Morphology Control by Incorporating an Asymmetric Small Molecule Donor for Efficient Ternary Organic Solar Cells

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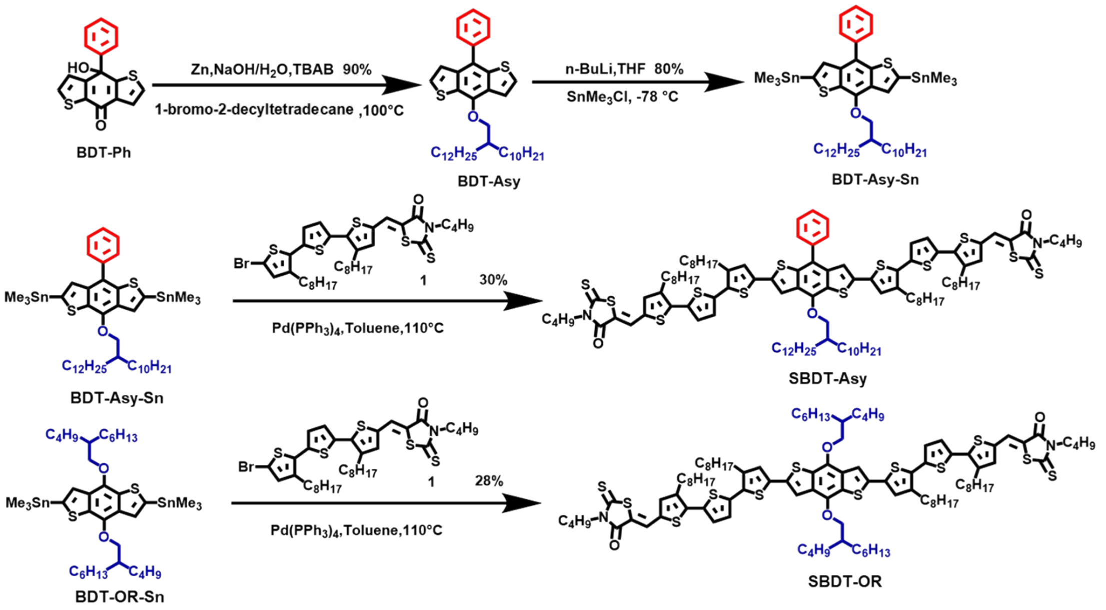
Experimental Section

Materials and Characterization Techniques. PM6, Y6 and BDT-OR-Sn were obtained from commercially as analytical grade and used directly without any purification. Compound 1 was synthesized as reported in the literature.[1] ^{1}H NMR spectra were taken on a Bruker-Avance III HD 500M and Bruker AVANCE III HD 600MHz Spectrometer. UV-Vis absorption spectrum was measured with a SHIMADZU UV-1750 spectrophotometer. Cyclic voltammetry (CV) was performed using a CS300M electrochemical workstation with a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode at a scan rate of 100 mV s^{-1}. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in acetonitrile was used as the supporting electrolyte. Donor film was prepared by drop-casting onto the glassy carbon working electrode from chloroform solution and dried before measurements. The redox potential of the Fc/Fc+ internal reference was 0.39 V vs. SCE. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels, were determined by calculating the empirical formulas of $E_{\mathrm{HOMO}} = -e(E_{\mathrm{ox}} + 4.8 - E_{1/2}^{(\mathrm{Fc/Fc+})})$, $E_{\mathrm{LUMO}} = -e(E_{\mathrm{red}} + 4.8 - E_{1/2}^{(\mathrm{Fc/Fc+})})$, where E_{ox} and E_{red} were the onset oxidation potential and the onset reduction potential, respectively. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. TEM samples of the blends were prepared under the corresponding optimized device conditions. The blend films were mounted on Formvar coated copper grids.

