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Ruthenium(II) complexes based on tridentate polypyridine ligands that feature long-lived room-temperature luminescence

Giulio Ragazzon,^{ab} Peter Verwilt,^a Sergey A. Denisov,^{ac} Alberto Credi,^b Gediminas Jonusauskas^c and Nathan D. McClenaghan^{*a}

Integrating a matched organic chromophore and a Ru(II) complex with optimized tridentate polypyridine ligands instils reversible electronic energy transfer giving an unusually long room temperature luminescence lifetime (42 μ s) without compromising the emission quantum yield.

Transition metal polypyridine complexes in general, and ruthenium complexes and dyads in particular, have been widely studied to better understand and harness their visible absorption, redox and photochemical processes.¹ This is typically with a view to application in the general areas of photosensitizers, dyes, sensors, LEDs, catalysts as well as nanotechnology.² Ligand modification is central in determining many of the key excited-state properties of the complexes, and hence emission (namely efficiency and luminescence decay rates). Polypyridine ligands generally bind in a bidentate or tridentate fashion, offering complexes with different coordination geometries and properties. Indeed, tridentate ligands can offer access to complexes with 1D-linear geometries (molecular rods and wires), but the luminescence properties are typically extensively hampered by thermally accessible metal-centred states which serve to diminish luminescence.¹ As an illustration, while $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) has a quantum yield (Φ_{em}) of 0.059 and a luminescence lifetime of 890 ns in degassed acetonitrile, the terpyridine analogue $[\text{Ru}(\text{tpy})_2]^{2+}$ (tpy = 2,2';6',2''-terpyridine) has much lower corresponding values of $<10^{-5}$ and 0.25 ns.³

Strategies to improve these parameters have reposed on defavouring thermally-activated loss by increasing the energy gap between states on lowering emissive ³MLCT levels, as a result of incorporating highly electron poor tpy-like ligands.⁴ Additionally, coupling with an organic auxiliary led to luminescence

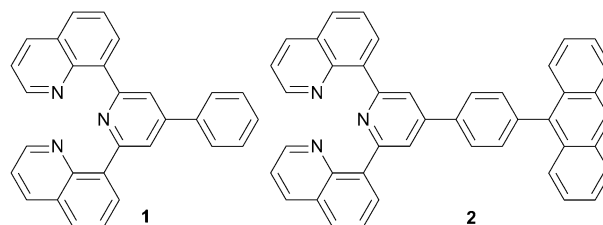


Fig. 1 Anthracene free (1) and appended (2) tridentate ligands employed in forming complexes $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$.

lifetimes as long as 1.8 μ s albeit with a small quantum yield of 10^{-4} .⁵ In two different approaches, microsecond luminescence lifetimes were recently obtained using heteroleptic ruthenium complexes based on tridentate ligands which comprise carbenes,⁶ or replacing the two external pyridine moieties of tpy with quinolines, giving emissive tridentate ligand-based octahedral ruthenium complexes.⁷

Herein we report a straightforward structural modification of the latter type of complex (*cf.* model complex $[\text{Ru}(\mathbf{1})_2]^{2+}$, Fig. 1), involving the judicious integration of an auxiliary chromophore with matched properties (*vide infra*), with the goal of giving access to a much longer-lived luminescent complex, while retaining a similar emission quantum yield. This modification could broaden the scope of functions in multicomponent artificial arrays by changing excited-state properties, including lifetime.

The auxiliary chromophore was anticipated to exert the desired role if the newly-introduced triplet level has a slow inherent deexcitation and is quasi-isoenergetic with the emissive MLCT state. This would permit reversible intercomponent excited-state energy transfer with the organic subunit acting as an energy reservoir and emission emanating from the metallic sub-unit with a net luminescence lifetime increase.⁸ Anthracene was anticipated to be an appropriate candidate (triplet energy at 1.8 eV; $\tau_{\text{phos}} = 3300 \mu\text{s}$), whose incorporation gave the prototype $[\text{Ru}(\mathbf{2})_2]^{2+}$, see Fig 1.³ Equally, this would add to the rather limited number of matched chromophore pairs.⁸

Model ligands **1** and **2** (Fig. 1) were both prepared from a common intermediate, 4-(4-bromophenyl)-2,6-di(quinolin-8-yl)pyridine (see the ESI† for detailed procedures).⁹ Ligand **1** was prepared by a palladium-catalysed hydro-dehalogenation.¹⁰

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Molecule **2** was prepared through a Suzuki coupling reaction with the pinacol ester of 9-anthryl boronic acid, with a yield of 34%. Complex formation was achieved upon reacting **1** or **2** with $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ in hot ethylene glycol under microwave irradiation, yielding the desired complexes $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$, respectively.

