

## **Terpolymerization Strategy to Achieve High-Efficient Organic Solar Cells *via* Constructing D1-A-D1-D2-Type Polymer Donors**

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## **Experimental Procedures**

### **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 PA14083) was obtained from Bayer Inc. BDT-2F, BDD, and BDT-2EST were purchased from SunaTech Inc and Solarmer Materials Inc. Pd<sub>2</sub>(dba)<sub>3</sub> and P(o-Tol)<sub>3</sub> were obtained from J&K.

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

<sup>1</sup>H NMR spectra of the polymers were recorded on a Bruker AVANCE III HD 400 MHz spectrometer using deuterated CDCl<sub>3</sub> 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<sup>-1</sup> tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the

supporting electrolyte. The scan rate was 0.05 V s<sup>-1</sup>. The  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are calculated as referring to the equation (1) and (2).

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

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

### **AFM characterizations.**

The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without PDINN/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  $\lambda = 1.10994 \text{ \AA}$ ) using a double crystal monochromator and focused both horizontally and vertically (450 (H) x 60 (V)  $\mu\text{m}^2$  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 (Rayonix 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,  $a = 10.8631 \text{ \AA}$ ,  $b = 8.7044 \text{ \AA}$ ,  $c = 7.7624 \text{ \AA}$ , and  $\beta = 102.938^\circ$ ) and the sample-to-detector distance was ~231 mm.

### **Device Fabrication and Characterizations**

The device was fabricated with a structure of ITO/PEDOT:PSS (40 nm)/active layer/PDINO/Ag. A thin layer of PEDOT:PSS was deposited through spin-coating on precleaned ITO-coated glass from a PEDOT: PSS aqueous solution (Baytron PVP AI 4083 from H. C. Starck) at 2,000 rpm and dried subsequently at 150°C for 15 min in air, the device was transferred to a nitrogen glove box. The device processing conditions were optimized via tuning the total concentration, altering the D/A ratio, and changing the content of the solvent additive. The champion device was fabricated from the total

concentration of  $14.0 \text{ mg ml}^{-1}$  with the D/A ratio was 1:1.2 (w/w) in chloroform and a trace amount of 1-chloronaphthalene (CN) (0.5%, v/v) as solvent additive with thermal annealing at  $110^\circ\text{C}$  for 10 min. Subsequently, methanol solution of PDINO at a concentration of  $1.0 \text{ mg ml}^{-1}$  was deposited atop the active layer at 3,000 r.p.m. for 30 s to afford a PDINO cathode buffer layer with a thickness of about 10 nm. Finally, the 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  $0.04 \text{ cm}^2$ . The current-voltage ( $J$ - $V$ ) characteristics were measured by a Keithley 2400 Source Meter under simulated solar light ( $100 \text{ mW/cm}^2$ , AM 1.5 G, Abet Solar Simulator Sun2000). The external quantum efficiency (EQE) spectra were detected on an EQE measuring system (Oriel Cornerstone 2601/4 m monochromator equipped with Oriel 70613NS QTH lamp). All the measurements were performed at room temperature under ambient atmosphere.

### **EQEEL measurements**

EQEEL of the solar cells were determined by using a digital source meter (Keithley 2400), to inject electric current into the solar cells, and a picoammeters (Keithley 6482) collected to a Si diode, to measure emitted photons from the solar cells.

### **EL spectra**

EL spectra of OSCs were measured by using a source meter (Keithley 2400) to inject electric current into the OSCs, and emitted photons were collected by an optical fiber and recorded by a fluorescence spectrometer (KYMERA-3281-B2, Andor), a Si EMCCD camera (DU970P-BVF, Andor), and an InGaAs camera (DU491A-1.7, Andor).

### **PL spectra**

PL spectra of the active layers were measured with a laser (SuperK EXU-6, NKT photonics) and narrowband filters (LLTF Contrast SR-VIS-HP8, NKT photonics) as the light source. The excitation wavelength was 480 nm. Photons emitted from the thin

films were collected and recorded by the same setup used for the EL spectra measurements.

