# Stepwise elongation effect on the two-photon absorption of self-assembled butadiyne porphyrins†

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**Butadiyne–porphyrin dimer arrays, which were generated by complementary coordination of the central zinc atom to imidazolyl followed by metathesis, were elongated stepwise and their 2PA properties were explored.**

Optical power limiting,[1] ultra-high density 3D optical memory,[2] high-resolution fluorescence microscopy,[3] 3D microfabrication,[4] and deep-site photodynamic therapy[5] are some of the potential applications of the rapidly growing field of two-photon absorption (2PA). However, most organic compounds exhibit only small off-resonant 2PA cross-sections values, $\sigma^{(2)}$, of less than a few tens GM (1 GM = $10^{-50}$ cm$^4$ s molecule$^{-1}$ photon$^{-1}$) measured using femtosecond pulses. Recently, highly conjugated π-systems have been shown to be most effective in enhancing 2PA.[6–9] In 2003, we first reported a giant $\sigma^{(2)}$ value of 7600 GM that was the largest among reported values measured by femtosecond pulses[9a,b] by combining conjugated butadiyne bisporphyrin with zinc–imidazolyl complementary coordination. On the other hand, acetylenic porphyrins[7a–c] having $\sigma^{(2)}$ of $10^4$ GM and self-assembled porphyrin ladders[7d,e] with a large $\sigma^{(2)}$ value of $1.2 \times 10^5$ GM were reported. Osuka and co-workers also synthesized conjugated porphyrins[8a–c] and hexaphyrins[8d] with $\sigma^{(2)}$ values with a maximum reaching $10^6$ GM. We have utilized zinc–imidazolyl complementary coordination[10,11] with exceptionally high stability constant of $10^{11}$ M$^{-1}$ towards the facile syntheses of large macrorings as light-harvesting systems[10a–c] and polymeric arrays as molecular wires.[10d,e] The combination of conjugated bisporphyrins using mono or bisacetylene linking with zinc–imidazolyl coordination provides a convenient pathway to generate not only polymers, but also discrete shorter porphyrin arrays by the addition of terminators.[10e] Herein, we present a butadiyne-bridged bisporphyrin monomer **TDT** and dimer **TDDT** terminated with a monomeric porphyrin unit on both ends to examine the effect of incremental elongation of butadiyne porphyrin arrays through self-coordination (Fig. 1).

In order to create the **TD$_n$T** array, **T′** and **D′**[12] were combined and initially dissociated to their respective monomers by the addition of pyridine. After removal of pyridine, these compounds were dissolved in CHCl$_3$ to reorganize into an oligomeric mixture, from which **(TDT)′** and **(TDDT)′** were separated using GPC. In order to permanently fix the oligomer structure, metathesis using Grubbs catalyst[13] was performed, followed by GPC separation to isolate finally the target compounds **TDT** and **TDDT**. The absorption spectra shown in Fig. 2 can provide information on the extent of conjugation in the porphyrin arrays. The simplest zinc–imidazolyl coordinated dimer **TT** exhibits the characteristic Soret band splitting[10f,11] centered at around 425 nm and emission maximum at 624 nm with a fluorescence quantum yield of 0.053. Upon insertion of a butadiyne bisporphyrin unit, the Soret band of **TDT** shows broader and red-shifted peaks at 434, 461 and 495 nm due to the extension of conjugation provided by the butadiyne linker. Furthermore, strong Q-bands appear at longer wavelengths at 666 and 728 nm, which are characteristic of butadiyne porphyrins.[14] As expected, the emission maximum of **TDT** was also bathochromically shifted to 737 nm with a fluorescence quantum yield of 0.084. **TDDT** also shows Soret bands at 434, 462 and 497 nm, and Q-bands

