

## Support Information

### **Regioselective acylation directing aromatic substituents in simple nonfullerene acceptors for efficient organic solar cells**

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**Materials:** All reagents and solvents were purchased from commercial sources (like J&K, Energy Chemical, Derthon, and Acros) and used without further purification unless otherwise specified. Compound 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde was synthesized according to a previous report.<sup>1</sup> All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon.

### **Device Fabrication and Characterization:**

The device structure was ITO/ZnO/Donor: Acceptor/MoO<sub>3</sub>/Al. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 15–20 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath that began with deionized water, followed by acetone and 2-propanol. A solution-processed zinc oxide (ZnO) interlayer of 30 nm was prepared according to a recent report.<sup>2</sup> The substrates were then transferred into a nitrogen-filled glove box. Active layer solutions with PM6 and acceptor (Ph-BDD or C4Ph-BDD) were prepared in chlorobenzene (CB) solvent. The active layer (ca. 110 nm) was spin-coated on the ZnO layer from a 20 mg/mL CB solution at a spin rate of 1800 r.p.m. The thickness of the active layer was verified by a surface profilometer (Tencor Alpha-500, USA). A 10 nm MoO<sub>3</sub> layer and a 100 nm Al layer were subsequently evaporated through a shadow mask to define the active area of the devices (5.8 mm<sup>2</sup>) and form the top anode.

The PCE was determined from *J-V* curve measurements (using a Keithley 2400 sourcemeter) under a 1 sun, AM 1.5G spectrum from a solar simulator (Oriel model 91192; 1000 W m<sup>-2</sup>). All the masked and unmasked tests gave consistent results with relative errors within 5%. The solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Enli/SRC2020, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). Theoretical *J<sub>sc</sub>* values obtained by integrating the product of the EQE with the AM 1.5G solar spectrum agreed with the measured value to within 5%.

Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of active layers using the space charge limited current (SCLC)

method with the hole-only device of ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al and electron-only device of ITO/ZnO/Active layer/PFN-Br/Al. The mobilities ( $\mu$ ) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where  $J$  is the current,  $E$  is the effective electric field,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the material relative permittivity,  $d$  is the thickness of the active layer, and  $V$  is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage ( $V_{bi}$ ) and the voltage drop ( $V_s$ ) from the substrate's series resistance from the applied voltage ( $V_{appl}$ ),  $V = V_{appl} - V_{bi} - V_s$ . The mobility can be calculated from the slope of the  $J^{1/2} \sim V$  curves.

The electrochemical behavior of the accepters was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution in CH<sub>3</sub>CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/s. A carbon plate working electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and the assumption that the energy level of Fc is 4.8 eV below vacuum.

The contact angle tests were performed on a Dataphysics OCA40 Micro surface contact angle analyzer. The surface energy of the polymers and accepters was characterized and calculated by the contact angles of the two probe liquids (water and Ethylene glycol) using the Wu model.<sup>3,4</sup>

### *Synthesis of compound 1a*

In a 50 mL two-necked flask, bromobenzene (2.34 g, 15 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (2.0 g, 6 mmol), Cs<sub>2</sub>CO<sub>3</sub> (9.77 g, 30 mmol), and tetrakis(triphenylphosphine)palladium (0.31 g, 0.26 mmol) were dissolved in 30 mL of ultra-dry *o*-xylene. And then the solution was heated at 110 °C overnight. After cooled to room temperature, the crude product was extracted with dichloromethane, washed with water, and dried with anhydrous magnesium sulfate. After removing the solvent, the product was purified by silica gel column chromatography. Compound **1a** was obtained as a white solid (0.82 g, 3.48 mmol, 58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.64-7.62 (m, 4H), 7.48-7.47 (m, 6H), 7.30 (s, 2H).

### *Synthesis of compound 1b*

The synthesis of compound **1b** was carried out similarly as described for compound **1a**, with *p*-bromobutylbenzene as the starting material. Compound **1b** was obtained as a white solid (1.68 g, 3.6 mmol, 60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 7.54 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.64-2.60 (m, 2H), 1.65-1.58 (m, 2H), 1.42-1.33 (m, 2H), 0.96-0.92 (m, 3H).

### *Synthesis of compound 2a*

In a 100 mL two-necked flask, 2,5-dibromo-3,4-thiophenedicarboxylic acid (1.15 g, 3.48 mmol) was dissolved in 30 mL of ultra-dry dichloromethane, and then 1 mL ultra-dry N,N-dimethylformamide was added. Subsequently, oxalyl chloride (1.77 g, 14 mmol) was added dropwise in the reaction. The reaction was proceeded at room temperature for more than 12 hours. After removing the solvent of the crude product, a yellow intermediate was obtained and directly used without further purification. The yellow intermediate and compound **1a** were dissolved in 30 mL of ultra-dry dichloromethane, and then aluminium chloride (1.86 g, 14 mmol) was added in three times at 0 °C. After that, the reaction was warmed to room temperature slowly and reacted overnight. The crude product was extracted with dichloromethane, washed with water, and dried with anhydrous magnesium sulfate. After removing the solvent, the product was purified by silica gel column chromatography. Compound **2a** was obtained

as a yellow solid (1.11 g, 2.1 mmol, 60% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.64-7.62 (m, 4H), 7.48-7.47 (m, 6H).

#### *Synthesis of compound 2b*

The synthesis of compound **2b** was carried out similarly as described for compound **2a** by replacing **1a** with **1b**. Compound **2b** was obtained as a yellow solid (1.5 g, 2.34 mmol, 65% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.56 (d,  $J = 6.4$  Hz, 4H), 7.29 (d,  $J = 6.8$  Hz, 4H), 2.69-2.66 (m, 4H), 1.69-1.53 (m, 4H), 1.45-1.38 (m, 4H), 0.98-0.95 (m, 4H).

