# Electronic Supplementary Information (ESI)

Understanding effects of two different acceptors in one small molecule for solution processable organic solar cells

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Synthesis and Characterization

Materials: Tetrahydrofuran (THF) and toluene were treated with sodium and distilled before use. Compound 1 was prepared according to literature method.[1] All other reagents were used directly as obtained from commercial sources.
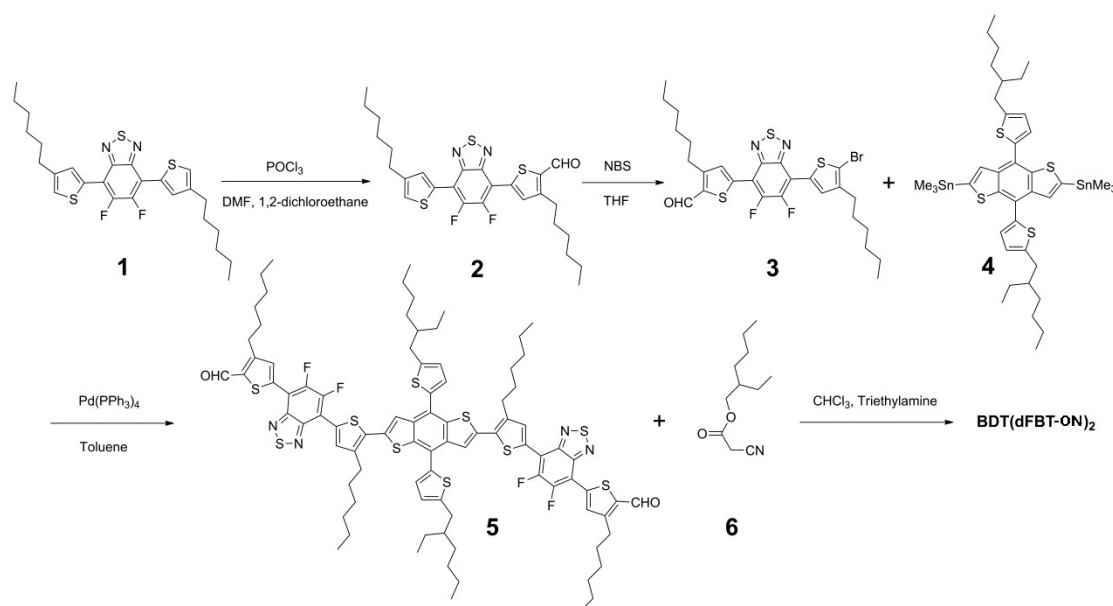
Scheme S1. Synthetic route of BDT(dFBT-ON)₂.

5-(5,6-difluoro-7-(4-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazol-4-yl)-3-hexylthiophene-2-carbaldehyde (**2**)

A solution of **1** (1.09 g, 2 mmol) in 20 ml anhydrous 1,2-dichloroethane and anhydrous DMF (0.31 ml, 4 mmol) was cooled down to 0 °C under nitrogen atmosphere. POCl₃ (0.44 ml, 4 mmol) was added dropwise into the solution within 10 min. The mixture were stirred at 0 °C for 30 min and room temperature for 1 hour respectively. After refluxing at 85 °C for 16 hours, the solution was cooled down to

room temperature and poured into water. The organic compounds were extracted with dichloromethane for twice, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ether (30:70) as eluent, affording compound **2** as a yellow solid (0.80 g, 75% yield). ^{1}H-NMR (400 MHz, $(CD_3)_2SO$) δ 10.18 (s, 1H), 8.20 (d, 2H), 7.62 (s, 1H), 3.09 (t, 2H), 2.70 (t, 2H), 1.66 (m, 4H), 1.40-1.23 (m, 12H), 0.87 (m, 6H). ^{19}F NMR (377 MHz, $CDCl_3$): δ -124.40 (d, J = 14.7 Hz), -128.09 (d, J = 14.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ182.40, 152.59, 152.39, 152.16, 150.53, 150.34, 149.97, 149.78, 148.71, 148.62, 148.56, 148.48, 147.95, 147.76, 143.93, 139.58, 139.52, 139.48, 138.81, 138.75, 133.57, 133.48, 133.08, 132.99, 130.90, 130.87, 130.84, 130.80, 125.05, 124.98, 113.80, 113.70, 110.04, 109.92, 31.71, 31.60, 31.48, 30.49, 30.44, 29.05, 29.04, 28.53, 22.65, 22.59, 14.12, 14.08. m/z (MALDI-TOF): 533.3 calcd. for $C_{27}H_{30}F_2N_2OS_3$: 532.7.

