

Supporting Information

Enlarged π -electronic network of a *meso-meso*, β - β , β - β triply linked dibenzoporphyrin dimer that exhibits a large two-photon absorption cross section

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General Procedure. All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry toluene was prepared by distillation over CaH_2 . ^1H - and ^{13}C -NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl_3 ($\delta = 7.260$) or CH_2Cl_2 ($\delta = 5.300$). Spectroscopic grade CH_2Cl_2 was used as solvents for all spectroscopic studies without further purification except where noted. UV/visible/NIR absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrometer with O_2 -degassed and Ar saturated spectroscopic grade solvents. Relative fluorescence quantum yields were estimated from that of tetraphenylporphyrin zinc(II) complex ($\Phi_f = 0.033$ in toluene). ESI-MS spectra were recorded on a BRUKER microTOF Focus using positive-ion mode. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736), silica gel gravity column chromatography (Wako gel C-300) and size exclusion gel permeation chromatography (Bio-Rad Bio-Beads S-X1, packed with toluene or CHCl_3 in a 4×100 gravity flow column: flow rate, 3.8 mLmin^{-1}). Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model 660. All retro Diels-Alder reactions were carried out in a glass tube oven SHIBATA GTO-250RS equipped with a vacuum pump.

Porphyrin monomer 4

4,7-Dihydro-4,7-ethano-2*H*-isoindole (350 mg, 2.41 mmol), 2,2'-dipyrrylmethane (177 mg, 1.21 mmol), and 4-*tert*-butylbenzaldehyde (0.605 ml, 3.62 mmol) were dissolved in dichloromethane 710 ml and the solution was stirred under Ar for 5 min in the dark. Then 2.5 M trifluoroacetic acid in dry dichloromethane solution (0.6 ml, 1.5 mmol) was added to the reaction mixture, and stirred for 3 h. DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (681 mg, 3.00 mmol) was added to the solution and stirred overnight. The whole reaction mixture was passed through a short alumina column, and the resulting mixture was concentrated to ca. 200 ml by a rotary evaporator. The concentrated solution was moved to a 500 ml round-bottom flask equipped with a condenser, to which were added triethylamine 0.1 ml and zinc(II) acetate dihydrate (266 mg, 1.21 mmol) in methanol 5 ml solution. After refluxing for 1 h, the solution was washed with water (50 ml x 2 times), dried over Na₂SO₄, and evaporated. The residue was once passed through a silica gel column (eluent : dichloromethane) to roughly remove polar materials. Products were separated by a gel permeation chromatography (GPC) (eluent : THF). The first yellow fraction contained some impurities and a trace amount of tetrakis(bicyclo[2.2.2]octadiene fused)porphyrin zinc(II) complex. The second deep red fraction was collected and recrystallized from dichloromethane/methanol to give porphyrin 4 (137.5 mg, 12%) as a *cis* and *trans* mixture. The last light red fraction was collected and recrystallized from dichloromethane/hexane to give 5,15-di-(4-*tert*-butylphenyl)porphyrin zinc complex (31.2 mg, 8.1%).

¹H NMR (600 MHz, CDCl₃) δ = 10.20 (s, 1H, *meso*), 9.36 (d, *J* = 4.6 Hz, 2H, β), 9.09 (d, *J* = 4.6 Hz, 2H, β), 8.15-8.10 (m, 6H, Aryl), 7.82-7.75 (m, 6H, Aryl), 6.49 (br, 4H, bicyclo -CH=CH-), 3.43 (br, 4H, bicyclo ¹C-H), 1.67 (s, 9H, *tert*-Bu), 1.66 (s, 18H, *tert*-Bu), and 1.53 (br, 4H, bicyclo -CH₂-CH₂-); ¹³C NMR (150 MHz, CDCl₃) δ = 152.3, 152.1, 151.9, 151.0, 150.3, 149.2, 143.5, 143.1, 141.7, 140.9, 137.1(2C), 133.8(2C), 133.6, 133.3, 132.2, 131.0, 123.4, 119.3, 105.6, 38.0, 37.7, 35.2, 35.1, 32.0(2C), and 26.9(2C); HR ESI-TOF Mass (positive mode) *m/z* = 925.4181 (calc. for C₆₂H₆₁N₄Zn = 925.4182 [M+H]⁺); UV/Vis (in CH₂Cl₂): λ_{max} [nm] (ε [M⁻¹cm⁻¹]) = 415 (533000) and 541 (27000); Fluorescence emission (excited at 415 nm in CH₂Cl₂) λ_{max} [nm] = 635, Φ_f = 0.019.

