

## Supporting Information

### **Bathocuproine as a cathode interlayer for nonfullerene organic solar cells with efficiency over 17%**

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## Experiment section

### Materials

Material for active layer (PM6, Y6, IT-4F and PC<sub>71</sub>BM) were purchased from Solarmer Materials Inc. PEDOT:PSS (Clevios PVP AI 4083, 1.3 -1.7 wt.% in water) was purchased from Xi'an Polymer Light Technology Corp. BCP (96%) and PDINN (98%) were purchased from Sigma-Aldrich and Solarmer Materials Inc respectively. Chloroform (99%), chloronaphthalene (95%) and methanol (99.8%) were purchased from Sigma-Aldrich.

### Device fabrication

First, the hole transporting layer PEDOT:PSS was deposited on ITO substrate (10 ohm sq<sup>-1</sup>) and annealed at 150 °C for 10 minutes to remove residual water. Then, the active layer was spin-coated on PEDOT:PSS and annealed at 100 °C for 10 minutes in N<sub>2</sub>-filled gloveboxes. The active layer was prepared by dissolving donor and acceptor (7:8.4 mg) in 1 ml mixed-solvent (The volume ratio of chloroform and chloronaphthalene is 99.5:0.5.) and stirred for over 6 hours. The donor is PM6 and the acceptor is the mixture of Y6 and PC<sub>71</sub>BM with different ratios (The weight ratio is from 1:1.2:0 to 1:0:1.2). Next, the CIL of BCP (0.5 mg in 1 ml methanol) or PDINN (1 mg in 1ml methanol) was spin-coated on the active layer at speed of 3000 rpm without further annealing. Finally, top Ag (70 nm) electrode was fabricated under a high vacuum ( $< 5 \times 10^{-7}$  Torr) through a shadow mask by thermal evaporating (Mini-spectros, Kurt J. Lesker). The effective active area is 4.1 mm<sup>2</sup>.

### Characterization

*J-V* curves of the cells were measured using a Keithley 2400 SourceMeter under 100 mW cm<sup>-2</sup> AM1.5 solar simulator (Newport, Sol3A, 450 W xenon lamp). The measurement was performed in a N<sub>2</sub>-filled glove box at the temperature of 25 °C. The light intensity of the light source was calibrated with a silicon photodiode (Hamamatsu, S1133-01). The scan rate was 0.2 V s<sup>-1</sup> and the dwell time was 0.1 s.

EQE test was characterized using a 150 W xenon lamp (Oriel) filtered with a monochromator (Cornerstone 74004) as a monochromatic light source.

Absorbance was measured with a UV-vis-NIR Spectrophotometer (UV3600, Shimadzu). The

concentration of acceptor is 0.1 mg/ml in chloroform. The weight ratio of acceptor to BCP is 5:1. The films were deposited by spin-coating the solvent at a speed of 2000 rpm and annealed at 100 °C for 10 min.

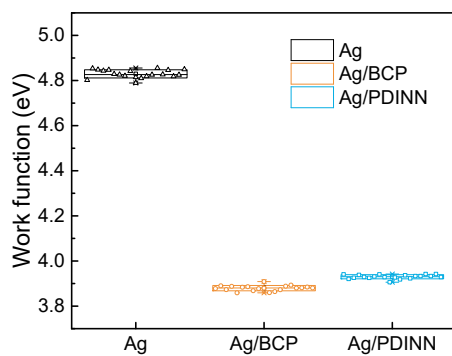
XPS measurements were carried out with a spectrometer (AXIS-ULTRA DLD-600W) in the analysis chamber at a base pressure of  $10^{-9}$  mbar. The data was collected with monochromatic Al ( $K\alpha$ ) radiation at  $h\nu = 1486.6$  eV. All recorded peaks were corrected for electrostatic effects by setting the C–C component of the C 1s peak to 285 eV.

Work function was measured by Kelvin probe (KP-020, KP Technology). A highly ordered pyrolytic graphite with a work function of 4.6 eV was used as the reference sample.

