

Vacuum level alignment in organic guest-host systems

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Using a combination of ultraviolet and x-ray photoelectron spectroscopies, we have studied the relative energy level alignment of two phosphorescent guest molecules, 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP) and tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$), doped in an electron transport host, tris(8-hydroxyquinolato) aluminum (III) (Alq_3), and in a hole transport host, 4,4'-bis(carbazol-9-yl)bi-phenyl. In each of the guest-host systems, we find that the vacuum levels of the guest and the host molecules align, and that the position of the highest occupied molecular orbital of the phosphorescent guest is independent of the guest molecule concentration (0.8%–56% by mass). The vacuum level alignment implies free movement of the Fermi level within the gaps of the guest and the host molecules manifesting the intrinsic nature of these organic semiconductors. These results give insights into the role that the phosphorescent molecules play in trapping and transporting charges within the emissive layer of an organic light-emitting device. © 2002 American Institute of Physics. [DOI: 10.1063/1.1487917]

I. INTRODUCTION

Following the progress in display applications involving organic light emitting diodes (OLEDs), a number of different schemes have been proposed to improve device efficiency and stability. Subsequently, increasing attention has been paid to modifying the electronic properties of an OLED thin film structure through doping. Introducing dopants in organic molecular films facilitates the control of a number of device properties such as electroluminescence (EL) quantum efficiency,^{1,2} thermal stability,² durability,³ and carrier injection and transport.⁴ Although doped organic molecular films bear some obvious similarities with doped inorganic semiconductor structures, the doping mechanism and the resulting electronic structure of the doped organic films can be quite different.^{5,6} Most notably, doping may or may not result in charge transfer between an organic host and a dopant.

Electrical doping of organic films refers to introducing a strong electron donor or acceptor in a host matrix, where charge transfer takes place between the donor/acceptor and the host molecules. Depending on the direction of the charge transfer, the Fermi level will shift either toward the host's highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) resulting in what is referred to as *p*-type or *n*-type doping of the host, respectively. The effects of electrical doping have recently been investigated in a number of alkali metal-doped (Li,Cs) organic charge transport layers.^{4,7–10} Incorporation of Li in an electron transport layer has been shown to reduce drive voltages, increase EL quantum efficiency and improve operational stability of an OLED.^{4,8–10} The benefits of alkali metal doping have been attributed to metal-induced gap states, which re-

sult in lower electron injection barriers at cathode contacts and higher bulk conductivities.⁴ Similar results have been observed when the dopant is an organic molecule with strong electron donating or accepting properties.^{5,6,11–14} In this case, the direction of electron transfer and the subsequent polarity of the doping have been found to depend strongly on the relative HOMO and LUMO positions of the dopant and the host molecules. For instance, a good match between the ionization potential (IP) of the host and the electron affinity (EA) of the dopant molecule appears to produce *p*-type doping,^{6,11,12} whereas alignment between the host LUMO and the dopant HOMO has been shown to lead to *n*-type doping.⁵

Molecular doping does not necessarily involve charge transfer, and hence, the *guest* and the *host* molecules may retain their electronic properties mostly unperturbed. Consequently, the Fermi level will move freely within the host and the guest HOMO–LUMO gaps upon film formation assuming that its movement is not limited by the band edges (no pinning). Therefore, the composite organic film can be considered intrinsic. The active emissive layer of an OLED doped with highly phosphorescent dye molecules is expected to have these intrinsic properties, and it has proven to be a viable and promising method to increase the overall EL quantum efficiency of a device.^{1,15–18} Upon electron and hole recombination, spin statistics limits the maximum production efficiency of singlet and triplet excitons to 25% and 75%, respectively. Hence, the incorporation of phosphor molecules in the active emitting layer provides an additional radiative channel through triplet emission.

