

Electronic Supplementary Material (ESI)

Naphthalene Diimide-Based Random Terpolymer Acceptors for Constructing All-Polymer Solar Cells with Enhanced Fill Factors

Baitian He,^{*a} Longfei Liu,^b Yan Liu,^a Guiting Chen,^{*a} Manjun Xiao^{*b}, Chuanbo Dai

^a

^a School of Chemistry and Environment, Jiaying University, Meizhou 514015, P. R.

China

^b College of Chemistry, Key Lab of Environment-Friendly Chemistry and Application

(Ministry of Education), Xiangtan University, Xiangtan 411105, P. R. China.

Corresponding Authors

*E-mail: baitian-he@foxmail.com

*E-mail: 576146400@qq.com

*E-mail: xmj0704@163.com

Experimental Section

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. All reactions were carried out under the nitrogen atmosphere. Anhydrous chlorobenzene (CB) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (M1) was purchased from Sigma-Aldrich and used as received. 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-octyldodecyl)diimide (M2) and (2*E*, 2'*E*)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(5-(trimethylstannyl)thiophen-2-yl)acrylonitrile) (M3) were prepared according to the previously reported literature.^{1,2}

Measurements: Molecular weights of the polymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 150 °C 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. ¹H NMR spectra were recorded on a Bruker AV-500 spectrometer in deuteriochloroform using tetramethylsilane (TMS; $\delta=0$ ppm) as an internal standard. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min⁻¹ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of 10 °C /min under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with ITO at a scan rate of 50 mV s⁻¹ against saturated calomel electrode (SCE) and a platinum wire as reference

electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Potentials were referenced to the 2 ferrocenium/ferrocene couple by using ferrocene as an internal standard. The deposition of a copolymer on the electrode was done by the evaporation of a CH₃Cl solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument.

Charge Carrier Mobility Measurements. The hole-only and electron-only devices were measured with device structures of ITO/PEDOT:PSS/PBDB-T:acceptor/MoO₃/Ag and ITO/ZnO/PBDB-T:acceptor/Ca/Al, respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the following equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 \frac{V^2}{d^3}$$

where J is the current, μ_0 is the carrier mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), i.e., $V = V_{appl} - V_{bi} - V_s$. The carrier mobility can be calculated from the slope of the $J^{1/2}$ - V curves.

Fabrication of all-polymer solar cells and Characterization: The indium tin oxide (ITO) glass substrates were cleaned sequentially under sonication for 30min with acetone, detergent, deionized water and isopropyl alcohol and then dried at 80 °C in baking oven overnight, followed by a plasma treatment for 4 min. The pre-cleaned ITO substrate were coated with PEDOT:PSS (filtered through a 0.22 μm PES filter) by spin-

coating (3000 rpm. for 30 s, thickness of ~40 nm) and then baked at 150 °C for 10 min in air. Then, the substrates were transferred into a nitrogen (N₂) protected glovebox. Afterwards the active layers spin coated from CB solution with 0.5vol% DIO as additive containing PBDB-T:acceptor (weight ratio 1:0.5) to obtain thicknesses of ~100 nm. Thermal annealing of the blend films was carried out by placing them onto a hot plate in a nitrogen atmosphere at 130°C for 10 min. A 5 nm PFN-Br cathode buffer layer was then spin-coated from methanol solution onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Al (100 nm) was deposited sequentially through a shadow mask under 10⁻⁷ Pa, with an active area of the cells of 0.04 cm². The current–voltage (*J-V*) curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, AM 1.5 G spectra from a class solar simulator(Taiwan, Enlitech), the light intensity was 100 mW cm⁻² as calibrated by a China general certification center (CGC) certified reference monocrystal silicon cell (Enlitech). Before the *J-V* test, a physical mask of an aperture with precise area of 0.04 cm² was used to define the device area. The EQE spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cel

