

# Supporting Information

## **Benzodifuran and Benzodithiophene Donor-Acceptor Polymers for Bulk Heterojunction Solar Cells**

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## Experimental

**Materials.** Most commercial chemicals were purchased from VWR, Aldrich, AK Scientific, Acros and Fisher. No further purification was applied unless otherwise noted. All reactions were conducted under purified nitrogen or argon from Airgas by Schlenk technique. The glassware and syringes were dried at 120 °C for more than 24 hours before use and cooled under nitrogen. Anhydrous tetrahydrofuran (THF) and toluene were kept over sodium/benzophenoneketyl and freshly distilled under nitrogen prior to use. 1-(4,6-dibromo-3-fluorothieno[3,4-*b*]thiophen-2-yl)-2-ethylhexan-1-one (**B1**) was purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd. Poly(3,4-ethylenedioxythiophene):Polystyrene sulfonate (PEDOT:PSS) type P VP AI 4083 was purchased from Heraeus Precious Metals. Phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) was purchased from Nano-C, Inc. Indium tin oxide (ITO) coated glass substrates were purchased from Luminescence Technology Corp. (Taiwan). 4,8-Dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (**1**), 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]difuran-4,8-dione (**2**), 2-dodecylthiophene (**3**) and 4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**M1**) were prepared according to the literature.<sup>1,2,3</sup>

### *Synthesis of 2-dodecylfuran (4)*

Freshly distilled furan (5g, 73.5mmol) was placed in a three-necked round bottom flask and dissolved in anhydrous THF (100 mL) under nitrogen. The solution was cooled to -40 °C with acetonitrile/liquid nitrogen mixture. Solution of *n*-butyl lithium in hexane (11.6mL, 2.5M) was added slowly. After 2.5 hours at -40 °C, 2-bromododecane was added with fast stirring. Then the reaction was kept at 25 °C overnight. The solution was poured into 200 mL ice water and extracted with hexane three times. Organic phase was dried with magnesium sulfate and concentrated by rotary evaporator. Colorless liquid (6.3g, 92%) was obtained after column chromatography with pure hexane as the final product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.866 (t, 3H), 1.261 (br, 18H), 1.626 (tt, 2H), 2.603 (t, 2H), 5.953 (dd, 1H), 6.257 (dd, 1H), 7.275 (dd, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: 14.10, 22.70, 28.00, 28.07, 29.22, 29.38, 29.29, 29.58, 29.66, 29.69, 31.95, 77.00, 104.49, 110.00, 140.59, 156.64 (Figure S1). MS *m/z*: 236.3 (M<sup>+</sup>).

### *Synthesis of 4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M1)*

2-Dodecylthiophene (0.72g, 2.85 mmol) was dissolved in 30 mL dry THF under nitrogen. The solution was cooled to -20 °C before adding *n*-butyl lithium solution in hexane (1.30 mL, 2.5 M). The reaction was kept for 2 hours to generate the anion. A suspension of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.30 g, 1.36 mmol) in 7 mL dry THF was transferred into the reaction at low temperature. The reaction was refluxed for 1 hour, and then followed by adding tin chloride (0.77 g, 4.1 mmol) aqueous solution at room temperature. The reaction was refluxed for 1 hour. The reaction mixture was diluted in ether and washed by DI water three times. Yellow solid (0.56 g, 59%), as the final product, was recovered from recrystallization in THF and methanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.92 (t, 6H), 1.30 (br, 32H), 1.48 (tt, 4H), 1.85 (tt, 4H), 2.84 (t, 4H), 6.94 (d, J=3.47, 2H), 7.33 (d, J=3.47, 2H), 7.48 (d, J=5.67, 2H), 7.69(d,J=5.67, 2H). <sup>13</sup>C

NMR (CDCl<sub>3</sub>, 125MHz)  $\delta$  ppm: 14.17, 22.74, 29.29, 29.41, 29.43, 29.63, 29.70, 29.73, 30.30, 31.66, 30.97, 123.46, 124.10, 124.29, 127.46, 127.80, 136.55, 137.02, 139.03, 147.18 (Figure S2).

*Synthesis of 4,8-bis(2-dodecylfuran-5-yl)benzo[1,2-b:4,5-b']dithiophene (M2)*

2-Dodecylfuran (0.66g, 2.79 mmol) was dissolved in 30 mL dry THF under nitrogen. The solution was cooled to -40 °C before adding n-butyl lithium solution in hexane (1.14 mL, 2.5 M). The reaction was kept for 2 hours to generate the anion. A suspension of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.3 g, 1.36 mmol) in 7 mL dry THF was transferred into the reaction at low temperature. The reaction was refluxed for 1 hour, and then followed by adding tin chloride (0.65 g, 3.5 mmol) aqueous solution at room temperature. The reaction was refluxed for 4.5 hours. The reaction mixture was diluted in ether and washed with deionized water three times. Yellow solid (0.2 g, 22%), as the final product, was recovered from recrystallization in THF and methanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz),  $\delta$  ppm: 0.92 (t, 6H), 1.30 (br, 32H), 1.48 (tt, 4H), 1.85 (tt, 4H), 2.84 (t, 4H), 6.30 (d, J=3.25, 2H), 7.01 (d, J=3.25, 2H), 7.58 (d, J=5.75, 2H), 8.01(d, J=5.75, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz)  $\delta$  ppm: 14.15, 22.72, 28.16, 28.33, 29.30, 29.40, 29.45, 29.64, 29.68, 29.70, 29.72, 31.95, 107.03, 111.40, 119.82, 123.72, 127.36, 134.51, 135.90, 150.07, 156.86. Elemental analysis calculated (%): C, 76.54; H, 8.87. found (%): C, 76.21; H, 8.80 (Figure S3).

*Synthesis of 4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-b:4,5-b']difuran (M3)*

2-Dodecylthiophene (0.60g, 2.4 mmol) was dissolved in 30 mL dry THF under nitrogen. The solution was cooled to -20 °C before adding n-butyl lithium solution in hexane (0.88 mL, 2.5 M). The reaction was kept for 2 hours to generate the anion. A suspension of benzo[1,2-*b*:4,5-*b'*]difuran-4,8-dione (0.21 g, 1.1 mmol) was refluxed for 1 hour followed by the addition of tin chloride (0.52 g, 2.7 mmol) aqueous solution at room temperature. The reaction mixture was refluxed for 1 hour. The reaction mixture was diluted in ether and washed with deionized water three times. The product was recovered as a yellow solid (0.27 g, 38%) by recrystallization in THF and methanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz),  $\delta$  ppm: 0.89 (t, 6H), 1.30 (br, 32H), 1.48 (tt, 4H), 1.82 (tt, 4H), 2.94 (t, 4H), 6.95 (d, J=3.61, 2H), 7.39 (d, J=2.28, 2H), 7.69 (d, J=3.61, 2H), 7.80(d, J=2.28, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz)  $\delta$  ppm: 14.14, 21.07, 22.71, 29.23, 29.38, 29.42, 29.60, 29.67, 29.68, 29.70, 30.22, 31.73, 31.94, 107.12, 110.15, 123.31, 124.61, 127.63, 133.83, 145.62, 146.66, 148.67. Elemental analysis calculated (%): C, 76.54; H, 8.87. found (%): C, 75.85; H, 8.60 (Figure S4).

*Synthesis of 4,8-bis(2-dodecylfuran-5-yl)benzo[1,2-b:4,5-b']difuran (M4)*

2-Dodecylfuran (0.78g, 3.3 mmol) was dissolved in 30 mL dry THF under nitrogen. The solution was cooled to -40 °C before adding n-butyl lithium solution in hexane (1.31 mL, 2.5 M). The reaction was kept for 2 hours to generate the anion. A suspension of benzo[1,2-*b*:4,5-*b'*]difuran-4,8-dione (0.3 g, 1.6 mmol) in 7 mL dry THF was transferred into the reaction at low temperature. The reaction was refluxed for 2.5 hours, and followed by the addition of tin chloride (0.75 g, 4.0 mmol) aqueous solution at room temperature. The reaction was refluxed for 1 hour. The reaction mixture was diluted in

ether and washed with deionized water three times. The product was recovered as a yellow solid (0.2 g, 20 from recrystallization in THF and methanol. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz), δ ppm: 0.92 (t, 6H), 1.28 (br, 32H), 1.48 (tt, 4H), 1.83 (tt, 4H), 2.83 (t, 4H), 6.27 (d, J=3.25, 2H), 7.27 (d, J=3.25, 2H), 7.59 (d, J=2.25, 2H), 7.80(d, J=2.25, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: 14.13, 22.70, 29.27, 29.38, 29.43, 29.61, 29.67, 29.68, 29.70, 31.73, 31.93, 106.04, 107.39, 108.26, 111.53, 121.33, 145.17, 147.37, 148.08, 156.47. Elemental analysis calculated (%): C, 80.74; H, 9.33. found (%): C, 80.51; H, 9.19 (Figure S5).

*Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-dodecyl-thiophene-5-yl)benzo[1,2-b:4,5-b']dithiophene (T1)*

**M1** (0.24 g, 0.347 mmol) was completely dissolved in 40 mL dry THF under nitrogen. n-Butyl Li solution in hexane (0.3 mL, 2.5 M) was added at -60 °C within 15 minutes. The reaction was kept at -60 °C for 1h. Then reaction temperature was brought to 20 °C for 20 min. Trimethyltin chloride solution in hexane (1.6 mL, 1 M) was added after the reaction was cooled to -60 °C. Reaction mixture was stirred at -60 °C for 10 minutes before warming it to room temperature. Ether was used to dilute the reaction mixture. Organic solution was washed with deionized water five times. Crude product was purified in a short column with pure hexane and neutral alumina. Light yellow solid (240 mg, 68%) was obtained as final product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.43 (s, 18H), 0.91 (t, 6H), 1.30 (br, 32H), 1.50 (tt, 4H), 1.83 (tt, 4H), 2.96 (t, 4H), 6.95 (d, 2H), 7.34 (d, 2H), 7.71 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: -8.31, 14.14, 22.71, 29.35, 29.38, 29.46, 29.64, 29.67, 29.70, 30.31, 30.95, 31.60, 31.94, 122.41, 124.18, 127.64, 131.18, 137.33, 137.77, 142.26, 143.29, 146.82 (Figure S6).

*Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-dodecyl-furan-5-yl)benzo[1,2-b:4,5-b']dithiophene (T2)*

Similar synthetic conditions and work-up processes in **T1** were applied (give full method with amounts and moles). Light yellow solid (0.48 g, 70%) was obtained as final product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.48 (s, 18H), 0.91 (t, 6H), 1.29 (br, 32H), 1.48 (tt, 4H), 1.86 (tt, 4H), 2.84 (t, 4H), 6.30 (d, 2H), 7.04 (d, 2H), 8.07 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: -8.36, 14.14, 22.70, 28.34, 28.40, 29.35, 29.37, 29.51, 29.63, 29.67, 29.69, 29.71, 31.93, 106.95, 111.17, 118.26, 131.58, 135.39, 140.37, 141.72, 150.74, 156.51 (Figure S7).

*Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-b:4,5-b']difuran (T3)*

Similar synthetic conditions and work-up processes in T1 were applied (give full method with amounts and moles). Light yellow solid (0.14 g, 80%) was obtained as final product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.49 (s, 18H), 0.91 (t, 6H), 1.30 (br, 32H), 1.48 (tt, 4H), 1.82 (tt, 4H), 2.95 (t, 4H), 6.94 (d, 2H), 7.53 (s, 2H), 7.74 (d, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: -8.94, 14.14, 22.71, 29.27, 29.38, 29.47, 29.64, 29.67, 29.70, 30.23, 31.76, 31.94, 108.46, 117.78, 123.38, 124.49, 127.15, 135.09, 145.99, 152.20, 166.13 (Figure 20).

*Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-dodecyl-furan-5-yl)benzo[1,2-b:4,5-b']difuran (T4)*

Similar synthetic conditions and work-up processes in **T1** were applied (give full method with amounts and moles). Light yellow solid (0.361 g, 81%) was obtained as final product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500MHz), δ ppm: 0.51 (s, 18H), 0.90 (t, 6H), 1.28 (br, 32H), 1.48 (tt, 4H), 1.83 (tt, 4H), 2.85 (t, 4H), 6.26 (d, 2H), 7.22 (d, 2H), 7.69 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125MHz) δ ppm: -9.01, 14.13, 22.70, 28.14, 28.36, 29.29, 29.37, 29.51, 29.60, 29.67, 29.70, 31.93, 31.94, 104.54, 107.23, 111.01, 118.92, 121.65, 148.88, 151.03, 156.08, 165.45 (Figure S8).

**General procedure for the polymerization.** All the polymers were synthesized by Stille coupling polymerizations. The reaction conditions were optimized with slight differences among the four polymers.

*Synthesis of poly(4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-b:4,5-b']dithiophene-2-yl)-alt-1-(3-fluorothiopheno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one (P1)*

To a dried Schlenk flask, **T1** (551.85 mg, 0.543 mmol), **B1** (240 mg, 0.542 mmol) and Pd(Ph<sub>3</sub>)<sub>4</sub> (12.6mg, 2% in mole) were mixed and dissolved in dry toluene with 0.25 mL anhydrous dimethylformamide (DMF) under argon. The solution was heated at 110 °C for 20 hours. Then the reaction mixture was cooled to room temperature before being quenched in 300 mL methanol. Then the precipitated polymer solid was filtered in thimble and washed by Soxhlet extraction with methanol, ether, and hexane. Finally, the polymer was extracted by hot chloroform. Dark blue solid (525 mg, 85.7%) was dried under vacuum as the final product. <sup>1</sup>H-NMR (Figure. S9) Mn: 23.0 kg/mol, PDI: 3.18.

*Synthesis of poly{4,8-bis(2-dodecylfuran-5-yl)benzo[1,2-b:4,5-b']dithiophene-2-yl}-alt-1-(3-fluorothiopheno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one} (P2).*

Similar synthetic conditions and work-up processes in **P1** were applied. Reaction time for **P2** here was 13 hours. Dark blue solid (360 mg, 96.3%) was dried under vacuum as the final product. <sup>1</sup>H-NMR (Figure. S10) Mn: 33.6 kg/mol, PDI: 2.57.

*Poly{4,8-bis(2-dodecylthiophene-5-yl)benzo[1,2-b:4,5-b']difuran-2-yl}-alt-1-(3-fluorothiopheno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one} (P3).*

Similar synthetic conditions and work-up processes in **P1** were applied. Reaction time for **P3** here was 35 hours. Dark blue solid (508 mg, 86.6%) was dried under vacuum as the final product. <sup>1</sup>H-NMR (Figure. S11) Mn: 50.6 kg/mol, PDI: 4.08.

*Synthesis of poly{4,8-bis(2-dodecylfuran-5-yl)benzo[1,2-b:4,5-b']difuran-2-yl}-alt-1-(3-fluorothiopheno[3,4-b]thiophen-2-yl)-2-ethylhexan-1-one} (P4)*

Similar synthetic conditions and work-up processes in **P1** were applied. Reaction time for **P4** here was 7 hours. Dark blue solid (446 mg, 86.9%) was dried under vacuum as the final product. <sup>1</sup>H-NMR (Figure. S12) Mn: 66.7 kg/mol, PDI: 5.06.

**General measurement and characterization.** Elemental analysis was carried out by the Galbraith Laboratories, Inc.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the purified products were recorded on Bruker Avance 500 MHz spectrometer at 25 °C. NMR data were obtained in deuterated chloroform ( $\text{CDCl}_3$ ) with tetramethylsilane (TMS) as the internal standard. The data are reported as follows: Chemical shifts are reported in ppm on  $\delta$  scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). GC/MS was carried on Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Helium was the carrier gas with the flow rate of 1 mL/min. The following parameters were set for all the GC/MS analyses: injector and detector temperature, 250 °C; initial temperature, 70 °C; temperature ramp, 10 °C/min; final temperature, 280 °C. Molecular weights ( $M_n$ ) and polydispersity indexes (PDI) of the synthesized polymers were estimated by Size Exclusion Chromatography (SEC) analysis on Viscotek VE 3580 system equipped with ViscoGEL™ columns (GMHHR-M) and refractive index (RI) detectors. The SEC system was based on HPLC grade THF as the eluent and calibrated by polystyrene standards from PSS Polymer Standards Service GmbH (PSS). The following parameters were set for all the SEC analyses: flow rate = 1.0 mL/min, injector volume = 100  $\mu\text{L}$ , detector temperature = 30 °C, column temperature = 35 °C. The polymers were dissolved in anhydrous THF with heat. The solutions were filtered by 0.45  $\mu\text{m}$  PTFE syringe filters before injection.

The UV-Vis absorption (UV-Vis) of polymer solutions and thin films were measured with Agilent 8453 UV-VIS spectrometer. Chloroform was used to prepare the polymer solutions. Thin-films of polymers were obtained by spin-coating concentrated polymer solutions in chlorobenzene on glass substrates.

Cyclic voltammetry (CV) experiments were performed by BAS CV-50W voltammetric analyzer. The three electrode system contains a platinum inert working electrode, a platinum wire auxiliary electrode and an Ag/AgNO<sub>3</sub> reference electrode. Non-aqueous electrochemical cell was prepared by 0.1M of electrochemical grade tetrabutylammoniumhexafluoro phosphate (THP) as electrolyte in freshly distilled acetonitrile over calcium hydride. Drops of the polymer solution in chloroform were deposited on tip of working electrode and dried by argon. The scan rate of the voltage is 100 mV/s. For calibration, the half of the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured under same condition and located at 0.09 V vs. Ag/AgNO<sub>3</sub> reference electrode. It is assumed that the HOMO level of Fc is -4.8 eV. The HOMO and LUMO levels were then calculated according to the following equations:

$$E_{\text{HOMO}} (\text{eV}) = -e(\varphi_{\text{ox}} + 4.8 - E_{1/2, \text{Fc/Fc}^+}) \quad (1)$$

$$E_{\text{LUMO}} (\text{eV}) = -e(\varphi_{\text{re}} + 4.8 - E_{1/2, \text{Fc/Fc}^+}) \quad (2)$$

where  $\varphi$  is the onset of oxidation/reduction potential vs. Ag/AgNO<sub>3</sub>.

