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<https://doi.org/10.1038/s42005-018-0101-9>

OPEN

Energy disorder and energy level alignment between host and dopant in organic semiconductors

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Energy level alignment between host and dopant molecules plays a critical role in exciton formation and harvesting in light emission zone of organic light-emitting diodes. Understanding the mechanism for predicting energy level alignment is thus important in materials selection for fabricating high-performance organic light-emitting devices. Here we show that host-dopant energy level alignment strongly depends on film thickness and substrate work function by using X-ray and ultraviolet photoemission spectroscopy. Invariant Gaussian density of states fails to explain the experimental data. We speculate that energy disorder in molecules next to the surface dictates the alignment. Ultraviolet photoemission spectroscopy measurements of several archetypical organic semiconductors confirm our speculation. An empirical interface disorder function is derived and used to construct a functional Gaussian density of states to compute host energy levels. Host-dopant energy level alignment is then computed by applying the universal energy alignment rule and is found in excellent agreement with the experimental data.

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An organic light-emitting diode (OLED) is a light-emitting device consisting of several organic layers. The low power consumption and the flexible form factor make the OLED display advantageous over traditional liquid crystal displays (LCD). Rapid development during the past few decades has already led to successful commercialization of OLED displays. However, there remain many fundamental scientific issues to be addressed in order to design future generations of OLEDs. The light-emitting layer inside an OLED pixel is usually a mixture layer, composed of host and dopant organic semiconductors. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are two most critical energy levels for organic materials since they are closely linked to charge transport, charge capturing and exciton formation in an OLED pixel. The frontier energy level alignment between the host and the dopant plays an important role in the process of light emission. Any mismatch in terms of the energy level leads to an insufficient excitonic energy transfer or carrier capturing in the emissive layer^{1,2}. This can significantly deteriorate the device performance. Thus, a clear understanding of the energy level alignment between host and dopant is crucial for materials selection in designing high-efficiency OLEDs. Currently, there are only a few studies on the energy level alignment in host-dopant systems³. More experimental and theoretical studies are required to fully understand the energy level alignment in the host-dopant system.

Molecular packing disorder is a typical characteristic of organic semiconductor solid films. This disorder broadens the density of states (DOS) of its energy levels^{4,5}. When the organic small molecule is deposited on top of a substrate, the DOS broadening of molecules near the interface is expected to be more significant than that of molecules positioned away from the interface^{6,7}. The interfacial disorder may have an impact on the energy level alignment between the host and dopant material, especially when the Fermi level of the substrate lies within the DOS of the organic's energy level. However, to the best of our knowledge, there is no report on the effect of interface disorder on energy level alignment.

In this work, we combine X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) to study the energy level alignment in a typical host-dopant system deposited on the molybdenum trioxide (MoO_3)-coated indium-tin-oxide (ITO) substrate. The host and dopant are 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) and bis[2-(2-pyridinyl-N)-phenyl-C](2,4-pentanedionato- O^2, O^4)iridium(III) ($\text{Ir}(\text{ppy})_2(\text{acac})$), respectively. And the host-to-dopant weight ratio is 10 to 1 in our study. We discovered that the energy level alignment between CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$ is thickness-dependent. Theoretically computed energy level alignment using an invariant Gaussian DOS model shows a large deviation from experimental results. The disagreement is attributed to the interfacial disorder of the host and the dopant. In order to verify the hypothesis, we utilize UPS to study the HOMO broadening at the substrate-organic interface. For their well-defined HOMO in UPS spectra, three organic small molecules, copper(II) phthalocyanine (CuPc), 4,4'-cyclohexylidenebis[N,N-bis(methylphenyl)benzenamine] (TAPC), and 60-carbon fullerene (C_{60}) are selected. The full width half maximum (FWHM), an indicator of disorder, is extracted by using the Gaussian distribution to fit the HOMO from each spectrum. An empirical interface disorder function is then introduced to describe the interfacial DOS broadening, and is found to describe well all three molecules studied. Furthermore, we have revised the Gaussian DOS model by including the interface disorder function. The theoretical calculation using the revised model shows an excellent agreement with the experimental result.

