Electronic Supplementary Material (ESI) for Polymer Chemistry.

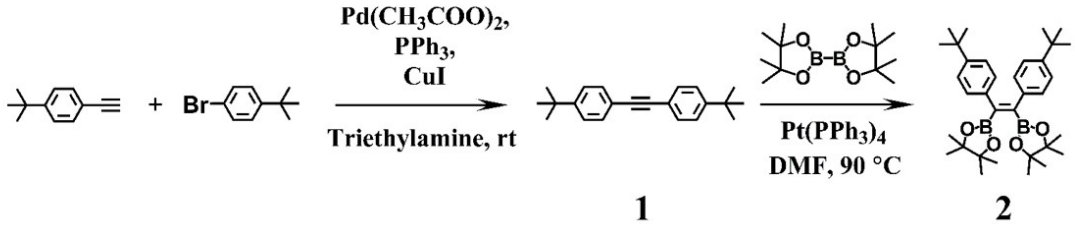
Supporting Information

The synthesis，characterization and flexible OFET application of three *(Z)*-1,2-bis(4-(tert-butyl)phenyl)ethane based copolymers

Yuli Huang, Wei Huang, Junwei Yang, Ji Ma, Moyun Chen, Haoyun Zhu and Weizhi Wang*

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science, Fudan University, Shanghai 200433, P. R. China.

E-mail: weizhiwang@fudan.edu.cn



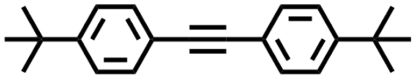
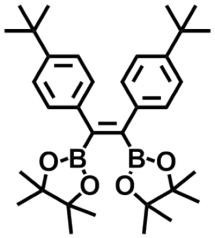
Scheme S1 Synthesis of *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane.

Synthesis of the monomers: 1,2-bis(4-tert-butylphenyl)ethyne (1) The purchased 1-bromo-4-tert-butylbenzene (11.35 g, 53.29 mmol) and 1-tert-butyl-4-ethynylbenzene (8.43 g, 53.35 mmol) were both dissolved in triethylamine in the nitrogen surroundings. Then stir the mixture for about 10 min, follow by a catalytic amount of triphenylphosphine, CuI and Pd(II) acetate (P:Cu:Pd =3:2:1) were added in the solution all at once. This reaction blend was heated under the reflux for 6 h until to appear absolute by a test named thin layer chromatogram, the mixture was chilled down, and the filtrate after filtering was concentrated in a vacuum circumstance. Finally, the product was purified through the column chromatography on silica gel to obtain the monomer 1 as white crystals in a yield of 86.5%. 1H NMR (400 MHz, CD2Cl2), δ (TMS, ppm): 7.52 – 7.42 (m, 4H), 7.42 – 7.33 (m, 4H), 1.33 (s, 18H); 13C NMR (100 MHz, CD2Cl2), δ (TMS, ppm): 151.56, 151.55, 151.54, 151.53, 151.52, 151.52, 131.19, 131.18, 131.16, 125.43, 125.43, 120.36, 88.79, 34.69, 34.68, 34.68, 31.01, 30.95, 30.92. Anal. Calcd for C22H26 (290.44): C, 90.90; H, 9.10; Found: C, 91.01, H, 8.99.

Synthesis of *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane *(2)*. A 100-mL flask equipped with a reflux condenser, a magnetic stirring bar and a septum inlet, was charged with a catalytic amount of tetrakis(triphenylphosphine)platinum ($Pt(PPh_3)_4$) and bis(pinacolato)diboron (10.08 g, 39.69 mmol) and then flushed with N_2. DMF (80 mL) and **1** (11.52 g, 39.72 mmol) were individually added. After stirring for around 24 h at 90 °C, the acquired mixture was extracted with CH_2Cl_2. About 10 times of cold-water washing was used to remove DMF in succession, and dried over anhydrous magnesium sulfate ultimately. Kugelrohr distillation (0.15 mm Hg) delivered the monomer **2**, white crystals with 78.4% yield. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (TMS, ppm): 7.13 – 7.06 (m, 4H), 6.87 – 6.73 (m, 4H), 1.32 (s, 24H), 1.24 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2), δ (TMS, ppm): 148.69, 138.77, 128.92, 128.91, 124.35, 84.01, 34.21, 34.20, 34.19, 31.03, 31.01, 31.00, 24.66. MS (MALDI-TOF): m/z (%): 567.320 (100) [M+Na]+. Anal. Calcd for $C_{34}H_{50}B_2O_4$ (544.38): C, 74.95; H, 9.18; Found: C, 74.58; H, 9.33.

Table S1 Summary of crystal data and reflection collection parameters for 1,2-bis(4-tert-butylphenyl)ethyne and *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-

tetramethyl-1,3,2-dioxaborolan-2-yl)ethane

		
Empirical formula	$C_{22}H_{26}$	$C_{34}H_{50}B_2O_4$
Formula weight	290.43	544.36
Crystal size, mm	0.32 x 0.28 x 0.24	0.26 x 0.21 x 0.18
Crystal system	Monoclinic, P21/c	Triclinic
space group	P2(1)/c	P-1
a, Å	11.731(4)	10.991(18)
b, Å	10.216(4)	12.54(2)
c, Å	15.667(6)	13.97(4)
a, deg	90	108.83(5)
β, deg	96.915(7)	103.58(5)
γ, deg	90	104.77(3)
V, Å^3	1863.9(12)	1653(6)
Z	4	2
Calculated density, Mg/m^3	1.035	1.094
F(000)	632	592
Temperature, K	293(2)	296(2)
Wavelength, Å	0.71073	0.71073
μ(Mo Ka), mm^{-1}	0.058	0.068
$2\theta_{max}$,deg (Completeness)	25.00 (99.8 %)	24.99(97.8 %)
no. of collected reflections	9206	8152
no. of unique ref.(R_{int})	3272 (0.0387)	5701 (0.0933)
Data/restraints/parameters	3272 / 6 / 200	5701 / 0 / 362
R_1, wR_2 [obs I>2σ (I)]	0.0967, 0.1832	0.1322, 0.2363
R_1, wR_2 (all data)	0.1394, 0.1951	0.1805, 0.2686
residual peak/hole, e. Å^{-3}	0.486 /-0.290	0.436/-0.302
transmission ratio	0.9863 /0.9817	0.9878/0.9824
Goodness-of-fit on F^2	1.013	1.196

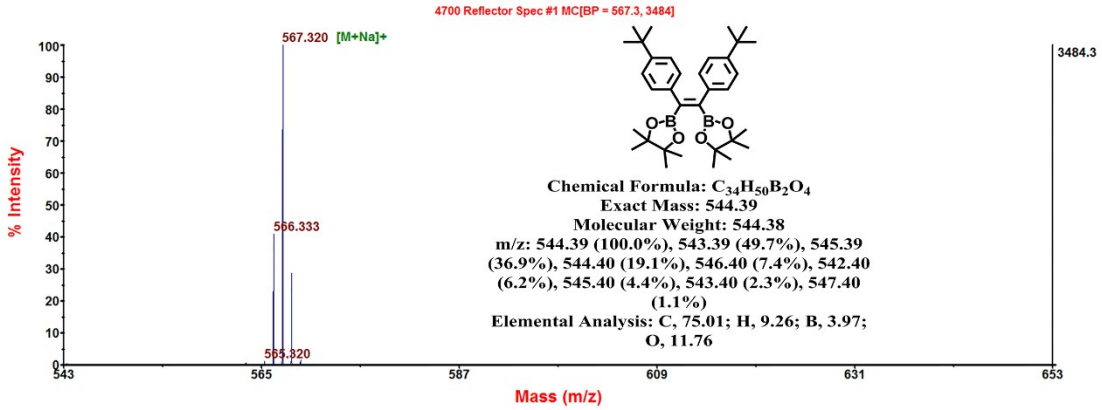


Fig. S1 The MALDI-TOF of *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane.

