Supporting Information

Self-assembled Perylene Bisimide J-Aggregates as Promising Cathode Modifier for Highly Efficient Inverted Polymer Solar Cells

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1. Experimental details

Materials: The synthesis of PBI-H was reported elsewhere.[14] Solvents and reagents were purchased from commercial sources, unless otherwise stated, and purified and dried according to standard procedures. Electron donor polymers PTB7 and PCDTBT were purchased from 1-Material Chemscitech Inc. (St-Laurent, Quebec, Canada), and used as received. ITO substrates with a sheet resistance of 15 Ω sq^{-1} were purchased from CSG HOLDING Co., LTD (Shenzhen, P. R. China), while PEDOT: PSS (Clevios P AI4083) was purchased from H.C. Starck Clevios.

Device fabrication: Pre-patterned ITO glass substrates were cleaned by subsequent ultrasonication in acetone, detergent, deionized water, and isopropyl alcohol. A thin PBI-H layer of about 10 nm was spin-coated at the pre-cleaned ITO substrate from anhydrous THF solution (with a concentration of 1mg mL^{-1}) at 1000 r.p.m. for 1 min. The blend ratio between PTB7 (10 mg mL^{-1}) and PCBM (15 mg mL^{-1}) is 1:1.5 by weight and the active blend layer with a thickness of 90 nm was prepared by spin-coating the chlorobenzene solution. Then, a 10 nm MoO_3 layer and a 100 nm Al layer were subsequently evaporated to form a top anode.

Characterization and measurement: 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 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). The film thickness of as-spun PBI-H film was measured by an Auto SE ellipsometer (Horiba). Absorption spectra were obtained using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3600).

Photoemission measurements were conducted on a ThermoFisher Scientific ESCALAB 250 system using a monochromated Al Kα photon source ($h\nu$ = 1486.6 eV) for XPS, a non-monochromated He I photon source ($h\nu$ = 21.22 eV) for UPS and a low energy electron source (about 1000 eV) for REELS. Chemical states of oxygen were identified using high-resolution core-level XPS. Work function and valence-band measurements were carried out using UPS with the sample tilted to a take-off angle of 90° and under an applied bias of –5 V. The REELS spectrum was recorded at a constant pass energy mode of 5 eV. The analysis chamber base pressure was ~10^{-10} mbar. In XPS fitting spectra the Shirley-type background due to inelastic scattering electrons was taken into account and the ratio of Lorentzian to Gaussian varied in the range of 30±5%.

2. Self-assembly of PBI-H into J-aggregates

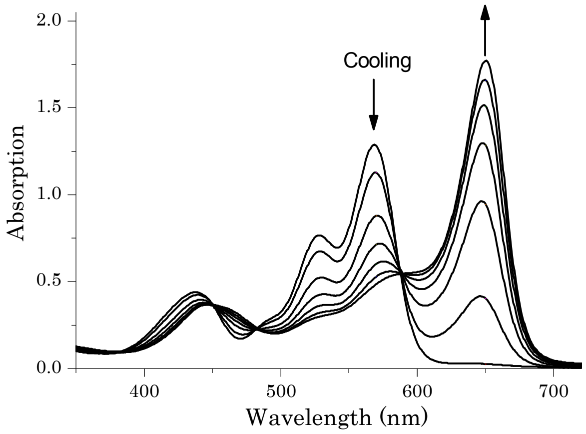

Figure S1. Formation of PBI-H J-aggregates (l_{max} = 650 nm) from PBI-H monomers (l_{max} = 568 nm) upon cooling of a 3.0×10^{-4} M PBI-H solution in toluene from 70 to 10 °C.

