Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Influence of metal phthalocyanine molecular orientation on charge separation at organic donor/acceptor interface

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Table S1. Ionization potential (IP) values marked in Figure 3 for C_{60}/MPc (M = Zn, Cu) bilayer without and with CuI layer by the UPS measurement.

IP		M = Zn(II)		M = Cu(II)	
Coverage		Without CuI	With CuI	Without CuI	With CuI
MPc	10nm	5.07	4.85	5.00	5.63
C_{60}	0.3nm	5.05	4.88	4.80	5.50
	0.6nm	5.05	4.95	4.70	5.50

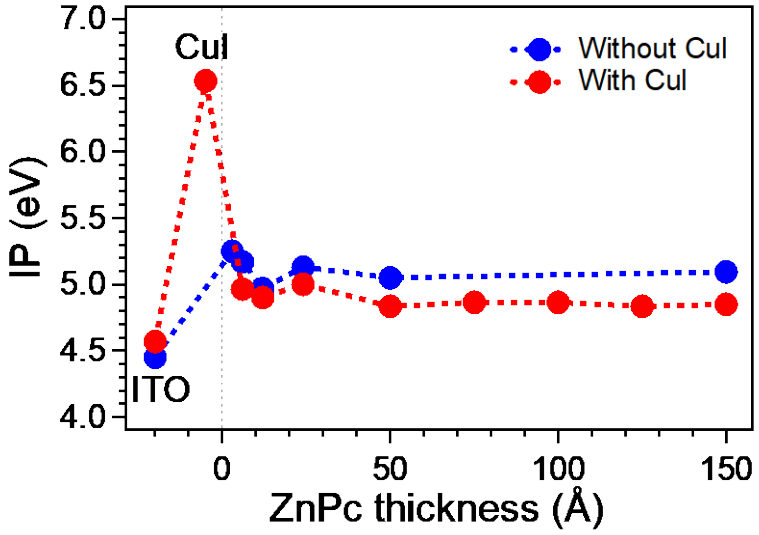

Fig. S1 Ionized potential (IP) versus ZnPc thickness with (red) and without (blue) CuI layer

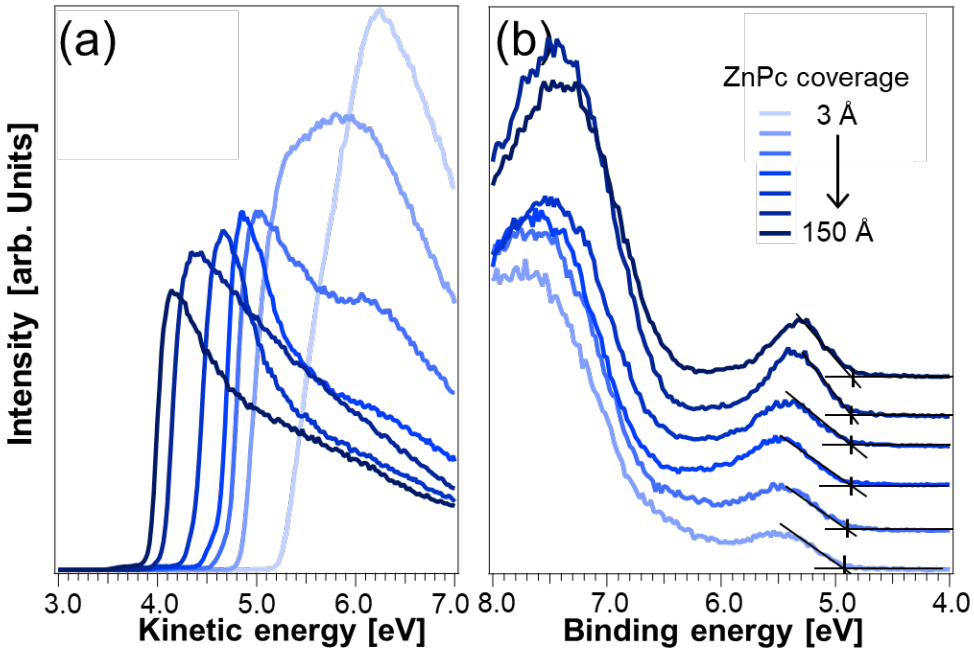

Fig. S2 (a) The secondary electron cutoff (SECO) and (b) the valence band spectra of ZnPc layer on CuI/ITO during the continuous ZnPc evaporation from 3 Å to 150 Å.

