

## Supporting Information

### Large Band-Gap Copolymers Based on 1,2,5,6-Naphthalenediimide Unit for Polymer Solar Cells with High Open Circuit Voltages and Power Conversion Efficiencies

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## 1. Materials.

All reagents were purchased from Aladdin, Alfa Aesar, Adamas-beta and Aldrich Co., and used as received without further purification. **BDTA**, **BDTT**, 2-octyldodecan-1-amine, and 3,7-dibromo-1,2,5,6-naphthalenediimide (**6**) were synthesized according to the previously reported procedures.<sup>1-4</sup>

## 2. Synthetic procedures.

**3,7-Dibromo-1,2,5,6-naphthalenediimide (6).** The solution of compound **5** (0.81 g, 0.91 mmol) and 2-octyldodecan-1-amine (2.27 g, 7.62 mmol) in glacial acetic acid (40mL) was refluxed for about 3 h. The reaction mixture was then cooled to room temperature. After removing the acetic acid under reduced pressure, the crude product was purified by column chromatography (silica gel; eluent: petroleum ether: dichloromethane = 2:1) to give pure compound **6** (1.16 g, yield: 62%) as a yellow solid. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.56 (s, 2H, ArH), 3.66 (d, *J* = 7.16, 4H, NCH<sub>2</sub>), 1.94 (d, 2H, CH), 1.41-1.21 (m, 64H, CH<sub>2</sub>), 0.89 (t, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 167.2, 165.9, 135.8, 130.7, 130.0, 128.0, 117.2, 42.8, 37.1, 31.8, 29.5, 26.3, 22.6, 14.0. Anal. calcd for C<sub>54</sub>H<sub>84</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub> (%): C, 65.84; H, 8.60; N, 2.84. Found (%): C, 65.79; H, 8.63; N, 2.78.

**3,7-Thienyl-1,2,5,6-naphthalenediimide (7).** A mixture of compound **6** (0.78 g, 0.90 mmol), tributyl(2-thienyl)stannane (0.89 g, 2.38 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (25 mg, 0.036 mmol), and degassed toluene (15 mL) was refluxed overnight. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was finally purified by column chromatography (silica gel; eluent: petroleum ether:dichloromethane = 5:2) to give pure compound **7** (0.62 g, yield: 79.1%) as an orange solid. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.49 (s, 2H, ArH), 7.84 (d, *J* = 3.48, 2H, ArH), 7.57-7.47 (dd, *J* = 1.95, 2H, ArH), 7.23-7.18 (t, *J* = 2.92, 2H, ArH), 3.61 (d, *J* = 1.24, 4H, NCH<sub>2</sub>), 1.92 (s, 2H, CH), 1.34-1.18 (t, 64H, CH<sub>2</sub>), 0.88-0.82 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 168.5, 167.7, 137.1, 132.2, 131.8, 130.4, 129.6, 129.3, 128.6, 128.1, 127.9, 42.6, 37.0, 31.9, 31.5, 30.0, 29.6, 29.3, 26.3, 22.6, 14.1. Anal. calcd for C<sub>62</sub>H<sub>90</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (%): C, 75.10; H, 9.15; N, 2.83. Found (%): C, 74.94; H, 9.22; N, 2.79.

**3,7-(5,5'-bromothieryl)-1,2,5,6-naphthalenediimide (M).** Compound **7** (0.62 g, 0.63 mmol) was first dissolved in the mixture of N,N-dimethylformamide (7 mL) and chloroform (21 mL) at room temperature. After N-bromosuccinimide (NBS) (0.25 g, 1.38 mmol) was added to above solution, the mixture was then stirred for 24 h at room temperature. Finally, the

reactant mixture was poured into 50 mL chloroform. The organic layer was then separated and washed with deionized water for several times. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed by rotary evaporation, the residue was purified by column chromatography (silica gel; eluent: petroleum ether:dichloromethane = 5:2) to give monomer **M** (0.44 g, yield: 59.0%) as an orange solid. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.33 (s, 2H, ArH), 7.65 (d, 2H, ArH), 7.13(d, 2H, ArH), 3.58 (d, 4H, NCH<sub>2</sub>), 1.89 (d, 2H, CH), 1.39-1.18 (m, 64H, CH<sub>2</sub>), 0.89 (t, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ/ppm): 168.2, 167.5, 138.4, 131.4, 131.0, 130.8, 129.4, 128.9, 128.6, 115.6, 42.7, 37.0, 31.9, 31.5, 30.0, 29.6, 29.3, 26.3, 22.7, 14.1. Anal. calcd for C<sub>62</sub>H<sub>88</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (%): C, 64.79; H, 7.22; N, 2.44. Found (%): C, 64.71; H, 7.19; N, 2.49.

