

Charge transfer induced enhancement of near-IR two-photon absorption of 5,15-bis(azulenylethynyl) zinc(II) porphyrins†

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Intramolecular charge transfer in 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrin leads to a significant enhancement of two-photon absorption at near-IR region, which has been investigated by femtosecond Z-scan method.

Recently, π -conjugated organic molecules with large two-photon absorption (TPA) cross section have attracted much attention due to numerous applications in material science¹ for optical limiters, optical data storage, 3-D microfabrication, optical switching, and in biological fields² for imaging with two-photon excited fluorescence. Among a variety of molecules studied, porphyrins and their derivatives have emerged as promising candidates for nonlinear optical materials because of their rigid two-dimensional and highly π -conjugated structures.^{3,4} One of the main issues in two-photon absorption is to find new molecular systems with large TPA cross sections. In parallel with this, a considerable progress has been made in elucidating structure–property relationships for large TPA cross section.⁵ A number of factors influence the TPA magnitudes, among which the two major considerations are π -electronic delocalization^{6,7} and charge separation efficiency.⁸ As a consequence, to increase TPA cross section values in molecular systems, molecular designs involving donor/acceptor sets intervened with a π -conjugation system in a symmetrical (D– π –D or A– π –A) or asymmetrical (D– π –A) arrangement have been proposed.⁹ The effect of varying the electron-donating or electron-accepting strength of the end groups, introducing additional groups to perturb the charge redistribution, and elongating the effective π -conjugation length has been considered to design new molecular structures with enhanced two-photon absorption behaviors. Asymmetric D– π –A perturbation is effective for enhancement of second-order polarizability of π -conjugated systems but has never been tested for enhancement of third order polarizability.

In this work, we examined the TPA properties of azulenylethynyl-linked zinc(II) porphyrins with a particular attention to the degree of charge separation in comparison with

bisphenylethynyl-linked zinc(II) porphyrin as a reference molecule (**1**, **2**, **3** and **4** in Fig. 1). Bisethynylated porphyrin was employed as a highly polarizable potent pigment on the basis of the previous extensive studies on this class of molecules. Therien and co-workers reported the large first-order hyperpolarizability for push–pull 5,15-bis(arylethynyl) zinc(II) porphyrins.¹⁰ Anderson *et al.* reported the very large third-order nonlinear optical properties for *meso-to-meso* butadiyne-linked porphyrin oligomers.¹¹ Azulene is also a polarizable group and can serve as either an electron donor or an electron acceptor depending on the nature and connectivity. The electron-rich nature of the five-membered ring and electron-deficient nature of the seven-membered rings are well known¹² and have been confirmed for directly azulene-linked zinc(II) porphyrins.¹³

Reference porphyrin **1** was prepared by the method by Therien and co-workers.^{10a} Azulene-linked molecules **2**, **3** and **4** were prepared by the route developed by Therien and Anderson with some modifications. Sonogashira coupling reactions of