Results

Measurement of host-dopant energy levels. In a host-dopant system, the optimized triplet dopant concentration is typically around 10 wt%^{8,9}, which makes it difficult to resolve the HOMO of the dopant in a UPS spectrum. Thus, UPS alone is not sufficient to determine the energy level alignment between the dopant and the host. Additional XPS measurement is then utilized to determine the HOMO offset of the dopant since the shift in HOMO of the organic. XPS core level shifts have been proven to carry the same magnitude of energy shifts as in UPS HOMOs, i.e., the energy separation between a core level and HOMO edge is a constant¹⁰ (see Supplementary Fig. 1). Fig. 1a shows the XPS Ir 4f core level spectrum and UPS valence band spectrum of a 3 nm $\text{Ir}(\text{ppy})_2(\text{acac})$ deposited on the MoO_3 -coated ITO substrate. The binding energy difference between the Ir 4f_{7/2} and the HOMO offset is measured to be 60.83 eV which is served as a reference to determine the HOMO offset of the $\text{Ir}(\text{ppy})_2(\text{acac})$ doped into the CBP matrix. Figure 1b shows photoemission spectra measured from 10 nm CBP: $\text{Ir}(\text{ppy})_2(\text{acac})$ layer. The measurement of Ir 4f core level helps determine the HOMO offset (measured in reference to Fermi level) of $\text{Ir}(\text{ppy})_2(\text{acac})$. In this case, the HOMO offset of $\text{Ir}(\text{ppy})_2(\text{acac})$ is determined to be 0.58 eV. Accordingly, the HOMO offset difference, δ , between CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$ is determined to be 0.54 eV. It is worth to note that, in Fig. 1b, a small HOMO peak, attributed to $\text{Ir}(\text{ppy})_2(\text{acac})$, can also be observed, whose energy offset is consistent with the HOMO offset determined from the XPS core level. The use of core levels is very useful for determining the HOMO offset of dopant when the host and dopant valence shell orbitals are convoluted. It should be noted that the low signal in Ir 4f core level spectrum may affect the accuracy of δ , especially when the film is very thin. For example, an error as large as ~0.1 eV is possible, as shown in Supplementary Fig. 2a.

Figure 2 shows the HOMO offset difference, δ , i.e., HOMO-HOMO offset between CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$ as a function of the thickness of the host-dopant layer. The experimental host and dopant HOMO offset data (open circles) are determined by using UPS and XPS, respectively. In this figure, we also show the experimental data determined solely by UPS band edge measurement (open squares). As shown in the figure, the data determined by both methods agrees with each other. The photoemission spectrum for each thickness is shown in the Supplementary Fig. 2. As clearly shown in the Fig. 2, the δ is dependent on the layer thickness. The δ decreases as the host-dopant layer reaches the substrate-organic interface and almost reaches ~0.7 eV, which coincides with the ionization energy difference between bulk CBP (6.0 eV) and bulk $\text{Ir}(\text{ppy})_2(\text{acac})$ (5.3 eV) (shown in the Supplementary Fig. 3), when the layer is thicker than 15 nm. This thickness-dependent δ may somewhat relate to the universal energy level alignment rule. Greiner et al. and Li et al. show that the HOMO offset of organic overlayers will universally pin to ~0.3 eV if the underlayer's work function exceeds the ionization potential (*IP*) of the overlayer organics^{11,12}. And in the present case, the substrate is MoO_3 , which has a high work function of ~6.8 eV¹³. The Fermi level is expected pin the HOMOs of both CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$. Therefore, the δ should diminish at the interface.

Theoretical modeling analysis. In order to explain the thickness variation of the δ , we first focus on the energy level alignment between CBP and MoO_3 , e.g., the equilibrium between the host matrix and the underlying substrate. Then, we study the energy level alignment between CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$.

