BODIPY-Modified Terpolymer Donors for Efficient Fullerene- and Nonfullerene-Polymer Solar Cells

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Materials and characterizations

All solvents were purchased from Sigma Aldrich Co., Energy Chemical Co., Alfa Aesar without further purification. $PC_{71}BM$ was purchased from Vizu Chem (Shanghai). IEICO-4F was purchased from Nanjing Zhiyan Technology Co., Ltd. As for the monomers in polymerizing, 8-Bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-T unit) and 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (TT-F unit) were purchased from Suna Tech without further purification. And bodipy monomer 2,8-dibromo-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine was purchased from chemextension Co., Ltd.

^1H NMR spectra was recorded on a Bruker DMX-400 spectrometer in deuterochloroform using tetramethylsilane (TMS; δ=0 ppm) as an internal standard. ^{19}F NMR spectra was detected on a Bruker DMX-400 spectrometer. The molecular weights of the polymers acceptors were estimated by gel permeation chromatography (GPC) on Agilent PL-GPC-220 using *o*-dichlorobenzene as the eluent at 120°C with polystyrenes as the internal standards. Thermogravimetric analysis (TGA) was undertaken with a METTLER TOLEDO TGA2 instrument. The thermal stability of the samples was determined by measuring their weight loss at a heating rate of 10°C min^{-1} from 25 to 500°C using 3 mg sample under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10°C min^{-1} from 25 to 350°C, under argon. Ultraviolet-visible (UV–vis) absorption spectra of solution in chloroform and thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. The simulated chemical geometry of the polymer monomers was conducted using the Gaussian 09 program package at B3LYP/(def2svp) level. The electrochemical cyclic voltammetry was conducted on a CHI voltammetric analyzer, in a 0.1 mol L^{-1} acetonitrile solution of tetrabutylammonium hexafluorophosphate (*n*-Bu$_4$NPF$_6$) at a potential scan rate of 100 mV s^{-1}. The conventional three electrode configuration consists of a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl wire pseudo-reference electrode. The polymer sample was coated on the

platinum sheet of working electrode. The reference electrode was checked versus ferrocenium-ferrocene (Fc$^+$/Fc) as internal standard as recommended by IUPAC (the vacuum energy level: 24.8 eV). All the solutions were deaerated by bubbling nitrogen gas for a few minutes prior to the electrochemical measurements. HOMO energy levels were calculated from the equation of E_{HOMO}=-($E_{onset(ox)}$+4.80) eV, and LUMO from E_{LUMO}=-($E_{onset(red)}$+4.80) eV. *J-V* curves of PSCs were measured on a computer-controlled Keithley 2400 Source Measure Unit. Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a silicon reference cell. EQE spectra was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The contact angle measurements were performed through KRUSS DSA1005 contact angle analyzer. Distilled deionized water and diiodomethane were employed as probe liquids. The surface energy were calculated via Owens-Wendt model: $\gamma_L(1+cos\vartheta)=2[(\gamma_d^S\times\gamma_d^L)^{1/2}+(\gamma_p^S\times\gamma_p^L)^{1/2}]$, where the superscripts γ_d and γ_p stand for the dispersion and polar components of the surface energy, as well as *L* and *S* refer to the probe liquid and film sample, respectively. Blend film morphologies were characterized via Bruker Dimension ICON atomic force microscopy.

Fabrication of Polymer Solar Cell Devices

Polymer solar cells (PSCs) in inverted structure of ITO/ZnO/active layer/MoO$_3$/Ag were fabricated. ITO (patterned indium tin oxide) glass was cleaned in an ultrasonic bath with acetone and isopropanol solvents, and treated in an ultraviolet-ozone chamber for 30 min. ZnO was prepared according to literature reported procedures and deposited through spin-coating onto ITO glass at 4000 rpm followed by thermal treatment at 200°C for 1 h.[1] The thickness of ZnO layer was calculated as 40 nm. Afterwards, the active layer was spin-coated. Finally, a layer of ca. 8 nm MoO$_3$ and then a Ag layer of *ca.* 100 nm were evaporated subsequently under high vacuum (*approx.* 8×10^{-5} Pa). For fullerene-based PSCs, polymer donors:PC$_{71}$BM (1:1.5, w/w) with total concentration of 25 mg mL^{-1} mixed in CB:DIO (97:3, v/v) solution were spin-

coated at 2000 rpm to form ~120 nm thickness active layers. On the other side, for non-fullerene PSCs, polymer donors:IEICO-4F (1:1.5, w/w, 25 mg mL^{-1}) blend in CB solution was spin-casting at 2000 rpm with 1% (v/v) DIO as the solvent additive. The thickness of active layers of non-fullerene systems were calculated around 130 nm. For both systems, no thermal-annealing process were employed.

Fabrication of hole- and electron-only devices for SCLC measurements

Hole and electron mobility were measured using the space charge limited current (SCLC) method. The hole-only devices with the device structure of ITO/PEDOT:PSS/active layer/Au were used to measure the hole mobility and the electron-only devices were fabricated with the configuration of ITO/ZnO/active layer/PDINO/Al. And the processing details of blend films were same with the fabricating conditions of all-PSCs. The thickness of active layers and buffer layers was measured with stylus profiler (KLA Tencor P-7). The hole and electron mobilities were calculated by Mott–Gurney equation.[2,3]

Polymerization of polymer donors

8-Bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene (BDT-T) (135 mg, 0.15 mmol), 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate (TT-F) (70.48 mg, 0.15 mmol) and the third monomer, 2,8-dibromo-5,5-difluoro-1,3,7,9-tetramethyl-10-phenyl-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (bodipy unit) were added according to different feed ratios together with anhydrous toluene (6 mL) were added to a 50 mL Schlenk bottle and purged with argon for 15 min. Then, 7.5 mg (4.3 mmol%) Pd(PPh$_3$)$_4$ was added to the reaction container. After flushing under argon for another 20 min, the reaction mixture was placed in an oil bath and stirred at 110°C for 12 h. The mixture was cooled to room temperature and poured into methanol (400 mL); then, the product was filtered with a Soxhlet thimble, where methanol, hexane, and chloroform (CF) were used for Soxhlet extraction. Finally, the extraction from chloroform was concentrated and precipitated with methanol again before drying under vacuum to get dried and dark solid.

