

A New Type of Organic Photovoltaic Materials: Poly(Rod-Coil) Polymers having Alternative Conjugated and Non-Conjugated Segments

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Experimental Section

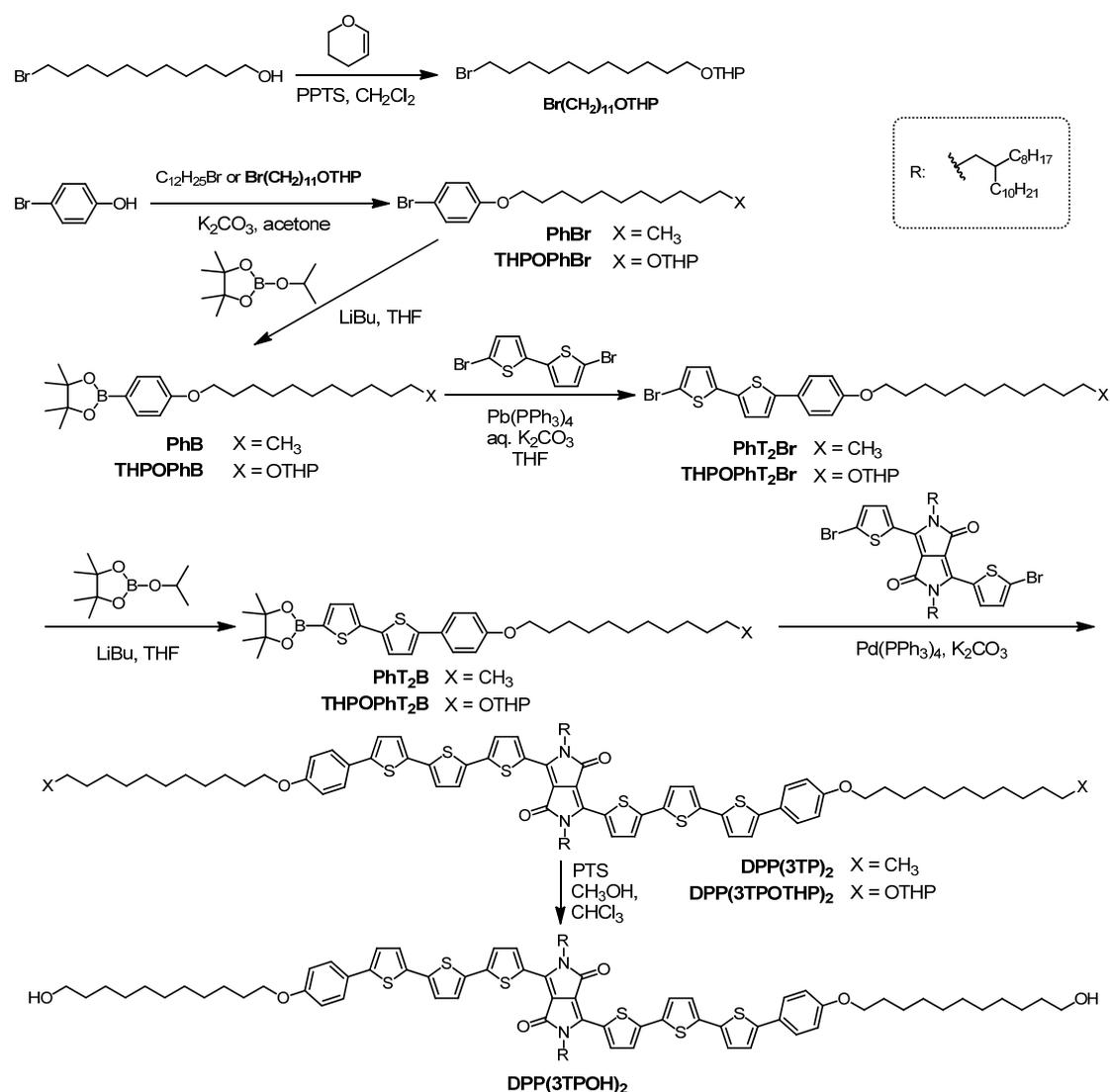
Methods and Characterizations

¹H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal reference. High temperature ¹H NMR was performed on a Varian 400 MHz spectrometer or a Agilent 600 MHz DD2 spectrometer at 110 °C using tetrachloroethane-*d*₂ as a solvent. Electron ionization (EI) mass spectra were measured on an Agilent 5973N mass spectrometer by an electron impact ionization procedure (70 eV). Gel permeation chromatography (GPC) was carried out on a Waters 1515 HPLC instrument equipped with a Waters 2489 UV detector, using THF as an eluent. The molecular weight and polydispersity index (PDI) were calculated based on polystyrene standards. UV-vis absorption spectroscopy was performed on a Hitachi U-3310 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 660C instrument using a three-electrode cell with a glassy carbon as working electrode, a platinum wire as counter electrode, and Ag/AgNO₃ as reference electrode. The samples were first casted on a glassy carbon electrode to form a film and then measured in CH₃CN in the presence of 0.1 M Bu₄NPF₆ with a scan rate of 50 mV s⁻¹. Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument under N₂ with a temperature rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed on a Q2000 modulated DSC instrument under N₂ with a heating rate of 10 °C min⁻¹ and a cooling rate of 15 °C min⁻¹. Transmission electron microscopy

(TEM) was performed on a Tecnai G2 Sphera TEM (FEI) operated at 200 kV. X-ray diffraction (XRD) was carried out on a PANalytical X'Pert Pro diffractometer with Cu K α beam (40 kV, 40 mA) in θ - 2θ scans (0.033 Å step size, 30 s/step). Polymer sample films were prepared by drop-casting from their CHCl₃ solutions onto a quartz plate.

Materials.

Unless indicated, all commercial reagents were used as received. The solvents for reactions were dehydrated following common methods, tetrahydrofuran (THF), ether, and NEt₃ refluxed over a mixture of Na and benzophenone while chlorobenzene dried over CaH₂ under argon, and freshly distilled prior to use.



Scheme S1. Synthesis of DPP(3TP)₂ and DPP(3TPOH)₂.

Br(CH₂)₁₁OTHP: A solution of 3,4-2H-dihydropyran (8 mL, 87.7 mmol) in dichloromethane (60 mL) was dropwise added to a solution of 11-bromoundecyl-1-alcohol (10 g, 39.8 mmol) and pyridinium *p*-toluenesulfonate (1.2 g, 4.7 mmol) in dichloromethane (60 mL) at 0 °C under argon. Then, the reaction

mixture was warmed to room temperature and stirred over 8 hours. After reaction, the organic solution was washed with deionized water, saturated salt water orderly and then dried over anhydrous MgSO_4 . After filtration, the filtrate was concentrated under reduced pressure. The residue was subjected to silica column chromatography using hexane/ CH_2Cl_2 (2/1, v/v) as eluent, allowing to separate 12.46 g compound **Br(CH₂)₁₁OTHP** as a colorless oil with a yield of 93%. ¹H NMR (300 MHz, CDCl_3) δ (ppm): 4.57 (m, 1H), 3.90–3.83 (m, 1H), 3.77–3.69 (m, 1H), 3.52–3.48 (m, 1H), 3.43–3.34 (m, 3H), 1.90–1.80 (m, 3H), 1.59–1.52 (m, 7H), 1.42–1.28 (m, 14H).

THPOPhBr: Into a refluxed mixture of 4-bromo-phenol (5 g, 2.89 mmol) and K_2CO_3 (5.438 g, 8.67 mmol) in acetone (50 mL), a solution of **Br(CH₂)₁₁OTHP** (9.69 g, 2.89 mmol) in acetone (15 mL) was dropwise added under argon. After stirred and refluxed overnight, the reaction mixture was filtrated. The filtrate was concentrated under a reduced pressure and the residue was subjected to silica column chromatography using hexane/ CH_2Cl_2 (1/1, v/v) as eluent. The product **THPOPhBr** was obtained as a colorless oil in a yield of 84% (10.44 g). ¹H NMR (300 MHz, CDCl_3) δ (ppm): 7.34 (d, $J=8.7$ Hz, 2H), 6.78 (d, $J=8.4$ Hz, 2H), 4.58 (br, 1H), 3.93–3.89 (m, 3H), 3.75–3.72 (m, 1H), 3.52 (m, 1H), 3.40 (m, 1H), 1.90–1.28 (m, 24H).

