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Supporting information

Image-force effects on energy level alignment at electron transport material/cathode interfaces

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Integer charge transfer (ICT) model: When organic semiconductors are deposited on a passivated substrate, *e.g.*, metal covered with a thin oxide layer or residual hydrocarbons, inorganic and organic semiconductor, physisorption will occur with a weak interaction at the interface. The electronic structure only changes via tunneling process and can be predicted and explained by the ICT model. In general, when the substrate work function (Φ_{sub}) is higher than the smallest energy required to take away one electron from the organic molecule near the interface producing a fully relaxed state (E_{ICT+}), electrons will transfer from substrate to the molecule and equilibrate until the Fermi level aligned to E_{ICT+}; when the substrate work function is lower than the largest energy gained when one electron is added to the molecule near the interface producing a fully relaxed state (E_{ICT-}), electrons will transfer from the molecule to substrate and equilibrate until the Fermi level aligned to E_{ICT-}. As a result, the relation curve of the organic/substrate work function ($\Phi_{sub/org}$) and Φ_{sub} is divided into three regimes: (i) $\Phi_{sub} < E_{ICT-}$, slope = 0, $\Phi_{sub/org} = E_{ICT-}$ with a positive interface dipole; (ii) $E_{ICT-} < \Phi_{sub} < E_{ICT+}$, slope = 1, $\Phi_{sub/org} = \Phi_{sub}$ with negligible interface dipole; (iii) $\Phi_{sub} > E_{ICT+}$, slope = 0, $\Phi_{sub/org} = E_{ICT+}$ with a negative interface dipole, as shown in Figure S1a.

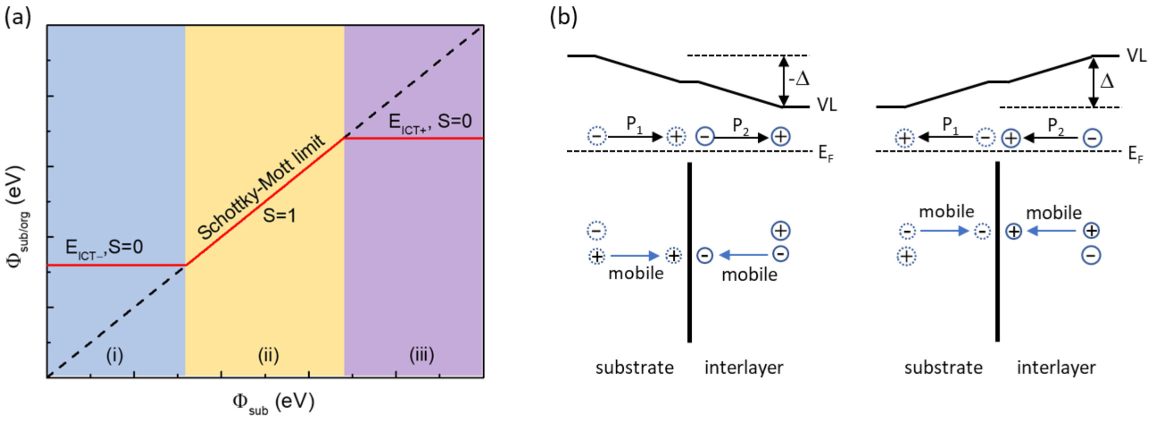

Figure S1. (a) The relationship between $\Phi_{sub/org}$ and Φ_{sub} when semiconductors follow typical ICT model. (b) Schematic illustration of work function downshift (left) and upshift (right) at the interface as the formation of “double dipole step”.

“double dipole step” model: Reenen et al[1] proposed this model firstly to explain the work function changes at the electrolyte/substrate interface. Except for the chemical hybridization and electron transfer, the image force effect also needs to be considered for the charged species near the substrate surface, which can be described by the attractive force between the opposite image

charges and themselves. As a result, the charged species will be driven towards the interface and equilibrate at the end. The positive and negative species usually show different ability to move, which may lead to a different position and hence form a dipole in the interlayer and an induced dipole in the substrate, creating a “double dipole step”. Both dipoles are perpendicular to the surface and point in a same direction, thus the substrate work function will be changed effectively. For example, if the negative species is more mobile, it will be closer to the substrate and form a double dipole pointing to the interlayer to downshift the vacuum level. Otherwise, if the positive species is more mobile, the vacuum level will be upshifted, see Figure S1b.

