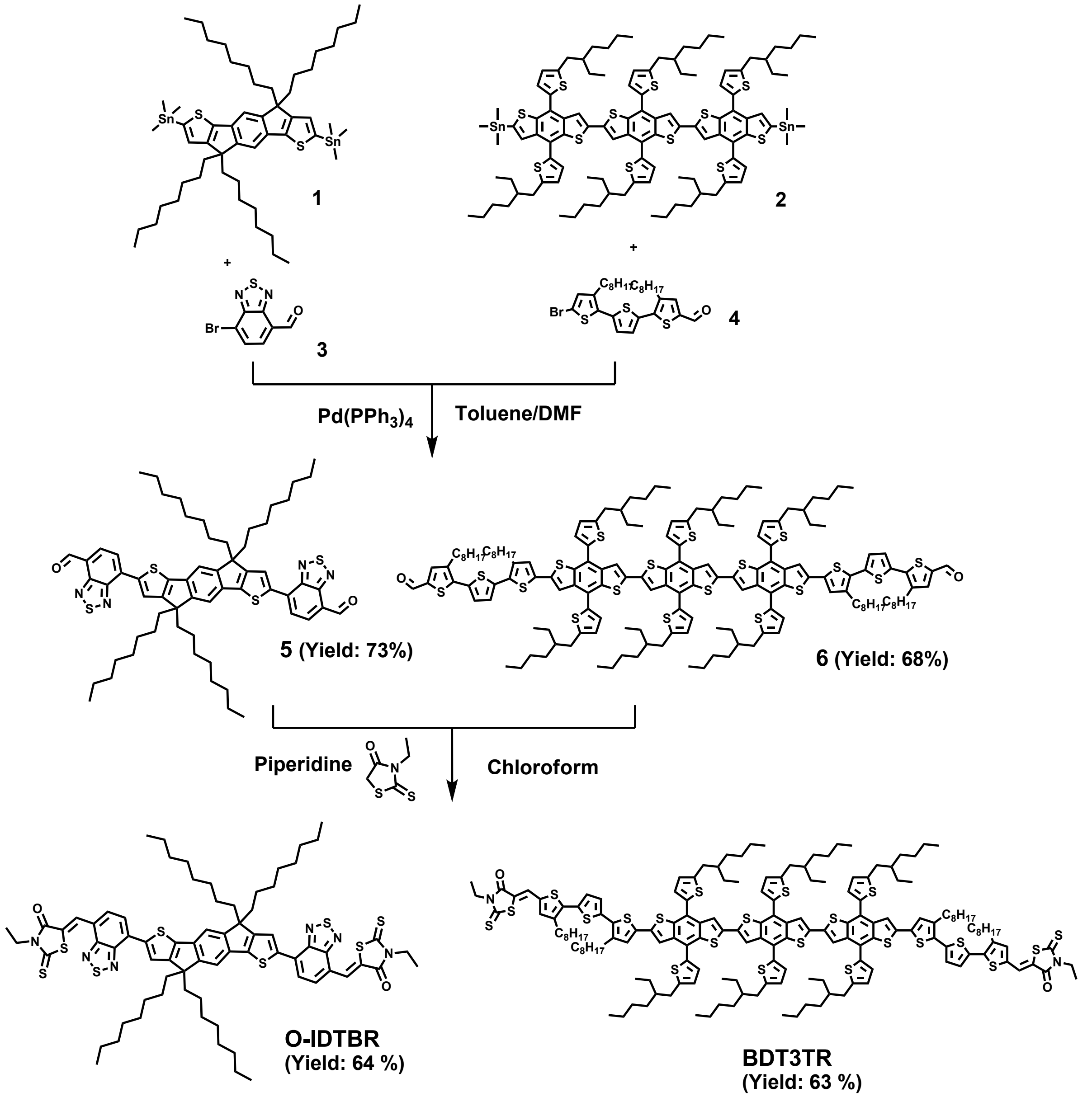
Electronic Supplementary Information

Highly Efficient and Thermally Stable Fullerene-Free Organic Solar Cells based on Small Molecule Donor and Acceptor

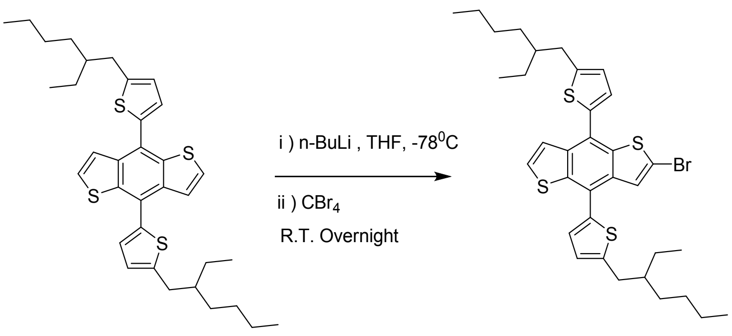
Sachin Badgujar,‡[a] Chang Eun Song,‡[a,b] Sora Oh,[a,b] Won Suk Shin,[a,b] Sang-Jin Moon,[a] Jong-Cheol Lee,[a,b] In Hwan Jung,[a,b]* and Sang Kyu Lee[a,b]*

[a]Division of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea

[b]Nanomaterials Science and Engineering Major, Korea University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea.



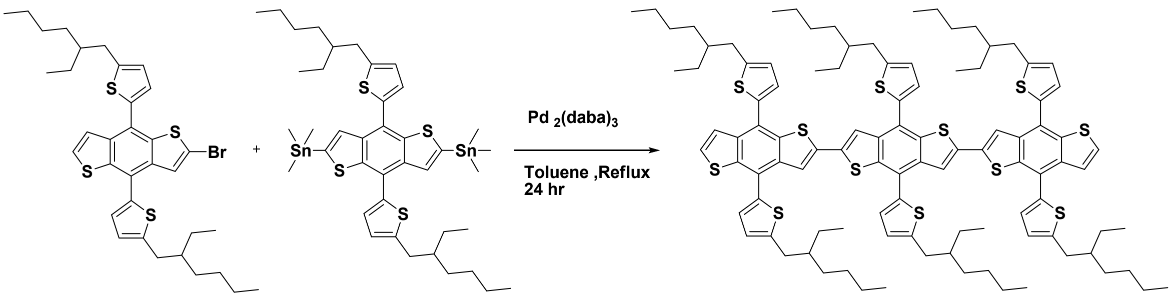
Scheme S1. Synthetic procedures used to prepare the rhodanine-based electron donor (BDT3TR) and acceptor (I-IDTBR).



2-1 (Yield: 74%)

Synthesis of compound 2-1.

Into a solution of 4-(5-(2-ethylhexyl)thiophen-2-yl)-8-(5-(2-ethylpentyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (2.0 g, 3.45 mmol) in THF (30 mL) at -78 ^{o}C was added 2.21 mL (3.54 mmol) of n-butyllithium (1.6M in hexane) by syringe. The mixture was stirred at -78 ^{o}C for 1 h and allowed to warm to room temperature. The mixture was stirred for 1h and cooled at -78 ^{o}C, and then carbon tetrabromide (1.25 mL, 3.79 mmol) was added. After being stirred at room temperature overnight, the mixture was then poured into 100 mL of cool water and extracted with diethyl ether. The organic layer was washed with brine (100 ml), dried over anhydrous MgSO$_4$ and concentrated under vacuum, the crude product was purified by column chromatography on silica gel using Hexane as eluent to afford compound 2-1 (1.69 g, 74%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 7.61 (d, J = 5.58 Hz, 1H), 7.60 (s, 1H), 7.47 (d, J = 5.6 Hz 1H), 7.25 (dd, J = 3.4 Hz, 2H), 6.88 (dd, J = 3.3 Hz, 2H), 2.86 (d, J = 6.78 Hz, 4H), 1.69 (m, 2H), 1.45 - 1.33 (m, 16H), 0.94 – 0.88 (m, 12H). Anal. Calcd: C, 62.08; H, 6.28; S, 19.50. Found: C, 62.06; H, 6.25; S, 19.51.