Dibenzoporphyrin 5

Porphyrin 4 (10.0 mg, 10.8 μmol) was placed in a glass tube oven, and heated to 210 °C under

reduced pressure (0.1 mmHg) for 30 minutes, to give dibenzoporphyrin **5** quantitatively.

^1H NMR (600 MHz, CD_2Cl_2 containing 1% butylamine) δ = 10.05 (s, 1H, *meso*), 9.21 (d, J = 3.7 Hz, 2H, β), 8.77 (d, J = 3.7 Hz, 2H, β), 8.11 (d, J = 7.3 Hz, 2H, Aryl), 8.06 (d, J = 7.8 Hz, 4H, Aryl), 7.93 (d, J = 7.3 Hz, 2H, Aryl), 7.84 (d, J = 7.8 Hz, 4H, Aryl), 7.35 (t, J = 7.7 Hz, 2H, Benzo), 7.31 (t, J = 7.8 Hz, 2H, Benzo), 7.28 (d, J = 7.8 Hz, 2H, Benzo), 7.10 (d, J = 7.8 Hz, 2H, Benzo), 1.71 (s, 9H, *tert*-Bu), and 1.67 (s, 18H, *tert*-Bu) ; ^{13}C NMR (150 MHz, CD_2Cl_2 (δ = 53.52) containing 1% butylamine) δ = 152.6, 151.3, 151.1, 147.3, 147.0, 143.7, 141.9, 141.2, 140.7, 140.5, 133.2, 133.0, 130.4 (2C), 125.9, 125.7, 125.5, 125.2, 124.8, 124.5, 117.8, 115.6, 107.9, 35.2, 35.0, 31.8, and 31.7 ; HR ESI-TOF Mass (positive mode) m/z = 868.3480 (calc. for $\text{C}_{58}\text{H}_{52}\text{N}_4\text{Zn}$ = 868.3478 [M] $^+$) ; UV/Vis (in CH_2Cl_2) : λ_{max} [nm] (ϵ [$\text{M}^{-1}\text{cm}^{-1}$]) = 430 (615000), 561 (27000), and 598 (34000). ; Fluorescence emission (excited at 430 nm in CH_2Cl_2) λ_{max} [nm] = 602, 658, Φ_f = 0.023.

Meso-meso linked porphyrin dimer 6

Commercially available chloroform was washed with water (3 times), and pre-dried over anhydrous K_2CO_3 . Pre-dried chloroform was distilled over anhydrous Na_2SO_4 .

(Method A) A solution of porphyrin **4** (50.0 mg, 54.1 μmol) in distilled CHCl_3 55 ml was bubbled with Ar gas for 15 min in the dark. Then a 0.12 M solution of AgPF_6 in dry acetonitrile (0.50 ml, 60.0 μmol) was added to the solution dropwise via a syringe. The reaction mixture was stirred under Ar in the dark for 3 h. The reaction was quenched with water (5 ml). The organic layer was washed with brine (50 ml \times 2 times), and dried over anhydrous Na_2SO_4 . To this solution, a solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (10 mg, 45.6 μmol) in MeOH (2 ml) and 3 drops of triethylamine were added and the resulting mixture was refluxed for 30 min. After cooling, the solution was washed with water (50 ml \times 2 times), dried over Na_2SO_4 , and the solvent was evaporated. The residual solid was dissolved in a small amount of CH_2Cl_2 , and passed through a short silica gel column (Wako gel C-300; eluent : CH_2Cl_2). Purified products were separated by a GPC column (eluent : THF), the first red fraction was collected and recrystallized from CH_2Cl_2 /MeOH, giving porphyrin dimer **6** (17.6 mg, 35%). The second fraction was also collected and recrystallized from CH_2Cl_2 /MeOH to recover **4** (17.8 mg, 36%).