Tapping mode atomic force microscopy (TMAFM) investigation of thin film surface morphology was carried out with Veeco dimension 5000 SPM, equipped OTESPA AFM tip. TMAFM analysis was performed directly on the active areas of solar cell devices. The AFM images were recorded at room temperature in air using silicon cantilevers with

normal spring constant of 42 N/m and normal resonance frequency of 320 KHz. A typical value of AFM detector signals corresponding to RMS cantilever oscillation amplitude was equal to 0.1 - 0.4 V and the images were collected at 1 Hz scan frequency in 10  $\mu$ m scan size.

Mettler Toledo TGA/DSC-1 system was used for both thermogravimetric analyses (TGA). For TGA, the measurements were carried out under nitrogen with the heating rate of 10  $^{\circ}$ C/min. Experiments of DSC were operated with the heating rate of 10  $^{\circ}$ C/min and cooling rate of -10  $^{\circ}$ C/min in the temperature range of 20  $^{\circ}$ C to 350  $^{\circ}$ C. Each polymer underwent three cycles of heating and cooling.

Photoelectron Spectroscopy in Air (PESA) Model AC-2 manufactured by Riken Keiki Instruments was used to measure the ionization potentials (IP) and estimated HOMO energy levels of polymers. Polymer solutions in chlorobenzene were spin coated on microscope cover glass substrate with thickness around 50 nm. The input power of UV light was set at 5 mW for organic semiconducting materials.

X-Ray diffraction (XRD) study was performed on a RIGAKU Ultima III diffractometer. Thin film samples were irradiated by Cu-K $\alpha$  ( $\lambda=1.54$   $\text{\AA}$ ) x-rays; data was collected from 1 $^{\circ}$  to 40 $^{\circ}$  ( $2\theta$ ) at 0.04 $^{\circ}$  intervals, at a rate of 2 degree/min. Thin films were obtained by drop casting a 10 mg/mL polymer solution in chloroform onto clean SiO $_2$  substrates. The solvent was evaporated slowly in a Petri dish saturated with chloroform.

Thicknesses of active layers were measured by AMBIOS XP1 Stylus Profiler. For each measurement, the contact force of the stylus was 0.2 mg and the scan rate was 0.01 mm/s.

**Organic Photovoltaics.** The structure of bulk heterojunction solar cell device is ITO/PEDOT:PSS/ Polymer:PC $_{71}$ BM/Ca/Al. S1813 photoresist was used to pattern the ITO anode. The patterned substrates were cleaned with ultrasonic bath for 20 minutes in each acetone, methanol, toluene and isopropanol. UV/ozone treatment was applied on the washed ITO-glass substrates for 20 minutes prior to use. PEDOT:PSS was spin-coated at speed of 3000 rpm for 90 seconds to obtain 30 nm thick films, followed with 180  $^{\circ}$ C annealing for 5 minutes. Polymer/PC $_{71}$ BM blends were dissolved in chlorobenzene (CB) with 3% v/v of 1,8-diiodooctane (DIO) as the additive. These solutions are spin-coated at 110  $^{\circ}$ C on the hot PEDOT:PSS covered substrates. The spin-coating was at 1000 rpm for 60 seconds. Metal electrodes comprised of 10 nm of calcium and 100 nm of aluminum were thermally deposited through shadow mask. The area of each pixel was calibrated as 10 mm $^2$ . Each device includes 6 active pixels.

I-V curves were measured by Keithley 2400 source meter interfaced with Labview software under nitrogen atmosphere. Thermo Oriel equipped with 250W xenon lamp and Spectra physics 69911 Power Supply was used to generate the AM 1.5 sun spectrum. The intensity of the incident light was calibrated to 100 mW/cm $^2$  by NREL certified Hamamatsu silicon photodiode. The efficiency was calculated by the following equation:

$$PCE(\eta) = \frac{P_{in}}{P_{out}} = FF \times \frac{J_{SC} \times V_{OC}}{P_{IN}}$$

External Quantum Efficiency (EQE) were measured directly on the OPV devices with QEX10 system manufactured by PV Measurement Inc. Monochromic light was generated by 10 nm optical grating between 300 nm to 900 nm. The intensity of the incident light was calibrated to by NREL certified Hamamatsu silicon photodiode in the wavelength range of 300 nm to 1100 nm.

$$J_{sc}^{calc} = \int eEQE(\lambda)N_p(\lambda)D\lambda$$

**Charge Carrier Mobility.** Shottky diodes were made with similar procedures as the solar cells with the device structure of ITO/PEDOT:PSS/Polymer/Al. The measurements of space charge limited current (SCLC) of pure polymers were carried out in the Cascade probe station equipped with Keithley 4200 systems. The voltage was increased by 0.005 V intervals from 0 V to 3 V. Each pixel had area of 10 mm<sup>2</sup> with film thickness around 60 nm.

The mobility was calculated by the following equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

where

$\mu$  is the charge mobility

$J$  is the current density

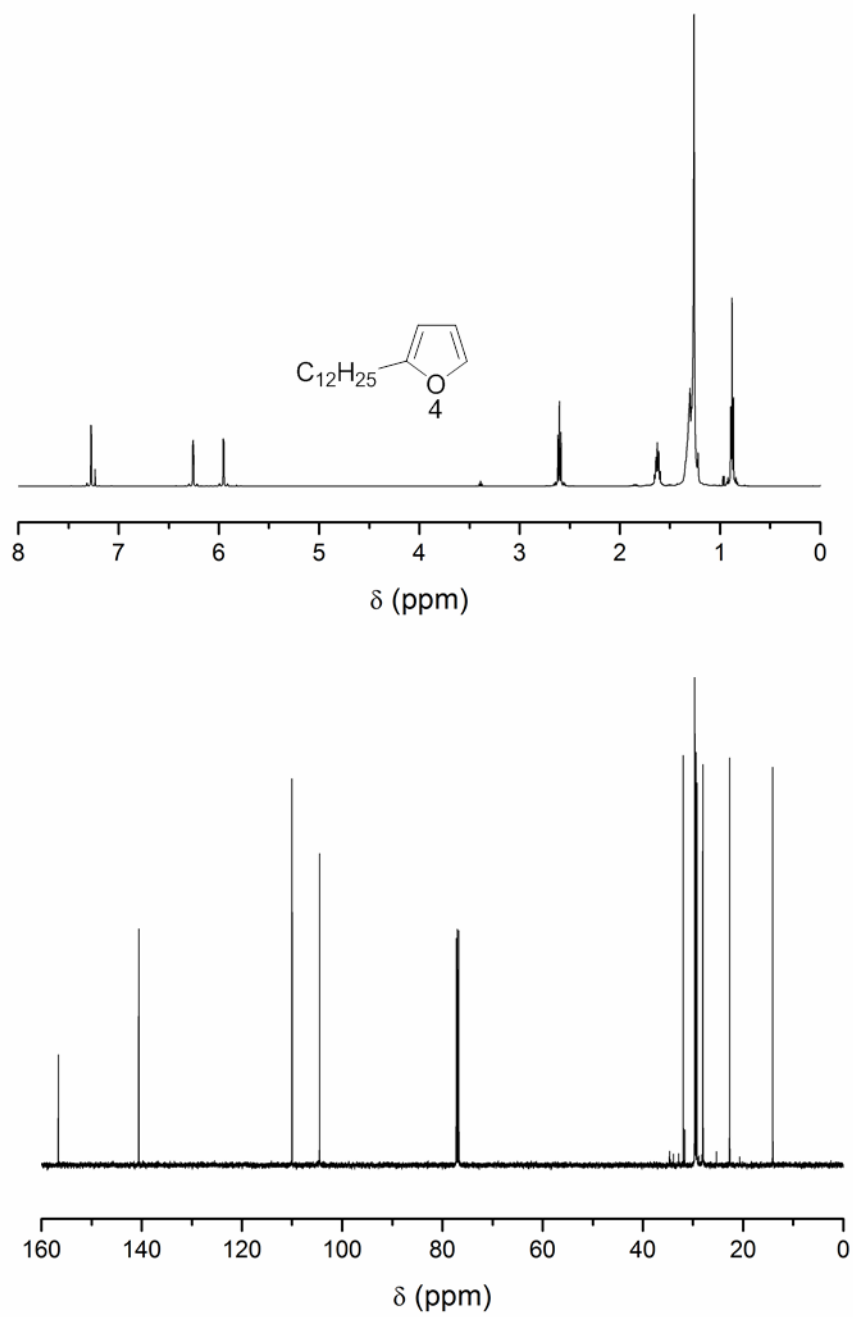
$\varepsilon_0$  is vacuum permittivity and equals to  $8.854 \times 10^{-12}$  F/m

