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Supporting Information

Indacenodithienothiophene–Naphthalene Diimide Copolymer as Acceptor for All–Polymer Solar Cells

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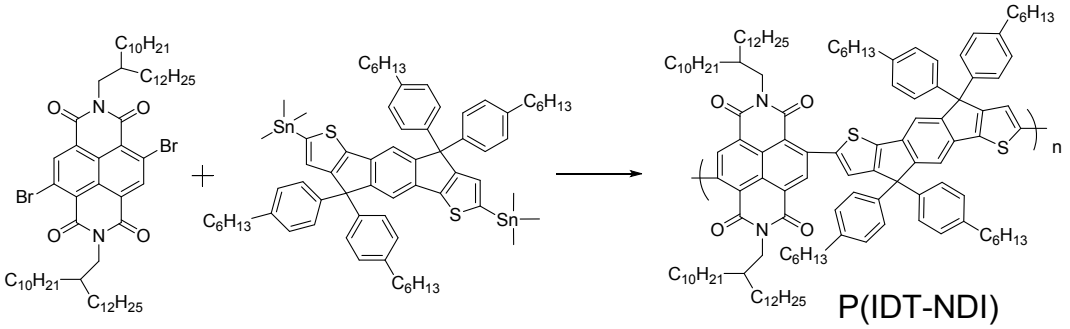

Scheme S1. Synthetic route of P(IDT-NDI)

Material synthesis: P(IDT-NDI) was synthesized using a palladium-catalyzed Stille coupling reaction, as shown in Scheme S1. In a Schlenk flask, 2,6-dibromo-N,N'-bis(2-decyltetradecyl)naphthalene-1,4,5,8-tetracarboxylic acid diimide) (0.1646 g, 0.15 mmol) and 4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (0.1835 g, 0.15 mmol) were dissolved in dry toluene (10 mL). After degassing under nitrogen for 30 min, $Pd_2(dba)_3$ (4.5 mg) and P(*o*-Tol)$_3$ (7.5 mg) were added to the mixture, which was then stirred for 12 h at 115 °C. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, hexane and chloroform, successively. The polymer was obtained by precipitation of the chloroform solution into methanol. Yield: (85%). GPC: M_w = 224.2 kDa, M_n = 101.7 kDa, M_w/M_n = 2.20. ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 8.75 (s, 2H), 7.53 (S, 2H), 7.27 (s, 2H), 7.16-7.08 (m, 16H) , 2.57 (m, 4H), 2.1 (m,2H), 1.60-1.19(m, 120H), 0.82-0.88 (t, 24H)

Measurements: Gel permeation chromatography (GPC) measurements was performed on Agilent PL-GPC 220 instrument with high temperature chromatograph, using 1,2,4-trichlorobenzene as the eluent at 160 °C. UV–vis absorption spectra of active layers of the all PSCs were measured on a Hitachi U-3010 UV–vis spectrophotometer. PL spectra were measured with a Shimadzu RF-5301PC

fluorescence spectrophotometer. The film morphology was measured using an AFM (SPA-400) with the tapping mode.