**PBDTA-INDI.** Monomer **M** (0.29 g, 0.25 mmol), **BDTA** (0.23 g, 0.25 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (4.6 mg, 2% mmol) and P(*o*-tol)<sub>3</sub> (6.8 mg, 8% mmol) were dissolved in degassed toluene (15 mL) under an argon atmosphere. The mixture was then stirred at 110 °C for 24 h in dark. After the mixture was cooled to room temperature, it was dropped into 500 mL methanol to form a green precipitate. The resulting precipitate was collected by filtration, and then purified by Soxhlet extraction successively with methanol, acetone, and hexane to remove the oligomers and impurities. The remaining polymer was dissolved in chloroform and precipitated again from methanol for several times. The pure copolymer was filtered and dried under vacuum as a dark-green solid (0.29g, yield: 82%). <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.27-8.78 (br, 2H, ArH), 8.64-7.79 (br, 2H, ArH), 7.69-7.34 (br, 2H, ArH), 7.14-6.86 (br, 2H, ArH), 4.31-3.55 (br, 8H, NCH<sub>2</sub>), 2.27-1.94 (br, 4H, CH), 1.40-1.25 (br, 80H, CH<sub>2</sub>), 0.98-0.75 (br, 24H, CH<sub>3</sub>). Anal. calcd for (C<sub>88</sub>H<sub>122</sub>N<sub>2</sub>O<sub>6</sub>S<sub>4</sub>)<sub>n</sub> (%): C, 73.70; H, 8.71; N, 1.95. Found (%): C, 73.96; H, 8.65; N, 2.08.  $M_w = 249.0$  kDa,  $M_n = 61.1$  kDa, PDI = 4.0.

**PBDTT-INDI.** Polymer **PBDTT-INDI** was synthesized as a dark-green solid according to a similar route as that followed for **PBDTA-INDI** with a yield of 81%. <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>, δ/ppm): 9.73-9.52 (br, 2H, ArH), 8.71-8.53 (br, 2H, ArH), 7.99-7.83 (br, 2H, ArH), 7.63-7.50 (br, 2H, ArH), 7.48-7.37 (br, 2H, ArH), 7.09-6.96 (br, 2H, ArH), 3.43-2.74 (br, 8H, NCH<sub>2</sub>), 2.09-1.92 (br, 4H, CH), 1.42-1.15 (br, 80H, CH<sub>2</sub>), 0.93-0.72 (br, 24H, CH<sub>3</sub>). Anal. calcd for (C<sub>96</sub>H<sub>130</sub>N<sub>2</sub>O<sub>6</sub>S<sub>4</sub>)<sub>n</sub> (%): C, 73.61; H, 8.24; N, 1.79. Found (%): C, 73.10; H, 8.26; N, 1.93.  $M_w = 165.9$  kDa,  $M_n = 48.3$  kDa, PDI = 3.4.

