

Unoccupied States of Tris-(8-hydroxyquinolate)-aluminum

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Tris-8-hydroxyquinolate-aluminum (Alq_3) is one of the key materials used in OLED's because of its excellent electron transport and light emitting properties.¹ For the understanding of these properties, the knowledge about occupied and unoccupied states is essential. In this report, the lowest unoccupied states of Alq_3 were probed by near-edge x-ray absorption fine structure (NEXAFS). The experimental results were compared with theoretical calculated unoccupied orbitals.

Thin films of Alq_3 were evaporated on Se-passivated n -GaAs(100) by organic molecular beam deposition (OMBD). The substrates were prepared by annealing to remove an As-cap, followed by an exposure to Se at a sample temperature of 400°C. This leads to a 2×1 reconstructed LEED pattern. Onto these GaAs(100):Se- 2×1 surfaces Alq_3 was deposited with a deposition rate of 1nm/min. During the deposition the substrate was kept at room temperature. At this temperature Alq_3 is likely to form an amorphous film. The fine structure in C-K, N-K, and O-K absorption edges was measured using the VLS-PGM monochromator at BESSY II. The energy scale and the resolution were calibrated using the $1s \rightarrow \pi^*$ absorption edge of nitrogen gas. The spectra were recorded in total electron yield (TEY) mode.

Figure 1 shows the NEXAFS spectra of the C, O, and N K-shell absorption taken at different angles of the incident photon beam relative to the sample surface normal. The spectra are characterized by the features corresponding to the excitation of

