Supporting Information

Isomerization effect of benzothiophene-substituted benzodithiophene-based donor polymer on the blend morphology and photovoltaic performance of all-polymer solar cells

Jinping Lin,[a] Jiejie Wan,[a] Haifen Liu,[b] Zejiang Li,[d] Shuqi Chang,[b] Guangsheng Fu,[a] Shaopeng Yang,[a] and Lixin Wang*[a,c]

[a]Hebei Key Laboratory of Photo-Electricity Information and Materials, College of Physics Science and Technology, Hebei University, Baoding 071002, China
[b]School of Quality and Technical Supervision, Hebei University, Baoding 071002, China
[c]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.
[d]College of Chemistry and Materials Science, Hebei University, Baoding 071002, China

*Corresponding author: E-mail: wanglx2015@hbu.edu.cn

Materials

All reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. THF was distilled over sodium and benzophenone under nitrogen. 5-Bromobenzo[b]thiophene was purchased from Zhengzhou Alfa Chemical Co., Ltd. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione was purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. PEDOT:PSS Clevios P VP (AI 4083) was purchased from Heraeus (Germany). 2-Methyltetrahydrofuran was bought from Aladdin Scientific Corp. N2200 and PFN-Br was purchased from Solarmer Materials Inc. The electron-deficient monomer of 4,8-bis(5-bromothiophen-2-yl)-2,6-dioctyl-[1,2,3]triazolo[4,5-f]isoindole-5,7(2H,6H)-dione was synthesized according to previous reports.[1-2]

Characterizations

The ^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker AVANCEIII 600 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. UV−vis absorption spectra were recorded using a Hitachi U-3000 spectrometer. The electrochemical measurements were performed in a deoxygenated solution of tetra-n-butylammonium hexa fluorophosphate (0.1 M) in CH_3CN with a CHI604E electrochemical workstation, wherein a Pt plate working electrode coated with samples, a Pt wire counter electrode, and a $Ag/AgNO_3$ reference electrode were applied. AFM images were measured with MFP-3D, OXFORD, Britain in tapping mode. The steady-state PL were measured under excitation of a 470 nm pulsed laser with a power density of 15 $\mu J/cm^2$, based on an FLS920 (Edinburgh Instruments)

fluorescence spectrometer. The PL mapping and TRPL were performed by confocal fluorescence microscopy (ISS fastFLIM) with 405 nm, 1 MHZ in ambient air. A Micro Capture Pro coupled with Image J software was applied to obtain the contact angles of the substrates. XPS and UPS measurements were performed using a surface analysis system (ThermoFisher, ESCALAB 250Xi) equipped with a He discharge lamp ($h\nu$ = 21.22 eV) and a monochromatic Al-Kα x-ray gun. The X-ray spot size was 500 μm in diameter.

Synthesis
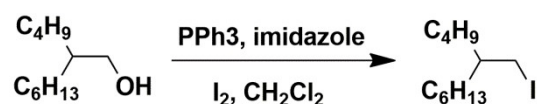
5-(iodomethyl)-undecane: Triphenylphosphine (6.3 g, 24 mmoL) and imidazole (1.63 g, 24 mmoL) were added to a 100 mL single-neck round-bottom flask, and then replaced the air in the flask by vacuuming and nitrogen filling. After injecting 2-butyl-1-n-octanol (3.88 g, 20.8 mmoL) and solvent dichloromethane (40 mL), cooled the system to 0℃, and then injected a solution of iodine in tetrahydrofuran (6.6 g iodine dissolved in 20 mL THF). After a few minutes, removed the cold bath and allow the system to react at room temperature for 24 hours. Added a saturated sodium sulfite solution and stirred vigorously until the system color no longer changed. After removing the solvent, added 150 mL petroleum ether to the remaining material, stirred and filtered off the white solid, and then the solution phase is extracted with ethyl acetate, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. After purification on a silica gel column, a colorless liquid (5.48 g, yield 89%) was obtained. ^{1}H NMR (CDCl$_3$, 600 MHz) δ 3.27 (d, J = 4.8 Hz, 2H), 1.31-1.20 (m, 16H), 1.12 (m, 1H), 0.91-0.87 (m, 6H).
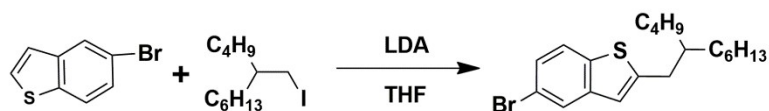

