

## Electronic Supplementary Information (ESI)

### Bulk Heterojunction Photovoltaic Cells Based on

### Tetra-methyl Substituted Copper (II)

### Phthalocyanine:P3HT:PCBM Composite

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**Materials Synthesis:** All materials were purchased from Aldrich and used as received. The synthesis of tetramethyl substituted copper (II) phthalocyanine (CuMePc) was carried out according to literature method,<sup>1</sup> and characterized by UV/Vis, elemental analysis. A mixture of 4-methylphthalonitrile and copper (II) salt was heated and stirred in quinoline at 180 °C for 3 hours under a nitrogen atmosphere. After cooling to room temperature, the mixture was washed with ethanol. The blue precipitate was filtered, washed with water and ethanol to form the raw product. The CuMePc nanocrystals were grown by horizontal physical vapor deposition under vacuum according to a literature process.<sup>2</sup> The evaporating material CuMePc was heated to 400 °C in the hot zone of two zone furnace. The second zone was held at room temperature. CuMePc nanocrystals spontaneously grew on a quartz tube wall between the zones as dark blue powder. UV/Vis spectra of sublimated CuMePc in DMF was recorded on a Perkin-Elmer Lambda 19 UV/Vis spectrophotometer. For CuMePc, UV/Vis (DMF):  $\lambda_{\max}$  = 612, 649, 680 nm; elemental analysis calcd (%) for C<sub>36</sub>H<sub>24</sub>CuN<sub>8</sub>; C 68.40, H 3.83, N 17.73; found C 67.84; H 3.87; N 17.62.

**Thin film fabrication:** Thin film samples (~100 nm) of CuMePc or P3HT or CuMePc:P3HT (weight ratio of 1:5, 1:3, 1:1, 3:1 and 5:1 which were denoted as P5C1, P3C1, P1C1, P1C3, and P1C5) composites were fabricated by spin coating

with a concentration of 10-20 mg/ml in dichlorobenzene (DCB) on the SiO<sub>2</sub>/Si or ITO substrates annealed at 120 °C for 15 minutes.

**Thermo Gravimetric Analysis (TGA):** A few milligrams of CuMePc nanocrystals were loaded on an aluminum/platinum crucible. Weight loss of sample was recorded using a Perkin-Elmer TGA-7 analyzer in the temperature range 50-800 °C under a flowing N<sub>2</sub> stream.

**UV/Vis measurement:** UV/Vis spectra of as spin-coated films made up of CuMePc nanocrystals and CuMePc:P3HT composite on ITO glass were recorded on a Perkin-Elmer Lambda 19 UV/Vis spectrophotometer.

**Ultraviolet Photoemission Spectroscopy (UPS):** All measurements were performed in a VG ESCALAB 220i-XL UHV photoelectron spectroscopy system comprising of an analysis chamber interconnected to a preparation chamber. A clean *p*-type Si with a native oxide layer was used as a substrate. CuMePc films were grown in steps by thermal evaporation on the substrate in the preparation chamber and transported to the analysis chamber. The film thickness and evaporation rate were monitored and controlled via a quartz crystal microbalance. UPS measurements were performed using a He I (21.2 eV) discharge lamp and with a sample biased of -4 V. The resolution of UPS measurements was 0.09 eV.

**Scanning Electron Microscopy (SEM):** Images of films surface morphology for the thin films made from CuMePc and CuMePc:P3HT composite by spin coating on Si/SiO<sub>2</sub> were recorded using scanning electron microscopy (LEO 1530). Prior to SEM image acquisition, all the film samples were individually pre-coated with a metallic gold layer having a thickness of 0.5 nm under vacuum.

**Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED):** CuMePc nanocrystals were sonicated in ethanol then dropped onto a holey carbon coated copper grid. TEM and SAED measurements were recorded using FEI Tecnai G2 20 STEM.