Fabrication of OSCs. The conventional binary and ternary device structure was prepared, with the structure being ITO / PEDOT:PSS / active layer / PDINN / Ag. The glass substrates coated with ITO were ultrasonically cleaned using detergent, deionized water, acetone and isopropyl alcohol. The cleaned indium tin oxide (ITO) substrates were dried with high-purity nitrogen gas and then treated with oxygen plasma for 1500 seconds. The PEDOT:PSS solution was filtered through a 0.22-micron filter membrane and then spin-coated onto the ITO substrates at a rotation speed of 5000 revolutions per minute for a spin-coating time of 25 seconds. Subsequently, the ITO substrates coated with the PEDOT:PSS film were heated in air at 150 °C for 15 minutes to remove the moisture in the film, and then they were transferred into a nitrogen-filled glove box. The chloroform solutions containing photovoltaic materials were stirred at 50 °C for 1 hour in advance and then spin-coated onto the PEDOT:PSS layer at a rotation speed of

3000 revolutions per minute for a spin-coating time of 30 seconds. After that, the intermediate layer material PDINN (with a concentration of 1 mg/mL in methanol) was spin-coated onto the active layer at a rotation speed of 3000 revolutions per minute for a spin-coating time of 30 seconds. Finally, 100-nanometer-thick silver was deposited under vacuum conditions. The effective area of the OSC device is 0.04 cm^2. The hole mobility and electron mobility were measured by space-charge-limited current (SCLC) method with a device configuration of ITO/ZnO/active layer/PDINN/Ag and ITO/PEDOT:PSS/active layer/MoO_3/Ag, respectively.

Synthesis



Scheme S1. Synthetic routes of the small molecules.

Synthesis of Compound BDT-Asy:

Compound BDT-Ph (440 mg, 1.47 mmol) and zinc powder (241 mg, 3.7 mmol) were put into a 100 mL flask under nitrogen, then 3.2 g of NaOH in water (40 mL) was added into the mixture. The mixture was well stirred and heated to reflux for 3 h. Then, 1-bromo-2-decyltetradecane (1.54 g, 3.7 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. After being refluxed overnight, the reactant was poured into cold water and extracted by petroleum ether. The organic phase was dried over Na_2SO_4. After removing the solvent under vacuum, residue was purified by silica column chromatography with petroleum ether to give compound BDT-Asy as a colorless oil (825 mg, 90%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 2H), 7.56-7.51 (m, 3H), 7.47-7.43 (m, 1H), 7.39-7.35 (m, 2H), 7.28-7.26 (m, 1H), 4.27 (d, J = 5.5 Hz, 2H), 1.93-1.88 (m, 1H), 1.68-1.62 (m, 2H), 1.53-1.26 (m, 38H), 0.90-0.85 (m, 6H).

Synthesis of Compound BDT-Asy-Sn:

To a solution of compound BDT-Asy (820 mg, 1.32 mmol) in THF (50 mL) at -78 °C was added dropwise *n*-BuLi (2.6 mL, 4.24 mmol, 1.6 M in tetrahydrofuran) under nitrogen. The mixture was stirred at -78 °C for 1 h and then warmed to room temperature for 0.5 h. After cooling back to -78 °C again, trimethyltin chloride (4.6 mL, 4.62 mmol, 1 M in hexane) was added in one portion. The mixture was brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and extracted by petroleum ether. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was recrystallized by ethanol. Compound BDT-Asy-Sn was obtained as a white solid (998 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 2H), 7.63-7.58 (m, 1H), 7.56-7.53 (m, 2H), 7.47-7.44 (m, 1H), 7.31-7.26 (m, 1H), 4.29 (d, J = 5.3 Hz, 2H), 1.93-1.88 (m, 1H), 1.71-1.65 (m, 2H), 1.51-1.26 (m, 38H), 0.90-0.86 (m, 6H), 0.46-0.33 (m, 18H).

Synthesis of Compound SBDT-Asy:

A solution of compound BDT-Asy-Sn (189 mg, 0.20 mmol) and compound 1 (376 mg, 0.50 mmol) in dry toluene (15 mL) was degassed several times with nitrogen followed by the addition of $Pd(PPh_3)_4$ (15 mg). After stirring at 110 °C for 24 h under argon, the mixture was poured into water and extracted with $CHCl_3$. The residue was purified by silica gel chromatography using a mixture of petroleum and dichloromethane (3/1, v/v) as eluent to afford compound SBDT-Asy as a black solid (115 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 2.0 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.61-7.59 (m, 2H), 7.55 (s, 1H), 7.27 (s, 1H), 7.24-7.21 (m, 5H), 7.15-7.12 (m, 3H), 7.10-7.08(m, 1H), 4.29 (d, J = 5.3 Hz, 2H), 4.14-4.10 (m, 4H), 2.83-2.76 (m, 8H), 1.96-1.93 (m, 1H), 1.70 (d, J = 6.1 Hz, 12H), 1.38-1.22 (m, 78H), 0.98-0.95 (m, 6H), 0.91-0.80 (m, 24H).

