J|A|C|S
COMMUNICATIONS

Time-Resolved X-ray Excited Optical Luminescence from Tris(2-phenyl bipyridine)iridium

Franziskus Heigl,[†,‡] Simone Lam,[†] Tom Regier,[§] Ian Coulthard,[§] and Tsun-Kong Sham*,[†,‡]

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7, Canadian Synchrotron Radiation Facility, Synchrotron Radiation Center, University of Wisconsin–Madison, Stoughton, Wisconsin 53589, and Canadian Light Source, University of Saskatchewan, Saskatoon, Canada S7N 0X4

Received January 12, 2006; E-mail: tsham@uwo.ca

fac-Tris(2-phenyl pyridine)iridium, Ir(ppy)$_3$, has attracted much attention lately in connection with its application in Organic Light Emitting Diode (OLED).[1] The luminescence from Ir(ppy)$_3$ exhibits a peak at ~530 nm with a shoulder at a longer wavelength.[2–5] This green luminescence has been attributed to the decay of the metal-to-ligand charge-transfer singlet state, ^{1}(MLCT), which relaxes to a lower energy triplet state via ^{1}(MLCT) → ^{3}(MLCT) intersystem crossing (enhanced by the spin–orbit coupling). The triplet then returns to the ground state radiatively. Despite the interest, the origin of the luminescence is still not fully understood.[2–9] A recent calculation shows that there is one lowest triplet (2.59 eV) and two slightly higher excited triplets that are very close in energy (2.60 eV).[9] The decay of the luminescence varies greatly depending on the molecular environment.[2–8] It has been reported that luminescence from a neat Ir(ppy)$_3$ film decays fast (nanosecond to 10 ns) due to "self-quenching" (triplet–triplet interaction resulting in a molecule in a higher excited state, which decays nonradiatively and another in the ground state),[2,3] while decays in solution can be as long as microseconds.[4–8]

In this communication, we report a study of the luminescence from Ir(ppy)$_3$ using a synchrotron technique called X-ray excited optical luminescence (XEOL)[10,11] and time-resolved X-ray excited optical luminescence (TRXEOL).[12] XEOL with excitation energy tuned across an absorption edge (element specific) can also be chemical and excitation-channel specific.[10–14] The optical yield, in turn, has been used to monitor the absorption; this technique is sometimes called optical XAFS (X-ray absorption fine structures). Although the mechanism for XEOL is complex for it involves the decay of super-excited states, it is generally realized that a radiative de-excitation channel results from the effective coupling of the super-excited state with the chromophore, producing electron–hole (e–h) pairs (e in the LUMO, h in the HOMO) that recombine radiatively. XEOL from organic light emitting materials has been investigated in a number of studies.[10–15]

The third generation synchrotron provides a desirable time structure for timing studies. The light pulses have subnanosecond duration and hundreds of nanosecond repetition rate. In this work, we measured the decay of the luminescence from Ir(ppy)$_3$ excited by X-ray pulses and the time-gated XEOL (counting photons coming through a selected time window) from a neat Ir(ppy)$_3$ film. The result provides new insight into the origin of the luminescence.

fac-Ir(ppy)$_3$ was obtained commercially (Alfa Aesar, product number 44282), and the specimens were prepared as a neat Ir(ppy)$_3$ film on a Si(100) substrate by spin coating. The luminescence was recorded with a JY-100 monochromator and a Hamamatsu photomultiplier tube (PMT), which has a ~2 ns response.[13] The measurements were made on the SGM beamline at the Canadian Light Source using a single electron bunch (60 ps pulse; 570 ns repetition; 10–15 mA current).[16] Briefly, the PMT signal is used as the start and the synchrotron pulse as the stop. The start is fed to a discriminator and an amplifier. The output signal together with the synchrotron pulse was fed to a TAC (time to amplitude converter). The TAC output with a suitable delay is stored in a MCA (multichannel analyzer). In the time-gated mode, a time window was selected (e.g., 0–10 ns for fast decay and 10–550 ns for slow decay).[12,17]

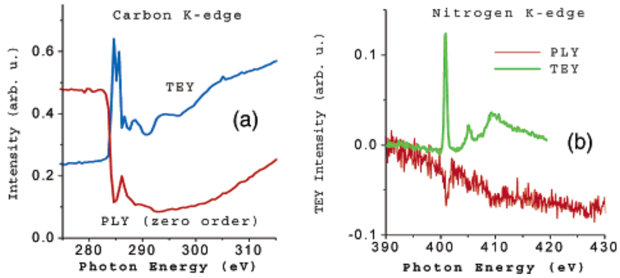

Figure 1. Graphs a and b show the C and N *K*-edge XANES, respectively, in total electron yield (TEY) and photoluminescence yield (PLY).

Figure 1a,b shows the XANES (X-ray Absorption Near Edge Structures) of Ir(ppy)$_3$ at the C and N *K*-edge recorded in TEY (total electron yield) and PLY (luminescence, zero order). The XANES (TEY) exhibits 1s to π^* transitions at ~285 and 286.5 eV from nonequivalent carbons and features at higher energies from 1s to σ^* transitions. The N *K*-edge (TEY) shows a single π^* followed by 1s to σ^* transitions. These observations are consistent with the XANES pattern of systems containing N.[13–15]

Figure 2 displays the luminescence from Ir(ppy)$_3$ excited at 278 eV (top panel), showing a peak at 534 nm and a shoulder at 580 nm as well as a less discernible one at 630 nm, in good agreement with previous findings.[2–8] The spectral feature changes little as the excitation energy is tuned from below the C *K*-edge to above the N *K*-edge, but the intensity (PLY) changes dramatically. Of particular interest is the abrupt decrease of the PLY at the π^* and resonance above the edge, resulting in an inverted XANES (PLY), as seen in Figure 1. PLY inversion occurs when the e–h pair production becomes less efficient across the absorption edge. This can be attributed to a less effective coupling of the excited state (by excitation above the edge) to the luminescence chromophore (triplet) than by excitation below the edge. In X-ray absorption, all the levels (core and valence) accessible by the X-ray will be excited. Below the C *K*-edge, all the shallow levels of carbon, nitrogen, and Ir are excited, producing e–h pairs. At the C *K*-edge π^* resonance, the 1s transition is turned on and the absorption cross-section of C increases abruptly. Since all the elements and all accessible levels are competing for the photons, a decrease in

---

[†] University of Western Ontario.
[‡] Canadian Synchrotron Radiation Facility.
[§] Canadian Light Source.

10.1021/ja060243c CCC: $33.50

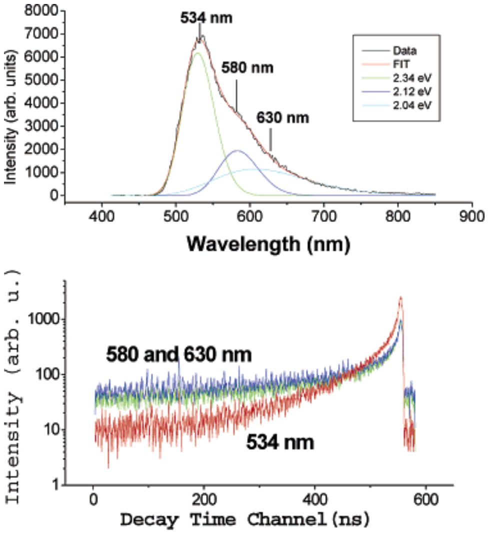

Figure 2. The luminescence spectrum of Ir(ppy)$_3$ excited at 278 eV (top) and decay curves for the three emission bands excited at 430 eV (bottom).

quantum yield of the radiative e−h pairs produced by the resonance produces an inverted XANES in PLY. This behavior in PLY ascribing to the decreasing effectiveness of e−h production across the edge has been studied extensively.[10−15]

The luminescence in Figure 2 is also fitted with three Gaussians at 2.34 (530 nm), 2.12 (585 nm), and 2.04 eV (608 nm), slightly different from the apparent maximum at 534, 580, and 630 nm, respectively, where decay measurements were performed as shown in the bottom panel of Figure 2. The three-peak feature compares favorably with the calculation of Hay,[9] which shows several possible triplet emission bands in this region (2.59−2.60 eV), and with the three triplet sub-state analysis of Finkenzeller and Yersin[6] and Tsuboi et al.[7,8] The latter results suggest that the two short wavelength peaks have higher transition probabilities (partially allowed) than the broad peak (nearly forbidden).

The decay curves (excited at 430 eV, log scale) in Figure 2 show that there are multi-lifetimes. Besides the slow decay, which dominates after the first 100+ ns, there are also some very fast decay components of which the discussion is beyond the scope of this report.[18] The 534 nm emission decays distinctly faster than the shoulder peaks. The 534 and 580 nm decay curves have been analyzed with curve fitting.[18] The 534 nm decay is best represented by three lifetimes of 15.8, 59.8, and 538 ns. Similarly, the decay at 580 nm has lifetimes of 5.89, 27.0, and 801 ns. These values are much faster than those (750 ns, 11 μs, and 145 μs) from solution using a pulse N_2 laser.[6] These lifetimes must be used with caution since the bands overlap. More importantly, these decays are strongly affected by the chemical environment (e.g., solution and thin film matrix) and temperature. Assuming no countervailing arguments, the lifetimes reported here can be attributed to the decay of the triplet sub-states to the ground state in a neat Ir(ppy)$_3$ film at room temperature.

The most interesting observation is displayed in Figure 3, where we show the XEOL recorded with zero order light time-gated with a fast (0−10 ns) and a slow (10−550 ns) time window. We see from Figure 3 that the fast window XEOL shows a dominant emission at 534 nm. This associates the 534 nm emission with a fast decay channel, while the 580 nm shoulder is not. This is confirmed in the slow window where the 580 nm peak is more intense than in the ungated XEOL (Figure 2). The observation of 534 nm emission in the slow window indicates that it is not entirely associated with the fast window.

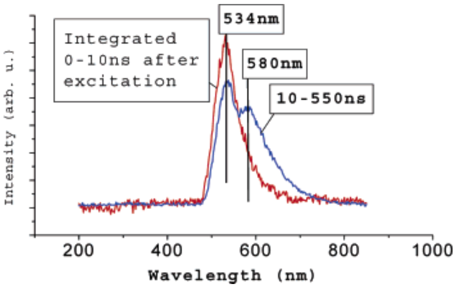

Figure 3. Time-gated XEOL collected with a fast (0−10 ns) and a slow (10−550 ns) time window excited with 430 eV photons.

The observations reported here clearly indicate that, with X-ray excitation, the triplet states of interest in neat Ir(ppy)$_3$ films can be produced very fast via direct excitation and core−hole de-excitation cascade. The time-gated XEOL technique can be used to uniquely probe the optical properties of OLED materials, semiconductor nanostructures, and light emitting soft matters. Experiments exploring metal center excitation are underway.

Acknowledgment. Research at UWO is supported by NSERC, CFI, and CRC of Canada; the operation of the Canadian Synchrotron Radiation Facility and the Canadian Light Source is supported by an NSERC MFA grant. Technical advice from Richard Rosenberg and the effort of the CLS accelerator group in producing a stable single bunch is greatly appreciated.

References

(1) Baldo, M. A.; O'Brien, Y. Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151−153.
(2) King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1431−1432.
(3) Adachi, C.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **2000**, 77, 904−907.
(4) Wang, Y.; Herron, N.; Grushin, V. V., LeCloux, D.; Petrov, V. *Appl. Phys. Lett.* **2001**, *79*, 449−451.
(5) Grushin, V. V.; Herron, N.; Lecroux, D. D.; Marshall, W. J.; Petrov, V. A.; Wang, Y. *Chem. Commun.* **2001**, 1494−1495.
(6) Finkenzeller, W. J.; Yersin, H. *Chem. Phys. Lett.* **2003**, *377*, 299−305.
(7) Holzer, W.; Penzkofer, A.; Tsuboi, T. *Chem. Phys.* **2005**, *308*, 93−102.
(8) Tsuboi, T.; Aljaroudi, N. *Phys. Rev. B* **2005**, *72*, 125109 (1−5).
(9) Hay, P. J. *J. Phys. Chem. A* **2002**, *106*, 1634−1641.
(10) Rogalev, A.; Goulon, J. In *Chemical Applications of Synchrotron Radiation, Part II: X-ray Applications*; Sham, T. K., Ed.; World Scientific: River Edge, NJ, 2002; Vol. 12B, pp 707−760.
(11) Sham, T. K.; Jiang, D. T.; Coulthard, I.; Lorimer, J. W.; Feng, H. X.; Tan, K. H.; Frigo, S. P.; Rosenberg, R. A.; Houghton, D. C.; Bryskiewicz, B. *Nature* **1993**, *363*, 331−333.
(12) Rosenberg, R. A.; Shenoy, G. K.; Heigl, F.; Lee, S.-T.; Kim, P.-S. G.; Zhou, X.-T.; Sham, T. K. *Appl. Phys. Lett.* **2005**, *86*, 263115 (1−3).
(13) Kim, P.-S.; Sham, T. K.; Zhang, P.; Fung, M.-K.; Lee, S. T.; Hu, Y.-F.; Yates, B. W. *J. Am. Chem. Soc.* **2001**, *123*, 8870−8871.
(14) Naftel, S. J.; Zhang, P.; Kim, P. S.; Sham, T. K.; Coulthard, I.; Antel, W. J., Jr.; Freeland, J. W.; Frigo, S. P.; Fung, M. K.; Lee, S. T.; Hu, Y. F.; Yates, B. W. *Appl. Phys. Lett.* **2002**, *78*, 1847−1849.
(15) Naftel, S. J.; Kim, P.-S. G.; Sham, T. K.; Sammynaiken, R.; Yates, B. W.; Hu, Y.-F. *J. Appl. Phys.* **2003**, *93*, 5191−5195.
(16) There are single bunch impurity issues. There are weak sidebands in the single bunch pulse, thus the width of the pulse is several nanoseconds. Note that we are triggering on the rising edge of the PMT pulse; the uncertainty is reduced since we trigger the signal above a certain threshold.
(17) Heigl, F.; Lam, S.; Zhou, X.-T.; Murphy, M.; Ko, P.; Sham, T. K.; Regier, T.; Coulthard, I.; Armelao, L. abstract submitted to SRI2006 (Korea).
(18) Three decay lifetimes, $y = a[\exp(-bt)] + c[\exp(-dt)] + f[\exp(-gt)]$, yield the best fit with the data set of 15−550 ns ($t = 0$ being the rising edge of the decay curve). The time response of the PMT (~2 ns) prohibits the extraction of any meaningful timing parameter less than 10 ns.

JA060243C