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Luminescent anion recognition: probing the interaction between dihydrogenphosphate anions and Ru(II) polypyridyl complexes in organic and aqueous media

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Abstract

A photophysical study of the interaction between dihydrogen phosphate anions and a series of ruthenium polypyridyl complexes containing anion receptor 4,4'-bis[(2-methoxyethyl)carbamoyl]-2,2'-bipyridine (**L1**) is reported. The complexes investigated are of the type $[\text{Ru}(\text{L})_2(\text{L1})\text{X}_2]$ and $[\text{Ru}(\text{L1})_3\text{X}_2]$, where **L** is 2,2'-bipyridyl or 1,10-phenanthroline and **X** is chloride or PF_6^- . The emission properties of the compounds are studied as a function of the anion concentrations using emission lifetime and steady-state measurements. For the mixed ligand complexes the emission intensity and lifetime increases upon the addition of 2.5 molar equivalents of H_2PO_4^- , further additions do not result in further increases. For $[\text{Ru}(\text{L1})_3\text{X}_2]$ the emission increases upon addition of the first 2.5 equivalents of dihydrogen phosphate, however, further increases lead to a decrease in both emission intensity and lifetime. The effect of the addition of trace amounts of water is also examined.

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Keywords: Anion; Receptor; Emission intensity; Complexes; Ruthenium

1. Introduction

In recent years there have been concerted efforts to design electrochemical and optical sensing devices based on transition metal based receptors [1]. Because of their stability and favourable redox and luminescent properties ruthenium(II)bipyridyl compounds have been extensively studied as potential sensing molecules [2–4]. To obtain receptor complexes based on these components chemical modification of 2,2'-bipyridyl ligands, mostly at the 4 and 4' positions, has been carried out. For anion recognition applications, this has often involved the addition of acyclic groups containing amide moieties, which serve as hydrogen bond donors. Steady-state emission data suggested that in solutions with receptor/anion ratios of between 5 and 50 $[\text{Ru}(\text{bpy})_2(\text{L1})]^{2+}$, where bpy is 2,2'-bipyridyl and **L1**

is 4,4'-bis[(2-methoxyethyl)carbamoyl]-2,2'-bipyridine, (Fig. 1) binds chloride and phosphate anions, whereas the emission properties of $[\text{Ru}(\text{L1})_3]^{2+}$ are sensitive to the addition of chloride [5,6]. For **1** the addition of chloride results in an increase of emission intensity, while upon the addition of phosphate anions this intensity is seen to decrease. For **3** the interaction with phosphate has not been reported.

In this contribution an emission study on the interaction between compounds of this type and dihydrogen phosphate anion is reported. The complexes investigated are of the type $[\text{Ru}(\text{L})_2(\text{L1})\text{X}_2]$ where **L** is 2,2'-bipyridyl, (compound **1**) 1,10-phenanthroline (compound **2**) and $[\text{Ru}(\text{L1})_3\text{X}_2]$, (compound **3**) and **X** is PF_6^- (**1–3**) or chloride (**1a** and **3a**). The results obtained show that an increase in emission intensity and lifetimes is observed for all three compounds up to 2.5 molar equivalents of phosphate added. At higher concentrations the behaviour of **1** and **2** is significantly different from that observed for **3**. It is also shown that the interaction between the receptor and the anion is extremely sensitive to the presence of traces of water.

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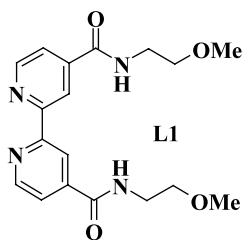


Fig. 1. Structure of the receptor ligand L1.

2. Experimental

2.1. Materials

All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. All other reagents were of HPLC grade or spectroscopic grade (Merck UVA-SOL). A 0.4 M solution of tetrabutylammonium dihydrogen phosphate in anhydrous acetonitrile (Sureseal, Aldrich) was used as a stock solution.