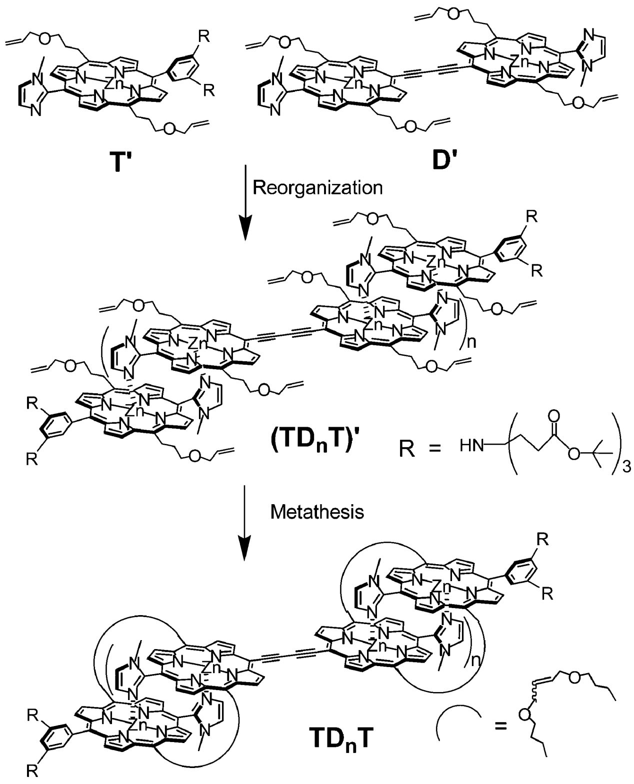

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**Fig. 1** Structure of butadiyne porphyrin array.

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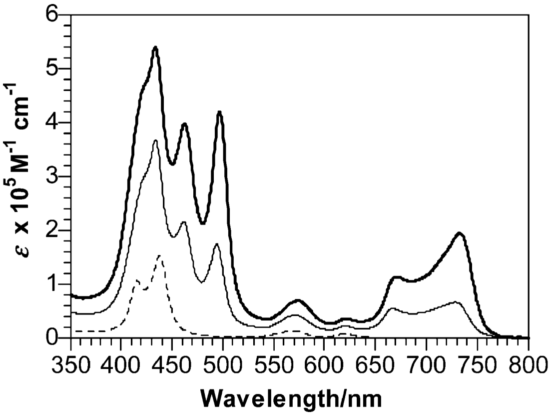

**Fig. 2** UV-Vis absorption spectra of **TT** (broken line), **TDT** (thin line), **TDDT** (solid line).

at 670 and 733 nm, slightly red-shifted with respect to **TDT**, and the amplification of the oscillator strength of the Q-bands is not only twice but almost thrice the intensity, indicating stronger dipole moments caused by excitonic interaction between the two bisporphyrins. Fluorescence also appeared at a longer wavelength of 733 nm with a higher quantum yield of 0.102.

The 2PA spectra were measured using an open-aperture Z-scan technique with 120 fs pulses at non-resonant wavelengths from 820 to 940 nm.[6d,9a,b] Fig. 3 shows typical Z-scan traces for **TDT** in toluene monitored at 867 nm (dotted trace) and theoretically fitted curves (solid line) with eqn (S1) and (S2) (see ESI†). The deviation of the baselines of the traces from 1.00 is due to the small one-photon absorption including the absorption of cell and solvent, which is corrected with eqn (S4) in further calculation. Fig. 4 shows plots of the two-photon absorbance $q_0$ against $I_0$ for **TDT** and **TDDT** in toluene monitored at 867 nm. The linear relationship between $q_0$ and $I_0$, which is predicted by eqn (S3), demonstrates that 2PA is the dominant process and the higher-order nonlinear processes are negligible under the experimental condition. **TDT** yields a maximum $\sigma^{(2)}$ value of $(1.00 \pm 0.099) \times 10^4$ GM at 870 nm. On the other hand, **TDDT** gives a maximum $\sigma^{(2)}$ value of $(6.10 \pm 0.88) \times 10^4$ GM at 870 nm (Fig. 5). This results in a 6× enhancement of $\sigma^{(2)}$ or a 3× amplification of $\sigma^{(2)}$ per butadiyne bisporphyrin. $\sigma^{(2)}$ of **TT** with femtosecond pulses was not measured due to its weak 2PA ($\sigma^{(2)}$ of ethynylimidazolylporphyrin dimer was $< 20$ GM).

