

Electronic Supplementary Information

Donor-Acceptor type conjugated copolymers based on alternating BNPB and oligothiophene units: from electron acceptor to electron donor and from amorphous to semicrystalline

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1. Experimental details

General. ^1H NMR spectra and ^{13}C NMR spectra were measured with a Bruker AV-400 MHz and 100 MHz NMR spectrometer at 25 °C. Elemental analysis was conducted on the VarioEL elemental analyzer. Gel permeation chromatography (GPC) was performed on a PL-GPC 220-type at 150 °C. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. Thermal analysis was measured on a Perkin-Elmer 7 instrument at a heating rate of 10 °C min⁻¹ under nitrogen flow. Differential scanning calorimetry (DSC) was performed with a TA DSC Q2000 instrument under nitrogen at the heating and cooling rates of 10 °C min⁻¹ for two heating/cooling cycles. Density functional theory (DFT) calculations were performed by Gaussian 09. The geometry structures were optimized at the b3lyp/6-31g(d,p) basis set. For clarity, the alkyl chains of the polymers were replaced with methyl chains. 2D grazing incidence wideangle X-ray scattering (2D-GIWAXS) were performed at the BL1W1A beamline at Beijing Synchrotron Radiation Facility (BSRF). Samples were prepared on silicon substrates. UV/Vis absorption spectra in solution and in films were measured with a Shimadzu UV-3600 spectrometer. Cyclic voltammetry (CV) were performed on a CHI660a electrochemical workstation using Bu_4NPF_6 (0.1 mol L⁻¹ in acetonitrile) as electrolyte solution and ferrocene as an internal reference at a scan rate of 100 mV s⁻¹. The CV cell was made up of a standard calomel reference electrode, a glassy carbon electrode, and a platinum wire counter electrode. The polymers were casted on the working electrode for measurements. Atomic force microscopy (AFM) hight and phase images were performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. The transmission electron microscopy (TEM) images were obtained on a TECNAI G2 transmission electron microscope (FEI Co., Netherlands). Photoluminescence (PL) spectra were measured with a Horiba Jobin-Yvon FL3C-111 fluorescence spectrophotometer. The thickness of films was measured by step profiler with a Dektak 6M Stylus Profile.

Materials and reagents. All of solvents, reagents and materials were purchased

from commercial suppliers and used as received without further purification unless otherwise mentioned. Dibromo-substituted double B←N bridged bipyridine (BNBP) unit and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene were synthesized in our laboratory. 2,5-dibromo-3,4-difluorothiophene,¹ 2,5-bis(trimethylstannyl)thiophene,¹ and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)² were prepared according to the literature methods. Toluene, DMF and THF were dried via standard methods.

2. Syntheses and characterizations

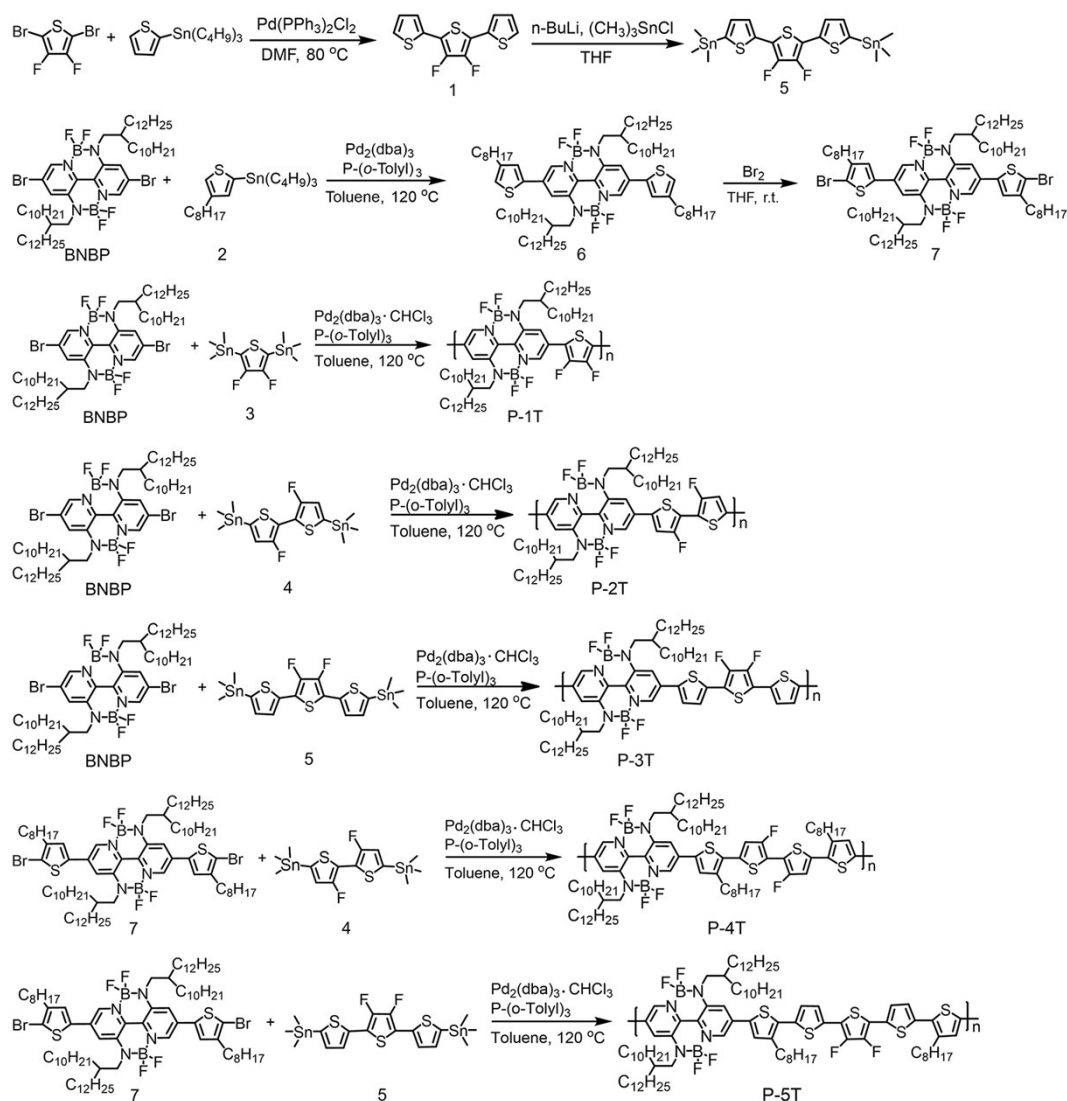
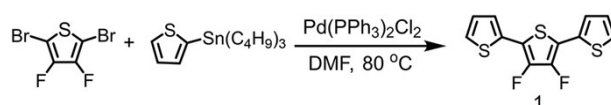
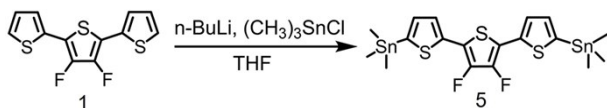


Figure S1. Synthetic routes of the polymers P-1T, P-2T, P-3T, P-4T and P-5T.

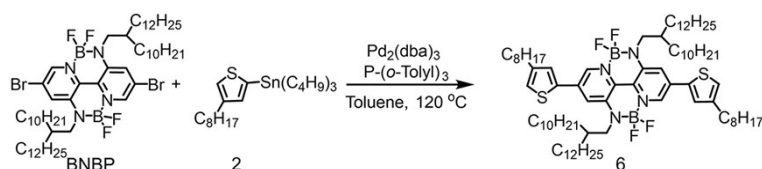


3',4'-difluoro-2,2':5',2''-terthiophene (1): 2,5-dibromo-3,4-difluorothiophene (1.32

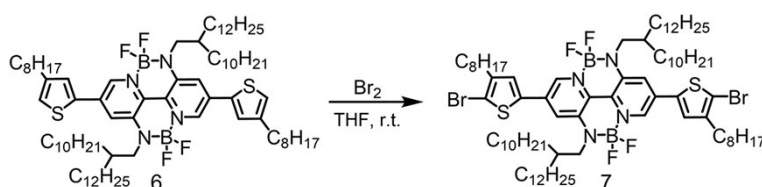
g, 4.74 mmol), tributyl(thiophen-2-yl)stannane (4.98 g, 13.32 mmol), Pd₂(PPh₃)₂Cl₂ (98 mg, 0.14 mmol) were placed in a two-necked flask under argon, then dried DMF (16 mL) was added. The mixture was allowed to stir at 80 °C for 7.5 h. After cooling, the reaction mixture was poured into KF solution, and extracted three times with dichloromethane. The organic phase was washed and dried over anhydrous Na₂SO₄, and then the solvent was removed by rotary evaporation. The crude product was purified by silica gel chromatography (petroleum ether) and recrystallization in methyl alcohol to obtain **3',4'-difluoro-2,2':5',2''-terthiophene** (0.24 g, yielded 18.8%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.35 (dd, J = 5.1, 1.0 Hz, 2H), 7.28 (dd, J = 3.7, 1.1 Hz, 2H), 7.08 (dd, J = 5.0, 3.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): 142.20, 140.09, 131.62, 127.70, 125.89, 124.95. Anal. Calcd for C₁₂H₆F₂S₃ (%): C, 50.68; H, 2.13. Found: C, 50.85; H, 2.18.



