

## Supporting Information

### Hydrogen-Bonded Polyazomethines for Efficient Organic Solar Cells

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#### 1. Experimental Section

##### 1.1 Materials

The reagents were purchased from Adamas, Sigma-Aldrich, J&K Scientific, Bide Pharmatech, SunaTech and Derthon. All chemicals were used as received. 5-Bromothiophene-3-carboxylic acid (1) was synthesized according to the procedure reported in literature. (2,2'-((2Z,2'Z)-((12,13-Bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]-thiadiazolo-[3,4-e]thieno[2, "3": 4' 5']thieno[2', 3': 4, 5]pyrrolo[3,2-g]thieno[2', 3': 4, 5]thieno[3,2-b]indole-2,10-diyl)bis(methanyl-ylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalono-nitrile (Y6) and 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-4F) were purchased from Solarmer Materials Inc. Zinc acetate dihydrate, methoxyethanol, and PEIE (80% ethoxylated solution, 37 wt% in water) were used for preparation of PEI-Zn precursor solutions. Tetrahydrofuran (THF) was freshly distilled over sodium wires and benzophenone prior to use.

##### 1.2 Instrumentation

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV-400 MHz spectrometer at room temperature. Chemical shifts were calibrated with tetramethylsilane (TMS) as the internal reference. Electrospray ionization mass

spectrometry analyses were performed on a Primer UPLC-Q-TOF mass spectrometer. Matrix-assisted laser desorption ionization time-of light mass spectrometry (MALDI-TOF MS) analyses were performed on a Bruker Autoflex system. Elemental analyses were carried out on an Elementar Vario EL Cube system. Gel permeation chromatography (GPC) analyses of polymers were carried out on a PL-GPC 220 high-temperature chromatography with chlorobenzene (CB) as eluent at 80 °C and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) measurements were conducted on a PerkinElmer Pyris 1 at a heating rate of 20 °C/min under nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch Instruments DSC 204f1 at a scan rate of 10 °C/min under nitrogen. Single crystal X-ray diffraction analysis was performed on a Bruker D8 VENTURE X-ray diffractometer. UV-vis absorption spectra of polymers in dilute chloroform (CF) solution and polymer thin-films were acquired from a PerkinElmer Lambda 20 UV-vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI600 electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M) in acetonitrile at scan rate of 100 mV s<sup>-1</sup>, platinum disk, platinum wire and Ag/Ag<sup>+</sup> ( $\text{AgNO}_3$ , 0.01 M in acetonitrile) were used as counter electrode, working electrode and reference electrode, respectively. The cell was calibrated with the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below vacuum level) as an external standard which was measured under the same conditions before and after the measurement of samples. The polymer film was coated on the surface of a platinum disk electrode. The theoretical calculation was performed with density functional theory (DFT) at B3LYP/6-31G(d) basis set to study molecular geometries and energy levels. All the branched side chains were substituted with methyl to simplify calculation. Atomic force microscopy (AFM) images were acquired with a Bruker JPK atomic force microscope. Grazing-incidence wide-angle X-ray scattering (GIWAXS) characterizations were carried out at the beamline 14B1 of Shanghai Synchrotron Radiation Facility (SSRF).

### **1.3 Organic photovoltaic device fabrication and measurement**

The device structure of solar cell was ITO/PEI-Zn/polymer:Y6/MoO<sub>3</sub>/Ag. The

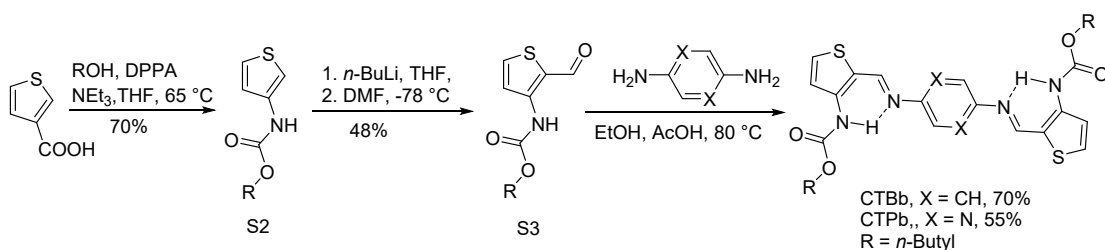
PEI-Zn was prepared by dissolving zinc acetate dihydrate (0.06 g) and PEIE (0.005 g) in 2-methoxyethanol (1.0 mL). A layer of PEI-Zn (30 nm) was deposited by spin-coating on the pre-cleaned ITO substrates and was annealed at 130 °C for 15 min in air. After deposition, the substrate was transferred to a glove box filled with nitrogen. The active layer was spin-coated at different speeds using a solution of polymer:Y6 (1:1.2 w/w, the total concentration of 10.3 mg mL<sup>-1</sup> in chloroform). A layer of MoO<sub>3</sub> (15 nm)/Ag (70 nm) was deposited on the active layer by vacuum evaporation at a base pressure of 2×10<sup>-7</sup> Torr. The effective device area was 4.1 mm<sup>2</sup> defined by shallow masks. The *J-V* characteristics were measured inside a nitrogen-filled glove box using Keithley 2400 source meter controlled by the LabVIEW program in dark and under illumination (AM 1.5G, 100 mW cm<sup>-2</sup>). Light intensity was calibrated with a silicon photodetector (Newport 818-UV). The external quantum efficiencies (*EQEs*) of the solar cells were measured on a system equipped with a 150 W xenon lamp fitted with a monochromator (Cornerstone 74004) as a monochromatic light source.

## 2. Synthesis of compounds

**2-Octyldodecyl (5-bromothiophen-3-yl)carbamate (2).** 5-Bromothiophene-3-carboxylic acid (8.00 g, 38.90 mmol), diphenylphosphoryl azide (DPPA) (14.40 g, 50.51 mmol) and triethylamine (7.87 g, 77.80 mmol) were added to a solution of 2-octyldodecan-1-ol (12.20 g, 40.85 mmol) in anhydrous THF (100.0 mL). After refluxing overnight, the solution was cooled and concentrated under reduced pressure. The residue was dissolved in diethyl ether and washed with aqueous solution of citric acid (5%), deionized water, and brine. The solution was dried with anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:100) as the eluent to give the titled compound as a light-yellow oil (8.90 g, 42% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (s, 1H), 6.96 (s, 1H), 6.73 (s, 1H), 4.06 (d, *J* = 5.6 Hz, 2H), 1.64 (m, 1H), 1.31 (m, 32 H), 0.90 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.92, 135.61, 123.69, 111.78, 109.05, 68.30, 37.59, 31.99, 31.97, 31.16, 30.05, 29.75, 29.73, 29.69, 29.65, 29.44, 29.41, 26.76, 22.76, 22.75, 14.18.

**2-Octyldodecyl (5-bromo-2-formylthiophen-3-yl)carbamate (3).** Anhydrous THF

(50.0 mL) and *n*-butyl lithium (8.00 mL, 20.00 mmol) were added to an around-bottom flask (250 mL) under nitrogen atmosphere at -78 °C. Diisopropylamine (2.02 g, 20.00 mmol) was added dropwise and the reaction was stirred at -78 °C for 1 h. A solution of compound **2** (5.00 g, 10.00 mmol) in dry THF (20.0 mL) was added dropwise to the flask. The mixture was stirred at -78 °C for 1 h, and *N*-formylpiperidine (2.27 g, 20 mmol) was added slowly and stirred for 2 h. The mixture was warmed to room temperature and was quenched by addition of hydrochloric acid solution (1.0 M). The mixture was extracted with dichloromethane (100 mL) and the combined organic layers were dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1:40) as the eluent to give the titled compound as a light-yellow oil (1.80 g, 34%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.95 (s, 1H), 9.50 (s, 1H), 8.00 (s, 1H), 4.09 (d, *J* = 6.0 Hz, 2H), 1.69 (m, 1H), 1.30 (m, 32 H), 0.88 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 182.11, 153.15, 144.88, 125.58, 125.47, 120.74, 69.00, 37.50, 31.94, 31.91, 31.03, 29.94, 29.67, 29.65, 29.62, 29.58, 29.37, 29.33, 26.70, 22.71, 22.70, 14.14.



**Scheme S1.** The synthesis of compounds with short sidechains for single crystal analysis.

**Butyl thiophen-3-ylcarbamate (S2).** The same procedure described for the synthesis of **2** was followed. The 3-thiophenecarboxylic acid (6.00 g, 46.80 mmol) 1-butanol, diphenylphosphoryl azide (16.70 g, 60.80 mmol) and triethylamine (9.50 g, 93.60 mmol) were used. The product was purified by column chromatography with ethyl acetate/petroleum (1:10) as the eluent to give the titled compound as a colorless solid (6.30 g, 70%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ. 7.29 (m, 2H), 7.22 (s, 1H), 7.05 (m, 1H), 4.21 (t, *J* = 6.6 Hz, 2H), 1.72 (m, 2H), 1.50 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H) <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 153.85, 136.17, 124.66, 120.79, 107.44, 65.19, 30.99,

19.08, 13.53.

**Butyl (2-formylthiophen-3-yl)carbamate (S3).** The compound **S2** (5.13 g, 25.70 mmol) and dry THF (100.0 mL) were added to a dry flask under nitrogen atmosphere. The mixture was cooled to -78 °C and a solution of *n*-butyl lithium (20.60 mL, 51.50 mmol) was added dropwise. The mixture was stirred at -78 °C for 1 h and dimethylformamide (3.8 g, 51.5 mmol) was added slowly. After stirring at -78 °C for 1 h, the mixture was warmed to room temperature and was quenched by addition of hydrochloric acid solution (1.0 M). The mixture was extracted with dichloromethane (100 mL) and the combined organic layers were dried with anhydrous sodium sulfate and was concentrated under reduced pressure. The residue was purified by chromatography on silica gel with ethyl acetate/petroleum (1:40) as the eluent to give the titled compound as a light-yellow oil (3.80 g, 67%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 9.94 (s, 1H), 9.69 (s, 1H), 7.93 (d, *J* = 5.6 Hz, 1H), 7.73 (d, *J* = 5.6 Hz, 1H), 4.22 (t, *J* = 6.8 Hz, 2H), 1.72 (m, 2H), 1.49 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 183.71, 153.07, 145.11, 136.05, 121.75, 119.74, 65.76, 30.82, 19.05, 13.52.

**Dibutyl (((1*E*,1'*E*)-(1,4-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(thiophene-2,3-diyl))dicarbamate (CTBb).** The same procedure described for the synthesis of **CTB-Br** was followed. The compound **S3** (0.86 g, 3.80 mmol) and 1,4-phenylenediamine (0.20 g, 1.90 mmol), absolute ethanol (30.0 mL), and several drops of acetic acid were used. A brown solid was washed with ethanol and was dried in vacuum at 45 °C to give the product (0.88 g, 90.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.10 (s, 2H), 8.53 (s, 2H), 7.96 (d, *J* = 4.4 Hz, 2H), 7.49 (d, *J* = 4.4 Hz, 2H), 7.28 (s, 4H), 4.23 (t, *J* = 5.4 Hz, 4H), 1.74 (m, 4H), 1.44 (m, 4H), 0.99 (t, *J* = 6.0 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.79, 152.69, 148.52, 141.70, 130.50, 122.35, 121.88, 117.56, 65.45, 30.99, 19.14, 13.81.

