

## Electronic Supporting Information

### **Manipulating the horizontal morphology and vertical distribution of the active layer in BHJ-PSC with multi-function solid organic additive**

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The optical microscopic images were taken from the SPM (E-sweep, SEIKO Inc., Japan) with the magnification of 1000. The black spots on the red-circles of Figure S1b are the aggregations of PC<sub>61</sub>BM.

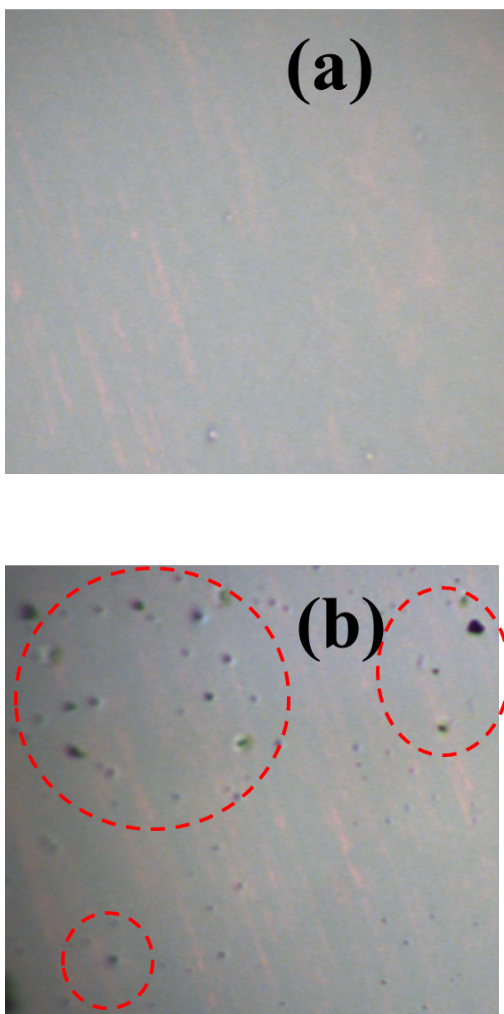


Figure S1: Optical microscopic images of (a) P3HT/PCBM/2,3-pyridinediol blended film without thermal annealing. (b) P3HT/PCBM/2,3-pyridinediol blended film with thermal annealing at 150 °C.

The cross section area on the P3HT/PC<sub>61</sub>BM blended film with additive was chosen randomly. The peak number of all area falls between 31~ 37 peaks. Figure S2 listed two extreme areas (which have 31 peaks and 37 peaks, respectively).