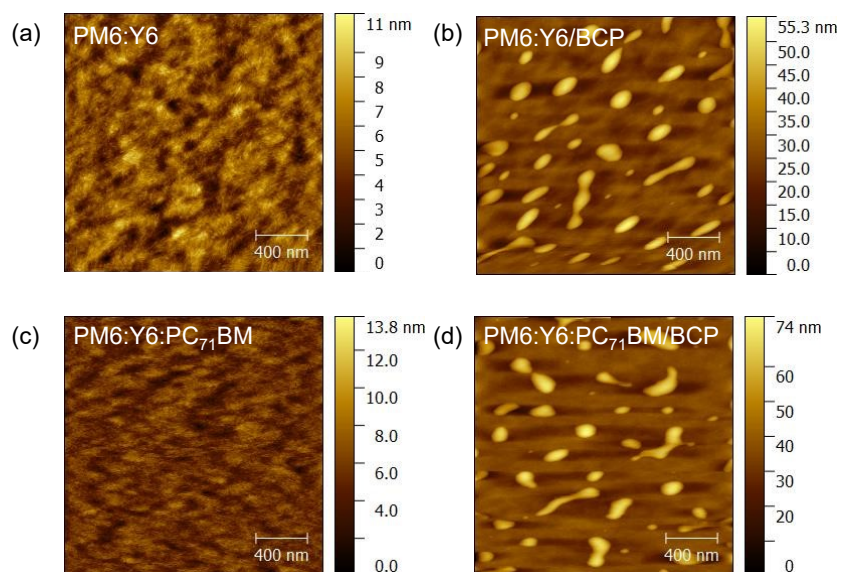
The NMR spectra were collected on a Bruker Ascend 400 MHz NMR spectrometer using deuterated chloroform as the solvent.

The mass spectrometry measurement was performed on an Agilent 1100 LC-MS Trap XCT System (Agilent Technologies, USA).

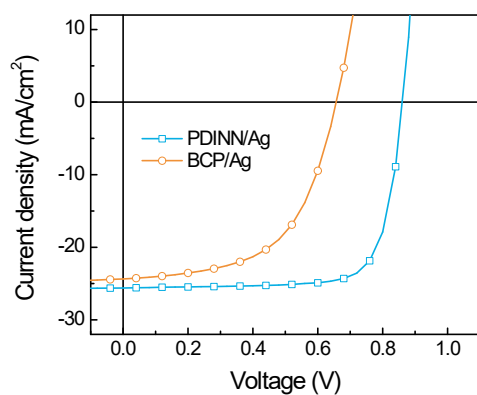
**Figure S1.** The changing of work function when using BCP and PDINN as CIL.



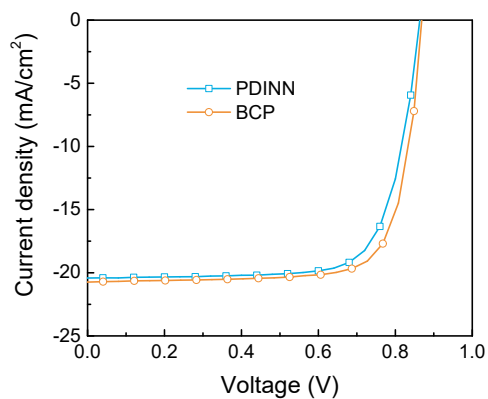
**Figure S2.** The morphology of BCP deposited on PM6:Y6 and PM6:Y6:PC<sub>71</sub>BM active layer.



