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ELECTRONIC SUPPLEMENTARY INFORMATION

Tetracene cyclophanes showing the controlled Intramolecular singlet fission by through-space orientations

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Experimental Section

General and Materials.

All reagents and solvents were purchased from FUJIFILM Wako Pure Chemical Corporation, Tokyo Kasei, Kanto Chemical, Merck, or Fluorochem. All reactions were carried out under nitrogen atmosphere unless otherwise noted. All reactions that require heating were conducted with an oil bath as the heat source. Flash silica gel column chromatography was conducted with a Biotage Isolera Flash system using SHOKO-scientific Purif-Pack-EX cartridges. Recycling preparative gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LaboACE. ^{1}H NMR spectra were measured with a JEOL JNM-ECZ400S spectrometer and all chemical shifts are reported on the δ-scale in ppm relative to the signal of tetramethylsilane (TMS at 0.00) or residual solvent protons (THF at 1.72) as the internal standard. Coupling constants (J) are quoted in Hz and relative intensities are reported. Proton-decoupled ^{13}C NMR spectra were acquired on a JEOL JNM-ECZ400S spectrometer and all chemical shifts are expressed in ppm using solvent as the internal standard ($CDCl_3$ at 77.16). High-resolution electrospray ionization (ESI) mass spectra were measured with a Bruker Daltonics micrOTOF II.

Spectroscopic Measurements. UV-VIS absorption spectra were recorded on Agilent (8453) UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on JASCO (FP-8500) spectrofluorophotometer.

Nanosecond Laser Flash Photolysis. Nanosecond transient absorption measurements were carried out using Unisoku TSP-2000 flash spectrometer. Surelite-I Nd-YAG (Q-switched) laser was employed for the flash photo-irradiation. A 150 W Xenon arc and halogen lamps were used as the monitor light source.

Picosecond Transient Absorption Measurement.[1] Picosecond transient absorption measurement was conducted by the device made by Unisoku Co., Ltd. Measurement method used in this measurement was Randomly Interleaved Pulse Train Method.

Femtosecond Pump-Probe System. The transient absorption spectroscopy measurements were carried out using a home-made femtosecond pump−probe system. Yb laser (PH2-10W, Light Conversion) was used to create fundamental light pulses at 1030 nm ± 10 nm at a repetition rate of 1 kHz. The pulse energy was 200 mJ, and the

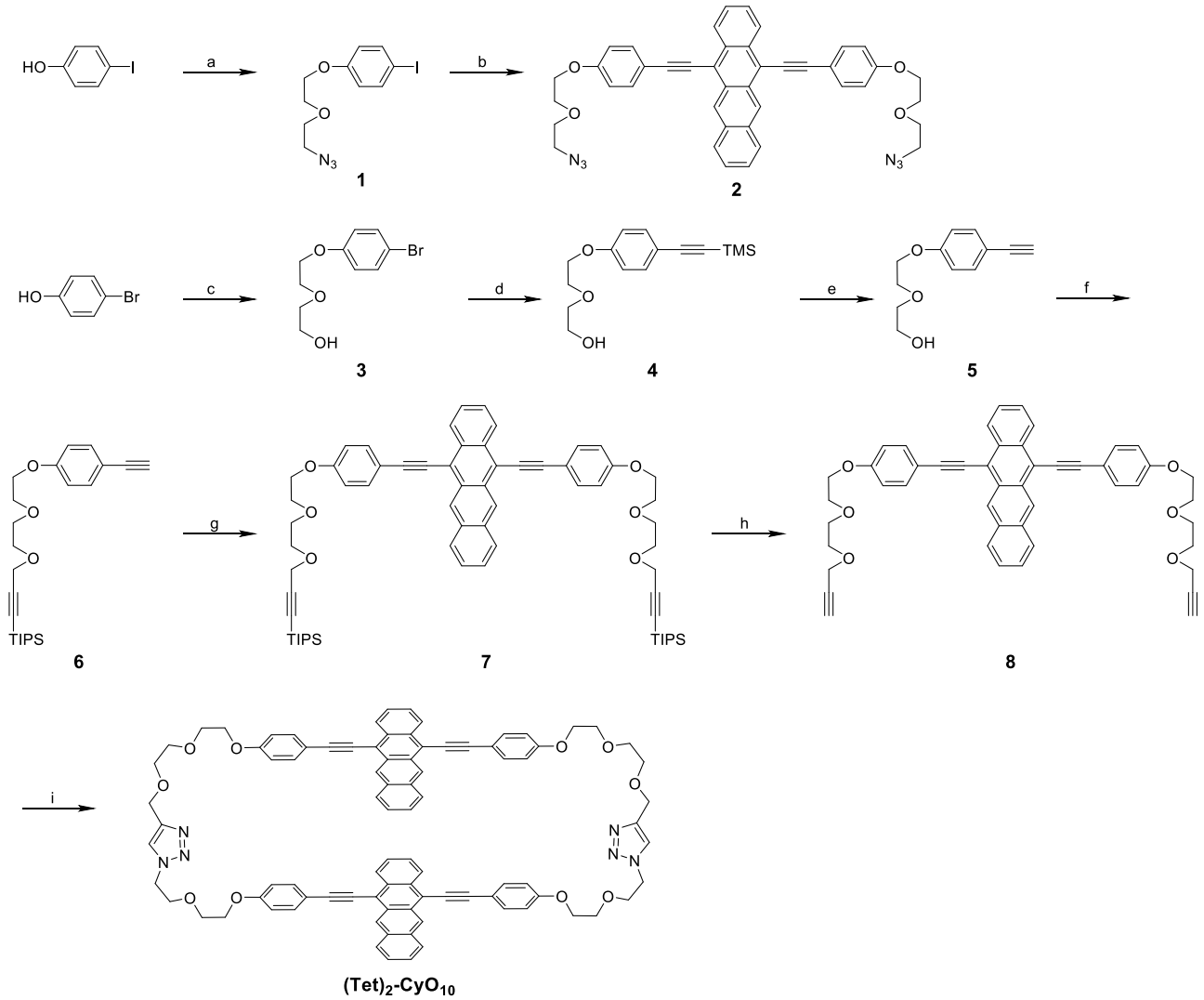
pulse duration was approximately 290 fs. 40 % of the fundamental beam was utilized to generate SHG (515 nm) and THG (343 nm) for sample pumping. The rest of the beam was delivered to a delay stage then attenuated appropriately and focused onto liquid D_2O or a sapphire crystal to generate a stable white light continuum for sample probing. The probe light was introduced to polychromators equipped with a CMOS array (USP-PSMM-PK120, Unisoku) for the visible part of the spectrum and an InGaAs diode array (USP-NIR-PDA256, Unisoku) for the near-infrared (NIR) wavelengths. The measurements were carried out by comparing responses with and without excitation using a chopper synchronized with the fundamental laser pulses. The spectra were typically acquired by recording 2000 shots, that is, averaging over 2 s. Excitation energies were sufficiently lowered to avoid multiple exciton generation; this was verified by recording a series of measurements with different excitation energies for the same sample. No excitation energy dependence of the response was observed.

Global and Target Analysis.[2] Global (singular value decomposition-based) and target (differential equation-based) analysis is accomplished using the Glotaran software package (http://glotaran.org).

Synthesis of $(Tet)_2$-CyO_{10}, $(Tet)_2$-CyO_{12}, and Tet-ref

The synthetic routes used to prepare compounds **$(Tet)_2$-CyO_{10}**, **$(Tet)_2$-CyO_{12}**, and **Tet-ref** are shown in the schemes S1, S2, and S3. 2-(2-Azidoethoxy)ethyl *p*-toluenesulfonate, 5,12-bis[(triisopropylsilyl)ethynyl]tetracene, 3-bromo-1-(triisopropylsilyl)-1-propyne, triethylene glycol *p*-toluenesulfonate, and 2-[2-(2-methoxyethoxy)ethoxy]ethyl *p*-toluenesulfonate were prepared according to reported procedures.[3-7]

Scheme S1 Synthesis of $(Tet)_2$-CyO_{10}



Conditions: (a) 2-(2-azidoethoxy)ethyl *p*-toluenesulfonate, K_2CO_3, DMF, 80 °C, 20 h; (b) 5,12-bis[(triisopropylsilyl)ethynyl]tetracene, tetrabutylammonium fluoride, $Pd(PPh_3)_4$, CuI, diisopropylamine, THF, 80 °C, 2 h; (c) 2-(2-chloroethoxy)ethanol, K_2CO_3, DMF,

110 °C, 24 h; (d) trimethylsilylacetylene, $Pd(PPh_3)_4$, CuI, triethylamine, THF, 80 °C, 24 h; (e) tetrabutylammonium fluoride, THF, r.t., 1 h; (f) 3-bromo-1-(triisopropylsilyl)-1-propyne, NaH, THF, 0 °C → r.t., 8 h; (g) i) *n*-butyllithium, THF, –78 °C → 0 °C, 40 min, ii) 5,12-naphthacenequinone, THF, r.t., 12 h, iii) H^+, iv) 10% aq. HCl, $SnCl_2$, r.t., 2 h; (h) tetrabutylammonium fluoride, THF, r.t., 1 h; (i) compound **2**, CuI, *N*,*N*-diisopropylethylamine, $CHCl_3$, 60 °C, 24 h.

Compound 1. A mixture of 4-iodophenol (1.28 g, 5.80 mmol), 2-(2-azidoethoxy)ethyl *p*-toluenesulfonate (1.83 g, 6.38 mmol), and K_2CO_3 (2.40 g, 17.4 mmol) in DMF (20 mL) was stirred at 80 °C for 20 h. The reaction mixture was then poured into ethyl acetate (100 mL) and washed with saturated aq. NH_4Cl (4 × 50 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 19:1 v/v to hexane/ethyl acetate = 4:1 v/v) to afford compound **1** (1.80 g, 5.40 mmol, 93%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 9.2 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 4.12–4.09 (m, 2H), 3.87–3.85 (m, 2H), 3.74 (t, J = 5.2 Hz, 2H), 3.42 (t, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 138.3, 117.2, 83.2, 70.4, 69.8, 67.6, 50.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{12}IN_3NaO_2$ 355.9866; Found 355.9874.

Compound 2. To a mixture of compound **1** (1.80 g, 5.40 mmol), 5,12-bis(triisopropylsilylethynyl)tetracene (1.45 g, 2.46 mmol), and triethylamine (20 mL) in THF (20 mL), a THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 6.15 mL, 6.15 mmol) was added and stirred under nitrogen atmosphere for 5 min. Then, $Pd(PPh_3)_2Cl_2$ (173 mg, 0.246 mmol) and CuI (46.8 mg, 0.246 mmol) were added and the reaction mixture was stirred under nitrogen atmosphere at 80 °C for 2 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (200 mL) and washed with 5% aq. HCl (2 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/ethyl acetate = 19:1 v/v) and recycling GPC (eluent: chloroform) to afford compound **2** (950 mg, 1.38 mmol, 56%) as a purple solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.25 (s, 2H), 8.66–8.63 (m, 2H), 8.11–8.08 (m, 2H), 7.76 (d, J = 8.8 Hz, 4H), 7.57–7.53 (m, 2H), 7.48–7.45 (m, 2H), 7.03 (d, J = 8.8 Hz, 4H),

4.23 (t, J = 4.8 Hz, 4H), 3.92 (t, J = 4.8 Hz, 4H), 3.78 (t, J = 5.2 Hz, 4H), 3.45 (t, J = 5.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.4, 132.2, 132.2, 130.0, 128.7, 127.6, 126.6, 126.2, 126.0, 118.4, 116.1, 115.0, 103.4, 86.3, 70.5, 69.8, 67.7, 50.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{34}N_6NaO_4$ 709.2534; Found 709.2520.

Compound 3. A mixture of 4-bromophenol (6.50 g, 37.5 mmol), 2-(2-chloroethoxy)ethanol (5.60 g, 45.0 mmol), and K_2CO_3 (20.7 g, 150 mmol) in DMF (40 mL) was stirred at 110 °C for 24 h. After cooling to the r.t., most of the DMF was evaporated under reduced pressure. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with saturated aq. NH_4Cl (4 × 100 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 v/v to hexane/ethyl acetate = 1:1 v/v) to afford compound **3** (6.48 g, 24.8 mmol, 66%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, J = 9.2 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 4.12–4.10 (m, 2H), 3.88–3.85 (m, 2H), 3.79–3.75 (m, 2H), 3.68–3.66 (m, 2H), 2.15 (t, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 132.2, 116.4, 113.1, 72.7, 69.4, 67.5, 61.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{13}BrNaO_3$ 282.9940; Found 282.9939.

Compound 4. A mixture of compound **3** (8.19 g, 31.4 mmol), trimethylsilylacetylene (15.4 g, 157 mmol), $Pd(PPh_3)_4$ (1.81 g, 1.57 mmol), CuI (299 mg, 1.57 mmol), and diisopropylamine (20 mL) in THF (20 mL) was stirred under nitrogen atmosphere at 80 °C for 24 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (200 mL) and washed with 5% aq. HCl (2 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 17:3 v/v) to afford compound **4** (6.99 g, 25.1 mmol, 80%) as a brown liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.13 (t, J = 4.4 Hz, 2H), 3.88–3.85 (m, 2H), 3.79–3.75 (m, 2H), 3.67 (t, J = 4.4 Hz, 2H), 2.14 (t, J = 6.0 Hz, 1H), 0.24 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 133.6, 115.6, 114.5, 105.1, 92.7, 72.7, 69.6, 67.4, 61.8, 0.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}NaO_3Si$ 301.1230; Found 301.1224.

Compound 5. A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 29.8 mL, 29.8 mmol) was added to a solution of compound **4** (6.90 g, 24.8 mmol) in THF (10 mL) and stirred at r.t. for 1 h. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with water (100 mL), and washed with saturated aq. NaCl (2 × 100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 17:3 v/v) to afford compound **5** (2.58 g, 12.5 mmol, 51 %) as a brown liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 9.2 Hz, 2H), 4.12–4.10 (m, 2H), 3.85–3.83 (m, 2H), 3.75 (t, J = 4.4 Hz, 2H), 3.65 (t, J = 4.4 Hz, 2H), 3.02 (s, 1H), 2.61 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 133.6, 114.6, 114.5, 83.6, 76.1, 72.7, 69.5, 67.4, 61.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}NaO_3$ 229.0835; Found 229.0829.

Compound 6. A THF solution (5 mL) of NaH (60% dispersion in paraffin liquid, 580 mg, 14.5 mmol) was added to a solution of compound **5** (2.49 g, 12.1 mmol) in THF (10 mL) at 0 °C. Then, 3-bromo-1-(triisopropylsilyl)-1-propyne (3.99 g, 14.5 mmol) was added to the mixture and stirred at r.t. for 8 h. After adding water (10 mL) dropwise to the reaction mixture, most of the THF was evaporated under reduced pressure. Ethyl acetate (100 mL) was added to the reaction mixture and washed with saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 4:1 v/v) to afford compound **6** (3.85 g, 9.61 mmol, 80%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.26, (s, 2H), 4.14 (t, J = 4.8 Hz, 2H), 3.87 (t, J = 4.8 Hz, 2H), 3.76 (s, 4H), 3.00 (s, 1H), 1.08–1.05 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 133.6, 114.6, 114.3, 103.2, 87.8, 83.7, 76.0, 70.7, 69.6, 68.7, 67.4, 59.2, 18.6, 11.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{36}NaO_3Si$ 423.2326; Found 423.2336.

Compound 7. A hexane solution of *n*-butyllithium (ca. 1.6 mol/L, 6.00 mL, 9.61 mmol) was added dropwise to a solution of compound **6** (3.85 g, 9.61 mmol) in THF (40 mL) at –78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 40 min. The reaction mixture was then cooled to –78 °C, and 5,12-naphthacenequinone (1.13 g, 4.37 mmol) was added at r.t. and stirred under nitrogen atmosphere for 12 h. Then, saturated aq. NH_4Cl (10 mL) was added to the reaction mixture and stirred for 20 min. The reaction

mixture was extracted with ethyl acetate (100 mL), and the organic layer was washed with saturated aq. NH_4Cl (2 × 100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. To the completely dried crude product, THF (20 mL) and $SnCl_2$ (2.07 g, 10.9 mmol) in 10% aq. HCl (10 mL) was added. The reaction mixture was stirred under dark and nitrogen atmosphere at r.t. for 2 h. The reaction mixture was extracted with ethyl acetate (100 mL), washed with water (2 × 100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 4:1 v/v) to afford compound **7** (970 mg, 0.946 mmol, 22%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 2H), 8.64–8.61 (m, 2H), 8.09–8.06, (m, 2H), 7.75 (d, J = 8.8 Hz, 4H), 7.54–7.51 (m, 2H), 7.47–7.44 (m, 2H), 7.02 (d, J = 8.8 Hz, 4H), 4.29 (s, 4H), 4.21 (t, J = 4.8 Hz, 4H), 3.92 (t, J = 4.8 Hz, 4H), 3.79 (s, 8H), 1.10–1.05 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.3, 132.2, 132.1, 130.0, 128.7, 127.5, 126.5, 126.2, 126.0, 118.3, 116.0, 115.0, 103.5, 103.2, 87.9, 86.2, 70.8, 69.7, 68.8, 67.6, 59.4, 18.7, 11.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{66}H_{80}NaO_6Si_2$ 1047.5400; Found 1047.5386.

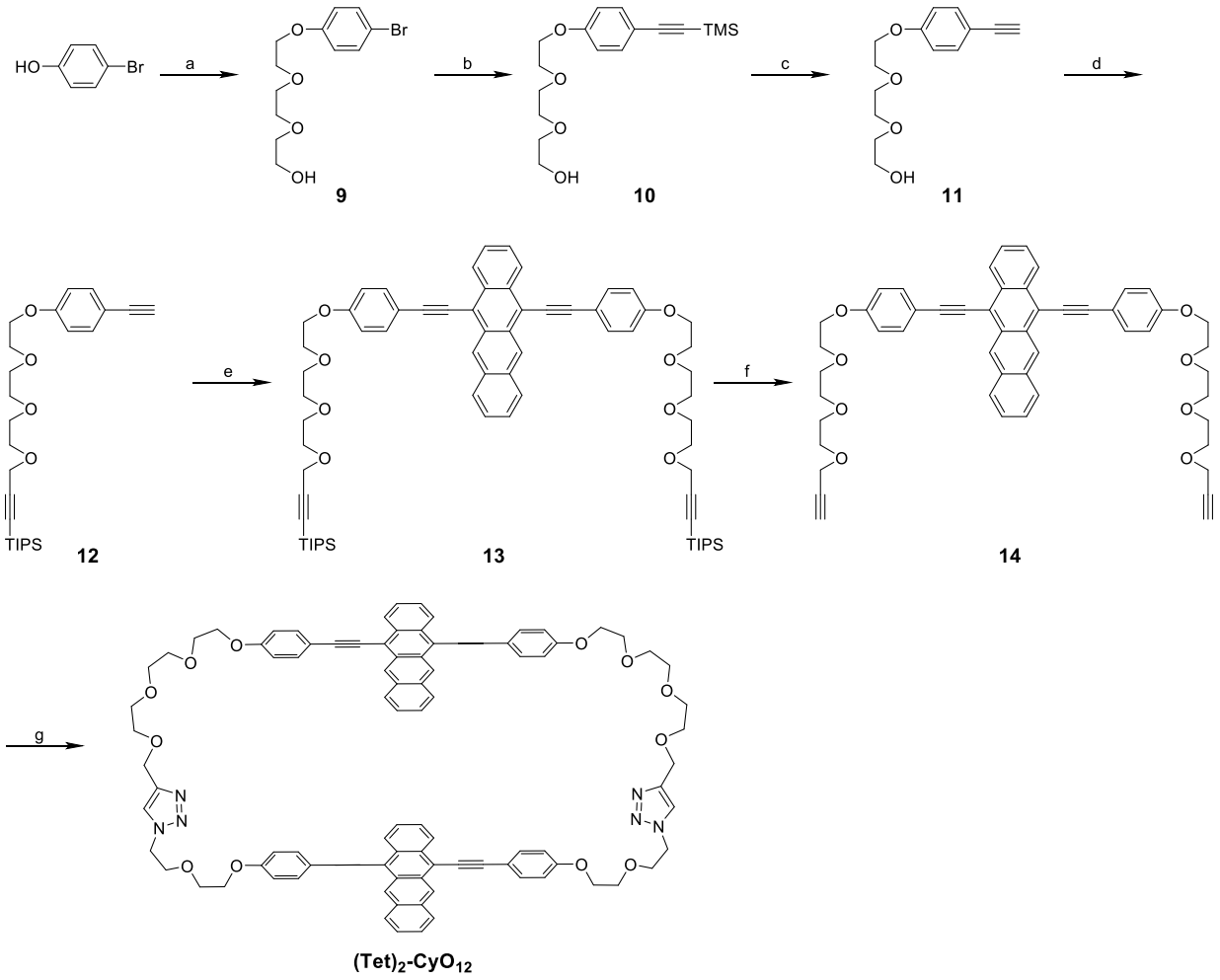
Compound 8. A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 0.70 mL, 0.70 mmol) was added to a solution of compound **7** (270 mg, 0.263 mmol) in THF (20 mL) and stirred at r.t. for 1 h. Ethyl acetate (100 mL) was added to the reaction mixture, and the organic layer was washed with water (100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 3:2 v/v to hexane/ethyl acetate = 11:9 v/v) to afford compound **8** (140 mg, 0.196 mmol, 75 %) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 2H), 8.64–8.61 (m, 2H), 8.09–8.06 (m, 2H), 7.75 (d, J = 8.8 Hz, 4H), 7.55–7.52 (m, 2H), 7.47–7.44 (m, 2H), 7.02 (d, J = 8.8 Hz, 4H), 4.24 (d, J = 2.4 Hz, 4H), 4.22 (t, J = 4.8 Hz, 4H), 3.91 (t, J = 4.8 Hz, 4H), 3.81–3.75 (m, 8H), 2.46 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.3, 132.2, 132.1, 130.0, 128.7, 127.5, 126.5, 126.2, 126.0, 118.3, 116.0, 115.0, 103.5, 86.2, 79.7, 74.8, 70.8, 69.8, 69.3, 67.6, 58.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{40}NaO_6$ 735.2717; Found 735.2723.

Compound (Tet)$_2$-CyO$_{10}$. A mixture of compound **8** (107 mg, 0.150 mmol), compound **2** (103 mg, 0.151 mmol), CuI (143 mg, 0.751 mmol), and *N*,*N*-diisopropylethylamine (130 mL) in $CHCl_3$ (300 mL) was stirred at 60 °C for 24 h. After cooling to r.t., the reaction mixture was washed with 5% aq. HCl (3 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from CH_2Cl_2 to CH_2Cl_2/acetone = 3:7 v/v) and further precipitation with chloroform and methanol to afford compound **(Tet)$_2$-CyO$_{10}$** (51.0 mg, 3.64×10^{-2} mmol, 24%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.68 (s, 4H), 8.20–8.12 (m, 4H), 7.86 (s, 2H), 7.81–7.74 (m, 4H), 7.55–7.48 (m, 8H), 7.35–7.29 (m, 4H), 7.26–7.21 (m, 4H), 6.89–6.80 (m, 8H), 4.77 (s, 4H), 4.59 (t, J = 4.8 Hz, 4H), 4.13 (t, J = 4.8 Hz, 4H), 4.08–4.03 (m, 4H), 3.93 (t, J = 4.8 Hz, 4H), 3.90–3.85 (m, 4H), 3.81–3.75 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 158.7, 145.5, 133.3, 133.2, 131.7, 131.6, 129.3, 128.7, 127.1, 126.0, 125.8, 125.5, 124.1, 117.8, 116.5, 116.3, 114.7, 114.6, 103.0, 102.9, 86.5, 86.4, 71.1, 70.0, 69.9, 69.9, 69.8, 67.7, 67.3, 65.1, 50.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{90}H_{74}N_6NaO_{10}$ 1421.5359; Found 1421.5321.

Scheme S2 Synthesis of $(Tet)_2$-CyO_{12}



Conditions: (a) triethylene glycol *p*-toluenesulfonate, K_2CO_3, DMF, 110 °C, 20 h; (b) trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, diisopropylamine, THF, 80 °C, 24 h; (c) tetrabutylammonium fluoride, THF, r.t., 1 h; (d) 3-bromo-1-(triisopropylsilyl)-1-propyne, NaH, THF, 0 °C → r.t., 8 h; (e) i) *n*-butyllithium, THF, −78 °C → 0 °C, 40 min, ii) 5,12-naphthacenequinone, THF, r.t., 12 h, iii) H^+, iv) 10% aq. HCl, $SnCl_2$, r.t., 2 h; (f) tetrabutylammonium fluoride, THF, r.t., 1 h; (g) compound **2**, CuI, *N*,*N*-diisopropylethylamine, $CHCl_3$, 55 °C, 12 h.

Compound 9. A mixture of 4-bromophenol (6.65 g, 38.5 mmol), triethylene glycol *p*-toluenesulfonate (12.9 g, 42.3 mmol), and K_2CO_3 (26.6 g, 193 mmol) in DMF (40 mL) was stirred at 110 °C for 20 h. After cooling to r.t., the reaction mixture was poured into

ethyl acetate (200 mL) and washed with saturated aq. NH_4Cl (4 × 100 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 v/v to hexane/ethyl acetate = 2:3 v/v) to afford compound **9** (8.36 g, 27.4 mmol, 71%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 9.2 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 4.11–4.08 (m, 2H), 3.86–3.83 (m, 2H), 3.74–3.67 (m, 6H), 3.62–3.59 (m, 2H), 2.61 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 132.3, 116.5, 113.1, 72.6, 70.9, 70.4, 69.7, 67.6, 61.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{17}BrNaO_4$ 327.0202; Found 327.0196.

Compound 10. A mixture of compound **9** (8.36 g, 27.4 mmol), trimethylsilylacetylene (13.5 g, 137 mmol), $Pd(PPh_3)_2Cl_2$ (962 mg, 1.37 mmol), CuI (261 mg, 1.37 mmol), and diisopropylamine (20 mL) in THF (20 mL) was stirred under nitrogen atmosphere at 80 °C for 24 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (200 mL) and washed with 5% aq. HCl (2 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 v/v to hexane/ethyl acetate = 2:3 v/v) to afford compound **10** (5.16 g, 16.0 mmol, 58%) as a brown liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 4.15–4.11 (m, 2H), 3.88–3.85 (m, 2H), 3.76–3.69 (m, 6H), 3.63–3.61 (m, 2H), 2.39 (t, J = 6.0 Hz, 1H), 0.24, (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 133.6, 115.6, 114.5, 105.2, 92.6, 72.6, 71.0, 70.5, 69.7, 67.4, 61.9, 0.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{26}NaO_4Si$ 345.1493; Found 345.1485.

Compound 11. A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 27.3 mL, 27.3 mmol) was added to a solution of compound **10** (7.35 g, 22.8 mmol) in THF (10 mL) and stirred at r.t. for 1 h. Ethyl acetate (100 mL) was added to the reaction mixture, and the mixture was then washed with water (100 mL) and saturated aq. NaCl (2 × 100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 v/v to hexane/ethyl acetate = 2:3 v/v) to afford compound **11** (5.05 g, 20.2 mmol, 89 %) as a brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.15–4.11 (m, 2H), 3.87–3.84 (m, 2H), 3.75–3.67 (m, 6H), 3.63–3.59 (m, 2H), 3.01, (s, 1H), 2.66, (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 133.6, 114.6, 114.4, 83.7, 76.0, 72.6, 70.9, 70.4, 69.6, 67.4, 61.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}NaO_4$ 273.1097; Found 273.1094.

Compound 12. A THF solution (10 mL) of NaH (60% dispersion in paraffin liquid, 969 mg, 24.2 mmol) was added to a solution of compound **11** (5.05 g, 20.2 mmol) in THF (20 mL) at 0 °C. Then, 3-bromo-1-(triisopropylsilyl)-1-propyne (6.67 g, 24.2 mmol) was added to the mixture and stirred at r.t. for 8 h. After adding water (15 mL) dropwise to the reaction mixture, most of the THF was evaporated under reduced pressure. Ethyl acetate (100 mL) was added to the reaction mixture, and the mixture was washed with water (100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 4:1 v/v) to afford compound **12** (5.39 g, 12.0 mmol, 60%) as a colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.24 (s, 2H), 4.12 (t, J = 4.8 Hz, 2H), 3.85 (t, J = 4.8 Hz, 2H), 3.74–3.67 (m, 8H), 3.00 (s, 1H), 1.09–1.04 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 133.6, 114.6, 114.3, 103.3, 87.7, 83.7, 75.9, 70.9, 70.7, 70.5, 69.7, 68.7, 67.5, 59.2, 18.6, 11.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{40}NaO_4Si$ 467.2588; Found 467.2598.

Compound 13. A hexane solution of *n*-butyllithium (ca. 1.6 mol/L, 2.1 mL, 3.38 mmol) was added dropwise to a solution of compound **12** (1.45 g, 3.23 mmol) in THF (40 mL) at –78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 40 min. Then, the reaction mixture was cooled to –78 °C and 5,12-naphthacenequinone (379 mg, 1.47 mmol) was added at r.t. and stirred under nitrogen atmosphere for 12 h. Saturated aq. NH_4Cl (10 mL) was added to the reaction mixture and stirred for 20 min. The reaction mixture was extracted with ethyl acetate (100 mL), and washed with saturated aq. NH_4Cl (2 × 100 mL) and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. To the completely dried crude product, THF (20 mL) and $SnCl_2$ (613 mg, 3.23 mmol) in 10% aq. HCl (10 mL) was added. The reaction mixture was stirred under dark and nitrogen atmosphere at r.t. for 2 h. The reaction mixture was extracted with ethyl acetate (100 mL), washed with water (2 × 100 mL) and saturated aq. NaCl (100 mL). The organic layer was

separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane to hexane/ethyl acetate = 3:1 v/v) to afford compound **13** (230 mg, 0.207 mmol, 14%) as a purple solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 2H), 8.65–8.62 (m, 2H), 8.10–8.07 (m, 2H), 7.75 (d, J = 8.8 Hz, 4H), 7.55–7.52 (m, 2H), 7.47–7.44 (m, 2H), 7.02 (d, J = 8.8 Hz, 4H), 4.27 (s, 4H), 4.21 (t, J = 4.8 Hz, 4H), 3.91 (t, J = 4.8 Hz, 4H), 3.79–3.70 (m, 16H), 1.09–1.04 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 133.3, 132.2, 132.1, 130.0, 128.7, 127.6, 126.5, 126.2, 126.0, 118.4, 116.0, 115.0, 103.5, 103.3, 87.8, 86.2, 71.0, 70.8, 70.6, 69.8, 68.8, 67.7, 59.3, 18.7, 11.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{70}H_{88}NaO_8Si_2$ 1135.5910; Found 1135.5913.

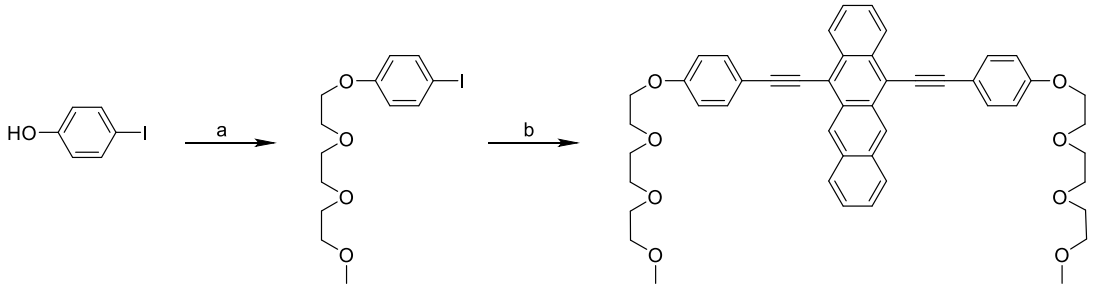
Compound 14. A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 0.593 mL, 0.593 mmol) was added to a solution of compound **13** (229 mg, 0.206 mmol) in THF (20 mL) and stirred at r.t. for 1 h. The reaction mixture was then extracted with CH_2Cl_2 (100 mL), washed with water (100 mL), and washed with saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 3:1 v/v to hexane/ethyl acetate = 2:3 v/v) and recycling GPC (eluent: chloroform) to afford compound **14** (162 mg, 0.202 mmol, 98 %) as a purple solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.24 (s, 2H), 8.66–8.63 (m, 2H), 8.11–8.07 (m, 2H), 7.76 (d, J = 8.8 Hz, 4H), 7.57–7.52 (m, 2H), 7.48–7.44 (m, 2H), 7.03 (d, J = 8.8 Hz, 4H), 4.24–4.19 (m, 8H), 3.91 (t, J = 4.8 Hz, 4H), 3.79–3.76 (m, 4H), 3.74–3.70 (m, 12H), 2.44 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 133.3, 132.2, 132.2, 130.0, 128.7, 127.6, 126.6, 126.2, 126.0, 118.4, 116.0, 115.0, 103.5, 86.2, 79.8, 74.7, 71.0, 70.8, 70.6, 69.8, 69.2, 67.7, 58.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{52}H_{48}NaO_8$ 823.3241; Found 823.3220.

Compound (Tet)$_2$-CyO$_{12}$. A mixture of compound **14** (140 mg, 0.191 mmol), compound **2** (120 mg, 0.191 mmol), CuI (182 mg, 0.954 mmol), and *N*,*N*-diisopropylethylamine (130 mL) in $CHCl_3$ (300 mL) was stirred at 55 °C for 12 h. After cooling to r.t., the reaction mixture was washed with 5% aq. HCl (3 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from

CH_2Cl_2 to CH_2Cl_2/acetone = 1:4 v/v) to afford compound **(Tet)$_2$-CyO$_{12}$** (29.5 mg, 1.98×10^{-2} mmol, 10%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 4H), 8.32–8.22 (m, 4H), 7.85–7.83 (m, 6H), 7.56–7.47 (m, 8H), 7.37–7.29 (m, 8H), 6.82–6.76 (m, 8H), 4.74 (s, 4H), 4.57 (t, J = 4.8 Hz, 4H), 4.10–4.05 (m, 4H), 4.03–3.99 (m, 4H), 3.92 (t, J = 4.8 Hz, 4H), 3.87–3.82 (m, 4H), 3.80–3.67 (m, 20H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 158.7, 145.4, 133.2, 133.1, 131.8, 131.7, 129.5, 128.6, 127.2, 126.1, 125.8, 125.6, 124.0, 117.9, 116.3, 116.1, 114.7, 114.6, 103.2, 103.1, 86.4, 86.4, 71.0, 70.8, 69.9, 69.9, 69.8, 69.7, 67.6, 67.3, 65.0, 50.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{94}H_{82}N_6NaO_{12}$ 1509.5883; Found 1509.5878.

Scheme S3 Synthesis of Tet-ref



15 **Tet-ref**

(a) 2-[2-(2-methoxyethoxy)ethoxy]ethyl *p*-toluenesulfonate, K_2CO_3, DMF, 80 °C, 14 h; (b) 5,12-bis[(triisopropylsilyl)ethynyl]tetracene, tetrabutylammonium fluoride, $Pd(PPh_3)_2Cl_2$, CuI, diisopropylamine, THF, 80 °C, 2 h.

Compound 15. A mixture of 4-iodophenol (1.10 g, 5.00 mmol), 2-[2-(2-methoxyethoxy)ethoxy]ethyl *p*-toluenesulfonate (1.91 g, 6.00 mmol), and K_2CO_3 (2.50 g, 15.0 mmol) in DMF (30 mL) was stirred at 80 °C for 14 h. After cooling to r.t., most of the DMF was evaporated under reduced pressure. The reaction mixture was then poured into ethyl acetate (200 mL) and washed with saturated aq. NH_4Cl (4 × 100 mL) and saturated aq. NaCl (200 mL). The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 9:1 v/v to hexane/ethyl acetate = 1:1 v/v) to afford compound **15** (1.63 g, 4.45 mmol, 89%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 9.2 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 4.12–4.06 (m, 2H), 3.87–3.82 (m, 2H), 3.75–3.71 (m, 2H), 3.70–3.63 (m, 4H), 3.57–3.53 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 138.0, 116.9, 82.8, 71.8, 70.7, 70.5, 70.4, 69.5, 67.4, 58.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{19}INaO_4$ 389.0220; Found 389.0217.

Compound Tet-ref. To a mixture of compound **15** (466 mg, 1.27 mmol), 5,12-bis[(triisopropylsilyl)ethynyl]tetracene (300 mg, 0.509 mmol), and diisopropylamine (20 mL) in THF (20 mL), A THF solution of tetrabutylammonium fluoride (ca. 1 mol/L, 1.27 mL, 1.27 mmol) was added and stirred under nitrogen atmosphere for 5 min. Then the catalysts $Pd(PPh_3)_2Cl_2$ (35.8 mg, 5.09×10^{-2} mmol) and CuI (10.0 mg, 5.09×10^{-2} mmol) were added and the reaction mixture was stirred under nitrogen atmosphere at 80 °C for 2 h. After cooling to r.t., the reaction mixture was poured into ethyl acetate (200 mL) and washed with 5% aq. HCl (2 × 100 mL), saturated aq. $NaHCO_3$ (100 mL), and saturated

aq. NaCl (100 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: gradient from hexane/ethyl acetate = 3:2 v/v to ethyl acetate) to afford compound **Tet-ref** (210 mg, 0.279 mmol, 55%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 2H), 8.64–8.62 (m, 2H), 8.09–8.07 (m, 2H), 7.75 (d, J = 8.8 Hz, 4H), 7.55–7.52 (m, 2H), 7.47–7.45 (m, 2H), 7.02 (d, J = 9.2 Hz, 4H), 4.21 (t, J = 4.8 Hz, 4H), 3.91 (t, J = 4.8 Hz, 4H), 3.79–3.76 (m, 4H), 3.73–3.65 (m, 8H), 3.59–3.56 (m, 4H), 3.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 133.3, 132.1, 132.1, 129.9, 128.7, 127.5, 126.5, 126.1, 125.9, 118.3, 116.0, 115.0, 103.4, 86.2, 72.0, 71.0, 70.8, 70.7, 69.7, 67.6, 59.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{48}NaO_8$ 775.3241; Found 775.3228.

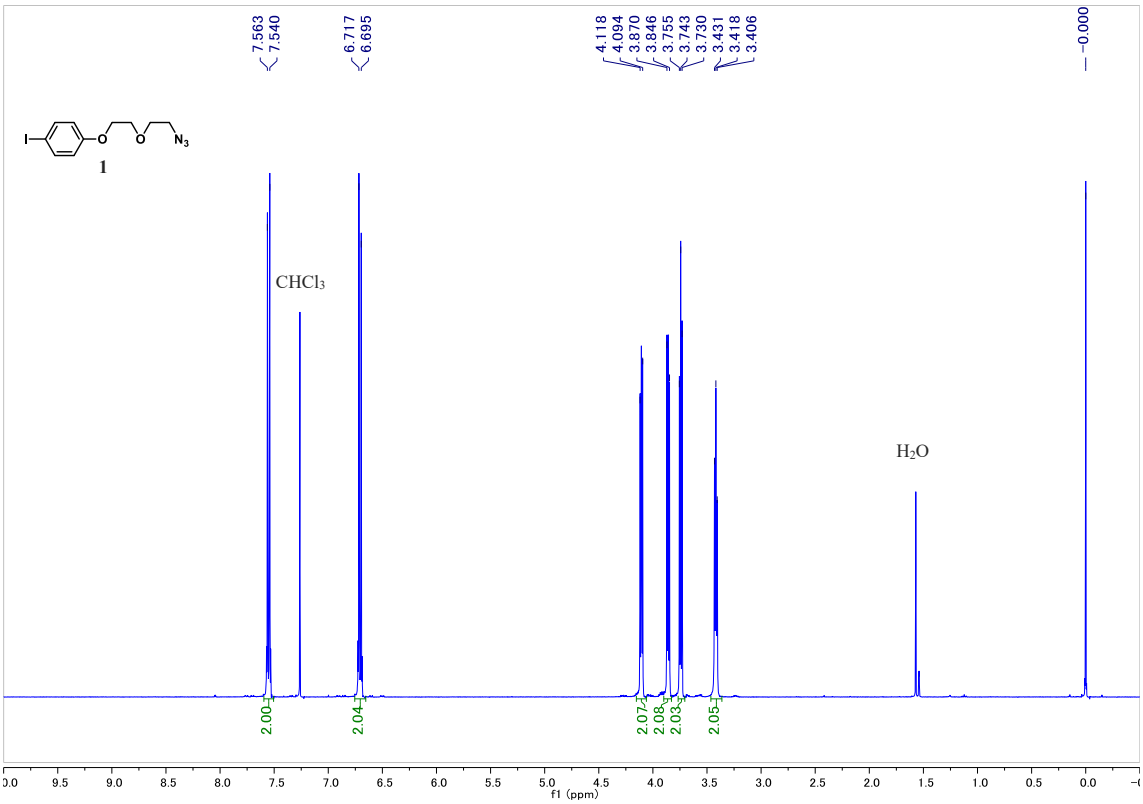


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**.

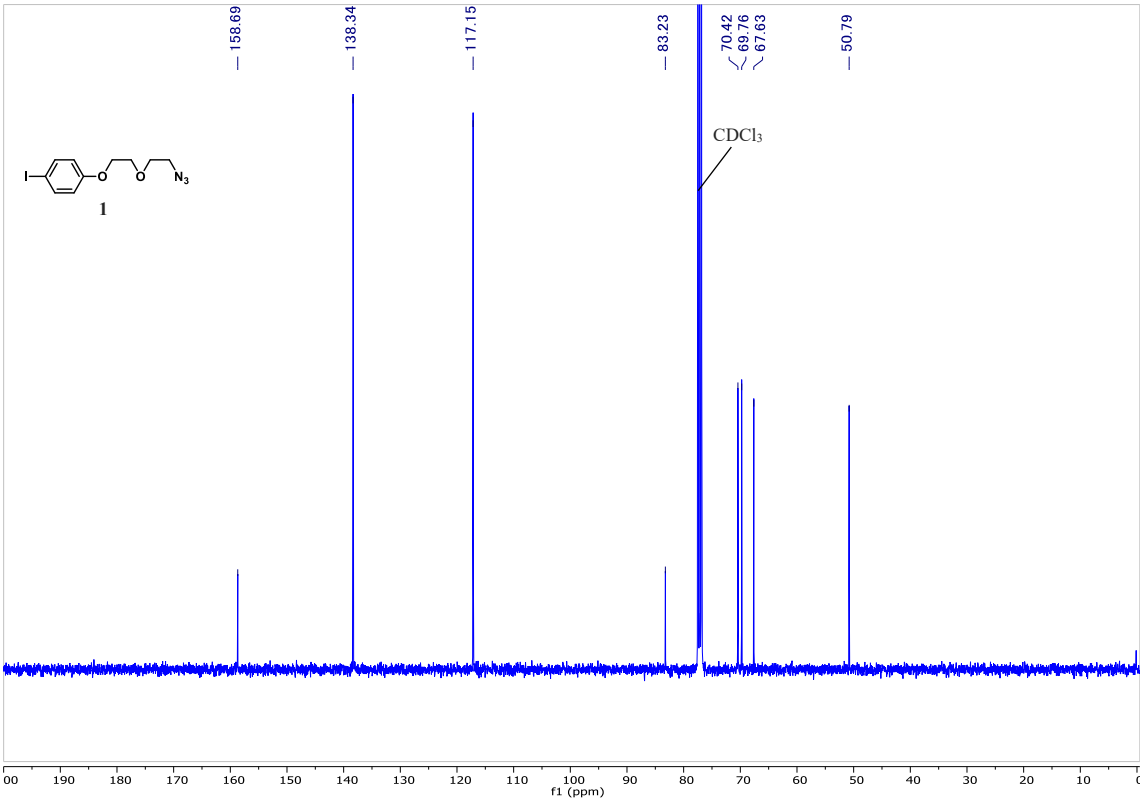


Fig. S2 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **1**.

