## Supporting Information

# Benzophenone-based small molecular cathode interlayers with various polar groups for efficient polymer solar cells

Zhiyang Liu,<sup>a,b</sup> Wang Li,<sup>a,b</sup> Ruixiang Peng,<sup>a</sup> Weigang Jiang,<sup>a,b</sup> Qian Guan,<sup>a,b</sup> Tao Lei,<sup>a,b</sup> Rongjuan Yang,<sup>a</sup> Amjad Islam,<sup>a,b</sup> Qiang Wei,<sup>a</sup> and Ziyi Ge<sup>\*a</sup>

<sup>a.</sup> Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, China. E-mail: geziyi@nimte.ac.cn

<sup>b.</sup> University of Chinese Academy of Sciences, Beijing, 100049, China

#### 1. Characterization and Measurement

Current density-voltage (*J-V*) characteristics of the devices were measured under the simulated solar light (100 mW cm<sup>-2</sup>; AM 1.5 G) provided by a Newport-Oriel® Sol3A 450W solar simulator and stored in Ar atmosphere without encapsulation. The device parameters were recorded with a Keithley 2440 Source Measure Unit. The intensity of the simulated solar light was calibrated by a standard Si photodiode detector (PV measurements Inc.), which was calibrated at National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) spectra were determined using a Newport-Oriel® IQE 200TM which was calibrated by standard Si/Ge solar cell under illumination with monochromatic light from a Xe lamp at room temperature in air. The thickness of films was performed using a surface profiler (Dektak 150).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were collected with a Bruker DMX-400 Spectrometer. The UV-vis absorption spectra were measured by a Perkin-Elmer Lambda 950 spectrophotometer. Surface images and the roughness were conducted on a Veeco Dimension 3100V atomic force microscope. Mass spectra were measured by XEVO Wafer high-performance liquid chromatography and mass spectrometer. Ultraviolet photoelectron spectroscopy (UPS) measurements were obtained by a Kratos ULTRADLD UPS/XPS system (Kratos analytical, Manchester, U. K.) with He I radiation at 21.2 eV from a discharge lamp operated at 20mA, a pass

energy of 5 eV, and a channel width of 25 meV.

#### 2. Device fabrication

The device structure was ITO/PEDOT:PSS (Baytron<sup>®</sup> P VP AI 4083) /PTB7:PC<sub>71</sub>BM/with or without interlayer/Al. PEDOT:PSS aqueous solution was filtered through 0.45  $\mu$ m filter and spin-coated at 4000 rpm for 1 min onto the treated ITO substrate and annealed at 120 °C for 20 min. Then, the active layer about 110 nm was spin-cast from a solution with PTB7: PC<sub>71</sub>BM ratio of 1:1.5 by weight (PTB7 concentration of 10 mg/mL) in chlorobenzene/1,8-diiodoctane (97:3 vol %) mixed solvent at 2000 rpm for 2 min and put in vacuum for 30 min. The interlayer materials were dissolved in methanol and their solutions (1 mg/ml) were spin-coated onto the active layer and put in vacuum for 30 min. Their thickness was controlled by the concentration of the solution and the spin speed between 1000 rpm to 6000 rpm. Al electrode (100 nm) was evaporated in vacuum chamber ( $3 \times 10^{-6}$  mbar) through a shadow mask to define the active area of the devices (4 mm<sup>2</sup>).

#### 3. J-V curves of PTB7:PC<sub>71</sub>BM-based PSCs with different interlayers



Fig. S1 J-V characteristics of PTB7:PC $_{71}$ BM-based PSCs (a) under AM 1.5G, 100 mW cm<sup>-2</sup> illumination

Table S1 Photovoltaic performance of PTB7:PC71BM-based PSCs with different interlayers.

CIM	$V_{\rm oc}$ [V]	J <sub>sc</sub> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
-----	------------------	--	--------	---------

LiF	0.70	15.83	65.58	7.35
ВРОН	0.75	15.45	66.83	7.78
BPN	0.76	16.87	70.28	8.98
BPO	0.76	17.09	71.58	9.34
BPS	0.76	16.94	70.15	9.03

The photovoltaic performance of LiF-based PTB7:PC<sub>71</sub>BM-based devices without the methanol treatment is lower than that of the devices with BPN, BPO or BPS interlayer. The  $J_{sc}$  of LiF-based devices is higher than that of BPOH-based devices.

## 4. UV-vis spectra



### 5. Hole and electron mobilities

BPS

Interlayer hole mobility (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) electron mobility (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) 8.12 3 10-4 Al 1.96 10-4 4.40 \$ 10-4 9.35 310-4 MeOH/Al 5.01 \$ 10-4 PFN 1.12/3 10-3 4.02 \$ 10-4 9.65 3 10-4 BPOH 5.30 \$ 10-4 1.15 🕫 10-3 BPN 5.75 3 10-4 1.75**6** 10<sup>-3</sup> BPO

5.01 \$ 10-4

1.21 3 10-3

Table S2 hole and electron mobilities of  $PTB7:PC_{71}BM$ -based devices with different treatment.

#### 6. Calculated J<sub>sc</sub> of the PTB7:PC<sub>71</sub>BM-based PSCs

Interlayer	J <sub>sc</sub>	J <sub>sc</sub> <sup>a</sup>
	[mA cm <sup>-2</sup> ]	[mA cm <sup>-2</sup> ]
None	14.30	13.85
MeOH	15.24	14.35
PFN	16.24	15.42
ВРОН	15.45	14.43
BPN	16.87	15.94
BPO	17.09	16.53
BPS	16.94	16.09

**Table S3**  $J_{sc}$ , calculated  $J_{sc}^{a}$  of the best PTB7:PC<sub>71</sub>BM-based PSCs with or without interlayer and methanol treatment.

The calculated  $J_{sc}$  obtained by integrating the EQE spectra show a ~5% mismatch compared with the  $J_{sc}$  value obtained from the *J*-*V* curves. The mismatch could be clarified as follow. First, the *J*-*V* curves of the devices were got in the glovebox filled with nitrogen. But the EQE measurements were finished in air without encapsulation, which affects the value. Second, the illuminating light for *J*-*V* measurements includes the full spectrum of simulated sunlight, while the EQE tests uses only single-wavelength light from 300 to 900 nm in intervals of 20 nm. Thus, the light for EQE tests does not span the full spectrum of simulated sunlight. Finally, the EQE is calculated according to the formula EQE= electrons (s)/photons (s). A small deviation (size of the light spot or flatness of the sample) will cause a decreased EQE. 7. The stability of devices with different interlayers



Fig. S3 The curves of PCEs versus time of devices with different interlayers

We monitored the device PCE versus time in a nitrogen atmosphere glovebox without encapsulation. The PCEs of the devices with PFN, BPN, BPO or BPS interlayers retained >83% of their original PCE values after 30 days storage. BPOH-based device only remained 79% of its original value of PCE.

8. <sup>1</sup>H and <sup>13</sup>C NMR spectra



Fig. S5 <sup>13</sup>C NMR spectrum of BPN in CDCl<sub>3</sub>.





Fig. S8  $^{1}$ H NMR spectrum of BPS in D<sub>2</sub>O.



**Fig. S9** <sup>13</sup>C NMR spectrum of BPS in  $D_2O$ .