

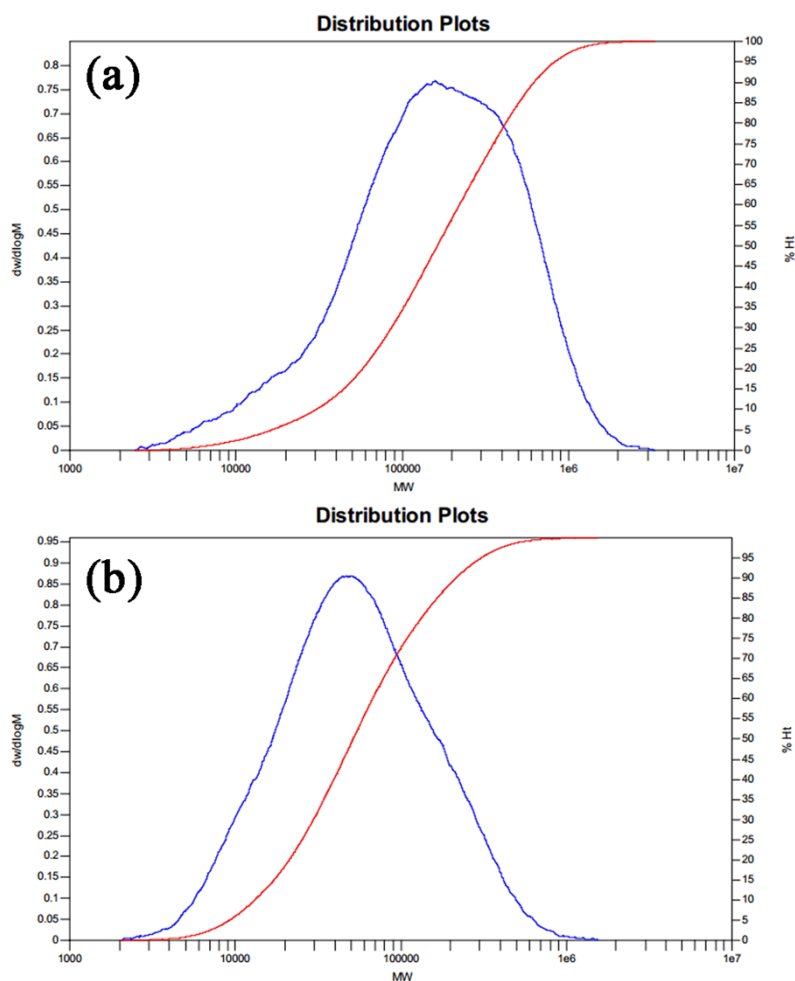
## Electronic Supplementary Information

# Naphtho[1,2-*b*;5,6-*b'*]difuran-based Donor-Acceptor Polymers for High Performance Organic Field-Effect Transistors

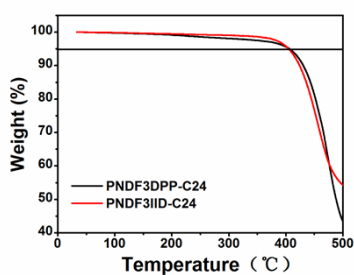
*Shaowei Shi,<sup>1,2</sup> keli Shi,<sup>1,3</sup> Gui Yu,<sup>3\*</sup> Xiaoyu Li,<sup>1,2\*</sup> Haiqiao Wang<sup>1,2\*</sup>*

1. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
2. Beijing Engineering Research Center for the Synthesis and Applications of Waterborne Polymers, Beijing University of Chemical Technology, Beijing 100029, China
3. Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

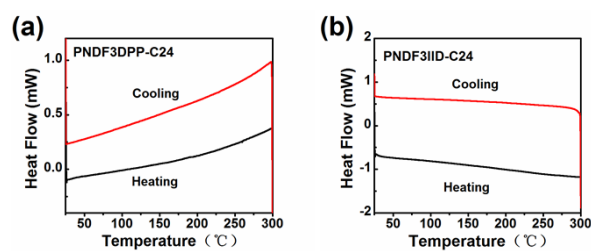
\* Corresponding authors: e-mail: wanghaiqiao@mail.buct.edu.cn (H. Wang); yugui@iccas.ac.cn (G. Yu); lixy@mail.buct.edu.cn (X. Li)



