

C 1s photoelectron energy loss spectra of organic electroluminescent materials

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Abstract – The C 1s photoelectron energy loss spectra of tris (8-hydroxy-quinoline) aluminum (Alq₃) and N,N'-diphenyl-N,N'-bis (3-methyl phenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD) thin films have been investigated. Two major loss structures, namely the plasmon dominated loss lines and shake-up satellites, have been observed. The shake-up spectrum of the C 1s photoelectron line is directly related to the π - π^* energy gap of the molecule which plays an important role in organic electroluminescent materials. The molecular orbitals of Alq₃ and TPD and their major components, quinoline and benzene, have been calculated with the AM1 semi-empirical method. The amount of the plasma-dominated loss of Alq₃ and TPD, which has to do with the delocalization of electrons through the molecule, was about 24 eV, alike in both cases. The main peak of the C 1s shake-up spectrum of Alq₃ and TPD, however, was 5.2 eV and 6.8 eV, respectively. It was found that the main shake-up peak reflects more the local π - π^* transition of quinoline and benzene component rather than the excitation of the whole molecule of Alq₃ and TPD. The C 1s shake-up spectra, however, revealed some correlation with the optical energy gap of the organic electroluminescent materials.

I. Introduction

In recent years, there has been considerable interest in developing organic electroluminescent (EL) devices for flat panel display (FPD) applications [1-3]. The basic structure of an organic light-emitting device (OLED) is a sandwich structure of electron and hole transport layer between metallic cathode and transparent anode on a glass substrate. Both conjugated polymers and functional molecules are currently used for the organic electroluminescent materials. In spite of low driving voltage, the performance of OLED such as quantum yield and reliability should be improved for the next generation display. A better understanding of the electronic structure of organic electroluminescent materials is needed for such improvement. Thus, calculations with various theoretical models and experiments with x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) have been performed in order to study the electronic structure of the organic materials [4-6]. Especially, the energy difference of the lowest unoccupied molecular orbital (LUMO) and the highest

occupied molecular orbital (HOMO), which is the π - π^* energy gap, plays an important role in OLED.

In this work, the C 1s photoelectron energy loss spectra of tris(8-hydroxy-quinoline) aluminum (Alq₃) [7] and N,N'-diphenyl-N,N'-bis(3-methyl phenyl)-1,1'-bi-phenyl-4,4'-diamine (TPD) thin films have been investigated. The π - π^* shake-up spectrum of the C 1s photoelectron line has been measured because it is directly related to the π - π^* energy gap of the molecule which has to do with the optical energy gap of the organic electroluminescent materials. The molecular orbitals of Alq₃ and TPD and their components, quinoline and benzene, have been calculated with the AM1 semi-empirical method and compared with each other.

II. Experiment and Calculation

The organic electroluminescent molecular thin films, Alq₃ and TPD, were deposited on a silicon wafer by thermal evaporation. The organic materials were purified powders and the base pressure of the evaporation chamber was about 2.5×10^{-6} Torr. The molecular structures of the organic molecules are

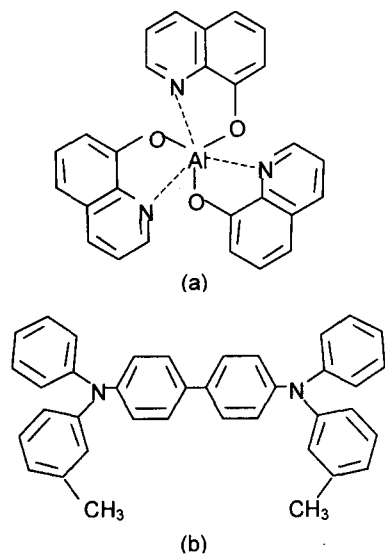


Fig. 1. Molecular structures of (a) Alq₃ and (b) TPD.

shown in Fig. 1. The thickness of each thin film was about 100 nm and the deposition rate was about 3 nm/min.