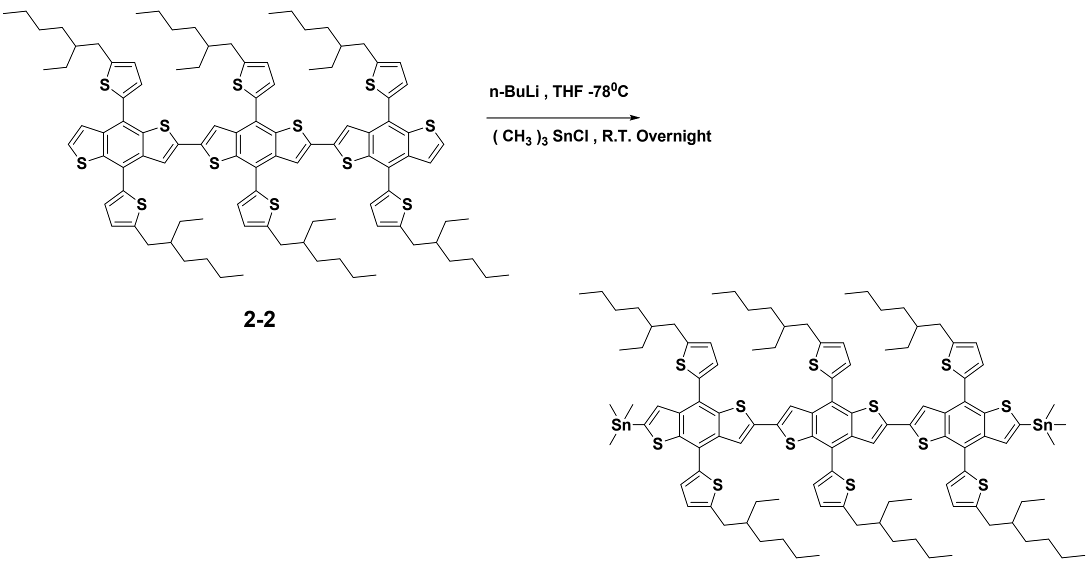


2-1

2-2 (Yield: 68%)

Synthesis of compound 2-2

A solution of compound 2-1 (1.0 g, 1.5 mmol) and 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (0.542 g, 0.600 mmol) in toluene (10 mL) was purges with argon for 5 minutes followed by the addition of tri(o-tolyl)phosphine (46 mg, 0.15 mmol) and tris(dibenzylideneacetone)dipalladium (77 mg, 0.075 mmol). The mixture was reacted at 110 ^{o}C for 24 hrs. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, and then dried over $MgSO_4$. After removal of solvent, the crude product was purified by column chromatography on silica gel with hexane as eluent to afford compound 2-2 (0.71 g, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.75(s, 2H), 7.71 (s , 2H), 7.60 (d, J = 5.57 Hz, 2H), 7.45 (d, J = 5.5 Hz, 2H), 7.30 (d, J = 3.3 Hz, 6H), 6.93 (m, 6H) 2.90 (m, 12H), 1.74–1.63 (m, 6H), 1.48–1.33 (m, 48 H), 0.98–0.89 (m, 36 H). Anal. Calcd: C, 70.70; H, 7.10; S, 22.21. Found: C, 70.65; H, 7.10; S, 22.23.



2-2

2 (Yield: 82%)

Synthesis of compound 2

Into a solution of compound 2-2 (0.700 g, 0.400 mmol) in THF (25 mL) at -78 ^{o}C was added 0.6 mL (0.96 mmol) of n-butyllithium (1.6M in hexane) by syringe. The mixture was stirred at -78 ^{o}C for 1 h and allowed to warm to room temperature. The mixture was stirred for 1h and cooled at -78 ^{o}C, and then 0.96 ml (0.96 mmol) of trimethyltinchloride (1M in THF) was added. After being stirred at room temperature overnight, the mixture was then poured into 100 mL of cool water and extracted with diethyl ether. The organic layer was washed with brine (100 ml), dried over anhydrous MgSO4 and concentrated under vacuum. The residue was recrystallized from ethanol to yield the compound 2 (0.682 g, 82%) as a red solid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 7.76(s, 2H), 7.71 (s, 2H), 7.64 (t, J = 14.5 Hz, 2H), 7.31 (m, 6H), 6.92 (m, 6H), 2.89 (d, J = 6.6 Hz, 12H), 1.72 (m, 6H), 1.54-1.33 (m, 48H), 0.99-0.89 (m, 36H), 0.39 (t, J = 28.2 Hz 18H). Anal. Calcd: C, 63.02; H, 6.76; S, 18.69. Found: C, 63.05; H, 6.75; S, 18.70.

Synthesis of compound 5

A solution of ((4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis (trimethylstannane) compound (1) (0.350 g, 0.33 mmol) and 7-

bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde compound (3) (0.204 g, 0.8 mmol) in toluene: DMF (5 mL,4:1 v/v) was purged with argon for 5 minutes followed by the addition of $Pd(PPh_3)_4$ (0.035 g, 0.004 mmol) again purging for 5 minutes. After being stirred at 110 °C overnight under argon, reaction mixture was poured into water (25 mL) and extracted with dichloromethane. The organic layer was washed with water, and then dried over Na_2SO_4. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (1:1) as eluent to afford compound 5 as a reddish brown solid (0.255 g, 73%). ^1H NMR (400 MHz, $CHCl_3$): δ 10.72 (s, 2H), 8.22 (s, 2H), 8.26 (d, J = 7.6 Hz, 2H), 8.06 (d, J = 7.6 Hz, 2H), 7.44 (s, 2H), 2.16 – 2.08 (m, 4H), 2.01 – 1.93 (m, 4H), 1.20 - 1.15 (m, 40H), 0.99 – 0.85 (m, 8H), 0.79 (t, J = 7.2 Hz, 12H). ^{13}C NMR ($CHCl_3$, 125 MHz, ppm): δ 188.4, 156.98, 154.23, 153.89, 152.19, 146.61, 140.61, 136.37, 134.07, 133.00, 124.80, 124.76, 122.72, 114.07, 54.37, 39.12, 31.75, 29.95, 29.27, 29.19, 24.24, 22.56, 14.037.

Synthesis of O-IDTBR

To a solution of compound 5 (0.250 g, 0.24 mmol) and 3-ethylrhodanine (0.193 g, 1.2 mmol) in 10 mL of chloroform, 5-drops of piperidine was added. The mixture was refluxed and stirred for overnight, under argon atmosphere. Reaction mixture was cooled to room temperature and poured in methanol 50 mL and stirred for 3 h. Solid was filtered off, residue was washed with enough methanol. Solid was dissolved in chloroform and slurried and it was chromatographed on silica gel using a mixture of dichloromethane and hexane (1:1) afford a purple blue solid (0.204 g, 64 % yield). ^1H NMR (400 MHz, $CHCl_3$): δ 8.53 (s, 2H), 8.21 (s, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 7.6 Hz 2H), 7.42 (s, 2H), 4.28 (qurt, J = 7.02 Hz, 4H), 2.15 – 2.08 (m, 4H), 2.00 – 1.93 (m, 4H), 1.35 (t, J = 7.3 Hz 12H), 1.20 - 1.12 (m, 40H), 0.99 – 0.83 (m, 8H), 0.79 (t, J = 7.2 Hz, 12H). ^{13}C NMR($CDCl_3$, 125 MHz, ppm): δ 167.54, 157.00, 154.58, 154.16, 151.71, 146.10, 140.97, 136.36, 131.33, 130.50, 127.25, 124.43, 124.19, 124.03, 123.78, 11.94, 54.34, 39.91, 39.15, 31.78, 29.99, 29.30, 29.21, 24.26, 22.58, 14.05, 12.32. MS (MALDI) m/z: calculated for $C_{72}H_{88}N_6O_2S_8$, [M]+, 1324.47; found, 1324.84. Anal. Calcd for $C_{72}H_{88}N_6O_2S_8$: C,65.22; H, 6.69; N, 6.34; O, 2.41; S, 19.34. Found: C, 64.78; H,6.65; N,6.24; S, 19.41.

