

## Understanding Strong Two-Photon Absorption in $\pi$ -Conjugated Porphyrin Dimers via Double-Resonance Enhancement in a Three-Level Model

Mikhail Drobizhev, Yuriy Stepanenko, Yuliya Dzenis, Aliaksandr Karotki, Aleksander Rebane,\*  
Peter N. Taylor, and Harry L. Anderson

Montana State University, Department of Physics, Bozeman, Montana, 59717, P. N. Lebedev Physics Institute, Leninsky Pr., 53, 119991, Moscow, Russia, Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland, and University of Oxford, Department of Chemistry, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, U.K.

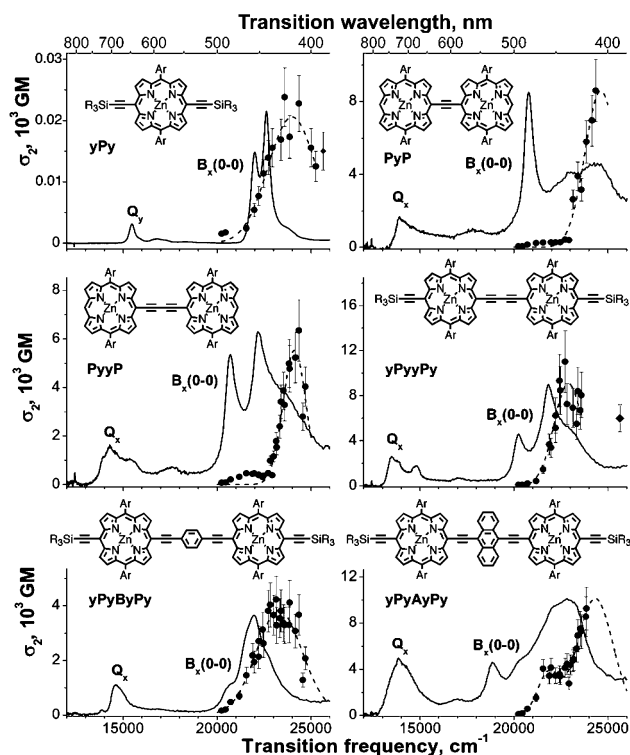
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Applications of two-photon absorption<sup>1</sup> (2PA), such as high-resolution 3D microscopy, deep tissue-penetrating photodynamic therapy (PDT), 3D micro- and nanofabrication, high-density optical data storage, and optical power limiting, depend critically on the availability of materials with high 2PA cross sections and on the ability of these chromophores to perform specialized photophysical, photochemical, or photobiological functions. Porphyrins are particularly well suited for biological applications and are widely used as PDT photosensitizers. Furthermore, photoinduced tautomerization of free-base tetrapyrroles is useful for optical memory applications.<sup>2</sup> However, the 2PA properties of tetrapyrroles were almost ignored until recently. We have investigated the intrinsic 2PA spectra of many tetrapyrrolic compounds using 100-fs pulses.<sup>3</sup> The 2PA cross section is generally low,  $\sigma_2 = 1\text{--}10$  GM (1 GM =  $10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>) in the Q-band region, while in the vicinity of the Soret band, it can be enhanced, up to  $\sigma_2 = 1 \times 10^3$  GM, by different mechanisms, including resonance enhancement, *gerade*-parity excited states, and electron-donating or -accepting substitutions.

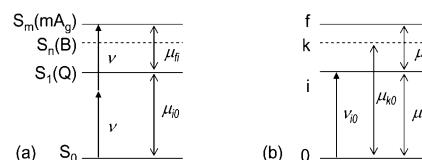
Here we present the 2PA spectra of a series of porphyrin dimers<sup>4</sup> and show that they possess extremely large intrinsic peak 2PA cross sections, up to  $\sigma_2 = 1 \times 10^4$  GM in the near-IR; these are among the highest values measured for any organic molecule.<sup>5</sup> Moreover, we demonstrate that the simple three-level model gives a perfect quantitative description of the observed 2PA cross section, which allows us to elucidate all the factors, contributing to an  $\sim 500$ -fold cooperative enhancement in  $\sigma_2$ , when going from porphyrin monomer to dimer. We also demonstrate generation of singlet oxygen upon one- and two-photon excitation of these porphyrin dimers.

The two-photon and one-photon absorption spectra of the monomer and dimers<sup>4</sup> are shown in Figure 1.<sup>6</sup> All the dimers show a pronounced 2PA peak at 820–890 nm, with  $\sigma_2 = (3\text{--}10) \times 10^3$  GM. The largest values are obtained for yPyyPy ( $9.1 \times 10^3$  GM) and yPyAyPy ( $10 \times 10^3$  GM).<sup>7</sup> In every case, the 2PA maximum occurs at higher energy than the corresponding one-photon Soret  $B_x(0-0)$  transition. This implies that the molecules are effectively centrosymmetric (i.e., the two porphyrin rings in each dimer are almost coplanar), and thus the final 2PA state can be assigned as *gerade*. It is interesting that INDO/MRD-CI calculations<sup>8</sup> predict a *gerade* state for a coplanar geometry of a yyPyyPy dimer very close in energy to what we observe for yPyyPy. Femtosecond pump-probe experiments on the PyP dimer<sup>9</sup> also show an excited  $S_m$  state in the energy region where we observe a strong 2PA peak.