(3',4'-difluoro-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (5): n-BuLi (0.79 mL, 1.26 mmol) was added dropwise to a solution of 3',4'-difluoro-2,2':5',2''-terthiophene (**1**) (0.16 mg, 0.57 mmol) in anhydrous THF (10 mL) at -78 °C under an argon atmosphere, and the mixture was kept at -78 °C for 2h. Then, (CH₃)₃SnCl (0.28 g, 1.43 mmol) was added to the mixture, then the mixture was allowed to warm and kept at room temperature for 7.5 h. The reaction was quenched by water and extracted by diethyl ether three times. The organic phase was washed with water three times, and dried over anhydrous Na₂SO₄ and the solvent was then removed by rotary evaporation. The crude product was purified by recrystallization in ethyl alcohol to obtain **(3',4'-difluoro-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane)** (0.16 g, yielded 45.0%). ¹H NMR (400 MHz, C₆D₆): δ (ppm) 7.33 (d, J = 3.4 Hz, 2H), 6.96 (d, J = 3.4 Hz, 2H), 0.20 (s, 18H). Anal. Calcd for C₁₈H₂₂F₂S₃Sn₂ (%): C, 35.44; H, 3.64. Found: C, 35.64; H, 3.73.

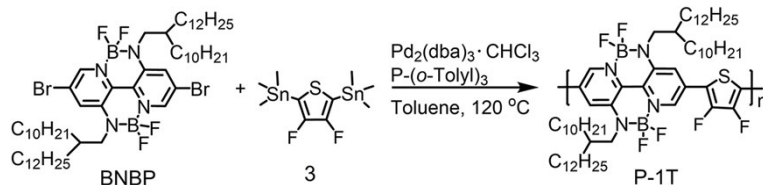


Compound 6: BNBP (0.80 g, 0.72 mmol), tributyl(4-octylthiophen-2-yl)stannane (**2**) (1.05 mg, 2.16 mmol), Pd₂(dba)₃ (13.19 mg, 0.014 mmol) and P(*o*-Tolyl)₃ (35.06 mg, 0.12 mmol) were placed in a two-necked flask under argon, then dried toluene (50 mL) was added. The mixture was allowed to stir at 120 °C overnight. After cooling, the reaction mixture was poured into water and extracted three times with dichloromethane. The organic phase was washed and dried over anhydrous Na₂SO₄, and then the solvent was removed by rotary evaporation. The crude product was purified by silica gel chromatography (petroleum ether:dichloromethane = 2:1) to obtain **6** (0.72 g, yielded 74.4%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.38 (s, 2H), 7.63 (s, 2H), 7.34 (s, 2H), 7.06 (s, 2H), 3.57 (d, J = 6.9 Hz, 4H), 2.67–2.64 (m, 4H), 1.78 (s, 1H), 1.70–1.64 (m, 4H), 1.39–1.21 (m, 100H), 0.90–0.83 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): 145.26, 143.66, 138.28, 132.96, 127.12, 125.32, 124.76, 122.54, 118.21, 48.04, 35.89, 32.10, 31.95, 31.93, 31.92, 31.89, 30.55, 30.44, 30.17, 29.72, 29.69, 29.68, 29.44, 29.38, 29.34, 29.28, 26.92, 22.70, 14.12.

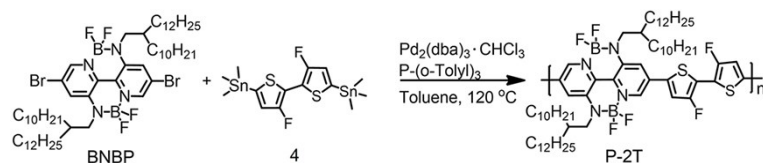


Compound 7: Compound **6** (0.36 g, 0.27 mmol) was added in anhydrous chloroform, and then bromine (0.26 mL, 5.08 mmol) was added to the solution. Then, the mixture was allowed to stir at room temperature for 24 h. Then the reaction mixture was poured into Na₂SO₃ solution, and the organic phase was extracted by dichloromethane three times. The organic phase was washed and dried over anhydrous Na₂SO₄, and then the solvent was removed by rotary evaporation. The crude product was purified by silica gel chromatography (petroleum ether:dichloromethane = 2:1) to obtain **7** (0.31 g, yielded 75.5%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.32 (s, 2H), 7.52 (s, 2H), 7.20 (s, 2H), 3.55 (d, J = 6.9 Hz, 4H), 2.62–2.59 (m, 4H), 1.75 (s, 2H), 1.66–1.55

(m, 4H), 1.36-1.22 (m, 100H), 0.91-0.85 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): 144.25, 143.77, 137.90, 132.20, 126.74, 125.41, 124.33, 117.93, 111.90, 48.07, 35.95, 32.13, 31.94, 31.89, 30.19, 29.72, 29.38, 29.28, 29.25, 26.98, 22.70, 22.67, 14.13.

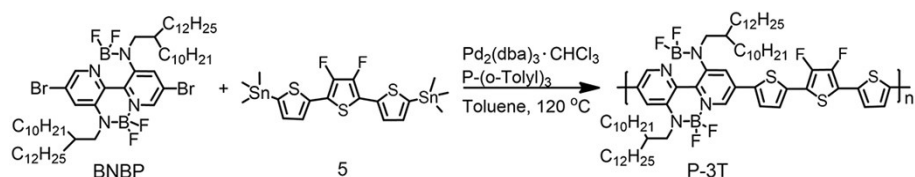


Polymer P-1T: Under the protection of argon, a mixture of BNBP (111.3 mg, 0.10 mmol), 2,5-bis(trimethylstannyl)thiophene (**3**) (41.0 mg, 0.10 mmol), Pd₂(dba)₃·CHCl₃ (2.1 mg, 0.002 mmol), P(*o*-Tolyl)₃ (4.9 mg, 0.016 mmol) and dried toluene were stirred at 120 °C for 24 h, then the end-capping reaction was carried out by adding bromobenzene (1 mL) for 5 h. After cooling, the product was concentrated by rotary evaporation and dispersed in methanol and then the precipitate was collected. The precipitate was purified by Soxhlet extraction using acetone and hexane to remove impurities and the residual monomers. The left residual was dissolved in chloroform, and then was dispersed in methanol. The product was collected and dried in vacuum overnight to give polymer **P-1T** (83.0 mg, yielded 80.2%). ¹H NMR (400 MHz, C₆D₄Cl₂, 100 °C): δ (ppm) 8.47 (s, 2H), 7.83 (s, 2H), 3.71 (s, 4H), 2.05 (m, 2H), 1.54-1.10 (m, 80H), 0.81 (s, 12H). GPC (TCB, polystyrene standard, 150 °C): Mn = 32.6 kDa, PDI = 2.46. Anal. Calcd for C₆₂H₁₀₂B₂F₆N₄S (%) : C, 69.52; H, 9.60; N, 5.23. Found: C, 69.71; H, 9.69; N, 5.11.

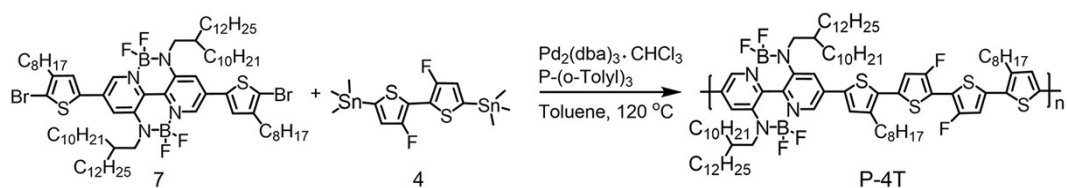


Polymer P-2T: **P-2T** was synthesized from BNBP (111.3 mg, 0.10 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**4**) (49.2 mg, 0.10 mmol) following a similar procedure as **P-1T**. Yield: (95.9 mg, 85.9%). ¹H NMR (400 MHz, C₆D₄Cl₂, 100 °C): δ (ppm) 8.64 (s, 2H), 7.90 (s, 2H), 7.39 (s, 2H), 3.95 (s, 4H), 2.27 (m, 2H), 1.79-1.36 (m, 80H), 1.08 (s, 12H). GPC (TCB, polystyrene standard, 150 °C): Mn = 40.8 kDa, PDI = 2.10. Anal. Calcd for C₆₆H₁₀₄B₂F₆N₄S₂ (%) : C, 68.73; H, 9.09; N, 4.86. Found:

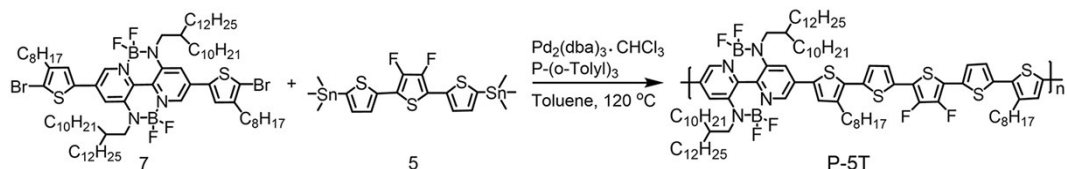
C, 68.50; H, 9.15; N, 4.73.