5-bromo-2-(2-butyl octyl) benzothiophene： 5-bromobenzothiophene (1.08 g, 5.07 mmoL) was dissolved in 15 mL tetrahydrofuran under a nitrogen atmosphere, and then the solution was cooled to -10 °C. LDA (1.0 M, 1.2 eqv.) was added dropwise, and then maintained the reaction at 0℃ for 1.5 h. Cooled the system again to -10℃, and 5-(iodomethyl)undecane (1.80 g, 1.2 eqv.) was added dropwise. The reactant was stirred at room temperature overnight. After quenching the reaction with water, extracted the crude product with petroleum ether. The organic phase was washed with water, dried over magnesium sulfate, and then the solvent was removed under reduced pressure. Purified the organic residue through a silica gel column (eluent: petroleum ether) to obtain 2.93 g of colorless liquid (yield 43%). (Contains some bromoalkane.) ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.79 (d, J = 1.9 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.33 (dd, J = 8.6, 1.9 Hz, 1H), 6.90 (s, 1H), 2.82 (d, J = 6.8 Hz, 2H), 1.70 (s, 1H), 1.32-1.08 (m, 16H), 0.95-0.78 (m, 6H).
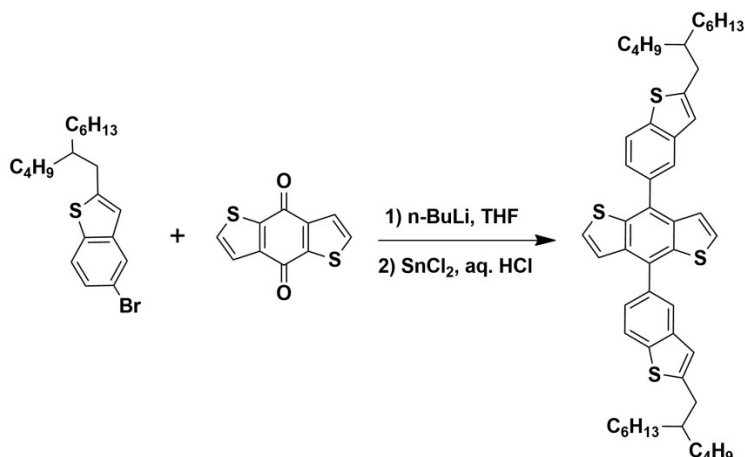
4,8-(2-(2-butyloctyl)benzothiophene-5-yl)benzodithiophene: In a 100 mL two-neck round-bottom flask, 5-bromo-2-(2-butyl octyl)benzothiophene (1.32 g, 3.46 mmoL) was dissolved in dry tetrahydrofuran (20 mL), and the air in the flask was removed by bubbling N_2. The reaction system was cooled to -78 °C using acetone/liquid nitrogen cold bath, and then n-BuLi (2.5 M, 1.05 eqv.) was added dropwise. The reaction was maintained below 0°C for 2 h. Benzodithiophene-4,8-dione (0.25 g, 1.13 mmoL) was added at low temperature, and after several moments, the cold bath was removed to allow the system to naturally return to room temperature. The reaction was stirred overnight. A dilute hydrochloric acid solution of $SnCl_2$ (3.3 g dissolved in 10 mL of 10% HCl) was added, and the reaction was allowed to proceed at room temperature for 12 h. 100 mL of CH_2Cl_2 was added for extraction and separation. The organic phase was dried and concentrated, and then the residue was purified using a silica gel column (eluent: petroleum ether:ethyl acetate = 50:1) to obtain 0.56 g of white solid (yield 63%). ^{1}H NMR (CDCl$_3$, 600 MHz) δ 8.01 (d, J = 1.7 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.60 (dd, J = 8.1, 1.7 Hz, 2H), 7.41-7.35 (m, 4H), 7.07 (s, 2H), 2.89 (d, J = 6.7 Hz, 4H), 1.79 (m, 2H), 1.42-1.27 (m, 32H), 0.92-0.87 (m, 12H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.86, 140.70, 139.36, 138.50, 136.42, 135.35, 130.62, 127.24, 124.76, 123.43, 123.13, 122.47, 121.75, 39.76, 35.48, 33.36, 33.07, 31.94, 29.68, 28.93, 26.65, 23.07, 22.72.
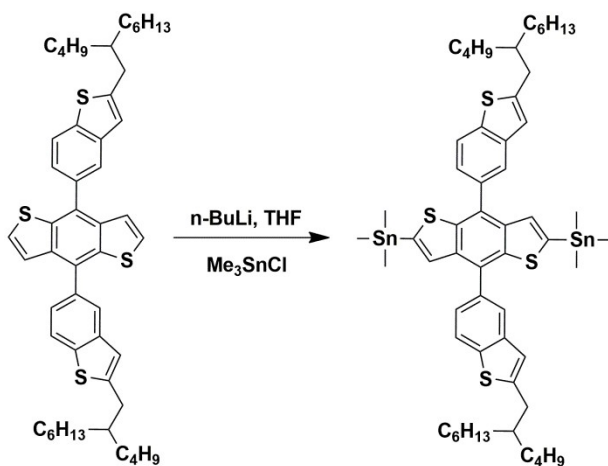
4,8-(2-(2-butyloctyl)benzothiophen-5-yl)benzodithiophene-2,6-trimethyltin: In a two-neck round-bottom flask, 4,8-(2-(2-butyloctyl)benzothiophen-5-yl)benzodithiophene (1.65 g, 2.1 mmoL) was dissolved in 50 mL degassed dry THF, and the system was cooled to -10 °C. n-BuLi (2.5 M, 6.3 mmoL) was added dropwise, and the reaction was stirred at -10 ~ -5 °C for 2 h. Then, trimethyltin chloride solution (1.38 g, 6.93 mmoL, 5 mL THF) was injected, and the reaction was stirred at room temperature overnight. Water was injected into the flask to quench the reaction, and the organics were extracted with dichloromethane. The organic phases were combined, washed with water, dried over $MgSO_4$, concentrated under reduced pressure, and the residue was purified using a silica gel column with 20:1 (v/v%) petroleum ether: ethyl acetate as the eluent. Finally, methanol was used for recrystallization to obtain 1.63 g of yellow solid (70% yield). ^1H NMR (CDCl$_3$, 600 MHz) δ 8.03 (s, 2H), 7.96 (d, $J =$ 8.1 Hz, 2H), 7.61 (d, $J =$ 8.1 Hz, 2H), 7.40 (s, 2H), 7.10 (s, 2H), 2.89 (d, $J =$ 6.7 Hz, 4H), 1.78 (m, 2H), 1.38-1.28 (m, 32H), 0.92-0.86 (m, 12H), 0.33 (s, 18H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 146.61, 142.78, 142.00, 140.67, 139.11, 137.24, 136.00, 130.85, 129.02, 124.99, 123.47, 122.38, 121.86, 39.73, 35.45, 33.34, 33.04, 31.91, 29.65, 28.89, 26.61, 23.04, 22.68, 14.17, 14.12, -8.35.
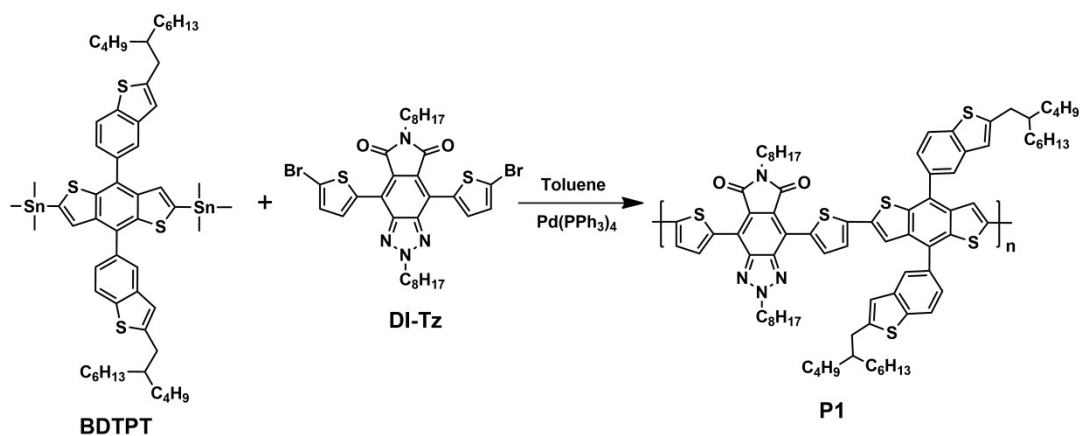
PBS-DIT: In a 5 mL microwave reaction tube, monomer BDTPT (77 mg, 0.069 mmol), monomer DI-Tz (51.3 mg, 0.069 mmol), and catalyst Pd(PPh3)4 (2.8 mg, 3.5 mol%) were added, respectively. The glass tube was sealed and subjected to vacuum and nitrogen gas filling operations. After injecting 2.5 mL of degassed toluene, the system was heated using an oil bath to 110°C, and maintained for 9 h. The reaction solution was cooled, added dropwise to methanol to precipitate a solid. Upon filtration, the filter cake was sequentially washed with methanol, acetone, and n-hexane using a Soxhlet extractor to remove impurities. Finally, the polymer was extracted into chloroform, concentrated under reduced pressure, and re-precipitated into methanol. Filtration to collect the target for vacuum drying to resulted in 74 mg of purple-black solid (yield 78%). GPC (THF): M_n = 84.4 kDa; PDI = 2.67.
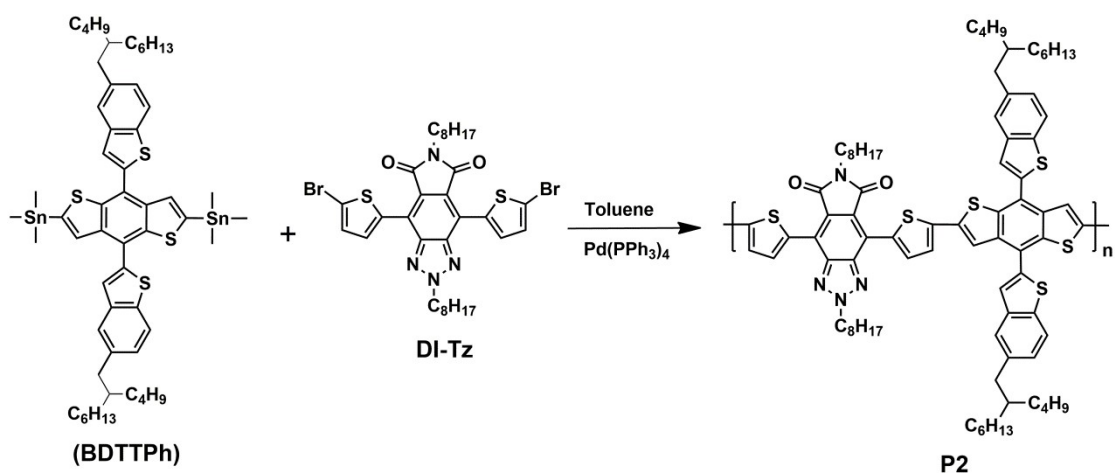
PTPh-DIT: The synthesis steps are the same as those of polymer **PBS-DIT**. The monomer BDTTPh was synthesized according to the literature (Macromolecules, 47(22), 7823-7830). Feeding and reaction conditions: BDTTPh (50 mg, 0.045 mmol), monomer DI-Tz (32.9 mg), 2 mL toluene, reaction for 6 hours, and 51 mg polymer product was obtained (yield 83%). GPC (THF): $M_n = 77.1$ kDa; PDI = 2.95.