3. UV/Vis absorption of PBI-H on glass substrate

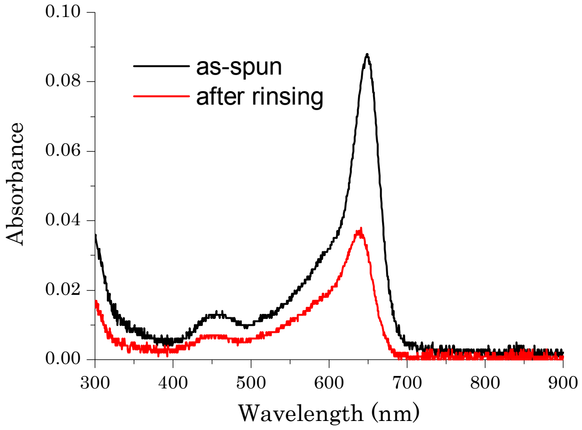

Figure S2. UV/Vis absorption spectra of the as-spun PBI-H film from 1 mg/mL THF solution used for device fabrication and after a rinse with chlorobenzene.

4. XPS characterization of ITO/PBI-H

The surface of PBI-H modified ITO was characterized by X-ray photoelectron spectroscopy (XPS). As shown in the XPS survey spectrum (see Figure S3a), the coexistence of carbon, nitrogen and oxygen elements indicates clearly the coverage of PBI-H on the surface; meanwhile, PBI-H layer is very thin or even does not cover ITO substrate completely as indicated by the existence of In XPS signals (which corresponds to an atomic percent of 5.66% for indium element). Figure S3b shows the high resolution XPS spectrum of oxygen element, and as expected there are several closed signals those corresponding to oxygen from metal oxide and organic molecules. It is very interesting to note that there is a component whose binding energy located at 532.6 eV that is slightly higher than that of carboxide group (C=O) (Figure S3b). This can be attributed to the hydrogen bonded carboxide group (C=O····H), which corresponding to the molecular aggregation model well (Figure 1a in maintext).[S1]

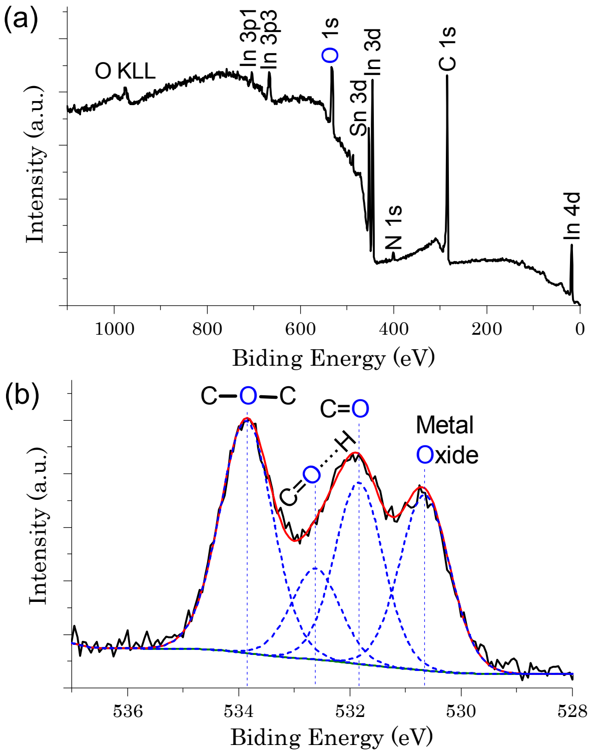

Figure S3. Surface property of the PBI-H modified ITO. a) XPS survey spectrum. b) O1s high resolution XPS spectrum.