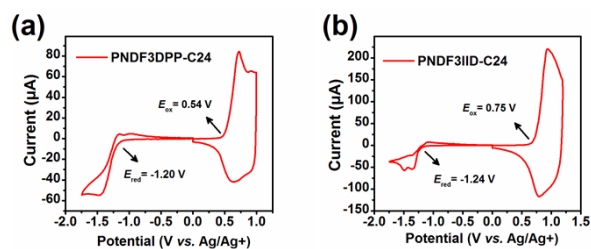
**Figure S1.** Gel permeation chromatography (GPC) traces of (a) PNDF3DPP-C24 and (b) PNDF3IID-C24.



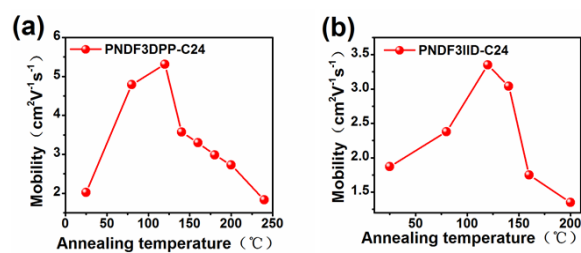
**Figure S2.** TGA plots of PNDF3DPP-C24 (5% loss, 407 °C) and PNDF3IID-C24 (5% loss, 403 °C) with a heating rate of 10 °C/min under an inert atmosphere.



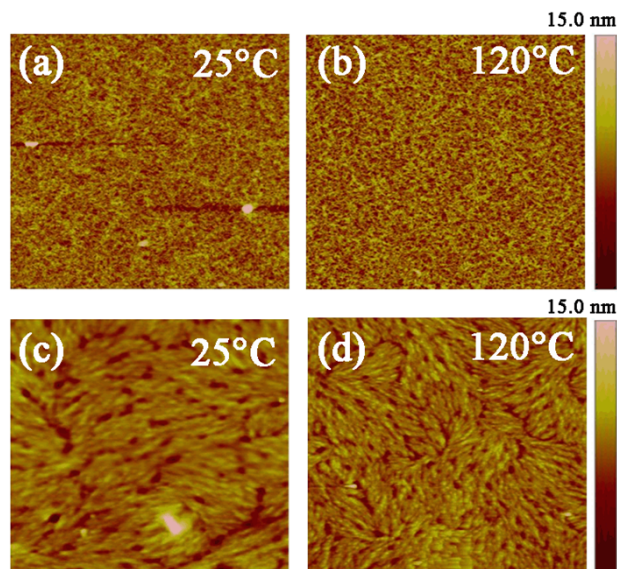
**Figure S3.** DSC thermograms of (a) PNDF3DPP-C24 and (b) PNDF3IID-C24.



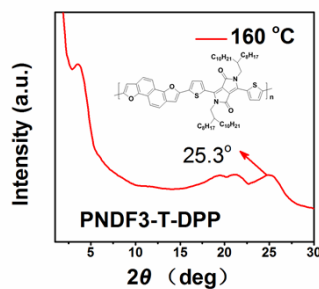
**Figure S4.** Cyclic voltammograms of (a) PNDF3DPP-C24 and (b) PNDF3IID-C24 films on a platinum electrode in 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at a scan rate of 100 mV s<sup>-1</sup>.



**Figure S5.** Evolution of hole mobilities of FETs based on (a) PNDF3DPP-C24 and (b) PNDF3IID-C24 films with different annealing temperatures.



**Figure S6.** AFM height images ( $3 \times 3 \mu\text{m}^2$ ) of PNDF3DPP-C24 (a,b) and PNDF3IID-C24 (c,d) thin films on OTS-modified  $\text{SiO}_2/\text{Si}$  substrates.



