

Determination of the energy levels of a phosphorescent guest in organic light emitting devices

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We have used photoelectron spectroscopy to study the relative binding energies of the highest occupied molecular orbitals (HOMOs) of the phosphorescent guest, 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-21H,23H-porphine platinum (PtOEP), and the organic electron transport host, tris(8-hydroxyquinolino) aluminum (III) (Alq₃) in PtOEP:Alq₃ composite films. The PtOEP HOMO position was found to be 0.50 ± 0.13 eV above that of the Alq₃ host, independent of the guest molecule concentration (0.8%–22% by mass). These results are consistent with the assumption that the vacuum levels of the guest and host align. © 2000 American Institute of Physics. [S0003-6951(00)00739-7]

It has recently been demonstrated that phosphorescent dyes, incorporated into the emissive layer of an organic light-emitting device (OLED), can greatly enhance device efficiencies.^{1–4} The quantum yield of the usual fluorescent decay of singlet excitons is limited to $\approx 25\%$ due to spin statistics. By utilizing a phosphorescent dye, both singlet and triplet excitons may decay radiatively, potentially resulting in a fourfold increase in quantum efficiency.

Despite the success of these devices, relatively little is known about the fundamental issue of molecular energy level alignment between the guest and host. For instance, the guest molecular energy levels occupied by the exciton should be such that neither the electron nor hole will hop to a neighboring host molecule, forming an exciplex. This implies that the guest highest occupied and lowest unoccupied molecular orbitals [(HOMO) and (LUMO), respectively] should be nested within the gap of the host material. However, if we assume that the host emissive layer is also the electron (hole) transport layer, it is usually undesirable to have a guest LUMO (HOMO) which is significantly higher (lower) in binding energy than the host LUMO (HOMO). In dilute concentrations, the guest molecules would then act as deep electron (hole) traps, and hinder transport through the device.

Ultraviolet photoelectron spectroscopy (UPS) has been used with great success to study the relative alignment of molecular orbital levels at organic/organic heterointerfaces.^{5–11} However, in a guest-host system, the guest concentration is typically only a few percent, and separation of the UPS spectral contributions of the guest and host is typically impossible, making direct observation of the relative HOMO levels unfeasible. The situation is further complicated, in the case of organic molecules, because most well-known fluorescent guest dyes do not contain any unique element(s), to identify the guest, and x-ray photoelectron spectroscopy (XPS) is therefore of little use.

In the case of phosphorescent dye molecules, we have a fortuitous situation: the heavy metal atom (ex, Pt, Ir),^{1–4} which provides the spin-orbit mixing of the singlet and triplet states, allows radiative decay of triplet excitons. It also represents a new constituent, unique to the guest molecule, which can be probed using XPS. In this letter, we present the first photoelectron spectroscopic study of a guest-host system, in which we have been able to determine the relative energies of the guest (PtOEP) and host (Alq₃)HOMO levels.

The substrates used in this study were Ag foils (99.99%, Sigma-Aldrich), which were prepared in ultrahigh vacuum (UHV) by Ar ion sputtering, and the cleanliness verified using XPS. The organic materials (PtOEP-Porphyrin Products; Alq₃-TCI America), purified by train sublimation, were deposited on these substrates under UHV conditions (typically 10^{-9} Torr) in a sample preparation chamber, connected to a main analysis chamber (base pressure 5×10^{-11} Torr) such that the samples were not exposed to air. UPS and XPS studies were conducted using an Omicron Multiprobe system, utilizing a hemispherical electrostatic energy analyzer, a He discharge lamp, and a Specs double anode (Mg and Al) x-ray source. The overall energy resolution was determined to be ≈ 50 meV for UPS, and ≈ 1 eV in XPS, which in practice was limited by the Al K α linewidth at low pass energies, and by the analyzer resolution at higher pass energies.

