

Supplementary Information

Achieving a solar power conversion efficiency exceeding 9% by modifying the structure of a simple, inexpensive and highly scalable polymer

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Experimental Section

General instrumental measurements

Nuclear magnetic resonance (NMR) spectra were analyzed on a Bruker AVANCE III HD 400 instrument operating at 400 MHz for ^1H NMR and operating at 100 MHz for ^{13}C NMR. Mass spectra (EIMS) were measured using JEOL JMS-700 Mstation. Thermogravimetric analysis (TGA) were recorded using Thermo plus EVOII TG8120, Samples were run under N_2 and heated from room temperature to 500 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$. UV-vis absorption measurements were carried out with a double-beam Shimadzu UV-2550 spectrophotometer with wavelength range 300–900 nm. All solution UV-vis experiments were run in chlorobenzene (CB) and films were prepared by spin-coating CB solutions onto quartz substrates. Cyclic voltammograms (CV) were determined by using an IviumStat instrument and at a scan rate of 50 mVs^{-1} at 25 $^\circ\text{C}$ under argon using 0.1 M tetrabutyl ammonium hexafluorophosphate in acetonitrile as the electrolyte. During measurement of CV, Pt wire was used as the counter electrode, Ag/AgCl electrode was used as the reference electrode and polymer was drop casted on a platinum electrode used as the working electrode. AFM measurements of size ($2 \times 2 \mu\text{m}^2$) were obtained using a scanning probe Multimode III instruments in a tapping mode.

GIWAXS Characterization.

2D-GIWAX measurements were performed on the PLS-II 3C beam line at the Pohang Accelerator Laboratory in South Korea. Active materials were coated on PEDOT:PSS/Silicon substrate with optimized device fabrication conditions. The monochromatic X-ray beam with intensity 11keV was adjusted with incident angle 0.110-0.140 on sample with irradiation time 5-10sec. The scattered X-ray patterns were recorded with charge coupled device (CCD) detector.

Hole and electron mobility measurements.

The hole and electron mobility of polymer: PC_{71}BM blends were measured by using SCLC method. The hole only (ITO/PEDOT:PSS/Active Layer/Au) and electron only (ITO/ZnO/Active Layer/Ca/Al) devices were fabricated in both CB and CB: DIO (97:3vol%DIO). The charge carrier mobility were determined by fitting dark J - V measurements results in the 0-5 V range into space charge limited form and mobility (μ) calculated using equation $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J = current density, ϵ_r = dielectric constant of the transport medium, ϵ_0 = permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), V = internal voltage and L =active layer thickness respectively.

Device fabrication.

The PSC were fabricated with conventional device architecture (ITO/PEDOT:PSS/Polymer: PC_{71}BM /Ca/Al) The ITO glass substrate was cleaned in order with detergent, de-ionized water, acetone and isopropyl alcohol in ultrasonicator and then dried in oven at 120 $^\circ\text{C}$ for about 5hour. Before spin coating, ITO glass was treated with UV-ozone for 20min and then thin layer of PEDOT:PSS ($\sim 35\text{nm}$) was spin coated and then annealed at 150 $^\circ\text{C}$ for 20min in air. Then substrates were transferred in to argon filled glove box. Then polymer: PC_{71}BM active layer was spin coated over ITO/PEDOT:PSS substrate from homogeneous blend solution (1.0:1.5) in CB/3 vol% DIO solution . The optimized thickness of active layer was $\sim 100\text{nm}$. After active layer deposition all substrates were dried on hot plate for 10min at 110 $^\circ\text{C}$. At the final stage, substrates were transferred to thermal evaporator; Ca (2nm) and

Al (100nm) were deposited on active layer in presence of high vacuum ($\sim 3 \times 10^{-6}$ Torr). The *J-V* characteristics were measured with computer controlled Keithley 236 source measure unit. The light source was Newport solar stimulator with illumination light intensity AM 1.5G, 100 mW cm^{-2} generated with xenon light source with an AM 1.5G. Mask was used to define device illumination area (9 mm^2) and EQE were measured with a reflective microscope objective to focus the light output from 100W Xenon lamp outfitted with a monochromator and optical chopper.

Large-area module fabrication.

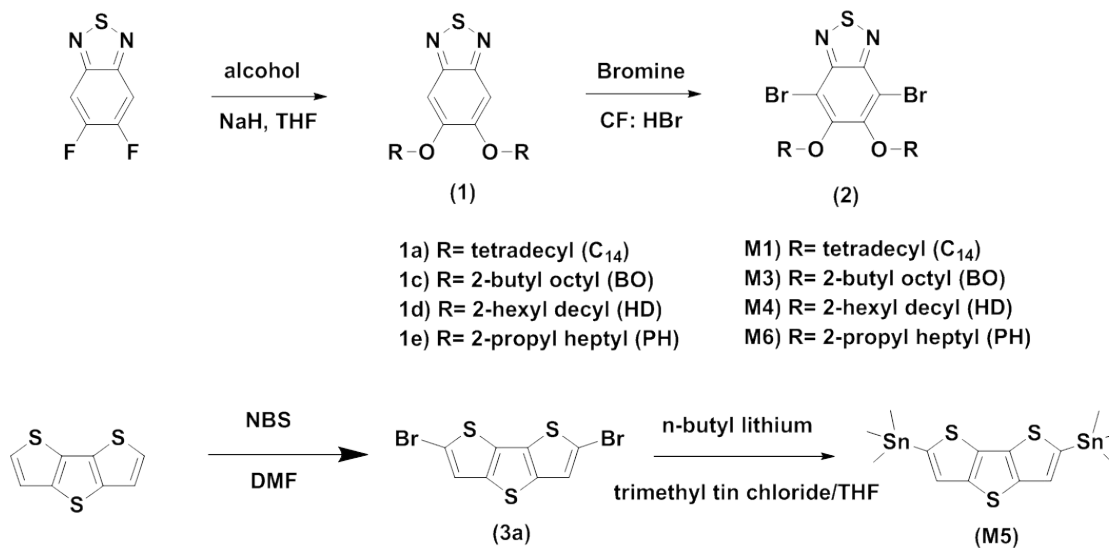
The stripe patterned ITO glass substrate (10cm x10cm) of 100 mm length and a stripe width of 8 mm was washed with detergent, de-ionized water, acetone and isopropyl alcohol using ultrasonicator and dried in oven at 120°C for 4 hours. Sub-module PSCs were fabricated with total 11 stripe cells. Before the fabrication, ITO glass was then treated with UV-ozone for 30min; ZnO NPs layer was coated on ITO substrate (thickness $\sim 25\text{nm}$) with flow rate $6\mu\text{l/s}$ at 80°C using slot-die coating technique. Then it was dried at 100°C for 10min in air. And then PEIE as a surface modifier to the ZnO layer was coated on the ZnO NPs/ITO substrate under same ZnO coating conditions. A solution of polymer: PC₇₁BM with concentration of 25 mg mL^{-1} dissolved in CB/DIO deposited on the PEIE/ZnO NPs layer at 80°C with flow rate of $3\mu\text{l/s}$. The moving speed of the slot-die head is 15 mm/s for deposition of all slot-die coated layers. Finally, MoO_x/Ag (10/80nm) metal electrode was deposited by thermal evaporator after the tape-masking for insulation of each stripe cell. The Photo-active area is defined by using the aperture ($6\text{mm} \times 11 \text{ cells} = 6,600 \text{ mm}^2$).

Materials and Methods.

All chemicals and solvents were purchased from Aldrich, Alfa Aesar and TCI Chemical Co., respectively.

5,6-Difluorobenzo[c][1,2,5]thiadiazole and dithieno[3,2-b:2',3'-d]thiophene was purchased from 4Chem Company.

Synthesis of Monomers:



Scheme S1. Synthetic route for monomers.

5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadiazole (1a)

Tetradecanol (4.7g, 21.8mmol) was added into 2-neck round bottom flask contained 150ml of anhydrous tetrahydrofuran under argon atmosphere. After cooling down to 0°C, sodium hydride (60% dispersion in paraffin) (1.4g, 34.88mmol) was added as one portion. After being stirred for 1h at 0°C, 5,6-difluorobenzo[c][1,2,5]thiadiazole (1.5g, 8.72mmol) was added and reaction mixture was refluxed overnight. Then mixture was brought to 0°C and slowly quenched by dropwise addition of 100 ml water and product was extracted with ethyl acetate. The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding 1a (3.8g, 78%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.13 (s, 2H); 4.09 (t, *J* = 6.5 Hz, 4H); 1.94-1.87 (m, 4H); 1.56-1.26 (m, 44H); 0.89-0.85 (m, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.1; 151.40; 98.4; 69.1; 31.9; 29.72; 29.68; 29.62; 29.4; 28.7; 26.0; 22.7; 14.1. MS (EI): Calculated *m/z* 560.44; found *M*⁺ 560.

4,7-dibromo-5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadiazole (M1)

To the stirred solution of 5,6-bis(tetradecyloxy)benzo[c][1,2,5]thiadiazole (1a) (2.5g, 4.45mmol) in chloroform (150ml), hydrobromic acid (30ml) and bromine (2.13g, 13.35mmol) was added at room temperature and reaction mass was refluxed overnight. Reaction mass was brought to 0°C and slowly quenched with sodium thiosulphate solution and extracted with chloroform (50ml x 3). The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding M1 (2.5g, 78%) as off white solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.16 (t, *J* = 6.64 Hz, 4H); 1.90-1.86 (m, 4H); 1.56-1.50 (m, 4H); 1.40-1.24 (m, 40H); 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.54; 150.4; 106.26; 75.17; 31.93; 30.27; 29.70; 29.69; 29.64; 29.62; 29.44; 29.37; 26.0, 22.7; 14.11. MS (EI): Calculated *m/z* : 718.26; found *M*⁺ 718.

5,6-Bis((2-butyloctyl)oxy)benzo[c][1,2,5]thiadiazole (1c)

2-Butyloctanol (2.7g, 14.53mmol) was added into 2-neck round bottom flask contained 100ml of anhydrous tetrahydrofuran under argon atmosphere. After cooling down to 0°C, sodium hydride (60% dispersion in paraffin) (0.94g, 23.3mmol) was added as one portion. After being stirred for 1h at 0°C, 5,6-difluorobenzo[c][1,2,5]thiadiazole (1g, 5.8mmol) was added and reaction mixture was refluxed overnight. Then mixture was brought to 0°C and slowly quenched by dropwise addition of 100 ml water and product was extracted with ethyl acetate. The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding 1c (2.5g, 86%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.10 (2H, s); 3.95 (4H, d, *J* = 5.4 Hz); 1.88 (2H, m); 1.54-1.28 (32H, m); 0.89 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.56; 151.44; 98.03; 71.51; 37.83 ; 31.88; 31.40; 31.08; 29.73; 29.20; 26.88; 23.06; 22.70; 14.10. MS (EI): Calculated *m/z*: 504.37; found *M*⁺ 504.

4,7-Dibromo-5,6-bis((2-butyloctyl)oxy)benzo[c][1,2,5]thiadiazole (M3)

To the stirred solution of 5,6-Bis((2-butyloctyl)oxy)benzo[c][1,2,5]thiadiazole (1c) (2.5g, 4.95mmol) in chloroform (150ml), hydrobromic acid (30ml) and bromine (2.37g, 14.85mmol) was added at room temperature and reaction mass was refluxed overnight. Reaction mass was brought to 0°C and quenched with sodium thiosulphate solution and extracted with chloroform (50ml x 3). The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding M3 (2.6g, 80%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.02 (4H, d, *J* = 6.2 Hz); 1.92 (2H, m); 1.58 (4H, m); 1.47-1.27 (28H, m); 0.90 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.84; 150.39; 105.99; 78.45; 39.20; 31.91; 31.09; 30.77; 29.76; 29.11; 26.87; 23.12; 22.69; 14.11. MS (EI): Calculated *m/z*: 662.2; found *M*⁺ 662.

5,6-bis((2-hexyldecyl)oxy)benzo[c][1,2,5]thiadiazole (1d)

2-hexyldecanol (3.52g, 14.53mmol) was added into 2-neck round bottom flask contained 100ml of anhydrous tetrahydrofuran under argon atmosphere. After cooling down to 0°C, sodium hydride sodium hydride (60% dispersion in paraffin) (0.94g, 23.3mmol) was added as one portion. After being stirred for 1h at 0°C, 5,6-difluorobenzo[c][1,2,5]thiadiazole (1g, 5.8mmol) was added and reaction mixture was refluxed overnight. Then mixture was brought to 0°C and slowly quenched by dropwise addition of 100 ml water and product was extracted with ethyl acetate. The organic extraction was dried over anhydrous magnesium

sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding 1d (2.5g, 70%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.10 (2H, s); 3.95 (4H, d, J= 5.46 Hz); 1.88 (2H, m); 1.54-1.25 (48H, m); 0.88 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.52; 151.40; 97.96; 71.41; 37.80 ; 31.90; 31.86; 31.34; 30.05; 29.71; 29.62; 29.36; 26.88; 26.85; 22.68; 14.10. MS (EI): Calculated m/z: 616.5; found M⁺ 617.