For copolymer PTB7-Th: The feed ratio of polymerizing monomers BDT-T:TT-F was 1:1 (mol %). Yield: 141 mg (68.4%). M_n=69 kg/mol, M_w=179 kg/mol, PDI=2.59.

For terpolymer PTB7-Th-bdp5: The feed ratio of BDT-T:TT-F:bodipy was 1:0.95:0.05 (mol %). Yield: 128 mg (62.1%). M_n=122 kg/mol, M_w=400 kg/mol, PDI=3.28.

For terpolymer PTB7-Th-bdp10: The feed ratio of BDT-T:TT-F:bodipy was 1:0.90:0.10 (mol %). Yield: 137 mg (66.5%). M_n=98 kg/mol, M_w=414 kg/mol, PDI=4.22.

Reference in Supporting Information

(1) Y. M. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.,* 2011, **23**, 1679-1683.

(2) P. W. M. Blom, J. M. Jong and M. G. Munster, *Phys. Rev. B*., 1997, **55**, R656-R659.

(3) G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys. Rev. B*., 1998, **58**, R13411-R13414.
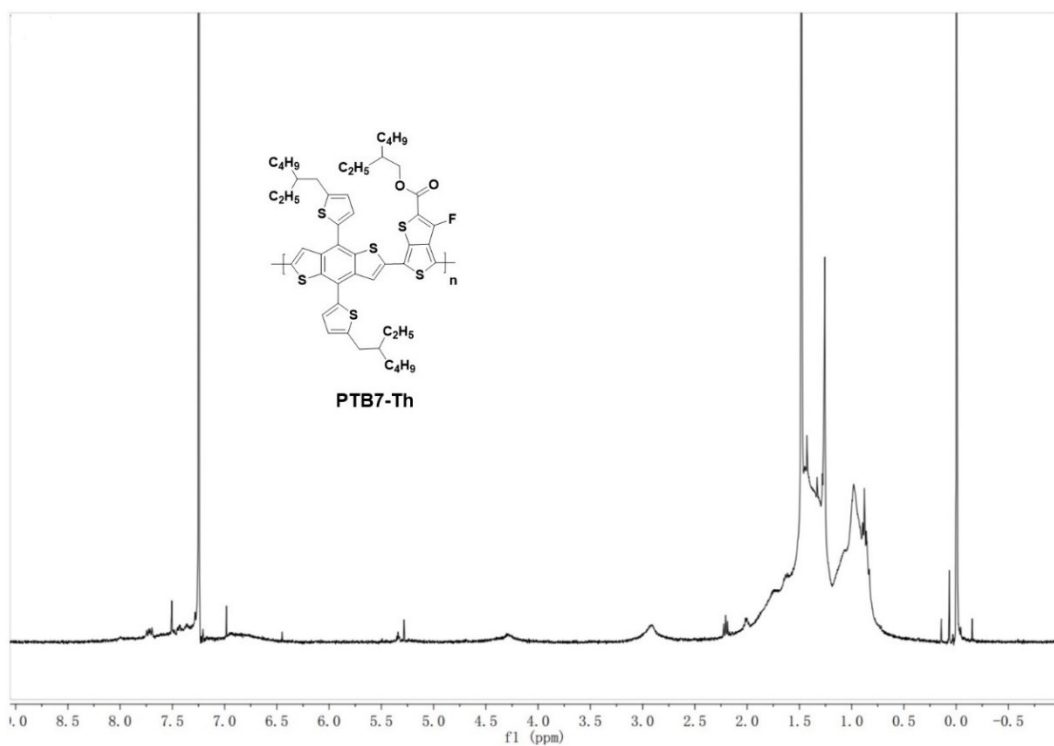
Figure S1. ^{1}H NMR spectra of copolymer PTB7-Th.
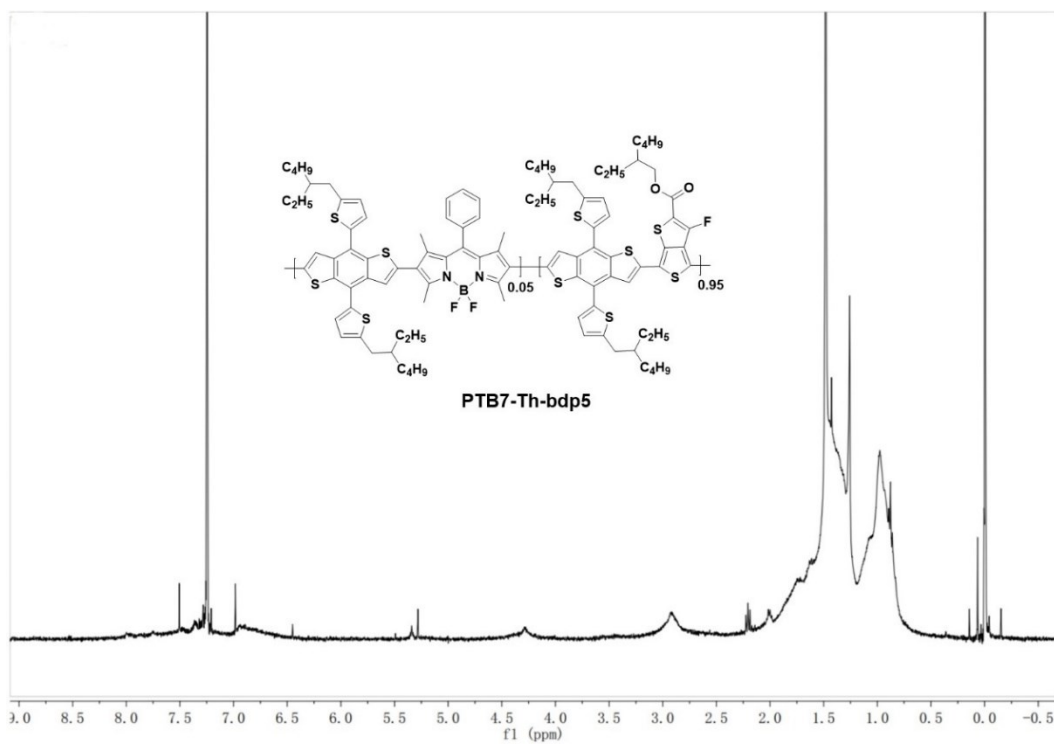
Figure S2. ^{1}H NMR spectra of terpolymer PTB7-Th-bdp5.
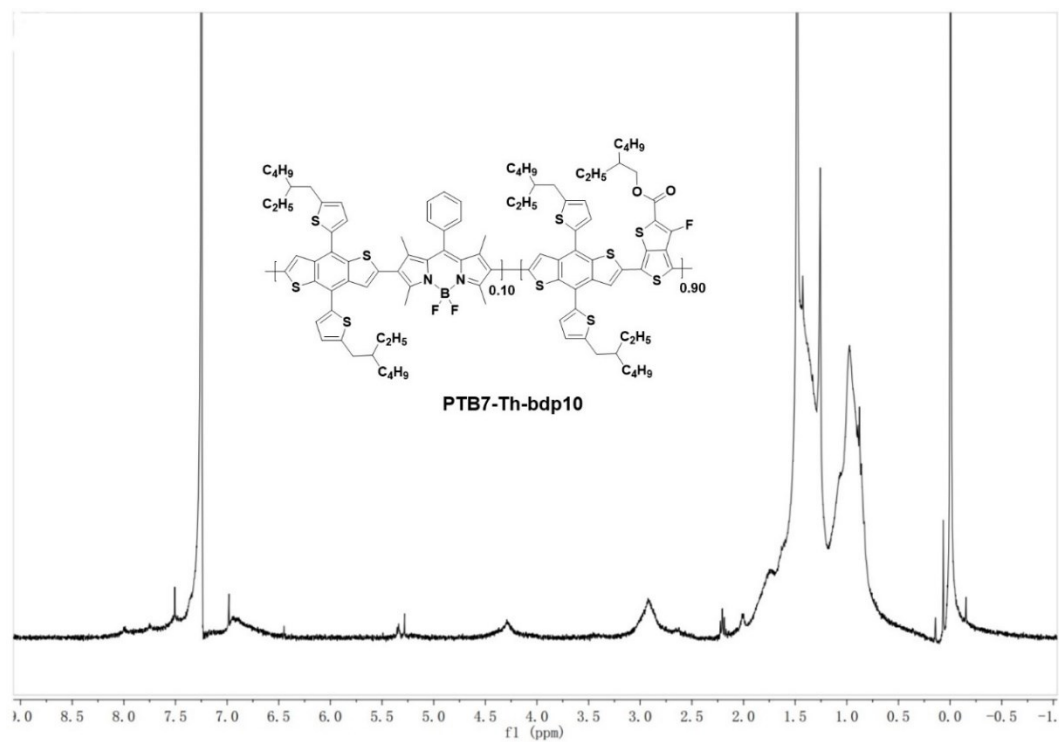
Figure S3. ^{1}H NMR spectra of terpolymer PTB7-Th-bdp10.
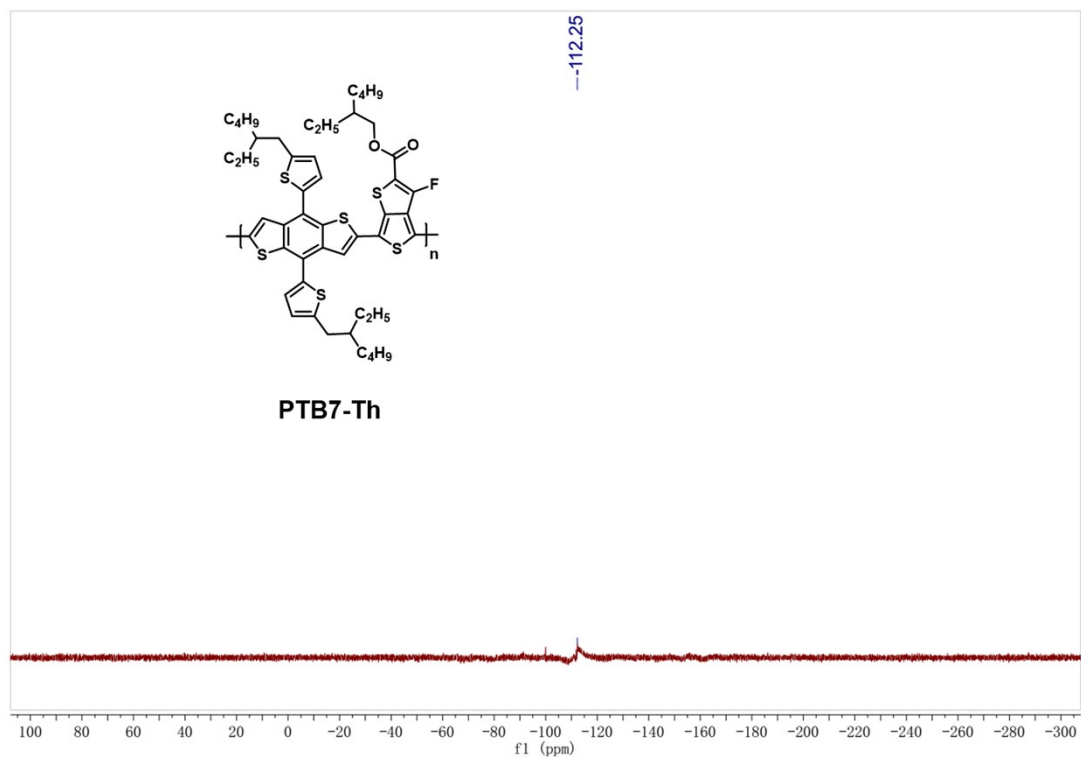
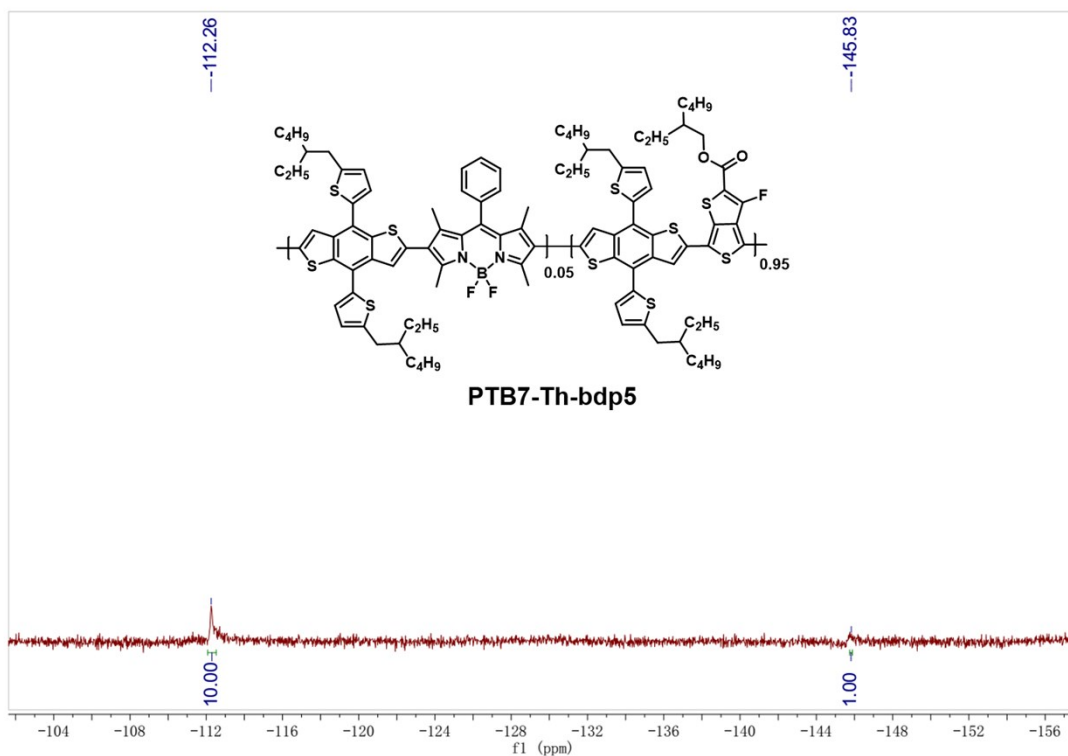**Figure S4**. ^{19}F NMR spectra of copolymer PTB7-Th.

