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Supporting Information

A New Copolymer Based on D-π-A or D-A-π Repeat Unit for Polymer Solar Cells Employing Non-halogenated Solvents

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Content

1. General material and method

2. Procedure for the preparation of the compounds and polymers

3. Copies of ^{1}H NMR and ^{13}C NMR spectra

4. Additional figures and tables

6. References

Material and method

All reagents were commercially available and were used as received without further purification unless otherwise stated. Anhydrous *N,N*-dimethylformamide (DMF) and toluene were distilled from CaH_2 and Na/benzophenone, respectively. [6,6]-phenyl C_{71} butyric acid methyl ether ($PC_{71}BM$) was purchased from American Dye Source Inc. Tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], 1,2-dichlorobenzene (*o*-DCB, 99+% purity), chlorobenzene (CB, 99+% purity), acetonitrile (99.8%, purity) and 1,8-diiodoctane (DIO) were purchased from Sigma-Aldrich. Anisole (AO, 99+% purity) and diphenyl ether (DPE, 98+% purity) were bought from Tokyo Chemical Industry and Alfa Aesar, respectively. 2,6-Bis(trimethyltin)-4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b'*]dithiophene(BDTT-Sn) was purchased from SunaTech Inc. 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole (ffBT) and 5,6-difluoro-4,7-dibromobenzo[2,1,3]thiadiazole (DT-ffBT) was acquired from Derthon Optoelectronic Materials Science Technology Co LTD.

^{1}H and ^{13}C nuclear magnetic resonance (NMR): The measurements were recorded on a Bruker AV-400 MHz spectrometer in *d*-chloroform with TMS as the internal standard. Chemical shifts were expressed in parts per million (ppm).

Thermogravimetric analysis (TGA): TGA was carried out on a METTLER TOLEDO TGA/DSC1/1100 LF apparatus operated at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

High temperature gel permeation chromatography (GPC): Molecular weight (M_n) and polydispersity index (PDI) were determined with Gel permeation chromatography (GPC) on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-Trichlorobenzene (TCB) as eluent. Samples were dissolved in 1,2,4-Trichlorobenzene (TCB) at 140 °C with shaking for 1 h for complete dissolution. The calibration method used to generate the reported data was the classical polystyrene method using polystyrene narrow standards.

UV-Vis: UV-vis absorption spectra were recorded on a PerkinElmer Lambda 750 spectrophotometer at room temperature. The solution absorption spectra were performed on *o*-DCB solution with sample concentration of 0.05 mg mL^{-1}. The film absorption spectra were collected from films spin-casted from 5 mg mL^{-1} *o*-DCB solutions.

Cyclic voltammetry (CV) measurements: The electrochemical properties of the polymer films were performed on a CHI600D electrochemical instrument in anhydrous acetonitrile at a scan rate 50 mV s^{-1} under nitrogen. Tetrakis-(n-butyl)ammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) was employed as the electrolyte. A glassy carbon electrode, a $Ag/AgNO_3$ electrode, and a Pt wire were used as the working electrode, reference and counter electrode, respectively. Polymer films were drop-casted onto the glassy carbon working electrode from a 5 mg ml^{-1} CB solution. The potential of $Ag/AgNO_3$ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The electrochemical onsets were determined at the position where the current starts to differ from the baseline. The HOMO energy levels were calculated from the equation: HOMO (eV) =-(E^{onset}_{ox} +4.8) eV, while the LUMO energy levels were obtained by combining the HOMO and optical band gap values of the films.

Space Charge Limited Current (SCLC): The hole mobilities were measured by the SCLC method on an hole-only device with a structure of ITO/PEDOT: PSS/active layer/Au/Al and electron-only device with a structure of ITO/ZnO/active layer/LiF/Al. SCLC device fabrication was almost the same as OPV device fabrication, and the film thickness was about 100 nm. The SCLC mobility was estimated following the Mott-Gurney square law, $\ln(I/V)^2=0.89\beta(V/L)^{1/2}+\ln(9\mu\varepsilon_0\varepsilon S/(8L^3))$, where I is the current, V is the applied voltage, β is the field activation factor, L is the thickness of polymer film, μ is the mobility, ε_0 is the permittivity of free space, ε is the relative permittivity, and S is the area of polymer film. The measurement of hole mobilities was conducted in the dark on a computer-controlled Keithley 2400 source-measure unit.

Transmission electron microscopy (TEM): The TEM images were acquired with a Tecnai G2 F20 high resolution transmission electron microscope operated at an acceleration voltage of 200 KV.

Grazing incidence wide angle X-ray scattering (GIWAXS): 2D GIWAXS patterns were obtained at 1W2A at Beijing Synchrotron Radiation Facility (BSRF) (λ=0.69 Å). Samples for GIWAXS were all prepared on top of Si (100) substrates.

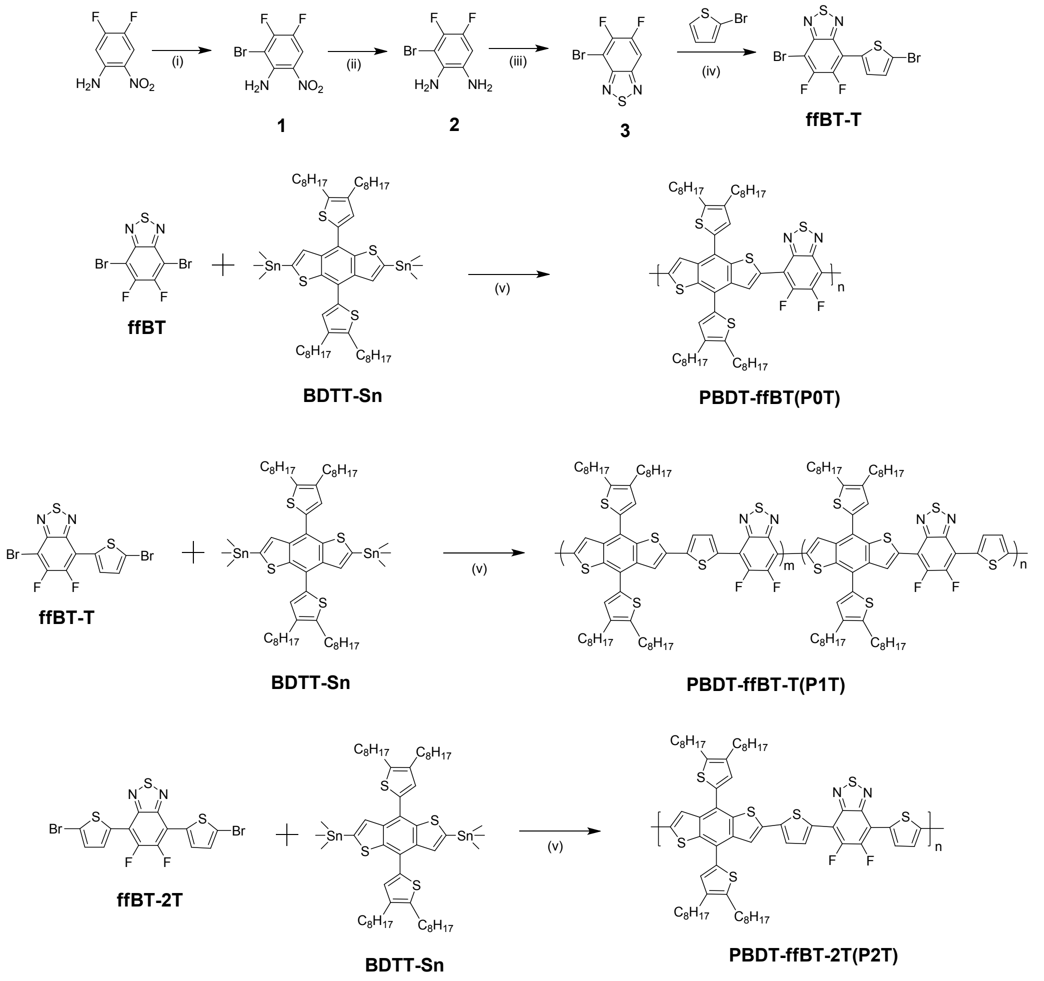
Film thickness: Film thickness of each thin film was measured by the profiler (D-100 Stylus Profilometer, KLA Tencor).