5-(7-(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)-3-hexylthiophene-2-carbaldehyde (**3**)

A solution of **2** (533 mg, 1 mmol) in 20 ml THF was stirred in dark at room temperature. A solution of NBS (296 mg 1.5 mmol) in 10 ml THF was added dropwise into the above solution and stirred at room temperature for 12 hours. The solution was washed with water and extracted with dichloromethane. After dried with $MgSO_4$, the solution was concentrated under low pressure. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ether (20:80) as eluent, affording compound **3** as an orange solid (537 mg, 88% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ10.15 (s, 1H), 8.15 (s, 1H), 8.02 (s, 1H), 3.05 (t, J = 7.7 Hz, 2H), 2.71-2.62 (t, J = 7.7 Hz, 2H), 1.81-1.72 (m, 2H), 1.72 -1.62 (m, 2H), 1.47- 1.26 (m, 12H), 0.90 (dd, J = 6.7, 5.6 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$): δ-124.40 (d, J = 14.5 Hz), -127.94 (d, J = 14.5 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ182.40, 152.16, 146.26, 143.93, 142.92, 142.82, 142.37, 139.30, 139.08, 138.97, 138.91, 138.18, 133.72, 133.62, 133.26, 132.99, 132.92, 132.45, 132.35, 131.36, 131.02, 130.96, 130.93, 126.47, 125.06, 115.56, 115.48, 112.76, 112.65, 110.34, 110.23, 31.63, 31.60, 31.48, 29.71, 29.55, 29.05, 28.95, 28.53, 22.64, 22.59, 14.11, 14.08. m/z (MALDI-TOF): 612.0 calcd. for $C_{27}H_{29}F_2N_2OS_3Br$: 611.6.

5,5'-(7,7'-(5,5'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(4-hexylthiophene-5,2-diyl))bis(5,6-difluorobenzo[c][1,2,5]thiadiazole-7,4-diyl))bis(3-hexylthiophene-2-carbaldehyde) (**5**)

To a solution of **3** (300 mg, 0.5 mmol) and **4** (148 mg, 0.16 mmol) in 50 ml toluene was added $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol). After degassing and purging with nitrogen for three times, the mixture was stirred at 110 °C for 48 hours. The mixture was cooled down to room temperature and precipitated in methanol. The crude dark purple solid was washed with ethanol, hexane and acetone several times each. Then it was precipitated from chloroform/methanol for three times. Due to the low solubility of **5**, the purple solid was used directly in the next step without further purification. m/z (MALDI-TOF): 1639.2 calcd. for $C_{88}H_{98}F_4N_4O_2S_{10}$: 1640.4.

