

## Two-Photon Characterization of Substituted (T8) Cage Silsesquioxanes<sup>1</sup>

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### Abstract

An efficient source of alternative energy has yet to be developed. Solar energy, the most viable and sustainable source of renewable energy, remains less effective due to limitations in absorbing materials to convert direct sunlight into useful solar cell devices. However, this flaw can be circumvented if solar panels had the capability to convert infrared radiation into useable energy. The focus of this study is the evaluation of the non-linear optical properties of silsesquioxane (caged {T8}) molecules through ultrafast two-photon spectroscopy to determine their applicability in creating more effective solar energy devices (Laine et al, 2010; Sulaiman et al, 2008). The two photon absorption measurements were carried out using 770 to 830nm, 30 femto-second pulses. The results revealed that there are maxima for the cross sections near 800nm for the different caged molecules studied. The increase in cross section is correlated with increasing substitution of electron donating groups on the cage. This data provides further support for these materials to be used in applications of near infrared solar absorption devices.

### Introduction

Although the contribution and significance of many fields of chemistry are being increasingly exposed to the public through mass media, the contributions of physical chemistry seem to be unseen and therefore insignificant in public view point. The primary purpose of this paper is to report the findings and the conclusions of the characterization study and through conveying the importance of these elements, the contributions of physical chemistry can be revealed. The investigations of physical chemistry are driven by global problems (energy, medicine, & technology) and gaps in scientific knowledge. In this respect, physical chemistry is no different; however, in this branch of chemistry the focus of solving these critical issues rely heavily on the application of materials' physical properties. One such property is the non-linear optical property of certain materials. This study will focus on the improvement of solar cell devices by evaluating the non-linear optical properties of cage (T8) silsesquioxanes molecules to determine their absorbing efficiency and sensitivity in near infrared spectral region.

Solar energy remains the most viable and sustainable form of alternative energy. However, with the vast supplies of cheap fossil fuels, historically, the underdevelopment solar technology was not a pressing issue. Recently, predictions of decreasing oil extraction efficiency of known oil reserves has intensified fears of oil peaking. These fears come at a time when projected energy estimates show that future demand for energy will be drastically increased (Rath, 2007). Concerns of oil peak could be alleviated with the ability to switch to cheap coal for increased energy production, but as concerns of global climate change are rising, the amount of coal generated power is being reduced. A better method of providing cheap energy production is needed globally and especially in the US.

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The United States is the largest consumer of oil production in the world. Rath (2007) reports that, "In the United States nearly 40% of energy usage is provided by petroleum oil". Much of the uses for oil are divided into transportation and generation of industrial electricity (Energy Administration, 2007). If no alternative source or combination of sources can be found to replace the energy output of coal and the declining efficiency of oil reserves, a national and global energy crisis could ensue. Governmental policies have tried to take steps to limit American dependence on foreign oil by investing in alternative energy and reducing dependence on oil for certain sectors such as transportation and "industrial only electricity generation". Nevertheless, no energy substitutes have been found; it is therefore necessary to systematically and incrementally improve upon the solar technology available today, in order to avert a possible energy crisis.

Stability in energy production for the future can be realized. Rapid improvements to solar technology can be achieved through the application of better absorbing materials. Currently, solar cell devices operate by converting ultraviolet radiation, a small portion of the sun's energy output, into electrical energy (via the photoelectric effect). Consequently, solar energy production would be more effective if the cell devices could absorb the infrared radiation in direct sunlight in order to maximize the transfer of solar energy into usable energy output.

- The primary research questions the study will address are:
- Can solar cell technology be improved?
- Does the cage silsesquioxanes molecules studied have high cross-section values in the infrared region?
- How does the addition of more electron donors affect the two-photon cross section of the molecules?

## Background and Research Plan

### *Background*

**Solar Technology.** The continued growth and expansion of society and the global economy needs energy. It is, therefore, prudent and essential that the production efficiencies of alternative energy sources are increased in order to create stability within the global economy for the future, as the inevitable depletion of fossil fuels draws closer. Fossil fuels are imperative to social-economic sustainability as they provide the means for industrial and commercial production, transportation, industrial agriculture and farming (rising of livestock for consumption), and electricity generation.

Fossil fuels provide  $37.4 \times 10^{14}$  btu of domestic electricity generation for the US. Currently, only coal burning can take on the burden of sustaining demand for domestic electricity production; however, due to international concerns of global climate change, political mandates have been implemented to regulate and decrease the amount of coal burning to decrease carbon dioxide emissions (Energy Administration, 2009). The inability to use coal for large scale energy production leaves the United States in a precarious position, as no forms of alternate energy can produce electricity to the required magnitude, yet, without energy its society will fall. The goal of alternate forms of energy is to relieve the load of energy production from fossil fuels.

Of the forms of alternative energy, solar energy production remains the most viable, renewable, and practical. Solar energy uses the phenomena created by the sun to produce energy. The sun, which is the source of all life on earth, is a constant source of energy which produces 89 petawatts of sunlight per year which is enough energy to sustain global demand with excess (Smil, 2003). The inherent problems with solar cell devices are efficiency, only a small fraction of the sun's output radiation can be currently transformed into useable energy, and production cost.