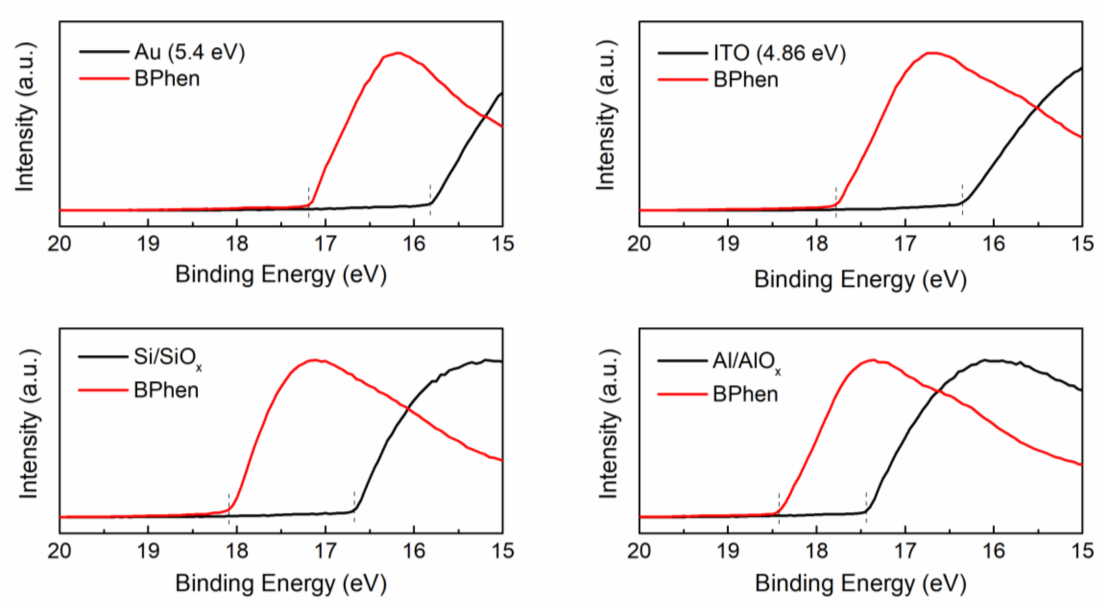

Figure S2. Photoemission cutoff of other four substrates with and without BPhen. These work function data are all involved in Figure 1b in the main text. The substrates Au and ITO used here are treated with UV-Ozone before evaporation.