Synthesis of compound ***6***

Compound 6 was synthesized according the procedure for compound 5. The stille scoupling of compound of (4,4',4",8,8',8"-hexakis(5-(2-ethylhexyl)thiophen-2-yl)-[2,2':6',2"-terbenzo[1,2-b:4,5-b']dithiophene]-6,6"-diyl)bis(trimethylstannane) (3) (0.426 g, 0.20 mmol) and 5"-bromo-3,3"-dioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde (5) (0.289 g, 0.50 mmol) and the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (1:1) then with with chloroform as eluent to afford compound 8 (0.384 g, 68%) as a red gummy mass. ^{1}H NMR (300 MHz, $CHCl_3$): δ 9.76 (s, 2H), 7.51 (s, 2H), 7.48 (d, J = 3.2 Hz, 4H), 7.41 (s, 2H), 7.29 (t, J = 3.3Hz, 6H), 7.13 (d, J = 3.8 Hz, 2H), 6.96 (d, J = 3.8 Hz, 2H), 6.92 (d, J = 3.35 Hz, 6H), 6.88 (s, 2H), 2.94 (d, J = 6.5 Hz, 12H), 2.73 (t, J = 7.5 Hz, 4H), 2.62 (t, J = 7.5 Hz, 4H), 1.79 (m, 6H), 1.64 (m, 8H), 1.51 - 1.38 (m, 48H), 1.33 - 1.28 (m, 40H) 1.03 (t, J = 7.3 Hz, 18H), 0.98 – 0.92 (m, 18 H), 0.89 – 0.85 (m,12H)

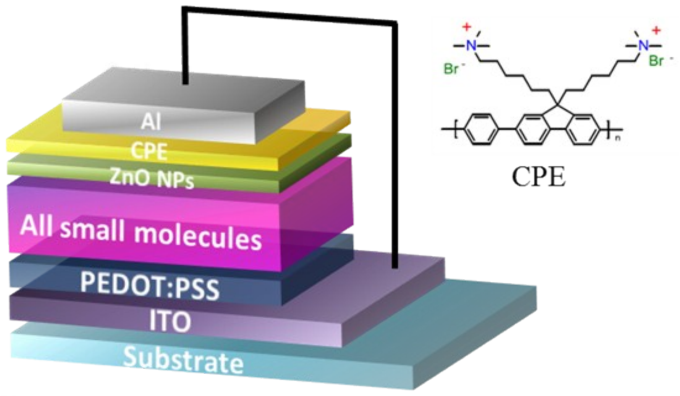
Synthesis of BDT3TR

Compound BDT3TR was synthesized according the procedure for *O-IDTBR.* Compound 6, 5",5'''''-(4,4',4",8,8',8"-hexakis(5-(2-ethylhexyl)thiophen-2-yl)-[2,2':6',2"-terbenzo[1,2-b:4,5-b']dithiophene] - 6,6"-diyl)bis(3,3"-dioctyl-[2,2':5',2"-terthiophene]-5-carbaldehyde) (0.30 g, 0.11 mmol), and 3-ethylrhodanine (0.088 g, 0.55 mmol) were used for the knoevenagel condensation. The crude Solid was dissolved in chloroform and slurried and it was chromatographed on silica gel using a mixture of dichloromethane and hexane (1:1) then chloroform as eluent to afford *BDT3TR* as a dark brown solid (0.160 g, 63 % yield). ^{1}H NMR (400MHz, $CHCl_3$): δ 7.64 (s, 2H) 7.57 (s, 2H) 7.37 (d, J = 5.6 Hz, 4H), 7.30(s, 2H), 7.28-7.25 (m, 6H) 7.05 (d, J = 3.6 Hz, 4H), 6.93- 6.89 (m, 8H,), 6.79 (s, 2H), 4.15 (q, J= 7.8Hz, 4H), 2.96(d, J= 6.71 Hz, 12H), 2.67 (t, J = 7.5 Hz, 4H), 2.58 (t, J = 7.5 Hz, 4H), 1.82- 1.78 (m, 6H), 1.61- 1.58 (m, 8H), 1.51- 1.41 (m, 48H), 1.35- 1.25 (m, 46H), 1.08 – 1.02 (m ,18H), 0.99 – 0.93(m, 18H), 0.90 (m, 12H). MS (MALDI) m/z: calculated for $C_{170}H_{208}N_2O_2S_{22}$, [M]+, 3017.01; found, 3017.5 Elemental Analysis(NCHS) C, 67.68; H, 6.95; N, 0.93; O, 1.06; S, 23.38 ,found : 67.43; H, 6.92; N, 0.97; S, 24.56.

General Experimental Details: All reagents, solvents, unless otherwise specified were obtained from Aldrich, TCI chemical company (japan) and were used as received. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). Compound 1[51], 3[34] and 4[54] were prepared according reported method. The synthesized compounds were characterized with ^{1}H NMR and ^{13}C NMR spectra obtained using a Bruker DPX-400 or 500 MHz NMR spectrometer. UV−visible analysis was performed with a Lambda 20 (Perkin-Elmer) diode array spectrophotometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) were performed on a Bruker Autoflex Ⅲ LRF200-CID instrument. Cyclic voltammetry (CV) was performed using a PowerLab/AD instrument model system in 0.1 M solution of tetrabutylammonium hexafluorophospate (Bu_4NPF_6) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mVs^{-1}. A glassy carbon disk (~0.05 cm^2) coated with a thin film, an Ag/AgNO3 electrode, and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. Ferrocene/ferrocenium redox couple was used as the internal standard. The HOMO energy level was calculated from the onset of the oxidation potential of the polymer using the following: $E_{HOMO} = -(4.8 + Eox\ onset)$ eV. The atomic force microscope (AFM) (Multimode IIIa, Digital Instruments) was operated in tapping mode to acquire images of the surfaces of blend films. SCLC devices' fabrication and testing. Mobility measurements of BDT3TR:O-IDTBR (w/w, 1:1) and pristine film of BDT3TR and O-IDTBR were done by a charge-only space-charge limited current (SCLC) method with the following diode structures: ITO/PEDOT–PSS/active layer/Au for hole-only devices and Al/active layer/Al for electron-only devices by taking current-voltage measurements and fitting the results to a space-charge limited form. The charge carrier mobilities were calculated using the SCLC model, where the SCLC is described by $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, L is the film thickness of the active layer, μ is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V is the internal voltage in the device, and $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance between the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Prepartaion of ZnO Nanoparticles (ZnO NPs)

ZnO get much attention in serve as the electron transport layer because it has good transparency across the whole visible spectral range, simple synthesis, relatively high electron mobility, and environmental stability. So we also used ZnO, especially as nanoparticles (NPs). The ZnO NPs were synthesized by sol-gel process,[63] detailed described as below; ZnO nanoparticles were synthesized by a solution-precipitation process using Zn acetate and tetramethylammonium hydroxide (TMAH)12. For a typical synthesis, a solution of zinc acetate in dimethyl sulphoxide (DMSO) (0.5 M) and 30 ml of a solution of TMAH in ethanol (0.55 M) were mixed and stirred for 1 h in ambient air, then washed and dispersed in ethanol at a concentration of ~30 mg ml^{-1}.



