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Towards ruthenium(II) polypyridine complexes with prolonged and predetermined excited state lifetimes†

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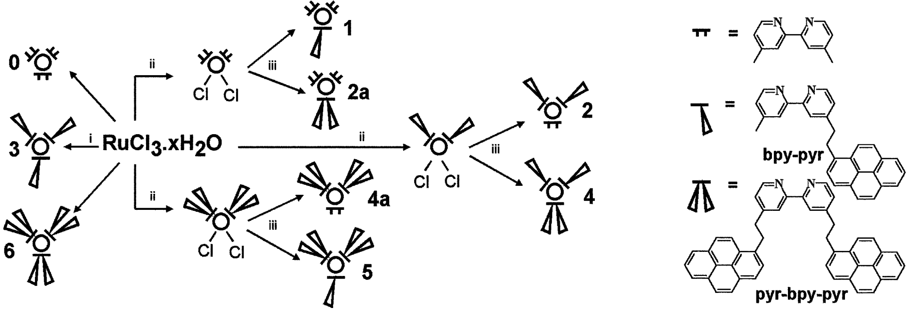
The excited state lifetime of a Ru(bpy)$_3$-motif is linearly related to the number of appended pyrenyl chromophores, but independent of connectivity; values for nine complexes range from 0.8 to 18.1 μs.

Transition metal complexes, such as those derived from $[Ru(bpy)_3]^{2+}$, have been extensively studied due to their unique combination of luminescence and redox properties.[1] Within this class of compounds, species with prolonged excited-state lifetimes are highly desirable in view of their use in diffusion-rate limited bimolecular processes and in multicomponent (supramolecular) systems featuring photoinduced energy and/or electron transfer processes, where Ru(II) complexes play the role of photo-active subunits.[2] In a seminal work, Ford and Rodgers[3] first noted that the luminescence lifetimes of Ru(II) polypyridine complexes can be prolonged by the presence of coupled aromatic chromophores having their lowest-lying, long-lived triplets at a similar energy to the luminescent metal-based triplet level(s). The basis of this behaviour is thermal equilibration between the relevant triplet states. In this and subsequent cases, an appended (organic) chromophore acts as an energy 'reservoir', whilst emission results almost exclusively from the ^{3}MLCT state.[4–6] Recently, Castellano and coworkers[4] noted that appending three pyrene (pyr) chromophores lengthens the excited-state lifetime compared to related species bearing only one pyrene unit. We have prepared the ligands bpy–pyr and pyr–bpy–pyr and a series of nine complexes bearing between 0 and 6 appended pyrenyl chromophores, Scheme 1. This allowed us to perform a systematic study of the role of a number of appended chromophores on the resulting excited-state lifetime, and other parameters. All permutations (with the exception of the tris-heteroleptic species) were prepared, additionally providing the opportunity to observe the influence of connectivity in the cases with two and four pyrenyl groups (**2** *cf.* **2a**; **4** *cf.* **4a**, respectively).

Electronic absorption and luminescence spectra‡ of both pyrene-bearing ligands (see data in Table 1) showed qualitatively similar features, with an enhanced absorption in the 310–350 nm region for ligand pyr–bpy–pyr. Similar luminescence properties suggest that minimal electronic interaction between pyrenyl units occurs in pyr–bpy–pyr. Absorption and luminescence spectra of all the complexes in oxygen-free acetonitrile solution at room temperature are also similar to one another, with absorption spectra dominated by ^{1}MLCT bands in the visible and by ^{1}LC (ligand centred) bands in the UV region and luminescence originating from ^{3}MLCT states, as established by comparing the relevant properties of the new compounds with literature examples.[1] Primary variations between the absorption and emission spectra of complexes **0–6** are enhanced absorption due to increasing numbers of appended pyrenes and small variations in the position of the emission maxima (Table 1), which are progressively shifted to higher energy as the number of points of substitution are increased, consistent with small electronic effects due to the presence of the pyrenylethyl substituents. The room temperature luminescence lifetimes (τ) are in all cases monoexponentials (Table 1) and quantum yields (Φ) are 0.065 ± 0.005 for all the complexes. Interestingly, a linear dependence is found for τ, with each successive pyrene adding approximately 2.7 μs to the lifetime of the complexes [Fig. 1(a)]. As in former observations concerning covalently-coupled Ru(II) polypyridine and pyrenyl chromophores,[3–6] this is attributed in each case to thermal equilibration between the lowest-lying triplet states located at the two electronically-distinct subunits.