#### *Synthesis of compound 3a*

In a 50 mL two-necked flask, compound **2a** (430 mg, 0.8 mmol), 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (0.94 g, 2.2 mmol), trimethylacetic acid (0.08 g, 0.8 mmol), and  $\text{Cs}_2\text{CO}_3$  (2.1 g, 6.4 mmol) were dissolved in 20 mL ultra dry *o*-xylene.  $\text{Pd}_2(\text{dba})_3$  (0.07 g, 0.08 mmol) and  $\text{P}(o\text{-CH}_3\text{OPh})_3$  (0.06 g, 0.16 mmol) were added in the reaction mixture and then the solution was heated at 120 °C for 16 hours. The crude product was extracted with dichloromethane, washed with water, and dried with anhydrous magnesium sulfate. After removing the solvent, the product was purified by silica gel column chromatography. Compound **3a** was obtained as a red solid (0.68 g, 0.54 mmol, 70% yield)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.86 (s, 2H), 7.76-7.74 (m, 2H), 7.69-7.67 (m, 4H), 7.59-7.58 (m, 2H), 7.49-7.48 (m, 6H), 2.01-1.93 (m, 8H), 0.99-0.93 (m, 36H), 0.77-0.73 (m, 16H), 0.65-0.60 (m, 12H).

#### *Synthesis of compound 3b*

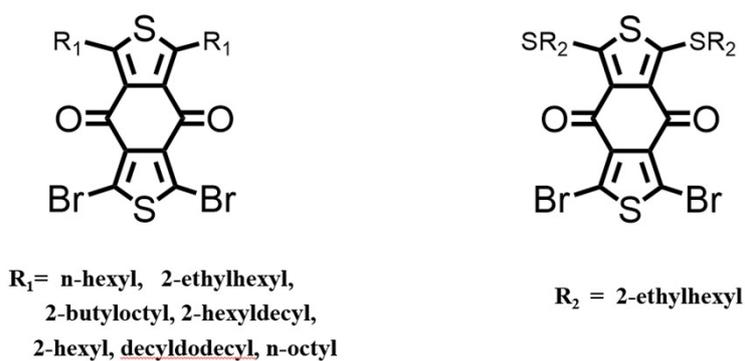
The synthesis of compound **3b** was carried out similarly as described for compound **3a** by replacing **2a** with **2b**. Compound **3b** was obtained as a red solid (0.73 g, 0.54 mmol, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 9.865 (s, 2H), 7.74-7.72 (m, 2H), 7.62 (d,  $J = 8$  Hz, 4H), 7.59 (d,  $J = 4$  Hz, 2H), 7.29 (d,  $J = 8$  Hz, 4H), 2.73-2.69 (m, 4H), 1.99-1.90 (m, 8H), 1.73-1.65 (m, 4H), 1.47-1.41 (m, 4H), 1.00-0.96 (m, 36H), 0.77-0.73 (m, 12H), 0.98-0.95 (m, 12H).

### *Synthesis of Ph-BDD*

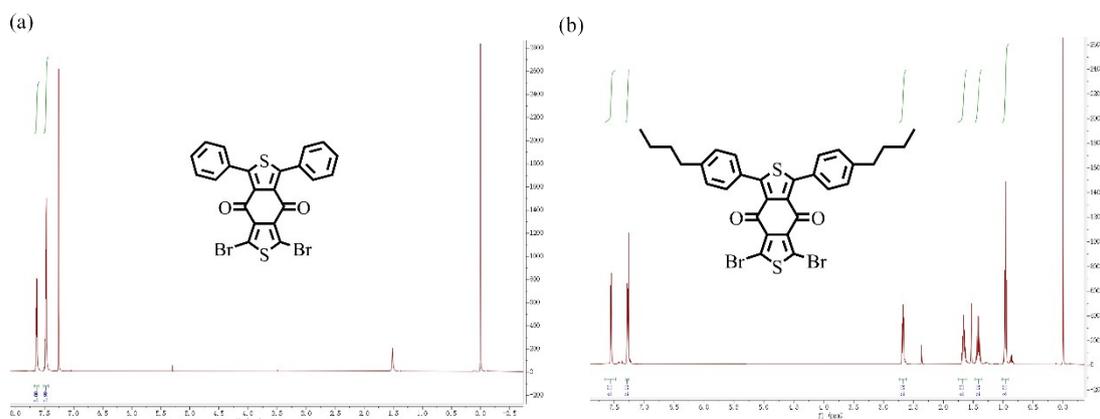
In 50 mL two-necked flask, the compound **3a** (180 mg, 0.15 mmol), (2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (100 mg, 0.45 mmol) and pyridine (0.1 mL) were dissolved in chloroform (25 mL). Then the mixture was heated at 60 °C and stirred for 4 h. After cooling to room temperature, the mixture was poured into methanol (150 mL) and filtered. The residue was purified by silica gel column chromatography using dichloromethane/petroleum ether (1/1, v/v) as the eluent to give a dark blue solid (190 mg, 0.12 mmol, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.92 (s, 2H), 8.56-8.52 (m, 2H), 7.78 (d, *J* = 8 Hz, 2H), 7.71-7.68 (m, 8H), 7.54-7.53 (m, 6H), 2.01-1.99 (m, 8H), 1.02-0.93 (m, 32H), 0.76-0.69 (m, 16H), 0.64-0.62 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 186.08, 176.36, 164.28, 164.20, 158.42, 157.55, 155.71, 155.37, 153.10, 152.97, 151.95, 142.75, 141.56, 141.44, 140.35, 139.85, 138.16, 138.08, 136.58, 134.52, 133.05, 132.02, 131.98, 129.84, 129.67, 128.40, 125.72, 124.83, 120.19, 115.04, 114.82, 114.55, 114.52, 114.48, 112.62, 112.43, 68.67, 54.18, 54.15, 43.15, 35.43, 34.29, 34.25, 34.06, 28.51, 28.47, 28.45, 27.50, 27.30, 22.83, 22.79, 14.15, 14.09, 10.59. MS (MALDI-TOF): *m/z* 1653.10 (M<sup>+</sup>).