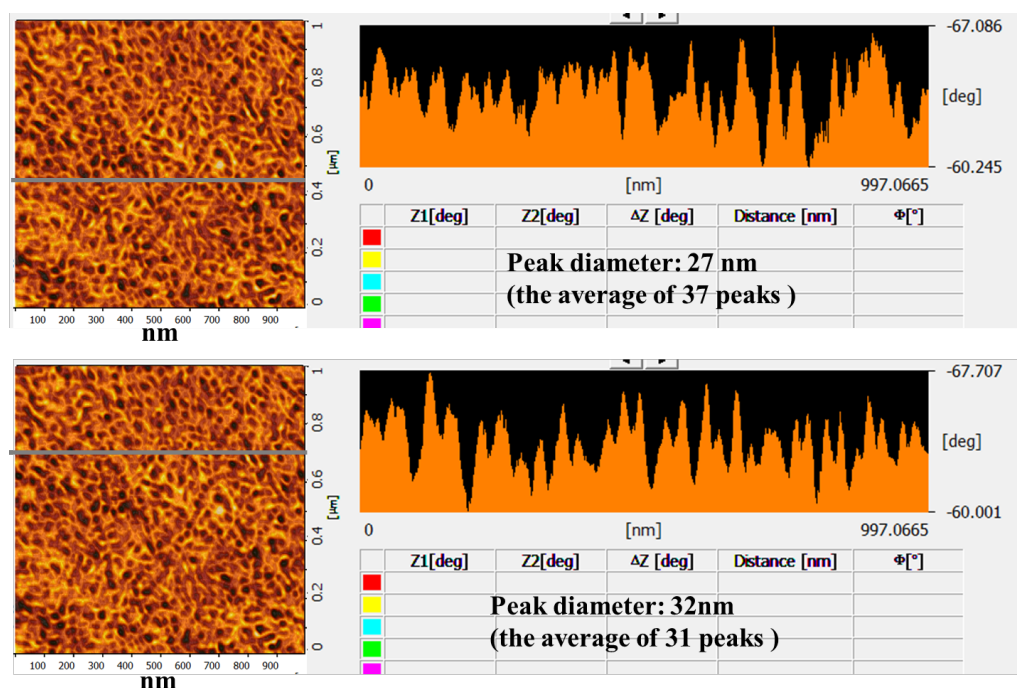


Figure S2: The cross section of P3HT/PC<sub>61</sub>BM blended film with additive at two different areas. 1000 nm length contains 37 and 31 peaks, corresponding to 27 nm and 32 nm for each peak, respectively.

In three NMR tubes containing 2 mL  $\text{CDCl}_3$ , 5 mg 2,3-pyrininediol, 5 mg 2,3-pyrininediol mixed with PCBM (1:1 weight ratio) and 5 mg 2,3-pyrininediol mixed with P3HT (1:1 weight ratio) were added in each tube. The tubes were shaken for 5 min and stand for 5 min, then the pictures were taken.  $^1\text{H}$ -NMR spectra (from Bruker 300 MHz-NMR spectrometer) of the sample in tube (a) and (c) are also taken immediately after the compounds were added and shaken.

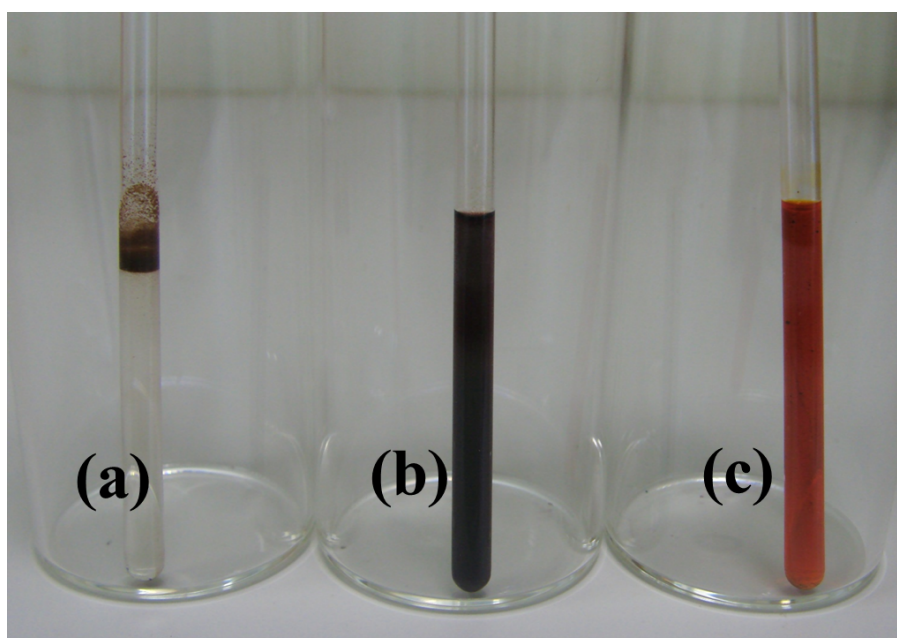


Figure S3: The photographs of (a) 2,3-pyrininediol in  $\text{CDCl}_3$ .

(b) 2,3-pyrininediol +  $\text{PC}_{61}\text{BM}$  in  $\text{CDCl}_3$ .

(c) 2,3-pyrininediol + P3HT in  $\text{CDCl}_3$ .