(Method B) A solution of porphyrin **4** (50.0 mg, 54.1 μmol) in distilled CHCl_3 (76 ml) containing DMA (*N,N*-dimethylacetamide) (0.38 ml) was bubbled with Ar gas for 15 min in the dark. Then a 0.12 M solution of AgPF_6 in dry acetonitrile (0.54 ml, 64.8 μmol) was added to the

solution dropwise via a syringe. The reaction mixture was stirred under Ar in the dark for 15 min. The reaction was quenched with water (5 ml), and then organic layer was washed with brine (50 ml x 2 times), and dried over anhydrous Na₂SO₄. To the resulting solution, a solution of Zn(OAc)₂•2H₂O (10 mg, 45.6 μmol) in MeOH (2 ml) and 3 drops of triethylamine were added and the resulting solution was refluxed for 30 min. After cooling, the solution was washed with water (50 ml x 2 times), dried over Na₂SO₄, and the solvent was evaporated. Residual solid was dissolved in a small amount of CH₂Cl₂, and passed through a short silica gel column (Wako gel C-300; eluent: CH₂Cl₂). Purified porphyrin dimer was recrystallized from CH₂Cl₂/MeOH, giving porphyrin dimer **6** (28.6 mg, 57%). No starting material was recovered in this method.

¹H NMR (600 MHz, CDCl₃) δ = 8.64 (br, 4H, β), 8.22 (m, 4H, Aryl), 8.14-8.03 (m, 12H, β and Aryl), 7.86 (m, 4H, Aryl), 7.67 (br t, 8H, Aryl), 6.52 (br, 8H, bicyclo -CH=CH-), 3.48 (br, 4H, bicyclo ⁱC-H), 3.40 (br, 4H, bicyclo ⁱC-H), 1.70 (s, 18H, *tert*-Bu), 1.54 (s, 36H, *tert*-Bu), and 1.6-1.5 (br, 16H, bicyclo -CH₂-CH₂-); ¹³C NMR (150 MHz, CDCl₃) δ = 154.3, 152.3(2C), 151.8(2C), 150.8, 149.8(2C), 143.6, 143.4, 141.6, 140.8, 137.0, 133.6(2C), 133.4, 131.3, 123.3(2C), 120.3, 119.5, 38.0, 37.6, 35.2, 34.9, 32.0, 31.8, 27.0, and 26.9; HR ESI-TOF Mass (positive mode) *m/z* = 1850.8057 (calc. for C₁₂₄H₁₁₈N₈Zn₂ = 1850.8059 [M]⁺); UV/Vis (in CH₂Cl₂): λ_{max} [nm] (ε [M⁻¹cm⁻¹]) = 420 (279000), 458 (295000), and 559 (76000).; Fluorescence emission (excited at 421 nm in CH₂Cl₂) λ_{max} [nm] = 656, Φ_f = 0.030.

Meso-meso linked dibenzoporphyrin dimer **8**

Meso-meso linked porphyrin dimer **6** (20 mg, 10.8 μmol) was placed in a glass tube oven, and heated to 210 °C under reduced pressure (0.1 mmHg) for 30 minutes, to give *meso-meso* linked dibenzoporphyrin dimer **8** quantitatively.

