

Supporting Information

Facile Construction of Metallo-supramolecular Poly(3-hexylthiophene)-*block*-Poly(ethylene oxide) Diblock Copolymers via Complementary Coordination and Their Self-Assembled Nanostructures

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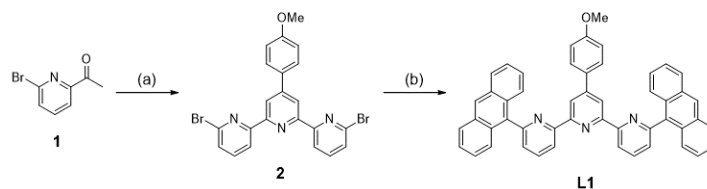
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1. General Information

Materials and General Methods. Unless otherwise noted, reagents and solvents were used as received from Fisher Scientific and Sigma-Aldrich without further purification. 2,2':6',2''-Terpyridine (**L2**),¹ 4'-(4-boronophenyl)-2,2':6',2''-terpyridine,² tosylated PEOME, tosylated PEG,³ tetrakis(triethylammonium) EDTA,⁴ 2,5-dibromo-3-hexylthiophene,⁵ and 2-acetyl-6-bromo-pyridine (**1**)⁶ were prepared according to the reported procedures. Column chromatography was conducted using silica gel (75-200 μm) from Fuji Silysia or basic Al_2O_3 (50-200 μm) from Acros. ^1H and ^{13}C NMR spectra were recorded at 25 $^\circ\text{C}$ on a Varian Mercury NMR 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to the nondeuterated solvents as a reference. Gel permeation chromatography (GPC) was conducted on the instrument equipped with two columns (Shodex KF-803 and KF-804), a Waters 515 HPLC pump, and a differential refractive index detector (LabAlliance RI2000), and the calibration curve was established by linear polystyrene standards. UV-vis absorption and photoluminescence spectra were recorded on JASCO V-650 and JASCO FP-8300, respectively. Photoluminescence spectra were collected using an excitation wavelength of 448 nm. Atomic force microscopy (AFM) was conducted on a Bruker Dimension Icon AFM system with ScanAsyst mode and the data were processed by NanoScope Analysis version 1.5 (Bruker Software, Inc.). Raman measurements were carried out using a Renishaw InVia Raman (UK) microscope with a Peltier cooled CCD detector and an excitation wavelength at 633 nm, where the laser beam used to excite the sample is directed to the sample through a 20 \times objective. The maximum laser power was measured to be 6.2 mW and the exposure time was set at 10s throughout the measurements. AFM samples were prepared by spin-coating (3000 rpm for 1 min) a sample solution (0.03 mg/mL) on a silicon wafer washed by piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 3:1$, v/v). Samples for Raman measurements were prepared by spin-coating (3000 rpm for 1 min) a sample solution (0.03 mg/mL) on a gold coated silicon wafer. Transmission electron microscope (TEM) images were recorded on a Hitachi Model H-7650 microscope operated at 120 kV. TEM samples were prepared by drop-casting a sample solution (0.03 mg/mL) onto a carbon-coated copper grid and dried *in vacuo* for 24 h. FTIR spectra were collected on a Thermo Scientific Nicolet iS5 spectrometer. FTIR samples were prepared by drop-casting a sample solution (1 mg/mL in CHCl_3) onto a KBr plate.

Solution Preparation for Nanostructure Studies. To a solution of diblock copolymers in CHCl_3 (0.5 mL, 6 mg/mL) which is filtered with a PTFE syringe filter (0.22 μm), MeOH (0.5 mL) was added slowly. The solution was allowed to age for 3 days at room temperature.

2. Synthesis and Characterization of L1.



Scheme S1. Synthesis of **L1**. *Reagents and conditions:* (a) 1) *p*-anisaldehyde, NaOH, EtOH, 25 °C, 2) NH₄OH, reflux; (b) 9-anthraceneboronic acid, Na₂CO₃, Pd(PPh₃)₄, toluene/H₂O/*t*-BuOH (3:3:1, v/v/v), reflux.

Compound 2. To an EtOH (80 mL) solution of **1** (4.0 g, 19.8 mmol), NaOH (0.9 g, 22.5 mmol) and *p*-anisaldehyde (1.2 g, 9.0 mmol) were successively added at 0 °C. After being stirred at 25 °C for 18 h, NH₄OH_(aq) (28 wt%, 25 mL) was added into the mixture, which then was refluxed for 18 h. After cooling to 25 °C, the reaction mixture was extracted with CH₂Cl₂, and the combined organic extract was washed with H₂O, dried over anhydrous MgSO₄, and then evaporated to dryness under reduced pressure. The crude product was recrystallized from MeOH to give **2** as a pale yellow solid (2.3 g, 4.6 mmol) in 51% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.64 (s, 2H), 8.56 (d, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), and 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.63, 157.32, 154.22, 150.10, 141.56, 139.08, 130.29, 128.57, 128.07, 119.94, 119.11, 114.37, and 55.40. MALDI-TOF-MS: calcd. for C₂₂H₁₆Br₂N₃O [M + H]⁺: *m/z* = 495.9660; found: 495.9666.

Compound L1. To a degassed two-neck flask containing **2** (5.0 g, 10.1 mmol), 9-anthraceneboronic acid (6.7 g, 22.0 mmol), and Na₂CO₃ (10.6 g, 0.1 mol), a mixed solvent (150 mL) of toluene/H₂O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N₂ for 30 min, Pd(PPh₃)₄ (577.8 mg, 0.5 mmol) was added into the mixture, which was refluxed for 1 day under N₂. After cooling to 25 °C, the mixture was extracted with CHCl₃, and the combined organic extract was dried over anhydrous MgSO₄ and then evaporated to dryness under reduced pressure. The residue was recrystallized from MeOH to give **L1** as a white solid (6.3 g, 9.1 mmol) in 90% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.90 (d, *J* = 7.9 Hz, 2H), 8.62 (s, 2H), 8.57 (s, 2H), 8.17–8.04 (m, 6H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.56 (m, 4H), 7.51–7.42 (m, 4H), 7.41–7.34 (m, 4H), 6.75 (d, *J* = 8.9 Hz, 2H), and 3.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 160.42, 157.80, 157.03, 156.22, 149.94, 137.29, 135.85, 131.69, 130.77, 130.42, 128.70, 127.72,

127.16, 126.61, 126.04, 125.42, 120.21, 119.16, 114.26, 72.08, and 55.41. FT-IR (cm⁻¹): 3075, 3051, 3001, 2960, 2930, 2831, 1674, 1603, 1577, 1567, 1545, 1516, 1460, 1443, 1412, 1395, 1354, 1296, 1205, and 1256. MALDI-TOF-MS: calcd. for C₅₀H₃₄N₃O [M + H]⁺: *m/z* = 692.2702; found: 692.2689.

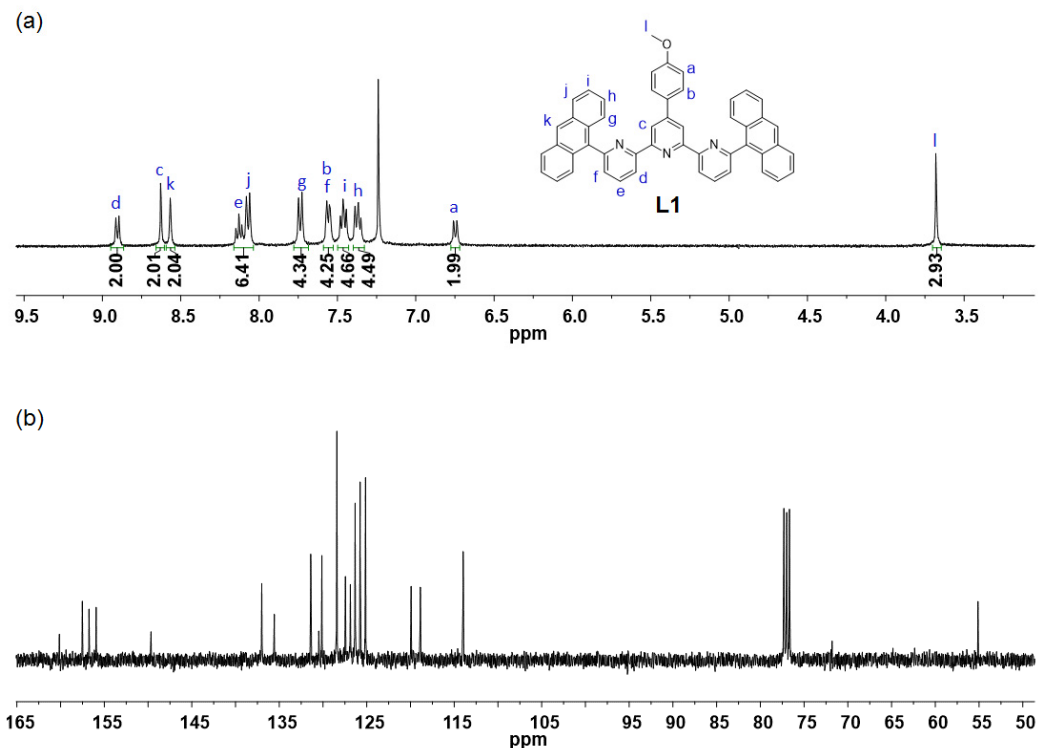


Figure S1. (a) ¹H and (b) ¹³C NMR spectra of **L1** taken in CDCl₃.

