

Published in final edited form as:

J Am Chem Soc. 2005 August 24; 127(33): 11608–11609. doi:10.1021/ja0537575.

Core-Modified Expanded Porphyrins with Large Third-Order Nonlinear Optical Response

Harapriya Rath, Jeyaraman Sankar, Viswanathan PrabhuRaja, Tavarekere K. Chandrashekar^{*,†}, Amit Nag, and Debabrata Goswami

Department of Chemistry, Indian Institute of Technology, Kanpur 208 106, India

The third-order NLO materials have attracted considerable attention due to their potential applications including 3-D optical memory and fabrication, optical limiting, and two-photon photo-dynamic therapy.¹ Thus, design and synthesis of new molecules with large macroscopic optical nonlinearities represent an active research field in modern chemistry and material science. In general, two-photon absorption (TPA/2PA) is a third-order nonlinear process, and the efficiency of the processes involving two-photon absorption require materials with large absorption cross sections (σ_2), which are directly related to the imaginary part of the second hyperpolarizability [$\text{Im}\gamma(-\omega, \omega, \omega, -\omega)$].² Research on the design and synthesis of such molecules not only requires synthetic skill but also an understanding of structure–property correlation. A handful of reports are available in the literature featuring the design and properties of such compounds.³ Porphyrins are considered suitable for such applications because of the presence of large polarizable conjugated π -electrons required for electronic communication as well as the versatile modifications of the structure possible in the basic framework of the macrocycle skeleton. In fact, TPA in tetrapyrrolic molecules has potential applications for optical power limiting^{4a} and for holographic data storage.^{4b} However, only a limited number of reports of the TPA cross-sections for porphyrins are available in the literature. The majority of regular porphyrins show small σ_2 values which typically do not exceed 1–10 GM (1 GM = 10^{-50} cm⁴ s photon⁻¹) in the range of near-IR wavelength⁵ and nearly 100–1600 GM in the Soret band region.⁶ On the other hand, the σ_2 value has been increased up to 50 000 GM in the case of the double-strand conjugated porphyrin polymer,⁷ whereas intermediate values have been observed in case of conjugated porphyrin dimers⁸ or triply linked fused porphyrin arrays.⁹ Thus, the TPA cross-section values given above are orders of magnitude too small for most of the applications mentioned above. Therefore, creating or finding new porphyrin analogues with higher values of σ_2 is of practical importance. A well-known fact is that oligothiophenes possess excellent electronic and optical properties;¹⁰ for example, α -sexthiophene, the α -linked hexamer of thiophene and its derivatives, has been successfully employed as an active component in organic field-effect transistors and light emitting devices.¹¹ In this context, aromatic core-modified expanded porphyrins where two or four pyrrole rings are replaced by thiophene rings as in 26π hexaphyrin analogues **1** or 34π octaphyrin analogues **2** can be chosen as suitable candidates for satisfying the most necessary and sufficient conditions for an organic material to be NLO active.

Thus, in this paper we wish to report the absolute TPA cross-section values of free base aromatic core-modified 26π hexaphyrin analogues and 34π octaphyrin analogues. TPA

E-mail:tkc@iitk.ac.in.

[†]Present address: Prof. T.K. Chandrashekar, Director, Regional Research Laboratory, Trivandrum, Kerala 695 019, India.

Supporting Information Available: Syntheses and spectroscopic characterization of **1c,e,d,f** and **2a–d**, UV–vis spectra of **1f** and **2b**; measurement technique; open aperture Z-scan traces of **1a–e**, **2a,c,d**, and rhodamine 6G; complete ref 3a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

cross-sections up to 90 600 GM measured by a femtosecond open-aperture Z-scan method for octaphyrin analogues are among the highest values known for any organic molecules to date. To the best of our knowledge, such types of macrocycles have never been studied for NLO response.

A schematic representation of core-modified expanded porphyrins **1** and **2** under investigation are shown in Chart 1. We have chosen very specifically these macrocycles for a better understanding of the most plausible deciding factors for affecting the σ_2 values and hence to know the structure–property correlation by adopting three strategies: (i) the effect of π conjugation, (ii) the effect of core heteroatoms (S vs Se), and (iii) the effect of *meso*-aryl substituents (electron-releasing vs electron-withdrawing). Following the general synthetic methodologies adopted in our laboratory, the macrocycles **1** and **2** have been achieved via a [3 + 3] or [4 + 4] MacDonald-type acid-catalyzed condensation of appropriate precursors.¹² The solid-state structural proof for octaphyrin analogues has been recently obtained by us.^{12b}