¹H NMR (600 MHz, CDCl₃) δ = 8.49 (d, *J* = 4.6 Hz, 4H, β), 8.22 (d, *J* = 7.7 Hz, 4H, Aryl), 8.13 (d, *J* = 4.6 Hz, 4H, β), 8.08 (d, *J* = 8.3 Hz, 8H, Aryl), 7.98 (d, *J* = 7.7 Hz, 4H, Aryl), 7.73 (d, *J* = 8.2 Hz, 8H, Aryl), 7.44 (t, *J* = 7.8 Hz, 4H, benzo), 7.41 (t, *J* = 6.9 Hz, 4H, benzo), 7.30 (d, *J* = 8.2 Hz, 4H, benzo), 7.23 (d, *J* = 8.3 Hz, 4H, benzo), 1.75 (s, 18H, *tert*-Bu), and 1.52 (s, 36H, *tert*-Bu); ¹³C NMR (150 MHz, CDCl₃) δ = 152.8, 152.6, 151.4, 150.8, 147.6, 144.4, 141.3, 140.5, 140.3, 140.1, 133.3, 133.0, 130.3, 126.2(2C), 125.9, 125.7, 125.0, 124.7, 122.3, 119.5(2C), 116.4, 35.4, 35.1, 32.1, and 31.8;

HR ESI-TOF Mass (positive mode) $m/z = 1738.6804$ (calc. for $C_{116}H_{102}N_8Zn_2 = 1738.6803 [M]^+$); UV/Vis (in CH_2Cl_2): λ_{max} [nm] ($\epsilon [M^{-1}cm^{-1}]$) = 434 (232000), 470 (188000), 578 (44000), and 619 (45000); Fluorescence emission (excited at 436 nm in CH_2Cl_2) λ_{max} [nm] = 628, and 684, $\Phi_f = 0.026$.

Meso-meso, β - β , β - β triply linked porphyrin dimer 9

A solution of *meso-meso* linked dibenzoporphyrin dimer **8** (15 mg, 8.63 μ mol) in distilled toluene (12 ml) was bubbled with Ar gas for 10 min, and heated to 50 °C with an oil bath. DDQ (9.8 mg, 43.2 μ mol) was added to the solution, then $Sc(OTf)_3$ (21.2 mg, 43.1 μ mol) was added. The reaction mixture was heated to 75 °C and stirred for 1 h under Ar. The reaction was quenched with 1 ml of THF (including no stabilizer), 1 drop of butylamine was added, and the solution was stirred for 1 h at room temperature. Resulting solution was passed through a short alumina column with THF (including no stabilizer). The solvent was removed by a rotary evaporator. After recrystallization from THF/MeOH, *meso-meso*, β - β , β - β triply linked porphyrin dimer **9** was obtained as dark green solids (10.6 mg, 71%).

1H NMR (600 MHz, CD_2Cl_2 containing 1% butylamine) $\delta = 7.71$ (d, $J = 7.9$ Hz, 4H, Aryl), 7.67 (d, $J = 8.3$ Hz, 4H, Aryl), 7.59 (br, 16H, Aryl), 6.94 (t, $J = 6.9$ Hz, 4H, benzo), 6.91 (t, $J = 6.8$ Hz, 4H, benzo), 6.53 (s, 4H, β), 6.32 (d, $J = 7.8$ Hz, 4H, benzo), 6.29 (d, $J = 7.7$ Hz, 4H, benzo), 1.56 (s, 18H, Ar- *t*Bu), and 1.51 (s, 36H, Ar- *t*Bu); HR ESI-TOF Mass (positive mode) $m/z = 1734.6496$ (calc. for $(C_{116}H_{98}N_8Zn_2)_2 = 1734.6497 [2M]^{2+}$); UV/Vis (in CH_2Cl_2 containing 1% butylamine: λ_{max} [nm] ($\epsilon [M^{-1}cm^{-1}]$) = 436 (178000), 579 (118000), 632 (126000), 676 (117000), and 1051 (27000).

