Supplementary Information for

Synthesis, Solvent-dependent Emission and Two-photon

Absorption of a Triangular -[D-π-A]₃- Macrocycle

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I. Methods and Materials

All chemicals were used as received unless otherwise indicated. Oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using the standard Schlenk technique. Reagent-grade tetrahydrofuran and toluene were distilled over sodium, while triethylamine and chloroform were distilled over CaH₂ prior to use. NMR spectra were recorded on a Mercury plus 300 (300 MHz), Bruker ARX 400 (400 MHz), Bruker ARX 500 (500 MHz) and Bruker AVANCE III 500 (500 MHz) instrument, using CDCl₃ or *d*-toluene as the solvent. Chemical shifts were reported in parts per million (ppm) relative to TMS (0 ppm) or toluene-*d*₈ (7.09 ppm) and CDCl₃ (77.0 ppm) or toluene-*d*₈ (137.0 ppm) for ¹H and ¹³C NMR spectra. MALDI-TOF was recorded on a Bruker Daltonics Inc. BIFLEX III mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer, and steady-state linear-excitation fluorescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. Fluorescence quantum yields were determined with 9,10-dibenzanthracene in ethanol ($\Phi_R = 0.95$; $\lambda_{ex} = 372$ nm) as the standard.

II. Synthetic Procedures and Characterization Data

General procedures of Sonogashira reaction A Schlenk tube containing aryl iodide, aryl acetylene, $Pd(PPh_3)_4$, and CuI was evacuated and back-filled with N₂ for three times. Degassed solvents of mixed Et₃N and THF were added via a syringe under N₂ atmosphere. The tube was then sealed and the reaction mixture was heated with stirring for 8~48 hours. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and diluted with dichloromethane, washed with saturated aq. NH₄Cl and brine sequentially, and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified with silica gel column chromatography to afford the products.



Reagents and conditions: a) ethylene glycol, toluene, 90 °C; b) Pd(PPh₃)₂Cl₂, Cul, Et₃N, THF, 2-methylbut-3yn-2-ol, 70 °C; c) KOH, THF, 70 °C; d) Pd(PPh₃)₄, Cul, Et₃N, THF, 45 °C; e) KOH, toluene, 110 °C

Scheme S1. Syntheses of oligomers 1 and 2



Compound **1a** was synthesized according to the procedures previously reported in the literature,¹ with some modifications, and toluene was used as the solvent.



1b. A tube containing **1a** (15.0 g, 33 mmol), $Pd(PPh_3)_2Cl_2$ (232 mg, 0.33 mmol), and CuI (64 mg, 0.33 mmol) was evacuated and back-filled with nitrogen for three times. Degassed 2-methylbut-3-yn-2-ol (10.5 mL, 99 mmol), Et_3N (70 mL) and THF (80 ml) were added to the tube under nitrogen atmosphere. The reaction mixture was stirred at 70 °C for 12 h and then worked up according to the general procedure. The crude product was purified with silica gel

column chromatography eluted with dichloromethane/ethyl acetate (DCM/EA=5/1, v/v) to afford the product (12.6 g, 88%); TLC (DCM/EA, 5/1) $R_f = 0.50$. ¹H NMR (300 MHz, CDCl₃): δ 7.94 (2H, d, J = 1.8 Hz), 7.69 (2H, d, J = 8.1 Hz), 7.46 (2H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.1$ Hz), 4.19 (4H, t), 3.62 (4H, t), 2.10 (2H, s), 1.65 (12H, s). ¹³C NMR (75 MHz, CDCl₃): δ 132.8, 132.5, 131.9, 127.2, 126.3, 124.5, 94.8, 92.3, 81.6, 65.6, 61.4, 31.4.



