Photoemission and X-ray absorption spectroscopies of phosphorescent organic iridium complexes


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Abstract

Phosphorescent materials represent an attractive route to high-efficiency organic LEDs, since their maximum theoretical quantum efficiency is 100%, compared to the 25% of fluorescent materials. We have studied the electronic structure of three phosphorescent iridium complexes, the red emitter Iridium bis(2-C-benzothienyl)pyridato-N,C (C) (acetylacetonate), the blue emitter Iridium bis(2,4,6-difluorophenyl)pyridato-N,C (C) picolinate, and the green emitter Iridium tris(2,4-tolyl)pyridato N,C) using electron spectroscopies. The materials were evaporated in situ onto a clean gold substrate in ultra-high vacuum. The valence band electronic structures were investigated using resonant photoemission, with the unoccupied states determined using X-ray absorption. The data suggests a hybridisation of the Ir 5d states with the p orbitals of the ligand. NEXAFS spectra are shown to be highly sensitive to the local environment.

Keywords: Photoelectron spectroscopy, X-ray absorption spectroscopy, organic semiconductors based on conjugated molecules

1. Introduction

A route towards the high efficiency organic LED is the use of phosphorescent active materials, which do not suffer the 25% limit in theoretical efficiency found in fluorescent materials. Following the work of Baldo, Forrest and Thompson [1], highly efficient organic LEDs have been fabricated using phosphorescent iridium complexes [2]. We have studied the electronic structure of three of these materials using electron spectroscopies.

The materials investigated were Iridium bis(2-C-benzothienyl)pyridato-N,C (C) (acetylacetonate), Iridium tris(2,4-tolyl)pyridato N,C), and Iridium bis(2,4,6-difluorophenyl)pyridato-N,C) picolinate which are, respectively, a red, a green and a blue emitter. The structures, and abbreviated names, of these molecules are shown in fig. 1. We have recently used two of these materials in a PFVK host to fabricate a white-emitting phosphorescent device [3].

Previous electron-spectroscopic investigations of phosphorescent organics [4-6] have been largely concerned with the question of band alignment with the polymer host typically employed with such materials. Here we investigate the electronic structure of the materials themselves.

![Fig. 1. Structures of the three molecules studied](image-url)
potential of the HOMO. The use of synchrotron radiation, on the other hand, permits the use of cross-section effects and resonant photoemission to determine the contribution of the Ir 5d state to the valence band structure. The unoccupied states were investigated using near-edge X-ray absorption (NEXAFS), at the absorption edges of each of the elements found in the molecular structure.

2. Experimental

Thin films (100nm) were evaporated in ultra-high vacuum, onto gold substrates, with the thickness determined using a quartz crystal microbalance. Line-source valence band photoemission spectra (hv=21.2 eV), and X-ray photoemission spectra (XPS) were taken using a Scienta 200 hemispherical analyser. Stoichiometry and purity were confirmed using XPS. Synchrotron radiation photoemission and NEXAFS spectra were taken on the BEAR beamline, ELETTRA, Trieste, Italy, using a 6mm-mradium hemispherical analyser. NEXAFS spectra were recorded using both total (drain current) and Auger yields. The energy resolution for photoemission and NEXAFS was < 100meV. The organic materials were obtained from American Dye Source, and used without further purification. Exposure to hard X-rays (Mg Ka) was found to induce defects in the films, thus shifting the apparent binding energy of the valence band. Valence band spectra were thus taken prior to XPS measurements.

3. Results and Discussion

Fig. 2 shows a series of photoemission spectra for Ir(Fpy)2pi. In the spectrum taken using a photon energy of 21.2 eV, note that the peak at a binding energy of 11 eV is significantly more intense than the other peaks, which is not the case in the spectra taken using photon energies around 60 eV. The relative cross-section of the Ir 5d level is much higher at 21.2 eV than at 60 eV [8], therefore the behaviour of this peak is consistent with that of the Ir 5d. Resonant photoemission can be used to extract the element-specific contributions to a photoemission spectrum, even if the element is relatively dilute. For example, resonant photoemission has recently been used to extract the 4f contribution to the valence bands of rare-earth complexes [9]. Rare earth resonances are particularly intense, but there will also be a finite enhancement at the Ir 4f edge, given the presence of unoccupied Ir d-states. The resonance energies were located using X-ray absorption of the evaporated films, using total yield. The Ir N\text{\textsubscript{d}} edge absorption spectrum is shown in fig. 3. There are two resonances, corresponding to the two spin-orbit split components of the Ir 4f level.