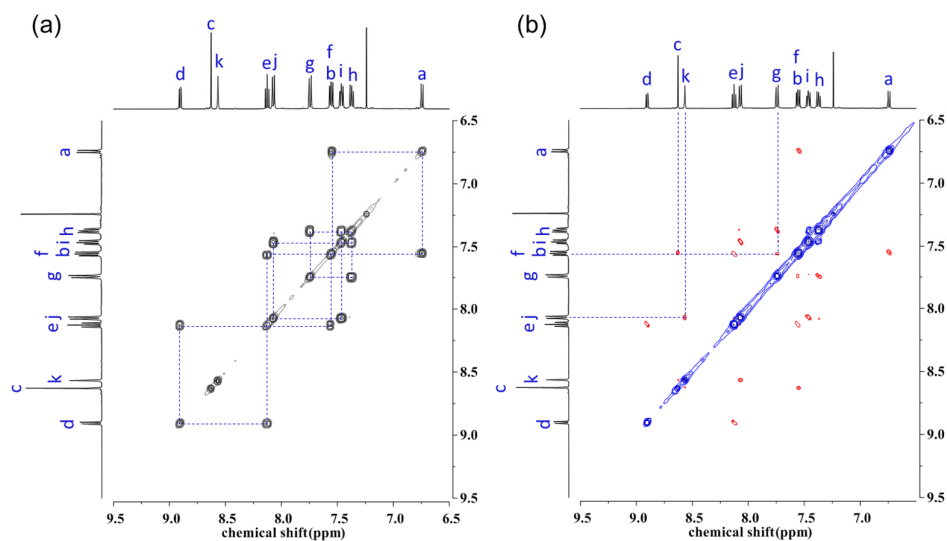


Figure S2. (a) ¹H COSY and (b) ¹H NOESY spectra of **L1**.

3. Synthesis and Characterization of [ZnL1L2].

[ZnL1L2]. To a CHCl₃ (5 mL) solution of **L2** (4.7 mg, 20.0 μmol) and **L1** (13.8 mg, 20.0 μmol), Zn(OTf)₂ (7.3 mg, 20.0 μmol) in MeOH (5 mL) was added. After the reaction mixture was stirred at room temperature for 30 min, the solvent was removed under reduced pressure and the residue was dried *in vacuo* to give [ZnL1L2] as a pale yellow solid (24.5 mg, 17.5 μmol) in 95% yield. ¹H NMR (400 MHz, CDCl₃/CD₃CN = 1/2, v/v): δ (ppm) 9.15 (s, 2H), 8.92 (d, *J* = 8.2 Hz, 2H), 8.35 (d, *J* = 8.9 Hz, 2H), 8.20 (dd, *J* = 8.1 and 7.7, 2H), 8.02 (s, 2H), 7.77–7.64 (m, 8H), 7.37 (d, *J* = 8.9 Hz, 2H), 7.30 (dd, *J* = 7.5 and 5.0 Hz, 2H), 7.21–7.09 (m, 8H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.55 (dd, *J* = 8.8 and 6.5 Hz, 4H), 6.48 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 9.7 Hz, 4H), and 4.02 (s, 3H). ¹³C NMR (100 MHz, CHCl₃/CD₃CN = 1/2, v/v): δ (ppm) 159.94, 156.83, 153.44, 151.58, 148.38, 147.68, 145.00, 142.46, 142.08, 142.01, 132.51, 131.68, 131.61, 131.36, 131.15, 130.43, 129.81, 129.25, 128.45, 128.25, 126.83, 125.31, 124.65, 123.97, 123.27, 121.94, 116.68, and 57.03. ESI-MS: calcd. for C₆₅H₄₄N₆OZn [M – 2OTf]²⁺: *m/z* = 494.1434; found: 494.1837.

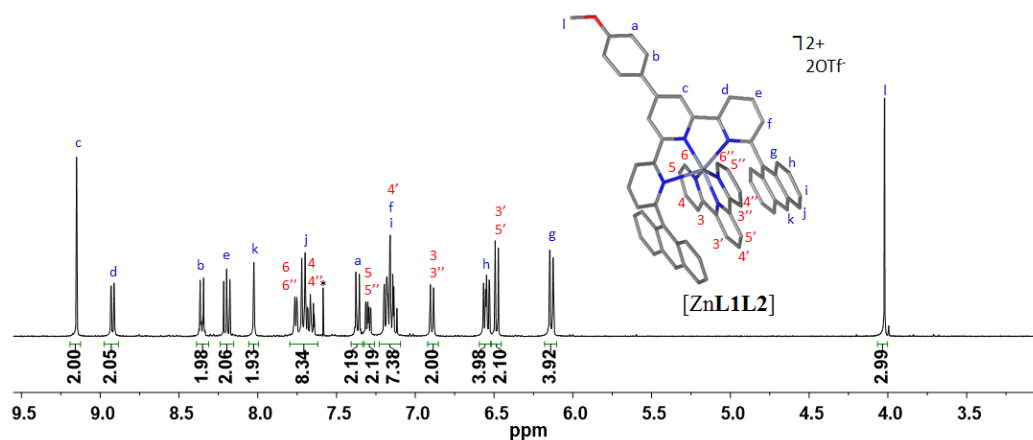


Figure S3. ¹H NMR spectrum of [ZnL1L2] (CDCl₃/CD₃CN = 1/2, v/v). The peak for CHCl₃ is denoted by an asterisk.

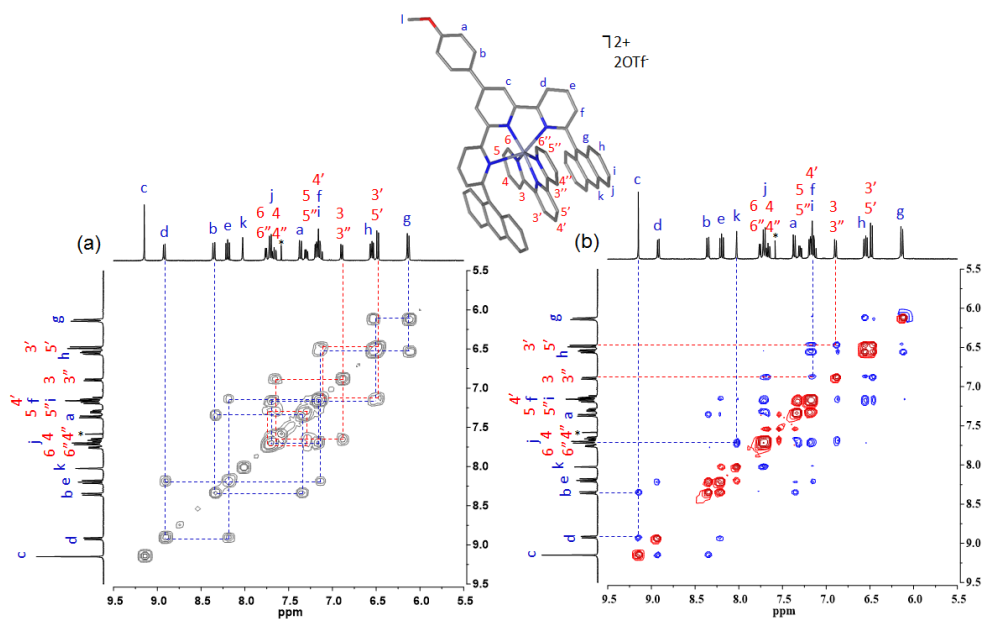


Figure S4. (a) ^1H COSY and (b) ^1H NOESY spectra of $[\text{ZnL1L2}]$. The peak for CHCl_3 is denoted by an asterisk.

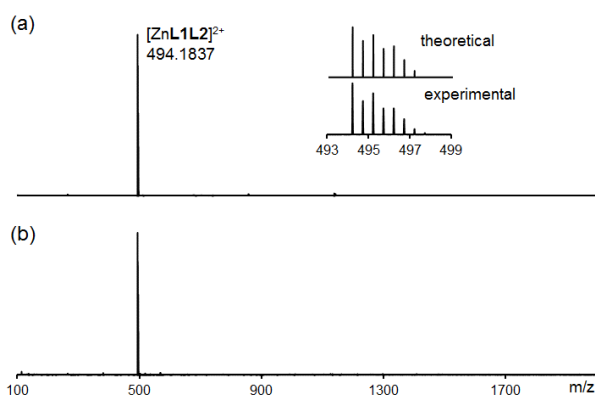


Figure S5. ESI-MS spectra of $[\text{ZnL1L2}]$ at concentrations of (a) 776.0 and (b) 2.3 μM in MeCN.

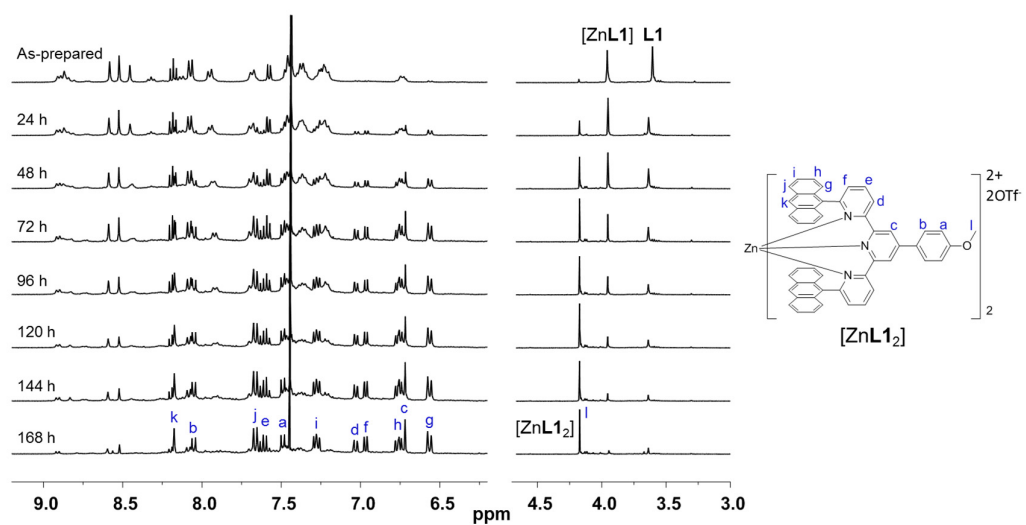
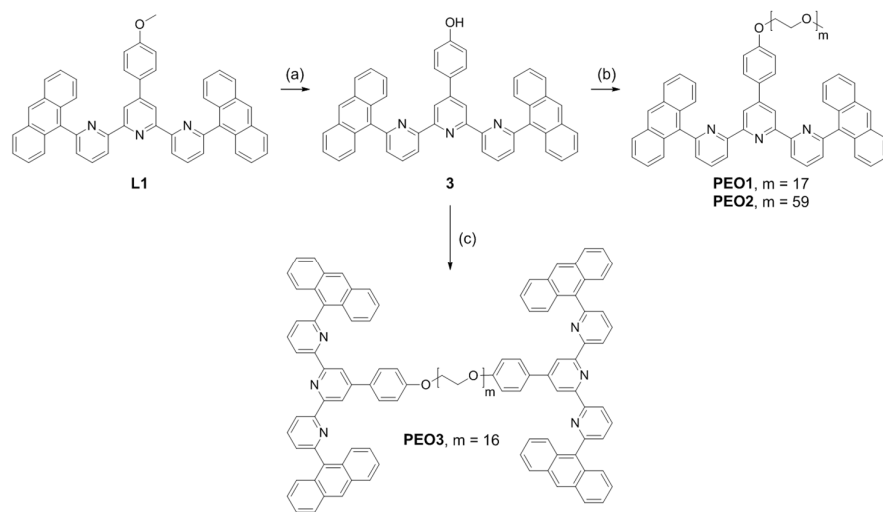


Figure S6. Time-dependent ^1H NMR spectra of a 2:1 mixture of **L1** and $\text{Zn}(\text{OTf})_2$ at room temperature ($[\text{L1}] = 11 \mu\text{M}$, $\text{CDCl}_3/\text{CD}_3\text{CN} = 1/2$, v/v).