THPOPhB: A solution of *n*-butyllithium (17 mL, 1.6 M in hexane, 27.2 mmol) was dropwise added into a solution of **THPOPhBr** (5.43 g, 12.7 mmol) in dry THF (100 mL) under argon at -78 °C and continued to stir for 2.5 hours. Then a solution of isopropoxyboronic acid pinacol ester (9.1 mL, 44.6 mmol) in THF (50 mL) was slowly added to the reaction system. The reaction mixture was warmed to room temperature and stirred overnight. After the reaction was quenched by a slow addition of water, the reaction mixture was extracted and the organic layer was collected, washed with water, and dried over anhydrous Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure. The residue was subjected to silica column chromatography using hexane/ CH_2Cl_2 (1/1, v/v) as eluent, allowing to separate 5.48 g the product **THPOPhB** as a light yellow oil with a yield of 91%. ¹H NMR (300 MHz, CDCl_3) δ (ppm): 7.72 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 4.55 (br, 1H), 3.95–3.91 (m, 3H), 3.74–3.68 (m, 1H), 3.48–3.45 (m, 1H), 3.38–3.32 (m, 1H), 1.81–1.27 (m, 36H).

THPOPhT₂Br: A mixture of 5,5'-dibromo-2,2'-bithiophene (3.4149 g, 10.5 mmol), **THPOPhB** (2.35 g, 5.25 mmol), methyltributylammonium chloride (3.71 g, 15.8 mmol), K_2CO_3 (8.186 g, 59.3 mmol), water (20 mL) and THF (100 mL) was degassed by argon bubbling for 10 min, and then added with $\text{Pd}(\text{PPh}_3)_4$ (0.2157 g, 0.187 mmol). The resultant mixture was subject to three circles of freeze-pump-thaw and finally backfilled with argon. After stirred and refluxed for 24 h, the reaction mixture was concentrated and extracted with CHCl_3 /water. The organic layers were collected and subsequently washed with water and saturated aqueous NaCl solution, dried over anhydrous MgSO_4 . After filtration, the filtrate was concentrated under reduced

pressure. The residue was subjected to silica column chromatography using hexane/CHCl₃ (10/1, v/v) as eluent, allowing to separate 1.6447 g product **THPOPhT₂Br** as a yellow solid with a yield of 57%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.51 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 3.9, 1H), 7.05 (d, *J* = 3.3, 1H), 6.97 (d, *J* = 4.2, 1H), 6.88–6.91 (m, 3H), 4.58 (m, 1H), 4.0 (t, *J* = 6.6 Hz, 2H), 3.87 (m, 1H), 3.75 (m, 1H), 3.52 (m, 1H), 3.40 (m, 1H), 1.79–1.29 (m, 24H).

THPOPhT₂B: Compound **THPOPhT₂B** (0.435 g) was synthesized as a yellow green solid in a yield of 72% following a method similar to that of compound **THPOPhB** using **THPOPhT₂Br** (0.5110 g, 0.86 mmol), *n*-butyl lithium (3.01 mL, 4.81 mmol) and isopropoxyboronic acid pinacol ester (1.30 mL, 6.34 mmol) as starting materials. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.53 (m, 2H), 7.24 (d, *J* = 3.6 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.58 (m, 1H), 4.0 (m, 2H), 3.88 (m, 1H), 3.75 (m, 1H), 3.52 (m, 1H), 3.40 (m, 1H), 1.82–1.25 (m, 36H).

DPP(3TPOTHF)₂: The synthesis of compound **DPP(3TPOTHF)₂** was followed a method similar to that of compound **THPOPhT₂Br** using 3,6-bis(5-bromothien-2-yl)-2,5-di(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.1915 g, 0.18 mmol), **THPOPhT₂B** (0.36 g, 0.56 mmol), methyltributylammonium chloride (0.13 g, 0.56 mmol), K₂CO₃ (0.12 g, 0.87 mmol) and Pd(PPh₃)₄ (0.0131 g, 0.011 mmol) as starting materials. After purified by silica column chromatography using CHCl₃/hexane (1/1, v/v) as eluent and recrystallization from CHCl₃/CH₃OH, 0.2869 g **DPP(3TPOTHF)₂** was obtained as purple solid in a yield of 81%. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.79 (s, 2H), 7.54 (d, *J* = 8.4 Hz, 4H), 7.33–7.14 (m, 10H), 6.95 (d, *J* = 8.8 Hz, 4H), 4.58 (m, 2H), 4.06–4.02 (m, 8H), 3.88 (m, 2H), 3.72 (m, 2H), 3.51–3.40 (m, 4H), 1.82 (m, 6H), 1.62–1.28 (m, 108H), 0.90 (m, 12H). MALDI-TOF MS for C₁₁₄H₁₆₄N₂O₈S₆: calcd 1882.9; found: 1881.7 (M⁺). Anal. calcd (%): C, 72.72; H, 8.78; N, 1.49. Found: C, 72.84; H, 9.02; N, 0.99.

DPP(3TPOH)₂: To a solution of **DPP(3TPOTHF)₂** (0.108 g, 0.057 mmol) in chloroform (6 mL) was added with a solution of *p*-toluene sulfonic acid (0.2 g, 1.16 mmol) in methanol (1.2 mL). After stirred at 50 °C for 2 days, the reaction mixture was washed with water and dried over anhydrous Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure. The residue was subjected to silica column chromatography using CHCl₃ as eluent, allowing to separate 0.094 g **DPP(3TPOH)₂** in a yield of 96%. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.78 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.32 (d, *J* = 4.0 Hz, 2H), 7.25–7.13 (m, 8H), 6.95 (d, *J* = 8.4 Hz, 4H), 4.04 (dd, *J*₁ = 12.4 Hz, *J*₂ = 6.4 Hz, 8H), 3.63 (t, *J* = 6.8 Hz, 4H), 1.83–1.80 (m, 6H), 1.58–1.27 (m, 117H), 0.90–0.86 (m, 12H). MALDI-TOF MS for C₁₀₄H₁₄₈N₂O₆S₆: calcd 1714.7; found: 1713.7 (M⁺). Anal. Calcd (%): C, 72.85; H, 8.70; N, 1.63. Found: C, 72.57; H, 8.88; N, 1.53.

PhBr: Compound **PhBr** (15.35 g) was synthesized as white solid in a yield of 90% following a method similar to that of compound **THPOPhBr** using 4-bromophenol (10 g, 57.8 mmol), 1-bromododecane (16.8 mL, 69.3 mmol), and potassium carbonate (23.96 g, 173.6 mmol) as starting materials. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.36 (d, $J = 8.7$ Hz, 2H), 6.78 (d, $J = 8.7$ Hz, 2H), 3.90 (t, $J = 6.6$ Hz, 2H), 1.78–1.71 (m, 2H), 1.43–1.26 (m, 18H), 0.88 (t, $J = 6.9$ Hz, 3H).

PhB: Compound **PhB** (5.93 g) was synthesized as yellow white solid in a yield of 93% following a method similar to that of compound **THPOPhB** using compound **PhBr** (6.0 g, 17.5 mmol), n-butyl lithium (15 mL, 24 mmol), and isopropoxyboronic acid pinacol ester (8 mL, 39 mmol) as starting materials. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.74 (d, $J = 8.1$ Hz, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 1.79–1.75 (m, 2H), 1.44–1.24 (m, 30H), 0.85 (t, $J = 6.9$ Hz, 3H).

PhT₂Br: Compound **PhT₂Br** (0.42 g) was synthesized as yellow solid in a yield of 65% following a method similar to that of compound **THPOPhT₂Br** using compound **PhB** (0.50 g, 1.3 mmol) and 5,5'-dibromo-2,2'-bithiophene (1.0 g, 3.1 mmol) as starting materials. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.51 (d, $J = 8.7$ Hz, 2H), 7.09 (d, $J = 3.6$ Hz, 1H), 7.05 (d, $J = 3.9$ Hz, 1H), 6.97 (d, $J = 3.9$ Hz, 1H), 6.91–6.88 (m, 3H), 3.97 (t, $J = 6.6$ Hz, 2H), 1.81–1.76 (m, 2H), 1.45–1.26 (m, 18H), 0.88 (t, $J = 6.9$ Hz, 3H).

PhT₂B: Compound **PhT₂B** (0.28 g) was synthesized as yellow green solid in a yield of 96% following a method similar to that of compound **THPOPhB** using compound **PhT₂Br** (0.23 g, 0.45 mmol), n-butyl lithium (0.4 mL, 0.64 mmol) and isopropoxyboronic acid pinacol ester (0.26 mL, 1.27 mmol) as starting materials. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 7.52–7.49 (m, 3H), 7.24 (d, $J = 3.6$ Hz, 1H), 7.17 (d, $J = 3.6$ Hz, 1H), 7.11 (d, $J = 3.9$ Hz, 1H), 6.91 (d, $J = 8.1$ Hz, 2H), 3.97 (t, $J = 6.9$ Hz, 2H), 1.79 (m, 2H), 1.46–1.26 (m, 24H), 0.87 (t, $J = 6.9$ Hz, 3H).

