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Structure-Function Relationships of Second Hyperpolarizabilities in Two-Dimensional Molecules

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ABSTRACT

The enhancement of the third order susceptibilities $\chi^{(3)}$ and second order molecular hyperpolarizabilities $<\gamma>$ in a series of covalently stacked dimer and trimer macrocycles (SiPc and SiNc) was observed through the phase conjugated signals from DFWM measurements at both 1064 and 532 nm. The FWHM of the phase conjugated signals at 532 nm is much smaller than those at 1064 nm and those of the reference compound CS_2. The $<\gamma>$ values at both wavelengths as a function of number of the monomer units (n) have an approximate n^3 dependence, differing only in the scaling constant. The origin of such enhancement is discussed and compared to those in one-dimensional π-conjugated systems.

Key words: phthalocyanine, naphthalocyanine, porphyrin, chlorophyll, exciton interaction, nonlinear optics, degenerate four wave mixing

1. INTRODUCTION

Porphyrins, phthalocyanines, and chlorophylls are molecules that possess two-dimensional π-conjugated electronic structures. They have very rich photophysics and photochemistry where a variety of their functions are performed[1,2]. One of the special characteristics of these two-dimensional π-conjugated macrocycles is the inter-macrocycle interaction. This inter-ring interaction, particularly in a dimer, is crucial in natural photosynthesis where the chlorophyll dimers act as antennae for light harvesting and as the primary electron donor in the initial charge separation reaction[3]. Because of the excitonic interactions between the macrocycles in a dimer, the electronic structures and energetics of each monomer have been affected, making the special functions possessed by those dimers. A number of studies were focused on the correlation of the electronic interactions between the macrocycles with the linear optical absorption spectrum which is proven to

be highly dependent on the molecular configuration and relative orientation of the macrocycles[4]. However, most of the previous studies on the relationship between the second hyperpolarizabilities and molecular structures are focused on expansion of π-conjugation in a linear or two-dimensional system with all π orbitals on the same plane. Only a few studies in that aspect have dealt with the interactions between the π-conjugated macrocycles, even though many NLO property measurements have been presented on these macrocycles[5].

Our investigation of the second hyperpolarizabilities of the macrocycles intends to answer the following two questions: (1) is there an enhancement of the second hyperpolarizabilities, γ_{zzzz}, in a molecular system which is known to have ring-ring interactions, and (2) can this enhancement, if it exists, be explained by the excitonic interactions between the macrocycles as those previously applied for interpretation of the linear absorption?

In our previous work, the third order optical susceptibilities $\chi^{(3)}_{zzzz}$ and γ_{zzzz} for a series of chlorophyll and tetraphenylporphyrin derivatives in solutions were measured via the degenerate four wave mixing (DFWM) technique at 532 nm[6]. The values of γ_{zzzz} for different macrocycle dimers (face-to-face, side-by-side, and tilted) were compared to their corresponding monomers, showing a factor of 2-3 increase, where the "face-to-face" dimers give the highest enhancement. However, the previous DFWM measurement at 532 nm could not completely eliminate the resonant effect and all the dimers except one were enforced through aggregation and electrostatic interaction which could be a dynamic process where the distance and the relative orientation between the monomers are dispersive.

In our current study, silicon phthalocyanine (SiPc) molecules with numbers of macrocycles from 1-3 and silicon naphthalocyanine (SiNc) molecules with 1-2 macrocycles were chosen, where the dimer and the trimer are covalently bonded and the face-to-face geometry is ensured through the bonding. In addition, we measured the $\chi^{(3)}_{zzzz}$ at both 1064 and 532 nm. In the IR region, no absorption of the molecules is observed, thus our results at 1064 nm will be from the off-resonant effect. The enhancement of γ_{zzzz} due to the interaction between the macrocycles is characterized by measuring the phase conjugated signal for the solutions of the SiPc monomer, dimer, and trimer, as well as SiNc monomer and dimer. The results will be explained via previous calculations of the interactions between the monomer macrocycles in a dimer[4] and the origin of the enhancement will be discussed.