1c & 1d. A mixture of **1b** (6.0 g, 13 mmol) and KOH (730 mg, 13 mmol) in THF (60 ml) was heated at 70 °C with stirring under N₂ atmosphere. TLC was performed every 5 min to monitor the reaction until the diethynyl product appeared. After cooling to r.t., the reaction mixture was washed with water, aq. NH₄Cl and brine, and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure, and the residue was purified with silica gel column chromatography using PE/DCM (2/1, v/v) to elute **1c** (1.2 g, 26%) and then DCM/EA (10/1, v/v) to elute **1d** (2.2 g, 42%). ¹H NMR (300 MHz, CDCl₃) of **1c**: δ 8.02 (2H, d, *J* = 1.5 Hz), 7.72 (2H, d, *J* = 8.1 Hz), 7.55 (2H, dd, *J* = 1.5 Hz, *J* = 8.1 Hz), 4.21 (4H, m), 3.64 (4H, m), 3.15 (2H, s). **1d**: δ 8.02 (1H, d, *J* = 1.5 Hz), 7.94 (1H, d, *J* = 1.5 Hz), 7.72 (1H, d, *J* = 8.4 Hz), 7.69 (1H, d, *J* = 7.8 Hz), 7.54 (1H, dd, *J* = 1.5 Hz, *J* = 7.8 Hz), 7.47 (1H, dd, *J* = 1.5 Hz, *J* = 8.4 Hz), 4.19 (4H, m), 3.63 (4H, m), 3.15 (1H, s), 2.08 (1H, s), 1.65 (6H, s). ¹³C NMR (75 MHz, CDCl₃) of **1c**: δ 133.5, 132.5, 132.4, 127.7, 126.4, 123.9, 92.2, 83.0, 78.3, 61.3. **1d**: δ 133.4, 132.8, 132.5, 132.4, 127.2, 126.35, 126.30, 124.5, 123.8, 95.0, 92.19, 92.17, 83.0, 81.5, 78.27, 78.24, 65.5, 61.3, 31.4.



1e. A mixture of 2,7-diiodophenanthrene-9,10-dione (8.0 g, 17 mmol),² tetrabutylammonium bromide (1.7 g, 5.2 mmol), sodium hydrosulfite (18.0 g, 102 mmol), H_2O (80 ml) and THF (80 ml)

was allowed to react at room temperature for 15 min. After a quickly extraction, solvent of the organic phase was evaporated under reduced pressure and the residue was added with 1-bromo-2-octyldodecane (9.2 g, 37 mmol), K₂CO₃ (12.0 g, 85 mmol) and DMF (100 ml). After heating at 100 °C for 6 h under N₂ atmosphere the reaction mixture was dissolved in PE and washed with 2M HCl and brine sequentially, and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified with silica gel column chromatography using PE as the eluent to afford **1e** (13.3 g, 75%) ¹H NMR (300 MHz, CDCl₃) of **1e**: δ 8.59 (2H, d, *J* = 1.5 Hz), 8.26 (2H, d, *J* = 8.7 Hz), 7.84 (2H, dd, *J* ₁ = 1.5 Hz, *J* ₂ = 8.7 Hz), 4.04 (4H, d), 2.10 (2H, m), 1.60~1.26 (64H, m), 0.88(12H, m) ¹³C NMR (75 MHz, CDCl₃): δ 142.8, 134.5, 131.5, 131.4, 127.2, 124.0, 108.4, 93.2, 48.8, 40.0, 39.3, 32.02, 31.99, 31.6, 30.3, 29.9, 29.84, 29.79, 29.73, 29.43, 29.40, 27.0, 22.7, 14.2.



