Supporting Information for

Molecular aggregation and crystallinity control enables improved performance of all-polymer solar cells

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Experiment section

Characterization

The molecular weight was determined by GPC using trichlorobenzene as the eluent and monodispersed polystyrene as the standard. The UV-Vis spectra of polymers were measured on with a TU-1601 spectrophotometer by using a 1 cm glass cuvette. Cyclic voltammetry (CV) was performed in 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 100 mV/s with ITO as the working electrode, Pt wire as the counter electrode and Ag/Ag^+ as the reference electrode. Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode.

Materials

Monomers FPDI-2Br was prepared by our previous work.[1-2] NDI-2Br and BT-Tin monomers were purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd., and polymer PTzBI was obtained from Solarmer Materials Inc. (Beijing). All other commercial reagents and solvents were obtained commercially and used without further purification unless stated otherwise.

Synthesis of PNDI-FPDI10%. In a 25-mL flask, NDI-2Br (177 mg, 0.180 mmol), FPDI-2Br (31.5 mg, 0.02 mmol) and BT-Tin (98.4 mg, 0.20 mmol) were first dissolved in degassed dry toluene (10 mL), and then $Pd_2(dba)_3$ (5.0 mg, 0.0055 mmol) and P(o-tol)$_3$ (10.0 mg, 0.033 mmol) were added under argon atmosphere. The reaction mixture was evacuated and refilled with nitrogen for three times, and then was heated to 110 ^oC for 72 hours. For end-capping, 2-(tributylstannyl)thiophene (0.2 mL) was added into the mixture and stirred for 12 hours, 2-bromothiophene (0.5 mL) was then added and stirred for 12 hours. After cooling to the room temperature, the mixture was poured into

methanol. The precipitation was collected and dissolved into cholorbenzene. The chlorobenzene solution was concentrated and poured into acetone. The precipitation was collected and dissolved into cholorbenzene again and the solution was concentrated and poured into hexane. The collected solid was then dried over vacuum to give PNDI-FPDI10% (172 mg, 82%).

Synthesis of PNDI-FPDI30%. It was prepared by the same procedure as described above, starting with NDI-2Br (138 mg, 0.140 mmol), FPDI-2Br (94.5 mg, 0.06 mmol) and BT-Tin (98.4 mg, 0.20 mmol). The collected solid was then dried over vacuum to give PNDI-FPDI30% (180 mg, 77%).

Synthesis of PNDI-FPDI70%. It was prepared by the same procedure as described above, starting with NDI-2Br (59.1 mg, 0.06 mmol), FPDI-2Br (221 mg, 0.14 mmol) and BT-Tin (98.4 mg, 0.20 mmol). The collected solid was then dried over vacuum to give PNDI-FPDI70% (211 mg, 75%).

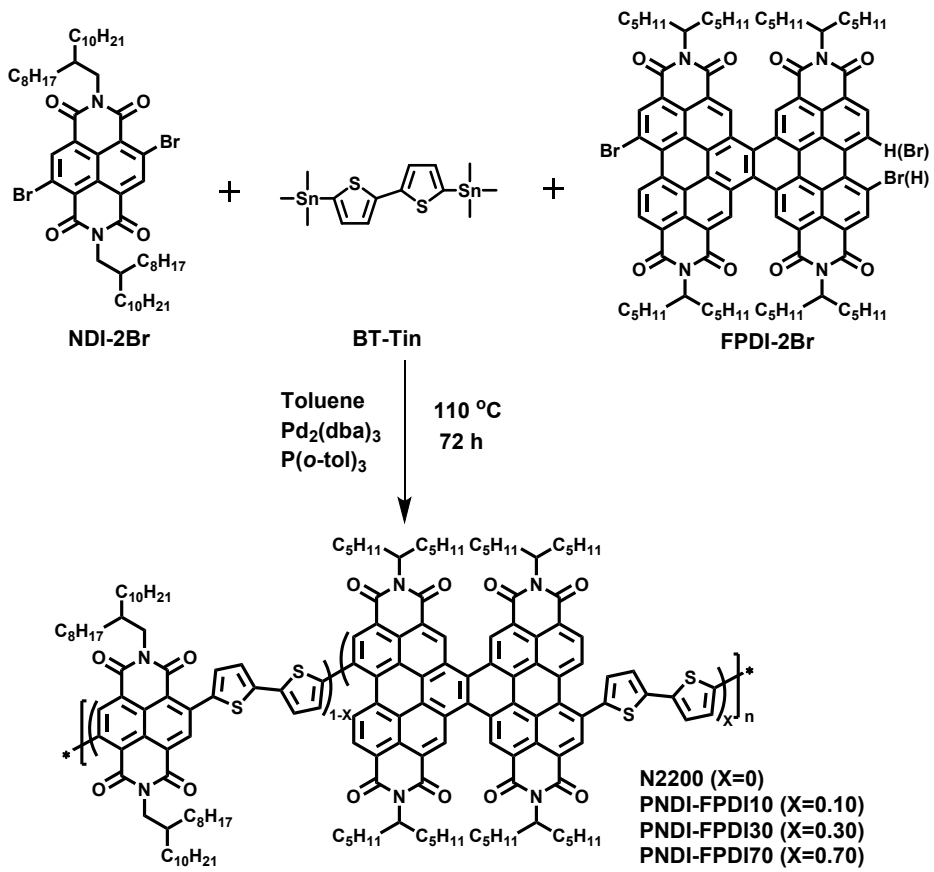
Synthesis of N2200. It was prepared by the same procedure as described above, starting with NDI-2Br (197 mg, 0.20 mmol) and BT-Tin (98.4 mg, 0.20 mmol). The collected solid was then dried over vacuum to give N2200 (159 mg, 80%).