$\varepsilon_r$  is relative permittivity of semiconducting materials. 3.5 is used here

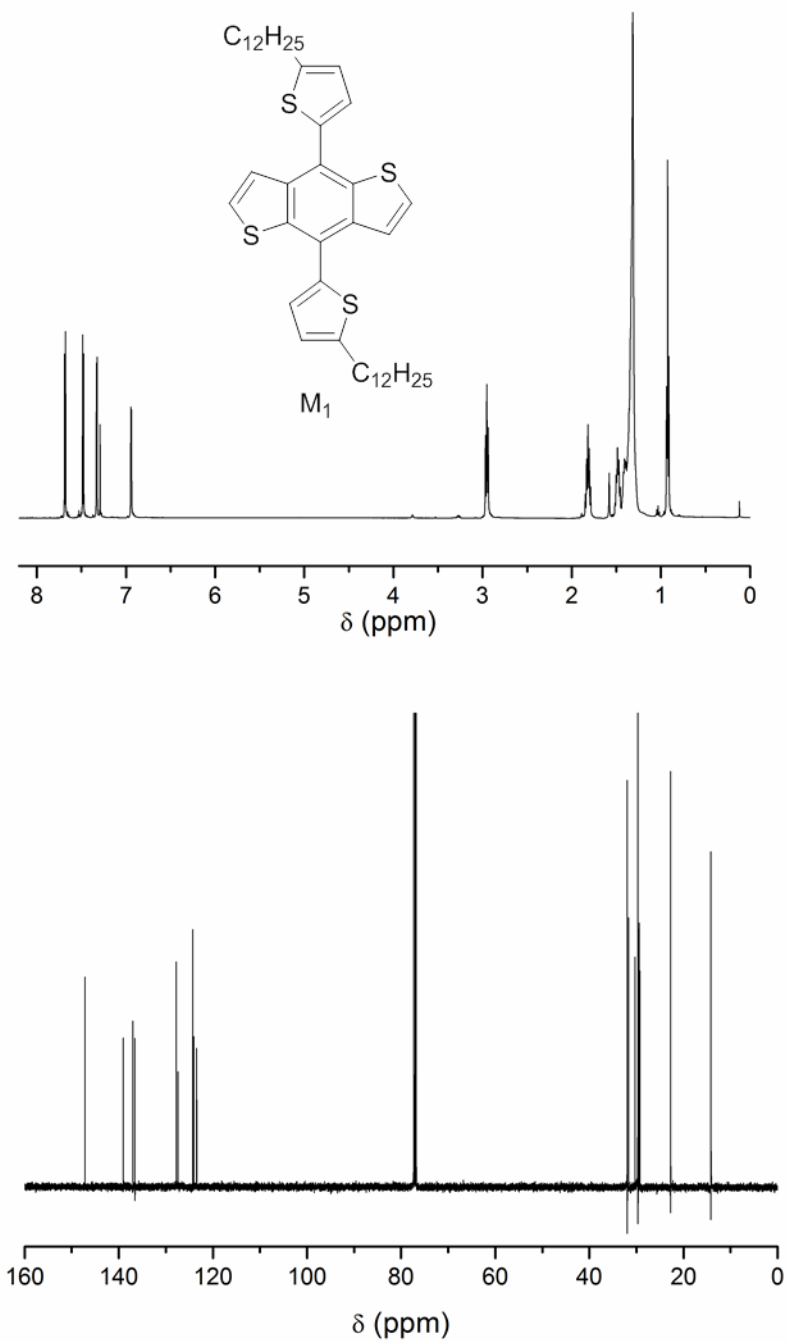
$V$  is the applied bias on the diode.

$L$  is the film thickness

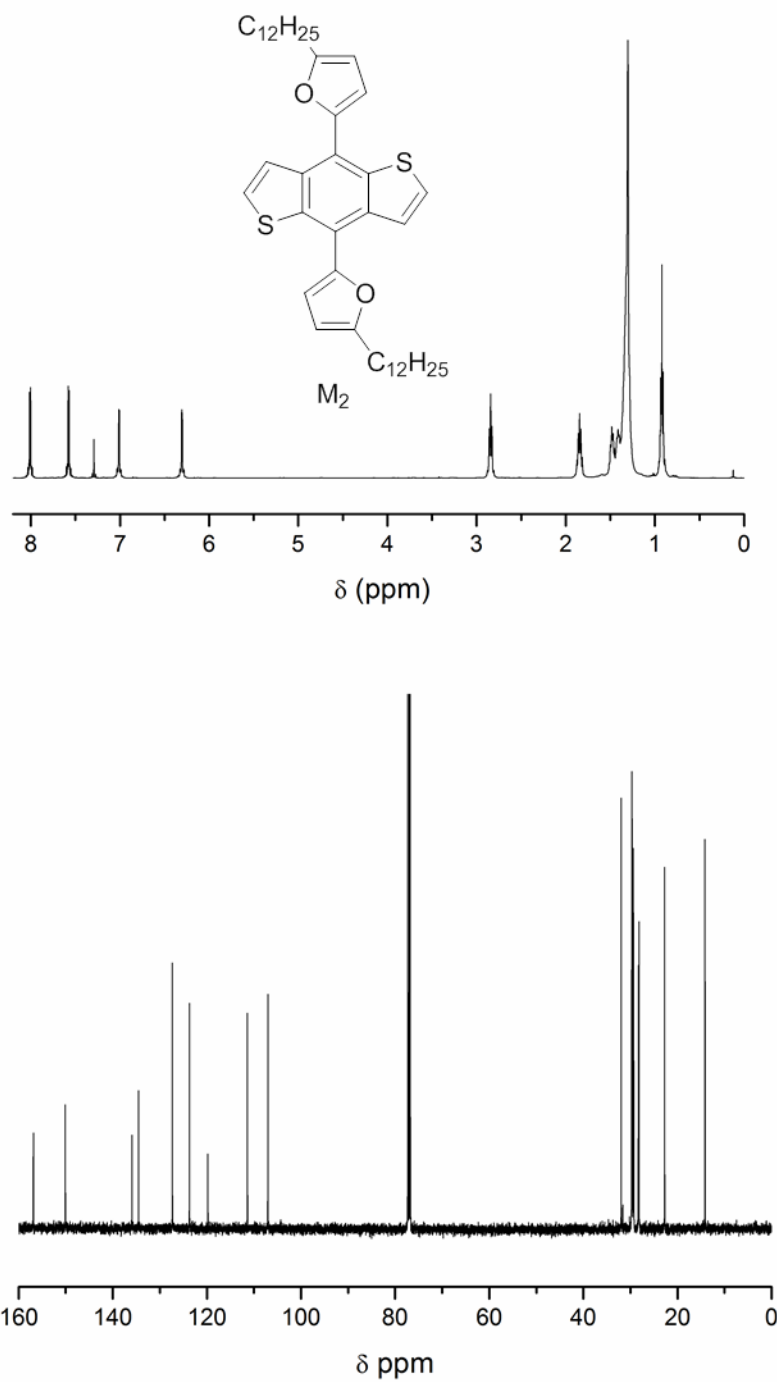




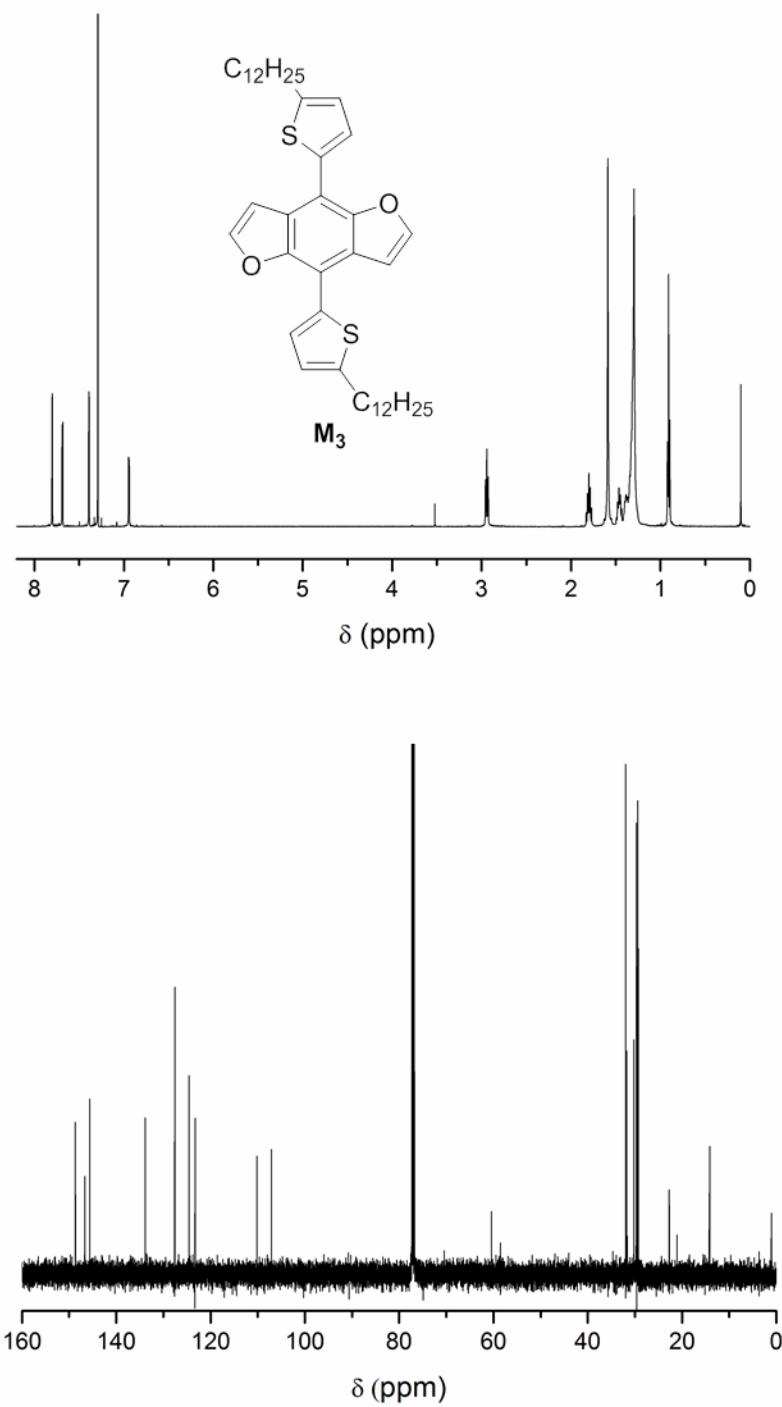
**Figure S1.** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of compound 4