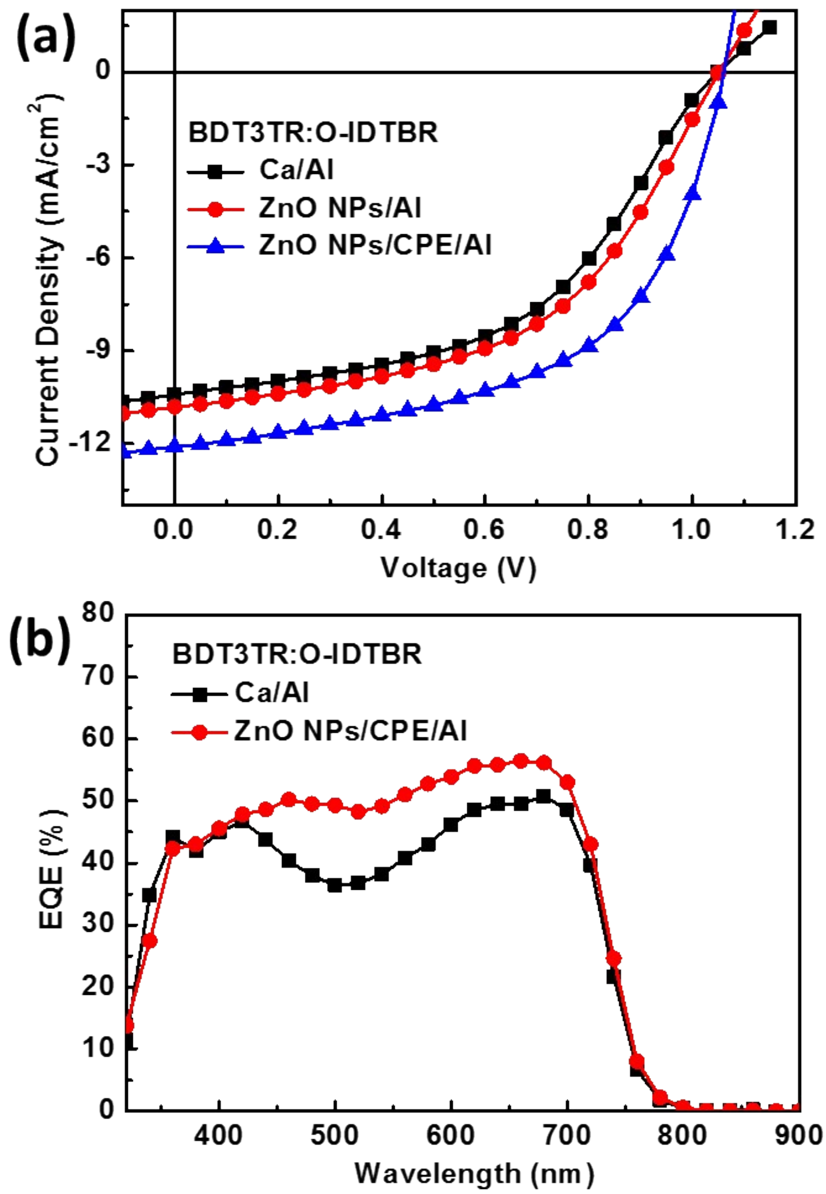


Fig. S1. (a) *J-V* characteristics of BDT3TR:O-IDTBR devices by top electrodes under AM 1.5G illumination, and (b) EQE of the corresponding devices.

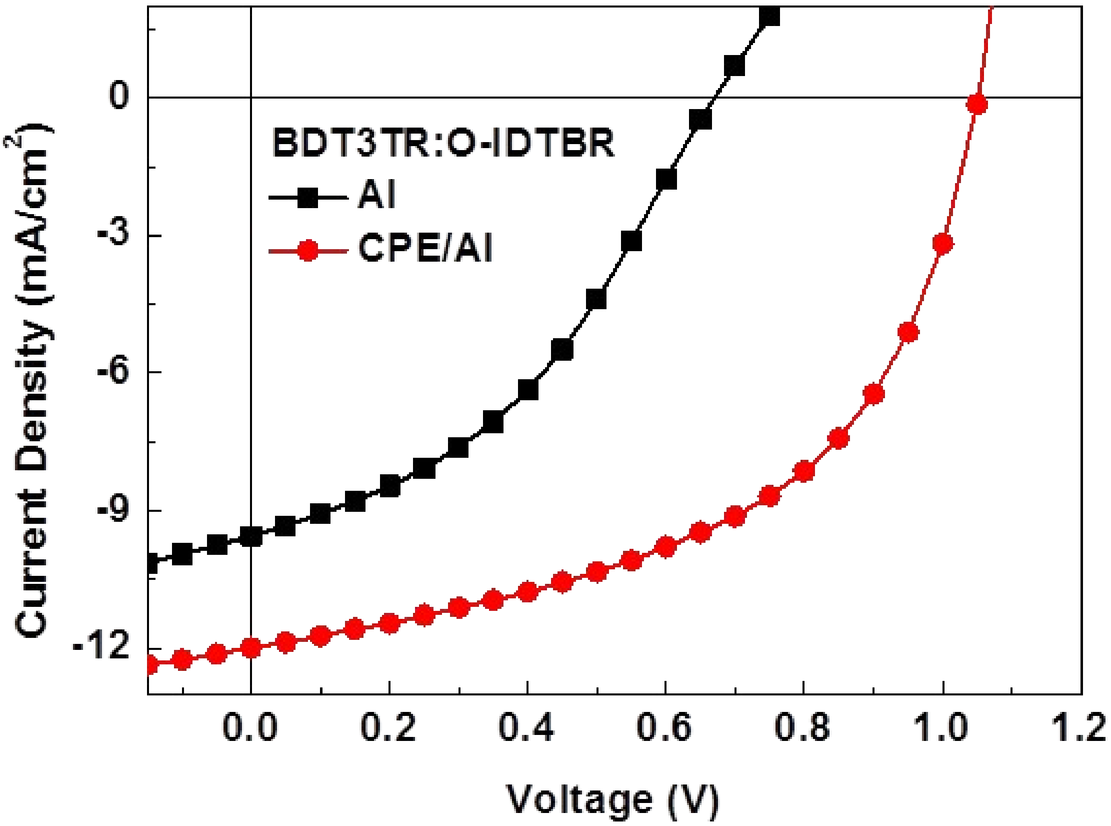


Fig. S2. *J-V* characteristics of BDT3TR:O-IDTBR devices by top electrodes (Al or CPE/Al) without ZnO NPs under AM 1.5G illumination