In order to understand the EL mechanism of an OLED based on a guest–host emissive layer, both the HOMO and the LUMO levels of the guest and the host molecules in the composite films need to be identified. Most recently, we have reported the first photoemission study of a guest–host molecular system consisting of an electron transport material tris(8-hydroxyquinolato) aluminum (III) (Alq_3) doped with

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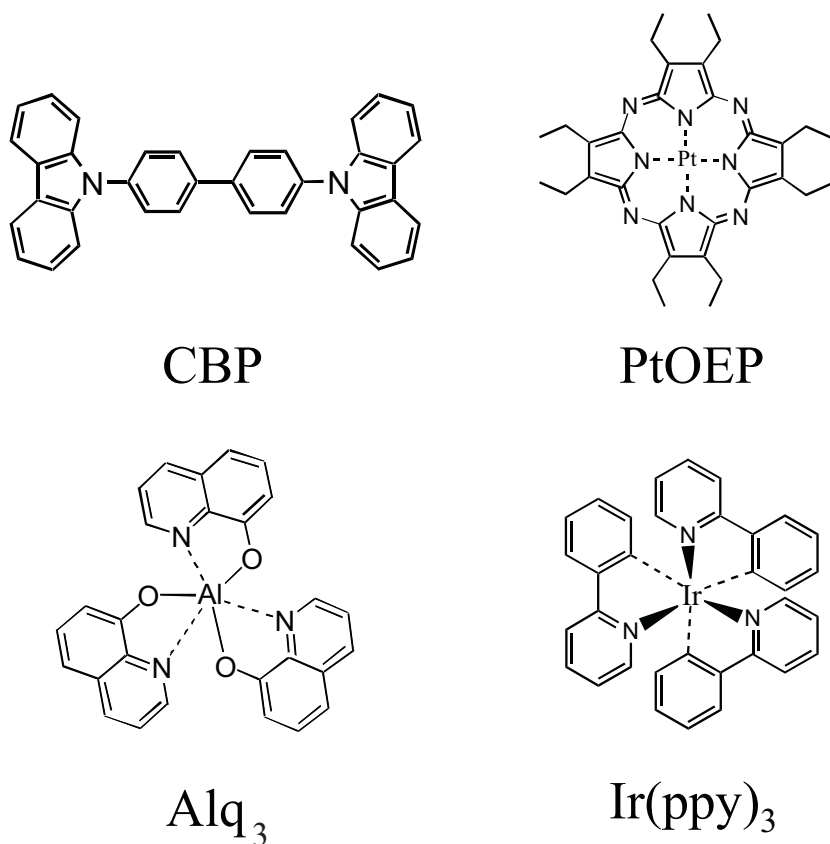


FIG. 1. The chemical structures of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP), tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$), tris(8-hydroxyquinolinato) aluminum (III) (Alq_3) and 4,4'-bis(carbazol-9-yl)biphenyl (CBP).

an organic phosphor 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP).¹⁹ In this work, it was found that the HOMO of PtOEP is located ~ 0.6 eV above the Alq_3 HOMO and that the vacuum levels of the guest and the host align. Most notably, the guest HOMO position was found to be independent of the guest molecule concentration (0.8%–28% by mass). The optical gaps of Alq_3 and PtOEP were used to estimate the LUMO positions of the two molecules which were found to align.

In this article, we extend our photoemission studies to two additional molecular guest–host systems, PtOEP:4,4'-bis(carbazol-9-yl)biphenyl (CBP) and tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$):CBP. (see Fig. 1 for the chemical structures of the molecules.) Both PtOEP:CBP and $\text{Ir}(\text{ppy})_3$:CBP composite films have been previously used as the light-emitting layers in OLED structures with external electroluminescence quantum efficiencies of 2.2% and 7.5% at 100 Cd/m^2 , respectively.^{1,15} This is an improvement compared with the earlier reported PtOEP: Alq_3 -based device with only 1.3% quantum efficiency at 100 Cd/m^2 .¹ Based on the results of the photoemission spectroscopy the characteristics of the guest and host energy levels in PtOEP:CBP and in $\text{Ir}(\text{ppy})_3$:CBP composite films were found to be very similar to those in PtOEP: Alq_3 films. The vacuum levels of the guest and the host molecules align bringing the guest HOMO at 0.7 and 0.8 eV above the host HOMO in PtOEP:CBP and in $\text{Ir}(\text{ppy})_3$:CBP composite films, respectively. As in the case of PtOEP: Alq_3 , the vacuum level alignment is independent of the guest concentration, which was varied from 8% to 51% (by mass) in PtOEP:CBP and from 14% to 56% (by mass) in $\text{Ir}(\text{ppy})_3$:CBP films.