**Figure S7.** 1D- in-plane GIXRD pattern of the PNDF3-T-DPP<sup>[1]</sup> thin film.

**Table S1.** Optical and Electrochemical Properties of the Polymers

Polymer	$\lambda_{\text{max}}$ in solution (nm) <sup>a</sup>	$\lambda_{\text{max}}$ in film (nm) <sup>b</sup>	$\lambda_{\text{onset}}$ in film (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) <sup>c</sup>	HOMO/ $E_{\text{ox}}$ (eV)/(V) <sup>d</sup>	LUMO/ $E_{\text{red}}$ (eV)/(V) <sup>d</sup>	$E_{\text{g}}^{\text{ec}}$ (eV) <sup>d</sup>
PNDF3DPP-C24	387, 734	394, 734	833	1.49	-5.25/0.54	-3.51/-1.20	1.74
PNDF3IID-C24	361, 681	360, 674	731	1.70	-5.46/0.75	-3.47/-1.24	1.99

<sup>a</sup>Measured in chloroform solution. <sup>b</sup>Measured on quartz plate by polymers cast from

chlorobenzene solution. <sup>c</sup>Bandgap estimated from the onset wavelength ( $\lambda_{\text{onset}}$ ) of the optical

absorption:  $E_g^{\text{opt}} = 1240 / \lambda_{\text{onset}}$  (eV). <sup>d</sup>The HOMO and LUMO energies as well as electrochemical bandgaps ( $E_g^{\text{ec}}$ ) are estimated with the following equations:  $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.71)$  (eV);  $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.71)$  (eV);  $E_g^{\text{ec}} = e(E_{\text{ox}} - E_{\text{red}})$  (eV).

**Table S2.** Optimized Electrical Parameters of Field-Effect Transistors at Different Annealing Temperatures

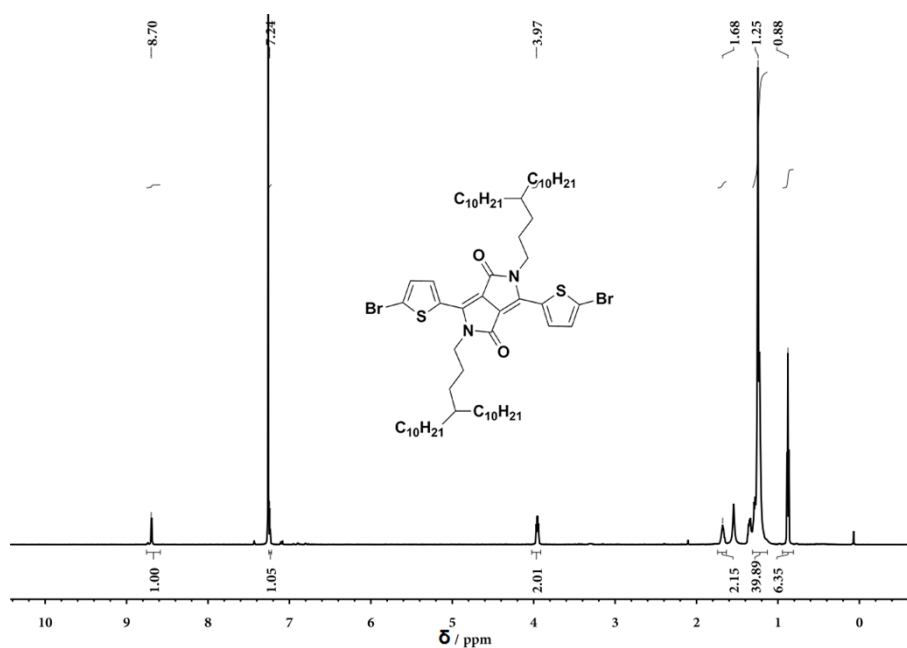
Annealing Temperature/°C	PNDF3DPP-C24			PNDF3IID-C24		
	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}}$ (V)	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$I_{\text{on}}/I_{\text{off}}$	$V_{\text{th}}$ (V)
25	2.02	10 <sup>6</sup> -10 <sup>7</sup>	15.2	1.87	10 <sup>7</sup> -10 <sup>8</sup>	10.3
80	4.79	10 <sup>6</sup> -10 <sup>7</sup>	15.3	2.38	10 <sup>6</sup> -10 <sup>7</sup>	15.7
120	5.31	10 <sup>6</sup> -10 <sup>7</sup>	14.6	3.35	10 <sup>7</sup> -10 <sup>8</sup>	8.6
140	3.57	10 <sup>5</sup> -10 <sup>6</sup>	13.7	3.04	10 <sup>7</sup> -10 <sup>8</sup>	10.2
160	3.30	10 <sup>6</sup> -10 <sup>7</sup>	14.2	1.75	10 <sup>7</sup> -10 <sup>8</sup>	13.8
200	2.73	10 <sup>6</sup> -10 <sup>7</sup>	11.1	1.35	10 <sup>7</sup> -10 <sup>8</sup>	12.7