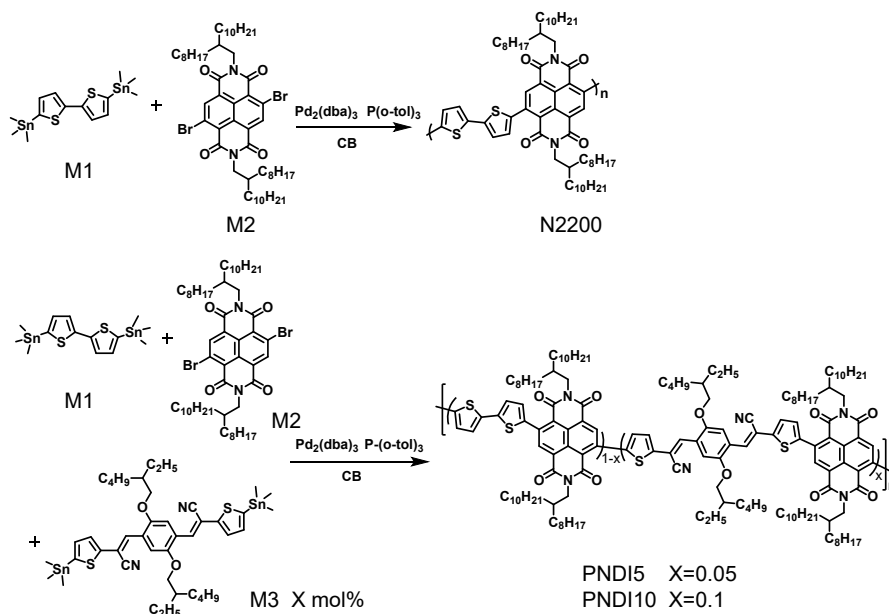


Figure S1. Chemical structures and synthesis to the polymer acceptors.

Synthesis of monomer and copolymers

(2E, 2'E)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(5-(trimethylstannyl)thiophen-2-yl)acrylonitrile) M3. Under N₂ atmosphere, (2E, 2'E)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(thiophen-2-yl)acrylonitrile) (3 g, 5.5 mmol) was dissolved in anhydrous THF (60 mL) and cooled to -78 °C for 30 min. Next, 1.0 M lithium diisopropylamide (12.1 mL, 12.1 mmol) was added to the resulting mixture, which was stirred for 2 hour in -78 °C. Then, trimethyltin chloride (13.2 mL in 1 M hexane solution, 13.2 mmol) was added to the resulting reaction mixture, which was stirred for 30 min and then warmed to RT. After the solvent was removed, the solid was then recrystallized from acetonitrile to get the product as deep red solid (3.5 g, yield 75%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 7.91 (s, 2H), 7.87 (s, 2H), 7.46 (d, J = 2.7 Hz, 2H), 7.15 (d, J = 3.4 Hz, 2H), 4.03~3.99 (d, 4H), 1.84~1.76 (m, 2H), 1.61~1.43 (m, 8H), 1.40~1.29 (m, 8H), 0.98 (t, J = 7.5 Hz, 6H), 0.93~0.86 (m, 6H), 0.49~0.32 (m, 18H). ¹³C NMR (125 MHz, CDCl₃), δ (ppm) 151.69, 145.91, 140.81,

136.94, 132.99, 128.89, 125.57, 117.54, 110.70, 105.65, 71.85, 39.58, 30.93, 29.27, 24.16, 23.13, 14.14, 11.38.

Synthesis of N2200. To a 25 mL flask was added bis(trimethylstannyl)-2,2'-bithiophene M1 (98.4 mg, 0.2 mmol), 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic-*N,N'*-bis(2-octyldodecyl)diimide M2 (197.01 mg, 0.2 mmol), tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (2.5 mg) and tri(*o*-tolyl)phosphine ($\text{P}(\text{o-Tol})_3$) (5.0 mg), anhydrous chlorobenzene (3.0 mL) under argon. The reaction mixture was heated to 130 °C for 48 h with stirring. Then the reaction mixture was cooled to ambient temperature and precipitated into methanol. The solid was collected by filtration and loaded into an extraction thimble and washed successively with methanol, acetone, hexane, dichloromethane and chloroform. The chloroform solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried in vacuo to get the polymer as a dark blue solid (179.3 mg, 88%). $M_n = 75.7$ kDa, $M_w = 137.2$ kDa, PDI = 1.83.