All-polymer solar cell fabrication

Prepatterned ITO-coated glasses were cleaned by sequential cycles of sonication in soap water, deionized water, ethanol, acetone, and isopropanol for 30 min, respectively. After UV/ozone treatment for 6 min, PEDOT:PSS hole transport layer was filtered and spin-coated on top of the treated-ITO at 3000 rpm for 30 s and dried over 150 ^{o}C for 15 min. The active layer solutions were prepared in CB (with a polymer concentration of

6 mg/mL and a D/A ratio at 1:1), and spin-coated on the PEDOT:PSS-coated substrates in a glove-box under N_2 atmosphere at 1800 rpm for 50 s. The blend films were then transferred to the heating platform and annealed at 120 ^oC for 10 min. A thin layer of PFN-Br (1 mg/mL) was spin coated on the top of active layer with 4000 rpm for 35 s. Finally, the Ag (100 nm) electrode was evaporated onto the active layer under a vacuum of 10^{-5} Torr. The current-voltage characteristics of the devices were measured using a computer-controlled Keithley 2400 source meter under stimulated AM1.5 G at an intensity of 100 mW/cm^2 provided by a solar simulator. The EQEs were measured by an Oriel Newport System. All above measurements were done at room temperature.

The hole-only device for the hole mobility was fabricated with a device structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag. The electron-only device for the electron mobility was fabricated with a device structure of ITO/ZnO/ active layer/PFN-Br/Ag. Both the hole and electron mobilities by space charge limited current (SCLC) were calculated with the following Mott-Gurney equation in the SCLC region: $J = (9/8)\varepsilon_0\varepsilon_r\mu(V^2/L^3)$, in which ε_0 is the permittivity of the vacuum, ε_r is the dielectric constant of the polymer and assumed to be 3, and L is the thickness of active layer.



Scheme S1 The synthetic routes of polymer acceptors PNDI-FPDIX.