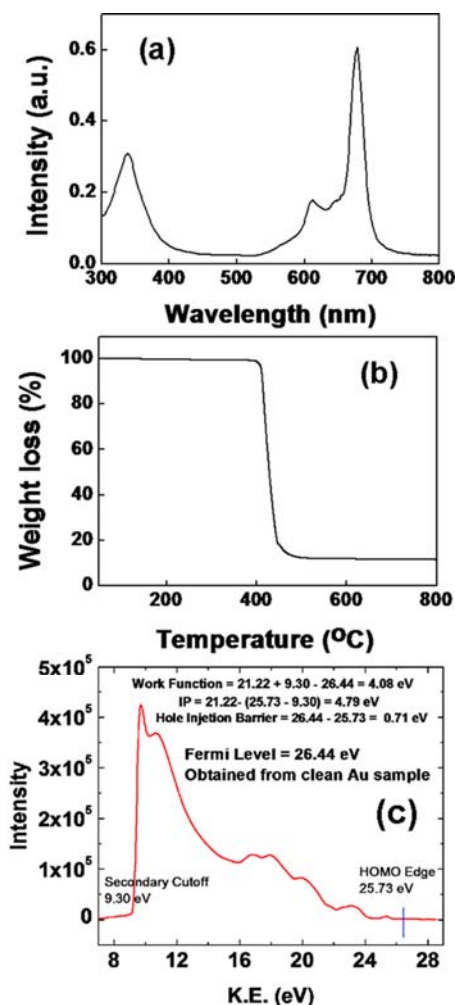
**Grazing Incidence X-ray Diffraction (GIXRD):** Grazing incidence X-ray diffraction patterns of as spin coated films formed on SiO<sub>2</sub>/Si substrate were recorded using a Bruker D8 Advance ( $\theta/\theta$ ) diffractometer with a Göbel mirror attachment. Irradiation of the parallel CuK <sub>$\alpha$ 1,2</sub> X-ray beam was fixed at a grazing incident angle of 1.000° ( $\theta$ ) and the detector was independently moved to collect the diffraction data in 2 $\theta$  range of 3-15° with a step-size of 0.02° (2 $\theta$ ) at a fixed speed of *ca* 5 second/step.

**Fabrication of Thin Film Transistors and Charge Mobility Measurements:** The bottom-contact thin film transistors based on thin film samples (~100 nm) of CuMePc or P3HT or CuMePc:P3HT (weight ratio of 1:5, 1:3, 1:1, 3:1 and 5:1 which were denoted as P5C1, P3C1, P1C1, P1C1, P1C3, and P1C5) composites were fabricated

by spin coating with a concentration of 10-20 mg/ml in dichlorobenzene (DCB) on the patterned SiO<sub>2</sub>/Si substrate and measured according a literature method.<sup>3</sup>

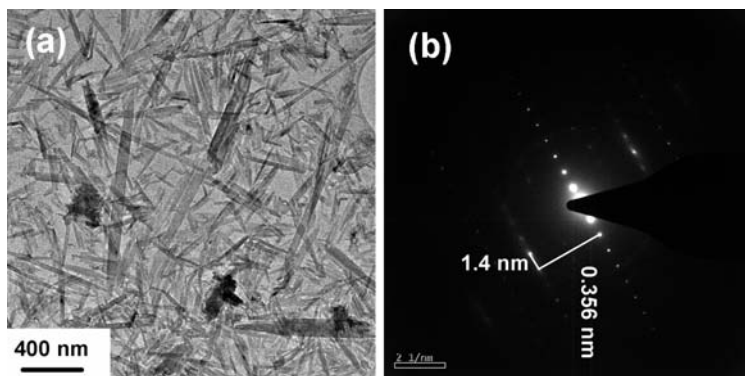
**Photovoltaic Cells Fabrication and Measurement:** The OPV cells were fabricated on precleaned glass substrates precoated with a ~1500-Å-thick transparent, conducting patterned indium tin oxide (ITO) anode with a sheet resistance of ~20 Ω / sq. The ITO glass substrate was first cleaned in ultrasonic bath for 20 min in Deconex detergent, distilled water and in acetone two times, and was dried in an oven at 100 °C. UV-ozone treatment was then performed for 20 min. Solution processed photovoltaic cells were fabricated by spin coating a dichlorobenzene (DCB) solution of CuMePc, P3HT or P3HT:CuMePc (3:1, 1:1 and 1:3 denoted as P3C1, P1C1 and P1C3) and PCBM composite in a weight ratio of 1:1 on pre-cleaned ITO substrate. The thickness of photoactive layer was controlled by the speed of spin coating. A 100 nm Al cathode was deposited through a shadow mask. The OPV cells with the following structures were fabricated:

ITO/CuMePc:PCBM or P3HT:PCBM or P3HT:CuMePc:PCBM (~100 nm)/Al (100nm). The current density–voltage (*J-V*) curves were recorded by a computer controlled Keithley 2400 source-measure unit. The photocurrent was measured in the dark and under AM 1.5 solar illuminations at an intensity of 100 mW/cm<sup>2</sup> with an Oriel 150 W solar simulator using a programmable Oriel mode 69907 power source. The light intensity was measured with an Oriel radiant power meter.

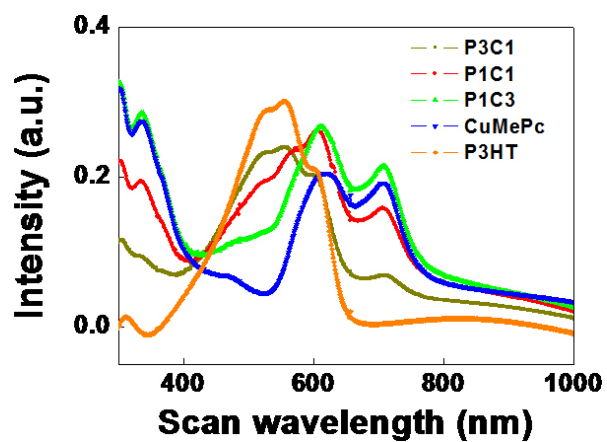


**Fig. 1S** (a) UV/Vis absorption spectrum for the solution of CuMePc in DMF; (b) TGA curve and (c) UPS spectrum of CuMePc nanocrystals.

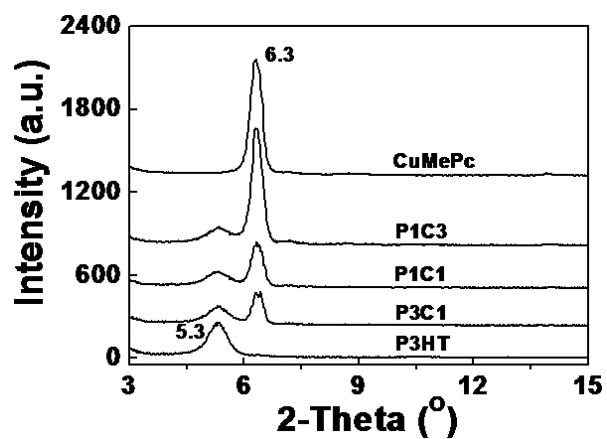
Fig. 1S (a) depicts the UV/Vis absorption spectrum of the CuMePc nanocrystals dissolved in dimethylformamide (DMF). Due to its poor solubility, the absorption spectrum of CuMePc in dichlorobenzene was not able to record. There are two sets of strong absorption bands, one is an intense single absorption at 680 nm and a shoulder at ~610 nm (Q band), both are attributed to  $\pi \rightarrow \pi^*$  transitions. The other absorption band is found to be at about 340 nm denoted as B band. The B band of phthalocyanine arises from the deeper  $\pi$  levels  $\rightarrow$  LUMO transitions.<sup>4</sup> CuMePc nanocrystal was found to exhibit good thermal stability with onset decomposition temperature of 410 °C as determined by thermo gravimetric analysis (TGA) under a nitrogen atmosphere (Fig. 1S b).



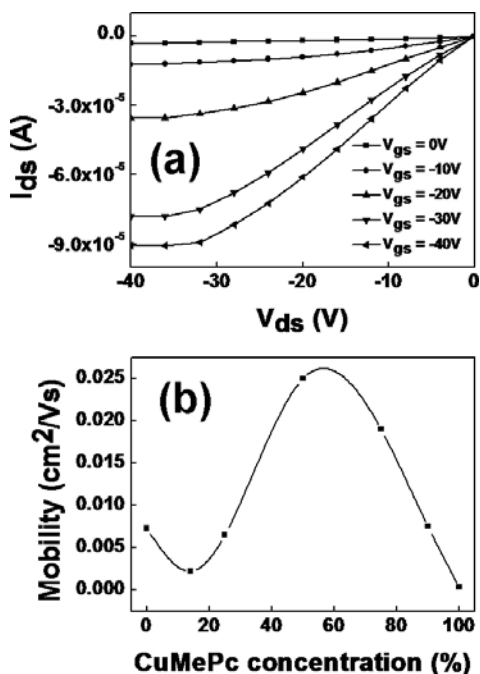
**Fig. 2S** (a) TEM image and (b) Selected area electron diffraction (SAED) pattern of CuMePc nanocrystals.