4. Synthesis and Characterization of PEO1, PEO2, and PEO3.



Scheme S2. Synthesis of **PEO1-PEO3**. *Reagents and conditions:* (a) HBr, AcOH, reflux; (b) tosylated PEOME, Cs₂CO₃, DMF, 80 °C; (c) tosylated PEG, Cs₂CO₃, DMF, 80 °C.

Compound 3. To an AcOH solution (10 mL) of **L1** (0.2 g, 0.3 mmol), HBr (10 mL, 59.0 mmol) was added at 0 °C. After the mixture was refluxed for 16 h, the solvent was removed by vacuum distillation and the residue was neutralized by NaOH_(aq). The aqueous solution was extracted with toluene. The combined organic extract was washed with H₂O, dried over anhydrous MgSO₄, and then evaporated to dryness under reduced pressure to give **3** as a pale yellow solid (106.0 mg, 45.0 mmol) in 54% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.88 (d, *J* = 7.8 Hz, 2H), 8.54 (s, 2H), 8.52 (s, 2H), 8.12 (t, *J* = 7.7 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 4H), 7.71 (d, *J* = 8.7 Hz, 4H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.47–7.39 (m, 4H), 7.34 (dd, *J* = 12.2 and 6.0 Hz, 6H), 6.49 (d, *J* = 8.5 Hz, 2H), and 3.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.57, 156.84, 156.44, 155.77, 149.86, 137.17, 135.29, 131.35, 130.14, 128.43, 128.35, 127.54, 126.91, 126.22, 125.82, 125.13, 120.15, 119.96, 118.96, and 115.46. FT-IR (cm⁻¹): 3313, 3052, 2954, 2924, 2852, 2357, 1600, 1581, 1566, 1519, 1456, 1443, 1396, 1257, and 1181. ESI-MS: calcd. for C₄₉H₃₂N₃O [M + H]⁺: *m/z* = 678.2545; found: 678.2556.

PEO1. To a DMF solution (10 mL) of **3** (0.4 g, 0.6 mmol), Cs₂CO₃ (121.0 mg, 0.9 mmol) was added. After the mixture was stirred at 80 °C for 1 h, a DMF solution of tosylated PEOME (121.0 mg, 213.4 μmol, DP = 17) was added. The mixture was stirred for 18 h at 80 °C. The solution was extracted with CH₂Cl₂ and NH₄Cl_(aq). The combined organic extract was washed with H₂O, dried over anhydrous MgSO₄ and then

evaporated to dryness under reduced pressure. The residue was purified by column chromatography (Al_2O_3 , $\text{CH}_2\text{Cl}_2/\text{MeOH} = 19:1$) to give **PEO1** as a colorless oil (175.0 mg, 161.0 μmol) in 75% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.90 (d, $J = 7.9$ Hz, 2H), 8.61 (s, 2H), 8.57 (s, 2H), 8.13 (t, $J = 7.8$ Hz, 2H), 8.07 (d, $J = 8.5$ Hz, 4H), 7.74 (d, $J = 7.9$ Hz, 4H), 7.55 (t, $J = 8.9$ Hz, 4H), 7.49–7.44 (m, 4H), 7.40–7.34 (m, 4H), 6.76 (d, $J = 8.9$ Hz, 2H), 4.01–3.98 (m, 2H), 3.76–3.72 (m, 2H), 3.69–3.46 (m, 62H), and 3.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.35, 157.49, 156.71, 155.90, 149.60, 136.99, 135.54, 131.38, 130.58, 130.10, 128.38, 127.41, 126.86, 126.30, 125.74, 125.12, 119.91, 118.81, 114.64, 71.86, 70.47, 69.49, 67.23, and 58.98. FT-IR (cm^{-1}): 3078, 3046, 2921, 2864, 1734, 1606, 1577, 1566, 1544, 1515, 1458, 1395, 1353, 1294, 1255, and 1106. GPC: $M_n = 1.2$ kDa, $M_w/M_n = 1.10$.

PEO2. By a similar procedure to that for **PEO1**, **PEO2** was obtained in 76% yield (160.0 mg, 52.0 μmol) from **3** (0.1 g, 150.0 μmol) and tosylated PEOME (196.0 mg, 70.0 μmol , DP = 57). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.90 (d, $J = 6.9$ Hz, 2H), 8.62 (s, 2H), 8.57 (s, 2H), 8.13 (t, $J = 7.8$ Hz, 2H), 8.07 (d, $J = 8.5$ Hz, 4H), 7.73 (d, $J = 8.8$ Hz, 4H), 7.58–7.52 (m, 4H), 7.49–7.44 (m, 4H), 7.40–7.34 (m, 4H), 6.76 (d, $J = 8.9$ Hz, 2H), 4.01–3.98 (m, 2H), 3.81–3.43 (m, 234H), and 3.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.30, 157.42, 156.64, 155.85, 149.54, 136.94, 135.48, 131.32, 130.52, 130.04, 128.33, 127.35, 126.80, 126.23, 125.68, 125.07, 119.86, 118.74, 114.59, 71.81, 70.45, 67.18, 58.93, and 53.38. FT-IR (cm^{-1}): 3078, 3047, 2924, 2864, 1731, 1606, 1579, 1567, 1545, 1515, 1455, 1395, 1350, 1296, 1251, and 1106. GPC: $M_n = 2.4$ kDa, $M_w/M_n = 1.13$.

PEO3. By a similar procedure to that for **PEO1**, **PEO3** was obtained in 19% yield (340.4 mg, 169.2 μmol) from **3** (1.49 g, 2.2 mmol) and tosylated PEG (0.8 g, 881.1 μmol , DP = 16). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.92 (d, $J = 7.8$ Hz, 4H), 8.64 (s, 4H), 8.58 (s, 4H), 8.17–8.04 (m, 12H), 7.76 (d, $J = 8.7$ Hz, 8H), 7.59–7.51 (m, 8H), 7.51–7.44 (m, 8H), 7.43–7.35 (m, 8H), 6.75 (d, $J = 7.9$ Hz, 4H), 3.98 (b, 4H), 3.73 (b, 4H), and 3.57 (b, 56H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.37, 157.51, 156.74, 155.92, 149.62, 137.01, 135.55, 131.40, 130.12, 128.41, 127.43, 126.88, 126.31, 125.76, 125.15, 119.94, 118.83, and 114.66. FT-IR (cm^{-1}): 3076, 3053, 2921, 2873, 1730, 1606, 1578, 1567, 1545, 1515, 1460, 1395, 1353, 1294, 1256, and 1115. GPC: $M_n = 1.6$ kDa, $M_w/M_n = 1.08$.

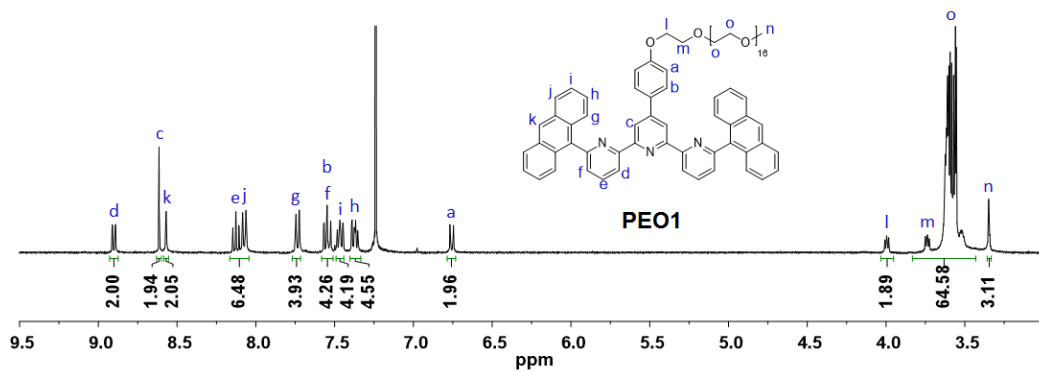


Figure S7. ^1H NMR spectrum of **PEO1**.