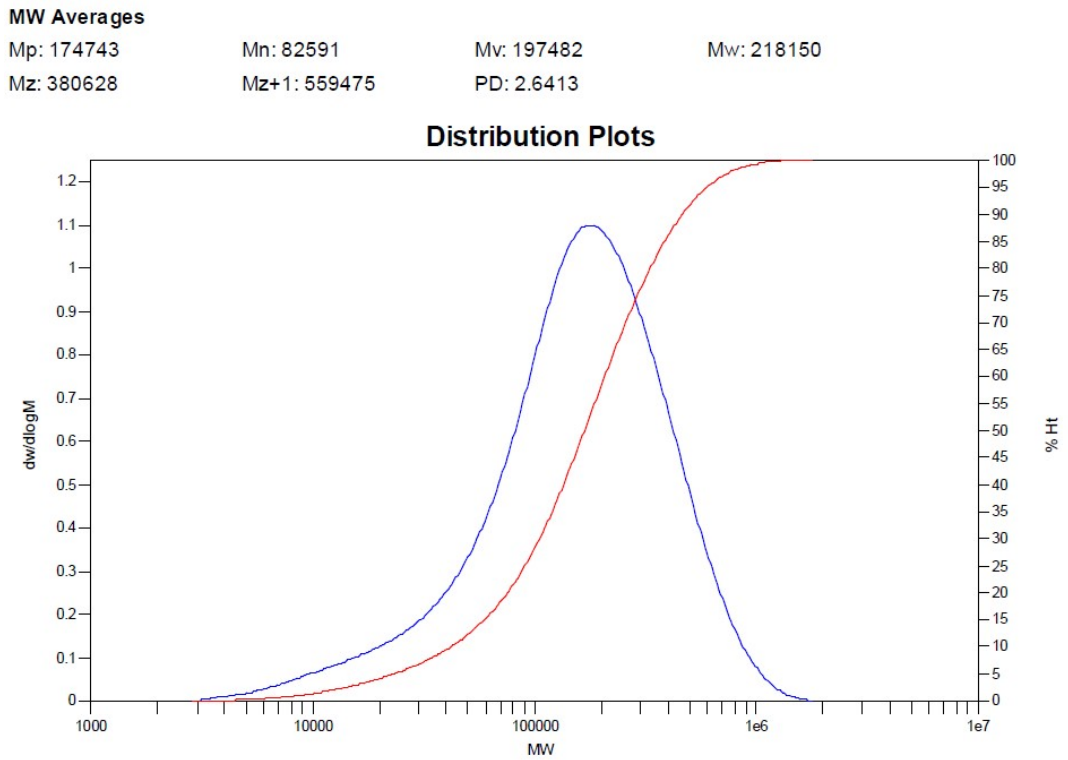


Fig. S1 The molecular weights of PNDI-FPDI10% measured by gel permeation chromatography.

MW Averages