II. EXPERIMENT

The guest and host molecules were evaporated from two resistively heated quartz crucibles and co-condensed onto a polycrystalline Ag foil, which was first cleaned by Ar^+ ion sputtering. The contamination levels of the Ag substrate were monitored with x-ray photoelectron spectroscopy (XPS). The thickness of the organic layers was monitored with a quartz crystal microbalance, and the composition of the films was varied by controlling the evaporation rates of guest and host molecules. After deposition, the samples were moved from the preparation chamber to the analysis chamber without breaking the vacuum. Photoemission spectra of the valence levels of both neat and composite films were recorded for He I ($h\nu = 21.22 \text{ eV}$) and He II ($h\nu = 40.82 \text{ eV}$) radiation, and core level spectra were obtained for $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) using a hemispherical energy analyzer for electron detection. The energy resolution was 50 meV in the ultraviolet photoelectron spectroscopy (UPS) and $\sim 1 \text{ eV}$ in the XPS measurements, where in the latter case, the resolution was limited by the width of the $\text{Al K}\alpha$ line. In the UPS measurements, the sample was biased at -3.0 V to compensate for the contact potential between the sample and the analyzer in order to resolve the vacuum level onset of the He I spectra.

The thickness of the studied neat and composite films was 75 \AA . The exact guest concentration in composite films was calculated from core level intensities of the heavy metal atom of the guest molecule normalized to those of the neat films. This method enabled the detection of a wide range of guest concentrations, from 0.8% to 56% (by mass), and it

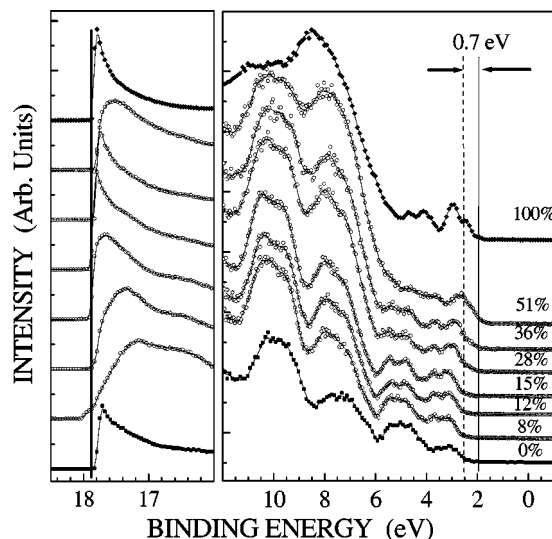


FIG. 2. He I spectra of PtOEP:CBP composite films. The PtOEP concentration is indicated by a mass percentage value. The binding energy is referenced to the Fermi level of the Ag substrate.

also accounted for possible fluctuations in evaporation rates. The HOMO–core level separation in energy was determined from the He I and the core level spectra of the neat films. Using this value we calculated the HOMO positions in the composite films based on the core level energies measured in these films. The underlying assumption in this method is that the ionization energy of the guest molecule is the same both in the neat and in the composite films, i.e., the polarization energy of the hole created in a photoemission process is approximately the same in each case. This assumption has previously been shown to be valid in the photoemission study of PtOEP:Alq₃ films,¹⁹ where the relative guest and host HOMO level positions were determined based on the core levels of both the guest and host materials. In the case of PtOEP:CBP and Ir(ppy)₃:CBP films, only the guest molecule had a distinct metal core level and therefore the host HOMO level position was determined with the help of the vacuum level onset in the He I spectra.

