Phosphate anion binding and luminescent sensing in aqueous solution by ruthenium(II) bipyridyl polyaza receptors

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Letter

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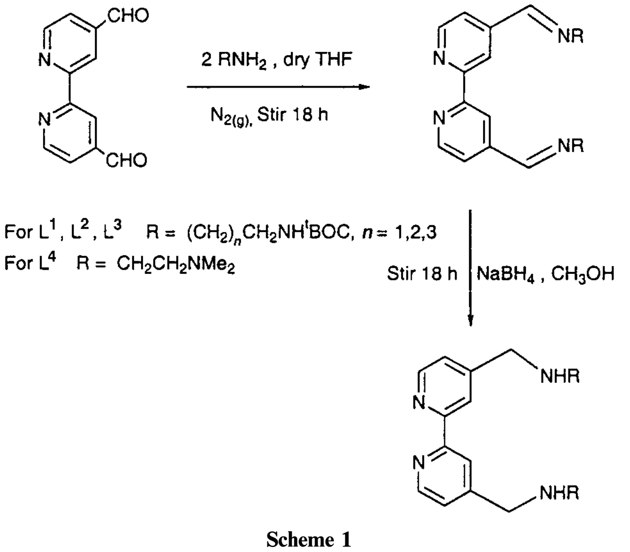
New ruthenium(II) bipyridyl polyaza receptors have been prepared and shown to bind and sense, *via* MLCT luminescent emission quenching, phosphate and ATP anions in aqueous solution.

Anionic guest species play a pivotal role in biological processes and their effects as environmental pollutants are now being realised.[1] In consequence of this there is a growing need for the construction of specific receptors containing signalling or reporter groups that have the capability of sensing anions in solution.[2] Water in particular is a challenging medium in which to detect the anion recognition event as anion hydration energies are large.[3] Rare examples of luminescent anion responsive systems have combined the anthracene fluorophore with polyammonium,[4] guanidinium[5] and zinc(II) amine[6] anion recognition sites. In addition cyclen appended phenanthridinium europium and terbium complexes are showing promise as luminescent sensors for halide and hydroxide ions in water.[7] We report here a new class of anion luminescent sensor consisting of a series of new ruthenium(II) bipyridyl polyaza receptors which bind and detect phosphate anions in water *via* MLCT luminescent emission quenching.

The condensation of 4,4′-diformyl-2,2′-bipyridine[8] with two equivalents of the appropriate mono-BOC protected diamine and *N*,*N*′-dimethylethylenediamine followed by *in situ* sodium tetrahydroborate reduction gave the new bipyridyl substituted amine compounds in 70–75% yield (Scheme 1).

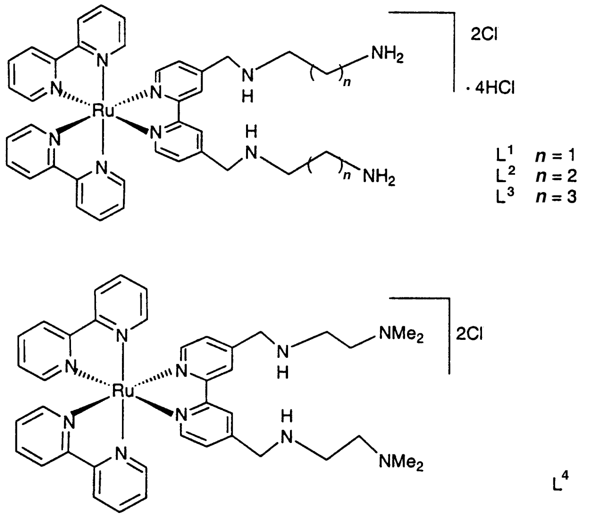
Refluxing these compounds with (bipy)$_2$RuCl$_2 \cdot 2$H$_2$O in aqueous ethanol for 18 hours and subsequent addition of hydrochloric acid afforded the new receptors L^1–L^4 isolated as hydrochloride salts in near quantitative yield (Scheme 2).

