

Supporting Information for:

**Synthesis and FRET Properties of Alternating Donor–Acceptor Copolymer Featuring  
Orthogonally Arrayed Transition Dipoles along Polymer Backbone**

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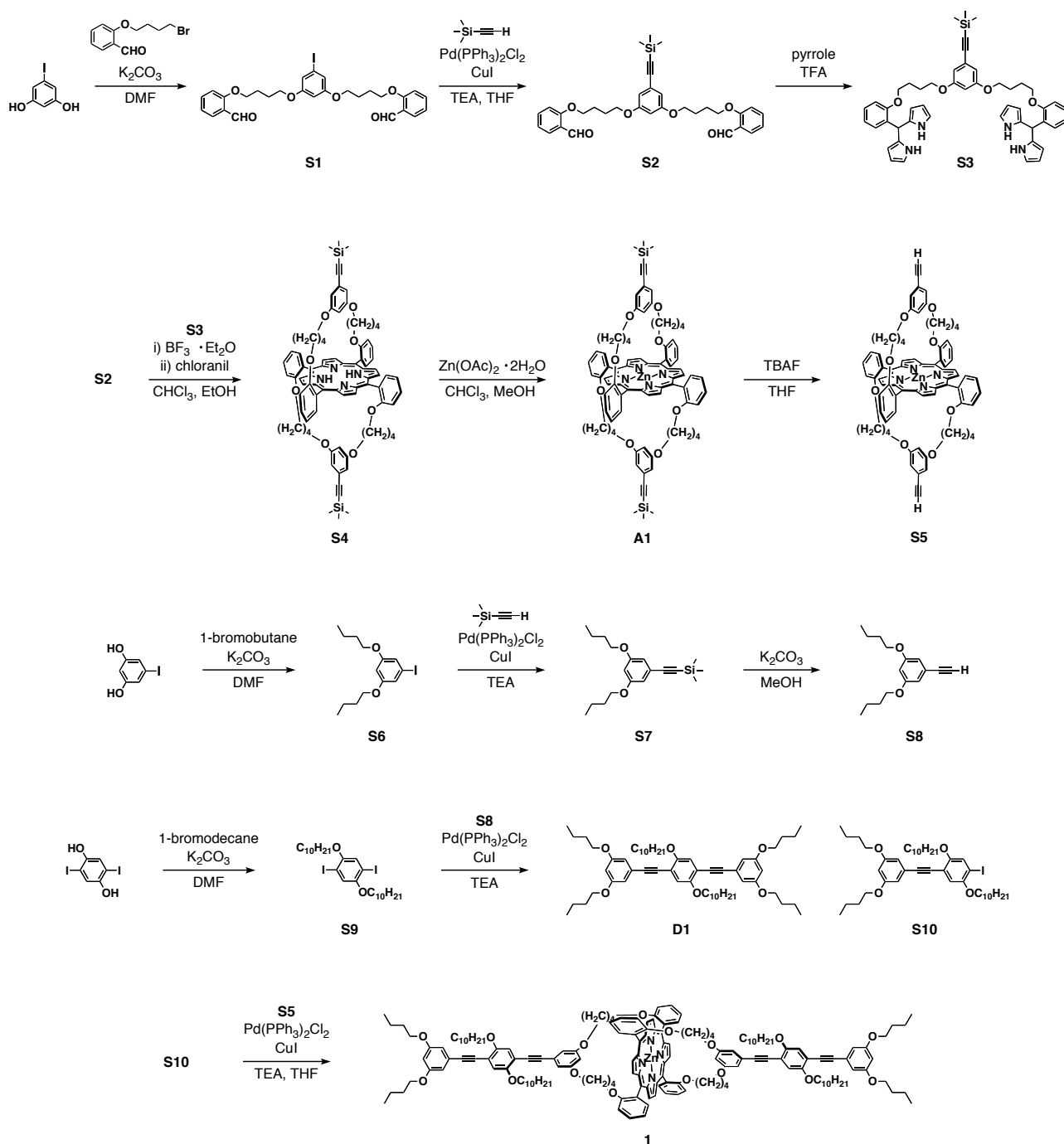
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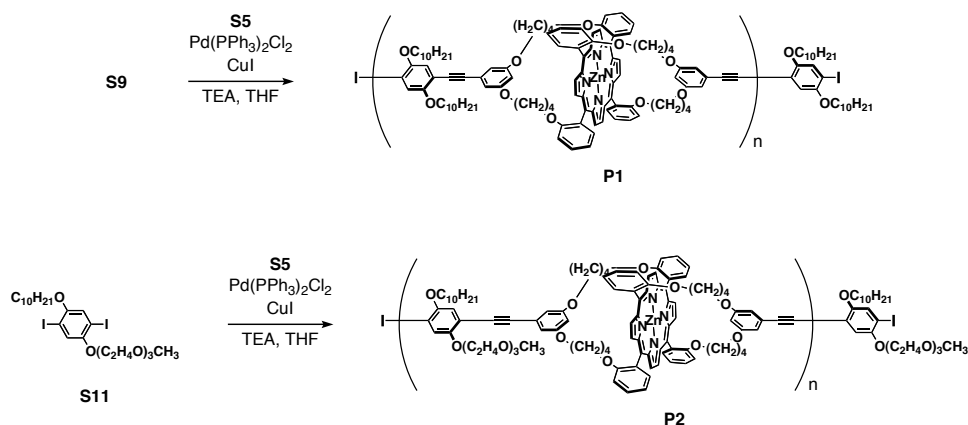
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**Measurements:** NMR spectra were recorded on a Bruker Biospin DRX-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (0 ppm for  $^1\text{H}$ ) or residual  $\text{CHCl}_3$  (77 ppm for  $^{13}\text{C}$ ) as an internal standard. Mass spectral data were obtained using a SHIMADZU AXIMA-CFR Plus MALDI TOF mass spectrometer. Melting points were determined with a Yanako NP-500P micro melting point apparatus. Recycling preparative HPLC was carried out on a Japan Analytical Industry model LC-9201, equipped with a column set consisting of JAIGEL-2.5H combined with JAIGEL-3.0H, with  $\text{CHCl}_3$  as the eluent at a flow rate of  $3.5 \text{ mL min}^{-1}$ . Gel permeation chromatography for copolymers was performed in THF solution using a TOSHO GPC system (HLC-8320GPC EcoSEC) equipped with two TSKgel Super-Multipore HZ-M columns and a UV detector (420 nm). The molecular weight ( $M_n$ ,  $M_w$ ) and polydispersity index (PDI) of the polymer samples were calculated on the basis of a polystyrene calibration. Electronic absorption and fluorescence spectra were recorded on a Hitachi U-2900 spectrophotometer and a Hitachi F-7000 spectrophotometer, respectively, in toluene solution at room temperature (298 K) in a quartz cuvette of 1 cm path length. Relative fluorescence quantum yield of **D1** was determined using quaterthiophene ( $\Phi = 0.18$ , benzene) as standard. Fluorescence lifetime measurements were performed by means of time correlated single photon counting (TCSPC) technique by using a FluoroCube spectrometer (HORIBA Jobin Yvon) equipped with a picosecond pulse laser (PB-375L, 375 nm) and a picosecond photon detection module (TBX). Decay analysis and the fitting routine to determine the lifetime(s) were performed using the DAS6 software provided by IBM. Spin coating was performed using OSHIGANE SC-300. Microfibers were fabricated by using NANON electrospinning setup (NANON-01A, MECC Co., Ltd.) and characterized with SEM (S-4800, Hitachi, 10kV) and an upright fluorescence microscopy (DMI6000 B, Leica).

**Part A:** This part describes the synthetic procedures and characterization data for copolymers (**P1** and **P2**) and the structural subunits (**D1**, **A1**, and **1**). 5-iodobenzene-1,3-diol,<sup>1</sup> 2-(4-bromobutoxy)benzaldehyde,<sup>2</sup> 2,5-diiodobenzen-1,4-diol,<sup>3</sup> and **S11**<sup>4</sup> were synthesized according to reported procedures. All other reagents and solvents were purchased from commercial sources and used without further purification. Air- and/or water-sensitive reactions were conducted under argon using dry solvents.

*Scheme S1.*





**1-iodo-3,5-bis(4-(2-formylphenoxy)butoxy)benzene (S1):** A mixture of 5-iodobenzene-1,3-diol (4.79 g, 20.3 mmol) and potassium carbonate (22.4 g, 162 mmol) in *N,N*-dimethylformamide (30 mL) was stirred at 70 °C for 1 hour, then, a solution of 2-(4-bromobutoxy)benzaldehyde (11.46 g, 44.6 mmol) in *N,N*-dimethylformamide (10 mL) was added to the solution with stirring. The resultant mixture was further stirred at 70 °C for 5 hours. After cooling to room temperature, the reaction was diluted with ether and washed with water, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was evaporated *in vacuo* and obtained liquid material was purified by column chromatography (SiO<sub>2</sub>; *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, from 1:1 to 0:1) to yield compound **S1** as light-yellow oily matter (9.07 g, 76%).

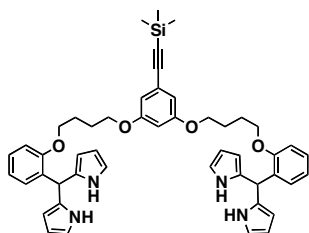
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  1.97–2.06 (m, 8H, –O–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>–CH<sub>2</sub>–O–), 3.99 (t, *J* = 6.0 Hz, 4H, –O–CH<sub>2</sub>–), 4.16 (t, *J* = 6.0 Hz, 4H, –O–CH<sub>2</sub>–), 6.38 (t, *J* = 2.1 Hz, 1H, 4-H of C<sub>6</sub>H<sub>3</sub>–I), 6.84 (d, *J* = 2.4 Hz, 2H, 2,6-H in C<sub>6</sub>H<sub>3</sub>–I), 6.98 (d, *J* = 8.4 Hz, 2H, 6-H in –C<sub>6</sub>H<sub>4</sub>–CHO), 7.03 (t, *J* = 7.5 Hz, 2H, 4-H in –C<sub>6</sub>H<sub>4</sub>–CHO), 7.54 (t, *J* = 7.8 Hz, 2H, 5-H in –C<sub>6</sub>H<sub>4</sub>–CHO), 7.84 (dd, *J* = 7.8, 1.8 Hz, 2H, 3-H of –C<sub>6</sub>H<sub>4</sub>–CHO), 10.51 (s, 2H, –CHO).

