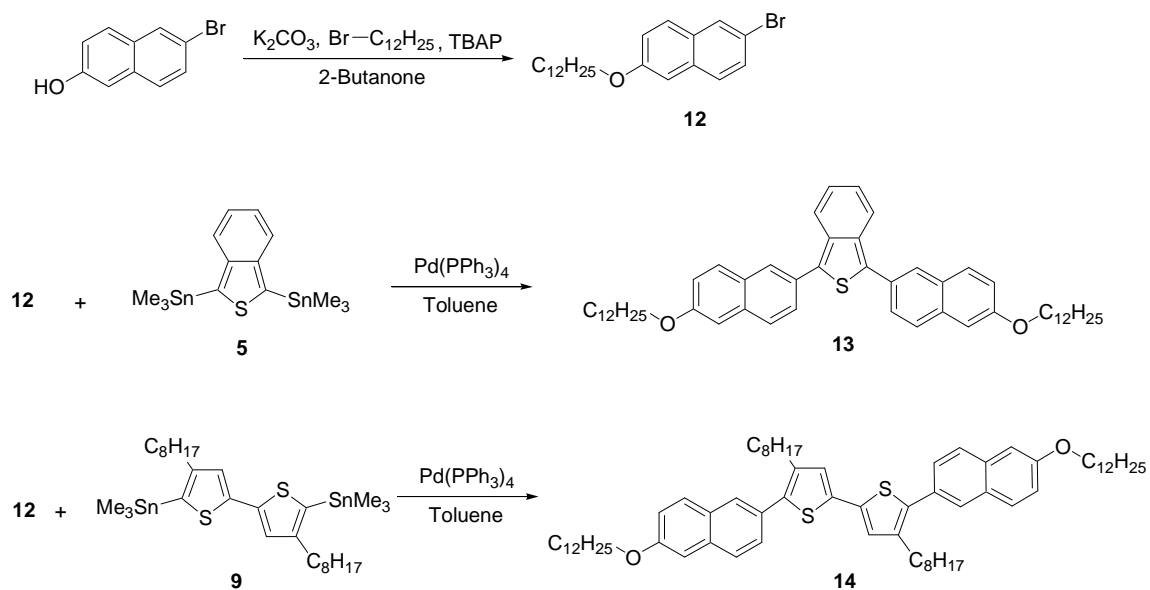


## Synthesis and Optical Properties of 1,1-Binaphthyl-Thiophene Alternating Copolymers with Main Chain Chirality

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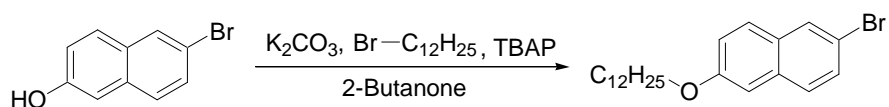
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Scheme S1. Synthesis of model compounds.

### 2-Bromo-6-dodecyloxy-naphthalene (12)

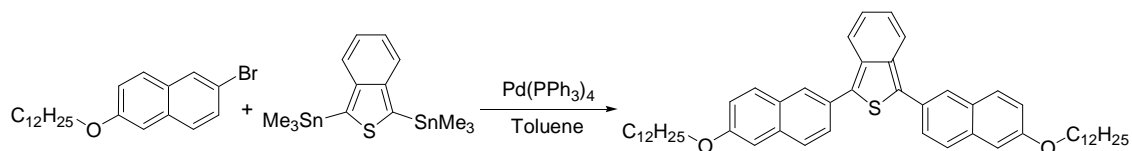


Scheme S2

6-Bromonaphthol (1.12 g, 5.0 mmol), potassium carbonate (0.83 g, 6.0 mmol), 1-bromododecane (1.50 g, 6.0 mmol), and TBAP (0.085 g, 0.25 mmol) were mixed in 10 mL of 2-butanone and refluxed at 80 °C for 24 hours. After evaporation of the solvent, the residue was extracted with dichloromethane, and dried over magnesium

sulfate. Recrystallization from ethanol to afford white solid (1.72 g, 4.4 mmol, yield = 88%).  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ; TMS)  $\delta$  0.88 (t, 3H,  $-\text{CH}_3$ ,  $J = 6.8$  Hz), 1.27 - 1.37 (m, 16H,  $-\text{C}_8\text{H}_{16}-\text{CH}_3$ ), 1.49 (quintet, 2H,  $-\text{CH}_2-\text{C}_9\text{H}_{19}$ ,  $J = 7.3$  Hz), 1.84 (quintet, 2H,  $-\text{CH}_2-\text{C}_{10}\text{H}_{21}$ ,  $J = 7.0$  Hz), 4.05 (t, 2H,  $\text{O}-\text{CH}_2-\text{C}_{11}\text{H}_{23}$ ,  $J = 6.8$  Hz), 7.08 (d, 1H,  $5\text{H}$ -(naphthalene),  $J = 2.4$  Hz), 7.16 (dd, 1H,  $7\text{H}$ -(naphthalene),  $J = 2.6$  Hz), 7.48 (dd, 1H,  $3\text{H}$ -(naphthalene),  $J = 1.8$  Hz), 7.58 (d, 1H,  $4\text{H}$ -(naphthalene),  $J = 8.8$  Hz), 7.63 (d, 1H,  $8\text{H}$ -(naphthalene),  $J = 8.8\text{Hz}$ ), 7.90 (d, 1H,  $1\text{H}$ -(naphthalene),  $J = 2.0$  Hz).  $^{13}\text{C}$  (100 MHz;  $\text{CDCl}_3$ ; TMS)  $\delta$  14.14, 22.70, 26.10, 29.20, 29.37, 29.41, 29.60, 29.61, 29.64, 29.67, 31.92, 68.10, 106.47, 116.86, 120.09, 128.33, 128.40, 129.52, 129.62, 129.90, 133.09, 157.42.

