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Soft x-ray-excited luminescence and optical x-ray absorption fine structures of tris (8-hydroxyquinoline) aluminum

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Photoluminescence from tris (8-hydroxyquinoline) aluminum (Alq_3) films has been observed using tunable soft x rays as an excitation source. The photons were tuned to energies above and below the K absorption edges of C, N, O, and Al. The luminescence was in turn used to monitor the absorption. It was found that the luminescence induced by soft x ray exhibits additional emission bands at shorter wavelengths compared to ultraviolet excitation. While all K edges exhibit optical x-ray absorption fine structures (XAFS) similar to those of total electron and fluorescence yield, the optical XAFS at the C K -edge resonance are enhanced for the $\text{C}1s$ to π^* transitions, indicating site specificity. These observations are attributed to the energetics of the process and the local electronic structure. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358360]

Tris (8-hydroxyquinoline) aluminum (Alq_3), a chiral compound with three chelating 8-hydroxyquinoline anions (henceforth denoted q , see Fig. 1) bonded to an aluminum ion Al^{3+} , has been the foundation for small-molecule organic light-emitting device (OLED) research.¹ Alq_3 is a green phosphor with high-luminescence efficiency and luminosity. Its application in OLED technology has led to the development of a new generation of flat-panel display devices.² It is not surprising that there have been extensive studies³⁻⁷ of the electronic structure and optical properties of Alq_3 . Here, we report another study of Alq_3 using soft x-ray-excited optical luminescence (XEOL) and x-ray absorption fine structure (XAFS).⁸⁻¹¹ The electronic structure of Alq_3 ,⁴⁻⁶ in turn, provides an opportunity to understand the origin of site specificity in XEOL in the soft x-ray region.¹²

In Alq_3 , the Al^{3+} ion stabilizes the molecular orbitals of the q anion via interaction between the metal ion and the oxygen that carries most of the negative charge of the ligand.⁴ The nitrogen-aluminum interaction is relatively weak. The moiety responsible for the luminescence is the anion of which the highest occupied molecular orbital (HOMO) is of primarily C and O character (the phenoxide ring), while the lowest unoccupied molecular orbital (LUMO) is largely on the pyridal side.⁴⁻⁶ A typical Alq_3 OLED device has an Alq_3 layer and an organic hole-transport (HT) layer sandwiched by a low-work-function cathode, and an optically transparent anode.¹ When a voltage is applied, hole transport to Alq_3 takes place at the organic

interface creating Alq_3^+ radicals. It was proposed that the biradical recombination of the anionic (Alq_3^-) and the cationic radicals of Alq_3 or the HT layer results in an excited state, Alq_3^* (hole in the HOMO, electron in the LUMO), which produces the luminescence. UV-excited luminescence produces essentially the same results, indicating a singlet exciton formation mechanism in both cases.¹³

XEOL arises from the de-excitation of a photoabsorption process. The absorption and the decay of the core holes lead to the production of photoelectrons, Auger electrons, and fluorescence photons. In solids, these processes and the associated secondary processes result 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.¹³ It has been observed that XEOL is often site selective when the excitation energy is tuned to an absorp-

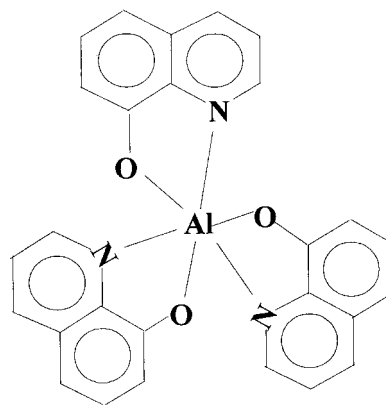


FIG. 1. Schematic drawing of Alq_3 .

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tion edge, although spectral features identical to the absorption cannot always be obtained.^{8–12,14} When the excitation photon energy changes from just below to just above the edge (e.g., at a white-line resonance), 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, with or without participation of the electron originally excited. The end result is similar to the formation of Alq_3^* in the electroluminescence process but there will be more channels than excitation with UV light. 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 scattering (RXRS).¹⁵ Thus, excitation with a photon energy tuned to an absorption-edge resonance is localized and would favor site-specific luminescence when the holes and electrons thus produced are in the relevant molecular orbitals (chromophore) responsible for the luminescence.