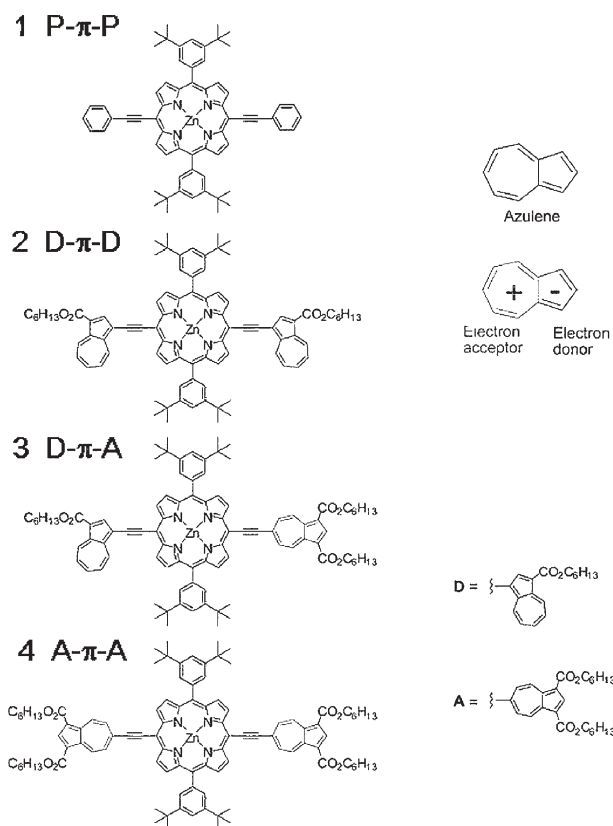


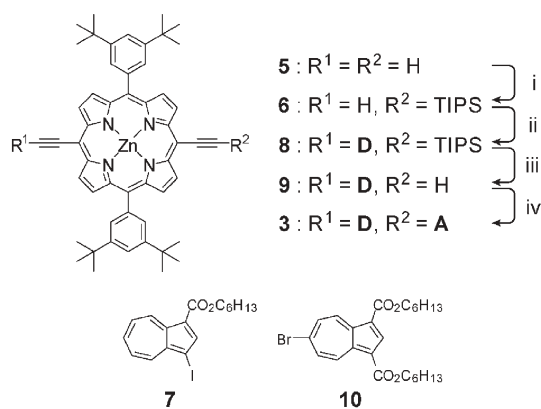
Fig. 1 Schematic molecular structures of **1**, **2**, **3** and **4**.

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† Electronic supplementary information (ESI) available: Two-photon absorption cross-section $\sigma^{(2)}$ and schematic diagram of femtosecond open-aperture Z-scan set-up. See DOI: 10.1039/b704986b



Scheme 1 Reagents and conditions: (i) LiHMDS, TIPSCl, pyridine, THF; (ii) **7**, Pd(PPh₃)₄, CuI, Et₃N, THF; (iii) TBAF, THF; (iv) **10**, Pd(PPh₃)₄, CuI, Et₃N, THF.

5.15-diethynyl zinc(II) porphyrin **5** with 1-iodo-3-hexyloxycarbonyl azulene (**7**) and 6-bromo-1,3-dihexyloxycarbonylazulene (**10**) provided **2** and **4** in 43 and 87% yields, respectively. Porphyrin **3** was prepared *via* partially silylated intermediate **6**, which was prepared from **5**. Sequential Sonogashira coupling reaction starting from **6** afforded **3** *via* intermediates **8** and **9** with a 87% isolated yield for the final reaction of **8** and **10** (Scheme 1).

In the steady-state absorption spectra, the Soret and Q-bands are observed at 449 and 641 nm for **1**, 471 and 685 nm for **2**, 473 and 713 nm for **3**, and 489 and 723 nm for **4**, respectively (Fig. 2). Since the Q-band (HOMO–LUMO transition) is sensitive to an enlarged π -conjugation pathway of porphyrin ring,¹⁴ the π -conjugation is estimated to increase in the order of $1 < 2 < 3 < 4$, which is also in line with the relative intensity of the Q-band. This may be caused by charge transfer property induced by electron-donating and electron-accepting azulenylethynyl substituents. The oscillator strengths calculated by TD-DFT method are shown in Fig. 2. Various transitions around the Soret band of **3** suggest the involvement of CT transitions in the absorption spectra, which is consistent with the broader spectral features of **3** in comparison with the relatively narrow absorption bands of **1**.

