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

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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.<sup>1</sup> 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 ( $\sigma_2$ ), which are directly related to the imaginary part of the second hyperpolarizability [ $\text{Im}\gamma(-\omega, \omega, \omega, -\omega)$ ].<sup>2</sup> 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.<sup>3</sup> Porphyrins are considered suitable for such applications because of the presence of large polarizable conjugated  $\pi$ -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<sup>4a</sup> and for holographic data storage.<sup>4b</sup> 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  $\sigma_2$  values which typically do not exceed 1–10 GM (1 GM =  $10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>) in the range of near-IR wavelength<sup>5</sup> and nearly 100–1600 GM in the Soret band region.<sup>6</sup> On the other hand, the  $\sigma_2$  value has been increased up to 50 000 GM in the case of the double-strand conjugated porphyrin polymer,<sup>7</sup> whereas intermediate values have been observed in case of conjugated porphyrin dimers<sup>8</sup> or triply linked fused porphyrin arrays.<sup>9</sup> 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  $\sigma_2$  is of practical importance. A well-known fact is that oligothiophenes possess excellent electronic and optical properties;<sup>10</sup> for example,  $\alpha$ -sexthiophene, the  $\alpha$ -linked hexamer of thiophene and its derivatives, has been successfully employed as an active component in organic field-effect transistors and light emitting devices.<sup>11</sup> In this context, aromatic core-modified expanded porphyrins where two or four pyrrole rings are replaced by thiophene rings as in  $26\pi$  hexaphyrin analogues **1** or  $34\pi$  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  $26\pi$  hexaphyrin analogues and  $34\pi$  octaphyrin analogues. TPA

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**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  $\sigma_2$  values and hence to know the structure–property correlation by adopting three strategies: (i) the effect of  $\pi$  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.<sup>12</sup> The solid-state structural proof for octaphyrin analogues has been recently obtained by us.<sup>12b</sup>

Typically, hexaphyrin analogues exhibit a split Soret-band with  $\lambda_{\text{max}}$  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.<sup>16</sup> 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**.<sup>16</sup> 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.<sup>13</sup> 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 ( $\sigma_2$ ) values were measured by using a standard open aperture Z-scan technique<sup>14</sup> 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).<sup>16</sup> 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 ( $\beta$ )<sup>9,15</sup> 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  $\beta$  = 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  $\beta$  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  $\sigma_2$  value is known<sup>15</sup> as the reference for calibrating our measurement technique.<sup>16</sup> From the theoretical fits to our experimental results, we find very high TPA cross-section ( $\sigma_2$ ) values for our conjugated macrocycles.

The high values of  $\sigma_2$  observed can be attributed to the extended conjugation effect which is further evident from our observation in an increase in the  $\sigma_2$  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  $26\pi$  to the  $34\pi$  systems. Furthermore, the  $26\pi$  hexaphyrin analogues are planar, whereas the  $34\pi$  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  $\sigma_2$  values for octaphyrin analogues are enhanced approximately 8–9 ( $\times 10^3$ ) times relative to regular porphyrins clearly showing the effect of extended  $\pi$ -conjugation due to the presence of larger number of  $\pi$ -electrons in octaphyrin analogues ( $34\pi$  vs  $18\pi$  electrons). The intermediate values obtained in case of porphyrin dimers where two  $18\pi$  porphyrin units are linked to each other by butadiyne<sup>8a</sup> or ethynyl linkers<sup>8b</sup> or are fused together<sup>9</sup> have been attributed to strong electronic coupling and the increase in  $\pi$ -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  $\pi$ -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.

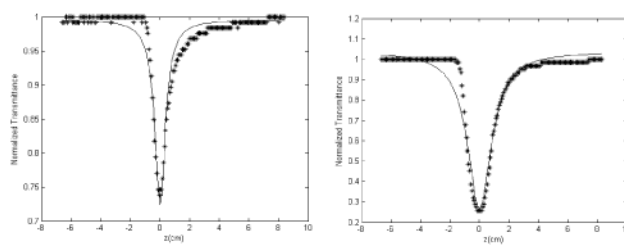
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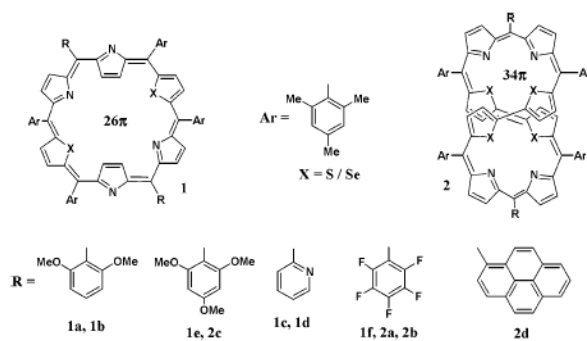
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16. See the Supporting Information for further details.



**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 1**Observed  $\sigma_2$  Values for Macrocycles **1** and **2**

compd	X	$\sigma_2$ (GM)
<b>1a</b>	S	2208
<b>1b</b>	Se	7800
<b>1c</b>	S	3828
<b>1d</b>	Se	9060
<b>1e</b>	S	4740
<b>1f</b>	S	24 000
<b>2a</b>	S	81 000
<b>2b</b>	Se	90 600
<b>2c</b>	S	67 340
<b>2d</b>	S	87 694