**1-(trimethylsilylethynyl)-3,5-bis(4-(2-formylphenoxy)butoxy)benzene (S2):** A mixture of **S1** (7.88 g, 13.4 mmol), dichlorobis(triphenylphosphine)palladium(II) (676 mg, 0.96 mmol), and copper iodide (92 mg, 0.48 mmol) in trimethylamine (55 mL) and tetrahydrofuran (25 mL) was stirred at 80 °C for 1.5 hours under argon atmosphere. Trimethylsilylacetylene (2.23 mL, 15.7 mmol) was then added to the solution with stirring and the resultant mixture was stirred at 80 °C for another 21 hours. After cooling to room temperature, the reaction was diluted with *n*-hexane and washed with water, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was evaporated *in vacuo* and obtained liquid material was purified by column chromatography (SiO<sub>2</sub>; *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>, from 3:7 to 0:1) to yield compound **S2** as yellow oily

matter (7.30 g, 97%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.24 (s, 9H,  $\text{SiMe}_3$ ), 1.96–2.07 [m, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 4.01 (t,  $J = 6.0$  Hz, 4H,  $-\text{O}-\text{CH}_2-$ ), 4.15 (t,  $J = 6.3$  Hz, 4H,  $-\text{O}-\text{CH}_2-$ ), 6.42 (t,  $J = 2.1$  Hz, 1H, 4-H in  $\text{C}_6\text{H}_3$ ), 6.61 (d,  $J = 2.4$  Hz, 2H, 2,6-H in  $\text{C}_6\text{H}_3$ ), 6.98 (d,  $J = 8.4$  Hz, 2H, 6-H in  $-\text{C}_6\text{H}_4-\text{CHO}$ ), 7.03 (t,  $J = 7.5$  Hz, 2H, 4-H in  $-\text{C}_6\text{H}_4-\text{CHO}$ ), 7.54 (t,  $J = 7.8$  Hz, 2H, 5-H in  $-\text{C}_6\text{H}_4-\text{CHO}$ ), 7.83 (dd,  $J = 7.8, 1.8$  Hz, 2H, 3-H in  $-\text{C}_6\text{H}_4-\text{CHO}$ ), 10.51 (s, 2H, Ar-CHO).

**Compound S3:** A mixture of 1,3-(4-(2-formylphenoxy)butoxy)-5-(trimethylsilyl)ethynyl)benzene

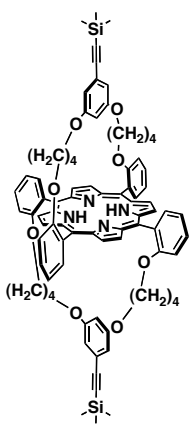


(**S2**) (5.00 g 8.9 mmol) and pyrrole (106 mL) was bubbled with argon for 2 hours. Trifluoroacetic acid (65  $\mu\text{L}$ ) was added to the solution with stirring under argon atmosphere and the mixture was stirred at room

temperature for 3 hours. The reaction was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with aqueous solution of NaOH (0.1 M) and brine, then, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removing  $\text{CH}_2\text{Cl}_2$  and pyrrole *in vacuo* at 90  $^\circ\text{C}$ , the crude product was purified by column chromatography ( $\text{SiO}_2$  washed with *n*-hexane containing 10% triethylamine, *n*-hexane/ $\text{CHCl}_3$ , from 1:1 to 1:4) to yield compound **S3** as a white solid (4.40 g, 62%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.24 (s, 9H,  $\text{SiMe}_3$ ), 1.70–1.84 [m, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 3.86 (t,  $J = 6.0$  Hz, 4H,  $-\text{O}-\text{CH}_2-$ ), 3.97 (t,  $J = 6.0$  Hz, 4H,  $-\text{O}-\text{CH}_2-$ ), 5.75 (s, 2H,  $\text{C}_4\text{H}_3\text{N}-\text{CH}-\text{C}_4\text{H}_3\text{N}$ ), 5.88 (m, 4H,  $-\text{C}_4\text{H}_3\text{N}-\text{H}$ ), 6.11–6.12 (m, 4H,  $-\text{C}_4\text{H}_3\text{N}-\text{H}$ ), 6.37 (t,  $J = 2.4$  Hz, 1H,  $\text{C}_6\text{H}_3$ ), 6.58 (d,  $J = 2.4$  Hz, 2H,  $\text{C}_6\text{H}_3$ ), 6.63–6.64 (m, 4H,  $-\text{C}_4\text{H}_3\text{N}-\text{H}$ ), 6.87–6.91 [m, 4H,  $-\text{C}_6\text{H}_4-\text{CH}(\text{C}_4\text{H}_3\text{N})_2$ ], 7.08 [dd,  $J = 7.8, 1.8$  Hz, 2H,  $-\text{C}_6\text{H}_4-\text{CH}(\text{C}_4\text{H}_3\text{N})_2$ ], 7.21 (t,  $J = 7.5$  Hz, 2H,  $-\text{C}_6\text{H}_4-\text{CHPy}_2$ ), 8.10 (br, 4H, N-H).

**Compound S4:** A mixture of **S2** (500 mg, 0.89 mmol) and **S3** (672 mg, 0.85 mmol) in  $\text{CHCl}_3$  (900

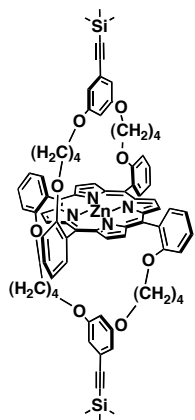


mL), EtOH (6.5 mL) was bubbled with argon for 3 hours. Boron trifluoride diethyl etherate (0.15 mL, 1.19 mmol) was added to the solution under argon atmosphere. After stirring for 3 hours at room temperature, chloranil (711 mg, 2.89 mmol) was added and the mixture was stirred for another 1.5 hours. After purification through flash column chromatography ( $\text{SiO}_2$ ;  $\text{CHCl}_3$ ) and column chromatography ( $\text{SiO}_2$ ; *n*-hexane/ $\text{CHCl}_3$ , from 1:3 to 1:4), compound **S4** was yielded as a purple solid (278 mg, 25%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  -2.58 (s, 2H, inner-NH), 0.15 (s, 18H,  $\text{SiMe}_3$ ), 0.80–0.85 [m, 8H, *meso*- $\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 1.05–1.09 [m, 8H, *meso*- $\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 2.64 [t,  $J = 6.3$  Hz, 8H, *meso*- $\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 3.92 [t,  $J = 5.7$  Hz, 8H, *meso*- $\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_2-\text{O}-$ ], 4.21 (t,  $J = 2.4$  Hz, 2H,  $\text{C}_6\text{H}_3$ ), 6.11 (d,  $J = 1.8$  Hz, 4H,

$C_6H_3$ ), 7.29–7.31 (m, 8H, *meso*- $C_6H_4$ ), 7.72 (t,  $J = 7.8$  Hz, 4H, *meso*- $C_6H_4$ ), 7.87 (dd,  $J = 7.2, 1.8$  Hz, 4H, *meso*- $C_6H_4$ ), 8.74 (s, 8H,  $\beta$ -pyrrole).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ , 298 K):  $\delta$  –0.12, 24.98, 25.22, 67.07, 68.08, 93.02, 101.87, 105.06, 110.42, 112.29, 115.67, 119.65, 123.39, 129.54, 131.82, 135.51, 158.89, 158.93. MALDI-TOF-MS (Matrix: dithranol): Found  $m/z = 1307.12$ , Calcd for  $[M]^+$  ( $C_{82}H_{82}N_4O_8Si_2$ ) = 1306.57.

**Compound A1:**  $Zn(AcO)_2 \cdot H_2O$  (2.35 g, 10.7 mmol) in methanol (70 mL) was added to a stirring solution of **S4** (700 mg, 0.53 mmol) in  $CHCl_3$  (340 mL) and the mixture was stirred overnight at room temperature. The reaction was washed with water, and the organic layer was dried over anhydrous  $Na_2SO_4$ . The organic solvents were removed *in vacuo* to dryness and the residue was purified by reprecipitation (methanol) to yield compound **A1** as a purple solid (682 mg, 93%).



M.p. 202.7–203.1 °C. Anal. Found: C, 70.36; H, 6.23; N, 4.06%. Calcd for  $C_{82}H_{80}N_4O_8Si_2Zn \cdot 2MeOH$ : C, 70.30; H, 6.18; N, 3.90%.  $^1H$  NMR ( $CDCl_3$ , 298 K):  $\delta$  0.14 (s, 18H,  $SiMe_3$ ), 0.68–0.73 [m, 8H, *meso*- $C_6H_4$ -O- $CH_2$ -( $CH_2$ ) $_2$ - $CH_2$ -O-], 1.09–1.14 [m, 8H, *meso*- $C_6H_4$ -O- $CH_2$ -( $CH_2$ ) $_2$ - $CH_2$ -O-], 2.54 [t,  $J = 6.9$  Hz, 8H, *meso*- $C_6H_4$ -O- $CH_2$ -( $CH_2$ ) $_2$ - $CH_2$ -O-], 3.92 (t,  $J = 2.1$  Hz, 2H, 4-H of  $C_6H_3$ ), 3.95 [t,  $J = 5.7$  Hz, 8H, *meso*- $C_6H_4$ -O- $CH_2$ -( $CH_2$ ) $_2$ - $CH_2$ -O-], 6.01 (d,  $J = 2.4$  Hz, 4H, 2,6-H of  $C_6H_3$ ), 7.27–7.32 (m, 8H, 4,6-H of *meso*- $C_6H_4$ ), 7.70 (t,  $J = 7.8$  Hz, 4H, 5-H of *meso*- $C_6H_4$ ), 7.83 (dd,  $J = 7.2, 1.8$  Hz, 4H, 3-H of *meso*- $C_6H_4$ ), 8.80 (s, 8H,  $\beta$ -pyrrole).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ , 298 K):  $\delta$  –0.12, 24.87, 25.07, 66.94, 68.20, 93.04, 101.34, 104.99, 110.15, 112.42, 116.43, 119.59, 123.37, 129.23, 131.28, 132.78, 135.50, 150.17, 158.67, 158.81. MALDI-TOF-MS (Matrix: dithranol): Found  $m/z = 1368.92$ , Calcd for  $[M]^+$  ( $C_{82}H_{80}N_4O_8Si_2Zn$ ) = 1368.48.