### 1,3-Bis-(6-dodecyloxy-naphthalen-2-yl)-isothianaphthene (13)

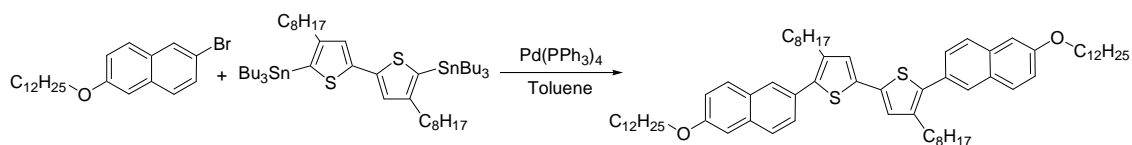


Scheme S3

A solution 1,3-bis-trimethylstannanyl-isothianaphthene (0.138 g, 0.30 mmol),

2-bromo-6-dodecyloxy-naphthalene (0.247, 0.63 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.007 g, 0.006 mmol) in toluene (2 mL) were refluxed at 90 °C for 24 hours. After cooling to room temperature, the mixture was purified silica gel column chromatography (contain 10 v/v% of potassium carbonate) (eluent: hexane/chloroform = 7/3) to afford an orange solid (0.116 g, 0.15 mmol, yield = 51%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; TMS) δ 0.88 (t, 6H, -CH<sub>3</sub>, *J* = 7.0 Hz), 1.28 - 1.41 (m, 32H, -O-C<sub>3</sub>H<sub>6</sub>-C<sub>8</sub>H<sub>16</sub>-CH<sub>3</sub>), 1.49 - 1.54 (m, 4H, -O-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-C<sub>9</sub>H<sub>19</sub>), 1.87 (quintet, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>10</sub>H<sub>21</sub>, *J* = 7.1 Hz), 4.11 (t, 4H, -O-CH<sub>2</sub>-, *J* = 6.6 Hz), 7.13 (dd, 2H, 5,6-*H*-(isothianaphthene), *J* = 3.2, 6.8 Hz), 7.18 (d, 2H, 5*H*-(naphthalene), *J* = 2.4 Hz), 7.21 (dd, 2H, 7*H*-(naphthalene), *J* = 2.2, 8.6 Hz), 7.79 - 7.85 (m, 6H, 3,4,7-*H*-(naphthalene)), 7.93 (dd, 2H, 4,7-*H*-(isothianaphthene), *J* = 3.2, 6.8 Hz), 8.08 (s, 2H, 1*H*-(naphthalene)). <sup>13</sup>C (100 MHz; CDCl<sub>3</sub>; TMS) δ 14.14, 22.70, 26.13, 29.25, 29.37, 29.45, 29.61, 29.63, 29.66, 29.69, 31.93, 68.14, 106.53, 119.78, 121.36, 124.20, 127.41, 127.61, 127.88, 129.13, 129.52, 133.87, 134.42, 135.27, 157.51.

### 5,5'-Bis-(6-dodecyloxy-naphthalen-2-yl)-4,4'-dioctyl-[2,2']bithiophenyl (14)



Scheme S4

A solution 4,4'-dioctyl-5,5'-bistrimethylstannyl-2,2'-bithiophene (0.215 g, 0.30 mmol), 2-bromo-6-dodecyloxy-naphthalene (0.247, 0.63 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.007 g, 0.006 mmol) in toluene (2 mL) were refluxed at 90 °C for 24 hours. After cooling to room temperature, the mixture was purified silica gel column chromatography (contain 10 v/v% of potassium carbonate) (eluent: hexane/dichloromethane = 8/2) to afford a yellow solid (0.120 g, 0.12 mmol, yield = 40%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>; TMS) δ 0.84 - 0.90 (m, 12H, -CH<sub>3</sub>), 1.23 - 1.37 (m, 52H, (Thophene)-C<sub>2</sub>H<sub>4</sub>-C<sub>5</sub>H<sub>10</sub>-CH<sub>3</sub>, -O-C<sub>3</sub>H<sub>6</sub>-C<sub>8</sub>H<sub>16</sub>-CH<sub>3</sub>), 1.47 - 1.53 (m, 4H, -O-C<sub>2</sub>H<sub>4</sub>-CH<sub>2</sub>-C<sub>9</sub>H<sub>19</sub>), 1.66 (quintet, 4H, (Thophene)-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>6</sub>H<sub>13</sub>, *J* = 7.5 Hz), 1.86 (quintet, 4H, -O-CH<sub>2</sub>-CH<sub>2</sub>-C<sub>10</sub>H<sub>21</sub>, *J* = 7.0 Hz), 2.69 (t, 4H, (Thophene)-CH<sub>2</sub>, *J* = 8.0 Hz), 4.09 (t, 4H, -O-CH<sub>2</sub>-, *J* = 6.6 Hz), 7.10 (s, 2H, 3,3'-*H*-(bithiophene)), 7.15 (d, 2H, 5*H*-(naphthalene), *J* = 2.4 Hz), 7.18 (dd, 2H, 7*H*-(naphthalene), *J* = 2.6, 9.0 Hz), 7.54 (dd, 2H, 3*H*-(naphthalene), *J* = 1.8, 8.2 Hz),

7.74 - 7.76 (m, 4H, 4,7-*H*-(naphthalene)), 7.83 (d, 2H, 1*H*-(naphthalene),  $J = 1.2$  Hz).