BDT(dFBT-ON)$_2$

To a solution of **5** (164 mg, 0.1 mmol) and **6** (394 mg, 2 mmol) in 25 ml anhydrous chloroform was added three drops of triethylamine. The mixture was stirred in nitrogen atmosphere for 24 hours at room temperature. Then the mixture was precipitated in methanol to get a dark purple solid. The crude product was further purified by silica gel chromatography with chloroform/petroleum ether (40:60) as eluent, affording BDT(dFBT-ON)$_2$ as an purple solid (179 mg, 54 % yield from **4**). ^{1}H-NMR (400 MHz, CDCl$_3$): δ8.29 (s, 2H), 8.07 (s, 2H), 8.02 (s, 2H), 7.57 (s, 2H), 7.38 (d, J = 3.3 Hz, 2H), 6.98 (d, J = 3.3 Hz, 2H), 4.18 (d, J = 2.6 Hz, 4H), 2.96 (d, J = 6.2 Hz, 4H), 2.78 (dd, J = 16.4, 9.3 Hz, 8H), 1.83-1.76 (m, 2H), 1.68 (m, 10H), 1.59-1.28 (m, 56H), 1.04 (t, J = 7.4 Hz, 6H), 0.99-0.89 (m, 30H). ^{19}F NMR (377 MHz, CDCl$_3$): δ-123.51 (s), -127.45 (s). ^{13}C NMR (101 MHz, CDCl$_3$): δ163.02, 162.94, 162.89, 161.20, 153.65, 153.54, 153.32, 153.13, 150.46, 149.83, 149.60, 148.35, 147.85, 147.50, 146.24, 145.26, 145.05, 144.83, 142.67, 142.16, 140.76, 139.44, 139.21, 138.65, 138.57, 137.61, 136.34, 136.13, 136.01, 135.69, 134.44, 133.50, 132.19, 131.60, 131.56, 129.10, 126.35, 125.38, 125.23, 122.44, 120.40, 119.07, 115.55, 114.10, 112.73, 109.23, 97.14, 97.05, 96.78, 96.57, 68.72, 41.54, 38.74, 34.48, 32.80, 31.87, 31.60, 31.08, 30.31, 29.80, 29.72, 29.30, 29.09, 28.88, 25.71, 23.75, 23.25, 22.99, 22.93, 22.66, 14.33, 14.29, 14.08, 14.05, 10.99. m/z (MALDI-TOF): 1998.9 calcd. for C$_{110}$H$_{132}$F$_4$N$_6$O$_4$S$_{10}$: 1996.2.
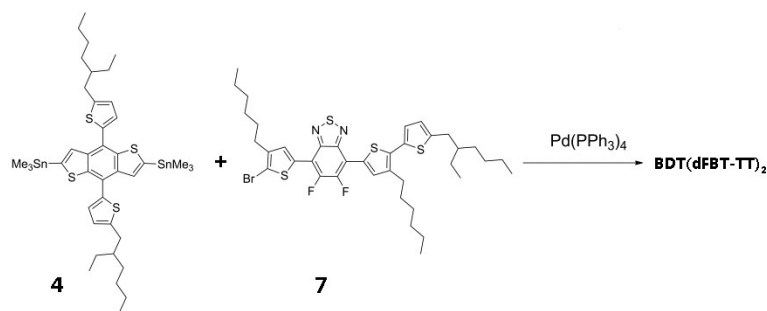
Scheme S2. Synthetic route of BDT(dFBT-TT)$_2$

BDT(dFBT-TT)$_2$

The compound **4** and **7** were prepared according to literature methods.[1] A solution of **4** (182 mg, 0.2 mmol) and **7** (345 mg, 0.44 mmol) in 35 ml toluene was added Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol). After degassing and purging with nitrogen for 3 times, the mixture was stirred at 115 °C for 72 hours. The mixture was cooled down to room temperature and precipitated in methanol. The crude dark purple solid was purified by silica gel chromatography with chloroform/petroleum ether (1:2) as eluent, affording **BDT(dFBT-TT)$_2$** as a purple solid (235 mg, 59% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (s, 2H), 8.08 (s, 2H), 7.73 (s, 2H), 7.40 (d, J = 3.4 Hz, 2H), 7.04 (d, J = 3.4 Hz, 2H), 6.96 (d, J = 3.4 Hz, 2H), 6.73 (d, J = 3.5 Hz, 2H), 2.91 (t, J = 8.8 Hz, 8H), 2.85 –

2.73 (m, 8H), 1.80 – 1.66 (m, 10H), 1.61 (d, J = 6.0 Hz, 2H), 1.50 – 1.24 (m, 56H), 0.99 (t, J = 7.4 Hz, 6H), 0.92 (dt, J = 7.3, 5.8 Hz, 30H).