While three distinct stereoisomers are possible (*mer*, *cis*, *fac* and *trans*, *fac*), the thermodynamically favourable *mer*-form can be formed predominantly upon heating at 200 °C.¹¹ Anion metathesis reactions and column chromatography afforded the pure complexes as hexafluorophosphate salts.

Electronic absorption spectra (see ESI†) are dominated by ligand-based absorption bands in the UV region and similar MLCT absorption in the visible region for both $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$. An additional anthracene absorption band is also observed, which retains its vibronic fine structure implying only weak ground-state coupling between the adjacent chromophores, suggesting an approach to orthogonality of the π -systems, as a result of steric constraints including peri-proton interactions. Consequently, each chromophore is anticipated to retain its own specific properties in the ensemble.

Steady-state luminescence shows red MLCT-based emission for both $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$ ($\lambda_{\text{em max}} = 686 \text{ nm}$) with similar emission quantum yields in degassed acetonitrile ($\Phi_{\text{em}} = 0.013$), see ESI.† However, a more pronounced oxygen sensitivity is observed in $[\text{Ru}(\mathbf{2})_2]^{2+}$ vs. $[\text{Ru}(\mathbf{1})_2]^{2+}$ (Table 1). While the latter molecule shows a low $\Phi_{\text{em deoxy}}/\Phi_{\text{em oxy}}$ ratio of 5.8, in contrast, a much higher value of 33 is obtained with $[\text{Ru}(\mathbf{2})_2]^{2+}$, which is consistent with a much longer excited-state lifetime.

Time-resolved spectroscopies in the sub-picosecond to microsecond regimes give supplementary information on the nature of the excited molecule and excited-state processes in the multi-component species. An emission lifetime of 2.7 μs was obtained for degassed $[\text{Ru}(\mathbf{1})_2]^{2+}$, which is similar to the previously reported tolyl analogue.¹¹ However, a luminescence lifetime which is over an order of magnitude longer (35 μs) was measured for a micromolar solution of $[\text{Ru}(\mathbf{2})_2]^{2+}$, see Fig. 2, which is conducive to enhanced oxygen sensitivity. Extrapolating to infinite dilution gave an apparent deexcitation rate of 23 800 s^{-1} or lifetime of 42 μs , much longer than the unelaborated chromophore (see Fig. S5, ESI†).

While emission data give information on the ultimate fate of the excited molecule, transient absorption spectroscopy elucidates the management of energy by the excited molecule and origin of the large lifetime enhancement. Excitation of $[\text{Ru}(\mathbf{2})_2]^{2+}$, either into the MLCT absorption band at 465 nm or predominantly in the anthracene-centred band at 355 nm rapidly led to the population of the anthracene triplet, denoted by a characteristic $T_n \leftarrow T_1$ absorption at 430 nm, see Fig. 3. The kinetics of deexcitation of this organic triplet

Table 1 Photophysical properties of ruthenium complexes $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$ in acetonitrile at room temperature

	$\lambda_{\text{em max}}^a$ (nm)	$\Phi_{\text{em oxy}}^b$	$\Phi_{\text{em deoxy}}^c$	τ^d (μs)	K_{eq}
$[\text{Ru}(\mathbf{1})_2]^{2+}$	686	2.2×10^{-3}	0.013	2.7	
$[\text{Ru}(\mathbf{2})_2]^{2+}$	686	4×10^{-4}	0.013	75×10^{-6} ; ^e 42	15.2 ± 2 ; ^f

^a Recorded on streak camera and uncorrected. ^b Luminescence quantum yield in air equilibrated CH_3CN solution cf. $[\text{Ru}(\text{bpy})_3]^{2+}$.³ ^c Idem in degassed CH_3CN solution. ^d Luminescence lifetime of ³MLCT in dilute degassed CH_3CN . ^e Determined *via* transient absorption spectroscopy in degassed CH_3CN . ^f Excited state equilibrium constant (see ESI).