In addition to the neat films of Alq₃ and PtOEP, four composite films were studied using both UPS and XPS. The PtOEP concentration of each of the four films was estimated from the Al(2s) and Pt(4f) core level intensities, relative to those of the neat films. The composite films had PtOEP concentrations, by mass, of 0.8%, 2.5%, 11%, and 22%, which correspond very closely to those reported in the earlier device work.^{1,2,4}

UPS data were collected from each of the neat films, to determine their ionization potentials, and the density of states of the pristine films. XPS was collected on each sample, following UPS, to avoid any influence of radiation damage on the UPS signal. The He I/UPS spectra of the two neat films are shown in Fig. 1. For PtOEP, the binding energy of

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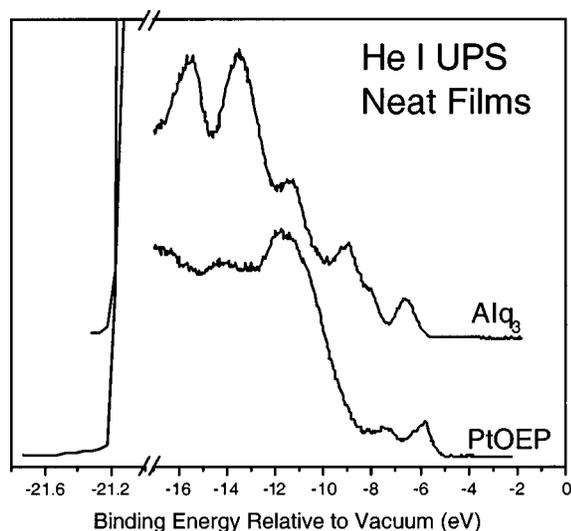


FIG. 1. He I (21.22 eV) UPS spectra of Alq₃ and PtOEP neat films. The ionization potentials, determined from the onset of photoemission and the low binding energy edge of the HOMOs are 5.9 and 5.3 eV, respectively.

the Pt(4*f*_{7/2} and 5/2) core levels were measured relative to the PtOEP HOMO. We initially assume that this binding energy does not change when the PtOEP is surrounded by the Alq₃ matrix. That is, we assume that the component of the electronic polarization screening of the core hole provided by the surrounding host material (Alq₃) is (nearly) the same as in pure PtOEP. We shall see that this assumption has been justified, for the 22% PtOEP sample, within the experimental uncertainties of UPS.

The UPS and XPS spectra of Alq₃ were used to determine the binding energy of the Al(2*s*) core level relative to the Alq₃ HOMO. A sharp Alq₃ spectral feature, ≈6.9 eV below the Alq₃ HOMO, was used to align the energy scales of the doped samples. The PtOEP neat film UPS spectrum is very flat in this region, and the doping of PtOEP therefore does not alter the shape or apparent position of this Alq₃ feature. The alignment of the energy scales was necessitated by a slight variation of the Fermi level within the Alq₃ gap upon doping, presumably due to the presence of both occupied and unoccupied PtOEP-derived states within the Alq₃ gap, which would shift the equilibrium Fermi level position.

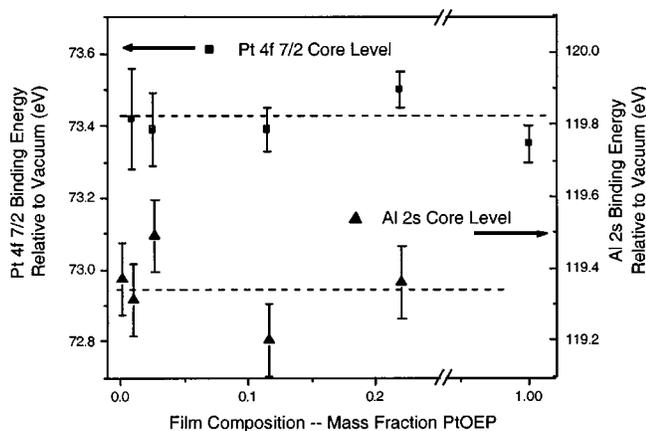


FIG. 2. Binding energies of the Al(2*s*) and Pt(4*f*_{7/2}) core levels measured relative to the Alq₃ vacuum level as a function of PtOEP concentration. Dashed lines indicate the mean binding energies.

