Luminescent pH Sensors based on *p-tert*-Butylcalix[4]arene-linked Ruthenium(II) Trisbipyridyl Complexes

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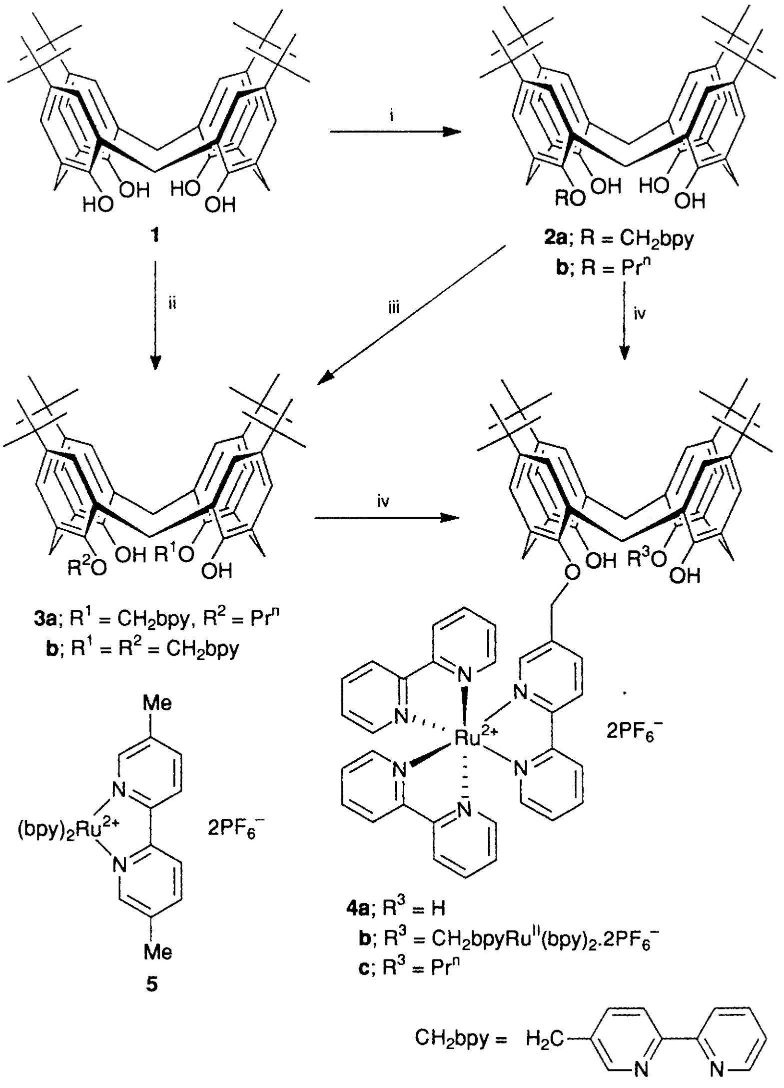
p-tert-Butylcalix[4]arene-linked trisbipyridylruthenium(II) complexes **4a** and **4b** show luminescent pH sensor action, in 50% (*v*/*v*) aqueous methanol, by operation of an intramolecular photoinduced electron transfer (PET) process.

Calixarenes and their derivatives have been extensively studied as hosts for both neutral and ionic species[1,2] and calixarene-based chromionophores[3] for Li^+, Na^+, K^+ and Ca^{2+}, and fluorionophores[4,5] for Na^+ and Li^+ have been prepared and shown to act as sensors. In addition to a calixarene-derived fluorescent sensor for neutral molecules[6] and an electrochemical sensor for anions,[7] luminescent lanthanide ion binding calixarenes are also known.[8] We have recently reported pH PET[9] sensors based on aminomethyltetraphenylporphyrin-tin(IV)[10] and aminomethylbipyridyl–ruthenium(II) complexes.[11] We now report the first example of a calixarene-based pH (PET) sensor.

The trisbipyridylruthenium(II) moiety was chosen as the luminophore with the free phenolic units of a calix[4]arene acting as the acid–base sites. These two units were coupled by a methylene spacer both to maximise the electron transfer rate and to buffer the units from one another. Formation of the phenolate anion(s) causes photoinduced intramolecular electron transfer to take place from the phenoxide ion to the trisbipyridylruthenium(II) moiety thus quenching the luminescence (an intermolecular PET process between phenoxide ions and the trisbipyridylruthenium(II) moiety is known[12]). Once the phenolate ions are protonated no such electron transfer takes place and hence luminescence is restored.

The synthesis of the trisbipyridylruthenium(II)-linked calixarenes **4a–c** is outlined in Scheme 1.[†] The ^1H and ^{13}C NMR spectra for **2a,b**, **3a,b** and **4a–c** indicated that they existed in the cone conformation.[13] This was also found to be the case in the solid state as shown by preliminary X-ray data for **4c**.

The metal-to-ligand charge transfer (MLCT) band of the complexes **4a** and **4c** are identical to that of unsubsituted bisbipyridyl(5,5'-dimethyl-2,2'-bipyridyl)ruthenium(II) **5**



Scheme 1 *Reagents and conditions*: i, RBr, BaO, $Ba(OH)_2 \cdot 8H_2O$, dimethylformamide; ii, for **3b**, 2 $BrCH_2bipy$, K_2CO_3, acetone, reflux; iii, for **3a**, $BrCH_2bipy$, K_2CO_3, acetone, reflux; iv, *cis*-$Ru^{II}(bipy)_2Cl_2 \cdot 0.5H_2O$, EtOH, reflux, then NH_4PF_6, MeOH

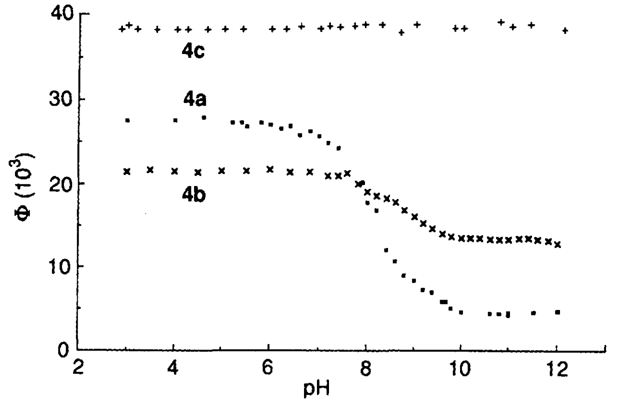


Fig. 1 Φ_{lum} for (**4a–c**) *vs.* pH in 50% *v*/*v*) aqueous methanol

whilst **4b** showed a bathochromic shift.‡ This can be attributed to an intramolecular stabilisation of the charge acquired by one of the bipyridine ligands in the excited state by the neighbouring trisbipyridylruthenium(II) moiety.

Emission spectral properties did not change with pH except for the luminescence intensity of complexes **4a** and **4b**. A plot of Φ_{lum} (quantum yield of luminescence) *vs.* pH for **4a** gave a single step (Fig. 1) with a pK_a of 8.1 (Table 1). However, the first deprotonation takes place at the distal phenol unit (pK_a 4.5)§ because the resulting phenolate anion can be stabilised by bifurcated hydrogen bonding with adjacent phenolic hydroxy groups. This, therefore, indicates that it is the proximal phenol unit which is responsible for the luminescence quenching observed in compound **4a**. Strong hydrogen bonding of the phenolate ion increases the oxidation potential of the distal phenoxide ion and the greater distance between the trisbipyridylruthenium(II) moiety and the distal phenol unit, compared to the proximal unit, also contributes to the lack of electron transfer from the distal phenoxide.

Compound **4c**, with a blocked distal phenol unit, was synthesised to probe this behaviour. However, **4c** showed no quenching. When the distal phenol unit of **4a** is functionalised with a second trisbipyridylruthenium(II) moiety, as in compound **4b**, then luminescence quenching is observed, to a certain extent, in the pH region 2–12 (Fig. 1) with a pK_a of 8.5 (Table 1). [A greater degree of quenching than that observed might be expected due to the presence of the two trisbipyridylruthenium(II) substituents]. The small degree of quenching seen in **4b** might be due to the fact that in polar solvents (in this case 50% *v*/*v* aqueous methanol) the first solvation shell for ionic species is very tightly bound compared to that of neutral species and this together with the steric crowding imposed by the two trisbipyridylruthenium(II) moieties on bound solvent molecules in **4b** impedes the solvent reorganisation required for electron transfer.[14] Compound **4c** is then also a victim of the effect of steric crowding on solvent reorganisation. The reduced PET rate in **4b** and **4c** could also be due to steric exclusion of polar solvent molecules from the PET sites. Rates of PET are known to be strongly influenced by solvent polarity.[15]

