Program and Book of Abstracts

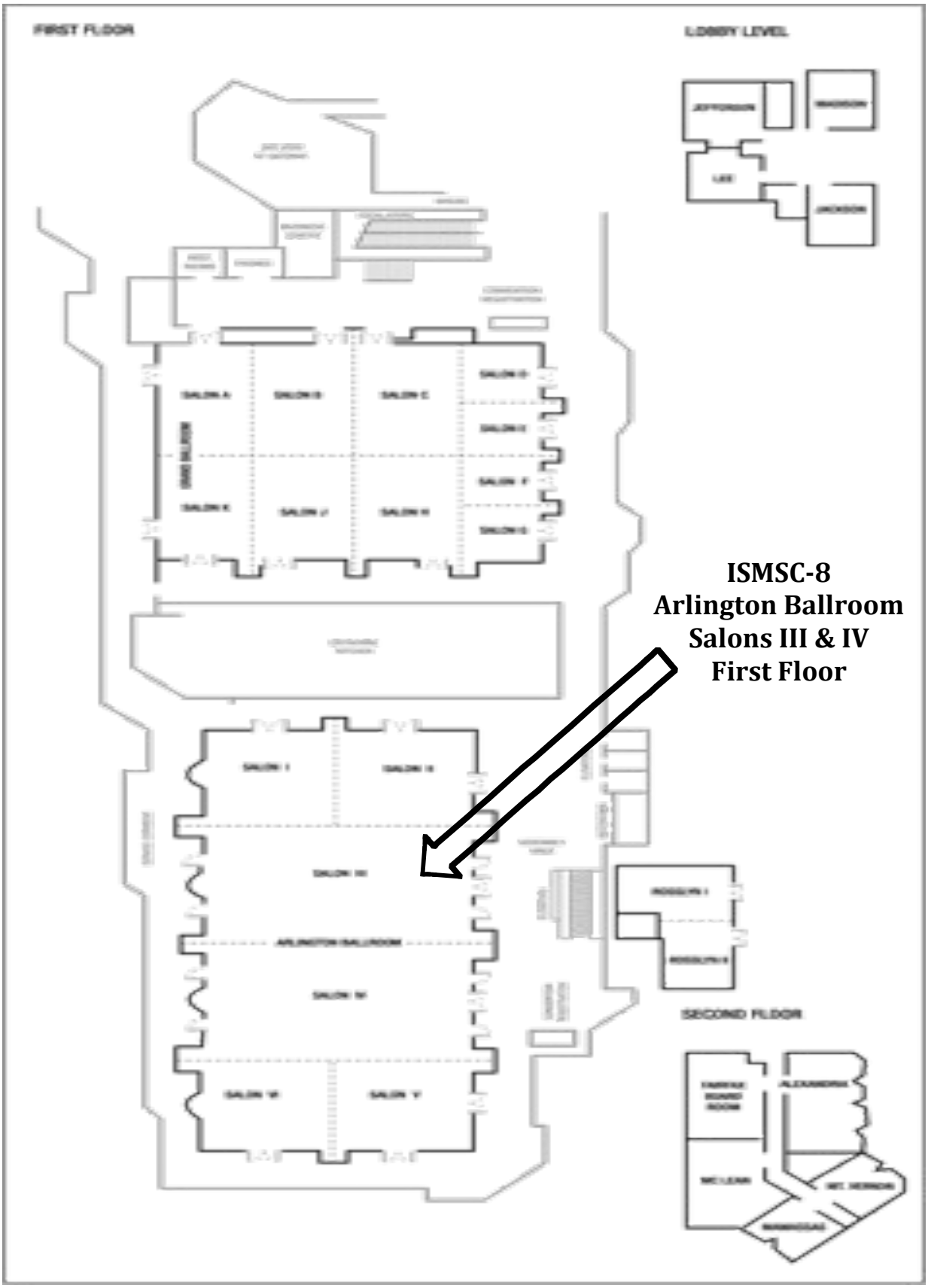
8th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC-8)



Crystal Gateway Marriott
Arlington, Virginia, USA

July 7–11, 2013
http://www.indiana.edu/~ismsc8

Floor Plan for Crystal Gateway Marriott



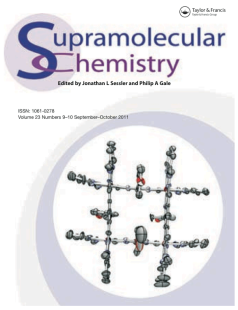
Welcome

The organizing committee welcomes you to ***ISMSC-8***. We hope that this meeting will continue the rich tradition of the previous 7 International Symposia on Macrocyclic and Supramolecular Chemistry. We intend ***ISMSC-8*** to encompass the broad scope and interdisciplinary nature of our field. We hope that interactions between attendees will help strengthen Macrocyclic and Supramolecular Chemistry.

Faculty from 4 universities organized ***ISMSC-8*** and we thank all those at the University of Maryland, Indiana University, Johns Hopkins University and Georgetown University for their support. We also thank the U.S. Department of Energy, the National Science Foundation, the Royal Society of Chemistry and many other organizations for their sponsorship of the ***ISMSC-8*** meeting.

Welcome to ***ISMSC-8*** and thank you for your participation,

Lyle Isaacs *Amar Flood* *Jeff Davis* *John D. Tovar* *Travis Holman*



We are pleased that *Supramolecular Chemistry* will publish a special issue dealing with chemistry presented at ***ISMSC-8***.

History of the International Symposium on Macrocyclic and Supramolecular Chemistry

Background. The International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC) came about from the merger of 2 regular meetings, the International Symposium on Macrocyclic Chemistry (ISMC) and the International Symposium on Supramolecular Chemistry (ISSC). The ISMC series, started in 1977 in Provo, Utah, was founded by Reed M. Izatt and James J. Christensen. The ISSC meetings began in 1980, in Warsaw, Poland and ISSC ran every other year until 2004. In 2006, the two meetings joined for a conference in Victoria, Canada, ISMSC-1. After this successful joint venture in 2006, the ISMSC has been held in a different country each year. For more details on the history of the ISMSC meetings see the website www://www.chem.byu.edu/node/1098 maintained at Brigham Young University.

The 8th International Symposium on Macrocyclic and Supramolecular Chemistry (***ISMSC-8***) will cover all aspects of macrocyclic and supramolecular chemistry. We hope it will bridge the traditional core areas of chemistry and interface with the biological, nanotechnological and materials arenas. The meeting will include a mix of established and younger speakers and will offer the chance for students and postdoctoral scholars to present their work in the form of oral presentations and posters.

Below is a list of the ISMSC meetings, along with the chief organizers:

2006 **Victoria, Canada** (T. Fyles)

2007 **Salice Terme, Italy** (L. Fabbrizzi)

2008 **Las Vegas, USA** (E. Anslyn / J. Sessler)

2009 **Maastricht, The Netherlands** (R. Nolte / A. Rowan)

2010 **Nara, Japan** (M. Fujita / Y. Inoue)

2011 **Brighton, England** (P. Gale)
http://www.ismsc2011.org/

2012 **Dunedin, New Zealand** (S. Brooker / K. Gordon)
http://www.otago.ac.nz/ismsc2012

2013 **Arlington, VA, USA** (L. Isaacs / A. Flood / J. Davis)
http://www.indiana.edu/~ismsc8/

2014 **Shanghai, China** (Z. Li)
http://www.ismsc2014.org

2015 **Strasbourg, France** (L. De Cola)

Table of Contents

Welcome 1
History of ISMSC 2
Table of Contents 3
ISMSC Organization 4
Sponsors, Donors & Gifts 5-7
Student Travel Award Winners 8
Poster Session and Award Information 8
Special Interest Sessions 8
General Information 9
Map of Metro Rail System 10
Izatt-Christensen Award in Macrocyclic Chemistry and Cram Lehn Pedersen Prize 11

Conference Schedule*
Sessions and Session Chairs 12
Conference Program 13-17
Poster Assignments 18-19

Lecture Abstracts
Sunday's Talks 20-26
Monday's Talks 27-39
Tuesday's Talks 40-47
Wednesday's Talks 48-59
Thursday's Talks 60-67

Poster Abstracts
Poster Session A PA1-90
Poster Session B PB1-78
Poster Session C PC1-82

Registered Participants and Presenters RP1-12

*A "*Conference at a Glance"* schedule is printed on the back cover of the program. This "Program and Book of Abstracts" was edited by Jeff Davis, Lyle Isaacs of the University of Maryland and Amar Flood of Indiana University. The abstracts in the program are printed in black and white, but a pdf with full color abstracts can be downloaded from the conference website.

Conference Organization

International Advisory Committee

Eric V. Anslyn - University of Texas at Austin, USA
Jerry L. Atwood - University of Missouri-Columbia, USA
Sally A. Brooker - University of Otago, New Zealand
Jeffery T. Davis - University of Maryland, USA
Luisa De Cola - University of Strasbourg, France
Amar H. Flood - Indiana University, USA
Mitsuhiko Shionoya - University of Tokyo, Japan
Philip A. Gale - University of Southampton, UK
Roger G. Harrison - Brigham Young University, USA
Itaru Hamachi - Kyoto University, Japan
Lyle Isaacs - University of Maryland, USA
Reed M. Izatt - Brigham Young University, USA
Kate A. Jolliffe - University of Sydney, Australia
Kimoon Kim - Postech, Korea
Roeland Nolte - University of Nijmegen, Netherlands
Alan E. Rowan - University of Nijmegen, Netherlands
Jonathan L. Sessler - University of Texas at Austin, USA
Zhanting Li - Fudan University, China
Marcey Waters - University of North Carolina, USA
Helma Wennemers - ETH, Switzerland

ISMSC-8 Local Organizing Committee

Lyle Isaacs (*University of Maryland, USA*), *Program*
Jeffery Davis (*University of Maryland, USA*), *Program*
Amar Flood (*Indiana University, USA*), *Program*
John D. Tovar (*Johns Hopkins University, USA*), *Poster Session*
K. Travis Holman (*Georgetown University, USA*),
Editor of Special Issue of Supramolecular Chemistry

Conference Web Site and Email Communication

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Caedmon Walters (University of Maryland) and
William R. Unrue (Indiana University), Email Communication
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Crystal Gateway Marriott
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www.marriott.com/wasum

Sponsors, Donors and Gifts

We thank the following organizations for their generous support of ***ISMSC-8***.

Patron Sponsors

United States, Department of Energy, Office of Basic Energy Sciences

http://www.science.doe.gov/bes/

Grant # DESC0010023

Basic Energy Sciences supports fundamental research in focused areas of the natural sciences in order to expand the scientific foundations for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy use. This support was provided by the Separations and Analysis Program and the Biomolecular Materials Programs in the Chemical Sciences, Geosciences and Biosciences Division.

National Science Foundation

http://www.nsf.gov

Grant # CHE1322204

The NSF is an independent federal agency created by Congress in 1950 "to promote the progress of science; to advance the national health, prosperity, and welfare; to secure the national defense…" With an annual budget of about $7.0 billion (FY 2012), the NSF is the funding source for approximately 20 percent of all federally supported basic research conducted by colleges and universities in the United States.

UNIVERSITY OF MARYLAND

http:// www.umd.edu

The **University of Maryland,** a public university located in College Park Maryland, is the largest university in the Washington Metropolitan area. Founded in 1856, the University of Maryland is the flagship institution of the University System of Maryland. Support was provided by the Department of Chemistry and Biochemistry, the College of Computer, Mathematics and Natural Sciences, The Vice-President of Research and the Office of the Provost.

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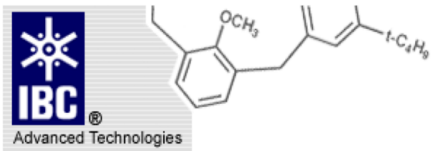
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Sponsors











Student & Post-Doc Travel Awards

Thanks to the support of the U.S. Department of Energy, we were able to make 21 competitive travel awards to students and post-docs who presented their research at ISMSC-8. The names and affiliations of the awardees are provided below:

Massimo Baroncini, Universita di Bologna, Italy
Parijat Borah, Nanyang University, Singapore
Jonathan Foster, University of Cambridge, UK
Youngdo Jeong, Univ. of Massachusetts, USA
Moridi Negar, Ecole Polytec. Lausanne, France
Nathan Strutt, Northwestern Univ., USA
Tyler Simmons, Florida State Univ., USA
Manolis Tzirakis, Swiss Fed. Inst. Tech., Switz.
Vedran Vukotic, Univ. of Windsor, Canada
Leah Witus, Northwestern University, USA
Yan Zhang, KTH Royal Institute Tech., Sweden

Jonathan Barnes, Northwestern Univ., USA
Marta Dal Molin, University of Padova, Italy
Mari Ikeda, Toho University, Japan
Semin Lee, Indiana University, USA
Severin Schneebeli, Northwestern Univ., USA
Hajime Shigemitsu, Osaka University, Japan

Wim Van Rossom, NIMS, Japan
Michelle Watt, University of Oregon, USA
Philip Young, Osaka University, Japan

Poster Talks and Awards

Poster Talks. From the 250+ posters being presented at ISMSC-8 the organizing committee selected the following 6 individuals to give 10-minute poster talks during the conference.

Guillaume De Bo, University of Manchester, UK
Tsuyoshi Minami, Bowling Green State Univ, USA
Maria del C. Rivera-Sanchez, Univ. Puerto Rico
Chenfeng Ke, Northwestern Univ., USA
Michelle Watt, University of Oregon, USA
Virginia Valderrey, ICR Catalonia, Spain

Poster Awards. There will be 250 posters on display during the first three poster sessions. From these, approximately 25 poster award finalists will be selected by the judges and by using votes cast by the conference attendees. These poster presenters will be able to display their posters for the remainder of the conference. The top 6 posters will receive an award that consists of $250, a free banquet ticket and a certificate. The grand prize winner will also receive a first-time award of the cover art for their peer-reviewed article in an issue of *Chemical Communications***.** The winners of the *ACS Poster Awards* (2 each)**,** *Nature Chemistry Awards* (2 each) and *RSC Poster Awards* (2 each) will be announced at the Banquet on Wednesday night, July 10, 2013.

Special Interest Sessions

"**Women in Science Networking Hour**" *Monday, July 8 at 5:45-6:45.* This cocktail hour will be kindly hosted by Linda Shimizu (University of South Carolina, USA) and is open to all women. This will be an informal event to meet and network with fellow scientists in the area of supramolecular and macrocyclic chemistry.

"Meet with NSF Program Managers" *Tuesday, July 9 at 1-2 pm (*Salon III Arlington Ballroom*).* Dr. Suk-Wah Tam-Chang and Dr. Timothy Patten, who are Program Directors for the Macromolecular, Supramolecular and Nanochemistry (MSN) Program at the National Science Foundation, will be available to answer questions about programs in the Division of Chemistry. Those who wish to learn more or have questions about the chemistry programs at NSF are encouraged to attend.

General Information and Social Events

Conference Venue The scientific sessions for ***ISMSC-8*** will be held at the Crystal Gateway Marriott, 1700 Jefferson Davis Hwy, Arlington, VA 22202. The hotel is located on the Metro's Yellow and Blue lines (Crystal City stop) and is minutes from downtown Washington, D.C. and from Reagan National Airport. For information on the hotel: www.marriott.com/hotels/travel/wasgw-crystal-gateway-marriott/ For an interactive map of Crystal City see http://dc.about.com/library/maps/blmapCrystalCity.htm

Registration The registration desk will be located in the Arlington Foyer, outside of the Arlington Ballroom (Salons III and IV). Registration will be open during the following times:

Sunday, July 7th	1:00 pm-8:00 pm	Monday, July 8th	7:30 am-4:00 pm
Tuesday, July 9th	8:00 am-1:00 pm	Wednesday, July 10th	8:00 am-4:00 pm
Thursday, July 11th	8:00 am-11:00 am		

Helpers with Yellow Name Tags and Conference Shirts. Members of the Organizing Committee and their groups (Davis, Isaacs and Flood) can be identified by yellow name tags. They will also be wearing a blue conference shirt on Sunday July 7th. Feel free to ask these individuals for help.

Location of Lecture Room The lectures will be held in Salon III of the Arlington Ballroom.

Uploading Presentations Presenters are asked to download their talks onto the computers in the lecture hall the day before their presentation if possible. If presenters want to use their own computers, then see the session chair (p. 12) before your session. Staff will be available to assist.

Poster Sessions Posters will be displayed in Salon IV, next door to the lecture room. Poster board assignments can be found on pages 18-19 of this Book of Abstracts. Posters can be a maximum size of 4 x 4 ft. There will be 3 poster sessions, one on Sunday evening, July 7th (**Session A** 7:00-9:00 pm with presenter last names A-H, set up before 6 pm Sunday, take down by 10:30 am on Monday, July 8). The other two sessions will occur on Monday, July 8th: **Session B** 1:30-3:30 pm, presenters I-Q, set up before 1 pm Monday, take down by 6 pm on Monday, July 8 and **Session C** 8-10 pm, presenters R-Z, set up by 7 pm on Monday, take down by 10:30 am on Tuesday, July 9. Poster award finalists (~25) will be identified Tues morning and are asked to set up posters after 10:30 am on Tuesday. Please also attend to your posters Wed 10-10:30 am for individual and group photographs.

Meals Continental breakfast will begin at 7:30 am in Salon IV. Catered lunches will be served in Salon IV on Monday and Wednesday. Box lunches will be available on Tuesday (free afternoon) and on Thursday (after conference ends). Refreshments provided during the day in the Arlington Foyer.

Sunday Night Welcome Reception Sunday evening, July 7th from 6-8 pm in Salon IV .

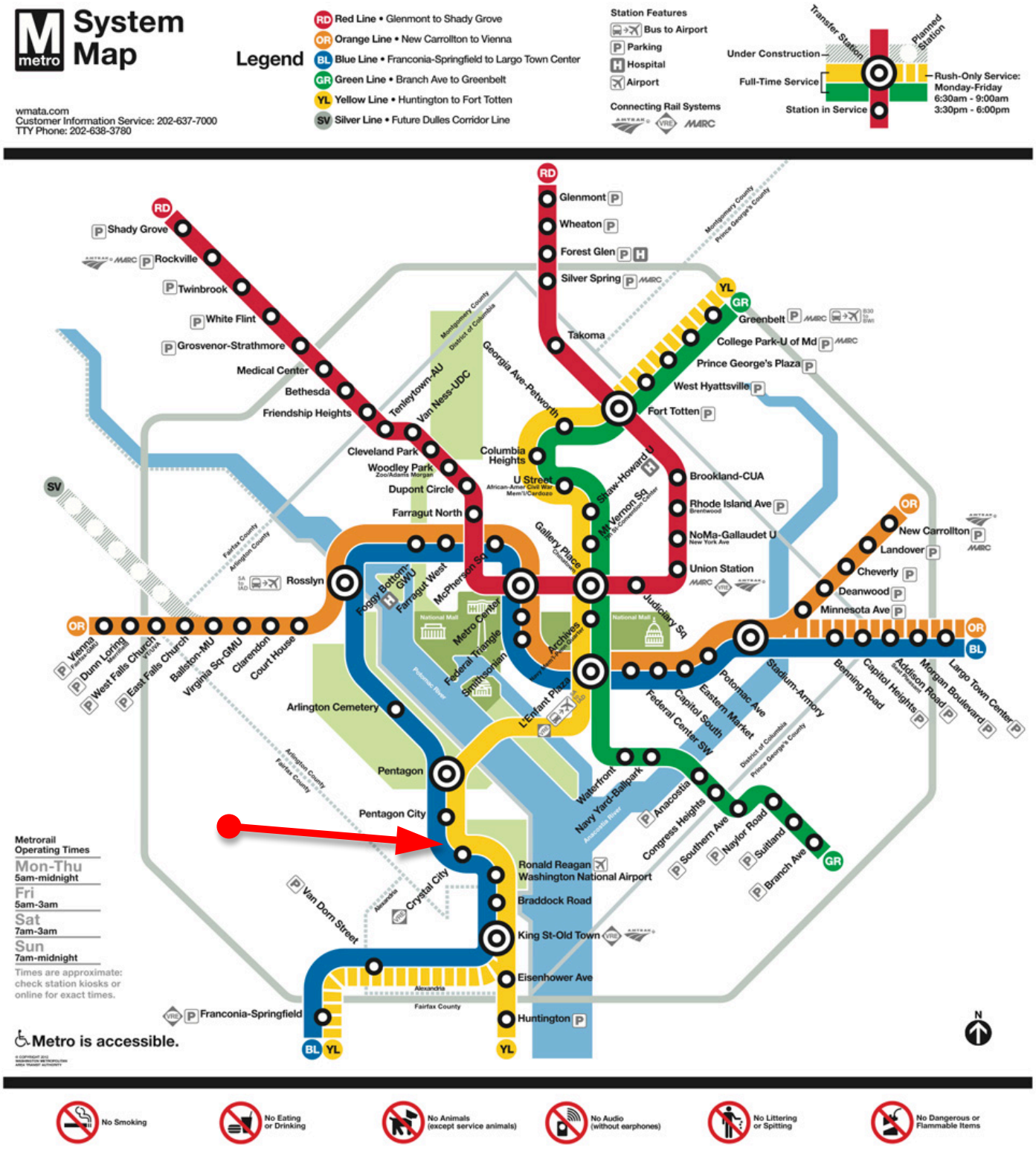
Conference Banquet Wednesday evening, July 10th at 7:30 pm in Salon IV.

Conference Photograph A conference photograph is scheduled for after lunch at 1:15-1:30 on Wednesday, July 10. Please meet in the lecture hall at 1:15 (Salon III of the Arlington Ballroom).

Free Time Tuesday afternoon and evening, July 9th is "free time". We encourage you to visit Washington DC or Old Town Alexandria. The hotel is conveniently located on the Metro rail (Crystal City stop). See http://www.wmata.com/ for details about the DC Metro system.

METRO RAIL SYSTEM

See http://www.wmata.com/ for details about the DC Metro system.



ISMSC 2013 Award Winners

Cram Lehn Pedersen Prize in Supramolecular Chemistry. The Cram Lehn Pedersen Prize, named in honor of the winners of the 1987 Nobel Prize in chemistry, recognizes significant, original and independent work in the area of supramolecular chemistry. *ChemComm*, a leader in publishing supramolecular chemistry research, sponsors the award.



The 2013 prize is awarded to **Professor Tomoki Ogoshi** from Kanazawa University for his outstanding work in macrocyclic and supramolecular chemistry. Professor Ogoshi has pioneered research on pillararenes, a new class of macrocyclic compounds.

Those within 10 years of receiving their PhD are eligible for the award. The winner receives a monetary honorarium, free registration for the ISMSC meeting and gives a lecture at ISMSC, as well as two additional presentations in the country where the meeting is held.

Izatt-Christensen Award in Macrocyclic Chemistry. Professor Izatt and the late Professor Christensen conceived the concept of the International Symposium on Macrocyclic Chemistry (ISMC) and they organized the first 5 ISMC Symposia starting in 1977. *IBC Advanced Technologies, Inc.*, of American Fork, Utah, USA, is the award's sponsor.



The 2013 prize goes to **Professor Eric Anslyn** from the University of Texas for groundbreaking work and international leadership in supramolecular chemistry and molecular recognition. The winner receives an honorarium and financial assistance for travel. The award is open to anyone working in macrocyclic chemistry who has not received an international award of $25,000 USD or more.

For a list of previous award and prize winners see the website https://www.chem.byu.edu/node/1100 maintained at Brigham Young University.

ISMSC-8 Sessions and Session Chairs

Sunday, July 7

3:15-6:00 pm **Session 1 Chair: Kate Jolliffe –** University of Sydney, Australia
Speakers: Meijer, Ashkenasy, Phillips, Aprahamian, Gibb, De Bo, Ke

Monday, July 8

8:30-10:00 am **Session 2 Chair: Mihail Barboiu –** Montpelier University, France
Speakers: Gale, Yang, Gellman

10:30-12:00 **Session 3 Chair: Pavel Anzenbacher –** Bowling Green State Univ., USA
Speakers: Rotello, O'Reilly, Minami, Watt

3:30-5:35 pm **Session 4 Chair: Mark MacLachlan –** University of British Columbia, Canada
Speakers: McNeil, Scherman, Zhao, Lee, Rivera-Sanchez, Valderrey

Tuesday, July 9

8:30-10:00 am **Session 5 Chair: Ali Trabolsi –** New York University, Abu Dhabi
Speakers: Zhao, Jeppesen, Hamachi, Dalcanale

10:30-11:45 am **Session 6 Chair: Penelope Brothers –** University of Auckland, New Zealand
Speakers: Würthner, Miljanić, Tobe

11:45-12:45 **Cram Lehn Pedersen Prize Chair: Yoshito Tobe –** Osaka University, Japan
Awardee: Ogoshi

Wednesday, July 10

8:30-10:00 am **Session 7 Chair: Darren Johnson –** University of Oregon, USA
Speakers: Sindelar, Batten, Wu, MacGillivray

10:30-12:00 pm **Session 8 Chair: Normand Voyer –** Universite de Laval, Canada
Speakers: Yang, Loeb, Stoddart

1:30-3:30 pm **Session 9 Chair: Kenji Kobayashi –** Shizuoka University, Japan
Speakers: Shionoya, Wennemers, Badjic, K. Shimizu

4:00-5:00 pm **Izatt-Christensen Award Chair: Roger Harrison –** Brigham Young, USA
Awardee: Anslyn

Thursday, July 11

8:30-10:00 am **Session 10 Chair: Janarthanan Jayawickramarajah –** Tulane Univ, USA
Speakers: Johnson, Fukuhara, Tucker, Hay

10:30-12:30 pm **Session 11 Chair: Kristin Bowman-James –** University of Kansas, USA
Speakers: Clever, Li, Shimizu, Fujita

ISMSC-8 Meeting Program and Schedule

Sunday, July 7, 2013

3:00 – 3:15pm	**Opening – Welcome**	
3:15 – 4:00pm	**E. W. Bert Meijer –** Eindhoven University, The Netherlands *Mastering Complexity: Functional Supramolecular Systems*	**(PL-1, p. 20)**
4:00 – 4:30pm	**Gonen Ashkenasy –** Ben Gurion University of Negev, Israel *The Systems Chemistry of Peptide Networks*	**(IL-1, p. 21)**
4:30 – 4:45pm	**Scott T. Phillips –** Pennsylvania State University, USA *Stimuli-Responsive Materials that Display Amplified Responses*	**(CL-1, p. 22)**
4:45 – 5:00pm	**Ivan Aprahamian –** Dartmouth College, USA *Hydrazone-Based Switches for Proton Relay Cascades*	**(CL-2, p. 23)**
5:00 – 5:30pm	**Bruce C. Gibb –** Tulane University, USA *The Assembly and Binding Properties of Deep-Cavity Cavitands in Water*	**(IL-2, p. 24)**
5:30 – 5:40pm	**Guillaume De Bo –** University of Manchester, UK *Sequence-Specific Synthesis by an Artificial Small-Molecule Machine*	**(CL-3, p. 25)**
5:40 – 5:50pm	**Chenfeng Ke –** Northwestern University, USA *A Molecular Gasket: Pillar[5]arene as a Promoter in Rotaxane Synthesis*	**(CL-4, p. 26)**
6:00 – 8:00pm	**Welcome Reception**	
7:00 – 9:00pm	**Poster Session "A"** (Presenters with last names A–H)	**(PA-1 thru PA-90)**

Monday, July 8, 2013

8:30 – 8:45am	**Philip A. Gale –** University of Southampton, UK *Towards Predictable Transmembrane Transport*	**(CL-5, p. 27)**
8:45 – 9:15am	**Dan Yang –** University of Hong Kong, Hong Kong *Self-Assembled Synthetic Ion Channels and Biomedical Applications*	**(IL-3, p. 28)**
9:15 – 10:00am	**Samuel H. Gellman –** University of Wisconsin, USA *Mimicry of Protein Recognition Surfaces with Foldamers*	**(PL-2, p. 29)**
10:00 – 10:30am	**Coffee Break**	
10:30 – 11:00am	**Vincent M. Rotello –** University of Massachusetts, USA *Nanoparticles and (Bio)molecular Recognition: Engineering the Interface for Sensing and Delivery*	**(IL-4, p. 30)**
11:00 – 11:30pm	**Rachel K. O'Reilly –** University of Warwick, UK *Reorganization of Polymeric Nanostructures for Controlled Release*	**(IL-5, p. 31)**
11:30 – 11:40pm	**Tsuyoshi Minami –** Bowling Green State University, USA *Intramolecular Indicator-dye Displacement Assay*	**(CL-6, p. 32)**
11:40 – 11:50pm	**Sankarapillai Mahesh –** IIST, India *Photoresponsive Transformation of Nanodots to Nanorods: Ostwald Ripening in Molecular Assemblies*	**(CL-7, p. 33)**
12:00 – 1:30pm	**Lunch Break**	
1:30 – 3:30pm	**Poster Session "B"** (Presenters with last names I–Q)	**(PB-1 thru PB-78)**
3:30 – 4:00pm	**Anne J. McNeil –** University of Michigan, USA *Developing Stimuli-Responsive Molecular Gels for Detection*	**(IL-6, p. 34)**
4:00 – 4:30pm	**Oren Scherman –** Cambridge University, UK *Cucurbiturils at the Interface between Supramolecular Chemistry and Materials Science*	**(IL-7, p. 35)**
4:30 – 4:45pm	**Yan Zhao –** Iowa State University, USA *Multivalent, Multifunctional Nanoparticles as Protein and Enzyme Mimics*	**(CL-8, p. 36)**
4:45 – 5:15pm	**Myongsoo Lee –** Seoul National University, Korea *Squeezable Tubules from Self-Assembly of Amphiphilic Macrocycles*	**(IL-8, p. 37)**
5:15 – 5:25pm	**Maria del C. Rivera-Sanchez –** Univ. of Puerto Rico, USA *A Hexadecameric Self-assembled Ligand for G-quadruplex DNA*	**(CL-9, p. 38)**
5:25 – 5:35pm	**Virginia Valderrey –** ICRC, Catalonia, Spain *Highly Cooperative Binding of Ion-Pair Dimers by a bis-Calix[4]pyrrole*	**(CL-10, p.39)**
5:45 – 6:45pm	**Special Interest Session I: Women in Science Networking Hour**	
5:45 – 8:00pm	**Dinner Break**	
8:00 – 10:00pm	**Poster Session "C"** (Presenters with last names R–Z)	**(PC-1 thru PC-82)**

Tuesday, July 9, 2013

8:30 – 8:45am	**Yanli Zhao –** Nanyang Technological Univ, Singapore *Photo-Switching on Nanoparticles*	**(CL-11, p. 40)**
8:45 – 9:15am	**Jan O. Jeppesen –** Univ. of Southern Denmark, Denmark *Unidirectional Linear Motion in Redox-Active Molecular Machines*	**(IL-9, p. 41)**
9:15 – 9:30am	**Itaru Hamachi –** Kyoto University, Japan *Design of Fluorescent ATP Chemsensors Useful Under Living Cells*	**(CL-12, p. 42)**
9:30 – 10:00am	**Enrico Dalcanale –** University of Parma, Italy *Molecular Recognition at Interfaces: Implications in Sensing and Polymer Science*	**(IL-10, p. 43)**
10:00 – 10:30am	**Coffee Break**	
10:30 – 11:00am	**Frank Würthner –** Universität Würzburg, Germany *Functional Nanosystems Based on Dye Aggregates*	**(IL-11, p. 44)**
11:00 – 11:15am	**Ognjen Miljanić –** University of Houston, USA *High-Fidelity Self-Sorting of Dynamic Combinatorial Libraries Under Irreversible Physical and Chemical Stimuli*	**(CL-13, p. 45)**
11:15 – 11:45am	**Yoshito Tobe –** Osaka University, Japan *Host-Guest Chemistry in Two-Dimensional Space*	**(IL-12, p. 46)**
11:45 – 12:45pm	***Cram Lehn Pedersen Prize*** **Tomoki Ogoshi –** Kanazawa University, Japan *Pillararenes: Easy-to-Make and Versatile Receptors for Supramolecular Chemistry*	**(AL-1, p. 47)**
12:45pm	**Free Time (Box Lunch Available)**	
1:00-2:00pm	**Special Interest Session II: Meet the NSF Program Officers**	

Wednesday, July 10, 2013

8:30 – 8:45am	**Vladimir Sindelar –** Masaryk University, Czech Republic *Bambusuril Macrocycles for Anion Binding*	**(CL-14, p. 48)**
8:45 – 9:15am	**Stuart R. Batten –** Monash University, Australia *Multifunctional Nanoballs and Variable Length Ligands*	**(IL-13, p. 49)**
9:15 – 9:30am	**Biao Wu –** Northwest University, China *Phosphate Coordination by Oligoureas*	**(CL-15, p. 50)**
9:30 – 10:00am	**Leonard R. MacGillivray –** University of Iowa, USA *Supramolecular Synthesis and Control of Reactivity in Organic Solids*	**(IL-14, p. 51)**
10:00 – 10:30am	**Coffee Break**	
10:30 – 10:45am	**Ying-Wei Yang –** Jilin University, China *Biocompatible Supramolecular Nanovalves for Controlled Cargo Release*	**(CL-16, p. 52)**
10:45 – 11:15am	**Stephen J. Loeb –** University of Windsor, Canada *Organizing Mechanically Interlocked Molecules to Function Inside Metal-Organic Frameworks*	**(IL-15, p. 53)**
11:15 – 12:00pm	**J. Fraser Stoddart –** Northwestern University, USA *Artificial Molecular Motors*	**(PL-3, p. 54)**
12:00 – 1:15pm	**Lunch Break**	
1:15 – 1:30pm	**Conference Photo**	
1:30 – 2:00pm	**Mitsuhiko Shionoya –** University of Tokyo, Japan *Metal-Centered Supramolecular Assembly*	**(IL-16, p. 55)**
2:00 – 2:30pm	**Helma Wennemers –** ETH, Switzerland *Peptides as Asymmetric Catalysts*	**(IL-17, p. 56)**
2:30 – 3:00pm	**Jovica Badjic –** Ohio State University, USA *Gated Molecular Recognition and Reactivity*	**(IL-18, p. 57)**
3:00 – 3:30pm	**Ken Shimizu–** University of South Carolina, USA *A Versatile Model System for Studying Non-covalent Interactions of Aromatic Surfaces*	**(IL-19, p. 58)**
3:30 – 4:00pm	**Coffee Break**	
4:00 – 5:00pm	***Izatt-Christensen Award in Macrocyclic Chemistry*** **Eric V. Anslyn –** University of Texas, Austin, USA *Three Short Stories of Analytical Supramolecular Chemistry*	**(AL-2, p. 59)**
7:30 pm	**Conference Banquet**	

Thursday, July 11, 2013

8:30 – 9:00am **Darren Johnson–** University of Oregon, USA **(IL-20, p. 60)**
Modular Supramolecular Fluorescent Receptors: Functional Materials and Applications as Probes for Anions

9:00 – 9:15am **Gaku Fukuhara –** Osaka University, Japan **(CL-17, p. 61)**
Supramolecular Oligosaccharide Sensing with Reporter-Modified Curdlans

9:15 – 9:30am **James H. R. Tucker –** University of Birmingham, UK **(CL-18, p. 62)**
Photo-active and Organometallic Nucleic Acid Oligomers

9:30 – 10:00am **Benjamin P. Hay –** Oak Ridge National Laboratory, USA **(IL-21, p. 63)**
Structural Design Principles for Self-assembled Coordination Polygons and Polyhedra

10:00 – 10:05am **Zhan-Ting Li –** Invitation to ISMSC-9, Shanghai, China

10:05 – 10:30am **Coffee Break**

10:30 – 10:45am **Guido H. Clever** – Universität Göttingen , Germany **(CL-19, p. 64)**
Control over Cavity Shape and Size in Anion Binding Coordination Cages

10:45 – 11:15am **Zhan-Ting Li –** Fudan University, China **(IL-22, p. 65)**
Aromatic Foldamers for Molecular Recognition and Supramolecular Materials

11:15 – 11:45am **Linda S. Shimizu –** University of South Carolina, USA **(IL-23, p. 66)**
Self-assembling Hosts as Functional Molecular Containers

11:45 – 12:30pm **Makoto Fujita –** University of Tokyo, Japan **(PL-4, p. 67)**
Nano-to-microgram Scale X-ray Analysis using Porous Complexes

12:30 – 12:35pm **Closing Remarks**

12:35pm **Lunch**

ISMSC-8 Poster Session Assignments

Session	Poster A	Poster B	Poster C
Date	Sun July 7	Mon July 8	Mon July 8
Time	7:00 PM	1:30 PM	8:00 PM
1	Ahn	Ikeda	Rastogi
2	Akutsu	Iritani	Reany
3	Al-Sayah	Isare	RiveraSanche
4	Alberti	Ito	Rodler
5	Alqurafi	Jayawickrmj	Roy
6	Alrawashdeh	Jensen	Rullaud
7	Ang	Jeong	Saha
8	Anzenbacher	Johnstone	Sashuk
9	Archer	Jones	Sawada
10	Avestro	Jordan	Schneebelli
11	Backes	Ju	Schnorr
12	Barboiu	Juricek	Shigemitsu
13	Barnes	Kakuta	Shimizu
14	Baroncini	Kanai	Silver
15	Basuray	Kanda	Simmons
16	Beaver	Kasera	Sinnwell
17	Belitsky	Kaur	Smith
18	Belskaya	Kawano	Sokolowski
19	Benson	Ke	Spence
20	Beyeh	Kerr	Sreejith
21	Bonizzoni	withdrawn	Stephenson
22	Borah	Kida	Stojakovic
23	Bordoli	Kikuchi	Strutt
24	Bowman Jms	Kim	Suhonen
25	Branson	Kobayashi	Sun
26	Braunschweig	Korevaar	Surbella
27	Brothers	Koutnik	Svoboda
28	Browne	Kouwer	Tan
29	Cantekin	Krupinski	Taylor
30	Cao, Dennis	Kulikov	Tkachenko
31	Cao, Liping	Kuwahara	Toth
32	Carnegie	Laird	Tovar
33	Carter	Lamb	Trabolsi
34	Catalán	Landis	Tresca
35	Chang	Larsen	Tripier
36	Charbonnaz	Laursen	Tulli
37	Chen	Lee, E	Turner
38	Cheng	Lee, S	Tyagi
39	Cho	Li, Hao	Tzirakis
40	Chui	Li, P	Ube
41	Collins, C	Liu, Yu	Ueshima
42	Collins, M	Liu, Yun	Ullmann
43	Cooper	Liu, Z	Vaganova
44	Crane	withdrawn	Valderrey
45	Crowley	Macartney	Valente
46	CruzVasquez	Mahesh	vanderZwaag

ISMSC-8 Poster Session Assignments

Session		Poster A		Poster B		Poster C
Date		Sun July 7		Mon July 8		Mon July 8
Time		7:00 PM		1:30 PM		8:00 PM
	47	Custelcean	47	Mandadapu	47	Van Rossom
	48	Dal Molin	48	Martinez, A	48	Vermeulen
	49	Dale	49	Martínez, M	49	Vinciguerra
	50	Dawn	50	Masson	50	Voloshin
	51	De Bo	51	McDonald	51	Vonnegut
	52	DeBlase	52	McGonigal	52	Vukotic
	53	Despotovic	53	Minami	53	Vurgun
	54	Destecroix	54	Miyake	54	Wakabayashi
	55	Dinake	55	Mizutani	55	Wallace
	56	Doonan	56	Moczar	56	Wang, Hao
	57	Duan	57	Moridi	57	Wang, Hui
	58	Duncan	58	Moriya	58	Wang, Y
	59	Edwards	59	Morzherin	59	Watt
	60	El Ayle	60	Mosca	60	Wei
	61	Elacqua	61	Mungalpara	61	Whitehead
	62	Elfeky	62	Murphy	62	Wilson
	63	Elliott	63	Nakahata	63	Winn
	64	Esipenko	64	Neves Filho	64	Witus
	65	Fantini	65	Nguyen	65	Wu
	66	Foster	66	Noguchi	66	Yamanaka
	67	Frasconi	67	Northrup	67	Yapar
	68	Früh	68	Ogden	68	Yasuhara
	69	Fujii	69	Orentas	69	Yeh
	70	Galán	70	Park	70	YesilbagTonga
	71	Gasparini	71	Parker	71	Yin
	72	Gilberg	72	Peacor	72	Yoneya
	73	Gong	73	Peck	73	Yoshihara
	74	Groeneman	74	Peters	74	Young
	75	Guo	75	Pfeffer	75	Yuen
	76	Habata	76	Pittelkow	76	Zhang, B
	77	Harrison	77	Qiao	77	Zhang, D
	78	Hartlieb	78	Quesada	78	Zhang, H
	79	Hatanaka			79	Zhang, Y
	80	Havel			80	withdrawn
	81	Helttunen			81	Zhu, K
	82	Hernández			82	Zhu, L
	83	HerreraEspña			83	Tsuchido, Y
	84	Hillyer				
	85	Hirsch				
	86	Ho				
	87	withdrawn				
	88	Hou, X				
	89	Huggins				
	90	Huszthy				

Mastering Complexity: Functional Supramolecular Systems

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Institute for Complex Molecular Systems, Laboratory of Macromolecular and Organic Chemistry, Laboratory of Chemical Biology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands
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The intriguing prospects of molecular electronics, nanotechnology, biomaterials, and the aim to close the gap between synthetic and biological molecular systems are important ingredients to study the cooperative action of molecules in the self-assembly towards functional supramolecular systems. The design and synthesis of well-defined supramolecular architectures requires a balanced choice between covalent synthesis and the self-assembly of the fragments prepared. The current self-assembly processes are primarily controlled by solvent, temperature or concentration. For synthetic chemists, the non-covalent synthesis of these supramolecular architectures is regarded as one of the most challenging objectives in science: How far can we push chemical self-assembly and can we get control over the kinetic instabilities of the non-covalent architectures made? How can we go from self-assembly to self-organization? Where the number of different components is increasing the complexity of the system is increasing as well. Mastering this complexity is a prerequisite to achieve the challenges in creating functional systems. In the lecture we illustrate our approach using a number of examples out of our own laboratories, with the aim to come to new strategies for multi-step non-covalent synthesis of functional supramolecular systems.

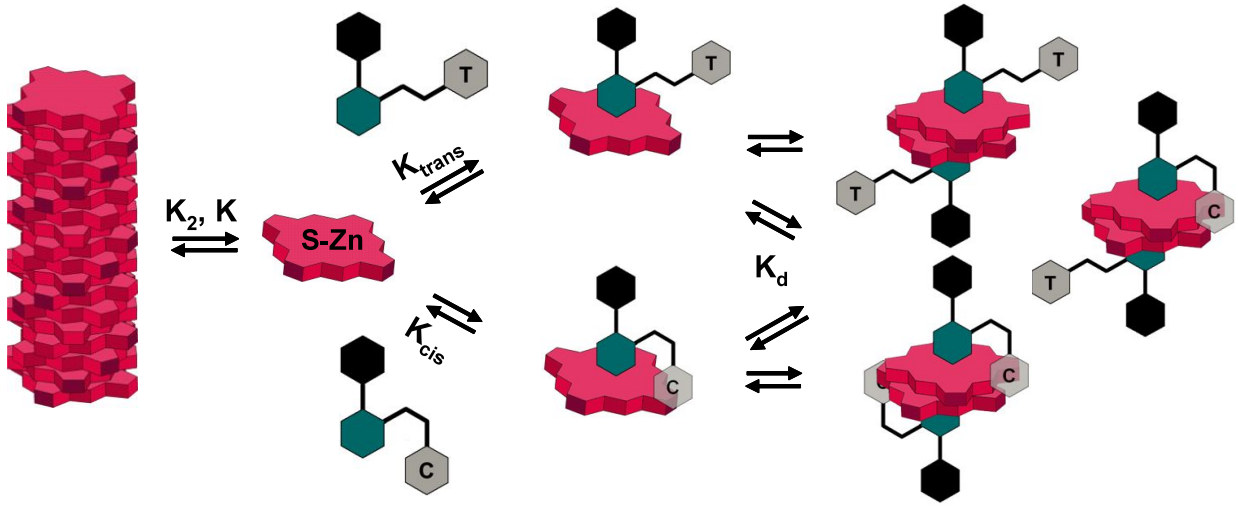


Fig: Photo-control over cooperative porphyrin self-assembly with phenylazopyridine auxiliaries.

Reference

1) Hirose, T.; Helmich, F.; Meijer, E.W. *Angew. Chem., Int. Ed*. **2013**, *52*, 304-309.

The Systems Chemistry of Peptide Networks

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Email: gonenash@bgu.ac.il

Non-enzymatic replication has been the subject of intense research, related to plausible scenarios in early molecular evolution and the origins of life. Several different synthetic replication systems have been prepared and analyzed, including nucleic acids, fatty acids, peptides, and organic molecules. We have been interested recently in the analysis of replication networks [1] operating far from equilibrium as better models for selection and adaptation in response to the ever-changing chemical environment. In this talk, we will present the following two new systems emphasizing the effects of transient supramolecular structures on the mechanism and dynamics of peptide self-organization and replication: (i) Light-dependent replication of α-helix proteins [2] and its utility for manipulating dynamic combinatorial libraries [3] and chemical logic operations [2,4], and (ii) one-dimensional assemblies as active traps facilitating β-sheet peptides replication [5,6].

[1] Dadon, Wagner, Ashkenasy *Angew. Chem. Int. Ed.* **2008**, 47, 6128.
[2] Dadon, Samiappan, Yishay, Ashkenasy *Chem. Eur. J.* **2010** *16*, 12096.
[3] Dadon, Samiappan, Wagner, Ashkenasy *Chem. Commun.* **2012**, 48, 1419.
[4] Samiappan, Dadon, Ashkenasy *Chem. Commun.* **2011**, *47*, 710.
[5] Rubinov, Wagner, Rapaport, Ashkenasy *Angew. Chem. Int. Ed.* **2009**, 48, 6683.
[6] Rubinov, Wagner, Matmor, Regev, N. Ashkenasy, G. Ashkenasy *ACS nano* **2012**, 6, 7893.

Designing Stimuli-Responsive Materials that Display Amplified Responses

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sphillips@psu.edu

This presentation will describe strategies for creating stimuli-responsive materials that are capable of responding (i) selectively to trace levels of signals, and (ii) continuously even after the signal has been removed. This ability to respond to trace—and even fleeting—signals occurs in the absence of applied reagents or energy, thus rendering the materials self-powered and autonomous. This responsive behavior is made possible via controlled depolymerization reactions as well as self-propagating autoinductive reactions that occur within the polymers that make up the materials. This presentation will describe several designs of polymers that convey amplified responses, as well as applications of the corresponding materials.

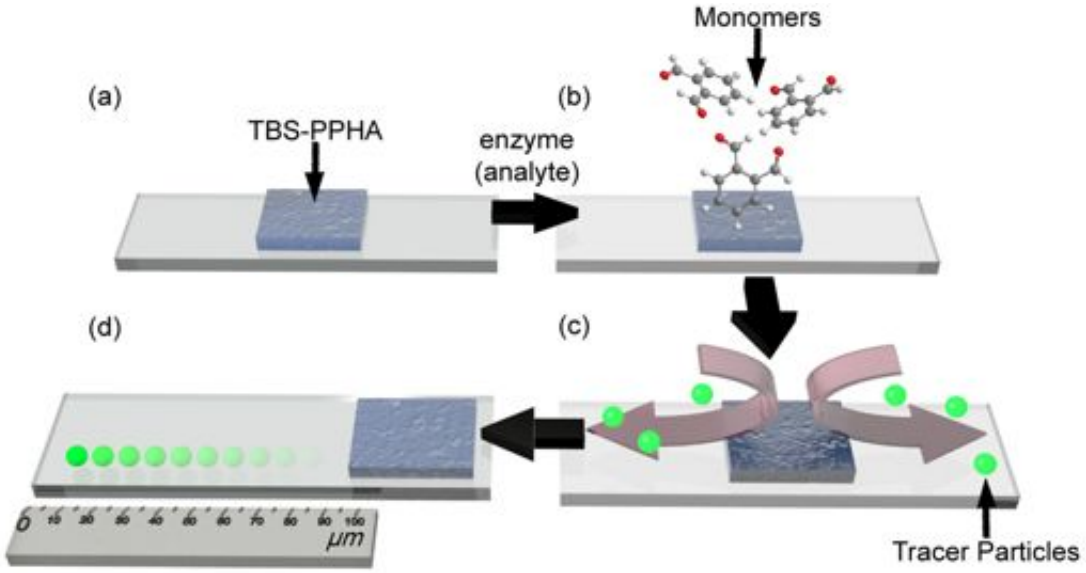


Figure 1. An analyte-responsive, non-mechanical plastic pump made from a depolymerizable polymer. The pump is the gray film, which is made from a depolymerizable poly(phthalaldehyde) (PPHA). The curved arrows show the direction that the fluid is pumped in the presence of an analyte.

Hydrazone-Based Switches for Proton Relay Cascades

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Can structurally simple molecular switches perform complicated functions? In order to answer this question, we have been developing for the past few years, simple, modular and tunable hydrazone-based rotary switches.[1-4] As part of this effort we took advantage of a bioinspired coordination-coupled deprotonation (CCD) process[2,3] to activate the switches without having to add protons to the system. The presentation will deal with CCD initiated multistep proton relays that can create switching cascades, and be utilized in signaling and signal amplification processes.

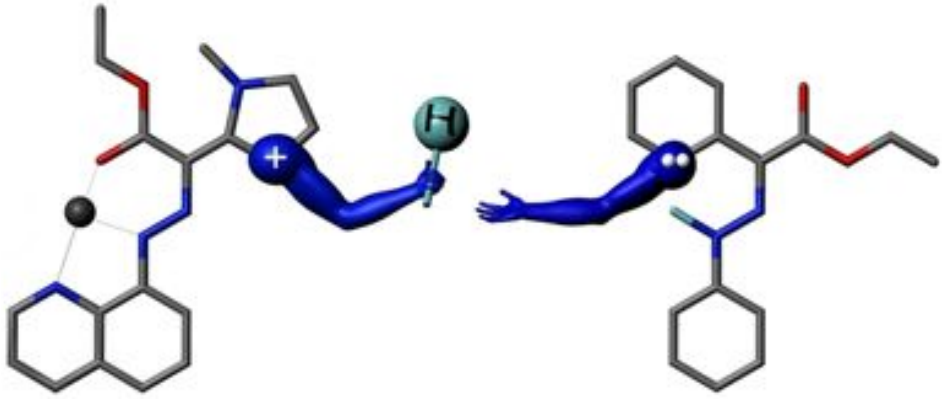


Figure 1. Zinc (II) initiated CCD leads to the activation of two different hydrazone switches through proton relay cascades.

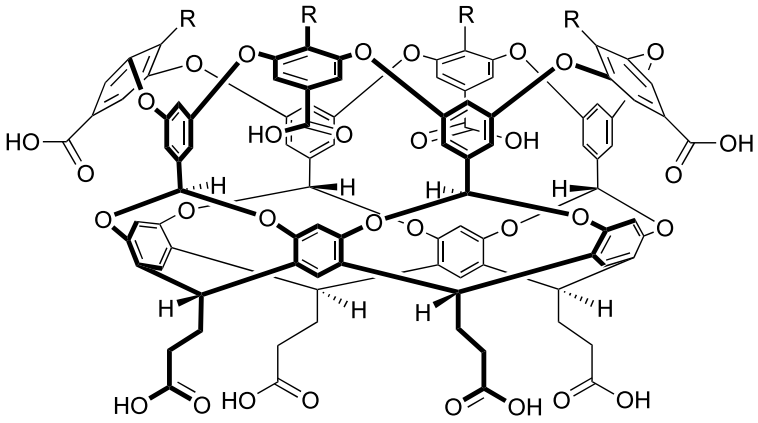
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2) Su, X.; Robbins, T. F.; Aprahamian**,** I. *Angew. Chem. Int. Ed.* **2011**, *50*, 1841.
3) Ray, D.; Foy, J. T.; Hughes, R. P.; Aprahamian, I. *Nature Chem.* **2012**, *4*,757.
4) Yang, Y.; Hughes, R. P.; Aprahamian, I. *J. Am. Chem. Soc.* **2012**, *134*, 15221.

The Assembly and Binding Properties of Deep-Cavity Cavitands in Water

Simin Liu,[†] Haiying Gan,[‡] Corinne L. D. Gibb[†] and Bruce C. Gibb[†]*
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[‡]*Department of Chemistry and Biochemistry, University of Notre Dame South Bend IN 46556*
bgibb@tulane.edu

Recent studies into the binding and assembly of water-soluble deep-cavity cavitands such as **1** and **2** (Figure 1) will be presented. More specifically, the affinity of chaotropic anions for hydrophobic concavity, and how this pertains to the Hofmeister Effect, will be discussed.[1] We will also present the structural requirements of these cavitands for orchestrating the hydrophobic effect and allowing them to assemble into dimeric,[2] and higher assemblies.[3]



1 R = H
2 R = Me

Figure 1. Deep-Cavity Cavitands.

References

1. Gibb, C. L.; Gibb, B. C., Anion Binding to Hydrophobic Concavity Is Central to the Salting-in Effects of Hofmeister Chaotropes. *J. Am. Chem. Soc.* **2011**, *133*, 7344-7347.
DOI: 10.1021/ja202308n
2. (a) Liu, S.; Gibb, B. C., High-definition self-assemblies driven by the hydrophobic effect: synthesis and properties of a supramolecular nanocapsule. *Chem. Commun.* **2008**, 3709-3716. **DOI**: 10.1039/c1cc10122f; (b) Gan, H.; Benjamin, C. J.; Gibb, B. C., Non-monotonic Assembly of a Deep-Cavity Cavitand. *J. Am. Chem. Soc.* 2011, *133*, 4770-4773. **DOI**: 10.1021/ja200633d.
3. *Guest-mediated switching of the assembly state of a water-soluble deep-cavity cavitand*, *Chem. Commun*., Gan, H. and Gibb, B. C., **2013**, Advanced Article. **DOI**: 10.1039/c2cc38227j.

Sequence-Specific Synthesis by an Artificial Small-Molecule Machine

Guillaume De Bo, Bartosz Lewandowski, John W. Ward, Marcus Papmeyer, Sonja Kuschel and David A. Leigh

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The ribosome is an enormous biological molecular machine that joins together amino acids derived from transfer RNA building blocks in an order determined by a messenger RNA strand, creating protein in a process known as translation. Here we report on the design, synthesis and operation of an artificial small-molecule machine that travels along a molecular strand, picking up amino acids that block its path, to synthesize a peptide in a sequence-specific manner.[1] The chemical structure is based on a rotaxane, a molecular ring threaded onto a molecular axle. The ring carries a thiolate group that iteratively removes proteinogenic amino acids from the strand and transfers them to a peptide elongation site through native chemical ligation. The synthesis is demonstrated using ~10^{18} molecular machines acting in parallel and generates milligram quantities of a peptide with a single sequence, determined by tandem mass spectrometry, corresponding to the original order of the amino acid building blocks on the strand.

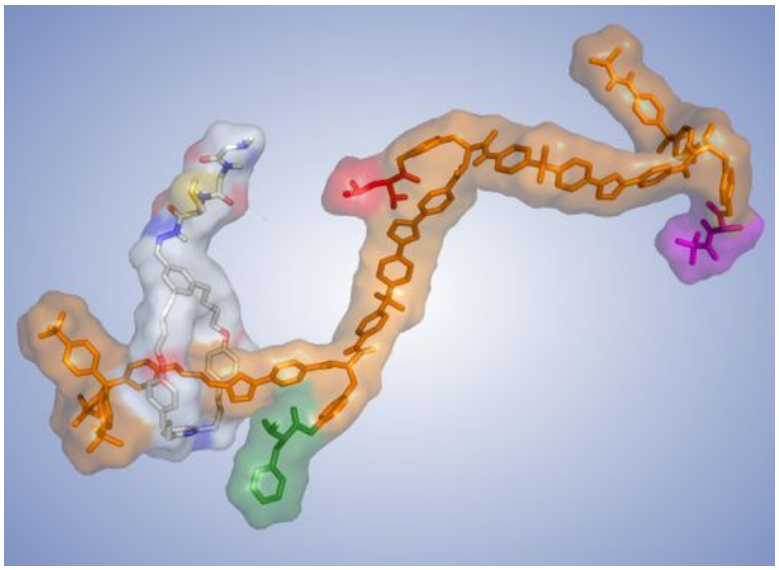


Figure 1. A molecule that makes molecules.

References

1) Lewandowski, B.; De Bo, G.; Ward, J. W.; Papmeyer, M.; Kuschel, S.; Aldegunde, M. J.; Gramlich, P. M. E.; Heckmann, D.; Goldup, S. M.; D'Souza, D. M.; Fernandes, A. E.; Leigh, D. A. **2013** *Science*, *339*, 189–193.

A Molecular Gasket: Pillar[5]arene as a Promoter in Rotaxane Synthesis

Chenfeng Ke, Nathan L. Strutt, Hao Li, Xisen Hou, Karel J. Hartlieb,
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The cucurbit[6]uril (**CB**) catalyzed alkyne-azide cycloaddition (AAC) is accelerated in the presence of cyclodextrin as a result of the formation of a cooperative hydrogen bonding network.[1] This strategy, which benefits considerably from positive cooperativity, has been applied[2] subsequently to the synthesis of rotaxanes. Here, we report that pillar[5]arene (**P**) also interacts with cucurbit[6]uril to promote the efficient cooperative capture of [4]- or [5]rotaxanes, along with the observation that this particular combination is tolerant to variations in the length of the azide guest (from 2-azidoethylpyridium to 5-azidopentylpyridium cations). The **P** rings not only serve as hydrogen bond donors in stabilizing the multicomponent assembly, but also act as 'molecular gaskets' to adjust the relative positioning of the alkyne and azide functions inside **CB** to allow their favorable alignment for cyclization, affording [4]- or [5]rotaxanes rapidly in excellent (90 – 96%) yields. ^{1}H NMR Spectroscopy reveals that the conformations adopted by the **P** rings are locked in the heterorotaxanes, allowing observation and assignment of all four conformational isomers. These findings expand the limited substrate scope of the CB-catalyzed AAC and provide a highly efficient way to template the formation of heterorotaxanes.

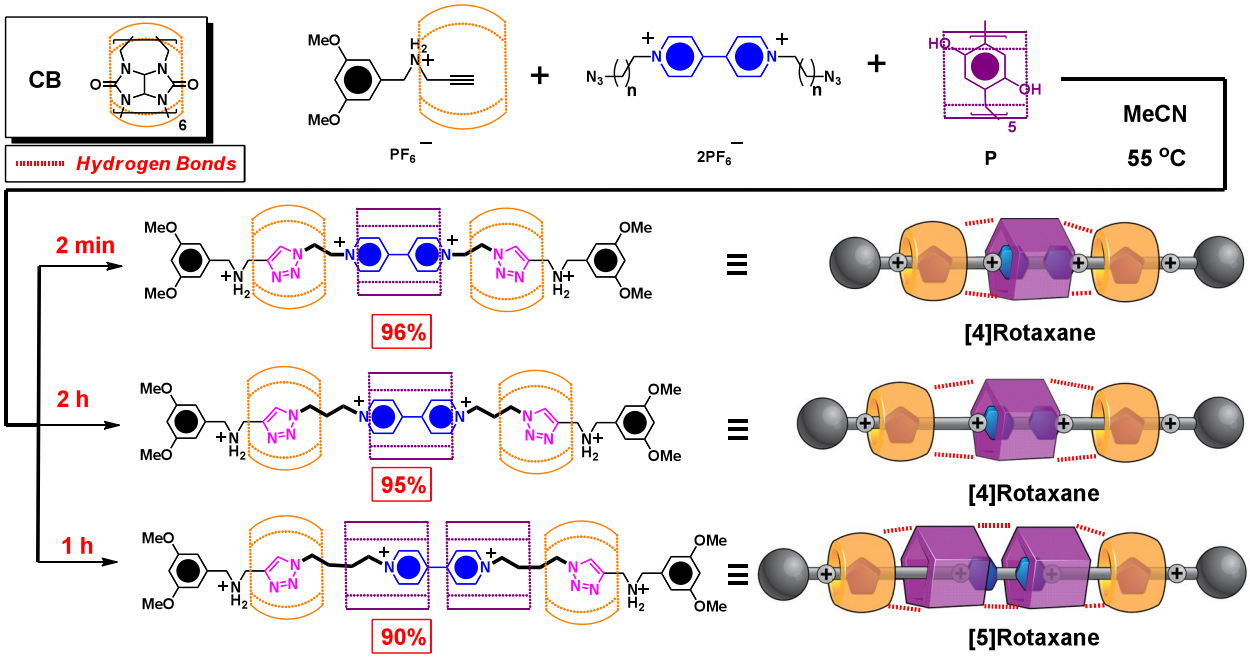


Figure 1. Synthesis of the hetero[4]- and [5]rotaxanes starting from a stopper precursor **CB** complex, viologen derivatives in the presence of **P** rings. The hatched lines in the graphical representation indicate the hydrogen bonding interactions between **CB** and **P** rings.

References

1) Ke, C.; Smaldone, R. A.; Kikuchi, T.; Li, H.; Davis, A. P.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2013**, *52*, 381–387.
2) Tuncel, D.; Steinke, J. *Chem. Commun.* **1999**, 1509–1510.

Towards Predictable Transmembrane Transport: QSAR Analysis of the Anion Binding and Transport Properties of Thioureas

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The transport of anions across biological membranes by small molecules is a growing research field due to the potential therapeutic benefits of these compounds.[1] However, little is known about the exact mechanism by which these drug-like molecules work and which molecular features make a good transporter. An extended series of 1-hexyl-3-phenylthioureas were synthesized (Figure 1), fully characterized (NMR, mass spectrometry, IR and single crystal diffraction) and their anion binding and anion transport properties were assessed using ^{1}H NMR titration techniques and a variety of vesicle-based experiments. Quantitative structure-activity relationship (QSAR) analysis revealed that the anion binding abilities of the mono-thioureas are dominated by the (hydrogen bond) acidity of the thiourea NH function. Furthermore, mathematical models show that the experimental transmembrane anion transport ability is mainly dependent on the lipophilicity of the transporter (partitioning into the membrane), but smaller contributions of molecular size (diffusion) and hydrogen bond acidity (anion binding) were also present. Finally, we provide the first step towards predictable anion transport by employing the QSAR equations to estimate the transmembrane transport ability of four new compounds.[2]

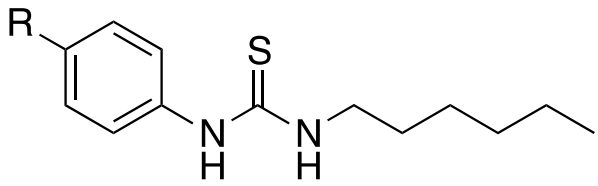


Figure 1. Twenty two 1-hexyl-3-phenylthioureas with different substituents in the *para*-position were used in this study.

References

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2) Busschaert, N.; Bradberry, S.J; Wenzel, M.; Haynes, C.J.E.; Hiscock, J.R.; Kirby, I.L.; Karagiannidis, L.; Moore, S.J.; Wells, N.J.; Herniman, J.; Langley, G.J.; Horton, P.N.; Light, M.E.; Félix, V.; Frey, J.G.; Gale, P.A. manuscript in preparation.

Self-Assembled Synthetic Ion Channels and Their Biomedical Applications

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Ion transport across cell membranes is regulated by ion channel proteins, and plays important roles in many physiological processes such as neuronal signaling, muscle contraction, cardiovascular function, and immune response. Many severe human diseases, such as cystic fibrosis, asthma, hypertension, epilepsy and myocardial infarction, are caused by dysfunction of natural ion channel proteins. Therefore, molecules that modulate the functions of ion channels or regulate ion transport across cell membranes have attracted significant attentions from both academia and pharmaceutical industry. Each year over US$6 billion are generated from the sales of drugs associated with ion channel functions. Most of those drugs control the functions of natural calcium, sodium or potassium channels through direct binding. In this talk, our recent discovery of small molecules that self-assemble into synthetic ion channels that transport small anions or cations across biological membranes will be presented. These synthetic ion channels can transport ions efficiently in living cells and epithelia, independent of natural ion channel proteins. They are easy to synthesize and their pharmacological properties can be readily modified. Explorations on their potential biomedical applications will also be presented.

Mimicry of Protein Recognition Surfaces with Foldamers

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Interactions between specific proteins are essential for in biology, with key roles in normal physiological signal transduction and disease-related processes. Many such interactions have proven recalcitrant to modulation with small molecules because the protein surface areas involved are large. In these cases, clinical modulation is generally achieved with large peptides or proteins. We are exploring an alternative approach to this challenge, based on unnatural oligomers that fold to specific conformations and display protein-like surfaces ("foldamers"). We have found that informational alpha-helices can be mimicked effectively with oligomers containing both alpha- and beta-amino acid residues ("alpha/beta-peptides"). Placement of beta residues throughout a sequence can confer substantial resistance to proteolysis. Successful alpha-helix mimicry has been demonstrated in the context of BH3 recognition by Bcl-2-family proteins (Figure 1) and formation of CHR+NHR helix-bundles from gp41-derived segments. Current efforts include expansion of protein-surface mimicry beyond isolated alpha-helices.

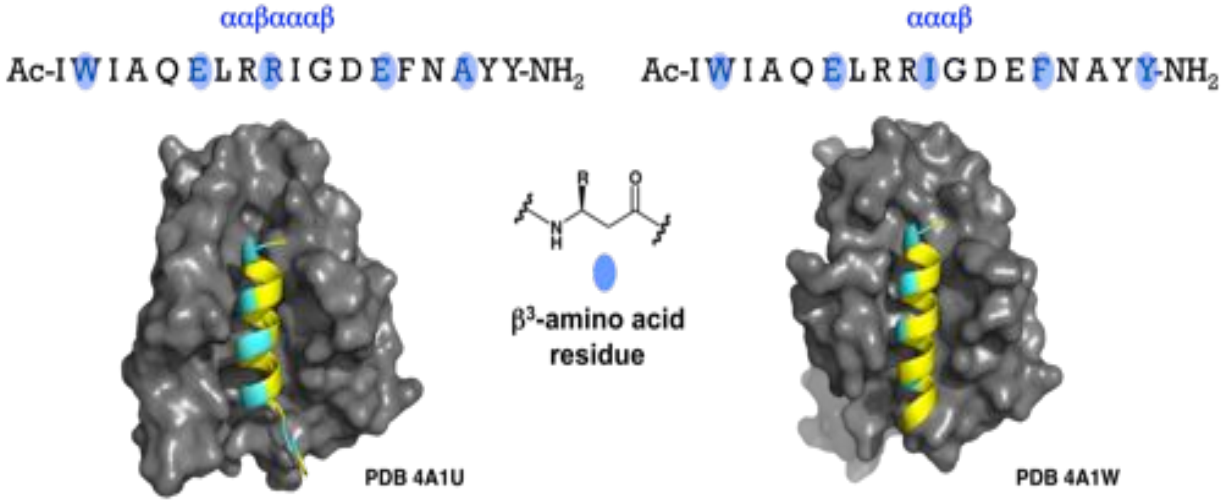


Figure 1. Crystal structures of Bcl-x_L bound to Bim-mimetic α/β-peptides.

Reference

Boersma, M. D.; Haase, H. S.; Peterson-Kaufman, K. J.; Lee, E. F.; Clarke, O. B.; Colman, P. M.; Smith, B. J.; Horne, W. S.; Fairlie, W. D.; Gellman, S. H. *J. Am. Chem. Soc.* **2012**, *124*, 315.

Nanoparticles and (Bio)molecular Recognition: Engineering the Interface for Sensing and Delivery

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Nanoparticles provide versatile scaffolds for multivalent recognition. Our research program focuses on the tailoring of nanoparticle surfaces for a variety of applications, coupling the atomic-level control provided by organic synthesis with the fundamental principles of supramolecular chemistry. We are using engineered nanoparticles for a range of biological applications, including drug/biomolecule delivery and sensing. This talk will focus on the interfacing of nanoparticles with biosystems, and will discuss our use of nanoparticles for sensing, delivery applications, and as therapeutics in their own right.

Reorganization of Polymeric Nanostructures for Controlled Release Applications

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Hollow nanoparticles of either spherical or cylindrical morphologies (nanocages and nanotubes) are highly desirable due to their potential utility as nanoreactors, nanocontainers, purification agents, delivery vehicles and nanofluidic materials. Several synthetic approaches have been developed for their fabrication in solution and in bulk; including layer by layer deposition, templated synthesis, and block copolymer (BCP) self-assembly. A number of reports illustrate the potential of BCP self-assembly for the synthesis of hollow nanoparticles, however they all involve additional synthetic and characterization steps. Efficient, reliable, and scalable processing methods for hollow nanoparticle generation are still needed to match the experimental simplicity of BCP self-assembly.

Herein, we demonstrate the spontaneous formation of hollow block copolymer nanoparticles examined through graphene oxide (GO) TEM supports.[1,2] Hollow spherical (nanocages) and open-end cylindrical (nanotubes) particles are produced by simple drop-casting of aqueous solutions of polyacrylic acid-block-poly(L-lactide) (PAA-*b*-PLLA) micelles onto a GO substrate. By altering the method of dehydration during the casting and drying process, core-compartmentalized or solid core-shell nanoparticles were produced in a controlled fashion. These reorganized nanostructures can be scaled up and harvested from the support and demonstrate interesting and tunable controlled release applications.

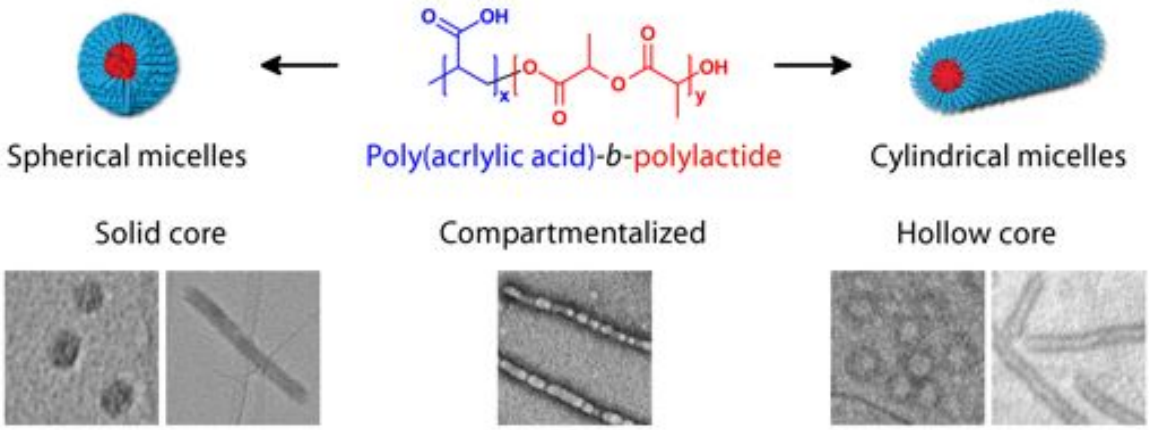


Figure 1. Proposed structural reorganization of PAA-*b*-PLLA micelles.

References

1) Petzetakis, N; Dove, A.P.; O'Reilly, R.K. *Chem. Sci*., **2011**, *2*, 955-960.
2) Patterson, J.P.; Sanchez, A.M.; Petzetakis, N.; Smart, T.; Epps III, T.H.; Portman, I.; Wilson, N.R.; O'Reilly, R.K. *Soft Matter*, **2012**, *8*, 3322-3328.

Intramolecular Indicator-dye Displacement Assay

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To date, much attention has been devoted to develop anion sensors.[1] One of the well-known strategies for anion detection is indicator-dye displacement assay, a term coined by Anslyn et al.[2] However, the major disadvantage of the dye displacement assays is that they are not reversible. To overcome this setback, we developed "Intramolecular Indicator-dye Displacement Assay (IIDA)" as a new approach toward anion sensing. The IIDAs comprises a receptor and a spacer with an attached anionic chromophore in a single-molecule assembly. In the resting state, the environment-sensitive anionic chromophore is bound by the receptor while the anionic substrate competes for binding into the receptor. The photophysical properties of the dye exhibits change in fluorescence when displaced by anions, which results in cross-reactive response.[3] To illustrate the concept, we have prepared sensors **1** and **2**. In this presentation, the characterization of sensors and micro-titer arrays comprising IIDA will be reported.

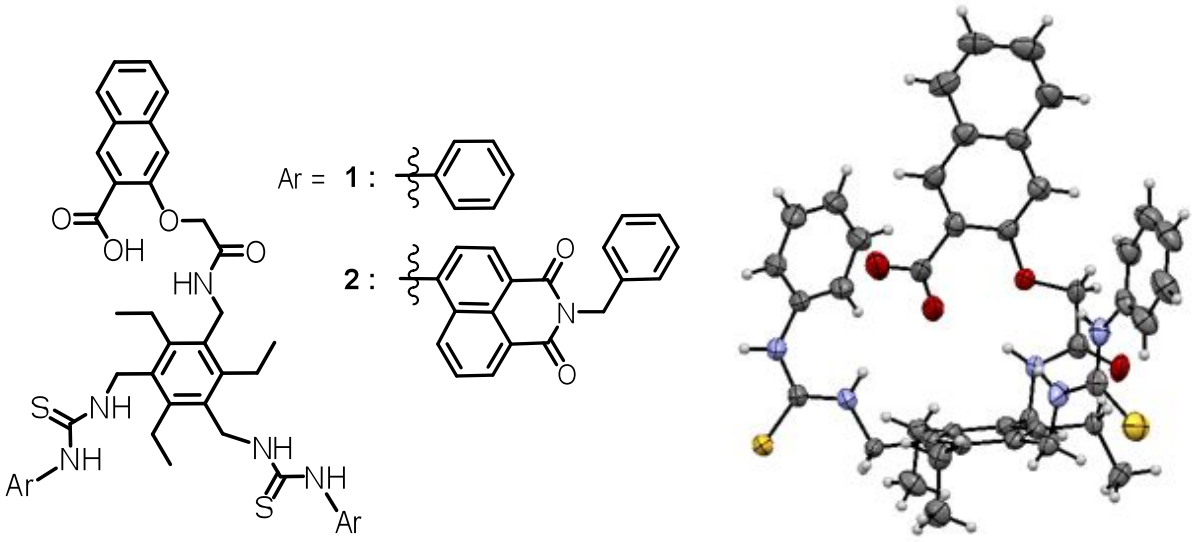


Figure 1. **Left**: Designed sensors **1** and **2** for Intramolecular Indicator-Dye Displacement Assay. **Right**: The structure of **1** determined by X-ray crystallography.

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Differential Anion Binding of a Tripodal Arylethynyl Urea Receptor Over Competitive Hydrogen Bonding Solvents

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Anion sensing is important due to the roles anions play in biological systems and the environment; selectivity in receptors is therefore crucial for applications. Arylethynylpyridine-based scaffolds have demonstrated a differential fluorescence response upon anion binding.[1-3] Expanding upon these systems, new tripodal 1,3,5-tris(arylethynyl)benzene receptors have been synthesized and show anion binding through hydrogen bonds to the three urea groups. The tripodal geometry and the position of the hydrogen bond donors of the ureas are ideal for binding trigonal planar anions such as nitrate. Excess nitrate in soil from over-fertilization is an important concern for the environment; run-off into water sources causes algal blooms, depriving the water of oxygen. Unfortunately, examples of strong and selective nitrate binding in competitive media are few. The tripodal receptor presented here demonstrates preferential binding of anions over competitive hydrogen bonding solvents. The binding mechanism in acetone-d_6 is complex and cannot be fit to a standard model. In 10% DMSO-d_6/$CDCl_3$ the higher order binding is broken up and the receptors bind anions in a 1:1 stoichiometry. A strong affinity for nitrate is observed even in the presence of DMSO, with an association constant of ~10^4 M^{-1} for nitrate and chloride for the trifluoro-substituted tris-urea receptor.

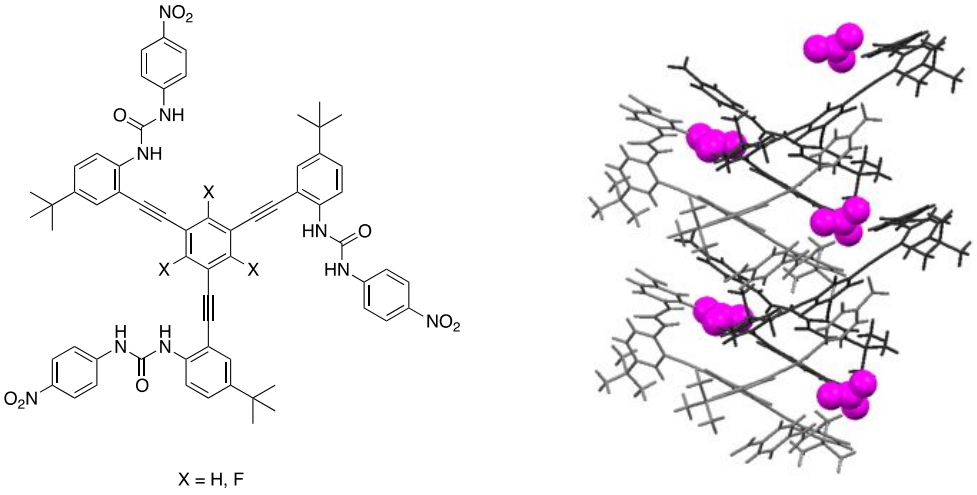


Figure 1. Tripodal 1,3,5-tris(arylethynyl)benzene receptors studied (left). X-ray structure of trifluoro-subsituted system binding nitrate in the presence of acetone (right).

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Developing Stimuli-Responsive Molecular Gels for Detection

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Materials that alter their properites in response to a change in their environment are useful for detecting the presence (or absence) of important chemical species, such as biomarkers, pollutants, and explosives. One promising class of stimuli-responsive materials are molecular gels, which are comprised of self-assembled small molecules that interact via non-covalent interactions. The principle advantage of these materials in a detection platform is that the solution-to-gel phase transition is unambiguous and readily observable without any instrumentation. Our group has been designing, developing and implementing molecular gels as sensors for a variety of different analytes over the past five years. This talk will highlight those efforts, discussing the challenges uncovered along the way, and will conclude with a summary of our generalizable approach to discover new small molecule gelators.

Cucurbiturils at the Interface between Supramolecular Chemistry and Materials Science

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Our research interests include development of controlled polymer architectures, hybrid nanoparticle assemblies, and the integration of dynamic supramolecular systems at interfaces. Using cucurbit[n]urils (CB[n]s) we adopt a simple bottom-up approach to achieve sophisticated designs, which are directed at the preparation of novel microcapsules, dynamic hydrogels, photonic devices and chemical and biological sensors.

Modification of solution viscosity using multivalent polymers and imidazolium-based ionic liquids has been accomplished through dynamic cross-linking in water using CB[8]. These hydrogels, with extremely high water content (up to 99.75% water by weight), have also been prepared by utilising renewable cellulose derivatives. Their rapid formation and shear-induced flow properties make these materials perfectly suited for use as injectable hydrogels for delivery of therapeutics. Indeed, model proteins can be easily encapsulated and their sustained release is observed over the course of 6 months. This far surpasses the current state-of-the-art for protein release from a hydrogel, highlighting these materials as important potential candidates for sustained therapeutic applications.

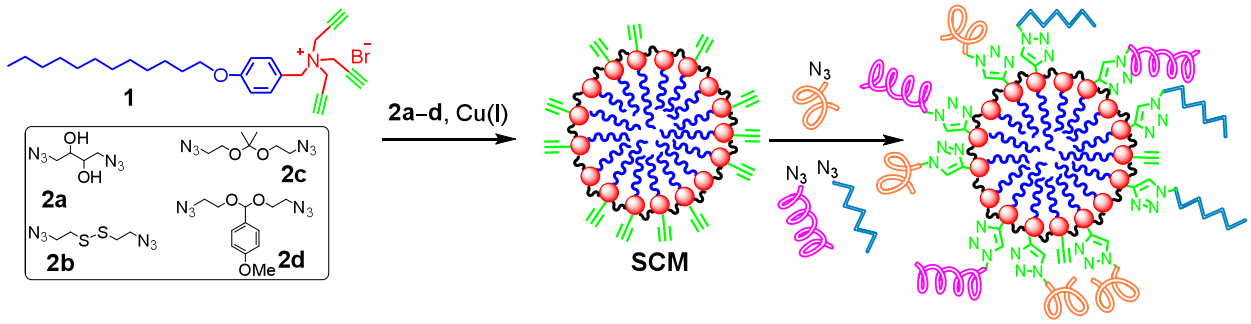
Furthermore, polymer-inorganic composite materials can be readily prepared based on the CB[8] coupling of multivalent gold nanoparticles (AuNPs) to functional copolymers. When these systems are attached onto gold surfaces intricate control is achieved over the site-selective immobilization of colloids and peptides. This has great scope for the development of optical materials, chemical sensors and biological separations. Additionally, we have developed an innovative new technique for manufacturing 'smart' microcapsules in large quantities using continuous flow in a single step from tiny droplets of water. The microdroplets are loaded with copolymers, AuNPs and CB[8]. The major advantage of this manufacturing platform over current methods is that a variety of cargos can be efficiently loaded during the microcapsule formation at room temperature, and the dynamic supramolecular interactions provide control over the porosity of the capsules and the timed release of their contents using stimuli. Our CB[n] based host-guest systems exhibit dynamic self assembly and are capable of responding to stimuli (photochemical, chemical, and thermal) allowing for external control and function to be built into the materials.

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Multivalent, Multifunctional Nanoparticles as Protein and Enzyme Mimics

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Multivalent nanoparticles were prepared by the surface-crosslinking of alkynylated surfactant micelles with a diazide crosslinker (Scheme 1). The click chemistry utilized in both crosslinking and post-functionalization ensures unparalleled functional group compatibility and allows the final functionalized nanoparticles to be prepared in a one-pot reaction at room temperature in water. These surface-crosslinked micelles (SCMs) have great resemblance to protein receptors in their hydrophilic exterior, functionalizable surface, tailored binding site in the interior, and nanodimension but are extremely robust and easy to prepare. When decorated with ligands on the surface, they represent multivalent water-soluble nanoparticles with potential biological applications.[1] When crosslinked by cleavable bonds, they act as "electrostatic bombs" to rapidly release entrapped cargo[2] or surface-active agents[3] on demand. They work as novel fusogens with their tunable size and charged surface to interact with lipid membranes.[4] They provide a tailored microenvironment for organometallic catalysts to form artificial metalloenzymes with high substrate selectivity and excellent recyclability in aqueous biphasic catalysis.[5] They serve as easy-to-synthesize scaffolds to construct artificial light harvesting systems.[6] Their surface and interior can be decorated with catalytic functionalities to make them water-soluble "synthetic enzymes". Hydrophobic binding cavities can be created in their interior with specific shape complementarity to desired guests.



Scheme 1. Preparation of SCM by click-crosslinking the alkynyl groups on the micellar surface.

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Squeezable Tubules from Self-Assembly of Amphiphilic Macrocycles

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Despite recent advances in synthetic nanometer-scale tubular assembly, conferral of dynamic response characteristics to the tubules remains a challenge. I will present supramolecular nanotubules that undergo a reversible contraction-expansion motion accompanied by an inversion of helical chirality. Bent-shaped aromatic amphiphiles self-assemble into hexameric macrocycles in aqueous solution, forming chiral tubules by spontaneous one dimensional stacking with a mutual rotation in the same direction. The adjacent aromatic segments within the hexameric macrocycles reversibly slide over one another in response to external triggers, resulting in pulsating motions of the tubules accompanied by a chiral inversion. The aromatic interior of the self-assembled tubules encapsulates hydrophobic guests such as C60. Using a thermal trigger, we could regulate the C60-C60 interactions through the pulsating motion of the tubules.

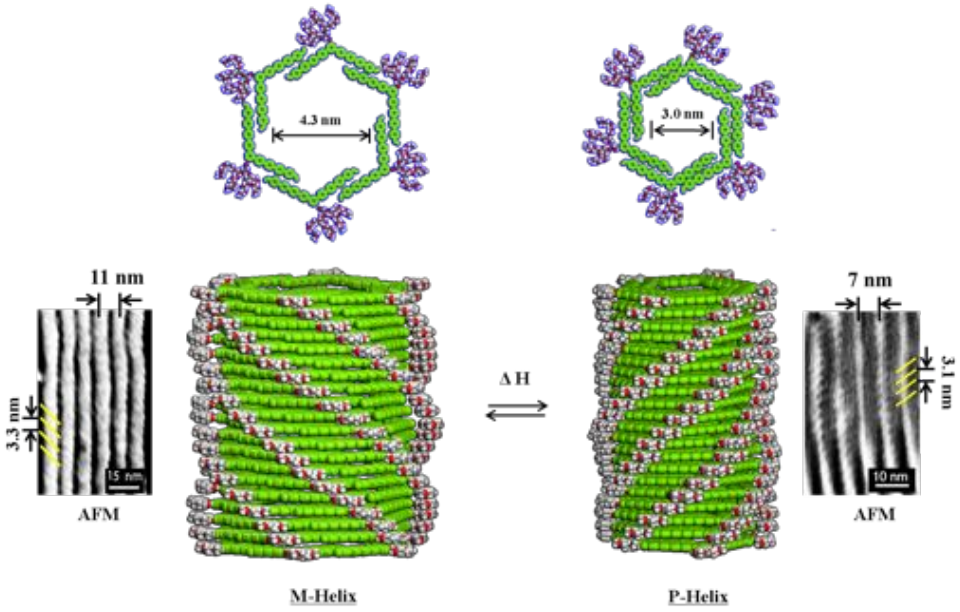


Figure. Self-assembled tubules with contraction-expansion motion

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A Hexadecameric Self-assembled Ligand for G-Quadruplex DNA

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The development of ligands that could target non-canonical DNA structures associated with the regulation of biological processes has recently gained a lot of interest. Particularly, the development of ligands that bind G-quadruplex DNA (QDNA) structures with high selectivity and affinity remains a challenge that must be overcome if QDNA is to become a viable target for pharmacological intervention.[1, 2] Our approach is focused on development of self-assembled ligands (SALs) where the constituent 8-aryl-2'-deoxyguanosine (8ArG) subunits form a supramolecular G-quadruplex (SGQ), which becomes the active ligand. Specifically, we report on the interactions between the hexadecameric SGQ from the 8ArG derivative**-1** and a dimer of tetramolecular QDNAs from the oligonucleotide 5'-d(TTAGGG)-3'.[3] Formation of $\mathbf{1}_{16}$ leads to a supramolecular ligand that binds to the 3'-terminal G-quartet surfaces at the interface between the QDNA dimer driven by the excellent size, shape and charge complementarity. The stoichiometry, thermodynamic stability and 3D-structure of the QDNA•$\mathbf{1}_{16}$•QDNA complex were evaluated by 1D/2D-NMR, DSC, DLS and molecular modeling studies. The results of these studies have validated 8ArG derivatives as a new generation of self-assembled QDNA ligands, paving the way to our long term goal of developing similar SALs as novel supramolecular anticancer treatments, cellular imaging probes and other biomedical applications.

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Highly Cooperative Binding of Ion-Pair Dimers by a Bis-Calix[4]pyrrole Macrocyclic Receptor

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Calix[4]pyrroles are known to function as heteroditopic receptors of ion-pairs.[1] On that basis, we have demonstrated that receptor **1**[2] (Figure 1) having two calix[4]pyrrole binding sites affords the effective binding of the ion-pair dimers **2a** and **2b** yielding $\mathbf{2}_2\subset\mathbf{1}$ complexes through a highly cooperative process ($\alpha > 10^5$). The cascade-like arrangement complexes of ion pairs are formed by: one ion-pair bound in a host-separated geometry and the other in a close contact binding mode. Interestingly, the exclusive and quantitative formation of the ion-pair hetero dimers **2a2b**$\subset$**1** can be also achieved. The use of the ion pair **3** containing a methyltrioctylammonium cation instead of the tetrabutylammonium renders a binding process significantly less cooperative. As result, the homodimeric complex $\mathbf{3}_2\subset\mathbf{1}$ places both ion-pairs bound in a receptor-separated binding mode. The equimolar combination of $[N(C_4H_9)_4]^+$ and $[NCH_3(C_8H_{17})_3]^+$ salts allows the self-assembly of hetero ion quartet complexes with cascade arrangement by means of a cooperative binding process. Importantly, in these latter mixed complexes, the $[NCH_3(C_8H_{17})_3]^+$ cation is selectively included in the shallow electron rich cavity formed by the pyrrolic rings of a calix[4]pyrrole scaffold.

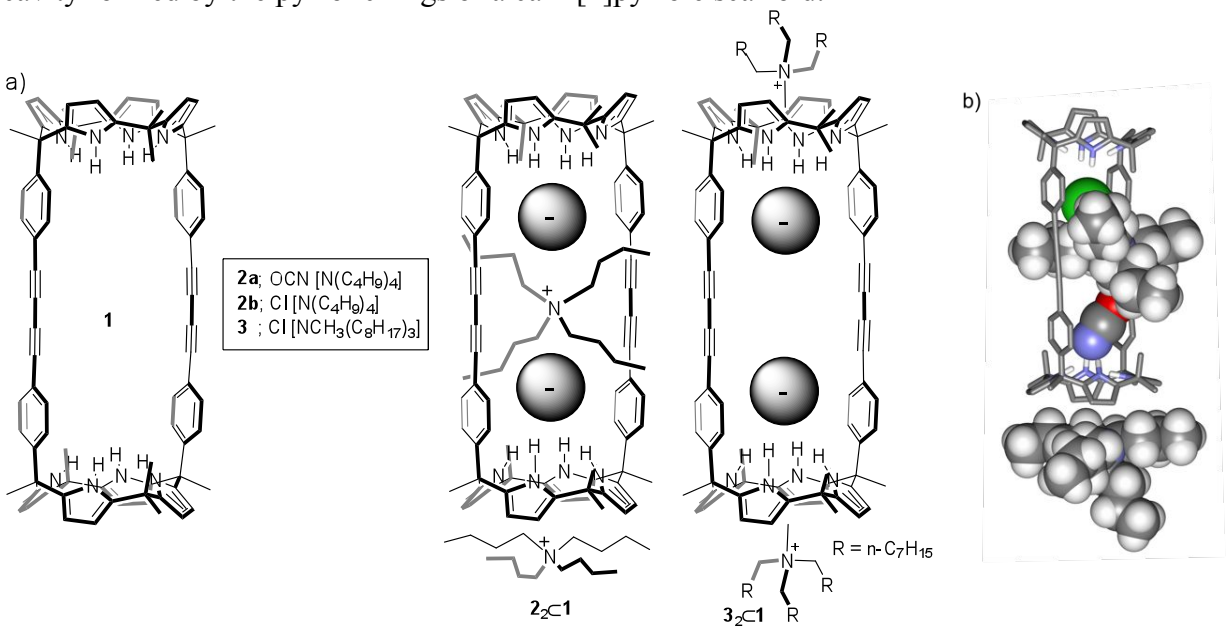


Figure 1. a) Molecular structures of bis-calix[4]pyrrole receptor **1**, the ion-pairs **2** and **3** and the dimeric ion-pair complexes $\mathbf{2}_2\subset\mathbf{1}$ and $\mathbf{3}_2\subset\mathbf{1}$; b) X-ray structure of the cascade complex **2a2b**$\subset$**1**.

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Photo-Switching on Nanoparticles

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Molecular and supramolecular switches have attracted considerable interest since their structures and properties can be tuned by external stimuli such as light and temperature. On account of unique and size-dependent optical, electronic, and catalytic properties of nanoparticles (e.g., gold nanoparticles, quantum dots, and mesoporous silica nanoparticles), the combination of the beneficial characteristics of molecular/supramolecular switches and nanoparticles can lead to the birth of novel hybrid materials. Our recent research indicates that the immobilization of photo-switches on the nanoparticle surfaces does not hamper their switching ability, and the photo-switching can be employed to modulate nanoparticle properties for further applications.[1-6]

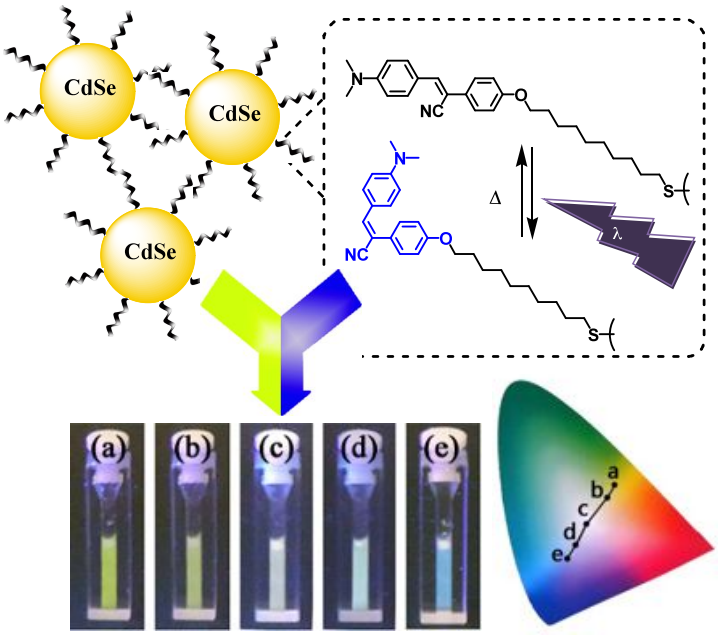


Figure 1. Photo-responsive organic dye based on cyanostilbene was functionalized onto the CdSe surface. The hybrids reveal a photo-tunable dual fluorescent characteristic.[5]

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Unidirectional Linear Motion in Redox-Active Molecular Machines

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Control of chemical processes is fundamental to the biological molecular machines of life.[1] These machines must operate with specific and precise timings in order to achieve controlled motion. In order to mimic nature, we have designed (Figure 1) and synthesized a supramolecular system based on the macrocyclic π-electron acceptor cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) and a thread containing two different redox-active π-electron donors in the shape of a tetrathiafulvalene (TTF) unit and a monopyrrolo-TTF (MPTTF) unit.[2]

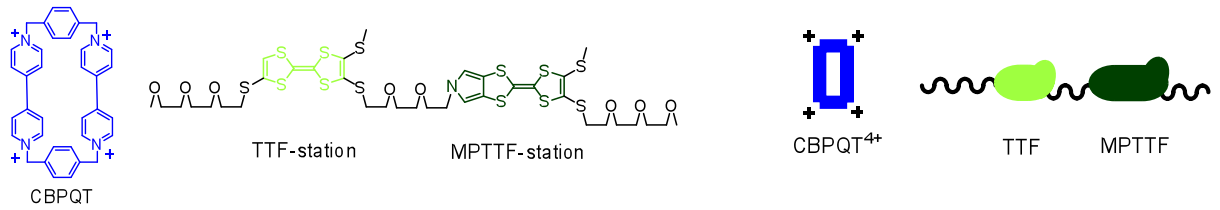


Figure. 1. Molecular structures and cartoons of $CBPQT^{4+}$ (blue) and a thread containing TTF (light green) and MPTTF (dark green) stations.

In this presentation, the synthesis of the TTF-MPTTF thread will be discussed, thereafter it will be demonstrated that the TTF-MPTTF thread upon mixing with $CBPQT^{4+}$ followed by thermodynamically equilibration and chemical oxidation leads (Figure 2) to a supramolecular system capable of performing unidirectional motion with an efficiency greater than 20%.

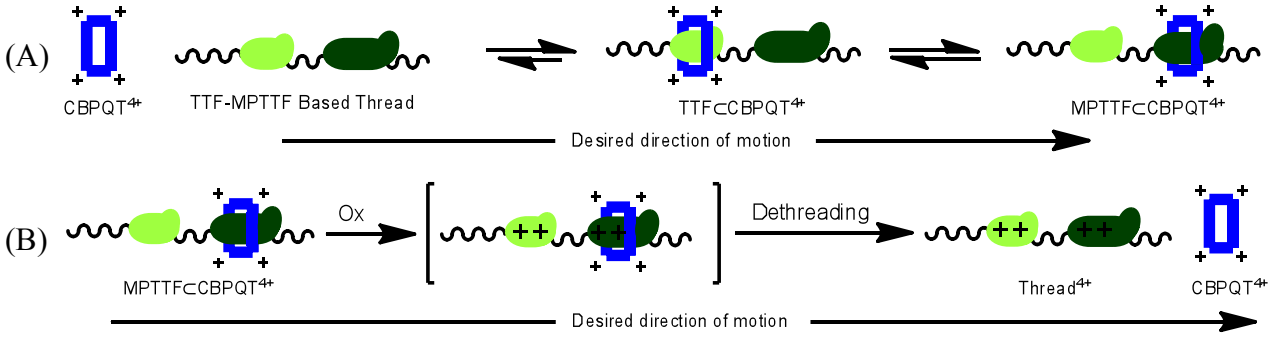


Figure 2. A cartoon representation illustrating (A) movement of $CBPQT^{4+}$ from left to right and (B) further movement of $CBPQT^{4+}$ to the right as a result of oxidation of the [2]pseudorotaxane $MPTTF\subset CBPQT^{4+}$.

References 1) Kinbara, K. ; Aida, T. *Chem. Rev.* **2005**, *105*, 1377–1400.
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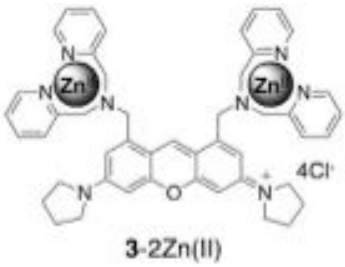
Design of Fluorescent ATP Chemsensors Useful Under Living Cells

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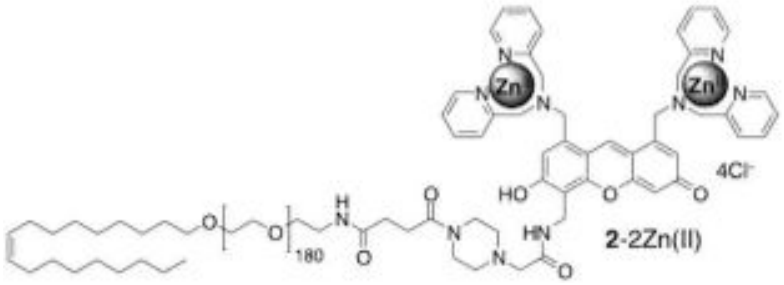
Since ATP and its derivatives (nucleoside polyphosphates (NPPs)) are implicated in many biological events, their rapid and convenient detection is of importance. In particular, live cell detection of NPPs could greatly contribute precise understanding of the complicated roles of NPPs. We report herein the molecular design of fluorescent chemosensors and their unique signal switching mechanisum that can detect NPPs in living cells. These chemosensors are based on xanthene (or pyronin)-based dinuclear Zn(II) complex **1**-2Zn(II). [1] Detailed spectroscopic and crystallographic studies revealed that these chemosensors can sense NPPs with about 10-fold increase of their fluorescence intensities through a sensing mechanism involving binding-induced recovery of the conjugated form of the xanthene or pyronin ring. More interestingly, these can work well not only in aqueous buffer solution, but also under live cell conditions. For example, **2**-2Zn(II) containing a lipid anchor selectively localized on the plasma membrane surface of live cells and detected the extracellular release of NPPs in cell necrosis induced by streptolysin O. On the other hand, rhodamine-type complex **3**-2Zn(II) spontaneously localized at mitochondria inside cells, and sensed the local increase of ATP concentration during apoptosis. [2,3] Multicolor images were also obtained through simultaneous use of them.



1-2Zn(II)



3-2Zn(II)



2-2Zn(II)

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Molecular Recognition at Interfaces: Implications in Sensing and Polymer Science

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Molecular recognition is one of the key functions to be implemented in responsive materials. The use of supramolecular structures has proven to be one of the best approaches to generate responsive materials. In order to make full use of them, general and effective strategies must be devised to attain the macroscopic expression of these molecular processes. The transfer of the intrinsic molecular recognition properties of a given receptor from solution to interfaces requires the mastering of weak interactions at interfaces.[1] In this contribution the following cases will be discussed, which have in common the use of phosphonate cavitands as receptors:
1. Molecular recognition at the solid-liquid interface: supramolecular sensors for drugs and cancer biomarkers in water and urine.[2] The energy of the molecular recognition between phosphonate cavitands and alkyl ammonium salts can be harnessed to perform a nanomechanical task in an univocal way (Figure 1).[3] 2. Molecular recognition at the solid-solid interface: Host-guest driven reversible polymer blending, the next challenge after the self-assembly of supramolecular host-guest polymers and copolymers.[4]

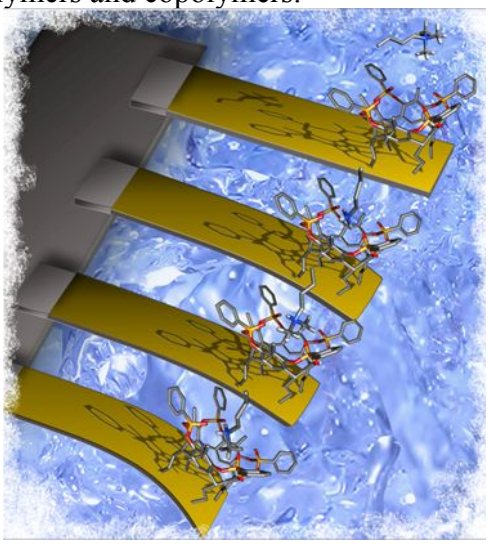


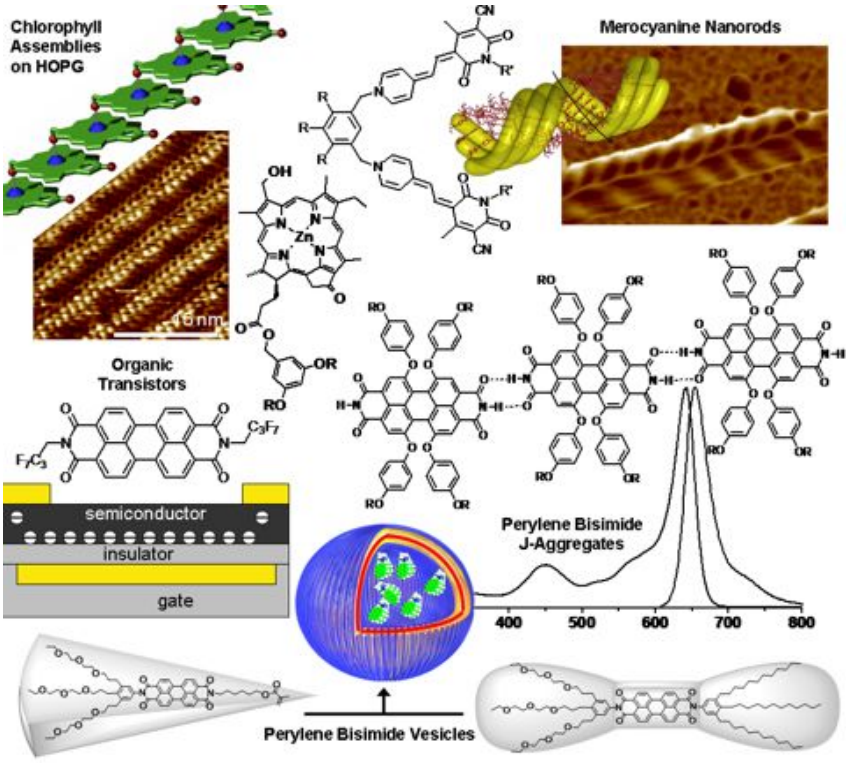
Figure 1. Nanomechanical sensing of alkyl ammonium salts.

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Functional Nanosystems Based on Dye Aggregates

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Research on dye molecules has been continuing to be at the forefront of new developments in chemistry owing to their versatile functional properties associated with π-conjugation. On a supramolecular level, appropriately controlled spatial arrangement of dyes enables pivotal functions in nature, the most intriguing examples being provided by the light-harvesting systems of purple and green bacteria which contain a large number of chlorophyll and carotene chromophores organized in cyclic arrays or tubular architectures by non-covalent interactions. During the last years, we have intensively investigated the self-assembly of chlorophyll, merocyanine, and perylene bisimide dyes by non-covalent forces into desirable nanoscale architectures. In this lecture, I will provide an overview on our achievements in the preparation of defined dye assemblies starting from a detailed characterization of binding strengths and self-assembly pathways.[1] Functional properties originating from electronic and excitonic interactions will be discussed as well.[2-4]



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High-Fidelity Self-Sorting of Dynamic Combinatorial Libraries Under Irreversible Physical and Chemical Stimuli

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Nature achieves absolutely selective synthesis of extremely complex molecules, starting from complicated "soups" of chemicals present in a cellular environment. In contrast, laboratory synthesis appears largely reductionist: most synthetic transformations combine just two high-purity precursors with a high-purity catalyst, often in the absence of air and moisture, to produce a third chemical. Our research aims to bridge this divide by introducing parallel synthesis into the realm of synthetic organic chemistry. To do that, we use equilibrating mixtures of compounds known as dynamic combinatorial libraries (DCLs), which respond to external stimuli by amplifying their components that best adapt to such stimuli. If that stimulus is an irreversible chemical reaction, a DCL will first express its most reactive constituent, which will in turn extract its components from other library members that contain them. Sequential application of this principle leads to self-sorting: spontaneous simplification of a DCL with n^2 members into just n pure products. We have shown that this process can operate under chemical[1] or physical—distillation[2] or precipitation[3]—conditions. This protocol could be of utility in basic chemical industry, where multiple value-added chemicals (e.g. esters) could be produced in a single reaction tower from a "messy" mixture of starting materials.

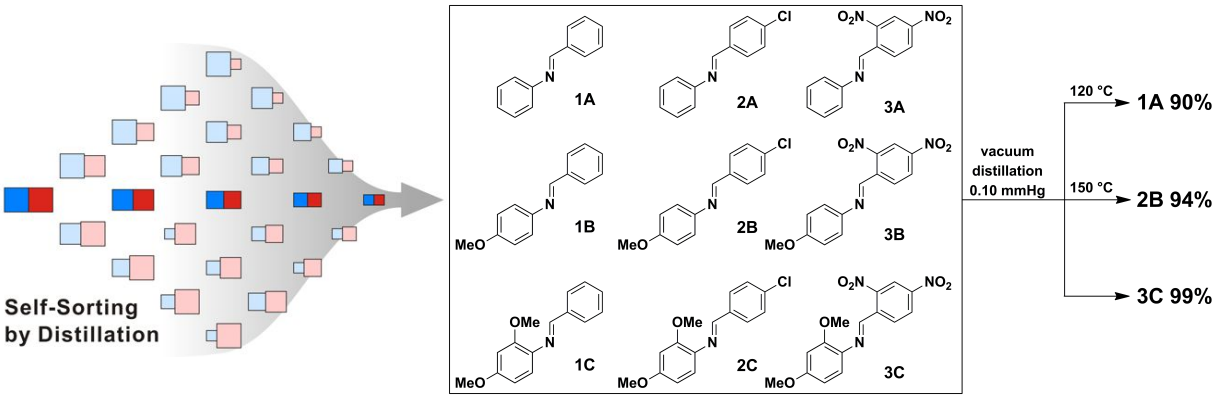


Figure 1. Schematic representation of a self-sorting process (left) and an example of its use in the distillative preparation of three high-purity imines (right).

References

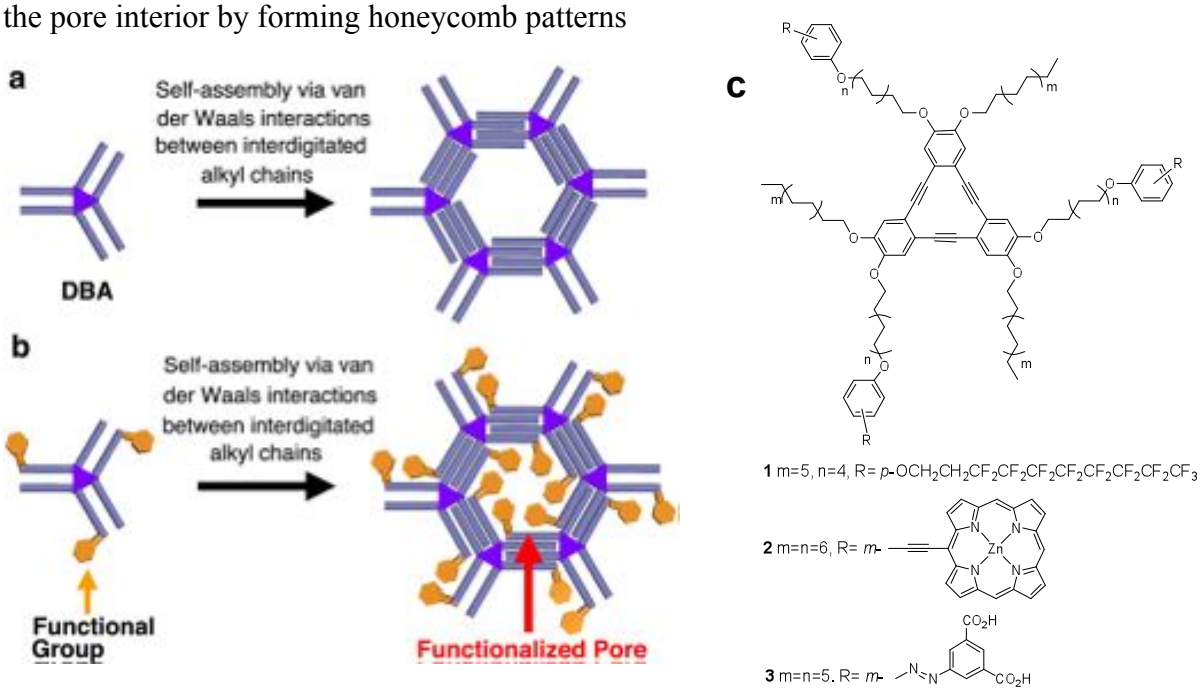
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Host-Guest Chemistry in Two-Dimensional Space

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Construction of two-dimensional (2D) porous patterns on solid surfaces using molecular self-assembly is a subject of intense current interest in view of perspectives for unique applications such as tailor-made catalysts. One of the challenges in the 2D porous system is physical (i.e. size and shape) or chemical (i.e. electrostatic properties) modification of the interior space of the porous networks to construct tailored functional pores.

Here we report on the functionalization of 2D pores formed by self-assembly of designed triangular building blocks bearing functional groups at a liquid-solid interface. To tailor pore interior alkoxylated dehydrobenzo[12]annulene (DBA) derivatives were chosen as building blocks because of their strong tendency for the formation of porous honeycomb patterns at the liquid/solid interface (Scheme 1a).[1] We designed DBAs **1**–**3** with functional groups such as perfluoroalkane, porphyrin, and dicarboxyazobenzene, respectively, attached at the end of three of the six alkyl chains in an alternating fashion. Consequently, the functional groups are located at the pore interior by forming honeycomb patterns



Scheme 1. A representation for self-assembly of DBAs: (a) the parent DBA forming a honeycomb 2D structure with *vacant* pores and (b) a DBA with functional groups at three alternating alkyl chains forming a honeycomb 2D structure with functionalized pores. (c) DBAs **1**–**3** bearing functional groups.

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Pillararenes: Easy-to-Make and Versatile Receptors for Supramolecular Chemistry

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The construction of supramolecular structures has attracted much attention not only from chemists but also from biologists and physicists as a bottom-up procedure to construct nano-scale architectures. Macrocyclic compounds play a major role in supramolecular chemistry because of their beautiful shape, nano-scale size and molecular recognition ability. Numerous supramolecular architectures have been constructed and studied as new components of materials as well as entities related to biological structural formation and functions using various macrocyclic hosts such as cyclodextrins, crown ethers, calixarenes and cucurbiturils.

In 2008, we reported a new class of macrocyclic hosts named "pillararenes" (Figure 1).[1] Pillararenes have repeating units connected by methylene bridges at the para-position, and thus they have a unique symmetrical pillar architecture differing from the basket-shaped structure of meta-bridged calixarenes. Synthesis of pillararenes is easy-to-make. They can be synthesized in high yield by reacting commercially available reagents. The reaction was completed in 3 minutes. Pillararenes also show versatile functionality similar to cyclodextrins. Based on the various synthetic approaches, position-selective mono-, di-, tetra-, penta- and per-functionalization of pillararenes can be achieved. Pillararene can capture electron accepting guest molecules within their cavity similarly to cucurbiturils. Because of their unique pillar-shaped architectures, high yield synthesis, outstanding host–guest properties, planar chirality and functionality, pillararenes are useful platform to construct various supramolecules including rotaxanes, catenanes, supramolecular polymers and sensors.[2]



Figure 1. Chemical and single X-ray crystal structures of pillar[5]arene

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Bambusuril Macrocycles for Anion Binding

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Bambusurils are family of macrocyclic compounds which consist of glycoluril building blocks connected by methylene bridges.[1,2] Since discovery of their first member, several bambusurils have been prepared differing by substitution on glycoluril units and a number of repeating units within a cycle. Based on the type of substitution, bambusurils are soluble in both non polar and aqueous solvents. The cavity interior of bambusuril macrocycles is significantly positively charged, whereas negative charge is located on the oxygen atoms at the portals. This is the reason why six-membered bambusurils are able to bind various anions inside their cavity. In our presentation we will summarize the most important supramolecular properties of bambusurils. Approaches to the bambusuril functionalization will be discussed as well as design of those derivatives with enhanced affinity and selectivity toward anions which play central roles in biology and also anions which represent a significant threat for the environment.

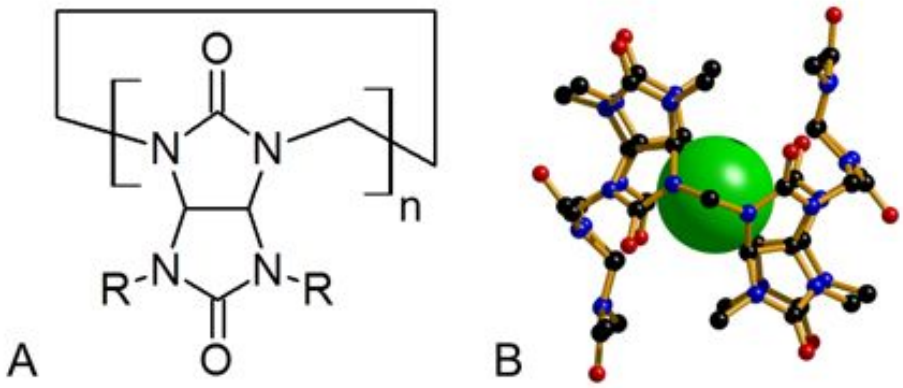


Figure 1. (A) General structure of bambusurils and (B) crystal structure of dodecamethylbambus[6]uril – chloride complex.

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Multifunctional Nanoballs and Variable Length Ligands

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We have synthesised large (2.7 nm) spherical metallosupramolecules ('nanoballs') with interesting properties.[1] Metal ions can be varied with retention of overall structure and crystal packing, or new nanoball packing arrangements achieved by varying counterions and solvent molecules. Properties include switching between two magnetic spin states (spin crossover) upon change in temperature or irradiation of light. The molecular packing creates cavities within the solid state, and the crystals will readily absorb solvents such as methanol, acetonitrile or acetone (which also changes the magnetic properties), and also absorb significant amounts of hydrogen and CO_2 (but not CH_4), pointing to a new class of porous materials. Preliminary results have also indicated the possibility of size-selective catalysis.

