

## Supporting Information

### Title:

Synthesis of functionalized insulated molecular wires by polymerization of an insulated  $\pi$ -conjugated monomer

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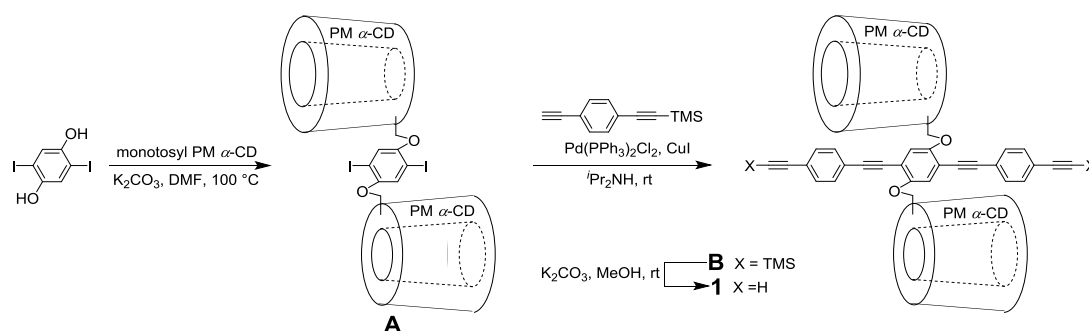
### I. General Comments.

1,4-Diiodotetrafluorobenzene, 4,7-dibromobenzo[2,1,3]thiadiazol, and other reagents were purchased from commercial sources and used without further purification. 6-*O*-monotosyl permethylated  $\alpha$ -cyclodextrin,<sup>1</sup> 2,6(7)-diiodo-tetrathiafulvalene,<sup>2</sup> 5,5'-diiodo-2,2'-bithiophene,<sup>3</sup> 4,4'-diiodo-azobenzene,<sup>4</sup> and [5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphinato]zinc(II),<sup>5</sup> were prepared by a method reported in the literature. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus or a Bruker Autoflex using  $\alpha$ -cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent. 400 MHz <sup>1</sup>H NMR, 100 MHz <sup>13</sup>C NMR, and ROESY spectra were recorded using a JEOL ECX-400 spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC9140 instrument equipped with JAIGEL-1H and -2H columns or equipped with JAIGEL-2.5H and -3H columns using CHCl<sub>3</sub> as the eluent. Analytical size-exclusion chromatography (SEC)

was carried out on a GL-Science GL-7400 HPLC system equipped with a GL-7410 HPLC pump, a GL-7400 UV detector, and GL-7454 RI detector through a column set consisting of Shodex KF-801, -802, -802.5, -803, -804 using THF as the eluent at a flow rate of 0.6 mL min<sup>-1</sup>. The average molecular weight ( $M_w$ ) and the polydispersity index (PDI) of polymers were determined by absolute molecular weight determination technique using SEC measurements equipped with low angle (7°) light scattering detector (Viscotek 270 viscosity).

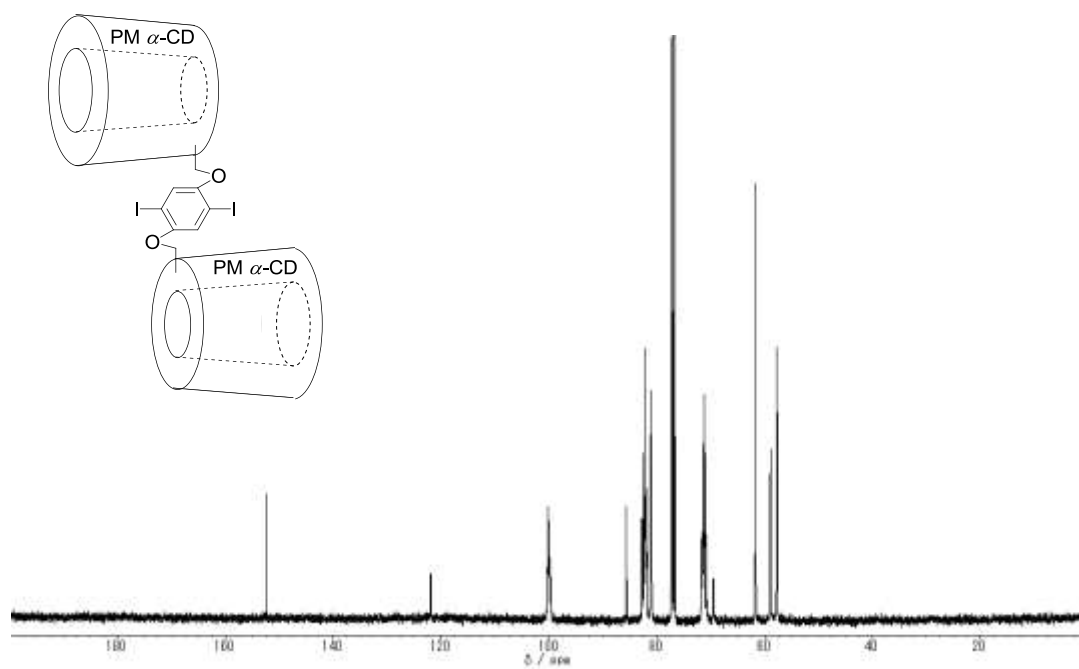
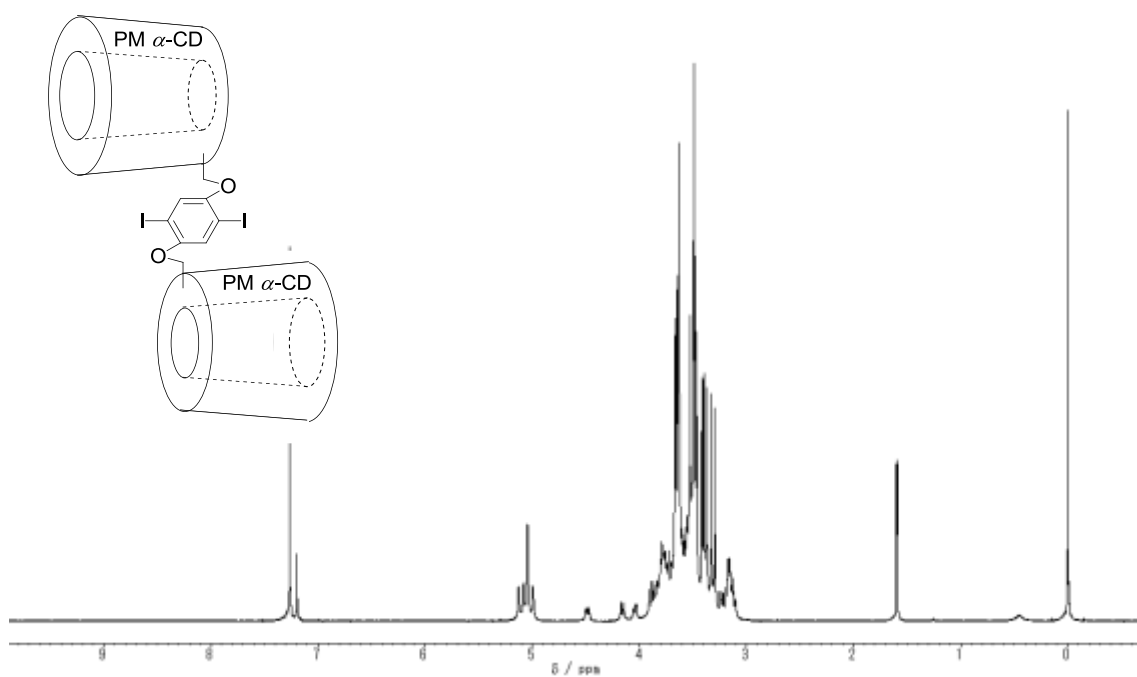
## II. Synthetic Procedures.

### Synthesis of **1**.<sup>6</sup>

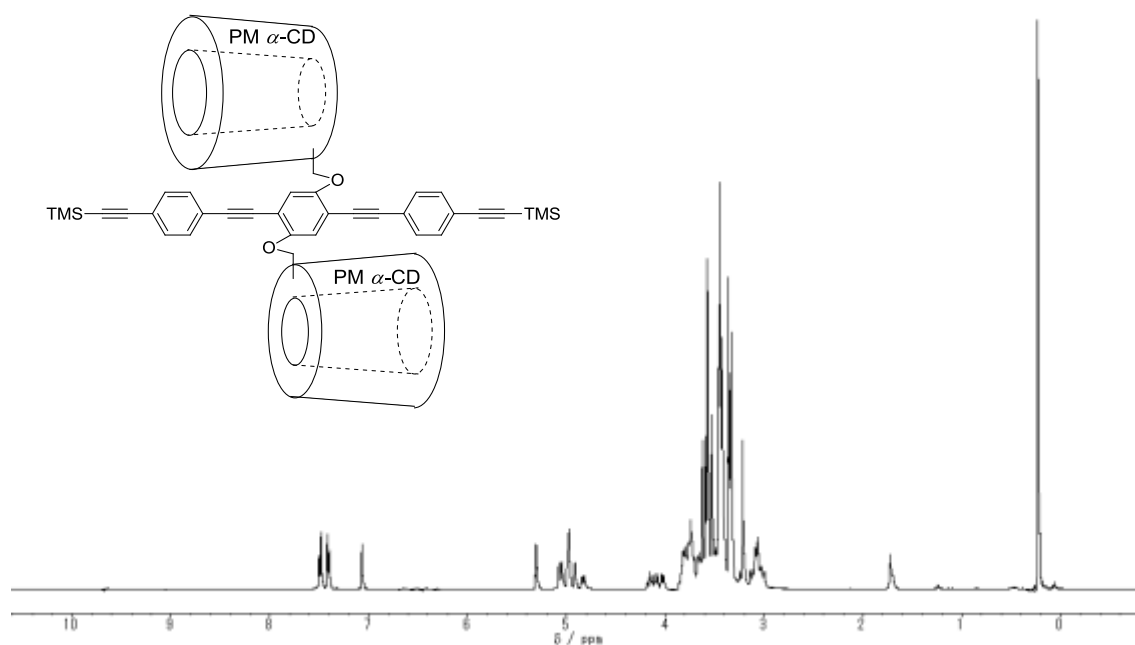


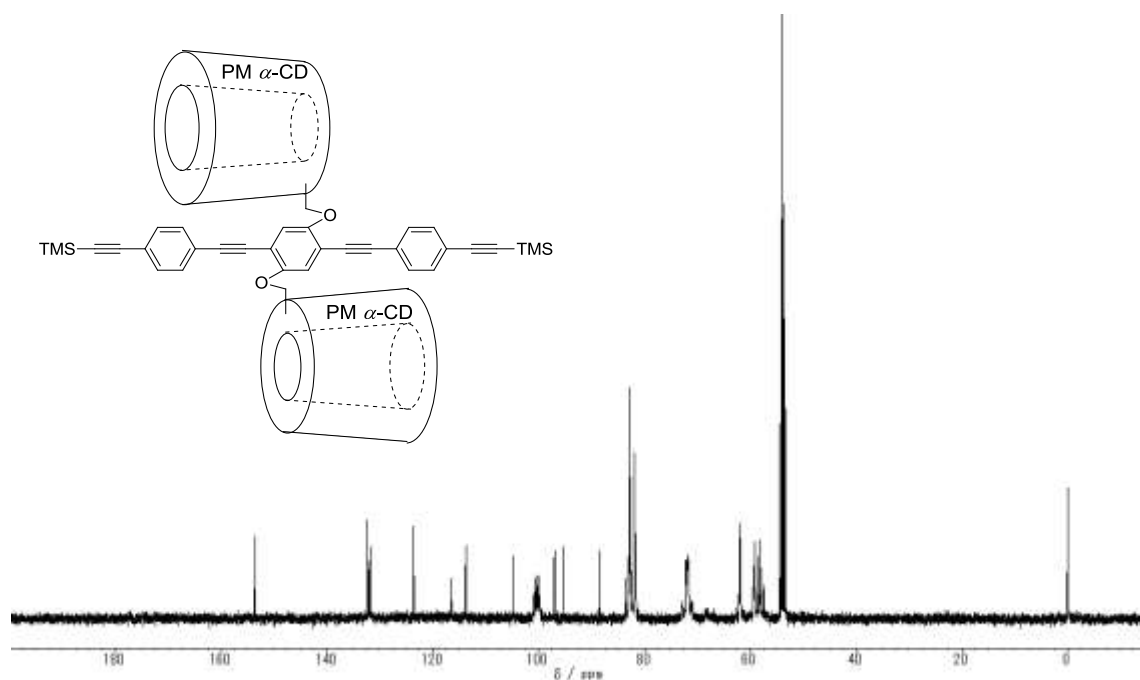
**A**: 1,4-Diiido-2,5-dihydroxybenzene (1.20 g, 3.33 mmol), 6-*O*-monotosyl  $\alpha$ -cyclodextrin permethylate (10.0 g, 7.32 mmol), and dry  $K_2CO_3$  (9.20 g, 66.6 mmol) were placed in a round-bottom flask and dried at 100 °C *in vacuo*. The mixture was dissolved in DMF (70 mL) and stirred at 100 °C overnight. The mixture was diluted with EtOAc and washed with saturated aqueous  $NaHCO_3$  and brine. The organic layer was separated and dried over  $Na_2SO_4$ . The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to give **A** (8.43g, orange solid, 93%). m.p.:138-141 °C; MALDI-TOF MS: ( $m/z$ ) 2767 ( $[M+Na]^+$ ,  $C_{112}H_{188}I_2O_{60}Na$ , calcd. 2771);  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 22.3 °C):  $\delta_H$  = 7.20 (s, 2H, ArH), 5.13-5.00 (m, 12H, CD-H<sub>1</sub>), 4.50-3.10 (m, 174H, CD-H, OCH<sub>3</sub>);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ , ):  $\delta_C$  = 152.43, 121.91, 100.3-99.6 (several peaks overlapped), 85.61, 82.74, 82.4-81.8 (several peaks overlapped), 81.2-81.0 (several peaks overlapped), 71.7-71.1 (several peaks overlapped), 70.80, 69.50, 61.77,

61.70, 59.1-58.9 (several peaks overlapped), 57.71; Anal. Calcd for  $C_{112}H_{188}I_2O_{60} \cdot H_2O$ :  
C, 48.94; H, 6.89. Found: C, 48.62; H, 6.92.