Polymer P-3T: P-3T was synthesized from BNBP (111.3 mg, 0.10 mmol) and (3',4'-difluoro-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (**5**) (61.0 mg, 0.10 mmol) following a similar procedure as **P-1T**. Yield: (114.8 mg, 88.3%). ¹H NMR (400 MHz, C₆D₄Cl₂, 100 °C): δ (ppm) 8.29 (s, 2H), 7.52 (s, 2H), 7.15 (s, 2H), 7.07 (s, 2H), 3.55 (s, 4H), 1.87 (s, 2H), 1.39-0.95 (m, 80H), 0.68-0.65 (m, 12H). GPC (TCB, polystyrene standard, 150 °C): Mn = 38.3 kDa, PDI = 1.91. Anal. Calcd for C₇₀H₁₀₆B₂F₆N₄S₃ (%): C, 68.05; H, 8.65; N, 4.54. Found: C, 68.45; H, 8.34; N, 4.62.



Polymer P-4T: P-4T was synthesized from compound **7** (111.3 mg, 0.08 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**4**) (42.4 mg, 0.08 mmol) following a similar procedure as **P-1T**. Yield: (100.2 mg, 81.0%). ¹H NMR (400 MHz, C₆D₄Cl₂, 100 °C): δ (ppm) 8.45 (s, 2H), 7.65 (s, 2H), 7.28 (s, 2H), 6.96 (s, 2H), 3.67 (s, 4H), 2.81 (s, 4H), 2.00 (s, 2H), 1.73-1.70 (m, 4H), 1.44-1.13 (m, 100H), 0.84-0.79 (m, 18H). GPC (TCB, polystyrene standard, 150 °C): Mn = 29.4 kDa, PDI = 1.91. Anal. Calcd for C₉₀H₁₄₀B₂F₆N₄S₄ (%): C, 70.10; H, 9.15; N, 3.63. Found: C, 70.35; H, 9.31; N, 3.74.



Polymer P-5T: P-5T was synthesized from compound **7** (125.0 mg, 0.08 mmol) and (3',4'-difluoro-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane) (50.8 mg, 0.08 mmol) following a similar procedure as **P-1T**. Yield: (120.3 mg, 89.0%). ¹H NMR

(400 MHz, $C_6D_4Cl_2$, 100 °C): δ (ppm) 8.73 (s, 2H), 7.92 (s, 2H), 7.56 (s, 2H), 7.45 (s, 2H), 7.44 (s, 2H), 3.95 (s, 4H), 3.09 (s, 4H), 2.27 (s, 2H), 2.00-1.97 (m, 4H), 1.78-1.36 (m, 100H), 1.11-1.06 (m, 18H). GPC (TCB, polystyrene standard, 150 °C): $M_n = 49.4$ kDa, PDI = 2.19. Anal. Calcd for $C_{94}H_{142}B_2F_6N_4S_5$ (%): C, 69.52; H, 8.81; N, 3.45. Found: C, 69.21; H, 8.90; N, 3.51.

3. Density functional theory calculations

Density functional theory (DFT) calculations were performed using Gaussian 09. Figure S1 shows the geometry structure of the polymers P-1T to P-5T, which were optimized by DFT calculations with the B3LYP/6-31G(d,p) basis set. The frontier molecular orbitals and LUMO/HOMO energy levels based on DFT calculations of these polymers are also shown. For simplification, all the long alkyl chains of the polymers are replaced by methyl groups.

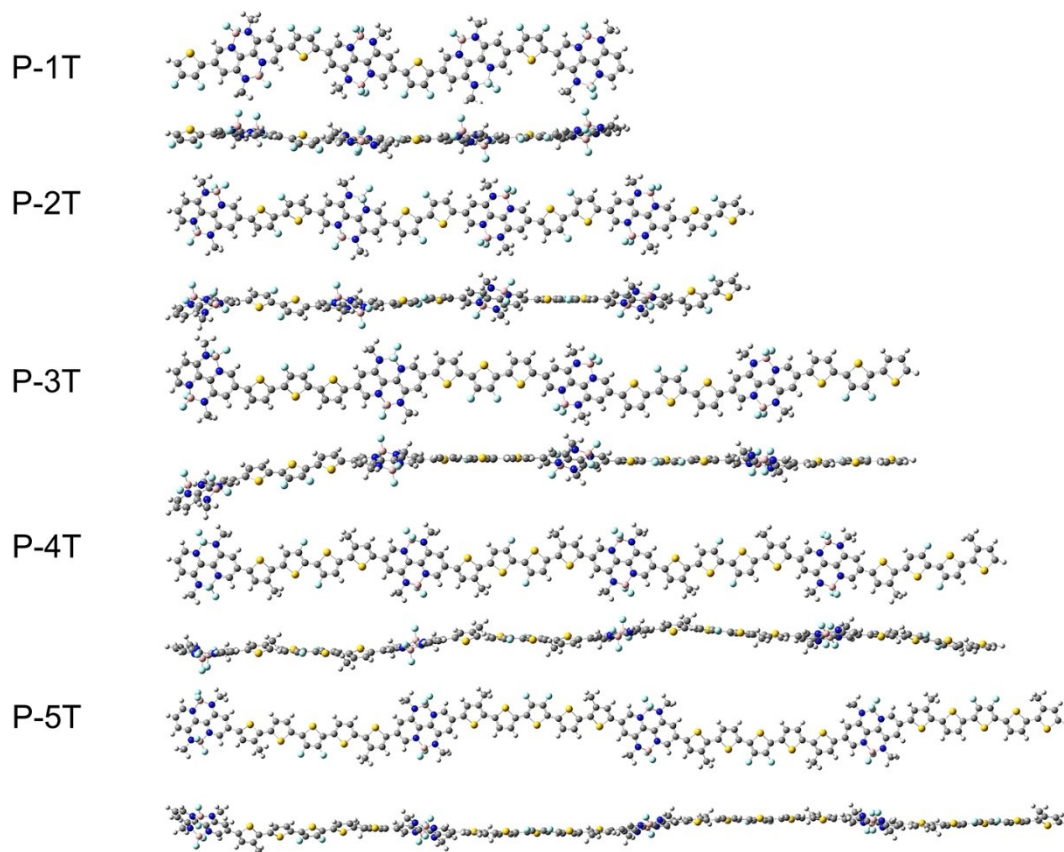


Figure S2. The geometry-optimized structure based on DFT calculations for the model molecules of P-1T, P-2T, P-3T, P-4T and P-5T, top view is up and side view is down for each polymer.

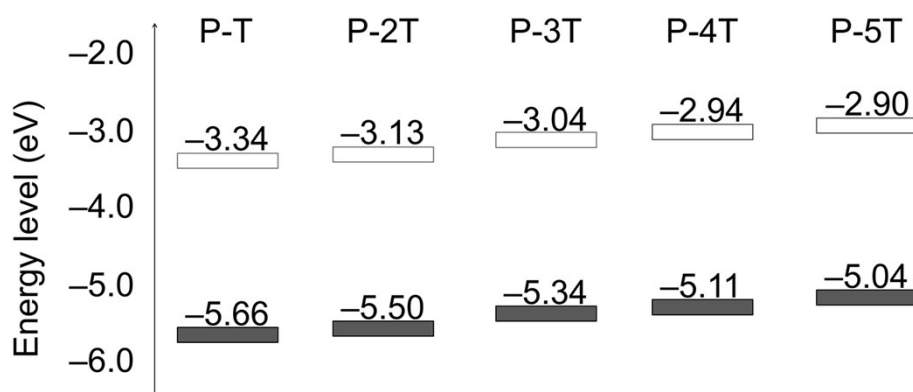


Figure S3. The LUMO/HOMO energy levels based on DFT calculations for the model molecules of P-1T, P-2T, P-3T, P-4T and P-5T.