DPP(3TP)₂: Compound **DPP(3TP)₂** (0.26 g) was synthesized as purple solid in a yield of 85% following a method similar to that of compound **THPOPhT₂Br** using 3,6-bis(5-bromothien-2-yl)-2,5-di(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (0.18 g, 0.17 mmol), and compound **PhT₂B** (0.39 g, 0.68 mmol) as starting materials. ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) δ (ppm): 8.74 (s, 2H), 7.50 (d, $J = 8.8$ Hz, 4H), 7.29 (d, $J = 4.0$ Hz, 2H), 7.20–7.09 (m, 8H), 6.91 (d, $J = 8.8$ Hz, 4H), 4.02–3.97 (m, 8H), 1.98 (m, 2H), 1.81–1.74 (m, 4H), 1.48–1.24 (m, 106H), 0.90–0.83 (m, 18H). MALDI-TOF MS for $\text{C}_{106}\text{H}_{152}\text{N}_2\text{O}_4\text{S}_6$: calcd 1710.7; found: 1710.3 (M^+). Anal. Calcd (%): C, 74.42; H, 8.96; N, 1.64. Found: C, 74.17; H, 8.82; N, 1.41.

General Procedure for Synthesis of Polymers: A mixture of **DPP(3TPOH)₂** (0.050 g, 0.03 mmol), diisocyanate (0.03 mmol), chlorobenzene (5 mL), and triethylamine (0.3 mL) was added into a reaction tube and the tube was sealed in a

N₂-filled glove box. After the reaction mixture was stirred at 95 °C for 24 h, 4-ethylphenyl isocyanate and methanol was subsequently added into the reaction system for end-capping the polymer. The crude polymer was separated by the precipitation with 100 mL of methanol and filtration, and further subjected to size-exclusion chromatography using a Bio-beads SX1 (Bio-Rad) column and chloroform as the eluent. The first green fraction was collected, evaporated to dryness, and further dried in vacuum for 1 day to get the final product. For **PU4-HW** having a large molecular weight, the polymerization reaction was carried out at 135 °C for 2 days.

PU1. Yield: 87%. M_n : 4.12 kDa, PDI: 1.08. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.76 (br), 7.49–7.47 (m), 7.28–7.26 (m), 7.22–7.19 (m), 7.15–7.08 (m), 6.91–6.89 (m), 4.03–3.98 (m), 3.63 (s), 3.13–3.09 (m), 1.97 (br), 1.80–1.75 (m), 1.67 (s), 1.62–1.57 (m), 1.47 (br), 1.38–1.23 (m), 0.86–0.83 (m). Anal. Calcd for (C₁₁₂H₁₆₀N₄O₈S₆)_x (%): C, 71.58; H, 8.75; N, 2.93. Found (%): C, 70.02; H, 8.70; N, 3.46.

PU2. Yield: 82%. M_n : 6.40 kDa, PDI: 1.15. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.75 (br), 7.47 (m), 7.26–7.09 (m), 6.89 (br), 6.38 (s), 4.13 (br), 3.98 (m), 3.73 (s), 1.96 (br), 1.76 (br), 1.66 (m), 1.41–1.23 (m), 0.85 (m). Anal. Calcd for (C₁₁₂H₁₅₁N₄O₈S₆)_x (%): C, 71.88; H, 8.36; N, 2.94. Found (%): C, 71.13; H, 7.91; N, 3.34.

PU3. Yield: 78%. M_n : 6.66 kDa, PDI: 1.40. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.76 (br), 7.47 (m), 7.27–7.08 (m), 7.02 (m), 6.90 (m), 6.45(s), 4.13 (m), 4.01–3.97 (m), 3.73 (br), 2.59 (m), 1.96 (br), 1.77 (m), 1.66 (m), 1.45–1.23 (m), 0.86–0.83 (m). Anal. Calcd for (C₁₁₂H₁₅₁N₄O₈S₆)_x (%): C, 71.88; H, 8.36; N, 2.94. Found (%): C, 71.66; H, 8.06; N, 3.37.

PU4-LW. Yield: 95%. M_n : 7.90 kDa, PDI: 1.39. ¹H NMR (400 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.75 (br), 7.47 (br), 7.27–7.20 (m), 7.13–7.06 (m), 6.89–6.88 (m), 6.38 (s), 4.12 (m), 4.01–3.96 (m), 3.86 (s), 3.72 (s), 2.59 (m), 1.96 (br), 1.77 (m), 1.66 (m), 1.41–1.23 (m), 0.84 (m). Anal. Calcd for (C₁₁₉H₁₅₇N₄O₈S₆)_x (%): C, 72.85; H, 8.29; N, 2.81. Found (%): C, 73.18; H, 8.12; N, 3.04.

PU4-HW. Yield: 86%. M_n : 16.7 kDa, PDI: 1.94. ¹H NMR (600 MHz, C₂D₂Cl₄, 110 °C) δ (ppm): 8.75 (br), 7.46 (m), 7.26–7.06 (m), 6.89–6.88 (m), 6.38 (s), 4.12 (m), 3.97 (m), 3.86 (s), 3.72 (s), 2.57 (m), 1.96 (br), 1.76 (m), 1.65 (m), 1.45–1.23 (m), 0.84 (m). Anal. Calcd for (C₁₁₉H₁₅₇N₄O₈S₆)_x (%): C, 72.85; H, 8.29; N, 2.81. Found (%): C, 72.22; H, 8.08; N, 2.74.

Fabrication and Characterization of Solar Cell Devices

The solar cell devices were fabricated with a structure of ITO/PEDOT:PSS/active

layer/Al. A layer of PEDOT:PSS (Heraeus Clevis P VP. Al 4083) with a thickness around 30 nm was spin-coated on top of well cleaned ITO glass at 6000 rpm for 1 min and baked at 120 °C for 15 min. After transferred into a N₂-filled glove box, the active layer with a thickness between 50–90 nm was spin-coated from a chloroform, chlorobenzene, or 1,2-dichlorobenzene solution of a mixture of the checked donor and PC₆₁BM (Lumitec LT-8905), and then subjected to thermal annealing at 80 °C for 10 min. Finally, the solar cell was finished by thermally deposition of a 100 nm-thick Al layer on the top of the active layer under a high vacuum (< 10⁻⁵ mbar) through a shadow mask. The effective cell area is 7 mm². Layer thickness was measured on a Veeco Dektak 150 profilometer. Current density–voltage (*J–V*) curves were recorded with a Keithley 2420 source meter. Photocurrent was acquired upon irradiation using an AAA solar simulator (Oriel 94043A, 450 W) with AM 1.5G filter. The intensity was adjusted to be 100 mW cm⁻² under the calibration with a NREL-certified standard silicon cell (Oriel reference cell 91150). External quantum efficiency (EQE) was detected with a 75 W Xe lamp, an Oriel monochromator 74125, an optical chopper, a lock-in amplifier and a NREL-calibrated crystalline silicon cell.

Measurement of Hole and Electron Mobilities for the Blend Films

Both hole and electron mobilities were measured by space-charge-limited current (SCLC) method. The hole mobility was measured with a device configuration of ITO/PEDPOT:PSS/blend film/Au, whereas that of electron with a device configuration of ITO/PEDPOT:PSS/blend film/Al. According to Mott-Gurney law, SCLC theory can be described by

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{(V_a - V_{bi})^2}{d^3}$$

where *J* is current density, ε_0 is permittivity of vacuum, ε_r is relative permittivity of the material (for conjugated polymer, ε_r is 3 in general), μ is mobility, V_a is applied voltage, V_{bi} is built-in voltage, and *d* is the thickness of the active film.

Supporting Figures and Tables

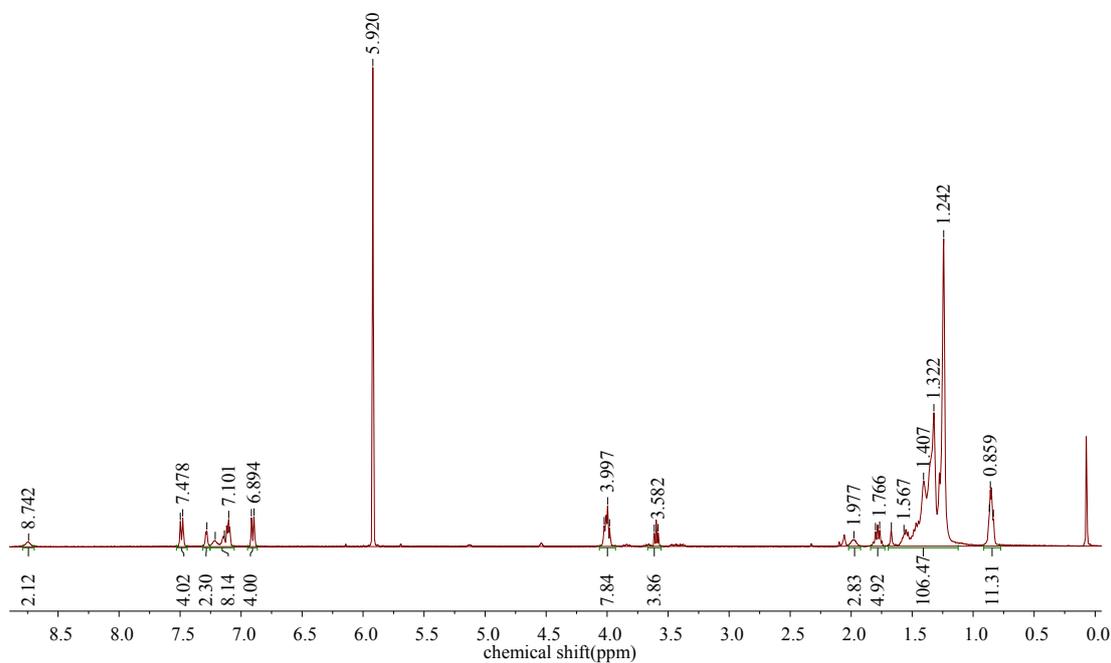


Fig. S1 ^1H NMR of $\text{DPP}(\text{3TPOH})_2$ ($\text{C}_2\text{D}_2\text{Cl}_4$, $110\text{ }^\circ\text{C}$).