4,7-Dibromo-5,6-bis((2-hexyldecyl)oxy)benzo[c][1,2,5]thiadiazole (M4)

To the stirred solution of 5,6-bis((2-hexyldecyl)oxy)benzo[c][1,2,5]thiadiazole (1d) (2.5g, 4.05mmol) in chloroform (150ml), hydrobromic acid (30ml) and bromine (1.94g, 12.15mmol) was added at room temperature and reaction mass was refluxed overnight. Reaction mass was brought to 0°C and quenched with sodium thiosulphate solution and extracted with chloroform (50ml x 3). The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding M4 (2.4g, 77%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.02 (4H, d, J= 6.2 Hz); 1.91 (2H, m); 1.56 (4H, m); 1.47-1.26 (44H, m); 0.89 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.84; 150.39; 105.99; 78.43; 39.22; 31.92; 31.09; 30.11; 29.77; 29.66; 29.38; 26.91; 26.88; 22.70; 14.11. MS (EI): Calculated m/z: 774.32; found M⁺ 774.

5,6-bis((2-propylheptyl)oxy)benzo[c][1,2,5]thiadiazole (1e)

2-propylheptan-1-ol (crude) (1.2g, 5.81mmol) was added into 2-neck round bottom flask contained 100ml of anhydrous tetrahydrofuran under argon atmosphere. After cooling down to 0°C, sodium hydride (60% dispersion in paraffin) (0.35g, 8.72mmol) was added as one portion. After being stirred for 1h at 0°C, 5,6-difluorobenzo[c][1,2,5]thiadiazole (0.25g, 1.45mmol) was added and reaction mixture was refluxed overnight. Then mixture was brought to 0°C and slowly quenched by dropwise addition of 100 ml water and product was extracted with ethyl acetate. The organic extraction was dried over anhydrous magnesium sulfate and then concentrated to get crude product. The crude product was taken for next step without further purification (0.4g, 61%).

4,7-dibromo-5,6-bis((2-propylheptyl)oxy)benzo[c][1,2,5]thiadiazole (M6)

To the stirred solution of crude 5,6-bis((2-propylheptyl)oxy)benzo[c][1,2,5]thiadiazole (1e)(0.4g, 0.89mmol) in chloroform (50ml), hydrobromic acid (5ml) and bromine (0.43g, 2.67mmol) was added at room temperature and reaction mass was refluxed overnight. Reaction mass was brought to 0°C and quenched with sodium thiosulphate solution and extracted with chloroform (50ml x 3). The organic extraction was dried over anhydrous magnesium sulfate and then concentrated. The crude product was purified by silica gel column with dichloromethane (30%) in hexane as eluent, yielding M6 (0.2g, 28% from 2 steps) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.01 (4H, d, J= 6.2 Hz); 1.95-1.90 (2H, m); 1.58 (4H, m); 1.47-1.29 (20H, m); 0.86-0.88 (12H, m). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.83; 150.39; 106.01; 78.43; 38.99; 33.32; 32.30; 31.03; 26.56; 22.69; 20.03; 14.47; 14.12. MS (EI): Calculated m/z: 606.13; found M⁺ 606.

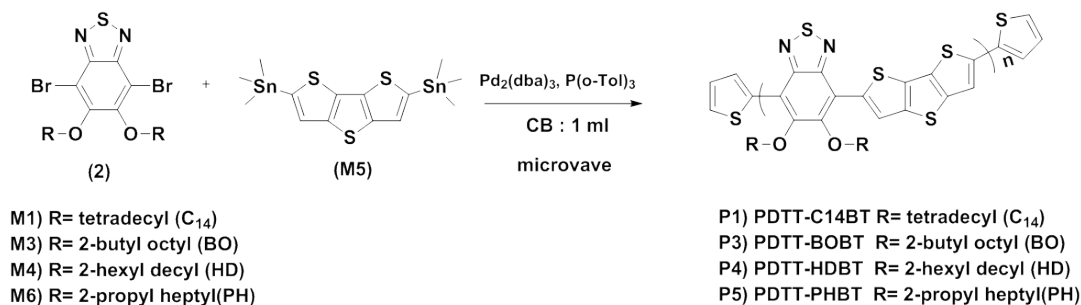
2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (3a)

N-bromosuccinimide (5.66g, 31.83mmol) was portion wise added to a solution of the compound dithieno[3,2-b:2',3'-d]thiophene (2.5g, 12.73mmol) in anhydrous DMF (150 ml) at 0°C. The mixture was heated up to room temperature, stirred overnight, and then poured into water, and the formed precipitate was taken out. The crude product was washed with methanol and recrystallized in chloroform/methanol to give of the compound as pale green crystals, 3a (4 g, 89%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) δ 7.26(s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 139.10; 130.85; 123.21; 112.37. MS (EI): Calculated m/z: 353.77; found M⁺ 354.

2,6-Bis(trimethyltin)dithieno[3,2-b:2',3'-d]thiophene (M5)

2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (2.5 g, 7.06mmol) was dissolved in 150 ml of anhydrous THF and cooled down to -78°C. n-butyl lithium solution (11 ml, 17.65mmol, 1.6 M in hexane) was added dropwise into the reaction mixture at the same temperature. After stirring for 30 min at -78°C, the reaction mass was allowed to stir at room temperature for 2h. Then it was cooled back to -78°C, trimethyltin chloride solution (22 ml, 21.12mmol, 1 M in THF) was added dropwise into the resulting solution and reaction mass was allowed to stir at RT for overnight. Then reaction was quenched by addition of 60 ml of water and product was extracted with diethyl ether. The organic phase was washed with water, and then dried anhydrous magnesium sulfate and evaporated in vacuum. Recrystallization of the residue from CH₂Cl₂ and isopropanol yields the di-stannylated compound M5 (1.86 g, 50%) as off-white solid. (To get more pure monomers some batches were purified by recycling preparative HPLC). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) δ 7.29 (s, 2H); 0.41 (t, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 143.78; 139.95; 135.81; 127.91; -8.41. MS (EI): Calculated m/z: 521.88; found M⁺ 522.

Synthesis of polymers:



Scheme S2. Synthetic routes polymers.

Synthesis of poly(5,6-bis((tetradecyl)oxy)-4-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)benzo[c][1,2,5] thiadiazole (PDTT-C14BT) (P1) or PDTTDABT.

To the clean dry 5ml microwave vial 4,7-dibromo-5,6-bis(tetradecyloxy)benzo[c][1,2,5] thiadiazole (M1) (216mg, 0.3mmol), 2,6-Bis(trimethyltin)dithieno[3,2-b:2',3'-d] thiophene (M5) (156mg, 0.3mmol), Pd₂(dba)₃ (3mole%), and tri-(o-tolyl)phosphine (6mole%) were added followed by 1 ml of anhydrous chlorobenzene (CB). The resulting reaction mixture was heated at 100°C for 10min, 120°C for 10min and then 140°C for 60min in a microwave reactor. 2-Bromothiophene (1 eq) and 2-(tributylstannyl)thiophene (1 eq) were sequentially added to the reaction mixture with a 20min interval for end-capping of the polymer. The reaction mixture was then cooled to room temperature, and the polymer was precipitated into methanol. The precipitated polymer was then filtered and purified by Soxhlet extraction using methanol 12h, acetone for 12h, hexane for 12h, chloroform for 12 h and finally chlorobenzene 12 hours. The chlorobenzene fraction was then concentrated under reduced pressure and precipitated into methanol and filtered to give dark brown solid. The polymer was dried in vacuum oven for 24 h before using to device fabrication. The chlorobenzene fraction (250mg, 91%) GPC analysis: Mn=82,580, Mw=313,824, PDI=3.80.

Synthesis of poly(5,6-bis((2-butyl octyl)oxy)-4-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)benzo [c] [1,2,5] thiadiazole (PDTT-BOBT) (P3)

To the clean dry 5ml microwave vial 4,7-dibromo-5,6-bis(2-butyl octyloxy)benzo[c] [1,2,5] thiadiazole (M3) (198mg, 0.3mmol), 2,6-Bis(trimethyltin)dithieno[3,2-b:2',3'-d] thiophene (M5) (156mg, 0.3mmol), Pd₂(dba)₃ (3mole%), and tri-(o-tolyl)phosphine (6mole%) were added followed by 1 ml of anhydrous chlorobenzene. The resulting reaction mixture was heated at 100°C for 10min, 120°C for 10min and then 140°C for 60min in a microwave reactor. 2-Bromothiophene (1 eq) and 2-(tributylstannyl)thiophene (1 eq) were sequentially added to the reaction mixture with a 20min interval for end-capping of the polymer. The reaction mixture was then cooled to room temperature, and the polymer was precipitated into methanol. The precipitated polymer was then filtered and purified by Soxhlet extraction using methanol 12h, acetone for 12h, hexane for 12h and finally chloroform 12 hours. The chloroform fraction was then concentrated under reduced pressure and precipitated into

methanol and filtered to give dark brown solid. The polymer was dried in vacuum oven for 24 h before using to device fabrication. The Chloroform fraction (220mg, 85%) GPC analysis: Mn= 41,910, Mw= 129,083, PDI=3.08.

Synthesis of poly(5,6-bis((2-hexyldecyl)oxy)-4-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)benzo[c] [1,2,5] thiadiazole (PDTT-HDBT) (P4)

To the clean dry 5ml microwave vial 4,7-dibromo-5,6-bis(2-hexyldecyloxy) benzo[c] [1,2,5] thiadiazole (M4) (232mg, 0.3mmol), 2,6-Bis(trimethyltin)dithieno[3,2-b:2',3'-d] thiophene (M5) (156mg, 0.3mmol), Pd2(dba)3 (3mole%), and tri-(o-tolyl)phosphine (6mole%) were added followed by 1 ml of anhydrous chlorobenzene. The resulting reaction mixture was heated at 100°C for 10min, 120°C for 10min and then 140°C for 60min in a microwave reactor. 2-Bromothiophene (1 eq) and 2-(tributylstannyl)thiophene (1 eq) were sequentially added to the reaction mixture with a 20min interval for end-capping of the polymer. The reaction mixture was then cooled to room temperature, and the polymer was precipitated into methanol. The precipitated polymer was then filtered and purified by Soxhlet extraction using methanol 12h, acetone for 12h and hexane for 12h. The hexane fraction was then concentrated under reduced pressure and precipitated into methanol and filtered to give dark brown solid. The polymer was dried in vacuum oven for 24 h before using to device fabrication. The hexane fraction (260mg, 89%) GPC analysis: Mn= 43,528, Mw= 129,686, PDI=2.9.

Synthesis of poly(4-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)-5,6-bis((2-propylheptyl)oxy)benzo[c][1,2,5]thiadiazole (PDTT-PHBT) (P5)

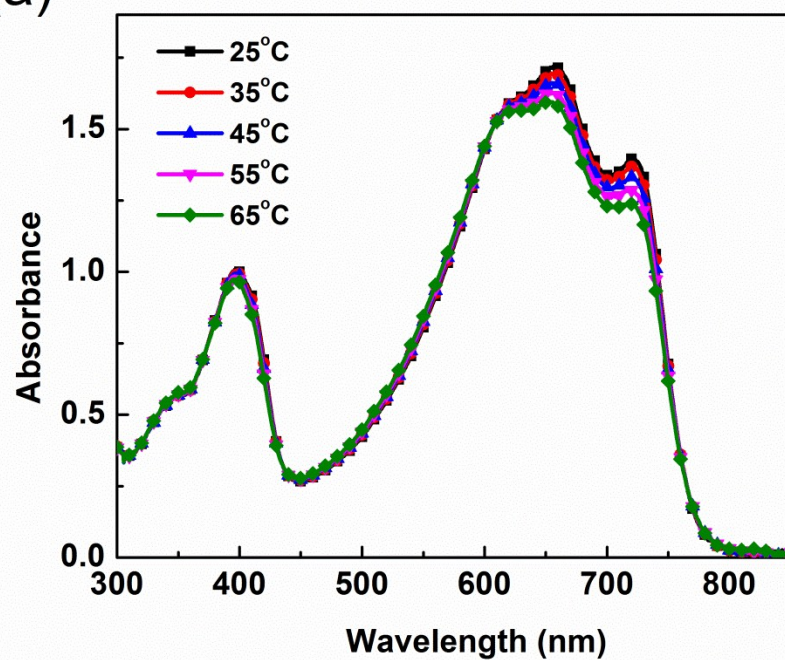
To the clean dry 5ml microwave vial 4,7-dibromo-5,6-bis((2-propylheptyl)oxy)benzo[c][1,2,5]thiadiazole (M6) (121mg, 0.2mmol), 2,6-Bis(trimethyltin) dithieno[3,2-b:2',3'-d] thiophene (M5) (104mg, 0.2mmol), Pd2(dba)3 (3mole%), and tri-(o-tolyl)phosphine (6mole%) were added followed by 1 ml of anhydrous chlorobenzene. The resulting reaction mixture was heated at 100°C for 10min, 120°C for 10min and then 140°C for 60min in a microwave reactor. 2-Bromothiophene (1 eq) and 2-(tributylstannyl)thiophene (1 eq) were sequentially added to the reaction mixture with a 20min interval for end-capping of the polymer. The reaction mixture was then cooled to room temperature, and the polymer was precipitated into methanol. The precipitated polymer was then filtered and purified by Soxhlet extraction using methanol 12h, acetone for 12h and hexane for 12h and finally chloroform 12 hours. The chloroform fraction was then concentrated under reduced pressure and precipitated into methanol and filtered to give dark brown solid. The polymer was dried in vacuum oven for 24 h before using to device fabrication. The Chloroform fraction (100mg, 75%) GPC analysis: Mn = 14,329, Mw= 34,750, PDI=2.4.