4. Thermal properties

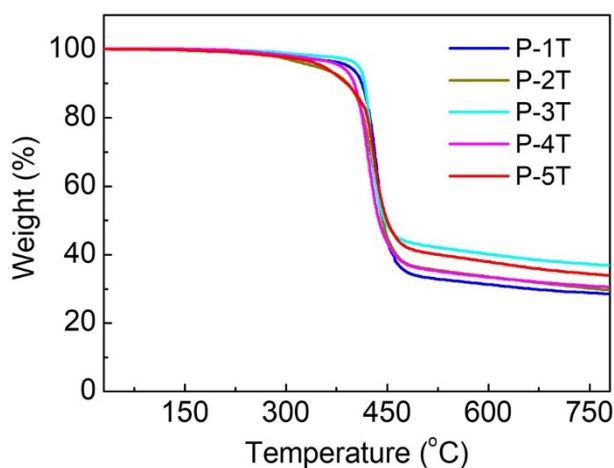


Figure S4. TGA curves of the polymers P-1T, P-2T, P-3T, P-4T and P-5T.

5. The molecular stacking properties

Table S1. GIWAXS characterization data of the polymers P-1T, P-2T, P-3T, P-4T and P-5T.

Films	Directions	100				010			
		Location [Å ⁻¹]	d-spacing [Å]	FWHM [Å ⁻¹]	CL [Å]	Location [Å ⁻¹]	d-spacing [Å]	FWHM [Å ⁻¹]	CL [Å]
P-1T	Out-of-plane	0.32	19.95	0.095	60				
	In-plane	0.30	20.94	0.101	56				
P-2T	Out-of-plane	0.31	20.53	0.135	42	1.59	3.95	0.322	18
	In-plane	0.27	23.28	0.080	71				
P-3T	Out-of-plane	0.30	20.81	0.147	38	1.64	3.83	0.253	22
	In-plane	0.27	23.02	0.106	53	1.64	3.84	0.217	26

P-4T	Out-of-plane	0.26	23.89	0.060	95	1.67	3.76	0.185	31
	In-plane	0.25	24.93	0.059	97	1.67	3.76	0.174	32
P-5T	Out-of-plane	0.28	22.36	0.071	79	1.69	3.72	0.163	35
	In-plane	0.26	23.80	0.071	79	1.70	3.70	0.170	33

6. Electron-only and hole-only devices fabrication and electron/hole mobility measurement

The electron/hole mobilities were measured using the space charge limited current (SCLC) method with the electron-only/hole-only devices structure of ITO/PEIE/film/Ca/Al or ITO/PEDOT:PSS/film/MoO₃/Al. The current-voltage curves in the range of 0–8 V were recorded using a computer-controlled Keithley 2400 source meter, and the results were fitted to a space-charge limited function:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89 \beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$

where J is the current density, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of 3 for polymers, μ is the zero-field mobility, V is the potential across the device ($V = V_{\text{applied}} - V_{\text{bias}} - V_{\text{series}}$), L is the thickness of film, and β is the field-activation factor. The series and contact resistance (V_{series}) of the device (10–15 Ω) were measured using blank device of ITO/PEIE/Ca/Al. The range of 0–5 V was used to extract the mobility values.

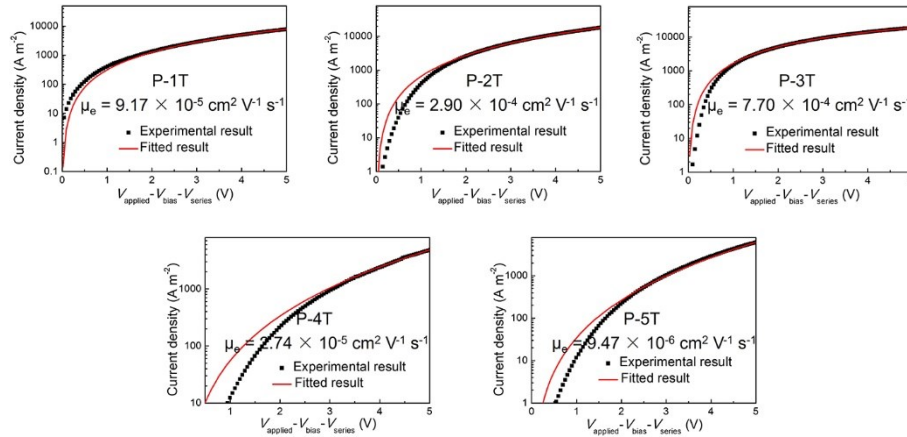


Figure S5. J–V curves and SCLC fittings of the electron-only devices of P-1T, P-2T, P-3T, P-4T and P-5T films.

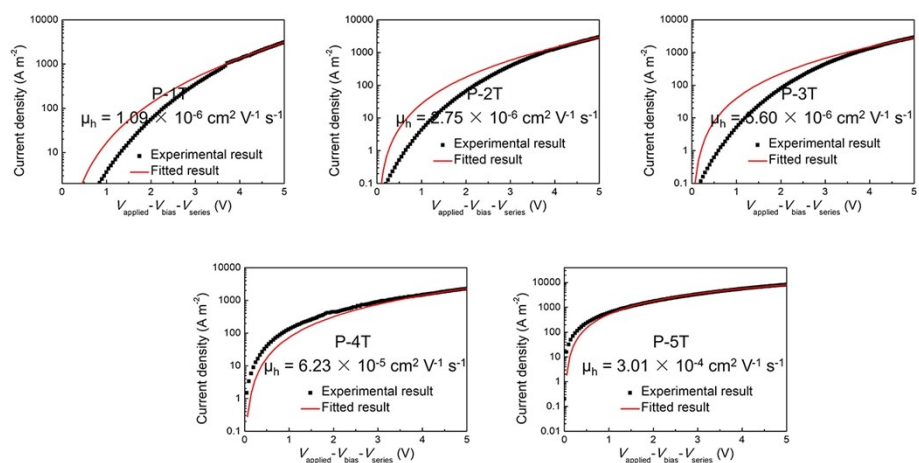


Figure S6. J–V curves and SCLC fittings of the hole-only devices of P-1T, P-2T, P-3T, P-4T and P-5T films.

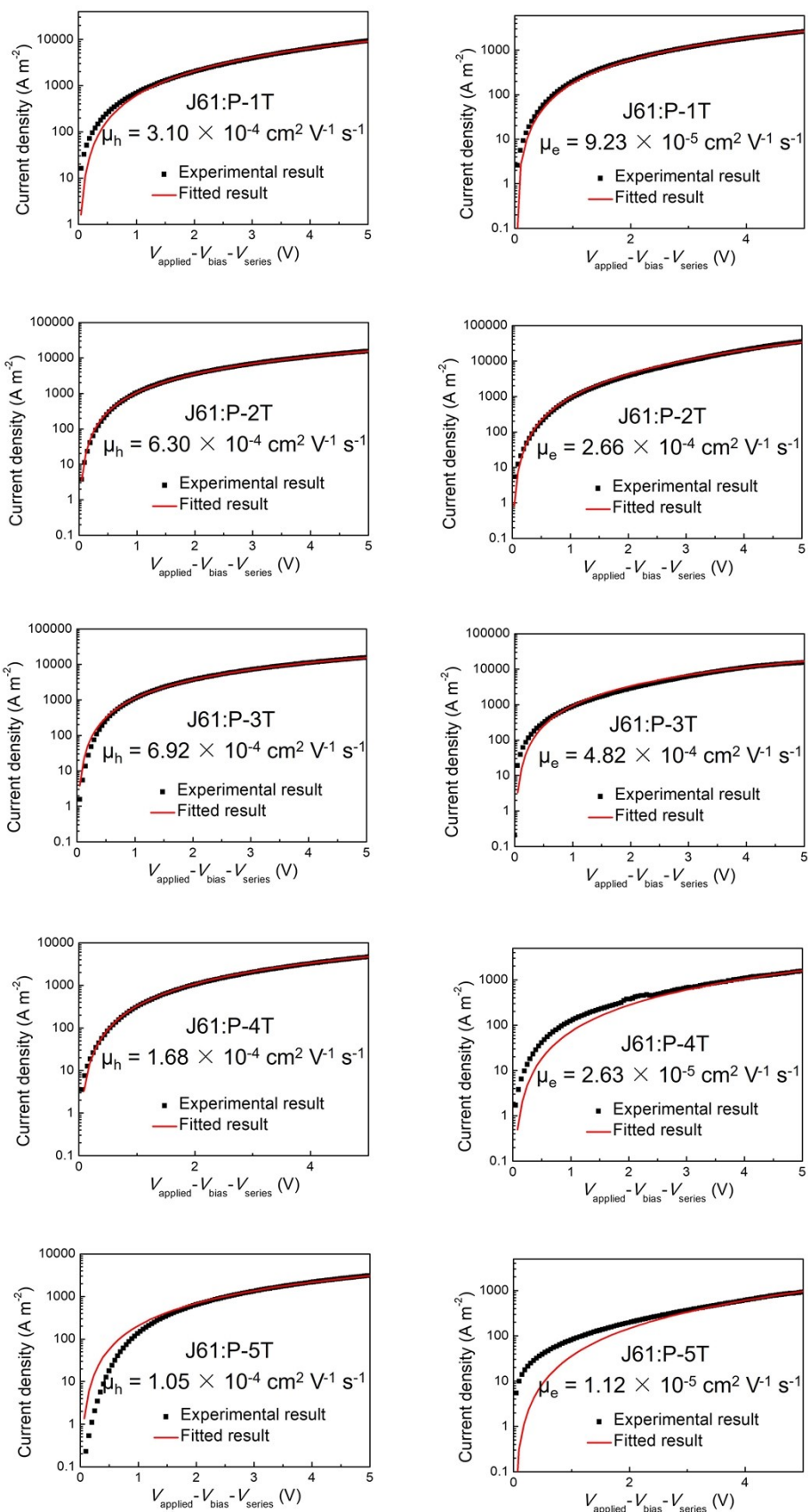


Figure S7. J–V curves and SCLC fittings of the hole-only and electron-only devices of J61:P-1T, J61:P-2T, J61:P-3T, J61:P-4T and J61:P-5T based blend films.

