Supporting Information

Stepwise Elongation Effect on Two-photon Absorption of Self-assembled Butadiyne Porphyrins

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Detailed procedures of synthesis and characterization.

Preparation (Reorganization) of (D)₂ and (**T**)_n and Isolation of the different length oligomers. **T**' (30mg, 22.3µmol) and **D**' (72mg, 44.6µmol) were dissolved in 400 mL of pyridine for dissociation. After 1 h, pyridine was completely removed and the porphyrins were dissolved in CHCl₃ for reorganization during which different oligomers (**TD**_n**T**)', i.e. n = 0, 1, 2, 3..., are formed. The target products (**TDT**)' and (**TDDT**)' were roughly separated by preparative GPC (JAIGEL 3H, eluent: CHCl₃, flow rate: 3.5 mL/min). Analytical GPC peaks (JAIGEL 3H-A, eluent: CHCl₃, flow rate: 1.2 mL/min): 13.032 (**TT**)', 12.506 (**TDT**)', 12.071 (**TDDT**)', 11.716 (**TDDDT**)'.

Olefin Metathesis Reaction for Covalent Linkage of (TDDT)'. (TDDT)' (5 mg, 0.87 µmol) containing a small amount of (TDT)' and (TDDDT)' was dissolved in 2 mL of CHCl₃. Grubbs catalyst (RuCl₂(PPh₃), 0.29 mg, 0.35 µmol) was added for metathesis. After 4 h, water was added to terminate the reaction and the target material was extracted with CHCl₃. The organic layers were washed with water and brine and dried over anhydrous Na₂SO₄. Preparative GPC (JAIGEL 3H, eluent: CHCl₃, flow rate: 3.5 mL/min) was performed for further purification/isolation of TDDT. UV-vis (λ_{abs} , CHCl₃): 434, 462, 497, 571, 622, 670, 733 nm. Fluorescence (λ_{em} , $\lambda_{ex} = 434$ nm, CHCl₃): 740, 822nm. MS (MALDI-TOF Mass, dithranol); Found *m*/*z* = 5744.00 [M + H⁺], calcd exact mass for C₂₄₄H₂₉₀N₂₈O₃₆Zn₄ 5742.76. Analytical GPC peak (JAIGEL 3H-A, eluent: CHCl₃, flow rate: 1.2 mL/min): 12.97 mins.

In ¹H-NMR, split signals due to isomers with respect to two internal olefin moieties were observed in a ca. 1:3 ratio. Asterisk (*) and prime (') indicate signals of major and minor isomers, respectively. No mark indicates that peaks of the isomers (*trans-trans, cis-trans, cis-cis*) are overlapped. $\delta_{\rm H}$ (600 MHz, CDCl₃; Me₄Si) 10.32 (*trans and cis*, 8H, m, Por β), 9.84 (*trans and cis*, 8H, m, Por β), 9.59 (*trans and cis*, 8H, m, Por β), 9.38* (*trans-trans*, 54% × 2H, s, Ph-4), 9.35' (*cis-trans*, 40% × 2H, s, Ph-4), 9.33' (*cis-cis*, 6% × 2H, s, Ph-4), 9.14-9.01 (*trans and cis*, 16H, m, Por β), 8.93 (*trans and cis*, 8H, m, Por β), 8.74 (2H, m, Ph-2,6), 8.58' (*cis-cis*, 6% × 2H, s, Ph-2,6), 8.54' (*cis-trans*, 40% × 2H, s, Ph-2,6), 8.50* (*trans-trans*, 54% × 2H, s, Ph-2,6), 7.15' (*cis-cis*, 6% × 2H, s, CONH), 7.11' (*cis-trans*, 40% × 2H, s, CONH), 7.08* (*trans-trans*, 54% × 2H, s, CONH), 6.53* (*trans*, 78% × 12H, two s, -CH=), 6.17' (*cis*, 22% × 12H, two s, -CH=), 5.70-5.40 (28H, m, imidazole-H₅ (6H), Por β (12H), Por-CH₂'-(40% × 24H)), 5.40-5.05* (60% × 24H, broad, Por-CH₂-), 4.80-4.70' (*cis*, 23% × 24H, two broad, -OCH₂CH=), 4.55-4.40* (*trans*, 77% × 24H, m, -OCH₂CH=), 4.35-4.20 (24H, m, Por-(CH₂)₂CH₂-), 3.50-2.94 (24H, broad m, Por-CH₂CH₂-), 2.55-2.20 (54H, m, amide ester -CH₂CH₂-(48H), imidazole-H₄ (6H)), 1.83-1.73 (*trans and cis*, 18H, m, NCH₃), 1.54 (54H, broad s, *t*Bu), 1.24-1.20 (*trans and cis*, 54H, three s*, *t*Bu). * indicates that doublet or singlet peaks overlap which makes the integration ratio difficult to determine. Approximately, the ratio is 1:6:8. All of these doublet peaks have a coupling constant of J = 4.2 Hz.

