

Supporting Information

Synthesis of Terpyridine End-modified Polystyrenes through ATRP for Facile Construction of Metallo-supramolecular P3HT-*b*-PS Diblock Copolymers

Tsung-Han Tu and Yi-Tsu Chan*

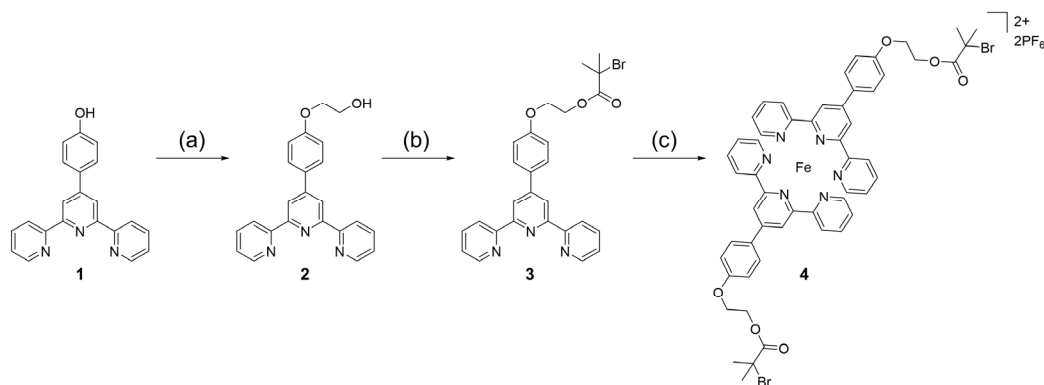
Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan; d02223101@ntu.edu.tw (T.-H.T.)

* Correspondence: ytchan@ntu.edu.tw (Y.-T.C.)

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1. Synthesis and Characterization of Metallo-initiator for ATRP



Scheme S1. Synthesis of metallo-initiator **4**. *Reagents and conditions:* (a) K_2CO_3 , DMF, 2-chloroethanol, 50 °C; (b) NEt_3 , α -bromoisobutyryl bromide, DCM, 0 °C; (c) 1) FeCl_2 , $\text{MeOH}/\text{CHCl}_3$, r.t., 2) NH_4PF_6 .

Compound 2. To a DMF (45 mL) solution of **1** (1.9 g, 5.8 mmol) and K_2CO_3 (4.8 g, 34.8 mmol), 2-chloroethanol (778.4 μL , 11.6 mmol) was added at room temperature. After being stirred at 50 °C for 18 h, the reaction mixture was extracted with ethyl acetate, and the combined organic extract was washed with H_2O , dried over anhydrous MgSO_4 , and then evaporated to dryness under reduced pressure. The crude product was recrystallized from MeOH to give **2** as a white solid (1.1 g, 3.0 mmol) in 51% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.71 (d, J = 4.7 Hz, 2H), 8.69 (s, 2H), 8.65 (d, J = 8.0, 2H), 7.82–7.90 (m, 4H), 7.34 (dd, J = 7.7, 4.6 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 4.15 (t, J = 4.4 Hz, 2H), and 4.00 (td, J = 4.7, 4.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 159.53, 156.34, 155.85, 149.66, 149.09, 136.86, 131.24, 128.61, 123.78, 121.37, 118.31, 114.91, 69.29, and 61.47. MALDI-TOF-MS: calcd for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}_2$ $[\text{M} + \text{H}]^+$: m/z = 370.1556; found: 370.1678.

Compound 3. To a DCM (20 mL) solution of **2** (200.0 mg, 541.4 μmol) and NEt_3 (0.1 mL, 0.8 mmol), α -bromoisobutyryl bromide (86.8 μL , 0.7 mmol) was added at 0 °C. After being stirred at room temperature for 22 h, the reaction mixture was extracted with CH_2Cl_2 and H_2O . The combined organic extract was washed with H_2O , dried over anhydrous MgSO_4 , and then evaporated to dryness under reduced pressure. The crude product was recrystallized from MeOH to give **3** as a white solid (227.3 mg, 438.5 μmol) in 81% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.73 (d, J = 4.6, 2H), 8.70 (s, 2H), 8.67 (d, J = 8.0, 2H), 7.86 (m, 4H), 7.35 (dd, J = 7.6, 5.4 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 4.57 (t, J = 4.9, 2H), 4.31 (t, J = 4.8, 2H), and 1.94 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.69, 159.38, 156.31, 155.84, 149.61, 149.08, 136.87, 131.38, 128.60, 123.78, 121.37, 118.31, 115.08, 65.73, 64.17, 55.48, and 30.73. MALDI-TOF-MS: calcd for $\text{C}_{27}\text{H}_{25}\text{BrN}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: m/z = 518.1079; found: 518.1349.

Compound 4. To a CHCl_3 (5.0 mL) solution of **3** (50.0 mg, 96.4 μmol), FeCl_2 (6.1 mg, 48.2 μmol) in MeOH (5.0 mL) was added. After being stirred at room temperature for 30 min, an excess amount of NH_4PF_6 (157.1 mg, 964.0 μmol) was added to precipitate the counterion-exchanged complex, and then the mixture was stirred for an additional 30 min. The precipitate was filtered, washed with H_2O , and dried *in vacuo* to give **4** as a dark purple powder (66.6 mg, 48.1 μmol) in 99% yield. ^1H NMR (400 MHz, CD_3CN): δ (ppm) 9.08 (s, 4H), 8.54 (d, J = 8.0 Hz, 4H), 8.24 (d, J = 8.8 Hz, 4H), 7.84 (dd, J = 8.5, 7.0 Hz, 4H), 7.30 (d, J = 8.7 Hz, 4H), 7.13 (d, J = 5.5 Hz, 4H), 7.02 (dd, J = 7.3, 5.9 Hz, 4H), 4.57 (t, J = 4.5 Hz, 4H), 4.42 (t, J = 4.5 Hz, 4H), and 1.94 (s, 12H). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) 172.86, 162.39, 161.65, 159.61, 154.55, 151.37, 140.13,

130.91, 130.69, 128.69, 125.19, 122.40, 117.36, 67.79, 65.61, 57.90, and 31.51. ESI-MS: calcd for $C_{54}H_{48}Br_2FeN_6O_6 [M - 2PF_6]^{2+}$: $m/z = 546.0699$; found: 546.0760.

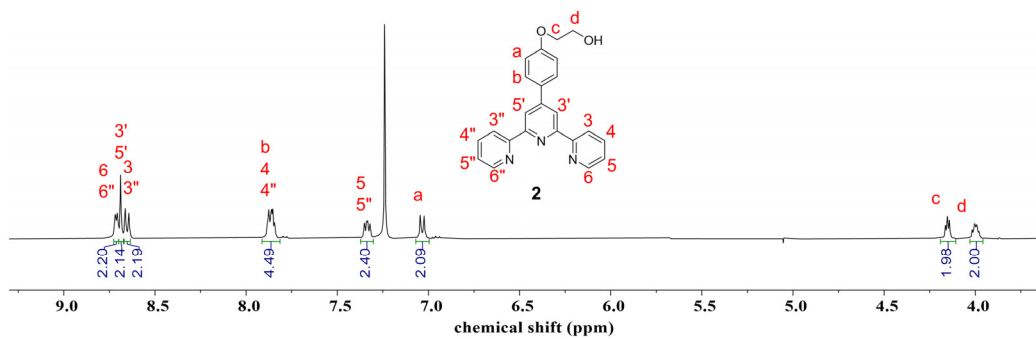


Figure S1. 1H NMR spectrum of **2** in $CDCl_3$.

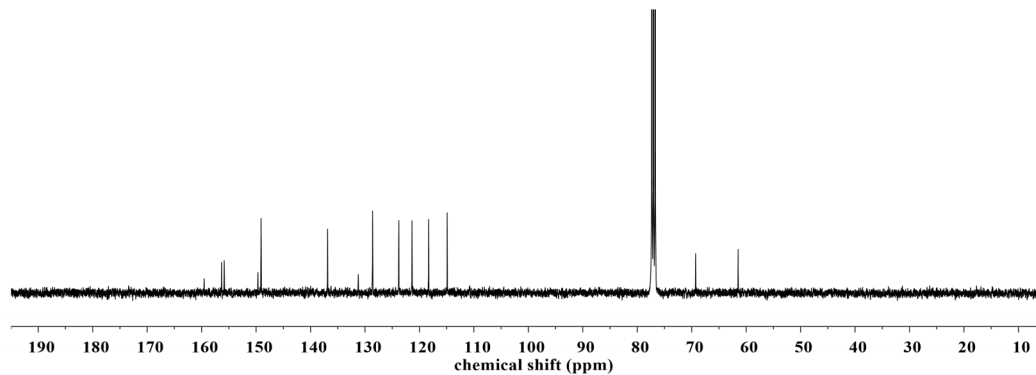


Figure S2. ^{13}C NMR spectrum of **2** in $CDCl_3$.

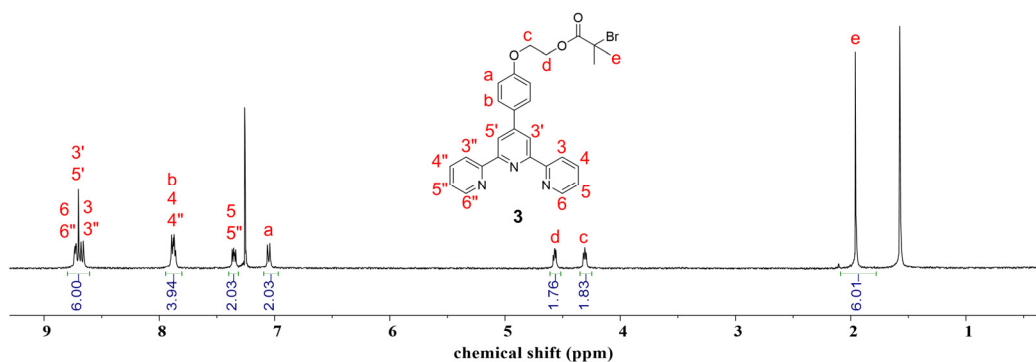


Figure S3. 1H NMR spectrum of **3** in $CDCl_3$.

