Proc. for Intl. Society
for Optical Engineering, Inc.
Jan. 18-22, 1993
Los Angeles, CA

RECEIVED BY
Nonlinear Optical Properties of Porphyrin and
Chlorophyll Dimers Studied by Degenerated Four Wave Mixing

Lin X.-Q. Chen

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

ANL/CHM/CP-78537

ABSTRACT

DE93 006411

As one of the important elements in natural and artificial electron transfer and energy transfer processes, porphyrin and its derivatives have received much attention in photoelectronics and photoelectronic materials. As our first attempt to relate the π - π electronic couplings between porphyrin macrocycles to apparent third order nonlinear susceptibilities, we measured $\chi^{(3)}$ for several porphyrin and chlorophyll *a* derivatives, including dimers with different configurations. Our preliminary results show that the dimers have enhanced $\chi^{(3)}$ compared to those of the monomer. This enhancement is related to the relative orientations between the two macrocycles in the dimers. The parallel dimers with close face-to-face distances seem to have the highest enhancement in $\chi^{(3)}$. Thus, we believe that $\chi^{(3)}$ is strongly related to the π - π electronic coupling between the two conjugated ring systems.

1. INTRODUCTION

Many studies have been done on nonlinear optical properties of organic polymers and small molecules.¹ In particular, certain correlations between the third order nonlinear susceptibility and the electronic conjugation length in the polymers have been established.² However, for a two-dimensional system such as the porphyrin derivatives, the problem becomes complicated. The porphyrin and its derivatives accommodate many electron transfer and energy transfer reactions in biological systems and in synthetic organic conductors and optical materials. In bacterial photosynthetic reaction centers, for example, two chlorophyll molecules form a slipped face-to-face dimer with a distance of 3 to 3.5 Å which acts as a primary electron donor upon absorption of light.³ The π - π electronic coupling between the two chlorophylls that occurs through their two-dimensional macrocycles modifies the photophysics of the dimer and enables it to function uniquely as the primary electron donor. In certain photosynthetic antenna proteins, chlorophyll dimers or oligomers are embedded in protein matrices, funneling light energy to the reaction centers.⁴ Since the early studies revealed the correlation between the electron delocalization in one dimension and the third order nonlinear susceptibilities $\chi^{(3)}$ in simple polymers², we expect that the π - π electron coupling via face-to-face "contact" would also affect $\chi^{(3)}$ of porphyrins in different conformations and different polymeric forms.

As our first attempt in making correlations between the molecular structural properties and the $\chi^{(3)}$ of the two-dimensional macrocycles, we present some preliminary results of $\chi^{(3)}$ measurements of several porphyrin and chlorophyll derivatives with different polymeric structures and relative ring orientations. The degenerate four wave mixing (DFWM) with picosecond laser pulses is used for the measurements. The correlation of the electronic interactions between the porphyrin in its polymeric form with the $\chi^{(3)}$ will be discussed.

2. EXPERIMENTAL

Tetraphenyl porphyrin (TPP), TPP-Fe(III)-Cl, TPP-Fe-O-Fe-TPP, Fe(III)-tetra(4-sulfonatophenyl)porphyrin (TSPP), and Fe(III)-tetra(N-methyl-4-pyridyl) porphyrin (TMPyP) were from Midcentury Chemicals and used without further purification. Chlorophyll *a* was from spinach, and the preparation method was presented elsewhere.⁵ The linear dimer of TPP, (TPP)₂, was from Dr. M. R. Wasielewski of Argonne National Laboratory. The organic solvents are all dried with molecular sieves and doubly distilled water was used for aqueous solutions. The concentrations of the samples were around 0.2 mM, except those having low solubilities. The accurate concentrations were determined

MASTER

by the absorption spectra. The absorbance of the samples were kept OD 0.02-0.06 at 532 nm in 1mm path quartz cells.

