Effect of With/Without Resonance-mediated Interactions on the Molecular Weight and Photovoltaic Performance of Polymers with Bis-Tolane as an Integrated Part of the Benzodithiophene Donor Unit for Efficient and Stable Organic Solar Cells

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■ EXPERIMENTAL SECTION

Materials. All reagents were purchased from Aldrich, Solarmer or Alfa-Aesar and used without further purification. (2,5-diethylhexyl-3,6-bis(5-bromothien-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione) was synthesized according to the reported procedure in the literature.[1] Moisture sensitive reactions were conducted in the presence of N_2 atmosphere. The other materials were common chemicals used as received. THF was dried over Na/benzophenone ketyl and freshly distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. The chemical shifts were accounted in ppm related to the singlet of $CDCl_3$ at 7.26 and 77 ppm for ^{1}H and ^{13}C NMR, respectively. The UV-visible absorption spectra were recorded on a JASCO V-570 spectrophotometer. Polymerization was performed in a CEM-focused microwave TM synthesis system. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and PDI of the polymers were determined by GPC using a PL gel 5 μm MLXED-C column on an Agilent 1100 series liquid chromatography system with THF as an eluent and calibration with polystyrene standards. Thermal analysis was carried out on a Mettler Toledo TGA/SDTA 851e, DSC 822e analyzer under N_2 atmosphere at a heating rate of 10 ^{o}C/min. The CV analysis was carried out in a 0.1 M solution of tetrabutylammonium perchlorate in anhydrous acetonitrile at a scan rate of 100 mV/s using a CHI 600C potentiostat (CH Instruments), a three-electrode cell with platinum electrode as the working electrode, Ag/AgCl as the reference electrode, and a platinum (Pt) wire as the counter electrode. Polymer thin films were coated on the Pt electrode and dried before the experiment. X-ray diffraction measurements were carried out with Cu Kα (λ=1.54 Å) in a diffractometer (X'pert PRO MRD, Philips) equipped with Göbel mirror. Incidence angle was fixed at 0.17°, the angle between the critical angle of the polymer and the substrate. The detector was scanned the angle (2Θ) from 10° to 90°, similar geometry as in the grazing incidence wide angle scattering.

Fabrication and Characterization of BHJ IOSCs. For the IOSCs, the device configuration is ITO/ZnO (60 nm)/polymer:$PC_{71}BM$ (100 nm) or polymer:$PC_{71}BM$ (100 nm)+3%DIO/Methanol treatment/PEDOT:PSS (10 nm)/Ag (100 nm). The ITO-coated glass substrates used for fabrication were ultrasonically cleaned with detergent, water, acetone, and isopropyl alcohol. The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 1.64 g) and ethanolamine ($NH_2CH_2CH_2OH$, 0.5 g) in 10g of 2-methoxyethanol, under vigorous stirring for 20 min for the hydrolysis reaction in air. The ZnO layer was spin cast from the precursor solution on top of the clean ITO-coated glass substrate, and annealed at 150 ^{o}C for 10 min in air. The photoactive layer of polymer:$PC_{71}BM$ was cast from a solution with the ratio of 1:0.7, 1:1.5, and 1:2 that was dissolved in 1 mL of CB and then spin coated at a rate of 1200 rpm for 30 s in a N_2 glove box. After drying in a vacuum, various solvent treatments were carried out. Finally, ~10 nm PEDOT:PSS (CLEVIOS PVP AI 4083):IPA (1:10 v/v%) and ~100 nm Ag layers were deposited on the photoactive layer. The top metal electrode area, comprising the active area of the solar cell, was 0.38 cm^2. The *J-V* characteristics of the devices were measured using a Keithley 2400 source measure unit under a calibrated AM 1.5G solar simulator (Oriel® Sol3A™ Class AAA solar simulator, models 94043A) at 100 mW/cm^2. The intensity of sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The IPCE measurement system (Oriel IQE-200) was composed of a 250 W quartz-tungsten-halogen lamp as the light source, and a monochromator, optical chopper, lock-in amplifier, and calibrated silicon photodetector. All IOSCs data were confirmed for more than 10 iterations under the same condition. While measuring the *J-V* curves for IOSCs, a black mask was used and only the effective area of the cell was exposed to light irradiation.

Hole and electron mobility. The hole mobility of bare polymers were calculated by fabricating the device structure of ITO/PEDOT:PSS/polymer/MoO_3/Al. The hole and electron mobility were evaluated from the *J-V* characteristics of single charge carrier devices and the results were subsequently fit using the SCLC method. The hole-only devices for BHJ composites were fabricated as follows: ITO/PEDOT:PSS(40 nm)/polymer:$PC_{71}BM$ (100 nm) or polymer:$PC_{71}BM$ (100 nm)+ 3%DIO or polymer:$PC_{71}BM$ (100 nm)+ 3%DIO (methanol treatment)/PEDOT:PSS (50 nm)/A1 (100 nm). The electron-only devices were fabricated using the following device configuration: ITO/ZnO (60 nm)/polymer:$PC_{71}BM$ (100 nm) or polymer:$PC_{71}BM$ (100 nm)+ 3%DIO or polymer:$PC_{71}BM$ (100 nm)+ 3%DIO (methanol treatment)/LiF/Al (150 nm). The mobility was determined by fitting the dark *J-V* curve into the SCLC model, based on the equation described by the Mott-Gurney law.

$J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$

Where ε_r is the dielectric constant (ε_r=3), ε_0 the permittivity of free space, L the thickness of the photoactive layer, μ the charge mobility and V the voltage drop across the device.

Impedance Spectroscopy. The impedance response was measured over the range of 1 Hz to 1MHz with an oscillation amplitude of 15 mV (Bio-Logic VMP-3). The experimental data were simulated using commercial *Z*-view software to estimate the values for each component of the corresponding equivalent circuits.

((3-Bromophenyl)ethynyl)trimethylsilane (1). To a 50 mL flask was added the 1,3-dibromobenzene (2 g, 8.41 mmol), bis (triphenylphosphine)palladium (II) dichloride (0.294 g, 5 mol %), and copper (I) iodide (0.079 g, 5 mol %). 30 mL of tetrahydrofuran (THF) was added followed by Et_3N (10 mL). Then, trimethylsilylacetylene (1.198 mL, 8.41 mmol) was added at room temperature and further stirred for 3 h. After the reaction was completed, solvent was removed under pressure and the resulting residue was extracted with methylene chloride (MC), dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as brown oil, which was then purified by column chromatography on silica gel using hexane as an eluent to obtain a colorless liquid (1.6 g, 72 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.64 (d, 1H), 7.42 (m, 2H), 7.16 (m, 1H), 0.23 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 133.74, 132.46, 130.40, 128.12, 126.12, 125.74 103.68, 100.12, 0.00.

((4'-(2-Ethylhexyloxy)biphenyl-3-yl)ethynyl)trimethylsilane (2). 2 M aqueous Na_2CO_3 (10 mL) was added to a mixture of ((3-bromophenyl)ethynyl)trimethylsilane (3 g, 11.8 mmol), 2-(4-(2-ethylhexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.58 g, 14.2 mmol), and tetrakis(triphenylphosphine)palladium (0.136 g, 0.03 mmol) dissolved in 24 mL of toluene. The mixture was refluxed for 12 h under N_2 atmosphere. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using ethylacetate (EA)/hexane (4:1) as the eluent to produce a colorless liquid. Yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.66 (s, 1H), 7.48 (m, 3H), 7.34 (m, 2H), 6.96 (d, 2H), 3.84 (d, 2H), 1.64-1.78 (m, 1H), 1.22-1.54 (m, 8H), 0.84 (m, 6H), 0.26 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 158.84, 141.42, 133.16, 131.79, 129.78, 127.31, 126.52, 125.81, 123.32, 115.37, 105.89, 94.32, 72.14, 39.84, 31.17, 29.82, 23.21, 22.84, 14.13, 11.84, 0.00.

4'-(2-Ethylhexyloxy)-3-ethynylbiphenyl [BPA(H)]. ((4'-(2-Ethylhexyloxy)biphenyl-3-yl)ethynyl)trimethylsilane (1.2 g, 3.12 mmol) was dissolved in 20 mL of MC and a solution of 1.4 g of potassium hydroxide dissolved in 25 mL of methanol was added. The reaction mixture was stirred at room temperature for 2 h before quenching with water (150 mL) and extracted with MC (80 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as yellow oil, which was then purified by column chromatography on silica gel using EA/hexane (3:1) as an eluent to obtain a colorless liquid (0.9 g, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68 (s, 1H), 7.52 (t, 3H), 7.38 (m, 2H), 6.94 (d, 2H), 3.92 (d, 2H), 3.08 (s, 1H), 1.74 (m, 1H), 1.38 (m, 8H), 0.92 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 158.84, 141.42, 133.16, 131.79,129.78, 127.31, 126.52, 125.81, 123.32, 115.37, 84.31, 72.14, 39.84, 31.17, 29.82, 23.21, 22.84, 14.13, 11.84.

4,8-Bis(4'-(2-ethylhexyloxy)-3-ethynylbiphenyl)benzo[1,2-b:4,5-b']dithiophene (3). n-BuLi (2.5 M, 1.1 mL) was added dropwise to a solution of 4'-(2-ethylhexyloxy)-3-ethynylbiphenyl (0.7 g, 2.9 mmol) in THF (25 mL) at 0 °C under N_2 atmosphere. The temperature of the reaction mixture was raised to 50 °C and stirred for 1.5 h. 4,8-Dihydrobenzo[1,2-b:4,5-b′]dithiophene-4,8-dione (0.3 g, 1.3 mmol) was added directly to the reaction mixture at 50 °C, which was then stirred for 2 h at the same temperature. Subsequently, the reaction mixture was cooled to room temperature and tin(II) chloride dihydrate (1.9 g, 19.75 mmol) in 15% HCl (20 mL) was added and further stirred for 1.5 h, before being poured into ice water. The reaction mixture was extracted with diethyl ether, the resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as brown oil, which was then purified by column chromatography on silica gel using hexane as an eluent to obtain a yellow solid (0.5 g, 45 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84 (s, 2H), 7.74 (d, 2H), 7.52–7.64 (m, 10H), 7.48 (d, 2H), 7.02 (d, 4H), 3.84 (d, 4H), 1.74 (m, 2H), 1.32–1.48 (m, 14H), 0.78–0.98 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 158.84, 141.84, 140.42, 138.74, 132.14, 129.76, 126.21, 125.79, 123.52, 115.43, 115.21, 112.26, 99.89, 86.24, 71.31, 39.84, 31.17, 29.82, 23.21, 22.84, 14.13, 11.84.