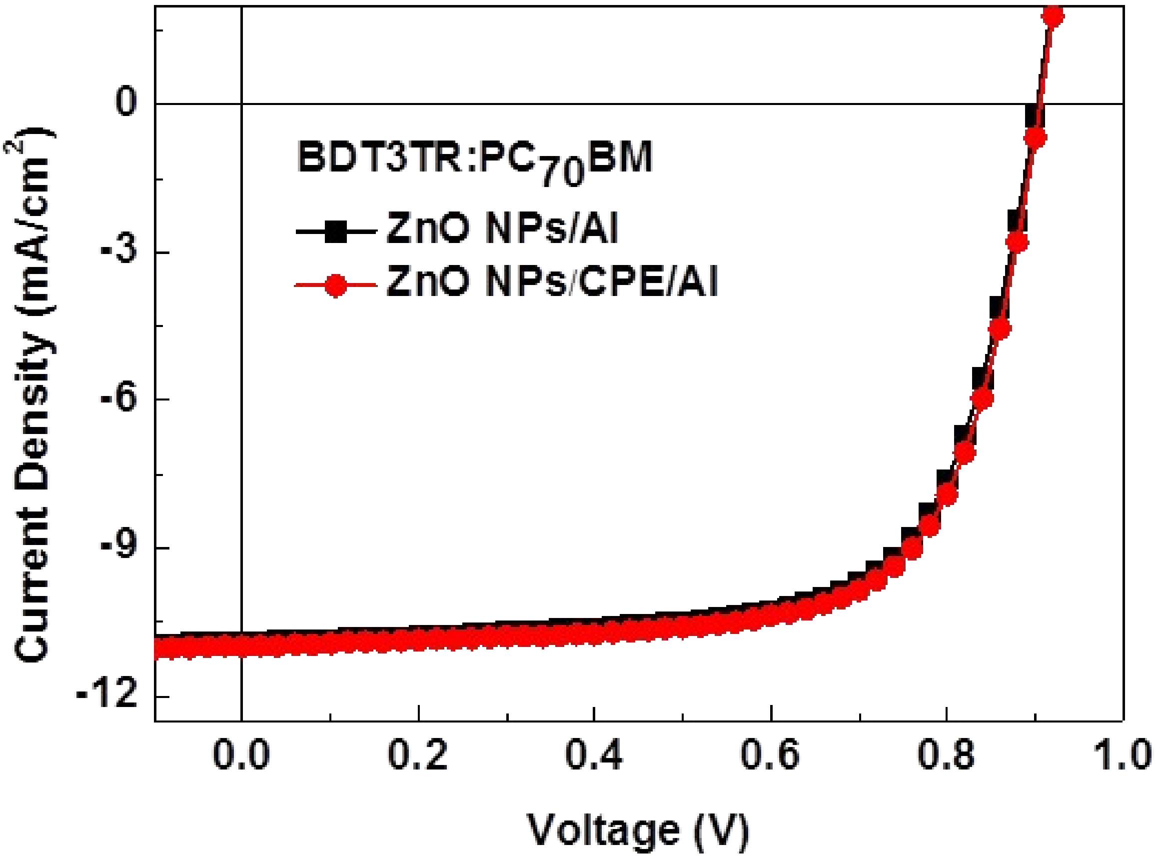


Fig. S3. *J-V* characteristics of BDT3TR:PC$_{70}$BM devices by top electrodes under AM 1.5G illumination

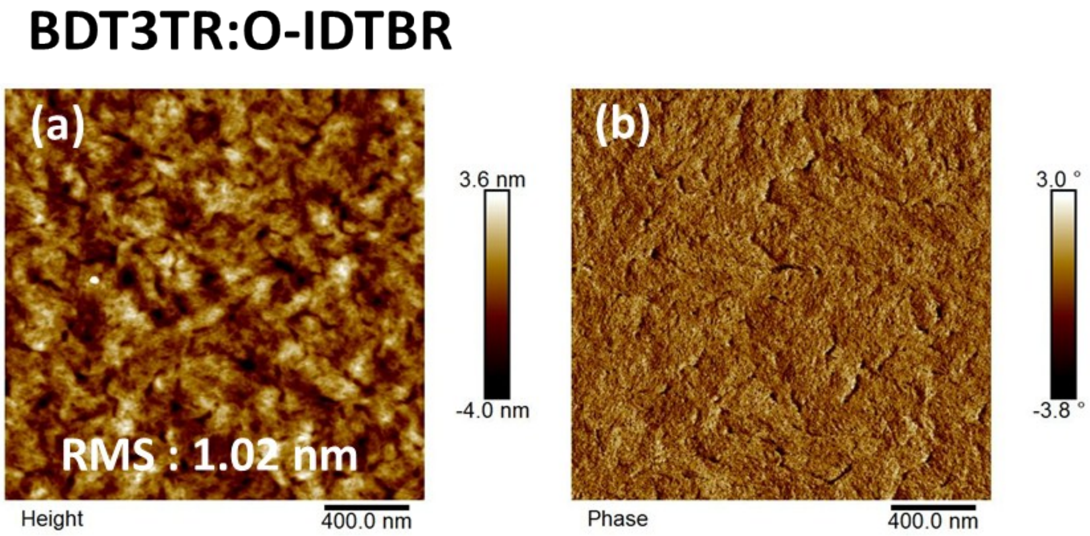


Fig. S4. (a) Topographic and (b) phase images of the BDT3TR:O-IDTBR blend films, measured in tapping-mode AFM.

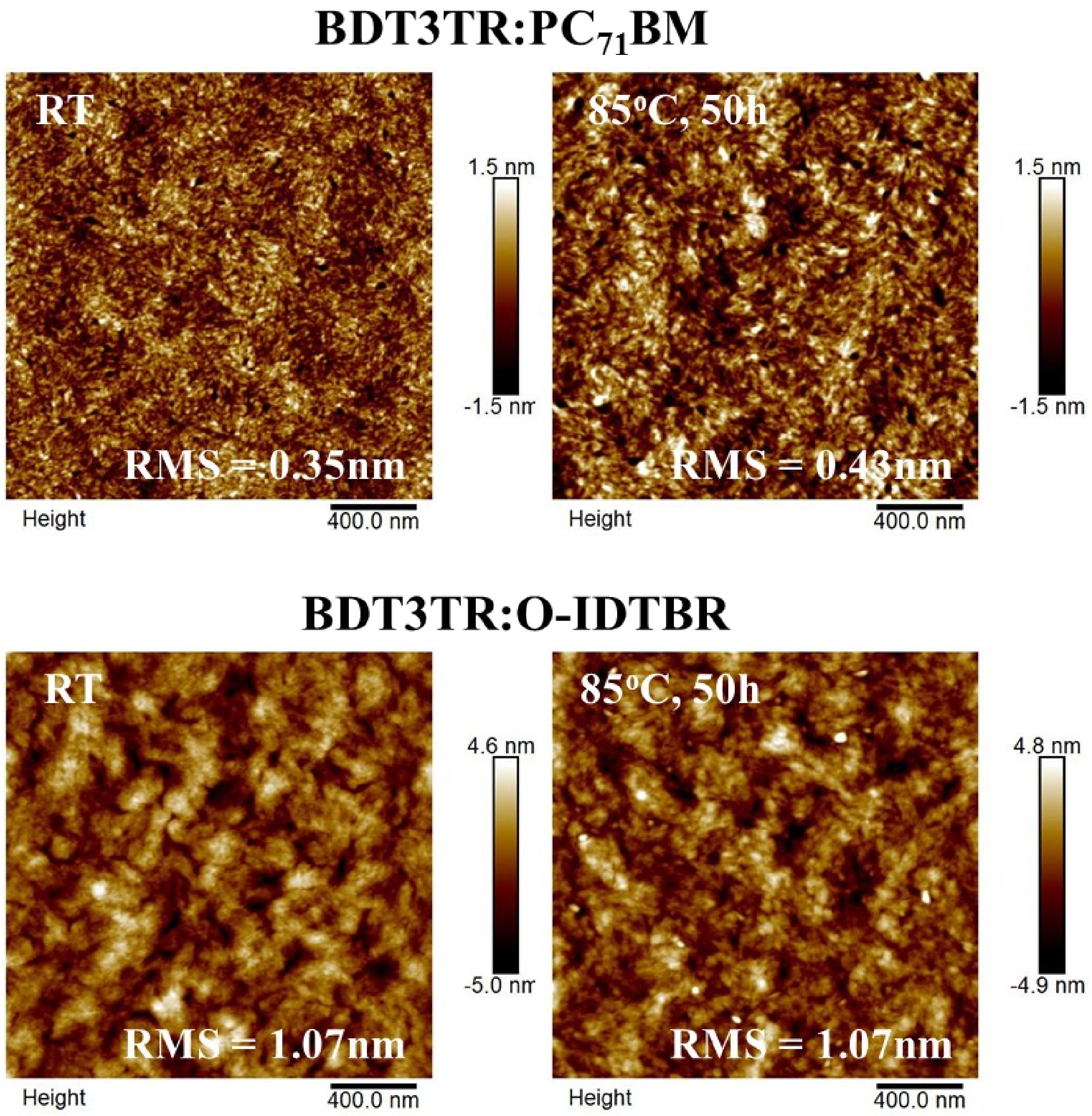


Fig. S5. Topographic images of the BDT3TR:PC$_{71}$BM and BDT3TR:O-IDTBR blend films before and after heat treatment at 85°C for 50 hours.

Photoluminescence (PL) properties

PL emission properties of BDT3TR, BDT3TR:O-IDTBR and BDT3TR:PC$_{71}$BM films at the almost identical thickness of around 100 nm were examined. As shown in **Fig. S4**, the excitation wavelength was fixed at 500 nm where the absorption of O-IDTBR is minimized. The emission of BDT3TR in the blend films was significantly decreased compared to neat BDT3TR film, implying the efficient charge separation by electron acceptor. However, the emission of BDT3TR was not completely quenched in BDT3TR:PC$_{71}$BM film. In case of BDT3TR:O-IDTBR film, the emission of O-IDTBR was mainly detected and the emission of BDT3TR was negligible. Thus, it is expected that the O-IDTBR accepter more effectively quenches emission of the BDT3TR donor.