Due to the low solubility of **9**, its clear ^{13}C NMR spectrum was not recorded.

Fig. S1. UV-Vis absorption spectra of **4** and **6** in CH₂Cl₂.

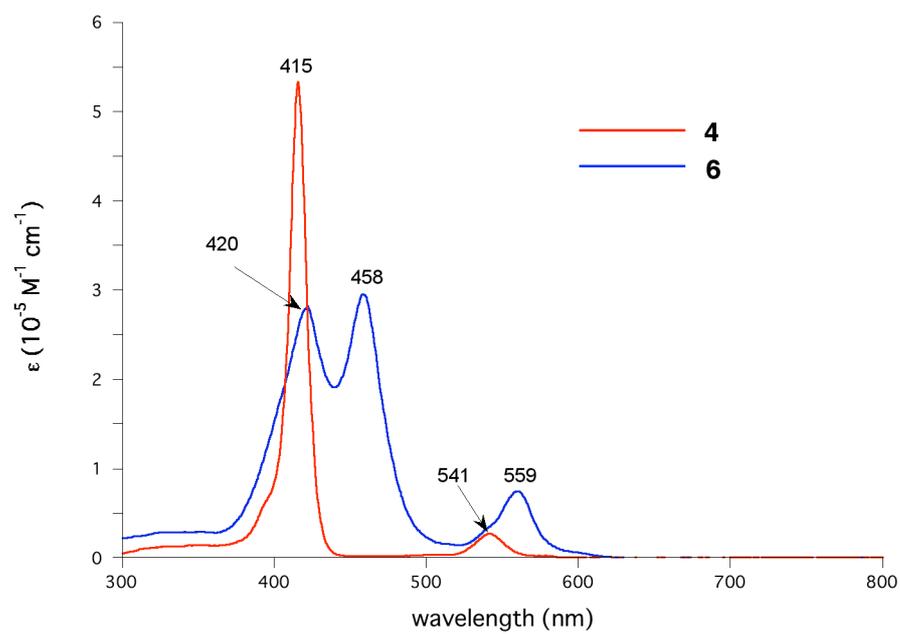


Fig. S2. Fluorescence spectra of 4, 6 (upper figure), and 6, 8 (lower figure) in CH₂Cl₂.