Potentiometric methods in water using the SUPERQUAD program[9] (0.1 M KNO$_3$, 25 °C) enabled speciation diagrams, protonation and receptor–phosphate complex stability constant values to be determined for L^1–L^4. Table 1 shows, as expected, pK_a values increase as the diamine alkyl spacer increases from L^1 to L^3. Taking into account speciation diagrams and the respective pK_a values of the receptors and phosphate and ATP, Tables 2 and 3 report the various receptor–anion complex species stability constant values. All the receptors bind both phosphate and ATP with the strength of binding dependent upon levels of protonation of receptor and guest anion.† As expected there is a general selectivity preference for ATP over phosphate and obviously chloride and nitrate.



Scheme 1

The luminescent properties of the Ru(bipy)$_3{}^{2+}$ centre are well documented[10] and we have recently shown that perturbation of the emission spectra of ruthenium(II) bipyridyl amide based receptors in polar DMSO and acetonitrile organic solvents occurs upon halide and dihydrogen phosphate binding.[11] It was of interest therefore to investigate whether



Scheme 2

Table 1 Protonation constants for L^1–L^4 receptors

Receptor	p$K_a{}^1$	p$K_a{}^2$	p$K_a{}^3$	p$K_a{}^4$
L^1	10.12(2)[a]	8.97(2)	5.00(3)	3.53(4)
L^2	10.37(1)	9.68(1)	6.71(1)	5.65(2)
L^3	10.77(1)	10.09(1)	7.57(1)	6.65(2)
L^4	8.37(2)	4.35(3)	2.78(3)	*ca.* 1.50[b]

[a] Figures in parentheses are the standard deviations of the last digit. [b] p$K_a{}^4$ was difficult to refine successfully with the program SUPERQUAD as it is low.

Table 2 Stability constants for receptor–phosphate complexes[a]

Receptor	LH_6PO_4 as $LH_4^{4+} \cdot H_2PO_4^-$	LH_5PO_4 as $LH_3^{3+} \cdot H_2PO_4^-$	LH_4PO_4 as $LH_2^{2+} \cdot H_2PO_4^-$	LH_3PO_4 as $LH_2^{2+} \cdot HPO_4^{2-}$	LH_2PO_4 as $LH^+ \cdot HPO_4^{2-}$
L^1	—	4.97(1)	3.78(2)	3.62(1)	3.09(1)
L^2	4.09(9)	3.22(7)	3.65(4)	3.39(3)	3.34(4)
L^3	—	2.03(9)	2.69(3)[b]	2.87(4)	3.41(4)
L^4	—	9.31(9)	7.91(6)	5.77(4)[c]	4.67(3)

[a] log β's for KH_2PO_4 in H_2O at 25 °C, 0.1 M KNO_3 are 12.03, 7.03, 2.64. [b] As $LH_3^{3+} \cdot HPO_4^{2-}$. [c] As $LH^+ \cdot H_2PO_4^-$.

these water soluble receptors were capable of sensing anions *via* MLCT emission perturbation in the aqueous environment.

The luminescent behaviour of L^1–L^4 in the pH range 2–10 was investigated *via* titration of the respective tetrahydrochloride compound with base, using HNO_3 to lower the pH. The emission intensity *versus* pH and MLCT λ_{max} profile for L^1 is shown in Fig. 1. As the solution becomes more acidic an increase in the emission intensity is observed which reaches a maximum at pH *ca.* 5.5 before a gradual quenching effect occurs towards lower pH values. Concomitant with this emission intensity variation there is a red shift of the MLCT λ_{max} from 605 nm at high pH values to 625 nm at pH ⩽ 4. Similar observations were also obtained with L^2 and L^3 receptors. At high pH where the amine groups remain largely unprotonated the luminescence is quenched *via* photoinduced electron transfer (PET) from the unprotonated amine groups to the $Ru(bipy)_3^{2+}$ moiety. Retrieval of quenched luminescence takes place as the pH is lowered and the amine groups become protonated. Why luminescence quenching occurs at pH values ⩽ 5.5 is difficult to rationalise. Grigg *et al.*[12] reported similar quenching behaviour at low pH with 5,5′-diaminomethyl-2,2′-bipyridyl ruthenium(II) complexes. They attributed the quenching to the location of proximal protonated amine positive charges in the vicinity of the $Ru(bipy)_3^{2+}$ moiety which may lead to Ru–N bond fission in the excited state. A similar mechanism could be in operation here, at lower pH the pK_a values of L^1–L^3 (Table 1) suggest protonation of the bipyridyl–CH_2–amino groups occurs generating positive charges in close proximity to the ruthenium(II) bipyridyl centre.

