

## **Supporting Information for**

# **Synthesis of an indacenodithiophene-based fully conjugated ladder polymer and its optical and electronic properties**

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**Synthesis of Monomers and Polymers.** Monomer 1 and 2 were synthesized according to the literature method.<sup>1-2</sup> All other chemicals were purchased from the commercial source and used without further purification unless otherwise indicated.

**Synthesis of PBTT.** A 25 mL glass flask was charged with monomer 1 (0.527 g, 1.02 mmol), monomer 2 (0.475 g, 1.02 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (8.0 mg, 0.00875 mmol), P(o-tol)<sub>3</sub> (16.0 mg, 0.0525 mmol) and chlorobenzene (8 mL). The flask was evacuated and refilled with nitrogen for three times, and then was heated to 110 °C for 48 hours. For end-capping, 2-(tributylstannyl)thiophene (0.2 mL) was added into the mixture and stirred for 12 hours, 2-bromothiophene (0.5 mL) was then added and stirred for 12 hours. After cooling to the room temperature (RT), the mixture was precipitated into methanol. The polymer was collected and further washed with acetone and hexane, then dried in vacuum to give product PBTT as a yellow solid (0.705 g, 80%).  $\lambda_{\text{max}}$  (solution)=403 nm; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 2H), 7.37 (s, 2H), 4.20 (s, 4H), 1.60 (s, 2H), 1.23 (s, 16H), 0.89 (d, J = 6.8 Hz, 6H), 0.83 (t, J = 7.4 Hz, 6H).

**Synthesis of PFIDT.** In a 125-mL flask, 1-bromo-4-hexylbenzene (900 mg, 3.78 mmol) was dissolved in THF (40 mL), and placed under a nitrogen atmosphere. The flask was then cooled to -78°C and stirred while 2.5 M n-BuLi (9.45 mL, 3.78 mmol) was added dropwise. The reaction mixture was stirred for one hour at -78°C, and then a solution of PBTT (200 mg, 0.378 mmol) in THF (20 mL) was added dropwise. The reaction was warmed to RT and stirred overnight. The reaction solution then poured into water and extracted with dichloromethane, and dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>.

After removal of the solvent, the crude product directly used for the next step without further purification. The crude product was dissolved in 20 mL of dry chloroform, and a solution of boron trifluoride diethyl etherate (>46.5 w%, 1.0 mL, 3.78 mmol) was added *via* a syringe. The reaction mixture was stirred for two hours at RT. Then, 10 mL of p.a. ethanol and 10 mL of water were added to terminate the reaction. The layers were separated and the organic layer was washed with water for four times. After removal of the solvents under reduced pressure, the polymer was precipitated and dried over vacuum to give product PFIDT as black solid (310 mg, 90%). GPC (chlorobenzene, 80 °C):  $M_n = 32400$  g/mol,  $M_w = 86700$  g/mol;  $\lambda_{\max}$  (film) = 564 nm;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 14.0$  Hz, 1H), 7.23-6.59 (m, 8H), 2.52 (s, 4H), 1.43-1.07 (m, 16H), 0.99-0.69 (m, 8H).

**Characterization.**  $^1\text{H}$  NMR spectra were recorded on a Bruker AV400 NMR spectrometer and used tetramethylsilane (TMS) as an internal standard in  $\text{CDCl}_3$ . The molecular weight was determined by GPC using THF as the eluent and monodispersed polystyrene as the standard. The IR spectra of polymers were characterized by a Spectrum One B FT-IR spectrometer (Perkin-Elmer Inc., USA). The UV-Vis spectra of polymers were measured on with a TU-1601 spectrophotometer by using a 1 cm glass cuvette. Cyclic voltammetry (CV) was performed in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 100 mV/s with ITO as the working electrode, Pt wire as the counter electrode and  $\text{Ag}/\text{Ag}^+$  as the reference electrode.

