Supporting Information

Rational Design of Terpolymer Acceptors for High-Efficiency All-Polymer Solar Cells

Jiawei Huang[a], Xintong Shi[a], Xiaoping Wang[a], Haokun Zheng[a], Yu Fang[a], Yujun Cheng[b], Sang Young Jeong[c], Han Young Woo[c], Qiao Zong[d], and Bin Huang[a]*

[a] School of Chemistry and Chemical Engineering, Jiangxi University of Science and Technology, 156 Ke Jia Avenue, Ganzhou, 341000 (P.R. China).

[b] School of Chemistry and Chemical Engineering, Jiangxi Science & Technology Normal University, NO.605, Fenglin Avenue, Nanchang, Jiangxi 330013, P.R. China.

[c] Department of Chemistry, College of Science, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul02841 (Republic of Korea).

[d] Wuhan Humanwell Innovative Drug Research and Development Center Limited Company.

Corresponding Author: Dr. Bin Huang.

E-mail addresses: binhuang@jxust.edu.cn (B. Huang).

Contents

1. **General Information**
2. **Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurement**
3. **Optical characterizations**
4. **Electrochemical characterizations.**
5. **AFM characterizations.**
6. **GIWAXS measurements**
7. **Device Fabrication and Characterizations**
8. **Results and Discussion.**

General Information

All reactions and manipulations were operated under argon atmosphere and all the starting materials were purchased from commercial suppliers and used without further purification. Chloroform, Chlorobenzene, Ag (99.999%) and other materials were purchased from Alfa, Aldrich (used without further purification). Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT: PSS (Baytron PAl4083) was obtained from Bayer Inc. BDT-2F, BDD, and BDT-2Cl were purchased from SunaTech Inc and Solarmer Materials Inc. $Pd_2(dba)_3$, $Pd(pph_3)_4$ and pio-meopph$_3$ were obtained from J&K. BTP-8-10-ICBr was purchased from Nanjing Zhiyan Technology Co.，Ltd.

Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurement

^{1}H NMR spectra of the polymers were recorded on a Bruker AVANCE III HD 400 MHz spectrometer using deuterated $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. The average number (M_n) and weight (M_w) molecular weight and PDI of the copolymer products were determined by Waters 2410 gel permeation chromatography (GPC) at 100 °C using 1,2,4-trichlorobenzene as an eluent.

Optical characterizations

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. All film samples were spin-cast on quartz slice substrates. Solution UV-*vis* absorption spectra at elevated temperatures also were collected on a Perkin Elmer Lambda 750 Spectrophotometer.

Electrochemical characterizations.

Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical work station, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the electrode from chloroform solutions to form thin films. 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The scan rate was 0.05 V s^{-1}. The E_{HOMO} and E_{LUMO} are calculated as referring to the equation (1) and (2).

$$E_{\mathrm{HOMO}}=-(E_{\mathrm{ox}}+4.4)\ \mathrm{eV}\ (1),$$

$$E_{\mathrm{LUMO}}=-(E_{\mathrm{red}}+4.4)\ \mathrm{eV}\ (2).$$

AFM characterizations.

The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without MoO_3/Ag on top of the active layer.

GIWAXS measurement

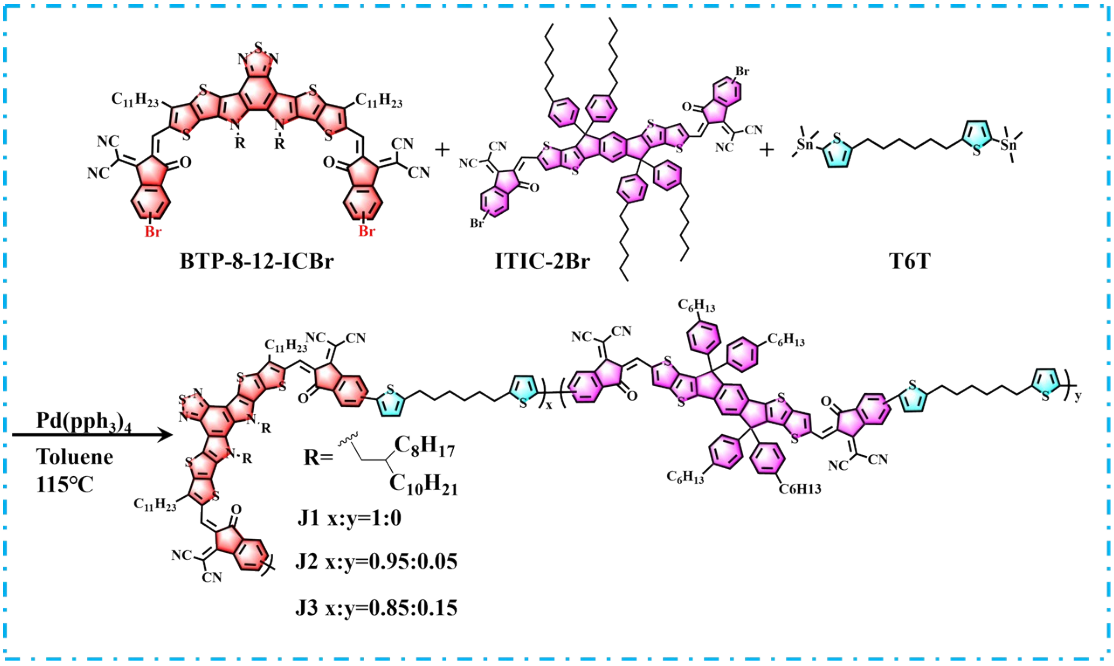
The GIWAXS measurement was carried out at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromatic (wavelength λ=1.10994 Å) using a double crystal monochromator and focused both horizontally and vertically (450 (H) x 60 (V) um^2 in FWHM @ the sample position) using K-B type mirrors. The grazing incidence wide-angle X-ray scattering (GIWAXS) sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angles of the X-ray beam were set to be 0.11°-0.13° for the neat and blend films. The GIWAXS patterns were recorded with a 2D CCD detector (Rayo nix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21, a=10.8631Å, b=8.7044Å, c=7.7624Å, and b=102.938Å) and the sample-to-detector distance was ~231 mm.