Solubility test by UV-Vis: The solutions with different concentrations of 0.05 mg ml^{-1}, 0.1 mg ml^{-1}, 0.2 mg ml^{-1}, 0.4 mg ml^{-1} and 0.5 mg ml^{-1} were firstly prepared. The standard curves are obtained by fitting the relationship between absorption strength at fixed wavelength and the concentration based on the Lambert beer's law. The concentrated solution was filtered to remove the insoluble polymeric particles. Then, the filtered solution was diluted to a low concentration to fulfill the requirement of Uv-Vis measurement. The absorption strength of the concentrated solutions was calculated by multiplying by dilution factors. If the calculated value of the absorption strength located on the standard curve, it is indicated that the polymer is completely dissolved in the solution. On the other hand, the polymer is not completely dissolved.

Fabrication of polymer solar cells: PSCs were fabricated as a conventional device architecture of ITO/PEDOT:PSS (30nm)/active layer/LiF (1 nm)/Al. ITO-coated glass (obtained from Lumtec, 7 Ωsq^{-1}) was cleaned with detergent, deionized water, isopropyl alcohol and acetone. After complete drying, the ITO-coated glass was treated with UV-ozone for 20 min. PEDOT:PSS was spin coated onto the ITO with 30 nm in thickness, and then the PEDOT:PSS film was annealed at 150 °C for 15 min in air. For P0T:$PC_{71}BM$ and P1T: $PC_{71}BM$ devices, the active layers were spin-coated from chlorobenzene and anisole (with polymer concentration of 10 mg

mL^{-1}) added with or without additive. Noticeably, P0T:$PC_{71}BM$ active layer was processed from hot AO solution at 120 ^{o}C. For P2T: $PC_{71}BM$ device, the active layers were spin-coated from *o*-DCB solution (with polymer concentration of 8mg ml^{-1}) at 150 ^{o}C. While for the non-fullerene and ternary device, the active layers were spin-coated from anisole solution with/without DPE as additive (with polymer concentration of 10 mg mL^{-1}). After the active layer deposited onto the PEDOT:PSS, LiF (8 nm in thickness) was thermally evaporated on its top, and then Al (100 nm) was thermally deposited on the LiF layer under high vacuum (<10^{-4} Pa). The mask shadow area was 0.09 cm^2. The *J–V* characteristics of PSCs were measured in nitrogen atmosphere employing a Keithley-2400 source meter and a solar simulator (SAN-EI, XES-70S1, San-Ei. Electric Co. Ltd., Osaka, Japan) at AM 1.5 G illumination of 100 mW cm^{-2} with a standard silicon solar cell as a reference to calibrate the light intensity. The EQE spectra of devices were examined using chopped monochromatic light from a xenon lamp under ambient conditions. A standard silicon solar cell was used as a reference to determine the light intensity at each wavelength.

Synthesis



Scheme S1. The synthetic routes of **P0T**, **P1T** and **P2T**. Reagents and conditions: (i) Br_2, CH_3COOH, 50 ^{o}C; (ii) $SnCl_2$, EA/EtOH, 75 ^{o}C; (iii) $SOCl_2$, $Et_3N/CHCl_3$, Reflux; (iv) $Pd(TFA)_2$, Ag_2O, DMSO, 80 ^{o}C; (v) $Pd_2(dba)_3/P(o\text{-}tol)_3$, toluene/DMF, reflux for 12~48 h.

2-Bromo-3,4-difluoro-6-nitroaniline(1)

To a solution of 4,5-difluoro-2-nitroaniline (8.7 g, 50 mmol) in acetic acid (60 mL) was added bromine (5.5 ml, 2 equiv) dropwise at 50 °C. The resulting mixture was kept at 50 °C for 2.5 hours. Subsequently, the reaction was cooled down to room temperature, and the reaction mixture was slowly poured into ice water (200 mL). The resulting precipitate was collected *via* filtration and washed with H_2O sufficiently. Then the raw product was dried to give compound 1 (10.5 g, 83% yield) as a yellow solid. The residue was used for the next step without further purification.

3-Bromo-4,5-difluorobenzene-1,2-diamine(2)

Compound 1 (3.8 g, 15 mmol) and $SnCl_2{\cdot}2H_2O$ (17 g, 75 mmol) were dissolved in 40 mL ethyl acetate and 20 mL ethanol in a 100 mL round-bottom flask. The solution was heated at 75 °C for 3 h. Then, the reactant was cooled down to room temperature, and poured into 100 mL water. The pH of the mixture was adjust to 5 by adding aqueous saturated solution of $NaHCO_3$. The residue was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$. After removing the solvent under vacuum, the crude product was achieved (2.2 g, 64% yield) without further purification.

4-Bromo-5,6-difluorobenzo[1,2,5]thiadiazole(3)

Compound **2** (4.3 g, 19 mmol) was dissolved in 150 mL $CHC1_3$ and 10.5 mL triethylamine in a 500 mL three-necked round bottom flask. After stirring for 15 min at room temperature, thionyl chloride ($SOCl_2$, 4.5 g, 2 equiv) was added dropwise. Following, the mixture was heated to reflux for 5 h. After cooling down to room temperature, the reactant was extracted with CH_2Cl_2. The organic layer was washed with water and brine, and dried over $MgSO_4$. After removing the solvent under vacuum, the residue was purified with silica gel column chromatography (Petroleum ether) to give compound **3** as a white solid (2.8 g, 59% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 7.75 (dd, *J*= 9.1, 7.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 154.64 (d, *J*=18.6 Hz), 152.28 (dd, *J*=47.2, 19.1 Hz), 149.51 (m), 148.88 (d, *J*=11.7 Hz), 104.7 (d, *J*=20.1), 99.65 (d, *J*=24.3 Hz).

4-Bromo-7-(5-bromothiophen-2-yl)-5,6-difluorobenzo[1,2,5]thiadiazole (ffBT-T)[1]

To a 50 mL of sealed tube were added $Pd(TFA)_2$ (2.5 mol%, 22 mg), Ag_2O (1.24 g, 2.0 equiv) and 4-bromo-5,6-difluorobenzo[1,2,5]thiadiazole (3) (0.67 g, 1 equiv) under Ar, followed by DMSO (10 mL) with stirring. 2-bromothiophene (0.87 g, 2 equiv) were then added subsequently. The reaction mixture was stirred at 80 ^{o}C for 6h. Then, the reaction mixture was cooled down to room temperature, filtered and diluted with dichloromethane, washed with brine. The organic layer was dried over $MgSO_4$, filtered and concentrated. Then, the residue was purified with silica gel chromatography (Petroleum ether) to provide pure product as a yellow solid (0.51, 46% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, δ): 8.01(d, *J*=4.0 Hz, 1H), 7.21(d, *J*=4.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 153.2 (dd, *J*=255.4 Hz, 20.0 Hz), 150.8(d, *J* = 5.5 Hz), 149.9 (dd, *J*=261.8 Hz, 19.5 Hz), 148.4 (d, *J*=8.4 Hz), 135.8 (d, *J*=8.0 Hz), 131.8 (d, *J*=10.3 Hz), 130.6 (m), 118.3, 112.4 (d, *J*=11.9 Hz), 97.4 (d, *J*=23.5 Hz)

Synthesis of the polymers

General procedure for the synthesis of P0T, P1T and P2T, by the Stille Coupling: To a degassed solution of bis(trimethyltin) BDT monomer (BDTT-Sn) (0.177 mmol), and dibrominated ffBT monomer (or ffBT-T, ffBT-2T) (0.177 mmol) in anhydrous toluene (8 mL) and anhydrous DMF (1.6 mL), $Pd_2(dba)_3$ (3.2 mg) and $P(o\text{-}tol)_3$ (8.6 mg) were added. For P0T and P2T, the reactions were terminated by stirring the sealed flask for 48 h and 12 h, respectively, when precipitations separated from the solutions. Three batches of P1T were synthesized by stirring the reaction flask for 18, 32 and 48 hours, respectively. End-capping was carried out by sequentially adding 0.1 mL 2-(tributylstanny)thiophene and 0.2 mL 2-bromothiophene to the reaction mixture. After cooling down to room temperature, the reaction mixture was poured into 100 mL of methanol, and stirred for 3 h. Then, the precipitated product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform as solvents to remove low molecular weight fractions. For P0T and P1T, The chloroform fraction was concentrated and precipitated into 200 mL of methanol with vigorous stirring. The precipitate was collected by filtration and dried in vacuum to yield a dark solid as the product. While for P2T, the residual fraction was collected and dried in vacuum to get a dark solid as the product. The yield and characterization of polymers were as follow:

Poly{(4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2-b:4,5-b']-dithiophen-2,6-diyl)-alt-(5,6-difluorobenzo[2,1,3]thiadiazole-4,7-diyl)} (P0T): (M_n/PDI=29 KDa/2.6, yield 55%). ^{1}H-NMR (400MHz, $CDCl_2CDCl_2$, δ): 7.47 (4H, br), 2.83~3.04 (8H, br), 1.41~1.94 (48H, br), 0.92 (12H, br).

