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Large Third-Order Optical Nonlinearity of Self-Assembled Porphyrin Oligomers

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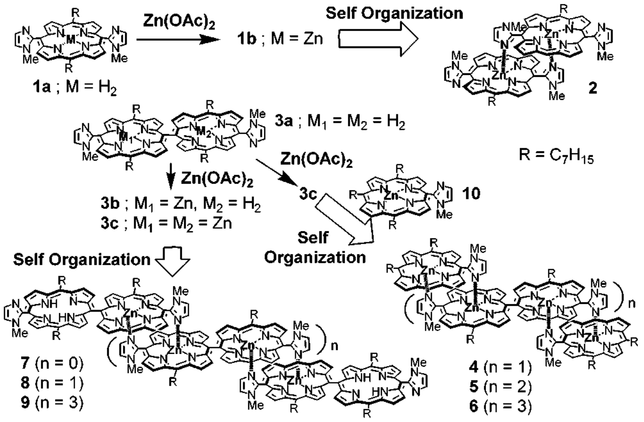
Third-order nonlinear optical (NLO) materials have attracted attention because of potential utilities for photonic applications such as ultrafast optical switching and modulations.[1-3] Various types of organic compounds have been studied to obtain materials with large third-order susceptibilities $\chi^{(3)}$. It has been generally accepted that donor and acceptor terminal sets separated by a π-conjugated system exhibit large $\chi^{(3)}$ values.[4-6] Porphyrins are promising candidates for such NLO materials in view not only of the large π-conjugated system but also of versatile modifications of the structures and various possibilities of central metal ions as well to create porphyrins with ideal properties.[7-14] In fact, linear porphyrin arrays linked by butadiyne were prepared and shown to exhibit among the largest $\chi^{(3)}$ values in any organic materials.[13,14]

We reported first that *meso*-(*N*-methyl)imidazolyl-porphyrinatozinc complex **1b** exists quantitatively as a slipped cofacial dimer **2** by the complementary coordination of the imidazolyl to Zn(II) in nonpolar media.[15] Recently, this idea was developed further to obtain a giant porphyrin array by linking two coordination units directly at the *meso*−*meso* positions.[16] The complementary coordination afforded a poly(porphyrin) containing up to 800 porphyrin units even in a dilute $CHCl_3$ solution. These porphyrin arrays are amenable to further synthetic elaboration just by exchange coordination. Therefore, specific donor and acceptor groups can be introduced at the molecular terminals of highly polarizable large π-electronic systems. This communication introduces such a porphyrin system with large nonlinear optical properties.

Porphyrin oligomers with porphyrinatozinc terminals, **4**, **5**, and **6** were obtained from a mixture of **3c** and monomeric imidazolylporphyrinatozinc **10**, followed by a gel permeation chromatography (GPC) separation from the resulting oligomers.[17] On the other hand, oligomers **7**, **8**, and **9** having free base at both molecular terminals were prepared by the reaction of **3a** with 1.5 equiv of zinc acetate in a mixture of chloroform and methanol.[17] Partial introduction of Zn(II) produced a mixture of **3b** and **3c**, which were self-assembled to give oligomeric mixtures by complementary coordination at the Zn site with leaving free bases at the terminals. Each oligomer was separated through a preparative GPC column (Scheme 1).

Figure 1, parts a and b show the absorption spectra of isolated compounds, dimeric zinc porphyrin **2**, **4**−**6**, and **7**−**9**, along with free base **3a** in $CHCl_3$. The Soret bands of **2** were split into twin peaks at 413 and 436 nm due to exiton interaction originated from slipped co-facial arrangement.[15] The split Soret band around 435 nm also appeared in the absorption spectra of **4**−**6**, and the absorbance of these peaks decreased with the chain length. The large split of the Soret bands that appeared in the spectra of **3a**−**9** around 410 and 450−490 nm were due to the exiton interaction from direct *meso*−*meso* linking. As shown previously,[16] the split Soret band at the longest wavelength was sensitive to the degree of organization, and the peaks shifted from 480 to 489 nm for the series of compounds, **4**−**6** and from 453 to 489 nm for **3a** and **7**−**9** with the increasing number of porphyrin units.