Device Fabrication and Characterizations

The PSCs were fabricated with a structure of glass/ITO/2PACz/Active layer /PNDIT-F3N-Br/Ag. The ITO-coated glasses were ultrasonic precleaned with detergent, deionized water, acetone and 2-propanol for 30min each and dried by a nitrogen blow. The ITO glasses were treated with UV-ozone for 20 min before use. 2PACz was spin-coated onto the ITO substrate and then annealed in an oven for 5min at 100 °C. Then the device was transferred to a nitrogen glove box. The active layer was spin-coated from 14.0 mg mL^{-1} solution dissolved in chloroform (PM6: Acceptor=1:1.2, 0.3% v/v DIO) at varied spinning speed for 30 s to form an active layer. Subsequently, ethanol (EtOH) solution of PNDIT-F3N with a small amount of acetic acid at a concentration of 0.5 mg ml^{-1} was deposited atop the active layer at 3,000 r.p.m. for 30 s to afford a PNDIT-F3N cathode buffer layer with thickness of about 10 nm. Finally, top Ag electrode was deposited over the active layer by thermal evaporation under a vacuum chamber to accomplish the device fabrication. The effective area of one cell was 0.04 cm^2. The current-voltage (J-V) characteristics were measured by a Keithley 2400 Source Meter under simulated solar light (100 mW/cm^2, AM 1.5 G, Abet Solar Simulator Sun2000). The incident photon-to-electron conversion efficiency (IPCE) spectra were detected on an IPCE measuring system (Oriel Cornerstone 2601/4 m monochromator equipped with Oriel 70613NS QTH lamp). All the measurements were performed at room temperature under nitrogen glove box.

Results and Discussion

Synthetic procedures



Synthesis of compound J1: In a round bottom flask, BTP-8-10-ICBr (30 mg, 0.017 mmol), 1,6-bis(5-(trimethylstannyl)thiophen-2-yl)hexane (9.8mg, 0.017 mmol) and $Pd(PPh_3)_4$ (0.6mg, 0.0005 mmol) were dissolved in ultra dry toluene (6.0 mL). The mixture was deoxygenated with nitrogen for 3 times and stirred at 115°C for 3 days. After cooling to room temperature, the mixture was dropped into methanol (50 mL) and filtered. The collected crude product was Soxhlet extracted with acetone and chloroform. Finally, the chloroform fraction was concentrated and dropped into methanol (50 mL), after filtered and dried under vacuum to obtain J1 as blue solid. Mn = 6.02kDa, PDI =1.96. Elemental Analysis for J1: C, 73.55; H, 7.80; N, 5.58; O, 1.64; S, 11.42.

Synthesis of compound J2 (5%ITIC): In a round bottom flask, BTP-8-10-ICBr (30mg, 0.017 mmol), 1,6-bis(5-(trimethylstannyl)thiophen-2-yl)hexane (10.3mg, 0.018 mmol), ITIC-2Br (1.4mg, 0.0009 mmol) and $Pd(PPh_3)_4$ (0.6mg, 0.0005 mmol) were dissolved in ultra dry toluene (6.0 mL). The mixture was deoxygenated with nitrogen for 3 times and stirred at 115°C for 3 days. After cooling to room temperature, the mixture was dropped into methanol (50 mL) and filtered. The collected crude product was Soxhlet extracted with acetone and chloroform. Finally, the chloroform fraction was concentrated and dropped into methanol (50 mL), after filtered and dried under vacuum to obtain J2 as blue solid. Mn = 5.56kDa, PDI =2.01. Elemental Analysis for J2: C, 75.25; H, 6.92; N, 4.62; O, 1.76; S, 11.45.

Synthesis of compound J3 (15%ITIC): In a round bottom flask, BTP-8-10-ICBr (30mg, 0.017 mmol), 1,6-bis(5-(trimethylstannyl)thiophen-2-yl)hexane (10.9mg, 0.019 mmol), ITIC-2Br (3.0mg, 0.0019 mmol) and $Pd(PPh_3)_4$ (0.65mg, 0.00057 mmol) were dissolved in ultra dry toluene (6.0 mL). The mixture was deoxygenated with nitrogen for 3 times and stirred at 115℃ for 3 days. After cooling to room temperature, the mixture was dropped into methanol (50 mL) and filtered. The collected crude product was Soxhlet extracted with acetone and chloroform. Finally, the chloroform fraction was concentrated and dropped into methanol (50 mL), after filtered and dried under vacuum to obtain J3 as blue solid. Mn = 4.75kDa, PDI =1.80. Elemental Analysis for J3: C, 73.95; H, 7.60; N, 5.35; O, 1.67; S, 11.43.