### 3. Characterization

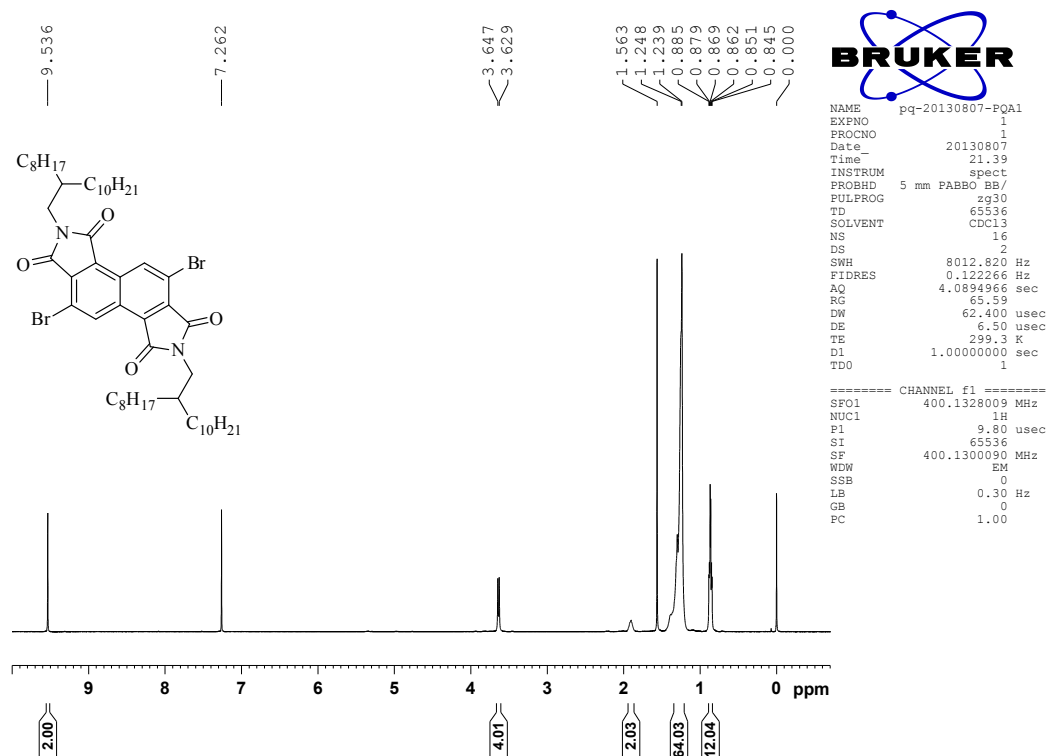
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance-400 spectrometer with *d*-chloroform as the solvent and tetramethylsilane as an internal standard. The elemental analysis was performed on a Thermo Electron SPA Flash EA 1112 series analyzer. Molecular weights of the copolymers were determined by using a Waters 1515 GPC instrument with THF as the eluent and polystyrene as a standard. Thermogravimetric analysis was conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  and under a  $\text{N}_2$  flow rate of  $90\text{ mL min}^{-1}$ . UV-vis spectra were obtained on a Cary 300 spectrophotometer. Cyclic voltammetry measurements were made on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of  $50\text{ mV s}^{-1}$ , with a platinum wire counter electrode and an Ag/AgCl reference electrode in an anhydrous and nitrogen-saturated  $0.1\text{ mol L}^{-1}$  acetonitrile solution of tetrabutylammonium perchlorate. The  $\text{CHCl}_3$  solutions of the resulting copolymers were drop-coated onto the platinum plate working electrodes. XRD patterns of the polymers were recorded on a Philips X-ray diffractometer operated in reflection geometry mode at  $30\text{ mA}$ ,  $40\text{ kV}$  with  $\text{Cu K}_\alpha$  radiation. AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode. SCLC is described by  $J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3$ , where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu$  is the hole or electron mobility,  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $\varepsilon_0$  is the permittivity of free space ( $8.85\times 10^{-12}\text{ F m}^{-1}$ ),  $V$  is the internal voltage in the device and  $V = V_{\text{appl}} - V_{\text{bi}} - V_{\text{a}}$ , where  $V_{\text{appl}}$  is the applied voltage to the device,  $V_{\text{bi}}$  is the built-in voltage due to the relative work function difference of the two electrodes and  $V_{\text{a}}$  is the voltage drop due to contact resistance and series resistance across the electrodes.