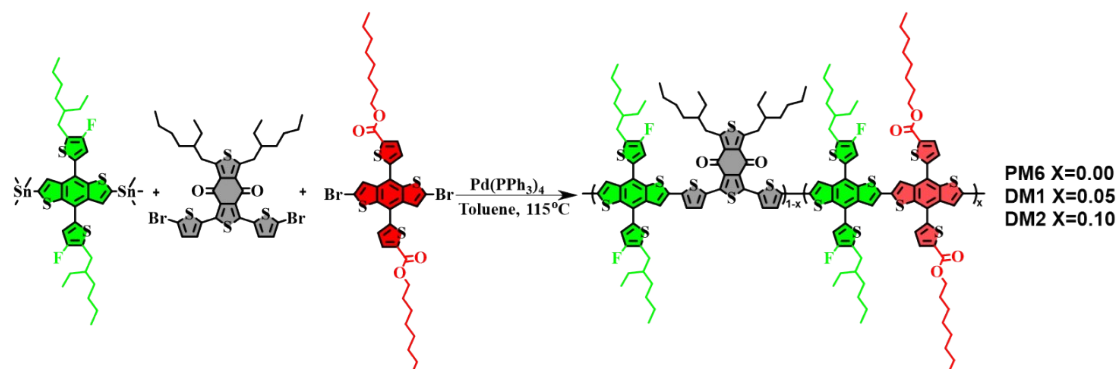
### **Transient photocurrent vs voltage curves**

Transient photocurrent vs voltage curves of the solar cells were measured using a green LED. The  $V_{oc}$  of the solar cell under the LED illumination is close to that under the simulated AM1.5G illumination. An oscilloscope (MDO4104C, Tektronix) was used to record the transient photocurrent signals. A Keithley 2400 is used to apply voltage to the solar cell. The impact of series resistance in the electrodes of the solar cells is minimized using a “4-point” method: the sensing of the voltage applied to the active layer of the solar cell is done via connecting an additional set of anode and cathode terminals to a voltmeter.

sphere.

## Results and Discussion

### Synthetic procedures



#### (1). copolymer PM6 was synthesized as follows:

The F-BDT is 0.047g mmol (0.050 mmol), BDD is 0.038g (0.050 mmol) and dry toluene (4 ml) were added to a 20 ml double-neck round-bottom flask. The reaction container was purged with argon for 20 min, then  $\text{Pd}_2(\text{dba})_3$  0.00091g (0.01 mmol) and  $\text{P}(\text{o-Tol})_3$  0.00091g (0.03 mmol) were added. After another flushing with argon for 20 min, the reactant was heated under  $115^\circ\text{C}$  to reflux for 4.0h. The reactant was cooled down to room temperature and poured into methanol (50 ml), then purified by Soxhlet extraction with hexane, acetone, and chloroform in sequence. The obtained PM6 (yield 74%) was recovered as solid from the chloroform by precipitation from methanol, and dried under vacuum 24h. Elemental analysis calculated for PM6: C, 67.27; H, 6.61; O, 2.56; S, 20.52. Found: C, 67.25; H, 6.62; O, 2.61; S, 20.55.

#### (2). terpolymer DM1 was synthesized as follows:

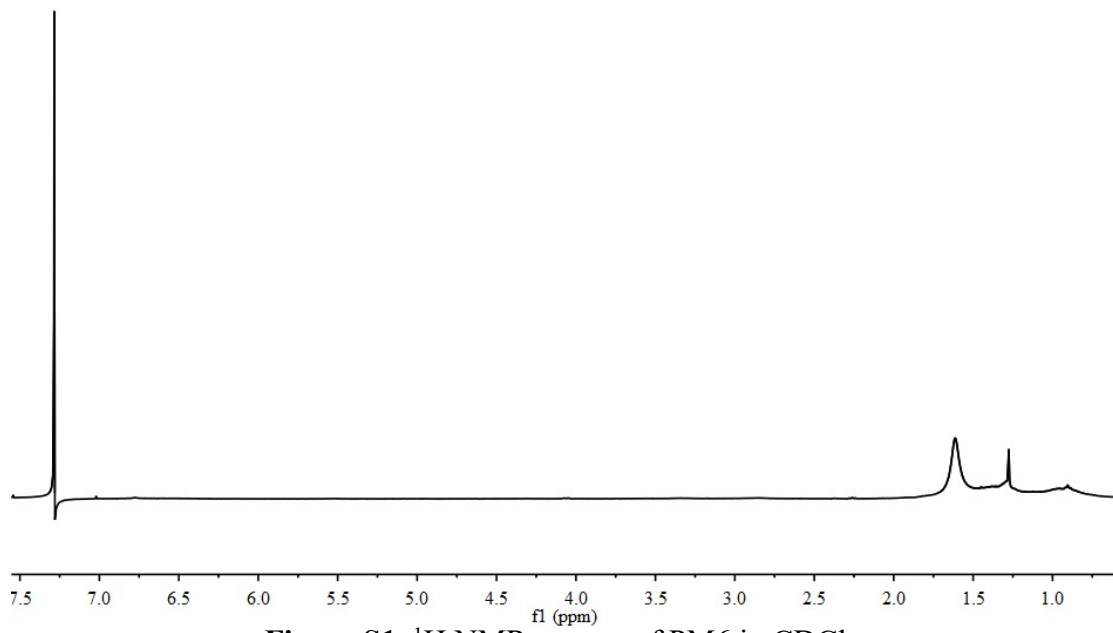
The F-BDT is 0.0300g (0.0319 mmol), BDT-2EST is 0.0014g (0.0016 mmol), BDD is 0.0257g (0.0335 mmol) and dry toluene (5 ml) were added to a 20 ml double-neck round-bottom flask. The reaction container was purged with argon for 20 min, then  $\text{Pd}_2(\text{dba})_3$  0.0023g (0.0020 mmol) was added. After another flushing with argon for 20 min, the reactant was heated under  $115^\circ\text{C}$  to reflux for 4.0h. The reactant was cooled down to room temperature and poured into methanol (50 ml), then purified by Soxhlet extraction with hexane, acetone, and chlorobenzene in sequence. The obtained terpolymer DM1 (yield 70%) was recovered as solid from the chloroform by precipitation from methanol, and dried under vacuum 24h. Elemental analysis