The XPS analyses were performed by PHI-5400 system with a monochromatized Al K α x-ray source ($E = 1486.6$ eV) at 12 kV and 350 W. Monochromator is essential for the study of organic materials because of the possible damage when standard source is used. The measured spectra were obtained

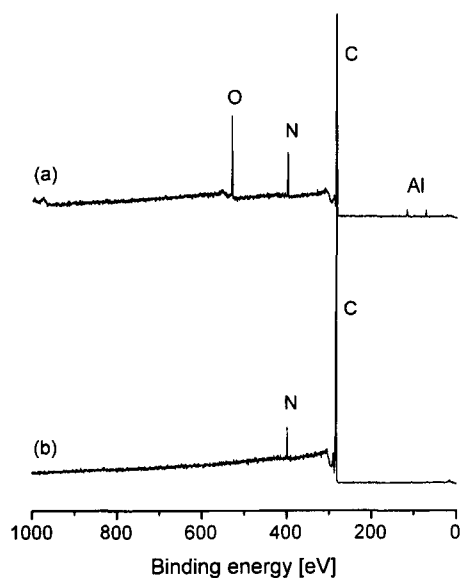


Fig. 2. XPS survey spectra of (a) Alq₃ and (b) TPD.

at the pass energy of 35.75 eV. The resolution was 0.7 eV FWHM for Ag 3d_{5/2}. The binding energy was calibrated at 84.0 eV for Au 4f_{7/2} and shifted to the reference of the hydrocarbon C 1s main peak at 285.0 eV. The base pressure in the analysis chamber was about 5×10^{-10} Torr. To reduce the charging effect at the sample surface, a neutralizer was used during the measurements. Fig. 2 shows the XPS survey spectra of Alq₃ and TPD. One can see the C 1s, O 1s, N 1s and the two weak Al photoelectron lines of Al 2s and Al 2p. No other elements, which can be originated from impurities, can be found. The measured atomic concentration is in good agreement with the theoretical values [8].

The molecular orbitals of the organic materials were calculated on a Silicon Graphics O² R10000 workstation (IRIX 6.x platform). All the calculations were performed utilizing a commercial program, Cerius², developed by Molecular Simulations Inc. The modules used were Open Force Field, Minimizer, and MOPAC, which is a well known semi-empirical quantum code. In this calculation, we used the AM1 Hamiltonian approximation [9].

III. Results and Discussion

Fig. 3 shows the valence band spectra of Alq₃ and TPD, which represents the occupied molecular orbitals. Because of the poor photoelectric cross-section of x-ray source, valence band spectra are often recorded using ultraviolet photoelectron spectroscopy (UPS). Here, we used the XPS valence band spectra only for the fingerprinting mode of analysis. The valence band is mainly composed of O 2s and N 2s (21-27 eV), C 2s (10-20 eV), and C 2p (6-10 eV). The result of Alq₃ is in good agreement with that of the Soft XPS measurements [4]. Except for the N 2s peak, the rest of the spectrum of TPD is astonishingly similar to the XPS valence band spectrum of polystyrene [10]. This may come from the fact that the benzene component is commonly present in both polystyrene and TPD. This means that the electronic structure of TPD is strongly affected by the benzene component. The calculation of the projected density of states (PDOS) of Alq₃ [4] showed that the contribution of Al to the electronic structure is vanishingly small. This means also that the electronic structure of Alq₃ is strongly affected by the quino-

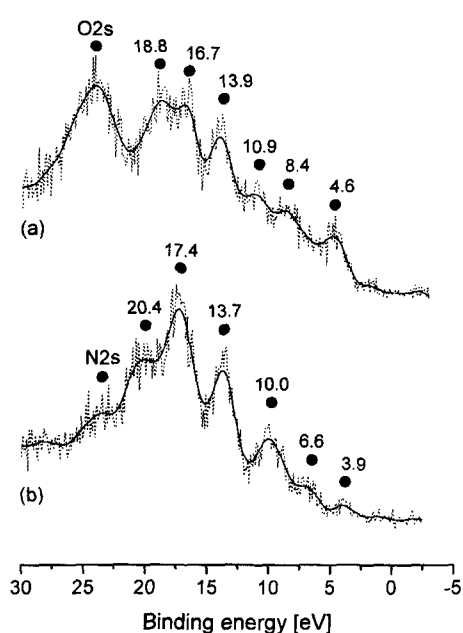


Fig. 3. Valence band spectra of (a) Alq₃ and (b) TPD.

line component.