**OFETs fabrication.** We fabricated the bottom-gate bottom-contact (BGBC) organic

field effect transistors (OFETs) with solution-processed semiconductor. Highly doped n-typed Si wafer with 300 nm thick thermally grown SiO<sub>2</sub> layers were used as gate substrates. The source-drain gold electrodes were formed by photolithography. We used octadecyltrichlorosilane (OTS) self-assembled-monolayers as the surface treatment layers for cleaning SiO<sub>2</sub> dielectrics, and then spin-coated the polymer solution (6 mg/mL in o-dichlorobenzene) onto the OTS-modified SiO<sub>2</sub> substrate at 3000 rpm for 40 s. For the annealing of OFETs, the samples were placed on a hotplate in air for 5 min. The device performance measured after each annealing step at room temperature in air by using a Keithley 4200 Semiconductor Characterization System. The carrier mobility ( $\mu$ ) was calculated from the data in the saturated regime according to the equation

$$I_{DS}=(W/2L)C_i\mu(V_G-V_T)^2$$

Where  $I_{DS}$  is the saturation drain current,  $W/L$  is the channel width/length,  $C_i$  is the capacitance per unit area of the gate dielectric layer, and  $V_G$  and  $V_T$  are the gate voltage and threshold voltage, respectively.

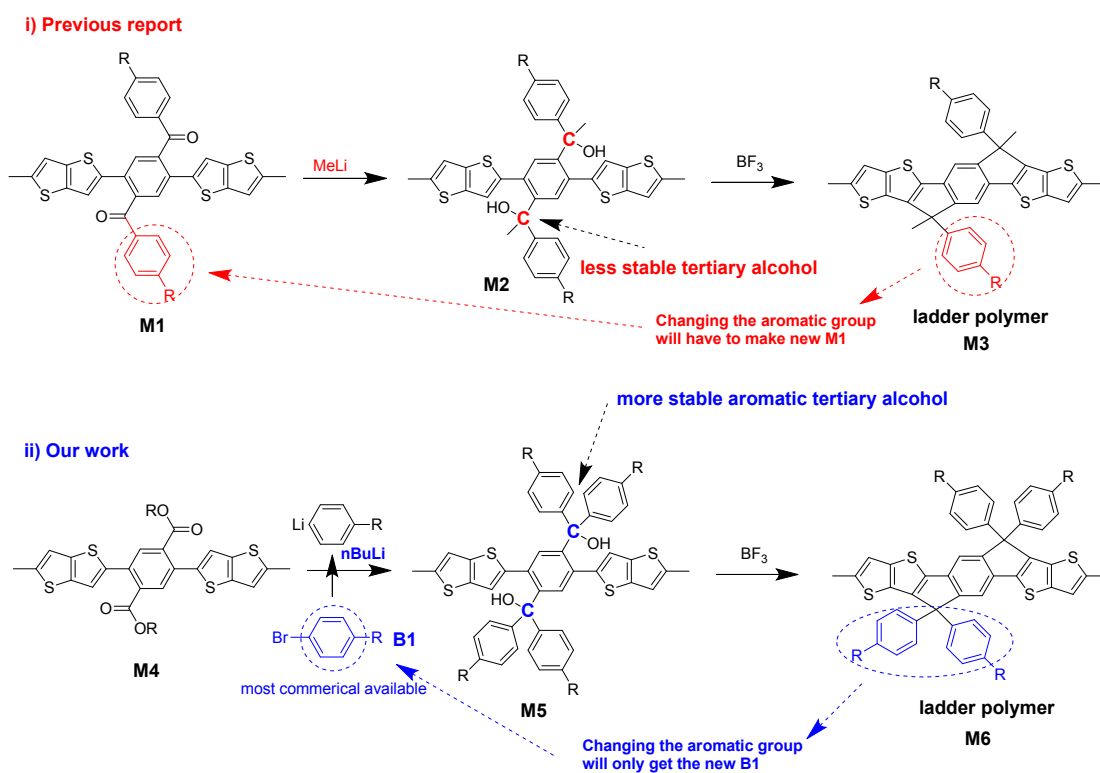


Fig. S1 The comparison of previous and current strategies toward the ladder polymer.

