

Supplementary Information

## **Nanoscale Phase Separation in Bulk Heterojunction Structure of Perylene Bisimide and Porphyrin by Controlling Intermolecular Interactions**

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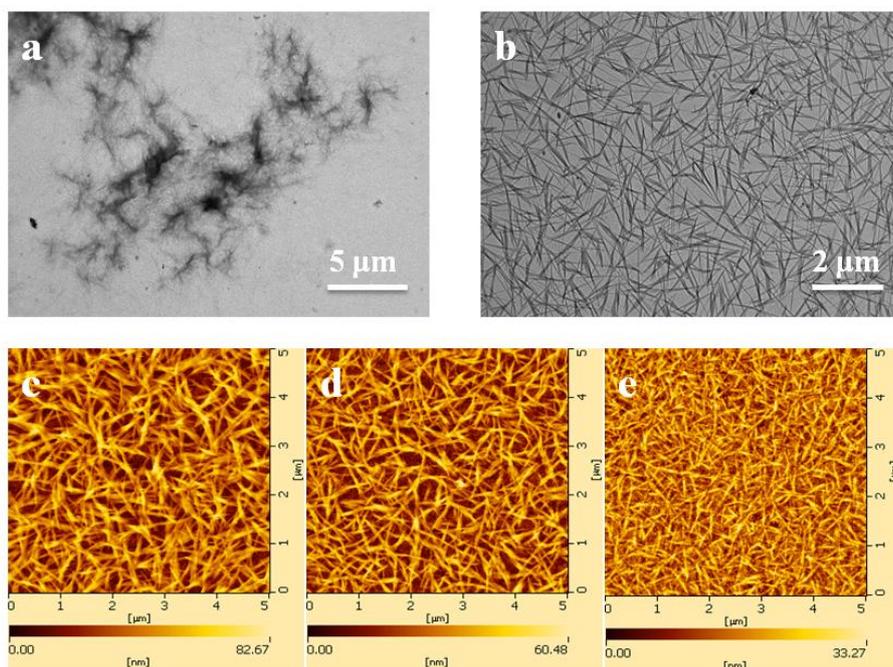
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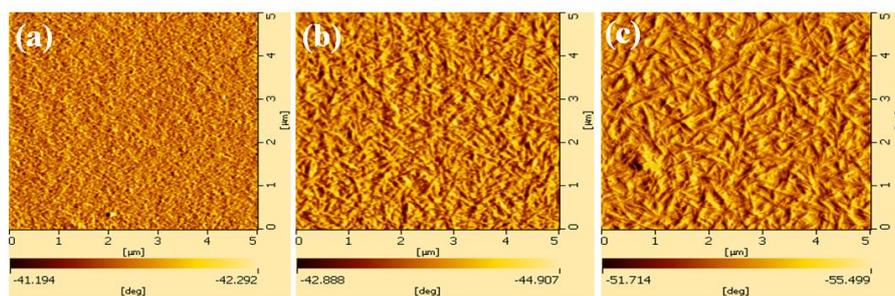
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## S1. Morphology characterization

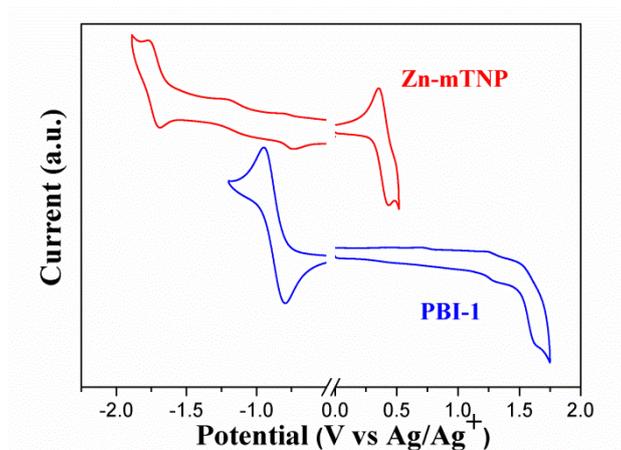


**Figure S1.** TEM image of **PBI-1** aggregates formed during drop-casting process on formvar stabilized with carbon support films from 1 mg/mL (a) chlorobenzene (b) THF solutions, AFM height images of **PBI-1** aggregates formed during spin-coating process on ITO from (c) 3 mg/mL, (d) 2 mg/mL, and (e) 1 mg/mL THF solutions at room temperature.