A mode-locked, Q-switched, and frequency doubled Nd:YAG laser (Coherent Antares) coupled with a Pockels cell pulse extractor was used in the DFWM experiments. The most energetic mode-locked pulse in each Q-switched envelop was extracted at 1000 Hz. The extracted pulse has a pulse energy of 90 μ J and FWHM of 70 ps at 532 nm. The laser beam was then split into two pump beams and one probe beam for a conventional counter propagating configuration of DFWM. Each of the three beams is focused and the spatial overlap is approximately at the focal point. A polarizer was placed in front of each focusing lens. Two photodiode detectors were used, one to collect the phase conjugated signal, and another to monitor the laser intensity. The photodiode signals were then sent to a boxcar integrator, which is connected to a Gateway PC/486 computer for data acquisition and analysis. A typical signal trace is presented in Fig. 1. The correlation between the signal and the laser intensity was closely checked by varying the laser intensity via neutral density filters and detuning the laser to a state where it generated considerable pulse-to-pulse fluctuation. The relationship between the conjugated signal and the laser pulse intensity is shown in Fig. 2.

Figure 1. The phase conjugated signal of TSPP/TMPyP dimer.

Figure 2. The laser pulse intensity I_0 vs. the phase conjugated signal I for TMPyP (both axes are in logarithm scale).

3. RESULTS AND DISCUSSION

The measured $\chi^{(3)}$ was extracted from the following equation:^{6,7}

$$\chi^{(3)} = \chi_{\text{ref}}^{(3)} \left(\frac{I/I_0}{I_{\text{ref}}/I_{0\text{ref}}} \right)^{1/2} \left(\frac{n}{n_{\text{ref}}} \right)^2 \frac{l_{\text{ref}}}{l} \frac{\alpha l}{(1 - e^{-\alpha l})e^{-\alpha l/2}} \quad (1)$$

where l is the pathlength of the sample; I and I_0 are the intensities of the conjugated signal and the signal proportional to the laser intensity; n is the index of refraction; and α is the absorption coefficient of the sample at the laser wavelength in cm^{-1} . The subscript "ref" refers to a reference compound. The $\chi^{(3)}$ of CS_2 , 4×10^{-13} esu,⁹ was used through the data analysis. To obtain the second hyperpolarizability $\langle \gamma \rangle$ of a molecule in isotropic media, the following relationship is applied:⁹

$$\langle \gamma \rangle = \frac{\chi^{(3)}}{L^4 N} \quad (2)$$

where L is the local field correction factor, $[(n^2+2)/3]^4$, and N is the number density of the molecule in solution in cm^{-3} . Thus, the measured $\chi^{(3)}$ is proportional to the concentration of the solution.

Table I lists the measured $\chi^{(3)}$ and $\langle \gamma \rangle$ according to equations (1) and (2). The χ values were scaled to those of 0.2 mM for all the samples, although the actual concentrations used in the measurements range from 0.11 to 0.28 mM.

TABLE I. $\chi^{(3)}$ and $\langle \gamma \rangle$ of porphyrins and chlorophylls measured by DFWM (20°C, normalized for $2 \times 10^{-4}\text{M}$)

Compound (solvent)	Configuration	$\chi^{(3)} \times 10^{13}$ esu	$\langle \gamma \rangle \times 10^{30}$ esu
Chl a (THF)	monomer	6.6 ± 0.9	1.8 ± 0.3
Chl a ($\text{C}_6\text{H}_6\text{CH}_3$)	mostly tilted dimer	9.9 ± 1.5	2.1 ± 0.3
Chl a ($n\text{-C}_6\text{H}_{14}$)	tilted oligomer	14.3 ± 2.0	4.2 ± 0.6
TPP (THF)	monomer	4.9 ± 0.7	1.3 ± 0.2
TPP ₂ (THF)	side-to-side dimer	13.7 ± 2.0	3.7 ± 0.5
TPP-Fe(III)Cl (THF)	monomer	7.4 ± 1.5	1.9 ± 0.4
TPP-Fe-O-Fe-TPP (THF)	face-to-face dimer	13.5 ± 2.0	3.6 ± 0.6
TSPP (H_2O)	mostly monomer	2.5 ± 0.4	0.9 ± 0.2
TMPyP (H_2O)	mostly monomer	2.2 ± 0.3	0.7 ± 0.1
TSPP/TMPyP ($\text{H}_2\text{O}/\text{MeOH}$)	mostly dimer	8.3 ± 1.0	2.8 ± 0.4