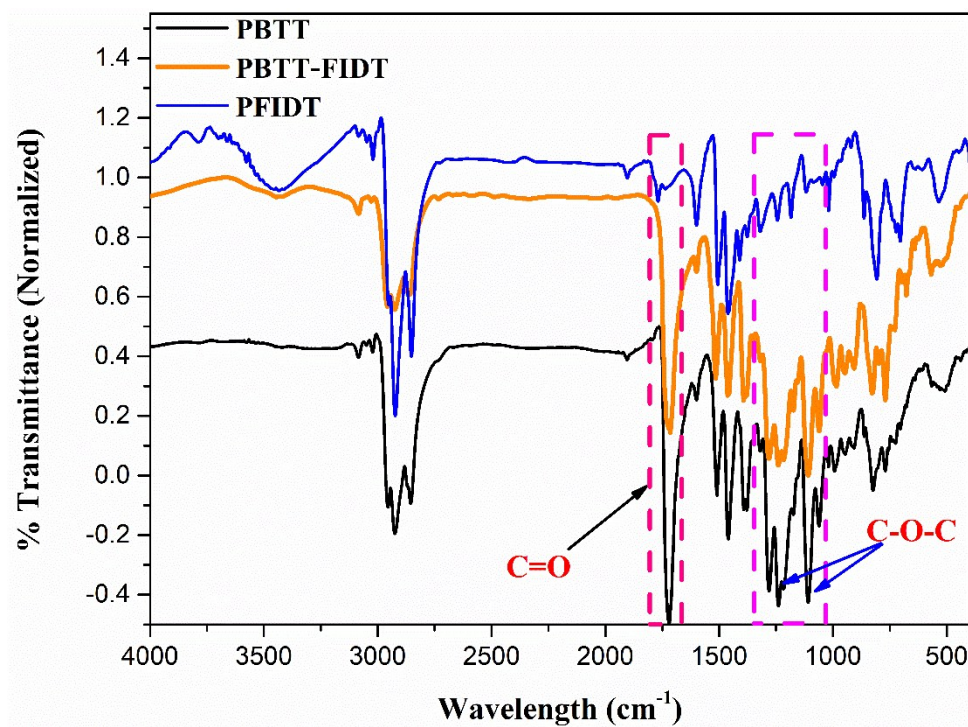


Fig. S2 FT-IR spectra of PBTT (before fusion), PBTT-FIDT (partial fusion) and PFIDT (after fusion).