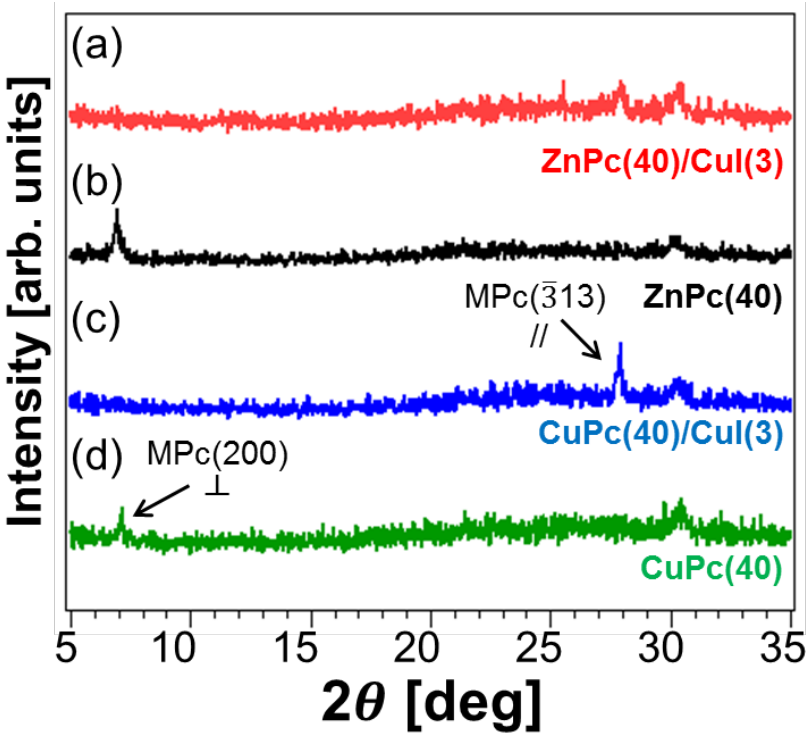

Fig. S3 X-Ray Diffraction (XRD) patterns of (a) ZnPc/CuI, (b) ZnPc, (c) CuPc/CuI, and (d) CuPc deposited on ITO substrates. The MPc is 40 nm-thick and CuI is 3 nm-thick. The molecular orientation of MPc films exhibits the α-form. The small peak at ~ 30.2 ˚ is attributed to ITO substrate.

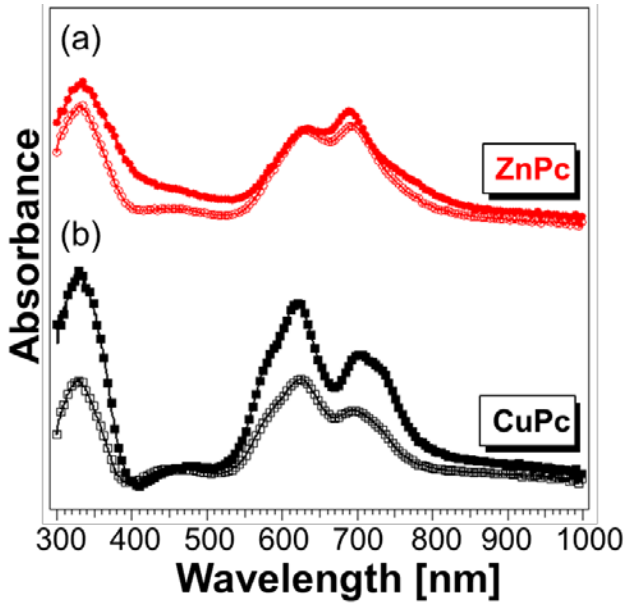

Fig. S4 UV absorption spectra of (a) 10 nm ZnPc and (b) 10 nm CuPc with (filled symbols) or without (open symbols) 3 nm CuI layer deposited on the ITO, respectively.