$^{13}\text{C}$  (100 MHz;  $\text{CDCl}_3$ ; TMS)  $\delta$  14.12, 14.14, 22.66, 22.70, 26.13, 28.90, 29.25, 29.38,

29.44, 29.49, 29.62, 29.65, 29.68, 30.92, 31.87, 31.93, 68.12, 106.42, 119.61, 125.91,

126.86, 127.77, 128.74, 129.49, 129.55, 133.71, 135.47, 136.83, 139.47, 157.46.

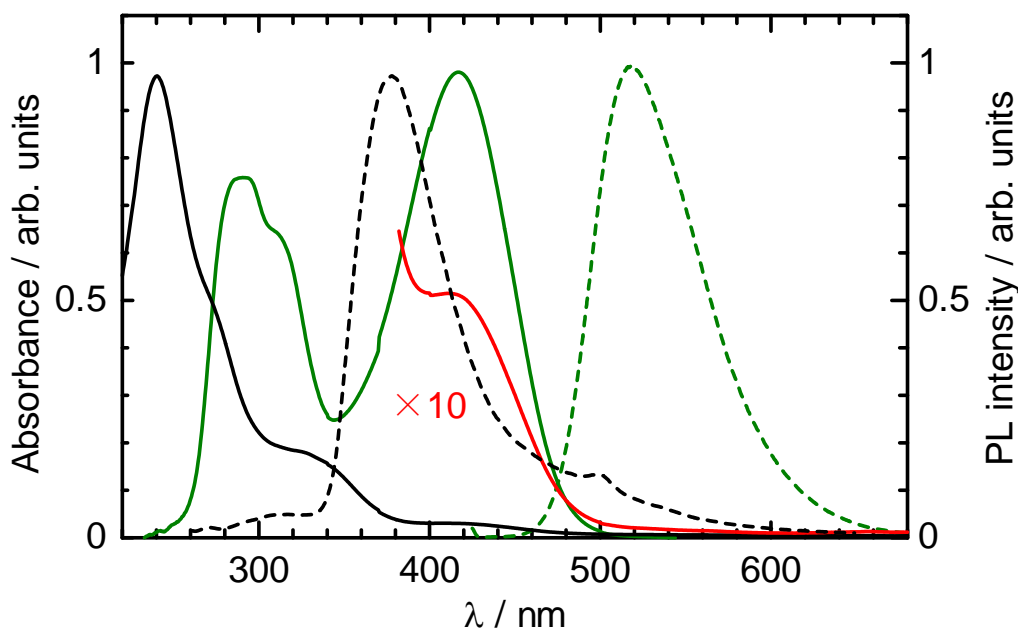


Figure S1. UV-vis absorption (solid) and PL (dashed) spectra of P(Bn-ITN) (black and red ( $\times 10$ )) and compound **13** (green) in THF.

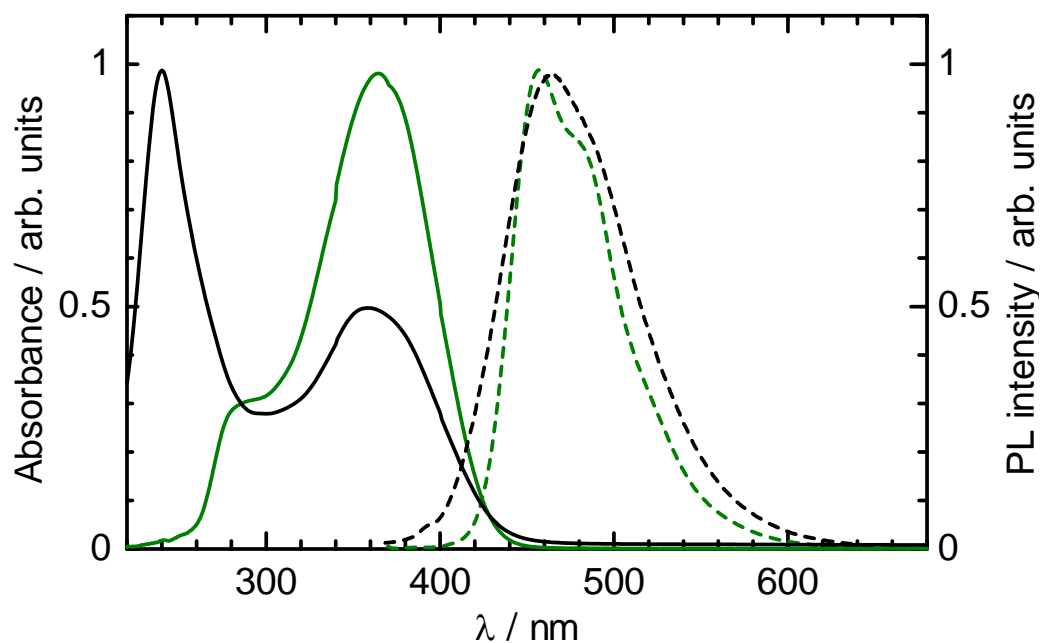


Figure S2. UV-vis absorption (solid) and PL (dashed) spectra of P(Bn-B8T) (black) and compound **14** (green) in THF.