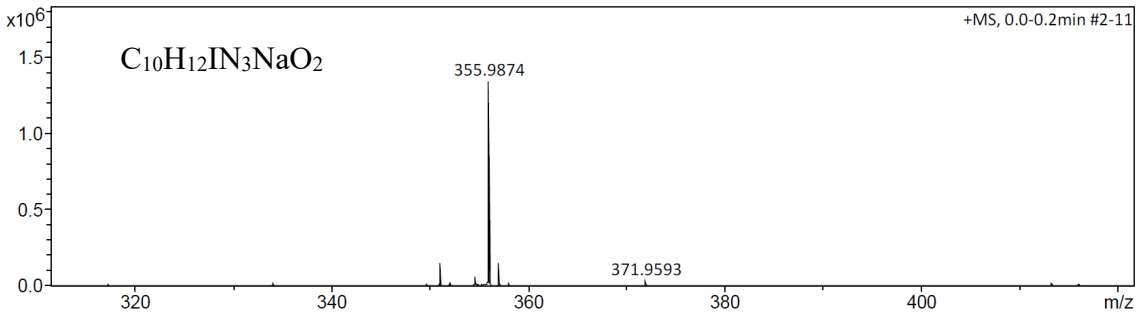


Fig. S3 High resolution ESI-TOF-MS spectrum of compound **1**.

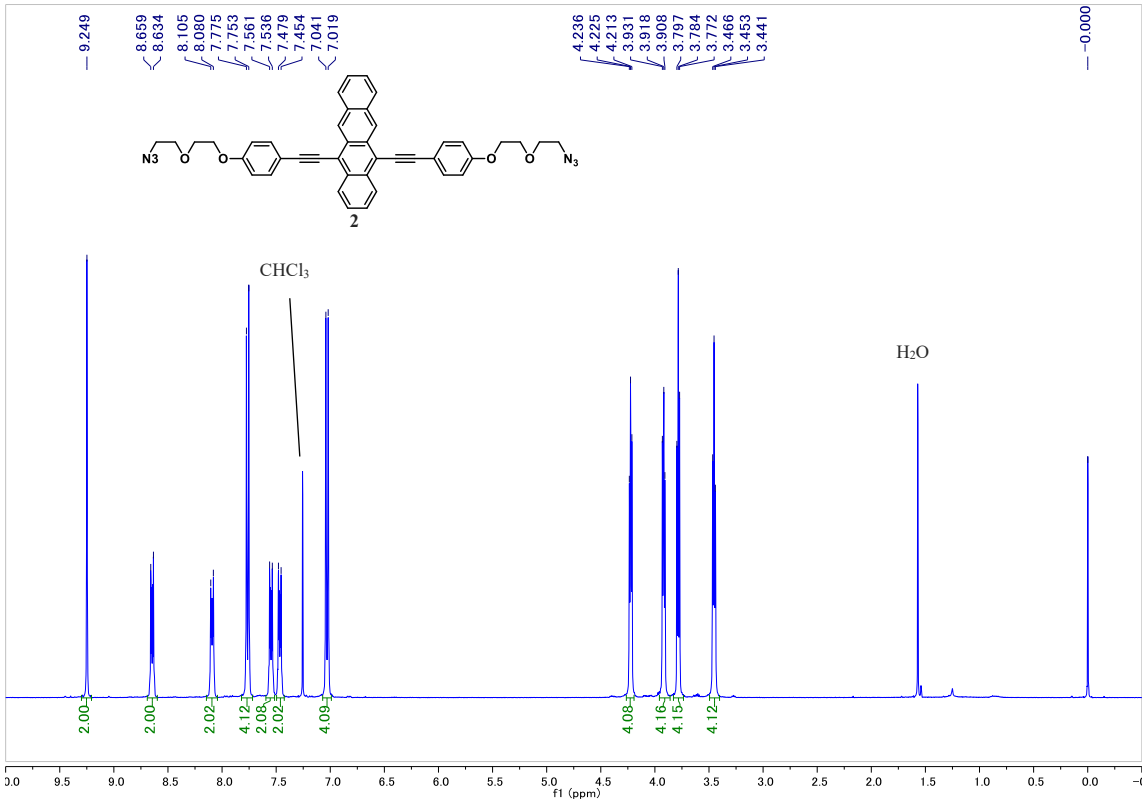


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **2**.

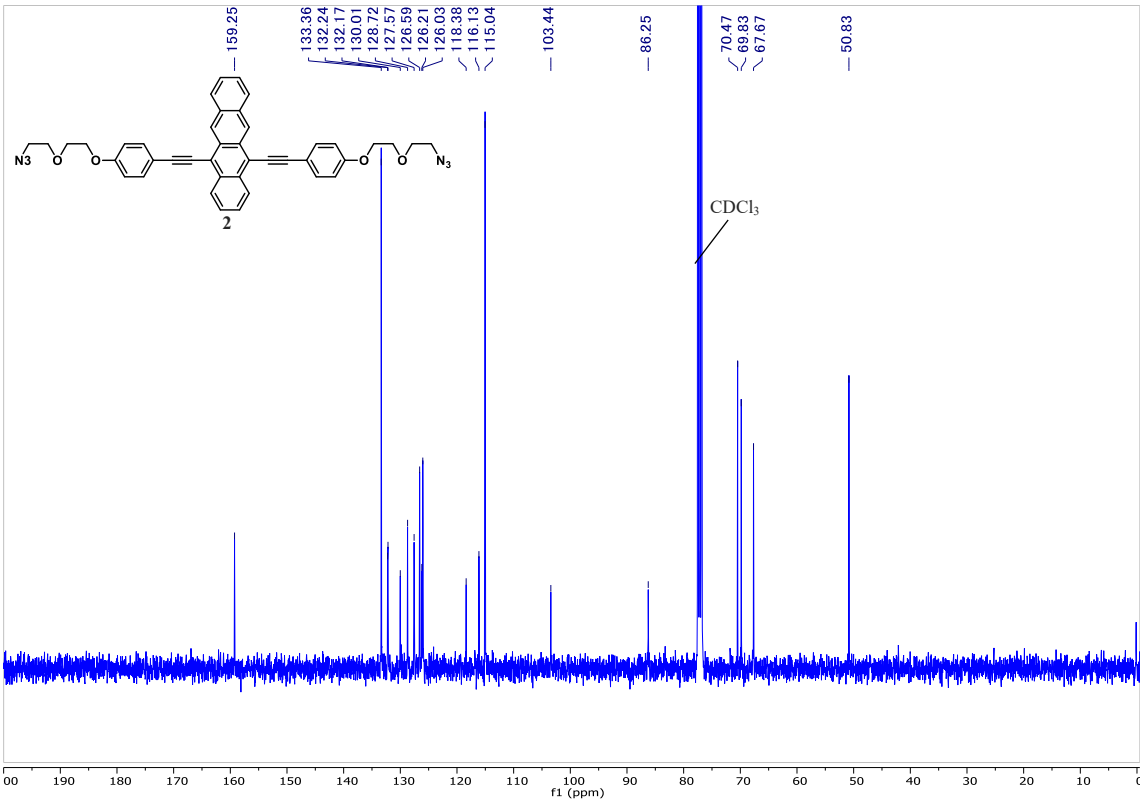


Fig. S5 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **2**.

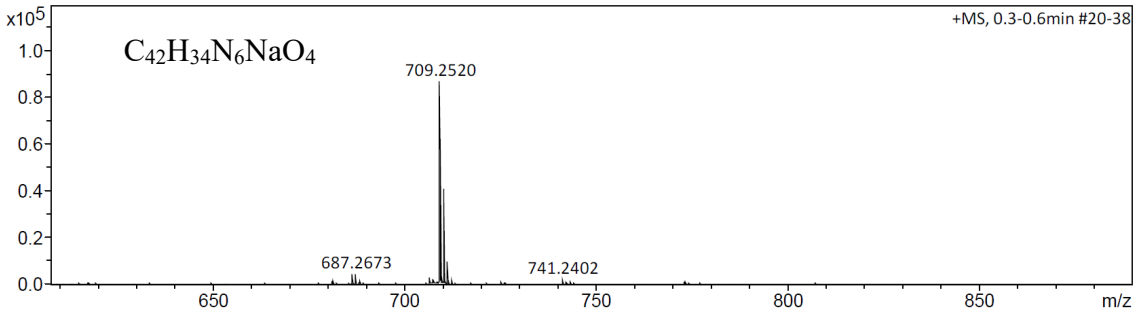


Fig. S6 High resolution ESI-TOF-MS spectrum of compound **2**.

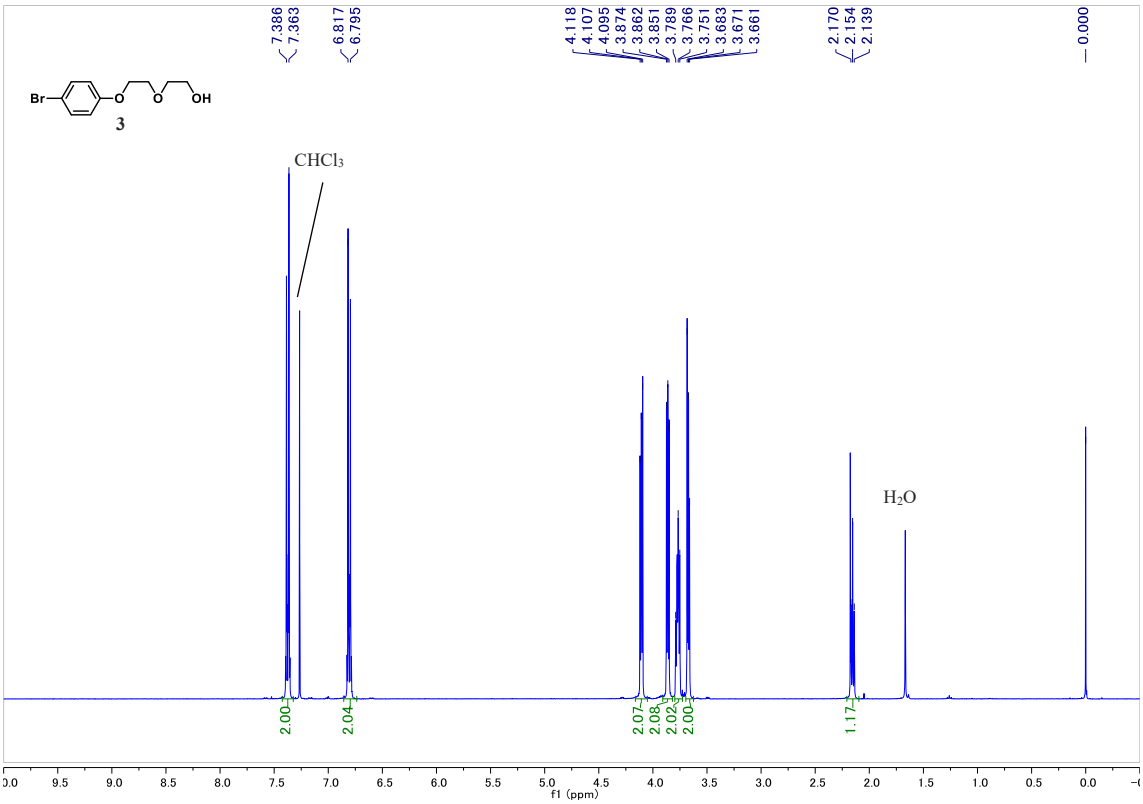


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

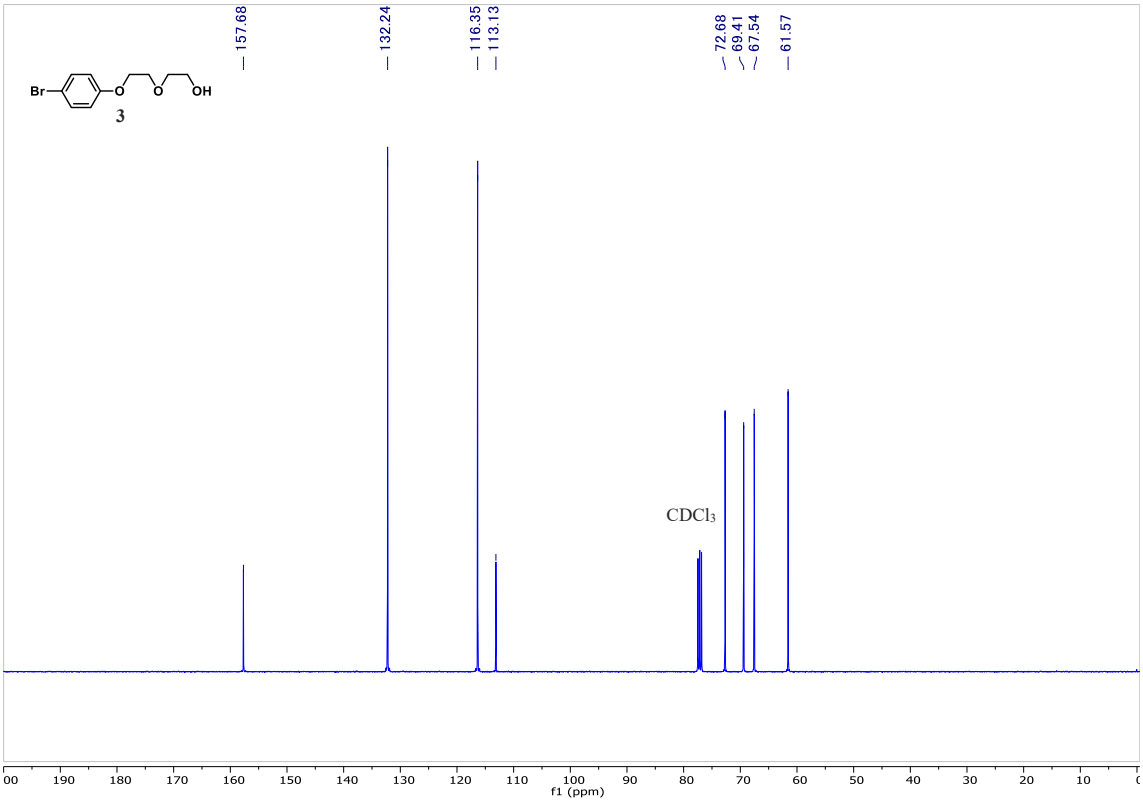


Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**.

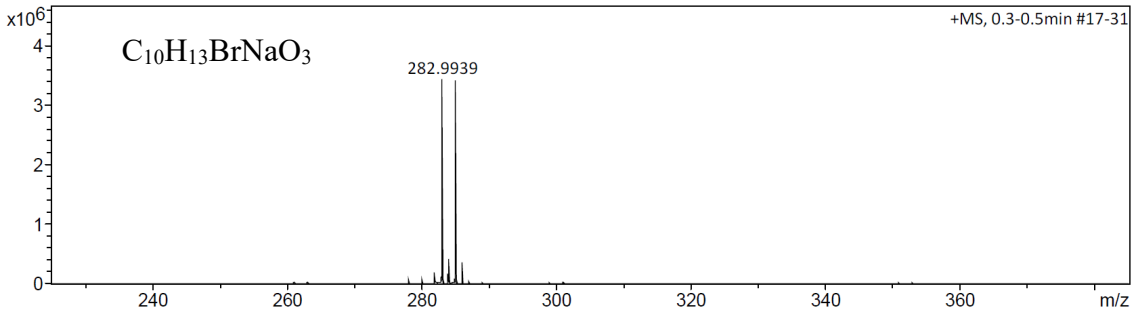


Fig. S9 High resolution ESI-TOF-MS spectrum of compound **3**.

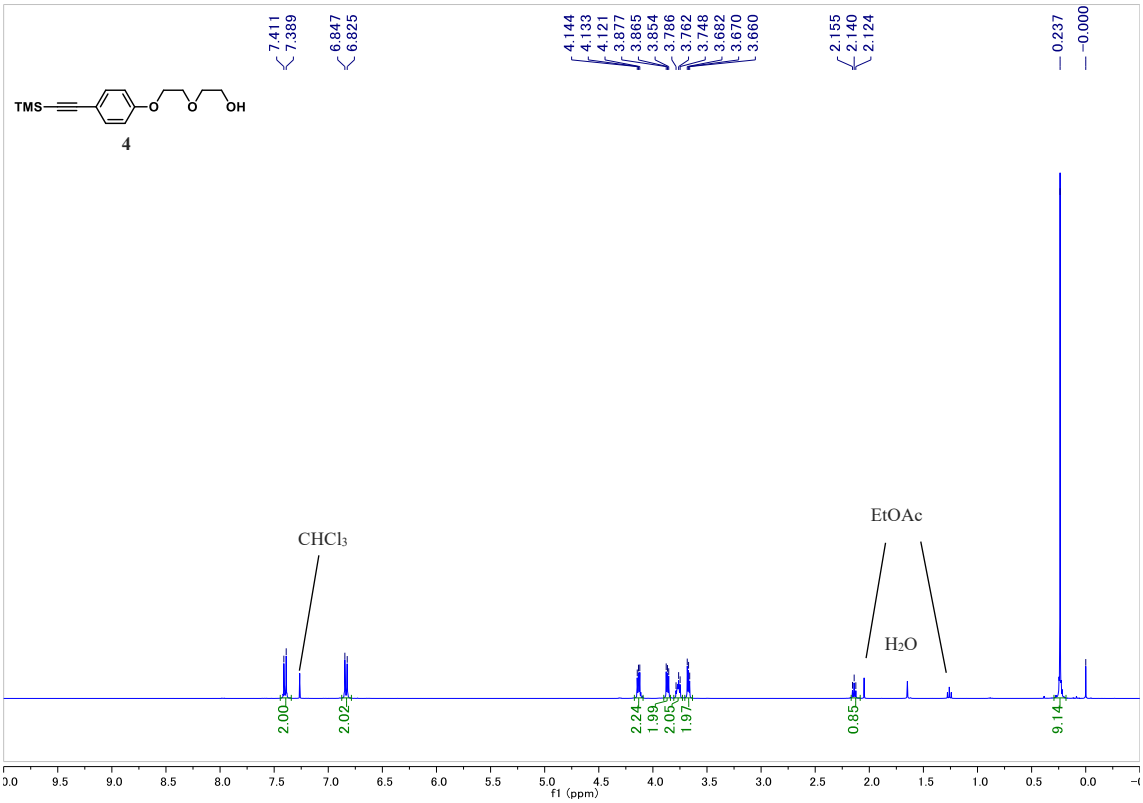


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**.

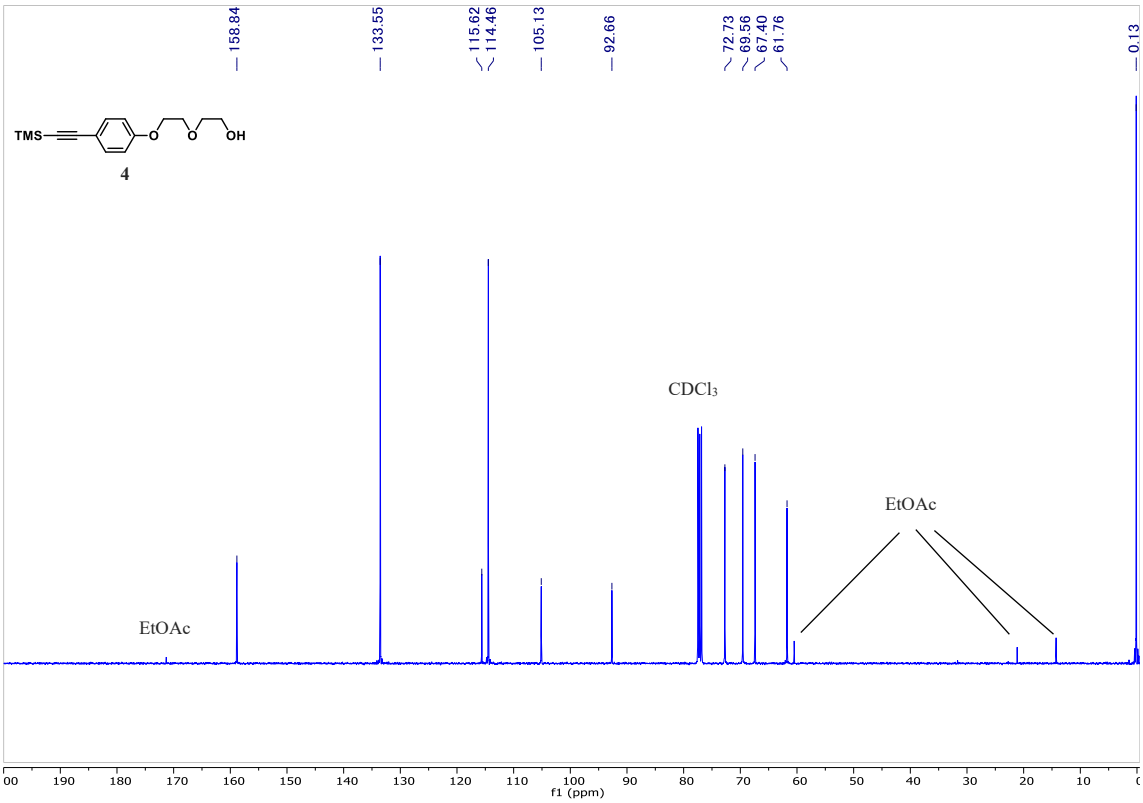


Fig. S11 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**.

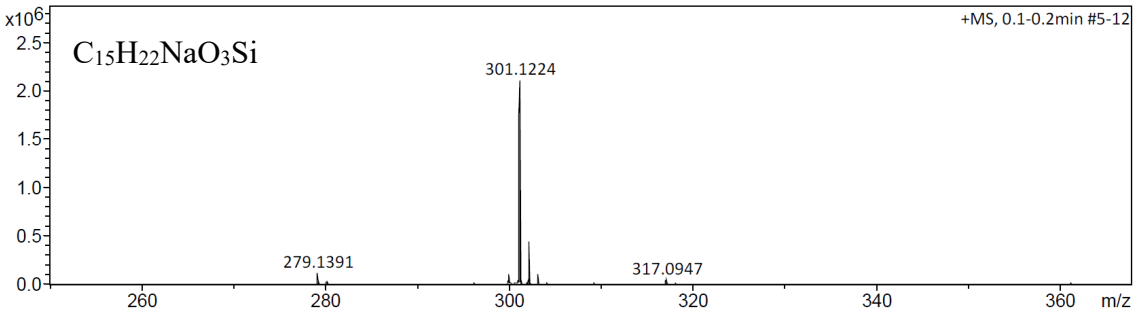


Fig. S12 High resolution ESI-TOF-MS spectrum of compound **4**.

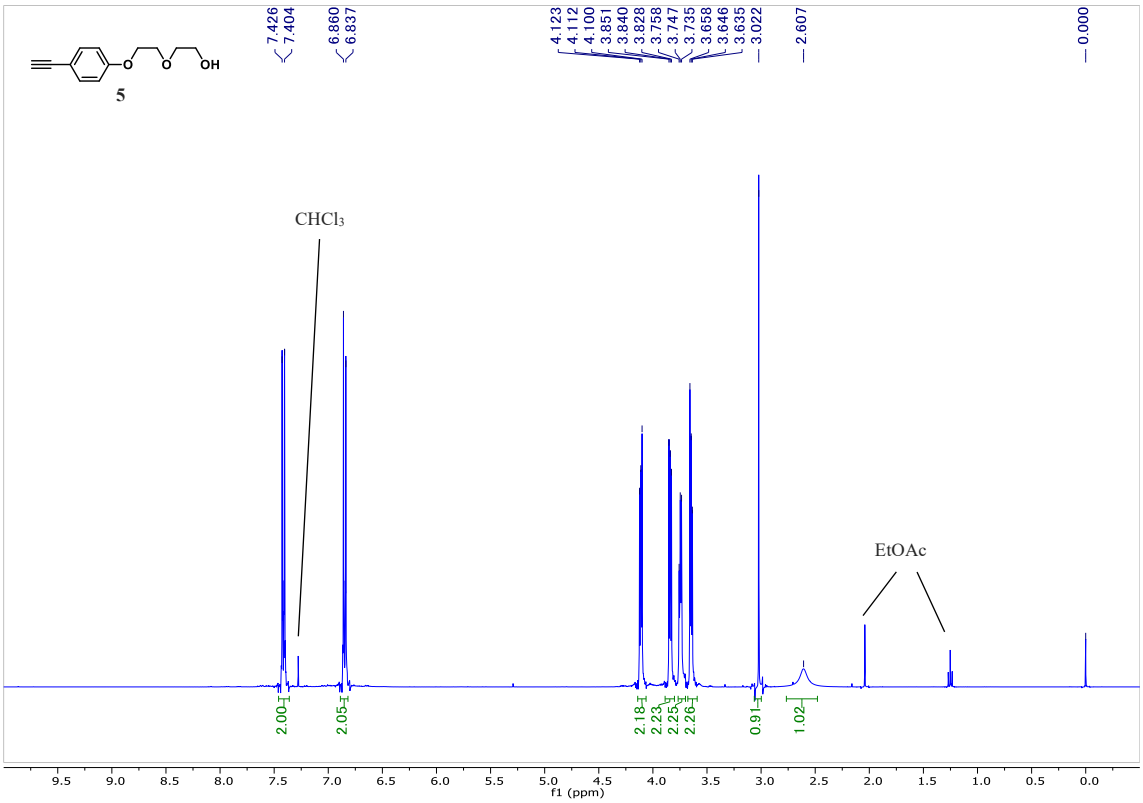


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**.

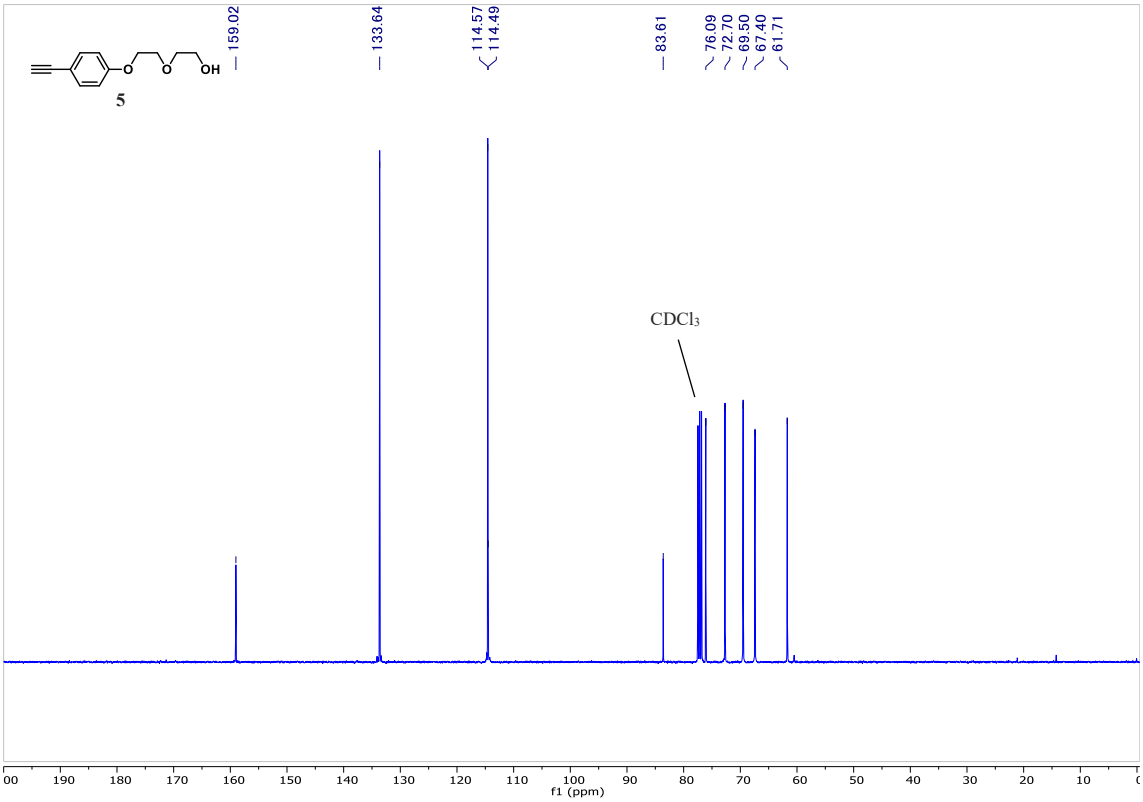


Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**.

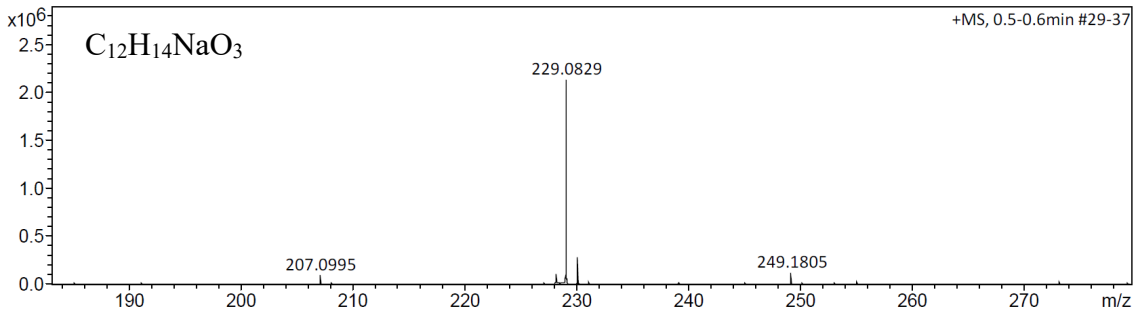


Fig. S15 High resolution ESI-TOF-MS spectrum of compound **5**.

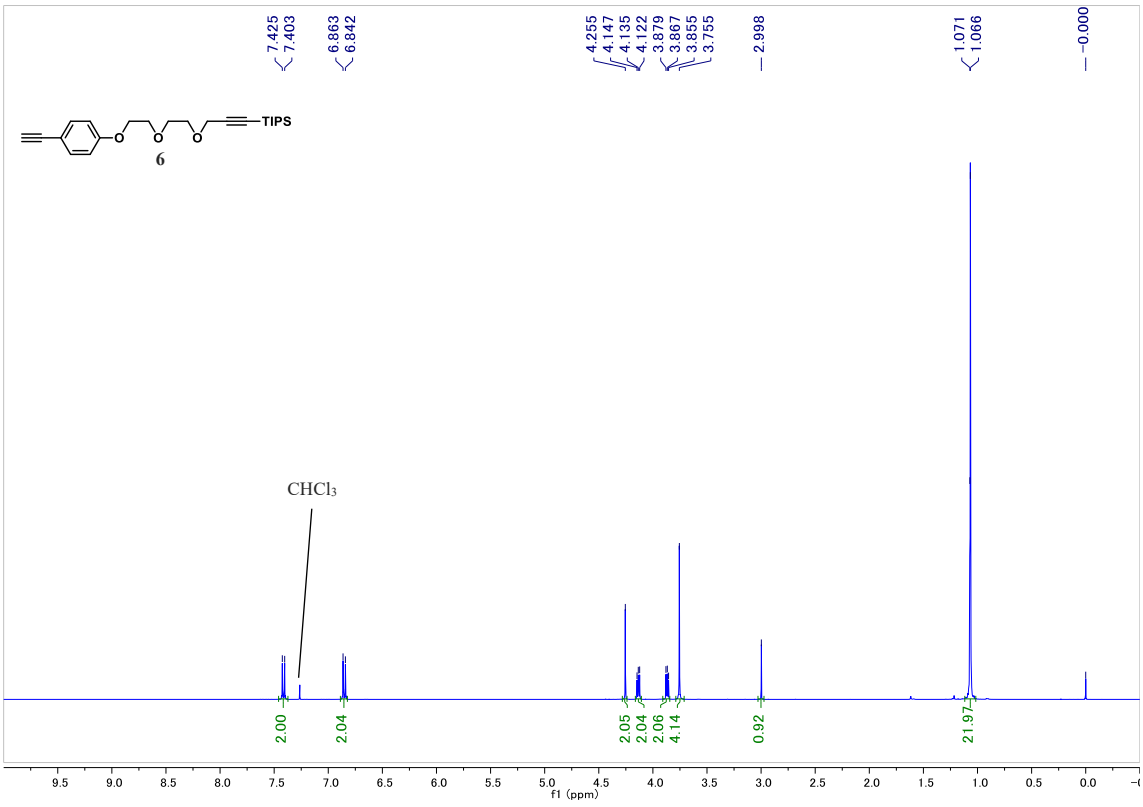


Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**.

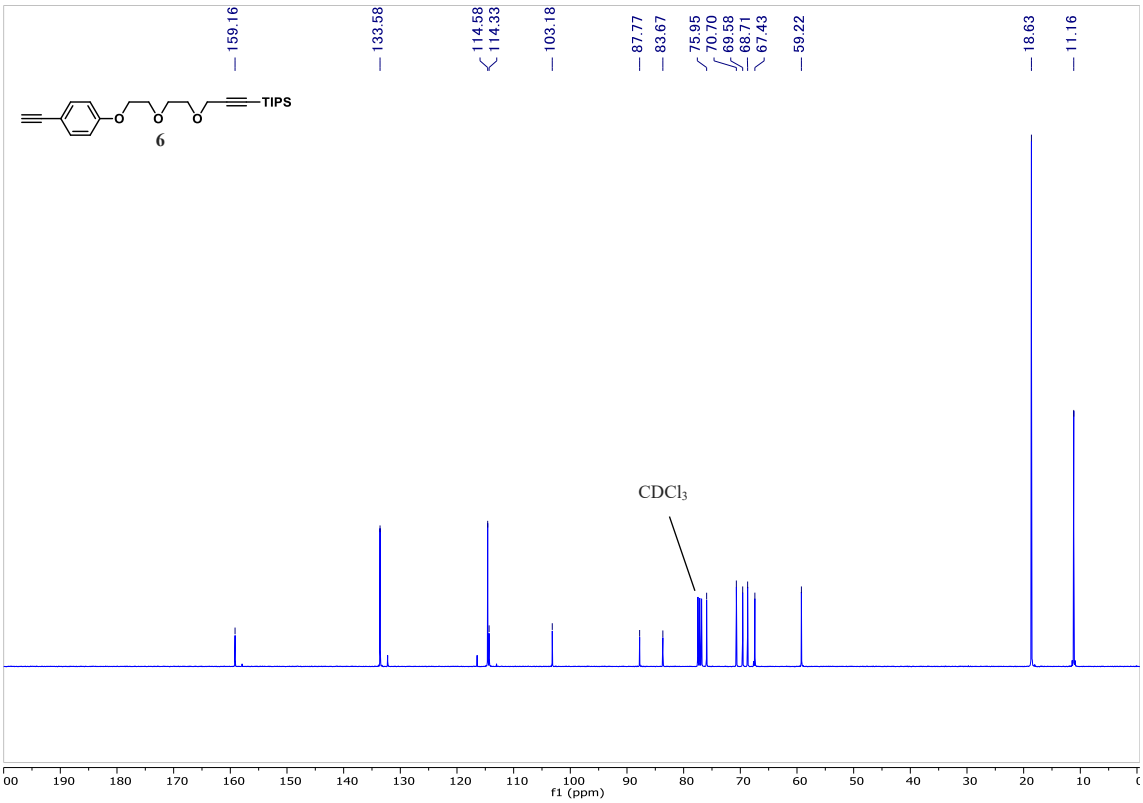


Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6**.

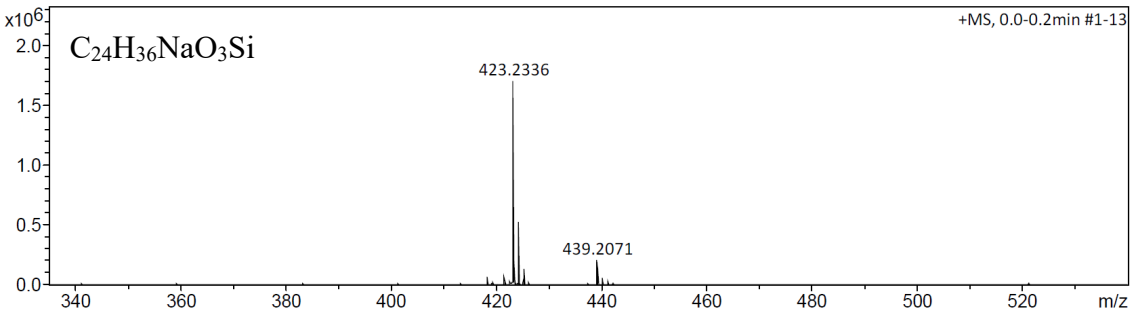


Fig. S18 High resolution ESI-TOF-MS spectrum of compound **6**.

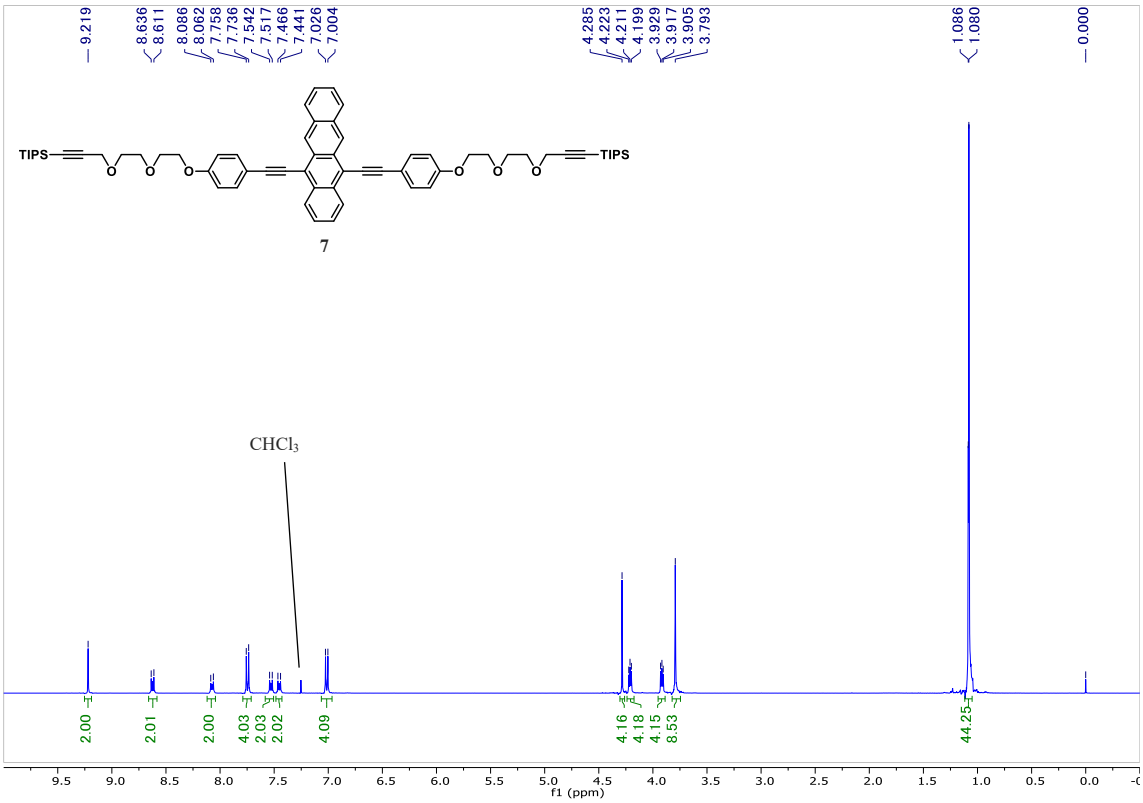


Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**.

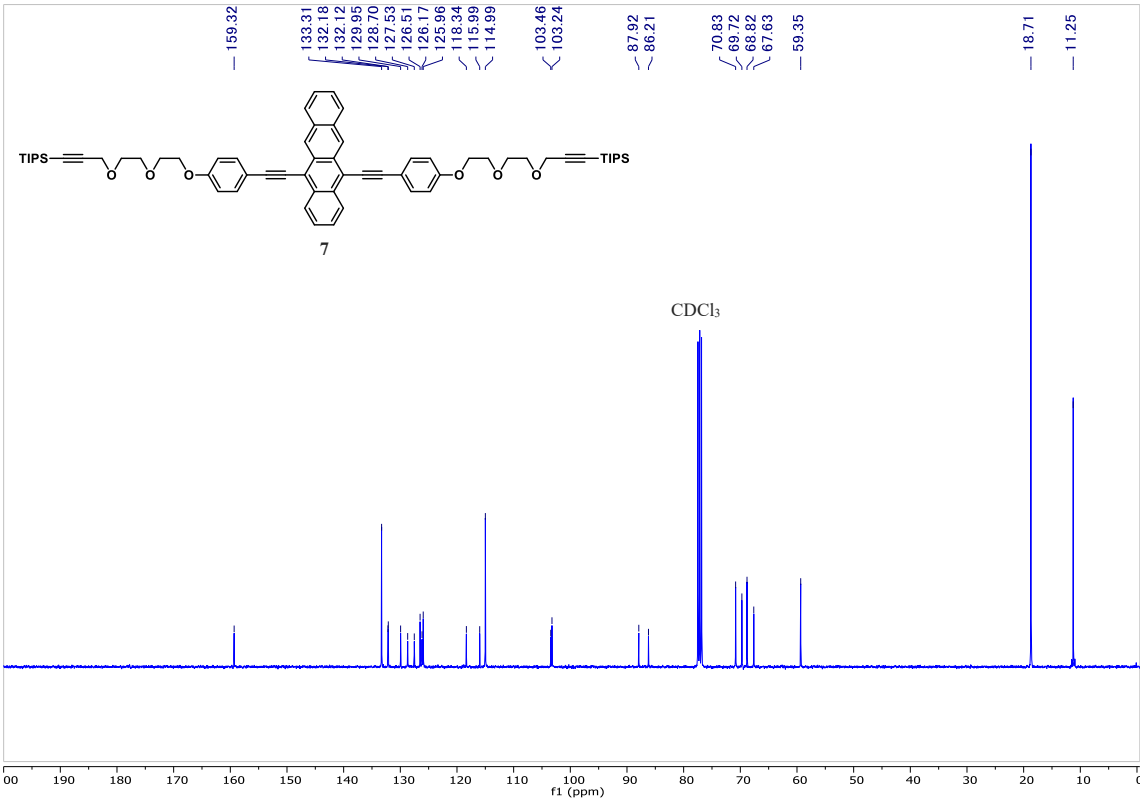


Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**.

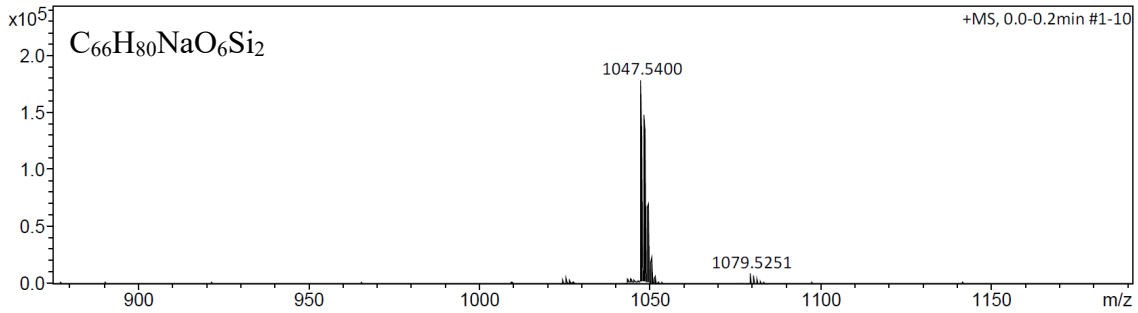


Fig. S21 High resolution ESI-TOF-MS spectrum of compound **7**.