1. A mixture of **1c** (447 mg, 1.3 mmol), **1e** (8.0 g, 7.8 mmol), Pd(PPh₃)₄ (35 mg, 0.03 mmol), CuI (6 mg, 0.03 mmol), Et₃N (10 ml), and THF (10 ml) was applied to the general Sonogashira reaction procedure and reacted at 45 °C for 10 h. The crude product was purified with silica gel column chromatography and eluted with PE/CH₂Cl₂ (4/1, v/v) to afford the product **1f** (1.4 g, 52%). TLC (PE/CH₂Cl₂, 3/1) R_f = 0.40. ¹H NMR (300 MHz, CDCl₃): δ 8.61 (2H, d, J = 2.1 Hz), 8.54 (2H, d, J = 8.7 Hz), 8.44 (2H, d, J = 1.8 Hz), 8.30 (2H, d, J = 8.7 Hz), 8.18 (2H, d, J = 0.9 Hz), 7.85 (2H, dd, J_1 = 2.1Hz, J_2 = 8.7 Hz), 7.79 (2H, d, J = 8.1 Hz), 7.76 (2H, dd, J_1 = 1.8 Hz, J_2 = 8.7 Hz), 7.65 (2H, dd, J_1 = 0.9Hz, J_2 = 8.1 Hz), 4.24 (4H, m), 4.08 (8H, m), 3.69 (4H, m), 1.92 (4H, m), 1.20~1.62 (128H, m), 0.87 (12H, t), 0.81 (12H, t). ¹³C NMR (100 MHz, CDCl₃): δ 143.5, 142.6, 134.3, 133.1, 132.7, 132.0, 131.6, 131.4, 129.6, 128.7, 127.8, 127.20, 127.16, 126.5, 126.0, 125.1, 124.4, 122.6, 121.6, 93.2, 92.4, 90.9, 89.7, 61.4, 39.2, 31.95, 31.91, 31.45, 31.44, 30.2, 29.77, 29.71, 29.42, 29.40, 29.39, 29.36, 27.00, 26.97, 22.71, 22.67, 14.13, 14.10.



2'. A mixture of **1d** (2.5 g, 6.2 mmol), **1e** (3.2 g, 3.1 mmol), Pd(PPh₃)₄ (116 mg, 0.1 mmol), CuI (19 mg, 0.1 mmol), Et₃N (10 ml), and THF (10 ml) was applied to the general procedure and reacted at 45 °C for 14 h. The crude product was purified with silica gel column chromatography and eluted with CH₂Cl₂ /EA (3/1, v/v) to afford the product **1g** (3.8 g, 83%). TLC (CH₂Cl₂ /EA, 3/1) $R_f = 0.20$. ¹H NMR (300 MHz, CDCl₃): δ 8.59 (2H, d, J = 8.7 Hz), 8.46 (2H, d, J = 1.8 Hz), 8.13 (2H, d, J = 1.2 Hz), 8.02 (2H, d, J = 1.5 Hz), 7.78 (2H, d, J = 8.1 Hz), 7.77 (2H, dd, $J_1 = 1.8$ Hz, $J_2 = 8.7$ Hz), 7.72 (2H, d, J = 8.1 Hz), 7.64 (2H, dd, $J_1 = 1.2$ Hz, $J_2 = 8.1$ Hz), 7.49 (2H, dd, $J_1 = 1.5$ Hz, $J_2 = 8.1$ Hz), 4.22 (8H, m), 4.12 (4H, d), 3.68 (8H, m), 2.09 (2H, s), 1.97 (2H, m), 1.67 (12H, s), 1.22-1.60 (64H, m), 0.81 (12H, t). ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 132.93, 132.90, 132.6, 132.5, 131.98, 131.93, 129.9, 128.6, 127.8, 127.2, 127.1, 126.4, 126.3, 125.9, 125.1, 124.5, 123.0, 121.5, 94.8, 92.31, 92.29, 91.0, 89.7, 81.6, 65.6, 61.4, 39.2, 31.9, 31.4, 30.2, 29.69, 29.68, 29.65, 29.64, 29.36, 29.31, 26.9, 22.6, 14.1.