**Materials and Synthetic Procedures.** 2,7-Bis(trimethylstannyl)naphtho[1,2-b:5,6-*b'*]difuran,<sup>[1]</sup> 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(4-decyltetradecan)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP-C24),<sup>[2]</sup> and (*E*)-6,6-dibromo-1,1-bis(4-decyltetradecan)-[3,3-biindolinylidene]-2,2-dione (IID-C24)<sup>[3]</sup> were synthesized according to the procedures reported in the literature. *N,N*-Dimethylformamide (DMF) was vacuum distilled with CaH<sub>2</sub> and tetrahydrofuran (THF) was distilled from Na/benzophenone prior to use. All reactions were carried out under an inert atmosphere of N<sub>2</sub>. The other chemicals are commercial available products and used without any further purification.

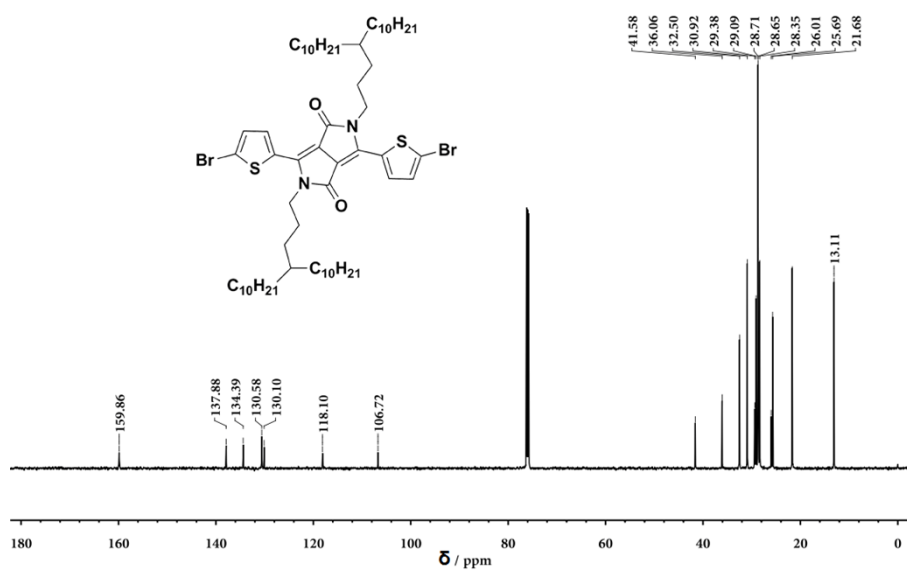
**Synthesis of P<sub>NDF3DPP</sub>-C24.** In a 25 mL two-necked flask, monomer 2,7-bis(trimethylstannyl)naphtho[1,2-b:5,6-b']difuran (53.4 mg, 0.1 mmol), 3,6-bis(5-bromothiophene-2-yl)-2,5-bis(4-decyltetradecan)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (113.1 mg, 0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mg, 0.005 mmol) and P(*o*-tol)<sub>3</sub> (12.5 mg, 0.04 mmol) were dissolved in anhydrous chlorobenzene (6 mL). The mixture was purged with nitrogen for 30 min and then the reaction mixture was heated at 110 °C for 24 h. After cooled down to room temperature, the reaction mixture was precipitated in methanol (200 mL) and then collected by filtration. Then the solid was subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), hexane(24 h) and chlorobenzene (12 h). The final chlorobenzene fraction was dried to afford the target polymer as a shiny, bronze-colored solid (92.5 mg, yield 78%, *M*<sub>n</sub> = 66.6 kDa, *M*<sub>w</sub> = 222.0 kDa, PDI = 3.85). Elemental analysis: calculated for (C<sub>76</sub>H<sub>108</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>)<sub>n</sub>, C, 77.50; H, 9.24; N, 2.38; found: C, 77.82; H, 9.11; N, 2.38.

