Dramatic enhancement of intrinsic two-photon absorption in a conjugated porphyrin dimer†

Aliaksandr Karotki,[a] Mikhail Drobizhev,[ab] Yuliya Dzenis,[a] Peter N. Taylor,[c] Harry L. Anderson[c] and Aleksander Rebane*[a]

[a] Department of Physics, Montana State University, Bozeman MT 59717-3840, USA.
E-mail: rebane@physics.montana.edu; Fax: +1 406 994 4452; Tel: +1 406 994 7831
[b] Lebedev Physics Institute, Leninsky Prospekt, 53, 119991, Moscow, Russia
[c] Dyson Perrins Laboratory, Chemistry Department, University of Oxford, South Parks Road, Oxford, UK OX1 3QY

We report strong cooperative enhancement of simultaneous two-photon absorption cross section in a porphyrin dimer. The two-photon cross section, $\sigma_2 = 6 \times 10^{-47}$ cm^{4}s/photon, corresponds to a 400-fold increase over the value measured for the monomer, and is one of the largest ever obtained for organic chromophore of similar size.

Promising applications of two-photon absorption (TPA) in high-density optical data storage,[1,2] two-photon fluorescence microscopy,[3] microfabrication,[2,4] photodynamic therapy,[5,6] and other areas of photonics have recently stimulated the search for novel materials with high efficiency of simultaneous (intrinsic) two-photon absorption (TPA). Porphyrins, notably porphyrin oligomers and polymers, deserve a particular attention since tetrapyrrolic chromophores are inherently suitable for medical and biological applications,[7,8] and also because their photophysical behaviour can easily be optimized by changing the central metal, as well as by peripheral substitution.[9–11] On the other hand, previous studies have revealed that the majority of regular porphyrins show rather small TPA cross sections, σ_2, which, typically, do not exceed 1–10 GM (1 GM $= 10^{-50}$ cm^4 s photon^{-1}) in the biologically important range of near-IR wavelengths.[12] This fact alone has so far largely precluded tetrapyrrolic compounds from being used in real TPA-based applications.

In this paper, we report on a π-conjugated porphyrin dimer molecule, which shows about 400 times greater two-photon absorptivity than the corresponding monomer. The intrinsic TPA cross section, measured with femtosecond pulses, is, $\sigma_2 = 6 \times 10^3$ GM at 780 nm illumination wavelength. This value is comparable to or even exceeds the largest simultaneous TPA cross sections measured for organic chromophores,[13–16] and is certainly the largest value measured for a tetrapyrrolic molecule.‡

It is known that in linear oligomers[17–19] and multi-branched[15,16] conjugated systems the lowest-energy TPA-allowed transition is well separated from other higher

TPA-energy levels, leading to characteristic peaks in near-IR TPA spectra. We have recently used this circumstance to study cooperative enhancement of σ_2 in a series of conjugated multi-branched systems.[16] In porphyrins, however, the relevant TPA transitions are known[9,20–22] to be devoid of distinct spectral features, and rather form a broad continuum due to several overlapping electronic transitions and their vibronic satellites. Another peculiar feature of porphyrins consists in a possibility of strong resonance enhancement, which occurs if the TPA excitation frequency is close to one-photon-allowed Q-transition(s). Depending on chemical structure, the lowest Q-band is located at 620–740 nm, i.e. close to the important near-IR region of wavelengths. In the experiments with two different porphyrins described below, we found that their TPA spectra correspond to very broad features in the excitation region of 780–900 nm. Therefore, we chose $\lambda = 780$ nm for excitation, which is close to the Q-band, and measure σ_2 for both the parent porphyrin monomer and its dimer at this particular wavelength. We then invoke the knowledge of linear absorption properties from the ground- and excited state to explain the very strong enhancement of σ_2 in dimer as compared to monomer.

The chemical structures of [5,15-bis(3,5-bi-tert-butylphenyl)-10,20-bis(trihexylsilylethynyl)porphyrinato]zinc(II) (monomer) and 5,5′-(1,3-butadiyne-1,4-diyl)bis[[10,20-bis(3,5-bi-tert-butyl-phenyl)-15-(trihexylsilylethynyl)porphyrinato]zinc(II) (dimer) are shown in the insets in Fig. 1. Linear absorption and fluorescence spectra of monomer and dimer in polyvinylbutyral (PVB) film are presented in Fig. 1. The extended conjugation in the dimer manifests itself in a pronounced red shift of the absorption and fluorescence maxima relative to monomer.