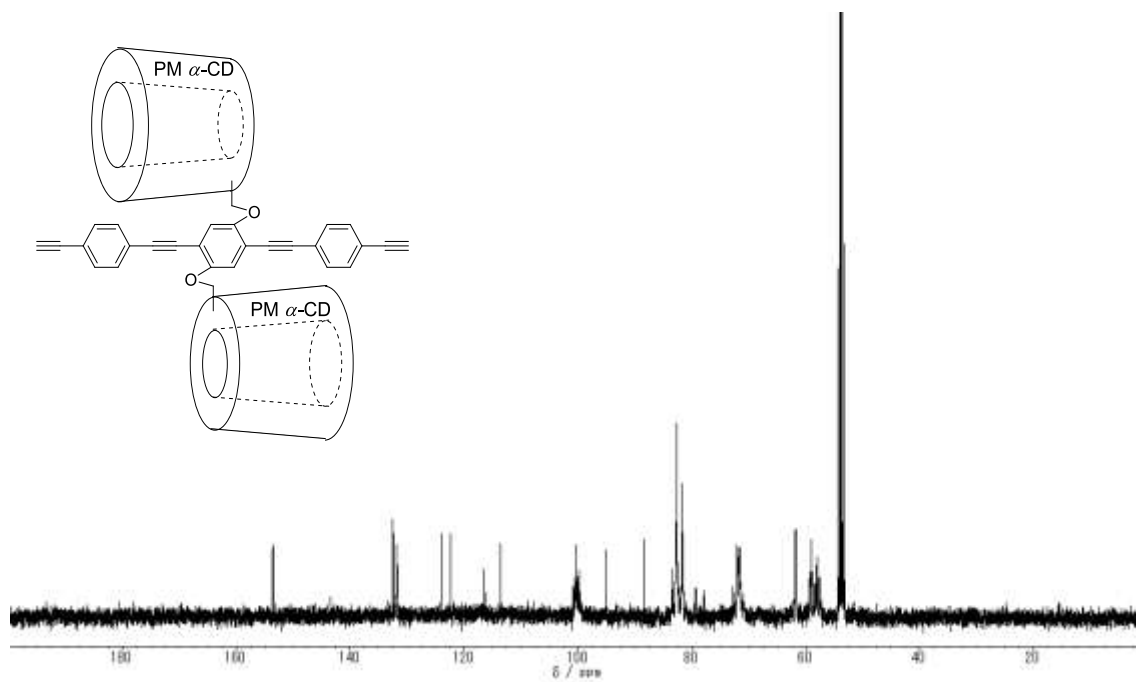
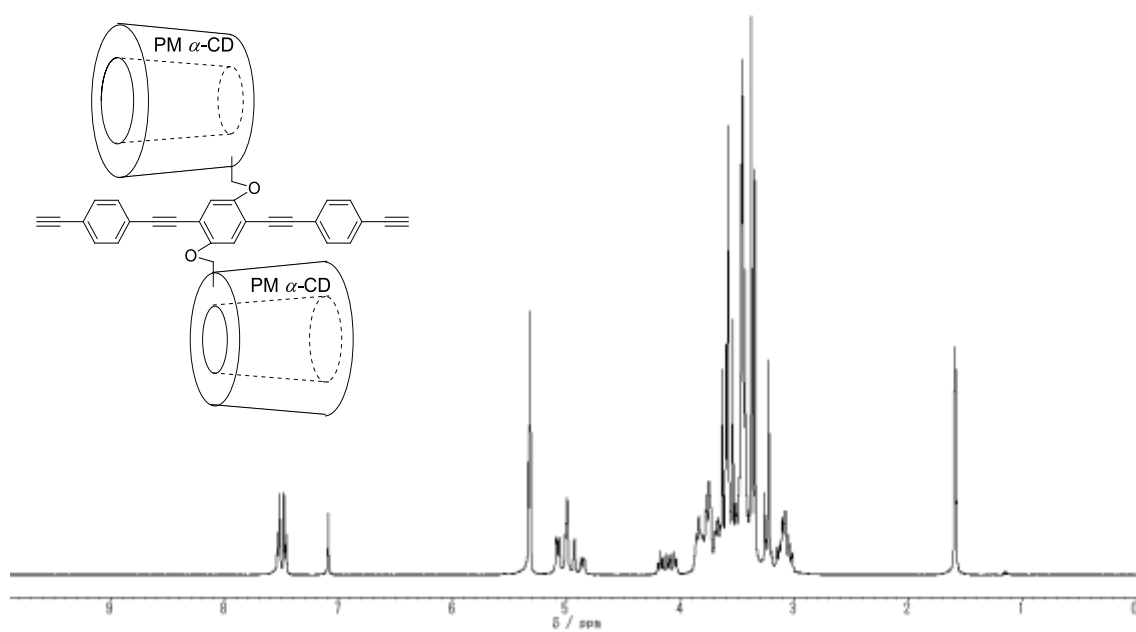


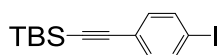
**B:** To a solution of **A** (5.49 g, 2.0 mmol) in  $i\text{Pr}_2\text{NH}$  (50 mL) degassed by 3 consecutive freeze-pump-thaw cycles was added  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (70 mg, 0.10 mmol),  $\text{CuI}$  (14 mg, 0.10 mmol), and 1-ethynyl-4-(trimethylsilylethynyl)benzene (1.19 g, 6.0 mmol) under Ar. After stirring for 1 h at room temperature, the mixture was filtered through a Celite pad and concentrated, followed by a chromatographic purification on silica gel with EtOAc-EtOH (9:1) as eluent to give **B** (4.64 g, orange solid, 80%). m.p.:138-141 °C; MALDI-TOF MS: ( $m/z$ ) 2909 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{138}\text{H}_{214}\text{O}_{60}\text{Si}_2\text{Na}$ , calcd. 2912);  $^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 21.4 °C):  $\delta_{\text{H}}$  = 7.49 (d,  $J$  = 8.4 Hz, 4H, ArH), 7.41 (d,  $J$  = 8.4 Hz, 4H, ArH), 7.07 (s, 2H, ArH), 5.08-4.92 (m, 12H, CD- $\text{H}_1$ ), 4.83-2.99 (m, 174H, CD-H,  $\text{OCH}_3$ ), 0.23 (s, 18H,  $(\text{CH}_3)_3\text{Si}$ );  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 20.6 °C):  $\delta_{\text{C}}$  = 153.63, 132.29, 131.82, 123.60, 123.58, 116.47, 113.73, 104.75, 100.9-99.7 (several peaks overlapped), 96.97, 95.27, 88.47, 83.53, 83.0-82.5 (several peak overlapped), 81.81, 81.62, 72.2-71.7 (several peaks overlapped), 62.1-61.8 (several peaks overlapped), 59.4-59.0 (several peaks overlapped), 58.44, 58.2-58.0 (several peaks overlapped), 57.50, 57.45, -0.03; Anal. Calcd for  $\text{C}_{138}\text{H}_{214}\text{O}_{60}\text{Si}_2 \cdot \text{H}_2\text{O}$ : C, 57.01; H,7.49. Found: C, 56.90; H, 7.28.



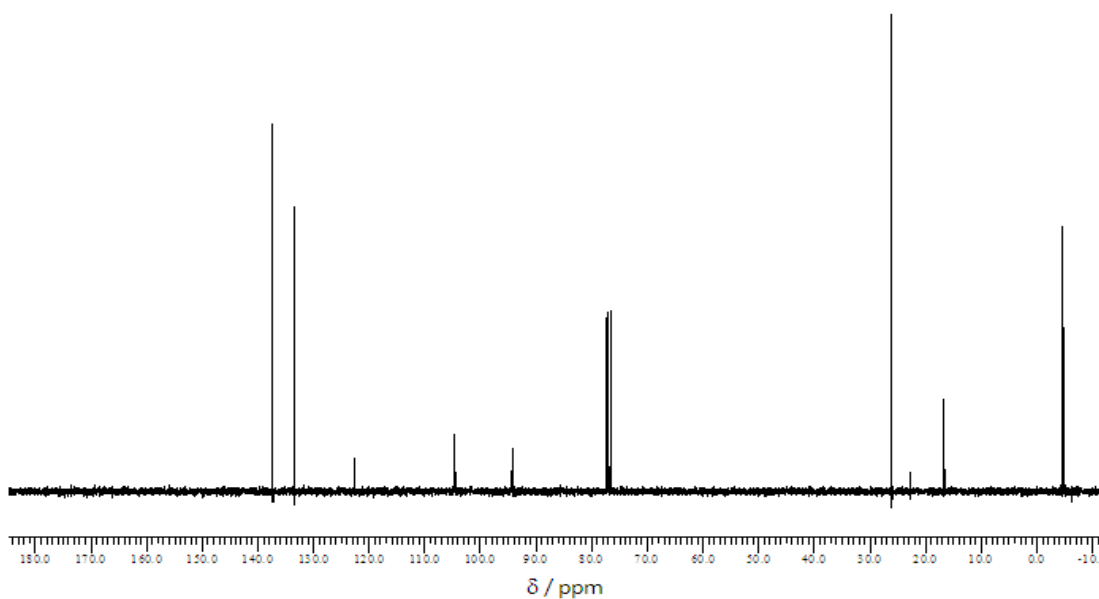
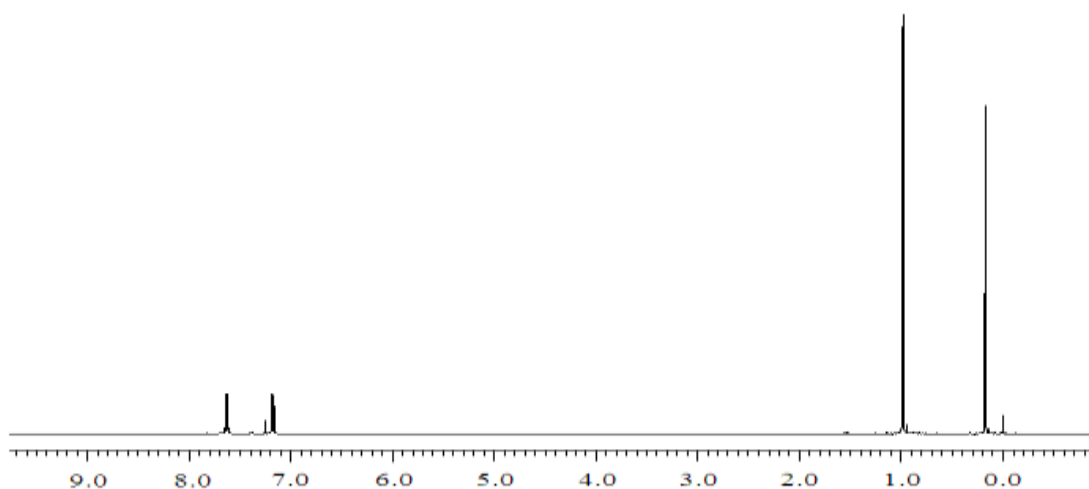


**1:** To a solution of **B** (644 mg, 0.223 mmol) in MeOH (8 mL) was added  $\text{K}_2\text{CO}_3$  (1.1 g, 8.0 mmol). After stirring for 30 min at 25 °C, the mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as an eluent to give **7** (573 mg, brilliant yellow solid, 94%). m.p. >201 °C (decomposed); MALDI-TOF MS: ( $m/z$ ) 2768 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{132}\text{H}_{198}\text{O}_{60}\text{Na}$ , calcd. 2768);  $^1\text{H}$ -NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 14.2 °C):  $\delta_{\text{H}}$  = 7.53 (d,  $J$  = 8.4 Hz, 4H, ArH), 7.47 (d,  $J$  = 8.4 Hz, 4H, ArH), 7.09 (s, 2H, ArH), 5.09-4.93 (m, 12H, CD- $\text{H}_1$ ), 4.86-3.01 (m, 176H, CD-H, CCH,  $\text{OCH}_3$ );  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 21.8 °C)  $\delta_{\text{C}}$  = 153.57, 132.47, 131.80, 123.94, 122.42, 113.64, 100.8-99.6 (several peaks overlapped), 95.01, 88.43, 83.4-83.3 (several peaks overlapped), 82.9-82.4 (several peaks overlapped), 81.71, 79.47, 79.32, 77.98, 77.88, 72.73, 72.1-71.4 (several peaks overlapped), 62.0-61.6 (several peaks overlapped), 59.3-58.9 (several peaks overlapped), 58.41, 58.33, 58.2-58.0 (several peaks overlapped), 57.45, 57.35; Anal. Calcd for  $\text{C}_{132}\text{H}_{198}\text{O}_{60}\cdot 2\text{H}_2\text{O}$ : C, 57.01; H, 7.32. Found: C, 56.82; H, 7.17.