The TPA cross-section values were measured by an open-aperture Z-scan method¹⁵ with wavelength tunable 130 fs pulses at 5 kHz repetition rate generated from a Ti:sapphire regenerative

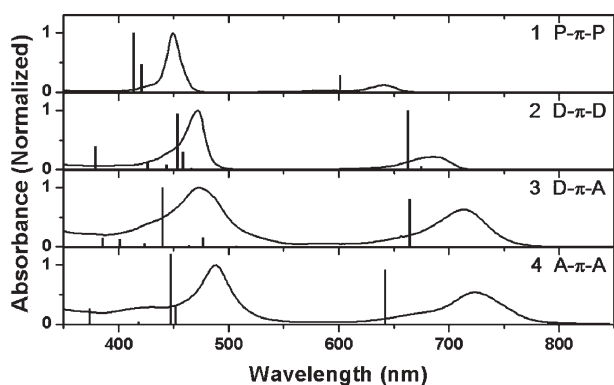


Fig. 2 Steady-state absorption spectra (solid line) of **1**, **2**, **3** and **4** in toluene and calculated oscillator strength (vertical line) by TD-DFT method.

Table 1 Excitation wavelength (nm), sample concentrations (mM) and TPA cross section values (GM) of **1**, **2**, **3** and **4** in toluene

Sample	Wavelength/nm	Concentration/mM	$\sigma^{(2)}/GM$
1 (P- π -P)	1260	0.12	1890
2 (D- π -D)	1360	0.14	3520
3 (D- π -A)	1400	0.13	8030
4 (A- π -A)	1430	0.13	5490

amplifier system (Spectra-Physics, Hurricane) (ESI[†]). Sufficiently high power pulses easily afford an adequate power density for TPA process without tight focusing, which eliminates unwanted nonlinear effects such as self-focusing and white-light continuum generation. The maximum TPA cross section $\sigma^{(2)}$ values are 1890 GM at 1260 nm for **1**, 3520 GM at 1360 nm for **2**, 8030 GM at 1400 nm for **3**, and 5490 GM at 1430 nm for **4**, respectively (Table 1).

Also, the TPA spectra of these porphyrin derivatives were recorded in the 600–850 nm region, indicating that two-photon allowed states should exist nearby 630–720 nm, slightly higher and wider than one-photon allowed Q bands (Fig. 3). Since the electron densities of the *meso*-carbon atoms of the Zn(II) porphyrin ring are very high, the attachment of acceptor moieties at *meso*-carbons is more effective in elongating the π -conjugation pathway throughout the molecular framework along the triple bond linkages. Thus, it is expected that A- π -A type **4** is more effective in elongating π -conjugation pathway than D- π -D type **2**, which is in accord with the red-shifted absorption spectra and larger $\sigma^{(2)}$ value of **4** as compared with **2**. Importantly, D- π -A type porphyrin **3** exhibits the TPA cross-section value of 8030 GM at 1400 nm, which is distinctly larger than that of **4**. The enhancement in the TPA value of **3** may be ascribed to CT character. It is noteworthy that the TPA cross section $\sigma^{(2)}$ values of **2**, **3** and **4** are larger than that of **1**, indicating that electron donating/accepting substituents play important roles in the enhancement of TPA values in addition to the elongation of the π -conjugation pathway through π -bond linkages. To gain further insight into the enhancement of TPA values, the molecular orbital structures of **1**, **2**, **3** and **4** were calculated on B3LYP/6-31G* level (Fig. 4). The HOMO and LUMO of **4** are characteristic of an elongated π -electron conjugation pathway throughout the molecular framework, which naturally results in an enhancement in the TPA value as compared with **2**. On the other hand, the CT

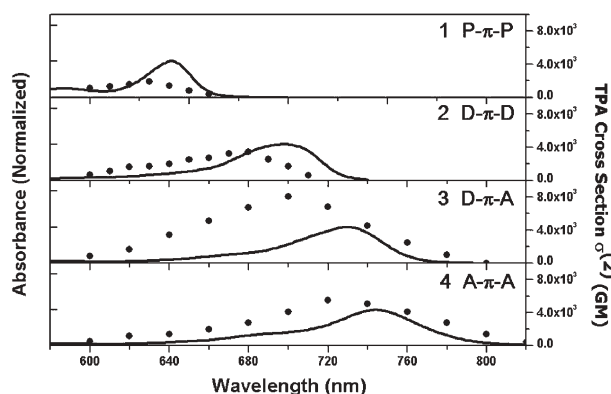


Fig. 3 One-photon absorption spectra (solid line) and two-photon absorption spectra (closed circle) of **1–4** in toluene.