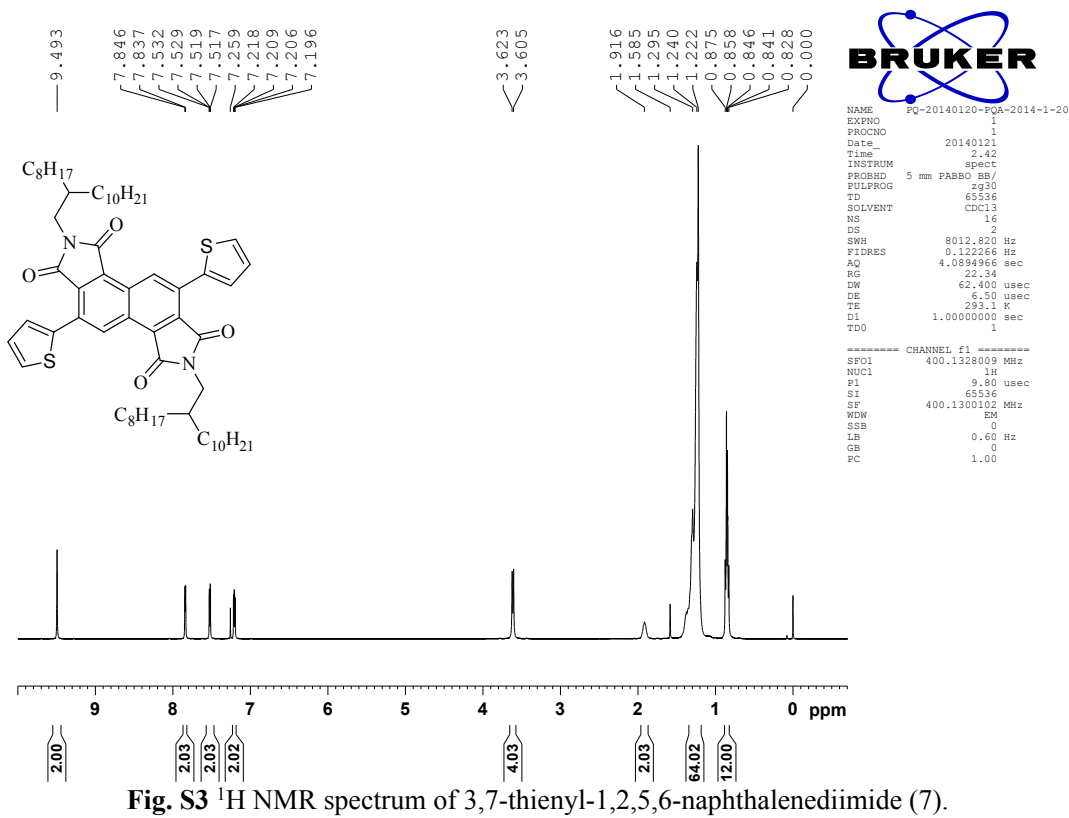
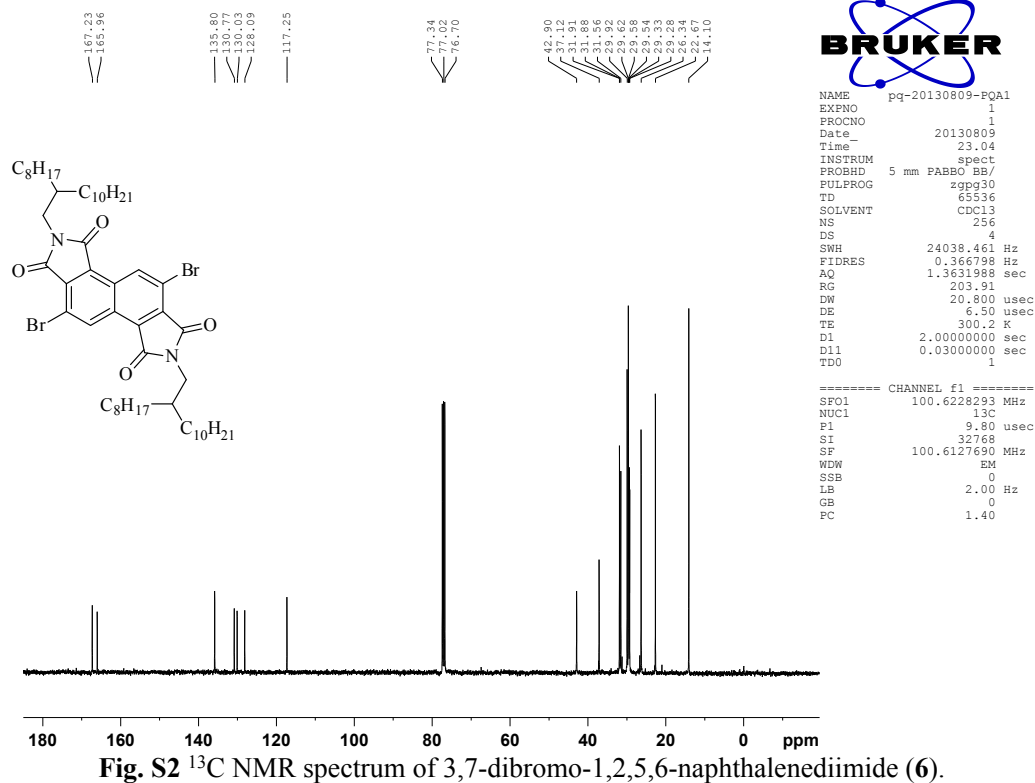
#### 4. Device fabrication