We have also discovered a new type of bridging ligand in which the bridging length can be controlled by the presence or nature of e.g. group I or II metals.[2] The ligand contains a central crown ether cavity and peripheral metal binding pyridyl groups. In the absence of a guest the bridging length is typically *ca.* 7.7 Å. In the presence of K^+, however, the bridging length more than doubles (*ca.* 16 Å). Other crown bound species give intermediate bridging lengths.

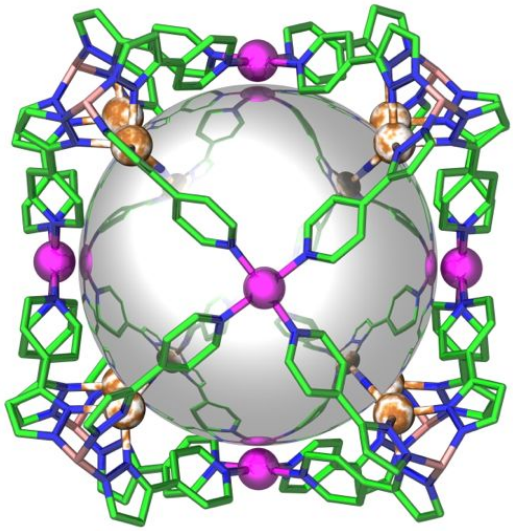


Figure 1. A nanoball.

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Phosphate Coordination by Oligoureas

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Phosphate ions play important roles in many biological, environmental and chemical processes, such as the transformation between ATP and ADP and eutrophication of aquatic systems, etc. However, study of the phosphate chemistry is challenging due to the different forms of phosphate (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4) varying with the external pH. The orthophosphate ion (PO_4^{3-}) has been theoretically proven to have the largest binding energy with six urea moieties compared to other tetrahedral oxoanions (ClO_4^-, SO_4^{2-}). We have synthesized a series of oligourea ligands by mimicking the oligopyridines, which show high affinity and complementarity to phosphate ion. The trisurea receptors display complementary binding with tetrahedral anions and achieve saturated coordination with PO_4^{3-} in a 2:1 (host/guest) complex (Figure 1a). An ethylene-bridged bis(bisurea) ligand assembles with PO_4^{3-} to generate the first triple anion helicate (Figure 1b). Moreover, a C_3-symmetric tris(bisurea) ligand was designed and assembles with phosphate to afford the first $[A_4L_4]$-type tetrahedral anion cage $[(PO_4)_4L_4]^{12-}$ held together by 48 hydrogen bonds (Figure 1c). These results demonstrate the coordination saturation (12 hydrogen bonds) and geometry (arrangement of six urea groups in an approximately octahedral environment) of phosphate ion, which ensures the formation of desired supramolecular structures based on anion coordination.

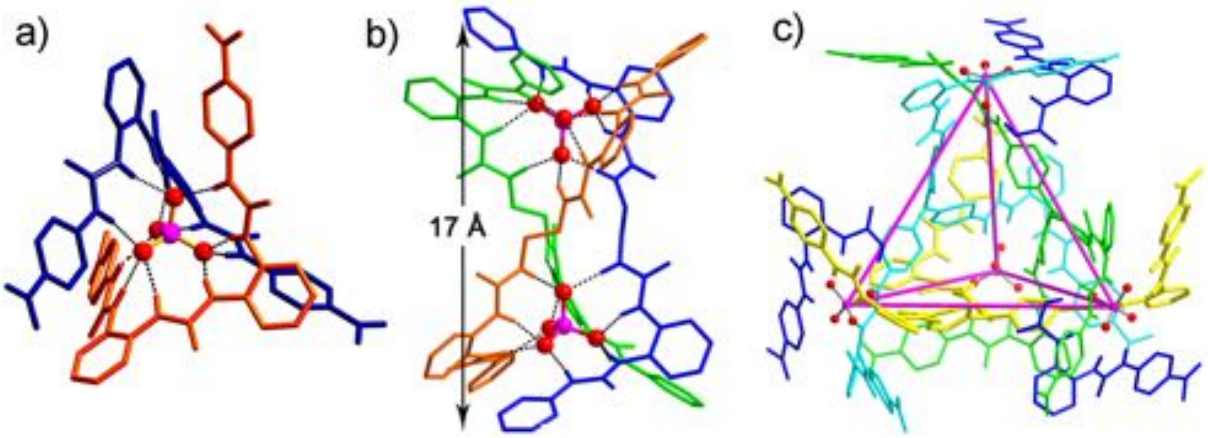


Figure 1. Phosphate coordination with oligoureas.

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Supramolecular Synthesis and Control of Reactivity in Organic Solids

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In this presentation, a method being developed in our laboratory that enables noncovalent bonds to be utilized, in a general way, to direct the formation of covalent bonds will be described. We show how small organic molecules and inorganic complexes act as templates by assembling olefins into prescribed geometries in the solid state to undergo photochemically induced [2+2] cycloadditions. We demonstrate how the template method effectively enables the crystal engineering of molecules (e.g. ladderanes) that form stereoselectively, in quantitative yield, and in gram amounts. Relevance and applications of the method to the fields of chemical synthesis (e.g. catalysis), materials science (e.g. optical properties), and molecular nanotechnology (e.g. organic nanocrystals) will be discussed. Related work in the fields of organic semiconductors will also be presented.

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Biocompatible Supramolecular Nanovalves for Controlled Cargo Release

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Encapsulation of anticancer drugs within nanocarriers that selectively target diseased cells promises to increase the effectiveness of conventional chemotherapy and decrease its side effects, representing a hot research topic in recent years. Mesoporous silica nanoparticles (MSNs) are particularly interesting candidates for powerful drug carriers because of their unique characteristics and abilities to efficiently and specifically entrap cargo molecules, and show great potential as superior intelligent drug delivery platform.[1] Synthetic macrocyclic compounds are promising candidates for applications in the field of drug delivery and cancer therapy. Installing supramolecular nanovalves based on molecular machines constructed from different macrocyclic compounds, i.e., crown ethers, cyclodextrins, cyclophanes, cucurbiturils, and pillararenes, on the surfaces of MSNs can significantly improve the biocompatibility and gated properties of this type of materials for on-command cargo delivery and release (Figure 1).[2-6] In this presentation, I will talk about some recent developed "smart" cargo/drug delivery systems in our research laboratory, which comprise MSNs functionalized with well-defined self-assembled layers of biocompatible supramolecular nanovalves based on macrocycles (cucurbiturils, calixarenes and pillararenes in particular) and with well-defined stimuli-responsive supramolecular polymers, and their successful operation under a range of external stimuli.

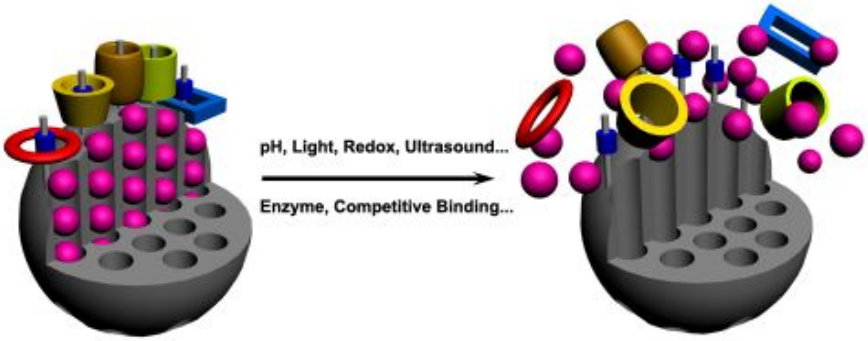


Figure 1. Schematic diagram of supramolecular nanovalves based on different macrocycles.

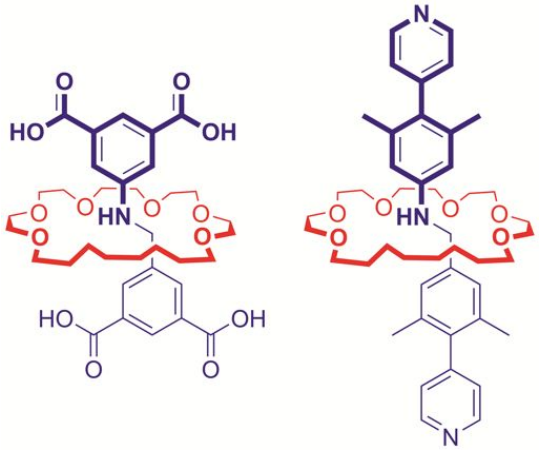
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Organizing Mechanically Interlocked Molecules to Function Inside Metal-Organic Frameworks

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A variety of artificial molecular switches and machines that are based on the relative motion of the constituent components of mechanically interlocked molecules (MIMs) have been reported.[1] However, these and other elaborate molecular systems only operate in solution or in a condensed phase where the molecular devices are randomly dispersed and their motion incoherent. If these tiny devices could be organized in a predictable and orderly manner, the ideas of creating ultra-dense molecular-based memory or controlling electronic properties of materials at the molecular level would be very much closer to realization. One way to achieve a higher level of molecular organization and coherency would be to precisely place the "soft" dynamic molecular components that undergo motion (*e.g.* rotation or translation) into the pores of metal organic framework (MOF) materials In this way, the "soft" MIM would be clearly separated from the "hard" structural skeleton of the MOF that holds it in place.[2] If this could be accomplished, the small size of a MIM unit (~1 nm^3) and the regularity of a MOF framework would allow for an incredibly high density of dynamic components in a material: ~10^{21} per cm^3. The ability to arrange mobile and functional molecular components in a highly dense and predictable array is a crucial step towards the generation of solid-state devices with multiple functions and properties. This presentation will describe our newest MOF materials containing MIM linkers capable of rotational and translational motion.



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Artificial Molecular Motors

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A long-term goal of modern science is to devise artificial, small molecule motors which harness energy, in the form of simple and versatile inputs such as light or electrical potential, in order to perform useful work.[1] Here, we report our recent progress in this arena, aided and abetted by the remarkable properties of the cyclophane cyclobis(paraquat-*p*-phenylene) (**CBPQT**$^{4+}$)—which has a well-established proclivity to bind electron-rich guests, and has recently been shown to possess rich redox chemistry.[2] We describe a prototypical pseudorotaxane system in which a ring repeatedly and autonomously traverses a dumbbell **D**$^{+}$ in one relative direction, powered by photons of light. We have also made progress towards a second generation system that can store some of the energy it processes in the form of a meta-stable inclusion complex, in which **CBPQT**$^{4+}$ is effectively snared in an unfavorable position on a viologen-containing dumbbell. The unique attributes of **CPBQT**$^{4+}$ – which acts as a conduit for the transformation of chemical, electrical, or light energy – are vital to the operation of both these systems.

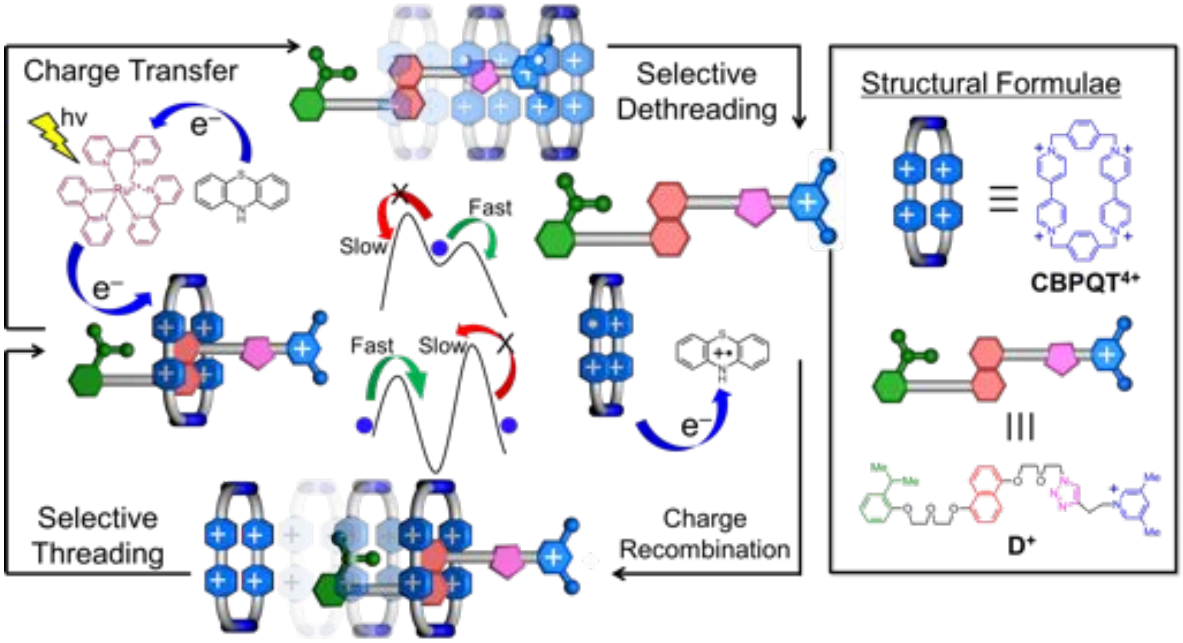


Figure 1. Graphical representation of the unidirectional and autonomous association and dissociation of a redox active macrocycle and linearly asymmetric dumbbell, powered by light.

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Metal-Centered Supramolecular Assembly

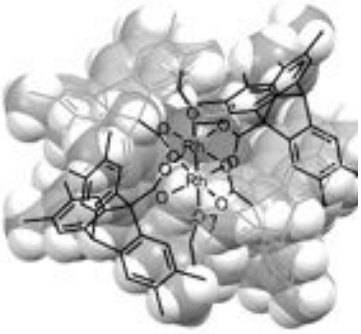
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Metal ions can provide a platform for molecular self-assembly leading to well-defined structures with specific physical and chemical properties. By rational ligand design, metal selection, and optimization of chemical surrounding, the metal-centered self-assembled structures and the self-assembly processes can be predicted more quantitatively.

Herein we present our recent advances in metal-centered supramolecular design and synthesis, taking examples of metal-aided stabilization of novel bio-related structures,[1] self-assembled hollow complexes by metal-metal interactions,[2] and metal-centered construction of multi-gear systems.[3]







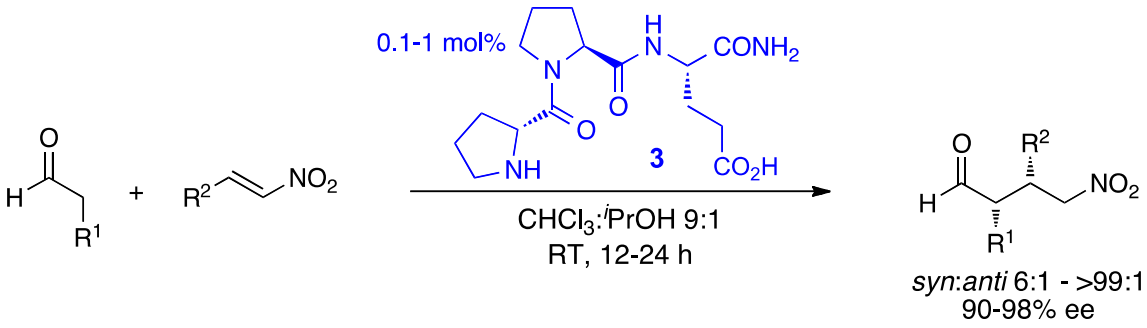
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Peptides as Asymmetric Catalysts

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In nature, proteins fulfill manifold different functions and are crucial as, for example, enzymes or templates for the controlled formation of structural components such as bones. The Wennemers group is intrigued by the question whether also peptides with significantly lower molecular weights compared to proteins can fulfill functions for which nature evolved large macromolecules. Specifically we ask whether peptides can serve as effective asymmetric catalysts, templates for the controlled formation of metal nanoparticles, synthetic collagen based materials, or tumor targeting vectors.

The lecture will focus on the development of peptides as asymmetric catalysts. Tripeptides of the general type H-Pro-Pro-Xaa (Xaa = amino acid with a carboxylic acid) will be presented that are effective catalysts for aldol reactions and conjugate addition reactions between aldehydes and nitroolefins.[1] The peptides allow for enamine catalysis with catalyst loadings of as little as 0.1-1 mol% and provide synthetically versatile products in high stereoselectivities. Several synthetically valuable compounds such as γ-amino acids, pyrrolidines, γ-butyrolactones and γ-butyrolactams are easily accessible using this methodology.



The scope of these peptide-catalyzed reactions will be presented and recent insight into the mechanism as well as the importance of the conformational properties for effective catalysis will be discussed.[1-4]

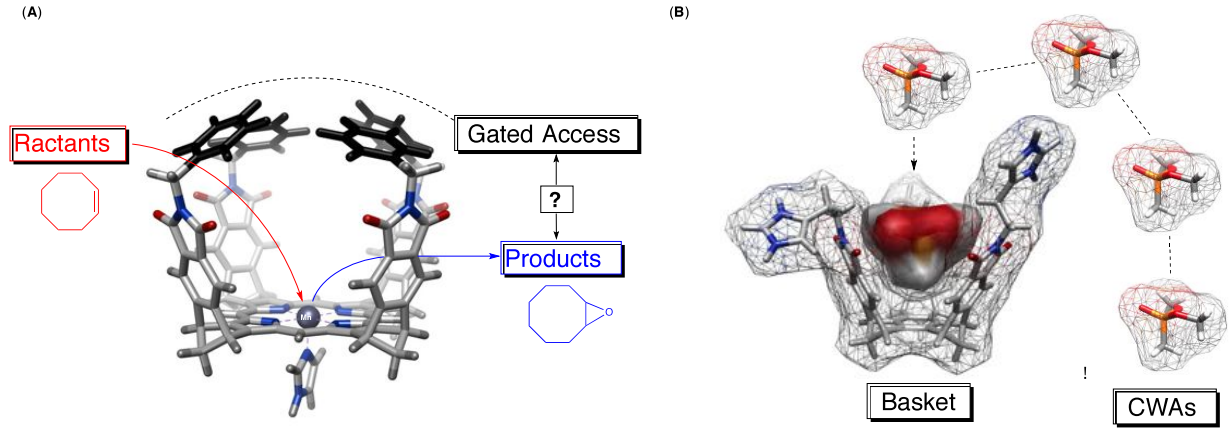
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Gated Molecular Recognition and Reactivity

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The entrapment of guest compounds with artificial hosts[1] allows for controlling local environment and properties of a variety of analytes. In particular, one can use molecular encapsulation for stabilizing reactive intermediates, promoting chemical reactions and modulating conformational dynamics of guests. Interestingly, the incorporation of dynamic elements of design, i.e. aromatic gates, into hosts is important for regulating the activation energy ($\Delta G^{\ddagger}_{in/out}$) characterizing the ingress/egress of guests.[2] Gated encapsulation thus allows for tuning the persistency (lifetime) of encapsulation complexes[3] yet not much is know about the utility of molecular gating for directing the outcome of chemical reactions and/or a precise delivery of useful compounds. The lecture will focus on presenting our efforts toward understanding working mechanisms[4,5] of gated baskets in controlling the kinetics of molecular recognition (see Figure A). We will also describe the utility of gated hosts for entrapment/degradation of nerve agents (see Figure B).



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A Versatile Model System for Studying Non-covalent Interactions of Aromatic Surfaces

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Non-covalent interactions of aromatic surfaces are important to the function of many synthetic and biological systems.[1] Yet, the fundamental origins and stability trends of these weak interactions are still a subject of considerable study and debate. One reason is the lack of accurate and comprehensive experimental data. To address this problem, we developed a small molecule model system that can form and accurately measure the strength of intramolecular interactions of aromatic surfaces.[2] Due to a central N-arylimide single bond with restricted rotation, the rigid bicyclic framework is in equilibrium between *folded* and *unfolded* confirmations, which can and cannot form the intramolecular noncovalent interaction. Thus, measurement of the folded/unfolded ratio by ^{1}H NMR integration provides a measure of the interaction of interest. Due to the synthetic versatility and ease of preparation, we have applied this model system to study a range of noncovalent interactions of aromatic services including: face-to-face π-stacking,[2] edge-to-face π-stacking, CH-π,[3] deuterium(CH)-π,[4] halogen-π, heterocyclic π-stacking, cation-π and lone pair-π interactions.

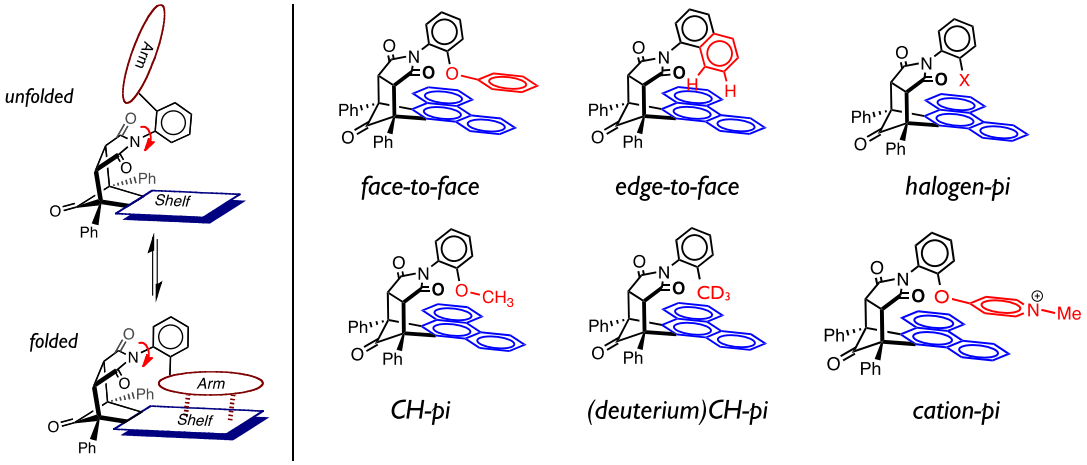


Figure 1. (*left)* Schematic representation of our molecular balance for measuring non-covalent interactions of aromatic surfaces. (*right*) Specific examples

Three Short Stories of Analytical Supramolecular Chemistry

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Over the last fourteen years our group has worked in a field we have referred to as supramolecular analytical chemistry, where our own pursuits meld covalent and non-covalent organic/inorganic reactivity with standard analytical techniques such as chemometrics to create assays for various real-life applications. In this lecture, three short stories, starting from the inspiration for the idea, up to the current implementation, will be presented.

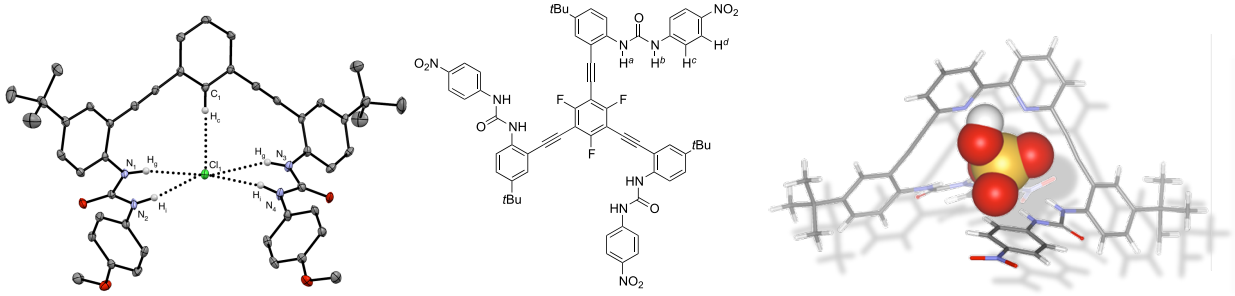
The first discussion will follow the history of citrate sensing in our group, starting with the initial design concept, moving to applications in soda-pop and flavored vodka, and finally utilization in hospitals for monitoring anti-coagulation therapy in dialysis procedures. This example highlights the use of indicator-displacement assays (IDAs) and the use of designed, pre-organized, and highly selective receptors. The second example will delineate the need for rapid and parallel analysis of enantiomeric excess (*ee*) values in optimizing catalytic asymmetric synthesis routines. Several approaches using enantioselective IDAs, as well as systems that create chiral assemblies, will be presented. The later approach relies on multi-component assembly that is triggered by the introduction of the analyte, thereby giving rise to a circular dichroism signal. The use of these assays in high-throughput screening will be given. The third and last short story will follow our thought process of moving away from highly selective receptors to low-selectivity receptors, and the creation of patterns that identify a single analyte in complex mixtures, or that qualitatively differentiate between complex mixtures. The inspiration for this approach to chemical sensing is the mammalian senses of taste and smell, which will be briefly reviewed. The discussion will center on differential sensing as a means of fingerprinting mixtures of analytes whose structures are not even known, with a particular focus on perfumes and beverages. Overall, this lecture will show that a combination of mechanistic organic chemistry with concepts from supramolecular chemistry and chemometrics lead to the creation of novel, but also practical, advances in the analytical sciences.

Modular Supramolecular Fluorescent Receptors: Functional Materials and Applications as Probes for Anions

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This talk will describe the development of modular, inherently fluorescent receptors based on a difunctionalized 2,6-alkynylpyridine scaffold as hosts for small molecules and ions. A new class of urea receptors will be described that form 1:1 complexes with halides. This receptor class exhibits tunable "off-on" or "on-off" fluorescence in the presence of anions, depending on the placement of electron-donating and -withdrawing groups on the periphery of the host. Protonation enhances binding over one order of magnitude, alters the binding selectivity, and provides a colorimetric indication of anion binding. Emerging applications in selective anion binding, sensing anions in wet and polar solvents, and fluorescent redox sensing will be discussed.

A related tripodal receptor will be described that exhibits selective and strong nitrate binding in wet acetone and other polar solvents. A water-soluble receptor related to parent bisurea **1** exhibits selective chloride binding in water with "turn on" fluorescence, providing insight into the mechanism of fluorescence in this receptor class. In addition, we describe efforts to adjust the receptor core (such as varying the bridging central arene from pyridyl to phenyl to bipyridyl). Such alterations result in hosts displaying strong C-H•••anion hydrogen bonds, new hosts that are selective for oxoanions, and a host that binds metal salts in their primary and secondary coordination spheres.



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Supramolecular Oligosaccharide Sensing with Repoter-Modified Curdlans

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Selective sensing of oligosaccharides in aqueous media is a challenge in current chemistry due to their heavy hydration and stereochemical diversity. Hence, the use of aqueous or protic media is often avoided in saccharide recognition studies, excepting a few recent ones. Indeed, precisely recognizing saccharide in aqueous media is a tricky task, which demands the host to form a highly structured multiple hydrogen-bonding network upon complexation with a specific saccharide that is heavily hydrated in the midst of bulk water. Thus, the development of selective saccharide sensor that functions in aqueous media is of particular significance and benefit not only from the scientific but also from the application point of view.

Curdlan (Cur) is a linear glucan composed of (1→3)-linked β-D-glucose units and is known to form a triple helical structure. The most intriguing feature of Cur is the ability to reversibly denature/renature by simply switching the solvent between water or aqueous acidic solution and DMSO or aqueous alkaline solution.[1] In this study, we synthesized reporter-modified curdlans, i.e. 6-*O*-(4-(dimethylamino)-benzoyl)Cur (**DABz-Cur**)[2] and free base/Zn porphyrin-modified Curs (**H_2Por-** and **ZnPor-Cur**), as saccharide sensors, and investigated their abilities for sensing a variety of oligosaccharides by using circular dichroism (CD) spectroscopy to find a specifically high sensitivity for one of tetrasaccharides, i.e. acarbose shown in Figure 1. Acarbose is a drug to treat type-2 diabetes mellitus and obesity by inhibiting α-glucosidase that releases glucose from higher carbohydrates, and therefore its detection is of particular significance from the diagnostic viewpoint. Acarbose added to an aqueous solution of **DABz-Cur** caused a significant reduction of the CD intensity without altering the couplet pattern, indicating strong interactions of acarbose with **DABz-Cur** among 24 saccharides examined in this study.

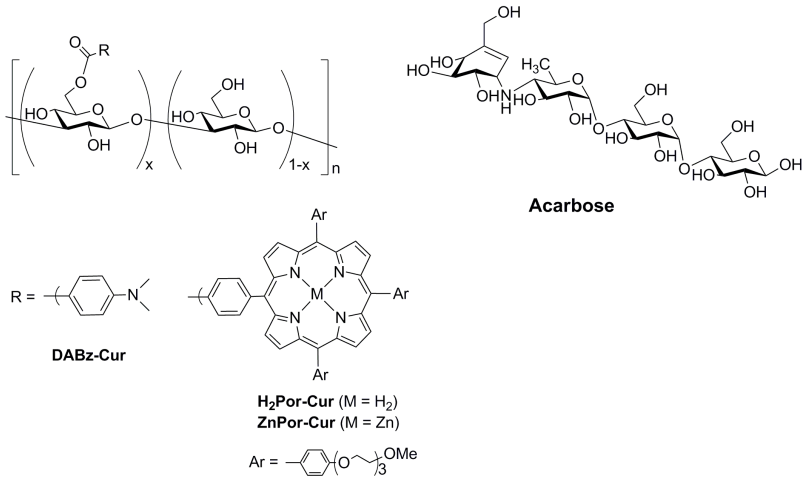


Figure1. Structures of reporter-modified curdlans (**DABz-**, **H_2Por-**, and **ZnPor-Cur**) and acarbose.

The detailed chiroptical properties and saccharide recognition behavior of **DABz-**, **H_2Por-**, and **ZnPor-Cur** will be discussed.

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Photo-active and Organometallic Nucleic Acid Oligomers

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The functionalization and modification of nucleic acids and their components is a topical area within supramolecular chemistry, not least due to continued interest in the sensing of various biomolecules and the development of synthetic biology. In our group, we focus on two themes within nucleic acid chemistry. In the first theme, we focus on the properties of functionalized DNA, in particular its modification with one or two photo-active anthracene units. Functionalization with one anthracene allows us to use hybridization assays to probe single base changes and base modifications in target DNA through changes in fluorescence for sensing applications.[1] Functionalization with two anthracenes creates a photochromic system in which anthracene photodimerisation results in drastic changes in duplex stability.[2]

Our second theme focuses on the development of synthetic nucleic acids as analogues of natural forms. Recently we reported an unprecedented example of an organometallic form of a nucleic acid, called *ferrocene nucleic acid* (FcNA).[3] The particular form of FcNA reported involves the replacement of repeating dinucleotide units within DNA with ferrocene units, as shown schematically below.

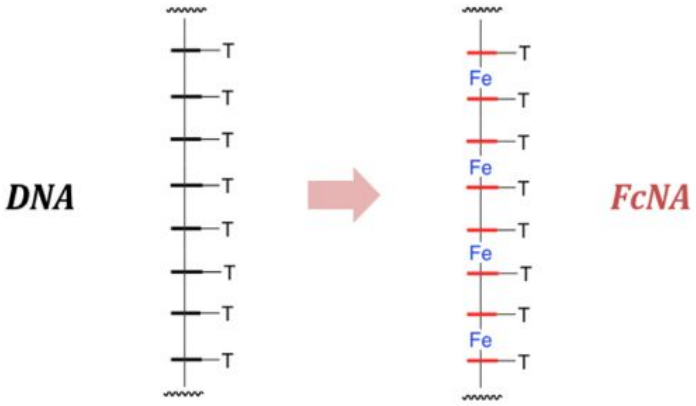


Figure 1. Schematic representation of the structural relationship between DNA and FcNA

We will present an overview of our results covering these two themes, involving a description of the sensing and spectroscopic properties of the various oligomers made.

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Structural Design Principles for Self-assembled Coordination Polygons and Polyhedra

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Strategies for the design of ligands that combine with metal ions to form high-symmetry coordination assemblies are reviewed.[1] Evaluation of crystal structure evidence reveals that prior structure-based design approaches,[2-5] based on the concept of complementary bonding vector angles, fail to predict the majority of known examples. After explaining the reasons for this failure, it is shown how an alternative approach, *de novo* computer-aided molecular design, provides a practical method that predicts a much wider range of component shapes encoded to direct the formation of such assemblies.

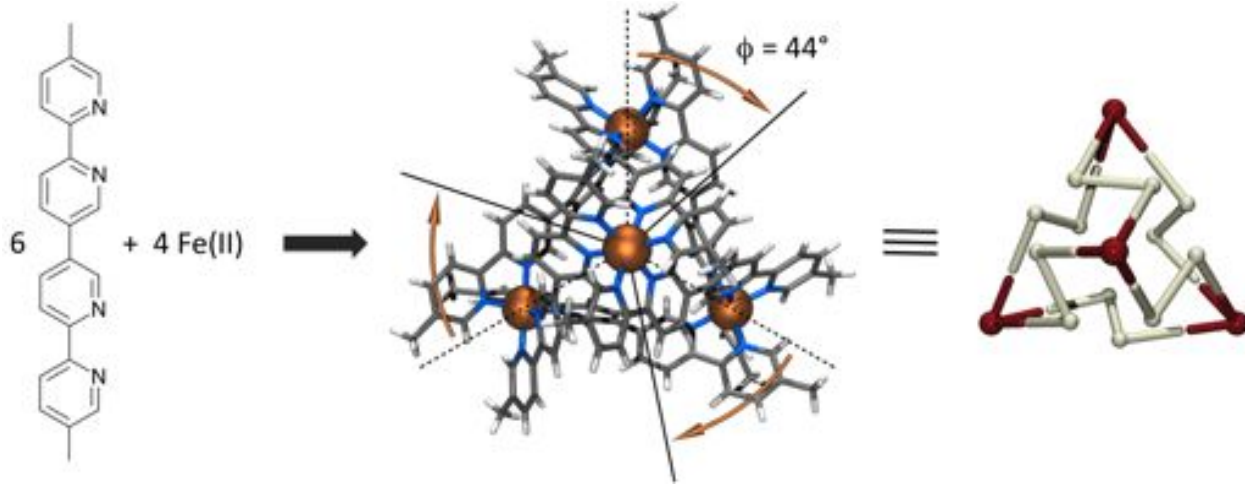


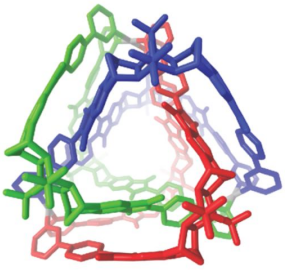
Figure 1. The most common reason why prior vector-based design rules fail is concerted vertex rotation. In the example shown above, a rotationally distorted, *T* symmetric M_4L_6 assembly, the degree of vertex rotation, ϕ, is defined as the angle between a vertex bonding vector (solid black line) and the plane containing the edge C_2 axis (dotted line). Previously published design rules apply only when ϕ = 0°.

References

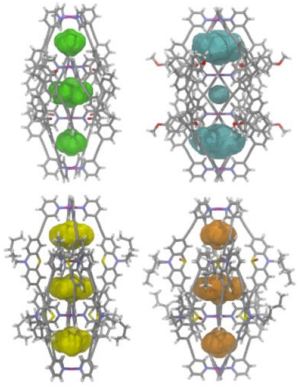
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Control over Cavity Shape and Size in Anion Binding Coordination Cages

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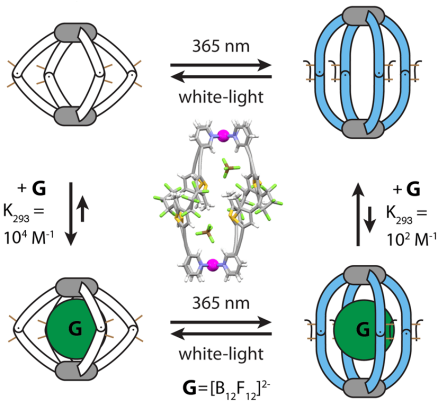


The research on supramolecular coordination cages is facing a transition from a primarily esthetic motivation to a focus on function and switchable control. Host-guest systems promise to find application in fields such as uptake, delivery & release of molecular cargo, sensing, separation and supramolecular catalysis inside confined environments. Our current research efforts include the realization of non-trivial cage topologies[1] and the implementation of static and dynamic control over cavity size and shape.



Previously, we have reported a dibenzosuberone-based interpenetrated double-cage [$Pd_4Ligand_8$] which is capable of allosteric anion binding with a tremendous affinity for the inclusion of two chloride anions in its outer pockets.[2-4] Recently, we found, that variation of the backbone structure as well as the size of the templating anion inside the central pocket of the interpenetrated double-cages allow for a static control of the size and hence anion binding capabilities of the outer pockets. Furthermore, we could show that the interpenetration principle can be extended onto other functional backbones such as the redoxactive compounds phenothiazine and anthraquinone when certain design requirements are fulfilled.

Based on light-switchable dithienylethene (DTE) ligands we prepared a novel coordination cage that exhibits a stimuli-responsive change of structure and conformational dynamics which in turn modulates its ability to bind negatively charged guests in its interior. This photochromic cage gives us reversible control over the uptake and release of guests such as $[B_{12}F_{12}]^{2-}$ by irradiation with UV and white light, respectively.[5]



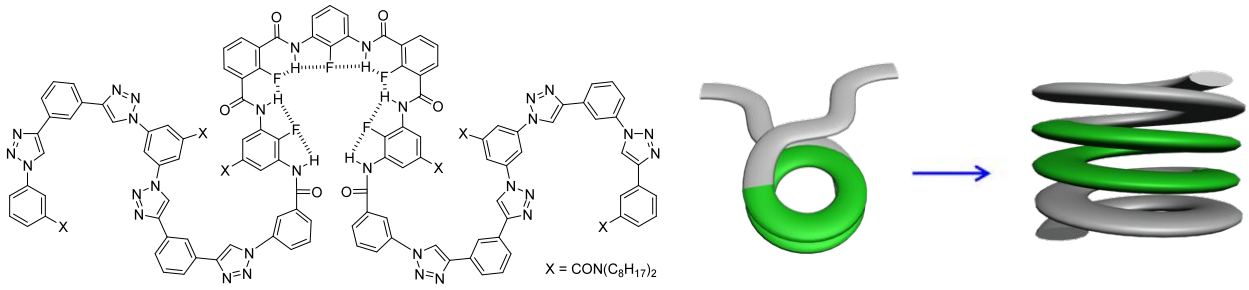
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Aromatic foldamers for molecular recognition and supramolecular materials design

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Hydrogen bonding-induced arylamide oligomers can adopt folded, zigzag or extended conformations.[1] This kind of compact aromatic backbones can be readily modified from the two ends or from the side chains. Thus, they can be utilized for self-assembling discrete ordered supramolecular architectures and for directing the formation of macrocyclic and capsule systems.[2-4] When folded segments are incorporated to polymer backbones as cross-links, the resulting copolymers display unique reversible mechanical properties due to the breaking and recovering of the intramolecular hydrogen bonds.[5] When they are attached with two quadruply hydrogen bonded UPy units, they can bind an intramolecular hydrogen bonding-free analogue to form supramolecular alternate block polymers.[6] When they are incooporated into the thread component, they are able to tune the shuttle behavior of the related [2]rotaxanes.[7] We also found that the C–H···O hydrogen bonding of the 1,4-diphenyl-1,2,3-triazole can induce aromatic triazole oligomers to form folded structures, which are good receptors for fluoroorganohalides in organic solvents through intermolecular N···X (I or Br) halogen bonding.[8] When one or two flexible aromatic/1,2,3-triazole oligomeric segments are attached to an aromatic amide folded segment, the central helical framework can induce the appended triazole segments to stack to form foldamer hybrids in less polar media:[9]



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Self-assembling Hosts as Functional Molecular Containers

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Our goal is to identifying simple molecular building blocks that predictably self-assemble into well-defined and functional supramolecular structures. We have focused on macrocyclic building blocks that use ureas or amides to guide the self-assembly of these small donut-shaped building blocks to form straw-like structures. These macrocycles probe a range of different ring sizes, shapes, and functionality. They assembled as designed into tubular structures forming porous crystals with guest-accessible channels (Figure 1). The urea macrocycles form non-covalent assemblies that are robust enough to be used as containers for facilitating photochemical reactions and for mediating oxidations with singlet oxygen with both high selectivity and conversion.[1,2] Other macrocycles contained functional groups that could undergo subsequent reactions and covalent stabilize the straws.[3] For example, macrocycles that contain diacetylene units within the walls of the straws polymerized to give porous conjugated polydiacetylenes. These new functionalized supramolecular assemblies may have applications in synthesis, for separations, and in flow and molecular transport.

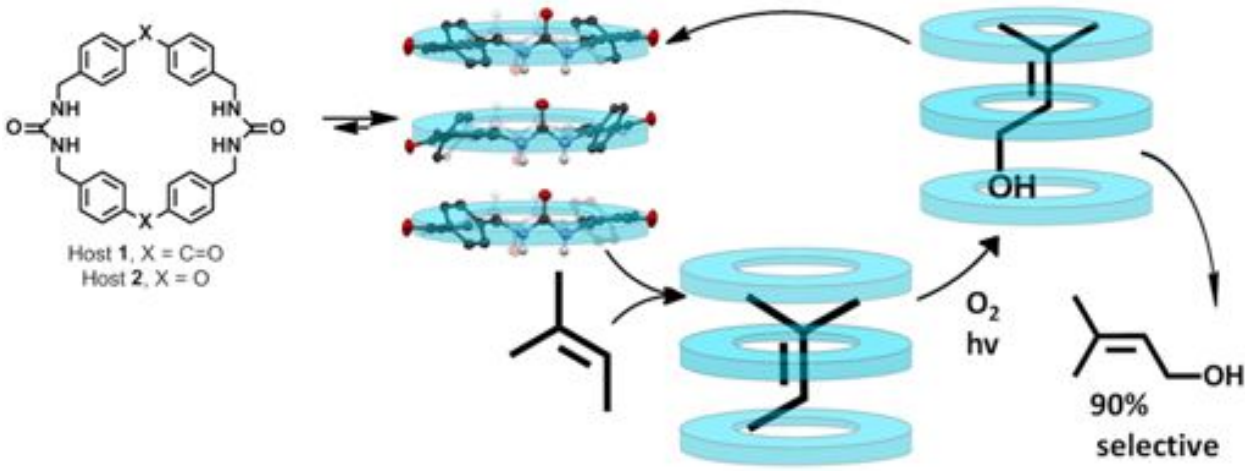


Figure 1. Bis-urea macrocycles stack into columns through three-centered urea hydrogen bonds to form porous crystals with guest accessible channels. A benzophenone bis-urea host facilitates the oxidation of an alkene upon UV-irradiation under an oxygen atmosphere.

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Nano-to-microgram Scale X-ray Analysis using Porous Complexes

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X-ray single crystal diffraction (SCD) analysis has the intrinsic limitation that the target molecules must be obtained as single crystals. Here, we report a new protocol for SCD analysis that does not require the crystallization of the sample. In our method, tiny crystals of porous complexes are soaked in the solution of a target, where the complexes can absorb the target molecules. The crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks (Figure 1). As the SCD analysis is carried out with only one tiny crystal, the required sample amount is of the nano-to-microgram order. We demonstrate that even ~50 ng of a sample is enough to be analyzed. When combined with high performance liquid chromatography (HPLC), multiple fractions were directly characterized, establishing a prototypical LC-SCD analysis. Furthermore, the structure of a scarce marine natural product was unambiguously determined using only 5 μg of the compound.

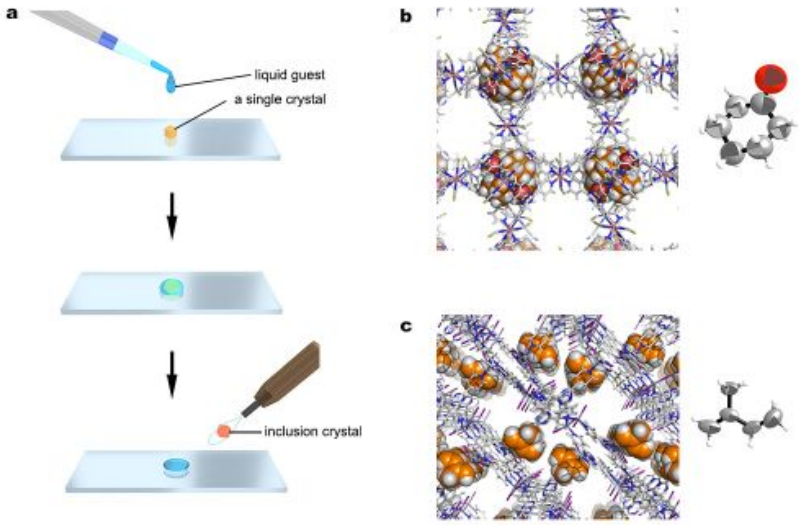


Figure 1. Schematic outline for the preparation of a guest-included network complex: a single piece of crystal **2** or **3** was treated for 2 d with a drop of a liquid guest and subjected to X-ray data collection. The experiment with isoprene was carried out in a sealed vial to avoid the evaporation of the guest.

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Fluorescent Hydrogels Formed By CH–π And π–π Interactions as Main Driving Forces: An Approach Toward Understanding the Relationship Between Fluorescence And Structure

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Amide-linked tripyridine derivatives **1**, with a *para*-substituent, and **2**, with a *meta*-substituent, were gelated in water or water-DMSO. The gelation capabilities of **1** and **2** were attributed to the cooperative effects of mainly CH-π and π-π stacking or strong intermolecular hydrogen bonding interaction between the amide groups. More interestingly, the fluorescence intensity of *meta*-substituted **2** was relatively smaller than that of the *para*-substituted **1**, indicating that the emission property is also dependent on the binding strength of the π-π stacking. As a complementary armory of dynamic oscillation, steady shear experiments indicated that the gel formed for the *para*-substituted gel **1** is relatively strong and is a thermally resistant network as compared to the gel **2** bearing the *meta*-substituent. In additions, the fluorescence property of the pyridine-based gels may be suitable for applications in optoelectronic devices.

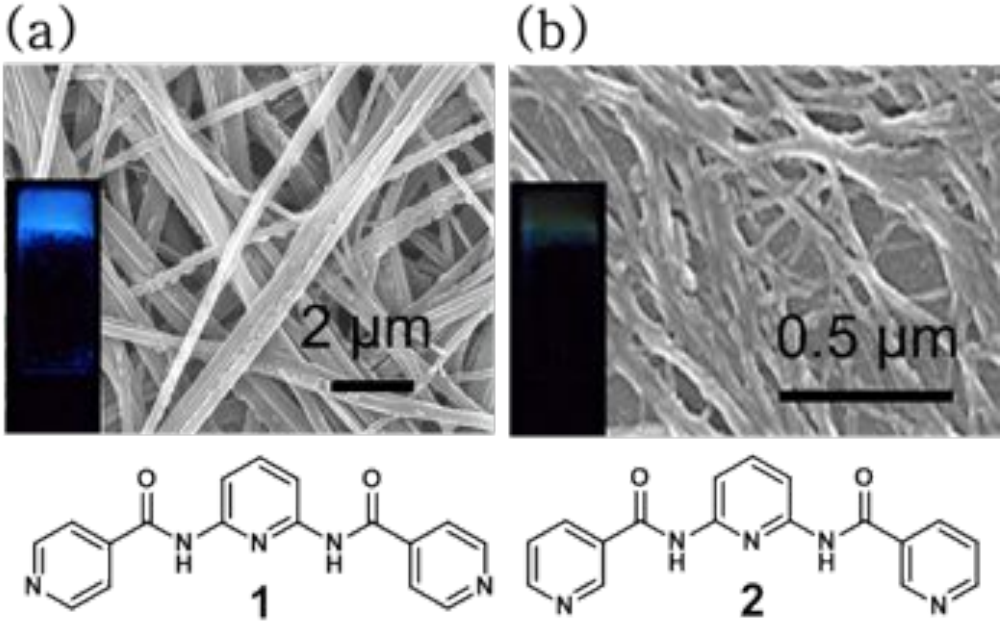


Fig 1. SEM images of hydrogels (a) **1** and (b) **2** and chemical structures of gelators **1** and **2**.

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Achiral Guests and Solvent-Triggered Chiral Inversions in a Planar-Chiral Cyclic *pseudo*[1]Catenane

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Pillar[5]arenes[1] are new macrocyclic hosts and were first reported in 2008 by our group. The planar chirality of pillar[5]arene is caused by the substitution position of the alkoxy groups, but the optical resolution is not posible because it is racemized by the rotation of the units at 25℃ in solution. We have succeeded in optical resolution of pillar[5]arenes by formation of rotaxanes.[2] In this study, we report dynamic planar-chiral inversions based on a new bicyclic structure based on pillar[5]arene, a *pseudo*[1]catenane **1**, in which the guest is an alkyl chain connected to one pillar[5]arene unit. The alkyl chain of **1** was included in cavity in chloroform (***Figure 2***). Two components were obtained in area ratio 1:1 and optical resolution planar chirality of **1** by chiral HPLC. CD spectra of these fractions were mirror images, indicating that enantiopure *pS*-**1** and *pR*-**1** can be collected. 1,4-Dicyanobutane was added to the first fraction (*pS*-**1**) in chloroform, CD spectra changed dramatically from positive to negative. Similar results were obtained for the second fraction (*pR*-**1**). Inclusion of 1,4-dicyanobutane in the cavity of **1** causes de-threading of the alkyl chain moiety from the cavity of **1**. Thus, the addition of the achiral guest 1,4-dicyanobutane induced the planar-chiral inversion.

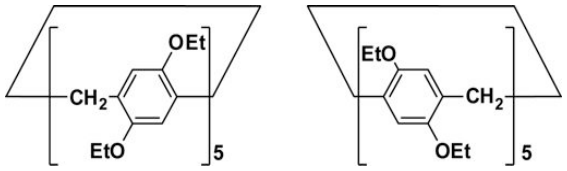
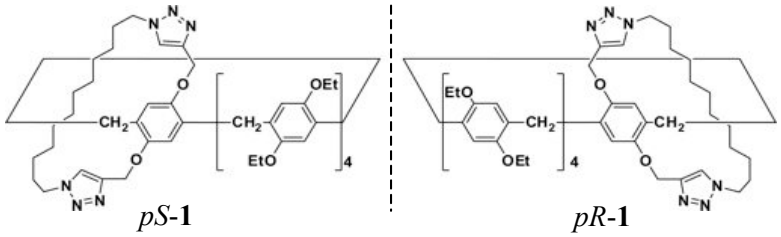


Fig 1. Planer chirality of per-ethylated pillar[5]arene



pS-**1** *pR*-**1**

Figure 2. Structure of cyclic *pseudo*[1]rotaxane **1**.

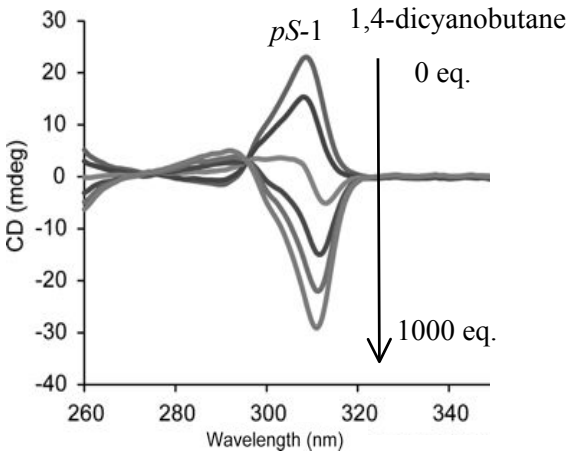


Figure 3. CD spectra of *pS*-**1** (10.5 μM) with 1,4-dicyanobutane (0 eq. – 1000 eq. to *pS*-**1**) in chloroform.

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Effect of Replacing $–CH_2CH_2CH_2–$ with –NHCONH– on Rates of Tunneling Across SAMs of Alkylthiols

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Charge transport across self-assembled monolayers (SAMs) predominantly occurs through off-resonant through bond tunneling. The influence of the molecular composition and structure of the SAM on the rate of charge transport as a function of voltage is still unclear. We previously reported that the substitution of a $–CH_2CH_2–$ for a –CONH– group in C12- to C18-alkanethiols has no statistically significant effect on charge tunneling properties of SAM.[1] Here, we report the effect of introducing a urea group, –NHCONH–, in lieu of a $–CH_2CH_2CH_2–$, $–CH_2CONH–$ or $–NHCOCH_2–$ group in C12-alkanethiols (Figure 1) on the tunneling currents across Ag-SAM//Ga_2O_3/EGaIn Junctions. Our results show that the values of $\langle \log|J| \rangle$ for urea-containing compounds are not distinguishable from that of the C12-thiol (or the amide-containing compounds). The values of $\langle \log|J| \rangle$ are thus independent of the molecular structure within the group investigated.

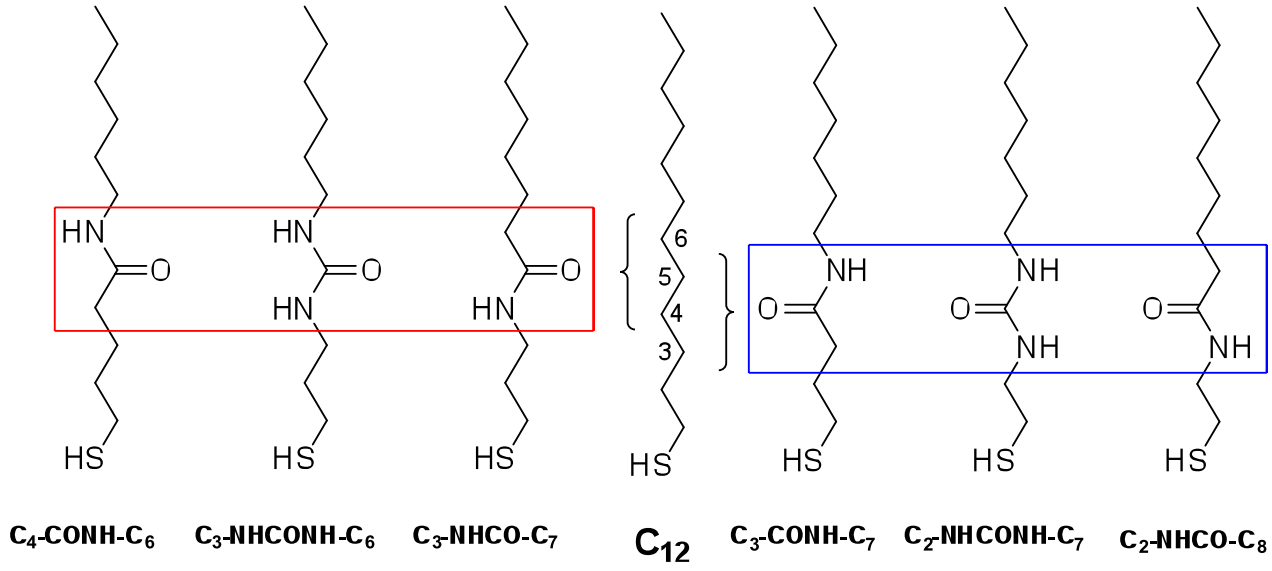


Figure 1. Schematic representation of the structural variations upon the inclusion of the amide and the urea groups in the structure of C12-alkanelthiol.

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Novel Model Compounds for Hemoglobin and Myoglobin: Exploring the Strength of the H-bond

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There is a great interest in understanding how the heme domain discriminates between O_2 and CO. The mechanism of this discrimination is a matter of controversy.[1] It is widely believed that the *distal* histidine stabilizes bound O_2 by H-bond interaction (*Pauling* hypothesis).[2] In our mimicry of biological dioxygen binding by hemoglobin and myoglobin we have proven, for the first time, the existence of this H-bond in Co(II)-oxymyoglobin, as well as in model complexes **1**-Co-O_2 and **2**-Co-O_2.[3,4] Our current efforts in this field are focused on investigating the strength of the H-bond by systematically varying the N–H acidity of the *distal* base in the model complex **1**-Co-O_2. Our most recent results towards this goal are presented.

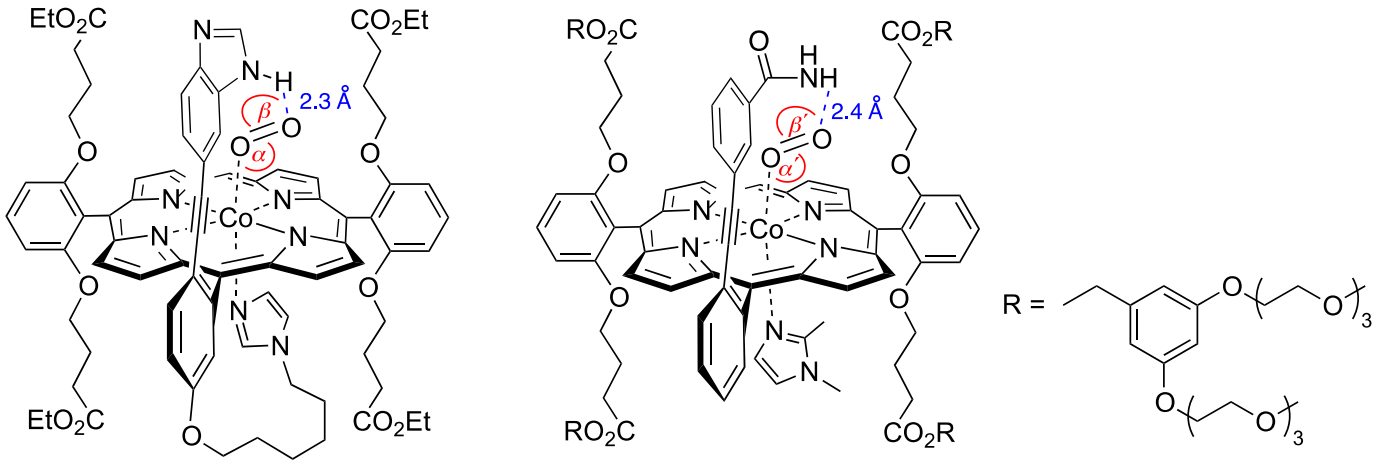


Figure 1. *Distal* H-bonds in hemoglobin/myoglobin model systems **1**-Co-O_2 and **2**-Co-O_2. The angles ($\alpha = \alpha' = \beta' = 110°$ and $\beta = 105°$) and distances were obtained from the frozen-solution EPR measurements.

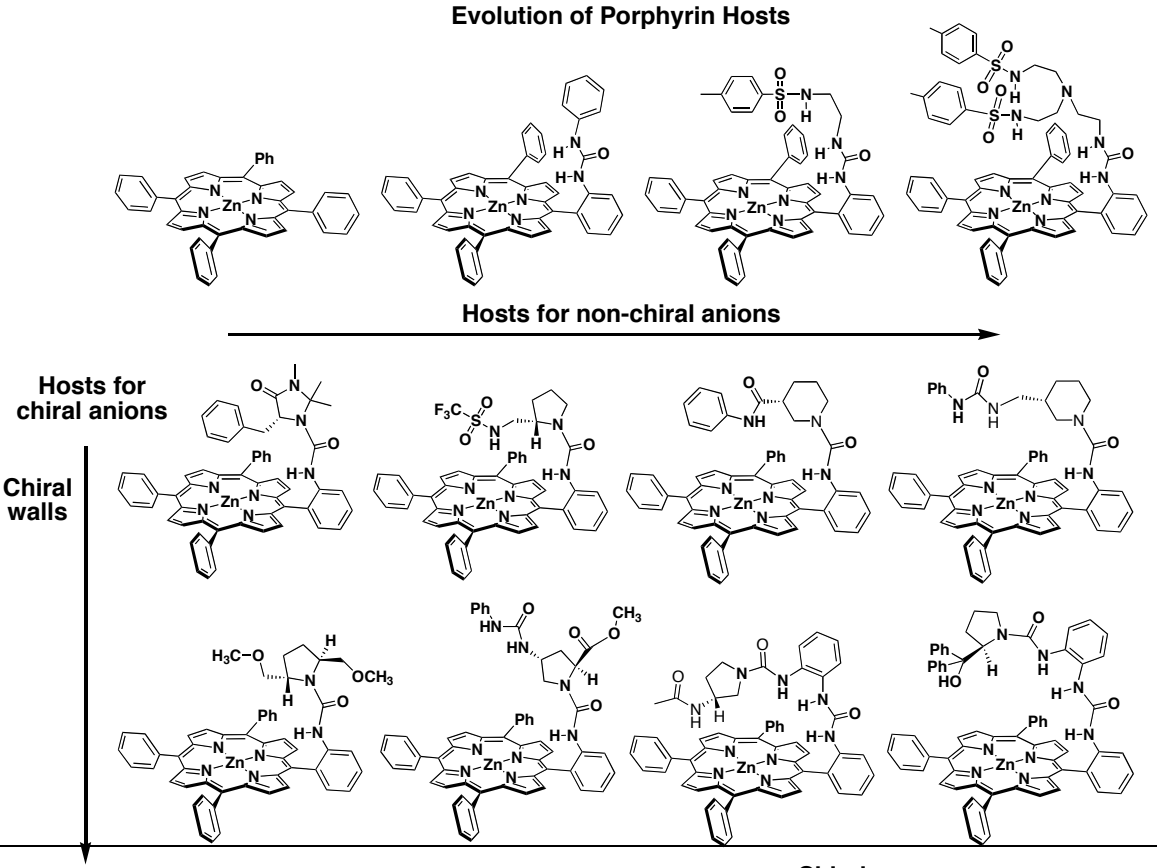
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Chiral Porphyrins: Hosts with Chiral Walls and Caps

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This project centers on the synthesis and recognition studies of chiral porphyrins characterized by the spatial positioning of asymmetric centers either within the wall of the porphyrin host or above the porphyrin surface which effectively serves to cap the porphyrin. Thus, these hosts have asymmetric centers positioned directly beside or above the metal center. The hosts have introverted functionality – guest recognition sites protrude into the interior of the host cavity from the wall or from the top of the porphyrin where they work in tune with the metal center for cooperative guest binding. These hosts are fairly rigid and exhibit complementary guest binding interactions (such as hydrogen bonding, pi-pi interactions, metal coordination) while minimizing steric interactions for the appropriate stereoisomer of a guest. For the creation of the hosts, a porphyrin isocyanate was reacted with a variety of commercially available chiral pyrrolidines and piperidines; the hosts are available in diversity in high yield with minimal synthetic effort. Guests studied were primarily chiral carboxylate containing guests; enantioselectivites in guest binding of approximately 2-4 have been achieved thus far with these types of hosts. Several of these hosts display a conformationally-induced organization upon binding to guests.



Strong Fluorescence Enhancement Of Cyclometalated Ir (III) Complexes In Cucurbit[10]uril

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Fluorescent cyclometalated iridium(III) complexes are attracting widespread interest due to their unique photophysical properties and promising fluorescence applications, especially as labeling reagents for biomolecules[1].The fluorescence properties of these Ir(III) complexes are very sensitive to their local environment[2]. With respect to this point, we have examined the fluorescence sensitivity of some Ir(III) polypyridine complexes by encapsulation within the large macrocycle cucurbit[10]uril (Q[10]). In this work we present for the first time the full encapsulation of Ir(III) polypyridine complexes in Q[10], which resulted in a strong fluorescence enhancement by a factor of ~40 and a blue shift of 34 nm. Binding constants were determined and the effect of pH was investigated. Preliminary electrochemical measurements were also carried out to complement the fluorescence work. We propose to take advantage of this fluorescence enhancement to improve fingerprint detection in terms of visualization.

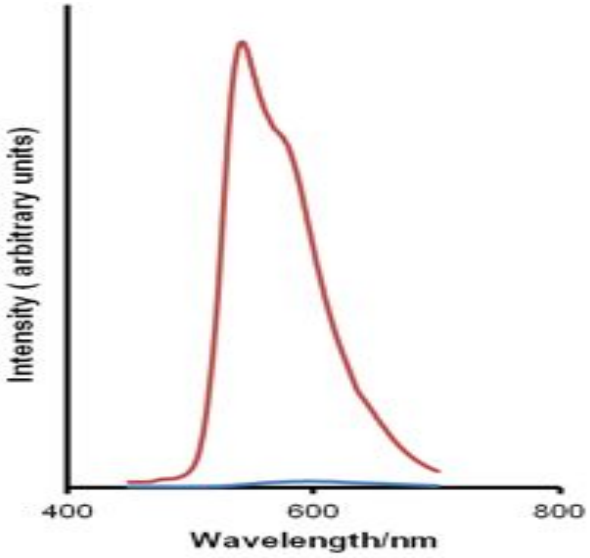


Fig 1. Fluorescence spectra of the free Ir(III) complex (blue) and the Q[10] encapsulated complex (red).

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Preparation of Polyacrylate-based Nanoparticles through Supramolecular Self-assembly for Target Specific Drug Delivery

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Supramolecular self-assembly techniques have been utilized in the preparation of polymer based nanoparticles (NPs) recently[1-2]. In this work, drug loaded polyacrylic acid (PAA) based NPs were prepared through the self-assembly technique for target specific drug delivery application. To begin, β-cyclodextrin and adamantane (AD) conjugated PAA was prepared. Together with AD conjugated PEG and folic acid, the four components would self-assemble into NPs with cancer targeting property[3]. This serve as a vehicular host in which anticancer drug, doxorubicin (DOX) was loaded in it. Cytotoxicity assays revealed that the drug loaded NPs have more toxicity towards the cancerous MDA-MB231 cells as compared to free DOX. When the same set of comparison was made on the healthy HEK293 cells, the contrary was observed. Furthermore, *in-vivo* experiments were also conducted onto tumor bearing nude mice. Similarly, the mice that received treatment from the drug loaded NPs have shown to suppress the tumor more than those mice with the intravenous injection of free DOX. In conclusion, both *in-vitro* and *in-vivo* experiments have shown the folate grafted NPs are an excellent platform for target specific drug delivery application. This work is in hope to search for a new platform for target specific delivery of anticancer drug.

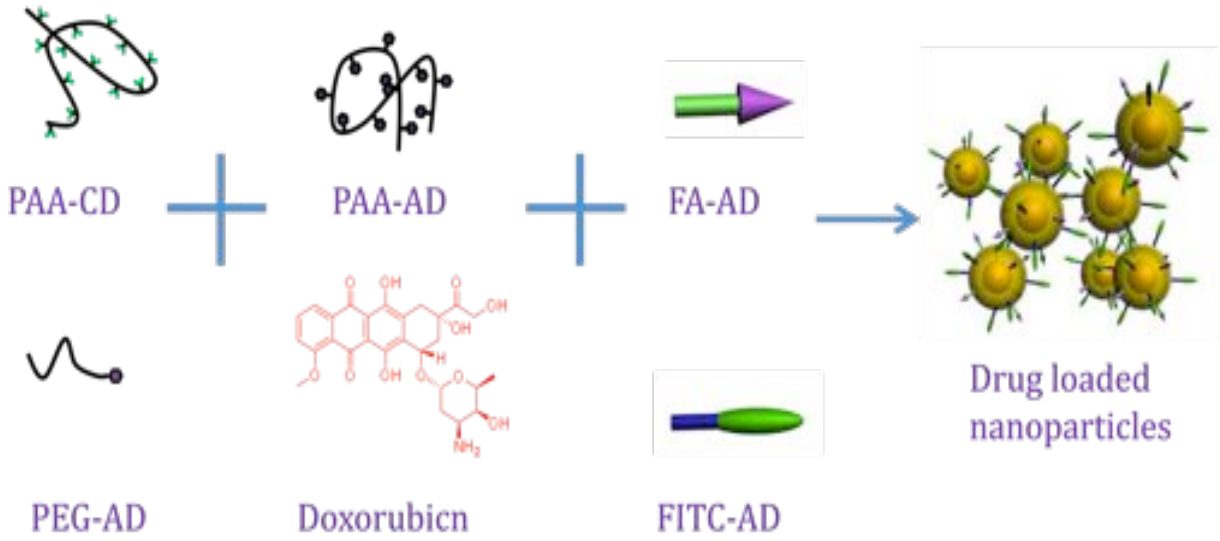


Figure 1. Schematic showing the supramolecular self-assembly of drug loaded nanoparticles. FITC (Fluorescence Isothiocyante) was included for tracing purposes.

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Supramolecular Analytical Chemistry: Assays for Multiple Analytes

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The ability of materials and compounds to form self-assemblies is utilized in a range of applications including supramolecular analytical chemistry, a term coined by Anslyn,[1] describing a new discipline focusing on applying the lessons learned from molecular recognition and self-assembly to analytical science. Here, the design of sensors for chemical species appears to be an excellent touchstone for the supramolecular analytical chemistry to prove its value. A number of chemosensor probes have been shown to successfully recognize and differentiate various analytes.[2] However, the design, preparation, and studies of sensing parameters are demanding research, and despite the demand, few materials suitable for selective analyses emerge. This is partly because many synthetic receptors and corresponding probes display cross-reactivity, i.e. bind more than one analyte, albeit each with different affinity. Such receptors and probes, while perhaps not ideally suitable for analysis of very low levels of key analytes,[3a] are conveniently used as sensor arrays that utilize differential sensing schemes and cross-reactive sensors.[3] The advantages of such cross-reactive sensor arrays are, among others, that they can be used in sensing of multi-component analytes,[3] are able to react to the presence of an unknown or unexpected analyte, and are able to escape the 1:1 stoichiometry limitations of selective probes operating on the lock-and-key principle.[4] Indeed, rational optimization of a cross-reactive array sensor was recently demonstrated to overcome the stoichiometry limitation.[5] Perhaps the most important is the fact that cross-reactive sensor arrays are capable of simultaneous recognition and quantification of multiple analytes.[6]

In this presentation we will discuss current progress in recognition of multiple analyte mixtures, cations, anions, and electroneutral species such as amines or N-nitrosoamines using cross-reactive arrays. We will also explain the design paradigms enabling simultaneous recognition and quantitation of various analytes to include various drug-related anions such as non-steroidal inflammatory drugs (NSAIDs) and amine derived drugs of abuse related to amphetamine and ephedrine, and other potential applications.

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Dinuclear Helicates as Spin Crossover Compounds

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As the interest in molecules with functional properties continues to grow, molecules that display Spin Crossover (SCO) properties are increasingly well researched.[1,2] The "*de novo*" design of compounds with abrupt spin transitions and thermal hysteric loops is of particular importance to creating compounds for use in a variety of applications including optical displays and sensors.[2,3] To this end the study of compounds that display SCO properties is a rapidly growing and rich area of research.

Following on from our previous research into dinuclear triple helicates which display SCO properties,[4] we discuss here the synthesis and characterization of two new dinuclear triple helicates which show interesting spin crossover behavior. Using a combination of solid state and solution based techniques the spin crossover properties of these compounds have been investigated and are discussed in depth.

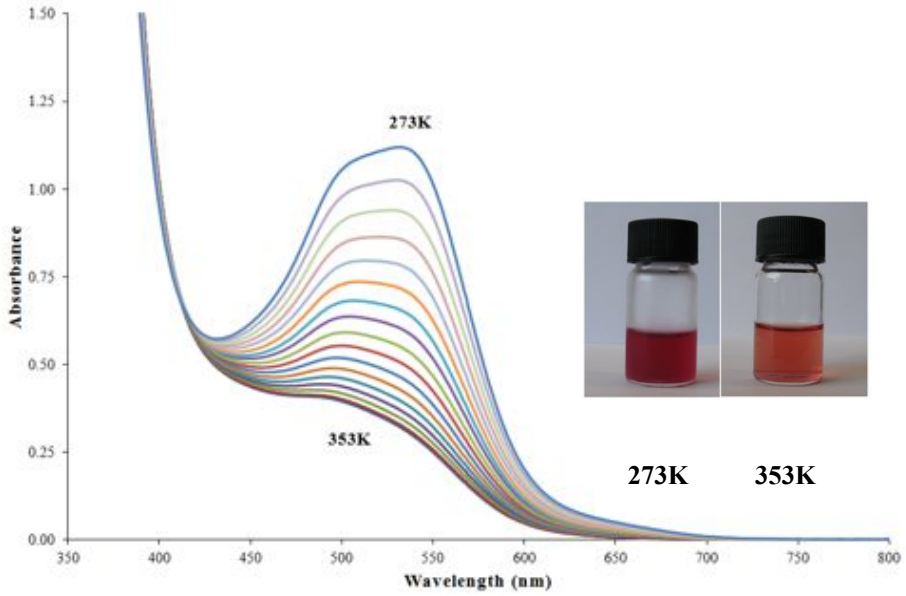


Figure 1: Change in the absorption spectra of Compound **1** with temperature.

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Template-Directed π-Mediated Self-Assembly and Photoinduced Properties of 1-Dimensional Molecular Arrays Featuring Naphthalene Diimide

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The efficiency of template-directed 'clipping' protocols coupled with dynamic covalent chemistry—specifically, those employing (i) crown ether–secondary dialkylammonium ion recognition and (ii) reversible, self-editing imine formation under thermodynamic control, respectively—have enabled chemists to prepare monodisperse 1-D mechanically interlocked assemblies in which a precise number of functional components are placed within well-defined geometries and distances relative to one another.[1,2] These assemblies present an attractive 'dynamically robust' scaffold for understanding the impact on through-space electron transfer (eT) events over discrete and potentially long distances.[3] Using this approach, we prepared rotaxane-based linear arrays featuring electron-accepting naphthalene diimides, which present access to various mixed-valence and radical anion states where the electrons generated are stabilized via π-stacking interactions. Taking steps further, model [2]rotaxane dyads were designed and their photophysical/electronic properties probed using steady-state and time-resolved spectroscopic techniques. Preliminary results indicate that, upon photo-excitation of a perylene donor stopper, efficient fluorescence quenching and charge separation are able to occur. These works are expected to enlighten our understanding of (1) through-space eT dynamics and (2) the design parameters necessary to realize 1-D photosynthetic mimics and light-harvesting relays incorporating the mechanical bond.

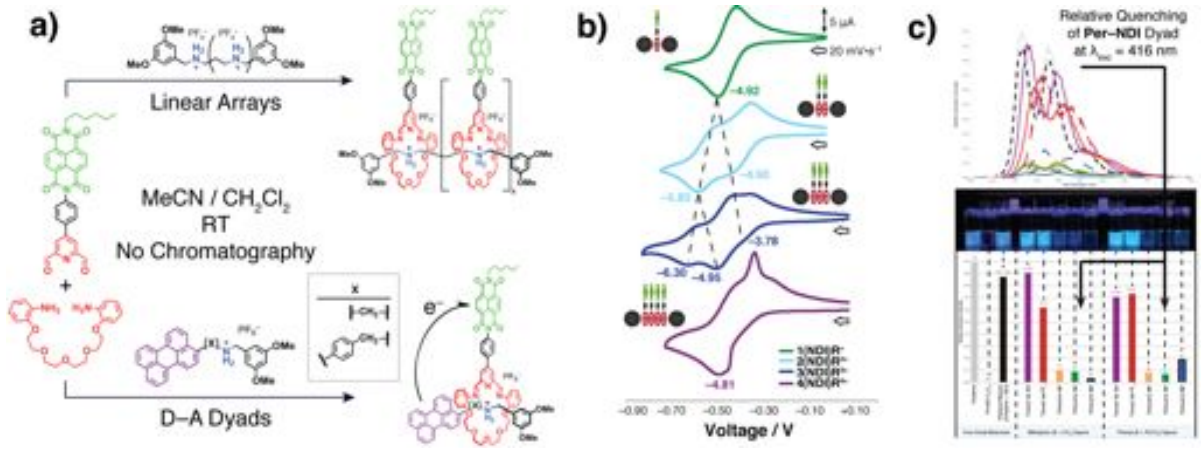


Figure 1. Dynamic assembly a) of mechanically interlocked arrays and dyads leading to b) enhanced $(NDI^{\bullet-})_n$ (n = 1, 2, 3, or 4) stabilization and c) photoinduced eT events.

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Self-Assembly of Novel Naphthlene-Derivatives for Selective Dispersion of Carbon Nanotubes in Water.

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Naphthalenediimides represent a class of compounds with electron-deficient π-system whose electronic and spectroscopic properties have led to their extensive study in the field of supramolecular chemistry.[1, 2] As an electron-acceptor motif, their ability to form donor-acceptor interactions has been widely exploited in the construction of molecular devices and machines.[3] Here we present the spontaneous self-assembley of novel water-soluble naphthalenediimides and their ability of selective dispersion of carbon nanotubes.

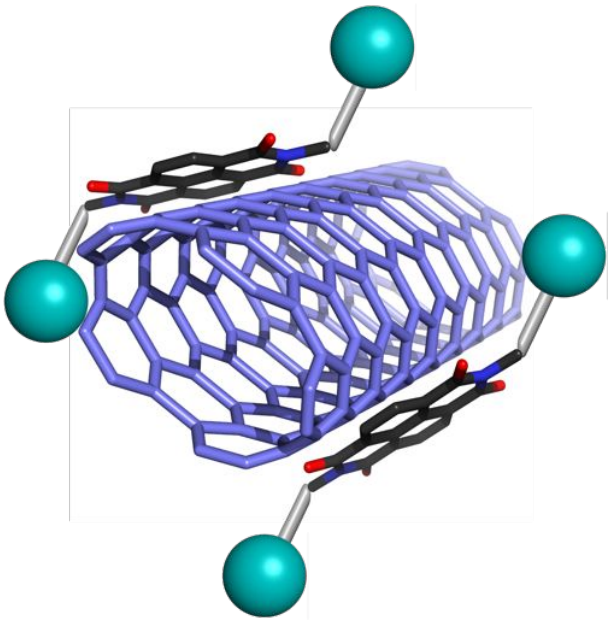


Figure 1. Dispersion of carbon nanotubes by van-der-waals interaction with naphthalendiimides, carrying solvophobic moieties

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Imidazole I-Quartet Water and Proton Dipolar Channels

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The complementarity of shape, dimensions and electrostatic profiles between interactional surfaces of biomolecules are considered to be major determinants of functions. Interfacial or encapsulated water molecules, necessarily present in contact space, are of crucial relevance for many biological scenarios like: biomolecular recognition and self-assembly, protein structure and activity, DNA conformation and recognition, proton(ion) and water-channel selectivity.

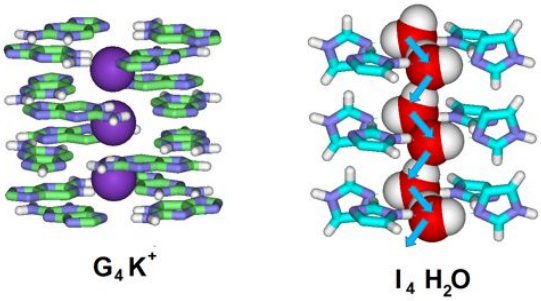


Fig 1. Imidazole I-quartets mutually stabilized by dipolar inner water wires are reminiscent of G-quartets stabilized by cations.

Regarding the basic principles of ion-transport along protein channels, they are related to large water-filled cavities in which the dipolar structure of the proteins help to overcome the high energy barrier of the translocation of the ions toward the selectivity filter. Synthetic robust counterparts have been developed with the hope of reproducing the complicate biological machinery. Electrostatic asymmetry, push and pull rigid rods or polarizable materials have been used to generate dipolar ion-pumping as observed with natural protein systems. Intuitively, interactions between chiral asymmetric surfaces and water might imply the generation of oriented dipolar surface-bonded water clusters. Within this context, it has been shown that chiral interactional surfaces are determinant for asymmetric tissue morphogenesis. Chiral imidazole-quartet nanotubes in which confined water molecules present a unique dipolar orientation can preserve the electrochemical potential along the channel. Further progress and mechanistic simplicity can be imagined by using dipolar water wires to control dipolar ion-pumping along chiral channels. Herein, nanosized pores with internal chiral surfaces have been used to generate electrostatic dipolar profiles of oriented water wires preserving electrochemical potential conservation along the channel in which protons and ions are envisioned to diffuse along the *dipolar hydrophilic pathways*. These systems has provided excellent reasons to consider that chirality and water induced polarization generating dipolar ion-pumping in ion-channels may in principle to be strongly associated.

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Host-Guest Radical Pairing Interactions in the Formation of Coulombically Challenged Mechanically Interlocked Compounds

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In the realm of host-guest chemistry, viologens typically function as either an electron-poor guest, or as a subunit in an electron-poor host, both of which enter into noncovalent donor-acceptor bonding interactions with an electron-rich compound.[1] In recent years, we have explored the use of viologens as the subunit in both the host and guest in the shape of a [2]pseudorotaxane, where the expected Coulombic repulsion that usually exists between two dicationic viologens is exchanged for more favorable radical pairing interactions by way of chemical reduction.[2] More specifically, it is possible to access the rich redox chemistry of viologens – described[3] by Michaelis 80 years ago – and convert a dicationic methyl viologen (MV^{2+}) and a tetracationic bis-viologen cyclophane (namely, cyclobis(paraquat-*p*-phenylene) $CBPQT^{4+}$) to their radical cations $MV^{\bullet+}$ and $CBPQT^{2(\bullet+)}$, respectively, which form stable 1:1 complexes under inert conditions that have binding affinites on the order of 10^4 M^{-1} (MeCN). Since making this discovery, we have explored carefully designed strategies which allow the mechanical bond in interlocked compounds to dictate the stability of unpaired viologen radicals.[4] In one extreme, we have demonstrated the interlocking of two $CBPQT^{4+}$ rings to form a homo[2]catenane (HC) that adopts preferentially a paramagnetic state ($HC^{\bullet 7+}$) by maintaining the unpaired electron indefinitely.[5,6]

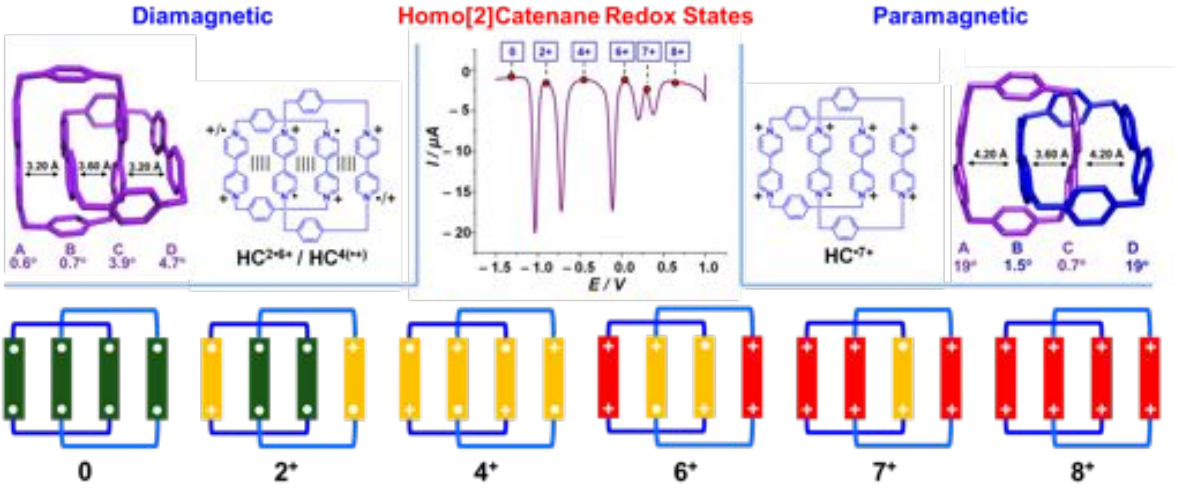


Figure 1. Electrochemical switching of magnetic states in a homo[2]catenane

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Photoactivated Directionally Controlled Transit of a Non-Symmetric Molecular Axle Through a Macrocycle

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The ability to control motion at the nanoscale is of fundamental importance in living organisms, and one of the most difficult challenges in nanoscience. In the last few year different research groups have developed artificial molecular machines able to control the movement of molecules and implemented such systems to make responsive materials and surfaces, to control catalytic processes, and to develop systems capable of controlling the storage of informations and the delivery of drugs upon controlled stimulation. But despite all this advancements, the development of synthetic molecular motors capable of directionally controlled linear or rotary movements is still a big challenge.[1] In this work we show as a simple supramolecular assembly constituted by a dibenzylammonium axle (*E*-**1**H$^+$) with two different end groups, namely an azobenzene unit at one end and a cyclopentyl unit at the other, can be operated to unidirectionally thread through a crown ether macrocycle, DB24C8 (**2**), using UV light and potassium ions as stimuli (Figure 1). The described system constitutes a first step towards the realization of an artificial molecular pump and can also be further developed to synthesize molecular linear motors based on rotaxanes and rotary motors based on catenanes.[2]

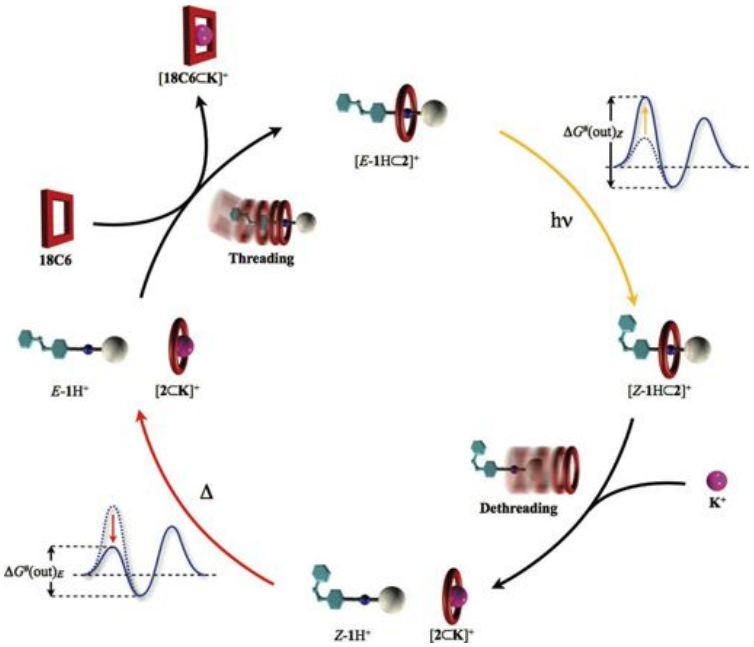


Figure 1. Schematic representation of the photoinduced unidirectional transit of a non-symmetric axle (*E*-**1**H$^+$) through a molecular ring (**2**).

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The Chameleonic Nature of the Diazaperopyrenium Dication

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Molecular recognition can be divided (Fig 1a) into two broad classes of processes, namely (i) homophilic recognition, the interaction of structurally and electronically similar, if not identical, species, and (ii) heterophilic recognition in which constitutionally different species come together as a result of stabilizing intermolecular noncovalent bonding interactions. Here, we use the 2,9-dimethyl diazaperopyrenium dication (**MP**$^{2+}$) to act in both a homophilic manner – forming nanowires in the solid state by capitalizing on p-p interaction across the large aromatic surface, as well as a heterophilic recognition unit for binding with p-electron rich guests, such as aromatic polyether macrocycles, e.g., **DN38C10** and **BPP34C10**. Isothermal calorimetry titration confirmed binding events with K_a values of 10^4 and 10^2 M^{-1} in MeCN for the binding of **MP**$^{2+}$ with **DN38C10** and **BPP34C10**, respectively. Based on these findings, we were able to modify the synthesis of the diazaperopyrenium unit to incorporate a functional azide handle, which was then used to form (Fig 1b) both the [2]- and [3]rotaxanes, harnessing template directed-synthesis for the formation of the rotaxanes.[1] Additionally, we have been able to encapsulate two **MP**$^{2+}$ dications within one CB[8], elucidated (Fig 1c) by X-ray crystallographic analysis.[2]

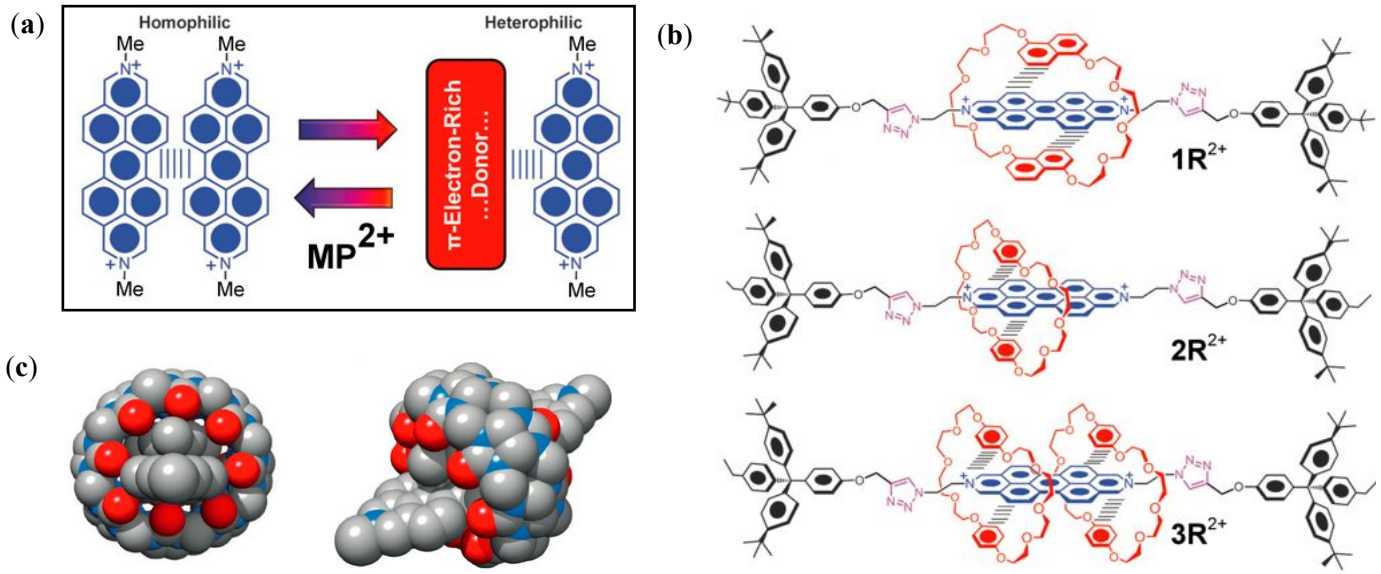


Fig 1. (**a**) The chameleonic nature of **MP**$^{2+}$ allows for homophilic molecular recognition even as a dicationic species, as well as donor–acceptor interactions with π-electron-rich compounds. (**b**) This donor–acceptor heterophilic recognition has been harnessed in the template-directed synthesis of the [2]rotaxanes **1R**$^{2+}$ and **2R**$^{2+}$ in addition to the [3]rotaxane **3R**$^{2+}$. (**c**) Solid-state superstructures of (**MP**$^{2+}$)$_2$⊂CB[8] obtained from single crystals grown from an aqueous solution of equimolar amounts of **MP**•2Cl and CB[8].

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A Synthetic Receptor for Asymmetric Dimethyl Arginine

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Dynamic combinatorial chemistry was utilized to identify a novel small molecule receptor, A_2D, for asymmetric dimethyl arginine ($aRMe_2$), which is a posttranslational modification (PTM) in proteins that is known to play a role in a number of diseases, including spinal muscular atrophy, leukemia, lymphoma, and breast cancer.[1] The receptor exhibits 2.5 to 7.5-fold selectivity over the isomeric symmetric dimethyl arginine, depending on the surrounding sequence, with binding affinities in the low micromolar range. The affinity and selectivity of A_2D for the different methylated states of Arg parallels that of proteins that bind to these PTMs. Characterization of the receptor-PTM complex indicates that cation-π interactions provide the main driving force for binding, loosely mimicking the binding mode found in the recognition of dimethyl arginine by native protein receptors.

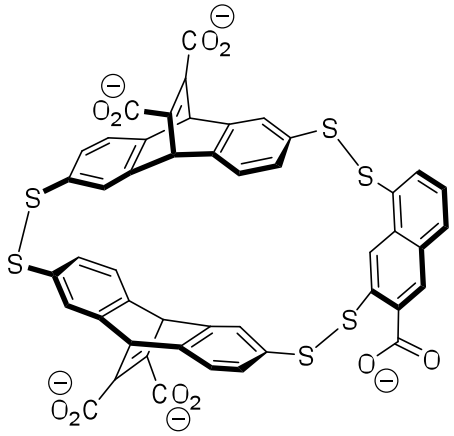


Figure 1. Synthetic macrocyclic mercaptophane, A_2D which selectively binds $aRMe_2$ over other methylation states of Arg.

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Supramolecular Chemistry of Melanins

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Biological pigments known as melanins are ubiquitous but poorly understood biomaterials with an emerging connection to supramolecular chemistry. Eumelanin, the black to brown human pigment, is currently thought to be a supramolecular assembly of organic nanoparticles derived from mixtures of heterogeneous oligomers of four to eight dihydroxyindole units. We are using a combination of synthesis, binding, and kinetics studies to attempt to understand eumelanin formation and structure in order to gain insight into its biological roles and develop non-biological applications. For example, eumelanin is known to bind a wide variety of metal ions and organic compounds, interactions that can potentially be exploited for water purification applications. We have recently shown that coatings derived from natural melanin extracted from human hair or synthetic eumelanin from the enzymatic polymerization of L-dopa act as lead-binding agents.[1] Attempts to develop a second-generation synthetic material led us to catechol-based coatings that change color upon binding metal ions. This presentation will describe our recent work with melanin-inspired coatings, small molecule control of synthetic eumelanin polymerization,[2,3] and synthesis of indole oligomers related to the molecular components of eumelanin.

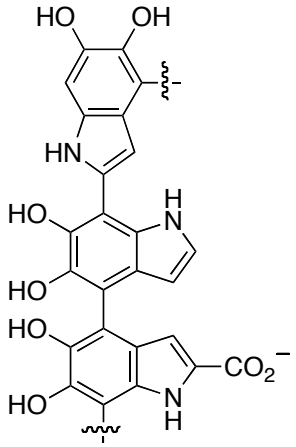


Figure 1. Eumelanin model.

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Reaction of Aryhydrazonoamides with Oxalyl Chloride Led to 14-Membered Macrocycles

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Arylhydrazonoamidines **1** and **2**, containing linear and cyclic amidine moiety are convenient building-blocks for the synthesis of various heterocyclic systems in reactions with electrophilic agents. We have studied the interaction of compounds **1** and **2** with oxalic chloride. Surprisingly, we have found that main products of 2:2 condensation of starting compounds were hexaazacyclotetradeca-6,8,12,14-tetraene **3** and dodecahydrodipyrimido[2,1-*h*:1',2'-l][1,2,5,6,9,12]hexaazacyclotetradecine **6**.

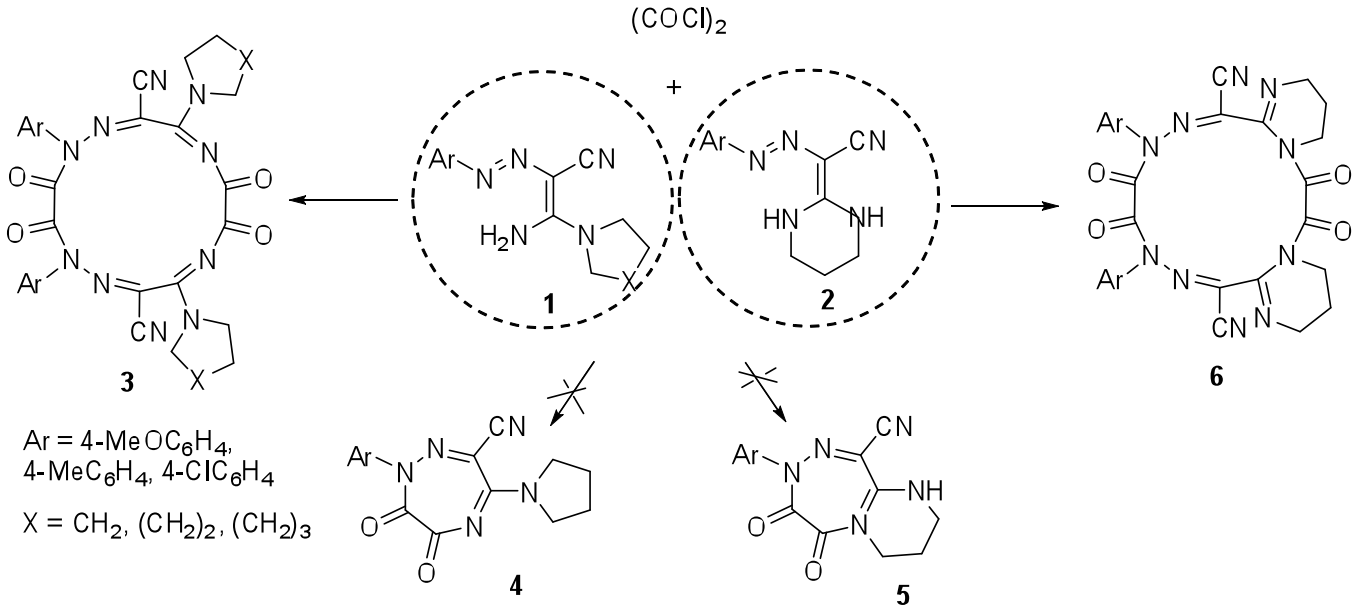


Figure 1. Synthesis of the hexaazacyclotetradeca-6,8,12,14-tetraenes **3** and dodecahydrodipyrimido- [2,1-h:1',2'-l][1,2,5,6,9,12]hexaazacyclotetradecines **4**

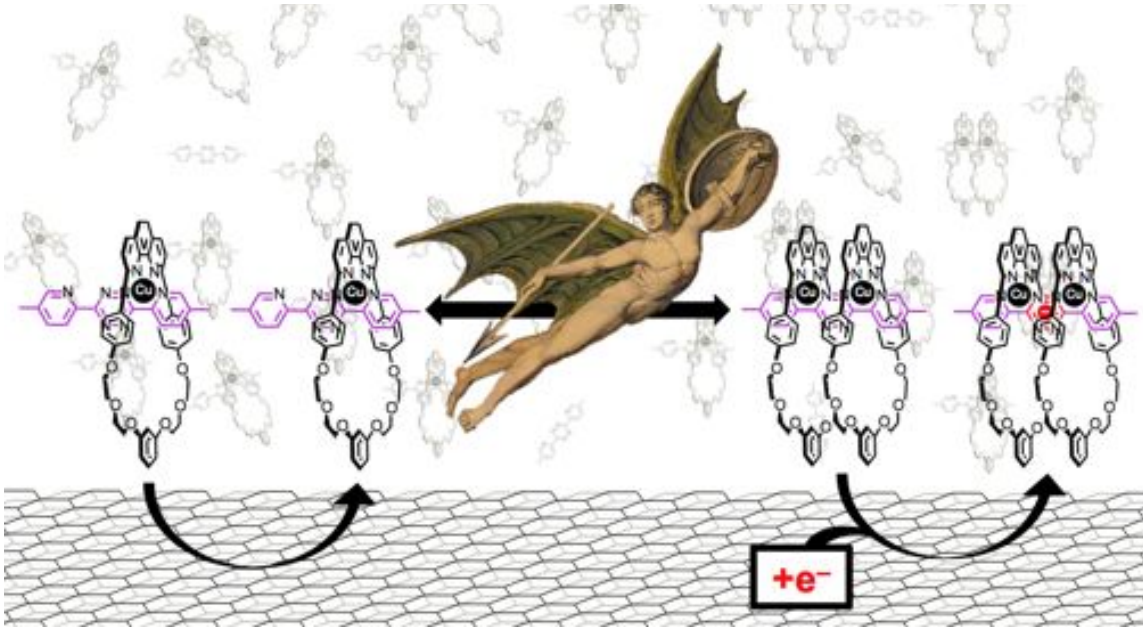
This reaction represents a new convenient method to obtain a library of hexaazacyclotetradecatetraene type **3** and dodecahydrodipyrimido[2,1-*h*:1',2'-l]hexaazacyclotetradecine type **4** from simple and available compounds. These macrocycles are of great interest because of their biological activity and ability to form complexes with metals.

Acknowledgments
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Diabolus Ex Machina: The Devilish Potential of Electrodes in Nanoscale Manipulations

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The Brownian universe inhabited by electochemically-actuated molecular switches may be accessed at the macroscale, allowing us to manipulate the mechanism of structural transformations. An example is a redox-active supramolecular switch that can be activated through both an energy-dissipating mechanism or an "alternate" mechanism that captures high-energy conformations, capitalizing on the pandemonium of the thermal bath. This allows us to create anisotropic flux between supramolecular morphologies from inherently isotropic stimuli, driving the system away from equilibrium. The selective capture of high-energy particles by the electrode calls to mind Maxwell's Demon, and has implications for the design and operation of molecular machinery.



Size-Selective Encapsulation of Hydrophobic Guests by Self-Assembled M_4L_6 Cobalt and Nickel Cages

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Supramolecular hosts can encapsulate guest molecules via weak interactions such as electrostatic, hydrogen bond and hydrophobic interactions.[1] Recently, the synthesis of tetrahedral $[M_4L_6]^{4-}$ anionic iron(II) cage in water through the reaction of 4,4'-diaminobiphenyl-2,2'-disulfonic acid, 2-formylpyridine and iron(II) sulfate was reported.[2] The reaction brings together 22 subcomponents through the formation of both dynamic-covalent (C=N) and coordinative (N→M) linkages to form a single complex structure.[3] This cage showed a remarkable ability to encapsulate and stabilize the air-sensitive white phosphorus P_4 and the worst greenhouse gas sulfur hexafluoride.[4]

The varied host-guest chemistry of the iron(II) cage led to the investigation of larger analogs to extend the range of guests that could be bound. Herein, cobalt(II) and nickel(II) cages and their recognition properties towards hydrophobic guests in solution and in the solid state is presented (Fig 1).[5] This study shows how subtle effect of altering the metal ion within an isostructural series of hosts results in perceivable differences in their guest binding abilities.

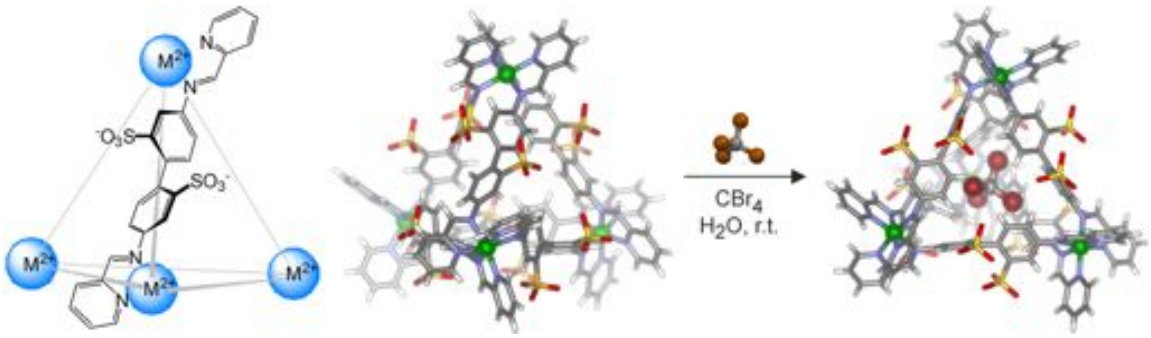


Figure 1. An example of the encapsulation of CBr_4 by an M_4L_6 Ni(II) cage in water.

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Water-Soluble Polyelectrolytes as Hosts for Small Organic Molecules

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Commercially available poly(amidoamine) (PAMAM) dendrimers are large hyperbranched water-soluble polyelectrolytes that can act as scaffolds for molecular assembly. Their capacity to uptake a number of small organic molecules, their well defined globular structure, and the ability to control their end-group functionality are all promising for use in the improvement of drug pharmacokinetics and, ultimately, as vectors for drug delivery.

Nevertheless, the high-stoichiometry soluble complexes of these polymers with small organic molecules have not yet been completely characterized. We concentrated our attention on carboxy-terminated "half-generation" dendrimers up to generation 6.5, whose surface is negatively charged in buffered aqueous solution at neutral pH. We conducted our binding studies using a dye-displacement assay based on optical signals (absorbance, fluorescence). Complex formation was assumed to be mainly guided by electrostatic interactions, but our findings suggest that significant secondary driving forces may be at play. We present results from our investigation of these interactions, together with a tentative interpretative model. We also compare the dendrimers' binding behavior to that of the more common linear polyelectrolytes. We are now moving towards the developments of these scaffolds for host applications including their use as drug vectors and as receptors in pattern-based chemical sensing systems.

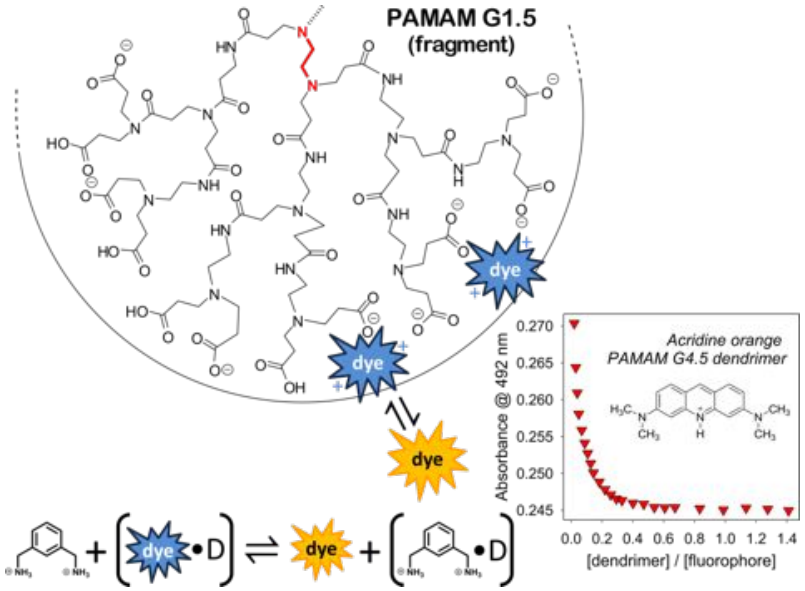


Fig 1.Fluorescent indicator binding and displacement with negatively charged PAMAM dendrimers.

Periodic Mesoporous Organosilica Grafted with Vanadyl Acetylacetonate: Novel Architecture for Catalyst Immobilization

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Designing catalytically active periodic mesoporous organosilica (PMO) is a novel strategy to transform various catalytically important transition-metal complexes into heterogeneous catalysts. Herein, we report a novel PMO synthesized through a surfactant-assisted approach. For the preparation of PMO, the essential organic precursor with two terminal alkoxy silanes was synthesized through the Schiff-base condensation between free amine of 3-aminopropyltriethoxysilane (APTES) and the carbonyl group of $VO(acac)_2$. The catalytic efficiency of PMO was evaluated for the selective hydroxylation of benzene to phenol, which is a fundamentally important catalytic reaction. The novel PMO catalysts show a benzene conversion with a remarkable selectivity of 100% towards the phenol formation, while $VO(acac)_2$, a homogeneous catalyst, presents a poor selectivity of 76.9% with a similar benzene conversion. In addition, PMO-1 exhibits a tremendous recyclability with a consistent catalytic activity in each cycle.[1]

In conclusion, a novel type of vanadyl complex-based PMO has been synthesized which serves as an excellent green catalyst for selective benzene hydroxylation not only with improved selectivity towards the phenol production, but also a robust recyclability, making the catalytic process more benign from environmental and commercial point of view.

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An Efficient Chiral Auxiliary Approach to Mechanically Planar Chiral Rotaxanes

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Mechanically planar chiral rotaxanes (Fig. 1), molecules which are chiral as a result of the mechanical bond between an achiral macrocycle and an achiral thread, are an intriguing and underexplored class of asymmetric molecules.[1] However, the synthesis of these materials in enantiopure form without the need for chiral stationary phase HPLC techniques remains an unsolved problem.

Taking inspiration from chiral auxiliary approaches in conventional asymmetric synthesis we have developed a method for the synthesis of enantiopure mechanically planar chiral rotaxanes without the need for chiral separation techniques and, for the first time, unambiguously assigned the absolute stereochemistry of the rotaxane products.[2] Our method, which employs readily available chiral pool materials as the source of chiral information and a high yielding, diastereoselective active template reaction for mechanical bond formation, finally opens the door to the detailed investigation of these challenging targets.[3]

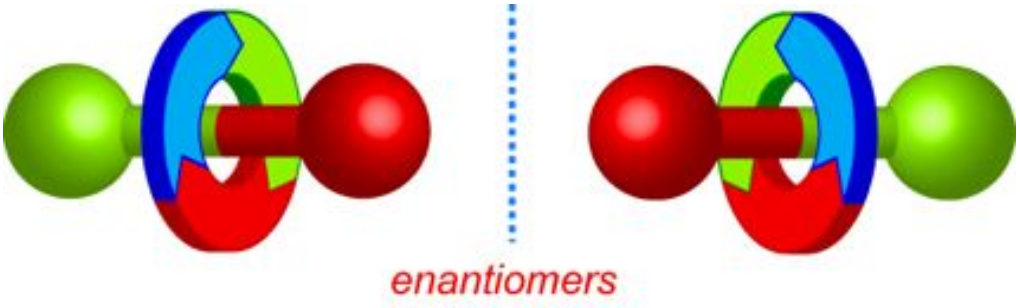


Figure 1. Schematic representation of enantiomeric mechanically planar chiral rotaxanes.

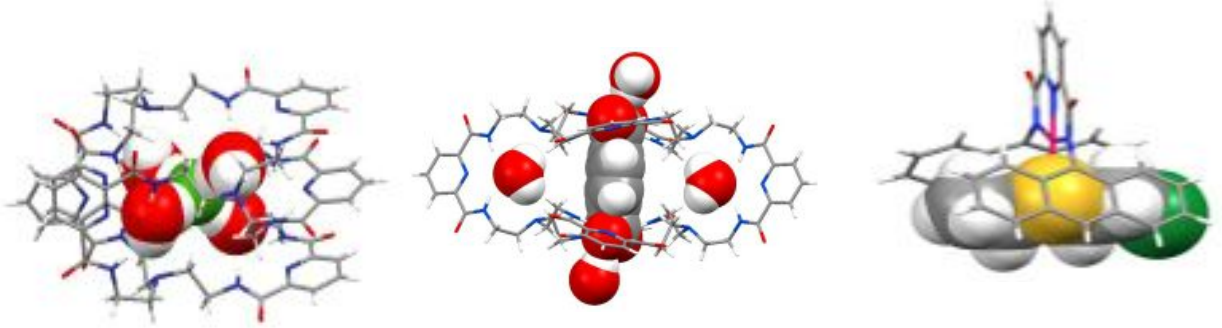
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Supramolecular Enclosures: Unraveling the Occupants

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Supramolecular chemistry is spectacularly versatile in the seemingly unlimited possibilities for building complex networks. One subset of these includes different classes of enclosures, where molecular or ionic occupants are held captive via weak hydrogen and/or π bonding supramolecular interactions. We have isolated and structurally characterized a number of such "enclosures," several of which are shown below. One consists of a totally covalent (not self-assembled) organic tetrahedron that has the ability to hold a limited number of small molecular/ionic guests, **1**.[1,2] A second is a tricyclic cylinder that is capable of shrinking or expanding in size depending on the length of encapsulated dicarboxylates, **2**.[3] A third consists of a Pd(II) pincer complex that, depending on its substituents, can provide a wall-like enclosure that holds a chemical mustard surrogate within its boundaries, **3**.[4] We have found that by combining the powerful capabilities of X-ray crystallography and NMR spectroscopy, we can unravel and compare host:guest associations in both the solid state and solution. Excerpts from these findings will be described in this presentation.



2 **3**

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The Self-Assembly of Nanoarchitectures via Protein-Ligand Interactions

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Nature has evolved proteins that can spontaneously self-assemble to create complex structures such as virus particles and molecular motors. The fields of bionanoscience and synthetic biology are based on the concept that by combining biological building blocks with synthetic molecules it will be possible to construct novel nanoscale structures and machines that can do useful work.

If nanoscale objects were constructed using weak supramolecular interactions between proteins and ligands, it should be possible to use competing high affinity ligands to bring about disassembly, or even reorganisation of the building blocks to give new reversible architectures.

In this project we are developing general strategies to use protein-ligand interactions to construct three-dimensional nanoscale architecture including polymers, networks and virus-like particles. Ligands including carbohydrate moieties and biotin, have been covalently attached to the cholera toxin B-pentamer (CTB), which can then bind to other CTB pentamers or Streptavidin. Multivalency can increase the overall strength of the interactions and bring proteins together to form different aggregates.[1] With a combination of different ligands and modified proteins, the build up of different structures can be controlled. The structures have been analysed and characterised by techniques including mass spectrometry, isothermal titration calorimetry and analytical ultracentrifugation.

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Accessing Molecular Complexity With Conformationally Dynamic Synthetic Carbohydrate Receptors

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Carbohydrate-lectin recognition encodes the formation of extracellular hierarchical structures and information processing in complex biological networks. Accessing the information content of oligosaccharides could open significant opportunities in molecular information storage and processing. Unlike DNA and peptides, however, binding conjugates to monosaccharides that could quickly decode oligosaccharide structures do not exist because of the subtleties of carbohydrate binding, where cooperativity, multivalency, and cross-specificity are common. We have developed a new carbohydrate receptor (Figure 1) and investigated its selectivity for different monosaccharides by 1D and 2D NMR methods.[1] Host **1** binds all monosaccharides tested in a 1:1 binding stoichiometry, with nearly equal K_as. In an excess of pyranoside, **1** binds α- and β-Man in a 1:2 receptor:pyranoside stoichiometry with a high degree of positive cooperativity (K_2/K_1 ~ 13.7 and 7.6 for α- and β-Man respectively) and selectivities as high as 16.8:1 α-Man:α-Gal. Moreover, this preference changes as a function of pyranoside concentration, favoring β-Glc at low concentration (<0.1 mM) and favoring mannosides at higher concentrations. By developing synthetic carbohydrate receptors that can distinguish between monosaccharides that differ only by the orientation of a single hydroxyl group, we hope to elucidate many of the subtleties of carbohydrate binding and understand how complexity arises in molecular systems.

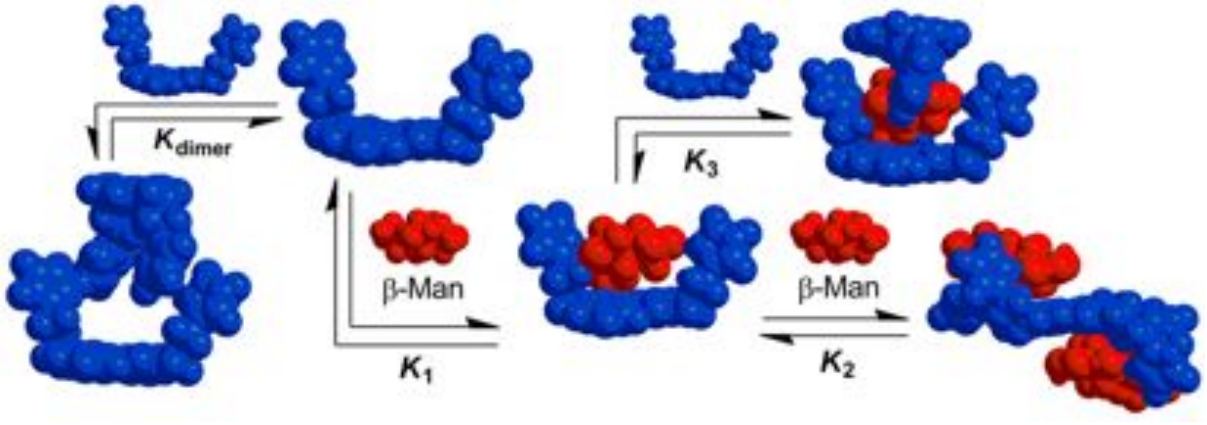


Figure 1. The equilibria present in a chloroform mixture of host **1** (blue) and β-Man (red) at 25°C. Upon increasing the β-Man:**1** ratio, K_2 determines the dominant species in solution. If instead, β-Man:**1** decreases, K_3 controls the dominant species present in the equilibrium mixture.