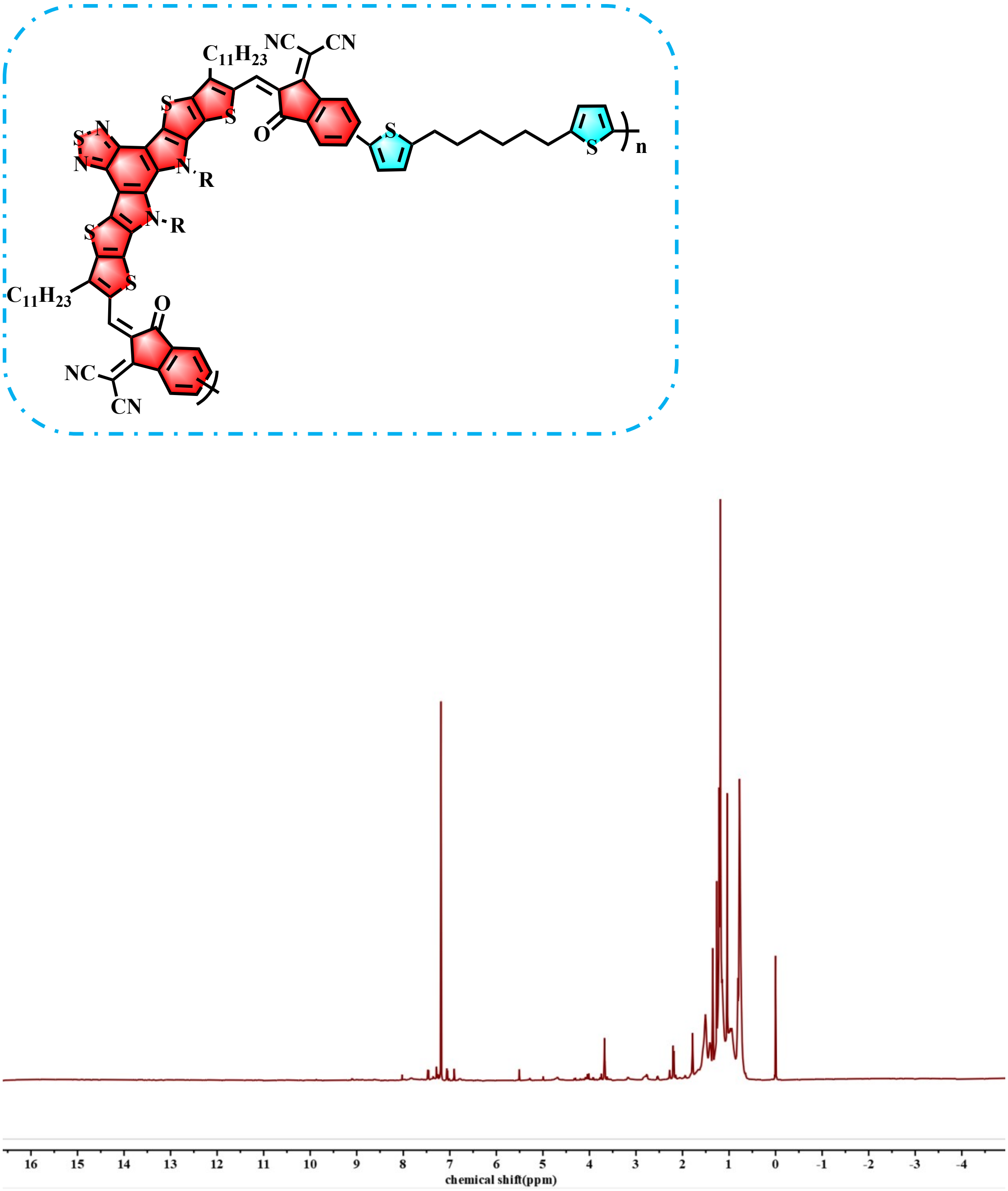


Figure S1. ^{1}H NMR spectra of J1 in $CDCl_3$.