2,6-(Trimethyltin)-4,8-bis(4'-(2-ethylhexyloxy)-3-ethynylbiphenyl)benzo[1,2-b:4,5-b']dithiophene [BDTBPA(H)]. A solution of compound 4 (0.5 g, 0.6 mmol) in THF (30 mL) was placed in a 50 mL flask, which was flushed with N_2 and the solution was cooled to -78 °C using dry ice/acetone. To the cooled solution, tert-BuLi (1.7 M, 0.73 mL) was added slowly and stirred for another 30 min at -78 °C and trimethyltin chloride (0.25 g, 1.2 mmol) was directly added as a solid. The solution was slowly warmed to room temperature and stirred overnight. Aqueous sodium carbonate (20 mL) was added slowly to the solution and extracted with MC (30 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford a yellow residue, which was recrystallized from ethanol to obtain a yellow solid (0.45 g, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 2H), 7.76 (d, 2H), 7.54–7.66 (m, 8H), 7.44–7.50 (m, 2H), 6.98–7.04 (d, 4H), 3.92 (d, 4H), 1.72-1.78 (m, 2H), 1.28-1.52 (m, 16H), 0.82-0.98 (m, 12H), 0.39-0.58 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 159.294, 144.77, 143.68, 141.26, 139.08, 132.54, 130.89, 130.05, 129.97, 128.87, 128.19, 127.15, 123.46, 114.90, 98.63, 86.28, 70.57, 39.38, 30.54, 29.10, 23.86, 23.09, 14.15, 11.15, -8.18. Anal. Calcd for $C_{60}H_{70}O_2S_2Sn_2$: C, 64.07; H, 6.27; O, 2.84; S, 5.70; Sn, 21.11. Found: C, 63.92; H, 6.38.

4'-(2-Ethylhexyloxy)-2,4-difluorobiphenyl (4). 2 M aqueous Na_2CO_3 (15 mL) were added to a mixture of 1-bromo-4-(2-ethylhexyloxy)benzene (3 g, 10 mmol), 2,4-difluorophenylboronic acid (2.15 g, 13 mmol), and tetrakis(triphenylphosphine)palladium (0.607 g, 0.1 mmol) dissolved in toluene (24 mL) and ethanol (12 mL). The mixture was refluxed for 12 h under N_2

atmosphere. After cooling to room temperature, the mixture was extracted with MC and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using EA/hexane (4:1) as an eluent to produce a colorless liquid (3.2 g, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32– 7.46 (m, 3H), 6.82–6.98 (m, 4H), 3.92 (d, 2H), 1.72−1.80 (m, 1H), 1.22−1.52 (m, 8H), 0.82−0.98 (m, 6H). ^{13}C NMR (300 MHz, CDCl3): δ (ppm) 162.89, 161.47, 160.02, 159.28, 158.74, 132.93, 130.76, 129.17, 127.73, 124.32, 114.82, 112.13, 104.98, 70.73, 38.94, 31.13, 28.95, 22.71, 14.15, 11.15.

4'-(2-Ethylhexyloxy)-2,4-difluoro-3-iodobiphenyl (5). A solution of compound 6 (2 g, 6.2 mmol) in THF (30 mL) was placed in a 50 mL flask, flushed with N_2 and cooled to -78 °C using dry ice/acetone. LDA (2 M in THF/pentane, 3.77 mL) was added slowly, the solution was stirred for another 30 min at -78 °C and iodine (1.75 g, 6.9 mmol) in 20 mL of THF was added. The solution was slowly warmed to room temperature and stirred overnight. The reaction was quenched with water, extracted with EA. The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford a yellow residue, which was purified by column chromatography on silica gel using EA/hexane (1:1) as an eluent to produce a colorless liquid (2.1 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.28−7.44 (m, 3H), 6.84−7.02 (m, 3H), 3.84 (d, 2H), 1.72−1.80 (m, 1H), 1.22−1.52 (m, 8H), 0.80−0.98 (m, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 162.89, 161.47, 160.02, 159.28, 158.74, 132.93, 130.76, 129.17, 127.73, 124.32, 114.82, 112.13, 70.73, 38.94, 31.13, 28.95, 22.71, 14.15, 11.15.

((4'-(2-Ethylhexyloxy)-2,4-difluorobiphenyl-3-yl)ethynyl)trimethylsilane (6). To a 100 mL flask was added the compound 7 (2 g, 4.51 mmol), bis (triphenylphosphine)palladium (II) dichloride (0.105 g, 5 mol %), and copper (I) iodide (0.025 g, 5 mol %). The vessel was then sealed with a rubber septum, evacuated and backfilled with argon three times. 25 mL of THF was added followed by 10 mL of Et_3N. Then, trimethylsilylacetylene (0.763 mL, 5.4 mmol) was added at room temperature and further stirred for 3 h. After the reaction was completed, solvent was removed under pressure and the resulting residue was extracted with MC, dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as brown oil, which was then purified by column chromatography on silica gel using hexane as an eluent to obtain a colorless liquid (1.5 g, 83 %). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.34−7.42 (m, 3H), 6.92−6.98 (m, 3H), 3.84 (d, 2H), 1.68−1.82 (m, 1H), 1.22−1.48 (m, 8H), 0.82−0.98 (m, 6H), 0.22−0.42 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 162.74, 161.32, 160.22, 159.48, 158.94, 133.03, 131.89, 129.82, 127.93, 125.32, 115.42, 112.43, 70.73, 38.94, 31.13, 28.95, 22.71, 14.15, 11.15, 0.00.

4'-(2-Ethylhexyloxy)-3-ethynyl-2,4-difluorobiphenyl [BPA(F)]. ((4'-(2-Ethylhexyloxy)-2,4-difluorobiphenyl-3-yl)ethynyl)trimethylsilane (1.4 g, 3.3 mmol) was dissolved in 30 mL of MC and a solution of 1.6 g of potassium hydroxide dissolved in 25 mL of methanol was added. The reaction mixture was stirred at room temperature for 2 h before quenching with water (100 mL) and extracted with MC (100 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as yellow oil, which was then purified by column chromatography on silica gel using EA/hexane (3:1) as an eluent to obtain a colorless liquid (0.9 g, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.32−7.46 (m, 3H), 6.92−7.04 (m, 3H), 3.92 (d, 2H), 3.52 (s, 1H), 1.68−1.82 (m, 1H), 1.32−1.52 (m, 8H), 0.82−0.98 (m, 6H). ^{13}C NMR (300 MHz,$CDCl_3$): δ (ppm) 162.74, 161.32, 160.22, 159.48, 158.94, 133.03, 131.89, 129.82, 127.93, 125.32, 115.42, 112.43, 86.42, 70.73, 38.94, 31.13, 28.95, 22.71, 14.15, 11.15.

4,8-Bis(4'-(2-ethylhexyloxy)-3-ethynyl-2,4-difluorobiphenyl)benzo[1,2-b:4,5-b']dithiophene (7). n-BuLi (2.5 M, 1.19 mL) was added dropwise to a solution of 4'-(2-

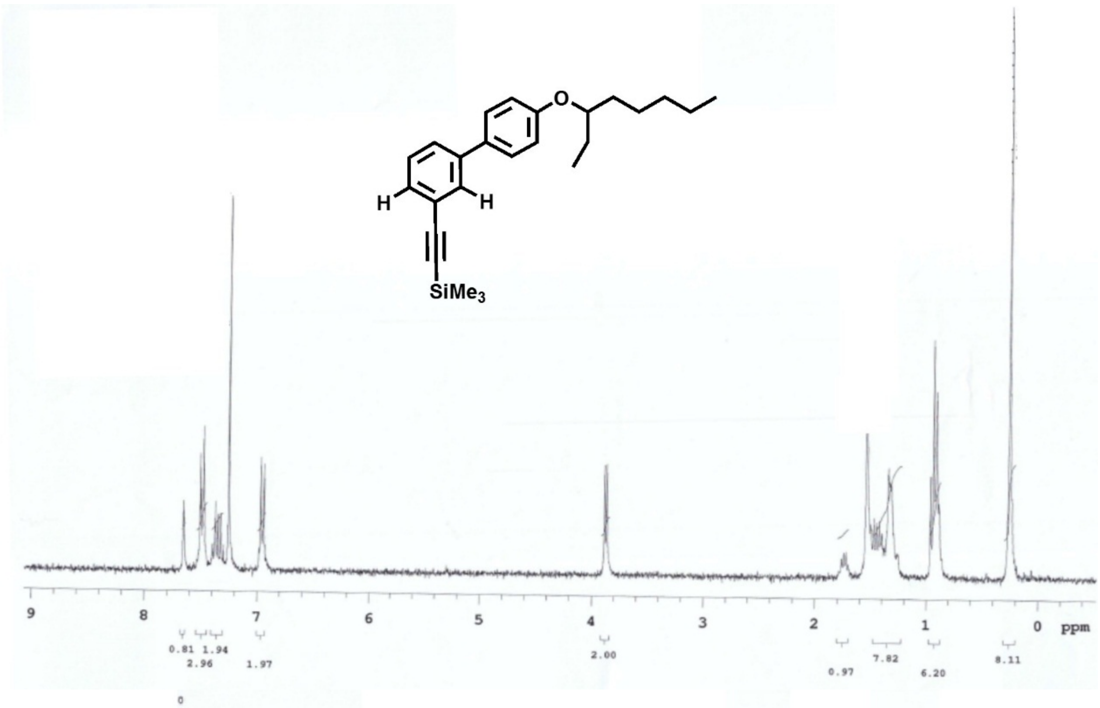
ethylhexyloxy)-3-ethynyl-2,4-difluorobiphenyl (1.02 g, 2.9 mmol) in THF (25 mL) at 0 °C under N_2 atmosphere. The temperature of the reaction mixture was raised to 50 °C and stirred for 1.5 h. 4,8-Dihydrobenzo[1,2-b:4,5-b′]dithiophene-4,8-dione (0.3 g, 1.3 mmol) was added directly to the reaction mixture at 50 °C, which was then stirred for 2 h at the same temperature. Subsequently, the reaction mixture was cooled to room temperature and tin(II) chloride dihydrate (1.9 g, 19.75 mmol) in 15% HCl (20 mL) was added and further stirred for 1.5 h, before being poured into ice water. The reaction mixture was extracted with diethyl ether, the resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude compound as brown oil, which was then purified by column chromatography on silica gel using hexane as an eluent to obtain a yellow solid (0.48 g, 40 %). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.76-7.80 (d, 2H), 7.60-7.66 (d, 2H), 7.38-7.52 (m, 6H), 6.98-7.08 (m, 6H), 3.92 (d, 4H), 1.72-1.78 (m, 2H), 1.28-1.52 (m, 16H), 0.82-0.98 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 163.10, 159.73, 159.60, 159.32, 157.57, 140.26, 138.41, 130.74, 130.02, 129.99, 128.73, 128.53, 126. 40, 125.30, 125.13, 125.12, 114.62, 111.73, 111.50, 111.17, 102.41, 95.34, 86.65, 70.50, 39.38, 30.52, 29.119, 23.86, 23.11, 14.16, 11.16.

