Improving the all-polymer solar cell performance by adding a narrow bandgap polymer as the second donor

Kai Wang,[a] Sheng Dong,*[b] Xudong Chen,[c] Ping Zhou,[c] Kai Zhang,[b] Jun Huang*[a] and Ming Wang*[a]

[a] Center for Advanced Low-Dimension Materials, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China.
[b] Institute of Polymer Optoelectronic Materials & Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.
[c] Shanghai International College of Design & Innovation, Tongji University, Shanghai 200080, China.
E-mail: M.W. mwang@dhu.edu.cn J. H. huangj@dhu.edu.cn S. D. dongsheng5175000@126.com

Supporting Information

Content

1. General materials and characterizations

2. Cyclic voltammetry measurements

3. SCLC Mobility measurements

4. Solar cell device characterizations

5. AFM measurements

1. General materials and characterizations

Materials: PF2 and PM2 were synthesized according to the literature[1-2]. N2200 were purchased from the Sunatech Co. Molecular weight of PF2: M_n = 20 kDa, PDI=1.8; molecular weight of PM2: M_n=42 kDa, PDI=2.2; molecular weight of N2200: M_n=42 kDa, PDI=2.2.

Chemical Properties: Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Cyclic voltammetry (CV) measurements were tested on a CHI-800 electrochemistry workstation. Molecular weights of the polymers were determined by Agilent Technologies PL-GPC 220 high-temperature (150 °C) chromatograph using 1,3,4-trichlorobenzene as the eluent and polystyrene as the standards.

Device characteristics: Current density-voltage (*J-V*) curves were recorded by Keithley 2400 source meter. PCEs were measured under the light of 100 mWcm^{-2} AM1.5 G from a solar simulator (Enlitech, Taiwan). The light intensity was calibrated by using a China General Certification Centre (CGC) certified reference monocrystal silicon cell (Enlitech). A physical mask containing an aperture with a precise area of 4 mm^2 was used to define the device area during the *J–V* measurements. The external quantum efficiency (EQE) spectra were recorded on a commercial EQE measurement system (Enlitech, QE-R3011, Taiwan). Film thickness was determined on KLA-Tencor P7 Profilometer.

2. Cyclic voltammetry measurements

Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, an Ag/AgCl reference electrode and a Pt wire counter-electrode. The measurements were performed in absolute acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s. Polymer films for CV test were drop-casted onto the glassy carbon working electrode from the chlorobenzene solution, and concentrations are 5

mg/mL. The absolute energy level of ferrocene/ferrocenium (Fc/Fc$^+$) was set to be 4.8 eV below vacuum. The HOMO level was calculated from the equation:

$$E_{HOMO} = -\left(4.8 + E_{onset}^{ox}\right) eV$$, and the LUMO level was calculated from:

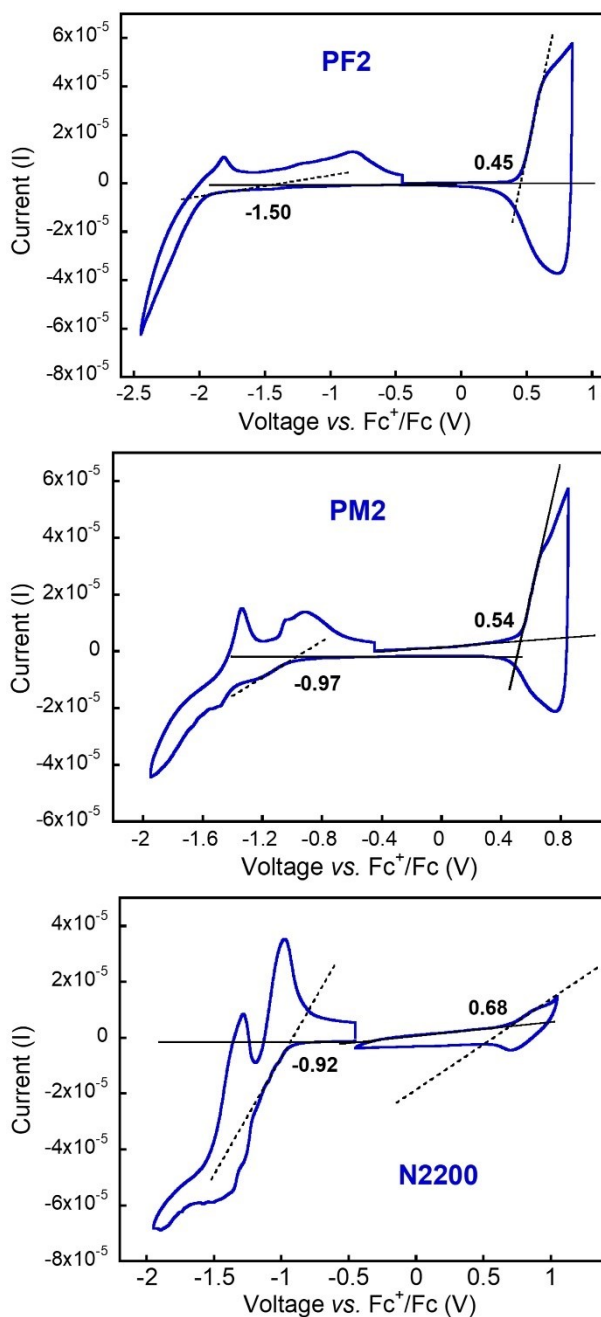$$E_{LUMO} = -\left(4.8 + E_{onset}^{re}\right) eV$$.