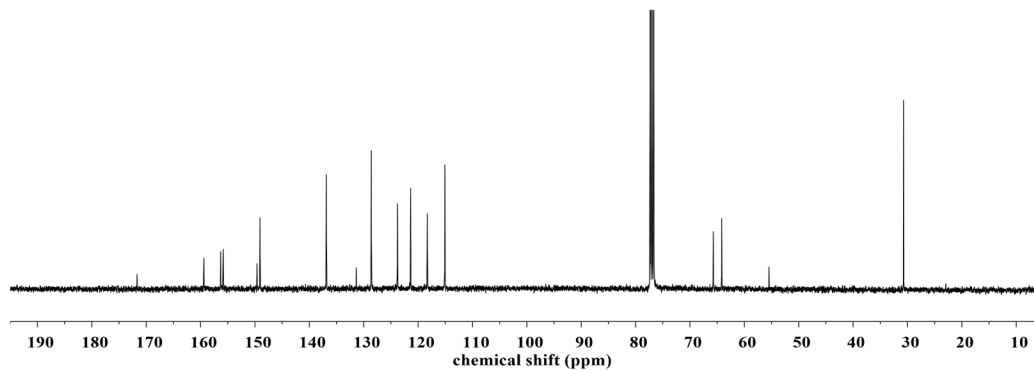


Figure S4. ^{13}C NMR spectrum of **3** in CDCl_3 .

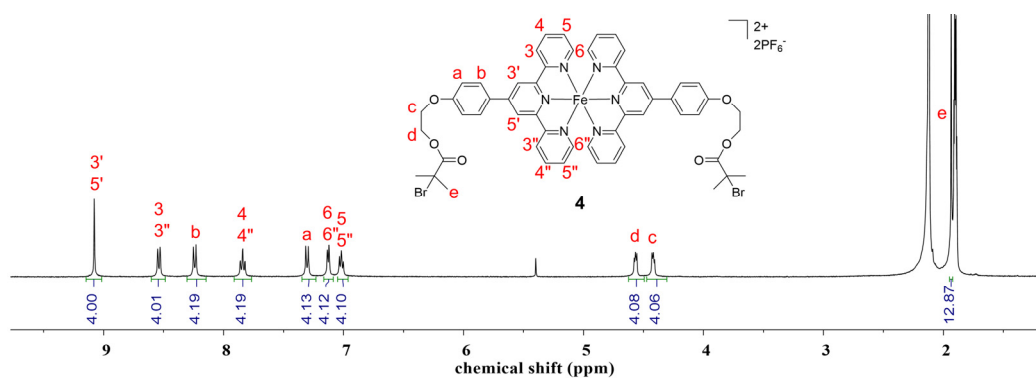


Figure S5. ^1H NMR spectrum of **4** in CD_3CN .

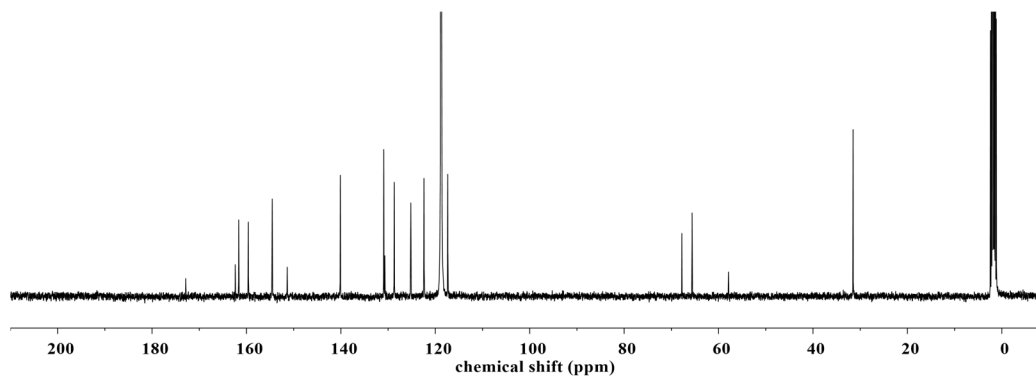


Figure S6. ^{13}C NMR spectrum of **4** in CD_3CN .

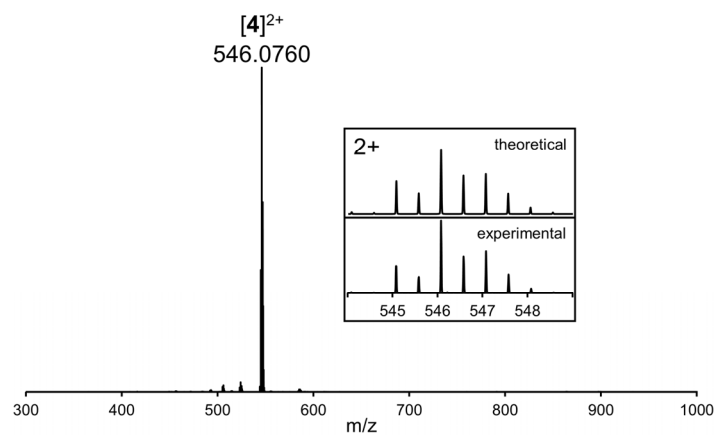


Figure S7. ESI-MS spectrum of **4**.

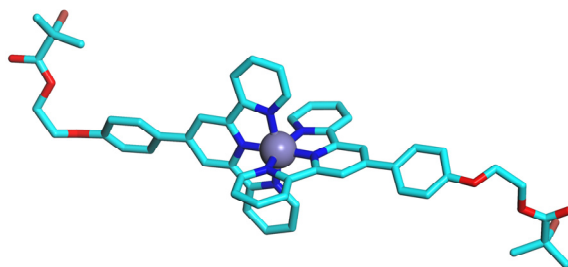
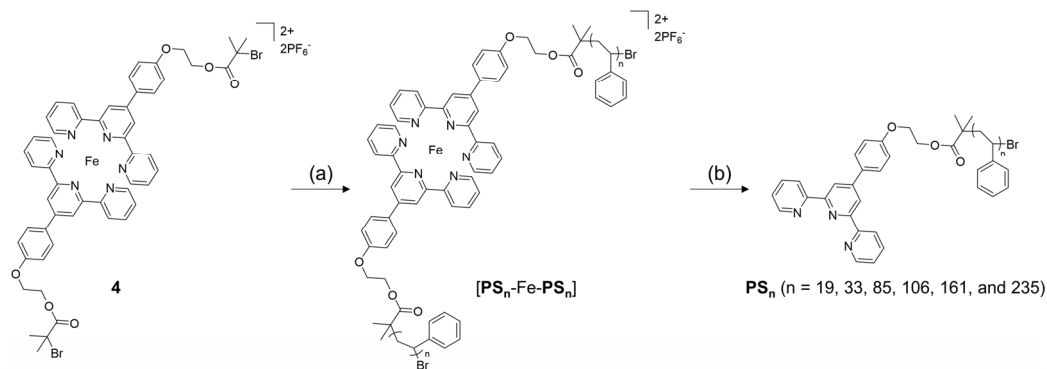


Figure S8. X-ray crystal structure of **4** (cyan, carbon; blue, nitrogen; red, oxygen; purple, iron; brown, bromine). Hydrogen atoms and PF_6^- ions are omitted for clarity.

2. Synthesis and Characterization of TPY-Functionalized PS



Scheme S2. Synthesis of tpy-functionalized polystyrene PS_n ($n = 19, 33, 85, 106, 161, \text{ and } 235$) from the metallo-initiator **4**. *Reagents and conditions:* (a) styrene, CuBr , PMDETA , MeCN , 110°C ; (b) EDTA , DMF , 25°C .

PS₁₉. To a degassed Schlenk flask containing CuBr (46.7 mg, $325.8\ \mu\text{mol}$) and **4** (150.1 mg, $108.6\ \mu\text{mol}$), the pre-degassed styrene (1.2 mL, $10.9\ \text{mmol}$) and MeCN ($466.0\ \mu\text{L}$) were added. The flask was further degassed by three freeze-pump-thaw cycles, and then PMDETA ($68.0\ \mu\text{L}$, $325.8\ \mu\text{mol}$) was added. After stirring at 110°C for 60 min, the reaction mixture was cooled to room temperature and then exposed to air. An excess amount of TEA-EDTA in DMF was added to the mixture, which was subsequently stirred at 25°C for 1 day. The reaction mixture was poured into MeOH and the precipitate was filtered and dried *in vacuo* to afford **PS₁₉** as a white powder (467.2 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.75–8.61 (m, 6H), 7.92–7.79 (m, 4H), 7.36 (dd, $J = 7.4, 5.1$, 2H), 7.23–6.86 (br, 57H), 6.86–6.26 (br, 38H), 3.97–3.79 (br, 4H), and 2.28–1.14 (br, 57H). GPC: $M_n = 1,900\ \text{Da}$, $M_w/M_n = 1.14$.

