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## Supporting Information for

# Facile End-Capping Strategy with Strong Electron Withdrawing Groups for Enhancing Field-Effect Mobility

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#### 1. Synthetic procedures of polymers



All Chemical reagents were purchased from SunaTech and used as received. Compound **4** and **6** were synthesized according to the literature.<sup>1</sup>

**2FIC-Br**: To a solution of **1** (0.42 g, 2.20 mmol) and **2** (0.75 g, 3.36 mmol) in anhydrous chloroform (15 mL), 0.50 mL of pyridine were added under Ar atmosphere. The mixture was then stirred at 60 °C for 10 h. After removing the solvent, the residue was purified by silica gel chromatography (PE:CH<sub>2</sub>Cl<sub>2</sub> = 2:1) to afford an orange solid. (0.60 g, 67.9%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.80 (s, 1H), 8.58–8.55 (q, *J* = 4 Hz, 1H), 7.74–7.72 (t, *J* = 4 Hz, 1H), 7.62–7.61 (d, *J* = 4.0 Hz, 1H), 7.29 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  185.86, 157.91, 156.05, 153.86, 144.74, 138.40, 137.50, 136.74, 134.64, 131.88, 123.00, 115.31, 115.13, 113.71, 113.55, 113.17, 113.02. HRMS (ESI, [M]<sup>+</sup>, C<sub>17</sub>H<sub>5</sub>BrF<sub>2</sub>N<sub>2</sub>OS): calcd, 401.9274; found, 401.69928.

**PDPPTT-2FIC**: **3** (70 mg, 0.151 mmol), **4** (155 mg, 0.137 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (2.8 mg, 0.003 mmol), P(o-tol)<sub>3</sub> (3.7 mg, 0.012 mmol), and dry chlorobenzene (8 mL) were added into a reaction tube under nitrogen atmosphere. Subsequently, the mixture was stirred at 130 °C for 48 h. 2FIC-Br

(23 mg, 0.056 mmol) in 1 mL of chlorobenzene was then injected into the reaction solution. The mixture was stirred at 130 °C for additional 12 h, and then poured into 100 mL of methanol. The raw polymer was filtered off and purified by Soxhlet extraction with methanol, acetone, and hexane to remove small molecules, oligomers, and catalyst residues. Notably, high-molecular-weight polymer PDPPTT-2FIC was obtained through Soxhlet extraction with chloroform. The chloroform fraction was concentrated and then precipitated into 100 mL of methanol and dried under vacuum to afford PDPPTT-2FIC as a dark solid (113 mg, 72.5%).  $M_w/M_n$  (GPC) = 59596/18337.

**PDPPTT**: PDPPTT was prepared using the similar procedure as above, except for the molar ratio of 3 to 4 (1:1) and no addition of 2FIC-Br. PDPPTT was acquired as a dark solid in a yield of 86.4%.  $M_w/M_n$  (GPC) = 129073/33908.

**PNDI2T-2FIC**: The synthetic procedure is similar as described for PDPPTT-2FIC (yield 67.3%).  $M_w/M_n$  (GPC) = 27331/14163.

**PNDI2T**: The synthetic procedure is similar as described for PDPPTT (yield 83.5%).  $M_w/M_n$ (GPC) = 32173/16307.

**PDPPTT-2FIC-a** and **PDPPTT-Benzene**: Prepolymer PDPPTT is similar as described for PDPPTT-2FIC. Subsequently, about half of the reaction solution was transferred to another reaction tube under nitrogen atmosphere. 2FIC-Br and bromobenzene were then injected into the two reaction tubes, respectively. The mixture was stirred at 130 °C for additional 12 h, and then poured into 100 mL of methanol. The raw polymers were filtered off and purified using Soxhlet extraction to afford PDPPTT-2FIC-a and PDPPTT-Benzene in a yield of 75.8% and 73.7%, respectively. 212535/65998 and 205092/67081 of  $M_w/M_n$  were achieved for PDPPTT-2FIC-a and PDPPTT-Benzene.