Poly{(4,8-di(2,3-dioctylthiophen-5-yl)-benzo[1,2-b:4,5-b']-dithiophen-2,6-diyl)-alt-((7-thiophen-2-yl)-5,6-difluorobenzo[1,2,5]thiadiazole-4,5-diyl)} (P1T): (M_n/PDI=39 KDa/2.5, yield 60%). ^{1}H-NMR (400MHz, $CDCl_2CDCl_2$, δ): 7.35~8.87 (6H, br), 2.81~3.01 (8H, br), 1.29~1.9 (48H, br), 0.97(12H, br)**.**

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-b:4,5-b']dithiophen-2,6-diyl)-alt-((4,7-di(thiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole)-5,5'-diyl)} (P2T): (M_n/PDI=34 KDa/4.0, yield 44%). ^{1}H-NMR (400MHz, $CDCl_2CDCl_2$, δ): 7.27~8.26 (8H, br), 2.67~2.87 (8H, br), 1.33~1.79 (48H, br), 0.89 (12H, br).

^{1}H NMR and ^{13}C NMR spectra

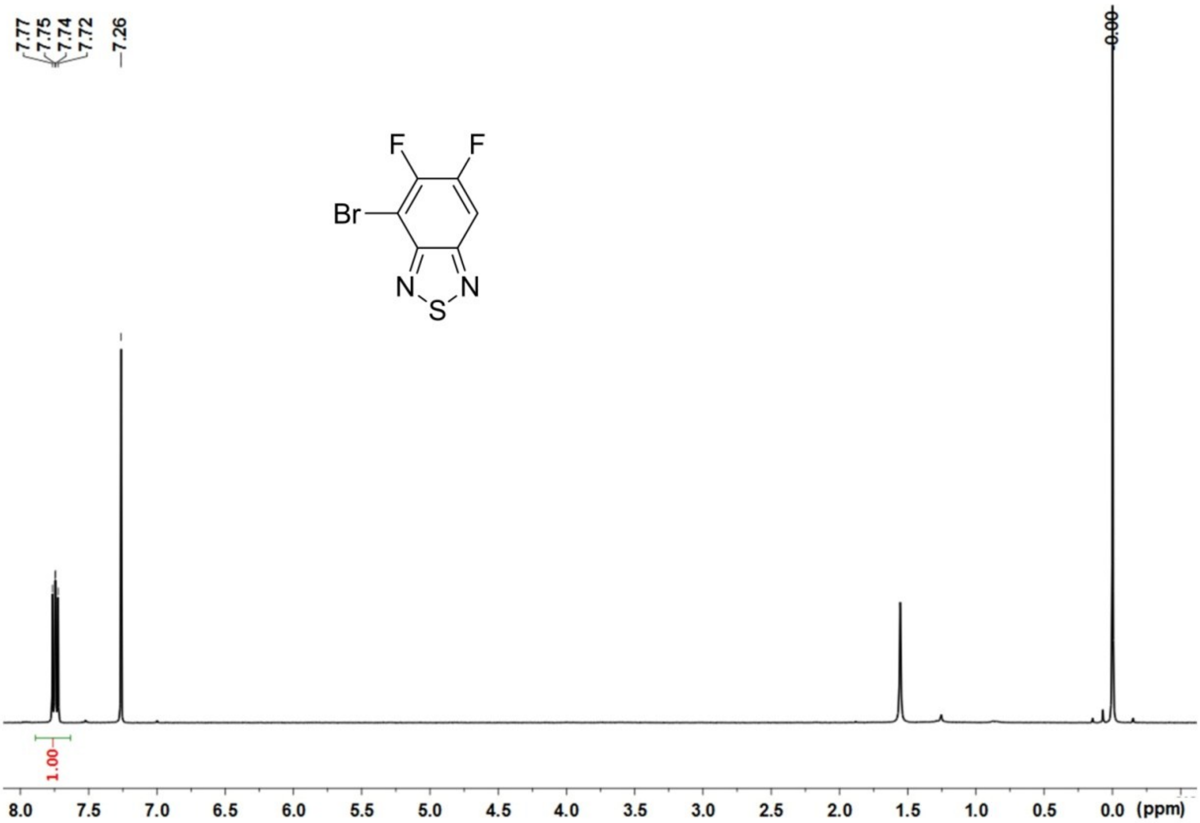


Figure S1. ^{1}H NMR spectrum of compound 3.

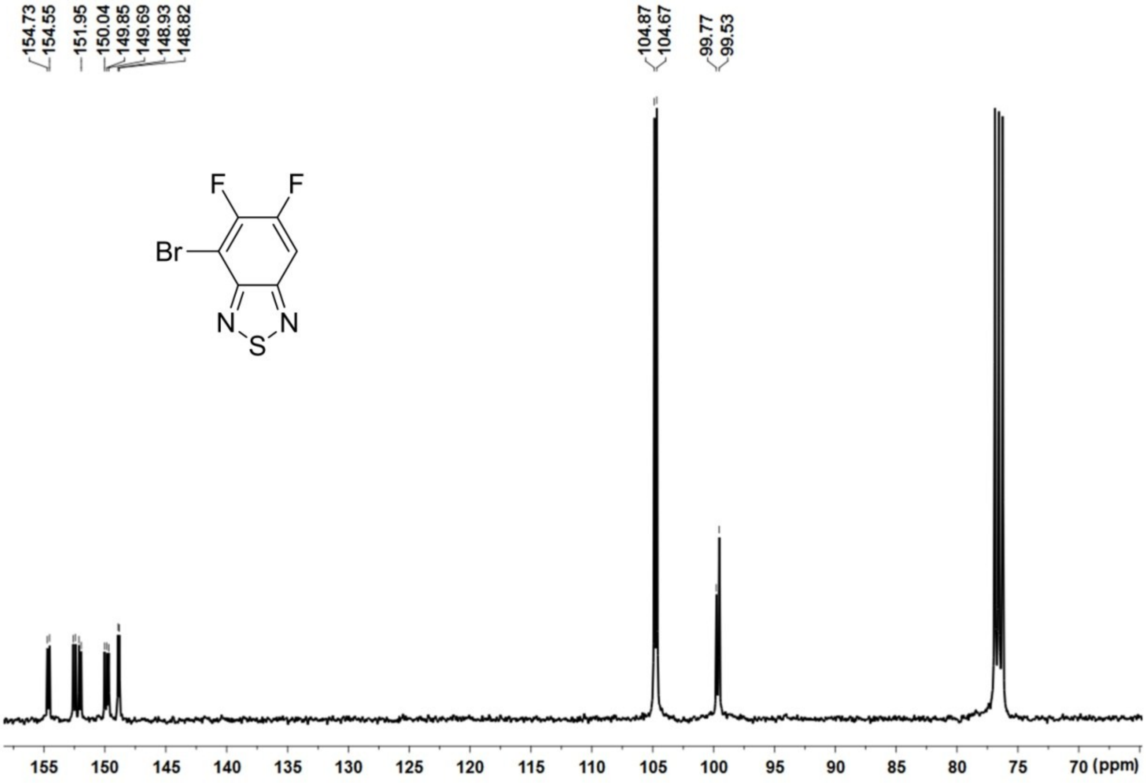


Figure S2. ^{13}C NMR spectrum of compound 3.