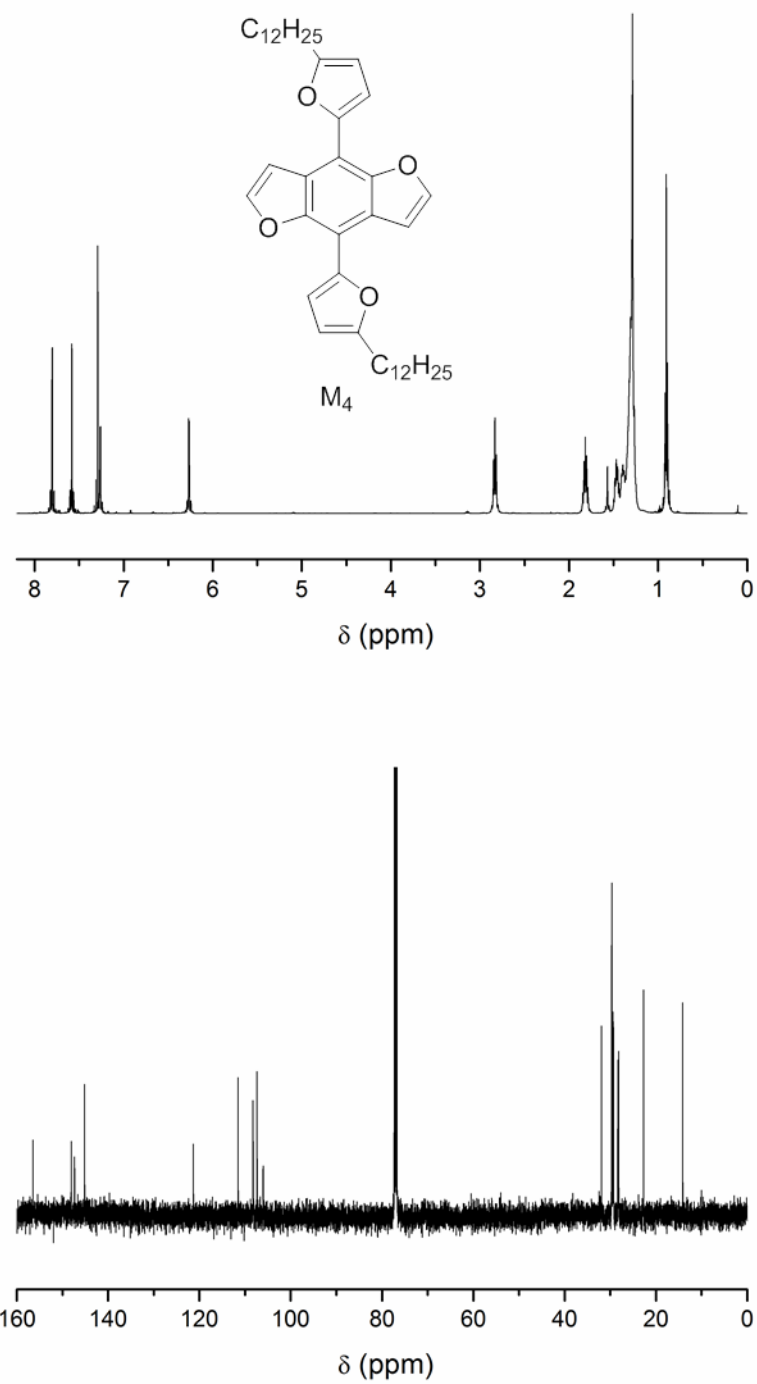
**Figure S2.** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of monomer **M1**



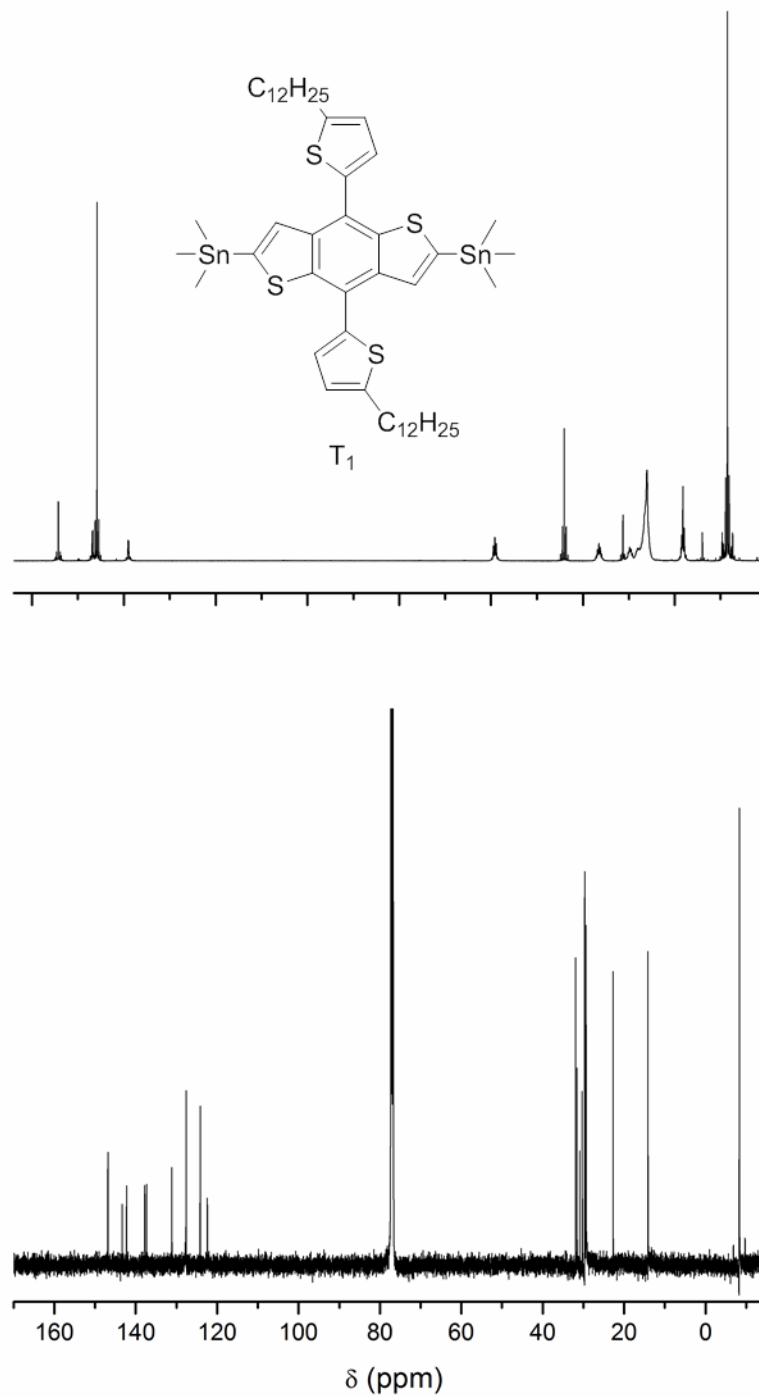
**Figure S3.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of monomer **M2**