calculated for DM1: C, 64.03; H, 6.60; S, 20.48; O, 2.80. Found: C, 64.05; H, 6.62; S, 20.45; O, 2.81.

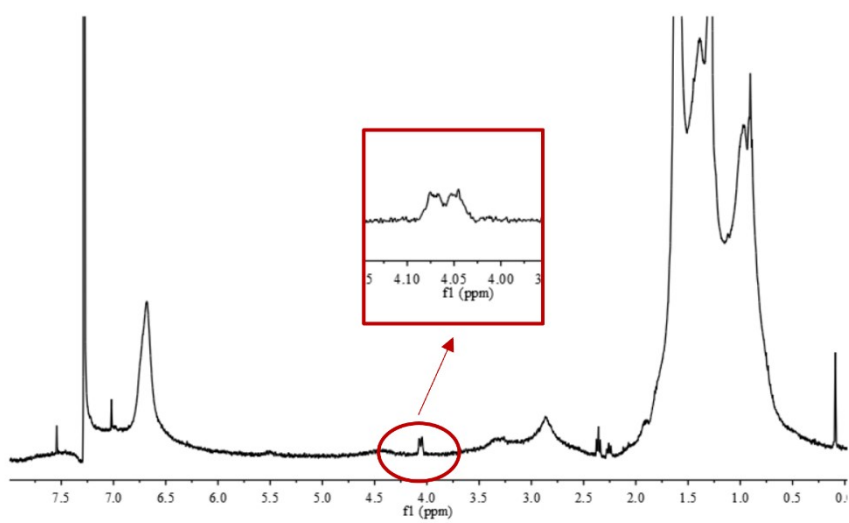
**(3). terpolymer DM2 was synthesized as follows:**

The synthetic method is same as terpolymer DM1, except the concentration of monomers with F-BDT is 0.0300g (0.0319 mmol), BDT-2EST is 0.0029g (0.0036 mmol), BDD is 0.0272g (0.0355 mmol), and the yield is 70%. Elemental analysis calculated for DM2: C, 67.19; H, 6.60; O, 3.04; S, 20.44. Found: C, 67.15; H, 6.58; O, 3.04; S, 20.45.