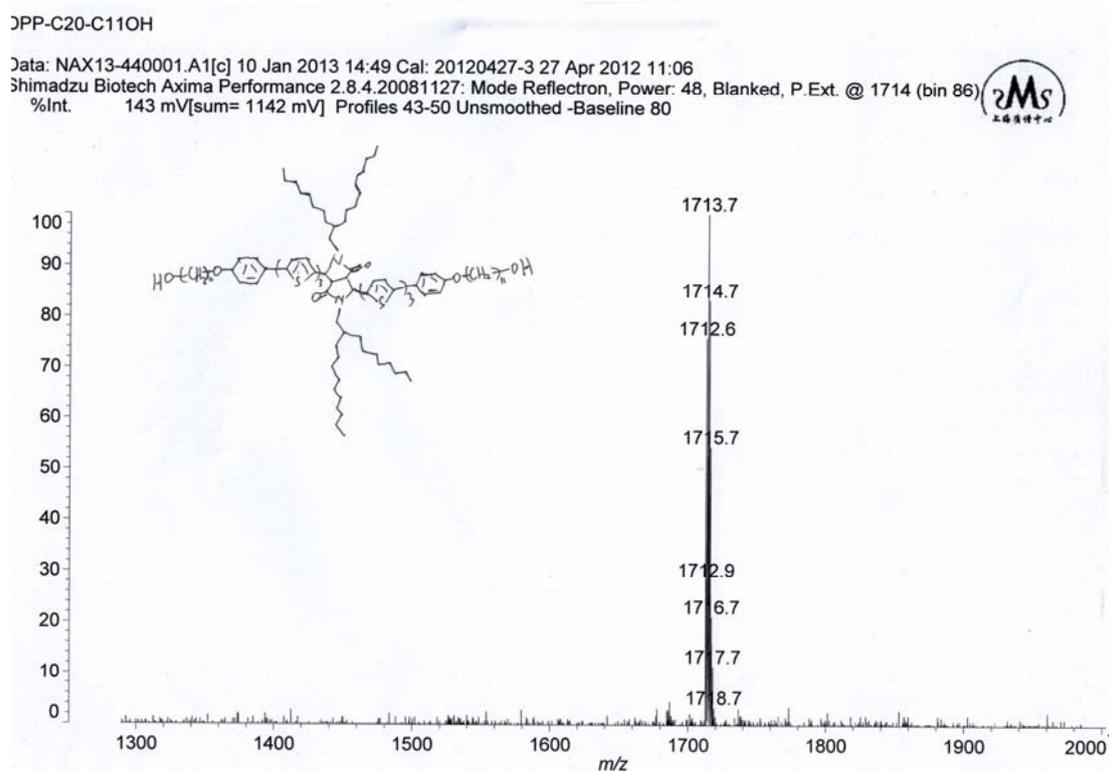


Fig. S2 MALDI-TOF mass spectrum of $\text{DPP}(\text{3TPOH})_2$.

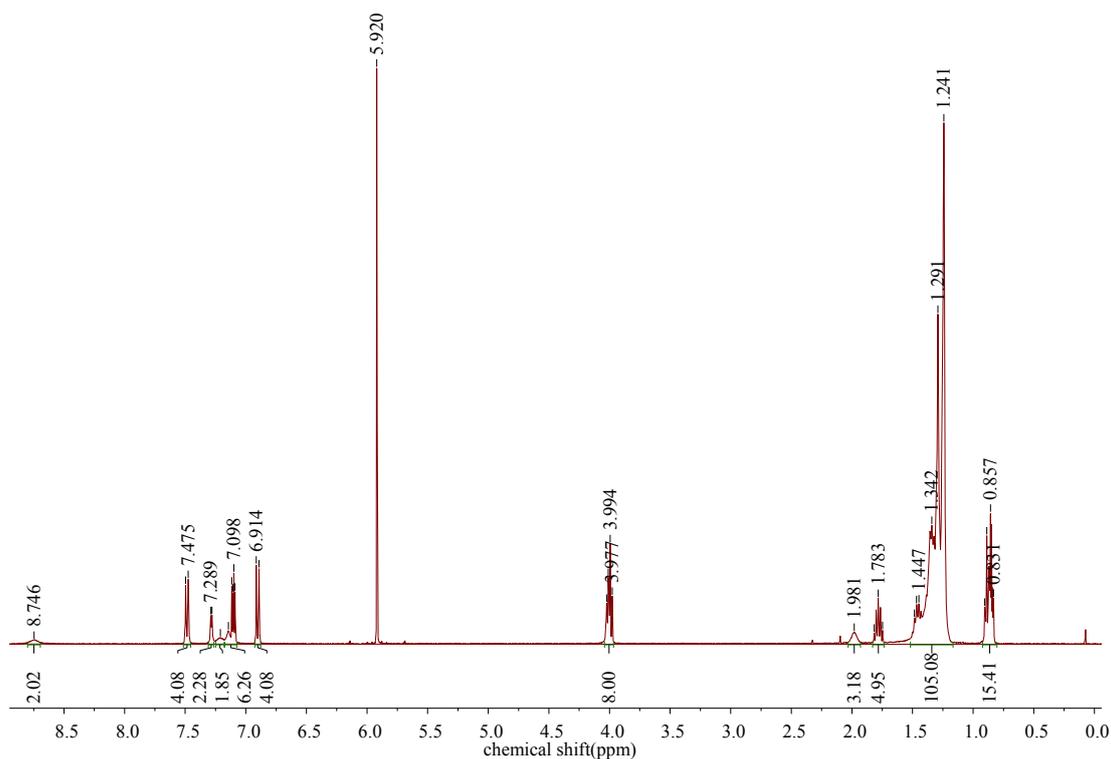


Fig. S3 ^1H NMR of $\text{DPP}(\text{3TP})_2$ ($\text{C}_2\text{D}_2\text{Cl}_4$, $110\text{ }^\circ\text{C}$).

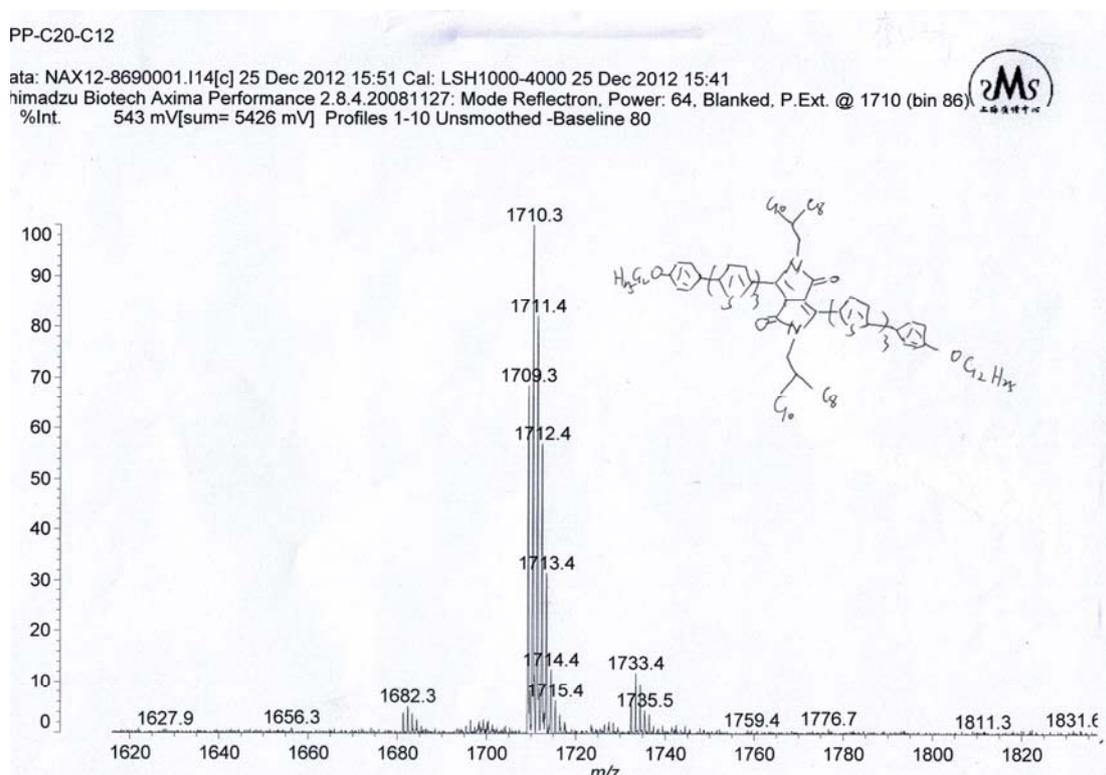


Fig. S4 MALDI-TOF mass spectrum of $\text{DPP}(\text{3TP})_2$.