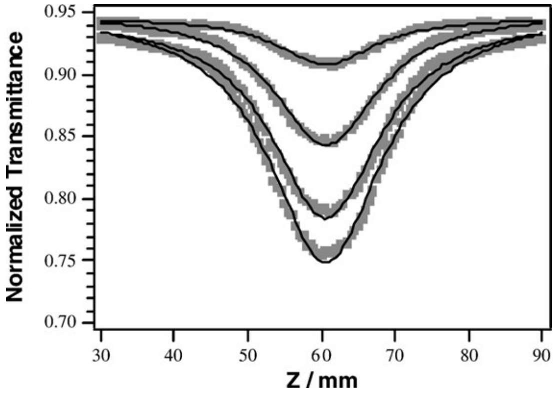

**Fig. 3** Typical open-aperture Z-scan traces (TDT in toluene, 0.5 mmol L$^{-1}$). Incident power = 0.07, 0.18, 0.29, 0.38 mW, respectively, from top to bottom.

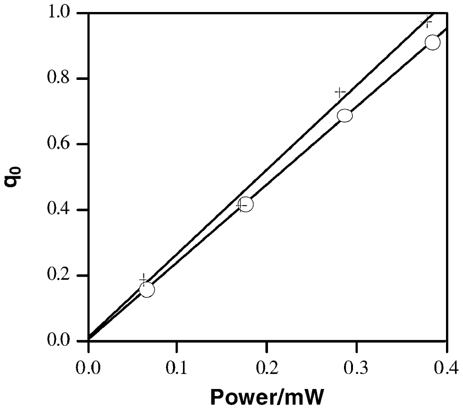

**Fig. 4** The plot of two-photon absorbance $q_0$ against the incident power of the laser beam for **TDT** (○) and **TDDT** (+) in toluene (0.5 and 0.08 mmol L$^{-1}$, respectively) monitored at 867 nm.

The high 2PA cross-section value in **TDT** is mainly attributed to the butadiyne π-bridge[7,9a,b] which increases conjugation as evidenced by the presence of large Q-band located at 728 nm. The intensification of the Q-band implies delocalization of the electron density throughout the bisporphyrin resulting in a lower energy $S_1 \leftarrow S_0$ transition. As a result, 2PA is considerably amplified.

The elongation of the array by complementary coordination of another butadiyne bisporphyrin unit resulted into a more amplified cross-section value. As described in the one-photon absorption spectra, the amplification of the oscillator strength of the Q-band of **TDDT** is almost three times that of **TDT** due to the larger transition dipole moments caused by the additional excitonic interaction between the two butadiyne bisporphyrins of **TDDT**. Since the $\sigma^{(2)}$ value is proportional to the square of the transition dipole moment of the one-photon absorption,[15] which is the $S_1 \leftarrow S_0$ transition in many cases, the intensification of the Q-band probably contributes to larger enhancement for **TDDT**.

In conclusion, we have established a convenient route of enhancing 2PA *via* a self-assembly approach rather than through the elongation of conjugated porphyrin arrays. Moreover, through stepwise extension of the arrays we were able to obtain a 6× intensification of $\sigma^{(2)}$ (3× per butadiyne unit)

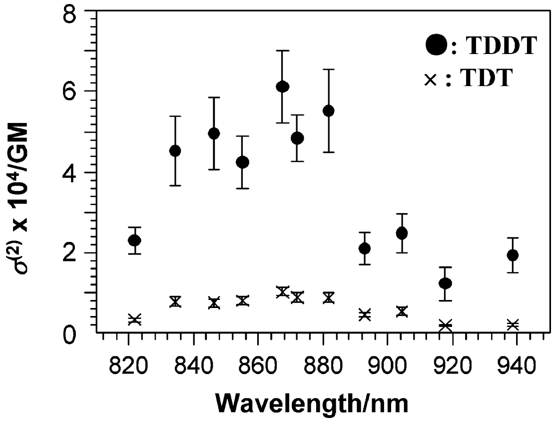

**Fig. 5** 2PA spectra of **TDT** and **TDDT** in toluene.

giving a maximum value of 6.1 × $10^4$ GM, which is one of the largest values for 2PA considering the length of the array. The properties of longer arrays are also interesting and are subject to further investigation.

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