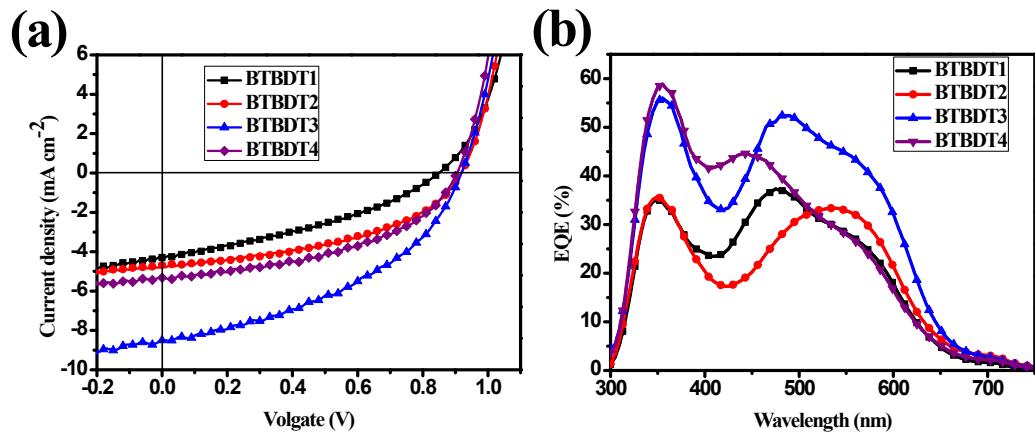


## **Electronic Supplementary Information**

### **Synthesis, characterization and photovoltaic properties of benzo[1,2-*b*:4,5-*b'*]dithiophene-bridged molecules**

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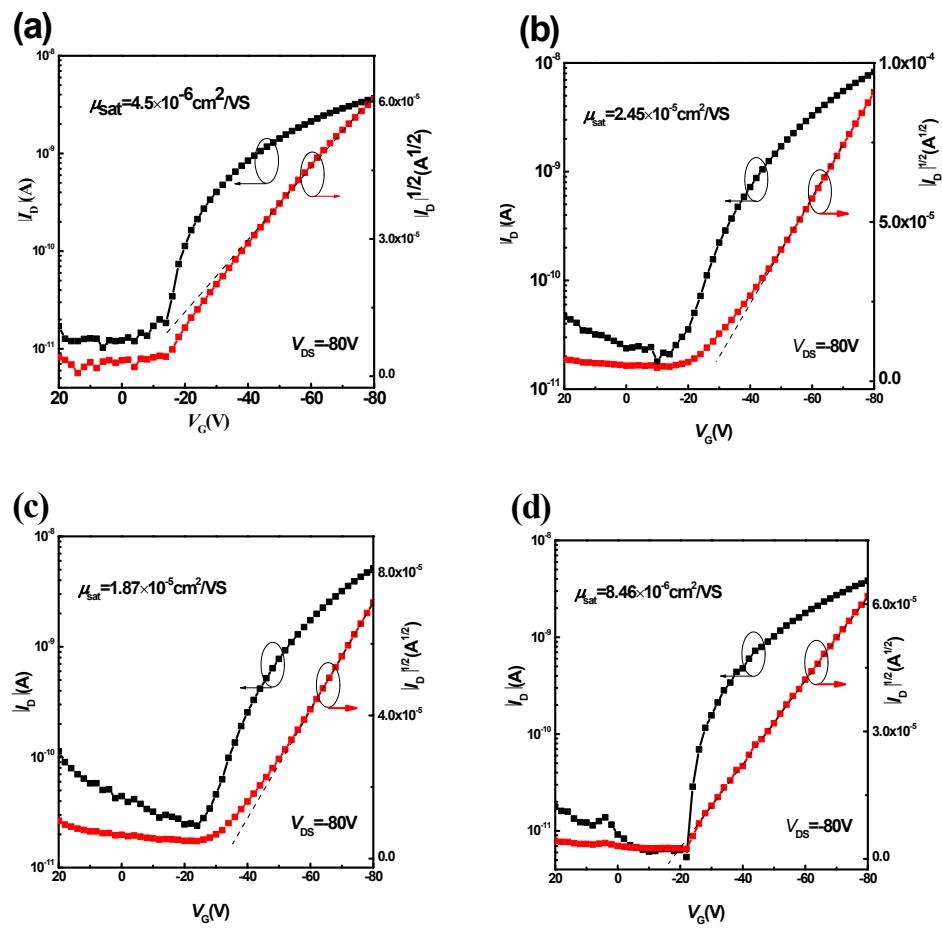
**Fig. S1** (a) Current–density ( $J$ – $V$ ) curves and (b) EQE spectra of the OSC devices with the blend ratio of **BTBDT1**–**BTBDT4**/PC<sub>61</sub>BM = 1:3 (w/w) under the illumination of AM 1.5G, 100 mW cm<sup>-2</sup>.

**Table S1** Photovoltaic properties of the OSCs based on donor/PC<sub>61</sub>BM (different ratio, w/w) under illumination of AM 1.5G, 100 mW cm<sup>-2</sup>.