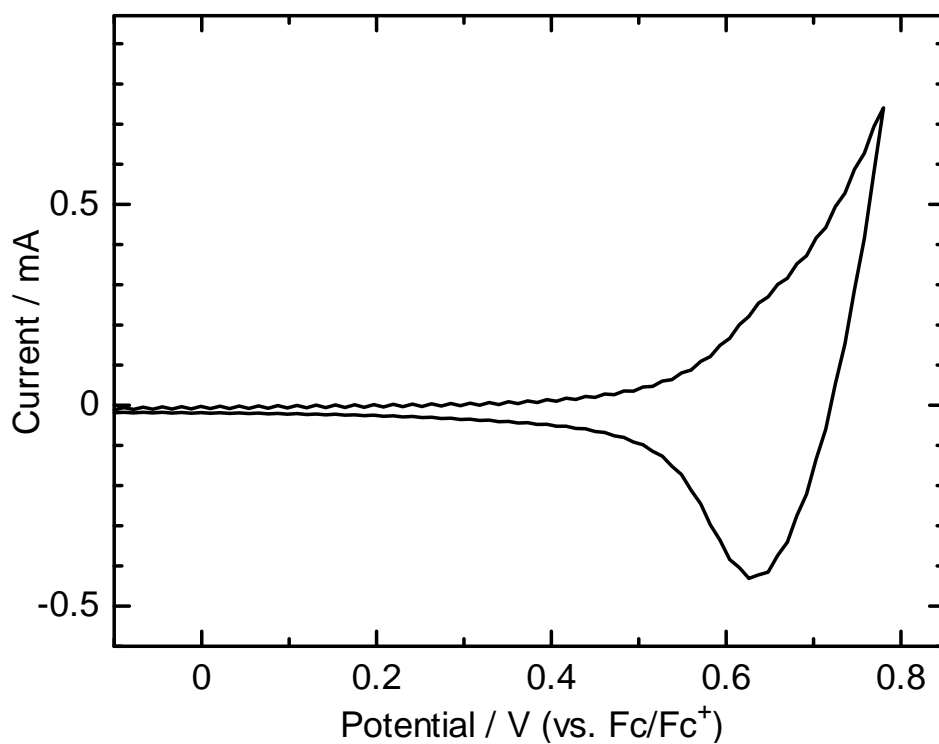


Figure S3. A cyclic voltammogram of EP(Bn-BT) on deposited an ITO glass electrode at a scan rate of  $100 \text{ mVs}^{-1}$ .

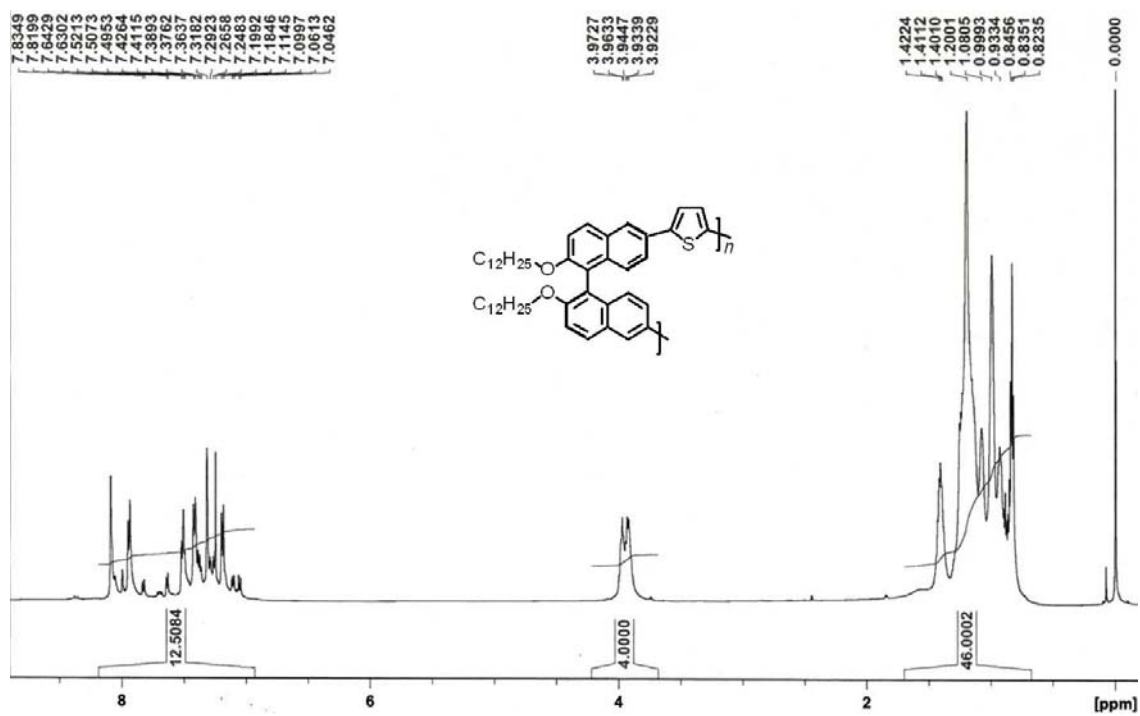


Figure S4. <sup>1</sup>H NMR spectrum (600 MHz) of P(Bn-T).