Solar energy can be used to create electric power or heat. Solar energy production can be categorized into two forms; the first uses the electromagnetic radiation sunlight to create electricity or heat and other use is wind energy to create electricity. Wind energy is actually due to the uneven heating of the planet. Generally, this term solar energy is used to describe the ability to use the sun's radiation output in order to harvest its energy in the form of electricity for industrial and domestic uses. It is this form of solar energy, the use of solar radiation to create electricity, which the paper will focus on.

Solar energy can be transformed into electricity in two ways. The first form is through the direct conversion of the ultra-violet radiation present in sunlight into electricity through the use of semiconductors. The second method of electricity generation is formed indirectly through steam, in which the thermal heat of the sunlight is concentrated through the use of mirrors, panels, and parabolic collectors to focus on to containers filled with water. As the water turns to steam, the steam causes the turbines to rotate. The rotation of the turbine acts as cranks to generate electricity.

This study will focus on the limitations of current photovoltaic cell devices and explore current research for the advancement of solar cell technology the possibilities to improve contemporary cell technology.

Semiconductor photovoltaic cells work by generating electric power by converting ultraviolet radiation from the sun into electricity through the photoelectric effect. The photoelectric effect can be described as reaction in which a photon of light interacts with a surface, usually metal, causing electrons to be released. The freed electrons can then flow from the p to n-junction in the presences of an electric filed causing a change in voltage across the junction, causing energy to be produced.

Semiconductor cells can uses various types of silicone, amorphous and crystalline, but crystalline is the most common. The greatest limitation of silicone is that in order to efficiently generate electricity the compound has to be ultra-pure. The purification is a costly and time consuming procedure. The silicone cells have a lifetime of about thirty years; however most of time is spent during the purification processes. As the demand for photovoltaic devices increases, the expanded production of these devices will cause the price of silicone to decrease.

Organic thin-films are the cheapest types of photovoltaic cells. However, the flaws with current organic films are their poor charge transfers and separation properties; these flaws decrease efficiency of the thin films far below that of silicone based devices.

As the need of alternative energy increases, this necessity will engender greater funding for solar research to extend the properties of absorption, charge transfer, and charge separation of cell devices. It is the extension of these properties which will create the next generation of highly effective and more powerful solar energy harvesting devices. Current research areas for extending the capabilities of cell devices are infrared absorbing material, quantum dots, microfabrication, organic thin films, the use of solar concentrators and photovoltaic cells (Boston College, 2010; Gesellschaft, 2008; Ludwigs, 2010; Naughton, 2010; Ohio State University, 2009; Vaynzof, 2010).

**Non-linear materials.** Non-linear optical materials are defined as “the modification of the optical properties of a material system by the presence of light” (Boyd, 1992). The term non-linear describes the interaction of light with the material as being different than that of normal chromophores or molecules that absorb, scatter, and/or transmit light. Usually, changes in material by a non-linear interaction is evident with a change in the refractive index of the material itself as a response to a high intensity light source such as a laser. Non-linear optical materials can be classified in two regimes inorganic compounds (crystals and nan-particles) and organic compounds.

Examples of these crystals are Ti: Sapphire, LBO (Lithium Tri-Borate) and BBO (Beta Barium Borate) crystals. These crystals are used in the application of advanced lasers systems and optical set-ups. The non-linear response of the Ti: sapphire allows for the creation of ultra-short pulses and also crystal's self-focusing ability (electronic Kerr effect) which stabilizes of the short-pulsed laser. The properties of LBO crystals allow them to be utilized for frequency doubling and tripling of pump lasers and for uses in optical parametric amplifiers (OPA) and oscillators (OPO) (Osico Technologies, 2008). BBO crystals are used in optical set to create sum frequency generation and harmonic generation.

Organic materials are gaining popularity because their low cost, manipulability, and variability in structure, synthesis, and properties. The chemistry concepts of bonding and electronic orbitals are central in describing the attributes of organic compounds. Molecules exhibit four types of energies; however only the electronic, vibrational, and rotational levels can interact with photons, to “exhibit quantization effects” (Parsad, 2008). In organic materials, it is their bonding structure of the  $\sigma$ - and  $\pi$ -bonds of the molecule which, is composed of overlapping electronic orbitals of individual atoms, allow the molecules to respond to light. Prasad (2008) defines this interaction of light as determined by the “symmetry elements of the molecule” which are composed of the behavior of the molecular orbitals and other energy states. In general the amount or increase of chain conjugations allows the absorption spectral of the organic molecules to be shift further down the electromagnetic spectrum.

Nano-particles such as gold and silver are also predicted to be valuable non-linear materials for biological imaging and sensing. Nano-cluster of gold and silver possess unique characteristic that are different from bulk materials which allows the electronic response to stimuli to resemble that of organic molecules than that of bulk metals or semi-conductors.

Non-linear optical materials are predicted to bring a revolution the major global concerns of health and medicine, energy, and technology through imaging and sensing, photodynamic therapy, optical limiting, non-linear data storage and absorption abilities of the materials.

**Health and Medicine.** While advances in medicine have come a long way in recent decades, gaps in knowledge and limited understanding still exist when it comes to the dynamic structures of molecules and the interactions that lead to the spread of disease. Through the uses of imaging, sensing, and photodynamic therapy, medical and biological fields

hope to gain increased knowledge of the body and its interaction with pathogens in order to devise more effective ways at eliminating disease.

Imaging allows for increased understanding of molecular interactions and dynamic conformations of molecular components such as protein, RNA, cell membranes within the body to determine their roles in disease prevention and proliferation. Non-linear microscopy allows for improved imaging over tradition microscopy techniques because the technique allow for deeper penetration and displays more surface details of the material (Denk, Strickler, & Webb, 1990).