III. RESULTS AND DISCUSSION

A. PtOEP:CBP films

The He I spectra of the neat and PtOEP:CBP composite films are shown in Fig. 2 for the studied guest molecule concentration range of 8%–51% (by mass). The binding energies are referenced to the Fermi level E_F , which was determined separately on a sputter-cleaned Ag substrate. As the PtOEP concentration of the film increases, the He I spectrum of the composite film appears to be a superposition of the orbitals of the neat films of CBP and PtOEP. As a result, emission from the sharp features of the HOMO and HOMO-1 orbitals of the neat PtOEP spectrum at 2.5 and 3.0 eV, respectively, and from the CBP HOMO at 2.5 eV produces one broad feature centered at 2.5 eV in the spectra of the composite films. Interestingly, the vacuum level onset is the same (17.9 ± 0.1 eV) in all the spectra of the neat and the PtOEP:CBP composite films. The apparent vacuum level

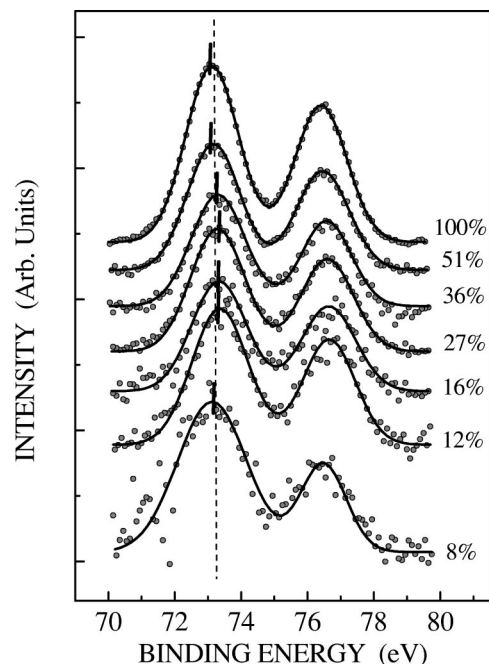


FIG. 3. Pt 4f core level spectra of a neat PtOEP film and PtOEP:CBP composite films at various guest molecule concentrations. The binding energy is referenced to the Fermi level of the Ag substrate.

alignment is further confirmed by the position of the Pt 4f_{7/2} core level line obtained from XPS which is the same (73.3 ± 0.1 eV) both in the neat PtOEP and in the PtOEP:CBP composite films. The core level positions shown in Fig. 3 were deduced from a nonlinear least-square fit of the sum of Gaussian functions to the data after Shirley-type background subtraction.

B. Ir(ppy)₃:CBP films

The He I spectra of the neat and Ir(ppy)₃:CBP composite films shown in Fig. 4 exhibit similar features to those of the PtOEP:CBP series films. The concept of spectral superposition is demonstrated even better by the He I spectra of the Ir(ppy)₃:CBP composite films. This is particularly well observed at the highest guest molecule concentration (56%) where the sharp feature at 3.7 eV can be attributed to an orbital found right below the Ir(ppy)₃ HOMO and HOMO-1 lines of the neat film spectrum. Again, independent of the guest molecule concentration the vacuum levels of the composite films align with the vacuum level of the neat CBP film. However, in stark contrast to the previous case, the vacuum level of the neat Ir(ppy)₃ film is shifted by 0.2 eV toward lower binding energy with respect to the vacuum level of the composite Ir(ppy)₃:CBP and the neat CBP films.