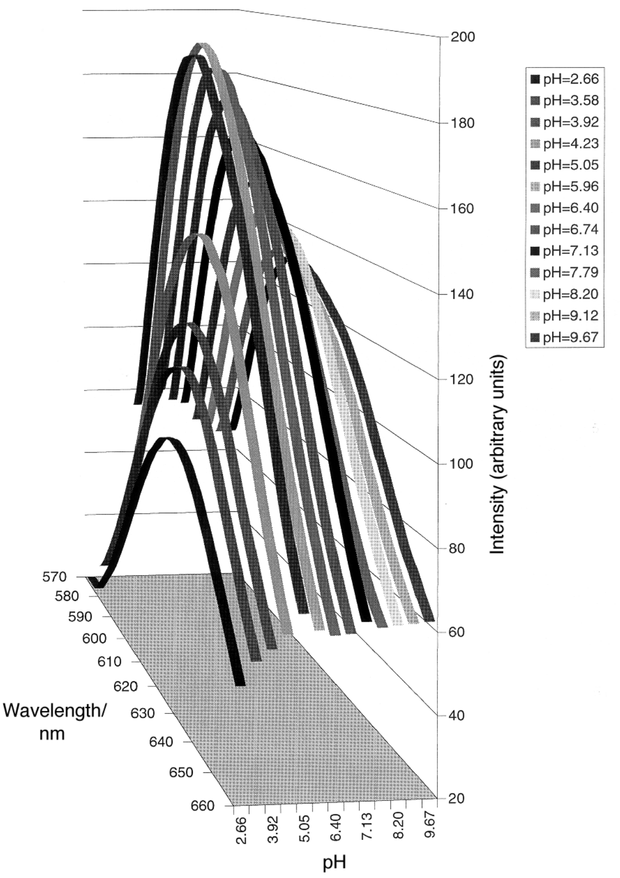


Fig. 1 pH dependence of luminescence intensity and wavelength for L^1 (10^{-5} M). Colour version available at: http://www.rsc.org/suppdata/nj/1999/347/.

The luminescence pH titration curve for L^4 (Fig. 2) displays similar quenching characteristics at lower pH, however, at higher pH values (pH > 7) there is a gradual increase in emission intensity.

The addition of KH_2PO_4 and Na_2H_2ATP salts to non-deaerated‡ buffered aqueous solutions of L^1–L^4 at pH 6 resulted in significant quenching of luminescence (Fig. 3) by up to 15%. Analogous anion titration experiments with $Ru(bipy)_3^{2+}$ produced no effect. These phosphate anion induced quenching effects contrast with ruthenium(II) bipyridyl amide systems exhibiting an intensity enhancement of luminescence emission response to chloride and dihydrogen phosphate anions in acetonitrile and DMSO solutions.[11] The

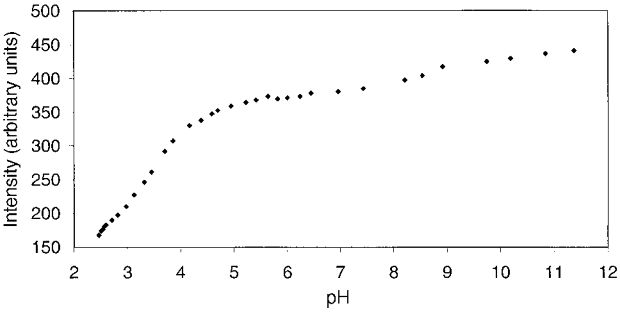


Fig. 2 pH dependence of luminescence intensity and wavelength for L^4 (10^{-5} M) in water, $T = 25$ °C.