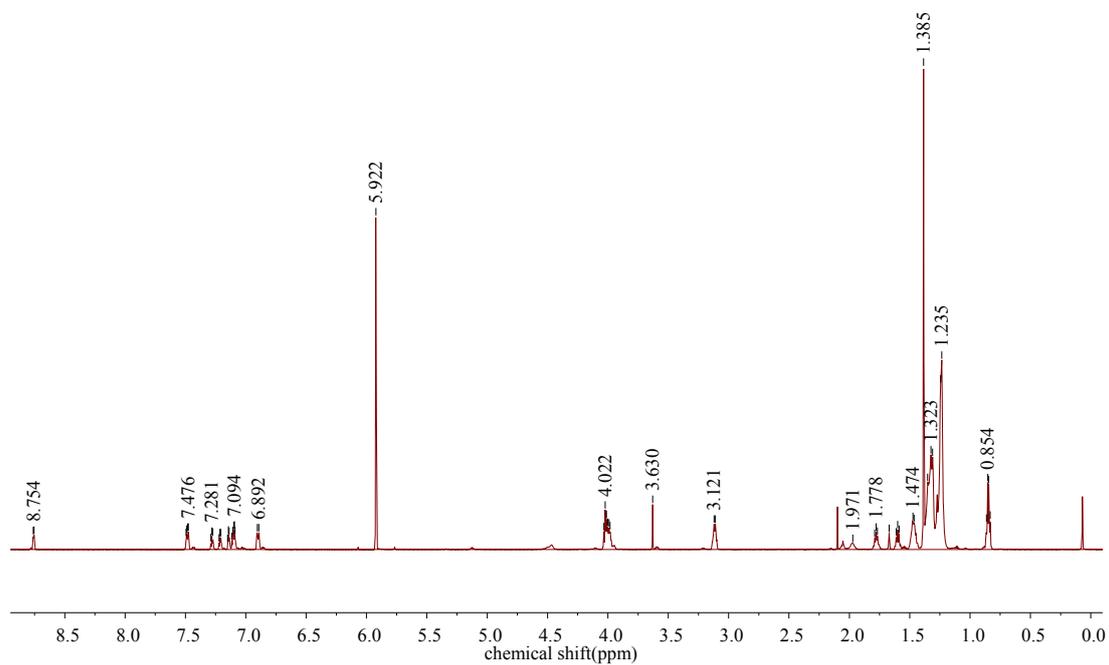


Fig. S5 ^1H NMR of **PU1** ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C).

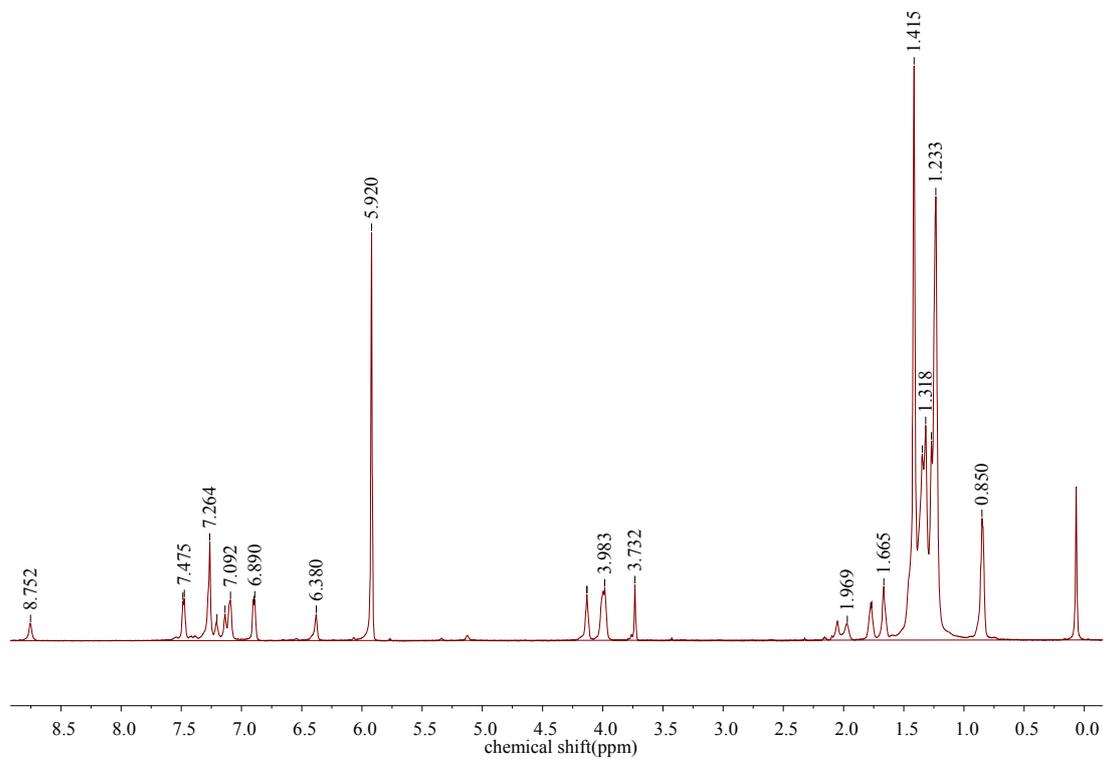


Fig. S6 ^1H NMR of **PU2** ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C).

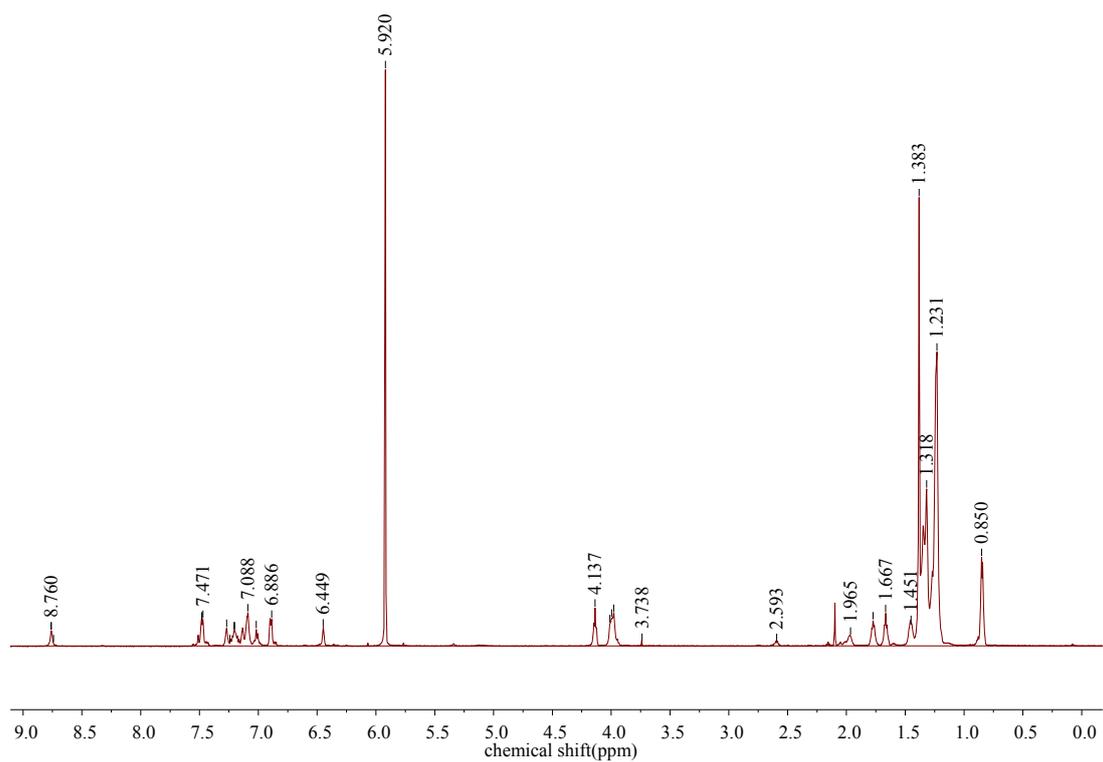


Fig. S7 ^1H NMR of **PU3** ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C).