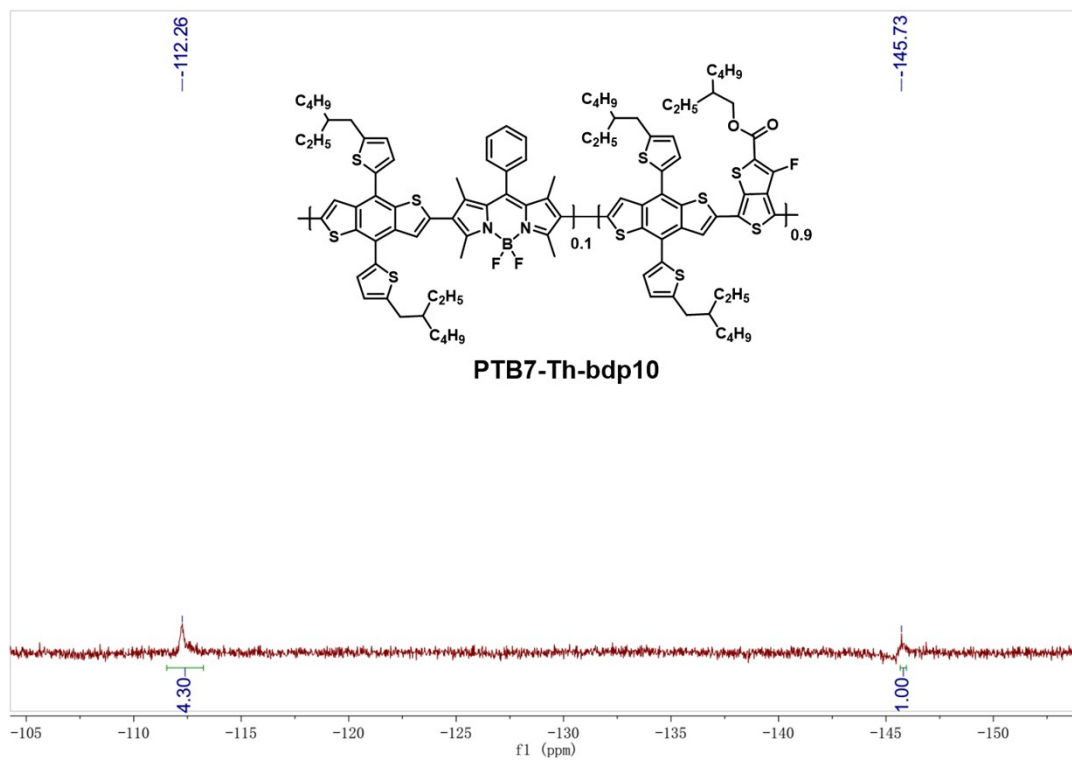**Figure S5**. ^{19}F NMR spectra of BODIPY-modified terpolymer PTB7-Th-bdp5.