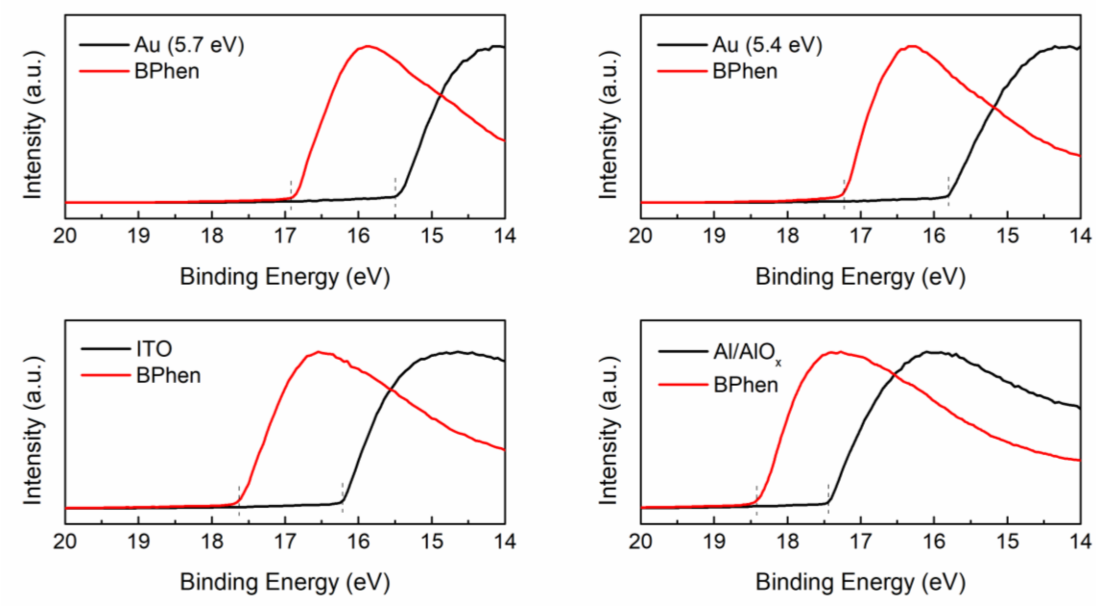

Figure S3. The work function downshift of various substrates with spin-coated BPhen. They show same displacement (−1.4 eV) with the vacuum-deposited samples.

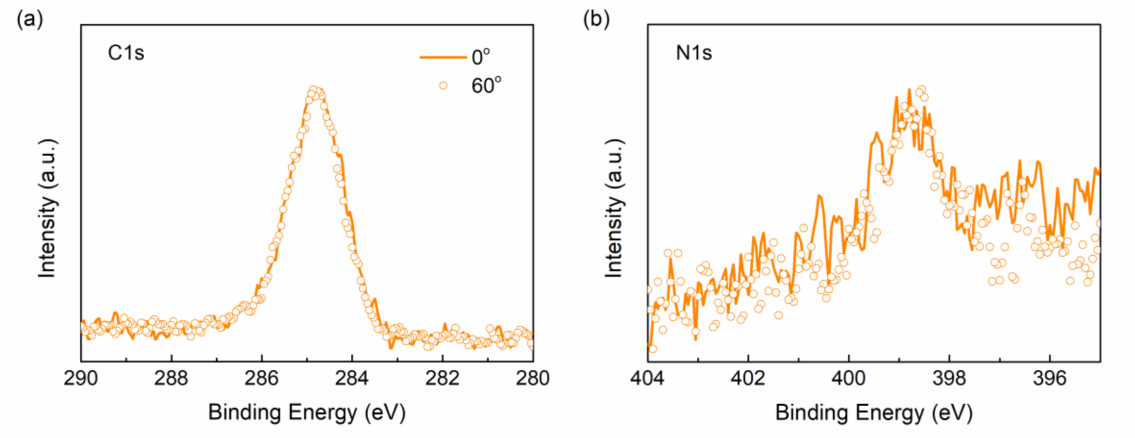

Figure S4. Comparison of the ARXPS spectra of C 1s (a) and N 1s (b) at emission angles of 0° and 60° for the sample with less than 0.8 nm-thick film.