Fabricaiton of all-polymer solar cells

A device configuration of ITO/PEDOT:PSS/Blend/PFN-Br/Ag was applied. The ITO-glass substrate was cleaned with detergent, deionized water, acetone, and isopropanol for 20 min each, and then was dried by a nitrogen flow before subjected to treatment with ultraviolet/ozone for 20 min. The thin layer of PEDOT:PSS was formed by spin-coating its solution on the surface of ITO at 3500 rpm for 50 s, followed by annealing at 130 °C for 15 min. Then, the device was transferred to a glove box to deposit the active layer. In a nitrogen-filled glove box, a mixture of PBS-DIT:N2200 (2:1, wt/wt) or PTPH-DT:N2200 (2:1, wt/wt) using 2-methyl tetrahydrofuran (MTHF) as a solvent was stirred at 90 °C in a capped vial for 30 min to ensure sufficient mixing. The active layer solution was spin-coated at 2000 rpm for 40 s. Afterward, the electron transport layer of PFN-Br was spin-coated at 3500 rpm for 30 s. Finally, the device was transferred to a vacuum evaporation chamber and metal electrodes were evaporated under low pressure (*ca.* 1×10^{-5} Pa). The overlapping area between the cathode and anode defined a pixel size of 0.08 cm². The *J-V* curves were measured using a computer-controlled Keithley 2400 source meter under AM 1.5G, 100 mW cm⁻² illumination, which was provided by a SAN-EIELS 155 (XE) solar simulator equipped with a standard monocrystalline silicon solar cell to calibrate the light intensity. The EQE data were measured by using a solar cell spectral response measurement system (Crowntech Inc.)
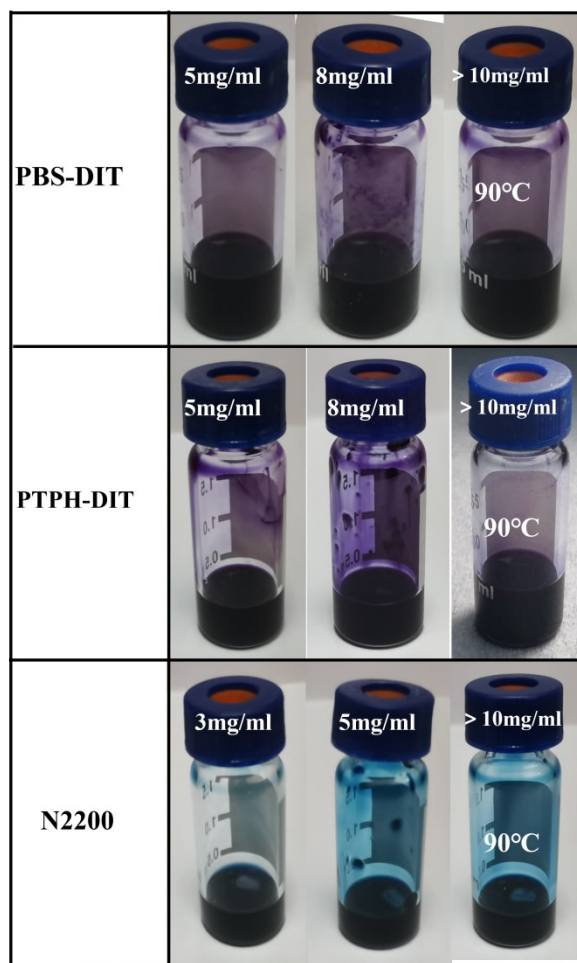
Figure S1. The solubility tests of PBS-DIT, PTPH-DIT, and N2200 in the MTHF solvent. The solubility changes were compared under a room temperature with two different concentrations and the 90 ℃ heating with an even higher concentration. The two polymer donors of PBS-DIT and PTPH-DIT and the polymer acceptor of N2200 all well dissolved in the hot solvent of MTHF with a concentration more than 10 mg/mL .
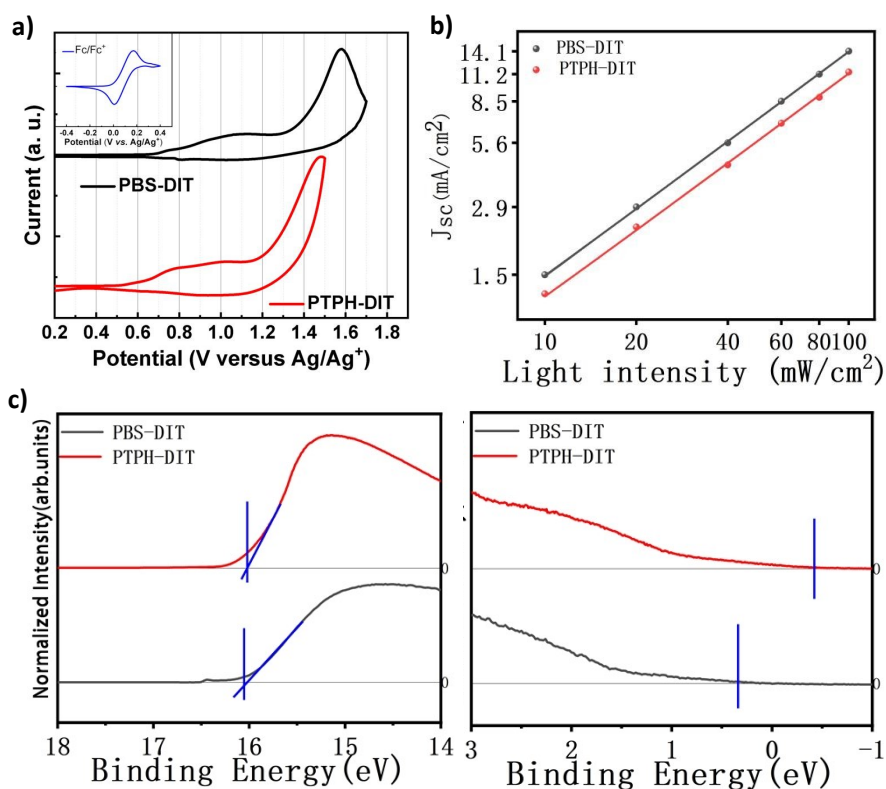
Figure S2. (a) Voltammetry cyclic curves of PBS-DIT, PTPH-DIT, and ferrocene; (b) J_{SC} dependence on light intensity for devices based on PBS-DIT and PTPH-DIT; c),d) UPS spectra of PBS-DIT and PTPH-DIT.
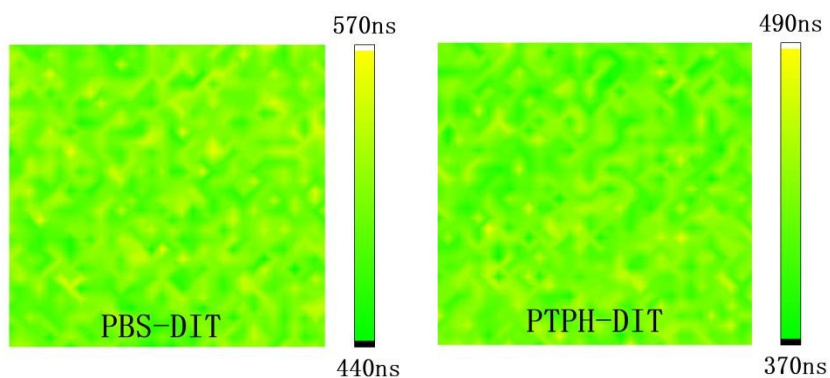
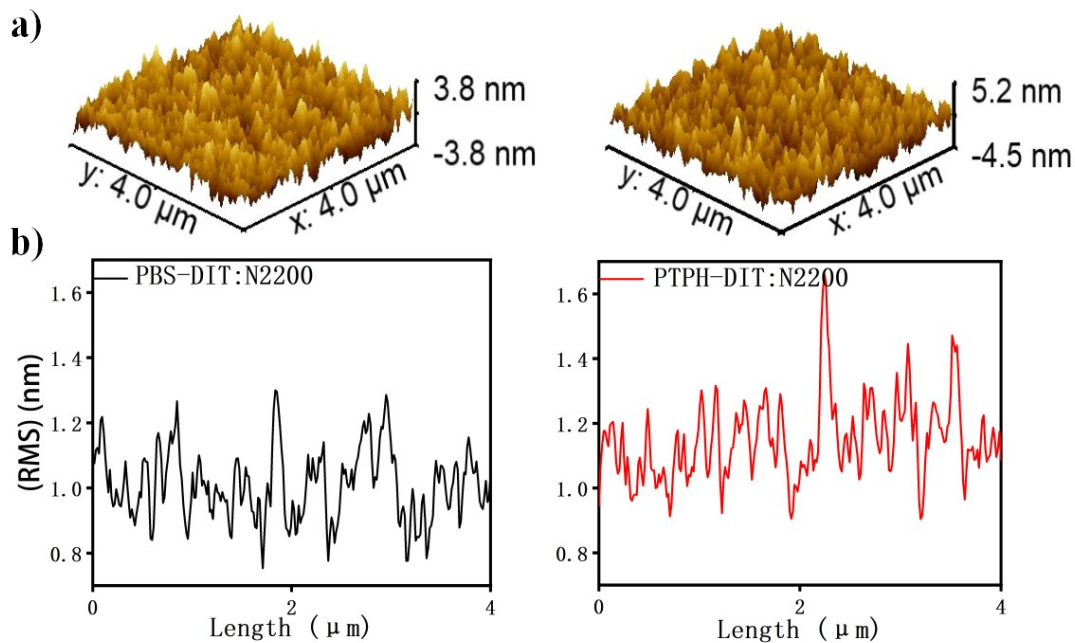**Figure S3.** Fluorescence lifetime mappings of PBS-DIT and PTPH-DIT pure films.