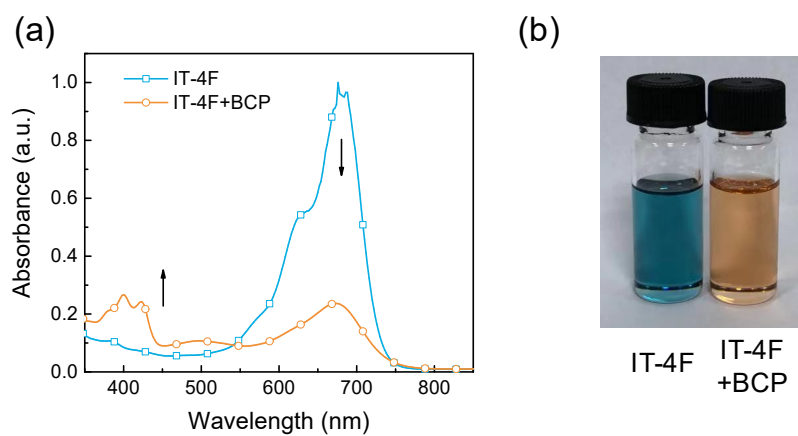
**Figure S3.** The  $J$ - $V$  curves of the ternary OSC with the structure of ITO/PEDOT:PSS/PM6:Y6:IT-4F/CIL/Ag, where the CIL is BCP or PDINN. The ratio of PM6:Y6:IT-4F is 1:1:0.2.



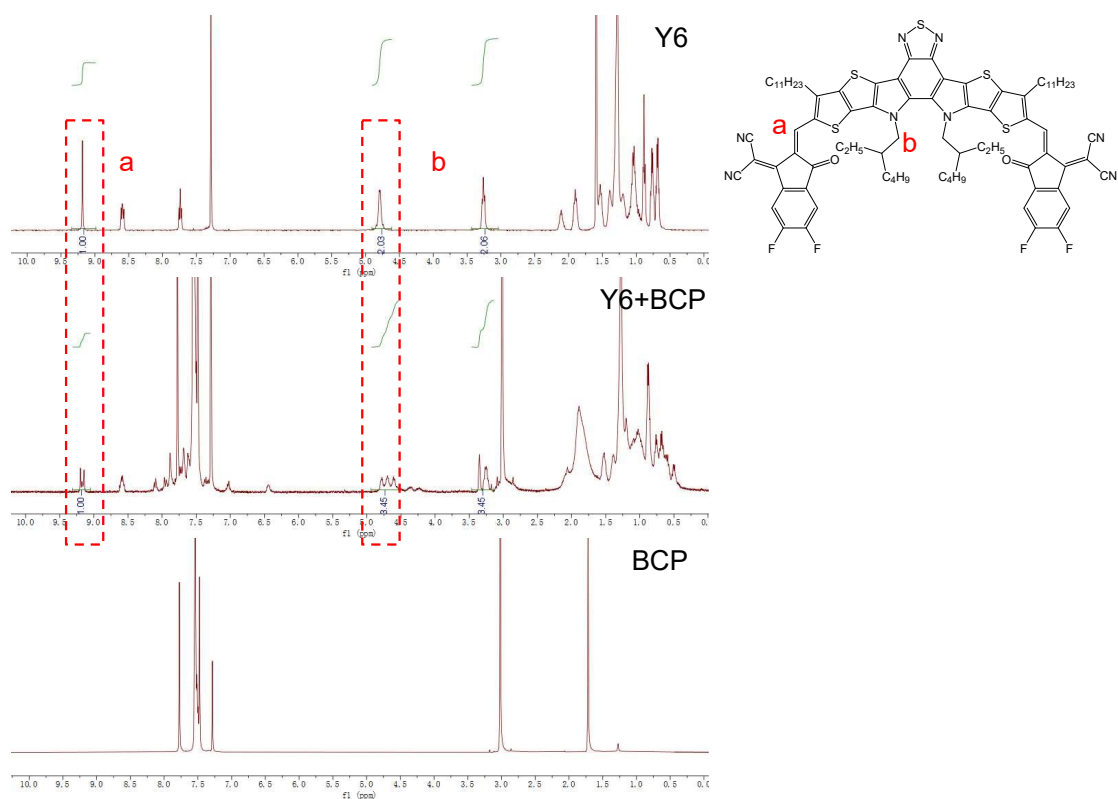
**Figure S4.** The  $J$ - $V$  curves of the ternary OSC with the structure of ITO/PEDOT:PSS/PM6:IT-4F:PC<sub>71</sub>BM/CIL/Ag, where the CIL is BCP or PDINN. The ratio of PM6: IT-4F:PC<sub>71</sub>BM is 1:1:0.2.