2. EXPERIMENTAL

2.1. Materials and sample preparation

The compounds used in this work were synthesized by the procedure described separately in another paper[7]. The synthesis of SiNc compounds is described in an upcoming publication[8]. The structures of the molecules are shown in Figure 1. DFWM measurements of the molecules were carried out in dioxane solution with sample concentrations ranging from 0.15 to 0.28 mM. For each molecule, three concentrations were prepared to ensure the precision of the measurements.

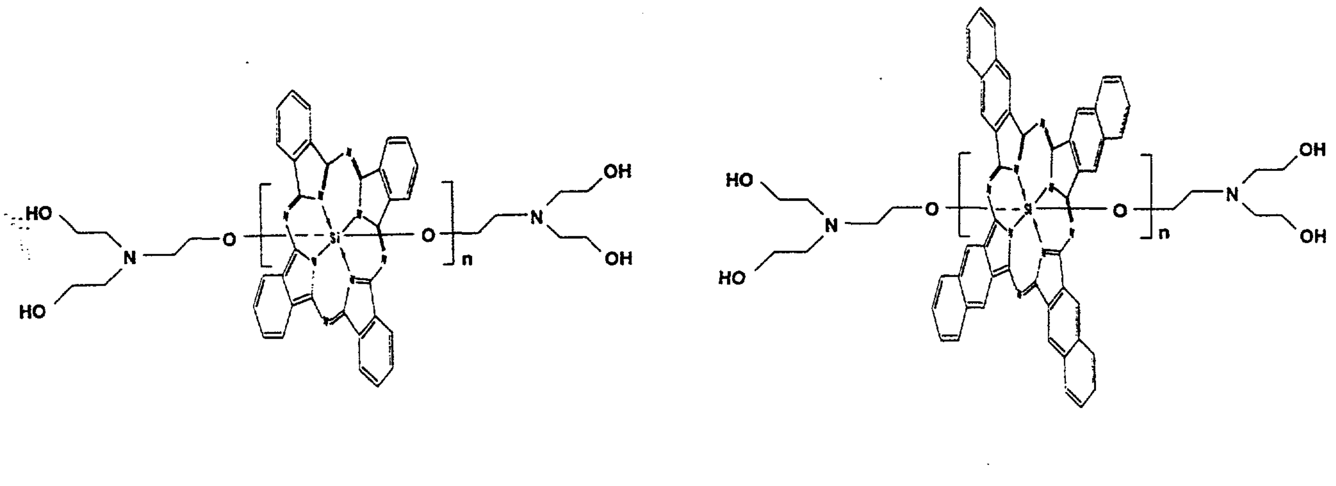


Figure 1. Molecular structures of the SiPc compounds (where n = 1-3) and the SiNc compounds (where n = 1,2) used in DFWM measurements.

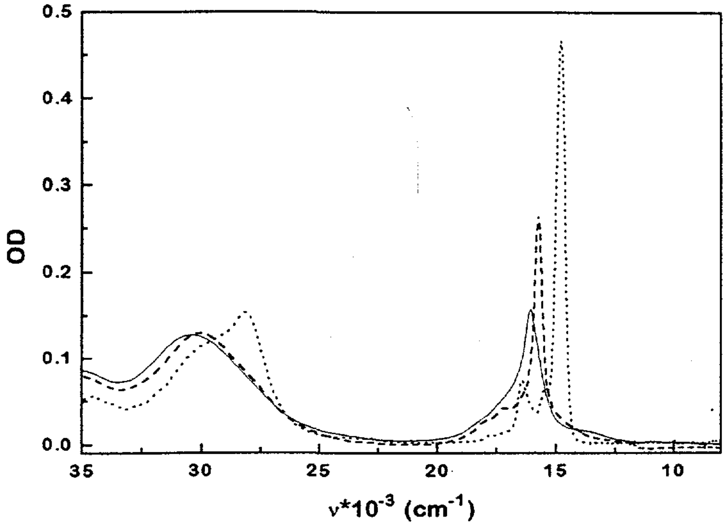
2.2. Optical absorption

The optical absorption of the samples were measured via Perkin-Elmer Lambda-19 UV-vis spectrometer with 1 cm path cells. The concentration of the samples were 0.6 - 1.8 × 10^{-6} M. All the measurements were carried out at room temperature.