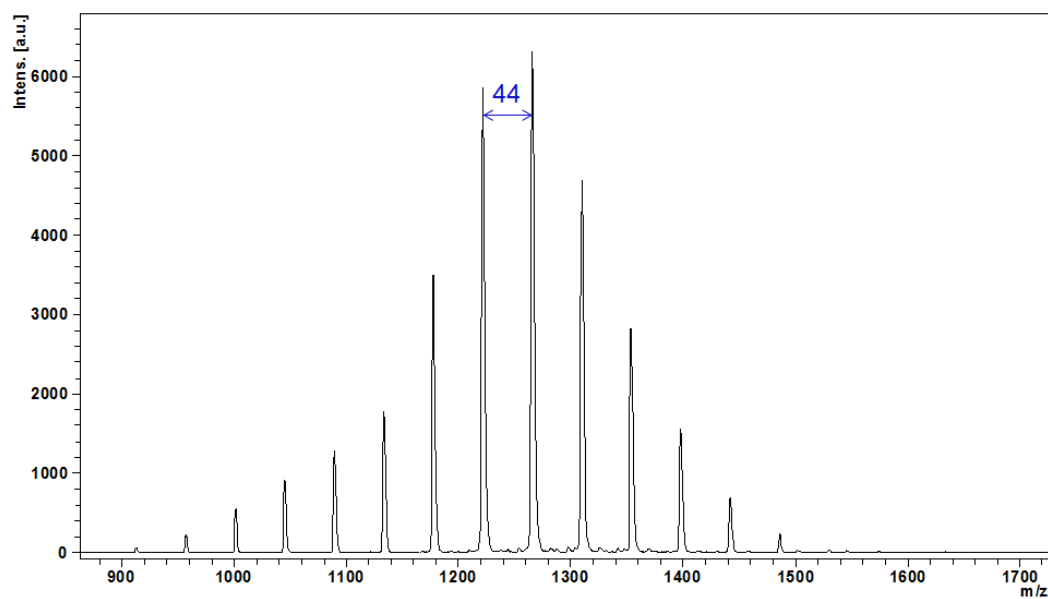


Figure S8. MALDI-TOF-MS spectrum of **PEO1**.

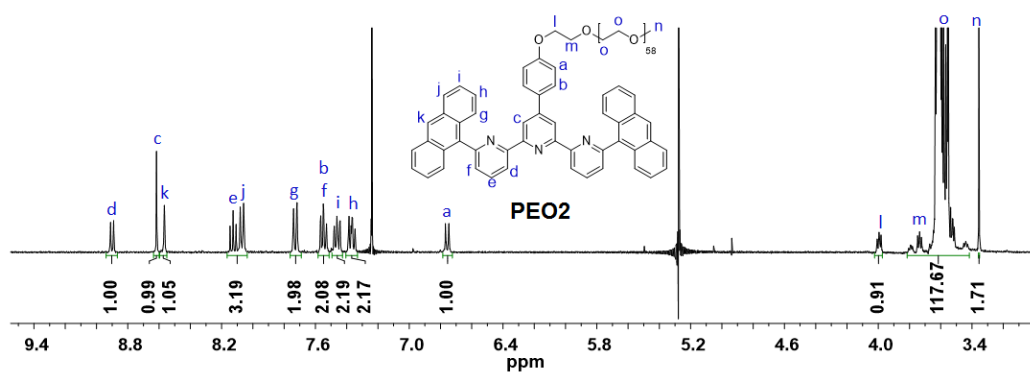


Figure S9. ^1H NMR spectrum of **PEO2**.

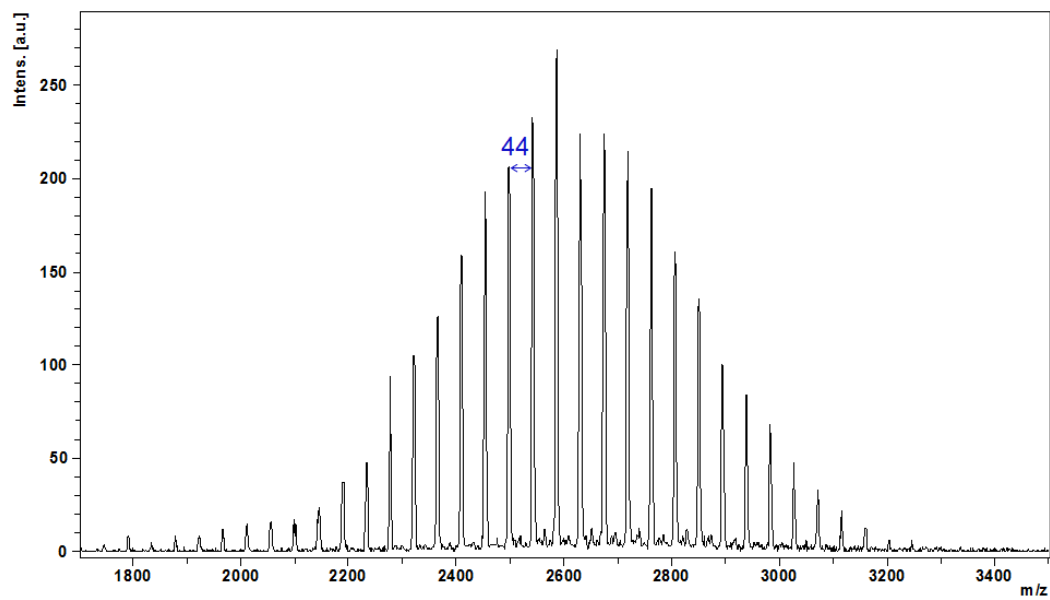


Figure S10. MALDI-TOF-MS spectrum of **PEO2**.

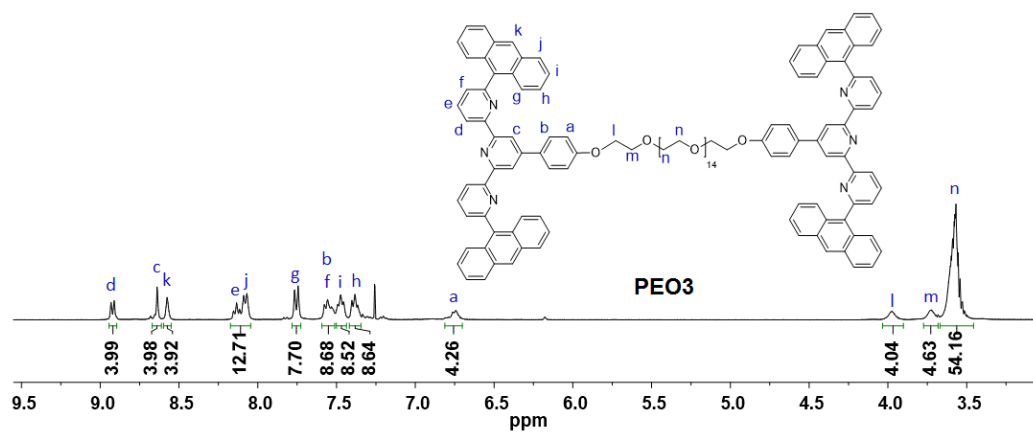


Figure S11. ¹H NMR spectrum of **PEO3**.

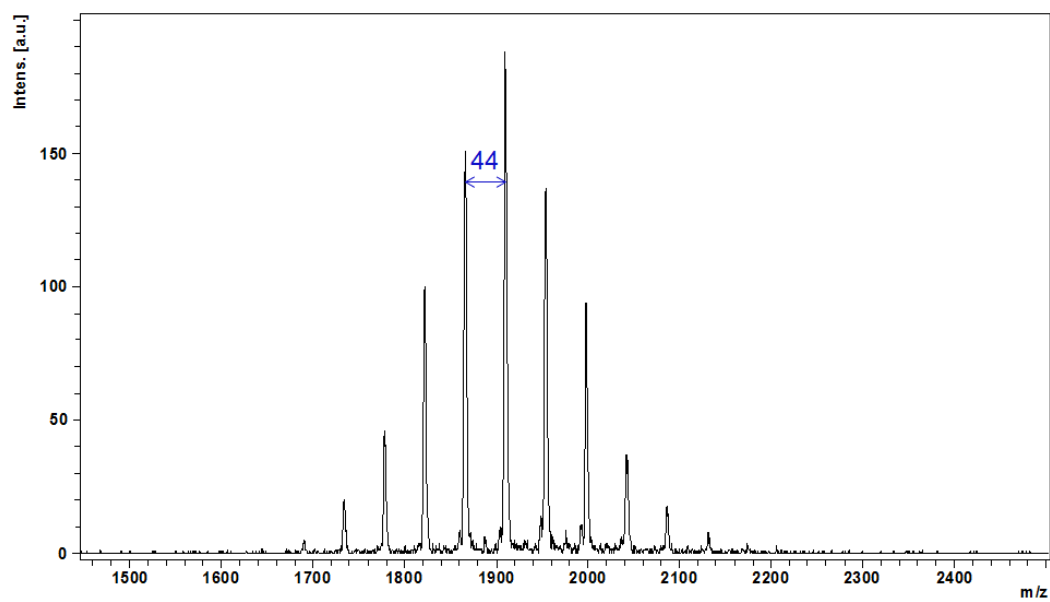
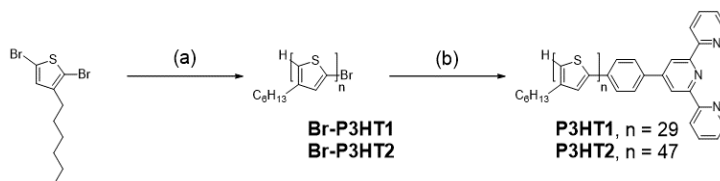


Figure S12. MALDI-TOF-MS spectrum of **PEO3**.

5. Synthesis and Characterization of Br-P3HT1, Br-P3HT2, P3HT1, and P3HT2.



Scheme S3. Synthesis of **P3HT1** and **P3HT2**. *Reagents and conditions:* (a) 1) *t*-BuMgCl, LiCl, THF, 2) Ni(dppp)Cl₂, THF, 0 °C. (b) 4'-(4-boronophenyl)-2,2':6',2''-terpyridine, Pd(PPh₃)₄, toluene/H₂O/*t*-BuOH (3:3:1, v/v/v), reflux.