Figure S1. CV measurements of PF2, PM2 and N2200 films.

3. SCLC Mobility measurements

Hole-only devices were fabricated to measure the hole mobility using the space charge limited current (SCLC) method. The diode structure is ITO/PEDOT:PSS/Active Layer/MoO$_3$/Ag. Polymer films were then spin-coated from the chlorobenzene solutions at the concentration. And the active layers were prepared under the similar condition of those OPV devices. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{(V - Vbi)^2}{d^3}$$

, where J is the current, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ is the zero-field mobility, d is the thickness of the polymer layer, V is the applied voltage and the V_{bi} is the built-in voltage. Then hole mobilities were calculated from the slope of the $J^{1/2}$-V curves in the SCLC region.

Table 1. Hole mobilities of active layers at different polymer ratios.

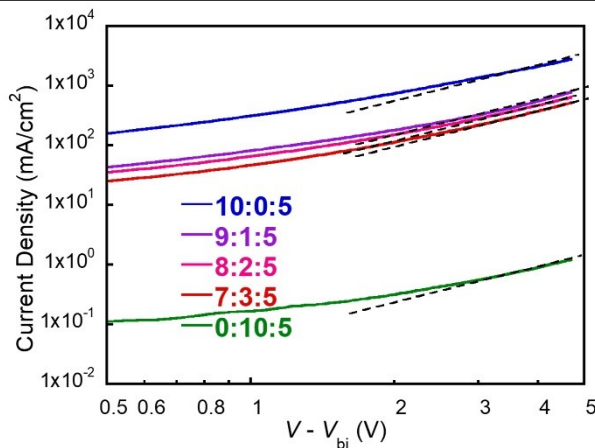| PF2:PM2:N2200 ratio	Hole mobility (cm^{2}V^{-1}s^{-1})
10:0:5	8.3*10^{-4}
9:1:5	2.9*10^{-4}
8:2:5	6.9*10^{-5}
7:3:5	4.6*10^{-5}
0:10:5	1.2*10^{-6}

Figure S2. *J-V* curves of SCLC measurements. Dashed lines indicating the fitting of SCLC region for mobility calculations.

4. Solid cell device characterizations

Table 2. PM2:N2200 devices performance at different D/A ratios. (device structures: ITO/ZnO/PM2:N2200/MoO$_3$/Ag, films were thermal annealed at 130 ^{o}C for 10 minutes.)

	D/A Ratio	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
PM2:N2200	1:0.5	4.99	0.78	40.09	1.57
	1:0.75	4.24	0.81	38.64	1.33
	1:1	4.12	0.82	40.09	1.35

Table 3. PM2:N2200 devices performance using DIO additive. (device structures: ITO/ZnO/PM2:N2200/MoO$_3$/Ag, films were thermal annealed at 130 ^{o}C for 10 minutes.)