2.3. DFWM measurements

The $\chi^{(3)}$ of the SiPc solutions were derived from the phase conjugated signals in counter propagating DFWM measurements. A Nd-YAG regenerative amplifier (RGA-60, Continuum) seeded by a cw, mode-locked Nd-YAG laser (Antares, Coherent) was used in the DFWM experiments. The laser repetition rate was 50Hz, and FWHM of the laser pulse was about 70 ps. The pulse energy at 1064 nm was about 20mJ, and at 532 nm, 2 mJ. The laser beam then was split into three, with 50/50 spilt for the two pump beams and about 5% of the pump for the probe beam. No focusing lens was used. The spatial and timing overlap of the laser beams was adjusted via the mirrors and the translation stages for one of the pumps and the probe beams. The polarization directions of all beams are vertical in the laboratory frame and parallel to each other. Thus, the $\chi^{(3)}$ and γ values in this paper all refer to $\chi^{(3)}_{zzzz}$ and $<\gamma>_{zzzz}$. After the phase conjugated signal was optimized, the translation stage for the pump beam was fixed. The time delay between the pump and the probe was varied during data collection. Two photodiode detectors were used to collect the phase conjugated signal and a signal proportional to the laser intensity. The photodiode signals were sent to a boxcar integrator that is connected to an A/D board (MIO-16, National Instruments) installed inside a 486/33MHz PC (Gateway 2000) for data acquisition and analysis. Neutral density filters (NG-5) were used to ensure no saturation of the photodiode, and the transmission of each filter at 1064 and 532 nm was measured on a UV-vis spectrometer to calibrate the signal intensity.

The phase conjugated signal as a function of the delay time of the probe was fitted into a Gaussian curve, where the amplitude of the phase conjugated intensity, I, was extracted from the height of the Gaussian curve. Each of the points on the experimental trace resulted from at least 50 or more pulses, where the signal to noise ratio was found to be satisfactory.



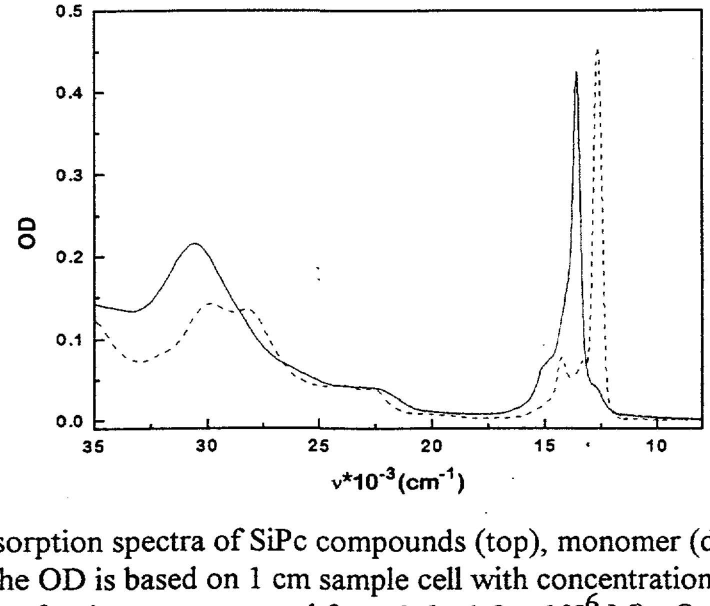


Figure 2. Optical absorption spectra of SiPc compounds (top), monomer (dotted), dimer (dashed), and trimer (solid). The OD is based on 1 cm sample cell with concentrations normalized to 10^{-6} M (the real concentrations for the spectra ranged from 0.6 - 1.8 × 10^{-6} M). Optical absorption spectra of SiNc compounds (bottom), no concentration normalization.

