Ruthenium(II) complex with a notably long excited state lifetime†

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A new Ru(II) diimine complex, [Ru(5-pyrenyl-1,10-phenanthroline)]$_3$(PF$_6$)$_2$ ([Ru(py-phen)$_3$]$^{2+}$), possesses a room temperature excited state lifetime of 148 ± 8 μs.

Visible-absorbing luminescence probes that display long decay times are becoming increasingly important in biophysics, high-throughput screening, clinical chemistry, and lifetime-based chemical sensing.[1–4] One particular class of luminophores based on transition metal complexes displaying metal-to-ligand charge transfer (MLCT) excited states[5] have shown promise in such luminescence-based technologies.[1–4] In the interest of expanding these initial efforts, new MLCT compounds with prolonged emission decay times deserve special attention.

The photophysical properties of transition metal complexes displaying MLCT excited states are dominated by non-radiative decay processes and can be largely predicted by the energy gap law.[6] Excited state lifetimes in such complexes are modulated through simple modifications of the ligands and/or the central metal atom. Although this approach has proven quite successful, complexes with very long lifetimes consequently possess large energy gaps, generally with MLCT absorption bands in the UV. Alternatively, MLCT complexes containing ligands with large π-systems extend excited state lifetimes by imparting significant electronic delocalization into the charge transfer excited state.[7] Even though such complexes absorb in the visible, useful for analytical luminescence applications, their lifetimes are only slightly larger than that observed in the parent diimine complexes.

The room temperature lifetimes of the charge transfer-based emission in Ru(II) diimine complexes can be dramatically extended (approaching 50 μs) by tethering a pyrene molecule to one of the ligands within the complex.[8–12] The observed MLCT-based emission in such complexes is substantially longer-lived relative to the parent compounds as a result of energy transfer processes between the MLCT fragment and the pyrene unit.[8–12] In previous work, we have suggested that the energy transfer process can be controlled by adding additional pyrene molecules to the ligand periphery, which has the effect of increasing the formation of 'pyrene-like' triplets, further extending the lifetime of the complex. The present work takes advantage of this concept and has successfully generated a new Ru(II) diimine complex, [Ru(py-phen)$_3$](PF$_6$)$_2$ (Fig. 1), where py-phen is 5-pyrenyl-1,10-phenanthroline, with a room temperature lifetime of 148 ± 8 μs.

Full details regarding the synthesis of py-phen and [Ru(py-phen)$_3$](PF$_6$)$_2$ are presented in the ESI†. Briefly, py-phen was prepared from 5-bromo-1,10-phenanthroline and 3-pyreneboronic acid using standard Suzuki coupling conditions. [Ru(py-phen)$_3$](PF$_6$)$_2$ was synthesized by refluxing Ru(DMSO)$_4$Cl$_2$ and py-phen in 95% ethanol, followed by precipitation of the PF$_6$-salt, and final purification accomplished through gel filtration chromatography. The absorption and emission spectra of [Ru(py-phen)$_3$]$^{2+}$ in MeCN are displayed in Fig. 2. The tethered pyrene chromophores are largely responsible for the structured π–π* absorption bands between 300 and 350 nm.

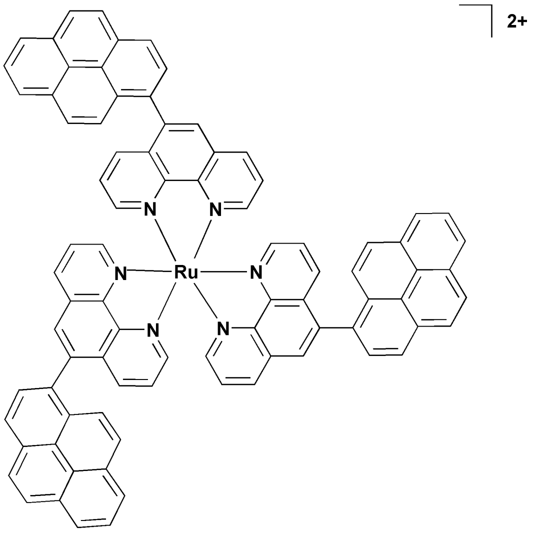

Fig. 1 Molecular structure of [Ru(py-phen)$_3$]$^{2+}$.

The absorption bands in the visible are due to the d$_\pi$(Ru) → π*(py-phen) MLCT transitions in the molecule. Regardless of excitation wavelength (300–532 nm), this complex displays only one visible emission band centered near 600 nm in MeCN at room temperature with a quantum yield of 0.071 ± 0.010. This emission band is characteristic of MLCT-based luminescence typically observed in Ru(II)–diimine complexes.[5] Using single photon counting techniques (342 nm excitation), no singlet emission could be observed from the pyrenyl units when grafted onto the metal complex. The corrected excitation spectrum of [Ru(py-phen)$_3$]$^{2+}$ (600 nm emission) is almost completely superimposible at all wavelengths with its absorption spectrum, suggesting a singlet energy transfer efficiency near unity. Similar behavior has been observed in related Ru(II)–pyrene chromophores.[9,11,12]

The excited state lifetime of [Ru(py-phen)$_3$]$^{2+}$ in thoroughly deaerated MeCN at infinite dilution is 148 ± 8 μs as measured with 458 nm laser pulses from an N$_2$-pumped dye laser (500 ps

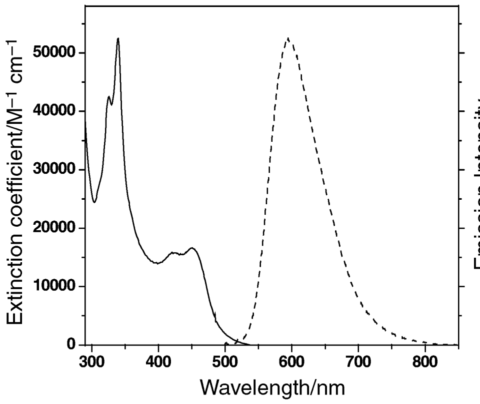

Fig. 2 Absorption (solid line) and emission (dashed line) spectra of [Ru(py-phen)$_3$]$^{2+}$ in MeCN at room temperature. The emission spectrum was recorded with 458 ± 2 nm excitation.