Figure S4. (a) AFM 3D topography of the surface of the blend of PBS-DIT:N2200 and PTPH-DIT:N2200. (b) Line-cut profiles of the rough surface of PBS-DIT:N2200 and PTPH-DIT:N2200.
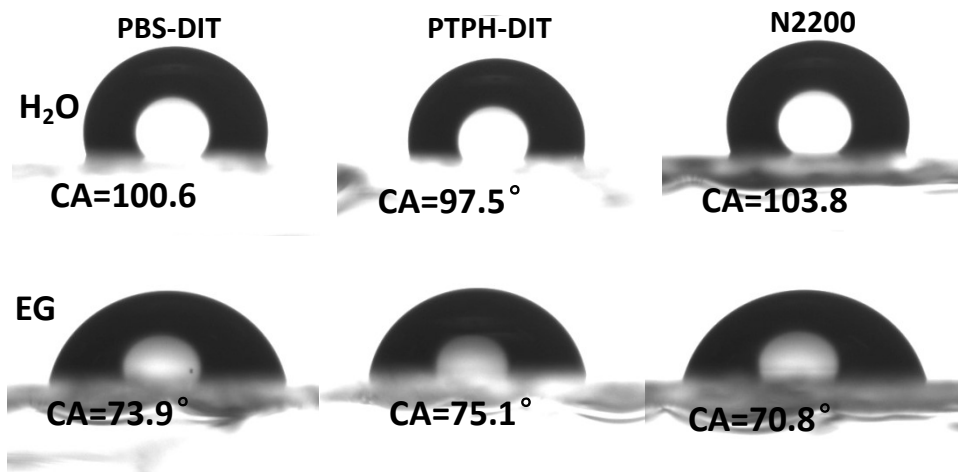

Figure S5. Contact angles of PBS-DIT, PTPH-DIT, and N2200 pure films under H_2O (top) and ethylene glycol (bottom) treatment.

Table S1. R_s and R_{rec} fitted according to different device impedance curves, and hole (μ_h) and electron (μ_e) mobilities calculated according to the space charge limited current (SCLC) method[a].

Blends	R_s (Ω)	R_{rec} (Ω)	μ_h(cm^2 V^{-1} s^{-1})	μ_e(cm^2 V^{-1} s^{-1})	μ_h/μ_e
PBS-DIT:N2200	12.1	824	4.2×10^{-4}	5.7×10^{-4}	0.74
PTPH-DIT:N2200	13.3	566	2.2×10^{-4}	4.2×10^{-4}	0.52

[a]Hole-only device of ITO/PEDOT:PSS/BHJ/MoO$_3$/Ag and electron-only device of ITO/ZnO/BHJ/PDINO/Ag was constructed. The film thickness of active layer was measured using a Bruker Dektak XT probe surface profilometer. The carrier mobilities were calculated according to $J = (9/8)\varepsilon_r\varepsilon_0\mu(V^2/L^3)$, where ε_0 is the permittivity of free space (8.85×10^{-12} F/m), ε_r is the dielectric constant of the organic active layer (assumed to be 3), μ is the hole or electron mobility, V is the voltage drop across the device, and L is the average active layer thickness. $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes.

Table S2. Lifetimes and weight fractions derived from time-resolved PL decay traces[a]; and summarized surface tension values and Flory-Huggins parameters for the films[b].

Films	A_1	τ_1	A_2	τ_2	τ_{ave}	γ^d (mN m^{-1})	γ^p (mN m^{-1})	γ (mN m^{-1})	$X_{D.A}$
PBS-DIT	32.8	6.4	92	68.7	66.7	21.16	1.32	22.48	-
PTPH-DIT	43.9	3.8	132	65.3	64.1	16.81	2.89	19.7	-
PBS-DIT:N2200	240	3.7	33	37.2	2.3	24.4	0.41	24.81	0.384 K
PTPH-DIT:N2200	109	13.3	40	43.9	30.1	18.49	2.25	20.74	0.883 K
N2200	-	-	-	-	-	28.52	0.19	28.71	-

[a]The TRPL decay curves were fitted by bi-exponential decay equation:

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) ; \quad I(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$$

Where τ_1 and τ_2 are the lifetimes of fast and slow decays. A1 and A2 are the corresponding weight fractions.

[b]The contact angles of water and ethylene glycol on the film were used to calculate the

surface tension by Fowkes approximation:[3]

$$\gamma_L(1+\cos\theta) = 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} + 2(\gamma_S^p \cdot \gamma_L^p)^{1/2}$$

$$\gamma = \gamma^d + \gamma^p$$

Where θ is the droplet contact angle on the organic thin film, γ is the surface tension of the film which is the sum of dispersion (γ^d) and polarity (γ^p) components. γ_s^d and γ_L^d refer to dispersion part of film surface and liquid, and γ_s^p and γ_L^p refer to polarity part of solid surface and liquid.

The compatibility between two materials can be deduced from the empirical formula of Flory- Huggins parameter:

$$X_{D.A} = K(\sqrt{\gamma_A} - \sqrt{\gamma_D})^2$$

Where K is a constant, and γ_D and γ_A are the surface free energies of the donor and acceptor materials.

Table S3. Investigation of device performance when using chlorobenzene and chloroform as solvents. The concentration of the active layer is 9 mg/mL. The data is derived from the average of 12 devices.