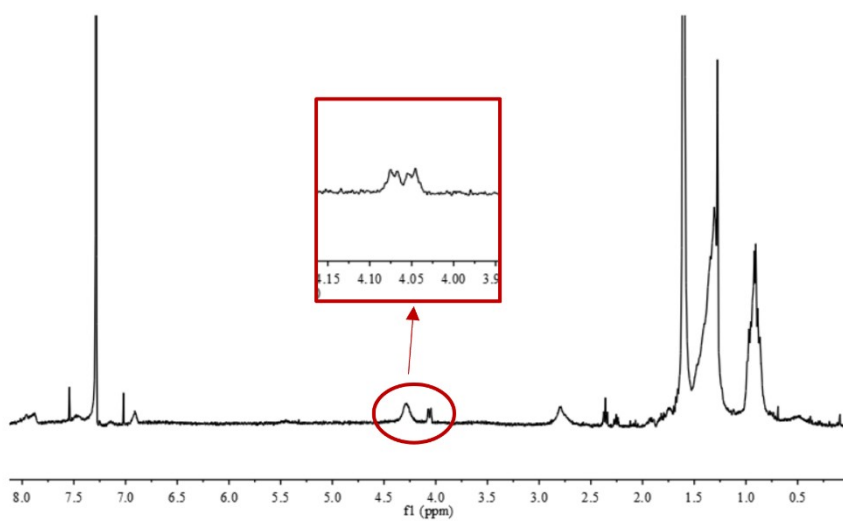




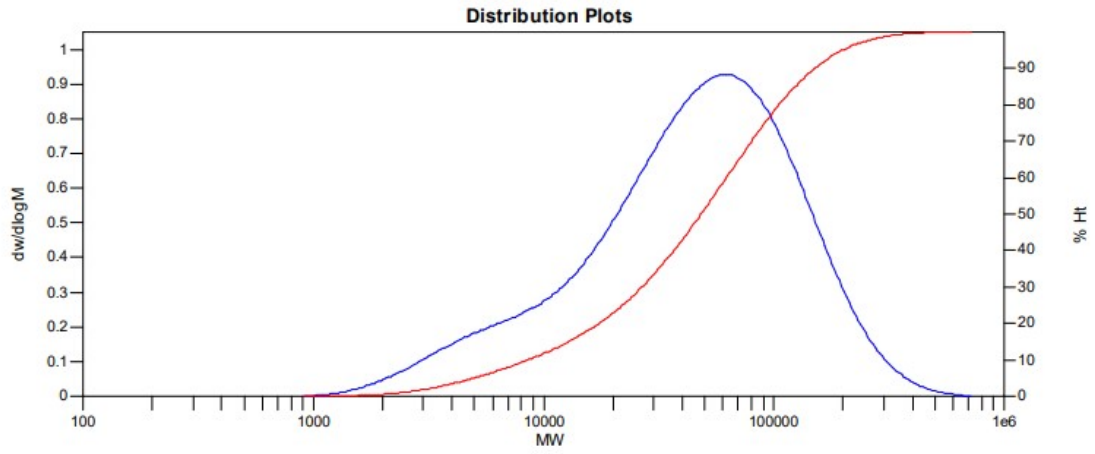
**Figure S1.**  $^1\text{H}$  NMR spectra of PM6 in  $\text{CDCl}_3$ .



**Figure S2.** <sup>1</sup>H NMR spectra of DM1 in CDCl<sub>3</sub>.



**Figure S3.**  $^1\text{H}$  NMR spectra of DM2 in  $\text{CDCl}_3$ .



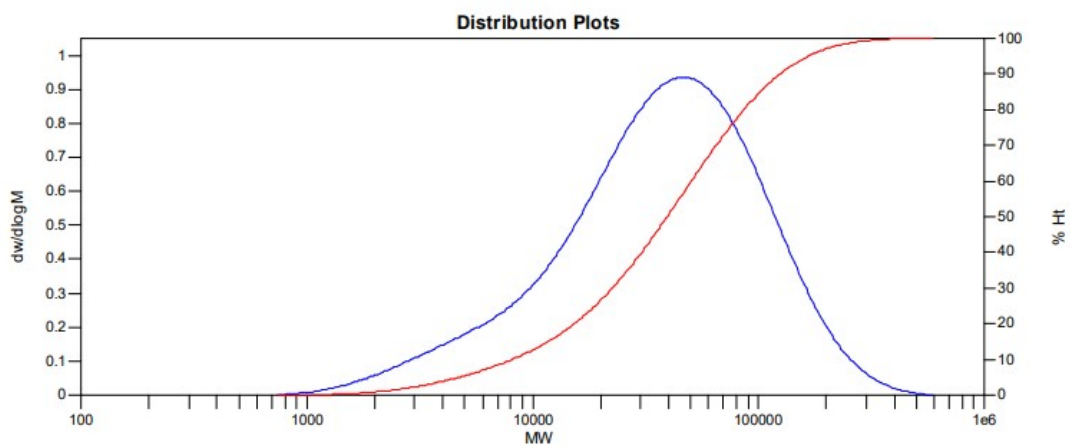
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	62668	20572	67078	132290	206606	59156	3.26065

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.07	13.77	16.72	-84.9305	100	8845.48	100