Device fabrication and characterization: The all-PSCs were fabricated with a structure of ITO/PEDOT: PSS (40 nm)/active layer/cathode. A thin layer of PEDOT: PSS was deposited through spin-coating on precleaned ITO-coated glass from a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 2000 rpm and dried subsequently at 150 °C for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer of polymers (J50, J51 or PTB7-Th) and **P(IDT-NDI)** was spin-coated from its chloroform solution onto the PEDOT: PSS layer under a spin-coating rate of 2000 rpm. For the investigation of the effect of the D:A weight ratios of the active layer on the photovoltaic performance of the all-PSCs, we used the polymer blend solution with a total blend polymer concentration of 12 mg/mL in chloroform and the D:A weight rations from 1:1 to 3:1. For the convenience to prepare the polymer blend solution, we selected the weight ratios of 6:6 (1:1), 7:5 (1.4:1), 8:4 (2:1) and 9:3 (3:1). After spin-coating, the active layers were annealed at 110 ^{o}C for 30 min for the devices with thermal annealing treatment. The thickness of the active layers is *ca*. 100 nm. Then methanol solution of PDINO at a concentration of 1.0 mg mL^{-1} was deposited atop the active layer at 3000 rpm for 30 s to afford a PDINO cathode buffer layer with thickness of *ca*. 10 nm. Finally, top Al electrode was deposited in vacuum onto the cathode buffer layer at a pressure of *ca*. 5.0 × 10 $^{-5}$ Pa. The active area of the device was 4.7 mm^2. The current density–voltage (*J–V*) characteristics of the PSCs were measured in glovebox on a computer-controlled Keithley 2450 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as the light source. The light intensity was calibrated to 100 mW cm^{-2} by a Newport Oriel 91150V reference cell. The input photon to converted current efficiency (IPCE) was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Charge Carrier Mobility Measurements: Hole and electron mobility were measured using the space charge limited current (SCLC) method. Device structures are ITO/PEDOT:PSS/Polymer donor : P(IDT-NDI) /Au (hole-only device) for hole mobility measurement and ITO/ZnO/Polymer donor: P(IDT-NDI) /PDINO/Al (electron-only device) for electron mobility measurement. The SCLC mobilities were calculated by the following equation:[P. W. M. Blom, M. J. M. de Jong and M. G. van Munster, *Physical Review B*, 1997, **55**, R656-R659.]

$$J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3} \qquad (1)$$

Where J is the current density, ε_r is the relative dielectric constant of active layer material (here we used a relative dielectric constant of 4), ε_0 is the permittivity of empty space, μ is the mobility of hole or electron, L is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{app}-V_{bi}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (in the hole-only and the electron-only devices, the V_{bi} values are 0.2 V and 0V respectively).

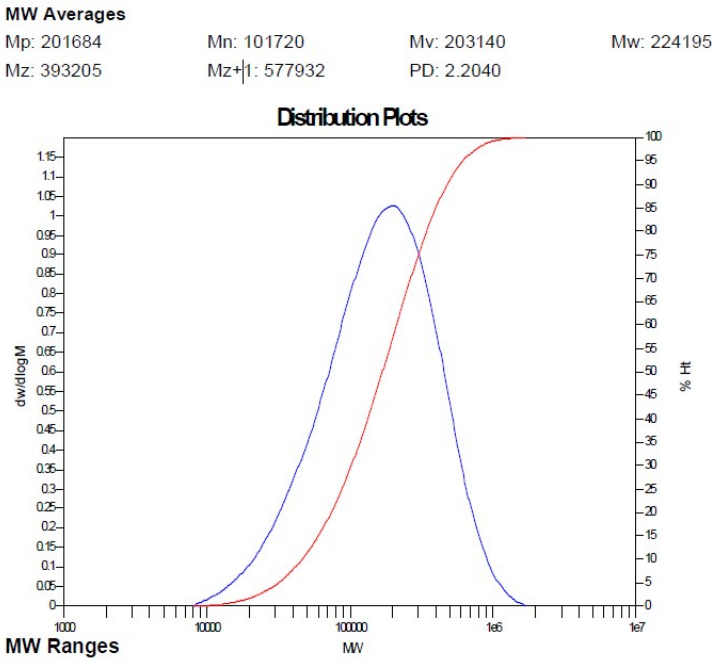

Figure S1. GPC measurement of P(IDT-NDI).

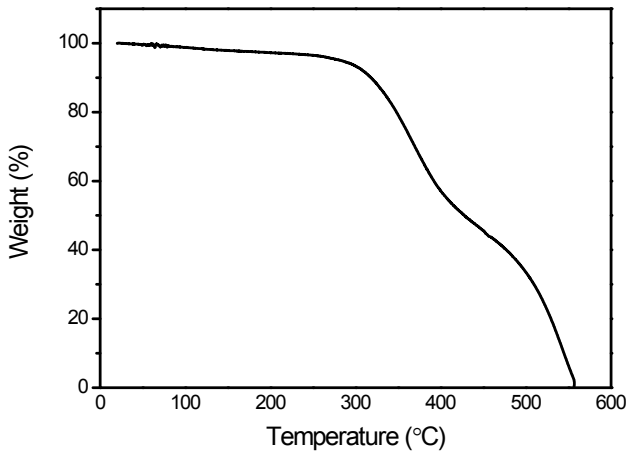

Figure S2. TGA plots of the acceptor polymer (PIDT-NDI) with a heating rate of 100 °C min^{-1} under an inert atmosphere.

