

Luminescent pH Sensors Based on Di(2,2'-bipyridyl) (5,5'-diaminomethyl-2,2'-bipyridyl)-ruthenium(II) Complexes¹

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Luminescent pH sensors based on $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridyl) display proton assisted retrieval of luminescence in **1b–d** and proton assisted quenching of luminescence in **1a** (both due to photoinduced electron transfer) and proton promoted luminescence quenching due to the generation of positive charges in the vicinity of the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ luminophore in **1e–g** probably leading to a Ru–N bond fission in the excited state.

In the accompanying communication we demonstrated the proton-controlled fluorescence of a series of aminomethylated tetraphenylporphyrin-tin(IV) complexes.² Owing to the close resemblance of spectral and electrochemical properties of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridyl) to those of the porphyrins³ similar studies were undertaken with a series of $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{L}]^{2+}$ complexes **1a–i** and have led to a new class of pH sensors **1e–g**. $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ complexes with conjugated ion-binding sites⁴ have recently been examined in sensing contexts. The luminescent properties (not the sensing action) of $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ complexes with nonconjugated ion-binding sites⁵ (such as azacrown ethers⁶) and amines⁷ have also been reported.

We now report the first series **1a–g** of pH sensors based on $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ where the acid–base sites are buffered from the bipyridine ligand by a methylene spacer. Complexes **1a–j** and **2a,b** were synthesised from $[\text{RuCl}_2(\text{bpy})_2] \cdot 3\text{H}_2\text{O}$ and the appropriately substituted bipyridyl ligand in ethanol (80 °C) and isolated as the hexafluorophosphate salts. The 5-amino-methyl- and 5,5'-diaminomethyl-substituted ligands were synthesised from the respective bromo derivatives and amines in benzene (80 °C) containing K_2CO_3 . The bromomethylbipyridyls were synthesised from their respective methyl derivatives using *N*-bromosuccinimide in CCl_4 .⁸

Upon diprotonation, the absorption spectra maxima of **1a–g** show a *ca.* 6 nm hypsochromic shift whilst the absorption onset shows a red shift. These changes are attributed to the interaction of the protonated side chain amine across the

methylene spacer with the localized charge acquired by the bipyridyl ligand in the metal to ligand charge transfer (MLCT) excited state of the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ moiety.⁹ In complexes **1b–d** the luminescence is completely quenched at a higher pH when the amine groups are unprotonated owing to photoinduced electron transfer (PET) from the side-chain amine groups to the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ moiety (see Table 1, $\Delta G_{\text{ET}} < 0$ **1b–d**). When one of the amine groups is protonated, the luminescence of **1b–d** remains completely quenched because the monoprotonated species is a better electron acceptor than $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ itself. Therefore the retrieval of the quenched luminescence takes place only when the pH is low enough to protonate both side-chain amine groups. The diprotonated species exhibits a maximum luminescence intensity at an emission maximum of 650 nm. During the pH titration the shape of the emission spectra was preserved and the luminescence intensity was the only variable. The $\text{p}K_{\text{a}2}$ values of **1b–g** were estimated *via* eqn. (1).

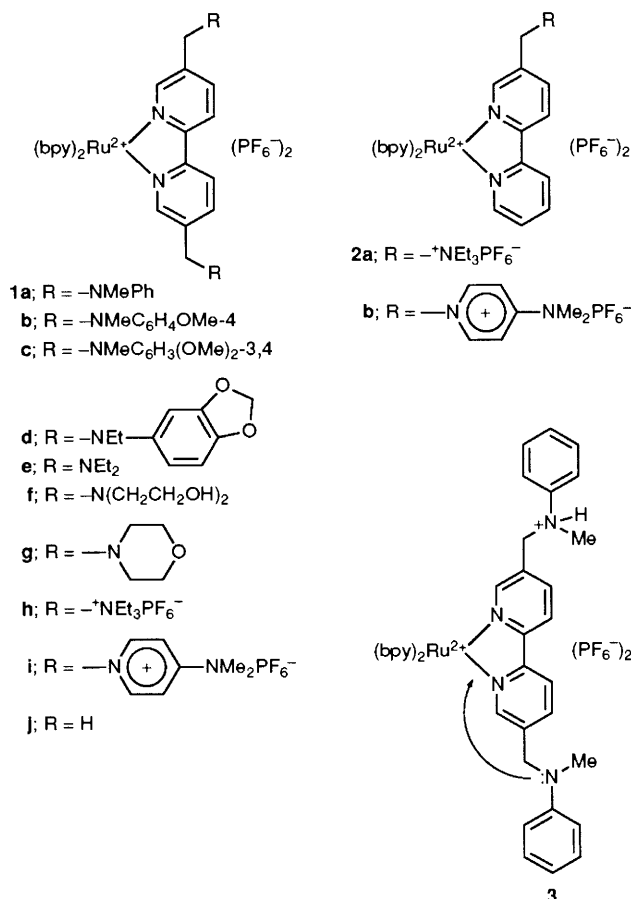
$$\log[(\phi_{\text{max}} - \phi)/(\phi - \phi_{\text{min}})] = \text{pH} - \text{p}K_{\text{a}}(\text{lum.}) \quad (1)$$