2.2. Titration studies

Steady-state emission titrations were carried out by the addition of 0.1 cm³ aliquots of a 0.4 M solution of dihydrogen phosphate in anhydrous acetonitrile with a micro syringe to a 250 cm³ acetonitrile solution of the appropriate ruthenium complex (1×10^{-5} M). Emission measurements were then made after a minimum of 10 min equilibration. Emission lifetime measurements were carried out in air saturated hplc grade acetonitrile containing the ruthenium compounds (1×10^{-5} M).

2.3. Spectroscopy

¹H NMR Spectra were obtained in [D₃]acetonitrile or [D₆]DMSO and recorded on a Bruker Avance 400 (400 MHz) NMR spectrometer. UV–Vis absorption spectra (accuracy ± 2 nm) were recorded on a Shimadzu UV–Vis–NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV–Vis data manager. Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a Perkin-Elmer LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R298 detector, interfaced with an Elonex PC466 employing Perkin-Elmer FL WINLAB custom built software. Emission and excitation slit widths were 10 nm at 298 K. Emission spectra are uncorrected for photomultiplier response. 10 mm pathlength quartz cells were used for recording spectra.

2.4. Single photon counting

Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) Time-

Correlated Single-Photon Counting apparatus comprising of two model J-yA monochromators (emission and excitation), a single photon photomultiplier detection system model 5300, and a F900 nanosecond flashlamp (N₂ filled at 1.1 atm pressure, 40 kHz), interfaced with a personal computer via a Norland MCA card. A 500 nm cut off filter was used in emission to attenuate scatter of the excitation light (337 nm), luminescence was monitored at 640 nm. Data correlation and manipulation was carried out using EAI F900 software version 5.1.3. Emission lifetimes were calculated using a single exponential fitting function; Levenberg–Marquardt algorithm with iterative reconvolution (Edinburgh instruments F900 software). The reduced χ^2 and residual plots were used to judge the quality of the fits. Lifetimes are $\pm 7\%$.

3. Synthetic procedures

3.1. Ligand synthesis

In a slight modification of the literature method [7] L1 was obtained via a condensation reaction of 4,4'-bisdiethylester of 2,2'-bipyridine with 2-methoxyethylamine. The use of the diester, which was obtained via the esterification [8] of 4,4'-bis(dicarboxy)-2,2'-bipyridyl [9] increases the ease of the preparation because of its increased stability with respect to the acid chloride originally used.

3.2. Synthesis of metal complexes

3.2.1. [Ru(bpy)₂(L1)](PF₆)₂·2H₂O, (I)

L1 (358 mg, 1 mmol) and [Ru(bpy)₂Cl₂]₂·2H₂O (550 mg, 1.06 mmol) were heated at reflux overnight in EtOH/H₂O 80/20 (80 cm³). Ethanol was removed by rotary evaporation and the orange oil further diluted with water. The product was precipitated by the addition of a saturated aqueous solution of NH₄PF₆. The resulting solid was filtered, washed with water, air dried, and recrystallised from acetone/water to yield the product as an orange solid (650 mg, 61%).

NMR *d*₆-DMSO, δ_{H} (400 MHz) 3.25 (6H, s, 2 \times CH₃), 3.5 (8H, m, 4 \times CH₂), 7.5 (4H, 2 \times t, bpy 5,5'), 7.71 (2H, d, pyr 5,5'), 7.76 (2H, d, pyr 3,3'), 7.84 (2H, d, pyr 6,6'), 7.91 (2H, d, bpy 6,6'), 8.18 (4H, q, bpy 5,5'), 8.84 (4H, d, and bpy 3,3'), 9.23[#] (4H, br s, 4 \times NH). # = exchanges with D₂O. δ_{C} ¹³C NMR (CD₃CN) 162.9 (CONH), 157.2 (Bpy 2,2', qC), 156.5 (Pyr 2,2', qC), 152.2 (Pyr 6,6'), 151.5 (Bpy 6,6'), 142.2 (Pyr 4,4', qC), 137.8 (Bpy 4,4'), 127.4 (Bpy 3,3'), 124.7 (Pyr 3,3'), 124.1 (Bpy 5,5'), 121.7 (Pyr 5,5'), 69.7 (OCH₂), 57.5 (OCH₃), 39.4 (NCH₂). Elemental analysis; C₃₈H₃₆N₈O₆RuP₂F₁₂ requires C, 41.80; H, 3.30; N, 10.25%; Found: C, 41.80; H, 3.47; N, 10.10.