**Dibutyl (((1*E*,1'*E*)-(pyrazine-2,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(thiophene-2,3-diyl))dicarbamate (CTPb).** The same procedure described for the synthesis of **CTB-Br** was followed. The compound **S3** (0.46 g, 2.00 mmol), pyrazine-2,5-diamine (0.10 g, 0.98 mmol), absolute ethanol (10.0 mL), and several

drops of acetic acid were used. A brown solid was washed with ethanol and was dried at 45 °C in vacuum to give the title compound (0.31 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.21 (s, 2H), 9.35 (s, 2H), 8.44 (s, 2H), 7.98 (d, *J* = 5.4 Hz, 2H), 7.61 (d, *J* = 5.4 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 4H), 1.75 (m, 4H), 1.50 (m, 4H), 1.01 (t, *J* = 7.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.89, 153.61, 153.22, 143.55, 140.86, 133.36, 122.25, 117.89, 65.63, 30.95, 19.17, 13.82.

**Synthesis of bis(2-octyldodecyl) (((1*E*,1'*E*)-(1,4-phenylenebis(azaneylylidene))-bis(methaneylylidene))bis(5-bromothiophene-2,3-diyl))dicarbamate (CTB-Br).** Compound **3** (1.60 g, 3.02 mmol) and 1,4-phenylenediamine (0.16 g, 1.47 mmol) were dissolved in absolute ethanol (12.0 mL) in a round bottom flask, and several drops of acetic acid was added to the mixture, The reaction was stirred at 80 °C for 18 h. The precipitate was filtered and then recrystallization from the mixed solvent of ethanol and chloroform. A brown solid was collected as the titled compound (1.10 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.19 (s, 2H), 8.47 (s, 2H), 8.01 (s, 2H), 7.31 (s, 4H), 4.15 (d, *J* = 5.6 Hz, 4H), 1.77 (m, 2H), 1.40 (m, 64 H), 0.91 (t, *J* = 6.6 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.47, 151.27, 148.15, 141.44, 125.41, 121.87, 118.79, 118.73, 68.60, 37.52, 31.94, 31.93, 31.29, 30.00, 29.71, 29.67, 29.62, 29.58, 29.39, 29.37, 26.75, 22.71, 13.91, 13.90. HRMS MALDI-TOF: *m/z* calcd for C<sub>58</sub>H<sub>92</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>, 1133.4940; found, 1133.4947.

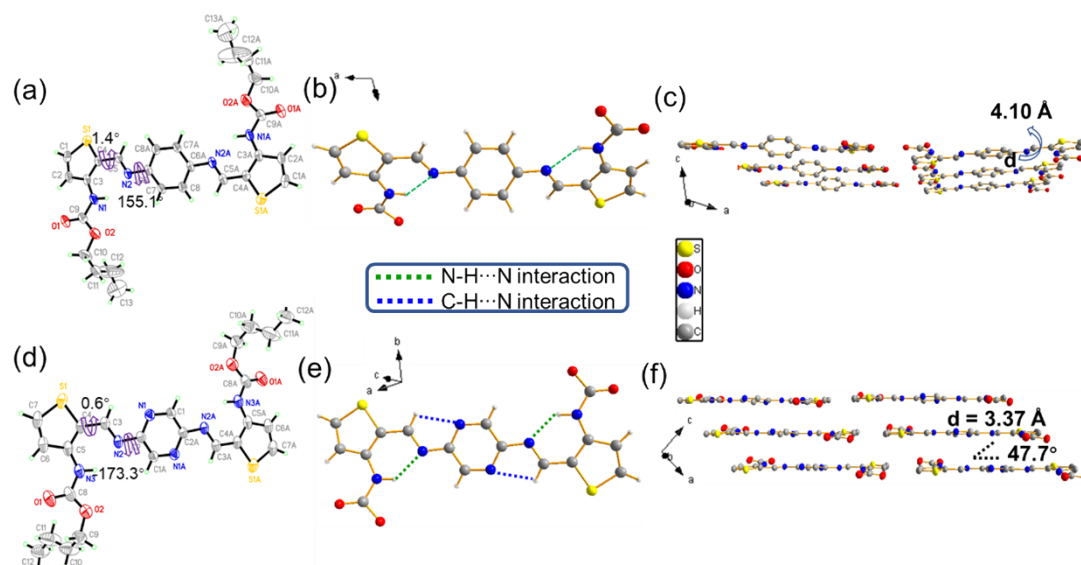
**Synthesis of bis(2-octyldodecyl) (((1*E*,1'*E*)-(pyrazine-2,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(5-bromothiophene-2,3-diyl))dicarbamate (CTP-Br).** The synthesis procedure was same as that of **CTB-Br**. Compound **3** (1.70 g, 3.20 mmol), pyrazine-2,5-diamine (0.17 g, 1.56 mmol) and absolute ethanol (12.0 mL) were used to afford precipitate, which was further purified by recrystallization from the mixed solvent of ethanol and chloroform to obtain an orange-red solid (0.68 g, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.27 (s, 2H), 9.22 (s, 2H), 8.36 (s, 2H), 8.01 (s, 2H), 4.15 (d, *J* = 6.0 Hz, 4H), 1.76 (m, 2H), 1.36 (m, 64 H), 0.87 (t, *J* = 6.8 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.36, 153.44, 152.92, 143.27, 140.98, 125.55, 122.11, 119.12, 68.82, 37.51, 31.94, 31.92, 31.36, 30.02, 29.71, 29.67, 29.66, 29.61, 29.39, 29.36, 26.81, 22.71, 14.15 HRMS MALDI-TOF: *m/z* calcd for C<sub>56</sub>H<sub>90</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>,

1135.4845; found, 1135.4840.

**Synthesis of polymer PBBDT.** CTB-Br (0.114 g, 0.100 mmol), compound **4** (0.091 g, 0.100 mmol), tris(dibenzylideneacetone)dipalladium (0.002 g, 0.0021 mmol), tris(*o*-tolyl)phosphine (0.003 g, 0.084 mmol) and dry chlorobenzene (7.0 mL) were added to a Schlenk flask, and the mixture was purged with nitrogen for 30 min. The reaction was stirred at 120 °C for 15 h. After cooling to room temperature, the mixture was precipitated in methanol and was filtered. The residue was sequentially washed with methanol, acetone, hexane, and chloroform in a Soxhlet extractor. The chloroform fraction was concentrated under reduced pressure and was precipitated in methanol to give a black solid with metallic luster (0.156 g, 98%). Anal. Calcd for C<sub>92</sub>H<sub>134</sub>N<sub>4</sub>O<sub>4</sub>S<sub>6</sub>: C 71.18, H 8.70, N 3.61; Found: C 71.05, H 8.62, N 3.58. GPC (chlorobenzene, 80 °C):  $M_n = 35.3$  kDa, PDI = 2.5.

**Synthesis of polymer PPBDT.** The PPBDT was synthesized in same way as PBBDT. CTP-Br (0.114 g, 0.100 mmol), compound **4** (0.091 g, 0.100 mmol), tris(dibenzylideneacetone)dipalladium (0.002 g, 0.0021 mmol), tris(*o*-tolyl)phosphine (0.003 g, 0.084 mmol) and dry chlorobenzene (7.0 mL) were used to afford a black solid with metallic luster (0.153 g, 95%). Anal. Calcd for C<sub>90</sub>H<sub>132</sub>N<sub>6</sub>O<sub>4</sub>S<sub>6</sub>: C 69.54, H 8.56, N 5.41; Found: C 69.40, H 8.44, N 5.32. GPC (chlorobenzene, 80 °C):  $M_n = 53.6$  kDa, PDI = 2.6.

### 3. Crystallographic results



**Fig. S1** The single crystal structure of (a, b) CTBb and (d, e) CTPb. Molecular arrangement in single crystal of (c) CTBb and (f) CTPb. The alkyl chains are omitted for clarity in (b, c) and (e, f).



**Table S1** Crystal data and structure refinement for CTBb

Empirical formula	C <sub>26</sub> H <sub>30</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	526.66
Temperature	228(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 19.267(3) Å α = 90°
	b = 11.683(2) Å β = 116.908(8)°
	c = 13.325(3) Å γ = 90°
Volume	2674.5(8) Å <sup>3</sup>
Z, Calculated density	4, 1.308 mg/m <sup>3</sup>
Absorption coefficient	2.124 mm <sup>-1</sup>
F(000)	1112
Crystal size	0.200 × 0.180 × 0.150 mm <sup>3</sup>
Theta range for data collection	4.577 to 69.064°
Limiting indices	-23 ≤ h ≤ 23, -12 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected / unique	18014 / 2459 [R(int) = 0.0559]
Completeness to theta	67.679 99.3 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2459 / 2 / 167
Goodness-of-fit on F <sup>2</sup>	1.123
Final R indices [I > 2σ(I)]	R1 = 0.0713, wR2 = 0.1932
R indices (all data)	R1 = 0.0806, wR2 = 0.2026
Extinction coefficient	n/a
Largest diff. peak and hole	0.908 and -0.678 e.Å <sup>-3</sup>

**Table S2** Selected bond distance and torsion angles for compound CTBb

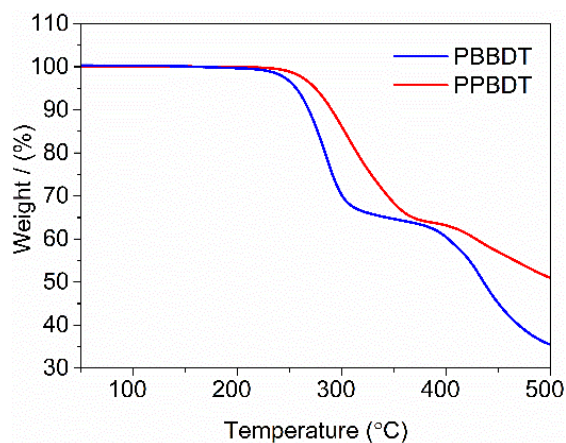
Bond type	Bond length (Å)	Torsion angles (°)
N(2)–H	0.88	
N(2)·····N(1)	2.71	
H·····N(1)	2.08	
C(4)–C(5)	1.45	
C(5)–N(2)	1.28	
N(2)–C(6)	1.42	
N(1)–C(1)–C(6)–S(1A)		169.28

**Table S3** Crystal data and structure refinement for CTPb

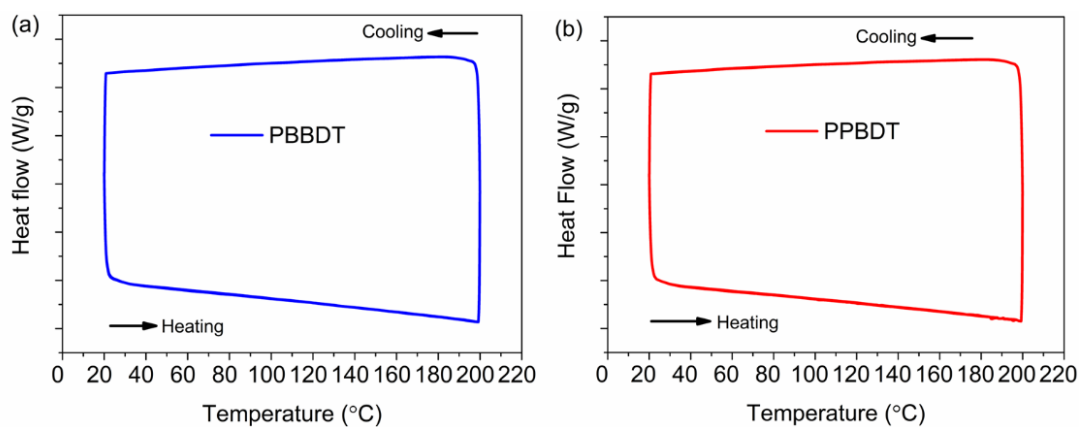
Empirical formula	C <sub>24</sub> H <sub>28</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	528.64
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 4.6081(2) Å $\alpha$ = 90°
	b = 21.1052(9) Å $\beta$ = 98.391(2)°
	c = 13.2174(5) Å $\gamma$ = 90 (2)°
Volume	1271.70(9) Å <sup>3</sup>
Z, Calculated density	2, 1.381 mg/m <sup>3</sup>
Absorption coefficient	2.260 mm <sup>-1</sup>
F(000)	556
Crystal size	0.180 × 0.160 × 0.140 mm <sup>3</sup>
Theta range for data collection	3.977 to 68.562°
Limiting indices	-5 ≤ h ≤ 5, -25 ≤ k ≤ 25, -14 ≤ l ≤ 15
Reflections collected / unique	17061 / 2346 [R(int) = 0.0732]
Completeness to theta	67.679 99.9 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2346 / 0 / 167
Goodness-of-fit on F <sup>2</sup>	1.089
Final R indices [I > 2σ(I)]	R1 = 0.0653, wR2 = 0.1737
R indices (all data)	R1 = 0.0837, wR2 = 0.1906
Extinction coefficient	n/a
Largest diff. peak and hole	0.772 and -0.629 e.Å <sup>-3</sup>