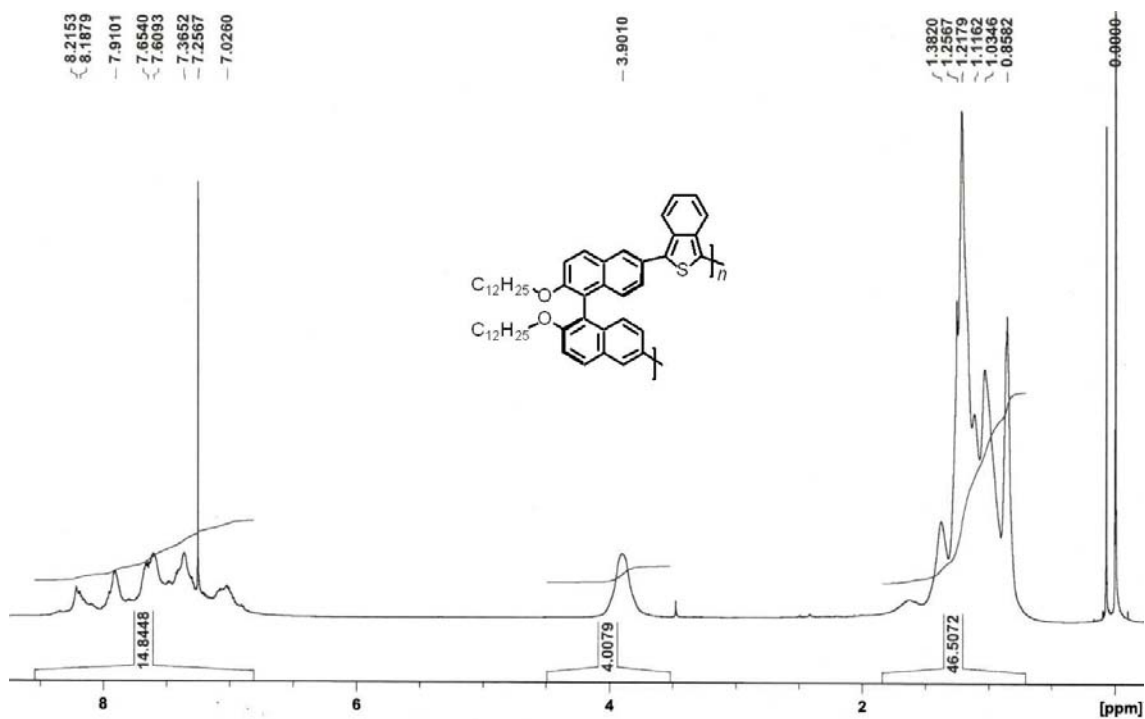


Figure S5. <sup>1</sup>H NMR spectrum (600 MHz) of P(Bn-ITN).