Synthesis of Compound SBDT-OR:

A solution of compound BDT-OR-Sn (133 mg, 0.15 mmol) and compound 1 (282 mg, 0.38 mmol) in dry toluene (10 mL) was degassed several times with nitrogen followed by the addition of $Pd(PPh_3)_4$ (15 mg). After stirring at 110 °C for 24 h under argon, the mixture was poured into water and extracted with $CHCl_3$. The residue was purified by silica gel chromatography using a mixture of petroleum and dichloromethane (2/1, v/v) as eluent to afford compound SBDT-OR as a black solid (80 mg, 28%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (s, 2H), 7.50 (s, 2H), 7.25-7.24 (m, 4H), 7.17-7.15 (m, 4H), 4.21

(d, J = 5.4 Hz, 4H), 4.14-4.11 (m, 4H), 2.85-2.80 (m, 8H), 1.91-1.88 (m, 2H), 1.72-1.68 (m, 12H), 1.43-1.28 (m, 76H), 0.99-0.97 (m, 6H), 0.92-0.87 (m, 24H).

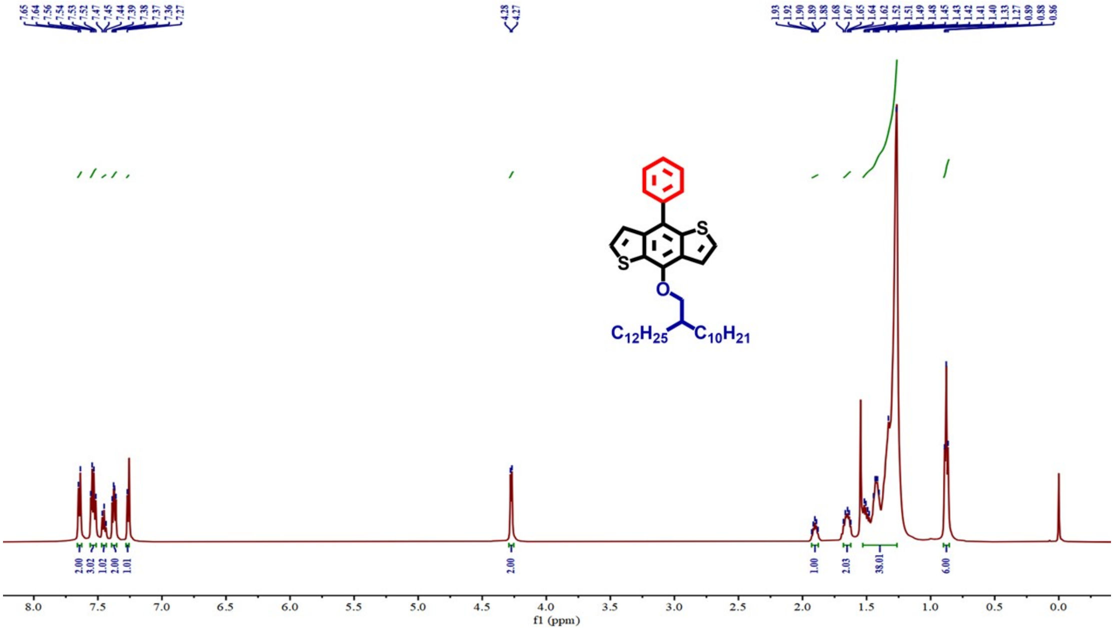


Fig. S1. ^{1}H NMR spectrum of compound BDT-Asy in $CDCl_3$ at room temperature.