**Figure S4.** GPC spectra of PM6.



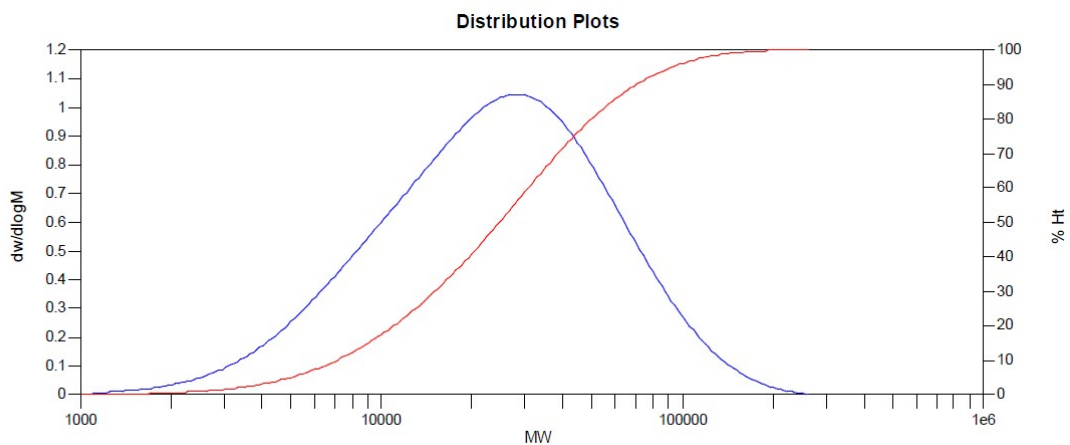
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	47061	18106	55604	110561	175397	49121	3.07103

**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.20	13.97	16.87	-68.9634	100	7108.51	100

**Figure S5.** GPC spectra of DM1.



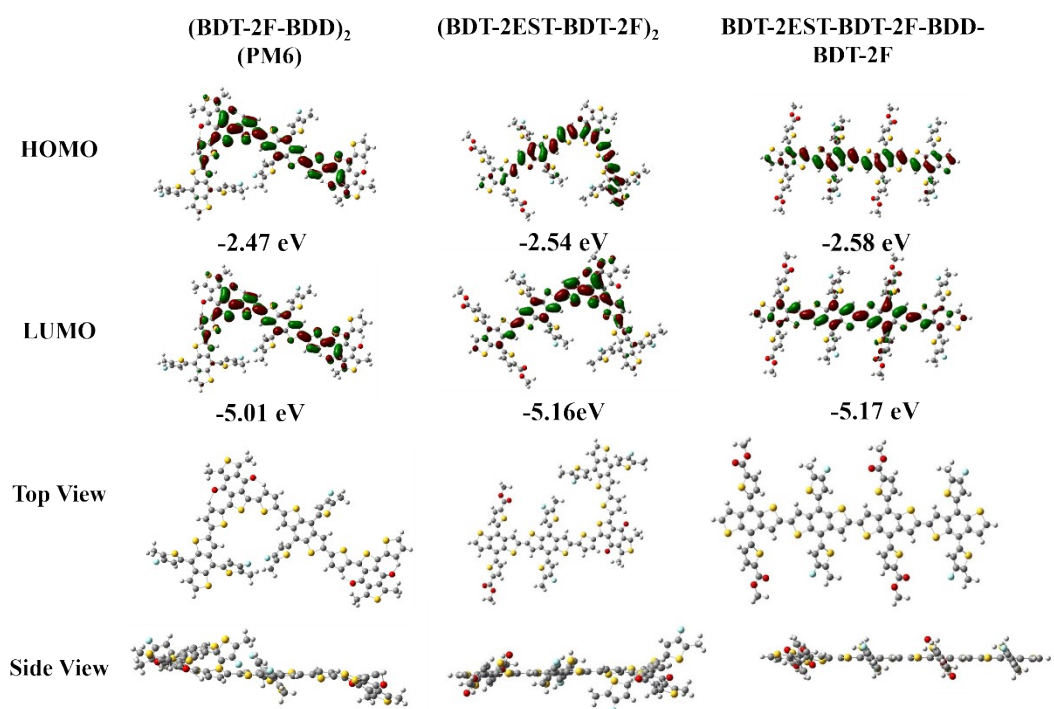
**MW Averages**

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27837	15326	32853	58351	87449	29763	2.14361