Synthesis of PNDI5. It was synthesized similarly as described for N2200. Starting with M1 (93.48mg, 0.19 mmol), M2 (197.01mg, 0.2mmol), M3 (9.3 mg, 0.01 mmol). Yield: 185.4 mg (91%). $M_n = 68.5$ kDa, $M_w = 126.7$ kDa, PDI = 1.85.

Synthesis of PNDI10. It was synthesized similarly as described for N2200. Starting with M1 (88.56 mg, 0.18 mmol), M2 (197.01 mg, 0.2 mmol), M3 (18.5 mg, 0.02 mmol). Yield: 167.5 mg (83%). $M_n = 60.6$ kDa, $M_w = 116.9$ kDa, PDI = 1.93.

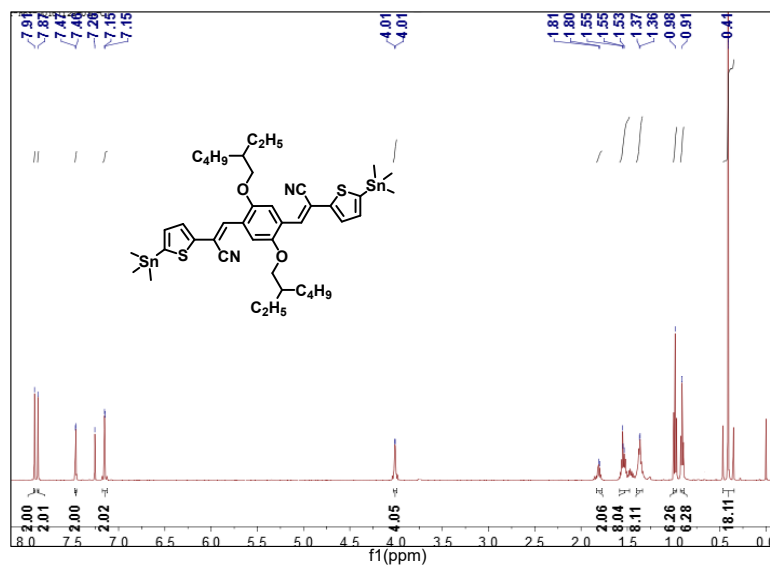


Figure S2. ^1H NMR spectra of M3 in CDCl_3

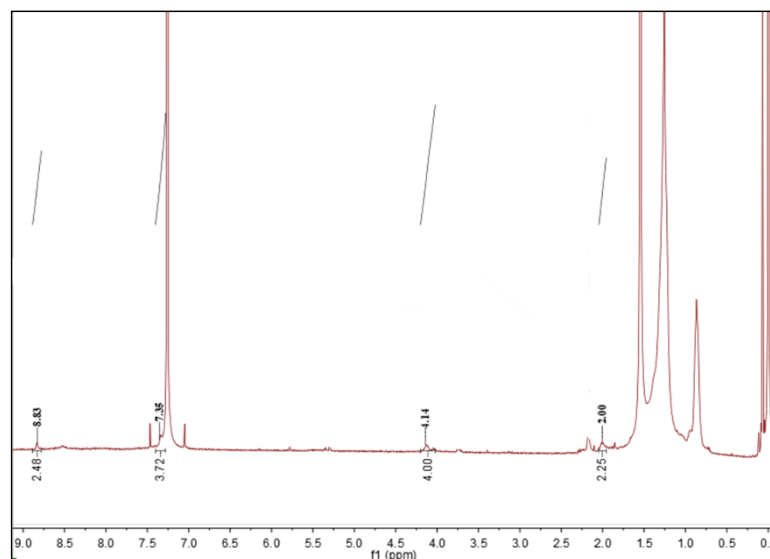


Figure S3 ^1H NMR spectra of N2200 in CDCl_3

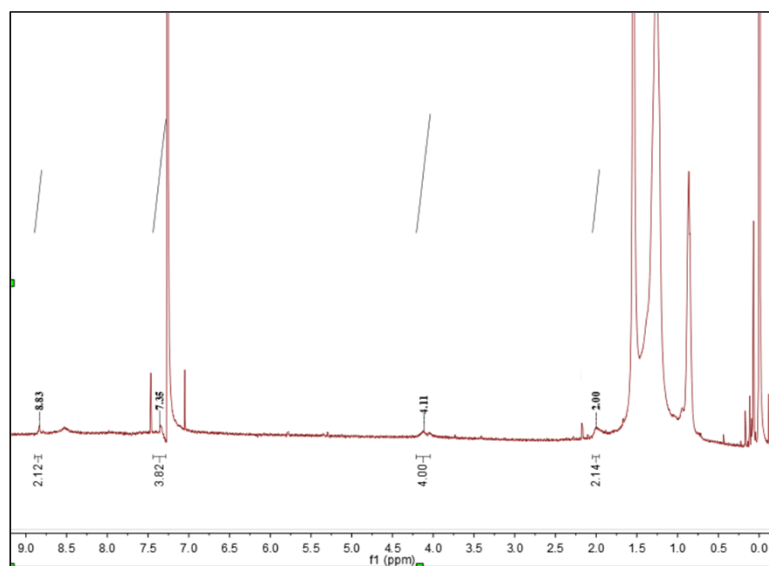


Figure S4 ^1H NMR spectra of PNDI5 in CDCl_3

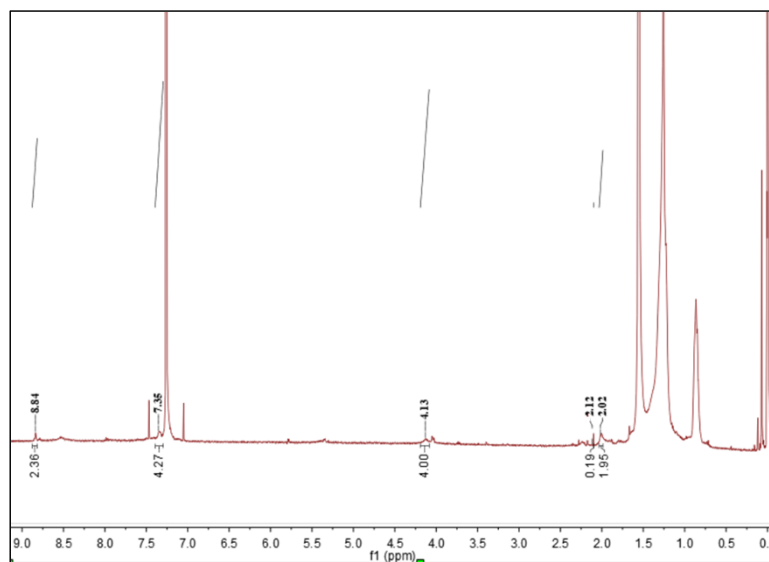


Figure S5 ^1H NMR spectra of PNDI10 in CDCl_3

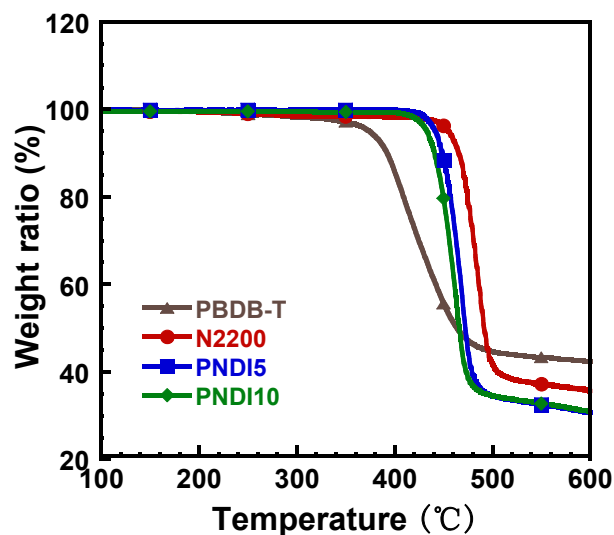


Figure S6. TGA plot of polymer acceptors.