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Molecular Quasicrystals: Penrose Tiling with Molecules

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Like a bathroom wall, a tiled plane is covered with no gaps or overlaps. This is easy to achieve using regular tiles like triangles, squares or hexagons but impossible using only shapes with 5-fold symmetry. In the 1960s Roger Penrose approached this intriguing mathematical problem by using tiles of more than one shape (Fig. 1).[1] The chemical manifestation of this phenomenon was the absence of 5-fold symmetry in classical crystallography. In 1984 Daniel Shechtman reported an Al-Mn alloy for which the electron diffraction pattern showed sharp reflections with 10-fold symmetry, the first 'quasicrystals',[3] for which he was awarded the 2011 Nobel Prize in chemistry.[4] Quasicrystals comprised of molecules have not yet been observed. Our approiach to preparing molecular quasicrystals by using 5-fold symmetric molecules to replicate Penrose tiling on a surface will be descibed. The key to creating a Penrose tiling pattern is to follow the rules for the edge-edge interactions between the tiles which mathematics show are essential to preserve the tiling. We are using the molecular design tools available to synthetic chemists to prepare 2D molecular quasicrystals using synthetically accessible 5-fold symmetric molecules as tiles and the techniques of coordination and supramolecular chemistry to control the edge-edge interactions.

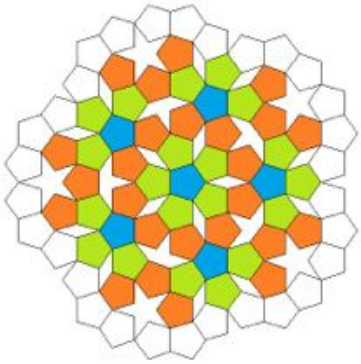


Figure 1. Penrose tiling.

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Subcomponent Self Assembly Using Palladium(II): A Versatile Strategy for the Synthesis of Supramolecular Complexes

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Subcomponent self-assembly has been used to create a variety of complex supramolecular structures, including 3D container molecules[1] and interlocked species,[2] via formation of imine bonds around a metal ion template. Condensing 2,6-diformylpyridine with amines around a palladium(II) metal ion in acetonitrile has proven a versatile method for synthesizing new assemblies, including macrocycles, interlocked structures such as rotaxanes and catenanes, as well as host-guest complexes.

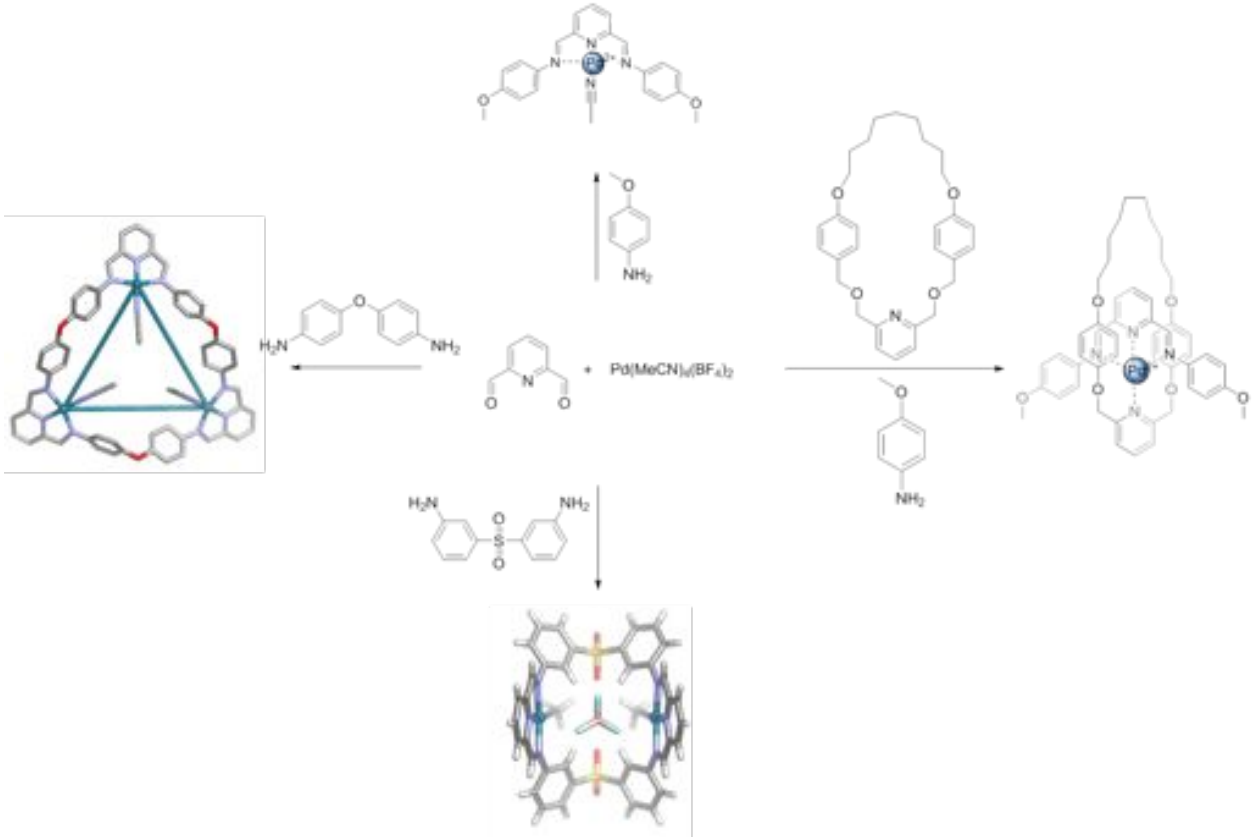


Figure 1. Examples of products synthesised using subcomponent self-assembly with palladium (II) in acetonitrile .

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Threading Polymers Through a Flexible Macrocycle Ring

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Despite being relatively simple systems, macrocycles comprising porphyrin and glycoluril moieties behave similar to complex enzyme architectures. As a virtue of their toroidal shape, they can accommodate linear polymer chains, which pass through their cavities, much like threading the eye of a needle. Valuable insight into the translocation mechanism of proteins through holes and channels can be gained by systematically studying the threading of polymers through synthetic analogs **1** and **2**. The rate of polymer threading through **1** is strongly dependent on the chain-length of the polymer and translocation speeds are usually fast.[1] Furthermore, the entropy of activation for threading becomes more negative with chain-length while enthalpy of activation remains constant.[2] The use of flexible macrocycle **2** for threading shows remarkable differences in length dependency and energy profile. Greater affinity of **2** for the polymer chain results in slower translocation speeds, and hence lower threading-on rates compared to **1**. The initial binding of **2** to the polymer chain shows an unprecedented negative activation enthalpy, which presumably results from the opening of an initially filled cavity at lower temperatures. This unusual conformational change exhibited by macrocycle **2** mimics some enzyme systems with negative enthalpy values for binding processes related to protein folding.

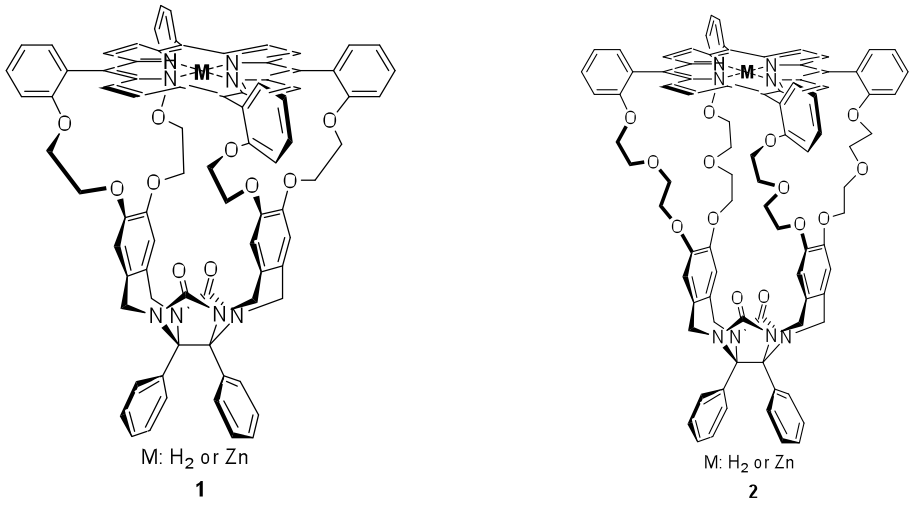


Figure 1. Regular and flexible macrocycles.

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Room-Temperature Ferroelectricity in a Family of Charge-Transfer Complexes

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Ferroelectrics—materials which exhibit spontaneous polarization that can be reversed by an external electric field—are of value[1] for a large variety of sensing, photonic, and memory applications, particularly for their versatility as tunable capacitors. In the drive to move away from toxic inorganic materials, organic ferroelectrics have gained stature because of their cheapness, light weight nature, and tailorability. The majority of organic ferroelectric materials are characterized by low phase transition temperatures, and are thus ineffective under ambient conditions. Recently, we reported[2] the discovery of above room-temperature ferroelectricity in three high-aspect ratio charge-transfer crystals (Figure 1a,b). Temperature-dependent dielectric constant measurements of the crystals indicate that they are always ferroelectric, and polarization hysteresis curves of the crystals measured (Figure 1c) at 300 K demonstrate remnant polarization values that are competitive with those of many inorganic ferroelectrics. The crystals assemble readily as a consequence of the lock arm supramolecular ordering (LASO) design, in which synergistic charge-transfer and hydrogen bonding interactions generate, not only an extended donor–acceptor stack, but also a dense 3D hydrogen bonding network. This supramolecular motif has guided the continuing development of other modular functional organic systems which exhibit unusual optical phenomena (Figure 1d) as well as ferromagnetism.

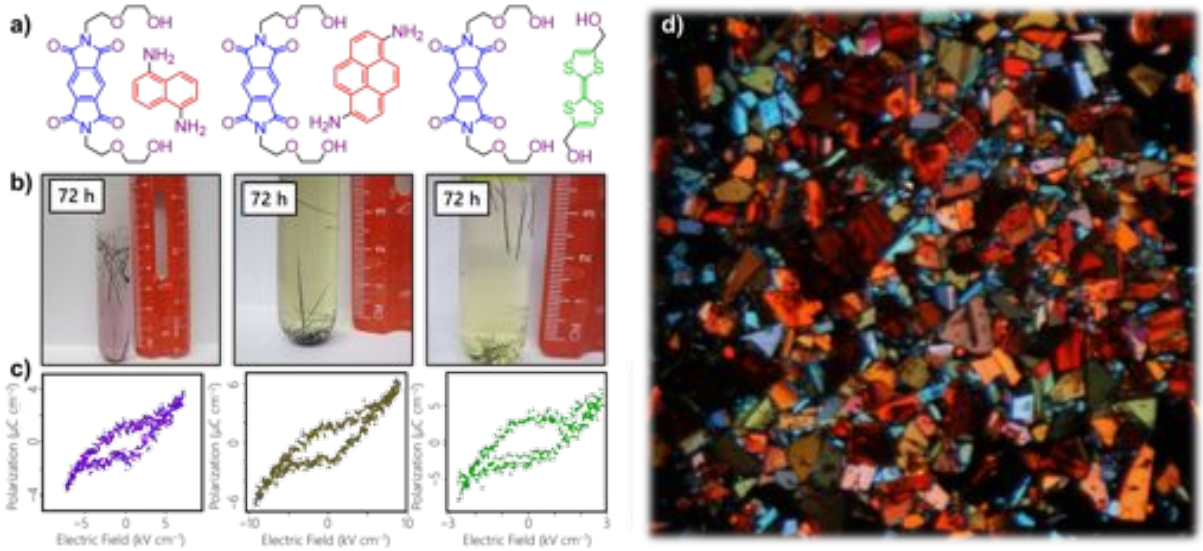


Figure 1. a) Structural formulas of the molecules which constitute the ferroelectric donor-acceptor complexes. b) Images of the high aspect ratio co-crystals. c) Room temperature (300 K, f = 0.1 Hz) polarization hysteresis curves. d) Pleochroism in charge-transfer crystals.

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Synthesis and Daisy-Chain Assembly of Monofunctionalized Cucurbit[6]uril Derivatives

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In order to further extend the supramolecular chemistry of CB[*n*] it is necessary to develop efficient synthetic methods to prepare functionalized CB[*n*] derivatives.[1] In this paper, we develop robust, scalable procedures for the synthesis of a series of monofunctionalized CB[6] derivatives (**1-5**) that bear reactive functional groups (eg. hydroxyl, nitro, amino, propargyl, or allyl group). First, compound **2** with propargyl or allyl bromide can be transformed to **4** or **5** which contain reactive propargyloxy or allyloxy substituents. The most significant aspect of the work, however, is the gram scale synthesis of monofunctionalized CB[6] derivative **4** which contains a clickable propargyloxy group. Finally, we are successful to get compound **1** from the reaction of **4** and azido amine in the presence of Pericàs' catalyst.[2]

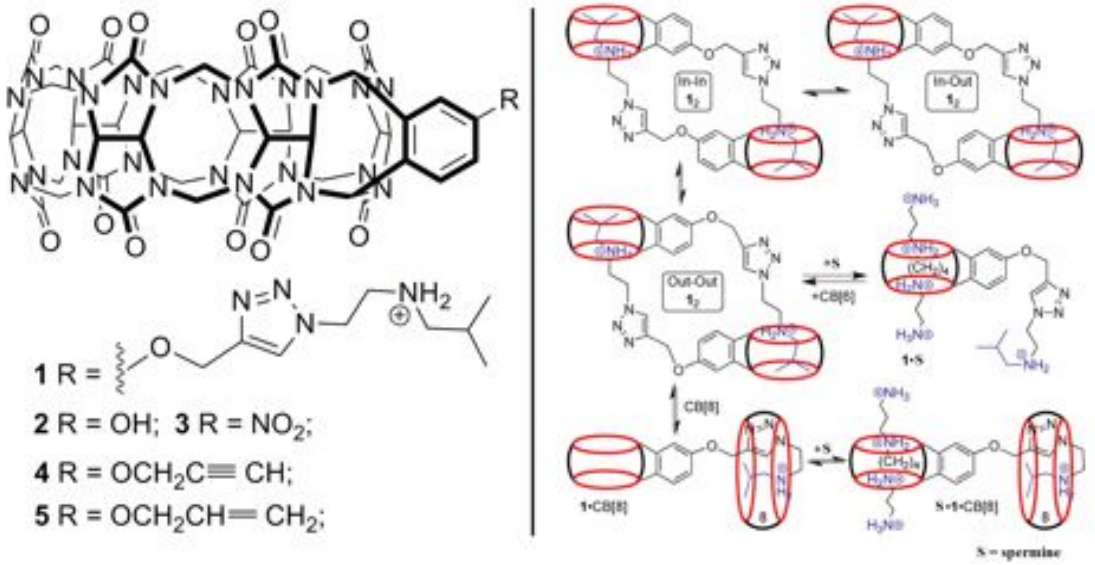


Figure 1. Monofunctionalized Cucubit[6]uril Derivatives and Its Assembly

The chemical structure of **1** features a CB[6] sized cavity covalently connected to an isobutylammonium group. Compound **1** can undergo self-assembly in water to give the cyclic [c2] daisy chain $\mathbf{1}_2$ which is responsive to various stimuli (e.g., guests and CB[n] receptors).[3] Monofunctionalized CB[6] derivatives with reactive functional groups has the potential to enlarge the utility of CB[6]-type receptors as components of more complex systems in the future.

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NMR Analysis of Anion Binding to a Hydrophobic Concavity and its Implications for the Hofmeister Effect

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Irrespective of the technique, studying the properties of aqueous solutions reveals that co-solute salts modulate the solution in predictable ways. This, "Hofmeister Series" is most evident with anions, and follows the order: F-, SO42-, AcO-, Cl-, Br-, NO3-, ClO3-, I-, ClO4- and SCN-. For example, kosmotropes such as F- decrease the solubility of solutes, while chaotropes such as SCN- increase it.[1] We have previously shown that host-guest associations driven by the hydrophobic effect are modulated by salts; in complete accord with the Hofmeister series.[2] Fundamental to this is selective anion binding to the concave binding site of the host. We will report further 1H NMR studies revealing how the thermodynamics of anion binding modulates host-guest binding. These studies are leading to new methods of anion recognition, and more importantly, demonstrate how anions can engender many Hofmeister phenomenon.

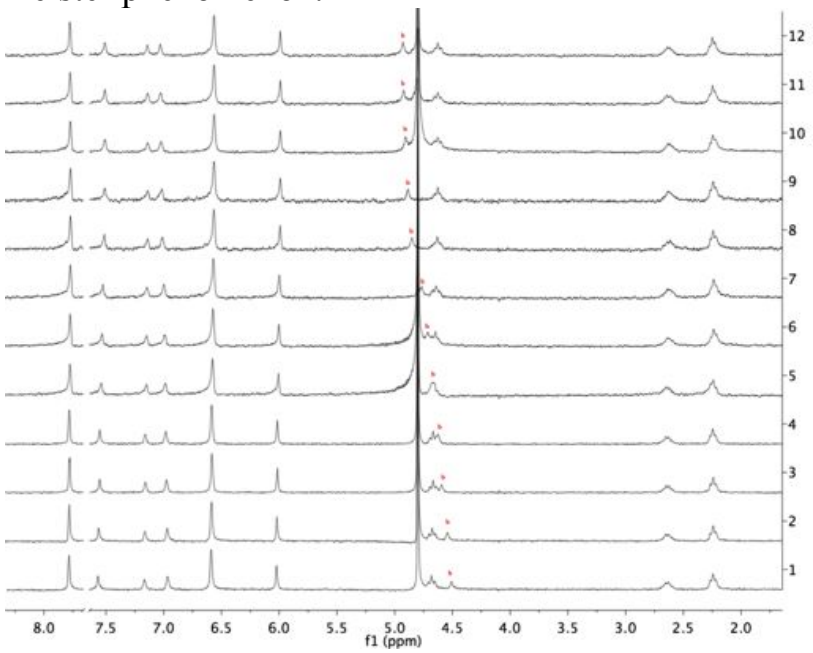


Fig. 1. With serial addition of a guest ion (with no salt at spectrum 1, and approximately .1 M of salt at spectrum 12) to the solution containing the host hydrophobic concavity, the migration of a benzal "b" proton absorption can be observed to shift across the NMR spectrum. The pattern can be fit to a curve proportional to the binding constant of the host-guest interaction.

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Supramolecular Interactions in Fluorescent Lanthanide Molecular Complexes

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Complexes of lanthanide ions with conjugated organic ligands are of significant interest due to their strong fluorescent properties.[1,2] As such, fifteen new lanthanide p-chlorobenzoic acid complexes, $[PrL_3(terpy)(H_2O)]_2$ **(1)**, $[LnL_3(terpy)(H_2O)]_2$ (Ln=Nd **(2)**, Sm **(3)**, and Eu **(4)**), and $[LnL_3(terpy)(H_2O)]$ (Ln=Sm **(5)**, Eu **(6)**, Gd **(7)**, Tb **(8)**, Dy **(9)**, Ho **(10)**, Er **(11)**, Tm **(12)**, Yb **(13)**, Lu **(14)**, and Y **(15)**; HL: p-chlorobenzoic acid; terpy: 2,2':6',2''-terprydine), have been synthesized hydrothermally at varying temperatures and structurally characterized by single crystal and powder X-ray diffraction. The series is comprised of dimers (Pr-Eu) that give way to monomers (Sm-Y) as the lanthanide contraction takes effect. All fifteen complexes feature a tridentate terpyridine, p-chlorobenzoic acid ligands exhibiting multiple binding modes, bidentate, bridging bidentate, and monodentate, and a bound water. Dimeric complexes **2, 3,** and **4** display intermolecular Type II halogen···halogen interactions.[3] Fluorescence studies were performed on complexes **3, 4, 5, 6, 8,** and **9** at room temperature and the characteristic luminescence of Sm(III), Eu(III), Tb(III), and Dy(III) was exhibited. Funding provided by the DOE.

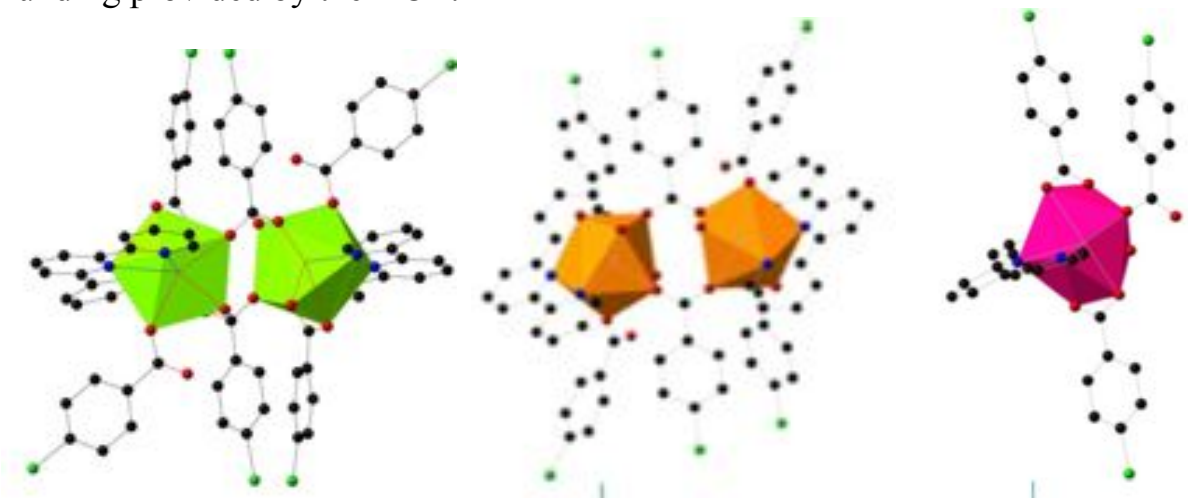


Fig 1. Polyhedral representations of different structure types in Ln-4-chlorobenzoic acid series

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Chemical Control of the Slippage Process in [2]Rotaxanes

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Interpenetrated molecules based on the 1,2-bis(pyridinium)ethane motif (*axles*) and 24-membered crown ethers (*wheels*) have been extensively studied by Loeb and coworkers.[1] It was observed that cyclohexyl groups on the axles can act as slippage stoppers, allowing to reduce the rate of association/dissociation.[2]

Nowadays, we are interested in slow-dissociating mono-charged supramolecular complexes, for their potential use in drug delivery, so we have investigated rotaxane-like systems with dibenzo-24-crown-8-ether (**DB24C8**) as the wheel and several different linear components containing a mono-(pyridinium)ethane recognition site with a bulky group stopper on one side, and a cyclohexyl-type group (cyclohexyl, piperidine, morpholine or thiomorpholine) on the other side as a slippage stopper.

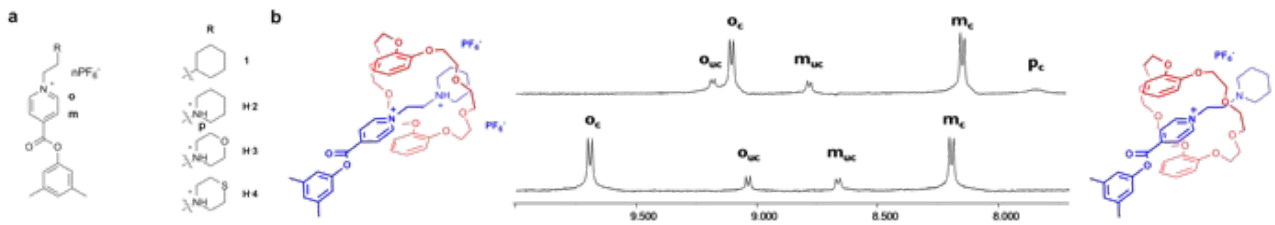


Fig 1. **a**, Monopyridinium-ethane-cyclohexyl axles. **b**, Partial ^{1}H NMR spectrum (400 MHz, 273 K, CD_3NO_2) of equimolar solution of $[\mathbf{H{\cdot}2}]^{2+}$ and **DB24C8** (top) and after addition of 1 equivalent of base (bottom) showing formation of a rotaxane-like complex (uc = uncomplexed axle; c = complexed axle).

A mixture of $[\mathbf{1}]^+$ with **DB24C8** in nitromethane reached equilibrium after 20 days yielding complex $[\mathbf{1}\subset\mathbf{DB24C8}]^+$ with a low association constant (K_a = 5 M^{-1}). Instead, the axle with a piperidinium moiety, $[\mathbf{H{\cdot}2}]^{2+}$ upon mixing with **DB24C8** produce complex $[\mathbf{H{\cdot}2}\subset\mathbf{DB24C8}]^{2+}$, attaining equilibrium in less than 5 minutes with a significant increase in the association constant ($K_a = 2\times10^3$ M^{-1}). Addition of base at 273 K to this solution, rendered the mono-charged rotaxane-like complex $[\mathbf{2}\subset\mathbf{DB24C8}]^+$. The dependency of the half-life time in solution of these complexes with the nature of the slippage stopper will be discussed.

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Synthesis of *Meso*-dipyrrole Calix[4]pyrroles as Anion Receptors

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Anions play a fundamental role in a wide range of biological and environmental processes.[1] Since the pioneering works three decades ago,[2] remarkable progress has been made in the design and application of anion receptors to develop new anion sensors. Previously, we have reported and easy-to-do method for preparation of chromogenic calix[4]pyrroles as anion sensors.[3, 4] Herein we report the design and synthesis of calix[4]pyrroles with double pyrroles pendant arms, *cis*-**1** and *trans*-**1** isomer (Figure 1), their solid state structures and anion binding studies. Both isomers were characterized by ^{1}H NMR, ^{13}C NMR and ESI mass spectra. Further, their solid state structure was elucidated by X-ray diffraction. The binding properties of *cis*-**1** and *trans*-**1** were then assessed by UV-vis titration experiments using various anions. For example, the bathochromic shifts of spectra of *cis*-**1** upon the titration with chloride (Figure 1, right panel) were used to calculate the binding constants. In general, *cis*-**1** exhibits higher overall affinity for anions compared to the *trans*-**1** isomer.

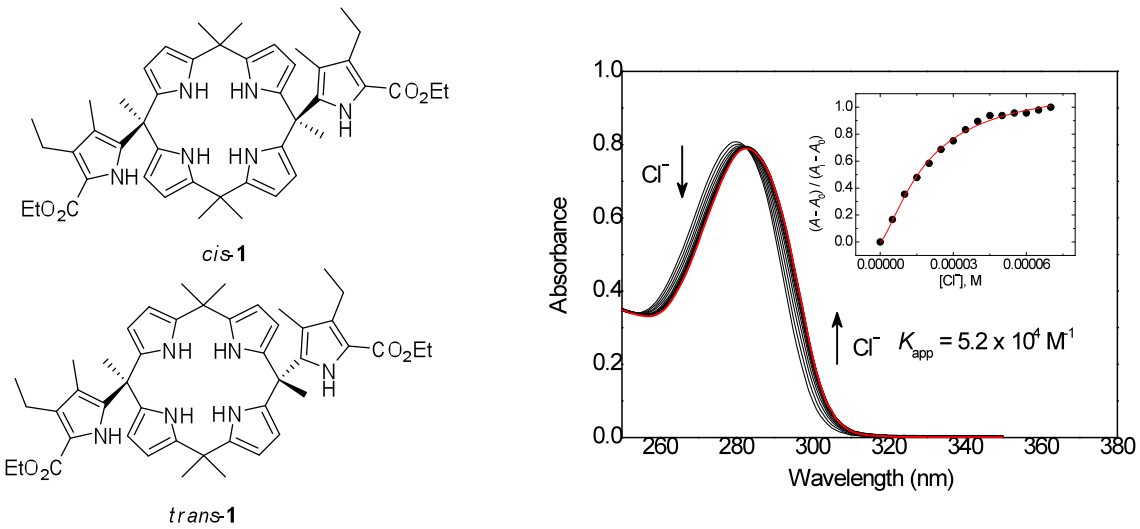


Figure 1. *Meso*-bispyrrole calix[4]pyrrole *cis*-**1** and *trans*-**1** and absorption spectral titrations of *cis*-**1** upon the addition of *n*-Bu_4NCl.

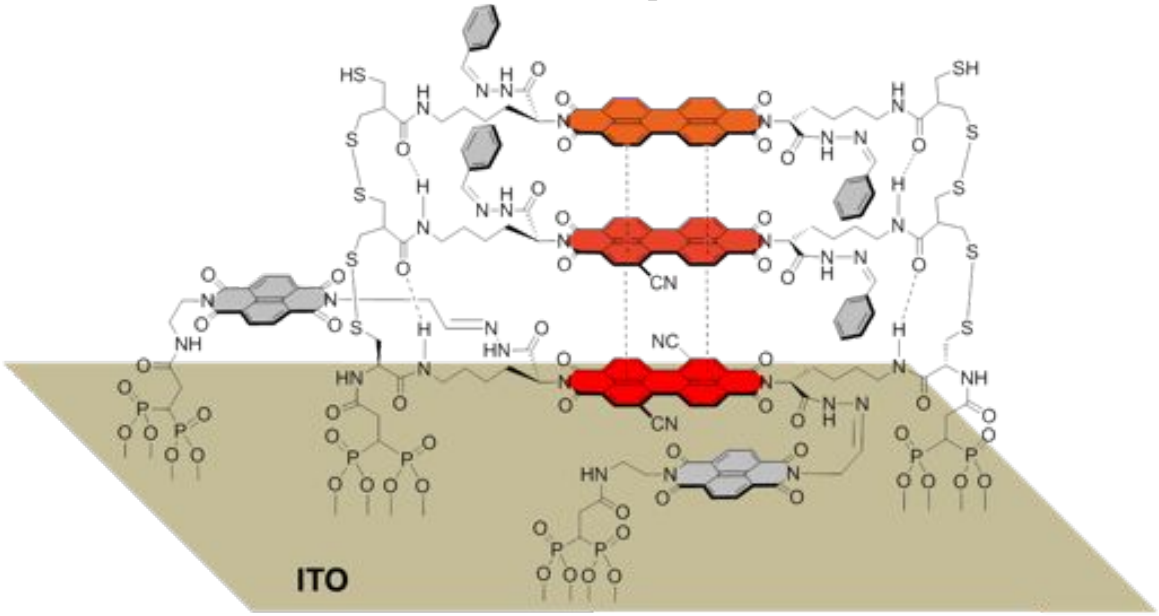
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Oriented Multicomponent Photosystems with Central Perylenediimide Stacks

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In the context of developing new processes to synthesize supramolecular functional materials, self-organizing surface initiated polymerization (SOSIP) has been successfully introduced to functionalize indium tin oxide (ITO)-covered glass surfaces with perylene diimide (PDI) chromophores.[1, 2] Herein, successive polymerizations with different propagators allow for the building of multicomponent central stacks where suitable HOMO and LUMO levels build up redox gradients.

Moreover, the architecture is modified one step further by making use of benzaldehyde-protected hydrazide moieties appended to the central structure. Those are available for chemoorthogonal dynamic hydrazone exchange with various aldehyde-bearing aromatic chromophores. Structured by π-π interactions and templated by the central stack, they arrange in lateral arrays. Taking advantage of the reversibility of the hydrazone linkage and using successive exchange steps, multicomponents lateral stacks are assembled. Judicious choice of partners with matching HOMO and LUMO for the central and lateral stacks leads to the idealized double channel, double gradient heterojunctions with oriented multicolored antiparallel redox gradients (OMARG). Herein, synthetic strategies leading to PDI components, conditions for processing them through SOSIP as well as characterization of the obtained functionalized ITO surfaces will be presented.



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Molecular Binding Thermodynamics of Aryl-β-Cyclodextrins Bearing Triazole Moieties

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Recently, great efforts have been put into designing and developing of novel cyclodextrin (CD) derivatives as well as their guest selectivity and host selectivity.[1-2] However, only a small number of studies focus on the comparison of molecular binding behaviors of CD derivatives with self-included, self-excluded or intermolecular inserted conformation. Herein, two aryl-*β*-CD derivatives bearing 1,2,3-triazole moieties, i.e. mono-6-deoxy-6-{4-(8-oxymethylquinolino) [1,2,3]triazolyl}-*β*-CD (**1**) and mono-6-deoxy-6-{4-(8-oxymethylnaphthol)[1,2,3]triazolyl}-*β*-CD (**3**), and their analogues without 1,2,3-triazole moieties, i.e. mono-6-deoxy-6-(8-oxymethylquinolino)-*β*-CD (**2**) and mono-6-deoxy-6-(8-oxymethylnaphthol)-*β*-CD (**4**) were selected as hosts.[3] Their molecular binding behaviors towards (±)-borneol and (±)-camphor were investigated to elucidate how aryl and triazole substituent moieties of host affects the binding abilities by circular dichroism, fluorescence, 2D NMR spectroscopy as well as microcalorimetric titrations in aqueous phosphate buffer solution (pH 7.20) at 298.15 K. The binding modes of host-guest interactions obtained from 2D NMR displayed that host aryl-*β*-CDs without triazole moieties gave better induce-fit efficiency between hosts and guests, leading to stronger binding abilities. Thermodynamically, the inclusion complexation was driven by enthalpy with the stoichiometry of 1:1. Another factor contributed to the enhanced binding abilities was the enthalpy gain with the smaller entropy loss. From the enthalpy-entropy compensation analysis, host aryl-*β*-CDs without triazole moieties were found to experience minor conformation changes and extensive desolvation effects upon complexation with guests.

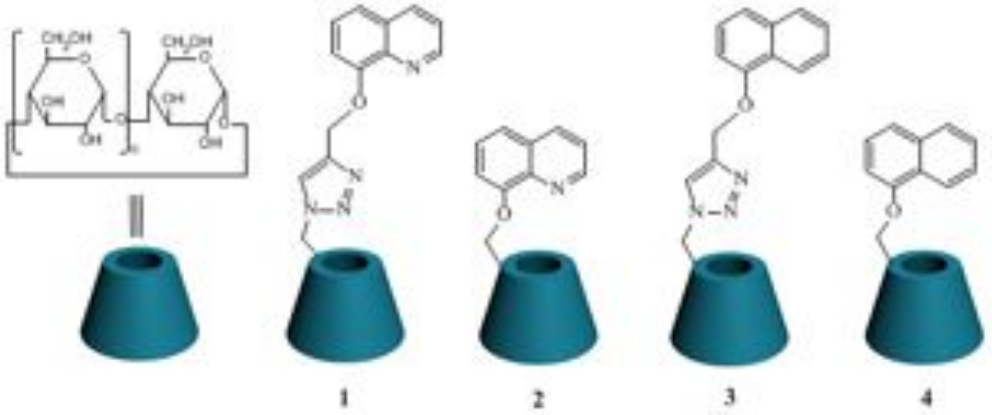


Figure 1. Structures of host aryl-*β*-CDs with and without triazole moieties.

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Driving a Molecular Pump away from Equilibrium

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A pressing goal for contemporary science is to build artificial molecular systems that can perform useful work. Here, we report a molecular pump that processes chemical energy (redox) to drive a molecule away from equilibrium, i.e., from a low to a high energy state. A series of molecular rods were synthesized containing 3,5-dimethylpyridinium (**Py**$^{+}$) and 4,4′-bipyridinium (**BIPY**$^{2+}$) units, connected to a bulky steric stopper by chains of different lengths. Cyclobis(paraquat-*p*-phenylene) (**CBPQT**$^{4+}$) is repelled by the **Py**$^{+}$ and **BIPY**$^{2+}$ initially: upon reduction with activated zinc dust, however, the Coulombic repulsion between **Py**$^{+}$ and **CBPQT**$^{2(+\bullet)}$ decreases dramatically and a thermodynamically stable trisradical complex[1,2] **BIPY**$^{+\bullet}\subset$ **CBPQT**$^{2(+\bullet)}$ is formed within seconds. Tris(4-bromophenyl)aminium hexachlorido-antimonate (Magic Blue) was used to oxidize the radical cation rapidly to the fully oxidized state. The electrostatic **Py**$^{+}$ barrier is recovered, causing the **CBPQT**$^{4+}$ ring to shuttle on to the glycol/oligoethylene chain, for which it has little affinity. Dethreading from this high energy, metastable [2]rotaxane state occurs slowly as a result of Coulombic repulsion between the **CBPQT**$^{4+}$ ring and **Py**$^{+}$/**BIPY**$^{2+}$ units. Experimental results and DFT calculations show that the molecular pump can raise the potential energy of **CBPQT**$^{4+}$ to 13 kcal/mol with an efficiency that reaches 8%.

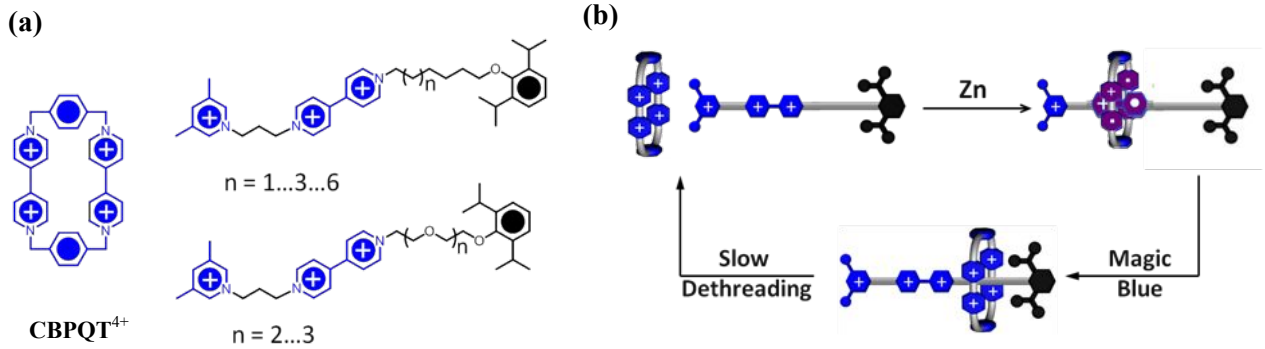


Figure 1. **(a)** Structure formulas of the components for building a molecular pump and **(b)** a graphical representation of the mechanism of action of the molecular pump.

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Ethereal Hosts for Lithium Ion: A Theoretical Study

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Since the host-guest chemistry field has been formulated, organic hosts for various ions have been studied extensively. It is widely accepted that structural and electrostatic complementarity is very important in host-guest chemistry. However, the detailed understanding which enables the chemists to design useful hosts is still in paucity. Furthermore, it's difficult to compare the experimental binding constants considering various experimental conditions such as solvent effect, different temperature, presence of other counter ion effects, etc. Since the computational accuracy of binding energy estimation has been greatly improved. Although the gas phase binding energy is not of direct use for many practical applications, it has an advantage. it could provide an objective measure for the intrinsic affinity. Here we calculated an approximate binding energies for famous organic hosts for lithium. The selectivity between lithium and sodium was also investigated. The 6-31G** basis set with B3LYP functional was used to calculate binding energy of Li^+ and Na^+ with four famous hosts with Gaussian03 package. The hosts comprise of 6-spherand, cryptand, 12-crown-4 and 6-starand as shown in Figure 1. The binding energies and analysis of the corresponding geometries will be presented in the poster.

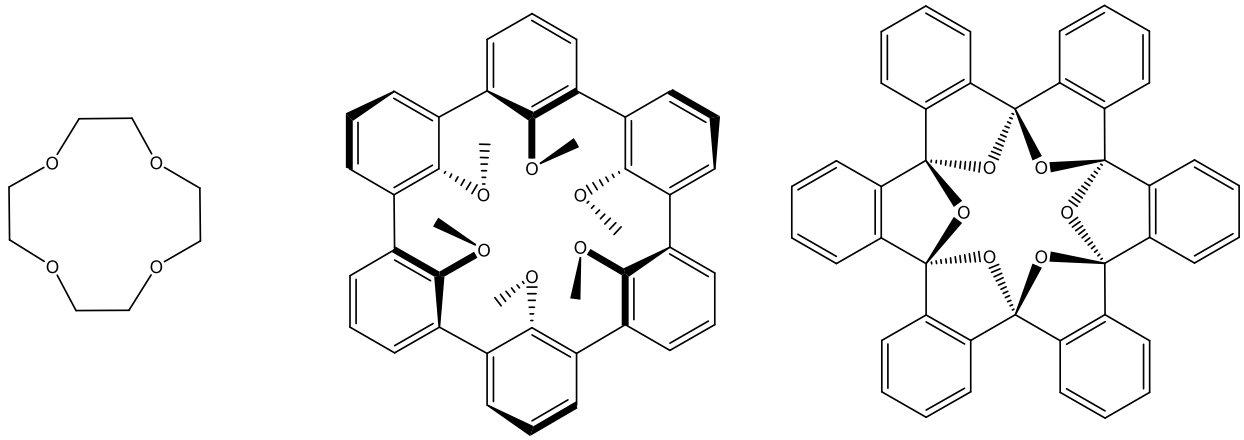


Figure 1. Representative ethereal hosts for Li^+.

References

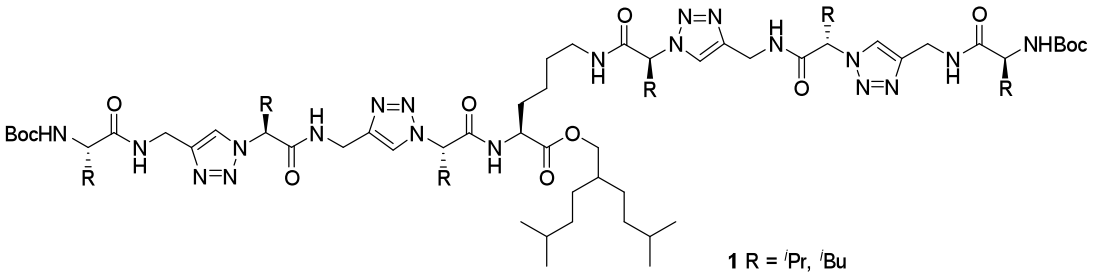
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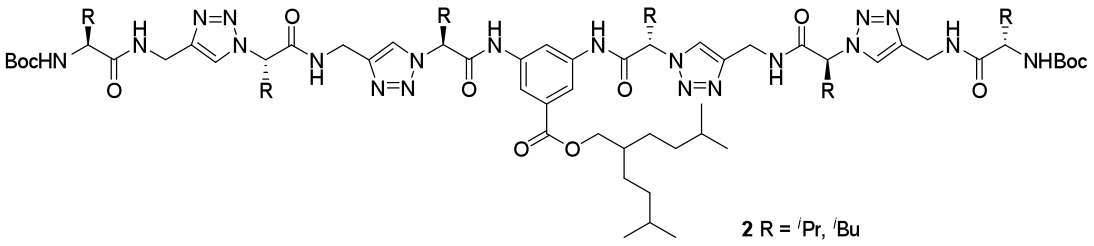
Synthesis and Supramolecular Properties of Branched Oligotriazole-based Peptidomimetics

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We have previously reported a novel class of peptidomimetics composed of an alternating sequence of amino acid units and 1,4-substituted 1,2,3-triazole units,[1] which could be easily accessed via the regioselective copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction. These peptidomimetics exhibited a head-to-tail dimerization and were good organogelators.

In this work we extended our idea to joining these peptidomimetics in a head-to-head manner through a bifunctional linker and to examine their supramolecular properties. Here we made use of L-lysine and 3,5-diaminobenzoate as the linkers and synthesized the corresponding compounds **1** and **2**. It was found that the geometry and symmetry of the linkers played an important role in determining their properties in terms of solubility and ability to form organogels. The lysine derivatives **1** formed very stable and strong gels in aromatic solvents whereas the benzoates **2** were non-gelators even at high concentrations. They also displayed a very different morphology under the scanning electron microscope. Circular dichroism studies revealed that all these peptidomimetics adopted a β-sheet structure. The formation of supramolecular aggregates was also evident for the benzoates **2** from viscometric studies.





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Synthesis, Characterization, and Evaluation of Pluronic based β-Cyclodextrin Polyrotaxanes for Mobilization of Accumulated Cholesterol from Niemann-Pick Type C Fibroblasts

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Niemann-Pick Type C is a rare disorder involving accumulation of cholesterol within the endosomal/lysosomal compartment and giving rise to various neurological, hepatic and pulmonary symptoms that increase in intensity over time.[1] NPC typically manifests in children and is ultimately fatal.[2] Treatment with β-cyclodextrin (CD) derivatives results in rapid egress of cholesterol from sites of abnormal storage both *in vitro* and *in vivo* and was shown to prevent neurodegeneration with continuous infusion into the central nervous system.[3] Unfortunately, cholesterol re-accumulation occurred shortly after dosing due to rapid CD clearance.[3] Increasing the efficiency of CD delivery with a high molecular weight, long circulating delivery vehicle may make it a more viable NPC therapeutic.

Polyrotaxanes (PRTx) are supramolecular assemblies that have been of considerable interest in biomaterials applications.[4] These complexes are prepared by threading macrocycles non-covalently onto a polymer core with subsequent endcapping by bulky moieties to prevent macrocycle dethreading. Endcap cleavage can be designed to be bioresponsive toward pH or enzyme activity, allowing for control over where the PRTx releases its macrocyclic cargo.[5] Here, a library of PRTx derivatives was synthesized using CD and Pluronic block copolymers as building blocks. PRTx macromolecules were subsequently evaluated as potential therapeutics against NPC.

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Pnictogen-Directed Synthesis of Discrete Disulfide Macrocycles

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The use of main-group elements as components in metal-directed self-assembly is not common and has led to new structure types that are inaccessible using the more traditional transition metals.[1] Arsenic(III), antimony(III) and bismuth(III) have unusual, but predictable, trigonal pyramidal coordination geometries that feature stereochemically active lone-pairs of electrons when coordinated by thiolates. Our laboratory has shown that this geometry can be targeted in the self-assembly of As and Sb macrocycles and cryptands (where L = a rigid dithiolate) from $AsCl_3$ or $SbCl_3$ and thiol ligands.[2,3] Current research illustrates these self-assemblies have been found to be more labile than previously thought. Both cryptand and macrocycle are both easily oxidized by mild oxidants such as iodine, DDQ, and NCS. In the case of iodine, discrete cyclic disulfide macrocycles are rapidly synthesized cleanly and selectively when activated by pnictogen additives (As and Sb). Macrocycles were confirmed by ^{1}H-NMR spectrscopy and X-ray crystallography. A *p*-xylyl-based disulfide trimer and tetramer crystallized in hollow, stacked columns stabilized by intermolecular, sulfur···sulfur close contacts.

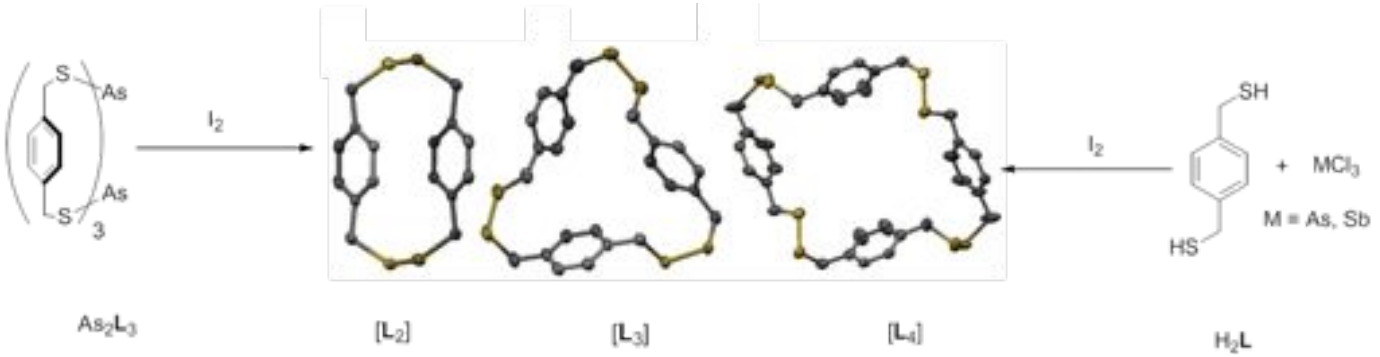


Figure 1. Oxidation of arsenic-activated dithiolates $H_2\mathbf{L}$ or $As_2\mathbf{L}_3$ to cleanly form disulfide macrocycles $\mathbf{L}_2$ (dimer), $\mathbf{L}_3$ (trimer), $\mathbf{L}_4$ (tetramer).

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Effective and Synthetically Simple Anion Transporters Based on a Cyclohexane Scaffold

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The transport of anions, such as chloride, across cell membranes is ubiquitous in biology and the malfunction of proteins that carry out this function can lead to a variety of diseases, such as Cystic Fibrosis[1] and Bartter's syndrome.[2] An effective synthetic anion transporter could work to replace lost activity and has been a goal for supramolecular chemists for two decades.

Our group has been very successful in this area with systems such as the cholapods (e.g. **1**),[3,4] however structures of this design are complex and time-consuming to synthesize. We now present a simpler, yet equally effective system based on a cyclohexane core (e.g. **2**) which utilizes elegant conformational control, due to the appended methyl groups, in order to pre-organize the molecule for anion binding and transport. The most powerful of these systems, **2**, can transport anions into vesicles (as shown in Figure 1 below) more effectively than an analogous cholapod, **1**, but is available in significantly fewer steps.

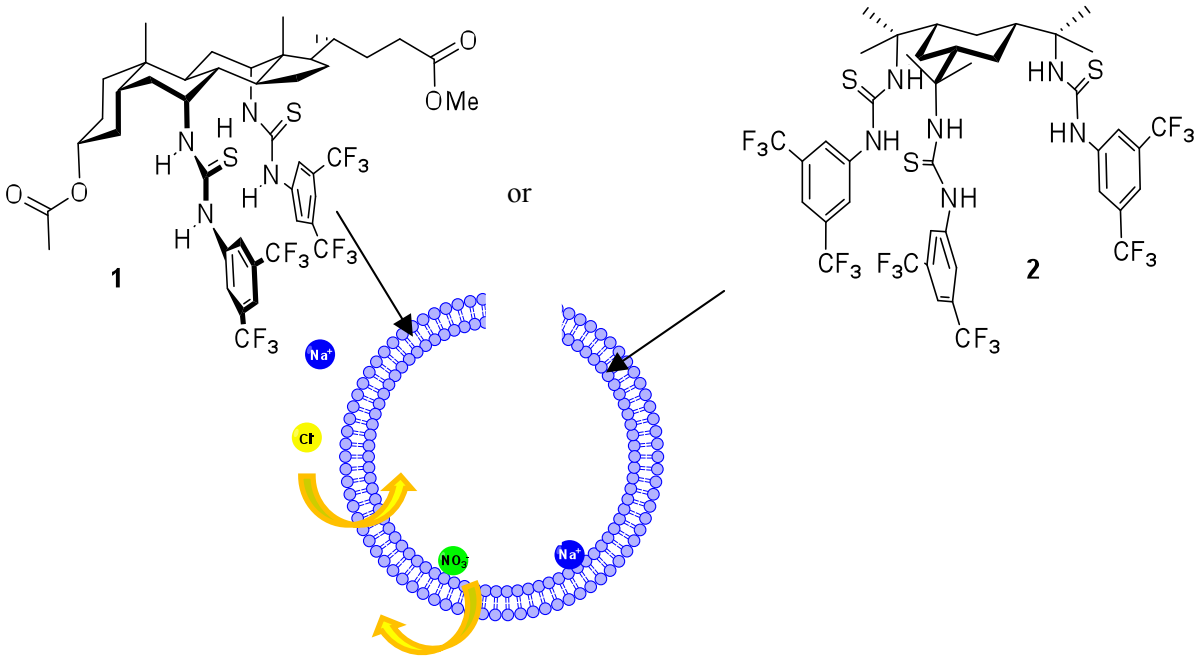


Figure 1. Chloride/Nitrate antiport due to **1** or **2** pre-incorporated into a vesicle membrane

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Novel Metal-Organic Frameworks using Structure Directing, Shape-Persistent Ligands

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Interest in developing porous materials is derived from their many potential applications in host-guest chemistry, molecular sensing and separation, gas storage and heterogeneous catalysis. Advances in synthetic techniques have led to many methods for introducing porosity into materials. Crystalline solids composed of extended structures in which metal ions are linked by organic spacers (binding ligands), or metal-organic frameworks (MOFs), provide highly porous and thermally stable (over 300°C) materials. Furthermore, the materials properties can easily be tuned toward a given application through modification of the organic bridging unit. By using bulky structure directing and shape-persistent ligands it may be possible to increase the overall surface area and void space within the crystal lattice of the material. Here, we highlight the synthesis of a family of new organic ligands chosen for their bulky, shape-persistent nature and high degree of aromaticity. Through incorporating bulky sub-units, we hope to amplify the ligands 'internal molecular free volume' (IMFV) into the corresponding crystalline material.

Exploiting Ferrocene as a Component of Synthetic Molecular Machines: Towards Organometallic Molecular Actuators.

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Biological molecular machines (nature's nanotechnology) exploit controlled molecular-level motion to carry out all of life's fundamental processes.[1] One of the key requirements of the nanotechnology revolution is to gain the ability to manipulate matter on the smallest of scales. In this regard, chemists have begun to synthesize molecular analogues of the fundamental components of machinery from both the macroscopic and biological realms.[1-2] While there have been some spectacular successes, including synthetic molecular "muscles" for the most part these successes have been obtained using complex and difficult to synthesize mechanically interlocked molecules (MIM).[2] Due to the difficulties associated with the synthesis of MIM many groups are now attempting to generate synthetic molecular machines from less synthetically challenging architectures. As part of these efforts a number of groups have begun examining the use ferrocene as a component of synthetic molecular machines.[3-4] Here we will describe our recent attempts to exploit ferrocene in the development of simple molecular switches (Fig. 1a) with a goal of extending these systems to readily synthesised organometallic molecular actuators (Fig. 1b).

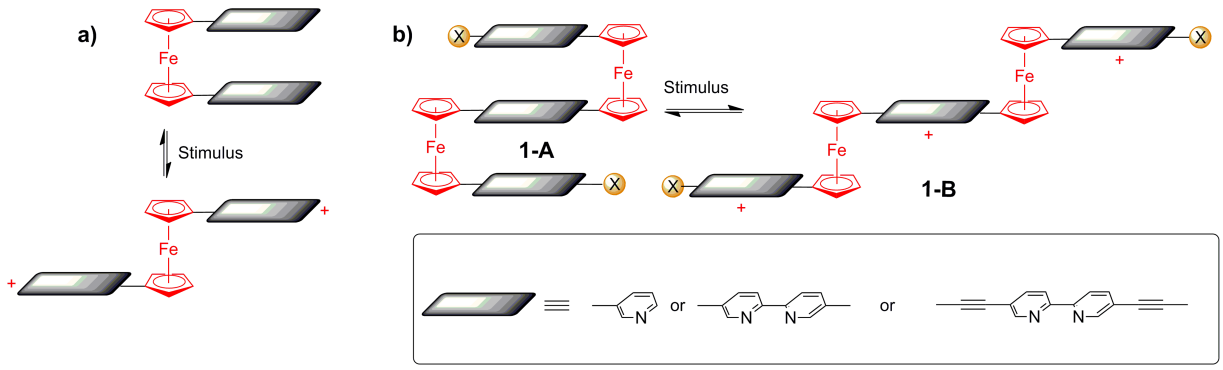


Figure 1. Ferrocene based a) molecular switches and b) actuators.

Acknowledgements: We thank the Marsden Fund, the Division of Science and the Department of Chemistry, University of Otago for providing financial support for this work.

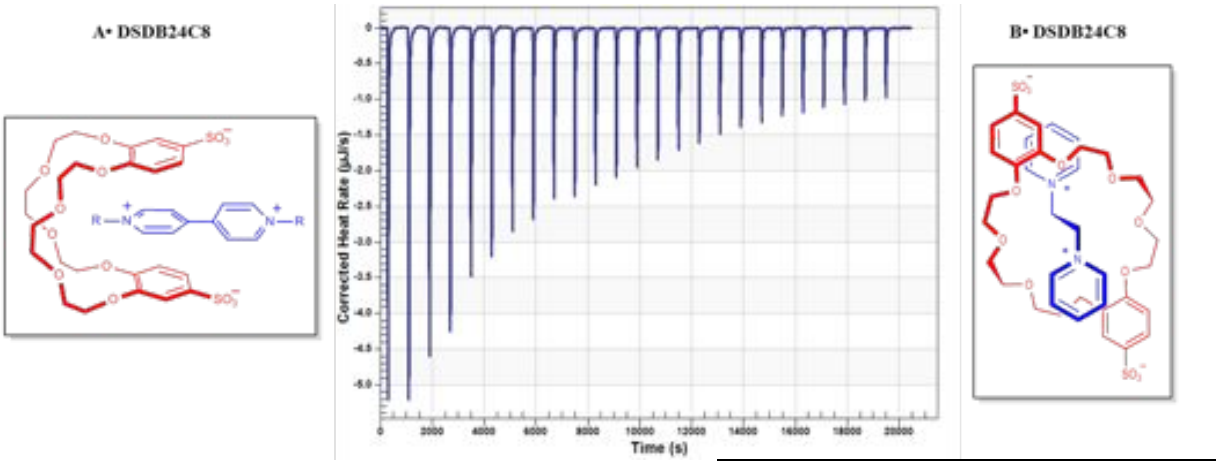
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Structural Effects on the Stability of Supramolecular Ion-Pairs

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We have previously reported the preparation and isolation of two different counter-ion free supramolecular ion-pairs and established their co-conformational preferences in solution and in the solid state; the observed behavior was attributed to the intrinsic stability of the complexes as were no counter-ions present.[1] In order to continue our investigation on the stability of the supramolecular ion pairs and its relationship with structural factors, we undertook calorimetric dilution experiments on two supramolecular isomers. These complexes are formed from two equally and opposite double-charged species, methyl-viologen $\mathbf{A}^{2+}$ or 1,2-bis(pyridinium)ethane $\mathbf{B}^{2+}$ as guests and the anti-disulfo-dibenzo[24]crown-8 $[\mathbf{DSDB24C8}]^{2-}$ as host; which gave rise to 1:1 complexes, **[A·DSDB24C8]** and **[B·DSDB24C8]** (Figure 1).



$\Delta_r H$	40.0	±2.0	kJmol^{-1}
$\Delta_r S$	193	± 6	Jmol^{-1}K^{-1}
$\Delta_r G$	17.8	± 0.2	kJmol^{-1}
K_a	(1.2	± 0.1) x 10^3	M^{-1}

$\Delta_r H$	22.2	± 0.5	kJmol^{-1}
$\Delta_r S$	105.1	± 0.3	Jmol^{-1}K^{-1}
$\Delta_r G$	9.1	± 0.5	kJmol^{-1}
K_a	(4.0	± 8) x 10^2	M^{-1}

Fig 1. Structures of supramolecular ion pairs **A** and **B**. In the middle, a typical thermogram of the dissociation ITC experiments, and thermodynamic data of the process for both structures.

The crystal structures of both complexes have been determined and related to their association constants. The results suggests that the relative stability of the supramolecular complex **[A·DSDB24C8]** is significantly higher than the stability of its isomer **[B·DSDB24C8],** proving the importance of the different non-covalent interactions on each geometrical arrangement.

Ion-Pair Recognition in Self-Assembled Helicates

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Triple-stranded helicates of M_2L_3 stoichiometry represent prototypical supramolecular architectures self-assembled from bidentate chelating ligands and metal cations with well-defined coordination geometries. Recent studies indicated that, analogous to metal coordination, anion coordination can also be effectively employed in the self-assembly of molecular ensembles with predictable architectures.[1] By combining cation and anion coordination chemistries, we show that heteroditopic ligands comprising 2,2'-bipyridine and *o*-phenylene-(bis)urea chelating groups self-assemble with MX salts (M = Ni^{2+}, Fe^{2+}, X = divalent tetrahedral oxoanions, e.g., SO_4^{2-}, SeO_4^{2-}) into ion-pair helicates or mesocates, in which the cations and anions are octahedrally coordinated by 6 pyridyl and 6 urea groups, respectively.[2] The self-assembly process is highly selective with respect to both the cation and the anion, discriminating based on shape, charge, and coordination preferences of the ions. The structures and dynamics of the helicates/mesocates, as determined by single-crystal X-ray diffraction and NMR and ESI-MS spectroscopies, will also be discussed.

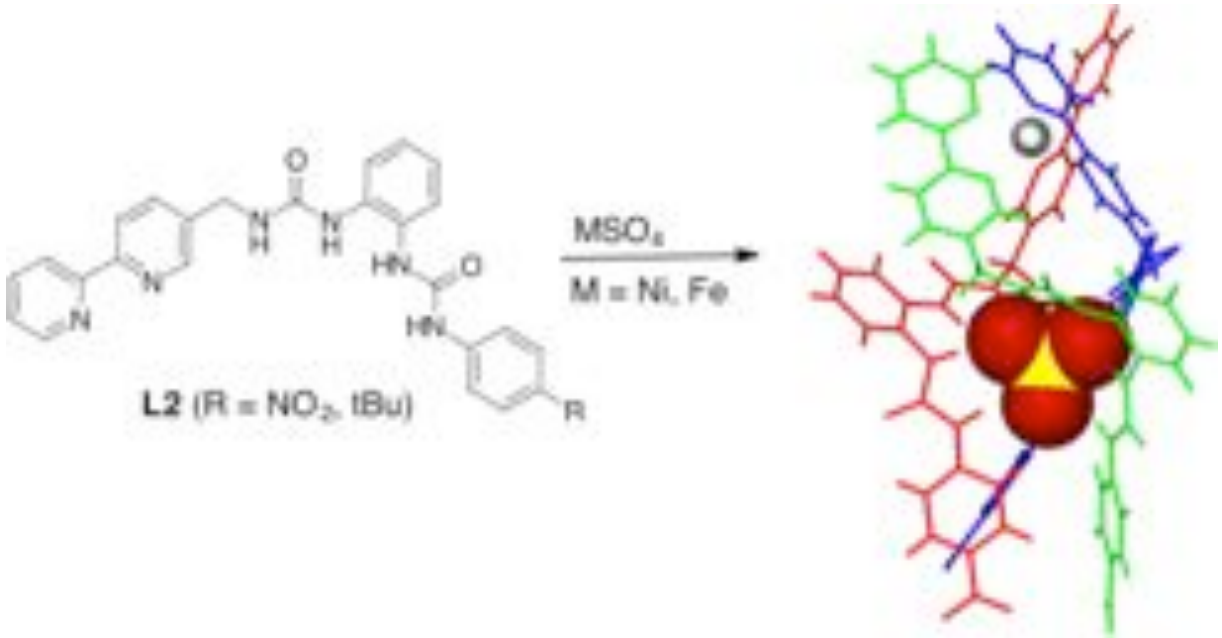


Figure 1. Self-assembly of ion-pair helicates from heteroditopic 2,2'-bipyridine-bis(urea) ligands and MSO_4 (M = Ni, Fe).

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Oligothiophene Based Fluorescent Membrane Probes

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Multiple biological processes such as recognition, transport and replication are mediated by changes in cellular membrane properties. As a consequence, the analysis of membrane fluidity or lateral tension became more and more important for the study of biological systems. Fluorescent probes represent nowadays the best analytical tool for the study of membrane characteristics, thanks to their high sensitivity and spatial resolution, driving the research towards molecules with always improved performances.

Recently our group proposed the use of a new class of fluorescent probes based on amphiphilic oligothiophenes push-pull systems,[1] in which planarization and polarization of the oligothiophene core is induced by environmental changes, enabling the sensing of membrane fluidity, homogeneity and tension (Figure 1).[2] The potentialities of the new probes were tested in DPPC (dipalmitoyl phosphatidylcholine) vesicle membrane model, showing good sensitivity toward the change in fluidity induced by a thermal phase change transition. In particular, the probe responds to a passage from liquid crystalline phase to gel phase with a bathochromic shift of its excitation maximum, as a consequence of the planarization of its ground state induced by the passage to a more rigid environment This poster presents the results of an improved design of the fluorophores, obtained by the systematic variation of the push-pull strength,[3] the degree of deplanarization of the oligothiophene backbone and the length of the conjugated oligomer.

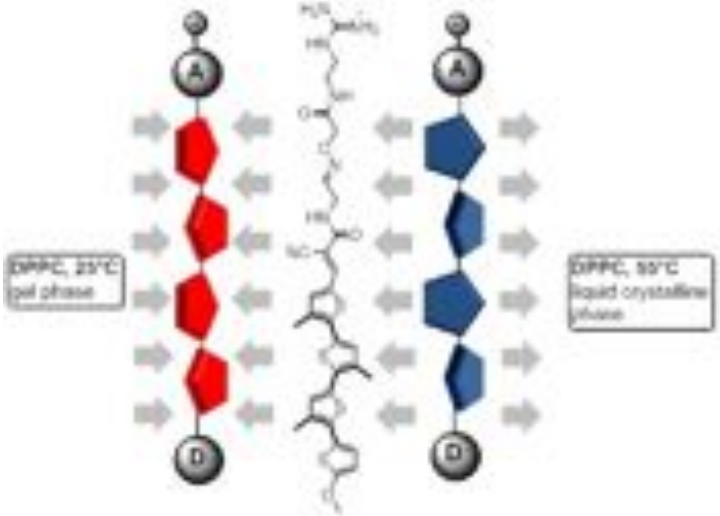


Figure 1. Amphiphilic oligothiophene push-pull systems.

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ExCage: A Three-Fold Symmetric Extended Viologen Cage

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The ability of viologens to enter into strong charge-transfer interactions is well-established in the literature.[1] Cyclophanes, and more recently, rigid cyclophanes—comprised of two viologen subunits—are capable of forming[2] inclusion complexes with polycyclic aromatic hydrocarbons (PAHs) with high affinity through a combination of charge-transfer and van der Waals interactions.[3] The synthesis of a three-fold symmetric, *ex*tended viologen *cage*-like receptor (**ExCage**$^{6+}$) has been achieved, containing a total of six π-electron poor pyridinium units displayed 1,3,5 around a benzenoid core and connected by three bridging *p*-xylylene units. Having an internal cavity measuring 12.6 Å between each *p*-xylylene unit and spanning from 6.6 up to 7.3 Å between opposing 1,3,5-tris(4-pyridinium)benzene moieties, **ExCage**$^{6+}$ is poised to bind a large number of PAHs of varying size and shape. Compared to two-dimensional cyclophanes, **ExCage**$^{6+}$ has the advantage of being a three-dimensional cavity, in which non-linear guests can engage in multiple charge-transfer interactions while still maintaining overlap with the core benzenoid unit. The utility of **ExCage**$^{6+}$ arises from its ability to host a diverse population of π-electron rich guests which are denied complexation with other cyclophanes, allowing future studies into their applications in filtration and/or separation.

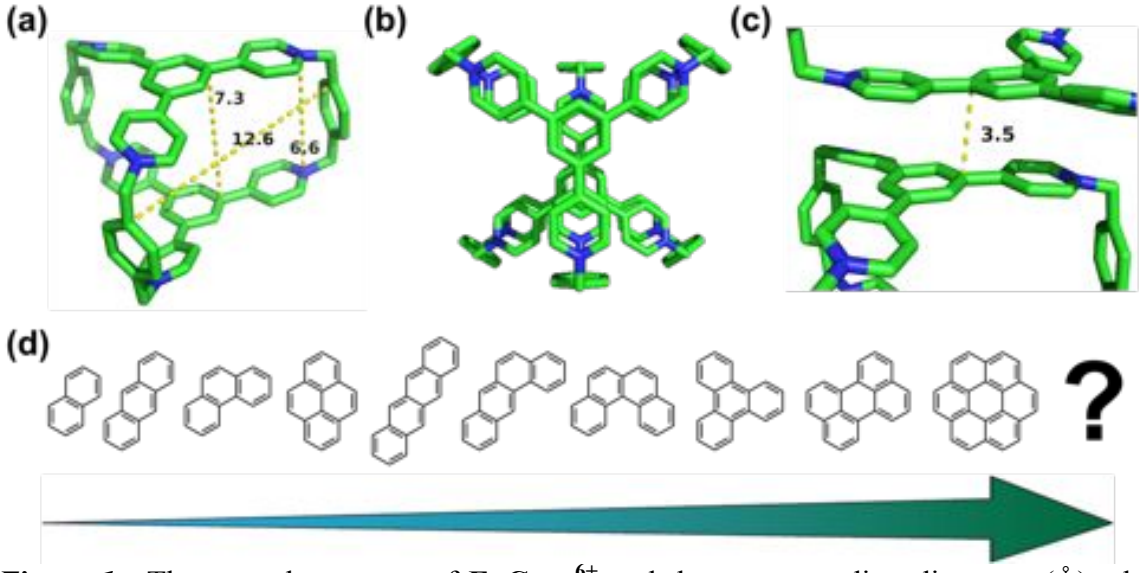


Figure 1. The crystal structure of **ExCage**$^{6+}$ and the corresponding distances (Å) which demonstrate the expanse of the cavity (**a**), and top view of two **ExCage**$^{6+}$ molecules stacked on one another in the superstructure (**b**), where an optimum π-π stacking distance exists between the two cages (**c**) are shown. Increasing size of π-electron rich PAHs that could bind favorably inside the **ExCage**$^{6+}$ (**d**).

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Self-assembled Bis-urea Macrocycles as a Tubular Molecular Container for Selective Chemical Reactions in the Solid-state

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Bis-urea macrocycles self-assemble to tubular structures giving crystal with nano sized channels that we use as molecular containers. These molecular containers alter the reactivity, stability, and chemical behavior of the reactants entrapped within them. We are investigating these containers to influence the outcome of photochemical reactions done within it. In the presentation, we will describe the applications of a self-assembled tubular molecular container as a flask for selective solid-state reaction. This crystalline straw-like container is developed from cyclic bis-urea macrocycles containing two C-shaped phenylethynylene units and it can absorb solid guests such as coumarin, its methylated derivatives and other similarly sized guests from their solution.[1] Coumarin usually undergoes a non selective photoreaction in solid state with very low percent conversion to produce four different isomers. Within our molecular container, coumarin photo-dimerization produced only one isomer with amazing selectivity and enhanced conversion in the solid-state. Derivatives of coumarin such as 6- or 7-methyl coumarin also showed selective product formation consistent with their subtle difference in dimension.[2,3] The synthesis and stability of the container along with the extensive characterization of these host•guest complexes will be discussed. The influence of the container on the dimerization of the guest molecules will be presented.

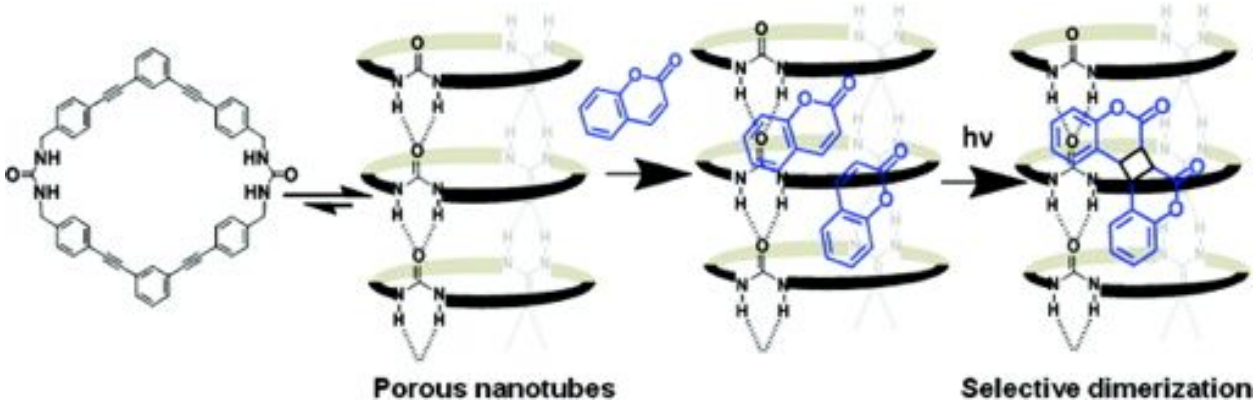


Fig 1. Self-assembly of bis-urea macrocycle and selective photodimerization within the tube.

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Sequence-Specific Synthesis by an Artificial Small-Molecule Machine

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The ribosome is an enormous biological molecular machine that joins together amino acids derived from transfer RNA building blocks in an order determined by a messenger RNA strand, creating protein in a process known as translation. We report on the design, synthesis and operation of an artificial small-molecule machine that travels along a molecular strand, picking up amino acids that block its path, to synthesize a peptide in a sequence-specific manner.[1] The chemical structure is based on a rotaxane, a molecular ring threaded onto a molecular axle. The ring carries a thiolate group that iteratively removes proteinogenic amino acids from the strand and transfers them to a peptide elongation site through native chemical ligation. The synthesis is demonstrated using ~10^{18} molecular machines acting in parallel and generates mg quantities of a peptide with a single sequence, determined by tandem mass spectrometry, corresponding to the original order of the amino acid building blocks on the strand.

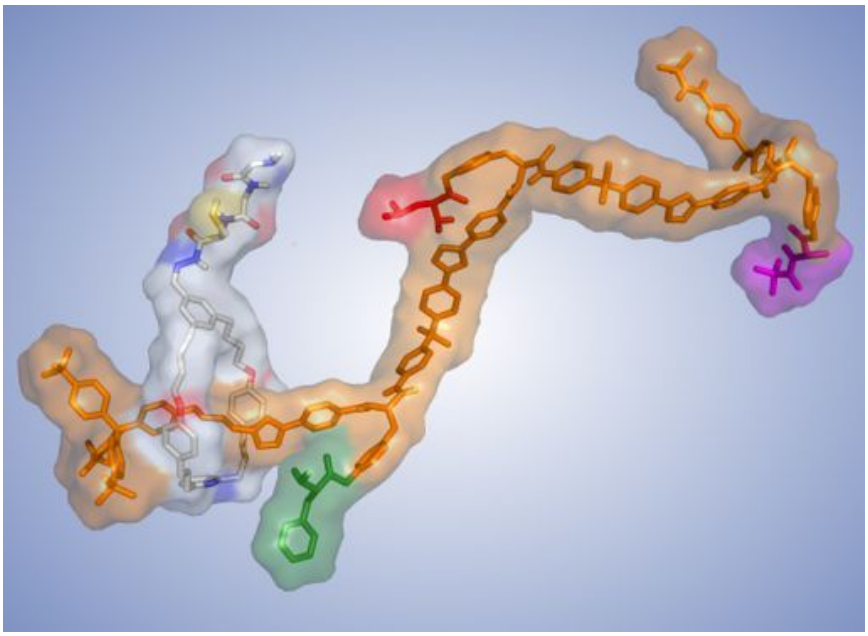


Figure 1. A molecule that makes molecules.

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A Novel, Robust, Electrochemically Active Covalent Organic Framework

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Covalent organic frameworks (COFs) are well ordered, inherently porous, high surface area, and crystalline, 2D or 3D polymers comprised of light elements (C, H, N, O, B). In the 2D case, they form layered π-stacked structures. This alignment of orbitals can enhance vertical charge transport throughout the polymer, a promising feature for electronic applications. Here, we present the solvothermal synthesis of a new enamine-linked redox-active COF. The framework incorporates quinone groups through a condensation of 2,6-diamino anthraquinone (DAAQ) with 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (TS) to form a layered 2D COF (DAAQ-TS, Figure 1). The material has been synthesized as a microcrystalline powder with a BET surface area as high as 800 m^2/g. For electrochemical energy storage applications, the high surface area of the COF should lead to increased double-layer capacitance, and, the redox processes of the anthraquinone moieties will provide pseudocapacitive charge storage. Structure-property relationships important to energy storage will be discusseed by comparing the DAAQ-TS COF to a recently reported[1] 1,4-diaminobenzene-TS COF (DAB-TS COF, Figure 1).

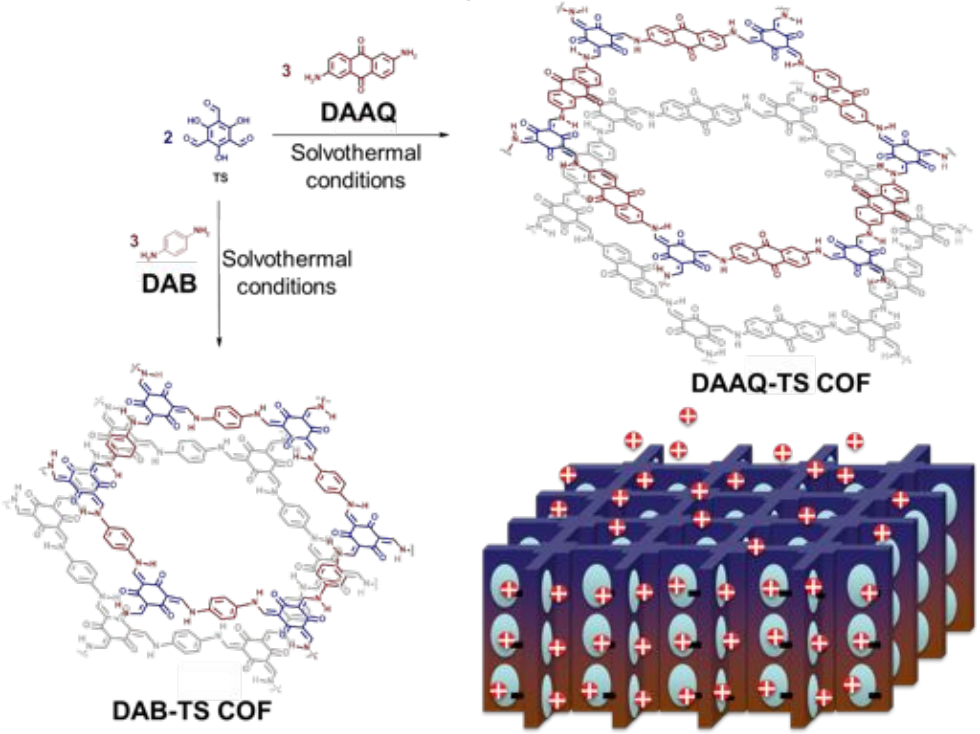


Figure 1. Solvothermal condensation of DAB-TS and redox-active DAAQ-TS enamine COFs. Bottom right is a schematic of a redox-active COF in an electrochemical capacitor.

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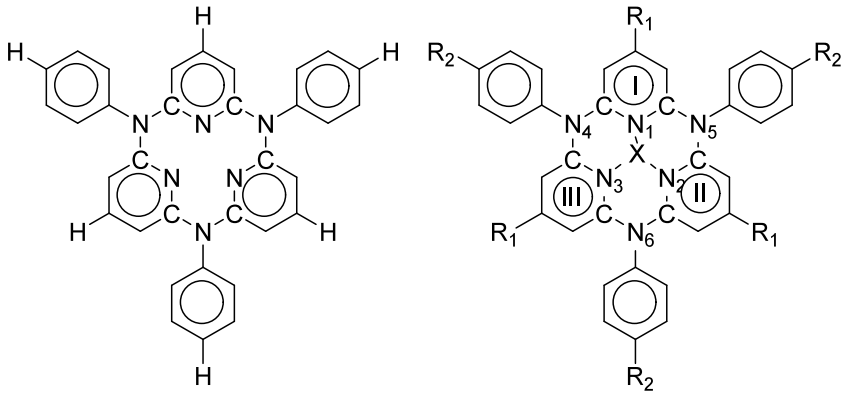
Azacalix[3](2,6)pyridine Derivatives are Powerful Trident Scavengers for some Alkali and Alkaline Earth Metal Cations

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It is a common wisdom that macrocyclic ligands have the ability to selectively bind the metal ions[1] which has proved to be very useful in ion transporting phenomena, chemosensing, metaloenzyme mimics, catalysis, and nuclear waste treatments.[2] Among a large variety of macrocycles synthesized to serve as scavengers of metal ions, calixarenes play a notable role.

This presentation reports on the results of the complexation of Li^+, Na^+ and Be^{2+} metal cations with several derivatives of the parent *N*-(phenyl)-substituted azacalix[3](2,6)pyridine (Figure 1.), both in gas phase and in acetonitrile solution. The gas phase molecular structures and complexation energies were calculated by the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) method including basis set superposition error (BSSE) calculated by counterpoise (CP) correction scheme at the same level of theory. The solvent effects were assessed using the polarized continuum method (PCM).

The results have shown that supramolecular structures **1a**, **1b** and **1c** offer useful ligands capable of efficient and selective sequestration of Li^+, Na^+ and Be^{2+} cations, being the most suitable for the Be^{2+} cation. The binding affinity for Be^{2+} is extremely high, both in the gas phase and in the acetonitrile,[3] which might be very useful in prevention of berylliosis disease.



1

1a (R_1=H, R_2=Me)
1b (R_1=R_2=NMe_2)
1c (R_1=R_2=[N=C(NMe_2)$_2$])

Figure 1. *N*-(phenyl)-substituted azacalix[3](2,6)pyridine scafold **1** and its derivatives **1a**, **1b** and **1c** serving as scavengers of cations X = Li^+, Na^+ and Be^{2+}.

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Selective and Tunable Carbohydrate Sensors from Synthetic Lectins

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Many biological processes involve the recognition of carbohydrates on the surfaces of cell membranes. Lectins "carbohydrate binding proteins" are vital to this information transfer and thus can be useful tools in science. Selective recognition of saccharides in aqueous media presents a particular challenge for supramolecular chemistry, due to the hydromimetic nature and structural similarity of the substrates. Despite this our group has meet with some success in the design of 'synthetic lectins', recently reporting a simple and fluorescent system for all equatorial substrates such as glucose[1]. Herein we report a simple modification to this system, which allows control and selectivity for all-equatorial positively and negatively charged carbohydrates, while improving solubility and binding and maintaining florescence output.

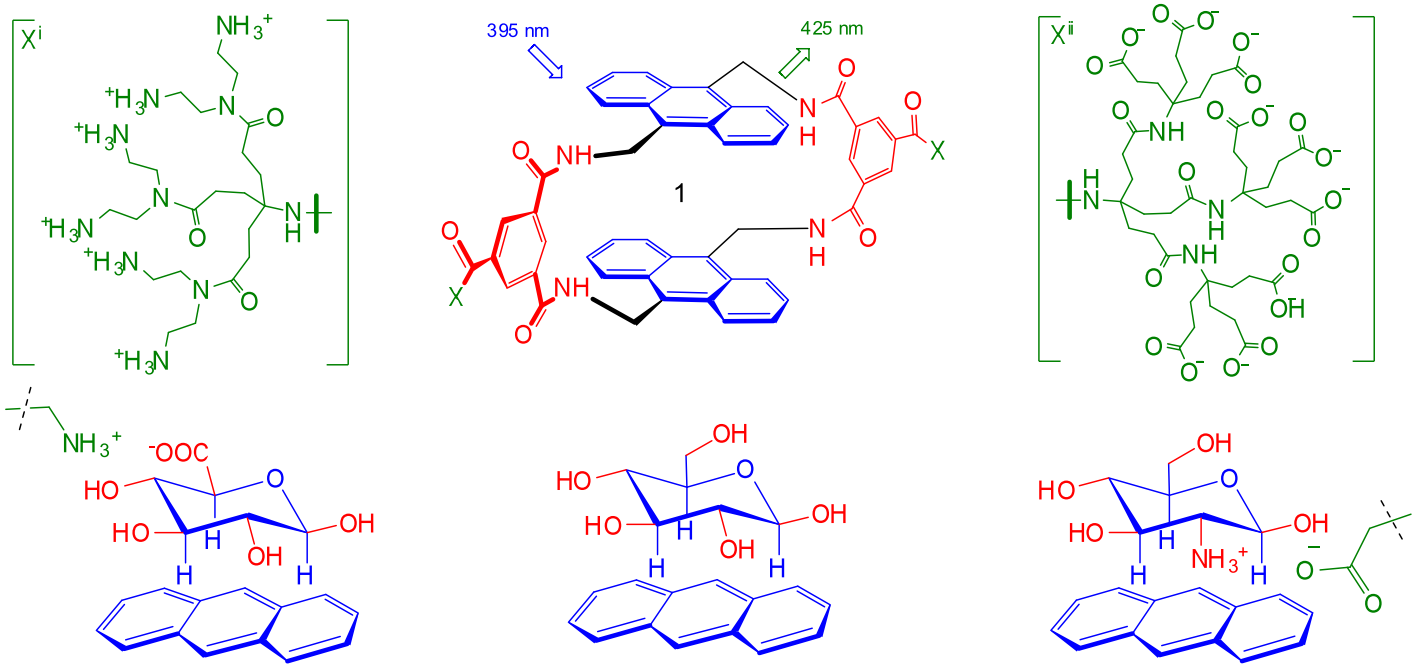


Figure 1.

References

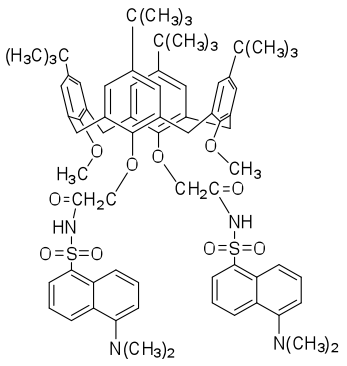
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The Influence of Conformation of Fluorogenic Calix[4]arenes on Selective Sensing of Toxic Mercury(II) Ions

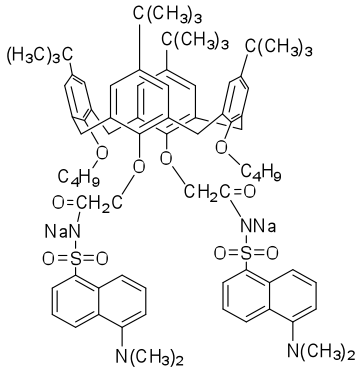
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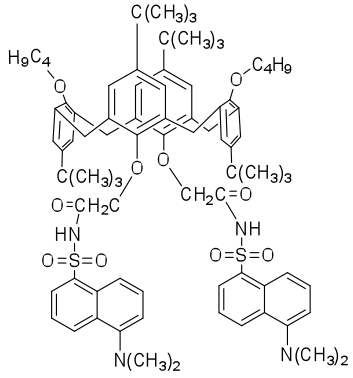
Calixarenes have shown promise in the efficient and selective sensing of toxic heavy metal ions, in particular, Hg^{2+}, which has harmful digestive, cardiac, kidney, neurological health effects on humans. During complexation with metal cations, flexible calixarenes adopt the conformations which are the most appropriate for accommodation of specific guests. This feature of calixarene-based ligands may be used for the design of complexing reagents for selective optical recognition of hazardous metal ions. Recent work by this research group has shown that a flexible calix[4]arene **1** demonstrated high selectivity and sensitivity towards Hg^{2+}, preferring the *cone* and *1,3 alternate* conformations upon complexation with this heavy metal ion.[1,2] In order to study systematically the effect from the conformational preorganization of the calixarene moiety on Hg^{2+} sensing by such fluorogenic ligands, two new fluorogenic calix[4]arenes, **2**[3] and **3**, fixed in the *cone* and *1,3-alternate* conformations, respectively, were obtained and their metal ion sensing characteristics studied. In both solvent extraction from aqueous solutions (with high content of competing Na^+, $C_{Na^+} \sim 0.1$ M; pH 5.0, acetate buffer) and acidic MeCN-H_2O (1:1 *v/v*) solutions, **2** and **3** showed selective optical recognition of Hg^{2+} over many alkali, alkaline earth and transition metal cations relative to their conformationally mobile analog **1**.



1 (Flexible)



2 (*Cone*, disodium salt)



3 (*1,3-Alternate*)

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Responsive Assemblies of Organic Cage Molecules

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Assemblies of porous molecular cages (PMCs) are a burgeoning field in materials science. By utilizing PMCs as discrete building blocks, solid state materials have been synthesized with unique propities.[1-3] A unique feature of PMCs is that they have all the benefits of extended porous structures such as microporous polymers, or metal organic frameworks (MOFs), whilst maintaining the solubility and versatility associated with small molecules. Hitherto, such cages have been constructed from dynamic covalent chemistry using 'one pot' synthetic methods. We have recently explored the design and synthesis of highly porous PMCs constructed solely from carbon atoms. Such materials promise important scientific outcomes through future practical opportunities as well as tackling a fascinating set of fundamental challenges in synthetic chemistry, materials science, crystal engineering, and crystallography. Here we report how individual cages can be modified to yield bulk samples that are responsive to external stimuli such as light.

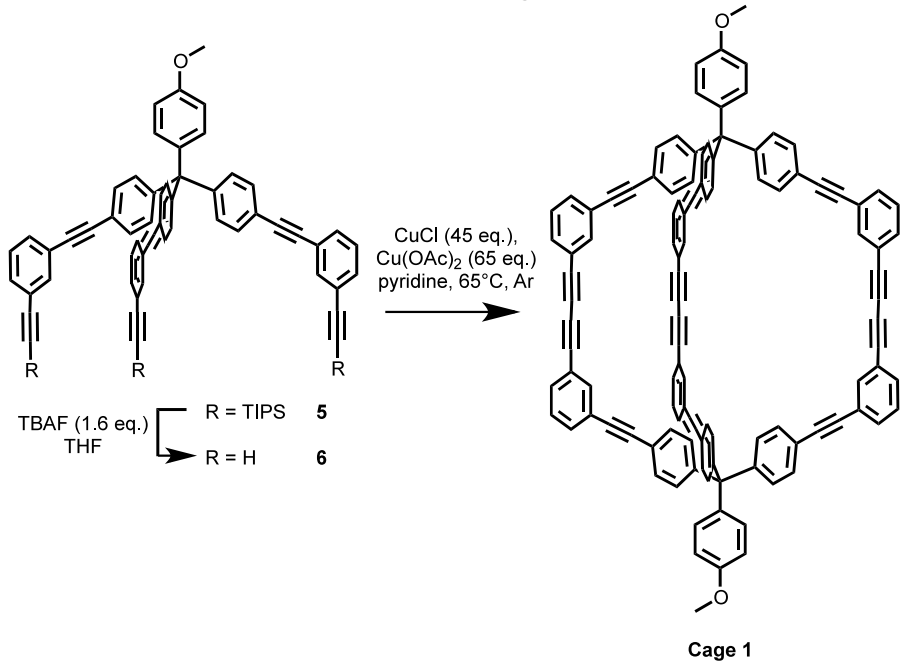


Figure 1. Intrinsically porous cage molecule

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Photo-responsive Supramolecular Coordination Polymers in Organic Media and Their Light-induced Morphological Transformations

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Pseudo one-dimensional (1D) transition metal complexes have been attracting much interest because of their specific electronic, magnetic and optical properties in the crystalline state. Studies on 1D metal-organic nanomaterials have mostly focused on the bulk phase such as single crystal and metal-organic frameworks, which were limited in flexible fabrication of miniaturized devices. To develop 1D metal complex dispersible in solution, it is necessary to convert them lipophilic by introducing lipophilic alkyl chains.[1] Lipid-converting technique is a general pathway to prepare lipophilic 1D complexes. In this work, mixed-valence diruthenium (II,III) paddlewheel complexes with the formulas $[Ru_2(\mu\text{-}O_2CR)_4X]_n$, where R is an azobenzene-contained lipid, X = Cl (**1**-Cl) or I (**2**-I), has been successfully synthesized. These diruthenium complexes showed good solubility in nonpolar solvents while solvatochromism can be observed in **2**-I solutions. The self-assembly of coordination polymers showed concentration dependent behaviors. Particularly, photoisomerization was observed for dilute solution (0.01 mM) while it hardly occurred at higher concentration (1.0 mM). In contrast, distinct morphological transformation could be observed by photoirradiation of the solid samples. These differences upon photoisomerization behaviors in solution and solid state might be the result of the different packing state of diruthenium complexes.

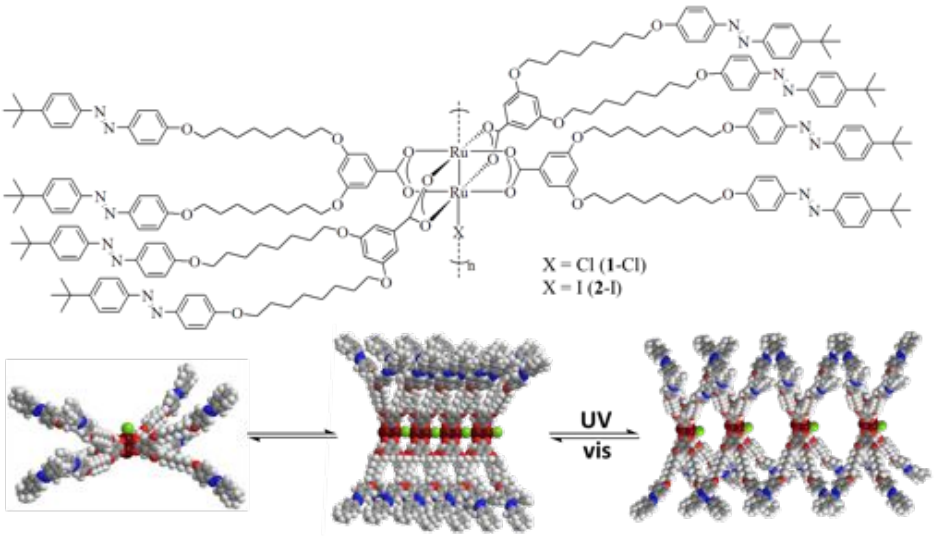


Figure 1. Unit molecular structure of halogen-bridged coordination polymers and the illustration of one-dimensional supramolecular polymer formation and photoinduced transformation.

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Supramolecular Dimers of Catechol as Templates for the [2+2] Photocycloaddition

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Control over the self-assembly and packing of molecules in organic crystals has been observed to be significant in the utility of the organic solid state as a medium for synthetic chemistry. Employing hydrogen-bond-donor templates based on resorcinol, our group has developed a means to organize reactive olefins into discrete assemblies suitable for [2+2] photocycloadditions. Attempts to expand the library of useful organic templates to include catechol and its derivatives were met with unique assemblies and varying degrees of photoreactivity. Photostable assemblies comprised of infinite 1D chains were observed,[1] as well as reactive, non-discrete assemblies that produced head-to-tail photodimers.[2]

Here we will show the first example of catechol forming a discrete and photoreactive assembly with 2,2'-bis(pyridyl)ethylene. Additionally, the assembly shows a unique character whereby the functional template consists of a supramolecular dimer of catechol molecules. Assessment of additional catechol-based templates has yielded a second cocrystal exhibiting analogous supramolecular templating.

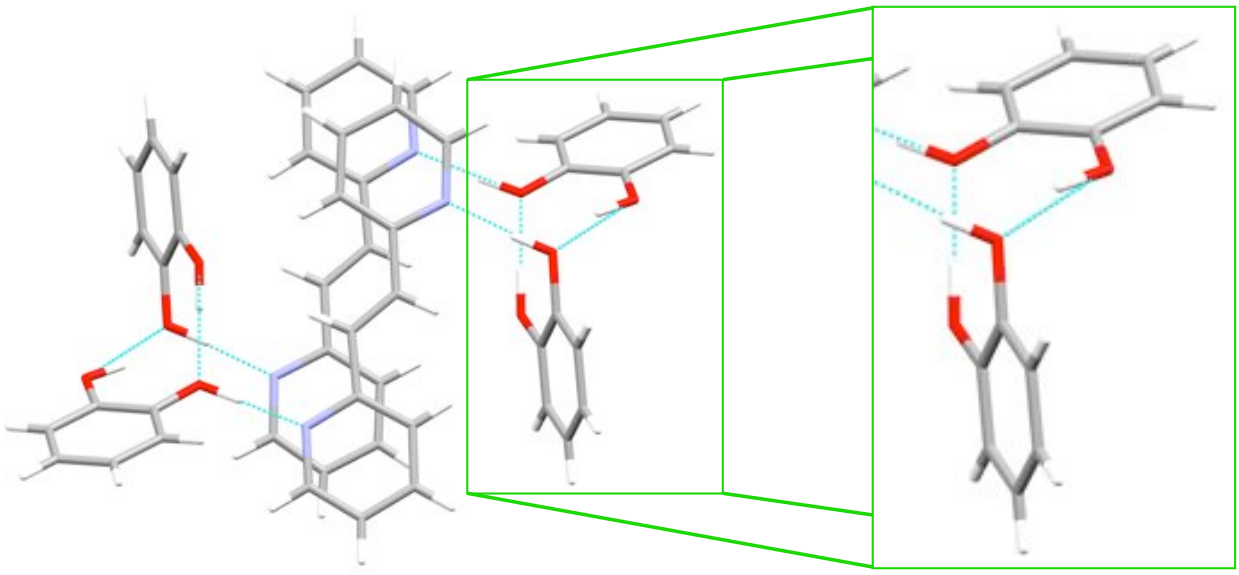


Figure 1. Catechol as a template for a [2+2] photodimerization.

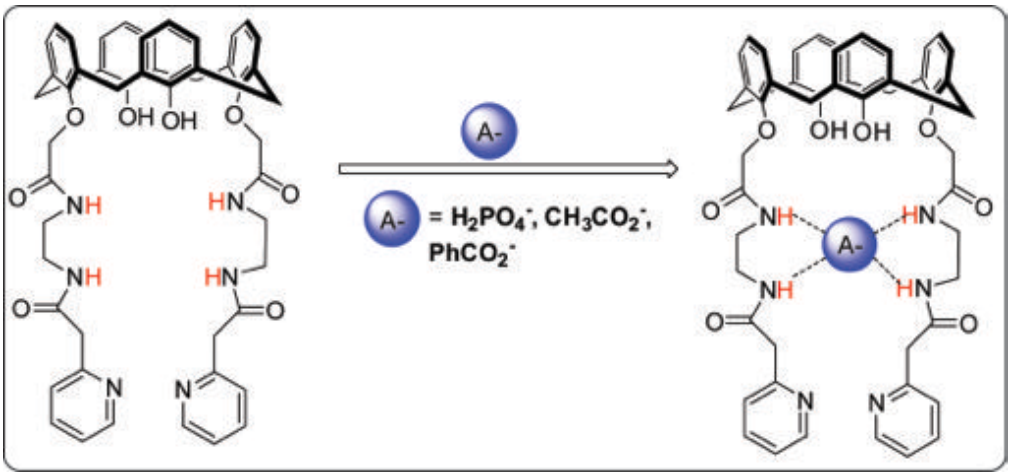
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Experimental and Computational Studies of Anion Recognition by Functionalized Calixarenes.

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There is continued interest in the development of anionic receptors in supramolecular chemistry due to the pivotal roles that anions play in many chemical, biological and medicinal processes. For example, phosphate ion and its key derivatives play important roles in energy storage and signal transduction in living systems. Calixarenes have proven to be versatile scaffolds for the development of anionic receptors due to the ease of functionalization at their lower or upper rims with linkers decorated with recognition motifs for anions, such as urea, thiourea and amide moieties. These modified calixarenes form a pre-organized core capable of improving the binding and selectivity of anions. This presentation will describe the synthesis and anion binding studies of functionalized calixarenes. Calix[4]arenes which contain pyridine and terpyridine moieties appended to the lower rim of calix[4]arene, have been synthesized in four steps. The binding ability of these calixarenes for various anions, including F^-, Cl^-, HSO_4^-, $H_2PO_4^{2-}$ and CH_3COO^-, was tested in organic media by monitoring the changes in their ^1H NMR, UV-Vis and fluorescence spectra as a function of added anions.



Functionalized Cryptophane-111 Derivatives by the Capping Approach

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Cryptophane-111, **(±)-C111**, is a molecular cage exhibiting the highest affinity for Xe (K_a = 10^4 M^{-1} at 293K) in organic solvents.[1] Designing functionalized water-soluble derivatives of **(±)-C111** is of interest in the context of magnetic resonance imaging and biosensing applications.[2] The only two water-soluble **(±)-C111** derivatives known to date were obtained after synthesizing **(±)-C111**.[3,4] In efforts in our group to make more available functionalized derivatives, trismethoxy-cryptophane-111, **(±)-(MeO)$_3$-C111**, and trisbromo-cryptophane-111, **(±)-Br$_3$-C111** were successfully synthesized by unsymmetrical capping of cyclotriphenolene **(±)-CTP** by cyclotriguaiacylene **(±)-CTG** and trisbromo-cyclotriphenolene **(±)-Br$_3$-CTP**, respectively. Preliminary binding studies of both cryptophanes show their ability to bind xenon. They were also shown to bind methane with a slow exchange regime over a wide range of temperatures. Compared to **(±)-C111**, the presence of the functional groups on one side of the cryptophane enhances the affinity for methane binding by creating a permanent dipole in the capsule. Unfortunately, their binding constant is lower because of a larger entropic cost. On the other hand, kinetic parameters reveal a slower exchange rate due to the large groups blocking the portals.[5] Further substitution of the methoxy and bromide groups by water solublizing and/or fluorescent groups for the formation of more valuable cryptophanes are currently underway.

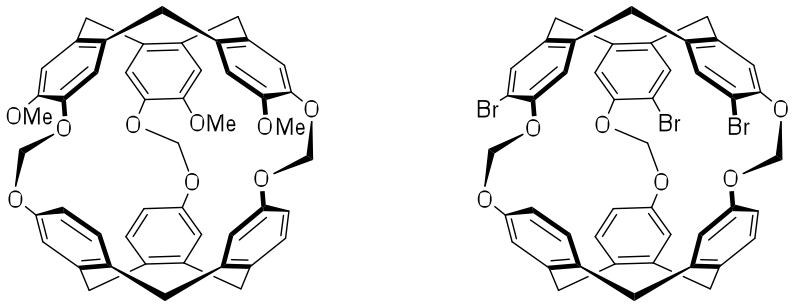


Figure 1. **(±)-(MeO)$_3$-C111** and **(±)-Br$_3$-C111**.

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Supramolecular Engineering of Polymeric Scaffolds Derived from Ring-Opening Metathesis Polymerization: Towards Synthetic Foldamers and Functional Materials

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The coalescence of supramolecular chemistry and materials science has resulted in the synthesis of polymers, with a focus on subsequent self-assembly.[1] Owing to the ability of Nature to engineer macromolecules utilizing noncovalent interactions, supramolecular polymers have emerged as attractive modules capable of sustaining a precise assembly, while providing access to functional building blocks.[2] The field of supramolecular polymer science can be divided into two categories: side-chain[3] and main-chain functionalized[4] polymers, both of which require highly-controlled polymerizations, such as ROMP,[5] to design well-defined architectures that can mirror the precision and fidelity demonstrated by Nature. Previous studies have demonstrated that ROMP can achieve the formation of both supramolecular main-chain ABC triblock copolymers[6] and side-chain functionalized ABC terpolymers[7] (Figure 1) containing a mixture of orthogonal recognition motifs.[8] Utilizing the expertise gained from these studies, we endeavor to achieve the formation of synthetic supramolecular polymer systems that fold into well-defined 3D structures so as to afford complex materials capable of mimicking Nature. This contribution will describe preliminary concepts that are being developed that utilize noncovalent interactions to drive the self-assembly of functional supramolecular polymers into ordered structures.

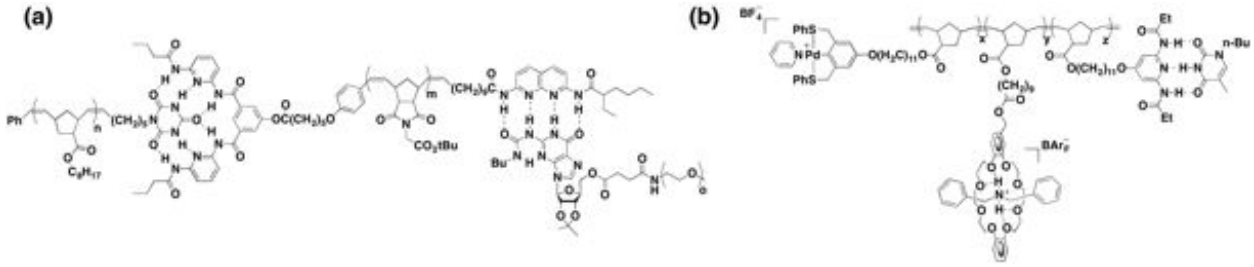


Figure 1. Representative supramolecular ABC triblock copolymer and terpolymer containing multiple recogntion motifs.

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Quantum Dot Sensor for Heavy Metal

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A highly sensitive and specific nanosensors was reported based on quantum dots (QDs) coated with acid for detection of heavy metal (HM) ions in water. The water-soluable acid-capped QDs were prepared through a hydrothermal route. The QD nanosensors were constructed by conjugating acid onto the surface of the QDs. Based upon the fact that the fluorescence of the QDs could be quenched by HM ions, a simple and rapid method for heavy metals detection was proposed. The response showed linear proportion to the concentration of HM.

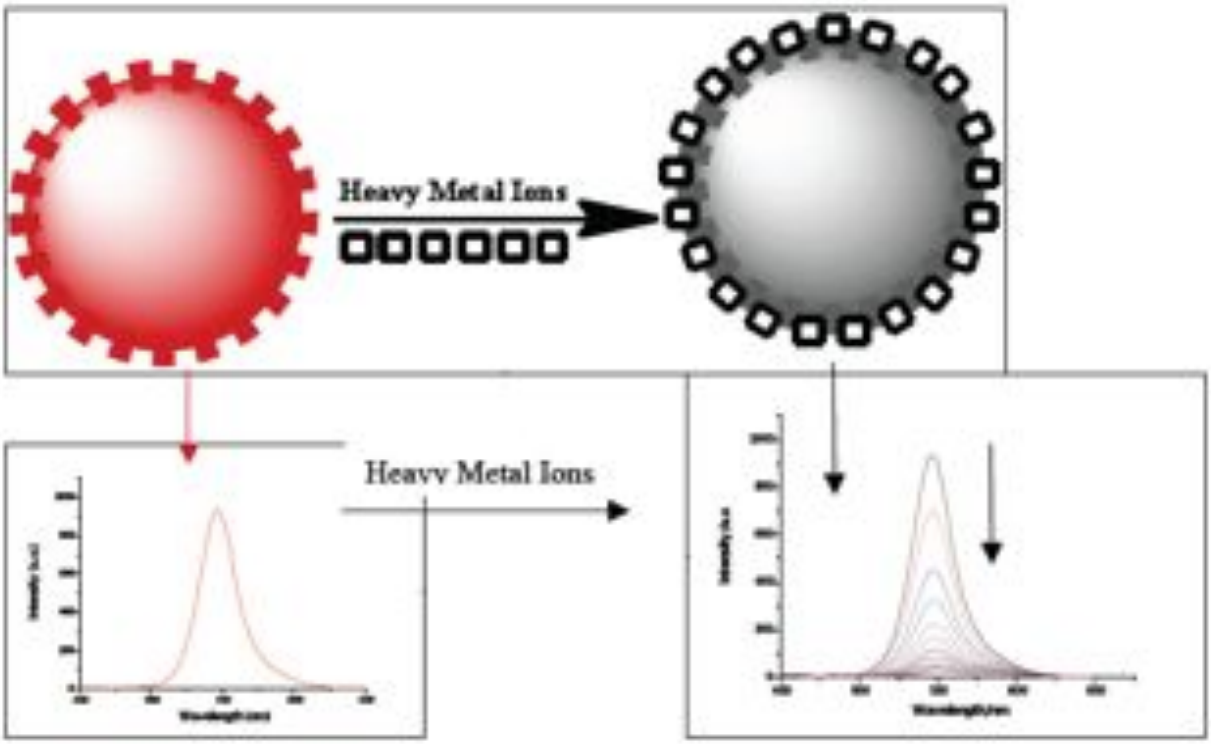


Figure 1. Quenching of QD fluorescence upon heavy metal ion complexation.

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Coordination Polymers Containing F_4TCNQ as its Dianion

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In addition to its neutral form, 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its tetrafluoro analogue, F_4TCNQ are known to exist in both a radical monoanionic and a dianionic form. The accessibility of a range of redox states offers some promise in regards to the generation of TCNQ/$TCNQF_4$-based materials that can exhibit unusual and possibly useful magnetic/electronic properties. We have found that the combination of metal ions with $TCNQF_4$ (and TCNQ) in its dianionic form provides access to a wide variety of coordination networks.[1,2]

When combined with metal ions in the presence of a range of cations or coligands, F_4TCNQ^{2-} forms an extensive range of 1D, 2D and 3D coordination polymers that exhibit a variety of topologies. For example, when Zn(II) and bpe (1,2-bis(4-pyridyl)ethylene) are combined with the dianion of $TCNQF_4$, a pillared structure is generated in which $Zn(F_4TCNQ)$ sheets are linked by bridging bpe ligands (*Figure 1*). The combination of Cu(I) and F_4TCNQ^{2-} in the presence of organic cations leads to the formation of an infinite anionic framework which has the topology of platinum sulfide. An example of such a network is presented in Figure 2. The cations, located within the channels of the framework, are shown to exert a significant structure-directing influence.

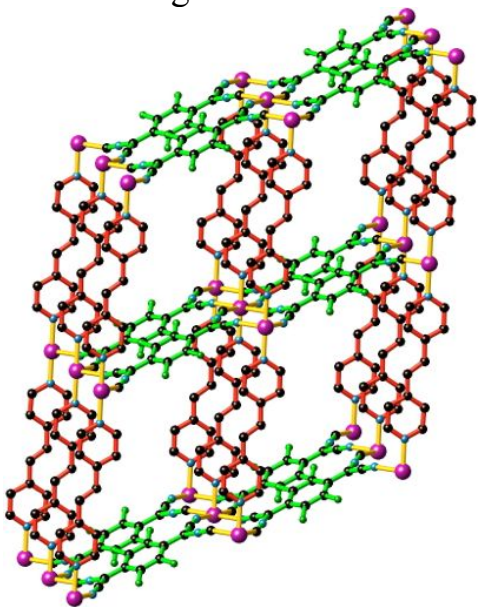


Figure 1. $[Zn(F_4TCNQ)(bpe)]$

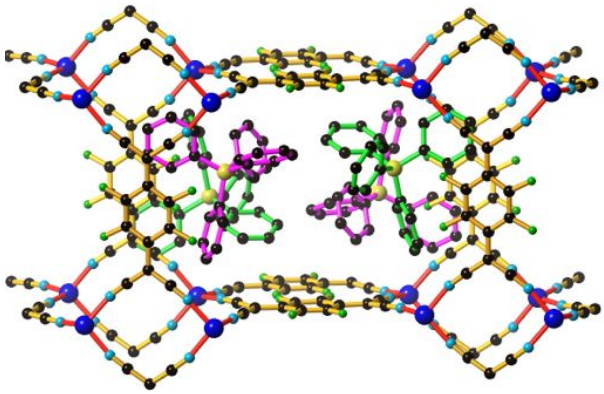


Figure 2. $(PPh_4)[Cu(F_4TCNQ)]$

References

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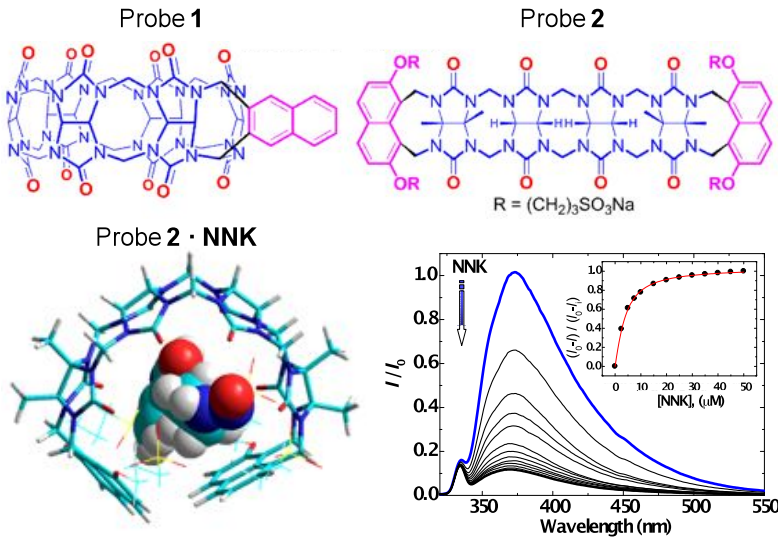
Sensing of Biologically Relevant Amines by Cucurbut[n]urils-Based Fluorescent Microarrays

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A supramolecular sensor array composed of two fluorescent cucurbit[*n*]uril-type receptors (probe **1**[1] and probe **2**) displaying complementary selectivity was tested for its ability to detect and quantify cancer-associated nitrosamines[2] and drug-related amines. The fluorimetric titration of the individual probes showed highly variable and cross-reactive analyte dependent change in fluorescence. An excellent ability to recognize a large number of analytes was demonstrated in qualitative as well as quantitative assays. Importantly, a successful quantitative analysis of analytes of interest was achieved in mixtures and in human urine. The throughput, sensitivity and LOD surpass the current state of the art methods that usually require analyte solid phase extraction (SPE). These results open up the opportunity for new applications of cucurbit[*n*]uril-type receptors in sensing and pave the way for the development of simple high-throughput assays for various drugs in the near future.



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Reactions of 2-halo-, 2-halomethyl-, and 2-(α-bromobenzyl)calix[4]arenes.

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Calixarenes with halo groups at the methylene bridge position offer an entry to new methylene-bridge-substituted calixarenes. Putative 2-bromo- and 2-iodo-*p*-*tert*-butyltetramethoxycalix[4]arenes formed when a 2-lithiocalixarene reacts with Br_2 or an iodoalkane are implicated in the formation of a novel 2,2′-dicalixarene with direct connection of the units at the bridge position.[1] This compound undergoes reactions typical of single calixarene baskets such as demethylation and de-*tert*-butylation though the demethylation with BBr_3 was slow, likely because of steric crowding in the intermediate borate esters.[1] The demethylated, de-*tert*-butylated species was characterized by single crystal x-ray diffraction and displays a configuration with the two baskets oriented opposite one another. 2-Chloro-*p*-*tert*-butyltetramethoxycalix[4]arene is a starting point for 2-alkoxy-, 2-amino-, and 2-hydroxycalixarenes.[1] Deprotonation of *p*-*tert*-butyl-tetramethoxycalix[4]arene followed by treatment with a dihalomethane (CH_2I_2 or CH_2ClI) gives 2-iodomethyl and 2-chloromethyl species respectively. Base-promoted elimination on these compounds yields 1,1-diaryl-substituted alkenes while thermal elimination (no base) gives 1,2-diaryl-substituted alkenes. Routes to similar triarylethenes via synthesis and reaction of 2-(α-bromobenzyl)-*p*-*tert*-butyl-tetramethoxycalix[4]arenes are also under investigation.

