

X-ray Excited Optical Luminescence Studies of Tris-(2,2'-bipyridine)ruthenium(II) at the C, N K-edge and Ru L_{3,2}-edge

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Tris-(2,2'-bipyridine)ruthenium(II), Ru(bpy)₃²⁺, is a prototype for transition metal-based photosensitization, charge separation, and photoinduced electron-transfer chemistry.^{1–9} Its luminescence has been intensively studied since Paris and Brandt assigned the optical transition to a metal-to-ligand charge transfer (MLCT).¹ The lowest excited state is the localized triplet MLCT state which has a high quantum yield, long lifetime, and strong photochemical stability.^{1–9} These properties led to the application of Ru(bpy)₃²⁺ in many photoprocesses and more recently in organic light-emitting diode (OLED).^{10,11} Despite intensive research, the electronic structure and the optical properties of this compound are still not fully understood.¹² We have chosen this complex to study the site and excitation channel specificity of X-ray excited optical luminescence (XEOL),¹³ which has already shown some promises in the characterization of quantum-confined nanostructures,¹³ and OLED materials and devices.^{14,15}

While UV–visible excites an electron from an occupied to an unoccupied molecular orbital (e.g., HOMO–LUMO), tunable X-rays from a synchrotron light source can induce site-selective excitation when the excitation photon is scanned across an absorption edge.¹³ An absorption edge arises from the excitation of a core electron from an atomic orbital (AO) into the lowest unoccupied electronic states (e.g., LUMO in molecules and the bottom of the conduction band in semiconductors). In Ru(bpy)₃²⁺,

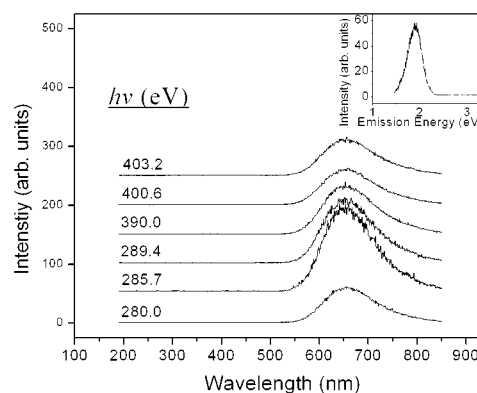


Figure 1. XEOL of Ru(bpy)₃(ClO₄)₂ at selected excitation energies.

this AO-to-MO excitation channel at the carbon atom, for example, turns on when the photon energy is scanned across the C K-edge, exciting a 1s electron into unoccupied bound, quasi-bound, and continuum states. This process, the associated Auger decay, and secondary events involving inelastic scattering of electrons produce holes in the valence band/HOMO, HOMO – 1, and so forth and electrons in the conduction band/LUMO, LUMO + 1, and so forth. The radiative recombination of holes and electrons produces luminescence. The XEOL technique can be site-specific and excitation-channel-specific when the excitation energy is tuned to the absorption edge of the element of which the local electronic structure is effectively coupled to the luminescence channel.^{13–15}

Ru(bpy)₃(ClO₄)₂ was obtained commercially (Strem). The specimen was prepared as a fine powder film. The C and N K- and Ru L_{3,2}-edge were recorded at the spherical grating monochromator (SGM) beamline and the double crystal monochromator (DCM) beamline, respectively, of the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center, University of Wisconsin-Madison. The optical photons were recorded with a J-YH100 monochromator.^{14,15} X-ray absorption near edge structures (XANES) were recorded simultaneously by total electron yield (TEY), fluorescence yield (FLY), and photoluminescence yield (PLY). FLY detects the fluorescence X-rays from the radiative decay of the core hole using a channel plate detector,¹⁶ while PLY detects optical photons in a total yield (zero-order) mode or at a selected wavelength. In general, TEY is sensitive to the surface and the near surface region of the film, while FLY and PLY are bulk sensitive; this is particularly the case with soft X-rays.^{14,15} All spectra were normalized to an appropriate light curve.¹⁷

Figure 1 shows the normalized XEOL obtained with selected excitation energies ranging from 280 eV (below the C K-edge) to 403.2 eV (above the N K-edge).¹⁷ All spectra exhibit a broad peak at 655 nm, in excellent agreement with the OLED electroluminescence reported by Gao and Bard.¹¹ The invariance of the spectral profile indicates that the origin of the luminescence is the same: recombination of electrons in LUMO, LUMO + 1, and so forth and holes in Ru-based HOMO, HOMO – 1, and so forth. The C and N K-edge XANES in TEY, FLY, and PLY are shown in Figure 2. The two peaks at 285.7 and 286.5 eV in Figure 2a are 1s-to-π* transitions of nonequivalent carbons on the bipyridine ring.^{15,18,19} The carbon atoms that are not bonded to

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(17) All spectra are normalized to an I₀ curve from a clean HF refreshed Si that has no carbon contamination, a Ni mesh I₀ monitor, and the ring current. This procedure removes contribution from the carbon contamination on the optics.