### *Synthesis of C4Ph-BDD*

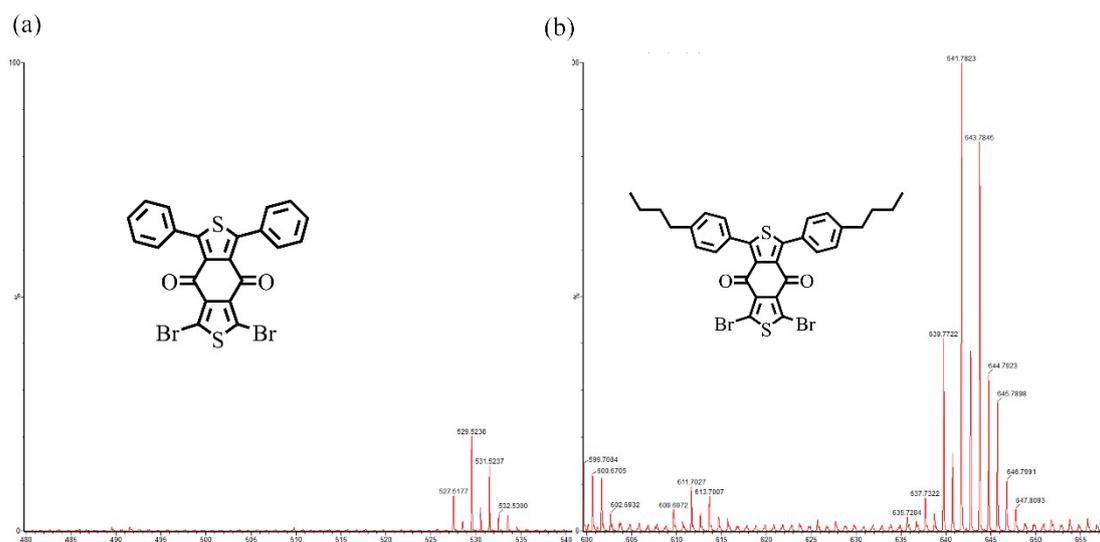
The synthesis of **C4Ph-BDD** was carried out similarly as described for compound **Ph-BDD** by replacing **3a** with **3b**. The **C4Ph-BDD** was obtained as a dark blue solid (158 mg, 0.09 mmol, 82% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.92 (s, 2H), 8.558-8.525 (m, 2H), 7.78-7.75 (d, *J* = 8 Hz, 2H), 7.69 (d, *J* = 4 Hz, 4H), 7.65 (d, *J* = 4 Hz, 4H), 7.35 (d, *J* = 4 Hz, 4H), 2.77-2.74 (m, 4H), 2.03-1.96 (m, 8H), 1.75-1.70 (m, 4H), 1.50-1.43 (m, 4H), 1.02-0.98 (m, 38H), 0.75-0.74 (m, 16H), 0.65-0.62 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm): 186.76, 176.49, 164.30, 160.22, 157.72, 153.12, 152.98, 152.25, 144.84, 142.58, 139.84, 138.20, 131.66, 129.73, 129.32, 128.44, 125.69, 120.14, 115.06, 114.84, 114.58, 112.62, 112.44, 68.33, 54.14, 43.23, 35.69, 35.43, 34.28, 34.07, 33.39, 28.53, 27.50, 27.32, 22.84, 22.81, 22.61, 14.16, 14.10, 14.03, 10.60, 10.58. MS (MALDI-TOF): *m/z* 1765.20 (M<sup>+</sup>).



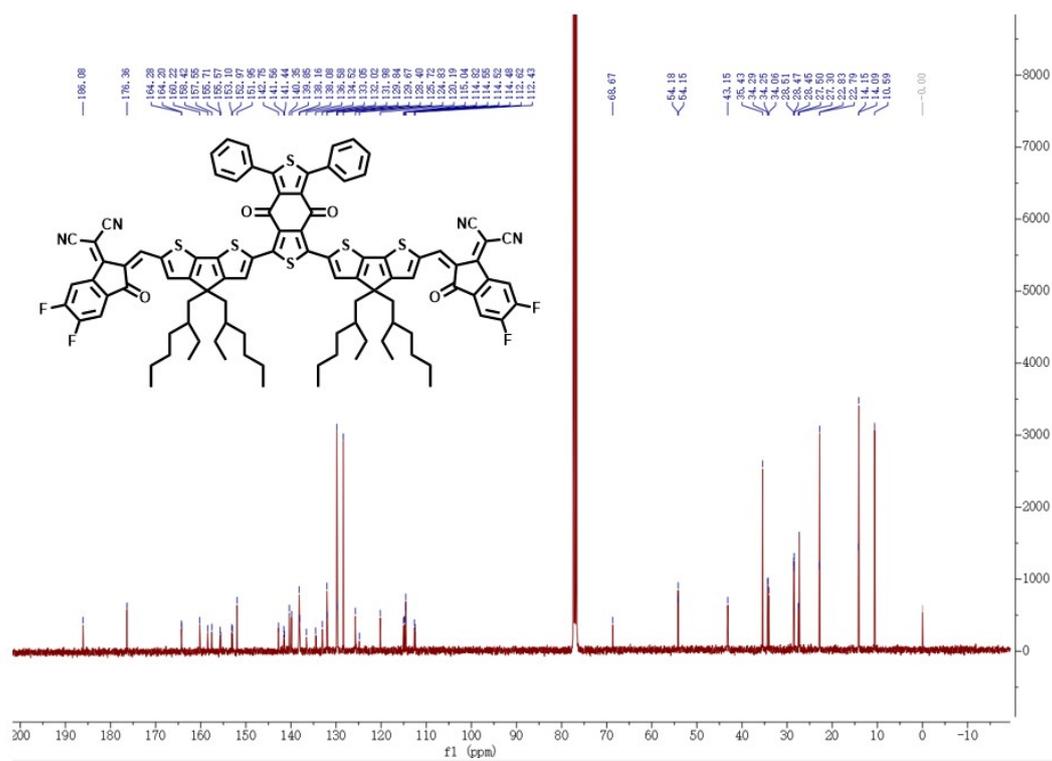
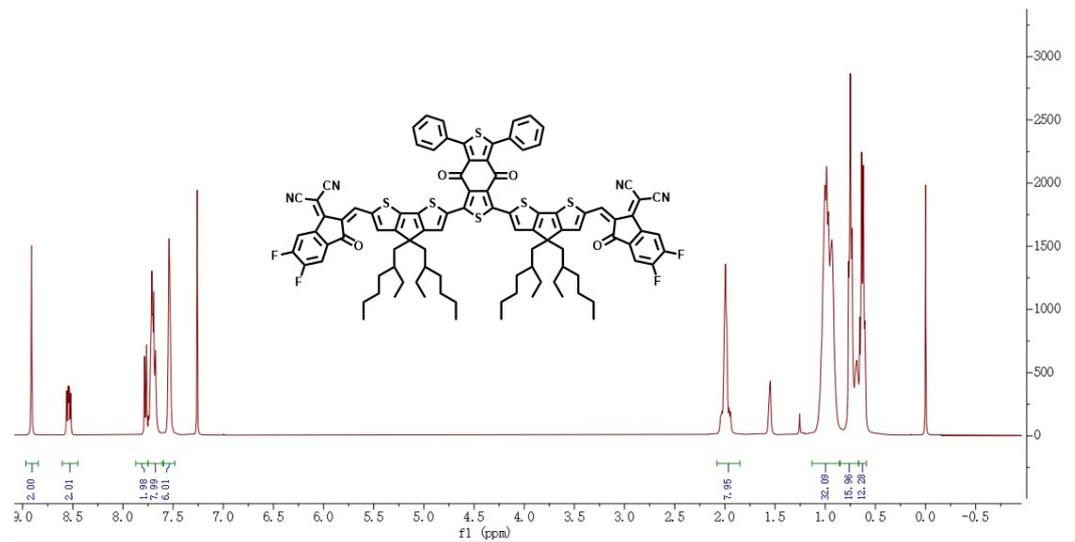
**Fig. S1** Summary of the various substitutions on benzodithiophenedione (BDD). So far, alkyl- and alkylthio-substitutions have been reported.