Mp: 156647	Mn: 70378	Mv: 155290	Mw: 170844
Mz: 293200	Mz+1: 432107	PD: 2.4275	

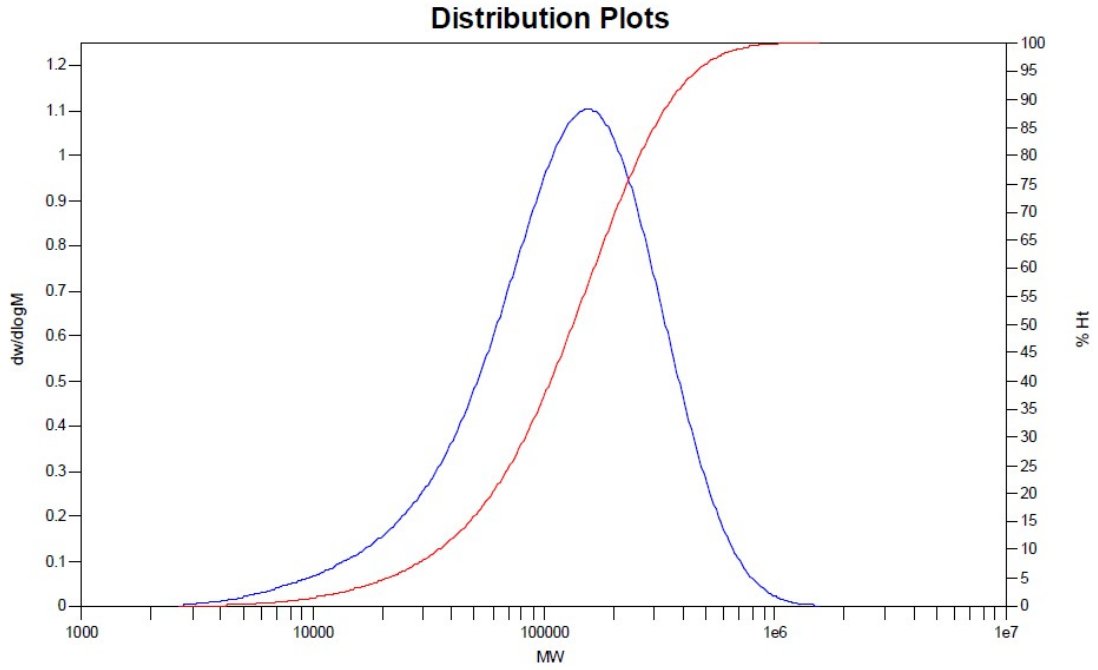
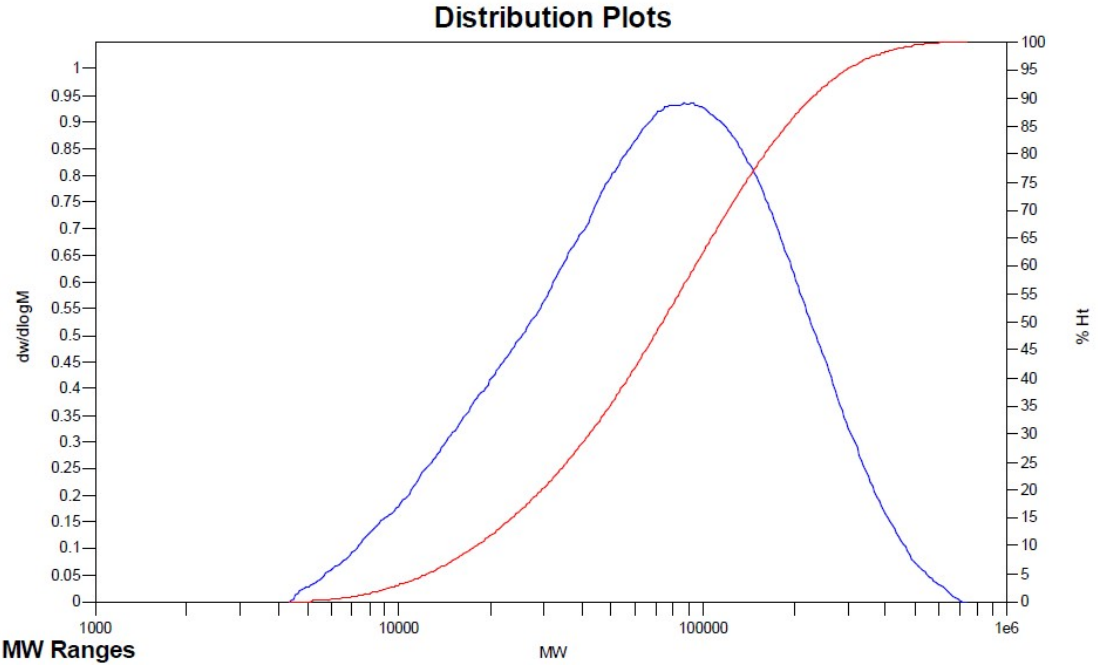