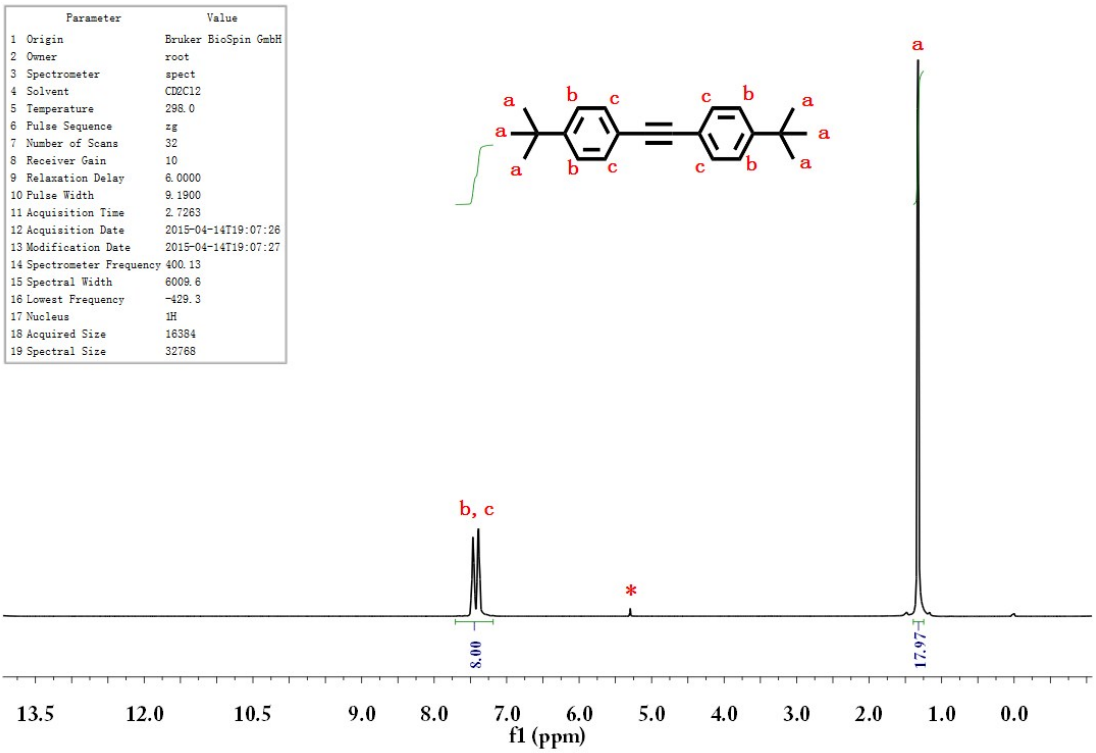


Fig. S2 The ^{1}H-NMR spectrum of 1,2-bis(4-tert-butylphenyl)ethyne**.**

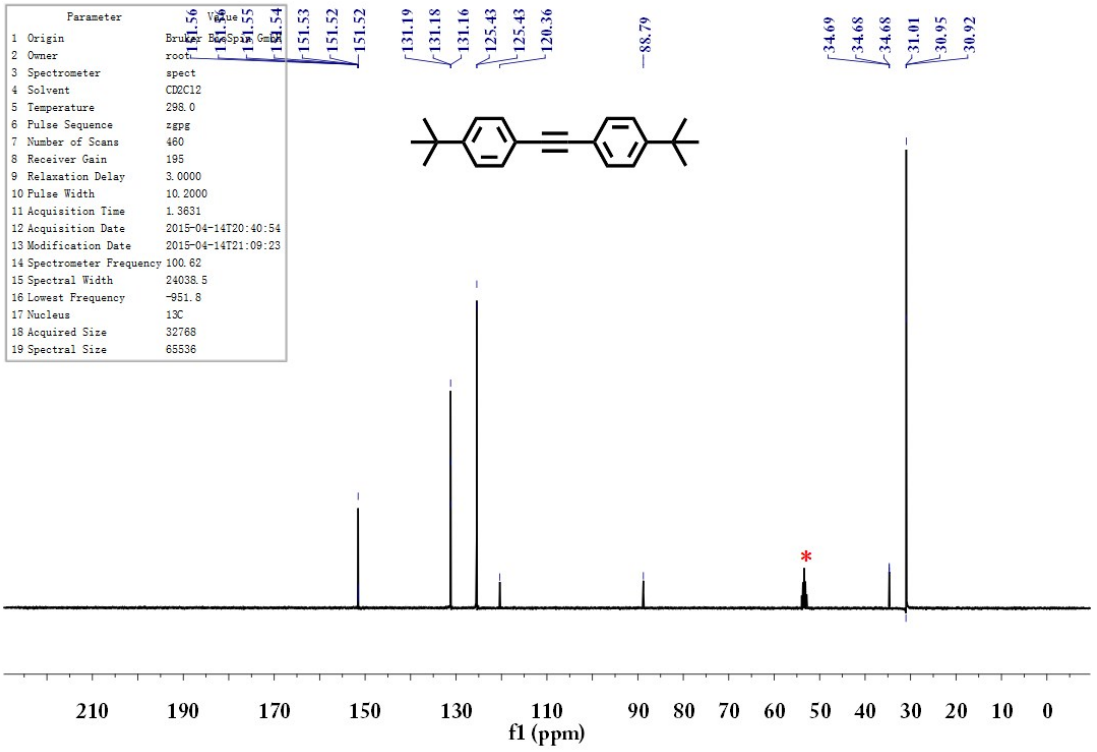


Fig. S3 The ^{13}C-NMR spectrum of 1,2-bis(4-tert-butylphenyl)ethyne.