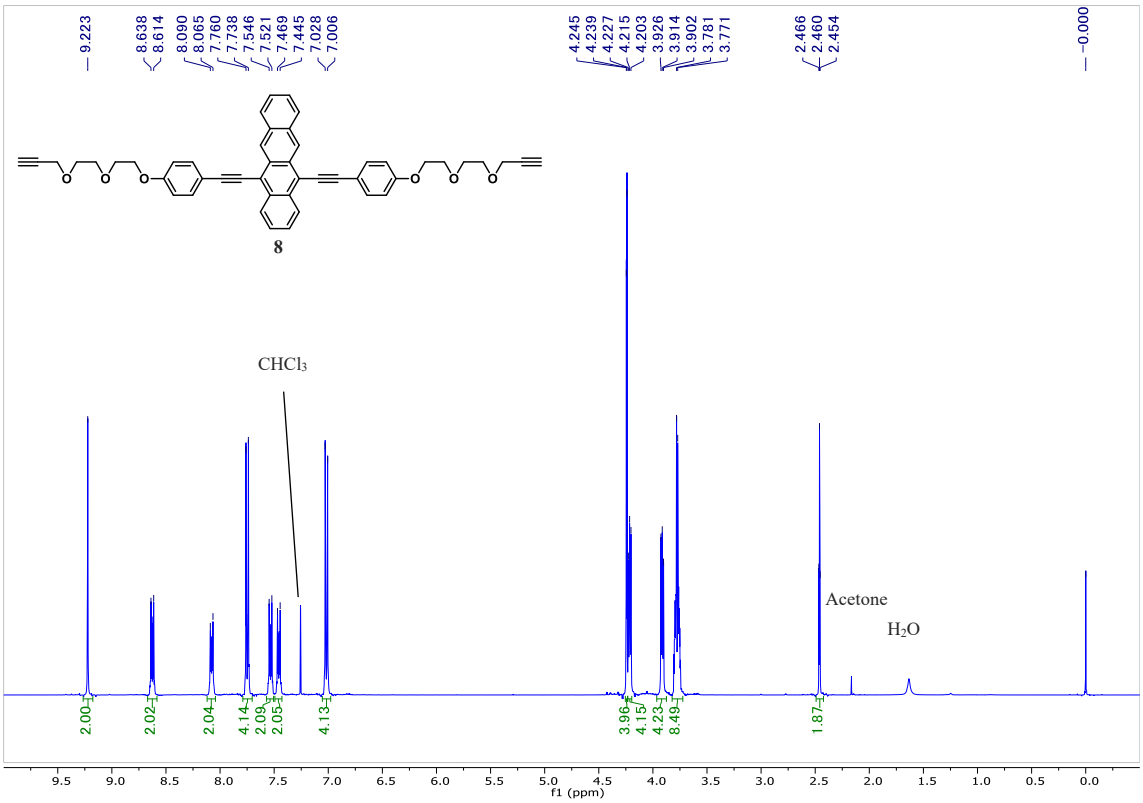


Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**.

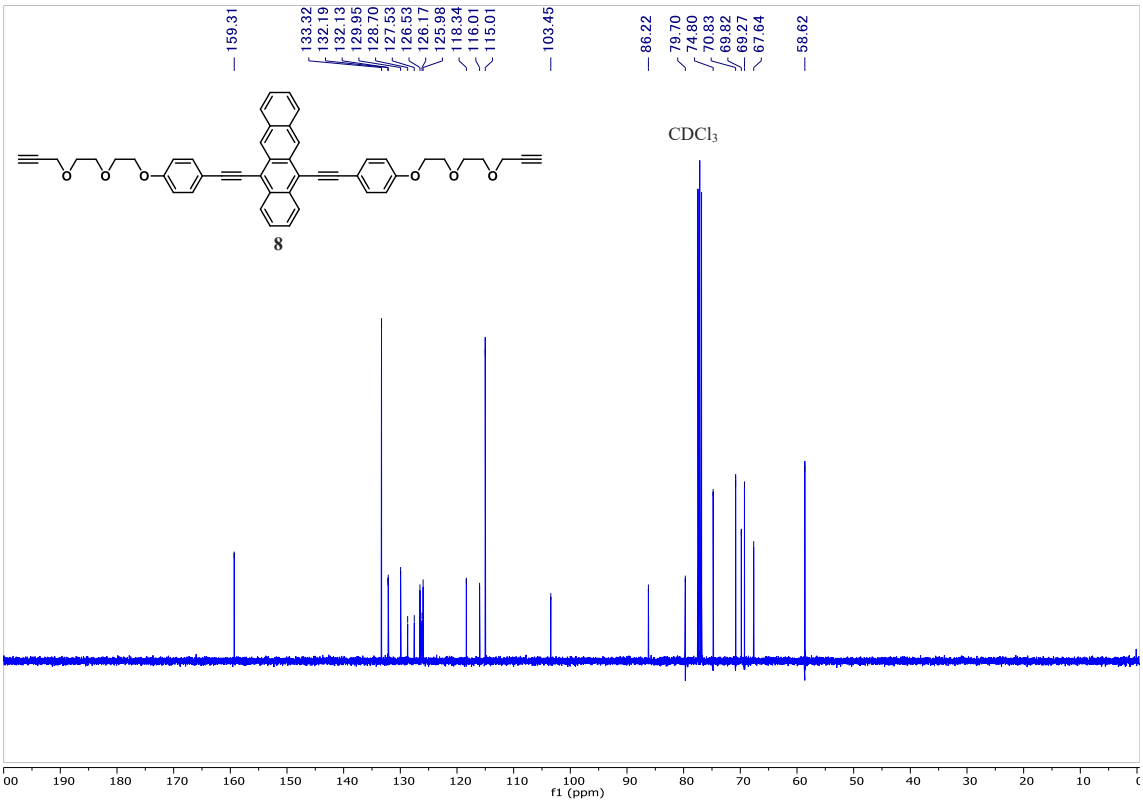


Fig. S23 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**.

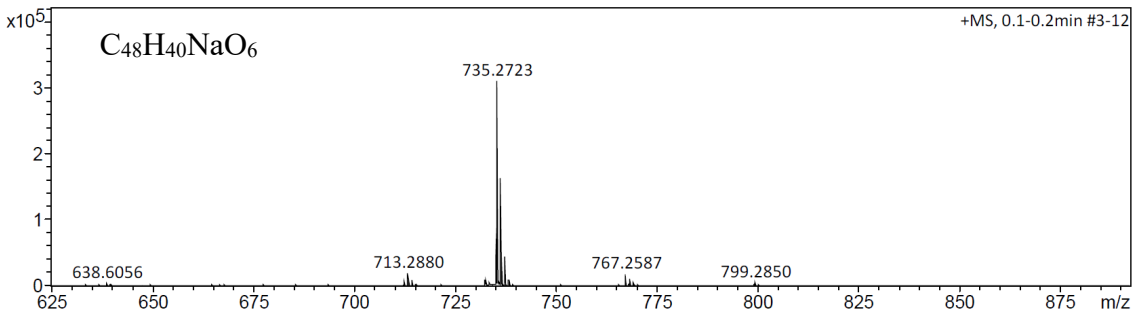


Fig. S24 High resolution ESI-TOF-MS spectrum of compound **8**.

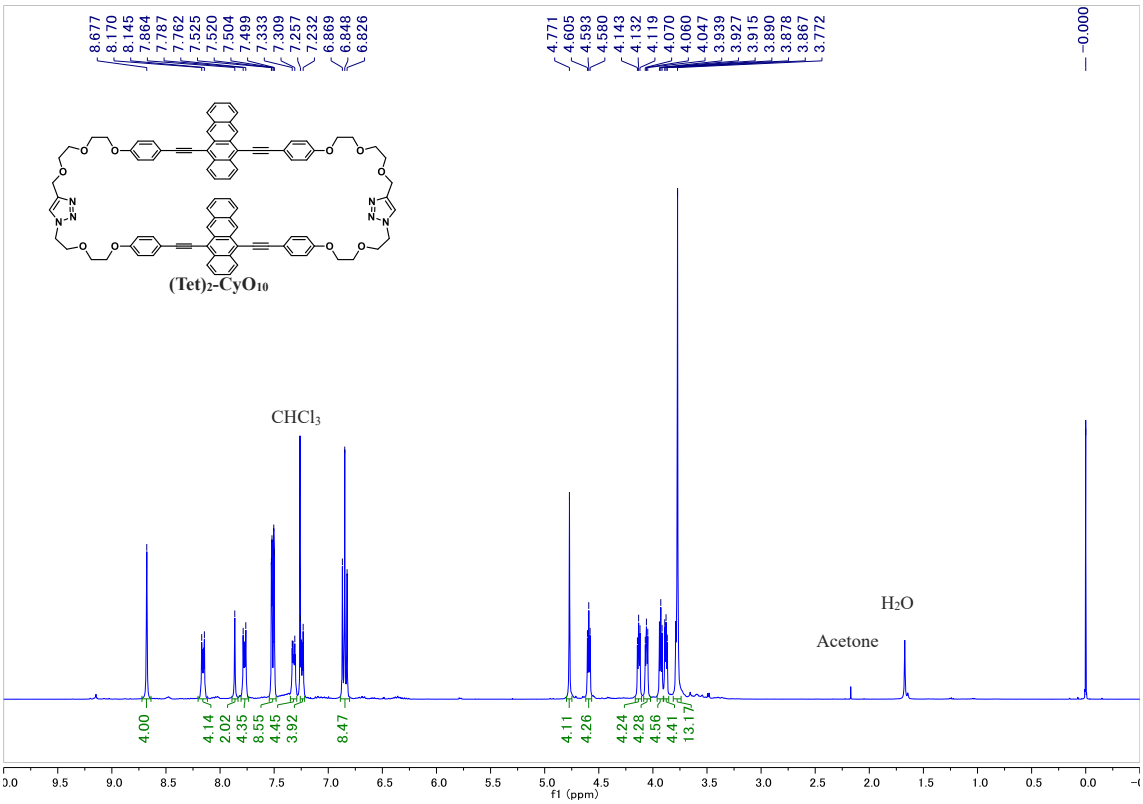


Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **(Tet)$_2$-CyO$_{10}$**.

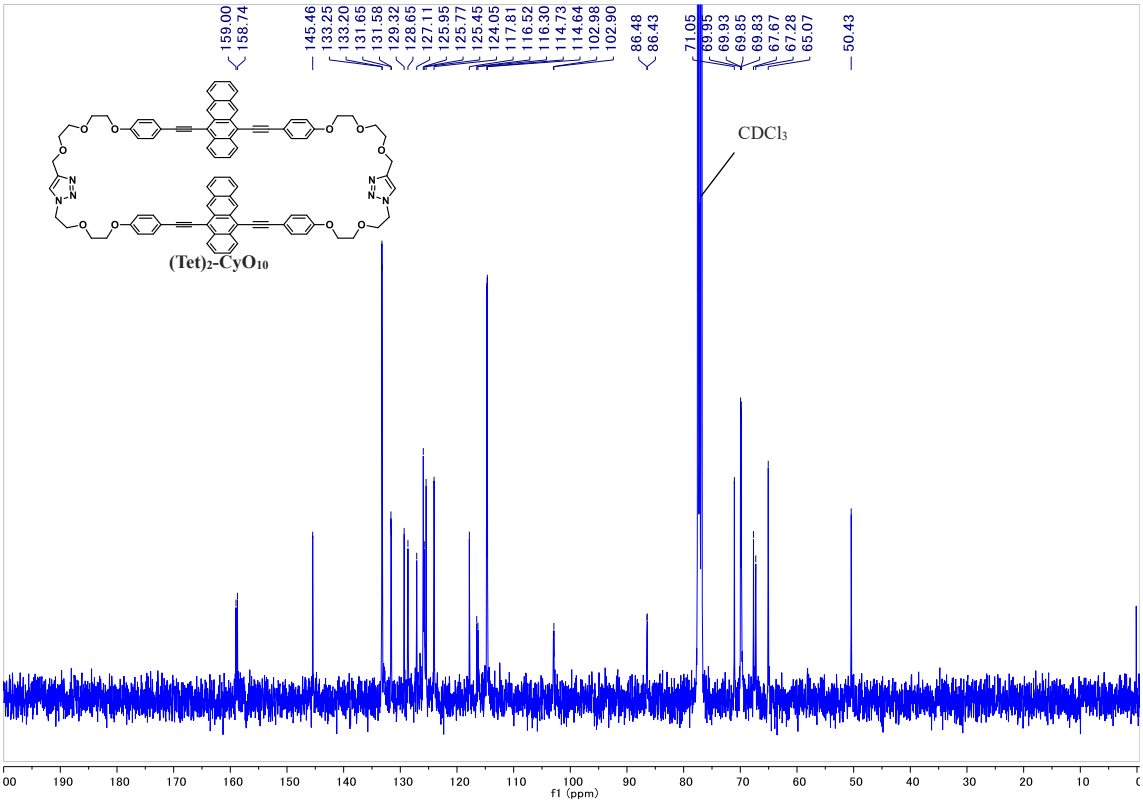


Fig. S26 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **(Tet)$_2$-CyO$_{10}$**.

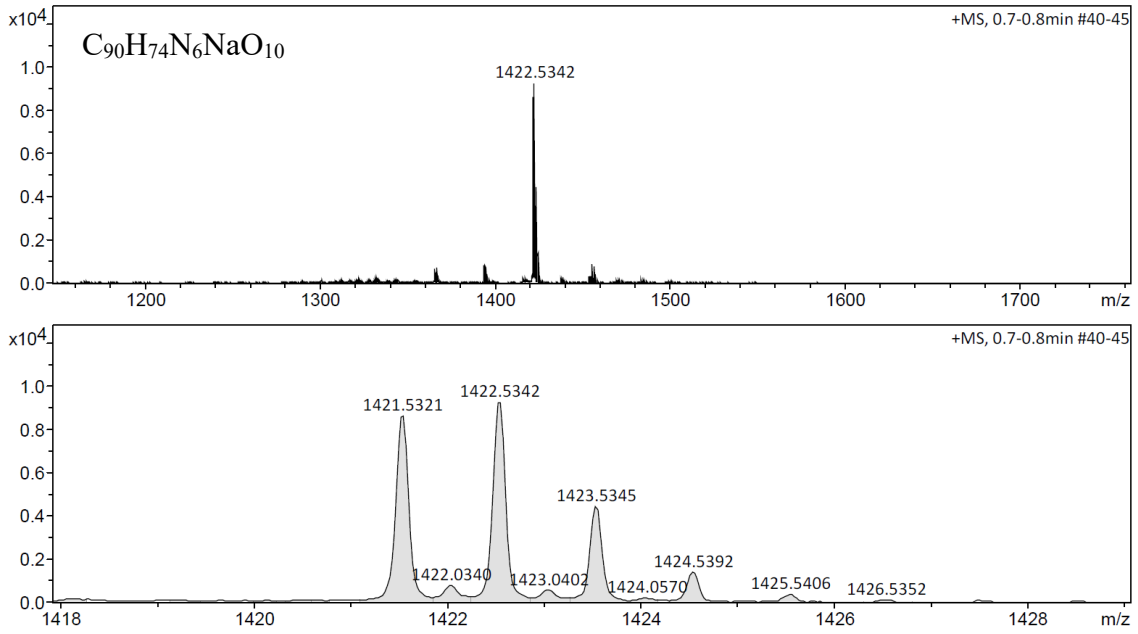


Fig. S27 High resolution ESI-TOF-MS spectrum of **(Tet)$_2$-CyO$_{10}$**.

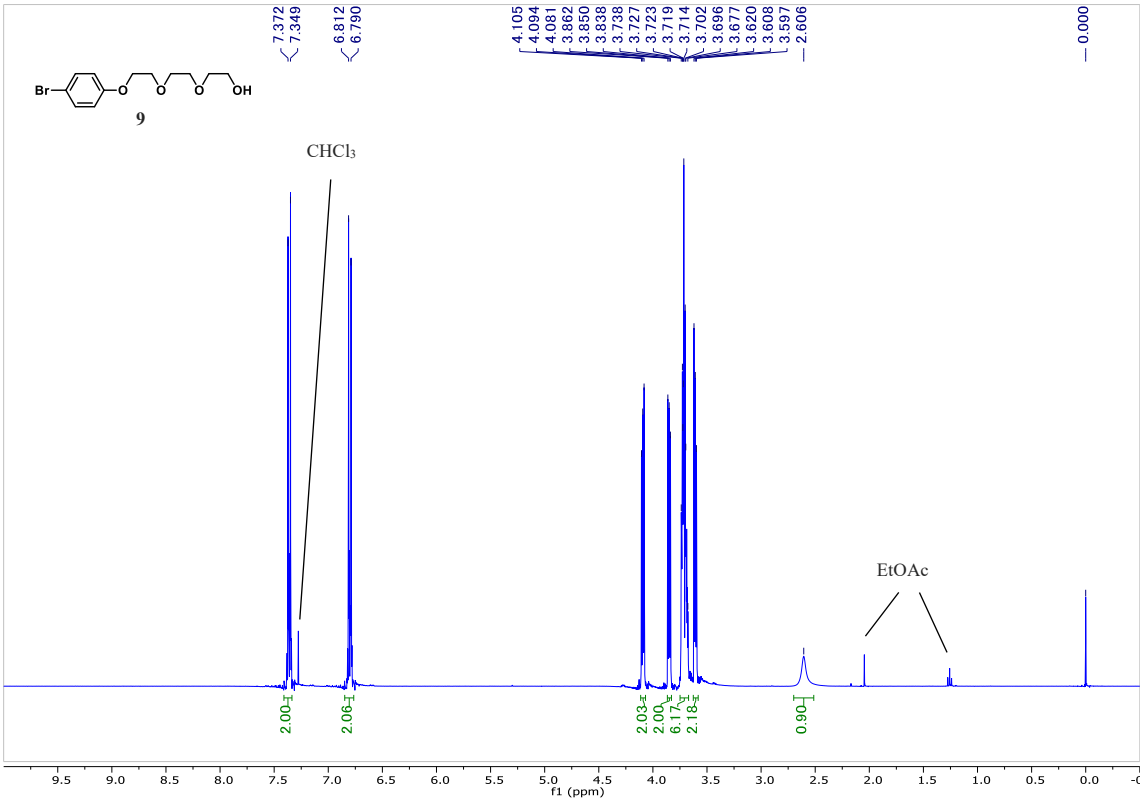


Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**.

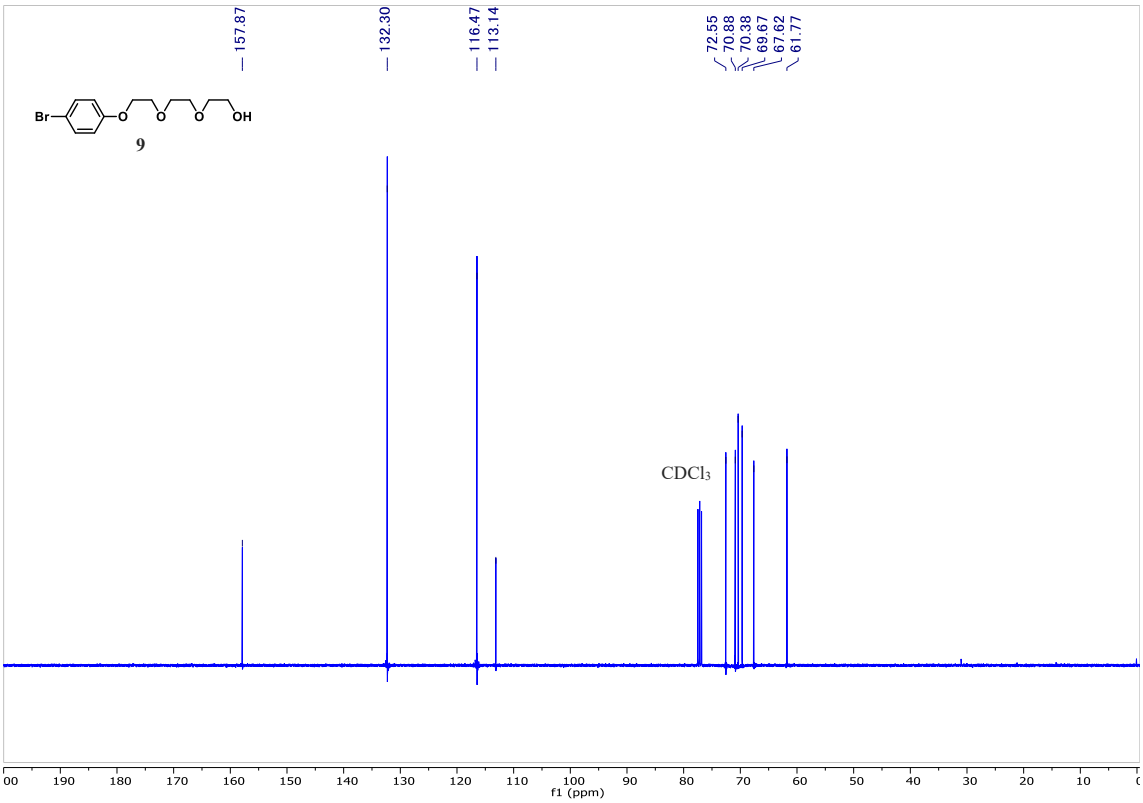


Fig. S29 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**.

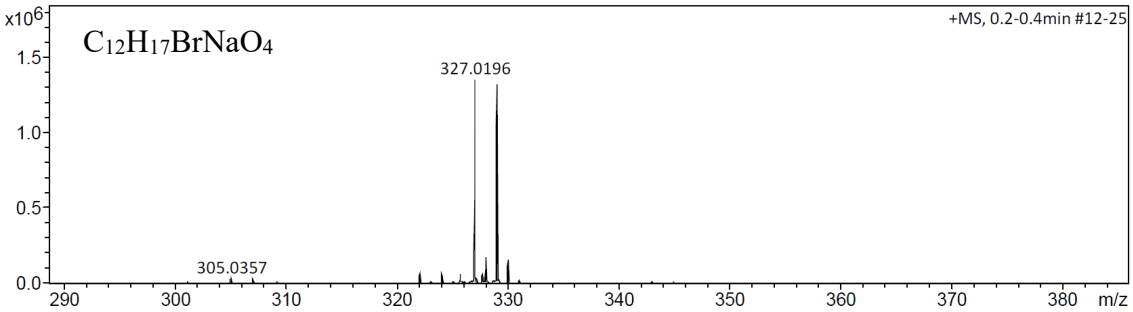


Fig. S30 High resolution ESI-TOF-MS spectrum of compound **9**.

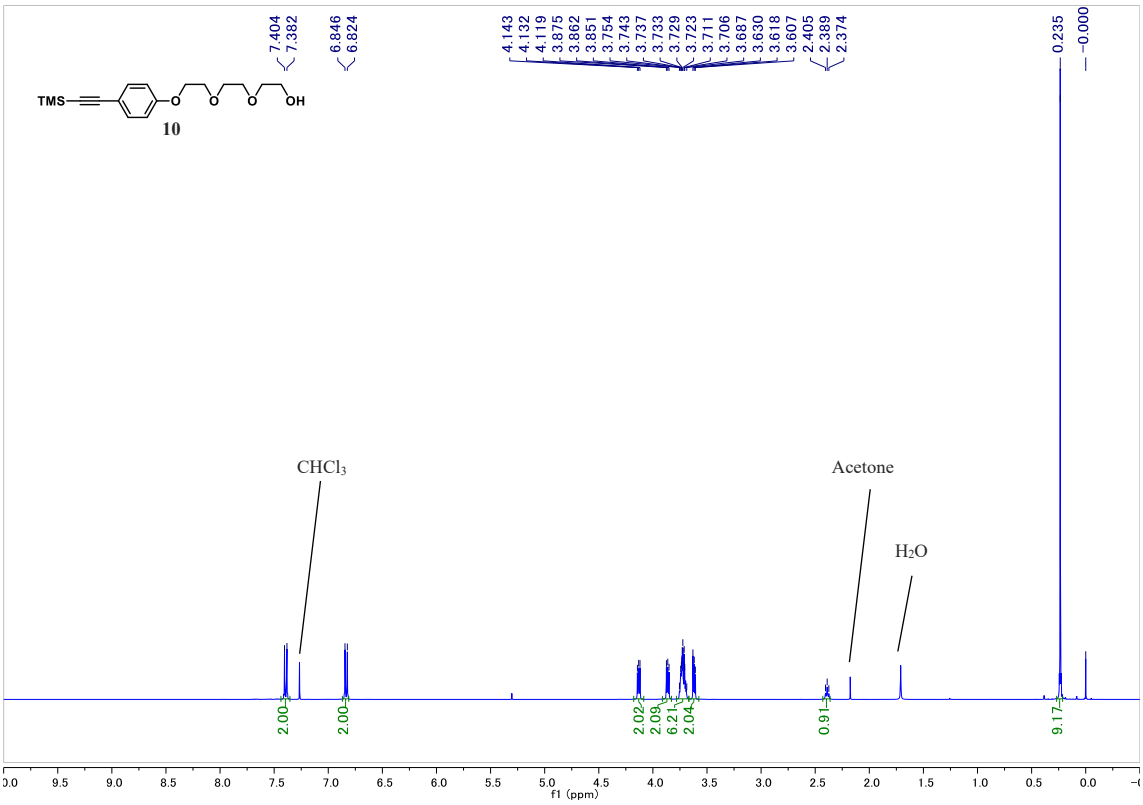


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **10**.

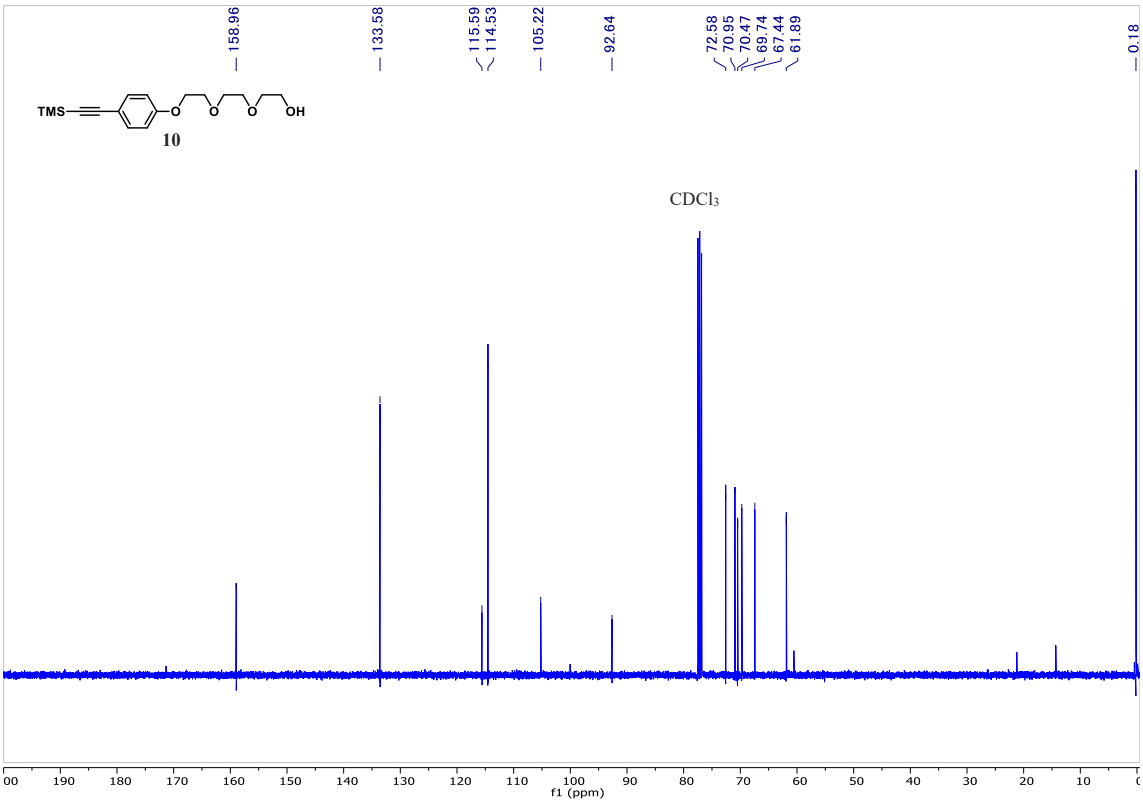


Fig. S32 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**.

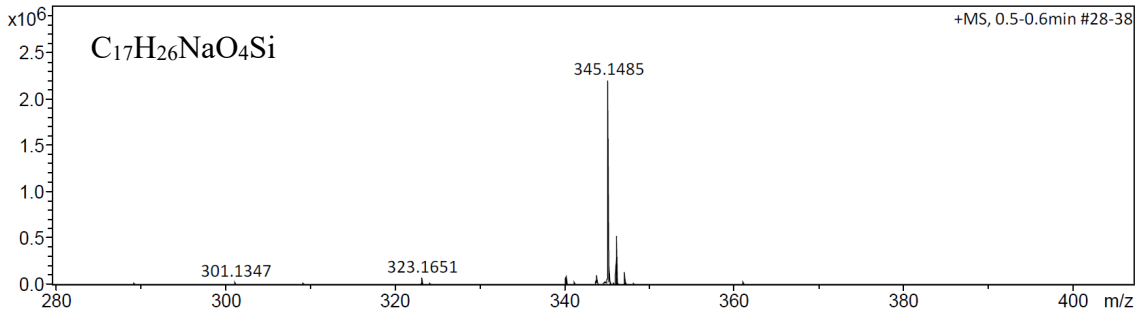


Fig. S33 High resolution ESI-TOF-MS spectrum of compound **10**.

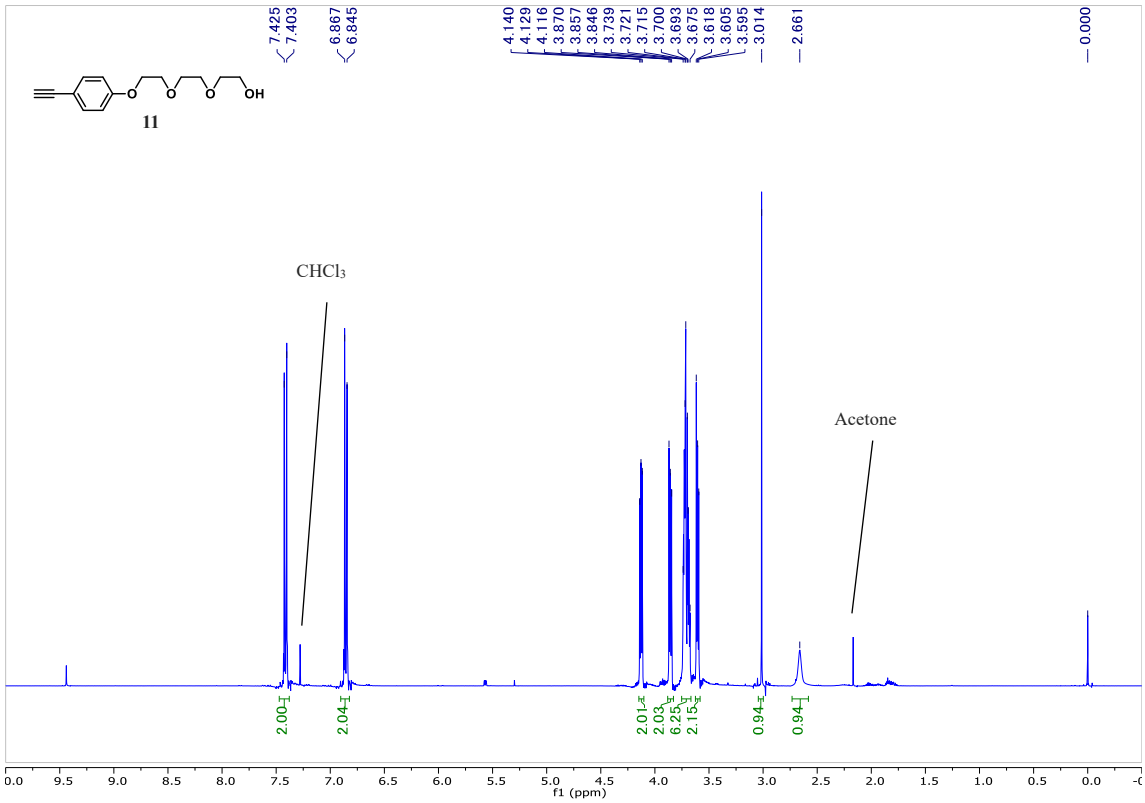


Fig. S34 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**.

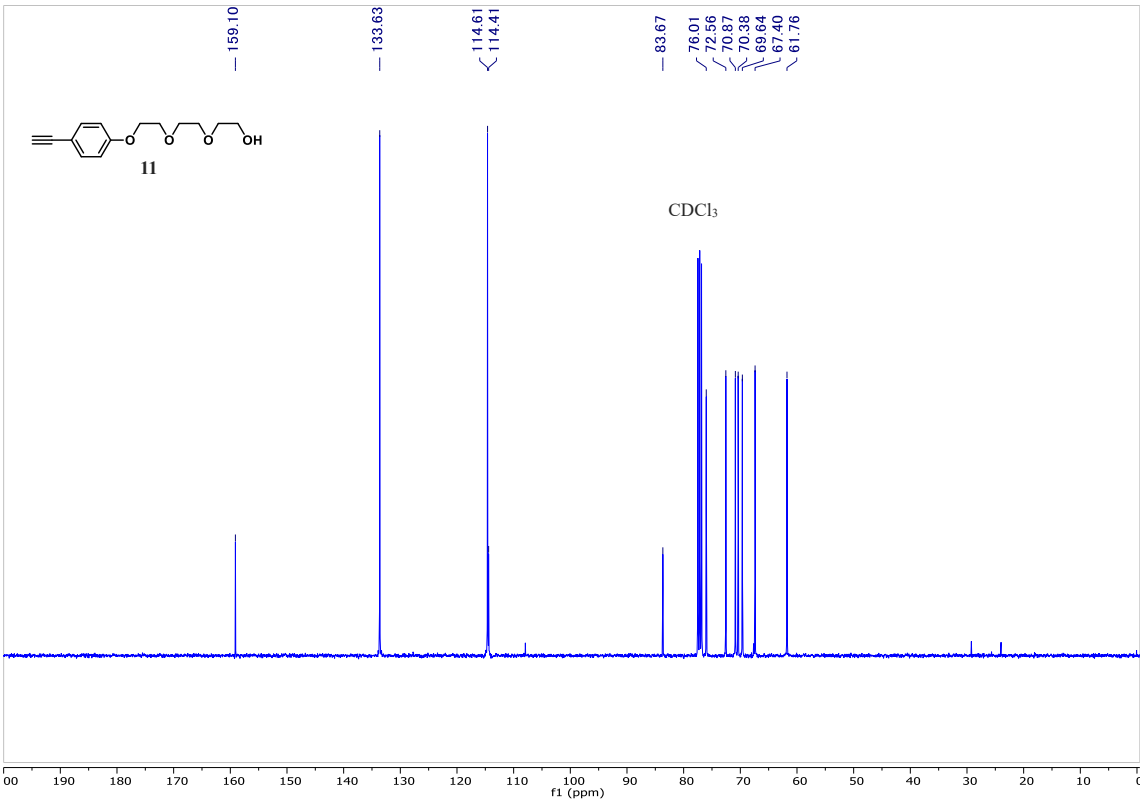


Fig. S35 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**.

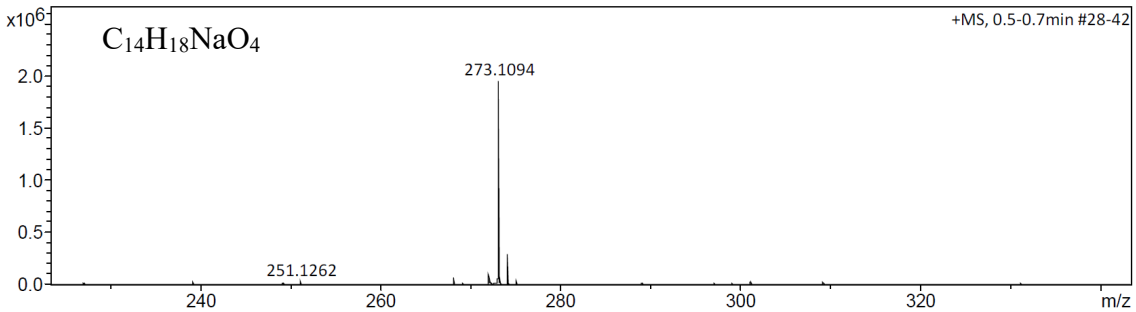


Fig. S36 High resolution ESI-TOF-MS spectrum of compound **11**.

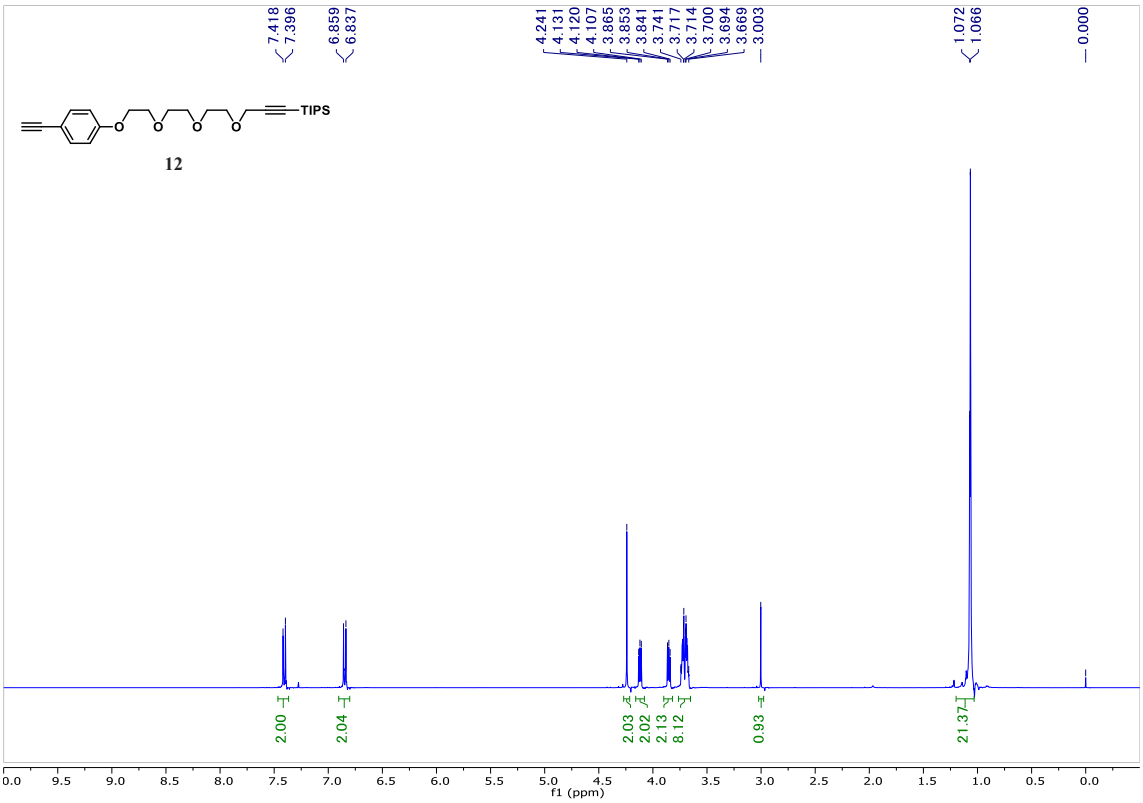


Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **12**.

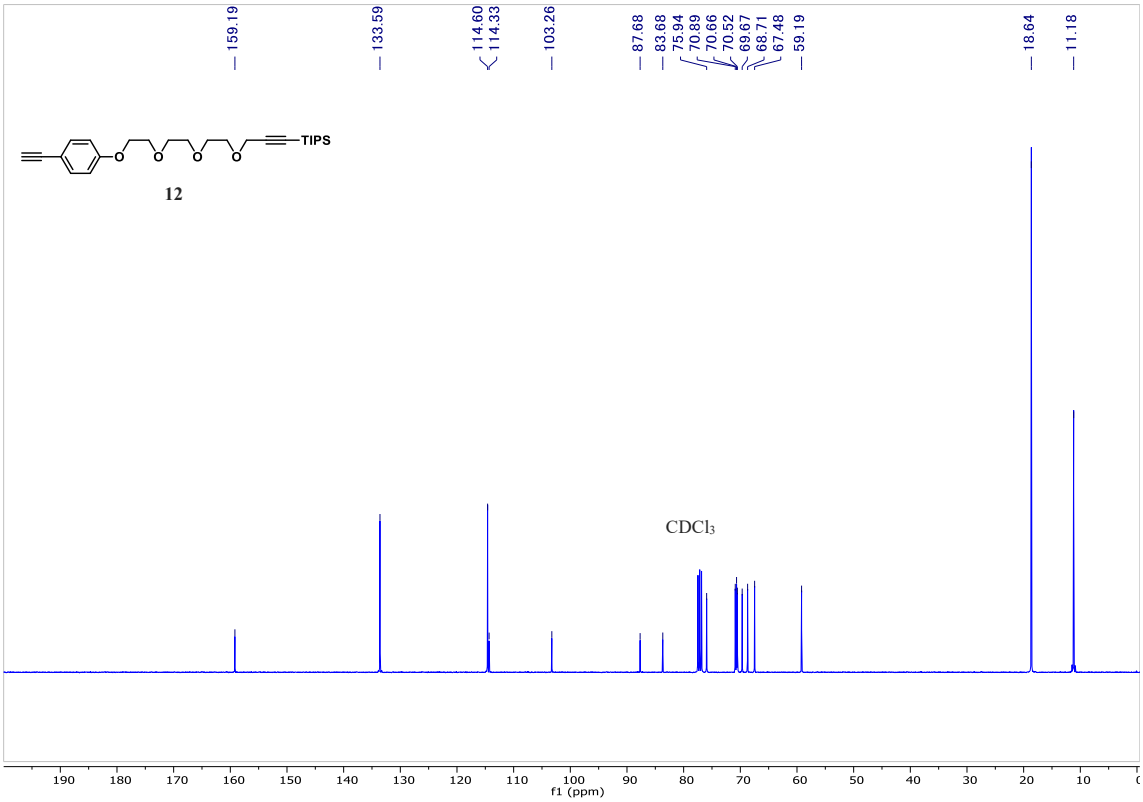


Fig. S38 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **12**.

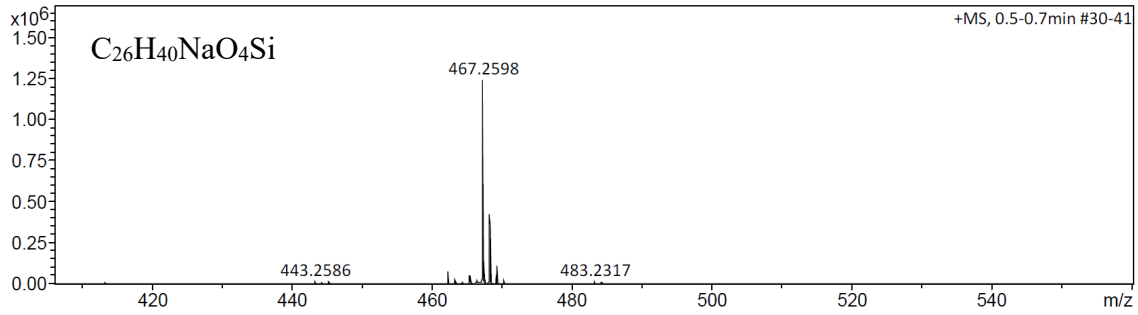


Fig. S39 High resolution ESI-TOF-MS spectrum of compound **12**.