Photovoltaic properties

Table S1 The photovoltaic performance of the devices under illumination of AM 1.5 G, 100 mW cm^{-2} and all the D:A ratio is 1:1 (w/w) for BDT(dFBT-ON)$_2$ based solar cells.

additive solvents	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
/	0.947	2.04	45.6	0.88
1%DIO	0.932	4.22	46.0	1.81
2%DIO	0.941	6.32	41.6	2.47
3%DIO	0.920	7.19	47.1	3.12
3%DIO+1%THF	0.953	7.48	49.6	3.54

Table S2 The photovoltaic performance of the devices under illumination of AM 1.5 G, 100 mW cm^{-2} and all the D:A ratio is 1:1 (w/w) for BDT(dFBT-TT)$_2$ based solar cells.

post treatments	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
/	0.863	9.19	65.9	5.55
0.5%DIO	0.853	6.16	54.7	2.88
1%DIO	0.828	5.71	53.8	2.55
2%DIO	0.779	5.50	45.5	1.96
TA[a]	0.905	6.90	54.5	3.41

a)   Thermal annealing (TA) 70 °C for 10 min on BDT(dFBT-TT)$_2$ based solar cells.

The performance of the photovoltaic properties was been studied. The current density was 2.03 mA/cm^2 without any additives and the PCE was 0.87%. Some post-treatments such as thermal annealing, solvent annealing and additive solvent were taken to improve the performance of BDT(dFBT-ON)$_2$. When the 1,8-diiodooctane (DIO) was added into the solution as additive, the PCE was improved a lot from 0.87% to 3.12%. The improvement of the efficiency was mostly depended on increasing of current density, which was changed from 2.03 mA/cm^2 (without DIO) to 7.19 mA/cm^2 (with 3% DIO, v/v). Any post treatments, including thermal annealing, solvent annealing and additive solvents, were not helpful to the performance of BDT(dFBT-TT)$_2$.
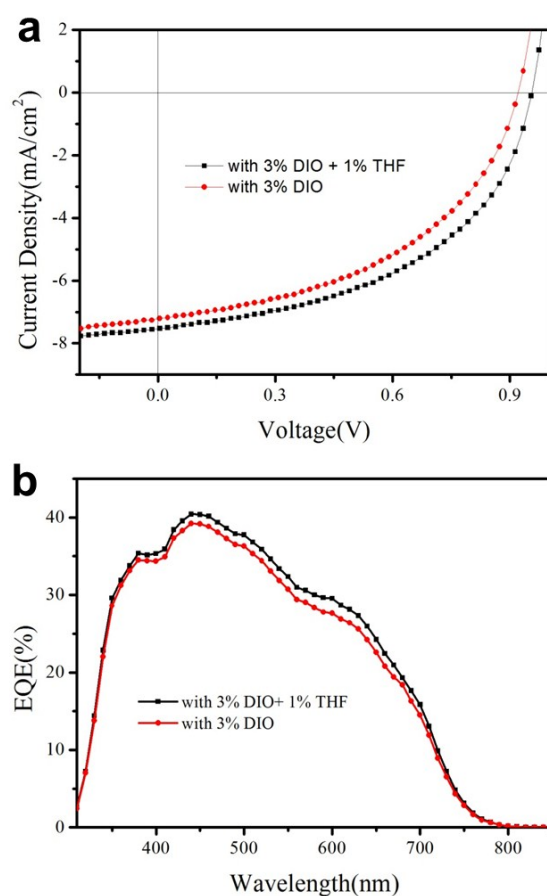
Fig S1. (a) *J-V* curve of BDT(dFBT-ON)$_2$ based BHJ solar device. (b) exteranl quantum efficiencies (EQEs) of BDT(dFBT-ON)$_2$:PC$_{71}$BM BHJ solar device.

Film morphology

The root mean square (RMS) roughness of BDT(dFBT-ON)$_2$ are 9.86 nm, 7.96 nm and 7.53 nm. However, a big difference between the phase images of these active layers was observed. For the film without any additive solvents, the scale of phase separation was large. This over-aggregation structure limits the J_{sc} and FF of solar cell. The film had been improved significantly after adding DIO or THF into the solution. The scale of phase was decreased and it was benefical for charge dissociation. THF was easy to volatilize for its low boiling point and played a role on the morphology adjustment. THF was easy to volatilize for its low boiling point and played a role on the morphology adjustment.[5] DIO might be extracted by THF during fabrication. The film became more compacted after the mixed solvents (DIO-THF) were used, and the interface area was increased which led to high charge mobility and J_{sc}.