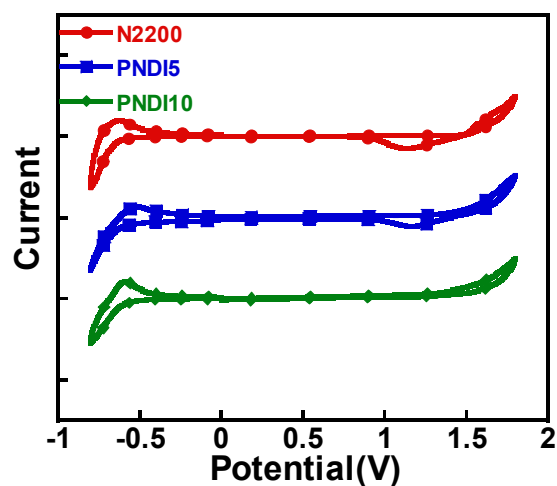


Figure S7. CV characteristics of polymer acceptors.

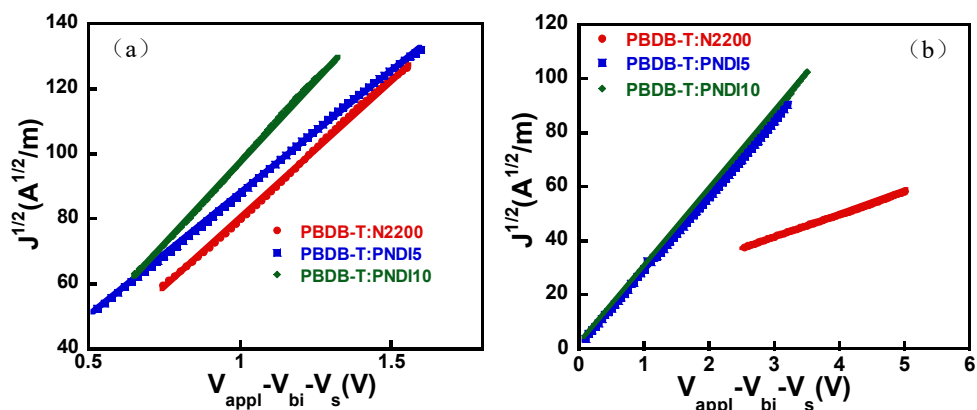


Figure S8. Space-charge limited current density mobility of (a) hole-only and (b) electron-only devices.

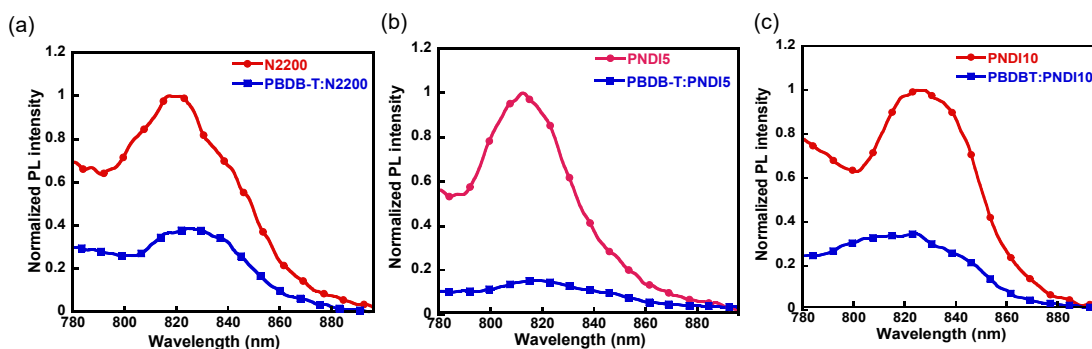


Figure S9. Photoluminescence spectra of (a) pure N2200 and PBDB-T:N2200 (1:0.5 w:w), (b) pure PNDI5 and PBDB-T:PNDI5 (1:0.5 w:w), (c) pure PNDI10 and PBDB-T:PNDI10 (1:0.5 w:w).