An estimation of the energy distribution between states at equilibrium can be obtained using experimental parameters, *i.e.* the ratio of Φ to τ for the examined complex divided by the ratio of Φ to τ for the model compound **0**.[5] This calculation gives an approximate value for α, the fraction of molecules in their excited-states with populated pyrene triplets after equilibration, whilst $1 - \alpha$ corresponds to the fraction of ^{3}MLCT states. The equilibrium constant is expressed as: $K_{eq} = \alpha/(1 - \alpha)$.[5] The dependence of α on the number of appended pyrenyl units is shown in Fig. 1(b).

We have also modelled the simultaneous equilibria involving the excited $[Ru(bpy)_3]^{2+}$ center and the lower-lying triplet levels of each of the individual pyrene groups.§ The parameters employed were: $T = 298$ K, $\tau(Ru) = 870$ ns, as in **0**, $\tau(pyr) = 150$ μs,[4] and $\Delta E = 260$ cm^{-1}; the prefactor for the forward and backward Arrhenius-type rates pertaining to the various



Scheme 1 Synthesis of complexes **0–6**. *Reactions and conditions*: (i) DMF, N_2, 120 °C, 24 h; (ii) dry DMF, N_2, 70 °C, 40 h; (iii), MeOH, H_20, reflux, 24 h. Complexes **0–6** were isolated as hexafluorophosphate salts, following anion metathesis.

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† Electronic supplementary information (ESI) available: synthesis of the new ligands bpy–pyr and pyr–bpy–pyr and of their ruthenium compounds. See http://www.rsc.org/suppdata/cc/b1/b110291e/

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Table 1 Photophysical properties measured for all species in deoxygenated acetonitrile at room temperature

Species	$\lambda_{\text{em max}}$/ nm	τ/μs	α^b	$K_{\text{eq}}{}^b$
bpy–pyr	375^a	0.19	—	—
pyr–bpy–pyr	375^a	0.21	—	—
0	616	0.87	—	—
1	614	2.5 (3.7)	0.71 (0.78)	2.5 (3.5)
2	614	6.6 (6.5)	0.89 (0.88)	8.1 (7.1)
2a	614	6.9	0.90	9.0
3	614	7.9 (9.1)	0.91 (0.91)	10.1 (10.6)
4	612	11.0 (11.8)	0.93 (0.93)	13.3 (14.2)
4a	610	11.3	0.94	15.7
5	610	15.0 (14.1)	0.95 (0.95)	19.0 (17.7)
6	608	18.1 (16.5)	0.96 (0.96)	24.0 (21.3)

^{a} Highest energy feature of a structured band. ^{b} Fraction of pyrene-like triplets calculated from experimental parameters. Estimated values from equilibria modelling (see text) are given in brackets.

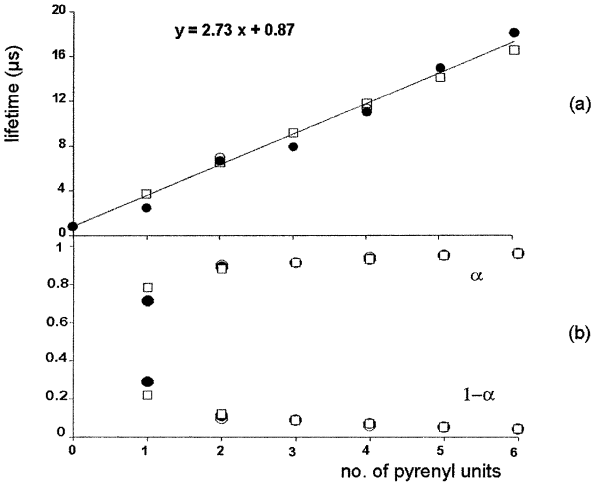

Fig. 1 Effect of number of appended pyrenes on: (a) excited-state lifetime; and (b) distribution of excitation energy; α is the fraction of pyrene-like triplets. Solid points are experimental (or calculated from experimental data), empty points are from modelling (see text).