For the energy level alignment between CBP and MoO_3 , the classical invariant Gaussian DOS model is applied to calculate the

Fig. 1 Core level and valence band spectra. **a** X-ray photoemission spectroscopy (XPS) Ir 4f core level and ultraviolet photoemission spectroscopy (UPS) valence spectrum for a 3 nm layer of bis[2-(2-pyridinyl-N)phenyl-C](2,4-pentanedionato-O²,O⁴)iridium(III) (Ir(ppy)₂(acac)) deposited on the molybdenum trioxide(MoO₃)-coated indium tin oxide (ITO) substrate. **b** XPS core level of Ir 4f and UPS valence spectrum for 3 nm 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP):Ir(ppy)₂(acac) layer deposited on top of the MoO₃-coated ITO substrate

Fig. 2 Highest occupied molecular orbital (HOMO) offset difference, δ , between 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) and bis[2-(2-pyridinyl-N)phenyl-C](2,4-pentanedionato-O²,O⁴)iridium(III) (Ir(ppy)₂(acac)) as a function of the layer thickness. The solid curve is calculated by using a revised Gaussian density of states (DOS) model including the interfacial disorder function. The dashed curve is calculated by using the invariant Gaussian DOS model. Error bars are the standard deviation of the measurement

HOMO offset profile, $\Delta E_{\text{H}}^{\text{CBP}}(x)$, of CBP. This invariant Gaussian DOS model has been proposed to calculate the energy level alignment at the substrate-organic interface^{14–16}. In the model, the HOMO DOS, $g(E)$, of the organic semiconductor is assumed to have a Gaussian function:

$$g(E) = \frac{N_0}{\sigma_{\text{CBP}} \sqrt{2\pi}} \exp \left[-\frac{(E - E_0)^2}{2\sigma_{\text{CBP}}^2} \right] \quad (1)$$

where N_0 is the total density of states in the HOMO, E_0 is the center energy of the Gaussian function and σ_{CBP} is the Gaussian width of CBP. In this study, N_0 of CBP is $2 \times 10^{21} \text{ cm}^{-3}$, estimated based on the typical density of organic small molecules, two spin states as well as the stoichiometry of CBP in the mixed film. The onset energy of the tangent of the inflection point of the Gaussian distribution is taken as the HOMO offset of the organic in the photoemission spectrum, and the center energy E_0 is $2\sigma_{\text{CBP}}$ away from this onset value¹⁵. The bulk IP ($I_{\text{CBP}}^{\text{bulk}}$) of CBP is experimentally determined to be 6.0 eV. By adding $2\sigma_{\text{CBP}}$ to this value, the E_0 of CBP is determined to be $I_{\text{CBP}}^{\text{bulk}} + 2\sigma_{\text{CBP}}$.

As the Fermi level E_{F} is constant across the CBP film, we can calculate the hole density $p(x)$ in CBP's HOMO at thickness x by the following equation:

$$p(x) = \int_{-\infty}^{+\infty} \frac{1}{1 + \frac{1}{g} \exp[(E_{\text{F}} - E)/k_{\text{B}}T]} g[E + eV(x)] dE \quad (2)$$

Fig. 3 Highest occupied molecular orbital (HOMO) broadening at the interface. **a** HOMO photoemission spectra of copper(II) phthalocyanine (CuPc) of different thickness deposited on the molybdenum trioxide (MoO_3)-coated indium tin oxide (ITO) substrate. **b** HOMO photoemission spectra of 1 nm CuPc deposited on different substrates (ITO and MoO_3), the interfacial dipole of each interface is shown in the figure. The HOMO maximum in each spectrum is normalized and the binding energy is set to 0

where $E_F = 6.8 \text{ eV}$ is determined by measuring the work function Φ_{MoO_3} of the MoO_3 , k_B is the Boltzmann constant and T is the temperature (300 K). e is the elementary charge, g is the HOMO degeneracies which is set to be 2 (spin degeneracies)¹⁵, and $V(x)$ is the electrostatic potential. $V(x)$ can be numerically solved by coupling the Eq. 2 with the Poisson's equation:

$$\frac{d^2 V(x)}{dx^2} = -\frac{ep(x)}{\epsilon_r \epsilon_0} \quad (3)$$

where ϵ_0 is the vacuum permittivity and $\epsilon_r = 3.5$ is the dielectric constant of CBP. The shift in $eV(x)$ is consistent with the HOMO offset shift and the HOMO offset profile $\Delta E_{\text{H}}^{\text{CBP}}(x)$ can be calculated. Boundary conditions^{9,10} for Eq. 3 are: (i) $-V(0)$ is the interface dipole Δ and (ii) electrical field vanishes at the film surface, and $V'(t)=0$. Since in our study, the work function of the MoO_3 is higher than the IP of CBP, and the HOMO offset at the interface is 0.3 eV. We calculate the interface dipole by:

$$\Delta = IP_{\text{CBP}}^{\text{bulk}} - 0.3 \text{ eV} - \Phi_{\text{MoO}_3} \quad (4)$$

The interface dipole Δ is determined to be -1.1 eV at MoO_3 -CBP interface in our simulation.