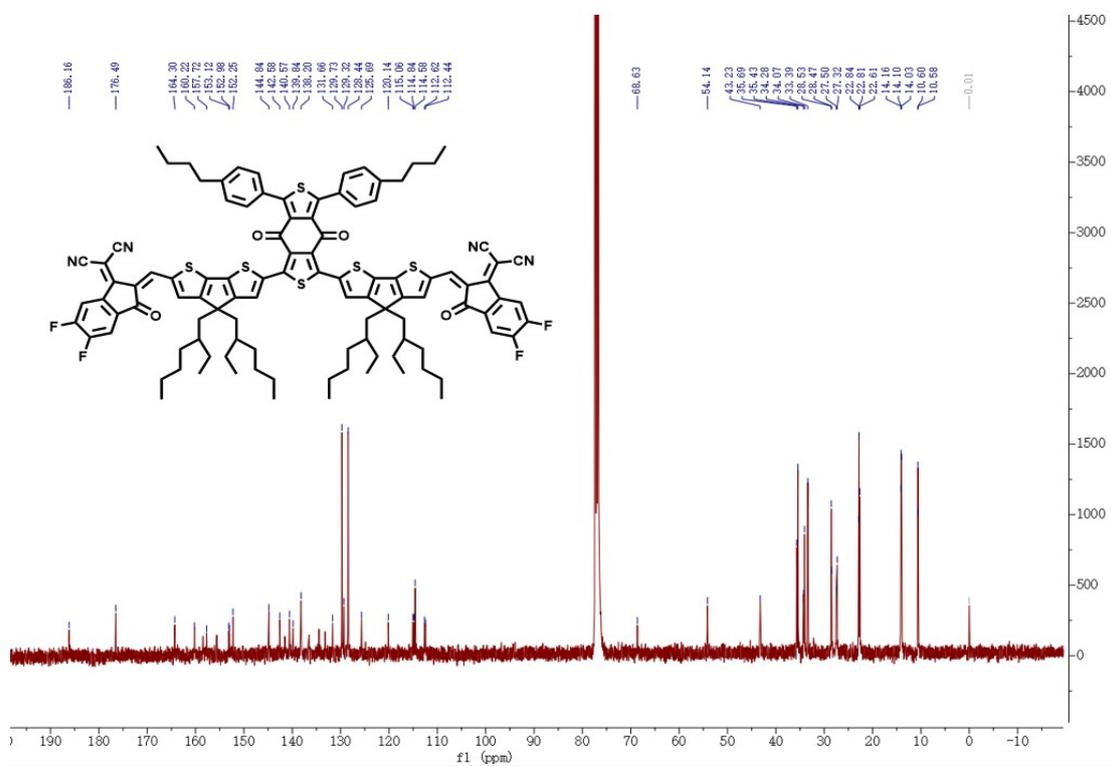
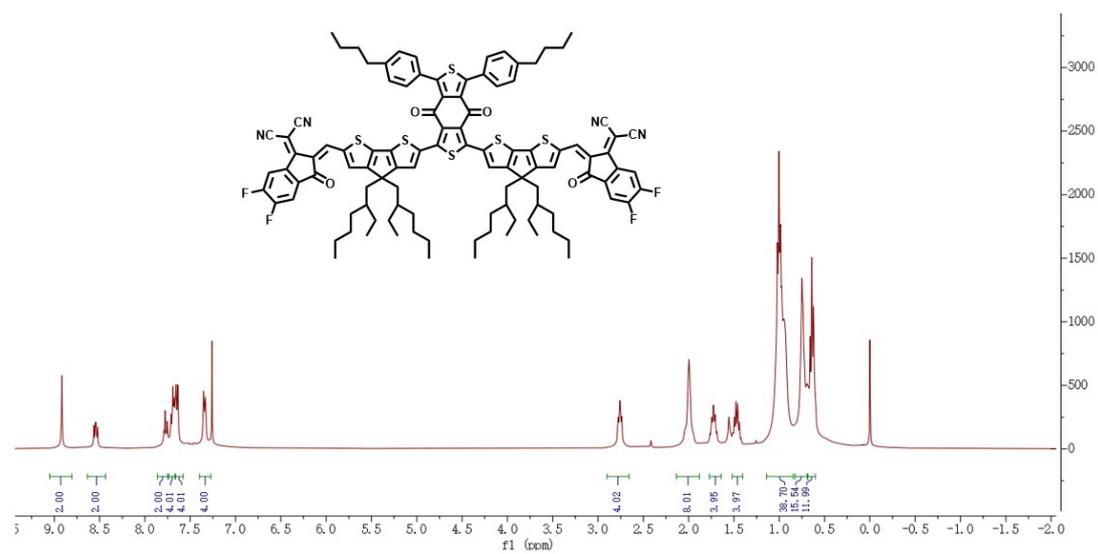
**Fig. S2**  $^1\text{H}$  NMR spectroscopy of compound (a) 2a and (b) 2b.