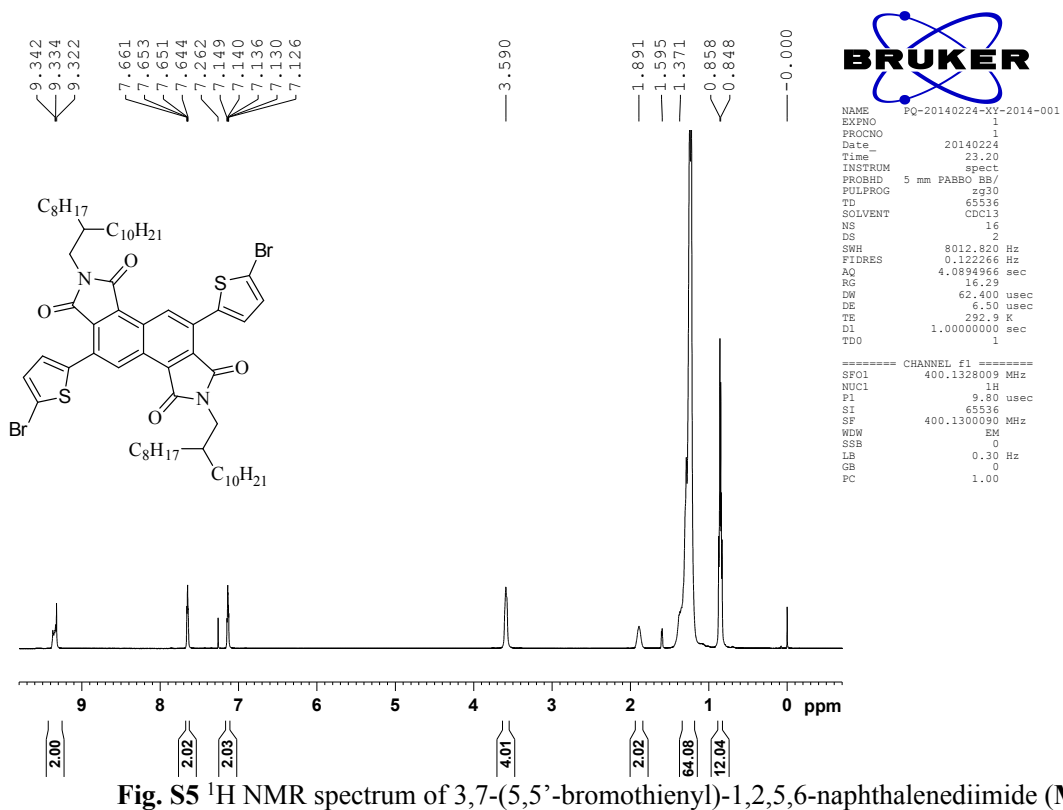
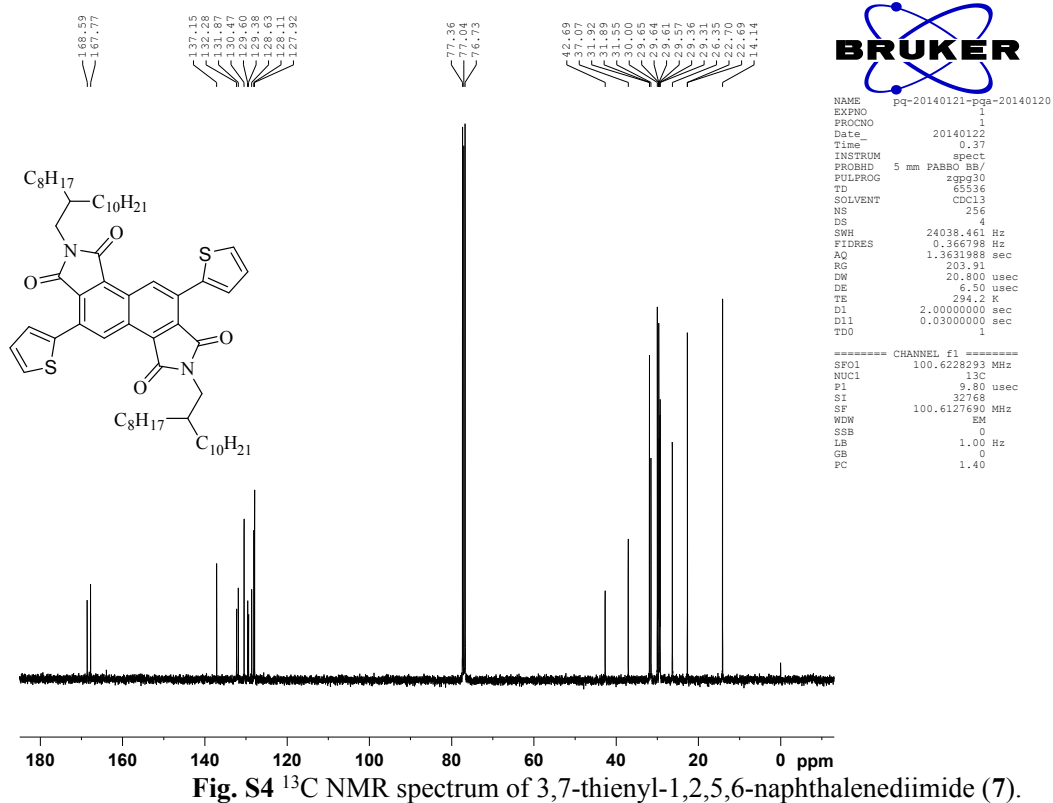
The device structure was ITO/PEDOT:PSS/copolymer:PC<sub>71</sub>BM/Ca/Al. A glass substrate with a pre-patterned ITO (sheet resistance =  $15\ \Omega\ \text{sq}^{-1}$ ) was first ultrasonicated in detergent, deionized water, acetone, and isopropanol in turn, and then modified by UV-ozone treatment for 20 min. After filtration through a  $0.45\ \mu\text{m}$  filter, PEDOT:PSS (Bay PVP AI 4083, Bayer AG) was spin-coated at 4000 rpm for 60 s to form a thin layer of 35 nm thickness on the cleaned ITO substrate, and baked on a hot plate at  $140\text{ }^\circ\text{C}$  for about 15 min. A blend film of copolymer:PC<sub>71</sub>BM (1:1.5 w/w) was prepared by spin-coating its mixed solvent of chlorobenzene (CB)/1,8-diiodooctane (DIO) (97:3, v:v) solution (concentration:  $25\text{ mg mL}^{-1}$ ) or chlorobenzene (CB)/chloroform (CF)/1,8-diiodooctane (DIO) (48.5:48.5:3, v:v:v) solution (concentration:  $20\text{ mg mL}^{-1}$ ) at 1500 rpm for 60 s. The thickness of the active layers was kept at about 100-105 nm. A Ca layer (15 nm) and an Al layer (140 nm) were finally deposited in