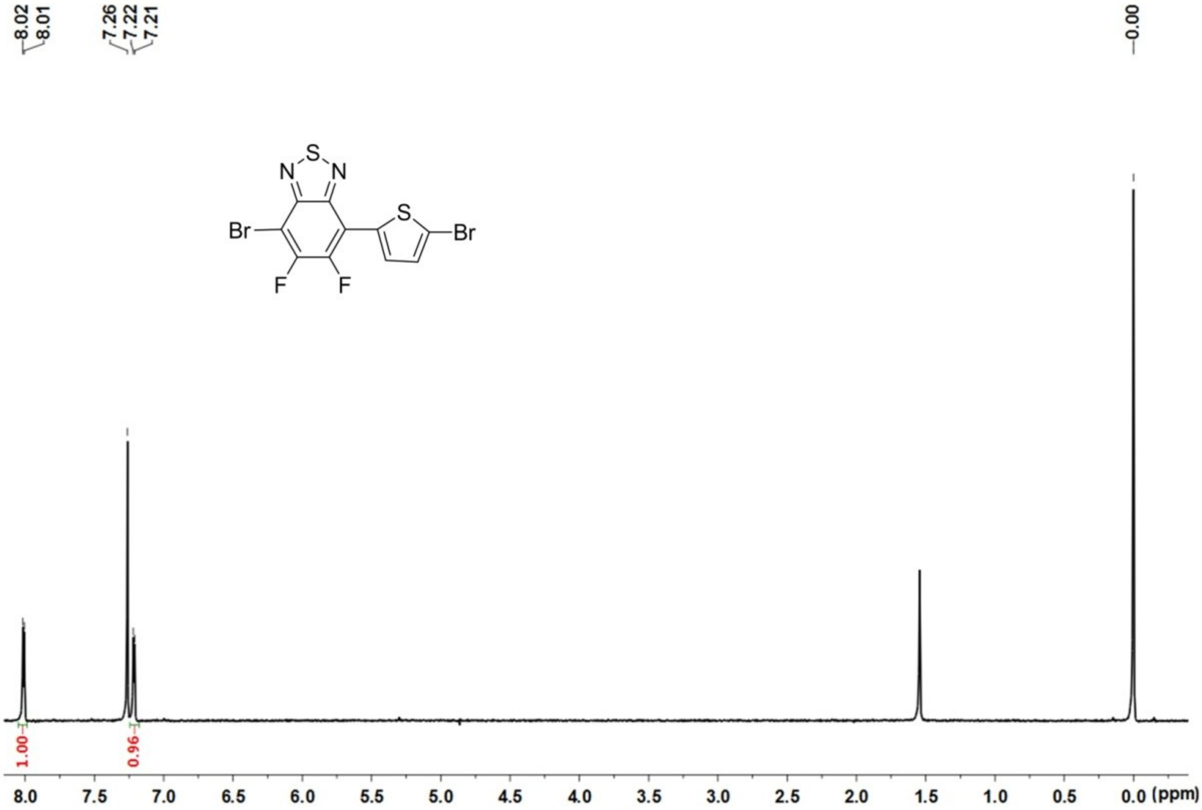


Figure S3. ^{1}H NMR spectrum of compound 4.

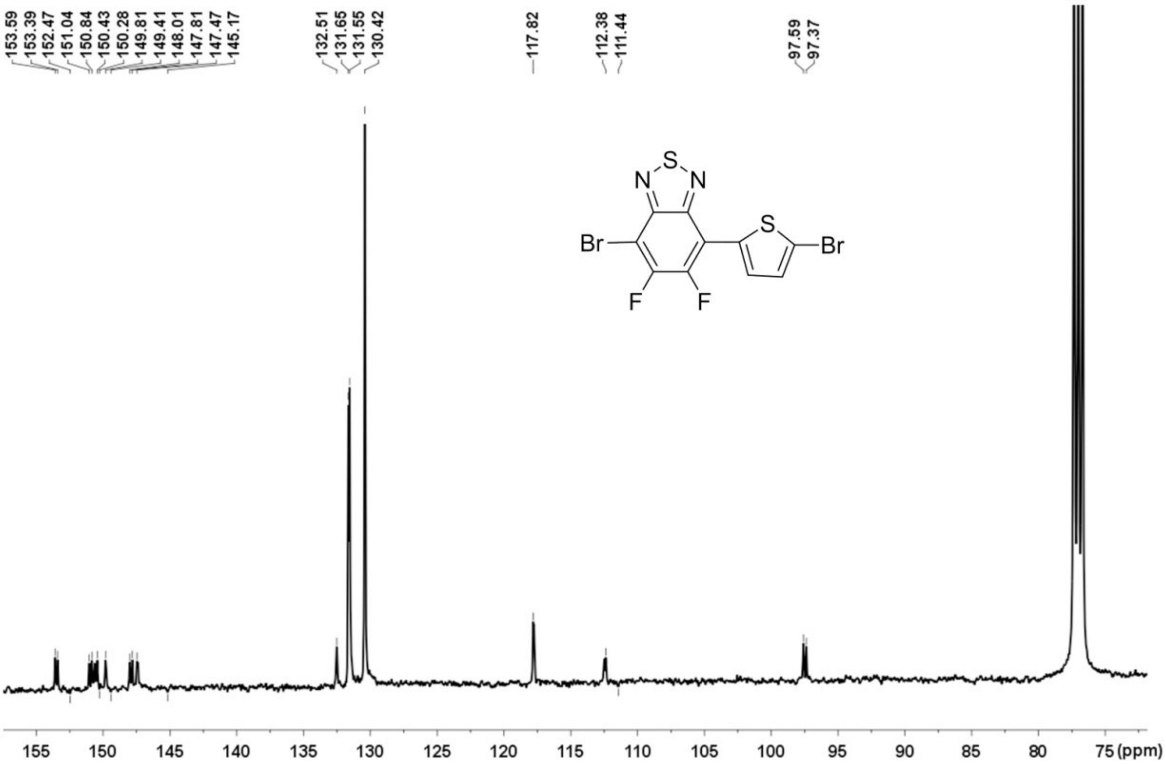


Figure S4. ^{13}C NMR spectrum of compound 4.

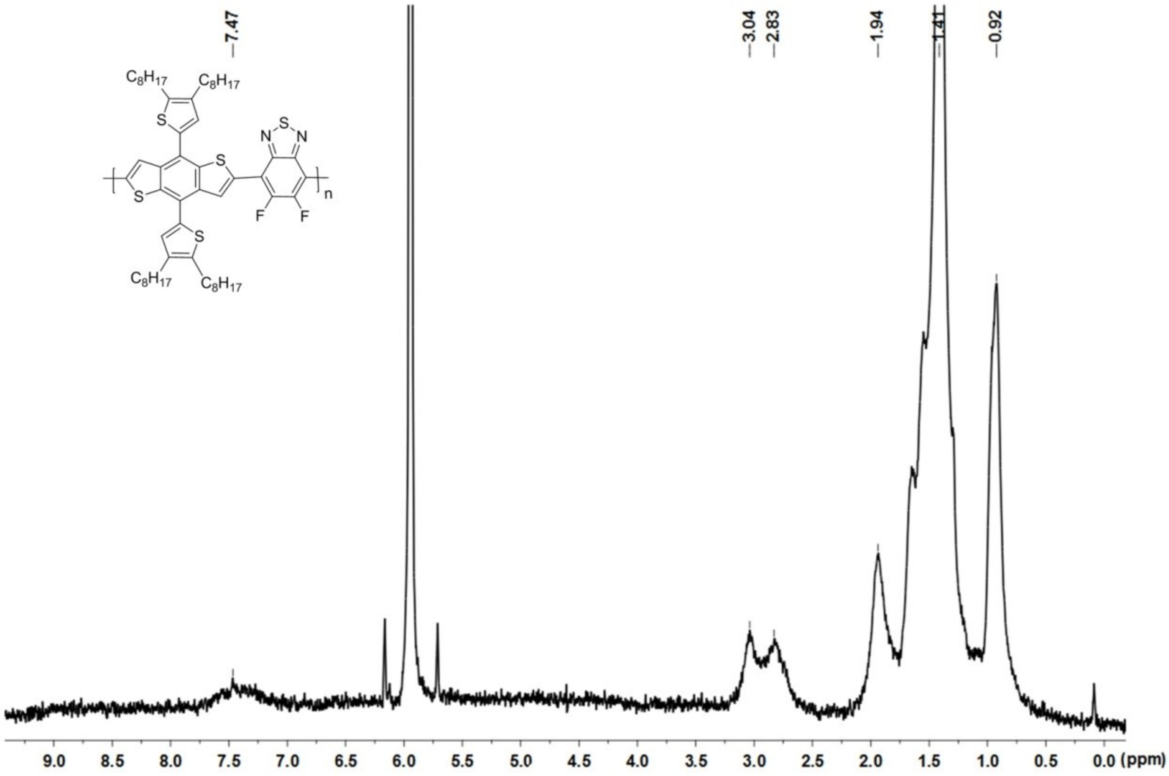


Figure S5. ^{1}H NMR spectrum of **P0T**.