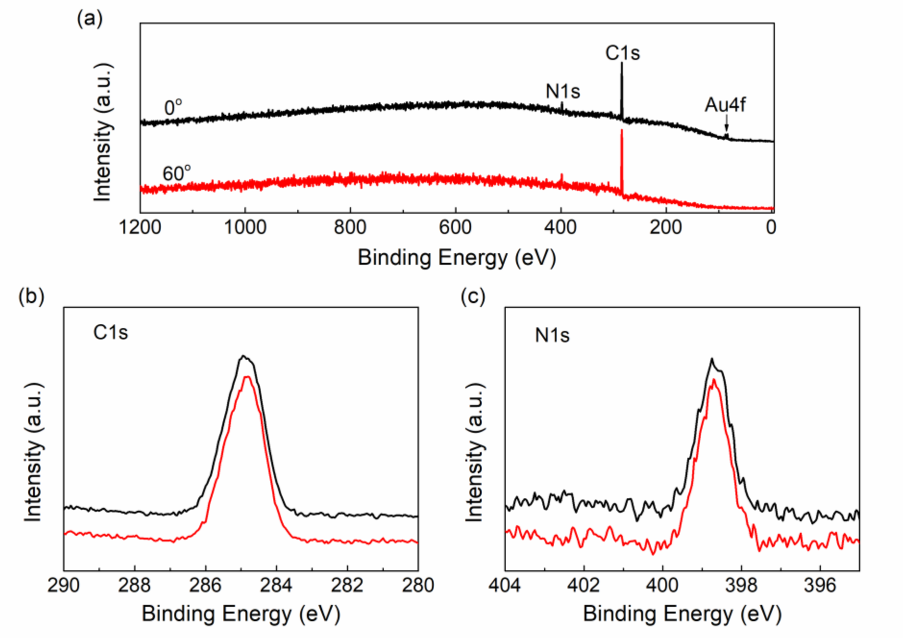

Figure S5. ARXPS spectra of full scan (a), C 1s (b) and N 1s (c) for the sample with 8 nm-thick film. Here we only show the emission angle of 0º and 60º. The signal of Au 4f is observed at the emission angle of 0º and disappears at 60º, indicating that the deepest detection layers locate at the interface. All spectra in figure (b) and (c) are normalized by the sweep times. After that the C 1s peaks at different emission angles are normalized by area, and the N 1s peaks are calibrated by their C 1s peak, respectively. The N 1s peaks show same area at different emission angles, suggesting the same atomic ratios of C: N.

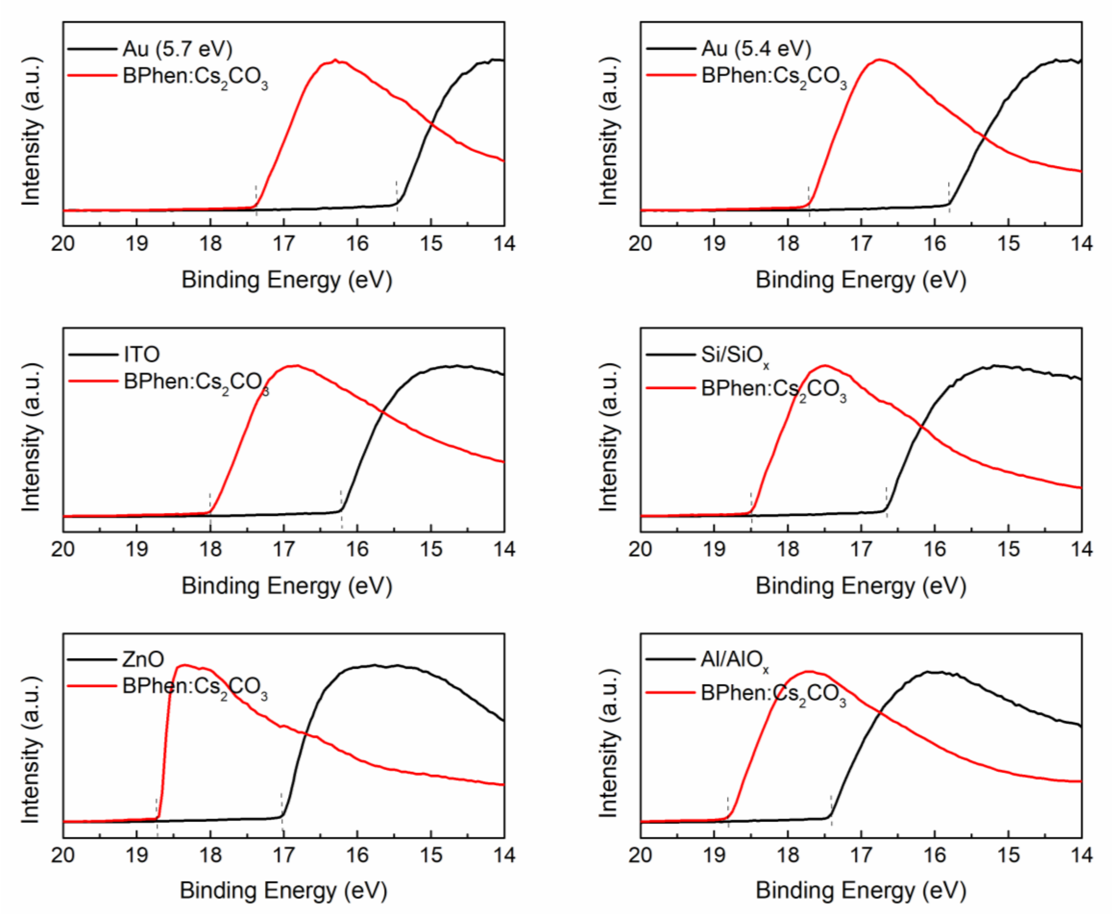

Figure S6. Photoemission cutoff for the secondary electrons of a series of substrates with and without Cs_2CO_3 doped BPhen. N-doping increases the displacement from −1.4 eV to −1.8 eV. All these data are summarized in Figure 6a.