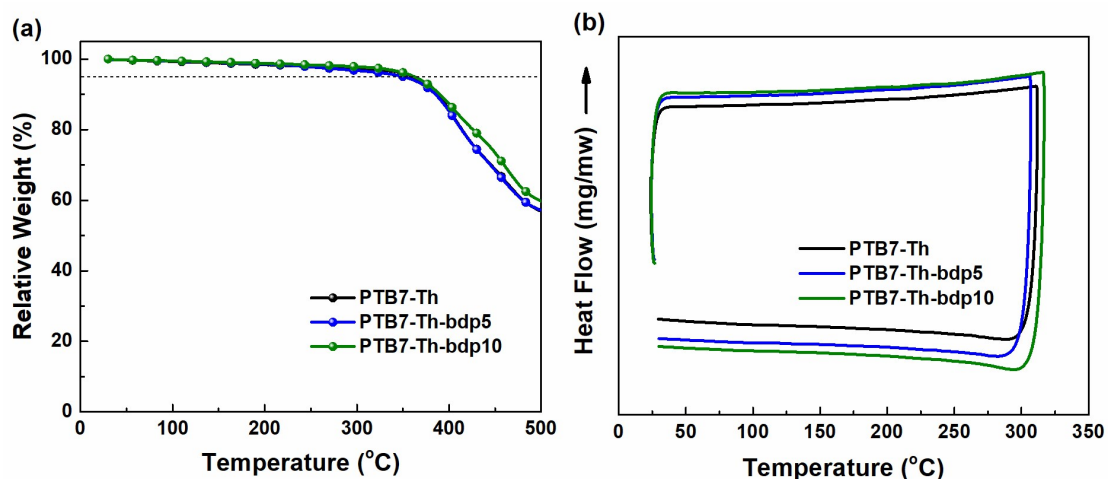**Figure S6**. ^{19}F NMR spectra of BODIPY-modified terpolymer PTB7-Th-bdp10.

Figure S7. Thermogravimetric analysis (TGA) curves (a) and differential scanning calorimetry (DSC) curves for as-synthesized polymers.
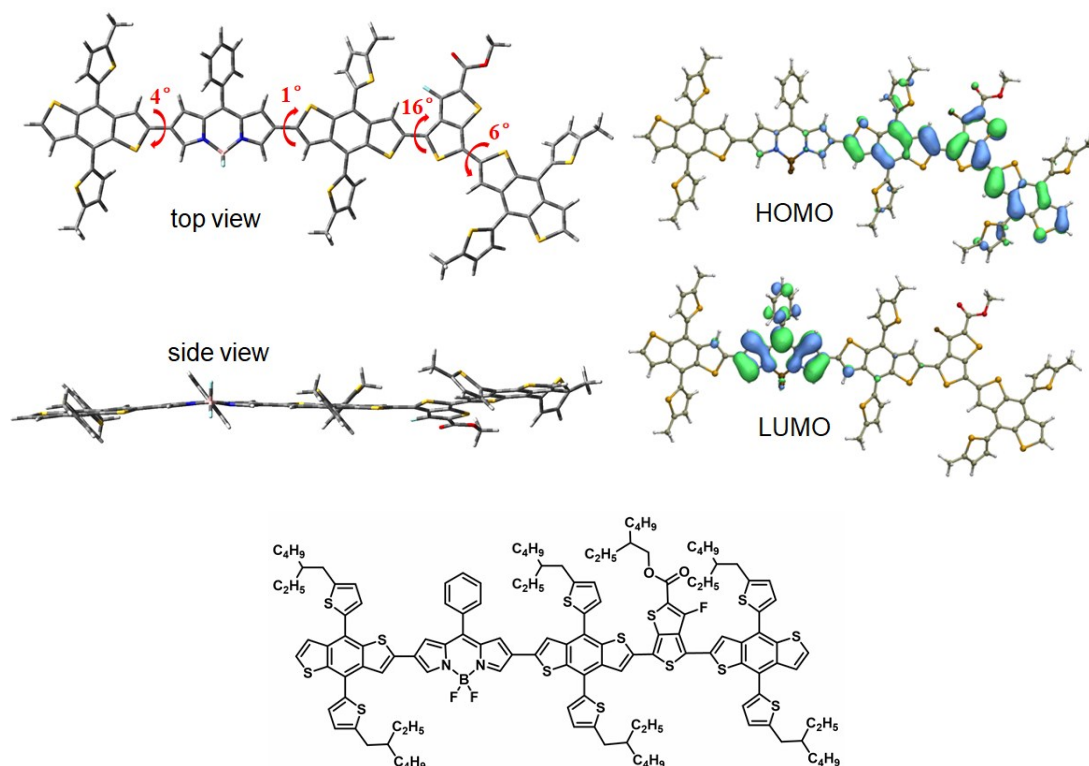