Br-P3HT1. To a degassed Schlenk flask containing 2,5-dibromo-3-hexylthiophene (8.0 g, 24.5 mmol) and LiCl (1.0 g, 24.5 mmol) under nitrogen atmosphere, anhydrous tetrahydrofuran (80 mL) was added. The mixture was degassed by three freeze-pump-thaw cycles, and then *t*-butyl magnesium chloride solution in THF (13.8 mL, 1.6 M, 23.6 mmol) was introduced by a syringe into the mixture at room temperature, which was stirred at room temperature for 1.5 h (solution A). To another degassed Schlenk flask containing Ni(dppp)Cl₂ (308.6 mg, 0.6 mmol), anhydrous THF (80 mL) was added under nitrogen atmosphere. The mixture was degassed by three freeze-pump-thaw cycles. The solution A was added into the reaction mixture at 0 °C. After being stirred for 1 h at 0 °C, HCl (1 mL, 1 M) was added to quench polymerization. The reaction mixture was poured into methanol and the precipitate was filtered and dried *in vacuo* to afford **Br-P3HT1** as a dark solid (2.9 g, 460.3 μmol) in 70 % yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.04–6.78 (m, 30H), 2.86–2.66 (m, 58H), 2.66–2.46 (m, 2H), 1.65 (m, 60H), 1.37 (m, 180H), and 0.97–0.71 (m, 90H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 139.87, 133.68, 130.47, 128.58, 31.69, 30.50, 29.46, 29.26, 22.65, and 14.12. GPC: *M*_n = 5.8 kDa, *M*_w/*M*_n = 1.15.

Br-P3HT2. By a similar procedure to that for **Br-P3HT1**, **Br-P3HT2** was obtained in 87% yield (1.4 g, 189.2 μmol) from 2,5-dibromo-3-hexylthiophene (4.0 g, 12.3 mmol) and LiCl (0.5 g, 12.3 mmol), *t*-butyl magnesium chloride in THF (6.9 mL, 1.6 M, 11.8 mmol), and Ni(dppp)Cl₂ (85.7 mg, 160.0 μmol). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.04–6.78 (m, 43H), 2.86–2.66 (m, 82H), 2.66–2.46 (m, 2H), 1.65 (m, 84H), 1.37 (m, 252H), and 0.97–0.71 (m, 126H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 139.85, 133.68, 130.44, 128.58, 31.70, 30.51, 29.46, 29.24, 22.64, and 14.12. GPC: *M*_n = 7.4 kDa, *M*_w/*M*_n = 1.25.

P3HT1. To a degassed two-neck flask containing 4'-(4-boronophenyl)-2,2':6',2''-terpyridine (0.1 g, 280.0 μmol), **Br-P3HT1** (1.0 g, 230 μmol, DP = 29), and NaOH (0.6

g, 14.0 mmol), a mixed solvent (42 mL) of THF/H₂O (3:1, v/v) was added. After being purged with N₂ for 30 min, Pd(PPh₃)₄ (13.3 mg, 11.5 μmol) was added into the mixture, which was then refluxed for 2 days under N₂. After cooling to 25 °C, the mixture was extracted with CHCl₃ and the combined organic extract was dried over MgSO₄ and then evaporated to dryness under reduced pressure. The residue was precipitated from CH₃OH/CHCl₃ to give **P3HT1** as a deep purple solid (0.6 g, 140.0 μmol) in 61% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.88–8.60 (m, 6H), 8.06–7.83 (m, 4H), 7.62 (m, 2H), 7.36 (m, 2H), 7.13–6.86 (m, 30H), and 3.03–2.46H (m, 60H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.45, 156.25, 149.83, 149.38, 143.89, 140.55, 140.11, 139.83, 137.48, 137.10, 135.73, 134.88, 133.92, 133.70, 131.22, 130.71, 129.77, 128.81, 127.73, 127.37, 126.80, 124.09, 121.59, 120.23, 118.89, 32.04, 30.75, 29.72, 29.52, 22.91, and 14.38. FT-IR (cm⁻¹): 2953, 2924, 2854, 1603, 1584, 1566, 1509, 1455, and 1377. GPC: *M*_n = 6.3 kDa, *M*_w/*M*_n = 1.21.

P3HT2. By a similar procedure to that for **P3HT1**, **P3HT2** was obtained in 56% yield (1.2 g, 69.0 μmol) from 4'-(4-boronophenyl)-2,2':6',2''-terpyridine (53 mg, 150.0 μmol), **Br-P3HT2** (2.1 g, 124.0 μmol, DP = 47), NaOH (0.6 g, 14.0 mmol), and Pd(PPh₃)₄ (7.2 mg, 6.2 μmol). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.83–8.65 (m, 6H), 8.03–7.85 (m, 4H), 7.62 (m, 2H), 7.40–7.32 (m, 2H), 7.11–6.85 (m, 48H), 2.97–2.54 (m, 96H), 1.80–1.52 (m, 96H), 1.52–1.20 (m, 51H), and 1.01–0.81 (m, 144H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.26, 156.03, 149.15, 143.65, 140.34, 139.89, 139.61, 136.85, 135.51, 133.72, 130.50, 129.65, 129.56, 129.49, 128.60, 128.45, 127.49, 127.16, 126.56, 123.83, 121.35, 120.00, 118.67, 117.78, 31.70, 30.51, 29.48, 29.27, 22.66, and 14.12. FT-IR (cm⁻¹): 2954, 2923, 2854, 1602, 1584, 1564, 1509, 1455, and 1377. GPC: *M*_n = 8.9 kDa, *M*_w/*M*_n = 1.26.

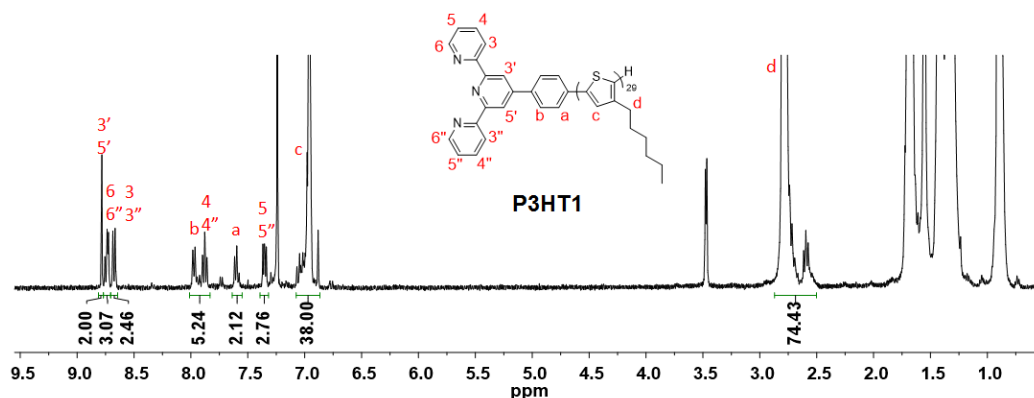


Figure S13. ¹H NMR spectrum of **P3HT1**.

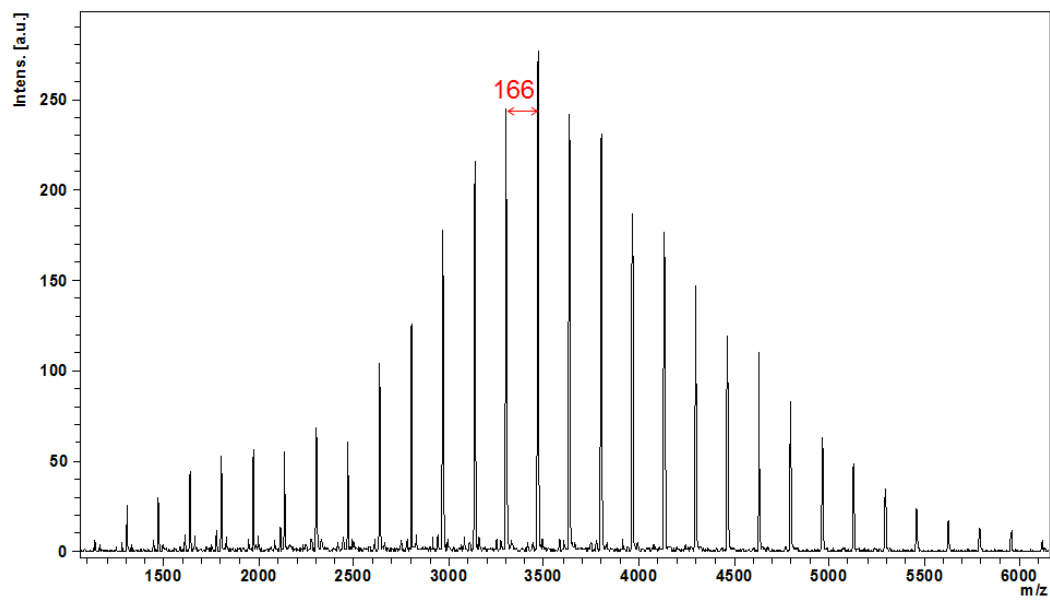


Figure S14. MALDI-TOF-MS spectrum of **P3HT1**.

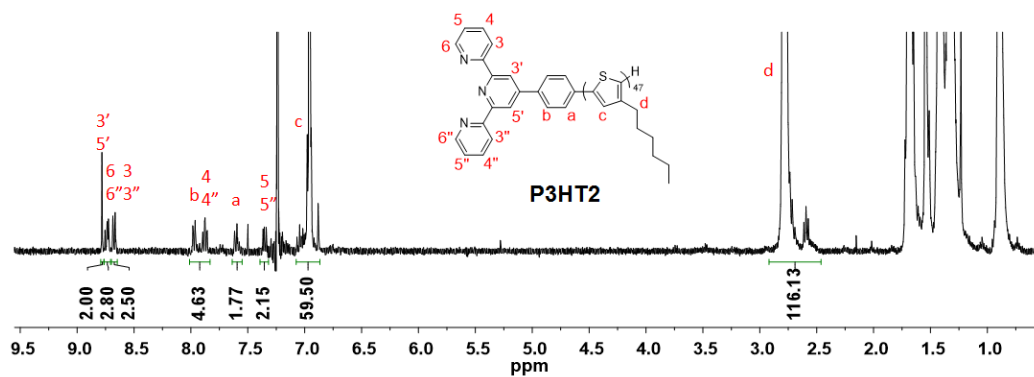


Figure S15. ¹H NMR spectrum of **P3HT2**.