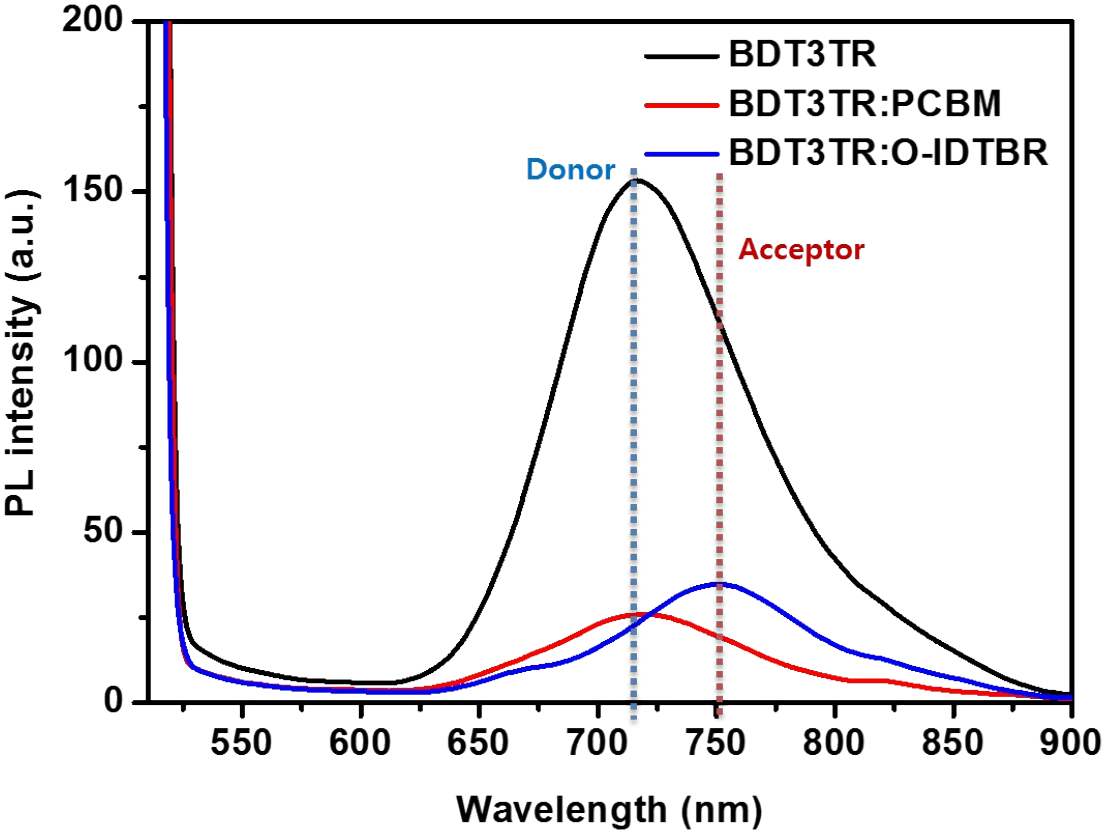


Fig. S6. PL emission properties of BDT3TR, BDT3TR:O-IDTBR and BDT3TR:PC$_{71}$BM films at the almost identical thickness of around 100 nm

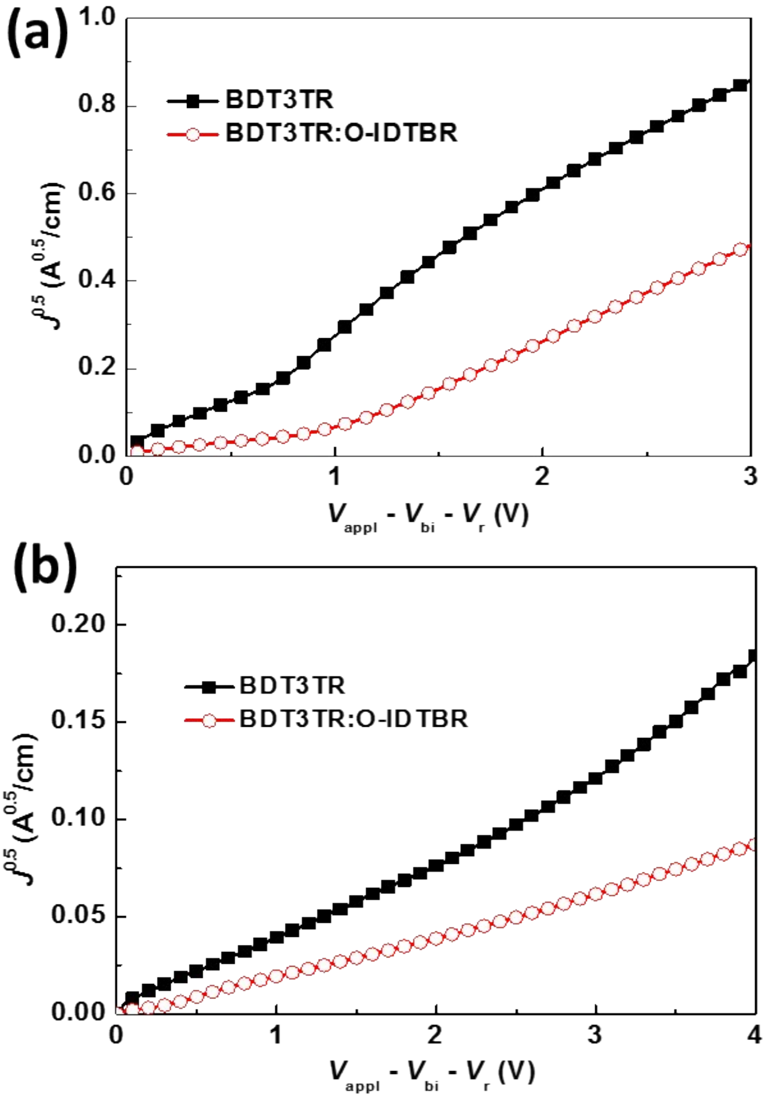


Fig. S7. (a) Hole mobility derived from SCLC method. Plots of $J^{0.5}$ vs. effective bias of hole-only devices with structure of ITO/PEDOT:PSS / Active layer/Au, and (b) electron mobility with structure of ITO/ZnO/Active layer/Ca/Al

2D-GIXD measurements: 2D-GIXD measurements were conducted at PLS-II 9A U-SAXS beamline of Pohang Acceleartor Laboratory (PAL) in Korea. The X-rays coming from the in-vacuum undulator (IVU) are monochromated using Si(111) double crystals and focused at the detector position using K-B type mirrors. GIXD patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time was 2~ 120 seconds dependent on the saturation level of detector. Diffraction angles were calibrated by a pre-calibrated sucrose (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, b = 102.938^{o}) and the sample-to-detector distance was about 223.2 mm.