Table 3 Stability constants for receptor–ATP complexes[a]

Receptor	LH_7ATP as $LH_4^{4+} \cdot H_3ATP^-$	LH_6ATP as $LH_4^{4+} \cdot H_2ATP^{2-}$	LH_5ATP as $LH_3^{3+} \cdot H_2ATP^{2-}$	LH_4ATP as $LH_3^{3+} \cdot HATP^{3-}$	LH_3ATP as $LH_2^{2+} \cdot HATP^{3-}$	LH_2ATP as $LH_2^{2+} \cdot ATP^{4-}$
L^1	—	5.02(8)	5.13(7)	5.22(5)	4.27(5)	3.74(3)
L^2	4.83(5)	3.79(6)	4.37(4)[b]	5.21(2)	4.62(2)	3.28(2)
L^3	4.12(4)	2.75(9)	3.41(4)[b]	4.99(1)	3.66(2)[d]	1.89(9)
L^4	—	—	4.28(9)	3.53(9)[c]	4.14(9)	—

[a] log β's for Na_2H_2ATP in H_2O at 25 °C, 0.1 M KNO_3 are 6.78, 4.01, 2.03. [b] As $LH_4^{4+} \cdot HATP^{3-}$. [c] As $LH_2^{2+} \cdot H_2ATP^{2-}$. [d] As $LH_3^{3+} \cdot ATP^{4-}$.

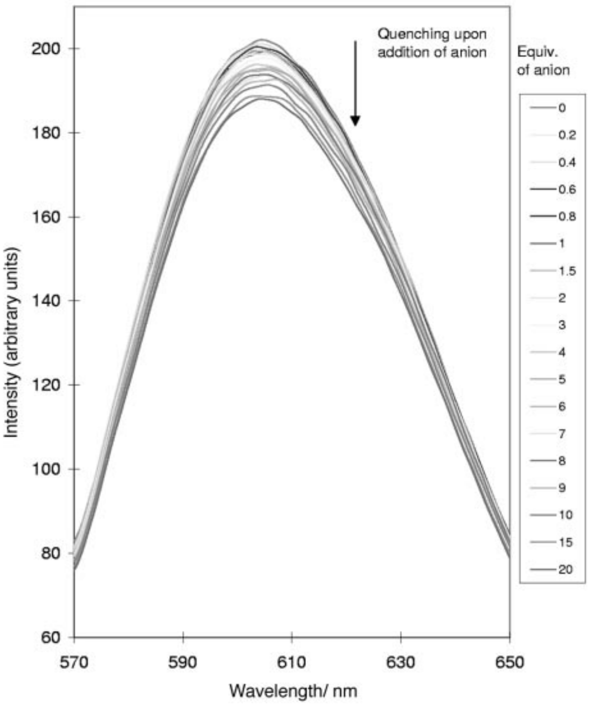


Fig. 3 Emission spectral titration of KH_2PO_4 with L^1 (10^{-5} M) in water at pH = 6.02 buffered with *N*-morpholinoethylsulfonic acid (MES) (10^{-2} M), $T = 25\,°C$. Colour version available at: http://www.rsc.org/suppdata/nj/1999/347/.

formation of a receptor–anion complex that increases the rigidity of the receptor, thereby disfavouring the non-radiative decay processes can tentatively explain the latter effect in organic solvents. However, further photophysical investigations are needed to determine the nature of this anion–receptor quenching mechanism in water.

This preliminary study has demonstrated that these new ruthenium(II) bipyridyl polyaza receptors represent a new class of anion luminescent sensor capable of binding and sensing phosphate and ATP anions in the aqueous environment.

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Notes and references

† ^{31}P NMR titration experiments in D_2O gave evidence for 1 : 1 stoichiometric complexes with ATP.

‡ Analogous anion titration experiments in argon aerated aqueous solutions gave very similar quenching observations.

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Letter 9/01534E