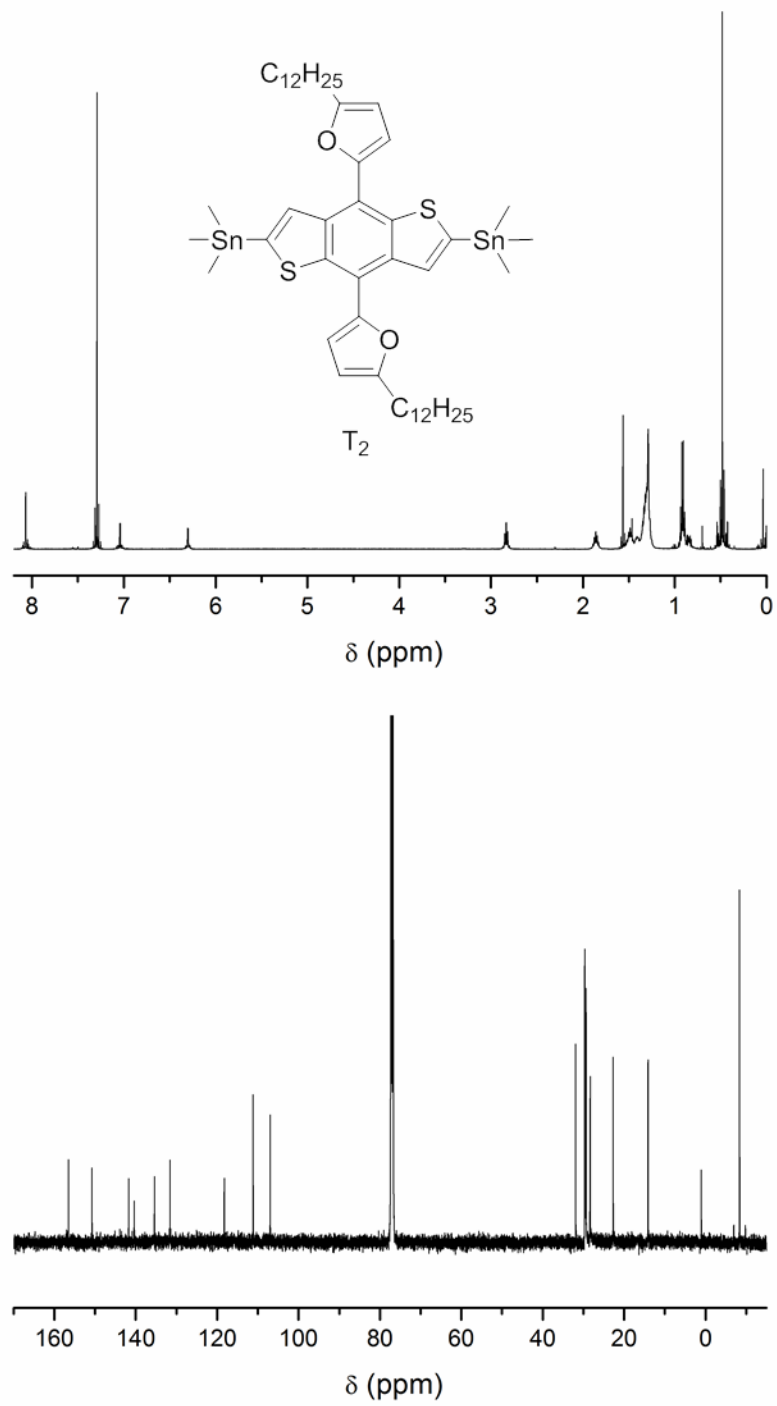
**Figure S4.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of **M3**



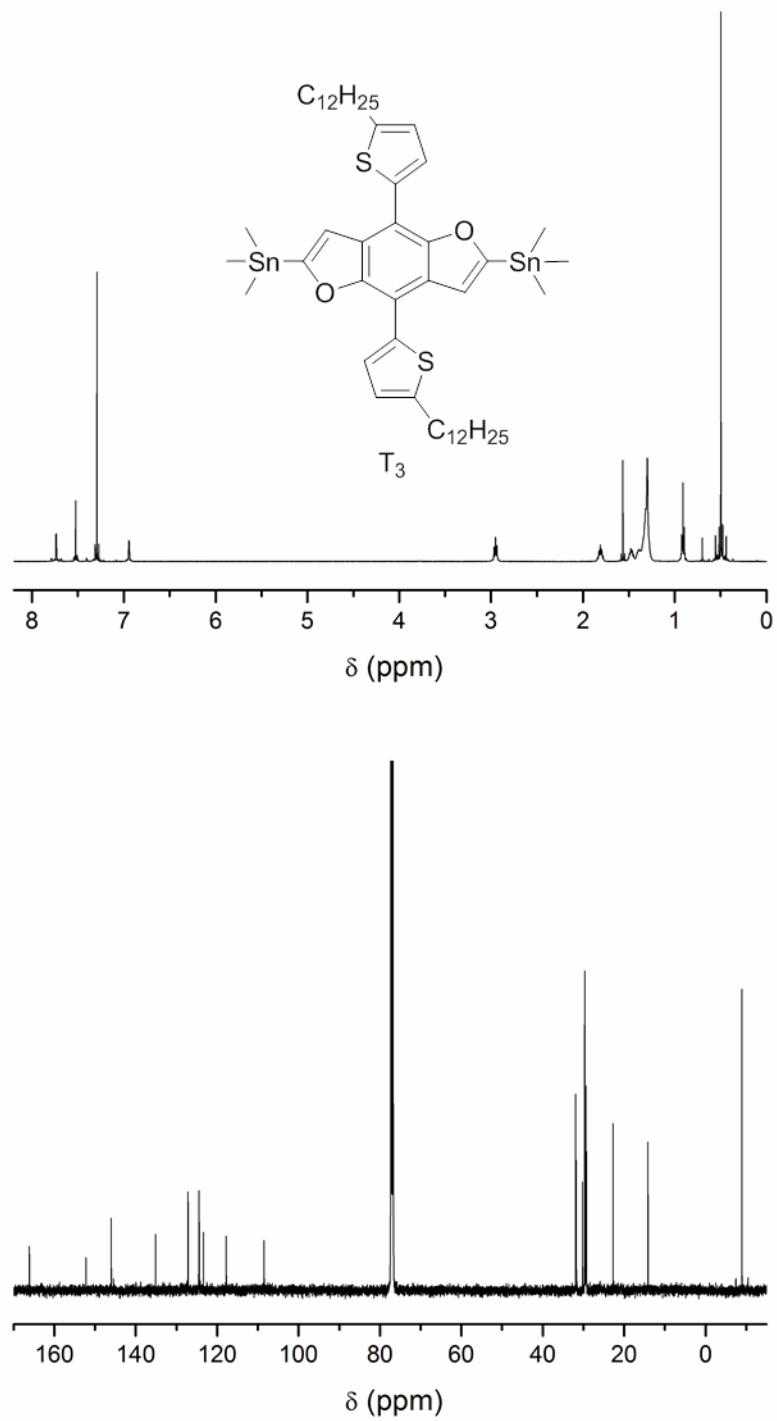
**Figure S5.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of monomer **M4**