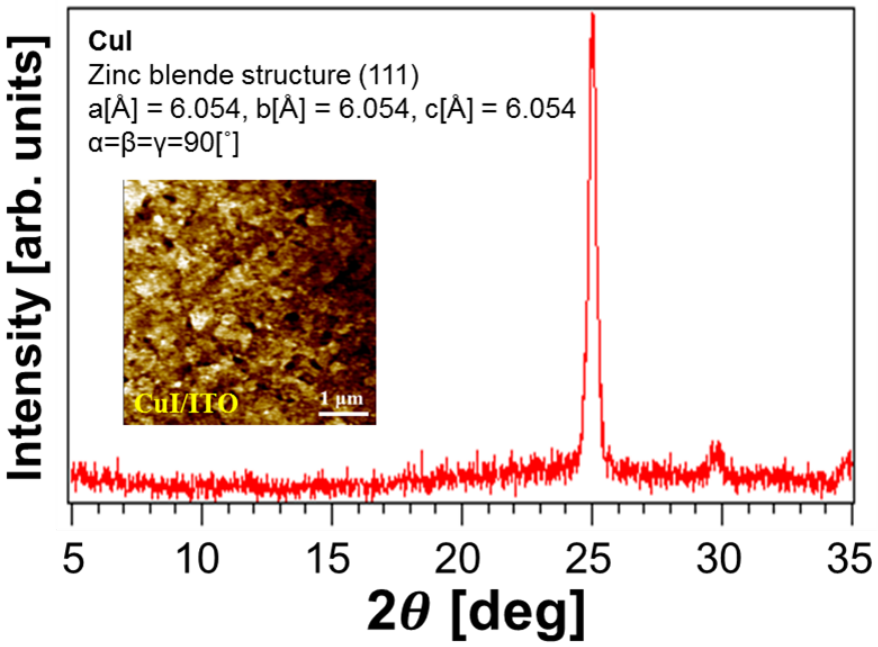

Fig. S5 X-Ray Diffraction (XRD) pattern and AFM image of 10 nm CuI deposited on ITO substrates.

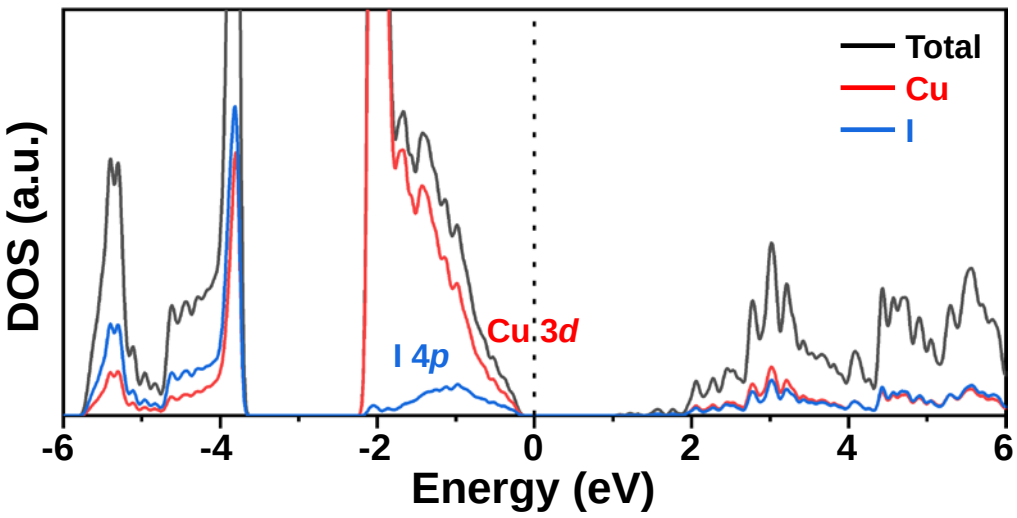

Fig. S6 Density of state (DOS) of CuI bulk. Black, red and blue lines indicate total DOS of CuI bulk, partial DOS of copper and iodine, respectively. Energy zero indicates the Fermi level.