Scheme 1. Molecular Structures and Synthetic Routes of Porphyrins Studied in This Work



The femtosecond time-resolved optical Kerr effect (OKE) was measured at 800 nm,[17] which was off-resonance from the electronic transition frequencies as shown in Figure 1. The results were summarized in Table 1. It must be noted here that extremely low concentrations such as 10^{-5}−10^{-6} M must have been employed for the measurements of **7**−**9** because of nonlinearities that were very large. The elucidated orders of the polarizabilities $|\gamma_{yyyy}|$ and the susceptibilities $|\chi^{(3)}{}_{yyyy}|$ of oligomers **7**−**9** were extremely large, ranging from 10^{-30} to 10^{-29} esu and from 10^{-14} to 10^{-13} esu, respectively. On the other hand, the $|\gamma_{yyyy}|$ of the series of compounds **4**−**6**, which were terminated by monomeric zinc porphyrin, ranged from 10^{-31} to 10^{-30} esu which were 10 times smaller than those of **7**−**9**. Slow equilibration of each compound occurred during the measurements but did not greatly affect the NLO properties. The measurements were finished within 2 h, after which 15% of the isolated oligomers were exchanged to generate satellite peaks in the chromatogram.

The $|\gamma_{yyyy}|$ of **4**−**6** and the real part of the polarizability per porphyrin unit, γ_{real}/unit obtained by heterodyning measurement[17] and giving more accurate values for **7**−**9**, showed an almost linear increase with the number of porphyrins. Such a linear increase on the unit polarizability has also been observed in butadiyne-linked conjugated porphyrin oligomers[13] evaluated through degenerate

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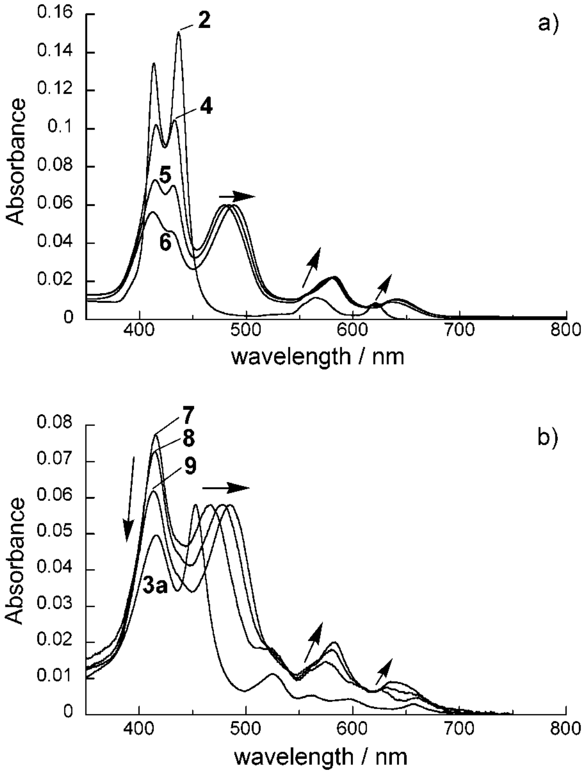

Figure 1. (a) Absorption spectra of isolated **2** and **4**−**6** and (b) **3a** and **7**−**9** in $CHCl_3$. Concentrations were ∼10 μM, and absorbance was normalized at the split Soret band appeared around 450 to 490 nm in each spectrum. The shifted peaks of split Soret band at the longest wavelength were as follows: **4**; 480, **5**; 484, **6**; 489, **3a**; 452, **7**; 467, **8**; 479, **9**; 485 nm.

Table 1. Nonlinear Optical Properties of Porphyrins by OKE Measurements

porphyrins (no. of units)	$\lvert\gamma_{yyyy}\rvert$ (10^{-32} esu)	γ_{real}/unit (10^{-32} esu)	$\lvert\chi^{(3)}_{yyyy}\rvert$ (10^{-15} esu)	$\chi^{(3)}_{real}$ (10^{-15} esu)	concentration (10^{-6} M)
1a (1)	14		91		320
2 (2)	8		24		150
3a (2)	7		4		25
4 (4)	13		55		200
5 (6)	61		38		30
6 (8)	120		39		15
7 (4)	180	55	50	57	13
8 (6)	950	120	165	130	8.3
9 (10)	1300	150	163	150	5.0

four-wave mixing (DFWM) measurement with 45 ps laser pulse at 1064 nm, which was also under off-resonant conditions.[18] The largest susceptibility, $|\chi^{(3)}_{xyyx}|$, reached 1.6 × 10^{-9} esu at the unit concentration of ∼1 mM for the polymer with the estimated degree of polymerization of 20. The third-order nonlinearities of porphyrin oligomers linked by groups of apparently less conjugation such as direct *meso*−*meso* and 1,4-phenylene bridges have also been measured by using a *z*-scan method.[12,18] These porphyrins showed only moderate polarizability increments with the number of porphyrin unit. The method and conditions for these measurements are not identical, and direct comparison of our results with these data is difficult, but the compounds **7**−**9** exhibited extremely large polarizabilities with a clear tendency to enhance the increments with the chain length.