Table S1. Device performance of the all-PSCs based on PBDB-T: PNDI5 with different D/A ratios under AM1.5 Illumination at 100 mW/cm².

Blend film ^a	D/A	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE(%)
	(wt/wt)				
PBDB-T:PNDI5	1:0.5	0.825	11.24	70.41	6.53
	1:1	0.848	11.33	66.67	6.41
	1:1.5	0.854	10.53	64.26	5.78

^a All of the blend films are processed by CB.

Table S2. Device performance of the all-PSCs based on PBDB-T: PNDI5 with different thermal annealing under AM1.5 Illumination at 100 mW/cm².

Blend film ^a	thermal	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE(%)
	annealing				
PBDB-T:PNDI5	NO	0.825	11.24	70.41	6.53
T:PNDI5	80°C 10min	0.826	11.50	72.54	6.89

100°C 10min	0.825	11.44	73.11	6.90
130°C 10min	0.823	11.63	73.75	7.06

^a Donor : Acceptor =1:0.5; all of the blend films are processed by CB.

Table S3. Device performance of the all-PSCs based on PBDB-T: PNDI5 with various proportion additive under AM1.5 Illumination at 100 mW/cm².

Blend film ^a	additive	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE(%)
	NO	0.823	11.63	73.75	7.06
PBDB- T:PNDI5	0.5% DIO	0.867	12.32	74.94	8.01
	1% DIO	0.878	11.37	75.72	7.56

^a Donor : Acceptor =1:0.5; all of the blend films are processed by CB with 130 °C thermal annealing for 10 min.

Table S4. Device performance of the all-PSCs based on PBDB-T: PNDI5 with different thickness under AM1.5 Illumination at 100 mW/cm².

Blend film	Rate	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE(%)
	1500	0.859	11.16	73.21	7.02
	1800	0.861	11.73	73.97	7.48
	2000	0.858	11.62	74.70	7.45
1:0.5	2200	0.863	11.98	74.21	7.68
	2500	0.867	12.32	74.94	8.01
	3000	0.861	11.95	75.05	7.72

^a Donor : Acceptor =1:0.5; all of the blend films are processed by CB with 0.5 vol% DIO and 130 °C thermal annealing for 10 min.

Table S5. Relevant parameters obtained from $J_{ph}-V_{eff}$ curves.

Blend films ^a	V_0 (V)	J_{ph}^b (mA cm ⁻²)	J_{sat} (mA cm ⁻²)	G_{max} (m ⁻³ s ⁻¹)	$P(E,T)^b$ (%)	L (nm)
PBDB-T:N2200	0.93	10.9	11.9	7.43×10^{27}	91.60%	100
PBDB-T: PNDI5	0.94	12.0	12.7	7.93×10^{27}	94.49%	100
PBDB-T: PNDI10	0.88	10.6	11.3	7.06×10^{27}	93.80%	100

^a Donor : Acceptor =1:0.5; all of the blend films are processed by CB with 0.5 vol% DIO and 130 °C thermal annealing for 10 min. ^b At the condition of $V_{eff} = V_0 - V_{appl}$ ($V_{appl} = 0$, under short-circuit condition).

1. Z. Chen, Y. Zheng, H. Yan and A. Facchetti, *J. Am. Chem. Soc.*, **2009**, *131*, 8-9.
2. B. He, Q. Yin, X. Yang, L. Liu, X.-F. Jiang, J. Zhang, F. Huang, Y. Cao, *J. Mater. Chem. C* **2017**, *5*, 8774.