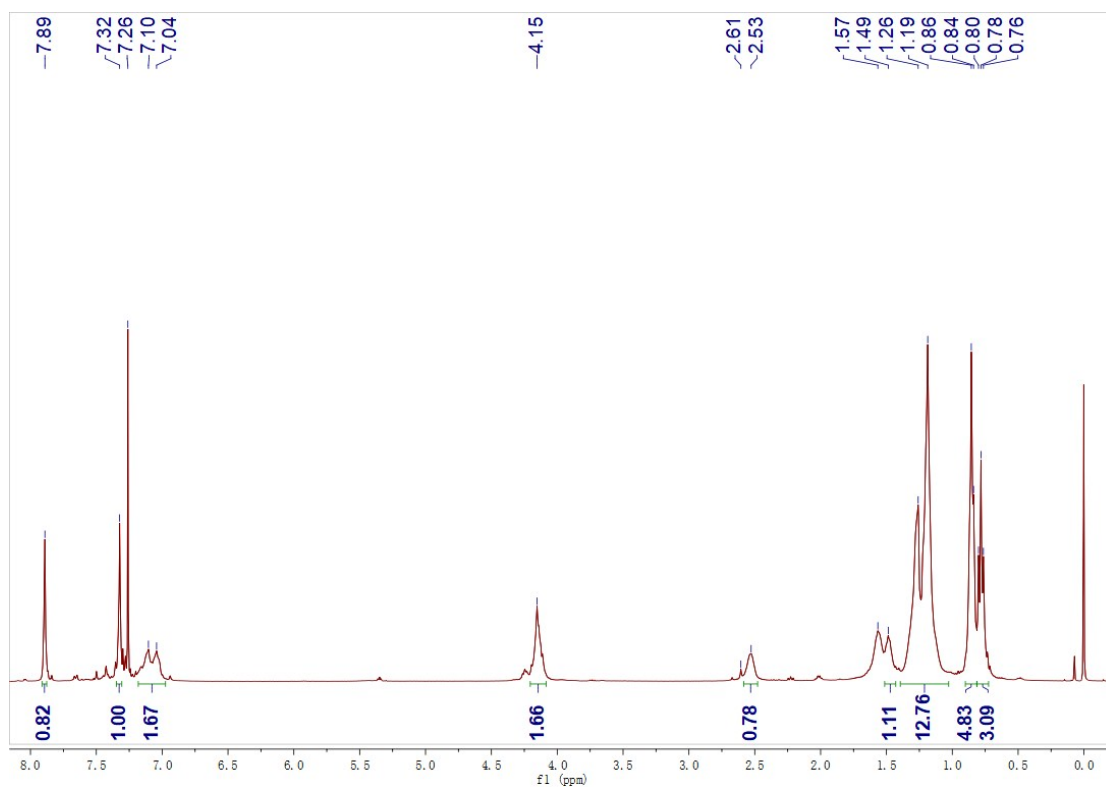


Fig. S3 The  $^1\text{H}$  NMR spectra (400 MHz) of PBTT-FIDT ( $\text{CDCl}_3$ , 298K).

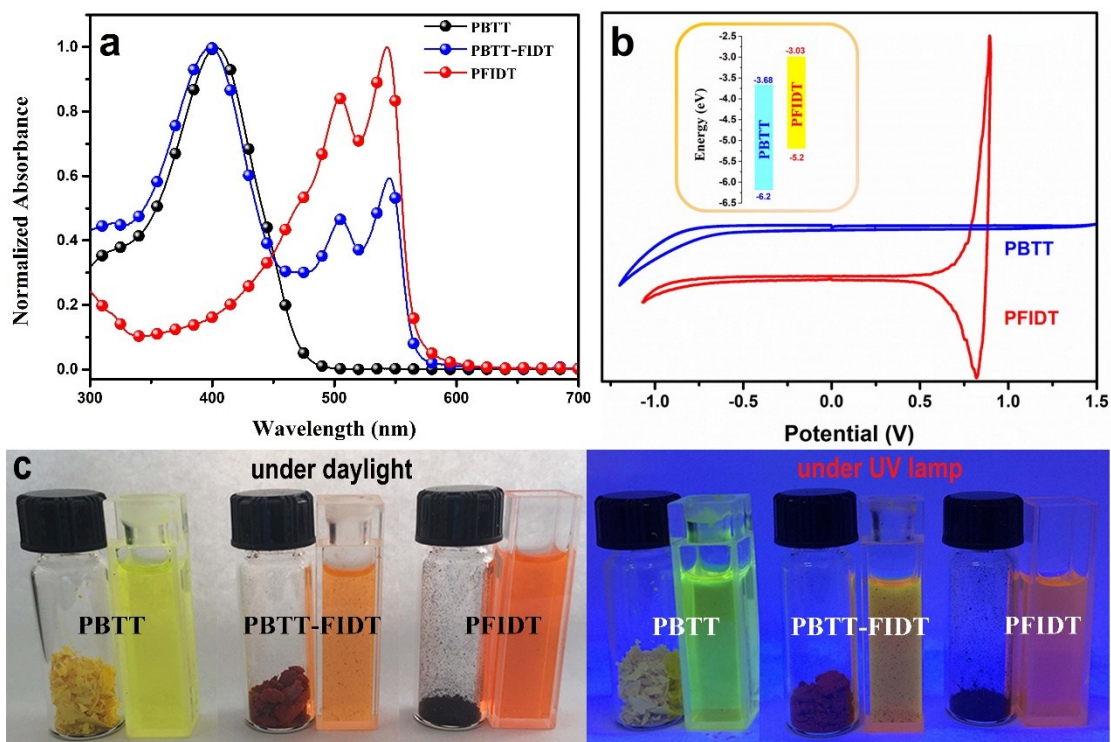
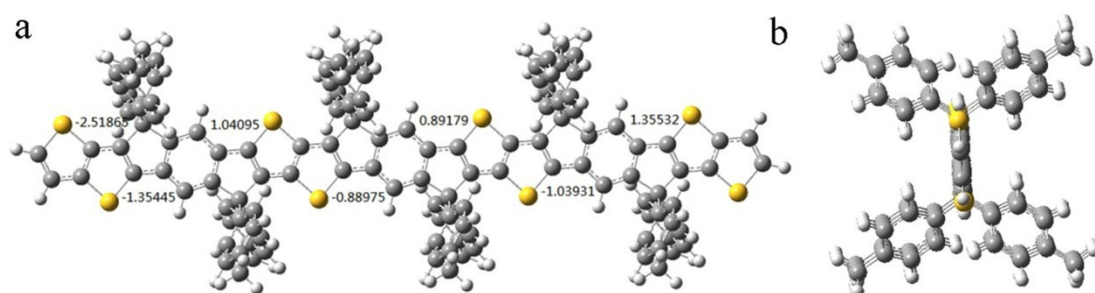