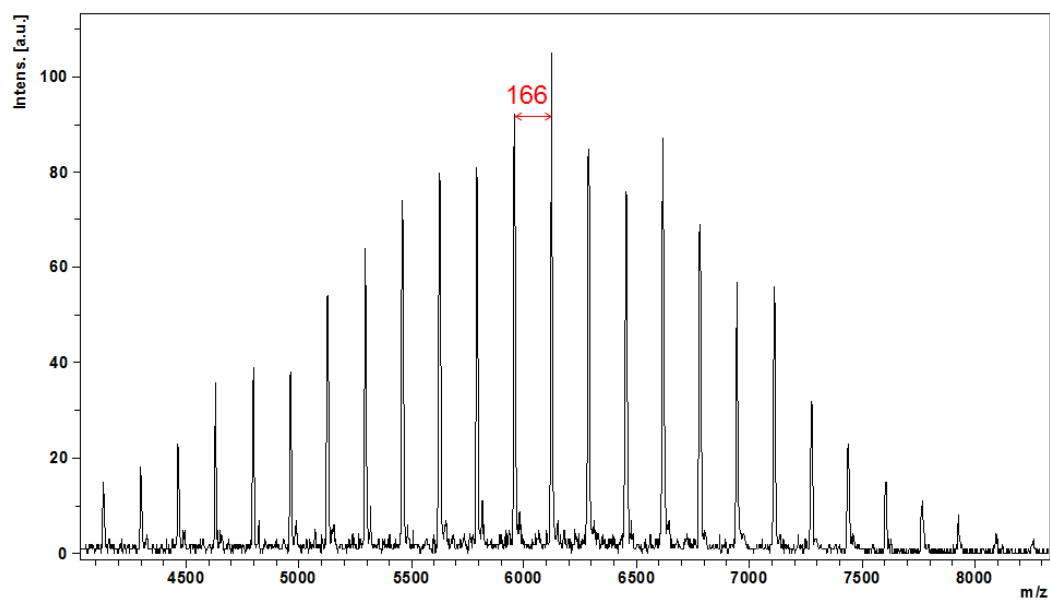
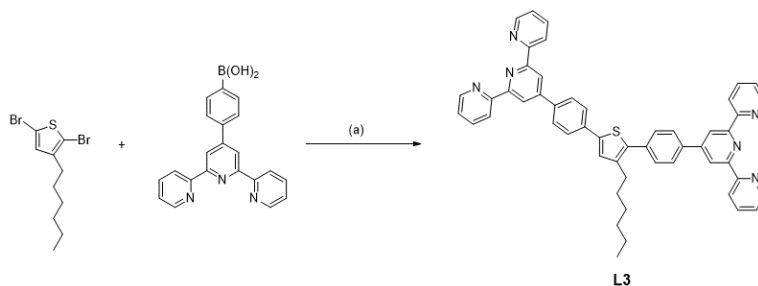


Figure S16. MALDI-TOF-MS spectrum of **P3HT2**.

6. Synthesis and Characterization of L3.



Scheme S4. Synthesis of **L3**. *Reagents and conditions:* (a) Na₂CO₃, Pd(PPh₃)₄, toluene/H₂O/*t*-BuOH (3:3:1, v/v/v), reflux.

L3. To a degassed two-neck flask containing 2,5-dibromo-3-hexylthiophene (0.5 g, 1.5 mmol), 4'-(4-boronophenyl)-2,2':6',2''-terpyridine (1.6 g, 4.6 mmol), and Na₂CO₃ (2.2 g, 15.3 mmol), a mixed solvent (56 mL) of toluene/H₂O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N₂ for 30 min, Pd(PPh₃)₄ (286.0 mg, 0.18 mmol) was added into the mixture, which was refluxed for 2 days under N₂. After cooling to 25 °C, the mixture was extracted with CHCl₃, and the combined organic extract was dried over anhydrous MgSO₄ and then evaporated to dryness under reduced pressure. The residue was recrystallized from MeOH to give **L3** as a white solid (1.1 g, 1.4 mmol) in 88% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.80–8.61 (m, 1H), 8.00–7.80 (m, 8H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.38–7.28 (m, 5H), 2.74 (t, *J* = 8.0, 8.0, 2H), 1.74–1.63 (m, 2H), 1.41–1.24 (m, 6H), and 0.92–0.83 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 156.19, 156.17, 155.94, 155.92, 149.52, 149.47, 149.11, 141.67, 140.45, 137.23, 137.13, 136.83, 135.34, 134.96, 129.49, 127.75, 127.45, 126.36, 125.84, 123.81, 121.34, 121.31, 118.61, 118.43, 31.64, 31.01, 29.27, 29.11, 22.62, and 14.10. FT-IR (cm⁻¹): 3059, 3051, 2951, 2923, 2852, 2360, 2343, 2330, 1734, 1602, 1564, 1566, 1507, 1466, 1442, 1413, 1389, 1264, 1115, 1089, 1076, and 1039. MALDI-TOF-MS: calcd. for C₅₂H₄₂N₆S [M + H]⁺: *m/z* = 783.3270; found: 783.3275.

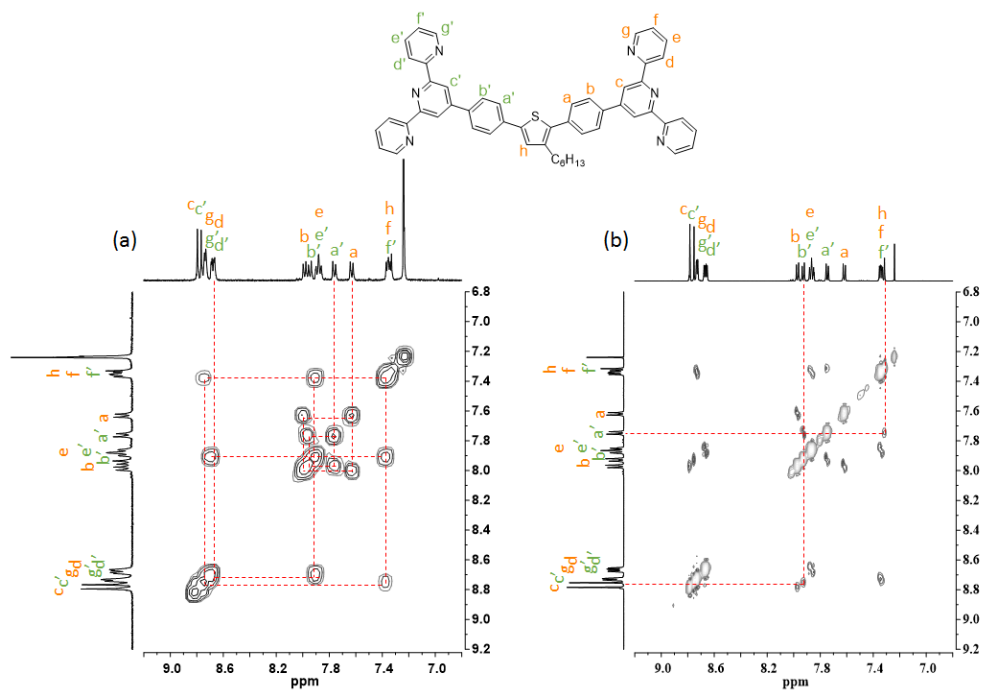


Figure S17. (a) ^1H COSY and (b) ^1H ROESY spectra of **L3**.

7. Synthesis and Characterization of [P3HT1-Zn-PEO1], [P3HT1-Zn-PEO2], [P3HT2-Zn-PEO1], and [P3HT2-Zn-PEO2].

General Procedure for Polymer Complexation Reactions. To a CHCl_3 solution (5 mL) of **PEO** and **P3HT** in an equimolar ratio, one equivalent of $\text{Zn}(\text{OTf})_2$ in MeOH (5 mL) was added. After the reaction mixture was stirred at room temperature for 5 min, the solvent was removed under reduced pressure to give the corresponding diblock copolymers.

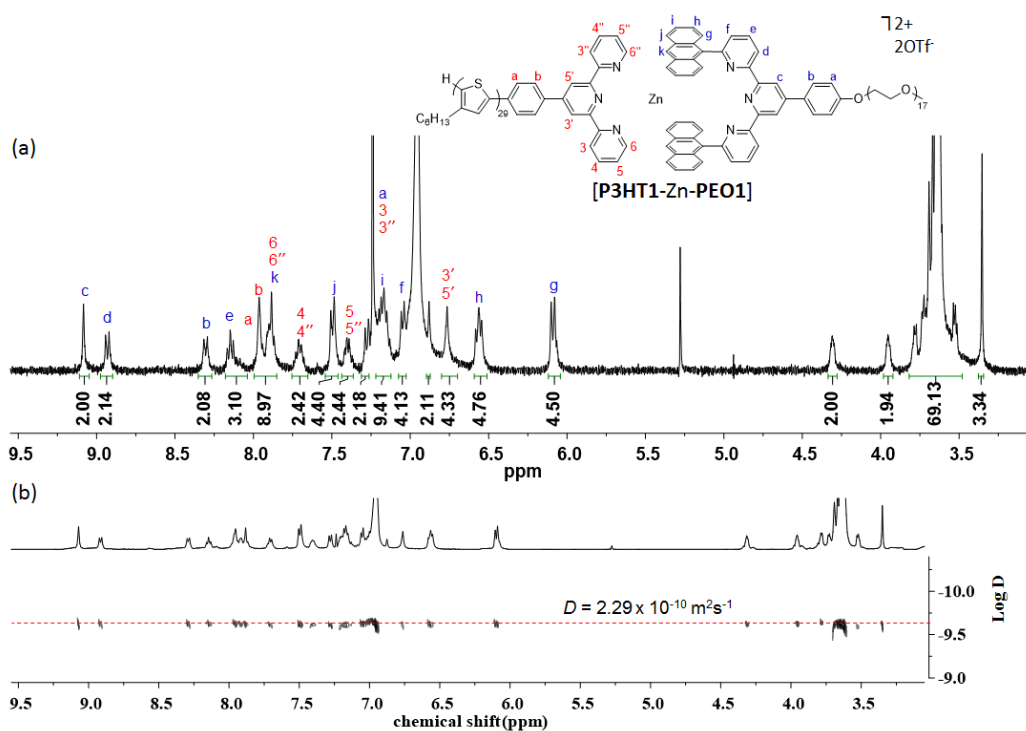


Figure S18. (a) ^1H NMR and (b) DOSY spectra of **[P3HT1-Zn-PEO1]**.