Figure S8. Simulated molecular geometries and frontier molecular orbitals from DFT calculations for terpolymers without tetramethyl structure and the corresponding simulated chemical structure (we employed methyl to replace other alkyl chains in DFT calculations).
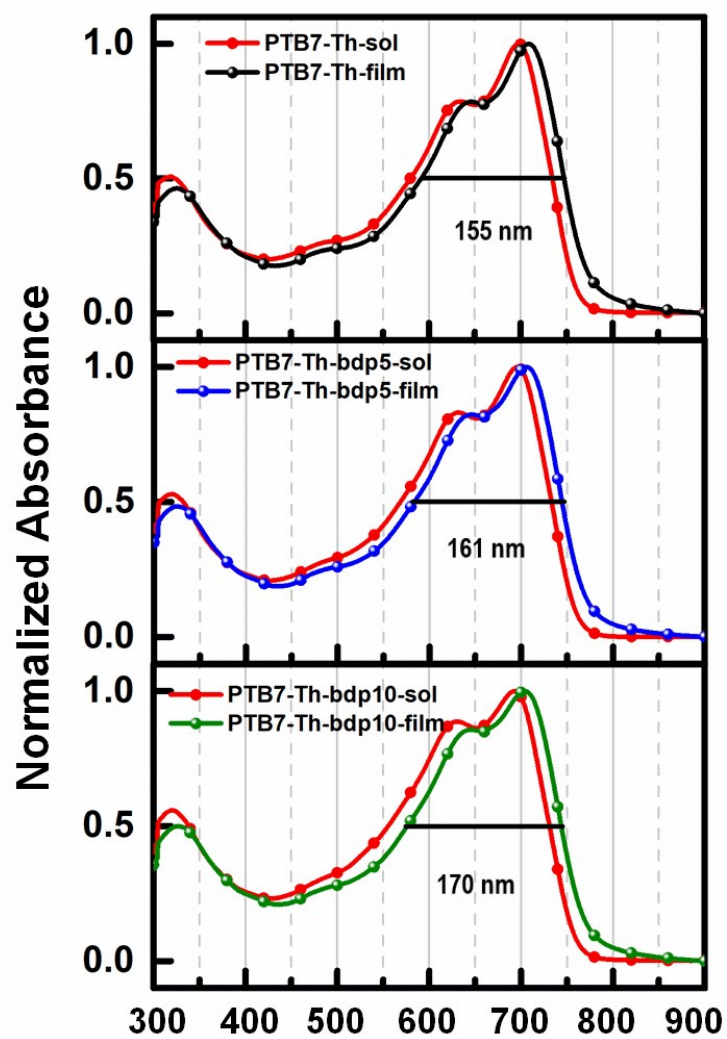
Figure S9. Comparison of absorption profiles of different polymer donors in dilute CB solution and film state.
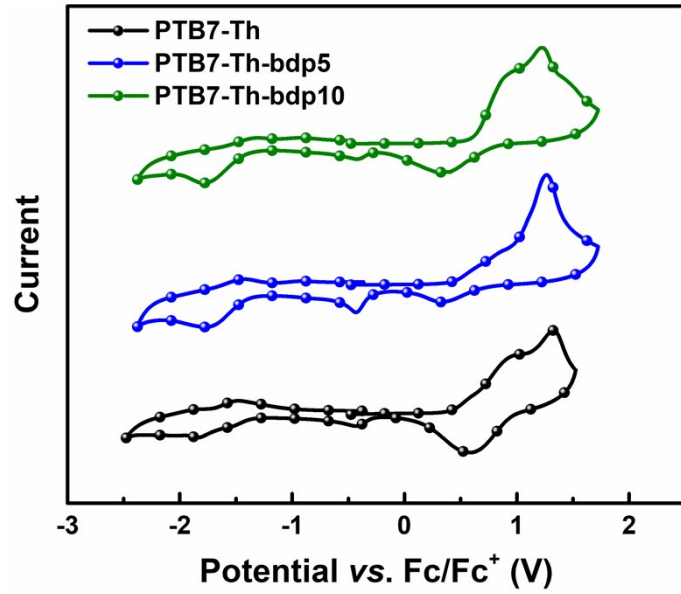
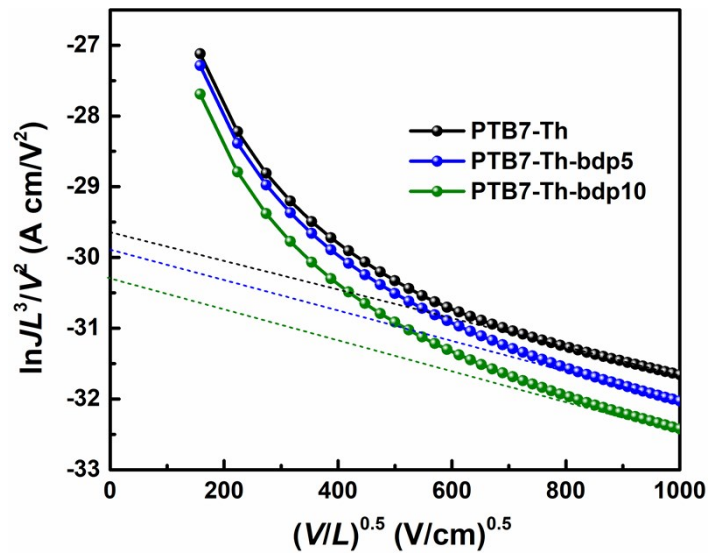**Figure S10**. CV curves for different as-synthesized polymers.

