

**Supporting Information:**

**Perylene Bisimide as Cathode Modifier in Organic Photovoltaics: The Role of Aggregation Morphology on the Interlayer Performance**

Wenqiang Zhang,<sup>a, c</sup> Shu Zhong,<sup>b</sup> Li Nian,<sup>a</sup> Yulan Chen,<sup>a</sup> Zengqi Xie,<sup>a,\*</sup> Linlin Liu,<sup>a</sup> Muddasir Hanif,<sup>a</sup> Wei Chen<sup>b,\*</sup> Yuguang Ma <sup>a</sup>

<sup>a</sup>Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology  
Guangzhou 510640, P. R. China

E-mail: [msxiez@scut.edu.cn](mailto:msxiez@scut.edu.cn);

<sup>b</sup>Department of Chemistry, National University of Singapore  
3 Science Drive 3, 117543, Singapore

E-mail: [phycw@nus.edu.sg](mailto:phycw@nus.edu.sg)

<sup>c</sup>State Key Laboratory of Supramolecular Structure and Materials, Jilin University  
Qianjin Avenue, Changchun, 130012, P. R. China

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## 1. Materials

The PBI-1 molecule was synthesized via the method from literature [30]. Solvents and reagents were purchased from commercial sources, unless otherwise stated, and purified and dried according to standard procedures. The rr-P3HT and PC<sub>61</sub>BM were purchased from 1-Material Chemsitech Inc. (St-Laurent, Quebec, Canada), and used as received. ITO substrates with a sheet resistance of 15  $\Omega/\square$  were purchased from CSG HOLDING Co., LTD (Shenzhen, P. R. China).

## 2. UPS measurements

*In-situ* ultraviolet photoemission spectroscopy (UPS) measurements were carried out in a custom-built ultrahigh vacuum (UHV) system with He I $\alpha$  ( $h\nu=21.2$  eV) as the excitation source. All UPS spectra were recorded with Omicron EA 125 hemispherical analyzer at normal emission angle under room temperature (RT). Vacuum level shifts were determined from UPS spectra at low-kinetic energy onset (secondary electron cutoff) with -5 V sample bias. The WF of the substrate was obtained through the equation  $WF = h\nu - W$ , where W is the spectrum width of the energy difference between substrate Fermi level and secondary electron cutoff (SECO). The Fermi level in the UPS spectra located at 16.9 eV. The binding energy of all UPS spectra were calibrated and referenced to the Fermi level of a sputtered clean silver sample. UPS spectra were measured at normal emission. The ITO glass substrates were cleaned and spin-coated with PBI-1 before loaded into the preparation chamber which is connected to the analysis chamber mounted with the UV source and the hemispherical analyzer. Vacuum-sublimation purified C<sub>60</sub> molecule was thermally evaporated onto the substrates at RT from a Knudsen cell in the preparation chamber. Deposition rate of  $\sim 0.2$  nm/min was precalibrated by a quartz-crystal-microbalance (QCM) under similar growth conditions. The nominal thickness of the organic films was estimated from the attenuation of the Si 2p peak intensity from the SiO<sub>2</sub> substrate before and after deposition.

## 3. Device fabrication

Pre-patterned ITO glass substrates were cleaned by subsequent ultrasonication in acetone, detergent, deionized water, and isopropyl alcohol successively. For the fabrication of inverted device,

a thin PBI-1 aggregate layer of about 10 nm was spin-coated onto the pre-cleaned ITO substrate from  $\text{CHCl}_3$  or THF solution (with a concentration of 1 mg/mL) at 3000 r/min for 1 min. The blend ratio between rr-P3HT (23 mg/mL) and  $\text{PC}_{61}\text{BM}$  (23 mg/mL) is 1:1 by weight and the active blend layer with a thickness of 200 nm was prepared by spin-coating the *o*-dichlorobenzene solution at 800 r/min for 30 s and dried in a covered glass petri dishes. Then the device was baked on a hot plate at 120 °C for 10 min. Finally,  $\text{MoO}_3$  (10 nm) and Al cathode (100 nm) was evaporated through a shadow mask to define the active area of the devices (0.16  $\text{cm}^2$ ).