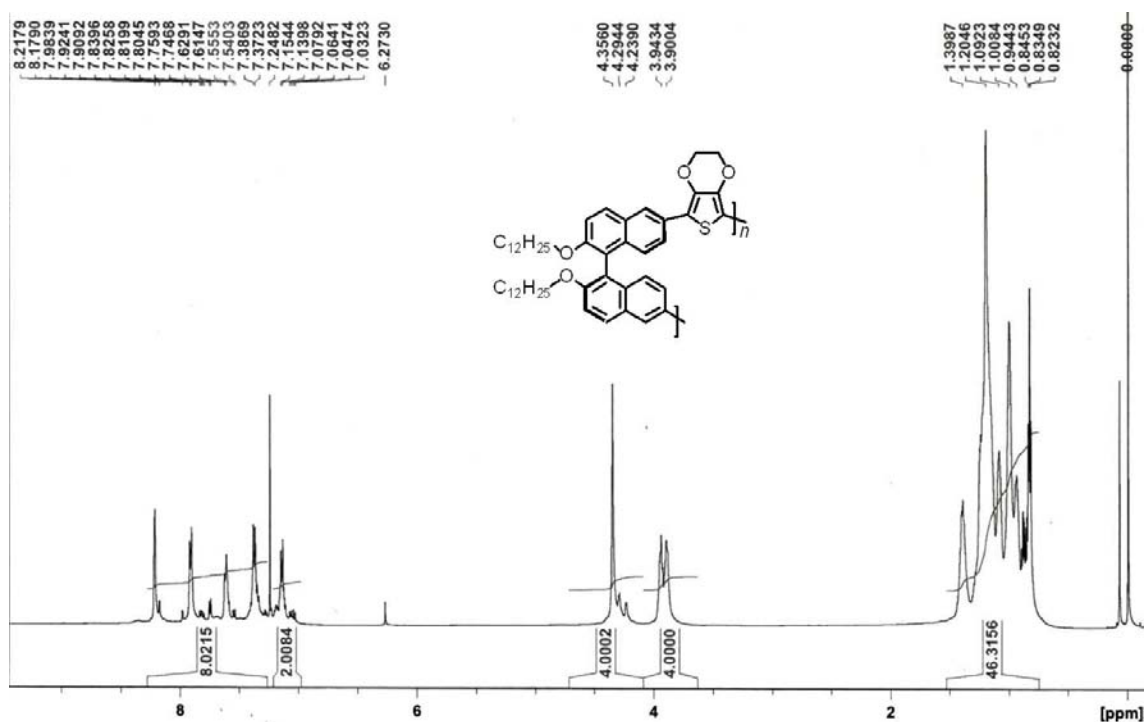


Figure S6. <sup>1</sup>H NMR spectrum (600 MHz) of P(Bn-EDOT).

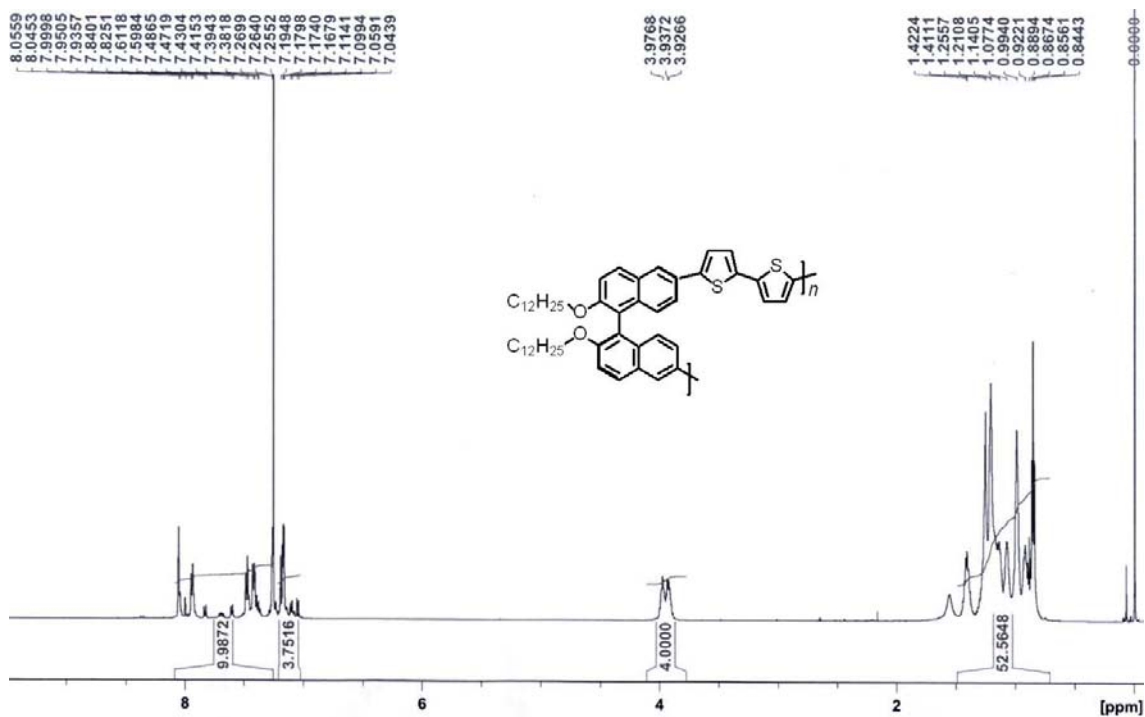


Figure S7. <sup>1</sup>H NMR spectrum (600 MHz) of P(Bn-BT).