For the energy level alignment between CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$, the HOMO offset profile $\Delta E_{\text{H}}^{\text{Ir}}(x)$ of $\text{Ir}(\text{ppy})_2(\text{acac})$ can be calculated using the universal energy level alignment rule for molecule-molecule interfaces reported by Li et al.¹² (see Supplementary Fig. 4). As per this rule, the molecule's HOMO offset depends on the substrate molecule's work function. Thus, the $\Delta E_{\text{H}}^{\text{Ir}}(x)$ can be determined from the following equations:

$$\Delta E_{\text{H}}^{\text{Ir}}(x) = \begin{cases} \gamma[\Phi_{\text{CBP}}(x) - IP_{\text{Ir}}^{\text{bulk}}] + 0.3 \text{ eV} & EA_{\text{Ir}}^{\text{bulk}} < \Phi_{\text{CBP}}(x) < IP_{\text{Ir}}^{\text{bulk}} \\ 0.3 \text{ eV} & \Phi_{\text{CBP}}(x) \geq IP_{\text{Ir}}^{\text{bulk}} \end{cases} \quad (5)$$

where $EA_{\text{Ir}}^{\text{bulk}}$ and $IP_{\text{Ir}}^{\text{bulk}}$ are the bulk electron affinity and the ionization potential of $\text{Ir}(\text{ppy})_2(\text{acac})$. The LUMO pinning scenario is neglected as the work function, $\Phi_{\text{CBP}}(x)$, of the CBP is expected to be much closer to the IP than EA of $\text{Ir}(\text{ppy})_2(\text{acac})$ due to the high work function substrate. $\Phi_{\text{CBP}}(x)$ can be calculated by:

$$\Phi_{\text{CBP}}(x) = \Phi_{\text{MoO}_3} + \Delta - eV(x) \quad (6)$$

and $\gamma = -0.78$ is an experimentally determined constant.¹²

Therefore, the HOMO offset difference, $\delta(x)$, can be calculated as follow:

$$\delta(x) = \Delta E_{\text{H}}^{\text{CBP}}(x) - \Delta E_{\text{H}}^{\text{Ir}}(x) \quad (7)$$

We tried several combinations of the host and dopant's Gaussian width and found none of them give a reasonable fit to the experimental data. One of the calculated $\delta(x)$, using 0.4 eV and 0.25 eV as the σ of CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$, is plotted in Fig. 2 (dashed line), which shows a significant deviation from the experimental data. The deviation is attributed to the interfacial disorder of the organic, as will be discussed in the following text. In the Gaussian DOS model, the Gaussian width is assumed to be constant across the whole organic layer. This means that molecular disorder is similar in the film. The disorder relates to molecular geometric shape and molecular packing. In a crystalline film, molecular packing is well-defined, i.e., less disorder. Whereas in a non-crystalline or amorphous film, molecular packing is less defined, i.e., more disorder. In the present case, CBP: $\text{Ir}(\text{ppy})_2(\text{acac})$ system is amorphous, and the disorder effect is expected to dominate the energy level alignment. In general, a constant Gaussian width is assumed in modeling analysis. However, as discovered below, this assumption is not true for the organic at the interface. The interfacial disorder will further broaden the HOMO DOS and the σ is no longer a constant near the interface.

Interfacial energy disorder. To validate the hypothesis, the interfacial disorder of the organic molecule must be investigated. Since the disorder in the organic semiconductor induces the broadening of the energy level, the FWHM of the HOMO observed in the UPS spectrum can be utilized to study the degree of disorder. However, for many molecules, such as CBP and $\text{Ir}(\text{ppy})_2(\text{acac})$, the HOMO is always convoluted with multiple energy levels (e.g., HOMO-1, HOMO-2) in the UPS spectrum^{17,18}. Arbitrary fitting the valence band spectrum may cause significant error and lead to inaccurate conclusion. Therefore, we selected three "model" organic small molecules with well-defined HOMO feature to study the interfacial disorder and the FWHM can be directly extracted by using only one Gaussian function to analyze the HOMO spectrum. These three molecules are CuPc, TAPC and C_{60} , respectively¹⁹⁻²¹.