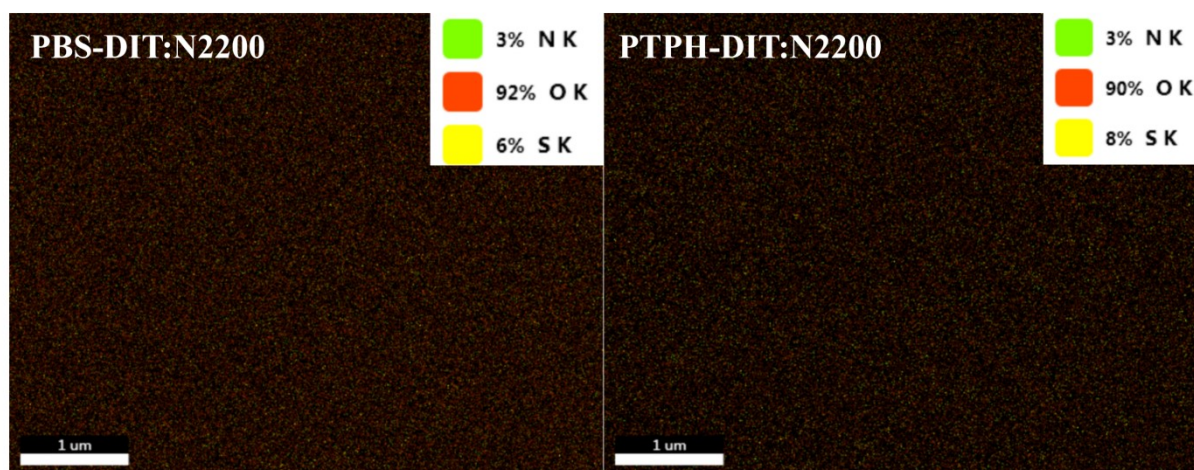| Solvent	Blend	Jsc (mA/cm²)	Voc (V)	FF (%)	PCE (%)
CF	PBS-DIT:N2200	10.5 ± 0.55	0.925	53.53 ± 2.2	6.29 ± 0.35
	PTPH-DIT:N2200	9.7 ± 0.42	0.920	54.5 ± 1.7	4.95 ± 0.34
CB	PBS-DIT:N2200	9.24±0.22	0.911	61.1±2.3	5.14±0.20
	PTPH-DIT:N2200	6.49±0.21	0.900	50.9±2.3	3.07±0.18

Figure S6. EDS mappings of N, O, and S on the surfaces of the two blended films of PBS-DIT:N2200 and PTPH-DIT:N2200.
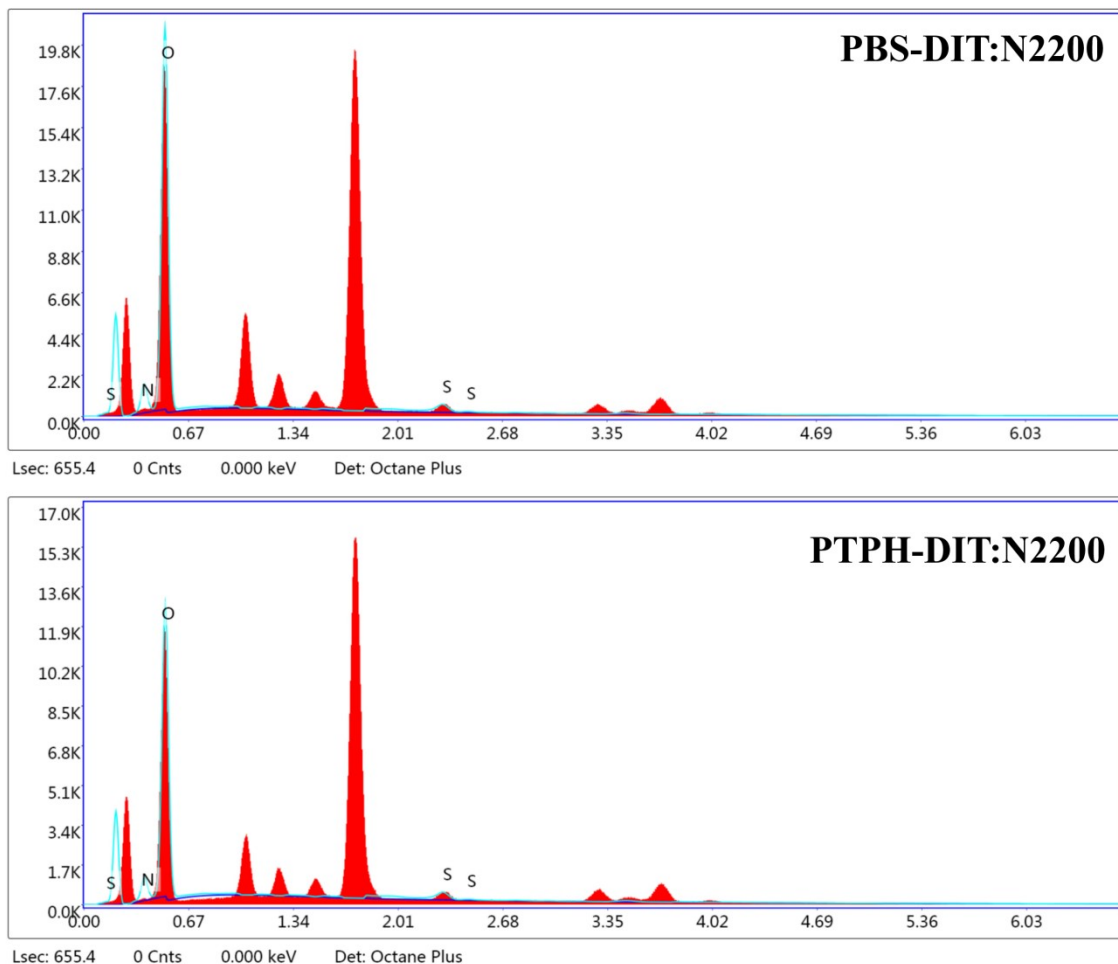
Figure S7. EDS element signal peaks of the two blended films of PBS-DIT:N2200 and PTPH-DIT:N2200.

Table S4.The proportion of N, S, and O elements on the surface of the thin film analyzed by EDS.