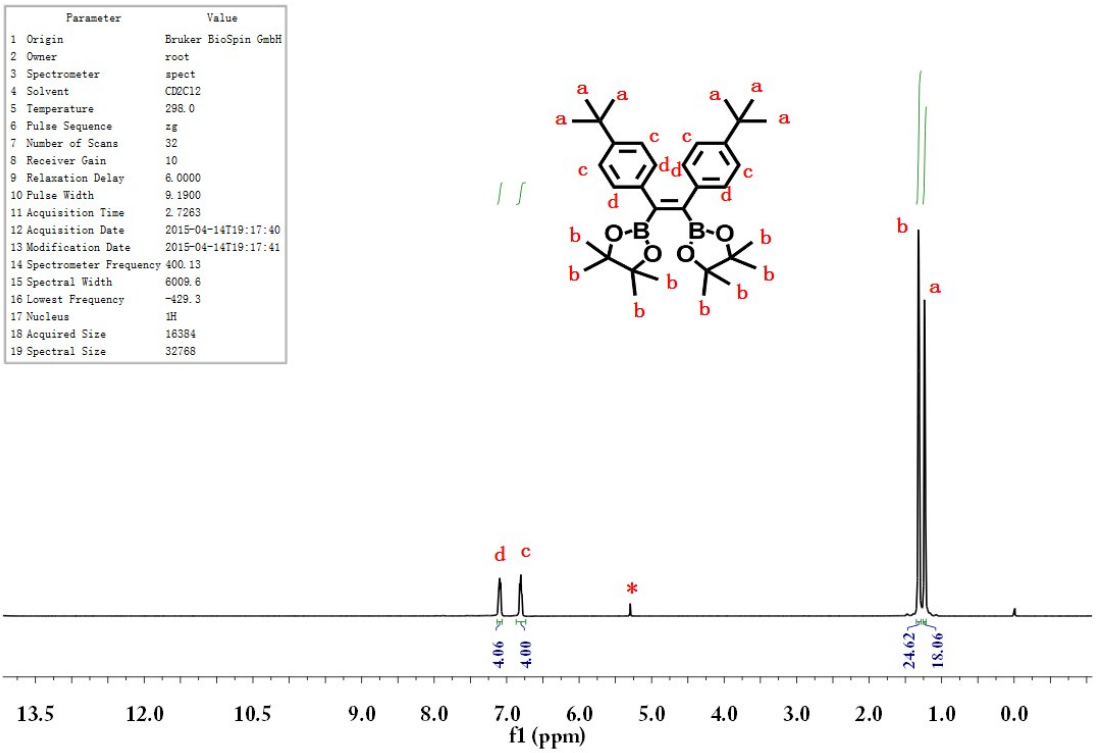


Fig. S4 The ^{1}H-NMR spectrum of *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane.

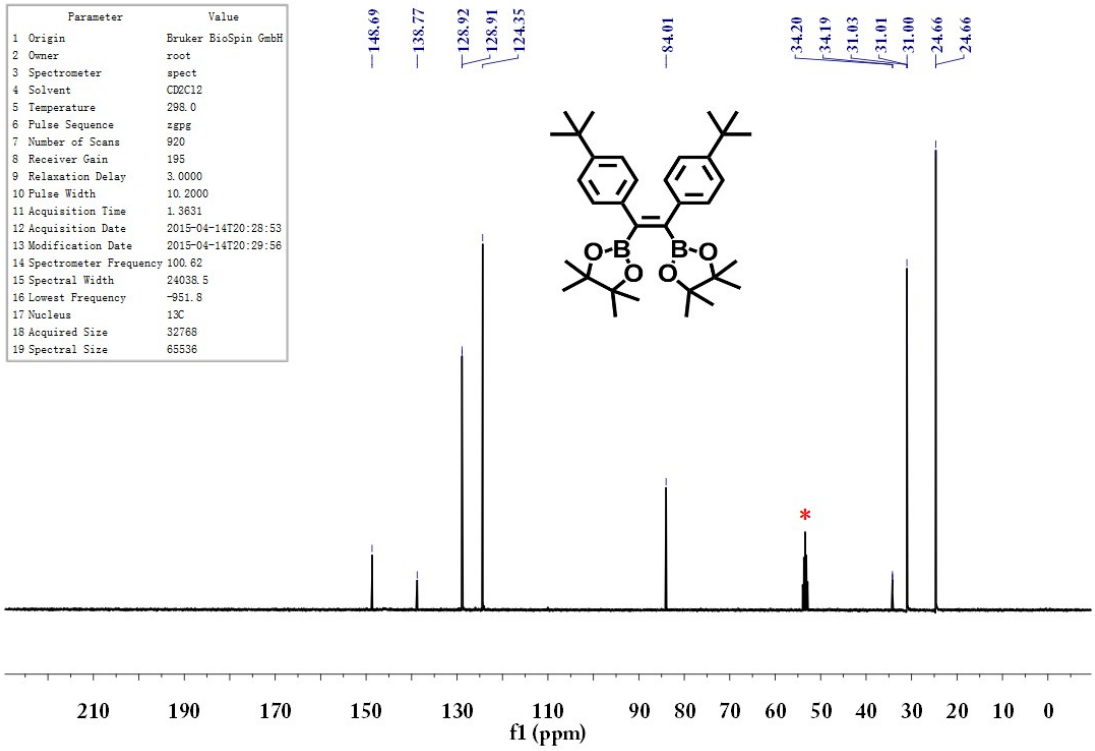


Fig. S5 The ^{13}C-NMR spectrum of *(Z)*-1,2-bis(4-tert-butylphenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethane.