Optimized Large-scale synthesis of polymer using thermal conditions.

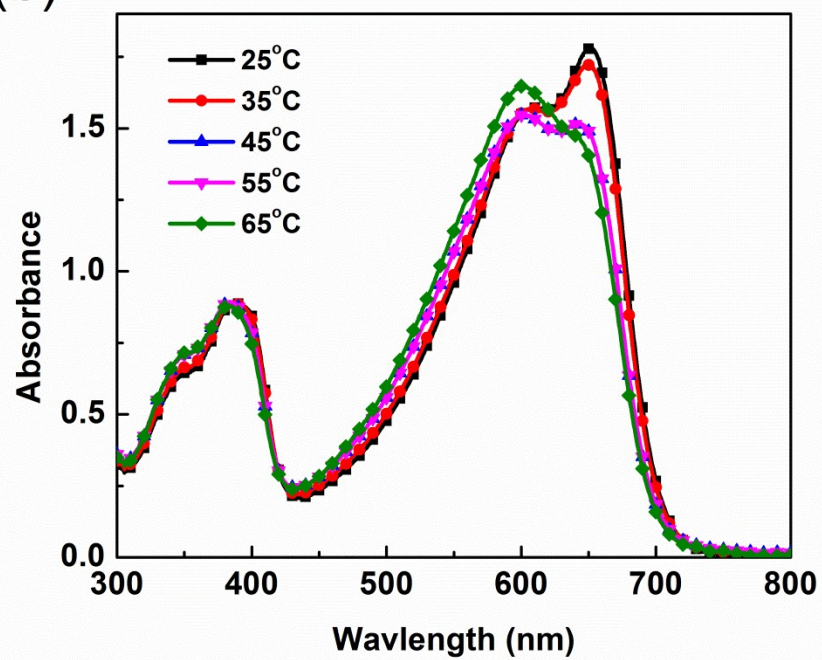
Synthesis of poly(5,6-bis((2-butyloctyl)oxy)-4-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)benzo [c] [1,2,5] thiadiazole (PDTT-BOBT) (P3).

In clean flame dried 25ml 2-neck round-bottom flask fitted with condenser 4,7-dibromo-5,6-bis(2-butyl octyloxy)benzo[c][1,2,5]thiadiazole (M3) (1.19g, 1.8mmol), 2,6-Bis (trimethyltin) dithieno[3,2-b:2',3'-d] thiophene (M5) (945mg, 1.8mmol) were charged. Pd(PPh₃)₄ (42mg, 2mole%) were charged in the glove box. Then, anhydrous Toluene (14.4ml): DMF (3.6ml) was added via a syringe. The polymerization was carried out at 110°C for 48h under nitrogen protection. The raw product was precipitated into methanol and collected by filtration. The precipitated polymer was then filtered and purified by Soxhlet extraction using methanol 12h, acetone for 12h, followed by hexane for 12h, dichloromethane 12h, and finally chloroform for 12 h. The dichloromethane and chloroform fractions were then separately concentrated under reduced pressure and precipitated into methanol and filtered to give dark brown solid. The polymers were dried in vacuum oven for 24 h before using to device fabrication. The dichloromethane fraction (600mg, 45%) GPC analysis: Mn=45,782, Mw= 185,875, PDI=4.0; Chloroform fraction (600mg, 45%) GPC analysis: Mn= 64,830, Mw= 228,958, PDI=3.5.

(a)



(b)



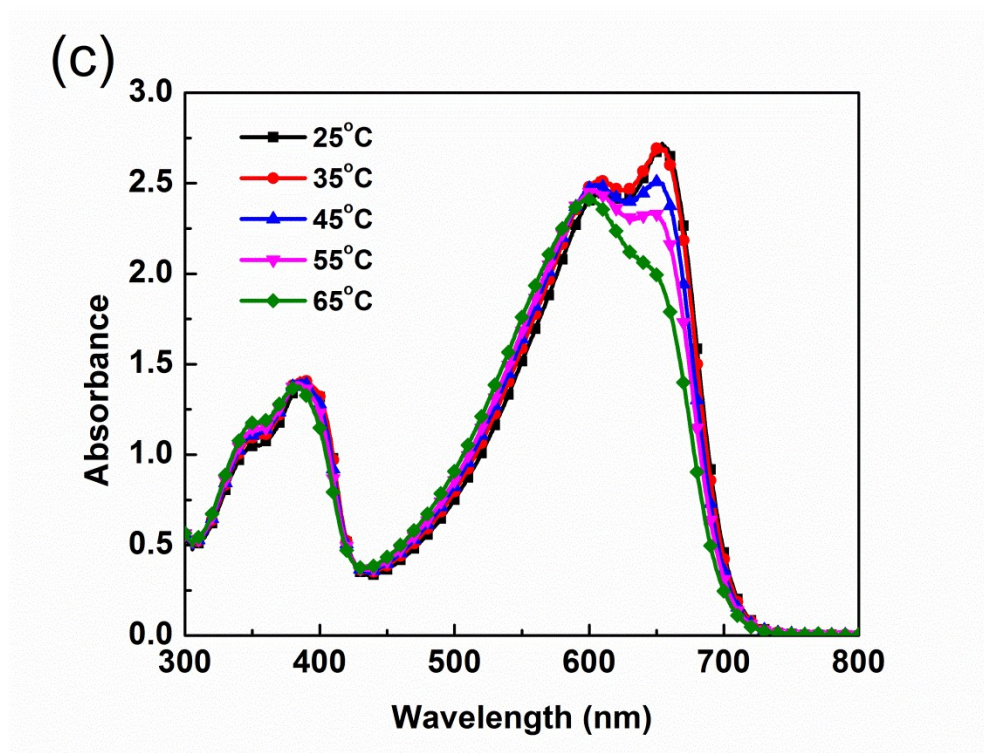


Fig. S1 The UV-vis absorption spectra of polymers in CB solution during heating process from 25°C to 65°C a) P1, b) P3 and c) P4.

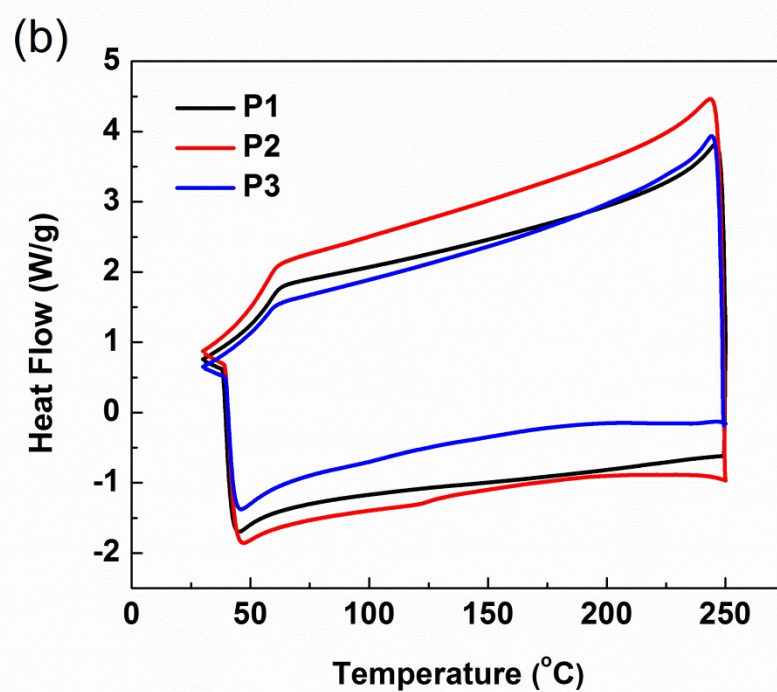
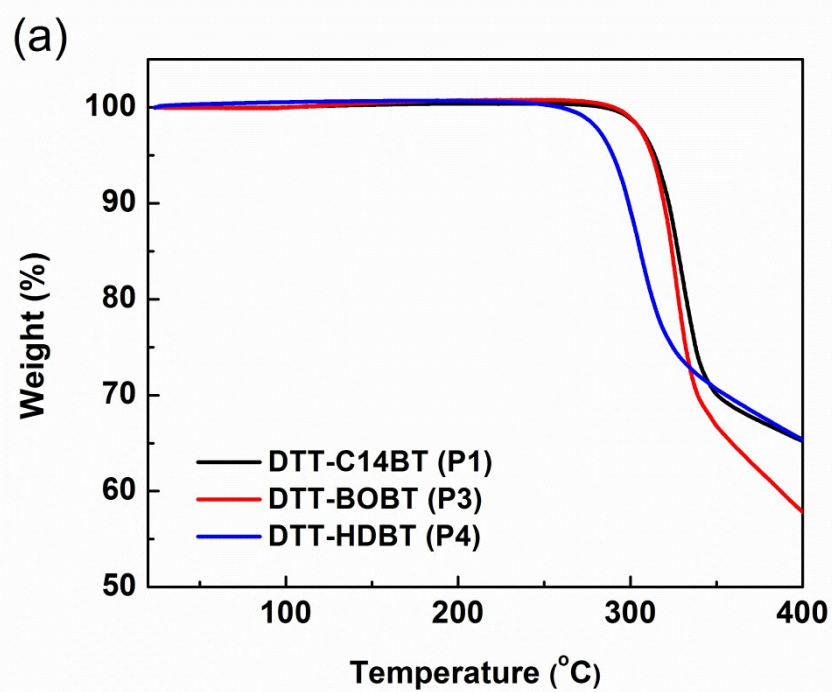


Fig. S2 (a) TGA and (b) DSC profiles of polymers.

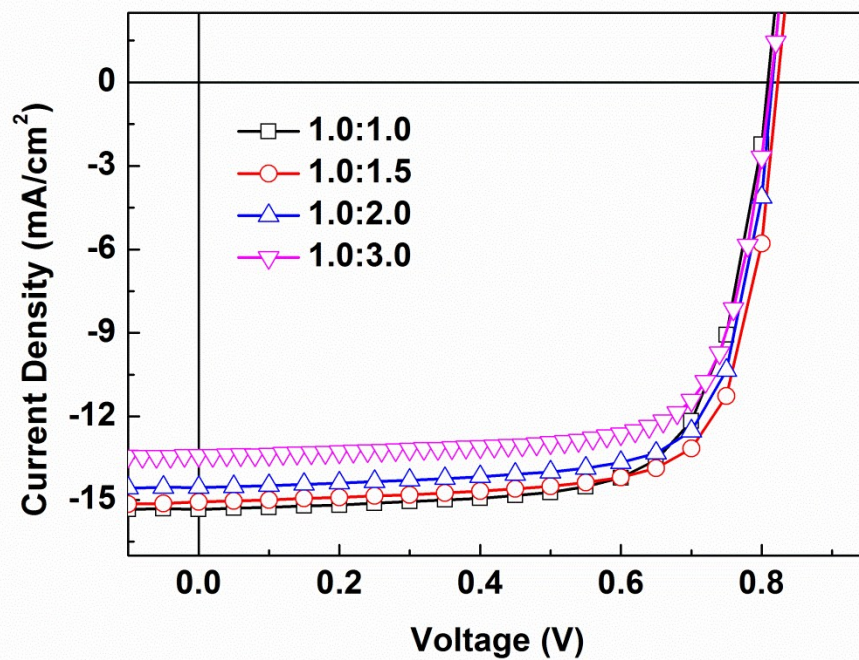


Fig. S3 The J - V characteristics of P3:PC₇₁BM PSCs with different D:A weight ratios (solvent: CB/DIO) under conventional device architecture (ITO/PEDOT:PSS/Photo-activelayer/Ca/Al).

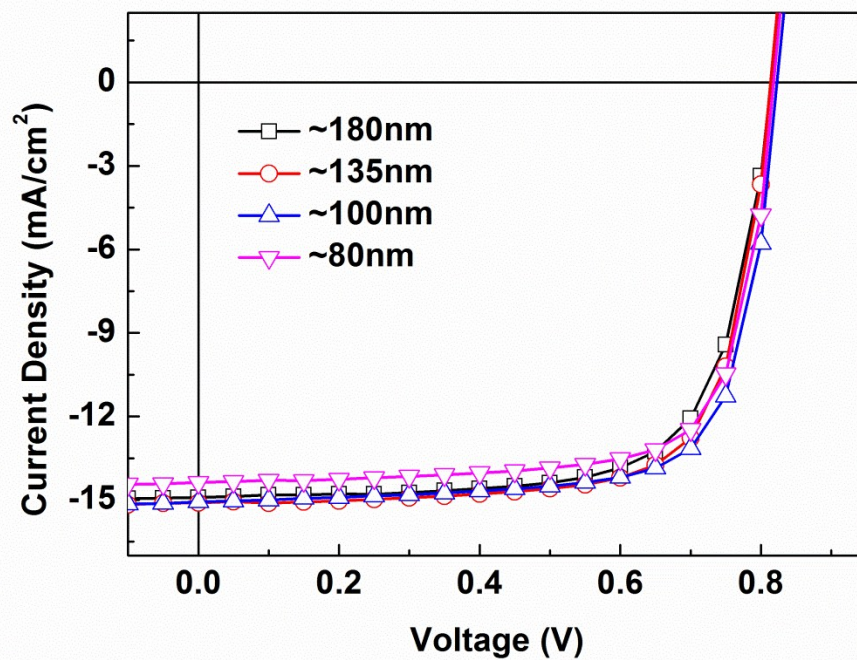


Fig. S4 The *J*-*V* characteristics of P3:PC₇₁BM PSCs with different thickness of the photo-active layer.