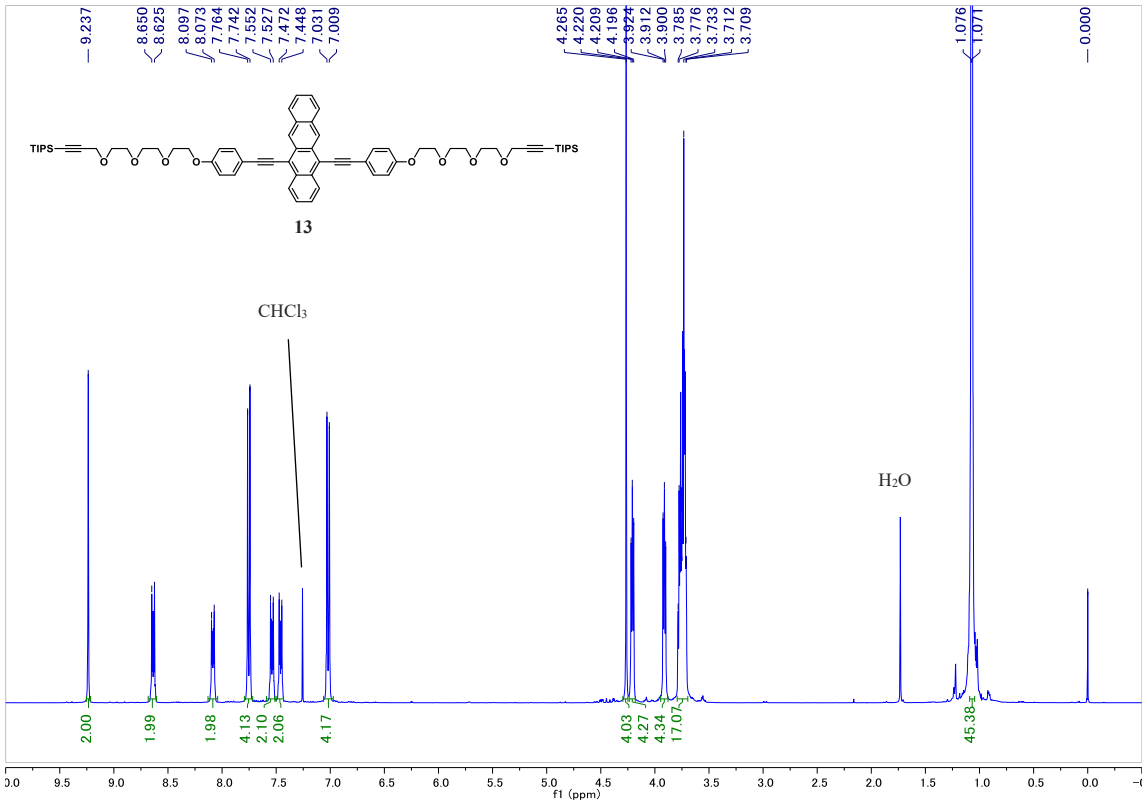


Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**.

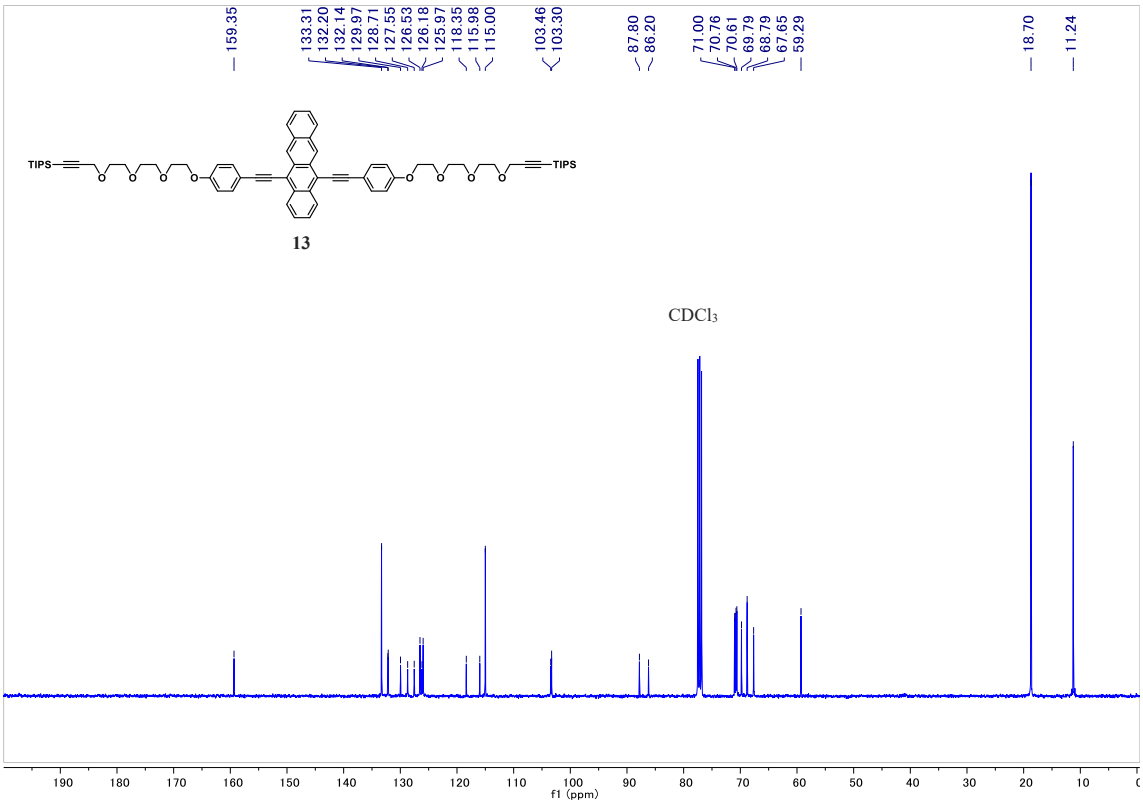


Fig. S41 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**.

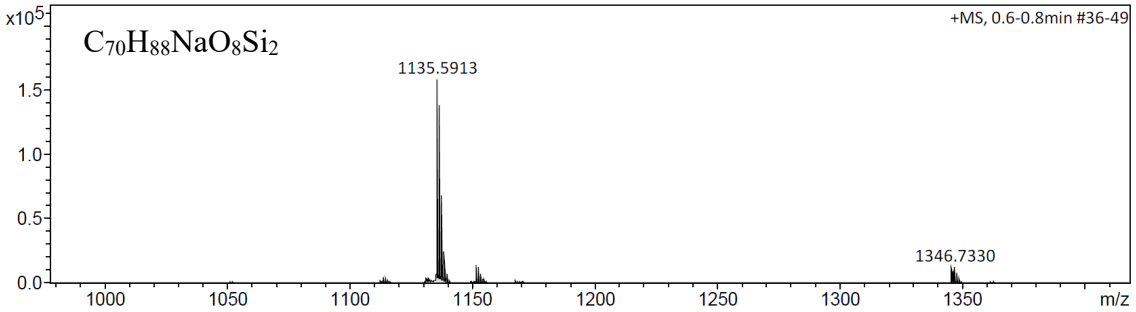


Fig. S42 High resolution ESI-TOF-MS spectrum of compound **13**.

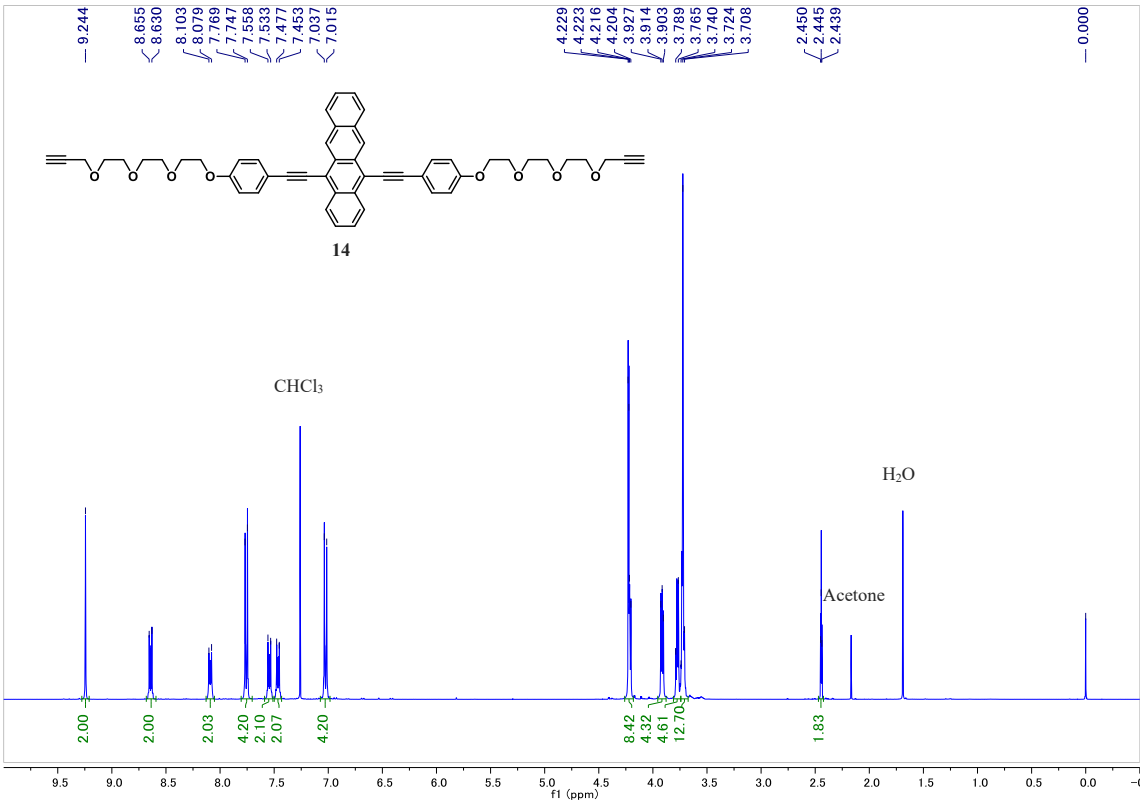


Fig. S43 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**.

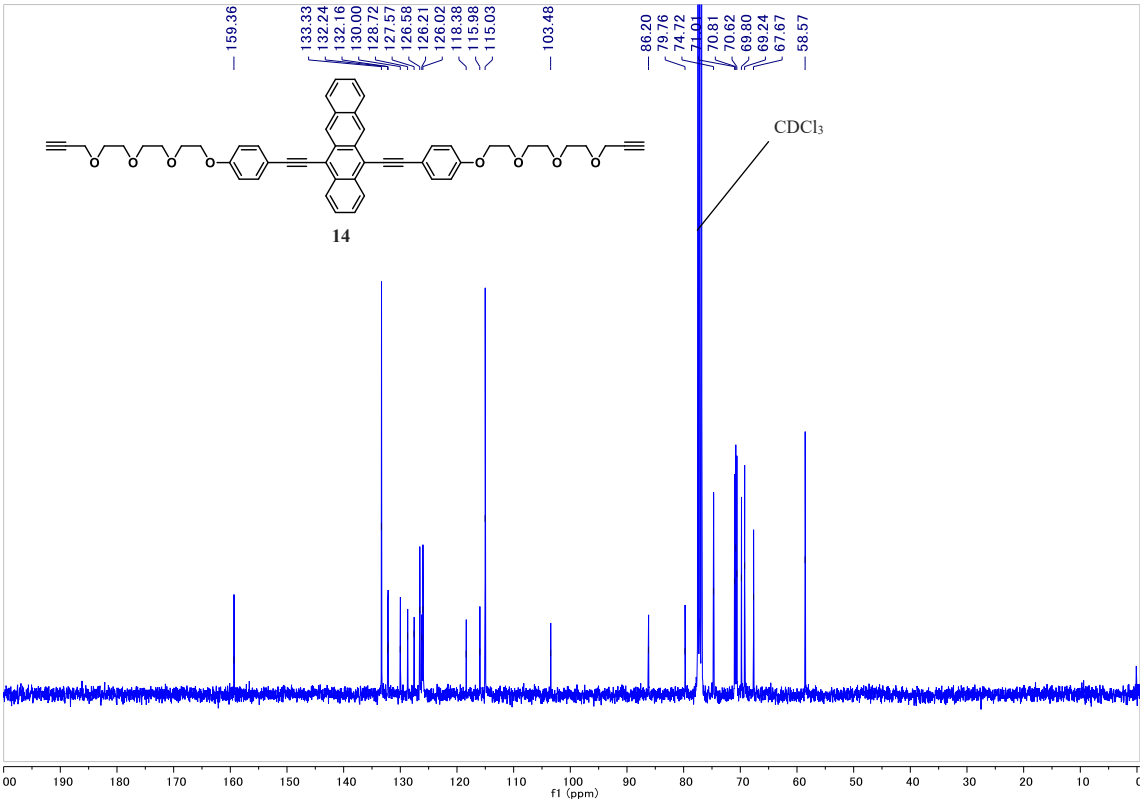


Fig. S44 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**.

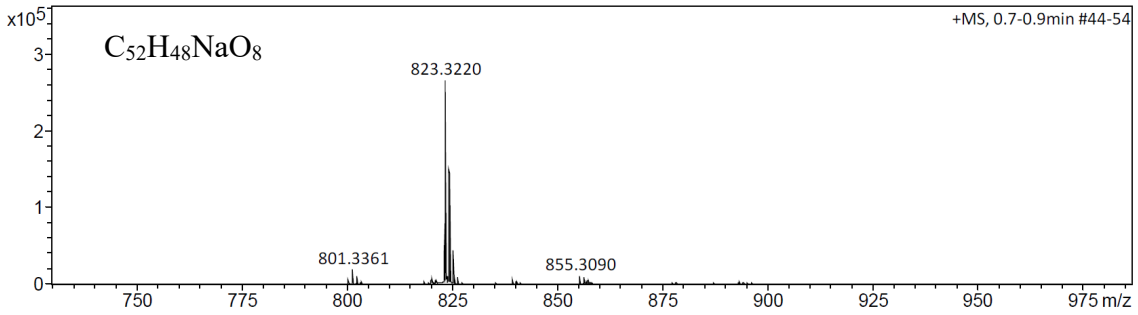


Fig. S45 High resolution ESI-TOF-MS spectrum of compound **14**.

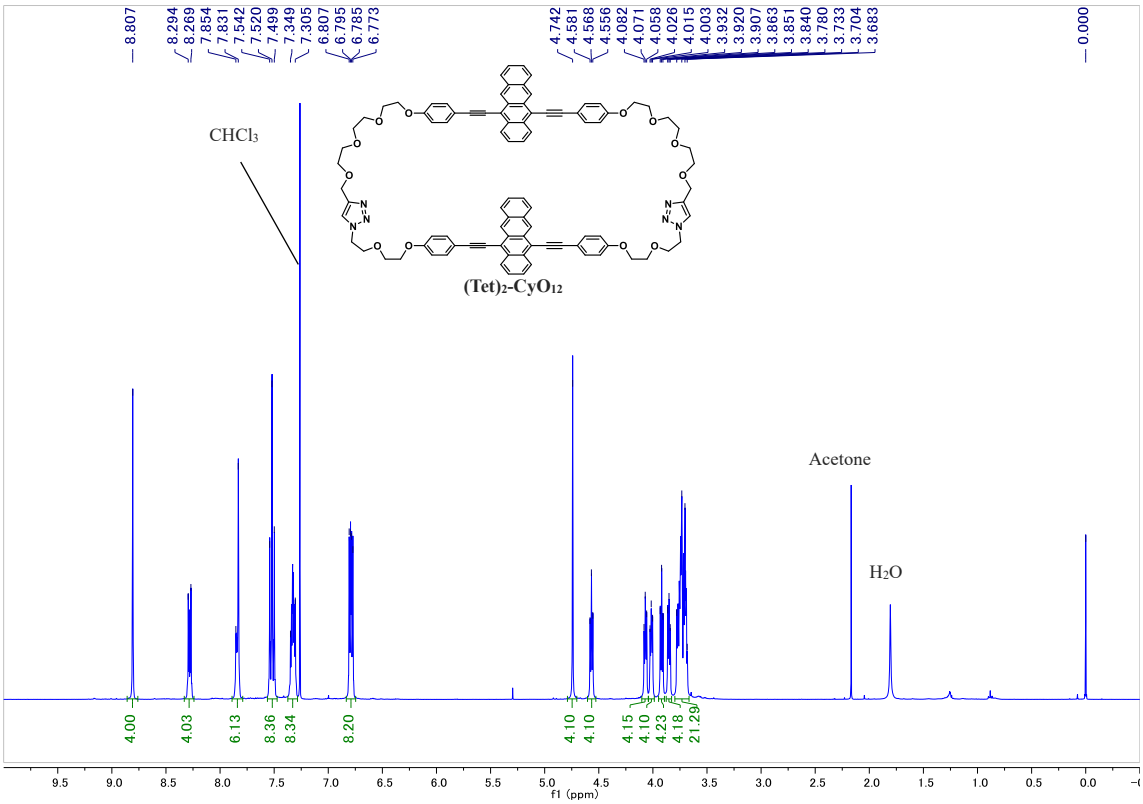


Fig. S46 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **(Tet)$_2$-CyO$_{12}$**.

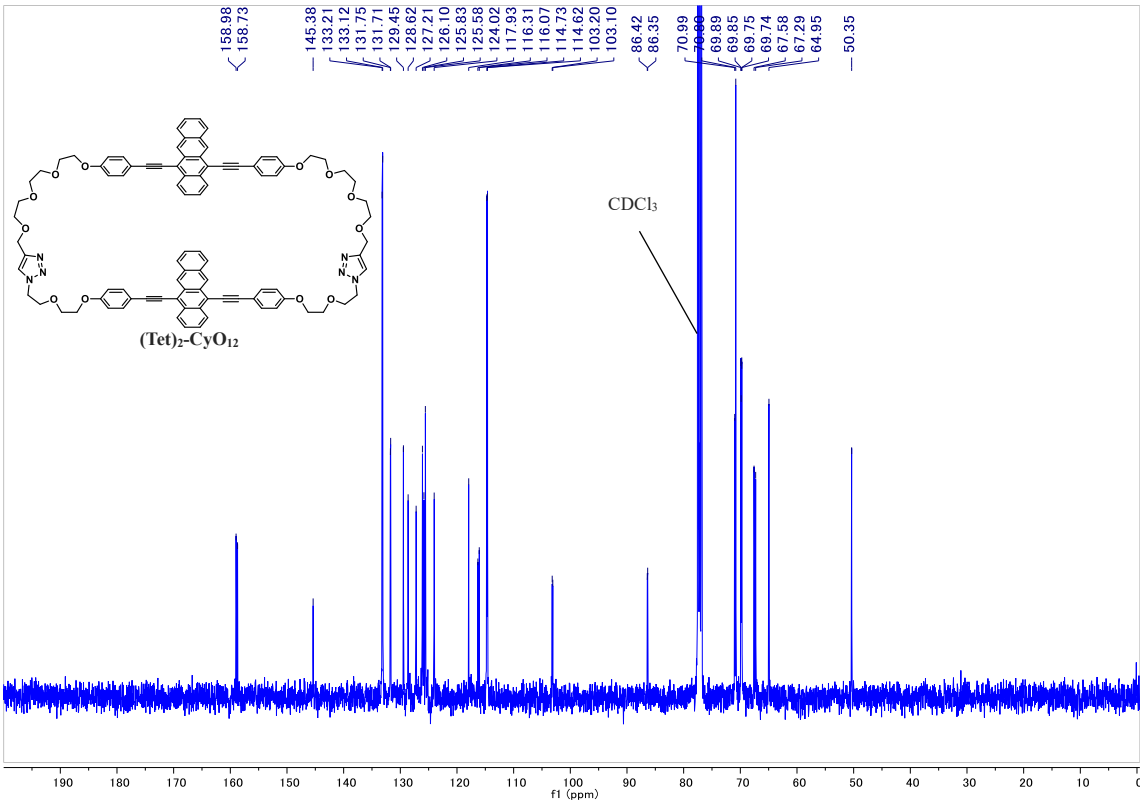


Fig. S47 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **(Tet)$_2$-CyO$_{12}$**.

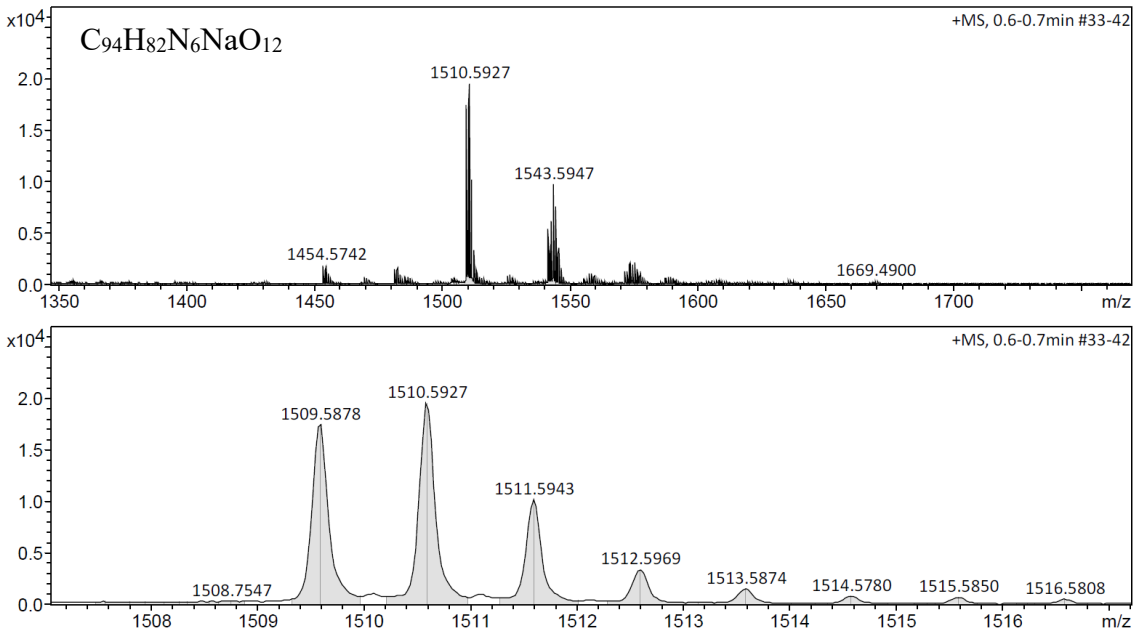


Fig. S48 High resolution ESI-TOF-MS spectrum of **(Tet)$_2$-CyO$_{12}$**.

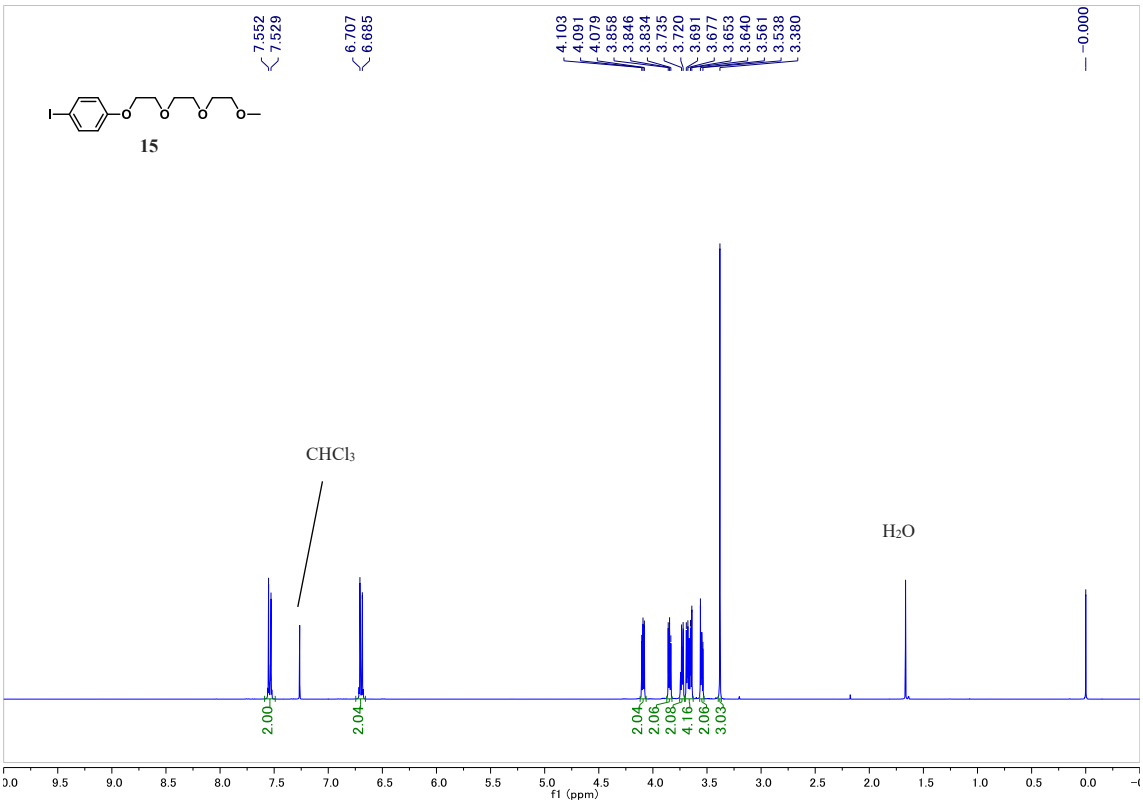


Fig. S49 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**.

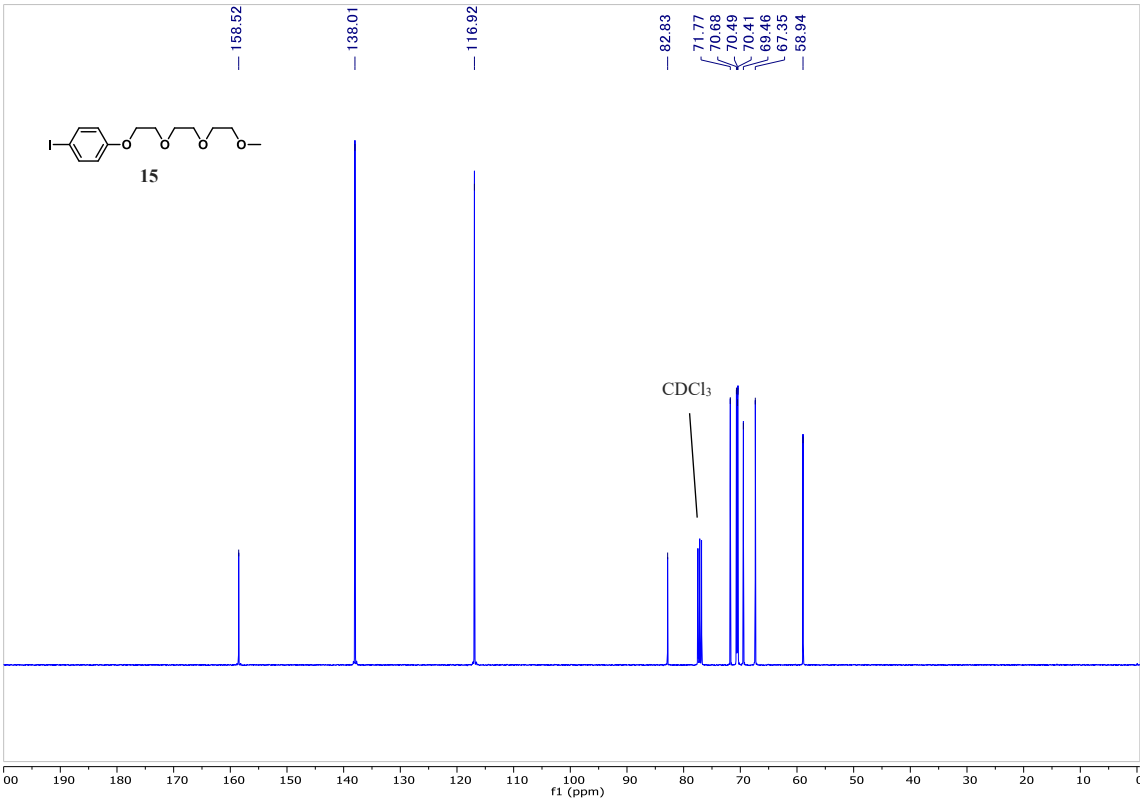


Fig. S50 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**.

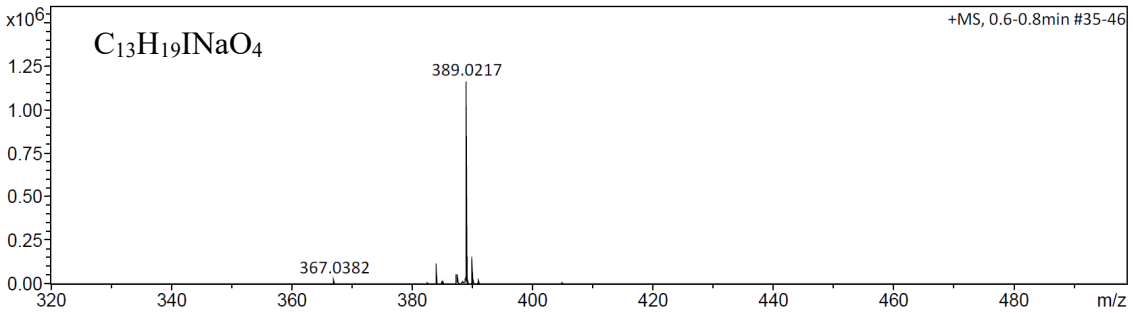


Fig. S51 High resolution ESI-TOF-MS spectrum of compound **15**.

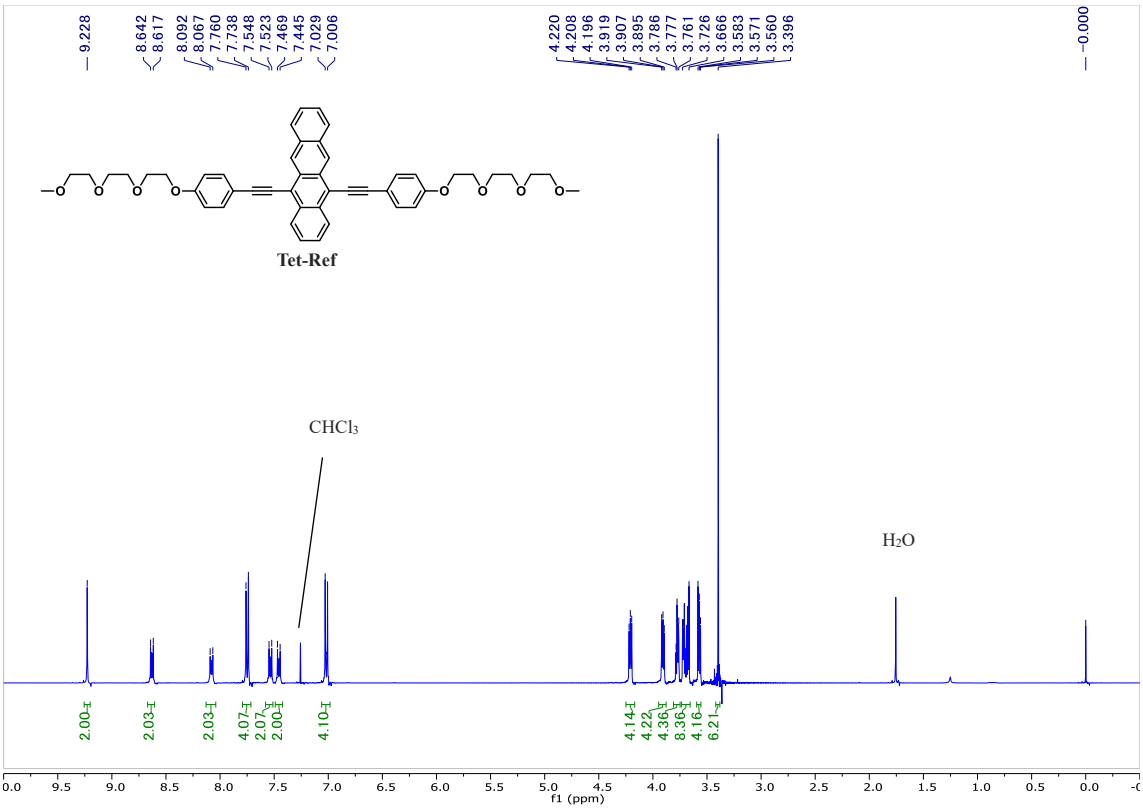


Fig. S52 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **Tet-ref**.

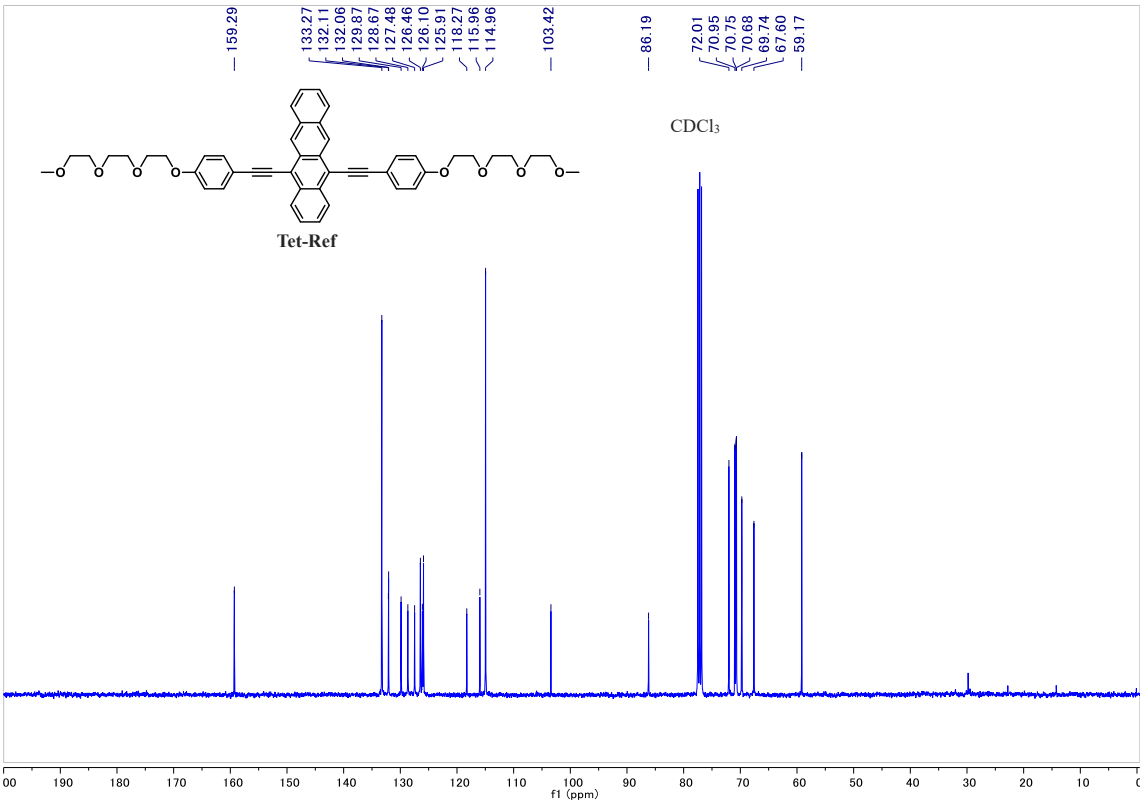


Fig. S53 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **Tet-ref**.

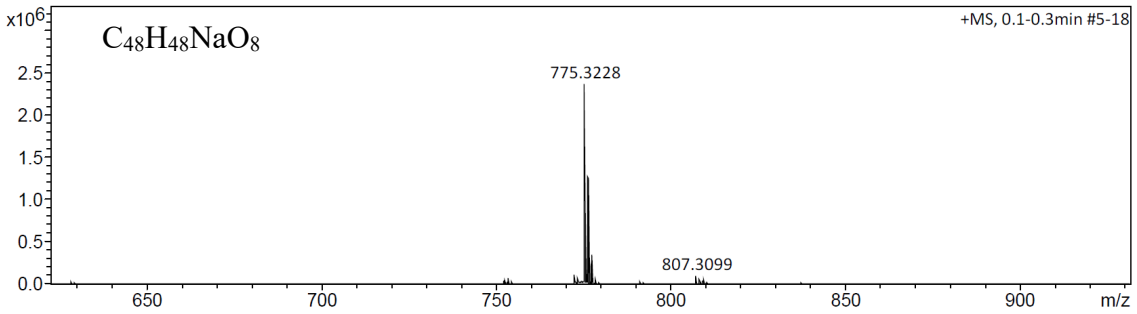


Fig. S54 High resolution ESI-TOF-MS spectrum of **Tet-ref**.

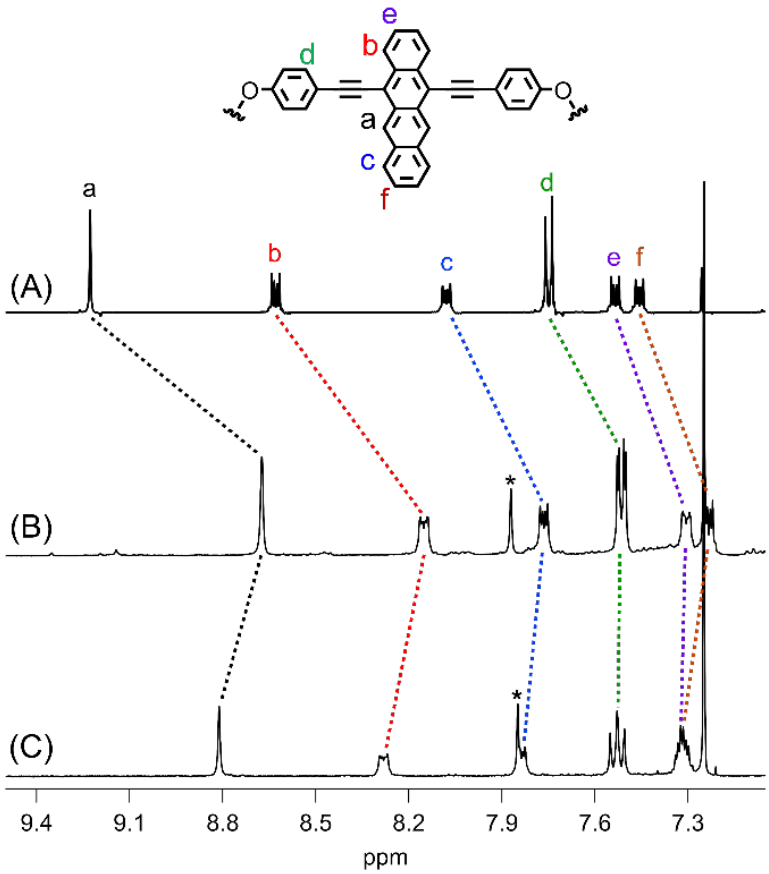


Fig. S55 ^{1}H NMR spectra of (A) Tet-ref, (B) $(Tet)_2$-CyO_{10} and (C) $(Tet)_2$-CyO_{12} in the range of 7.0-9.5 ppm (protons of phenylene and Tet units) in $CDCl_3$. The asterisk (*) shows the protons of the 1,2,3-triazole unit.

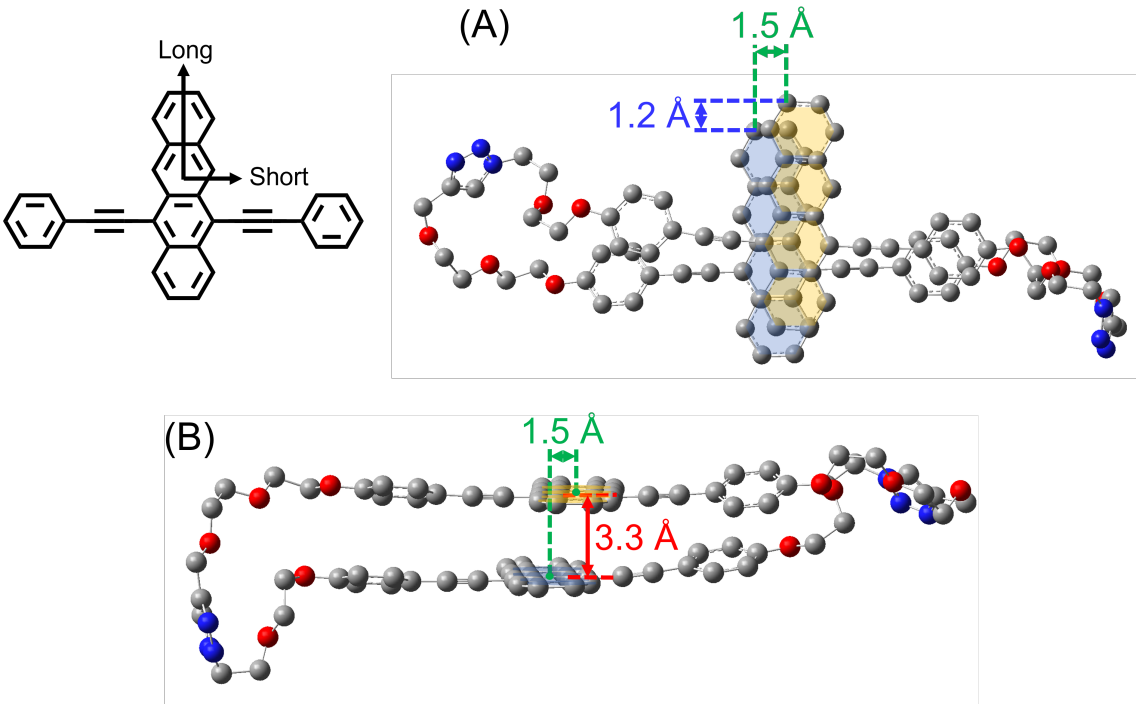


Fig. S56 The optimized structure of $(Tet)_2$-CyO_{10} calculated by DFT method at the ωB97XD/DGTZVP level. The oxygen and nitrogen atoms are highlighted in red and blue, respectively. The hydrogen atoms are omitted for simplicity. (A) Top view and (B) side view.

The π-stacking distance between two Tet units was estimated to be 3.3 Å (red arrow). The slip distance is 1.5 Å (green arrow) in the direction of short molecular axis, whereas the lateral displacement between the two Tet units is 1.2 Å (blue arrow) along the long molecular axis.