3. RESULTS

3.1. Absorption spectra

The absorption spectra of the SiPc monomer, dimer, and trimer in dioxane are shown in Figure 2. The spectra are very indicative of the structural arrangement of the Pc rings in the dimer and the trimer, assuming the π-π^* transitions correspond to these bands with their electronic dipoles in the SiPc planes. The most obvious change as the number of SiPc rings increase is the blue shifts for both Q and B bands, suggesting a parallel dipole arrangement. These spectra are very similar to those observed earlier in another series of SiPc compounds[9]. The main peak positions of the Q and B bands for the SiPc compounds are listed in Table I.

TABLE I. ABSORPTION BAND POSITIONS OF SiPc COMPOUNDS IN DIOXANE (290K)

	MONOMER		DIMER		TRIMER	
	ν(cm^{-1})	$\Delta\nu$(cm^{-1})^a	ν(cm^{-1})	$\Delta\nu$(cm^{-1})^a	ν(cm^{-1})	$\Delta\nu$(cm^{-1})^a
Q- band	14771	0	15723	952	16051	1280
B- band	28089	0	29940	1851	30581	2492

^{a}band position shift relative to the monomer.

The optical absorption spectra of SiNc compounds are also included in Figure 2. The Q band position of the monomer SiNc at 12658 cm^{-1} is over 2000 cm^{-1} lower in energy compared to the SiPc monomer, while the blue shift in the dimer SiNc Q band is 947 cm^{-1}, similar to 952 cm^{-1} of the SiPc dimer. There is some absorption between 20,000 - 25,000 cm^{-1} in the SiNc spectra, which is absent in those for SiPc compounds. The red shift of the Q band in SiNc may be due to its larger π conjugated system than SiPc, which may lower the energy of the excited state. The ratio of the Q and B band shifts in the dimer and the ratio of the integrated intensities of the Q and B band in the monomer are both about 2. This fact results from a simple exciton coupling between the neutral-excitation transitions of the two rings, as suggested by Hush and Woolsey[10]. The same analogy can be applied to the trimer. The widths and band shapes of the Q and B bands also become increasingly broader and less structured as the number of SiPc units increase. This broadening of the bands may result from the distribution of the relative dipole orientations between the rings due to a rotational motion around Si-O-Si bonds. Although the general trend of the blue shift is correlated to the parallel dipole arrangement, the absolute values of the spectral shift of the dimer and the trimer relative to the monomer cannot be described by dipole-dipole interaction[10]. The failure of this dipole-dipole interaction model in these spectra is attributed to the small inter-ring distances (3.32Å) relative to the size of the rings. Similar phenomena of the blue shift in macrocycle dimers were also observed in modeling the optical absorption of chlorophyll dimers, a model system for natural photosynthesis[4]. The solution to this problem is to use monopole-monopole interactions instead of dipole-dipole interactions. This method has successfully obtained theoretical results in agreement with the electronic spectra in several macrocycle dimer systems[4]. Similar trends are also observed for SiNc compounds shown in Figure 2.

At the wavelengths of the DFWM experiments, 532 and 1064 nm, although there is no absorption band present, the residual absorption at 532 nm is known to be able to create the excited singlet and triplet state whose absorption coefficients are much larger than that of the ground state. Minimum absorption is observed at 1064 nm.

3.2. DFWM measurements

Figure 3 presents normalized phase conjugated signals of the monomer, dimer, and trimer at 1064 nm. Clearly the magnitude of the peak increases one order of magnitude as each additional SiPc unit is attached to the system.