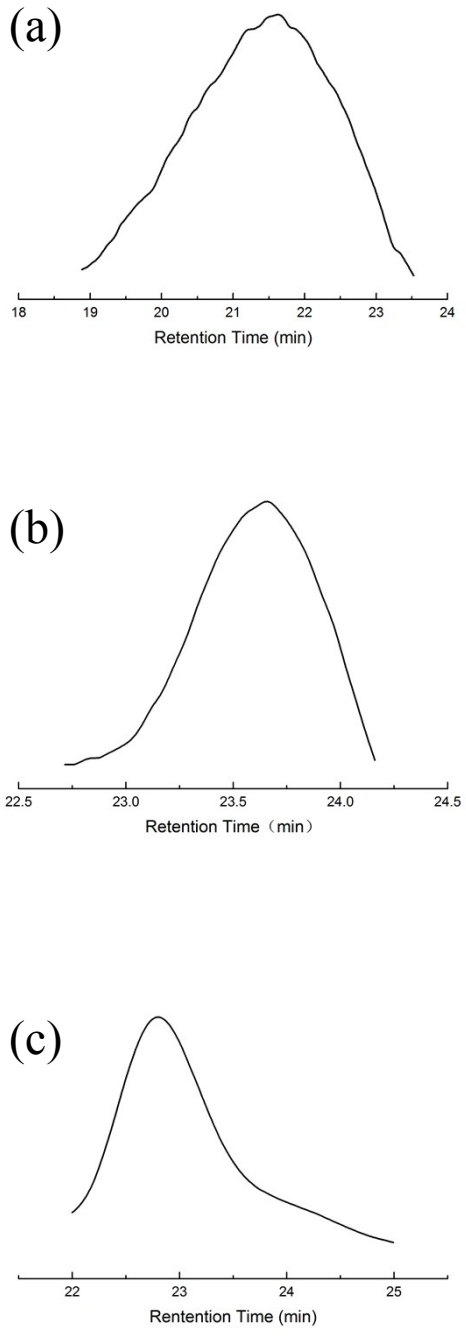


Fig. S6 GPC data of (a) PBPT, (b) PBPTT and (c) PBPDT

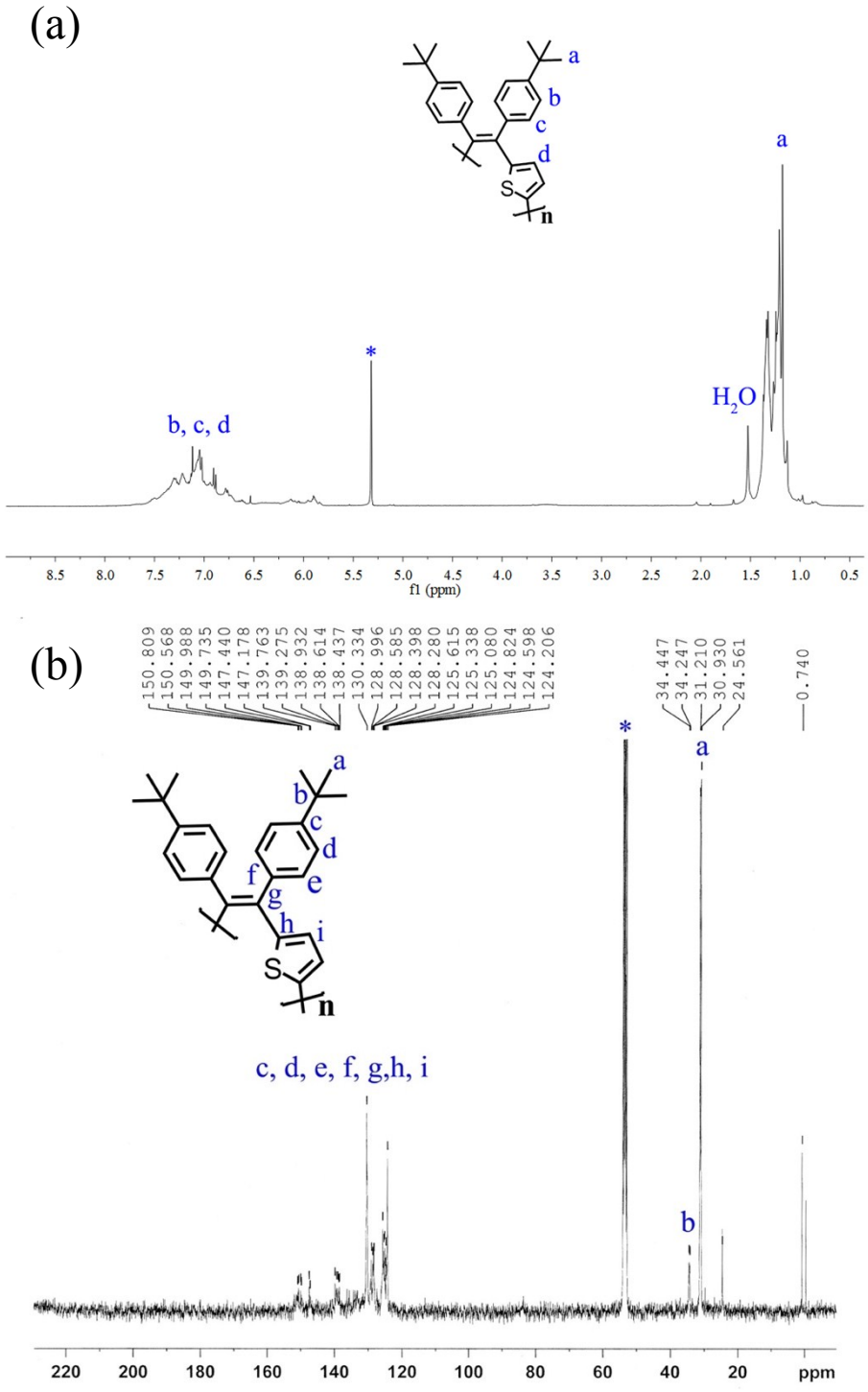


Fig. S7 (a)^{1}H-NMR and (b)^{13}C-NMR spectra of PBPT

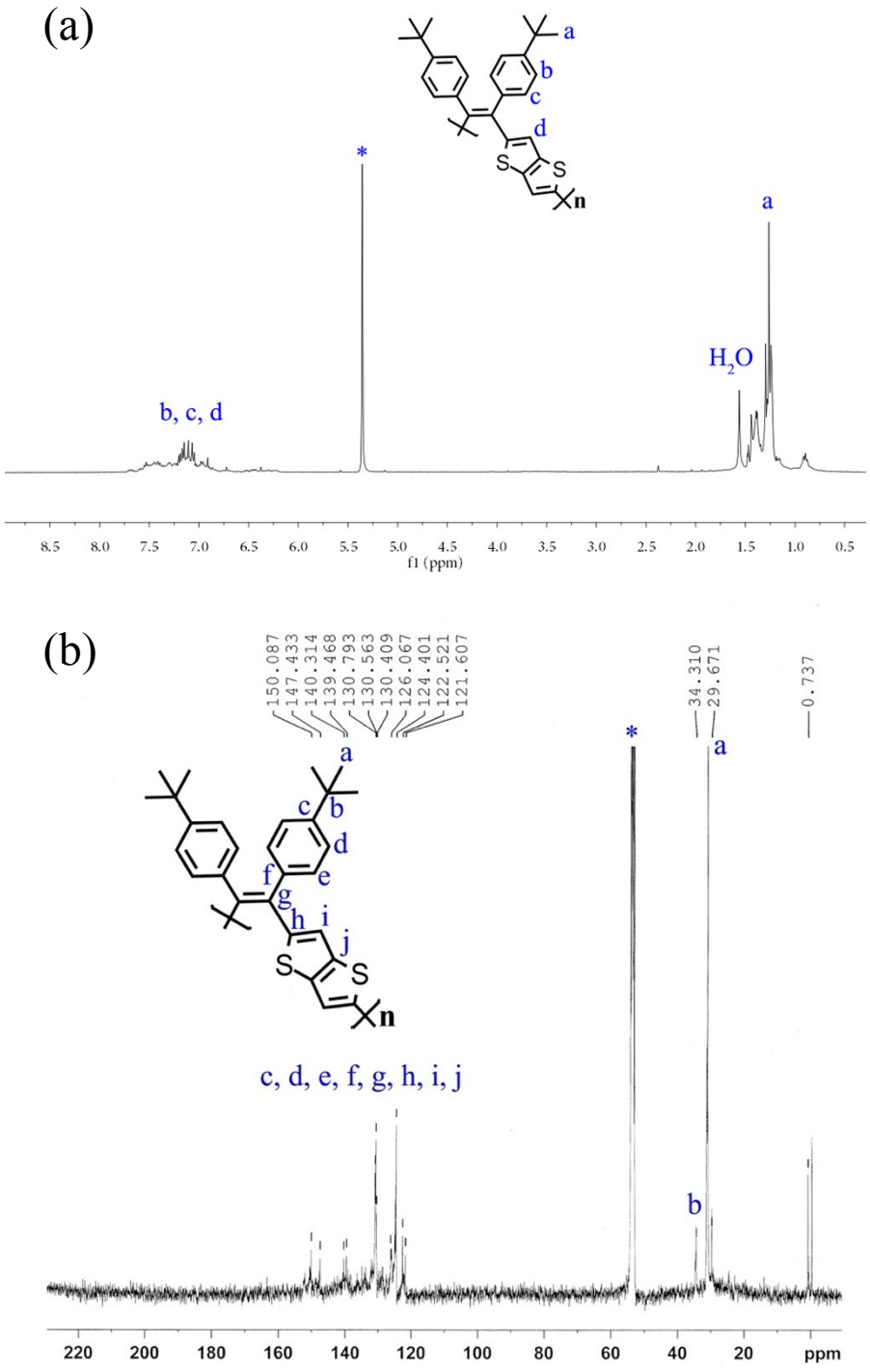


Fig. S8 (a)^{1}H-NMR and (b)^{13}C-NMR spectra of PBPTT