#### 4. Device and film characterization

The thickness of the films was characterized by a Dektak 150 surface profiler. The characterization of the diverse nanostructures was performed by the field emission scanning electron microscope (FESEM) of LEO 1530 VP at room temperature. PCE values were determined from J-V characteristics measured by a Keithley 2400 source-measurement unit under AM 1.5G spectrum from a solar simulator (Oriel model 91192). Masks made from laser beam cutting technology with well-defined area of 16.0  $\text{mm}^2$  were attached to define the effective area for accurate measurement. Solar simulator illumination intensity was determined using a monocrystal silicon reference cell (Hamamatsu S1133, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL).

#### 5. SEM characterization of the film on glass.

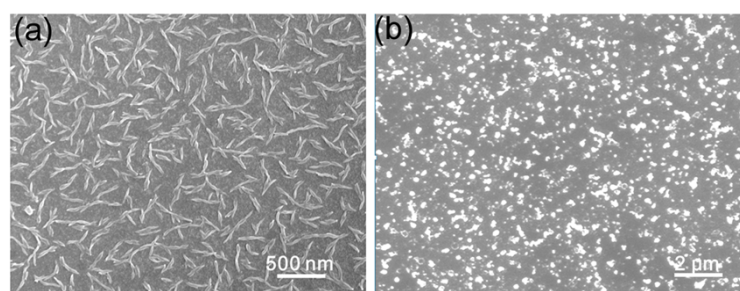


Figure S1. SEM characterization of the morphologies of the PBI-1 by spin-coating on glass substrates: a) PBI-1 formed nanorods from chloroform solution (1 mg/mL) with ca. 0.01 time equivalent of acetic acid as additive; b) PBI-1 formed nanoparticles from chloroform solution (1 mg/mL) with ca. 2 times equivalent of acetic acid as additive.

If the hydrogen bonding interactions between two adjacent molecules were prohibited to a certain degree, the long nanofibres would be separated into smaller fragments, such as nanorods or nanoparticles. This hypothesis was realized by adding some special molecules which can form hydrogen bond with the PBI-1 more easily and grab the preemption of other adjacent PBI-1 molecules. To this end, 0.01 times equivalent molecule  $\text{CH}_3\text{COOH}$  was added into the chloroform system, and plenty of small homogeneous fragments formed as shown in Figure S1b. The hydrogen bonds between PBI-1 and  $\text{CH}_3\text{COOH}$  were rather strong. The length of the nanorods was concentrated on the range of 500-600 nm. Along with the increase of the amount of  $\text{CH}_3\text{COOH}$ , the length of nanorods decreased until the formation of nanoparticles (Figure S1b), which indicated that the PBI molecules were separated thoroughly by  $\text{CH}_3\text{COOH}$  molecules. The PBI-1 was surrounded by the invasive acid molecules. The process of self-assembly into micro/nano-structure can be accurately controlled and the morphology of the film can be regulated precisely.

## 6. Device performance

**Table S1.** Device performance under  $1000\text{W}/\text{m}^2$  AM illumination with various interlayers <sup>a)</sup>. The device structure is ITO/PBI-1aggregates(10 nm)/P3HT:PC<sub>61</sub>BM(200 nm)/MoO<sub>3</sub> (10 nm)/Al (100 nm). PBI-1 nanofibers and nanoparticles were applied as the cathode interlayers in Device A and Device B, respectively.

device	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	PCE (%) <sup>b)</sup>
DeviceA (nanofibers)	0.62±0.004	9.28±0.14	63.2±0.11	3.55±0.11(3.69)
Device B (nanoparticles)	0.58±0.005	8.98±0.16	59.5±0.15	3.01±0.13 (3.16)

a) Statistic data achieved from 15 independent devices. b) The maxima PCEs in the brackets.