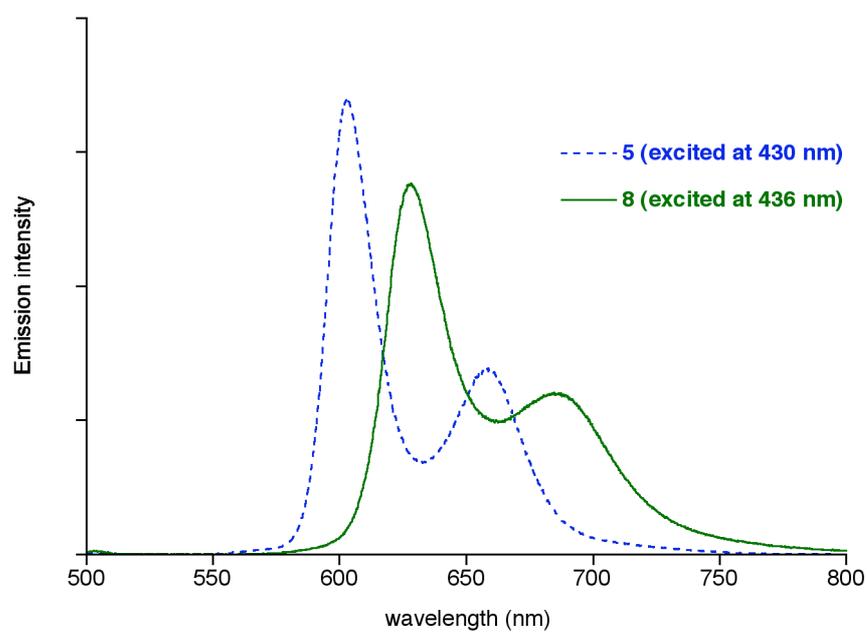
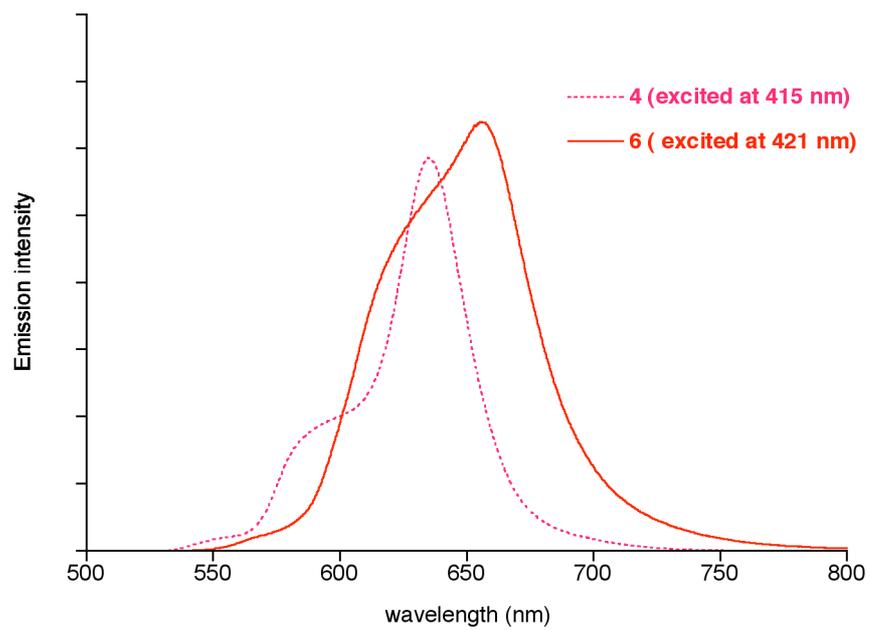
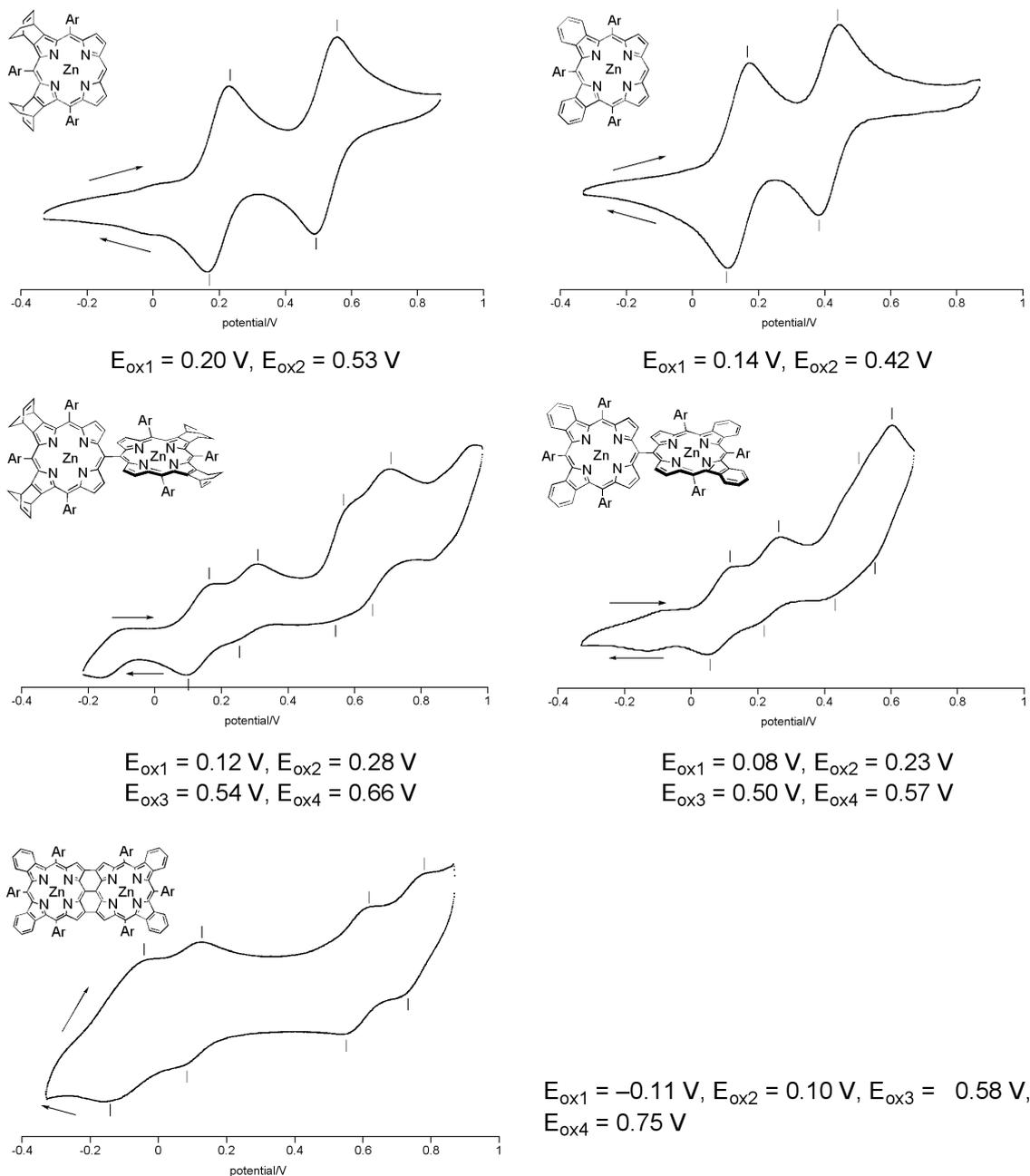