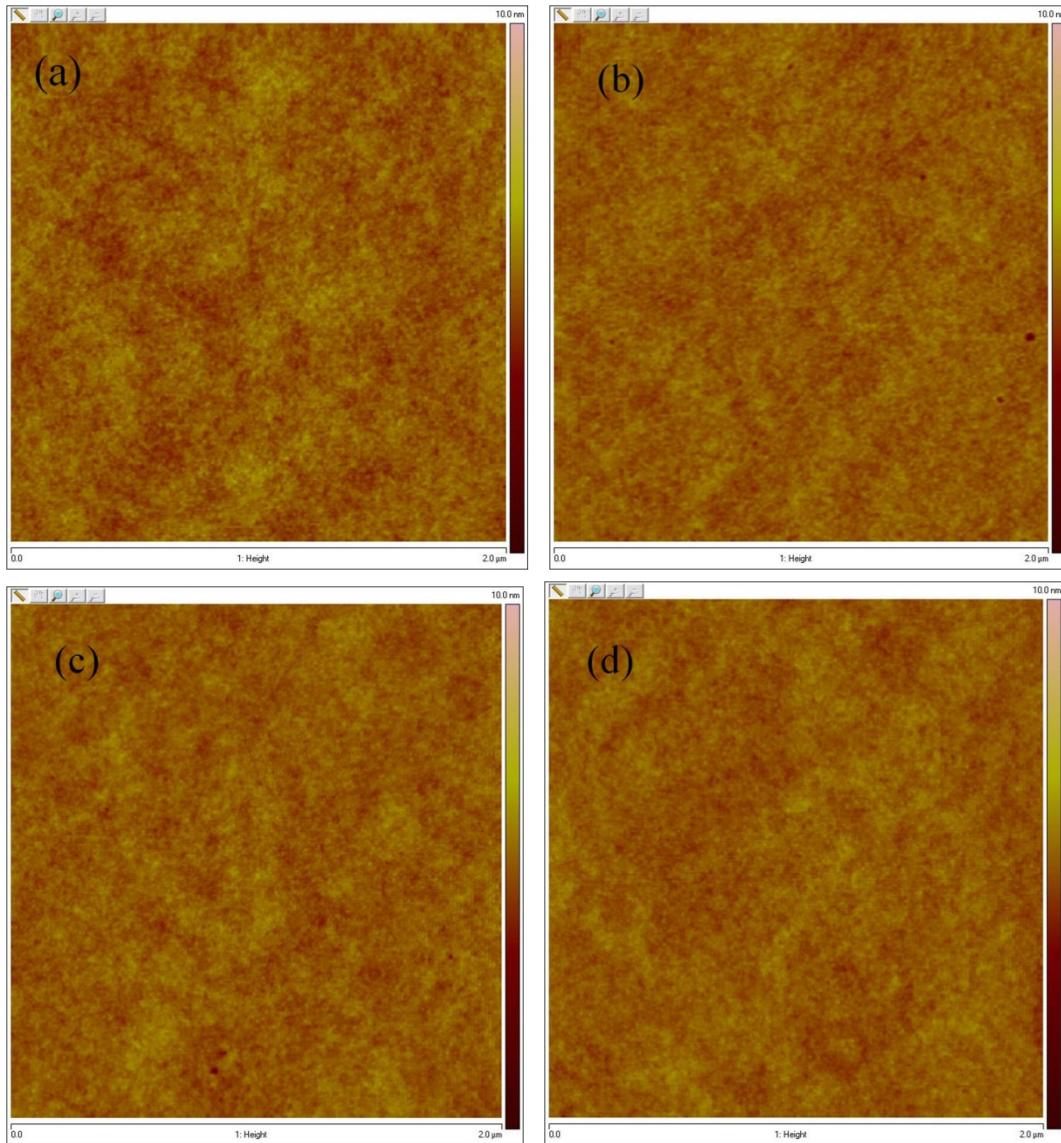
Donor	Donor : PC <sub>61</sub> BM (w/w)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF	PCE (%)
BTBDT1	1 : 2	0.88	3.57	37.9	1.19
	1 : 3	0.85	4.29	35.6	1.30
	1 : 4	0.81	3.01	35.7	0.87
BTBDT2	1 : 2	0.92	4.61	41.8	1.78
	1 : 3	0.92	4.68	45.9	1.98
	1 : 4	0.90	4.85	42.6	1.86
BTBDT3	1 : 2	0.95	5.50	36.2	1.89
	1 : 3	0.92	8.50	42.6	3.33
	1 : 4	0.91	5.88	46.6	2.49
BTBDT4	1 : 2	0.88	5.38	40.8	1.93
	1 : 3	0.90	5.32	46.8	2.24
	1 : 4	0.73	3.94	34.6	0.99

**Table S2** HOMO-1, HOMO, LUMO and LUMO+1 energy levels and  $E_g$  as determined by theoretical calculations for **BTBDT1–BTBDT4**.

	<b>HOMO-1</b> (eV)	<b>HOMO</b> (eV)	<b>LUMO</b> (eV)	<b>LUMO+1</b> (eV)	<b><math>E_g</math> (eV)</b>
<b>BTBDT1</b>	-5.57	-4.98	-3.09	-2.89	1.89
<b>BTBDT2</b>	-4.88	-4.69	-2.85	-2.66	1.70
<b>BTBDT3</b>	-4.97	-4.74	-2.92	-2.75	1.82
<b>BTBDT4</b>	-4.86	-4.73	-2.88	-2.79	1.85



**Fig. S2** Transfer characteristics at  $V_{\text{DS}} = -80$  V from (a) **BTBDT1**, (b) **BTBDT2**, (c) **BTBDT3** and (d) **BTBDT4**.



**Fig. S3** Topography images obtained by tapping mode AFM of the blend films spin-coated from chloroform solutions of **BTBDT1–BTBDT4:PC<sub>71</sub>BM** in a weight ratio of 1:2: (a) **BTBDT1/PC<sub>71</sub>BM**, (b) **BTBDT2/PC<sub>71</sub>BM**, (c) **BTBDT3/PC<sub>71</sub>BM** and (d) **BTBDT4/PC<sub>71</sub>BM**.