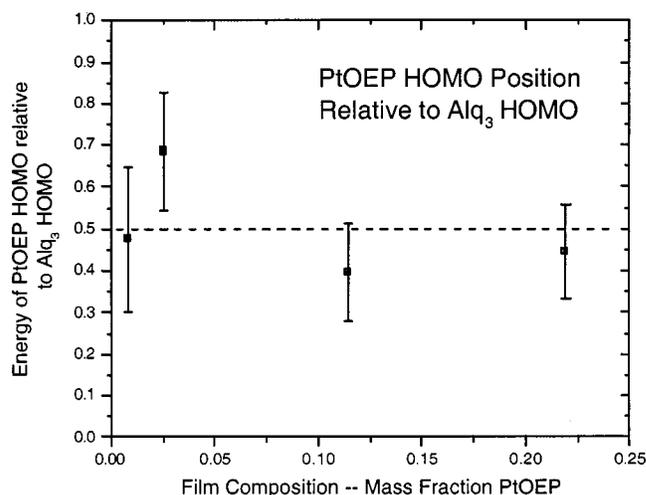


FIG. 3. PtOEP HOMO energy relative to the Alq₃ HOMO in PtOEP-doped Alq₃ films.

UPS and XPS spectra of each of the doped films were collected. All spectra were shifted rigidly to align the sharp Alq₃ spectral feature 6.9 eV below the Alq₃ HOMO, as discussed above. The difference in binding energies of the Al(2*s*) and Pt(4*f*) core levels was determined in each film. Using the Pt(4*f*) to PtOEP HOMO and Al(2*s*) to Alq₃ HOMO energy differences measured on the neat films, the position of the PtOEP HOMO relative to the Alq₃ HOMO was then determined for each film.

The He I UPS spectra of the neat films (Fig. 1) are clear and well resolved. The Alq₃ spectrum is in excellent agreement with previously published results.^{6,8,9,12,13} No UPS data of PtOEP has been published, however, the overall appearance of the spectrum, particularly in the HOMO region, indicates a high-quality film. The ionization potentials, defined as the energy difference between the vacuum level and the low binding energy edge of the HOMO, of the Alq₃ and PtOEP films are 5.9±0.1 and 5.3±0.1 eV, respectively.

A summary of the XPS peak positions, in binding energies relative to the vacuum, is presented in Fig. 2. All peak positions were determined using standard nonlinear least-squares fitting techniques, assuming a Gaussian peak shape due to the resolution-limited nature of the XPS technique. During the fitting of the Pt(4*f*) peaks, the spin-orbit splitting between the *j*=7/2 and 5/2 peaks was fixed, as well as the branching ratio. When we examine the Pt(4*f*_{7/2}) core level binding energy as a function of PtOEP concentration, we find that it is constant within experimental uncertainty. The small amount of scatter in the reported binding energies is due to experimental noise, and agrees well with the constant energy within the estimated error bars. The data show no systematic dependence on the PtOEP concentration. Similarly, the Al(2*s*) energy is constant with respect to the PtOEP concentration.

Given the constant binding energies of the Pt(4*f*) and Al(2*s*) core levels as a function of PtOEP concentration, we conclude that the PtOEP HOMO is ≈0.50±0.13 eV above the Alq₃ HOMO in the doped films, which implies, within experimental uncertainty, that the vacuum levels of the PtOEP and Alq₃ align. The measured PtOEP HOMO position relative to the Alq₃ HOMO is shown for each film in

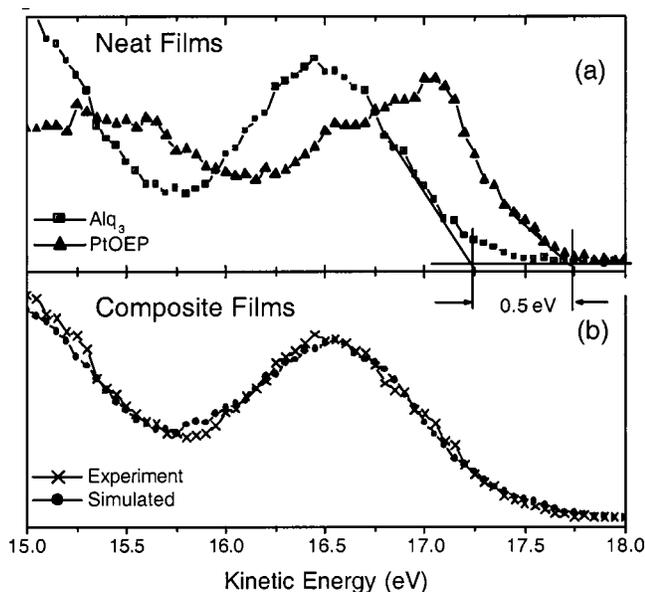


FIG. 4. UPS spectra of the HOMO region for the Alq₃ and PtOEP neat films, as well as an Alq₃ film doped with 22% PtOEP. The fourth data set represents a simulated spectrum of the doped film obtained by adding $0.78 \times$ the neat Alq₃ spectrum + $0.22 \times$ the neat PtOEP spectrum. All energy scales have been shifted to the relative positions of the Alq₃ and PtOEP HOMOs derived from the XPS results.