PS₃₃. By a similar procedure to that for **PS₁₉**, **PS₃₃** was obtained as a white powder (862.0 mg) from CuBr (40.3 mg, $280.8\ \mu\text{mol}$), **4** (129.4 mg, $93.6\ \mu\text{mol}$), styrene (2.1 mL, $18.7\ \text{mmol}$), MeCN ($0.7\ \text{mL}$), and PMDETA ($58.6\ \mu\text{L}$, $280.8\ \mu\text{mol}$). The polymerization was conducted at 110°C for 2 h before quenched. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.75–8.63 (m, 6H), 7.90–7.80 (m, 4H), 7.33 (dd, $J = 7.1, 4.9$, 2H), 7.23–6.84 (br, 99H), 6.84–6.22 (br, 66H), 3.98–3.82 (br, 4H), and 2.10–1.17 (br, 99H). GPC: $M_n = 3,600\ \text{Da}$, $M_w/M_n = 1.13$.

PS₈₅. By a similar procedure to that for **PS₁₉**, **PS₈₅** was obtained as a white powder (530.0 mg) from CuBr (20.3 mg, $141.3\ \mu\text{mol}$), **4** (65.1 mg, $47.1\ \mu\text{mol}$), styrene (1.1 mL, $9.4\ \text{mmol}$), MeCN ($360\ \mu\text{L}$), and PMDETA ($20.3\ \mu\text{L}$, $141.3\ \mu\text{mol}$). The polymerization was conducted at 110°C for 8 h before quenched. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.86–8.66 (m, 6H), 8.02–7.86 (m, 4H), 7.49–7.37 (br, 2H), 7.23–6.85 (br, 255H), 6.85–6.25 (br, 170H), 3.98–3.81 (br, 4H), and 2.41–1.06 (br, 255H). GPC: $M_n = 7,900\ \text{Da}$, $M_w/M_n = 1.21$.

PS₁₀₆. By a similar procedure to that for **PS₁₉**, **PS₁₀₆** was obtained as a white powder (463.1 mg) from CuBr (9.3 mg, $64.8\ \mu\text{mol}$), **4** (29.9 mg, $21.6\ \mu\text{mol}$), styrene (1.0 mL, $8.6\ \text{mmol}$), MeCN ($498.6\ \mu\text{L}$), and PMDETA ($13.5\ \mu\text{L}$, $64.8\ \mu\text{mol}$). The polymerization was conducted at 110°C for 8 h before quenched. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.80–8.64 (m, 6H), 7.96–7.80 (m, 4H), 7.42–7.30 (br, 2H), 7.23–6.86 (br, 318H), 6.86–6.19 (br, 212H), 4.03–3.82 (br, 4H), and 2.33–1.12 (br, 318H). GPC: $M_n = 11,900\ \text{Da}$, $M_w/M_n = 1.14$.

PS₁₆₁. By a similar procedure to that for **PS₁₉**, **PS₁₆₁** was obtained as a white powder (613.4 mg) from CuBr (9.3 mg, 64.8 μ mol), **4** (29.8 mg, 21.6 μ mol), styrene (2.0 mL, 17.3 mmol), MeCN (990.7 μ L), and PMDETA (13.5 μ L, 64.8 μ mol). The polymerization was conducted at 110 °C for 16 h before quenched. ¹H NMR (400 MHz, CDCl₃): δ 8.79–8.66 (m, 6H), 7.94–7.84 (m, 4H), 7.40–7.30 (br, 2H), 7.30–6.88 (br, 483H), 6.88–6.24 (br, 322H), 3.95 (br, 4H), and 2.32–1.18 (br, 483H). GPC: M_n = 16,200 Da, M_w/M_n = 1.17.

PS₂₃₅. By a similar procedure to that for **PS₁₉**, **PS₂₃₅** was obtained as a white powder (1.0 g) from CuBr (9.3 mg, 64.8 μ mol), **4** (29.8 mg, 21.6 μ mol), styrene (2.0 mL, 17.3 mmol), and PMDETA (13.5 μ L, 64.8 μ mol). The reaction mixture was conducted at 110 °C for 3 h before quenched. ¹H NMR (400 MHz, CDCl₃): δ 8.82–8.65 (m, 6H), 7.97–7.83 (m, 4H), 7.40–7.33 (br, 2H), 7.23–6.86 (br, 705H), 6.86–6.25 (br, 470H), 3.99–3.85 (br, 4H), and 2.29–1.14 (br, 705H). GPC: M_n = 22,000 Da, M_w/M_n = 1.26.

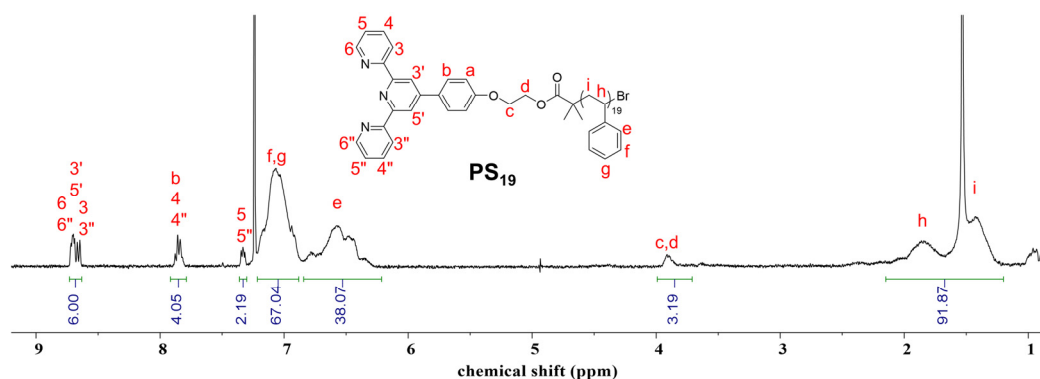


Figure S9. ¹H NMR spectrum of **PS₁₉** in CDCl₃.

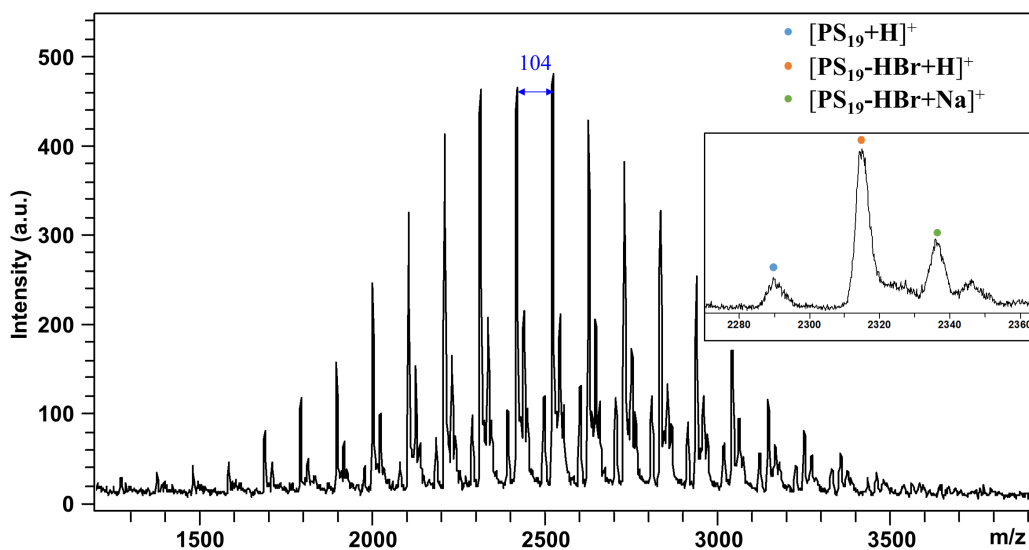


Figure S10. MALDI-TOF-MS spectrum of **PS₁₉**.

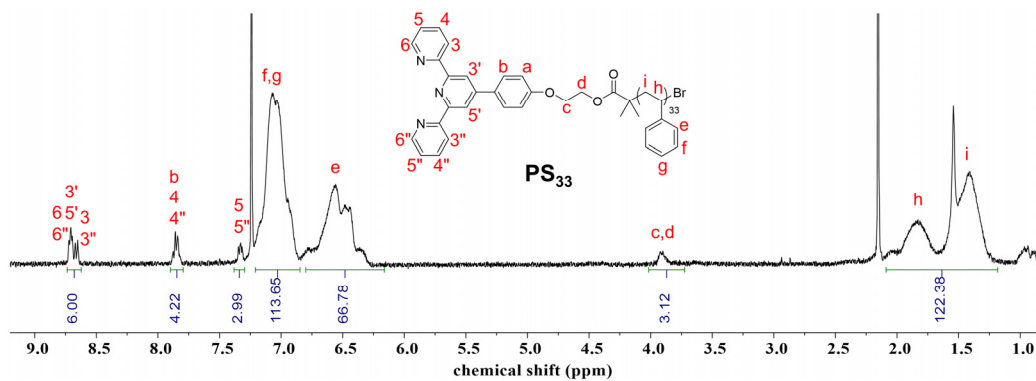


Figure S11. ^1H NMR spectrum of PS_{33} in CDCl_3 .