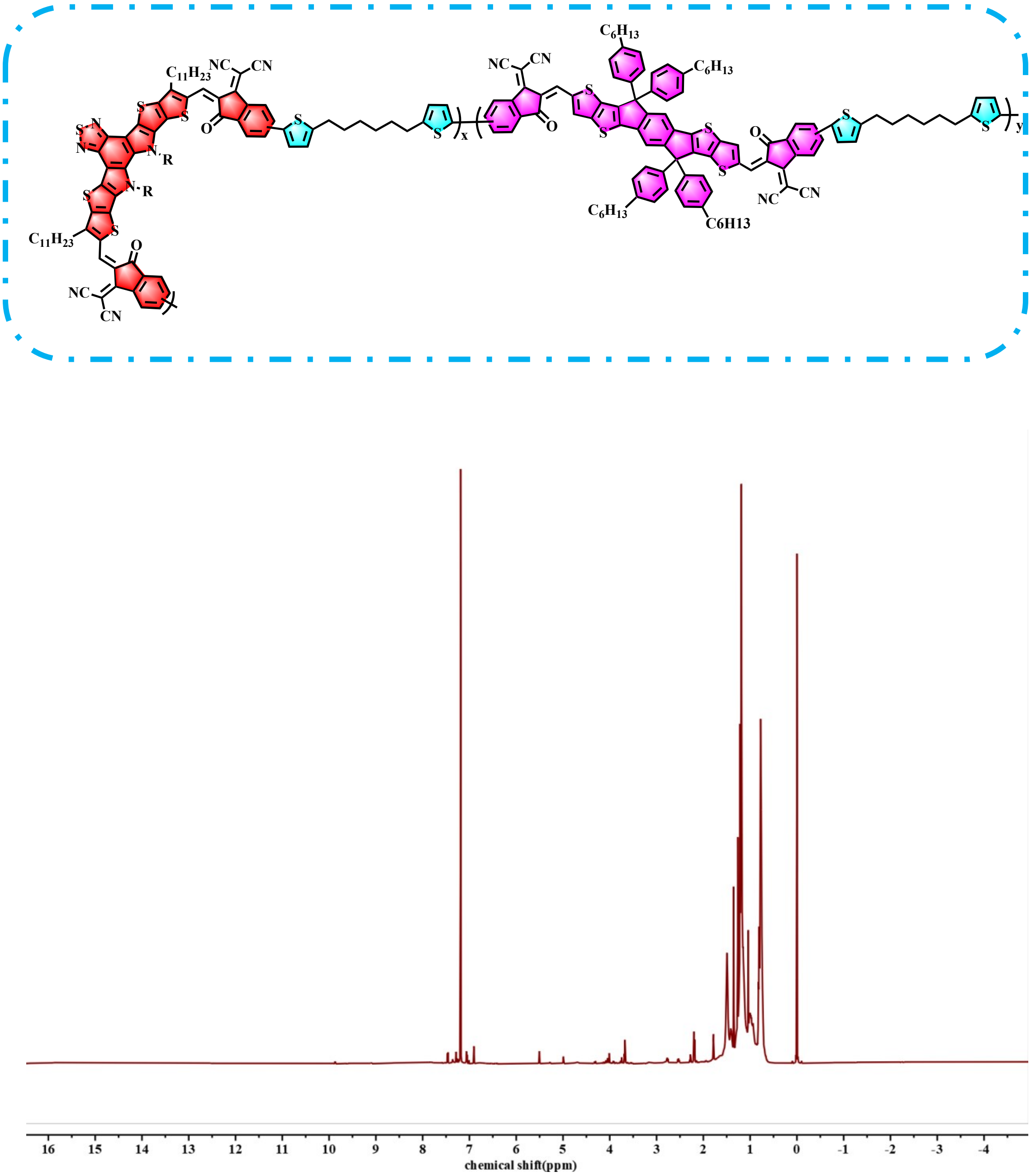


Figure S2. ^{1}H NMR spectra of J2 in $CDCl_3$.

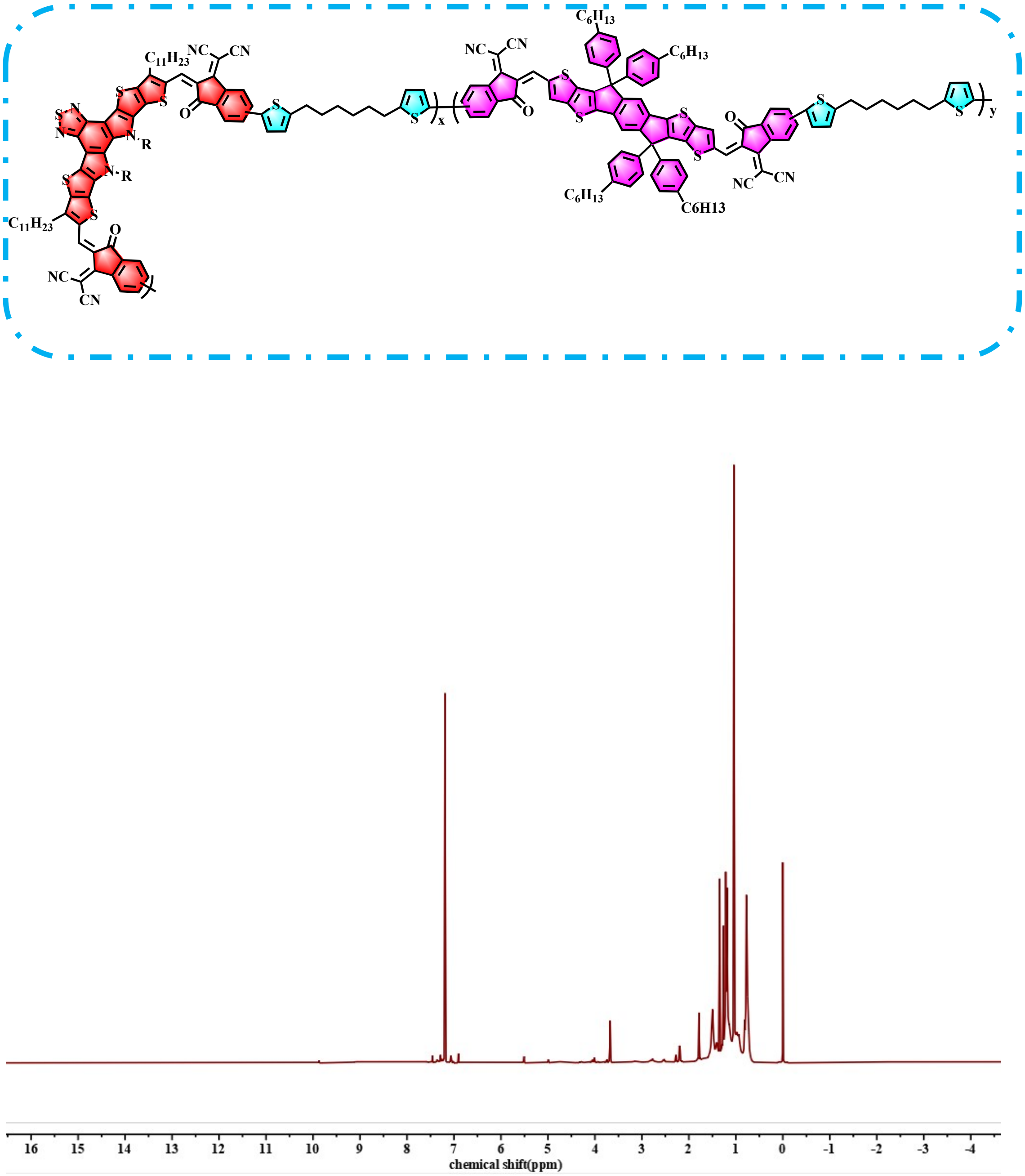


Figure S3. ^{1}H NMR spectra of J3 in $CDCl_3$.