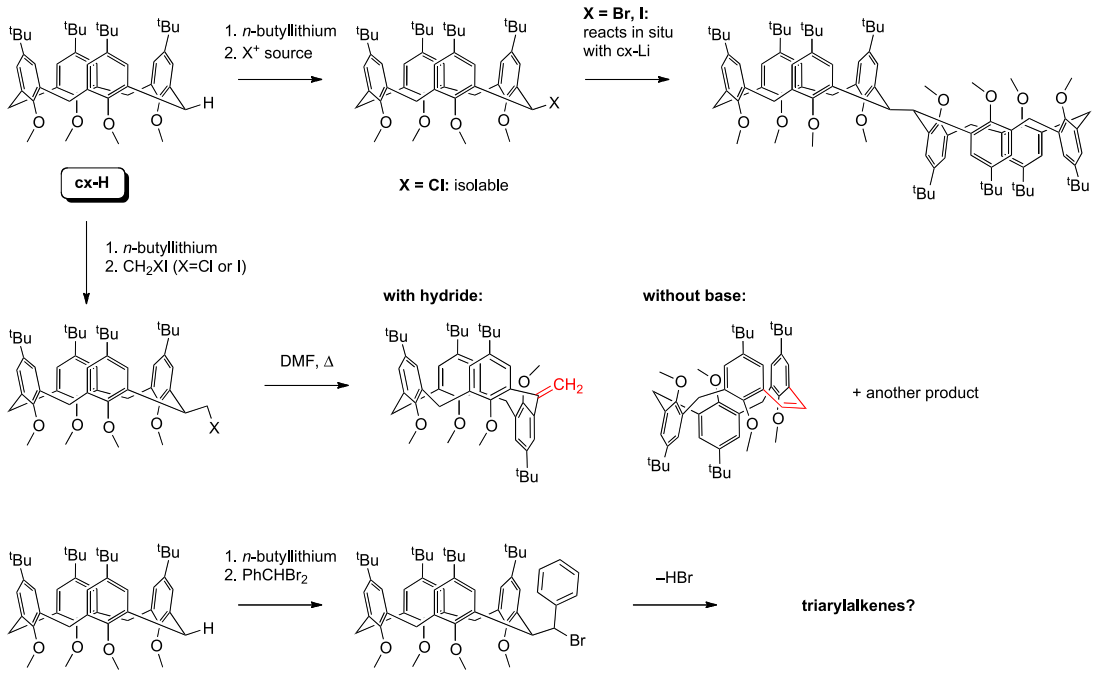


Figure 1. Synthesis and reactions of 2-substituted calixarenes.

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Electroluminescence and heat-set gelation in a series of dynamic-covalent metallo-polymers

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Unlike conventional polymers which are irreversibly formed, supramolecular polymers can reform and reconfigure their structure and properties in response to stimuli. We report a series of dynamic-covalent metallo-polymers that are readily synthesized by the condensation of linear diamine and dialdehyde subcomponents around copper(I) templates in the presence of bidentate phosphine ligands. When fabricated into light-emitting electrochemical cells (LECs) the polymers show electroluminesce, making them part of an increasingly important class of LEC device not dependent on expensive, earth-scarce elements such as platinum(II), iridium(III) and osmium(II).[1] The devices emit red light when a low bias is applied but undergo a hypsochromic shift in emission as the voltage is increased, eventually emitting yellow light. In solution, the red polymers undergo a sol-gel transition upon heating to form a yellow gel which shows rapid self-healing behavior. The mechanism underlying these apparently disparate responses is deduced to be due to rearrangement at the copper centres from heteroleptic $[CuN_2P_2]^+$ polymers to homoleptic cross-linked $[CuN_4]^+$ polymers and free $[CuP_4]^+$ complexes.[2] The distinct changes in photophysical and rheological properties observed as a result of rearrangement of the polymer system holds potential for use in a variety of sensing, imaging and information storage applications.

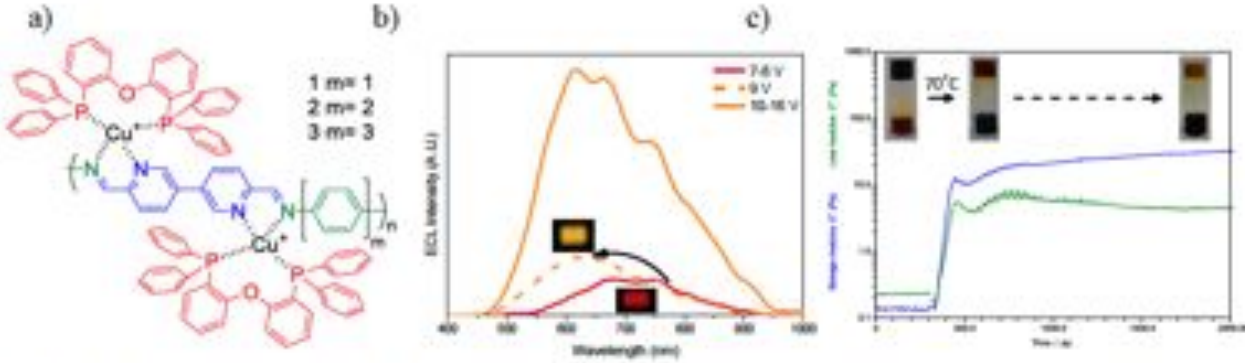


Figure 1. A series of dynamic-covalent metallo-polymers (a) show a hypsochromic shift in electroluminescent emission with increasing voltage (b) and the formation of self-healing gels at high temperatures (c).

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Redox Control of Relative Motion in a Switchable Molecular Solomon Link

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The natural tendency of biological molecules to fold into different topologies is a determining factor[1] in the recognition and catalytic processes that drive living systems. The importance of topology in defining the biological activity of proteins and DNA has inspired[2] chemists to design and synthesize mechanically interlocked molecular compounds. We present the template-directed synthesis of a molecular Solomon link, designed to generate stabilized, redox-controlled tetrathiafulvalene (TTF) dimers, whose properties can be configured reversibly by altering the applied redox potential. The molecular Solomon link ($\mathbf{4}^{8+}$) is comprised (Figure 1) of a crown ether (**1**) containing four alternating TTF and 1,5-dioxynaphthalene (DNP) units, doubly interlocked with an octacationic organoplatinum square, formed under templation from $\mathbf{2}^{2+}$ and **3** in the presence of **1** acting as the template. The unique arrangement of the TTF moieties in the molecular Solomon link in a face-to-face manner with each other, leads to the formation of a stable mixed-valence dimer $[(TTF)_2]^{\bullet+}$ upon one-electron oxidation. Further redox stimulation of TTF induces the switching of the crown ether to attain a stable conformation in which the two DNP units are located inside the structural framework of the metallo-organic square. The structural control that emerges through electronic stimulation and the fascinating molecular motion of the macrocycle within this unique structural topology heralds the entry to a high level of dynamic structural complexity for mechanically interlocked molecules.

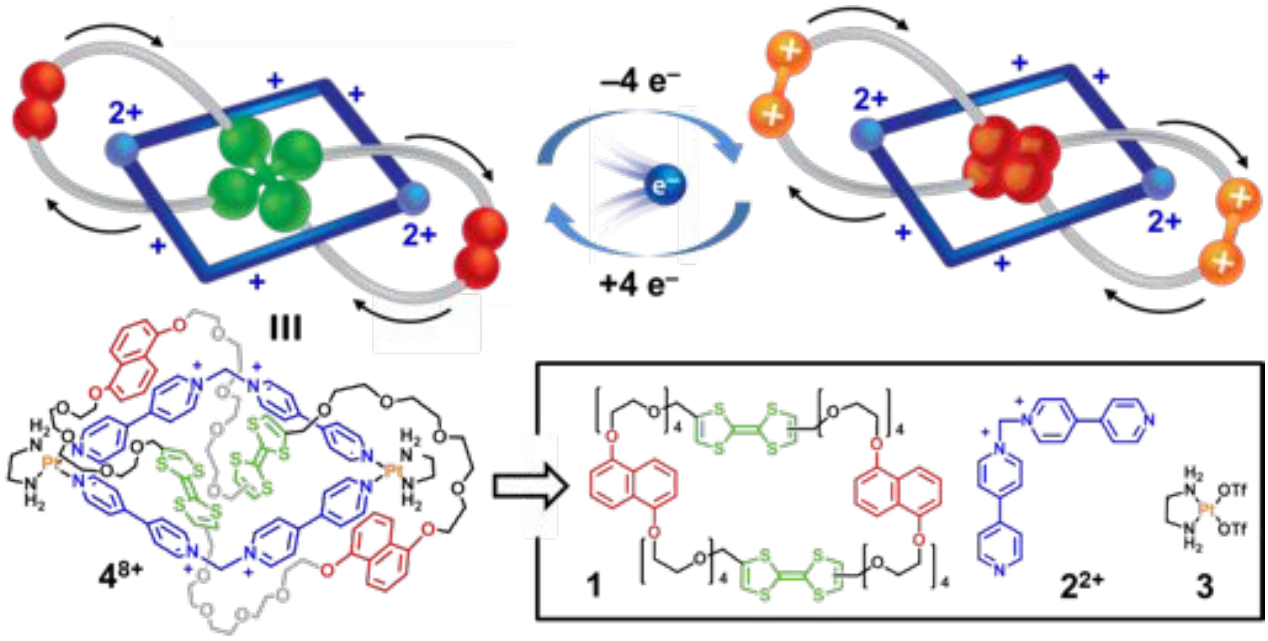


Figure 1. Redox-activated switching of a bistable Solomon link

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Preparation of Tetrakis(tetrathiafulvalene)-calix[4]pyrrols Functionalized with Pyrene Units

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Calix[4]pyrrole incorporating four appended tetrathiafulvalene (TTF) units can be used as colorimetric chemosensors, e.g. for nitroaromatic explosives, on account of their ability to form host-guest complexes with electron-deficient compounds.[1] Compounds containing pyrene units are known to form nanohybrids with single-walled carbon nanotubes (SWCNT).[2] To combine those two properties and to immobilize tetrakis(TTF)-calix[4]pyrrole derivatives on SWCNT in order to develop new sensors for electron-deficient compounds, tetrakis(TTF)-calix[4]pyrrole derivatives containing one or several azide linkers were synthesized in a multistep synthesis and functionalized with pyrene units using click chemistry. The ability of those compounds to bind 1,3,5-trinitrobenzene (TNB) as well as their interactions with buckminsterfullerene (C60) and SWCNT, as in Figure 1, has been investigated and will be presented.

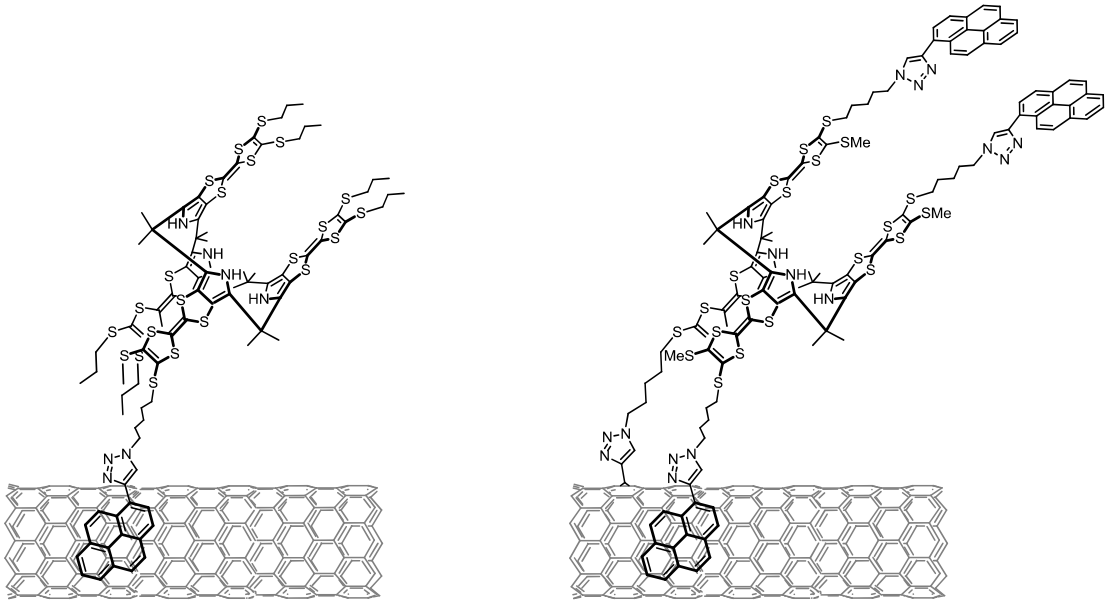


Figure 1. Two possible nanohybrids consisting of SWCNT and tetrakis(TTF)-calix[4]pyrroles functionalized with pyrene units.

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pH-Dependent Transition of Polyhedral Micelle Formed by Amphiphilic Calix[4]arene Derivative

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Controlled self-assembly of amphiphilies is an important field in material science. Among many functional amphiphilies, calix[4]arene moiety is particular useful as a rigid segment to provide a well-defined nanometer-sized structure.[1] We previously independently synthesized a new cataionic lipid denoted by CaL[4]C3 from calix[4]arene with propyl tails and primary amines and found that six CaL[4]C3 molecules can self-assemble into a cubic-like micelle at low pH.[2] Interestingly, there was no distribution in the aggregation number. (Figure 1) On the other hand, the calix[4]arene derivatives attached hexyl tails instead of propyl ones do not show the shape persistency. Although the effect of hydrophobic moiety on the shape persistency is shown, the effect of chemical structure of hydrophilic part is not investigated. Here, we synthesized the amphiphilic calix[4]arene bearing glutamic acid groups instead of amines (denoted by GCaLC3, see Figure 2) and small angle X-ray scattering (SAXS) measurements revealed the structure of GCaL3 micelles was sphere at both pH = 3.2 and 10.1 while the aggregation numbers were six and twelve at pH = 3.2 and 10.1, respectively. This results indicate that the GCaL3 micelles are cubic at low pH similar to CaL[4]C3 system and it changes to dodecahedral shape with increasing pH.

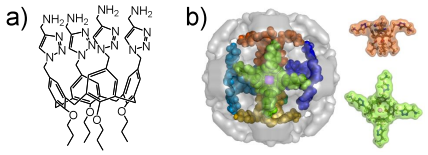


Figure 1. (a) Chemical structure of CaL[4]C3 and (b) schematic representation of cubic-like micelle.

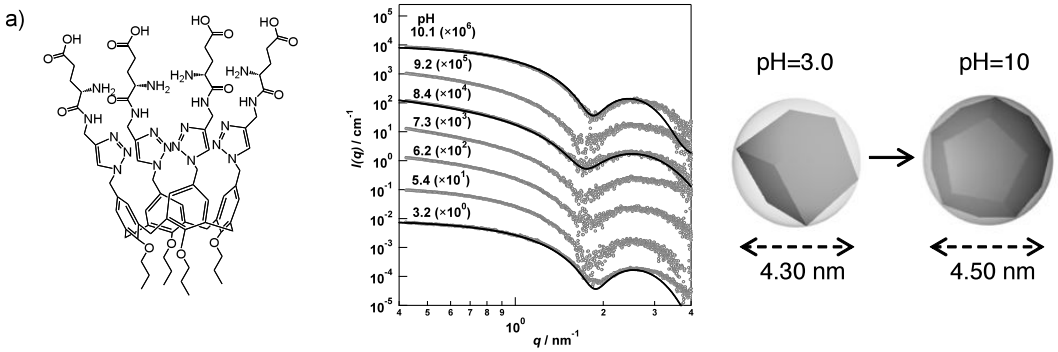


Figure 2. (a) Chemical Structure of GCaL3 and (b) SAXS profiles of GCaL3 micelles in 50 mM NaCl solutions at pH = 3.2 ~ 10.1.

References

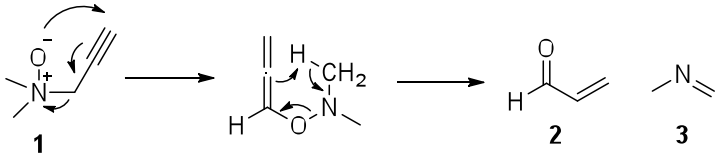
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Stabilization of the Chemical Reactivity of Prop-2-ynylic Amine *N*-oxide by Encapsulation in a Molecular Container

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In non-polar solvents prop-2-ynylic amine *N*-oxides experience concerted [2,3]-sigmatropic rearrangement yielding acrolein and an imine. [1] We envisaged that the intrinsic chemical reactivity of the prop-2-ynylic amine *N*-oxide **1** could be modified by encapsulation in a molecular container.[2] The main idea is to difficult the molecule to achieve the geometry of the transition state required for the decomposition reaction. Our reasoning included the reduction of the nucleophilicity of the *N*-oxide oxygen by hydrogen bonding and the reversible confinement of the substrate in a molecular reactor of suitable dimensions, in which by steric reason the energy of the transition state increased significantly. Kinetic measurements have shown that decomposition is slowed down when 1 equivalent of calix[4]pyrrole **4** is present in solution. Furthermore, the encapsulation in the molecular container **5** featuring a bis[2]catenane topology with a polar interior stabilizes the *N*-oxide **1** for months.[3] The encapsulation process is reversible and by addition of a competitive guest the *N*-oxide **1** is slowly released in the solution, where it experiences the aforementioned decomposition.



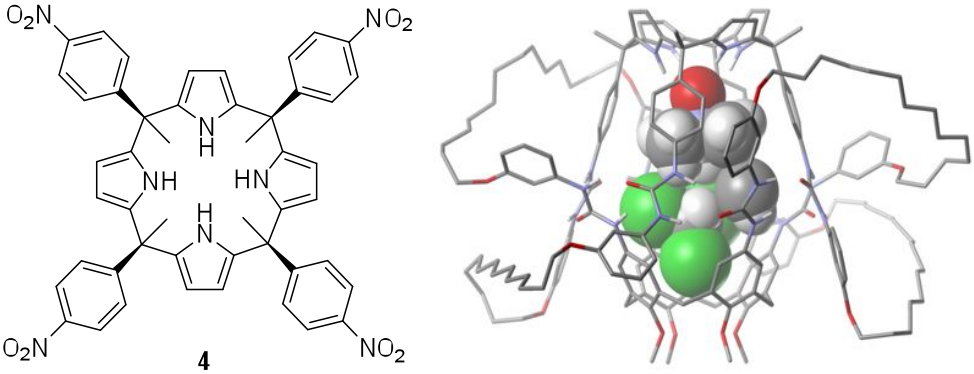


Figure 1. Reaction mechanism of decomposition of prop-2-ynyl amine *N*-oxides. Line drawing structure of calix[4]pyrrole **4** and energy minimized (CAChe/MM3) structure of the *N*-oxide **1** encapsulated in bis[2]catenane **5** with a molecule of chloroform co-included.

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Cell-Penetrating Poly(disulfide)s Generated by Substrate-Initiated Polymerization

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The success of a drug or a cellular probe depends on reaching its target. Typically this means crossing the cell membrane and it may set unwanted restrictions on the molecule's design. Cell-penetrating poly(disulfide)s (CPDs) are currently emerging as molecular transporters thanks to their ability to bind different cargoes. Once they cross the biological barrier, they are degraded by endogenous glutathione, releasing the substrate and eliminating toxicity.[1]

The formation of a complex between the active molecule and the vector is one of the major drawback of CPDs, limiting the type and the number of substrates that can be delivered. Applying lessons from surface-initiated polymerization,[2] we developed a conceptually new approach to grow cell-penetrating poly(disulfides) directly on substrates of free choice through ring-opening disulfide-exchange polymerization.[3]

Thiolated substrates are used as initiators in the polymerization on strained cyclic disulfides (propagators), controlling the size of the polymer using iodoacetamides as terminators. The formation of CPDs takes place in very mild conditions and can be followed directly through the appearance of transport activity in fluorogenic vesicles. The process is further characterized by gel-permeation chromatography and fluorescence resonance energy transfer. Polymers obtained using this new methodology are tested for cellular uptake on HeLa cells, revealing good transmembrane activity.

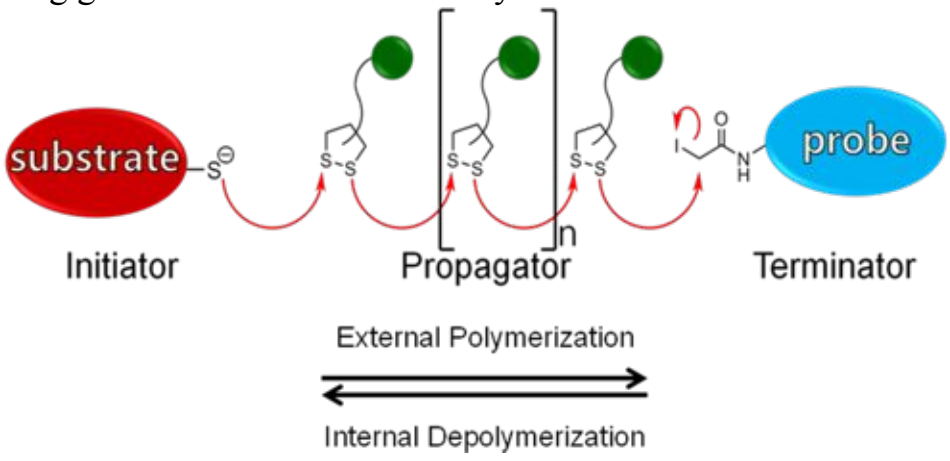


Figure 1. Substrate-initiated ring-opening disulfide-exchange polymerization.

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Isomerization of Glycoluril Dimer and Trimer Related to Cucurbituril Formation

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Cucurbiturils (CB) are excellent host molecules in supramolecular chemistry with possible applications e.g. as receptors, sensor or catalysts.[1] Limitations to their applications are mainly due to their limited solubility and the complexity of the functional group introduction. A detailed knowledge of the cucurbituril forming mechanism is the key to synthesize new functionalized derivatives. Mechanistic studies focused on the reaction conditions, variation of reactant concentration and addition of templates and their effect on the product distribution.[2]

The dimerization reaction of glycoluril units is the initial step in the synthesis of CB. Isaacs and co-workers studied reactions of glycolurils bearing different *o*-xylylene units with formaldehyde in nonpolar solvent under acidic conditions. They identified a mixture of S- and C-shaped dimer as kinetic product.[3] We decided to choose the methyl protected glycoluril **1** (figure 1) and investigate its reaction with formaldehyde in aqueous media. These conditions should closer resemble those from CB formation. We demonstrated that, in the presence of water, the S-shaped dimer **2** is the solely kinetic product that is subsequently transformed to the thermodynamic C-shaped product **3**.[4] Similar results have been observed in trimer synthesis. Detailed information about these investigations will be presented on this poster.

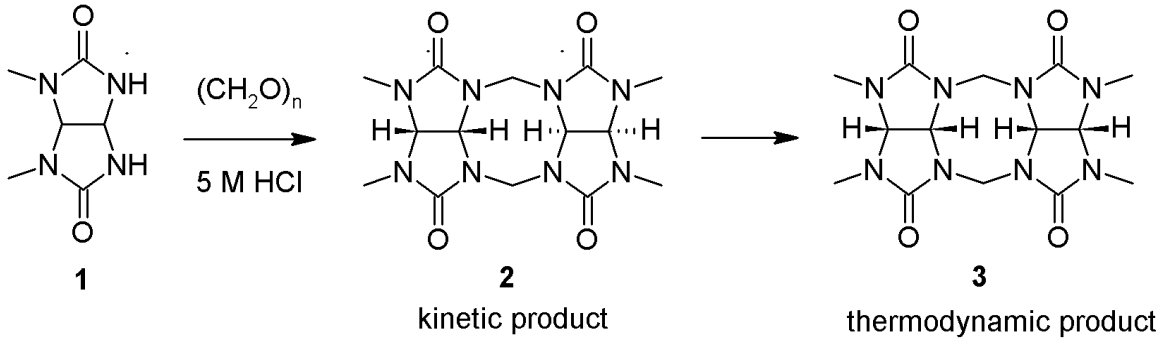


Figure 1. Dimerization and isomerization reaction of glycoluril **1**.

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Single Vesicle Fusion Events Mediated by SNAREs Using a Synthetic Host–Guest Binding Pair

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Understanding the molecular mechanism of synaptic vesicle fusion triggered by a conserved family of proteins called SNAREs (N-ethylmaleimide-sensitive factor attachment protein receptors) is a key issue in neuronal communication.[1-3] In order to study the protein-mediated vesicle fusion mechanism, we designed a synthetic system to observe the synaptic vesicle fusion events at the single-molecular level with the course of time. A SNARE protein based single-vesicle fusion assay monitored by fluorescence enables simultaneous measurement of vesicle fusion.[4] Here, we report a new, reliable and efficient single-vesicle content mixing assay for a SNARE-mediated membrane fusion using a fluorophore (Cy3, Cy5) tagged host-guest pair cucurbit[7]uril–adamentane derivative (CB[7]-Ad), on the basis of fluorescence resonance energy transfer (FRET) analysis. A change in FRET signal occured when a CB[7]-Cy3 binds to a Ad-Cy5, which is a mark of two different SNARE embedded vesicle (CB[7]-Cy3@t-Vesicle, Ad-Cy3@v-Vesicle) fusion. This synthetic host-guest system may be useful to monitor the vesicle fusion events in detail. Results from this study and their implication in synaptic vesicle fusion will be presented.

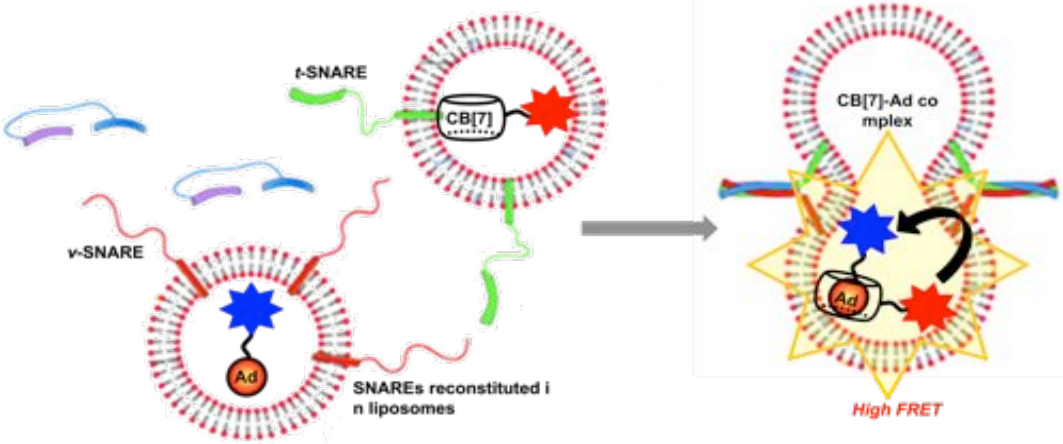


Figure 1. Single-vesicle content mixing assay based on CB[7] and Ad pair.

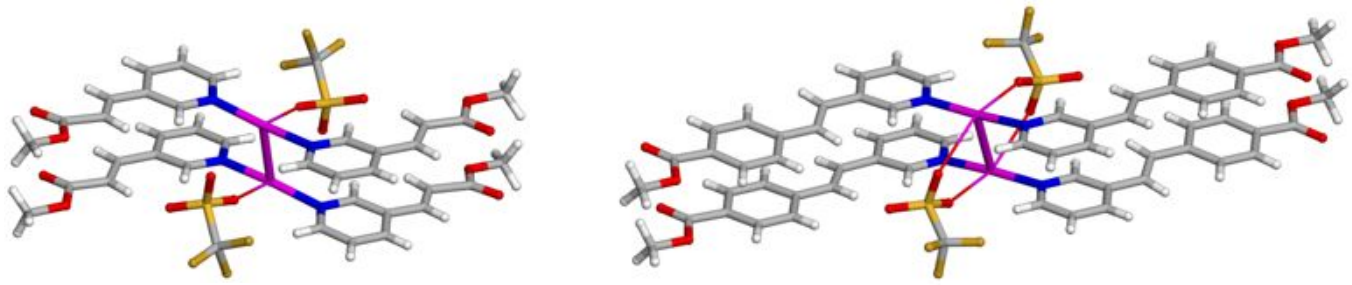
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Sulfonate Anion Assisted Argentophilic Interactions as Templates for [2+2] Cycloaddition Reactions in the Solid State

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The ability to align olefins within the solid state that can undergo [2+2] cycloaddition reactions utilizing argentophilic interactions has gained attention in the chemical literature. Argentophilic bonding is a closed shell interaction that is found with silver atoms and has been successful in orienting pyridine-based molecules to photoreact upon exposure to ultraviolet radiation.[1] The Ag-Ag distance within such a complex can vary based upon the different components in the crystal such as the anion. Anions that interact with silver atoms can assist in the formation of these argentophilic interactions that will hopefully lead to photoreactive solids. [2] In this presentation, we will discuss the formation of photoreactive silver complexes based upon sulfonate anions. We will address not only the overall structure of the complex but how the sulfonate anions assist in the formation of these reactive solids. Two bonding motifs were realized within these complexes: a monodentate and a bridging interaction as shown in Figure 1. In all examples a quantitative yield of the photoreaction was achieved to form the cyclobutane-based product.



a. b.

Figure 1. Argentophilic complexes with trifluoromethanesulfonate with a monodentate (a) and a bridging interaction (b) that form photoreactive crystals.

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Photomodulated Fluorescence of Supramolecular Assemblies of Sulfonatocalixarenes and Tetraphenylethene

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Self-assembled fluorescent nanoparticles that respond to specific stimuli are highly appealing as potential labels, probes, memory devices, and logic gates.[1] However, organic analogues are challenging to prepare, owing to unfavorable aggregation-caused quenching.[2] We herein report the self-assembly of fluorescent organic nanoparticles in water by means of calixarene-induced aggregation of a tetraphenylethene derivative (QA-TPE) mediated by *p*-sulfonatocalix[4]arenes. The fluorescence of the self-assembled nanoparticle showed interesting photo-switching, and the fluorescence emission behavior of the host-guest assembly was opposite to that of free QA-TPE both before and after irradiation. Free QA-TPE is non-fluorescent, owing to intramolecular rotations. In contrast, the self-assembled nanoparticle that formed upon complexation of QA-TPE with *p*-sulfonatocalix[4]arene exhibited aggregation-induced emission fluorescence (λ_{em} = 480 nm, Φ = 14%), owing to restricted rotation. Upon UV-light irradiation, free QA-TPE was cyclized to the corresponding diphenylphenanthrene (QA-DPP), which showed typical fluorescence of a π-conjugated system (λ_{em} = 385 nm, Φ = 9.3%); whereas the nanoparticle was non-fluorescent upon irradiation, as a result of aggregation-caused quenching. In effect, this system allows programmed modulation of TPE fluorescence at two different emission wavelengths by means of host-guest complexation and irradiation. Relative to single-mode stimulus-responsive system, this system of highly integrated modes into a single molecular unit that can exhibit modulation of fluorescence by multiple stimuli is expected to be more adaptable for practical applications and to show enhanced multifunctionality.

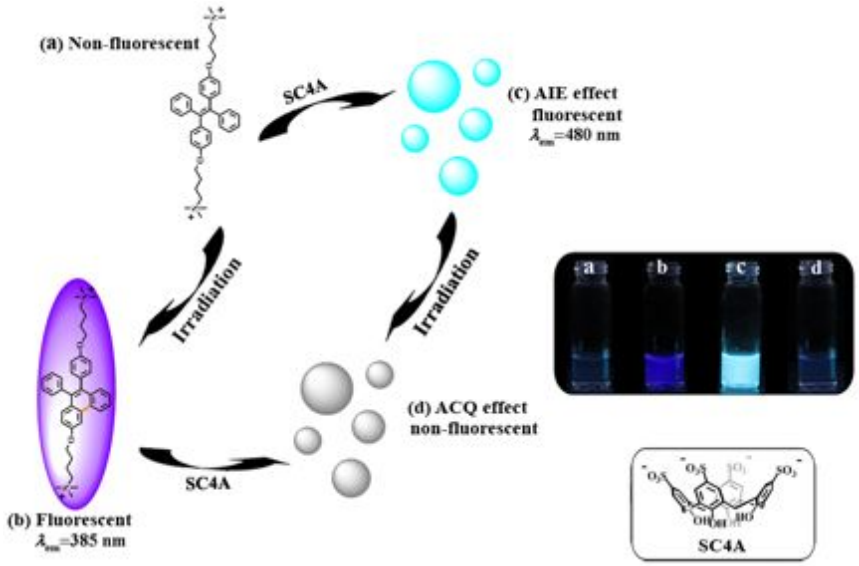


Figure 1. Schematic illustration of the fluorescence transitions of QA-TPE induced by through host–guest complexation and irradiation.

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Allosteric Behavior of Silver(I) Complex with Cyclen-Based Cylindrical Cryptand

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Recently we have reported that tetra-armed and double-armed cyclens bearing aromatic rings act as an insectivorous plant (*Venus Flytrap*) when they form complexes with Ag^+ ion.[1-4] We therefore called the tetra-armed and double-armed cyclens "argentivorous molecules". During the research project, we found that the Ag^+ complexes with the argentivorous molecules form atropisomers by the aromatic side-arms (Fig. 1). The results prompted us to make new cyclen-based cylindrical cryptands having two argentivorous molecules bridged with ethyleneoxy units; **1a**, **1b**, **1c**, and **1d** cross-linked by OCH_2CH_2O, $O(CH_2CH_2O)_2$, $O(CH_2CH_2O)_3$, and $O(CH_2CH_2O)_4$ units, respectively (Fig. 2). We expected that the molecules would show allosteric behaviours in the reaction kinetics and/or stereochemistry when they form complexes with Ag^+ ions (Fig. 3).

Here we report that the allosteric behavior of the Ag^+ complexes with the cyclen-based cylindrical cryptands depend on the lengths of the diethyleneoxy units.

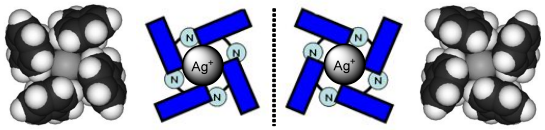
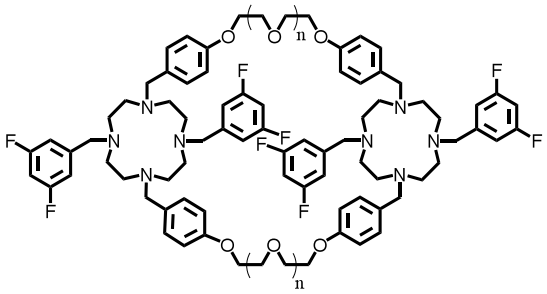


Figure 1. Atropisomers in the argentivorous molecules.



1a: n = 0, **1b**: n = 1,**1c**: n = 2, **1d**: n = 3

Figure 2. Cyclen-based cylindrical cryptands.

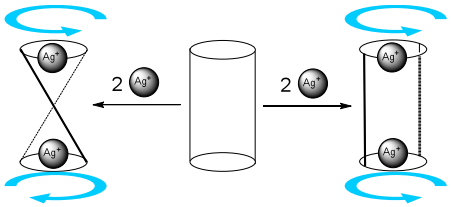


Figure 3. Schematic drawing of diastereomers in the Ag^+ complex with the cyclene-based cylindrical cryptand.

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Cavitands based on resorcinarenes with amino acids on their upper rims used for chiral amine recognition

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Cavitands based on resorcinarenes with alanine and glycine on their upper rims have been synthesized. The upper rim of the resorcinarenes have been elongated with four identical substituents topped with alanine and glycine groups. The new resorcinarenes were characterized by NMR, MS and sustained *off*-resonance irradiation collision induced dissociation (SORI-CID) technique in FTICR-MS. Eight water molecules were found to associate to the cavitand. The alanine substituents are proposed to form a kite-like structure around the resorcinarene scaffold. The binding of chiral *R*- and *S*-methyl benzyl amines was studied by ^{1}H NMR titration, and compared to that of a binary *L*-tartaric acid and model compound. The results showed that these resorcinarenes interact with several amine guests and with four carboxylic acid groups, several amines strongly. The ^{1}H NMR titration of one resorcinarene with primary, secondary, and tertiary chiral amines showed that it can discriminate between these three types of amines and showed chiral discrimination for chiral secondary amines.[1]

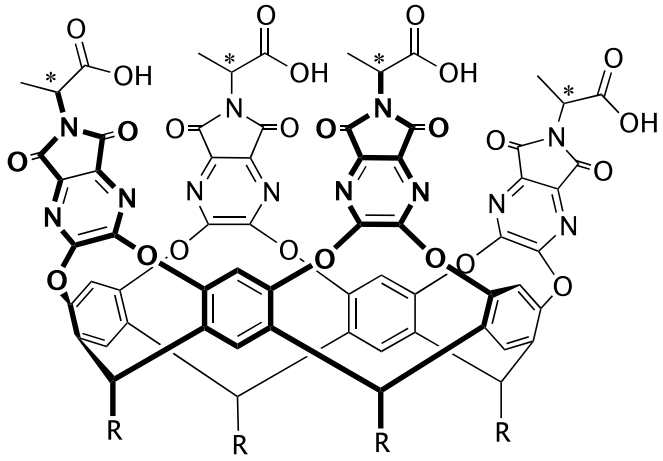


Figure 1. Resorcinarenes with amino acid substituents. (R = CH_3 or $C_{11}H_{23}$)

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Topological Diastereoisomerism in a Chiral Handcuff Catenane

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A handcuff catenane is an example of a mechanically-interlocked molecule (MIM) with an architecture that consists of two covalently bound macrocycles (a ditopic host or bis-macrocycle) interlocked by a third macrocycle that is threaded through both binding sites of the ditopic host. Three previous examples[1–3] of this molecular topology have been reported, with the most recent publication[3] also describing the first solid-state structure of this particular MIM. The self-assembly of a topologically unique, chiral handcuff catenane has been achieved by utilizing a template-directed protocol, wherein the crown ether, bis-1,5-dioxynaphthalene[50]crown-14 (DN50C14), templates the formation a ditopic host consisting of two fused π-electron-deficient cyclobis(paraquat-*p*-phenylene) rings. The ditopic host contains a plane of chirality and is observed as a mixture of two pairs of enantiomers. Characterization using ^{1}H nuclear magnetic resonance spectroscopy and single crystal X-ray diffraction, with supporting density functional theory calculations, suggests that two topological diastereoisomers have been obtained, as a result of the two possible ways in which the polyether chains can wrap around the ditopic host. The ratio of major to minor isomers is approximately 85:15. The solid-state structure of the major topological diastereoisomer has been elucidated by single crystal X-ray diffraction.

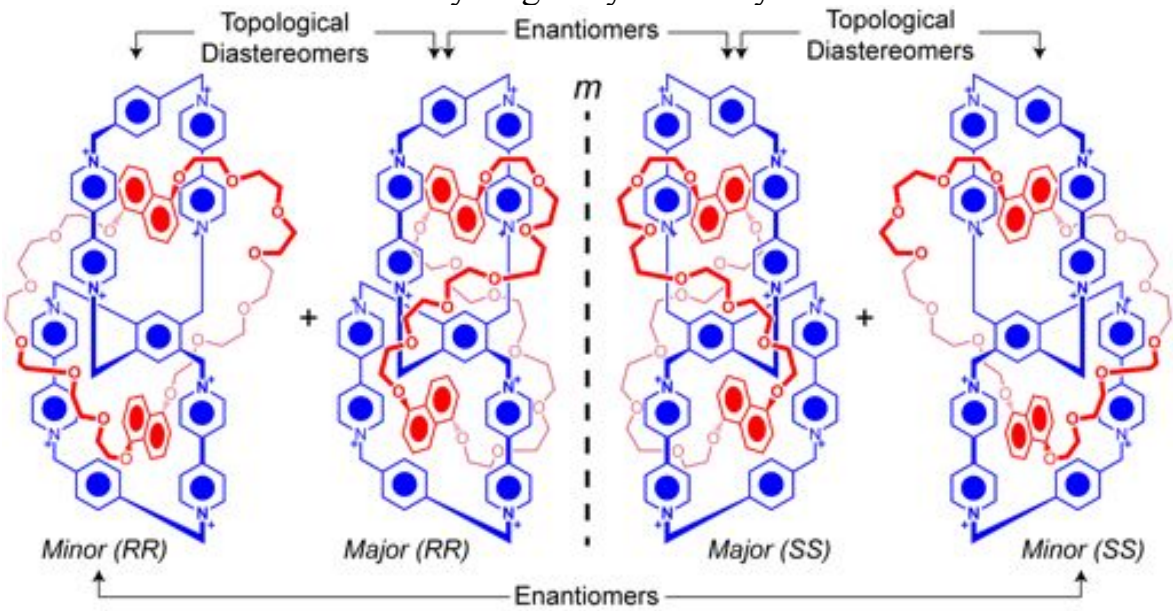


Figure 1. Planar chirality in a ditopic host, together with topological diastereoisomerism, results in the existence of four isomers of a handcuff catenane.

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Expansion–contraction of photoresponsive artificial muscle regulated by host–guest interactions

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We prepared supramolecular hydrogel actuators based on host-guest interaction between cyclodextrin (CD) and azobenzene (Azo) at the side chain. The supramolecular hydrogel actuator showed reversible macroscopic deformations in both size and shape when irradiated by ultraviolet(UV λ = 365 nm) or visible light(Vis λ = 430 nm).

Fig 1 depicts the chemical structure of the host-guest gel (αCD-Azo gel). Acrylamide (AAm), *N*,*N'*-methylenebis(acrylamide) (MBAAm), host monomer (αCD-AAm), and guest monomer (Azo-AAm) were copolymerized in DMSO. We regulated the volume of the αCD–Azo gels in water using photo irradiation. UV light (λ = 365 nm) irradiation of aCD–Azo gels increases the weight of the hydrogels, whereas continuous irradiation of Vis light (λ = 430 nm) to the αCD–Azo gels restores the initial weight and volume. These volume changes of αCD–Azo gels are correlated with the inclusion complex formation between αCD and Azo units (Fig 2).

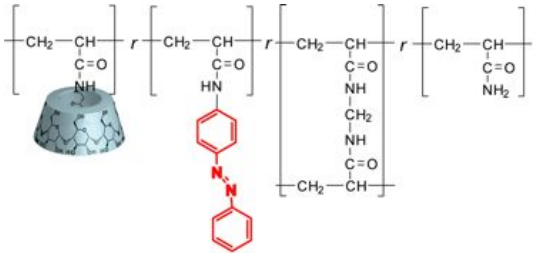


Figure 1. Chemical structure of αCD-Azo gel.

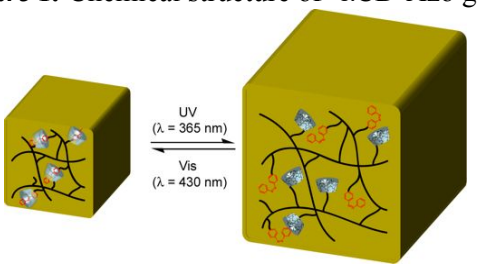


Figure 2. Schematic illustration of the expansion-contraction of αCD–Azo gel in response to photo stimuli.

Finally, we prepared photoresponsive actuators using expansion–contraction ability of αCD–Azo gels. Irradiating the plate gel with ultraviolet light (λ = 365 nm) from the left side bends the gel to the right, whereas irradiating the bent gel with Vis light (λ = 430 nm) from the same side for an hour restores the initial condition (Fig 3(a)) The same result was obtained similarly, considering the side opposite to (Fig 3(b)). In conclusion, we developed a light-driven supramolecular actuator with αCD and Azo that stems from formation and dissociation of an inclusion complex by uv or visible light irradiation. [1]

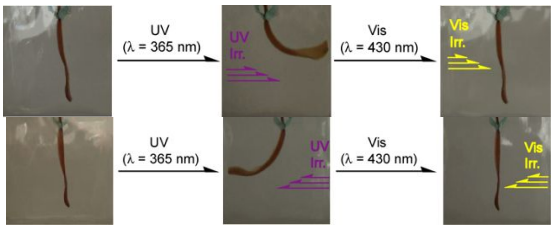


Figure 3. Light irradiation to plate-like αCD–Azo gel with UV light following Vis light from left (a) and right (b) side.

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Bambusurils – Receptors for Organic Anions

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Bambusurils are an interesting, growing family of anionic receptors. They are formed by an acid-catalyzed and templated condensation reaction from glycoluril and formaldehyde. These cheap building blocks form a rigid yet still sufficiently flexible structure ideal for the supramolecular interactions.[1] Since the publication of the first bambusuril, several other members differing by the substitution and size were prepared.[2] Depending on the substitution it is possible to tune its properties such as solubility or its supramolecular affinities. It is well established, that six-membered bambusurils are capable of forming complexes with wide variety of inorganic anions, but recently we found out, that some of them are even able to interact with organic ones.

In this meeting we would like to present our findings about interactions of $Bn_{12}BU[6]$ with organic anions, namely carboxylates and sulphonates.

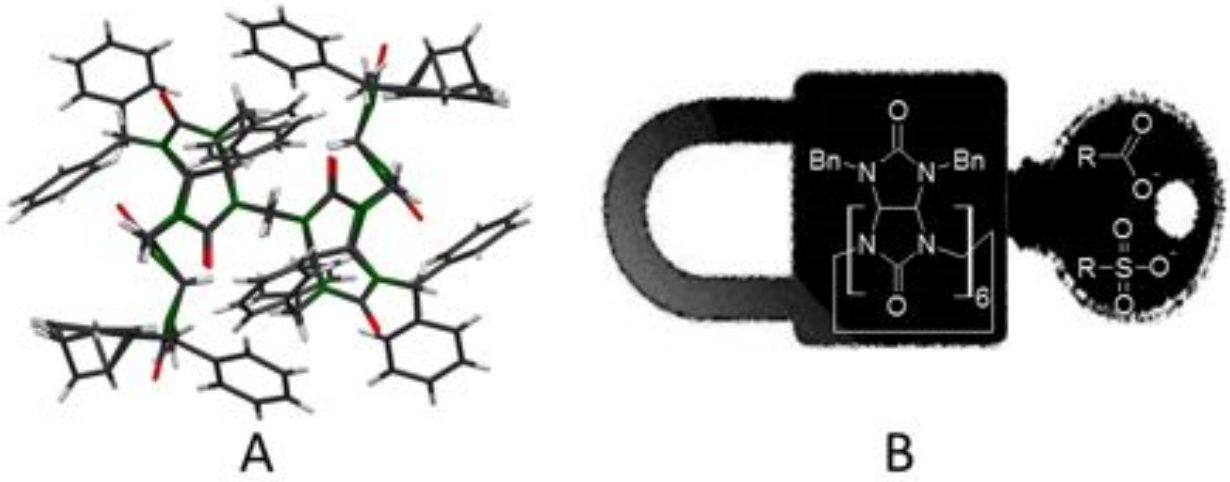


Figure 1. **(A)** Crystal structure of $Bn_{12}BU[6]$ and **(B)** a representation of its binding interactions with organic anions.

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Acknowledgments Support for this work was provided by the Czech Science Foundation (P207/10/0695), the project CETOCOEN (no. CZ.1.05/2.1.00/01.0001) from the European Regional Development Fund and Brno Ph.D. Talent Scholarship program sponsored by Brno City Municipality.

Self-assembly of Resorcinarene Bis-crowns

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Resorcinarenes, as well as closely resembling calixarenes, are widely used as supramolecular receptors for cations, anions, and small organic molecules.[1] The bowl-shaped binding cavity of resorcinarenes can be modified, for example, by bridging with crown ether units to enhance selectivity towards cations.[2] Self-assembly of the resorcinarene hosts into thin films and particles mainly depend on the length of the lower rim alkyl groups. Resorcinarene bis-crowns (Fig. 1) with alkyl groups from ethyl to undecyl show increasing tendency to form bilayers upon crystallization while maintaining approximately constant affinity towards Cs^+ and Ag^+.[3] In addition, the reduced flexibility of resorcinarene bis-crown binding site makes them interesting building blocks for Langmuir-films. Herein, we present a block-shaped C-methyl bis-crown derivative, and discuss the effect of the lower rim alkyl chain length on complexation and self-assembly into Langmuir-films.

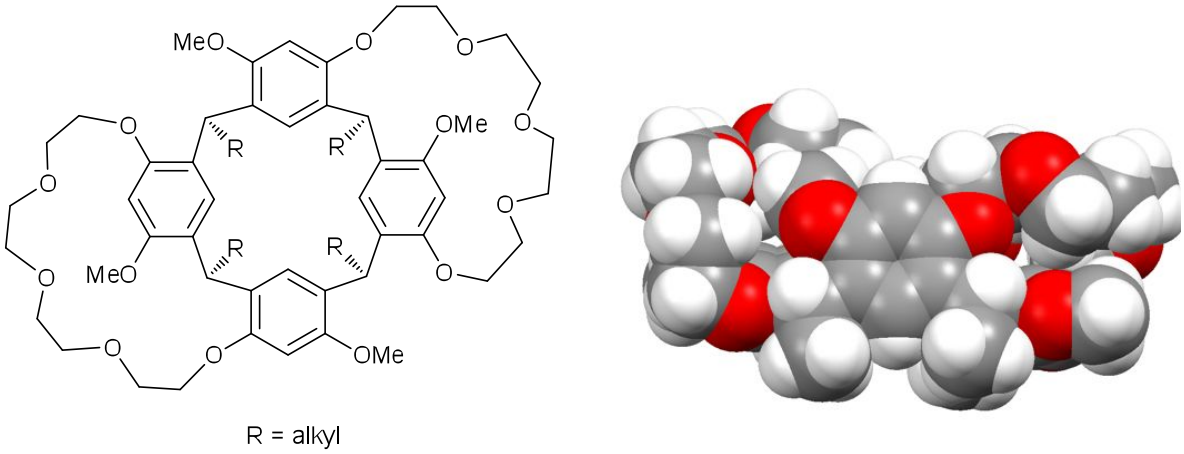


Figure 1. Structure of resorcinarene bis-crowns (left) and crystal structure of *C*-methyl resorcinarene bis-crown (right).

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Photo- and Chemically-Induced [2]pseudorotaxane Formation Using Spiropyran-based Axles

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Rotaxanes and catenanes are interlocked molecules which can convert an energy input (optical, electrochemical or chemical) into mechanical motion of their constituents, so they have been regarded as prototypes of molecular machines. There are several techniques for synthesis of rotaxanes, one of them is using pseudorotaxane complexes as precursors.[1]

We have previously demonstrated that macrocyclic ethers, like neutral dibenzo-24-crown-8 ether [**DB24C8**] and anionic *anti*-disulfonated-dibenzo-24-crown-8 ether [**DSDB24C8**]$^{2-}$, are capable to assembly with cationic 1,2-bis(pyridinium)ethane axles to form [2]pseudorotaxanes, which can then be transformed into [2]rotaxanes.[2]

Currently, we have built up [2]pseudorotaxane systems where the axle has been modified by adding a spiropyran moiety (SP) instead of a pyridinium unit; this moiety can be isomerized reversibly into a monocationic fragment, called merocyanine (ME), by chemical or optical stimulation.[3] We have observed that changing SP to ME form promotes the assembly between axle and macrocycle ethers (Figure 1). In order to study the influence of functional groups attached to the pyridinium unit in the SP-ME isomerization process, we have obtained several axles. Herein, we report the chemical behavior of each axle by itself (towards optical or chemical stimulus) and in the presence of [**DB24C8**] and [**DSDB24C8**]$^{2-}$ using diverse solvents.

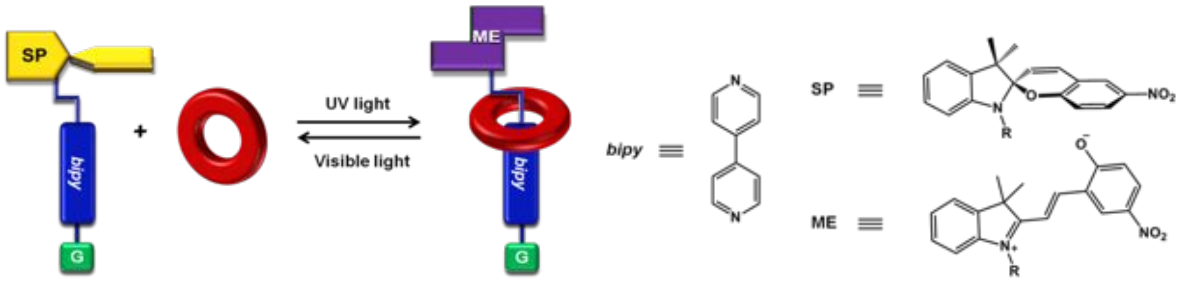


Figure 1. Schematic representation of [2]pseudorotaxane systems. **G** correspond to different groups attached to the *bipy* unit, such as -CH_3, -Bn, and -(*α*-bromo-*p*-xylene). [**DB24C8**] or [**DSDB24C8**]$^{2-}$ are indicated by a wheel.

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Towards Formation of Tweezer-like Receptors by Self-assembly

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The reversible formation of boronic esters due to the interaction of boronic acids and diols, as well as the intra or intermolecular adduct formation with amines, have been widely employed to assemble several supramolecular systems such as macrocycles, cages, capsules, covalent organic frameworks, and polymers.[1,2]

With the aim to generate tweezer-like receptors starting from these building blocks, we have studied the N-B adduct stability of several arylboronic esters in the presence of both aliphatic and aromatic amines and diamines. The study was carried out in solution by isothermal NMR titrations and optical spectroscopy, and also by analysis X-Ray crystal structures elucidated from isolated single cystals. The solid-state structures (Figure 1a) showed features resembling tweezer-like receptors, indicating its potential to bind aromatic or other kind of guest compounds. In solution, N-B adducts showed good to moderate stability (Figure 2b) and such stability further depends on the structure of the selected diol and the length of the diamine spacer. The only stable 2:1 adduct (ester:amine) in solution with $K_{ass} > 10^5$ was characterized for aromatic diamines containing aliphatic spacers. Currently a wide variety of guest compounds, which could lead to self-assembled tweezers-type complexes, are being explored.

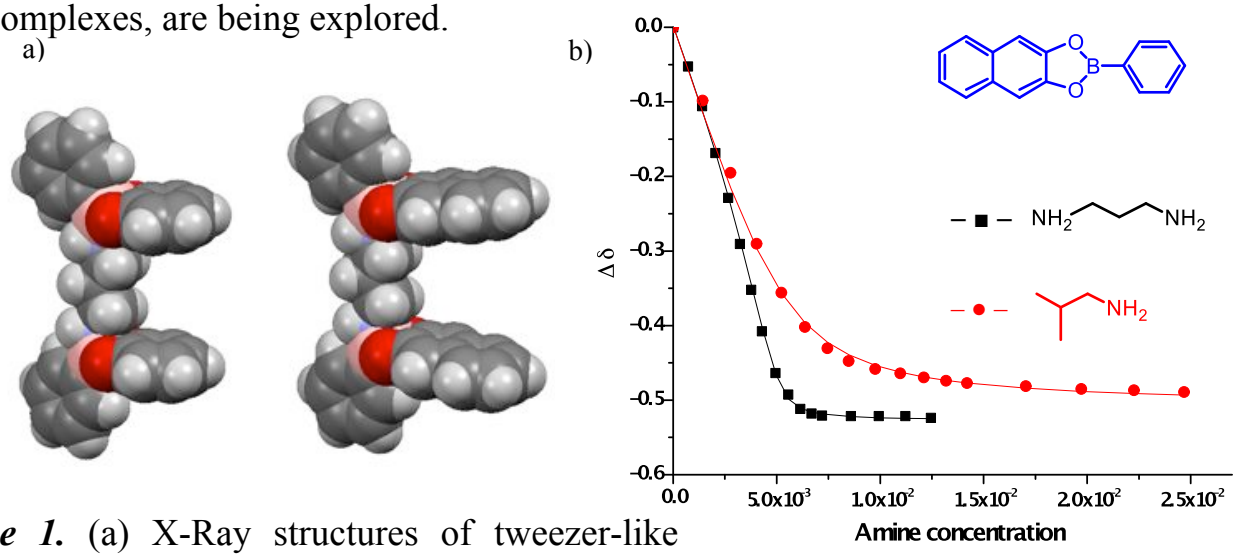


Figure 1. (a) X-Ray structures of tweezer-like adducts assembled by diamines and boronic esters (b) NMR Binding isoterms titrations of **1** with isobutylamine (circle) and 1,3-diaminoprapane (square).

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Computational Modeling of Deep-Cavity Cavitand Host:Guest Complexes, and in Aqueous Media

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Various binding and assembly motifs have been observed with a water-soluble deep-cavity cavitand. Computational studies, and corresponding empirical binding and assembly studies,[1] of the cavitand will be discussed, including: molecular dynamics simulations of cavitand in aqueous media with alkane guests of varying length, docking simulations of the host with non-polar guests, and models giving insight to the binding motifs observed in situ.[2]

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Anion-Triggered Switching of Supramolecular Architectures at the Liquid-Solid Interface

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Two-dimensional crystals of organic adsorbates that self-assemble from solution on surfaces can be switched using a variety of different stimuli. We demonstrate anion binding ($X = Cl^-$, Br^-, I^-) inside pre-programmed cavities of adsorbed aryl-triazole based receptors as observed using scanning tunneling microscopy. The anion binding events drive a surface morphology switch that can be explained by the interruption of long-range dipolar coupling forces. Indicative of the adsorption of the anion-receptor complex, bright spots in the binding pockets are observed. Additionally, the surface bias can be used to locally switch the structure. This work demonstrates the hierarchical character of supramolecular self-assemblies.

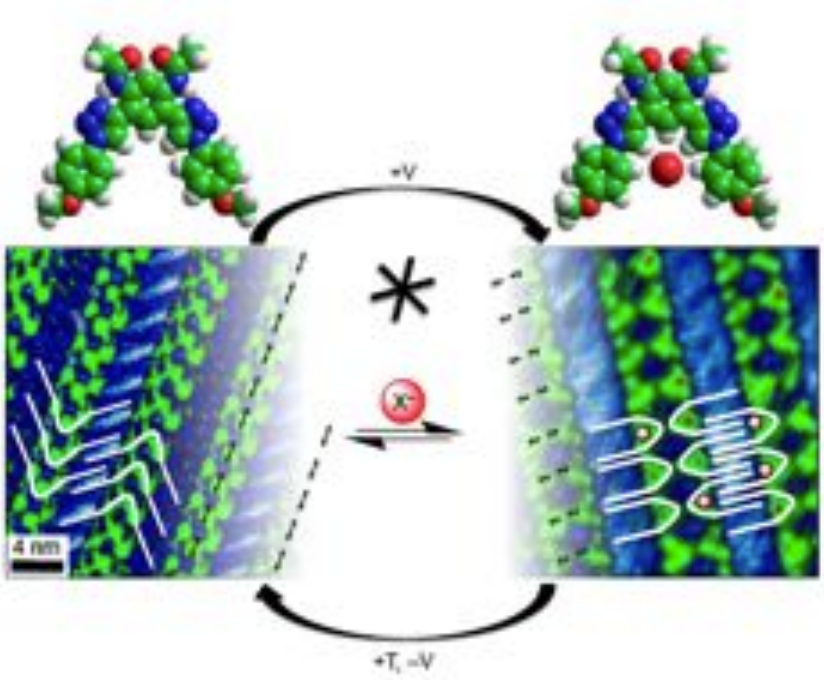


Figure 1. Summary of anion-induced supramolecular switching.

Synthesis and Preliminary Studies of a Cyclo[1]furan[1]pyridine[4]pyrrole Fused Macrocycle

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A novel hybrid cyclo[1]furan[1]pyridine[4]pyrrole **F1P1P4** has been synthesized using Suzuki coupling. Based on previous studies of **P3P3** and **P2P4**,[1] we propose that the protonated form of non-aromatic macrocycle **F1P1P4** might exist as a fully conjugated, annulene-like structure. This protonated form would be expected to reflect the presence of an electronically delocalized 24 π-electron antiaromatic resonance contributor within an overall structure dominated by localized aromaticity. The protonated form of **F1P1P4** was produced by treating with 10 equiv. of TFA in $CHCl_3$. Both the neutral and protonated forms were then studied by UV-Vis and ^{1}H NMR spectroscopy, which revealed an increase in the extent of π-electron conjugation within the macrocycle upon protonation. The present furan-pyrrole derived macrocycle is currently being studied as a ligand for larger metal cations, such as samarium and uranium. A summary of these latter efforts will be provided.

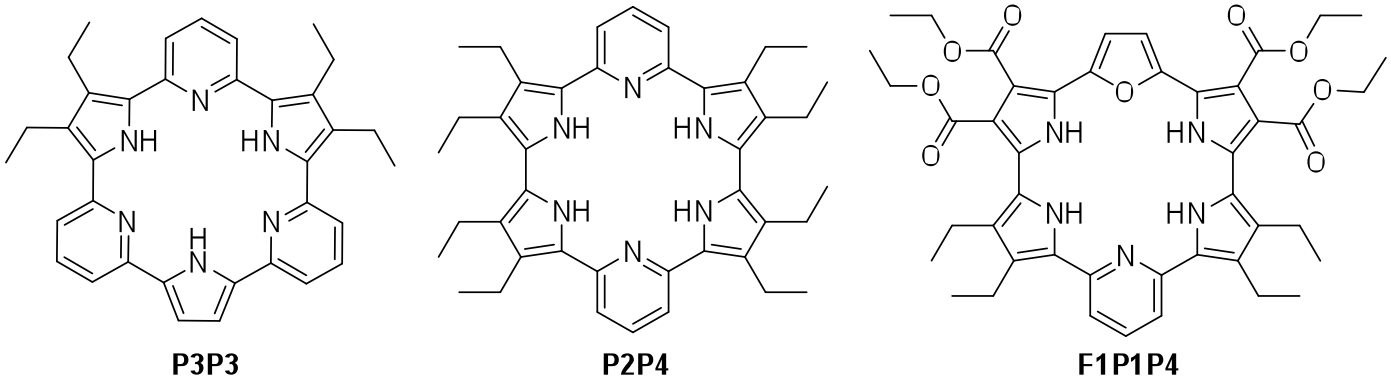


Figure 1. Structure of **P3P3**, **P2P4** and **F1P1P4**.

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Highly Efficient Fluorescent Output of a Pyrene-Diazaperopyrenium Pair Achieved by Rotaxanation

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Förster resonance energy transfer (FRET), a distance-dependent energy transfer between donor and acceptor fluorophores, has been widely used in chemical and biochemical sensors. The challenge in the development of new FRET fluorophore pairs is the prevention of self-quenching as a result of dye aggregation, which can be achieved[1] by the formation of a supramolecular complex. Herein, we report (Figure 1) a new FRET donor-acceptor fluorophore pair, namely pyrene ($\mathbf{1}^{+}$) and 2,9-diazaperopyrenium ($\mathbf{2}^{2+}$), by incorporation into a [4]rotaxane using cyclodextrin (**CD**) accelerated cucurbit[6]uril (**CB**) catalyzed azide-alkyne 1,3-dipolar cycloaddition.[2] Aggregation of the 2,9-diazaperopyrenium unit is effectively prevented by the encircling γ-CD, affording efficient FRET in the [4]rotaxane **R**•$4PF_6$ upon excitation of the pyrene unit in MeCN. More significantly, the [4]rotaxane **R**•$4PF_6$ powder exhibits red fluorescence (Figure 1d), indicating additional electronic interactions in the solid state.

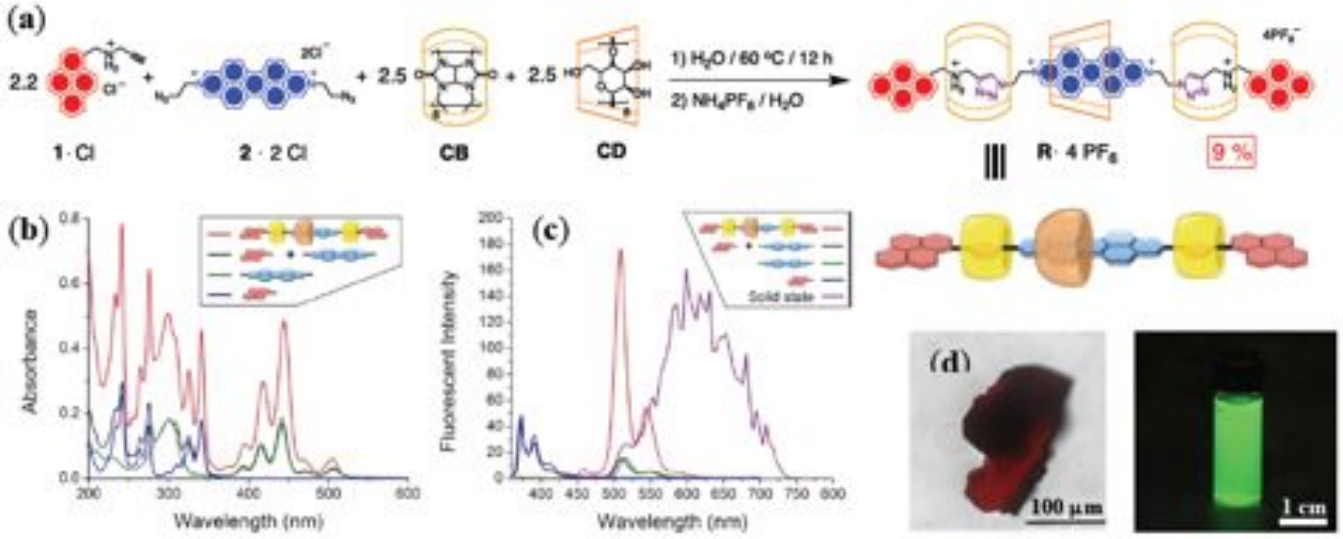


Figure 1. (**a**) Synthesis of the [4]rotaxane **R**•$4PF_6$, (**b**) UV-Vis spectra of **1**•PF_6 (50 μM, blue), **2**•$2PF_6$ (50 μM, green), a physical mixture of **1**•PF_6 and **2**•$2PF_6$ (50 μM, black) and **R**•$4PF_6$ (50 μM, red) in MeCN at 298 K, (**c**) fluorescent spectra of **1**•PF_6 (25 μM, blue), **2**•$2PF_6$ (25 μM, green), the physical mixture of **1**•PF_6 and **2**•$2PF_6$ (25 μM, black) and **R**•$4PF_6$ (25 μM, red) excited at 347 nm in MeCN at 298 K, and the solid-state fluorescent spectrum of **R**•$4PF_6$ (purple) excited at 405 nm at room temperature, (**d**) confocal microscopic image of **R**•$4PF_6$ excited at 405 nm, (**e**) image of **R**•$4PF_6$ in MeCN solution excited at 365 nm.

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Interesting New Chemistry of Pyrrole β-Amides

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Pyrrole β-amides are useful building blocks for the preparation of novel molecular architectures that can be used in supramolecular chemistry and sensor development. Under basic conditions, pyrrole β-amides and an α-aldehyde produce different condensation products with pyrrolinones depending on the amide substitution. Secondary amides formed the expected dipyrrinones, but expected underwent a subsequent trans-amidation with the pyrrolinone nitrogen to produce an unsymmetrical imide. Additional studies of this highly fluorescent material will be presented. Under the same conditions, tertiary amides produced the expected dipyrrinone carboxylic acid, which have been shown to have strong self-association properties. The X-ray structure of the dipyrrinone carboxylic acid was found to show a dimeric structure with a network of six intermolecular hydrogen bonds in a dipyrrinone to carboxylic acid motif. Additional characterization of this dimeric structure will be presented.

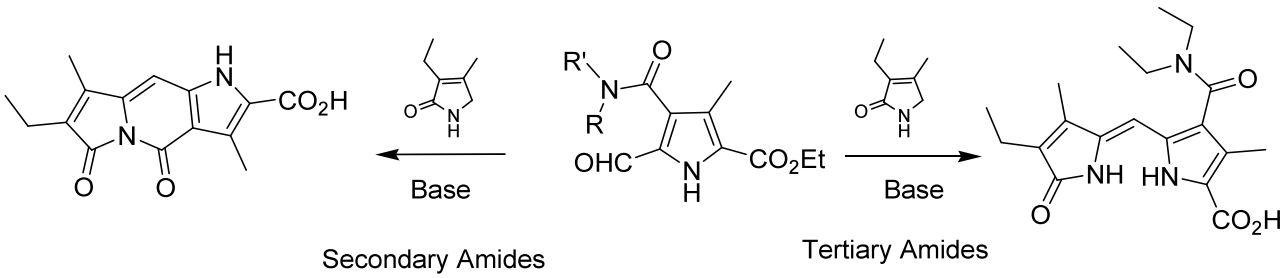


Figure 1. Synthetic Scheme.

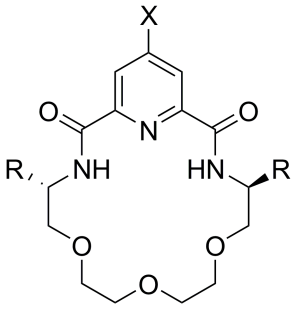
Synthesis of Enantiopure Pyridino-Crown Ether–Based Bis-amides as Potential Organocatalysts

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Asymmetric organocatalysis is a relatively new and popular field within the domain of enantioselective synthesis. It can be interpreted as chemical processes in which the small metal free molecules are active and catalyse stereoselective organic reactions. Stereoselective bifunctional organocatalysts bear two functional groups in a chiral skeleton which provide chiral induction. These type of catalysts yield the products with high stereoselectivity owing to the simultaneous activation of the electrophile by its hydrogen bonding donor moiety (eg. amide, urea, thiourea) and the nucleophile by the Brønsted basic group.

Up to now there is only one example in the literature when a crown ether containing a pyridine subunit was used as an enantioselective catalyst in an asymmetric synthesis.[1] In this case only moderate enantioselectivities were observed. The applied crown ether catalyst contained only Brønsted basic functionalities.

Amide-type organocatalysts are versatile ones for various asymmetric reactions.[2–4] Six new enantiopure amide-type pyridino-crown ethers (*S,S*)-**1**–(*S,S*)-**6** were prepared by cyclization of chiral diamines with 4-substituted pyridine-2,6-dicarbonyl dichlorides using established procedures[5]. The pyridino-crown ether–based catalysts are intented to test in asymmetric Michael reactions. The effect of the substituents at position 4 of the pyridine ring and the alkyl groups at chiral centers, respectively for the efficiency of enantiomeric induction will be studied.



macrocycle	X	R
(*S,S*)-**1**	H	Me
(*S,S*)-**2**	H	iBu
(*S,S*)-**3**	Cl	Me
(*S,S*)-**4**	Cl	iBu
(*S,S*)-**5**	OMe	iBu
(*S,S*)-**6**	NO_2	iBu

Fig 1. New enantiopure pyridino-crown ether–based bis-amides as potential organocatalysts.

Acknowledgement: Financial support of the Hung. Sci. Res. Fund (K81127) is acknowledged.

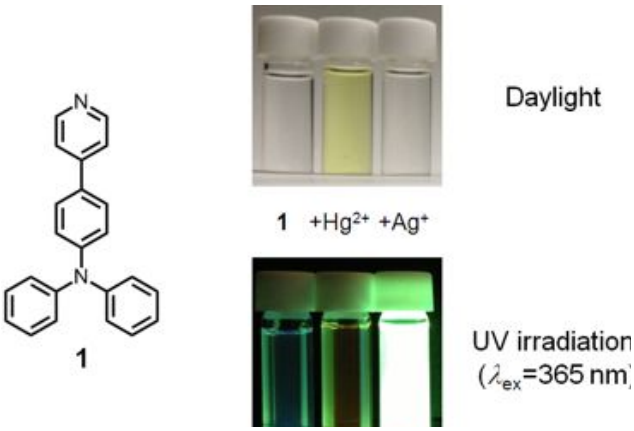
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Silver and Mercury Ions-Specific Pyridine-Containing Dual Mode Sensor

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Fluorescence sensor molecules for metal ions have much advantage than the other sensing systems, because of their high sensitivity. To develop fluorescence sensor molecules with specific metal ions, many researcher have reported well-designed molecules, which are prepared via multistep and in low yields. However, they are in far stage from practical use. To develop practical fluorescence sensor molecules, it is important to develop multifunctional sensor molecules with a simple structure and small molecular weight. Recently, Jiang[1] and Kim[2] reported dual-mode sensor molecules which can detect 2 metal ions. Based on above, we have been interested in developing practical fluorescence sensor molecules.



1

We here report a dual-mode sensor molecule (N,N-diphenyl-4(pyridin-4-yl)aniline, (1)[3] with small molecular weight and simple structure, which can detect two metal ions by different spectroscopy. 1 was prepared by the Suzuki-Miyaura reaction from 4-Iodopyridine and 1.1 equivalents of 4-(N,N-diphenylamino)phenylboronic acid in 75% yield. Complexing property of 1 toward several metal ions was examined based on metal ion-induced fluorescence and UV-vis spectral changes in methanol. 1 shows a weak fluorescence emission at 468 nm upon excitation at 350 nm in methanol. A significant enhancement of the fluorescence intensity was observed upon addition of 100 equivalents of Ag^{+} to 1. On the other hand, upon addition of Hg^{2+}, the emission of 1 quenched. No spectral changes were observed upon addition of Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rb^{+}, La^{3+} and Pb^{2+} ions. When Cd^{2+} was added, small enhancement of the fluorescence intensity was observed. In the UV-vis experiment, redshift (from 350 to 405 nm) was observed, when equimolar amounts of Hg^{2+} were added. On the other hand, no spectral changes were observed upon addition of equimolar amounts of Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rb^{+}, Ag^{+}, Cd^{2+}, La^{3+}, and Pb^{2+} ions. The UV-vis and fluorescent spectral data suggest that 1 would be used to detect both Hg^{2+} and Ag^{+} ions by UV-vis and fluorescence spectroscopy, respectively.

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Construction of Functionalized Two-Dimensional Pores by Zinc Porphyrin Units

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Recently, the construction of two-dimensional (2D) porous molecular networks by using self-assembly of organic molecules has attracted intense interest because 2D pores can be used as space to immobilize guest molecules. We previously reported that self-assembly of dehydrobenzo[12]annulene (DBA) derivatives having six alkoxy chains formed honeycomb networks at the liquid/solid interfaces via van der Waals interactions as revealed by scanning tunneling microscopy (STM) observations. [1] Moreover, polycyclic aromatic compounds were co-adsorbed within the 2D pores formed by DBAs.[2] One of the challenges in this field is functionalization of the 2D pores which can host target guest molecule(s) via specific guest recognition. We report the construction of 2D pores functionalized by zinc porphyrin units.

We designed DBA **1** having a zinc porphyrin at the end of each three alkyl chains. Modeling predicts that 6 zinc porphyrin units would be located in a hexagonal pore formed by self-assembly of **1**. STM observations revealed that a honeycomb structure of DBA **1** was formed and the zinc porphyrin units were placed in the pores (Fig 1). Moreover, in the presence of C_{60}, C_{60} molecules were immobilized on the zinc porphyrin via charge transfer interaction.

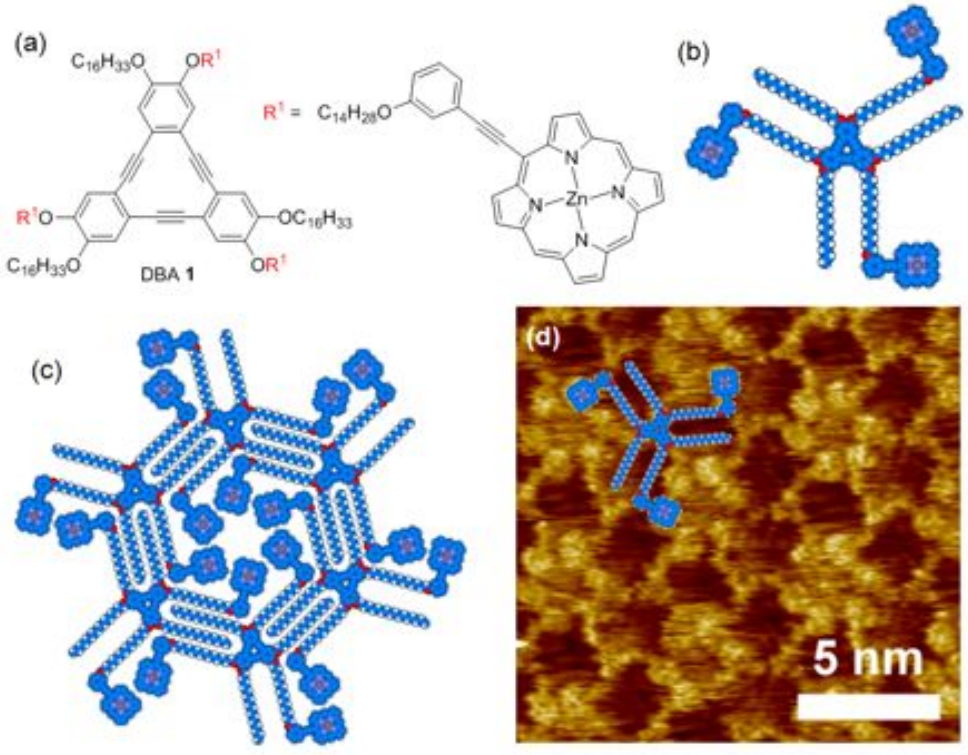


Fig. (a) Chemical structure of DBA **1** (b) Schematic model of DBA **1** (c) Model of hexagonal structure formed by DBA **1** (d) STM of monolayer formed by DBA **1** at the 1,2,4-trichlorobenzene/graphite interface.

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Chirality Amplification in Supramolecular Copolymers: Chiral Hierarchy and Stereomutation Effects

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Supramolecular polymers are ideal platforms to study chirality amplification because they can form very long helical assemblies at thermodynamic equilibrium. For instance, studying mixtures of enantiomers (majority-rules principle) or mixtures of chiral and non-chiral monomers (sergeants-and-soldiers principle) has revealed subtle effects of intermolecular interactions on chirality amplification.[1]

In order to expand these concepts, we have focused our attention on mixtures of monomers bearing both distinct self-assembling units and enantiomeric side-chains. The competing chirality introduced in such a non-symmetrical system is unprecedented. In particular, we report highly surprising stereomutation effects that prove that it is not possible to predict the helical bias of an assembly based on the helical bias of its constituents. Chirality amplification in supramolecular copolymers is actually ruled by the diastereomeric interactions between the comonomers.

References

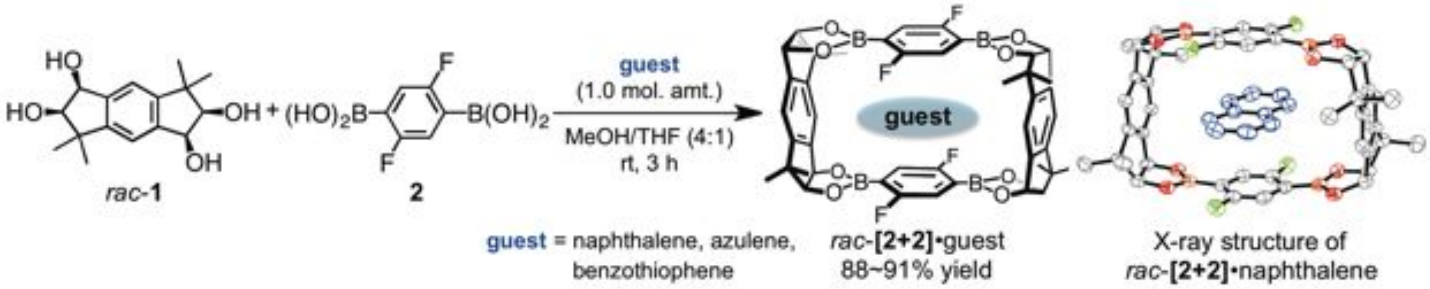
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Release and Recovery of Guest Molecules During the Reversible Borate Gel Formation of Guest-Included Macrocyclic Boronic Esters

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We have already reported the guest-induced self-assembly of discrete boronic esters based on the reversible nature of boronic ester formation.[1] Herein, we realized the release and recovery of the guest molecule during the formation and collapse of the borate gel by utilizing the dynamic nature of both boronic ester formation and borate formation. Guest-included macrocyclic boronic esters *rac*-**[2+2]**•guest were obtained by the self-assembly of *rac*-**1** with diboronic acid **2** in the presence of suitable guest compounds (Scheme 1).

Scheme 1. Self-assembly of guest-included macrocyclic boronic esters *rac*-**[2+2]**•guest.



Blue-coloured borate gel was obtained when *rac*-**[2+2]**•azulene (5.0 wt%) was treated with 2 molar amounts of 1,3-diaminopropane in methanol/THF (4:1) at room temperature (Figure 1a,b). Azulene was released into the borate gel at this stage. The released azulene was efficiently recovered from the borate gel as *rac*-**[2+2]**•azulene in 84% when the gel was treated with 1M aqueous HCl at room temperature and stirred for 24 h (Figure 1c).

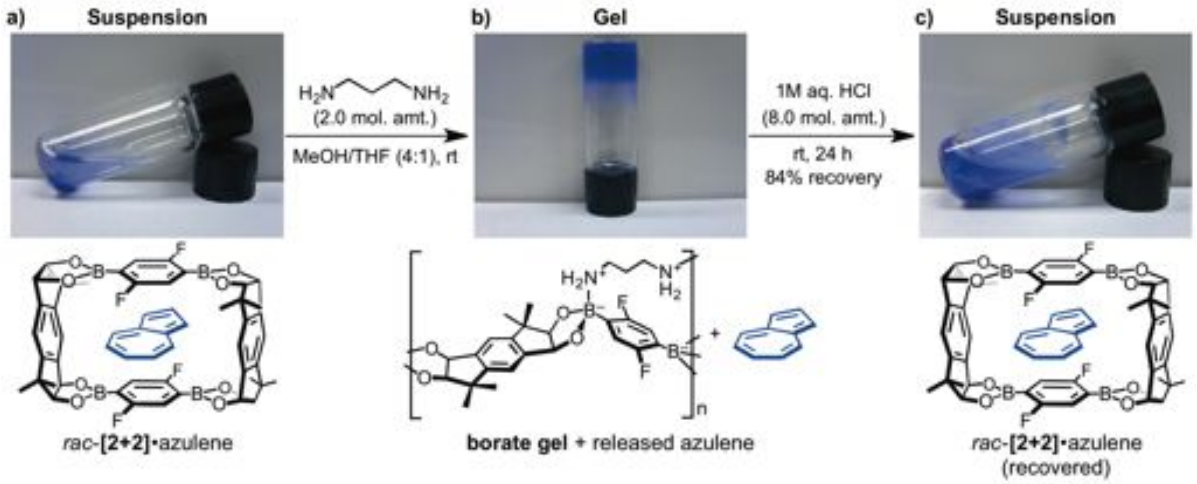


Figure. Release and recovery of the guest molecule during the reversible borate gel formation.

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Photonic Nanomaterials and Protein-binding Molecular Switches Prepared using Cyclodextrin Based Host-Guest Interactions

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This presentation will focus on the supramolecular chemistry associated with (a) multi-chromophore containing nanomaterials and (b) stimuli responsive molecular switches prepared in water. The central supramolecular synthon utilized for these systems is the β-cyclodextrin (β-CD)-based host-guest interaction. However, the use of other complementary interactions (including nucleic acid base-pairing, cation coordination, and electrostatic interactions) help to expand the versatility and functionality of the resultant systems. First, we will illustrate host-guest interaction driven construction of photonic porphyrinic nanowires and porphyrin-perylenediimide multi-layer thin films. This portion of the presentation will include materials characterization studies (including TEM, STM, and AFM measurements). The second segment of the presentation will detail how sterically precluded "smart" protein-binders (that are deactivated, inter-alia, via β-CD-based inclusion complex formation) can be activated to inhibit protein targets in response to oligonucleotide stimuli. Here, molecular switching and protein-binding studies will be discussed (including FRET, UV-vis, circular dichrosim, and fluorescence anisotropy experiments).

Anions Effect on the Complexation between Electron Donors and Cyclobis(paraquat-p-phenylene)

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In the last decade, the electron accepting macrocyclic tetracationic host cyclobis(paraquat-*p*-phenylene) has been used intensively as the ring component for construction of switchable donor-acceptor bistable [2]catenanes[1,2] and [2]rotaxanes.[3] In these constructions, derivatives of the electron donating tetrathiafulvalene (TTF) and 1,5-dioxynaphtalene (DNP) have been widely used as guests.

In this poster, we show that the complexation between an electron donor and cyclobis(paraquat-*p*-phenylene) is not only influenced by the nature of the donor, but also by the nature of the counteranions.[4] Binding studies between cyclobis(paraquat-*p*-phenylene) and derivatives of TTF and DNP in the presence of differently sized counteranions reveal that both the nature and the concentration of the anion have a large impact on the association strength of the resulting host-guest complex.

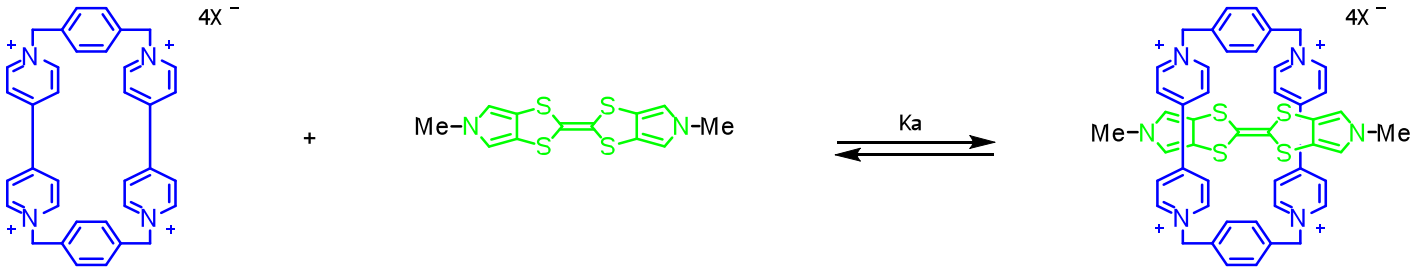


Figure. The complexation between cyclobis(paraquat-*p*-phenylene)•4X and a tetrathiafulvalene derivative (X = PF_6 and TRISPHAT).

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Solublization of Hydrophobic Catalysts using Nanoparticle Hosts

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Metal-mediated catalysis is a powerful tool in organic synthesis due to high reactivities under mild conditions coupled with regio-, and stereoselectivity. [1] However, use of these catalysts in water is challenging due to their meager solubility and instability in water.[2] We have developed a general strategy for solublizing hydrophobic catalysts using nanoparticle hosts. Through supramolecular interactions between catalysts and the hydrophobic region of the NP monolayer, various hydrophobic metal-based catalysts were encapsulated in the monolayer of water-soluble nanoparticles (NPs). (Fig 1.) To test the range of compatible catalysts, 2nd generation of Hoveyda-Grubb catalysts, Wilkinson catalysts and complex [Cp*Ru(cod)Cl] (Cp* = pentamethylcyclopentadienyl) were encapsulated. Ring-opening metathesis, hydrogenation and allylcarbamate cleavage were subsequently performed successfully in water, respectively.

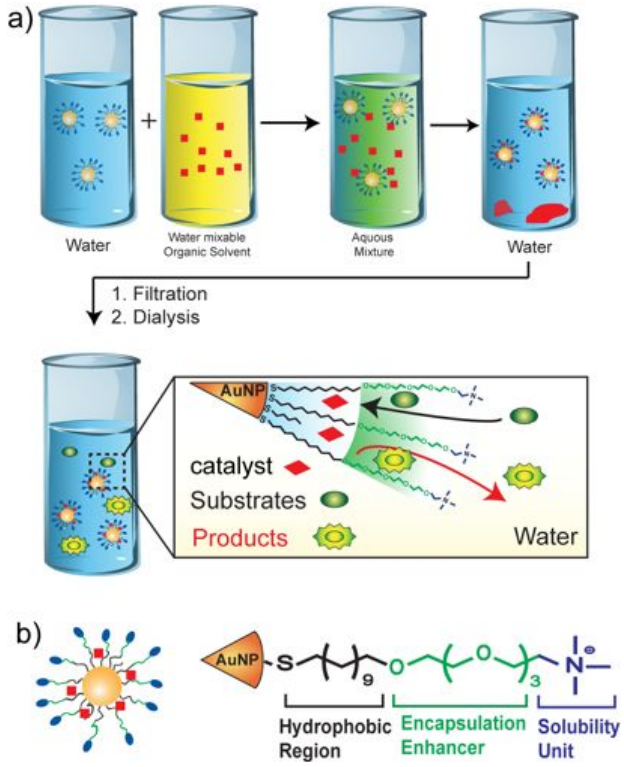


Fig a) Encapsulation of hydrophobic catalysts in water-soluble NPs. b) Structure of water-soluble NPs.

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Fused [*n*]polynorbornane Frameworks in Supramolecular Chemistry

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In previous studies within the Pfeffer group, [*3*] and [*5*]polynorbornane based-frameworks have been successfully employed for strong and selective anion recognition. Using [*n*]polynorbornane based-frameworks, with appropriate functionalisation, we are currently investigating a number of anion recognition related applications.

A major theme of this project is the design and synthesis of antimicrobial agents inspired by the naturally occurring antimicrobial peptide family of θ-defensins. This involves the incorporation of cationic guanidino-groups onto the norbornane frameworks, which are designed to target the anionic section of lipid A found in gram-negative bacteria.

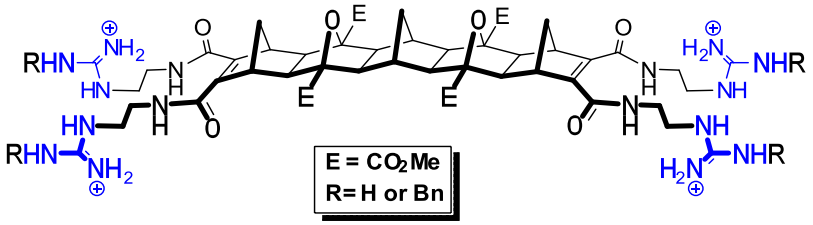


Figure 1. Guanidine-functionalised [*5*]polynorbornane

We are also investigating the use of highly pre-organised hosts, namely symmetric macrocyclic [*n*]polynorbornanes, and evaluating their anion binding properties. Furthermore, we have developed a one-pot multi-component approach for the synthesis of [*n*]polynorbornanes, designed for the construction of metal-organic frameworks. Similar metal-organic frameworks[1] have been shown to be suitable supramolecular assemblies for use in anion recognition applications.

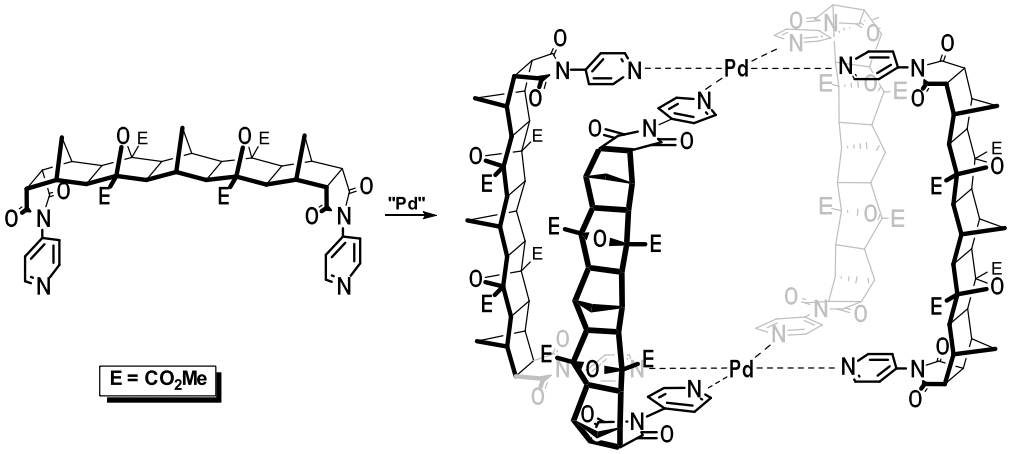


Figure 2. Interesting MOF.

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Supramolecular Assembly of Metal Nanoparticles *via* Cucurbit[8]uril Ternary Complex Formation

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Cucurbit[*n*]uril's (CB[*n*]s) are a class barrel shaped macrocyclic host molecules where *n*=5-8 and 10. The smaller CB[*n*] homologues (< 7) are capable of encapsulating single small molecules. CB[8] is capable of encapsulating two molecules to create a 1:1:1 ternary complex. The most commonly studied guests are methyl viologen (MV^{2+}) and naphthol (Np) moieties, which are capable of forming a 1:1:1 ternary complex with CB[8]. This pairing exhibits a very high binding constant of 10^{12} with CB[8]. The use of CB[8] ternary complexes to assemble polymers, biopolymers and polymer colloids has been well studied. However, the combination of CB[8] ternary complexes to assemble metal nanoparticles has not before been studied. Nobel metal nanoparticles, such as gold nanoparticles (AuNPs), are particularly interesting due to their unique optical properties.

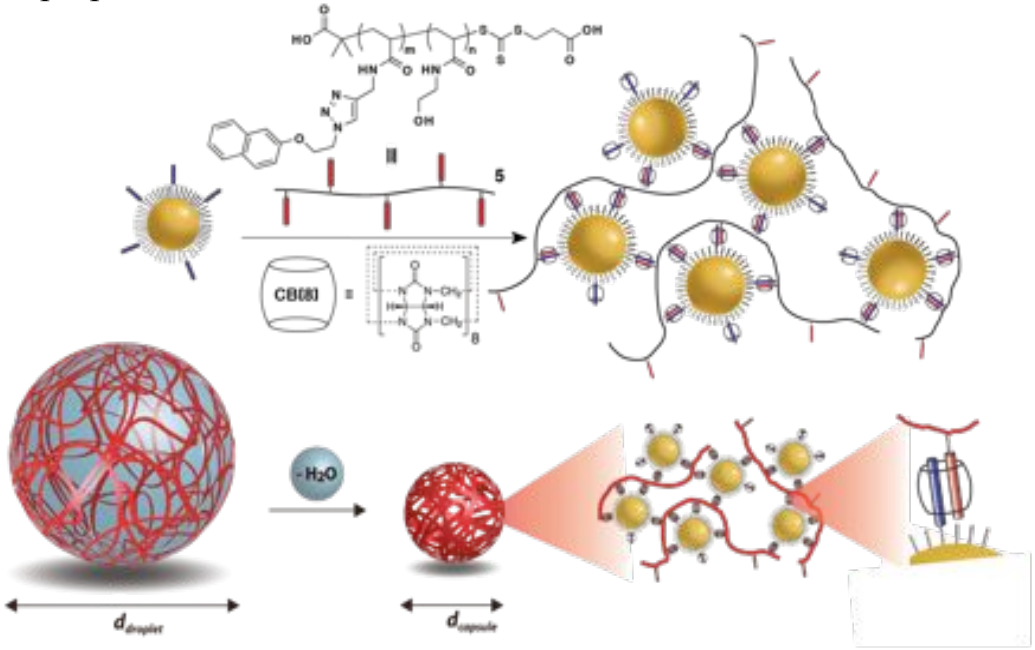


Fig. Assembly of AuNPs using cucurbit[8]uril ternary complex formation into microcapsules

Through CB[8] ternary complex formation we have assembled MV^{2+}-functional AuNPs with a Np-functional polymers to give nanoparticle-polymer composite materials.[1] These materials were shown to self-assemble into microcapsules when assembled in a micro-fluidic device.[2] Additionally, we have shown that CB[8] ternary complexes are capable of aligning gold nanorods (AuNRs) in a controllable and reversible fashion.

References: [1] Coulston *et al.*, *Chem. Commun.*, 2011, **47**, 164. [2] Zhang *et al.*, Science, **335**, 690 (2012)

Binding of Octa-Acid Deep-Cavity Cavitand to Specific Protein Targets

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Recent studies into the binding of octa-acid deep cavity cavitands and its derivatives to specific protein targets will be presented. Additionally we will discuss the different synthetic routes to the cavitand derivatives, and the preparatory method for obtaining target proteins.[1] We will describe the computational and analytical approaches used to identify specific binding especially between the negatively charged guest molecule octa-acid and charged protein surfaces and potential inhibition of protein activity.[2] More specifically, we will focus on the spectroscopic techniques used to determine whether specific binding has occurred and what this information tells us about protein inhibition.[3]

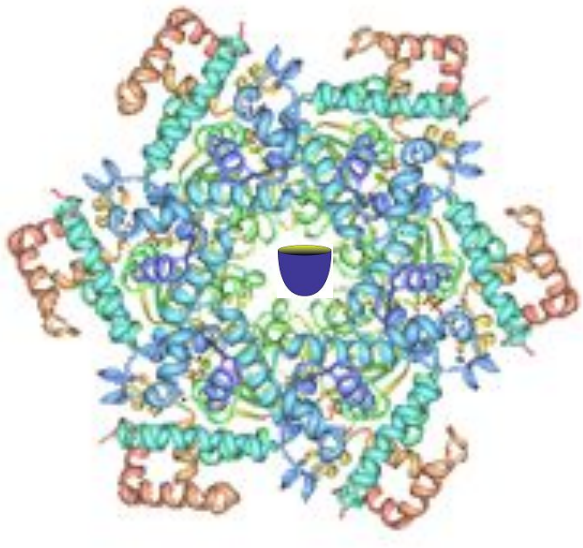


Figure 1. Schematic of specific binding between a cavitand and sv40 hexamer.

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Soft Metal Complexes of an O_4S_2-Macrocycle with Different Coordination Modes: Monomers, Molecular Dumbbells, and 1D Polymers

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Exo-coordination is synthetically attractive because it would provide a means of connecting macrocyclic building blocks in diverse arrangements.[1,2] In this presentation, a range of thiaphilic (Ag^+, Cu^+, Hg^{2+}, and Pd^{2+}) mono-, di-, and multinuclear complexes (**1**-**8**) of the O_4S_2-macrocycle **L** with discrete (**1**-**6**) and continuous (**7**, **8**) forms are reported (Fig 1).[3] First, reactions of **L** with $AgClO_4$, $Hg(NO_3)_2$, and K_2PdCl_4 afforded a typical endocyclic 1:1 complexes $[Ag\mathbf{L}]ClO_4$ (**1**) without anion binding, $[Hg\mathbf{L}(NO_3)_2]$ (**2**), and $[Pd\mathbf{L}Cl_2]$ (**3**), respectively. One-pot reaction of **L** with $AgClO_4$ together with linker coligands (**L'**: bpy, dabco, and bpp) afforded unique dumbbell-shaped complexes $[Ag_2\mathbf{L}_2(\mu_2\text{-bpy})](ClO_4)_2$ (**4**), $[Ag_2\mathbf{L}_2(\mu_2\text{-dabco})](ClO_4)_2$ (**5**), and $[Ag_2\mathbf{L}_2(\mu_2\text{-bpp})](ClO_4)_2$ (**6**) with an **L**Ag-**L'**-Ag**L** pattern. Comparative NMR studies suggest the existence of corresponding structures of this type in solution. Contrasting with the discrete complexes, reactions of **L** with CuBr and AgSCN yielded continuous 1D network complexes $\{[(Cu_2Br_2)\mathbf{L}_2]\cdot 2CH_2Cl_2\}_n$ (**7**) and $[Ag_4\mathbf{L}_2(SCN)_4]_n$ (**8**), respectively. The latter complex features an unusual fishbone-like structure, in which endocyclic Ag(I) complexes attached to a "looped" exocyclic backbone of type $\{Ag\text{-}(1,3\text{-}\mu_2\text{-}SCN)_2\text{-}Ag\text{-}(1,1,3\text{-}\mu_3\text{-}SCN)\text{-}Ag\}_n$ via Ag-SCN bonds.

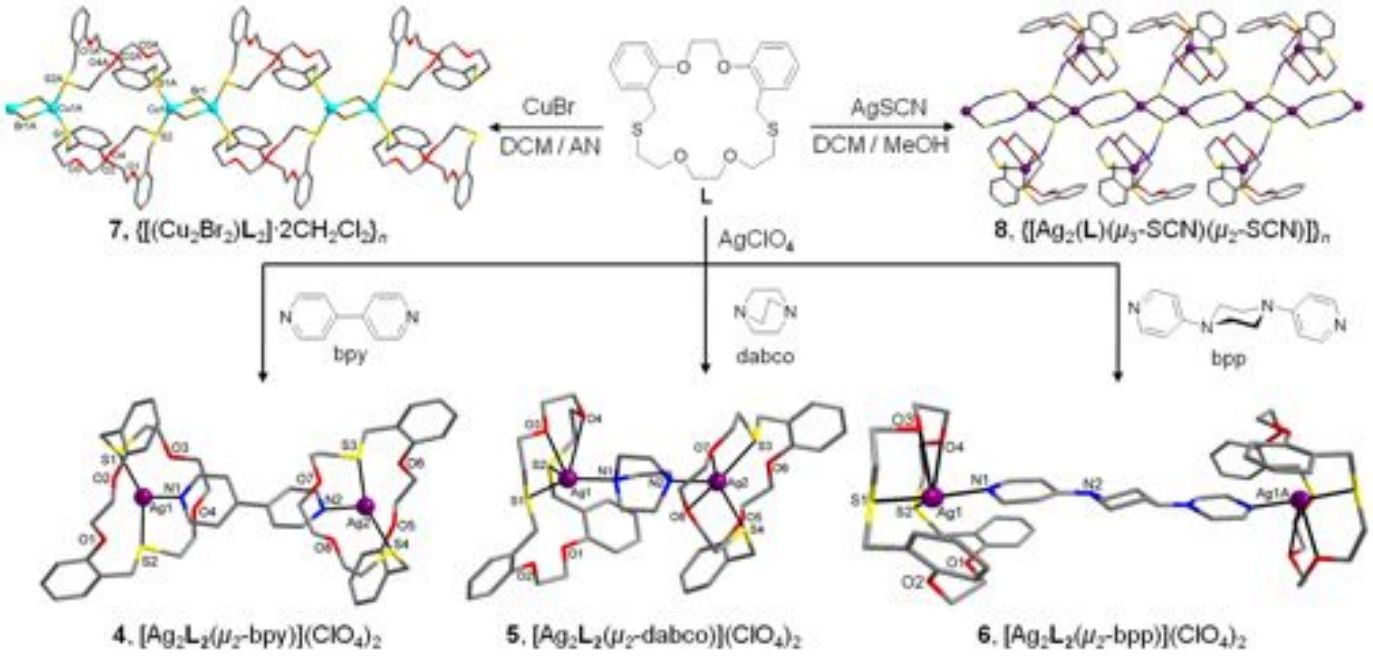


Figure 1. Synthetic routes leading to complexes with diverse topologies.

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Apertures, Binding and Catalysis Inside ExBox

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A series of rigid, box-like tetracationic cyclophanes comprised of two bis(pyridinium) units, also referred to as extended viologens, have been synthesized in our lab and shown[1] to function as high-affinity supramolecular hosts for polycyclic aromatic hydrocarbons (PAHs). These "extended viologen boxes"—or Ex^{n}Box for short—display a remarkable ability to scavenge PAH molecules of any shape and size up to 14.6 Å in ExBox and even larger guests in Ex^{n}Box (n > 1). The scope of ExBox to bind PAHs is not limited to planar aromatic guests and involves non-planar PAHs, such as [4]helicene and corannulene. By expanding the structure of ExBox by an additional phenylene and/or acetylene units, the cavity of Ex^{2}Box and its larger analogues becomes electron-deficient in the corners and relatively electron-rich in the middle and binds both π-electron-rich and -poor guests, as well as macrocyclic polyethers comprising two electron-rich subunits or an aligned molecule of tetracene. In addition to the ability of ExBox to extract PAHs from Saudi Arabian crude oil and catalyze bowl-inversion of corannulene, recognition in large apertures of Ex^{n}Box could be particularly useful (1) in the realm of the template-directed synthesis of topologically challenging molecular knots or (2) to exfoliate graphene nanoribbons.

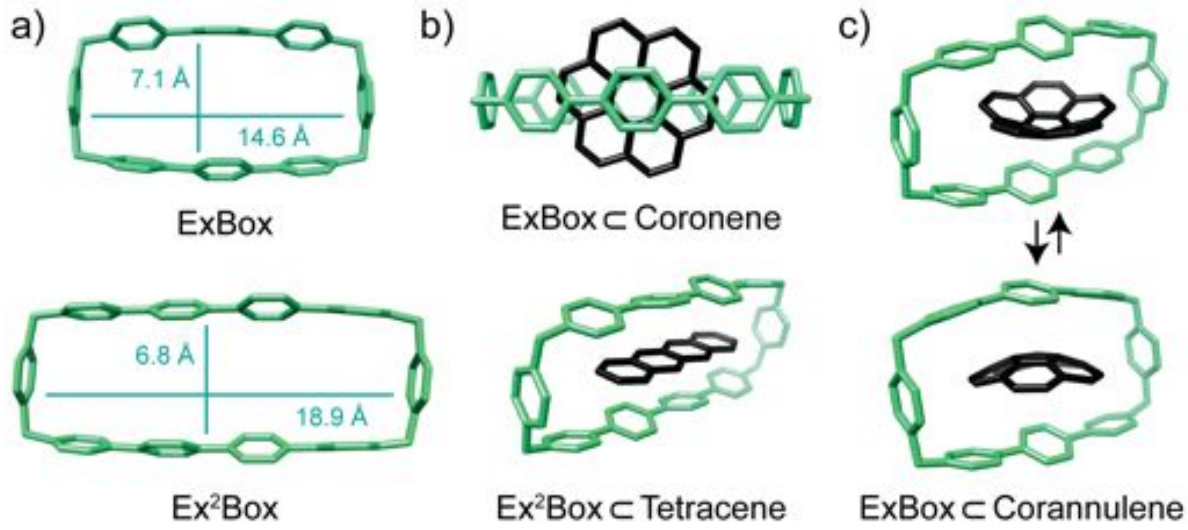


Fig 1. X-Ray crystallography sheds light on (**a**) apertures, (**b**) binding and (**c**) catalysis inside ExBox.

References 1) Barnes, J. C.; Juríček, M.; Strutt, N. L.; Frasconi, M.; Sampath, S.; Giesener, M. A.; McGrier, P. L.; Bruns, J. C. ; Stern, C. L.; Sarjeant, A. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 183–192.

Formation of Supramolecular Hydrogel Polymerizing Inclusion Complexes and Functional Properties

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Supramolecular materials have attracted attention due to their unique properties, because the non-covalent bonds can reversibly connect and disconnect inside these materials. To create new supramolecular materials with specific functional properties, we chose host-guest interactions using non-covalent bonds. We succesfully formed supramolecular materials by the polymerization of inclusion complexes between CD and guest monomers in aqueous solutions. These materials showed high stretching and self-healing properties.

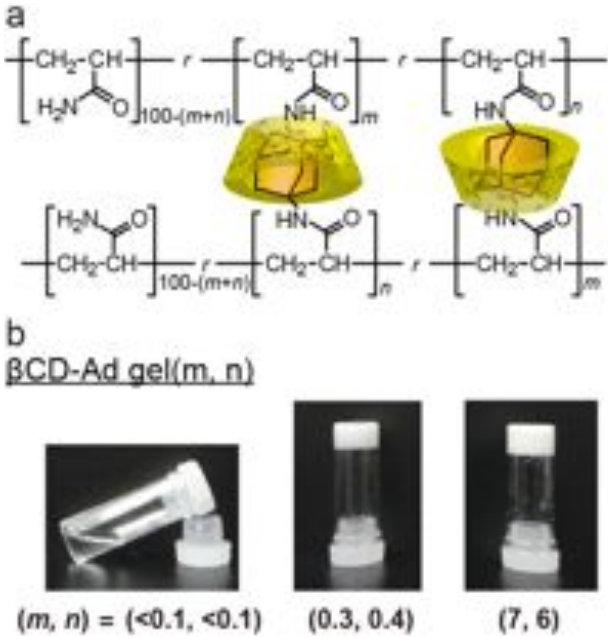


Figure 1. (a) Chemical structure of the βCD-Ad gel(*m, n*). (b) Photographs of the βCD-Ad gel(*m, n*). *m* and *n* denote the mol% of host unit and guest unit, respectively.

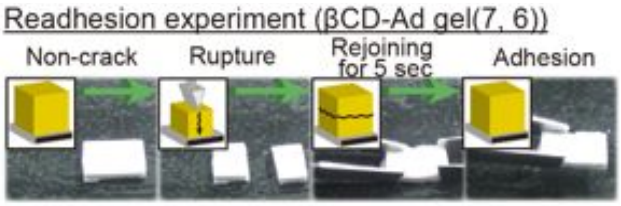


Fig 2. Self-healing behavior of βCD-Ad gel (7, 6).

β-Cyclodextrin-adamantane gel (βCD-Ad gel(*m, n*)) formed self-standing gels even though these supramolecular hydrogels do not have covalently-crosslinking units (Figure 1). Storage elastic modulus (*G´*) of these supramolecular hydrogels are larger than loss elastic modulus (*G´´*) in low frequency. When the rectangular shape of the βCD-Ad gel(0.3, 0.4) was stretched with tweezers and released, the morphology of the βCD-Ad gel(0.3, 0.4) recovered the initial state. Additionally, the βCD-Ad gel (1.6, 1.9) did not show the same behavior, suggested that the supramolecular materials having a little cross-linking of inclusion complex exhibited high stretching property and shape recovery behavior. On the other hand, the βCD-Ad gel (7,6) showed self-healing properties. The self-healing properties of the supramolecular hydrogels were studied by re-adhesion experiments. The fracture surface of βCD-Ad gel (7,6) adhered after rejoining between cut surfaces for 5 seconds (Figure 2). The adhesive strength was studied by the compression test using wedge-shaped plunger. After 24 hours, the adhesive strength of βCD-Ad gel (7,6) recovered to 99% of initial rupture strength[1].

References

1) Kakuta, T.; Takashima, Y.; Nakahata, M.; Otsubo, M.; Yamaguchi, H.; Harada, A. *Adv. Mater.* **2013** (DOI: 10.1002/adma.201205321).

Conformational and Fluorescence Change of an *N*-phenylbenzohydroxamic Acid Derivative Depending on the Solvent Properties

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N-Phenylbenzohydroxamic acid changes its conformation, depending on the solvent properties.[1] We newly synthesized derivative **1** that consists of two pyrene moieties separated from the phenyl rings of *N*-phenylbenzohydroxamic acid skeleton by ethylene linkers (Fig. 1). Compound **1** showed solvent-dependent fluorescence spectra due to conformational change, that is, only monomer fluorescence of pyrene was observed in DMSO or DMF, whereas excimer fluorescence was observed in CH_2Cl_2 or $CHCl_3$. Thus, the structural characteristics could be converted to fluorescence change as output. These results demonstrate that structural characteristics of *N*-hydroxybenzanilide can be applied as a core structure of fluorescent sensor for solvent property. [2] We have reported several types of aromatic amides, which exhibit conformational change in response to various types of environmental change such as pH and redox state. By utilizing the similar strategy shown here, fluorescent sensors for various environmental conditions would be developed.

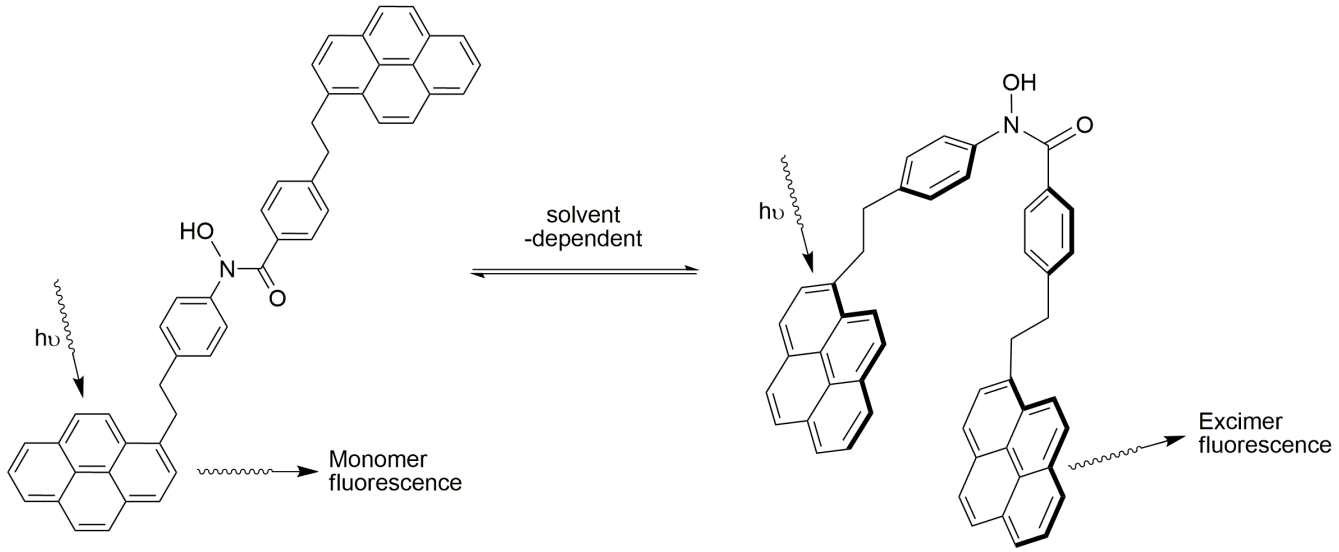


Figure 1. Solvent-dependent conformational and fluorescence change of **1**.

References
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2) Kanai, M.; Hirano, T.; Azumaya, I.; Okamoto, I.; Kagechika, H.; Tanatani, A. *Tetrahedron* **2012**, *68,* 2778-2783.

Formation of Chiral Helical Chain Structures of *N,N'*-Bis(*ortho*-substituted phenyl)squaramides in the Crystals

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Squaramide is a squaric acid derivative with two amino groups, and is used as key structural motif of anion receptors or bifunctional organocatalysts or as a bioisostere of urea in medicinal chemistry. *N,N'*-Diarylureas generally form one-dimensional chain structures by hydrogen bonds between the carbonyl oxygen atom and two hydrogen atoms on nitrogen atoms of the adjacent molecule in the crystals (Fig. 1a). Since *N,N'*-diarylsquaramides have two NH groups and two carbonyl oxygens, we expected that they construct unique hydrogen bonding interactions such as shown in Fig. 1b, and examined the crystal structures of various *N,N'*-diarylsquaramides.

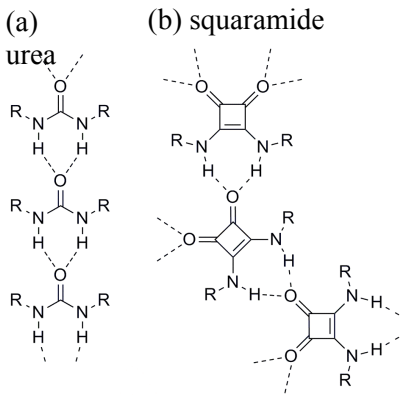


Figure 1. Supposed hydrogen bonding interactions of urea and squaramide

Many *N,N'*-bis(*ortho*-substituted phenyl)squaramides afforded pseudo-polymorphs, including chiral crystals. In most chiral crystals, the one-handed helical chain structures were observed, which were classified into 3 types (Fig. 2). In two types, 4-membered rings and phenyl groups were nearly perpendicular to the helical axis as observed in compounds **1** (2_1 helix) and **2** (6_1 helix), while 4-membered rings of third type was nearly parallel to the axis as observed in compound **3** (4_1 helix). The helical chain structures of squaramides, and the high frequency of spontaneous resolution are very interesting from viewpoints of molecular chirality. The detailed helical properties of *N,N'*-bis(*ortho*-substituted phenyl)squaramides are under investigation.