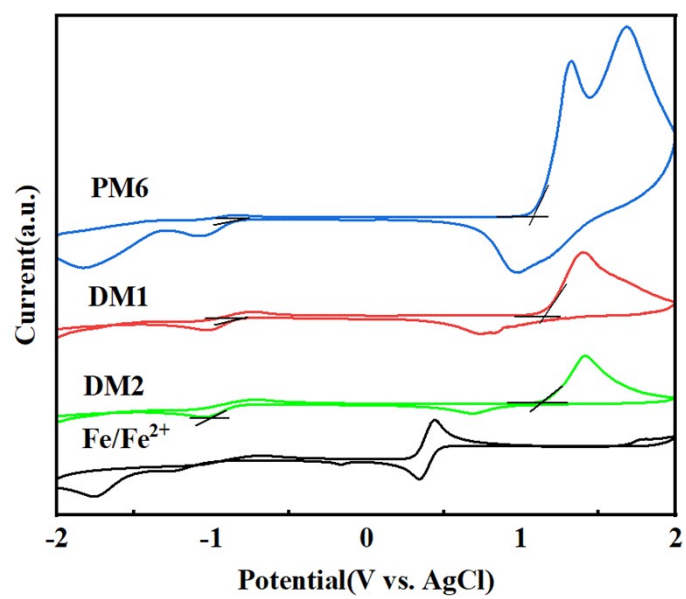
**Processed Peaks**

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.77	14.33	16.65	93.6377	100	8636.24	100

**Figure S6.** GPC spectra of DM2.

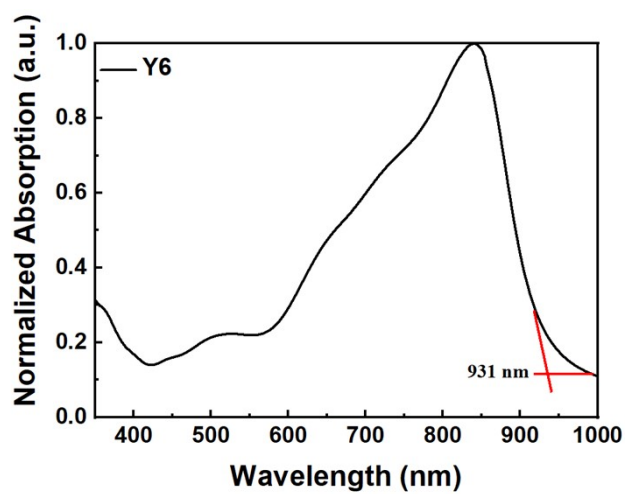


**Figure S7.** The density functional theory (DFT) calculations on molecular energy levels and optimal molecular geometries.

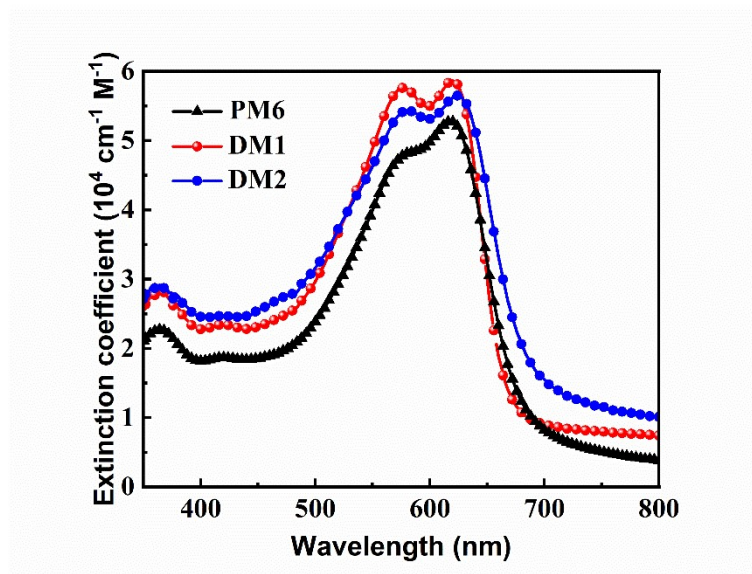


**Figure S8.** Cyclic voltammetry (CV) measurement of the related thin films (ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple used as an internal reference).