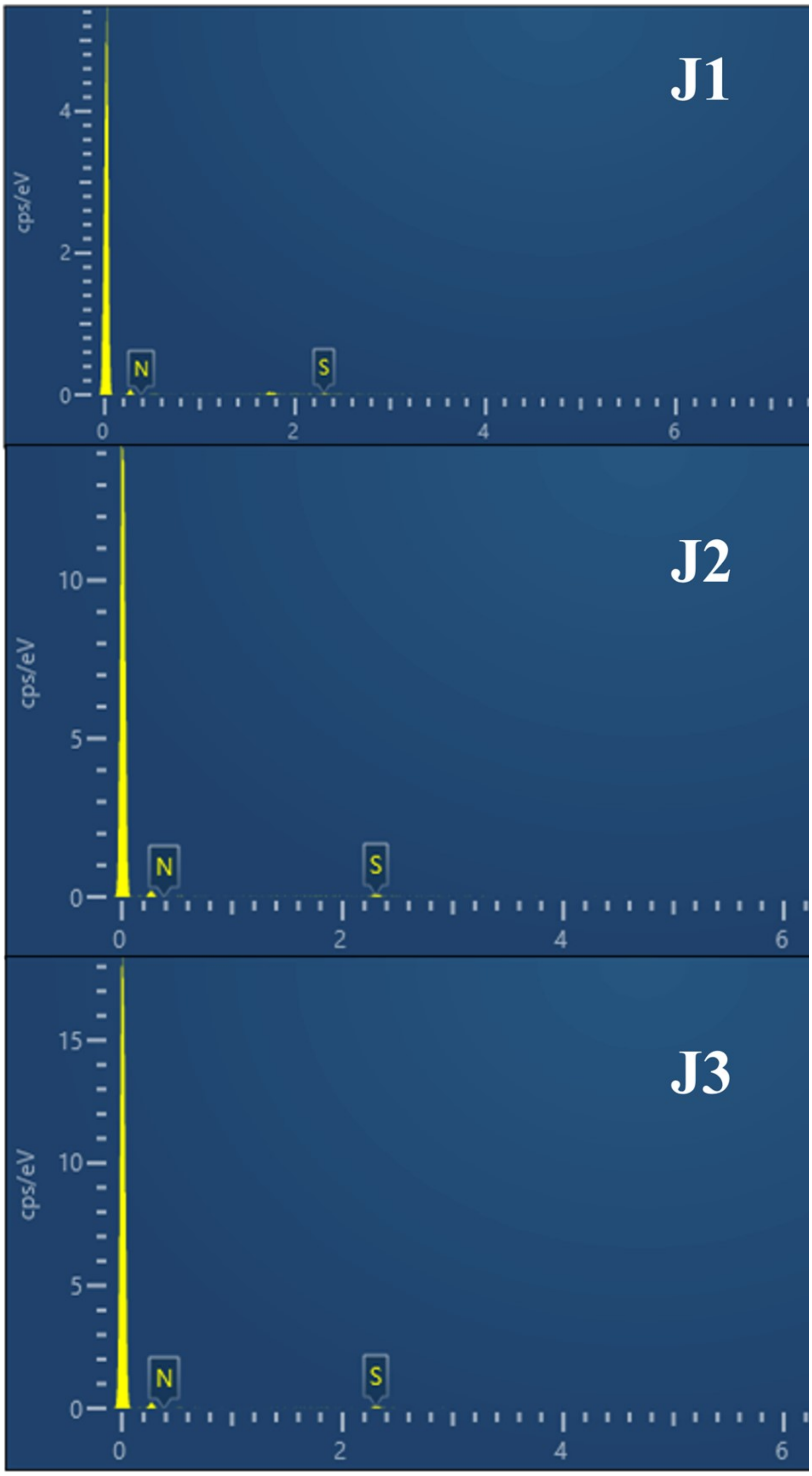
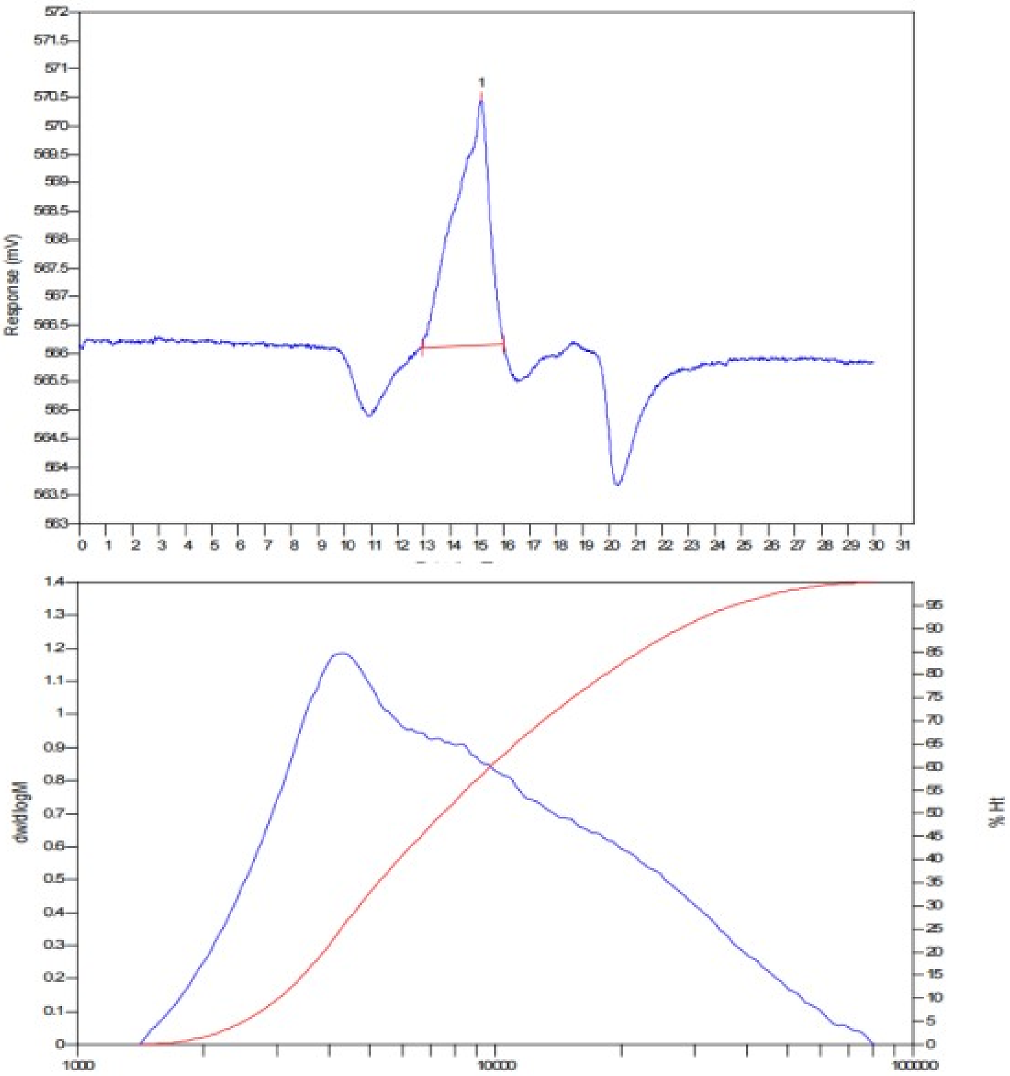