Complex **1a** behaves in a different manner to **1b–d**. At higher pH **1a** exhibits an emission maximum at 605 nm [*cf.* $\Delta G(\mathbf{1a}) = -0.09$, $\Delta G(\mathbf{1b}) = -0.28$]. Luminescence is quenched to a certain extent owing to PET compared to **1j**, at a higher pH when the amine groups are unprotonated [$\phi(\mathbf{1j}) = 0.033$, $\phi(\mathbf{1a}) = 0.023$]. In the pH range 3.8–1.8 the intensity of emission drops while the emission spectral maximum and

Table 1 Luminescence and pK_a data for the complexes **1a-g**^a

Complex	pK_a^d (abs.)	pK_{a1}^e (lum.)	pK_{a2}^e (lum.)	pK_a (model)	ΔpK_a^i (lum.)	Diprotinated		Unprotonated		$\Delta G(ET)/$ eV ^h
						λ_{em}^c	ϕ^b	λ_{em}^c	ϕ^b	
1a	1.50	2.4 ^f	—	5.00	2.6	653	0.009	605	0.023	-0.09
1b	2.0	—	2.4 ^g	—	—	653	0.011	—	>0.001	-0.28
1c	1.9	—	1.9 ^g	—	—	653	0.011	—	>0.001	-0.049
1d	2.2	—	2.3 ^g	—	—	653	0.010	—	>0.001	(>0)
1e	6.0	7.8	5.9	10.3	4.4	653	0.012	610	0.038	0.00
1f	4.1	5.4	4.1	8.6	4.5	653	0.010	610	0.039	(>0)
1g	3.5	5.8	3.9	7.4	3.5	653	0.009	610	0.038	(>0)

^a 50% (v/v) aqueous methanol (10^{-6} mol dm⁻³). pH range 0–12, 25 °C, $\mu = 0.01$ mol dm⁻³,¹⁰ $\lambda_{ex} = 473$ nm for **1a–j**; 20 nm slits. Data analysis: least squares, average gradient 0.9–1, correlation coefficient 0.9–1, no of points >10. ^b Quantum yields were measured on aerated solutions by comparison with [Ru(bpy)₃]²⁺ in aerated H₂O.¹¹ **1j** in 50% (v/v) aqueous methanol had $\phi = 0.033$ (λ_{em} 610 nm). ^c λ_{em} Values reported are from uncorrected emission spectra. The spectra were corrected for the photomultiplier response using the usual standards, *i.e.* aluminium complex of 2,2'-dihydroxy-1,1'-azonaphthalene-4-sulfonic acid¹² and 4-*N,N*-dimethylamino-4'-nitrostilbene¹³ (for example the corrected λ_{em} for diprotinated **1a–g** was 680 nm). Corrected spectra were used to calculate quantum yields. ^d pK_a (abs.) was calculated using $(A_{max} - A)/(A - A_{min}) = pH - pK_a$ (abs.) measuring absorbance at 450 nm in a pH titration. The isobestic point was 473 nm in **1a–g**. ^e pK_a (lum.) was calculated using eqn. (1) measuring luminescence intensity at 606 nm with pH. (Quantum yield vs. pH plots gave the same pK_a values within experimental error.) ^f First protonation leads to luminescence quenching. ^g Only the second protonation leads to luminescence in **1b–d**. ^h Calculated from the Weller equation¹⁴ $\Delta G = -E_s + E_{ox}(\text{amine}) - E_{red}[\text{Ru}^{II}(\text{bpy})_3]^{2+} - E_{i.p.}$. E_s and reduction potential of [Ru^{II}(bpy)₃]²⁺ are from ref. 3 and E_i oxidation potentials for amines are from refs. 14 and 15. The ion-pairing energy (0.1 eV; $E_{i.p.}$) is from ref. 16. ⁱ ΔpK_a (lum.) = pK_a (model) - pK_{a2} (lum.).



shape are retained. This is attributed to PET from the free amino group of monoprotonated **1a** to the [Ru^{II}(bpy)₃]²⁺ moiety (**3**, arrow). In **3** the effect of the additional positive charge in the vicinity of the [Ru^{II}(bpy)₃]²⁺ moiety will be to lower the reduction potential of **3** which in turn makes the $\Delta G(ET)$ for **3** sufficiently negative for the remaining unprotonated amine moiety to transfer an electron to the [Ru^{II}(bpy)₃]²⁺ group. From pH 1.8 to 0.6 the emission maximum shifts gradually to a limiting value of 650 nm at lower pH when both side-chain amine groups are protonated.