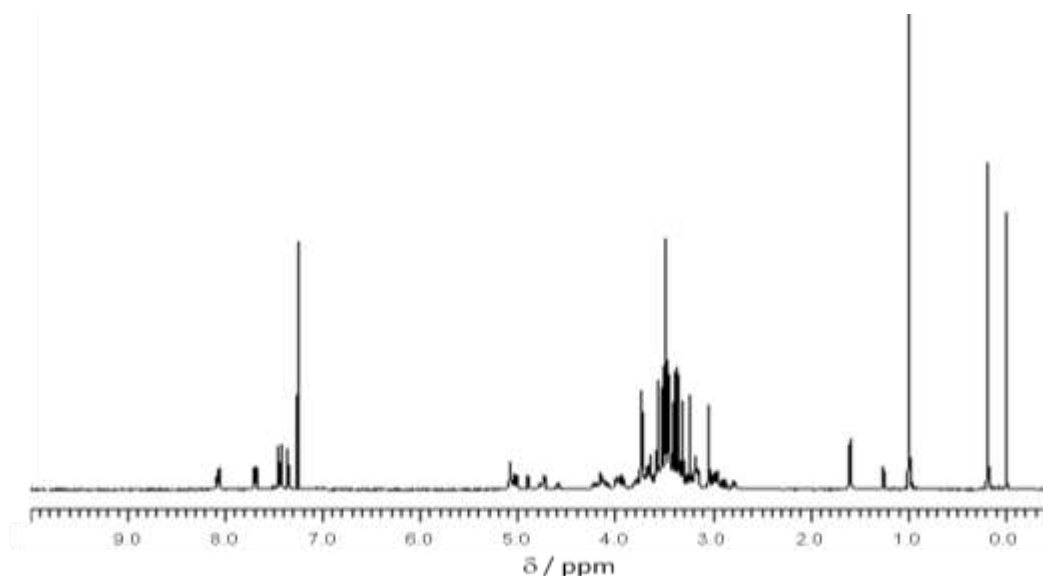


Diiodobenzene (4.95 g, 15 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (421.1 mg, 0.6 mmol), and CuI (57.1 mg, 0.3 mmol) were dissolved in *i*Pr<sub>2</sub>NH (150 mL). The solution was then cooled to 0 °C and *tert*-butyldimethylsilylacetylene (2.8 mL, 15 mmol) was added dropwise to the solution. After gradually warming to ambient temperature, the solution was further stirred for 4 h. The solution was filtered on a Celite pad and the filtrate was concentrated *in vacuo*. The residue was purified by preparative SEC using CHCl<sub>3</sub> as the eluent, to give a white solid. HRMS-EI: (m/z) 342.0307 (calcd for [M + H]<sup>+</sup>, 342.0301). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ<sub>H</sub> = 8.08 (d, *J* = Hz, 4H, ArH), 7.69 (d, *J* = Hz, 4H, ArH), 7.46(s, *J* = Hz, 2H, ArH), 1.00 (s, 18H, CH<sub>3</sub>), 0.19 (s, 12H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, r.t.): δ<sub>c</sub> = 137.33, 133.44, 122.71, 104.61, 94.35, 94.26, 26.11, 16.68, -4.69; Anal. Calcd for C<sub>14</sub>H<sub>19</sub>SiI; C, 49.12; H, 5.59. Found: C, 49.00; H, 5.39.

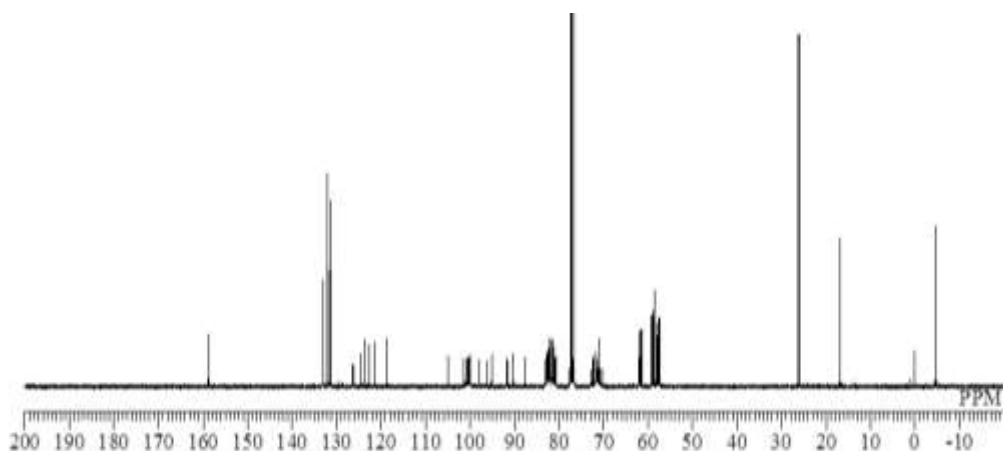


### Synthesis of **2**.

**1** (1.00 g, 0.36 mmol) was dissolved in water (25 mL) and MeOH (50 mL). This solution was stirred at 55 °C for 30 min. After cooling to ambient temperature, the solution was added dropwise to another reaction vessel containing 1-(4-iodophenyl)-2-(*tert*-butyldimethylsilyl)acetylene (297 mg, 0.86 mmol), Pd(OAc)<sub>2</sub> (13.5 mg, 0.06 mmol), TXPTS (117 mg, 0.18 mmol), CuI (3.40 mg, 0.018 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (295 mg, 0.90 mmol) dissolved in water (25 mL), MeOH (50 mL) and Et<sub>3</sub>N (3.5 mL) under Ar atmosphere. The mixture was stirred at 50 °C for 16 h and the mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using EtOAc-toluene(1:1), followed by EtOAc-MeOH(9:1), to yield **2** as a pale yellow solid (1.03 g, 90%). MALDI-TOF MS(CHCA): (*m/z*) 3194 ([M+Na]<sup>+</sup>, C<sub>160</sub>H<sub>234</sub>NaO<sub>60</sub>Si<sub>2</sub>, calcd. 3196); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> = 8.08 (d, *J* = 8.4 Hz, 4H, ArH), 7.69 (d, *J* = 8.0 Hz, 4H, ArH), 7.46 (s, 2H, ArH), 7.44 (d, *J* = 8.8 Hz, 4H, ArH), 7.36 (d, *J* = 8.8 Hz, 4H, ArH), 5.08-4.90 (m, 12H, CD-H<sub>1</sub>), 4.74-2.80 (m, 174H, CD-H, OCH<sub>3</sub>), 1.00 (s, 18H, CH<sub>3</sub>), 0.19 (s, 12H, SiCH<sub>3</sub>); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, r.t.): δ<sub>c</sub> = 158.78, 132.99, 131.57, 131.40, 131.35, 126.31, 124.40, 123.62, 122.59, 121.44, 118.63, 105.04, 101.33, 100.80, 100.43, 100.18, 99.98, 97.86, 96.32, 95.20, 91.64, 90.24, 87.84, 83.12, 82.94, 82.83, 82.64, 82.61, 82.43, 82.11 (several peaks overlapped), 81.91 (several peaks overlapped), 81.78, 81.42, 81.40, 81.37, 81.27, 81.19, 80.94, 80.70 (several peaks overlapped), 72.85, 72.57, 72.16, 71.85, 71.67, 71.64, 71.16-71.12 (several peaks overlapped), 70.86, 70.32, 62.13, 62.04, 61.97, 61.76, 61.53, 61.49, 59.22, 59.09, 59.03, 58.95, 58.81, 58.58, 58.10, 57.80, 57.66, 57.58, 57.44, 26.13, 16.74, -4.65; Anal. Calcd for C<sub>160</sub>H<sub>234</sub>O<sub>60</sub>Si<sub>2</sub>: C, 60.55; H, 7.43. Found: C, 60.37; H, 7.47.

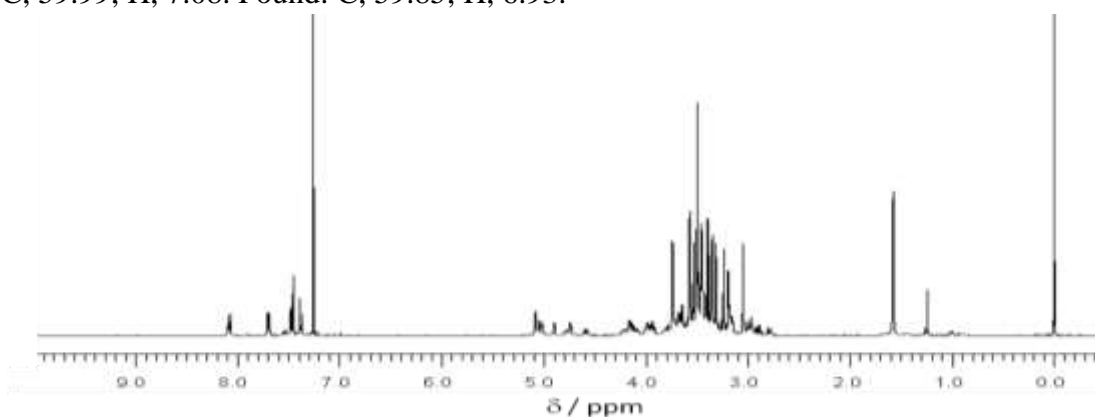


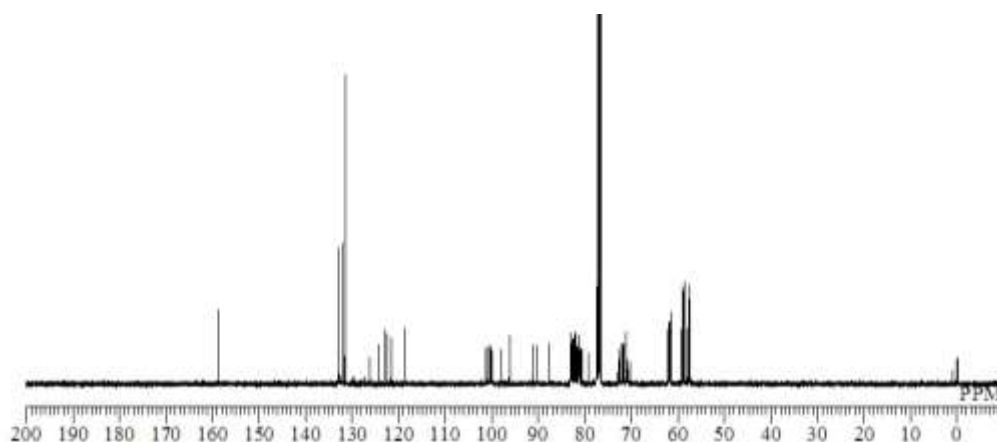




### Synthesis of **3**.

TBAF (3.0 mmol, 1M in THF, 3.0 mL) was added to a solution of **2** (1.00 g, 0.315 mmol) in THF (50 mL). The solution was stirred under nitrogen at ambient temperature for 30 min. MeOH (10 mL) was then poured into the solution and the resulting solution was concentrated *in vacuo*. The residue was purified by preparative SEC using CHCl<sub>3</sub> as the eluent, to give **3** as a yellow solid (899 mg, 97%). MALDI-TOF MS: ( $m/z$ ) 2967 ( $[M+Na]^+$ , C<sub>148</sub>H<sub>206</sub>O<sub>60</sub>Na, calcd. 2968); <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, r.t.): δ<sub>H</sub> = 8.08 (d,  $J$  = 8.8 Hz, 4H, ArH), 7.69 (d,  $J$  = 7.6 Hz, 4H, ArH), 7.46 (m, 6H, ArH), 7.38 (d,  $J$  = 8.4 Hz, 4H, ArH), 5.09-4.90 (m, 12H, CD-H<sub>1</sub>), 4.80-2.79 (m, 176H, CD-H, OCH<sub>3</sub>, CCH); <sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, r.t.): δ<sub>C</sub> = 158.74, 132.97, 132.11, 131.54, 131.42, 126.27, 124.26, 123.06, 122.41, 121.48, 118.60, 101.29, 100.77, 100.39, 100.14, 99.95, 97.83, 96.25, 91.29, 90.26, 87.83, 83.08, 83.02, 82.89, 82.79 (several peaks overlapped), 82.60, 82.57, 82.38, 82.08, 81.88, 81.86, 81.75, 81.39, 81.36, 81.23, 81.15, 80.91, 80.66, 79.29, 72.80, 72.53, 72.11, 71.82, 71.65, 71.62, 71.10 (several peaks overlapped), 70.81, 70.27, 62.08, 62.00, 61.92, 61.70, 61.49, 61.46, 59.17, 58.99, 58.91, 58.77, 58.54 (several peaks overlapped), 58.05, 57.75, 57.62, 57.53, 57.40; Anal. Calcd for C<sub>148</sub>H<sub>206</sub>O<sub>60</sub>·H<sub>2</sub>O: C, 59.99; H, 7.08. Found: C, 59.85; H, 6.93.