**Synthesis of P<sub>NDF3IID</sub>-C24.** In a 25 mL two-necked flask, monomer 2,7-bis(trimethylstannyl)naphtho[1,2-b:5,6-b']difuran (53.4 mg, 0.1 mmol), (*E*)-6,6-dibromo-1,1-bis(4-decyltetradecan)-[3,3-biindolinylidene]-2,2-dione (109.3 mg, 0.1 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (5 mg, 0.005 mmol) and P(*o*-tol)<sub>3</sub> (12.5 mg, 0.04 mmol) were dissolved in anhydrous chlorobenzene (6 mL). The mixture was purged with nitrogen for 30 min and then the reaction mixture was heated at 110 °C for 48 h. After cooled down to room temperature, the reaction mixture was precipitated in methanol (200 mL) and then collected by filtration. Then the solid was subjected to Soxhlet extraction with methanol (24 h), acetone (24 h), hexane(24 h) and chloroform (12 h). The final chloroform fraction was dried to afford the target polymer as a shiny, bronze-colored solid (108 mg, yield 94%, *M*<sub>n</sub> = 31.2 kDa, *M*<sub>w</sub> = 89.5 kDa, PDI =

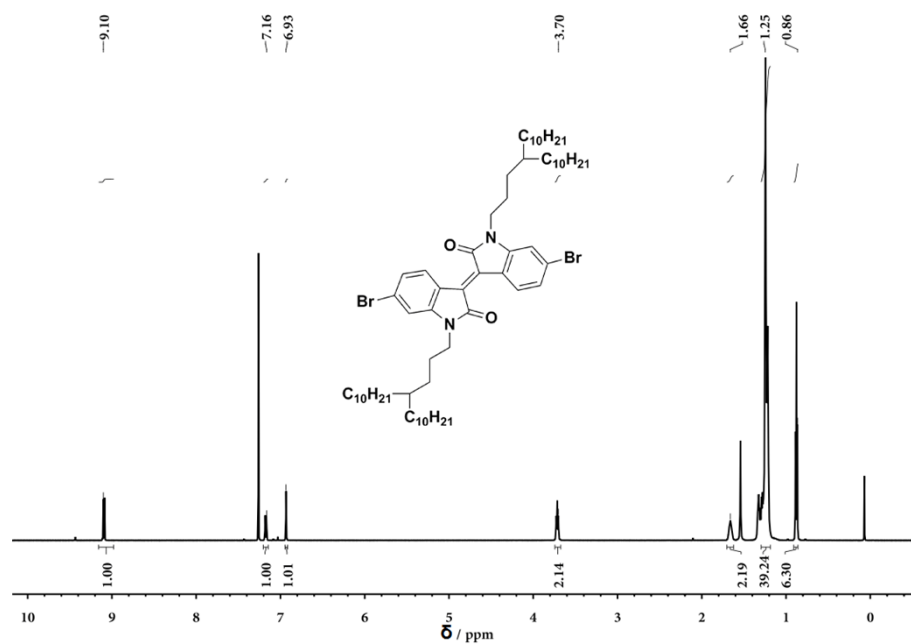
2.87). Elemental analysis: calculated for  $(C_{78}H_{110}N_2O_4)_n$ , C, 82.20; H, 9.73; N, 2.46; found: C, 82.19; H, 9.51; N, 2.46.