7. PSC device fabrication and measurement

The PSC devices were fabricated with the configuration of ITO/PEDOT:PSS/Active layer/Ca/Al. Polymer J61 was used as donor and P-1T, P-2T, P-3T, P-4T or P-5T were used as acceptor. Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonication in deionized water, acetone, and isopropyl alcohol, followed by drying at 125 °C for 30 min and treatment with UV-ozone for 30 min. PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO glass substrates at 5000 rpm for 40 s to give a film thickness of 40 nm, followed by baking at 120 °C for 30 min. Then, the substrates were transferred to a nitrogen-filled glove box. The blends of donor and acceptor were spin-coated onto the PEDOT:PSS layers to produce the active layers. Finally, the active layers were transferred to a vacuum chamber, and Ca (20 nm) and Al (100 nm) were deposited by thermal evaporation at the pressure of 2×10^{-4} Pa. The active area of each device was 2 mm². The current density ($J-V$) curves of the devices were measured by the computer-controlled Keithley 2400 source meter under 100 mW cm⁻² AM 1.5G simulated solar light illumination provided by an XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd). The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd). The light intensity at each wavelength was calibrated using a calibrated monosilicon diode.

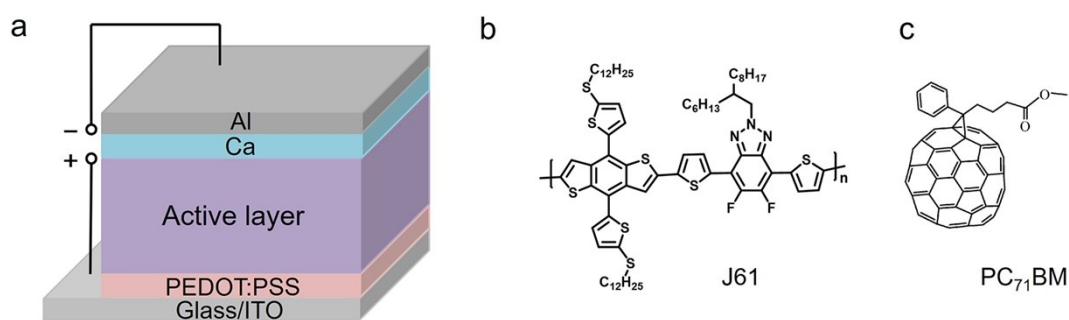


Figure S8. (a) The PSC device structure. The chemical structures of (b) polymer electron donor J61 and (c) electron acceptor PC₇₁BM.

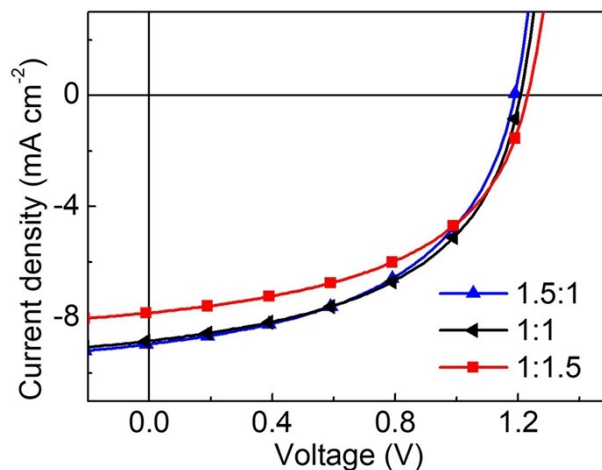


Figure S9. J - V plots of the OSCs based on J61:P-3T blend films with different D:A ratios.

Table S2. Photovoltaic parameters of the solar cells based on J61:P-3T blend films with different D:A ratios under illumination of AM 1.5 G, 100 mW cm^{-2} .

D:A ratio	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
1.5:1	1.19	8.95	49.23	5.24
1:1	1.21	8.84	50.40	5.39
1:1.5	1.23	7.83	50.46	4.86

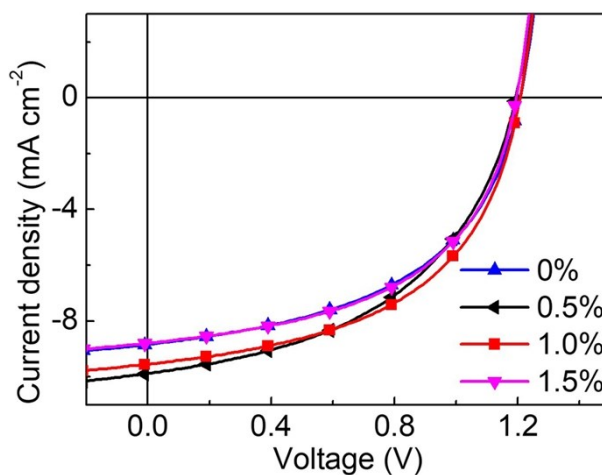


Figure S10. J - V plots of the OSCs based on J61:P-3T blend films (1:1, w/w) with different CN contents.

Table S3. Photovoltaic parameters of the solar cells based on J61:P-3T blend films (1:1, w/w) with different CN contents under illumination of AM 1.5 G, 100 mW cm^{-2} .

CN content (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
0	1.21	8.84	50.40	5.39
0.5	1.19	9.88	48.23	5.67

1.0	1.21	9.55	51.68	5.97
1.5	1.19	8.80	52.18	5.47

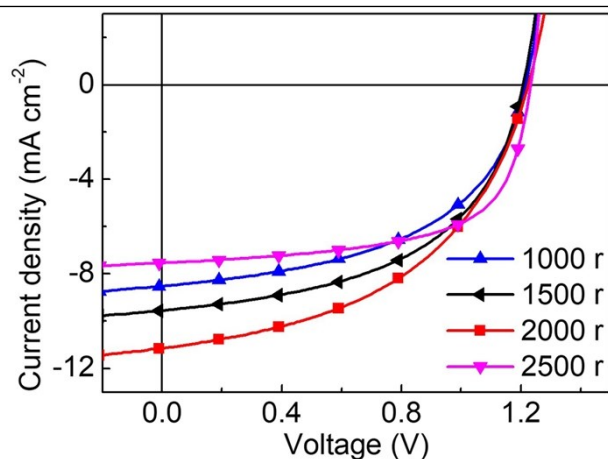


Figure S11. J - V plots of the OSCs based on J61:P-3T blend films (1:1, w/w) with different spinning speed.

Table S4. Photovoltaic parameters of the solar cells based on J61:P-3T blend films (1:1, w/w) with different spinning speed under illumination of AM 1.5 G, 100 mW cm^{-2} .

spinning speed (r)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
1000	1.21	8.52	51.35	5.29
1500	1.21	9.55	51.68	5.97
2000	1.22	11.15	47.95	6.52
2500	1.23	7.54	63.04	5.85

8. Morphology of the blend films

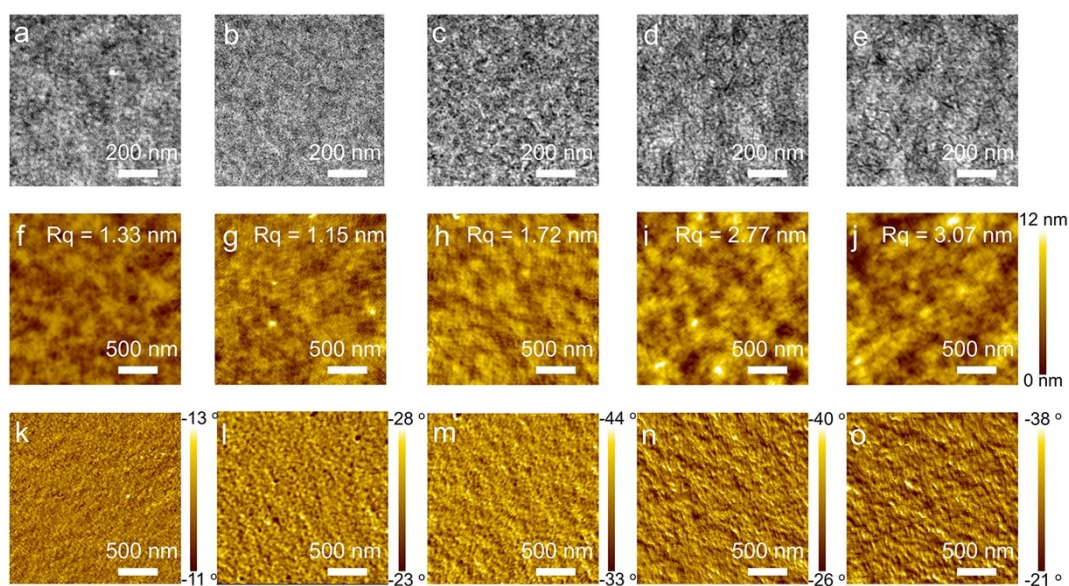


Figure S12. (a-e) TEM images, (f-j) AFM height images and (k-o) AFM phase images of the J61:P-1T, J61:P-2T, J61:P-3T, J61:P-4T and J61:P-5T-based blend films, respectively.