sequence under a vacuum of  $2 \times 10^{-6}$  Torr to form the negative electrode. Hole-only devices were fabricated similarly to the PSCs with a structure of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM (1:1.5)/MoO<sub>3</sub>/Ag. 10 nm MoO<sub>3</sub> was evaporated onto the surface of the photoactive layer with or without surface modification before Al evaporation. All devices were fabricated in a nitrogen-filled glove box (<0.1 ppm O<sub>2</sub> and H<sub>2</sub>O). The thickness of the films was measured using a Dektak 6 M surface profilometer. The device area was 0.04 cm<sup>2</sup>. The J-V characterization of the devices was carried out on a computer-controlled Keithley 2400 Source Measurement system. The EQE values were tested with a Newport Model 77890 (Newport Co. Ltd.) during illumination with monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by using a standard Si solar cell. All fabrication and characterization processes, except for the EQE measurements, were conducted in a glove box.

## 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra.







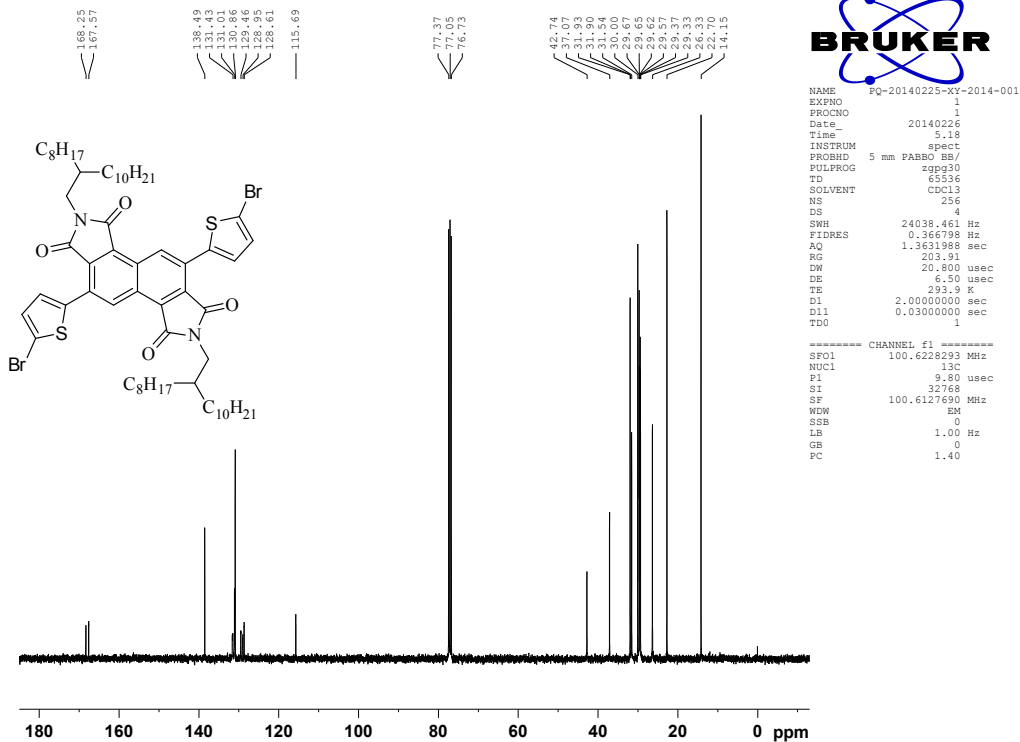


Fig. S6  $^{13}C$  NMR spectrum of 3,7-(5,5'-bromothieryl)-1,2,5,6-naphthalenediimide (M).