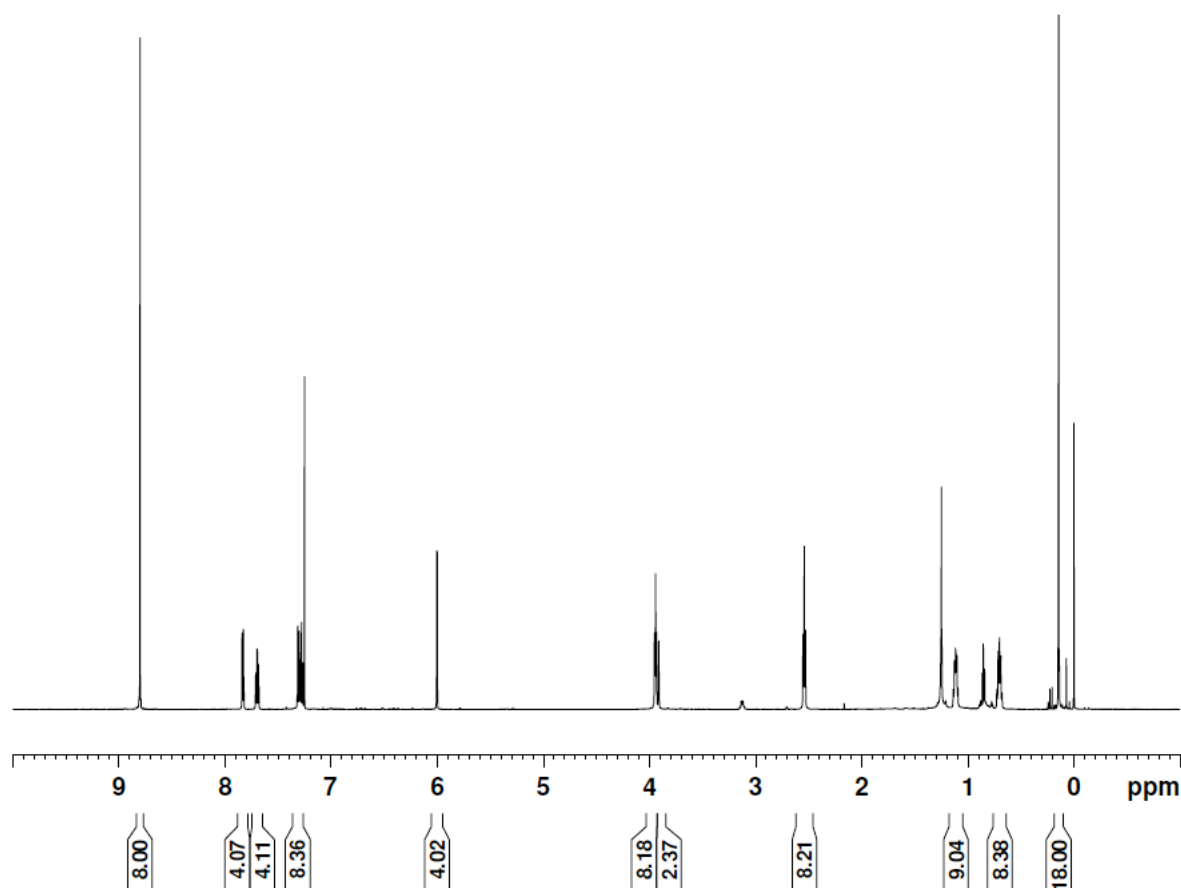
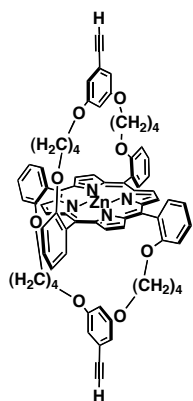


Figure S1.  $^1\text{H}$  NMR spectrum of **A1** in chloroform- $d_1$  at 298 K.

**Compound S5:** Tetra-*n*-butylammonium fluoride (1.0 M in tetrahydrofuran, 1.14 mL) was added to a stirring solution of **A1** (682 mg, 0.49 mmol) in tetrahydrofuran (10 mL) and the mixture was stirred at room temperature for 2.5 hours. The solvent was removed *in vacuo* to dryness and the residue was purified by column chromatography ( $\text{SiO}_2$ ; *n*-hexane/ $\text{CHCl}_3$ , from 3:7 to 1:9) to yield compound **S5** as a purple solid (557 g, 91%).



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.69–0.74 [m, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>2</sub>- $\text{CH}_2$ -O-], 1.10–1.15 [m, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>2</sub>- $\text{CH}_2$ -O-], 2.50 [t,  $J$  = 6.9 Hz, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>2</sub>- $\text{CH}_2$ -O-], 2.82 (s, 2H,  $\text{H}-\text{C}\equiv\text{C}-$ ), 3.92 (t,  $J$  = 2.4 Hz, 2H, 4-H in  $\text{C}_6\text{H}_3$ ), 3.95 [t,  $J$  = 5.7 Hz, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ )<sub>2</sub>- $\text{CH}_2$ -O-], 5.98 (d,  $J$  = 2.4 Hz, 4H, 2,6-H in  $\text{C}_6\text{H}_3$ ), 7.28 (t,  $J$  = 7.5 Hz, 8H, 4-H in *meso*- $\text{C}_6\text{H}_4$ ), 7.31 (d,  $J$  = 8.1 Hz, 8H, 6-H in *meso*- $\text{C}_6\text{H}_4$ ), 7.70 (t,  $J$  = 8.1 Hz, 4H, 5-H in *meso*- $\text{C}_6\text{H}_4$ ), 7.82 (dd,  $J$  = 7.5, 1.5 Hz, 4H, 3-H in *meso*- $\text{C}_6\text{H}_4$ ), 8.81 (s, 8H,  $\beta$ -pyrrole).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  24.87, 24.99, 66.95, 68.25, 76.14, 83.44, 101.26, 110.27, 112.48, 116.42, 119.59, 122.32, 129.26, 131.29, 132.77, 135.52, 150.16, 158.66, 158.75. MALDI-TOF-MS (Matrix: dithranol): Found  $m/z$  = 1224.91, Calcd for  $[\text{M}]^+$  ( $\text{C}_{76}\text{H}_{64}\text{N}_4\text{O}_8\text{Zn}$ ) = 1224.40.

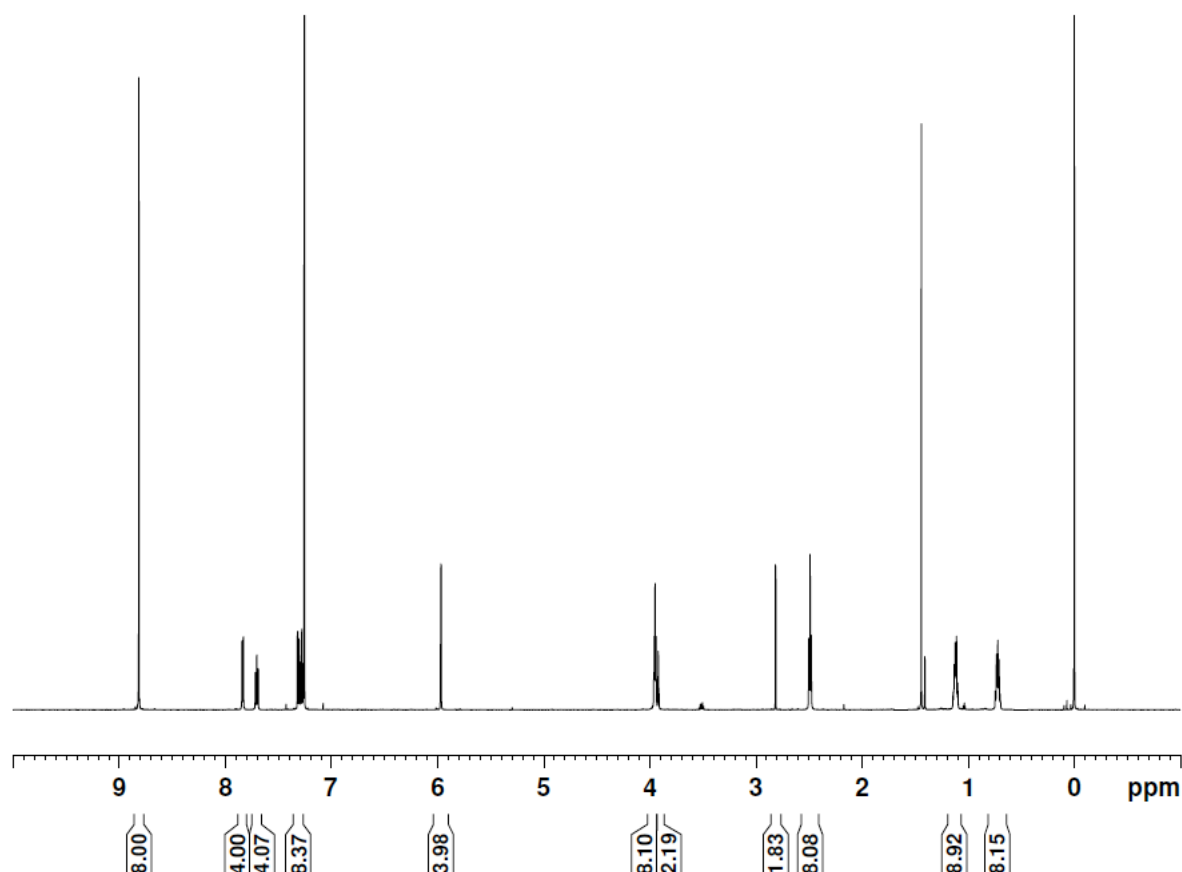


Figure S2.  $^1\text{H}$  NMR spectrum of **S5** in chloroform- $d_1$  at 298 K.