2,6-(Trimethyltin)-4,8-bis(4'-(2-ethylhexyloxy)-3-ethynyl-2,4-difluorobiphenyl)benzo[1,2-b:4,5-b']dithiophene [BDTBPA(F)]: A solution of compound 4 (1 g, 1.1 mmol) in THF (30 mL) was placed in a 50 mL flask, which was flushed with N_2 and the solution was cooled to -78 °C using dry ice/acetone. To the cooled solution, tert-BuLi (1.7 M, 1.3 mL) was added slowly and stirred for another 30 min at -78 °C and trimethyltin chloride (0.45 g, 2.2 mmol) was directly added as a solid. The solution was slowly warmed to room temperature and stirred overnight. Aqueous sodium carbonate (20 mL) was added slowly to the solution and extracted with MC (30 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated to afford a yellow residue, which was recrystallized from ethanol to obtain a yellow solid (0.9 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 2H), 7.76 (d, 2H), 7.54–7.66 (m, 8H), 7.44–7.50 (m, 2H), 6.98–7.04 (d, 4H), 3.92 (d, 4H), 1.72-1.78 (m, 2H), 1.28-1.52 (m, 16H), 0.82-0.98 (m, 12H), 0.39-0.58 (m, 18H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 163.13, 159.86, 159.73, 159.48, 157.67, 140.47, 138.61, 130.92, 130.18, 130.03, 128.82, 128.56, 126.60, 125.39, 125.23, 125.18, 111.86, 111.62, 111.24, 95.24, 86.85, 70.58, 39.48, 30.72, 29.31, 23.76, 23.21, 14.18, 11.22, -8.18. Anal. Calcd for $C_{60}H_{66}F_4O_2S_2Sn_2$: C, 60.22; H, 5.56; F, 6.35; O, 2.67; S, 5.36; Sn, 19.84. Found: C, 60.12; H, 5.72.

Polymerization for PBDTBPA(H)-DPP. BDTBPA(H) (200 mg, 0.5 mmol) and DPP (121 mg, 0.5 mmol) were dissolved in CB (10 mL). The reaction mixture was flushed with argon for 15 min and $Pd_2(dba)_3$ (6 mg, 2 mole%), and (*o*-tolyl)$_3$P (14 mg, 16 mole%) was added and purged five times continuously with vacuum and argon. The reaction mixture was heated to 120 ^{o}C for 6 h. After cooling to room temperature, the reaction mixture was poured into methanol to afford a precipitate, which was purified by Soxhlet extraction method using methanol, hexane and acetone, and then extracted in CF, which was evaporated to afford PBDTBPA(H)-DPP (58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.12–7.48 (m, 6H), 7.20–7.16 (m, 14H), 4.20–3.60 (m, 8H), 2.10–0.64 (64H); Anal. Calcd for $C_{84}H_{92}N_2O_4S_4$: C, 76.32; H, 7.01; O, 4.84; S, 9.70. Found: C, 76.56; H, 7.12; O, 4.98; S, 9.92.

Polymerization for PBDTBPA(F)-DPP. Microwave-assisted Stille polymerization reaction conditions were employed to synthesize PBDTBPA(F)-DPP. The procedure for the synthesis of polymer PBDTBPA(F)-DPP is as follows: To a 10 mL microwave tube, monomer PBDTBPA(F) (200 mg, 0.5 mmol), DPP (114 mg, 0.5 mmol), $Pd_2(dba)_3$ (8 mg, 2 mole%), and (*o*-tolyl)$_3$P (18 mg, 16 mole%) were dissolved in anhydrous CB (5 mL). The reaction mixture was purged with

N_2 for 15 min. The microwave tube was placed in the reactor and heated to 120 ^{o}C for 30 min. After cooling to room temperature, the reaction mixture was poured into methanol to afford a precipitate, which was purified by Soxhlet extraction method using methanol, hexane and acetone, and then extracted in CF, which was evaporated to get PBDTBPA(F)-DPP (47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.12–7.48 (m, 6H), 7.20–7.16 (m, 10H), 4.20–3.60 (m, 8H), 2.10–0.64 (64H); Anal. Calcd for $C_{84}H_{88}F_4N_2O_4S_4$: C, 72.38; H, 6.36; O, 4.59; S, 9.20. Found: C, 72.18; H, 6.14; O, 4.72; S, 9.42.



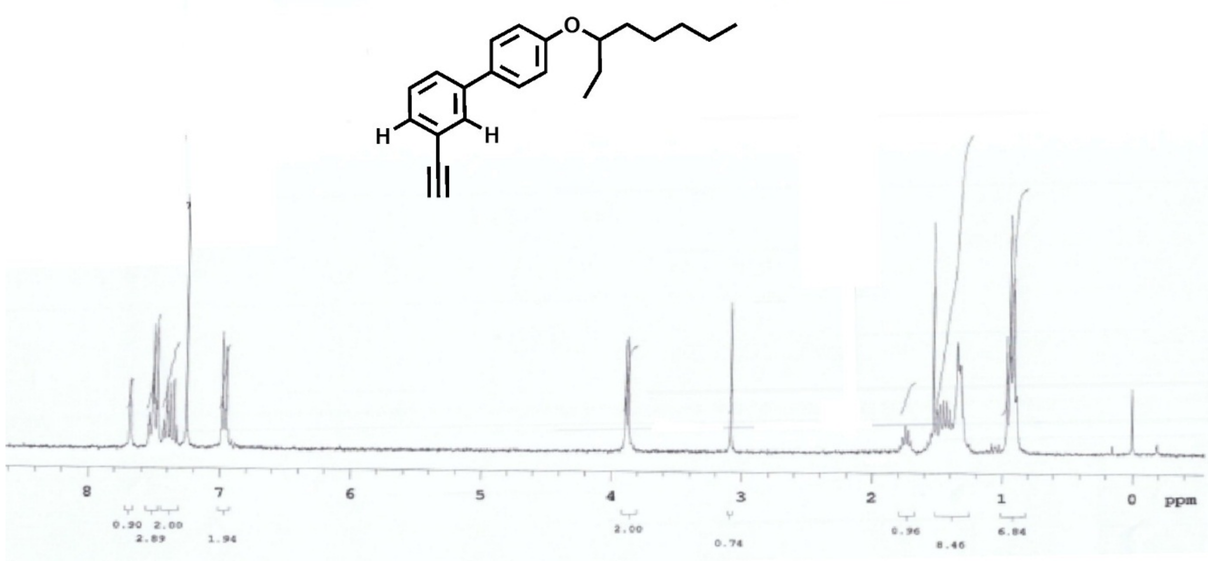


Figure S1. ^{1}H NMR of 2 and BPA(H).