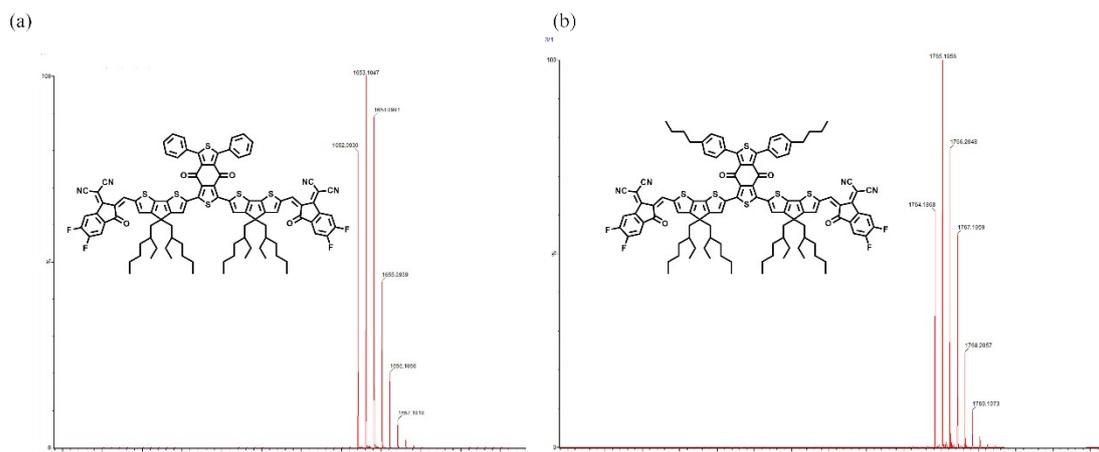
**Fig. S3** MALDI-TOF mass spectrometry of compound (a) 2a and (b) 2b.



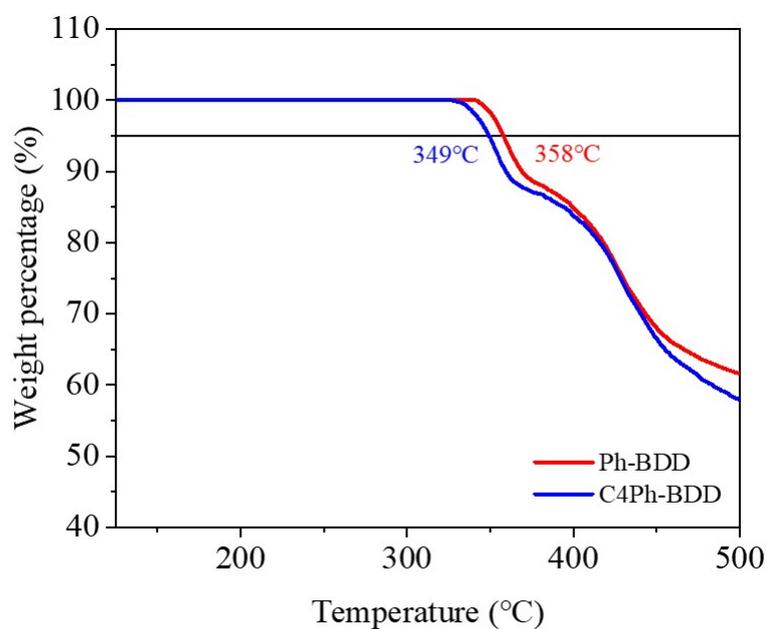
**Fig. S4**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy of Ph-BDD.