In generally, the tendency was very apparent that the domain size was getting decreasing while the additive solvents were added into the solution. Dense dark

domains attributed to $PC_{71}BM$ rich regions and no obvious crystallization can be observed. Then the linear fiber structures were found when DIO was added, which had a positive effect on the charge separation and transfer.
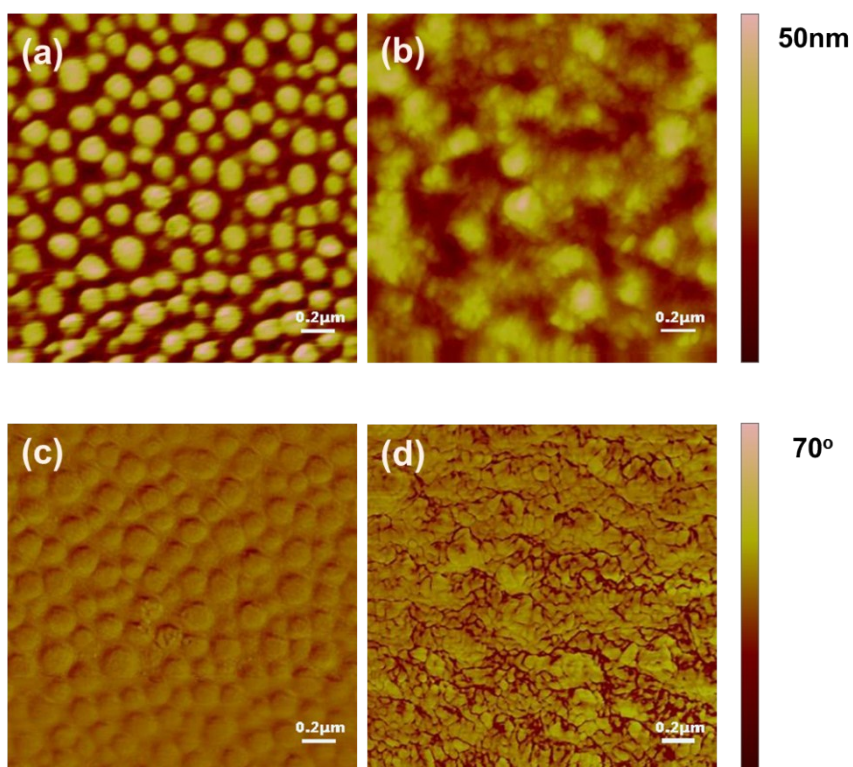

Fig. S2 AFM images of the solar cell active layer of BDT(dFBT-ON)$_2$: (a),(c) without DIO (b),(d) with 3% DIO. All the images scale are 2 μm × 2 μm.
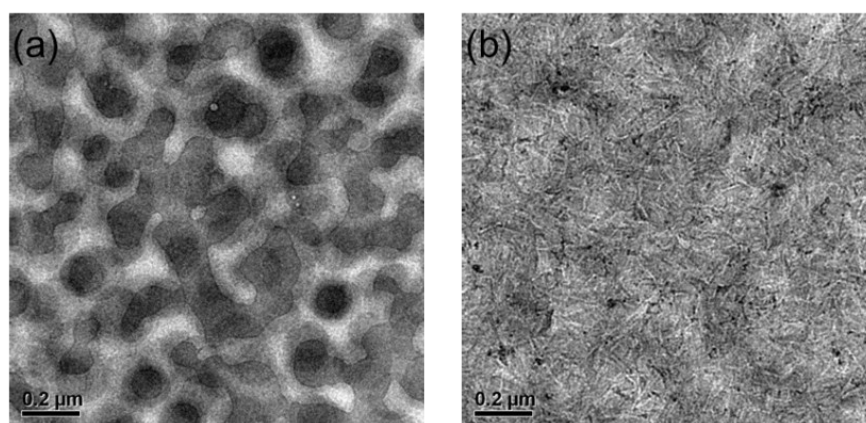

Fig. S3 TEM images of solar cell active layer of BDT(dFBT-ON)$_2$: (a) without DIO and THF, (b) with 3% DIO. The scale are all 200 nm.