2. A mixture of **1g** (3.1 g, 2.0 mmol) and KOH (1.1 g, 20 mmol) in toluene (30 ml) was heated at 110 °C under N₂ atmosphere with stirring for 2 h. After cooling to r.t., the reaction mixture was washed with 2M HCl and brine sequentially, and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduce pressure and the residue was purified with silica gel column chromatography and eluted with PE/DCM (2/1, v/v) to afford **1h** (2.5 g, 86%) TLC (PE/CH₂Cl₂, 2/1) $R_f = 0.3$. ¹H NMR (300 MHz, CDCl₃): δ 8.59 (2H, d, J = 8.7 Hz), 8.46 (2H, d, J = 1.5 Hz), 8.13 (2H, s), 8.10 (2H, s), 7.77 (2H, dd, $J_1 = 1.5$ Hz $J_2 = 8.7$ Hz), 7.76 (2H, d, J = 6.9 Hz), 7.73

(2H, d, J = 6.9 Hz), 7.64 (2H, d, $J_2 = 6.9$ Hz), 7.56 (2H, d, J = 6.9 Hz), 4.22 (8H, m), 4.13 (4H, d), 3.67 (8H, m), 3.17 (2H, s), 1.98 (2H, m), 1.22-1.60 (64H, m), 0.81 (12H, t). ¹³C NMR (100 MHz, CDCl₃): δ 143.5, 133.7, 133.1, 132.7, 132.6, 132.5, 132.2, 130.0, 128.7, 128.0, 127.8, 127.2, 126.6, 126.1, 125.2, 124.0, 123.1, 121.6, 92.4, 92.3, 91.2, 89.8, 83.2, 78.3, 61.4, 39.3, 32.0, 31.5, 30.3, 29.81, 29.79, 29.76, 29.44, 29.43, 27.0, 22.7, 14.2.



MC3. A mixture of 1 (293 mg, 0.14 mmol), 2 (200 mg, 0.14 mmol), Pd(PPh₃)₄ (80 mg, 0.07 mmol), CuI (13 mg, 0.07 mmol), Et₃N (300 ml) and THF (300 ml) was allowed to react according to the general procedure at 45 °C for 48 hrs. The crude product was further purified by column chromatography on silica gel with PE/CH₂Cl₂ (1/1, v/v) as the eluent to afford the product (250 mg, 55%). TLC (PE/CH₂Cl₂, 1/1) R_f = 0.50. ¹H NMR (400 MHz, CDCl₃): δ 8.63 (6H, d, J = 8.4 Hz), 8.48 (6H, s), 8.24 (6H, s), 7.83 (6H, d, J = 8.4 Hz), 7.80 (6H, d, J = 7.6 Hz), 7.67 (6H, d, J= 7.6 Hz), 4.26 (12H, m), 4.15 (12H, d), 3.72 (12H, m), 2.00 (6H, m), 1.98~1.21 (192H, m), 0.83 (36H, t). ¹³C NMR (100 MHz, CDCl₃): δ 143.5, 133.1, 132.7, 131.8, 130.0, 128.7, 127.9, 127.5, 126.5, 126.0, 125.2, 123.0, 121.6, 92.5, 91.2, 89.8, 61.5, 39.4, 32.0, 31.9, 31.6, 30.3, 30.0, 29.79, 29.78, 29.76, 29.73, 29.44, 29.39, 27.1, 22.7, 14.1. Calc. for C₂₂₈H₃₀₆O₁₈: C, 82.12; H, 9.25. Found: C, 82.05; H, 9.21.