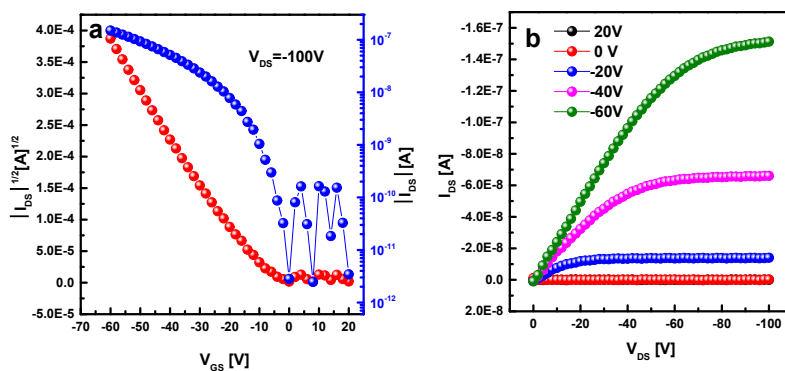
Fig. S4 a) Normalized absorption spectra of PBTT, PBTT-FIDT and PFIDT in  $\text{CHCl}_3$ ; b) The CV and the energy level diagrams of PBTT and PFIDT; c) Color changes under different light condition (PBTT, PBTT-FIDT and PFIDT, respectively).

The electrochemical properties of PBTT and PFIDT were investigated by cyclic voltammetry (CV) method in film. Cyclic voltammetry was carried out in a standard

three-electrode electrochemical cell employed with a platinum working electrode and an Ag/AgCl reference electrode while using ferrocene as an internal standard. The energy level referenced for ferrocene compared to vacuum was 4.80 eV. PFIDT exhibits a distinct oxidation wave and less obvious reduction wave, whereas PBTT shows a reduction wave and very weak oxidation wave (Figure S3b). The highest occupied molecular orbital (HOMO) energy level of PFIDT and the lowest occupied molecular orbital (LUMO) energy level are estimated to be -5.20 eV and -3.68 eV, respectively (Table 1).