The Alq_3 sample in high purity was obtained commercially from Aldrich. Alq_3 specimens were prepared by evaporation from a Ta evaporator heated resistively in a vacuum chamber onto a *p*-type Si(100) wafer. The evaporation rate and dosage were monitored with a UTI quadropole mass spectrometer. A typical thickness of hundreds of nm was obtained. In all cases, the thickness of the film was significantly larger than the one-absorption length (63% absorption) of C, N, and O at their *K* edges, resulting in total absorption conditions for the experiments. The measurements of the C, N, and O *K* edges of Alq_3 were carried out at the spherical grating monochromator (SGM) beamline¹⁶ of the Canadian Synchrotron Radiation Facility (CSR) at the Synchrotron Radiation Center, University of Wisconsin–Madison (Aladdin). The Al *K*-edge measurements were made at the SRI-CAT 2-ID-C SGM beamline¹⁷ at the advanced photon source (APS) at Argonne National Laboratory. The photoluminescence was recorded with a J-Y H-100 optical monochromator equipped with a Hamamatsu R943-02 photomultiplier tube (PMT). X-ray absorption near-edge structures (XANES) were monitored simultaneously by total electron yield (TEY), fluorescence yield (FLY), and photoluminescence yield (PLY). A Ti filter was used to remove high-order light at the C *K* edge. All the yields were normalized to an appropriate light curve.

Figure 2 shows the normalized XEOL of Alq_3 obtained with selected excitation energies ranging from 275 eV (below the C *K* edge) to 560 eV (above the O *K* edge). It is interesting to note that all spectra exhibit a two-peak pattern. This observation differs somewhat from the UV-excited luminescence and electroluminescence which often appear as a broad peak at ~ 530 nm (with a short wavelength shoulder).³ The separation of the two optical bands is ~ 0.2 eV, in good accord with the notion of electron–hole recombination: the calculated values of ~ 0.13 eV between HOMO and HOMO–1 and ~ 0.04 eV between LUMO and LUMO+1

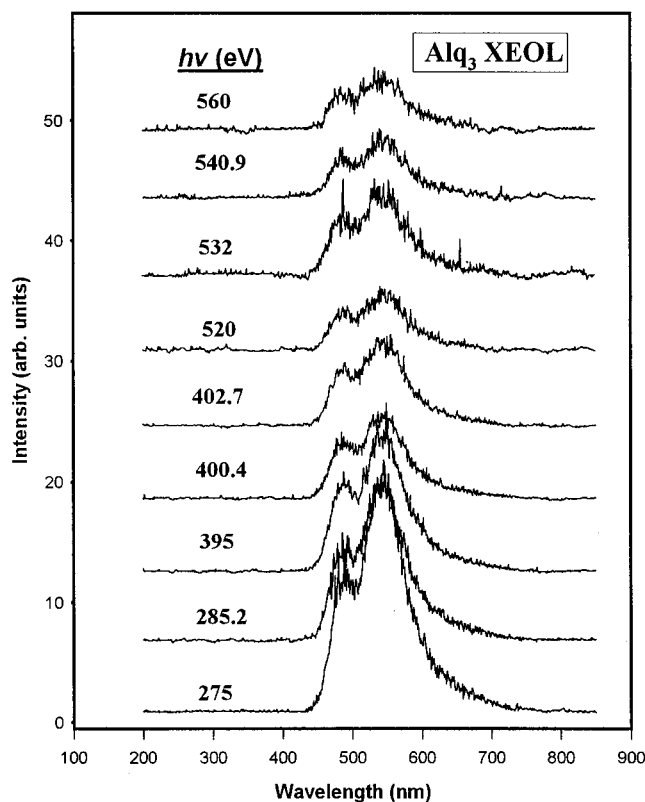


FIG. 2. XEOL excited with selected photon energies from 275 to 560 eV.

(Ref. 4) suggest that the HOMO triplets (from all three ligands) are involved in the luminescence. Figure 2 also shows that the luminescence is most intense when the excitation is tuned to the carbon *K* edge. This is expected since a majority of the atoms in the molecule are carbon.

The C, N, and O XANES spectra are shown in Fig. 3, where several interesting features are apparent. First, all yields exhibit essentially the same spectral patterns at all edges, in good agreement with recent observations.^{5,6} The resonances just above the C *K* edge are associated with transitions from the core (*1s*) to LUMO and LUMO+1, etc., which contain a significant contribution of the absorbing atoms to the unoccupied molecular orbital. The resonance at ~ 400.4 eV is the *1s* to π^* transition localized at the N site. As pointed out recently,^{5,6} carbon exhibits a more complex *K*-edge XANES because the C *1s* binding energy in the molecule varies. Each carbon contributes differently to the unoccupied densities of states depending upon where it is on the phenoxide or pyridal ring.¹⁸ We attribute the first two sharp resonances at the C *K* edge to *1s* to π^* transitions from the aromatic carbons, especially those farthest away from the N and O.⁶ These features are enhanced noticeably in the PLY in relation to the intensities of the other C *K*-edge XANES features. Since these transitions arise from the *1s* to π^* transition from the aromatic carbons, the LUMO is directly populated by the transition, and associated Auger decay populates the HOMO holes. Thus, we argue that in the absence of strong secondary events and countervailing arguments, these transitions will produce enhanced luminescence, hence, some degree of site specificity. A similar behavior, albeit less dramatic, is also seen at the N *K*-edge π^* resonance.