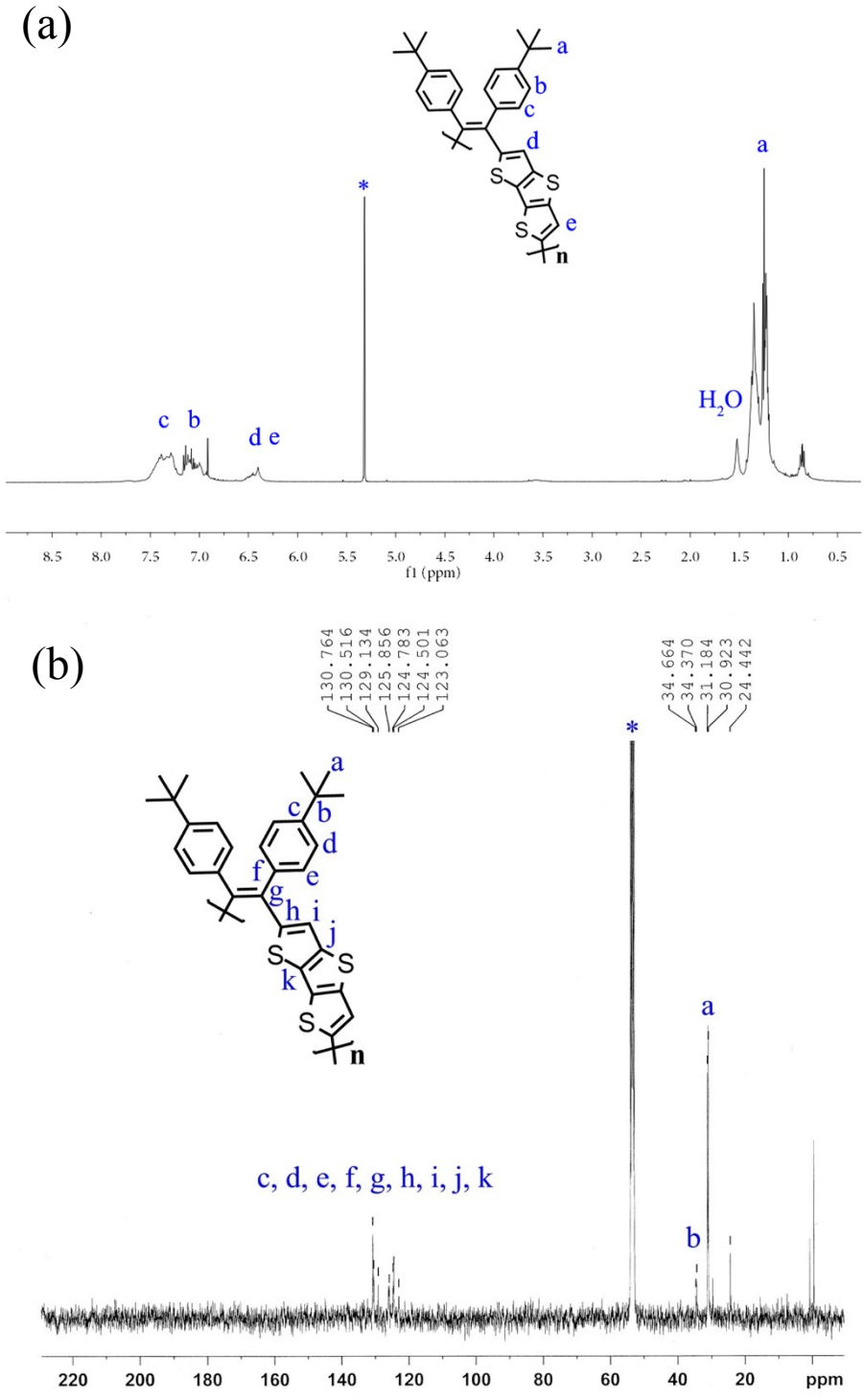


Fig. S9 (a)^{1}H-NMR and (b)^{13}C-NMR spectra of PBPDT

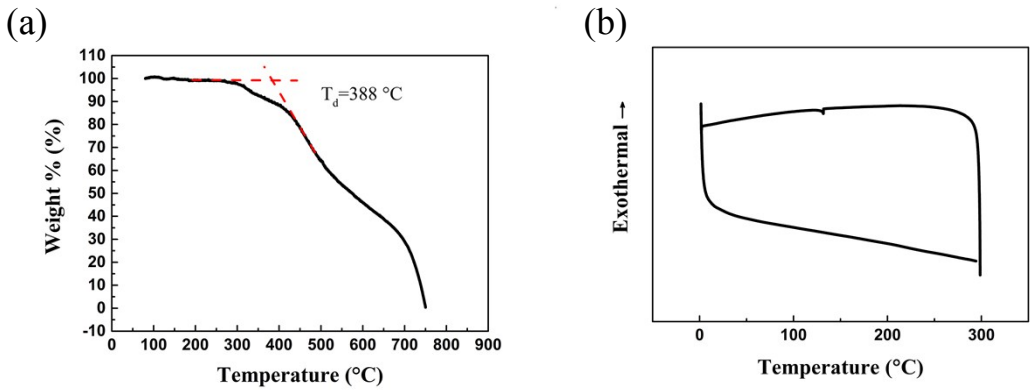


Fig. S10 (a)TGA and (b)DSC curves of PBPT

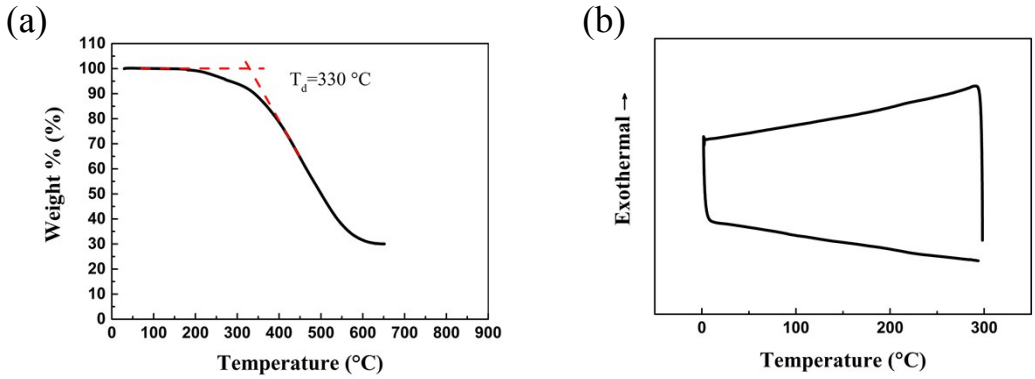


Fig. S11 (a)TGA and (b)DSC curves of PBPTT

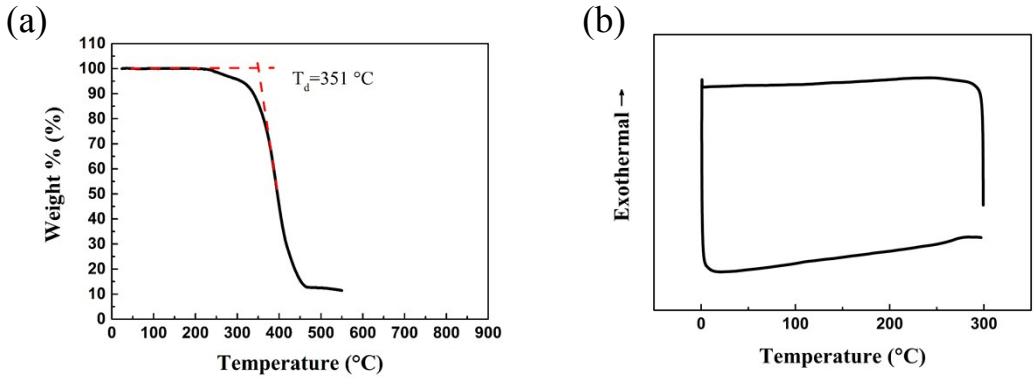