Figure 3a shows UPS spectra of CuPc with different layer thickness deposited on top of the MoO_3 -coated ITO substrate. All

Fig. 4 Full width half maximum (FWHM) of the highest occupied molecular orbital (HOMO). HOMO FWHM, Σ , of **a** CuPc, **b** 4,4'-cyclohexylidenebis[N,N-bis(methylphenyl)benzenamine] (TAPC) and **c** fullerene (C₆₀) as a function of layer thicknesses. The dashed and solid curves are fitted curves using the interface disorder function. **d** Summary of fitting parameters β and λ . Error bars for FWHM are the standard deviation of HOMO fitting. Error bars for β and λ are the standard deviation of empirical FWHM fitting

spectra are normalized and aligned to the HOMO maximum with binding energy set to zero. As clearly shown in Fig. 3a, the HOMO of CuPc is significantly broadened as the molecule reaches the interface. Figure 3b shows the UPS spectra of 1 nm CuPc deposited on top of ITO and MoO₃-coated ITO substrate, respectively. It is interesting to note that the interfacial HOMO broadening also depends on the underlying substrate. As compared with the CuPc deposited on ITO, the HOMO is much broader on the MoO₃ substrate. The additional HOMO broadening is likely caused by the interface dipole at the substrate-organic interface. The magnitude of interface dipole is experimentally determined to be -1.53 eV at MoO₃-CuPc interface and -0.16 eV at ITO-CuPc interface (see Supplementary Fig. 5). As compared with ITO-CuPc interface, the large dipole field at the MoO₃-CuPc interface may further distort the electron cloud distribution on the molecules near the interface, and induce valence shell static charge fluctuations by additional structural disorder such as the bond-angle and bond-length configurations of the interface molecules²². UPS spectra for the TAPC and C₆₀ (see Supplementary Figs. 6–9) also show the same trend: the HOMO will be further broadened if there exists a larger interface dipole.

The FWHM, Σ , of the HOMO of CuPc, TAPC, and C₆₀ is plotted as a function of the layer thickness, which is shown in Figs. 4a–c respectively. In all cases, the Σ increases when the organic reaches the interface, and the Σ of the organic on the MoO₃ is larger than that on the ITO substrate, indicating an increased disorder due to the interface dipole. Here, we introduce an empirical interface disorder function to quantify the thickness-dependent FWHM, $\Sigma(x)$:

$$\Sigma(x) = \Sigma(\infty) \cdot [1 + \beta \exp(-x/\lambda)] \quad (8)$$

where $\Sigma(\infty)$ is the HOMO FWHM of the organic in the bulk phase and is only dependent on the properties of the organic molecule. β is a pre-factor which is related to the interface dipole strength, molecular rigidity as well as the molecular packing on the substrate surface. λ is a characteristic decay length which is not only dependent on three properties as discussed above, but also dependent on molecular packing across the film as well as the screening of the molecule to the interface dipole field. We use the interface disorder function to fit the experimentally measured Σ and find that all six sets of data can be well fitted, as shown in Figs. 4a–c. The fitting parameters β and λ are summarized in Fig. 4d (the detailed fitting parameters can be found in

Fig. 5 Schematic diagram of energy level alignment in a host-dopant system. Gaussian density of states (DOS) is refined by including an interface disorder function to accurately compute the energy level alignment between the host and dopant. The Fermi level (E_F) is shown in the figure. The alignment of highest occupied molecular orbital (HOMO) is subject to the interfacial DOS broadening

Supplementary Table 1). As shown, β of the organic deposited on MoO_3 is larger than that on ITO. This is due to the large interface dipole at the MoO_3 -organic interface. However, λ has no general trend and is probably due to the convolution of multiple properties of the system as discussed above. In our case, the value of β ranges from ~ 0.1 to ~ 1.6 , and λ ranges from ~ 1.3 to ~ 2.7 nm.

Inclusion of interfacial disorder function in modeling analysis.