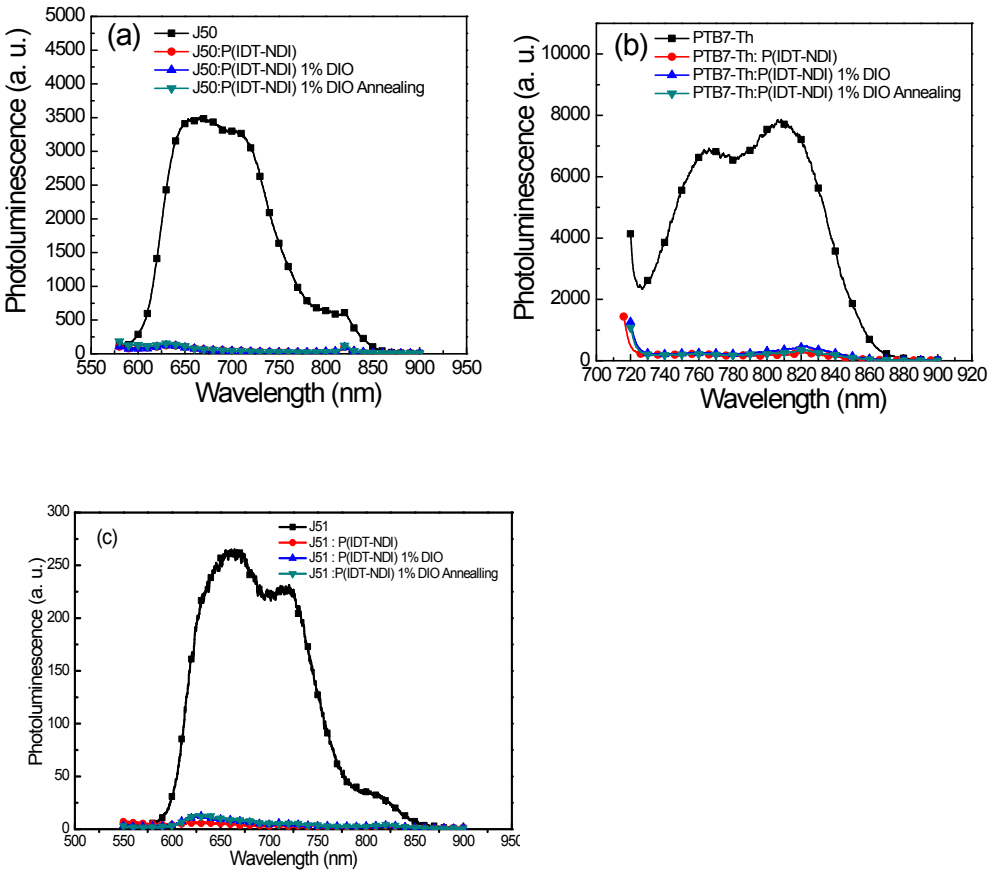

Figure S3. Photoluminescence spectra of the polymer donor and polymer blend films of J50 : P(IDT-NDI) (1.4: 1, w/w), PTB7-Th: P(IDT-NDI) blends (2: 1, w/w) and J51: P(IDT-NDI) blends (2: 1, w/w)