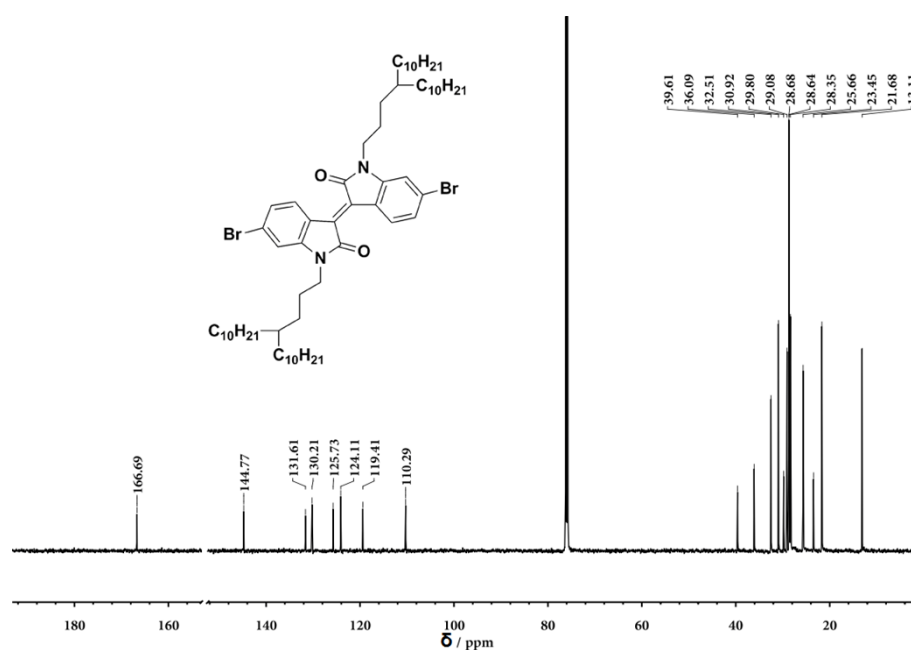
**Figure S8.**  $^1H$  NMR spectrum of DPP-C24.



**Figure S9.**  $^{13}C$  NMR spectrum of DPP-C24.



**Figure S10.** <sup>1</sup>H NMR spectrum of IID-C24.



**Figure S11.** <sup>13</sup>C NMR spectrum of IID-C24.

**Measurements and Characterization.** Gel permeation chromatography was carried out at 150 °C using a Polymer Labs PL 220 system using a refractive index detector and 1, 2, 4-trichlorobenzene as the eluent. All new compounds were



characterized by nuclear magnetic resonance spectra (NMR). The NMRs ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) were recorded on a Bruker AV 600 MHz spectrometer in  $\text{CDCl}_3$  at room temperature using tetramethylsilane (TMS;  $\delta = 0$  ppm) as an internal standard. Elemental analyses were performed on a Flash EA 1112 elemental analyzer. Thermal gravimetric analysis (TGA) measurements were carried out on PerkinElmer TGA 4000 under a nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Differential scanning calorimetry (DSC) measurements were recorded using a Mettler Toledo DSC 1 under nitrogen at a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$ . UV–vis–NIR absorption spectra were measured on Shimadzu spectrometer model UV-3150. The electrochemical cyclic voltammetry was conducted on a Zahner Ennium Electrochemical Workstation with a glass carbon disk (coated with the polymer film), a Pt wire, and  $\text{Ag}/\text{Ag}^+$  electrode as working electrode, counter electrode and reference electrode respectively in a  $0.1\text{ mol/L}$  tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) acetonitrile solution. The potential of  $\text{Ag}/\text{Ag}^+$  reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple ( $\text{Fc}/\text{Fc}^+$ ). The grazing incidence X-ray diffraction (GIXRD) data were obtained at 1W1A, Beijing Synchrotron Radiation Facility. For GIXRD, the drop-coated films were illuminated at a constant incidence angle of  $0.2^\circ$  ( $\lambda = 2d\sin\theta = 1.54\text{ \AA}$ ). Atomic force microscopy (AFM) measurements were carried out on a Digital Instruments Nanoscope V instrument, and operated in a tapping mode. The thickness of thin film was measured by XP-2 Profiler (Ambios Technology).