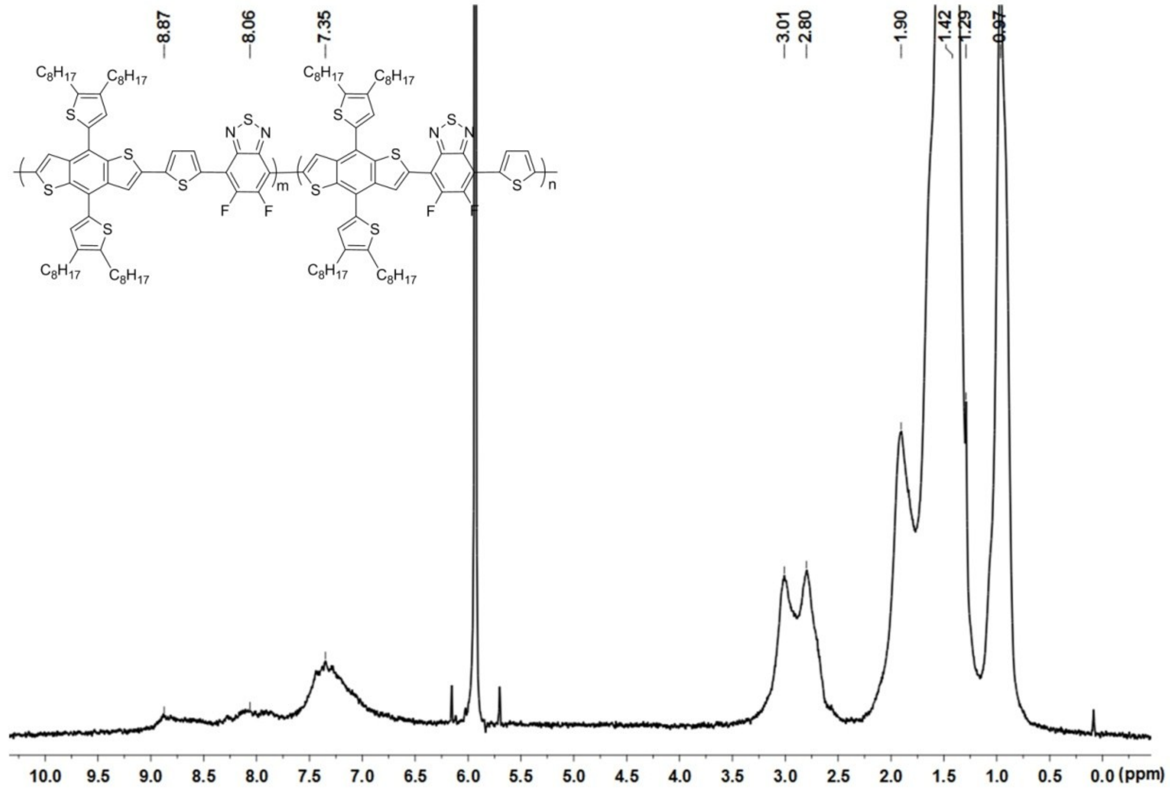


Figure S6. ^{1}H NMR spectrum of **P1T**.

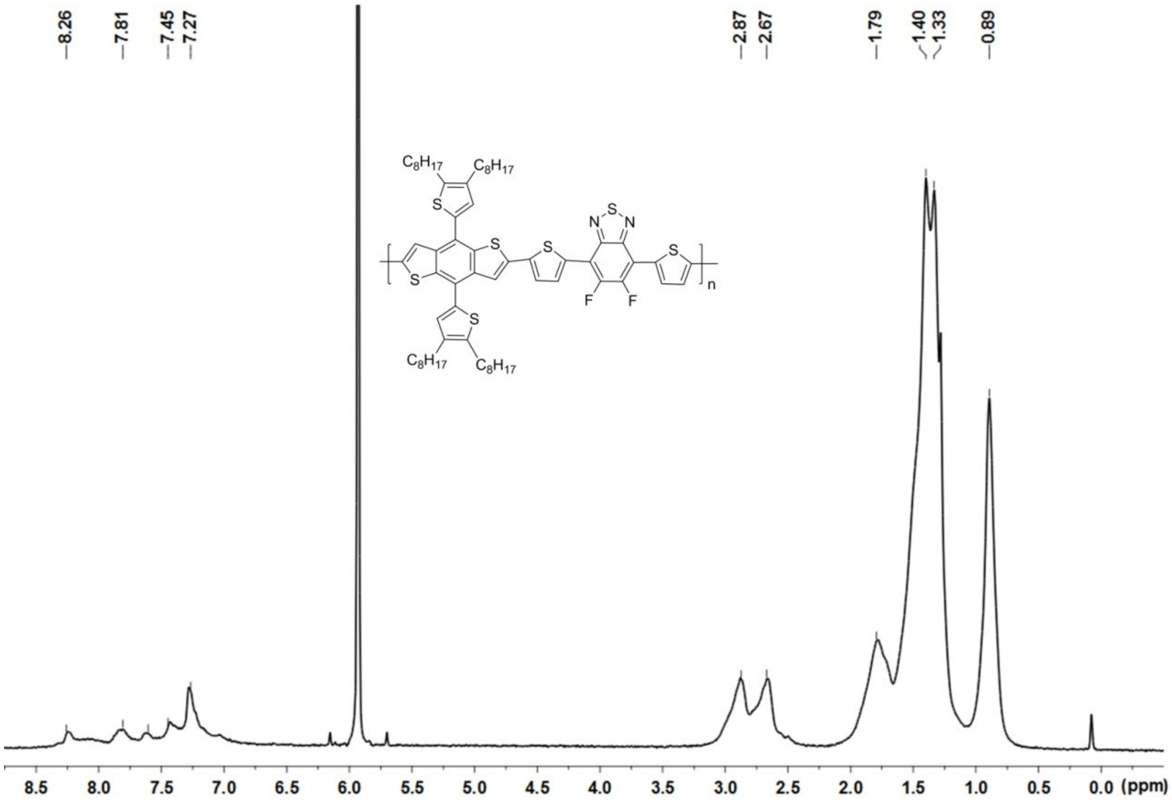


Figure S7. ^{1}H NMR spectrum of **P2T**.

Additional figures and tables

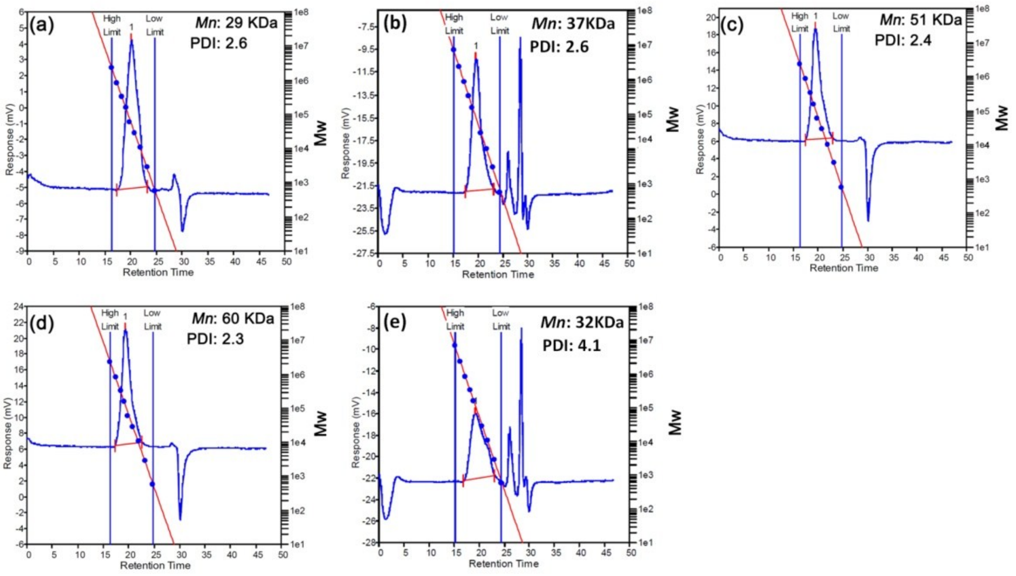


Figure S8. GPC traces of the polymers measured with 1,3,5-trichlorobenzene as eluent at 140 ^{o}C (a for P0T; b, c, d for P1T; e for P2T, respectively).