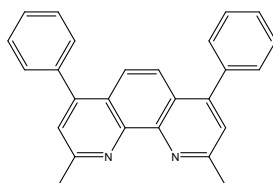
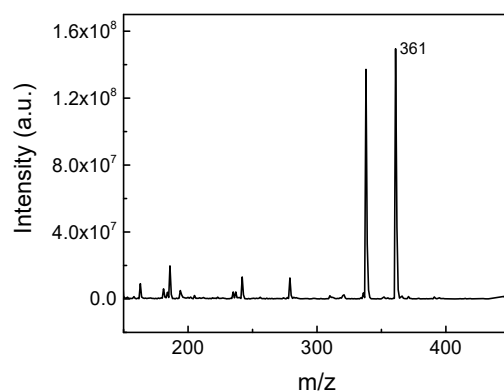
**Figure S5.** The (a) absorbance and (b) relevant optical photograph of IT-4F solution and a mixture of IT-4F and BCP.



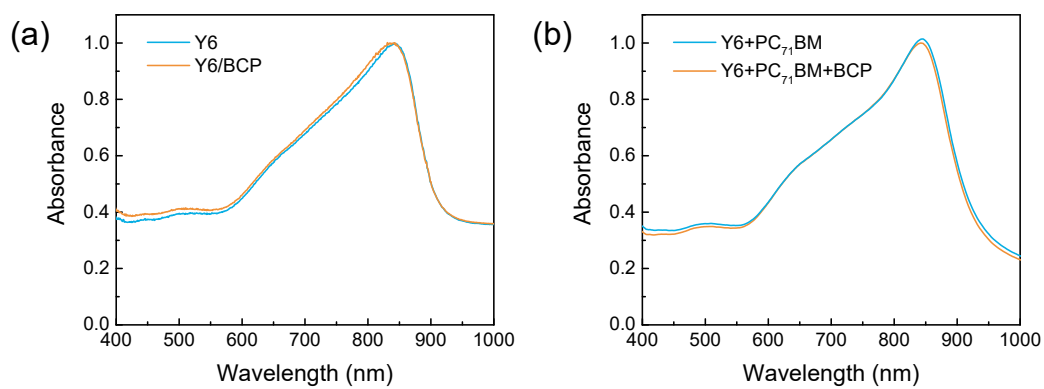
**Figure S6.**  $^1\text{H}$  NMR spectra of Y6, Y6+BCP and BCP. The reagent is  $\text{CDCl}_3$ . The marked dash box is to show the intensity change of H at the position of marked "a" and "b" in the chemical structure of Y6.



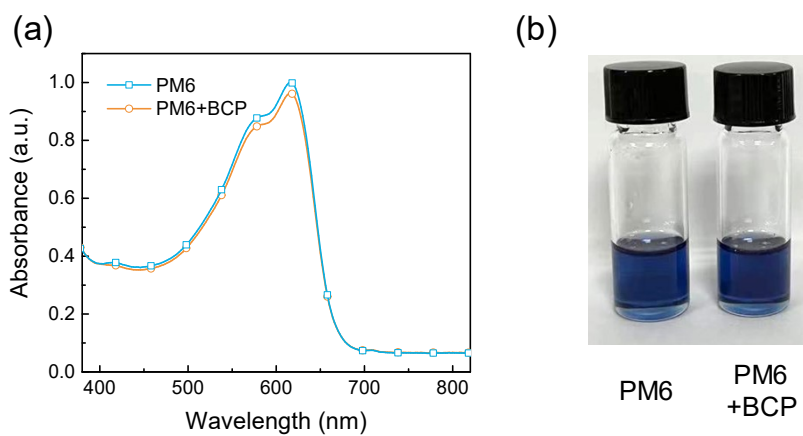
**Figure S7.** Mass spectra of BCP.



**Figure S8.** The absorbance of (a) Y6 and (b) Y6:PC<sub>71</sub>BM film after depositing BCP layer.



**Figure S9.** The (a) absorbance and (b) relevant optical photograph of PM6 solution and a mixture of PM6 and BCP.



**Figure S10.** The absorbance of BCP and PDINN.