**Fabrication of Field-Effect Transistor Devices.** Polymer field-effect transistors were fabricated in a bottom-gate bottom-contact (BGBC) configuration (gold electrode on  $\text{n}^+\text{-Si}/\text{SiO}_2$  substrates). The gold (Au) source-drain electrodes were prepared by a

photolithography technique. The substrates were first cleaned with UVO for 20 min and immersed in Piranha solution (7:3 mixture of sulfuric acid and 30% hydrogen peroxide) for 5 min, then subjected to cleaning using ultrasonication in deionized water (twice), ethanol (once) and acetone (once). The cleaned substrates were dried under vacuum at 80 °C. Before the deposition of polymer semiconductors, octadecyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS to form an OTS self-assembled monolayer. Then the polymer thin films (*ca.* 30 nm) were spin-coated on the OTS modified SiO<sub>2</sub>/Si substrates from the solutions in hot *o*-dichlorobenzene (7 mg/mL for PNDF3DPP-C24, 5 mg/mL for PNDF3IID-C24) at a speed of 3000 rpm for 60s. The FETs devices were annealed on a hotplate for 5 minutes in air directly and measured in air by using a Keithley 4200 Semiconductor Characterization System. Different channel lengths (L) of the FET devices (L = 5, 10, 20, 30, 40, and 50 μm) and the same channel widths (W) of 1400 μm were used to optimize device performance. The FET mobilities were calculated from the saturation regime ( $V_{SD} = -100$  V) in the transfer plots of  $V_G$  versus  $I_{SD}$  by extracting the slope of the linear range of  $V_G$  vs.  $I_{SD}^{1/2}$  plot and using the following equation:

$$\left. \frac{\partial I_{SD}^{1/2}}{\partial V_{GS}} \right|_{V_{SD}} = \left[ \mu_h C_i \left( \frac{W}{2L} \right) \right]^{1/2}$$

where  $I_{SD}$ ,  $V_{SD}$  and  $V_{GS}$  are the source-drain current, source-drain voltage and the gate voltage, respectively;  $W/L$  is the channel width / length;  $C_i$  ( $C_i = 11$  nF/cm<sup>2</sup>) is the capacitance per unit area of gate dielectric layer;  $\mu_h$  represents the hole mobility in the regime saturation.

In the following equation:

$$I_{DS} = (W / 2L) Ci \mu_h (V_{GS} - V_{th})^2$$

the threshold voltage  $V_{th}$ , was calculated by extrapolating  $V_{th} = V_{GS}$  at  $I_{SD} = 0$  in the  $V_{GS}$  vs.  $I_{SD}$  curve in the saturation regime ( $V_{SD} = -100$  V). Current on and off ratio,  $I_{on/off}$ , was determined through dividing maximum  $I_{SD}$  ( $I_{on}$ ) by the minimum  $I_{SD}$  ( $I_{off}$ ).

[1] Shi, S.; Xie, X.; Gao, C.; Shi, K.; Chen, S.; Yu, G.; Guo, L.; Li, X.; Wang, H. *Macromolecules*, **2014**, *47*, 616.

[2] Kang, I.; Yun, H.-J.; Chung, D. S.; Kwon, S.-K.; Kim, Y.-H. *J. Am. Chem. Soc.*, **2013**, *135*, 14896.

[3] Lei, T.; Dou, J. H.; Pei, J. *Adv. Mater.*, **2012**, *24*, 6457.