Several factors may contribute to the large enhancement of the nonlinearity. In the series of compounds **1**−**9** here examined, free base monomer **1a**, dimer **3a**, or dimeric zinc complex **2** did not show such a tendency. The series of oligomer **4**−**6** terminated by monomeric zinc porphyrin showed relatively large $|\gamma_{yyyy}|$ values with a linear increase. However, abruptly large $|\gamma_{yyyy}|$ values were observed when free base porphyrins are attached at the terminal positions of core zinc complexes, **7**−**9**. These data clearly showed that the combination of the terminal free base and the core zinc moiety is important to enhance the nonlinearity. The terminal free base, working as a primary electron acceptor in photosynthetic reaction centers, is certainly regarded as the acceptor with respect to the inner Zn porphyrin. Compounds **7**−**9** are therefore regarded as a class of linear quadrapolar molecules,[6] which consist of polarizable π-electronic systems as the central core and acceptors at the molecular terminal. π-Stacked complementary coordination of imidazolyl to Zn porphyrin must be an efficient method to produce polarizable π-electronic systems. The polarizability increments are remarkably enhanced by the increase of the number of central Zn porphyrin units, being 2, 4, and 8 for the series of compounds **7**, **8**, and **9**, respectively.

Judging from these large off-resonant third-order optical nonlinearities, porphyrin oligomers are of potential utility as materials of optoelectronics, optical-switching devices, and integrated optics. According to the methodology here presented, the molecular length and the structure of central π-conjugation system are easily modified. Specific terminal groups, not only of acceptors, but also of donors and donor/acceptor pairs, can be introduced simply by coordination reorganization. Facile introduction of the terminal groups constitutes the outstanding merit of this method. Efforts are being undertaken to further enhance and characterize the optical nonlinearities.

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Supporting Information Available: Preparation of compounds, experimental details, and analytical methods for OKE measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Prasad, P. N., Williams, D. J., Eds. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.
(2) Zyss, J., Ed. *Molecular Nonlinear Optics: Materials, Physics and Devices*; Academic Press: Boston, 1994.
(3) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*; Gordon and Breach: Amsterdam, 1995.
(4) Chen, G.; Mukamel, S. *J. Phys. Chem.* **1996**, *100*, 11080.
(5) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Günter, P. *J. Phys. Chem. B* **1998**, *102*, 4451.
(6) S. Hahn, D. Kim, M. Cho, *J. Phys. Chem. B* **1999**, *103*, 8221 and references therein.
(7) Chou, J.-H.; Kosal, M. E.; Nalwa, H. S.; Rakow, N. A.; Suslick, K. S. In *The Porphyrin Handbook*; Kadish, K., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 1987; Vol. 6, Chapter 41, p 43.
(8) Maloney, C.; Byrne, H.; Dennis, W. M.; Blau, W.; Kelly, J. M. *Chem. Phys.* **1988**, *121*, 21.
(9) Sakaguchi, T.; Shimizu, Y.; Miya, M.; Fukumi, T.; Ohta, K.; Nagata, A. *Chem. Lett.* **1992**, 281.
(10) Guha, S.; Kang, K.; Porter, P.; Roach, J. F.; Remy, D. E.; Aranda, F. J.; Rao, D. V. G. L. N. *Opt. Lett.* **1992**, *17*, 264.
(11) Henari, F. Z.; Blau, W. J.; Milgrom, L. R.; Yahioglu, G.; Phillips, D.; Lacey, J. A. *Chem. Phys. Lett.* **1997**, *267*, 229.
(12) Terazima, M.; Shimizu, H.; Osuka, A. *J. Appl. Phys.* **1997**, *81*, 2946.
(13) Thorne, J. R. G.; Kuebler, S. M.; Denning, R. G.; Blake, I. M.; Taylor, P. N.; Anderson, H. L. *Chem. Phys.* **1999**, *248*, 181.
(14) Kuebler, S. M.; Denning, R. G.; Anderson, H. L. *J. Am. Chem. Soc.* **2000**, *122*, 339.
(15) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111.
(16) Ogawa, K.; Kobuke, Y. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4070.
(17) Experimental details and methods are described in the Supporting Information.
(18) Since these measurements were carried out with picosecond time scale laser pulses, there was a nuclear orientational contribution rather than electronic response measured by femtosecond laser in this study.

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