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† Electronic supplementary information (ESI) available: experimental details, self quenching plot and excited state absorption difference spectra. See http://www.rsc.org/suppdata/cc/b0/b007336i/

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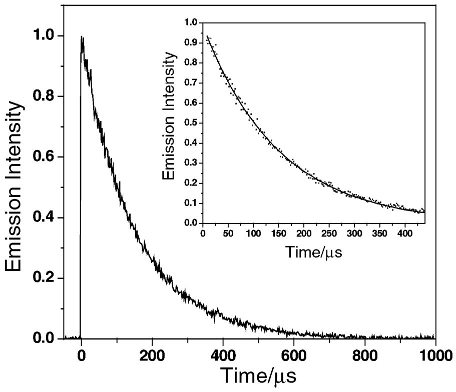

Fig. 3 Time-resolved emission decay of $[Ru(py\text{-}phen)_3]^{2+}$ in deaerated MeCN obtained with 458 ± 2 nm pulsed excitation (500 ps fwhm) detected at 600 nm. The decay represents an average of 128 laser pulses. Inset: data fit to a single exponential decay model.

fwhm), Fig. 3. A fast luminescence decay component (< 16 ns) was also observed, consistent with data obtained on related compounds.[8,10,11] This exceptionally long lifetime agrees well with the decay kinetics observed in the transients from the nanosecond laser flash photolysis experiments. However, the transient absorption profiles observed in $[Ru(py\text{-}phen)_3]^{2+}$ at all times following a 460 or 532 nm laser pulse are similar to that obtained with the uncoordinated py-phen ligand following 355 nm excitation. Therefore, the absorption transients provide evidence for the existence of a 'pyrene-like' triplet state at all delay times while there is no direct observation of a MLCT-based triplet state. The only observed radiative decay pathway for the $[Ru(py\text{-}phen)_3]^{2+}$ complex at room temperature is MLCT-based photoluminescence. In the model complex $[Ru(Ph\text{-}phen)_3]^{2+}$, where Ph-phen is 5-phenyl-1,10-phenanthroline, the lifetime under similar conditions is 1.15 μs.[13] In $[Ru(py\text{-}phen)_3]^{2+}$, the lifetime is extended *ca.* 129-fold relative to $[Ru(Ph\text{-}phen)_3]^{2+}$ as a consequence to the stabilization imparted by the energy transfer processes.

The observed excited state lifetime in $[Ru(py\text{-}phen)_3]^{2+}$ is very sensitive to subtle changes in oxygen concentration. Under our experimental conditions, high purity argon gas was continuously flowed through the cuvette during the measurement cycle, while maintained at a constant temperature of 20 ± 1 °C. Significant changes in lifetime could be correlated to the argon flow rate and temperature.

The long lifetime associated with the $[Ru(py\text{-}phen)_3]^{2+}$ complex permits a dynamic excited state self-quenching reaction at relatively dilute concentrations. Under our experimental conditions we did not observe any deviation in Beer's law behavior in the ground state absorption spectrum nor were we able to identify any new bands in the steady-state emission spectrum at concentrations between 2×10^{-6} and 2×10^{-5} M. Over this concentration range, the rates of emission decay are well modeled by a Stern–Volmer expression, recently used to describe self-quenching processes in Pt(II) diimine compounds.[14] The derived self-quenching rate constant of 1.3×10^8 $M^{-1}\ s^{-1}$ is valid under optically dilute conditions and is clearly not a result of ground state aggregation.

The uncoordinated py-phen ligand displays structured phosphorescence at 77 K in 4:1 EtOH:MeOH in the presence of ethyl iodide when excited in the UV (342 nm). Visible excitation (458 nm) of $[Ru(py\text{-}phen)_3]^{2+}$ in the same frozen matrix yields a similarly structured emission, reflecting the dominance of pyrene-like triplets in the excited states. The decay kinetics of $[Ru(py\text{-}phen)_3]^{2+}$ at 77 K are complex, containing a long component of 46 ± 2 ms.

Energy transfer processes between the excited MLCT and pyrene states at room temperature facilitates the extension of the excited state lifetime in $[Ru(py\text{-}phen)_3]^{2+}$. The observed 148 μs lifetime is substantially beyond the range of any previously measured lifetime in this class of chromophores. Importantly, this lifetime was obtained without relying on energy gap law predictions. The complex is susceptible to dynamic self-quenching processes under optically dilute conditions. To our knowledge, this is the first example of such behavior in a Ru(II)–diimine complex. The room temperature emission in $[Ru(py\text{-}phen)_3]^{2+}$ is MLCT-based, however at 77 K, the emission emerges as a π–π*-based phosphorescence.

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