#### Synthesis of 4.

A solution of **3** (58.9 mg, 20.0  $\mu\text{mol}$ ), 1,4-diiodobenzene (6.60 mg, 20.0  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (1.83 mg, 2.00  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (1.05 mg, 4.00  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (2 mL) and THF (4 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over  $\text{Na}_2\text{SO}_4$  and to the mixture was added 50 mg of QuadraSil TA silica supported metal scavenger (Sigma-Aldrich) to remove palladium residues, which caused decolorization and filtered through a Celite pad followed by a 0.22 mm nylon filter. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **4** ( $M_w = 1.21 \times 10^5$ , PDI = 3.21,  $\bar{n} = 40$ ) as a pale yellow film (56.5 mg, 94%).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} = 8.10$  (br, ArH), 7.73 (br, ArH), 7.54-7.43 (br, ArH), 5.11-4.92 (m, CD-H<sub>1</sub>), 4.79-2.80 (m, CD-H, OCH<sub>3</sub>); Anal. Calcd for  $(\text{C}_{156}\text{H}_{208}\text{O}_{60} \cdot \text{H}_2\text{O})_n$ : C, 61.21; H, 6.91. Found: C, 61.35; H, 6.73.

#### Synthesis of 5.

A solution of **3** (29.4 mg, 10.0  $\mu\text{mol}$ ), 5,5'-diiodo-2,2'-bithiophene<sup>2</sup> (4.18 mg, 10.0  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (0.91 mg, 1.00  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (0.52 mg, 2.00  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm

nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **5** ( $M_w = 9.15 \times 10^4$ , PDI = 3.42,  $\bar{n} = 29$ ) as a pale yellow film (24 mg, 77% yield).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} = 8.11$  (br, ArH), 7.72 (br, ArH), 7.52-7.42 (br, ArH), 7.12 (br, ArH), 5.09-4.90 (m, CD- $\text{H}_1$ ), 4.78-2.81 (m, CD-H,  $\text{OCH}_3$ ); Anal. Calcd for  $(\text{C}_{156}\text{H}_{208}\text{O}_{60}\text{S}_2 \cdot 2\text{H}_2\text{O})_n$ : C, 59.61; H, 6.80; S, 2.04. Found: C, 59.45; H, 6.73; S, 1.85.

#### Synthesis of 6.

A solution of **3** (22.8 mg, 7.8  $\mu\text{mol}$ ), 1,4-diodotetrafluorobenzene (3.13 mg, 7.8  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (0.71 mg, 0.78  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (0.41 mg, 1.56  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **6** ( $M_w = 9.45 \times 10^4$ , PDI = 3.01,  $\bar{n} = 31$ ) as a pale orange film (19 mg, 79% yield).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} = 8.10$  (br, ArH), 7.71 (br, ArH), 7.58-7.47 (br, ArH), 5.08-4.91 (m, CD- $\text{H}_1$ ), 4.79-2.80 (m, CD-H,  $\text{OCH}_3$ ); Anal. Calcd for  $(\text{C}_{154}\text{H}_{204}\text{F}_4\text{O}_{60})_n$ : C, 59.84; H, 6.65. Found: C, 59.66; H, 6.51.

#### Synthesis of 7.

A solution of **3** (29.4 mg, 10.0  $\mu\text{mol}$ ), 4,7-dibromobenzo[2,1,3]thiadiazol (2.94 mg, 10.0  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (0.91 mg, 1.00  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (0.52 mg, 2.00  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **7** ( $M_w = 8.41 \times 10^4$ , PDI = 4.27,  $\bar{n} = 27$ ) as a pale orange film (30 mg, 96% yield).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} =$

8.10 (br, ArH), 7.71 (br, ArH), 7.66 (br, ArH), 7.52-7.46 (br, ArH), 5.09-4.92 (m, CD-H<sub>1</sub>), 4.79-2.80 (m, CD-H, OCH<sub>3</sub>); Anal. Calcd for (C<sub>154</sub>H<sub>206</sub>N<sub>2</sub>O<sub>60</sub>S·2H<sub>2</sub>O)<sub>n</sub>: C, 59.41; H, 6.80; N, 0.90. Found: C, 59.32; H, 6.77; N, 0.78.

#### Synthesis of 8.

A solution of **3** (29.4 mg, 10.0 μmol), 2,6(7)-diiodotetrathiafulvalene<sup>3</sup> (4.55 mg, 10.0 μmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.91 mg, 1.00 μmol), and PPh<sub>3</sub> (0.52 mg, 2.00 μmol) in Et<sub>3</sub>N (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using CHCl<sub>3</sub> as an eluent and evaporated to give **8** ( $M_w = 1.59 \times 10^5$ , PDI = 3.81,  $\bar{n} = 50$ ) as a pale orange film (27 mg, 81% yield). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, r.t.): δ<sub>H</sub> = 8.10 (br, ArH), 7.71 (br, ArH), 7.54-7.46 (br, ArH), 6.60 (br, ArH), 5.09-4.91 (m, CD-H<sub>1</sub>), 4.79-2.80 (m, CD-H, OCH<sub>3</sub>); Anal. Calcd for (C<sub>154</sub>H<sub>206</sub>O<sub>60</sub>S<sub>4</sub>·H<sub>2</sub>O)<sub>n</sub>: C, 58.47; H, 6.63; S, 4.05. Found: C, 58.55; H, 6.43; S, 3.89.

#### Synthesis of 9a (M = Zn).

A solution of **3** (50.0 mg, 17.0 μmol), [5,15-Dibromo-10,20-bis-(3,5-di-*tert*-butylphenyl) porphyrinato]zinc (II)<sup>5</sup> (15.42 mg, 17.0 μmol), Pd<sub>2</sub>(dba)<sub>3</sub> (1.55 mg, 1.70 μmol), and PPh<sub>3</sub> (0.89 mg, 3.40 μmol) in Et<sub>3</sub>N (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 40 °C for 48 h under Ar. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using CHCl<sub>3</sub> as an eluent and evaporated to give **9a** ( $M_w = 2.11 \times 10^4$ , PDI = 3.97,  $\bar{n} = 57$ ) as a green film (31 mg, 85% yield). <sup>1</sup>H NMR (400MHz, THF-d<sub>8</sub>, r.t.): δ<sub>H</sub> = 10.85 (br, meso-H), 9.76-9.63 (br, β-H), 8.92-8.86 (br, β-H), 8.17-8.09 (br, ArH), 7.92-7.43 (br, ArH), 5.16-4.83 (m, CD-H<sub>1</sub>), 4.70-2.81 (m, CD-H, OCH<sub>3</sub>), 1.60-1.58 (br, *t*-Bu); Anal. Calcd for (C<sub>196</sub>H<sub>254</sub>N<sub>4</sub>O<sub>60</sub>Zn)<sub>n</sub>: C, 63.77; H, 6.94; N, 1.52. Found: C, 63.67; H, 6.78; N, 1.32.

#### Synthesis of **9b** (M = H<sub>2</sub>).

A solution of polymer **9a** (33 mg) in CHCl<sub>3</sub> (10.0 mL) was stirred for 3h, under Ar, in the presence of TFA (10.0 mL). The mixture was extracted with CHCl<sub>3</sub> and washed with NaHCO<sub>3</sub> aq. and brine. The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, to give **9b** as a green film (32 mg, 97% yield). <sup>1</sup>H NMR (400MHz, THF-d<sub>8</sub>, r.t.): d<sub>H</sub> = 9.61-9.53 (br, b-H), 8.84-8.78 (br, b-H), 8.03-7.02 (br, ArH), 5.16-4.83 (m, CD-H<sub>1</sub>), 5.04-2.73 (m, CD-H, OCH<sub>3</sub>), 1.36 (br, *t*-Bu), -1.94–2.31(br, N-H); Anal. Calcd for (C<sub>196</sub>H<sub>256</sub>N<sub>4</sub>O<sub>60</sub>·2H<sub>2</sub>O)<sub>n</sub>: C, 64.25; H, 7.15; N, 1.53. Found: C, 64.37; H, 6.98; N, 1.30.

#### Synthesis of **9c** (M = FeCO).

A suspension of polymer **9b** (16 mg) and FeCl<sub>2</sub>·4H<sub>2</sub>O (5 mg) in a mixed solvent of CHCl<sub>3</sub> (10 mL) and CH<sub>3</sub>CN (5 mL) was stirred at 55 °C for 20 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. A suspension of thus formed polymer (16 mg) and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (100 mg) in a mixed solvent of toluene (10 mL) and H<sub>2</sub>O (5 mL) was stirred at r.t. under CO (1 atm) for 50 h. The mixture was diluted with toluene and washed with brine. The organic layer was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, to give **9c** (15 mg, 94%) as an ocher film. Anal. Calcd for (C<sub>197</sub>H<sub>254</sub>N<sub>4</sub>O<sub>61</sub>Fe·H<sub>2</sub>O)<sub>n</sub>: C, 63.47; H, 6.92; N, 1.50. Found: C, 63.20; H, 6.99; N, 1.22.

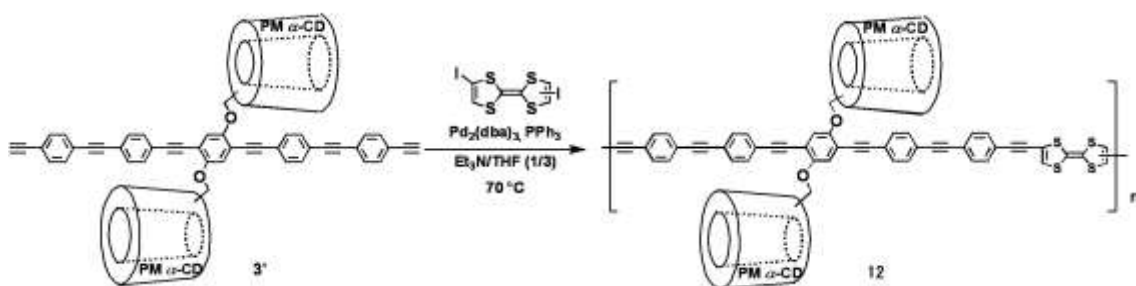
#### Synthesis of **10**.

A solution of **3** (29.4 mg, 10.0 μmol), 4,4'-diiodoazobenzene<sup>4</sup> (4.34 mg, 10.0 μmol), Pd<sub>2</sub>(dba)<sub>3</sub> (0.52 mg, 2.00 μmol), and PPh<sub>3</sub> (1.05 mg, 4.00 μmol) in Et<sub>3</sub>N (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub>, added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using CHCl<sub>3</sub> as an eluent and evaporated to give **10** (*M<sub>w</sub>* = 1.32 × 10<sup>5</sup>, PDI = 3.61,  $\bar{n}$  =

42) as a pale yellow film (26 mg, 84% yield).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} = 8.10$  (br, ArH), 7.93 (br, ArH), 7.70-7.62 (br, ArH), 7.55-7.45 (br, ArH), 7.42-7.33 (br, ArH), 5.09-4.90 (m, CD- $\text{H}_1$ ), 4.79-2.79 (m, CD-H,  $\text{OCH}_3$ ); Anal. Calcd for  $(\text{C}_{160}\text{H}_{212}\text{O}_{60}\text{N}_2 \cdot 2\text{H}_2\text{O})_n$ : C, 61.45; H, 6.96; N, 0.90. Found: C, 61.20; H, 6.88; N, 0.77.