Sensing is related to imaging; however, the main goal of sensing is to be used as an early detection tool in order to predict the onset of disease. Currently, sensing has been used particularly with Alzheimer's disease to tract and visualize the disease as it progresses. Recently a method of detection was identified with the sensing of amyloid  $\beta$  to determine if a patient has or is developing the neurodegenerative disease (Elsevier, 2010; Wang et al, 2010).

Photodynamic therapy and medicine delivery systems allow for hyper-branched molecules to connect to disease cells such as cancers and destroy them by acting either as a cytotoxin or by releasing encapsulated cancer medication. The medicines can activate with the use of infrared radiation to provide medicines to a particular target area (Prasad, 2003).

**Energy and Technology.** Optical limiting is a non-linear optical property that absorbs high intensity light or more accurately the material output intensity varies only by a small amount with large changes in input intensity. In many military advanced fighter systems the aircrafts rely on sensors to operate; however, the advantage of this military technology has a major flaw that could leave it to be susceptible to attack, high intense light. To improve upon this defect, optical limiters could be used to absorb the high intensity while allowing the sensors to operate with the less intense light.

Non-linear optical storing method improve memory capacity through the use of a three dimensional storage technique that allows data to not only be stored on the surface of the materials, but also at certain depths within the materials. This technique has the potential to create tetra-byte or higher storage capacity with a small amount of material.

**Silsesquioxanes.** Within the macromolecule science there is big push to document and understand the properties of silsesquioxanes, which are silicone based molecules whose structures have the empirical formula  $R_nSiO_n$ , in which R group substituent can be a hydrogen or any type of alkyl, alkylene, aryl, arylene, or organo-functional derivatives of alkyl, alkylene, aryl, or arylene groups. There several core structures of silsesquioxane; these cores come about with the parameter in which the molecules are synthesized. In particular, recent research has placed a special interest on the cage molecules also called cage (T8) silsesquioxanes, polysilsesquioxanes, or POSS for their unique properties. These qualities categorized by the molecules' non-linear properties, the robustness, versatility, and compatible with a variety compounds (Baney, 1995; Laine, 2005, Sulaiman, 2008). In addition silsesquioxanes, provide property control over uncooperative synthesized polymers or compounds. Studies have recorded the molecules' ability to allow for physical property controls such as radiation absorption and in situ formation of nanoscopic glass layers on material surfaces, improving gas and liquid barrier, stain resistance, resistance to environmental degradation, radiation absorption, adhesion, printability, time dependent mechanical and thermal properties such as heat distortion, creep, compression set, shrinkage, modulus, hardness and abrasion resistance, electrical and thermal conductivity, and fire resistance (Baney, 1995; Li, 2003; Lichtenhan, 2005; Lin, 2003; Lu, 2005; Zhao, 2005). The high applicability of these molecules lead to massive interests from diverse fields, the implication and research of these materials even has influences on nanotechnology and micromachining.

The first commercialization of silicones began with silsesquioxane chemistry, in 1930 propelled by the research teams of Corning Glass Works and General Electric Company (Baney, 1995). Historically, the early uses for silsequioxanes were in resin used for electrical wiring at high temperatures due to the materials extreme heat resistance and low electrical conductivity. As knowledge and patents began to devise more techniques to create and modify the silsesquioxane molecules, more applications were developed for the uses of the materials.

The applications of the molecules can be best described by the category in which they fit in; however, some of the base properties of silsesquioxanes seem to overlap although the specific strengths of the properties vary depending on the composition and preparation of the materials. These core properties are high heat resistance, low electric conductivity, oxidative stability, hydrophobicity, strong chemical resistances, high dielectric strength and volume resistivity. The three categories can be represented by polyphenylsilsesquioxanes, polymethylsilsesquioxanes, and co-polymers, a mixture of the first two categories.

The first category, polyphenylsilsesquioxanes, is mainly used for coating of electronics and optical devices with a major emphasis on the utilization for photoresists, interlay dielectrics, protective films for semiconductor devices and optical fiber coatings (Baney, 1995; Lichtenhan, 2005; Zhao, 2005). Other non-related applications for the molecules are used in separation membranes, and carcinostatic drugs. The molecules in this study will fall into this grouping. These materials possess non-linear optical properties and can even be synthesized to be transparent which allows for their use with current solar cell technology.

Polymethylsilsesquioxanes have many diverse applications. Utilized as a coating, it can be used to provide adhesion to rubber and plastics and protective (non-stick, water resistant and abrasion resistant) films on paper, plastic, rubber, metal surfaces, integrated circuits and electrical devices (Baney, 1995; Li, 2003; Lin, 2003; Lu, 2005; Zhao, 2005). Its uses have also found their way into cosmetics and binders for ceramics (Baney, 1995).

Co-polymers are mixtures of polyphenylsilsesquioxanes and polymethylsilsesquioxanes in order to improve the weakness of one compound with the inherent qualities of the other. For example, polyphenylsilsesquioxanes exhibit brittleness, but by incorporating polymethylsilsesquioxanes helps to create better cohesion.