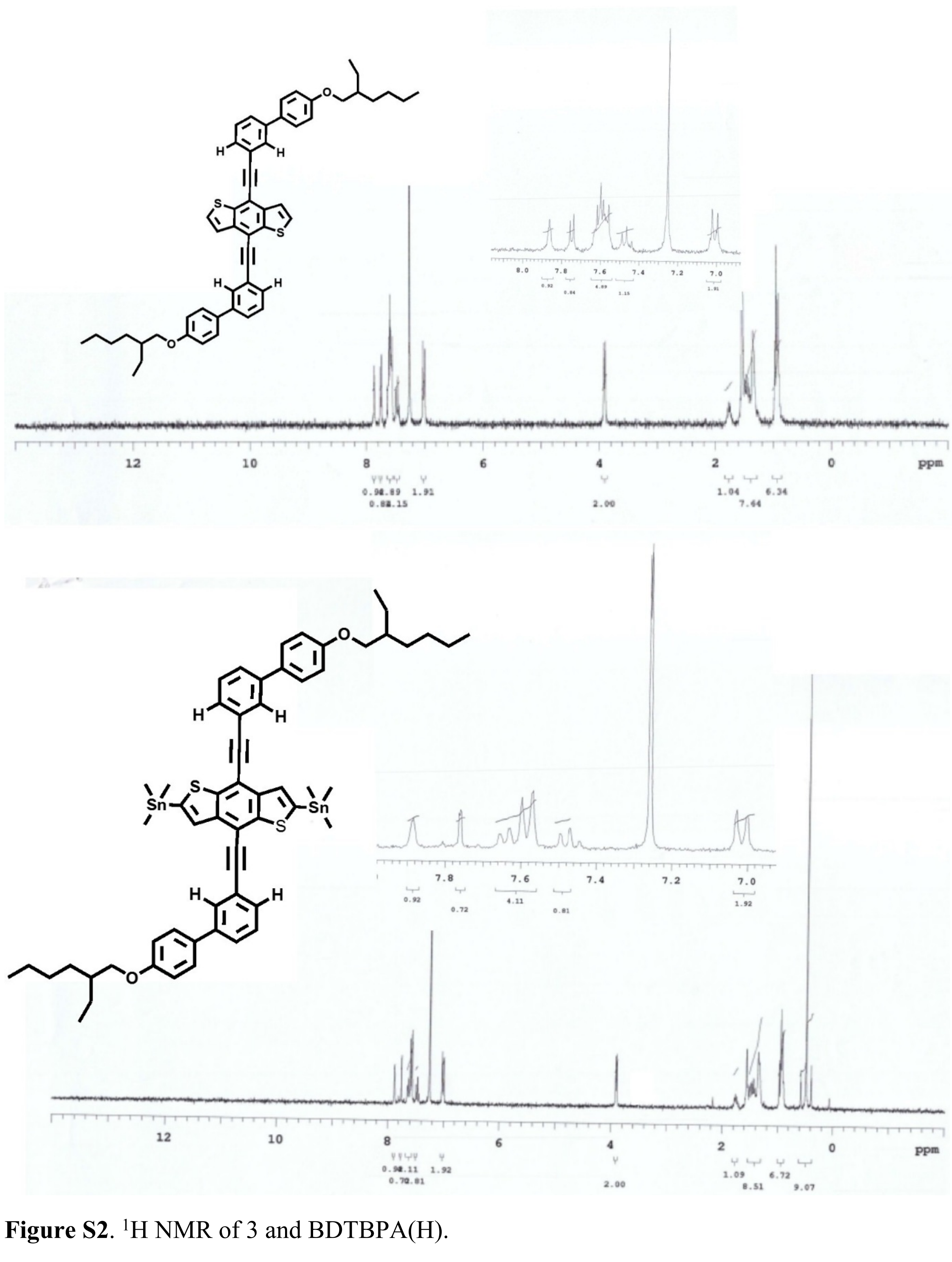
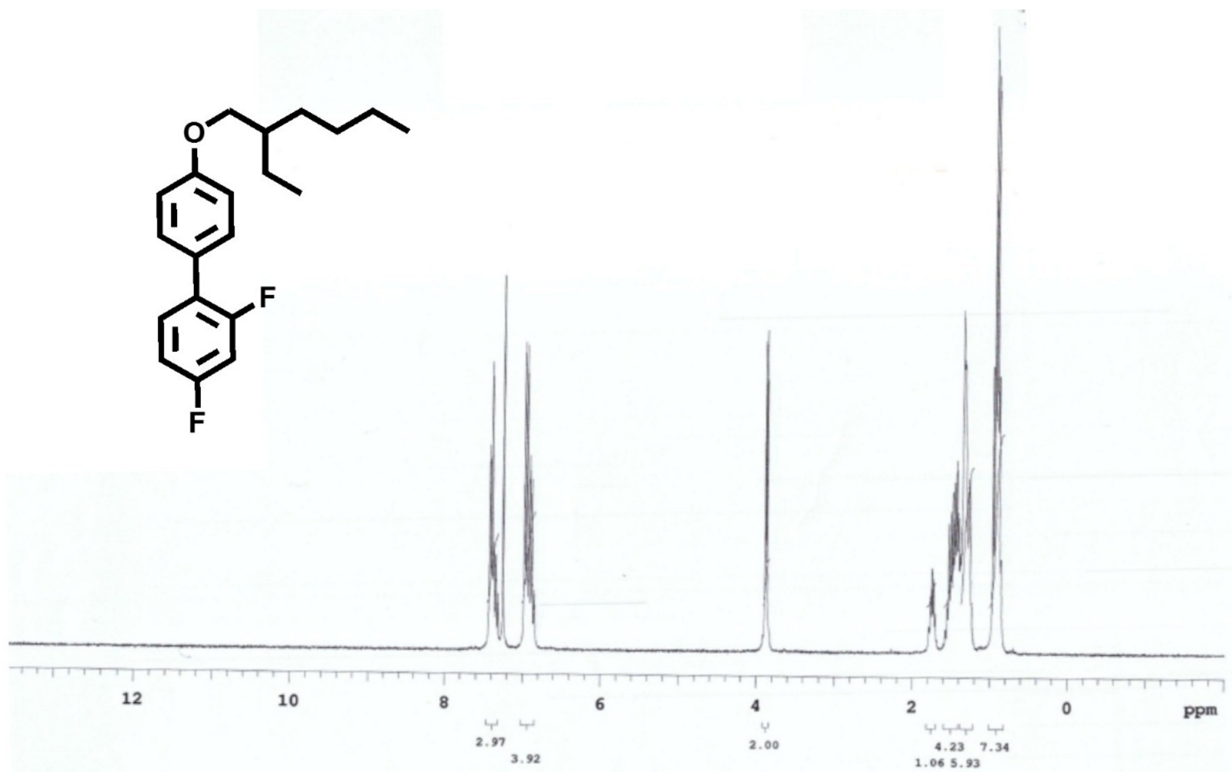


Figure S2. ^{1}H NMR of 3 and BDTBPA(H).



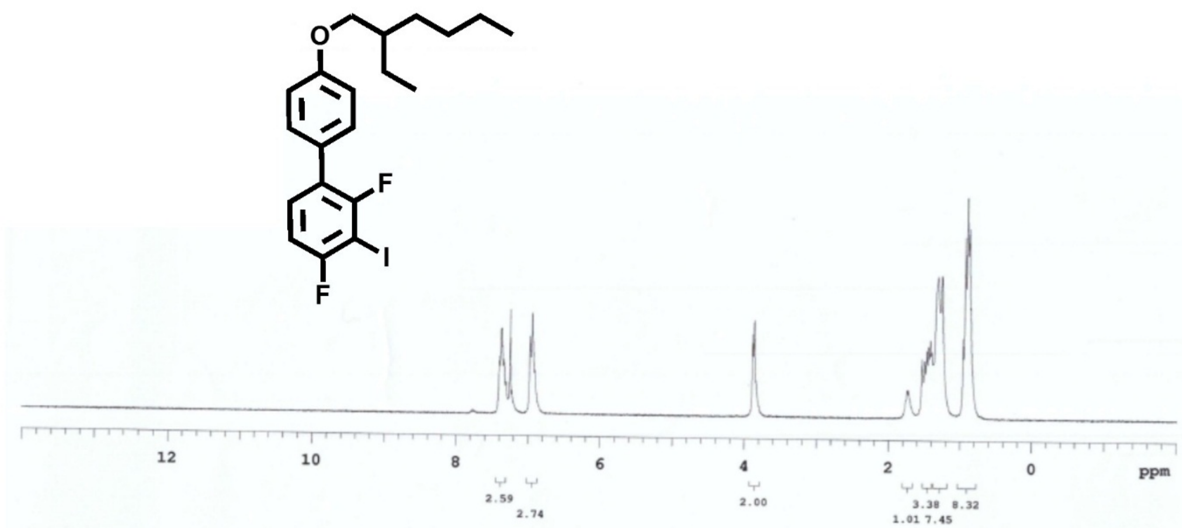
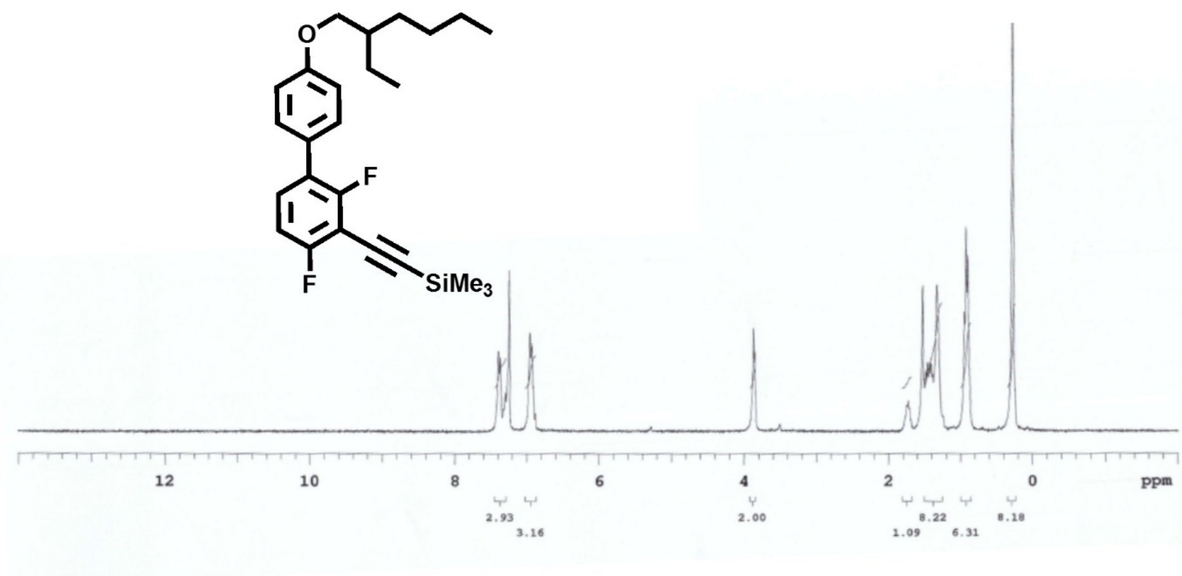


Figure S3. ^{1}H NMR of 4 and 5.