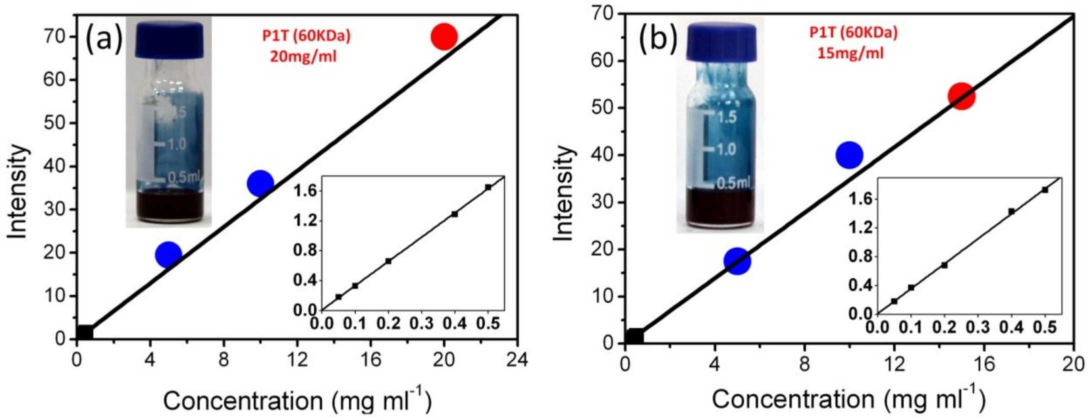


Figure S9. The Solubility of P1T with a higher M_n of 60 KDa. (a in *o*-DCB solution; b in anisole solution).

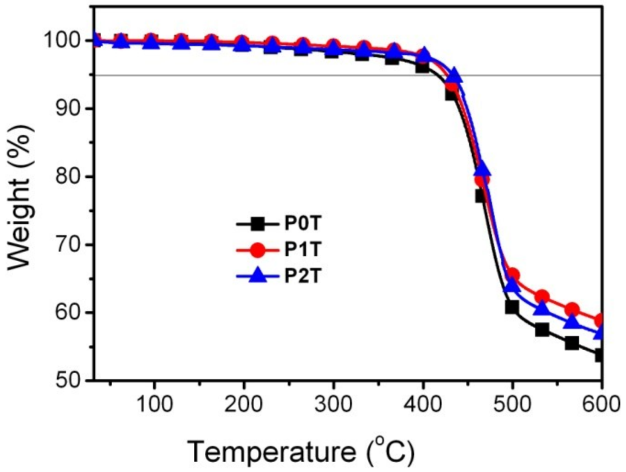


Figure S10. Thermo gravimetric analysis (TGA) curves of **P0T**, **P1T** and **P2T**.

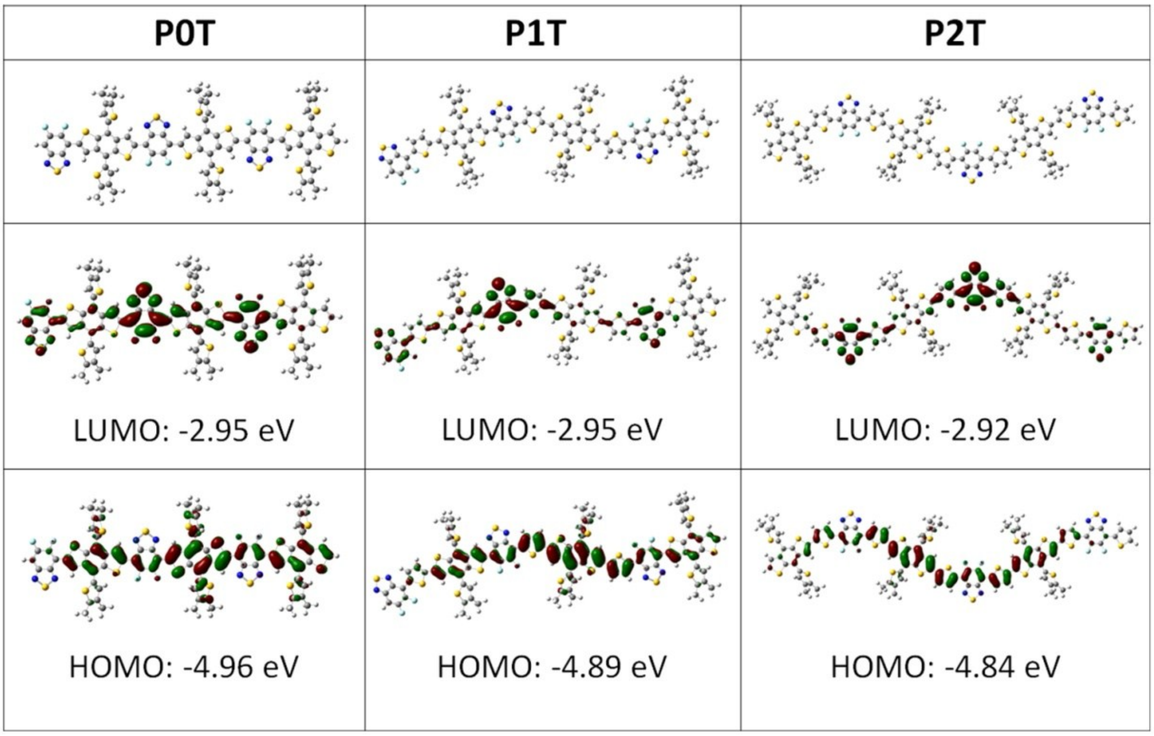


Figure S11. B3LYP/6-31G** electronic density contours for P0T, P1T and P2T trimers.

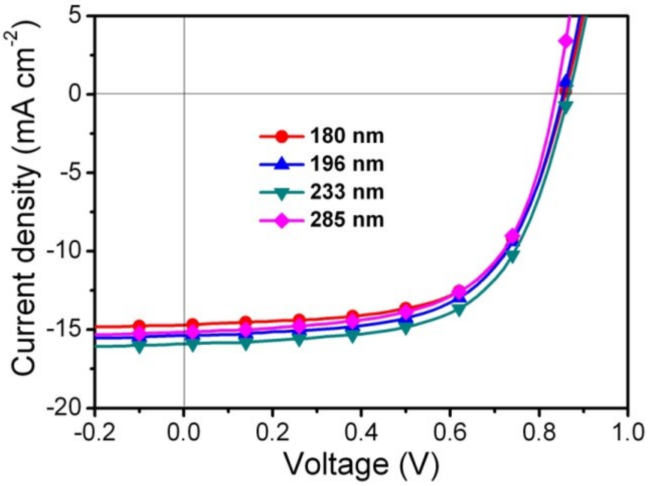


Figure S12. *J*-*V* characteristics of P1T:PC$_{71}$BM processed from AO/DPE with different film thickness.