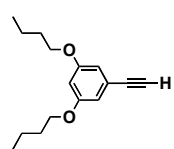
**1-iodo-3,5-dibutoxybenzene (S6):** A mixture of 5-iodobenzene-1,3-diol (0.44 g, 1.8 mmol) and potassium carbonate (2.08 g, 15.1 mmol) in *N,N*-dimethylformamide (3.8 mL) was stirred at 70 °C for 1.5 hour under argon atmosphere, and 1-bromobutane (0.61 mL, 5.6 mmol) was then added to the solution with stirring. The resultant mixture was stirred at 70 °C for 3 hours. After cooling to room temperature, the reaction solution was diluted with ether and washed with water, and then the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The filtrate was evaporated *in vacuo* and obtained liquid material was purified by column chromatography ( $\text{SiO}_2$ ; *n*-hexane/ $\text{CHCl}_3$ , from 1:0 to 0:1) to yield compound **S6** as colorless oily matter (524 mg, 80%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.96 [t,  $J$  = 7.2 Hz, 6H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.44–1.50 [m, 4H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.71–1.76 [m, 4H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 3.90 [t,  $J$  = 6.6 Hz, 4H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 6.39 (t,  $J$  = 2.1 Hz, 1H, 4-H in  $\text{C}_6\text{H}_3$ ), 6.83 (d,  $J$  = 1.8 Hz, 2H, 2,6-H in  $\text{C}_6\text{H}_3$ ).



**1-trimethylsilylethynyl-3,5-dibutoxybenzene (S7):** A mixture of **S6** (1.20 g, 3.4 mmol), dichlorobis(triphenylphosphine)palladium(II) (174 mg, 0.25 mmol), and copper iodide (23 mg, 0.12 mmol) in trimethylamine (17 mL) was stirred at 80 °C for an hour under argon atmosphere. Trimethylsilylacetylene (0.57 mL, 4.1 mmol) was then added to the solution with stirring and the resultant mixture was stirred at 80 °C for another 6 hours. After cooling to room temperature, the reaction solution was diluted with *n*-hexane and washed with water, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was evaporated *in vacuo* and obtained liquid material was purified by column chromatography (SiO<sub>2</sub>; *n*-hexane/CHCl<sub>3</sub>, from 1:0 to 8:1) to yield compound **S7** as colorless oily matter (1.03 g, 94%).

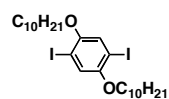
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 0.24 (s, 9H, -SiMe<sub>3</sub>), 0.96 [t, *J* = 7.2 Hz, 6H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 1.44–1.50 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 1.71–1.76 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 3.92 [t, *J* = 6.3 Hz, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 6.43 (t, *J* = 2.4 Hz, 1H, 4-H in C<sub>6</sub>H<sub>3</sub>), 6.59 (d, *J* = 1.8 Hz, 2H, 2,6-H in C<sub>6</sub>H<sub>3</sub>).



**1-ethynyl-3,5-dibutoxybenzene (S8):** A solution of **S7** (0.93 g, 2.9 mmol) in methanol (85 mL) was added to potassium carbonate (4.0 g, 29 mmol) and the mixture was stirred at 60 °C overnight. The reaction solution was diluted with *n*-hexane and washed with water, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed *in vacuo* to yield compound **S8** as colorless oily matter (687 mg, 96%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 0.97 [t, *J* = 7.5 Hz, 6H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 1.44–1.50 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 1.72–1.77 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 3.93 [t, *J* = 6.6 Hz, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>3</sub>], 6.46 (t, *J* = 2.4 Hz, 1H, 4-H in C<sub>6</sub>H<sub>3</sub>), 6.62 (d, *J* = 2.4 Hz, 2H, 2,6-H in C<sub>6</sub>H<sub>3</sub>).

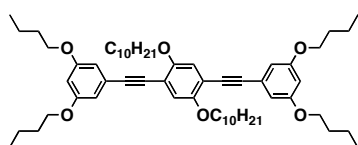
**1,4-didecyloxy-2,5-diiodobenzene (S9):** A mixture of 1,4-diiodo-2,5-benzenediol (1.00 g, 2.7 mmol) and potassium carbonate (3.06 g, 22.1 mmol) in *N,N*-dimethylformamide (5.5 mL) was stirred at 70 °C for 1.5 hour under argon atmosphere, and 1-bromodecane (1.83 g, 8.3 mmol) was then added to the solution with stirring. The resultant mixture was stirred at 70 °C for 6 hours. After cooling to room temperature, the reaction solution was diluted with ether and washed with water, and then the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was evaporated *in vacuo* and obtained liquid material was purified by column chromatography (SiO<sub>2</sub>; *n*-hexane/CHCl<sub>3</sub>, from 1:0 to 4:1) to yield compound **S6** as colorless oily matter (1.56 g, 88%).



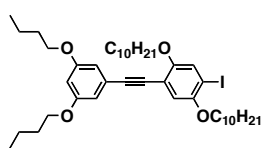
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 0.88 [t, *J* = 6.9 Hz, 6H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub>], 1.25–1.38 [m, 24H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub>], 1.47–1.51 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub>], 1.77–1.82 [m, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub>], 3.92 [t, *J* = 6.6 Hz, 4H, -O-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>8</sub>-CH<sub>3</sub>], 7.17 (s, 2H, 3,6-H in C<sub>6</sub>H<sub>2</sub>).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  14.13, 22.68, 26.02, 29.13, 29.27, 29.32, 29.54, 29.55, 31.90, 70.34, 86.28, 122.75, 152.83.

**Compound D1 and S10:** A mixture of **S9** (500 mg, 0.78 mmol), dichlorobis(triphenylphosphine)palladium(II) (39 mg, 0.05 mmol), and copper iodide (5 mg, 0.02 mmol) in trimethylamine (4 mL) was stirred at 80 °C for an hour under argon atmosphere. Compound **S8** (0.25 mL, 1.0 mmol) was then added to the solution with stirring and the resultant mixture was stirred at 80 °C overnight. After cooling to room temperature, the reaction solution was diluted with *n*-hexane and washed with water, and then the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography ( $\text{SiO}_2$ ; *n*-hexane/ $\text{CH}_2\text{Cl}_2$ , from 9:1 to 7:3) to yield compound **D1** (143 mg, 21%) and **S10** (278 mg, 47%) as white solids.



**D1:** M.p. 72.4–72.8 °C. Anal. Found: C, 79.17; H, 10.13. Calcd for  $\text{C}_{58}\text{H}_{86}\text{O}_6$ : C, 79.22; H, 9.86%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.87 [t,  $J$  = 6.9 Hz, 6H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 0.98 [t,  $J$  = 7.5 Hz, 12H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.20–1.55 [m, 36H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.74–1.78 [m, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.82–1.86 [m, 4H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 3.95 [t,  $J$  = 6.6 Hz, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 4.02 [t,  $J$  = 6.3 Hz, 4H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 6.45 (t,  $J$  = 2.4 Hz, 2H,  $\text{C}_6\text{H}_3$ ), 6.67 (d,  $J$  = 1.8 Hz, 4H,  $\text{C}_6\text{H}_3$ ), 7.00 (s, 2H,  $\text{C}_6\text{H}_2$ ).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  13.83, 14.10, 19.23, 22.67, 26.05, 29.33, 29.43, 29.60, 29.65, 31.25, 31.90, 67.81, 69.63, 85.26, 95.05, 102.76, 109.79, 113.93, 117.03, 124.50, 153.65, 160.00. MALDI-TOF-MS (Matrix: dithranol): Found  $m/z$  = 878.92, Calcd for  $[\text{M}]^+$  ( $\text{C}_{58}\text{H}_{86}\text{O}_6$ ) = 878.64.



**S10:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.85–0.89 [m, 6H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 0.96–0.99 [m, 6H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ], 1.20–1.55 [m, 32H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 1.72–1.85 [m, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 3.92–4.00 [m, 8H,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3$ ,  $-\text{O}-\text{CH}_2-(\text{CH}_2)_8-\text{CH}_3$ ], 6.45 (t,  $J$  = 2.4 Hz, 1H,  $\text{C}_6\text{H}_3$ ), 6.66 (d,  $J$  = 2.4 Hz, 2H,  $\text{C}_6\text{H}_3$ ), 6.90 (s, 1H,  $\text{C}_6\text{H}_2-\text{I}$ ), 7.30 (s, 1H,  $\text{C}_6\text{H}_2-\text{I}$ ). MALDI-TOF-MS (Matrix: dithranol): Found  $m/z$  = 634.89, Calcd for  $[\text{M}-\text{I}+\text{H}]^+$  ( $\text{C}_{42}\text{H}_{66}\text{O}_4$ ) = 634.50.