Figure S4. Energy dispersive spectrometer (EDS) analysis of J1, J2 and J3.



MW Averages

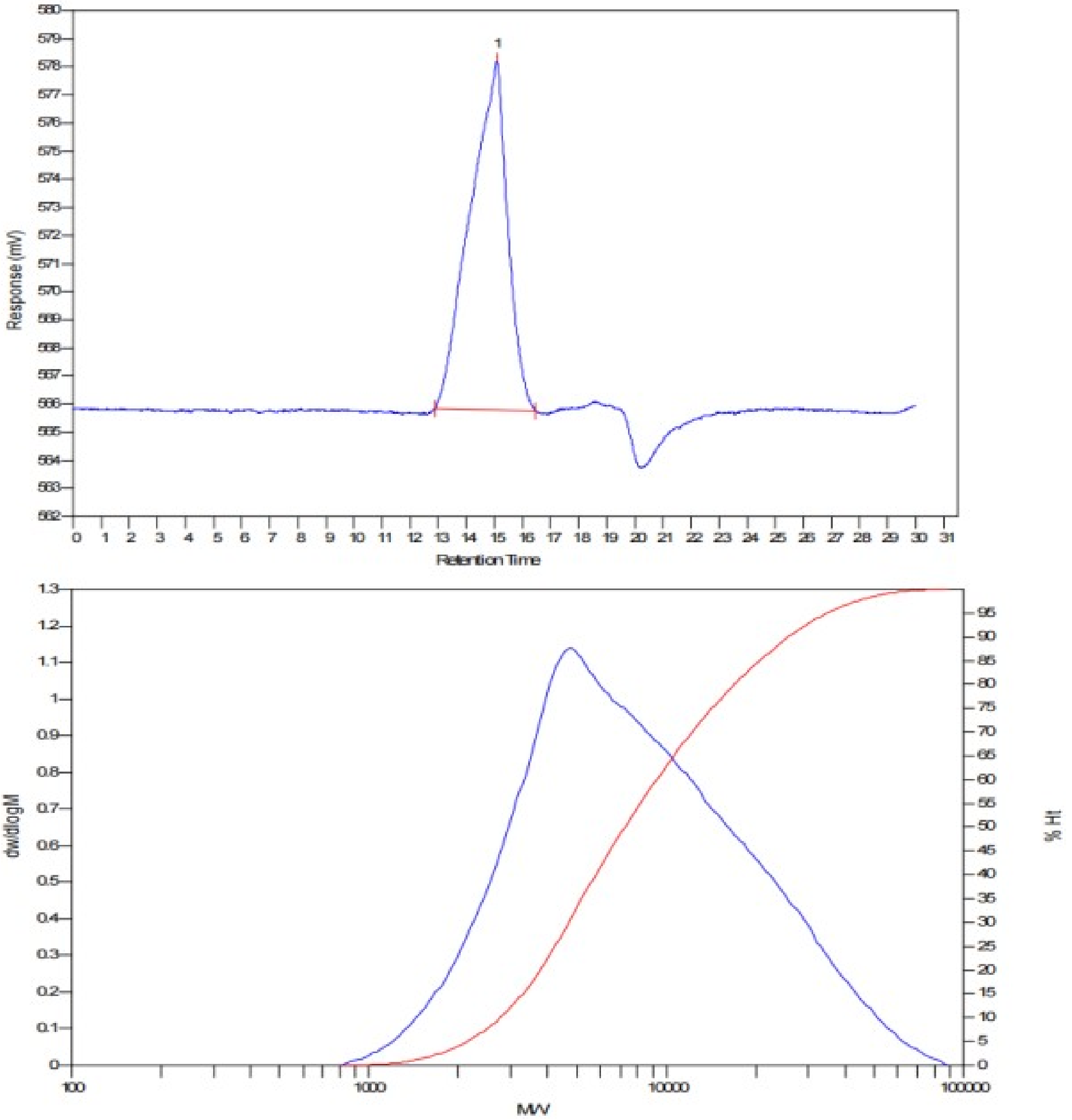
Mp: 4359 Mn: 6027 Mv: 10546 Mw: 11788

Mz: 22992 Mz+1: 35101 PD: 1.9559

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.95	15.15	16.02	4.29932	0	382.2	100

Figure S5. High temperature gel permeation chromatography (HT-GPC) trace of J1.