**Two-Photon Absorption.** Before explaining the technique of two-photon absorbance spectroscopy, it is imperative to have the knowledge of two-photon absorbance and understand its relationship to non-linear optical materials. First, however, it is customary to recognize the physicist that formed the theory of two-photon absorbance in 1931, Maria Goppert-Mayer. This conclusion was made an astounding 30 years before the first laser was constructed to demonstrate the theoretical concepts.

Two-photon absorption is a quantum, non-linear optical phenomena in which two coherent photons are absorbed simultaneously by a material. As the two-photon absorption is a quantum effect it can be represented by the equation:

$$P(t) = \chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \chi^{(4)}E^4(t) + \dots + \chi^{(n)}E^n(t)$$

The equation represents the anharmonic oscillator model which describes the displacement of the charges of an organic system by the interactions of an incoming electric field. This displacement of charge is defined as polarization.  $P(T)$  represents the polarizability of the material model as a power series in an electrical field strength.  $E(t)$  represents the electric field strength and the terms  $\chi^{(n)}$  are known as the  $n$ th order susceptibility coefficients. The discussion of nonlinear two-photon absorption would be incomplete without mentioning the mathematical representation of the wave interaction with nonlinear material because the nonlinear absorption effect is defined as a quantum event (having both the properties of a particle and a wave). The wave equation in nonlinear media given as:

$$\nabla^2 E - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c} \frac{\partial^2 P}{\partial t^2}$$

where  $n$  is the refractive index and  $c$  is the speed of light in a vacuum.

The two-photon absorption process is described as a third order polarizability of the material given by the equation.

$$P^{(3)}(t) = \chi^{(3)}E^3(t)$$

Conceptually polarizability of the material means that:

if a small signal at frequency  $\omega_s$  is propagated through the medium in the presence of a strong pump signal  $\omega_p$ , the frequencies chosen such that  $\omega_s + \omega_p$  equals some transition frequency of the material, then the transition can take place through simultaneous absorption of those two photons. (Bhaskar, 2007); (Boyd, 1992)

Two-photon absorption process can be described in two ways non-degenerative and degenerative absorption. Degenerative two-photon absorption, utilized in this experimentation, can be more easily explained through comparisons with traditional one-photon absorbance. This effect differs from one-photon absorbance because the chromophores or light absorbing molecules in solution are absorbing two long-wavelength photons to reach the similar first singlet excited state as opposed to one shorter wavelength (higher energy) photon. The word similar is used to describe the first singlet state because in principle, one-photon and two-photon excitation follow different selection rules meaning that the energy state reached by one-photon excitation is different from that reached by two-photon excitation (Webb, 1997). Nevertheless, it is easy to understand the idea of two-photon absorption conceptually by



saying that the initial interaction of a photon with a material excites the material by a certain amount from the ground state and the second interaction of the material with a coherent photon excites to materials by the same amount so that the material reaches the first singlet excited state (Ajat thesis; Lakowicz, 2003). It is again important to emphasize the photons interactions are simultaneous, meaning no intermediate levels or steps are involved. Two-photon absorbance also varies from one photon absorbance through the Beers and Lambert law which states that for one photon absorption the amount of light absorbed is linearly related to the intensity of the incident light. However, two-photon absorbance is related to the square of the intensity of the incident light which graphically represents a quadratic dependence intensity of the incident light. "As a result of the quadratic dependence two-photon excitation, most of the excitation occurs at the focal point of the excitation, where the local intensity is highest." (Lakowicz, 2003). Physically, this concept can be observed as a narrow band of fluorescence as the intensity beam enters the solution that becomes focused and intensified at the focal point of material (usually observed to be near the center of the solution). It is this property of two-photon absorption that allows the technique to have diverse applications.

Two photon absorbance (excitation) is gaining popular in through techniques such as lithography, fluorescence microscopy, imaging, photon dynamic therapy, and optical limiting; however, for the sake of this paper the focus will be on the use of two-photon absorbance as a spectroscopic tool to characterize non-linear optical properties of the cage silsesquioxane molecules which forms the theoretical framework or research plan of this investigation.

Two-Photon Excitation Fluorescence (TPEF) employs picosecond or femtosecond pulsed laser sources to concentrate the available light energy into ultra-short pulses. In the spectroscopy set-up, the intensity of incident light can then be varied through the use of a neutral density filter. By changing laser intensity, the quadratic dependence of input intensity to fluorescence intensity can be verified. Fluorescence intensity is measured orthogonal by PMT in photo counting mode. The spectroscopic technique utilizes a known standard that absorbs around the same wavelength as the samples for comparisons of the two-photon absorption measurements. The absorption measurements are used to determine the two-photon cross sections to characterize the sample's two-photon excitation response.