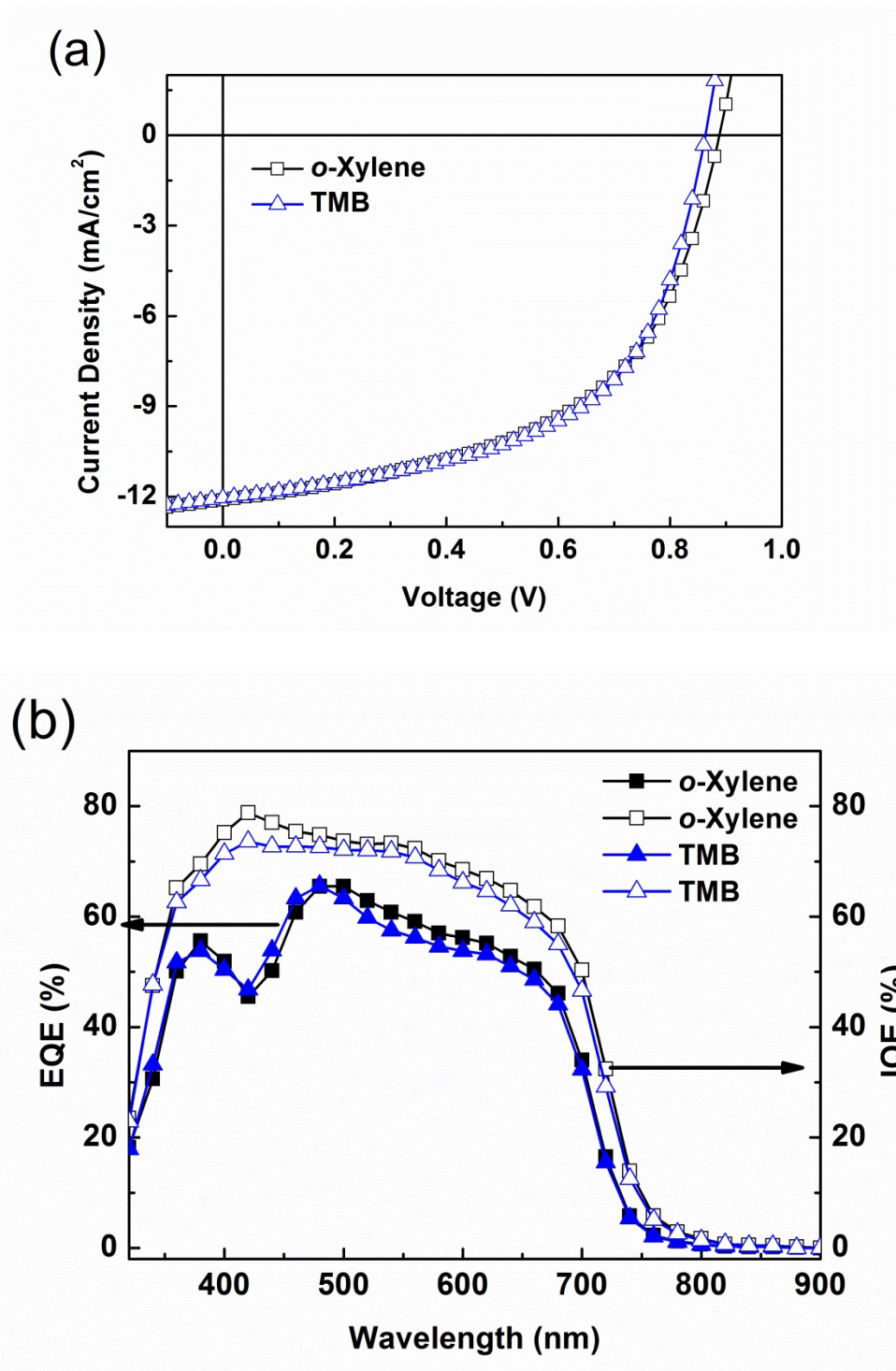


Fig. S5 The J - V characteristics (a) and EQE and IQE curves (b) of P3:PC₇₁BM (1.0:1.5, w/w) dissolved in non-halogenated solvent under conventional device architecture (ITO/PEDOT:PSS/ Photo-active layer/Ca/Al).

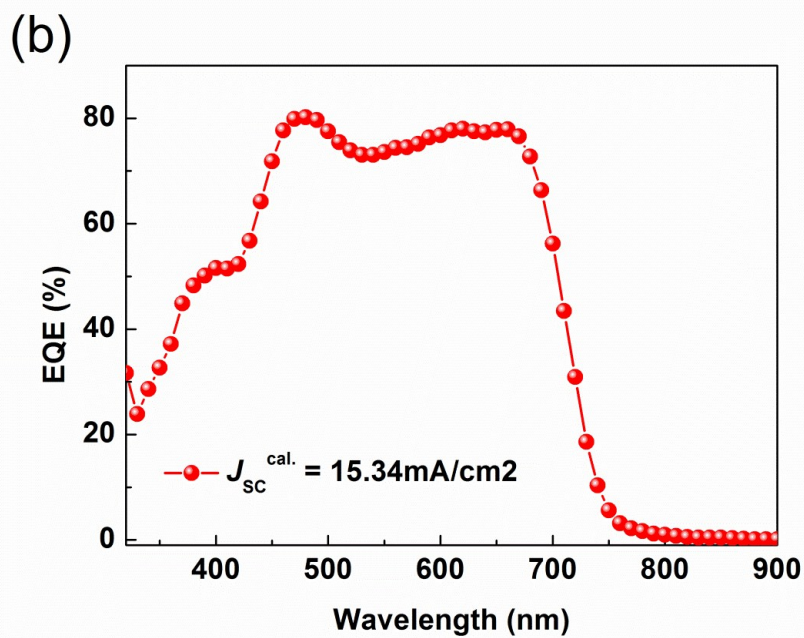
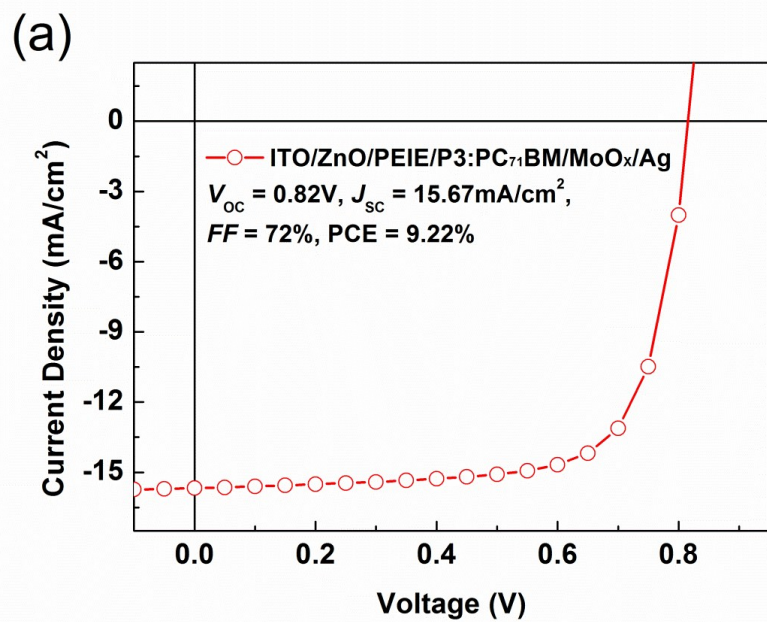


Fig. S6 The J-V characteristics and EQE curves of P3:PC₇₁BM with optimum conditions employing inverted device structure (ITO/ZnO/PEIE/polymer:PC₇₁BM/MoO₃/Ag).

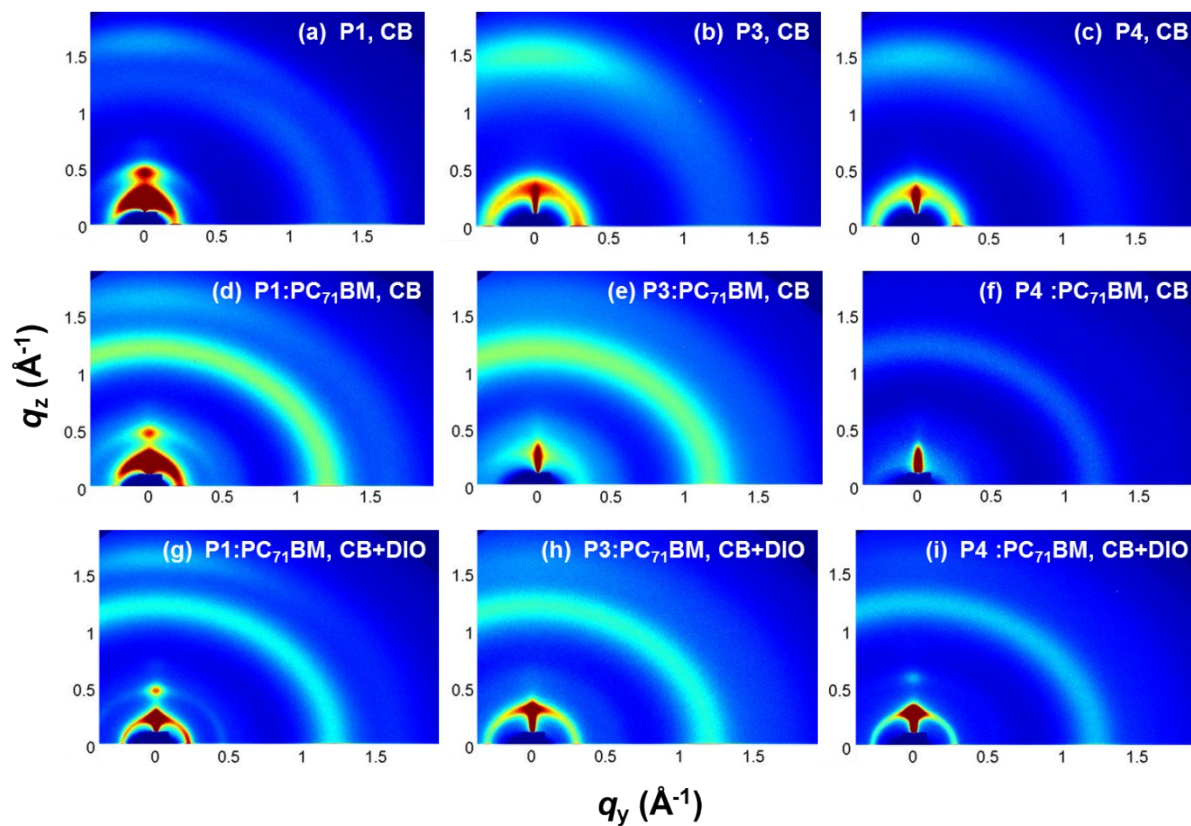
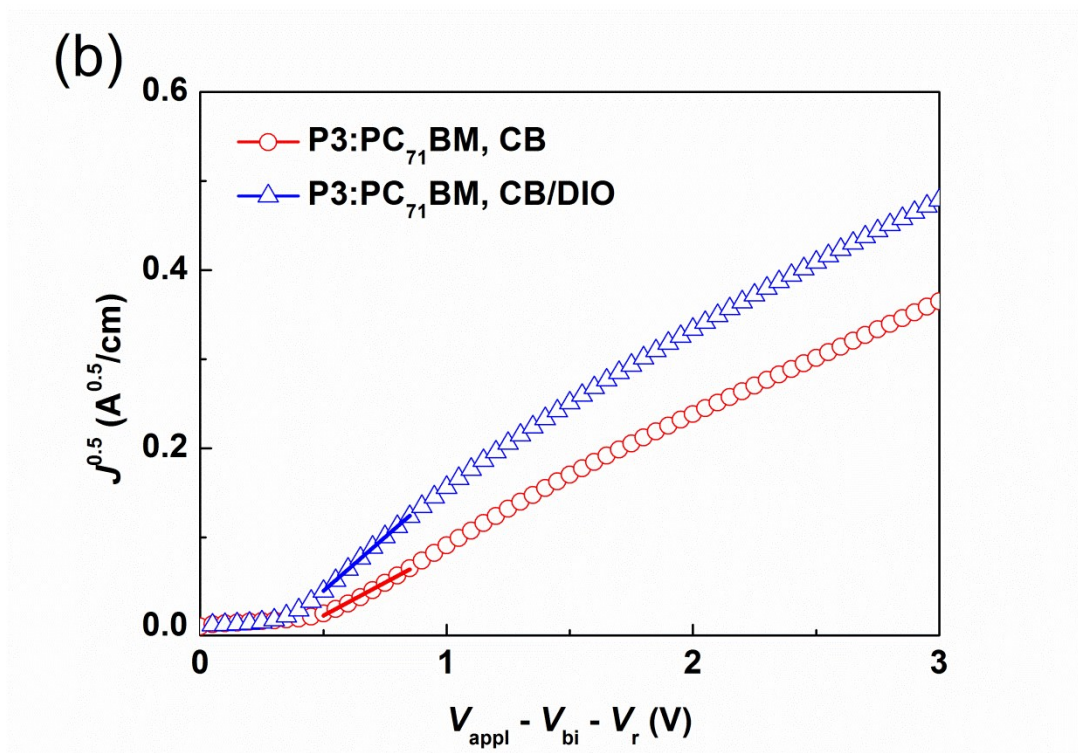
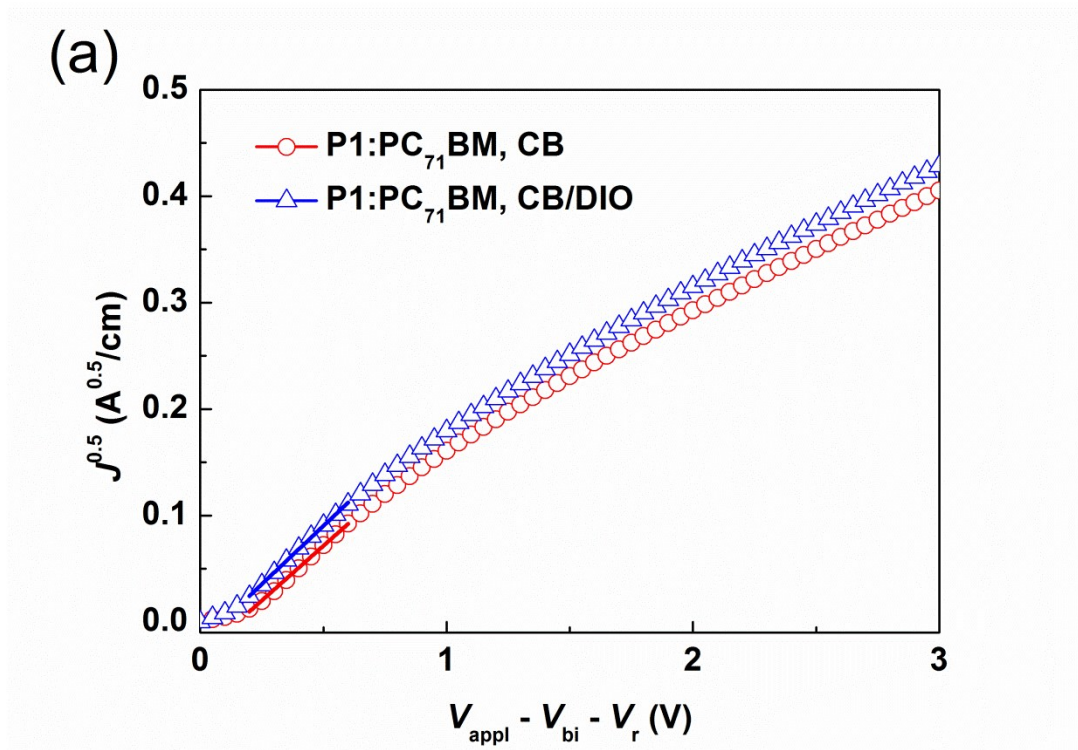