Blend	Element Atomic %		
	N K	O K	S K
PBS-DIT:N2200	10.98	86.95	2.08
PTPH-DIT:N2200	11.20	86.24	2.56
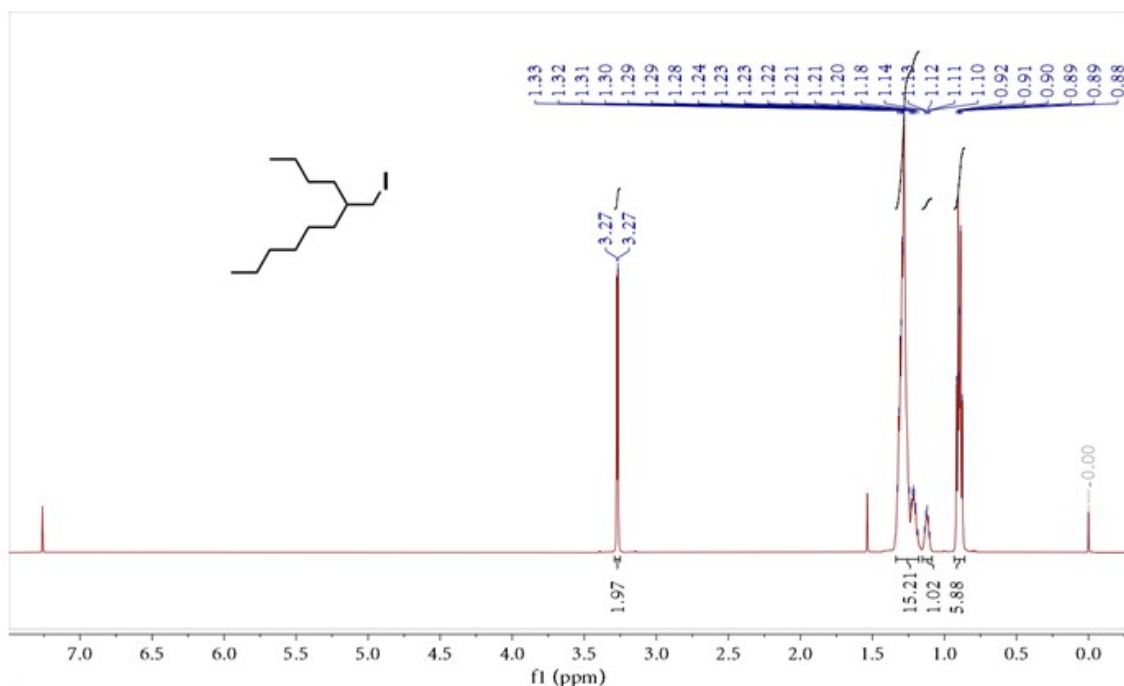
Figure S8. ^{1}H NMR spectrum of 5-(iodomethyl)-undecane.
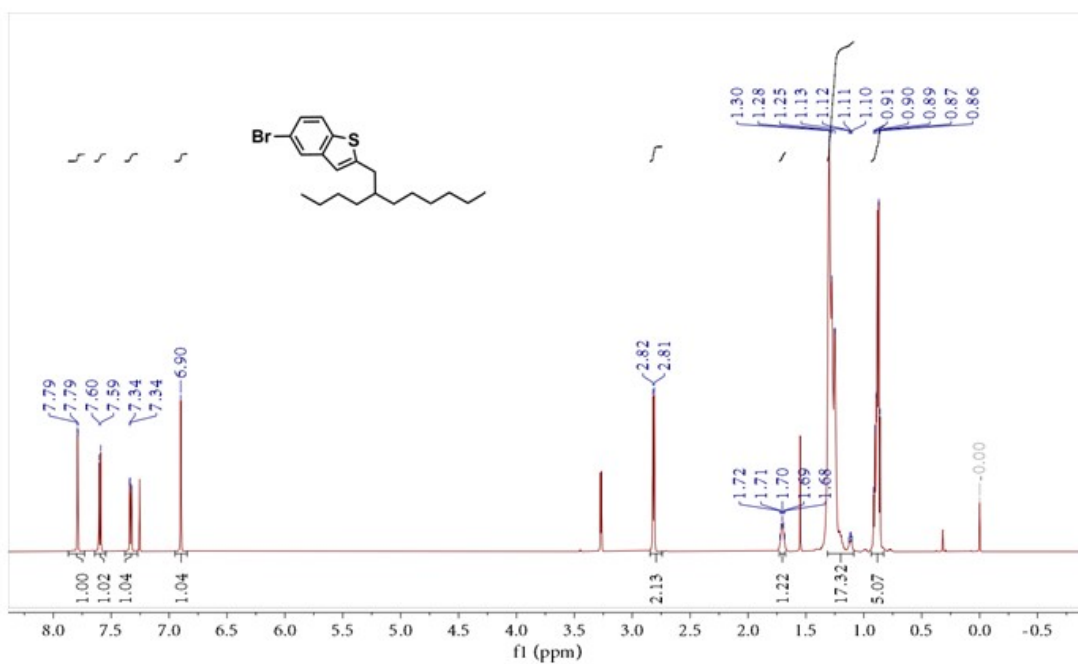
Figure S9. ^{1}H NMR spectrum of 5-bromo-2-(2-butyloctyl) benzothiophene (containing some 5-(iodomethyl)-undecane).
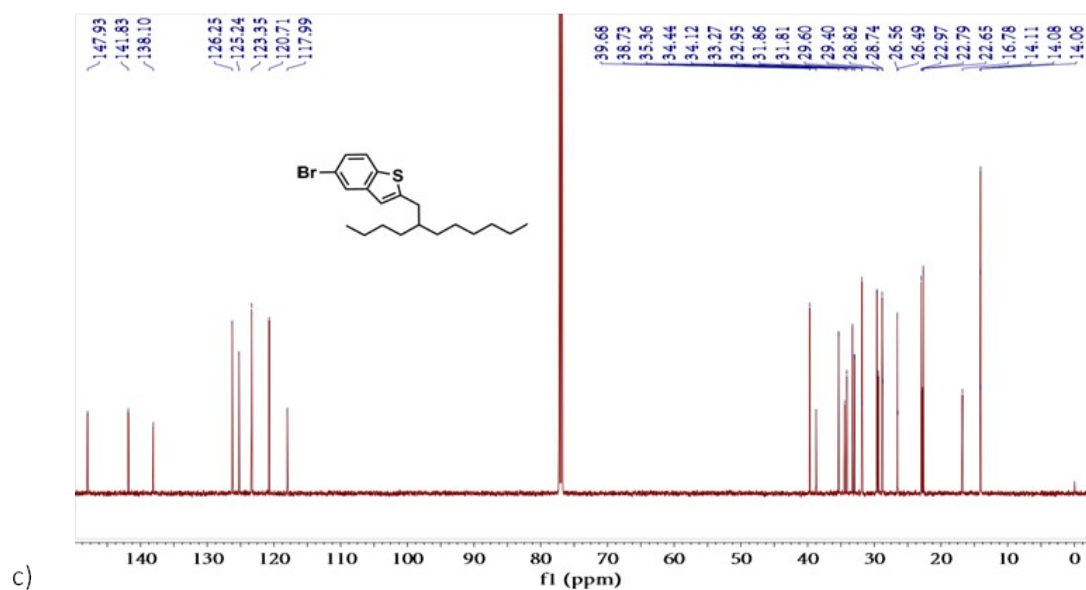
Figure S10. ^{13}C NMR spectrum of 5-bromo-2-(2-butyloctyl)benzothiophene (containing some 5-(iodomethyl)-undecane).
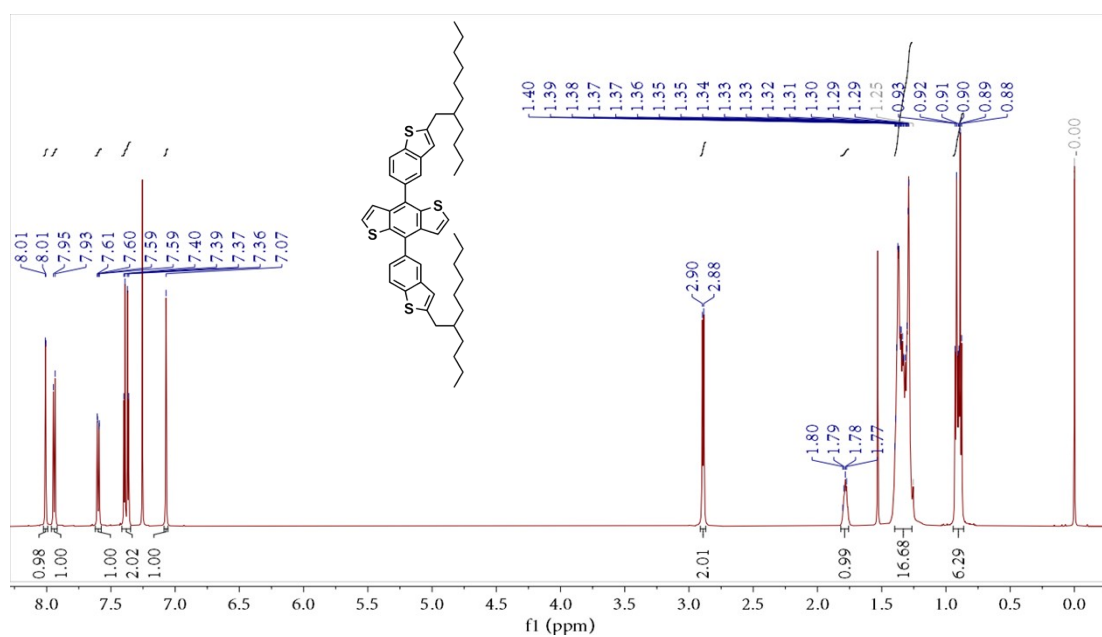
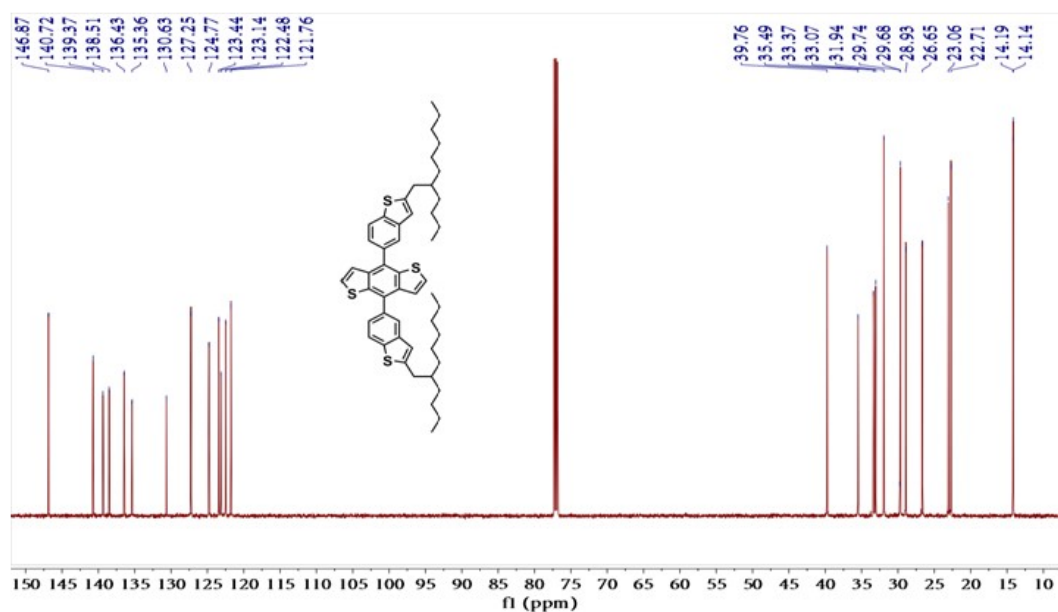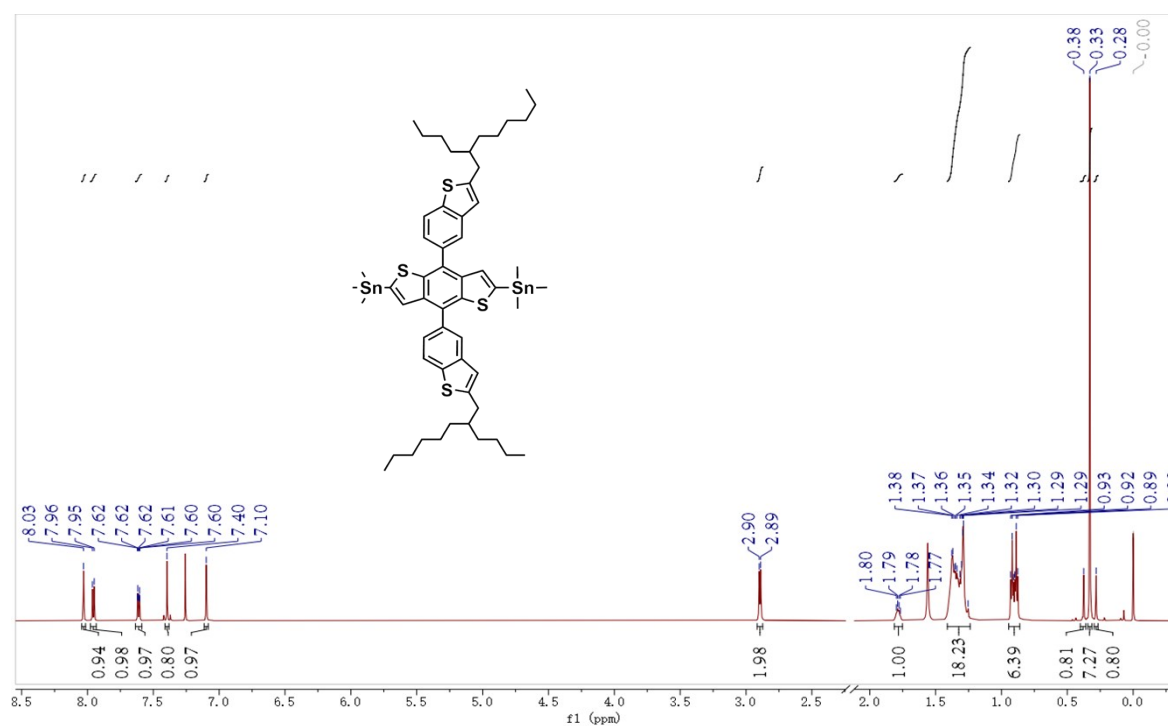**Figure S11**. ^{1}H NMR spectrum of 4,8-(2-(2-butyloctyl)benzothiophene-5-yl)benzodithiophene