In order to maximize the resonance enhancement, we chose the excitation wavelength $\lambda = 780$ nm on the red side of dimer's longest wavelength absorption band. The excitation is performed by 150 fs time duration laser pulses with the repetition rate of 1 kHz (see electronic supplementary information (ESI)† for experimental details). Even though the linear extinction at 780 nm is rather small (the corresponding one-photon absorption (OPA) cross section is $\sigma_1 \sim 3 \times 10^{-17}$ cm^2), it can still surpass the TPA, especially at room temperature. In our recent paper[23] we showed that this residual OPA in porphyrins originates from thermal population of higher-lying vibrational levels of the ground electronic state, and that one can reduce this side effect by lowering the temperature of the sample. Upon lowering temperature, the population of these states depletes, thus decreasing the efficiency of OPA. Fig. 2 shows

---

† Electronic supplementary information (ESI) available: Experimental procedures. See http://www.rsc.org/suppdata/cp/b3/b313399k/

‡ Degenerate four wave mixing (DFWM) studies on a polymer analogue of this dimer indicate that it may have a two-photon cross section as high as 50 000 GM per macrocycle at 1064 nm,[11] but DFWM is a much more indirect method of determining two-photon cross sections than the femtosecond two-photon excited fluorescence measurements reported here.
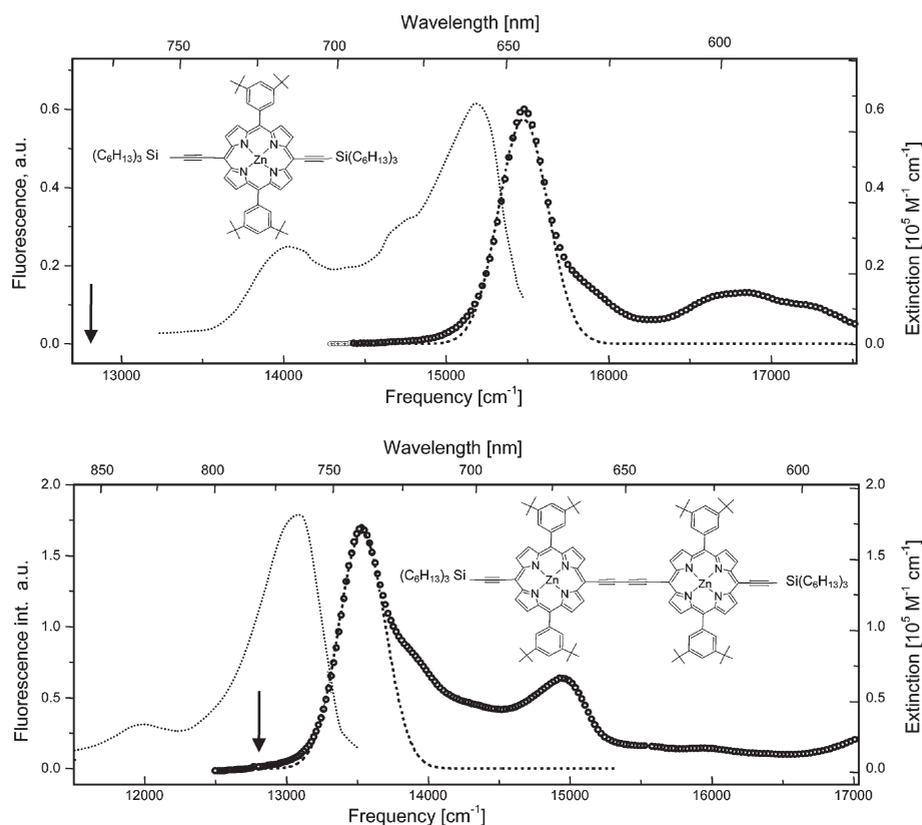
Fig. 1 Linear absorption (open circles) and fluorescence (dotted line) spectra of monomer, top, and dimer, bottom, in PVB film. All spectra are measured at room temperature, except the absorption spectrum of dimer, which is measured at low temperature. The fitting of the first absorption band to a Gaussian is shown by a dashed line. This function is used to calculate the oscillator strength of the $0 \rightarrow i$ transition. Arrows show the TPA laser excitation wavelength.