Even though there are no changes in the MLCT band, examination of the absorption spectra, as a function of pH, for compounds **4a–c** revealed that small but significant changes do occur in the region 190–270 nm. This allowed the estimation of ground state pK_a values for compounds **4a–c** (Table 1) and since ground and excited state pK_a values are the same[16] for **4a** and **4b** then compound **4c** should have a pK_a of *ca.* 8.8 in the excited state.

The notion that the order of Φ_{max} in aerated solutions (Table 1) arises from a varying degree of steric hindrance imposed, by the calixarene itself, upon oxygen quenching of luminescence in **4a–c** can be ruled out since the Φ_{max} order is preserved in degassed solutions (**4c** > **4a** > **4b**).

Table 1 Properties of complexes **4a–c**[a]

Complex	λ_{abs}/nm ($\varepsilon \times 10^4$)	λ_{em}/nm[b]	Φ_{max}[c,d] (degassed)	Φ_{max}[c] (aerated)	pK_a[e] Abs.	pK_a[e] Lum.
4a	452 (2.0)	606	0.055	0.027	8.1	8.1
4b	450 (2.1)	606	0.047	0.021	8.6	8.5
4c	453 (2.3)	610	0.072	0.038	8.8	—

[a] Solutions were made up in 50% (*v*/*v*) aqueous methanol (10^{-6} mol dm^{-3}) containing 0.02 mol dm^{-3} tetraethylammonium chloride; excitation slit 5 nm, emission slit 10 nm; data analysis by least squares; average gradient 0.9–1, correlation coefficient 0.9–1, number of points > 10 for luminescence studies, > 6 for absorption studies. [b] Uncorrected. [c] Quantum yields were estimated by comparison with an aerated solution of compound **5** in 50% *v*/*v* aqueous methanol (Φ = 0.033).[11] [d] Samples were degassed by passing a stream of argon through them until no further change in emission intensity was observed. [e] pK_a (abs.) could be estimated from small but significant changes in the absorption spectra in the region 190–270 nm. pK_a (abs.) and pK_a (lum.) were calculated using the Henderson–Hasselbalch-type mass action equations: (1) $\log[(A_{max} - A)/(A - A_{min})] = pK_a$ (abs.) −pH, and (2) $\log[(\Phi_{max} - \Phi)/(\Phi -_{min})] = pK_a$ (lum.) − pH, respectively.

The Φ_{max} value for compound **5** is also larger in degassed solution (0.083 in 50% *v*/*v* aqueous methanol).

Since the luminescence quenching of trisbipyridylruthenium(II) by electron-rich phenols *via* a PET process is known,[12] then by taking 2,4,6-trimethylphenol as a mimic for the relevant calixarene acid–base site a ΔG(ET)¶ of −0.10 can be estimated; the luminescence quenching in **4a** and **4b** at lower pH, compared to **5**, most probably arises owing to a varying degree of PET processes taking place from the calixarene to the trisbipyridylruthenium(II) moiety. A ΔG(ET) for a PET process between *p-tert*-butylcalix[4]arene and the trisbipyridylruthenium(II) moiety cannot be estimated owing to the non-availability of electrochemical data for the calixarene.

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Footnotes

† All new compounds were characterised by ^{1}H NMR and IR spectroscopy, FAB MS and elemental analysis.

‡ Compounds **4a–c** obeyed the Beer–Lambert law in the concentration region 10^{-5}–10^{-6} mol dm^{-3} (*i.e.* there were no complications due to aggregation).

§ Value obtained from absorption *vs.* pH studies.

¶ The ΔG(ET) value was estimated using the Weller equation: $\Delta G(\text{ET}) = -E_s + E_{ox}$ (phenol) $-E_{red}[\text{Ru(bpy)}_3]$ $-E_{i.p.}$ (for parameters used see ref. 14).

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