Modulation of the luminescence properties of a ruthenium–terpyridine complex by protonation of a remote site

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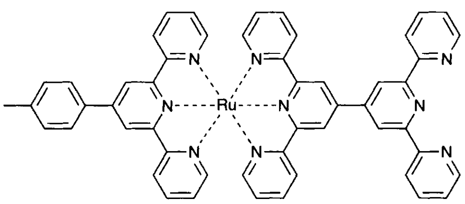
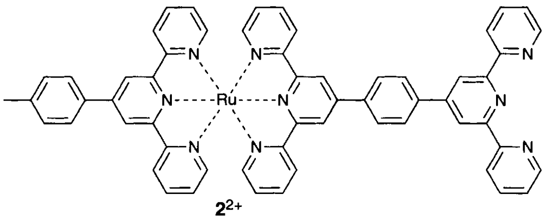
In a series of complexes $[(ttp)Ru\{tpy(C_6H_4)_ntpy\}]^{2+}$, the Ru–tpy type chromophore and the free tpy site are separated by a variable number (n = 0–2) of phenylene spacers [tpy = 2,2′:6′,2″-terpyridine, ttp = 4′-(p-tolyl)-2,2′:6′,2″-terpyridine]; for the complex with n = 0, modulation of the luminescence properties of the Ru-based chromophore can be performed by protonation at the free tpy site suggesting a new approach for affording long-lived excited species of the basic Ru–tpy type unit.

The control of vectorial energy and electron transfer on multicomponent assemblies requires the synthesis of rigid rod-like molecular species. With this aim the use of tpy (tpy = 2,2′,6′,2″-terpyridine) is particularly appealing since functionalization of the ligand at the right position allows the construction of multicomponent systems based on the electro- and photo-active $Ru(tpy)_2{}^{2+}$ unit and its analogues, with a very strict control over the geometry of the assembly.[1]

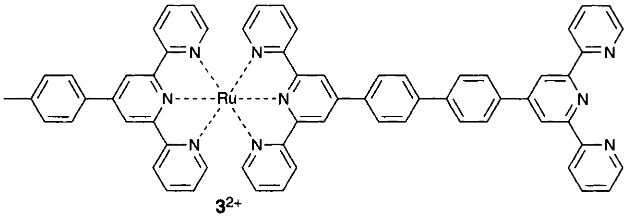
In previously studied systems[2–6] containing a $Ru(tpy)_2{}^{2+}$ component and various electron or energy acceptors attached to it, the Ru-based complex was excited (Ru → *Ru), the ensuing process being subsequently monitored. Intrinsic deactivation of the $Ru(tpy)_2{}^{2+}$ unit competes with these photoinduced processes and is thus a serious limitation. The main drawback, inherent to $Ru(tpy)_2{}^{2+}$, is that the lowest lying excited state is short-lived (*ca.* 1 ns at room temperature).[7] Several groups have tried to increase the lifetime of Ru–tpy type centres by structural modifications, knowing that the photophysics of ruthenium–polypyridine complexes is governed by the energy gap, ΔE, between the luminescent level, of metal-to-ligand charge transfer (MLCT) electronic configuration, and a higher lying metal-centred (MC) level. The latter level provides an activated pathway for fast radiationless decay of the luminescent state.[8] Thus one tries either to push the MC level to higher energy or to stabilize the MLCT level with the aim of increasing ΔE. For instance, this has been done by using (*i*) electron-withdrawing or repelling groups at 4′ positions,[7] (*ii*) cyclometallating ligands,[9] and (*iii*) large tpy-type ligands.[10,11] We present here an alternative approach for obtaining long-lived excited species for Ru–tpy chromophores, based on the influence of protonation in the series of complexes, as illustrated in Scheme 1. The synthesis and the characterization of the complexes 1^{2+}–3^{2+} were described previously.[4]