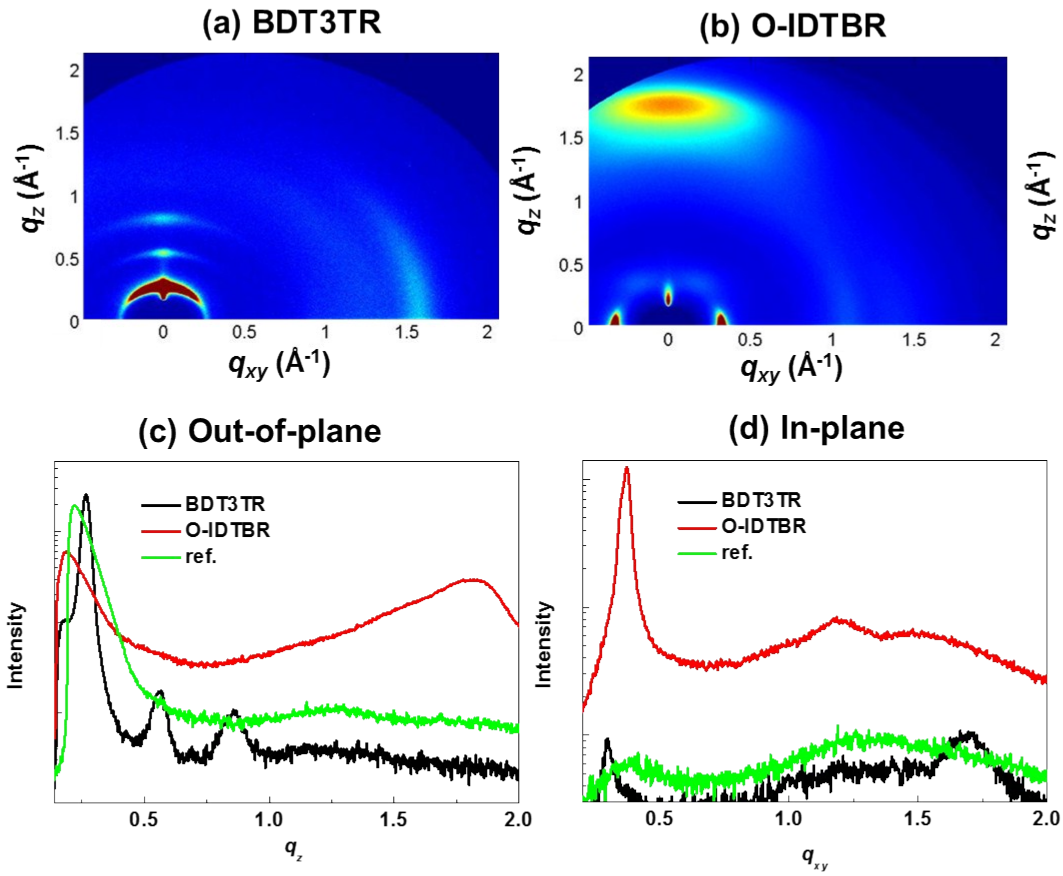
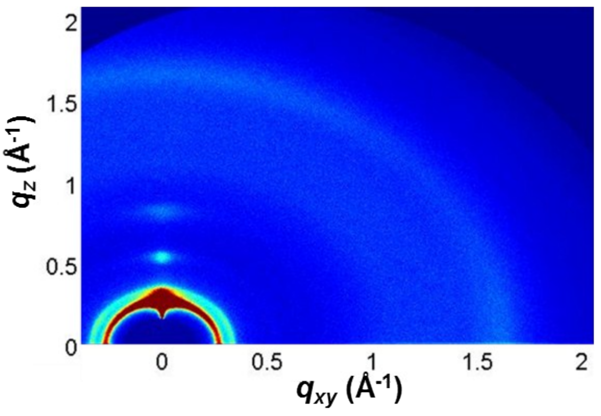
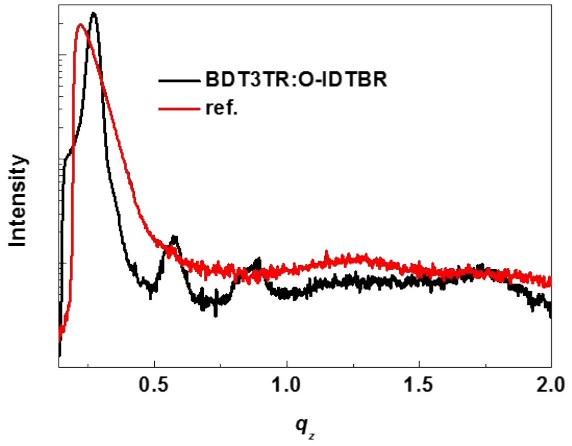


Fig. S8. Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) image of neat (a) BDT3TR and (b) O-IDTBR. (c) Out-of-plane and (e) in-plane line cuts of BDT3TR and O-IDTBR from the 2D-GIXD images.

(a) BDT3TR:O-IDTBR



(b) Out-of-plane



(c) In-plane

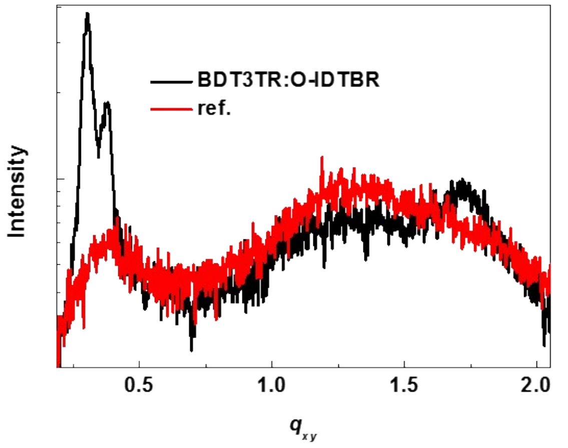


Fig. S9. Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) image of blend films of (a) BDT3TR:O-IDTBR. (c) Out-of-plane and (d) in-plane line cuts from the corresponding 2D-GIXD image.

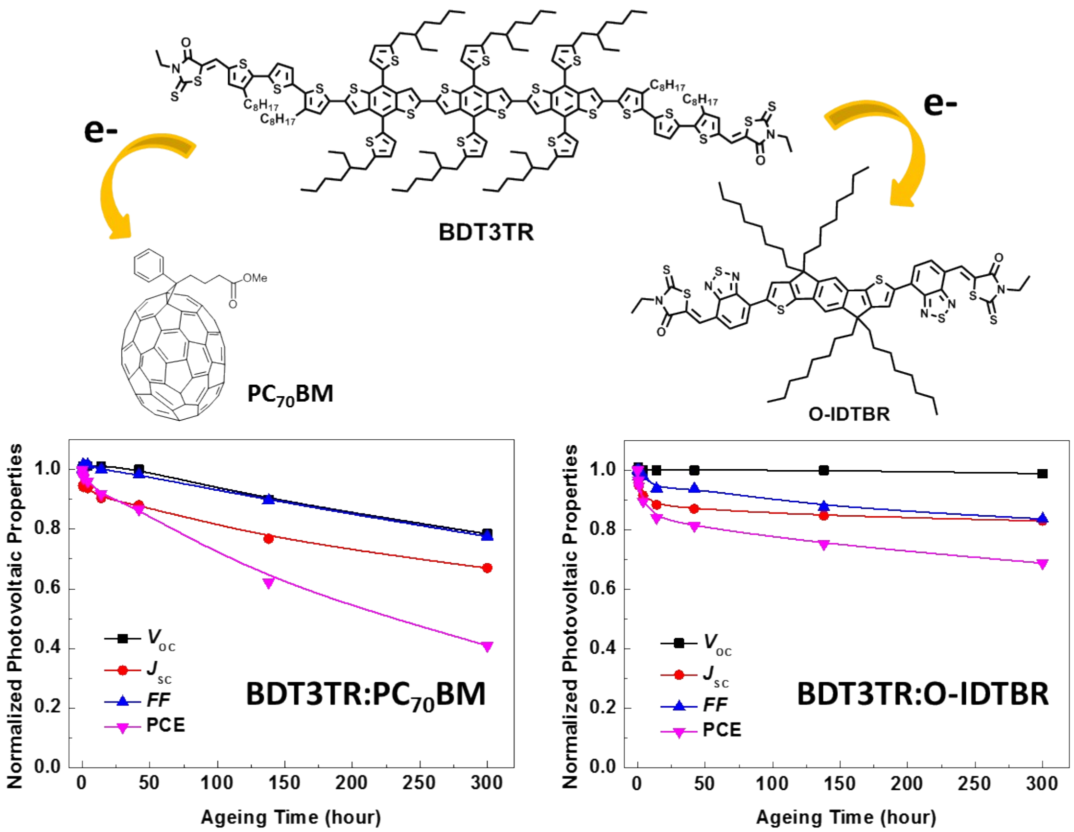


Fig. S10. Normalized photovoltaic properties of BDT3TR:PC$_{70}$BM and BDT3TR:O-IDTBR devices