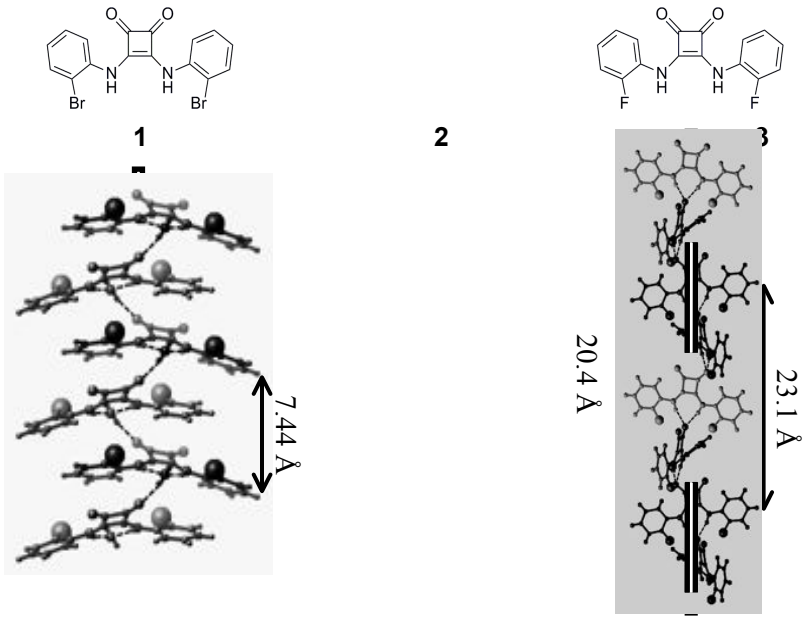


Fig2. Three types of helical chain structures in chiral crystals

Quantitative SERS Using the Sequestration of Small Molecules Inside Precise Plasmonic Nanoconstructs

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Surface-enhanced Raman spectroscopy (SERS) is a powerful analytical technique, which is increasingly being used as a tool for direct molecular detection, particularly with colloidal nanoparticles.[1] Macrocyclic host, cucurbit[8]uril (CB[8]), serves to create precise nanojunctions between gold nanoparticles[2] for reproducible SERS while its hydrophobic cavity can accommodate small aromatic molecules that enables their SERS detection with improved sensitivity. We report, for the first time, explicit shifts in the SERS frequencies of CB[8] on complexation with guest molecules. Based on this observation we demonstrate a strategy for determination of binding constants and quantification of a range of molecules with detection limits at 10^{-11} M level.[3] This method represents a new analytical paradigm for quantitative characterization of small aromatic molecules with SERS.

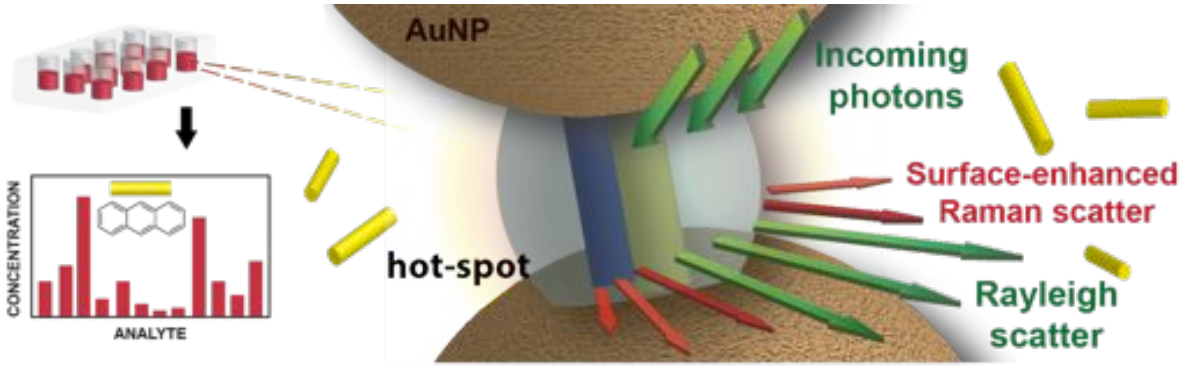


Figure 1. Cucurbit[8]uril bridged gold nanoparticles for ultrasensitive SERS analysis.

References
1) Alvarez-Puebla, R. A.; Liz-Marzán, L. M. *Chem. Soc. Rev.* **2012**, *41*, 43–51.
2) Taylor, R. W.; Lee, T.-C.; Scherman, O. A.; Esteban, R.; Aizpurua, J.; Huang, F. M.; Baumberg, J. J.; Mahajan, S. *ACS Nano* **2011**, *5*, 3878–3887
3) Kasera S.; Biedermann F.; Baumberg J. J.; Scherman O.A.; Mahajan S. *Nano Lett.*, **2012**, *12*, 5924.

Decanickel Wheels – Syntheses, X-ray Structures & Related Complexes

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A novel 2,2′:6′,2″-terpyridine–picolylamine-based bridging ligand L has been synthesized and fully characterized. As shown in figure 1(a), the ligand has tridentate and bidentate metal binding sites available to coordinate with various metal ions. By varying the size of anions both dinuclear complexes and supramolecular assemblies have been produced.

Addition of metal salts containing small anions like halides result in formation of Cu_2L and Zn_2L dinuclear complexes, where one metal ion binds at each of the binding sites of the ligand. These complexes will be used to study kinetics of hydrolysis of phosphatediesters.

Larger anions like PF_6^-, ClO_4^-, SO_4^{2-}, NO_3^- result in formation of Zn_4L_4 type squares *via*. head-to-head and tail-to-tail, HH-TT, (H=tridentate site, T=bidentate site) coordination of the ligand. The octahedrally bound Zn(II) ion between two tridentate sites can be replaced with Fe(II) to prepare $Fe_2Zn_2L_4$ squares. A flat molecule of terephthalic acid was also deliberately encapsulated in the middle of the $Fe_2Zn_2L_4$ square.

The head-to-tail, HT, coordination of the ligand in case of Ni(II) results in formation of decanickel wheels, like $[Ni_{10}L_{10}Cl_4(H_2O)_6](Cl)_{15}Br\bullet\sim 140H_2O$ shown in figure 1(b). Due the large structure of the molecule X-ray crystallographic studies rather have been quite challenging.

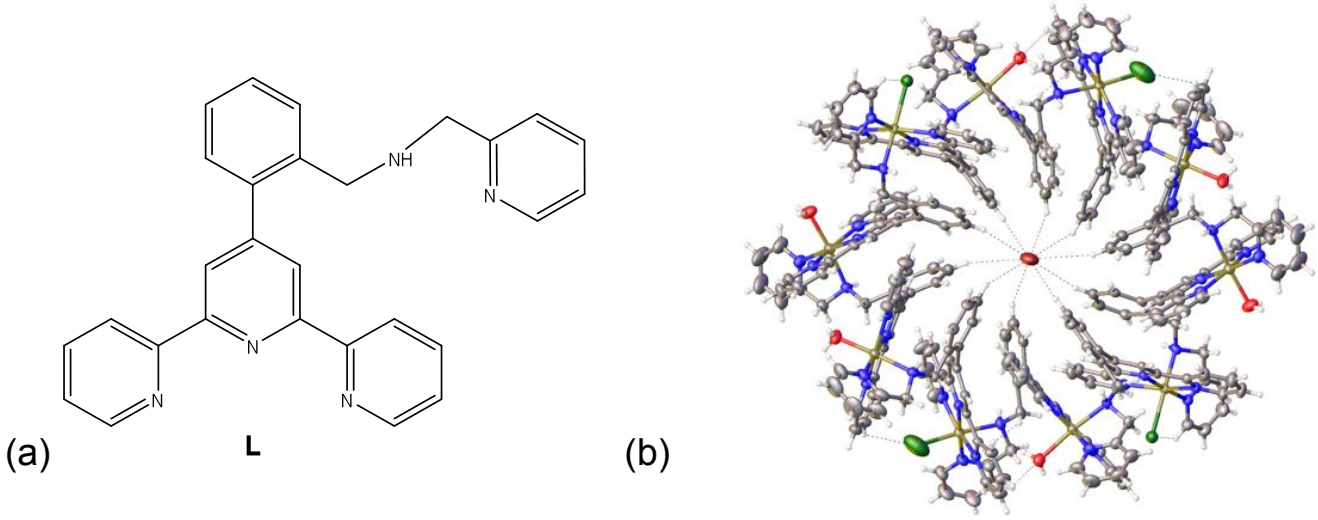


Fig (a) Diagram of the polydentate ligand L (b) X-ray crystallographic structure of a Decanickel complex, 140 uncoordinated water molecules and 19 chloride ions are omitted for clarity.

Removal of Polychlorobiphenyls Contaminated in Oil by Crosslinked Cyclodextrin Polymers

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Polychlorobiphenyls (PCBs) (**Fig 1**) were widely used as insulating fluids in electric equipment, such as capacitors and transformers, but their manufacture and commercial use have been prohibited in many countries due to their strong toxicity, environmental persistence, and bioaccumulation. From an environmental protection standpoint, the development of a facile and environmentally benign method to treat large amounts of oil stockpiles contaminated with PCBs is a crucial subject. In this work, we prepared γ-cyclodextrin (γ-CD) polymers by polycondensation reactions of γ-CD with aromatic linkers, and examined their adsorption capability towards PCBs in oil (**Fig 2**). We found that a terephthaloyl-crosslinked γ-CD polymer (TP-γ-CD polymer) revealed an adsorption capability towards any type of PCB from mono- to decachlorobiphenyls in insulating oils. When PCB (100 ppm)-contaminated oil was passed through a column packed with the TP-γ-CD polymer at 80–110 °C, the PCBs were completely removed with a removal efficiency of >99.9999 % and pure oil yield of >80%. Additionally, methyl esterification of the free carboxylic groups of the TP-γ-CD polymer enabled the complete recovery of the PCBs adsorbed on the polymer by simply washing with acetone. The methyl-esterified TP-γ-CD polymer could be recycled at least ten times for PCB adsorption without any loss in the adsorption capability (**Fig 3**).

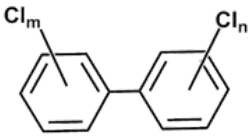


Figure 1. Chemical structure of polychlorobiphenyls.

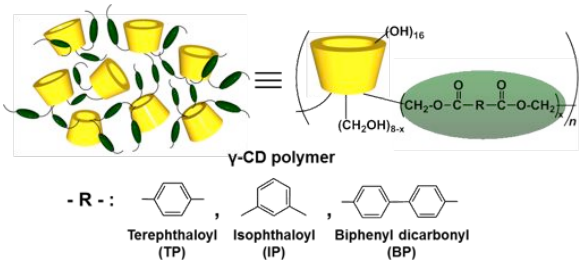


Fig 2. γ-Cyclodextrin (γ-CD) polymers crosslinked with various dibasic acid dichlorides.

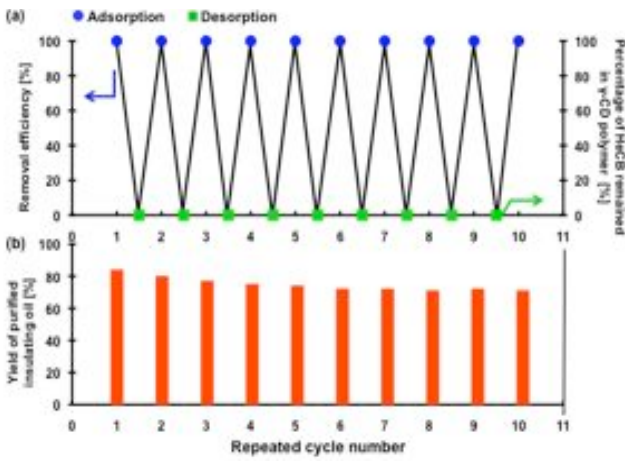


Fig 3. (a) Removal efficiency of 2,2',4,4',5,5'-hexachlorobiphenyl from insulating oil by methylated TP-γ-CD polymer and percentage of 2,2',4,4',5,5'-hexachlorobiphenyl remain in the CD polymer after the desorption process, (b) yield of the resulting pure insulating oil.

A Molecular Gasket: Pillar[5]arene as a Promoter in Rotaxanes Synthesis

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The cucurbit[6]uril (**CB**) catalyzed alkyne-azide cycloaddition (AAC) is accelerated in the presence of cyclodextrin as a result of formation of a cooperative hydrogen bonding network.[1] This strategy, which benefits considerably from positive cooperativity, has been applied[2] subsequently to the synthesis of rotaxanes. Here, we report that pillar[5]arene (**P**) also interacts with cucurbit[6]uril to promote the efficient cooperative capture of [4]- or [5]rotaxanes, along with the observation that this particular combination is tolerant to variations in the length of the azide guest (from 2-azidoethylpyridium to 5-azidopentylpyridium cations). The **P** rings not only serve as hydrogen bond donors in stabilizing the multicomponent assembly, but also act as 'molecular gaskets' to adjust the relative positioning of the alkyne and azide functions inside **CB** to allow their favorable alignment for cyclization, affording [4]- or [5]rotaxanes rapidly in excellent (90 – 96%) yields. ^{1}H NMR Spectroscopy reveals that the conformations adopted by the **P** rings are locked in the heterorotaxanes, allowing observation and assignment of all four conformational isomers. These findings expand the limited substrate scope of the CB-catalyzed AAC and provide a highly efficient way to template the formation of heterorotaxanes.

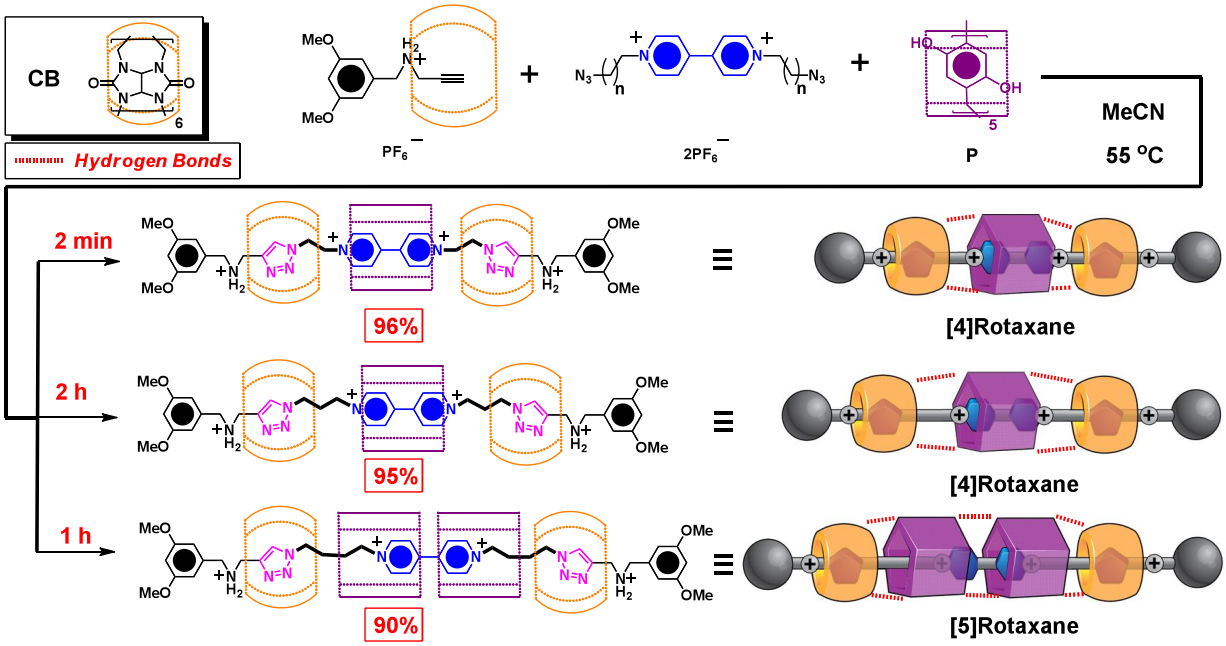


Figure 1. Synthesis of the hetero[4]- and [5]rotaxanes starting from a stopper precursor **CB** complex, viologen derivatives in the presence of **P** rings. The hatched lines in the graphical representation indicate the hydrogen bonding interactions between **CB** and **P** rings.

References 1) Ke, C.; Smaldone, R. A.; Kikuchi, T.; Li, H.; Davis, A. P.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2013**, *52*, 381. 2) Tuncel, D.; Steinke, J. *Chem. Commun.* **1999**, 1509–1510.

Bimetallic Uranyl Containing Coordination Polymers: Synthesis, Structure, and Photophysical Properties

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Uranyl (UO_2^{2+}) bearing hybrid materials have maintained significant interest owing to their diverse topological and photophysical properties. Incorporating a secondary metal center into these materials may influence structures as well as photoluminescent or catalytic properties. Such bimetallic coordination polymers may be synthesized in a number of ways (e.g. direct assembly, post synthetic modification, and the use of metalloligands). Direct assembly often requires the use of heterofunctional, multitopic ligands with "harder" and "softer" functionalities that can selectively bind to two different metal centers. Post synthetic modification may be employed to alter a pre-synthesized coordination polymer to incorporate another metal center. Finally, metalloligands, i.e. ligands with "pre-packaged" metal centers and open coordination sites elsewhere on the molecule, may also be used to synthesize bimetallic compounds. The use of all three of these synthetic routes has yielded a number of the bimetallic uranyl hybrid materials. Herein, we discuss the use of these methods to synthesize several uranium containing bimetallic coordination polymers, their crystal structures and their photophysical properties.

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Poster Withdrawn

Chiral Recognition and Kinetic Resolution with Supramolecular Cyclodextrin Nanocapsules in Nonpolar Solvents

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Supramolecular nanocapsules constructed by the self-assembly of molecular building blocks have attracted considerable attention in the fields of supramolecular and synthetic chemistry,[1] because they exhibit unique guest discrimination properties as well as high stabilization effect towards reactive intermediates utilizing their isolated nanocavity from the bulk solution. We recently reported that a supramolecular nanocapsule formed by an assembly of 6-*O*-triisopropylsilylated β-cyclodextrin (TIPS-β-CD) exhibits a high affinity for pyrene in benzene or cyclohexane.[2] Because this nanocapsule possesses an asymmetric cavity derived from the constituent D-glucose units, it has potential for enantioselective recognition of specific chiral guests, such as chiral aromatic amines and chiral aromatic alcohols, in nonpolar solvents through multi-point interactions, including hydrogen bonding between the CD hydroxyl groups and the guest polar groups as well as the inclusion of the guest aromatic moiety into the CD cavity. Herein, we present the extremely high chiral recognition of an aromatic amine by a supramolecular chiral nanocaspsule assembled by TIPS-β-CD in a nonpolar solvent.[3] In addition, the selective sequestration of one enantiomer by the supramolecular chiral nanocapsule in the nonpolar solvent successfully realized the kinetic resolution of racemic aromatic amines (Fig 1).

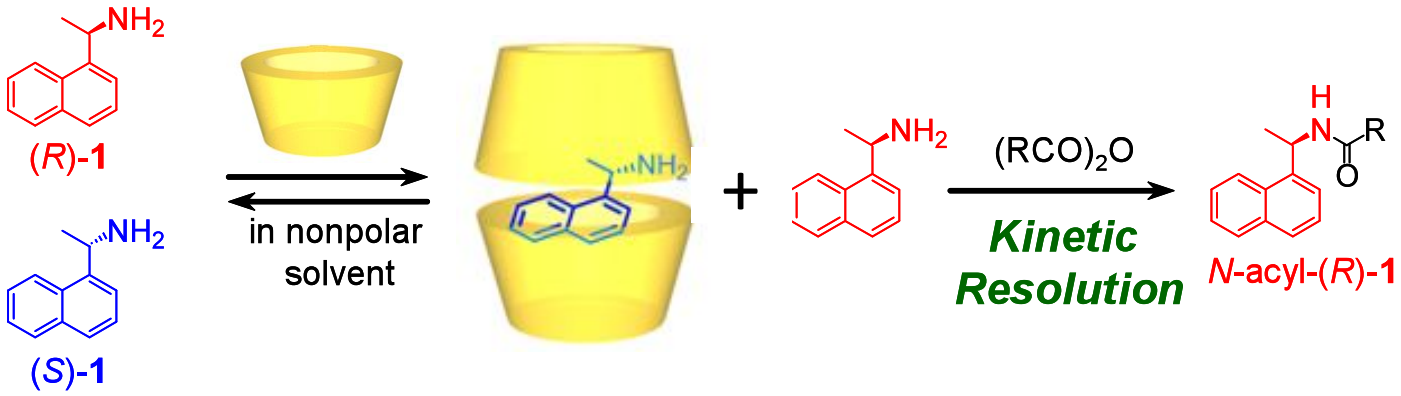


Fig 1. Illustration of chiral recognition and kinetic resolution with supramolecular cyclodextrin nanocapsule.

References 1) (a) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647–1668. (b) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *Angew. Chem. Int. Ed.* **2002**, *41*, 1488–1508. (c) Liu, S.; Gibb, B. C. *Chem. Commun.* **2008**, 3709-3716. (d) Amouri, H.; Desmarets, C.; Moussa, J. *Chem. Rev.* **2012**, *112*, 2015–2041. 2) Kida, T.; Iwamoto, T.; Fujino, Y.; Tohnai, N.; Miyata, M.; Akashi, M. *Org. Lett.* **2011**, *13*, 4570. 3) Kida, T.; Iwamoto, T.; Asahara, H.; Hinoue, T.; Akashi, M. *J. Am. Chem. Soc.* **2013**, *135*, 3371-3374.

Construction of Macrocyclic Boronic Esters Capable of Including Two Aromatic Molecules

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We have already reported the construction of macrocyclic boronic esters which can include one aromatic molecule by using a tetrol with benzene skeleton **1** and various diboronic acids[1].

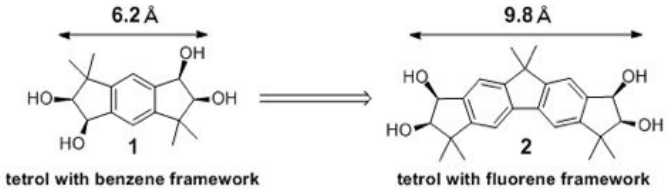
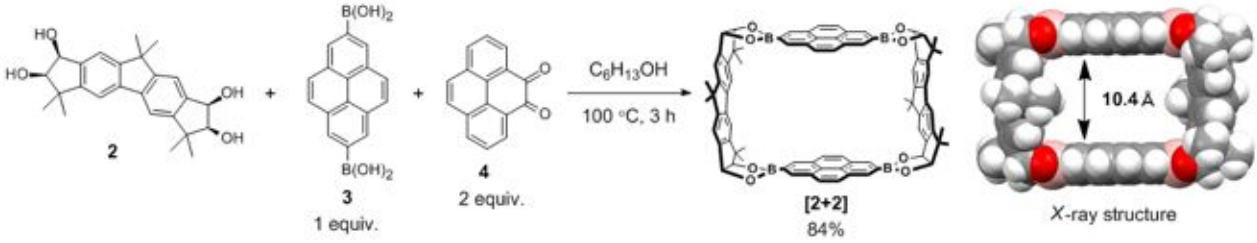


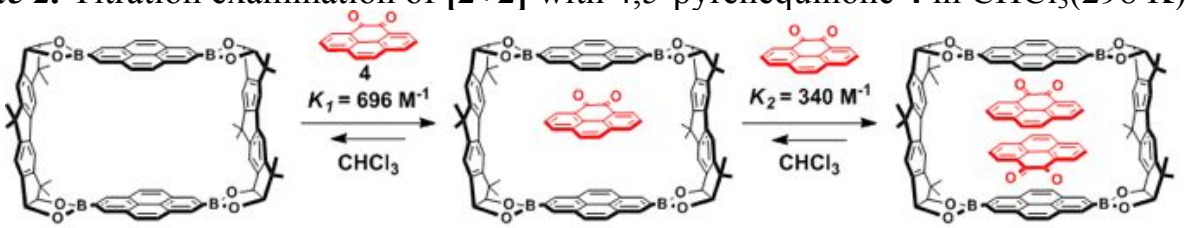
Figure 1. Design of tetrol

To construct a reaction vessel which can include two molecules inside, we prepared a novel tetrol with fluorene skeleton **2** (**Fig 1**). The macrocyclic boronic ester **[2+2]** was constructed successfully with fluorene tetrol **2** and pyrene diboronic acid **3** using 4,5-pyrenequinone **4** as a guest (**Scheme 1**). ITC study revealed that **[2+2]** could include two molecules of 4,5-pyrenequinone **4** in chloroform (**Scheme 2**). Furthermore, it was found that only one molecule of naphthalimide **5**, a very electron-deficient aromatic molecule, was included in **[2+2]** but pyrene **6**, an electron-rich aromatic molecule, could be included as the second guest molecule as judged by ITC and NMR study (**Scheme 3**).

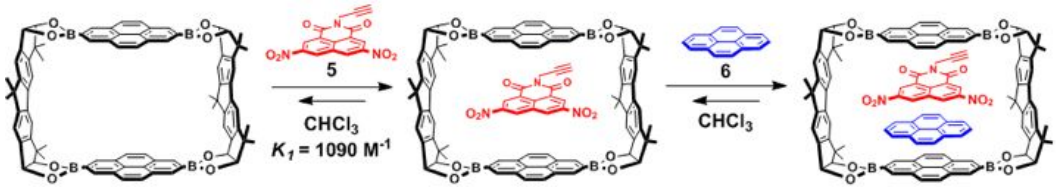
Scheme 1. Construction of macrocyclic boronic ester **[2+2]**.



Scheme 2. Titration examination of **[2+2]** with 4,5-pyrenequinone **4** in $CHCl_3$(298 K).



Scheme 3. Titration examination of **[2+2]** with naphthalimide **5** and pyrene **6** in $CHCl_3$ (298 K).



Reference 1) Iwasawa, N.; Takahagi, H., *J. Am. Chem. Soc.* **2007**, *129*, 7754 -7755.

Switchable Nanoporous Sheets from Aqueous Self-Assembly of Aromatic Macrobicycles

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A rationally designed macrobicyclic amphiphile consisting of a hydrophilic dendron at the center of the aromatic plane self-assembles into a porous 2D structure with nano-sized lateral pores through the lateral association of faced dimers with a uniform size in diameter of 3.5 nm. The porous sheets efficiently intercalate flat aromatic molecules such as coronene through the conformational inversion of the basal planes of the dimeric micelles. Notably, the intercalation of a flat conjugated aromatic guest enforces the porous sheets to reversibly transform into closed sheets without sacrificing the 2D structure in shape. This switch is also accompanied by flexibility change of the self-assembled 2D structure from flexible to rigid states. Such a unique supramolecular structure with switchable functions might provide a new strategy for the design of intelligent materials simultaneously with biological and electro-optical functions.

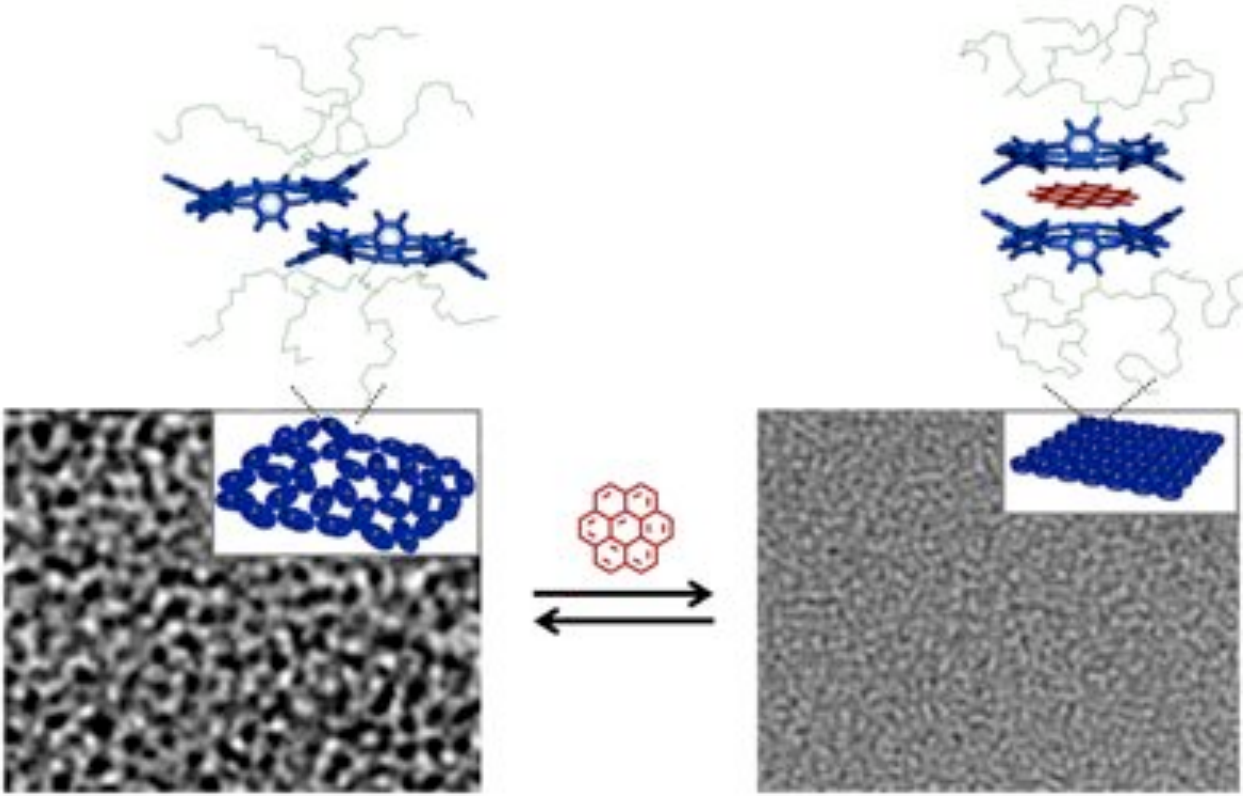
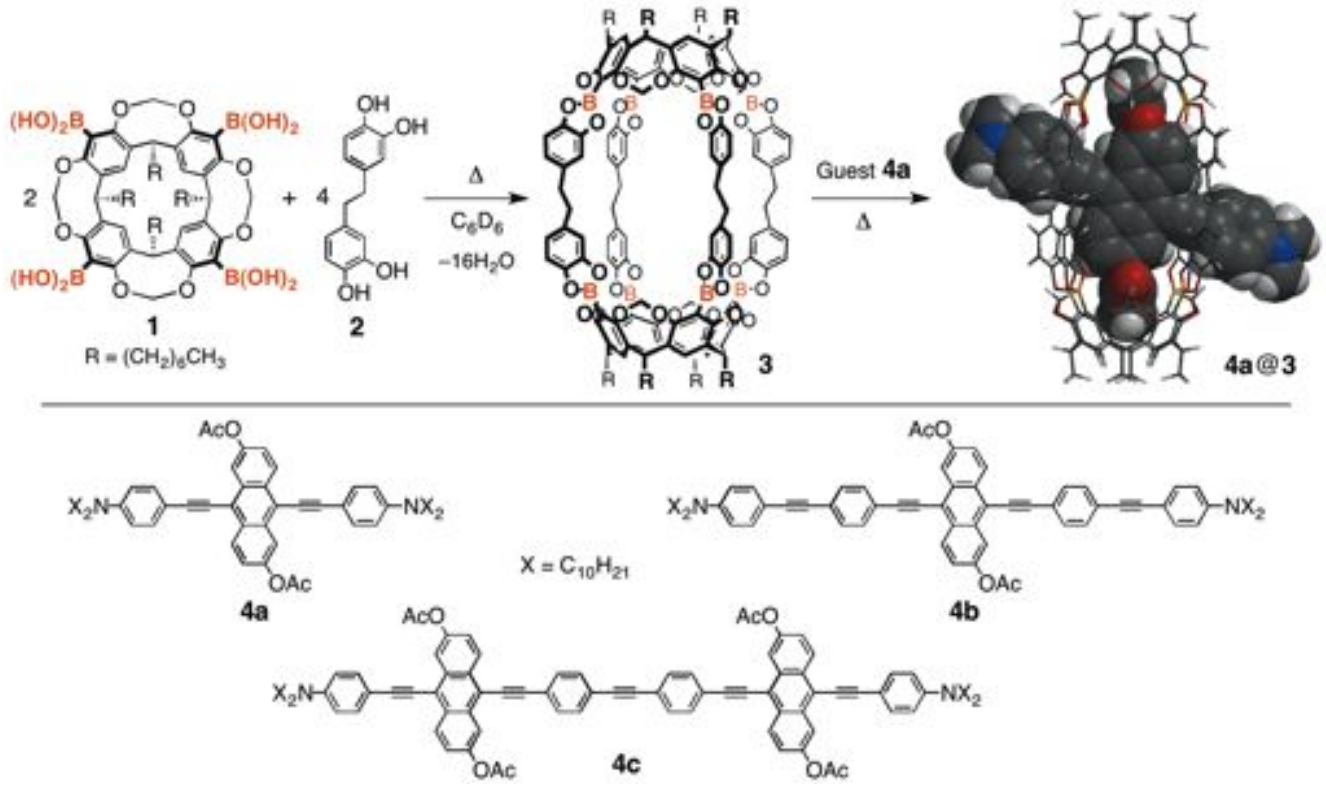


Figure 1. Schematic representation of the switch between a nanoporous sheet and a closed sheet triggered by coronene intercalation.

Self-Assembled Boronic Ester Cavitand Capsule as a Guard Nanocontainer for Cruciform 9,10-Bis(arylethynyl)anthracene Derivatives

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Two molecules of a cavitand tetraboronic acid **1** and four molecules of 1,2-bis (3,4-dihydroxyphenyl) ethane **2** quantitatively self-assemble into capsule **3** by dynamic boronic ester formation.[1] We describe that capsule **3** quantitatively and tightly encapsulates 2,6-diacetoxy-9,10-bis(arylethynyl)anthracene derivatives **4a**–**c** as highly fluorescent cruciform guests to form **4a**–**b**@**3** and **4c**@(**3**)$_2$. The structural features of **3**, which possesses two polar bowl-shaped aromatic cavity ends and four equatorial windows, make it possible to encapsulate cruciform guests **4a**–**c** with protection of the reactive anthracene core inside **3** and with two protruding arylethynyl groups as π-conjugated arms of **4** from two equatorial windows of **3**. Thus, **4a**–**b**@**3** and **4c**@(**3**)$_2$ were more resistant to photochemical reactions in solution and fluorescence quenching in solid state than free **4**. Furthermore, two-photon absorption properties of **4a**–**b**@**3** and **4c**@(**3**)$_2$ in solution were found to be enhanced compared with free **4**.



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Consequences of Pathway-Complexity in Self-Assembly: How to Recognize and How to Optimize

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The performance of one-dimensional self-assembled systems in functional organic materials with electronic or bioactive properties critically depends on the organization and dynamics of the molecular building blocks. Hence, understanding the self-assembly pathways involved in the formation of these supramolecular materials is essential. Here, we disclose a crucial step in the quantitative understanding of pathway complexity in self-assembly processes. Combining kinetic experiments with the development of a kinetic model, we unravel two parallel operating assembly pathways in the nucleated assembly of chiral, π-conjugated molecules into helical aggregates. These pathways–resulting in metastable right-handed helices and stable left-handed helices–compete for the same molecular building block. As a consequence of this competition, entrapment of monomers in metastable helices slows down assembly of the equilibrium structure.[1] By obtaining this kinetic information, hidden pathways during assembly processes can be revealed. Furthermore, insights into kinetic pathways allow us to avoid entrapment of material in metastable assemblies by manipulating parameters like concentration, temperature or solvent-composition. New model-driven strategies are developed and assessed by simulation to optimize the assembly rate into the desired equilibrium structure.

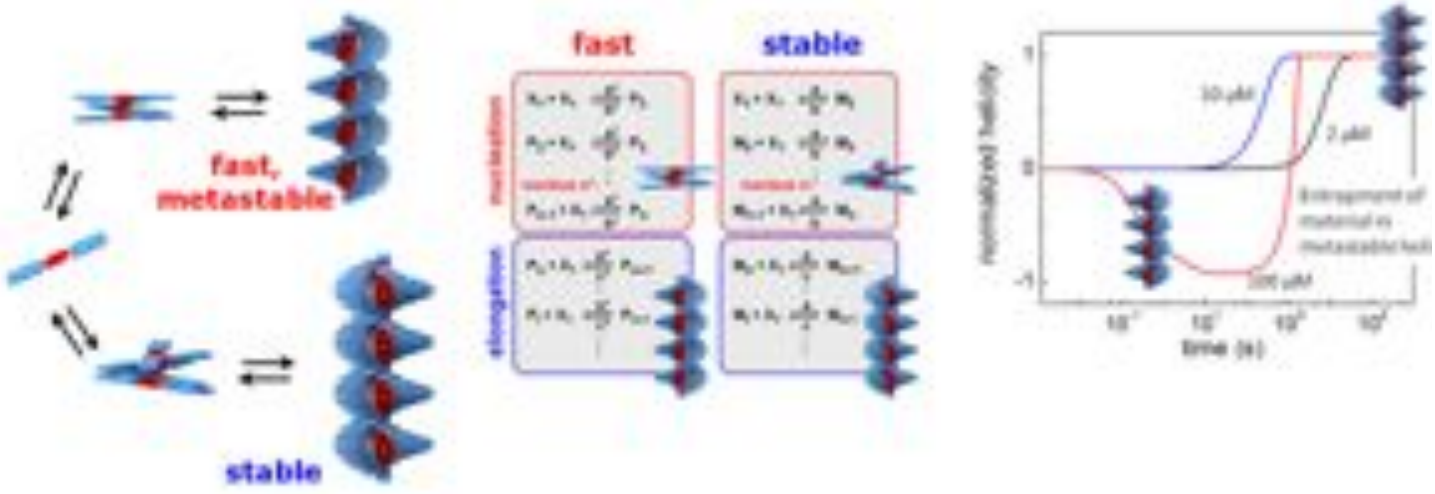


Figure 1. Parallel assembly into metastable and stable assemblies. A kinetic model is developed which predicts a decrease in assembly rate of the equilibrium structures at high concencentration, due to entrapment of monomers in metastable assemblies, as is observed experimentally. Kinetic insights resulting from the model allow us to develop new strategies to optimize assembly processes in which multiple pathways are involved.

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Tripodal Anion Receptors with 1,3,5-Triethylbenzene Core: Synthesis and Optical Phosphate Sensing

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Both inorganic and organic phosphates are important species involved in many key processes in a living matter and in the environment as anthropogenic pollutants.[1] Over the last years, synthesis of various types of artificial phosphate sensors has received significant attention.[2] Here, we describe a design and synthetic approach to tripodal fluorescent sensors based on pyrrole and thiourea moieties connected to 1,3,5-triethylbenzene core[3] (**1**-**8**). The supramolecular behavior of the sensors has been studied by fluorescence titration, VT-NMR, and X-ray crystallography. The structures **3**-**8** have been found displaying desirable *turn-on* fluorescence response to dihydrogenphosphate. To broaden the spectrum of potential analytes, the sensing of hydrolytic products of sarin nerve agent, methylphosphonate and isopropylmethylphosphonate has been investigated. We believe that this study opens up new avenues for the sensing of phosphates and phosphonates in the future.

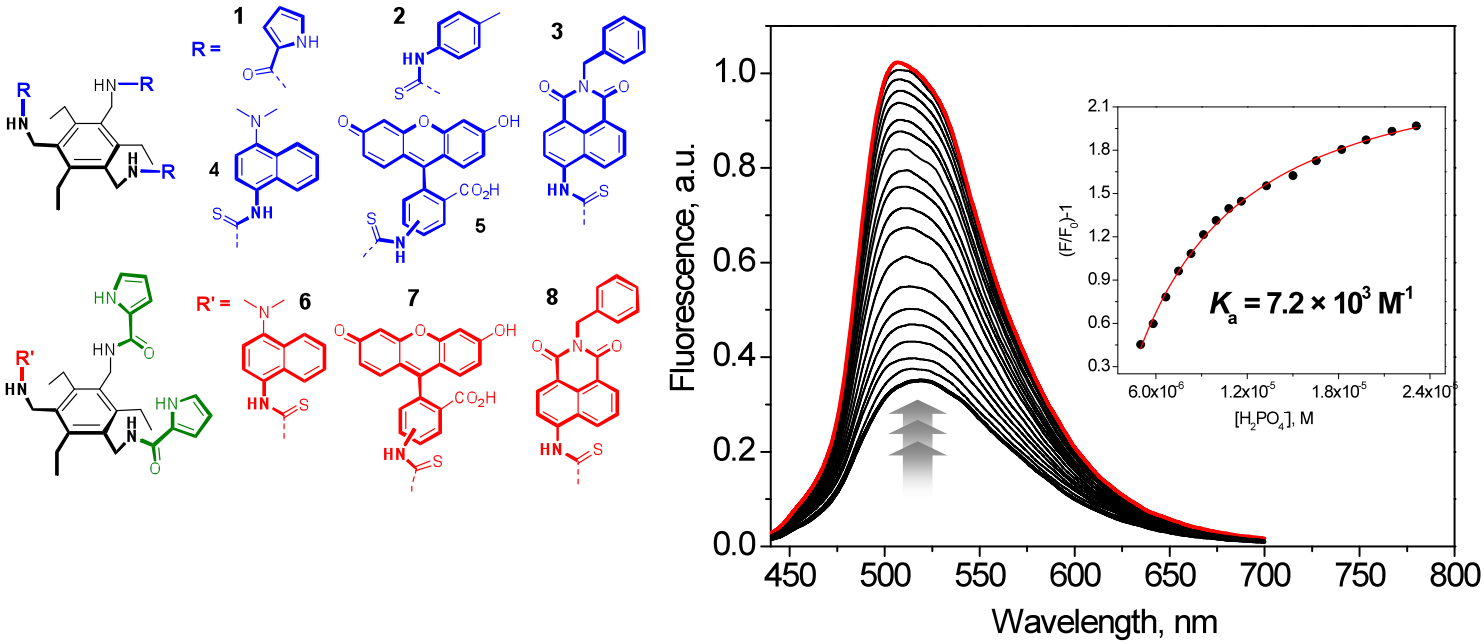


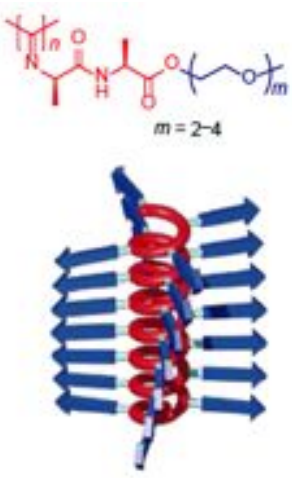
Figure 1. Left: Structure of tripodal sensors for phosphates and phosphonates; ***Right:*** fluorescence spectra of **3** (10 μM) upon addition of $H_2PO_4^-$ in DMSO,

References 1) Bronner, F. *et al. Extra- and Intracellular Calcium and Phosphate Regulation: From Basic Research to Clinical Medicine.* CRC Press, Boca Raton, 1992. 2) (a) Martínez-Máñez, R. *et al. Chem. Rev.* **2003**, *103*, 4419. (b) Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 486. (c) Anzenbacher, P., *et al. Angew. Chem., Int. Ed.* **2007**, *46*, 7849. 3) (a) Raymond, K. N. *et al. J. Am. Chem. Soc.* **1993**, *115*, 6466. (b) Anslyn, E. *et al. Synthesis* **2005**, 2080.

Hierarchically Assembled Responsive Hydrogels: Towards Cytoskeletal Mimicry

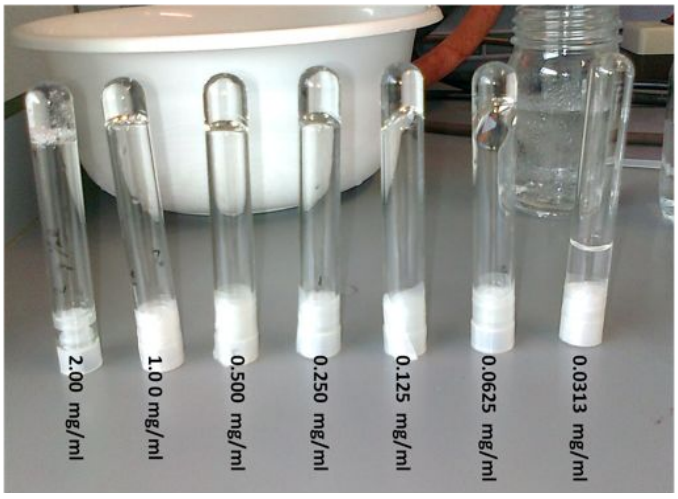
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Mechanical responsiveness is essential to all biological systems down to the level of tissues and cells. Their intra and extracellular mechanics are governed by a series of proteins, such as microtubules, actin, intermediate filaments and collagen. As a general design motif, these proteins self-assemble into helical structures and superstructures that differ in diameter and persistence length to cover the full mechanical spectrum. Contrary to man-made gels, these these biogels display particular mechanical responses (stress stiffening), directly linked to their filamentous structure. We present synthetic gels that mimic in nearly all aspects gels prepared from intermediate filaments. They are prepared from polyisocyanopeptides grafted with oligo(ethylene glycol) side chains (Fig 1). These polymers possess a stiff and helical architecture and show a tuneable thermal transition where the chains bundle to generate transparent gels at extremely low concentrations. We demonstrate the hierarchical relationship between bulk mechanical properties and single molecule parameters using characterisation techniques operating at different length scales combined with an appropriate theoretical network model.[1,2] Our results show that to develop artificial cytoskeletal or extracellular matrix mimics, essential design parameters are not only the molecular stiffness,[3] but also bundling. Moreover, the polyisocyanide polymers are readily modified, which marks the starting point for functional biogel mimics with potentially a variety of biomedical applications.



ig 1. Structure and 3D ketch of the (ethylene ycol)-grafted polyiso- anoidepeptides.

ig 2. Inversion test ows gel formation at tremely low ncentrations (up to 006 wt-%).



References 1) Kouwer, P. H. J.; Koepf, M.; Le Sage, V. A. A.; Jaspers, M.; Van Buul, A. M.; Eksteen-Akeroyd, Z., H. ; Woltinge, T.; Schwartz, E.; Kitto, H., J.; Hoogenboom, R.; Picken, S. J.; Nolte, R. J. M.; Mendes, E.; Rowan, A. E. *Nature* **2013**, *493*, 651. 2) Koepf, M.; Kitto, H. J.; Schwartz, E.; Kouwer, P. H. J.; Nolte, R. J. M.; Rowan, A. E. *Eur. Polym. J.* **2013**, *in press* (DOI: j.eurpolymj.2013.01.009). 3) van Buul, A. M.; Schwartz, E.; Brocorens, P.; Koepf, M.; Beljonne, D.; Maan, J. C.; Christianen, P. C. M.; Kouwer, P. H. J.; Nolte, R. J. M.; Engelkamp, H.; Blank, K.; Rowan, A. E. *Chem. Sci.* **2013**, *4*, 2357.

Cyclodextrin-Promoted Synthesis of Bio-ready ZnO Quantum Dots from Zinc Oxo-clusters

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During the last decade Quantum Dots (QDs) have been applied dominantly in biological sciences.[1] Among quantum dots, ZnO nanoparticles can be regarded as most promising for applications in biology due to their interesting optical properties and enhanced biocompatibility compared to toxic heavy metal-based materials. Up to date, they have been synthesized by hydrolysis of inorganic salts or organozinc precursors. However, even though zinc oxo-compounds are well-known as secondary building units of metal-organic frameworks (MOFs),[2] they have never been regarded as predesigned molecular precursors of ZnO nanocrystals. We aimed at creating a material combining the advantages of fluorescent QDs and cyclodextrins (CD)–oligosaccharides that play an important role in supramolecular chemistry as well as in pharmaceutical sciences.

We report a novel room-temperature synthetic pathway towards CD-coated water-soluble ZnO QDs from well-defined Zn oxo-clusters as precursors. The nucleation and growth processes of semiconductor nanoparticles are promoted by cyclodextrin and depend on the type of oxo-precursor used. *In-vitro* cytotoxicity tests show that toxic effect of as-synthesized ZnO QDs is negligeable for concentrations lower than 100 mg / L and is visible only after more than a few hours of exposition. During imaging experiments on CCD human foreskin fibroblast cells intensive signal was observed in confocal microscope images. The obtained results demonstrate that ZnO@CD QDs can permeate cell membranes and enter the cells. Nanoparticles were localized in perinuclear part of the cytosol and did not enter the nuclei. Furthermore, ZnO NPs show high stability of fluorescence and were resistant to photobleaching.

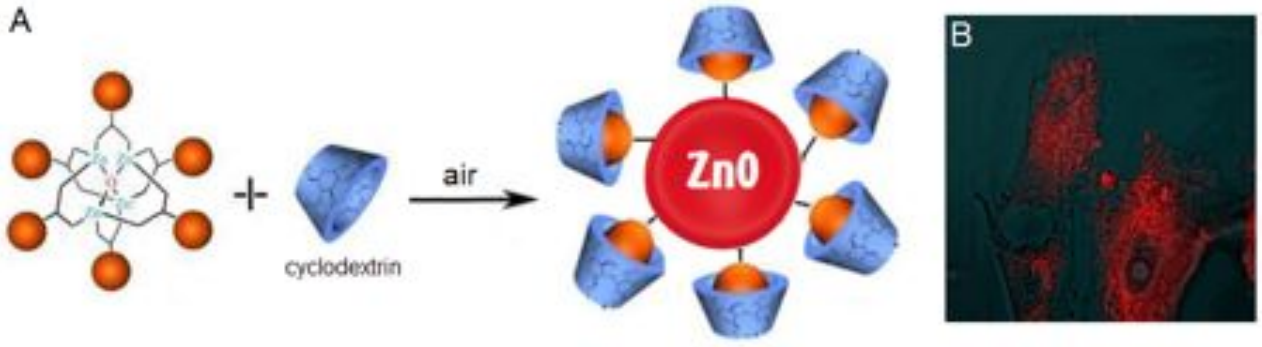


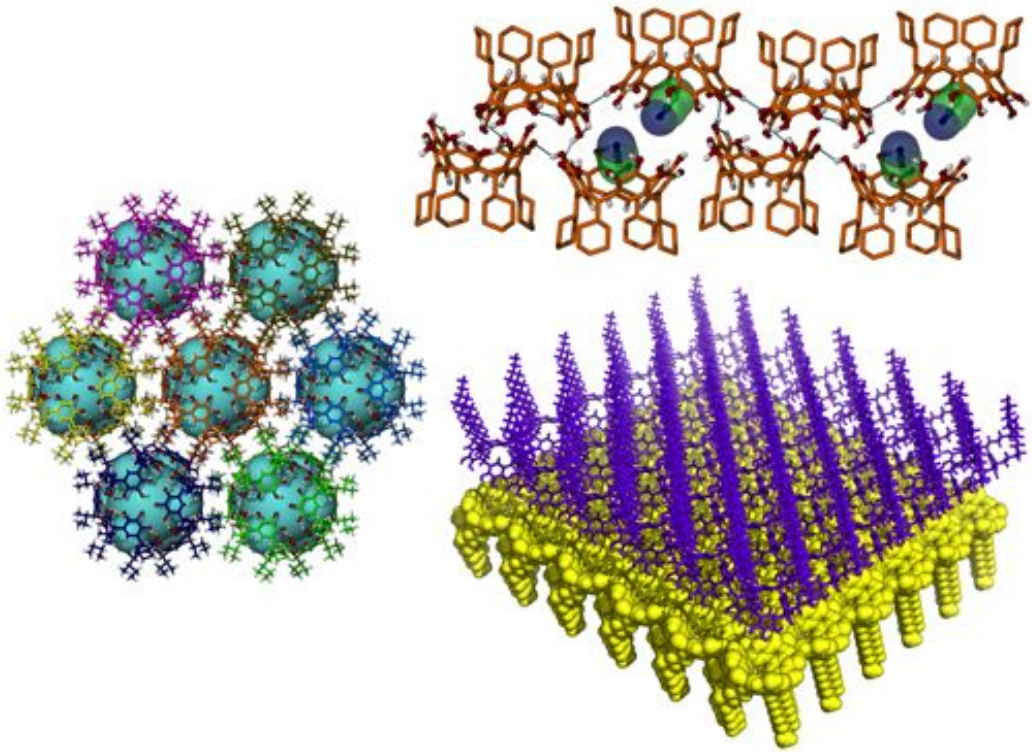
Figure 1. CD-coated ZnO QDs: synthesis from zinc oxo-cluster (a) and cell staining image (b).

References 1) Michalet, X et al *Science*, **2005**, *307*, 538–44. 2) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276–279

X-Ray and TEM studies of Pyrogallol[4]arenes Obtained from Branched Aldehydes: "Bilayer" Motif and the Hexameric Capsule Formation

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The enclosure of chemical space is one of the essential attributes of a biological system (living cell, virus capsid, etc.) Self-assembly has proved to be an efficient method of constructing capsules that uses either hydrogen-bonding or metal-coordination. We have prepared "branched chain" pyrogallol[4]arenes that were obtained by a "[4+4]condensation" of pyrogallolarene with an appropriate aldehyde. We have found that both 2-butylpyrogallol[4]arene and isopropylpyrogallol[4]arene may form capsules from the solvent mixtures EtOAc/MeCN (1:1) and $PhNO_2$/MeOH (1:1), respectively. In contrast, 3-heptyl- and 4-heptylpyrogallol[4]arenes are both prone to pack into a multilayer arrangement (EtOAc/EtOH). Cyclohexylpyrogallol[4]arene crystallized from mixtures of EtOAc/EtOH (1:1) or EtOAc/MeCN (1:1) to give the multilayer motif rather than the spherical hexamer. TEM studies of branched pyrogallolarenes revealed the formation of large spherical aggregates on the order of ~10-500 nm in size.



Chirality Transcription of Primary and Secondary Ammonium Salts by Forming [2]Pseudorotaxane

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Chirality recognition in supramolecular interaction plays an important role in many natural systems such as the DNA double helix and secondary α-helix structure of proteins. Recently various artificial and biomimetic supramolecular systems for chirality recognition have been extensively studied. More recently, we have reported the synthesis of a new benzo-2',2''-quaterphenyl-26-crown-8 ether (**1**).[1] The 2',2''-quaterphenyl group can flip like a co-axis rotor blade, and the macrocyclic ring can form [2]pseudorotaxanes with cationic organic guests such as secondary ammonium salts. Information on the chirality of the ammonium salts is detected directly by CD spectroscopy.

We report the application of the [2]pseudorotaxane system for a variety of chiral *sec*-ammonium salts (*R*)-**2a-d**-H·PF_6. Formation of [2]pseudorotaxane of [**1**·(*R*)-**2c**-H][PF_6] was confirmed by ^{1}H and ^{13}C NMR, Cold Spray Ionization-MS (CSI-MS). The CD spectrum of [**1**·(*R*)-**2c**-H][PF_6] showed typical exciton split Cotton effects of negative and positive exciton chirality around 260 nm, indicating that the two long axes in the quaterphenyl group constitute clockwise and counterclockwise screw sense. When the crown ether formed the chiral [2]pseudorotaxane with various (*R*)-*sec*-ammonium ions, the same signs of the Cotton effects were also observed in the CD spectrum. The application of the system for primary ammonium salts (*R*)-**2e**-H·PF_6.will be reported.

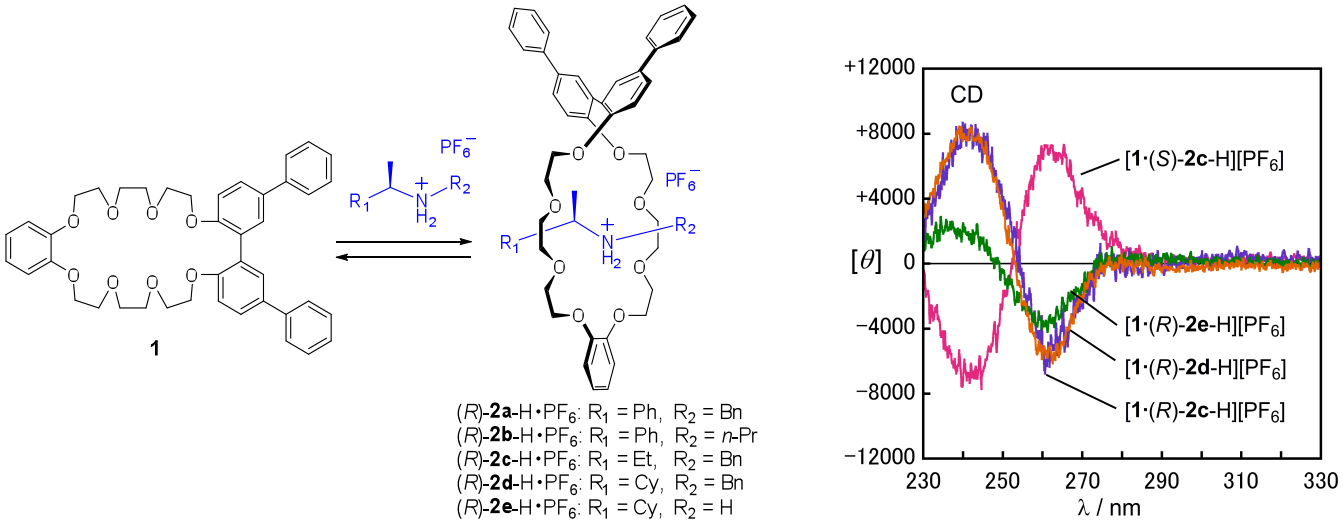


Figure 1. The chirality transcription and amplification system using CD spectroscopy.

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Crystal Engineering Reactivity in the Organic Solid State

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Our group is focused on using principles of supramolecular chemistry based on templates to direct reactions in the solid state. Templates provide a reliable means to achieve reactions of olefins in [2+2] photodimerizations. In this presentation, we will discuss expansion of functional group diversity through utilization of Copper-Catalyzed Azide-Alkyne Cycloaddition (click) reaction as well as demonstrate the first intramolecular templated [2+2] photocycloaddition.

The click reaction provides a reliable method of integrating triazole rings as synthetic linkers. In this work, the click reaction has been employed to combine various azides with stilbazole-based molecules. Using the triazole containing compounds, we have investigated the effects of molecular shape on [2+2] photocycloaddition reactions. Additionally, we have investigated the electronic bridging capabilities of triazole bearing molecules within the crystalline phase and demonstrated that electronic properties are maintained between the solution phase and the crystalline state (Fig. 1).[1]

Where intermolecular [2+2] photocyloadditions have been a major theme, we have designed the first templated assembly that undergoes an intramolecular [2+2] photocycloaddition.[2] This work, as well as our work with the click reaction will be discussed.

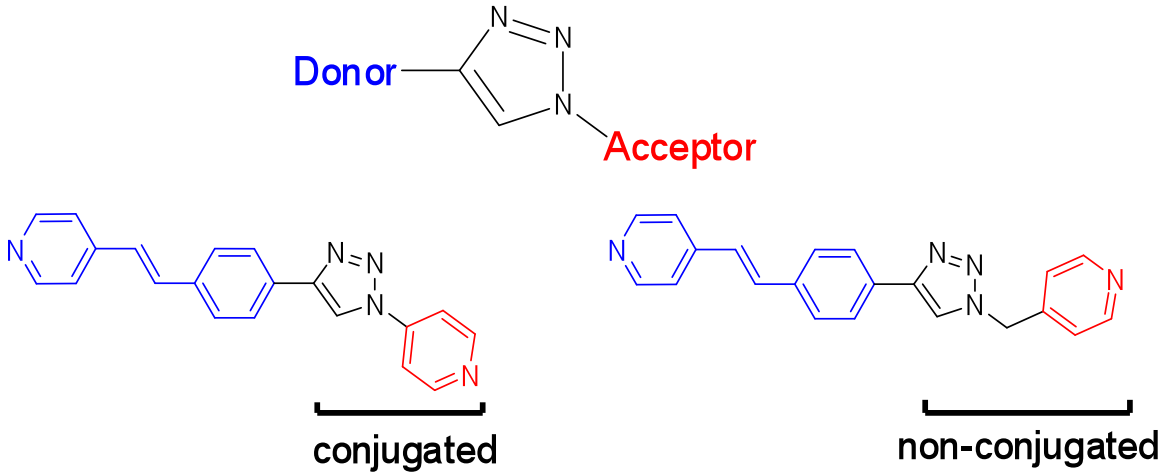


Figure 1. Conjugated and non-conjugated molecules for electronic studies.

References 1.) Laird, R. C.; Nguyen, N. P.; Rusch, S. F.; Baltrusaitis, J.; MacGillivray, L. R., *Org. Lett. Submitted.*
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Ion Chromatographic Separations Using a Cyclen-Resorcinarene Host

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Resorcinarenes are cyclic tetramers which are synthesized from the condensation of resorcinol and various aldehydes. The phenolic hydroxyl groups on the upper rim of resorcinarenes can be modified to provide a preorganized host cavity. In this work, the upper rim of the resorcinarene was substituted with cyclen groups which serve to bind transition metal cations, while the lower rim was substituted with undecyl groups to render the molecule more hydrophobic. (Figure 1) The resulting cyclen-resorcinarene host was adsorbed onto styrene-divinylbenzene resin beads for use in HPLC ion chromatographic separations. The separation of transition metal ions was achieved on this column using post-column complexation and uv-vis detection. The stability constants of cyclen with transition metal ions demonstrate that cyclen has high selectivity for Cu^{2+} over other transition metals.[1] Thus, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+} ions were baseline separated from Cu^{2+} using HNO_3 eluent with this column. Addition of oxalic acid to the eluent provided a very good separation among all the cations. The preconcentration of Cu^{2+} at the parts per billion level from a large matrix background of transition metal cations was also achieved using a nitric acid gradient. Recovery of Cu^{2+} at >98% was obtained.[2]

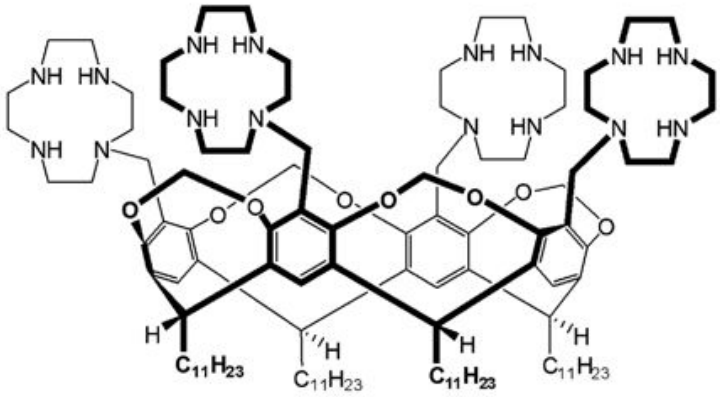


Figure 1. Cyclen-resorcinarene host

References

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2) Li, Na; Harrison, R.G.; Allen, L.; Lamb, J.D. *Analyst,* **2013,** *138*, 1467-1474.

Solvatochromic Probe Detecting Hydrogen Bond Donating Solvents

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Solvatochromism is a valuable tool to investigate polarity in solution by monitoring a change in the absorption or emission band.[1] Solvatochromic dyes have the potential to probe environmental changes of supramolecular assemblies in biomembranes [2] and at oil-water interface.[3] Currently, these dyes lack the ability to distinguish between dipoles and hydrogen bonding, limiting their use in applications such as water sensing.[4] To address this issue we developed a dye, 6-(3-aminophenyl)-1,3,5-triazine-2,4-diamine (MADAT), that detects hydrogen bond donating solvents (Fig 1). Emission of MADAT was largely unchanged in all non-protic solvents however a large bathochromic shift was found in protic solvents. Detecting water impurities in tetrahydrofuran at low concentrations was possible using MADAT.

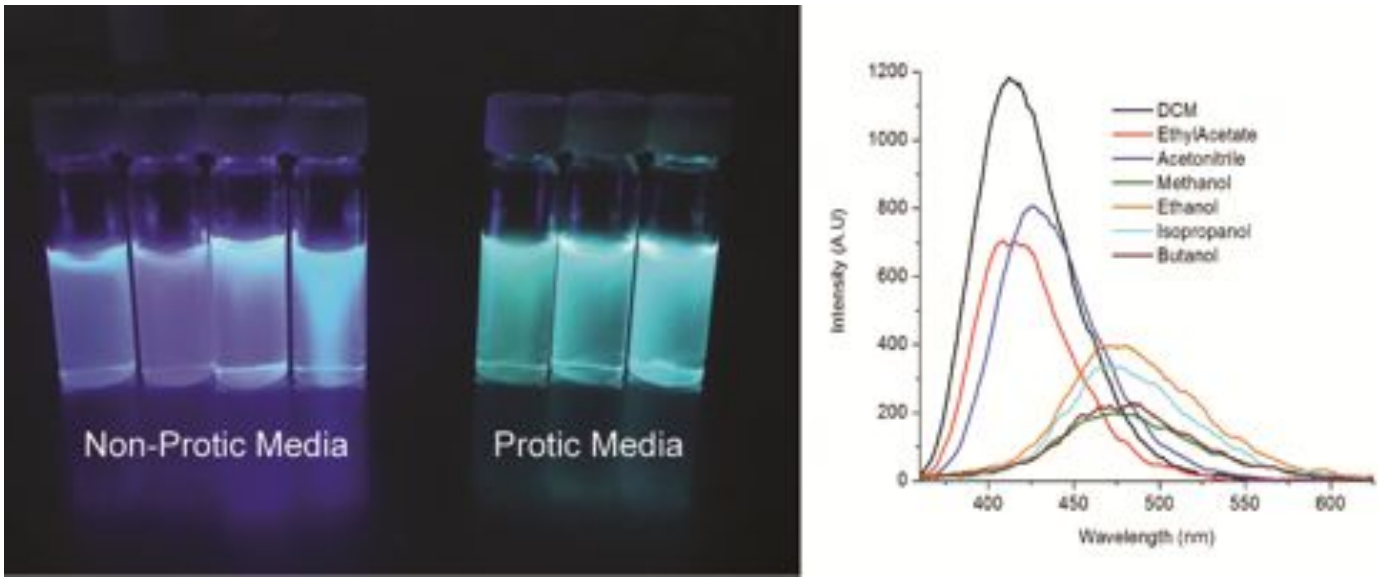


Figure 1. Bathochromic shift of MADAT emission in protic media

References
[1] (a) Buncel, E.; Rajagopal, S. *Acc. Chem. Res.* **1990**, *23*, 226. (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319. [2] Yan, P.; Xie, A.; Wei, M.; Loew, L. *J. Org. Chem.* **2008**, *73*, 6587-6594. [3] Vitha, M. ACS Symposium Series. **2011**, *1062*, 51-97. [4] Pinheiro, C.; Lima, J.; Parola, A. *Sensors and Actuators B: Chemical*. **2006**,*114*, 978-983.

Asymmetric Tetrakis(tetratihiafulvalene)-calix[4]pyrroles for Click-enabled Surface Functionalization

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Some years ago a tetrakis(tetrathiafulvalene)-calix[4]pyrrole receptor[1] was synthesized and it was shown that it can act as a molecular sensor for electron deficient molecules such as the explosive 1,3,5 trinitrobenzen (TNB). However, the potential of this unique receptor has not fully explored and development of this promising molecular sensor need to be carried out. To improve the performance of new sensors based on calix[4]pyrroles, it is essential to interface them to the macroscopic world, e.g. by ordering them on various surfaces.[2] A type of modified surfaces, introduced here, is based on a Click-enabled platform. By using simple aliphatic thiol chains and functionalized azide-terminated aliphatic thiol chains in different ratios the composition of the resulting self-assembled monolayers (SAMs)[3] can be controlled (Figure 1, A), so that non-regularly shaped sensors bearing alkyne functional groups can be "clicked" onto the protruding azide tails to create ordered and well–spaced structures (Figure 1, B). It is anticipated that, the calix[4]pyrroles subsequently can bind TNB (Figure 1, C). In order to obtain this functionalization of surfaces, the design and synthesis of non-symmetric calix[4]pyrroles functionalized with an alkyne unit is essential.

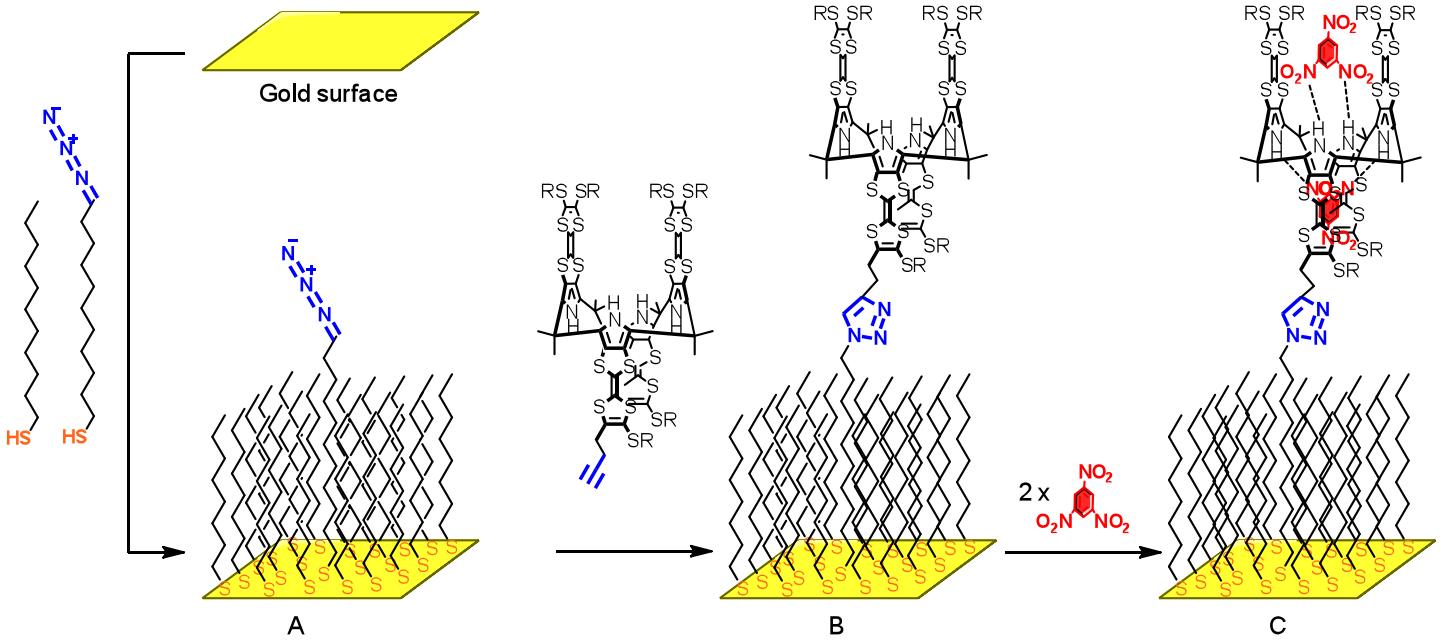


Figure 1. Suface functionalization using click-enabled platforms.

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Counterion Controlled Self-Assembly of Supramolecular Nanotubes

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Self-assembly of planar π-conjugated molecules into columnar aggregates with rod-like or tubular superstructures is a promising strategy for formation of nanostructures for charge and exciton transport. The use of charged π-systems provides additional opportunities to tune electronic properties and superstructures via the counterions. The talk will focus on the self-assembly of amphiphilic derivatives of the amino-trioxatriangulenium ion[1] ($ATOTA^+$, Fig 1). In Langmuir[2] and Langmuir-Blodgett[3] films as well as in lipid composite systems[4] and bulk aqueous solution the $ATOTA^+$ salts form closely packed columnar aggregates with a strong tendency to form bilayers. By choice of the associated counterions it is possible to tune the amphiphilic properties of these aggregates and thus modify the aggregate superstructures. It is demonstrate how the interaction between bilayers of the positively charged pi-stacks can be tuned from attractive to repulsive by choice of anion, leading to either multilayer nanorods (Fig 1b) or to monodisperse single-walled nanotubes (Fig1c).

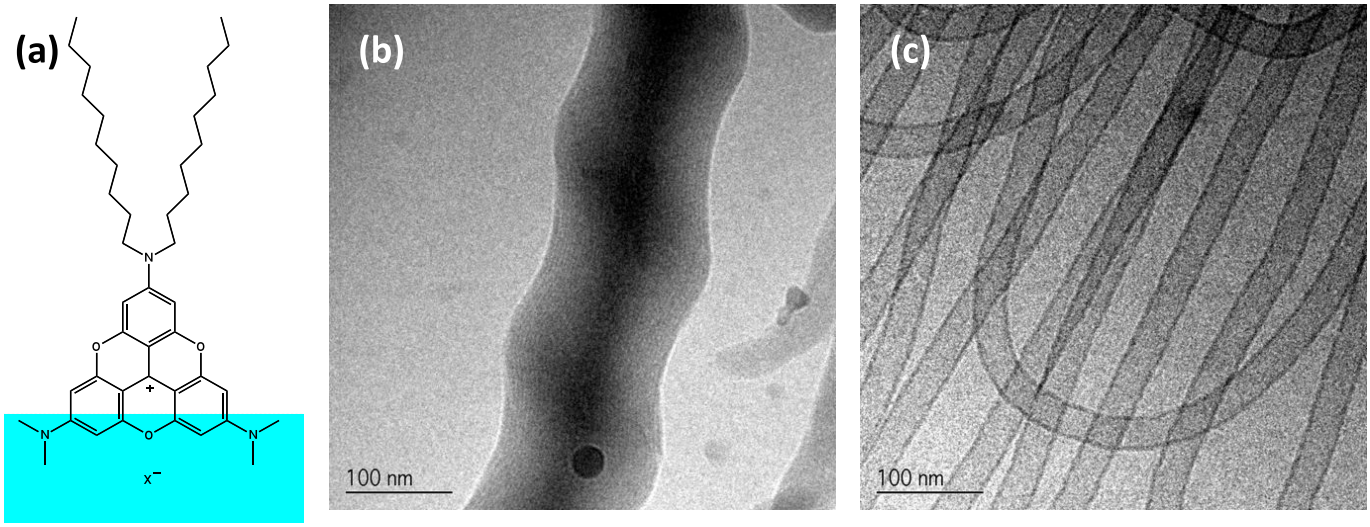


Figure 1. (a) Molecular structure of the amphiphilic $ATOTA^+$ X^- salts. Cryo-TEM of aggregates formed in aqueous solutions: (b) multi-layer nanorods (c) 29 nm mono-disperse single walled nanotubes.

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Rational Approach toward Endo/Exocyclic Complexes: Homo- and Heterometallic Coordination Polymers Exhibiting SCSC Transformation

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A rationally designed NS_4-macrocycle **L** which employs an NS_2 donors in one side to accommodate a metal cation in the cavity (endocoordination) and the two sulfur donors as bridgeheads for the exocoordination has been synthesized (*see* Figure 1). The proposed approach allowed us to prepare an endocyclic monocopper(II) complex **1** and an exocyclic dimercury(II) complex **2**. As might be expected, reaction of **L** with a mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and HgI_2 yielded an endo/exocyclic heterometallic 1D coordination polymer **3**, in which endocyclic copper(II) complexes are linked with exocyclic mercury iodide backbone.

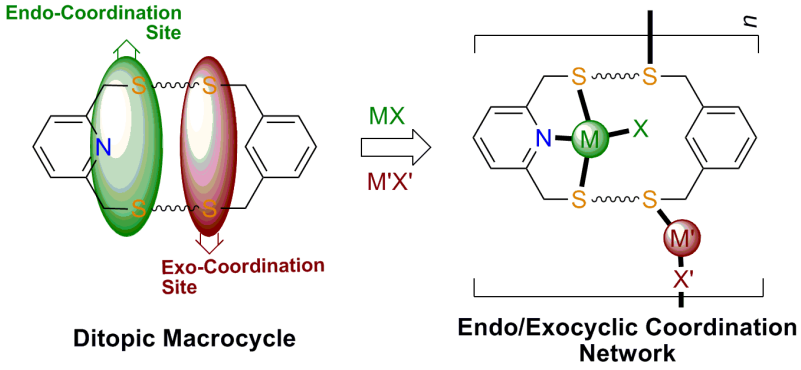


Fig 1. Concept of ligand-directed endo/exocyclic coordination networking**.**

Meanwhile, reaction of **L** with $AgClO_4$ afforded an endo/exocyclic 1D coordination polymer **4** (*see* Figure 2). Exposure of **4** to different solvent system induces a single-crystal to single-crystal (SCSC) transformation, resulting in an anion-coordinated 1D coordination polymer **5** formed through rearrangement of the metal coordination environment coupled with a framework distortion.

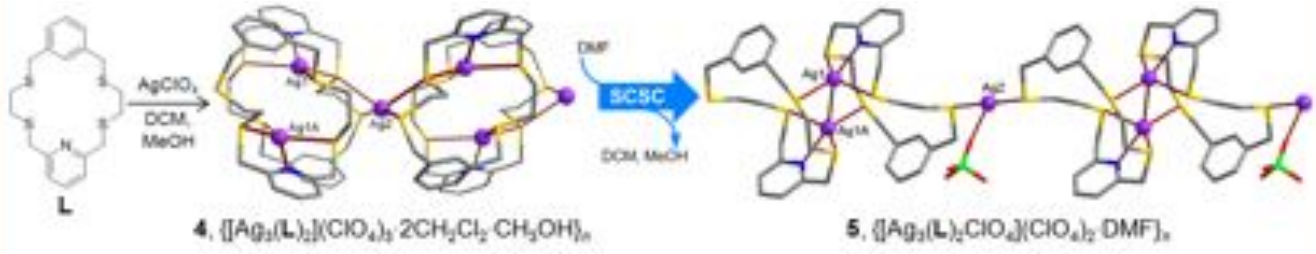


Figure 2. Formation of the endo/exocyclic Ag(I) coordination polymer **4** and its solvent-induced SCSC transformation to **5**.

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Cyanostars: Pentagonal Macrocycles with Cyanostilbene CH donors for Binding Anions and Forming Dialkylphosphate [3]Rotaxanes

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Functional macrocycles are key platforms for supramolecular chemistry, however, their efficient preparation remains a challenge. Here, we present the creation of a C_5-symmetric macrocycle, cyanostar,[1] that was prepared in a one-pot Knoevenagel condensation with high yields (>80%) conducted on multi-gram scales. The central cavity is electropositive with CH hydrogen bonding units that are activated by electron-withdrawing cyano groups. In solution, the cyanostar shows unusually high-affinity binding as 2:1 sandwich complexes, log $\beta_2 \sim 12$, towards large anions (BF_4^-, ClO_4^- and PF_6^-) usually considered weakly coordinating. The cyanostar's size preference allowed formation of an unprecedented [3]rotaxane templated around a dialkylphosphate.

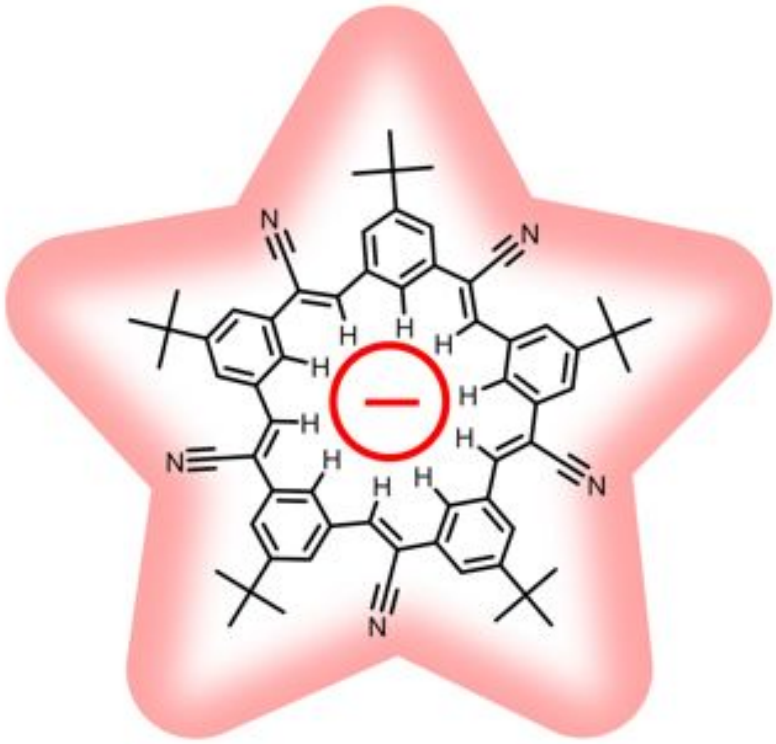


Figure 1. Cyanostar macrocycle binds large anions

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Benzobisimidazolium – A Novel Building Block for the Constructions of Supramolecular and Mechanically Interlocked Architectures

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In the fields of supramolecular chemistry[1] and mechanostereochemistry,[2] 4,4′-bipyridinium ($BIPY^{2+}$) units have been investigated extensively as a π-electron deficient building block for the constructions of supramolecular and mechanically interlocked architectures. However, the toxicity[3] of $BIPY^{2+}$ limits its applications in biological systems. This is providing an incentive to search of alternative building blocks. Here, we report that benzo-bisimidazolium (BBI^{2+}) acts as a π-electron deficient guest, forming supramolecular complexes (Figure 1) with some π-electron rich hosts, such as 1,5-dinaphtho[38]crown-10[4] (DN38C10). The formation of the threaded structures appears to be driven by π-electron donor-acceptor interactions and hydrogen bonding. Proton NMR spectroscopic titrations reveal that the effective binding constant for the 1:1 interaction between BBI^{2+} and DNP38C10 is on the order 10^3 M^{-1}, which is higher than that between $BIPY^{2+}$ and DNP38C10, i.e., 4×10^2 M^{-1}. These findings provide initial support for the suggestion that BBI^{2+} may have a role to play as an alternative to $BIPY^{2+}$ in the construction of elaborated supramolecular constructs. Further explorations of this postulate are ongoing in our laboratory.

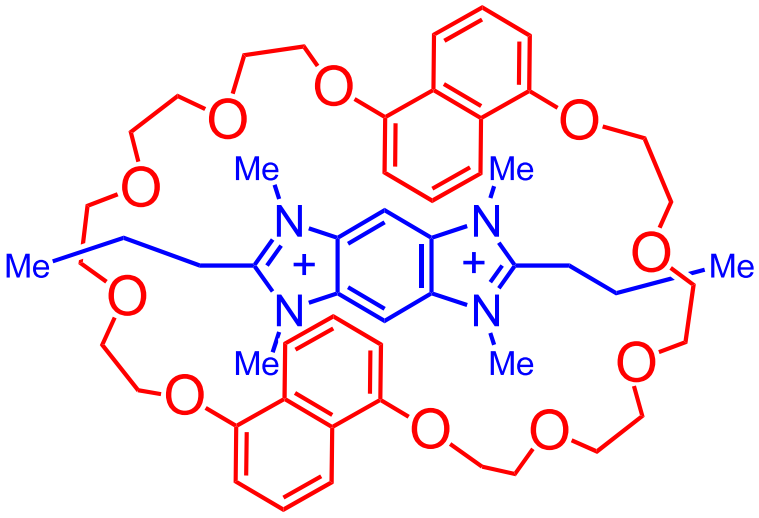


Figure 1. Schematic representation of a new pseudorotaxane, namely $BBI^{2+}\subset$DNP38C10.

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Rational Design and Construction of Nitrogen-Rich Metal-Organic Framework for CO_2 and H_2 Capture and Storage

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On the way towards a sustainable low-carbon future, the design and construction of adsorbents for CO_2 capture and clean energy storage are vital technology. The incorporation of accessible nitrogen-donor sites into the pore walls of porous adsorbents can dramatically affect the CO_2 uptake capacity and selectivity on account of the dipole-quadrupole interactions between the polarizable CO_2 molecule and the accessible nitrogen site.

Based on rational design, a dendritic hexacarboxylate ligand, referred as **H_6-1**, was conveniently synthesized via "click chemistry" (Figure 1a).[1,2] Subsequently, a nitrogen-rich *rht*-type metal-organic framework (MOF), referred as **NTU-105**, was constructed (Figure 1b). The MOF presents exceptionally high CO_2 uptake capacity not only for CO_2 (36.7 wt% at 273 K and 1 atm) but also for H_2 (2.75 wt% at 77 K and 1 atm) (Figure 1c) comparing with its isoreticular *rht*-MOFs, which is attributed to favorable interactions between the CO_2 molecules and the nitrogen-rich triazole units of the MOF proved by both experimental measurements and theoretical molecular simulations.[1]

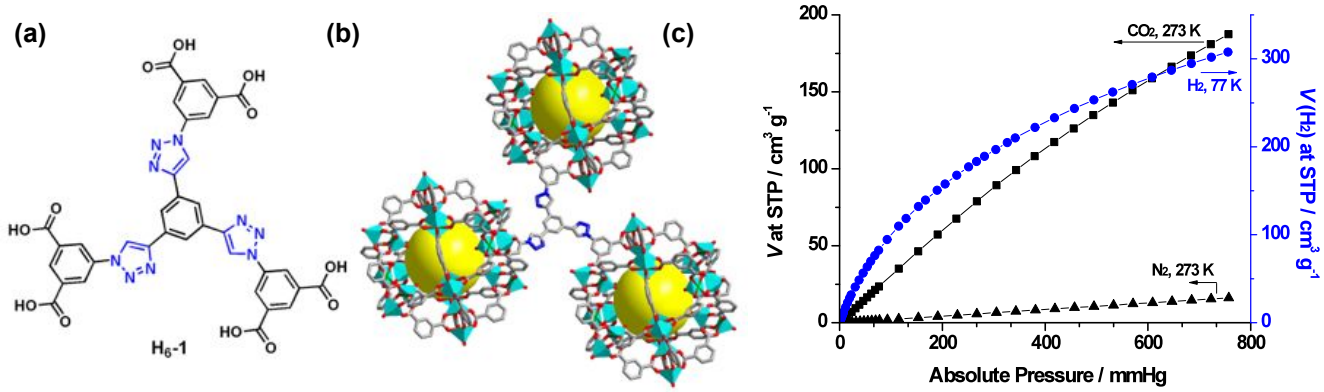


Figure 1. (a) Chemical structure of ligand **H_6-1** and (b) crystal structure of (3,24)-connected *rht*-type framework of **NTU-105**. In the crystal structure, carbon atoms are colored in gray, nitrogen atoms are colored in blue, oxygen atoms are colored in red, copper atoms are colored in green, and hydrogen atoms and solvent molecules were omitted for sake of clarity; (c) gas adsorption isotherms of activated **NTU-105** for CO_2 and N_2 measured at 273 K, and H_2 measured at 77 K.

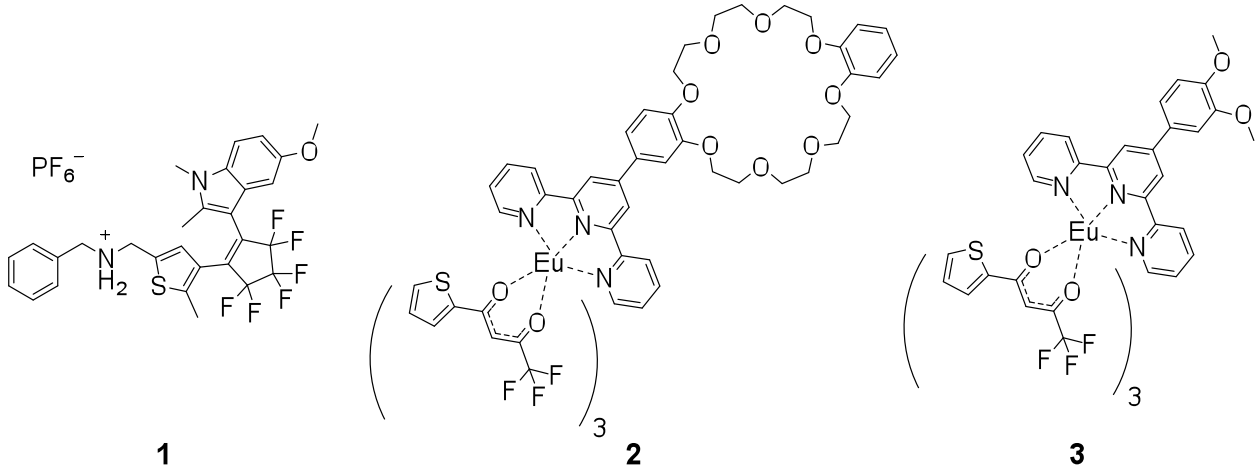
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Dual Stimulus Luminescent Lanthanide Molecular Switch Based on Unsymmetrical Perfluorocyclopentene Diarylethene

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Photochromic compounds can be interconverted by light between two states of different spectroscopic properties,[1,2] which makes them good candidates for realizing smart optical modulation. Diarylethene derivatives (DTEs) are the most promising optically responsive compounds, featuring notable thermally irreversible photochromic behavior, high photoisomerization quantum yields, and outstanding fatigue resistance.[3,4] The integration of photochromic DTEs with luminescent lanthanide component has displayed a few remarkable potential applications. In this work, we have noncovalently combined unsymmetrical perfluorocyclopentene-fused photochromic diarylethene derivative (**1**) to a Eu^{3+} complex of dibenzo-24-crown-8 (DB24C8) derivative bearing a terpyridine moiety (**2**) through the interaction of the dialkylammonium moiety in **1** with the 24C8 ring in **2**, to demonstrate how the Eu^{3+} luminescence is reversibly modulated by the ring-closing and ring-opening reactions of **1** caused upon UV and visible light irradiation. We introduced an indole chromophore to **1** in order to lower the excitation energy for facilitating the resonant energy transfer (RET) from the excited lanthanide ion to one of the isomers of the photochromic switch. We also introduced thermally stable thiophene-based unsymmetrical diarylethene as a RET acceptor of **1**, and a perfluorocyclopentene as the central ethene linker because of its resistance to fatigue.



1 **2** **3**

Fig 1. Structures of diarylethene **1** and Eu^{3+} complex **2** and reference **3** without DB24C8.

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Foldameric Anion Receptors: Encapsulation, Duplex Formation and Hydrophobic Collapse

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Nature creates microenvironments that facilitate ion recognition and transport. Inspired by this approach, we are investigating the use of foldameric anion receptors to bind biorelevant chloride by means of excluding solvent from the binding sites. These designs protect the anion by using hydrophobic 'caps' and the CH hydrogen-bonding triazoles by forming double helices. These processes mimic the recognition between vancomycin and bacterial cell walls as well as hydrogen bondings between base pairs inside DNA. Here, we present an example of chloride extraction from aqueous media with the assistance of hydrophobic caps where significant enhancement in chloride binding is observed. This work can help provide better understanding of the solvent's role in anion recognition and more guidance on the design of receptors in competitive media like water.

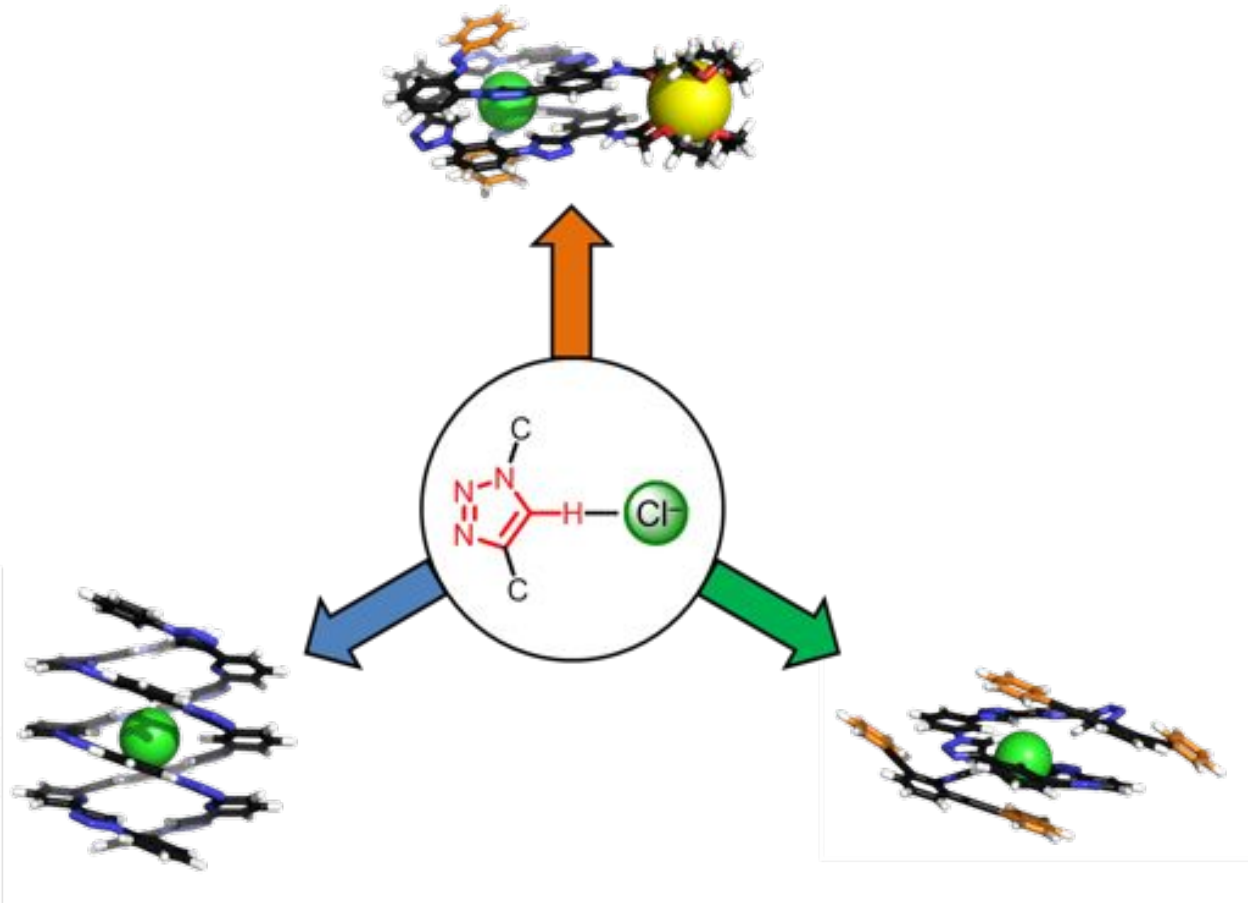


Figure 1. Examples of new foldamer designs (clockwise from top): chloride extraction, chloride encapsulation and duplex formation.

Selective Isolation of Gold Facilitated by Second-Sphere Coordination with α-Cyclodextrin

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Gold recovery using environmentally-benign chemistry is imperative from an environmental perspective.[1] Here, we report spontaneous assembly of a 1D supramolecular complex ***α*•Br** with an extended $\{[K(OH_2)_6][AuBr_4]\subset(\alpha\text{-CD})_2\}_n$ chain superstructure[2] formed (Figure 1a) during rapid co-precipitation of α-cyclodextrin (α-CD) with $KAuBr_4$ in water. The bulk co-precipitation is unique (selective) for α-CD and $KAuBr_4$, and does not occur if β-CD or γ-CD is substituted for α-CD, or, if $KAuCl_4$ is employed instead of $KAuBr_4$. This phase change in aqueous solution is also selective for gold, even in the presence of other square-planar palladium and platinum complexes. From the single-crystal X-ray analyses (Figure 1b) of the six inclusion complexes ***α*•Br**, ***β*•Br**, ***γ*•Br**, ***α*•Cl**, ***β*•Cl**, and ***γ*•Cl** between α-, β-, and γ-CDs with $KAuBr_4$ and $KAuCl_4$, we hypothesize that a perfect match in molecular recognition between α-CD and $[AuBr_4]^-$ leads to a near-axial orientation of the ion with respect to the α-CD channel, facilitating a highly specific second-sphere coordination[3] involving $[AuBr_4]^-$ and $[K(OH_2)_6]^+$ and driving the co-precipitation of the 1 : 2 adduct. This discovery heralds a green host-guest procedure for gold recovery from gold-bearing raw materials making use of α-cyclodextrin — an inexpensive and environmentally-benign carbohydrate.

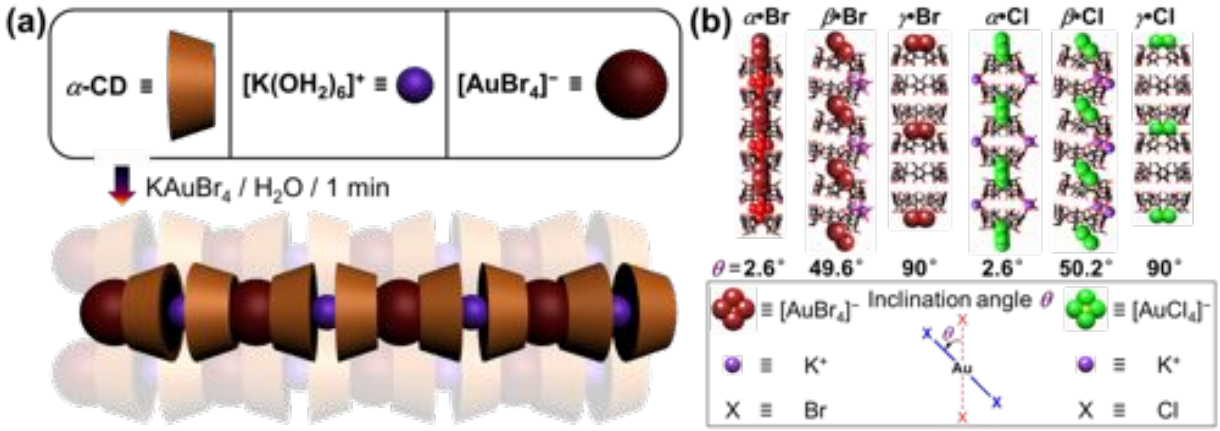


Fig 1. (**a**) Representation of the spontaneous co-precipitation of a 1:2 adduct between $KAuBr_4$ and α-CD in aqueous solution to afford ***α*•Br**. (**b**) Single crystal superstructures of ***α*•Br**, ***β*•Br**, ***γ*•Br**, ***α*•Cl**, ***β*•Cl**, and ***γ*•Cl**. The inclination angle of the $[AuX_4]^-$ anion viewed from the side with respect to the central axis of the CD tori is defined as θ. C Black, O Red, Br Brown, Cl Green, Au Yellow, K Purple.

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Poster B-44 Withdrawn

Selective Recognition of Methylated Lysines and Arginines by Cucurbit[7]uril

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Cucurbit[7]uril selectively binds the epigenetic mark $N^{\varepsilon},N^{\varepsilon},N^{\varepsilon}$-trimethyllysine ($LysMe_3$, $K_{CB[7]}$ = (1.8±0.6) x 10^6 dm^3 mol^{-1}) by 3500-fold over lysine ((5.3±0.7) x 10^2 dm^3 mol^{-1}) in aqueous solution,[1] using ion-dipole interactions and the hydrophobic effect, rather than cation-π interactions, as in the "aromatic cages" of *p*-SO_3-calix[4]arene hosts or chromodomain proteins which recognize $LysMe_3$.[2] The trend in $K_{CB[7]}$ of $LysMe_3$ > $LysMe_2$ > LysMe > Lys (Figure 1) follows the recognition pattern of the chromodomain HP1 and other $LysMe_n$ protein readers. With CB[6], protonation of the guest carboxylate group is required for the formation of inclusion complexes with the $LysMe_n$ series. The CB[7] host also displays modest selectivity between the asymmetric ((2.0±0.3) x 10^3 dm^3 mol^{-1}) and ((6.1±0.6) x 10^3 dm^3 mol^{-1}) dimethylarginines, both of which bind more strongly than the parent arginine or monomethylarginine.

The work on the methylated free amino acids is being extended to methylated lysines on the surface of proteins to examine the effects of the neighbouring residues on the CB[7] binding. Bovine serum albumin and hen egg white lysozyme will be reductively mono- and dimethylated with ^{13}C labels at the lysine sites[3] and the complexations by CB[7] will be monitored by ^1H-^{13}C 2D NMR spectroscopy and MALDI-TOF mass spectrometry.

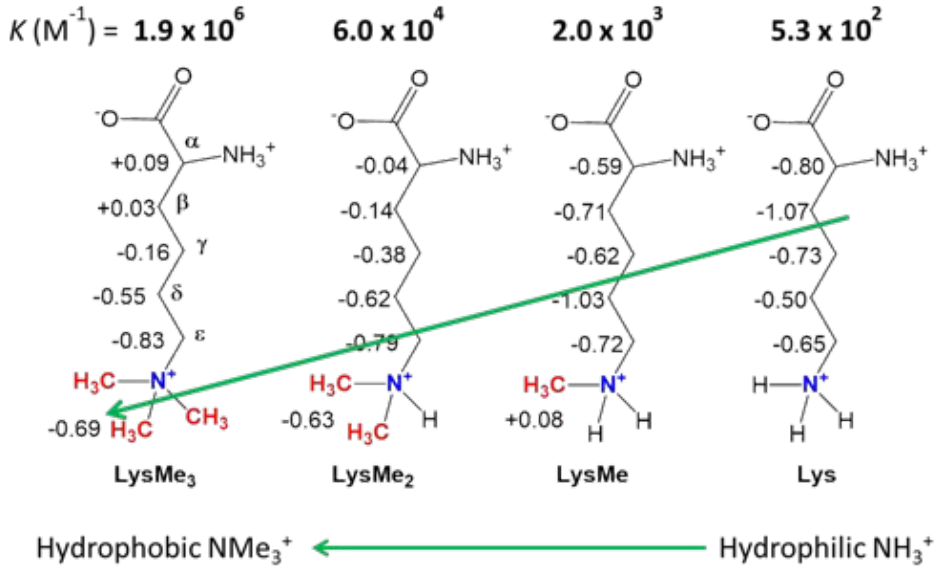


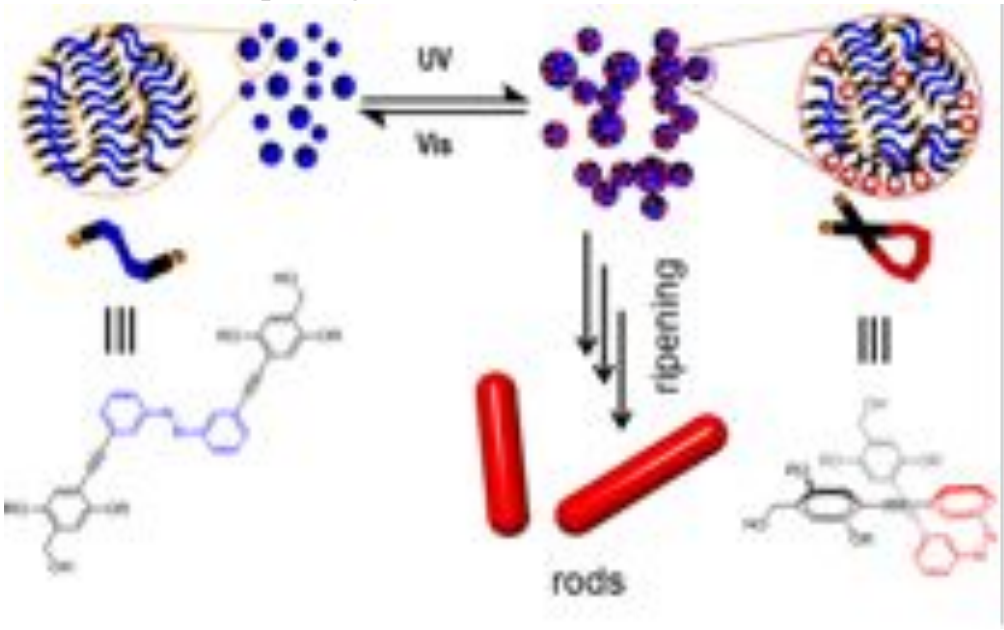
Figure 1. Host-guest stability constants and limiting ^1H NMR chemical shift changes for the complexation of methylated lysines by cucurbit[7]uril.

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Photoresponsive Transformation of Nanodots to Nanorods: Ostwald Ripening in Molecular Assemblies

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Formation of shape persistent one-dimensional (1D) nano- and microstructures is a topic of current interest in the field of advanced materials research.[1] Ostwald ripening is one of the reasons to the formation of 1D nanostructures from nanoparticles of metals and semiconductors.[2] For example, CdTe, CdSe and ZnO nanoparticles have been shown to form nanorods by Ostwald type ripening process. Herein we report the light induced reversible morphology change from the initially formed nanodots of a trans azobenzene derivative to shape controlled rods.[3] For the self-assembly of π-systems to nano- and microrods with controlled aspect ratio, it is important to prevent the usually occurring spontaneous extended aggregation of molecules. π-systems derived from phenyleneethynylene units are appropriate for this purpose since they are known to form spherical or circular assemblies due to weak π-interaction. This method allows the preparation of organic supramolecular rods with controlled aspect ratio that can be assembled and disassembled by light of appropriate wavelengths. The new observation described here reveals another property of the versatile azobenzene chromophore that may encourage further studies enroute to stimuli responsive hierarchical structures with controlled morphological features.



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Hydrogels for the Slow Release of Hydrophobic Drugs Using Cucurbit[n]uril

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Hydrogels are generally polymers which contain hydrophilic networks capable of holding large amounts of water, but are not soluble in water. Hydrogels derived from alginate can be formed by cross-linking with sodium or calcium ions. These hydrogels are biocompatible. [1]Alginate cross-linking can be improved with the macrocycles Q[5] and Q[6] to give robust gels. Q[*n*] is the abbreviation of the family of macrocyclic molecules known as cucurbit[*n*]uril. The homologues Q[7-8] have been shown to encapsulate the hydrophobic benzimidazole anticancer drugs such as ABZ and MEABZ and these complexes can be embedded into hydrogels.[2,3] These Q[7-8]@drug complexes loaded into Q[5] or Q[6] mediated alginate hydrogels release the complex slowly over a period of several days. This demonstrates a method for the slow release of hydrophobic drugs from hydrophilic hydrogels. The details of our findings will be presented.

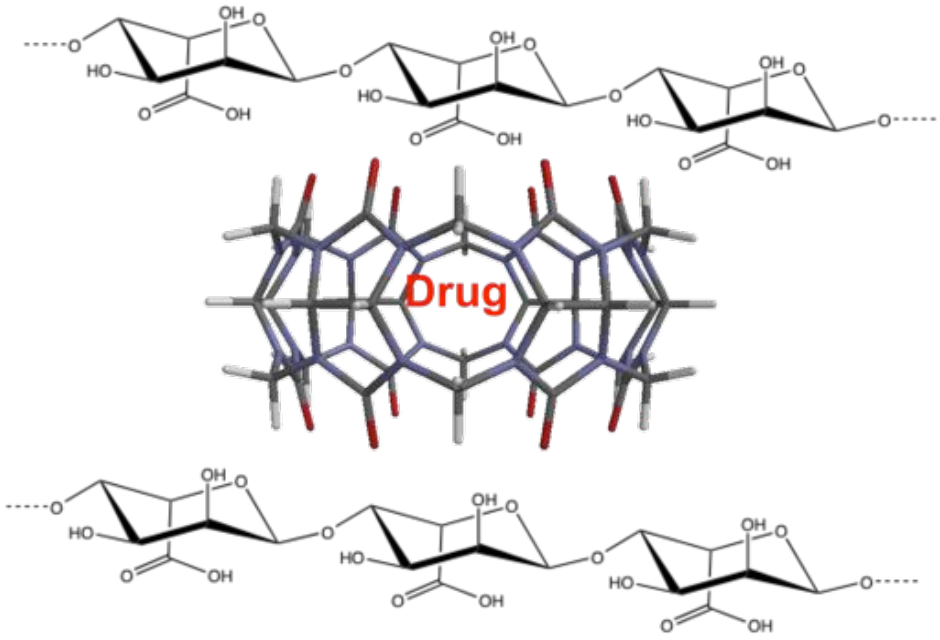


Fig 1. Structure of alginate hydrogel with a hydrophobic drug encapsulated in cucurbit[*n*]uril.

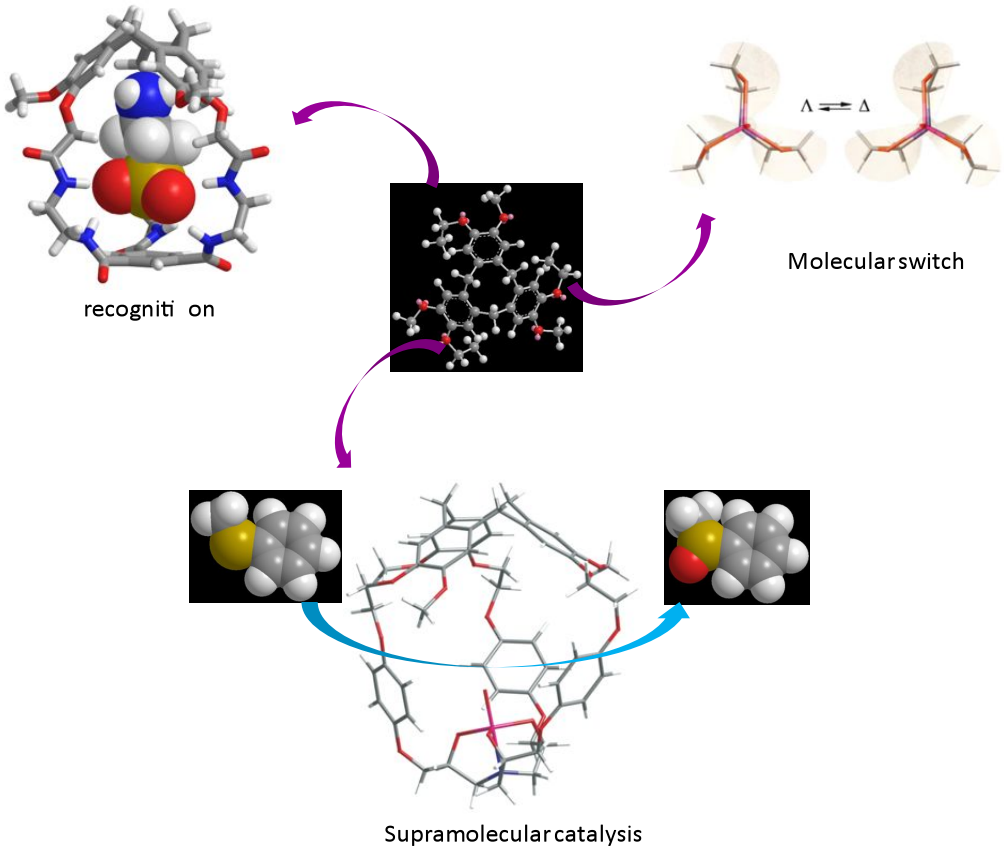
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Revival of the Chemistry of Hemicryptophanes

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The hemicryptophanes, combining a CTV unit with another C_3 symmetrical moiety, are ditopic host molecules. Although their synthesis was described for the first time by A. Collet and J.-M. Lehn in 1982,[1] their complexation properties and their catalytic activities have received little attention. Here, we will described new aspects of the chemistry of hemicryptophanes since recently they were found to be efficient supramolecular catalysts,[2] ion-pairs,[3] zwitterions,[4] or enantioselective carbohydrates receptors,[5] and led to the design of novel molecular mechanical components as propellers.[6]



References [1] Canceill, J.; Collet, A.; Gabard, J.; Kotzyba-Hibert, F.; Lehn, J.-M. *Helv. Chim. Acta* **1982**, *65*, 1894. [2] (a) Dimitrov-Raytchev, P.; Martinez, A.; Gornitzka, H.; Dutasta, J.-P. *J. Am. Chem. Soc.* **2011**, *133*, 2157; (b) Martinez, A.; Dutasta, J.-P. *J. Catal.* **2009**, *267*, 188. (c) O. Perraud, A. B. Sorokin, J.-P. Dutasta, A. Martinez *Chem. Comm.* **2013**, *in press* DOI:10.1039/C2CC37829A. [3] Perraud, O.; Robert, V.; Martinez, A.; Dutasta, J.-P. *Chem. Eur. J.* **2011**, *17*, 4177. [4] (a) Perraud, O.; Robert,V.; Gornitzka, H.; Martinez, A.; Dutasta, J. P. *Angew. Chem. Int. Ed.* **2012**, 504.*(b)* Perraud, O.; Robert, V.; Gornitzka, H.; Martinez, A.; Dutasta, J. P. *Org. Bio. Chem.* **2012**, 1056 [5] Perraud, O.; Martinez, A.; Dutasta, J.-P. *Chem. Commun.* **2011**, *47*, 5861.[6] (a) Martinez, A.; Robert, V.; Gornitzka, H.; Dutasta, J.-P. *Chem. Eur. J.* **2010**, *16*, 520. (b) Martinez, A.; Guy, L.; Dutasta, J.-P. *J. Am. Chem. Soc.* **2010**, *132*, 16733.

Stability of Boronic Acid-Diol Esters as a Function of Acidity of Both Components: A Quantitative Study

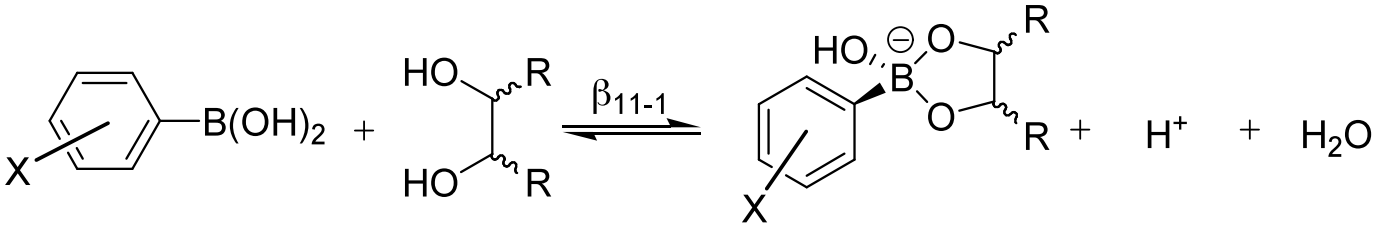
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Boronic acids interact rapidly and reversibly with diols to form boronic esters and these reactions find numerous applications for development of sugar sensors and self-assembled supramolecular structures.[1] Acidities of both components play important role in stability of esters,[2] but the effect has not been yet studied quantitatively. In this work the equilibrium constants corresponding to the reaction shown in Scheme 1 with boronic acids and diols of variable acid strength shown in Chart 1 were determined by potentiometric titrations and by UV-Vis, fluorescence and ^{11}B NMR titrations at variable pH to address the existing concern regarding the consistency of stability constants determined by different techniques.[2a] The constants $\beta_{11\text{-}1}$ follow the Hammett equation with ρ depending on pK_a of diol and varying from 2.0 for glucose to 1.2 for ARS. Results of UV-Vis and fluorometric titrations agree well with those expected on basis of $\beta_{11\text{-}1}$, but stability constants determined by ^{11}B NMR titrations are one order of magnitude smaller than expected. A general equation, which makes possible an estimate of $\beta_{11\text{-}1}$ for any pair of boronic acid and diol from their pK_a values, is proposed on basis of established Brönsted-type correlation of Hammett parameters for $\beta_{11\text{-}1}$ with acidity of diols.