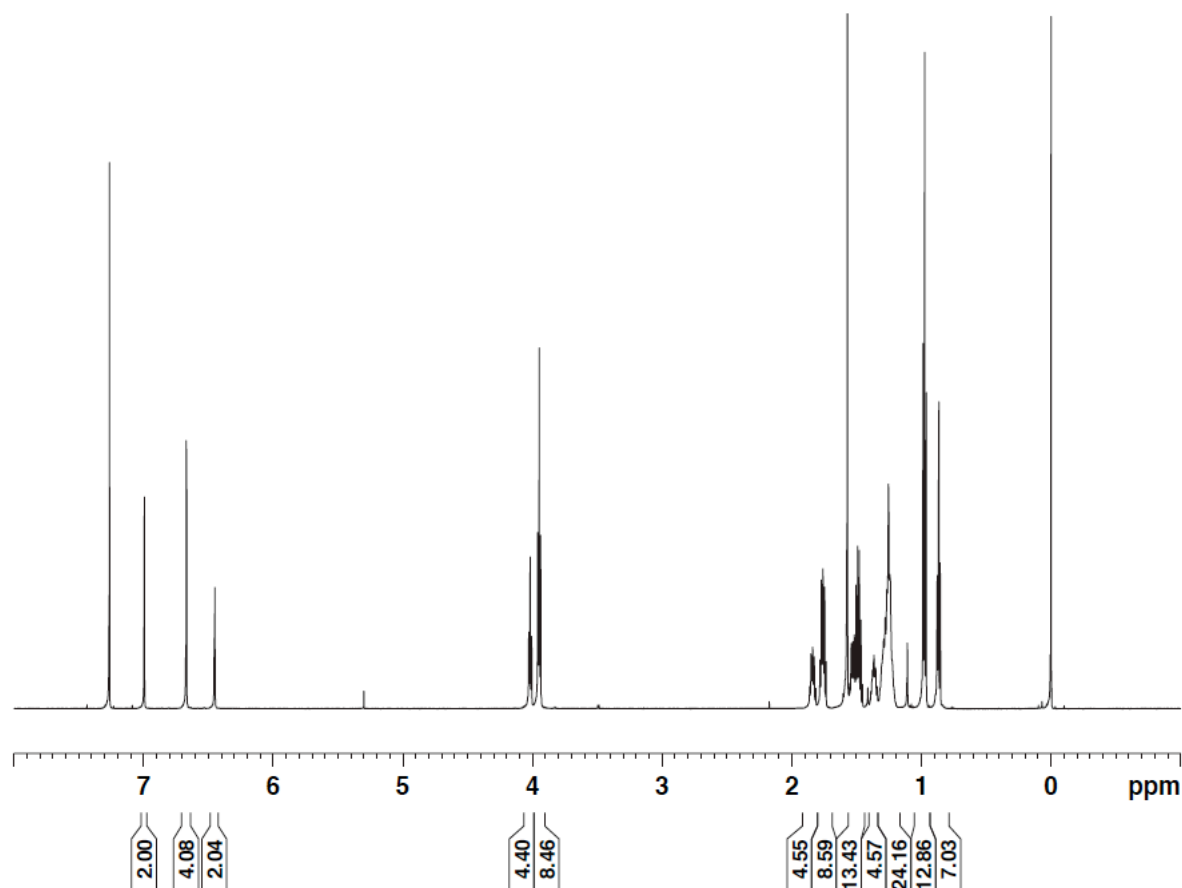
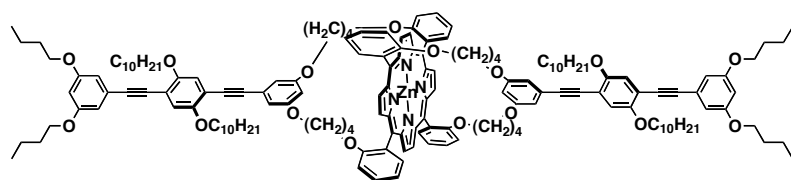


Figure S3.  $^1\text{H}$  NMR spectrum of **1D** in chloroform- $d_1$  at 298 K.

**Compound 1:** A mixture of **S5** (52.0 mg, 42  $\mu\text{mol}$ ), **S10** (77.4 mg, 102  $\mu\text{mol}$ ),



tetrakis(triphenylphosphine) palladium (0) (2.3 mg, 2  $\mu\text{mol}$ ), and copper iodide (0.4 mg, 2  $\mu\text{mol}$ ) in dehydrated toluene (2.0 mL) was

stirred at 70  $^{\circ}\text{C}$  for an hour under argon atmosphere. Redistilled diisopropylamine (0.5 mL) was then added to the solution and the resultant mixture was stirred at 70  $^{\circ}\text{C}$  for 8 hours. After cooling to room temperature, methanol was added to the solution with stirring. Insoluble matter was separated by filtration and purified by column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2$ ) and SEC (bio-beads S-X1,  $\text{CH}_2\text{Cl}_2$ ,  $\phi$  22 mm  $\times$  100 cm) to yield compound **1** (35 mg, 34%) as a purple solid.

M.p. 75.6–76.0  $^{\circ}\text{C}$ . Anal. Found: C, 76.85; H, 7.89; N, 2.34%. Calcd for  $\text{C}_{160}\text{H}_{192}\text{N}_4\text{O}_{16}\text{Zn}$ : C, 77.09; H, 7.76; N, 2.25%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.71–0.76 [m, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_2$ -O-], 0.82–0.86 [m, 12H, -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_8$ - $\text{CH}_3$ ], 0.96 [t,  $J$  = 7.5 Hz, 12H, -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_3$ ], 1.11–1.52 [m, 72H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_2$ -O-, -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_8$ - $\text{CH}_3$ , -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_3$ ], 1.71–1.82 [m, 16H, -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_3$ , -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_8$ - $\text{CH}_3$ ], 2.56 [t,  $J$  = 6.6 Hz, 8H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_2$ -O-], 3.91–3.97 [m, 24H, *meso*- $\text{C}_6\text{H}_4$ -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_2$ -O-, -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_8$ - $\text{CH}_3$ , -O- $\text{CH}_2$ -( $\text{CH}_2$ ) $_2$ - $\text{CH}_3$ ,

$C_6H_3]$ , 6.08 (d,  $J = 2.4$  Hz, 4H,  $C_6H_3$ ), 6.43 (t,  $J = 2.4$  Hz, 2H,  $C_6H_3$ ), 6.64 (d,  $J = 2.4$  Hz, 4H,  $C_6H_3$ ), 6.87 (s, 2H,  $\equiv C-C_6H_2-C\equiv$ ), 6.93 (s, 2H,  $\equiv C-C_6H_2-C\equiv$ ), 7.28–7.33 (m, 8H, *meso*- $C_6H_4$ ), 7.70 (t,  $J = 7.5$  Hz, 4H, *meso*- $C_6H_4$ ), 7.87 (dd,  $J = 7.2, 1.8$  Hz, 4H, *meso*- $C_6H_4$ ), 8.83 (s, 8H,  $\beta$ -pyrrole).  $^{13}C$  NMR ( $CDCl_3$ , 298 K):  $\delta$  13.81, 14.10, 19.21, 22.64, 24.30, 25.06, 25.91, 26.02, 29.21, 29.27, 29.31, 29.40, 29.54, 29.58, 29.62, 31.23, 31.87, 66.94, 67.79, 68.25, 69.53, 69.58, 85.00, 85.25, 94.80, 94.98, 100.93, 102.73, 109.77, 109.81, 112.46, 113.80, 113.93, 116.49, 116.98, 119.64, 123.73, 124.49, 129.26, 131.31, 132.78, 135.52, 150.20, 153.52, 153.57, 158.74, 158.79, 159.98. MALDI-TOF-MS (Matrix: dithranol): Found  $m/z = 2489.64$ , Calcd for  $[M]^+$  ( $C_{160}H_{192}N_4O_{16}Zn$ ) = 2489.36.

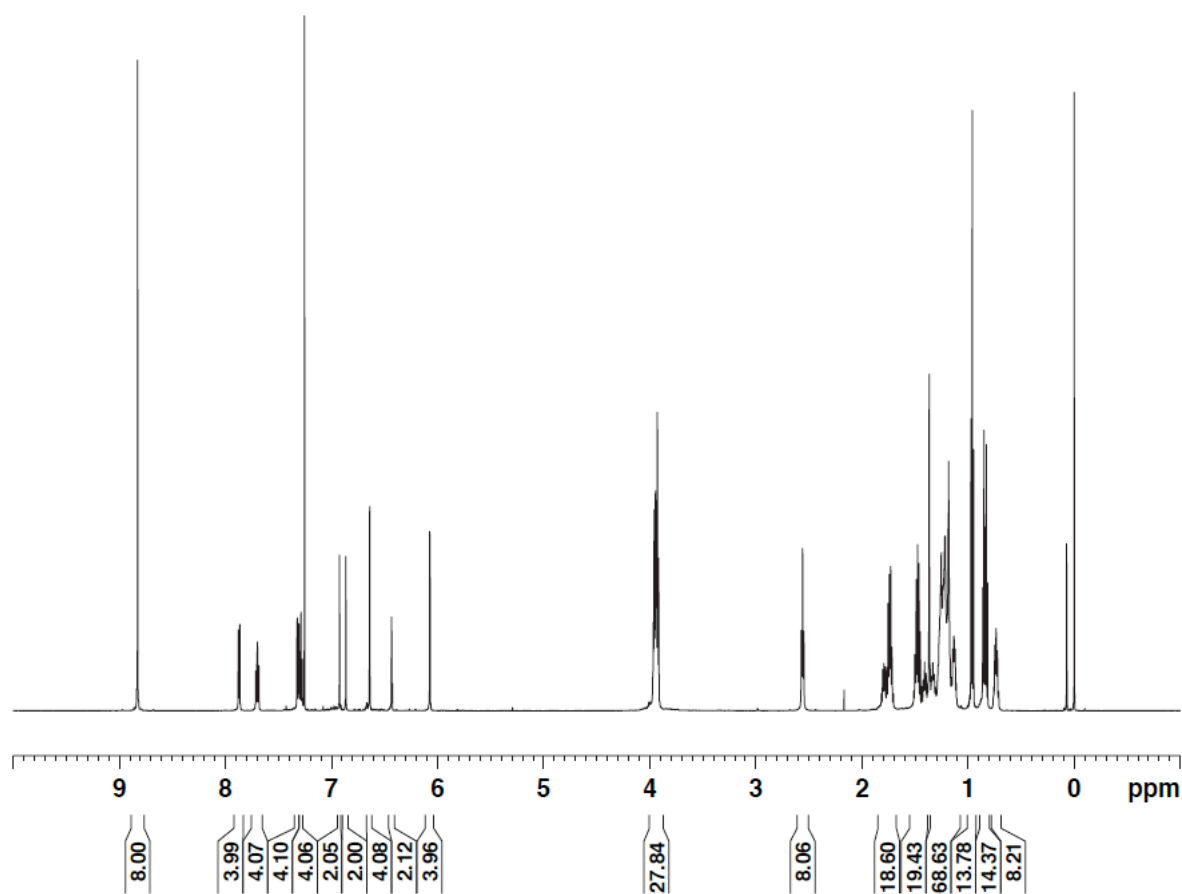
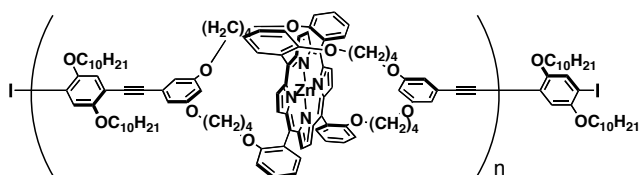


Figure S4.  $^1H$  NMR spectrum of **1** in chloroform- $d_1$  at 298 K.