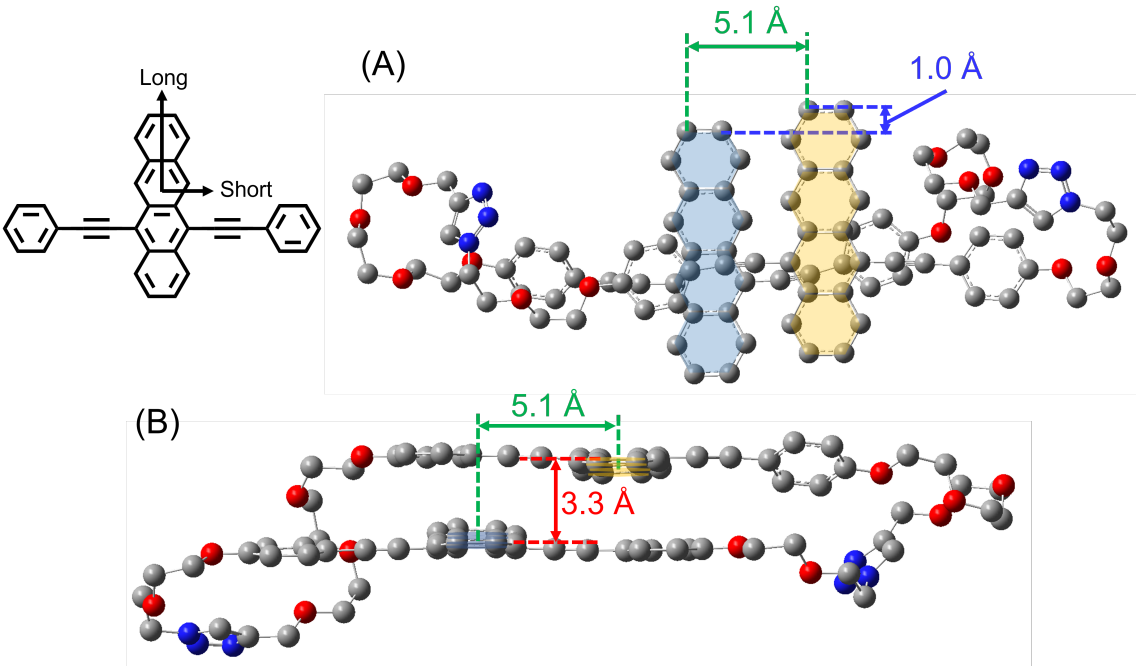
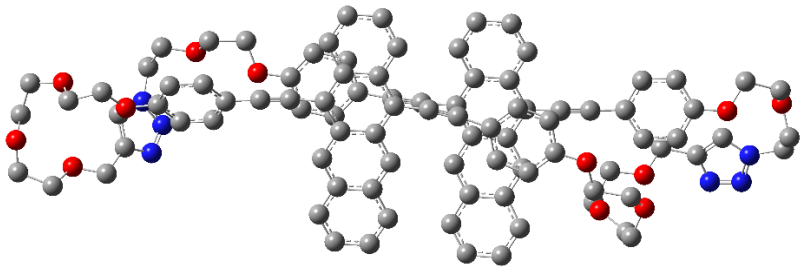


Fig. S57 The optimized structure of $(Tet)_2$-CyO_{12} calculated by DFT method at the ωB97XD/DGTZVP level. The oxygen and nitrogen atoms are highlighted in red and blue, respectively. The hydrogen atoms are omitted for simplicity. (A) Top view. (B) Side view.

The π-stacking distance between two Tet units was estimated to be 3.3 Å (red arrow). The slip distance is 5.1 Å (green arrow) in the direction of short molecular axis, whereas the lateral displacement between the two Tet units is 1.0 Å (blue arrow) along the long molecular axis.

Cartesian coordinates and energies of $(Tet)_2$-CyO_{12} optimized by ωB97XD/DGTZVP level



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	16.630035	-1.395687	0.872444
2	6	0	16.455991	-0.367415	-0.229108
3	8	0	15.834162	-1.046618	-1.356602
4	6	0	15.430111	-0.209710	-2.477735
5	6	0	14.080076	-0.690414	-2.958723
6	8	0	13.128958	-0.305586	-1.925532
7	8	0	6.221989	4.124527	-0.066770
8	6	0	-3.997604	3.004353	0.631209
9	6	0	-2.577103	3.283670	0.636150
10	6	0	-1.779852	2.717555	1.650526
11	6	0	-2.310075	1.896822	2.645862
12	6	0	-3.729293	1.610304	2.636714
13	6	0	-4.525113	2.169358	1.636318
14	6	0	-1.500091	1.325197	3.683625
15	6	0	-2.052335	0.518910	4.642969
16	6	0	-3.454469	0.231350	4.631063
17	6	0	-4.264240	0.760649	3.662323
18	6	0	-4.830459	3.575799	-0.388330
19	6	0	-4.270557	4.444800	-1.356479
20	6	0	-2.851148	4.718863	-1.354234
21	6	0	-2.011880	4.123265	-0.381974
22	6	0	-5.078528	5.057701	-2.368860

23	6	0	-4.532959	5.886342	-3.312955
24	6	0	-3.132319	6.154101	-3.312243
25	6	0	-2.322588	5.585356	-2.365746
26	6	0	-0.606552	4.309217	-0.411783
27	6	0	-6.206057	3.233911	-0.422774
28	6	0	0.608731	4.370719	-0.393779
29	6	0	-7.366176	2.866596	-0.415502
30	6	0	2.028692	4.317151	-0.316824
31	6	0	-8.691927	2.354224	-0.354841
32	6	0	2.643568	3.208269	0.299380
33	6	0	4.028098	3.109711	0.397862
34	6	0	4.829959	4.131390	-0.122143
35	6	0	4.241966	5.243332	-0.740378
36	6	0	2.859790	5.334965	-0.838132
37	6	0	-9.762466	2.955014	-1.044262
38	6	0	-11.055663	2.433105	-0.969152
39	6	0	-11.298241	1.295264	-0.190930
40	6	0	-10.245188	0.677423	0.498058
41	6	0	-8.963661	1.197327	0.416602
42	8	0	-12.546333	0.693685	-0.036404
43	6	0	2.939913	-1.559464	-0.476202
44	6	0	4.379381	-1.448578	-0.597895
45	6	0	5.117881	-0.976069	0.505659
46	6	0	4.512722	-0.616931	1.710841
47	6	0	3.073921	-0.737433	1.835610
48	6	0	2.335198	-1.198323	0.744370
49	6	0	5.268477	-0.128788	2.831464
50	6	0	4.638281	0.209429	4.000426
51	6	0	3.218428	0.080761	4.129790
52	6	0	2.462439	-0.376567	3.083200
53	6	0	2.164425	-2.024579	-1.590006
54	6	0	2.814860	-2.420943	-2.787466
55	6	0	4.250806	-2.313613	-2.906658
56	6	0	5.020623	-1.812648	-1.828392
57	6	0	2.077649	-2.925193	-3.907872
58	6	0	2.703770	-3.299741	-5.066814

59	6	0	4.119771	-3.188923	-5.185426
60	6	0	4.863251	-2.710203	-4.139936
61	6	0	6.422717	-1.646138	-1.955403
62	6	0	0.749540	-2.054240	-1.508543
63	6	0	7.623036	-1.458589	-2.027022
64	6	0	-0.467709	-2.035571	-1.484896
65	6	0	9.019646	-1.187022	-2.049302
66	6	0	-1.888372	-1.974619	-1.525802
67	6	0	9.591632	-0.361628	-1.050676
68	6	0	10.949117	-0.084950	-1.053482
69	6	0	11.774083	-0.626515	-2.045931
70	6	0	11.235193	-1.436628	-3.049918
71	6	0	9.865401	-1.710590	-3.046711
72	6	0	-2.577894	-2.266731	-2.719428
73	6	0	-3.964724	-2.160346	-2.799415
74	6	0	-4.694917	-1.755485	-1.674989
75	6	0	-4.030991	-1.483451	-0.470677
76	6	0	-2.650226	-1.589788	-0.396534
77	8	0	-6.076118	-1.583623	-1.661499
78	6	0	-6.801061	-1.694876	-2.920604
79	6	0	-8.251606	-1.344148	-2.691896
80	8	0	-8.936574	-2.481043	-2.095224
81	6	0	-10.373124	-2.468616	-2.296205
82	6	0	-10.962738	-3.685096	-1.594792
83	7	0	-11.195995	-3.496383	-0.166808
84	6	0	-12.076500	-2.660952	0.454045
85	6	0	-11.934660	-2.931783	1.802201
86	7	0	-10.979713	-3.918909	1.957811
87	7	0	-10.515554	-4.273571	0.763612
88	6	0	-12.667602	-2.356517	2.956302
89	6	0	-14.919106	0.456771	-0.315925
90	6	0	-13.704177	1.246808	-0.731690
91	8	0	-14.097799	-2.619122	2.762470
92	6	0	-15.000862	-1.769574	3.515958
93	6	0	-16.392464	-1.947998	2.938072
94	8	0	-16.493782	-1.441345	1.574839

95	6	0	-16.159950	-2.409384	0.528155
96	6	0	-16.051746	-1.676235	-0.791041
97	8	0	-14.842068	-0.867081	-0.920362
98	8	0	9.115826	2.138286	1.055501
99	6	0	9.356378	2.275059	2.488873
100	6	0	9.870743	0.963682	3.026178
101	8	0	8.750393	0.028921	3.111313
102	6	0	9.044254	-1.228520	3.784890
103	6	0	9.754025	-2.245292	2.914798
104	8	0	11.141915	-1.840583	2.736776
105	6	0	6.891233	2.975769	0.535953
106	6	0	8.386066	3.241709	0.442447
107	6	0	11.956609	-2.882944	2.104348
108	7	0	15.422544	-2.182771	2.856285
109	7	0	14.201133	-2.594976	3.167391
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116	1	0	17.440579	0.018531	-0.513861
117	1	0	16.170367	-0.294373	-3.278358
118	1	0	15.351692	0.836156	-2.171197
119	1	0	13.815557	-0.214841	-3.907889
120	1	0	14.092948	-1.774897	-3.086999
121	1	0	-0.721475	2.936557	1.660367
122	1	0	-5.586160	1.962989	1.634906
123	1	0	-0.440568	1.549510	3.692820
124	1	0	-1.432820	0.093920	5.421560
125	1	0	-3.869359	-0.408904	5.398021
126	1	0	-5.325750	0.546646	3.654554
127	1	0	-6.139055	4.849893	-2.369280
128	1	0	-5.163066	6.340984	-4.065987
129	1	0	-2.712447	6.807565	-4.065307
130	1	0	-1.259804	5.780968	-2.363618

131	1	0	2.028220	2.411378	0.692072
132	1	0	4.458043	2.239267	0.868035
133	1	0	4.886042	6.015878	-1.134699
134	1	0	2.409527	6.194566	-1.314845
135	1	0	-9.578540	3.838471	-1.639844
136	1	0	-11.852499	2.917880	-1.512913
137	1	0	-10.452522	-0.208691	1.079292
138	1	0	-8.152741	0.707763	0.936673
139	1	0	6.192661	-0.897656	0.417930
140	1	0	1.261256	-1.288398	0.835577
141	1	0	6.344272	-0.031022	2.736330
142	1	0	5.215042	0.576476	4.839187
143	1	0	2.746768	0.348066	5.066327
144	1	0	1.388428	-0.478262	3.179791
145	1	0	1.004836	-3.008895	-3.815158
146	1	0	2.125550	-3.681668	-5.897657
147	1	0	4.604366	-3.485138	-6.106336
148	1	0	5.936743	-2.622951	-4.226085
149	1	0	8.975371	0.074379	-0.278028
150	1	0	11.380939	0.554241	-0.298685
151	1	0	11.858664	-1.856853	-3.825557
152	1	0	9.446508	-2.339249	-3.820287
153	1	0	-2.016422	-2.568328	-3.592859
154	1	0	-4.456288	-2.390763	-3.732024
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156	1	0	-2.145150	-1.362144	0.531403
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160	1	0	-8.336067	-0.464560	-2.049798
161	1	0	-10.593899	-2.533521	-3.369773
162	1	0	-10.814168	-1.543496	-1.911894
163	1	0	-10.272148	-4.519760	-1.684613
164	1	0	-11.908382	-3.959179	-2.065953
165	1	0	-12.718234	-1.970765	-0.065606
166	1	0	-12.314609	-2.823556	3.877951

167	1	0	-12.522047	-1.272553	3.025916
168	1	0	-15.816039	0.970697	-0.683254
169	1	0	-14.985644	0.381685	0.767630
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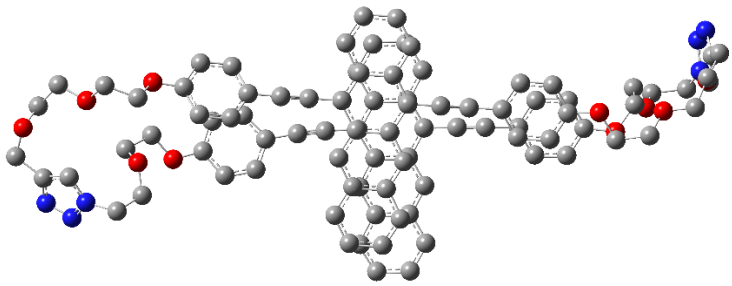
171	1	0	-13.557284	1.178546	-1.812032
172	1	0	-14.693206	-0.721752	3.427187
173	1	0	-14.999393	-2.046068	4.578486
174	1	0	-17.107448	-1.368758	3.522843
175	1	0	-16.681348	-3.002586	2.973178
176	1	0	-15.225276	-2.909763	0.771247
177	1	0	-16.963780	-3.154457	0.457569
178	1	0	-16.935567	-1.048527	-0.947006
179	1	0	-15.989757	-2.402693	-1.601359
180	1	0	8.437744	2.548805	3.014666
181	1	0	10.104749	3.059035	2.653366
182	1	0	10.657233	0.556428	2.392839
183	1	0	10.282358	1.122060	4.030267
184	1	0	8.070142	-1.623251	4.073021
185	1	0	9.634465	-1.042360	4.688129
186	1	0	9.718906	-3.223632	3.413055
187	1	0	9.253428	-2.329634	1.944495
188	1	0	6.578757	2.867318	1.577020
189	1	0	6.637273	2.063175	-0.005534
190	1	0	8.701826	3.279284	-0.596916
191	1	0	8.635968	4.192403	0.921245
192	1	0	11.863344	-3.798921	2.696035
193	1	0	11.580455	-3.074242	1.094710
194	1	0	13.875370	-1.703240	0.001792

Total Energy : -4861.04759561 Hartree, Imaginary Freq : 0

Cartesian coordinates and energies of $(Tet)_2$-CyO_{10} optimized by ωB97XD/DGTZVP level



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	6.158621	4.338067	1.423099
4	6	0	7.548607	4.344686	1.508251
5	6	0	8.298523	5.096404	0.593208
6	6	0	7.637430	5.832019	-0.404774
7	6	0	6.255282	5.821988	-0.482557
8	6	0	-6.233867	5.788376	-0.740879
9	6	0	-7.617699	5.813641	-0.713667
10	6	0	-8.319762	5.178540	0.324507
11	6	0	-7.609165	4.512359	1.332469
12	6	0	-6.217093	4.489219	1.297526
13	6	0	5.480530	5.074149	0.433741
14	6	0	-5.498505	5.124728	0.268006
15	6	0	4.061385	5.069447	0.365263
16	6	0	-4.077852	5.103932	0.247963
17	6	0	-2.857864	5.089771	0.239490
18	6	0	2.842111	5.067157	0.319369
19	6	0	1.425302	6.732712	-1.551270
20	6	0	0.751380	7.532601	-2.434331
21	6	0	-0.672256	7.539122	-2.453116
22	6	0	-1.376617	6.745155	-1.588650

23	6	0	1.426319	5.062109	0.286153
24	6	0	0.729425	5.887375	-0.631511
25	6	0	-0.713144	5.893199	-0.651223
26	6	0	-1.441659	5.073214	0.246490
27	6	0	1.359578	3.380271	2.106111
28	6	0	0.699651	4.220632	1.191493
29	6	0	-0.747160	4.226021	1.171278
30	6	0	-1.438894	3.389695	2.066053
31	6	0	1.337820	1.692360	3.917263
32	6	0	0.667663	2.552772	2.988965
33	6	0	-0.778176	2.557380	2.968070
34	6	0	-1.480237	1.700859	3.876281
35	6	0	-0.800864	0.893452	4.746841
36	6	0	0.628620	0.889187	4.767719
37	8	0	-9.644968	-4.639784	-0.694553
38	8	0	9.646816	-4.580751	-1.033218
39	6	0	6.250790	-4.972229	0.170772
40	6	0	7.627807	-5.059884	0.055217
41	6	0	8.293617	-4.413512	-0.998779
42	6	0	7.558062	-3.663842	-1.926008
43	6	0	6.173081	-3.578926	-1.802943
44	6	0	-6.200596	-3.716815	-1.668052
45	6	0	-7.588231	-3.816805	-1.739749
46	6	0	-8.292094	-4.466853	-0.717482
47	6	0	-7.592166	-4.998004	0.377850
48	6	0	-6.212673	-4.896669	0.441632
49	6	0	5.488006	-4.232994	-0.762151
50	6	0	-5.481803	-4.257699	-0.585984
51	6	0	4.071793	-4.166662	-0.664196
52	6	0	-4.063367	-4.180350	-0.537967
53	6	0	-2.844559	-4.131961	-0.514873
54	6	0	2.854105	-4.124459	-0.601123
55	6	0	1.376621	-2.401550	-2.365238
56	6	0	0.673301	-1.594033	-3.217641
57	6	0	-0.750156	-1.595114	-3.195560
58	6	0	-1.425381	-2.403971	-2.322013

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60	6	0	0.712010	-3.259863	-1.434611
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62	6	0	-1.428234	-4.098863	-0.506842
63	6	0	1.434347	-5.754895	1.291602
64	6	0	0.743681	-4.926937	0.388309
65	6	0	-0.703240	-4.928889	0.409709
66	6	0	-1.364571	-5.759866	1.331973
67	6	0	1.473203	-7.417804	3.126012
68	6	0	0.772407	-6.574024	2.204850
69	6	0	-0.673621	-6.576808	2.225449
70	6	0	-1.344742	-7.423469	3.165815
71	6	0	-0.636657	-8.215038	4.028147
72	6	0	0.792910	-8.212097	4.007996
73	6	0	-10.452684	4.684225	1.302341
74	6	0	-11.915765	4.936619	1.002114
75	8	0	-12.311515	4.122939	-0.079497
76	8	0	-12.436735	-3.853324	-0.627401
77	6	0	-11.838828	-4.673428	-1.614913
78	6	0	-10.404134	-4.237562	-1.828377
79	8	0	12.306685	4.070325	0.246545
80	6	0	11.864792	4.776208	1.384590
81	6	0	10.391320	4.497859	1.598495
82	6	0	10.374411	-4.054360	-2.136630
83	6	0	11.816368	-4.497997	-2.002016
84	8	0	12.430737	-3.781083	-0.946490
85	7	0	-14.715989	-2.037881	-0.060607
86	6	0	-14.348005	-3.245509	0.662974
87	6	0	-13.720990	-4.302002	-0.237715
88	6	0	-13.644142	4.362446	-0.490758
89	6	0	-14.025936	3.359280	-1.560228
90	6	0	14.080257	3.452312	-1.231650
91	6	0	13.653152	4.349238	-0.087544
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93	6	0	14.353512	-3.323585	0.387943
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103	8	0	-14.198216	2.089981	-0.961833
104	8	0	14.239414	2.132853	-0.749224
105	6	0	14.631829	1.224809	-1.771161
106	6	0	-14.557092	1.088487	-1.905823
107	1	0	5.583351	3.755642	2.136244
108	1	0	8.033323	3.764862	2.285030
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110	1	0	5.753567	6.395949	-1.255563
111	1	0	-5.700117	6.283101	-1.546511
112	1	0	-8.186093	6.321858	-1.486188
113	1	0	-8.126091	4.011825	2.142847
114	1	0	-5.672159	3.973942	2.082560
115	1	0	2.509914	6.724630	-1.531560
116	1	0	1.302096	8.166644	-3.123967
117	1	0	-1.198740	8.178506	-3.156604
118	1	0	-2.461381	6.747445	-1.597347
119	1	0	2.445027	3.376622	2.117612
120	1	0	-2.524250	3.393073	2.046008
121	1	0	2.425144	1.689643	3.928670
122	1	0	-2.567428	1.704535	3.856041
123	1	0	-1.344571	0.245705	5.429200
124	1	0	1.148344	0.238321	5.465614
125	1	0	5.743698	-5.481022	0.984715
126	1	0	8.216004	-5.631749	0.765973
127	1	0	8.048651	-3.145401	-2.741684
128	1	0	5.607603	-3.001360	-2.527633
129	1	0	-5.659577	-3.218165	-2.466293
130	1	0	-8.105779	-3.388527	-2.590479

131	1	0	-8.156083	-5.493172	1.162065
132	1	0	-5.678971	-5.315859	1.288961
133	1	0	2.461219	-2.400749	-2.374952
134	1	0	1.200361	-0.945190	-3.911752
135	1	0	-1.299504	-0.946838	-3.872709
136	1	0	-2.509789	-2.404697	-2.297738
137	1	0	2.519823	-5.751537	1.272689
138	1	0	-2.450138	-5.761109	1.343806
139	1	0	2.560476	-7.413541	3.107882
140	1	0	-2.432099	-7.423613	3.178197
141	1	0	-1.157384	-8.853705	4.736566
142	1	0	1.336005	-8.848480	4.701524
143	1	0	-10.192202	5.136313	2.270121
144	1	0	-10.269740	3.603083	1.357069
145	1	0	-12.508215	4.703871	1.903951
146	1	0	-12.061694	6.005064	0.772223
147	1	0	-11.852881	-5.730302	-1.306719
148	1	0	-12.386992	-4.589749	-2.567933
149	1	0	-10.012145	-4.714973	-2.737640
150	1	0	-10.359759	-3.147763	-1.959080
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152	1	0	12.016819	5.861691	1.264973
153	1	0	10.208907	3.416703	1.541369
154	1	0	10.089486	4.854866	2.593591
155	1	0	9.963825	-4.437374	-3.081699
156	1	0	10.319307	-2.957349	-2.150810
157	1	0	12.343416	-4.311496	-2.952350
158	1	0	11.842501	-5.581017	-1.806085
159	1	0	-15.271430	-3.628902	1.102867
160	1	0	-13.653041	-2.984572	1.466899
161	1	0	-14.366112	-4.467133	-1.114920
162	1	0	-13.647561	-5.252935	0.315091
163	1	0	-13.743613	5.383783	-0.896651
164	1	0	-14.339940	4.266734	0.358494
165	1	0	-13.239975	3.330050	-2.333046
166	1	0	-14.961306	3.689707	-2.044348

167	1	0	13.322567	3.493160	-2.031692
168	1	0	15.030111	3.829622	-1.648672
169	1	0	13.763496	5.404550	-0.390680
170	1	0	14.316090	4.174093	0.775228
171	1	0	14.351322	-4.367723	-1.500147
172	1	0	13.627441	-5.279243	-0.149877
173	1	0	15.271100	-3.760227	0.788660
174	1	0	13.661801	-3.130653	1.213667
175	1	0	-12.862733	-1.030386	-0.403790
176	1	0	12.900055	-1.007972	-0.492720
177	1	0	13.852861	1.184475	-2.551138
178	1	0	15.566537	1.554053	-2.250097
179	1	0	-15.475440	1.368962	-2.443838
180	1	0	-13.753161	0.976318	-2.652745

Total Energy : -4553.43772269 Hartree, Imaginary Freq : 0

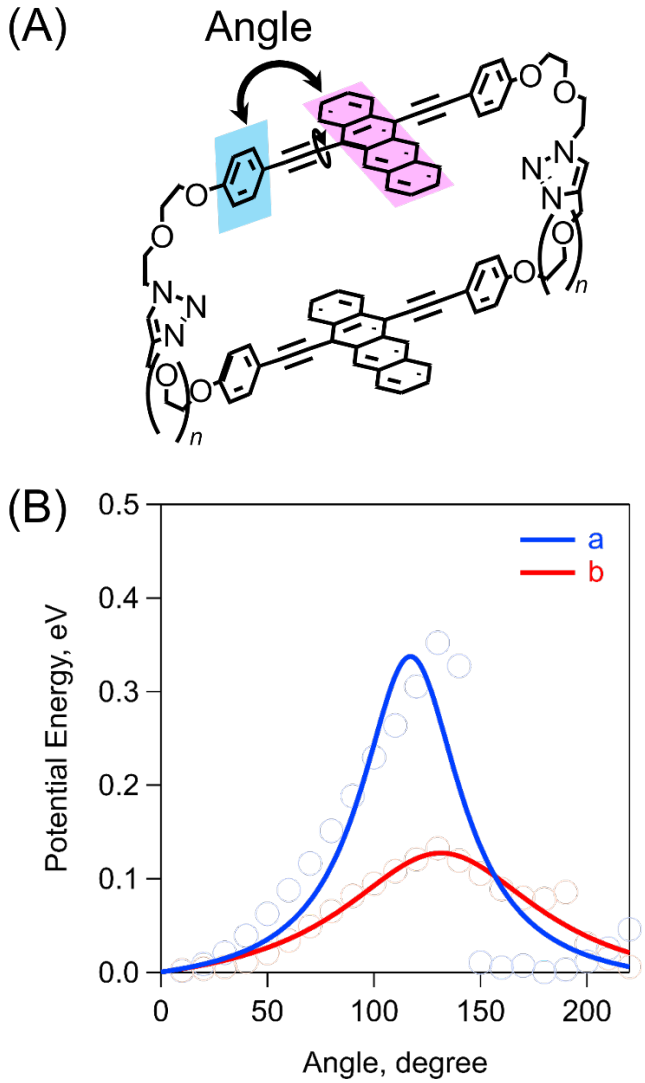
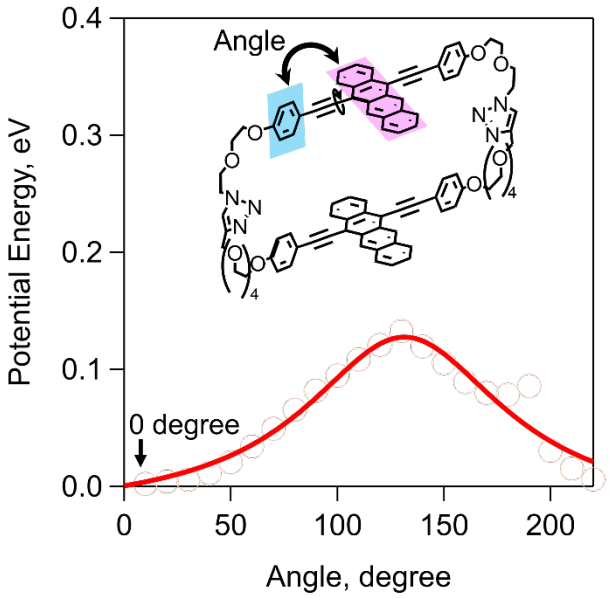


Fig. S58 (A) Schematic illustration of the dihedral angle between a tetracene and phenylene units in $(Tet)_2$-CyO_n. The potential energies were calculated by changing the dihedral angle between tetracene (pink) and phenylene (light blue) units. (B) Potential energies landscape scanning over rotation of one pentacene–phenylene dihedral angles of (a) $(Tet)_2$-CyO_{10} (blue) and (b) $(Tet)_2$-CyO_{12} (red) calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level. The horizontal axis represents the dihedral angle differences from the optimized geometries between tetracene and phenylene units. Therefore, the difference of 0° in the dihedral angle correspond to the optimized structures.

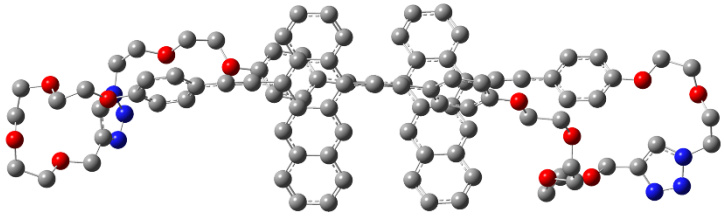
The rotational barriers of $(Tet)_2$-CyO_n are defined as the difference between the lowest and highest energy states when rotating the dihedral angle between tetracene and phenylene units in the range of 0° to 220° from the optimized structure. As an example,

for $(Tet)_2$-CyO_{12}, the relative energy for rotation increased with increasing the angles, attaining a maximum value of 0.13 eV at 130° rotation, which corresponds to the rotational barrier. In contrast, the rotational barrier in $(Tet)_2$-CyO_{10} was calculated to be 0.34 eV at 120°. The smaller rotational barrier in $(Tet)_2$-CyO_{12}relative to $(Tet)_2$-CyO_{10} suggests that the conformational flexibility of $(Tet)_2$-CyO_{12} is larger than that of $(Tet)_2$-CyO_{10}. The similar discussion was performed in previous work (See: ref. 13 in the text).

Cartesian coordinates of $(Tet)_2$-CyO_{12} at 0 degree calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{12} at 0 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	15.294804	0.908397	2.267424
2	6	0	15.402902	-0.163830	1.200061
3	8	0	14.996594	-1.399458	1.763293
4	6	0	14.827768	-2.453320	0.832158
5	6	0	13.362091	-2.811999	0.704132
6	8	0	12.698801	-1.698088	0.134139
7	8	0	6.975147	-0.525813	-3.103832
8	6	0	-3.106344	-0.616906	-1.983740
9	6	0	-1.676596	-0.675419	-2.086827

10	6	0	-0.955377	0.520921	-2.240754
11	6	0	-1.586375	1.753908	-2.282469
12	6	0	-3.020221	1.813808	-2.189823
13	6	0	-3.741251	0.636137	-2.058372
14	6	0	-0.847185	2.978430	-2.404018
15	6	0	-1.487977	4.179119	-2.416696
16	6	0	-2.917092	4.241553	-2.315807
17	6	0	-3.655151	3.101865	-2.211809
18	6	0	-3.840167	-1.817671	-1.762199
19	6	0	-3.170542	-3.036338	-1.590513
20	6	0	-1.739936	-3.094206	-1.697264
21	6	0	-1.012316	-1.932436	-1.984873
22	6	0	-3.878342	-4.241312	-1.271235
23	6	0	-3.215297	-5.411631	-1.057605
24	6	0	-1.790186	-5.467383	-1.162009
25	6	0	-1.081083	-4.348853	-1.479454
26	6	0	0.398699	-1.960772	-2.168334
27	6	0	-5.259789	-1.740723	-1.654834
28	6	0	1.590653	-1.845924	-2.366810
29	6	0	-6.459661	-1.589652	-1.552197
30	6	0	2.966675	-1.533392	-2.588203
31	6	0	-7.848005	-1.307378	-1.355479
32	6	0	3.323695	-0.195170	-2.784655
33	6	0	4.649123	0.179667	-2.959606
34	6	0	5.649945	-0.794001	-2.949460
35	6	0	5.304710	-2.140196	-2.768857
36	6	0	3.981702	-2.504549	-2.586775
37	6	0	-8.850373	-2.194326	-1.754756
38	6	0	-10.196456	-1.909760	-1.524651
39	6	0	-10.552380	-0.715453	-0.891694
40	6	0	-9.554839	0.182524	-0.488356
41	6	0	-8.224796	-0.111056	-0.717673
42	8	0	-11.830474	-0.338692	-0.620631
43	6	0	2.445383	0.422549	0.537786
44	6	0	3.873953	0.338096	0.415197
45	6	0	4.592084	1.486610	0.035131

46	6	0	3.951385	2.681857	-0.258126
47	6	0	2.523859	2.776129	-0.098700
48	6	0	1.809087	1.655020	0.298181
49	6	0	4.669151	3.827757	-0.746098
50	6	0	4.015581	4.990684	-1.019092
51	6	0	2.600186	5.099223	-0.815963
52	6	0	1.881387	4.031723	-0.372159
53	6	0	1.698449	-0.744340	0.858294
54	6	0	2.339334	-1.989117	0.965587
55	6	0	3.764761	-2.074651	0.840213
56	6	0	4.520273	-0.914393	0.605505
57	6	0	1.592672	-3.196880	1.160833
58	6	0	2.213551	-4.406764	1.222635
59	6	0	3.634764	-4.491803	1.107597
60	6	0	4.380356	-3.365973	0.929096
61	6	0	5.938392	-1.007753	0.512879
62	6	0	0.289361	-0.668618	1.037248
63	6	0	7.143941	-1.135953	0.448451
64	6	0	-0.913134	-0.673591	1.201549
65	6	0	8.560548	-1.310729	0.371023
66	6	0	-2.325160	-0.794302	1.373229
67	6	0	9.388691	-0.242226	-0.005445
68	6	0	10.759401	-0.404380	-0.087324
69	6	0	11.337602	-1.639073	0.218621
70	6	0	10.529044	-2.716630	0.591535
71	6	0	9.149140	-2.546122	0.663953
72	6	0	-2.879500	-2.053910	1.622837
73	6	0	-4.251581	-2.223216	1.762154
74	6	0	-5.100011	-1.118737	1.642192
75	6	0	-4.554945	0.150773	1.406280
76	6	0	-3.187720	0.310649	1.273010
77	8	0	-6.452818	-1.180825	1.718509
78	6	0	-7.033160	-2.423590	2.062679
79	6	0	-8.539027	-2.311123	2.037416
80	8	0	-8.973670	-1.328238	2.948770
81	6	0	-10.368128	-1.343417	3.126409

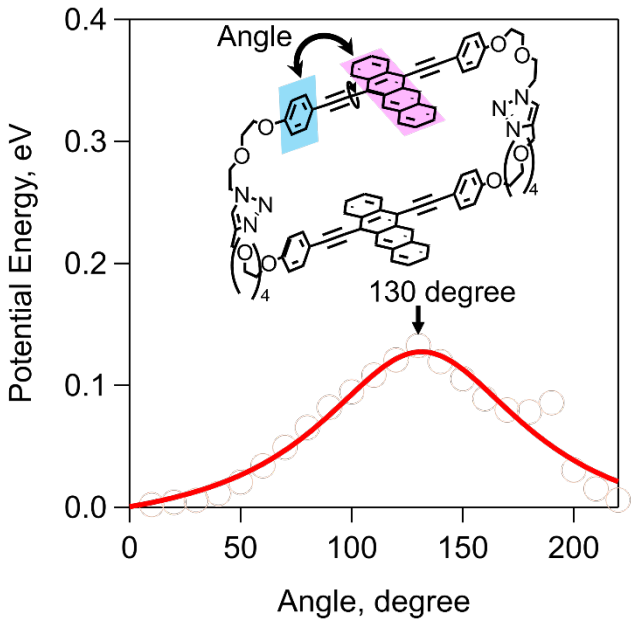
82	6	0	-10.792819	-0.061337	3.826076
83	7	0	-10.933807	1.061032	2.915784
84	6	0	-11.916245	1.264984	2.012228
85	6	0	-11.583117	2.460636	1.422662
86	7	0	-10.432865	2.914293	1.987749
87	7	0	-10.039288	2.061142	2.892094
88	6	0	-12.290254	3.168030	0.316586
89	6	0	-14.196641	-0.518988	-0.672050
90	6	0	-12.891043	-1.180420	-1.041726
91	8	0	-13.681066	3.088094	0.567948
92	6	0	-14.493344	3.483538	-0.512065
93	6	0	-15.933851	3.134947	-0.180467
94	8	0	-16.135577	1.737744	-0.071360
95	6	0	-15.961332	1.213198	1.237958
96	6	0	-15.707008	-0.279759	1.158145
97	8	0	-14.402961	-0.633344	0.725321
98	8	0	9.559324	1.774161	-2.268505
99	6	0	9.132851	3.124164	-2.279903
100	6	0	9.017454	3.620200	-0.854533
101	8	0	7.880658	3.013534	-0.252125
102	6	0	7.692867	3.349963	1.115721
103	6	0	8.289700	2.337315	2.070271
104	8	0	9.693196	2.343380	1.932072
105	6	0	7.389548	0.820465	-2.921981
106	6	0	8.904882	0.881571	-3.146102
107	6	0	10.342096	1.537689	2.895133
108	7	0	13.726067	2.704953	2.638990
109	7	0	12.451441	2.883208	2.812696
110	6	0	11.820032	1.678716	2.739807
111	6	0	12.770009	0.707890	2.522244
112	7	0	13.936767	1.388420	2.464640
113	1	0	15.878244	1.783644	1.981751
114	1	0	15.690643	0.520780	3.209454
115	1	0	14.780122	0.097754	0.336431
116	1	0	16.448987	-0.229052	0.871578
117	1	0	15.375235	-3.326932	1.200156

118	1	0	15.235413	-2.185233	-0.148705
119	1	0	13.244326	-3.703474	0.074149
120	1	0	12.957832	-3.027778	1.700471
121	1	0	0.127064	0.476626	-2.296774
122	1	0	-4.822300	0.681907	-1.973556
123	1	0	0.235525	2.927448	-2.484227
124	1	0	-0.919710	5.099862	-2.507451
125	1	0	-3.408242	5.209436	-2.326181
126	1	0	-4.737944	3.150674	-2.137104
127	1	0	-4.959684	-4.197782	-1.190026
128	1	0	-3.767882	-6.312255	-0.808092
129	1	0	-1.276937	-6.408290	-0.990427
130	1	0	0.001019	-4.384199	-1.559604
131	1	0	2.555810	0.571618	-2.767832
132	1	0	4.877368	1.231761	-3.071916
133	1	0	6.097076	-2.880322	-2.746264
134	1	0	3.726507	-3.545137	-2.415989
135	1	0	-8.577556	-3.121184	-2.248757
136	1	0	-10.946026	-2.623433	-1.845171
137	1	0	-9.837460	1.099365	0.016668
138	1	0	-7.458120	0.573336	-0.373248
139	1	0	5.669588	1.418630	-0.086808
140	1	0	0.729660	1.719297	0.406201
141	1	0	5.741970	3.737010	-0.899601
142	1	0	4.564866	5.850040	-1.391338
143	1	0	2.104580	6.043378	-1.019746
144	1	0	0.808416	4.110770	-0.221514
145	1	0	0.513110	-3.129325	1.236833
146	1	0	1.629526	-5.311949	1.356561
147	1	0	4.119831	-5.461607	1.160262
148	1	0	5.458100	-3.432294	0.829569
149	1	0	8.959034	0.725067	-0.235934
150	1	0	11.390881	0.428383	-0.376427
151	1	0	10.953704	-3.688465	0.814624
152	1	0	8.521457	-3.383064	0.952488
153	1	0	-2.227635	-2.919403	1.686460

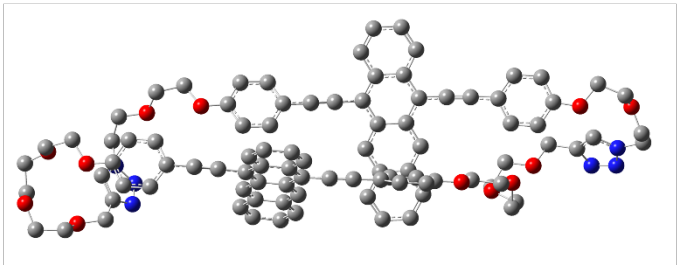
154	1	0	-4.636895	-3.219569	1.938035
155	1	0	-5.227817	0.997933	1.326456
156	1	0	-2.775507	1.293991	1.071637
157	1	0	-6.746556	-3.195560	1.336552
158	1	0	-6.693346	-2.727837	3.060645
159	1	0	-8.942359	-3.300083	2.308869
160	1	0	-8.888527	-2.071402	1.026929
161	1	0	-10.663424	-2.205682	3.744145
162	1	0	-10.889337	-1.429658	2.161352
163	1	0	-10.047845	0.218370	4.570749
164	1	0	-11.751903	-0.212212	4.326195
165	1	0	-12.725280	0.569811	1.832303
166	1	0	-11.951958	4.210842	0.266266
167	1	0	-12.062580	2.685510	-0.645847
168	1	0	-15.010908	-1.023016	-1.211533
169	1	0	-14.183710	0.529604	-0.983628
170	1	0	-12.853284	-1.314733	-2.130127
171	1	0	-12.819051	-2.162132	-0.558149
172	1	0	-14.193587	2.958822	-1.431784
173	1	0	-14.407860	4.566022	-0.695547
174	1	0	-16.577846	3.486083	-0.991287
175	1	0	-16.238772	3.646542	0.741022
176	1	0	-15.121321	1.696728	1.743697
177	1	0	-16.875735	1.383205	1.826888
178	1	0	-16.461606	-0.750400	0.512599
179	1	0	-15.807935	-0.702617	2.160921
180	1	0	8.165268	3.244020	-2.780310
181	1	0	9.867159	3.737578	-2.818051
182	1	0	9.926311	3.372010	-0.296779
183	1	0	8.895898	4.713180	-0.861867
184	1	0	6.612888	3.392251	1.288237
185	1	0	8.109639	4.342984	1.323051
186	1	0	7.999803	2.617789	3.095415
187	1	0	7.878460	1.337347	1.866376
188	1	0	6.866728	1.474623	-3.628502
189	1	0	7.156679	1.146844	-1.901329

190	1	0	9.324098	-0.101303	-2.924927
191	1	0	9.132750	1.124952	-4.192426
192	1	0	10.040945	1.855643	3.903986
193	1	0	10.057880	0.482617	2.771651
194	1	0	12.715880	-0.361210	2.393221

Cartesian coordinates of $(Tet)_2$-CyO_{12} at 130 degrees calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{12} at 130 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	16.427773	1.244670	-0.819283
2	6	0	16.181382	0.168647	0.225165
3	8	0	15.721782	0.838026	1.434632
4	6	0	15.259963	-0.025954	2.512221
5	6	0	13.894343	0.448468	2.965317
6	8	0	12.981286	0.146419	1.872626
7	8	0	6.468912	-4.048009	-0.191815
8	6	0	-3.756972	-2.920754	-0.675373

9	6	0	-2.333680	-3.191556	-0.690749
10	6	0	-1.539790	-2.591340	-1.689562
11	6	0	-2.079164	-1.747244	-2.663420
12	6	0	-3.501889	-1.468654	-2.643542
13	6	0	-4.294038	-2.060145	-1.655609
14	6	0	-1.275001	-1.151680	-3.692743
15	6	0	-1.836751	-0.327553	-4.636035
16	6	0	-3.240961	-0.046272	-4.612220
17	6	0	-4.046160	-0.600088	-3.648909
18	6	0	-4.586228	-3.534818	0.323300
19	6	0	-4.021369	-4.436653	1.259934
20	6	0	-2.599309	-4.702078	1.248185
21	6	0	-1.763075	-4.065206	0.297024
22	6	0	-4.827918	-5.089260	2.248761
23	6	0	-4.276092	-5.950940	3.163791
24	6	0	-2.872603	-6.211133	3.153225
25	6	0	-2.063803	-5.602027	2.226520
26	6	0	-0.356111	-4.248138	0.316575
27	6	0	-5.966960	-3.207576	0.362979
28	6	0	0.865771	-4.308109	0.284384
29	6	0	-7.137173	-2.851191	0.342729
30	6	0	2.285406	-4.243938	0.191016
31	6	0	-8.468026	-2.351115	0.256930
32	6	0	2.893633	-3.047382	-0.247356
33	6	0	4.277452	-2.944146	-0.375178
34	6	0	5.083619	-4.049406	-0.070433
35	6	0	4.501461	-5.246124	0.378649
36	6	0	3.120240	-5.341628	0.509849
37	6	0	-9.590235	-3.160107	0.527827
38	6	0	-10.889719	-2.662812	0.393744
39	6	0	-11.084251	-1.338436	-0.024144
40	6	0	-9.979192	-0.508586	-0.276594
41	6	0	-8.690515	-1.006036	-0.135261
42	8	0	-12.330490	-0.750437	-0.220073
43	6	0	2.770390	1.520188	0.413535
44	6	0	4.213729	1.414084	0.506188