**Figure S6.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of **T1**

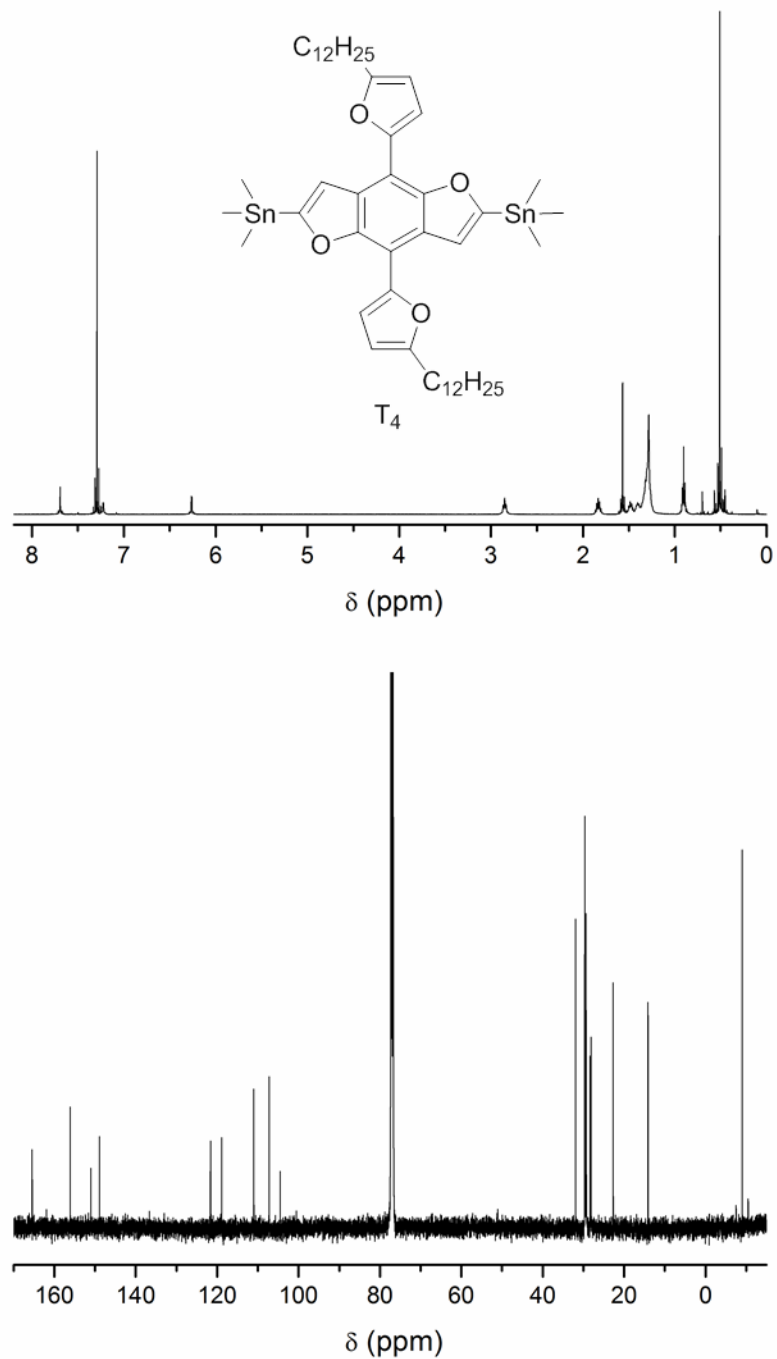


**Figure S7.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of **T2**

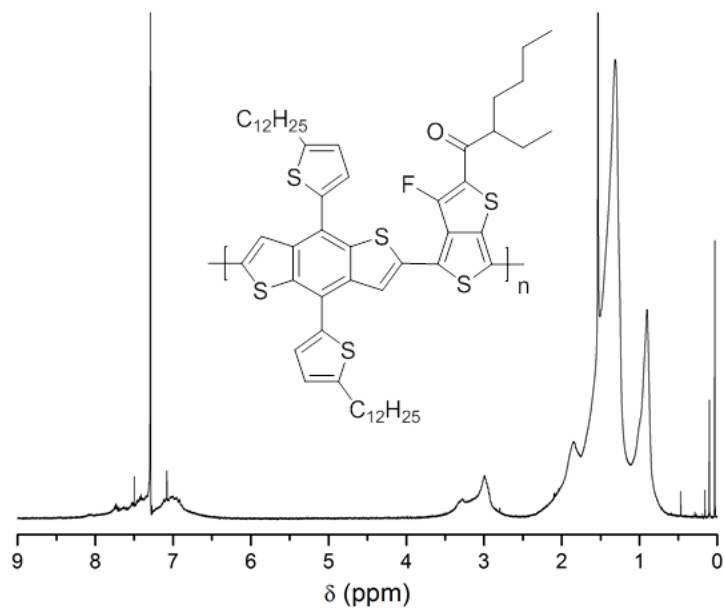


**Figure S8.** <sup>1</sup>H-NMR (top) and <sup>13</sup>C-NMR (bottom) spectra of **T3**

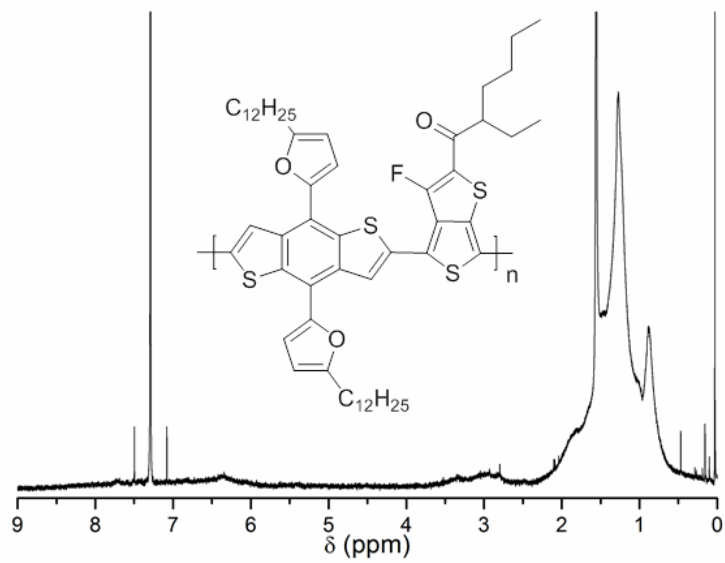




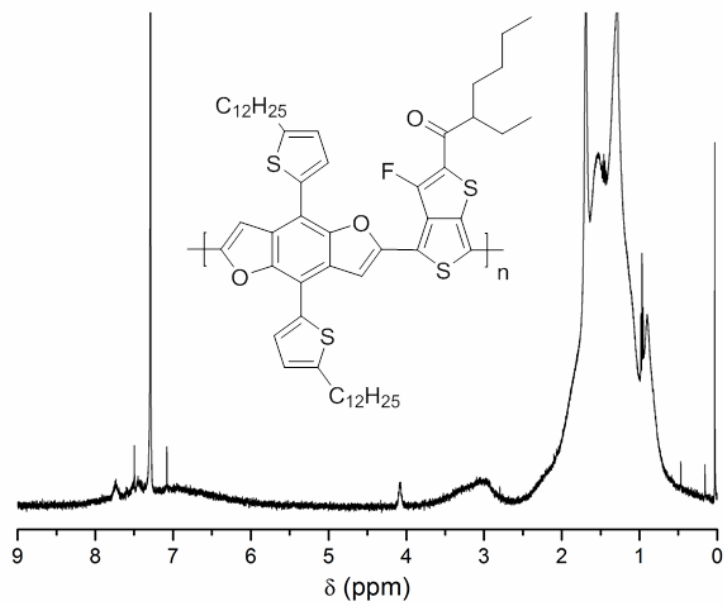
**Figure S9.**  $^1\text{H-NMR}$  (top) and  $^{13}\text{C-NMR}$  (bottom) spectra of **T4**



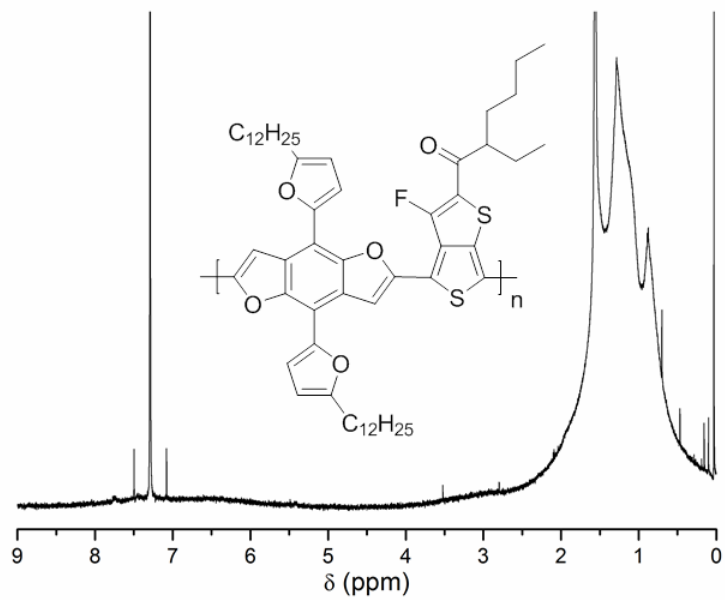
**Figure S10.**  $^1\text{H-NMR}$  of P1



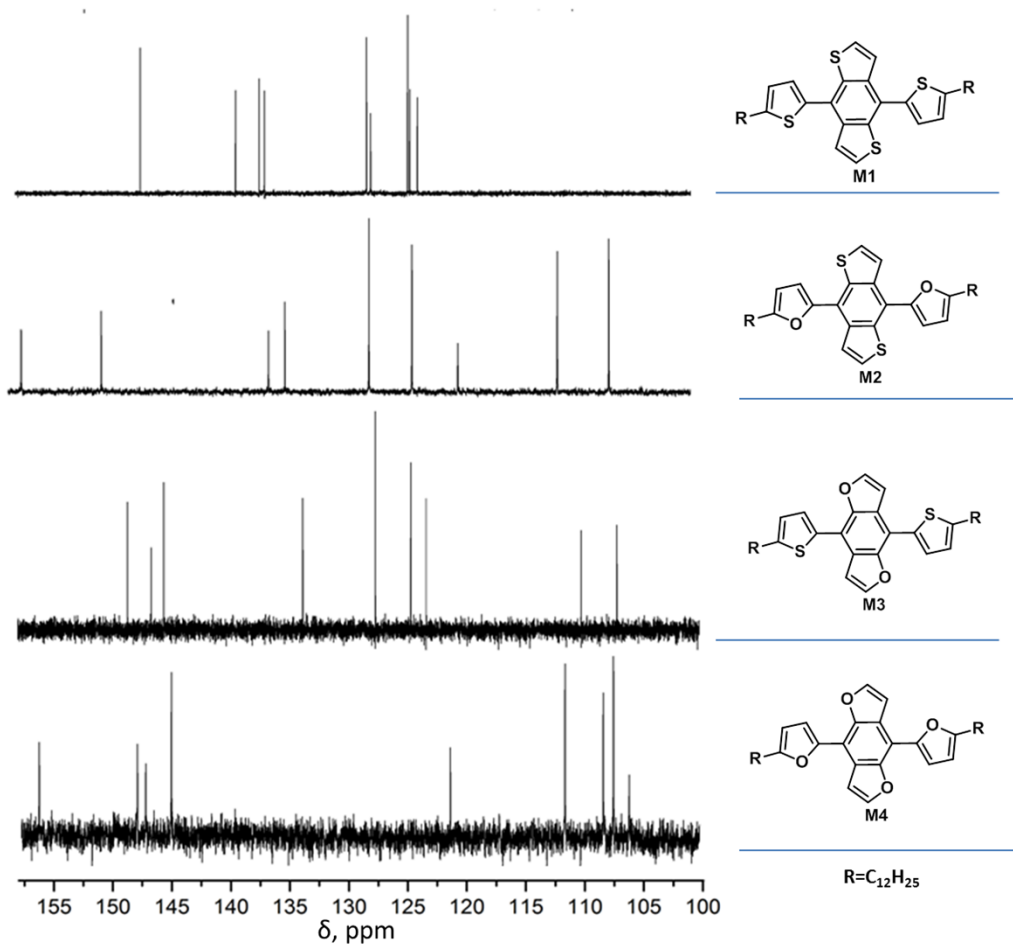
**Figure S11.**  $^1\text{H-NMR}$  of P2