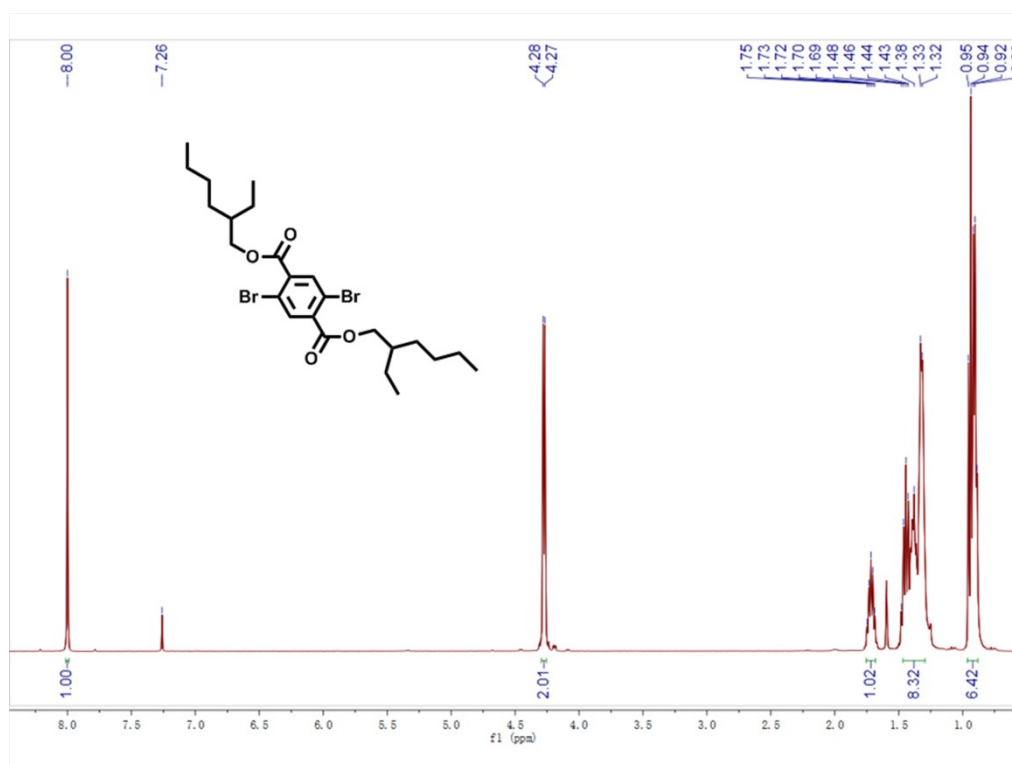
**Fig. S5** a) The model fragment for studying the dihedral angle in PFIDT; b) The optimized geometry of PFIDT.



**Fig. S6** The typical transfer (a) and output characteristics (b) of OFETs (channel length,  $L=10\ \mu\text{m}$ ) based on PFIDT.