9. The photoluminescence (PL) measurements

Photoluminescence (PL) spectroscopy was used to study the exciton dissociation and charge transfer behavior in the blends. According to the maximum absorptions, the excitation wavelengths of P-nT ($n = 1-5$) were selected to be 550 nm. Figure S13 shows the PL spectra of the blend films in comparison with those of pristine polymer acceptor P-nT films. For the blend films, the PL quenching efficiency of P-1T, P-2T, P-3T, P-4T and P-5T are 97.3%, 76.4%, 91.9%, 45.1% and 48.0%, respectively. Compared with J61:P-1T, J61:P-2T and J61:P-3T, the J61:P-4T and J61:P-5T blends exhibit low PL quenching efficiency, which mainly due to the mismatched energy levels for exciton dissociation.

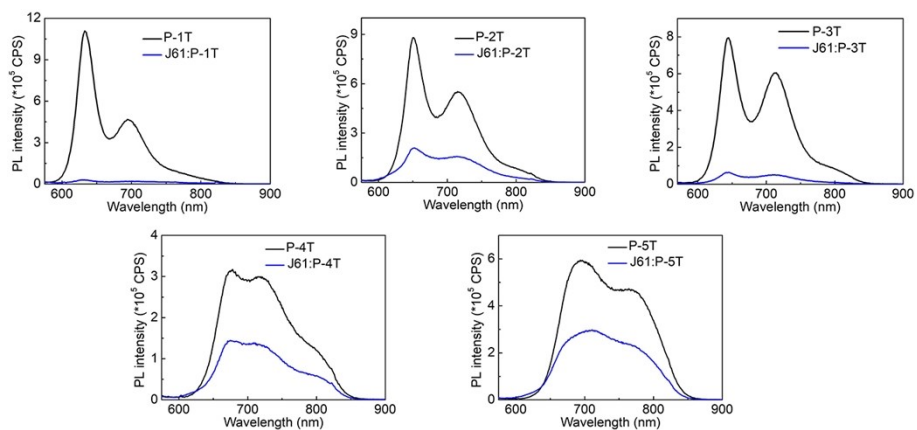


Figure S13. Photoluminescence spectra of pure P-nT (n = 1-5) and the blend films of J61:P-nT (excited at 550 nm).

10. ^1H NMR and ^{13}C NMR spectra

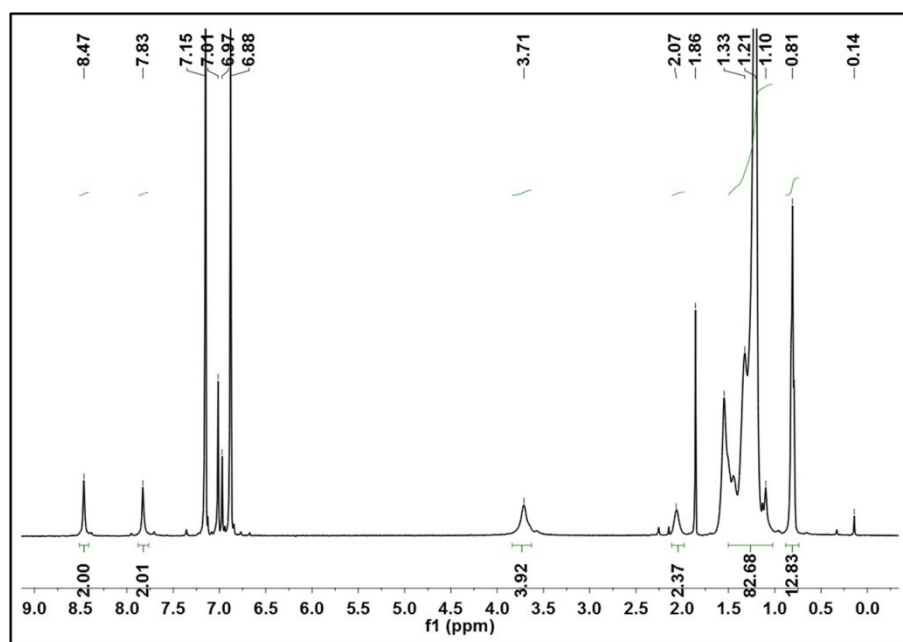


Figure S14. ^1H NMR spectrum of P-1T.

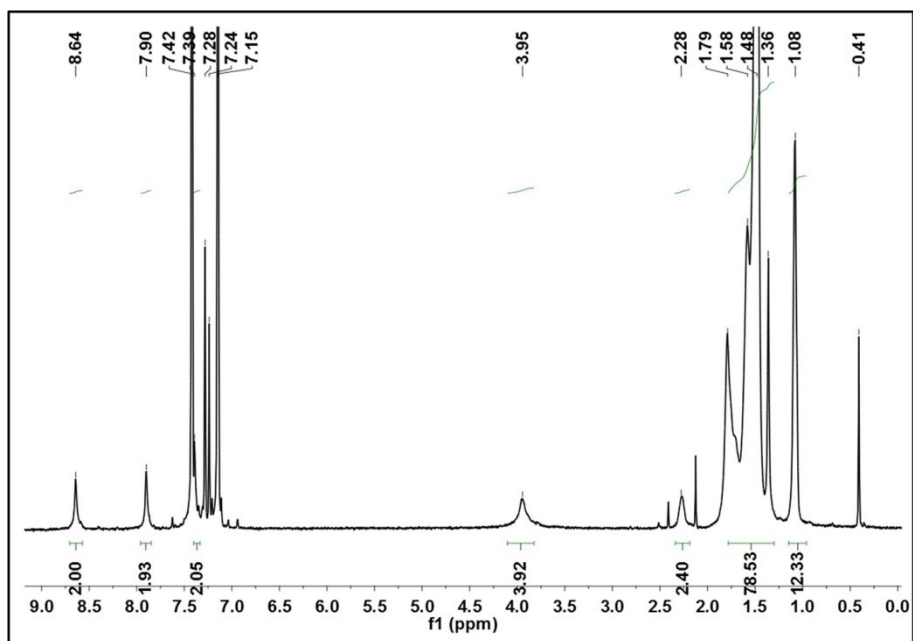
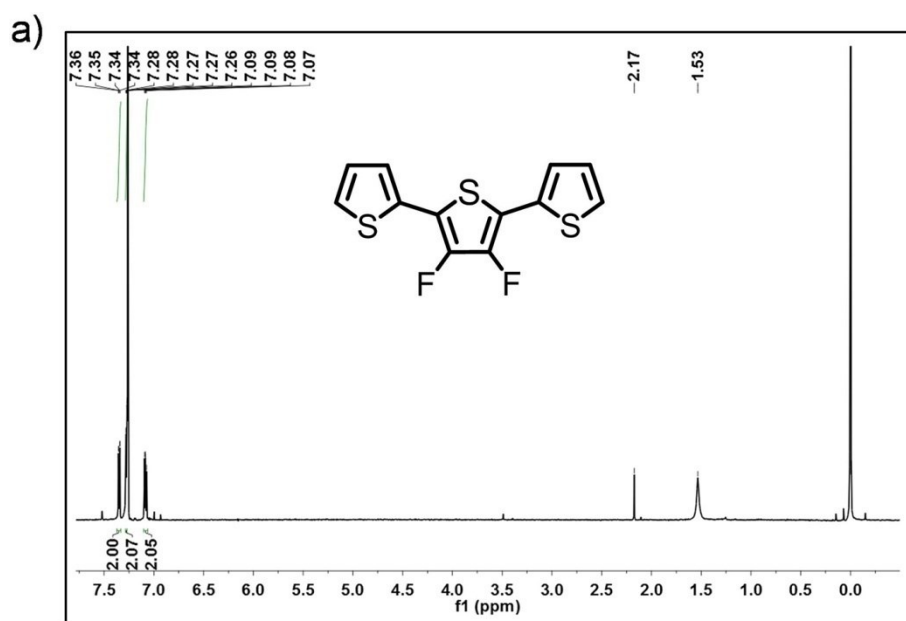


Figure S15. ^1H NMR spectrum of P-2T.