Figure S11. *J-V* curves of the hole-only devices based on polymer neat films fitted by SCLC method.
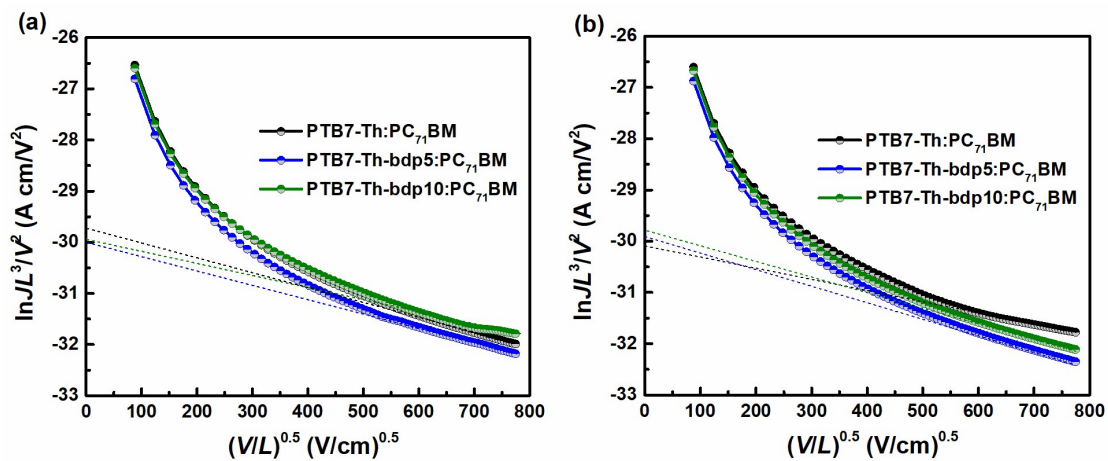
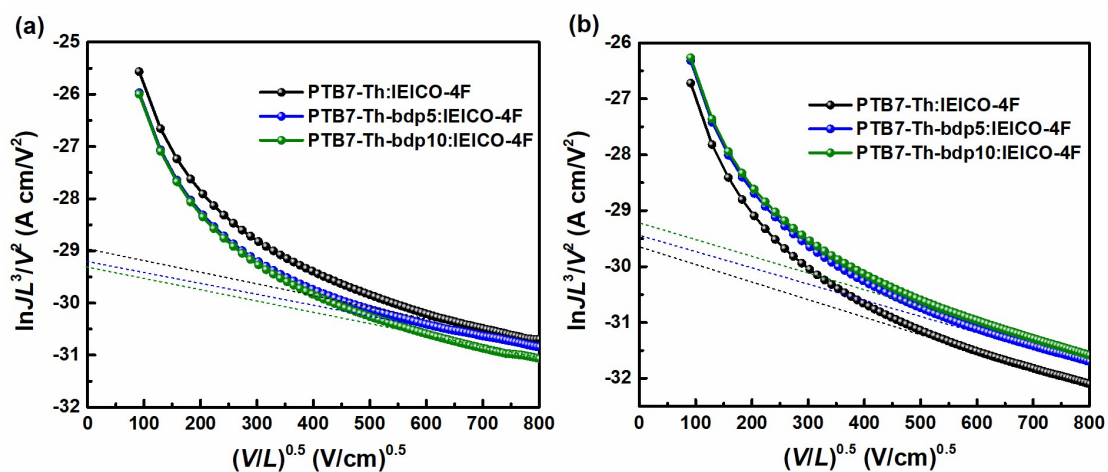**Figure S12**. *J-V* curves of the hole-only (a) and electron-only (b) devices based on fullerene acceptor $PC_{71}BM$.