**P1:** A Schlenk flask was charged with **S5** (100.0 mg, 81.5  $\mu$ mol), **S9** (52.4 mg, 81.6  $\mu$ mol), copper(I)iodide (0.7 mg, 3.8  $\mu$ mol), and tetrakis(triphenylphosphine)palladium (0) (4.8 mg, 4.1  $\mu$ mol). The flask was vacuumed and back-filled with argon. Dehydrated toluene (2.2 mL) was added by syringe and the mixture was heated at 70  $^\circ$ C for an hour under argon atmosphere. Redistilled diisopropylamine (0.5 mL) was added by syringe, and the mixture was stirred at 70  $^\circ$ C

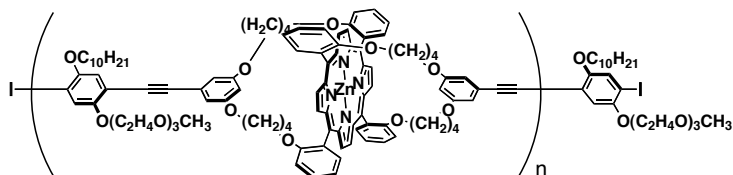


for 3 days. A solution of **S9** (26.2 mg, 40.9  $\mu\text{mol}$ ) in dry toluene dehydrated (0.5 mL) and diisopropylamine redistilled (0.1 mL) was added to the reaction, and the mixture was stirred at 70 °C overnight. The generated polymer was precipitated in methanol, filtered, and rinsed with water and methanol (113 mg, 86%,  $M_w/M_n > 2.0$ ). The polymer was purified through gel permeation chromatography (GPC, JAIGEL 2.5H + JAIGEL 3H,  $\text{CHCl}_3$ ) to remove the low molecular weight fraction. A purple solid was obtained with number average molecular weight  $M_n = 61.7\text{K}$  (12 mg, 9%,  $M_w/M_n = 1.31$ ) and 25.8K (46 mg, 35%,  $M_w/M_n = 1.18$ ) estimated by comparison with polystyrene standard.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.60–0.90 [br m, 14H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ], 1.10–1.50 [br m, 32H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ], 1.60–1.80 [br m, 8H,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ], 2.53 [br, 8H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ], 3.80–4.00 [br m, 14H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ,  $\text{C}_6\text{H}_3$ ], 6.04 (br, 4H,  $\text{C}_6\text{H}_3$ ), 6.78 (br, 2H,  $\equiv\text{C--C}_6\text{H}_2\text{--C}\equiv$ ), 7.26–7.30 (br m, 8H, *meso*- $\text{C}_6\text{H}_4$ ), 7.67 (br, 4H, *meso*- $\text{C}_6\text{H}_4$ ), 7.85 (br, 4H, *meso*- $\text{C}_6\text{H}_4$ ), 8.80 (s, 8H,  $\beta$ -pyrrole).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  14.08, 22.62, 24.90, 25.07, 25.87, 29.18, 29.24, 29.28, 29.51, 29.69, 31.84, 66.95, 68.27, 69.53, 84.97, 94.72, 100.96, 109.83, 112.49, 113.84, 116.46, 117.01, 119.64, 123.73, 129.25, 131.29, 132.82, 135.51, 150.20, 153.47, 158.73, 158.80.

**P2:** The same procedure for the synthesis of **P1** was applied using **S5** and **S11** as starting materials.



The obtained solid material was purified through gel permeation chromatography (GPC, JAIGEL 2.5H + JAIGEL 3H,  $\text{CHCl}_3$ ) to yield **P2** with number average

molecular weight  $M_n = 40.9\text{K}$  ( $M_w/M_n = 1.39$ ) estimated by comparison with polystyrene standard.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  0.70–0.90 [m, 11H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ], 1.10–1.80 [m, 24H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ], 2.55 (m, 8H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ), 2.65–3.80 (m, 13H,  $\text{--O--(CH}_2)_2\text{--O--(CH}_2)_2\text{--O--(CH}_2)_2\text{--O--CH}_3$ ), 3.85–4.10 (m, 14H, *meso*- $\text{C}_6\text{H}_4\text{--O--CH}_2\text{--(CH}_2)_2\text{--CH}_2\text{--O--}$ ,  $\text{--O--(CH}_2)_2\text{--O--(CH}_2)_2\text{--O--(CH}_2)_2\text{--O--CH}_3$ ,  $\text{--O--CH}_2\text{--(CH}_2)_8\text{--CH}_3$ ,  $\text{C}_6\text{H}_3$ ), 6.04 (br, 4H,  $\text{C}_6\text{H}_3$ ), 6.80 (br, 2H,  $\equiv\text{C--C}_6\text{H}_2\text{--C}\equiv$ ), 7.24–7.28 (m, 8H, *meso*- $\text{C}_6\text{H}_4$ ), 7.67 (m, 4H, *meso*- $\text{C}_6\text{H}_4$ ), 7.86 (m, 4H, *meso*- $\text{C}_6\text{H}_4$ ), 8.79 (s, 8H,  $\beta$ -pyrrole).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta$  14.07, 22.61, 24.83, 25.09, 25.86, 29.15, 29.23, 29.27, 29.50, 29.69, 31.84, 66.95, 67.02, 68.12, 68.26, 69.49, 69.58, 70.08, 70.28, 70.89, 71.00, 109.84, 112.35, 116.42, 119.60, 123.63, 129.24, 131.27, 132.78, 135.51, 150.19, 158.80.

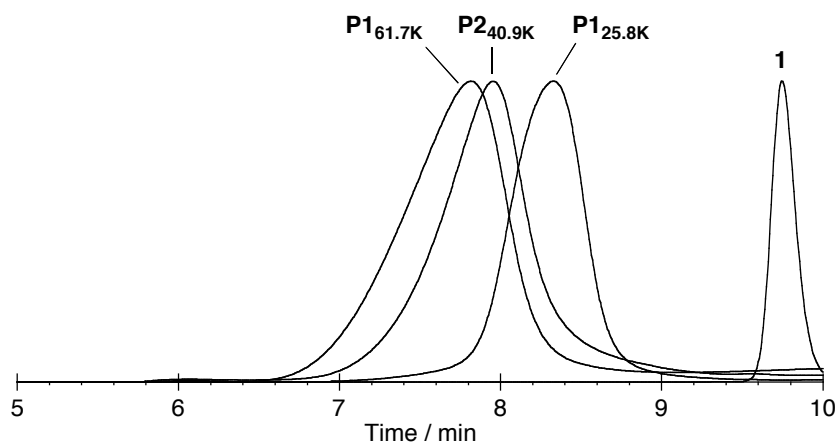


Figure S5. GPC chromatogram of **P1**, **P2**, and **1**.

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**Part B:** This part describes the photophysical properties of copolymer **P1** and the structural subunits (**D1**, **A1**, and **1**) in toluene solution.

*Table S1.* Photophysical parameters of **D1**, **A1**, and **1** in toluene.

Compound	Absorption		Emission		
	$\lambda_{\max}$ [nm] (log( $\epsilon$ ))	log( $\epsilon_{375}$ )	$\lambda_{\max}$ [nm]	$\Phi_f$ [%] <sup>a</sup>	$\tau$ [ns] ( $\lambda_{\text{moni}}$ [nm])
<b>D1</b>	369 (4.56)	4.53	402	86	1.28 (430)
<b>A1</b>	426 (5.68), 552 (4.35)	3.90	601, 652	4	2.47 (650)
<b>1</b>	367 (4.93), 426 (5.68), 552 (4.35)	4.90	601, 652	–	< 0.05 <sup>b</sup> (430), 2.54 (650)

<sup>a</sup>Benzene solution of 2,5':2',5'':2'',5'''-quaterthiophene ( $\Phi = 0.18$ ) was used as the standard. <sup>b</sup>Shorter than instrumental limitations.