The compounds are grouped into four subgroups. The first group consists of three chlorophyll *a* solutions, corresponding to monomers, tilted dimers and oligomers; the second one is TPP vs. TPP-TPP (a linear dimer of TPP, covalently bond via a phenyl group); the third one is TPP-Fe-Cl and the dimer TPP-Fe-O-Fe-TPP, where the dimer is face-to-face covalently bond but with greater distances compared to those without a middle atom (e.g. O atom); and the fourth group contains two ionic monomers and a heterodimer formed between the two monomers with opposite charges.

In the concentration range (10^{-4} M) applied in our measurements, chlorophyll *a* is known to form dimers and oligomers in nonpolar solvents (e.g. hydrocarbons, toluene, benzene etc.) and monomers in nucleophilic solvents (e.g. ethanol, pyridine, tetrahydrofuran, etc., where the solvent and the solute form a complex).¹⁰ In toluene solution, chlorophyll *a* forms a tilted or T-dimer, where the keto group ($\text{C}=\text{O}$) of ring 9 interacts with the Mg atom of another chlorophyll. Although the apparent $\chi^{(3)}$ of chlorophyll *a* in toluene increased by 50% compared to that of the THF solution, the second hyperpolarizability $\langle \gamma \rangle$ of the T-dimer after local field correction only increases by a margin of the experimental error, implying small change in electron delocalization. However, the larger enhancement was observed in hexane solution, where $\chi^{(3)}$ and $\langle \gamma \rangle$ increase by a factor of 2. The optical spectrum of chlorophyll *a* in hexane (not shown) strongly suggested the formation of the oligomer. The exact reason for the enhancement is yet to be revealed because the configuration of the oligomer was proposed to be the extension of the T-dimer. However,

the real situation may be more complicated when dynamic equilibrium of the dimer or oligomer formation is considered. Thus, at room temperature, the toluene and hexane solutions of chlorophyll *a* are not very good models to characterize the effect of the electronic coupling via π - π interaction between the rings.

The $\chi^{(3)}$ and $\langle \gamma \rangle$ of TPP₂, a covalently linked TPP dimer where the linkage is a shared phenyl group, has a factor of three increase compared to those of TPP. This increase seems much smaller compared to the results of thiophene oligomer⁹, where the increase is a factor of five from monomer to dimer. One possible explanation is that thiophene dimer is more rigid in terms of keeping the π conjugation plane, whereas TPP₂ has an imperfect planar structure reducing the π conjugation.

The other covalently linked dimer, TPP-Fe-O-Fe-TPP, is face-to-face bonded with an O atom in the middle. Compared to its corresponding monomer, TPP-Fe-Cl, $\chi^{(3)}$ and $\langle \gamma \rangle$ of this dimer increased only by a factor of two, indicating that the bridging O prevents a strong π - π interaction between the rings. However, it is also likely that the $\chi^{(3)}$ and $\langle \gamma \rangle$ values of TPP-Fe-Cl have resonance enhancement due to an absorption peak centered at 507 nm, which causes its $\langle \gamma \rangle$ value to be 1.5 and 3 times those for TPP and TSPP, respectively.

The dimer shows that the largest enhancement on $\chi^{(3)}$ and $\langle \gamma \rangle$ is the heterodimer formed between TSPP and TMPyP. A factor of four enhancement is the most significant among the four dimers we have studied. The enhancement suggests a relatively strong coupling between the porphyrins. This dimer is formed with face-to-face configuration, via electrostatic interactions between the negative charges on four -SO₃⁻ groups of TSPP and positive charges on four N atoms of N-methylpyridyl groups. However, without a covalent linkage, the dimer formation is a dynamic process, and the distance between the macrocycles fluctuates. Therefore, the factor of four enhancement is still much smaller than a factor of ten in the bis(phthalocyanines)¹¹, where a transition metal atom is sandwiched between the macrocycles.