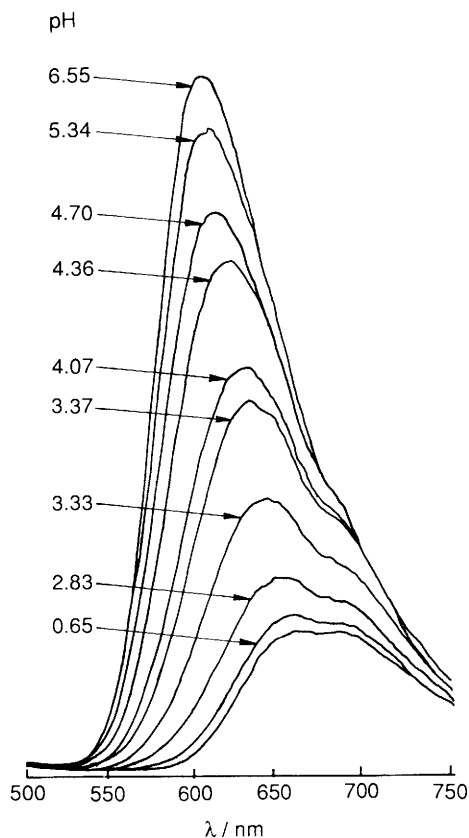


Fig. 1 Emission spectral variations of **1f** as a function of pH in 50% (v/v) MeOH-H₂O. The pH values are, in order of decreasing intensity, 6.55, 5.34, 4.70, 4.36, 4.07, 3.37, 3.33, 2.83 and 0.65.

When both amine groups are protonated **1a** exhibits the same emission spectrum as **1b–d** and the ϕ values are comparable with those of the diprotinated forms of **1b–d** (Table 1).

The shifted emission maximum of **1a–d** (650 nm) compared to **1j** (610 nm) and the low quantum yield of **1a–d** when diprotinated led us to investigate further the effect of positive charges on the excited state properties of the [Ru^{II}(bpy)₃]²⁺ moiety. For this purpose we chose the complexes **1e–g** where the complications due to photoinduced electron transfer are

Table 2^a Absorption and emission data for selected complexes

Complex	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon \times 10^4$)	$\lambda_{\text{em}}/\text{nm}$	ϕ
1j	450 (1.52)	610	0.033
2b	450 (1.16)	630	0.030
2a	446 (1.16)	640	0.021
1i	446 (1.39)	645	0.020
1h	437 (1.18)	653	0.008

^a Absorption and emission characteristics of all the complexes are independent of pH (0–12) in 50% (v/v) aqueous methanol. The effective positive charge of the side chain(s) increases in the order **1j** < **2b** < **2a** (monosubstitution) and **1j** < **1i** < **1h** (disubstitution).

minimised [$\Delta G(\text{ET}) = 0$ or >0 for **1e–g**]. These complexes show a red shift in the emission maximum from 610 nm to 653 nm (*cf.* emission maxima and quantum yield for diprotonated **1a–d**) as well as a drop in luminescence intensity as both side-chain amines become protonated (Fig. 1). The ϕ vs. pH profiles of **1e–g** show that ϕ varies across 3–3.5 pH units and arises from two discrete protonation equilibria, each of which fit eqn. (1). The corresponding pK_a values are given in Table 1.

Luminescence quenching in **1e–g** arises from location of the double positive charge, consequent on protonation of both amine groups, in the vicinity of the $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ moiety and this represents a new mechanism for luminescent pH sensing action. That diprotonation of the amino groups is responsible for these effects is shown by the spectral data of **1h** (Table 2) which are very similar to data of diprotonated **1a–g**. This is further confirmed by observations on **1i** in which the positive charges are delocalised and on the monosubstituted versions **2a** and **2b**. Table 2 clearly shows the correlation between effective positive charge on the side chain and the ϕ and λ_{em} values. A closely related example is where the luminescence is quenched upon bringing an external positive charge (Ag^+) close to $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$.¹⁷ The quenching of luminescence in this latter case was thought to be due to the formation of a luminescent exciplex between $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and Ag^+ . Our results suggest that the proximity of the cation is the major causative factor.

How do the proximal charges cause the luminescence quenching required for sensor action? The presence of cationic side chains can encourage the photofission of an Ru–N bond possibly *via* a d–d state,¹⁸ to a five-coordinate intermediate which may hydrate to restore six-coordination.¹⁹ The monoquo complex would then thermally return to the original trisbipyridyl coordination, since sensors **1** and **2** are photostable as is the model compound **1j**.^{18–20}

In conclusion, the use of MLCT lumophores results in luminescent pH sensors *via* two mechanisms. One involves

photoinduced electron transfer and the other originates from the presence of proximal charges.

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