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’ (30 mg, 22.3 μmol) and D’ (72 mg, 44.6 μmol) 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 (TDₙT)’, 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, λ_ex = 434 nm, CHCl₃): 740, 822 nm. 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. δ_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-H9 (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, tBu), 1.24-1.20 (trans and cis, 54H, three s*, tBu). *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$^6$ 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.$^2$ The laser intensities were attenuated using filters to give on-axis peak intensities ranging from 0.2 to $2.2 \times 10^{15}$ W/m$^2$. 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.$^2$

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

\[
q(\zeta) = \frac{q_0}{1 + \zeta^2} \quad (2)
\]

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

\[
L_{eff} = \frac{[1-\exp(-\alpha^{(1)}L)]/\alpha^{(1)}} \quad (4)
\]
\[ \sigma^{(2)} = \hbar \omega \alpha^{(2)} / N \]  \hspace{1cm} (5)

where \( \zeta \) is the normalized z-position \( \left( \zeta = (z-z_0)/z_R \right) \), 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, \( L_{\text{eff}} \) 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.
The 3 types of environments experienced by the allylic and imidazolyl protons can be divided into these 3 categories:

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**Figure S2.** $^1$H-NMR spectra of TT, TDT, and TDDT in CDCl$_3$ at r.t., 600 MHz.
Figure S3. HHCOSY spectrum of TDDT in CDCl$_3$ at r.t., 600 MHz.
**Figure S4.** Excitation Spectrum of TDDT in CHCl₃ monitored at 740 nm.

References:
