

X-Ray Excited Optical Luminescence from $\text{Ru}(\text{bipy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ in the Energy and Time Domains

Simone Lam¹, Franziskus Heigl¹, P.-S. Grace Kim¹, T.K. Sham¹, Robert A. Gordon², Dale Brewe², Tom Regier³, Ian Coulthard³ and Robert I. R. Blyth³

¹ Department of Chemistry, University of Western Ontario, London Ontario Canada N6A 5B7,

² PNC-CAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL USA,

³ Canadian Light Source, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0X4

Abstract. Recent observations of XEOL (X-ray Excited Optical Luminescence) from prototype Ru(II) complexes with excitation energies at various absorption edges of Ru, C and N, and corresponding optical XAFS (photoluminescence yield) are reported. Time-resolved XEOL using the synchrotron light pulse from the Advanced Photon Source in top-up mode and the Canadian Light Source operating in single bunch mode are also noted. These results are discussed in terms of the electronic structures of the complexes, spin-orbit coupling and radiative decay dynamics of the systems.

Keywords: XEOL, Synchrotron Radiation, Ru(II) complexes, time-resolved, optical EXAFS

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INTRODUCTION

The strong interaction between organic ligands and metal ions creates unique properties for applications in electroluminescence, solar energy conversion, sensors and nonlinear optics [1]. Ru(II) complexes with nitrogen containing ligands are mostly studied due to their rich photophysical and redox properties [2].

Tris-(2,2-bipyridine)ruthenium, $\text{Ru}(\text{bipy})_3^{2+}$, and tris-(1,10-phenanthroline)ruthenium, $\text{Ru}(\text{phen})_3^{2+}$, an analogue of $\text{Ru}(\text{bpy})_3^{2+}$, are involved in many photo processes in addition to being triplet emitters in organic light emitting diode [3,4]. In its 2+ oxidation state, Ru adopts a low spin $4d^6$ configuration, in which the t_{2g} d orbitals are doubly occupied and the e_g orbitals are empty. The ligand field around the Ru ion shows a quasi-octahedral symmetry (Fig.1).

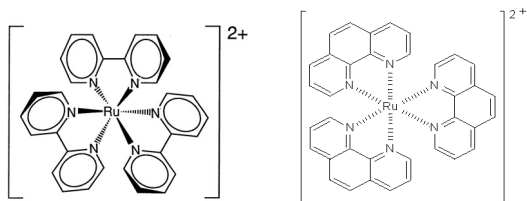


FIGURE. 1. Molecular structure of $\text{Ru}(\text{bipy})_3^{2+}$ (left) and $\text{Ru}(\text{phen})_3^{2+}$ (right).

Both Ru(II) complexes involve π -bonding and π^* -antibonding orbitals located on the ligands, and t_{2g} and e_g orbitals from Ru 4d. In the ground state, only π and t_{2g} orbitals are filled [5]. Upon photoexcitation, there are three typical transitions: (1) t_{2g} to e_g , d-d transition, which is forbidden (2) π - π^* transition which is localized on the ligands and appears in the UV; and (3) metal-to-ligand charge transfer (MLCT) from metal d to π^* located in the ligands. The reason that MLCT luminescence is observed as the most intense transition instead of π , π^* lies in the interaction between the metal d (large spin-orbit splitting) and ligand π orbitals, resulting in a significant mixing between singlet and triplet states and an effective intersystem crossing. The emission is considered to be from the spin-orbital states rather than from a single triplet state.

In $\text{Ru}(\text{bipy})_3^{2+}$, it has been shown that optical absorption in the visible [6] populates the singlet metal-to-ligand charge-transfer ($^1\text{MLCT}$) excited states, which rapidly decays by intersystem crossing [7] to the lowest lying MLCT triplet state ($^3\text{MLCT}$). These ($^3\text{MLCT}$) excited states include three nearly degenerate triplet states as well as fourth one, slightly higher in energy [8]. In the excited states of $\text{Ru}(\text{bipy})_3^{2+}$, it is known that the transferred electron is localized on one of the 'bipy' ligands, rather than

delocalized over all three [9]. In this work we report X-ray Excited Optical Luminescence (XEOL) [10] and Time-Resolved X-ray Optical Luminescence (TRXEOL) [11,12] of these complexes at various excitation energies.