Typically, hexaphyrin analogues exhibit a split Soret-band with λ_{max} 536 nm and the one photon absorption spectral intensity goes to zero level nearly at 780 nm as shown in the inset in Figure 1 for **1f** as a representative example.¹⁶ On the other hand, octaphyrin analogues exhibit Soret-like absorption at 517 nm and Q-band-like absorption at 671 nm as shown in Figure 2 for **2b**.¹⁶ Here we would like to mention that the one-photon absorption spectra of the macrocycles **1** and **2** remain invariant with respect to the different meso substituents, and also so far as the effect of core atom on electronic absorption spectra of core modified porphyrins are considered, thiophene and selenophene analogues behave in a similar way.¹³ Hence, from the UV–vis spectra of these macrocycles, it is clear that all the macrocycles investigated in this work are transparent in the near-infrared region. Thus, nonlinear optical measurements were performed with nonresonant excitation. The TPA cross-section (σ_2) values were measured by using a standard open aperture Z-scan technique¹⁴ for 1 cm long sample cells. We use 100 fs pulses at 780 nm with 50 MHz repetition rate from Femtolite laser (IMRA) operating at the second-harmonic wavelength of the Er-doped fiber laser. The 20 cm lens used for the Z-scan experiments produce GW-level laser intensities at the focus, which easily induces two-photon absorption (TPA).¹⁶ All of the samples were measured at 10^{-4} M solution in dichloromethane solvent and showed negligible single-photon absorption at 780 nm. The solvent itself does not show any TPA under our experimental conditions. We obtain the observed nonlinear absorption coefficient values (β)^{9,15} by fitting our measured transmittance values to the following expression: $T(z) = 1 - \beta I_0 L / [2(1 + z^2/z_0^2)]$, where β = nonlinear absorption coefficient, I_0 = on-axis electric field intensity at the focal point in absence of the sample, L = sample thickness, z_0 = Rayleigh range ($z_0 = \pi w_0^2/\lambda$), where w_0 is the minimum spot size at the focal point. The β values are obtained by curve fitting the measured open-aperture traces with the above equation. Figure 1 shows the open aperture traces of **1f** and **2b**. We have taken rhodamine 6G for which the σ_2 value is known¹⁵ as the reference for calibrating our measurement technique.¹⁶ From the theoretical fits to our experimental results, we find very high TPA cross-section (σ_2) values for our conjugated macrocycles.

The high values of σ_2 observed can be attributed to the extended conjugation effect which is further evident from our observation in an increase in the σ_2 values as a function of substituents from electron-releasing to electron-withdrawing groups within the same type of conjugated macrocycles. Moreover, changing the inner heterocyclic rings from thiophene to selenophene provides a marked enhancement in TPA values. The details of these observations are summarized in Table 1. However, as expected from our electron-conjugation argument, a drastic change occurs as we go from 26π to the 34π systems. Furthermore, the 26π hexaphyrin analogues are planar, whereas the 34π octaphyrin

analogues are a nonplanar figure-eight configuration; thus, the drastic enhancement in the values of the TPA cross-section in the case of octaphyrin analogues can also be ascribed partly due to the electronic interactions between the two porphyrin like pockets in the basic framework of the macrocycle.

The σ_2 values for octaphyrin analogues are enhanced approximately 8–9 ($\times 10^3$) times relative to regular porphyrins clearly showing the effect of extended π -conjugation due to the presence of larger number of π -electrons in octaphyrin analogues (34π vs 18π electrons). The intermediate values obtained in case of porphyrin dimers where two 18π porphyrin units are linked to each other by butadiyne^{8a} or ethynyl linkers^{8b} or are fused together⁹ have been attributed to strong electronic coupling and the increase in π -conjugation between two monomer units. However, in the expanded porphyrin system the conjugation is much larger in the porphyrin skeleton itself because of the presence of more number of π -electrons relative to dimers.

In conclusion, the aromatic core-modified expanded porphyrins can be attempted as the best suitable candidates especially as organic nonlinear optical materials due to exceptionally large nonresonating two-photon absorption cross-sections. Further studies to exploit these structure–property correlations are currently in progress.

Acknowledgments

T.K.C. thanks DST, New Delhi, India; D.G. thanks DST, MCIT (India) and International SRF Program of Welcome Trust (U.K.) for the financial grant. H.R., J.S., and V.P.R. thank CSIR, India, for their Senior Research Fellowships.