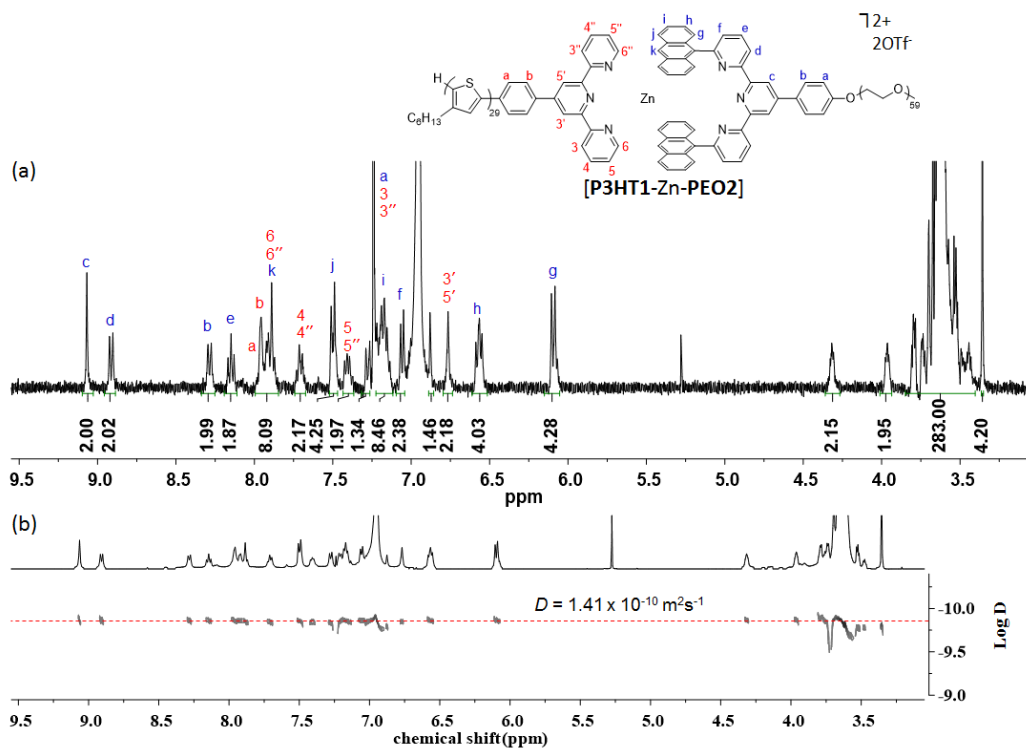


Figure S19. (a) ^1H NMR and (b) DOSY spectra of [P3HT1-Zn-PEO2].

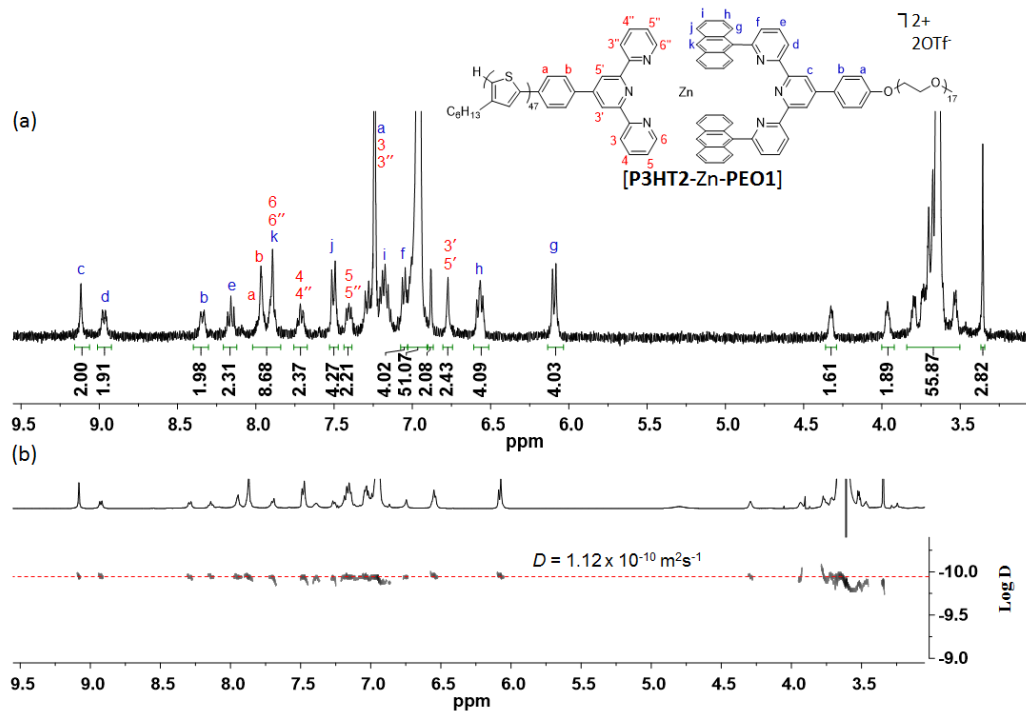


Figure S20. (a) ^1H NMR and (b) DOSY spectra of [P3HT2-Zn-PEO1].

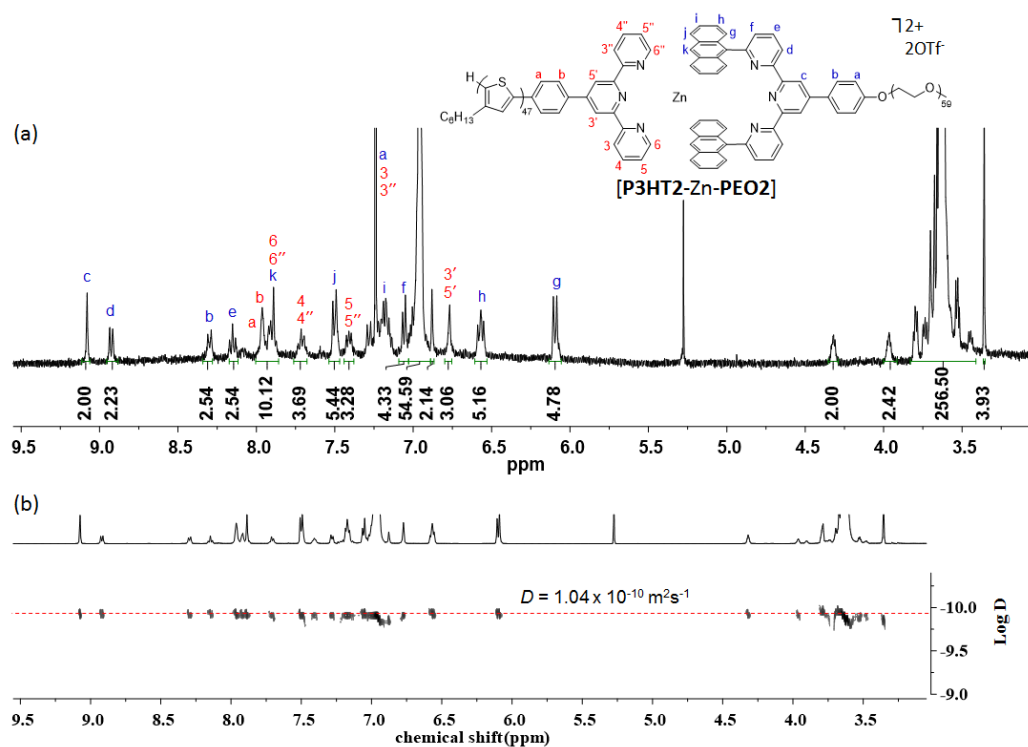


Figure S21. (a) ^1H NMR and (b) DOSY spectra of **[P3HT2-Zn-PEO2]**.

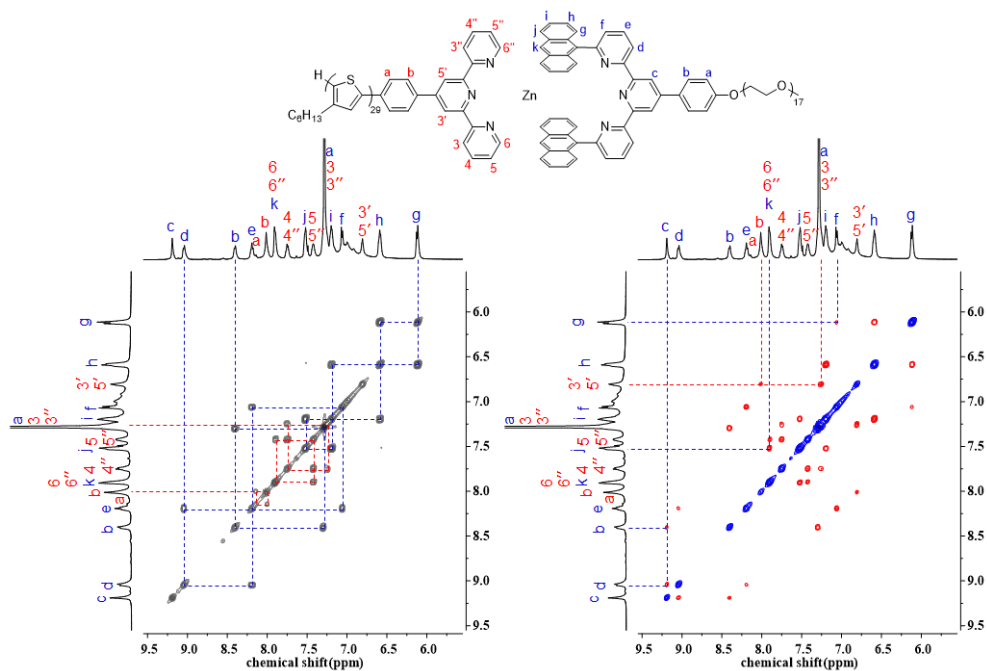


Figure S22. (a) COSY and (b) NOESY spectra of **[P3HT1-Zn-PEO1]**.