EXPERIMENTAL

$\text{Ru}(\text{bipy})_3^{2+}$ and $\text{Ru}(\text{phen})_3^{2+}$ in the form of perchlorate salt were obtained commercially. Specimens were prepared either on a Si wafer by spin coating or on a carbon tape. Measurements were made with a JY100 monochromator and a Hamamatsu photomultiplier (PMT) at the PNC-XOR bending magnet line of the Advanced Photon Source (APS) operating in top-up mode (153 ns repetition rate), the Al Seya, the HERMON and the DCM beamlines at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison, as well as the SGM beamline of the Canadian Light Source (CLS). Timing experiments were performed at the APS and CLS, the latter with a single bunch (570 ns repetition rate). The experimental setup for timing has been described elsewhere [10,11]. In time-gated experiments, a time window was used for time-resolved XEOL and optical XAFS measurements.

RESULTS AND DISCUSSION

Fig. 2 shows the XEOL from $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bipy})_3^{2+}$ excited with synchrotron UV and soft x-rays, respectively. The UV excited XEOL from $\text{Ru}(\text{phen})_3^{2+}$ shows an asymmetric peak at ~ 610 nm tailing towards longer wavelengths while the XEOL from $\text{Ru}(\text{bipy})_3^{2+}$ exhibits a similar peak at ~ 658 nm. These features arise from the decay of the ($^3\text{MLCT}$) excited states. The blue shift resulting from replacing 'bipy' with 'phen' is attributed to the more extended delocalization in 'phen'. XEOL from $\text{Ru}(\text{bipy})_3^{2+}$ has been reported earlier [13], here we will concentrate on $\text{Ru}(\text{phen})_3^{2+}$.

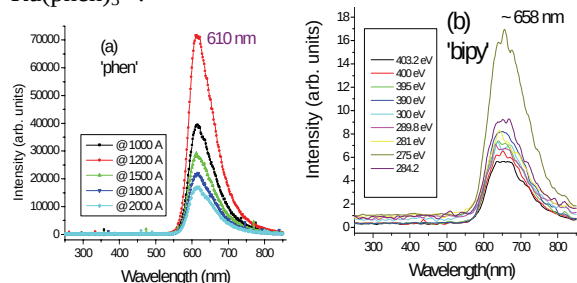


FIGURE 2. XEOL from (a) $\text{Ru}(\text{phen})_3^{2+}$ and (b) $\text{Ru}(\text{bipy})_3^{2+}$ excited with UV (6.2 – 12.4 eV) and soft x-ray (from below the C K-edge to above the N K-edge), respectively.

Fig. 3 (a) shows the XEOL from $\text{Ru}(\text{phen})_3^{2+}$ excited with 500 eV photons and the time-gated

XEOL using the fast (0-50 ns) and slow time window (520 – 570 ns), showing the ($^3\text{MLCT}$) emission as well as that from the ligand in the UV. Fig. 3(b) shows the inverted PLY (photoluminescence yield) at the N K-edge XANES. Similar inversion was observed at the C K-edge PLY XANES (not shown). Fig. 4 shows optical XANES together with FLY (fluorescence yield) of the two Ru complexes at the Ru $L_{3,2}$ -edge. The intense whiteline (~ 2820 eV) just below the Ru $L_{3,2}$ -edge arises from the Cl K-edge of the perchlorate ion. The PLY yield of the Ru is enhanced compared to that of the FLY. Fig. 5 shows the decay curves for the $^3\text{MLCT}$ maximum and the UV luminescence

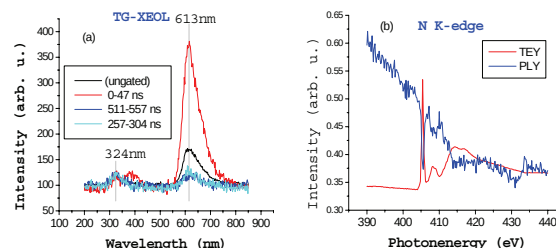


FIGURE 3. (a) XEOL from $\text{Ru}(\text{phen})_3^{2+}$ and (b) N K-edge XANES from photoluminescence yield (PLY) and total electron yield.