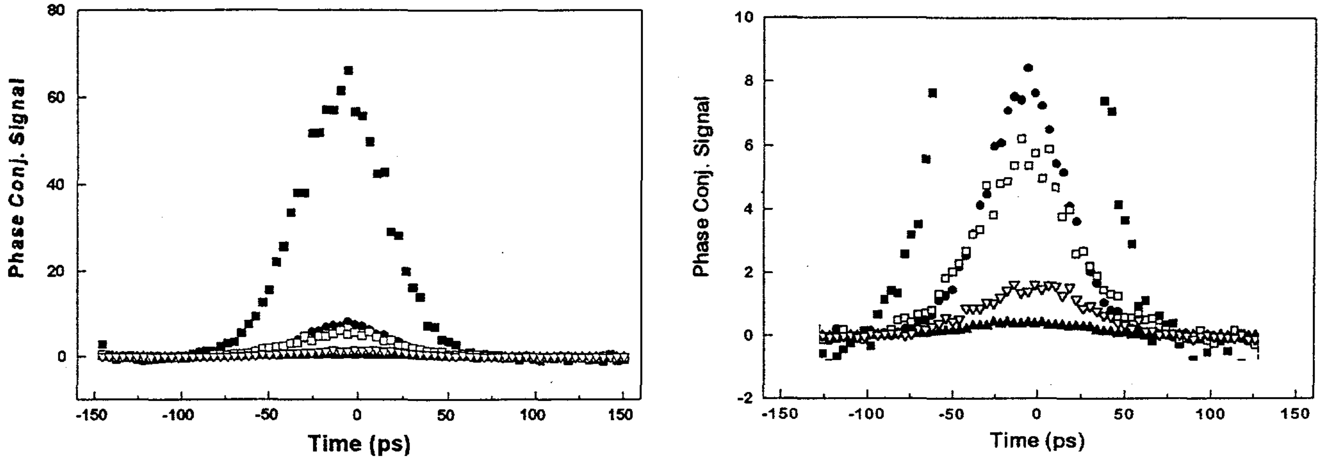


Figure 3. Normalized phase conjugated signals (for 1 mM SiPc or SiNc unit, and normalized by a signal proportional to the cubic of the laser power) for SiPc monomer (▲), dimer (●), and trimer (■) and for SiNc monomer (▽) and dimer (□), obtained by DFWM at 1064 nm, 290K.

The measured $\chi^{(3)}$ can be extracted from the following equation:

$$\chi^{(3)}=\chi^{(3)}_{ref}\cdot\left(\frac{I/I_o^{\,3}}{I_{ref}/I_o^{\,3}{}_{ref}}\right)^{1/2}\left(\frac{n}{n_{ref}}\right)^{2}\left(\frac{l_{ref}}{l}\right)\frac{\alpha l}{(1-e^{-\alpha l})e^{-\alpha l/2}}\quad (1)$$

where subscript ref stands for reference parameter, l is the optical path in cm, I and I_0 are the phase conjugated signal and the signal proportional to the laser intensity, n is the index of refraction and α is the OD of the sample in cm^{-1}. The reference for the DFWM is CS_2, assuming $\chi^{(3)}$ is 6.8×10^{-13}

esu at 532 nm, as according to a previous report. The $\chi^{(3)}$ of CS_2 at 1064 nm was not available for DFWM technique in the literature to our knowledge. Because our emphasis here is on the trend of the molecular hyperpolarizabilities in a stacked macrocycle system with an increasing number of SiPc units, we assumed the $\chi^{(3)}$ value of CS_2 remained unchanged with the laser wavelength. The $\chi^{(3)}$ for the pure solvent was measured with the same setup or extrapolated from $\chi^{(3)}$ vs. concentration plot to zero concentration. The "net" $\chi^{(3)}$ of the solute is obtained by subtracting $\chi^{(3)}_{solvent}$ from $\chi^{(3)}_{total}$ from equation (1). To obtain the average molecular second hyperpolarizability <γ> in an isotropic medium, the following relationship is applied:

$$<\gamma> = \frac{\chi^{(3)}}{L^4 N} \tag{2}$$

where L is the local field correction factor, $L = (n^2+2)/3$, and N is the number density of the molecules in solution in cm^{-3}. The experimental results of $\chi^{(3)}$ and <γ> for SiPc and SiNc (naphthalocyanine) are listed in Table II.