**Table S4** Selected bond distance and torsion angles for compound CTPb

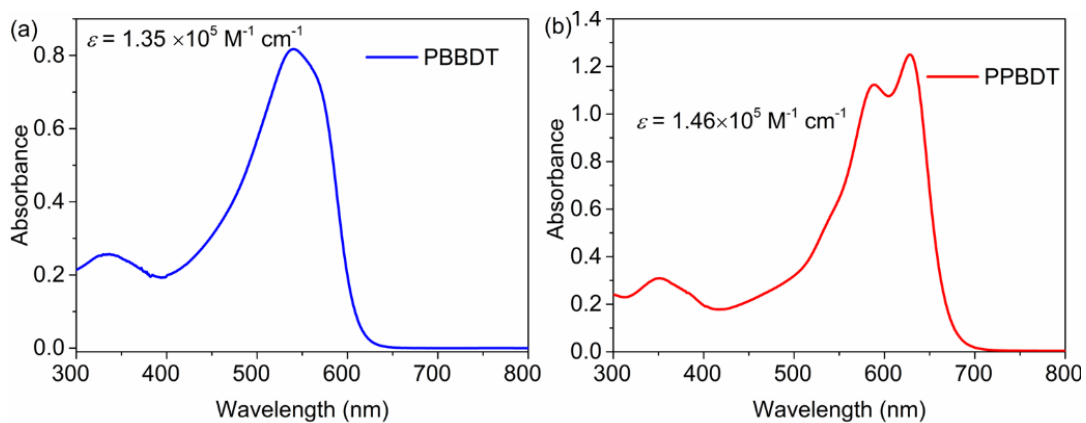
Bond type	Bond length (Å)	Torsion angles (°)
N(2)–H	0.88	
N(2)·····N(1)	2.71	
H·····N(1)	2.08	
C(4)–C(3)	1.43	
C(3)–N(2)	1.29	
N(2)–C(2)	1.40	
N(1)–C(1)–C(6)–S(1A)		169.28



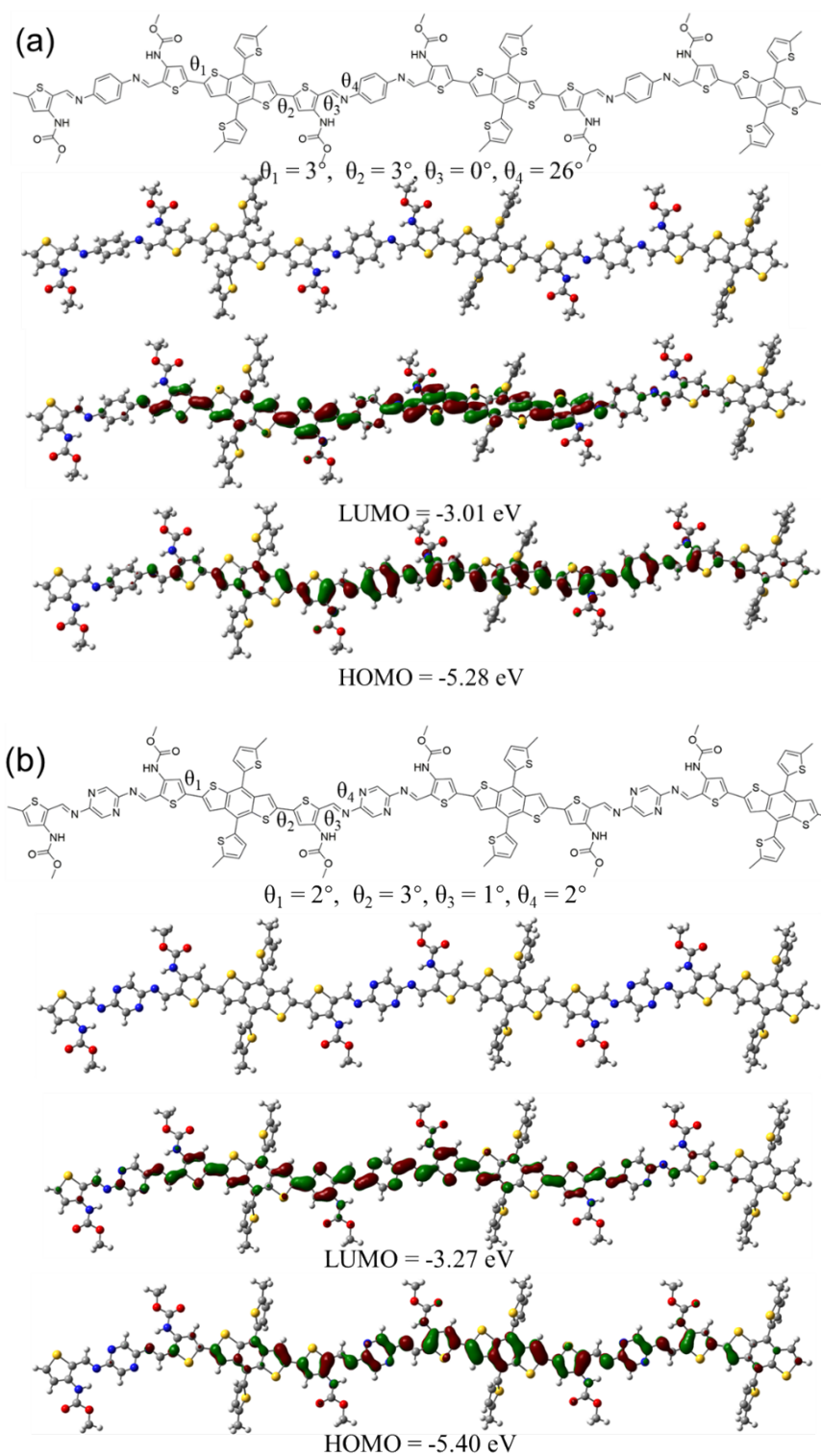
**Fig. S2** The TGA curves of polymer **PBBDT** and **PPBDT**.



**Fig. S3** DSC traces of the polymer (a) **PBBDT** and (b) **PPBDT**.



**Fig. S4** Absorption spectra of the polymer solutions at room temperature (a) **PBBDT** and (b) **PPBDT**.



**Fig. S5** Optimized geometry and calculated frontier orbitals of (a) **PBBDT** and (b) **PPBDT** trimers at B3LYP/6-31(d) level.

#### 4. NMR spectra of compounds

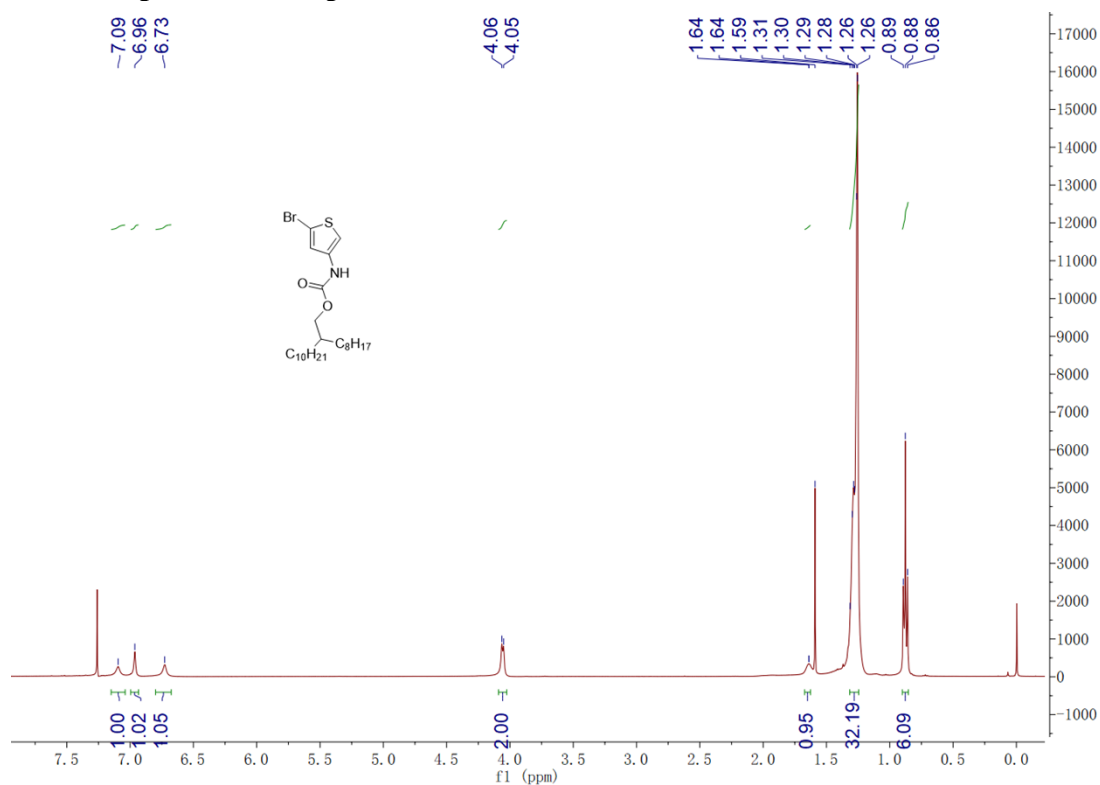


Fig. S6 The  $^1\text{H}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$ .

