Fluorescence dynamics of Ir(PPy)₃

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Introduction

The growing reliance on derivatives of $Ir(PPy)_3$ as the emitters in organic light emitting devices (OLED) presents a need to better understand its basic photophysics. $Ir(PPy)_3$, shown in Figure 1, represented a breakthrough in the design of efficient OLEDs.¹ Its success is largely attributed to its ability to emit light efficiently from the excited triplet state, due to enhancement of the intersystem crossing (ISC) induced by the Ir atom. The ISC efficiency is a result of mixing of singlet and triplet states, so that the normally forbidden singlet-triplet transitions become allowed. For example, the weakest ground state absorption band at 485 nm (molar absorptivity, $\varepsilon = 1550 \text{ M}^{-1}\text{cm}^{-1}$) is usually assigned to a



Figure 1. Structure of Ir(PPy)_{3.}

singlet-triplet absorption. Due to the strength of the mixing, the states are not completely singlet or triplet, so it is not correct to describe any of the states in this way.² It is therefore not clear what the absorption bands represent, and the most recent attempt to clarify this using time resolved spectroscopy suffered from low signal-to-noise ratios and vague conclusions.³ In an effort to obtain a more accurate and detailed description of the excited states of this molecule, we employed time-resolved emission spectroscopy to probe the lifetimes of the excited states following excitation at various wavelengths.

Results and Discussion

The results of our emission studies show that excitation of $Ir(PPy)_3$ at 400 nm results in an emission decay curve that can be fitted with 2 decay components. The faster decay occurs with a time constant of 1.8 ps, and the slower one has a time constant of 2 µs. The relative amplitude of the fast decay component becomes larger at shorter wavelengths, indicating a time-dependent red-shift in the emission spectrum, as shown in Figure 2. However, there is a gap between the excitation wavelength and the earliest observable fluorescence, at -0.1 ps, indicating non-radiative energy loss on a time-scale shorter than the 120 fs instrument response



Figure 2. Absorption, fluorescence and time-resolved upconverted fluorescence spectra of $Ir(PPy)_3$ in DMF.

time. Attempts to observe the dynamics of this process using transient absorption (TA) were unsuccessful, as the TA spectrum exhibited no changes on this time scale. Excitation of $Ir(PPy)_3$ at 375 nm gives the same result, except that the fast component of the emission decay occurs with a time constant of 750 fs.

The long-lived emission can be assigned to decay from the lowest emitting state, denoted $SM_{3,5}$, for spin-mixed states 3 and 5, based on an earlier, theoretical study.² Its long lifetime indicates that it contains a large triplet contribution, in agreement with that study. The fast component of the emission decay must occur during the relaxation to $SM_{3,5}$. However, as noted in Figure 2, the earliest observable emission spectrum is significantly red-shifted from the excitation wavelength, indicating that there is at least one, rapid relaxation process preceding the other two. The assignments of the ground state absorption spectrum that have been provided indicate that the band excited at 400 nm and 375 nm is electronically different



Figure 3. Schematic for $Ir(PPy)_3$ relaxation. SM represents a spin-mixed state.

from the emitting state. This suggests assignment of this initial process to radiationless relaxation between electronic states.

To assign the remaining component of the relaxation, we consider both the time-dependent red-shift of the emission spectrum, and the excitation wavelength-dependence of the decay time constant. A time-dependent red-shift usually indicates a solvatochromic effect or vibrational relaxation. We did not observe any solvent-dependence of the emission spectrum, which suggests negligible solvatochromism. Furthermore, recent studies on other complexes exhibiting extremely efficient spin-orbit coupling indicates that rapid relaxation between electronic states can populate a vibrationally excited emitting state. In this case, higher energy excitation could lead to a more highly excited emitting state, which could have a more rapid relaxation to the ground state. A schematic of this mechanism is presented in Figure 3.

The previous work on this material included a proposed a mechanism invoking thermal equilibration between the triplet substates of $Ir(PPy)_3$.² However, since only the highest energy triplet substate is emissive, this thermal equilibration is not consistent with the time-dependent shift of the emission spectrum or with the excitation wavelength-dependence of the emission time constant. It seems likely that equilibration between substates in the previous work was proposed because its inclusion was necessary to explain a third emission decay component, which was observed in those experiments but not in ours.

Conclusion

In this study, we examined the emission dynamics of $Ir(PPy)_3$ in order to better understand the result of exciting the various bands of the material. We have shown that the initial relaxation process is faster than our instrumental time resolution, and it is followed by an emissive process that exhibits a biexponential decay. We propose electronic relaxation, followed by internal conversion, as the origins of the two initial decay processes.

References

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