the excitation power dependence of fluorescence intensity at several different temperatures measured for porphyrin dimer in PVB film. The degree of the power dependence progressively increases with decreasing temperature (Fig. 2) because of the lowering of OPA, and turns into purely quadratic one at $T = 20$ K. However, analysis of these dependencies with the expression $F(P) = aP + bP^2$ shows that the value of two-photon cross section, proportional to coefficient b,[23] does not depend on temperature. This is not surprising, because,
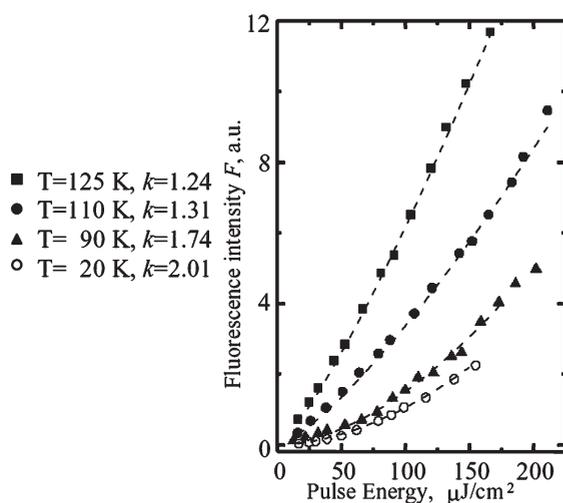
in contrast to OPA, two-photon transitions predominantly occur from the ground state and do not depend on the depletion of the thermally populated vibronic states.

The two-photon cross section was measured at 20 K, where only TPA is present. The measurement was performed by the method based on the comparison of fluorescence intensity upon two- and one-photon excitation. We thus obtained $\sigma_2 = (6 \pm 1) \times 10^3$ GM.§ This constitutes one of the largest intrinsic molecular TPA cross section values known to date.[13–16]

To clarify the origin of such a large nonlinear cross section, we performed similar measurements for the monomeric porphyrin in PVB film. The obtained value, $\sigma_2 = 15 \pm 4$ GM, falls well in the range that is typical for regular porphyrins.[12] In this case, the excitation at 780 nm was sufficiently far away to the red from the closest Q-band absorption peak at 646 nm, such that no detectable OPA was present, even at room temperature.

We conclude that the porphyrin dimer exhibits at 780 nm an σ_2 value that is about 400 times larger than the corresponding porphyrin monomer. This experimental result is in agreement with the recent quantum mechanical calculations[24] showing that, upon transition from a similar porphyrin monomer to a dimer about a hundredfold enhancement of TPA cross section is expected.

Our task now is to explain how such drastic enhancement occurs. Quantitatively, σ_2 for porphyrins in the near-IR excitation wavelength region may be calculated in the so-called

Fig. 2 Dependence of fluorescence intensity on average excitation power for dimer at different temperatures. Dashed lines present fits to $F = cP^k$ function at each temperature. The corresponding k-values are listed in the upper left corner. Fitting to the function $F = aP + bP^2$ is also appropriate and is discussed in the text.

§ Recently we performed TPA cross section measurements for a number of porphyrin dimers, including the one studied in this paper, at room temperature in solvent upon excitation further in the near-IR, $\lambda \approx 860$ nm, where OPA is absent. Preliminary results indicate that the σ_2 amounts up to several thousand GM, confirming the measurements at low temperature reported here. These results will be reported elsewhere.

single intermediate state approximation. This is because the real intermediate level (the first Q-band) in porphyrins is close to the excitation wavelength ($\lambda_{ex} = 780$ nm). As a result, the contribution of this level into the two-photon cross section dominates over the rest of the intermediate levels. Ref. 22 discusses the application of the single intermediate level model to porphyrins in detail. In the framework of this model, the two-photon cross section is proportional to:

$$\sigma^2 \propto \frac{|M_{i0}|^2 |M_{if}|^2}{(\nu_{i0} - \nu_p)^2 + \Gamma^2} g(2\nu_p). \tag{1}$$

Here, subscripts 0, i and f refer to the ground, intermediate, and final excited states, respectively, M_{i0} and M_{if} are the $0 \rightarrow i$ and $i \rightarrow f$ transition dipole moments, respectively, Γ is the half width at the half maximum of the $0 \rightarrow i$ transition, $g(2\nu_p)$ is the normalized lineshape function (in Hz^{-1}), proportional to the cross-sectional contour of the final state, ν_p and ν_{i0} are the photon frequency and the frequency of the $0 \rightarrow i$ transition.