Spatially periodic order

From **Fig. S4**, it is clearly seen that only the (100) peak was present without any additive solvent; while, a (200) peak was appeared after adding additive solvent, which means better crystalline structure was formed. Interestingly, the position of (100) peaks of **BDT(dFBT-ON)$_2$** was changed with additive solvent and it shifted to a lower value of 2.24 nm^{-1}, corresponding to the *d*-spacing of 2.8 nm (shown in **Fig. S4**). It means that the distance between the molecules of **BDT(dFBT-ON)$_2$** was increased, indicating that alkyl chains of **BDT(dFBT-ON)$_2$** were actually twisted and bended between the molecules without additive solvent forming a disordered arrangement on planarity.
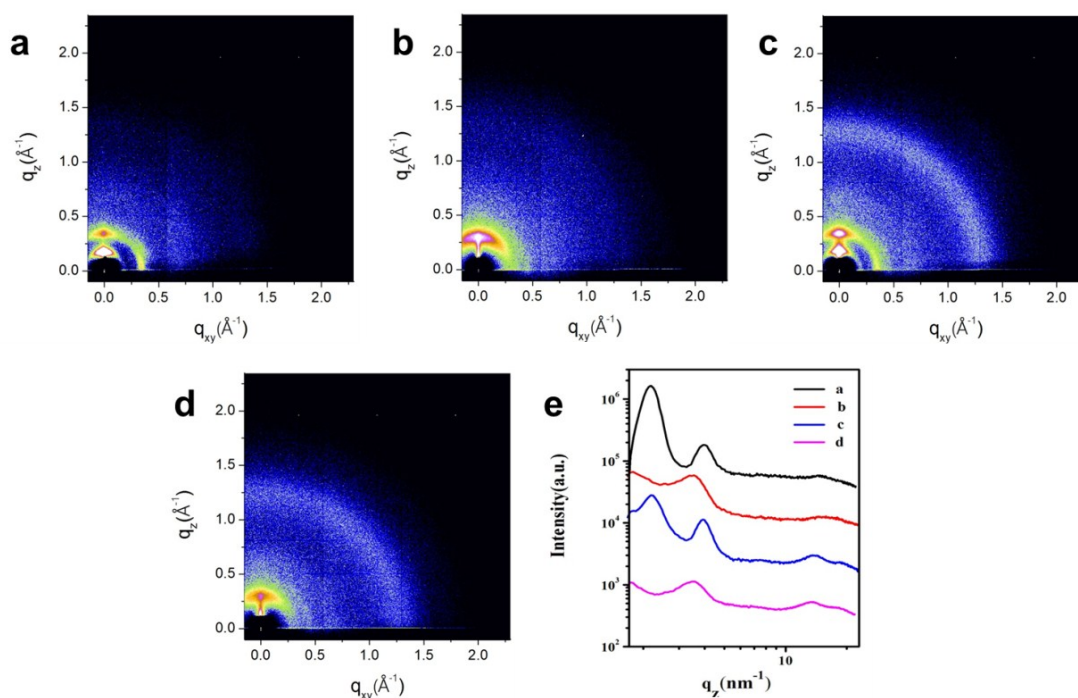