References

1. a Ehrlich JE, Wu XL, Lee IY, Hu ZY, Röckel H, Marder SR, Perry JW. *Opt Lett.* 1997; 22:1843. [PubMed: 18188382] b Köhler RH, Cao J, Zipfel WR, Webb WW, Hanson MR. *Science.* 1997; 276:2039. [PubMed: 9197266] c Kawata S, Sun HB, Tanaka T, Takada K. *Nature.* 2001; 412:697. [PubMed: 11507627] d Bhawalkar JD, Kumar ND, Zhao CF, Prasad PN. *J Clin Laser Med Surg.* 1997; 15:201. [PubMed: 9612170]
2. Liu XJ, Feng JK, Ren AM, Zhou X. *Chem Phys Lett.* 2003; 373:197.
3. a Albota M, et al. *Science.* 1998; 281:1653. [PubMed: 9733507] b Reinhardt BA, Brott LL, Clarkson SJ, Dillard AG, Bhatt JC, Kannan R, Yuan L, He GS, Prasad PN. *Chem Mater.* 1998; 10:1863. c Kim OK, Lee KS, Woo HY, Kim KS, He GS, Wicz JS, Prasad PN. *Chem Mater.* 2000; 12:284.
4. a Wood GL, Miller MJ, Mott AG. *Opt Lett.* 1995; 20:973. [PubMed: 19859394] b Drobizhev M, Sigel C, Rebane A. *J Lumin.* 2000; 86:391.
5. Karotki A, Drobizhev M, Kruk M, Spangler C, Nickel E, Mamardashvili N, Rebane A. *J Opt Soc Am B.* 2003; 20:321.
6. a Drobizhev M, Karotki A, Kruk M, Rebane A. *Chem Phys Lett.* 2002; 355:175. b Drobizhev M, Karotki A, Kruk M, Mamardashvili N, Zh, Rebane A. *Chem Phys Lett.* 2002; 361:504.
7. Screen TEO, Thome JRG, Denning RG, Bucknall DG, Anderson HL. *J Am Chem Soc.* 2002; 124:9712. [PubMed: 12175222]
8. a Ogawa K, Ohashi A, Kobuke Y, Kamadaand K, Ohta K. *J Am Chem Soc.* 2004; 126:4050. b Karotki A, Drobizhev M, Dzenis Y, Taylor PN, Anderson HL, Rebane A. *Phys Chem Chem Phys.* 2004; 6:7.
9. Kim D, Osuka A, Shigeiwa M. *J Phy Chem A.* 2005; 109:2996.
10. Mullen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, 1998.
11. a Horowitz G, Fichou D, Peng XZ, Xu ZG, Garnier F. *Solid State Commun.* 1989; 72:381. b Dimitrakopoulos CD, Malenfant PRL. *Adv Mater.* 2002; 14:99. c Dodabalapur A, Torst L, Katz HE. *Science.* 1995; 268:270. [PubMed: 17814790]

12. a Rath H, Anand VG, Sankar J, Venkatraman S, Chandrashekar TK, Joshi BS, Khetrpal CL, Schilde U, Senge MO. *Org Lett.* 2003; 5:3531. [PubMed: 12967317] b Rath H, Sankar J, Prabhuraja V, Chandrashekar TK, Joshi BS, Ray R. *Chem Commun.* 2005:3343.
13. Chandrashekar TK, Venkatraman S. *Acc Chem Res.* 2003; 36:676. [PubMed: 12974651]
14. Sheik-Bahaei MA, Said A, Wei TD, Hagan J, Van Stryland EW. *IEEE J Quantum Electron.* 1990; 26:760.
15. Sengupta P, Balaji J, Banerjee S, Philip R, Ravindra Kumar G, Maiti S. *J Chem Phys.* 2000; 112:9201.
16. See the Supporting Information for further details.

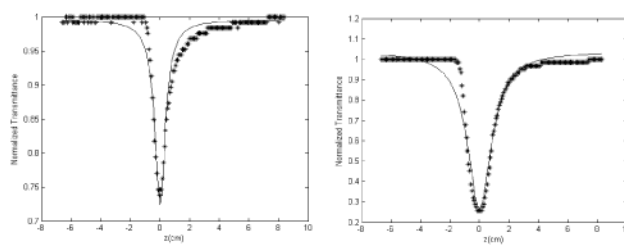


Figure 1. Open-aperture Z-scan traces of **1f** and **2b**. Solid lines are the best-fitted curves of experimental data.

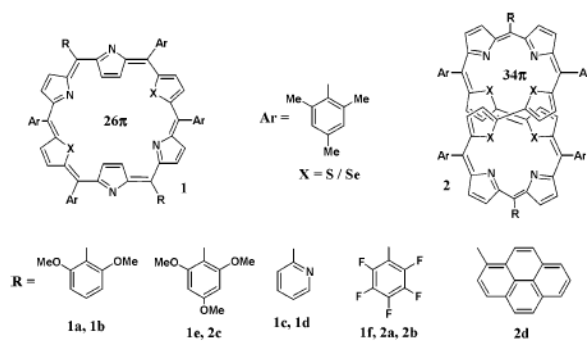


Chart 1.
Core-Modified Hexaphyrin and Octaphyrin Analogues

Table 1Observed σ_2 Values for Macrocycles **1** and **2**

compd	X	σ_2 (GM)
1a	S	2208
1b	Se	7800
1c	S	3828
1d	Se	9060
1e	S	4740
1f	S	24 000
2a	S	81 000
2b	Se	90 600
2c	S	67 340
2d	S	87 694