### Synthesis of **11**.

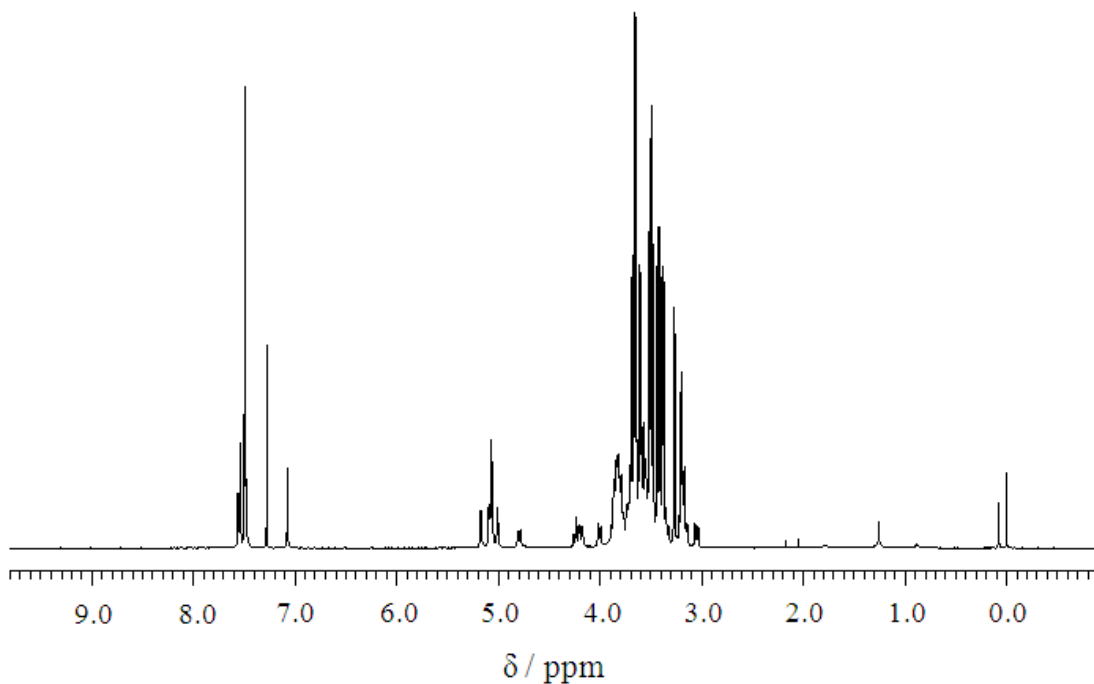
A solution of **3** (29.5 mg, 10  $\mu\text{mol}$ ), diiododiarylethene (7.2 mg, 10  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (0.92 mg, 1.0  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (0.52 mg, 2.0  $\mu\text{mol}$ ) in a mixed solvent of  $\text{Et}_3\text{N}$  (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 40  $^\circ\text{C}$  for 48 h and subsequently filtrated on a Celite pad. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **11** (31 mg, 91 %). ( $M_w = 9.35 \times 10^4$ , PDI = 2.50,  $\bar{n} = 27$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{H}} = 8.09$  (brd, Ph-H), 7.89 (brs, diarylethene-H), 7.71 (brd, Ph-H), 7.52-7.39 (br, Ph-H, diarylethene-H), 5.09-4.58 (br, CD-H), 4.20-2.79 (br, CD-H,  $\text{OCH}_3$ ), 2.50 (brs, parallel:diarylethene- $\text{CH}_3$ ), 2.23 (brs, antiparallel:diarylethene- $\text{CH}_3$ ); Anal. Calcd for  $(\text{C}_{171}\text{H}_{216}\text{O}_{60}\text{S}_2\text{F}_6 \cdot 2\text{H}_2\text{O})_n$ : C, 59.61.45; H, 6.44; S, 1.86. Found: C, 59.20; H, 6.38; S, 1.77.

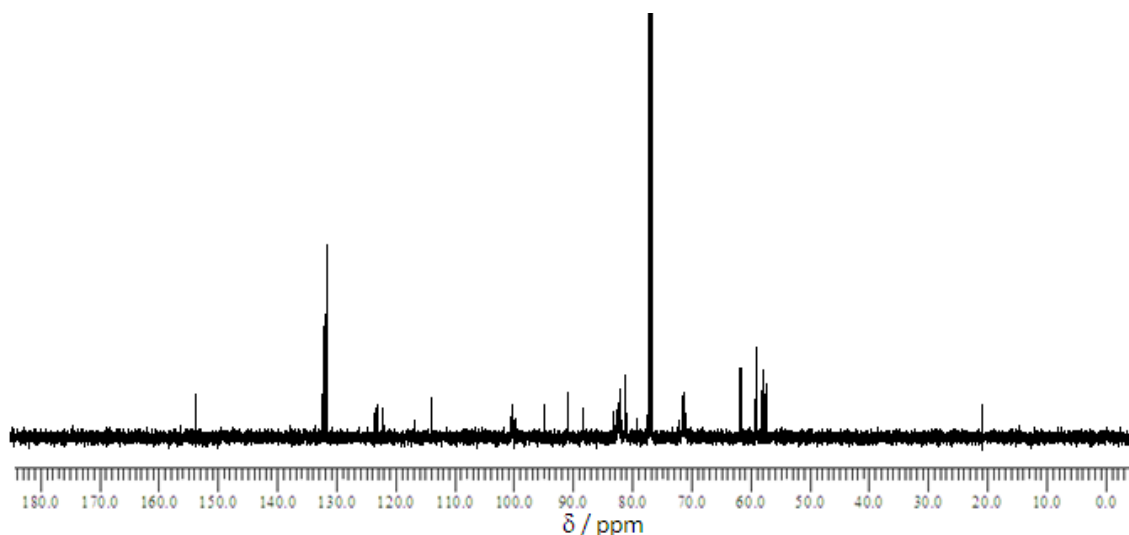


### Synthesis of **3'**

1-(4-Iodophenyl)-2-(*tert*-butyldimethylsilyl)acetylene (60.0 mg, 0.17 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (20.5 mg, 29.2  $\mu\text{mol}$ ), and  $\text{CuI}$  (1.39 mg, 7.30  $\mu\text{mol}$ ) were added to a

solution of **1** (200 mg, 73.0  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (6 mL) and THF (3 mL) subjected to freeze-pump-thaw cycling three times prior to use. After stirring at 45  $^\circ\text{C}$  for 4 h under Ar, the mixture was filtered on a Celite pad and concentrated. Purification by flash column chromatography on silica gel using EtOAc-EtOH (9:1) as an eluent yielded a pale yellow solid, which was subsequently dissolved in THF (10 mL) and treated with TBAF (0.50 mmol, 1M in THF, 0.5 mL). This solution was stirred under nitrogen at ambient temperature for 30 min. MeOH (5 mL) was then poured into the solution and the resulting solution was concentrated *in vacuo*. The residue was purified by preparative SEC using  $\text{CHCl}_3$  as the eluent, to give **3'** as a light yellow solid (204 mg, 89%). MALDI-TOF MS: ( $m/z$ ) 2967 ( $[\text{M}+\text{Na}]^+$ ,  $\text{C}_{148}\text{H}_{206}\text{O}_{60}\text{Na}$ , calcd. 2967);  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.): 7.55 (d,  $J = 8.4$  Hz, 4H, ArH), 7.49 (m, 12H, ArH), 7.08 (s, 2H, ArH), 5.17-5.00 (m, 12H, CD- $\text{H}_1$ ), 4.81-3.04 (m, 176H, CD-H,  $\text{OCH}_3$ , CCH);  $^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.):  $\delta_{\text{c}} = 153.43, 132.08, 131.54, 131.43, 123.32, 123.23, 122.83, 122.14, 116.67, 113.80, 100.46, 100.22-100.00$  (several peaks overlapped), 99.48, 94.76, 90.87, 88.30, 83.13-82.05 (several peaks overlapped), 81.73, 81.17, 81.01, 79.13, 72.23, 71.47-70.88 (several peaks overlapped), 61.83, 61.78, 61.71, 59.19, 59.07, 59.04, 58.99, 58.18, 57.86, 57.84, 57.77, 57.73, 57.30; Anal. Calcd for  $\text{C}_{148}\text{H}_{206}\text{O}_{60}\cdot 3\text{H}_2\text{O}$ : C, 59.27; H, 7.12. Found: C, 59.02; H, 6.98%.





### Synthesis of **8'**

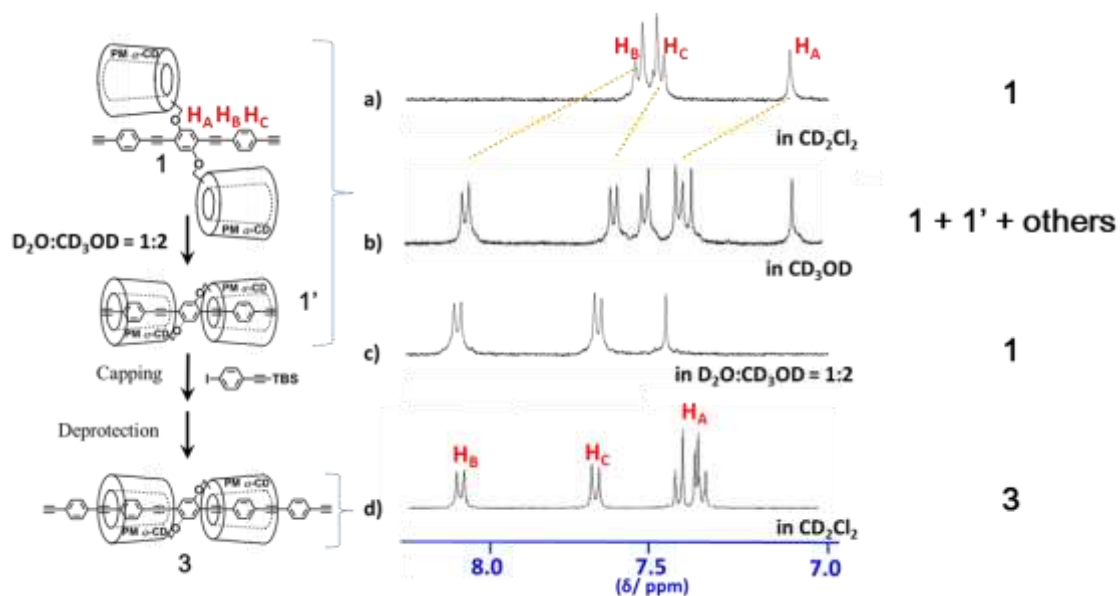
A solution of **3'** (29.4 mg, 10.0  $\mu\text{mol}$ ), 2,6(7)-diiodotetrathiafulvalene<sup>3</sup> (4.55 mg, 10.0  $\mu\text{mol}$ ),  $\text{Pd}_2(\text{dba})_3$  (0.91 mg, 1.00  $\mu\text{mol}$ ), and  $\text{PPh}_3$  (0.52 mg, 2.00  $\mu\text{mol}$ ) in  $\text{Et}_3\text{N}$  (1 mL) and THF (5 mL) subjected to freeze-pump-thaw cycling three times prior to use was stirred at 70 °C for 48 h under Ar. The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$ , added 50 mg of QuadraSil TA, filtered through a Celite pad followed by a 0.22 mm nylon filter, and concentrated under reduced pressure. The polymer was purified from low molecular weight material by preparative recycling gel permeation chromatography using  $\text{CHCl}_3$  as an eluent and evaporated to give **8'** ( $M_w = 1.27 \times 10^5$ , PDI = 2.69,  $\bar{n} = 40$ ) as a pale orange film (24 mg, 72% yield).  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ , r.t.): 7.75-7.70 (br, ArH), 7.55-7.45 (br, ArH), 7.07 (s, 2H, ArH), 6.60 (br, ArH), 5.17-5.00 (m, CD-H<sub>1</sub>), 4.81-2.87 (m, CD-H, OCH<sub>3</sub>); Anal. Calcd for  $(\text{C}_{154}\text{H}_{206}\text{O}_{60}\text{S}_4 \cdot \text{H}_2\text{O})_n$ : C, 58.47; H, 6.63; S, 4.05. Found: C, 58.30; H, 6.31; S, 3.81.