Fig. S12 (a)TGA and (b)DSC curves of PBPDT

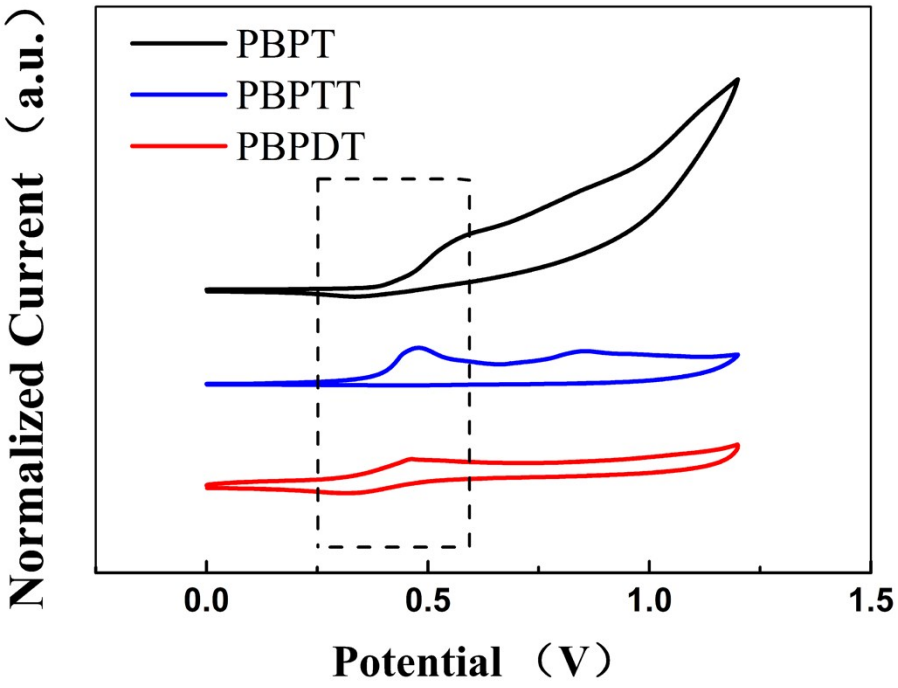


Fig. S13 Cyclic voltammograms of PBPT, PBPTT and PBPDT

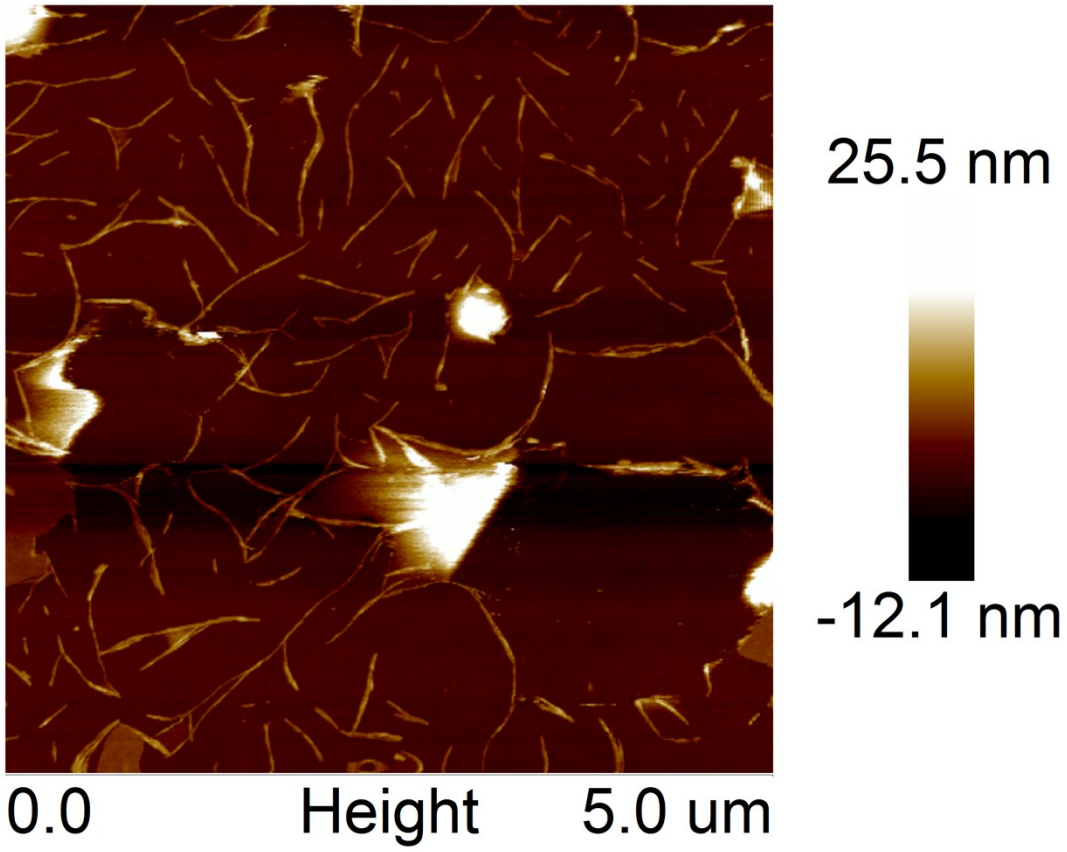


Fig. S14 AFM photo of PBPTT film.

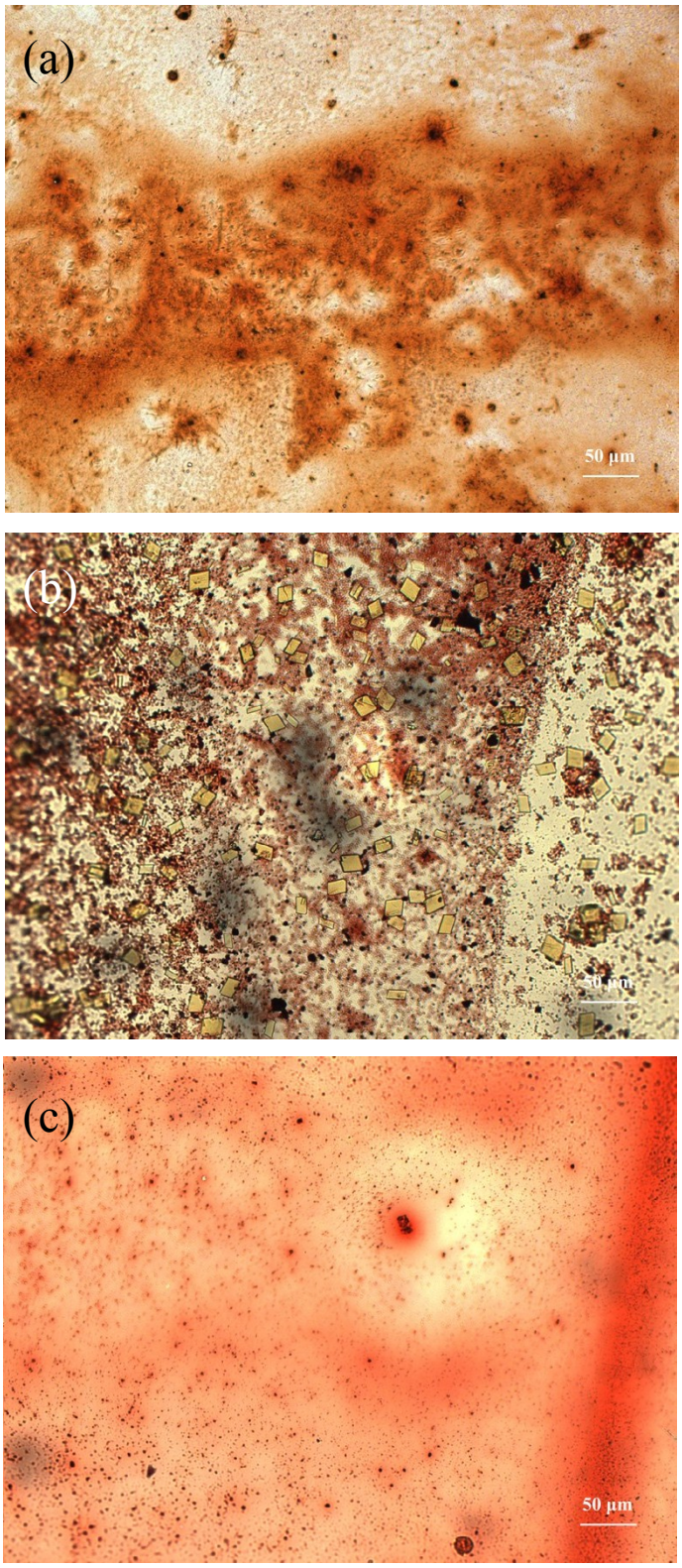
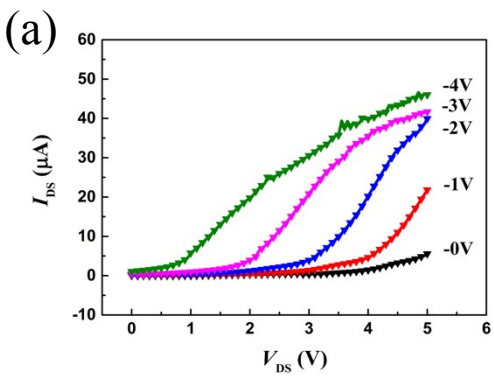