Figure S12. ^{13}C NMR spectrum of 4,8-(2-(2-butyloctyl)benzothiophene-5-yl)benzodithio phene-5-yl)benzodithiophene.

Figure S13. ^{1}H NMR spectrum of 4,8-(2-(2-butyloctyl)benzothiophen-5-yl)benzodithiophene -2,6-trimethyltin.
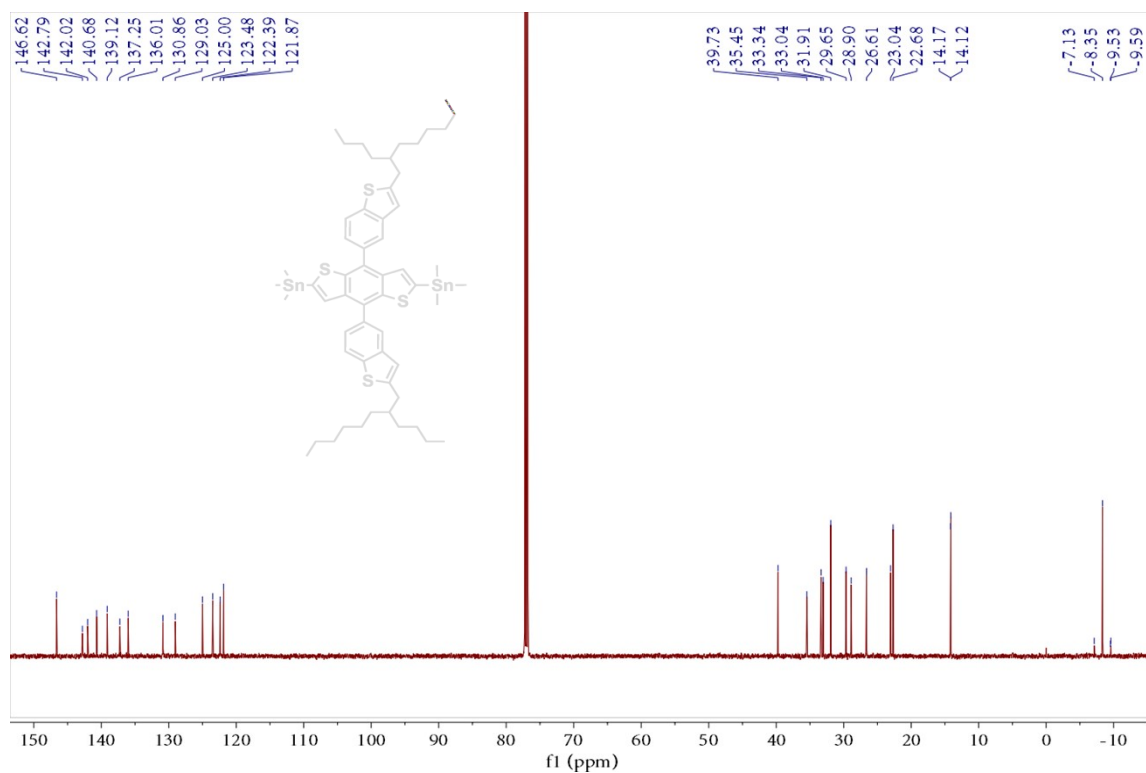
Figure S14. ^{13}C NMR spectrum of 4,8-(2-(2-butyloctyl)benzothiophen-5-yl)benzodithiophene -2,6-trimethyltin.
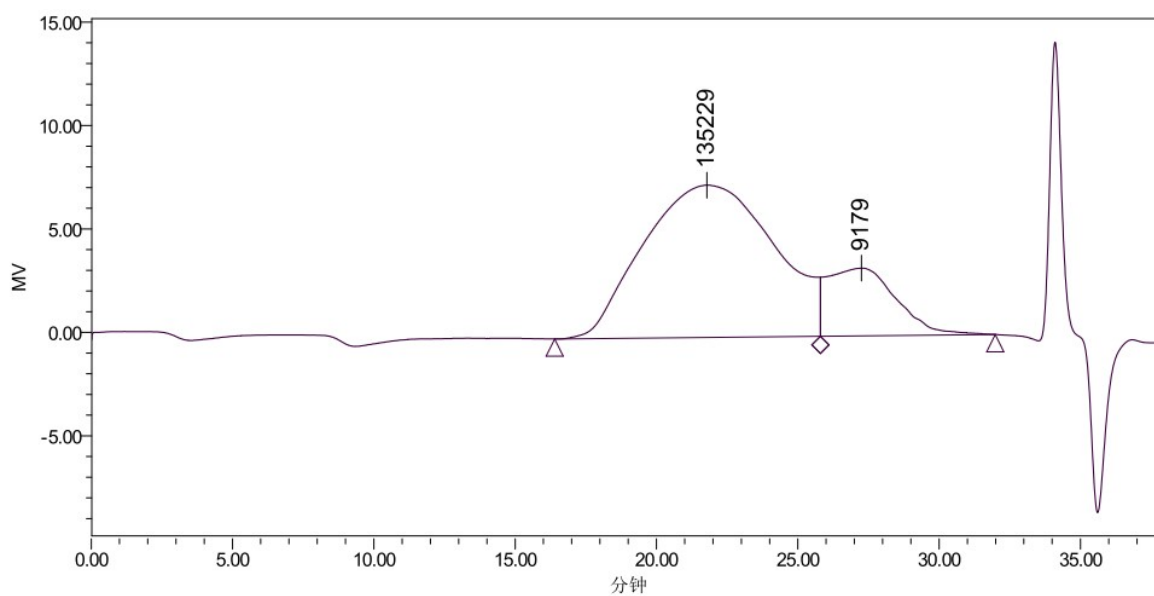