### **Research Plan**

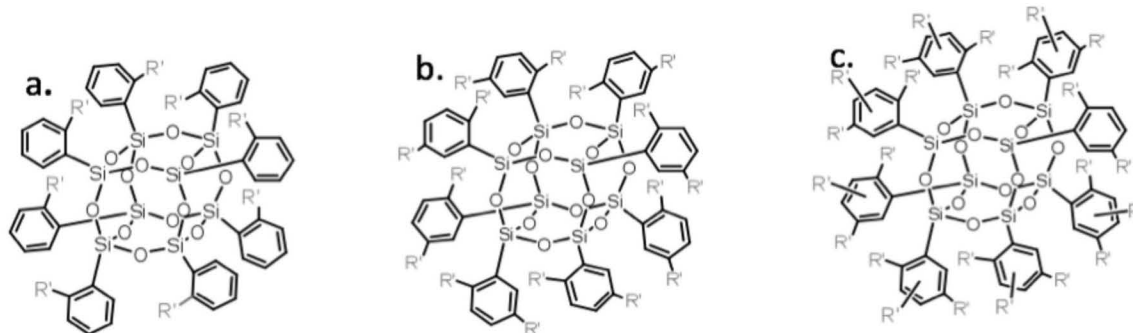
Since the caged (T8) molecules exhibit the properties of durability against chemical and biological degradation, are highly weather resistance, have high heat resistance, can be manipulated to have versatile structures, have recorded non-linear properties and are transparent in UV light, then theoretically, the compounds represent effective material to improve the efficient of solar cell devices by absorbing infrared radiation. First, however, caged (T8) silsesquioxanes absorption efficiencies and sensitivity to two-photon excitation in the infrared region must be evaluated. Although, not much literature can be found confirming abilities of silsesquioxane as solar cell devices there has been extensive research in using the caged molecules in improving or developing more sensitive photo-resist and the applications of the molecules in providing effective coatings of electronics and absorptive coatings for radiation (Baney et al, 1995). The study conducted by Sulaiman showed quantitative data that the  $\text{NH}_2$ VinylStilbeneOS molecule has a high cross section of 810 GM at 780nm. By increasing conjugated with pi-conjugated systems and long conjugated carbon side chains to similar  $\text{NH}_2$ VinylStilbeneOS molecules, a method can be devised to extend the absorption maximum of the similar molecules into the infrared range of the electromagnetic radiation spectrum.

In order to confirm hypothesis that the caged molecules represent better absorbing materials, the sensitivity to two-photon excitation of  $\text{Nboc}_n\text{StilOS}$  and  $\text{Ace}_n\text{StilOS}$  molecules are required to be tested through the use of infrared and near-infrared ultrafast laser pulses to evaluate the prospective design of creating more efficient solar cell devices.

### **Methodology**

**Investigated systems.** The molecules investigated have the same T8 caged silsesquioxane core structure, composed of eight silicon atoms which act as the vertices of the cubic structure. The phenyl groups attached to the silicon atoms allow for various r-groups to be substituted onto the cage molecule (figure 1). Two types of substituent groups are attached the cubic structure for investigation which are Nboc and Ace groups (figure 2). The molecules will have the name of  $\text{Nboc}_n\text{StilOS}$  and  $\text{Ace}_n\text{StilOS}$ , respectively with the number n to represent how many group of the type Nboc and Ace are present on the cube. Each of the systems of molecules were accurately weighed and dissolved in a known amount of the solvent DCM (di-chloromethane) so that the stock concentration was approximately on the order of  $1 \times 10^{-4}$  molar.

**Figure 1.** The figure displays the chemical structure from the 8 substituted core to the 16 and 23 substituted caged molecules.



**Figure 2 (a)** The R-group classified as the Noboc. **(b)** The chemical structure of the substituent Ace.



**Quantum Yield.** In order to determine the quantum yield or quantum efficiency, steady measurements and photoluminescence emission data were needed. Steady state measurements were carried out on an Agilent (Model No. 8341). The initial absorbance measurements were also used to determine extinction coefficients of the compounds. Photoluminescence measurements were carried out on Fluoromax-2 fluorimeter; the concentrations of the compounds were diluted so that the absorbance of the compounds was below .1 to avoid saturating the fluorimeter. Bis-MSB [p-bis (o-methyl-styryl) benzene] was used as the emissions standard. Quantum yield was calculate using the formula

$$\Phi_{PL(x)} = \left(\frac{A_x}{A_s}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 \Phi_{PL(s)}$$

where  $\Phi_{PL(x)}$  is the quantum yield, A is the absorbance at the excitation wavelength, F is the integrated area of the curve for the emission spectra, n is the refractive index of the solvent, and  $\Phi_{PL(s)}$  is the known quantum yield of the standard.

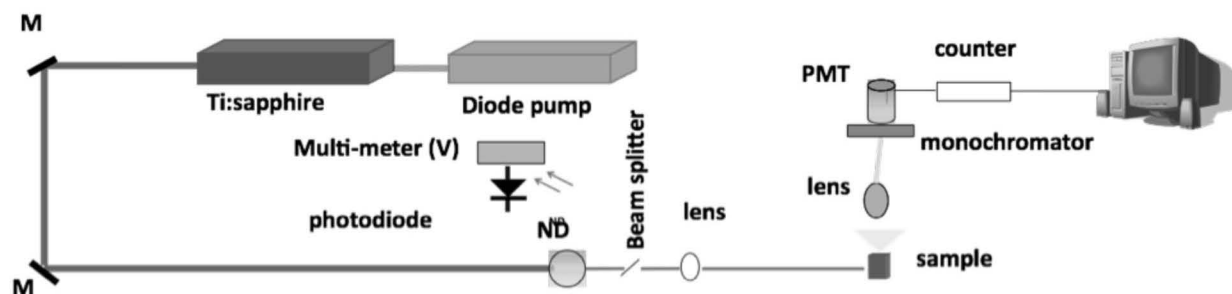
**Cross Section.** The cross section values were determined using the equation

$$F(t) = \frac{1}{2} \eta \delta c n \frac{g_p}{\pi \lambda f \tau} \phi \langle P(t) \rangle^2$$