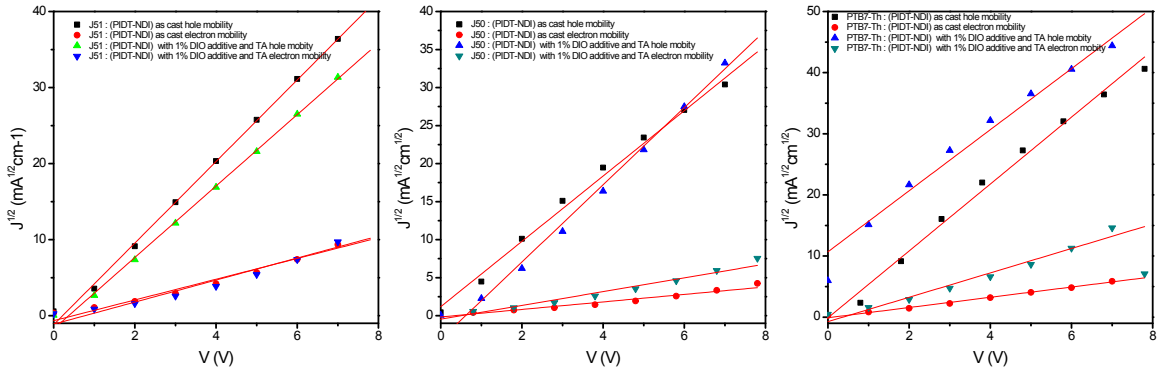

Figure S4. *J-V* characteristics of the device for the hole and electron mobility measurements in dark.

Table S1. Photovoltaic performance parameters of the all-PSCs based on J50:P(IDT-

NDI) with thermal annealing at 110°C for 30 min, under the illumination of AM1.5G, 100 mW/cm^2.

D/A (w/w)	V_{oc} (V)	J_{sc} (mA•cm^{-2})	FF (%)	PCE (%)
1:1	0.74	9.36	56.6	3.91
1.4:1	0.78	9.68	54.5	4.12
2:1	0.74	10.38	43.7	3.37
3:1	0.76	9.88	46.9	3.51

Table S2. Photovoltaic performance parameters of the all-PSCs based on PTB7-Th: P(IDT-NDI) with thermal annealing at 110°C for 30 min, under the illumination of AM1.5G, 100 mW/cm^2.

D/A (w/w)	V_{oc} (V)	J_{sc} (mA•cm^{-2})	FF (%)	PCE (%)
1:1	0.92	6.81	52.3	3.29
1.4:1	0.93	7.00	53.3	3.45
2:1	0.91	7.35	54.4	3.63
3:1	0.92	7.08	50.1	3.25

Table S3. Photovoltaic performance parameters of the all-PSCs based on J51:P(IDT-NDI) with thermal annealing at 110°C for 30 min, under the illumination of AM1.5G, 100 mW/cm^2.

D/A (w/w)	V_{oc} (V)	J_{sc} (mA•cm^{-2})	FF (%)	PCE (%)
1:1	0.93	9.23	58.4	5.00
1.4:1	0.93	8.71	61.0	4.93
2:1	0.93	9.55	60.3	5.33
3:1	0.92	9.50	53.8	4.73

Table S4. Photovoltaic performance parameters of the PSCs based on polymer donor(J50, J51 and PTB7-Th) : $PC_{70}BM$, reported in literatures.

Polymer	V_{oc} (V)	J_{sc} (mA•cm^{-2})	FF (%)	PCE (%)	References
J50	0.58	7.41	56.5	2.43	1
J51	0.75	11.90	67.2	6.00	1
PTB7-Th	0.80	15.73	74.30	9.37	2

References

1. J. Min, Z.-G. Zhang, S. Zhang and Y. Li, Chem. Mater., 2012, 24, 3247-3254.
2. S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng and S.-A. Chen, Adv. Mater., 2013, 25, 4766-4771.

Table S5. Hole and electron mobilities of the active layers of the all-PSCs.

Blend films	w/o DIO			With 1% DIO additive and thermal annealing		
	μ_h 10^{-5}cm^{2}V^{-1}s^{-1}	μ_e 10^{-5}cm^{2}V^{-1}s^{-1}	μ_h/μ_e	μ_h 10^{-5}cm^{2}V^{-1}s^{-1}	μ_e 10^{-5}cm^{2}V^{-1}s^{-1}	μ_h/μ_e
J50 : P(IDT-NDI)	1.78	0.07	23.09	3.94	1.59	2.48
PTB7-Th: P(IDT-NDI)	5.12	0.17	30.11	2.80	0.51	5.48
J51 : P(IDT-NDI)	4.23	1.49	2.84	6.58	3.06	2.15