MC2. In a round-bottom flask, **MC3** (100 mg, 0.03 mmol) was dissolved in a mixture of CHCl₃ (20 ml), H₂O (4 ml), CH₃CN (4 ml) and CF₃CO₂H (10 ml). The mixture was heated at reflux for 2 days. After cooling to rt, it was washed with water and aq. NaHCO₃. Then the organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified with silica gel column chromatography and eluted with CHCl₃/EtOH (50/1, v/v) to afford the product (87 mg, 95%). TLC (CHCl₃/EtOH, 50/1) R_f = 0.20. ¹H NMR (300 MHz, CDCl₃): δ 8.25 (6H, s), 8.03 (6H, d, *J* = 8.4 Hz), 7.99 (6H, s), 7.98 (6H, d, *J* = 8.1 Hz), 7.52 (6H, d, *J* = 8.4 Hz), 7.46 (6H, d, *J* = 8.1 Hz), 4.08 (12H, d), 1.98 (6H, m), 1.69~1.23 (192H, m), 0.83 (36H, t). ¹H NMR (500 MHz, toluene-*d*₈): δ 8.83 (6H, s), 8.39 (6H, d, *J* = 8.5 Hz), 8.09 (6H, s), 8.03 (6H, d, *J* = 8.5 Hz), 7.47 (6H, d, *J* = 8.0 Hz), 4.33 (12H, d), 2.18 (6H, m), 1.87~1.28 (192H, m), 0.89 (36H, m). ¹³C NMR (125 MHz, toluene-*d*₈): δ 178.0, 143.7, 134.9, 131.9, 131.1, 130.6, 130.2, 130.0, 128.7, 126.8, 126.7, 123.1, 121.6, 94.9, 89.9, 77.5, 39.8, 32.0, 31.80, 31.74, 30.25, 30.24, 29.69, 29.63, 29.58, 29.3, 29.2, 27.3, 22.44, 22.41, 13.47, 13.46. MALDI-TOF MS: Calc. for C₂₁₆H₂₈₂O₁₂: 3070.2 (m/z). Found: 3093.2 (M+Na⁺).



MC1. A Schlenk tube containing the MC2 (50 mg, 0.02 mmol) and diaminomaleonitrile (16 mg, 0.15 mmol) was evacuated and back-filled with N_2 for three times. Then, a mixture of CF_3CO_2H (5 ml) and chloroform (5 ml) was added via a syringe under N2 atmosphere. The tube was then sealed and the reaction mixture was heated at 70 °C with stirring for 3 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and washed with water and NaHCO₃ to pH=7, and then dried over anhydrous Na₂SO₄. The solvent was evaporated and the residue was purified with silica gel column chromatography and eluted with PE/toluene = (1/1, 1)v/v) to afford product MC1 (43 mg, 80%). TLC (PE/ toluene, 1/1) $R_f = 0.50$. ¹H NMR (300 MHz, CDCl₃): δ 8.77 (6H, s), 8.45 (6H, s), 8.34 (6H, s), 8.14 (6H, s), 7.76 (6H, s), 7.61 (6H, s), 4.08 (12H, d), 2.01 (6H, m), 1.64 ~ 1.21 (192H, m), 0.83 (36H, t). ¹H NMR (500 MHz, toluene- d_8): δ 8.91 (6H, s), 8.87 (6H, d, J = 8.5 Hz), 8.72 (6H, s), 8.44 (6H, d, J = 8.5 Hz), 7.89 (12H, d, J = 8.5 Hz), 4.38 (12H, d), 2.12 (6H, m), 1.93 ~ 1.30 (192H, m), 0.90 (36H, m). ¹³C NMR (125 MHz, toluene-d₈): δ 143.8, 141.5, 132.1, 131.4, 130.6, 128.8, 127.8, 126.8, 126.7, 126.3, 123.2, 121.6, 113.3, 94.4, 90.1, 77.6, 39.8, 32.0, 31.9, 31.8, 30.3, 29.8, 29.6, 29.4, 29.2, 27.3, 22.5, 22.4, 13.51, 13.47. MALDI-TOF MS: Calc. for C₂₂₈H₂₈₂N₁₂O₆: 3286.2 (m/z). Found: 3286.2 (m/z). Calc. for C₂₂₈H₂₈₂N₁₂O₆: C, 83.32; H, 8.65, N, 5.11. Found: C, 83.26; H, 8.67, N, 5.03.

III. DFT Calculations of MC1

Density functional theory (DFT) calculations were carried out using Gaussian09 program.³ Molecular geometry was optimized using B3LYP hybrid functional 9 with 6-31G basis set, and visualized by Chem3D program. The polarized continuum model method (PCM) with toluene as the solvent was used to calculate the electronic structures in solution. In these calculations, side chains are shortened to methoxyl groups.



Figure S1. Selected MOs of ground-state **MC1** with energy levels (eV) calculated in the optimized geometry in toluene solution.