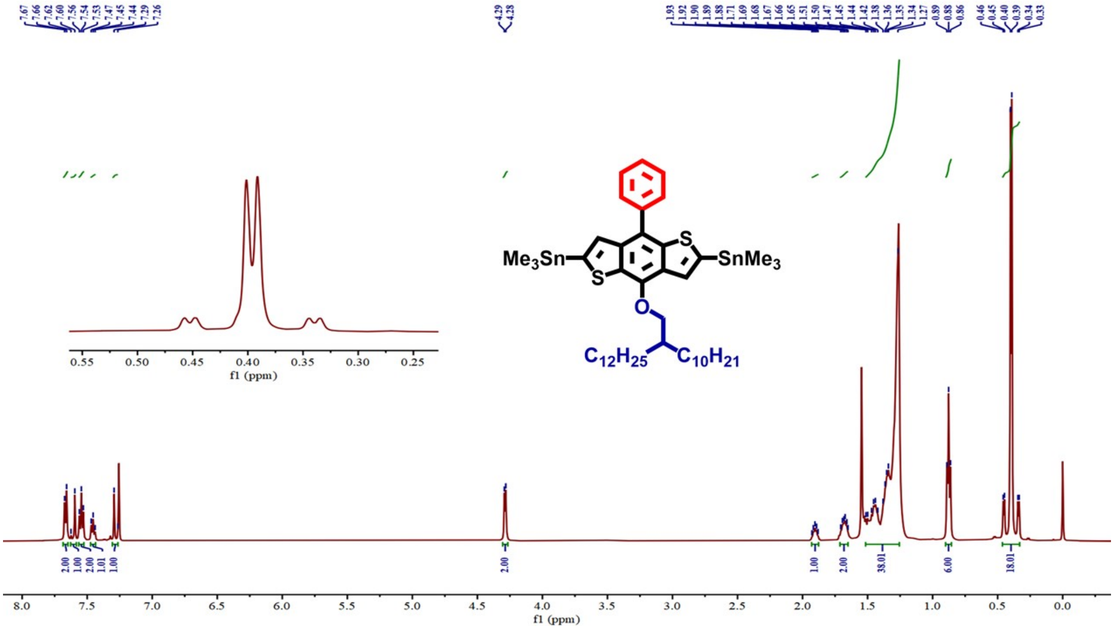


Fig. S2. ^{1}H NMR spectrum of compound BDT-Asy-Sn in $CDCl_3$ at room temperature.

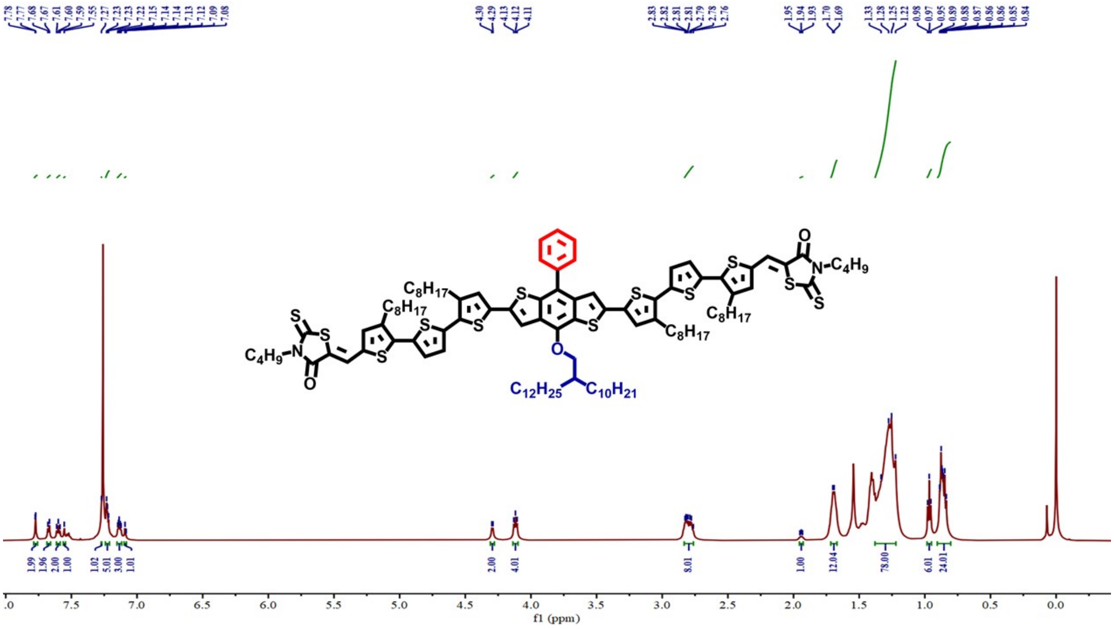


Fig. S3. ^{1}H NMR spectrum of compound SBDT-Asy in $CDCl_3$ at room temperature.