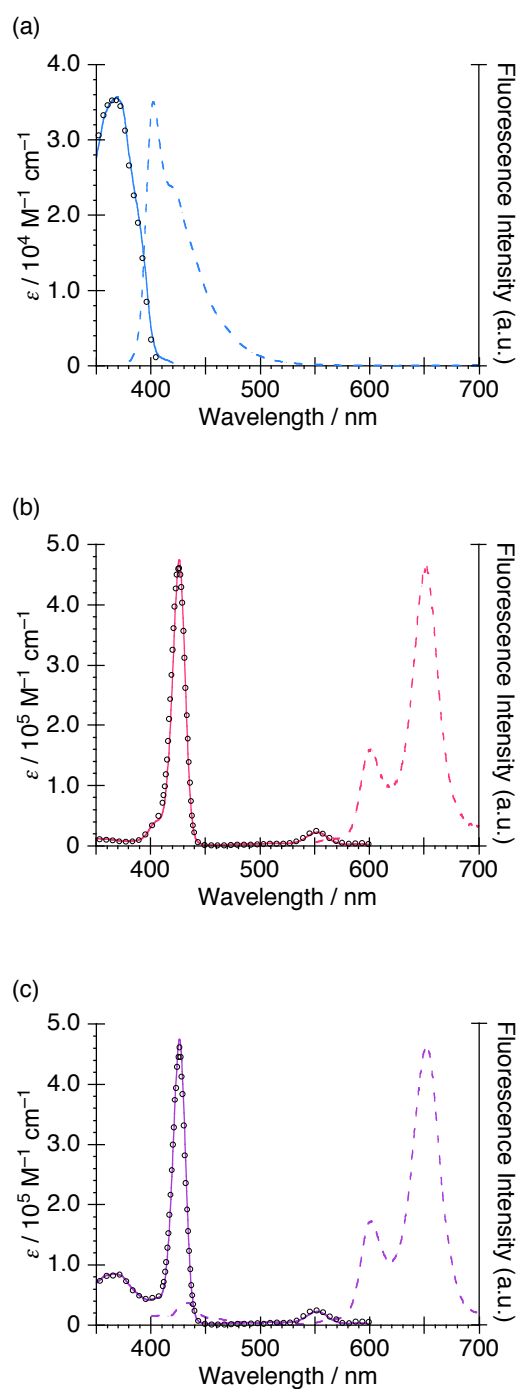


Figure S6. Absorption (solid line), fluorescence (dash line), and corrected fluorescence excitation ( $\circ$ ) spectra of **D1** (a), **A1** (b), and **1** (c) in toluene:  $[\mathbf{D1}] = 2.0 \times 10^{-6} \text{ M}$ .  $[\mathbf{A1}] = [\mathbf{1}] = 0.5 \times 10^{-6} \text{ M}$ ;  $\lambda_{\text{ex}} = 375 \text{ nm}$  (for **D1**) and  $425 \text{ nm}$  (for **A1** and **1**);  $\lambda_{\text{moni}} = 410 \text{ nm}$  (for **D1**) and  $650 \text{ nm}$  (for **A1** and **1**); RT.



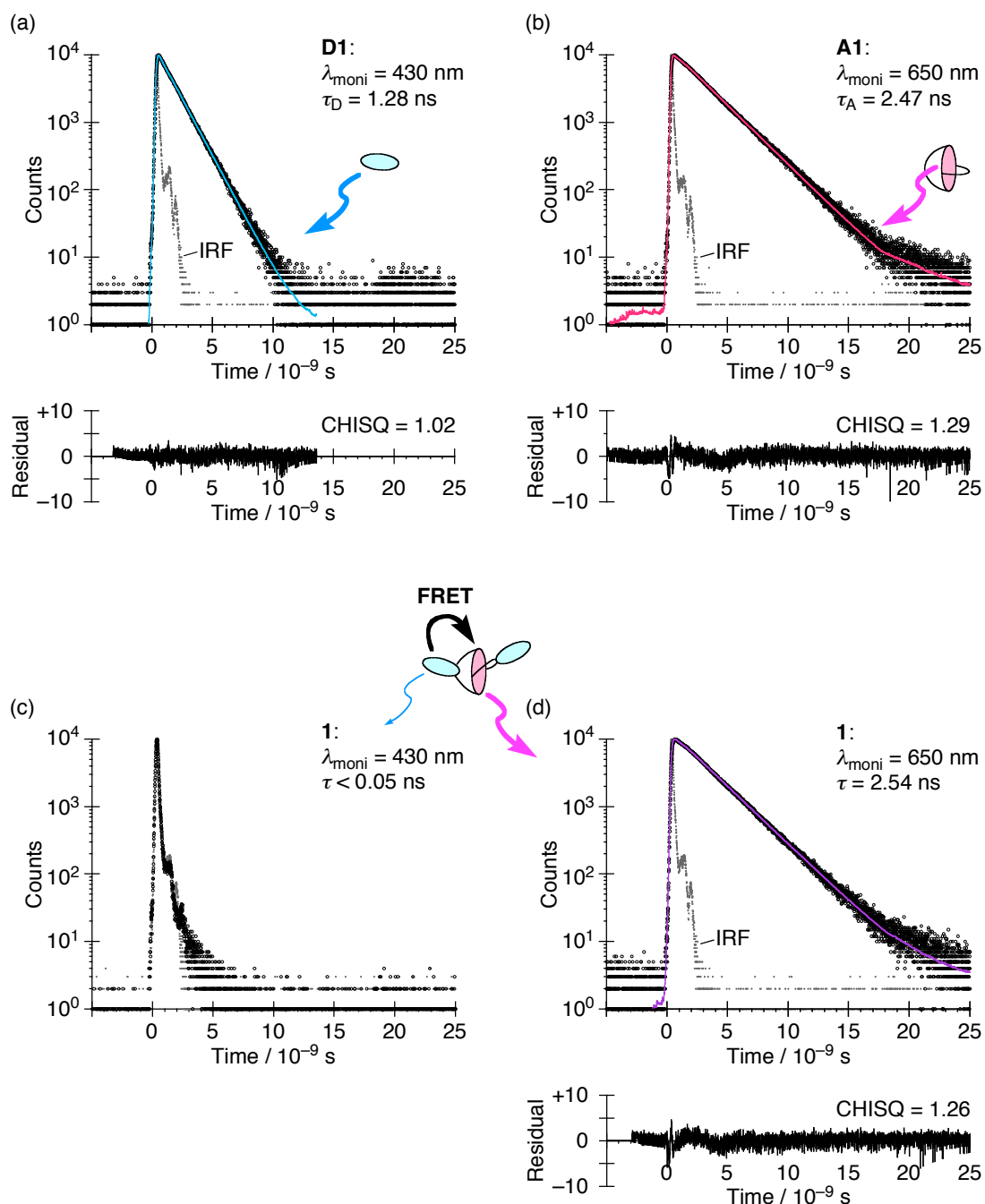


Figure S7. Time-resolved fluorescence decays of (a) D1, (b) A1, (c, d) 1 in toluene at room temperature obtained with excitation at 375 nm and detection at 430 or 650 nm as indicated in the figure.

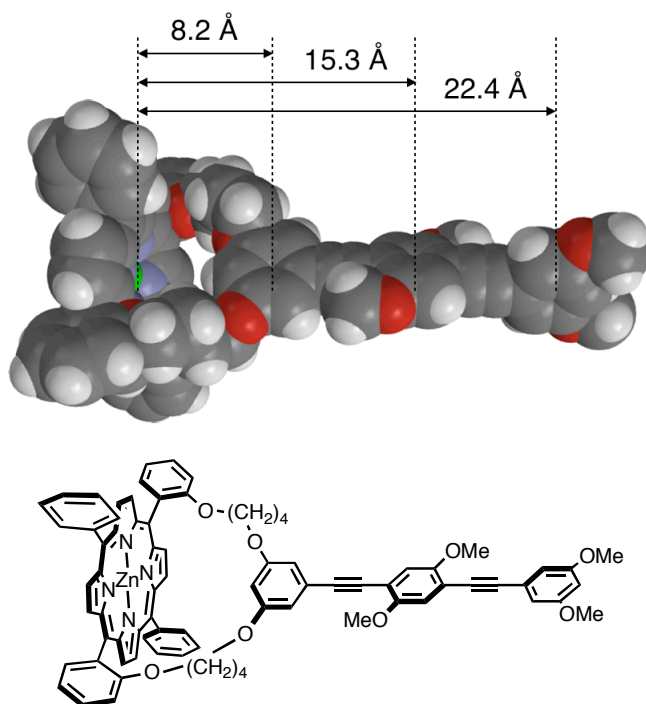


Figure S8. A computer-generated partial molecular model and the corresponding chemical structure for **1** and **P1**.

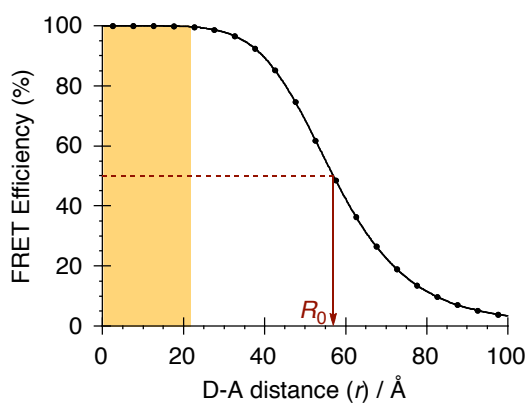
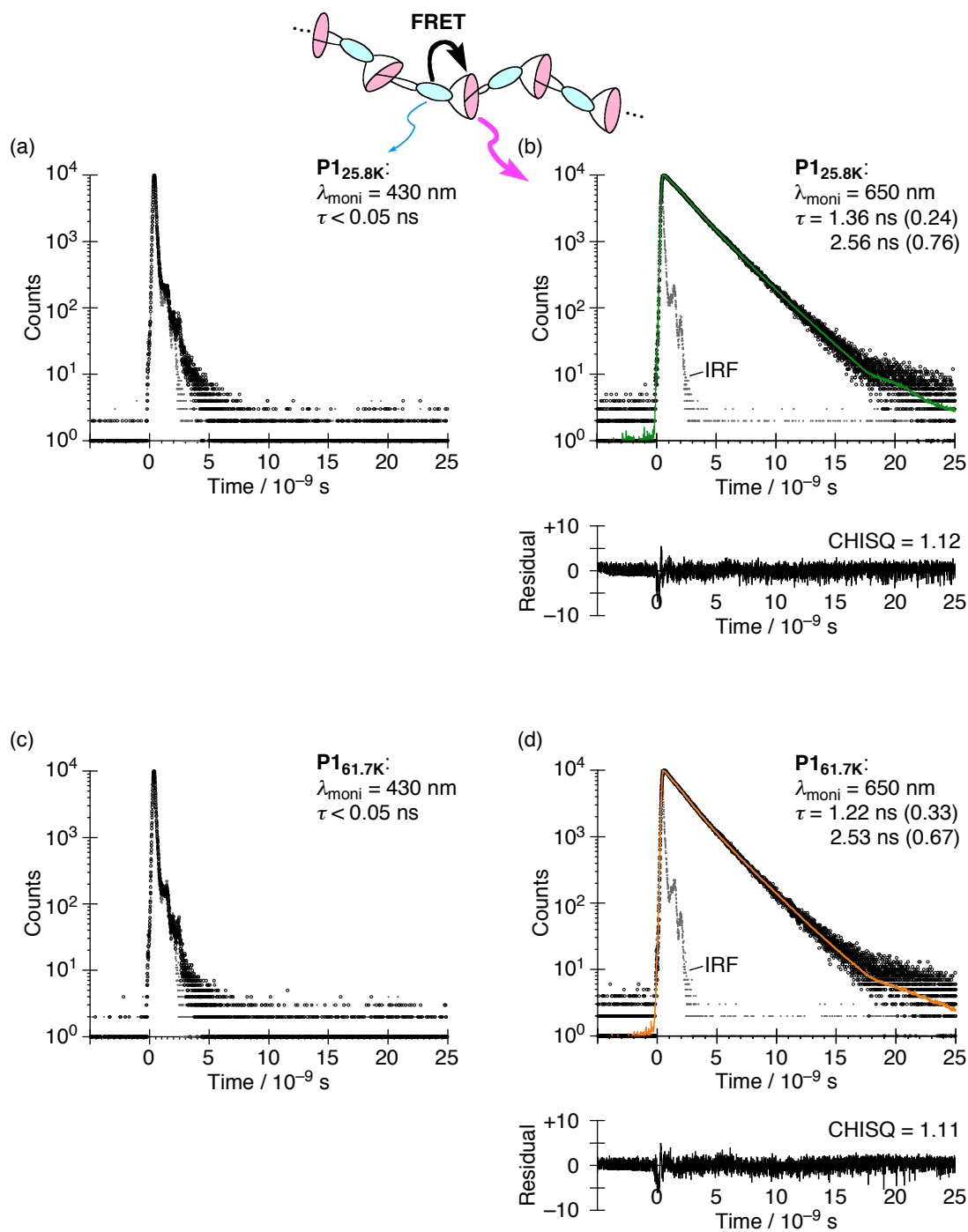