45	6	0	4.940403	1.021866	-0.637387
46	6	0	4.317473	0.743848	-1.857964
47	6	0	2.875167	0.867164	-1.954730
48	6	0	2.147863	1.242411	-0.820985
49	6	0	5.059644	0.342833	-3.021812
50	6	0	4.413637	0.093139	-4.207665
51	6	0	2.991537	0.229446	-4.309064
52	6	0	2.246760	0.603711	-3.218253
53	6	0	2.007167	1.902265	1.568242
54	6	0	2.673250	2.229448	2.780854
55	6	0	4.112602	2.130975	2.870666
56	6	0	4.870963	1.704346	1.749305
57	6	0	1.947157	2.649344	3.942435
58	6	0	2.589630	2.958631	5.115548
59	6	0	4.009802	2.860880	5.203568
60	6	0	4.742862	2.457595	4.115311
61	6	0	6.275041	1.537649	1.850758
62	6	0	0.590516	1.919770	1.512171
63	6	0	7.482559	1.348382	1.917569
64	6	0	-0.633649	1.886588	1.518649
65	6	0	8.878591	1.073654	1.943401
66	6	0	-2.052288	1.814927	1.603322
67	6	0	9.482425	0.380821	0.863398
68	6	0	10.838500	0.084066	0.881353
69	6	0	11.628258	0.478798	1.970934
70	6	0	11.057873	1.164447	3.051358
71	6	0	9.690451	1.454869	3.033038
72	6	0	-2.717659	2.263398	2.764694
73	6	0	-4.100832	2.144984	2.898340
74	6	0	-4.852461	1.569122	1.862490
75	6	0	-4.212592	1.140058	0.688130
76	6	0	-2.834390	1.259417	0.559885
77	8	0	-6.228223	1.370781	1.920343
78	6	0	-6.896545	1.601090	3.196852
79	6	0	-8.336299	1.144670	3.100435
80	8	0	-9.136964	2.213938	2.525956

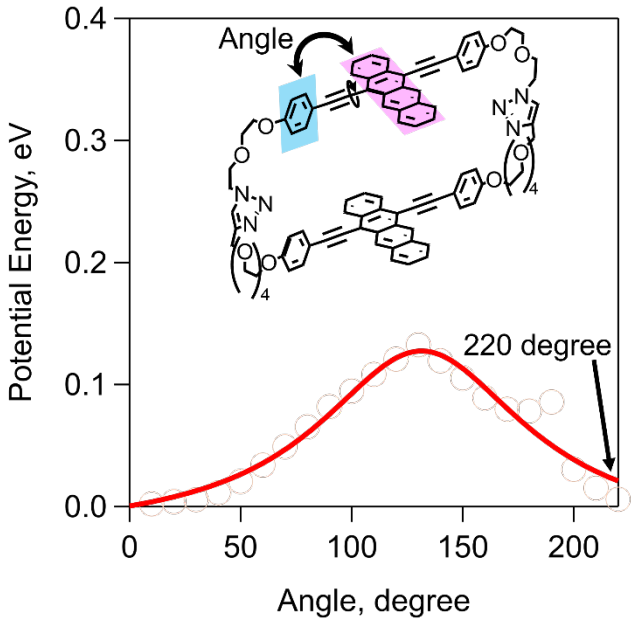
81	6	0	-10.561579	2.039710	2.722676
82	6	0	-11.270393	3.295912	2.226827
83	7	0	-11.395754	3.377142	0.775604
84	6	0	-12.147479	2.611086	-0.066678
85	6	0	-11.911999	3.136848	-1.327707
86	7	0	-11.035763	4.200603	-1.208977
87	7	0	-10.706842	4.358786	0.065823
88	6	0	-12.489438	2.730059	-2.632630
89	6	0	-14.725688	-0.699515	-0.390130
90	6	0	-13.536935	-1.529844	0.033555
91	8	0	-13.943139	2.906358	-2.562582
92	6	0	-14.702336	2.201219	-3.576610
93	6	0	-16.157539	2.186801	-3.137590
94	8	0	-16.360518	1.388712	-1.936050
95	6	0	-16.204284	2.122131	-0.678068
96	6	0	-16.147255	1.118905	0.457576
97	8	0	-14.880766	0.400494	0.551941
98	8	0	9.318878	-2.015327	-1.344107
99	6	0	9.316307	-1.907521	-2.799442
100	6	0	9.713419	-0.501668	-3.182422
101	8	0	8.581829	0.382828	-2.904337
102	6	0	8.756636	1.756782	-3.355821
103	6	0	9.553635	2.620241	-2.396065
104	8	0	10.948505	2.207351	-2.431579
105	6	0	7.124097	-2.838290	-0.675359
106	6	0	8.606270	-3.168638	-0.811425
107	6	0	11.825506	3.139406	-1.717146
108	7	0	15.238331	2.379860	-2.648419
109	7	0	14.038187	2.894229	-2.870555
110	6	0	13.229943	2.666935	-1.769513
111	6	0	13.965436	1.979001	-0.816378
112	7	0	15.198117	1.810625	-1.374609
113	1	0	16.986777	0.834148	-1.664036
114	1	0	17.024856	2.044366	-0.367777
115	1	0	15.431408	-0.554833	-0.120172
116	1	0	17.122965	-0.364294	0.419430

117	1	0	15.973643	0.030397	3.343695
118	1	0	15.189869	-1.067272	2.175605
119	1	0	13.583452	-0.079677	3.876710
120	1	0	13.913426	1.527049	3.161405
121	1	0	-0.476893	-2.804379	-1.706485
122	1	0	-5.360870	-1.865919	-1.648667
123	1	0	-0.211431	-1.371592	-3.709437
124	1	0	-1.221263	0.115594	-5.412592
125	1	0	-3.663361	0.609257	-5.366959
126	1	0	-5.112214	-0.392125	-3.631540
127	1	0	-5.892413	-4.883442	2.255207
128	1	0	-4.905204	-6.436944	3.902793
129	1	0	-2.447885	-6.891348	3.884448
130	1	0	-0.996096	-5.789883	2.215414
131	1	0	2.272516	-2.190041	-0.481527
132	1	0	4.704683	-2.006497	-0.704953
133	1	0	5.148865	-6.083170	0.612246
134	1	0	2.672166	-6.268476	0.851184
135	1	0	-9.439698	-4.189345	0.835311
136	1	0	-11.729521	-3.311818	0.609069
137	1	0	-10.152012	0.516944	-0.580061
138	1	0	-7.840224	-0.356152	-0.308699
139	1	0	6.020391	0.945349	-0.570472
140	1	0	1.068918	1.333357	-0.889481
141	1	0	6.139745	0.238982	-2.943054
142	1	0	4.980096	-0.208699	-5.083194
143	1	0	2.507081	0.034847	-5.260877
144	1	0	1.168236	0.709921	-3.291401
145	1	0	0.868371	2.720243	3.871089
146	1	0	2.018883	3.278155	5.981577
147	1	0	4.508032	3.106341	6.136036
148	1	0	5.822176	2.379047	4.175874
149	1	0	8.890997	0.065194	0.012460
150	1	0	11.289788	-0.464726	0.064862
151	1	0	11.655977	1.472484	3.900655
152	1	0	9.244188	1.982321	3.869226

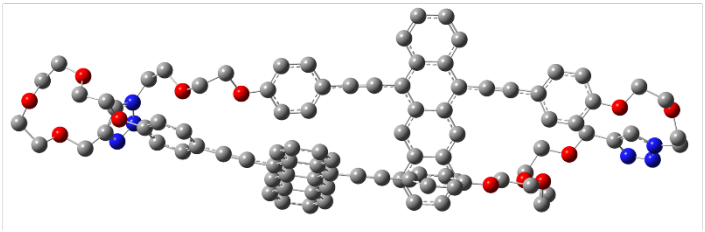
153	1	0	-2.138495	2.700644	3.570880
154	1	0	-4.574882	2.500107	3.804341
155	1	0	-4.808434	0.695516	-0.099303
156	1	0	-2.346048	0.903377	-0.340222
157	1	0	-6.377309	1.027757	3.976442
158	1	0	-6.870626	2.666149	3.454134
159	1	0	-8.701227	0.922899	4.116923
160	1	0	-8.408155	0.231789	2.497044
161	1	0	-10.778396	1.912983	3.796543
162	1	0	-10.926461	1.146956	2.195774
163	1	0	-10.703950	4.176843	2.534786
164	1	0	-12.272810	3.345942	2.666374
165	1	0	-12.773768	1.792935	0.255424
166	1	0	-12.063730	3.350616	-3.429915
167	1	0	-12.275636	1.673552	-2.852689
168	1	0	-15.627655	-1.330221	-0.373324
169	1	0	-14.595298	-0.322072	-1.407073
170	1	0	-13.509409	-2.456397	-0.555470
171	1	0	-13.601649	-1.780614	1.099126
172	1	0	-14.335205	1.168724	-3.676590
173	1	0	-14.607957	2.697801	-4.555739
174	1	0	-16.770255	1.718685	-3.914727
175	1	0	-16.513193	3.213871	-2.980415
176	1	0	-15.294249	2.725083	-0.708208
177	1	0	-17.073104	2.784630	-0.533583
178	1	0	-16.976829	0.402532	0.367439
179	1	0	-16.238990	1.646944	1.411647
180	1	0	8.322288	-2.130425	-3.207569
181	1	0	10.035914	-2.626508	-3.218307
182	1	0	10.595948	-0.169964	-2.629941
183	1	0	9.944581	-0.467911	-4.258270
184	1	0	7.741466	2.156032	-3.442269
185	1	0	9.231146	1.770786	-4.347038
186	1	0	9.464966	3.674050	-2.708410
187	1	0	9.154387	2.526027	-1.376412
188	1	0	6.699786	-2.543936	-1.643141

189	1	0	6.978827	-2.015731	0.033879
190	1	0	9.045794	-3.374302	0.166209
191	1	0	8.742500	-4.050660	-1.450855
192	1	0	11.749657	4.126549	-2.193421
193	1	0	11.491004	3.228459	-0.674478
194	1	0	13.716869	1.606494	0.162175

Cartesian coordinates of $(Tet)_2$-CyO_{12} at 220 degrees calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{12} at 220 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	15.294804	0.908397	2.267424
2	6	0	15.402902	-0.163830	1.200061
3	8	0	14.996594	-1.399458	1.763293
4	6	0	14.827768	-2.453320	0.832158
5	6	0	13.362091	-2.811999	0.704132
6	8	0	12.698801	-1.698088	0.134139
7	8	0	6.975147	-0.525813	-3.103832
8	6	0	-3.106344	-0.616906	-1.983740

9	6	0	-1.676596	-0.675419	-2.086827
10	6	0	-0.955377	0.520921	-2.240754
11	6	0	-1.586375	1.753908	-2.282469
12	6	0	-3.020221	1.813808	-2.189823
13	6	0	-3.741251	0.636137	-2.058372
14	6	0	-0.847185	2.978430	-2.404018
15	6	0	-1.487977	4.179119	-2.416696
16	6	0	-2.917092	4.241553	-2.315807
17	6	0	-3.655151	3.101865	-2.211809
18	6	0	-3.840167	-1.817671	-1.762199
19	6	0	-3.170542	-3.036338	-1.590513
20	6	0	-1.739936	-3.094206	-1.697264
21	6	0	-1.012316	-1.932436	-1.984873
22	6	0	-3.878342	-4.241312	-1.271235
23	6	0	-3.215297	-5.411631	-1.057605
24	6	0	-1.790186	-5.467383	-1.162009
25	6	0	-1.081083	-4.348853	-1.479454
26	6	0	0.398699	-1.960772	-2.168334
27	6	0	-5.259789	-1.740723	-1.654834
28	6	0	1.590653	-1.845924	-2.366810
29	6	0	-6.459661	-1.589652	-1.552197
30	6	0	2.966675	-1.533392	-2.588203
31	6	0	-7.848005	-1.307378	-1.355479
32	6	0	3.323695	-0.195170	-2.784655
33	6	0	4.649123	0.179667	-2.959606
34	6	0	5.649945	-0.794001	-2.949460
35	6	0	5.304710	-2.140196	-2.768857
36	6	0	3.981702	-2.504549	-2.586775
37	6	0	-8.850373	-2.194326	-1.754756
38	6	0	-10.196456	-1.909760	-1.524651
39	6	0	-10.552380	-0.715453	-0.891694
40	6	0	-9.554839	0.182524	-0.488356
41	6	0	-8.224796	-0.111056	-0.717673
42	8	0	-11.830474	-0.338692	-0.620631
43	6	0	2.445383	0.422549	0.537786
44	6	0	3.873953	0.338096	0.415197

45	6	0	4.592084	1.486610	0.035131
46	6	0	3.951385	2.681857	-0.258126
47	6	0	2.523859	2.776129	-0.098700
48	6	0	1.809087	1.655020	0.298181
49	6	0	4.669151	3.827757	-0.746098
50	6	0	4.015581	4.990684	-1.019092
51	6	0	2.600186	5.099223	-0.815963
52	6	0	1.881387	4.031723	-0.372159
53	6	0	1.698449	-0.744340	0.858294
54	6	0	2.339334	-1.989117	0.965587
55	6	0	3.764761	-2.074651	0.840213
56	6	0	4.520273	-0.914393	0.605505
57	6	0	1.592672	-3.196880	1.160833
58	6	0	2.213551	-4.406764	1.222635
59	6	0	3.634764	-4.491803	1.107597
60	6	0	4.380356	-3.365973	0.929096
61	6	0	5.938392	-1.007753	0.512879
62	6	0	0.289361	-0.668618	1.037248
63	6	0	7.143941	-1.135953	0.448451
64	6	0	-0.913134	-0.673591	1.201549
65	6	0	8.560548	-1.310729	0.371023
66	6	0	-2.325160	-0.794302	1.373229
67	6	0	9.388691	-0.242226	-0.005445
68	6	0	10.759401	-0.404380	-0.087324
69	6	0	11.337602	-1.639073	0.218621
70	6	0	10.529044	-2.716630	0.591535
71	6	0	9.149140	-2.546122	0.663953
72	6	0	-2.879500	-2.053910	1.622837
73	6	0	-4.251581	-2.223216	1.762154
74	6	0	-5.100011	-1.118737	1.642192
75	6	0	-4.554945	0.150773	1.406280
76	6	0	-3.187720	0.310649	1.273010
77	8	0	-6.452818	-1.180825	1.718509
78	6	0	-7.033160	-2.423590	2.062679
79	6	0	-8.539027	-2.311123	2.037416
80	8	0	-8.973670	-1.328238	2.948770

81	6	0	-10.368128	-1.343417	3.126409
82	6	0	-10.792819	-0.061337	3.826076
83	7	0	-10.933807	1.061032	2.915784
84	6	0	-11.916245	1.264984	2.012228
85	6	0	-11.583117	2.460636	1.422662
86	7	0	-10.432865	2.914293	1.987749
87	7	0	-10.039288	2.061142	2.892094
88	6	0	-12.290254	3.168030	0.316586
89	6	0	-14.196641	-0.518988	-0.672050
90	6	0	-12.891043	-1.180420	-1.041726
91	8	0	-13.681066	3.088094	0.567948
92	6	0	-14.493344	3.483538	-0.512065
93	6	0	-15.933851	3.134947	-0.180467
94	8	0	-16.135577	1.737744	-0.071360
95	6	0	-15.961332	1.213198	1.237958
96	6	0	-15.707008	-0.279759	1.158145
97	8	0	-14.402961	-0.633344	0.725321
98	8	0	9.559324	1.774161	-2.268505
99	6	0	9.132851	3.124164	-2.279903
100	6	0	9.017454	3.620200	-0.854533
101	8	0	7.880658	3.013534	-0.252125
102	6	0	7.692867	3.349963	1.115721
103	6	0	8.289700	2.337315	2.070271
104	8	0	9.693196	2.343380	1.932072
105	6	0	7.389548	0.820465	-2.921981
106	6	0	8.904882	0.881571	-3.146102
107	6	0	10.342096	1.537689	2.895133
108	7	0	13.726067	2.704953	2.638990
109	7	0	12.451441	2.883208	2.812696
110	6	0	11.820032	1.678716	2.739807
111	6	0	12.770009	0.707890	2.522244
112	7	0	13.936767	1.388420	2.464640
113	1	0	15.878244	1.783644	1.981751
114	1	0	15.690643	0.520780	3.209454
115	1	0	14.780122	0.097754	0.336431
116	1	0	16.448987	-0.229052	0.871578

117	1	0	15.375235	-3.326932	1.200156
118	1	0	15.235413	-2.185233	-0.148705
119	1	0	13.244326	-3.703474	0.074149
120	1	0	12.957832	-3.027778	1.700471
121	1	0	0.127064	0.476626	-2.296774
122	1	0	-4.822300	0.681907	-1.973556
123	1	0	0.235525	2.927448	-2.484227
124	1	0	-0.919710	5.099862	-2.507451
125	1	0	-3.408242	5.209436	-2.326181
126	1	0	-4.737944	3.150674	-2.137104
127	1	0	-4.959684	-4.197782	-1.190026
128	1	0	-3.767882	-6.312255	-0.808092
129	1	0	-1.276937	-6.408290	-0.990427
130	1	0	0.001019	-4.384199	-1.559604
131	1	0	2.555810	0.571618	-2.767832
132	1	0	4.877368	1.231761	-3.071916
133	1	0	6.097076	-2.880322	-2.746264
134	1	0	3.726507	-3.545137	-2.415989
135	1	0	-8.577556	-3.121184	-2.248757
136	1	0	-10.946026	-2.623433	-1.845171
137	1	0	-9.837460	1.099365	0.016668
138	1	0	-7.458120	0.573336	-0.373248
139	1	0	5.669588	1.418630	-0.086808
140	1	0	0.729660	1.719297	0.406201
141	1	0	5.741970	3.737010	-0.899601
142	1	0	4.564866	5.850040	-1.391338
143	1	0	2.104580	6.043378	-1.019746
144	1	0	0.808416	4.110770	-0.221514
145	1	0	0.513110	-3.129325	1.236833
146	1	0	1.629526	-5.311949	1.356561
147	1	0	4.119831	-5.461607	1.160262
148	1	0	5.458100	-3.432294	0.829569
149	1	0	8.959034	0.725067	-0.235934
150	1	0	11.390881	0.428383	-0.376427
151	1	0	10.953704	-3.688465	0.814624
152	1	0	8.521457	-3.383064	0.952488

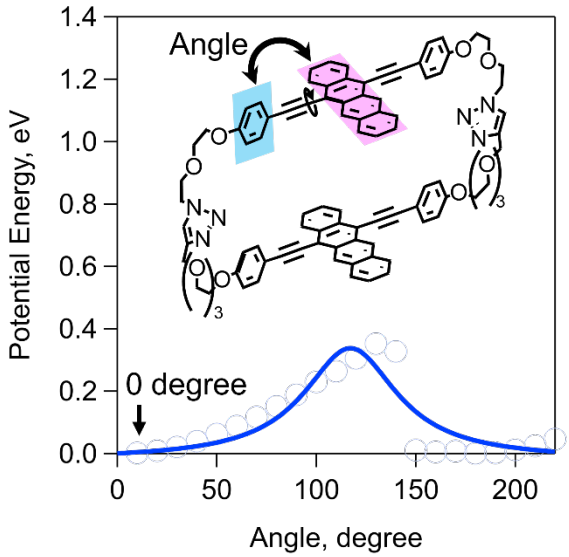
153	1	0	-2.227635	-2.919403	1.686460
154	1	0	-4.636895	-3.219569	1.938035
155	1	0	-5.227817	0.997933	1.326456
156	1	0	-2.775507	1.293991	1.071637
157	1	0	-6.746556	-3.195560	1.336552
158	1	0	-6.693346	-2.727837	3.060645
159	1	0	-8.942359	-3.300083	2.308869
160	1	0	-8.888527	-2.071402	1.026929
161	1	0	-10.663424	-2.205682	3.744145
162	1	0	-10.889337	-1.429658	2.161352
163	1	0	-10.047845	0.218370	4.570749
164	1	0	-11.751903	-0.212212	4.326195
165	1	0	-12.725280	0.569811	1.832303
166	1	0	-11.951958	4.210842	0.266266
167	1	0	-12.062580	2.685510	-0.645847
168	1	0	-15.010908	-1.023016	-1.211533
169	1	0	-14.183710	0.529604	-0.983628
170	1	0	-12.853284	-1.314733	-2.130127
171	1	0	-12.819051	-2.162132	-0.558149
172	1	0	-14.193587	2.958822	-1.431784
173	1	0	-14.407860	4.566022	-0.695547
174	1	0	-16.577846	3.486083	-0.991287
175	1	0	-16.238772	3.646542	0.741022
176	1	0	-15.121321	1.696728	1.743697
177	1	0	-16.875735	1.383205	1.826888
178	1	0	-16.461606	-0.750400	0.512599
179	1	0	-15.807935	-0.702617	2.160921
180	1	0	8.165268	3.244020	-2.780310
181	1	0	9.867159	3.737578	-2.818051
182	1	0	9.926311	3.372010	-0.296779
183	1	0	8.895898	4.713180	-0.861867
184	1	0	6.612888	3.392251	1.288237
185	1	0	8.109639	4.342984	1.323051
186	1	0	7.999803	2.617789	3.095415
187	1	0	7.878460	1.337347	1.866376
188	1	0	6.866728	1.474623	-3.628502

189	1	0	7.156679	1.146844	-1.901329
190	1	0	9.324098	-0.101303	-2.924927
191	1	0	9.132750	1.124952	-4.192426
192	1	0	10.040945	1.855643	3.903986
193	1	0	10.057880	0.482617	2.771651
194	1	0	12.715880	-0.361210	2.393221

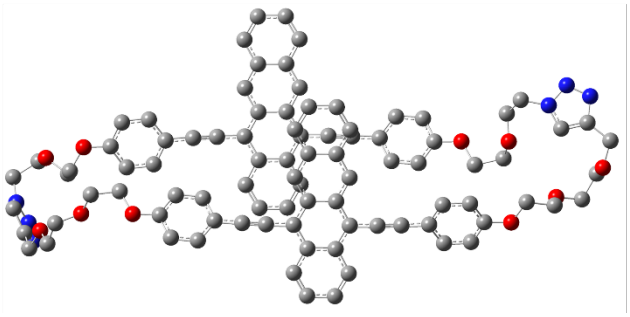
DFT-computed energy landscape scanning over rotation of one pentacene–phenylene dihedral angles of $(Tet)_2$-CyO_{12} calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.

Angle, degree	Total Energy (Hartree)	Potential Energy, eV
0	-4860.89438434	0.00
10	-4860.89429823	0.00
20	-4860.89423228	0.00
30	-4860.89417085	0.00
40	-4860.89396193	0.01
50	-4860.89362397	0.02
60	-4860.89312974	0.03
70	-4860.89257167	0.05
80	-4860.89198444	0.06
90	-4860.89136603	0.08
100	-4860.89089777	0.09
110	-4860.89039718	0.11
120	-4860.88993609	0.12
130	-4860.88951289	0.13
140	-4860.88998612	0.12
150	-4860.89051365	0.11
160	-4860.89111384	0.08
170	-4860.89144699	0.08
180	-4860.89149825	0.08
190	-4860.89122734	0.09
200	-4860.89326241	0.03
210	-4860.89381778	0.02
220	-4860.89416092	0.01

Cartesian coordinates of $(Tet)_2$-CyO_{10} at 0 degrees calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{10} at 0 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	10.035569	-2.993095	0.205103
2	8	0	-8.911459	-0.809235	2.902591
3	6	0	-5.451622	0.237444	2.178864
4	6	0	-6.808139	0.353439	2.466305
5	6	0	-7.587355	-0.798443	2.600145
6	6	0	-6.999497	-2.056932	2.419454
7	6	0	-5.651483	-2.161433	2.127593
8	6	0	6.455457	-3.219361	-0.311211

9	6	0	7.817347	-3.461185	-0.392330
10	6	0	8.712567	-2.704385	0.371106
11	6	0	8.230018	-1.687735	1.199374
12	6	0	6.861139	-1.448892	1.270826
13	6	0	-4.848843	-1.012867	2.010801
14	6	0	5.952883	-2.213719	0.529785
15	6	0	-3.449938	-1.129560	1.740063
16	6	0	4.543492	-1.993299	0.638497
17	6	0	3.345279	-1.839976	0.757623
18	6	0	-2.259055	-1.250130	1.538065
19	6	0	-1.170283	-3.776317	0.741213
20	6	0	-0.651465	-4.979367	0.372092
21	6	0	0.755386	-5.125913	0.175369
22	6	0	1.590848	-4.066094	0.357679
23	6	0	-0.857164	-1.393037	1.326893
24	6	0	-0.327911	-2.634734	0.944367
25	6	0	1.085806	-2.782340	0.747081
26	6	0	1.938753	-1.684369	0.934642
27	6	0	-0.506632	0.981695	1.909792
28	6	0	-0.000865	-0.272111	1.522091
29	6	0	1.413533	-0.419933	1.322105
30	6	0	2.246778	0.697970	1.503855
31	6	0	-0.184424	3.356503	2.500366
32	6	0	0.324380	2.074523	2.102632
33	6	0	1.738479	1.929626	1.886229
34	6	0	2.582689	3.077357	2.066957
35	6	0	2.058581	4.274615	2.446721
36	6	0	0.650548	4.416465	2.671374
37	8	0	8.916434	1.116754	-1.403295
38	8	0	-10.196979	1.185884	-0.206384
39	6	0	-6.748228	2.110008	-0.771087
40	6	0	-8.110720	2.177433	-0.536678
41	6	0	-8.880170	1.008132	-0.494699
42	6	0	-8.262129	-0.229762	-0.697638
43	6	0	-6.893685	-0.288150	-0.935576
44	6	0	5.631301	-0.286058	-2.300182

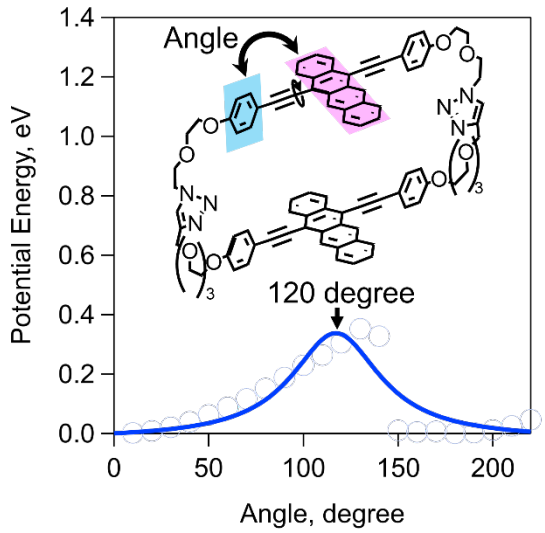
45	6	0	7.014961	-0.178914	-2.204485
46	6	0	7.580857	0.918345	-1.552036
47	6	0	6.750920	1.905716	-1.007019
48	6	0	5.376104	1.793686	-1.111824
49	6	0	-6.114740	0.872984	-0.972614
50	6	0	4.791248	0.692727	-1.762128
51	6	0	-4.701055	0.802788	-1.167500
52	6	0	3.369049	0.598784	-1.850547
53	6	0	2.155989	0.581828	-1.862047
54	6	0	-3.496222	0.745328	-1.302719
55	6	0	-2.204278	-1.685705	-2.104716
56	6	0	-1.583270	-2.839318	-2.474054
57	6	0	-0.163695	-2.883965	-2.620320
58	6	0	0.585349	-1.770947	-2.391006
59	6	0	-2.081738	0.700463	-1.463881
60	6	0	-1.453998	-0.489973	-1.859364
61	6	0	-0.027581	-0.532936	-2.011233
62	6	0	0.735275	0.619208	-1.774990
63	6	0	-1.919784	3.079117	-0.810746
64	6	0	-1.317356	1.877552	-1.225573
65	6	0	0.106671	1.840806	-1.400961
66	6	0	0.848263	3.015990	-1.185229
67	6	0	-1.783191	5.455568	-0.149921
68	6	0	-1.178167	4.229938	-0.589383
69	6	0	0.243686	4.201875	-0.799422
70	6	0	0.997212	5.403777	-0.584234
71	6	0	0.384605	6.547970	-0.175305
72	6	0	-1.030514	6.571840	0.052522
73	6	0	10.921983	-2.719343	1.287444
74	6	0	12.280721	-3.273488	0.922165
75	8	0	12.923800	-2.368374	0.048497
76	8	0	10.833736	0.472144	0.512284
77	6	0	11.080129	0.290636	-0.876516
78	6	0	9.788349	0.016223	-1.616866
79	8	0	-11.726322	-0.583193	2.788469
80	6	0	-10.935848	0.166386	3.681570

81	6	0	-9.571719	0.431105	3.091342
82	6	0	-11.110343	0.115091	-0.428686
83	6	0	-11.359990	-0.140922	-1.900768
84	8	0	-11.988790	1.002693	-2.461700
85	7	0	13.222504	1.918318	0.936575
86	6	0	12.034034	2.167801	1.730058
87	6	0	10.766788	1.812535	0.955081
88	6	0	13.988804	-2.936110	-0.689075
89	6	0	14.756377	-1.820596	-1.363430
90	6	0	-13.765955	-1.784716	2.424102
91	6	0	-13.032102	-0.782727	3.282006
92	6	0	-12.504520	0.812662	-3.761513
93	6	0	-14.033021	0.736599	-3.725041
94	7	0	-14.467332	-0.315595	-2.825957
95	7	0	13.682763	2.847735	0.085941
96	7	0	14.668437	2.314772	-0.581310
97	6	0	14.843742	1.033036	-0.163768
98	6	0	13.910603	0.762145	0.808682
99	6	0	-14.577632	-0.246788	-1.480669
100	6	0	-14.671946	-1.558651	-1.083359
101	7	0	-14.616427	-2.346713	-2.190061
102	7	0	-14.485497	-1.590824	-3.243300
103	8	0	15.633360	-1.226853	-0.424150
104	8	0	-13.981141	-1.245341	1.139396
105	6	0	-14.716916	-2.115671	0.299701
106	6	0	15.927178	0.132447	-0.682468
107	1	0	-4.852793	1.134630	2.061656
108	1	0	-7.243027	1.341482	2.553133
109	1	0	-7.622123	-2.939758	2.519058
110	1	0	-5.201080	-3.140158	1.997430
111	1	0	5.765458	-3.816058	-0.899028
112	1	0	8.210822	-4.240869	-1.036142
113	1	0	8.912827	-1.062234	1.761715
114	1	0	6.488379	-0.655627	1.910126
115	1	0	-2.239183	-3.657685	0.880120
116	1	0	-1.306695	-5.831591	0.221419

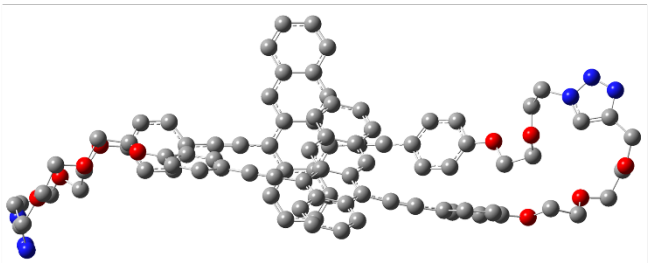
117	1	0	1.158429	-6.090312	-0.118085
118	1	0	2.659617	-4.178602	0.211371
119	1	0	-1.576800	1.094126	2.053469
120	1	0	3.312666	0.591196	1.324982
121	1	0	-1.254447	3.468274	2.649332
122	1	0	3.650889	2.966121	1.899565
123	1	0	2.704680	5.137239	2.577424
124	1	0	0.251599	5.384290	2.956644
125	1	0	-6.159675	3.021447	-0.801013
126	1	0	-8.608248	3.129598	-0.385658
127	1	0	-8.823569	-1.154897	-0.650974
128	1	0	-6.415391	-1.253068	-1.066144
129	1	0	5.194592	-1.146222	-2.796499
130	1	0	7.634982	-0.956273	-2.634651
131	1	0	7.208752	2.751765	-0.505077
132	1	0	4.734535	2.559733	-0.686912
133	1	0	-3.280891	-1.654080	-1.977985
134	1	0	-2.164700	-3.739588	-2.645200
135	1	0	0.318198	-3.816960	-2.893214
136	1	0	1.665948	-1.807036	-2.481500
137	1	0	-2.995082	3.101426	-0.661096
138	1	0	1.924375	2.988447	-1.322388
139	1	0	-2.856881	5.475987	0.016262
140	1	0	2.071098	5.377486	-0.745370
141	1	0	0.963735	7.451708	-0.013492
142	1	0	-1.499475	7.493192	0.383903
143	1	0	10.546536	-3.206998	2.195314
144	1	0	11.009177	-1.642215	1.459900
145	1	0	12.881222	-3.406201	1.833196
146	1	0	12.153889	-4.255602	0.448139
147	1	0	11.597380	1.161821	-1.294778
148	1	0	11.732380	-0.581329	-0.972302
149	1	0	9.988301	-0.117310	-2.688087
150	1	0	9.341405	-0.898550	-1.223467
151	1	0	-11.405994	1.139053	3.892377
152	1	0	-10.825099	-0.371600	4.634682

153	1	0	-9.661106	0.963957	2.138639
154	1	0	-9.018560	1.057227	3.802706
155	1	0	-10.781778	-0.798589	0.075198
156	1	0	-12.035146	0.421465	0.058426
157	1	0	-11.997362	-1.031154	-1.984730
158	1	0	-10.421446	-0.344681	-2.432907
159	1	0	12.030542	3.221989	2.011861
160	1	0	12.106135	1.562219	2.635053
161	1	0	10.631521	2.500047	0.116376
162	1	0	9.899964	1.914656	1.615299
163	1	0	13.591266	-3.628558	-1.444455
164	1	0	14.668658	-3.494893	-0.032135
165	1	0	14.040438	-1.087493	-1.756511
166	1	0	15.334130	-2.222371	-2.206974
167	1	0	-13.179035	-2.711314	2.355855
168	1	0	-14.725343	-2.020768	2.909037
169	1	0	-12.997008	-1.176730	4.308945
170	1	0	-13.584632	0.168198	3.301672
171	1	0	-12.104238	-0.097910	-4.220062
172	1	0	-12.207971	1.665481	-4.379732
173	1	0	-14.434542	0.526958	-4.717478
174	1	0	-14.449430	1.678551	-3.365210
175	1	0	13.672480	-0.138537	1.351958
176	1	0	-14.532986	0.681909	-0.935141
177	1	0	-14.274495	-3.120139	0.283932
178	1	0	-15.748779	-2.209548	0.668151
179	1	0	16.867623	0.339954	-0.167242
180	1	0	16.089758	0.319165	-1.751291

Cartesian coordinates of $(Tet)_2$-CyO_{10} at 120 degrees calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{10} at 120 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	10.035569	-2.993095	0.205103
2	8	0	-8.911459	-0.809235	2.902591
3	6	0	-5.451622	0.237444	2.178864
4	6	0	-6.808139	0.353439	2.466305
5	6	0	-7.587355	-0.798443	2.600145
6	6	0	-6.999497	-2.056932	2.419454
7	6	0	-5.651483	-2.161433	2.127593
8	6	0	6.455457	-3.219361	-0.311211
9	6	0	7.817347	-3.461185	-0.392330

10	6	0	8.712567	-2.704385	0.371106
11	6	0	8.230018	-1.687735	1.199374
12	6	0	6.861139	-1.448892	1.270826
13	6	0	-4.848843	-1.012867	2.010801
14	6	0	5.952883	-2.213719	0.529785
15	6	0	-3.449938	-1.129560	1.740063
16	6	0	4.543492	-1.993299	0.638497
17	6	0	3.345279	-1.839976	0.757623
18	6	0	-2.259055	-1.250130	1.538065
19	6	0	-1.170283	-3.776317	0.741213
20	6	0	-0.651465	-4.979367	0.372092
21	6	0	0.755386	-5.125913	0.175369
22	6	0	1.590848	-4.066094	0.357679
23	6	0	-0.857164	-1.393037	1.326893
24	6	0	-0.327911	-2.634734	0.944367
25	6	0	1.085806	-2.782340	0.747081
26	6	0	1.938753	-1.684369	0.934642
27	6	0	-0.506632	0.981695	1.909792
28	6	0	-0.000865	-0.272111	1.522091
29	6	0	1.413533	-0.419933	1.322105
30	6	0	2.246778	0.697970	1.503855
31	6	0	-0.184424	3.356503	2.500366
32	6	0	0.324380	2.074523	2.102632
33	6	0	1.738479	1.929626	1.886229
34	6	0	2.582689	3.077357	2.066957
35	6	0	2.058581	4.274615	2.446721
36	6	0	0.650548	4.416465	2.671374
37	8	0	8.916434	1.116754	-1.403295
38	8	0	-10.196979	1.185884	-0.206384
39	6	0	-6.748228	2.110008	-0.771087
40	6	0	-8.110720	2.177433	-0.536678
41	6	0	-8.880170	1.008132	-0.494699
42	6	0	-8.262129	-0.229762	-0.697638
43	6	0	-6.893685	-0.288150	-0.935576
44	6	0	5.631301	-0.286058	-2.300182
45	6	0	7.014961	-0.178914	-2.204485

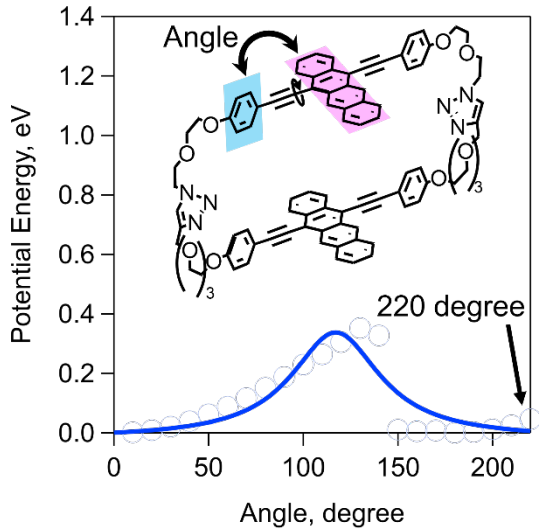
46	6	0	7.580857	0.918345	-1.552036
47	6	0	6.750920	1.905716	-1.007019
48	6	0	5.376104	1.793686	-1.111824
49	6	0	-6.114740	0.872984	-0.972614
50	6	0	4.791248	0.692727	-1.762128
51	6	0	-4.701055	0.802788	-1.167500
52	6	0	3.369049	0.598784	-1.850547
53	6	0	2.155989	0.581828	-1.862047
54	6	0	-3.496222	0.745328	-1.302719
55	6	0	-2.204278	-1.685705	-2.104716
56	6	0	-1.583270	-2.839318	-2.474054
57	6	0	-0.163695	-2.883965	-2.620320
58	6	0	0.585349	-1.770947	-2.391006
59	6	0	-2.081738	0.700463	-1.463881
60	6	0	-1.453998	-0.489973	-1.859364
61	6	0	-0.027581	-0.532936	-2.011233
62	6	0	0.735275	0.619208	-1.774990
63	6	0	-1.919784	3.079117	-0.810746
64	6	0	-1.317356	1.877552	-1.225573
65	6	0	0.106671	1.840806	-1.400961
66	6	0	0.848263	3.015990	-1.185229
67	6	0	-1.783191	5.455568	-0.149921
68	6	0	-1.178167	4.229938	-0.589383
69	6	0	0.243686	4.201875	-0.799422
70	6	0	0.997212	5.403777	-0.584234
71	6	0	0.384605	6.547970	-0.175305
72	6	0	-1.030514	6.571840	0.052522
73	6	0	10.921983	-2.719343	1.287444
74	6	0	12.280721	-3.273488	0.922165
75	8	0	12.923800	-2.368374	0.048497
76	8	0	10.833736	0.472144	0.512284
77	6	0	11.080129	0.290636	-0.876516
78	6	0	9.788349	0.016223	-1.616866
79	8	0	-11.726322	-0.583193	2.788469
80	6	0	-10.935848	0.166386	3.681570
81	6	0	-9.571719	0.431105	3.091342

82	6	0	-11.110343	0.115091	-0.428686
83	6	0	-11.359990	-0.140922	-1.900768
84	8	0	-11.988790	1.002693	-2.461700
85	7	0	13.222504	1.918318	0.936575
86	6	0	12.034034	2.167801	1.730058
87	6	0	10.766788	1.812535	0.955081
88	6	0	13.988804	-2.936110	-0.689075
89	6	0	14.756377	-1.820596	-1.363430
90	6	0	-13.765955	-1.784716	2.424102
91	6	0	-13.032102	-0.782727	3.282006
92	6	0	-12.504520	0.812662	-3.761513
93	6	0	-14.033021	0.736599	-3.725041
94	7	0	-14.467332	-0.315595	-2.825957
95	7	0	13.682763	2.847735	0.085941
96	7	0	14.668437	2.314772	-0.581310
97	6	0	14.843742	1.033036	-0.163768
98	6	0	13.910603	0.762145	0.808682
99	6	0	-14.577632	-0.246788	-1.480669
100	6	0	-14.671946	-1.558651	-1.083359
101	7	0	-14.616427	-2.346713	-2.190061
102	7	0	-14.485497	-1.590824	-3.243300
103	8	0	15.633360	-1.226853	-0.424150
104	8	0	-13.981141	-1.245341	1.139396
105	6	0	-14.716916	-2.115671	0.299701
106	6	0	15.927178	0.132447	-0.682468
107	1	0	-4.852793	1.134630	2.061656
108	1	0	-7.243027	1.341482	2.553133
109	1	0	-7.622123	-2.939758	2.519058
110	1	0	-5.201080	-3.140158	1.997430
111	1	0	5.765458	-3.816058	-0.899028
112	1	0	8.210822	-4.240869	-1.036142
113	1	0	8.912827	-1.062234	1.761715
114	1	0	6.488379	-0.655627	1.910126
115	1	0	-2.239183	-3.657685	0.880120
116	1	0	-1.306695	-5.831591	0.221419
117	1	0	1.158429	-6.090312	-0.118085

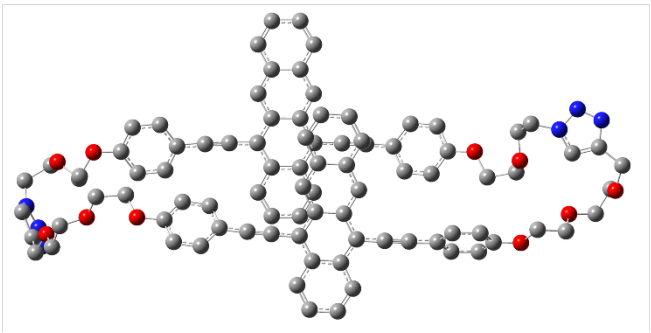
118	1	0	2.659617	-4.178602	0.211371
119	1	0	-1.576800	1.094126	2.053469
120	1	0	3.312666	0.591196	1.324982
121	1	0	-1.254447	3.468274	2.649332
122	1	0	3.650889	2.966121	1.899565
123	1	0	2.704680	5.137239	2.577424
124	1	0	0.251599	5.384290	2.956644
125	1	0	-6.159675	3.021447	-0.801013
126	1	0	-8.608248	3.129598	-0.385658
127	1	0	-8.823569	-1.154897	-0.650974
128	1	0	-6.415391	-1.253068	-1.066144
129	1	0	5.194592	-1.146222	-2.796499
130	1	0	7.634982	-0.956273	-2.634651
131	1	0	7.208752	2.751765	-0.505077
132	1	0	4.734535	2.559733	-0.686912
133	1	0	-3.280891	-1.654080	-1.977985
134	1	0	-2.164700	-3.739588	-2.645200
135	1	0	0.318198	-3.816960	-2.893214
136	1	0	1.665948	-1.807036	-2.481500
137	1	0	-2.995082	3.101426	-0.661096
138	1	0	1.924375	2.988447	-1.322388
139	1	0	-2.856881	5.475987	0.016262
140	1	0	2.071098	5.377486	-0.745370
141	1	0	0.963735	7.451708	-0.013492
142	1	0	-1.499475	7.493192	0.383903
143	1	0	10.546536	-3.206998	2.195314
144	1	0	11.009177	-1.642215	1.459900
145	1	0	12.881222	-3.406201	1.833196
146	1	0	12.153889	-4.255602	0.448139
147	1	0	11.597380	1.161821	-1.294778
148	1	0	11.732380	-0.581329	-0.972302
149	1	0	9.988301	-0.117310	-2.688087
150	1	0	9.341405	-0.898550	-1.223467
151	1	0	-11.405994	1.139053	3.892377
152	1	0	-10.825099	-0.371600	4.634682
153	1	0	-9.661106	0.963957	2.138639

154	1	0	-9.018560	1.057227	3.802706
155	1	0	-10.781778	-0.798589	0.075198
156	1	0	-12.035146	0.421465	0.058426
157	1	0	-11.997362	-1.031154	-1.984730
158	1	0	-10.421446	-0.344681	-2.432907
159	1	0	12.030542	3.221989	2.011861
160	1	0	12.106135	1.562219	2.635053
161	1	0	10.631521	2.500047	0.116376
162	1	0	9.899964	1.914656	1.615299
163	1	0	13.591266	-3.628558	-1.444455
164	1	0	14.668658	-3.494893	-0.032135
165	1	0	14.040438	-1.087493	-1.756511
166	1	0	15.334130	-2.222371	-2.206974
167	1	0	-13.179035	-2.711314	2.355855
168	1	0	-14.725343	-2.020768	2.909037
169	1	0	-12.997008	-1.176730	4.308945
170	1	0	-13.584632	0.168198	3.301672
171	1	0	-12.104238	-0.097910	-4.220062
172	1	0	-12.207971	1.665481	-4.379732
173	1	0	-14.434542	0.526958	-4.717478
174	1	0	-14.449430	1.678551	-3.365210
175	1	0	13.672480	-0.138537	1.351958
176	1	0	-14.532986	0.681909	-0.935141
177	1	0	-14.274495	-3.120139	0.283932
178	1	0	-15.748779	-2.209548	0.668151
179	1	0	16.867623	0.339954	-0.167242
180	1	0	16.089758	0.319165	-1.751291

Cartesian coordinates of $(Tet)_2$-CyO_{10} at 220 degrees calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.