	DIO	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
PM2:N2200	0	5.20	0.81	40.63	1.71
	1%	7.35	0.85	44.66	2.80
	2%	7.59	0.84	43.88	2.81
	3%	7.61	0.85	43.94	2.84

Table 4. J_{ph} - V_{eff} parameters of PF2:PM2:N2200 devices.

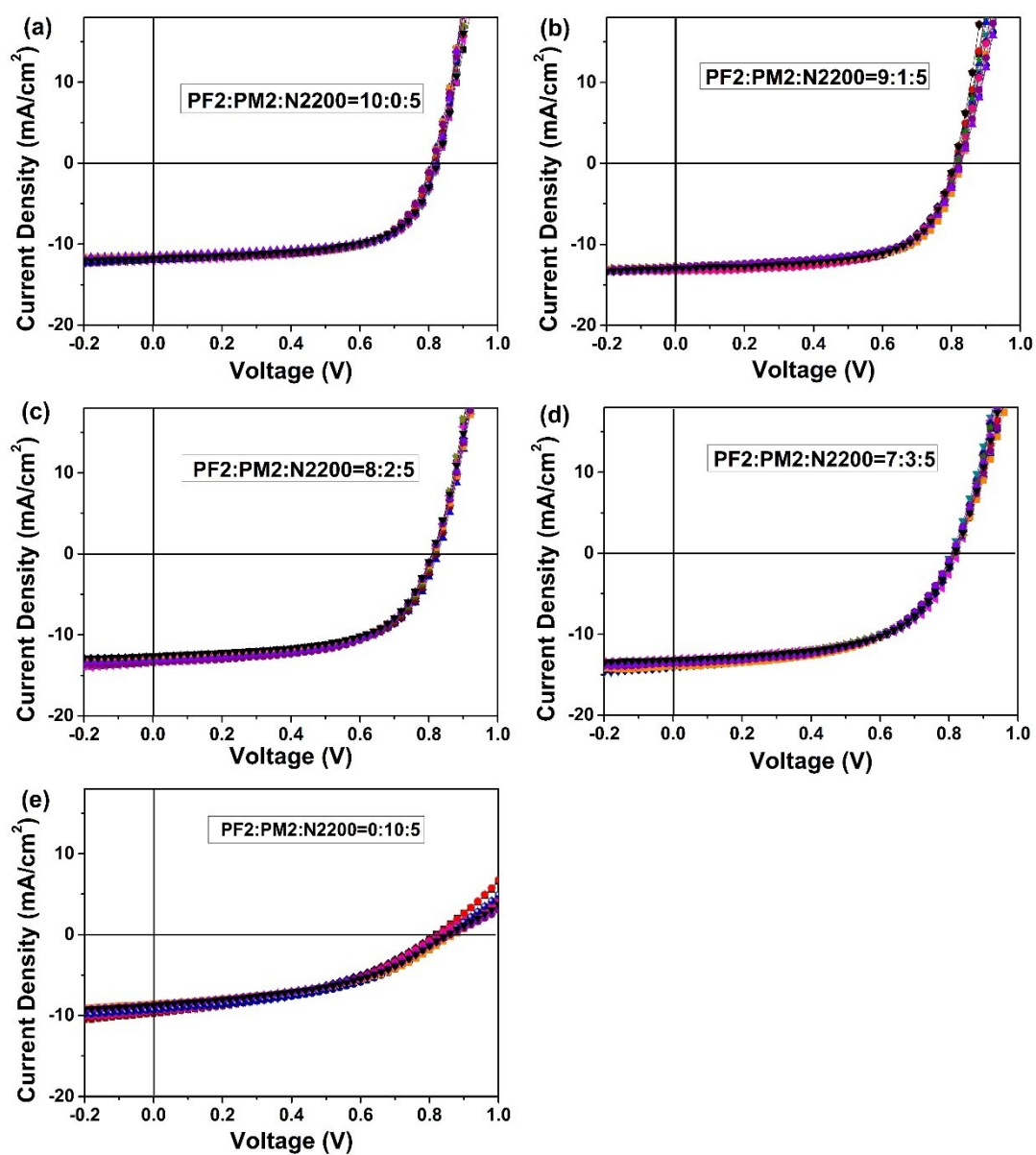| PF2:PM2:N2200 (wt%:wt%:wt%)	J_{sat} (mA/cm^2)	J_{ph} (mA/cm^2)	J_{ph} /J_{sat} (%)	G_{max} (10^{27}m^{-3}s^{-1})
10:0:5	11.17	10.95	98.1	6.78
9:1:5	13.02	12.04	92.5	7.75
8:2:5	13.70	12.52	91.4	7.44
7:3:5	16.01	14.39	89.9	8.70