TABLE II. $\chi^{(3)}$ AND <γ> VALUES OF SiPc AND SiNc DERIVATIVES AT 1064 nm BY DFWM (290K, DIOXANE)

	$\chi^{(3)}$ (10^{-11}esu/M)[a]	$\chi^{(3)}$ (10^{-11}esu/M Pc or Nc)[b]	<γ> (10^{-32}esu)	σ (ps)
SiPc-monomer	0.4	0.4	0.2	52
SiPc-dimer	9.8	4.9	5.04	52
SiPc-trimer	39.0	13	20.7	48
SiNc-monomer	2.5	2.5	1.2	62
SiNc-dimer	8.6	4.3	4.52	62

[a] normalized with 1 M, assuming a linear relationship between $\chi^{(3)}$ and concentration.
[b] normalized with 1 M macrocycle unit concentration.

TABLE III. $\chi^{(3)}$ AND <γ> VALUES OF SiPc DERIVATIVES AT 532 nm BY DFWM (290K, DIOXANE)

	$\chi^{(3)}$ (10^{-11}esu/M)[a]	$\chi^{(3)}$ (10^{-11}esu/M Pc or Nc)[b]	<γ>(10^{-32}esu)	σ (ps)
SiPc-monomer	7.3	7.3	3.8	26
SiPc-dimer	82	41	43	34
SiPc-trimer	120	60	160	36

[a,b] same as in TABLE II.

Minimum optical densities (OD/mm) at 1064 nm were observed in the samples, ranging from 0.0003 to 0.02/mm, whereas the OD at 532 nm range from 0.07 to 1.05/mm. Thus, the phase conjugated signal at 532 nm will contain resonance effect in addition to the excited state absorption between 400 - 600 nm. For a comparison, the same measurements were also conducted at 532 nm for the SiPc series. The results are shown in Table III.

Figure 4 shows the γ of the compounds as a function of the macrocycle unit number at both 1064 and 532 nm. The relationship between $<\gamma>$ values and the unit number can be approximated with a third power dependence, with only different scaling constants. These approximation curves can be written as $<\gamma> = 0.7\ n^3$ at 1064 nm and $<\gamma> = 5.8\ n^3$ at 532 nm.

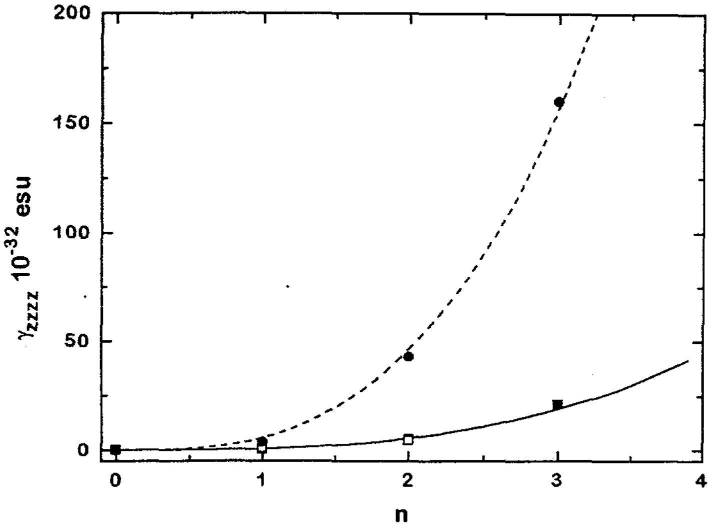


Figure 4. $<\gamma>$ at 1065 nm vs. number of macrocycles in the molecules for SiPc (■) and SiNc (□) and a curve approximate with $<\gamma>_{zzzz} = 0.7\ n^3$ (solid) as compared to $<\gamma>$ at 532 nm vs. number of macrocycles in the molecules for SiPc (●) and a curve approximate with $<\gamma>_{zzzz} = 5.8\ n^3$ (dashed).