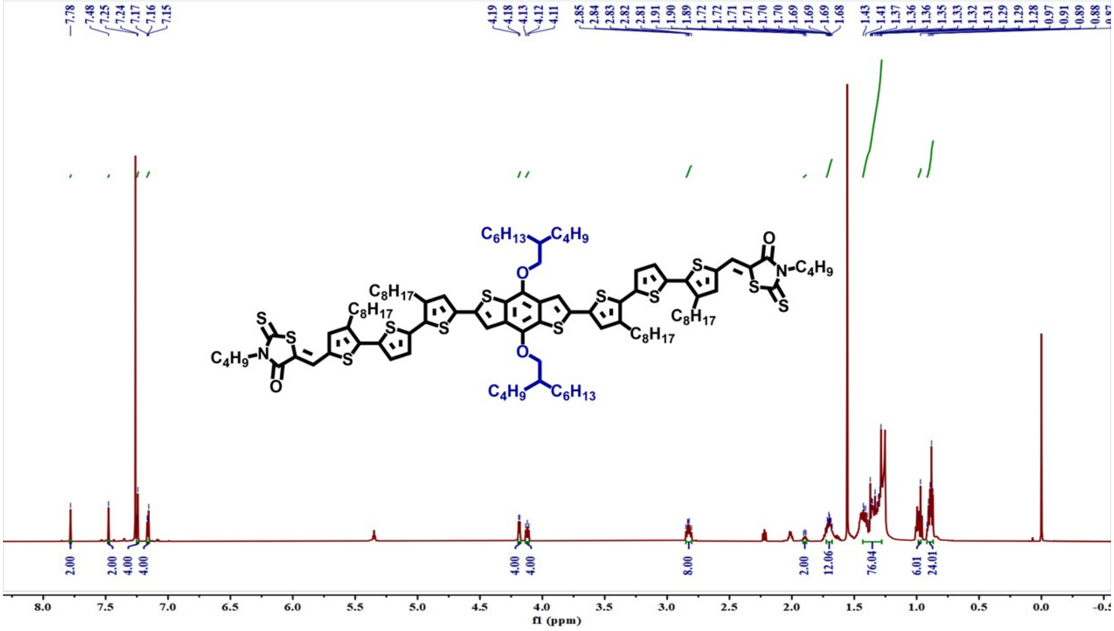


Fig. S4. ^{1}H NMR spectrum of compound BDT-OR in $CDCl_3$ at room temperature.

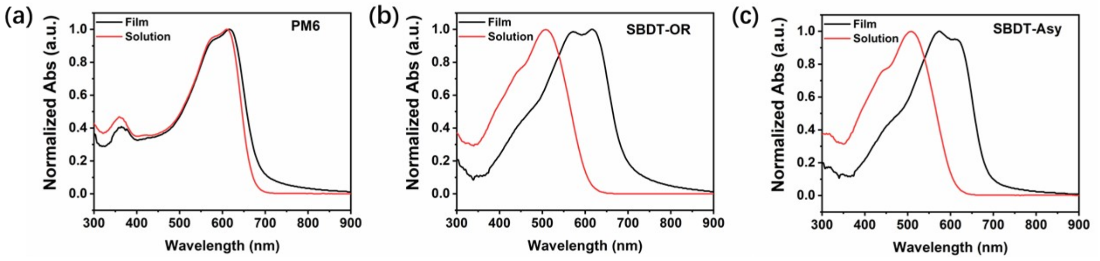


Fig. S5. Normalized UV-vis absorption spectra of the (a) PM6, (b) SBDT-OR, and (c) SBDT-Asy in thin film and in chloroform solution at room temperature (~20 °C).