Fig. S2 The molecular weights of PNDI-FPDI30% measured by gel permeation chromatography.

MW Averages

Mp: 87105	Mn: 42050	Mv: 91308	Mw: 102052
Mz: 188396	Mz+1: 275731	PD: 2.4269	



MW Ranges

Fig. S3 The molecular weights of PNDI-FPDI70% measured by gel permeation chromatography.

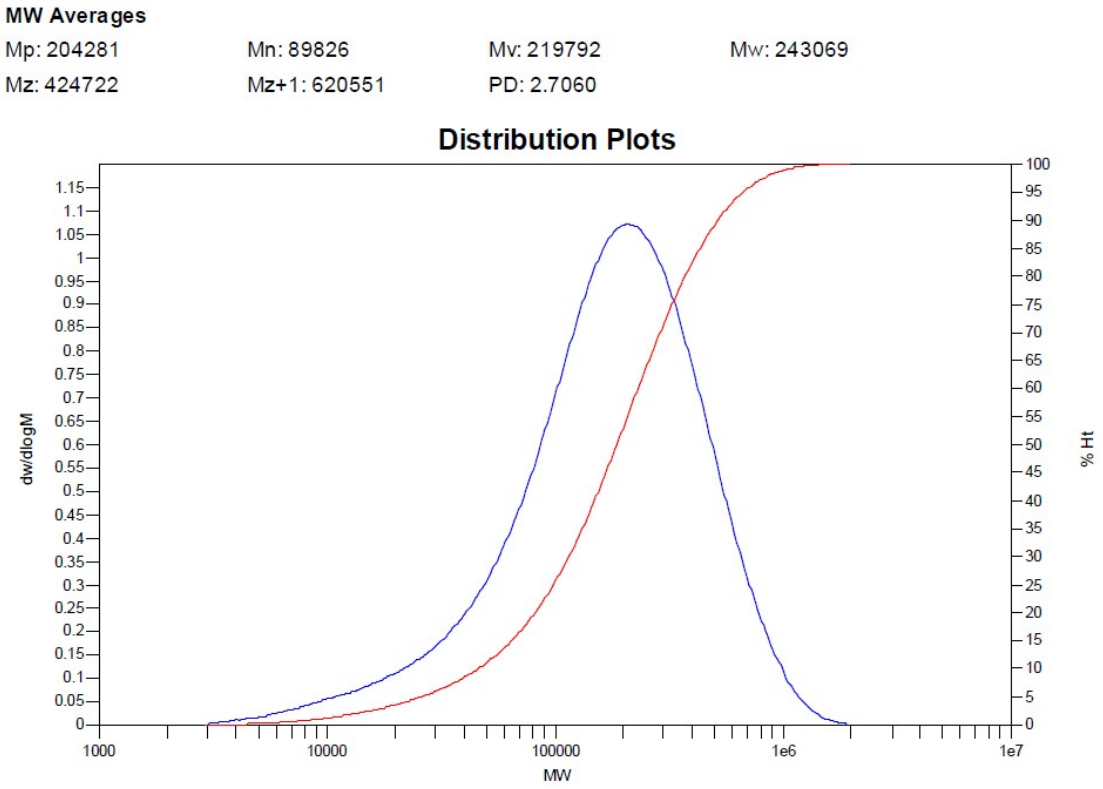


Fig. S4 The molecular weights of N2200 measured by gel permeation chromatography.

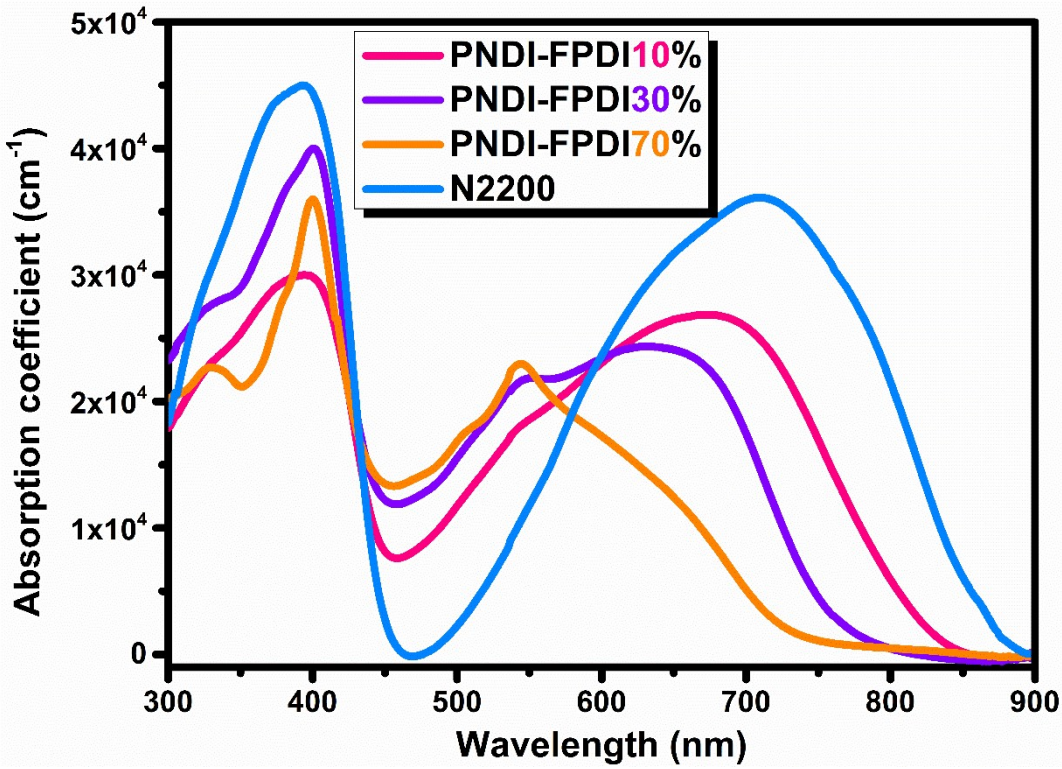


Fig. S5 The absorption coefficient of these PAs in film state.