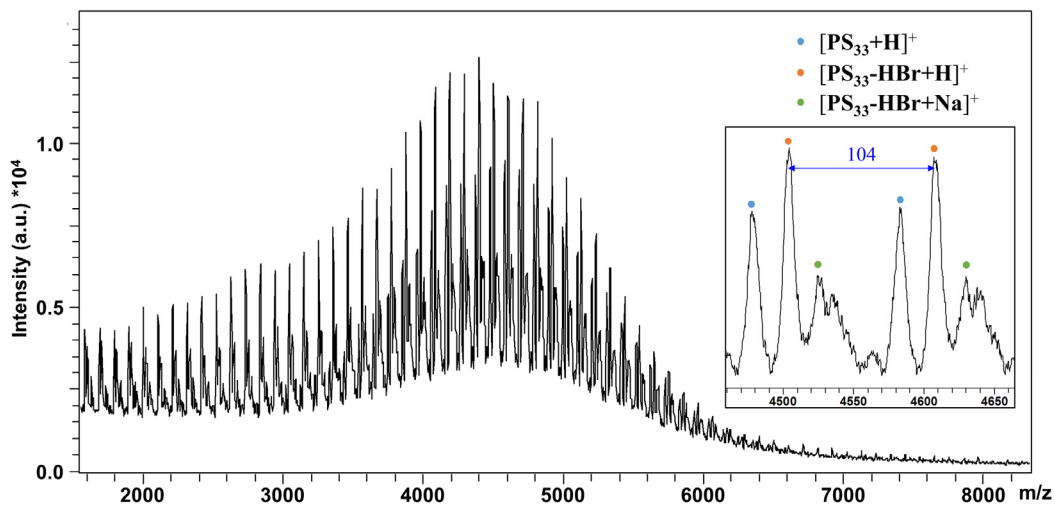


Figure S12. MALDI-TOF-MS spectrum of PS_{33} .

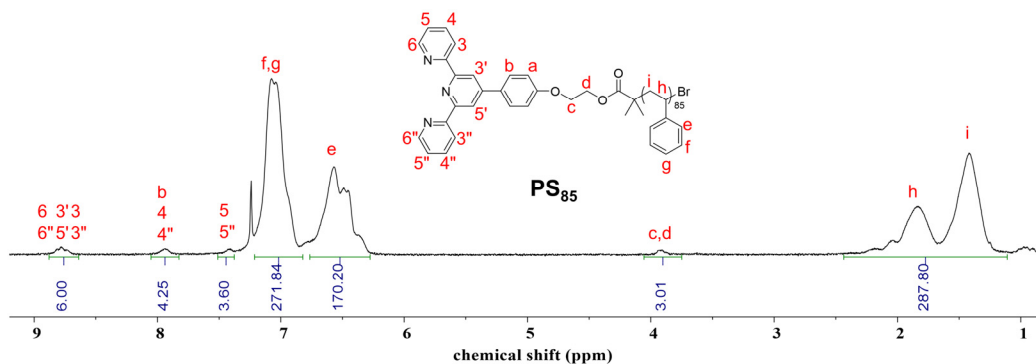


Figure S13. ^1H NMR spectrum of PS_{85} in CDCl_3 .

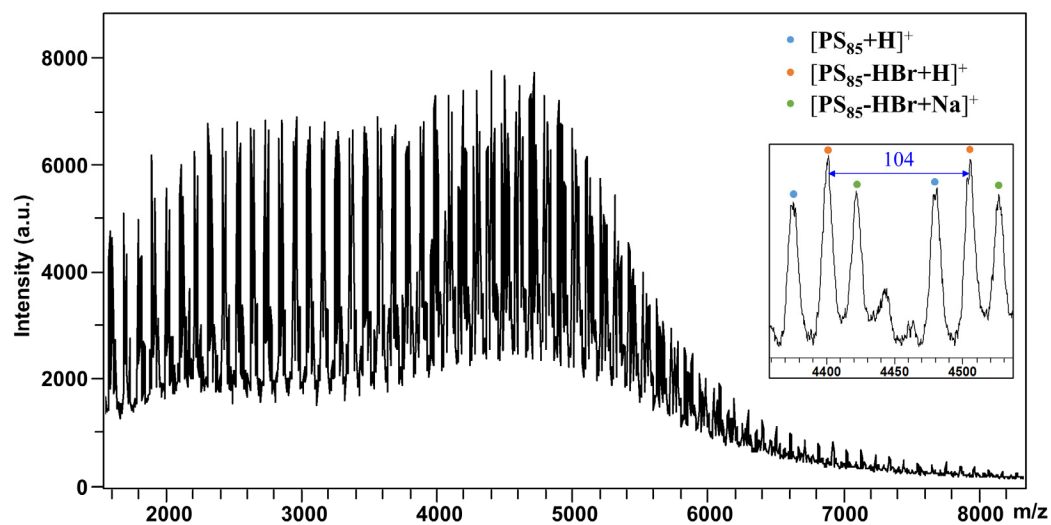


Figure S14. MALDI-TOF-MS spectrum of PS_{85} .

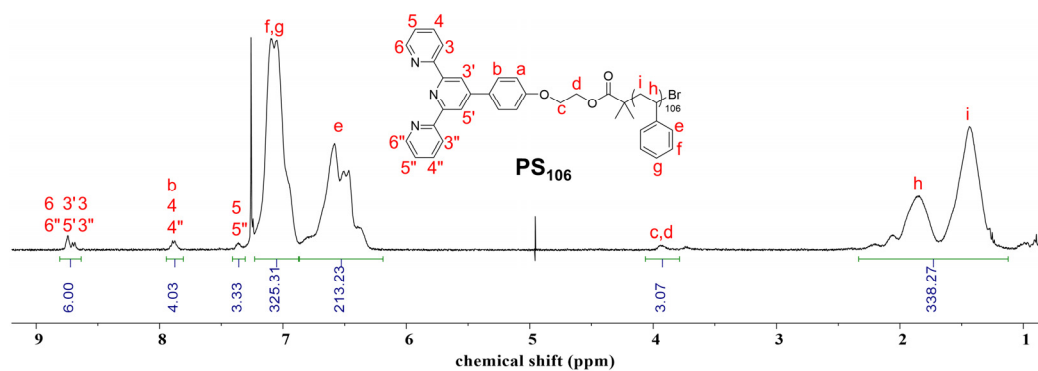


Figure S15. ^1H NMR spectrum of PS_{106} in CDCl_3 .

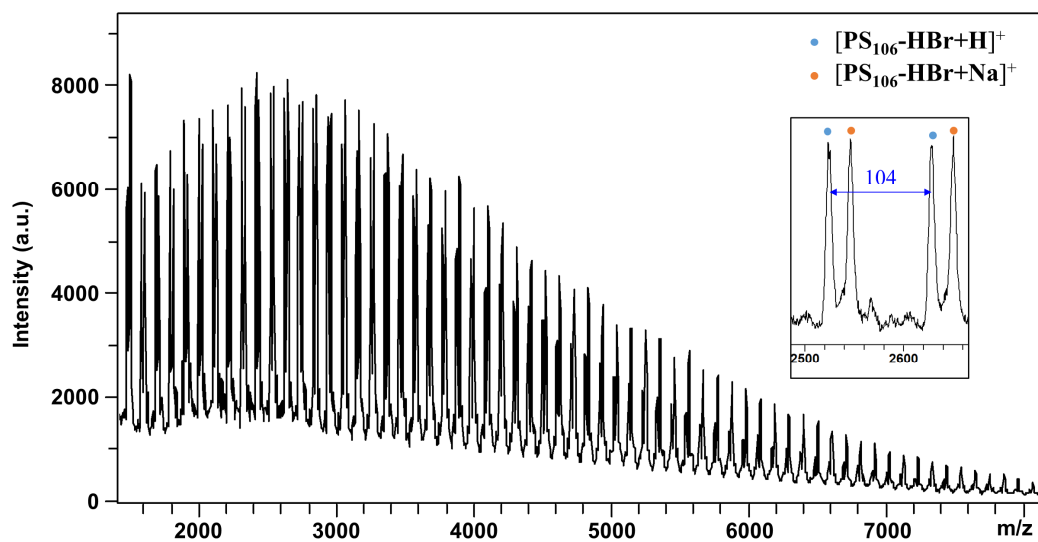


Figure S16. MALDI-TOF-MS spectrum of PS_{106} .

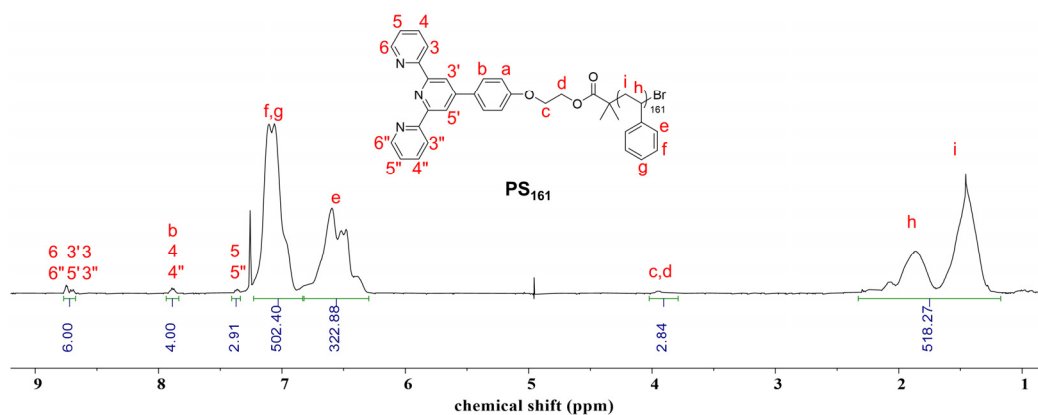


Figure S17. ^1H NMR spectrum of **PS₁₆₁** in CDCl_3 .