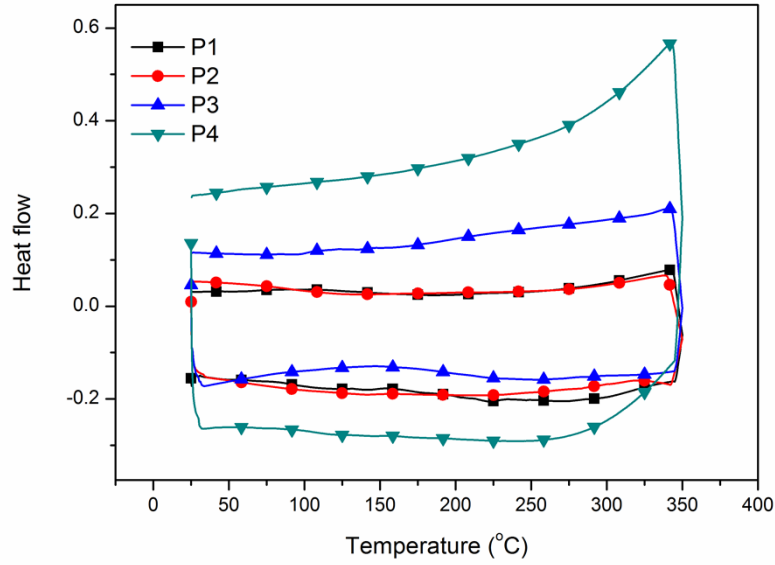
**Figure S12.** <sup>1</sup>H-NMR of P3



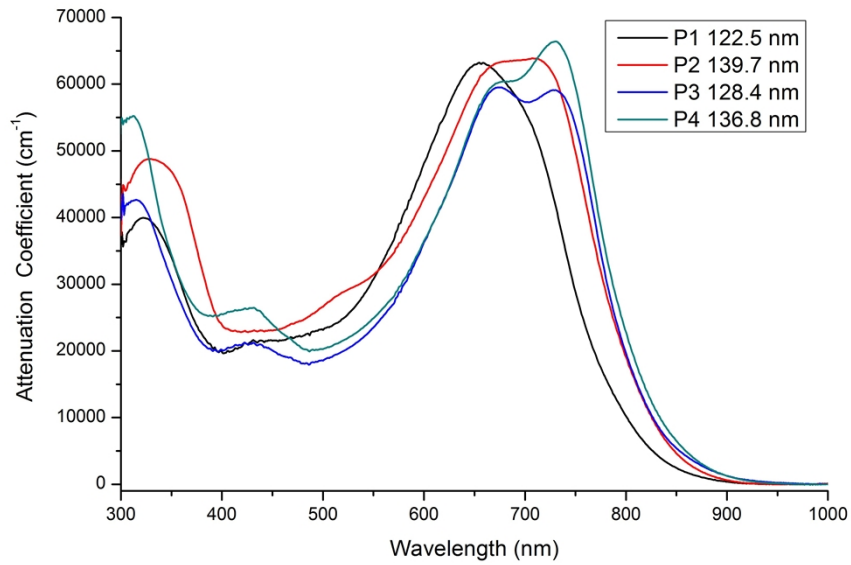
**Figure S13.** <sup>1</sup>H-NMR of P4



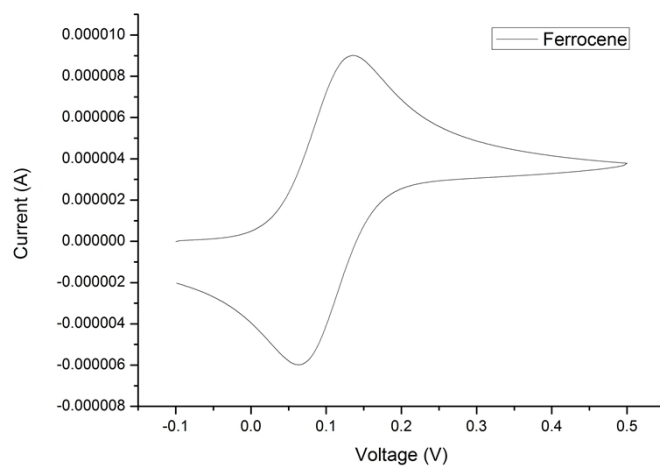
**Figure S14.** Chemical shifts in  $^1\text{H-NMR}$  spectra of the aromatic protons in the monomers M1, M2, M3, and M4



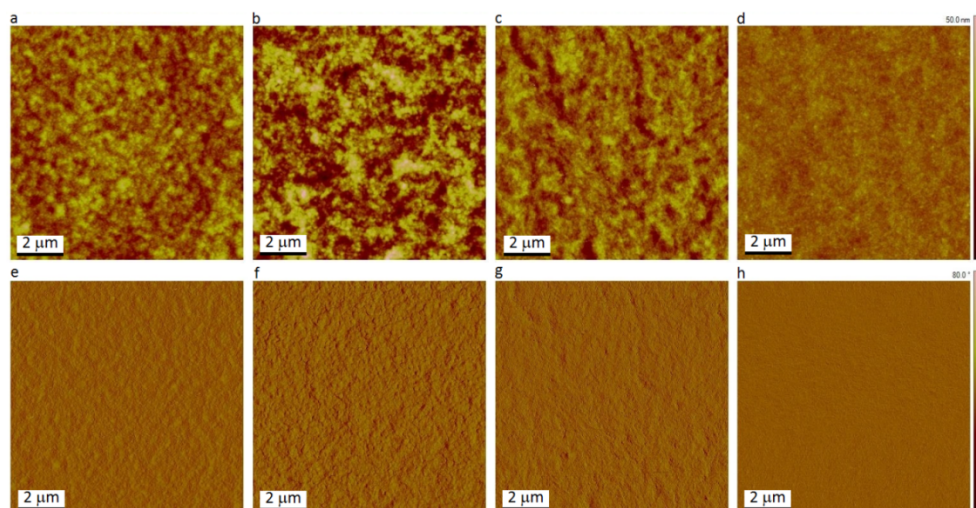
**Figure S15.** DSC thermograms of **P1**, **P2**, **P3**, and **P4** with heating and cooling rate of 10 °C/min under nitrogen



**Figure S16.** Attenuation coefficients (extinction coefficients), measured on polymer thin films on glass substrate



**Figure S17.** Redox curve of ferrocene (in 0.1M  $\text{Bu}_4\text{N}^+\text{PF}_6^-/\text{MeCN}$ , vs.  $\text{Ag}/\text{AgNO}_3$  reference electrode)



**Figure S18.** AFM height images (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4** and phase images (e) **P1**, (f) **P2**, (g) **P3**, (h) **P4/PC<sub>71</sub>BM** blend in ratio 1:1.5 w/w spin casted from chlorobenzene solutions with 3% DIO followed by high vacuum for 20 hours

**Table S1. Measured parameters for attenuation coefficients**

|           | Absorbance<br>(a.u.) | Average of 10 film thickness<br>measurements |
|-----------|----------------------|--|
| <b>P1</b> | 0.806                | 122.5  |
| <b>P2</b> | 0.912                | 139.7  |
| <b>P3</b> | 0.801                | 128.4  |
| <b>P4</b> | 0.949                | 136.8  |

**Table S2. Highest  $J_{sc}$  obtained from OPV and EQE measurements with P1, P2, P3, and P4**

|           | $J_{sc}$ (mA cm <sup>-2</sup> ) |       |
|-----------|---------------------------------|-------|
|           | OPV                             | EQE   |
| <b>P1</b> | 6.75                            | 7.90  |
| <b>P2</b> | 6.45                            | 7.13  |
| <b>P3</b> | 8.14                            | 9.78  |
| <b>P4</b> | 12.35                           | 13.60 |

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