Fig. S4 GIWAXS of BDT(dFBT-ON)$_2$ based solar cell active layer: (a) BDT(dFBT-ON)$_2$-3% DIO, (b) BDT(dFBT-ON)$_2$, (c)BDT(dFBT-ON)$_2$-PC$_{71}$BM-3% DIO, (d)BDT(dFBT-ON)$_2$ - PC$_{71}$BM, (e)XRD patterns of BDT(dFBT-ON)$_2$ films.
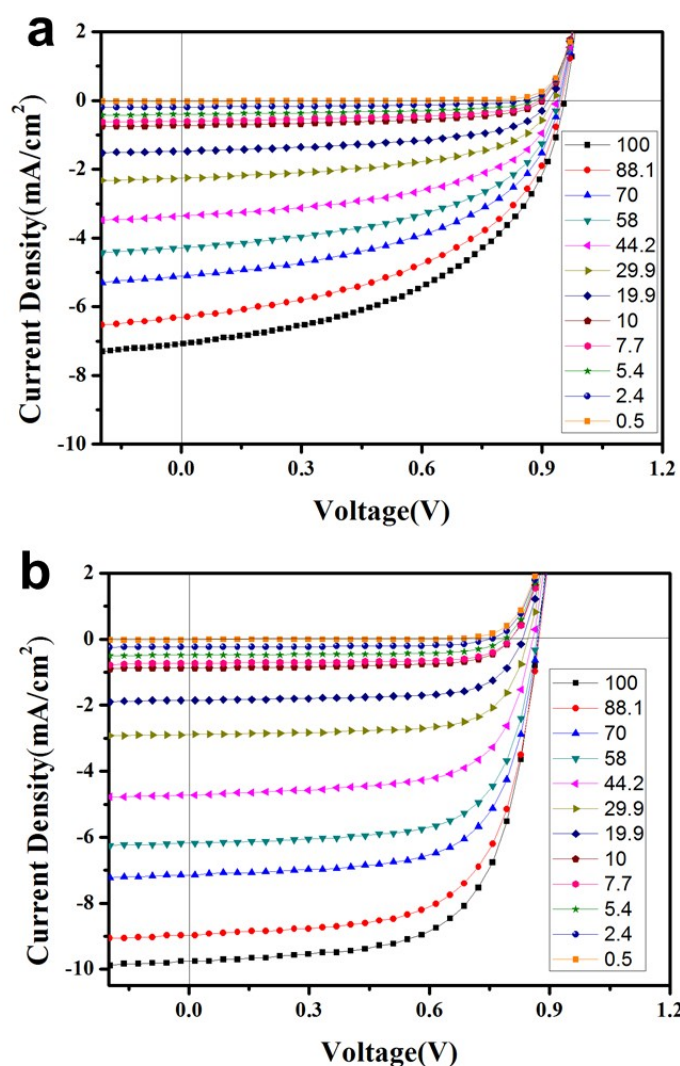
Fig. S5. J-V characteristics of SMs based solar cells under various light intensities ranging from 100 to 0.5 mW/cm2.(a)BDT(aFBT-ON)2:PCB71M with 3% DIO and 1% THF. (b)BDT(dFBT-TT)2:PC71BM.

Device fabrication and testing

ITO-coated glass substrate ($15\Omega/\square$) were cleaned by DI-water, acetone and isopropyl alcohol under ultrasonication for 20 min and then keep the substrates into the isopropyl alcohol for subsequent use. Ultraviolet ozone (UVO) for 10 min before spinning-coating the PEDOT:PSS (4083) to form a neat film with the thickness of 25~30 nm and then keeping them at 150°C for 10 min. An active layer 50 nm was coated onto the PEDOT:PSS and vacuum evaporated Ca and Al as the electron transport layer and top electrode, respectively. We investigated and studied the photovoltaic properties of this small molecules under illumination of AM 1.5 (100 mW cm^{-2}) with the device structure of ITO/PEDOT:PSS/Active layer (50 nm)/Ca (20 nm)/Al (80 nm). The ratio of the donor and acceptor ($PC_{71}BM$) is 1:1 (w/w). The

concentration of the solution is 8 mg/ml (stirred for 4 hours at room temperature in CF) for the BHJ solar device. The cathode of Ca (20 nm)/Al (80 nm) was deposited at the pressure of 2×10^{-6} Torr in the vacuum thermal evaporator. The current density–voltage (J–V) curves were obtained by a Keithley 2420 Source-Measure Unit. The photocurrent was measured under illumination using an Oriel Newport 150WSolar simulator (AM 1.5G).The EQE measurements of the devices were performed with an Oriel Newport System (Model 66902). All the measurements were performed at room temperature in air. Hole mobility was measured using the space-charge limited current (SCLC) model.[2-4] The hole only devices were fabricated in a configuration of ITO/PEDOT:PSS (35 nm)/active layer/MoO_3 (5 nm)/Au. Hole mobility can be calculated from the equation:

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where J is the current density, L is the film thickness of active layer, m is the hole mobility, ε_r (assumed to be 3) is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space, 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 across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. The dark current density–voltage curves were obtained by a Keithley 2420 Source-Measure Unit.

References

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