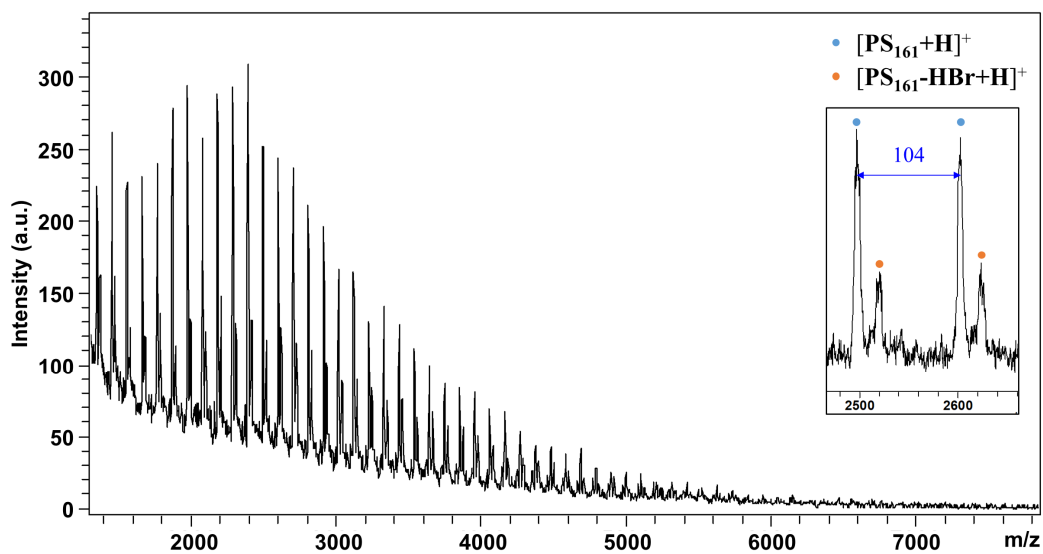


Figure S18. MALDI-TOF-MS spectrum of **PS₁₆₁**.

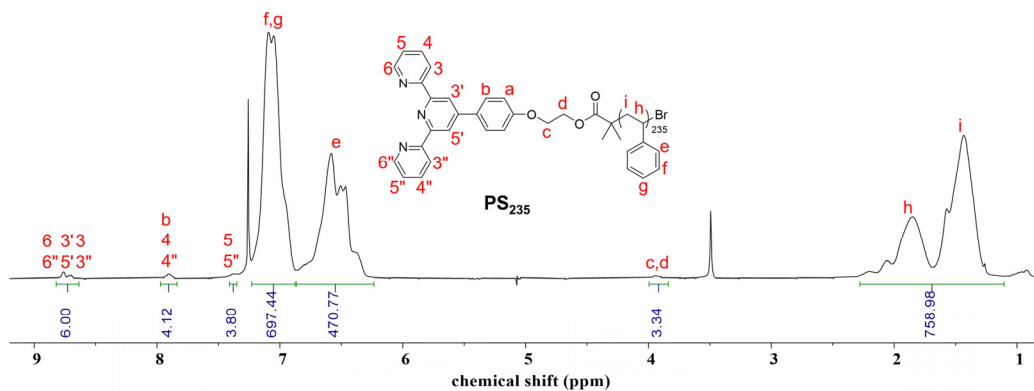


Figure S19. ^1H NMR spectrum of **PS₂₃₅** in CDCl_3 .

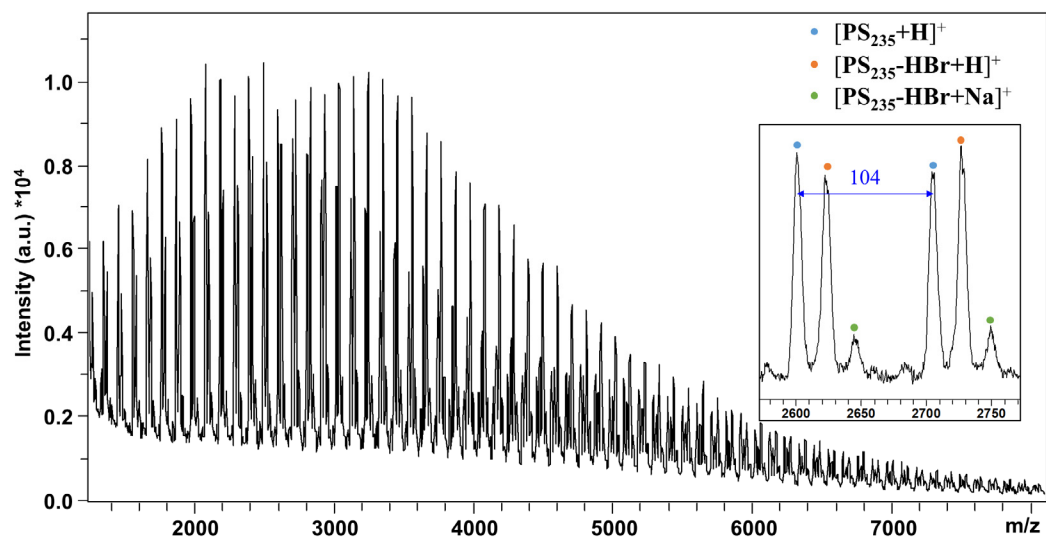


Figure S20. MALDI-TOF-MS spectrum of **PS₂₃₅**.

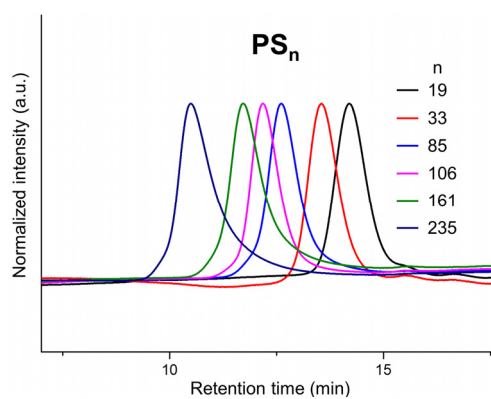
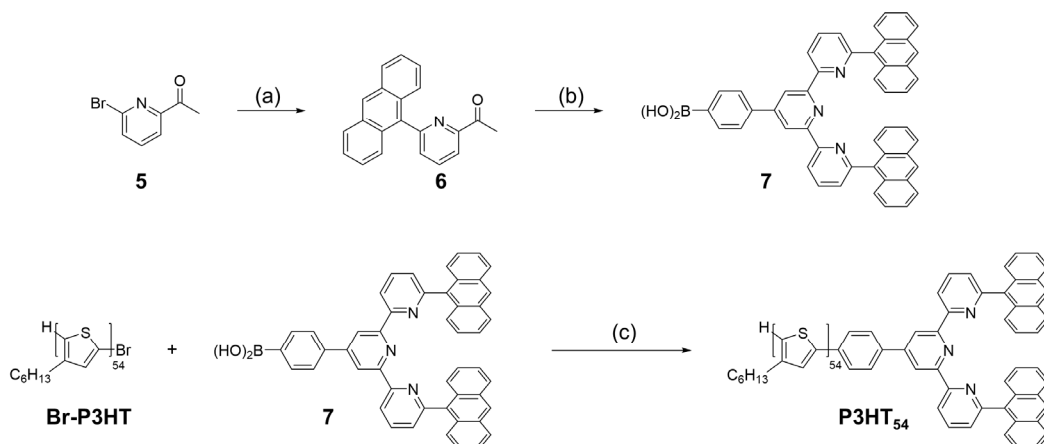


Figure S21. GPC traces of **PS₁₉** ($M_n = 1,900$, $M_w/M_n = 1.14$), **PS₃₃** ($M_n = 3,600$, $M_w/M_n = 1.13$), **PS₈₅** ($M_n = 7,900$, $M_w/M_n = 1.21$), **PS₁₀₆** ($M_n = 11,900$, $M_w/M_n = 1.14$), **PS₁₆₁** ($M_n = 16,200$, $M_w/M_n = 1.17$), and **PS₂₃₅** ($M_n = 22,000$, $M_w/M_n = 1.26$).

3. Synthesis and Characterization of P3HT₅₄



Scheme S3. Synthesis of **P3HT₅₄**. *Reagents and conditions:* (a) 9-anthraceneboronic acid, Na₂CO₃, Pd(PPh₃)₄, toluene/H₂O/*t*-BuOH (3/3/1, v/v/v), reflux; (b) 1) 4-formylphenylboronic acid, NaOH, EtOH, 25 °C, 2) NH₄OH, reflux; (c) Pd(PPh₃)₄, NaOH, THF/H₂O (3/1, v/v), reflux.

Compound 6. To a degassed two-neck flask containing **5** (15.0 g, 75.0 mmol), 9-anthraceneboronic acid (21.6 g, 97.5 mmol), and Na₂CO₃ (79.5 g, 750.0 mol), a mixed solvent (466.0 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 (808.9 mg, 0.7 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 **6** as a pale-yellow solid (20.0 g, 9.1 mmol) in 90% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.57 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.10 – 8.00 (m, 3H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.47 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.37 (dd, *J* = 8.7, 7.1 Hz, 2H), and 2.68 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 200.93, 157.90, 154.16, 137.31, 134.63, 131.62, 130.60, 130.24, 128.83, 128.17, 126.27, 126.01, 125.46, 120.44, and 26.25. MALDI-TOF-MS: calcd for C₂₁H₁₆NO [M + H]⁺: *m/z* = 298.1232; found: 298.1245.