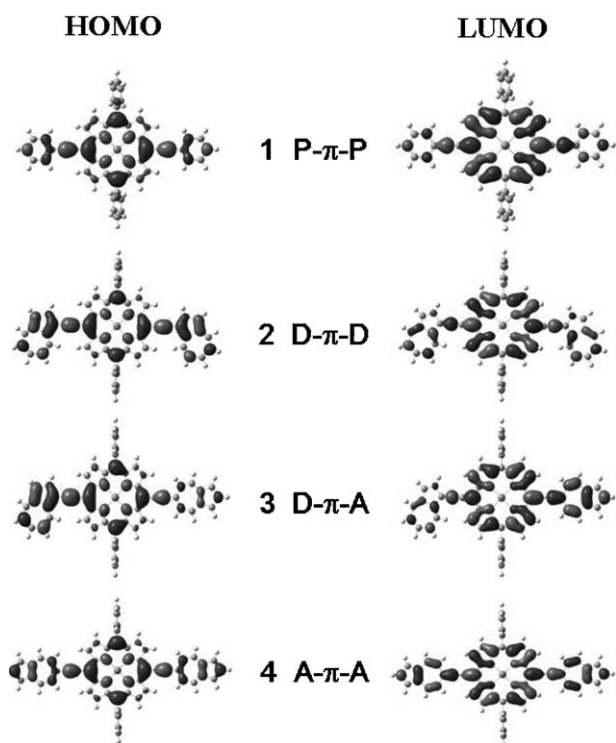


Fig. 4 Frontier orbitals (HOMO and LUMO) of **1**, **2**, **3** and **4** from the geometry optimization process based on the *ab initio* calculation on B3LYP/6-31G* level.

transition between HOMO and LUMO levels becomes manifest in **3**, which leads to even larger TPA value.¹⁶

In summary, this study demonstrates that the prominent enhancement of two-photon absorption properties in porphyrins of which the structures are modified with azulene substituents can be understood in terms of an interplay of enlarged π -electronic interaction and efficient charge separation. We anticipate these molecules will find applications as optical power limiters in this wavelength range and as efficient TPA sensitizers for NIR photorefractive composites.

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Notes and references

1 (a) F. Kajar and J. M. Nunzi, *Functional Organic and Polymeric Materials*, ed. T. H. Richardson, 2000, John Wiley & Sons Ltd, New