By applying the above formula to both dimer and monomer, we can express the ratio of the two cross sections as:

$$\frac{\sigma_2^{(D)}}{\sigma_2^{(M)}} = \frac{\left[\left(\nu_{i0}^{(M)} - \nu_p\right)^2 + \Gamma^{(M)2}\right]}{\left[\left(\nu_{i0}^{(D)} - \nu_p\right)^2 + \Gamma^{(D)2}\right]} \frac{\left|M_{i0}^{(D)}\right|^2}{\left|M_{i0}^{(M)}\right|^2} \frac{\left|M_{if}^{(D)}\right|^2 g^{(D)}(2\nu_p)}{\left|M_{if}^{(M)}\right|^2 g^{(M)}(2\nu_p)} \tag{2}$$

where superscript D and M refer to dimer and monomer, respectively. The three main factors contributing to the large TPA cross section of the dimer are the resonance enhancement term[12,22] $[(\nu_{i0} - \nu_p)^2 + \Gamma^2]^{-1}$, the $0 \rightarrow i$ transition dipole squared $|M_{i0}|^2$, and the product of the $i \rightarrow f$ transition dipole squared and the normalized lineshape function $|M_{if}|^2 g(2\nu_p)$. At 780-nm, the resonance enhancement factor for the dimer is *ca.* 13 times larger than that for the monomer. If the two porphyrin units forming the dimer were not coupled, then we could assume that each unit absorbs independently. Excluding the above resonance enhancement factor, the resulting dimer TPA cross section would be just twice as large as that of the monomer. However, our experiment gives 400/$13 \approx 30$ times enhancement, which serves as an evidence of strong electronic coupling between the two units. This further significant enhancement has to come from the product $|M_{i0}|^2 |M_{if}|^2 g(2\nu_p)$. The $0 \rightarrow i$ transition dipoles can be quite easily obtained from the linear absorption spectra. Indeed, since the oscillator strength f_{i0} is proportional to the transition dipole squared times ν_{i0}, then it is straightforward to calculate the ratio (Fig. 1):

$$\frac{\left|M_{i0}^{(D)}\right|^2}{\left|M_{i0}^{(M)}\right|^2} \propto \frac{f_{i0}^{(D)}}{\nu_{i0}^{(D)}} : \frac{f_{i0}^{(M)}}{\nu_{i0}^{(M)}} = 2.6 \tag{3}$$

The last remaining factor in eqn. (2) consists of the product of the $i \rightarrow f$ transition dipole squared and the normalized lineshape function. In this case, however, we know neither the oscillator strength of the transition from the first excited state nor the TPA spectral shape $g(2\nu_p)$. On the other hand, since we know the TPA cross sections we can calculate the ratio:

$$\frac{\left|M_{if}^{(D)}\right|^2 g^{(D)}(2\nu_p)}{\left|M_{if}^{(M)}\right|^2 g^{(M)}(2\nu_p)} = \frac{1}{13} \frac{1}{2.6} \frac{\sigma_2^{(D)}}{\sigma_2^{(M)}} = 12 \tag{4}$$

The product $|M_{if}|^2 g(2\nu_p)$ is proportional to the excited state absorption $\varepsilon_{if}(2\nu_p - \nu_{i0})$. In effect, (4) gives us the ratio of the excited-state extinction coefficients of dimer and mono-

mer $\varepsilon_{if}^{(D)}(2\nu_p - \nu_{i0})/\varepsilon_{if}^{(M)}(2\nu_p - \nu_{i0})$. Singlet–singlet excited-state absorption spectra of related monomer and dimer systems were calculated in ref. 9 and are in good qualitative agreement with our experiment. In particular, a dimer with cumulenic structure of butadiyne linker in the first singlet excited state exhibits an order of magnitude enhancement in $\varepsilon_{if}(2\nu_p - \nu_{i0})$, as compared to monomer. The cumulenic structure of the linker in the first excited state was favoured over the alternated in ref. 9 to explain the linear optical properties of the dimer.

Therefore, the extremely large two-photon cross section of the dimer can be explained by the very favourable position of the energy levels. The strong conjugation between porphyrin units in the dimer brings first one-photon transition close to one-half of one of the strong two-photon transitions giving rise to nearly double-resonance TPA conditions. In fact, the only known reported system,[15] with larger TPA cross section is a second-generation dendrimer based on diphenylaminostilbene. The porphyrin dimer molecule, studied in this article, holds a record large σ_2 among relatively small molecules. One possible way to compare the two-photon cross sections of different molecules is to calculate the ratio of the σ_2 to molecular weight. For the porphyrin dimer studied here this ratio is equal to 2.8 GM amu^{-1}, while for the dendrimer from[15] it is only about 1 GM amu^{-1}, making it a less efficient two-photon absorber in this sense than the porphyrin dimer.