#### 2. Film characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 500MHz NMR spectrometer. High-Resolution Mass Spectrometry (HRMS) was acquired from a Thermo Scientific Q Exactive. X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo Scientific K-Alpha instrument using monochromatized Al  $K\alpha$  (hv = 1486.6eV). The relative molecular weight and polydispersity index (PDI) were determined by gel-permeation chromatography (GPC) using an Agilent PL-GPC 220 at 150 °C with 1,2,4-trichlorobenzene as the eluent. Thermal gravimetric analysis (TGA) measurements were performed on a Netzsch TG 209 F1 Libra under nitrogen atmosphere at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) tests were conducted on a Netzsch DSC 200 F3 under nitrogen atmosphere at a heating/cooling rate of 20 °C/min. Ultraviolet-visible (UV-vis) absorption spectra were measured using a Shimadzu UV-3600i Plus spectrophotometer. Polymer solutions dissolved in chlorobenzene (0.02 mg/mL) were used as solution samples. Polymer solutions (5 mg/mL) were spin-coated on glass substrates as thin-film samples. Cyclic voltammograms (CV) were obtained on a CHI 760E workstation, where a platinum wire was used as the counter electrode, an Ag/AgCl electrode was used as the reference electrode, and a glassy carbon electrode (4 mm in diameter) was used as the working electrode. Ferrocene (E<sub>HOMO</sub> of 0.45 eV) was used as a control. Tetrabutylammonium hexafluorophosphate was dissolved in acetonitrile as the electrolyte solution (0.1 mol/L). The redox reaction was conducted in the electrolyte solution under an argon atmosphere at a scan rate of 20 mV/s. Polymer solutions were drop-coated on the glassy carbon electrode and then dried to prepare the samples for CV testing. Atomic force microscopy (AFM) height images were obtained from a Bruker Dimension Icon in tapping mode. Polymer solutions were spin-coated on glass substrates and then annealed at 180 °C for 30 minutes as thin-film

samples. The grazing incidence X-ray diffraction (GIXRD) tests were performed on the 14B1/15U1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). Polymer solutions were spin-coated on silicon wafers and then annealed at 180 °C for 30 minutes as thin-film samples.

#### 3. Device Fabrication and Measurement

In order to reduce the impact of  $O_2$  and  $H_2O$  on the charge transport performance and stability, the OFETs based on all polymers adopted a TGBC architecture, and the preparation and testing processes of the OFETs were conducted in a nitrogen glove box. Commercial glass that was washed with isopropyl alcohol and acetone was used as a substrate. Au (35 nm) was thermally evaporated through a shadow mask with interdigital electrode patterns to form the source/drain electrodes. Polymer solutions (5 mg/mL) were stirred overnight at 60 °C, spin-coated on glass substrates at 1500 rpm for 60 s, and then annealed at 180 °C for 30 minutes in a vacuum oven. PMMA with  $M_w = 120$  kg/mol was dissolved in n-butyl acetate (80 mg/mL) and then spin-coated on semiconductor layers at 1500 rpm for 60 s as dielectric layers. The thickness of dielectric layers was approximately 800 nm, and then the devices were annealed on a hot plate at 90 °C for 30 minutes. Ag (80 nm) was thermally evaporated through a shadow mask to form the gate electrodes. The charge transport properties of OFETs were investigated using a Keithley S4200 SCS semiconductor parameter tester. The carrier mobilities in the saturation regions were calculated according to the following equation:

$$\mu_{\rm sat} = \frac{2L \, 1 \, \partial \sqrt{I_{\rm DS}}}{WC_{\rm i} \, \partial V_{\rm G}}$$

where L and W are the semiconductor channel length and width, respectively;  $C_i$  is the capacitance per unit area of the gate dielectric layer;  $I_{DS}$  is the drain current; and  $V_G$  is the gate voltage.

## 4. Additional graphs



**Fig. S1** GPC chromatograms of (a) PDPPTT, (b) PDPPTT-2FIC, (c) PNDI2T, and (d) PNDI2T-2FIC using 1,2,4-trichlorobenzene as an eluent at 150 °C.



Fig. S2 <sup>1</sup>H NMR spectrum of 2FIC-Br (400 MHz, CDCl<sub>3</sub>, 55 °C).



Fig. S3 <sup>13</sup>C NMR spectrum of 2FIC-Br (100 MHz, CDCl<sub>3</sub>, 55 °C).



Fig. S4 XPS spectra of F 1s for (a) DPP- and (b) NDI-based polymers.



Fig. S5 TGA plots of (a) DPP- and (b) NDI-based polymers.



Fig. S6 DSC curves for the second heating and cooling scans of (a) DPP- and (b) NDI-based polymers in a  $N_2$  atmosphere.



Fig. S7 The  $\mu_{sat}$ - $V_{G}$  curves of OFETs based on DPP- and NDI-based polymers.



**Fig. S8** The GPC chromatograms, transfer and output curves of OFETs based on PDPPTT-2FICa and PDPPTT-Benzene.

### REFERENCES

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