Figure S13. *J-V* curves of the hole-only (a) and electron-only (b) devices based on nonfullerene acceptor IEICO-4F.
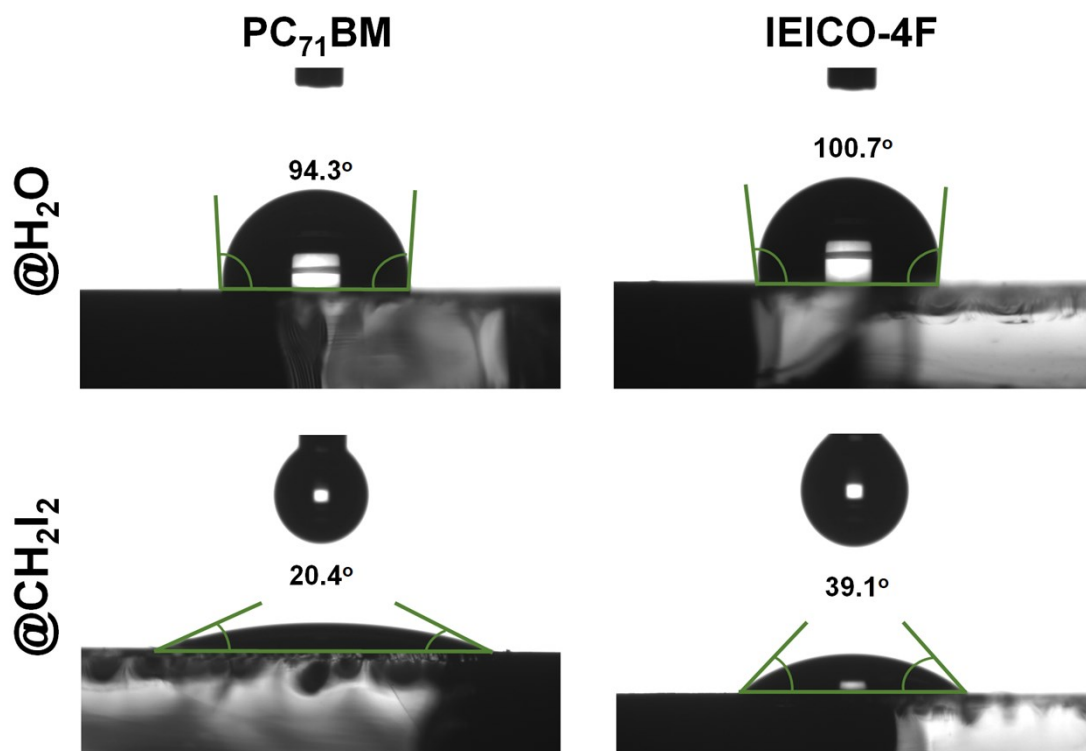
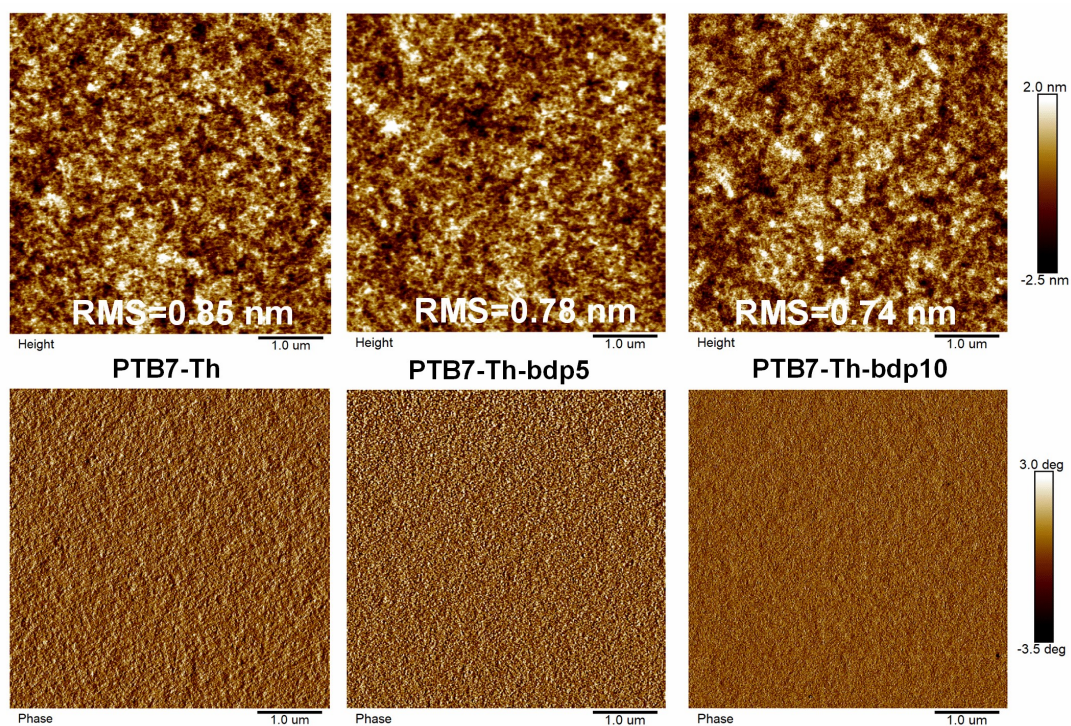**Figure S14**. Images of contact angel measurements for neat acceptor films.

Figure S15. AFM height and phase images (5 μm × 5 μm) for neat polymer films.

Table S1. I_{0-0}/I_{0-1} values of different polymers upon varied test temperature.

polymer	temperature [°C]	relative I_{0-0} value	relative I_{0-1} value	I_{0-0}/I_{0-1}
PTB7-Th	15	1	0.77	1.30
	30	0.97	0.77	1.26
	45	0.93	0.76	1.22
	60	0.89	0.76	1.17
	75	0.85	0.76	1.12
	90	0.83	0.77	1.08
	105	0.80	0.77	1.04
	120	0.75	0.77	0.97
PTB7-Th-bdp5	15	1	0.81	1.23
	30	0.96	0.81	1.19
	45	0.93	0.81	1.15
	60	0.89	0.80	1.11
	75	0.87	0.80	1.09
	90	0.83	0.80	1.04
	105	0.81	0.81	1
	120	0.77	0.82	0.94
PTB7-Th-bdp10	15	1	0.89	1.12
	30	0.97	0.89	1.09
	45	0.92	0.89	1.03
	60	0.88	0.88	1
	75	0.85	0.88	0.97
	90	0.83	0.88	0.94
	105	0.80	0.89	0.90
	120	0.76	0.89	0.85

Table S2. Detailed parameters for contact angle measurements.

film surface	ϑ_{water} [°]	ϑ_{oil} [°]	γ_d [mJ m^{-2}]	γ_p [mJ m^{-2}]	γ [mJ m^{-2}]
PTB7-Th	100.6	55.6	31.10	0.26	31.36
PTB7-Th-bdp5	100.6	53.3	32.42	0.19	32.61
PTB7-Th-bdp10	101.3	51.4	33.49	0.10	33.59
PC$_{71}$BM	94.3	20.4	47.66	0.04	47.70
IEICO-4F	100.7	39.1	40.06	1.6×10^{-4}	40.06