$Ru\rightleftharpoons pyr$ equilibria was assumed to be $\geq 1 \times 10^9$ s^{-1}, in accordance with the fact that none of the luminescence decays showed multiple components on the nanosecond time scale; no interpyrene interaction was considered. Results are displayed in Fig. 1, and are in fair agreement with the experimental data, confirming that the τ *vs.* number of pyrene units linear behaviour is consistent with the adopted equilibrium scheme.

Temperature is expected to affect strongly the equilibrium described above. Indeed, the steady-state luminescence spectra of the complexes, measured at 77 K, are quite different to one another. Whilst **0** and **1** exhibit typical ^{3}MLCT emission profiles and lifetimes (*e.g.* τ = 5 μs for **0**),[1] the higher members of this series exhibit progressively more pyrene phosphorescence character, further indicated by the luminescence lifetimes (550 μs for **4a**, very close to that of an alkylpyrene[3]). As examples, the 77 K emission spectra of **0** and **4a** are shown in Fig. 2. The 77 K steady-state emission spectra also allowed us to estimate the energy separation between ^{3}MLCT and ^{3}pyrene levels, found to be of the order of a few hundreds of cm^{-1}, in agreement with the energy gap ΔE used for the calculation described above.

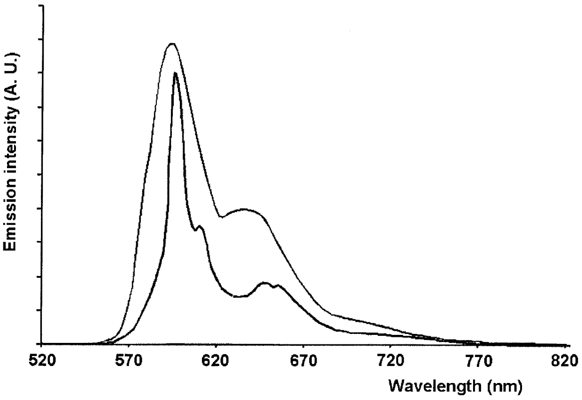

Fig. 2 Luminescence spectra obtained at 77 K, excitation at 450 nm: upper curve is for complex **0**; lower is for complex **4a**.

In conclusion, the excited state lifetime for species with a $[Ru(bpy)_3]^{2+}$ unit connected to pyrenyl chromophores by short, saturated hydrocarbon spacers can be qualitatively and quantitatively tailored upon introducing the appropriate number of pyrenyl chromophores. We have shown that each successive substitution adds 2.7 μs to the observed lifetime giving a value of 18.1 μs for **6** (with six appended chromophores), which is clearly not the upper limit that can be reached by this type of system. As the linear behaviour is maintained even with six individual excited-state equilibria having been established, further additional chromophores should increase the lifetime further, and one may suggest using a dendritic architecture to this end.

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Notes and references

‡ Absorption and luminescence spectra were measured in vacuum-line degassed acetonitrile at room temperature with a Perkin-Elmer Lambda 5 UV/Vis spectrophotometer and a Spex Fluorolog II spectrofluorimeter, respectively. Luminescence quantum yields (Φ) were evaluated with reference to air-equilibrated $[Ru(bpy)_3]Cl_2$ in water as a standard (Φ = 0.028).[1] Luminescence lifetimes (τ) on the μs and ms time scales were obtained with an IBH single photon counting equipment and a Perkin-Elmer LS50B luminescence spectrometer, respectively. The experimental uncertainty on the absorption and luminescence maxima is 2 and 1 nm, respectively, while that for the Φ and τ values is 10%.

§ Calculations were performed by using the matrix formalism of Matlab 5.0.

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