Figs. 4 and 5 show the C 1s photoelectron main peaks (dotted line) and their energy loss spectra (solid line) of Alq₃ and TPD, respectively. The num-

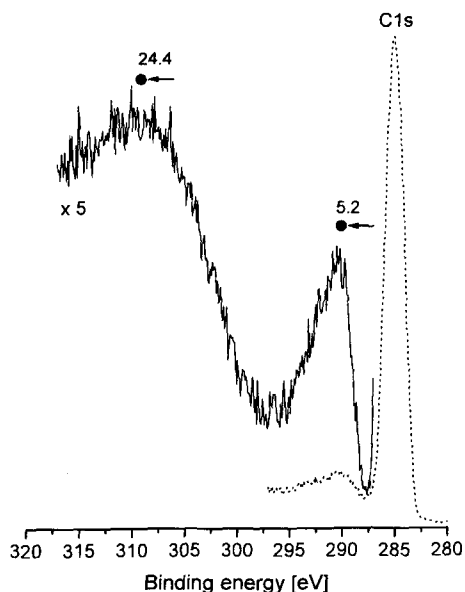


Fig. 4. C1s main peak and its energy loss spectrum of Alq₃.

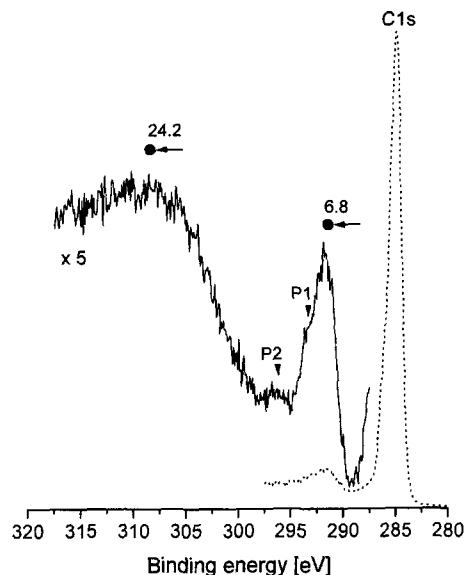


Fig. 5. C1s main peak and its energy loss spectrum of TPD.

bers on the top of the peaks reveal the amount of the energy loss from the C 1s binding energy of 285.0 eV. Two major loss structures, namely the plasmon dominated loss lines and the shake-up satellites, have been observed. The broad shapeless region at about 24 eV in both Alq₃ and TPD represents the plasmon dominated loss line. This reflects the extent of delocalization of electrons through the molecule and is sensitive to the sp² and sp³ bonding [11]. The plasmon dominated loss line of polyethylene and polypropylene lies in about 20 eV and that of the highly oriented pyrolytic graphite (HOPG) in about 30 eV. This means that if the potential π density in the carbon system is maximized as in graphite, it becomes an interlaced collective network of electrons that form a near perfect free electron plasmon [11]. Thus, the degree of π network reduction in Alq₃ and TPD is apparently about 20%. The sharp peaks at 5.2 eV (Fig. 4) and 6.8 eV (Fig. 5) are the main peaks of the C 1s shake-up spectrum of Alq₃ and TPD, respectively. The intensity of the shake-up peak reaches about 8% of the C 1s main peak intensity. The shake-up spectrum of the C 1s photoelectron line is directly related to the π - π^* energy gap of the molecule which plays an important role in organic electroluminescent materials. Minor loss peaks at P1 and P2 in TPD can be slightly seen in

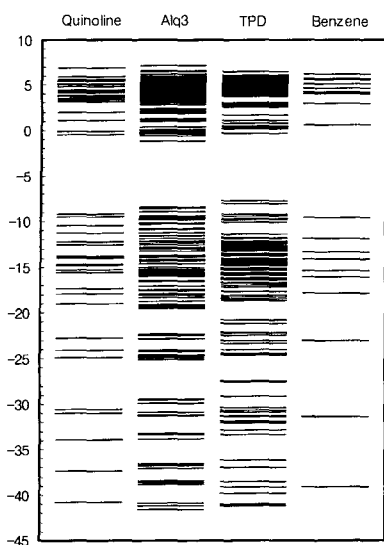


Fig. 6. Molecular energy levels of quinoline, Alq₃, TPD, and benzene (Vertical axis: arbitrary unit).

Fig. 5. Such loss structure with the main loss peak at 6.8 eV is also observable in the $\pi \rightarrow \pi^*$ shake-up spectrum of polystyrene [10]. According to the study of the C 1s shake-up spectra from benzene and biphenyl [12], the peak at 6.8 eV comes from the intra ring benzene like excitation.