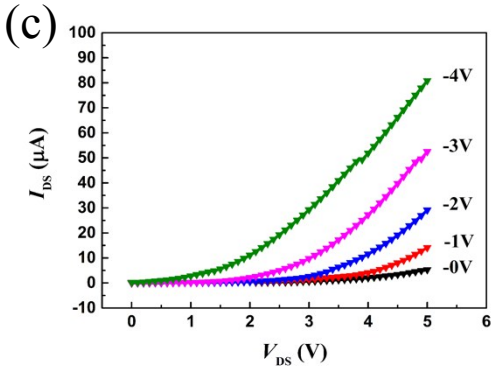
Fig. S15 POM photos of (a) PBPT, (b) PBPTT and (c) PBPDT in the bright field.



(b)

Summary

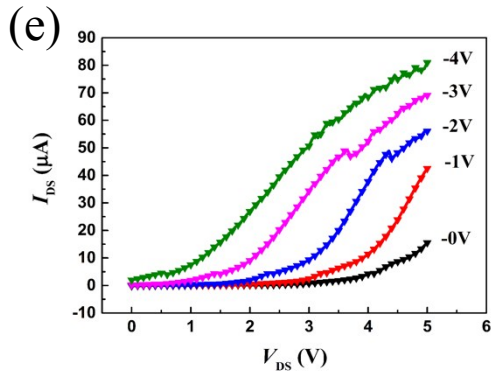
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	0.00109	1.63026E-5	-0.00118	7.4762E-6	0.98809



(d)

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
B	-2.37392E-4	1.85772E-5	-0.00184	8.50148E-6	0.99872



(f)

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	-1.93988E-4	3.33355E-5	-0.00173	1.52873E-5	0.97708

Fig. S16 The output curves of OFET devices based on (a) PBPT, (c) PBPTT and (e) PBPDT. The linear fitting information of OFET devices based on (b) PBPT, (d) PBPTT and (f) PBPDT.

(a)

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
B	-5.10854E-4	2.04896E-5	-0.00176	9.39635E-6	0.99155

(b)

Summary

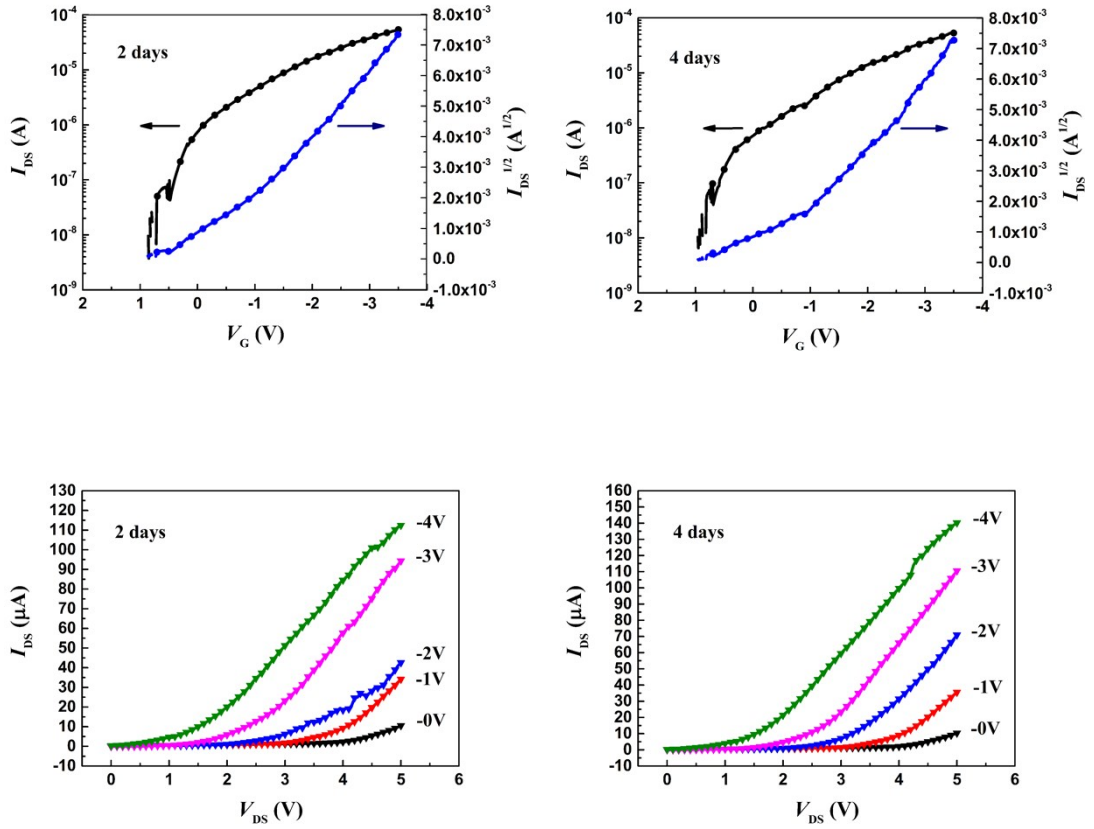
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
B	-3.73099E-4	1.56039E-5	-0.00173	7.15581E-6	0.99491

Fig. S17 The linear fitting information of OFET device based on PBPTT in two bending condition. (a) belongs to the condition shown in Fig. 5 (a), while (b) belongs to the condition shown in Fig. 5 (d)

Table S2 The characteristics and performance of the OFET device based on PBPTT during two weeks.