Figure S9. The relationship between the energy-transfer efficiency ( $E$ ) and the distance between the donor and acceptor molecules ( $r$ ) for **1** obtained from eq S1,

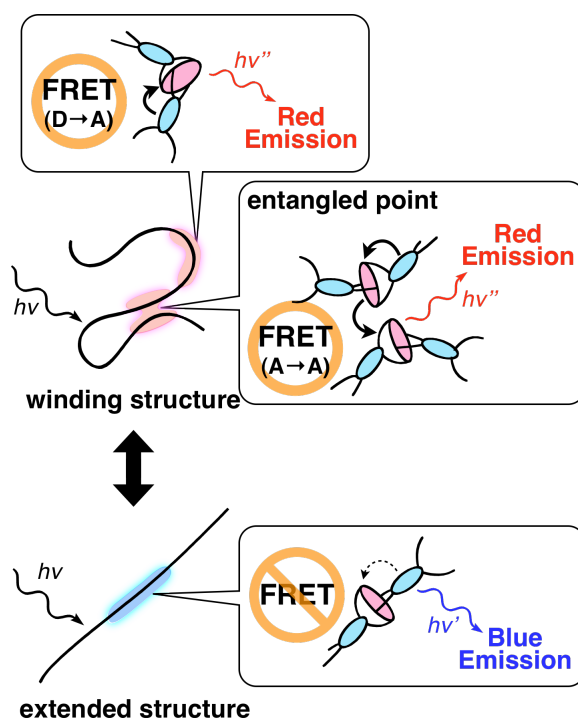
$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (\text{S1})$$

where Förster distance ( $R_0$ ) is 57.0 Å as described in the text.

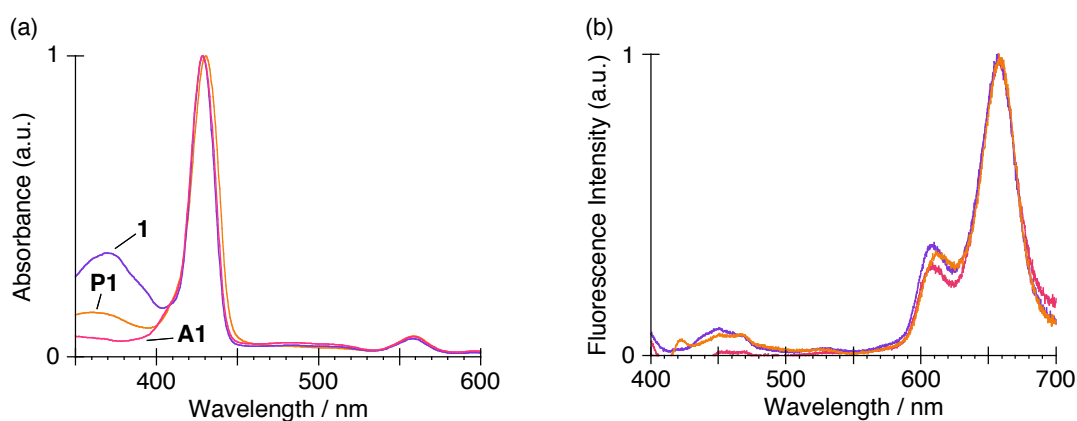


*Figure S10.* Time-resolved fluorescence decays of (a, b) **P1<sub>61.7K</sub>**, (c, d) **P1<sub>25.8K</sub>** in toluene at room temperature obtained with excitation at 375 nm and detection at 430 or 650 nm as indicated in the figure.

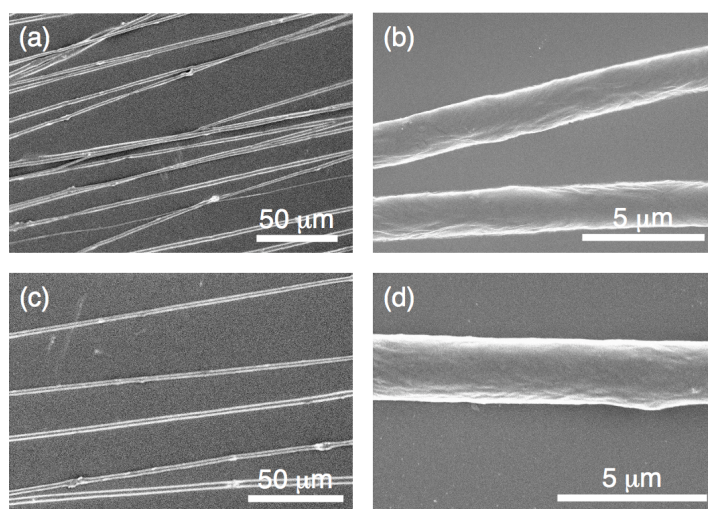
**Part C:** This part describes the photophysical properties of the composite materials, in which the copolymer **P1** was incorporated into a polymeric matrix.



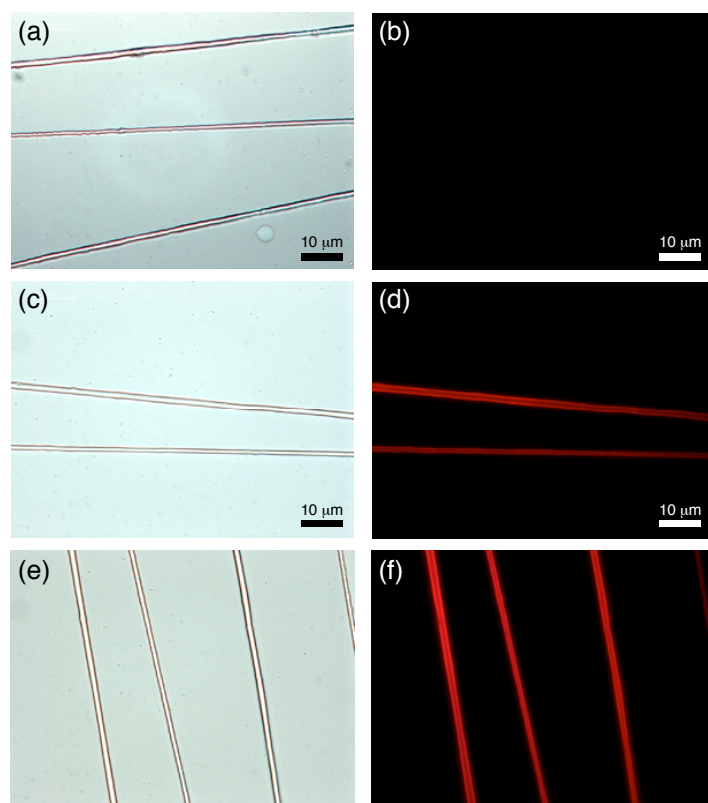
*Figure S11.* Schematic illustration of examples of the positional relationship between the donor and acceptor units on a copolymer backbone and corresponding energy transfer properties.



*Figure S12.* (a) Absorption and (b) fluorescence spectra of **1** (purple line), **A1** (pink line), and **P1<sub>61.7K</sub>** (orange line) in film state. Each film sample was prepared from a chloroform solution of the compound and polyethylene oxide (PEO) through spin coating method at a speed of 3000 rpm. The content of each compound is 6.2 wt% in the film.



*Figure S13.* SEM images for (a, b) PEO nanofibers and (c, d) **P1<sub>61.7K</sub>**/PEO nanofibers obtained from viscous chloroform solutions through electrospinning method (**P1<sub>61.7K</sub>** content: 6.2 wt%). Each solution was pumped through a metal syringe needle at a constant rate of 0.01 mL hour<sup>-1</sup> by a syringe pump. Application of a high voltage (30 kV) to the metal syringe needle allowed generation of microfibers, which were collected on the surface of a grass substrate attached to a rotating disk collector at a distance of 20 cm from the syringe needle. Both of nanofibers have smooth surfaces with diameters of about 2.5 μm.



*Figure S14.* (a, c, e) Optical and (b, d, f) fluorescence microscopic images of **P1<sub>61.7K</sub>**/PEO microfibers with different **P1<sub>61.7K</sub>** contents. The **P1<sub>61.7K</sub>** content is 0 wt% (a, b), 6.2 wt% (c, d), and 12.5 wt% (e, f) in the fibers.