Fig. 6 shows the calculated energy diagrams of the molecular orbitals of Alq₃ and TPD and their components, quinoline and benzene. Though some re-scaling of vertical axis would have to be done to compare the calculated values with the experimental data, the untreated values are good enough for our purpose since we are only interested in the relative changes among the molecules. In these diagrams, the energy difference between HOMO and LUMO, namely the $\pi\text{-}\pi^*$ energy gap, of Alq₃ and TPD is reduced to about 83% and 73% compared with that of the quinoline and benzene component, respectively. The proportion of reduction in TPD is stronger than in Alq₃. Such reduction of the $\pi\text{-}\pi^*$ energy gap can be understood with the quantum calculation of polyacetylene [13]. Here, the band gap is reduced as the conjugation length of the conductive polymer is increased. The relative shift of the $\pi\text{-}\pi^*$ energy gap at the Alq₃/TPD interface in Fig. 6 is similar to the energy band diagram in an OLED with double structure (Mg/Alq₃/TPD/ITO) [2]. The energy band gap in this simple OLED, however, is 2.7 eV in Alq₃ and

3.2 eV in TPD. These values are usually obtained by optical absorption and photoluminescence (PL) measurements. The energy of the absorption line is normally higher than the energy of the PL. So, the above values are taken from the wavelength where the optical absorption is just beginning. In case of the C 1s shake-up spectra of Alq₃ (Fig. 4) and TPD (Fig. 5), the energy point where the $\pi \rightarrow \pi^*$ transition is just beginning is 2.9 eV and 4.5 eV, respectively.

IV. Conclusions

Thermally evaporated Alq₃ and TPD thin films have been characterized by XPS. The C 1s photoelectron energy loss spectra have been investigated. Two major loss structures, namely the plasmon dominated loss lines and shake-up satellites, have been observed. The shake-up spectrum of the C 1s photoelectron line is directly related to the $\pi\text{-}\pi^*$ energy gap of the molecule which plays an important role in organic electroluminescent materials. The amount of the plasmon dominated loss of Alq₃ and TPD was about 24 eV alike in both cases. The main peak of the C 1s shake-up spectrum of Alq₃ and TPD, however, was 5.2 eV and 6.8 eV, respectively. It was found that the main shake-up peak reflects more the local $\pi \rightarrow \pi^*$ transition of quinoline and benzene component rather than the excitation of the whole molecule of Alq₃ and TPD. The C1s shake-up spectra, however, revealed some correlation with the optical energy gap of the organic electroluminescent materials.

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References

- [1] J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, and A. Stocking, *Science* **273**, 884 (1996).
- [2] *Organic electroluminescent materials and devices*, edited by S. Miyata and H. S. Nalwa, Gordon and Breach Publishers (1997).
- [3] *Polymeric and organic electronic materials and applications*, edited by A. J. Epstein and Y. Yang, *MRS Bulletin* **22**(6), 13 (1997).

- [4] A. Curioni, W. Andreoni, R. Treusch, F. J. Himpsel, E. Haskal, P. Seidler, C. Heske, S. Kakar, T. van Buuren, and L. J. Terminello, *Appl. Phys. Lett.* **72**, 1575 (1998).
- [5] V. E. Choong, Y. Park, B. R. Hsieh, and Y. Gao, *J. Phys.* **D30**, 1421 (1997).
- [6] V. E. Choong, Y. Park, Y. Gao, M. G. Mason, and C. W. Tang, *J. Vac. Sci. Technol. A* **18**, 1838 (1998).
- [7] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [8] J. W. Lee, T. H. Kim, S. H. Kim, and S. T. Kim, *J. Surf. Anal.* **6**, 66 (1999).
- [9] Cerius² User's Reference, Molecular Simulations Inc.
- [10] G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, John Wiley & Sons (1992).
- [11] T. L. Barr, *Modern ESCA: The Principles and Practice of X-Ray Photoelectron Spectroscopy*, CRC Press (1994).
- [12] C. Enkvist, S. Lunell, and S. Svensson, *Chem. Phys.* **214**, 123 (1997).
- [13] M. C. Petty, M. R. Bryce, and D. Bloor, *An Introduction to Molecular Electronics*, Edward Arnold (1995).