**Fig. S5** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy of C4Ph-BDD.



**Fig. S6** MALDI-TOF mass spectrometry of (a) Ph-BDD and (b) C4Ph-BDD.

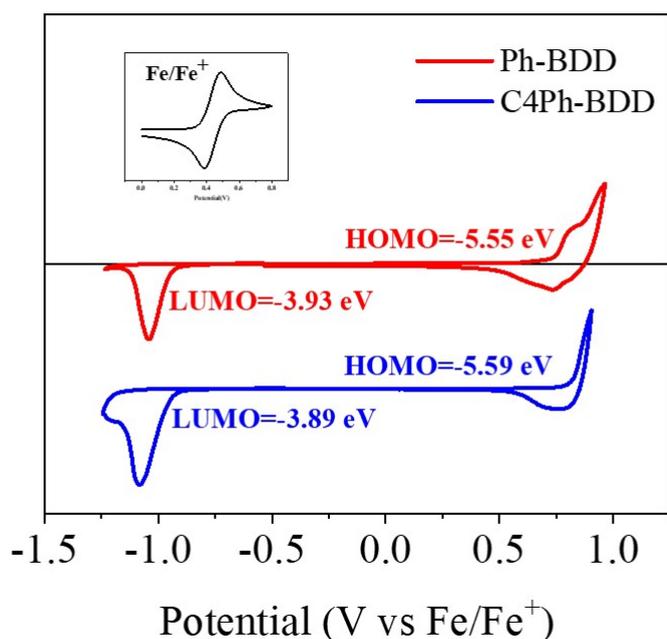


**Fig. S7** TGA curves of Ph-BDD and C4Ph-BDD under  $N_2$  atmosphere.

**Table S1.** Optical and electrochemical properties of Ph-BDD and C4Ph-BDD.

Acceptor	$\lambda_{\max}$ (nm)		$\epsilon$ ( $10^5 \text{ M}^{-1}\text{cm}^{-1}$ )	$E_g^{\text{opt}}$ (eV)	HOMO <sup>a</sup> (eV)	LUMO <sup>a</sup> (eV)
	Solution	Film				
Ph-BDD	705	692	1.85	1.46	-5.55	-3.93
C4Ph-BDD	714	694	1.63	1.39	-5.59	-3.89

<sup>a</sup> Calculated with equation  $E_{\text{HOMO/LUMO}} = -e (E_{\text{ox/red}} + 4.80)$  (eV)



**Fig. S8** Cyclic voltammetry measurements of Ph-BDD and C4Ph-BDD.

**Table S2.** Structural parameters of the pristine and/or blend films of PM6, Ph-BDD, and C4Ph-BDD obtained from the GIWAXS measurements

Film	In-plane direction peak		Out-of-plane direction peak	
	Scattering vector ( $q$ ) [ $\text{\AA}^{-1}$ ]	$d$ -spacing [ $\text{\AA}$ ]	Scattering vector ( $q$ ) [ $\text{\AA}^{-1}$ ]	$d$ -spacing [ $\text{\AA}$ ]
PM6	0.277	22.68	0.322/1.671	/3.76
Ph-BDD	0.331/0.435	14.44/	0.441/1.754	/3.59
C4Ph-BDD	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>	-- <sup>a</sup>
PM6:Ph-BDD	0.277/0.393	22.68/--	0.305/0.406/ 0.621/1.715	/3.66/ /
PM6:C4Ph-BDD	0.277	22.68	0.296/1.693	/3.71

<sup>a</sup> The pristine film of C4Ph-BDD showed very weak diffraction in the GIWAXS measurement, and no relevant diffraction peak could be defined.

**Table S3.** Summary of X-ray crystallographic data for Ph-BDD.

Identification code	2169440
Empirical formula	0.5(C <sub>89</sub> H <sub>46</sub> F <sub>4</sub> N <sub>4</sub> O <sub>4</sub> S <sub>6</sub> ),0.5(C <sub>92</sub> H <sub>52</sub> F <sub>4</sub> N <sub>4</sub> O <sub>4</sub> S <sub>6</sub> )
Formula Weight	1580.97
Temperature/K	150K
Crystal system	triclinic
Space group	P-1
a/Å	20.8350 (7)
b/Å	21.5807 (7)
c/Å	23.5080 (9)
$\alpha$ /°	67.313 (3)
$\beta$ /°	88.729 (3)
$\gamma$ /°	75.359 (3)
Volume/Å <sup>3</sup>	9401.8(6)
Z	4
$\rho_{\text{calc}}$ g/cm <sup>-3</sup>	1.117
Reflections collected	101062
Independent reflections	35965
Final R indexes [ $I \geq 2\sigma(I)$ ]	9399

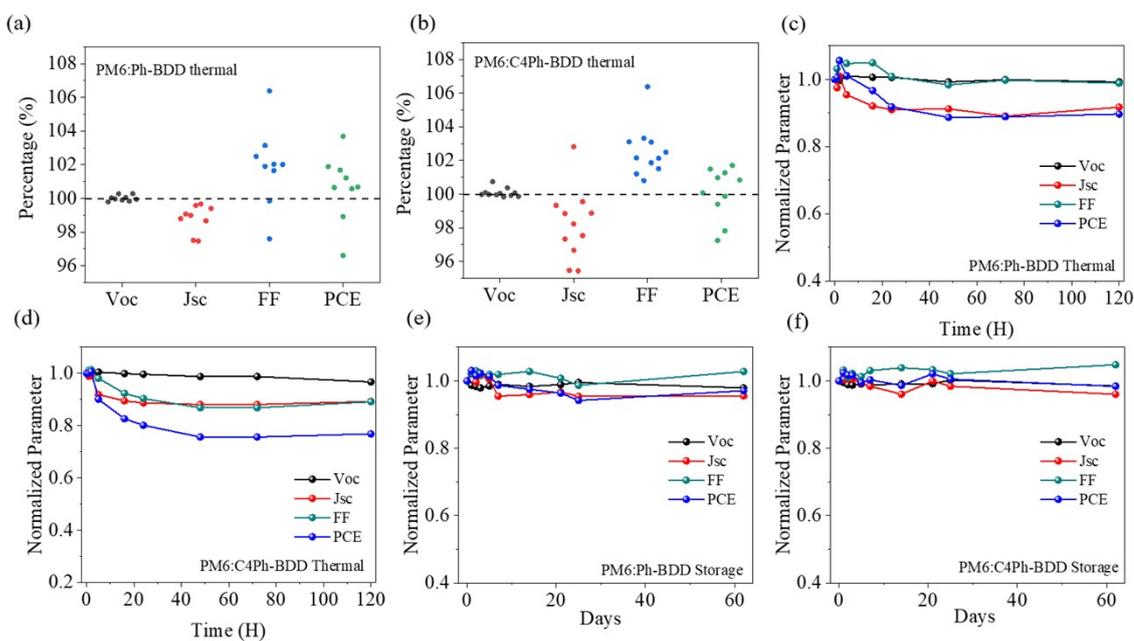
<sup>a</sup> The structure is of insufficient quality due to the disorder by alkyl side chain, but it is solid to analyze the stacking patterns of molecular backbones. There are A and B level alerts when checking the CIF file of Ph-BDD (CDCC2169440).

