

Modeling photodecay as mixed second-order relaxation in phosphorescent metal complexes

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Several metal complex compounds are interesting as triplet emitters and have application as dopants in optoelectronic devices, such as organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LEECs). A series of tridentate Pt^{II} complexes with tunable emission wavelength was designed, synthesized and recently characterized [1]. However, proper understanding of the phosphorescent process is required for optimizing performance, and to date the phosphorescent decay has only been fit with empirical double-exponential fits to yield an approximate average lifetime τ . Such heuristic bi-exponentials require *four* fit parameters (two amplitudes and two decay times) without an obvious microscopic justification for these *two* time scales.

Here, a generalized differential equation is used to describe a mixed 2nd order relaxation process which requires only *three* fit parameters and *one* time scale, as follows:

$$(1) \quad f'(t) = -\frac{1}{\tau} \left[(1-m)f(t)m \frac{f^2(t)}{f_{\Delta}} \right],$$

where the initial ratio of minority-to-majority reactant is m , which also describes the weighting factors for first-order $(1-m)$ and second order m relaxation terms in Eq. (1), respectively. For example, $m = 0$ corresponds to a pure uni-molecular reaction, $m = 1$ corresponds to a pure bi-molecular reaction and $0 < m < 1$ indicates mixed behaviour. By integrating this differential equation, we solve an expression for $f(t)$, where molecularity m , time constant τ , and decay amplitude f_{Δ} can be fitted to the relaxation data.

We implemented a fitting algorithm to this function with a simulated annealing Monte Carlo algorithm which automatically identifies confidence intervals for each parameter. This algorithm was used to analyze the luminescence decay of Pt^{II} complex triplet emitters at different temperatures (77 K and room temperature), ambient gases (air and Ar) and different excitation powers. The m , τ , and f_{Δ} are observed to fit the experimental relaxation curve with high confidence, offering a microscopic model for the relaxation. The resulting fits are as good as, or better than, the bi-exponential fits with one less fit parameter, strongly suggesting that we have identified the proper underlying origin of this behavior. In the low-temperature Ar-ambient data, $m = 0.13$ was observed with error less than 0.01, indicating that a considerable component of second order relaxation was present. We report data on power dependent experiments to investigate the possible physical nature of the majority and minority components in the mixed second order reaction described by Eq. (1).

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REFERENCES

- [1] Jan Sanning, Cristian A. Strassert, et al., Scanning-tunneling-spectroscopy-directed design of tailored deep-blue emitters. *Angew. Chem. Int. Ed.* **54** (2015), 786–791.