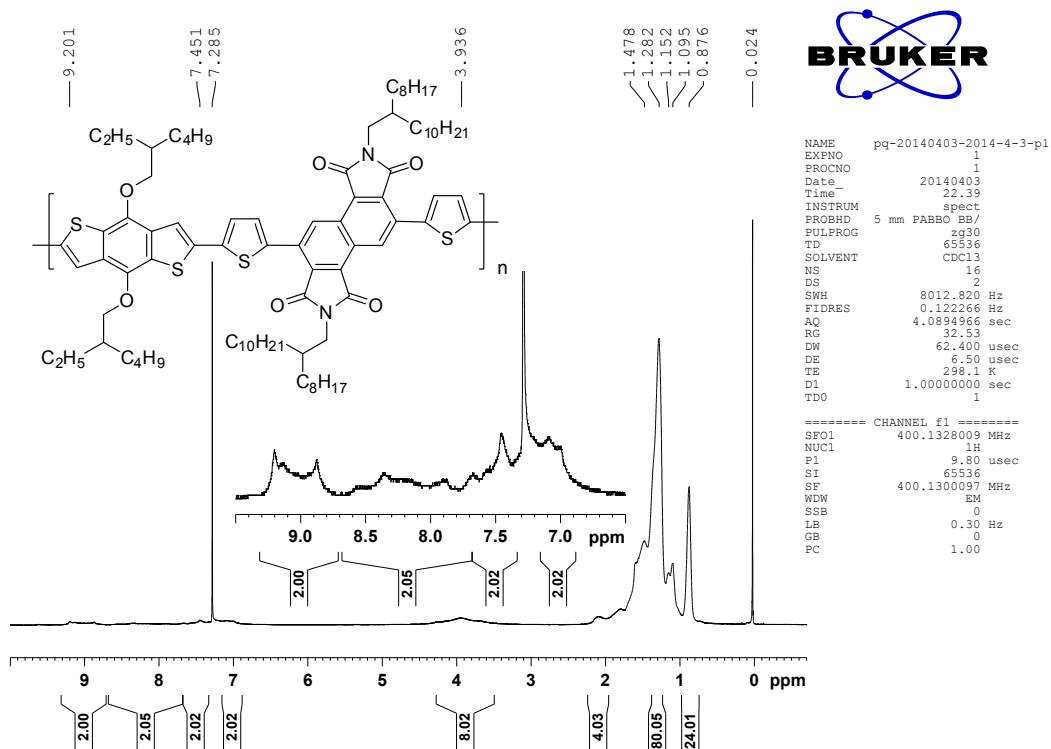


Fig. S7  $^1H$  NMR spectrum of PBDTA-INDI.



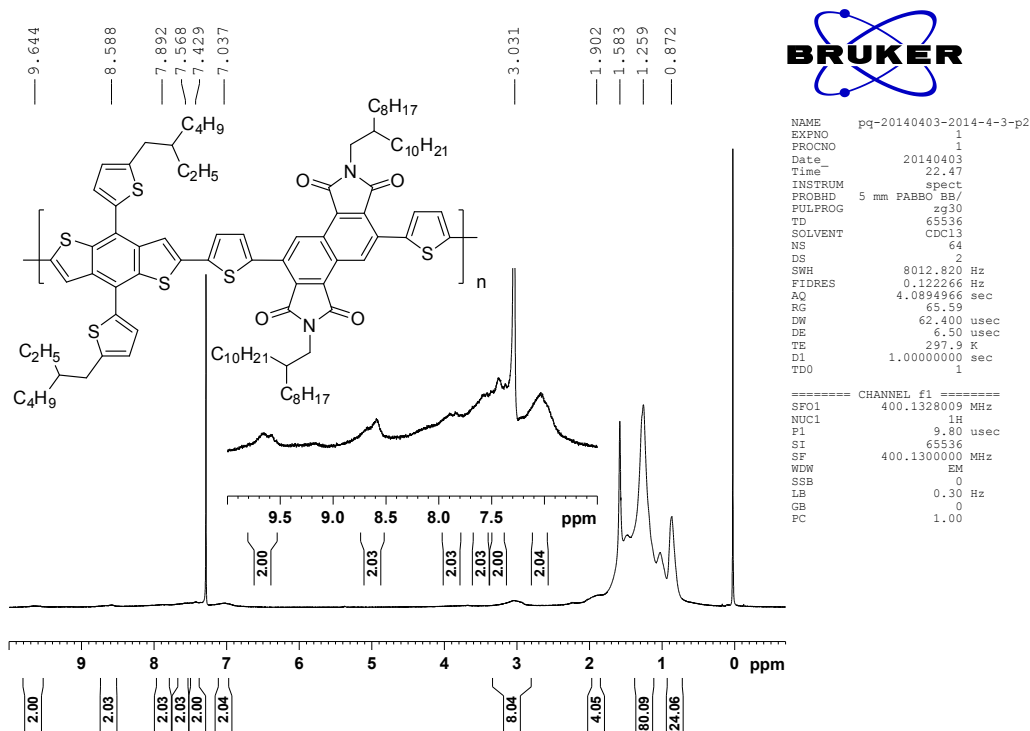


Fig. S8 <sup>1</sup>H NMR spectrum of PBDTT-INDI.

## 6. References

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