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## **Electronic Supporting Information**

## Precise Tracking and Modulating Aggregation Structures of Conjugated Copolymers in Solutions

Zi-Yuan Wang,<sup>a</sup> Ze-Fan Yao,<sup>a</sup> Yang Lu,<sup>a</sup> Li Ding,<sup>a</sup> Zi-Di Yu,<sup>a</sup> Hao-Yang You,<sup>a</sup> Xin-Yi Wang,<sup>a</sup> Yang-Yang Zhou,<sup>a</sup> Lin Zou,<sup>\*b</sup> Jie-Yu Wang,<sup>a</sup> and Jian Pei<sup>\*a</sup>

<sup>a</sup>Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center of Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

<sup>b</sup>Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621999, China

Email: jurling@pku.edu.cn; jianpei@pku.edu.cn

## **1.** General Procedure and Experimental Details.

All chemicals and solvents are of reagent grade unless otherwise indicated. All air and water sensitive reactions were performed under N2 atmosphere. Molecular weights were determined by gel permeation chromatography (GPC) performed on Polymer Laboratories PL-GPC220 at 150 °C using 1,2,4trichlorobenzene (TCB) as eluent. Absorption spectra were recorded on PerkinElmer Lambda 750 UV-vis spectrometer. Varied-temperature absorption spectra were recorded on Shimadzu UV3600Plus spectrometer. Thermal gravity analyses (TGA) were carried out on a TA Instrument O600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter. Cyclic voltammetry measurements were performed on a SP-300 Bio-Logic potentiostat and were carried out in acetonitrile containing 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte for polymer thin films. Glassy carbon electrode was served as a working electrode and a platinum wire as a counter one, and all potentials were recorded versus AgCl (saturated)/Ag as a reference electrode (scan rate: 50 mV s<sup>-1</sup>). Ultraviolet Photoemission Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS) were conducted on a Kratos AXIS Supra/Ultra Photoelectron Spectrometer under an ultrahigh vacuum of about  $3 \times 10^{-9}$  Torr with an unfiltered He I gas discharge lamp source (21.22 eV) and a monochromatic Al K $\alpha$  source (1486.7 eV,  $\theta = 90^{\circ}$ ) as the excitation source, respectively. Al K $\alpha$  source operated at 14 kV and 15 mA. The instrumental energy resolution for UPS and XPS were 0.1 eV and 0.5 eV, respectively. For sample preparation, all doped films were deposited on heavily doped n-type Si wafers in a N<sub>2</sub> glove box and transferred through a transport system without air exposure into the spectrometer analysis chamber. The GIWAXS was performed at beamline BL14B1 of Shanghai Synchrotron Radiation Facility at a wavelength of 1.2398 Å. BL14B1 is a beamline based on bending magnet and a Si(111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection.

Small angle neutron scattering (SANS) measurements were conducted on *Suanni* instrument at the 20 MW China Mianyang Research Reactor (CMRR) in China Academy of Engineering Physics. The neutron wavelength,  $\lambda$ , was 5.3 Å ( $\Delta\lambda/\lambda \sim 10\%$ ). The samples were contained in 20 mm quartz cells with a path length of 2 mm. SANS scattering profiles were collected at ambient temperature, scattering in samples containing up to 3 mg mL<sup>-1</sup> concentration in deuterated 1,2-dichlorobenzene ( $d_4$ -o-DCB). Samples were corrected for background scattering using empty cells with deuterated solvent only. The scattering profiles were reduced to absolute scale using Igor Pro, and the data were analyzed using National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR)-supplied Igor Pro software tools. The scattering length density was calculated according to the scattering length per molecule and the molecular volume. BDOPV-T and BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> were used classic Lorentz model, while BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> and BDOPV-2T were adopted FlexCyc\_Polylen model to fit the experimental data.<sup>1,2</sup> The data obtained from Lorentz model is coherence length, which multiply by  $\sqrt{3}$  is the mean-squared radius of gyration ( $R_g$ ). The scattering lengths of  $d_4$ -o-DCB, BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> and BDOPV-2T are 4.59 × 10<sup>-6</sup> Å<sup>-2</sup>, 5.69 × 10<sup>-7</sup> Å<sup>-2</sup> and 5.78 × 10<sup>-7</sup> Å<sup>-2</sup>, respectively. In addition, the molecular weights of BDOPV-T and BDOPV-2T monomers are 1650.65 and 1732.77, respectively. Therefore, a single polymer chain would contain 22 monomers. According to the theoretical computation, the optimized length of a monomer is 24.0 Å (the geometries of monomer were optimized at the B3LYP/6-311G\* level, using the Gaussian 09 software package). Therefore, the length of a single polymer chain is about 53 nm.