The origins of these high 2PA cross sections can be elucidated quantitatively by considering a three-level model (Figure 2a). We identify the *i*-state with the lowest Q-state,<sup>3</sup> and the well-defined peak in the 2PA spectrum is assigned to a *gerade* final state, *f*. This latter state can be either of  $A_g$  or  $B_g$  symmetry. Second-order



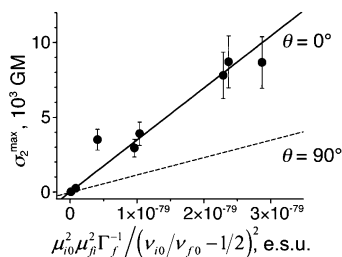
**Figure 1.** One-photon (solid line) and two-photon (symbols) absorption spectra. Gaussian fits to 2PA spectra are shown by dashed lines. (Structures have R = C<sub>6</sub>H<sub>13</sub> and Ar = 3,5-di-*tert*-butylphenyl.<sup>4</sup>)



**Figure 2.** (a) Three-level model describing the 2PA process. (b) Corresponding four-level model explaining the origin of excess excited-state polarizability. Soret band (state *k*) accounts for an important part of the polarizability in the ground state.

perturbation theory allows one to express the peak 2PA cross section,<sup>10</sup> averaged over space and for Gaussian line shape, as follows:

$$\sigma_2^{\max} = \frac{(2\pi)^4 (2 \cos^2 \theta + 1)}{15} \sqrt{\frac{\ln 2}{\pi}} \frac{L^4}{(hcn)^2} \frac{|\mu_{i0}|^2 |\mu_{f1}|^2}{\Gamma_f} \left( \frac{\nu_{i0}}{\nu_{f0}} - \frac{1}{2} \right)^{-2} \quad (1)$$



**Figure 3.** Dependence of maximum 2PA cross section (for all molecules and all observed 2PA bands) on a combination of molecular parameters, entering right-hand side of eq 1, and measured independently.

where  $n$  is the refractive index of medium,  $L = (n^2 + 2)/3$  is the local field factor,  $\Gamma_f$  is the line width of the  $f$ -th state, and  $\theta$  is the angle between the two transition dipole moment vectors,  $\mu_{i0}$  and  $\mu_{fi}$ . Our measurements give absolute values for all the parameters in eq 1, except for  $\mu_{fi}$ . The latter can be obtained from the excess linear polarizability,  $\Delta\alpha$ ,<sup>11</sup> which can be measured by either electroabsorption or time-resolved microwave conductivity techniques. It is easy to show that for a four-level model (as in Figure 2b).

$$|\mu_{fi}|^2 = \hbar\nu_{fi} \left( \frac{3}{2} \Delta\alpha + 2 \frac{|\mu_{i0}|^2}{\hbar\nu_{i0}} + \frac{|\mu_{k0}|^2}{\hbar\nu_{k0}} \right) \quad (2)$$

We use this information to plot the maximum  $\sigma_2$  values of all molecules versus a combination of parameters from the right-hand side of eq 1 in Figure 3. Theoretical lines corresponding to  $\theta = 0^\circ$  and  $\theta = 90^\circ$  are shown without any fitting parameters. In the dimers, the best agreement between experiment and theory is obtained if  $\mu_{i0}$  and  $\mu_{fi}$  are parallel, whereas in the monomer the transition dipoles are probably perpendicular. Since the lowest Q-transition in the dimers is polarized parallel to the long molecular axis<sup>8,12</sup> ( $A_g \rightarrow 1B_{3u}$  transition), the final 2PA state must have  $A_g$  symmetry.

We can now quantitatively compare the molecular parameters of the dimers with those of the yPy monomer. For example, in the yPyyPy dimer, the first transition dipole squared,  $\mu_{i0}^2$ , is approximately 4-fold larger, the detuning denominator in eq 1 is reduced almost 3-fold, the sharpening of 2PA transition gives a 2-fold enhancement, and the second transition dipole squared,  $\mu_{fi}^2$ , is about 10 times larger than in yPy. The first two factors result from amplification and red shift of the first Q-transition, which, in turn, can be seen as a manifestation of a strong perturbation of the four-orbital Gouterman model<sup>8,12b</sup> and elongation of  $\pi$ -conjugation. The effect of narrowing of the 2PA peak could be due to a spectral focusing of several 2PA states into a single dominant peak caused by linear extension of the system. The most important enhancement factor is, however, due to the 10-fold increase in the strength of the second excited-state transition. On the basis of eq 2 and the  $\Delta\alpha$  values,<sup>11</sup> we estimate that  $|\mu_{fi}| \approx 30\text{--}40$  D, depending on particular dimer structure. Such huge values of the excited-state transition dipoles in porphyrin dimers can be compared to one-dimensional  $\pi$ -conjugated polymers, where the absorption from the  $1B_u$  excited state is strongly concentrated in the  $1B_u \rightarrow mA_g$  transition.<sup>13</sup> The gigantic transition strength can be understood if one considers a  $\pi$ -conjugated system as an organic semiconductor with restricted size. Then, the states lying slightly below the conduction band will concentrate a huge oscillator strength, because of their large delocalization radius (large electron-hole separation),<sup>14</sup> which is limited in our case only by molecular length.

As for the role of molecular structure, we see that for a series of dimers with the same side substituents,  $\sigma_2$  increases in the series

yPyByPy < yPyyPy < yPyAyPy. Increasing conjugation length does not necessarily lead to stronger 2PA; for example,  $\sigma_2$  is larger for PyP than for PyyP, which can be explained by much better (smaller) detuning factor for the former.

One of the most promising applications of the extremely large 2PA cross sections of these porphyrin dimers is 2PA-induced PDT. We have demonstrated singlet oxygen generation upon both one- and two-photon excitation of these dimers. The quantum efficiencies of oxygen sensitization in 1% pyridine/toluene are between 0.3 (for yPyAyPy) and  $\sim 1$  (for yPyByPy). We are currently investigating the scope of these chromophores for two-photon excited PDT.

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**Supporting Information Available:** Experimental details and table of oxygen sensitization quantum yields. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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