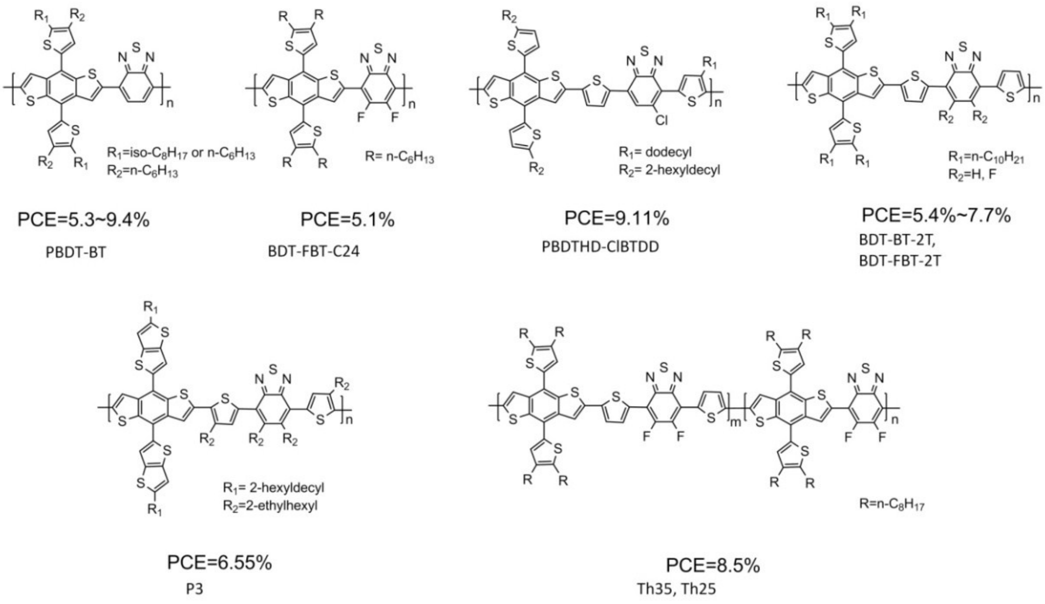


Figure S13. The chemical structure and general PCEs of the analogs of P1T.[2-8]

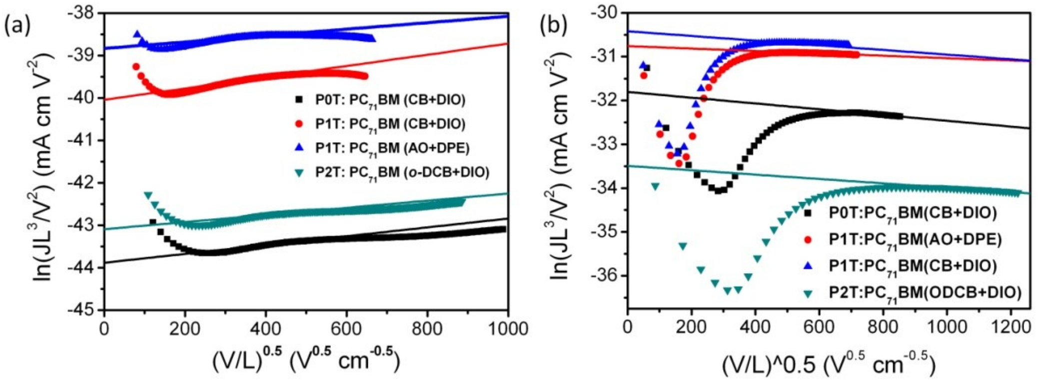


Figure S14. (a) electron-only and (b) hole-only curves of the devices.

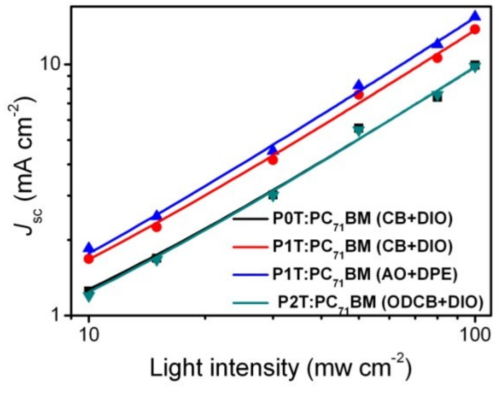
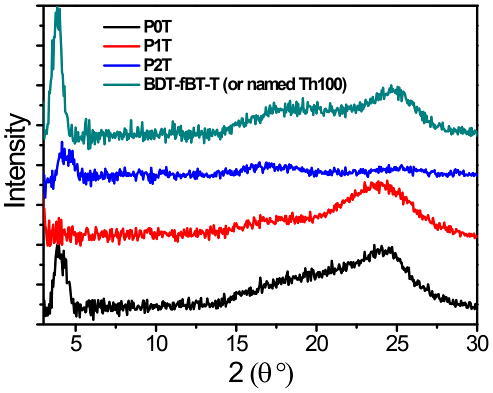


Figure S15. Dependence of J_{sc} on light intensity of the PSCs based on different polymers.



Fgure S16. The out-of plane XRD spectra of P0T, P1T, P2T and BDT-FBT-2T (or named Th100) pure films.

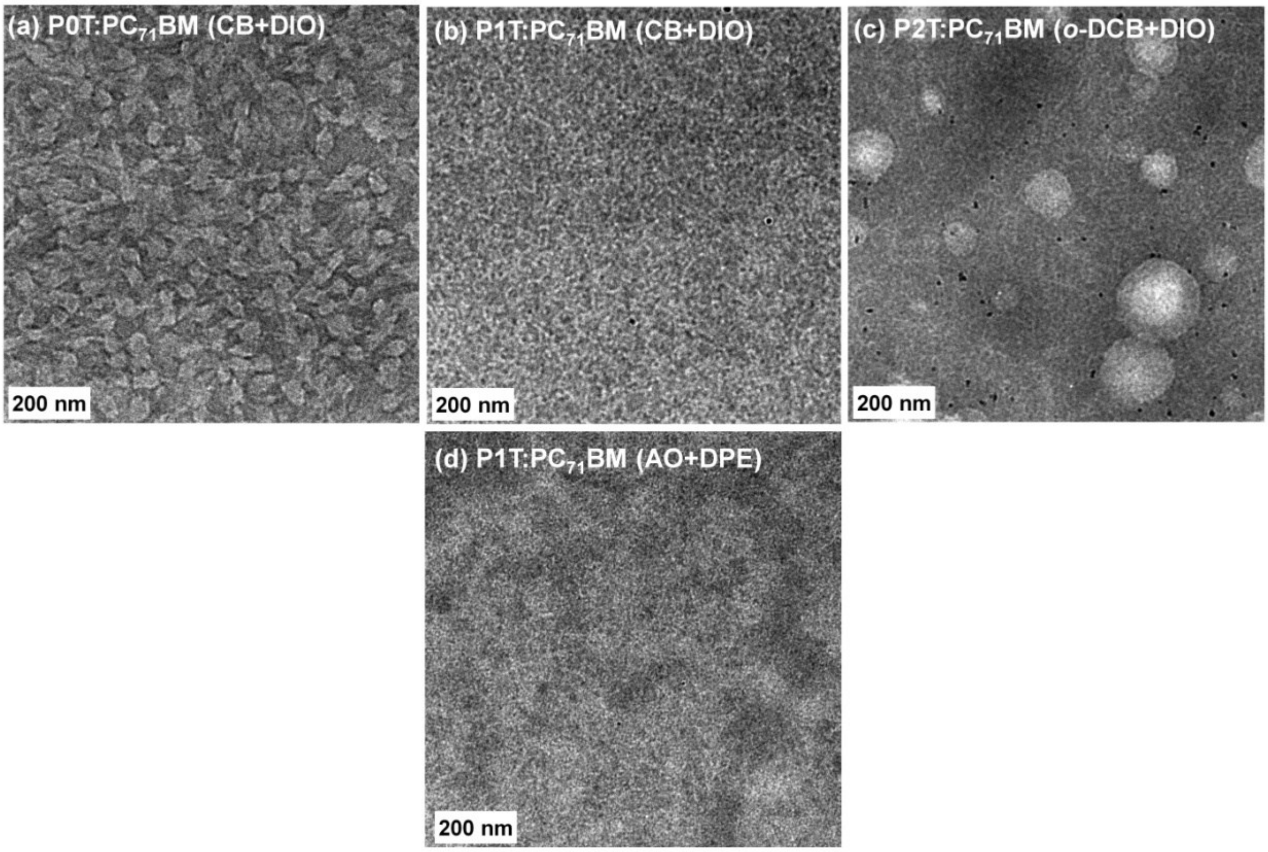


Figure S17. Bright field TEM images of the polymer:$PC_{71}BM$ blend films.