5. Device performance of PSCs using PCDTBT as the donor polymer

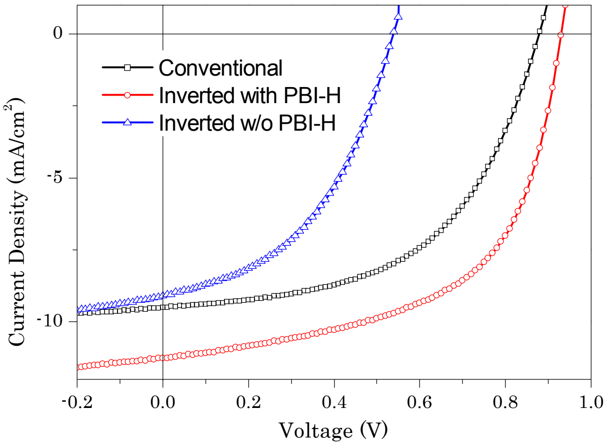

Figure S4. The current density versus voltage characteristics (*J*-V) of the devices with a conventional device structure of ITO/PEDOT:PSS/PCDTBT:$PC_{71}BM$/Al (black squares), an inverted device structure of ITO/without PBI-H (blue triangles) and with PBI-H (red circles)/ PCDTBT:$PC_{71}BM/MoO_3$/Al, respectively. The measurements were performed under 1000 W m^{-2} air mass 1.5 global (AM 1.5 G) illumination.

Table S1. Device performance/parameters from photovoltaic cells with conventional and inverted device structures using PCDTBT as the donor polymer, measured under 1,000Wcm^{-2} AM 1.5G illumination.

Device structure	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
ITO/PBI-H / PCDTBT:$PC_{71}BM/MoO_3$/Al	0.93	11.28	57.4	6.01
ITO/PEDOT:PSS/ PCDTBT:$PC_{71}BM$/Al	0.88	9.50	53.5	4.47
ITO/ PCDTBT:$PC_{71}BM/MoO_3$/Al	0.54	9.12	45.3	2.23

6. Electron-dominated device investigation

Electron-dominated devices were fabricated to measure the electron mobility using the space charge limited current (SCLC) method. The device structures are ITO/Al/interlayer (*x* nm)/PC$_{61}$BM (60 nm)/Ba/Al, where the interlayer represented PBI-H and the conventional PFN. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation: $J = (9/8)\varepsilon_0\varepsilon_r\mu((V^2)/(d^3))$, where J is the current, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the interlayer/PC61BM double layers, and V is the effective voltage. The V 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 electron -mobility can be calculated from the slope of the $J_{1/2}$~V curves.

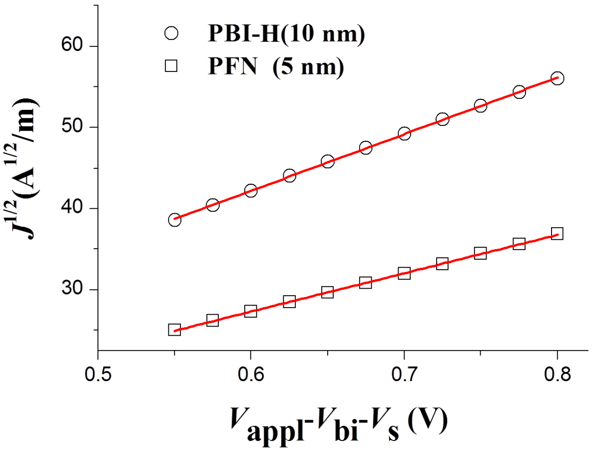

Figure S5. $J_{1/2}$~V characteristics of electron-dominated devices with PFN (5nm) (squares) and PBI-H (10nm) (circles) interlayers measured at room temperature. Device configuration: ITO/Al/interlayer (*x* nm)/PC$_{61}$BM (60 nm)/Ba/Al.

The average electron mobility (μ) of the PBI-H (10nm)/PC$_{61}$BM (60nm) double layers was determined as 4.9 ± 0.6 $cm^2 \cdot v^{-1} \cdot s^{-1}$, while that of PFN (5 nm)/PC$_{61}$BM (60nm) double layers was 2.0 ± 0.5 $cm^2 \cdot v^{-1} \cdot s^{-1}$.

7. Fluorescence quenching of PBI-H by P3HT by charge transfer

In order to test the charge transfer property between PBI-H and conjugated polymers, we did fluorescence quenching experiment using poly(3-hexylthiophene) (P3HT) as the electron donating polymer. The reason to replace PTB7 by P3HT is to avoid the effect of Forster energy transfer from PBI-H to the polymers, because P3HT showed a blue-shifted absorption compared with PTB7 in film state which enable P3HT does not absorb the emission from PBI-H.