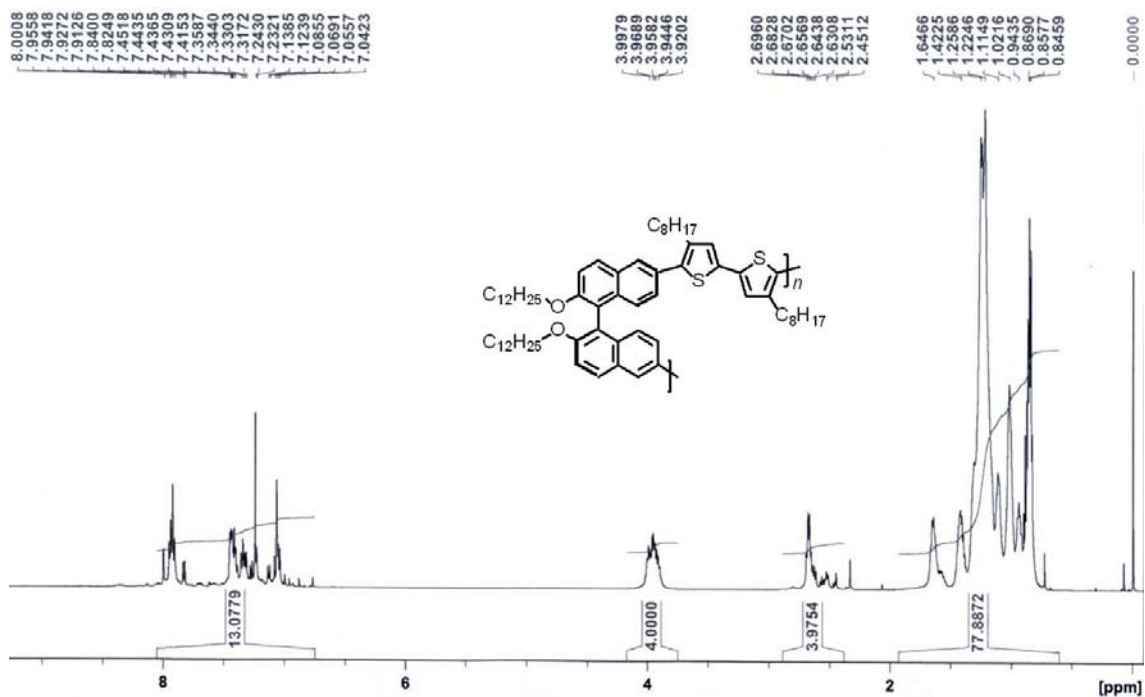


Figure S8. <sup>1</sup>H NMR spectrum (600 MHz) of P(Bn-B8T).

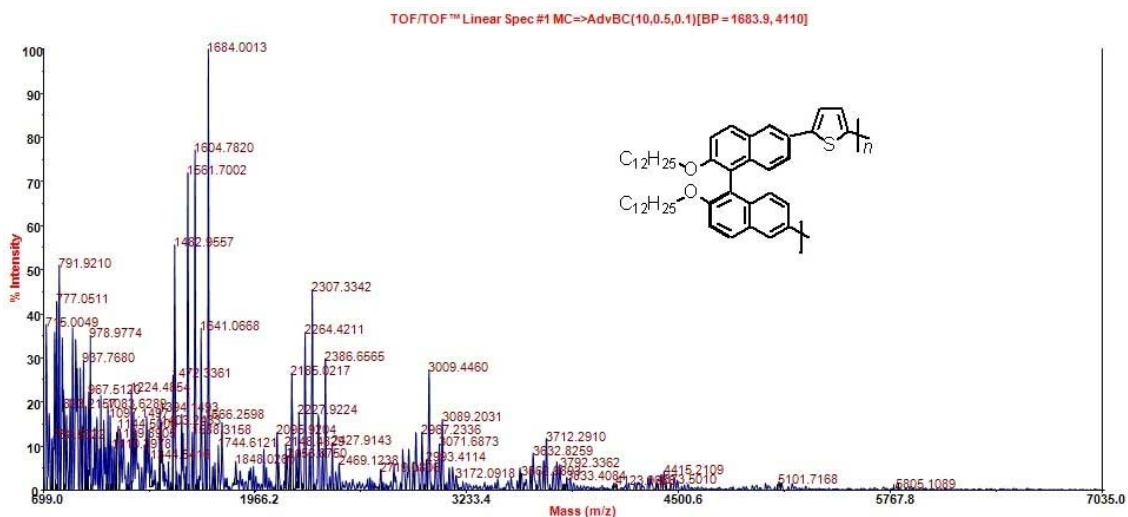


Figure S9. MALDI-TOF-MS spectrum of P(Bn-T).

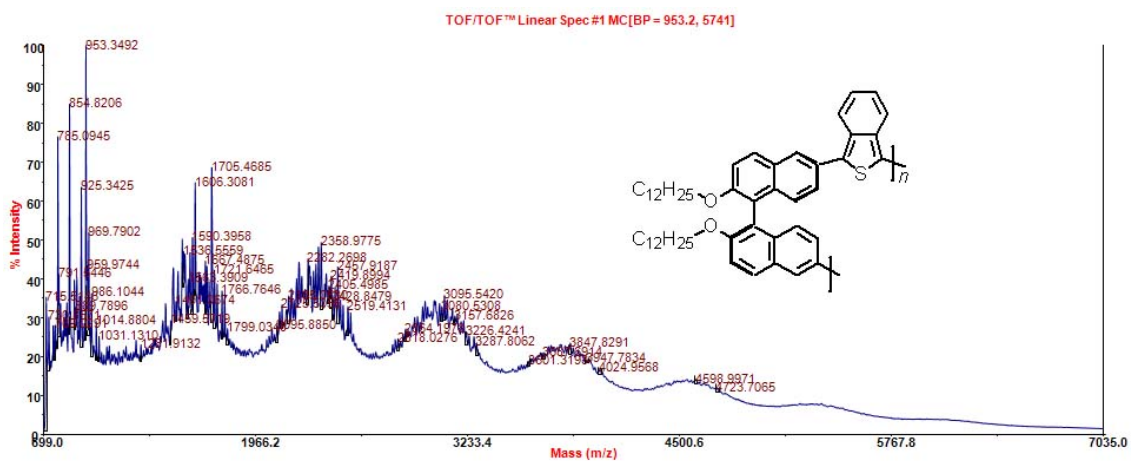


Figure S10. MALDI-TOF-MS spectrum of P(Bn-ITN).