Fig. S7 2D-GIWAXS images of pristine polymers (upper row), polymer: PC₇₁BM blend without DIO (middle row) and polymer:PC₇₁BM blend with DIO(lower row) for polymer P1, P3 and P4.



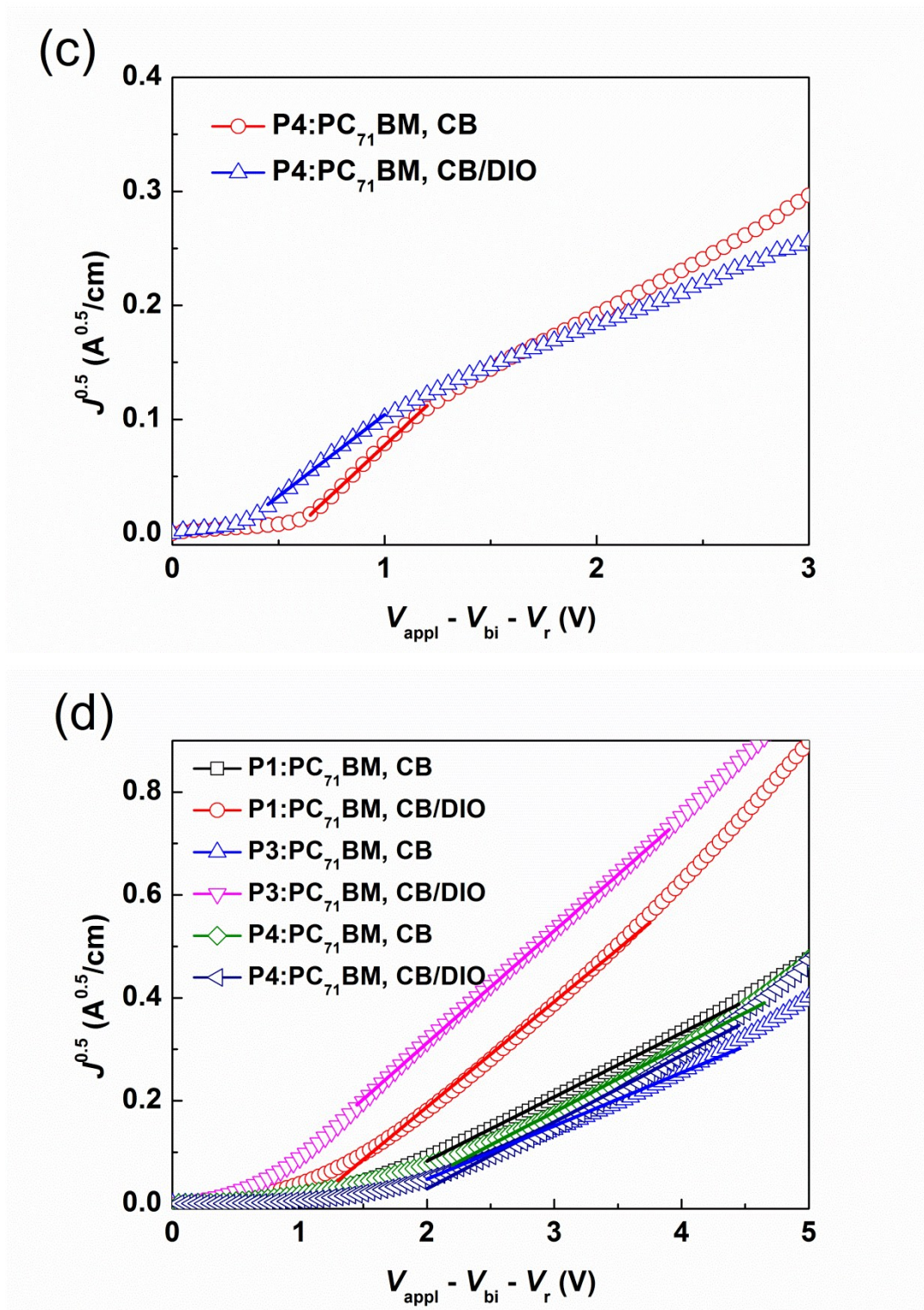


Fig. S8 The dark J - V curves of (a), (b) and (c) of hole-only and (d) electron-only devices based on polymer: PC₇₁BM blend films casting from CB and CB/DIO conditions.

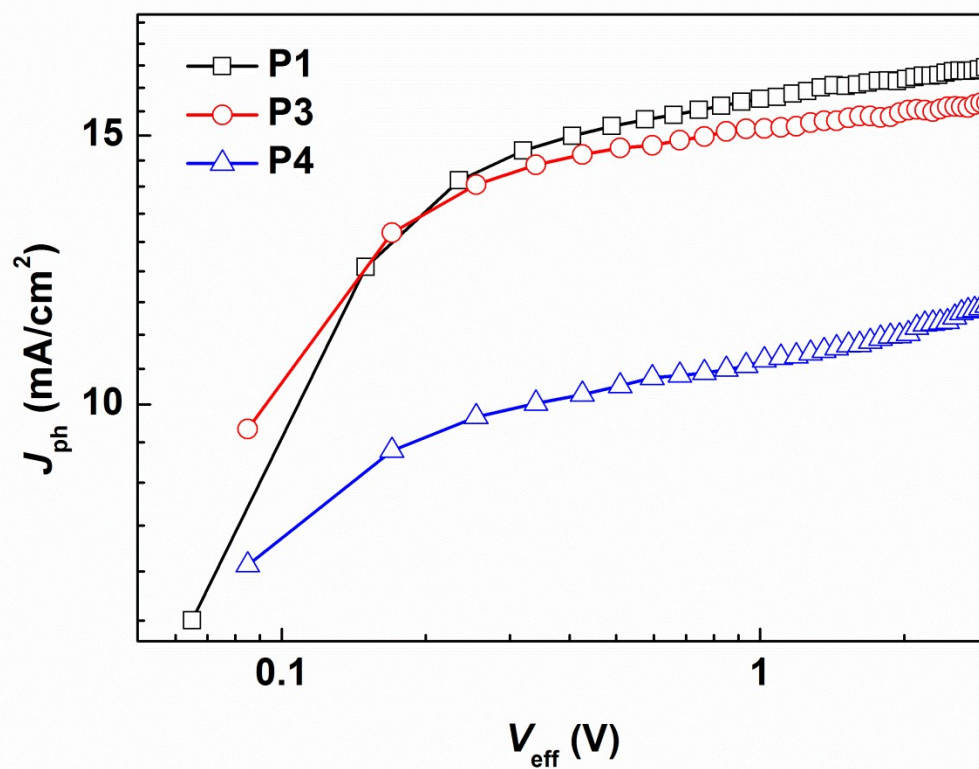


Fig. S9 The plot of J_{ph} Vs V_{eff} for polymers P1, P3 and P4.

(a)



(b)

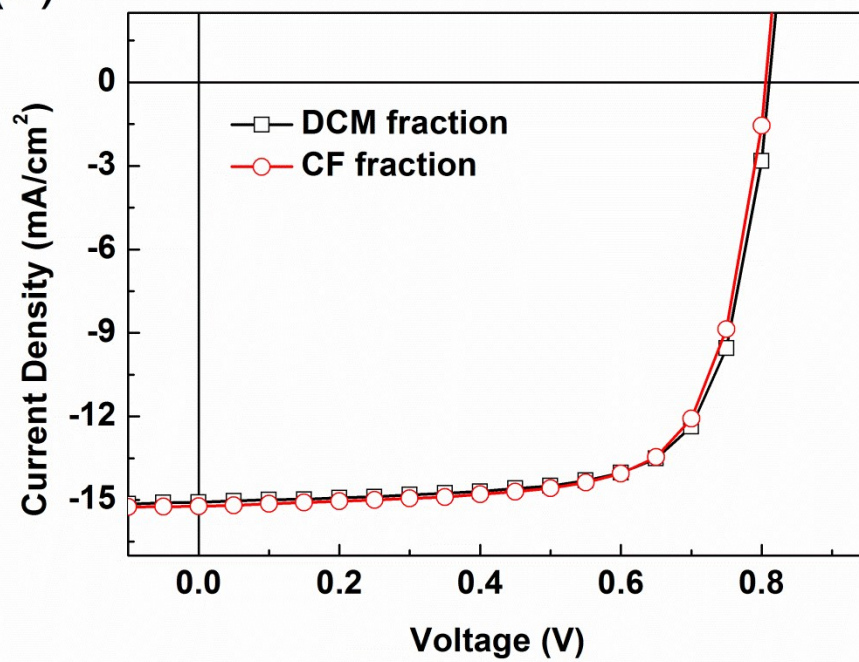


Fig. S10 (a) image of large scale synthesized polymer P3, b) J-V curves of the large scale synthesized polymer.