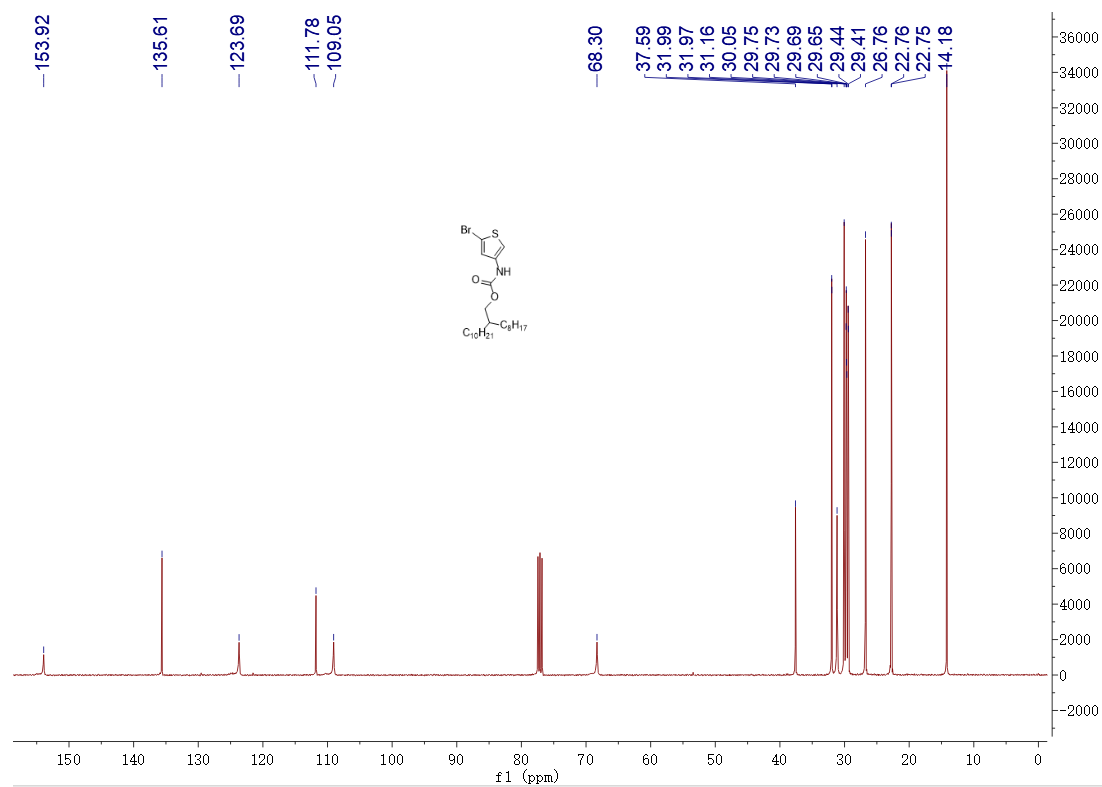


Fig. S7 The  $^{13}\text{C}$  NMR spectrum of compound 2 in  $\text{CDCl}_3$ .

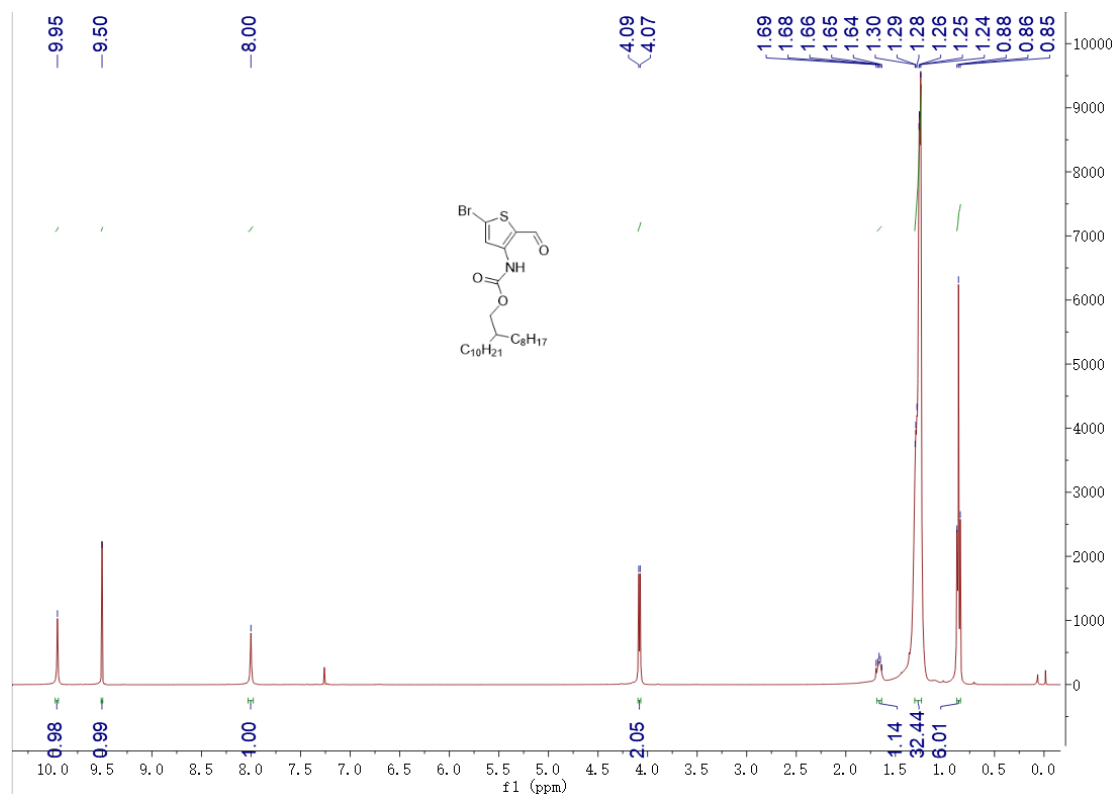


Fig. S8 The  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$ .

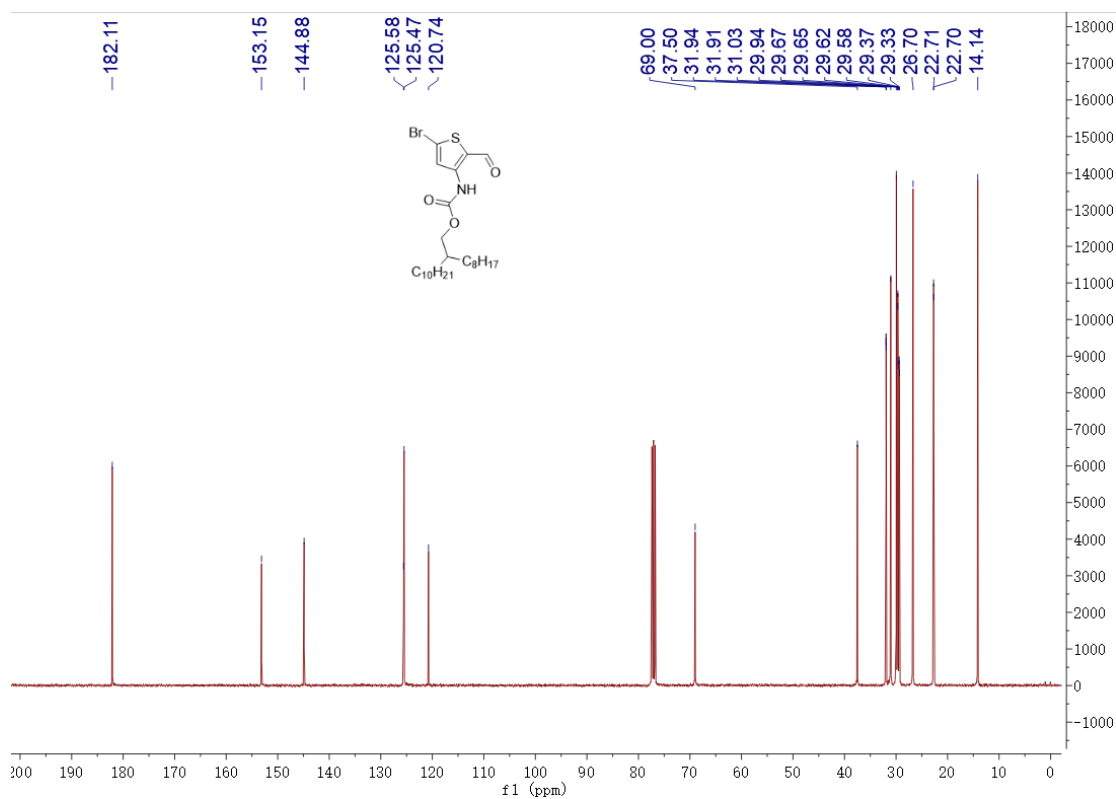
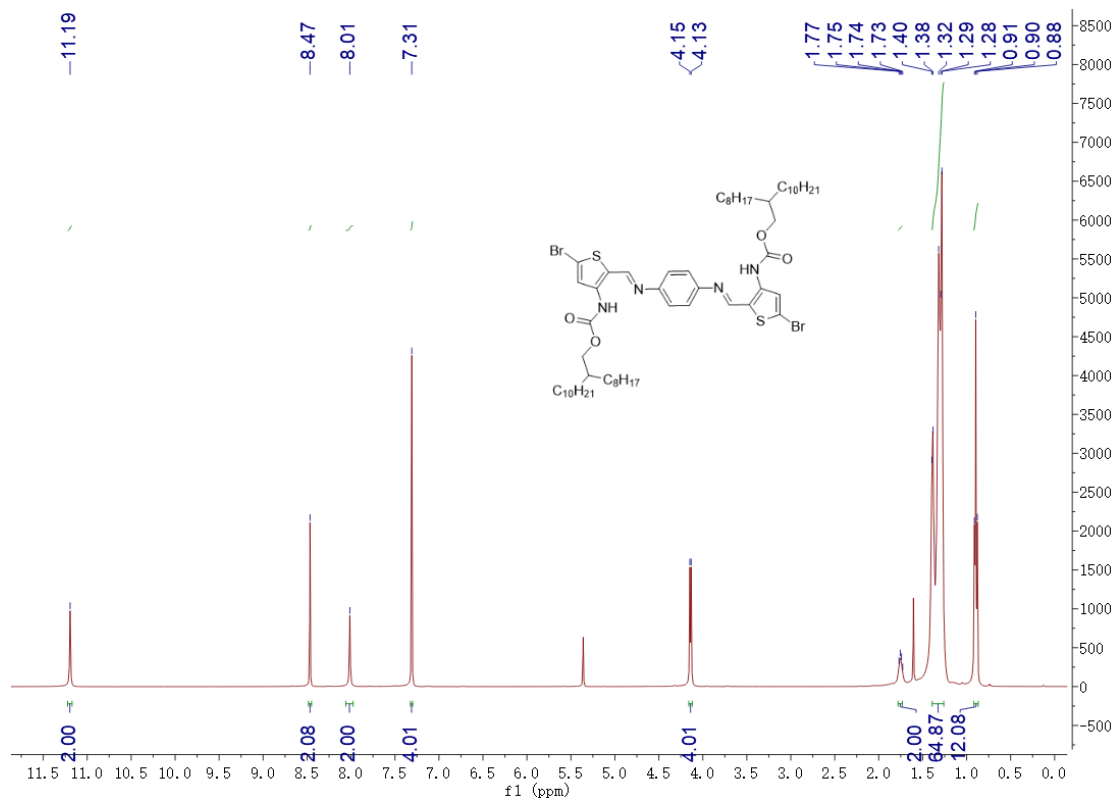
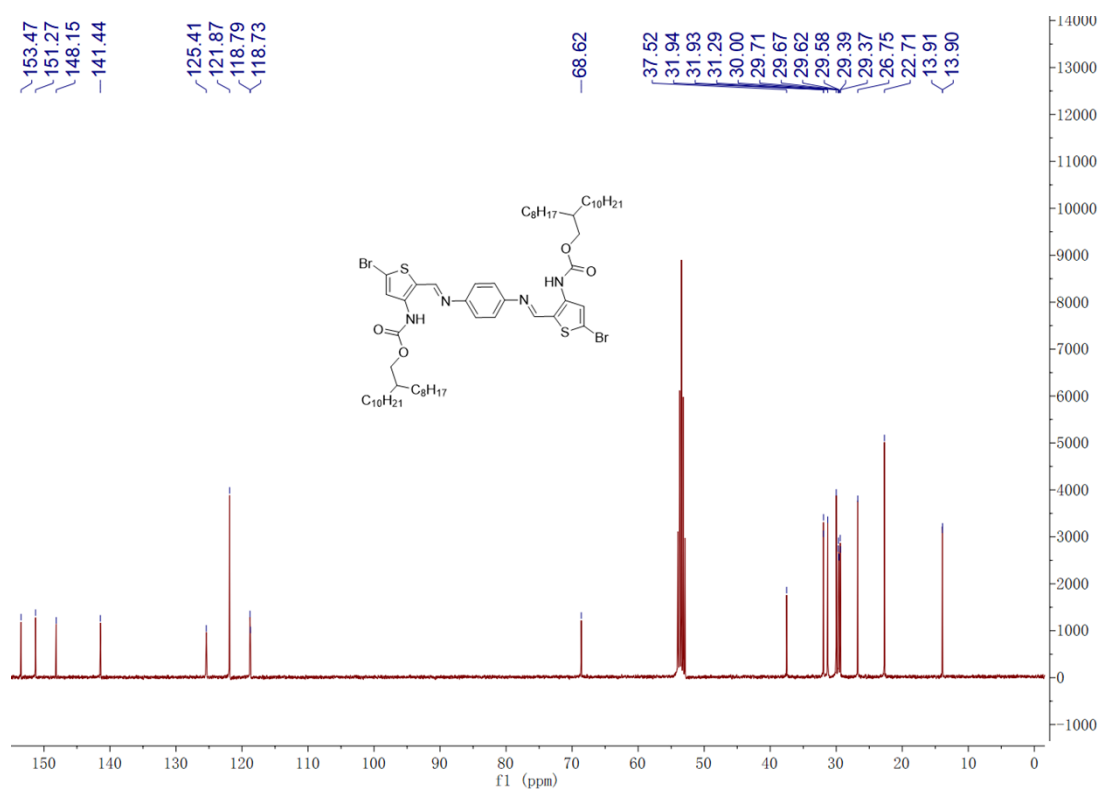