1^{2+}

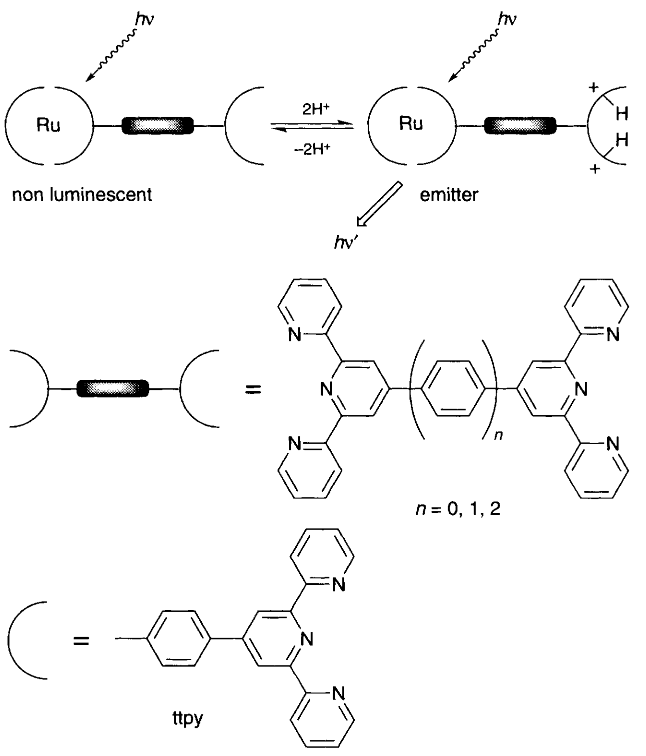


2^{2+}



3^{2+}

The free tpy site of compounds 1^{2+}–3^{2+} can be protonated in slightly acidic medium (pK_{a2} = 3.42 and pK_{a1} = 4.64 for H_2tpy^{2+} and $Htpy^+$ respectively[12]).



Scheme 1

While the visible absorption spectra of 2^{2+} and 3^{2+} are practically unchanged at pH ⩾ 1, the absorption maximum of complex 1^{2+} gradually shifts from 490 to 500 nm on passing from pH 7 to 1 [as revealed by titration experiments with HCl in acetonitrile–water (1 : 1) in the presence of 1 mol dm^{-3} KNO_3]. Thus, for $\mathbf{1}^{2+}$ the spectroscopic properties (*i*) are consistent with a Ru ⟶ (tpy–tpy) CT electronic configuration for the Ru-based chromophore and (*ii*) can be varied by protonation at the appended tpy fragment.[13] In our case, the influence of acidic solvent could be investigated best by luminescence titration (air-equilibrated solutions were employed in all cases). In the interval pH 1–7, three luminescent species were detected for $\mathbf{1}^{2+}$ exhibiting λ_{max} at 650, *ca.* 680 and 700 nm, respectively, and lifetime values of 4, 22 and 80 ns, respectively. Fig. 1 summarizes the results of a global fitting analysis performed over 11 luminescence decays obtained in the indicated pH interval by monitoring the full spectral range from 610 to 750 nm and according to eqn. (1).

$$I(t) = B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2) + B_2\exp(-t/\tau_3) \quad (1)$$

As one can see, the relative contributions, B_i change with pH. In particular, at both pH 2.2 and 1, the luminescence is mostly due to a single species. According to the protonation behaviour of the free tpy ligand[12] these species should be the protonated forms of $\mathbf{1}^{2+}$, *i.e.* $H\mathbf{1}^{3+}$, $[(ttp)Ru(tpy{-}tpyH)]^{3+}$ at pH 2.2 and $H_2\mathbf{1}^{4+}$, $[(ttp)Ru(tpy{-}tpyH_2)]^{4+}$ at pH 1.