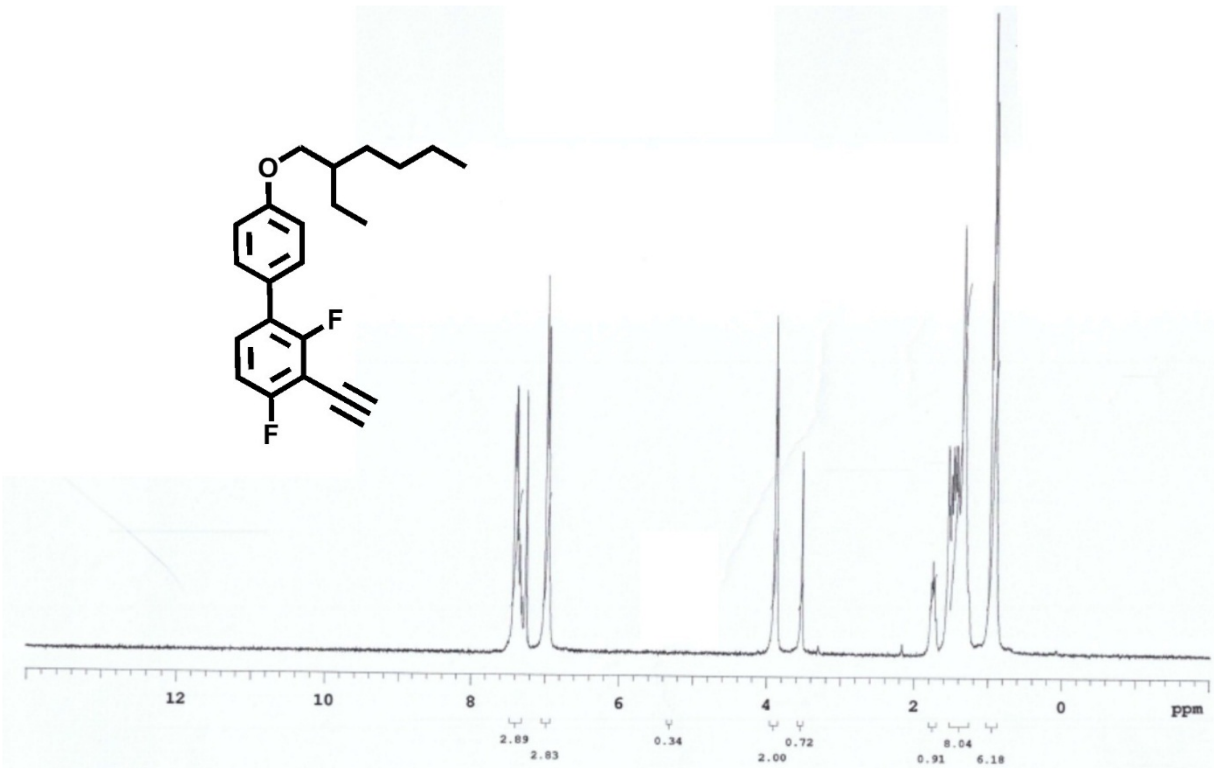
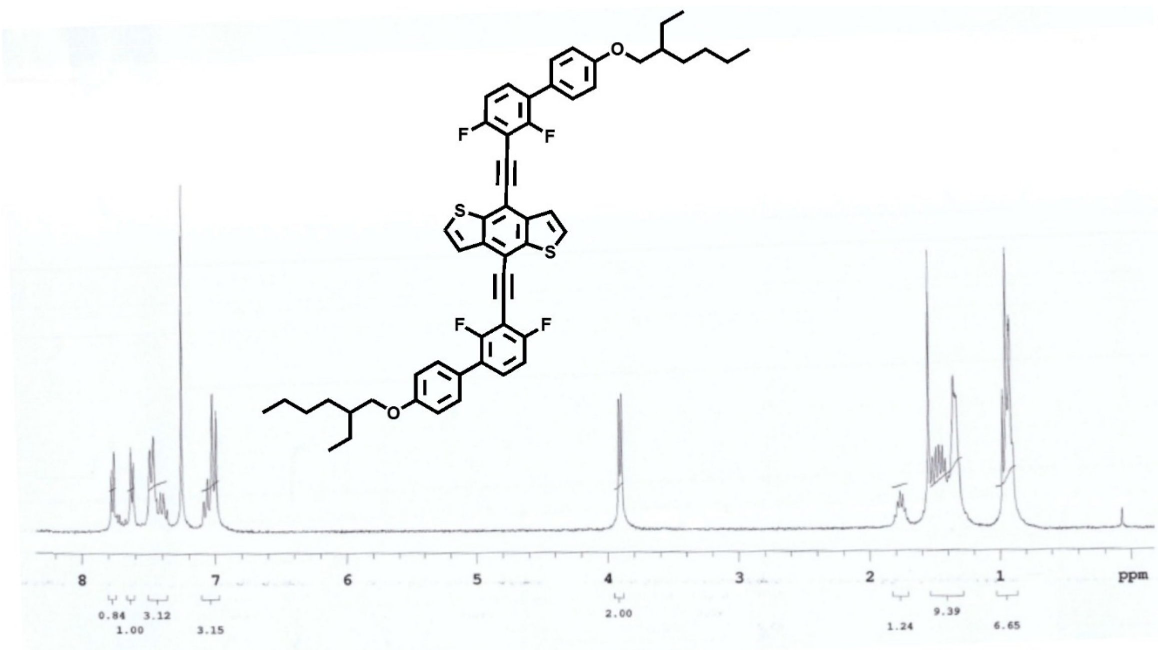


Figure S4. ^{1}H NMR of 6 and BPA(F).



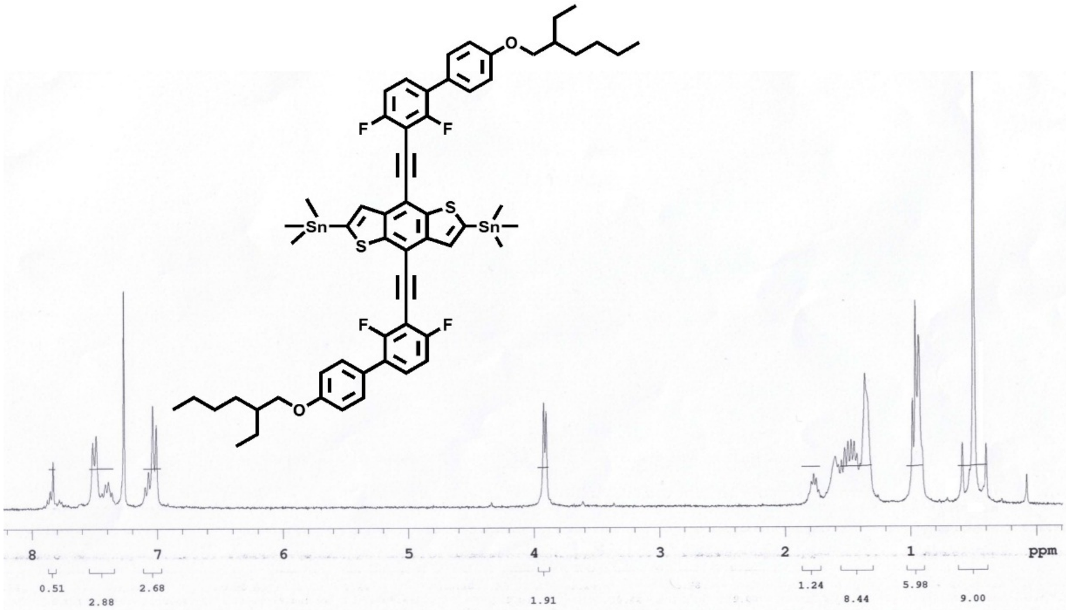
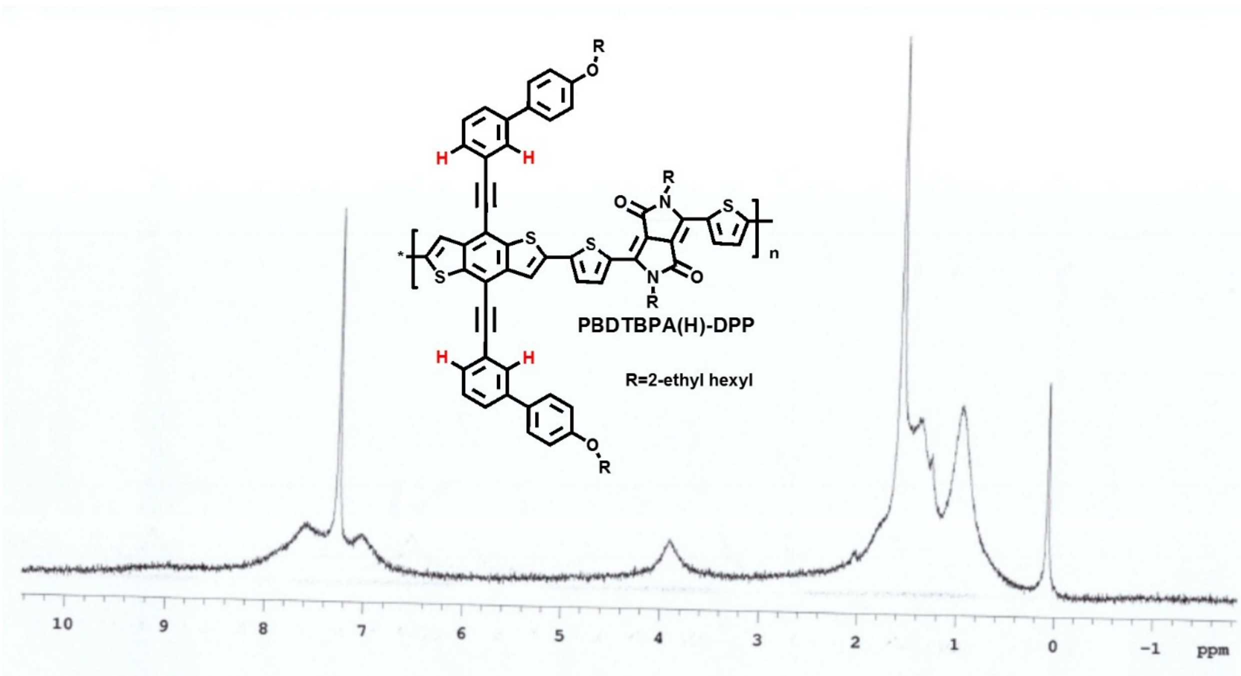


Figure S5. ^{1}H NMR of 7 and BDTBPA(F).