Figure S3. All *J-V* curves of PF2:PM2:N2200 devices
(ITO/PEDOT:PSS/PF2:PM2:N2200/PFN-Br/Ag): (a) 10:0:5; (b) 9:1:5; (c) 8:2:5; (d)
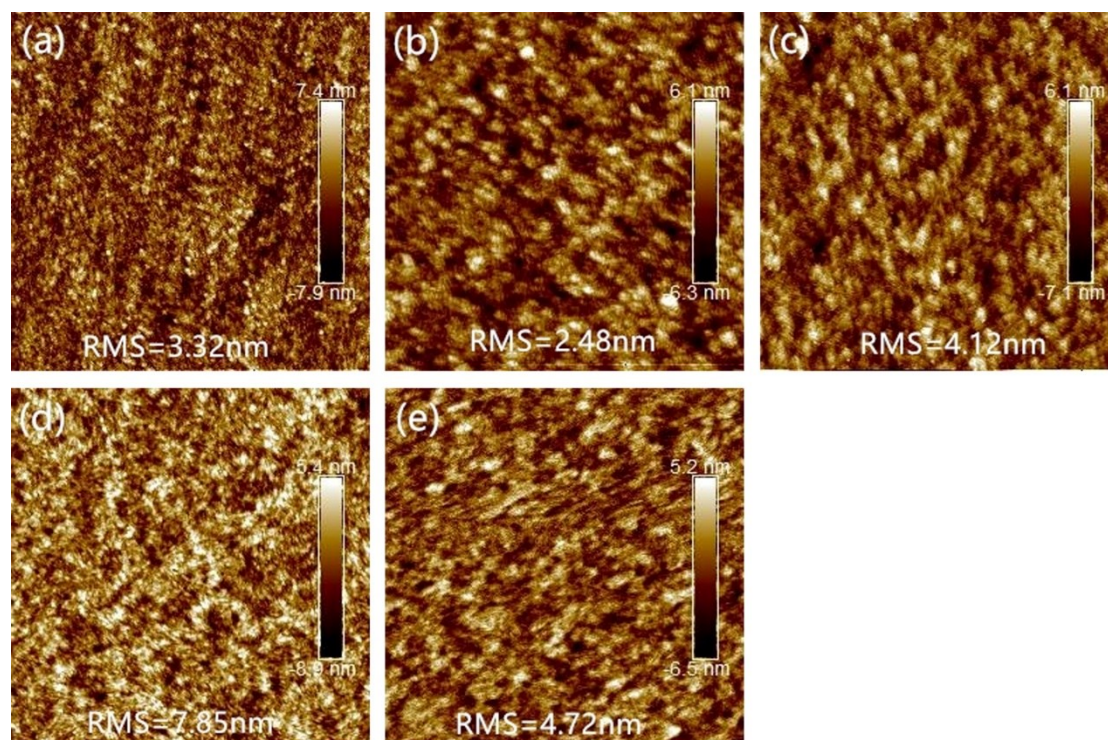7:3:5; (e) 0:10:5.

5. AFM measurements

Figure S4. AFM topography measurement of different PF2:PM2:N2200 blend films: (a) 10:0:5; (b) 9:1:5; (c) 8:2:5; (d) 7:3:5; (e) 0:10:5.

References:

1. J. Min, Z.-G. Zhang, S. Zhang, Y. Li, *Chem. Mater.* **2012**, *24*, 3247.

2. M. Wang, H. Wang, M. Ford, J. Yuan, C.-K. Mai, S. Fronk, G. C. Bazan, *J. Mater. Chem. A*, **2016**, *4*, 15232.