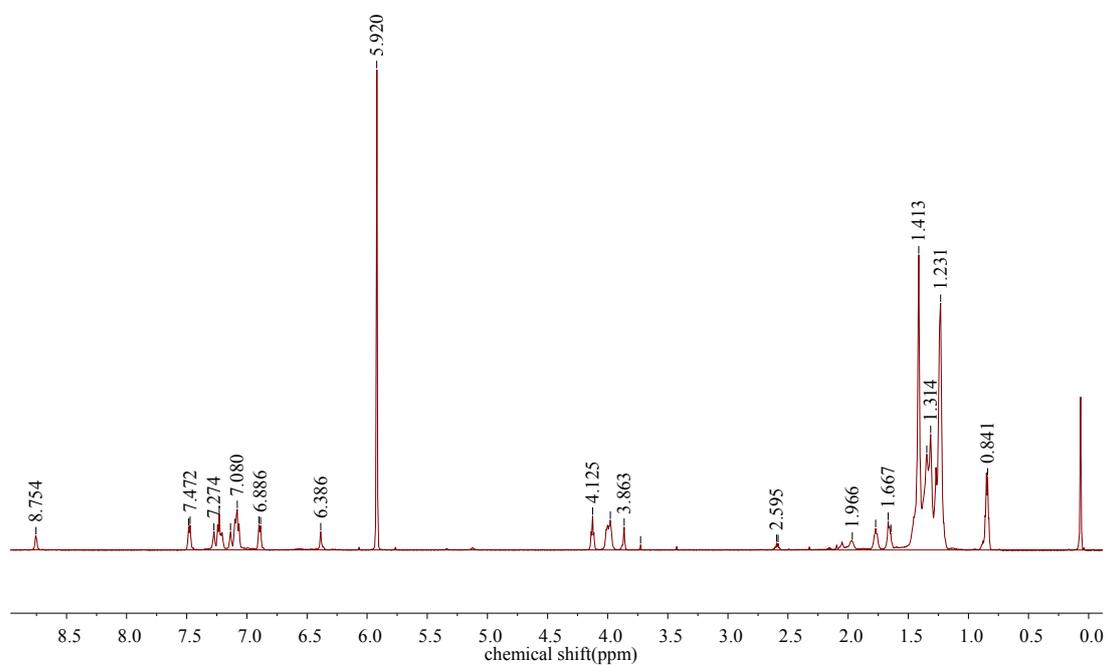


Fig. S8 ^1H NMR of **PU4-LW** ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C).

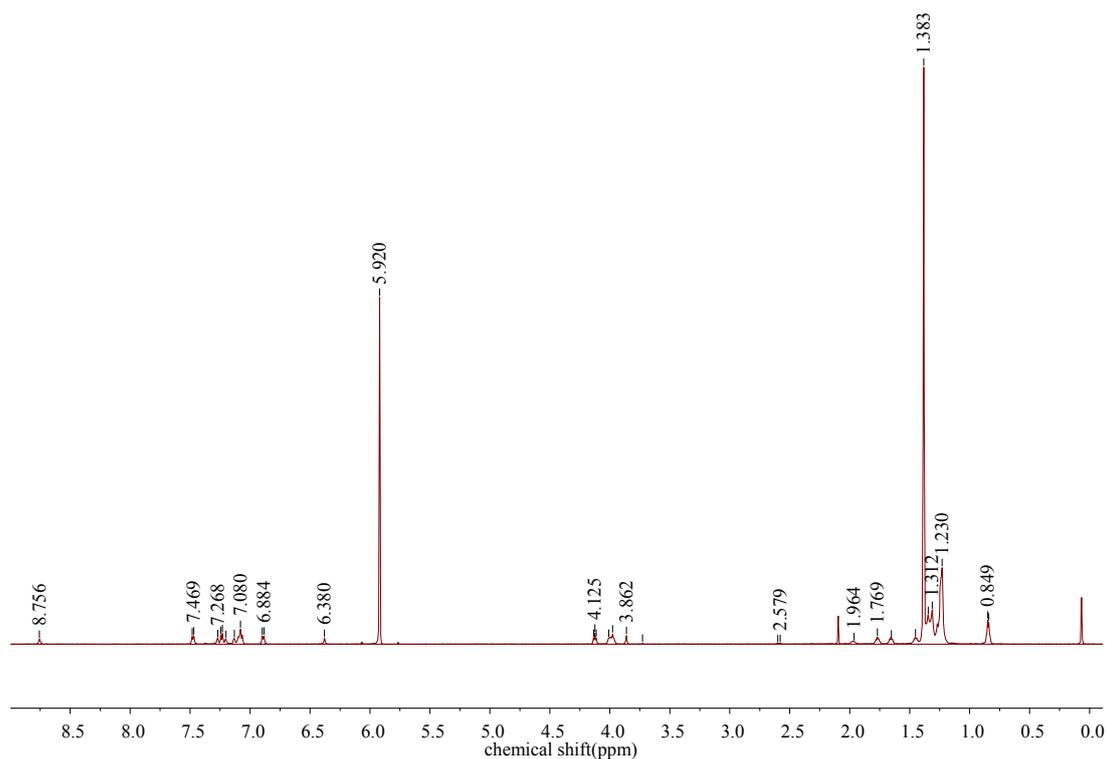


Fig. S9 ^1H NMR of **PU4-HW** ($\text{C}_2\text{D}_2\text{Cl}_4$, $110\text{ }^\circ\text{C}$).

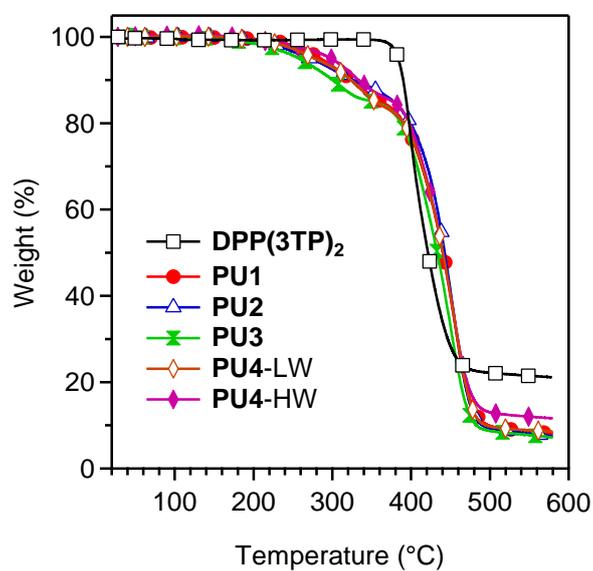


Fig. S10 TGA traces of **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW** with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a N_2 flow.

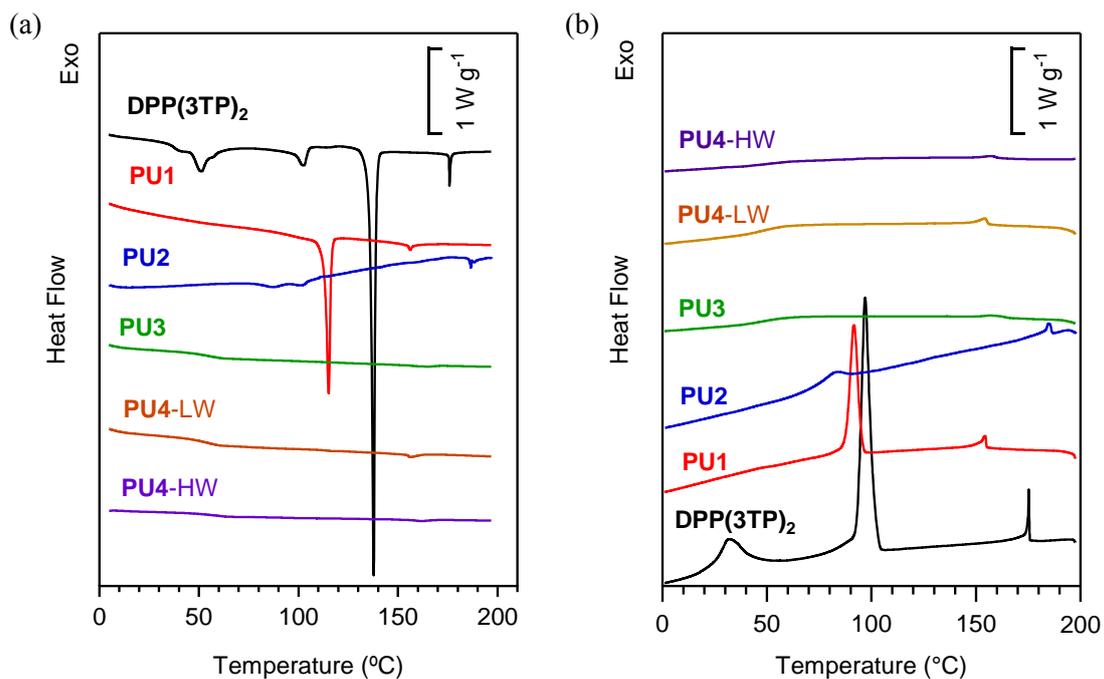


Fig. S11 The second (a) heating and (b) cooling DSC traces of **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW** under a N₂ atmosphere. Heating rate: 10 °C min⁻¹, cooling rate: 15 °C min⁻¹.