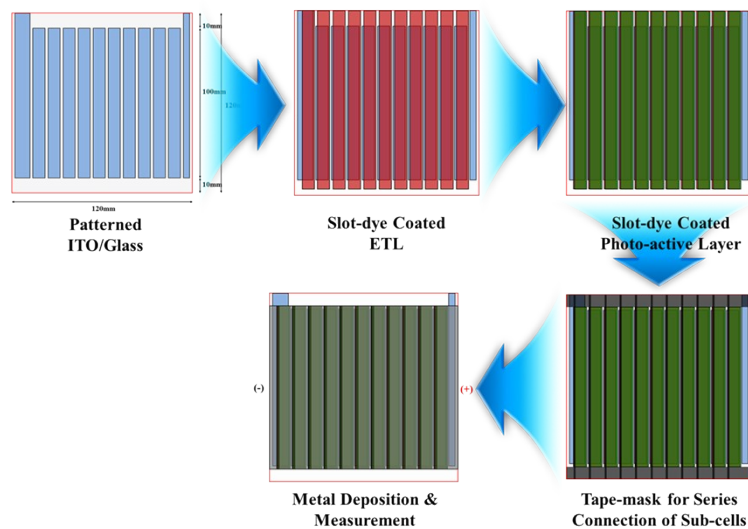


Fig. S11 Schematic diagram for preparing large-area module

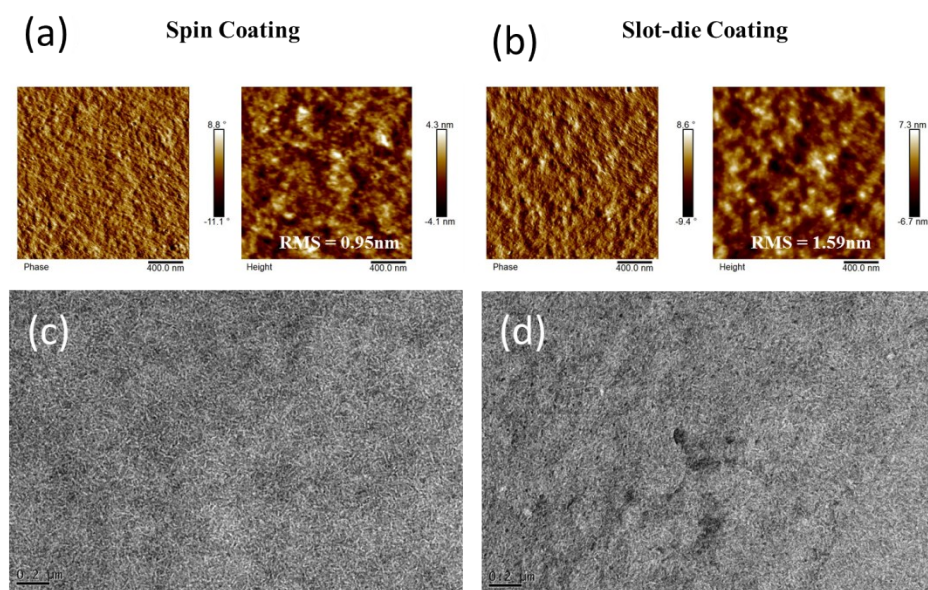
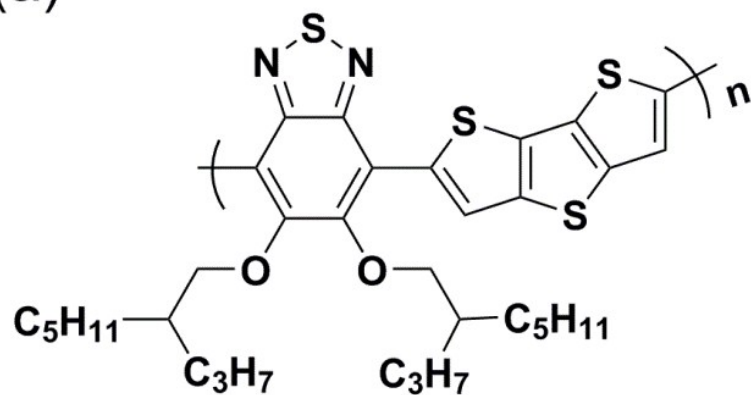
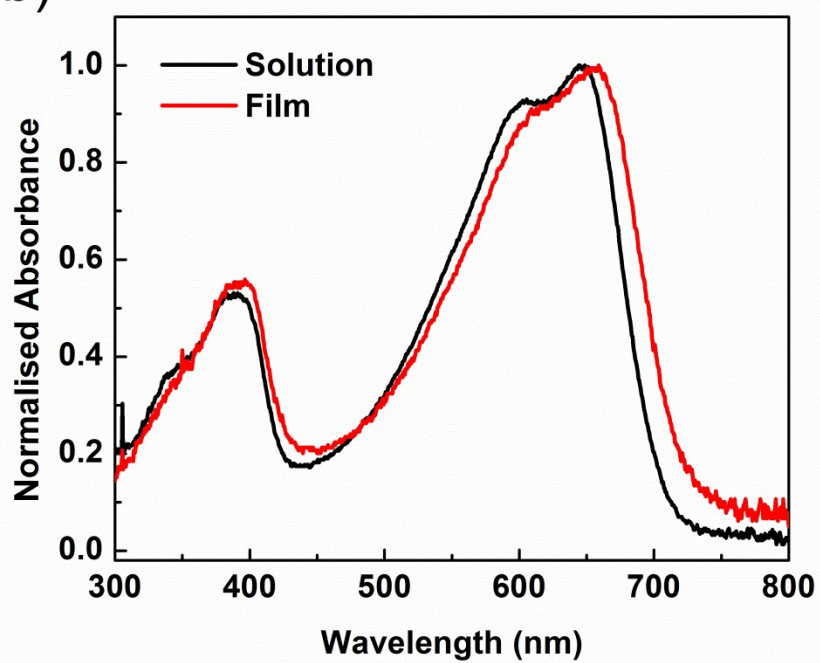


Fig. S12 (a,c) and (b,d) represents the AFM and TEM images of the P3:PC₇₁BM films casted from spin coating and slot-die coating technique, respectively.

(a)



(b)



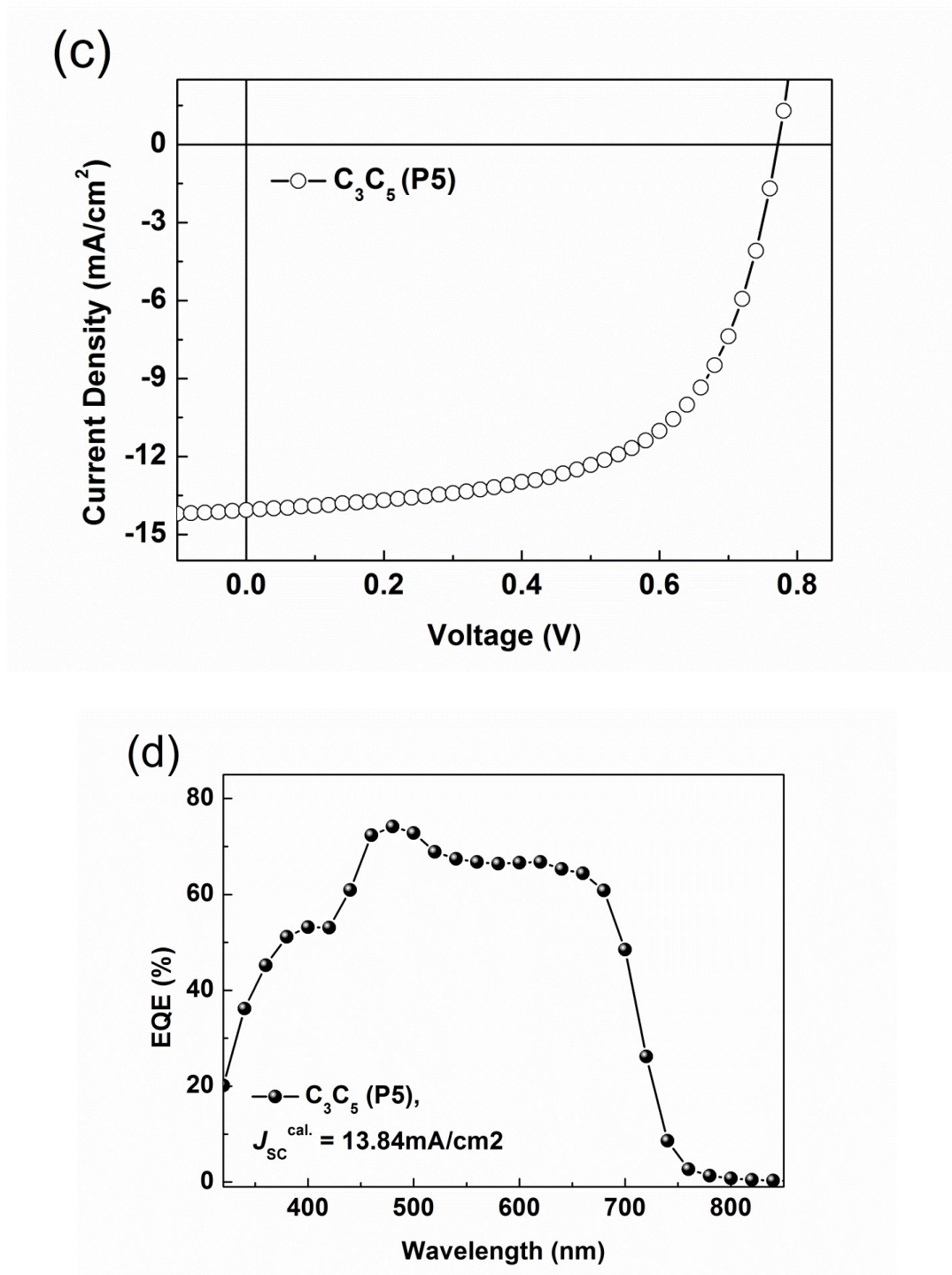


Fig. S13 (a) polymer structure of P5, (b) UV-visible spectra of P5 in solution and film state , (c) & (d) J-V and EQE curves of the P5 with device structure (ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al) processed with CB/DIO.

Table S1 Device characteristics of P3:PC₇₁BM PSCs with different D:A blend ratios (solvent: CB/DIO) under conventional device architecture ITO/PEDOT:PSS/Photo-active layer/Ca/Al.

Polymer	Weight Ratio	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
P3	1.0:1.0	0.81	15.34	71	8.82
	1.0:1.5	0.82	15.07	74	9.21
	1.0:2.0	0.81	14.55	74	8.77
	1.0:3.0	0.81	13.41	74	8.07

Table S2 Conventional PSCs results of P3:PC₇₁BM PSCs with variable film thickness.

Polymer	Thickness	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
P3	~180 nm	0.81	14.91	71	8.62
	~135 nm	0.81	15.10	73	8.94
	~100 nm	0.82	15.07	74	9.21
	~80 nm	0.82	14.38	74	8.73

Table S3 Photovoltaic properties of P3:PC₇₁BM (1.0:1.5, w/w) PSCs with non-halogenated solvent conditions under conventional device architecture (ITO/PEDOT:PSS/ Photo-active layer/Ca/Al).

Solvent	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]
<i>o</i> -Xylene	0.89	12.11	53	5.73
TMB	0.86	12.05	56	5.80

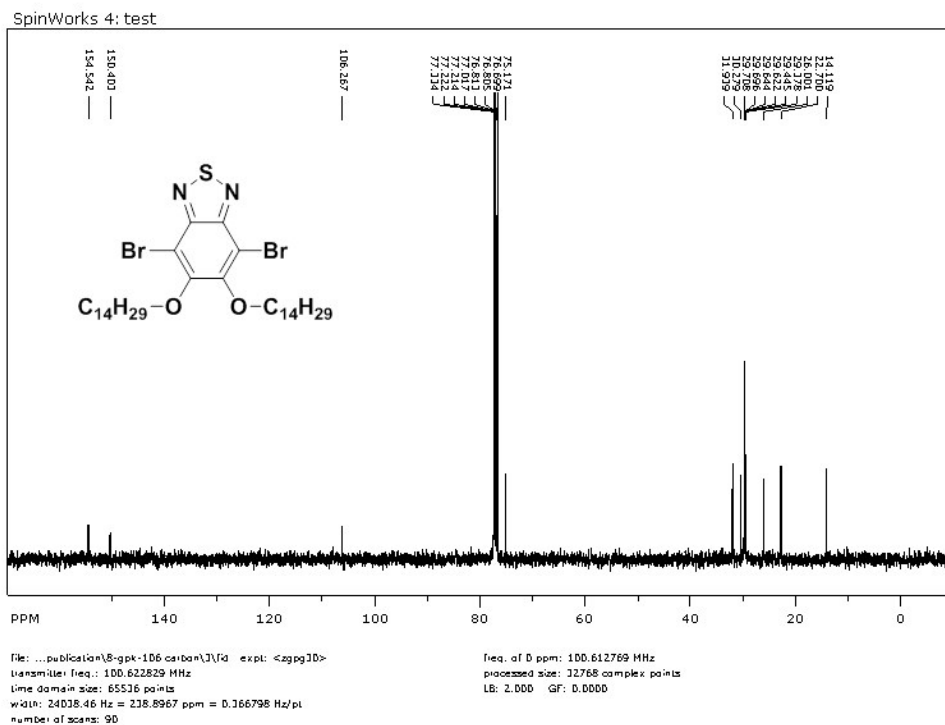
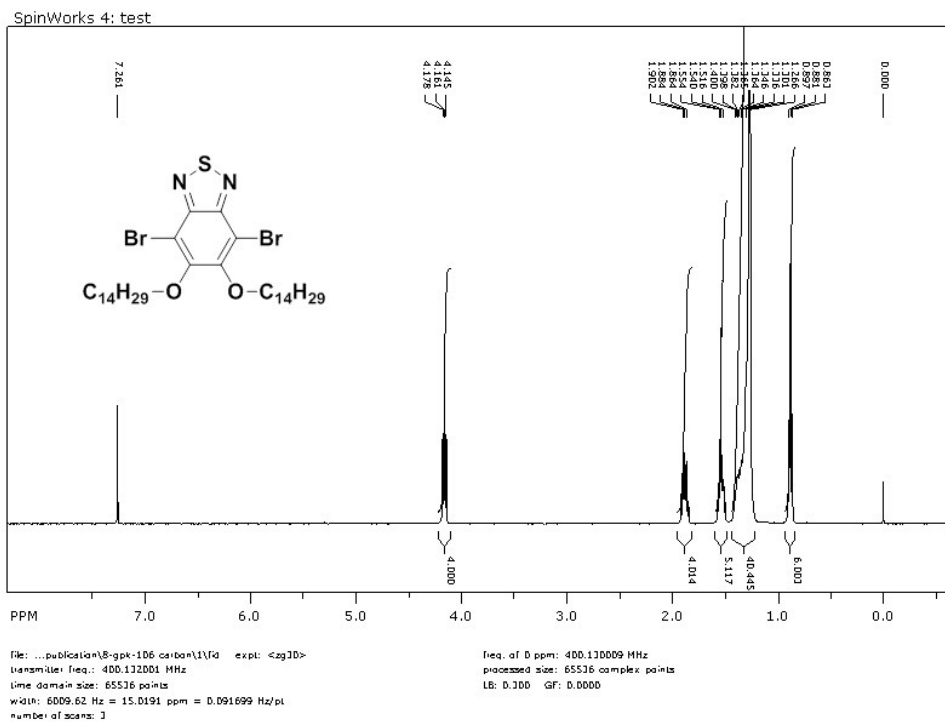
Table S4 Conventional device results of P3 in optimized large scale synthesis using thermal reactions.