MW Averages

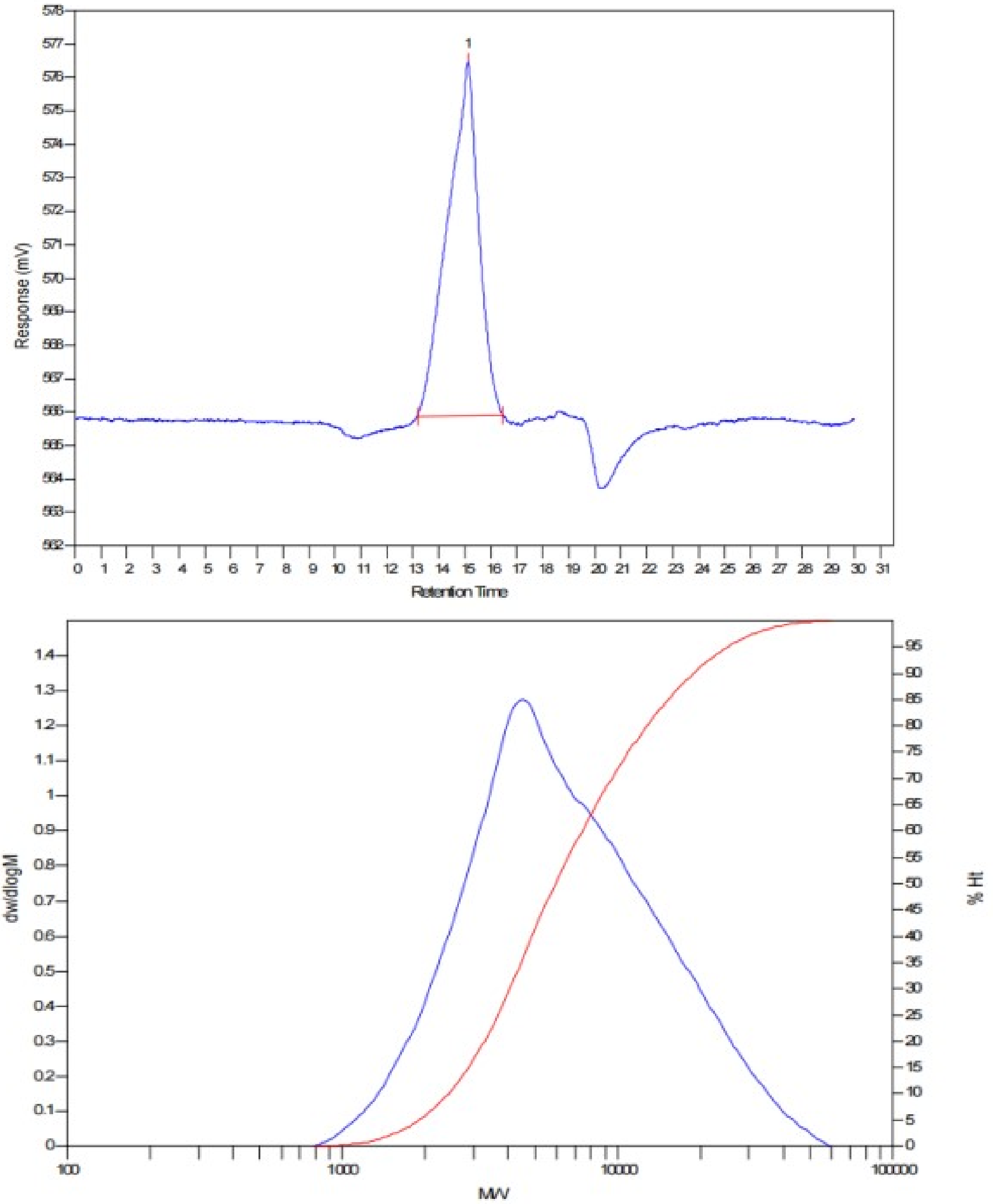
Mp: 4757 Mn: 5557 Mv: 9993 Mw: 11170

Mz: 21939 Mz+1: 34381 PD: 2.0101

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.88	15.08	16.45	12.3993	0	1148.5	100

Figure S6. High temperature gel permeation chromatography (HT-GPC) trace of J2.



MW Averages

Mp: 4554 Mn: 4746 Mv: 7796 Mw: 8563

Mz: 15367 Mz+1: 23377 PD: 1.8043

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.18	15.12	16.47	10.5787	0	873.995	100

Figure S7. High temperature gel permeation chromatography (HT-GPC) trace of J3.

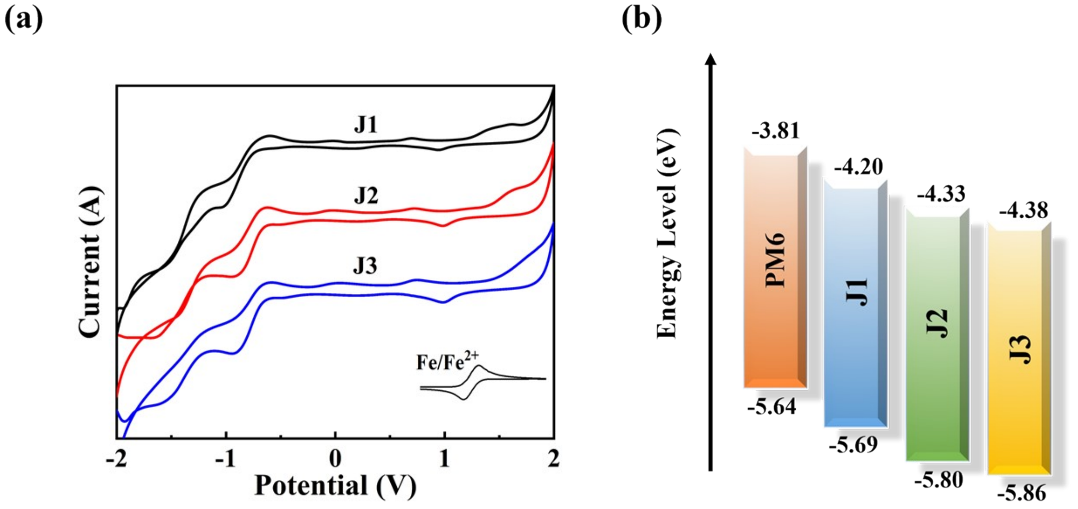


Figure S8. (a) CV curves of the three polymers. (b) Molecular energy level diagram of the related polymers and donor.