FET Devices Fabrications and Testing. Top-gate bottom-contact (TG/BC) FET devices were fabricated using n<sup>++</sup>-Si/SiO<sub>2</sub> (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the SiO<sub>2</sub> surface. The substrates were subjected to cleaning using ultrasonication in acetone, detergent, deionized water (twice), and isopropyl alcohol. The cleaned substrates were dried under vacuum at 80 °C. All the above processes were performed under ambient conditions. The substrates were transferred into a glovebox. 1.8 g L<sup>-1</sup> of 4-methylbenzenethiol (MBT) in acetonitrile were used to change the energetic mismatch between Au electrodes and polymers.<sup>3</sup> A thin film of the polymer was deposited on the substrates by spin-coating the solution (3 mg mL<sup>-1</sup> in o-DCB) at 1000 rpm for 60 s, optionally followed by annealing at 180 °C for 10 min. After the deposition of the polymer thin film, a CYTOP solution (CTL809M/CT-solv180 = 3/1) was spin-coated onto the semiconducting layer at 2000 rpm for 60 s, resulting in a 500 nm thick dielectric layer. The CYTOP layer was then annealed at 100 °C for 60 min in a glovebox. Gate electrodes comprising a layer of Al (45 nm) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation under high vacuum ( $10^{-4}$  Pa). The evaluations of the FETs were carried out under ambient conditions (22 °C,  $R_{\rm H} = 50-60\%$ ) on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility ( $\mu$ ) was calculated from the data in the saturated regime according to the equation  $I_{\rm SD} = (W/2L)C_{\rm i}\mu(V_{\rm G} - V_{\rm T})^2$ , where  $I_{\rm SD}$  is the drain current in the saturated regime. W and L are, respectively, the semiconductor channel width and length,  $C_i$  ( $C_i = 3.7$ nF) is the capacitance per unit area of the gate dielectric layer, and  $V_{\rm G}$  and  $V_{\rm T}$  are the gate voltage and threshold voltages.  $V_{\rm G} - V_{\rm T}$  of the device was determined from the relationship between the square root of  $I_{\rm SD}$  and  $V_{\rm G}$  at the saturated regime.

**Solution Doping and Thin Film Fabrication.** BDOPV-based copolymers and *N*-DMBI were dissolved in *o*-DCB with a concentration of 3 mg mL<sup>-1</sup>. The aliquots mixture of *N*-DMBI and polymer solutions were

stirred at 50 °C for 5 min. Thin films were deposited on the treated substrates by spin-coating the mixture at 1500 rpm for 60 s and annealed at 120 °C for 8 h. The film thickness ( $\sim$ 8 nm) is determined by AFM. 4-Point conductivity measurements were conducted in an N<sub>2</sub> glovebox with Keithley 4200 SCS.

Figures S1-S14 and Tables S1-S3.



Figure S1. N(1s) and S(2p) X-ray photoelectron spectroscopy of the intrinsic films of BDOPV-T ( $\mathbf{a}$ ,  $\mathbf{b}$ ), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub>( $\mathbf{c}$ ,  $\mathbf{d}$ ), BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub>( $\mathbf{e}$ ,  $\mathbf{f}$ ), and BDOPV-2T ( $\mathbf{g}$ ,  $\mathbf{h}$ ).

**Table S1.** Summary of the ratio of N(1s) and S(2p) of BDOPV- $T_{0.8}$ -2 $T_{0.2}$  and BDOPV- $T_{0.2}$ -2 $T_{0.8}$  from X-ray photoelectron spectroscopy measurements.

	Calculated Value	1 <sup>st</sup> N/S ratio	2 <sup>nd</sup> N/S ratio	3 <sup>rd</sup> N/S ratio
BDOPV-T <sub>0.8</sub> -2T <sub>0.2</sub>	1.36	1.44 (5.6%)	1.36 (0)	1.36 (0)
BDOPV-T <sub>0.2</sub> -2T <sub>0.8</sub>	0.84	0.82 (-2.4%)	0.79 (-6%)	0.81 (-3.6%)

\* the relative error ( $\delta$ ) was presented in the parentheses, which is equal to the ratio of absolute error ( $\mu$ ) and

calculated value (x) as 
$$\frac{\delta}{\mu} = \frac{x - \mu}{\mu} \times 100\%$$



**Figure S2.** Thermal gravity analysis (TGA) under air (**a**) and differential scanning calorimeter traces (DSC) of BDOPV-T (**b**), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> (**c**), BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> (**d**), and BDOPV-2T (**e**).