Compared to the results at 1064 nm, the $<\gamma>$ value for the same molecule at 532 nm is much larger because of the resonance enhancement and the excited state absorption. However, the change of the $<\gamma>$ value due to the addition of each macrocycle unit follows the same cubic power of n as in the non-resonant case. The only difference is that the scaling factor is about 8 - 9 times larger than the non-resonant case at 1064.

Another noticeable difference between the 1064 and 532 nm data is the FWHM of the phase conjugated signals, σ, listed in TABLES II and III. For the 532 nm data, σ is from 26 - 36 ps, about half of 60-70 ps for the CS_2 signal, whereas σ at 1064 nm is nearly the same as that of CS_2. This is an indication of the additional effect from the excited state absorption of Pc and Nc in the region of 400 - 600 nm. This signal narrowing also distinguishes the non-resonant phase conjugated signal at 1064 nm from that at 532 nm.

4. DISCUSSIONS

As mentioned earlier, we intended to answer the two questions in the Introduction through our experimental results. First, we have confirmed an enhancement of the second hyperpolarizabilities γ_{zzzz} in two molecular systems with stacked macrocycles, known to have strong interactions between the rings. The second question cannot be answered so clearly and briefly until we complete further theoretical calculations. However, there is an apparent structural difference between the stacked macrocycles in our study and planar π-conjugated molecules. The enhancement of γ_{zzzz} with the number of π-conjugated electrons in various molecular systems, such as polyene and thiophene oligomers, is well documented[11]. The origin of such enhancement was attributed to delocalization of the π-electrons, so-called "particles in a box". This can be visualized based on possible resonant electronic structures with certain charge separation characters, which can be produced via a perturbation using light excitation. However, in the stacked macrocycles that we studied here, the enhancement of γ_{zzzz} with the addition of each monomer unit cannot be described by "particles in a box", rather, "a pile of boxes". Despite the difference in electronic structure and the spectral shifts between the planar π-conjugated molecules and the stacked macrocycles, there is something in common between the two systems. The π-π interaction always generates more frontier molecular orbitals which compose those electronic states involved in the state transition pathways described using a perturbation theory[11]. As the density of the states increases, the probability of finding an allowed electronic transition with an energy close to the laser photon energy becomes greater, thus γ is enhanced. The revelation of the origin for the enhancement will rely on theoretical modeling and more experimental results. However, the complexity of such molecular systems forbids effective calculations of the NLO properties. Based on the previous success of a semi-empirical method using only a few molecular orbitals in each monomer to predict electronic spectra of dimer macrocycles, we are going to use a similar approach on NLO property calculations.

Another question raised by our experimental results is the origin of the cubic power dependence of the macrocycle number for both non-resonant and resonant nonlinear optical effects. According to previous studies on thiophene oligomers, such power dependence is a function of the monomer unit number which will eventually reach zero when the unit number becomes large. The number of the units will give us information on the delocalization range in a planar π-conjugated system. We plan to study the tetramer of SiPc in the near future, at that time we may be able to extract more information on this issue.

5. CONCLUSION

We have observed a significant enhancement of the second hyperpolarizabilities of the molecules with the number of monomer units in a stacked macrocycle system. This result suggests another approach of designing effective nonlinear optical materials and devices. Moreover, the correlation between the molecular structures and the enhancement of the NLO properties in such stacked macrocycle systems motivates theoretical modeling to reveal the origin of the enhancement, based on excitonic interactions.

6. ACKNOWLEDGEMENTS

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