### III. Confirmation of the formation of [3]rotaxane.

#### $^1\text{H}$ NMR analysis in different solvents and concentrations.



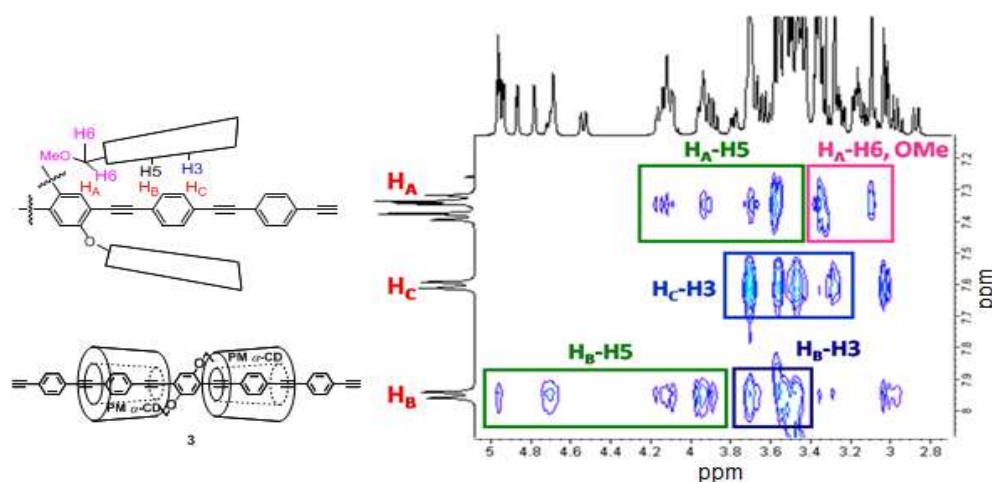
**Answer:** The double intramolecular self-inclusion phenomenon of **1** has been confirmed by  $^1\text{H}$  NMR employing different solvents and concentrations (Figure SII). The NMR spectrum of aromatic protons of **1** in  $\text{CD}_2\text{Cl}_2$  reveals the exclusion of the OPE moiety from the cavity of the PM  $\alpha$ -CDs (Figure SIIa). A spectrum in  $\text{CD}_3\text{OD}$  at room temperature showed an equilibrium mixture of **1**, pseudo linked [3]rotaxane **1'**, and its oligomeric supramolecular complexes (Figure SIIb). When a more hydrophilic medium ( $\text{CD}_3\text{OD}:\text{D}_2\text{O} = 2:1$ ) has been used, **1** was completely converted to the supramolecular complex **1'** at room temperature (Scheme SIIc). The evidence that the NMR spectra of **1'** at different concentrations in  $\text{CD}_3\text{OD}$  showed no new peaks ascribable to oligomeric and/or polymeric supramolecular complexes supports the formation of double intramolecular self-inclusion complex **1'** as a sole product. In order to fix the pseudo-linked [3]rotaxane structure by elongating the OPE, **1'** was treated with *tert*-butyldimethylsilyl (TBS)-protected *p*-iodophenylacetylene in the presence of a catalytic amount of  $\text{Pd}(\text{OAc})_2$ , TXPTS, and  $\text{CuI}$ , followed by the deprotection of the TBS group, the desired insulated monomer **3** was obtained as a sole product after purification. The aromatic region of  $^1\text{H}$  NMR spectra of fixed [3]rotaxane **3** was quite similar as that of **1'** (Figures SIIc and SII d). The thermal stability of this fixed [3]rotaxane structure of **3** was validated using  $^1\text{H}$  NMR as the insulation was retained under toluene reflux condition for 24 h.



**Figure S11.** a), b), c) The aromatic region of 400 MHz  $^1\text{H}$  NMR spectra of **1** in  $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{OD}$ , and  $\text{D}_2\text{O} : \text{CD}_3\text{OD} = 1 : 2$ , respectively. d) The aromatic region of 400 MHz  $^1\text{H}$  NMR spectrum of **3** in  $\text{CD}_2\text{Cl}_2$ .

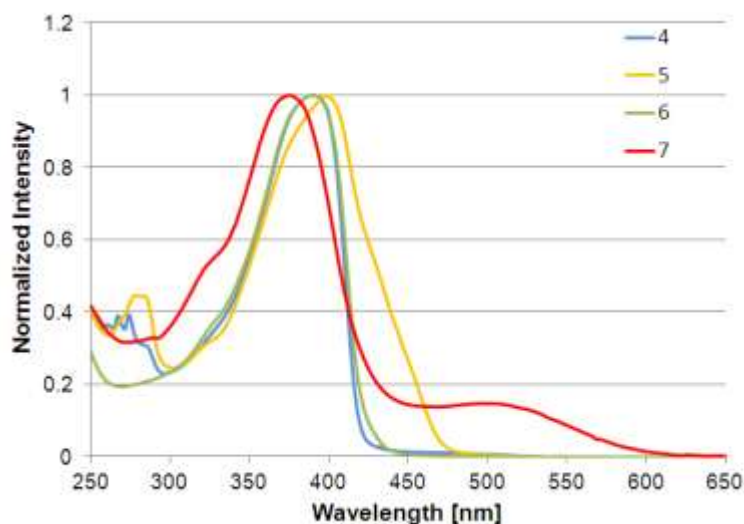
#### ROESY NMR of insulated monomer **3**.

The 2D-ROESY NMR spectrum of **3** was acquired in  $\text{CDCl}_3$ . Strong correlations between the aromatic protons of the axial oligo(phenylene ethynylene) ( $\text{H}_\text{A}$ ,  $\text{H}_\text{B}$  and  $\text{H}_\text{C}$ ) and the inner protons of the cyclodextrins ( $\text{H}_3$  and  $\text{H}_5$ ) were observed.

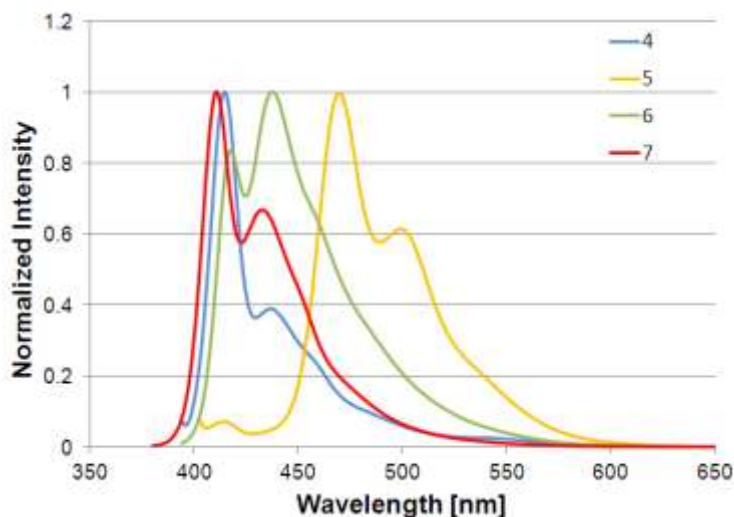


**Figure S12.** Partial 2D-ROESY NMR spectrum of **3** (600 MHz,  $\text{CDCl}_3$ ) showing the correlations between aromatic protons of the axial oligo(phenylene ethynylene) and inner protons of cyclodextrins.

#### IV. Absorption and Emission spectra of copolymer **4-7**.



**Figure SI3a.** UV/Vis absorption spectra of copolymer 4-7.

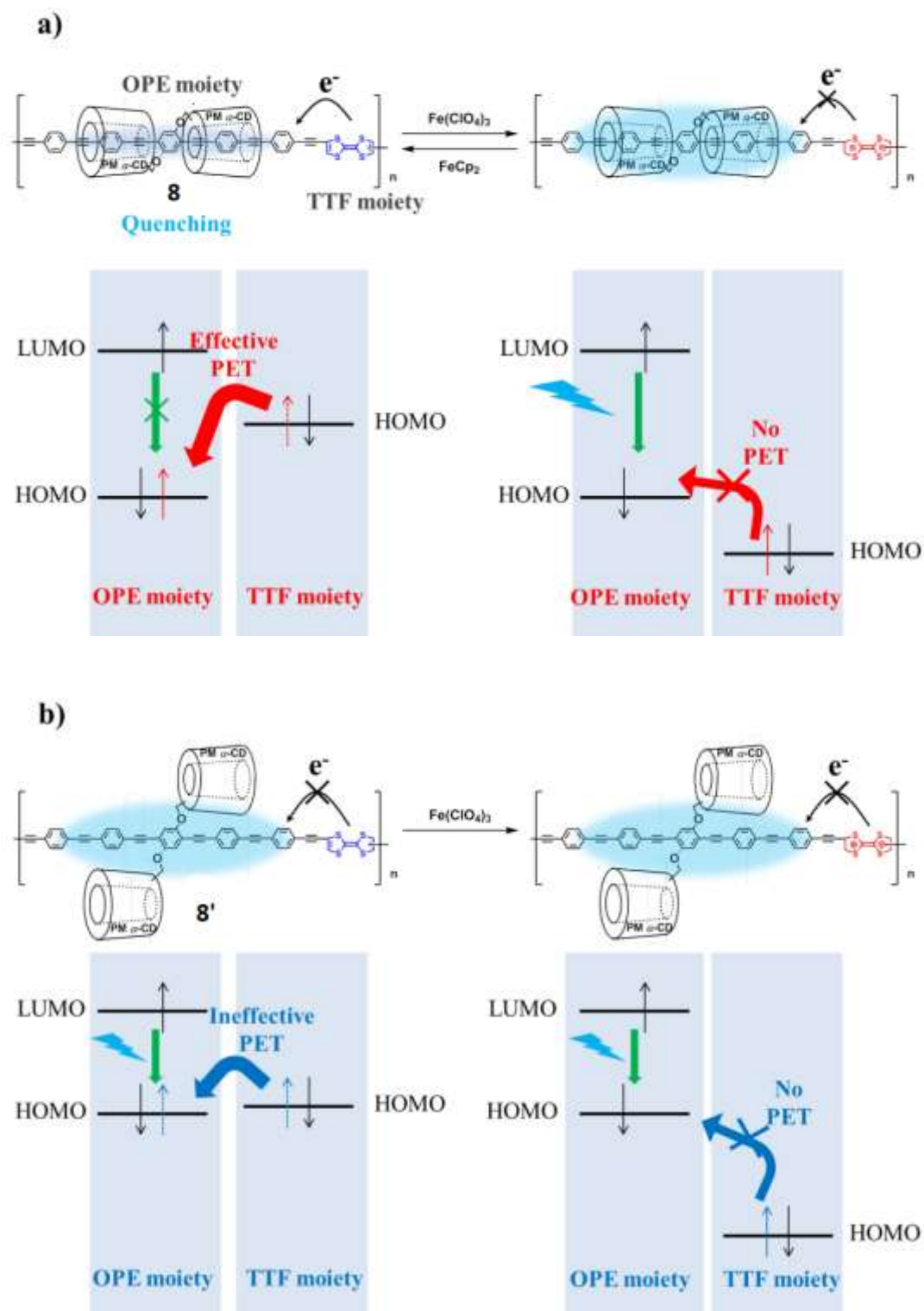


**Figure SI3b.** Fluorescence emission spectra of copolymer 4-7.

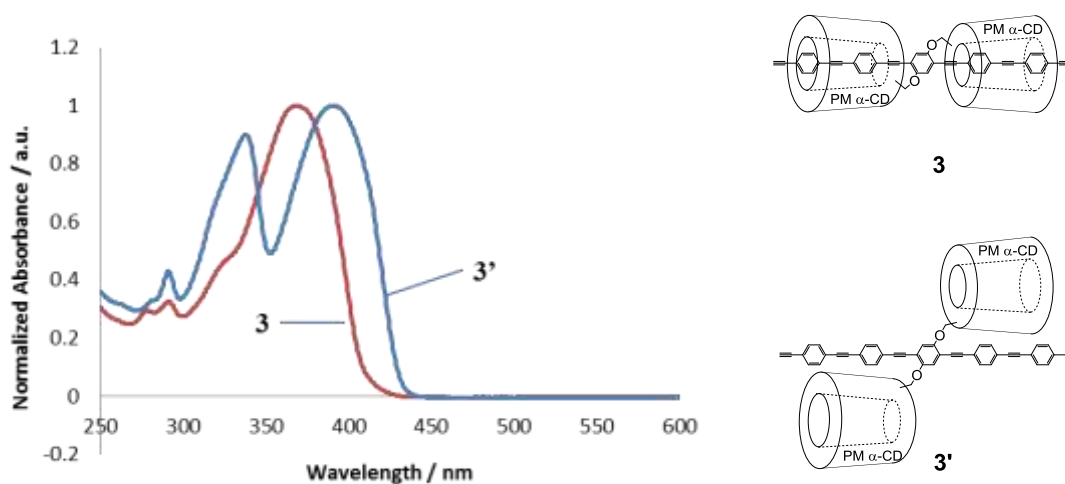
#### V. Explanation of change in emission spectra of copolymers 8 and 8'.