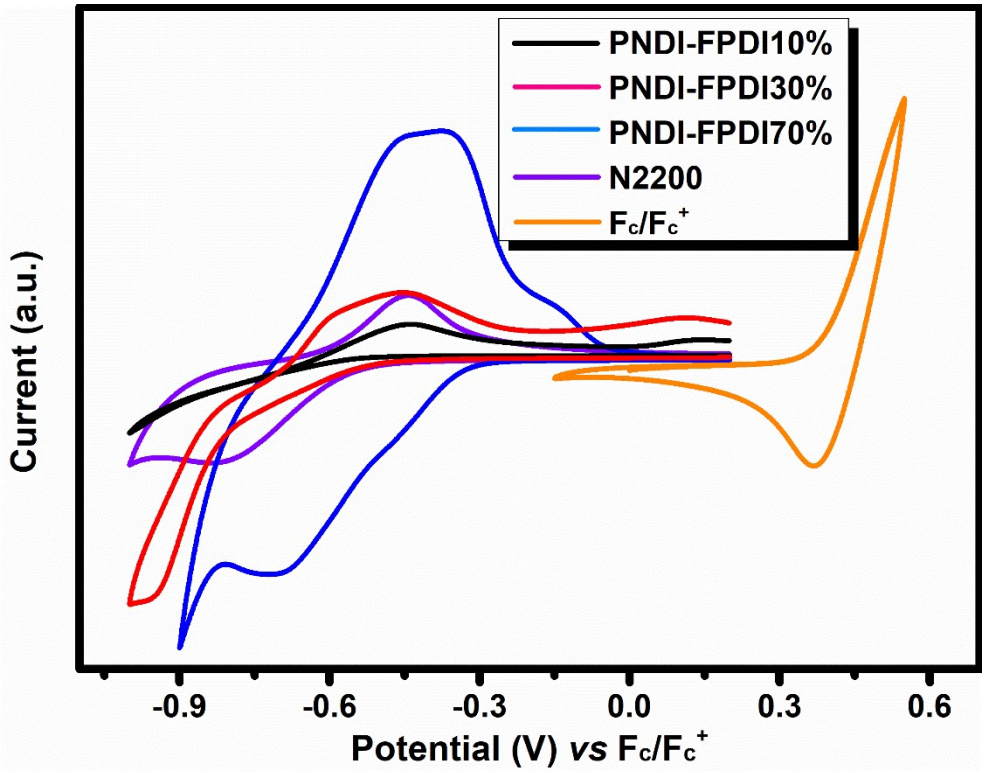


Fig. S6 Cyclic voltammetry (CV) of the PAs in the film measured in a 0.1 M Bu_4NPF_6-CH_3CN solutions with a Pt electrode and an $Ag/AgNO_3$ reference electrode.

Table S1 The photovoltaic performances of all-PSCs based on PTzBI:PNDI-FPDI10% with various blend weight ratios.

PAs	D/A Ratio (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PNDI-FPDI10%	2:1	0.83	9.86	55.8	4.57
	1:1	**0.84**	**10.49**	**55.63**	**4.90**
	1:2	0.84	9.18	51.45	3.97

Table S2 The photovoltaic performances of all-PSCs based on PTzBI:PNDI-FPDI10% annealed at different temperature for 10 min.

Temperature (^{o}C)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)[a]
100	0.84	10.88	59.47	5.44
120	**0.84**	**11.99**	**61.29**	**6.17**
130	0.83	11.03	60.74	5.56
150	0.84	10.74	55.08	4.97

Table S3 The photovoltaic performances of all-PSCs based on PTzBI:PAs with different additives under the annealing temperature of 120 ^{o}C.

PAs	Additive	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PNDI-FPDI10%	0.5% CN	0.85	12.63	60.4	6.48
PNDI-FPDI10%	1% CN	0.84	13.85	63.3	7.36
PNDI-FPDI10%	3% CN	0.83	11.76	57.1	5.57
PNDI-FPDI10%	0.5% DIO	0.84	12.76	59.6	6.39
PNDI-FPDI10%	1% DIO	0.84	13.12	61.7	6.80
PNDI-FPDI10%	3% DIO	0.83	11.83	57.8	5.68
PNDI-FPDI10%	**1% CN+1%DIO**	**0.84**	**14.81**	**66.0**	**8.21**
PNDI-FPDI10%	1% CN+2%DIO	0.83	11.52	59.2	5.66
PNDI-FPDI10%	2% CN+1%DIO	0.83	10.89	62.3	5.63
PNDI-FPDI30%	1% CN+1%DIO	0.82	6.92	53.1	3.01
PNDI-FPDI70%	1% CN+1%DIO	0.78	5.70	42.3	1.86
N2200	1% CN+1%DIO	0.90	5.36	58.0	2.80

References:

[1] Y. Yin, J. Yang, F. Guo, E. Zhou, L. Zhao, Y. Zhang, *ACS Appl. Mater. Inter.*, 2018, **10**, 15962-15970.

[2] Y. Yin, Z. Zheng, Y. Lu, D. Chen, M. Liu, F. Guo, S. Gao, L. Zhao, Y. Zhang, *ACS Appl. Mater. Inter.*, 2019, **11**, 29765-29772.