The observed vacuum level shift in the He I spectra is replicated by the shifts in the core level spectra of Ir 4f_{7/2} and 5/2 lines in the composite films with respect to the neat Ir(ppy)₃ films. The XPS peak positions of the Ir 4f_{7/2} and 5/2 lines shown in Fig. 5 were determined as described above. As indicated in Fig. 5, the 4f_{7/2} line position of the neat Ir(ppy)₃ film is shifted by 0.2 eV toward lower binding energies with respect to the line position in the Ir(ppy)₃:CBP composite films. As it turns out, the position

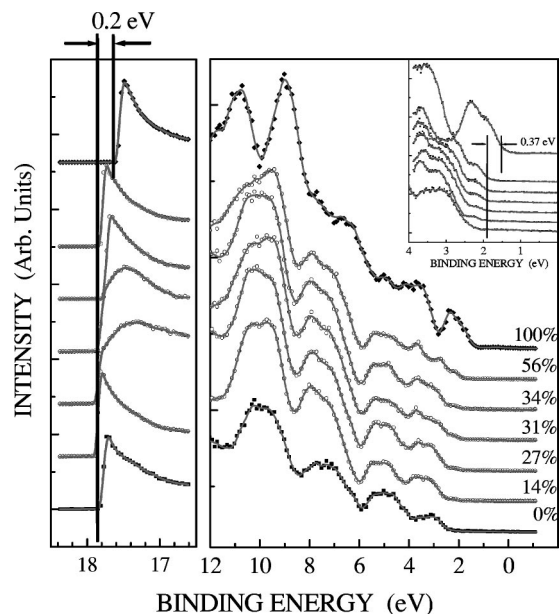


FIG. 4. He I spectra of $\text{Ir}(\text{ppy})_3$:CBP composite films. The $\text{Ir}(\text{ppy})_3$ content of the films is indicated by a mass percentage value. The inset shows a detailed view of the HOMO part of the spectra. The binding energy is referenced to the Fermi level of the Ag substrate.

of $\text{Ir} 4f_{7/2}$ line is the same (61.4 ± 0.1 eV) in all the studied $\text{Ir}(\text{ppy})_3$:CBP composite films. Since the shift of the core level position is practically identical to the measured vacuum level shift, we conclude that the vacuum levels of $\text{Ir}(\text{ppy})_3$ and CBP align. Based on our earlier assumption of the ionization potential of the guest molecule remaining the same both in the neat and in the composite films, we also expect the $\text{Ir}(\text{ppy})_3$ HOMO level to shift rigidly with the core level position.

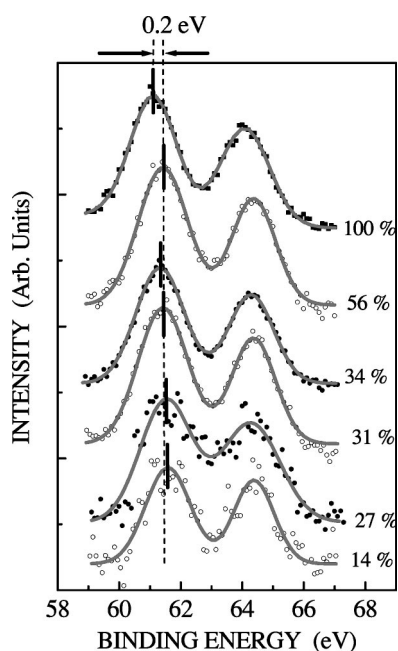


FIG. 5. $\text{Ir} 4f$ core level spectra of a neat $\text{Ir}(\text{ppy})_3$ film and $\text{Ir}(\text{ppy})_3$:CBP composite films at various guest molecule concentrations. The binding energy is referenced to the Fermi level of the Ag substrate.

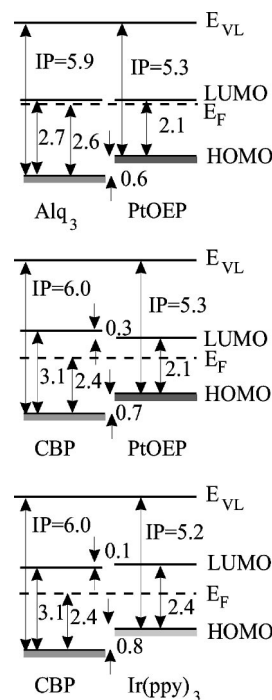


FIG. 6. Guest and host energy levels in the studied composite films. The energy values are expressed in electron volts.