**Figure S3**. Temperature-dependent UV-*vis*-NIR absorption spectra of BDOPV-T (**a**), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> (**b**), BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> (**c**), and BDOPV-2T (**d**) in *o*-DCB solution. With the solution temperature increasing, the intensity of long-wavelength band decreased and the absorption maximum peak  $\lambda_{max}$  around 800 nm showed blue-shift.



**Figure S4**. Cyclic voltammetry of ferrocene (**a**), BDOPV-T (**b**), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> (**c**), BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> (**d**), and BDOPV-2T (**e**).



Figure S5. LUMO distributions on BDOPV-T and BDOPV-2T (the repeating units is 1, 2, and 3 respectively).<sup>5</sup>



**Figure S6**. Measured SANS data of four polymers (**a**), simulated SANS data of BDOPV-T (**b**), BDOPV- $T_{0.8}$ - $2T_{0.2}$  (**c**), BDOPV- $T_{0.2}$ - $2T_{0.8}$  (**d**), and BDOPV-2T (**e**) and Kratky data<sup>4</sup> of the four polymers (**f**).



**Figure S7**. Representative 1D GIWAXS plots of the films of BDOPV-T, BDOPV-T<sub>0.8</sub>- $2T_{0.2}$ , BDOPV-T<sub>0.2</sub>- $2T_{0.8}$ , and BDOPV-2T.

Table S2. Coherence length of four intrinsic polymers. Coherence length  $(L_c)$  is calculated from breadth

$$(\Delta_q)$$
 of a diffraction peak:  $L_c = 0.89 \times \frac{2\pi}{\Delta_q}$ 

Polymer	BDOPV-T	BDOPV-T <sub>0.8</sub> -2T <sub>0.2</sub>	BDOPV-T <sub>0.2</sub> -2T <sub>0.8</sub>	BDOPV-2T
FWMH (Å <sup>-1</sup> )	0.09374	0.09566	0.05737	0.0489
Coherence Length (Å)	59.6	58.4	98.5	114.4



Figure S8. Transfer and output curves for BDOPV-T (**a**, **b**), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> (**c**, **d**), BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub> (**e**, **f**), and BDOPV-2T (**g**, **h**).

<b>Table S3</b> . Summary of OFET	performance of the	polymers
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Polymer	$\mu_{\rm ave}/\mu_{\rm max} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$		<sup>-1</sup> s <sup>-1</sup> )	$V_{\rm th}({ m V})$	$I_{\rm on}/I_{\rm off}$
BDOPV-T	(	0.011/0.013		1.2	105
BDOPV-T <sub>0.8</sub> -2T <sub>0.2</sub>	(	0.060/0.088		3.1-8.5	105
BDOPV-T <sub>0.2</sub> -2T <sub>0.8</sub>		0.50/0.58		5.9-18.0	105
BDOPV-2T		0.84/1.31		1.0-16.9	106
	-4.09	-4.08	-3.98	-4.00	
	-5.79	-5.73	-5.63	-5.47	
	BDOPV-T	BDOPV- T <sub>0.8</sub> -2T <sub>0.2</sub>	BDOPV- T <sub>0.2</sub> -2T <sub>0.8</sub>	BDOPV-2T N-DMBI	

**Figure S9.** Molecular structure of *N*-DMBI and the different HOMO and LUMO level of four polymers and *N*-DMBI.



**Figure S10**. Normalized UV-*vis*-NIR absorption spectra of intrinsic and doped (5 wt% and 15 wt%) solutions of BDOPV-T (**b**), BDOPV- $T_{0.8}$ -2 $T_{0.2}$  (**c**), BDOPV- $T_{0.2}$ -2 $T_{0.8}$  (**d**), and BDOPV-2T (**e**).



**Figure S11**. Normalized UV-*vis*-NIR absorption spectra of both intrinsic and doped (5 wt% (**a**) and 15 wt% (**b**)) films of BDOPV-T, BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub>, BDOPV-T<sub>0.2</sub>-2T<sub>0.8</sub>, and BDOPV-2T.



Figure S12. AFM height images of intrinsic film of BDOPV-T (a), BDOPV-T<sub>0.8</sub>-2T<sub>0.2</sub> (d), BDOPV-T<sub>0.2</sub>- $2T_{0.8}$  (g), and BDOPV-2T (j) and the corresponding doped films with 24 mol% (b, e, h, k) and 48 mol% (c, f, i, l) *N*-DMBI.



**Figure S13**. Representative 1D GIWAXS plots of intrinsic and doped films of BDOPV-T (**a**), BDOPV- $T_{0.8}$ -2 $T_{0.2}$ (**b**), BDOPV- $T_{0.2}$ -2 $T_{0.8}$ (**c**), and BDOPV-2T (**d**).



**Figure S14**. Electronic conductivities of the doped polymers at different concentration of the dopant *N*-DMBI.

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