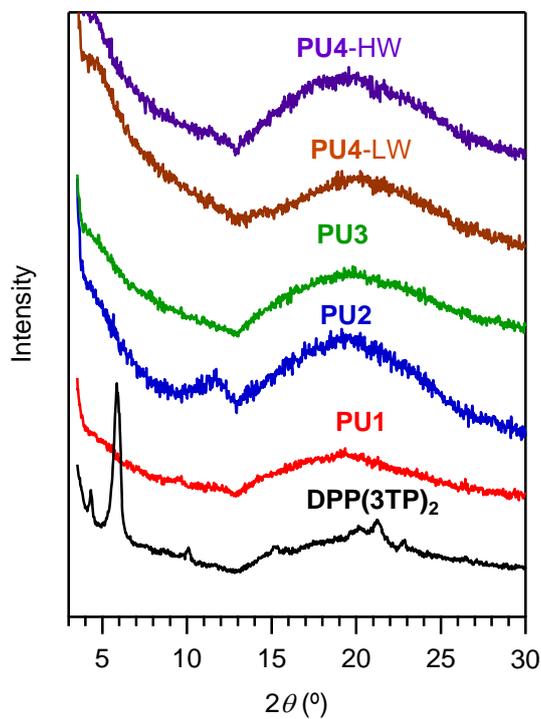


Fig. S12 XRD profiles of **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW** films.

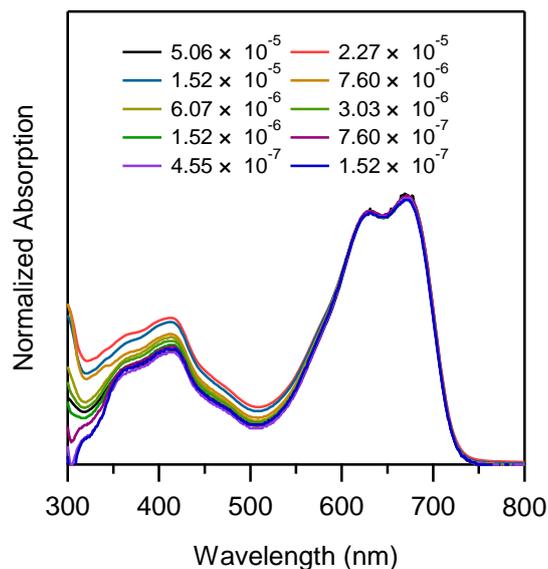


Fig. S13 UV-vis absorption spectra of the solutions of **DPP(3TP)₂** in *o*-dichlorobenzene with different concentrations (mol/L).

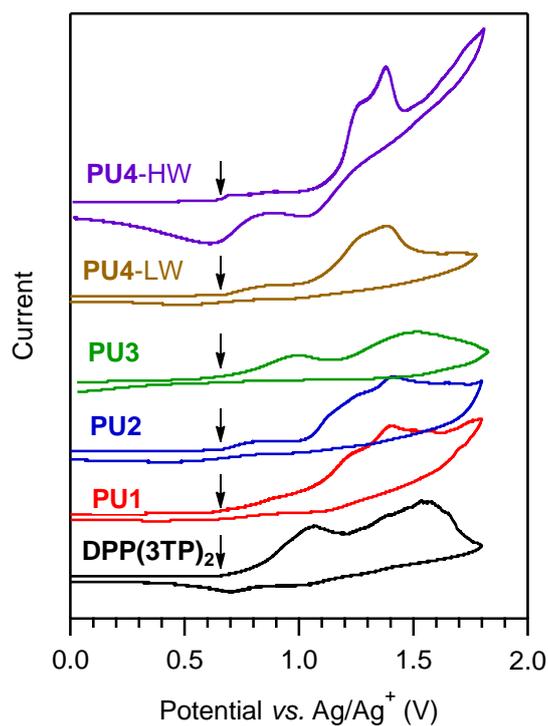


Fig. S14 CV profiles of **DPP(3TP)₂**, **PU1**, **PU2**, **PU3**, **PU4-LW** and **PU4-HW**. All the polymers and DPP(3TP)₂ have been found to have the onset oxidation peak around 0.65 V versus Ag/Ag⁺, giving their HOMO energy level of -5.3 eV.

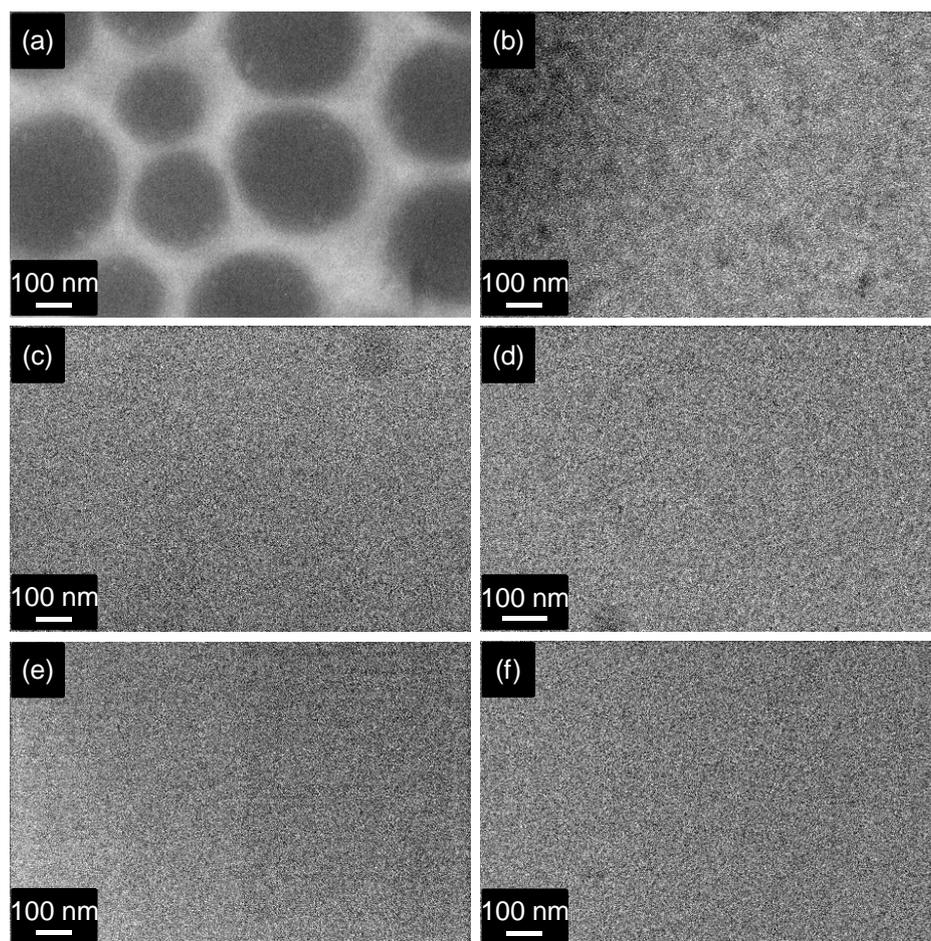


Fig. S15 TEM images of the blend films based on (a) **DPP(3TP)₂**, (b) **PU1**, (c) **PU2**, (d) **PU3**, (e) **PU4-LW**, or (f) **PU4-HW** with **PC₆₁BM**.

Table S1. Device parameters for the BHJ solar cells fabricated with **DPP(3TP)₂** and **PC₆₁BM** under different conditions.

DPP(3TP)₂:PC₆₁BM (w/w)	Solvent	Concentration (mg/mL)	Spin-coating Speed (rpm)	Annealing ^[a] (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE ^[b] (%)
1:1	CHCl ₃	20	3000	-	0.71	0.95	46.0	0.31 (0.29)
1:2	CHCl ₃	20	3000	-	0.71	0.97	48.4	0.33 (0.32)
1:3	CHCl ₃	20	3000	-	0.70	0.57	51.8	0.21 (0.19)
1:2	CHCl ₃	20	3000	80	0.72	1.46	47.6	0.50 (0.49)
1:2	CHCl ₃	20	3000	100	0.68	1.64	39.3	0.44 (0.43)
1:2	CHCl ₃	20	3000	120	0.22	0.51	31.4	0.04 (0.03)
1:2	CHCl ₃	20	2500	-	0.67	0.88	53.2	0.32 (0.31)
1:2	CHCl ₃	20	3500	-	0.67	1.06	55.5	0.39 (0.38)
1:2	CHCl ₃	20	4000	-	0.69	0.93	54.3	0.35 (0.33)
1:2	CHCl ₃	20	3500	80	0.76	1.82	43.2	0.59 (0.55)

[a] for 10 min. [b] Data in parentheses are the average values.