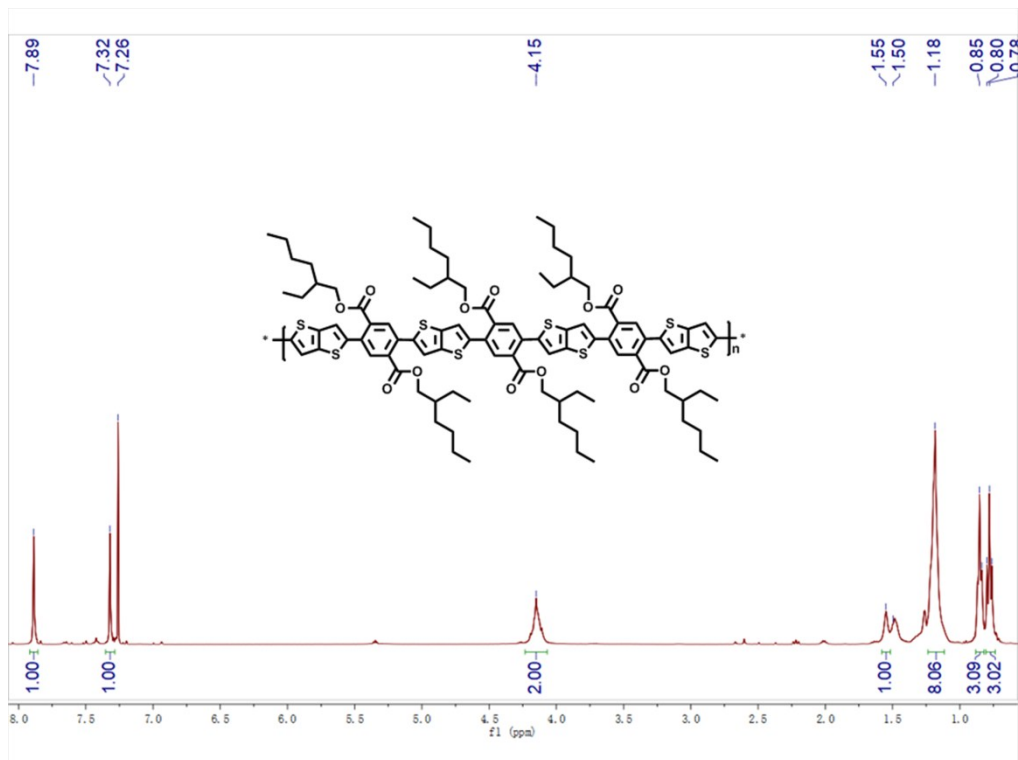
**Table S1** Summary of PFIDT-n-Based OFET Device Performances.

$L[\mu\text{m}]$	$T(^{\circ}\text{C})$	$\mu\ [\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}]$	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}}\ [\text{V}]$
10	RT	$4.56\times 10^{-5}$	$10^4$	-9.42
	80	$5.62\times 10^{-5}$	$10^5$	-11.58
	120	$5.37\times 10^{-5}$	$10^4$	-12.11
	200	$4.56\times 10^{-5}$	$10^2$	-11.35
5	RT	$1.47\times 10^{-4}$	$10^3$	-11.50
	80	$1.70\times 10^{-4}$	$10^5$	-12.32
	120	$1.91\times 10^{-4}$	$10^6$	-12.65
	200	$1.54\times 10^{-4}$	$10^3$	-12.30

