Soft X-ray Excited Luminescence and Optical X-ray Absorption Fine Structures of Tris (8-Hydroxyquinoline) Aluminum at the Al K Edge

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Introduction

Tris (8-hydroxyquinoline) aluminum (Alq_3), has been the foundation for small molecule organic light-emitting device (OLED) research since the report of Tang and Van Slyke.[1] Its application in OLED technology has led to the development of a new generation of flat-panel display devices.[2-3] In Alq_3 (Fig. 1), the moiety responsible for the luminescence is the chelating anion.[4-6] Here we report a study of Alq_3 using soft x-ray excited optical luminescence (XEOL)[7] and x-ray absorption fine structure (XAFS) at the Al K edge.

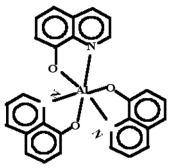

FIG. 1. Scematic drawing of Alq_3.

It was proposed that the biradical recombination of the anionic (Alq_3^-) and the cationic radicals of Alq_3 or hole transport layer results in an excited state, Alq_3* [hole in the highest occupied molecular orbital (HOMO), electron in the lowest unoccupied molecular orbital (LUMO)], which produces the luminescence.[3] UV-excited luminescence produces essentially the same results, indicating a singlet exciton formation mechanism in both cases.[8]

XEOL arises from the de-excitation of a photoabsorption process that results in the formation of thermalized holes and electrons, respectively, in the valence band/HOMO and the conduction band/LUMO. The radiative recombination of electrons and holes produces luminescence.[7-10] When the excitation photon energy changes from just below to just above the edge, the absorption and decay dynamics change abruptly, and the atoms of interest will absorb a larger fraction of the incoming photons. In a many-body picture, the result is a new core hole (a channel not accessible at energies below the edge), and electron(s)/hole(s) in the vicinity of the molecule. Resonant excitation in the near edge region can produce holes in the HOMO, HOMO-1, etc., and electrons in the LUMO, LUMO+1, etc., locally through Auger decay. The end result is similar to the formation of Alq_3* in the electroluminescence process, but there will be more populated channels than electro- and UV excitation. This mechanism is unique for resonant excitation where the excitation of the core electron and the associated core-hole decay (Auger and fluorescence) must be viewed as a concerted process, a phenomenon known as resonant x-ray Raman (RXR).[11]

Results and Discussion

The Al K-edge measurements were made at the SRI-CAT 2-ID-C spherical grating monochromator beamline.[12] The photoluminescence was recorded with a J-Y H-100 optical monochromator equipped with a Hamamatsu R943-02 photomultiplier tube (PMT), which has a nearly flat response from ~290-850 nm. X-ray absorption near-edge structures (XANES) were monitored simultaneously by total electron yield (TEY), fluorescence yield (FLY), and photoluminescence yield (PLY).

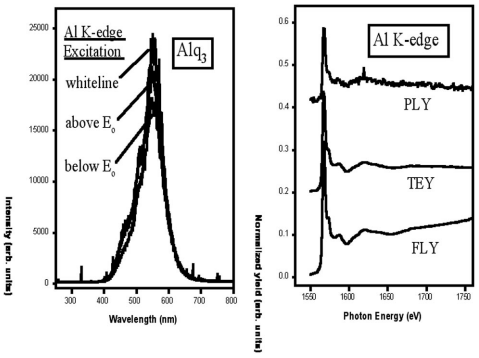

FIG. 2. XEOL (left panel) and Al K-edge XANES (right panel) of Alq_3.

Figure 2 shows the XEOL excited with energies above and below the Al K edge, and the Al K-edge XAFS recorded in TEY, FLY, and PLY. The luminescence below and above the edge shows that there are high-energy (shorter wavelength) shoulders not seen in UV excitation. The shoulders are enhanced with excitation at and above the edge indicating that there are more channels that get populated for conduction band-valence band recombination. The Al valence electrons are not directly involved in the luminescence process since there is no occupied densities of states of Al character for a nominally 3^+ ion. When the excitation energy is below the Al K edge, the luminescence is induced by the excitation of the lower Z elements, especially carbon. At photon energies above the edge, a larger fraction of the photon flux will be absorbed by Al. This produces energetic Auger electrons and subsequently thermalized electrons and holes (ligand). The end result is that the PLY XAFS follows that of the TEY and FLY. This result has been used together with low-energy results (at the K edge of the low-Z elements) to illustrate site selectivity.[13] This technique can beapplied to the characterization of OLED device.

Acknowledgments

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