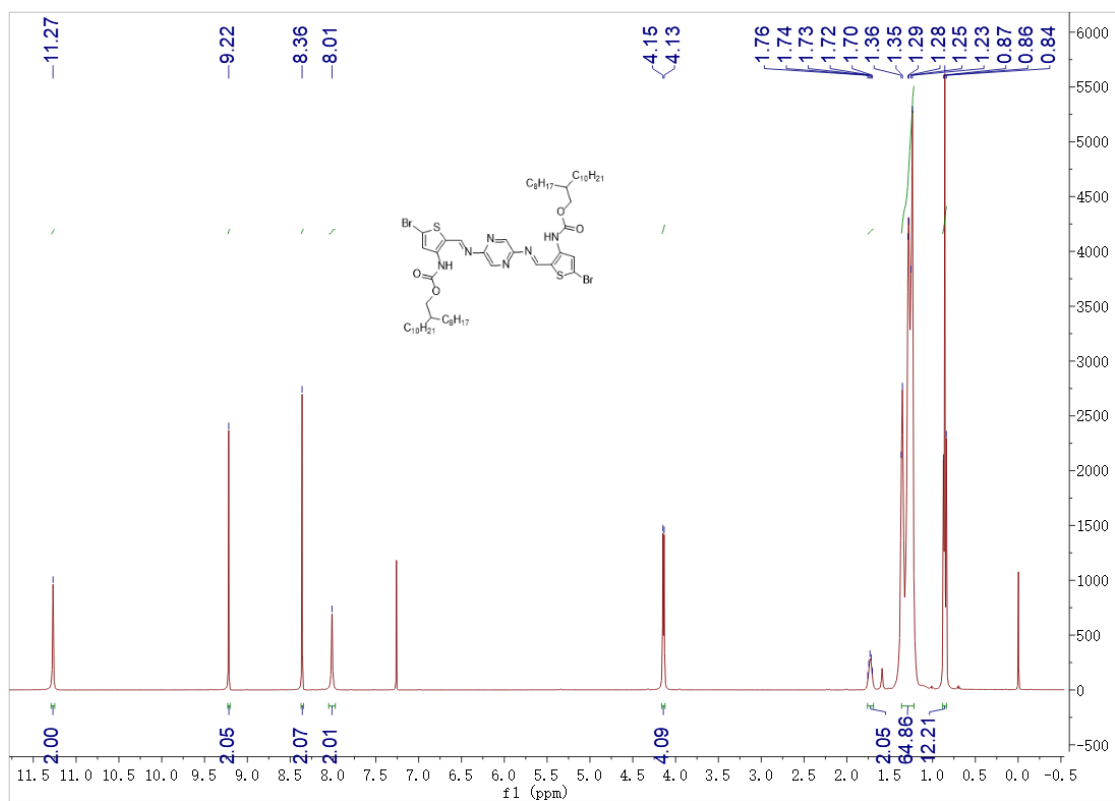
Fig. S9 The  $^{13}\text{C}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$ .



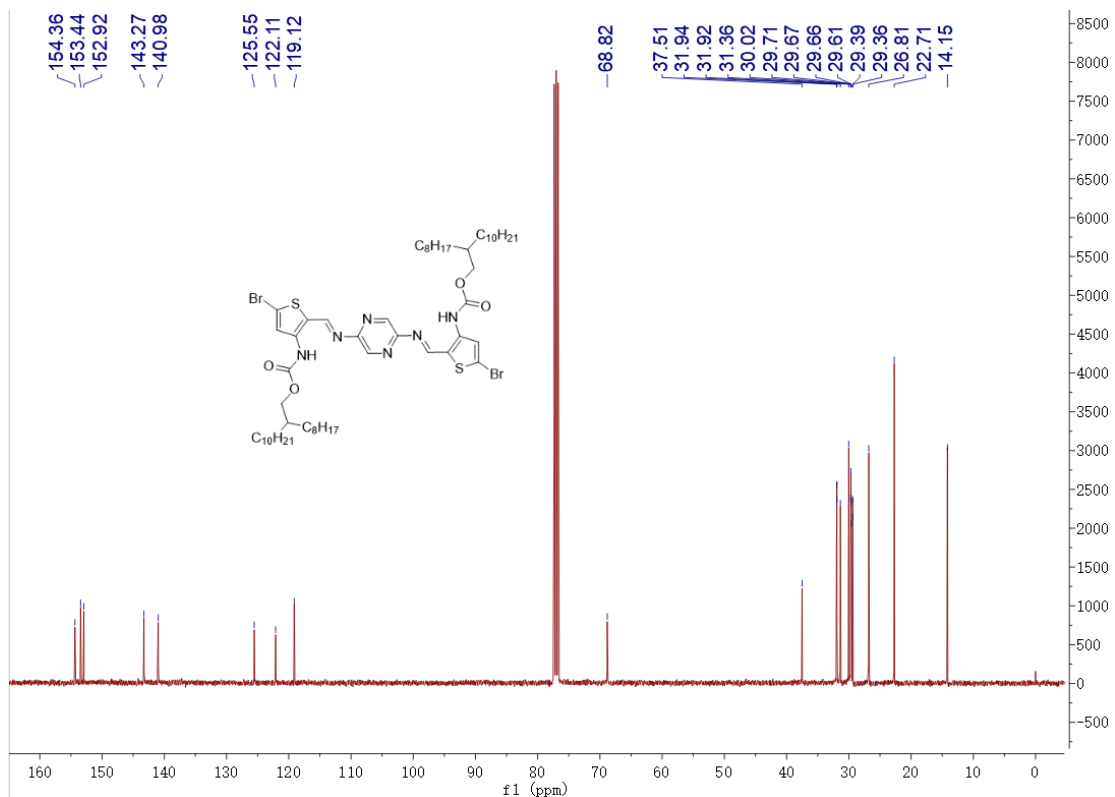
**Fig. S10** The <sup>1</sup>H NMR spectrum of compound **CTB-Br** in CD<sub>2</sub>Cl<sub>2</sub>.