Time (day)	μ ($cm^2V^{-1}s^{-1}$)	on/off ratio	V_{TH} (V)
0	0.27	1×10^4	-0.13
2	0.36	1.4×10^4	-0.09
4	0.38	8.1×10^3	-0.27
6	0.40	6.8×10^3	-0.19
8	0.28	3.8×10^3	-0.09
10	0.38	2.9×10^3	-0.14
12	0.32	1.5×10^3	-0.20
14	0.50	1.6×10^3	-0.70

Fig. S18 The transfer plots, output curves and linear fitting information of the OFET device based on PBPTT during two weeks:



2 days

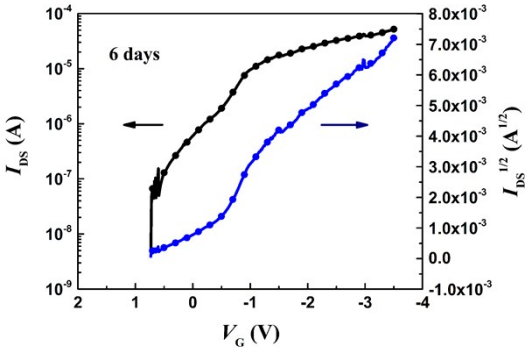
Summary

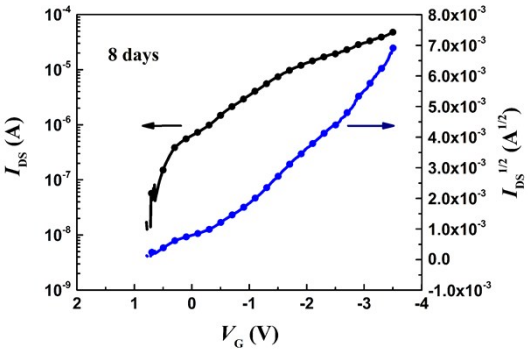
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	-1.88655E-4	1.37592E-5	-0.00211	5.82084E-6	0.9981

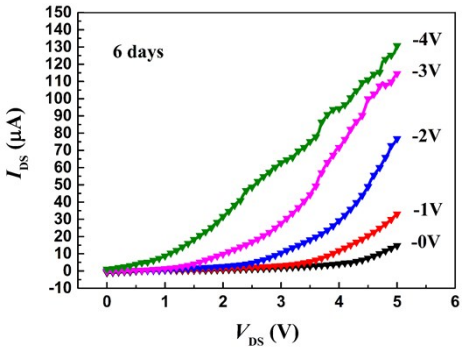
4 days

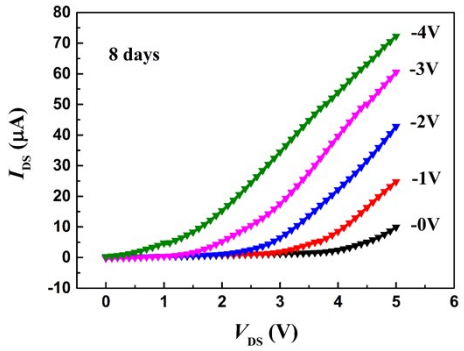
Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	-5.85365E-4	2.69769E-5	-0.00218	1.14126E-5	0.9932









6 days

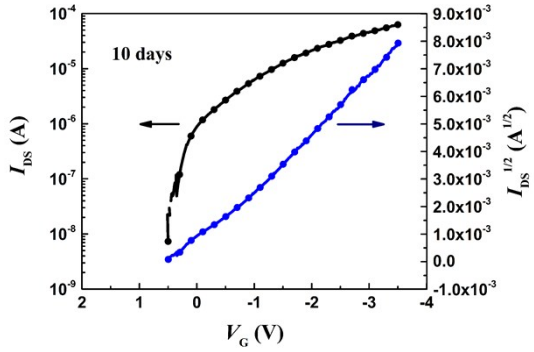
Summary

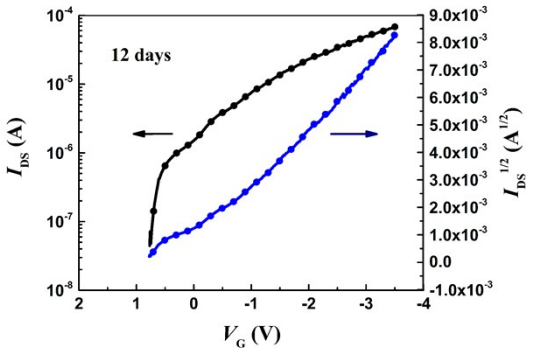
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	0.00182	1.89393E-5	-0.00151	8.01226E-6	0.99302

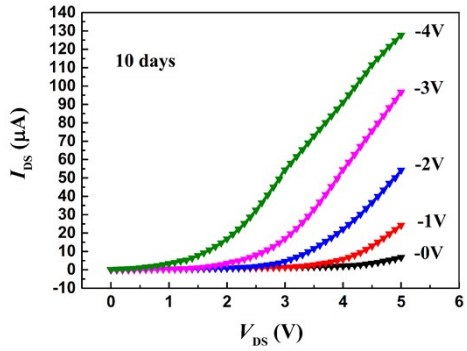
8 days

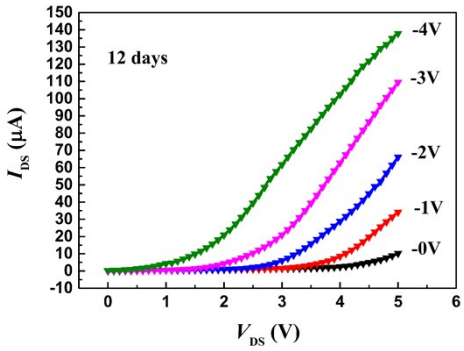
Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	-1.62886E-4	2.35618E-5	-0.0019	9.9678E-6	0.99319









10 days

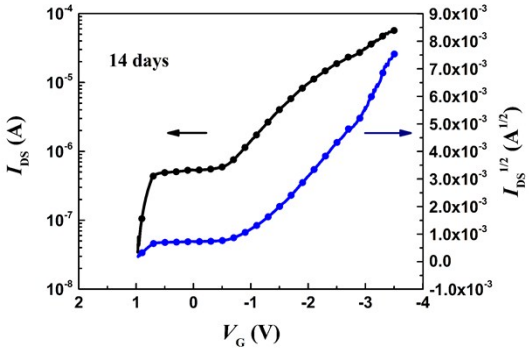
Summary

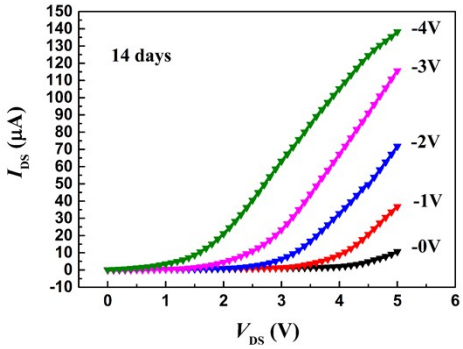
	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	2.9309E-4	5.58783E-6	-0.00217	2.36393E-6	0.9997

12 days

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	4.01014E-4	1.47514E-5	-0.0022	6.24056E-6	0.99798





14 days

Summary

	Intercept		Slope		Statistics
	Value	Standard Error	Value	Standard Error	Adj. R-Square
C	-0.00174	4.71887E-5	-0.00249	1.99632E-5	0.98419