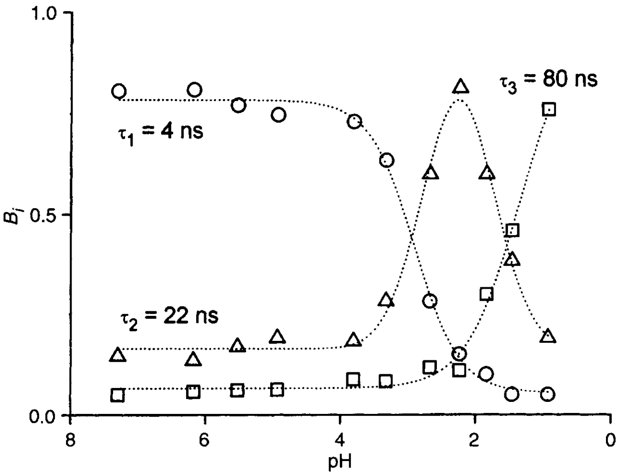


Fig. 1 Calculated contributions (relative intensities, B_i) for the three components of the luminescence decays in the case of $\mathbf{1}^{2+}$ [see eqn. (1) in text]. Given that the estimated uncertainties on B_i are *ca.* 20%, it is presumed that only the component with τ = 4 ns is present at pH > 4.

Table 1 Luminescence data[a]

	λ_{max}/nm		I_{rel}[b]		τ/ns	
	N	A	N	A	N	A
$\mathbf{1}^{2+}$	649	700	2.0	16.0	2.8	80.0
$\mathbf{2}^{2+}$	648	656	1.1	1.7	1.7	3.1
$\mathbf{3}^{2+}$	648	648	1.0[c]	1.1	1.5	2.4

[a] From uncorrected spectra, in neat acetonitrile (N) and acetonitrile containing 0.1 mol dm^{-3} CF_3COOH (A). [b] Excitation of isoabsorbing samples, λ_{exc} 490 nm. [c] $\phi = 5.0 \times 10^{-5}$.

Table 1 compares luminescence data for the investigated complexes in pure acetonitrile and in acetonitrile containing 0.1 mol dm^{-3} CF_3CO_2H.

The photophysical results indicate that acidification has no effect on $\mathbf{3}^{2+}$ but causes a small shift on the MLCT band in $\mathbf{2}^{2+}$, in accordance with the length of the spacer separating tpy fragments in each complex (two or one phenylene units, respectively). By contrast, the acidic solvent induces a very significant bathochromic shift of the emission for $\mathbf{1}^{2+}$. It also gives rise to an enhanced luminescence intensity and a longer excited-state lifetime as compared to the situation in neat acetonitrile (τ = 80 *vs.* 2.8 ns). In this case, the direct back-to-back connection between the two tpy units ensures a relatively strong coupling between the protonatable site and the ruthenium-containing site. This is reflected by the strong influence of protonation of the free tpy on the luminescence properties of the complex.

The spectroscopic and luminescence properties of complexes $\mathbf{1}^{2+}$–$\mathbf{3}^{2+}$ and their diprotonated forms, $H_2\mathbf{1}^{4+}$–$H_2\mathbf{3}^{4+}$ can be rationalized in terms of energy difference ΔE between the emitting MLCT and the MC states combined with the degree of delocalization[14] of the promoted electron in the MLCT excited state over the bis-tpy ligand. The protonable tpy fragment provides a remote site for control of the luminescence properties of the ruthenium(II) complex component.

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References

1 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
2 J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1991, **30**, 4230.
3 J.-P. Collin, J. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1992, **31**, 4112.
4 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Sauvage, J. P. Collin, A. Sour, E. C. Constable and A. M. W. Cargill Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7692 and references cited therein.
5 F. Barigelletti, L. Flamigni, V. Balzani, J.-P. Collin, J.-P. Sauvage and A. Sour, *New J. Chem.*, 1995, **19**, 793.
6 V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2705.
7 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.
8 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84**, 85.
9 F. Barigelletti, L. Flamigni, M. Guardigli, A. Juris, M. Beley, S. Chodorowsky-Kimmes, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 1996, **35**, 136.
10 A. C. Benniston, V. Goulle, A. Harriman, J.-M. Lehn and B. Marczinke, *J. Phys. Chem.*, 1994, **98**, 7798.
11 A. C. Benniston, V. Grosshenny, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1884.
12 K.-Y. Kim and G. H. Nancollas, *J. Phys. Chem.*, 1977, **10**, 948.
13 J. G. Vos, *Polyhedron*, 1992, **11**, 2285.
14 G. F. Strouse, J. R. Schoonover, R. Duesing, S. Boyde, W. E. Jones Jr. and T. J. Meyer, *Inorg. Chem.*, 1995, **34**, 473 and references cited therein.

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