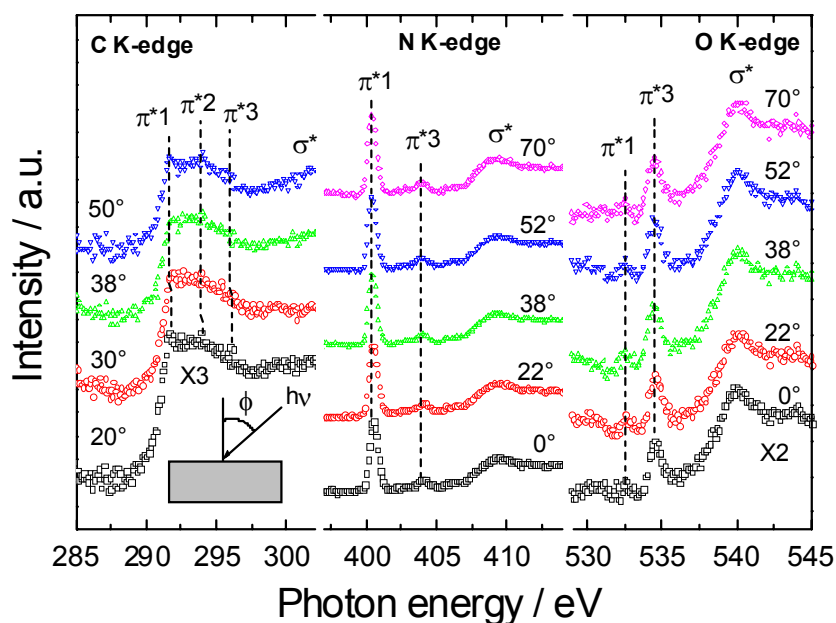


Figure 1. NEXAFS spectra of the Alq_3 film on GaAs(100):Se- 2×1

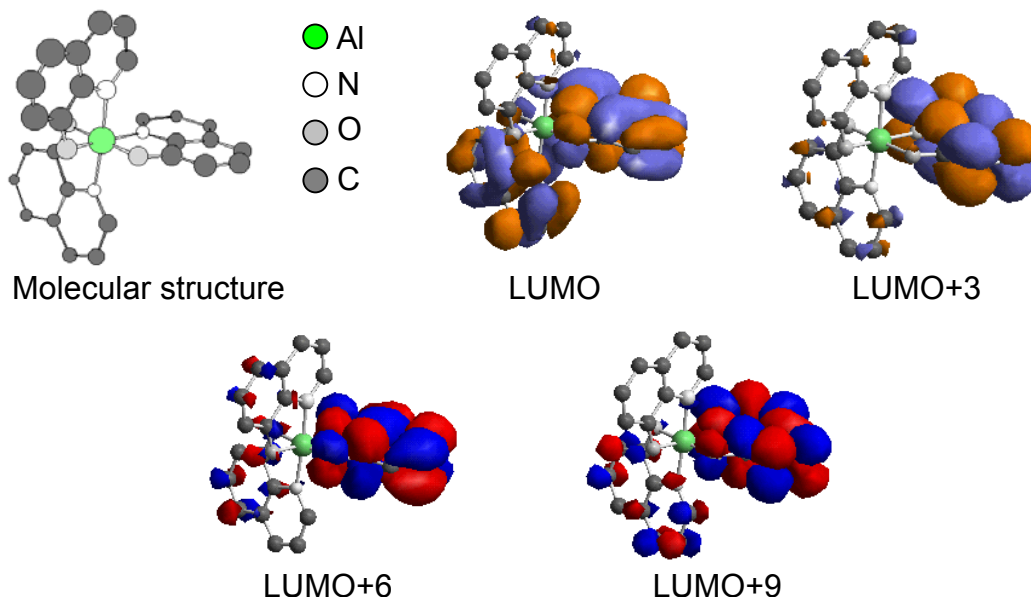


Figure 2. Molecular orbital surface of Alq₃ molecule corresponding to π^* resonance. Only one of each set of triplets is shown, e.g. LUMO+1 and LUMO+2 have the same orbital character as LUMO but the molecular orbital is distributed on two other ligands. The same holds for LUMO+3, LUMO+6, and LUMO+9.

localized 1s core level electron into unoccupied π^* orbitals below the ionization potential (IP) of each 1s core level, followed by broad features corresponding to σ^* resonances. In C K-edge spectra three peaks can be distinguished at 291.6, 294.0, and 298.8 (π^*1 , π^*2 , π^*3) leading to quite broad features, while the excitation from nitrogen and oxygen atoms shows narrow peaks, namely at 400.5 and 404.0 eV (π^*1 , π^*3) for N-edge and 532.5 and 534.5 eV (π^*1 , π^*3) for O-edge spectra. The narrow character of the peaks corresponding to N and O-K edge can be accounted for by the fact that the three N and O atoms in an Alq₃ molecule are chemically equivalent while for C K-edge the different chemical environments induce splitting of the core levels resulting in a more complex lineshape. For all absorption edges, no angular dependence is observed. This is understandable because of the isotropic characteristics of the Alq₃ molecular structures.

For a better understanding of NEXAFS results calculations of the molecular electronic structure were performed. Geometry optimization was performed for the meridional isomer using Gaussian'98 Software with the B3LYP method on the STO-3G level of approximation. The molecular orbital surfaces corresponding to π^* resonance are presented in Figure 2. The calculated molecular orbitals can be grouped according to the same orbital character on each of the three ligands. In the figure, only one of each molecular orbital sets is shown. The energy positions of the calculated molecular orbitals relative to that of LUMO is presented in Table 1. The observation of four LUMO sets corresponding to π^* resonances agrees well with the previous calculation using density functional theory by Curioni *et al.*² From the energy separation of each orbital set, it can be seen that each of the π^* resonance peak corresponds to a set of molecular orbitals. Discrepancy is also observed in that for the O K-edge the energy separation of ~ 3 eV between two sets of molecular orbitals (LUMO, LUMO+6) having the contribution of O atoms is slightly larger than the energy distance of 2.3 eV between π^*1 and π^*3 . This may be caused by the core

Table 1. Calculated energy positions (eV) of the molecular orbital relative to the LUMO. The corresponding π^* resonances are also included.

LUMO	0	LUMO+1	0.2	LUMO+2	0.22	π^*1
LUMO+3	1.42	LUMO+4	1.58	LUMO+5	1.68	π^*2
LUMO+6	2.96	LUMO+7	3.10	LUMO+8	3.24	π^*3
LUMO+9	4.32	LUMO+10	4.48	LUMO+11	4.58	π^*3

hole effect of the NEXAFS spectra which is not considered in the molecular orbital calculation. A main feature of all unoccupied states is that the molecular orbitals are distributed on the quinolate ligand side groups while the contribution of the central Al atom is vanishingly small. For the LUMO the molecular orbitals are mainly localized on C and N atoms, thus the pyridyl side of the molecule. This agrees well with the NEXAFS spectra in that the C and N K-edge spectra show relatively strong π^*1 resonance peaks while only a weak peak is observed in the O K-edge spectra. The LUMO+3 corresponding to the π^*2 resonance are mostly contributed by C atoms while the molecular orbital of LUMO+6 and LUMO+9 are distributed over all of the quinolate part of the molecule. Accordingly π^*3 resonance corresponding to the LUMO+6 and LUMO+9 sets are observed in all K-edge spectra.

In this report, the NEXAFS spectra of the Alq₃ film on GaAs(100):Se-2×1 are compared with the calculated molecular orbital surfaces using B3LYP method on the STO-3G level of approximation. The contribution of each atom in the molecule to the molecular orbitals agrees very well with the NEXAFS spectra while a discrepancy of the energy position is assigned to the excited nature of the molecules in the NEXAFS spectra. From the angular dependent measurements the isotropic character of the Alq₃ film is also confirmed.

¹ C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51** (1987) 913.

² 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** (1998) 1575