Based on UPS experimental data, we proceed to include the interface disorder function to explain the thickness-dependent HOMO alignment between CBP and $\text{Ir(ppy)}_2(\text{acac})$. Figure 5 shows the schematic energy level alignment in a host-dopant system with consideration of the interfacial disorder effect. As schematically shown in this figure, we still use the Gaussian DOS function as discussed above to calculate the $\Delta E_{\text{H}}^{\text{CBP}}(x)$. However, we revise the model by including the interface disorder function. Therefore, the Gaussian width $\sigma(x)$ is given by:

$$\sigma(x) = \sigma(\infty) \cdot [1 + \beta \exp(-x/\lambda)] \quad (9)$$

where $\sigma(x)$ is the width of the Gaussian DOS of the molecule far away from the interface. In this study, $\sigma(\infty)$ is chosen to be 0.40 eV for CBP and 0.25 eV for $\text{Ir(ppy)}_2(\text{acac})$, as these values provide the best fit to experimental data. Other parameters remain the same as those in the previous calculation. The pre-factor β and decay constant λ are assumed to be constant for both CBP and $\text{Ir(ppy)}_2(\text{acac})$ to minimize the number of free parameters in the model. In this calculation, β and λ is set to be 1.5 and 2.5 nm, respectively, which is within the range as shown in Fig. 4d. However, the HOMO DOS broadening is highly dependent on the molecule. The β and λ for CBP and $\text{Ir(ppy)}_2(\text{acac})$ may have different values. The other assumption is that the interfacial disorder only causes the broadening of the DOS but it does not shift the center energy of the DOS with reference to the vacuum level. Therefore, the IP of the molecule, which is determined by the energy difference between DOS onset and the vacuum level, is dependent on the DOS broadening:

$$\text{IP}(x) = \text{IP}^{\text{bulk}} - 2\sigma(\infty) \cdot \beta \exp(-x/\lambda) \quad (10)$$

with IP^{bulk} , the bulk IP of the molecule. The DOS broadening will affect the Eq. 1 and the boundary condition for host calculation:

$$\Delta = \text{IP}_{\text{CBP}}^{\text{bulk}} - 2\sigma_{\text{CBP}}(\infty) \cdot \beta - 0.3 \text{ eV} - \Phi_{\text{MoO}_3} \quad (11)$$

with $\sigma_{\text{CBP}}(\infty)$, the bulk Gaussian width of CBP's HOMO. And the $\text{IP}_{\text{Ir}}^{\text{bulk}}$ in Eq. 5 should be replaced by the thickness-dependent $\text{IP}_{\text{Ir}}(x)$ in the calculation:

$$\text{IP}_{\text{Ir}}(x) = \text{IP}_{\text{Ir}}^{\text{bulk}} - 2\sigma_{\text{Ir}}(\infty) \cdot \beta \exp(-x/\lambda) \quad (12)$$

with $\sigma_{\text{Ir}}(\infty)$, the bulk Gaussian width of $\text{Ir(ppy)}_2(\text{acac})$'s HOMO. The HOMO-HOMO offset difference, $\delta(x)$ between CBP and $\text{Ir(ppy)}_2(\text{acac})$ can be calculated according to Eq. 7. Figure 2 also shows the calculated δ as a function of the thickness by using the revised Gaussian DOS model (solid curve), which shows an excellent agreement with the experimental data. This clearly shows that energetic disorder function is critical in the quantitative analysis of HOMO-HOMO energy level alignments in host-dopant systems.

In order to further prove our claim, we conducted additional photoemission measurement and theoretical calculation on another host-dopant system: CBP- $\text{Tris(1-phenylisoquinoline)iridium(III)}$ (Ir(piq)_3) - (see Supplementary Fig. 10 and 11). This system also shows a similar thickness dependence of energy level alignment between host and dopant. The theoretical calculation also indicates that the interfacial disorder plays a significant role in determining the host-dopant energy level alignment at the interface.