Scheme1. Interaction between arylboronic acids and 1,2-diols.

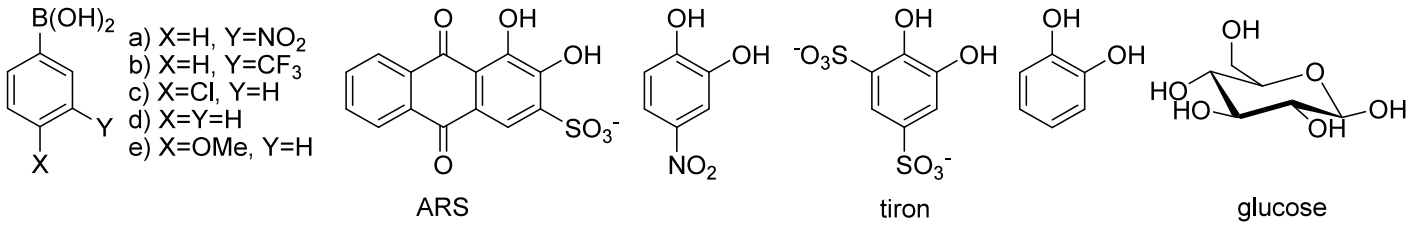


Chart 1. Arylboronic acids and diols employed in this study.

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Reactions and Conformational Changes In and Around Cucurbiturils

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After a brief overview of the recognition properties of Cucurbit[n]urils (CB[n]), we will present (1) the impact of these macrocycles on the rates and activation parameters of intramolecular Diels-Alder reactions between furfuryl and allyl groups, both being connected to a central dimethylammonium cation; these cycloadditions were carried out in the cavity of CB[7] and CB[8] (see Figure 1a);[1] (2) the use of CB[n]s as tools to determine the torsional isomerization barriers of substituted biphenyls (Figure 1b);[2] (3) the regio- and diastereoselective recognition of fluorine-substituted di- and tribenzyl ammonium cations by CB[8] (Figure 1c),[3] and (4) subtle "supramolecular buttressing effects" in CB[7]/guest assemblies (Figure 1d); we defined "supramolecular buttressing effects" as the alteration, by a neighboring unit, of a substituent effect on intermolecular recognition. To illustrate this notion, we showed that the geometry of complexes formed with CB[7] and biphenyls bearing *meta*-dimethylsulfonium groups could be affected by additional substituents at the *para*-position; the latter exert pressure on the neighboring sulfonium groups, and subsequently on the portal of CB[7].[4]

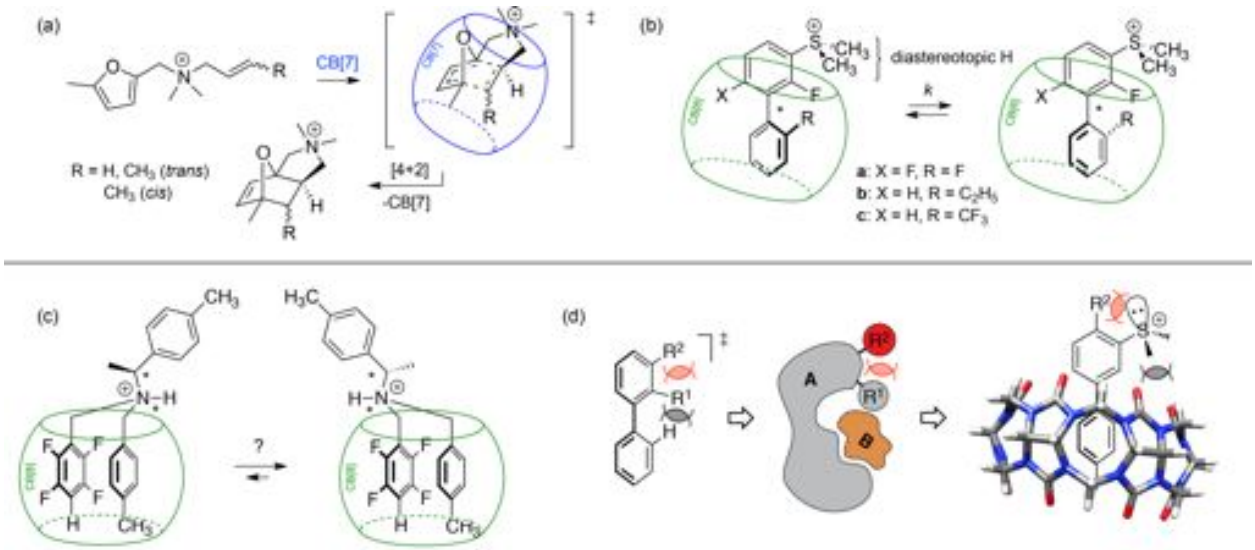


Fig 1. (a) Intramolecular Diels-Alder cycloadditions promoted by CB[n]s; (b) Torsional isomerization of biphenyl derivatives inside CB[8]; (c) diastereoselective recognition of fluorine-substituted tribenzyl ammonium cations; (d) buttressing effects: from molecules to host/guest complexes.

References

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Tunable Selectivity in Expanded, Shape Persistent-Triazolophanes

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Tetraphenylene triazolophanes have demonstrated many hallmark lessons of supramolecular chemistry in receptor design for the size-selective binding of chloride. Taking advantage of its shape-persistence, we aimed to tune its selectivity by installing flanking 1,8-naphthalimide spacers to create a new class of triazolophanes with elliptical cavities (MC, X = CH) for enhanced binding of linear anions (i.e. N_3^-, SCN^-). The stepwise and modular synthesis of these macrocycles also allowed for the systematic installation of pyridyl head groups (X = N) by which its internally directed dipole was found to promote formation of sandwich complexes around tetrahedral anions (i.e. ClO_4^-) with high binding affinities ($\beta_2 \sim 10^{12}$ M^{-1}).



Figure 1. A series of expanded triazolophanes (**MC**) were found to bind linear anions (X = CH, i.e., N_3^-) within its expanded cavity while modulating the local dipole with pyridines (X = N) drove formation of sandwich complexes ($\mathbf{MC}_2$•ClO_4^-) around tetrahedral anions.

Intramolecular Indicator-Dye Displacement Assay

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To date, much attention has been devoted to develop anion sensors.[1] One of the well-known strategies for anion detection is indicator-dye displacement assay, a term coined by Anslyn et al.[2] However, the major disadvantage of the dye displacement assays is that they are not reversible. To overcome this setback, we developed "Intramolecular Indicator-dye Displacement Assay (IIDA)" as a new approach toward anion sensing. The IIDAs comprises a receptor and a spacer with an attached anionic chromophore in a single-molecule assembly. In the resting state, the environment-sensitive anionic chromophore is bound by the receptor while the anionic substrate competes for binding into the receptor. The photophysical properties of the dye exhibits change in fluorescence when displaced by anions, which results in cross-reactive response.[3] To illustrate the concept, we have prepared sensors **1** and **2**. In this presentation, the characterization of sensors and micro-titer arrays comprising IIDA will be reported.

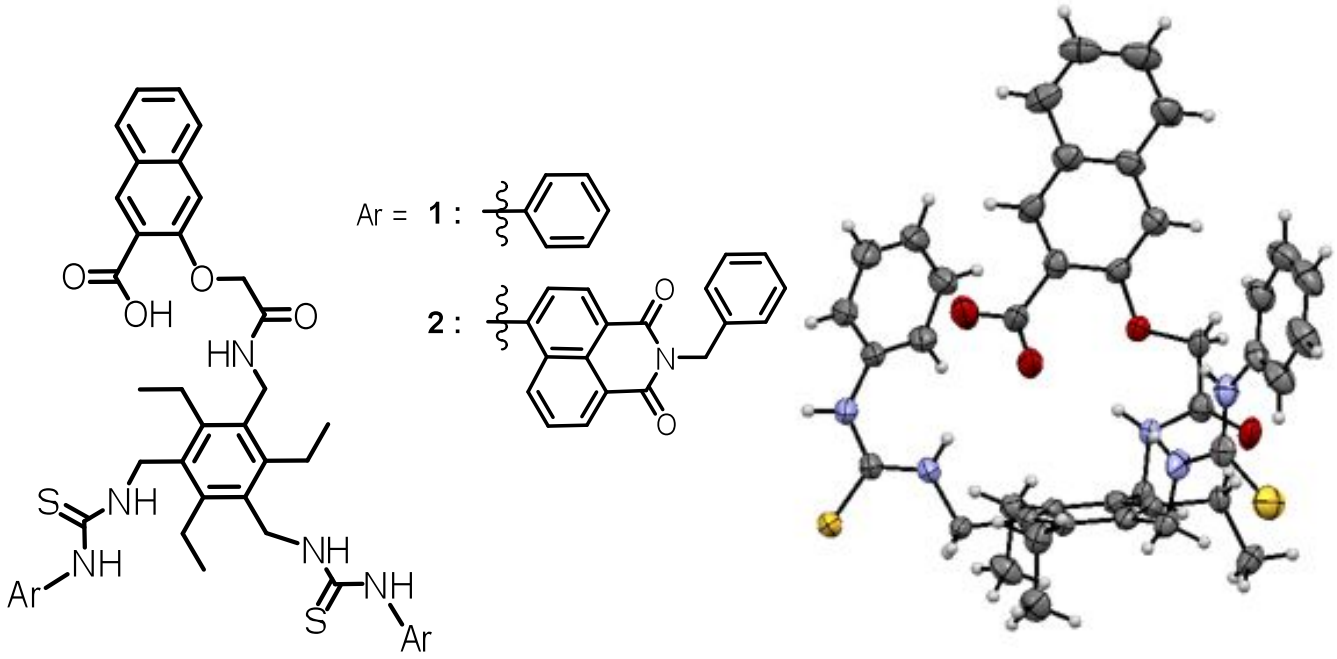


Figure 1. **Left**: Designed sensors **1** and **2** for Intramolecular Indicator-dye Displacement Assay. **Right**: The structure of **1** determined by X-ray crystallography.

References 1) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry, Monographs in Supramolecular Chemistry*; Royal Society of Chemistry: Cambridge, 2006. 2) Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687–699. 3) (a) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3118–3130. (b) Umali, A. P.; Anslyn, E. V. *Curr. Opin. Chem. Biol.* **2010**, *14*, 685–692. (c) Anzenbacher, P., Jr.; Lubal, P.; Bucek, P.; Palacios, M. A.; Kozelkova, M. E. *Chem. Soc. Rev.* **2010**, *39*, 3954–3979.

Catalytically-Driven Unidirectional Shuttling of γ-Cyclodextrin Along a Symmetrical Dumbbell

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Motor proteins, whose locomotion is driven by catalytic ATP hydrolysis in their active sites, are vital components of nature's molecular machinery that convert chemical energy into mechanical work. Wholly synthetic systems that accomplish similar feats are currently being developed on account of their potential to power artificial molecular machines.[1] We present the design (Figure 1) of rotaxanes incorporating a γ-cyclodextrin (γ-CD, Figure 1b) ring component which, by virtue of the orientational asymmetry of the ring and its well-known ability to enhance the rate of anthracene photodimerization,[2] can undergo catalytically-driven unidirectional shuttling. Studies on a single station model **1** (Fig 1a) inform the design of an extended three-station analog (Figure 1c) that, from an initial 1:1:1 population of co-conformers, will be driven towards a single product in which the ring has been transported to one end of the dumbbell. By analogy to motor proteins, the γ-CD 'active site' in this design moves along the dumbbell with directional bias which is linked to a catalytic reaction, and it does so autonomously whilst fuel is supplied, in the form of anthracene and light.

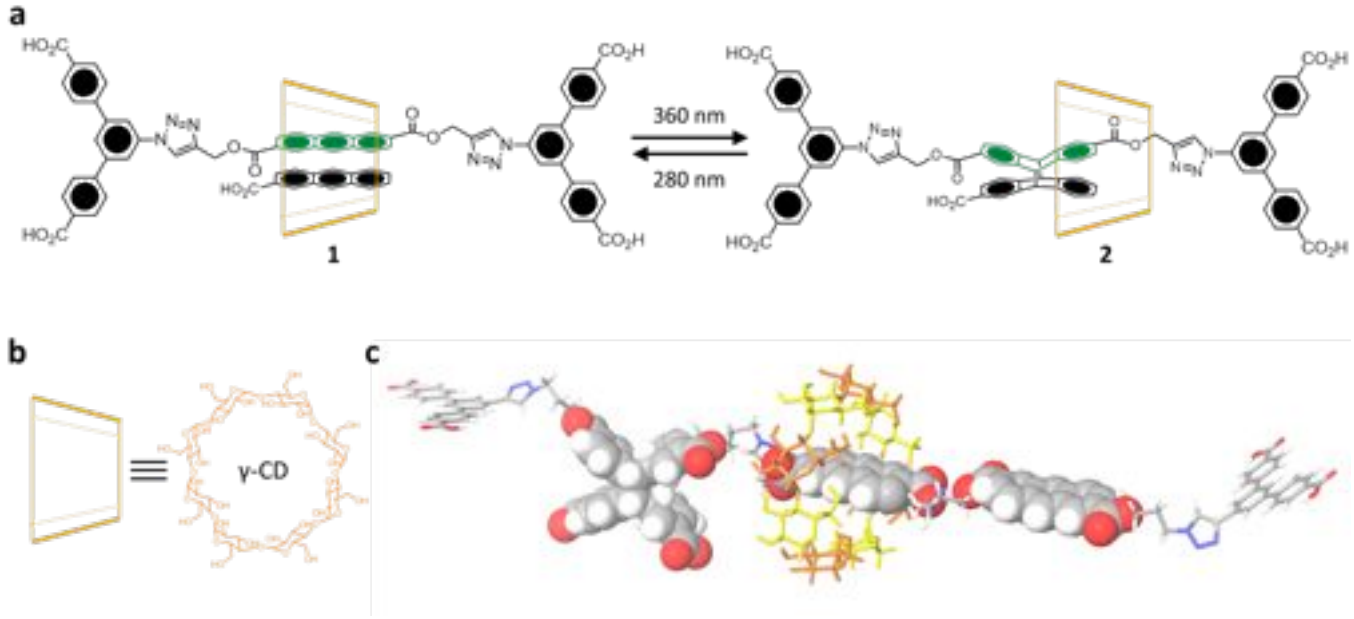


Fig. **a**, Model rotaxane **1** encorporates a single anthracene station. **b**, Structural formula of γ-CD. **c**, Computational simulation of a three-station analog after photocycloaddition of one anthracene unit – starting from a 1:1:1 population of co-conformers, the ring will be driven to one end of the dumbbell preferentially.

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Reversible Structural Switch in Crystalline Nano-cavities of Peptide Metallo-Macrocycles with Smooth Ligand Exchange by Water Contents

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Crystalline materials often undergo stimulus-responsive structural transition leading to new functions. Based on high design possibility and structural diversity of peptides, we envisioned that molecular crystals of cyclic metallo-peptides would demonstrate dynamic behaviors in the solid state within a flexible hydrogen-bonding network. We have previously reported crystalline Ni(II)-macrocycles $[Ni_4\mathbf{1}_4]^{8+}$ consisting of β-dipeptides with a nano-cavity (Fig. 1a).[1] Herein we demonstrate the reversible structural switch of nano-cavities by ligand exchange in the single crystal of peptide metallo-macrocycles as the nitrate (NO_3^-) salts.

By single crystal X-ray structural analysis and thermal studies (TG·DSC), we observed two-step structural changes accompanying the release of included water molecules with keeping single crystallinity. At the second strucutral change, crystal-to-crystal structural transformation was found with the release of all water molecules, which regulates the opening and closing of the cavities through close cooperation between ligand exchange and switch of hydrogen-bonding between β-dipeptides (Fig. 1b).[2] This structural transformation accompanied the switch of functional groups assembled in the cavities. Indeed, this structural switch was reversible and proceeded very smoothly above -40 °C under the control of external temperature and humidity.

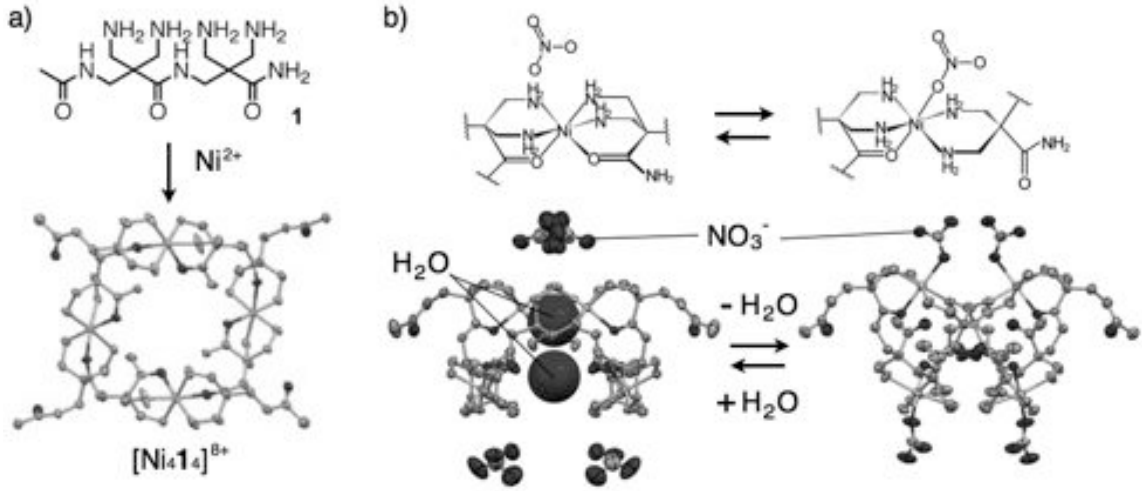


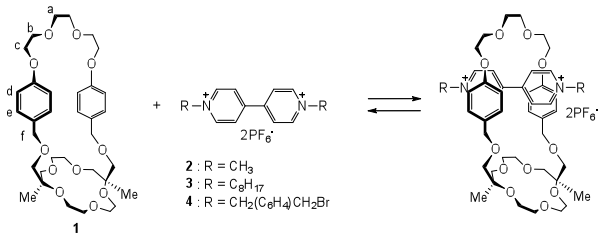
Figure 1. (a) The crystal structure of Ni(II)-macrocycles $[Ni_4\mathbf{1}_4]^{8+}$with β-dipeptide **1** and (b) ligand exchange behaviors in the NO_3 salts of crystalline Ni(II)-macrocycles at 20 °C depending on the humidity: wet condition (left) and dry condition (right).

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Preparation of Rotaxanes from a Cryptand and Bipyridinium Salts

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Recently, various interlocked molecules, such as rotaxanes and catenanes, have been investigated as both chemosensors and molecular machines. These interlocked molecules can bind specific guest molecules, including alkali metal cations and chloride and sulfate anions, inside three-dimensional cavities. Because cryptands have been employed to achieve strong binding of metal cations within a three-dimensional cavity,[1] molecular motion of rotaxanes composed of a bipyridinium salt as an axle component and a cryptand as a wheel component can be expected to occur upon addition of metal cations.[2] Here, we report preparation of new rotaxanes utilizing a novel cryptand, containing two aromatic rings, as a wheel component combined with bipyridinium salts as axle components.

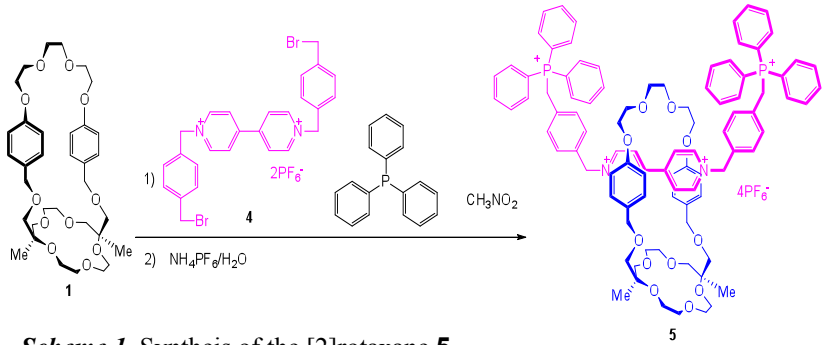


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Table 1. Association constants, K_a (M^{-1}), obtained by monitoring proton (d), of cryptand **1** with bipyridinium salts **2**, **3** and **4** in acetone-d_6 at 293 K. Error < 8%

	K_a / M^{-1}		
Cryptand	**2**	**3**	**4**
1	180	130	210

The binding properties of cryptand **1** were estimated by quantitative ^{1}H NMR titration experiments involving the cryptand **1** with dimethyl bipyridinium salt **2** as well as the bipyridinium salt derivatives **3** and **4** in acetone–d_6. During these titrations, the ^{1}H NMR shift changes of the phenylene protons of the macrocycle (d) were monitored. Measuring the upfield shift in proton (d) upon the addition of bipyridinium salts **2** – **4** allowed association constants (K_a) to be determined. The association constants for the complexation are given in ***Table 1***. The association constants for the complexation of cryptand **1** with the bipyridinium salts **2** – **4** proved to be on the same order of magnitude. The reaction of the cryptand **1**, the bipyridinium salt **4**, and PPh_3 in CH_3NO_2 gave the [2]rotaxane **5** in 11% yield (***Scheme***). As expected, upfield shifts were observed in the signals of the phenylene protons (d and e) of cryptand **1**, implying π–π interactions between the benzene rings of the macrocycle and the positively charged bipyridinium salt.



1 5

Scheme 1. Syntheis of the [2]rotaxane **5**.

References 1) Nakatsuji, Y.; Sunagawa, T.; Masuyama, A.; Kida, T.; Ikeda, I. *Chem. Lett.* **1995**, 445–446.
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Unique Fluoride Complexation in Basic Media by Urea and Thiourea Derivatives of Phenothiazine 5,5-dioxide

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We synthesized a novel phenothiazine 5,5-dioxide containing two urea units (**1**) and its thio analogue (**2**), and studied their anion recognition ability in acetonitrile using UV–vis spectroscopy.

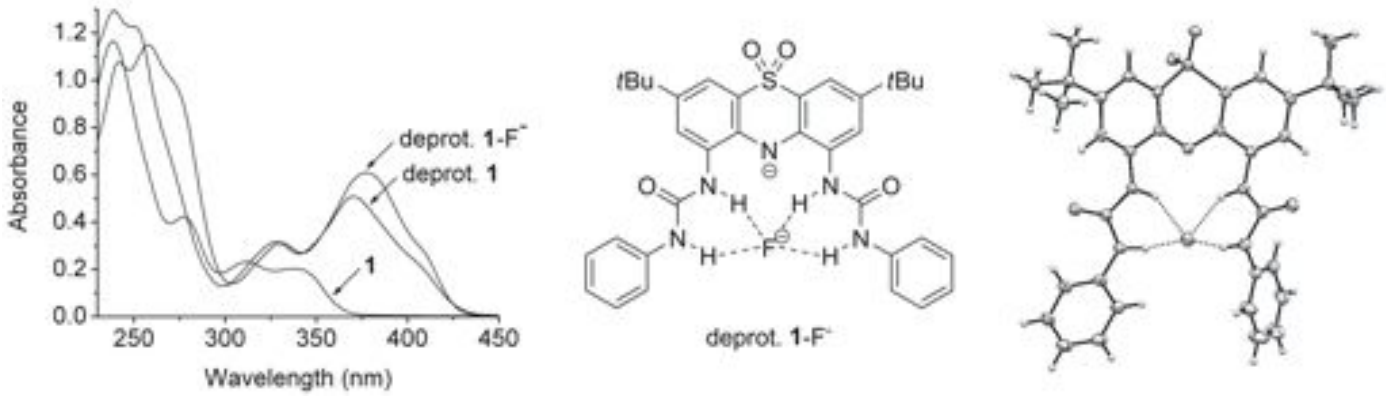


Figure 1. UV–vis spectrum and crystal structure of the deprotonated **1**–F^- complex.

While most of the studied anions (chloride, bromide, hydrogen sulfate, sulfate and dihydrogen phosphate) were bound only by the neutral receptors, fluoride and acetate were complexed even by the deprotonated ones. The deprotonated receptors showed stronger complexing ability toward fluoride than acetate. The formation of the deprotonated **1**–F^- complex was also examined by ^{1}H NMR spectroscopy and X-ray crystallography.

Acknowledgements. Financial support of the Hungarian Scientific Research Fund (OTKA K 81127 and PD 104618) is gratefully acknowledged.

References 1) Kormos, A.; Móczár, I.; Pál, D.; Baranyai, P.; Holczbauer, T.; Palló, A.; Tóth, K.; Huszthy, P. submitted to *Tetrahedron*.

Reversible Supramolecular Modification of Surfaces

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In this poster, the development of a versatile strategy for the reversible surfaces functionalization of polymeric filtration membranes following a supramolecular surface modification approach is presented.[1-4] This work is expected to generate important insights to better understand surface supramolecular modification. The developed system will give the possibility to regenerate and change the functionality of filtration membranes "in-place" during their industrial use.

As a first step, we developed a chemical approach allowing the controlled introduction of a relevant number of β-cyclodextrin derivatives ("hosts") on the surface of the selected polymeric membrane (polyethersulfone). The modified membranes were characterized by Fourier transform infrared spectroscopy and water flow ability measurements. As the next step, a multivalent polymeric guest, with functional groups able to form inclusion complexes with immobilized "hosts" on the surface of the membranes were synthesized and fully characterized. This polymer was fluorescently labelled and used to assess its reversible adsorption on the modified membranes. This polymer was further modified in order to introduce additional bio-catalytic functionalities (*e.g.* enzyme) in the system. The supramolecular binding, bio-catalytic activity and reversibility of the system were investigated by fluorescent microscopy, gel electrophoresis and spectroscopic methods.

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4) A. Barnard and D. K. Smith, *Angew. Chem., Int. Ed.*, **2012**, 51, 6572-6581.

Lithium Conductive Molecular Crystals having Diamine and Bis(trifluoromethanesulfonyl)amide Framework

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Molecular crystals (MCs) that show ionic conductivity are one of the most interesting materials because of their potential application as next-generation solid electrolytes with safety and reliability. We recently reported the synthesis of novel MC, $Li_3[B(C_6H_4O_2)\{O(CH_2CH_2O)_3CH_3\}_2][N(SO_2CF_3)_2]_2]$, with ionic conduction paths consisting of glyme chains.[1] Owing to the existence of the conduction paths, This MC showed the selective lithium ion conductivity under solid state. Based on the result, we investigate the structural control of the ionic conduction paths by modification of the component units of MCs for improving ionic conductivity. In this work, we attended the amine framework as a building block of conduction paths instead of glyme chains. We herein report the synthesis, crystal structure, and ionic conductive properties of MCs, $Li\{N(SO_2CF_3)_2\}(R^1{}_2NCHR^2CH_2NR^1{}_2)$ (**1**; $R^1 = CH_3$, $R^2 = H$, **2**; $R^1 = CH_3$, $R^2 = CH_3$, **3**; $R^1 = CH_2CH_3$, $R^2 = CH_3$). The relationship between crystal structure and ionic conductivity of these MCs suggests that the values of ionic conductivity and activation energy are affected by the molecular arrangement and the molecular structure, respectively.

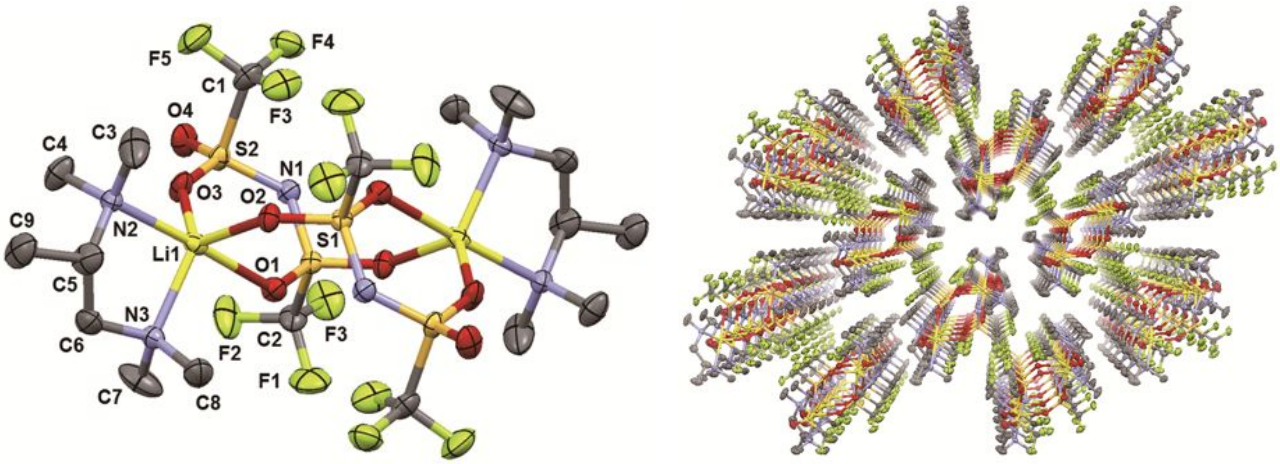


Figure 1. Crystal structure (left) and packing view along *b*-axis (right) of MC **2**.

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Facilitated Kinetic Transport of Co^{2+}, Cu^{2+}, Cd^{2+} Through a Supported Liquid Membrane with Calix[4]arene as a Carrrier

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In the present study, we investigate the process behavior of the transport of alkali, alkali-earth, and transitions metal ions through the bulk liquid membrane by a calix[4]arene derivatives (**1** and **2**, as presented in Fig 1) as the new liquid membranes and analysis of kinetics parameters by means of experimental data. The guest metal cations are transported from the source phase to the receiving phase in this study. After metal ion complexing with the carrier host on the interface between the source phase and the membrane, transporting into the membrane and on the interface between the membrane and receiving phase the metal ion is released into the receiving phase by diffusing down its concentration gradient.

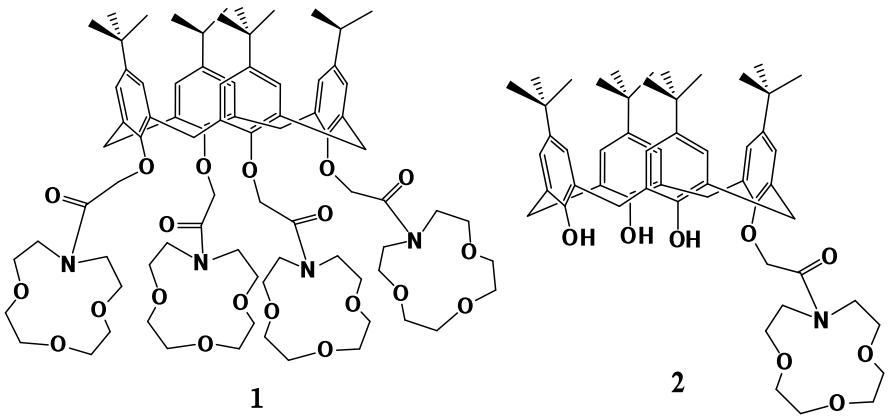


Figure 1. The structures of calix[4]arene derivatives.

To measure the binding ability of the **1** toward alkali and alkaline-earth and transition metal ions, firstly we used a bulk liquid membrane system. Among alkali metal ions, Li^+ ion was found to move the most rapidly from source into receiving phase medium by a rate of $1.26 \cdot 10^{-8}$ mol s^{-1} cm^{-2}. For alkaline-earth metal ions, the transport rate of Mg^{2+} ion was the largest by $4{,}23 \cdot 10^{-8}$ mol s^{-1} cm^{-1}. So, it is presumed that Mg^{2+} ion is selectively bound to the calix[4]arene **1**. For transition metals, the relative frequency for copper low Cu^{2+} $9.54 \cdot 10^{-8}$ mol s^{-1} cm^{-1} and cobalt Co^{2+} $2.41 \cdot 10^{-8}$ mol s^{-1} cm^{-1} has a high transfer rate. Whereas, for nickel transfer rate is low Ni^{2+} $1.59 \cdot 10^{-8}$ mol s^{-1} cm^{-1}. While the average rate of transport of cadmium Cd^{2+} $5.49 \cdot 10^{-8}$ mol s^{-1} cm^{-1}

Fluorimetric Indicators for Nitroaromatic Explosives

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Detection of explosives and improvised explosive devices (IEDs) is an issue of paramount importance in many of the volatile geographical areas. In particular, we face everyday the tremendous death-toll that anti-personnel landmines and IEDs cause (70 between military and civilians injured or killed daily), most of them children.

We will present a new class of indicators based on the brightly fluorescent pyren-1-yl and 10-phenylanthracen-9-yl fluorophores that are able to detect nitroaromatic explosives (e.g. TNT). The fluorescent molecules display a unique mode of interaction with nitroaromatics, and their fluorescence is quenched by photoinduced electron transfer. Extensive solution studies carried out using common photophysical techniques and NMR show that the formation of stable Meisenheimer complexes is responsible for the intramolecular PET quenching process. The Meisenheimer complex between the analyte and a nucleophilic amine moiety of the indicator acts as an electron trap to prevent radiative decay within the signaling fluorophore. As a result, fluorescence quenching is observed.

Interestingly, due to the excellent film-forming properties, the fluorescent indicators can be easily deposited on many surfaces including glass, polymer films, paper) by Ink-Jet printing and spray deposition techniques. The fluorescent material films obtained can be used for a rapid and robust screening of materials that have been exposed to TNT or its vapors.

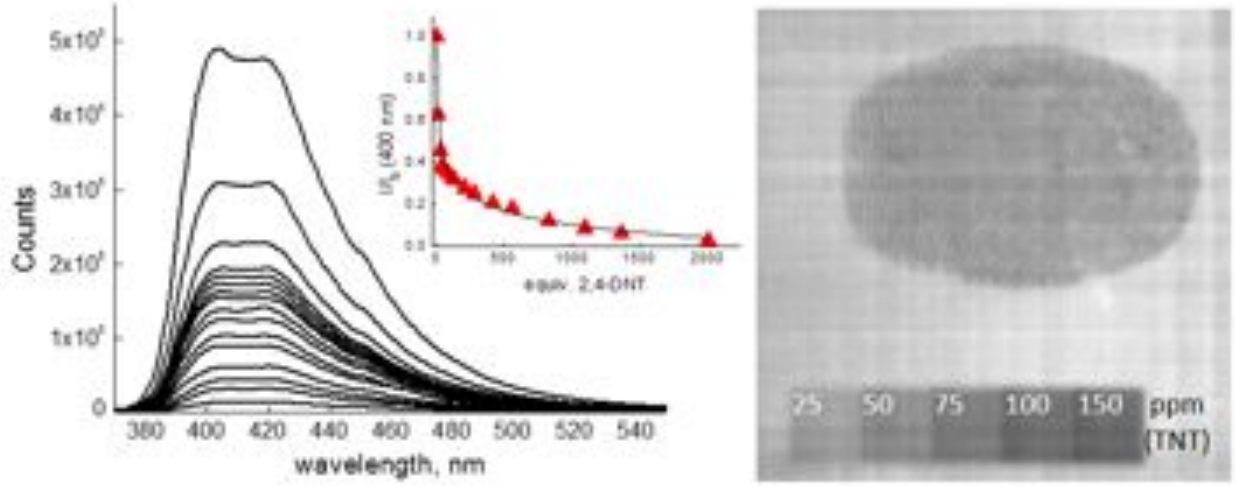
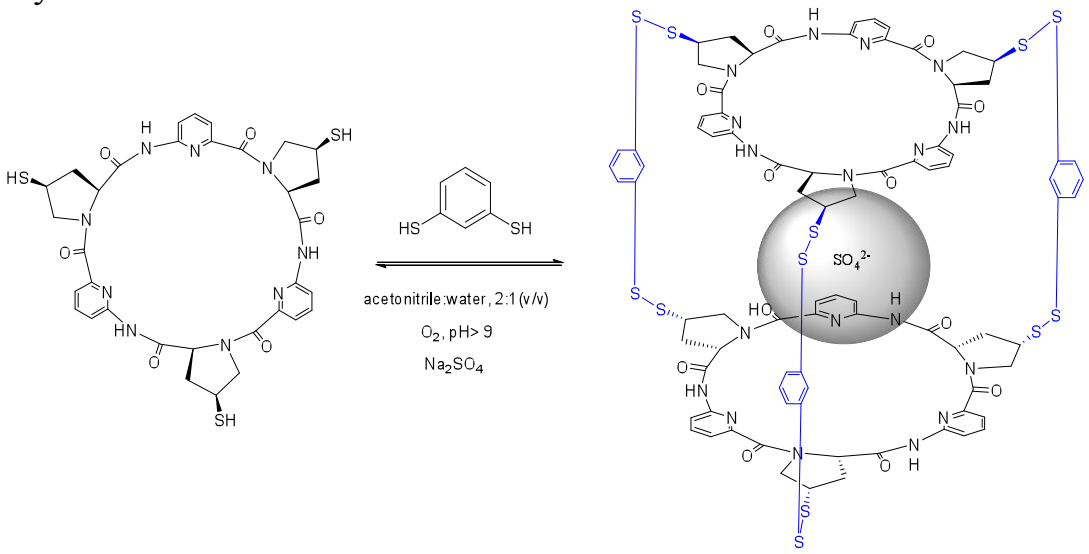


Figure 1. Titration of a pyrene-1-yl indicator with 2,4-dinitrotoluene (left). The printed material can be used to examine objects and surfaces, for example, a fingerprint that is positive for nitroaromatics (right).

Synthesis of a Triply Linked Bis(cyclopeptide) Receptor for Sulfate Anions

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Dynamic combinatorial libraries (DCL) are mixtures of compounds equilibrating under thermodynamic control by continuously exchanging building blocks.[1] Generation of such libraries requires suitable reversible reactions. Thiol-disulfide reversible exchange is one of the most widely used reactions for the generation of DCLs in aqueous media. Addition of a suitable template into a dynamic library can lead to amplification of one library member at the expense of others which is thermodynamically stabilized by interaction with the template. By using this concept our group succeeded in the synthesis of singly and doubly-linked anion-binding bis(cyclopeptides).[2,3] Current efforts are directed toward the synthesis of the corresponding triply linked system.



1 2

To achieve the synthesis of the desired compound, we are using cyclopeptide trithiol **1** and 1,3-benzenedithiol as building blocks and disulfide exchange chemistry as the reversible reaction. Both building blocks are equilibrated under appropriate conditions in absence and the presence of a solute salt whose anions serves as template to mediate the formation of the desired bis(cyclopeptide) **2**. Synthetic approaches and results of these investigations are summarized in this poster.

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2) Otto; S., Kubik, S., *J. Am. Chem. Soc.* **2003**, 125, 7804.
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Bis-porphyrin Molecular Tweezers with Varying Degrees of Rotational Freedom

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The synthesis of molecular tweezers for the fabrication of nanoscale molecular devices continues to be a highly active area of research in supramolecular chemistry. We have recently reported bis-metalloporphyrin molecular tweezer **1a** (Figure 1),[1] which was synthesised by coupling linker and receptor modules via a microwave-accelerated alkene plus cyclobutane epoxide (ACE) cycloaddition.[2] **1a** has several positions of rotational degrees of freedom; about the porphyrin *meso*-phenyl group with respect to the norbornyl linker, and between each half of the norbornyl linker about the central phenyl diimide. This allows changes in both interporphyrin distance and angle. Using UV-Vis and ^{1}H NMR spectroscopy with multivariate global spectral analysis, **1a** was found to form a strong 1:1 intramolecular sandwich complex with the diamino ligand DABCO (1,4-diazabicyclo[2.2.2]octane) (**1a**:DABCO, K_{11} = 8.1 x 10^7 M^{-1}), transforming to a 1:2 open complex (**1a**:$(DABCO)_2$, K_{12} = 2.7 x 10^9 M^{-2}) at high concentrations of DABCO.

We will discuss our current work with **1**, and contrast **1a** with **1b**, the latter of which exhibits significantly restricted rotation about a sterically bulky 2,3,5,6-tetramethylphenyl diimide core (R = CH_3, Fig 1). This has allowed isolation of the *syn*- and *anti*- isomers of **1b**, and the study of each configuration when complexed with DABCO. Furthermore, our efforts towards expanding tweezer **1** to incorporate a second (allosteric) binding site will be discussed.

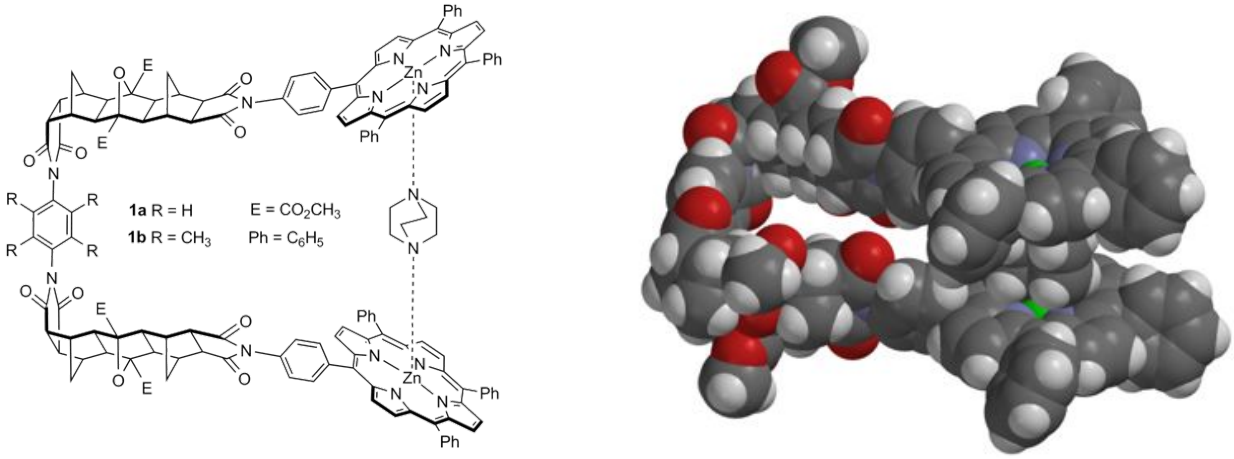


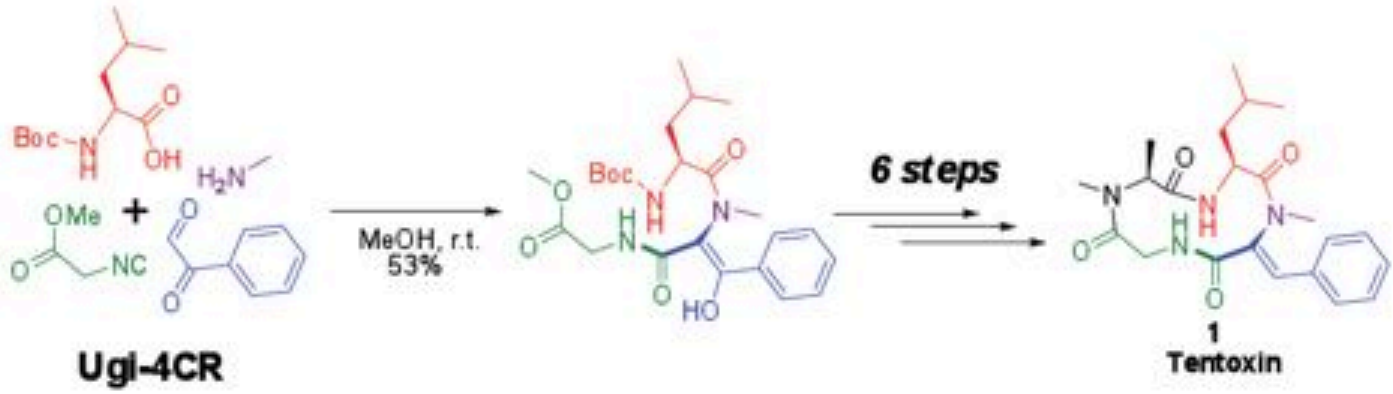
Figure 1. Molecular tweezers **1**:DABCO; semi-empirical molecular model of **1a**:DABCO.

References 1) Murphy, R.B., Pham, D.-T., Lincoln, S.F., Johnston, M.R., *Eur. J. Org. Chem.*, **2013**, *published online 5th April 2013*, DOI: 10.1002/ejoc.201300207 2) Foitzik, R.C., Lowe, A.J. and Pfeffer, F.M. *Tetrahedron Letters*, **2009**, *50*, 2583-2584.

The Multicomponent Approach to Tentoxin, a Macrocyclic Herbicide

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Tentoxin **1** is a metabolite isolated from several phytopathogenic fungi of the *Alternaria* genus[1] This cyclopeptide has been found to induce chlorosis in some sensitive higher plants while it does not affect other cultures.[2,3] The compound acts by inactivating the F(1)-ATPase motor of sensitive plants at nanomolar concentrations while at higher concentrations it stimulates the activity of the enzyme.[4] Therefore, it is a lead compound for crop protection. After analyzing the structure of tentoxin, we set out to synthesize it in only seven diastereoselective steps beginning with an Ugi-4CR employing commercially available L-Boc-Leu, methylamine, phenylglyoxal, and methyl isocyanoacetate.[5] (Scheme 1)



Scheme 1

References

1) Fulton, N.D.; Bollenbacher, K.; Templeton, G.E. *Phytopathology* **1965**, *55*,49–51.
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5) Zhu, J.; Bienaymé, H Multicomponent Reactions Wiley-VCH, Weinheim, **2005**.

Redox-Generated Mechanical Motion of Supramolecular Polymeric Actuator Based on Host-Guest Interactions

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Formation of supramolecular materials through host-guest interactions is a powerful method to create innovative materials. Here we prepared a host-guest gel (βCD-Fc gel) consisting of water-soluble polymer cross-linked with inclusion complexes between β-cyclodextrin (βCD) and ferrocene (Fc). Association and dissociation of inclusion complexes by redox stimuli led to expansion and contraction of the gel on a macroscale. The βCD-Fc gel was utilized as a redox-responsive actuator.

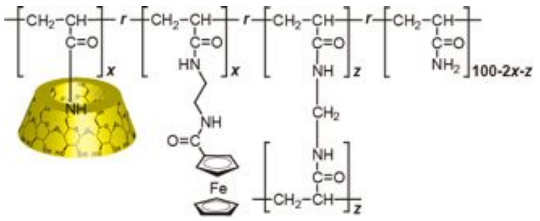


Figure 1. Chemical structure of βCD-Fc gel.

Fig 1 depicts the chemical structure of host-guest gel (βCD-Fc gel). Acrylamide (AAm), *N,N'*-methylenebis(acrylamide) (MBAAm), host monomer (βCD-AAm), and guest monomer (Fc-AAm) were copolymerized in the mixed solvent of water/DMSO(95/5). We regulated the size of the βCD-Fc gel using redox reaction. By oxidizing Fc moiety, the gel changed its color from orange to green and the length of the gel was increased. Subsequent reduction shrank the gel to the original size.This indicates that oxidized ferrocenium cations (Fc^+) were excluded from the cavity of βCD to swell the gel (Fig 2).

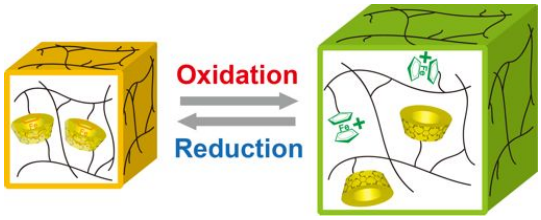


Figure 2. Schematic illustration of the expansion-contraction of the βCD-Fc gel in response to redox stimuli.

Finally, we estimated the mechanical work done by the βCD-Fc gel. A rectangular βCD-Fc gel with a weight attached at the bottom was used as a gel actuator. Oxidation expanded the gel and the weight became down. Reduced βCD-Fc gel contracted and restored the weight to the original position (Fig 3). The mecanical work done by the actuator was estimated to be ca. 2.0 μJ. In conclusion, we developed redox-responsive polymeric actuator using βCD-Fc inclusion complexes. This type of hydrogel can be applied to artificial muscles.[1)]

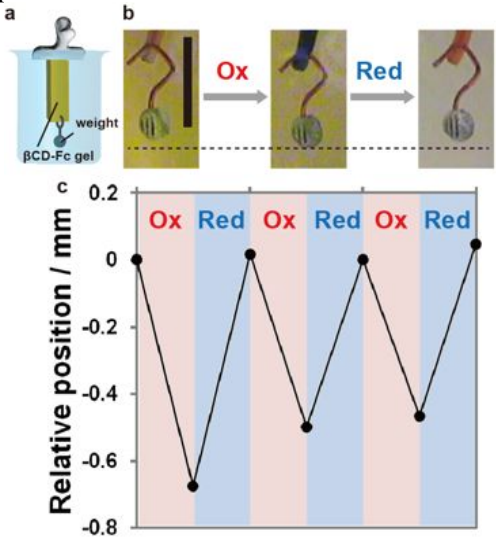


Figure 3. Schematic illustration (a), photographs (b) and the relative position of a weight (c) of a βCD–Fc gel actuator.

Reference 1) Nakahata, M.; Takashima, Y.; Hashidzume, A.; Harada, A. *Angew. Chem. Int. Ed.* **2013**, in press. (DOI: 10.1002/anie.201300862)

Graphene Oxide-Mesoporous Silica Nanohybrid: A 'Nano-Beehive' for Two-Photon Bio-imaging

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Extensive research has been focused on developing organic and hybrid materials for non-linear optics (NLO) and imaging.[1, 2] For applications such as multiphoton imaging, addressing issues such as variation in the NLO properties of organic materials when comparing to the sum of properties from isolated molecules is a challenging task.[3] In many cases, intermolecular interactions are found to be determinant to the achievement of good performance from either second order or third order (e.g. two photon absorption) materials. In contrast here we investigate the possibility reducing intermolecular interactions by loading two-photon active molecules on a two dimensional (2D) surface and demonstrate the use of these materials for bioimaging. We prepared a 2D carrier vessel by growing mesoporous silica on either sides of thin layer graphene oxide (GO) to get a hybrid material termed '*nano-beehive*'(NB). We have selected a linear donor-acceptor (D-π-A) based *π*-conjugated two-photon dye **1** and loaded inside the mesopores. Poly(acrylic acid) polymer matrix was used to coated **NB1** to prevent the diffusion of dye to outer environment, the final hybrid was named as **PAA@NB1**(Fig). Detailed materials characterization and photophysical investigations were carried out with **PAA@NB1**. The hybrid exhibits high cell viability, lower cytotoxicity and excellent two-photon emission *in vitro* indicating the potential of this new material for two-photon bio-imaging. Details of the experiments for two-photon bio-imaging will be presented in the poster.

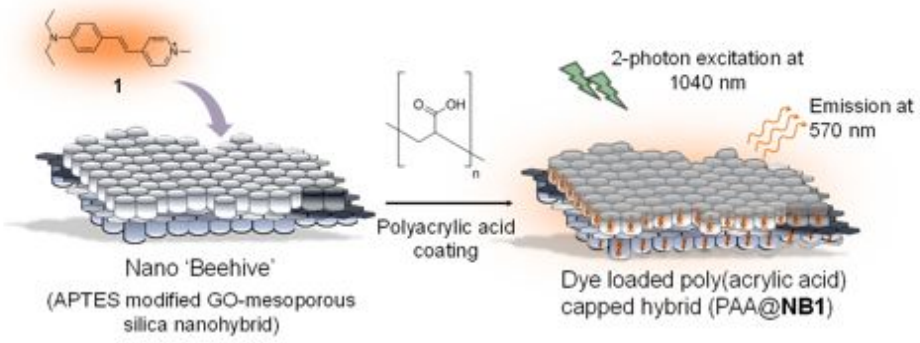


Figure 1. Scheme showing preparation of hybrid PAA@NB1. (GO refers graphene oxide and PAA refers to poly acrylic acid respectively)

References

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Self-Assembly as a Tool for Fluorescence Sensing of ATP

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Challenges underlying the fluorescence sensing of biologically important molecules have been focused on the selective detection of a target molecule from its structural analogues. As a typical example, nucleotides (AMP, ADP, and ATP) can be raised. To probe ATP, we need to differentiate it only on the basis of the net-charges from the others. However, conventional fluorescence sensors have limited precise discrimination of ATP because the defined mode of 1:1 binding operates between the receptor and the phosphate, leading to the concomitant detection of ADP and ATP. To overcome this limitation derived from the 1:1-type recognition-based sensing, the development of a novel fluorescence sensing strategy is indispensable.

The principle of self-assembly is expected to afford a new dimension to the fluorescence sensing, because subtle difference in the molecular information encoded can be amplified into the resulting self-assembled structures as an output. To utilize the self-assembly as a practical tool, we thus focused on aggregation-induced emission (AIE) dye, which is endowed to show the "turn-on" fluorescence switching in response to self-assembly formation.

We demonstrate here that synergistic marriage of fluorescence sensing and self-assembly makes selective recognition of ATP possible by a steep turn-on fluorescence response (Figure 1).[1] This allosteric-like turn-on response is utilized more generally to differentiate concerned target out of its structural analogues.[2]

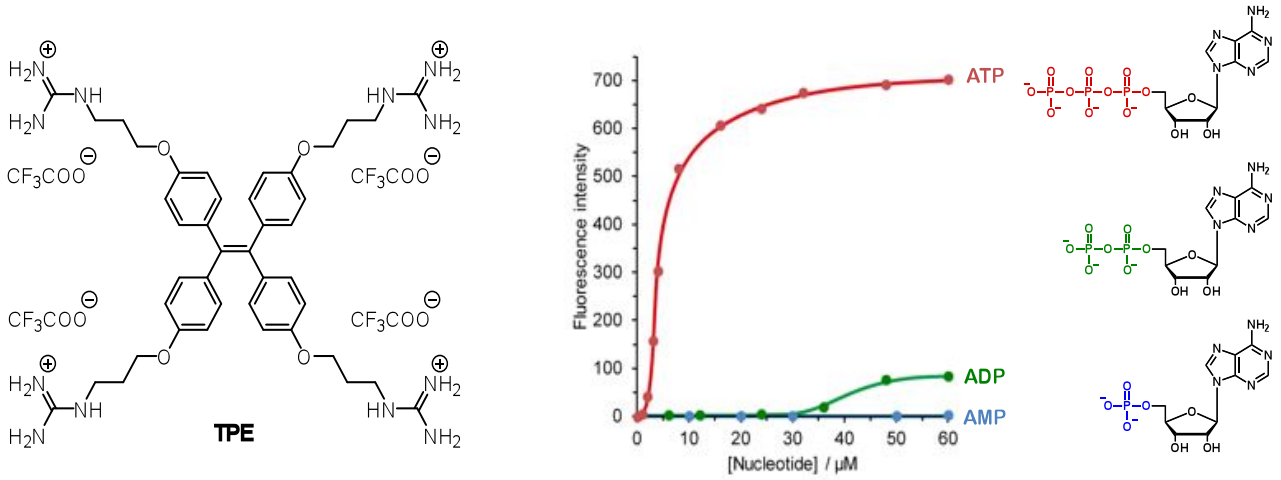


Fig 1. AIE-based fluorescence sensor, TPE and its fluorescence response toward nucleotides.

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Spiroligomer Talon Macrocycles as New Moieties for Potential Protein-Surface Ligands

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Binding to protein surfaces with synthetically-based molecules poses a unique challenge, since this inherently requires large areas to facilitate interactions. Furthermore, the use of synthetic proteins as drugs is difficult due to proteases that can process the protein before it has a chance to interact with the target. Peptoids have been shown to interact with proteins, and combinatorial libraries of peptoids have been proven to be effective in discovering new ligands for protein binding.[1] Unfortunately, peptoids are flexible molecules, and they also lack the surface area required to compete with larger protein interactions (e.g. surface interactions). To combat these problems, we have created spiroligomers that have a rigid backbone, exhibit functionality comparable to proteins, and are resistant to proteases.[2] Recently, we have developed methods to tether spiroligomers together utilizing a peptoid backbone to create 'talon' molecules that have a potential interacting surface area of over 2000 Å^2. We have also shown that these spiroligomer talons can be incorporated into peptoid macrocycles to further rigidify the peptoid backbone. The spiroligomers on this talon macrocycle could then be cross-coupled to form hinged receptors.

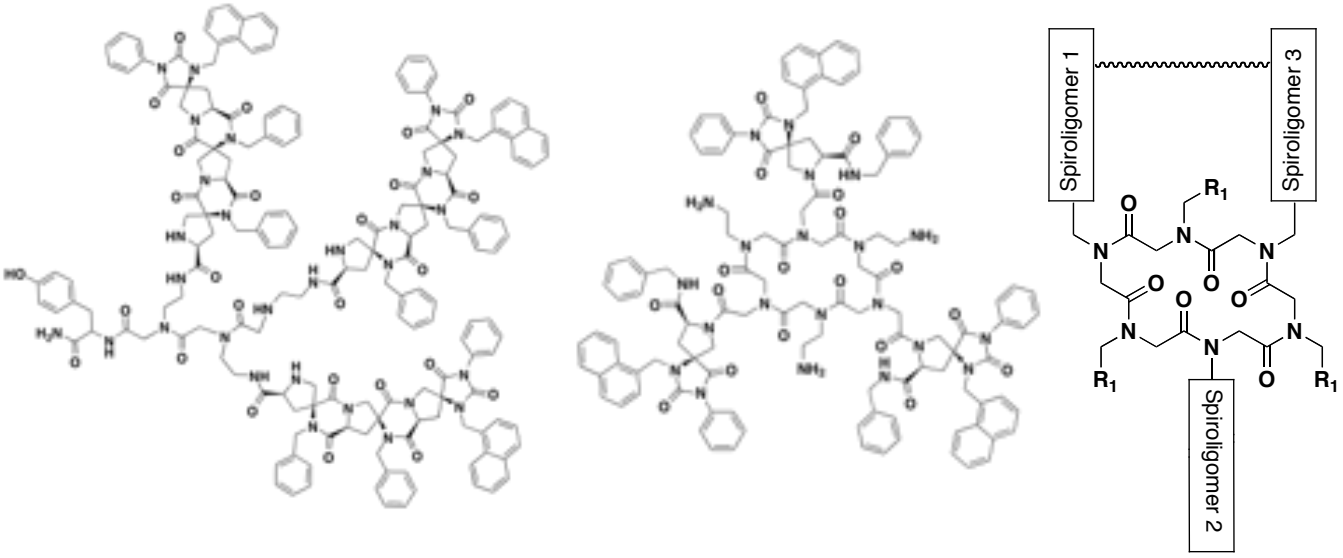


Fig 1. The molecule on the left represents a Spiroligomer Talon. The molecule in the center shows a Talon Macrocycle. The image shown on the right is a conceptual mock-up for a spiroligomer hinged-receptor.

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Tetrazole-Functionalised Calixarenes Support Lanthanoid Supraclusters

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We have recently reported the synthesis of a calix[4]arene ionophore functionalized at the lower rim with tetrazole moieties (**1**), the first example of such, to our knowledge.[1] We found that the interaction of the calix[4]arene bis-tetrazole ligand (**1**) with metal cations, when deprotonated with triethylamine or similar base, is entirely as would be expected, with the four phenol O atoms and two N atoms binding to the metal centre (Figure 1).[1] The initial aim of this work was to extend the range of ligands available to incorporate into polymeric monoliths, to produce light emitting lanthanoid-based materials.[2]

Subsequently, we have found that changing the base added to the metal – calixarene solution has a dramatic impact on the complex formed. Adding ammonium acetate resulted in the formation of large oxo / hydroxo lanthanoid clusters with unprecedented "cluster of cluster" (or supracluster) structures (Figure 1). We will discuss here the structures of these clusters, which are the first to be supported by tetrazole ligands of any type, along with preliminary investigation of their properties.

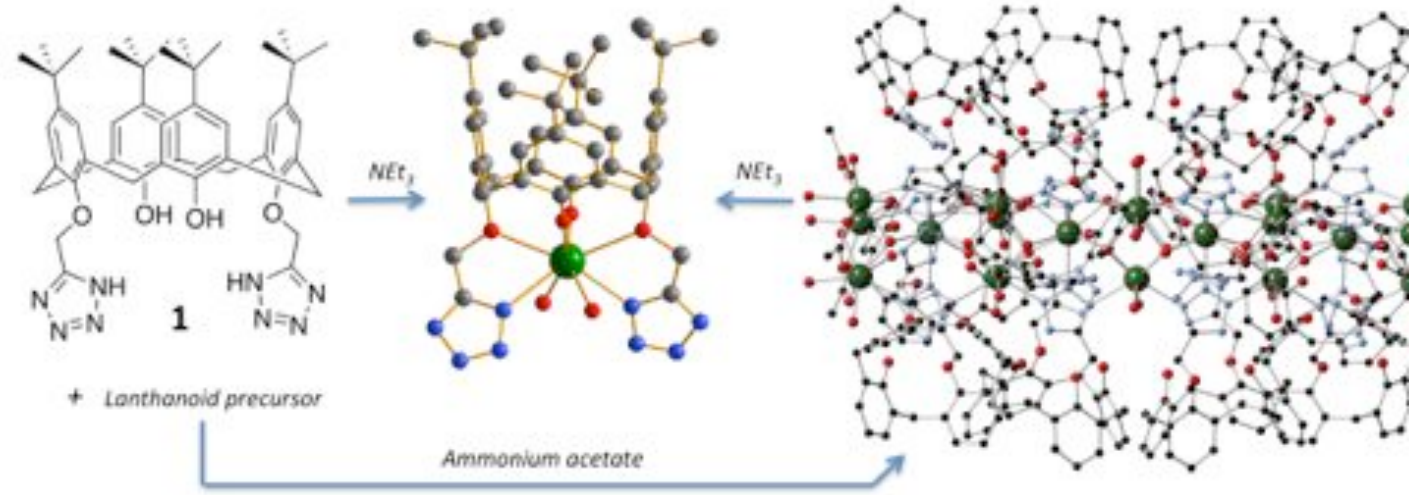


Fig 1. Bis-tetrazole calix[4]arene, **1**, forms a typical 1:1 complex in the presence of triethylamine,[1]whereas addition of ammonium acetate results in cluster formation. The supracluster shown here is $[Er_{19}(\mathbf{1}\text{-}3H)(\mathbf{1}\text{-}2H)_{11}(CH_3CO_2)_6(OH)_{26}(H_2O)_{30}]$, with t-butyl groups and H atoms removed; the supracluster core comprises of apex-fused trigonal bipyramidal clusters.

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Enantiomerically Pure Hydrogen-Bonded Supramolecular Belts

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The assembly of monomers to chiral cavities by hydrogen bonding is one of the major themes in supramolecular chemistry. Self-assembled cavity compounds can be potentially used in asymmetric catalysis and enantioselective recognition. An attractive approach to such chiral constructs is to build them from enantiomerically pure monomers.[1]

Herein, we report the first example of chiral supramolecular belt compounds that possess adjustable cavity size, assembled by using 4H bonding bicyclic C_2-symmetric monomers **1** and **2** (Fig 1).[2] The monomers undergo a unique solvent-mediated selective self-assembly to the cyclic tetramers in chloroform and to a mixture of cyclic tetramers, and pentamers in toluene, respectively. In addition, these monomers show self-sorting properties, which can be modulated by the choice of solvent or insertion of C_{60}. The exclusive formation of kinetically inert homoleptic tetrameric assemblies $\mathbf{1}_4$ and $\mathbf{2}_4$ was observed in chloroform, whereas in toluene, a mixture of scrambled tetramers and pentamers was obtained. The tetrameric belts $\mathbf{1}_4$ and $\mathbf{2}_4$ constitute a new class of efficient fullerene receptors based on unconventional π-acidic structural units that complex C_{60} and C_{70} selectively in aromatic solvents.

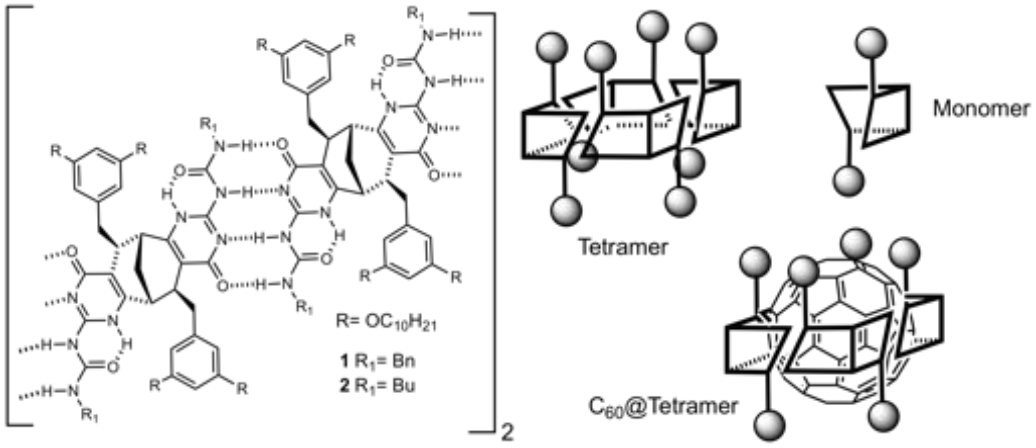


Fig. Chemical structure (left) and schematic representation (right) of supramolecular cavity tetramers (belts).

Acknowledgement: This research is funded by the European Social Fund under Global Grand measure (VP1-3.1-ŠMM-07-K-03-007).

References 1) Orentas, E.; Wallentin, C. J.; Bergquist, K. E.; Lund, M.; Butkus, E.; Wärnmark, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 2071. 2) Shi, Q.; Bergquist, K. E.; Li, J.; Lund, M.; Sundin, A.; Butkus, E.; Orentas, E.; Wärnmark, K. manuscript under preparation.

K^+- and Rb^+-Triggered Supramolecular Gels Based on Calix[4]arene Derivative: Relationship between Structure & Property

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Calixarene derivatives with multiple binding sites and flexible conformation frequently promote an effective cross-linking to form a polymeric network that is critical for gelation. To investigate the calix[4]arene derivative-based gelator, $(Et_3NH)_2{\cdot}H_2CTA$ was prepared from the reaction of calix[4]arene tetraacetic acid (H_4CTA) and triethylamine in methanol.[1] Upon addition of the aqueous solution of K^+ and Rb^+ to the methanolic solution of $(Et_3NH)_2{\cdot}H_2CTA$, the respective supramolecular gels with network structures possessing solvents were generated immediately. The K^+-triggered gel (**1**) is occurred the growth of microcrystals together with the deformation of gel with the lapse of time, whereas the Rb^+-triggerd one (**2**) maintained permanently the stable gel state. Such relative stability of both gels could arise from the structural characteristics of gels formed.

In order to investigate the structure-property relationship for gels **1** and **2**, the related single crystals of each species were obtained. According to the crystal structures, **1** and **2** exhibit a self-assembled network topologies of a typical polymer gel formed by only H-bonds and a coordination polymer gel linked by coordination bonds and H-bonds, respectively (Figure 1). In this presentation, we report the formation and the properties of the metal-triggered supramolecular gels based on calix[4]arene derivative as well as their crystal structures.

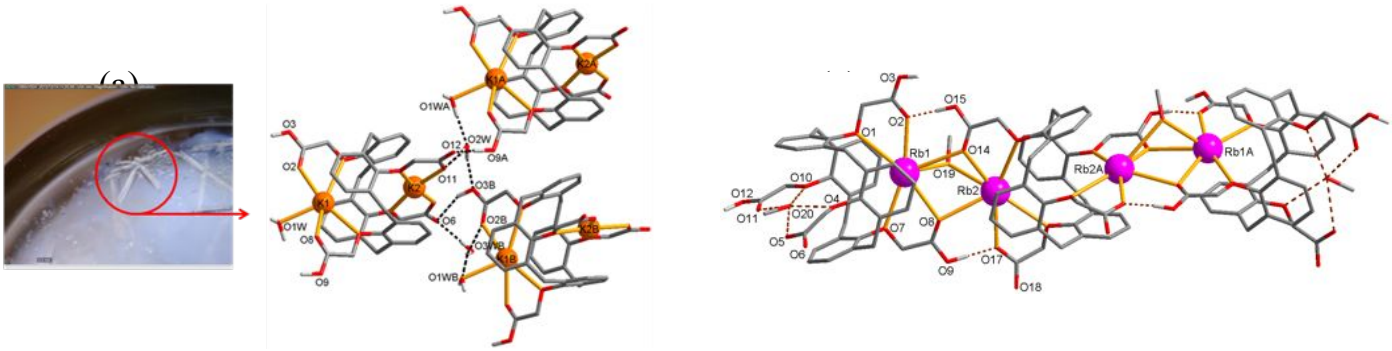


Fig. (a) Photo of crystals formed from process of sol-gel transition of K^+-induced gel and crystal structures of (b) $\{[K_2{\cdot}H_2CTA{\cdot}(H_2O)]{\cdot}(H_2O)_2\}_n$ (**1**) and (c) $\{[Rb_4(H_2\mathbf{CTA})(H_3\mathbf{CTA})_2(MeOH)_2]{\cdot}MeOH{\cdot}(H_2O)_3\}_n$ (**2**) showing H-bonds (dashed lines) and coordination bonds (yellow lines).

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Design and Synthesis of Highly Functionalized and Complex Bis-Peptide Assemblies: Progress Toward Artificial "Tertiary Structure"

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Proteins are in a category all their own as supramoleular entities enriched with both chirality and functionality. Inspired by them, we have created Bis-Peptides, a new technology for making molecules several kilodaltons in size that are also enriched with both functionality and chirality. Bis-Peptides are shape-programmable macromolecules assembled from a collection of building blocks called bis-amino acids that are connected to one another through pairs of amide bonds.[1] They serve as water-soluble, rigidified scaffolds capable of presenting collections of functional groups in different spatial orientations by virtue of the sequence, shape and stereochemistry inherent in each chiral building block. We have previously demonstrated short sequences of bis-amino acids that create "secondary structures" and locally present functional groups for applications of catalysis[2], binding protein surfaces[3], and control of election transfer in water[4], three essential processes of native proteins. In order to expand on this, we have set our sights on developing a strategy for introducing "tertiary structure" into our bis-peptide oligomers. We have synthesized linear sequences of two and three bis-peptide oligomers spaced by short, flexible linkers and cross-linked them into large macrocycles and covalently linked bundles. With these macromolecules (Fig 1), we can now position multiple functional groups with larger surface areas for mimicry of protein-protein interactions, recreate complex active sites of enzymes, and form unique, chiral pockets for host-guest molecular recognition.

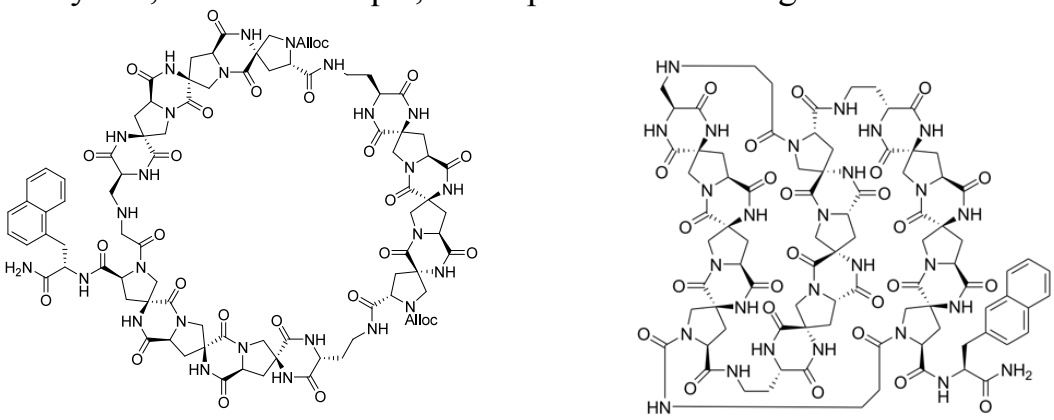


Figure 1. Examples of Bis-Peptide Macrocycles and Covalent Bundles.

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A Fluorescence Based Assay for the Study of Enzymatic Methylation of Lysine

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The installation of covalent post-translational modifications (PTMs), specifically methylation marks, has been implicated in several disease states.[1] While several methods currently exist for the detection of these PTMs, there is a strong drive for a continuous, label-free method for the study of the enzyme kinetics and substrate influence. Such a method could enable the quick examination of the "cross-talk" between PTMs in enzyme substrates and prove useful for understanding binding modes as well as drug discovery.

Using three water soluble small-molecule receptors with different affinity for trimethyl lysine, a fluorescence displacement assay has been developed to monitor the kinetics of methylation.[2] This assay takes advantage of the differential affinity each receptor has for trimethyl lysine to produce a fingerprint for each methylation state that is sensitive to neighboring amino acids and PTMs. The assay utilizes a "turn-on" event with the organic dye Lucigenin; the dye is non-fluorescent when complexed to the receptors but upon displacement by a methylated lysine, the fluorescence is recovered. This displacement can be monitored in real time, enabling the quantification of substrate effects on enzymatic activity. Qualitatively, the assay allows for rapid screening of potential new inhibitors for specific lysine methylation states.

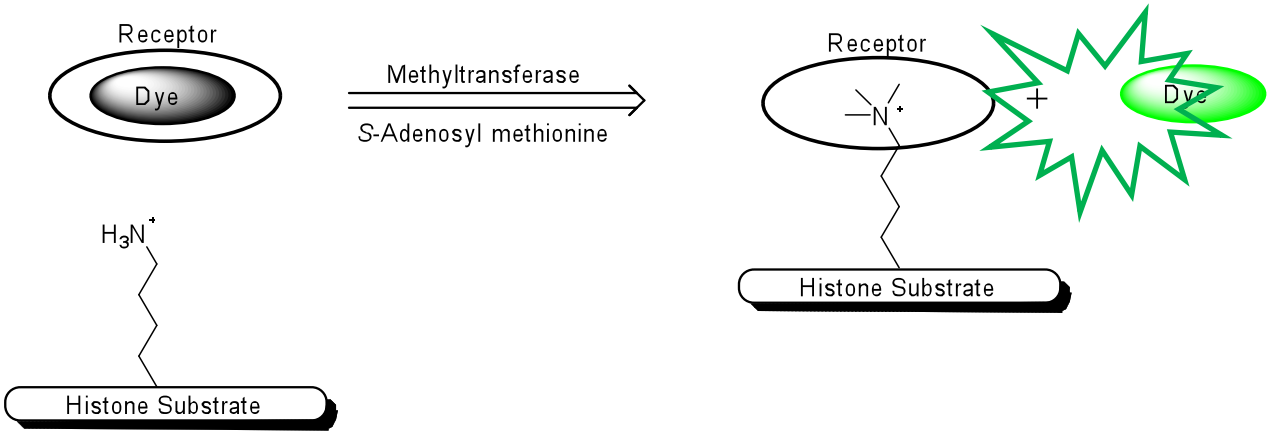


Figure 1. Fluorescence displacement assay for the enzymatic methylation of lysine.

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Thiosquaraine Rotaxanes: Synthesis, Dynamic Structure and Oxygen Photosensitization

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Photodynamic therapy (PDT) is a non-invasive cell-death therapy that relies on irradiation of a photosensitizer to generate reactive oxygen species, most notably singlet oxygen ($^1O_2$). In recent years, there has been an interest in developing near-infrared fluorophores as PDT agents, because they can be excited at longer wavelengths, allowing for deeper tissue penetration *in vivo*. Specifically, squaraine dyes have been investigated for potential PDT applications, and suitably substituted squaraines have progressed to cell toxicity and small animal model studies.[1] More recently, thio-substituted squaraines with impressive singlet oxygen quantum yields have been reported.[2] However, thiosquaraines are significantly less photostable than oxygen analogs and more susceptible to chemical degradation.

In the past, the Smith group has shown that encapsulation of squaraine dyes inside a protective tetralactam macrocycle greatly enhances the stability of the chromophore.[3] Similarly, in this work, encapsulation of a thiosquaraine derivative yielded the first thiosquaraine rotaxane (Figure 1, left) and led to a dramatic increase in stability for the thiosquaraine (Figure 1, right). Furthermore, the thiosquaraine rotaxane was found to generate singlet oxygen at a rate comparable to methylene blue (MB), demonstrating the potential of thiosquaraine rotaxanes to be used as efficient photosensitizers in PDT applications. Thiosquaraine rotaxanes exhibit novel molecular dynamic properties that are dependent on co-conformation. These properties open up the possibility of developing thiosquaraine rotaxanes as molecular machine-like devices with controlled movement.

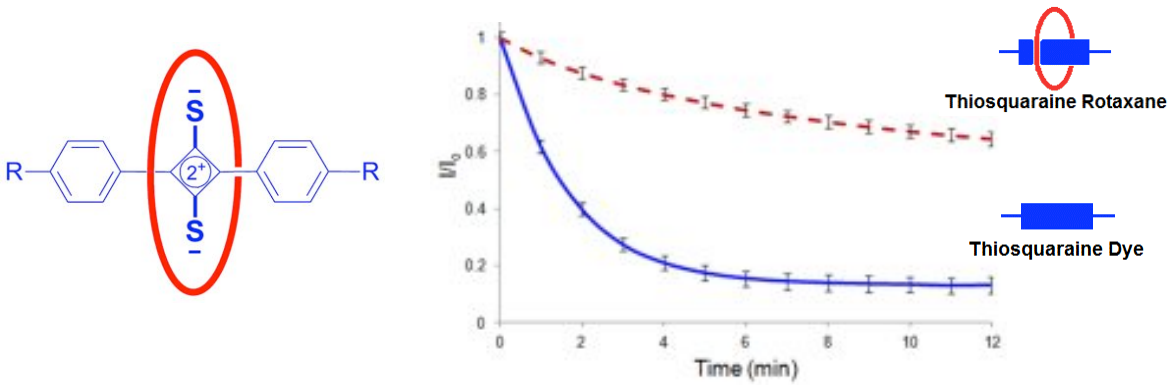


Figure 1. **Left:** General structure of thiosquaraine rotaxane. **Right:** Degredation of thiosquaraine dye and thiosquaraine rotaxane in methanol (5 μM, 25°C).

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Lipophilic Nucleoside Derivatives for Molecular Recognition and Selective Transmembrane Transport

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The unique non-covalent binding potential of nucleobases makes them desirable candidates for molecular recognition, supramolecular assembly, and small molecule transmembrane transport (Figure **1**). Guanosine, in particular, is unique in that it has both a Watson-Crick and a Hoogsteen edge, providing multiple faces for non-covalent interactions, including self assemblies.[1,2]

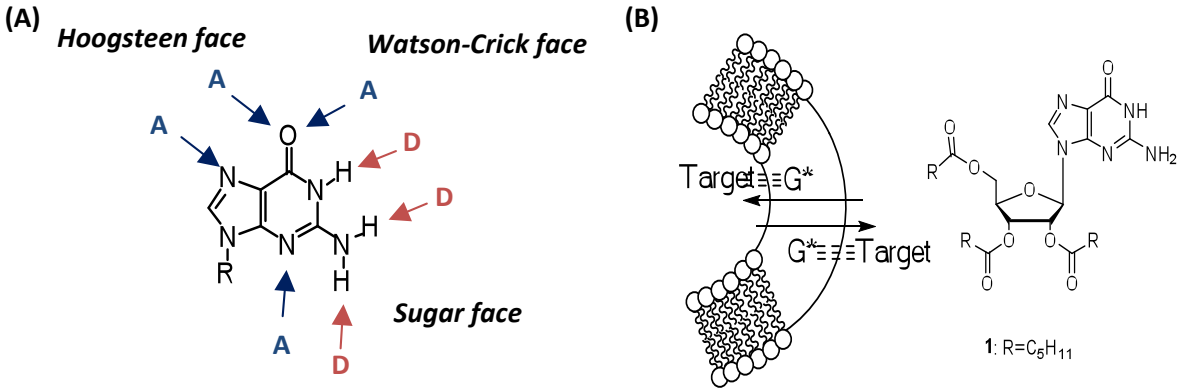


Figure 1. (A) The four hydrogen bond acceptors and three hydrogen bond donors of the G nucleobase allow for its unique ability to form non-covalent interactions with applications for molecular recognition and supramolecular assemblies. **(B)** Addition of acyl chains to the ribose increases lipophilicity and thus allow **1** to act as a transmembrane transporter.

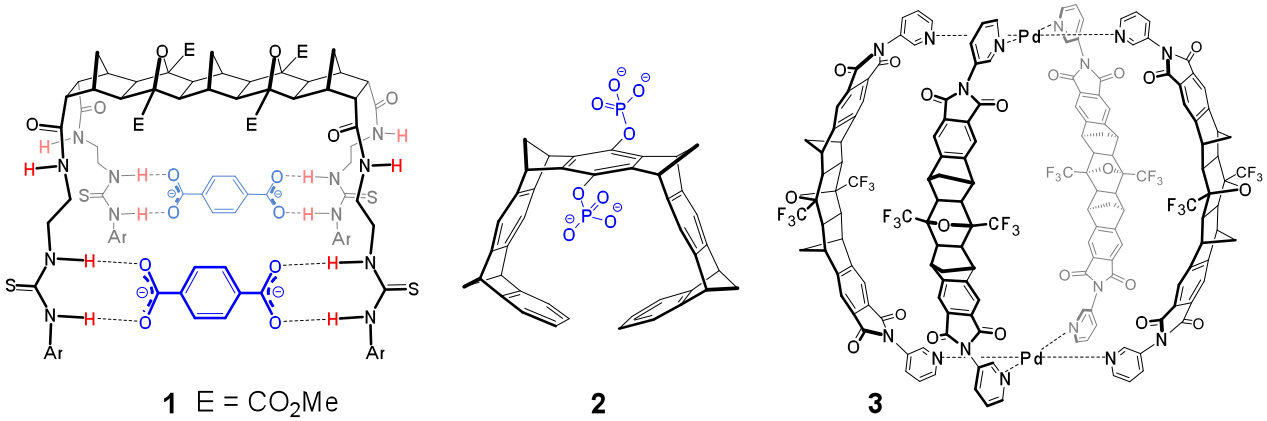
Most nucleosides and nucleoside analogue drugs are not capable of permeating the phospholipid membrane to enter cells, because of their relative hydrophilicity. Thus, membrane bound transporters are required for cellular uptake.[1] It is advantageous to enhance the biological activity of nucleosides and nucleoside analogues by utilizing artificial transporters. *O*-acylated hexanoate guanosine **1** is capable of selectively extracting and transporting nucleosides across an organic interface. The lipophilicity of the nucleoside target, specifically the structural identity of the sugar (i.e. ribose vs. arabinose vs. 2‘-deoxyribose), plays a Role in the extraction and transport selectivity. Additionally, formation of supramolecular guanosine structures, such as the G-quartet or the C-G base pair, in the organic layer inhibits the transmembrane transport of cytosine moieties. Interestingly, however, the lipophilic base pair does not inhibit, but rather enhances transmembrane transport of purines. These results provide insight towards the ultimate goal of carrying out selective small molecule transport with supramolecular structures.

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Multicomponent Synthesis of Fused Polynorbornane Frameworks for Cage Formation

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Fused polynorbornanes have proven to be valuable scaffolds in a number of supramolecular settings including both anion[1] and cation recognition[2] (**1** and **2** respectively) as well as the construction of M_2L_4 metal organic cages such as **3**.[3]



1 E = CO_2Me **2** **3**

Figure 1. Macrocyclic clefts and cages based on fused polynorbornanes.

Unfortunately these polynorbornane frameworks are sometimes overlooked due to the lengthy linear synthesis that is often required for their construction. For example 12 synthetic steps were required to construct the ligand used to construct cage **3** and hence only small quantities of the desired target were obtained.

Herein a one-pot multicomponent approach to symmetric pyridine substituted frameworks will be presented. The approach involves (i) twin 1,3-dipolar cycloaddition and (ii) imide formation. The new methodology affords the complete frameworks in good yield in less than 30 minutes. Initial experiments have indicated that these frameworks are suitable ligands to form M_2L_4 cages and it is hoped that the new approach will accelerate the development of fully functionalised variants of this interesting class of macrocycle.

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New Strategies for Dynamic Combinatorial Chemistry in Water

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Selection approaches to enable the discovery of new supramolecular receptors have been explored over the past decade, and in particular the concept of *dynamic combinatorial chemistry* has proven successful (Fig. 1).[1] It is especially challenging to identify receptors that are strong and selective in competitive solvents such as water, and the use of dynamic combinatorial libraries to achieve this is appealing.

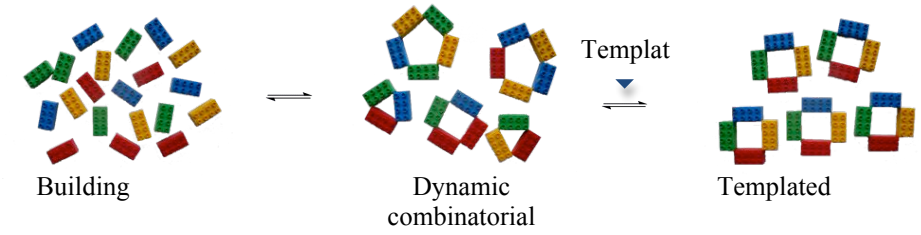


Figure 1. Dynamic combinatorial chemistry illustrated using LEGO building blocks.

Firsly, development of diselenide- and disulfide exchange chemistry for dynamic combinatorial chemistry in water will be discussed. Diselenide exchange has the advantage over other reversible reactions that it proceeds extremely quickly in water at physiological pH. Secondly, study of the reaction between biotin and formaldehyde (aminal exchange) has enabled us to identify a cyclic hexamer, biotin[6]uril, that is formed in high yield and perfect regio-isomeric purity will be described. The macrocycle binds anions in water with selectivity towards chaotropic anions (Fig. 2).

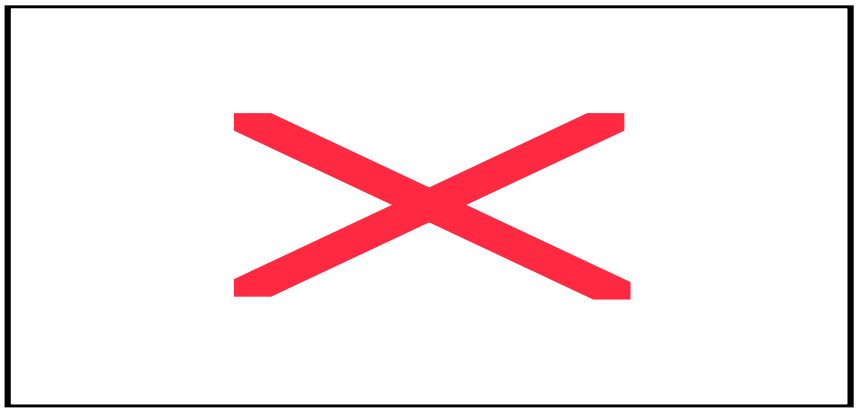


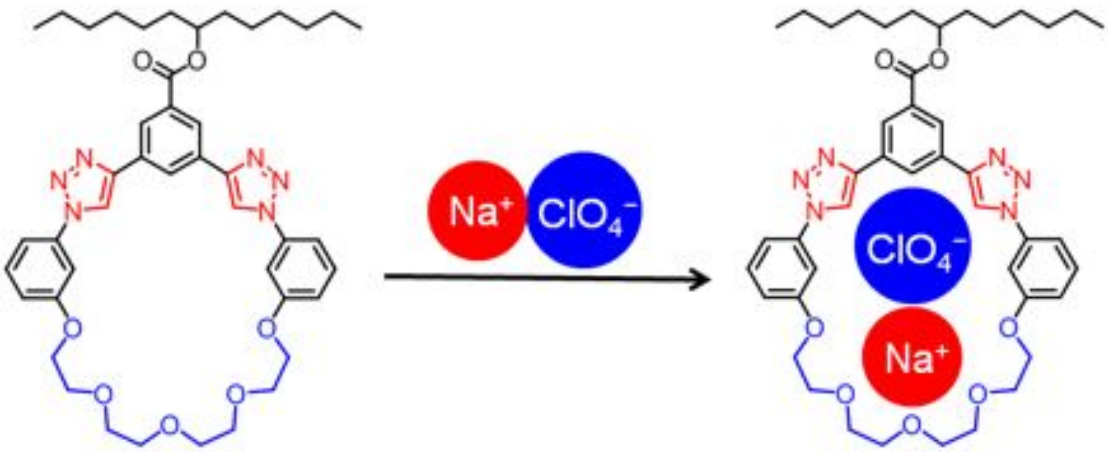
Figure 2. Biotin[6]uril, a water soluble macrocycle that binds anions.

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Aryl-Triazole Derived Janus Macrocycle as Ion Pair Receptor

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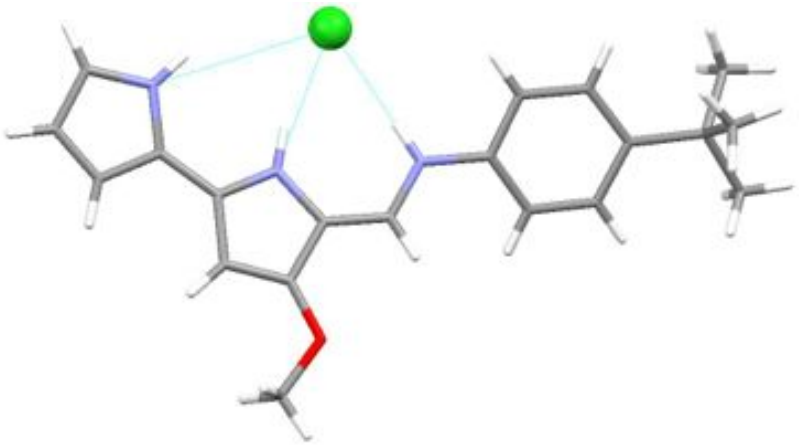
The creation of receptors that can bind ion pairs may afford unique selectivities that can be exploited in the sensing and extraction of salts in biology and chemistry. Compared to the large number of cation and anion receptors that have been developed over the past decades, the examples of synthetic molecules that can selectively bind ions as pairs are not common. To explore this area, a triazole-based macrocyclic ion pair receptor has been designed and synthesized. The Janus-type macrocycle has both hydrogen bond donors and acceptors that can face into the cavity's center. It has been found that the macrocycle binds the sodium perchlorate ion pair in a mixture of CD_2Cl_2 and CD_3CN as a 1:1:1 complex with an apparent association constant that exceeds those observed for the perchlorate anion or sodium cation alone. It is believed that the contact between the ion pairs in the complex's cavity serves as the driving force for the putative cooperativity. Progress towards characterizing the binding mode and the ion pair selectivity will be presented.



Transmembrane Anion Transport Facilitated by Small Molecules

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Facilitated transmembrane anion transport is an emerging topic in supramolecular chemistry.[1] Small molecule anion transporters are able to disturb the normal ionic balance across cell membranes inducing cell death (either apoptosis or complete cell-lytic processes), and this approach can be useful for killing cells with an abnormal growth, like tumour cells, or to eliminate harmful microorganisms.[2] Prodiginines and tambjamines are two class of natural products with anion transport properties.[3] This ionophoric activity has been linked to the biological activity of these compounds.[4] We have explored the structure-activity relationships between ion transport and biological activity of these natural alkaloids and related synthetic analogs.[5] Our latest results in this area will be presented.



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C-Ring Modifications Alter Basicity and Transmembrane Chloride Transport Ability of Synthetic Prodigiosenes

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Prodigiosin belongs to a family of tripyrrole natural products, the prodiginines, with anti-bacterial, anti-malarial, anti-cancer and immunosuppressive properties. Prodigiosin also acts as an ionophore, facilitating transport of charged ions across cellular membranes. However, in order to understand the mode of action for prodigiosin in ion transport across membranes, many analogs have been synthesized and studied over the years.

In this study, the influence of C-ring substitution on transmembrane anion transport, protonation and conformation distribution of prodigiosin and its analogs was investigated.[1] Transport experiments using EYPC liposomes showed that changes in substitution on ring C affected the transport activity of analogs. Even though the presence of an ester linkage on ring C of these synthetic prodigiosenes decreases the pK_a (6.5) and chloride transport efficiency as compared to prodigiosin (pK_a = 8.2), the analogs still exhibit a high rate of chloride transport. In fact, chloride transport by ester analogs increased as pH was decreased from 8.5 to 6.5. Further, a series of NMR experiments were used to study the inter conversion between protonated and deprotonated forms of the prodiginine analogs. The NMR experiments also revealed the change in conformations for prodigiosin and its analogs, in the presence of a counter-anion.

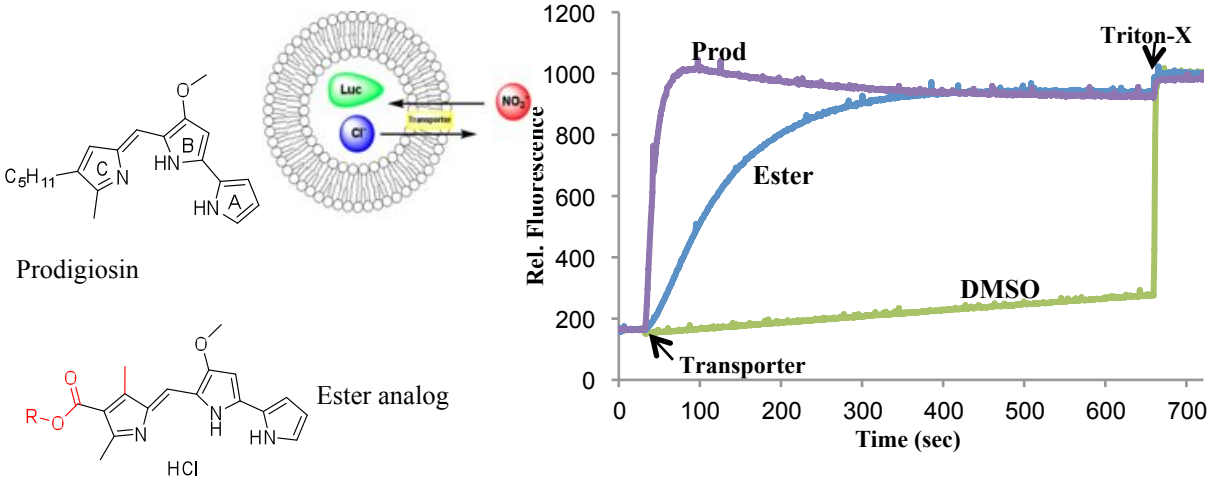


Figure 1. Anion exchange assay for prodigiosenes. Change in fluorescence due to chloride transport by prodigiosin and its synthetic ester analog in EYPC liposomes.

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Lateral Tetraazadecalin Podands: Synthesis, Structure and Unique Binding Mode

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Since the first reported *cis*- and *trans*-1,3,5,7-tetraazadecalins (*Figure 1*, **1** & **2**) and the smallest *cis*-TAD cage (**3**),[1] macrocyclic aminal systems are known by now as viable, reasonably stable and useful dynamic entities.[2] Currently, we wish to report the elaboration of diaminal podands based on *cis*-1,3,5,7-tetraazadecalin (*cis*-TAD). Beside the basic interest in their reach stereoelectronic features and concave shape of *cis*-TAD, this class of compounds comprise the skeleton of various podands capable of heavy metal ion inclusion.

The synthesis of 2,6-bis(hydroxymethylene)-*cis*-TAD (**4**) and 2,6-bis(α,α'-dimethyl-β-hydroxyethyl)-*cis*-TAD (**5**) as well as of suitably substituted 2,6-diaryl-*cis*-TAD podands is presented. For the latter, the effect of electron donating or withdrawing substituents on the benzaldehyde reagents was examined while **4** and **5** were probed and showed considerable propensity for heavy metal-ion chelation.[3] X-ray analyses of the [Cd^{II}·(**4**)] and [Pb^{II}·(**4**)] complexes show a particularly interesting 5-amino-1,3-diazane chelation type with intramolecular donor exchamge in solution. The structural and dynamic properties of the various complexes, as well as the spectroscopic characterization of the complexes by heavy nuclear NMR (^{113}Cd and ^{207}Pb) will be discussed.

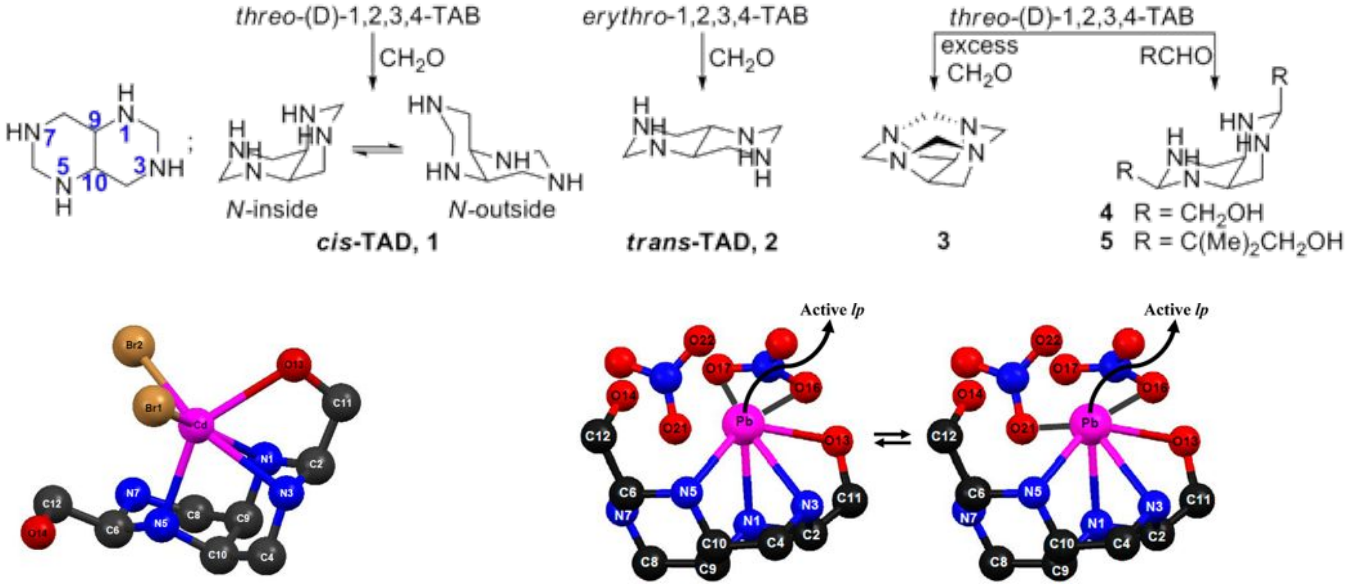


Fig 1. *Top:* 1,3,5,7-Tetraazadecalins diastereomers (*left)*, smallest *cis*-TAD cage and podands (*right*). *Bottom:* Stereoview of the X-ray crystal structures [Cd^{II}·(**4**)] (*left*) and [Pb^{II}·(**4**)] (*right*).

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A Hexadecameric Self-Assembled Ligand for G-quadruplex DNA

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Development of ligands that could target non-canonical DNA structures associated with the regulation of biological processes has recently gained a lot of interest. Particularly, the development of ligands that bind G-quadruplex DNA (QDNA) structures with high selectivity and affinity remains a challenge that must be overcome if QDNA is to become a viable target for pharmacological intervention.[1, 2] Our approach is focused on development of self-assembled ligands (SALs) where the constituent 8-aryl-2'-deoxyguanosine (8ArG) subunits form a supramolecular G-quadruplex (SGQ), which becomes the active ligand. Specifically, we report on the interactions between the hexadecameric SGQ from the 8ArG derivative-**1** and a dimer of tetramolecular QDNAs from the oligonucleotide 5'-d(TTAGGG)-3'.[3] Formation of $\mathbf{1}_{16}$ leads to a supramolecular ligand that binds to the 3'-terminal G-quartet surfaces at the interface between the QDNA dimer driven by the excellent size, shape and charge complementarity. The stoichiometry, thermodynamic stability and 3D-structure of the QDNA•$\mathbf{1}_{16}$QDNA complex were evaluated by 1D/2D-NMR, DSC, DLS and molecular modeling studies. Results of these studies have validated 8ArG derivatives as a new generation of self-assembled QDNA ligands, paving the way to our long term goal of developing similar SALs as novel supramolecular anticancer treatments, cellular imaging probes and other biomedical applications.

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Self-Assembly of Novel Amphiphilic Dendrocalix[4]arenes as Prospective Systems for Carbon Allotrope Dispersion

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Supramolecular calixarene assemblies are described in numerous reports.[1,2] Inhere we present highly water soluble, well designed amphiphilic calixarenes, with a calix[4]arene cage as a structure forming entity between the hydrophilic and the hydrophobic units. The hydrophobic sphere, built up from large aromatic systems, enables a non covalent interaction with e.g. carbon allotropes like single walled carbon nanotubes. The hydrophilic part provides water solubility at slight basic conditions up to physiological pH-values. That in turn can be exploited for subsequent highly hydrophobic self associating processes. The extraordinary T-shaped structure affords highly efficient self aggregation phenomena down to concentrations as low as 10^{-6} mol/l and is elaborated using a calix[4]arene, carrying highly fluorescent perylen moieties. These large aromatic building blocks offer the opportunity to screen and characterize the molecules by numerous analytic methods like uv/vis-spectroscopy.

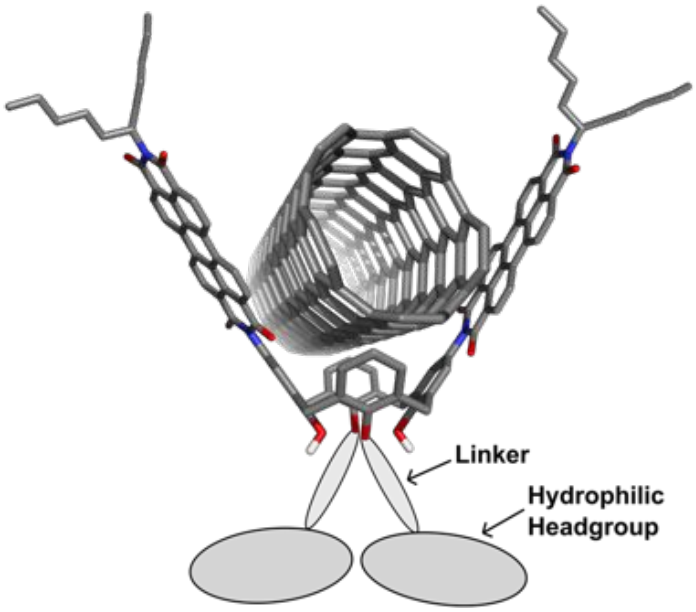


Figure 1. Schematical presentation of a van-der-waals interaction between novel, highly functionalized watersoluble calix[4]arene derivatives and single walled carbon nanotubes.

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Solid-to-Solid Expansion of Pyridyl *Bis*-Urea Crystals

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Materials that contain open channels and pores like, zeolites, porous aluminosilicates as well as synthesized metal organic framework, display microporosity. Seemingly non-porous solids can also have the ability to transport or uptake guests by changing their three dimensional structures. In self-assembled structures, the supramolecular interactions between the building blocks may alter or shift in the presence of guests. We synthesized *bis*-urea pyridyl macrocycles[1] that assemble via urea-urea hydrogen bonding and π-π stacking to afford closed pack one dimensional solid pillars with no pores.[2] We showed that despite the lack of pores, these seemingly nonporous pillars can expand in presence of polar guests. One urea oxygen lone pair, remain unsatisfied during the pillar formation. A guest that satisfies this interaction can drive its absorption to generate well-ordered host:guest complexes with repeatable stoichiometry. For example, hydrogen bonding interactions between guest alcohols and unsatisfied urea lone pairs were observed in the solid complexes and are likely the driving force for these solid-to-solid transitions. Halogen bonding can also be used to induce absorption.[3] This presentation will describe how the organic solids are dynamic in nature in the presence of some guest molecules.

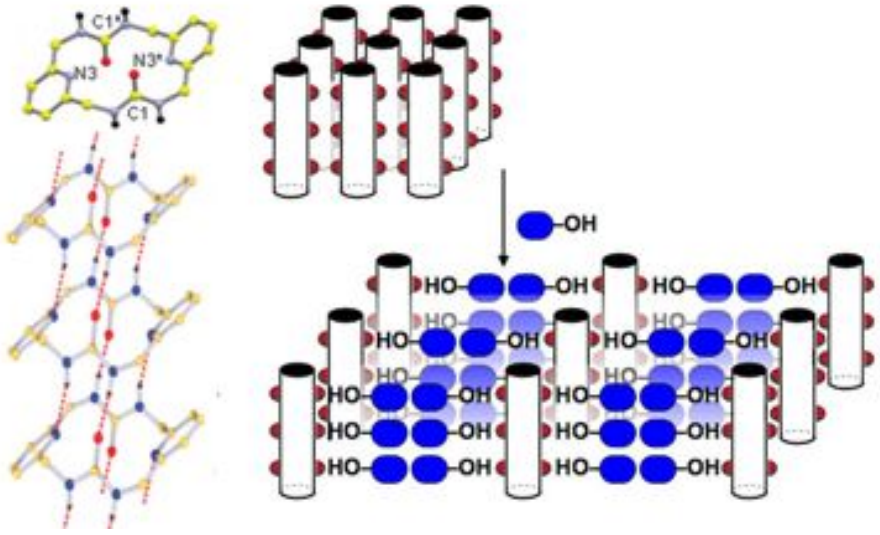


Figure 1. Expansion in the Solid State

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Calixarene-Based Solid Lipid Nanoparticles: DNA Binding, a Sequence-Dependent Interaction

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Successful gene therapies require the design of efficient vectors to deliver DNA to its target.[1] Many synthetic amphiphiles used as non-viral vectors have been developed. Among them, calixarenes, are very attractive molecules. Indeed, their conical structure allows regioselective modification, and therefore the design of complex amphiphiles.[2] One of challenges in gene therapies is the transfection rate. A natural cationic biopolymer like chitosan able to interact with anionic molecules as nucleic acids can increase the amount of DNA delivered into the cell.[3] In this poster, we report on a new cationic amphiphilic calixarenes able to interact with DNA as solid lipid nanoparticles (SLNs) in water.[4] A calix[4]arene, functionalized with four guanidino moieties as recognition site, and four dodecyl chains as hydrophobic part has been synthetized and was able to self-assemble in water as nanoparticles. We demonstrated that the interaction between these nanoparticles and DNA is not purely electrostatic, but is also a groove binding mechanism. To deliver DNA into the target cell, the SLNs were modified to pass through the cell membrane. Successive layers of DNA-chitosan were added around the calixarene-SLNs via the layer-by-layer technique. Our results highlight the importance of the double-stranded DNA sequence upon interaction with calixarene-based SLNs.

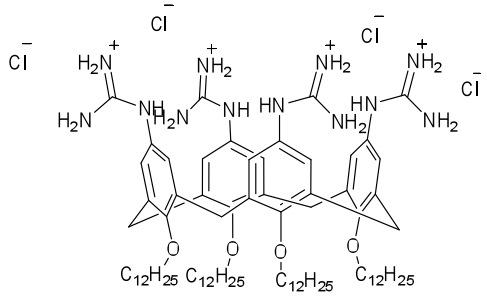


Figure 1. Para-guanidino-calix[4]arene.

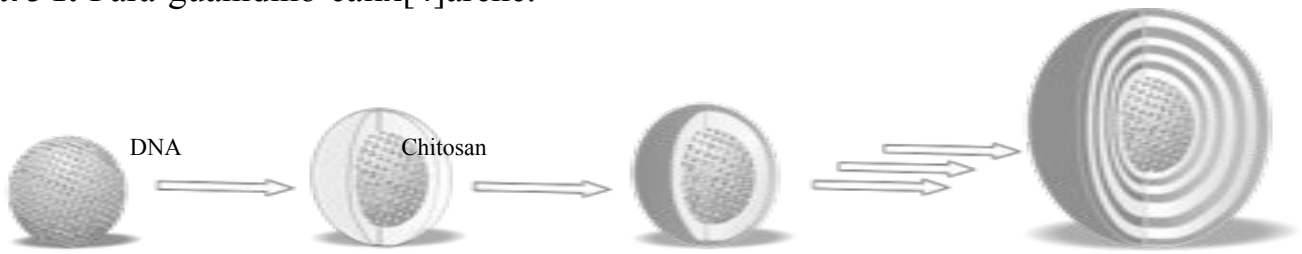
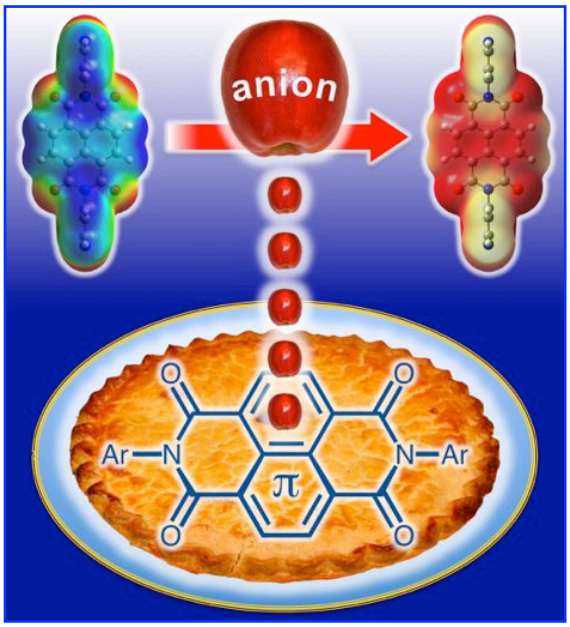


Figure 2. Layer by Layer assembly of DNA-chitosan onto calixarene-based SLNs.

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Boundaries of Anion/π-Acid Interactions: From Anion–π and Charge Transfer Interactions to Thermal and Photoinduced Electron Transfer Events

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The recent discovery of anion–π interactions has added a new dimension to anion recognition chemistry.[1] In this presentation, I will demonstrate that depending on the Lewis basicity of anions and π-acidity of electron-deficient receptors, e.g., naphthalenediimides and perylenediimides, modes of anion/π-acid interactions vary between four distinct pathways:[2] (1) strongly Lewis basic anions (hydroxide, fluoride, cyanide) trigger thermal ET to π-acids generating corresponding radical anions and dianions, (2) moderate Lewis basic anions (acetate and choride) undergo photoinduced ET that produces radical anions of π-acids, (3) poor Lewis basic anions (bromide, iodide) form CT complexes (no radical anion was formed), and (4) non-Lewis basic anions (triflate, perchlorate) form nonchromogenic anion–π complexes. Extensive spectroscopic data[2–4] backed-up by advanced theorical studies[4,5] have not only established formal ET from Lewis basic anions to neutral π-acceptors as a new paradigm of supramolecular chemistry, but also challenged a log-held notion that these anions can only attack as nucleophiles[6] instead of triggering ET to π-acids. While anion-induced ET has been already exploited for colorimetric sensing of toxic anions[2,3] and the synthesis of NDI-based conjugated polymers,[7] noncovalent anion/NDI interations could be used for template directed synthesis of MOFs and cooperative binding and release of ion-pairs.

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Thiolate-Protected Nanoparticles *via* Organic Xanthates: Fundamental and Practical Aspects

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Herein I want to present a new route for attachment of functional ligands to gold nanoparticles (NPs) *via* covalent Au-S bond by using organic xanthates.[1] In its classical, commonly used version, the functionalization of NPs is achieved using thiols that possess desired functional groups.[2] However, the classical method has serious limitations because, due to high nucleophilicity of SH group, preparation of ligands incorporating many important functional groups is impossible. My method enables to circumvent the thiol incompatibility problem. By employing the xanthate approach I was able to introduce onto NP surface ligands containing thiol-sensitive olefin and acetylene functionalities, which offer a powerful tool for further NP chemical transformations, such as metathesis, click chemistry, or polymerization.

My studies provided also an insight into the fate of hydrogen under exposure of thiol to gold - a fundamental puzzle of the nanoscience. Since the discovery of the self-assembly of thiols on gold surfaces (mid 1980's), hydrogen was widely believed to leave the thiol in a molecular form (H_2). However, by studying the mechanism of Au-S bond formation, I found that the hydrogen releases as a proton (H^+). Obtained results indicate that the behavior of hydrogen depends on the local chemical environment, and the current views on the Au-S bonding mechanism must be revised.

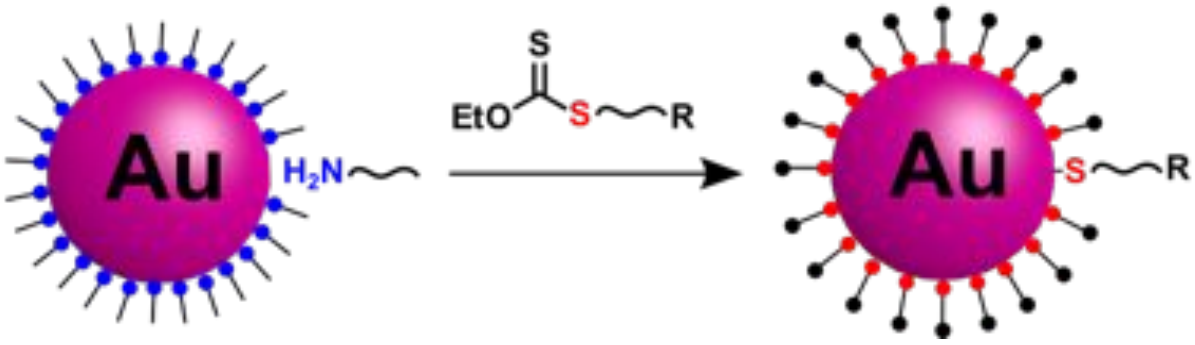


Figure 1. Schematic illustration for the preparation of thiolate-protected NPs from xanthates

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A Crystalline Folded Peptide Coordination Network with Nanometer-Size Channels

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Construction of crystalline coordination networks with large cavities has been carried out only by use of rigid organic ligands so far. In this work, we successfully created such a structure from a flexible oligopeptide ligand by using a concerted self-assembly process of networking and folding. A flexible peptide ligand of the Gly-Pro-Pro sequence was folded into the collagen helix conformation and also three-dimensionally networked during metal coordination, which resulted in a crystalline peptide material containing nanometer-size cavities.

The tetrapeptide with N- and C-terminal pyridyl groups (ligand **1**, Figure 1A) was treated with Ag(I) ion in aqueous ethanol. Colorless block single crystals **2** were obtained after one week at room temperature (Figure 1B). X-ray diffraction analysis revealed the formation of an infinite honeycomb structure of $[\mathbf{1}–\mathrm{Ag(I)}]_n$ complex (Figure 1C). In **2**, both two types of the peptide ligands were revealed as the typical collagen helix conformation (Figure 1D, dihedral angles of each residue; ω=180º, $-64º<\varphi<-74º$, $149º<\psi<173º$). Such folded-peptide ligands chains were hexagonally entangled, and as a result large helical channels (diameter: 2 nm) were formed along crystallographic *c* axis.