PBI-H may form gel in chlorobenzene at a concentration of 1mg/mL as we reported before.[S2] Because the majority of conducting polymers show the best solubility in chloroaromatic solvents a further gelation experiment was carried out in chlorobenzene at a perylene bisimide PBI-H concentration of 1 mg/mL in the presence of electron donating P3HT (Figure S6). Thin films of both gels, without and with P3HT, were prepared by shaking the gels and subsequent drop-casting onto glass. As shown in Figure 6a, the pure PBI gel film exhibits red emission under UV light (365 nm) irradiation, while in the case of composite gel the emission from PBI-H is quenched effectively by P3HT as shown in Figure 6b. This fluorescence quenching can be attributed to the intermolecular charge transfer between PBI-H and P3HT which is an exothermic process at the interface between the two components.[S3] The efficient fluorescence quenching provides evidence that excitons can migrate with high efficiencies within both domains of the P3HT and PBI-H manifolds, respectively to reach the interface where the charge separation takes place. Figure S6d shows the absorption spectra of PBI-H films with and without P3HT. The J-type absorption band of PBI-H is remained in UV/vis spectrum of the mixture of PBI-H and P3HT, indicating strong self-assembly ability of PBI-H also in P3HT matrix. Thus, the hydrogen-bond and π–π-stacking codes implemented in PBI-H building blocks clearly outweigh the interactions between the electron donor and acceptor molecules.

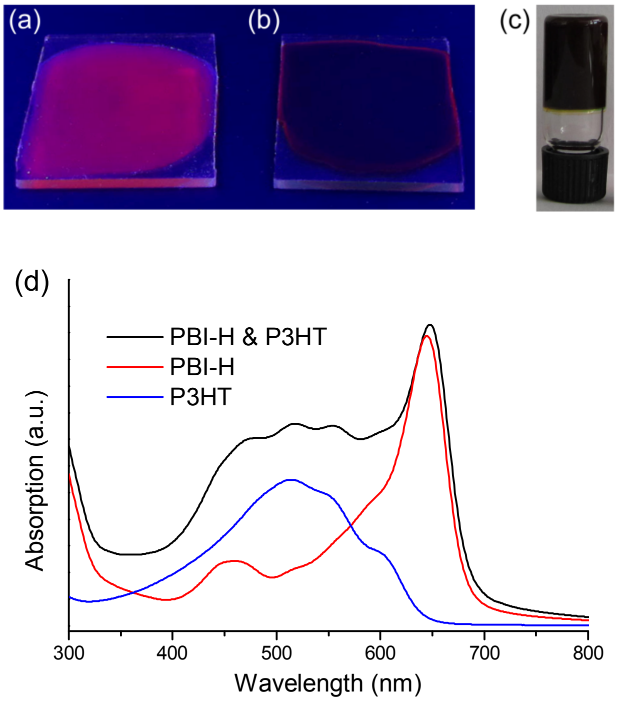

Figure S6. (a, b) Photographs of drop-cast films under UV light (365 nm) irradiation that were prepared from (a) 1 mg/mL PBI-H in chlorobenzene and (b) mixture of 1 mg/mL PBI-H and 1 mg/mL P3HT in chlorobenzene. (c) Photograph of the composite gel (1 mg/mL PBI-H and 1 mg/mL P3HT in chlorobenzene). (d) UV/vis absorption spectra of the drop-cast films from PBI-H (red line, gel, 1 mg/mL), P3HT (blue line, solution, 1 mg/mL), and PBI-H P3HT mixture (black line, gel, 1 mg/mL of each) in chlorobenzene.

8. Additional references

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[S2] Z. Xie, V. Stepanenko, B. Fimmel, F. Würthner, *Mater. Horiz.* **2014**, *1*, 355.

[S3] A. Wicklein, S. Ghosh, M. Sommer, F. Würthner, M. Thelakkat, *ACS Nano* **2009**, *3*, 1107.