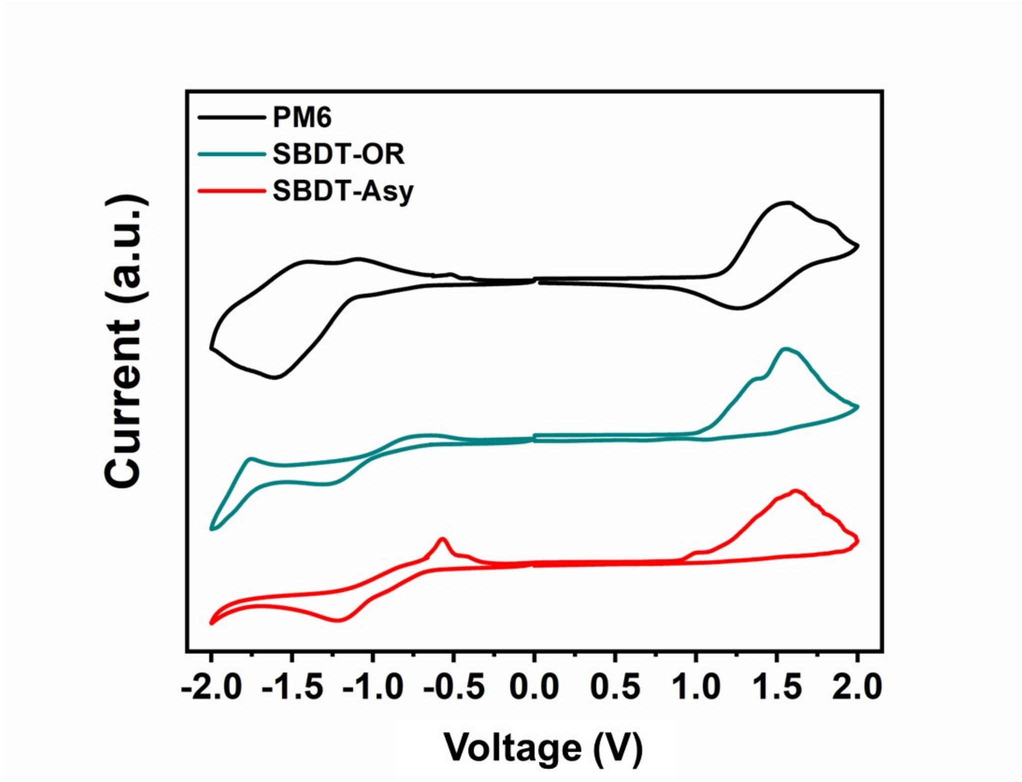


Fig. S6. Electrochemical cyclic voltammogram curves of PM6, SBDT-OR and SBDT-Asy.

Table S1. Optical and electrochemical properties of the donor.

Donor	λFilm max (nm)	λFilm onset (nm)	λSol max (nm)	λSol onset (nm)	$E_g^{opt(a)}$ (eV)	HOMO[b] (eV)	HOMO[b] (eV)	HOMO[c] (eV)	LUMO[c] (eV)
PM6	614	686	608	668	1.81	-5.59	-3.73	—	—
SBDT-OR	614	700	508	606	1.77	-5.48	-3.71	-5.32	-3.01
SBDT-Asy	576	686	508	606	1.81	-5.48	-3.70	-5.31	-3.00

(a) Calculated from the empirical formula: $E_g^{opt} = 1240/\lambda_{onset}$; (b) Cyclic voltammetry (CV) method by measuring film. (c) Calculated from the DFT.