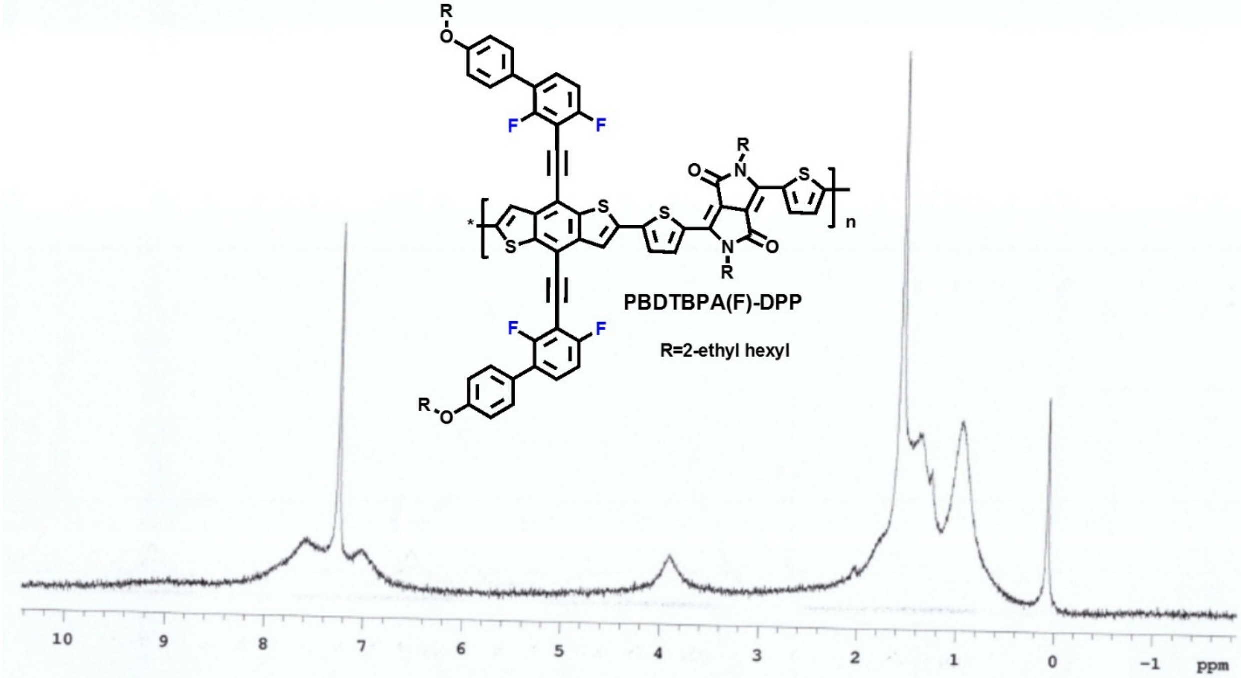
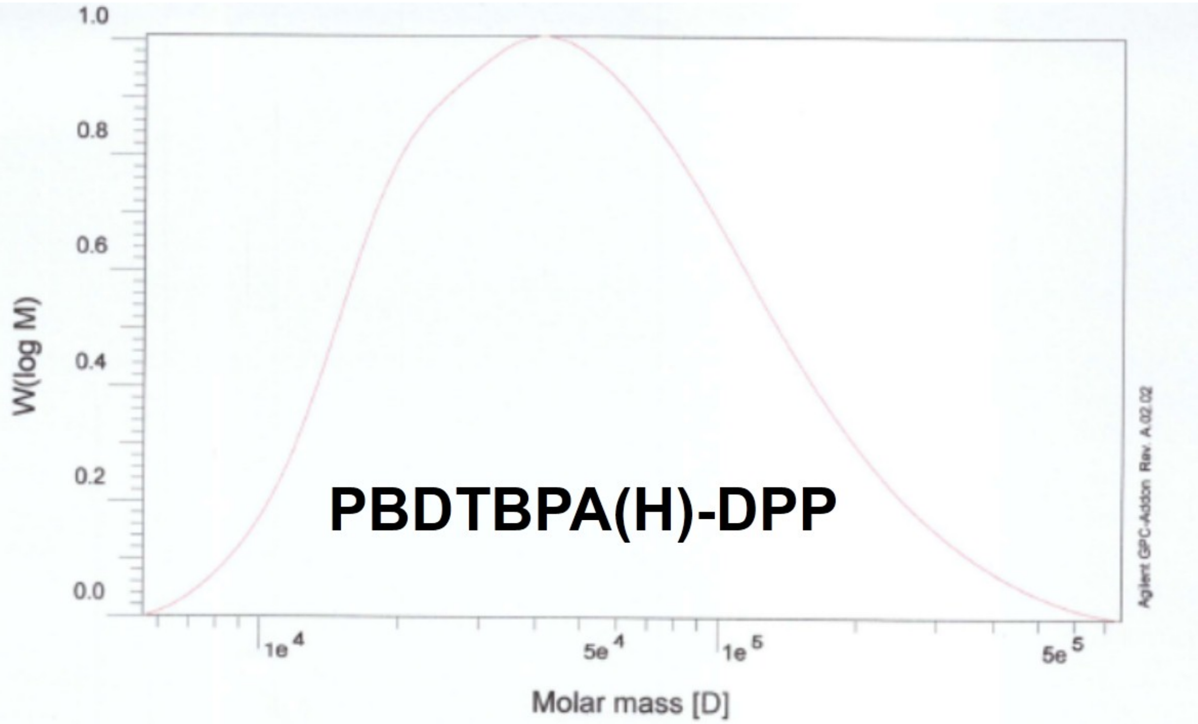


Figure S6. ^{1}H NMR of PBDTBPA(H)-DPP and PBDTBPA(F)-DPP.

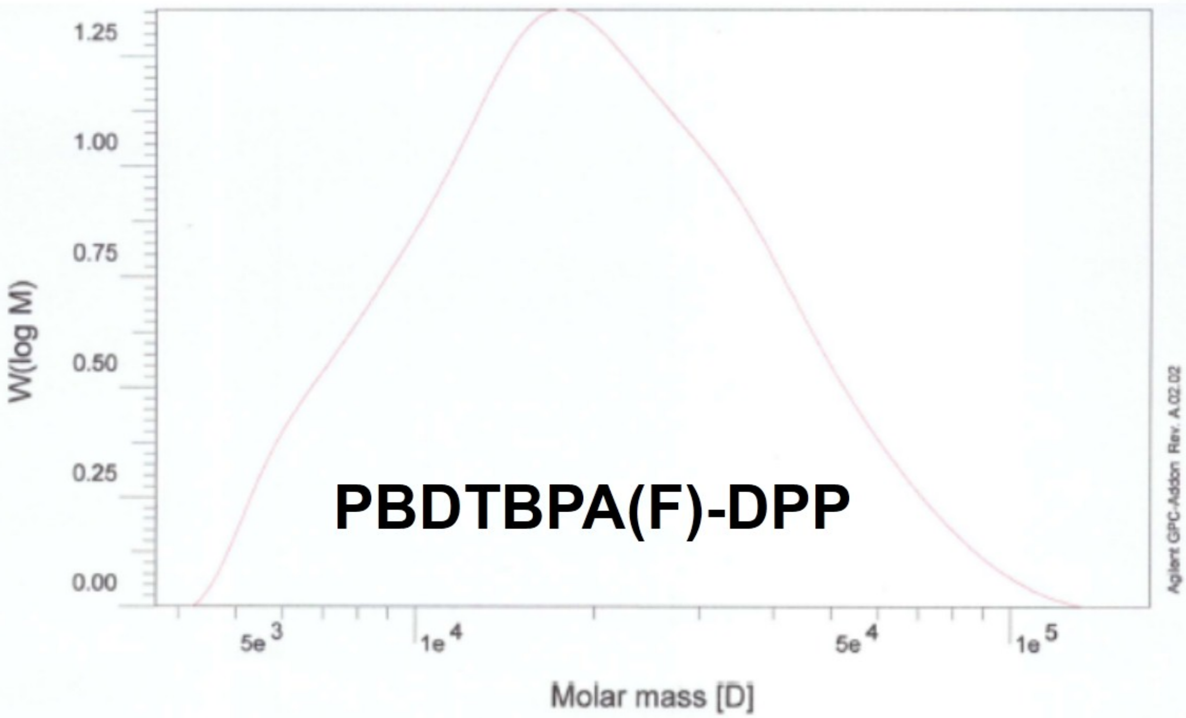


Sample :			
Injection Date :			
Calibration File :	TEST-CAL.CAL		
Calibration Date :			
Baseline from :	6.103 min	**Baseline to :**	8.465 min
Integration from:	6.103 min	**Integration to :**	8.465 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :	....?	**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 ul
Column 1 :	....?	**Temperature :**	23.000 C
Detector 1 :	RID A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	KRANTHI	**Acquisition interval :**	0.430 sec

rid1A

Mn :	3.4830e4	g/mol
Mw :	7.1324e4	g/mol
Mz :	1.4989e5	g/mol
Mv :	0.000000	g/mol
D :	2.0478e0	
[n]:	0.000000	ml/g
Vp :	7.4663e0	ml
Mp :	4.1557e4	g/mol
A :	5.7927e3	ml*V
10%	1.6520e4	g/mol
30%	2.8836e4	g/mol
60%	5.8142e4	g/mol
85%	1.2321e5	g/mol
90%	1.5606e5	g/mol

Figure S7. GPC graph of PBDTBPA(H)-DPP.



Sample :			
Injection Date :			
Calibration File :	TEST-CAL.CAL		
Calibration Date :			
Baseline from :	6.782 min	**Baseline to :**	8.671 min
Integration from:	6.782 min	**Integration to :**	8.671 min
MHK - A (Cal.):	0.000000E+0	**MHK - K (Cal.):**	1.000000E+0 ml/g
Eluent :	....?	**Flowrate :**	1.000 ml/min
Concentration :	1.000 g/l	**Inject volume :**	20.000 ul
Column 1 :	....?	**Temperature :**	23.000 C
Detector 1 :	RID A, Refractive Index Signal	**Delay volume :**	0.000 ml
Operator :	KRANTHI	**Acquisition interval :**	0.430 sec

rid1A

Mn :	1.5930e4	g/mol
Mw :	2.4270e4	g/mol
Mz :	3.6484e4	g/mol
Mv :	0.000000	g/mol
D :	1.5235e0	
[n]:	0.000000	ml/g
Vp :	7.8912e0	ml
Mp :	1.7601e4	g/mol
A :	2.4380e3	ml*V
10%	8.1593e3	g/mol
30%	1.3494e4	g/mol
60%	2.2903e4	g/mol
85%	4.0041e4	g/mol
90%	4.7220e4	g/mol

Figure S8. GPC graph of PBDTBPA(F)-DPP.