Polymer	<i>d</i> [nm]	<i>V</i> _{oc} [V]	<i>J</i> _{sc} [mA/cm ²]	<i>FF</i> [%]	PCE [%]
P3					
DCM fraction	~115	0.81	15.08	72	8.78
Mn=45.7kDa , PDI=4.0					
P3					
CF Fraction	~105	0.81	15.23	71	8.75
Mn=64.8kDa , PDI=3.5					

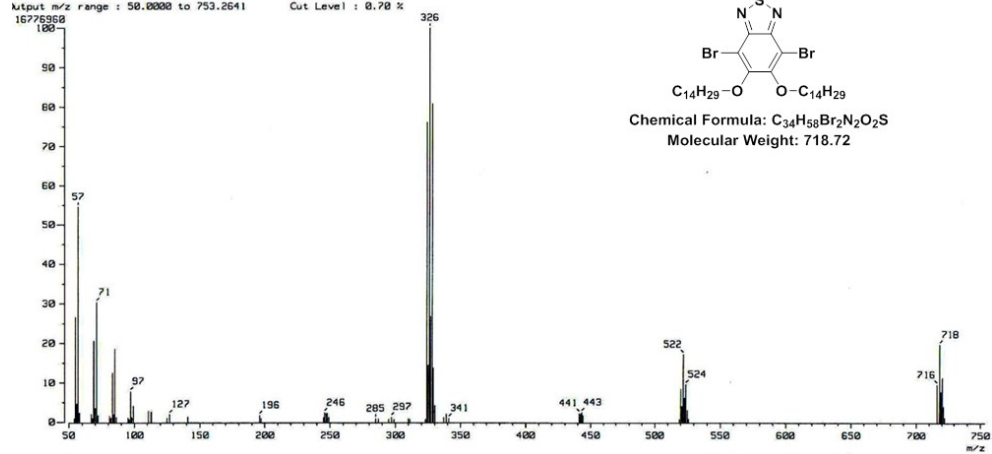
Table S5 Conventional device performance of PSCs based on P5:PC₇₁BM (1.0:1.5, w/w) dissolved in CB/DIO.

Polymer	Solvent	<i>d</i> [nm]	<i>V</i> _{oc} [V]	<i>J</i> _{sc} [mA/cm ²]	<i>FF</i> [%]	PCE [%]
P5	CB/DIO	~95	0.77	14.06	61	6.61

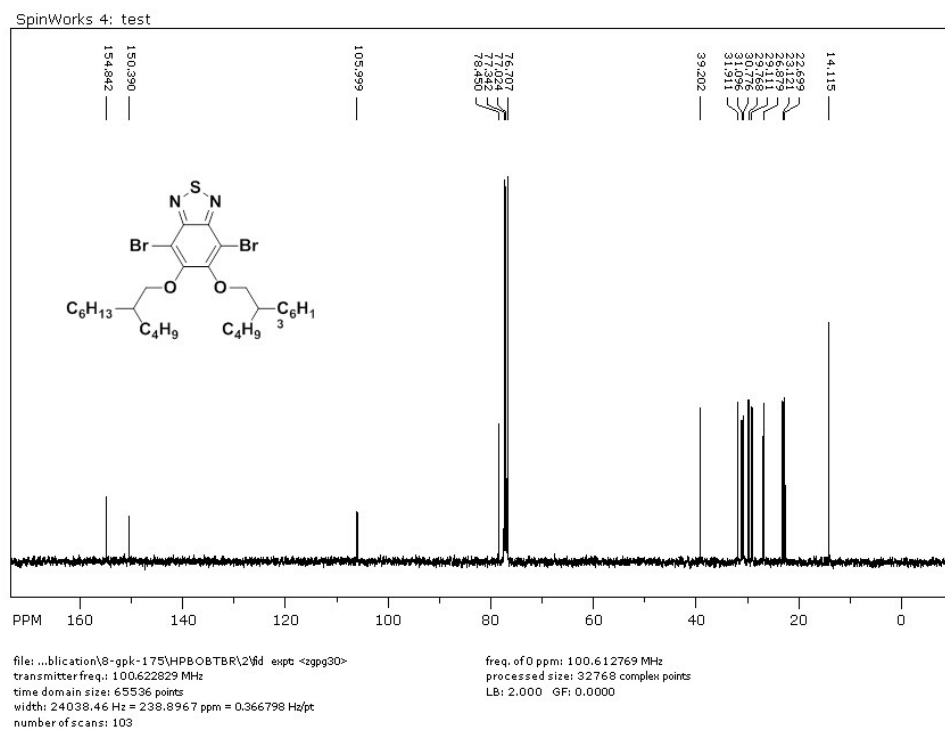
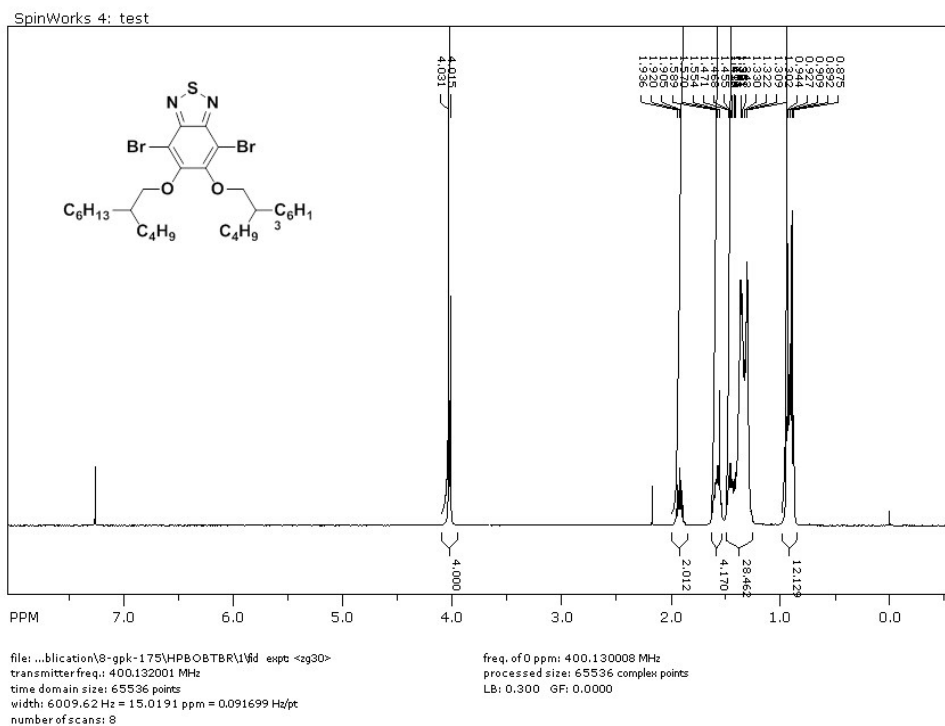
¹H NMR, ¹³C NMR (in CDCl₃) and Mass spectra of compound M1



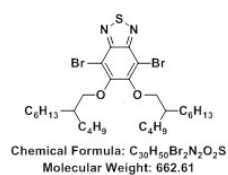
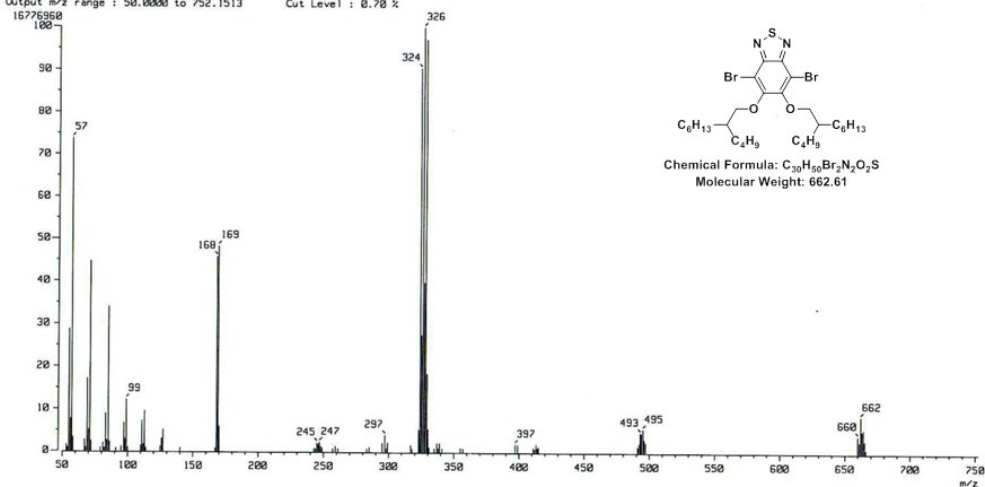
Mass Spectrum
 Date : 17-Feb-2016 15:06
 Sample: 8-6PK-186
 Ion Mode: EI+
 Spectrum Type: Normal Ion (MF-Linear)
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 Output m/z range: 50.0000 to 753.2641
 Cut Level: 0.70 %



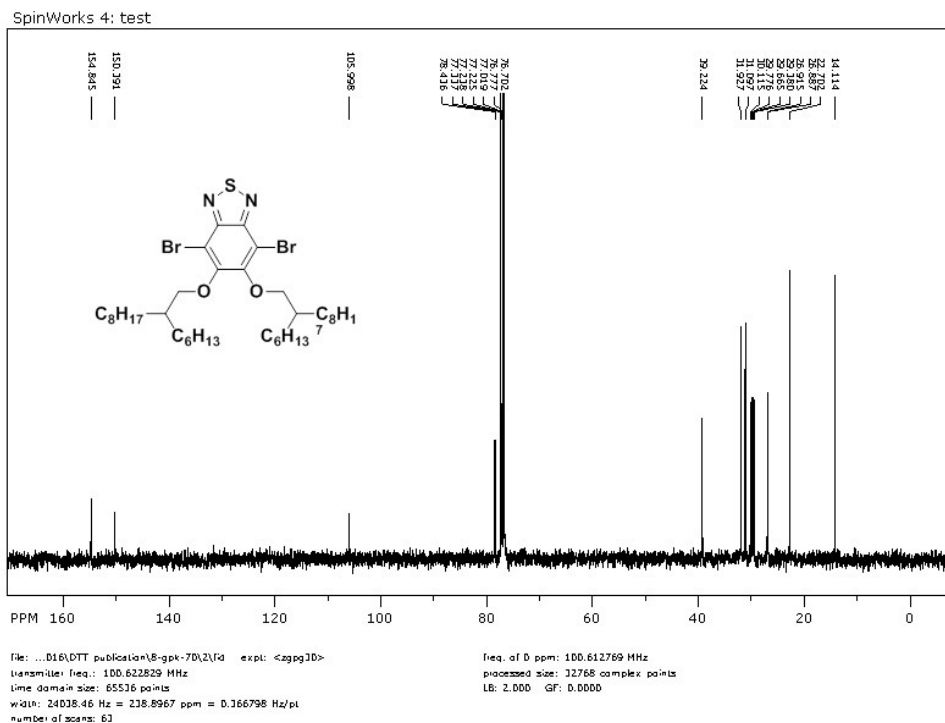
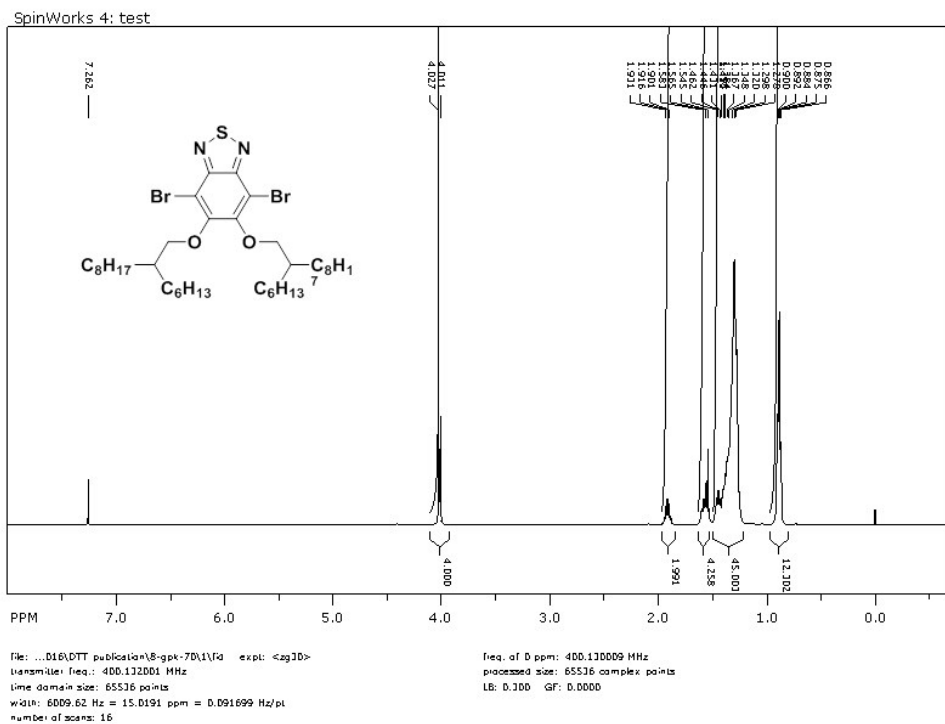
^1H NMR, ^{13}C NMR (in CDCl_3) and Mass spectra of compound M3