As shown in Figure S4a, an electron from the HOMO level of the tetrathiafulvalene (TTF) moiety is transferred to the SOMO orbital of the oligo(phenylene ethynylene) (OPE) moiety generated by excitation of the OPE moiety. This electron transfer inhibits the return of the excited electron to the original orbital with the emission of fluorescence, which means no fluorescence is emitted. However, when the TTF moiety is oxidized to the di-cation, the HOMO level of the moiety is lowered such that electron transfer cannot take place, which allows the excited electron of the conjugated chain to fall back to the ground state with consequent fluorescence emission. On the other hand, as shown Figure S4b, given that the HOMO level of the OPE moiety of uninsulated copolymer **12** is higher than that of the insulated copolymer **8**, efficient PET does not occur even in the original form of the polymer. Thus, the difference in the emission intensity of the TTF moiety before and after oxidation is smaller. Based on the UV spectra of **3** and that of the corresponding uninsulated monomer **3'**, the respective maximum absorptions occurred at wavenumbers of 368 nm and 391 nm (Figure S5). This result suggests that

the HOMO-LUMO gap of the uninsulated OPE unit is smaller than that of the insulated OPE unit given that the planarity of the OPE unit of **3'** is higher than that of **3** because the OPE unit of the former was fixed in a twisted manner owing to the cyclodextrin covering.

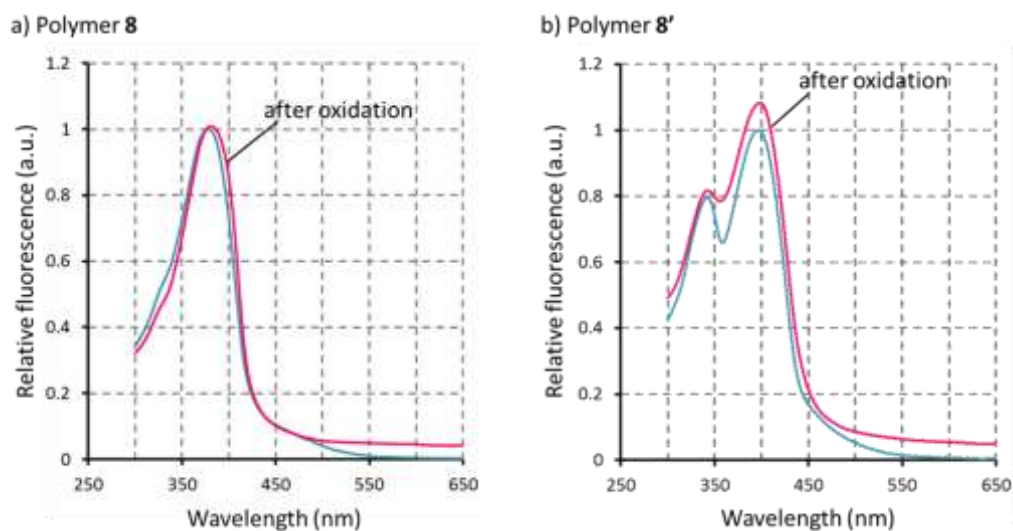


**Figure SI4a-b.** Explanation of the emission intensity changes in TTF copolymers **8** and **8'** due to redox manipulations using energy level diagrams.



**Figure SI5.** UV/Vis absorbance spectra of insulated OPE monomer **3** (red) and uninsulated OPE monomer **3'** (blue) in  $\text{CHCl}_3$ .

Insulation constrains the conformation of the OPE chain in a somewhat twisted orientation, which prevents the delocalization of electrons along the conjugated chain and results in a decrease in the HOMO level. Indeed, the absorption maxima of **3** and **3'** occurred at 368 nm and 391 nm, respectively. These results suggested that the dihedral angles between the benzene units of **3** were more twisted than those between the benzene units of **3'** due to the cyclodextrin covering.



**Figure SI6.** a,b) UV spectra of polymer **8** and **8'** in CHCl<sub>3</sub> in different redox states: natural form (blue) and di-cation form (red).

**VI. Flash-Photolysis Time-Resolved Microwave Conductivity Measurement (FP-TRMC).**

The nanosecond laser pulses from a Nd: YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDY-HG, FWHM 3-5 ns) have been used as excitation sources. The photon density of the laser was set at  $1.9 \times 10^{15}$  photons/cm<sup>2</sup>. For time-resolved microwave conductivity (TRMC) measurement, the microwave frequency and power were set at ~ 9.1 GHz and 3 mW respectively, and the film of the samples (casted from 1~2 wt% CHCl<sub>3</sub> solutions at 0.9-2.3 μm thick) was set at the electric field maximum in the cavity. The TRMC signal picked up by a diode (rise time < 1 ns) is monitored by a digital oscilloscope (Tektronix, TDS3032B, rise time 1.4 ns). All the above experiments were carried out at room temperature. The transient photoconductivity ( $\Delta\sigma$ ) of the samples is related to the reflected microwave power ( $\Delta P_r/P_r$ ) and sum of the mobilities of charge carriers via:

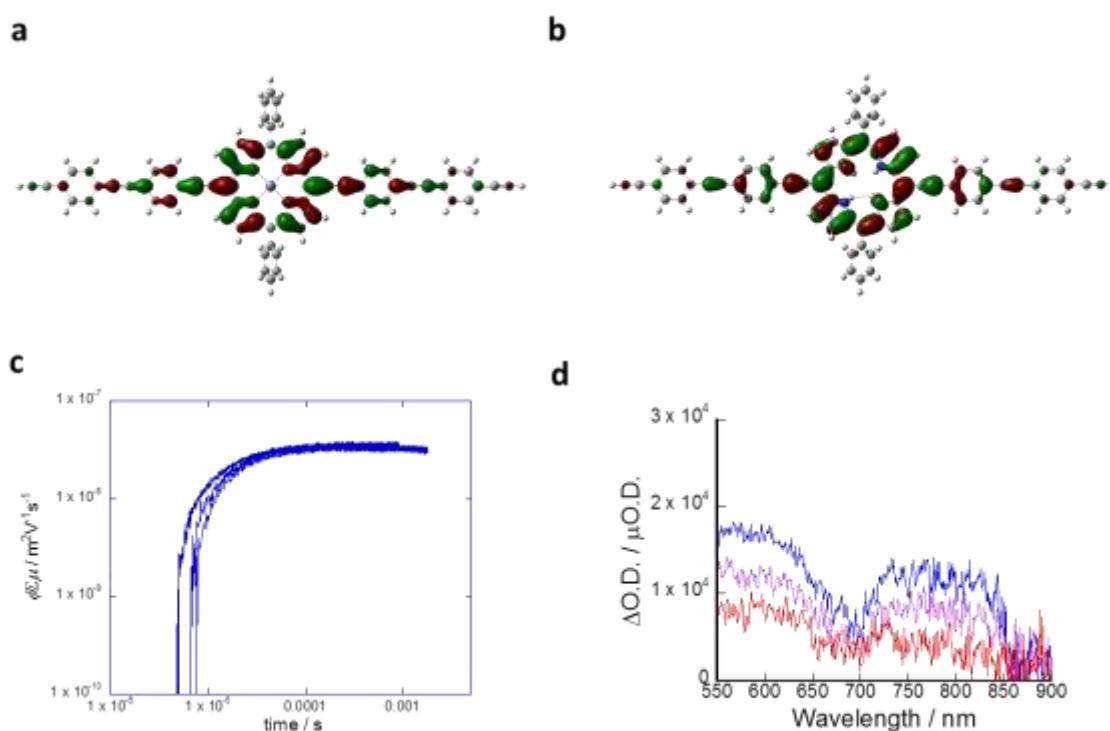
$$\langle \Delta\sigma \rangle = \frac{1}{A} \frac{\Delta P_r}{P_r} \quad (1)$$

$$\Delta\sigma = e \sum \mu \phi N \quad (2)$$

where  $A$ ,  $e$ ,  $\phi$ ,  $N$ , and  $\sum\mu$  are a sensitivity factor, elementary charge of electron, photo carrier generation yield (quantum efficiency), the number of absorbed photons per unit volume, and sum of mobilities for negative and positive carriers respectively. The number of photons absorbed by the sample was estimated based on the power loss of an incident laser pulses averaged over 100 shots. The values of  $\phi$  in the polymer films were determined by transient absorption spectroscopy (TAS). The other details of the set of apparatus were described elsewhere.<sup>7,8</sup>

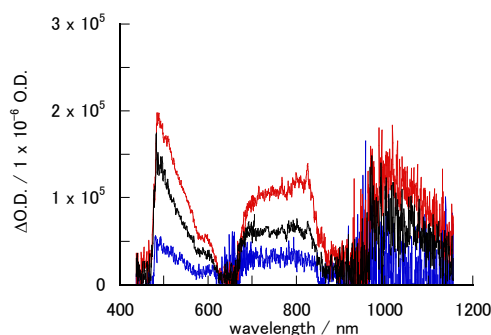
## VII. Transient Absorption Spectroscopy Measurement (TAS).

The TRMC measurement directly gives the value of  $\phi\Sigma\mu$ , which is the product of the quantum yield of charge carriers ( $\phi$ ) and the sum of their mobilities ( $\Sigma\mu$ ). In-situ TAS measurement assigns the conductivity kinetics to negative or positive charge species and to determine its concentration quantitatively. The value of  $\phi$  was determined based on the transient absorption observed at 620 nm attributed to Zn-porphyrin radical cations with  $\epsilon^+$  of  $7 \times 10^4 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$ .<sup>9</sup> The THG laser pulses from the nanosecond laser were used as excitation light sources. The incident photon densities in the present paper were set at  $2.4 \times 10^{16} \text{ photon/cm}^2$ . The same films used in the TRMC measurement were irradiated with continuum white light for absorption spectroscopy perpendicularly with respect to the laser pulse. The spot size of the light probe was approximately 1 mm in diameter at the sample. After passing through the sample, the white light and/or emission was led to a grating unit (Hamamatsu, C5094) and scanned by a wide-dynamic-range streak camera (Hamamatsu, C7700). The streak image was collected via a CCD camera (Hamamatsu, C4742-98).<sup>10</sup>



**Figure SI7:** **a)** Optimized structures of a model compound of **9a** calculated using the DFT, including a schematic representation of the HOMO orbitals. **b)** HOMO of radical cations of the model molecule of **9b** calculated by the DFT method with B3LYP/6-31G(d,p) level. **c)** Conductivity transient observed for **9c** in logarithmic time scale. The transients were observed for the identical sample in Figure 3a upon excitation at 355 nm,  $1.9 \times 10^{15}$  photons  $\text{cm}^{-2}$ . **d)** Transient absorption spectra of a solid film of **9b** upon excitation at 355 nm,  $2.4 \times 10^{16}$  photons  $\text{cm}^{-2}$ . The spectra were recorded at 1(blue), 3(violet), and 10(red)  $\mu\text{s}$  after pulse exposures, respectively.

We attempted to clarify the photochemical dynamics of the present molecular systems not only in the thin solid films but also in the solution and polymer matrices. Photo-excitation of the Zn-porphyrin molecules in the non-polar solution phase predominantly produces the triplet excited state because of the lower energy required for re-organization of the charged species, giving rise to the characteristic transient spectra of the triplet state of **9b** as shown in Figure S7. The kinetic trace of the transient spectra apparently mismatched with those of the conductivity transients observed in the thin solid film of the compounds (Figure 3), and the yield of the triplet states shows a distinct decrease under oxygen saturated conditions. This is also the signature that the TRMC conductivity transient originates from the positively charged species on the conjugated backbone.

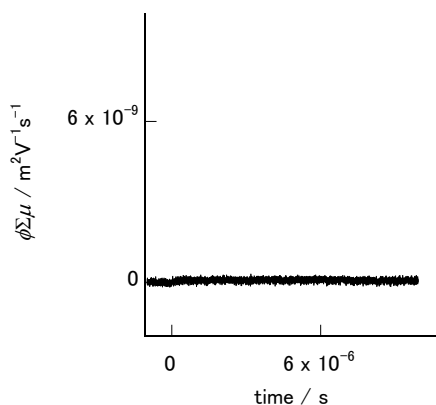


**Figure SI8.** Transient absorption spectra of **9b** (100 mM) in toluene acquired using a quartz cell (optical path length = 10 mm) under ambient conditions (black), saturated Ar



(red), and O<sub>2</sub> (blue) upon exposure to 355 nm pulses at  $1.8 \times 10^{16}$  photons cm<sup>-2</sup>, recorded 1 ms after excitation.

However, unfortunately, because of the preferred formation of the triplet state in the non-polar solvent, only an indistinguishable conductivity transient was observed in the solution upon excitation at 355 nm (Figure S8). Note that the TRMC measurement cannot be performed using a polar solvent, which increases the reorganization energy of the charged species, hence leading to the higher yield of holes on the Zn-porphyrin molecules due to the considerable static absorbance of microwave radiation by the polar medium.



**Figure S19.** Conductivity transient of **9b** (100 mM) observed upon excitation with 355 nm at  $3.7 \times 10^{16}$  photons cm<sup>-2</sup> in toluene using a quartz cell (optical path length = 1 mm) under ambient conditions.