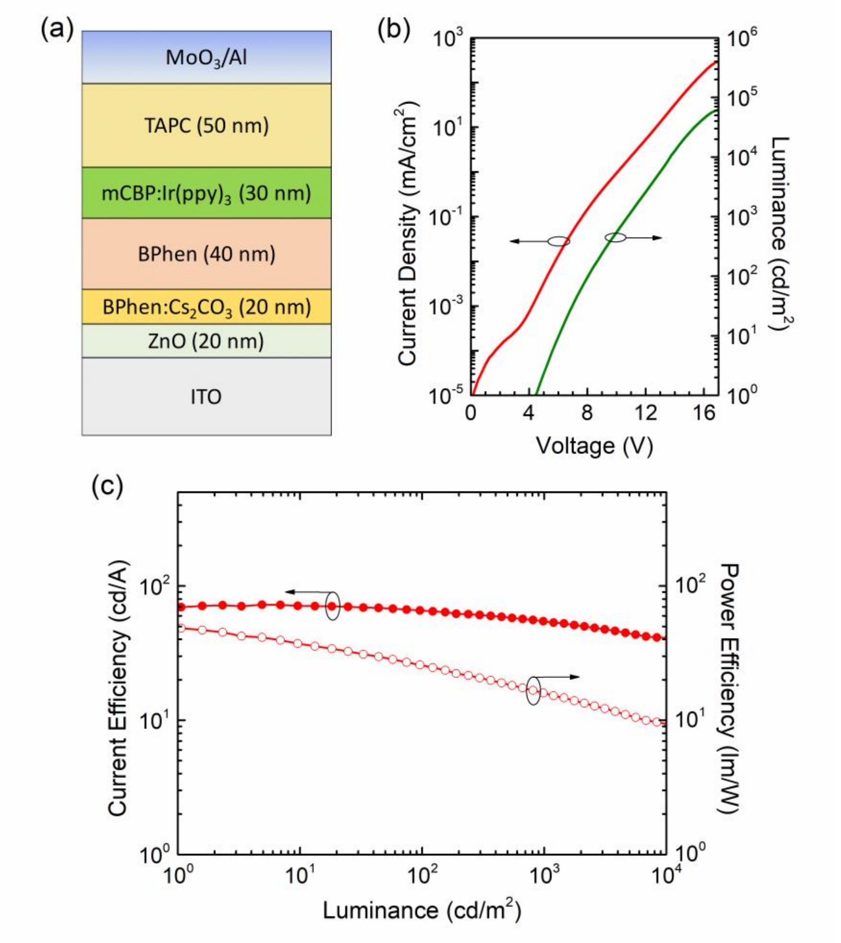

Figure S7. (a) Device structure of the inverted OLED. (b) Current density and luminance versus voltage characteristics. (c) Current efficiency and power efficiency versus luminance characteristics.

Table S1. Summary of device performance for the inverted OLED.

V_{on} [V][a]	EQE [%] / CE [cd/A] / PE [lm/W]				L_{max} [cd/m^2]
	Maximum	At 100 cd/m^2	At 1000 cd/m^2	At 10000 cd/m^2	
4.4	20.8/72.5/48.5	18.8/65.7/25.8	15.6/54.6/15.9	11.8/41.2/9.4	62000

[a] Turn-on voltage (at brightness of 1 cd/m^2).

Reference

(1) S. van Reenen, S. Kouijzer, R. A. J. Janssen, M. M. Wienk and M. Kemerink, *Adv. Mater. Interfaces*, 2014, **1,** 1400189.