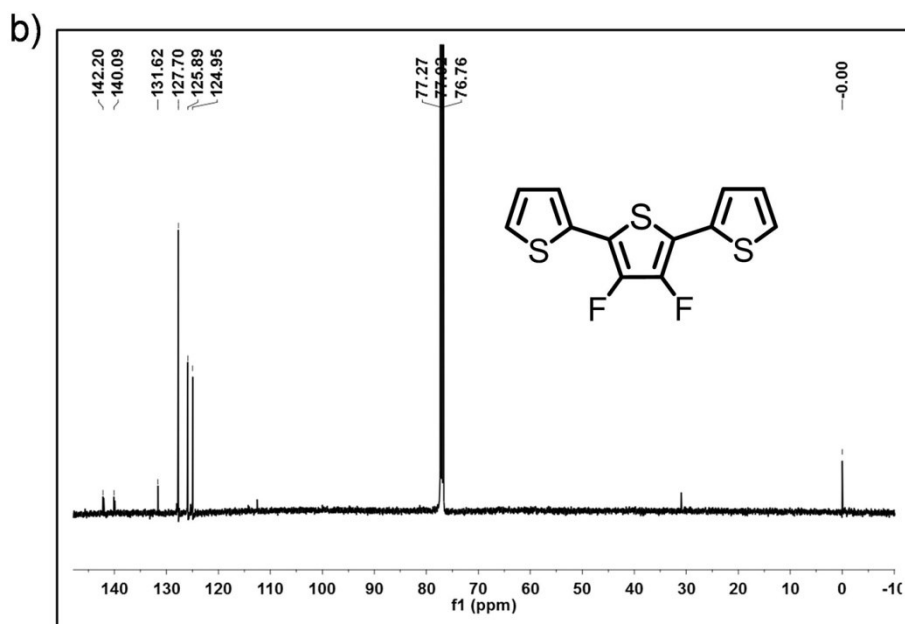


Figure S16. ^1H NMR and ^{13}C NMR spectra of 3',4'-difluoro-2,2':5,2''-terthiophene.

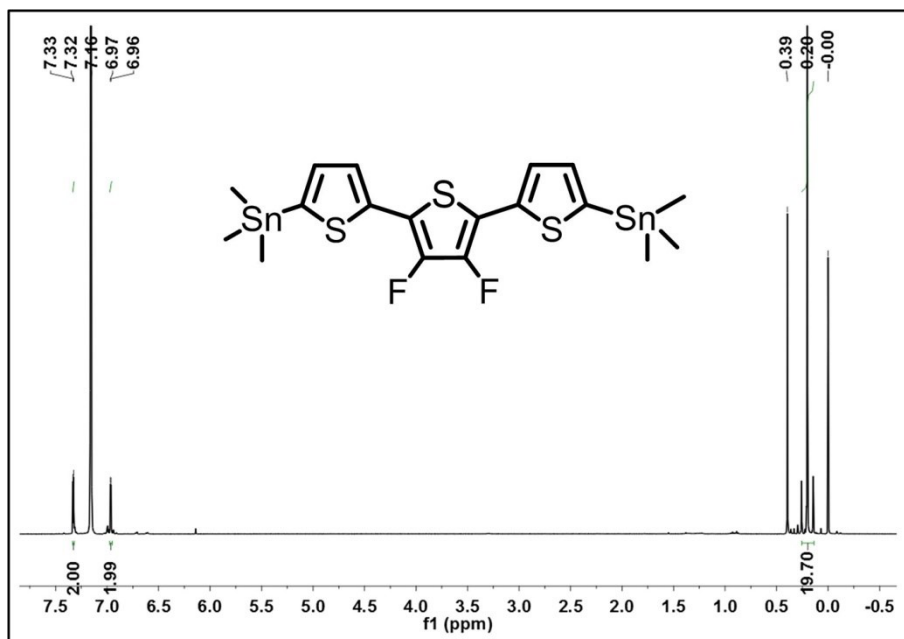


Figure S17. ^1H NMR spectrum of (3',4'-difluoro-[2,2':5,2''-terthiophene]-5,5''-diyl)bis(trimethylstannane).

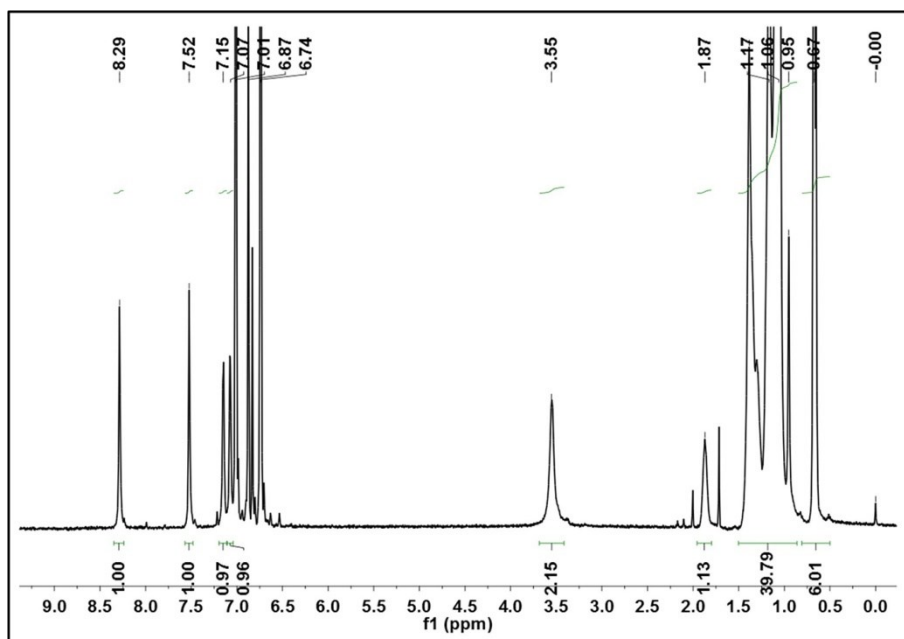
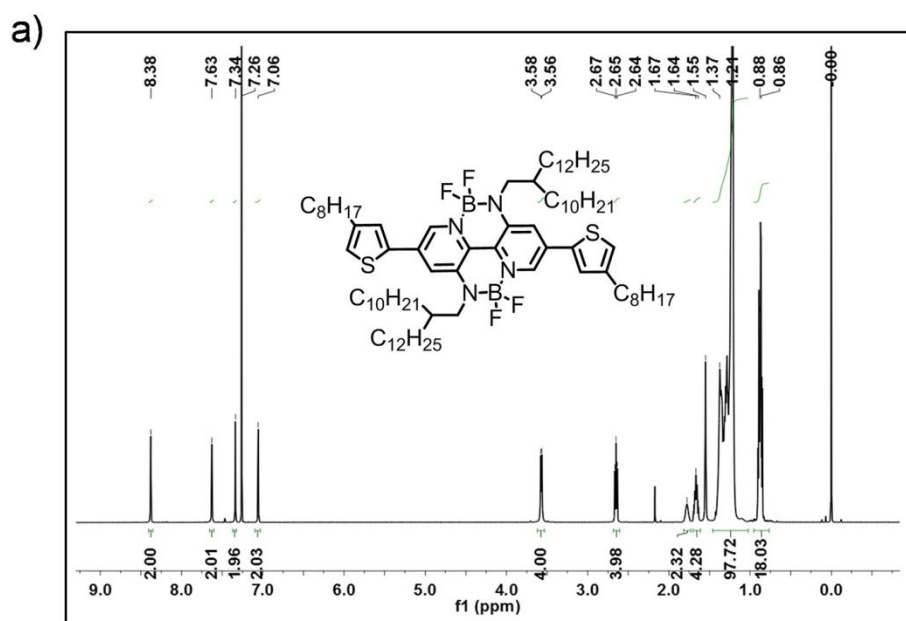


Figure S18. ^1H NMR spectrum of P-3T.