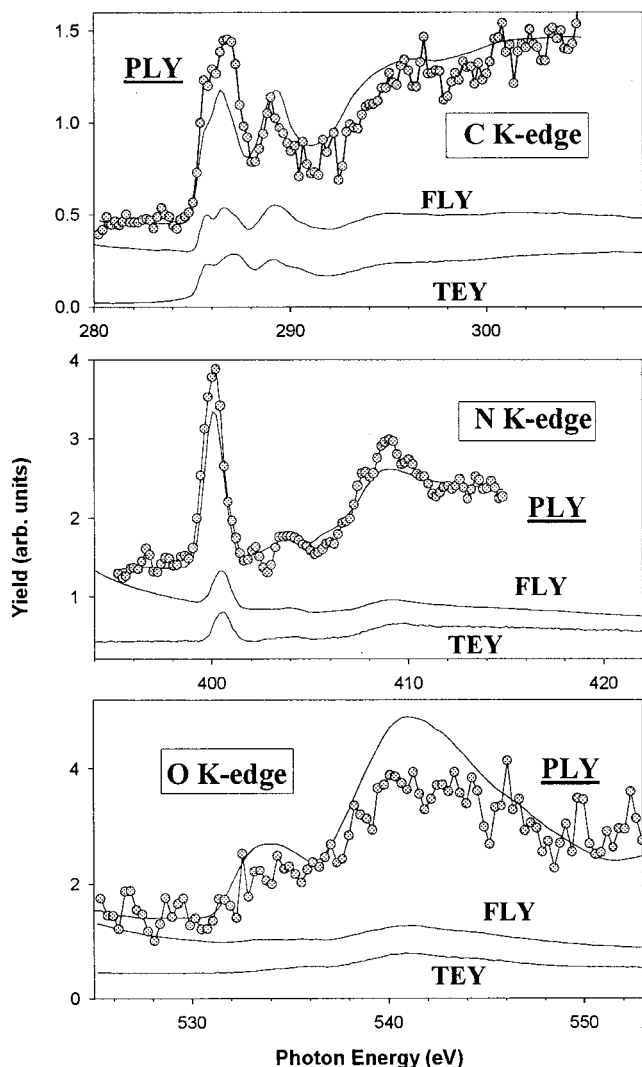


FIG. 3. TEY, FLY, and PLY (total) XANES at the C, N, and O K edges of Alq_3 . Normalized PLY and TEY are compared in some details.

Figure 4 shows the XEOL excited with energies above and below the Al K edge and the Al K -edge XAFS. The Al valence electrons are not involved in the luminescence process (Al is nominally a 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 large fraction of the pho-

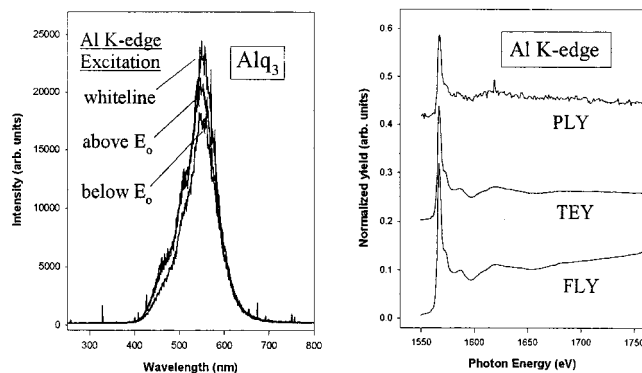


FIG. 4. XEOL (left panel) and Al K -edge XANES (right panel) of Alq_3 in TEY, FLY, and PLY.

ton flux will be absorbed by the Al. This produces energetic Auger electrons and subsequently thermalized electrons and holes (ligand). Thus the PLY XAFS follows that of the TEY and FLY.

As noted above, Fig. 3 shows enhanced optical response following C K -edge $1s$ to π^* absorption. We reiterate that this indicates that the excitation process and the associated decay localized at the C sites farthest away from O and N are coupled effectively to the luminescence. This can be understood in terms of the effectiveness of the C K -edge $1s$ to π^* excitation in creating holes in the HOMO and HOMO-1, and electrons in the LUMO, and LUMO+1. When the atom was not directly connected to or contributed very little to the chromophore in the π ring, no enhancement was observed, as was the case for aluminum and oxygen.

In summary, we have reported excitation-energy-dependent photoluminescence associated with the energy of x rays and the C localized excitation-enhanced luminescence. The results indicate site specificity in terms of the projected densities of states of elements in relevant molecular orbitals. It should also be noted that this technique could be applied to the characterization of actual OLED devices.

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