**Fig. S11** The <sup>13</sup>C NMR spectrum of compound **CTB-Br** in CD<sub>2</sub>Cl<sub>2</sub>.

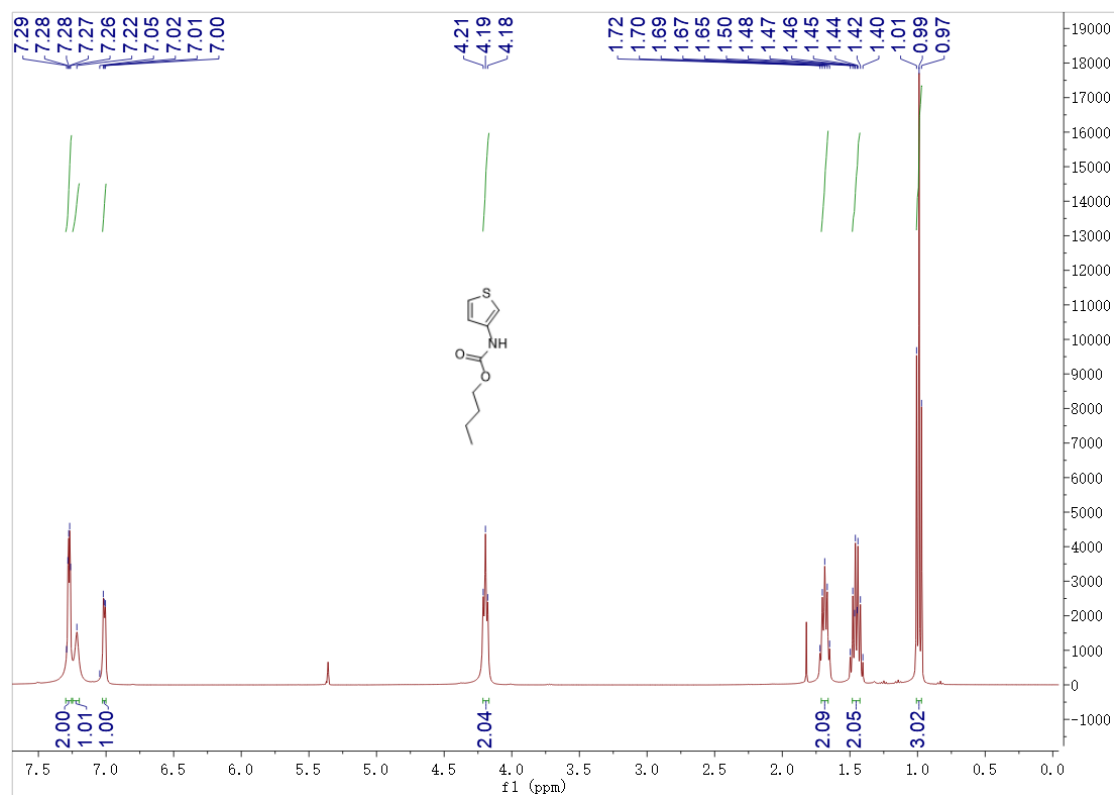


**Fig. S12** The <sup>1</sup>H NMR spectrum of compound CTP-Br in CDCl<sub>3</sub>.

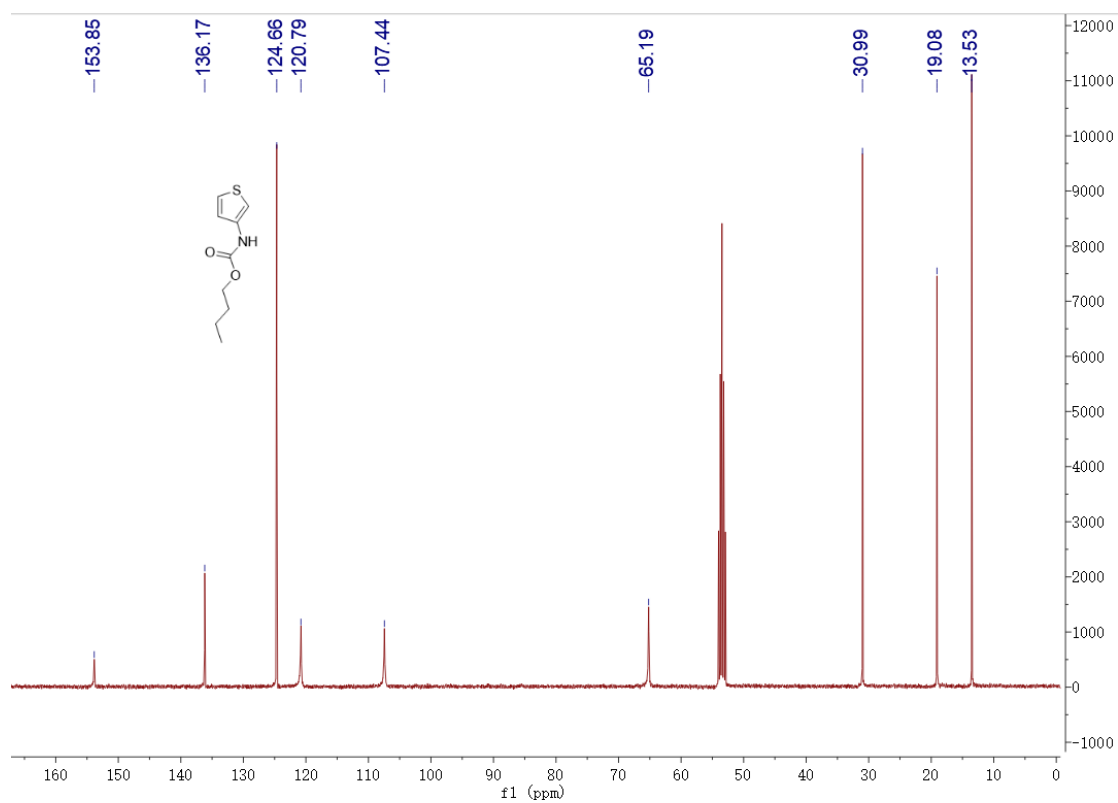


**Fig. S13** The <sup>13</sup>C NMR spectrum of compound CTP-Br in CDCl<sub>3</sub>.





**Fig. S14** The  $^1\text{H}$  NMR spectrum of compound S2 in  $\text{CD}_2\text{Cl}_2$ .



**Fig. S15** The  $^{13}\text{C}$  NMR spectrum of compound S2 in  $\text{CD}_2\text{Cl}_2$ .

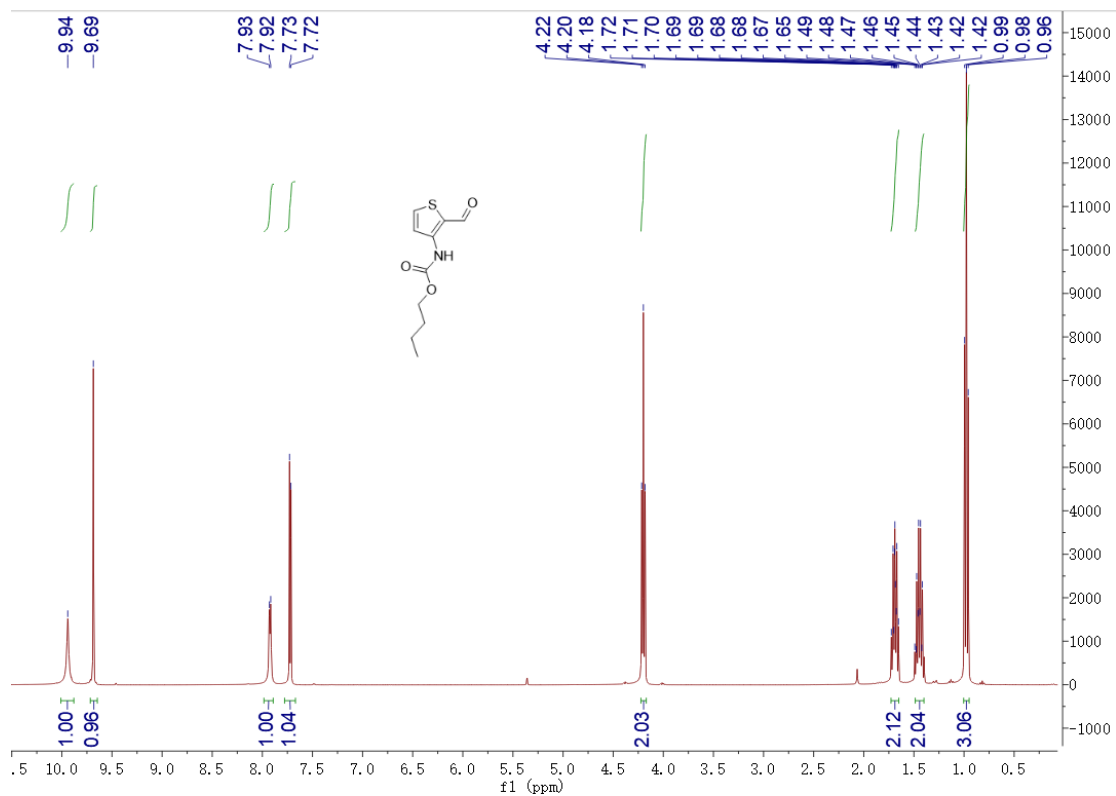


Fig. S16 The  $^1\text{H}$  NMR spectrum of compound S3 in  $\text{CD}_2\text{Cl}_2$ .

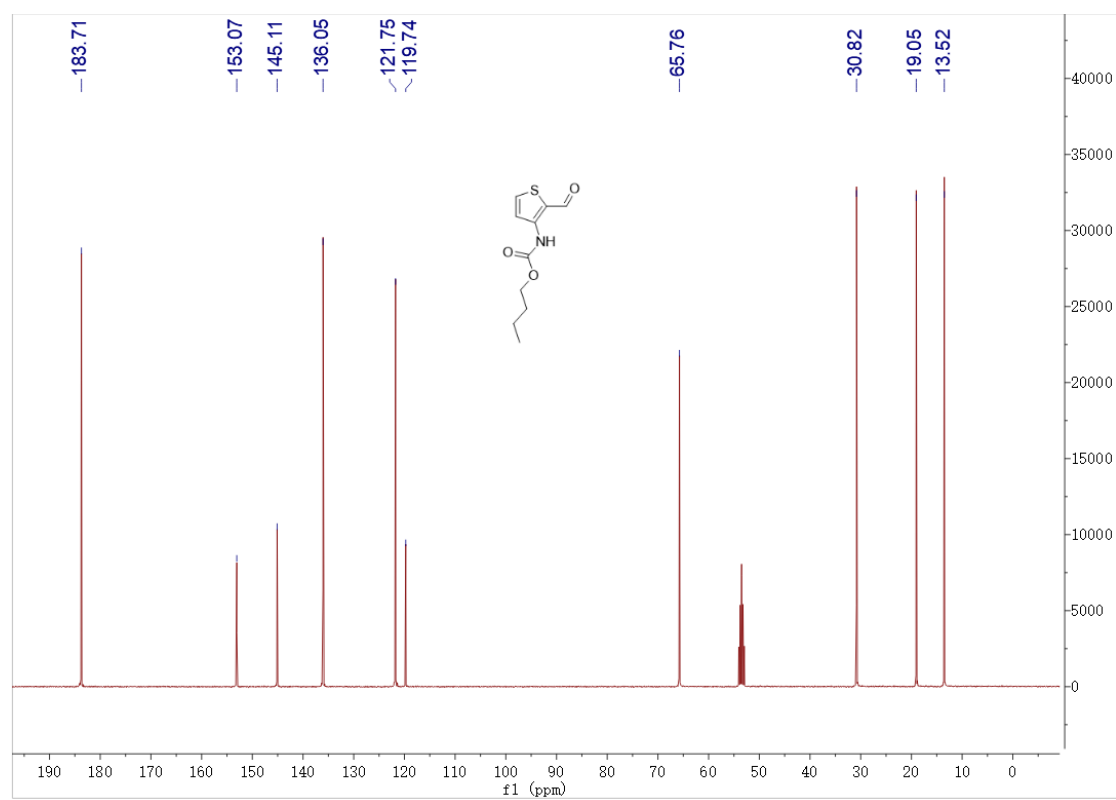
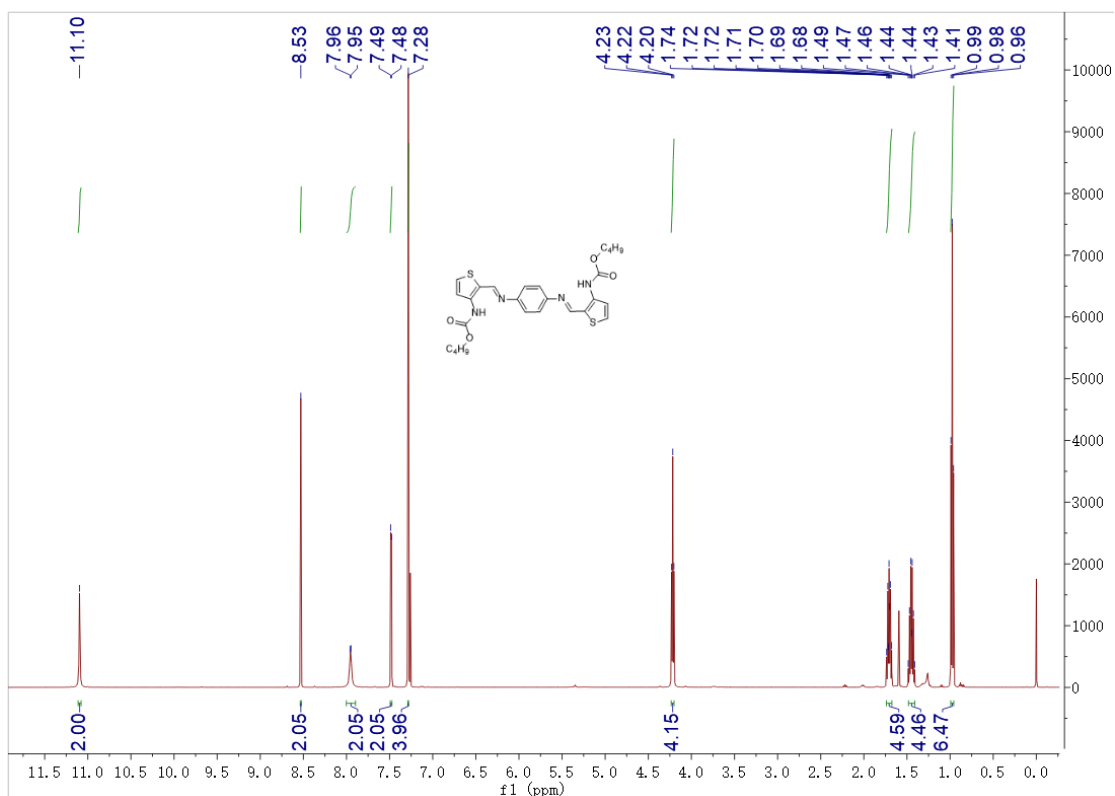
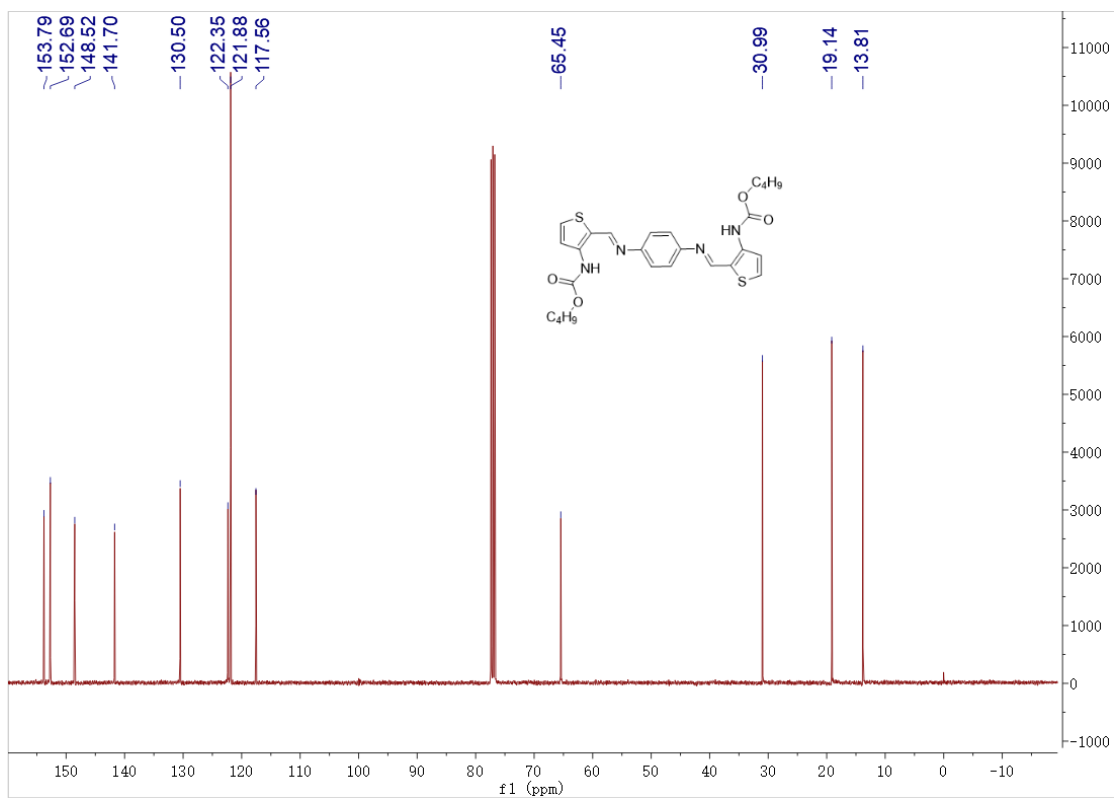