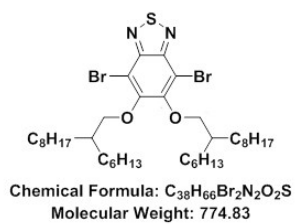
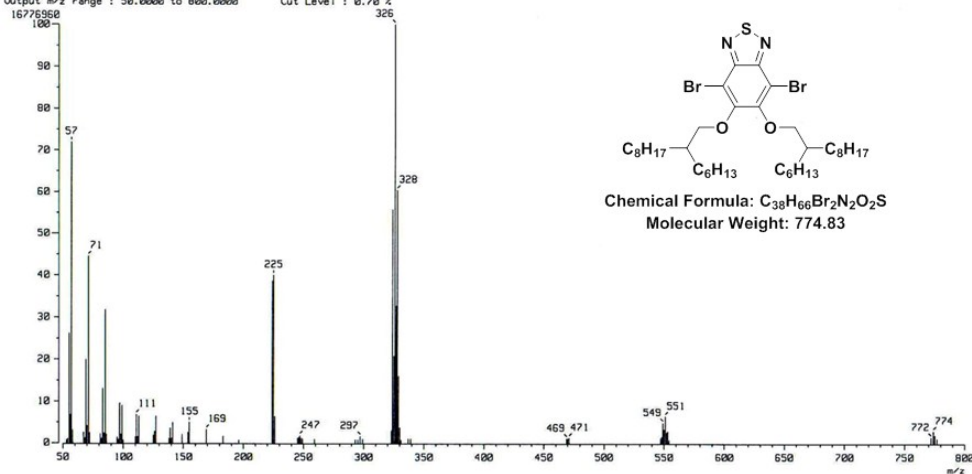
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 Sample: B-GPK-175
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 Spectrum Type : Normal Ion (MF-Linear)
 RT : 1.48 min Scan# : 43
 BP : m/z 325.0000 Int. : 1599.98
 Output m/z range : 50.0000 to 752.1513 Cut Level : 0.70 %



¹H NMR, ¹³C NMR (in CDCl₃) and Mass spectra of compound M4

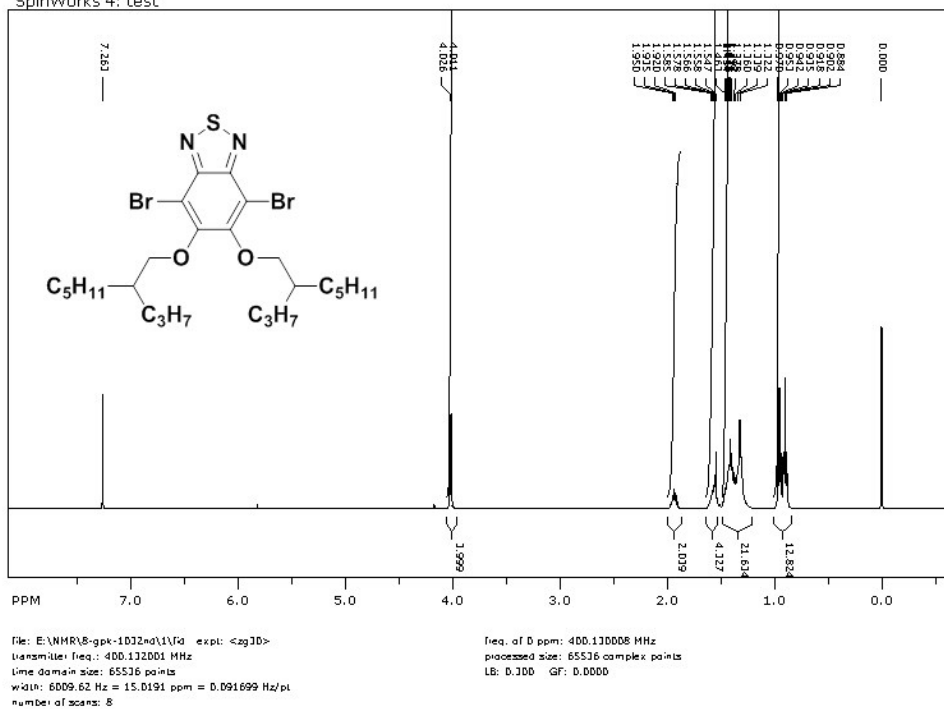


[Mass Spectrum]
 Date : 2-17-007 Date : 17-Feb-2016 15:16
 Sample: 8-6PK-70
 Note : -
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 Spectrum Type : Normal Ion (MF-Linear)
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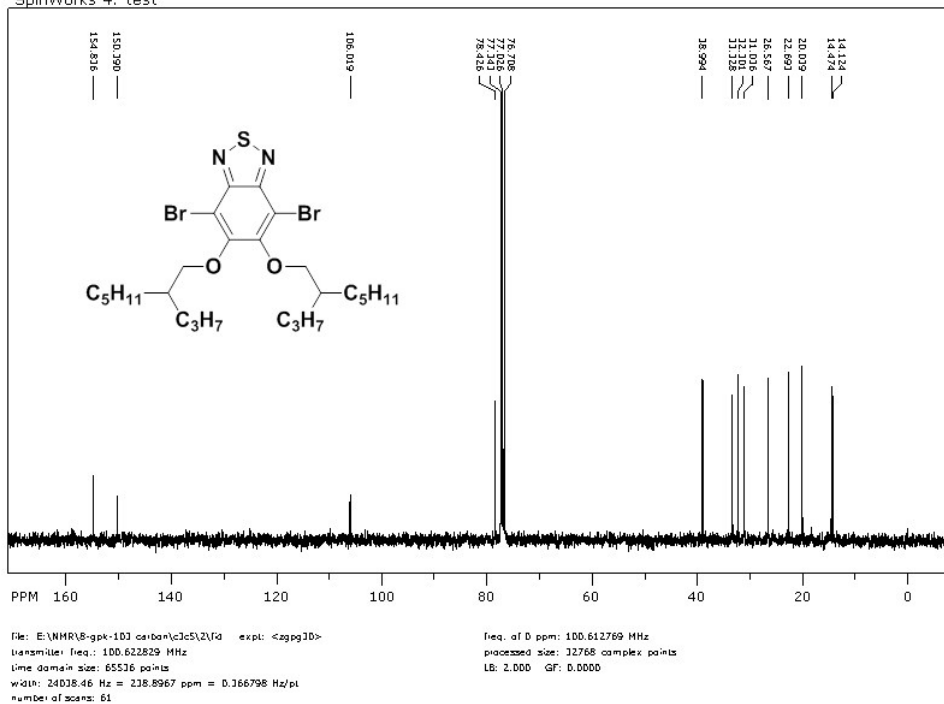


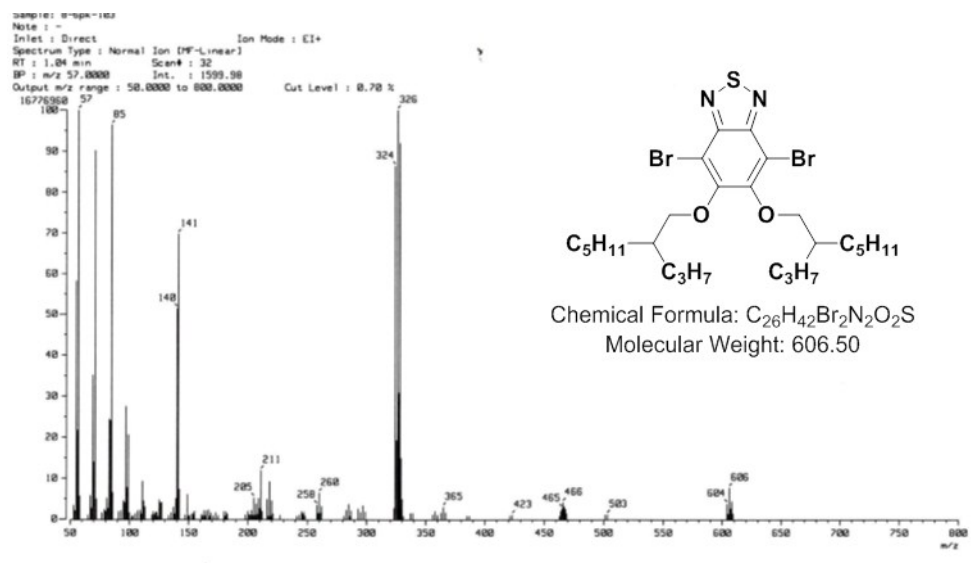
¹H NMR, ¹³C NMR (in CDCl₃) and Mass spectra of compound M6

SpinWorks 4: test

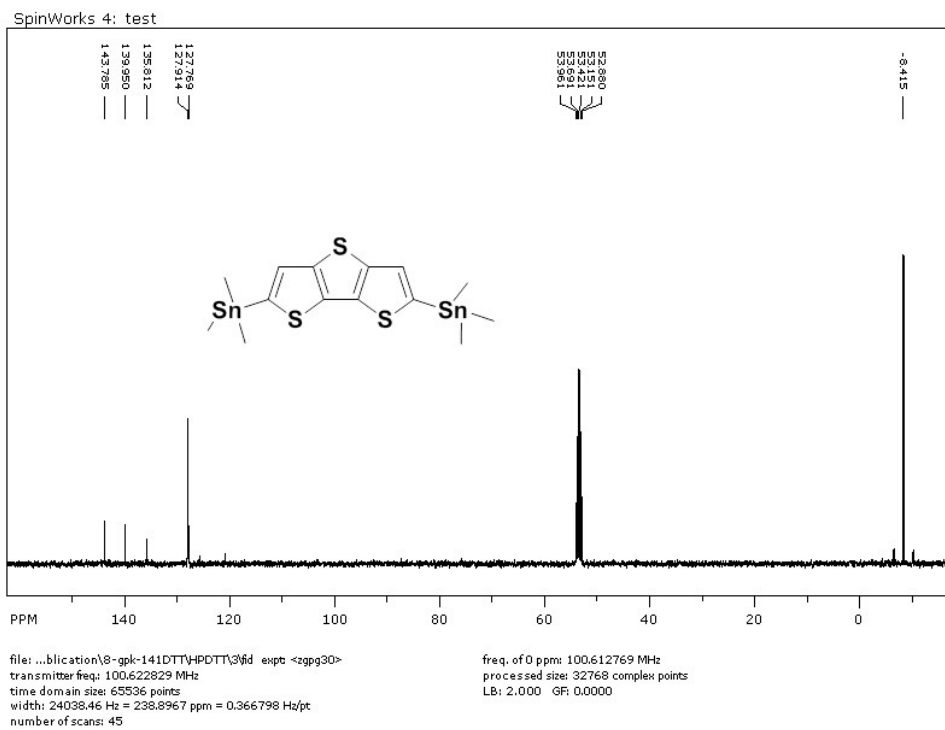
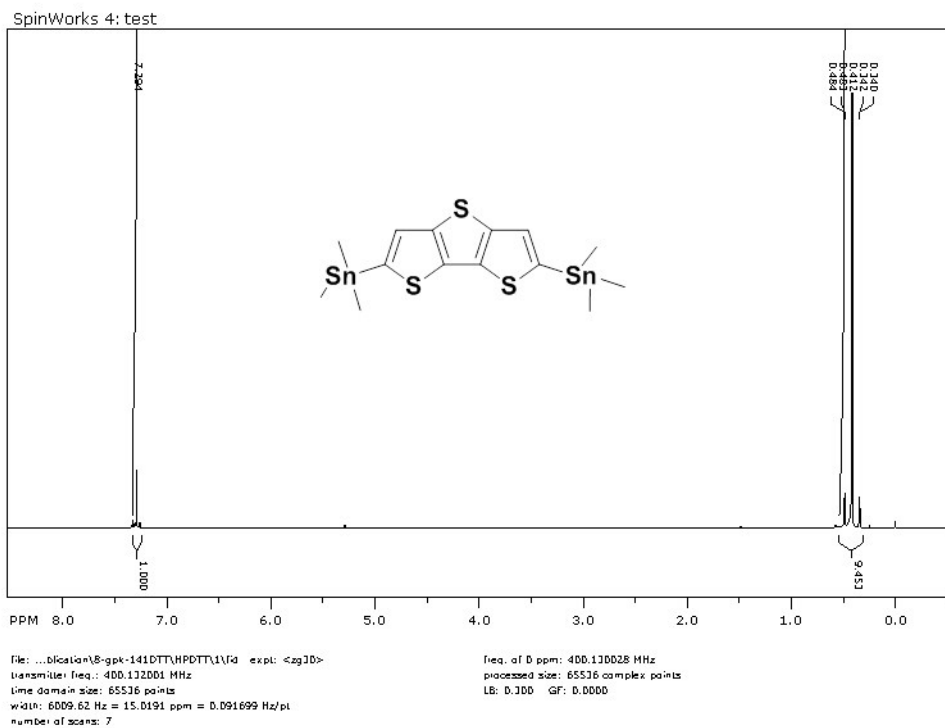


SpinWorks 4: test





¹H NMR, ¹³C NMR (in CDCl₃) and Mass spectra of compound M5



Note : -
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 Spectrum Type : Normal Ion [MF-Linear]
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