**Figure S9.** Normalized UV-vis absorption spectra of Y6 thin film.



**Figure S10.** the absorption coefficients of the films (film thickness is 100 nm).

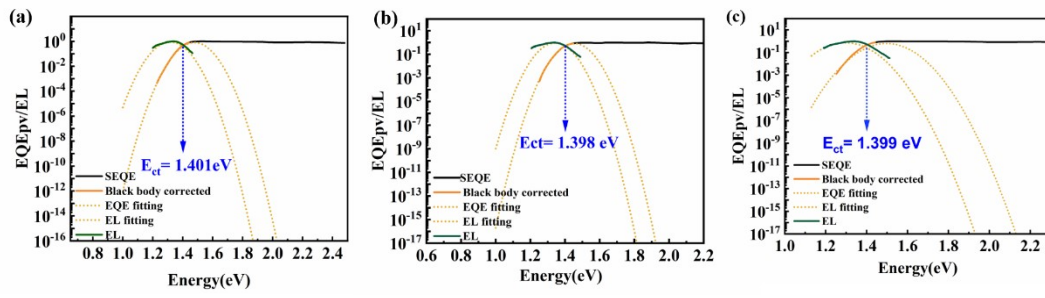
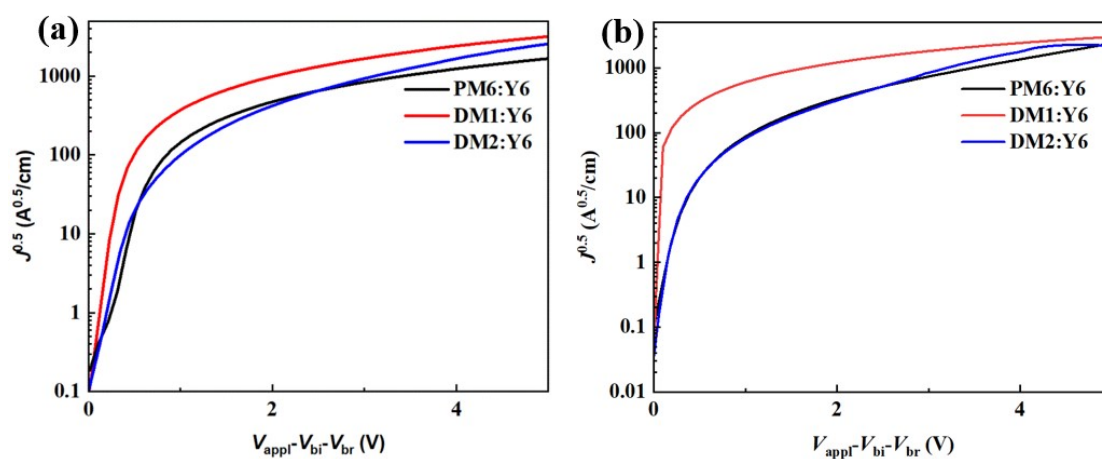
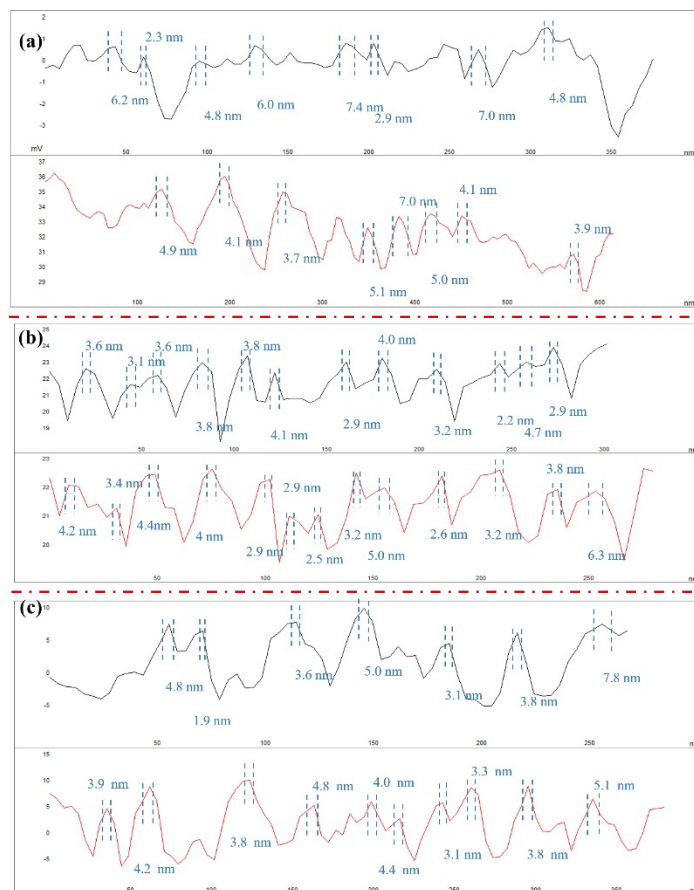


Figure S11. Normalized EL and sEQE spectra of (a) PM6:Y6, (b) DM1:Y6, (c) DM2:Y6-based devices.