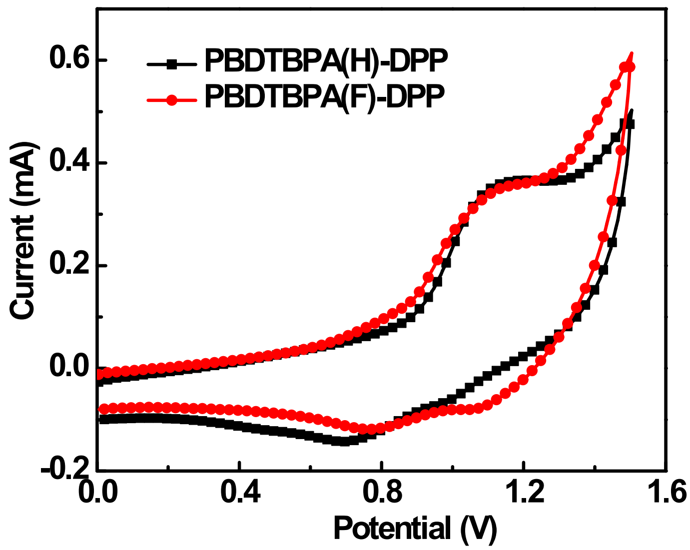


Figure S9. CV curves of PBDTBPA(H)-DPP and PBDTBPA(F)-DPP.

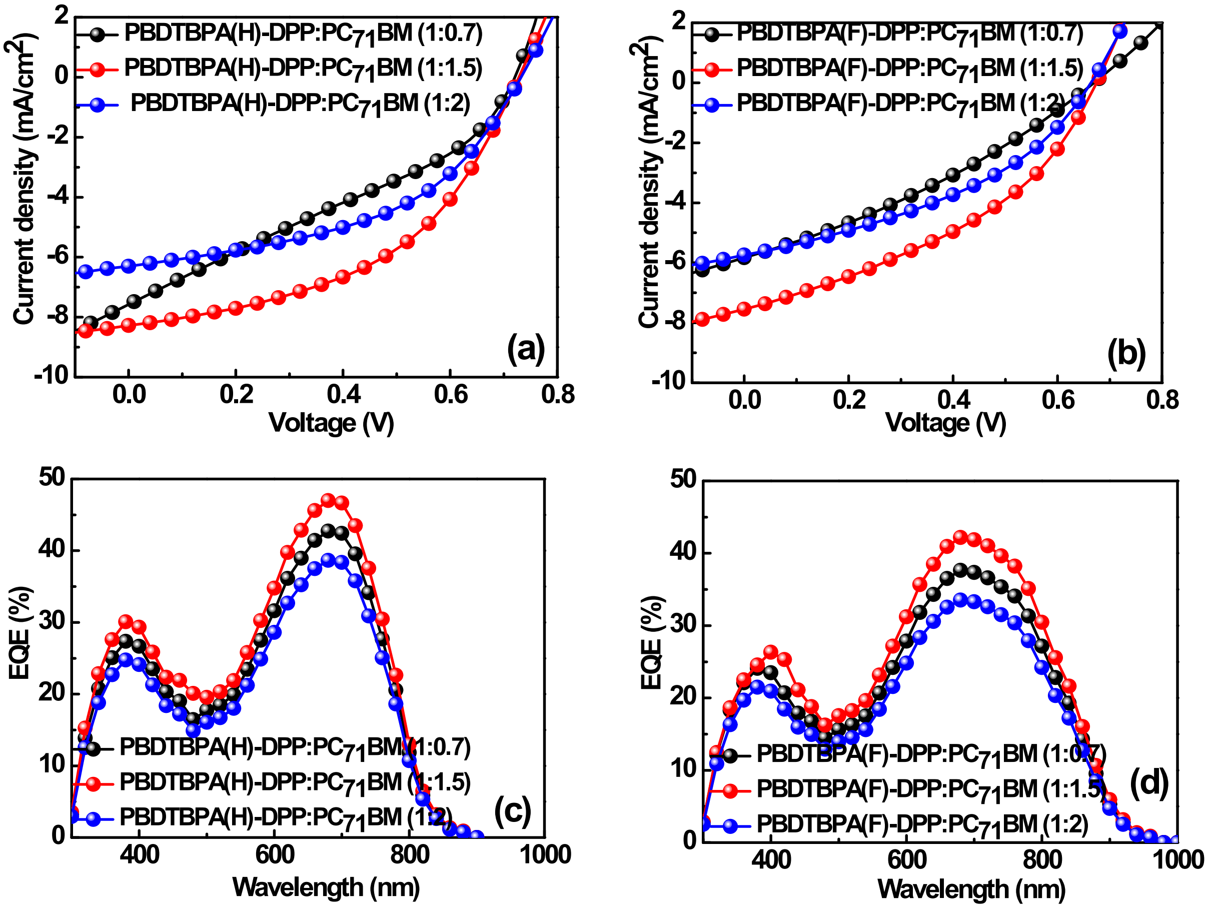


Figure S10. Current density-voltage (*J*-*V*) and EQE curves of the IOSCs based on PBDTBPA(H)-DPP and PBDTBPA(F)-DPP at different ratios.

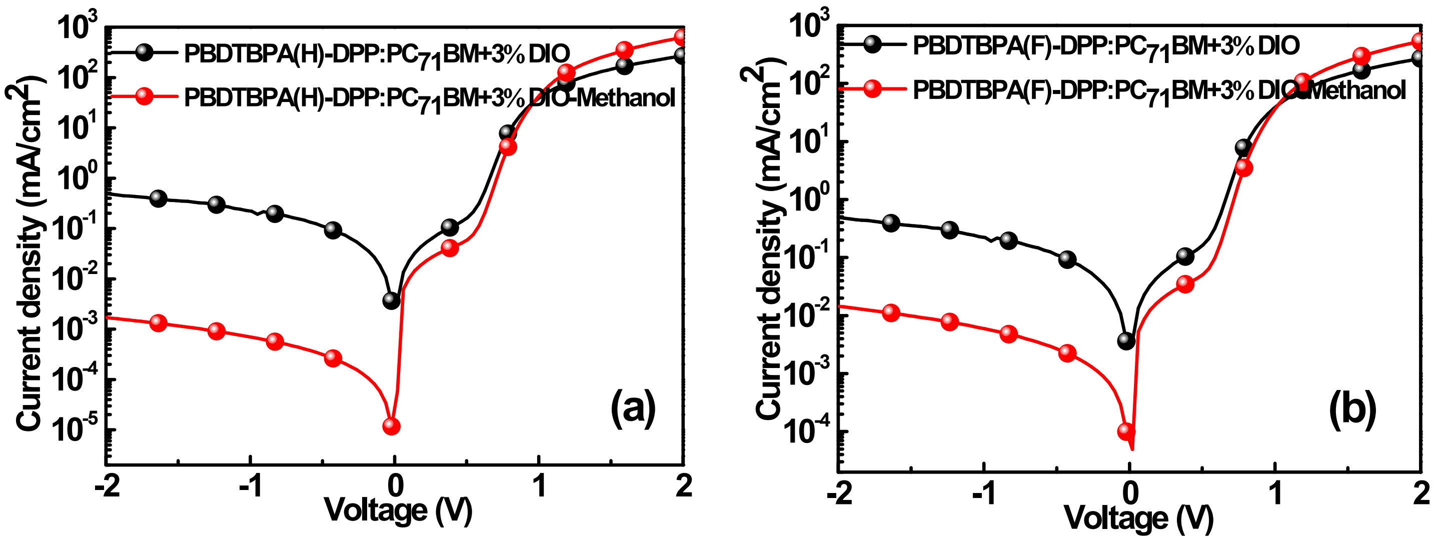


Figure S11. Dark current curves of IOSCs based on PBDTBPA(H)-DPP and PBDTBPA(F)-DPP.

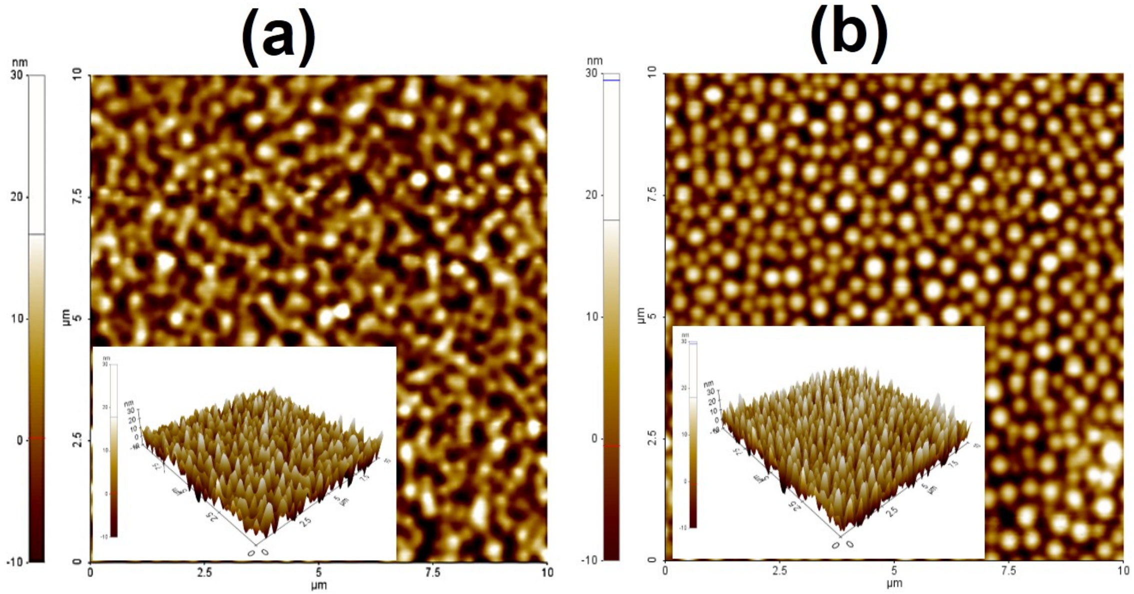


Figure S12. AFM images of a) PBDTBPA(H)-DPP:$PC_{71}BM$ (1:1.5) and b) PBDTBPA(F)-DPP:$PC_{71}BM$ (1:1.5).