**Table S4.** Photovoltaic performances of the PM6:Ph-BDD based OSCs

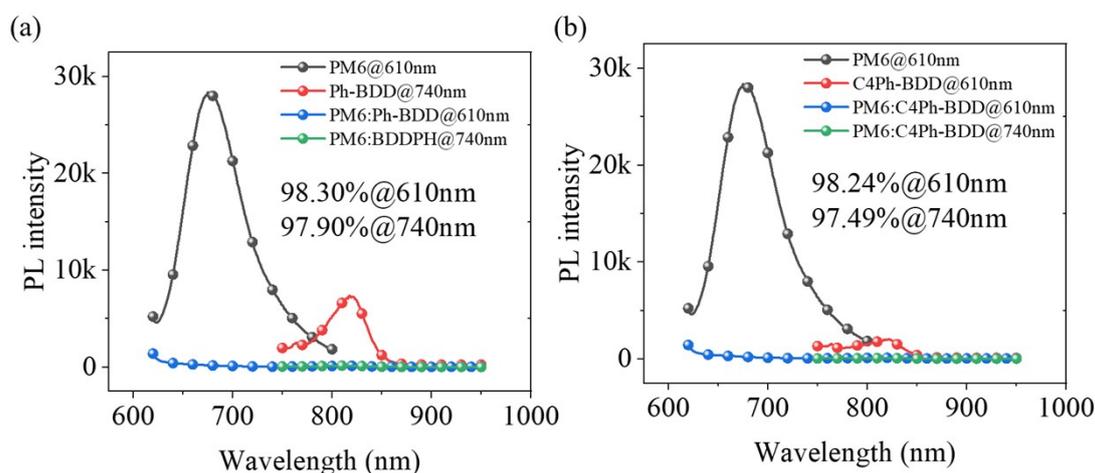
D: A	Treatment	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
	As cast	0.90	17.19	52.64	8.15
	140 °C+10min	0.87	19.87	60.75	10.51
1:1	160 °C+10min	0.88	21.16	63.54	11.85
	170 °C+10min	0.87	22.44	65.04	12.71
	180 °C+10min	0.85	20.29	68.71	11.87
1:1.2	160 °C+10min	0.86	22.40	60.20	11.61
1:1.5	160 °C+10min	0.87	21.17	63.18	11.65

**Table S5.** The effect of 1-chloronaphthalene (CN) on photovoltaic performances of the PM6:Ph-BDD based OSCs, with a D:A ratio of 1:1 and an annealing at 170 °C for 10 min

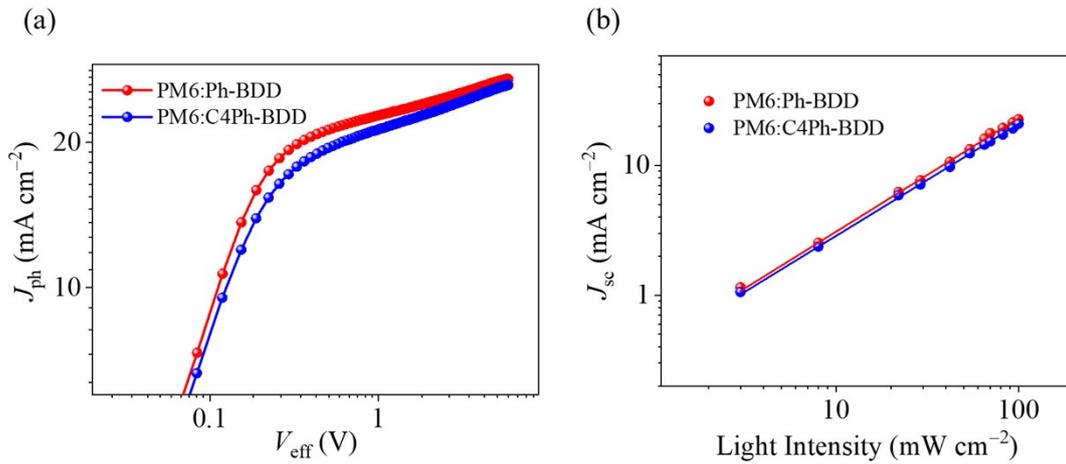
CN (vol%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
0	0.87	22.44	65.04	12.71
0.5%	0.86	24.07	65.80	13.64
1%	0.86	23.49	63.88	12.92
1.5%	0.86	23.40	64.06	12.91