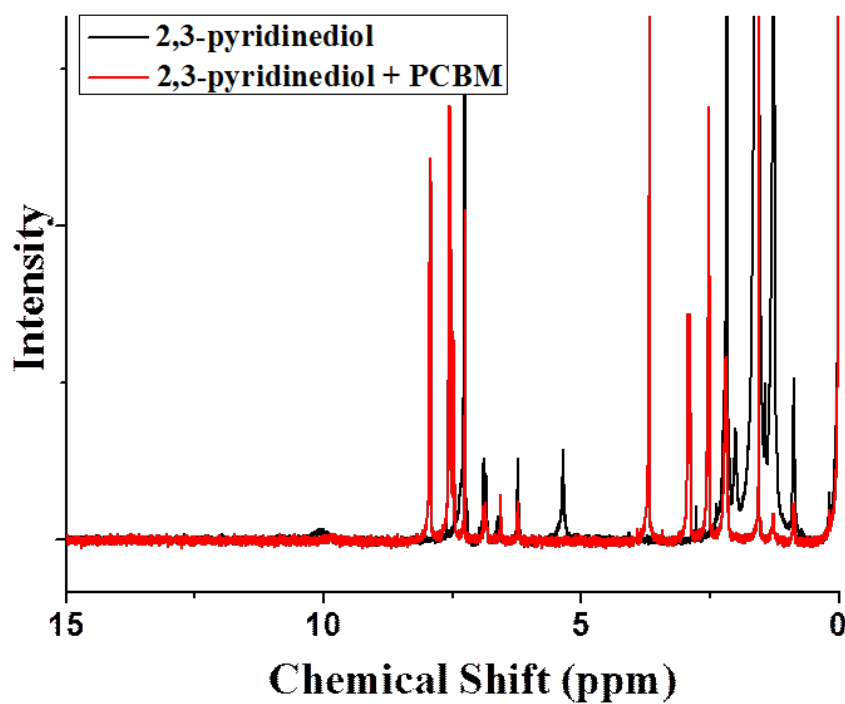


Figure S4: <sup>1</sup>H-NMR spectra of 2,3-pyridinediol and 2,3-pyridinediol mixed with PC<sub>61</sub>BM. (the impurity peaks (for 2,3-pyridinediol) showed between 5-0 ppm come from the solvent residues in NMR tube).

The thermal stability of PTB7/PC<sub>71</sub>BM blended film was test by heating the active film at 100 °C during the process of BHJ-PSC devices assembly. All devices are fabricated at the same condition except the thermal annealing of the active layer.

Table S1: The photovoltaic parameters of devices based on PBT7/PC<sub>71</sub>BM films processed under different conditions.

| <b>Additive</b>           | <b>Thermal treated<br/>Temperature/Times</b> | <b><i>J</i><sub>sc</sub><br/>(mA/cm<sup>2</sup>)</b> | <b><i>V</i><sub>oc</sub><br/>(V)</b> | <b>FF</b> | <b>PCE<br/>(%)</b> |
|---------------------------|----------------------------------------------|------------------------------------------------------|--------------------------------------|-----------|--------------------|
| None                      | None                                         | 15.79                                                | 0.78                                 | 0.43      | 5.31               |
| None                      | 100 <sup>o</sup> C/10 min                    | 15.09                                                | 0.78                                 | 0.44      | 5.27               |
| None                      | 100 <sup>o</sup> C/30 min                    | 13.56                                                | 0.76                                 | 0.45      | 4.69               |
| DIO <sup>a</sup>          | None                                         | 17.16                                                | 0.73                                 | 0.53      | 6.62               |
| DIO <sup>a</sup>          | 100 <sup>o</sup> C/10 min                    | 15.40                                                | 0.75                                 | 0.47      | 5.44               |
| DIO <sup>a</sup>          | 100 <sup>o</sup> C/30 min                    | 13.16                                                | 0.75                                 | 0.42      | 4.26               |
| Pyridinediol <sup>b</sup> | None                                         | 18.35                                                | 0.77                                 | 0.53      | 7.54               |
| Pyridinediol <sup>b</sup> | 100 <sup>o</sup> C/10 min                    | 18.19                                                | 0.76                                 | 0.53      | 7.39               |
| Pyridinediol <sup>b</sup> | 100 <sup>o</sup> C/30 min                    | 16.91                                                | 0.74                                 | 0.58      | 7.30               |

a: 3 % in volume of DIO (diiodo-octane) in DCB, b: 3wt% pyrininediol in DCB