Fig. S3. Cyclic voltammograms of **4**, **5**, **6**, **8**, and **9**. (versus ferrocene/ferrocenium cation)



These measurements were performed using a platinum working electrode, a platinum wire counter electrode, and Ag/0.01 M AgNO₃ reference electrode in dichloromethane solution containing 0.1 M *n*-Bu₄NBF₄ as a supporting electrolyte.

Measurement of two-photon absorption cross-section ($\sigma^{(2)}$).

The TPA spectra were measured from 1180 to 1420 nm by using the open-aperture Z-scan method¹ with ~130 fs pulses from an optical parametric amplifier (*Light Conversion, TOPAS*) operating at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (*Spectra-Physics, Hurricane*) (Figure S4). The laser beam was divided into two parts. One was monitored by a Ge/PN photo-diode (*New Focus*) as intensity reference and the other was used for transmittance measurement. After passing through an $f = 10$ cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (z-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell is 1 mm. The transmitted laser beam from the sample cell was then detected by the same photo-diode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0 ranged 0.20 to 0.25×10^{15} Wm⁻². Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open-aperture traces with the following equation:¹

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)}, \quad (1)$$

where α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam.

After obtaining the nonlinear absorption coefficient β , the TPA cross-section $\sigma^{(2)}$ of one solute molecule (in units of 1 GM = cm⁴·s/photon·molecule) can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{h\nu}, \quad (2)$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.

References

1. M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. G. Hagan, E. W. van Stryland, *IEEE J. Quant. Electr.* 1990, **26**, 760.