Compound 7. To an EtOH (80 mL) solution of **6** (6.1 g, 20.5 mmol), NaOH (820.6 mg, 20.5 mmol) and 4-formylphenylboronic acid (1.4 g, 9.3 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 filtered and washed with CHCl₃ to afford **7** as a yellow solid (4.0 g, 5.7 mmol) in 61% yield. ¹H NMR (400 MHz, CD₃OD/CDCl₃ = 4/1, v/v): δ (ppm) 8.90 (d, *J* = 7.8 Hz, 2H), 8.66 (s, 2H), 8.63 (s, 2H), 8.25 (dd, *J* = 7.8, 7.8 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 4H), 7.70 (d, *J* = 8.8 Hz, 4H), 7.64 (d, *J* = 7.2 Hz, 2H), and 7.54–7.38 (m, 10H). ¹³C NMR (100 MHz, CD₃OD/CDCl₃ = 4/1, v/v): δ (ppm) 159.06, 158.58, 157.19, 153.17, 138.94, 138.85, 136.46, 136.39, 134.79, 132.90, 131.60, 129.83, 129.01, 128.41, 127.43, 127.29, 126.56, 121.99, 120.78, and 119.99. MALDI-TOF-MS: calcd for C₄₉H₃₃BN₃O₂ [M + H]⁺: *m/z* = 706.2666; found: 706.2579.

P3HT₅₄. To a degassed two-neck flask containing **7** (302.1 mg, 428.5 μmol), monobrominated **Br-P3HT** (2.0 g, 219.4 μmol, *M_n* = 9,100, *M_w*/*M_n* = 1.18), and NaOH (2.0 g, 50.0 mmol), a mixed solvent (170 mL) of THF/H₂O (3/1, v/v) was added. After being purged with N₂ for 30 min, Pd(PPh₃)₄ (30.5 mg, 26.4 μmol) was added into the mixture, which was then refluxed for 2 days under N₂. After cooling to room temperature, the mixture was extracted

with CHCl_3 and the combined organic extract was dried over MgSO_4 and then evaporated to dryness under reduced pressure. The residue was purified by precipitation from $\text{CH}_3\text{OH}/\text{CHCl}_3$ to give **P3HT**₅₄ as a deep purple solid (2.0 g, 248.6 μmol , DP = 54) in 87% yield. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.92 (m, 2H), 8.73 (s, 2H), 8.59 (s, 2H), 8.21 (m, 2H), 8.16 (m, 4H), 7.76 (m, 4H), 7.67 (m, 2H), 7.56 (s, 2H), 7.47 (s, 4H), 7.41 (s, 6H), 6.98 (s, 54H), 2.79 (s, 108H), 1.71 (s, 108H), 1.30 (d, 324H), and 0.92 (s, 108H). GPC: M_n = 8,800 Da, M_w/M_n = 1.23.

Isomeric structures of P3HT₅₄. The mono-brominated P3HT prepared by GRIM have two kinds of chain ends, namely head-to-head and head-to-tail orientations. The difference could be distinguished by the ^1H NMR spectra of **P3HT**₅₄ [1]. The chain-end head-to-tail content is about 22% (Figure S26).

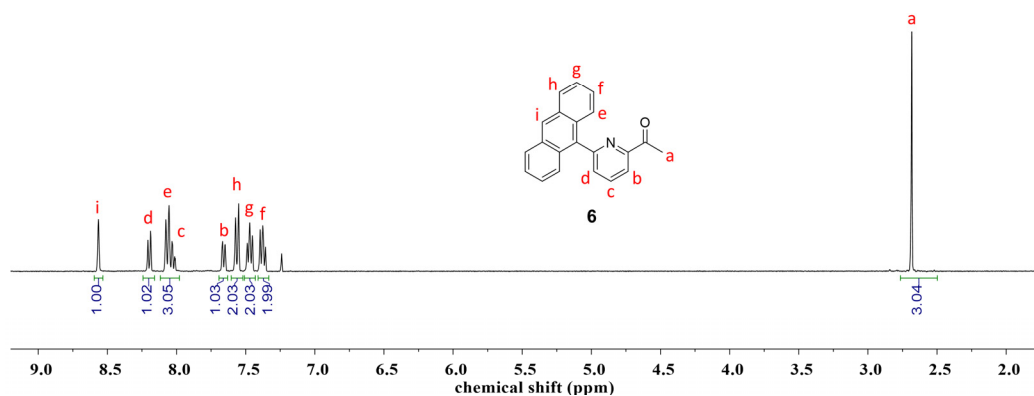


Figure S22. ^1H NMR spectrum of **6** in CDCl_3 .

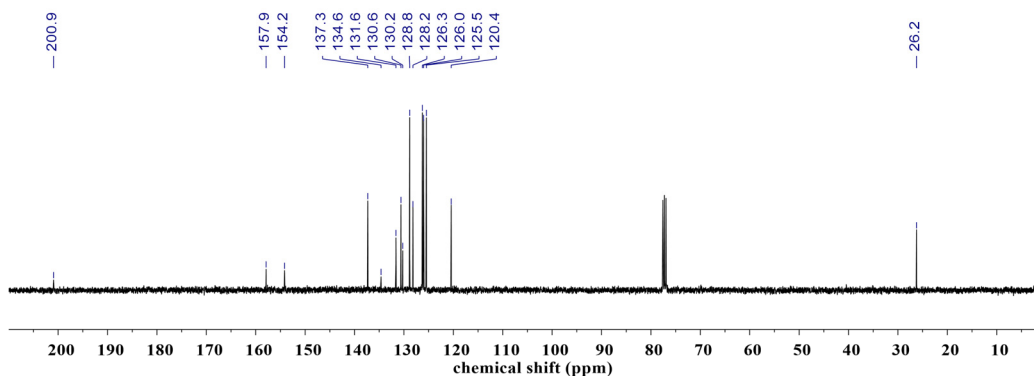


Figure S23. ^{13}C NMR spectrum of **6** in CDCl_3 .

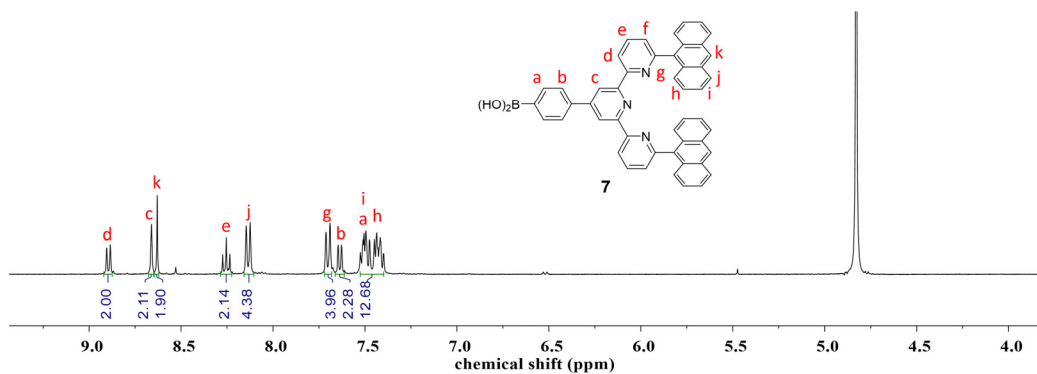


Figure S24. ^1H NMR spectrum of **7** in $\text{CD}_3\text{OD}/\text{CDCl}_3$ (4/1, v/v).

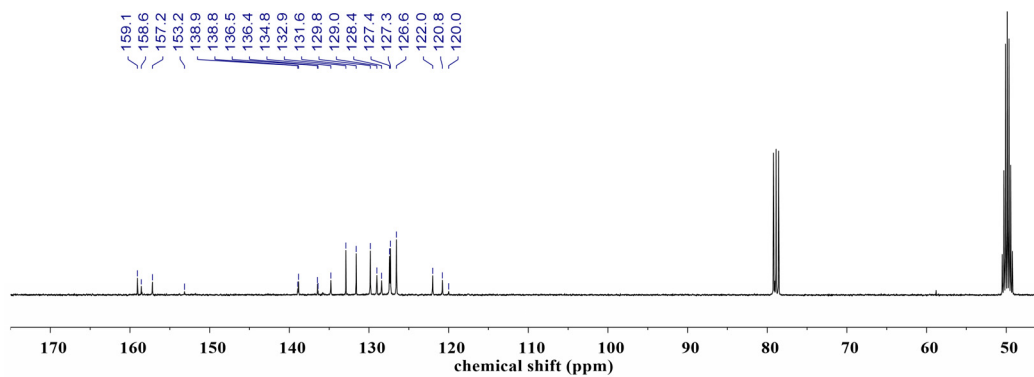


Figure S25. ^{13}C NMR spectrum of **7** in $\text{CD}_3\text{OD}/\text{CDCl}_3$ (4/1, v/v).

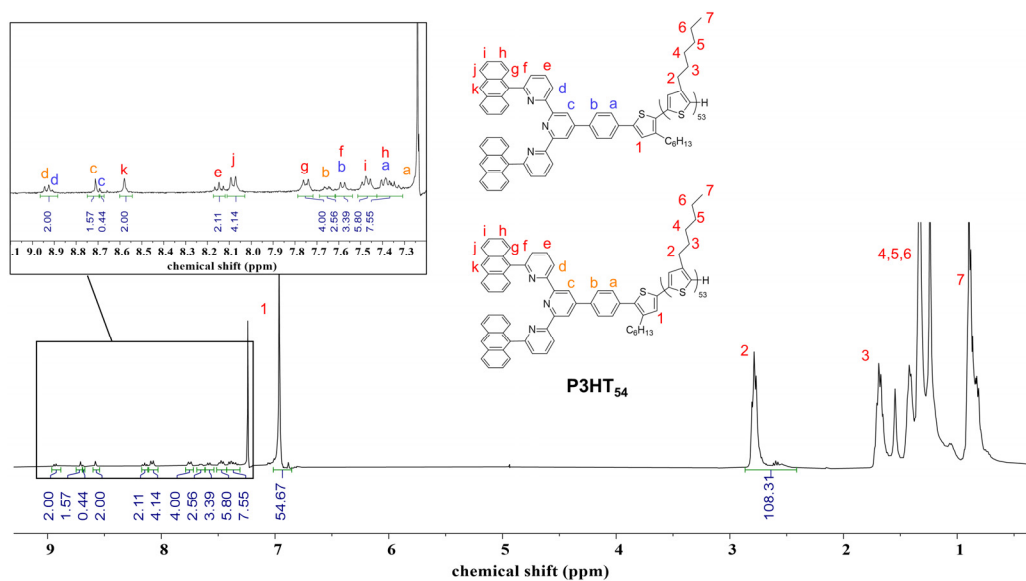


Figure S26. ^1H NMR spectrum of **P3HT₅₄**.