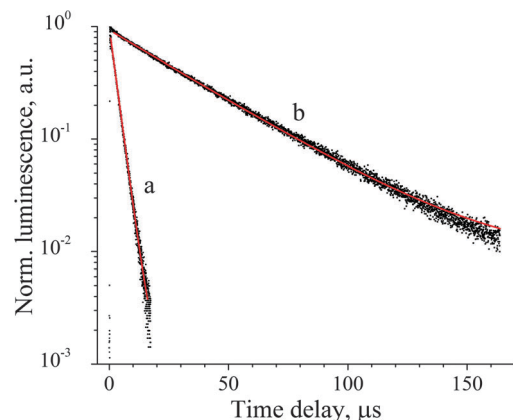


Fig. 2 Luminescence decay of dilute $[\text{Ru}(\mathbf{1})_2]^{2+}$ (a) and anthracene appended $[\text{Ru}(\mathbf{2})_2]^{2+}$ (b) in acetonitrile at 700 nm ($\lambda_{\text{exc}} = 465 \text{ nm}$).

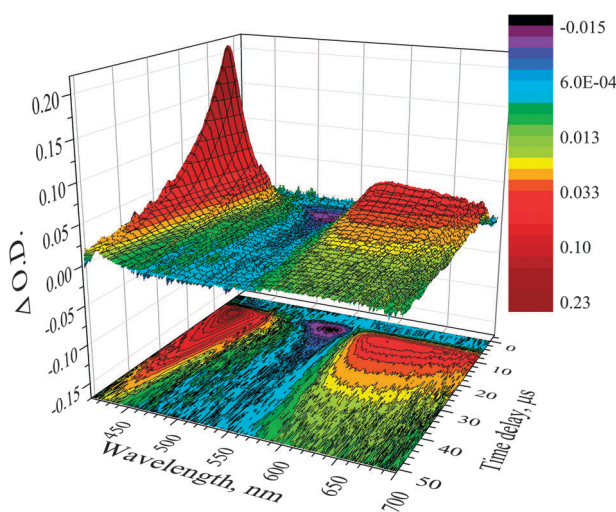


Fig. 3 Transient absorption map of $[\text{Ru}(\mathbf{2})_2]^{2+}$ showing deexcitation of the equilibrated bichromophoric molecule in acetonitrile ($\lambda_{\text{exc}} = 465 \text{ nm}$).

band mirrors those of the red emission (see ESI†). This behaviour is attributed to a dynamic excited-state equilibrium involving the two chromophores confirming that excited states on the adjacent chromophores may be considered quasi-isoenergetic, thus permitting rapid and reversible electronic energy transfer (REET). As a similar quantum yield was obtained for both $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$, this implies the energy shuttling in $[\text{Ru}(\mathbf{2})_2]^{2+}$ is essentially quantitative.

To gain further insight into the energies of the pertinent states, low temperature phosphorescence measurements were undertaken with both $[\text{Ru}(\mathbf{1})_2]^{2+}$ and $[\text{Ru}(\mathbf{2})_2]^{2+}$. At 77 K, slightly blue-shifted MLCT emission ($\lambda_{\text{em max}} = 672 \text{ nm}$) could be observed from $[\text{Ru}(\mathbf{1})_2]^{2+}$ with respect to room temperature, while in the bichromophoric complex the emission of $[\text{Ru}(\mathbf{2})_2]^{2+}$ was located further to the red ($\lambda_{\text{em max}} = 712 \text{ nm}$) and attributed to a slightly lower-lying anthracene emission, with only a small energy difference between high energy emission features. While such a small value cannot be measured directly without significant error, kinetic analysis (see ESI†) allows determination of the energy gap at 430 cm^{-1} , which is consistent with reversible interchromophore electronic energy transfer at room temperature.

