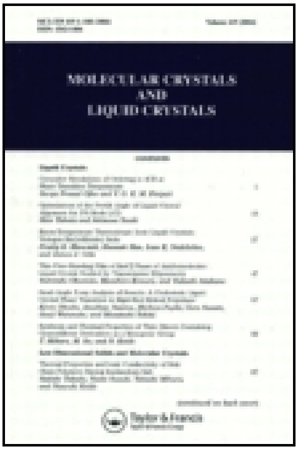

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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K. Sugiyama [a], D. Yoshimura [a], E. Ito [a], T. Miyazaki [a], Y. Hamatani [a], I. Kawamoto [a], Y. Ouchi [a], K. Seki [a] & H. Ishii [b]

[a] Department of Chemistry, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-01, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

To cite this article: K. Sugiyama , D. Yoshimura , E. Ito , T. Miyazaki , Y. Hamatani , I. Kawamoto , Y. Ouchi , K. Seki & H. Ishii (1996): Uv Photoemission Study of 8-Hydroxyquinoline Aluminum (ALQ_3) / Metal Interfaces, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 239-244

To link to this article: http://dx.doi.org/10.1080/10587259608042292

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 239–244
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UV PHOTOEMISSION STUDY OF 8-HYDROXYQUINOLINE ALUMINUM (ALQ_3) / METAL INTERFACES

K. SUGIYAMA, D. YOSHIMURA, E. ITO, T. MIYAZAKI, Y. HAMATANI,
I. KAWAMOTO, Y. OUCHI, AND K. SEKI
Department of Chemistry, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
H. ISHII*
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract Electronic structure of tris(8-hydroxyquinolino) aluminum (Alq_3) / metal interface was directly investigated as a model interface of electroluminescent (EL) devices by UV photoemission spectroscopy (UPS). Simulated spectrum of Alq_3 calculated by a MNDO / PM3 molecular orbital calculation showed a good correspondence with the observed UPS spectrum. Highest occupied molecular orbitals (HOMOs) of Alq_3 was assigned to HOMO of the ligands. At Alq_3 / metal interfaces, shift of the vacuum level was observed, in contrast to the traditional assumption with common vacuum level at the interface. Interfacial energy diagrams determined by the results of UPS corresponds well to actual carrier-injecting character at the interface.

INTRODUCTION

Recently, organic electroluminescent (EL) devices have attracted much attention in relation to the application to a flat panel display, and great efforts have been made to improve the performance of the devices.[1,2,3] The operation of organic EL devices roughly consists of three processes; (1) carrier injection from metal electrode to organic layer, (2) carrier transport, and (3) carrier recombination. Although carrier injection is one of these important processes, the mechanism is not clear. For understanding its mechanism, it is indispensable to elucidate the electronic structure of interface between the organic layer and the metal electrode. However, only few reports have been published for the direct measurements of the interfacial electronic structure.[4,5] In most studies, interfacial energy diagram have been estimated by combining separately observed electronic structures of the two components at the interface, with assumption of a common vacuum level at interface. However, recently we found a shift of vacuum level at the porphyrin / metal interface,[6] by directly studying the interface by UV photoemission spectroscopy (UPS), which is a useful method for probing the surface electronic structure. This is contrast to the concept of common vacuum level. Thus,we have shown that direct examination of the interface is necessary for clarifying the interfacial electronic structure.

In this work, we have extended our UPS study to tris(8-hydroxyquinolino) aluminum (Alq_3) / metal (Au, Al) interfaces as model interfaces of organic EL device. Alq_3 is a typical light-emitting material in the organic EL devices. By analyzing the interfacial electronic structure deduced from UPS experiments, the correlation between the observed electronic structure of the model interface and carrier-injecting nature of the real interface was investigated. The validity of traditional assumption of common vacuum level is also discussed.

EXPERIMENT

The sample of Alq_3 was supplied from Toshiba R&D Center, and was purified by sublimation. Photoelectron spectroscopic measurements were carried out using synchrotron radiation with an angle resolving UPS spectrometer at BL8B2 of UVSOR Facility at Institute for Molecular Science. Alq_3 thin films were prepared by vacuum deposition onto Al or Au evaporated substrate. UPS spectra were measured under vacuum of 10^{-8} Pa by a concentric hemispherical analyzer with a total resolution of about 0.2 eV. In order to assign the observed spectra, the molecular orbital (MO) calculations of Alq_3 were carried out with a MOPAC semi-empirical PM3 program.[7,8] The simulated spectra were obtained by convoluting the delta functions located at each orbital energy with a Gaussian function with a half width of 0.8eV.