**Figure S12.** (a)  $J^{0.5}$ - $V$  plots of hole-only devices with active layer. (b)  $J^{0.5}$ - $V$  plots of electron-only devices with active layer.



**Figure S13.** the calculated average values of FWHM of (a) PM6:Y6, (b) DM1:Y6, and (c) DM2:Y6.

**Table S1.** The energy levels of polymer donors obtained from the DFT calculation.

<b>Polymers</b>	<b>HOMO<sup>a</sup> (eV)</b>	<b>LUMO<sup>a</sup> (eV)</b>
<b>PM6</b>	-5.01	-2.47
<b>DM1</b>	-5.16	-2.54
<b>DM2</b>	-5.17	-2.58

**Table S2.** the device performance with Y6 as the acceptor under 100 mW cm<sup>-2</sup> AM 1.5G solar illumination (all the active layer blends were prepared with CN (0.5%, v/v) as solvent additive).

Total concentration (mg/ml)	Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
13.0	DM1:Y6	0.85	25.01	75.27	16.00
14.0		0.85	25.86	78.29	17.21
15.0		0.84	25.81	74.42	16.13
13.0	DM2:Y6	0.86	25.57	74.62	16.41
14.0		0.86	25.63	75.48	16.65
15.0		0.85	25.70	72.27	15.79

**Table S3.** the device performance with Y6 as the acceptor under 100 mW cm<sup>-2</sup> AM 1.5G solar illumination (all the active layer blends were prepared with the total concentration is 14.0 mg/ml).

CN (v/v)	Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0	DM1:Y6	0.86	24.39	74.86	15.70
0.5%		0.85	25.86	78.29	17.21
1.0%		0.83	25.27	76.57	16.06
0	DM2:Y6	0.87	24.02	74.36	15.54
0.5%		0.86	25.63	75.48	16.65
1.0%		0.84	25.03	75.08	15.79



**Table S4.** the device performance with Y6 as the acceptor under 100 mW cm<sup>-2</sup> AM 1.5G solar illumination CN (0.5%, v/v) as solvent additive and the total concentration is 14.0 mg/ml).

Annealing temperature (°C)	Active layer	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
0	DM1:Y6	0.86	24.61	74.19	15.70
100		0.85	25.86	78.29	17.21
150		0.85	25.48	77.57	16.80
0	DM2:Y6	0.87	24.91	73.14	15.85
100		0.86	25.63	75.48	16.65
150		0.85	25.18	74.98	16.05

**Table S5.** Parameters measured or calculated from EL and sEQE measurements.

Active layer	$E_g$ (eV)	$E_{\text{loss}}$ (eV)	$\Delta E_1$ (eV)	$\Delta E_2$ (eV)	$\Delta E_3$ (eV)
PM6:Y6	1.419	0.528	0.263	0.057	0.208
DM1:Y6	1.419	0.511	0.263	0.050	0.198
DM2:Y6	1.419	0.515	0.263	0.051	0.201

**Table S6.** The effect of  $M_n$  on photovoltaic properties.

Active layer	$M_n$ (kDA)	PCE (%)
PM6:Y6	20.57	15.67
	46.62	14.05
DM1:Y6	18.11	17.21
	46.77	16.50

**Table S7.** The surface energies of the related films.

Active layer	Water (°)	R (mN m <sup>-1</sup> )	Glycerol (°)	R (mN m <sup>-1</sup> )
PM6	102.99	21.23	86.26	25.66
DM1	101.21	22.31	86.10	25.75
DM2	102.41	21.58	86.73	25.39
Y6	95.30	25.93	83.70	27.11

**Table S8.** The related parameters of the GIWAXS measurements on the neat polymer films and the blend films.

Samples	Out-of-Plane				In-Plane			
	$\pi$ - $\pi$ stacking cell axis (010)				Unit cell long axis (100)			
	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )
PM6	1.69	3.80	0.144	39.7	0.291	21.6	0.023	246.0
DM1	1.68	3.70	0.179	32.0	0.229	27.4	0.038	148.1
DM2	1.68	3.70	0.206	27.7	0.293	21.5	0.049	116.3
PM6:Y6	1.70	3.70	0.205	27.90	0.306	20.5	0.051	110.9
DM1:Y6	1.68	3.74	0.206	27.76	0.293	21.5	0.049	115.4
DM2:Y6	1.70	3.70	0.203	28.17	0.308	20.4	0.050	113.1