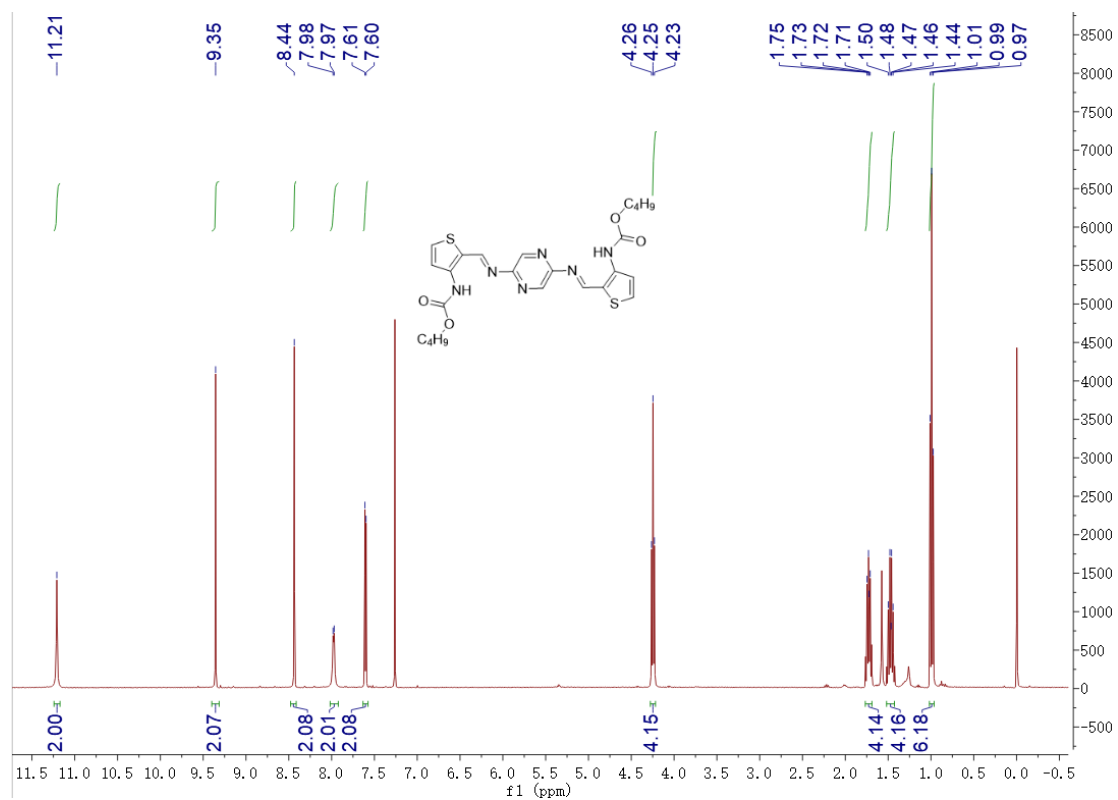
Fig. S17 The  $^{13}\text{C}$  NMR spectrum of compound S3 in  $\text{CD}_2\text{Cl}_2$ .



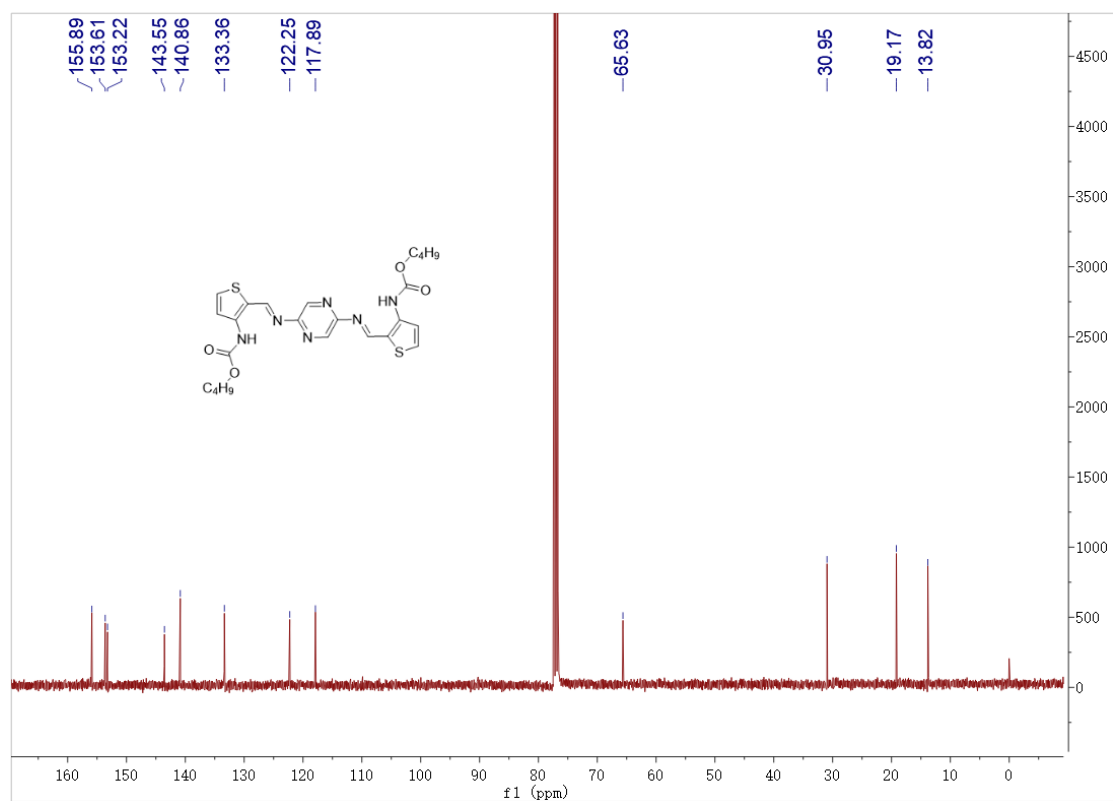
**Fig. S18** The  $^1\text{H}$  NMR spectrum of compound **CTBb** in  $\text{CDCl}_3$ .



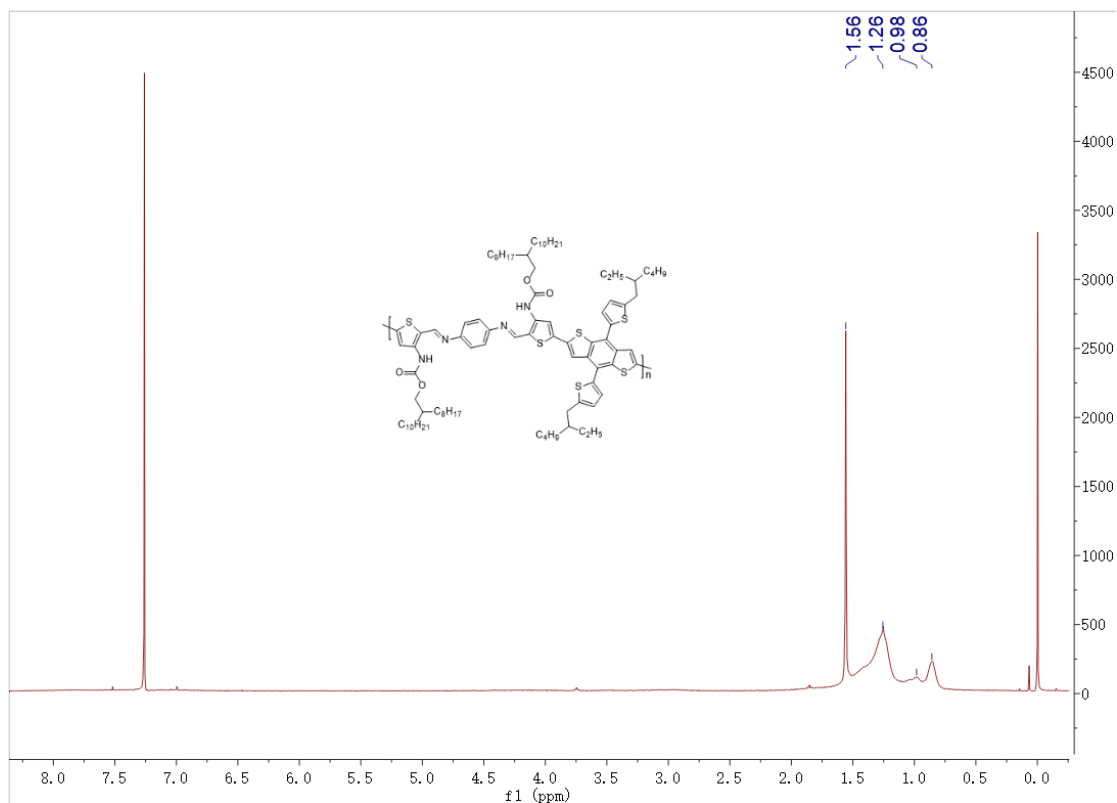
**Fig. S19** The  $^{13}\text{C}$  NMR spectrum of compound **CTBb** in  $\text{CDCl}_3$ .