Two-photon absorption cross-section measurement using an open aperture z-scan technique. The effective 2PA cross section $\sigma^{(2)}$ of **TDT** and **TDDT** in toluene from 840-940 nm was determined by an open aperture z-scan method^{S1} with femtosecond pulses generated by an optical parametric amplifier (*SpectraPhysics OPA-800*) operating at 1 kHz pumped by a Ti:sapphire regenerative amplifier system (*SpectraPhysics Spitfire, Merlin, Tsunami,* and *Millenia*). The optical set-up used for the z-scan measurements is similar to previously reported methods.^{S2} The laser intensities were attenuated using filters to give on-axis peak intensities ranging from 0.2 to 2.2×10^{15} W/m². The repetition rate was reduced from 1 kHz to 10 Hz using a mechanical chopper for all measurements. The samples were placed in a 1 mm quartz cuvette and scanned at a range of 60 mm around the focal point.

The curve fits were performed according to the theoretical expression for the transmittance.^{S2}

$$T(\zeta) = \frac{(1-R)^2 e^{(-\alpha^{(1)}L)}}{\sqrt{\pi}q(\zeta)} \int_{-\infty}^{\infty} \ln[1+q(\zeta)e^{(-x^2)}] dx$$
(1)

$$q(\zeta) = \frac{q_0}{1 + \zeta^2} \tag{2}$$

$$q_0 = \alpha^{(2)} (1 - R) I_0 L_{eff}$$
(3)

$$L_{eff} = [1 - \exp(-\alpha^{(1)}L)]/\alpha^{(1)}$$
(4)

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$$\sigma^{(2)} = \hbar \omega \, \alpha^{(2)} \,/\, N \tag{5}$$

where ζ is the normalized z-position ($\zeta = (z-z_0)/z_R$), and z_0 and z_R are the focal position and the Rayleigh range, respectively. q_0 is the two-photon absorbance, $\alpha^{(1)}$ is the one-photon absorption coefficient, R denotes the Fresnel reflectance, and L is the path length (1 mm). $\alpha^{(2)}$ is the 2PA coefficient, L_{eff} denotes the effective path length, and I_0 is the peak intensity at the focal position. N is the number density of the solute molecules and $\hbar \omega$ is the photon energy of the incident light. Finally, the $\sigma^{(2)}$ value was estimated from equation (5).



Figure S1. Analytical GPC elution curve of **TT** (green), **TDT** (blue), and **TDDT** (orange) using a JAIGEL 3H-A column with $CHCl_3$ as the eluent, flow rate = 1.2 mL/min.



Figure S2. ¹H-NMR spectra of TT, TDT, and TDDT in $CDCl_3$ at r.t., 600 MHz.

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Figure S3. HHCOSY spectrum of **TDDT** in CDCl₃ at r.t., 600 MHz.



Figure S4. Excitation Spectrum of TDDT in CHCl₃ monitored at 740 nm.

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