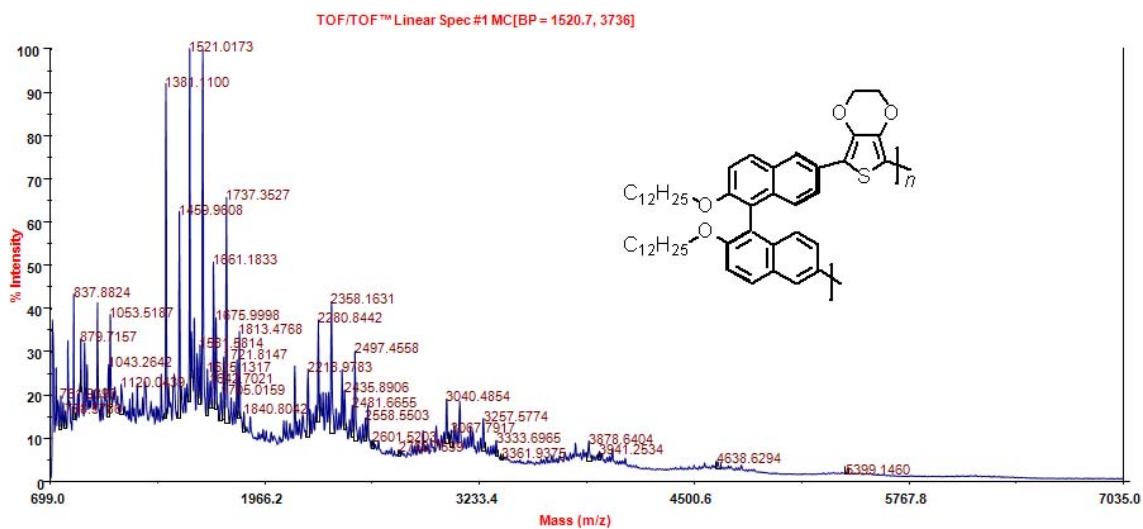


Figure S11. MALDI-TOF-MS spectrum of P(Bn-EDOT).

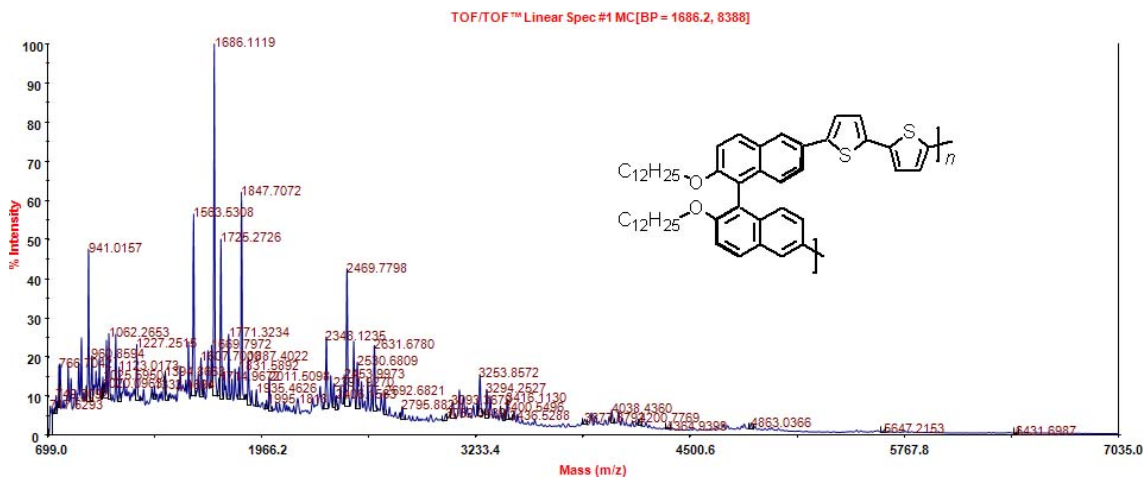


Figure S12. MALDI-TOF-MS spectrum of P(Bn-BT).

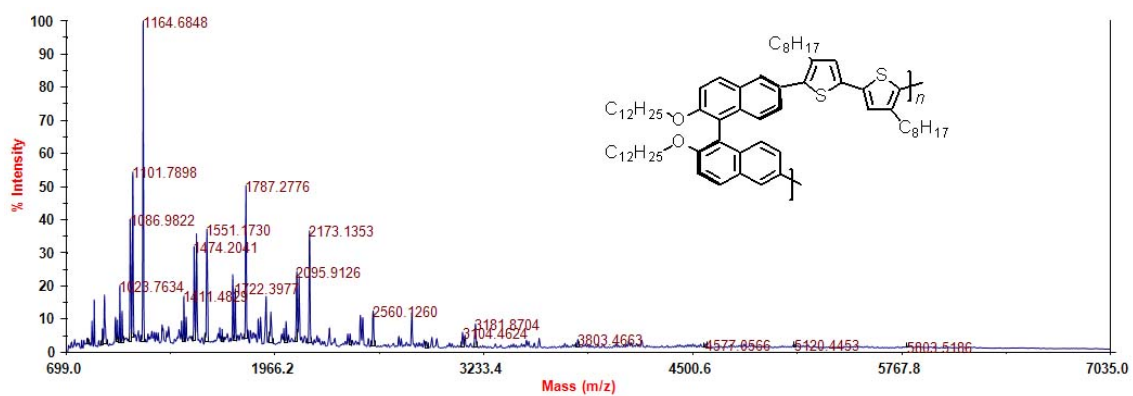


Figure S13 MALDI-TOF-MS spectrum of P(Bn-B8T).