Optimized structure of $(Tet)_2$-CyO_{10} at 220 degree



Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	10.035569	-2.993095	0.205103
2	8	0	-8.911459	-0.809235	2.902591
3	6	0	-5.451622	0.237444	2.178864
4	6	0	-6.808139	0.353439	2.466305
5	6	0	-7.587355	-0.798443	2.600145
6	6	0	-6.999497	-2.056932	2.419454
7	6	0	-5.651483	-2.161433	2.127593
8	6	0	6.455457	-3.219361	-0.311211
9	6	0	7.817347	-3.461185	-0.392330

10	6	0	8.712567	-2.704385	0.371106
11	6	0	8.230018	-1.687735	1.199374
12	6	0	6.861139	-1.448892	1.270826
13	6	0	-4.848843	-1.012867	2.010801
14	6	0	5.952883	-2.213719	0.529785
15	6	0	-3.449938	-1.129560	1.740063
16	6	0	4.543492	-1.993299	0.638497
17	6	0	3.345279	-1.839976	0.757623
18	6	0	-2.259055	-1.250130	1.538065
19	6	0	-1.170283	-3.776317	0.741213
20	6	0	-0.651465	-4.979367	0.372092
21	6	0	0.755386	-5.125913	0.175369
22	6	0	1.590848	-4.066094	0.357679
23	6	0	-0.857164	-1.393037	1.326893
24	6	0	-0.327911	-2.634734	0.944367
25	6	0	1.085806	-2.782340	0.747081
26	6	0	1.938753	-1.684369	0.934642
27	6	0	-0.506632	0.981695	1.909792
28	6	0	-0.000865	-0.272111	1.522091
29	6	0	1.413533	-0.419933	1.322105
30	6	0	2.246778	0.697970	1.503855
31	6	0	-0.184424	3.356503	2.500366
32	6	0	0.324380	2.074523	2.102632
33	6	0	1.738479	1.929626	1.886229
34	6	0	2.582689	3.077357	2.066957
35	6	0	2.058581	4.274615	2.446721
36	6	0	0.650548	4.416465	2.671374
37	8	0	8.916434	1.116754	-1.403295
38	8	0	-10.196979	1.185884	-0.206384
39	6	0	-6.748228	2.110008	-0.771087
40	6	0	-8.110720	2.177433	-0.536678
41	6	0	-8.880170	1.008132	-0.494699
42	6	0	-8.262129	-0.229762	-0.697638
43	6	0	-6.893685	-0.288150	-0.935576
44	6	0	5.631301	-0.286058	-2.300182
45	6	0	7.014961	-0.178914	-2.204485

46	6	0	7.580857	0.918345	-1.552036
47	6	0	6.750920	1.905716	-1.007019
48	6	0	5.376104	1.793686	-1.111824
49	6	0	-6.114740	0.872984	-0.972614
50	6	0	4.791248	0.692727	-1.762128
51	6	0	-4.701055	0.802788	-1.167500
52	6	0	3.369049	0.598784	-1.850547
53	6	0	2.155989	0.581828	-1.862047
54	6	0	-3.496222	0.745328	-1.302719
55	6	0	-2.204278	-1.685705	-2.104716
56	6	0	-1.583270	-2.839318	-2.474054
57	6	0	-0.163695	-2.883965	-2.620320
58	6	0	0.585349	-1.770947	-2.391006
59	6	0	-2.081738	0.700463	-1.463881
60	6	0	-1.453998	-0.489973	-1.859364
61	6	0	-0.027581	-0.532936	-2.011233
62	6	0	0.735275	0.619208	-1.774990
63	6	0	-1.919784	3.079117	-0.810746
64	6	0	-1.317356	1.877552	-1.225573
65	6	0	0.106671	1.840806	-1.400961
66	6	0	0.848263	3.015990	-1.185229
67	6	0	-1.783191	5.455568	-0.149921
68	6	0	-1.178167	4.229938	-0.589383
69	6	0	0.243686	4.201875	-0.799422
70	6	0	0.997212	5.403777	-0.584234
71	6	0	0.384605	6.547970	-0.175305
72	6	0	-1.030514	6.571840	0.052522
73	6	0	10.921983	-2.719343	1.287444
74	6	0	12.280721	-3.273488	0.922165
75	8	0	12.923800	-2.368374	0.048497
76	8	0	10.833736	0.472144	0.512284
77	6	0	11.080129	0.290636	-0.876516
78	6	0	9.788349	0.016223	-1.616866
79	8	0	-11.726322	-0.583193	2.788469
80	6	0	-10.935848	0.166386	3.681570
81	6	0	-9.571719	0.431105	3.091342

82	6	0	-11.110343	0.115091	-0.428686
83	6	0	-11.359990	-0.140922	-1.900768
84	8	0	-11.988790	1.002693	-2.461700
85	7	0	13.222504	1.918318	0.936575
86	6	0	12.034034	2.167801	1.730058
87	6	0	10.766788	1.812535	0.955081
88	6	0	13.988804	-2.936110	-0.689075
89	6	0	14.756377	-1.820596	-1.363430
90	6	0	-13.765955	-1.784716	2.424102
91	6	0	-13.032102	-0.782727	3.282006
92	6	0	-12.504520	0.812662	-3.761513
93	6	0	-14.033021	0.736599	-3.725041
94	7	0	-14.467332	-0.315595	-2.825957
95	7	0	13.682763	2.847735	0.085941
96	7	0	14.668437	2.314772	-0.581310
97	6	0	14.843742	1.033036	-0.163768
98	6	0	13.910603	0.762145	0.808682
99	6	0	-14.577632	-0.246788	-1.480669
100	6	0	-14.671946	-1.558651	-1.083359
101	7	0	-14.616427	-2.346713	-2.190061
102	7	0	-14.485497	-1.590824	-3.243300
103	8	0	15.633360	-1.226853	-0.424150
104	8	0	-13.981141	-1.245341	1.139396
105	6	0	-14.716916	-2.115671	0.299701
106	6	0	15.927178	0.132447	-0.682468
107	1	0	-4.852793	1.134630	2.061656
108	1	0	-7.243027	1.341482	2.553133
109	1	0	-7.622123	-2.939758	2.519058
110	1	0	-5.201080	-3.140158	1.997430
111	1	0	5.765458	-3.816058	-0.899028
112	1	0	8.210822	-4.240869	-1.036142
113	1	0	8.912827	-1.062234	1.761715
114	1	0	6.488379	-0.655627	1.910126
115	1	0	-2.239183	-3.657685	0.880120
116	1	0	-1.306695	-5.831591	0.221419
117	1	0	1.158429	-6.090312	-0.118085

118	1	0	2.659617	-4.178602	0.211371
119	1	0	-1.576800	1.094126	2.053469
120	1	0	3.312666	0.591196	1.324982
121	1	0	-1.254447	3.468274	2.649332
122	1	0	3.650889	2.966121	1.899565
123	1	0	2.704680	5.137239	2.577424
124	1	0	0.251599	5.384290	2.956644
125	1	0	-6.159675	3.021447	-0.801013
126	1	0	-8.608248	3.129598	-0.385658
127	1	0	-8.823569	-1.154897	-0.650974
128	1	0	-6.415391	-1.253068	-1.066144
129	1	0	5.194592	-1.146222	-2.796499
130	1	0	7.634982	-0.956273	-2.634651
131	1	0	7.208752	2.751765	-0.505077
132	1	0	4.734535	2.559733	-0.686912
133	1	0	-3.280891	-1.654080	-1.977985
134	1	0	-2.164700	-3.739588	-2.645200
135	1	0	0.318198	-3.816960	-2.893214
136	1	0	1.665948	-1.807036	-2.481500
137	1	0	-2.995082	3.101426	-0.661096
138	1	0	1.924375	2.988447	-1.322388
139	1	0	-2.856881	5.475987	0.016262
140	1	0	2.071098	5.377486	-0.745370
141	1	0	0.963735	7.451708	-0.013492
142	1	0	-1.499475	7.493192	0.383903
143	1	0	10.546536	-3.206998	2.195314
144	1	0	11.009177	-1.642215	1.459900
145	1	0	12.881222	-3.406201	1.833196
146	1	0	12.153889	-4.255602	0.448139
147	1	0	11.597380	1.161821	-1.294778
148	1	0	11.732380	-0.581329	-0.972302
149	1	0	9.988301	-0.117310	-2.688087
150	1	0	9.341405	-0.898550	-1.223467
151	1	0	-11.405994	1.139053	3.892377
152	1	0	-10.825099	-0.371600	4.634682
153	1	0	-9.661106	0.963957	2.138639

154	1	0	-9.018560	1.057227	3.802706
155	1	0	-10.781778	-0.798589	0.075198
156	1	0	-12.035146	0.421465	0.058426
157	1	0	-11.997362	-1.031154	-1.984730
158	1	0	-10.421446	-0.344681	-2.432907
159	1	0	12.030542	3.221989	2.011861
160	1	0	12.106135	1.562219	2.635053
161	1	0	10.631521	2.500047	0.116376
162	1	0	9.899964	1.914656	1.615299
163	1	0	13.591266	-3.628558	-1.444455
164	1	0	14.668658	-3.494893	-0.032135
165	1	0	14.040438	-1.087493	-1.756511
166	1	0	15.334130	-2.222371	-2.206974
167	1	0	-13.179035	-2.711314	2.355855
168	1	0	-14.725343	-2.020768	2.909037
169	1	0	-12.997008	-1.176730	4.308945
170	1	0	-13.584632	0.168198	3.301672
171	1	0	-12.104238	-0.097910	-4.220062
172	1	0	-12.207971	1.665481	-4.379732
173	1	0	-14.434542	0.526958	-4.717478
174	1	0	-14.449430	1.678551	-3.365210
175	1	0	13.672480	-0.138537	1.351958
176	1	0	-14.532986	0.681909	-0.935141
177	1	0	-14.274495	-3.120139	0.283932
178	1	0	-15.748779	-2.209548	0.668151
179	1	0	16.867623	0.339954	-0.167242
180	1	0	16.089758	0.319165	-1.751291

DFT-computed energy landscape scanning over rotation of one pentacene–phenylene dihedral angles of $(Tet)_2$-CyO_{10} calculated with Gaussian 09 using DFT method at the B3LYP/6-31G level.

Angle, degree	Total Energy (Hartree)	Potential Energy, eV
0	-4553.32775777	0.00
10	-4553.32769680	0.00
20	-4553.32743358	0.01
30	-4553.32699047	0.02
40	-4553.32632195	0.04
50	-4553.32545602	0.06
60	-4553.32452998	0.09
70	-4553.32348054	0.12
80	-4553.32219640	0.15
90	-4553.32083514	0.19
100	-4553.31932435	0.23
110	-4553.31806889	0.26
120	-4553.31653586	0.31
130	-4553.31482110	0.35
140	-4553.31573227	0.33
150	-4553.32737406	0.01
160	-4553.32757187	0.01
170	-4553.32749051	0.01
180	-4553.32775344	0.00
190	-4553.32765484	0.00
200	-4553.32733476	0.01
210	-4553.32682181	0.03
220	-4553.32606264	0.05

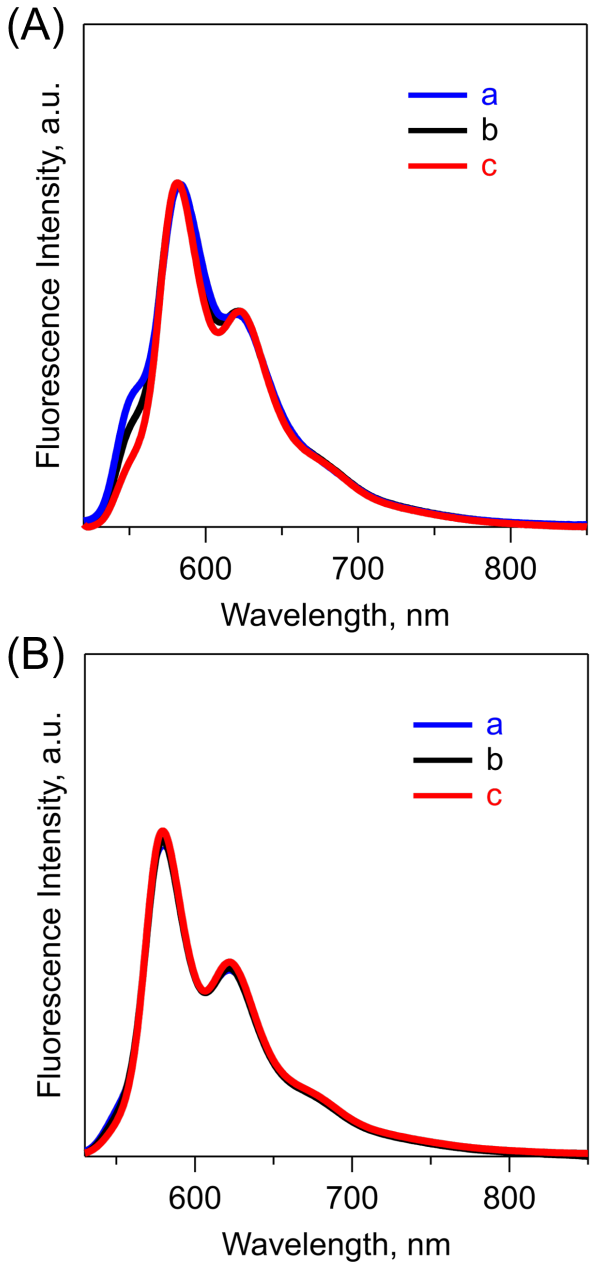


Fig. S59 (A) Normalized fluorescence emission spectra of $(Tet)_2$-CyO_{10} upon excitation at (a) 340 nm, (b) 480 nm and (c) 515 nm in THF. (B) Normalized fluorescence spectra of $(Tet)_2$-CyO_{12} upon excitation at (a) 360 nm, (b) 480 nm and (c) 520 nm in THF.

In contrast with the no spectral changes of $(Tet)_2$-CyO_{12}, the emission intensity of $(Tet)_2$-CyO_{10} derived from the *H*-type excited state complex (at ca. 550 nm) is relatively higher at the shorter excitation wavelength at 340 nm. Since the *H*-type excited state complex

should be a competitive reaction with ISF, the ISF becomes more efficient at the longer excitation wavelength. Our picosecond transient absorption measurement (ps-TAS) system has two different excitation wavelengths such as 355 and 532 nm. Therefore, 532 nm is appropriate for high-yield ISF because the *H*-type excited state complex is relatively suppressed.

Table S1 Summarized emission quantum yields in THF

	Tet-ref	$(Tet)_2$-CyO_{10}	$(Tet)_2$-CyO_{12}
Φ_{FL}	0.73	0.16	0.21

Table S2 Summarized fluorescence lifetimes in $(Tet)_2$-CyO_n and Tet-ref in THF

	λ_{obs} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
Tet-ref	575	7.6	–	–
$(Tet)_2$-CyO_{12}	580	0.72	13.7	–
$(Tet)_2$-CyO_{10}	582	0.59	6.6	15.2

First, fluorescence decay profiles of Tet-ref (line a: gray) and $(Tet)_2$-CyO_{12} (line b: red) in THF were evaluated (Fig. 4). The fluorescence lifetimes of $(Tet)_2$-CyO_{12} were determined to be 0.72 ns and 13.7 ns by di-exponential function. This is in contrast with that of Tet-ref, which was evaluated by mono-exponential function (τ_S = 7.6 ns). Therefore, τ_1 and τ_2 corresponds to ISF and TTA, respectively. Next, the fluorescence lifetimes (τ_S) of $(Tet)_2$-CyO_{10} (line c : blue) in THF were calculated by tri-exponential fitting of the corresponding decay profiles. In addition to the first component: ISF and the second component: TTA, the third component is attributable with the emission process derived from the *H*-type excited complex (*H*-Comp). Finally, the kinetic values such as rate constants of ISF (k_{ISF}), TTA (k_{TTA}), *H*-Comp formation (k_{Comp}) and emission from *H*-Comp (k_{Lum}) were estimated by performing target analysis on the transient absorption with reference to the above lifetimes estimated for Tet compounds. The calculated values of the rate constants were summarized in Table 1 in the text.

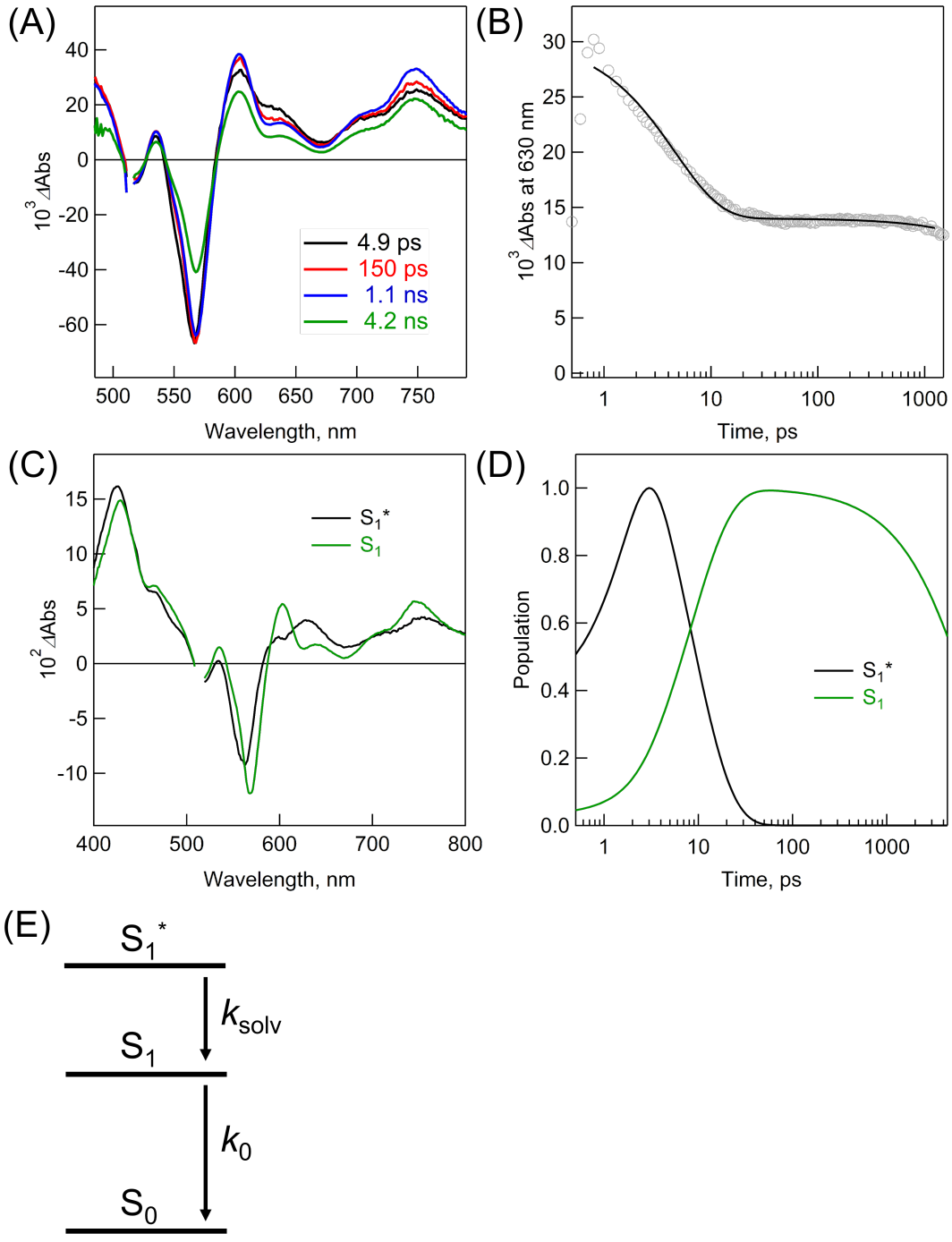


Fig. S60 (A) fs-TAS of Tet-ref in THF (λ_{ex} = 515 nm). (B) Time profile at 602 nm. (C) The species-associated spectra of the initial singlet excited state (S_1^*) (black line) and solvent-relaxed S_1 (S_1) (green line). (C) Time-dependent population profiles of S_1* (black line) and S_1 (green line). (E) A kinetic model for target analysis of Tet-ref.

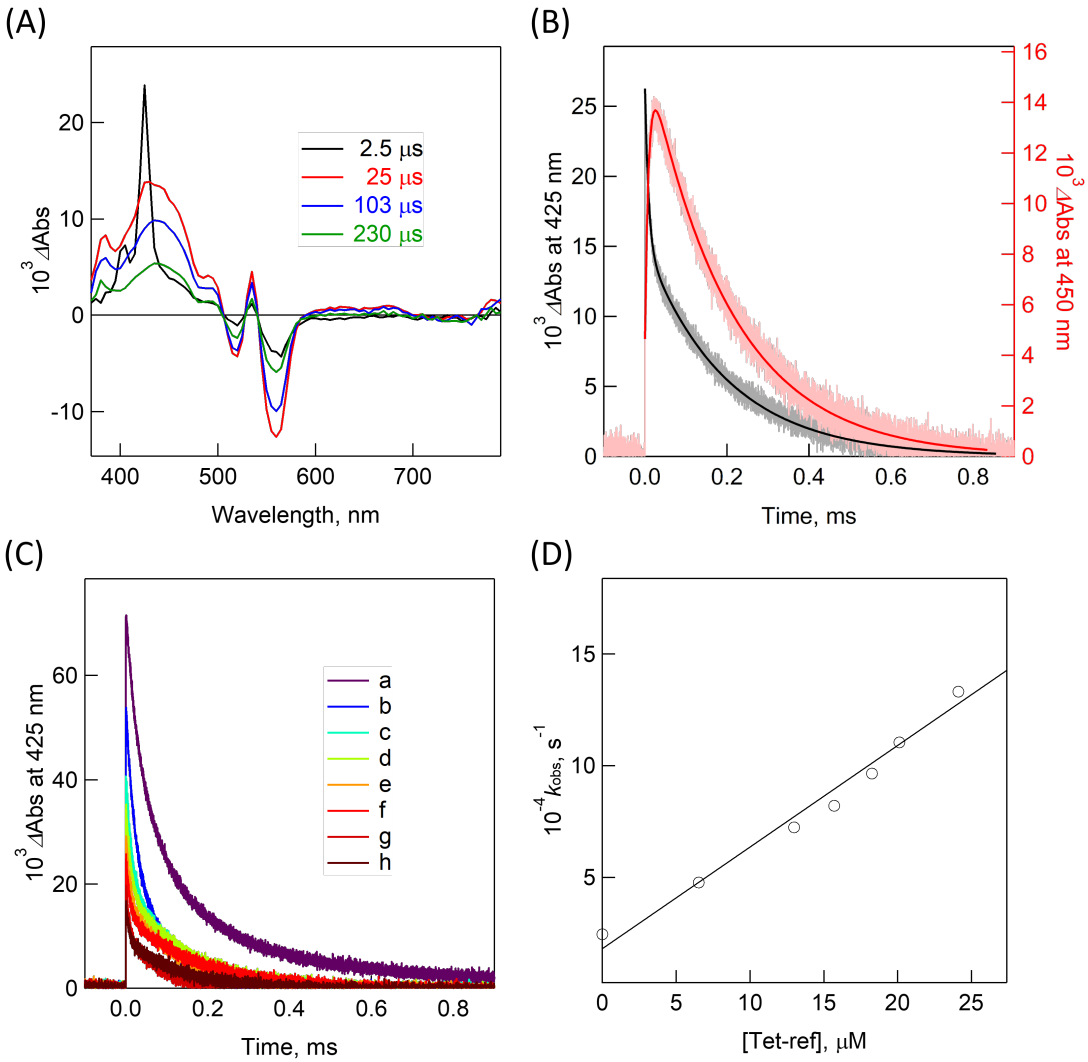


Fig. S61 (A) Nanosecond transient absorption spectra (ns-TAS) of anthracene (ca. 200 μM) in the presence of Tet-ref (24 μM) excited at 355 nm in THF. (B) The corresponding time profiles at 425 nm and 450 nm. (C) The time profiles of absorption at 425 nm in the presence of different concentrations of Tet-ref. (a) 0 μM, (b) 6.5 μM, (c) 13 μM, (d) 16 μM, (e) 18 μM, (f) 20 μM, (g) 24 μM and (h) 27 μM. (D) The pseudo-fist order plot vs. the concentration of Tet-ref monitored at 425 nm. The rate constant of energy transfer was determined to be $4.5 \times 10^9\ M^{-1}\ s^{-1}$.

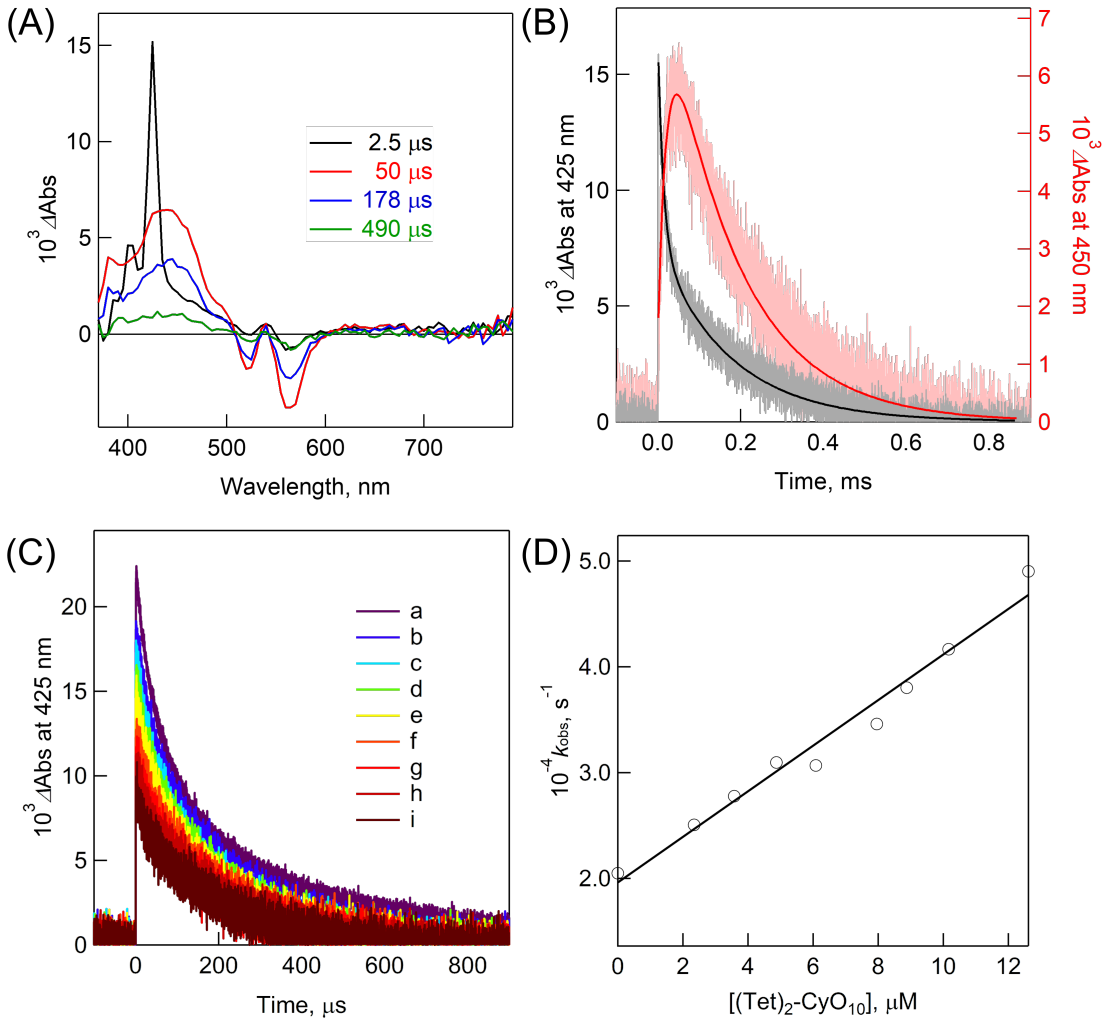


Fig. S62 (A) Nanosecond transient absorption spectra (ns-TAS) of anthracene (ca. 200 μM) in the presence of $(Tet)_2$-CyO_{10} (6.1 μM) excited at 355 nm in THF. (B) The corresponding time profiles at 425 nm and 450 nm. (C) The time profiles of absorption at 425 nm in the presence of different concentrations of $(Tet)_2$-CyO_{10}. (a) 0 μM, (b) 2.3 μM, (c) 3.6 μM, (d) 4.9 μM, (e) 6.1 μM, (f) 8.0 μM, (g) 8.9 μM, (h) 10 μM and (i) 13 μM. (D) The pseudo-fist order plot vs. the concentration of $(Tet)_2$-CyO_{10} monitored at 430 nm. The rate constant of energy transfer was determined to be $2.1 \times 10^9\ M^{-1}\ s^{-1}$.

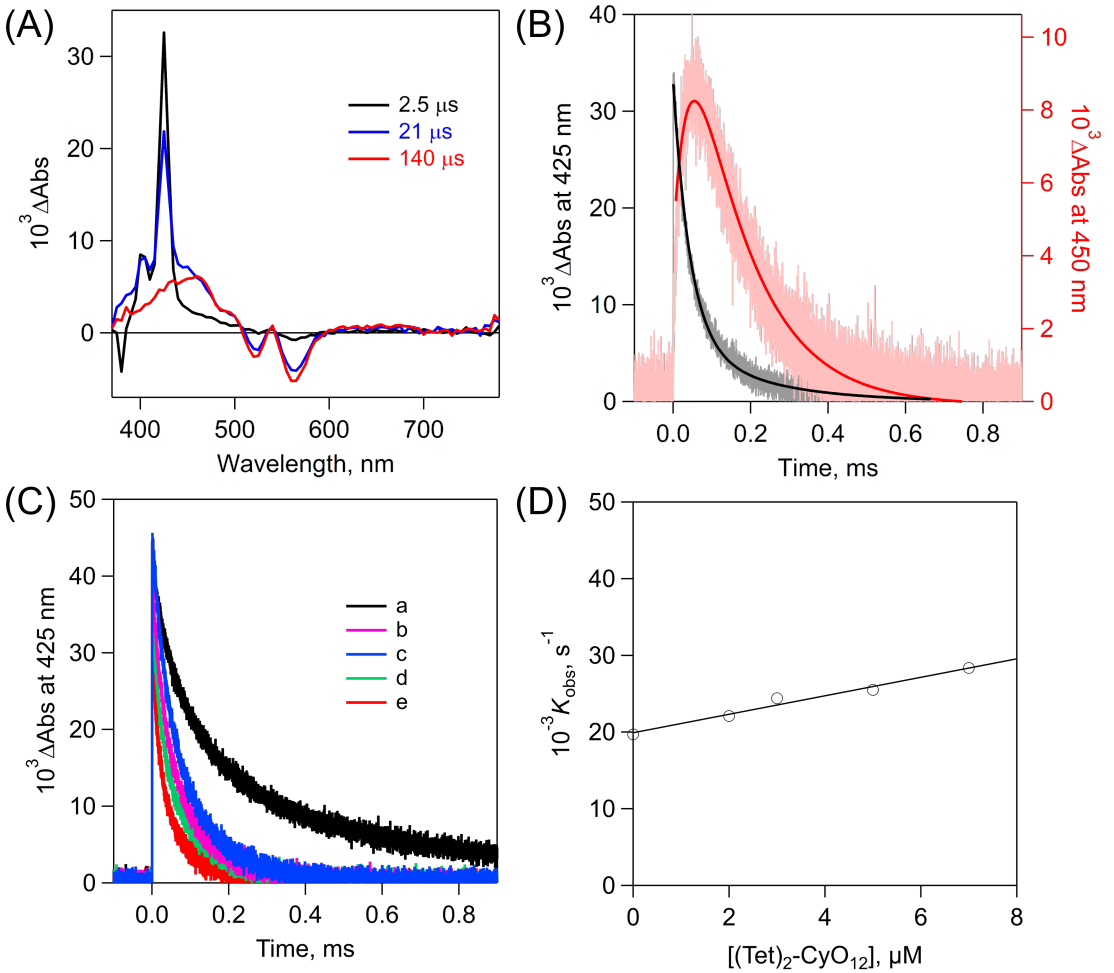


Fig. S63 (A) Nanosecond transient absorption spectra (ns-TAS) of anthracene (ca. 300 μM) in the presence of $(Tet)_2$-CyO_{12} (5.0 μM) excited at 355 nm in THF. (B) The corresponding time profiles at 425 nm and 435 nm. (C) The time profiles of absorption at 425 nm in the presence of different concentrations of Tet-ref. (a) 0 μM, (b) 2.0 μM, (c) 5.0 μM, and (d) 7.0 μM. (D) The pseudo-fist order plot vs. the concentration of $(Tet)_2$-CyO_{12} monitored at 450 nm. The rate constant of energy transfer was determined to be $4.0 \times 10^9\ M^{-1}\ s^{-1}$.

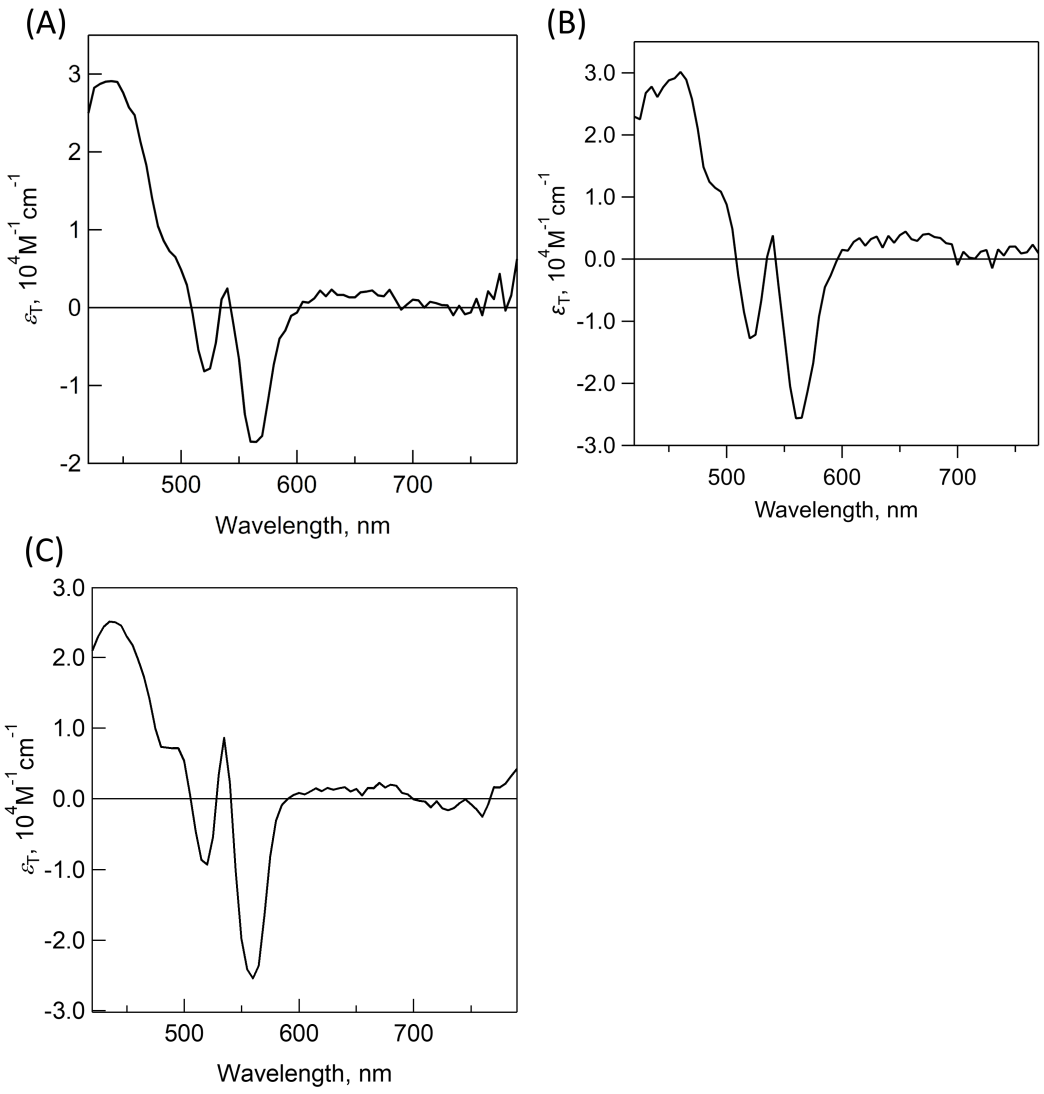


Fig. S64 Sensitized T-T absorption spectra of (A) $(Tet)_2$-CyO_{10}, (B) $(Tet)_2$-CyO_{12}, and (C) Tet-ref in THF (λ_{ex} = 355 nm, sensitizer: anthracene). The extinction coefficient of T-T absorption (ε_T) of (A) $(Tet)_2$-CyO_{10} is 27,600 M^{-1} cm^{-1} at 450 nm, (B) that of $(Tet)_2$-CyO_{12} is 28,800 M^{-1} cm^{-1} at 450 nm, and that of Tet-ref is 23,000 M^{-1} cm^{-1} at 450 nm.

Calculation Processes of Triplet Yields

1. Concentration of Excited Singlet States[8]

Concentrations of the excited singlet states ([^{1}S]) of Tet derivatives were calculated by analyzing ps-TAS. When the solution in a cuvette is irradiated by the pump laser, the fraction of light intensity transmitted (I/I_0) through a solution can be calculated as follows:

$$(I/I_0) = 1 - 10^{-\mathrm{Abs(532\ nm)}}$$

Where Abs(532 nm) represents absorbance at 532 nm in absorption measurement. The calculation of [^{1}S] depends on the total number of photons per pump pulse:

$$\text{(photons) / (pulse)} = \text{(laser power) / [(repetition rate) × (energy per photon)]}$$

We assumed the number of absorbed photons in the photo-interaction volume is equal to the initial population of the excited molecules. Then, a cylindrical volume (V) was calculated by the excitation spot area times the call path length (d), that is:

$$V = (\pi \times r^2) \times d = \pi \times (0.1\ \mathrm{cm})^2 \times [(0.2\ \mathrm{cm}) \times (0.001\ \mathrm{L\ cm^{-3}})] = 6.28 \times 10^{-6}\ \mathrm{L}$$

Where r is the laser radius. Based on these values, [^{1}S] can be calculated as follows:

$$[^1\mathrm{S}] = [(\text{photon / pulse}) \times (I/I_0)] / (N_\mathrm{A} \times V)$$

Where N_A is Avogadro constant ($N_\mathrm{A} = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$). The values of [^{1}S] obtained here are summarized in Table S3.

Table S3 Concentrations of excited singlet states.

	[^{1}S*] (M)
$(Tet)_2$-CyO_{10}	7.8×10^{-7}
$(Tet)_2$-CyO_{12}	9.0×10^{-8}
Tet-ref	2.7×10^{-7}

2. Concentrations of Excited Triplet States[9, 10]

The energy transfer (EnT) method was utilized to determine the extinction coefficient of the triplet excited state of Tet derivatives. The kinetic model is represented as follows:

$^3D^* \rightarrow D$ (Intersystem crossing of donor: $t_{0,\,D} = 1/k_{0,\,D}$)

$^3D^* + A \rightarrow D + {}^3A^*$ (Energy transfer from donor to acceptor: k_{EnT})

$^3A^* \rightarrow A$ (Intersystem crossing of acceptor: $t_A = 1/k_A$)

Where D and A are the energy donor and acceptor, respectively. The quantum yield of EnT and related equations are

$$\Phi_{EnT} = k_{EnT}[A] / (k_{EnT}[A] + k_{0,D})$$

$$\varepsilon_A = \varepsilon_D \times (\Delta Abs._A / \Delta Abs._D) / \Phi_{EnT}$$

Where ε_D, ε_A, $\Delta Abs._A$, and $\Delta Abs._D$ are molar absorption coefficients and delta absorbance of D and A, respectively. Then, considering the ratio of the intersystem crossing of acceptor generated by EnT and the rate constant of EnT, the value of $\Delta Abs._A$, is corrected by the delta absorbance ($\Delta Abs._{A,\,corr.}$), which is taken at the time (t_{max}) of the maximum concentration of $^3A^*$ and the raw data of delta absorbance ($\Delta Abs._{A,\,raw}$) at t_{max} as follows:

$$\Delta Abs._{A,\,corr.} = \Delta Abs._{A,\,raw} \times \exp(k_A t_{max})$$

$$t_{max} = \ln(k_A / (k_{EnT}[A] + k_{0,\,D})) / (k_A - k_{EnT}[A] - k_{0,\,D})$$

In this study, anthracene (Anth) was employed as an energy donor (D) because EnT process is energetically feasible considering the energy of triplet excited state of Ant (1.8 eV)[11] and Tet (1.2 eV).[9, 10] The molar extinction coefficient of triplet excited state of Anth was reported as 47,700 M^{-1} cm^{-1} at 425 nm in THF. The obtained rate constant of the EnT (k_{EnT}) shows that EnT process approximately proceeded in all systems according to the diffusion-limited mechanism in THF. The concentrations of Tet derivatives in the measurement were corrected by steady-state absorption spectra.