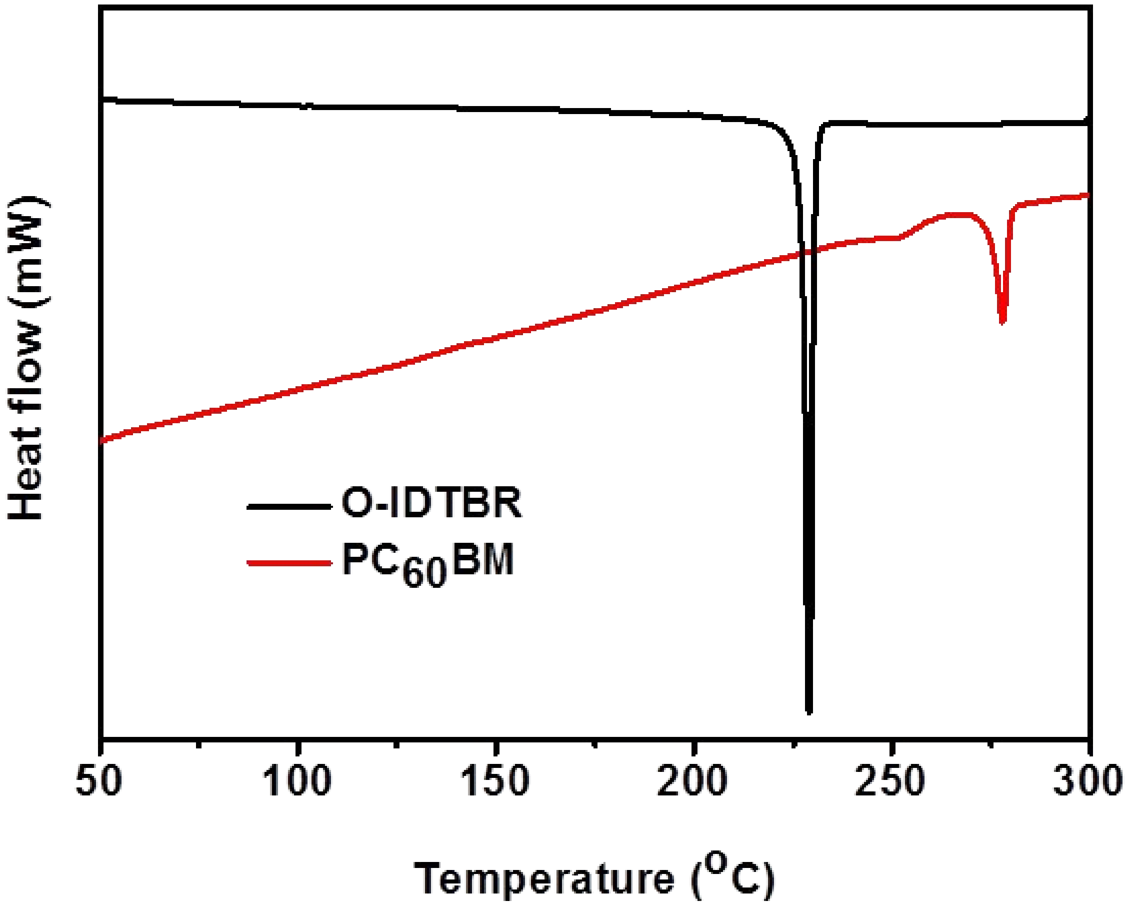


Fig. S11. Differential scanning calorimetry (DSC) curves of O-IDTBR and $PC_{60}BM$ under N_2 at a heating rate of 10 °C min^{-1}

Table S1. **Optical and electrochemical properties of the rhodanine-terminated small molecules.**

Small Molecule	$\lambda_{max, sol}$ [nm]$^{a)}$	$\lambda_{max, film}$ [nm] $^{b)}$	$\lambda_{onset, film}$ [nm]	E_g^{opt} [eV] $^{c)}$	$E_{ox, onset}$ [V]	$E_{re, onset}$ [V]	$E_{HOMO, CV}$ [eV] $^{d)}$	$E_{LUMO, CV}$ [eV] $^{e)}$	E_g^{cv} [eV] $^{f)}$
BDT3TR	505	572	681	1.82	0.44	-	– 5.10	-	-
O-IDTBR	664	689	785	1.57	0.80	1.04	– 5.46	– 3.62	1.84

a) Dilute solution in chloroform, b) Spin-cast film on quartz plate from 1 wt.% chloroform solution for 30 s at 1500 rpm, c) Band gap calculated from the absorption edge in solid film, d) HOMO levels were determined from the E_{onset} of the first oxidation potential of ferrocene, –4.8 eV, e) LUMO levels were determined from the E_{onset} of the first reduction potential of ferrocene, –4.8 eV, f) The electrochemical bandgap determined by cyclic voltammetry.

Table S2. Summary of photovoltaic properties of BDT3TR:O-IDTBR by weight ratio.

Active layer$^{a)}$	Weight ratio [w/w]	Annealing	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
BDT3TR:O-IDTBR	1.0:0.5	W/O	1.01	8.11	44	3.60
		80°C, 10min	0.98	9.32	48	4.37
		110°C, 10min	0.99	8.77	51	4.41
	1.0:1.0	W/O	1.04	9.21	45	4.28
		80°C, 10min	1.03	10.35	49	5.27
		110°C, 10min	1.01	7.77	53	4.16
	1.0:2.0	W/O	1.04	7.49	44	3.46
		80°C, 10min	1.04	9.64	49	4.93
		110°C, 10min	1.01	5.80	54	3.14
	1.0:3.0	W/O	1.05	7.73	44	3.53
		80°C, 10min	1.04	8.86	50	4.56
		110°C, 10min	1.00	6.10	54	3.28

a) ITO/PEDOT:PSS/Photo-active layer/Ca/Al

Table S3. Summary of photovoltaic properties by top electrodes

Active layer$^{a)}$	Top Electrode	V_{OC} [V]	J_{SC} [mA cm^{-2}]	*FF* [%]	PCE [%]
BDT3TR:O-IDTBR	Ca/Al	1.05	10.42	49	5.35
	ZnO NPs/Al	1.05	10.82	50	5.70
	ZnO NPs/CPE/Al	1.06	12.10	55	7.09

a) ITO/PEDOT:PSS/Photo-active layer/Top Electrode

Table S4. Photovoltaic properties of BDT3TR:O-IDTBR devices without ZnO NPs

Active layer	**Top Electrode**	**V_{OC} [V]**	**J_{SC} [mA/cm^2]**	***FF* [%]**	**PCE [%]**
BDT3TR:O-IDTBR	Al	0.67	9.55	40	2.55
	CPE/Al	1.05	11.98	52	6.51

Conventional device architecture is ITO/PEDOT:PSS/Photo-active layer/Top Electrode.

Table S5. Photovoltaic properties of BDT3TR:$PC_{70}BM$ devices by top electrodes

Active layer	**Top Electrode**	**V_{OC} [V]**	**J_{SC} [mA/cm^2]**	***FF* [%]**	**PCE [%]**
BDT3TR:$PC_{70}BM$	ZnO NPs/Al	0.90	10.91	69	6.83
	ZnO NPs/CPE/Al	0.91	10.99	70	6.95

Conventional device architecture is ITO/PEDOT:PSS/Photo-active layer/Top Electrode.

Table S6. Summary of SCLC mobilities

Active layer	thickness [nm]	$\mu_h{}^{a)}$ [cm^2 V^{-1}s^{-1}]	$\mu_e{}^{b)}$ [cm^2 V^{-1}s^{-1}]
BDT3TR	85	3.39×10^{-4}	
O-IDTBR	85		4.30×10^{-6}
BDT3TR:O-IDTBR	100	1.21×10^{-4}	1.07×10^{-6}

a) The hole-only devices with structure of ITO/PEDOT:PSS/Active layer/Au, b) The electron-only devices with structure of ITO/ZnO/Active layer/Ca/Al