The variation of host-dopant energy level alignment is expected to occur when the mixed film is deposited on a high work-function substrate, as expected in the theoretical calculation. At the substrate-organic interface, the work function of the substrate must be high enough to pin the Fermi level to the HOMO of both host and dopant. We also studied the energy level alignment between CBP and $\text{Ir(ppy)}_2(\text{acac})$ on a bare ITO substrate with a work function of 4.8 eV¹³. The host-dopant energy level alignment is constant across the whole layer, with a δ of around 0.55 eV (see Supplementary Fig. 12 and 13).

The knowledge of varied host-dopant energy level alignment at the interface can be potentially applied to optimize the device performance of the OLED. When charge carriers transport through the host-dopant layer, the charge trapping, and de-trapping process can be significantly tuned, resulting in a change of carrier population in the device and, therefore, the position of recombination zone. From theoretical calculation, the significant change of the energy level alignment between host and dopant occurs within the first 3 nm layer, which gives us an opportunity to tune the charge transport in the device. Thus, we fabricated hole-only devices with a structure of $\text{ITO/MoO}_3/\text{CBP:Ir(ppy)}_2(\text{acac})/\text{CBP/MoO}_3/\text{Al}$ and measured their current density-voltage characteristic. By varying the thickness of the $\text{CBP:Ir(ppy)}_2(\text{acac})$ layer from 0 to 3 nm, we are able to significantly tune the hole population in the device (see Supplementary Fig. 14). The remaining challenge to fabricate high-performance OLED is to synthesize a high work-function charge transporting material, on which the host-dopant layer is deposited.

Discussion

In conclusion, it is discovered that the host-dopant energy level alignment is dependent on the film thickness when deposited on a high work function substrate. Conventional invariant Gaussian DOS model fails to describe the thickness dependence of the host-dopant HOMO-HOMO alignment. An energetic disorder function of organic molecule is empirically derived based on UPS measurement. This disorder function is found to have a strong impact on the energy level alignment. Interface dipole is discovered to play an important role in driving interface energetic

disorder. A revised Gaussian DOS model including the interface disorder function shows an excellent agreement with the experimental results. Furthermore, we found that the universal energy level alignment rule is applicable to quantify the HOMO alignment between host and dopant.

Methods

Substrates used in this study are ITO-coated glass substrates. All substrates were cleaned (ultra-sonicated) in soap, DI water, acetone, and methanol, and then were treated by ultraviolet ozone for 15 min. Cleaned substrates were then loaded into PHYSICAL ELECTRONICS 5500 multi-technique system. To prepare MoO₃-coated ITO substrates, a 3 nm MoO₃ layer was grown on top of the ITO substrate by thermal vapor evaporation under a base pressure of 10^{−9} torr. All the organic was deposited under a base pressure of 10^{−8} torr. CBP and Ir(ppy)₃(acac) (or Ir(ppy)₃) were co-deposited at the rate of 0.20 Å/s and 0.02 Å/s, respectively. CuPc, TAPC and C₆₀ were all deposited at a rate of 0.10 Å/s. The deposition rate was monitored by a calibrated quartz crystal microbalance. After the deposition, samples were transferred in situ into the analysis chamber for photoemission study without breaking vacuum. The radiation source was the Al Kα emission line (1486.7 eV) for XPS and He Iα emission line (21.22 eV) for UPS. The take-off angle was 75 degrees for XPS and 88 degrees for UPS. A bias of -15 V was applied for UPS to measure the work function. XPS and UPS were conducted under a base pressure of 10^{−9} torr.

Data Availability

The data that support the finding and the model are available from the corresponding author upon reasonable request.

Received: 25 June 2018 Accepted: 23 November 2018

Published online: 03 January 2019

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Acknowledgements

Funding support for this work is provided by Canada Research Chair (Z. H. Lu, Tier I CRC chair in organic optoelectronics), the Natural Science and Engineering Research Council of Canada, and the National Natural Science Foundation of China (Grant No. U1402273, 11774304).

Author contributions

P.L. and Z.-H.L. conceived the concept and theory. P.L. conducted the photoemission spectroscopy studies and implemented the theoretical calculation. G.I. and J.-J.L. assisted the program coding for the theoretical calculation. Y.Z. participated in the data analysis. P.L. and Z.-H.L. co-wrote the manuscript.

Additional information

Supplementary Information accompanies this paper at <https://doi.org/10.1038/s42005-018-0101-9>.

Competing interests: The authors declare no competing interests.

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