In summary, we observed various enhancements of $\chi^{(3)}$ and $\langle \gamma \rangle$ in porphyrin dimers with different relative orientations and linkages, which imply different electronic couplings. A close face-to-face distance and parallel ring orientation enhances $\chi^{(3)}$ and $\langle \gamma \rangle$ significantly. Our observations are preliminary at this stage due to the limited model compounds studied. Moreover, the dimer-monomer equilibrium is a dynamic process, where the exchange rate may also affect the apparent values of $\chi^{(3)}$ and $\langle \gamma \rangle$. To quantitatively characterize the electronic coupling, extensive theoretical calculations must be conducted. Work on this aspect of the chemistry is underway.

5. ACKNOWLEDGEMENT

The author would like to thank Dr. James Norris for inspiring the work, and Dr. M. R. Wasielewski for his TPP₂ sample and many helpful discussions. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

6. REFERENCES

1. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, New York, 1990.
2. G. P. Agrawal, C. Cojan, and C. Flytzanis, "Nonlinear optical properties of one-dimensional semiconductors and conjugated polymers", *Physical Review B*, Vol. 17, pp. 776-789, 1974.
3. J. Deisenhofer, O. Epp, K. Miki, R. Huber, and H. Michel, "X-ray structural analysis of a membrane protein complex: electron density map at 3Å resolution and the models of the chromophores of the photosynthetic reaction center from *Rhodospseudomonas viridis*", *J. Mol. Biol.*, Vol. 180, pp. 385-398, 1984.

4. H. Zuber and R. A. Brunisholz, "Structure and function of antenna polypeptides and chlorophyll-protein complexes: principles and variability", in Chlorophylls, H. Scheer, Ed., Chapter 3.6, pp. 627-703, CRC Press, Boca Raton, 1991.
5. W. A. Svec, "The isolation, preparation, characterization, and estimation of the chlorophylls and bacterial chlorophylls", in The Porphyrins, D. Dolphin, Ed., Vol. 5, pp. 341-399, Academic Press, New York, 1978.
6. R. Dorsinville, L. Young, R. R. Alfano, R. Zamboni, R. Daniels, G. Ruane, and C. Taliani, "Nonlinear optical response in polythiophene film using four-wave mixing techniques", *Opt. Lett.*, Vol. 14, pp. 1321-1323, 1989.
7. D. J. McGraw, A. E. Siegman, G. M. Wallraff, and R. D. Miller, "Resolution of the nuclear and electronic contributions to the optical nonlinearity in polysilanes", *Appl. Phys. Lett.*, Vol. 54, pp. 1713-1715, 1989.
8. R. W. Hellwarth, "Third-order optical susceptibilities of liquids and solids", *Prog. Quant. Electr.*, Vol. 5, pp. 1-68, 1977.
9. M.-T. Zhao, B. P. Singh, and P. N. Prasad, "A systematic study of polarizability and microscopic third-order optical nonlinearity in thiophene oligomers", *J. Chem. Phys.*, Vol. 89, pp. 5535-5541, 1988.
10. J. J. Katz, L. L. Shipman, T. M. Cotton, and T. R. Janson, "Chlorophyll aggregation: coordination interactions in chlorophyll monomers, dimers, and oligomers", in Porphyrins, D. Dolphin, Ed., Vol. V, Chapter 9, pp. 401-458, Academic Press, New York, 1979.
11. J. S. Shirk, J. R. Lindle, F. J. Bartoli, and M. E. Boyle, "Third-order optical nonlinearities of bis(phthalocyanines)", *J. Phys. Chem.*, Vol. 96, pp. 5847-5852, 1992.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

DATE
FILMED

3 / 23 / 93