C. Energy levels in the guest–host systems

1. Vacuum level alignment

The observed vacuum level alignment in the studied guest–host systems implies that the relative positions of the guest and host HOMOs can be obtained from the difference of their neat film ionization potentials. A summary of the energy level positions in the three guest–host systems, including the $\text{PtOEP}:\text{Alq}_3$ composite from the previous studies,¹⁹ is shown in Fig. 6. The HOMO positions are referenced to the common vacuum level of the guest and the host. The HOMO–LUMO gaps were estimated from the optical absorption spectra of the guest and host materials.^{20–22} It is evident from Fig. 6 that in each one of the guest–host systems, the guest HOMO is located deep in the host gap. The separation between the guest and the host HOMOs ranges from 0.6 eV ($\text{PtOEP}:\text{Alq}_3$) to 0.8 eV ($\text{Ir}(\text{ppy})_3$:CBP). The estimated LUMO positions of the guest–host systems imply LUMO alignment except in $\text{PtOEP}:\text{CBP}$ film, where the PtOEP LUMO is located 0.3 eV below the CBP LUMO.

Here it is worth noting that the shift of the HOMO positions of the neat and the composite films is 0.14 eV larger when estimated from the high-energy cutoff of the He I spectra shown in detail in the inset of Fig. 4. The deviation is within the error margin of the measurements (0.15 eV), but it clearly illustrates the difficulties involved in determining the line positions solely from broad spectral features. The above conclusions on the LUMO level positions in the guest–host systems are based on the assumption that the host and the guest have similar exciton binding energies in the host matrix, i.e., the true LUMO levels are shifted by equal amounts from their estimated positions. The exciton binding energies

are typically 0.5–1.0 eV in molecular solids,^{23,24} and the uncertainties in estimating these energies constitute the biggest error in the deduced LUMO level positions.

Since there is no evidence for charge transfer (no mid gap states are observed in the UPS spectra), the guest and the host are expected to retain their electronic properties mostly unperturbed. Consequently, the Fermi level will move accordingly within the band gaps assuming that its movement is not hindered by the band edges (no pinning) leading to the vacuum level alignment between the guest and the host. Therefore, the sudden shift of the vacuum level between the neat Ir(ppy)₃ and the Ir(ppy)₃-doped films implies free movement of the Fermi level within the gaps of the guest and the host as the guest–host system is formed. As shown in Fig. 6 the Fermi level is located in the upper half of the CBP gap (2.4 eV from the HOMO edge), and slightly above the mid gap of Ir(ppy)₃ (1.6 eV above the HOMO edge). For comparison, in a neat Ir(ppy)₃ film, the Fermi level is at 1.4 eV as measured from the HOMO edge, which is fairly close to the mid gap (1.2 eV).

The Fermi level position in the neat Ir(ppy)₃ and CBP films is determined by the interaction between the molecular overlayer and the Ag substrate dominated by the formation of a dipole layer^{25–27} at the metal–organic interface. The interface dipole results in the shift of the vacuum level and consequently a change in the work function of the substrate surface. The mechanism of interface dipole formation is still under investigation; likely mechanisms affecting the formation of a dipole layer are chemical reaction between the metal and the organic adlayer, ion formation through charge transfer, image potential interaction, a surface rearrangement and orientation of polar molecules.²⁶ In the case of nonpolar molecules, and in the absence of a chemical reaction and a charge transfer between the metal and the organic, a dipole layer can be attributed to electrostatic effects (image potential interaction and surface rearrangements) at the interface. The electrostatic nature of the dipole layer including final state effects (screening of the photohole) in photoemission experiments have recently been discussed in detail elsewhere.^{28,29}