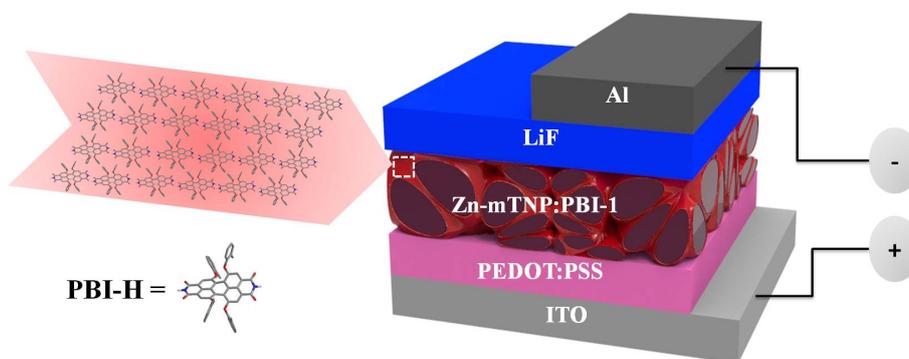
**Figure S2.** AFM height images of blend films with ratio of **PBI-1:Zn-mTNP** = (a) 1:9, (b) 2:8, (c) 3:7.

## S2. Electrochemistry behavior

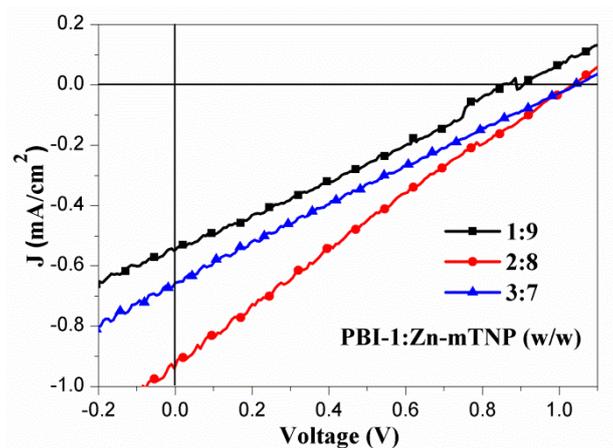


**Figure S3.** Cyclic voltammograms of **PBI-1** and **Zn-mTNP**. A glass-carbon disk electrode was used as the working electrode, a Pt wire as the counter electrode, Ag/Ag<sup>+</sup> as the reference electrode with ferrocene as the internal standard and Bu4NPF6 (0.1 M) as the electrolyte. The oxidation and reduction cycles were measured in CH<sub>2</sub>Cl<sub>2</sub> and N, N-dimethylformamide (DMF), respectively.

## S3. OPV performances



**Figure S4.** Schematic illustration of the device structure.



**Figure S5.** J-V curves of OPVs based on **PBI-1/Zn-mTNP** (w/w) under the illumination of AM 1.5G,  $100\text{mW cm}^{-2}$ .

**Table S1.** Photovoltaic properties of OPVs based on **PBI-1/Zn-mTNP** (w/w) under the illumination of AM 1.5G,  $100\text{mW cm}^{-2}$ .

<b>PBI-1/Zn-mTNP</b> (w/w)	Jsc ( $\text{mA cm}^{-2}$ )	Voc (V)	FF	PCE (%)
<b>1:9</b>	0.53	0.95	0.26	0.13
<b>2:8</b>	0.93	1.03	0.23	0.22
<b>3:7</b>	0.66	1.03	0.25	0.17
<b>4:6</b>	0.28	1.06	0.20	0.06
<b>5:5</b>	0.06	0.71	0.22	0.01