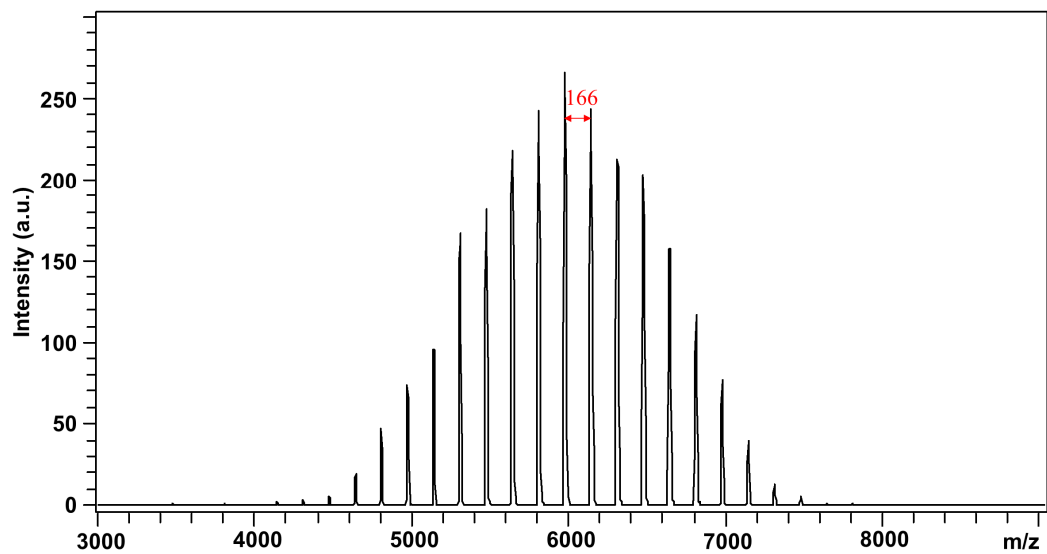


Figure S27. ^1H NMR spectrum of P3HT_{54} .

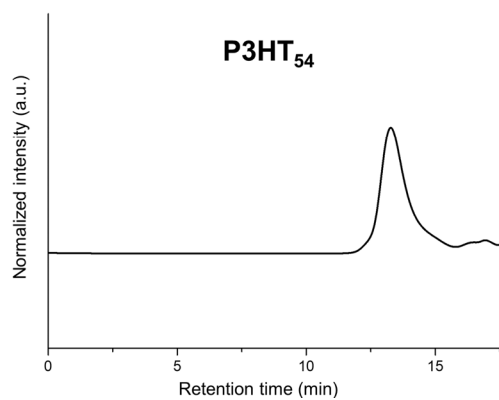
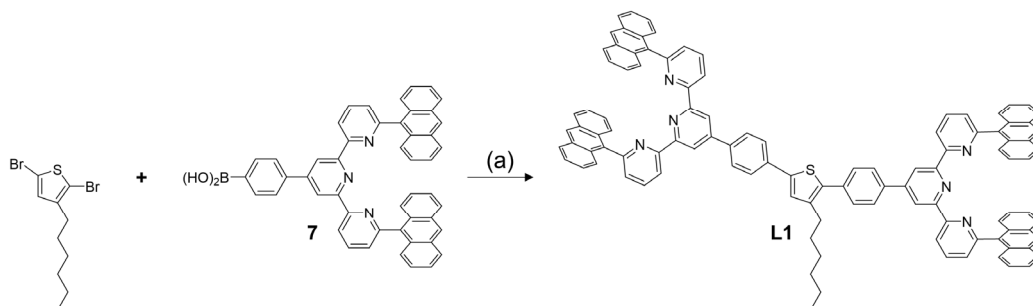


Figure S28. GPC trace of P3HT_{54} (THF was used as eluent. $M_n = 8,800$ Da, $M_w/M_n = 1.23$).



Scheme S4. Synthesis of **L1**. Reagents and conditions: (a) Na_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene/ H_2O / t -BuOH (3/3/1, v/v/v), reflux.

Compound L1. To a degassed two-neck flask containing 2,5-dibromo-3-hexylthiophene (0.2 g, 0.6 mmol), **7** (1.3 g, 1.8 mmol), and Na_2CO_3 (2.2 g, 20.7 mmol), a mixed solvent (56 mL) of toluene/ H_2O / t -BuOH (3/3/1, v/v/v) was added. After being purged with N_2 for 30 min, $\text{Pd}(\text{PPh}_3)_4$ (208.0 mg, 0.2 mmol) was added into the mixture, which was refluxed for 2 days under N_2 . After cooling to 25°C , the mixture was extracted with CHCl_3 and H_2O . The combined organic extract was dried over anhydrous MgSO_4 and then evaporated to dryness under reduced pressure. The residue was purified by column chromatography (Al_2O_3 , CH_2Cl_2 /hexane = 3/1). The crude was recrystallized from MeOH to give **L1** as a yellow solid (757.2 mg, 0.5 mmol) in 83% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.93–8.86 (m, 4H), 8.67 (s, 2H), 8.65 (s, 2H), 8.56 (s, 4H), 8.13 (dd, $J = 8.5, 7.5$ Hz, 4H), 8.06 (d, $J = 8.1$ Hz, 4H), 7.75–7.70 (m, 8H), 7.76–7.71 (m, 8H), 7.45 (dd, $J = 8.6, 6.5$ Hz, 8H), 7.41–7.32 (m, 10H), 7.25 (d, $J = 8.6$, 2H), 7.00 (s, 1H), 2.43 (t, $J = 7.8$ Hz, 2H), 1.46–1.37 (m, 2H), 1.31–1.22 (m, 6H), and 1.15–1.03 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 157.60, 157.58, 156.65, 156.61, 156.07, 149.56, 149.47, 141.43, 140.09, 137.03, 137.00, 136.88, 135.55, 135.49, 134.97, 134.61, 131.42, 130.14, 129.20, 128.43, 127.61, 127.53, 127.49, 127.45, 127.36, 127.33, 126.97, 126.32, 126.30, 125.98, 125.78, 125.76, 125.52, 125.15, 119.95, 119.92, 119.26, 119.10, 31.47, 30.72, 29.00, 28.79, 22.43, and 13.95. MALDI-TOF-MS: calcd for $\text{C}_{108}\text{H}_{75}\text{N}_6\text{S}$ [$\text{M} + \text{H}$] $^+$: $m/z = 1487.5773$; found: 1487.5695.

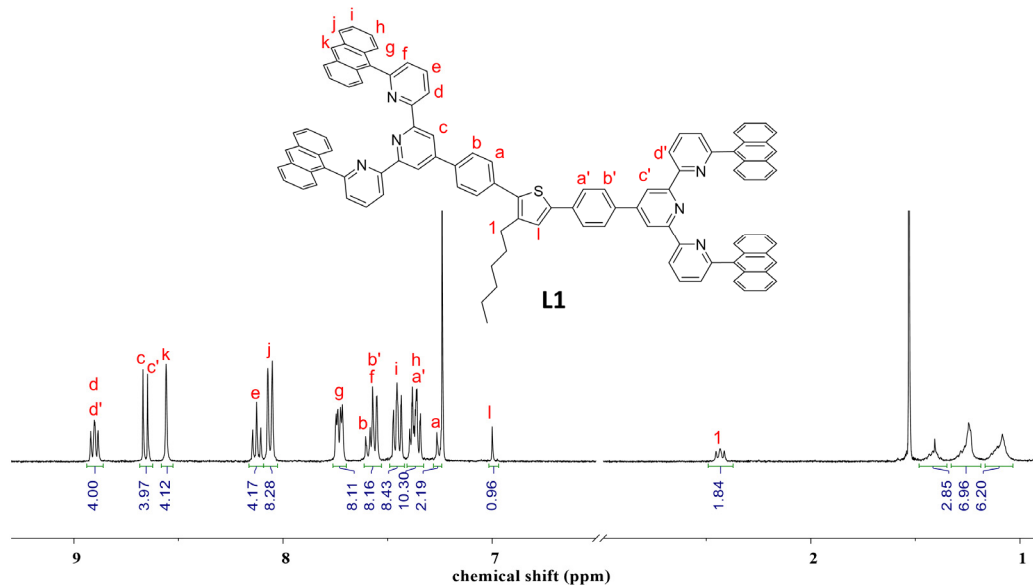


Figure S29. ^1H NMR spectrum of **L1** in CDCl_3 .