In the PtOEP:CBP system, the Fermi level is similarly located in the top half of the guest and the host gaps, at 2.4 and 1.7 eV measured from the CBP and PtOEP HOMOs, respectively. The Fermi level is somewhat closer to PtOEP LUMO (0.4 eV) because of the smaller gap energy of PtOEP. In the PtOEP:Alq₃ composite, the Fermi level is yet closer to the LUMOs of PtOEP and Alq₃, 0.1 eV in the scale of Fig. 6. The apparent alignment between the Fermi level and the guest and the host LUMOs in the latter case is, however, misleading. As discussed earlier, the LUMO positions were estimated from optical absorption measurements in solutions and are therefore not absolute (versus Fermi level). The true LUMO position of Alq₃ is likely to be ~1.4 eV higher than shown based on recent inverse photoemission measurements.²⁴ We also want to note that the position of the Fermi level was nearly constant throughout the guest concentrations studied in PtOEP:CBP and in Ir(ppy)₃:CBP films with standard deviations of 0.03 and 0.07 eV, respectively. In PtOEP:Alq₃ films, the scatter in the measured

Fermi level position was slightly higher resulting in a standard deviation of 0.13 eV.

2. Implications for electroluminescence mechanisms

Based on the deduced HOMO positions, at low guest concentrations, PtOEP and Ir(ppy)₃ are likely to act as hole traps in Alq₃ and in CBP host matrices when incorporated in an OLED structure. Upon charge injection, the trapped holes on guest molecules may provide sites for electron–hole recombination and subsequent triplet exciton formation. Hence, direct carrier recombination becomes a viable electroluminescence mechanism in the studied guest–host systems in addition to energy transfer from host to guest.¹

The LUMO level alignment in the PtOEP:Alq₃ films suggests that PtOEP does not act as a trap for electrons in this system. This finding is consistent with the analysis of device structures utilizing a PtOEP:Alq₃ composite film as the emissive layer.¹ However, in the PtOEP:CBP system, the guest LUMO level is located approximately 0.3 eV lower in energy with respect to the host LUMO. Because of its relatively low LUMO position PtOEP will act as an electron trap at low guest concentrations. However, at high guest concentrations, PtOEP may provide an electron hopping site,³⁰ leading to more efficient direct electron–hole recombination on the guest molecule in the PtOEP:CBP system. This may explain the better performance observed for the PtOEP:CBP-based devices compared with that of the PtOEP:Alq₃-based devices. Analogous findings were obtained when films of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine doped with 5,6,11,12-tetraphenylnaphthacene (rubrene) were used as the emissive layers. In these earlier studies, it was found that rubrene molecules can act as both hole trapping and electron hopping sites when the guest concentration exceeds 3 mol %.³⁰ Direct electron–hole recombination on rubrene molecules was proposed as the dominant electroluminescence mechanism, which was further enhanced by the dual nature of rubrene molecules as both hole trapping and electron hopping sites.

IV. CONCLUSION

We have been able to determine the relative HOMO level positions of guest molecules dispersed in organic hosts by using a combination of UPS and XPS. The vacuum levels of the guest and the host molecules align in all the composite films, and consequently, the guest–host HOMO separation is equal to the difference of the ionization potentials of the neat films. The vacuum level alignment implies free movement of the Fermi level within the guest and the host gaps upon the formation of the guest–host composite films. The guest HOMO level lies between 0.6 and 0.8 eV above the host HOMO level, suggesting that the guest molecules can act as trapping sites for holes. The estimated LUMO levels of the guest and the host align in PtOEP:Alq₃ and in Ir(ppy)₃:CBP but in PtOEP:CBP, the PtOEP LUMO is found 0.3 eV below the CBP LUMO. Additional electron hopping sites provided by PtOEP molecules at high guest concentrations and subsequent enhanced carrier recombination on the guest molecules

in the latter structure are proposed to explain the better performance of the PtOEP:CBP-based device compared with that of the PtOEP:Alq₃-based device.

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