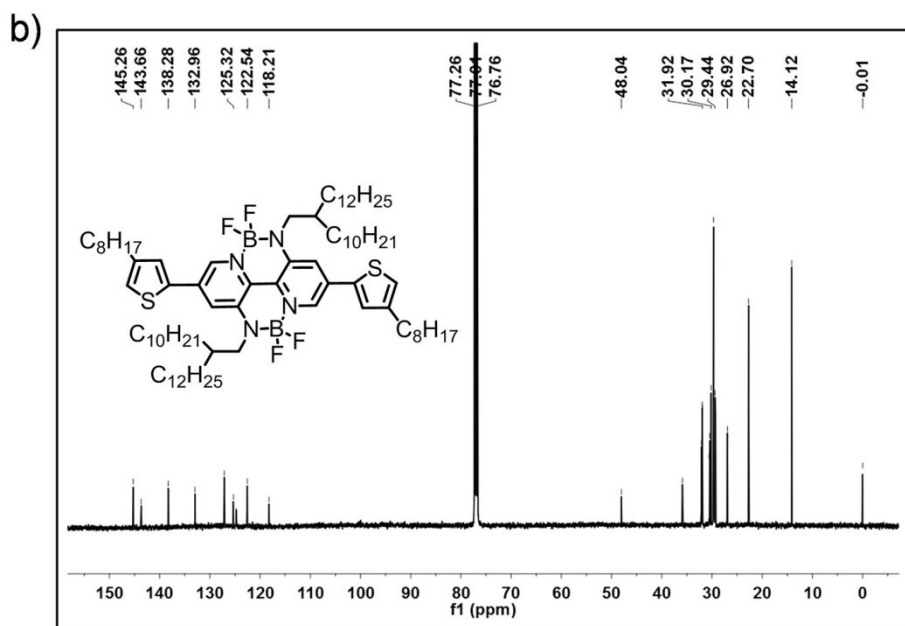
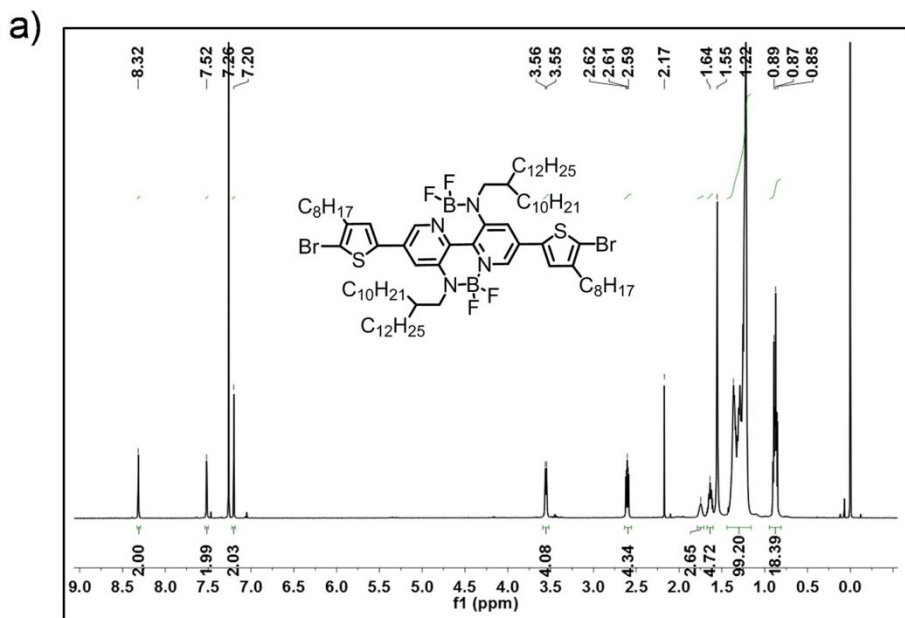


Figure S19. ¹H NMR and ¹³C NMR spectra of compound 2.



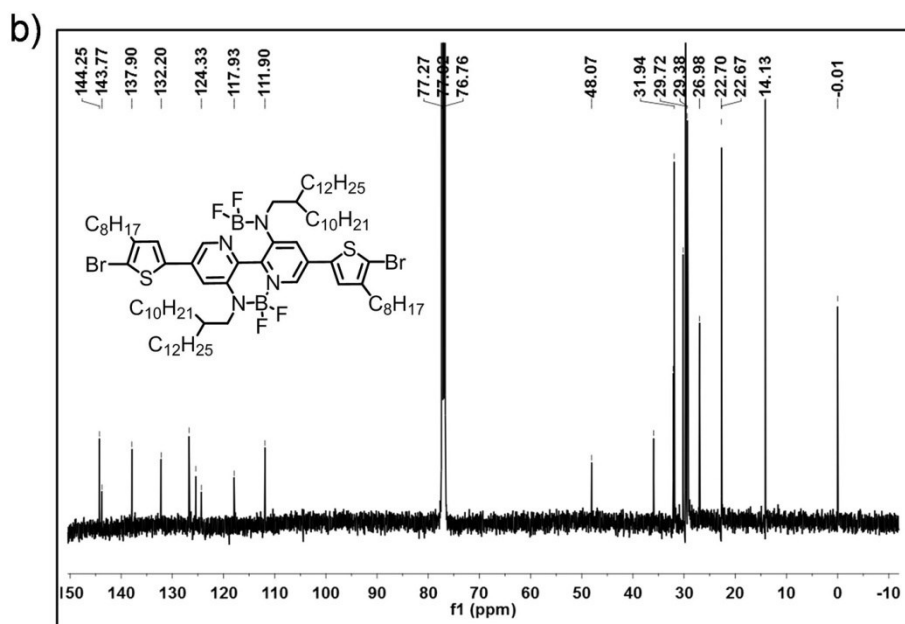


Figure S20. ¹H NMR and ¹³C NMR spectra of compound 3.

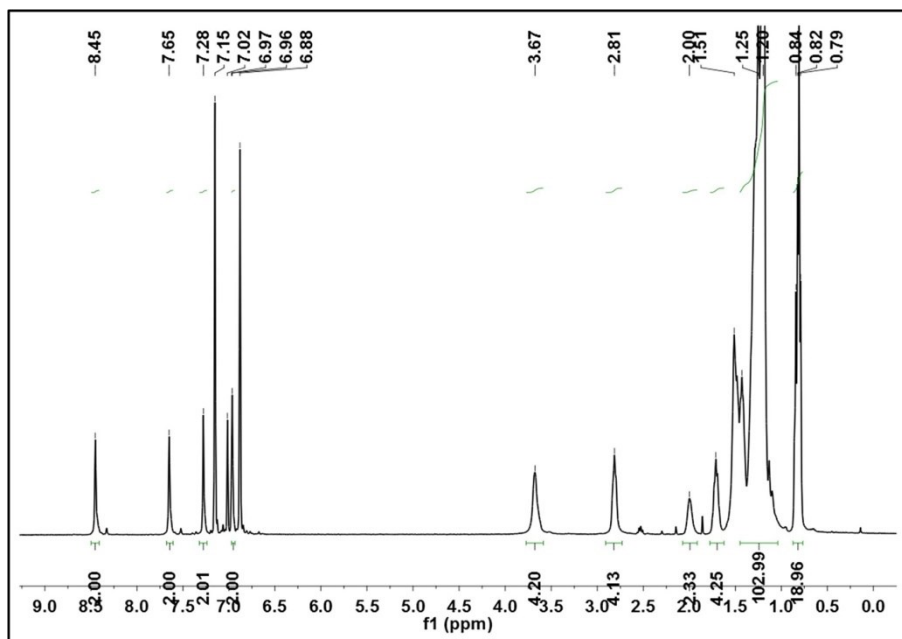


Figure S21. ¹H NMR spectrum of P-4T.

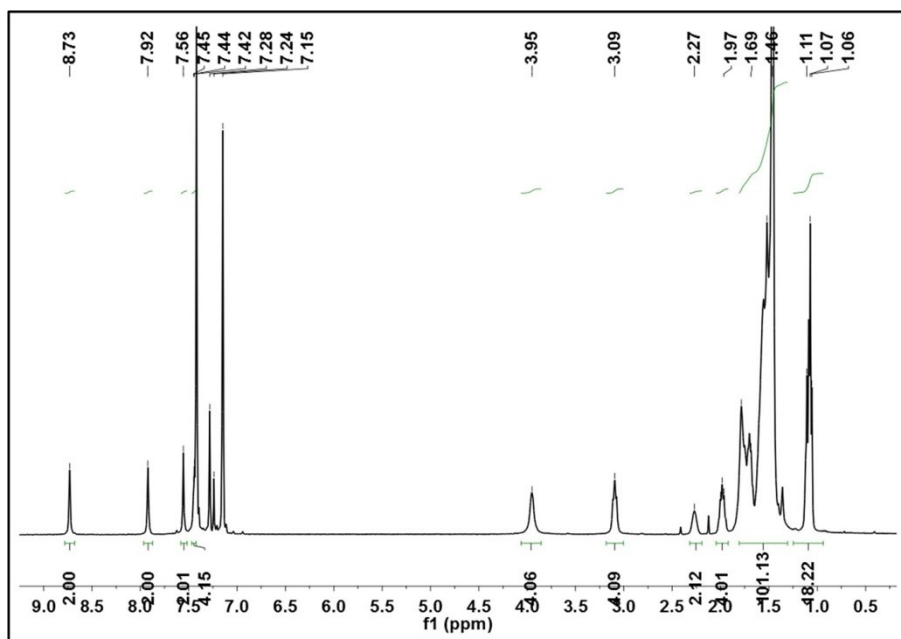


Figure S22. ^1H NMR spectrum of P-5T.

11. Reference

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- (2) K. Kawashima, T. Fukuhara, Y. Suda, Y. Suzuki, T. Koganezawa, H. Yoshida, H. Ohkita, I. Osaka and K. Takimiya, *J. Am. Chem. Soc.*, 2016, **138**, 10265-10275.