![Fig. 2. Photoemission spectra of Ir(Fpy)2pi at different photon energies. Also shown is a spectrum of a dilute MgIr alloy [7], taken using hv=21.2 eV.](image1)

![Fig. 3. Ir N\text{\textsubscript{d}} absorption spectrum of Ir(Fpy)2pi.](image2)

There is a small enhancement of the 11 eV peak at the N\text{\textsubscript{r}} resonant photon energy of 65 eV. This is perhaps not so evident in the spectrum of fig. 2, but is more clearly seen in Fig. 4, which shows superimposed flux-normalised spectra. The enhancement of this peak at the Ir N\text{\textsubscript{r}} resonance further suggests its Ir 5d character. However, fig. 2 shows that the peak at 3eV binding energy is enhanced at the Ir N\text{\textsubscript{b}} resonance energy. This suggests that there is some Ir 5d character in this peak, although clearly it is very weak at 21.2eV. This implies that while this peak is likely to be largely composed of organic \pi orbitals, there is also a finite amount of Ir 5d character. Note that this peak is close to the HOMO energy, although the 21.2eV data, which have intrinsically higher resolution, show that they are not degenerate.
Very similar behaviour in the photoemission spectra was seen for the other two iridium complexes, suggesting that the nature of the metal-organic bonding is similar in all three materials. The apparent Ir 5d behaviour in these materials is very different to that of a purely metallic dilute Ir system, a Mg alloy [7] shown in fig. 2. The Ir 5d peak is at a very low binding energy, and shows clear spin-orbit splitting, i.e. is rather atomic-like.

The spectra of the iridium complexes clearly imply more complex Ir behaviour, with the implication of Ir 5d hybridization with organic orbitals.

Fig. 5 shows a comparison of the nitrogen NEXAFS spectra for the three molecules. Unlike photoemission, NEXAFS is element specific, so the peaks seen correspond to unoccupied orbitals with significant weight on nitrogen sites.

As can be seen in fig. 1, the nearest-neighbour configuration of the N sites in all three molecules is identical, significant differences occurring only in next-nearest neighbours. Fig. 5 shows that the NEXAFS spectra are not identical, with, in particular, the peaks at 405 eV being rather different. Following the building block principle of NEXAFS [10], the nitrogen spectra of the three iridium complexes should be very similar to that of AQ$_3$ [11], and in fact the overall lineshape is similar. However the unoccupied states with weight on the N sites also have weight across the whole moiety in AQ$_3$ [11]. Therefore the NEXAFS spectra should be sensitive to the differences in the organic ligands, independent of the nearest neighbours of the N atoms. In this respect NEXAFS is a more sensitive probe of the local chemical environment than XPS.

This sensitivity has been noted in comparing the nitrogen NEXAFS spectra of metal 8-hydroxyquinolates – subtle differences in energy and lineshape have been noted in comparing data for AQ$_3$ [11] with that obtained from rare-earth quinolates [12]. This demonstrates that in NEXAFS spectra with sufficient resolution, the building block principle breaks down, notwithstanding the localisation of the core hole.

In principle the carbon NEXAFS spectra should yield more detailed information on the electronic structure of the
complexes, given the far higher presence of carbon. In practice there is rather too much information - each distinct carbon site has distinct NEXAFS transitions, giving rise to a superposition of multiple spectra. The result is the complex spectra shown in fig. 6. The multiple carbon sites are further evidenced by the multiple components visible in the carbon K-edge photoemission spectra, such as that shown for Ir(Fpy)2Cl in fig. 7. Here the aromatic carbon gives rise to the major component, at 285 eV, with higher oxidation states resulting in the components at higher binding energies. The C=C bond of the picolinate group is responsible for the small peak at 289 eV.

Very detailed calculations are needed for even a basic interpretation of the carbon NEXAFS spectra for such molecules, as has, for example, proven the case for AlQ3 [11].

A basic analysis of the S 2p 3 NEXAFS data of (bpy)3Ir(acac) and the K edge spectrum of Ir(Fpy)3Cl shows, as might be expected, great similarities to those of thiophene [10] and fluorene [13] respectively.

4. Conclusions

Although the iridium represents only a very small percentage of the content of the organic iridium complexes studied, we have shown that the iridium contribution to the valence band density of states can be identified by exploiting the tunability of synchrotron radiation. The triplet states responsible for phosphorescence are, of course, intrinsically invisible to the spectroscopies used here, as they involve optical transitions. The photoemission results are nevertheless relevant to phosphorescence since they imply that there is some hybridization of the Ir 5d states with the organic orbitals, in particular the 3e peak, close to the HOMO energy. This is consistent with recent theoretical results [14] which suggested that in general the Ir 5d states are hybridised with ligand π-orbitals in these complexes. Ir 5d states are therefore located both energetically and spatially close to organic π states. This would assist inter-system crossing from singlet excitations to triplets via the so called “heavy-ion effect”, which is facilitated by the spin-orbit coupling of the metal, consistent with the high triplet generation rates of these materials.

Nitrogen NEXAFS spectra have been shown to be highly sensitive to the different structures of the organic ligands, although the local chemical environment of the N atoms in each of the iridium complexes is identical.

The many different chemical environments of the individual carbon atoms in these molecules are evidenced by the multiple components to the C 1s spectra. This contributes to the complexity of the C K-edge NEXAFS spectra.

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References