Table S2. Device parameters for the BHJ solar cells fabricated with **PU1** and **PC₆₁BM** under different conditions.

PU1:PC₆₁BM	Solvent ^[a]	Concentration	Spin-coating Speed	DIO ^[b]	Annealing ^[c]	V _{OC}	J _{SC}	FF	PCE ^[d]
(w/w)		(mg/mL)	(rpm)		(°C)	(V)	(mA cm ⁻²)	(%)	(%)
1:1	CB	10	800		80	0.68	0.99	44.2	0.30 (0.28)
1:2	CB	10	800		80	0.69	1.40	51.8	0.50 (0.47)
1:3	CB	10	800		80	0.69	1.60	56.0	0.62 (0.59)
1:4	CB	10	800		80	0.68	1.92	57.0	0.75 (0.71)
1:5	CB	10	800		80	0.68	1.69	59.4	0.68 (0.63)
1:4	o-DCB	10	500		80	0.65	1.37	57.7	0.51 (0.48)
1:4	CHCl ₃	10	1500		80	0.69	1.06	56.8	0.42 (0.37)
1:4	CB	10	500		80	0.70	1.64	56.3	0.65 (0.61)
1:4	CB	10	1000		80	0.68	1.66	55.1	0.62 (0.60)
1:4	CB	10	1200		80	0.65	1.54	54.3	0.54 (0.53)
1:4	CB	10	800		115	0.69	1.52	50.0	0.52 (0.51)
1:4	CB	10	800		120	0.72	1.38	52.6	0.52 (0.49)
1:4	CB	10	800	1%	80	0.67	1.54	55.2	0.57 (0.55)
1:4	CB	10	800	2%	80	0.66	1.05	53.9	0.38 (0.31)
1:4	CB	10	800	3%	80	0.65	0.79	53.1	0.27 (0.23)

[a] CB: chlorobenzene; o-DCB: o-dichlorobenzene. [b] DIO: 1,8-diiodooctane. [c] for 10 min. [d] Data in parentheses are the average values.

Table S3. Device parameters for the BHJ solar cells fabricated with **PU2** and **PC₆₁BM** under different conditions.

PU2:PC₆₁BM	Solvent ^[a]	Concentration	Spin-coating Speed	DIO ^[b]	V _{OC}	J _{SC}	FF	PCE ^[c]
(w/w)		(mg/mL)	(rpm)		(V)	(mA cm ⁻²)	(%)	(%)
1:1	CHCl ₃	10	1000	-	0.77	0.64	39.1	0.19(0.18)
1:2	CHCl ₃	10	1000	-	0.80	1.31	50.8	0.54(0.52)
1:3	CHCl ₃	10	1000	-	0.82	1.80	51.2	0.75(0.72)
1:4	CHCl ₃	10	1000	-	0.80	2.09	58.8	0.98(0.95)
1:5	CHCl ₃	10	1000	-	0.80	1.94	54.7	0.85(0.82)
1:4	o-DCB	10	800	-	0.68	3.39	41.1	0.94(0.93)
1:4	CB	10	800	-	0.70	1.37	54.7	0.52(0.47)
1:4	CHCl ₃	10	1500	-	0.82	1.76	54.1	0.78(0.75)
1:4	CHCl ₃	15	1000	-	0.80	1.18	53.4	0.50(0.48)
1:4	CHCl ₃	15	2000	-	0.80	1.52	53.9	0.65(0.63)
1:4	CHCl ₃	10	1000	1%	0.78	2.01	59.2	0.93(0.89)
1:4	CHCl ₃	10	1000	2%	0.71	2.05	49.6	0.72(0.70)
1:4	CHCl ₃	10	1000	3%	0.68	2.76	44.6	0.83(0.80)
1:4	CHCl ₃	10	1000	4%	0.67	1.79	46.6	0.56(0.52)

[a] CB: chlorobenzene; o-DCB: o-dichlorobenzene. [b] DIO: 1,8-diiodooctane. [c] Data in parentheses are the average values.

Table S4. Device parameters for the BHJ solar cells fabricated with **PU3** and **PC₆₁BM** under different conditions

PU3:PCBM (w/w)	Solvent ^[a]	Concentration (mg/mL)	Spin-coating Speed (rpm)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE ^[b] (%)
1:1	o-DCB	30	800	0.75	1.22	51.8	0.48 (0.46)
1:2	o-DCB	30	800	0.76	1.49	53.7	0.61 (0.58)
1:3	o-DCB	30	800	0.77	1.67	55.1	0.71 (0.68)
1:4	o-DCB	30	800	0.75	1.57	57.9	0.68 (0.67)
1:5	o-DCB	30	800	0.73	1.50	61.5	0.67 (0.66)
1:4	CB	20	500	0.76	1.08	60.6	0.50 (0.48)
1:4	CHCl ₃	20	1000	0.75	1.19	56.7	0.50 (0.47)
1:4	o-DCB	20	500	0.73	1.62	58.9	0.70 (0.68)
1:4	o-DCB	20	800	0.70	1.40	57.4	0.57 (0.54)
1:4	o-DCB	20	1000	0.69	1.15	58.5	0.47 (0.45)
1:4	o-DCB	30	1000	0.75	1.61	57.3	0.69 (0.67)
1:4	o-DCB	40	800	0.73	1.30	61.1	0.58 (0.54)
1:4	o-DCB	40	1000	0.75	1.46	60.7	0.66 (0.64)

[a] CB: chlorobenzene; o-DCB: o-dichlorobenzene. [b] Data in parentheses are the average values.

Table S5. Device parameters for the BHJ solar cells fabricated with **PU4-LW** and **PC₆₁BM** under different conditions

PU4-LW:PCBM (w/w)	Solvent ^[a]	Concentration (mg/mL)	Spin-coating Speed (rpm)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE ^[b] (%)
1:1	CHCl ₃	10	1500	0.72	1.13	49.4	0.40 (0.39)
1:2	CHCl ₃	10	1500	0.73	1.39	52.8	0.54 (0.52)
1:3	CHCl ₃	10	1500	0.75	1.59	56.4	0.67 (0.63)
1:4	CHCl ₃	10	1500	0.78	1.80	53.3	0.75 (0.70)
1:5	CHCl ₃	10	1500	0.75	1.75	58.4	0.77 (0.76)
1:4	o-DCB	10	800	0.78	1.47	52.7	0.60 (0.56)
1:4	CB	10	800	0.74	1.37	51.3	0.52 (0.50)
1:4	CHCl ₃	10	1000	0.77	1.39	52.1	0.56 (0.55)
1:4	CHCl ₃	10	2000	0.75	1.53	50.7	0.58 (0.53)
1:4	CHCl ₃	20	1000	0.75	0.73	50.7	0.28 (0.27)
1:4	CHCl ₃	20	1500	0.75	0.89	52.3	0.35 (0.34)
1:4	CHCl ₃	20	2000	0.77	1.02	51.5	0.40 (0.39)

[a] CB: chlorobenzene; o-DCB: o-dichlorobenzene. [b] Data in parentheses are the average values.

Table S6. Device parameters for the BHJ solar cells fabricated with **PU4-HW** and **PC₆₁BM** under different conditions

PU4-HW:PC₆₁BM (w/w)	Solvent ^[a]	Concentration (mg/mL)	Spin-coating Speed (rpm)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE ^[b] (%)
1:2	CHCl ₃	20	1500	0.75	0.53	33.8	0.13 (0.12)
1:3	CHCl ₃	20	1500	0.73	0.73	43.0	0.23 (0.22)
1:4	CHCl ₃	20	1500	0.74	0.92	45.7	0.31 (0.26)
1:5	CHCl ₃	20	1500	0.74	0.76	50.7	0.29 (0.26)
1:4	CHCl ₃	20	2500	0.75	1.61	52.4	0.63 (0.60)
1:4	CHCl ₃	10	1000	0.75	1.76	51.6	0.68 (0.63)
1:4	CHCl ₃	10	2000	0.76	1.71	57.6	0.75 (0.73)
1:4	o-DCB	20	1000	0.78	1.99	53.0	0.82 (0.77)
1:4	CB	10	500	0.77	1.78	56.6	0.78 (0.73)

[a] CB: chlorobenzene; o-DCB: o-dichlorobenzene. [b] Data in parentheses are the average values.