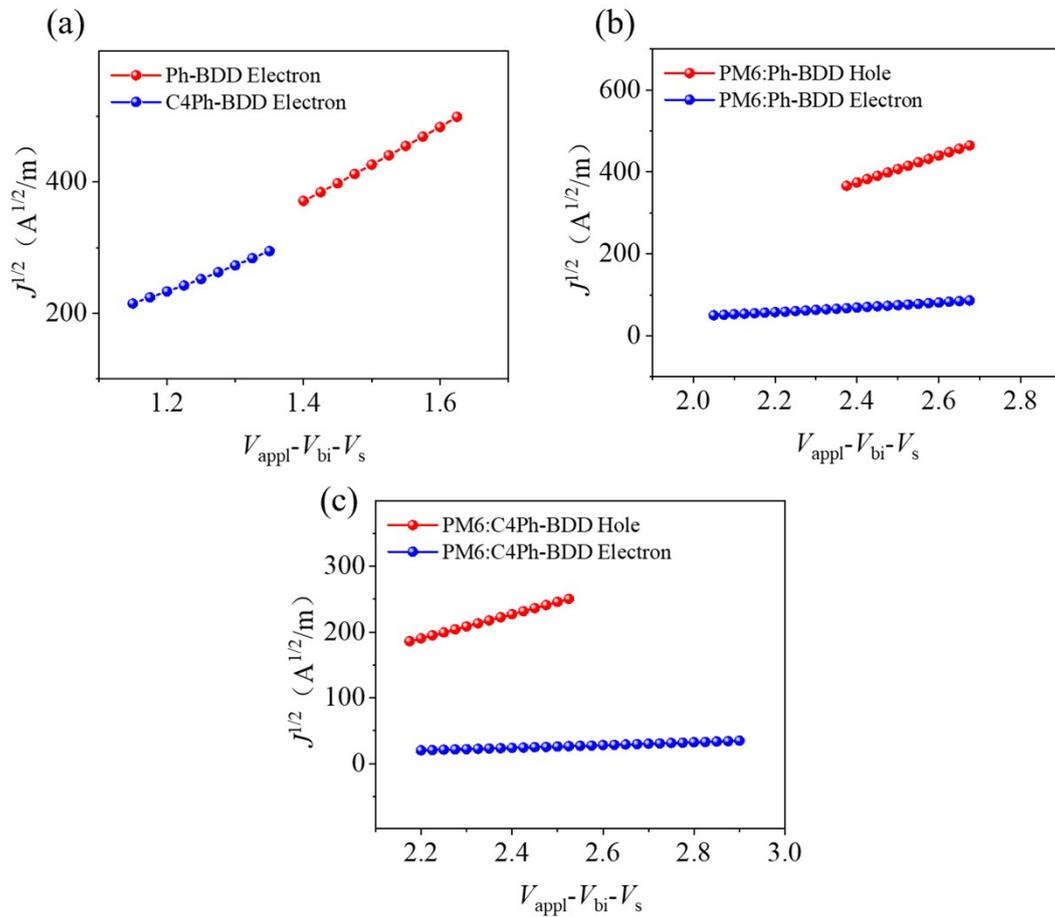
**Fig. S9** Variation of relevant performance parameters of all the (a) Ph-BDD and (b) C4Ph-BDD-based devices after being heated for an hour. Variation of relevant performance parameters of (c) Ph-BDD and (d) C4Ph-BDD-based devices during the test of thermal stability. Variation of relevant performance parameters of e) Ph-BDD and f) C4Ph-BDD-based devices in storage.



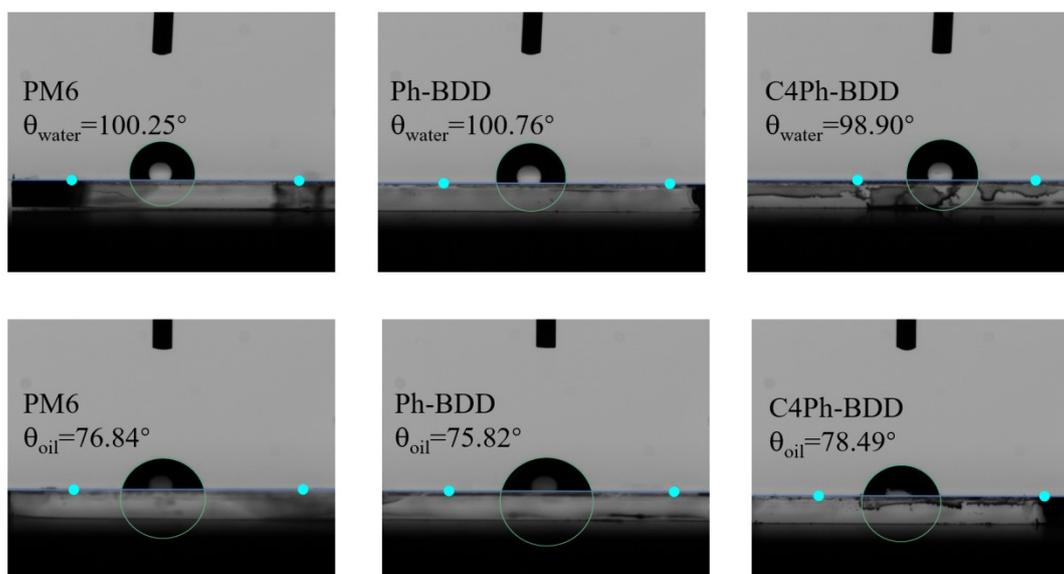
**Fig. S10** PL spectra of the neat films and optimized PM6: Ph-BDD (a) and PM6: C4Ph-BDD (b) blend films. Polymer PM6 and acceptors are excited at 610 and 740 nm, respectively.



**Fig. S11** Photocurrent density versus effective voltage (a) and dependence of  $J_{sc}$  on light intensity (b) for the optimized PM6: Ph-BDD and PM6: C4Ph-BDD based devices.



**Fig. S12** (a) SCLC  $J^{1/2}$ - $V$  characteristics of Ph-BDD and C4Ph-BDD pristine films in electron-only devices. SCLC  $J^{1/2}$ - $V$  characteristics of blend films of (b) PM6:Ph-BDD and (c) PM6:C4Ph-BDD in hole-only and electron-only devices.



**Fig. S13** Views of surface contact measurements for the films of PM6 and acceptors

**Table S6.** The contact angles and surface energy parameters of the films.

Film	Contact angle		$\gamma^d$ [mN/m]	$\gamma^p$ [mN/m]	$\gamma$ [mN/m]	$\chi$
	$\theta_{\text{water}}$	$\theta_{\text{oil}}^a$				
PM6	100.25°	76.84°	3.29	13.20	16.49	
Ph-BDD	98.90°	78.49°	4.24	11.82	16.06	$2.84 \times 10^{-3} \text{K}$
C4Ph-BDD	100.76°	75.82°	0.79	13.98	16.87	$2.16 \times 10^{-3} \text{K}$

<sup>a</sup>  $\theta_{\text{oil}}$  represents the contact angle of Ethylene glycol.  $\gamma^d$  and  $\gamma^p$  represent the surface free energy ( $\gamma$ ) generated from the dispersion forces and the polar forces, respectively.

## Reference

1. S. Pang, X. Zhou, S. Zhang, H. Tang, S. Dhakal, X. Gu, C. Duan, F. Huang and Y. Cao, *ACS Appl. Mater. Interfaces*, 2020, **12**, 16531-16540.
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