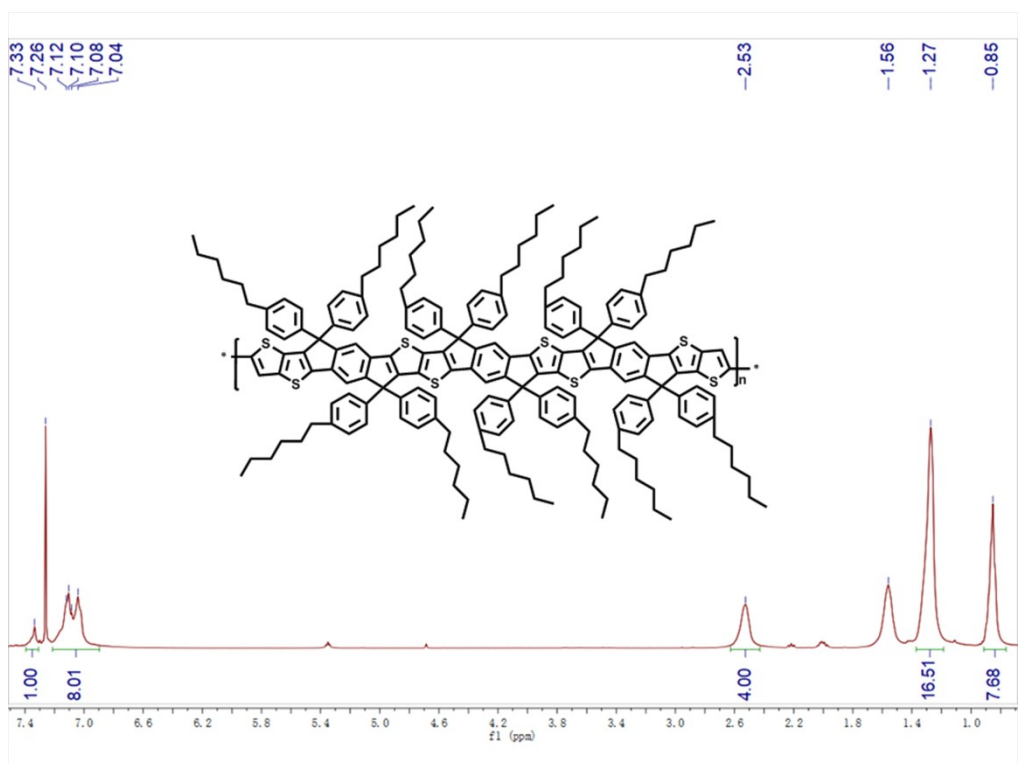


**Fig. S7**  $^1\text{H}$  NMR (400 MHz) spectrum of monomer 1 ( $\text{CDCl}_3$ , 298K).

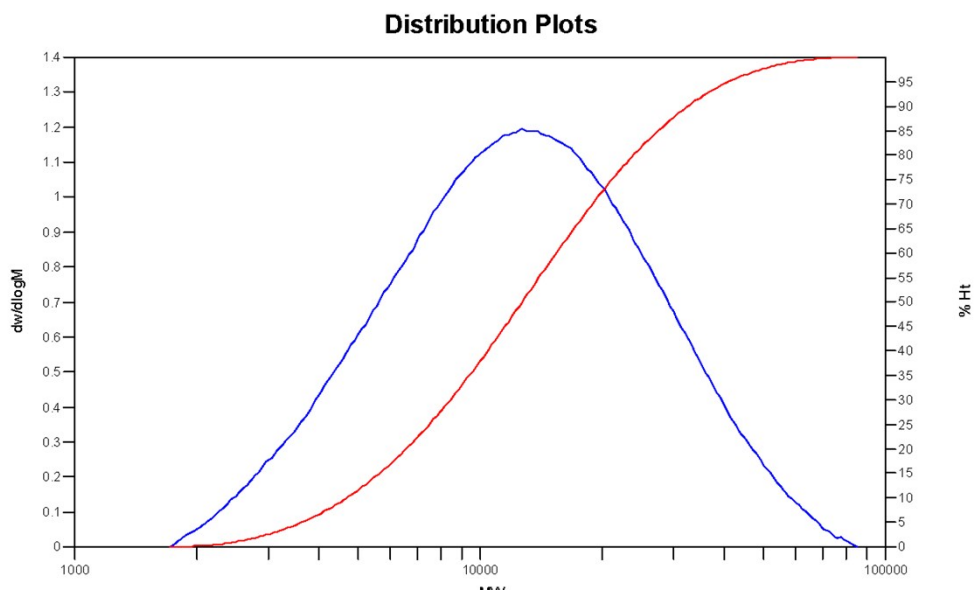




**Fig. S8** <sup>1</sup>H NMR (400 MHz) spectrum of PBTT (CDCl<sub>3</sub>, 298K).



**Fig. S9** <sup>1</sup>H NMR (400 MHz) spectrum of PFIDT (CDCl<sub>3</sub>, 298K).



**Fig. S10** The GPC curve of PFIDT with trichlorobenzen as the solvent.

- 1 D. Choi, B. S. Jeong, B. Ahn, D. S. Chung, K. Lim, S. H. Kim, S. U. Park, M. Ree, J. Ko and C. E. Park, *ACS Appl Mater Interfaces*, 2012, **4**, 702.
- 2 X. T. Zhang, L. M. Fan, W. L. Fan, B. Li, G. Z. Liu, X. Z. Liu and X. Zhao, *Crystal Growth & Design*, 2016, **16**, 3993.