IV. Concentration-dependent Absorptions and Self-association Constants

By fitting the extinction coefficient changes as a function of concentration to an isodesmic (i.e., equal *K*) self-association model at the longer wavelength, the aggregation constants (K_{agg}) were obtained for **MC1**. The apparent extinction coefficients measured in the concentration-dependent absorption spectra were fitted by the nonlinear regression analyses to the following expression,^{4,5}

$$\varepsilon = (2K_{\text{agg}}c + 1 - (4K_{\text{agg}}c + 1)^{0.5}) / 2 / K_{\text{agg}}^2 / c^2 \times (\varepsilon_{\text{m}} - \varepsilon_{\text{a}}) + \varepsilon_{\text{agg}}^2 / c^2 \times (\varepsilon_{\text{m}} - \varepsilon_{\text{a}}) + \varepsilon_{\text{a}}^2 / c^2 \times (\varepsilon_{\text{m}} - \varepsilon_{\text{m}}) + \varepsilon_{\text{a}}^2 / c^2 \times (\varepsilon_{\text{m}} - \varepsilon_{\text{m}}) + \varepsilon_{\text{m}}^2 / c^2$$

where ε is the apparent extinction coefficient; $\varepsilon_{\rm m}$ and $\varepsilon_{\rm a}$ are the extinction coefficient of the monomer and aggregated species, respectively; $K_{\rm agg}$ is the association constant, and *c* is the total concentration of the compounds.



Figure S2. Concentration-dependence of absorption spectra of **MC1** in (a) chloroform, (b) chlorobenzene and (c) toluene (insets showing the fitting of absorption data).



Figure S3. Concentration-dependent emission spectra of **MC1** in chloroform (arrow indicates the direction of intensity change at increased concentration).

V. Nonlinear Optical Characterizations

Open-aperture Z-scan measurements were conducted with a femtosecond laser system composed of a Spectra-Physics TOPAS optical parametric amplifier (OPA) pumped by a Spfire ACE-F-1KXP Ti:sapphire amplifier (~120 fs, 1KHz) as the light source. With the Z-scan technique,⁶ the 2PA cross section experiments were carried out at a number of wavelengths in the range of 670-800 nm. To obtain these wavelengths, the second harmonic of the signal wavelength was used. The spatial profile of the laser beam was a nearly Gaussian distribution. The beam was focused by a plano-convex lens with a focal length of 200 mm. by fitting the T-(z) curve using the 2PA theoretical equation:⁷

$$T(z) = \frac{1}{q_0 \sqrt{\pi}} \int_{-\infty}^{+\infty} l n \left(1 + q_0 e^{-\delta^2} \right) d\delta, \quad q_0 = \frac{I_0 \beta L w_0^2}{w^2(z)} \tag{1}$$

where T(z) is the sample transmittance, I_0 was the laser peak power density at z = 0, L was the optical distance, w_z and w_0 were the laser beam areas at z and z = 0, being $w^2(z)/w_0^2 = 1 + z^2/z_0^2$, where z_0 is the Rayleigh distance of the beam. The two-photon absorption coefficient β was obtained. The absolute 2PA cross sections were calculated according to Eq. (2):

$$\sigma_{2PA} = \frac{\beta}{N_0} (hv) \tag{2}$$

Where hv is one photon energy; N_0 is the concentration of absorbing species/cm³.

Two-photon excited fluorescence (2PEF) spectra were recorded on SD2000 spectrometer (Ocean Optical), excited by a mode-locked Ti-sapphire femtosecond laser (Mai Tai HP, Spectra

Physics) with pulse width and repetition rate of 100 fs and 82 MHz. The fluorescence emission curves were detected at 2.0×10^{-4} M from 720 nm to 870 nm.



Figure S4. Emission spectra of MC1 in toluene upon excitation at indicated wavelengths

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Copies of ¹H and ¹³C NMR Spectra













Copies of ¹H and ¹³C NMR Spectra in toluene- d_8 at 80 °C