in which F(t) is fluorescence counts measured in number of photons per seconds.  $\eta$  is fluorescence quantum yield (dimensionless).  $\delta$  is two-photon absorption cross section with the units centimeters<sup>4</sup>\*second per photon-molecule. c is defined as concentration of the molecule; its units are molecules per centimeters<sup>3</sup>. n represents the refractive index of the solvent (dimensionless), used to approximate the refractive index of the sample.  $g_p$  is shape factor of the beam pulses which is 0.664(dimensionless) for Gaussian pulses.  $\lambda$  is wavelength which is measured in centimeters. f is frequency of laser source.  $\tau$  is pulse duration in seconds.  $\phi$  is collection efficiency which is also dimensionless. P(t) is the input intensity with the units of photons per centimeters<sup>2</sup> per second. Courmarin 307 was used in as the two-photon absorbance standard (Xu and Webb, 1996).

**TPEF Laser Set-up.** The laser used for the Two-Photon Excitation Fluorescence (TPEF) measurements is a mode-locked Ti: Sapphire laser that is pump using a diode laser (figure 3). The diode pumping beam (Millennium Laser) is produced by two lanthanide bars within the laser cavity which are placed in a direct current source of about 34.7 Amps or 3.75 Watts of power. The bars emit 1064nm beam which strikes a temperature controlled LBO (Lithium Tri-Borate) to produce 532nm beam green light used to activate the Ti: Sapphire crystal within the Kapteyn-Murane oscillator cavity.

Figure 3



The femto-second pulses are generated within the laser and the nonlinear effective occurs within in the crystal which creates 800nm infrared light with the change of the crystal's refractive index. The beam passes through the cavity and compresses until the gain increases to exceed the output coupler and a powerful collimated laser beam is produced.

The resulting beam first travels through a colored filter to eliminate any scattered green light from the pump beam. A small portion of the beam is siphoned off using clear optical glass (beam splitter) onto a fiber optic cable connected to a spectrometer. Next, the majority beam is directed through a series of mirrors around the table, through a neutral density (ND) filter, and onto a beam splitter (optical glass) which directs a portion of the beam to a semiconductor diode which is connect to a voltmeter. The ND filter is used to relate the power of the laser to voltage. The main beam then passes through a focusing mirror and on to the sample.

As the beam strikes the sample it is focused within the material of the sample (non-linear effect) and a focused fluorescence is emitted from the sample. A collect mirror orthogonal from the sample collects the fluorescence; the fluorescence passes from the mirror through a monochromator, tuned to a specific wavelength, and is measured by a photomultiplier tube (PMT).

The PMT relates the amount of counts to a voltage difference. This voltage difference is converted into a current by a semiconductor diode contained within the counter. The counter is interfaced with a computer through a bus card which displays the fluorescence intensity as counts/seconds using the Lab View Software.

## Results/Discussion

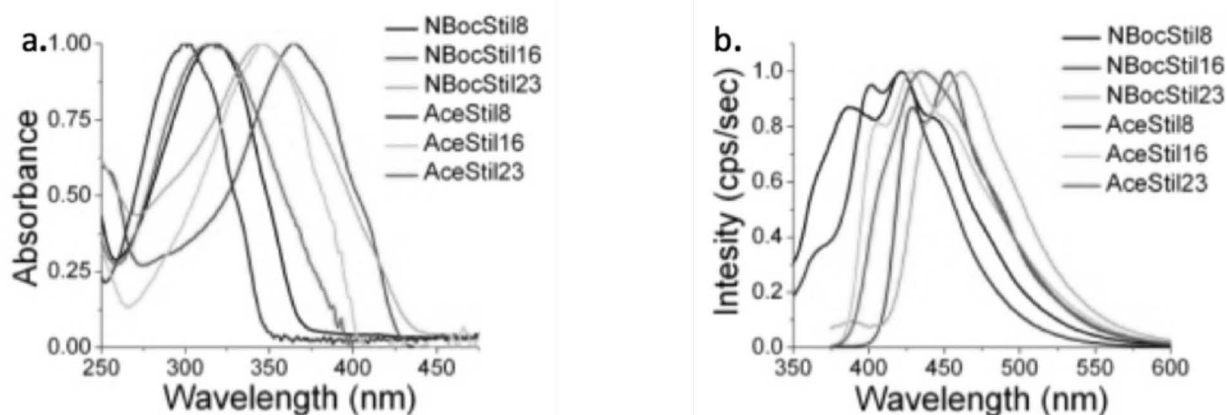
### Results/Discussion

The discussion of results will only provide a general picture of what the measured values (cross section, quantum yield, stoke shift) represent toward the application of improved solar technology. Explanations of the red-shifted absorbance and emissions spectra of the Nbc<sub>n</sub>StilOS and Ace<sub>n</sub>StilOS systems using their molecular orbital structure, of HOMO and LUMO, or the possible 3-D electronic orbital configuration of the caged molecules will not be examined in this paper.

**Steady State Analysis.** The spectra shown in figure four displays the absorbance and emission data of the studied Nbc and Ace compounds. One obvious trend in the data is that both the absorbance and emission spectra are shifted with the addition of increasing electron donating groups with the exception of Nbc<sub>16</sub>StilOS and Ace<sub>16</sub>StilOS which have absorbance red-shifts larger than Nbc<sub>23</sub>StilOS and Ace<sub>23</sub>StilOS, respectively.