Then, the concentrations of the triplet excited state ($[^3T^*]$) were estimated as follows:

$$[^3T^*] = \Delta Abs\ (1.0\ \mu s) / (\varepsilon_T \times d)$$

Where, ΔAbs (1.0 μs) and d are the delta absorbance of T-T absorption spectra at 1.0 μs

in ps-TAS and cell length, respectively. Finally, the triplet quantum yields (Φ_T) were obtained by the following equation:

$\Phi_T = [^3T^*] / [^1S]$

The average and standard deviation values were calculated following the reported method.[12]

Table S4 Calculation of Φ_T of $(Tet)_2$-CyO_{10} at different five wavelengths

Wavelength (nm)	440	445	450	455	460
ε_T (M^{-1} cm^{-1})	29,000	29,000	27,600	25,700	24,700
ΔAbs (1.0 μs)	0.0036	0.0036	0.0030	0.0026	0.0024
$[^3T^*]$ (M)	1.2×10^{-7}	1.2×10^{-7}	1.1×10^{-7}	1.0×10^{-7}	0.97×10^{-7}
Φ_T (%)	15	15	14	13	12

The Φ_T of $(Tet)_2$-CyO_{10} in THF was estimated to be 14 ± 1.2%.

Table S5 Calculation of Φ_T of $(Tet)_2$-CyO_{12} at different five wavelengths

Wavelength (nm)	440	445	450	455	460
ε_T (M^{-1} cm^{-1})	26,000	27,700	28,800	29,100	30,000
ΔAbs (1.0 μs)	0.0027	0.0030	0.0028	0.00276	0.00282
$[^3T^*]$ (M)	1.0×10^{-7}	1.0×10^{-7}	0.97×10^{-7}	0.95×10^{-7}	0.94×10^{-7}
Φ_T (%)	111	111	108	106	104

The Φ_T of $(Tet)_2$-CyO_{12} in THF was estimated to be 108 ± 2.5%.

Table S6 Calculation of Φ_T of Tet-ref at different five wavelengths

Wavelength (nm)	440	445	450	455	460
ε_T (M^{-1} cm^{-1})	25,000	24,500	23,000	21,700	19,700
ΔAbs (1.0 μs)	0.00025	0.00013	0.00027	0.00014	0.000071
$[^3T^*]$ (M)	5.1×10^{-8}	2.6×10^{-8}	5.8×10^{-8}	3.1×10^{-8}	1.8×10^{-8}
Φ_T (%)	1.2	0.58	1.2	0.68	0.40

The Φ_T of Tet-ref was estimated to be 0.80 ± 0.33%.

The k_{ISC} value was included in k_0. The rate constant of solvent relaxation process from S_1^* to S_1 (k_{solv}) was determined to be 1.2×10^{11} s^{-1} by fitting of decay profile of S-S absorption at 602 nm with bi-exponential function. Additionally, the rate constant of deactivation process of S_1 (k_0) was determined to be 1.3×10^8 s^{-1} by using fluorescence lifetime measurement of Tet-ref (Fig. S26). The Φ_T value was already estimated in Table S5 ($\Phi_T = 0.8 \pm 0.3\%$) together with $k_0 = 1.3 \times 10^8$ s^{-1}. Then, the k_{ISC} value of Tet-ref was estimated as follows: $k_{ISC} = k_0 \times \Phi_T = 1.1 \times 10^6$ s^{-1}.

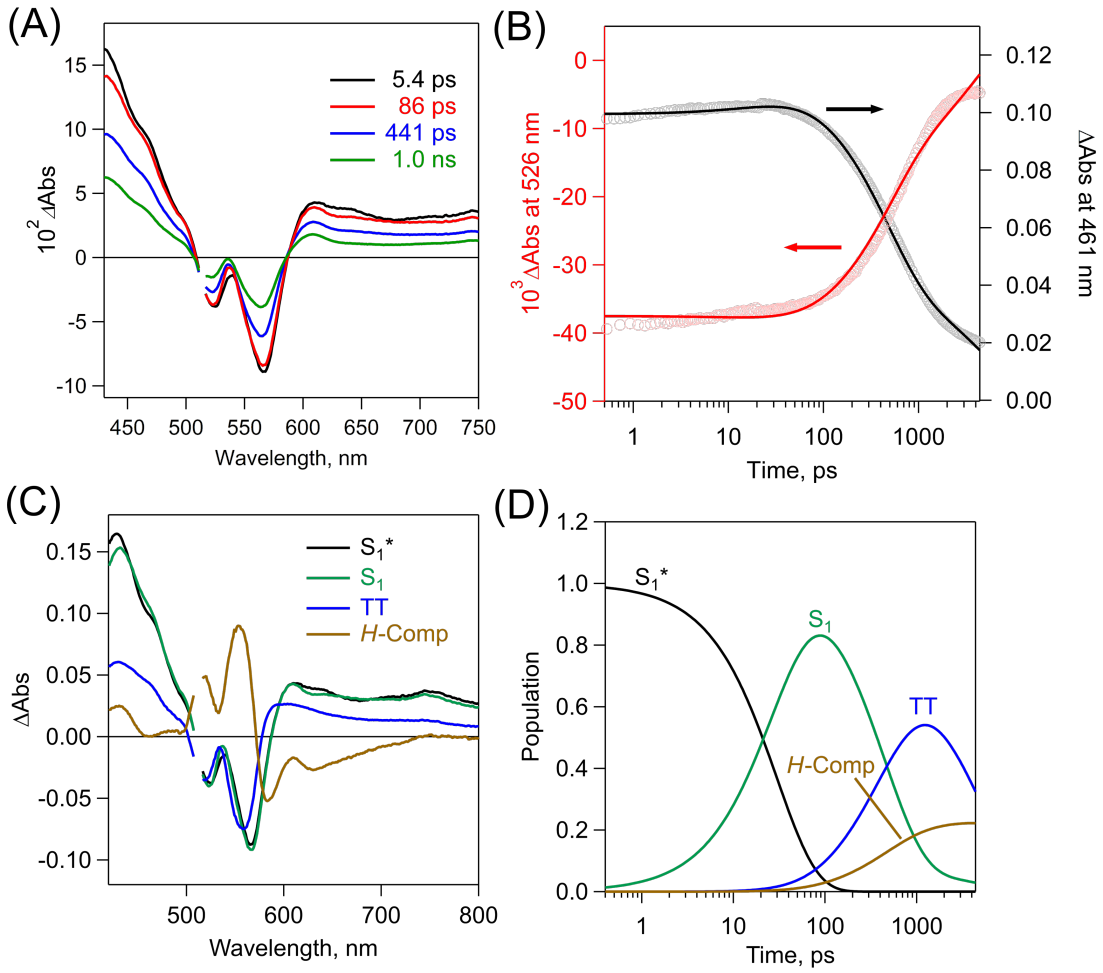


Fig. S65 (A) fs-TAS of $(Tet)_2$-CyO_{10} in THF (λ_{ex} = 532 nm). (B) The time profiles at 461 and 526 nm. (C) SAS of $(Tet)_2$-CyO_{10}: S_1* (black), S_1 (green), TT (blue) and *H*-Comp (brown). (D) The time-dependent population profiles.

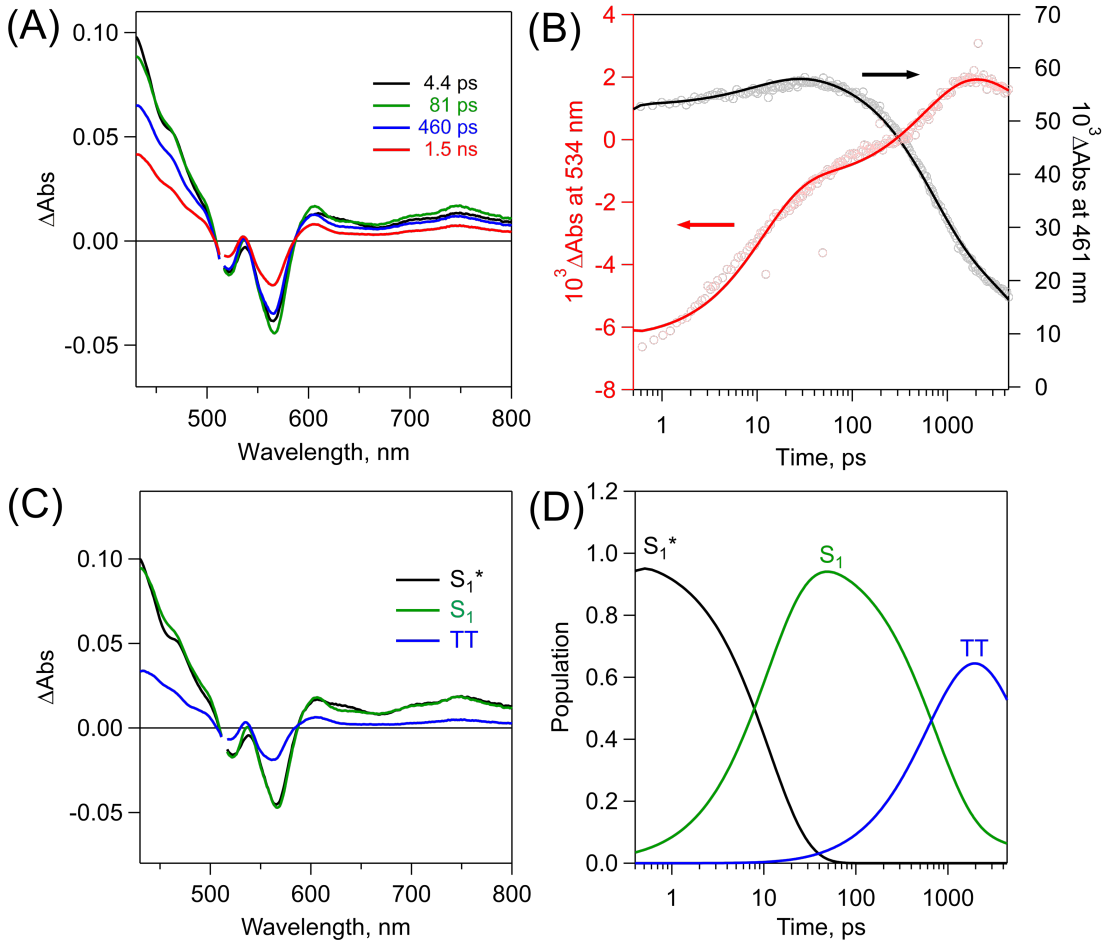
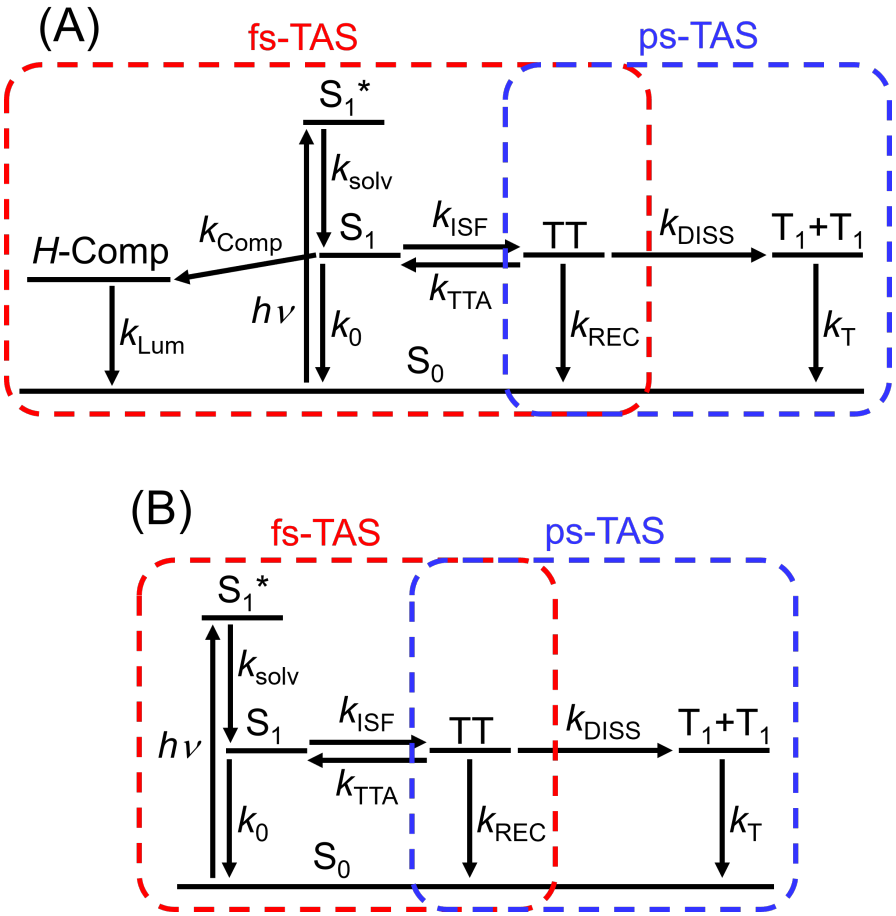


Fig. S66 (A) fs-TAS of $(Tet)_2$-CyO_{12} in THF (λ_{ex} = 532 nm). (B) The time profiles at 461 and 534 nm. (C) SAS of $(Tet)_2$-CyO_{12}: S_1* (black), S_1 (green) and TT (blue). (D) The time-dependent population profiles.

Global and Target Analysis[2]

Target (differential equation-based) analysis can be performed using the Glotaran software package (http://glotaran.org) for analysis of species-associated spectra (SAS) (Fig. 5 in the text and Figs. S65 and S66 in ESI†). To describe the transient absorption data of $(Tet)_2$-CyO_n, the normalized concentrations of S_1^*, S_1, TT, *H*-Comp and T_1+T_1were modelled using the following scheme (Scheme S4).

Scheme S4 Proposed kinetic scheme of (A) $(Tet)_2$-CyO_{10} and (B) $(Tet)_2$-CyO_{12}.



Then, the population of S_1*, S_1, TT and T_1+T_1 in $(Tet)_2$-CyO_{10} can be described using the following kinetic equations. The rate constant of the initial solvent relaxation process from S_1* to S_1 is denoted as k_{solv}. Then, the ISF from S_1 to TT (k_{ISF}), deactivation process from S_1 (k_0) to the ground state (S_0), reverse process of ISF: triplet-triplet annihilation (TTA) (k_{TTA}), the direct recombination process (k_{REC}) from the TT to S_0, the dissociation process (k_{DISS}) from TT to T_1+T_1 and deactivation process (k_T) from the T_1+T_1 to S_0 are

included.

$$\frac{d\,[S_1{}^*]}{dt} = -\,k_{solv}\,[S_1{}^*]$$

$$\frac{d\,[S_1]}{dt} = k_{solv}\,[S_1{}^*] + k_{TTA}[TT] - (k_0 + k_{ISF})\,[S_1]$$

$$\frac{d\,[TT]}{dt} = k_{ISF}\,[S_1] - (k_{TTA} + k_{DISS} + k_{REC})\,[TT]$$

$$\frac{d\,[T_1 + T_1]}{dt} = k_{DISS}\,[TT] - k_T\,[T_1 + T_1]$$

These equations were solved using the method described in a previous report.[13] In the case of the target analysis of fs-TAS and ps-TAS, the analysis was performed with the equation: $1/\tau_{TT} = k_{TT}$. The k_0 is the value of Tet-ref. In contrast, in $(Tet)_2$-CyO_{12}, the concentrations of S_1*, S1, TT, T_1+T_1 and *H*-Comp can be described by the following kinetic equations: the rate constant for the initial solvent relaxation process from S_1 to S_1* is denoted as k_{solv}. Then, the ISF from S_1 to TT (k_{ISF}), the deactivation process from S_1 to the ground state (k_0), the inverse process of the ISF: triplet-triplet annihilation (TTA) (k_{TTA}), the *H*-Comp formation from S_1 (k_{Comp}), the deactivation process from *H*-Comp to the ground state (k_{Lum}), the direct recombination process (k_{REC}) from the TT to S_0, the dissociation process (k_{DISS}) from TT to T_1+T_1 and deactivation process (k_T) from the T_1+T_1 to S_0 are included.

$$\frac{d\,[S_1{}^*]}{dt} = -\,k_{solv}\,[S_1{}^*]$$

$$\frac{d\,[S_1]}{dt} = k_{solv}\,[S_1{}^*] + k_{TTA}[TT] - (k_0 + k_{ISF} + k_{Comp})\,[S_1]$$

$$\frac{d\,[TT]}{dt} = k_{ISF}\,[S_1] - (k_{TTA} + k_{DISS} + k_{REC})\,[TT]$$

$$\frac{d\,[H-\mathrm{Comp}]}{dt} = k_{\mathrm{Comp}}\,[\mathrm{S_1}] - k_{\mathrm{Lum}}[H-\mathrm{Comp}]$$

$$\frac{d\,[\mathrm{T_1}+\mathrm{T_1}]}{dt} = k_{\mathrm{DISS}}\,[\mathrm{TT}] - k_{\mathrm{T}}\,[\mathrm{T_1}+\mathrm{T_1}]$$

The results of target analysis were summarized in Table 1 in the text and Tables S7 and S8 in the ESI†.

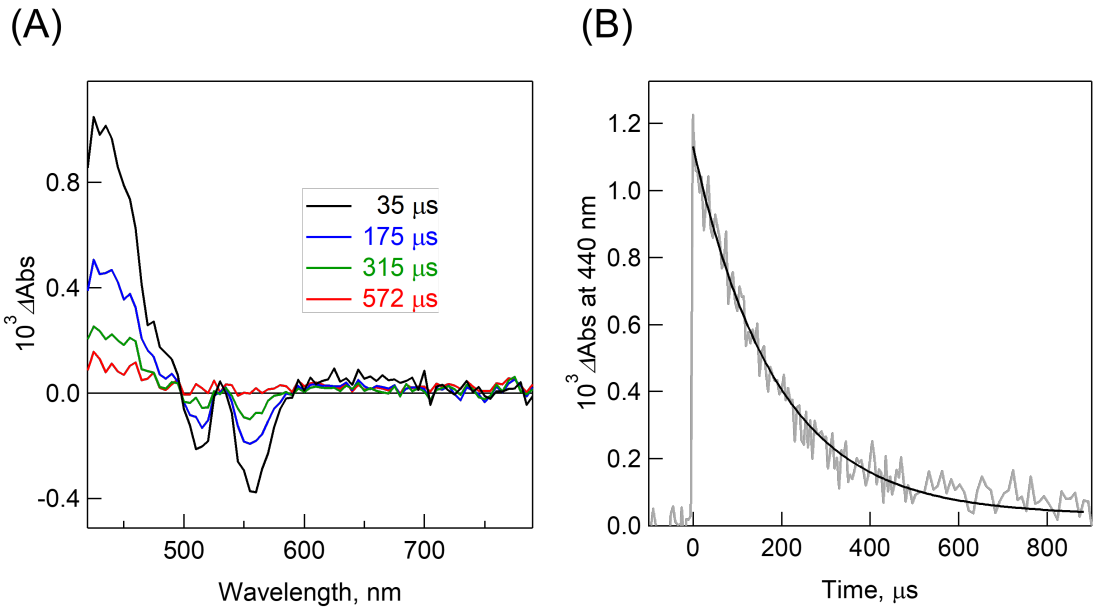


Fig. S67 ns-TAS of (A) $(Tet)_2$-CyO_{10} in THF (λ_{ex} = 532 nm) and (B) time profile at 430 nm. The individual triplet lifetime of $(Tet)_2$-CyO_{10} was determined to be 186 μs.

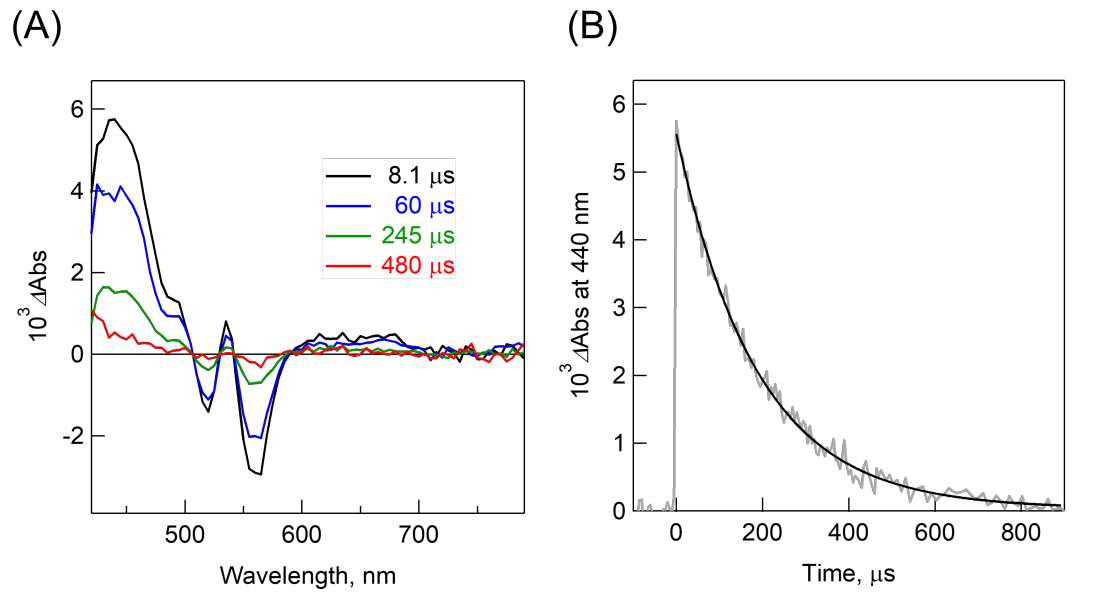


Fig. S68 ns-TAS of (A) $(Tet)_2$-CyO_{12} in THF (λ_{ex} = 532 nm) and (B) time profile at 430 nm. The individual triplet lifetime of $(Tet)_2$-CyO_{12} was determined to be 187 μs.

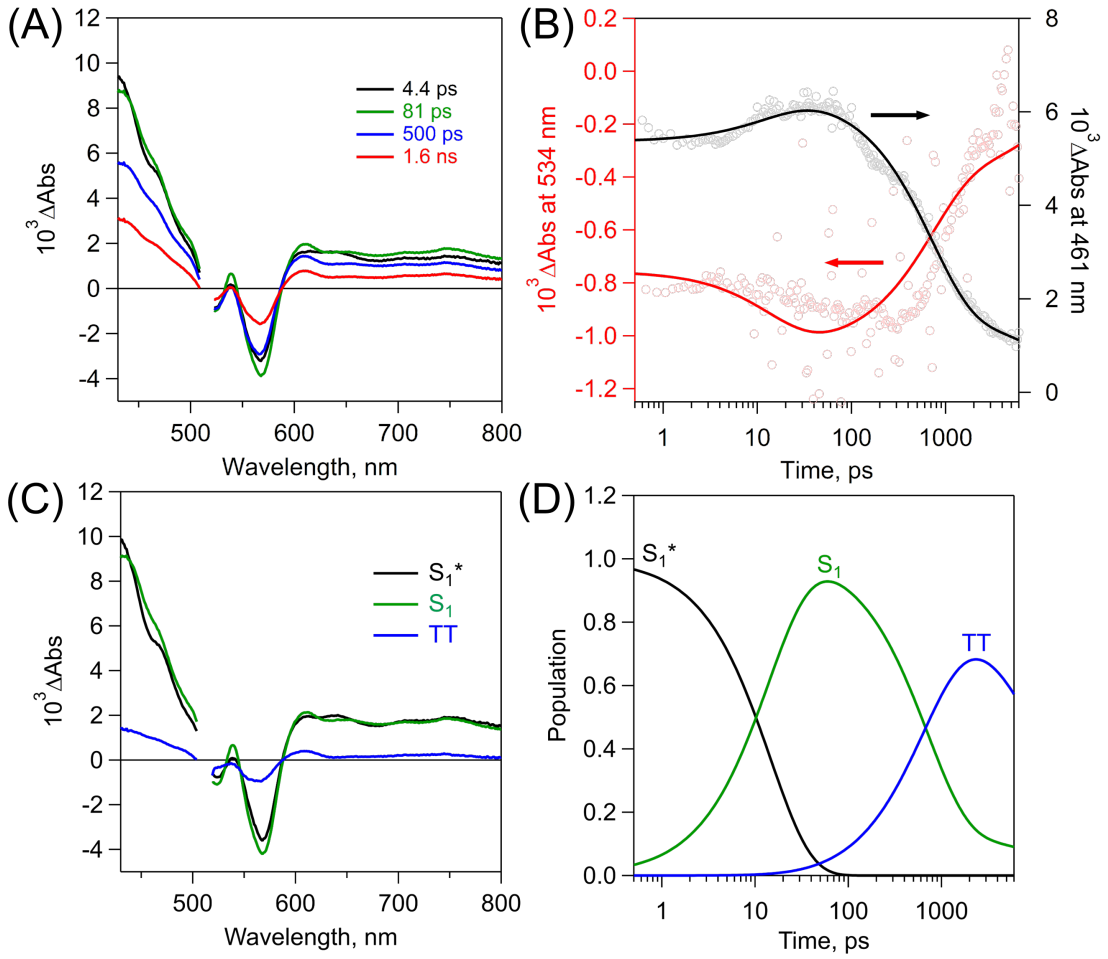


Fig. S69 (A) fs-TAS of $(Tet)_2$-CyO_{12} in toluene (λ_{ex}: 515 nm). (B) The time profiles at 534 and 461 nm. (C) SAS of $(Tet)_2$-CyO_{12}: S_1* (black), S_1 (green) and TT (blue). (D) The time-dependent population profiles.

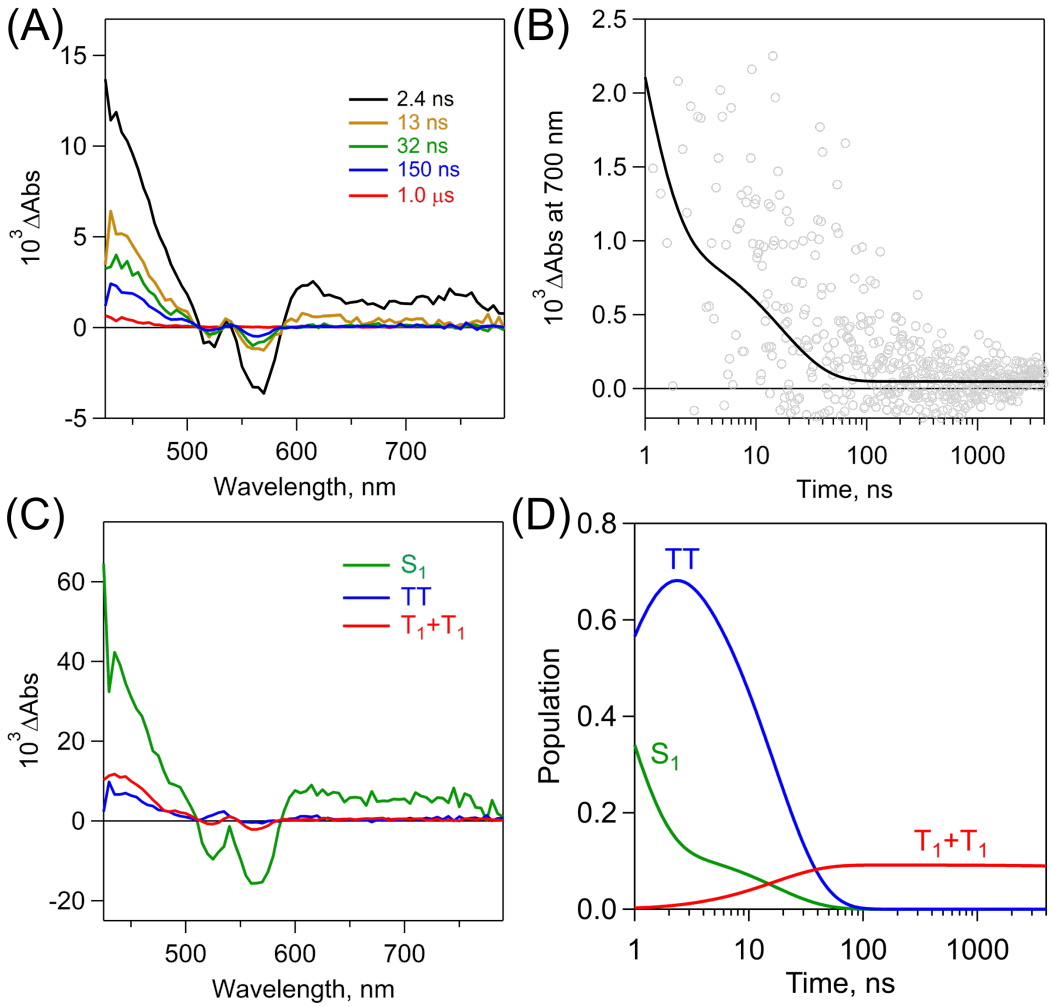


Fig. S70 (A) ps-TAS of $(Tet)_2$-CyO_{12} in toluene (λ_{ex}: 532 nm). (B) The time profile at 700 nm. (C) SAS of $(Tet)_2$-CyO_{12}: S_1 (green), TT (blue) and T_1+T_1 (red). (D) The time-dependent population profiles.

Table S7 Summarized kinetic parameters and quantum yields of $(Tet)_2$-CyO_{12} in THF and toluene.

	k_{solv},[a] 10^{10} s^{-1}	k_0,[b] 10^8 s^{-1}	k_{ISF},[a] 10^9 s^{-1}	k_{TTA},[a] 10^8 s^{-1}	k_{REC},[c] 10^7 s^{-1}	k_{DISS},[d] 10^7 s^{-1}	k_{ISF}/k_{TTA} (k_{DISS}/k_{REC})	k_T, 10^3 s^{-1} (τ_T, ms)	Φ_{TT},[f] %	Φ_T, %
THF	8.8	1.3	1.1	1.1	6.1	5.7	10 (0.93)	5.5[e] (0.19[e])	69	108±2.5[g]
toluene	6.8	1.3	1.0	1.9	4.2	0.70	5.3 (0.17)	–	67	18[h]

[a] Estimated by target analysis of fs-TAS. [b] Calculated by $k_0 = (\tau_S)^{-1}$, τ_S was estimated by fluorescence lifetime of Tet-ref (τ_S: 7.6 ns). [c] Calculated by $k_{REC} = k_{TT} - k_{DISS} = (\tau_{TT})^{-1} - k_{DISS}$, τ_{TT} was estimated by target analysis of ps-TAS. [d] Calculated by $k_{DISS} = k_{TT} \times \Phi_T/(2\Phi_{TT})$. [e] Calculated by $k_T = (\tau_T)^{-1}$, τ_T was estimated by ns-TAS. [f] Estimated by the population of TT (target analysis) considering k_{TTA} (Fig. 4C and Figs. S66 and S69-S70 in ESI†). [g] Estimated by ps-TAS (Fig. 5A). [h] Estimated by the population of T_1+T_1 (target analysis) (Fig. S70 in ESI†).

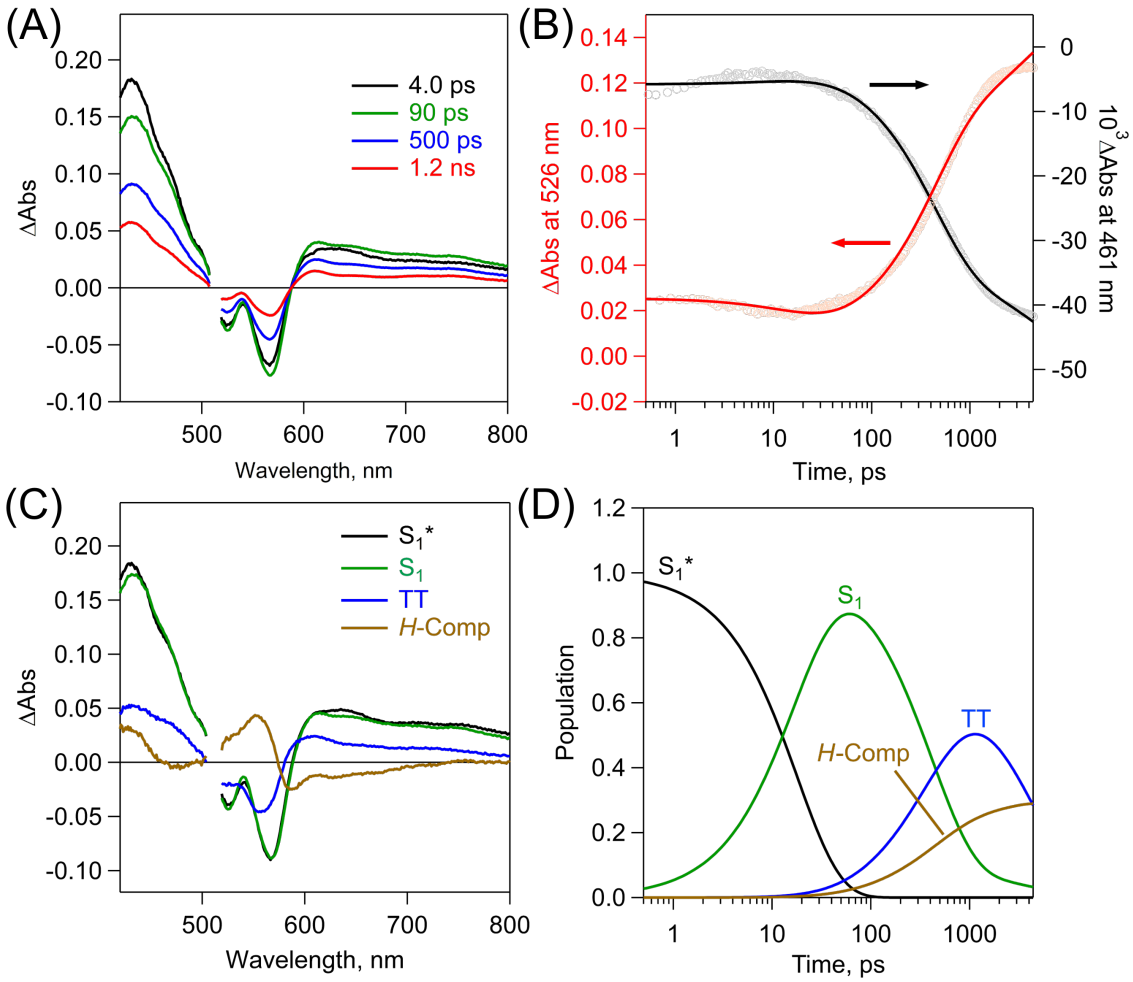


Fig. S71 (A) fs-TAS of $(Tet)_2$-CyO_{10} in toluene (λ_{ex}: 515 nm). (B) The time profile at 700 nm. (C) SAS of $(Tet)_2$-CyO_{10}: S_1* (black), S_1 (green), TT (blue) and *H*-Comp (brown). (D) Time-dependent population profiles.

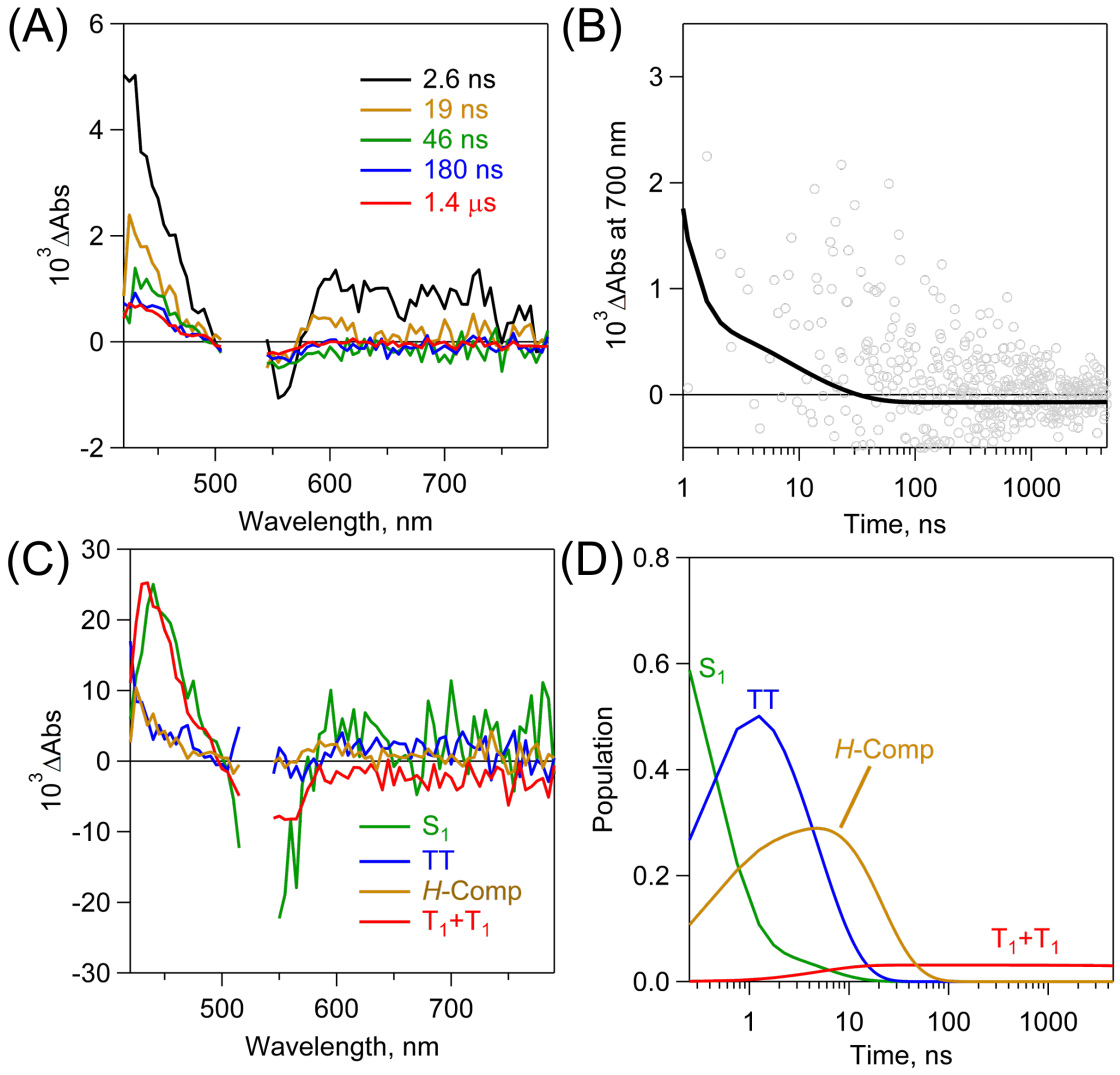


Fig. S72 (A) ps-TAS of $(Tet)_2$-CyO_{10} in toluene (λ_{ex}: 532 nm). (B) The time profile at 700 nm. (C) SAS of $(Tet)_2$-CyO_{10}: S_1 (green), TT (blue), *H*-Comp (brown) and T_1+T_1 (red). (D) Time-dependent population profiles.

Table S8 Summarized kinetic parameters and quantum yields of $(Tet)_2$-CyO_{10} in THF and toluene.

	k_{solv},[a] 10^{10} s^{-1}	k_0,[b] 10^8 s^{-1}	k_{Comp},[a] 10^8 s^{-1}	k_{Lum}, 10^7 s^{-1}	k_{ISF},[a] 10^9 s^{-1}	k_{TTA},[a] 10^8 s^{-1}	k_{REC},[e] 10^7 s^{-1}	k_{DISS},[f] 10^7 s^{-1}	k_{ISF}/k_{Comp}	k_{ISF}/k_{TTA} (k_{DISS}/k_{REC})	k_T, 10^3 s^{-1} (τ_T, ms)	Φ_{TT},[h] %	Φ_T, %
THF	3.3	1.3	4.5	6.7[c]	1.5	1.7	14	1.4	3.3	8.8 (0.10)	5.4[g] (0.19[g])	65	14±1.2[h]
toluene	5.5	1.3	5.8	6.0[d]	1.5	2.3	13	1.2	2.6	6.5 (0.071)	–	50	8.0[i]

[a] Estimated by target analysis of fs-TAS. [b] Calculated by $k_0 = (\tau_S)^{-1}$, τ_S was estimated by fluorescence lifetime of Tet-ref (τ_S: 7.6 ns). [c] Calculated by $k_{Lum} = (\tau_{Lum})^{-1}$, τ_{Lum} was estimated by fluorescence lifetime of $(Tet)_2$-CyO_{10} (τ_{Lum}: 15.2 ns). [d] Estimated by target analysis of ps-TAS. [e] Calculated by $k_{REC} = k_{TT} - k_{DISS} = (\tau_{TT})^{-1} - k_{DISS}$, τ_{TT} was estimated by target analysis of ps-TAS. [f] Calculated by $k_{DISS} = k_{TT} \times \Phi_T/(2\Phi_{TT})$. [g] Calculated by $k_T = (\tau_T)^{-1}$, τ_T was estimated by ns-TAS. [h] Estimated by the population of TT (target analysis) considering k_{TTA} (Fig. 5E and Figs. S66 and S71-S72 in ESI†). [h] Estimated by ps-TAS (Fig. 5C). [I] Estimated by the population ratio of T_1+T_1 (target analysis) (Fig. S72 in ESI†).

References

1. T. Nakagawa, K. Okamoto, H. Hanada and R. Katoh, *Opt. Lett.*, 2016, **41**, 1498-1501.
2. J. J. Snellenburg, S. Laptenok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, *J. Stat. Softw.*, 2012, **49**, 1-22.
3. R. Shiraishi, S. Matsumoto, Y. Fuchi, T. Naganuma, D. Yoshihara, K. Usui, K. Yamada and S. Karasawa, *Langmuir*, 2020, **36**, 5280-5286.
4. F. Pineux, S. Federico, K.-N. Klotz, S. Kachler, C. Michiels, M. Sturlese, M. Prato, G. Spalluto, S. Moro and D. Bonifazi, *ChemMedChem*, 2020, **15**, 1909-1920.
5. J. Hoogboom and T. M. Swager, *J. Am. Chem. Soc.*, 2006, **128**, 15058-15059.
6. W. Fudickar and T. Linker, *J. Am. Chem. Soc.*, 2012, **134**, 15071-15082.
7. Y.-S. Wang, S. Bai, Y.-Y. Wang and Y.-F. Han, *Chem. Commun.*, 2019, **55**, 13689-13692.
8. B. J. Walker, A. J. Musser, D. Beljonne and R. H. Friend, *Nat. Chem.*, 2013, **5**, 1019-1024.
9. S. Nakamura, H. Sakai, H. Nagashima, Y. Kobori, N. V. Tkachenko and T. Hasobe, *ACS Energy Lett.*, 2019, **4**, 26-31.
10. T. Sakuma, H. Sakai, Y. Araki, T. Mori, T. Wada, N. V. Tkachenko and T. Hasobe, *J. Phys. Chem. A*, 2016, **120**, 1867-1875.
11. P. Avakian, E. Abramson, R. G. Kepler and J. C. Caris, *J. Chem. Phys.*, 1963, **39**, 1127-1128.
12. T. Saegusa, H. Sakai, H. Nagashima, Y. Kobori, N. V. Tkachenko and T. Hasobe, *J. Am. Chem. Soc.*, 2019, **141**, 14720-14727.
13. I. H. M. van Stokkum, D. S. Larsen and R. van Grondelle, *Biochim. Biophys. Acta, Bioenerg.*, 2004, **1657**, 82-104.