The establishment of a dynamic excited-state equilibrium from the non-equilibrated initial excited state can be observed in real-time

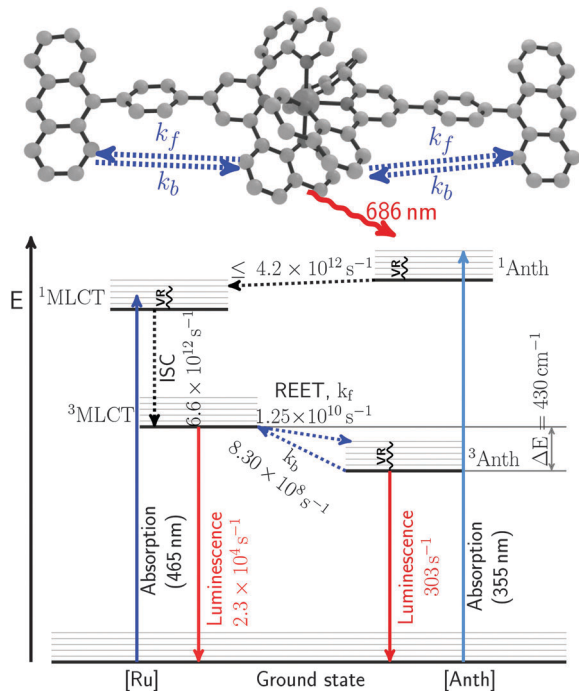


Fig. 4 Jablonski diagram showing pertinent energy levels and kinetics of reversible electronic energy transfer (REET) and delayed luminescence. ISC = intersystem crossing; VR = vibrational relaxation.

by picosecond transient absorption spectroscopy. Indeed, the rise time of the anthracene triplet absorption signature (see ESI[†]) is measured to be 75 ps. This value gives the rate of establishment of equilibrium ($k = 13.5 \times 10^9 \text{ s}^{-1}$), and is equal to the sum of forward (k_f) and backward (k_b) energy transfer processes.⁸ The relative k_f and k_b values can be determined by direct observation based on transient absorption signatures, while the excited-state equilibrium constant (K_{eq}), is a ratio of k_f to k_b . This can also be indirectly estimated using inherent deexcitation and lifetime decay data (see ESI[†]). Concerning direct observation, changes in absorption of the MLCT band at 485 nm (Fig. S7, ESI[†]) denote the relative populations immediately after excitation, as well as the subsequent metastable equilibrated system. This then allows determination of the equilibrated population to be largely (94%) in favour of the organic chromophore, and equilibrium constant K_{eq} at 15.2 ± 2 . This value agrees well with that estimated at 14.8 *via* the aforementioned luminescent decay method. Consequently k_f and k_b were determined at $1.25 \times 10^{10} \text{ s}^{-1}$ and $8.30 \times 10^8 \text{ s}^{-1}$, respectively, see Fig. 4 and ESI[†].

Ultrafast processes of intersystem crossing and formal singlet-singlet energy transfer were estimated using femtosecond transient absorption spectroscopy, upon exciting the MLCT absorption band or predominantly into the anthracene absorption band, respectively. Based on rapid changes in the spectrum at around 600 nm following visible excitation ($\lambda_{exc} = 490 \text{ nm}$) the ¹MLCT to ³MLCT intersystem crossing was observed to occur with a time constant of 150 fs (Fig. S9, ESI[†]). Meanwhile, on exciting anthracene at 370 nm and observing changes in the visible ground-state MLCT absorption band at 530 nm (Fig. S10, ESI[†]), an upper limit could be estimated for the electronic energy transfer rate from an excited singlet anthracene to lower-lying ¹MLCT level at around $4.2 \times 10^{12} \text{ s}^{-1}$. Indeed, a small amount of direct MLCT excitation and cooling would

effectively change the apparent rate to some extent, while remaining on the same order of magnitude. The ensemble of excited-state processes and rates describing energy transfer, energy distribution at equilibrium and subsequent emission are given in Fig. 4.

To summarise, reversible electronic energy transfer and an optimised coordination geometry conspire to give a tridentate ruthenium complex with an unprecedented luminescence lifetime, without compromising the luminescence efficiency. Time-resolved spectroscopies showed that due to reversible intercomponent electronic energy transfer, excited-state equilibration is reached in less than 400 picoseconds with an average of 94% of energy being stocked on the organic energy reservoir in the equilibrated system and that subsequent emission occurs on the microsecond timescale ($\tau_{em} = 42 \mu\text{s}$) from the metal-centre. Interestingly, this energy-shuttling was instilled in a predetermined fashion based on a rudimentary knowledge of energies of excited-states and intrinsic deexcitation rates in respective molecular sub-units. As well as offering the possibility of more efficient photosensitizers and improving underperforming chromophores, these REET processes are of potential interest in molecule-based machines, detection and light-emitting devices.

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