**Figure 4: The figure displays (a.) the absorbance spectra and (b.) the emission spectra of the studied compounds.**



Using the steady state values reported by Sulaiman, comparisons can be constructed using the similar StilbeneOS values and the values measured from either parent molecule from this study (chart 1). The absorbance values of  $\text{Nboc}_8\text{StilOS}$  (max: 317nm) is lower than that of the un-substituted silsesquioxane molecule (HVinylStilbeneOS) which has an absorbance max of 335 nm. The emission spectra of  $\text{Nboc}_8\text{StilOS}$  displays a maximum at 421 nm compared to the maximum of HVinylStilbeneOS at 385 nm. The longer range between the absorption maximum and emission maximum of  $\text{Nboc}_8\text{StilOS}$  allows for a greater Stokes shift of 104nm than the 50 nm shift of HVinylStilbeneOS. The increase in Stokes shift is indicative of increased charge transfer among the eight ligands for the  $\text{Nboc}_8\text{StilOS}$ . The charge transfer can be further supported with quantum yield of  $\text{Nboc}_8\text{StilOS}$  which has a value of 7% which is much lower than value measured for un-substituted silsesquioxane molecule (36%).

$\text{Nboc}_{16}\text{StilOS}$  and  $\text{Nboc}_{23}\text{StilOS}$  exhibit red-shifts in the absorbance and emission spectra. The shift in absorbance of the  $\text{Nboc}_{16}\text{StilOS}$  molecule was particularly interesting because its red-shift was greater than that of  $\text{Nboc}_{23}\text{StilOS}$ ; however, an explanation for the increased shift in absorbance spectra could be that it allows for a smaller Stoke shift for  $\text{Nboc}_{16}\text{StilOS}$ . The Stokes shifts were 87nm ( $\text{Nboc}_{16}\text{StilOS}$ ) and 118 nm ( $\text{Nboc}_{23}\text{StilOS}$ ). Quantum efficiency values were 43% ( $\text{Nboc}_{16}\text{StilOS}$ ) and 5% ( $\text{Nboc}_{23}\text{StilOS}$ ).

Comparisons of  $\text{Ace}_8\text{StilOS}$  and HVinylStilbeneOS showed a lower absorbance maximum at 300nm and a higher emission maximum of 422 nm. Since the stoke shift with this compound (122 nm) is greater than that of the value measured for un-substituted silsesquioxane molecule, it was also indicator for increased ligand interactions for the  $\text{Ace}_8\text{StilOS}$  molecules. The quantum yield of  $\text{Ace}_8\text{StilOS}$  (4%) was also shown to be lower than that of HVinylStilbeneOS (36%) and  $\text{Nboc}_8\text{StilOS}$  (7%).

Both  $\text{Ace}_{16}\text{StilOS}$  and  $\text{Ace}_{23}\text{StilOS}$  are red-shifted in absorbance and emission from the initial eight-substituted parent molecule shown in figure 4. The quantum yield of  $\text{Ace}_{16}\text{StilOS}$  (45%) is larger than  $\text{Ace}_{23}\text{StilOS}$  (19%), but the quantum yield of  $\text{Ace}_{23}\text{StilOS}$  is closer to  $\text{Ace}_8\text{StilOS}$ . The molecule  $\text{Ace}_{23}\text{StilOS}$  has a Stokes shift of 122 nm, which is almost identical to the eight-substituted molecule.

The increase in ligand interactions is emphasized through-out this section because these interactions are imperative for better absorbing materials as it allows charged to be delocalized around individual molecules and clusters of molecules which increase the probability and efficiency of charge separation that can be used to generate electricity.