Fig. 3. The scatter appears to be random, and does not indicate any systematic dependence on PtOEP concentration.

If we now estimate the relative positions of the two LUMO levels, using the optical absorption gaps of Alq₃ (2.7 eV) and PtOEP (≈ 2.1 eV¹) as the HOMO–LUMO splittings (ignoring excitonic effects, which will increase these splittings by ≈ 0.5 eV), we conclude that within our experimental uncertainty, the LUMO levels align. This conclusion is based on the assumption that the exciton binding energies of Alq₃, and a PtOEP molecule in an Alq₃ matrix are similar. We note that while we have directly measured the energy of a hole state in the HOMOs using UPS, the energy of an extra electron in the LUMO contains the uncertainty of this assumption. Thus, on the basis of this rough estimate, we would not expect the PtOEP to act as a deep electron trap in the electron transporting Alq₃ layer. This result was anticipated by Baldo *et al.*¹ on the basis of their OLEDs doped with DCM2 (2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl) ethenyl]-4H-pyran-4-ylidene] propane-dinitrile) in the recombination zone, and PtOEP 200 Å away.

As expected, we are unable to separate the contributions from the PtOEP and Alq₃ valence features in the UPS spectra of the doped films. With increasing PtOEP concentration, we observed a broadening of the apparent HOMO peak, and the Alq₃ related feature ≈ 4.7 eV below the Alq₃ HOMO peak, due to the strong PtOEP features in these energy ranges. At the highest PtOEP concentration (22%), we are able to further analyze the UPS spectrum in the following way. We can simulate the UPS spectrum of this film by creating a hypothetical spectrum through the superposition of $0.78 \times$ the neat Alq₃ spectrum and $0.22 \times$ the neat PtOEP spectrum, aligned such that the PtOEP HOMO edge is 0.50 eV above that of the Alq₃, as derived from the XPS results. This simulated spectrum was then compared with that collected from the 22% PtOEP-doped film. The neat, doped, and simulated spectra are presented in Fig. 4. The simulated spectrum is in excellent agreement with that measured on the doped film, thus justifying our earlier assumption of a constant Pt(4*f*) to PtOEP HOMO energy difference.

In conclusion, we have measured the HOMO energy of the phosphorescent guest molecule, PtOEP, relative to the Alq₃ host HOMO in doped films. The PtOEP HOMO is 0.50 ± 0.13 eV above that of the Alq₃ implying that the vacuum levels of the guest and host align within experimental uncertainties.

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- ¹M. A. Baldo, D. F. O'Brien, Y. You, A. Soutikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- ²D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **74**, 442 (1999).
- ³M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- ⁴R. C. Kwong, S. Sibley, T. Dubovoy, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Chem. Mater.* **11**, 3709 (1999).
- ⁵N. Sato and M. Yoshikawa, *J. Electron Spectrosc. Relat. Phenom.* **78**, 387 (1996).
- ⁶A. Rajagopal, C. I. Wu, and A. Kahn, *J. Appl. Phys.* **83**, 2649 (1998).
- ⁷H. Ishii, K. Sugiyama, D. Yoshimura, E. Ito, Y. Ouchi, and K. Seki, *IEEE J. Sel. Top. Quantum Electron.* **4**, 24 (1998).
- ⁸I. G. Hill and A. Kahn, *J. Appl. Phys.* **84**, 5583 (1998).
- ⁹R. Schlaf, B. A. Parkinson, P. A. Lee, K. W. Nebesny, and N. R. Armstrong, *Appl. Phys. Lett.* **73**, 1026 (1998).
- ¹⁰I. G. Hill and A. Kahn, *J. Appl. Phys.* **86**, 2116 (1999).
- ¹¹I. G. Hill and A. Kahn, *J. Appl. Phys.* **86**, 4515 (1999).
- ¹²A. Rajagopal and A. Kahn, *Adv. Mater.* **10**, 140 (1998).
- ¹³I. G. Hill, A. J. Mäkinen, and Z. H. Kafafi, *J. Appl. Phys.* **88**, 889 (2000).