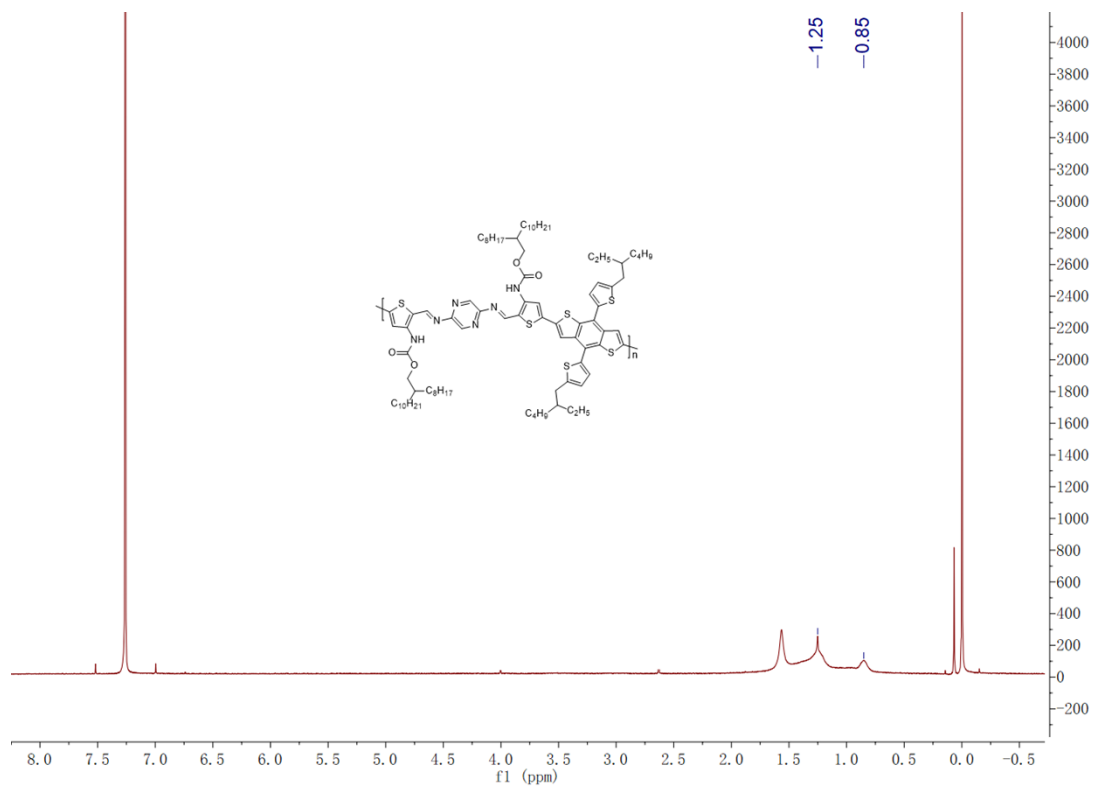
**Fig. S20** The  $^1\text{H}$  NMR spectrum of compound **CTPb** in  $\text{CDCl}_3$ .



**Fig. S21** The  $^{13}\text{C}$  NMR spectrum of compound **CTPb** in  $\text{CDCl}_3$ .

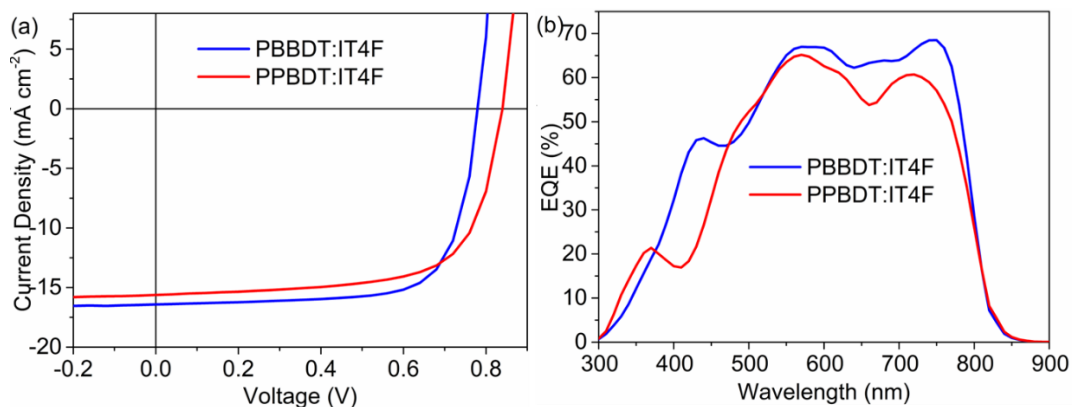


**Fig. S22** The  $^1\text{H}$  NMR spectrum of **PBBDT**  $\text{CDCl}_3$  at room temperature.



**Fig. S23** The  $^1\text{H}$  NMR spectrum of **PPBDT** in  $\text{CDCl}_3$  at room temperature.

## 5. Solar cell device data



**Fig. S24** (a)  $J$ - $V$  curves and (b) EQE spectra of the optimized OSCs based on polymers:IT-4F.

**Table S5** Photovoltaic parameters for polymer:IT-4F-based solar cells under AM1.5G illumination ( $100 \text{ mW cm}^{-2}$ )

Polymer	$V_{oc}^a$ (V)	$J_{sc}^a$ ( $\text{mA cm}^{-2}$ )	FF <sup>a</sup> (%)	PCE <sup>a</sup> (%)
<b>PBBDT</b>	$0.77 \pm 0.01$ (0.78)	$16.2 \pm 0.2$ (16.4)	$73.0 \pm 0.2$ (73.1)	$9.2 \pm 0.2$ (9.4)
<b>PPBDT</b>	$0.83 \pm 0.01$ (0.84)	$14.8 \pm 0.1$ (14.9)	$55.8 \pm 0.2$ (55.9)	$8.3 \pm 0.2$ (8.5)

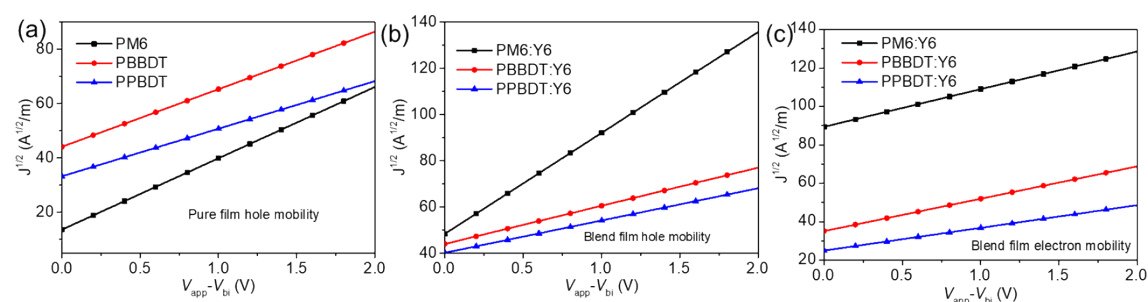
<sup>a</sup>The average values with standard deviations are obtained from 12 devices, and the values in parentheses are the highest values.

**Table S6** Device performance of the Polymers:Y6 solar cells fabricated with different annealing temperature

Polymer	Thickness (nm)	Annealing temperature ( $^{\circ}\text{C}$ )	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
<b>PBBDT</b>	98	w/o	0.79	21.8	42.6	7.3
		80	0.82	17.7	64.8	9.4
		100	0.81	20.3	61.9	10.2
<b>PPBDT</b>	103	w/o	0.83	15.6	46.7	6.1
		80	0.84	15.6	51.6	6.8
		100	0.86	15.3	55.9	7.3

**Table S7** Device performance of the Polymers:Y6 solar cells fabricated with different thickness of active layers

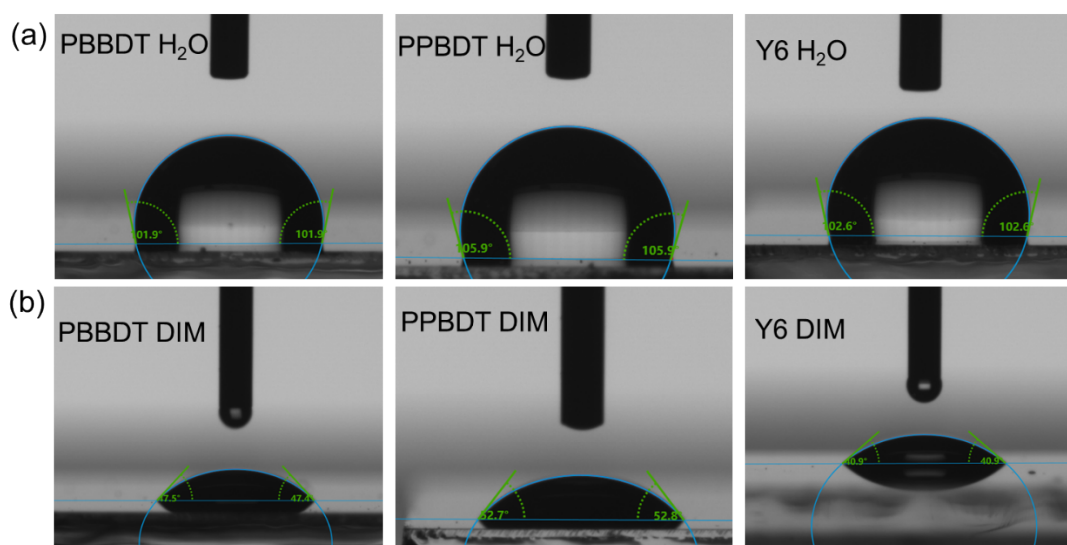
Polymer	Annealing temperature (°C)	Thickness (nm)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
<b>PBBDT</b>	100	98	0.81	20.3	61.9	10.2
		115	0.80	20.3	60.1	9.8
		138	0.82	18.1	62.7	9.3
<b>PPBDT</b>	100	103	0.86	15.3	55.9	7.3
		118	0.85	13.0	58.6	6.5
		135	0.84	15.6	51.6	6.8



**Fig. S25** The  $J$ - $V$  characteristics for (a) neat films, (b) blend films of hole-only devices, (c) blend films of electron-only devices.

**Table S8** Hole and Electron mobilities obtained by SCLC method

Active layer	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_h/\mu_e$
<b>PM6</b>	$3.10 \times 10^{-4}$	—	—
<b>PBBDT</b>	$1.90 \times 10^{-4}$	—	—
<b>PPBDT</b>	$1.56 \times 10^{-4}$	—	—
<b>PM6:Y6</b>	$3.40 \times 10^{-4}$	$2.73 \times 10^{-4}$	1.2
<b>PBBDT:Y6</b>	$1.81 \times 10^{-4}$	$1.68 \times 10^{-4}$	1.1
<b>PPBDT:Y6</b>	$1.44 \times 10^{-4}$	$0.98 \times 10^{-4}$	1.5



**Fig. S26** Contact angle measurements of **PBBDT**, **PPBDT**, and **Y6** thin-films by using deionized water and diiodomethane.

**Table S9** Contact angle of water and diiodomethane and the parameters for active layer materials

Surface	$\theta_{\text{H}_2\text{O}}$ (°)	$\theta_{\text{CH}_2\text{I}_2}$ (°)	$\gamma$ (mN/m)	$\chi^a$
<b>PBBDT</b>	101.9	47.5	37.20	0.13 <i>K</i>
<b>PPBDT</b>	105.9	52.8	34.63	0.33 <i>K</i>
<b>Y6</b>	102.6	40.9	41.67	

<sup>a</sup>The Flory-Huggins interaction parameter between polymers and acceptors, calculated via formula

$$\chi = K(\sqrt{\gamma_D} - \sqrt{\gamma_A})^2.$$