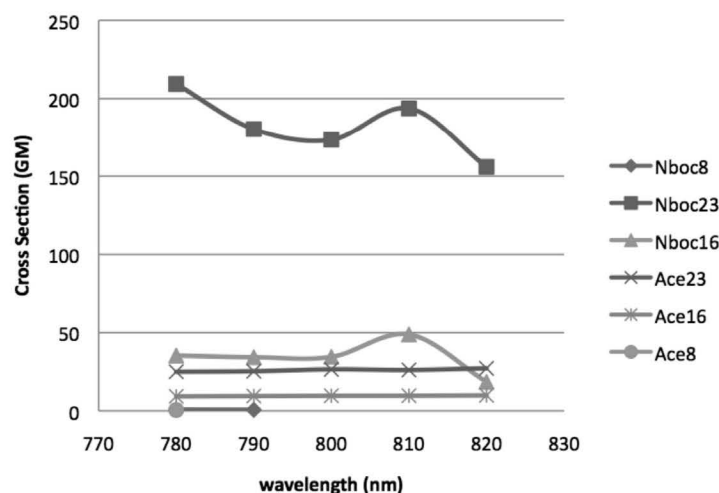
Chart 1

|  | Abb.               | $\lambda_{\text{abs}}$ | $\lambda_{\text{emis}}$ | $\epsilon$                        | QY   | Cross Section (@780nm) | Cross Section Maxima | Stokes Shift (nm) $ \lambda_{\text{abs}} - \lambda_{\text{emis}} $ | Cross Section per ligand (GM) |
|--|--------------------|------------------------|-------------------------|-----------------------------------|------|------------------------|----------------------|--|-------------------------------|
|  |                    | (nm)                   | (nm)                    | ( $\text{M}^{-1}\text{cm}^{-1}$ ) |      |                        |                      |  |                               |
|  | Nboc               |                        |                         |                                   |      |                        |                      |  |                               |
|  | R <sub>8</sub>     | 317                    | 421                     | 4.05E+04                          | 0.07 | 0.751                  |                      | 104  |                               |
|  | R <sub>16</sub>    | 366                    | 453                     | 5.66E+04                          | 0.43 | 35                     | 49 (810nm)           | 87   | 3.1                           |
|  | R <sub>23</sub>    | 345                    | 463                     | 6.33E+04                          | 0.05 | 209                    | 194 (810nm)          | 118  | 8.4                           |
|  | Ace                |                        |                         |                                   |      |                        |                      |  |                               |
|  | R <sub>8</sub>     | 300                    | 422                     | 6.86E+04                          | 0.04 | 0.485                  |                      | 122  |                               |
|  | R <sub>16</sub>    | 345                    | 429                     | 1.29E+05                          | 0.45 | 9.24                   | 9.86 (820nm)         | 84   | 0.6                           |
|  | R <sub>23</sub>    | 314                    | 435                     | 1.09E+05                          | 0.19 | 25                     | 27.15 (820nm)        | 121  | 1.2                           |
|  | HVinylStilbeneOS   | 335                    | 385                     |                                   | 0.36 | 25                     |                      | 50   | 3.1                           |
|  | MeVinylStilbeneOS  | 338                    | 394                     |                                   | 0.22 |                        |                      | 56   |                               |
|  | MeOVinylStilbeneOS | 345                    | 418                     |                                   | 0.16 | 110                    |                      | 58   | 13.8                          |
|  | NH2VinylStilbeneOS | 358                    | 482                     |                                   | 0.06 | 810                    |                      | 124  | 101                           |

Chart 1 displayed the steady state values determined for the Nboc<sub>n</sub>StilOS and Ace<sub>n</sub>StilOS molecules. The values displayed below the chart are values reported by Salaiman, 2009.

**Cross-Section Analysis.** While the steady state measurements of Although, Nboc<sub>8</sub>StilOS and Ace<sub>8</sub>StilOS resembled Stoke shift and quantum yield values more similar to NH2VinylStilbeneOS than HVinylStilbeneOS, the cross section values were nonexistence in the infrared region, which was expected, as the absorbance spectra of the studied molecules indicate maximum two-photon absorption in the 600 nm range. Cross section values did appear for the molecules Nboc<sub>16</sub>StilOS, Nboc<sub>23</sub>StilOS, Ace<sub>16</sub>StilOS, and Ace<sub>23</sub>StilOS (see chart 1). Yet, only the molecules Nboc<sub>16</sub>StilOS (49GM) and Nboc<sub>23</sub>StilOS (118GM) showed peaks in the near infrared region of 810 nm.

In addition to the peak at 810nm, Nboc<sub>23</sub>StilOS shows a potential peak at 780 nm which was an indicated peak in Sulaiman study for NH2VinylStilbeneOS. The appearance of the potential maximum could suggest that the occurrence could be a response solely of the attached amine addition or a combination of both the electronic structure of amine group contribution and ether-type addition. The peak is classified as a potential peak because cross values have yet to be determined for wavelengths lower than 780nm.

**Figure 5: The graph contains the cross section results for all studied compounds.**

Data for both systems displayed a correlation in two-photon cross section with the addition of more electron donating groups. Although, the correlation between donating groups and cross is apparent, more evidence would be needed to determine if the correlation is linear or logistic and to determine if the increase of donating groups will display increased charge transfer capabilities.

## Conclusion and Recommendations

### Conclusion

Cross section data supports the use of Nboc<sub>23</sub>StilOS as a more efficient absorbing material for future solar cells devices. Nboc<sub>23</sub>StilOS showed across section maximum in the near infrared region of ~ 810nm of about 200GM, with another suspected peak at 780 nm. The decrease in quantum yield from Nboc<sub>16</sub>StilOS (43%) to Nboc<sub>23</sub>StilOS (5%) can be interpreted as an increase in ligand interactions which allow for charge transfer or delocalization of charges across the surfaces of the molecules. The charge transfer characteristic can also be seen by plotting the cross section per ligand which increases to a maximum of 3.1GM /ligand (Nboc<sub>16</sub>StilOS) to a maximum of 8.4GM/ligand (Nboc<sub>23</sub>StilOS). Cross section data showed a correlation of increasing donating groups with increasing cross section in the infrared region for both systems of compounds, Nboc<sub>n</sub>StilOS and Ace<sub>n</sub>StilOS. Strong charge-transfer abilities promotes to the possibility to then insert metals within the core of the cages to separate the charges shared on the ligands. These findings allow for a small step forward in the direction of achieving a more efficient use of solar power. This small step could in turn create a prospective future where energy production would be dominated by clean and renewable energy sources and not fossil fuels.

### Recommendations

Results have shown Nboc<sub>23</sub>StilOS to have the characteristics of better absorbing material; therefore, more knowledge is need to understand the excited-state dynamics, molecular orbital configuration, and possible 3-D electronic structure of the caged molecule that enable the molecule to have a cross section maximum in the near-infrared region. Since solar cell devices also require strong charge separation properties, research into devising and implementing methods to insert molecules or atoms with high charge separation properties into the center of the cage must also be explored. The implementation of these fore-mentioned strategies would allow construction of more efficient infrared solar cell devices to begin, providing substantial increases in solar energy production for a future with increasing energy demand.

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