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 electronaccepting 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-n-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.^{10*a*} 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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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 electrondonating 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 openaperture 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 1Excitation wavelength (nm), sample concentrations (mM)and TPA cross section values (GM) of 1, 2, 3 and 4 in toluene

Sample	Wavelength/nm	Concentration/mM	$\sigma^{(2)}/GM$
$ \frac{1 (P-\pi-P)}{2 (D-\pi-D)} \\ 3 (D-\pi-A) \\ 4 (A-\pi-A) $	1260	0.12	1890
	1360	0.14	3520
	1400	0.13	8030
	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 mesocarbons is more effective in elongating the π -conjugation pathway throughout the molecular framework along the triple bond linkages. Thus, it is expected that A $-\pi$ -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, $D-\pi$ -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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