8. AFM Images of Nanostructures Generated from [P3HT-Zn-PEO].

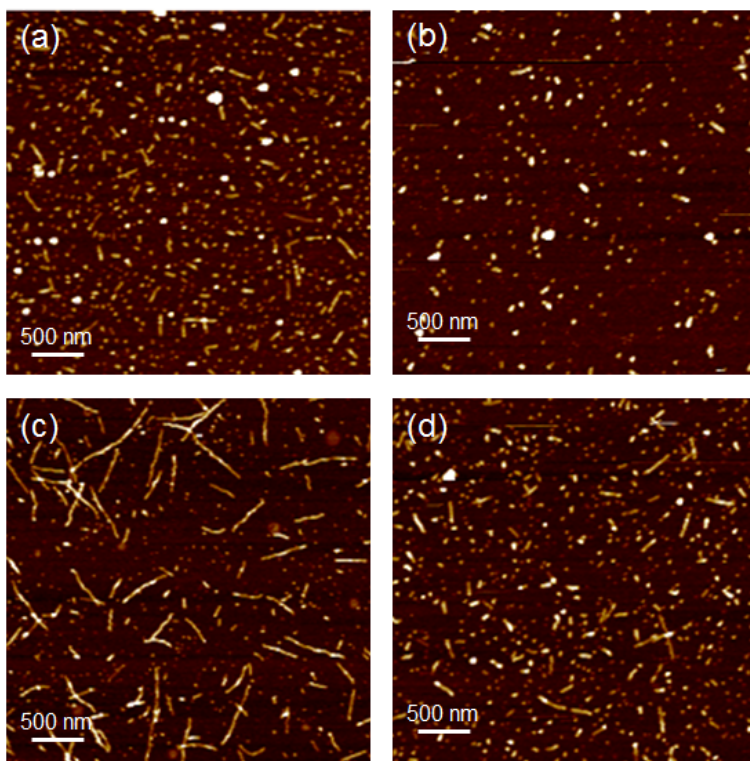


Figure S23. AFM images of the solutions of (a) [P3HT1-Zn-PEO1], (b) [P3HT1-Zn-PEO2], (c) [P3HT2-Zn-PEO1], and (d) [P3HT2-Zn-PEO2].

9. TEM Images of Nanostructures Generated from P3HT1 and P3HT2.

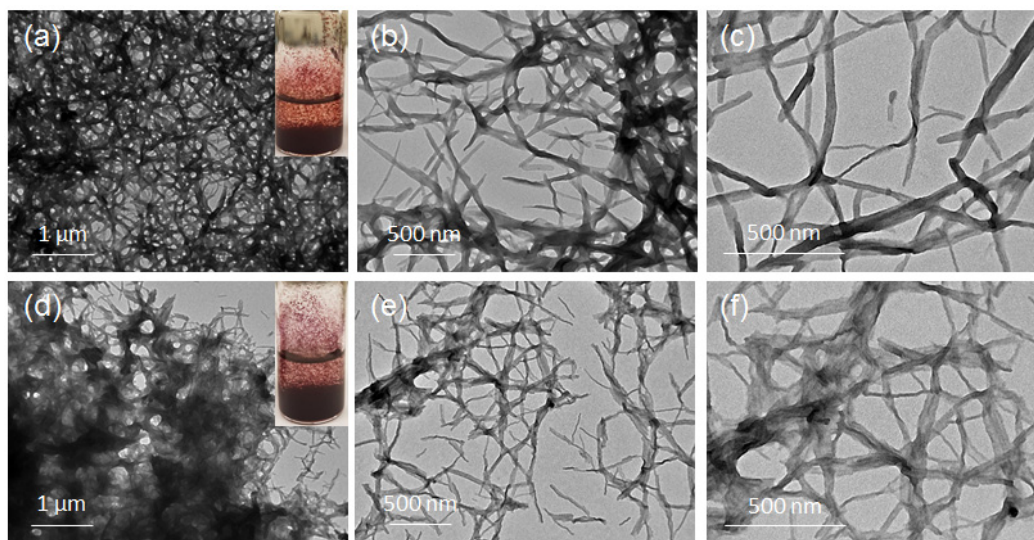


Figure S24. TEM images of the solutions of **P3HT1** (a–c) and **P3HT2** (d–f) in a mixed solvent of $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1, v/v). Insets show the photographs of the corresponding solutions.

10. Raman Spectra

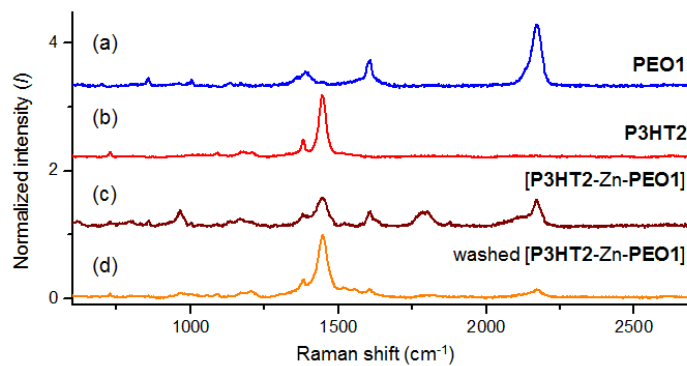


Figure S25. Raman spectra for (a) **PEO1**, (b) **P3HT2**, (c) **[P3HT2-Zn-PEO1]**, and (d) washed **[P3HT2-Zn-PEO1]**.

11. X-ray Crystallographic Data of [ZnL1L2].

Crystallographic data were acquired at 150(2) K on an Oxford Diffraction Gemini A CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structure was deposited at the Cambridge Crystallographic Data Center with the deposition number of CCDC 1529691.

Table S1. Crystal data and structure refinement for [ZnL1L2].

Identification code	ic18130	
Empirical formula	C ₇₂ H ₄₄ F ₆ N ₈ O _{7.5} S ₂ Zn	
Formula weight	1384.64	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7756(4) Å b = 13.0805(4) Å c = 18.7153(5) Å	a = 93.233(2)° b = 90.756(2)° g = 94.444(2)°
Volume	3112.69(16) Å ³	
Z	2	
Density (calculated)	1.477 Mg/m ³	
Absorption coefficient	0.545 mm ⁻¹	
F(000)	1416	
Crystal size	0.25 x 0.20 x 0.15 mm ³	
Theta range for data collection	3.10 to 25.00°.	
Index ranges	-11 ≤ h ≤ 15, -15 ≤ k ≤ 15, -22 ≤ l ≤ 19	
Reflections collected	19725	
Independent reflections	10889 [R(int) = 0.0246]	
Completeness to theta = 25.00°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.96758	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10889 / 600 / 983	
Goodness-of-fit on F ²	1.063	
Final R indices [I > 2σ(I)]	R1 = 0.0686, wR2 = 0.1816	
R indices (all data)	R1 = 0.0855, wR2 = 0.1960	
Largest diff. peak and hole	0.987 and -0.909 e.Å ⁻³	

12. Kinetic Stability of [ZnL1₂].

Pure [ZnL1₂] obtained by recrystallization from MeCN/ether (Figure S26a) was treated with one equivalent of 4'-(4-methoxyphenyl)-terpyridine. After mixing for 1 day at room temperature, no heteroleptic complex was observed by ¹H NMR (Figure S26c). Even after heating at 60 °C for 1 day, no significant change was found in the ¹H NMR spectrum (Figure S26d), suggesting that [ZnL1₂] has high kinetic stability against free unmodified terpyridine ligands.

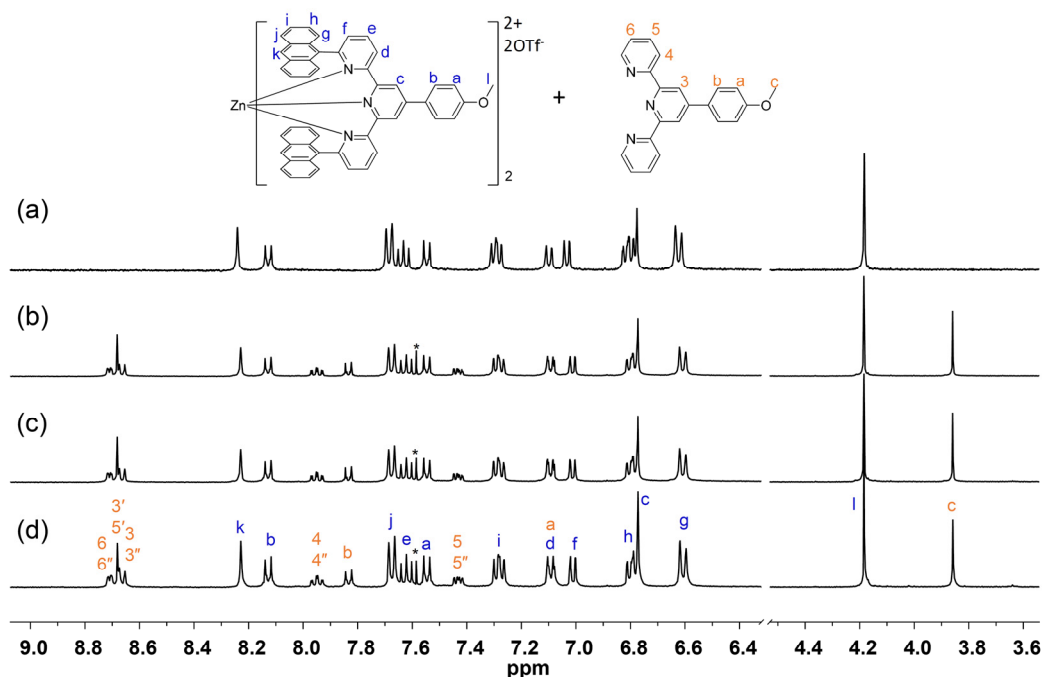


Figure S26. ¹H NMR spectra of (a) [ZnL1₂] in CD₃CN, (b) an as-prepared equimolar mixture of [ZnL1₂] and 4'-(4-methoxyphenyl)-terpyridine (CDCl₃/CD₃CN = 1:1, v/v), (c) after 1-day mixing at room temperature, and (d) after 1-day heating at 60°C. The peak for CHCl₃ is denoted by an asterisk.

References

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