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**ELECTRONIC STRUCTURES AND NONLINEAR OPTICAL PROPERTIES
OF MACROCYCLES IN MODEL COMPOUNDS AND
IN PHOTOSYNTHETIC SYSTEMS**

Lin X. Chen
Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

Ultrafast energy and electron transfer processes are carried out in natural photosynthetic systems via chlorophyll molecules attached to proteins. The chlorophyll molecules are held by the protein matrices with different relative distances and orientations. The environment around each chlorophyll determines its energetics and function in initial photochemical reactions. One of the most important factors that modify the energetics of the chlorophylls is the electronic interactions between the chlorophylls. This has been demonstrated by the structural details of the two chlorophyll arrays, B800 and B850 in photosynthetic bacterial antenna LHII, as well as the special pair chlorophylls in the bacterial photosynthetic reaction center. The former conducts the energy transfer to LHI, then to the reaction center, the latter, the electron transfer. The electronic interactions between chlorophylls in model systems and natural photosynthetic systems have been studied extensively with various techniques, e.g., linear optical absorption, but the nonlinear optical properties, such as high order nonlinear optical susceptibilities, are not well characterized. In this study, we intend to characterize the nonlinear optical susceptibility $\chi^{(3)}$ in various molecular systems consisting of chlorophyll, porphyrin and phthalocyanine with different configurations and aggregation states. The goal of this research is twofold, (1) to establish the correlation between the electronic couplings in macrocycles and $\chi^{(3)}$ with experimental measurements (e.g., degenerated four wave mixing, DFWM) and theoretical modeling, and (2) to explore the potential applications of biophotonics device based on the $\chi^{(3)}$ measurements of various chlorophyll arrays which perform ultrafast energy and electron transfer similar to those desirable functions in photonic devices.

Since many important functions in photosynthesis are performed via chlorophyll pairs with "face-to-face" configuration, we started to investigate the effect of electronic coupling in such a system on $\chi^{(3)}$. $\chi^{(3)}$ of a series of model systems consisting of chlorophylls, porphyrins and phthalocyanines have been measured using DFWM technique. In a μ -oxo silicon phthalocyanine monomer, dimer and trimer series with well-defined structures, we have found that nonresonant $\chi^{(3)}$ is enhanced when each unit of PcSi is added in this stacked "face-to-face" macrocycle system. This enhancement corresponds to an increase of the molecular second hyperpolarizability $\langle\gamma\rangle$ as a cubic function of the number of the units. A similar trend was also observed for naphthalocyanine derivatives. Such a significant enhancement in the third order nonlinear optical susceptibility due to "face-to-face" configuration of the macrocycles was not examined before. The observation differs from some of previous work that suggested "face-to-face" encounter of the macrocycles does not contribute significantly to the third order nonlinear optical susceptibilities. In conjunction with the $\chi^{(3)}$ measurement with DFWM, we also started theoretical

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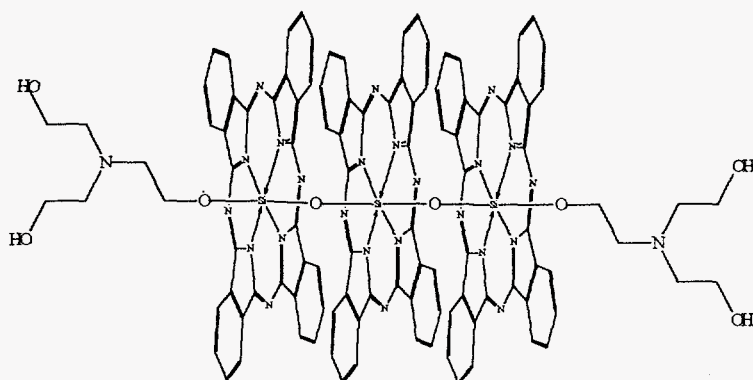


Figure 1. Molecular structure of μ -oxo silicon phthalocyanine trimer.

properties in the macrocycle systems. The calculation attempts to model the trend of the $\chi^{(3)}$ enhancement as a function of the number of the monomer units. The sum of state (SOS) expression of $\langle \gamma \rangle$ was used in the calculation based on perturbation expansion of the Stark energy as a function of electric field. The calculated results reproduce the trend of the $\chi^{(3)}$ enhancement and linear optical absorption spectra change very well. The agreement between the experimental and calculated results also suggests that Q-band only is sufficient in such calculations for this molecular series. The origin of the $\chi^{(3)}$ enhancement in the "face-to-face" macrocycles, according to the calculations, appears mainly from a low energy component of the Q-band due to the configuration interactions between the charge transfer and Q-state exciton configurations. The exciton interactions only in a macrocycle dimer cannot produce the experimentally observed trend of $\chi^{(3)}$ enhancement. We are in a process of modeling $\chi^{(3)}$ in LHII system and other model systems.

In order to further confirm our findings on the effect of the charge transfer configuration on $\chi^{(3)}$, we will conduct similar studies on the macrocycle dimers as well as other electronically strongly coupled systems, such as donor-acceptor supermolecules in artificial photosynthetic systems with synthetically modified charge transfer characters as well as solvation effect. Meanwhile, we will try to model $\chi^{(3)}$ in structurally well defined model systems with other geometries and aggregates of macrocycles, such as the B850 array in LHII system. In addition, the $\chi^{(3)}$ of the excited states in our previously studied systems will also be investigated by experiments and theoretical modeling. Other related studies include investigating the global movements of the reaction center proteins due to electron transfer using transient grating technique.

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modeling of $\chi^{(3)}$ in such "face-to-face" macrocycle system, trying to find origin of the enhancement based on the electronic structures. Differing from *ab-initio* quantum mechanical calculations with a complete basis set of the molecules, we modeled this $\chi^{(3)}$ enhancement with semi-empirical quantum mechanical calculations based on the "four orbital model" proposed by Gouterman. Similar approximations have been successfully used in predicting linear optical absorption of macrocycle dimers in previous studies. However, this is the first effort using such approach to model the nonlinear optical

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