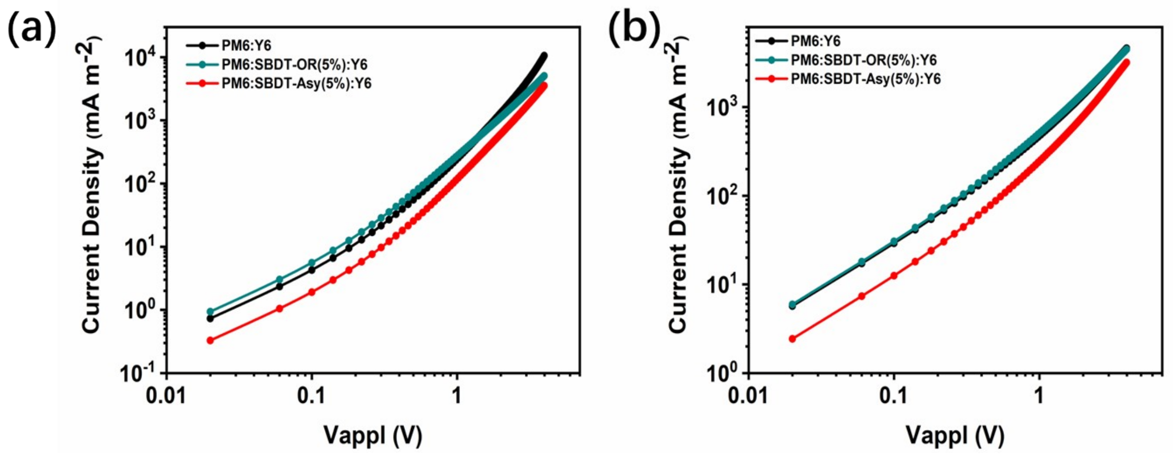


Fig. S7. The current-density-voltage (*J-V*) plots for the optimized hole-only (a) and electron-only (b) devices.

Table S2. Photovoltaic parameters of the OSCs based on PM6:Y6, PM6:SBDT-OR:Y6 and PM6:SBDT-Asy:Y6.

Active Layer	D/A(*w*/*w*)	V_{oc} a) (V)	J_{sc} a) (mA/cm^2)	FF a) (%)	PCE$_{max}$ a) (%)
PM6:Y6	1:1.2	0.86(0.84±0.01)	26.42(26.01±0.37)	71.55(71.00±0.52)	16.24(15.94±0.30)
PM6:SBDT-OR:Y6	0.95:0.05:1.2	0.86(0.84±0.01)	26.72(26.25±0.41)	72.68(71.56±1.10)	16.79(16.34±0.30)
	0.9:0.1:1.2	0.87(0.85±0.01)	25.82(25.45±0.31)	71.95(70.90±1.01)	16.16(15.82±0.31)
	0.8:0.2:1.2	0.87(0.85±0.01)	25.50(25.10±0.41)	71.51(70.40±1.12)	15.81(15.45±0.34)
PM6:SBDT-Asy:Y6	0.95:0.05:1.2	0.86(0.86±0.01)	26.99(26.68±0.32)	76.23(75.54±0.64)	17.68(17.28±0.30)
	0.9:0.1:1.2	0.87(0.86±0.01)	26.94(26.54±0.36)	72.04(71.41±0.61)	16.90(16.49±0.30)
	0.8:0.2:1.2	0.86(0.85±0.01)	26.82(26.51±0.28)	70.44(69.75±0.72)	16.33(16.01±0.31)

a) Values for the highest PCE device, with average values were obtained from 10 devices listed in parentheses.

Table S3. Photovoltaic parameters of the OSCs based on SBDT-OR:Y6 and SBDT-Asy:Y6.

Active Layer	D/A (*w*/*w*)	V_{OC} a) (V)	J_{SC} a) (mA/cm^2)	FF a) (%)	PCE a) (%)
SBDT-OR:Y6	1.1:1	0.75(0.73±0.01)	10.01(9.56±0.44)	40.86(39.74±1.01)	3.05(2.82±0.13)
SBDT-Asy:Y6	1.1:1	0.80(0.79±0.01)	11.58(11.25±0.31)	44.38(43.66±0.52)	4.09(3.74±0.26)

a) Values for the highest PCE device, with average values were obtained from 10 devices listed in parentheses.

Table S4. Hole mobilities and electron mobilities of active layers.

Active Layer	D/A(*w*/*w*)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PM6:Y6	1:1.2	5.51×10^{-4}	4.85×10^{-4}	1.14
PM6:SBDT-OR:Y6	0.95:0.05:1.2	5.62×10^{-4}	5.08×10^{-4}	1.11
PM6:SBDT-Asy:Y6	0.95:0.05:1.2	5.78×10^{-4}	5.55×10^{-4}	1.04

Reference

1. D. Han, M. Ding, B. Tang, K. Song, J. Lv, X. Bao and M. Sun, *J. Mater. Chem. C.*, 2024, **12**, 18472.