**Fig. 3S** UV/Vis absorption spectra for the films of CuMePc, P3HT and P3HT:CuMePc (weight ratio of 1:3, 1:1 and 3:1, denoted as P1C3, P1C1 and P3C1) composites (fabricated on ITO by spin coating and annealed at 120 °C for 15 minutes).



**Fig. 4S** GIXRD patterns for the films of CuMePc, P3HT and P3HT:CuMePc (weight ratio of 1:3, 1:1 and 3:1, denoted as P1C3, P1C1 and P3C1) composites (fabricated on SiO<sub>2</sub>/Si by spin coating and annealed at 120 °C for 15 minutes).



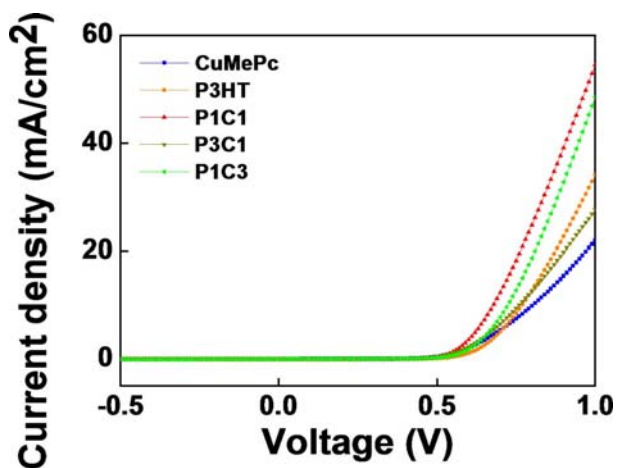
**Fig. 5S** (a) Output characteristics of the bottom-contact TFT device fabricated with the spin-coating P3HT:CuMePc composite (weight ratio of 1:1, channel length = 10  $\mu\text{m}$  and width = 3000  $\mu\text{m}$ ) and (b) Correlation between the TFT mobility and concentration of CuMePc nanocrystals in P3HT:CuMePc composite.

All devices showed *p*-type characteristics. Fig. 5S a shows the typical TFT output characteristics with a device made up of P1C1 composite as an example. The output characteristics exhibit standard linear and saturation regions, and the negative source-drain current ( $I_{ds}$ ) increases with an increasing negative gate voltage ( $V_{gs}$ ) bias. Fig. 5S b depicted the correlation between the carrier mobility and the concentration of CuMePc nanocrystals in P3HT:CuMePc composite.

**Table 1S.** Photovoltaic performance of the as-fabricated devices made from the thin film samples of CuMePc:PCBM, P3HT:PCBM and P3HT:CuMePc:PCBM composites.

Device	Hole mobility ( $\text{cm}^2/\text{Vs}$ )	Series resistance ( $\Omega/\text{cm}^2$ )	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	$V_{oc}$ (V)	$FF$ (%)	$PCE$ (%)
CuMePc	$2.9 \times 10^{-4}$	15.5	4.8	0.54	43	1.1

<b>P3HT</b>	$7.3 \times 10^{-3}$	8.3	10.7	0.61	50	3.2
<b>P1C1</b>	$2.5 \times 10^{-2}$	6.5	16.3	0.58	56	5.3
<b>P3C1</b>	$6.5 \times 10^{-3}$	12.9	12.1	0.58	47	3.3
<b>P1C3</b>	$1.9 \times 10^{-2}$	6.4	13.8	0.58	54	4.4



**Fig. 6S** Current ( $J$ )-voltage ( $V$ ) characteristics of solar cells made from CuMePc, P3HT and P3HT:CuMePc composites measured in the dark.

#### References

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