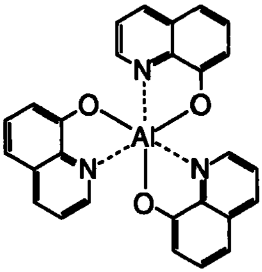

FIGURE 1. The molecular structure of Alq_3

RESULTS AND DISCUSSION

UPS spectra of Alq_3

Figure 2 (a) shows the UPS spectrum of Alq_3 of thickness of 10 nm on Au at the incident photon energy $h\nu$ of 40 eV. The abscissa is the binding energy E_b from the vacuum level.

Ionization threshold energy I_{th}, corresponding to the right-hand onset, was 5.9 ± 0.1 eV, which is consistent with that by other workers.[9] The simulated spectrum of Alq_3 is also shown in figure 2 (b), with each orbital energies marked by a vertical line. The contraction of the energy scale for the simulated spectrum by 1.1 times and a shift by 0.7 eV offer good agreement with the observed spectrum as shown in figure 2. The comparison with the simulated spectrum of 8-quinolinol showed that the features in the low energy region (5 - 10 eV) are derived from the π-orbitals of 8-quinolinol. The structures at 10 - 20 eV and around 25 eV were ascribed to the $\sigma + \pi$ and C2s orbitals, respectively. The topmost feature at 6.5 eV which dominates the electric properties of Alq_3 is assigned to the nearly degenerate three orbitals originating from π HOMO of 8-quinolinol ligands (the MO pattern is shown in the inset of figure 2). The small energy separation among these orbitals of Alq_3 indicates that the interaction among the HOMOs of the ligands is weak.

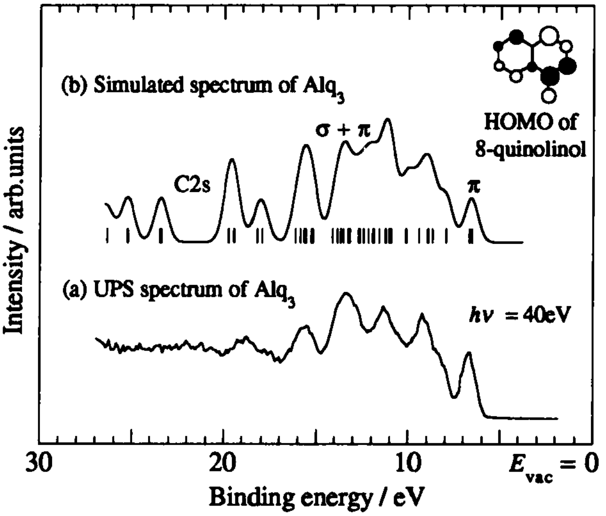

FIGURE 2. (a) The observed UPS spectrum of thick film (10nm) of Alq_3 on Au and (b) the simulated spectrum of Alq_3. Calculated orbital energies are also shown as vertical lines. The abscissa is the binding energy relative to vacuum level.

Electronic structure of Alq_3 / metal interfaces

Figure 3 shows UPS spectra of Alq_3 of (a)1nm and (b) 10nm thickness on Al. The abscissa is the binding energy relative to the Fermi level of Al. The line shapes of these two spectra are similar to that of the film of 10nm thickness on Au in figure 2 (a), indicating that the formation of interface does not change the molecular electronic structure of Alq_3.

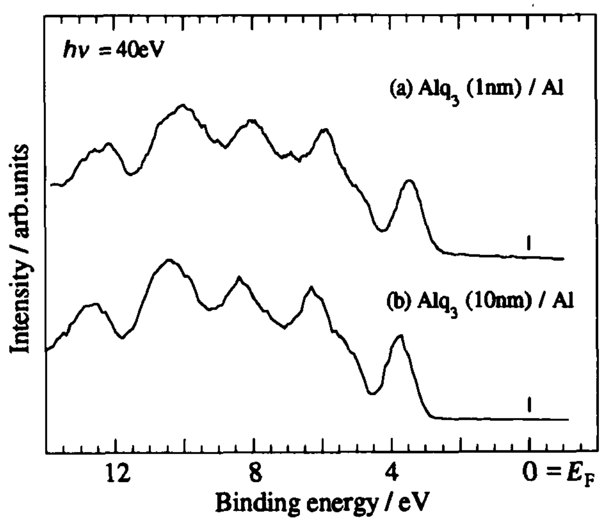

FIGURE 3. UPS spectra of Alq_3 of (a) 1nm and (b) 10nm on Al. The abscissa is the binding energy relative to Fermi level of Al, shown as the vertical lines.