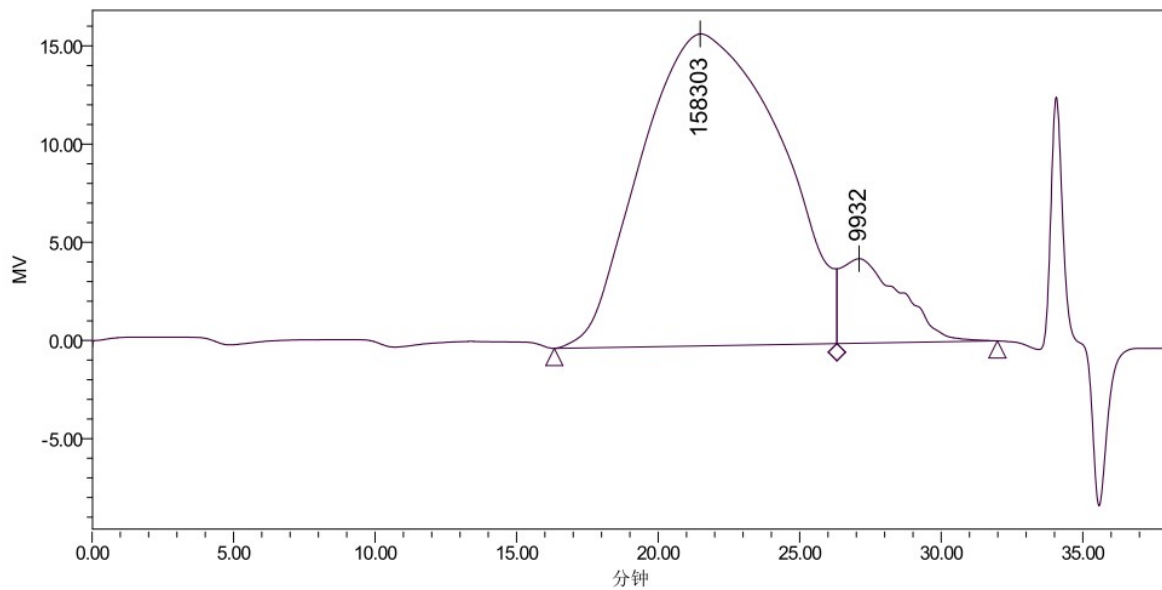**Figure S15**. The GPC eluting curve of PBS-DIT measured with THF as the solvent.

Figure S16. The GPC eluting curve of PTPH-DIT measured with THF as the solvent.
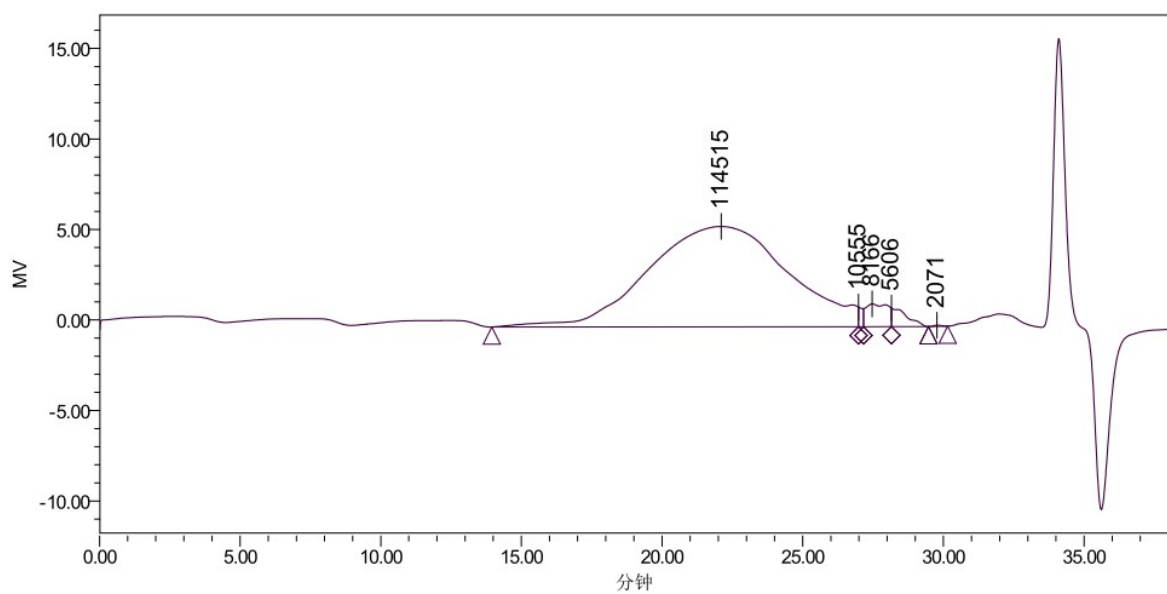

Figure S17. The GPC eluting curve of N2200 measured with THF as the solvent.

1. Wang, L.; Cai, D.; Zheng, Q.; Tang, C.; Chen, S.-C.; Yin, Z., Low Band Gap Polymers Incorporating a Dicarboxylic Imide-Derived Acceptor Moiety for Efficient Polymer Solar Cells. *ACS Macro Lett.* **2013,** *2* (7), 605-608.

2. Lan, L.; Chen, Z.; Hu, Q.; Ying, L.; Zhu, R.; Liu, F.; Russell, T. P.; Huang, F.; Cao, Y., High-Performance Polymer Solar Cells Based on a Wide-Bandgap Polymer Containing Pyrrolo[3,4-f]benzotriazole-5,7-dione with a Power Conversion Efficiency of 8.63%. *Adv. Sci.* **2016,** *3* (9), 1600032.

3. Comyn, J., Contact Angles and Adhesive Bonding. *Int. J. Adhesion and Adhesives* **1992,** *12* (3), 145-149.