### VIII. DFT Calculation.

Optimized structural coordinates of **9b** by B3LYP/6-31G(d,p).

Stoichiometry C<sub>68</sub>H<sub>40</sub>N<sub>4</sub>(1+,2)

Framework group C1[X(C<sub>68</sub>H<sub>40</sub>N<sub>4</sub>)]

Deg. of freedom 330

Full point group C1 NOp 1

Largest Abelian subgroup C1 NOp 1

Largest concise Abelian subgroup C1 NOp 1

Standard orientation:

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	6.093860	-0.089021	-0.064969
2	6	0	4.872523	-0.097895	-0.066245
3	6	0	17.216182	0.000134	0.050548
4	6	0	16.508778	-1.218051	0.009215
5	6	0	15.122278	-1.229017	-0.008931
6	6	0	14.394749	-0.020573	0.013996
7	6	0	15.103583	1.198435	0.055277
8	6	0	16.490110	1.207780	0.073117
9	6	0	18.642617	0.010621	0.069428
10	6	0	19.852768	0.019540	0.085570
11	6	0	10.338536	-0.053097	-0.031874
12	6	0	9.627361	-1.272829	-0.086399
13	6	0	8.243040	-1.285640	-0.099016
14	6	0	7.510583	-0.078122	-0.056281

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15	6	0	8.220703	1.142349	-0.001453
16	6	0	9.605058	1.153900	0.009765
17	6	0	12.974097	-0.031250	-0.003454
18	6	0	11.756166	-0.040969	-0.017507
19	6	0	1.193401	-2.960070	-0.133408
20	6	0	2.468207	-3.565960	-0.377476
21	6	0	3.432164	-2.597078	-0.323589
22	6	0	2.802510	-1.334542	-0.075356
23	7	0	1.445118	-1.588380	0.004588
24	6	0	-0.052131	-3.580181	-0.040651
25	6	0	3.460105	-0.086489	-0.038248
26	6	0	2.838872	1.210541	-0.120962
27	6	0	3.443332	2.375955	-0.612275
28	6	0	2.499236	3.400926	-0.598329
29	6	0	1.293497	2.891889	-0.094663
30	7	0	1.504925	1.518635	0.158635
31	6	0	0.052100	3.580440	0.041778
32	6	0	-1.193429	2.960336	0.134481
33	6	0	-2.468264	3.566186	0.378505
34	6	0	-3.432218	2.597319	0.324459
35	6	0	-2.802533	1.334808	0.076156
36	7	0	-1.445116	1.588642	-0.003614
37	6	0	-3.460110	0.086761	0.038915
38	6	0	-2.838889	-1.210267	0.121705
39	6	0	-3.443423	-2.375648	0.613017
40	6	0	-2.499335	-3.400623	0.599276
41	6	0	-1.293544	-2.891651	0.095644
42	7	0	-1.504930	-1.518406	-0.157718
43	6	0	-0.106107	-5.067771	-0.025471
44	6	0	-0.992349	-7.149417	-0.916589
45	6	0	-0.942405	-5.757243	-0.922027
46	6	0	0.664159	-5.811068	0.886716
47	6	0	0.605230	-7.203623	0.894659
48	6	0	-0.219473	-7.876425	-0.008557
49	6	0	0.106125	5.068028	0.026741
50	6	0	-0.605160	7.204008	-0.893132

51	6	0	-0.664132	5.811452	-0.885347
52	6	0	0.942482	5.757368	0.923343
53	6	0	0.992470	7.149540	0.918064
54	6	0	0.219586	7.876678	0.010142
55	6	0	-18.642597	-0.011365	-0.072020
56	6	0	-19.852743	-0.020277	-0.088467
57	6	0	-7.510599	0.078219	0.056263
58	6	0	-8.220617	-1.142300	0.001182
59	6	0	-9.604968	-1.153954	-0.010312
60	6	0	-10.338544	0.052985	0.031288
61	6	0	-9.627472	1.272764	0.086076
62	6	0	-8.243154	1.285677	0.098973
63	6	0	-6.093876	0.089220	0.065215
64	6	0	-4.872542	0.098139	0.066692
65	6	0	-14.394744	0.020155	-0.015516
66	6	0	-15.103475	-1.198904	-0.057063
67	6	0	-16.489995	-1.208356	-0.075252
68	6	0	-17.216167	-0.000768	-0.052776
69	6	0	-16.508868	1.217469	-0.011176
70	6	0	-15.122373	1.228541	0.007320
71	6	0	-11.756171	0.040752	0.016619
72	6	0	-12.974098	0.030941	0.002281
73	1	0	17.062055	-2.150777	-0.008375
74	1	0	14.585054	-2.170906	-0.040785
75	1	0	14.551951	2.132332	0.073139
76	1	0	17.029011	2.148509	0.104951
77	1	0	20.918463	0.027272	0.099775
78	1	0	10.180898	-2.204928	-0.118604
79	1	0	7.710302	-2.229929	-0.140403
80	1	0	7.669888	2.076385	0.035250
81	1	0	10.141418	2.095570	0.052661
82	1	0	2.609727	-4.612290	-0.600371
83	1	0	4.492331	-2.712528	-0.488129
84	1	0	0.759931	-0.964257	0.396023
85	1	0	4.453736	2.423296	-0.988653
86	1	0	2.631878	4.406561	-0.967770

87	1	0	1.041213	1.099704	0.955794
88	1	0	-2.609808	4.612484	0.601532
89	1	0	-4.492401	2.712733	0.488923
90	1	0	-0.759940	0.964679	-0.395336
91	1	0	-4.453876	-2.422951	0.989271
92	1	0	-2.632041	-4.406214	0.968809
93	1	0	-1.041003	-1.099454	-0.954732
94	1	0	-1.632022	-7.666992	-1.624623
95	1	0	-1.537351	-5.197039	-1.636273
96	1	0	1.289356	-5.292001	1.606196
97	1	0	1.197135	-7.762342	1.612915
98	1	0	-0.262925	-8.961009	-0.002584
99	1	0	-1.197065	7.762829	-1.611309
100	1	0	-1.289358	5.292489	-1.604878
101	1	0	1.537443	5.197059	1.637495
102	1	0	1.632187	7.667014	1.626132
103	1	0	0.263073	8.961262	0.004294
104	1	0	-20.918435	-0.028068	-0.102884
105	1	0	-7.669722	-2.076290	-0.035500
106	1	0	-10.141249	-2.095660	-0.053406
107	1	0	-10.181085	2.204819	0.118262
108	1	0	-7.710495	2.230003	0.140560
109	1	0	-14.551765	-2.132758	-0.074856
110	1	0	-17.028816	-2.149124	-0.107290
111	1	0	-17.062221	2.150150	0.006345
112	1	0	-14.585231	2.170469	0.039380

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Rotational constants (GHZ): 0.0554511 0.0063199 0.0056904

Optimized structural coordinates of **9a** by B3LYP/LANL2DZ.

Stoichiometry C<sub>68</sub>H<sub>36</sub>N<sub>4</sub>Zn(1-,2)

Framework group C1[X(C<sub>68</sub>H<sub>36</sub>N<sub>4</sub>Zn)]

Deg. of freedom 321

Prev. full point group        C1    NOp 1  
Prev. largest Abelian subgroup    C1    NOp 1  
    concise Abelian subgroup        C1    NOp 1

Standard orientation:

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Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	30	0.000000	-0.000004	-0.000093
2	1	-21.114703	-0.015156	-0.014764
3	6	-20.049082	-0.014150	-0.013919
4	6	-18.823120	-0.013009	-0.012949
5	1	-17.208363	2.147879	-0.024515
6	6	-17.388274	-0.011851	-0.011812
7	6	-16.662047	1.208247	-0.018469
8	1	-17.204903	-2.171287	0.001180
9	6	-16.660091	-1.230777	-0.004006
10	6	-15.263734	1.210252	-0.017370
11	1	-14.719726	2.150741	-0.022567
12	6	-15.261778	-1.230534	-0.002906
13	6	-14.529357	-0.009549	-0.009565
14	1	-14.716264	-2.170145	0.003144
15	6	-13.103869	-0.008412	-0.008464
16	6	-11.871742	-0.007468	-0.007541
17	1	-10.257493	2.155961	-0.015883
18	6	-10.447060	-0.006479	-0.006502
19	6	-9.712813	1.214912	-0.011363
20	1	-10.254553	-2.168656	0.003166
21	6	-9.711151	-1.226866	-0.000591
22	6	-8.318025	1.216773	-0.010181
23	1	-7.774819	2.158073	-0.013435
24	6	-8.316364	-1.226826	0.000175
25	6	-7.575894	-0.004520	-0.004499
26	1	-7.771881	-2.167385	0.004184
27	6	-6.158739	-0.003572	-0.003561
28	6	-4.922391	-0.002806	-0.002808

29	1	-4.588754	-2.679813	0.100515
30	1	-4.591683	2.674617	-0.105576
31	6	-3.516833	-2.551314	0.062085
32	6	-3.507260	-0.001989	-0.001987
33	6	-3.519657	2.547328	-0.066028
34	1	-2.686477	-4.599159	0.110278
35	1	-2.691554	4.596112	-0.113337
36	6	-2.839067	-1.271365	0.012421
37	6	-2.541578	-3.529659	0.062591
38	6	-2.840498	1.268145	-0.015649
39	6	-2.545507	3.526773	-0.065506
40	1	0.843956	-5.187681	1.983457
41	1	0.844830	-7.678545	1.992057
42	1	0.837927	7.679417	-1.991694
43	1	0.839905	5.188548	-1.982991
44	7	-1.468627	-1.468852	-0.016906
45	6	-1.256704	-2.860878	0.006028
46	7	-1.470316	1.467177	0.015139
47	6	-1.259940	2.859442	-0.007588
48	6	0.481454	-5.733797	1.116272
49	6	0.479115	-7.141204	1.119498
50	6	0.472021	7.141689	-1.119452
51	6	0.475975	5.734285	-1.116166
52	6	0.001988	-3.506001	-0.000122
53	6	0.002842	-5.010301	-0.000151
54	6	0.004472	-7.852105	-0.000207
55	1	0.005095	-8.940162	-0.000229
56	1	-0.005095	8.940147	-0.000239
57	6	-0.004472	7.852089	-0.000215
58	6	-0.002842	5.010290	-0.000156
59	6	-0.001988	3.505990	-0.000126
60	6	-0.474945	-5.734301	-1.116600
61	6	-0.470988	-7.141704	-1.119882
62	6	-0.480149	7.141190	1.119052
63	6	-0.482484	5.733783	1.115826
64	6	1.259948	-2.859450	-0.006251

65	7	1.470297	-1.467185	0.016719
66	6	1.256697	2.860870	0.007359
67	7	1.468646	1.468844	-0.015329
68	1	-0.838077	-5.188566	-1.983761
69	1	-0.836087	-7.679431	-1.992463
70	1	-0.846670	7.678534	1.991272
71	1	-0.845784	5.187665	1.982675
72	6	2.545579	-3.526776	-0.062807
73	6	2.840512	-1.268149	-0.012577
74	6	2.541507	3.529656	0.065283
75	6	2.839053	1.271361	0.015490
76	1	2.691681	-4.596112	-0.110518
77	1	2.686350	4.599159	0.113088
78	6	3.519727	-2.547330	-0.062254
79	6	3.507261	0.001984	0.001858
80	6	3.516763	2.551313	0.065853
81	1	4.591794	-2.674615	-0.100664
82	1	4.588643	2.679815	0.105422
83	6	4.922391	0.002794	0.002727
84	6	6.158739	0.003540	0.003528
85	1	7.771843	2.167377	0.013476
86	6	7.575894	0.004509	0.004526
87	6	8.316342	1.226824	0.010244
88	1	7.774857	-2.158081	-0.004157
89	6	8.318046	-1.216775	-0.000119
90	6	9.711129	1.226880	0.011491
91	1	10.254514	2.168676	0.016039
92	6	9.712834	-1.214898	0.000711
93	6	10.447060	0.006501	0.006660
94	1	10.257531	-2.155940	-0.003024
95	6	11.871742	0.007504	0.007771
96	6	13.103869	0.008417	0.008758
97	1	14.716226	2.170165	0.022962
98	6	14.529357	0.009568	0.009938
99	6	15.261756	1.230558	0.017790
100	1	14.719764	-2.150721	-0.002773



101	6	15.263755	-1.210228	0.003313
102	6	16.660070	1.230814	0.018968
103	1	17.204864	2.171328	0.025051
104	6	16.662068	-1.208211	0.004492
105	6	17.388274	0.011894	0.012345
106	1	17.208401	-2.147838	-0.000669
107	6	18.823120	0.013064	0.013564
108	6	20.049082	0.014071	0.014605
109	1	21.114703	0.014945	0.015511

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Rotational constants (GHZ): 0.0559120 0.0061986 0.0055988

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