In conclusion, we have observed a 400 times enhancement of TPA in conjugated porphyrin dimer, as compared to its related monomer at 780 nm. The very strong enhancement of the TPA cross section in dimer is explained by the π-conjugation-induced red shift, strengthening of the one-photon allowed Q-transition, and strengthening of transitions from the first excited state, which all result in almost double-resonance conditions for two-photon absorption. The resulting values of the intrinsic TPA cross section, 6×10^3 GM, and TPA cross section per molecular weight are the largest intrinsic values obtained so far for tetrapyrrolic compounds and are among the largest for any organic chromophore. The fact that conjugated porphyrin dimer has such high two-photon cross section implies that it can have practical applications in high-density optical data storage, 3D fluorescence imaging, microfabrication and photodynamic therapy.

References

1   D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843–845.
2   B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder and J. W. Perry, *Nature*, 1999, **398**, 51–54.
3   W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73–76.
4   W. H. Zhou, S. M. Kuebler, K. L. Braun, T. Y. Yu, J. K. Cammack, C. K. Ober, J. W. Perry and S. R. Marder, *Science*, 2002, **296**, 1106–1109.
5   J. D. Bhawalkar, N. D. Kumar, C.-F. Zhao and P. N. Prasad, *J. Clin. Lasers Med. Surg.*, 1997, **15**, 201–204.
6   A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, E. Nickel and C. W. Spangler, *IEEE J. Sel. Top. Quantum Electron.*, 2001, **7**, 971–975.
7   R. Bonnett, *Chemical Aspects of Photodynamic Therapy*, Gordon and Breach Science Publishers, Amsterdam, 2000.
8   R. K. Pandey, F.-Y. Shiau, C. J. Medforth, T. J. Dougherty and K. M. Smith, *Tetrahedron Lett.*, 1990, **31**, 789–792.
9   D. Beljonne, G. E. O'Keefe, P. J. Hamer, R. H. Friend, H. L. Anderson and J. L. Brédas, *J. Chem. Phys.*, 1997, **106**, 9439–9460.
10 H. L. Anderson, *Chem. Commun.*, 1999, 2323–2330.

11 T. E. O. Screen, J. R. G. Thorne, R. G. Denning, D. G. Bucknall and H. L. Anderson, *J. Am. Chem. Soc.*, 2002, **124**, 9712–9713.

12 A. Karotki, M. Drobizhev, M. Kruk, C. Spangler, E. Nickel, N. Mamardashvili and A. Rebane, *J. Opt. Soc. Am. B*, 2003, **20**, 321–332.

13 M. Albota, D. Beljonne, J -L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. R. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X. -L. Wu and C. Xu, *Science*, 1998, **281**, 1653–1656.

14 S. J. K. Pond, M. Rumi, M. D. Levin, T. C. Parker, D. Beljonne, M. W. Day, J.-L. Brédas, S. R. Marder and J. W. Perry, *J. Phys. Chem. A*, 2002, **106**, 11 470–11 480.

15 M. Drobizhev, A. Karotki, A. Rebane and C. W. Spangler, *Opt. Lett.*, 2001, **26**, 1081–1083.

16 M. Drobizhev, A. Karotki, Yu. Dzenis, A. Rebane, Z. Suo and C. W. Spangler, *J. Phys. Chem. B*, 2003, **107**, 7540–7543.

17 B. S. Hudson, B. E. Kohler and K. Schulten, in: *Excited States*, ed. E.C. Lim, Academic Press, New York, 1982, vol. 6, p. 1–95.

18 R. R. Birge and B. M. Pierce, *J. Chem. Phys.*, 1979, **70**, 165–178.

19 D. Beljonne, Z. Shuai and J. L. Brédas, *J. Chem. Phys.*, 1993, **98**, 8819–8828.

20 M. B. Masthay, L. A. Findsen, B. M. Pierce, D. F. Bocian, J. S. Lindsey and R. R. Birge, *J. Chem. Phys.*, 1986, **84**, 3901–3915.

21 J. Rodriguez, C. Kirmaier and D. Holten, *J. Am. Chem. Soc.*, 1989, **111**, 6500–6506.

22 M. Drobizhev, A. Karotki, M. Kruk and A. Rebane, *Chem. Phys. Lett.*, 2002, **355**, 175–182.

23 M. Drobizhev, A. Karotki, M. Kruk, A. Krivokapic, H. L. Anderson and A. Rebane, *Chem. Phys. Lett.*, 2003, **370**, 690–699.

24 X. Zhou, A.-M. Ren, J.-K. Feng, X.-J. Liu and Y.-D. Zhang, *ChemPhysChem*, 2003, **4**, 991–997.