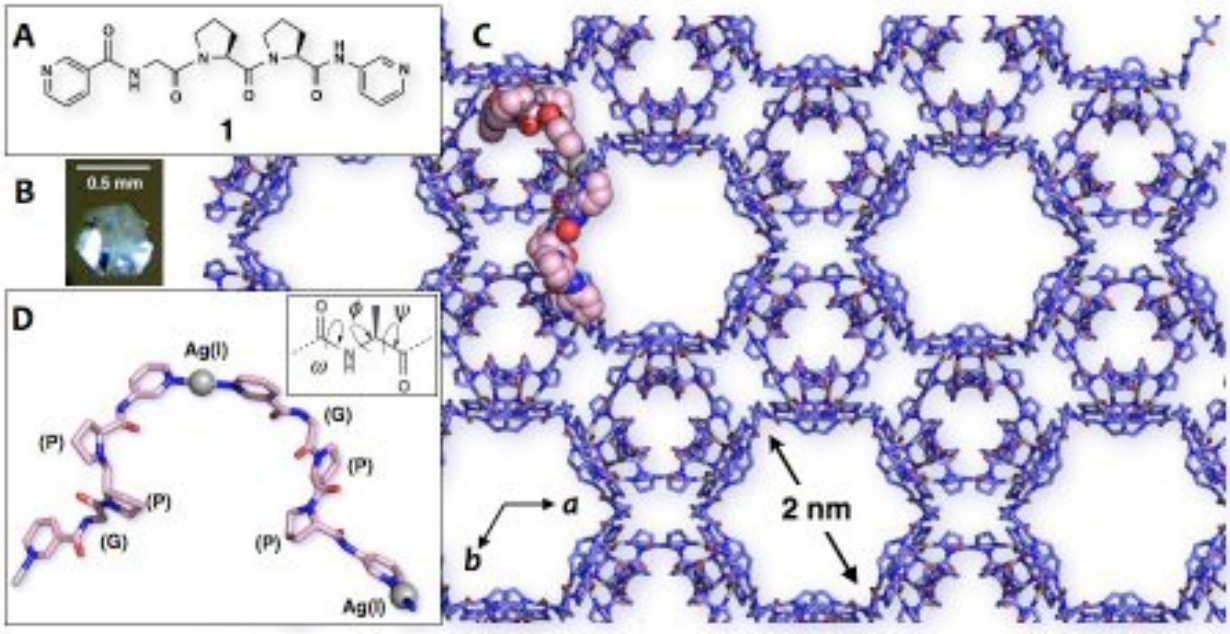


Figure 1. (A) Ligand **1**, (B) photograph of single crystal **2**, (C) crystal structure of **2** (solvents and counter anions were omitted for clarity, space-filling representation shows the asymmetric unit), and (D) close-up of peptide ligands conformations in **2** (*inset:* peptide dihedral angles).

Macrocycles as Building Blocks for Functional Nanostructures

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Macrocyclic compounds with a range of different constitutions, sizes, and shapes play an ever-increasing role in chemistry and nanotechnology.[1] To push the applications of macrocyclic chemistry further into the future, we are creating novel macrocycles designed to act as rigid building blocks for nanostructures with selectively functionalized cavities and well-defined shapes. Of particular interest are semi-conducting nanostructures with tubular shapes, which might find applications in catalysis, as chemical and mechanical sensors, as components of miniature electronic devices, and as vessels for targeted drug delivery systems in the fullness of time. This presentation will focus on the family of the newly discovered asararene macrocycles,[2] which were specifically designed to form tubular, semi-conducting nano-assemblies held together by coordinative metal-ligand bonds (Figure 1a). Asararenes with 6–12 aromatic units have been synthesized and isolated as pure crystalline compounds and their solid-state superstructures have been elucidated by single crystal X-ray diffraction. In the solid-state superstructure of asar[10]arene (Figure 1b), for example, the individual macrocycles stack on top of each other to form cylindrical nanotube-like channels packed together in a regular checkerboard array. In addition, triangular, shape-persistent macrocycles, composed of naphthalenediimide (NDI) units exhibiting intriguing redox-behavior will be discussed.

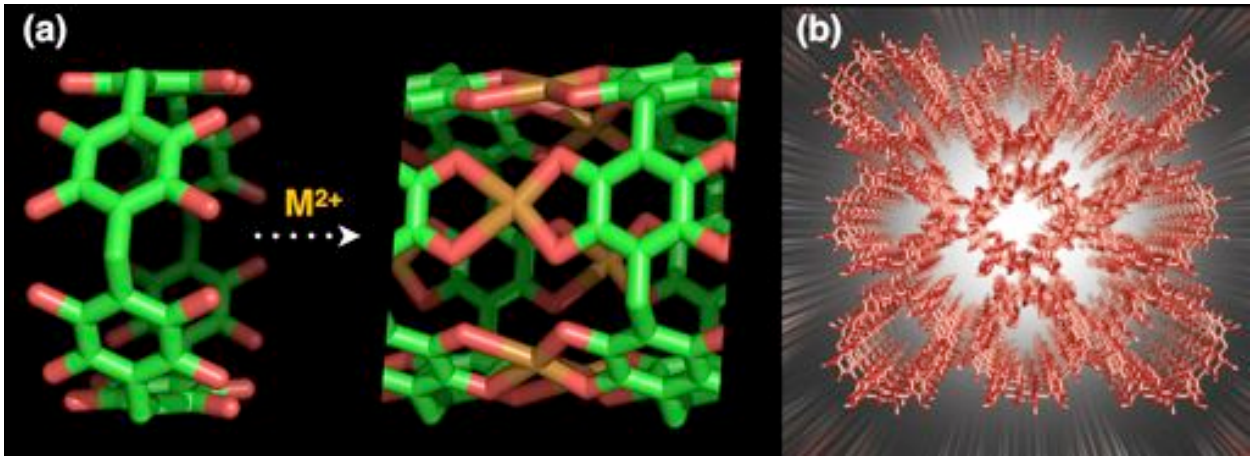


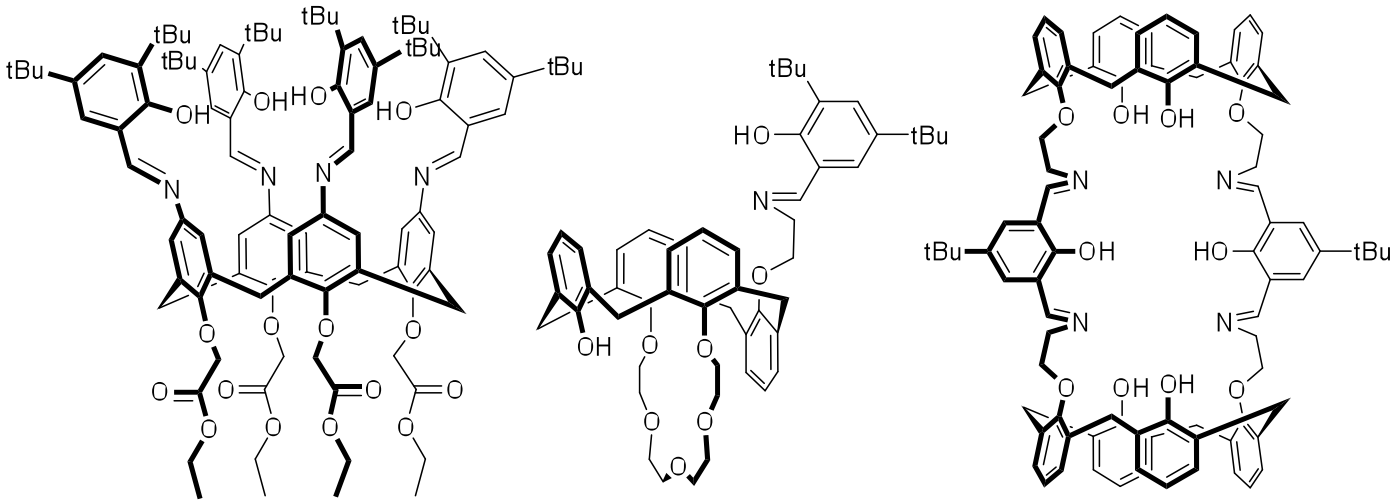
Figure 1. (**a**) Proposed assembly of asar[6]arene macrocycles into semi-conducting nanotubes. (**b**) Illustration of the solid-state superstructure of asar[10]arene.

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Calix[4]arenes as Scaffolds for Salicylidene and Robson-type Ligands

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Calix[4]arenes are very interesting host molecules and their conformational properties have been widely exploited to induce selectivity in the recognition of ions and neutral molecules.[1] Moreover, calix[4]arenes have been found to be excellent building blocks in supramolecular chemistry for the design of versatile receptor sites.[2] They can be selectively functionalized both at the phenolic hydroxyl groups (*lower rim*) and at the *para* positions of the phenol rings (*upper rim*) and thus, groups with divergent chemical and physical properties may be readily introduced at either face. Our groups interest has its focus on the coordination chemistry of binucleating Robson-type polyaza-phenolate and -thiophenolate ligands,[3] and given the many applications of calix[4]arenes, we became interested in calix[4]arene-based derivatives of these versatile ligand systems.



L¹ **L²** **L³**

Figure 1. Bifunctional Calix[4]arenes with Salicylidene and Robson-type binding sites.

Hence, we do not use the calix[4]arene itself as ligand or receptor, but as scaffold that bears two coordination sites with various chemical affinities, leading to bifunctional complexing agents, in which salicylidene or bis(iminomethyl)phenol units are attached to the *lower* or *upper rim*. Their synthesis, characterization and complexation behavior will be reported.

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Stimuli-Responsive Supramolecular Nanofibers Consisting of Non Stimuli-Responsive Molecules

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Stimuli-responsive supramolecular nanofibers composed of π-conjugated molecules have attracted attention because their promising properties, such as light-harvesting, photoluminescence and conductivity are controlled by external stimuli. Therefore, they are expected as a smart material for optoelectronics. To make supramolecular nanofibers, stimuli-responsive groups such as photo-responsive azobenzene, diarylethene and electro-responsive tetrathiafulvalene groups are needed. To date, various stimuli-responsive supramolecular nanofibers using stimuli-responsive groups have been reported. Most of them show transformations between nanofibers and amorphous assemblies. This is because superstructures are much affected by changes of molecular shapes and electron states. Therefore, nanofiber-to-nanofiber transformation is rare despite their potential utility as a smart material.

On the other hand, we found that nanofiber-to-nanofiber transformation of dehydrobenzoannulene (DBA) **1**[1,2] (Figure 1) which has only DBA core and two methyl ester groups. This phenomenon is surprised us because DBA **1** has no stimuli-responsive groups and ultrasound is not recognized as a stimulus for transformation of molecular arrangements. Furthermore, the obtained two nanofibers showed much different conductivity although they are constructed from same molecules. In this work, we discuss the reason why such a simple compound constructs stimuli-responsive supramolecular nanofibers and they showed drastically different conductivity.

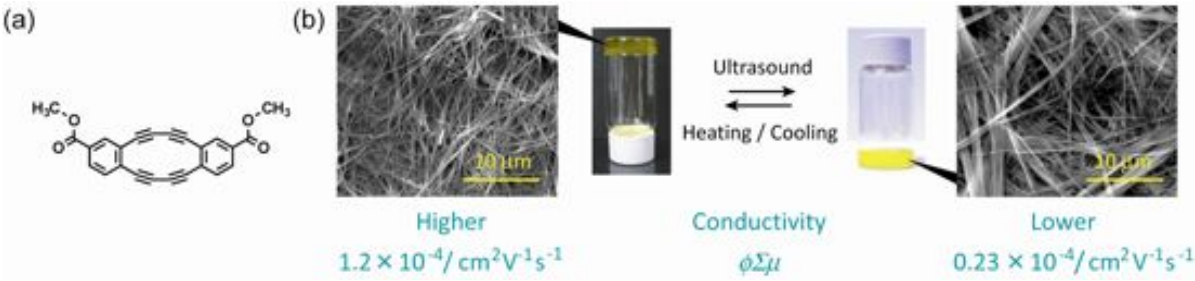


Figure 1. (a) The chemical structure of DBA **1**. (b) The response of the supramolecular nanofibers of DBA **1** to heat and ultrasound. The grayscale photos are SEM images of air-dried materials of the gel and suspension.

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A Versatile Model System for Studying Non-covalent Interactions of Aromatic Surfaces

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Non-covalent interactions of aromatic surfaces are important to the function of many synthetic and biological systems.[1] Yet, the fundamental origins and stability trends of these weak interactions are still a subject of considerable study and debate. One reason is the lack of accurate and comprehensive experimental data. To address this problem, we developed a small molecule model system that can form and accurately measure the strength of intramolecular interactions of aromatic surfaces.[2] Due to a central N-arylimide single bond with restricted rotation, the rigid bicyclic framework is in equilibrium between *folded* and *unfolded* confirmations, which can and cannot form the intramolecular noncovalent interaction. Thus, measurement of the folded/unfolded ratio by ^{1}H NMR integration provides a measure of the interaction of interest. Due to the synthetic versatility and ease of preparation, we have applied this model system to study a range of noncovalent interactions of aromatic services including: face-to-face π-stacking,[2] edge-to-face π-stacking, CH-π,[3] deuterium(CH)-π,[4] halogen-π, heterocyclic π-stacking, cation-π and lone pair-π interactions.

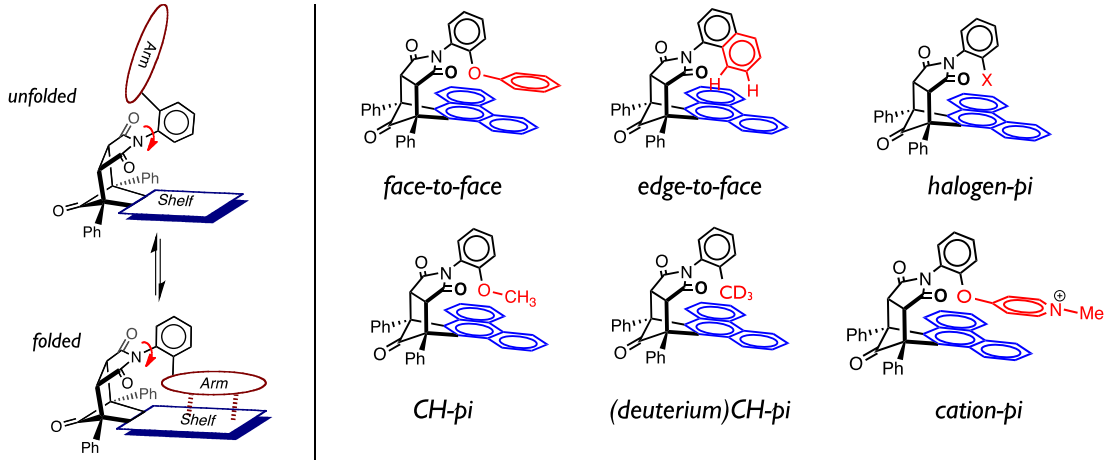


Figure 1. (*left)* Schematic representation of our molecular balance for measuring non-covalent interactions of aromatic surfaces. (*right*) Specific examples of

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Anions as Supramolecular Polymer Crosslinkers

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The self-assembly of polymers through interchain interactions is an area of current interest in materials chemistry.[1] The intrinsic material properties of polymeric systems, such as the material strength and elasticity or nanoscale patterning, can be altered by fine-tuning these interactions.[2] Through these means, the reversibility and strength of polymer cross-linking has been investigated using such molecular interactions as hydrogen-bond donor-acceptors, charge-transfer interactions, and cation-crown ether associations.[3,4] We wish to add another instrument to this molecular toolbox by developing anion-neutral receptor interactions. In our previous work we synthesized poly(methyl methacrylate) copolymers containing neutral receptors, including calix[4]pyrroles, a well-known set of anion binding agents. In this work, we have utilized controlled radical polymerizations to synthesize poly(calix[4]pyrrole-*co*-MMA) polymers and studied their crosslinking with various mono- and bis-anions (e.g. fluoride and terephthalate).[5] The systems demonstrate a noticeable increase in viscosity, as measured by Ubbelohde viscometry, when titrated with increasing amounts of bisanions. In addition, the solid-state films of the supramolecularly cross-linked polymers were studied by dynamic mechanical analysis (DMA) to determine the changes in storage modulus and T_g.

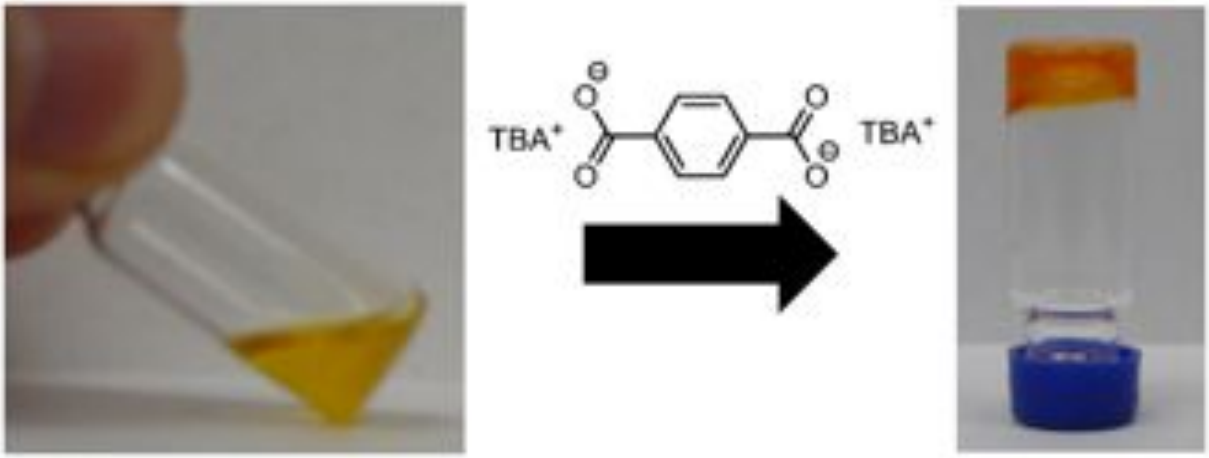


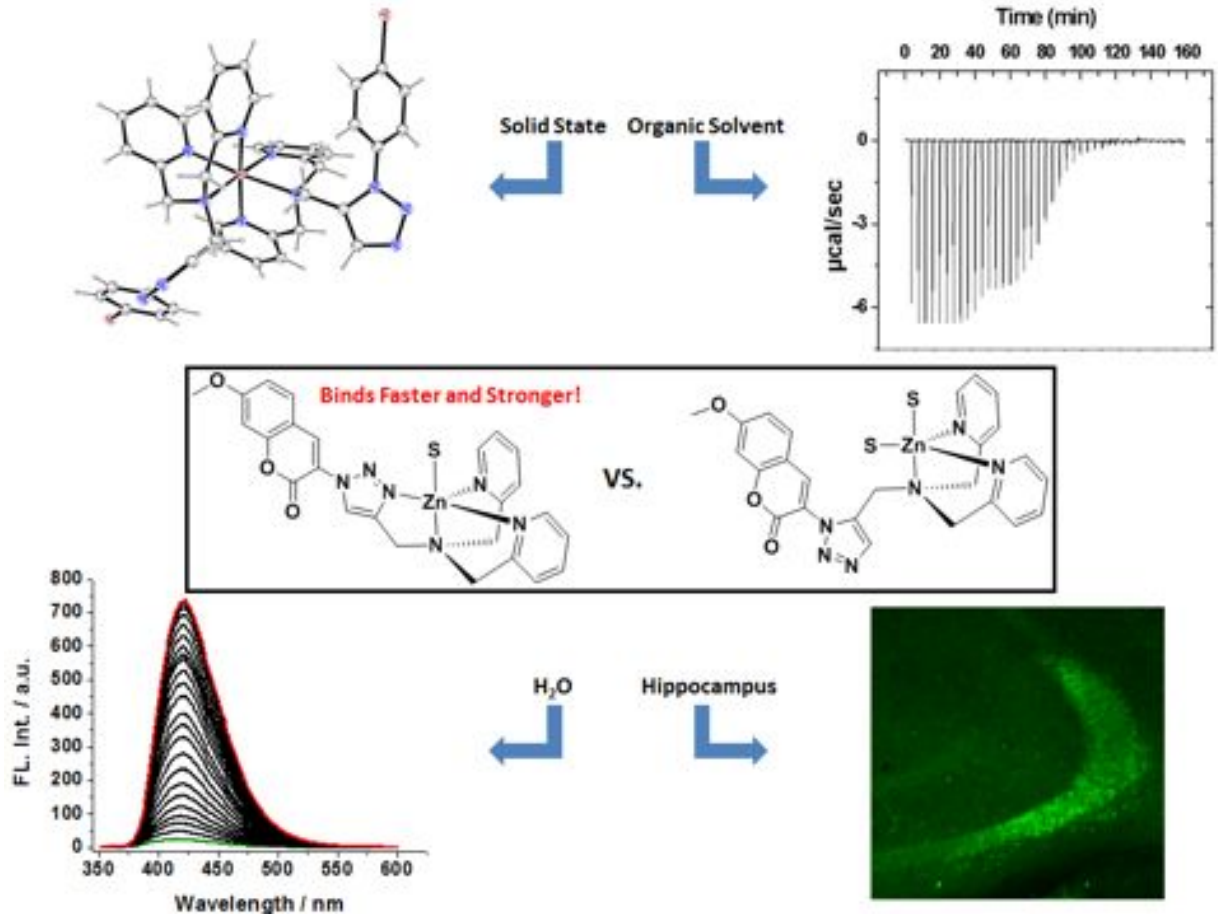
Fig Polymer solution becoming a gel upon addition of bis(tetrabutyl ammonium) terephthalate.

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Integrated and Passive 1,2,3-Triazolyl Groups in Fluorescent Indicators for Zinc(II) Ions – Thermodynamic and Kinetic Evaluations[1]

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The 1,2,3-triazolyl group is now receiving considerable attention as a versatile ligand for metal ions. In this work, we investigate the thermodynamic and kinetic effects of incorporating the 1,2,3-triazolyl moiety within a multidentate ligand scaffold for zinc(II) ions. In order to achieve this, different isomeric triazolyl-containing compounds were utilized. The 1,4-substituted triazoles participate in binding within a multidentate ligand system and are classified as integrated binders. Their isomeric, 1,5-counterparts do not participate within the chelation unit and are termed passive linkers. The effects of incorporating triazolyl binding were studied in the solid state, quantified in both organic and aqueous solvents, and investigated in live cell and hippocampal imaging experiments. The results found in this study should prove beneficial to future ligand design where the triazolyl moiety is to be used.



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Towards a Supramolecular Protecting Group Strategy Applied to Solid-State [2+2] Photodimerizations

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The use of principles of supramolecular chemistry to direct reactions in the crystalline state has emerged as a reliable means to control and direct organic synthesis of molecules in solids. In this context, chemists have utilized fixed spatial arrangements of molecules in crystal lattices to promote intermolecular [2+2] photodimerizations. A supramolecular approach to overcome packing effects that typically leads to photostability is to preorganize olefins for [2+2] photodimerizations using hydrogen-bond templates. Understanding features that control molecular packing within a crystalline lattice is crucial if solid-state synthesis is to be conducted by design.

In this presentation, we will describe our efforts to develop a supramolecular protecting group strategy to direct [2+2] photodimerizations of olefins decorated with alkoxy- groups. 4-(2-(4-methoxyphenyl)vinyl)pyridine (**1**) and 4-(2-(3,4-dimethoxyphenyl)vinyl)pyridine (**2**) were individually co-crystallized with a variety of resorcinol-based templates, and we have discovered preferences for edge-to-face packing within the discrete assemblies. Additional supramolecular protecting groups and templates will be discussed.

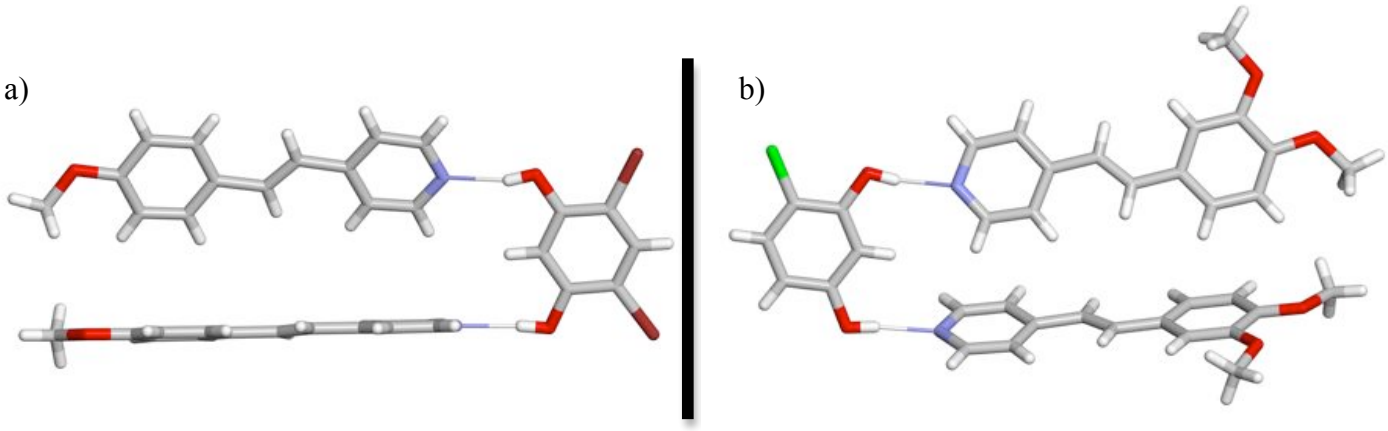


Figure 1. X-Ray structures of (a) 2(**1**)·4,6-dibromoresorcinol and (b) 2(**2**)·4-chlororesorcinol showing edge-to-face packing.

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Rapid Synthesis of Covalent Organic Frameworks from Homogeneous Conditions and Kinetic Characterization

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The emerging class of porous, crystalline materials known as covalent organic frameworks (COFs) offer high surface areas, low densities, and preparation from designed molecular building blocks. Despite expanding interest in these materials, limited work has examined the mechanism of COF formation, in part due to the difficulty in characterizing the heterogeneous suspensions associated with COF growth. We recently identified conditions for preparing 2D layered COFs that begin as homogenous solutions, allowing detailed rate measurements to be made for the first time. COF formation is observed within minutes, and the precipitation rate is readily measured from optical turbidity experiments. We characterize the systematic impact of concentration, temperature, and competitive inhibitors on the rate of COF formation, and use these observations to gain insights into the mechanism. We also demonstrate the broad applicability of this approach and progress towards using this information to rationally identify ideal growth conditions for framework materials.

A Non-covalent Porous Material Based on Zinc Carbonate Nanoclusters with Unique Gas Sorption and Photoluminescent Properties

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Over the last decade much attention has been paid to non-covalent porous materials (NPMs), constructed by non-covalent interactions driven self-assembly of discrete molecules and exhibit remarkable stability and high permanent porosity.[1] These materials poses some distinguishing features in comparison to covalently bonded metal-organic frameworks (MOF) such as solubility, which is a very important advantage in processing, *e.g.* for the formation of thin, porous films or simple modification of structure by co-crystallization of different building-blocks.[2] Herein we report on successful utilization of the tetranuclear hydroxo cluster $[Zn(q)_2]_2[t\text{BuZn(OH)}]_2$ (**1**) (where q = 8-hydroxyquinolinate)[3] as a predesigned organozinc precursor for activation of CO_2, which led to the unique and permanently porous fluorescent NPM **WUT-1** based on discrete molecules of heteroleptic zinc carbonate-hydroxyquinolinate clusters. **WUT-1** exhibits an interesting 3D microporous structure involving packing of clusters in a diamondoid manner and one of the highest BET surface areas for NPM materials.The experimental gas adsorption isotherms and grand canonical Monte Carlo (GCMC) simulations show that strong H_2 binding of **WUT-1** rigid structure with initial enthalpy of adsorption of 11.6 kJ mol^{-1} is an effect of occupation in the first step of ultramicropockets on the surface of **WUT-1** discrete clusters. We believe that the reported synthetic approach utilizing unique reactivity of well-defined organozic precursors could provide new perspectives on the preparation of model metallo-supramolecular architectures with desired functionalities.

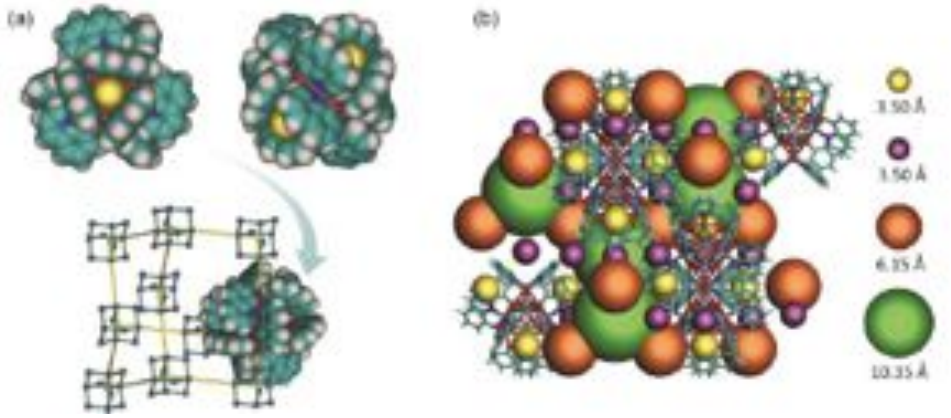


Fig 1. (a) Molecular cluster of **WUT-1** and representation of diamondoid lattice of **WUT-1**; (b) projection of the unit cell in **WUT-1** with color spheres representing the largest cavities.

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Near-Infrared Croconaine Rotaxanes as a New Class of Nanoscale Heat Generators

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There are numerous applications for heat generation at the molecular level, not least in photothermal cancer therapy, in which high energy laser light induces localised heating through the use of highly absorbing probes. Light around 800 nm has significant technical advantage, and currently gold nanoparticles are most commonly exploited.[1] However, limitations of gold nanoparticles include their large size, slow rates of diffusion and relative synthetic inflexibility. In addition, while a small number of organic dyes absorb efficiently in the desired region, they suffer from poor stability, aggregation and photobleaching.

Here we report the synthesis, photophysical properties and heat generation ability of the first Croconaine Rotaxane. Croconaine dyes have very high molar absorptivities at around 800 nm, but suffer from modest chemical stability and self-aggregation.[2,3] Previously, similar problems have been solved for fluorescent squaraine imaging probes by incorporation within interlocked rotaxane systems.[4] The efficient encapsulation of a croconaine dye (Figure 1a) inside a tetralactam macrocycle yields the target Croconaine Rotaxane (Figure 1b). Crucially, the interlocked product displays enhanced stability and highly favourable laser-induced hyperthermia properties. Furthermore, encapsulation-induced changes in croconaine absorbance demonstrates the potential for 'selective multicolor hyperthermia', a new concept based on the enhancement of heat generation *via* controlled molecular recognition events.

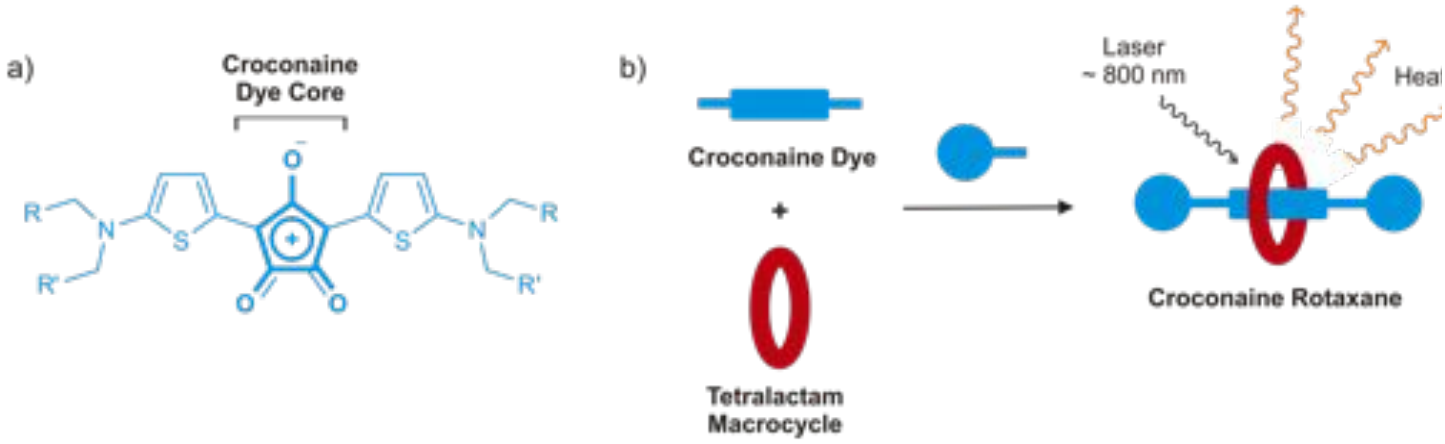


Fig 1. a) Croconaine dye, and b) schematic formation of the rotaxane hyperthermia agent.

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Graphene Oxide Wrapped Plasmonic Core Shell Nanohybrids for Photoacoustic Imaging

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Optical imaging with sub-millimeter spatial resolution in diffuse photon regime has become a reality with the advent of photoacoustic imaging.[1] Further, photoacoustic imaging[2] technique is getting evolved and often demand the usage of exogenous contrast agents with enhanced optical absorption cross-sections at the visible wavelength. In the present study, we illustrate the synthesis of a novel graphene oxide (GO) wrapped plasmonic core-shell nanohybrid material GO-SiO_2@AuNP, which exhibits an absorption enhancement in visible region of the electromagnetic spectrum (Figure 1).

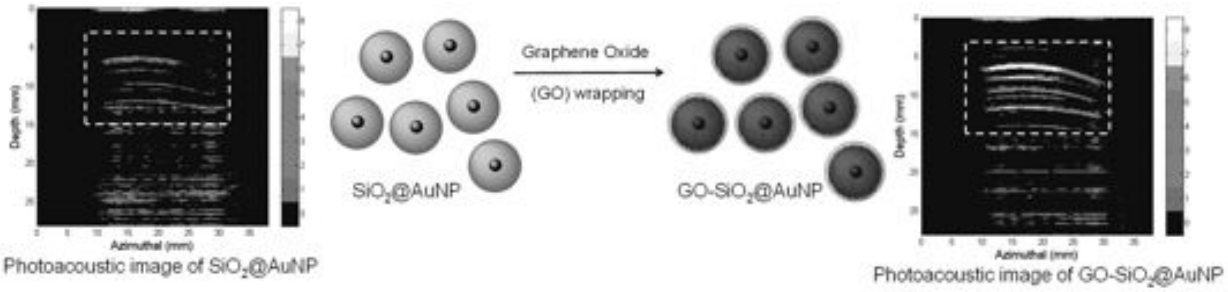


Figure 1. Scheme showing photoacoustic contrast enhancement in GO wrapped SiO_2@AuNP.

An ultrathin GO coating enhances the residual plasmonic absorption of the new hybrids at 527 nm while maintaining its compact size. An unprecedented enhancement in photoacoustic contrast was observed with the new nanohybrid. Thus, this unique strategy opens up new avenues for enhancing photoacoustic contrast using plasmonic nanoparticles with considerably lower toxicity and without any structural modifications for photoacoustic imaging in visible region. Details of the preparation of nanomaterials, photophysical and photoacoustic experiments will be presented in the poster.

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Cd_{16} Coordination Cages and the Role of Inter-ligand π-Stacking in Stabilising Cage Complexes

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Coordination cages have attracted much recent interest due to the increasing complexity and functionality that they can possess.[1]

The ligands L^{pp} and L^{14naph} have both been shown to form $[Cd_{16}(L)_{24}]^{32+}$ coordination cages by X-ray crystallography, ^{1}H NMR and ESMS. The $[Cd_{16}(L^{pp})_{24}]^{32+}$ cage undergoes a cage-to-cage interconversion in solution over a number of days to a smaller cage, $[Cd_6(L^{pp})_9]^{12+}$ (figure 1).[2] However the $[Cd_{16}(L^{14naph})_{24}]^{32+}$ cage is stable in solution indefinitely.[3] The additional inter-ligand π-stacking between ligand fragments associated with replacement of a phenyl group by a naphthyl group allows the complex to be stable in solution, providing conclusive proof of the importance of inter-ligand π-stacking in the assembly of this family of cages.

When L^{14naph} is combined with $Cd(BF_4)_2$ or $Cu(BF_4)_2$ in a 1:1 ratio, the trinuclear $[M_3(L^{14naph})_3]^{6+}$ (M = Cd or Cu) complex is afforded.[3] This unit has been shown to be a key component of a number of cages in this series. The coordinatively unsaturated unit has been reacted with L^{mes} in a 1:1 ratio to afford a $[M_{12}(L^{14naph})_{12}(L^{mes})_4]^{24+}$ (M = Cd or Cu) cuboctahedron cage.

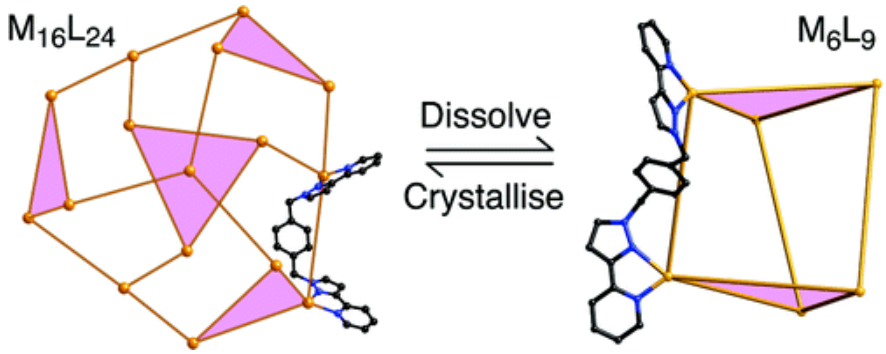


Figure 1. Cage-to-cage interconversion with the ligand L^{pp}

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Supramolecular Chemistry in the Solid State: Catalysis and Vortex-grinding for Mechanochemistry and Templates

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The organic solid state provides constrained yet flexible environment to conduct covalent-bond-forming reactions. However, catalysis in the organic solid state is expected to be difficult to achieve due to low diffusion rates of molecules in the crystals. A recently reported supramolecular catalysis in the organic solid state was achieved using a linear-template approach and mechanochemistry to achieve catalytic turnover.[1] We expanded the scope to new substrates where, remarkably, turnover proceeds spontaneously.

In related work, we developed a method based on the use of a vortex mixer that enables automated grinding and simultaneous irradiation of a solid sample.[2] Using the vortex mixer, the reported supramolecular catalysis proceeds four times faster than when conducted through manual grinding. The method has also been applied to preparation of cocrystals and metal-organic frameworks.

We will also present a concept of using a product of a template-directed solid-state reaction as a template for a subsequent solid-state photoreaction.[3] The reported photoreaction proceeds within a cocrystal that exhibits a unique form of polymorphism, and in a single-crystal-to-single-crystal manner. In addition, we will present a sequential integration of aromatics into discrete double-to-quadruple stacks within the cocrystals based on indolocarbazole.

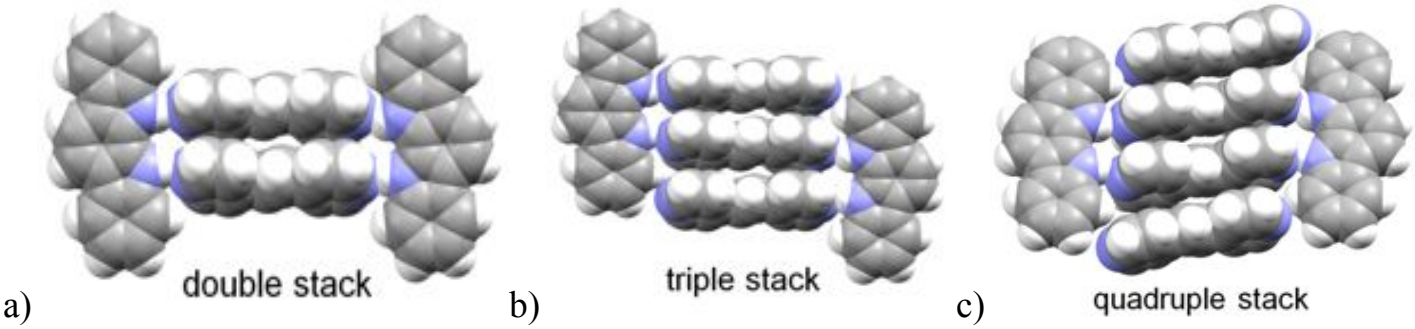


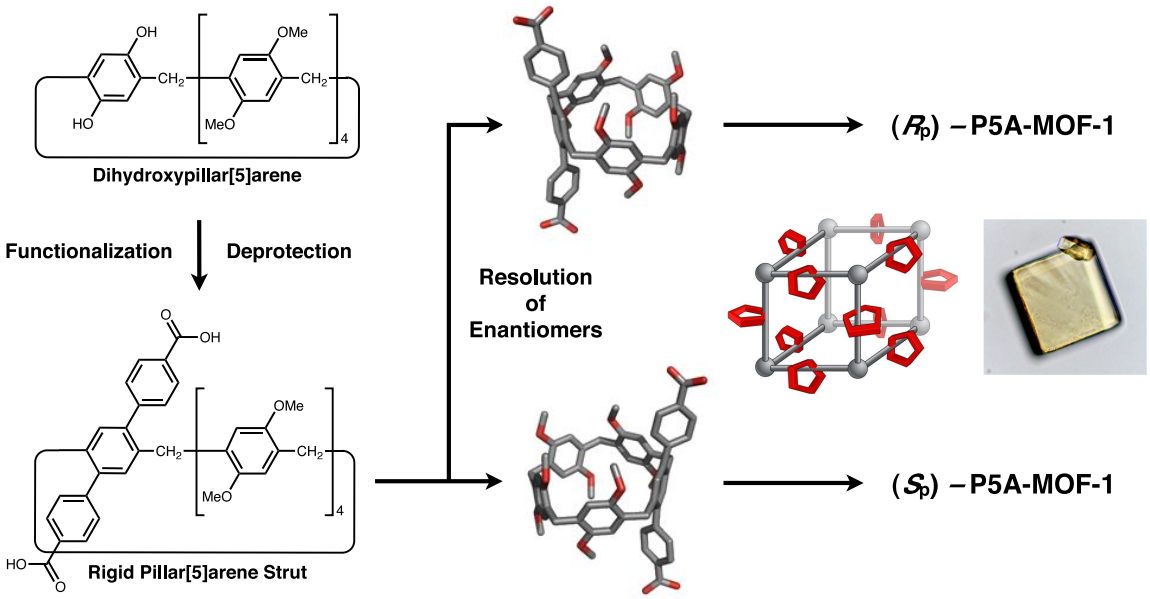
Figure 1. Discrete aromatic stacks in the cocrystals based on indolocarbazole: a) double, b) triple, and c) quadruple stack.

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Novel Porous Materials Utilizing Pillararene Macrocycles

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Pillararenes are a new class of π-electron-rich macrocycles with a cylindrical structure composed of hydroquinone units connected by methylene bridges in their *para* positions.[1] Recently, we have become interested in incorporating pillararenes into metal-organic frameworks (MOFs) to examine how electron-poor guests interact with the macrocyclic active domain of the material.[2] A rigid organic strut with a pillar[5]arene (P5A) backbone has been synthesized, and P5A-MOF-1 was grown with Zn_4O secondary building units. P5A-MOF-1 takes up large quantities of electron-poor guests from solution, including nitroaromatics. A color change occurs in the crystal upon guest binding on account of charge-transfer interactions between the encapsulated guest and the π-electron-rich cavity, indicating that P5A-MOF-1 may find application as a sensor for electron-deficient aromatics. The rigid difunctionalization of pillar[5]arene needed to create the organic strut imparts planar chirality onto the macrocycle. A racemic modification of the strut has been resolved through use of a chiral auxiliary protecting group and the synthesis of a homochiral version of P5A-MOF-1 was achieved (Scheme 1). The structural properties of homochiral P5A-MOF are now being investigated along with its ability to act as a solid-phase support for the separation of small molecule racemates.



Scheme 1. Synthesis of homochiral pillar[5]arene containing metal-organic frameworks.

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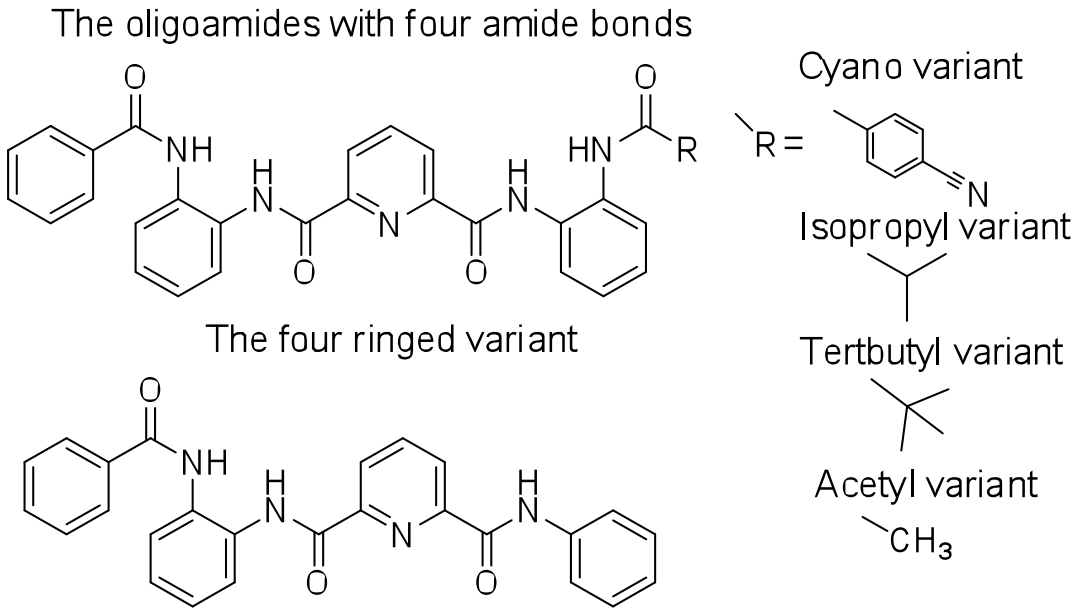
Crystal Forms of Five Asymmetric Oligoamides

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Oxyanion holes are catalytically active sites found in enzymes. They can stabilize reaction intermediates with strong hydrogen bond acceptor groups like enolates and tetrahedral intermediates.[1] The stabilizing effect is caused by the oxyanion holes ability to form several hydrogen bonds to a single hydrogen bond acceptor group.

To study the formation of oxyanion holes five asymmetric oligoamides capable of folding into a conformation with several hydrogen bonds to a single carbonyl oxygen were synthesized and studied with X-ray diffraction methods.[2]

The oligoamides were found to fold in two distinct conformations. The @-conformation where the intramolecular hydrogen bonds are formed with one carbonyl oxygen and the S-conformation where there are two hydrogen bond acceptors for intramolecular hydrogen bonds.



Scheme 1. The oligoamides presented in the poster.

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Mechanized Silica Nanoparticles Based on a Sulfocalix[4]arene-[2]Pseudorotaxane for Controlled Cargo Release

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Mechanized silica nanoparticles (MSNPs), as smart nanocontainers, have been accorded much attention[1] in recent years owing to their excellent performance for drug delivery, sensing, imaging. As the core component of MSNPs, mesoporous silica nanoparticles (MSNs) are good candidates for bio-related applications[2] because of the large surface areas, large pore volumes, tunable pore sizes, chemically modified surfaces and excellent biocompatibility. In order to fine-tune the gate components of these MSNPs for on demand cargo/drug release, a series of compounds and/or materials, including organic molecules, inorganic nanoparticles, polymers and molecular machines, have been located at the orifices of MSN pores. In addition, various external stimuli, i.e., pH changes, light, redox, enzyme, temperature, etc, have been applied[1,3] to regulate the gate operation to entrap and release the cargos from the pores of MSNs.

Calix[n]arenes are a class of macrocycles with widespread applications in the fields[4,5] of separation, sensing, self-assembly, and biomedicine. They have been shown to form 1:1 host-guest complexes with choline derivatives. Hence, MSNs have been modified on their surfaces with choline groups (of different lengths) which bind sulfocalix[4]arene as the gate molecules. Upon MSN functionalization, two enzyme cleavable sites are presented in each stalk component for the employment of specific enzymes to control (Figure 1) the pore openings and closings on the surface of MSNPs. The nanovalves can also be operated by increasing pH or by competitive binding. Fluorescent rhodamine B (RhB) is loaded into the pores of MSNs as model drugs and UV-vis spectroscopy is used to monitor the release of RhB and hence the enzyme specificity.

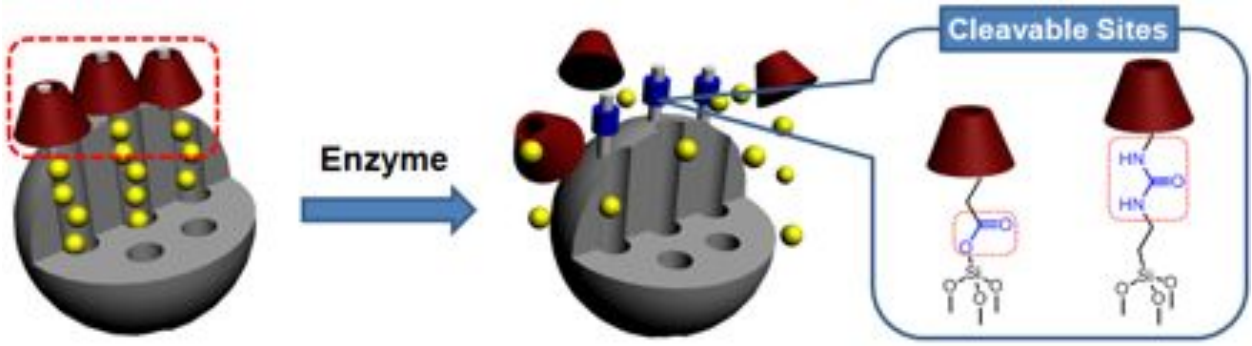


Fig 1. Enzyme-responsive SC[4]A-[2]pseudorotaxane-based mechanized silica nanoparticles

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Supramolecular Assembly of $[UO_2(NCS)_4(H_2O)]^{2+}$ Tectons with Substituted Pyridinium Cations

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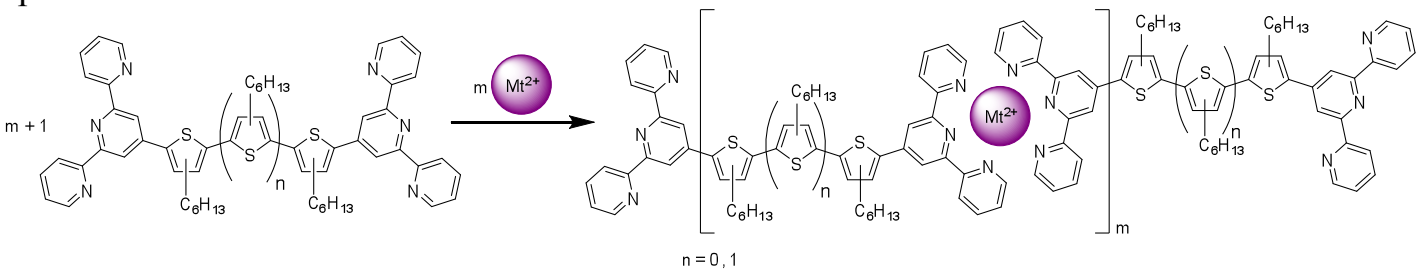
Coordination polymers and hybrid materials containing the uranyl cation $(UO_2)^{2+}$ have been the subject of extensive study due to their unique chemical and photophysical properties. Hydrothermal syntheses of these compounds can lead to a wide variety of oligomeric hydrolysis products, a complex system which can be manipulated via low pH, high halide aqueous media. This well-studied method controls uranyl hydrolysis and provides a limited speciation profile, yielding uranyl tetrahalide units $[UO_2X_4]^{2-}$ ($X=Cl^-,Br^-$) almost exclusively. This system provides a sound foundation for future studies focusing on crystal packing and supramolecular interactions (synthons). Anions, such as the pseudohalogens, are ideal candidates for utilizing high anion media; due to their ability to mimic traditional halogen chemistry and are also under-explored with in the field of actinides. Thiocyanate, SCN^-, is an ideal choice owning to its ambidentate nature, its ability to participate in solid-state interactions, and its relevance to liquid nuclear waste separation. The ionic uranyl thiocyanate tecton, $[UO_2(NCS)_4(H_2O)]^{2-}$, can be utilized to systematically study weak, less directional interactions (H-bonding, halogen-halogen, VDW) and their relative effects on crystal assembly. Presented herein will be a systematic study of the types and relative strengths of packing consideration in these uranly containing materials.

Funding for this work is provided by the DOE.

Metallo-supramolecular Polymers Based on Zn^{2+} and Fe^{2+} Complexes of Conjugated Bis-Terpyridines

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Reversible linking of α,ω-functionalized oligomer molecules by non-covalent interactions or appropriately labile covalent or coordination bonds gives a constitutional-dynamic polymer called dynamer (Scheme 1). The main advantage of dynamers is possibility of their post-synthesis modification allowing tuning or tailoring their properties or self-healing of their chains by exchanges or reshufflings their components. An ideal dynamer can be repeatedly switched between polymeric and oligomeric state in contrast to polymers composed of "permanent" macromolecules.



Scheme 1. Formation of metallo-supramolecular polymers

In this contribution we present new results concerning the metallo-supramolecular polymers prepared from oligothiophenes with 2,2':6',2"-terpyridine (*tpy*) end-groups and Zn^{2+} and Fe^{2+} ion couplers. The results include the complexation of 4′-ethynyl-*tpy*, 4′-thiophene-3-yl-*tpy* and unsubstituted *tpy* (for a comparison) with the ions,[1] optical properties of the species formed, synthesis and properties of α,ω-bis(*tpy*)bi- and ter-thiophenes substituted with hexyl group in different position,[2] complexation of the oligomers with the ions and optical properties of the obtained metallo-supramolecular polymers.

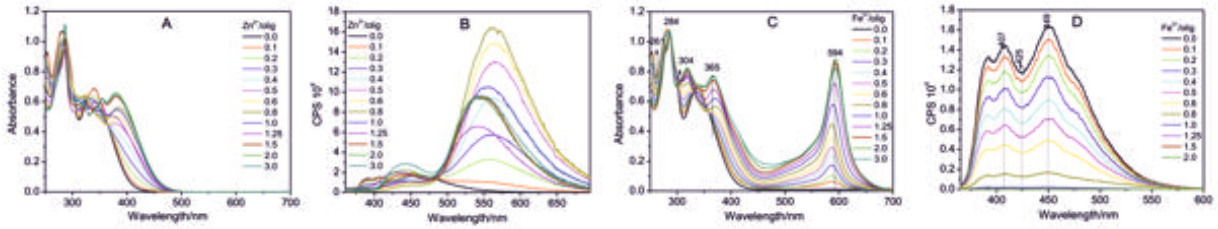


Figure 1. Changes in UV/vis (A, C) and photoluminescence (B, D) spectra accompanied titration of ligand with Zn^{2+} (A, B) and Fe^{2+} (C, D).

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Delivery of Polyamine-functionalised Mesoporous Silica Nanoparticles into Cancerous Cells

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The ability of polyamine amides to bind to glutamate receptors have made them useful in studying cancer propagation.[1] In order to harness this ability, 4-hydroxyphenylacetyl spermine was conjugated onto the mesoporous silica nanoparticles (MSNPs) for delivery into cancerous cells[2] by targeting the glutamate receptors on the cell surface. MSNPs were synthesized via a condensation reaction which was followed by a "click" reaction to couple the alkyne functionalized 4-hydroxyphenylacetyl spermine onto the MSNP surface. Thereafter, a cleavable disulphide ligand was attached on the surface of the nanoparticles and serves to release drugs from the mesopores upon a trigger. MSNPs were characterized by a series of techniques such as TEM, XRD and BET to study the morphology and surface properties of MSNPs. In addition, XPS and zeta potential were also conducted to confirm the presence of the different ligands on the surface of the nanoparticles. Thereafter, release profiles were conducted with various reducing agents, showing successful release of the drugs. Further studies can be conducted to compare the cell viability of MSNPs containing the polyamine amide groups and those without. Fluorescence microscopy images can also be used to further confirm cellular uptake of the MSNPs.

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^{207}Pb NMR studies of Pb^{2+} complexes with linear and macrocyclic ligands

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Studies employing Pb-207 and ^{1}H-^{207}Pb HMQC NMR techniques were used to investigate Pb^{2+} complexes three groups of branched, macrocyclic and macrobicyclic multidentate ligands. These ligands include EDTA analogues, $(R'CH_2)_2N$-R-$N(CH_2R'')_2$, where R = $-CH_2CH_2-$, $-CH_2C(CH_3)H-$, $-(CH_2)_3-$, cyclohexano, Cl-phenyl and R', R" = CO_2H, $C(=O)NH_2$, CH_2OH, $C(CH_3)HOH$ and 2-pyridyl. Also studied were tetraazamacrocyles with pendent arms, 12-ane-4$N(CH_2R)_4$, where R = CO_2H, $C(=O)NH_2$ and $C(=O)OCH_2CH_3$. Macrobicyclic cryptands 3.1.1, 2.2.1, 2.2.2 and $2_{NH}.2_{NH}.2_{NH}$ comprised the third group of ligands. The chemical shift values ($\delta^{207\text{-}Pb}$) for Pb-207 ranged from +2471 ppm (cyclohexanediaminetetraacetic acid) to -64 ppm (cryptand 2.2.2). For each of the groups of ligands a correlation between $\delta^{207\text{-}Pb}$ and the stability constant, K_{PbL}, of the 1:1 PbL complex was observed. For most of the ligands, ^{1}H-^{207}Pb HMQC NMR spectra revealed three-bond coupling between the hydrogen atom on the methylene group adjacent to the N or O donor atoms attached to Pb (Pb-N-C-H(H), Pb-O-C-H(H)). These studies showed that ^{1}H-^{207}Pb HMQC NMR can provide information regarding the solution structure of Pb complexes with multidentate ligands as reported previously by Claudio et al.[1]

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A Novel Photocontrollable Three Component System on the Basis of Crown-Containing Styrylbenzothiazole and Host Molecules

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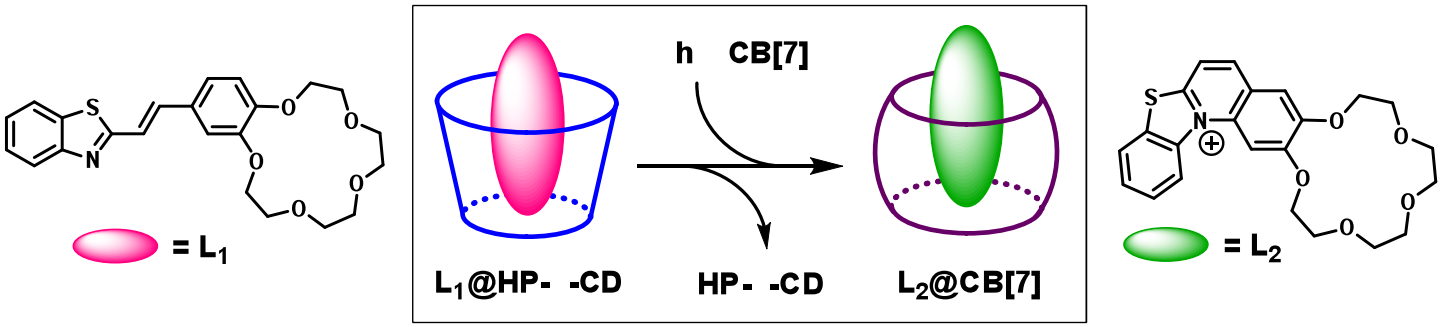
[2] *Laboratory of Photoactive Supramolecular Systems, A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Moscow, Russia*

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At the present time different molecular devices, created on the basis of organic supramolecular host-guest complexes, are becoming increasingly popular.

In this paper the photocontrollable molecular system, consisting of crown-containing 2-styrylbenzothiazole (**L_1**) as guest molecule, as well as 2-hydroxypropyl-β-cyclodextrin (**HP-β-CD**) and cucurbit[7]uril (**CB[7]**) as host molecules, is advanced. The aim of the research was to study the processes of self-assembly and breakage of this molecular ensemble, taking place under the action of UV irradiation.



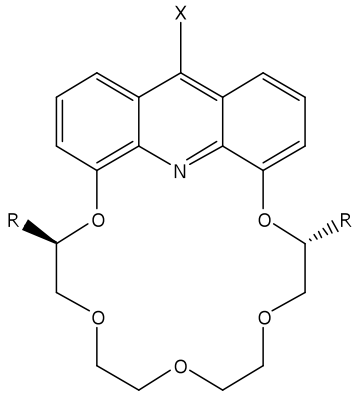
The particular features of the complex formation and photochemical transformation of 2-styrylbenzothiazole (**L_1**) in the presence of two host molecules were studied with a combination of physical methods: electronic absorption and 1D and 2D NMR-spectroscopy. UV irradiation of **L_1@HP-β-CD** supramolecular complex leads to a chain of transformations, including the ligand *trans*-to-*cis*-isomerisation, photocyclization and subsequent oxidative elimination. An important peculiarity of this phototransformation in the three component system is the selective binding of *trans*- and *cis*-forms of ligand **L_1** with **HP-β-CD,** and the oxidative photocyclization **L_2** product selective binding with **CB[7]** in accordance with the scheme presented above.

In summary, simultaneously with the photochemical reactions process, the movement of the guest molecule from the cavity of one "host" to the cavity of the other is observed.

Preparation and Studies of Chiral Stationary Phases Containing Enantiopure Acridino-18-crown-6 Ether Selectors

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The crown ether based chiral stationary phases have been proved to be successful in separating protonated primary amines, amino acids and their derivates both analitically and preparatively. Starting from commercially available and relatively cheap materials new acridino-18-crown-6 ethers (*R,R*)-**1** and (*R,R*)-**2** containing a carboxyl group were prepared. The latter crown ethers were used for the acylation of 3-(triethoxysilyl)propylamine using DCC in dichloromethane to obtain (*R,R*)-**3** and (*R,R*)-**4**. The crude crown ethers containing a terminal triethoxysilyl group were then treated with HPLC quality silica gel in refluxing toluene to give (*R,R*)-CSP-**5** and (*R,R*)-CSP-**6**. These novel chiral stationary phases were tested for the separation of the enantiomers of racemic protonated naphthylethylamines (1-NEA and 2-NEA), phenylethylamine (PEA) and 4-nitrophenylethylamine (NO_2-PEA), 4-bromophenylethylamine (Br-PEA).



(*R,R*)-**1**: R = Me, X = -COOH
(*R,R*)-**2**: R = *i*Bu, X = -COOH
(*R,R*)-**3**: R = Me, X = -CONH$(CH_2)_3Si(OEt)_3$
(*R,R*)-**4**: R = *i*Bu, X = -CONH$(CH_2)_3Si(OEt)_3$
(*R,R*)-CSP-**5**: R = Me, X = -CONH$(CH_2)_3SiO_3$-silica gel
(*R,R*)-CSP-**6**: R = *i*Bu, X = -CONH$(CH_2)_3SiO_3$-silica gel

Figure 1. New enantiopure crown ethers and chiral stationary phases.

Acknowledgements . The HPLC measurements were carried out in Richter Gedeon Ltd.
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Supramolecular Construction of Optoelectronic Biomaterials: "Polymerization" of Pi-conjugated Peptides

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We developed synthetic approaches to incorporate a wide variety of pi-conjugated functionality into the backbones of water-soluble peptides, such as fluorophores, reactive polymer precursors, and typical n-type and p-type semiconductors. These molecules self-assemble in aqueous media into 1-D nanomaterials with diameters under 10 nm and lengths of microns. These materials ultimately lead to the formation of self-supporting hydrogels that can be prepared with either randomly dispersed or globally aligned nanostructure components. This presentation will describe the synthesis and optoelectronic characterization of these new nanomaterials using electronic spectroscopy and their integration into functional bioelectronic transistors. Prospects for eliciting biological adhesion or other specific responses will be addressed.

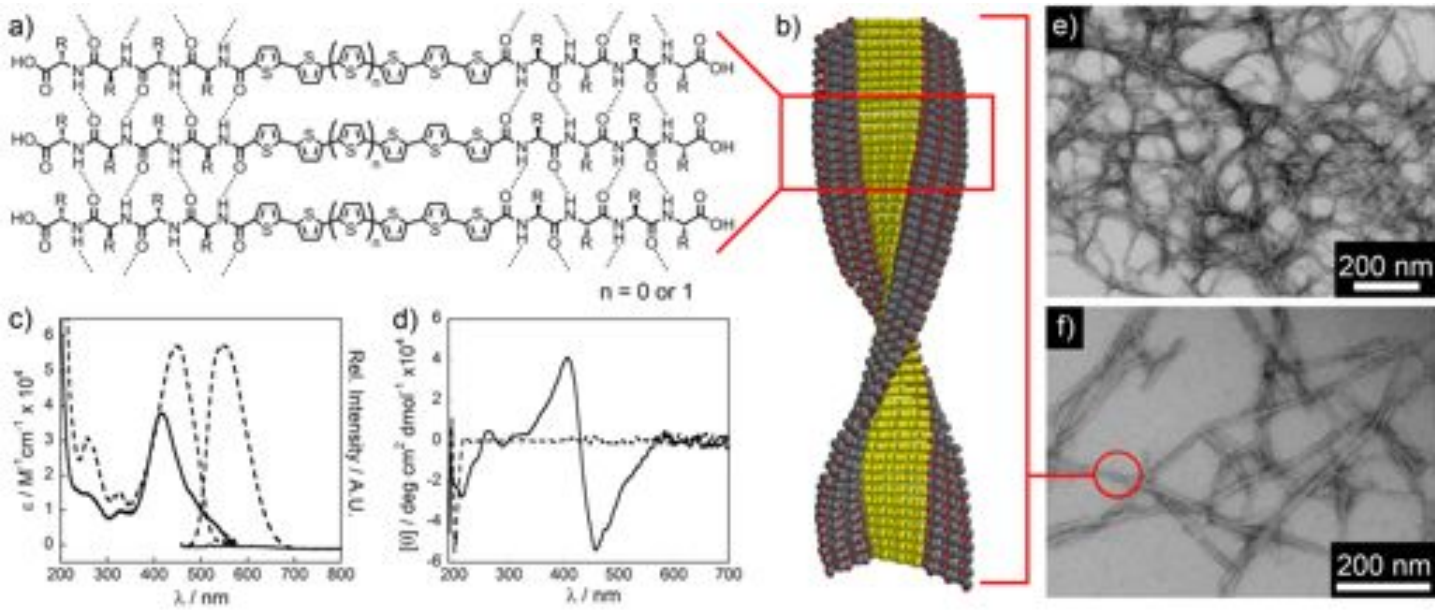


Figure 1. Peptide-pi-conjugated hybrid molecules undergo self assembly in water (a/b) leading to delocalized electronic structures (solid lines, c/d) thus defining "supramolecular conjugated polymers" within 1-D nanomaterials (TEMs e/f). (Image taken from Ref. 5)

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All-in-One Self-Assembly of a Trefoil Knot and a [2]Catenane

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Programing molecular building blocks for the controlled formation of organized supramolecular entities had always been and remains a challenge for synthetic chemist. Although, Complex molecular knots and links are being synthesized[1, 2] with increasing frequency, the power of "all-in-one"[3] self-assembly methods have yet to be fully exploited for this purpose. Here we describe a new ligand system comprised of a diaminobipyridine and a diformylpyridine, which, when combined with Zn(II) ions, forms a trefoil knot (**TK**) in 56% chemical yield. Alongside the formation of the **TK**, a [2]catenane was also isolated in 22% yield. Both structures were confirmed by ^{1}H NMR spectroscopy and mass spectrometry and an X-ray crystal structure of the [2]catenane was also obtained. These results highlight the synthetic efficiency of combining metal-templation and dynamic covalent imine bond formation for the construction of topologically demanding molecular architectures.

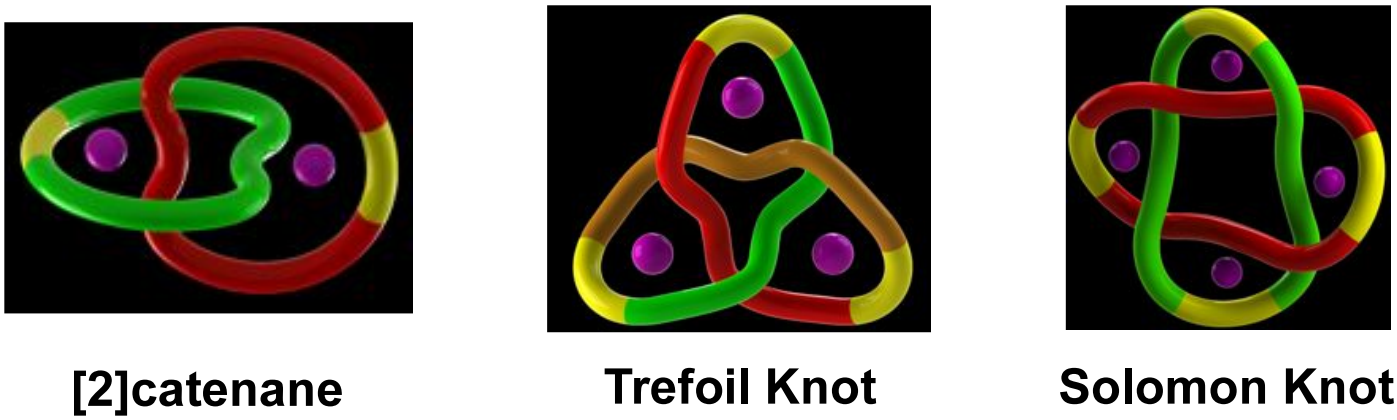


Figure 1. Graphical representation of three molecular links that can be obtained in an all-in-one synthesis strategy.

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Aryl C–H•••Cl$^-$ Hydrogen Bonding in a Fluorescent Anion Sensor

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Previous work in our labs has demonstrated the application of 2,6-bis(4-urea-phenylacetylene)pyridine as fluorescent probes for anions in solution.[1-3] Protonation of this class of receptor by acidic guests activates anion binding where by the pyridinium acts as a strong hydrogen bond donor and counter-cation for anionic guests. A phenyl analog of the original pyridine sensor was constructed to avoid the influences of pH on this system, and binding studies were performed to determine the effectiveness of the phenyl variant versus the pyridinium sensor. ^{1}H NMR and UV-Vis titrations in $CHCl_3$ show a ten-fold increase in anion association (K_a) over the bis-urea-pyridine. The increase in affinity is attributed to an aryl C–H•••Cl$^-$ hydrogen bond (Figure 1), demonstrated by a large downfield shift (>2 ppm) of the interior aryl proton (H_a) upon binding. An X-ray crystal structure supports the importance of the aryl C–H•••Cl$^-$ hydrogen bond observed in solution. Importantly, the ability to control fluorescence upon anion binding is preserved in the new phenyl sensor.

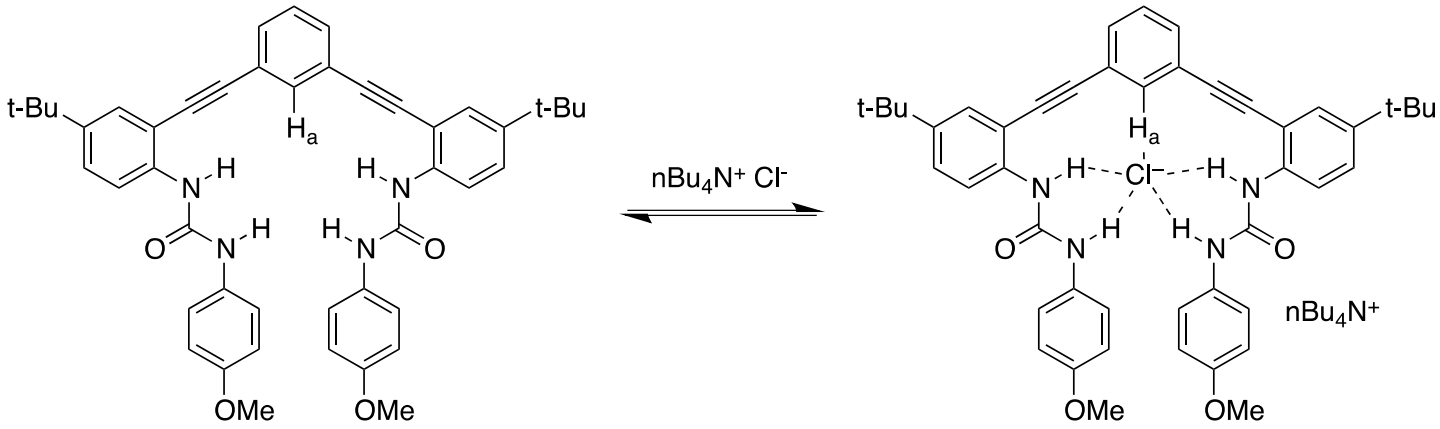


Figure 1. Anions are bound by an aryl C–H and four urea hydrogen bonds.

References

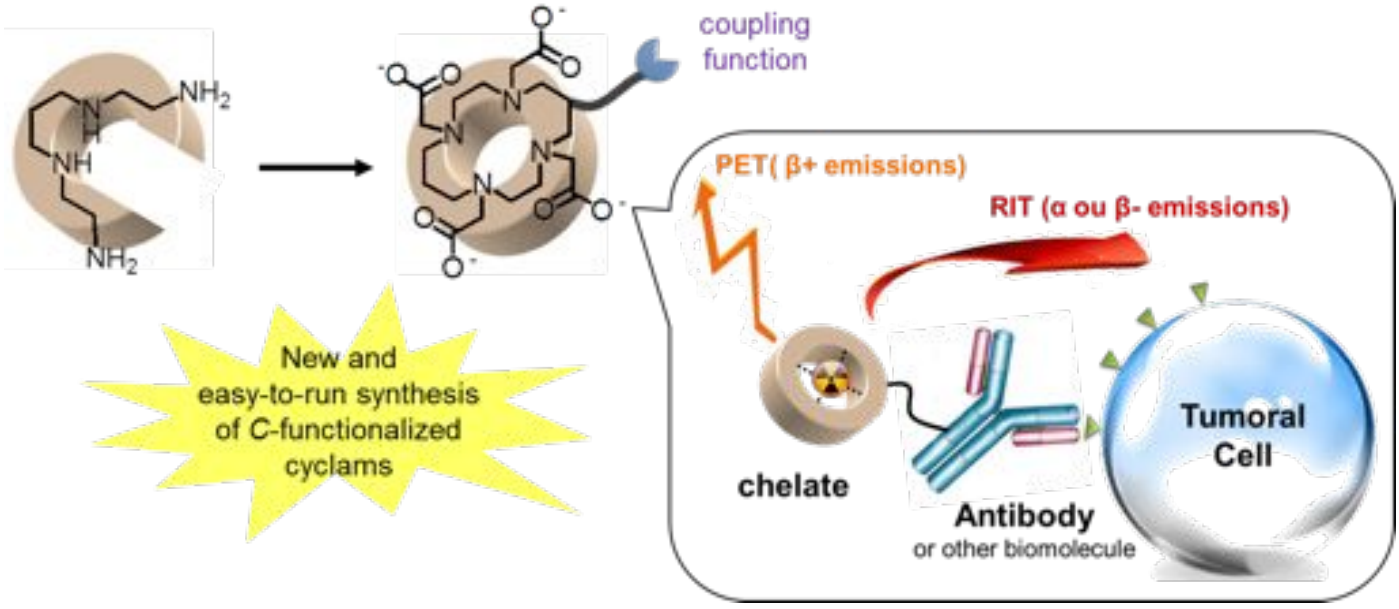
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New Polyfunctional Cyclam Based Chelators: Attracting Macrocycles For Inovating Medicinal Applications

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Lanthanides, transition or heavy metals, are very interesting metal cations for applications in medicine, for diagnostic (bioluminescence, MRI or Positron Emission Tomography: PET) and therapy (Radio-ImmunoTherapy: RIT,...). For instance, Gd^{3+} is the metal of choise to build a powerfull MRI contrast agent and Cu^{2+} is of growing interest since some of its radioisotopes have suitable radioactive properties for PET imaging (^{64}Cu) or for radioimmunotherapy (^{67}Cu).

Thus, many chelators have been proposed for the complexation of such metals in search of better contrats agents or radiopharmaceuticals, especially including systems allowing for coupling of the radiochelate to a targeting biomolecule to form bifunctional chelates, leading to remarkable labelling agents. Among the different types of macrocyclic structures, those based on the well-known tetraazamacrocyclic frameworks, as cyclam, have been demonstrated to be among the most efficient, due to their favourable physico-chemical properties.[1] However, the complexity of such structures makes difficult their coupling to biological materials to increase their targeting specificity, without losing their coordinating properties. We recently proposed new chelates with astonishing properties[2] and especially developed powerful and easy to run synthetic routes leading to their bifunctional derivatives.[3]



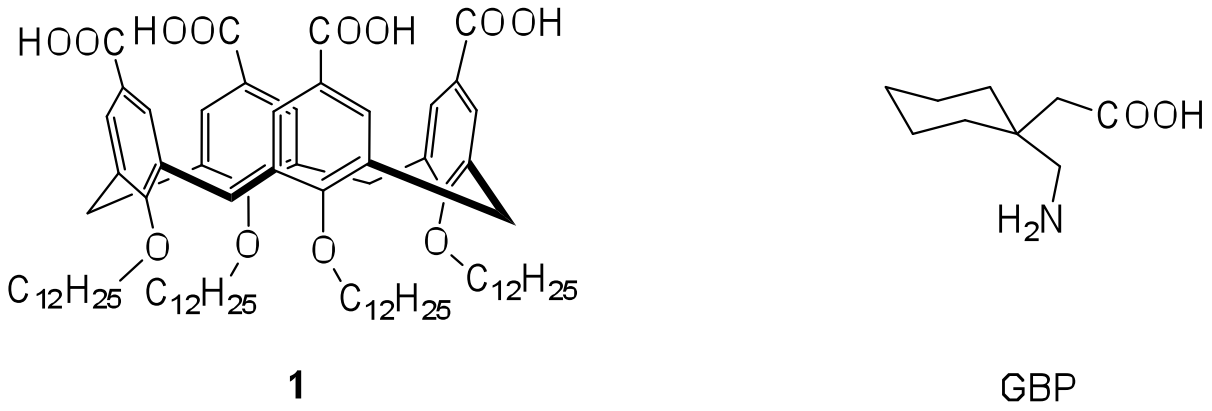
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Polymorphism Control of Active Pharmaceutical Ingredients Using Langmuir Monolayers

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Polymorphism is the ability of a substance to exist as two or more crystalline phases.[1] Nanostructured surfaces, in addition to the control of chemical and physical conditions, may represent another strategy to template the crystallization of active pharmaceutical compounds (APIs). Several types of surfaces have been explored including single crystal face, [2] polymers [3] and self-assembled monolayers (SAM) on gold. [4] Here we demonstrated that Langmuir monolayers of **1** interact with gabapentin (GBP), an API. The molecular arrangement of **1** had been studied by means of grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity (XRR) techniques. Interestingly, the control over the polymorphism of the API has been gained by varying the molecular packing within the monolayer. Two distinct polymorphic forms have been obtained.



1 GBP

Figure 1. Chemical structures of **1** and gabapentin.

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Chiral Framework Materials for Separation

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Chiral separation of racemic mixtures remains a significant challenge in organic syntheses and it is often easier to synthesize an enantiomerically pure compound than to separate a mixture. One potential medium for separation that we are currently exploring is the use of porous chiral coordination frameworks.

One of the routes that we have taken towards chiral materials is the use of racemically pure dicarboxylate ligands which can be derived from amino acids. The choice of spacer group between the amino acid termini is readily altered using rigid aromatic groups to give ligand lengths of between 1 and 1.5 nm. A number of framework materials have been successfully made using this approach.

Results have shown significant promise in terms of chiral resolution, as well as some intriguing structural assemblies that are templated by π-interactions. One example of both features is formed when using an alanine-derived ligand which generates a 2D→3D interpenetrated structure that retains solvent-accessible voids (Figure 1). On a small scale this material has been shown to separate a racemic mixture of pantolactone with high enantiomeric excess. A summary of our results in this area will be presented, highlighting the potential for chiral separation using these classes of materials.

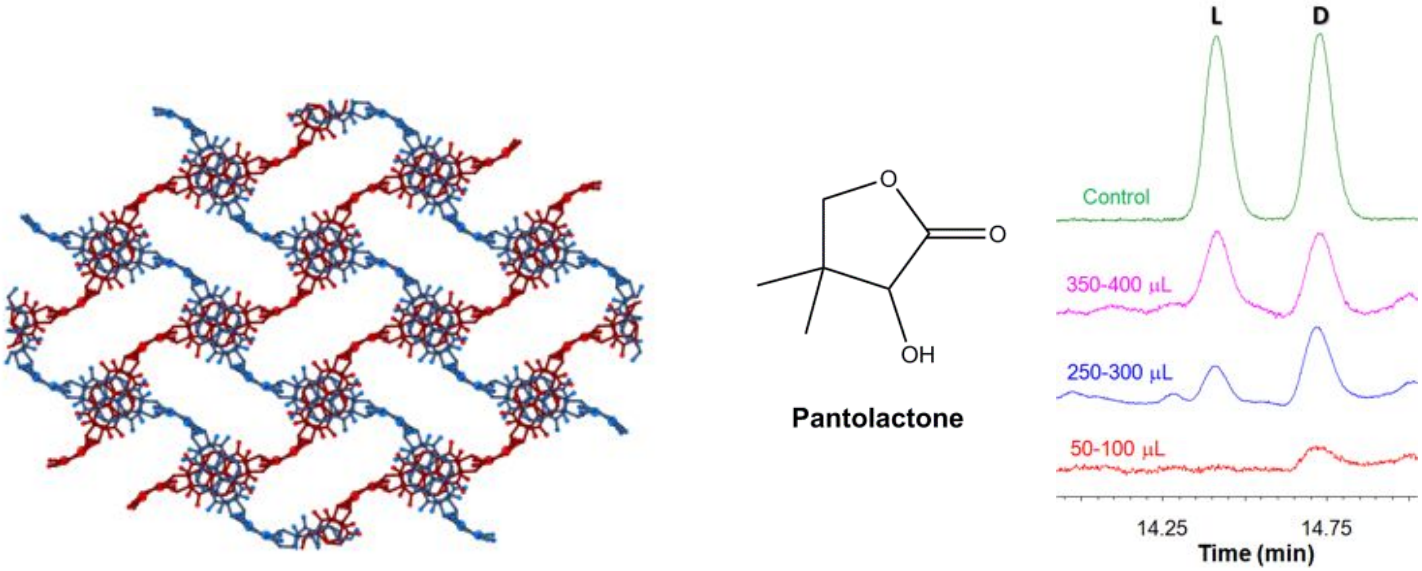


Figure 1. A racemically pure 2D→3D interpenetrated framework shows separation of a racemic mixture of pantolactone.

Click reaction as a tool for making self-assembling materials

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Triazole-based macrocycles possessing different pseudo-symmetry elements have be synthesized using the CuAAC reaction (***Figure 1***). The formation of the macrocycles w accompanied by their spontaneous self-assembly leading to solids with distinct layered structu as confirmed by scanning electron microscopy and supported by Density Functional Theory. T self-assembling property of the product and the "on water" reaction media seemed to form t driving force for the reaction in *t*-butanol-water system.[1] These observations on clic macrocycles led us to check the self-assembly of carbohydrate based click-conjugates. Molecul are diversified into two series. In series I, various click glycolipids are made, which exists in t form of long rods in water.[2] In series II, hexanoate protected click-glycoclusters are made, whi shows gelation abilities in long chain hydrocarbons (***Figure 2***). These phase selective gelat can have a potential application in oil spill recovery from water. Solvent-free mechanochemic glycosylation is used for the scalable preparation of required propargyl glycosides, which serv as a building block for making self-assembling materials.[3]

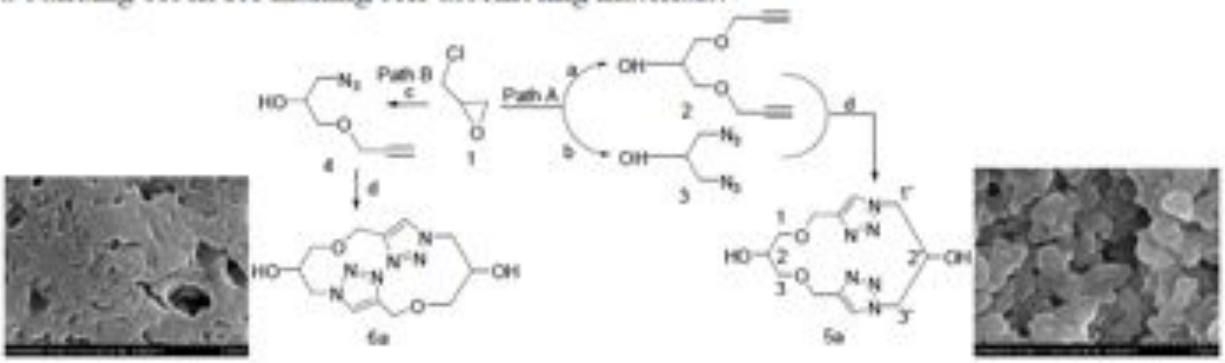


Figure 1. Synthesis of self-assembling glycerotriazolophanes

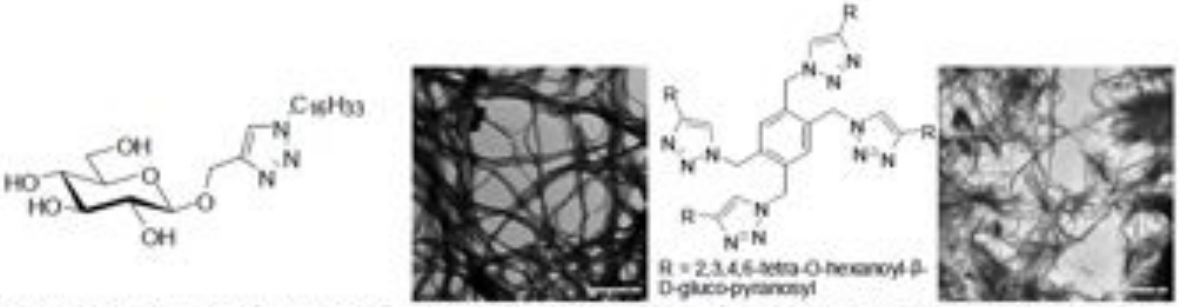


Figure 2. Synthesis and self-assembling properties of carbohydrate based click-conjugates

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Enantiopure lleno-acetylenic macrocycle wth modifiable periphery: Synthesis, chiroptical properties, and H-bond-driven self-assembly in the solid phase

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Chiral 1,3-diethynylallenes (DEAs) have proven to be very versatile building blocks for a number of carbon-rich scaffolds, such as alleno-acetylenic oligomers and macrocyles, which have shown exceptional chiroptical properties.[1,2] Our current efforts in this field have focused on the lateral functionalization of DEAs with the aim of triggering self-association of the corresponding macrocycles into chiral, columnar super-structures with amplified chiroptical properties. Our most recent results towards this goal include the preparation and optical resolution of the phenol-substituted alleno-acetylenic monomer **1**, as well as the development of the appropriate chemistry for the macrocyclization of monomer **1** to **2**. Macrocycle **2** exhibits a very intense Cotton effect centered at 254 nm ($\Delta\varepsilon$ = 375 $M^{-1}cm^{-1}$). Also, as expected by virtue of its large number of OH groups in the periphery of the central macrocyclic framework, **2** stacks in pillars in the solid state to form channels, which further self-assemble through H-bonding interactions into a 3D microporous architecture. Macrocycle **2** may also serve as a common platform for further chemical functionalization, thus providing access to a series of laterally-functionalized alleno-acetylene macrocycles.

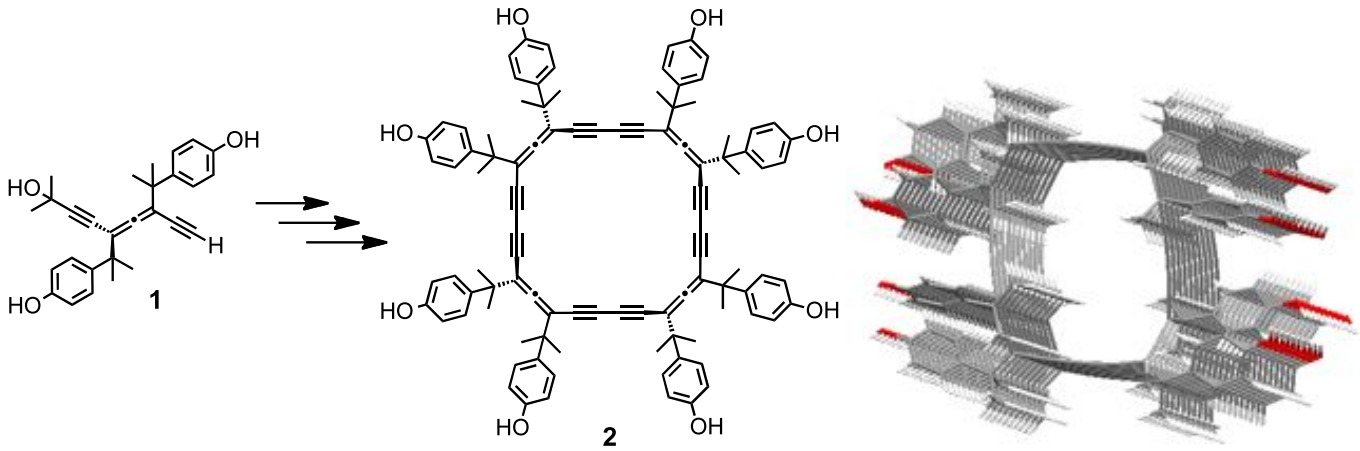


Figure 1. Left: Preparation of an optically active alleno-acetylenic macrocycle bearing lateral OH groups. Right: Columnar self-assembly of optically active alleno-acetylenic macrocycle **2** in the solid state.

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Water-Mediated Desymmetrization Self-Assembly of a Tetrakis(2,2′-bipyridyl)porphyrin Ligand

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Coordination-driven self-assembly of designer organic ligands and metal ions is a powerful method for constructing large and well-defined molecular architectures. When symmetrical ligands possessing chemically equivalent metal binding sites are employed, the resulting supramolecular complexes also tend to form symmetric frameworks. In this context, construction of unsymmetrically self-assembled architectures would provide a chemical system to have elaborate functions by arranging molecular components in less symmetric but well-organized manners.[1] Herein, we report desymmetrization self-assembly of a C_4-symmetric Zn-porphyrin ligand **L** with four 2,2′-bipyridin-5-yl (= bpy) groups to form a supramolecular cage complex $[Zn_{11}\mathbf{L}_6(H_2O)_{18}](OTf)_{22}$ with three different Zn(II) centers.[2] This unsymmetrical yet well-defined self-assembled structure was formed under well-balanced aqueous conditions, in which water ligands with adequate coordinating ability to Zn(II) served as stopper ligands to generate both tris(bpy) and hydrated bis(bpy) Zn(II) units in a finite cage structure. We also observed Δ-Λ isomerism in the middle of the complex in dry media. The moderate coordination ability of H_2O to Zn(II) centers plays an important role in the isomerism. Thus, metal-organic self-assembly in solution containing a moderate amount of coordinating molecules would add a fresh dimension to the construction of elaborate and intricate self-assembled systems.

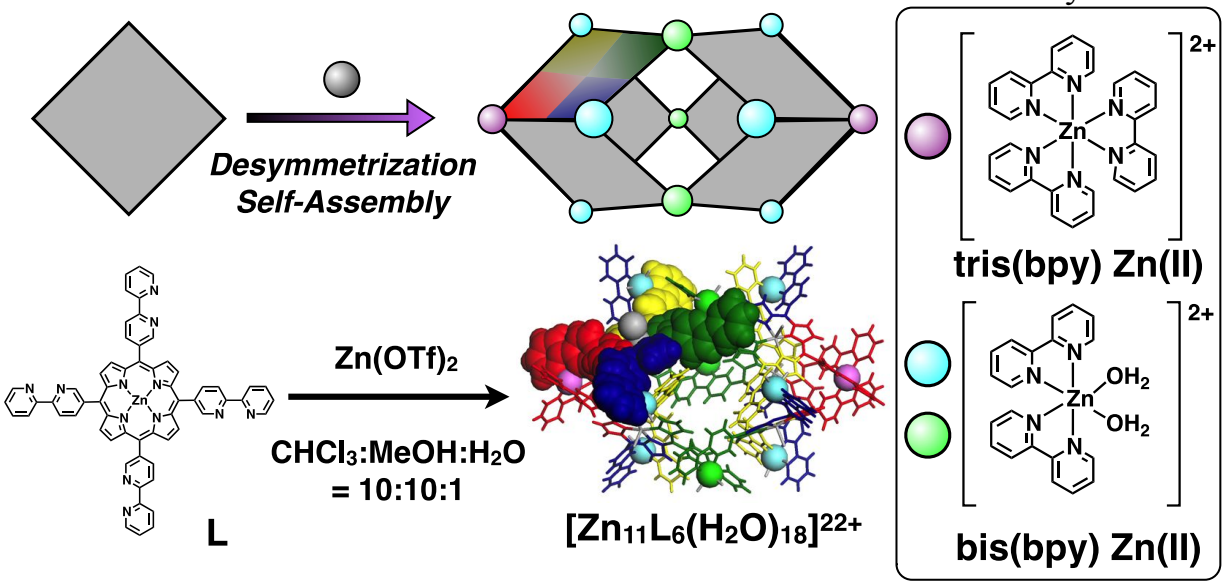


Figure 1. Desymmetrization self-assmbly of Tetrakis(2,2′-bipyridyl)porphyrin Ligand **L**.

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An Amphiphilic Pillar[5]arene: Its Application to High Efficient and Substrate-Selective Phase-Transfer Catalyst

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Phase-transfer catalysts enable the two-phase reaction between water and organic solvent. Pillar[5]arenes[1], first reported by our group, are good hosts for linear guests in organic[2] and aqueous[3] media. Pillar[5]arene has 10 reactive sites at its rims, and introduction of functional groups on these rims affects the physical properties of the pillar[5]arene because these groups cover the core. In the present study, we synthesized a pillar[5]arene derivative containing 10 phosphonium cations **1** (Fig1). Due to the amphiphilic property of the phosphonium cations, **1** was soluble in various kinds of solvents including chloroform and water. Using **1** as a PTC, we investigated oxidation of alkenes by $KMnO_4$ in a two-phase chloroform-water solvent system. Oxidation of the linear alkene 1-hexene by $KMnO_4$ was complete (>99%) in the presence of small amounts of **1** (Table 1, Run 1). On the other hand, the reaction was not complete (35%) with model **2** (Table 1, Run 2). By contrast, oxidation of 1-hexene using **1** in the presence of a competitive guest 1,4-dicyanobutane, was not complete (conversion 32%) and neither was that of the branched alkene 4-methyl-1-hexene (conversion 31%) (Table 1, Runs 3, 4). From these results, we considered the oxidation proceeded efficiently by capturing the substrate in the ring of **1**.

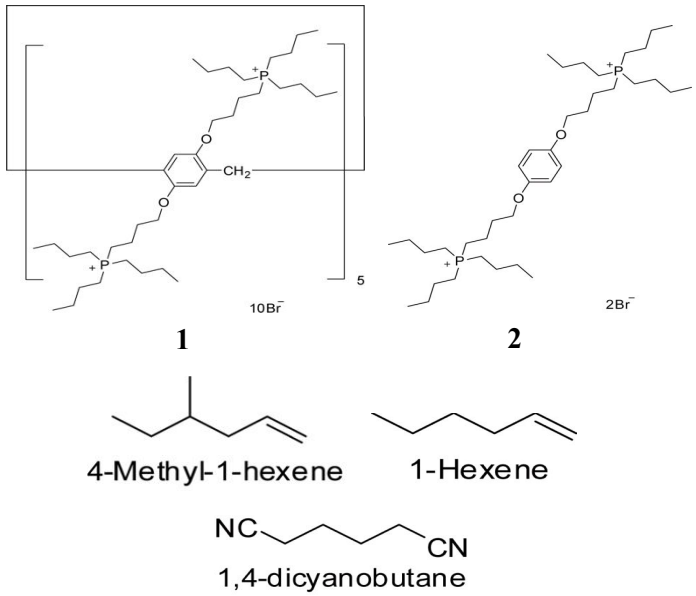


Figure 1. Phase-transfer catalysts: pillar[5]arene **1**, unit model **2**. Substrates: 1-hexene and 4-methyl-1-hexene. A competitive guest: 1,4-dicyanobutane.

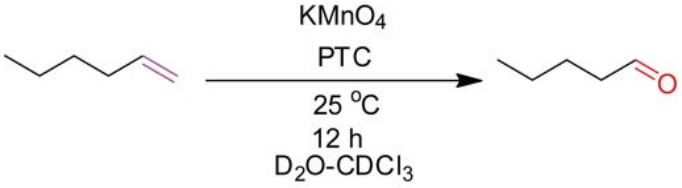


Table 1. Oxidation of alkenes with PTCs.

Run	PTC	Substrate	Conversion (%)
1	1	1-Hexene	>99
2	2	1-Hexene	35
3[a]	1	1-Hexene	32
4	1	4-Methyl-1-hexene	31

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Tail-to-Tail Bridged Calix[4]arenes as Complexation Agents for d- and f-Elements

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Calix[4]arenes are very potent host molecules and their conformational properties have been widely exploited to induce selectivity in the recognition of ions and neutral molecules.[1] Their controlled synthetic functionalization and versatile complexation properties along with unique three-dimensional structures arouse considerable attention in the field of supramolecular chemistry. They are commonly employed as molecular building blocks for the design of various receptor sites for the specific recognition of several guests.[2] They can be selectively functionalized both at the phenolic hydroxyl groups (*lower rim*) and at the *para* positions of the phenol rings (*upper rim*).

In our case we don't use the calix[4]arene itself as ligand or receptor, but as scaffold that bears coordination sites with various chemical affinities. Particularly, we are interested in the synthesis of novel biscalixarenes, whereas two calix[4]arene moieties in the *cone* or *1,3-alternate* conformation are linked at their *lower rim* via Schiff base like spacers or their corresponding aromatic amines.[3] Therefore, an up-to-date outline of the syntheses towards such novel tail-to-tail bridged biscalix[4]arenes with a *N,O*- or *N,S*-donor set for the complexation of of *d*- and *f*-elements shall be described. Furthermore, we present complexation studies, fluorescence behavior and structural characterizations of selected compounds.

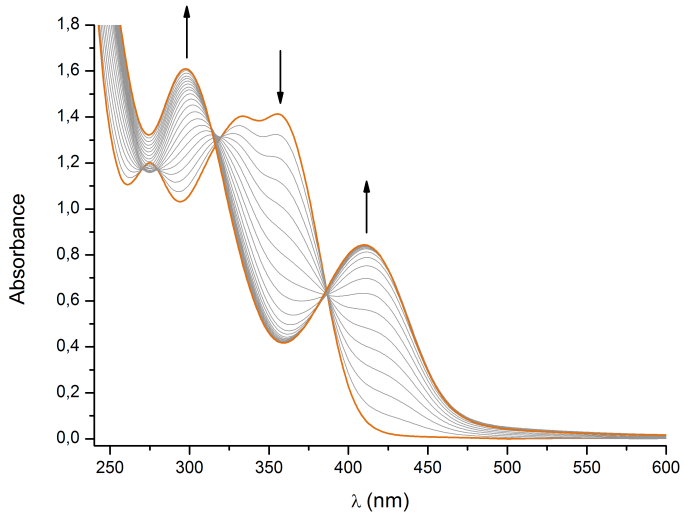


Figure 1. Titration of L^1 (5×10^{-5} M) with $Cu(OAc)_2$ (5×10^{-5} M) in MeCN at constant ionic strength (10^{-2} M $(Bu)_4N(PF_6)$) at room temperature

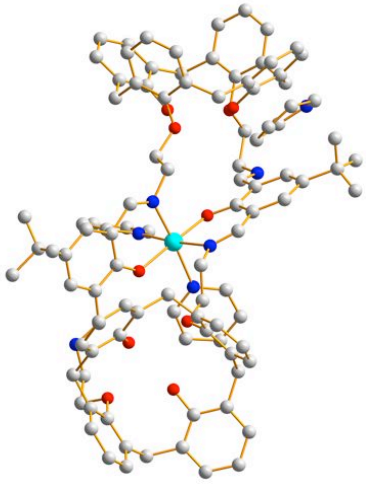


Fig 2. A Zn(II)-complex supported by a novel salicylidene-linked double-calix[4]-arene (L^1)

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White Light and Heat Sensitivity in a Pyridine Based Polymer Blend

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Soft polymer gels constitute a particularly flexible state of matter in which the tuning of molecular electronic and geometrical properties is markedly enhanced by collective effects. The gel blend of poly(4-vinyl pyridine) (P4VP) and poly(4-vinyl pyridine-*co*-butyl methacrylate) (P4VP/P(4VP-BMA)) swollen in pyridine, to be presented here , is a dielectric material which, following prolonged application of DC bias, displays changes in electrical conductivity in response to white light and, with the addition of a small amount of 4-hydroxypyridine, also to low level thermal perturbation. The unusually high thermal sensitivity can reach TCR=(0.1-0.16)/1^{o}C.[1] Spectroscopic data show that this behavior derives in part from a combination of the following field induced processes: 1) appearance of ionic species with associated electron transfer; 2) increased proton transfer to the nitrogen atom of the pyridine ring, producing pyridinium groups; 3) increased hydrogen bonding and a more rigid molecular organization.[2] The optimized system demonstrates, for the first time, that a polymer gel may have potential application as the active layer in light or thermal sensing devices.

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Highly Cooperative Binding of Ion-Pair Dimers by a bis-Calix[4]pyrrole Macrocyclic Receptor

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Calix[4]pyrroles are known to function as heteroditopic receptors of ion-pairs.[1] On that basis, we have demonstrated that receptor **1**[2] (Figure 1) having two calix[4]pyrrole binding sites affords the effective binding of the ion-pair dimers **2a** and **2b** yielding $\mathbf{2_2}\subset\mathbf{1}$ complexes through a highly cooperative process ($\alpha > 10^5$). The cascade-like arrangement complexes of ion pairs are formed by: one ion-pair bound in a host-separated geometry and the other in a close contact binding mode. Interestingly, the exclusive and quantitative formation of the ion-pair hetero dimers **2a2b**$\subset$**1** can be also achieved. The use of the ion pair **3** containing a methyltrioctylammonium cation instead of the tetrabutylammonium renders a binding process significantly less cooperative. As result, the homodimeric complex $\mathbf{3_2}\subset\mathbf{1}$ places both ion-pairs bound in a receptor-separated binding mode. The equimolar combination of $[N(C_4H_9)_4]^+$ and $[NCH_3(C_8H_{17})_3]^+$ salts allows the self-assembly of hetero ion quartet complexes with cascade arrangement by means of a cooperative binding process. Importantly, in these latter mixed complexes, the $[NCH_3(C_8H_{17})_3]^+$ cation is selectively included in the shallow electron rich cavity formed by the pyrrolic rings of a calix[4]pyrrole scaffold

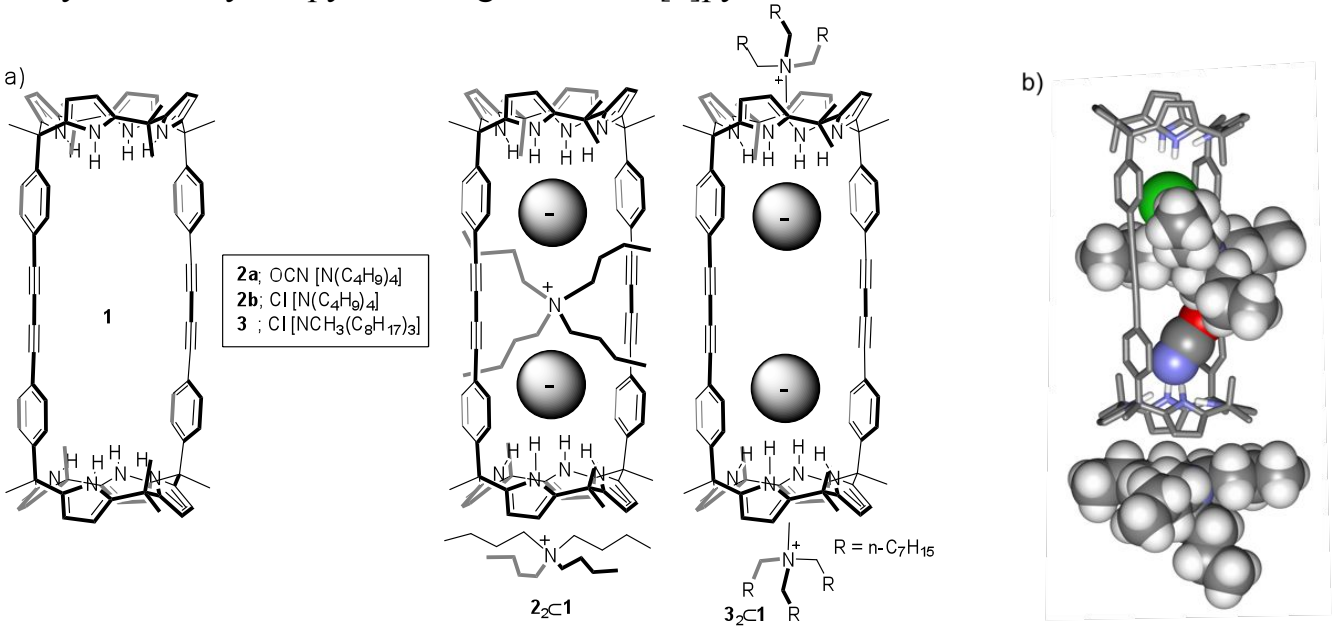


Figure 1. a) Molecular structures of bis-calix[4]pyrrole receptor **1**, the ion-pairs **2** and **3** and the dimeric ion-pair complexes $\mathbf{2_2}\subset\mathbf{1}$ and $\mathbf{3_2}\subset\mathbf{1}$; b) X-ray structure of the cascade complex **2a2b**$\subset$**1**.

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Truncated Porous Organic Cages

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Microporous materials are of significant interest due to their central role in gas storage, separation processes and catalysis.[1] Microporous molecular solids composed of discrete, shape-persistent organic cages have received growing attention[2] as they possess unique properties that set them apart from conventional, extended network materials. Our group recently reported[3] the synthesis and characterization of a novel, permanently porous, shape-persistent cage molecule that is constructed entirely from thermodynamically robust carbon-carbon bonds **C1**, (*Fig 1*). Following this work we will describe the synthesis of two new truncated versions of this cage, **C2** and **C3** (*Fig 1*). The structure and characterisation of these compounds will be discussed.

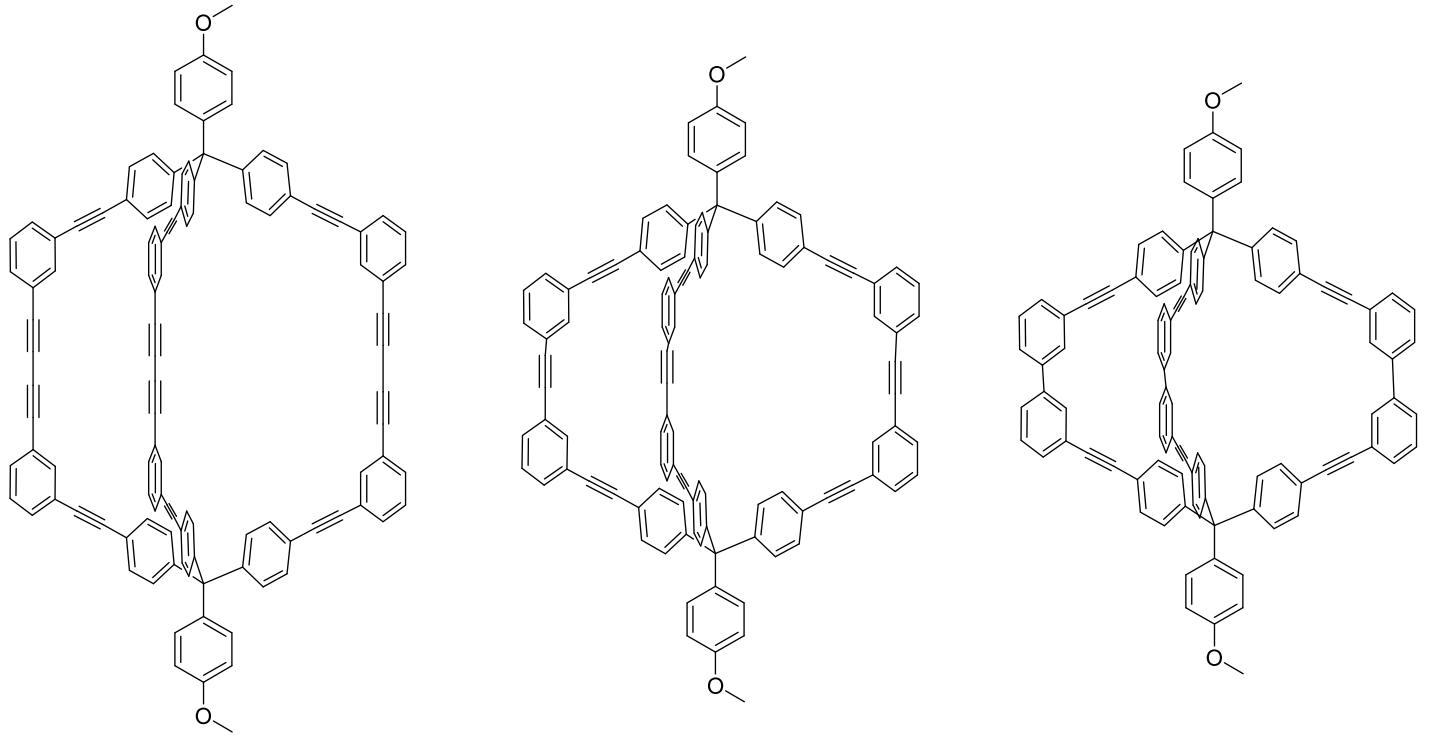


Figure 1. Porous Organic Cages.

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Multiple Aggregate States in Supramolecular Polymers

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Recently, considerable effort has been put into understanding the growth of synthetic, one-dimensional self-assembled nanostructures, inspired by the properties of natural fibrils such as microtubules and actin filaments. Korevaar *et al.* have investigated the self-assembly of an OPV-derivative, showing that a single pathway is not always sufficient to accurately explain aggregation behaviour, even if only one thermodynamic product exists.[1] Instead, a model including two parallel assembly pathways was proposed, and a similar model can be envisaged if multiple thermodynamic products occur. Transitions between different aggregated phases have also been extensively studied in polymer physics and solid-state chemistry, and contrastingly, usually models involving direct conversion are proposed, as for example by Koehler *et al.*[2] These models are illustrated in Figure 1.

Analysis of the morphology interconversion mechanism starts with a thermodynamic analysis, and subsequently kinetics are examined as a function of concentration. Simulations of a temperature-jump experiment have been performed using ODE-models based on the two different conversion scenarios, and a plot of time to half-completion versus concentration shows marked differences. Currently, work is being performed on verifying the presence of these differences for different parameter values, and on experimentally measuring these t_{50}-concentration graphs using temperature-jump spectroscopy.

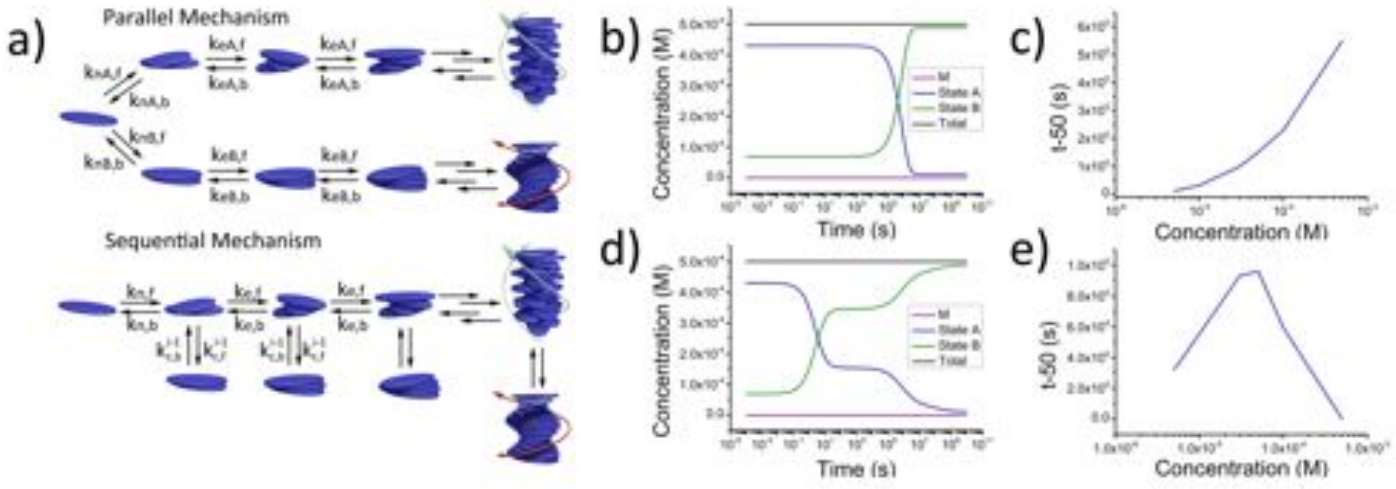


Figure 1. a) Two scenarios for the interconversion of different aggregate morphologies. b) Kinetic simulation using parallel pathway model. c) t_{50}-plot using parallel pathway model. d) Kinetic simulation using sequential pathway model. e) t_{50}-plot using sequential pathway model.

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Anion Recognition by Aryl-Pyrrole Oligomers

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A large set of genetic diseases has been associated with malfunctioning ion channels and has been brought together under the term channelopathies. Synthetic low molecular weight transport molecules can exert powerful effects on biological systems by mimicking the action of natural ion channels. At present, the few synthetic transporters that have been evaluated for chloride ion transport in epithelial cells have yielded promising results. An immediate goal is to provide lead compounds for channel replacement therapies.

Experience in anion recognition by oxacalix[2]arene[2]pyrimidine-based (thio)ureido[1] and selenacalix[3]triazine[2,3] receptors let to the design of a new class of anion receptors, aryl-pyrrole oligomers,[4] designed for chloride/bicarbonate selectivity and compatibility with cell membrane lipids. The compounds were analyzed for their anion binding properties and compared to known anion receptors/transporters. In addition, these synthetic anion transporters can be employed in technologies such as membrane-based sensors, separation processes and organocatalysis.