- York, ch. 12, p. 327; (b) W. Denk, J. H. Strickler and W. W. Webb, *Science*, 1990, **248**, 73; (c) A. Diaspro and M. Robello, *J. Photochem. Photobiol., B*, 2000, **55**, 1; (d) B. H. Cumpston, S. P. Anathavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kueble, 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; (e) J. H. Strickler and W. W. Webb, *Proc. SPIE-Int. Soc. Opt. Eng.*, 1990, **107**, 1398; (f) J. Oberlé, L. Bramerie, G. Jonusauskas and C. Rullière, *Opt. Commun.*, 1999, **169**, 325.
- 2 (a) W. R. Zipfel, R. M. Williams and W. W. Webb, *Nat. Biotechnol.*, 2003, **21**, 1369; (b) D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843; (c) J. D. Bhawalkar, N. D. Kumar, C. F. Zhao and P. N. Prasad, *J. Clin. Laser Med. Surg.*, 1997, **15**, 201.
- 3 (a) L. Jaquinod, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, Oxford, 2003, vol. 6, 43; (b) H. S. Nalwa and S. Miyata, *Nonlinear Optics of Organic Molecules and Polymers*, Chemical Rubber Corp., Boca Raton, FL, 1997.
- 4 N. K. M. Naga Srinivas, S. V. Rao, D. V. G. L. N. Rao, B. K. Kimball, M. Nakashima, B. S. Decristofano and D. N. Rao, *J. Porphyrins Phthalocyanines*, 2001, **5**, 549.
- 5 (a) O.-K. Kim, K.-S. Lee, H. Y. Woo, K.-S. Kim, G. S. He, J. Swiatkiewicz and P. N. Prasad, *Chem. Mater.*, 2000, **12**, 284; (b) S.-J. Chung, K.-S. Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz and P. N. Prasad, *J. Phys. Chem. B*, 1999, **103**, 10741; (c) G. S. He, J. Swiatkiewicz, Y. Jiang, P. N. Prasad, B. A. Reinhardt, L.-S. Tan and R. Kannan, *J. Phys. Chem. A*, 2000, **104**, 4805; (d) M. Drobizhev, A. Karotki, A. Rebane and C. W. Spangler, *Opt. Lett.*, 2001, **26**, 1081.
- 6 D. Kim, C. Kirmaier and D. Holten, *Chem. Phys.*, 1983, **75**, 305.
- 7 Y. Inokuma, N. Ono, H. Uno, D. Y. Kim, S. B. Noh, D. Kim and A. Osuka, *Chem. Commun.*, 2005, 3782.
- 8 (a) 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; (b) M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Röckel, S. Thayumanavan, S. R. Marder, D. Beljonne and J.-L. Brédas, *J. Am. Chem. Soc.*, 2000, **122**, 9500; (c) L. Ventelon, S. Charier, L. Moreaux, J. Mertz and M. Blanchard-Desce, *Angew. Chem., Int. Ed.*, 2001, **40**, 2098; (d) J. Yoo, S. K. Yang, M.-Y. Jeong, H. C. Ahn, S.-J. Jeon and B. R. Cho, *Org. Lett.*, 2003, **5**, 645; (e) A. Abbotto, L. Beverina, R. Bozio, A. Facchetti, C. Ferrante, G. A. Pagani, D. Pedron and R. Signorini, *Chem. Commun.*, 2003, 2144; (f) F. Meng, B. Li, S. Qian, K. Chen and H. Tian, *Chem. Lett.*, 2004, **33**, 470.
- 9 L. Cristian, I. Sasaki, P. G. Lacroix, B. Donnadiou, I. Asselberghs, K. Clays and A. C. Razus, *Chem. Mater.*, 2004, **16**, 3543.
- 10 (a) S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, 1996, **118**, 1497; (b) S. Priyadarshy, M. J. Therien and D. Beratan, *J. Am. Chem. Soc.*, 1996, **118**, 1504.
- 11 (a) H. L. Anderson, S. J. Martin and D. D. C. Bradley, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 655; (b) S. M. Kuebler, R. G. Denning and H. L. Anderson, *J. Am. Chem. Soc.*, 2000, **122**, 339; (c) T. E. O. Screen, J. R. G. Throme, R. G. Denning, D. G. Bucknall and H. L. Anderson, *J. Am. Chem. Soc.*, 2002, **124**, 9712.
- 12 R. S. H. Liu and A. E. Asato, *J. Photochem. Photobiol., C*, 2003, **4**, 179.
- 13 K. Kurotobi and A. Osuka, *Org. Lett.*, 2005, **7**, 1055.
- 14 (a) A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79; (b) A. Tsuda, H. Furuta and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 10304.
- 15 M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. G. Hagan and E. W. van Stryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.
- 16 D. Y. Kim, T. K. Ahn, J. H. Kwon, D. Kim, T. Ikeue, N. Aratani, A. Osuka, M. Shigeiwa and S. Maeda, *J. Phys. Chem. A*, 2005, 109.