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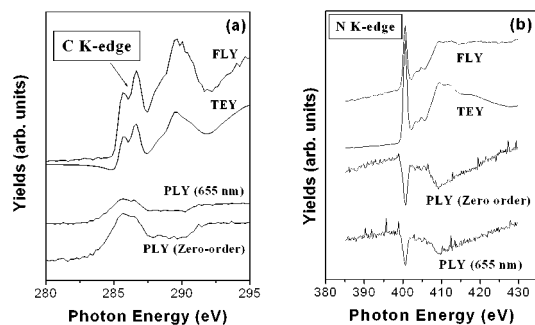


Figure 2. (a) C K-edge, and (b) N K-edge XANES in TEY, FLY, and PLY

the electronegative N directly are less tightly bound, in good accord with the results of tris-(8-hydroxyquinolate)aluminum(III).^{15,19} The Ru $M_{5,4}$ -edge ($3d_{5/2,3/2}$ to Ru 4p transition) are at ~ 280 and 284 eV, respectively, but not noticeable in TEY and FLY due to a smaller edge jump and absorption cross-section relative to carbon. From Figure 2a, we see that both zero-order and 655 nm PLY are similar as expected from a single emission profile. The PLY exhibits two interesting features. First, relative to TEY, the first resonance is tailing toward lower energy and is more intense than the second. This is attributed to a combination of the PLY of the Ru M_4 edge just below the C K-edge and a higher quantum yield of the C absorption. A Ru AO-MO transition facilitates the production of Ru holes in the valence band, hence, the luminescence. Second, and perhaps more dramatic, is the suppression of the broad resonance at ~ 289 eV. This feature is associated with the transition from C 1s to σ^* quasi bound states where the electron can tunnel out into the continuum suppressing luminescence. This observation validates that XEOL can be site and excitation channel specific.¹³⁻¹⁵

Figure 2b shows the XANES of the N K-edge. Both TEY and FLY show an intense $1s$ -to- π^* resonance at 400.6 eV, while the PLY is inverted. Inversion in PLY is not uncommon in soft X-ray optical XANES when the specimen is thick (total absorption) as is the case here in the 280 – 430 eV region, and all the elements are competing for the incoming photons.²⁰ It should be noted that the increase in absorption coefficients from below to above the N K-edge is large for N but negligible for C, while the total number of photons is essentially the same. Thus, there is an abrupt change in the distribution of the photons absorbed by N and the rest of the system (mostly carbon) across the N K-edge. A negative edge jump implies that N is less effective (smaller quantum yield) than C in producing luminescence per photon absorbed. In addition, the probing depth of PLY decreases above the N edge for a thick sample, resulting in a decrease in the number of more effective luminescent sites (carbon) per photon absorbed,¹⁵ facilitating an inversion.²⁰

Figure 3 shows the Ru $L_{3,2}$ -edge XANES. Absorption for C and N is smaller ($\sim 10^2$ cm²/g) at these energies than at their

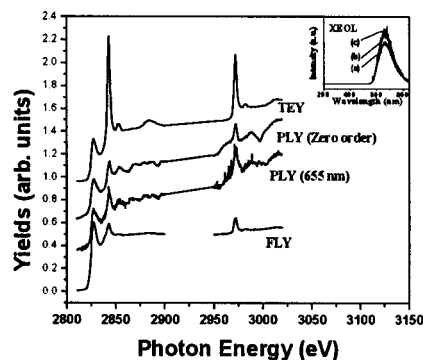


Figure 3. Ru $L_{3,2}$ -edge XANES in TEY, FLY, and PLY. (Inset) XEOL with excitation energy (a) below, (b) above, and (c) Ru L_3 -edge whiteline.

K-edge ($\sim 5 \times 10^4$ cm²/g).²¹ Thus, not all of the incoming photons are absorbed by the Ru(bpy)₃(ClO₄)₂ film. The peak at 2827.5 eV is the Cl K-edge from the ClO₄⁻. Both FLY and PLY exhibit all Ru XANES features in TEY. The Cl contribution at the Ru L_3 -edge is nearly flat and has little effect on the Ru spectrum. The intense Ru L_3 whiteline (WL) at 2842.2 eV arises from Ru $2p_{3/2}$ to $3d$ (e_g) transition; the corresponding L_2 -edge WL is at ~ 2973 eV.²² The Cl K-edge is more intense than that of Ru L_3 -edge in the FLY due to a more efficient Cl (K-shell) fluorescence channel. The secondary process for the decay of the Cl core hole can lead to the formation of holes and electrons in the HOMO and LUMO, respectively, in Ru(bpy)₃²⁺, resulting in PLY at the Cl K-edge. Similar Ru L-edge XANES was also observed in Ru-(bpy)₃(PF₆)₂ with the absence of the Cl K-edge. A detailed report of the XEOL of these two compounds will be published elsewhere. The inset in Figure 3 shows the XEOL at excitation energies near the Ru L_3 -edge. When the excitation energy is below the Ru L_3 -edge, for example, at 2800 eV, the luminescence is induced by the excitation of primarily C, and to a lesser extent, the rest of the molecule. At the Ru L_3 -edge, Ru absorbs a larger fraction of the photon flux (absorption above and below the edge: $\sim 5 \times 10^4$ and $\sim 1.6 \times 10^4$ cm²/g, respectively),²¹ and PLY follows.

We have used XEOL in conjunction with the XANES to study the optical property of Ru(bpy)₃(ClO₄)₂. The significance of the finding is that C and Ru localized excitation enhances PLY and N does not. The implication is that site and excitation specificity can be observed. This technique can be used to analyze OLED materials and devices.

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