Using the results of UPS measurements of the films with 1nm thickness, energy diagrams of Alq_3 / Al, Au interfaces were determined as shown in figure 4. Φ_m means the work function of the metal, while ε^F_{vac}, ε^F_v denote the energy of the vacuum level and the HOMO of Alq_3 relative to Fermi level of metal substrate, respectively. ε^F_v is determined as the right-hand onset of a spectrum of Alq_3 relative to the Fermi level of the metal substrate. In the case of Alq_3 / Au interface, the right-hand onset is overlapped with the strong emission from the d band of the Au substrate, making it difficult to determine ε^F_v. Therefore the HOMO energy of the diagrams was estimated by using the measured value of the lowering of the vacuum level Δ determined from the left-hand cutoff of the spectra and I_{th} = 5.9eV for Alq_3.

The energy position of the lowest unoccupied molecular orbital (LUMO) was estimated by regarding optical excitation energy of 2.9eV as the band gap. The actual band gap, however, may be slightly larger since optical excitation corresponds to the transition to the exciton state. At the interfaces with both metals, the vacuum level abruptly shifts within the thickness of a few nms by Alq_3 deposition, in contrast to the traditional assumption of a common vacuum level at the interface. Similar abrupt shift of vacuum level was also observed at organic semiconductor / metal interfaces (Zinc tetraphenylporphyrin / metal),[2] inorganic semiconductor / metal interfaces,[10] and organic / inorganic interfaces (merocyanine dyes / Ag halides).[11]

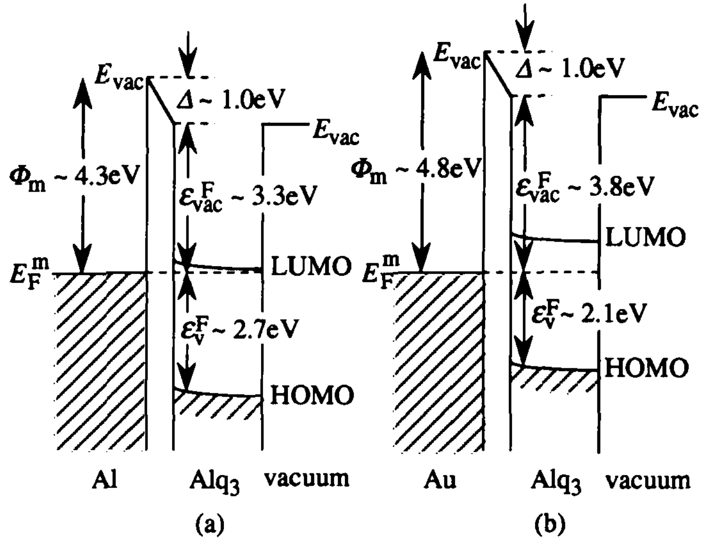

FIGURE 4. Energy diagrams of Alq_3 / Al (a), and Alq_3 / Au (b) interfaces, determined directly by using the results of UPS measurements.

Now let us consider the carrier-injecting character of the interfaces on the basis of the observed energy diagram. In the case of Alq_3 / Al interface, the barrier height to electron injection, corresponding to the energy difference between the LUMO of Alq_3 and the Fermi level of Al, is very small, while that to hole injection is very large, as seen in figure 4 (a). We can expect good electron-injecting character of the interface, which consistent with the nature of the real device.[12] In contrast, using a traditional assumption with a common vacuum level at interface, Fermi level of the substrate should be located around the center of the gap, suggesting poor electron injecting nature of the interface. In the case of Alq_3 / Au interface (figure 4 (b)), the Fermi level of Au is around the center of the gap, suggesting the poor injecting character for both carriers. This is consistent with the fact that hole-injection from Au electrode to Alq_3 is assisted by inserting hole-injection layer between Alq_3 and anode in most EL devices fabricated from Alq_3.

Thus a neglect of vacuum level shift at the interface Δ leads to an incorrect prediction of carrier-injecting nature of interfaces, since Δ plays an important role in determining interfacial electrical structure. These findings indicate the necessity of the direct observation of the interfacial electronic structure by UPS or other techniques for understanding EL devices.

ACKNOWLEDGMENTS

The authors thank Dr. Syun Egusa and Dr. Takashi Sasaki of Advanced Research Laboratory, Toshiba R&D Center for the gift of the sample material. This work was performed as a Joint Studies Program of the UVSOR facility of the Institute for Molecular Science (No.6-H217). This work was supported in part by the Grant-in Aids for Scientific Research (Nos. 07CE2004, 07NP0303, 04403001) and by the Venture Business Laboratory Program, both from the Ministry of Education, Science and Culture of Japan.

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