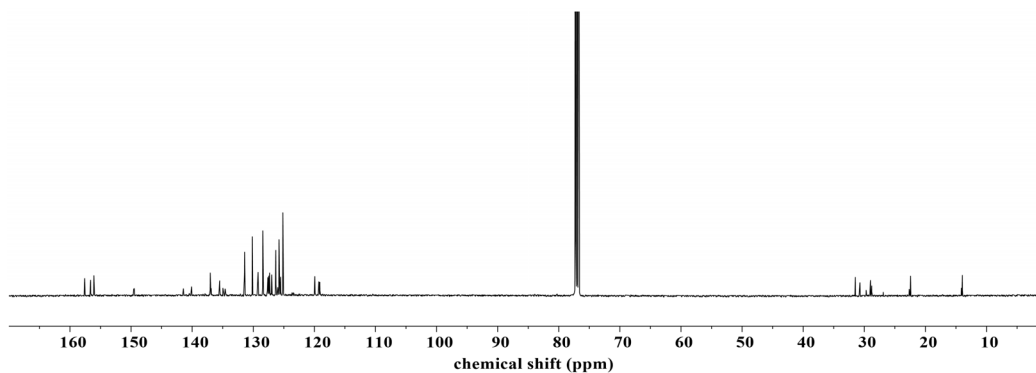


Figure S30. ^{13}C NMR spectrum of **L1** in CDCl_3 .

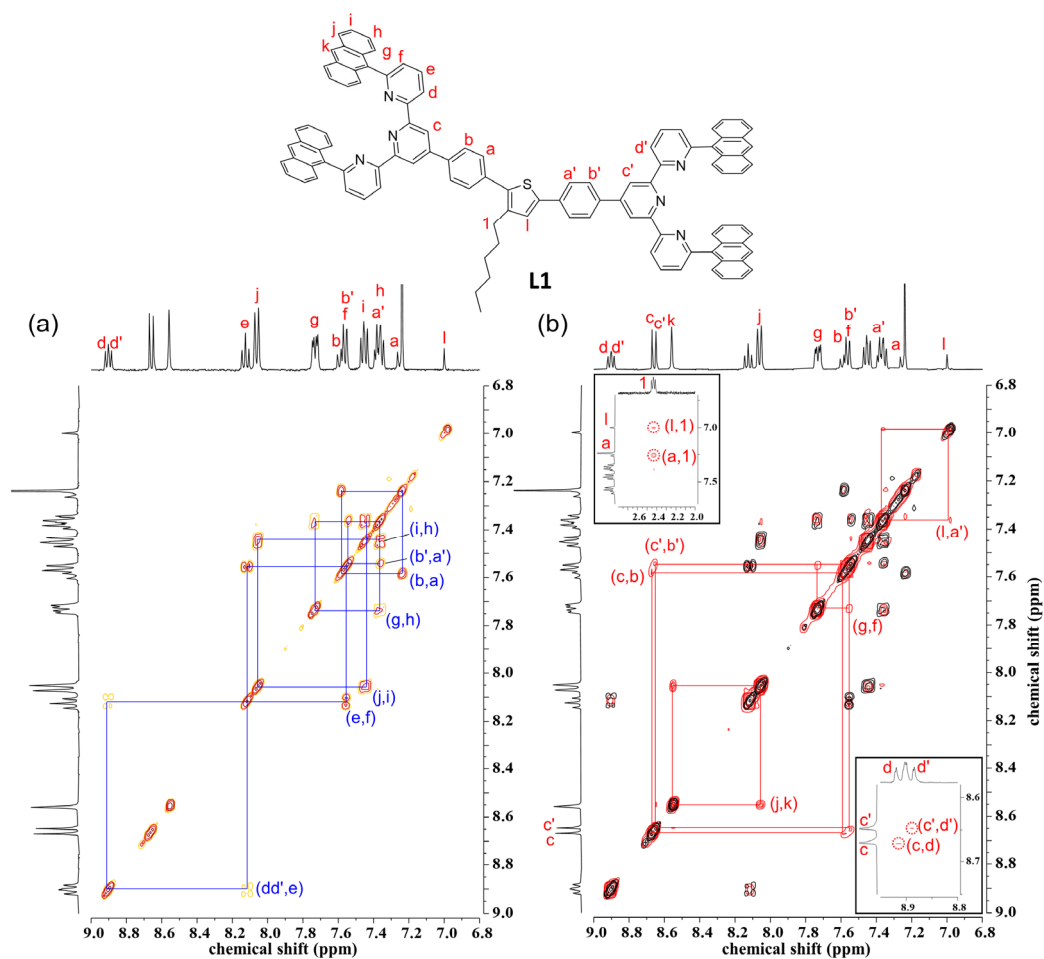


Figure S31. (a) COSY NMR spectrum of **L1** in CDCl_3 . (b) Overlapped NOESY (red) and COSY (black) NMR spectra of **8** (insets: partial NOESY spectra).

4. Crystal data

Crystallographic data were acquired on an Oxford Diffraction Gemini A CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structures of **4** and [L2-Zn-L3] were deposited at the Cambridge Crystallographic Data Center with the deposition numbers of CCDC 2043189 and 2043188, respectively.

Table S1. Crystal data and experimental details for metallo-initiator **4**.

| | | |
|--------------------------------------|--|-----------------------------|
| Identification code | ic20571 | |
| Empirical formula | C ₅₄ H ₄₈ Br ₂ F ₁₂ FeN ₆ O ₆ P ₂ | |
| Formula weight | 1382.59 | |
| Crystal system | Monoclinic | |
| Space group | Pn | |
| Unit cell dimensions | a = 16.473(2) Å | $\alpha = 90^\circ$. |
| | b = 9.0854(7) Å | $\beta = 98.448(8)^\circ$. |
| | c = 37.973(3) Å | $\gamma = 90^\circ$. |
| Volume | 5621.5(9) Å ³ | |
| Z | 4 | |
| F(000) | 2784 | |
| Density (calculated) | 1.634 Mg m ⁻³ | |
| Wavelength | 0.71073 Å | |
| Cell parameters reflections used | 4192 | |
| Theta range for Cell parameters | 3.1550 to 22.2550°. | |
| Absorption coefficient | 1.842 mm ⁻¹ | |
| Temperature | 100(2) K | |
| Crystal size | 0.300 x 0.250 x 0.010 mm ³ | |
| Data collection | | |
| Diffractometer | Xcalibur, Atlas, Gemini | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000 and 0.68911 | |
| No. of measured reflections | 23625 | |
| No. of independent reflections | 14606 [R(int) = 0.0749] | |
| No. of observed [$I > 2\sigma(I)$] | 7263 | |
| Completeness to theta = 25.242° | 99.7 % | |
| Theta range for data collection | 3.136 to 27.499°. | |
| Refinement | | |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0914, wR2 = 0.2037 | |
| R indices (all data) | R1 = 0.2073, wR2 = 0.2762 | |
| Goodness-of-fit on F ² | 1.277 | |
| No. of reflections | 14606 | |
| No. of parameters | 1538 | |

| | |
|------------------------------|------------------------------------|
| No. of restraints | 519 |
| Absolute structure parameter | 0.19(2) |
| Largest diff. peak and hole | 1.258 and -1.244 e.Å ⁻³ |

Table S2. Crystal data and experimental details for [L2-Zn-L3].

| | | |
|----------------------------------|--|-----------------------------|
| Identification code | ic20502 | |
| Empirical formula | C ₇₈ H ₆₀ F ₆ N ₆ O ₉ S ₂ Zn | |
| Formula weight | 1468.81 | |
| Crystal system | Monoclinic | |
| Space group | Cc | |
| Unit cell dimensions | a = 24.443(4) Å | $\alpha = 90^\circ$. |
| | b = 17.210(3) Å | $\beta = 124.58(3)^\circ$. |
| | c = 20.276(4) Å | $\gamma = 90^\circ$. |
| Volume | 7023(3) Å ³ | |
| Z | 4 | |
| F(000) | 3032 | |
| Density (calculated) | 1.389 Mg m ⁻³ | |
| Wavelength | 0.71073 Å | |
| Cell parameters reflections used | 3806 | |
| Theta range for Cell parameters | 4.0900 to 26.5370°. | |
| Absorption coefficient | 0.489 mm ⁻¹ | |
| Temperature | 110(2) K | |
| Crystal size | 0.20 x 0.15 x 0.10 mm ³ | |

Data collection

| | |
|--------------------------------------|---------------------------------|
| Diffractometer | Xcalibur, Atlas, Gemini |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.76530 |
| No. of measured reflections | 16379 |
| No. of independent reflections | 10909 [R(int) = 0.0415] |
| No. of observed [$I > 2\sigma(I)$] | 6767 |
| Completeness to theta = 25.242° | 99.5 % |
| Theta range for data collection | 3.115 to 27.498°. |

Refinement

| | |
|--------------------------------------|---------------------------|
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0754, wR2 = 0.1860 |
| R indices (all data) | R1 = 0.1281, wR2 = 0.2309 |
| Goodness-of-fit on F ² | 1.130 |
| No. of reflections | 10909 |
| No. of parameters | 919 |

No. of restraints 50
Absolute structure parameter 0.015(13)
Largest diff. peak and hole 0.862 and -0.638 e.Å⁻³

References

1. He, Y.-J.; Tu, T.-H.; Su, M.-K.; Yang, C.-W.; Kong, K.V.; Chan, Y.-T. Facile Construction of Metallo-Supramolecular Poly(3-hexylthiophene)-*block*-Poly(ethylene oxide) Diblock Copolymers via Complementary Coordination and Their Self-Assembled Nanostructures. *J. Am. Chem. Soc.* **2017**, *139*, 4218-4224, doi:10.1021/jacs.7b01010.