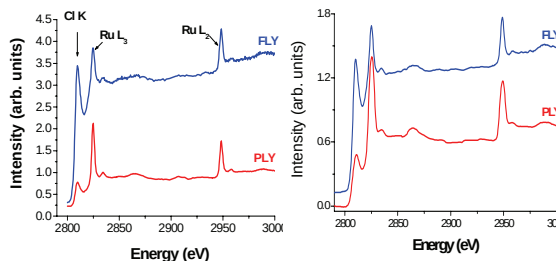


FIGURE 4. Ru $L_{3,2}$ edge XANES of $\text{Ru}(\text{bipy})_3^{2+}$ (left) and $\text{Ru}(\text{phen})_3^{2+}$ (right).

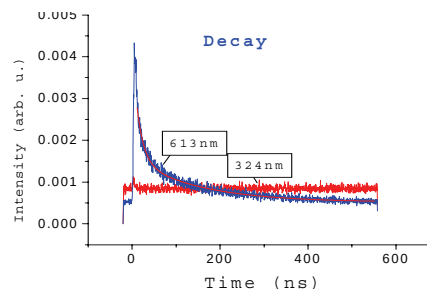


FIGURE 5. Decay curves at 613 nm and 324 nm emission together with a two exponent fit for the 613 nm emission.

Fig. 6 shows the XEOL and the optical XAFS of the $\text{Ru}(\text{phen})_3^{2+}$ complex at the Ru K-edge (~ 22 keV). These are hard x-rays, which has some interesting implications.

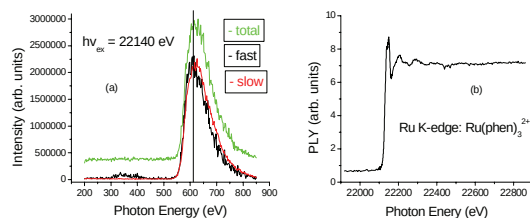


FIGURE 6. (a) time-gated XEOL from Ru(phen)_3^{2+} with a fast (0 -10 ns) and a slow (10 – 150 ns) window. UV emission is noticeable in the fast window. (b) Ru K-edge XAFS (PLY).

From Fig.1, we see that the ‘phen’ ligand has a slightly more delocalized π system, leading to a blue shift in the luminescence relative to ‘bipy’ (Fig. 2). There is no significant change in the spectral pattern as a function of excitation energy from UV to x-rays although the intensity and branching ratio varies somewhat. XEOL and TRXEOL in Fig. 3(a) show the normal $^3\text{MLCT}$ emission as well as emission in the UV region, characteristic of the ligand. Note that the fast decay component enhances the emission at 613 nm, while the slow decay favors the UV emission. This indicates that these two luminescence channels are of different origin. The conventional wisdom [10] suggests that generally the shorter the wavelength the faster the decay. For this not to be the case, the emission must have a different origin. Fig. 3(b) shows the inverted PLY at the N K-edge. Inversion is not uncommon in total absorption situations and is due to either a saturation effect or ineffective coupling and energy transfer of the excitation to the luminescence chromophore. Similar inversion is observed at the C K-edge although normal PLY was observed in a much thinner sample of Ru(bipy)_3^{2+} [13]. At the Ru $L_{3,2}$ -edge (Fig. 4) however, the optical XANES exhibits a normal edge jump indicating that the metal-center excitation enhances the emission chromophore.

Fig. 5 shows the decay curve of the main peak. A two-exponential fit yields a slow time of 149 ns and a fast time of 15.6 ns. The UV emission has a very fast (too fast to be detected with the PMT time resolution of ~ 2 ns) and a very slow ($> \mu\text{s}$) component. Returning to Fig. 3, we can attribute the XEOL from the fast window to ($^3\text{MLCT}$) de-excitation [12]. The UV emission is too weak for a meaningful fitting analysis.

Fig. 6 shows the XEOL and TRXEOL excited at 22140 eV, just above the Ru K-edge where the Ru 1s electron is excited to the LUMO containing Ru 5p character. It is interesting to note that the UV emission is weaker than those excited with soft x-rays (Fig. 3) and is only visible in the fast window. It is not clear why this is the case. We propose two possibilities: first, with 500 eV photons, there are many excitation

channels leading to energy transfer to the radiative de-excitation from the ligand. Second, at the Ru K-edge, Ru abruptly absorbs a large fraction of the incident photons creating a deep Ru core hole; thus all the subsequent decays are of primarily Ru character, which results in a fast, but less effective energy transfer to the ligand chromophore (C and N have very low cross-sections at these energies). More work is needed to resolve this interesting problem.

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