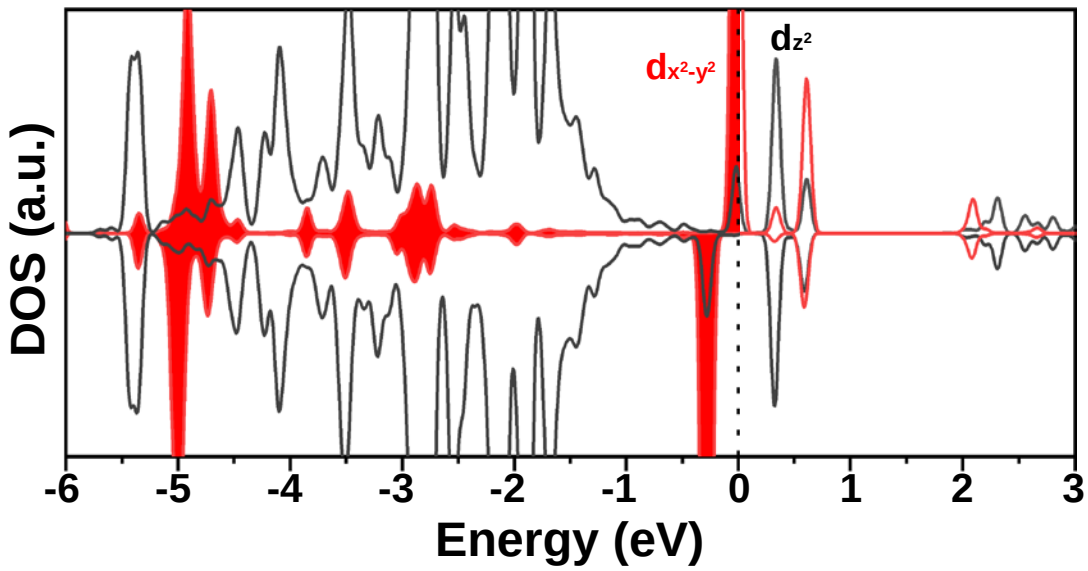

Fig. S7 Partial density of states (PDOS) of binding model of CuPc to CuI($\bar{1}\bar{1}\bar{1}$)-3Cu_{adatom} $\sqrt{3}\times\sqrt{3}$ R30° surface. Black line indicates the d_{z2} states of surface Cu atoms and red line indicates the d_{x2-y2} states of Cu in CuPc. Energy zero indicates the Fermi level.

Table S2. The cell structures and corresponding device parameters.

Cell structure	V_{OC} (V)	J_{SC} (EQE) (mA/cm^2)	FF	PCE (%)
ITO/CuPc(20)/C_{60}(40)/BCP(8)/Al(100)	0.47	3.89 (3.86)	0.56	1.01
ITO/CuI(3)/CuPc(20)/C_{60}(40)/BCP(8)/Al(100)	0.51	4.27 (4.82)	0.60	1.31
ITO/ZnPc(20)/C_{60}(40)/BCP(8)/Al(100)	0.53	3.98 (4.04)	0.62	1.30
ITO/CuI(3)/ZnPc(20)/C_{60}(40)/BCP(8)/Al(100)	0.55	5.28 (5.56)	0.63	1.84

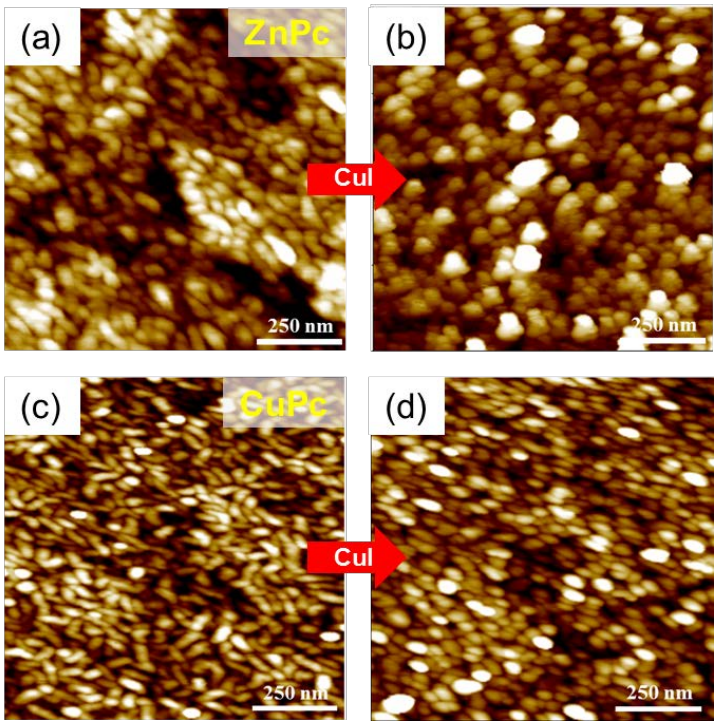

Fig. S8 AFM images of 40 nm thin films of (a) ZnPc, (b) ZnPc/CuI, (c) CuPc, and (d) CuPc/CuI deposited on ITO, respectively. The thickness of CuI layer is 3 nm. All MPc and CuI layers are deposited at the rate of 0.1 Å/s.