Table S1. Device characteristics of PSCs based on P0T with various DIO contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DIO content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1	3%	0.94	9.26	48.80	4.25
1:1.5	3%	0.96	10.19	54.34	5.31
1:2	3%	0.94	7.28	44.26	3.03
1:3	3%	0.94	5.68	49.12	2.62
1:1.5	1%	0.92	6.07	45.37	2.53
1:1.5	3%	0.96	10.19	54.34	5.31
1:1.5	5%	0.94	6.49	45.51	2.78

Table S2. Device characteristics of PSCs based on P1T with various DIO contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DIO content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	3%	0.86	13.28	57.18	6.53
1:1	3%	0.88	14.05	60.33	7.46
1:1.5	3%	0.86	13.38	70.90	8.16
1:2	3%	0.88	13.24	64.93	7.56
1:1.5	1%	0.86	13.14	60.09	7.69
1:1.5	3%	0.86	13.38	70.90	8.16
1:1.5	5%	0.88	13.24	64.93	7.56

Table S3. Device characteristics of PSCs based on P2T with various DIO contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DIO content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1	3%	0.84	10.05	54.68	4.61
1:1.5	3%	0.82	10.49	66.46	5.72
1:2	3%	0.80	9.46	56.37	4.27
1:1.5	1%	0.82	8.36	64.66	4.43
1:1.5	2%	0.80	9.69	63.67	4.94
1:1.5	3%	0.82	10.49	66.46	5.72
1:1.5	5%	0.80	11.18	52.08	4.66

Table S4. Device characteristics of PSCs based on P1T with various DPE contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DPE content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	3%	0.88	12.48	55.19	6.06
1:1	3%	0.88	13.26	64.17	7.49
1:1.2	3%	0.86	15.22	60.04	7.86
1:1.5	3%	0.86	15.68	63.22	8.53
1:1.8	3%	0.86	14.05	63.67	7.69
1:2	3%	0.84	14.29	59.36	7.13
1:1.5	1%	0.86	11.40	56.76	5.56
1:1.5	3%	0.86	15.68	63.22	8.53
1:1.5	5%	0.84	15.39	59.46	7.68

Table S5. Device Characteristics of PSCs based on P1T:PC$_{71}$BM processed from AO/DPE with various film thickness under AM 1.5G solar spectrum.

Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
180	0.86	14.71	61.79	7.82
198	0.86	15.39	60.90	8.06
233	0.86	15.68	63.22	8.53
285	0.84	15.16	61.46	7.83

Table S6. Device characteristics of PSCs based on P0T: PC$_{71}$BM processed from AO/DPE with various DPE contents and D/A proportions AM 1.5G solar spectrum.

D/A ratio	DPE content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE$_{best}$ (PCE^{a}) [%]
1:1.5	3%	0.94 (0.95 ± 0.01)	7.98 (6.93 ± 1.17)	45.10 (43.03 ± 3.15)	3.38 (2.82 ± 0.51)
1:1.5	0%	0.92 (0.91 ± 0.01)	7.82 (6.92 ± 1.32)	42.71 (42.52 ± 0.44)	3.07 (2.69 ± 0.53)

[a] Statistical data obtained from 5 independent devices.

Table S7. Comparison of photovoltaic properties of the polymers with analogs.

Polymer	Solvent	Extra Effort	Thickness [nm]	PCE [%]	PCE[a] [%]	Ref.
PBDT-BT	*o*-DCB	Interlayer modification	~90	8.5	9.5	Chem. Mater. 2016, 28, 3481[2]
PBDT-BT	*o*-DCB	Interlayer modification	~90	8.5	9.4	Adv. Mater. 2015, 27, 702[3]
BDT-FBT-C24	CB	---	---	5.3	---	J. Mater. Chem. A, 2016, 4, 1855[5]
BDT-BT-2T	*o*-DCB	---	~89	5.4	---	Adv. Mater. 2015, 27, 4461[4]
BDT-FBT-2T	*o*-DCB	---	~100	7.7	---	
PBDTHD-ClBTDD	CB	chlorinated benzothiadiazole units and asymmetric alkyl chain	~250	---	9.1	Chem. Mater. 2017, 29, 2819[6]
P1-P3		---	~100	5.3-6.5	---	Adv. Mater. 2015, 27, 6999[7]
Th00	CB	---	~100	4.9	---	J. Am. Chem. Soc., 2016, 138, 10782[8]
Th100	*o*-DCB	---	~100	6.9	---	
Th35	TMB	With retroreflective foil	~100	7.9	8.4	
P1T	**AO**	**---**	**~230**	**8.53**	**---**	**This work**

[a] PCE was achieved with extra effort.

Table S8. The recombination parameters, hole and electron mobility values based on different devices.

	recombination parameter α [%]	Hole mobility μ_h [cm^2 V^{-1}S^{-1}]	Electron mobility μ_e [cm^2 V^{-1}S^{-1}]	μ_e/μ_h
P0T/PC$_{71}$BM(CB+3%DIO)	0.902	5.17×10^{-5}	1.03×10^{-5}	0.2
P1T/PC$_{71}$BM(CB+3%DIO)	0.925	1.40×10^{-4}	3.77×10^{-4}	2.7
P1T/PC$_{71}$BM(AO+3%DPE)	0.934	1.88×10^{-4}	5.46×10^{-4}	2.7
P2T/PC$_{71}$BM(*o*-DCB+3%DIO)	0.918	2.08×10^{-5}	1.24×10^{-4}	6.0

Table S9. Device characteristics of PSCs based on P1T:$PC_{71}BM$ processed from AO/DPE with different molecular weights (M_n) under AM 1.5G solar spectrum.

Mn	V_{oc} [V]	J_{sc} [mA cm^{-2}]	J_{cal} [mA cm^{-2}]	FF [%]	PCE [%]
37kDa	0.86	15.68	15.38	63.22	8.53
51KDa	0.86	16.31	15.54	58.98	8.27
60KDa	0.86	15.92	15.74	62.19	8.51

Table S10. Device characteristics of PSCs based on P1T:ITIC-Th processed from AO/DPE with various DPE contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DPE content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.8	0%	0.92	14.65	53.57	7.22
1:1	0%	0.92	15.16	61.60	8.59
1:1.2	0%	0.92	13.96	62.38	8.01
1:1.5	0%	0.92	14.89	59.03	7.91
1:1	0%	0.92	15.16	61.60	8.59
1:1	0.5%	0.92	14.98	58.07	8.00
1:1	1%	0.90	13.30	59.04	7.07

Table S11. Device characteristics of PSCs based on P1T:ITIC-Th:$PC_{71}BM$ processed from AO/DPE with various DPE contents and D/A proportions AM 1.5G solar spectrum.

P1T:ITIC-Th : $PC_{71}BM$	DPE content	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1:0.5	3%	0.92	14.89	60.67	8.31
1:0.3:1.2	3%	0.90	14.67	67.70	8.94
1:0.25:1.25	3%	0.90	14.55	66.66	8.73
1:0.2:0.8	3%	0.92	13.38	60.45	7.44
1:0.4:1.6	3%	0.90	14.29	69.26	8.91
1:0.36:1.44	3%	0.92	14.59	68.56	9.21
1:1:0.5	0%	0.92	14.84	56.54	7.72
1:1:0.5	0.5%	0.92	14.12	58.05	7.54
1:1:0.5	1.5%	0.92	14.28	54.86	7.21
1:1:0.5	3%	0.92	14.89	60.67	8.31
1:0.36:1.44	3%	0.92	14.59	68.56	9.21
1:0.36:1.44	5%	0.92	14.48	70.16	9.14

Table S12. Photovoltaic performance of PSCs based P0T:$PC_{71}BM$ and P1T:$PC_{71}BM$ from o-xylene and 1, 2, 4-Trimethylbenzene, respectively, under AM 1.5G illumination, 100mW cm^{-2}.

Polymer	Solvent	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
P0T	O-xylene	0.98	9.07	55.29	4.91
	1, 2, 4-Trimethylbenzene	0.96	9.57	50.30	4.62
P1T	O-xylene	0.88	13.09	68.22	7.86
	1, 2, 4-Trimethylbenzene	0.86	13.22	66.73	7.58

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