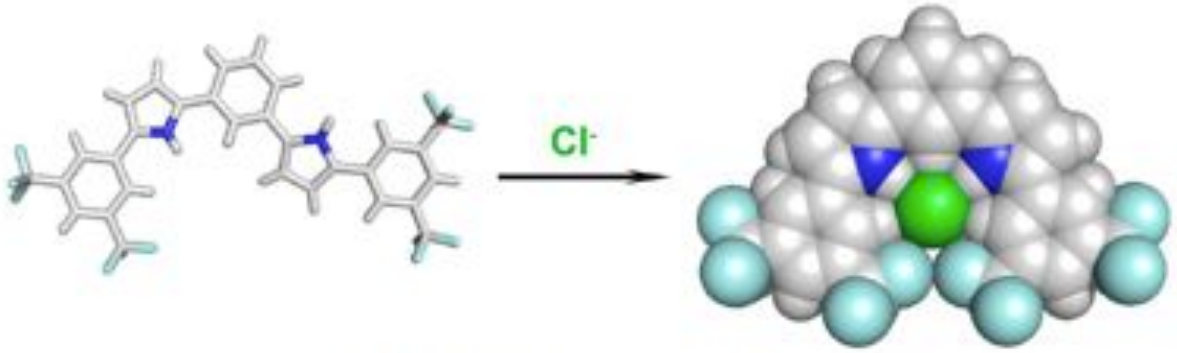


Figure 1. Aryl-pyrrole oligomer as anion receptor.

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Post-Synthesis MOF Modification Using a Grubbs Catalyst

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The transformative ability of the olefin metathesis reaction, popularized by the extensive use of Grubbs' catalysts, is both unique and chemically enabling. In addition to the extensive use of this reaction in the fields of polymer chemistry and materials science, Grubbs catalysts have been employed in the preparation of complex small molecules. One example of the power of this chemical transformation, in the context of small molecule synthesis, is the generation of aromatic motifs from vinyl benzene starting materials, known as the aromatizing ring closing metathesis (ARCM) reaction.[1] Despite the wide utility of olefin metathesis reactions, this transformation is notably missing from the metal organic framework (MOF) literature. The use of the ARCM reaction inside MOFs would introduce a new class of post-synthesis modifications into this type of three-dimensional porous material and enable the synthesis of new extended frameworks.[2] To this end, a strategy utilizing solvent-assisted linker exchange (SALE) on a pre-formed framework has been used to generate (Figure 1) a MOF containing open struts which can function as a testing ground for the ability of an olefin metathesis catalyst to form polyaromatic ring systems inside the pores of a MOF.[3] The "open" form of the MOF has been exposed to the Hoveyda-Grubbs first generation catalyst and transformed into the "closed" form without destruction of the porous framework. This proof-of-concept, not only shows the potential for carrying out advanced chemical transformations inside MOFs, but it also anticipates the formation of otherwise difficult-to-prepare porous materials.

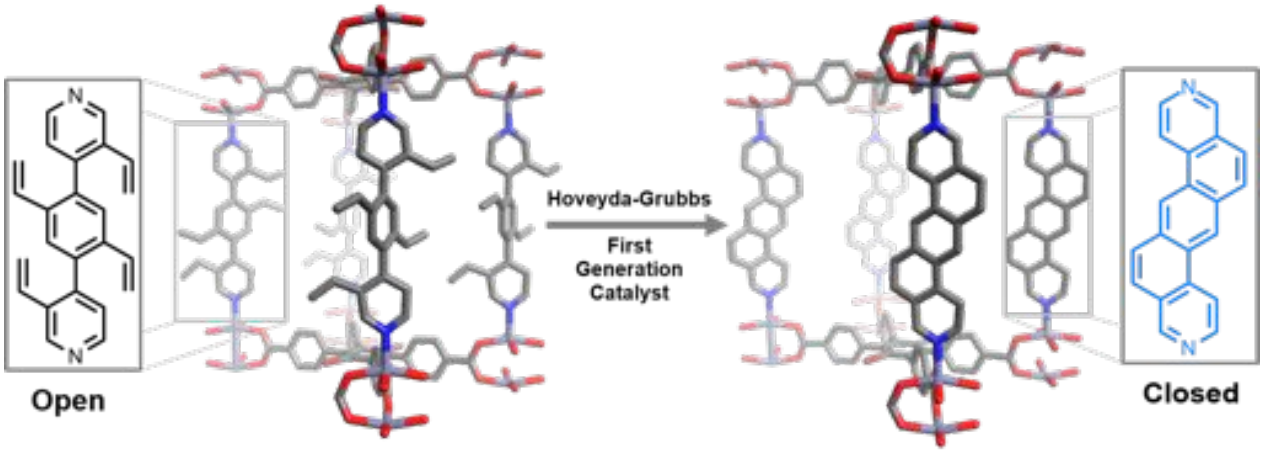


Fig 1. The crystal structures of a MOF with a tetracarboxylate-Zn paddlewheel floor and ceiling, and dipyridyl pillars in the "open" form transformed to a modified MOF with pillars in the "closed" form.

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Synthesis and Self-Assembly Processes of Monofunctionalized Cucurbit[7]uril

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The cucurbit[n]uril family of molecular containers has been well-researched over the past two decades, leading to remarkable derivatives of especially CB[5] and CB[6] with interesting properties and applications. However synthesizing derivatives of the larger CB[7] analogue, which is highly water soluble and binds a wider range of guests with strong affinity, has proven to be a synthetic challenge over the years which has greatly hindered its progress in a variety of applications.[1] We present a building-block approach towards monofunctionalized CB[7] derivatives by the condensation of gylcoluril hexamer and glycoluril bis(cyclic ether).[2] The resulting CB[7] derivatives Me_2CB[7] and CyCB[7] exhibit high intrinsic water solubility (264 mM and 181 mM, respectively). Due to this high water solubility, Me_2CB[7] is able to solubilize the insoluble drugs albendazole and camptothecin. The reaction of glycoluril hexamer and glycoluril bis(cyclic ether) gives a CB[7] derivative **1** which bears a reactive primary alkyl chloride group. Elaboration on compound **1** yields CB[7] derivative **2** which bears a covalently attached triazolyl ammonium group, a well-known guest for the CB[7] cavity. Compound **2** undergoes self-assembly to form a cyclic tetrameric assembly the structure of which was confirmed by NMR spectroscopy (^{1}H, variable-temperature, and DOSY) and electrospray mass spectrometry.

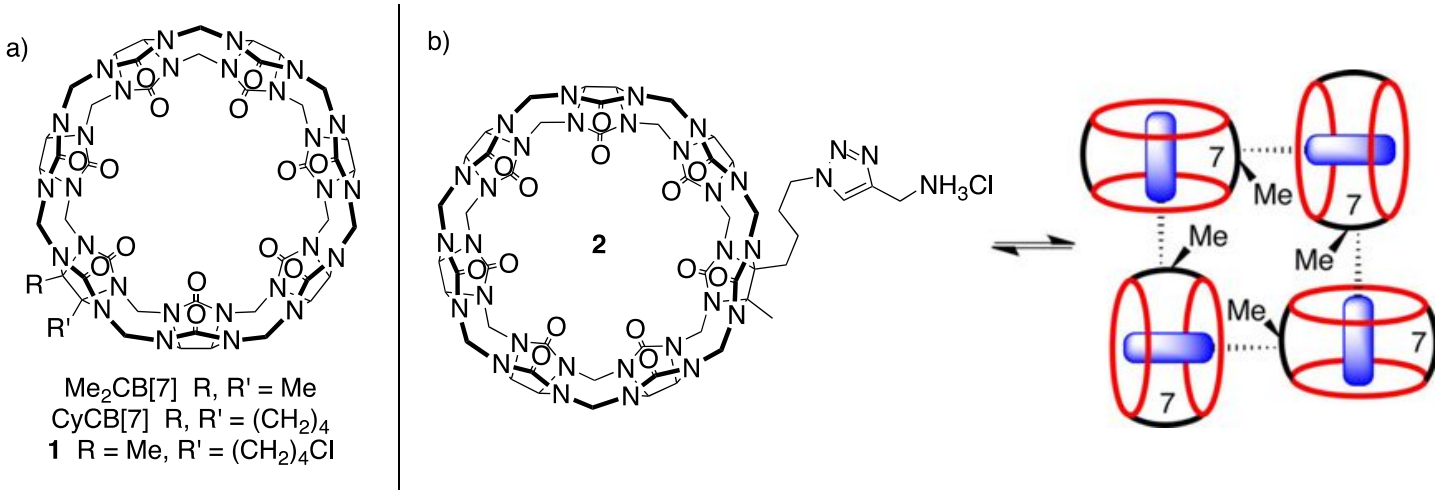


Fig 1. a) Structure of CB[7] derivatives Me_2CB[7], CyCB[7], and Cl-CB[7] **1**. b) Structure of the triazaloyl-bearing CB[7] derivative **2** and the self-assembly of **2** into a tetrameric assembly.

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The Rational Molecular Design and Supramolecular Assemblies of Cage Metal Complexes as "Smart" Electrocatalysts of HER

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During the last decades, the traditional methods of generating heat and electricity give way to the modern hydrogen energetics. Many scientists are now focused on search for highly efficient catalytic systems that can make it possible to split water and to generate H_2 from aqueous solutions; the developing the suitable electrocatalysts for the redox process $2H^+/H_2$ still remains a daunting challenge. The rationally designed and immobilized on a surface of the working electrode the iron and cobalt clathrochelate electrocatalysts are among the so-called "smart molecules"[1,2]: they are cheap, synthetically available and environmentally friendly compounds with both the chemical and thermodynamical stability in at least two oxidation states as well as in the wide range of the redox potentials, pH and temperature. The specific reactivity of the cage metal complexes as molecular scaffolds allows for both their functionalization with different pendants and an immobilization on the working electrode with formation of SAM. They demonstrate high rate of an electron transfer and the fine redox-tuning of their redox potentials to the potential of the reduction $2H^+/H_2$ in a given system; the rational design of such immobilized cage electrocatalysts allows obtaining those with lowest overpotential. In aqueous solutions at low pHs, their pendants substituents with activated hydrogen atoms undergo a fast deprotonation – reprotonation reaction working as "proton pump". This resulted in dramatic increase in the rate of H_2 evolution due to a fast intramolecular formation of the H – H bond and in the substantial improvement of the characteristics of electrocatalytic process.

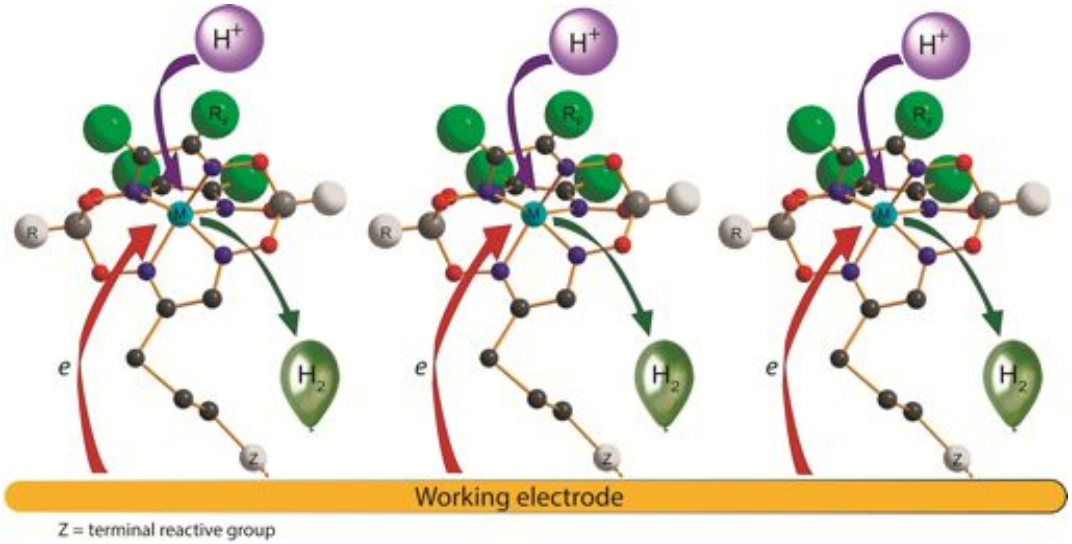


Figure 1. Formation of the clathrochelate SAM on a surface of the working electrode.

References 1) Pantani, O; Naskar, S.; Guillot, R.; Millet, M.; Anxolabéhère-Mallart, E.; Aukauloo, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 9948–9950. 2) Voloshin, Y.Z. *et al*. *Chem. Commun*. **2011**, *47*, 7737–7739; *Dalton Trans.* **2012**, *41*, 6078–6093; **2013**, *42*, 4373–4376; *J. Phys. Chem. C* **2013**, *117*, 2753−2759.

Arylethynylamide-Based Dithiol Sensors

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A series of redox active disulfides based on the 2,6-bis(2-anilinoethynyl)pyridine scaffold[1-3] have been synthesized for use as potential oxidative stress sensors in vitro (Figure 1). Reduction of the sulfur moiety within the sensor revealed a distinct fluorescence response dependent on the oxidation state of the sulfur linkage. The reduction potentials of the pertinent disulfide bond have been measured through cyclic voltammetry in non-aqueous solutions. The potentials can be affected by the steric and electronic influences of neighboring functionality. These sensors are currently under investigation as molecular probes to demonstrate the location and severity of oxidative stress within cells. In addition to sensing changes in redox potential, the dithiol sensor is being investigated as an indicator for various metal ions. For example, reaction of thiophilic metals to bridge the dithiol dramatically changes the fluorescence response through various mechanisms.

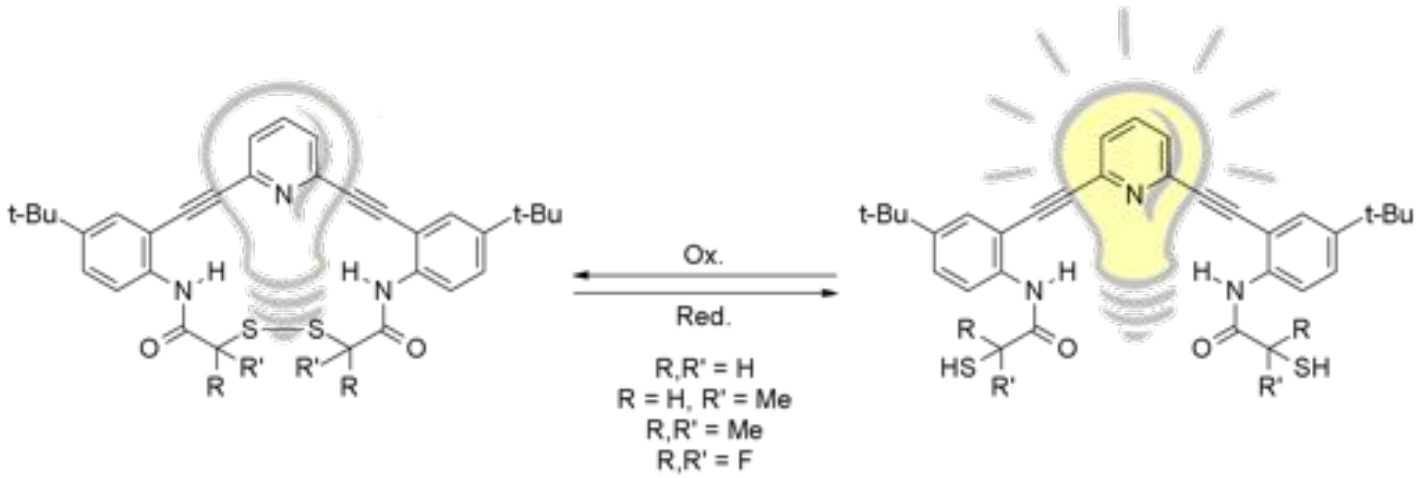


Figure 1. Redox sensing behavior of ethynylarene scaffolds.

References 1) Engle, J. M.; Carroll, C. N.; Johnson, D. W.; Haley, M. M. *Chem. Sci.* **2012**, *3*, 1105. 2) Carroll, C. N.; Coombs, B. A.; McClintock, S. P.; Johnson II, C. A.; Berryman, O. B.; Johnson, D. W.; Haley, M. M. *Chem. Commun*. **2011**, *47*, 5539. 3) Carroll, C. N.; Naleway, J. J.; Haley, M. M.; Johnson, D. W. *Chem. Soc. Rev.* **2010**, *39*, 3875.

Metal-Organic Frameworks with Interlocked Dynamic Components

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There has been a variety of molecular based switches and machines reported which are based on the relative movement of interlocked molecules in solution. These current systems only operate in solution or a condensed phase in which the molecules are randomly dispersed and there motion incoherent. If these tiny devices could be organized in a predictable manner the idea of creating ultra-dense molecular memory and/or controlling the opto-electronic properties at a molecular level could be much closer to realization. In order to achieve a higher level of organization we have placed mechanically interlocked molecule (MIMs) into the pores of metal organic frameworks (MOFs).[1,2] UWDM-1 (University of Windsor Dynamic Material) is constructed from a [2]rotaxane ligand in which the axle contributes to the rigid MOF skeleton while the macrocycle functions as the soft dynamic component, capable of undergoing thermally controlled rapid rotation inside the material. This presentation will describe the synthesis and characterization of UWDM-1 with various ring sizes in addition to a new metal-organic rotaxane framework.

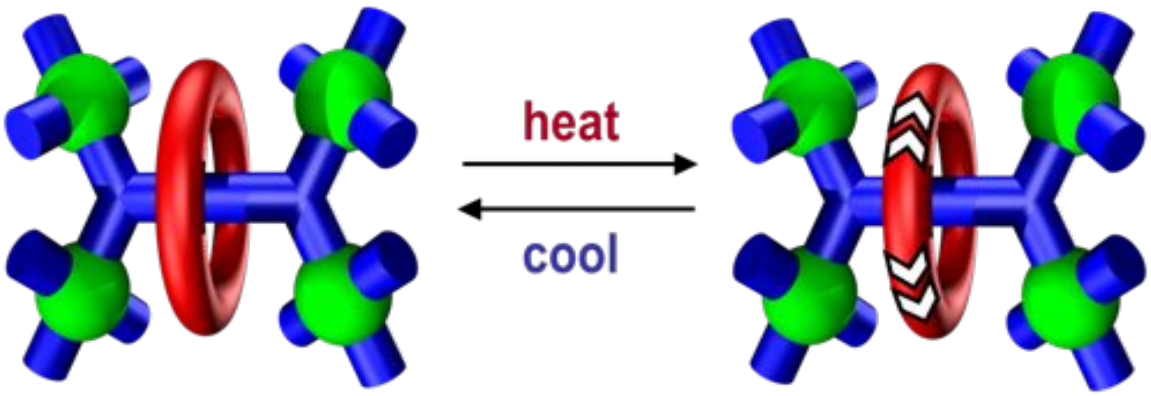


Figure 1. Cartoon dipicting thermally induced rapid rotation.

References

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2) V. Nicholas Vukotic, Kristopher J. Harris, Kelong Zhu, Robert W. Schurko, and Stephen J. Loeb, *Nature Chemistry*, **2012**, 4, 456-460

Access to Versatile β-Cyclodextrin Scaffolds Through Guest-Mediated Mono-Acylation

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Functionalized β-cyclodextrins (β-CDs) have a wide range of applications including catalysts, biological sensors, and drug delivery agents.[1, 2] The synthesis of mono-derivatized β-CDs usually necessitates multiple synthetic steps involving the mono-tosylation of an alcohol on the primary rim, followed by the introduction of a nucleophile. To complement existing approaches, we previously developed the synthesis of mono-derivatized heptakis-[6-deoxy-6-(2-aminoethylsulfanyl)]-β-CD, **1**, achieved through a one-step, highly-selective, guest-mediated S→N acyl transfer.[3] We have recently modified this methodology to feature disulfide and oxime functionalized linkers. Following mono-derivatization, these linkers enable the cleavage of the guest molecule, and yield an orthogonal group as a handle for further transformations to the β-CD scaffold. Using this new methodology, mono-derivatized β-CDs, **2**, and, **3**, were obtained in modest yields and high purity. We have also demonstrated that small molecules and peptides can be appended to the cleaved linkers in order to create β-CD constructs that may serve as catalysts and as sensors for macromolecules.

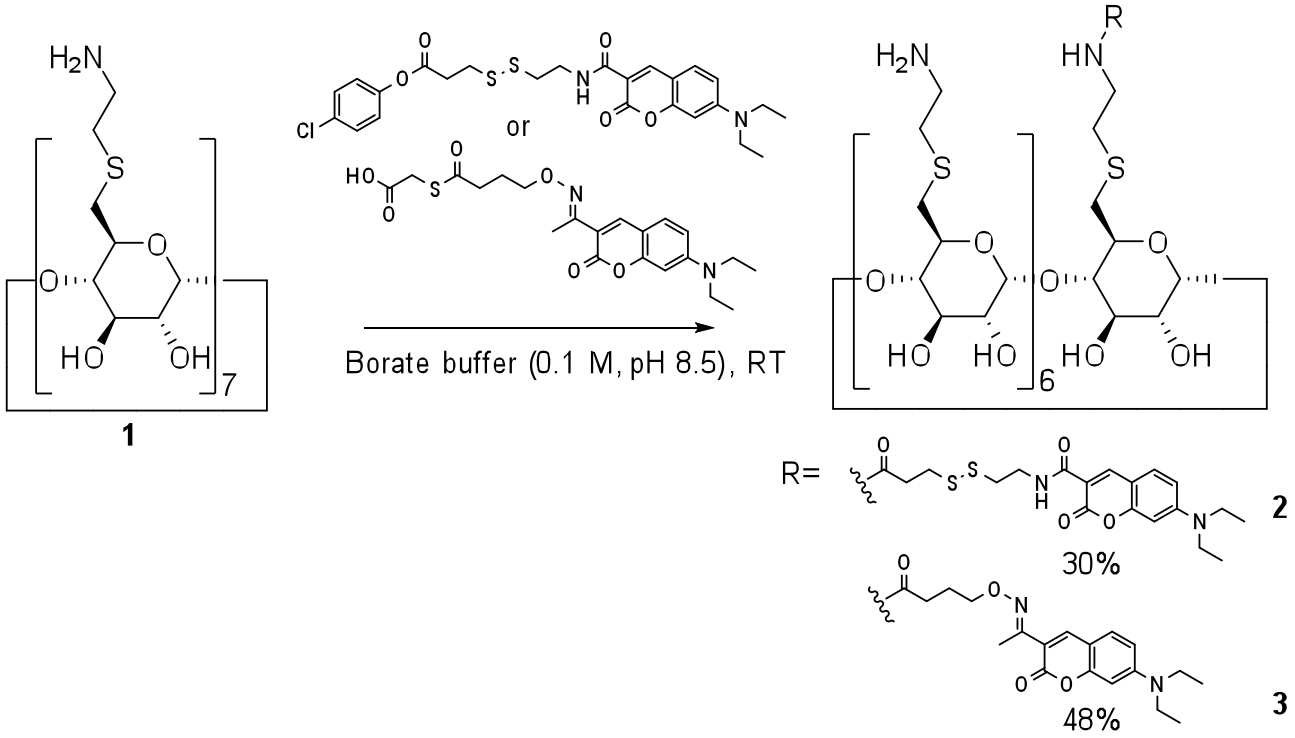


Figure 1. Mono-derivatization of **1** using guest molecules appended to cleavable linkers.

References 1) Breslow, R.; Dong, S. D. *Chem. Rev.* **1998**, *98*, 1997. 2) Wenz, G. *Angew. Chem. Int. Ed.* **1994**, *33*, 803. 3) Gómez-Biagi, R. F.; Nitz, M. *Chem. Commun.* **2011**, *47*, 8614–8616.

Nanostructured Peptide Amphiphile Assemblies for Bioactivity Control

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Peptide amphiphiles (PAs) have been shown to self-assemble into a variety of well-defined nanostructures, such as nanofibers, nanotubes, and nanosheets.[1] Bioactive materials can be realized with PAs by adding bioactive peptides. Such materials are especially important to develop artificial extracellular matrices, regenerative medicine, and drug delivery systems.[2] In this study, we fabricated PA-based hydrogels for cell culture and investigated the relationship between their nanostructure and the bioactivity.

PA molecules were designed to display a peptide sequence for cell-adhesion (arginine–glycine–asparatic acid; RGD). When different hydrophobic moieties were introduced, a variety of self-assembled nanostructures of PA were observed depending on the structure of the hydrophobic parts. Moreover, mixing two PAs could provide a way to precisely control the properties of the hydrogel. In this presentation, we will report the properties of PA-based hydrogels and the influence of the nanostructure on cellular functions.

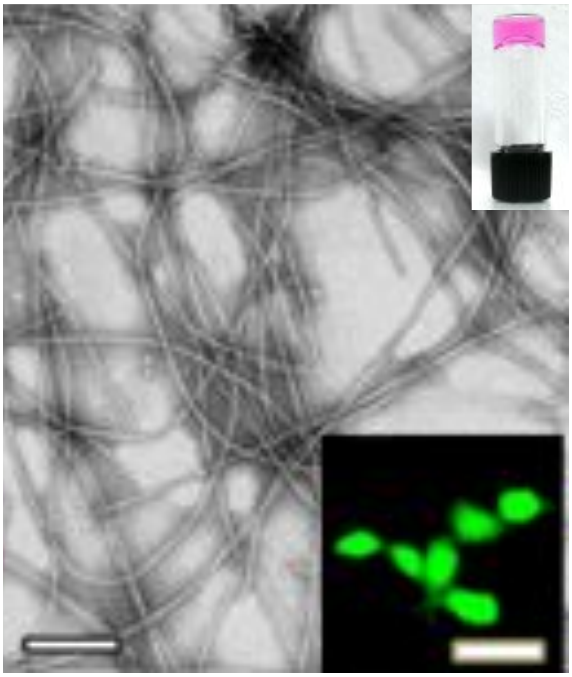


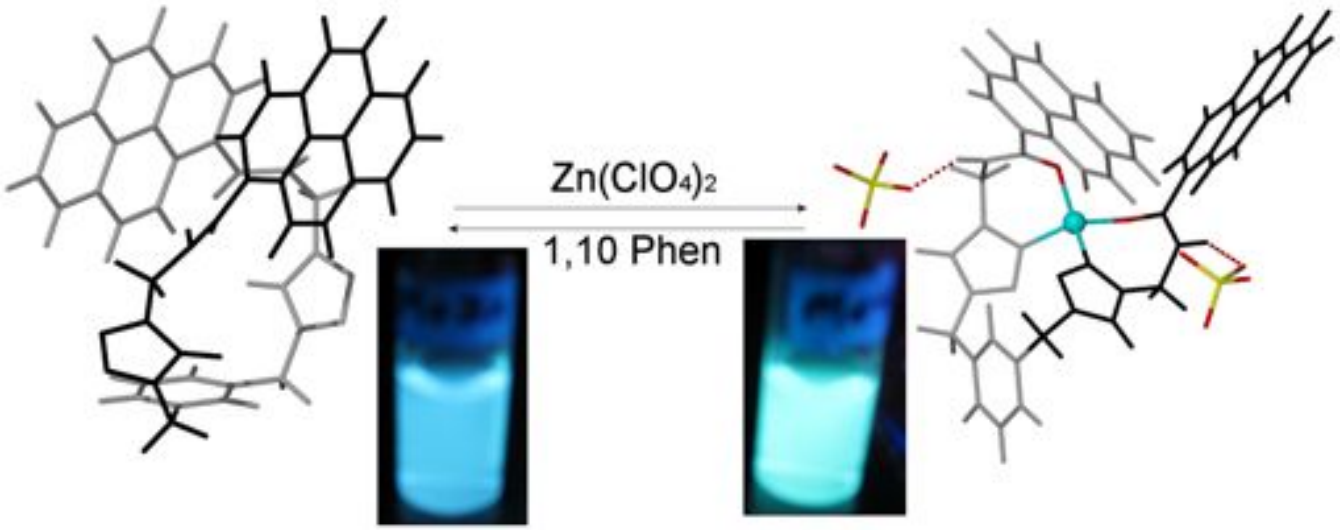
Fig 1. TEM image of PA hydrogel (inset: picture of hydrogel and fluorescence image of L929 cell on the gel).

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Ratiometric Detection of Zn^{2+} by Fluorescent Pyrene-Derived Molecular Probes

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Two pyrene-based molecular probes have been synthesized from *ortho*-and *meta*-bis(azidodimethyl)benzene and their coordination of Fe^{3+}, Al^{3+}, Fe^{2+}. Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Ca^{2+}, Mg^{2+} and Na^{+} cations is described. The greatest spectral changes were observed with Zn^{2+} salts, which are important analytical targets in environmental and biological chemistry, and a detailed investigation on the influence of the counterion (F^-, Cl^-, Br^-, I^-, ClO_4^-, NO_3^-, $CH_3CO_2^-$, SO_4^{2-} and BF_4^-) was undertaken. DFT studies suggest that Zn^{2+} is bound in the cleft of the probes in a 1:1 host:guest A significant hypsochromic shift is observed in the excimer band in the presence of metal salts and is greatest upon the addition of $Zn(ClO_4)_2$. The limit of Zn^{2+} detection is in the nanomolar range for the *meta* isomer and the binding process is reversible allowing the system to be recycled several times. A protocol is proposed that would allow detection of Zn^{2+} in aqueous samples.



Supramolecular Adducts of Squaraine and Protein for Noninvasive Tumor Imaging and Photothermal Therapy In Vivo

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Near-infrared (NIR) dyes with absorption between 650 and 1200 nm have gained increasing attention in recent years due to their promising applications in the fields of material science, biology and medicine.[1] Since the tissue transmission of NIR light is optimal owing to the low body scattering, energy absorption and enhanced irradiation penetration[2] with minimized the autoabsorption and autofluorescence *in vivo*,[3] the NIR dye-based optical imaging technology has been widely used in fundamental biology and pre-clinic diagnostics in living animals. Meanwhile, NIR materials can absorb light and convert the energy to heat by tumor-specific photoabsorbers for photothermal therapy.[4] Compared with other tumor treatment methods, the photothermal therapy is a laser-based minimally invasive treatment modality.

In this abstract, we introduce highly stable and biocompatible supramolecular adducts of SQ and the natural carrier protein, i.e., bovine serum albumin (BSA) (**SQ⊂BSA**) for tumor targeted imaging and photothermal therapy *in vivo*. SQ was selectively bound to BSA hydrophobic domain *via* hydrophobic and hydrogen bonding interactions with up to 80-fold enhanced fluorescence intensity. The highly emissive property of **SQ⊂BSA** did not compromise in the presence of cysteine or homocysteine. By covalently conjugating target ligands to BSA, the **SQ⊂BSA** was capable of targeting tumor sites and allowed for monitoring the time-dependent biodistribution of **SQ⊂BSA**, which consequently determined the protocol of photothermal therapy *in vivo*.

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Hybridized Foldamers

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Hydrogen bonding-induced aromatic amide foldamers exist in solvents of discrete polarity,[1] while 1,2,3-triazole oligomers adopt flexible conformations in solution in the absence of intramolecular hydrogen bonding.[2,3] When the two kinds of oligomers are contacted together, the folded aromatic amide backbones induce the contacted triazole chains to fold into a compact conformation to give rise to a hybrid secondary structure. This phenomenon mainly occurs in less polar solvents in which the intramolecular hydrogen bonding of the aromatic amides is strong to enable the formation of the stable folded state, while the stacking of the triazole backbones is weak. The F···H–N hydrogen bonding pattern is used because the F atom is smaller than RO,[4] the most common hydrogen bonding acceptor,[5] and the resulting aromatic amide foldamers would suffer a smaller steric hindrance when they undergo the intramolecular stacking for the formation of the folded conformation. The hybridized foldamers have been confirmed by ^{1}H NMR, UV-Vis experiments, as well as DFT calculations.

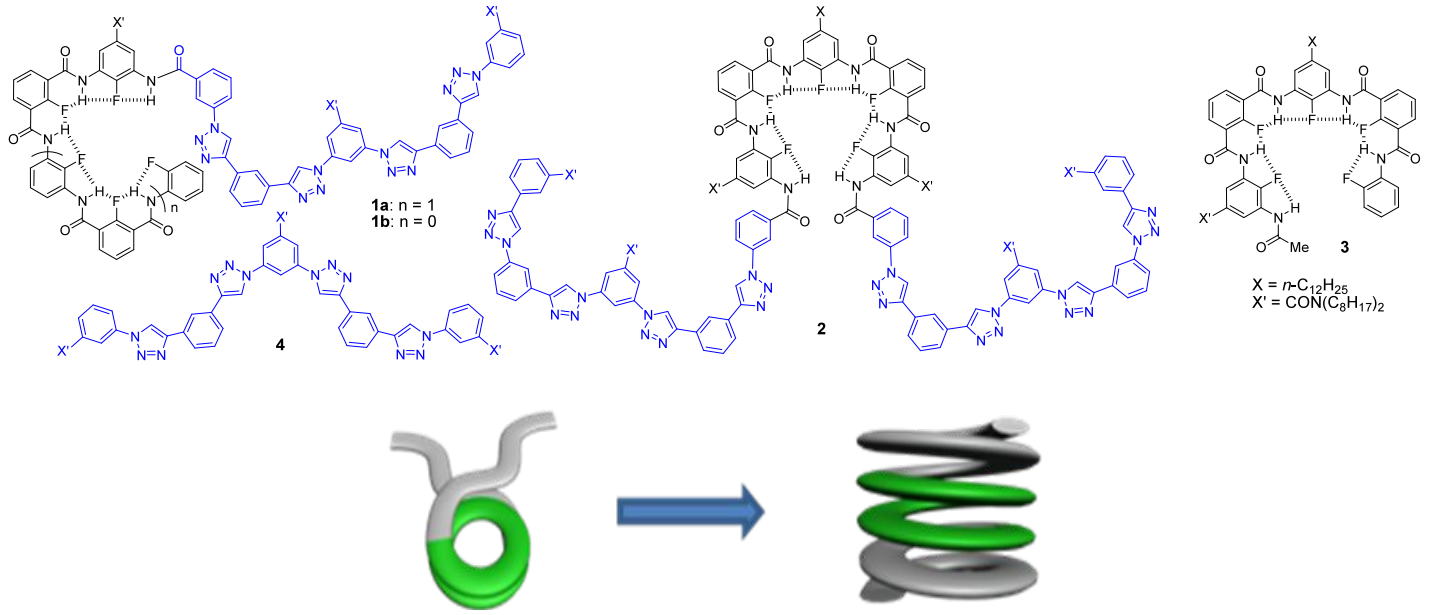


Figure 1. The folded aromatic amide segment induces the attached triazole segments to fold to form hybridized foldamer in solvents of low polarity.

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DNA-Mediated Rotaxane-Like Artificial Muscles

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Artificial muscle is one kind of molecular machine which can fulfill the transduction of chemical electrical or photochemical energy *i*nto controllable molecular motion. The study of this specific area, which holds potential for producing controllable nano- and mesoscale mechanical systems driven by molecular machinery, has received attention increasingly in recent years. Hitherto, several materials, such as conducting polymers,[1] single-walled carbon nanotubes, and dielectric elastomers, have been developed which exhibit muscle-like behavior at the nanoscale level. However, in these systems, the molecules show either non-directional movement or sliding motion rather than compressing and stretching, and are not satisfying when it comes to imitating authentic muscles in animals. In order to address this challenge, doubly bistable rotaxane molecules based on cyclobis-(paraquat-*p*-phenylene) $(CBPQT^{4+})^2$ were introduced in the system, in which the rings can shuttle reversibly along the rod under redox control, thus providing the essential factor to realize the specific directional movement, as well as the compression and stretching. Furthermore, DNA hybridization with its rigid and highly programmable linking nature will be used to assemble rotaxanes into linear assemblies, which will amplify the length change from microscopic to macroscopic (Figure 1). Based on this design, we expect to incorporate the molecule into biological systems and observe its function *in vivo*.

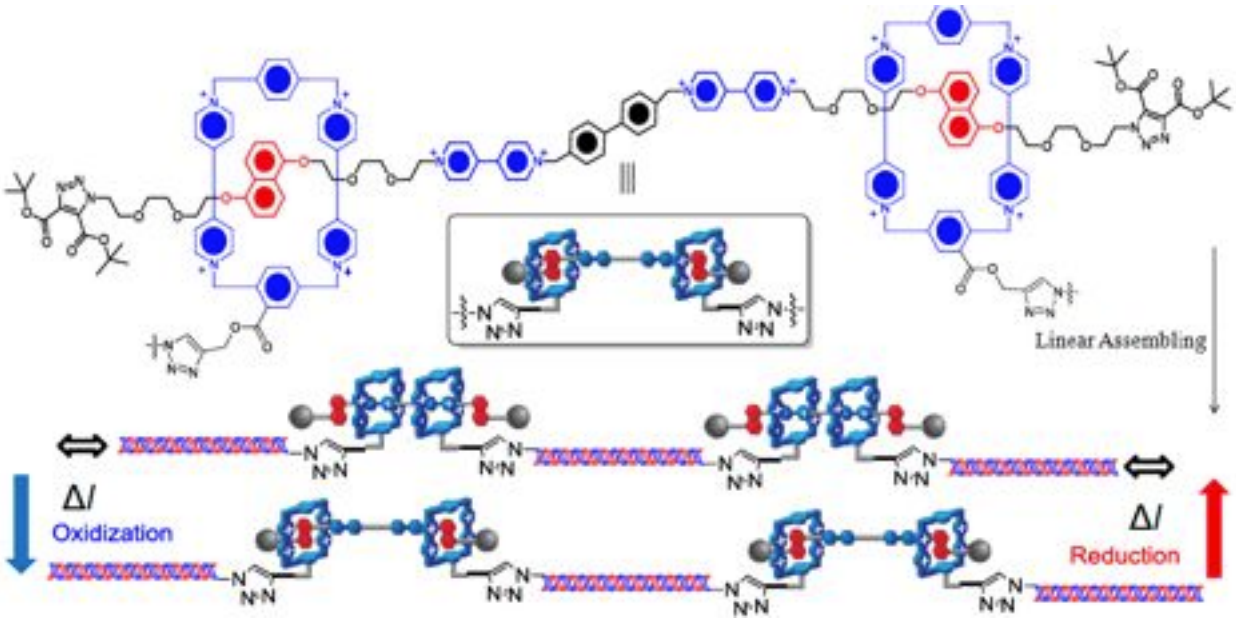


Fig. Length change of the repeating unit could be amplified through DNA-mediated linear assembling.

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Differential Anion Binding of a Tripodal Arylethynyl Urea Receptor Over Competitive Hydrogen Bonding Solvents

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Anion sensing is important due to the roles anions play in biological systems and the environment; selectivity in receptors is therefore crucial for applications. Arylethynylpyridine-based scaffolds have demonstrated a differential fluorescence response upon anion binding.[1-3] Expanding upon these systems, new tripodal 1,3,5-tris(arylethynyl)benzene receptors have been synthesized and show anion binding through hydrogen bonds to the three urea groups. The tripodal geometry and the position of the hydrogen bond donors of the ureas are ideal for binding trigonal planar anions such as nitrate. Excess nitrate in soil from over-fertilization is an important concern for the environment; run-off into water sources causes algal blooms, depriving the water of oxygen. Unfortunately, examples of strong and selective nitrate binding in competitive media are few. The tripodal receptor presented here demonstrates preferential binding of anions over competitive hydrogen bonding solvents. The binding mechanism in acetone-d_6 is complex and cannot be fit to a standard model. In 10% DMSO-d_6/$CDCl_3$ the higher order binding is broken up and the receptors bind anions in a 1:1 stoichiometry. A strong affinity for nitrate is observed even in the presence of DMSO, with an association constant of ~10^4 M^{-1} for nitrate and chloride for the trifluoro-substituted tris-urea receptor.

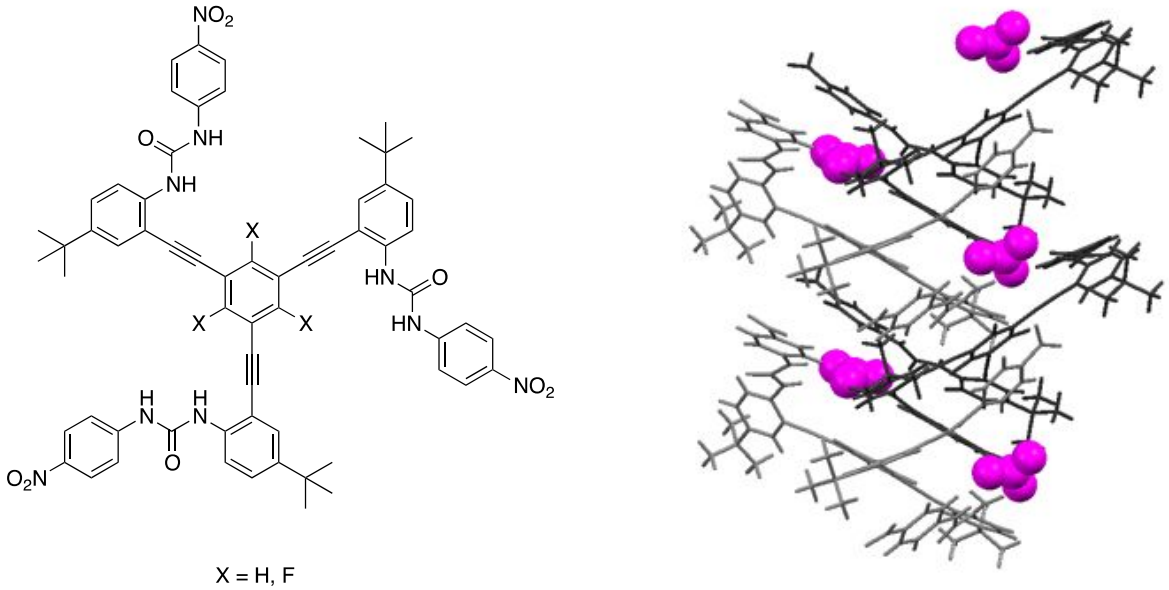


Figure 1. Tripodal 1,3,5-tris(arylethynyl)benzene receptors studied (left). X-ray structure of trifluoro-subsituted system binding nitrate in the presence of acetone (right).

References 1) Engle, J. M.; Carroll, C. N.; Johnson, D. W.; Haley, M. M. *Chem. Sci.* **2012**, *3*, 1105. 2) Carroll, C. N.; Coombs, B. A.; McClintock, S. P.; Johnson II, C. A.; Berryman, O. B.; Johnson, D. W.; Haley, M. M. *Chem. Commun.* **2011**, *47*, 5539. 3) Carroll, C. N.; Naleway, J. J.; Haley, M. M.; Johnson, D. W. *Chem. Soc. Rev.* **2010**, *39*, 3875.

Synthesis, Characterization of Macrocyclic Compounds with A Hydroxyl Functional Group

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Over the past few decades, macrocyclic compounds have attracted much attention due to their wide application in supramolecular and materials chemistry.[1-3] In the present study, a new 26-membered Schiff-base macrocycle **1** bearing a hydroxyl function group has been synthesized from 1,3-bis(2'-formylphenoxy)-2-propanol and resorcinol-bis(4-aminophenyl)ether via condensation and cyclization using Ba^{2+} as a templating metal. The cyclic Schiff base product **1** has also been reduced to the corresponding saturated macrocycle **2** employing $NaBH_4$ in THF/ethanol solution. The [1+1] macrocyclic structures of **1** and **2** were confirmed by single crystal X-ray analysis. The X-ray determination confirmed that **1** has the 26-membered macrocyclic structure shown in Figure 1(a) and that it exists in the solid state in a folded conformation [Figure 1(c)]. The crystal structure of **2** is shown in Figure 1(b). Unlike the structure of **1**, the increased flexibility of **2** in this case is reflected by the adoption of the twisted-folded conformation shown in Figure 1(d).

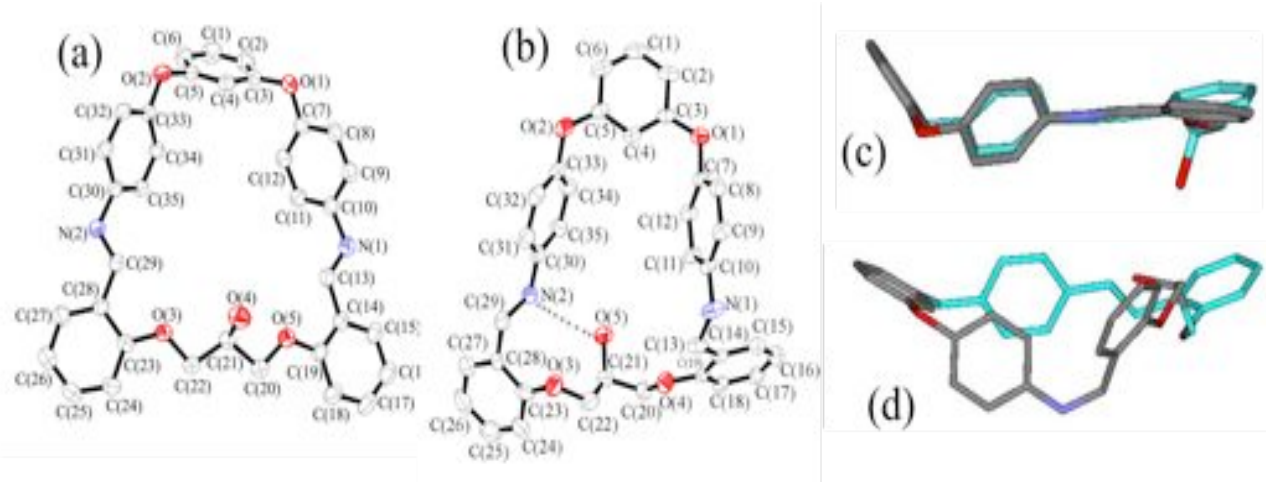


Fig 1. (a) Molecular structure of compound **1;** (b) Molecular structure of **2;** (c) Molecular structure of **1** viewed along side chain; (d) Molecular structure of **2** viewed along side chain.

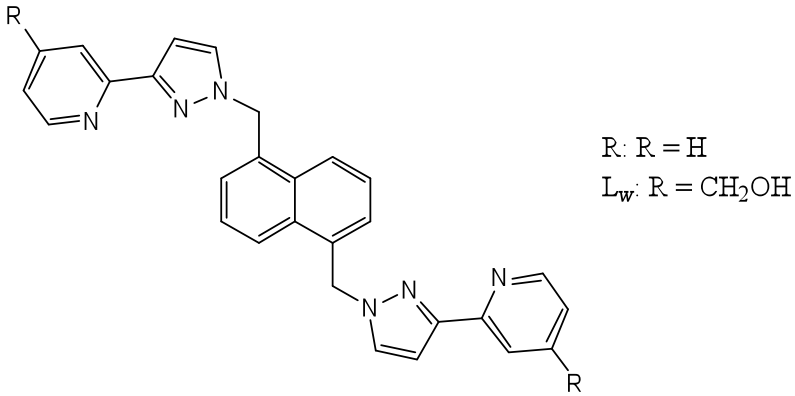
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Quantification of Solvent Effects on Molecular Recognition in Polyhedral Coordination Cage Hosts

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A water-soluble cubic coordination cage (**Hw**) has been prepared, which is isostructural with a previously reported organic-soluble cage (**H**) apart from the hydroxy groups on the external surface which render it water-soluble.[1,2] These two cages act as hosts for small organic molecules which bind *via* a combination of (i) hydrogen-bonding interactions with specific sites on the internal surface of the cages; (ii) non-polar interactions such as aromatic and van der Waals' interactions between aromatic rings in the guest and the cage internal surface; and (iii) solvophobic interactions. By comparing $\Delta G°$ values for guest binding in water (using **Hw**) and MeCN (using **H**), and using pairs of related guests that differ in the presence or absence of an aromatic ring substituent, it is possible to construct thermodynamic cycles that allow quantification of the solvophobic contribution to binding. Specifically, this is the difference between the solvophobic contributions to $\Delta G°$ in water and MeCN associated with desolvation of both guest and the internal surface of the cage when complexation occurs. A highly consistent value of *ca.* –10 kJ mol-1 is determined for this solvophobic contribution to $\Delta G°$ associated with the aromatic ring in water compared to MeCN. The ability to prepare related pairs of guests with the presence or absence of a wide range of substituents provides a potentially general way to quantify the solvophobic contributions to guest binding of these substituents.[3,4]



R: R = H
L_w: R = CH_2OH

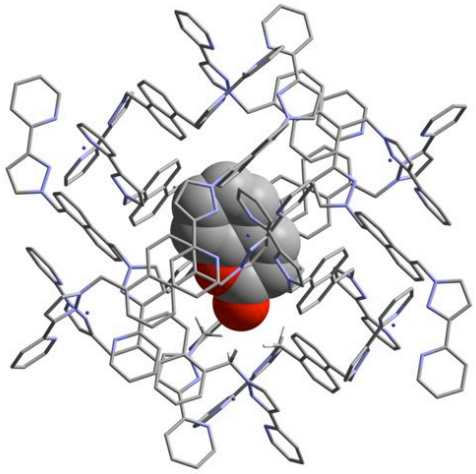


Figure 1. Structural formulae of the ligands used to prepare the host cages (right), molecular model of guest in cage cavity (left).

Rotaxane Formation by Donor–Acceptor Mediated Assembly

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Various aromatic donors (D) and acceptors (A) have been studied[1] both experimentally and *in silico* in order to gain a deeper understanding of D–A pairing energetics and morphologies which arise from their π–π stacking interactions. Rotaxanes obtained by the clipping approach[2,3] serve as useful scaffolds for studying the assembly of different D–A pairs while being able to control the number of units that assemble as a result of using monodisperse templates and thermodynamic equilibria. Rotaxane templates, featuring $-NH_2^+-$ binding sites located 3.5 Å apart,[2] provide an ideal distance for π–π stacking between the D/A-functionalized rings which encircle them. It was postulated[1,4] that the D–A pairing energies in a model [3]rotaxane system would be high enough to overcome homo-dimer formation on account of the significant differences in their quadrupole moments. Indeed, preliminary spectroscopic results point to the formation of alternating D–A π-stacks. By tuning the donating or accepting properties of the clipping precursors, we should be able to assess D–A pair selectivity and impart a high degree of ordered self-assembly. Upon completing model [3]rotaxane studies, we aim to construct larger oligo/poly[n]rotaxane systems where the long-range D–A-mediated self-assembly may lead to highly ordered thermodynamic products with emergent material properties.

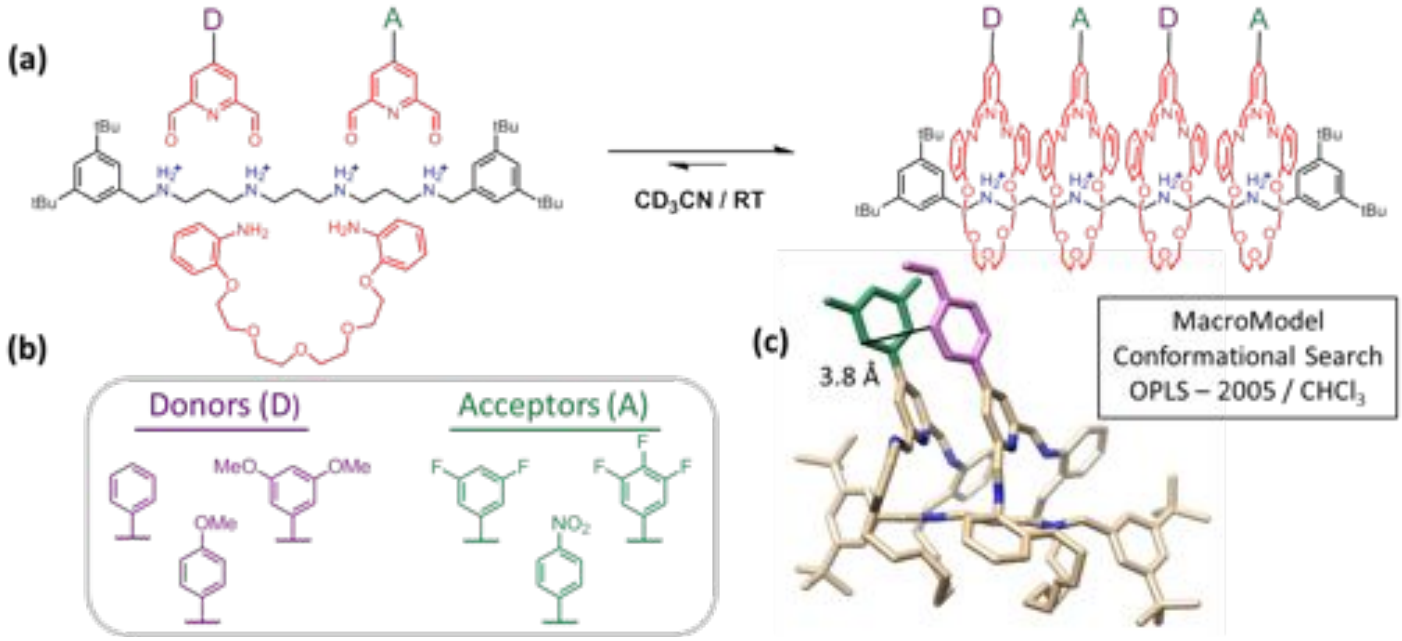


Figure 1. **(a)** D-A-Mediated assembly of a [5]rotaxane. **(b)** Different aromatic D/A compounds used in the assembly process. **(c)** Computational model of a D/A [3]rotaxane.

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Arrested Development: The Accidental Isolation of a Stable Cu^{I} Triazolide Rotaxane

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The active template approach, introduced by Leigh and co-workers in 2006, is a powerful method for the synthesis of mechanically bonded molecules. Recent work from the Goldup Group has demonstrated the use of "small" macrocycles in the active template synthesis of rotaxanes and that these reactions proceed in excellent yield.

During an active template Cu^{I} mediated alkyne-azide cycloaddition reaction (AT-Click) using one of these small macrocycles, we unexpectedly isolated a Cu^{I} triazolide rotaxane. Amazingly, this species has proven stable to aqueous work-up and silica gel column chromatography. Quantitative protonation of the Cu^{I}-C bond to give the corresponding rotaxane can be achieved by addition of acid or heating to above 80 °C once the AT-click reaction has completed, although these processes are remarkably slow.

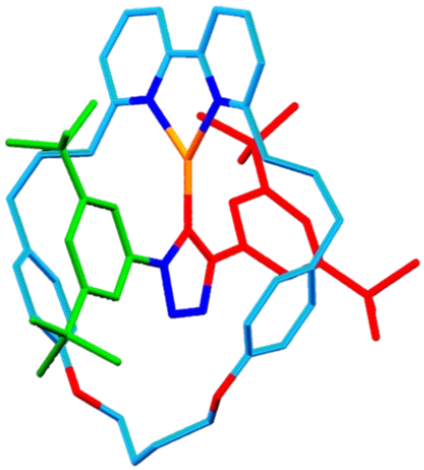


Figure 1. Crystal structure of stable Cu^{I} triazolide rotaxane.

Mechanistic studies of the triazole "click" reaction have implied the existence of a Cu^{I} triazolide intermediate with the presence of such a species confirmed by Straub and co-workers who isolated a Cu^{I} triazolide through reaction of a sterically hindered NHC-ligated Cu^{I} acetylide with a bulky azide under strictly anhydrous conditions.[2] Our results indicate that the sterically hindered environment of the mechanical bond in small, crowded rotaxanes is an even more effective method for stabilizing highly reactive intermediates.

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A Water-Switchable Doubly Bistable Palindromic [3]Rotaxane for Use in Artificial Muscle Materials

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Artificial muscles are an essential component for the development[1] of next-generation prosthetic devices, minimally invasive surgical tools, and robotics. Presented here is the design, synthesis, and characterization of a mechanically interlocked molecule (MIM) capable of switchable and reversible relative molecular motions that mimic muscular contraction. The doubly bistable palindromic [3]rotaxane design uses radical-based switching chemistry[2] and is compatible with aqueous media. In order to utilize the molecular actuation of this MIM in an artificial muscle material, an ordered assembly that coordinates the individual molecular motions of the palindromic [3]rotaxane is also required. Towards this end, [3]rotaxane derivatives containing versatile functionalization handles are being pursued to allow conjugation to macromolecules such as DNA and peptides. Thus, known motifs of biomolecule self-assembly will be utilized to integrate the switachble [3]rotaxanes into highly ordered structures and translate their molecular motions into macroscale movements.

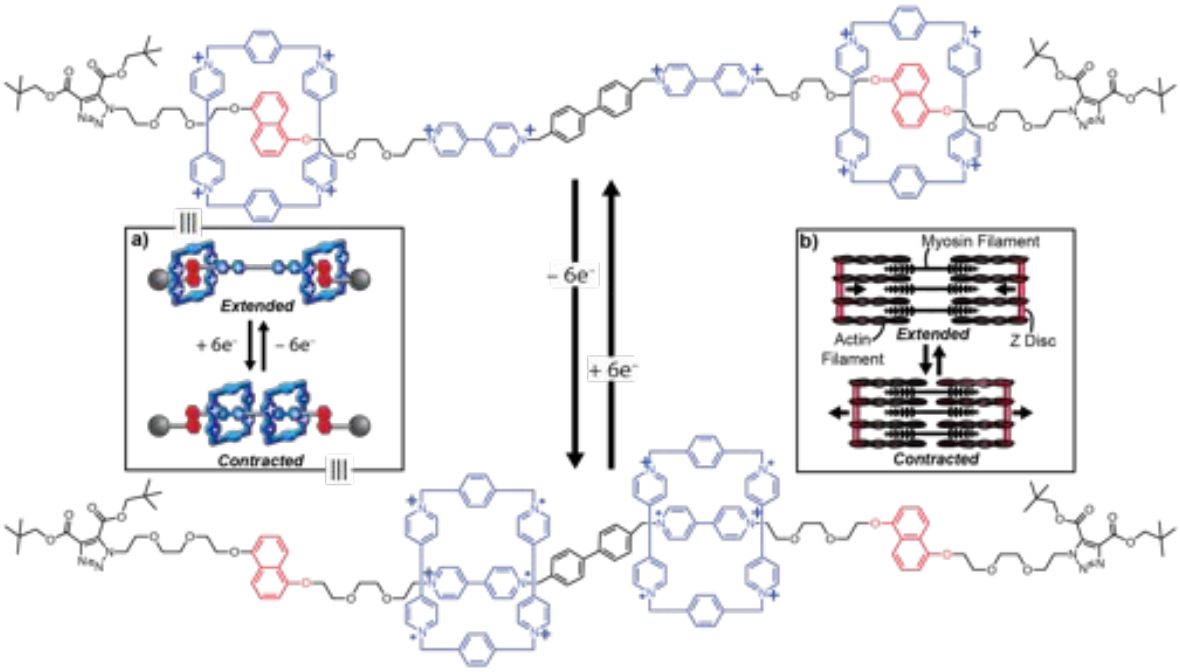


Figure 1 Structural formulas of the oxidized (top) and reduced (bottom) forms of a doubly bistable palindromic [3]rotaxane. **a**) Graphical representation of the relative motion of the macrocylic components, which undergo a contraction and expansion that mimics muscular motion. **b**) The contraction of the sarcomere in biological muscle is achieved through the molecular motion of actin and myosin proteins sliding relative to each other.

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A Molecular Electromechanical Brake

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Molecular devices are of interest on accounts of their potential applications in electronics, catalysis, sensing, and nanomedicine.[1] A common class of molecular devices is a molecular rotor which converts chemical or photochemical energy into circular motion.[2] Among stimuli-responsive rotors are molecular brakes which can be slowed down or even stopped upon application of an external stimuli, typically chemical or photochemical ones.[3]

Here, we describe how we have designed and synthesized a switchable [2]rotaxane formed between a $CBPQT^{4+}$ ring and a dumbbell containing TTF and a fluorescent molecular rotor, namely BODIPY[4] as a stopper. This [2]rotaxane has only one switchable binding site and therefore exists as one translational form in its ground state. Upon oxidation of TTF, the $CBPQT^{4+}$ ring is forced towards the BODIPY rotor as result of Coulombic repulsions. The friction between the ring and BODIPY increases the energy barrier of the rotation and halts the fluorescent rotor. The system is investigated using 1-D and 2-D NMR spectroscopies, steady-state and ultrafast time-resolved laser spectroscopies, electrochemical methods and quantum mechanical calculations. The co-conformational changes arising from the switching of the rotaxane were readily monitored by the fluorescent output of the BODIPY unit. The results confirm that the system operates as a molecular brake, actuated by electromechanical means.

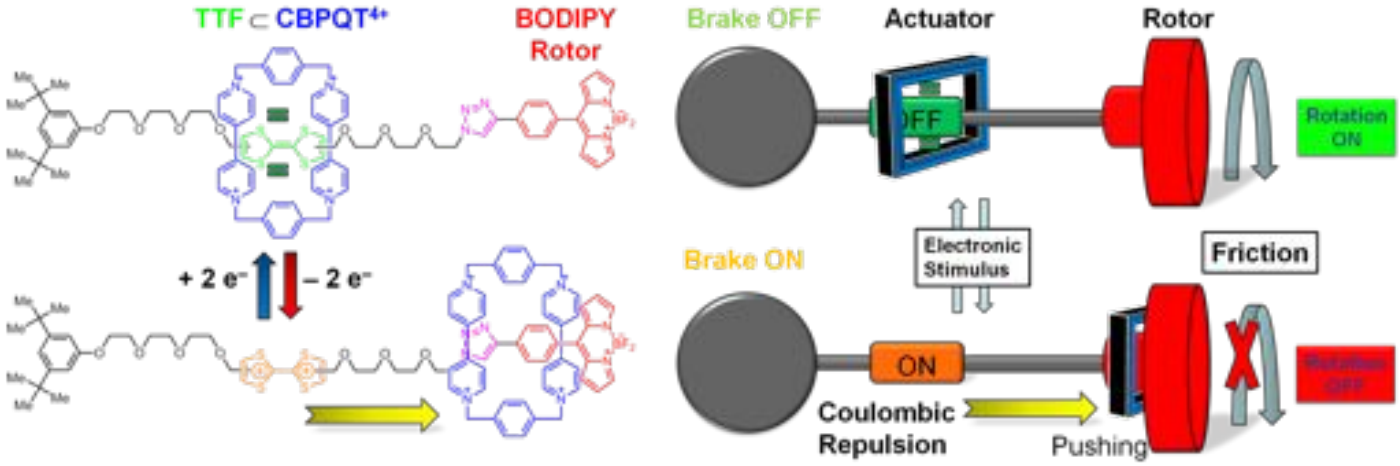


Figure 1. Operation of the switchable molecular brake actuated by an electrochemical stimulus.

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Thixotropic Hydrogel Formations in Universal Aqueous Solutions through Self-assembly of an Amphiphilic Tris-urea

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Development of supramolecular hydrogels has been an attractive field in supramolecular chemistry because of their use in a range of biological applications for tissue engineering, cell culture, drug delivery, and others. An amphiphilic tris-urea **1** was designed and synthesized as a low-molecular-weight gelator. The minimum gelation concentration of **1** was 0.25 wt% (1.9 mM). The hydrogel had a thixotropic property, and showed reversible gel−sol phase transition in response to mechano-stress. Low viscosity liquid was obtained after brief shaking the hydrogel of **1** using vortex vibrator for 5 seconds. Hydrogel was recovered from the liquid state within 10 minutes. The mechano-responsive gel−sol phase transition was repeatable at least 30 times. The amphiphilic tris-urea **1** formed gels with universal aqueous solutions such as saturated sodium chloride solution, 8 M hydrochloric acid, and 7 M potassium hydroxide solution. These hydrogels still retain their thixotropic nature.[1)]

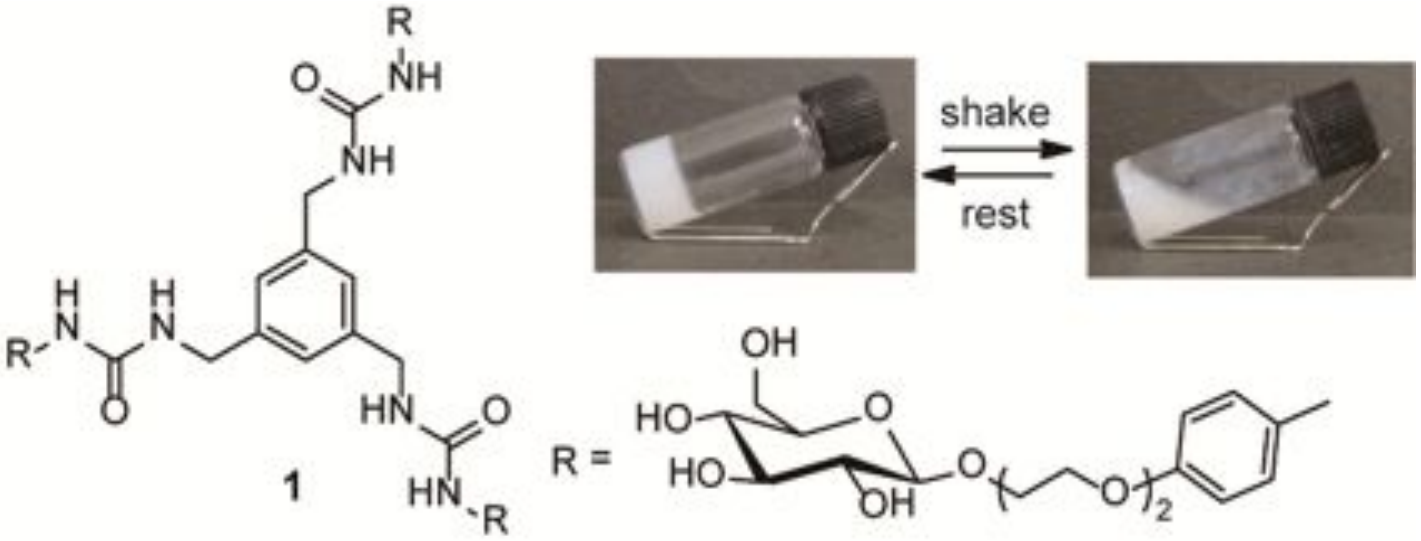


Figure 1. Chemical structure of amphiphilic tris-urea **1**, and the thixotropic property

References

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Novel Water Soluble Gold Nanoparticles for Peptide Recognition

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Mixed monolayer-protected gold clusters (MMPC) comprise a gold core of variable size whose surface is covered with ω-functionalized alkyl thiols. The functional groups that are distributed across the nanoparticle surface are responsible for the MMPC properties. Appropriate binding sites, for example, allow interactions with a complementary binding partner. The possibility to vary the size of gold nanoparticles and the type of number of functional groups on their surface in a wide range makes these systems interesting for a number of applications including the specific recognition of biomolecules. In this context it is crucial that MMPCs are able to interact with the potential binding partners in aqueous solution. Thus, not only have the MMPCs to be water soluble and stable in aqueous media, also the binding event has to tolerate water. So far, there is only a limited number of artificial receptors which have high affinity for biomolecules in aqueous solutions.[1-5]

In our group, a novel approach is pursued to synthesize MMPCs with peripheral functional groups that bind short peptides in water. Specifically, MMPCs are generated by replacing the ligands of amine-protected gold clusters with different ω-functionalized alkyl thiols. The functional groups are chosen to target characteristic functional groups of the potential substrate. In this poster, our synthetic work in this context and first results are presented.

References

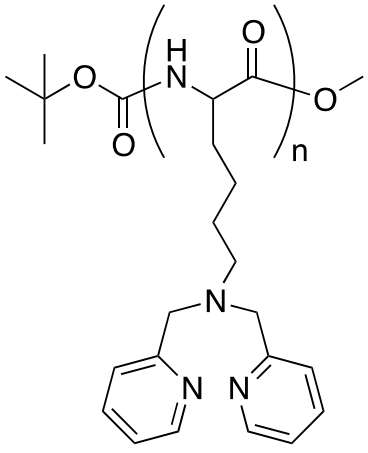
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Antimicrobial Action of Metal-Chelating Artificial Oligopeptides

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Various antimicrobial peptides (AMPs) are found in many living organisms as an innate immune system. AMPs are known to minimize development of drug resistance, because AMPs attack bacterial membrane rather than specific proteins. Inspired by the nature of AMPs, we designed artificial oligopeptides (Oligo-DPA, ***Figure 1***) with a dipicolylamine (DPA) moiety to selectively perturb bacterial membrane. DPA strongly binds to anionic phospholipids, which are enriched in bacterial membrane, through the complexation with zinc ion (Zn^{2+}). A series of oligopeptides with different amino acid lengths was obtained by repeating liquid-phase synthesis. In the presence of Zn^{2+}, Oligo-DPA displayed antimicrobial activity against *E. Coli* and *S. Aureus* depending on the number of amino acid units. The octamer and 12 mer expressed the highest antimicrobial activity for *S. aureus* and *E. coli*, respectively, whereas the monomer and short peptides (dimer and trimer) were inactive, reflecting the presence of optimal length of the peptide for the antimicrobial action. Oligho-DPA did not display antimicrobial activity in the absence of Zn^{2+}. In contrast to the high antimicrobial activity, Oligo-DPAs did not show hemolytic toxicity regardless of peptide length. The detailed action mechanism of Oligo-DPA is further discussed based on the model membrane study using liposomes.



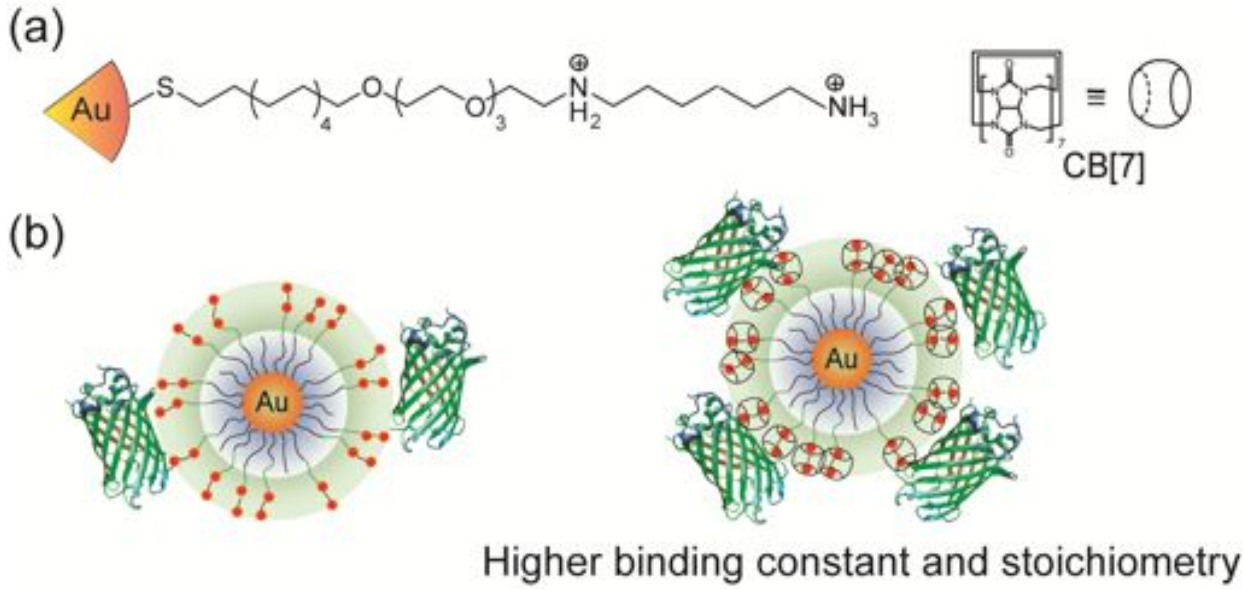
Oligo-DPA
(n = 1, 2, 4, 8, 12 and 16)

Figure 1. Chemical structure of Oligo-DPA

Supramolecular Tailoring of Protein-Nanoparticle Interactions

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Supramolecular chemistry is a versatile tool to extend the applications of nanoparticle in biology, such as regulating of nanoparticle toxicity and labeling of cellular biomarkers.[1,2] The inherent modularity of supramolecular chemistry provides a promising strategy to change the surface properties of nanoparticles as well as their interaction with biomolecules. Herein, a supramolecular host-guest complexation is utilized for effective regulation of protein-nanoparticle interactions. We synthesize gold nanoparticles (AuNPs) featuring diaminohexane as the terminal moiety to be recognized by cucurbit[7]uril (CB[7]). The binding of CB[7] on AuNP surface modulates the surface properties of AuNPs and change the interactions toward green fluorescent protein (GFP). Supramolecular modulated complex stability constants (*Ks*) and binding stoichiometries (*n*) of GFP-AuNP conjugates were quantified through the fluorescence titration curve fitting. The results indicate that higher binding constants and higher binding ratios were observed in the GFP and CB[7] encapsulated-AuNP complexes. Interestingly, the extent of ligand exchange on AuNP surface determines the degree of CB[7] effect on the protein-nanoparticle interaction. Effective modulation of the protein-nanoparticle interactions through supramolecular strategy will allow a better control of protein behavior/function using nanoparticles for potential biomedical applications.



Scheme 1. (a) Structure of a diaminohexane-functionalized gold nanoparticle and cucurbi[7]uril (CB[7]). (b) Schematic of the protein-nanoparticle interaction in the absence and presence of the guest molecules CB[7].

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Nanoparticle Encapsulation of Synthetic Catalysts for Intracellular Catalysis

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Metal mediated catalytic compounds are currently playing an increasingly important role in chemical biology for applications such as amplification of signals, catalytically labelling or deactivating target molecules, or prodrug activation.[1] However, designing catalysts and controlling their activity under physiological conditions is challenging due to the presence of air, water, and cellular components such as thiols.[2] By virtue of reversible noncovalent interactions, gold nanoparticles (AuNPs) can serve as a platform to solubilize and deliver hydrophobic catalysts, while controlling catalytic activity in biosystems. The alkanethiol monolayer of the AuNPs creates hydrophobic pockets inside the monolayer of the AuNPs. These stabilizing pockets can be used to successfully encapsulate hydrophobic catalysts.[3] We have designed a host-guest supramolecular system for the delivery of hydrophobic catalysts and control their reactivity with substrates. We studied a ruthenium-catalyzed release of amines from their allylcarbamate derivatives in biosystems. For this study we decorated the surface of AuNPs with functionalities that are recognized by cucurbit[7]uril (CB[7]). In the absence of CB[7], the catalyst catalyzed the allylcarbamate cleavage and the fluorescent rhodamine 110 was obtained both in solutions and in cells. However, with CB[7], serving as a steric stopper, the catalytic activity was inhibited.

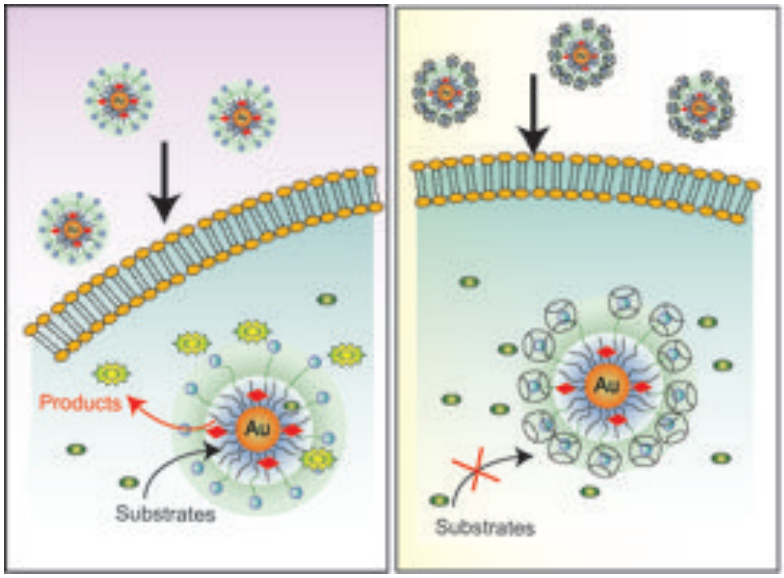


Figure. Supramolecular control of catalytic reactions in biosystems

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Chiral Recognition and Chiral Selection during the Self-Assembly Process of Protein-mimic Macroanions

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The homo-chirality of biological molecules, as one of the biggest puzzles in understanding how life began, is still remained unsolved. This process certainly involves the recognition and competition between the enantiomers. We demonstrate that for two inorganic chiral macroions (as simple models of biomolecules but without involving any hydrophobic and chemical interactions), they can demonstrate strict self-recognition controlled by weak physical intermolecular interactions when self-assembling in dilute aqueous solutions. Furthermore, a convincing chiral selection process was achieved when chiral co-ions are present in solution.

Macroions are able to self-assemble into viral capsid-like supramolecular aggregates driven by like-charge attraction. The solution study (light scattering, TEM, and CD) of the racemic mixtures can provide evidence for self-recognition between the enantiomers by showing that the two enantiomers self-assemble into individual homo-assemblies. Chiral co-ions (lactic acid and tartaric acid) are able to selectively slow down the self-assembly process of corresponding chiral macroioins. Moreover, by adding the chiral co-ions in the racemic mixture of the chiral macroions, separating individual macroionic enantiomers can be achieved.

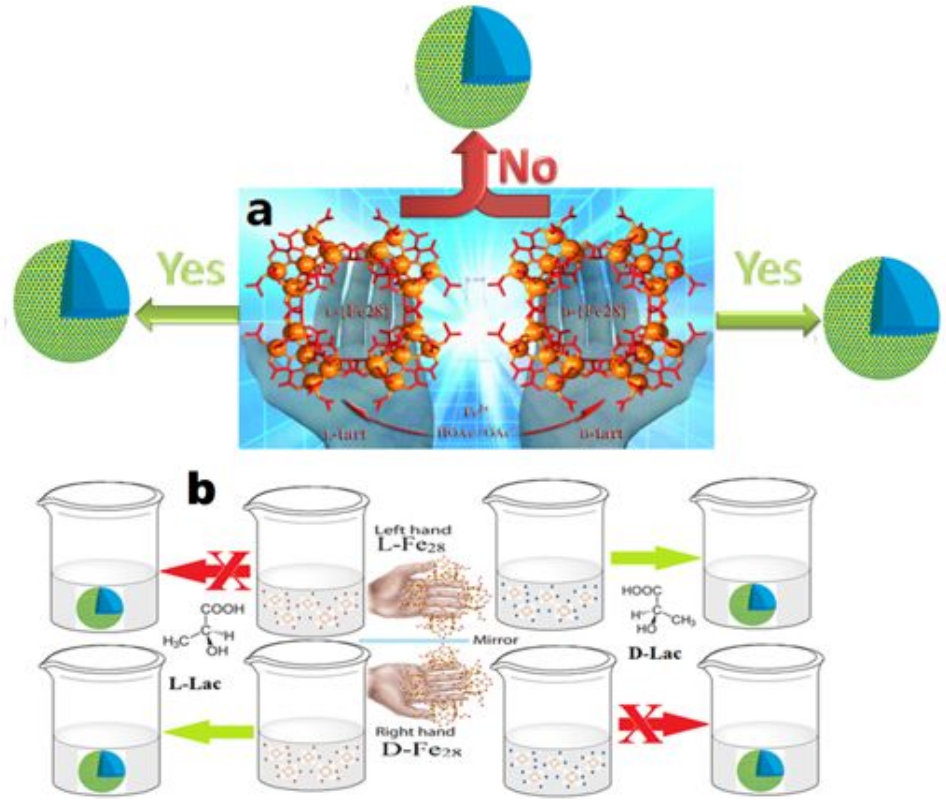


Fig 1. Representation of chiral recognition and chiral selection in self-assembly process of chiral macroions.

Simulation of Metal-Ligand Self-Assembly into Spherical Complex

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Molecular dynamics simulations were performed to study the self-assembly of a spherical complex through metal-ligand coordination interactions. M_6L_8, a nanosphere with six palladium ions and eight pyridine-capped tridentate ligands[1] was selected as a target system. We successfully observed the spontaneous formation of spherical shaped M_6L_8 cages over the course of our simulations, starting from random initial placement of the metals and ligands.[2] To simulate spontaneous coordination bond formations and breaks, the cationic dummy atom method was employed to model nonbonded metal-ligand interactions. A coarse-grained solvent model was used to fill the gap between the time-scale of the supramolecular self-assembly and that accessible by common molecular dynamics simulation. The simulated formation process occurred in the distinct three-stage (assembly, evolution, fixation) process that is well correlated with the experimental results.[3] We found that the difference of the life-time (or the ligand exchange rate) between the smaller-sized incomplete clusters and the completed M_6L_8 nanospheres is crucially important in their supramolecular self-assembly.

We also discuss our simulation results on $M_{12}L_{24}$ spherical complex with banana-shaped bidentate ligands.[4]

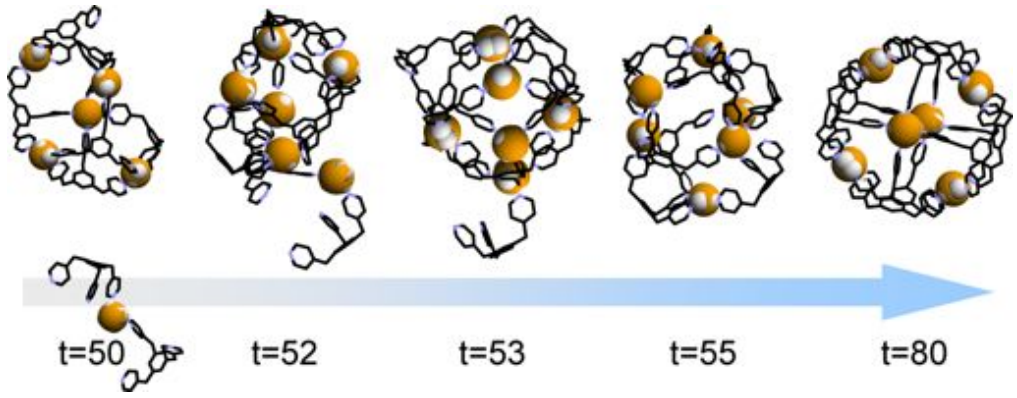


Figure 1. Spontaneous formation of M6L8 cage over the course of simulation.

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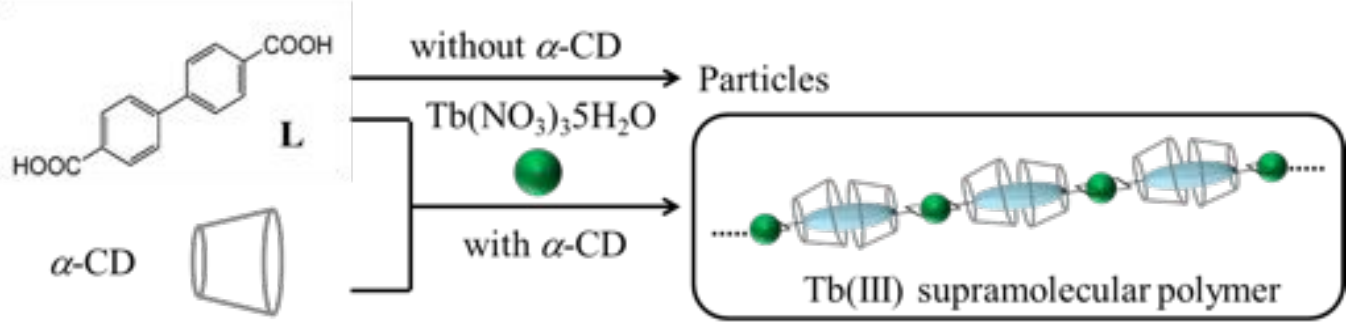
Construction, Fluorescent Property and Chiral Recognition of Polyrotaxane Type Metallosupramolecular Tb(III) Polymer

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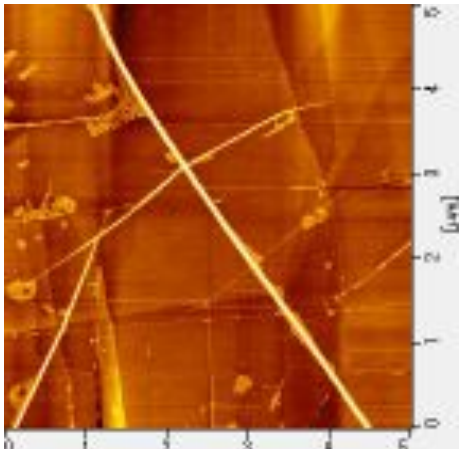
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Supramolecular polymers containing lanthanide ions (Ln(III)) in their main chain have attracted much attention in optically and magnetically points of view. However, it is difficult to regulate the coordination number of Ln(III), so we usually have to synthesize complicated ligand or use complicated method for complexation to construct Ln(III) polymers. This time, we report a novel and simple way for constructing Ln(III) supramolecular polymer by inclusion of bridging ligand 4,4'-Biphenyldicarboxylic acid: **L**) within the alpha-cyclodextrin (α-CD) followed by complexation with Tb(III) as lanthanide ion (Scheme 1)



Scheme 1. Preparation of Tb(III) supramolecular polymer.

Construction of Tb(III) supramolecular polymer was proved by fluorescent spectra (FL), circular dichroism spectra (CD) and atomic force microscopy (AFM, Figure 1). From Job's plot we could estimate the polymer consists of **L** : α-CD : Tb(III) = 1 : 2 : 1. Furthermore, when we added D- or L-tartaric acid to the aqueous solution of the supramolecular polymer, different FL and CD spectra between D- and L-tartaric acid were found. This meant that this polymer could recognize chirality of compounds by coordination with them. We will discuss the properties of this new Tb(III) supramolecular polymer in detail.



Effect of Length and Structure of Axle Components on Shuttling Dynamics in [2]Rotaxane Molecular Shuttles

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The shuttling motion of a ring component within a degenerate rotaxane system is of considerable interest due to the potential application of this property in molecular devices.[1] Such motion is strongly influenced by non-covalent binding interactions, as well as conformational effects, however, the influence of length and structure of axle components is not entirely understood. We therefore designed and prepared [2]rotaxanes which incorporate rigid phenylene (**1n**) or phenylene-ethynylene (**2n**) axles to allow us to ascertain the effect of length and structure on shuttling motion in such systems (Fig 1). Rigid spacers separate two secondary ammonium binding stations which a dibenzo-24-crown-8 ether ring can shuttle between.

The rates at which the DB24C8 ring shuttles between two stations in **1n** and **2n** were determined from line shape analyses of variable temperature ^{1}H NMR experiments in DMSO-d_6 and DMF-d_7. This allowed kinetic parameters of ring shuttling to be determined from the temperature dependence of rate constants. The variation in the enthalpic and entropic contributions across the series of rotaxanes is small in each solvent. This implies that axle length does not significantly influence the activation barrier for ring shuttling in these solvents.

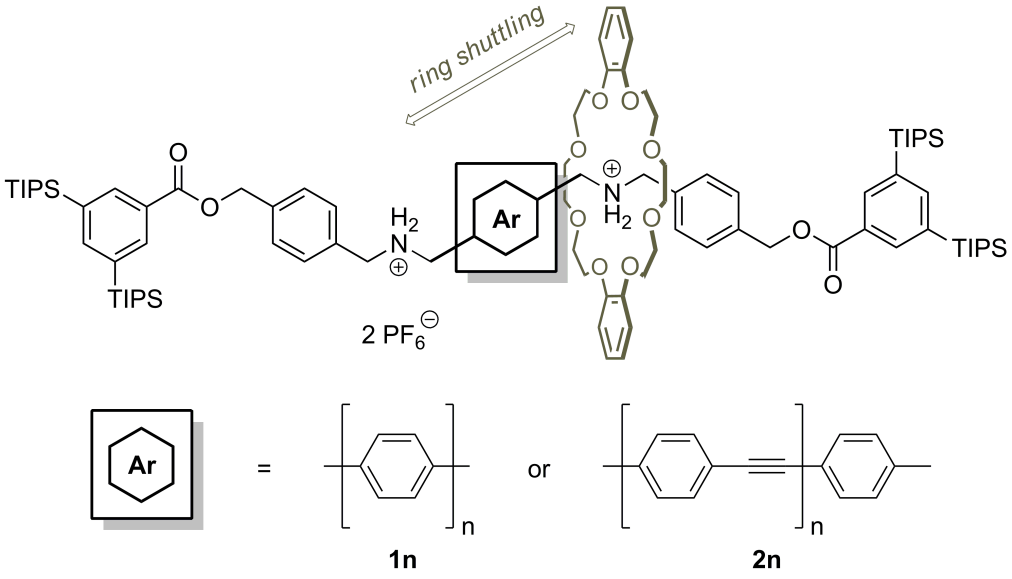


Figure 1. Structures of the [2]rotaxanes investigated.

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Ligand Functionalised Linear Peptides for Selective Recognition and Sensing of Biological Anions

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Anions undertake crucial roles in a diverse range of biological and chemical processes.[1] The ability to selectively sense anions in aqueous media has applications in areas including diagnostics and medicinal chemistry. Hence, the development of receptors capable of binding to biological anions is of intense recent interest.[1] Cyclic peptides in particular provide excellent scaffolds for anionic recognition as they allow for a preorganised binding site; however, the experimentally complex and tedious nature of their synthesis has proved to be challenging.[2] Therefore, novel linear peptide based anion receptors were synthesised using a solid phase peptide synthesis protocol, which is efficient and operationally simple.

We report here the synthesis of new linear receptors which are functionalised with different anion binding moieties such as Zn(II)/dipicolylamine (DPA) ligands and thioureas. Several structural variants were examined including different length peptides; different non-binding amino acid residues and amino acid chirality. The ability of these receptors to bind anions was evaluated using physical techniques including ^{1}H NMR and UV-vis (colorimetric indicator displacement assays). Our Zn(II)-DPA receptors demonstrate remarkable affinity for pyrophosphate with observed selectivity over adenosine triphosphate and adenosine diphosphate under mimicked physiological conditions; our thiourea functionalised receptors show high affinity towards sulfate and carboxylate ions.

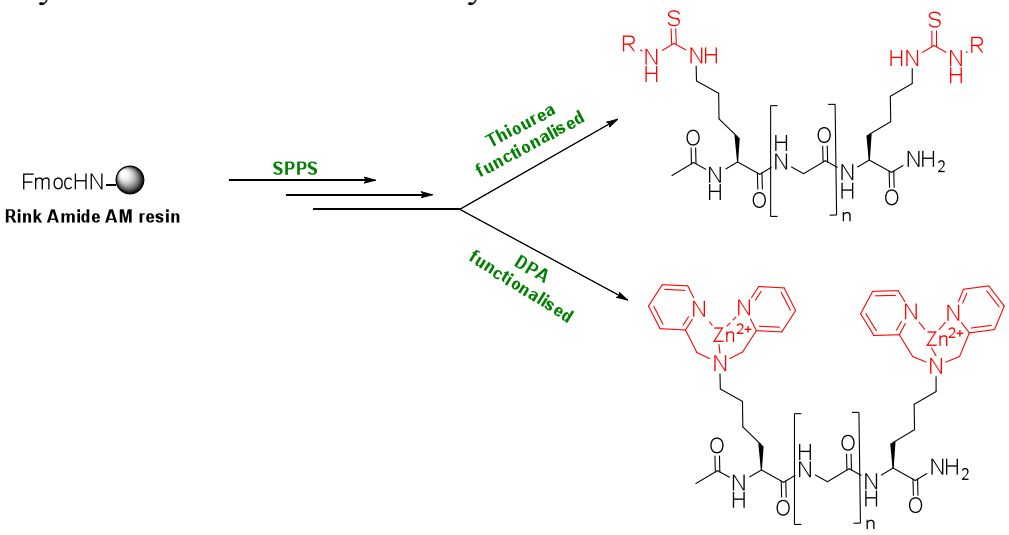


Figure 1. Simplified representation of synthetic strategy

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Biomedical Applications of Acyclic Cucurbit[n]uril Molecular Containers

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Recently, we reported the synthesis of two acyclic cucurbit[n]uril (CB[n]) molecular containers (**1a** and **2**).[1] Molecular containers **1** and **2** have very good water solubility and are able to increase the solubility of a variety of insoluble pharmaceutical agents including anti-cancer agents paclitaxel, camptothecin, tamoxifen, and melphalan by factors ranging from 23-fold to 2750. Recently, we discovered that container **2** displays a very high affinity toward the neuromuscular blocking agent rocuronium ($K_a = 3.4\times10^9$ M^{-1}) as determined by UV/Vis competition assay.[2] This high affinity reflects the preference of CB[n] containers for hydrophobic and cationic species and also the better electrostatic complementation provided by tetrasulfonate **1** toward the 11.0 Å N•••N separation in rocuronium. Significantly, rocuronium is a neuromuscular blocking agent widely used during surgery on humans. In collaboration with Prof. Eikermann at Massachusetts General Hospital we determined that **2** is capable of reversing rocuronium induced neuromuscular block *in vivo* in rats.

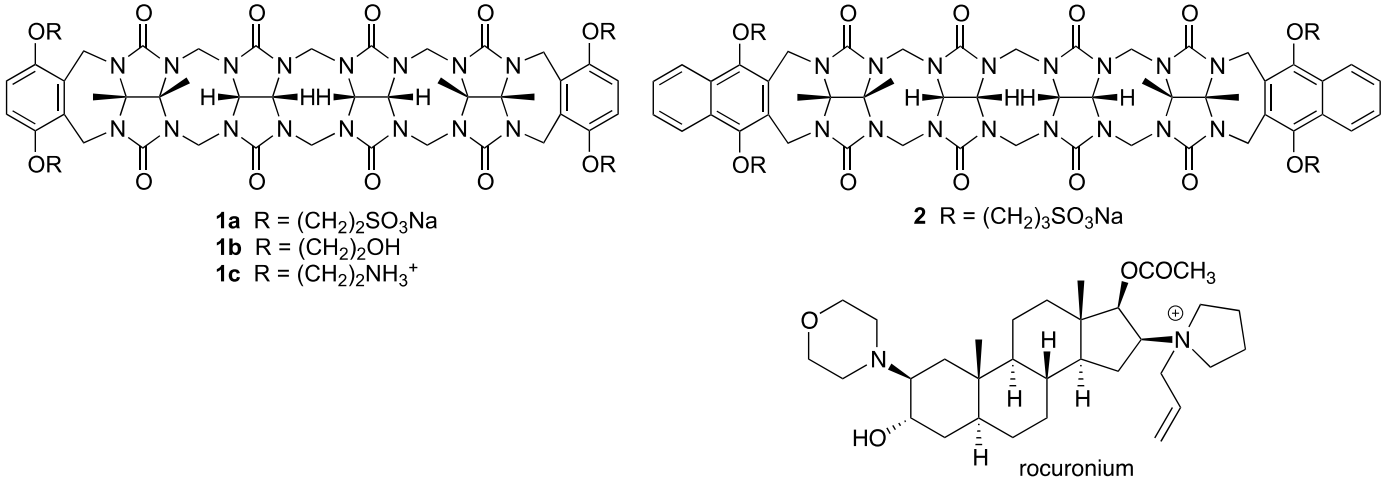


Figure 1. Chemical structures of acyclic CB[n] containers and rocuronium.

In ongoing work we have been optimizing the structure of acyclic CB[n]-type receptors for use as solubilizing agents for insoluble pharmaceutical agents. For example, we have studied the relative solubilizing ability of compounds **1a** – **1c** (Figure 1) which differ in the charge on the solubilizing group (e.g. **1a**, negative; **1b**, neutral; **1c**, positive). Phase-solubility diagrams were created for those hosts with positive, negative, and neutral drug molecules. A combination of phase solubility diagrams, x-ray crystallography, and UV/Vis binding assay (pK_a shift) were performed which allowed us to elucidate the reasons why negatively charged host **1a** is the most versatile solubilizing agent.

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Supramolecular Organic Frameworks Formed through Tetrathiafulvalene Radical Cation Dimerization

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Currently, metal-organic and covalent organic frameworks (MOFs and COFs) have found various applications in gas storage, catalysis, luminescence and biotechnology.[1,2] However, the construction of soluble soft supramolecular organic frameworks (SOFs) has been a challenge due to the lack of strong selective binding motifs. We envision that, as a new kind of structurally unique ordered supramolecular polymers,[3,4] SOFs are potentially useful in, such as, absorption, separation, sensing as well as delivery. In this poster, we will report the formation of two 3D self-assembled porous networks from rigid tetrahedral building blocks **1** and **2** through the intermolecular strong dimerization of the $TTF^{\bullet+}$ units in organic and aqueous media, respectively (Figure 1). The self-assembled 3D structures have been confirmed by the UV-Vis, ESR, CV, and DLS experiments.

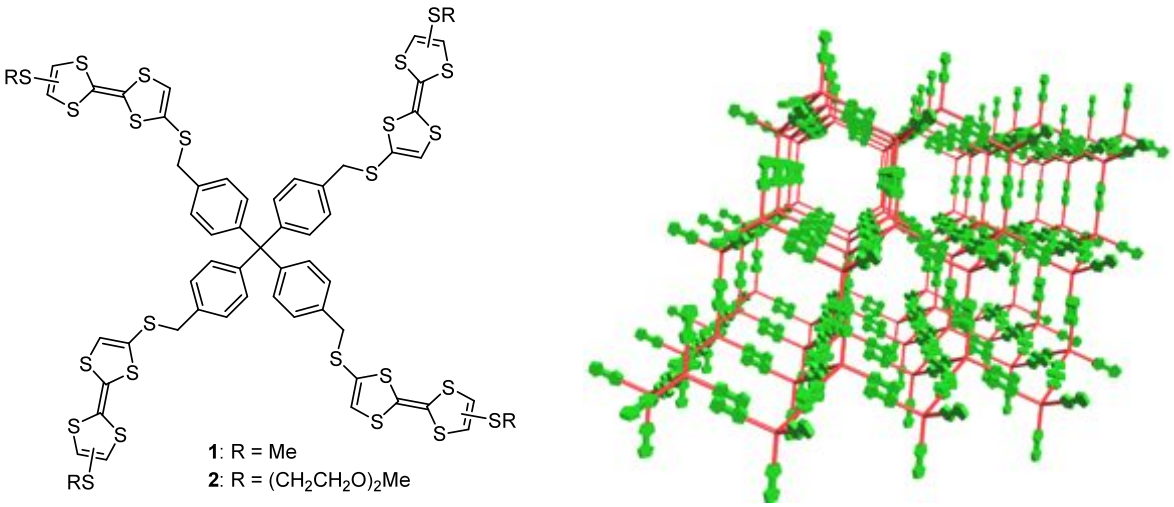


Figure 1. Monomers **1** and **2** and the schematic presentation of the formed 3D SOFs.

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Biocompatible Pillararene Assembly Based Carriers for Dual Bioimaging

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The current research has provided a successful example for delivering mixed dyes for dual bioimaging with biocompatible pillararene based assemblies by fully using pillararene cavities and assembled vesicular architectures. A series of tadpole-like and bola amphiphilic pillararenes **1**~**4** (Figure 1) were synthesized by selectively employing aqueous soluble biocompatible ethylene glycols and hydrophobic alkyl groups. In comparison with their monomers, these amphiphilic pillararenes not only improve the biocompatibility to cells but also form homogeneous supramolecular self-assemblies. Interestingly, different types of amphiphilic pillararenes also exhibited various performance on the delivery of dyes with different aqueous solubility. All assemblies here can deliver water soluble RhB to cells, while only tadpole-like amphiphilic pillararenes performed better on delivering hydrophobic FITC for imaging. Pillararenes **1**, **3** and **4** complexed with fluorescent **12**, and further formed stable assemblies for bioimaging. During the test of delivering mixed dyes, the tadpole-like amphiphile **1** performed best. Finally, the real cancer chemotherapy drug—doxorubicin, was successfully delivered by pillararene based assemblies to cells. The current research shows the capacities of pillararene based assemblies on delivering different dyes, and paves the way to using these biocompatible materials for the delivery of mixed drugs, and accomplishing the combination cancer therapy.[1]

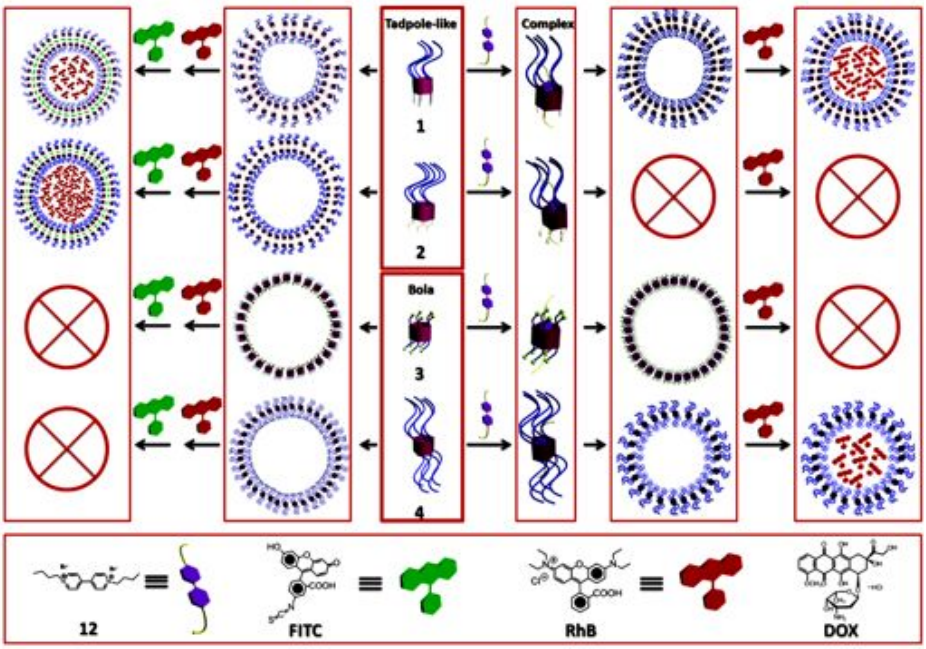


Figure 1. Illustrative mechanism for dual bioimaging with **12**, FITC and RhB delivered by biocompatible pillararene based assemblies.

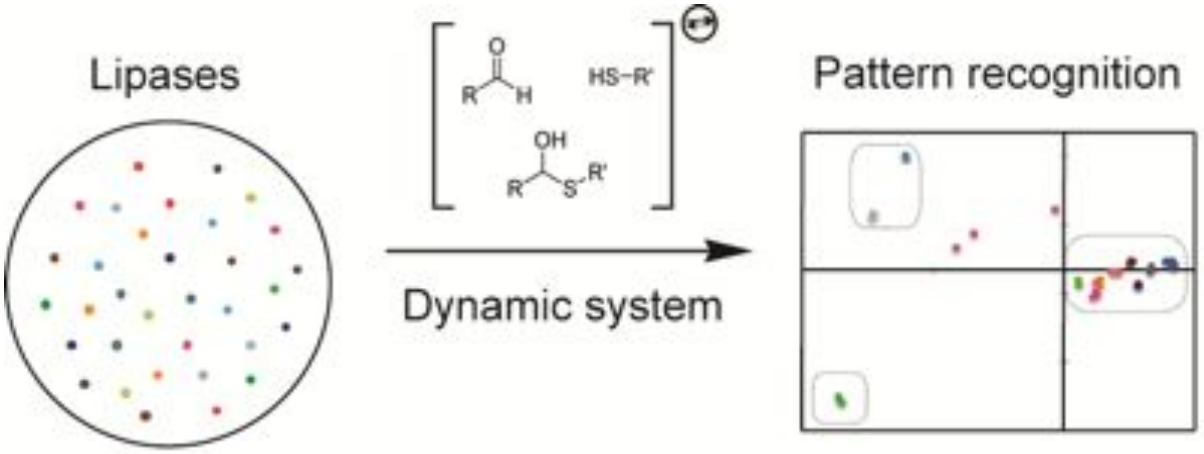
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Lipase Pattern Recognition Through Transformation of Dynamic Hemithioacetal Systems

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Dynamic systemic resolution (DSR) is a concept derived from constitutional dynamic chemistry (CDC)[1]. With added external selectors, such as enzymes, into the dynamic systems, a secondary, irreversible transformation will select and amplify the best constituent from the system. In addition, the enzyme activities are also challenged. Thus, this method provides a potential platform for evaluation and classification of enzyme activities.

In the present study, a dynamic hemithioacetal system with a complexity of 101 possible different compounds was generated and connected to lipase catalysis.[2] By using pattern recognition methodology as a tool for data analysis, twelve different lipases were successfully classified into three distinct groups, with good correlation to their reaction selectivities and reactivities. A probe lipase was further recognized within the same pattern following the predicted reactivity.



References

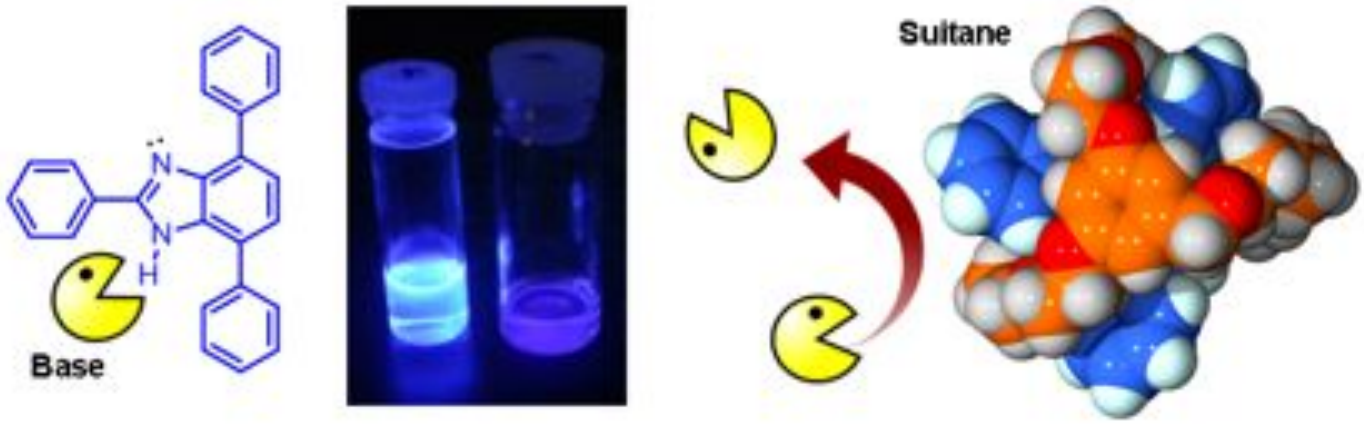
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C-80
WITHDRAWN

Fabricating a "Bullet-Proof" Vest for a Vulnerable Molecule Utilizing Supramolecular and Macrocyclic Chemistry

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[2]Pseudorotaxanes can be efficiently formed by using T-shaped benzimidazolium axles and crown ether wheels.[1] This new templating motif has recently been exploited to prepare [2]rotaxane molecular shuttles with crown ether macrocycles of various shapes and sizes.[2,3] In the structures of this type of [2]pseudorotaxane, the macrocycle wheel usually adopts a C-shaped conformation and clamps around the benzimidazolium ring *via* π-stacking. Inspired by this unique interpenetrated structure, a permanently interlocked, suitane,[4,5,6] was developed in which the T-shaped axle is completely enclosed by a cryptand-like host. This new supermolecule has been fully characterized by NMR spectroscopy, single X-ray diffraction, fluorescence spectroscopy, and DFT calculations. The encapsulated benzimidazole unit at the interior of the suitane shows a dramatic resistance to deprotonation by base due to the protection from the outer cryptand layer. This tactic of dressing a vulnerable molecule in a protective "vest"[7] or "suit" provides us with a supramolecular methodology for restricting access and therefore the reactivity of a particular functional group.



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Fluorescent Indicators for Zinc Ions – Photophysics and Microscopic Imaging

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The significance of developing fluorescent indicators targeting zinc(II) ions arises from the intimate involvement of zinc(II) ions in many biological processes. On the fundamental front, zinc(II) indicator research has enriched the knowledge base of the photophysical processes of organic fluorophores. In this presentation, several classes of synthetic indicators for zinc(II) ions that have been developed in our laboratory are described, with an emphasis on delineating how coordination with the redox-innocuous zinc(II) ions drastically changes the fluorescence of the organic ligand.[1-3] The utilities of selected compounds in microscopic imaging, including confocal and super-resolution techniques, of biological specimens are demonstrated.[4,5]

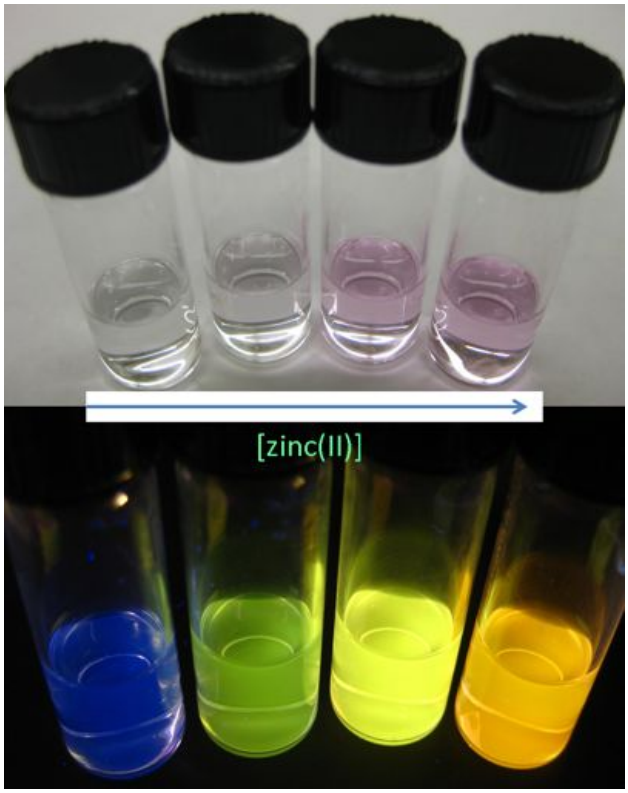


Figure 1. Color change over an increasing concentration gradient of zinc(II) ions.

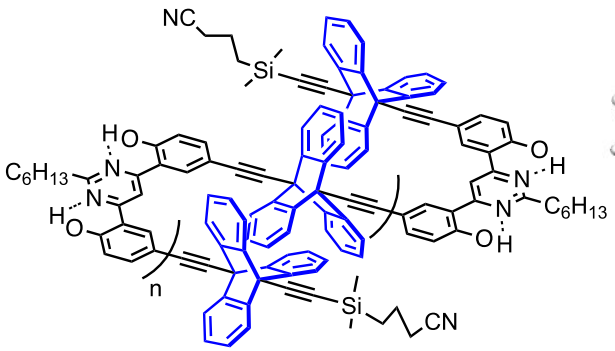
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Synthesis and Dynamic Motion of Molecular Spur Gears with Multiple Triptycene Units and a 4,6-Bis(2-hydroxyphenyl)pyrimidinyl Unit.

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Molecular gears, which are composed of intermeshed triptycene units, have attracted attention due to its plausible application as a molecular machine. However, reports on a molecular spur gear comprising parallel-intermeshed triptycene (Tp) units are limited. In this study, we have successfully synthesized a series of novel multiple molecular spur gears with a 4,6-bis(2-hydroxyphenyl)-2-hexylpyrimidinyl[4] backbone unit (Figure 1).

The molecular gears (**2**, **3**, **4**, **5**) were synthesized *via* Sonogashira cross-coupling reaction and fully characterized by ^{1}H, ^{13}C, IR and MALDI-TOF-MS spectroscopy. ^{1}H NMR spectra of the molecular gears, **2**-**5**, in $CDCl_3$ at 298 K show a characteristic signal at δ_H = 14 ppm, assigned to the hydroxyl hydrogen. The lower magnetic field position of the OH signal is ascribed to the intramolecular OH…N hydrogen bonds. Figure 2 shows the crystal structure of molecular gear (**3**) having three Tp units. The Tp units adapted a fully intermeshed conformation, which is attributed to OH…N hydrogen bonds. The dynamic motions of the molecular gears (**5**) in $CDCl_3$ solution were investigated by variable-temperature ^{1}H NMR (T = 293 – 213 K) and ROESY spectroscopy (T = 223 K). Rotation frequency of Tp units of [5]Gear (**5**) becomes smaller at the lower temperature (T ~ 213 K).



n = 0; [2]Gear (**2**)
n = 1; [3]Gear (**3**)
n = 2; [4]Gear (**4**)
n = 3; [5]Gear (**5**)

Figure 1. Molecular spur gears

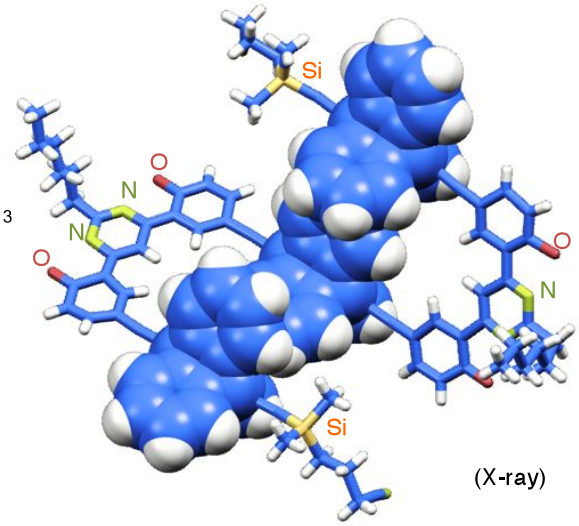


Figure 2. Crystal structure of [3]Gear (**3**)

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ISMSC-8 Program at a Glance

Time	Sunday, July 7th	Monday, July 8th	Tuesday, July 9th	Wednesday, July 10th	Thursday, July 11th
8:30 – 8:45a		Gale – CL5	Zhao – CL11	Sindelar – CL14	Gazit – IL20
8:45 – 9:15a		Yang – IL3	Jeppesen – IL9	Batten – IL13	Fukuhara – CL17
9:15 – 9:45a		Gellman – PL2	Hamachi – CL12	Wu – CL15	Tucker – CL18
9:45 – 10:00a			Dalcanale – IL10	MacGillivray – IL14	Hay – IL21
10:00 – 10:30a		Coffee break	Coffee break	Coffee break	Coffee break
10:30 – 11:00a		Rotello – IL4	Würthner – IL11	Yang – CL16	Clever – CL19
11:00 – 11:30a		O'Reilly – IL5	Miljanić – CL13	Loeb – IL15	Li – IL22
11:30a – 12:00p		Minami – CL6	Tobe – IL12	Stoddart – PL3	Shimizu – IL23
12:00 – 12:30p		Watt– CL7	*Cram Lehn Pedersen Prize* Ogoshi – AL1		Fujita – PL4
12:30 – 1:30p		Lunch		Lunch 12:00-1:15 Photo 1:15-1:30	Closing Remarks
1:30 – 2:00p		**Poster Session B** 1:30-3:30p	Lunch	Shionoya – IL16	Lunch
2:00 – 2:30p				Wennemers – IL17	
2:30 – 3:00p				Badjic – IL18	
3:00 – 3:30p	Welcome			Reinaud – IL19	
3:30 – 4:00p	Meijer – PL1	McNeil – IL6		Coffee break	
4:00 – 4:30p	Ashkenasy – IL1	Scherman – IL7	Free Time	*Izatt-Christensen Award* Anslyn – AL2	
4:30 – 5:00p	Phillips – CL1	Zhao – CL8			
	Aprahamian – CL2	Lee – IL8			
5:00 – 5:30p	Gibb – IL2	Rivera-Sanchez – CL9			
		Valderrey – CL10			
5:30 – 6:00p	De Bo – CL3				
	Ke – CL4				
Evening	6-8p Reception 7-9 **Poster Session A**	8-10p **Poster Session C**		7:30p Conference Banquet	