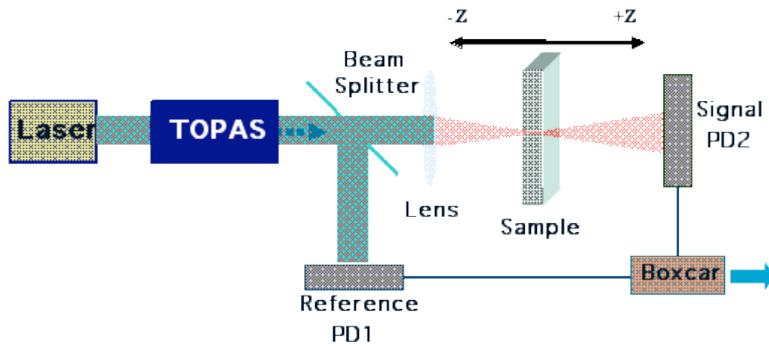


Figure S4. Schematic diagram of open-aperture Z-scan experimental setup.

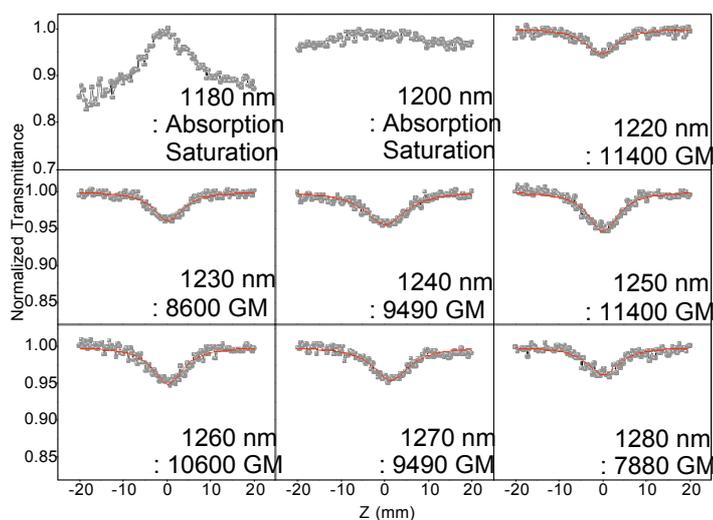


Figure S5. Open-aperture Z-scan traces (circles) of **7** in CH_2Cl_2 . The sample concentration is 0.10 mM. The peak irradiance at the focal point is $25 \text{ GW}/\text{cm}^2$. The solid lines are the best fitted curves of experimental data.

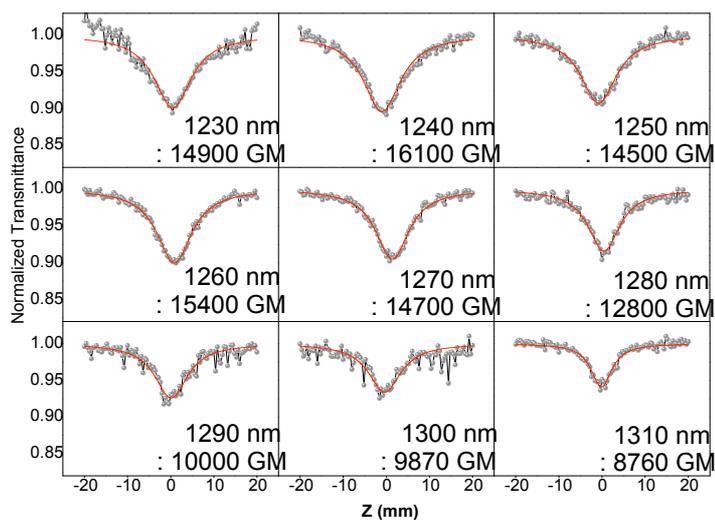


Figure S6. Open-aperture Z-scan traces (circles) of **9** in CH_2Cl_2 . The sample concentration is 0.17 mM. The peak irradiance at the focal point is $20 \text{ GW}/\text{cm}^2$. The solid lines are the best fitted curves of experimental data.