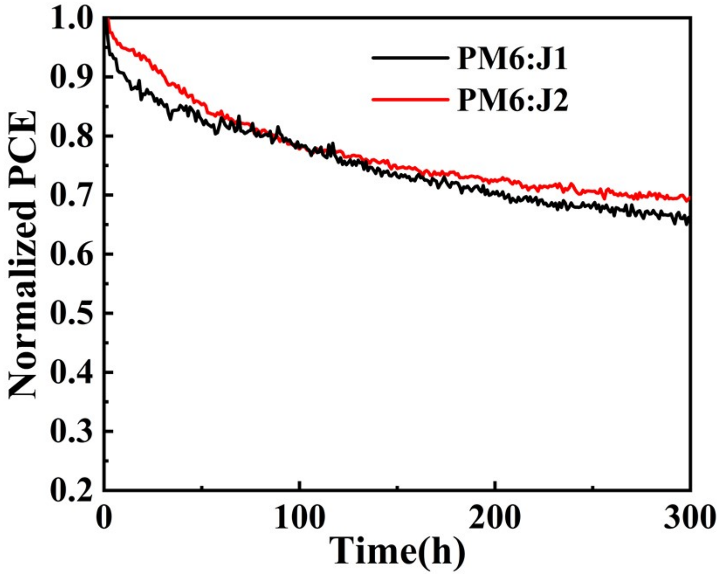


Figure S9. Normalized PCE change with time under constant heat at 60°C.

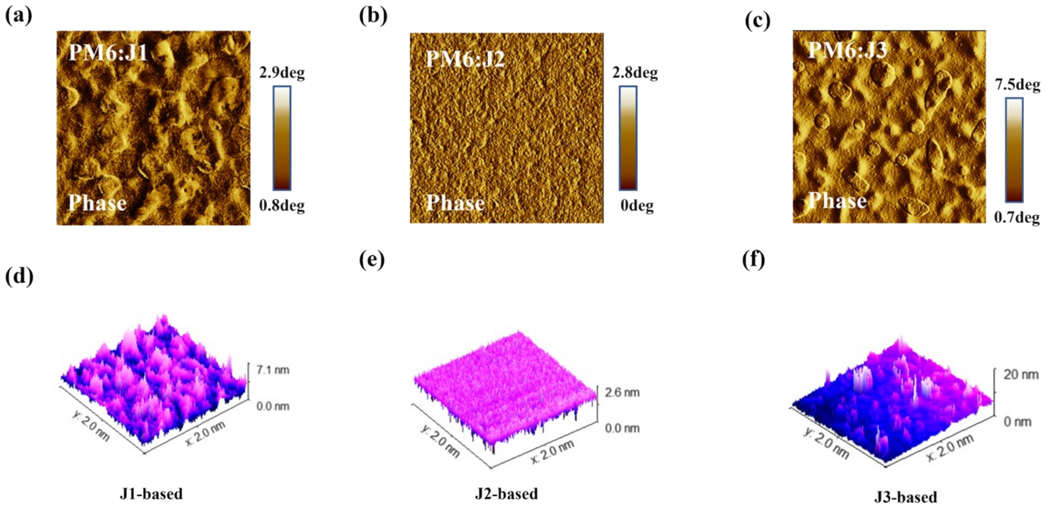


Figure S10. Phase images of (a) PM6:J1, (b) PM6:J2 and (c) PM6:J3 blend films. Height images of (d) PM6:J1, (e) PM6:J2 and (f) PM6:J3 blend films.

Table S1 The elemental analysis data of the photoactive materials.

Photoactive material	**Characteristic Element**	**Mass Fraction (%)**	**Atomic Fraction (%)**
J1	N	33.31	53.33
	S	66.69	46.67
J2	N	32.84	52.88
	S	67.16	47.12
J3	N	31.88	51.93
	S	68.12	48.07

Table S2 Surface tension and the Flory-Huggins interaction parameter of neat film of polymer donors and polymer acceptors.

Film	**θ_{water} [°]**	**$\theta_{glycerin}$ [°]**	**γ_w [mN m^{-1}]**	**γ_g [mN m^{-1}]**	**Blend film**	**χ/K $(\gamma_D^{-2}-\gamma_A^{-2})^2$**
J1	88.10	87.70	30.39	24.83	PM6:J1	0.115
J2	104.20	99.30	20.52	20.88	PM6:J2	0.006
J3	106.60	96.0	19.10	20.24	PM6:J3	0.021
PM6	103.20	93.60	21.56	20.47	/	/

Tables S3. Summarized parameters for the ordering structures of neat films and blend.

Samples	**π-π stacking (010) along OOP direction**				**Lamella stacking (100) along IP direction**			
	q ($Å^{-1}$)	*d*-spacing (Å)	FWHM ($Å^{-1}$)	CCL (Å)	q ($Å^{-1}$)	d-spacing (Å)	FWHM ($Å^{-1}$)	CCL (Å)
PM6	1.64	3.82	0.312	18.31	0.22	28.5	0.060	94.3
J1	1.65	3.80	0.07415	77	0.14	43.9	0.049	115
J2	1.68	3.75	1.345	4.24	0.17	37.5	0.038	150
J3	1.65	3.80	1.80	3.16	0.15	40.8	0.051	111.3
PM6:J1	1.64	3.82	0.028	204	0.14	45.7	0.0488	115.9
PM6:J2	1.68	3.74	0.321	17.8	0.16	39.8	0.044	127.4
PM6:J3	1.66	3.79	1.42	4.0	0.165	38.1	0.049	116