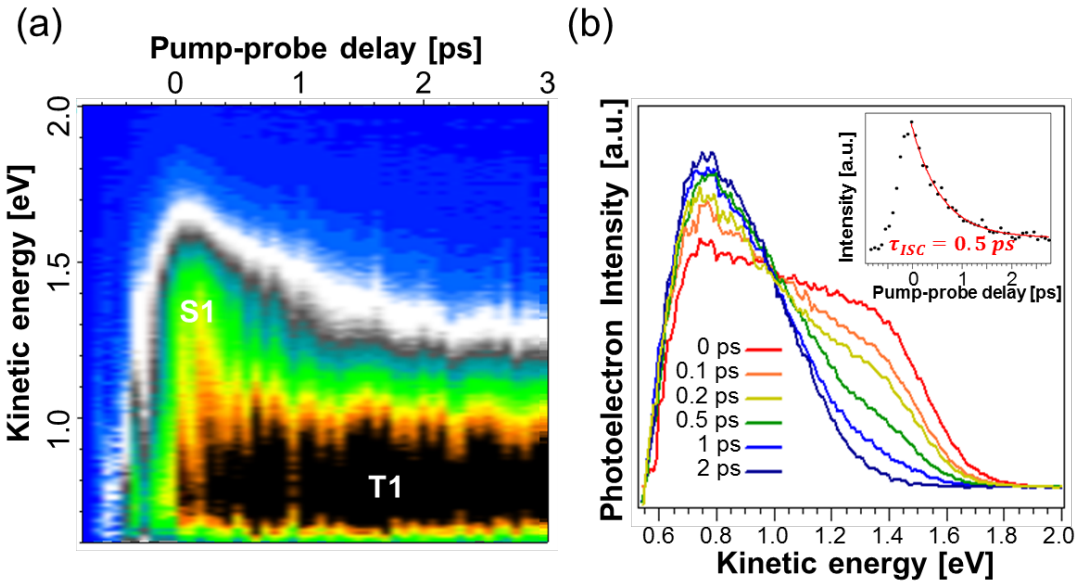

Fig. S9 (a) Two-dimensional TR-2PPE trace of 10 nm CuPc film deposited on Au(111) substrate with 5 nm CuI layer. The pump (hv_1) and probe energies (hv_2) are 1.65 eV and 4.96 eV, respectively. (b)

Energy-resolved 2PPE spectra at the different delay times (0.1, 0.2, 0.5, 1 and 2 ps). Inset: Intensity change at S1 peak (~1.35 eV) as a function of time delay.

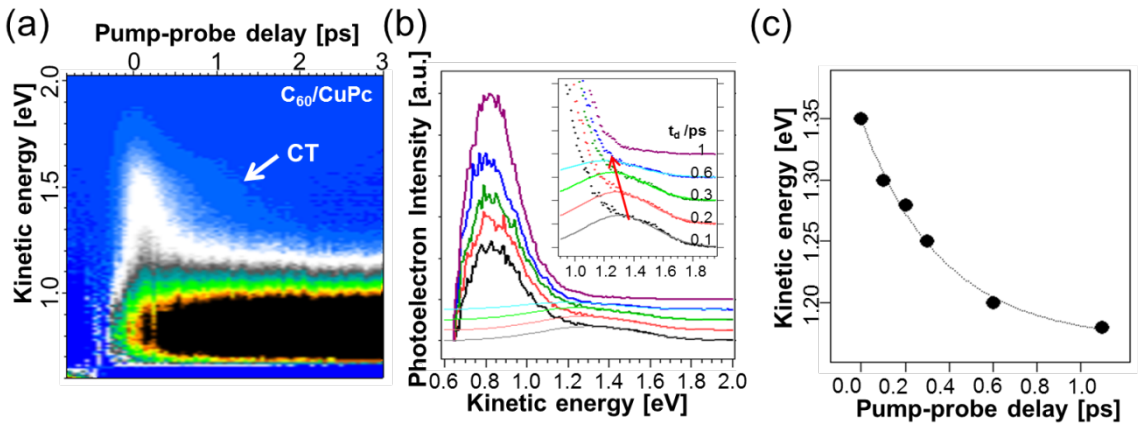

Fig. S10 Two-dimensional TR-2PPE trace of (a) 1 nm C_{60}/10 nm CuPc on Au(111) substrate with 5 nm CuI layer. (b) Energy-resolved 2PPE spectra at the early delay times (0.1, 0.2, 0.3, 0.6 and 1 ps). Inset: Magnified 2PPE spectra at high kinetic energy range. (c) Change of CT position as a function of pump-probe delay ($\triangle t$). The pump (hv_1) and probe energies (hv_2) are 1.65 eV and 4.96 eV, respectively.