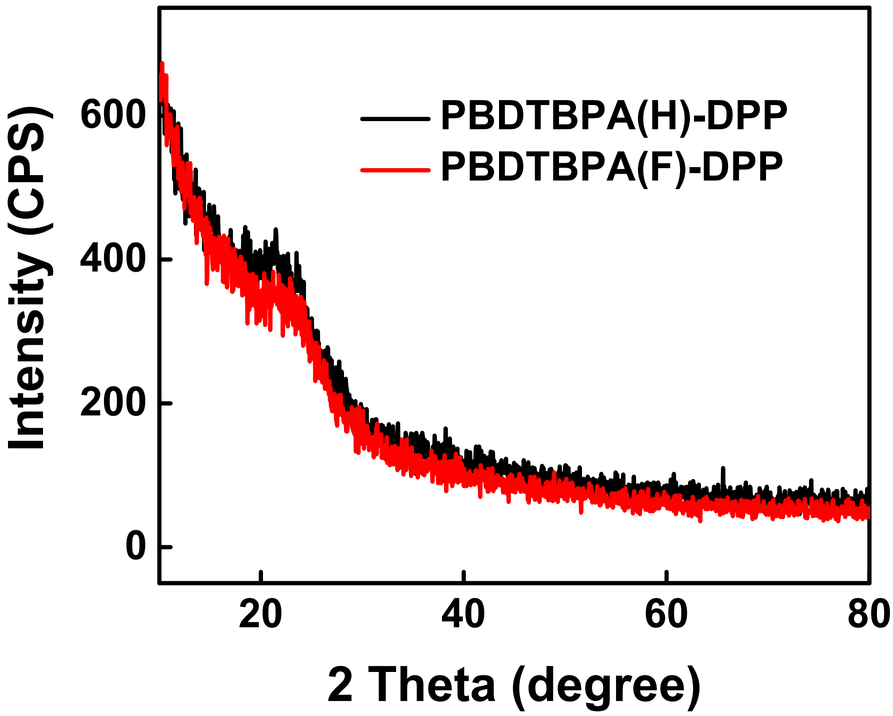


Figure S13. X-ray diffraction patterns of PBDTBPA(H)-DPP and PBDTBPA(F)-DPP.

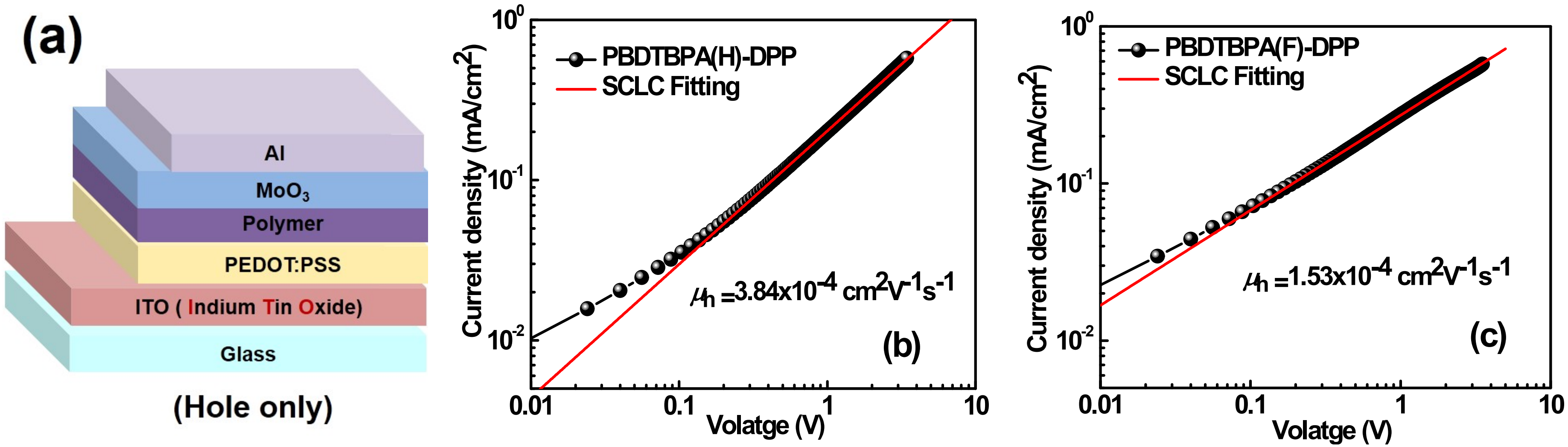


Figure S14. Hole mobility of bare PBDTBPA(H)-DPP and PBDTBPA(F)-DPP.

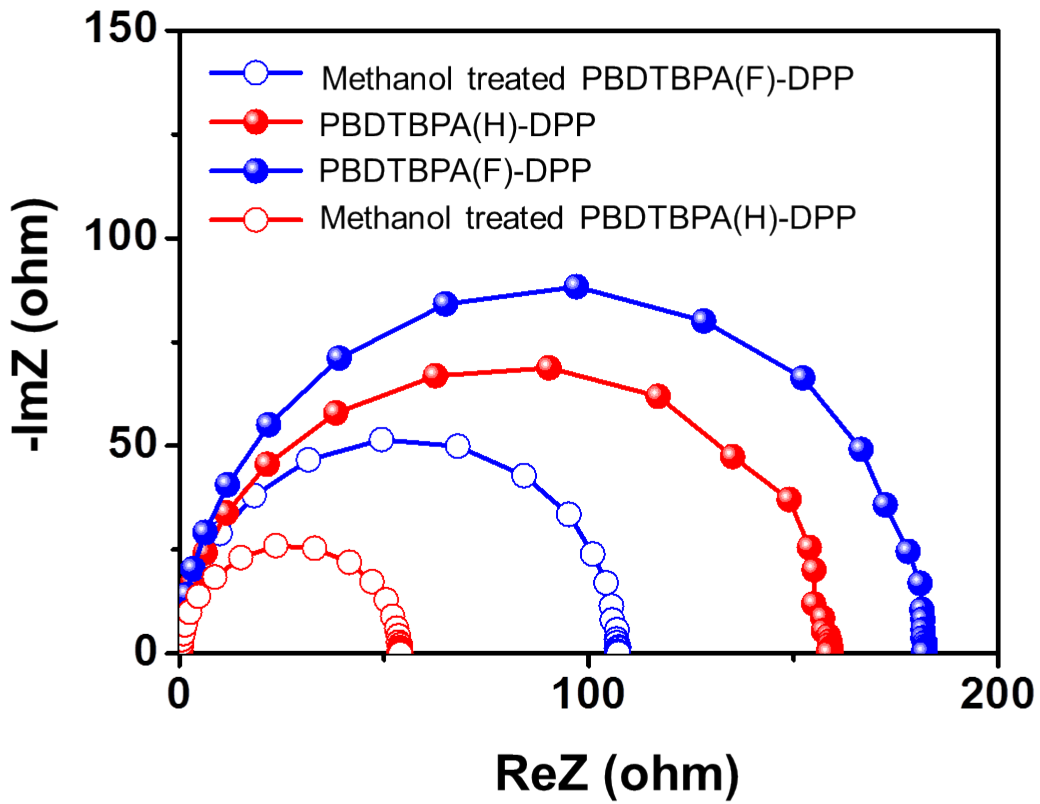


Figure S15. Impedance curves of polymer:$PC_{71}BM$ at the blend ratio of 1:1.5.

Table S1. Photovoltaic Properties of BHJ OSCs of Polymer:$PC_{71}BM$ at the Blend Ratios of 1:0.7 and 1:2

polymer	polymer:$PC_{71}BM$	thickness	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE[a] (%)
PBDTBPA(H)-DPP	1:0.7	100	7.34	0.71	32.58	1.69±0.03
PBDTBPA(H)-DPP	1:2	100	6.42	0.72	44.70	2.08±0.10
PBDTBPA(F)-DPP	1:0.7	100	6.03	0.67	31.48	1.27±0.11
PBDTBPA(F)-DPP	1:2	100	5.55	0.65	36.70	1.32±0.20

[a]PCE is average of 10 IOSCs.

Table S2. Hole and Electron Mobilities of Polymer: $PC_{71}BM$ at the Blend Ratio of 1:1.5 Under Various Processing Conditions

polymer	processing condition	hole mobility (μ_h,$cm^2V^{-1}s^{-1}$)	electron mobility (μ_e,$cm^2V^{-1}s^{-1}$)	charge balance ($\mu h/\mu e$)
PBDTBPA(H)-DPP	Pristine	1.04×10^{-5}	2.98×10^{-4}	0.03
PBDTBPA(H)-DPP	3% DIO	6.55×10^{-5}	3.01×10^{-4}	0.21
PBDTBPA(H)-DPP	methanol	1.76×10^{-4}	3.05×10^{-4}	0.58
PBDTBPA(F)-DPP	Pristine	8.25×10^{-6}	2.90×10^{-4}	0.02
PBDTBPA(F)-DPP	3% DIO	3.37×10^{-5}	2.95×10^{-4}	0.11
PBDTBPA(F)-DPP	methanol	7.44×10^{-5}	3.12×10^{-4}	0.23

REFERENCE

1. Tang, A.; Li, L.; Lu, Z.; Huang, J.; Jia, H.; Zhan, C.; Tan, Z.; Li, Y.; Yao, J. *J. Mater. Chem. A*., **2013**, *1*, 5747.