3.2.2. $[Ru(bpy)_2(L1)](Cl)_2$ (**1a**)

1a was prepared using the procedure outlined above for the PF_6 salt with the following modification. After removal of all of the solvent from the reaction mixture, the residue was taken up in a minimum volume of ethanol. Small quantities of the orange solid could be isolated by the slow addition of the ethanol solution into a large quantity of well-stirred, cold, diethyl ether. 1H NMR and hplc indicate that the metal cation is identical to that obtained in **1**.

3.2.3. $[Ru(phen)_2(L1)](PF_6)_2 \cdot 2H_2O$ (**2**)

A solution of $[Ru(phen)_2Cl_2]$ (75 mg, 0.13 mmol) and **L1** (50 mg, 0.14 mmol) in 80% ethanol (50 cm³) heated at reflux for 5 h. After removal of ethanol by rotary evaporation the product was precipitated as the PF_6 salt by addition of a concentrated aqueous solution of ammonium hexafluorophosphate. The orange solid was filtered, washed with water and recrystallised from acetone:water 50:50 (136 mg, 89%).

NMR: δ_H CD_3CN (400 MHz) 8.97 (2H, d, $J = 1.2$ Hz, pyr 3, 3'), 8.70 (2H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, phen 4,4'), 8.61 (2H, dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, phen 7,7'), 8.28 (4H, q, pyr 5,5', 6,6'), 8.21 (2H, dd, $J_1 = 5.6$ Hz, $J_2 = 1.2$ Hz, phen 2,2'), 7.9 (2H, dd, $J_1 = 5.2$ Hz, $J_2 = 1.2$ Hz, phen 9,9'), 7.85 (2H, d, $J_1 = 6.0$ Hz, phen 5,5'), 7.81 (2H, q, phen 3,3'), 7.6 (4H, m, phen 6,6', 8,8'), 7.56 (2H, br s, CONH), 3.58 (8H, m, pyr-4,4'- CH_2CH_2), 3.33 (6H, s, pyr-4,4'- OCH_3). δ_C CD_3CN (400 MHz) 162.9, 157.71, 152.7, 152.3, 147.3, 142.15, 136.8, 136.7, 130.8, 127.75, 124.4, 1211.6, 117.0, 116.5, 69.9, 57.45, 39.4. Elemental analysis; $C_{42}H_{42}N_8O_6P_2F_{12}Ru$ requires 43.97, H, 3.69, N, 9.77%; Found: C, 43.11; H, 3.26; N, 9.56.

3.2.4. $[Ru(L1)_3](PF_6)_2 \cdot 2H_2O$ (**3**)

L1 (358 mg, 1 mmol) was dissolved in refluxing EtOH/ H_2O 50/50 (30 cm³), and to this was added dropwise, a solution of $RuCl_3 \cdot 2H_2O$ (72 mg, 0.31 mmol) in the same solvent mixture (8 cm³). The reaction mixture was heated at reflux for 16 h. The solvent was removed by rotary evaporation and the product precipitated by the addition of a saturated aqueous solution of NH_4PF_6 . The resulting solid was filtered, washed with water, air dried, and recrystallised from acetone/water 50:50 to yield the product as a red/orange solid (320 mg, 71%). NMR, d_6 -DMSO, δ_H (400 MHz) 3.35 (18H, s, $6 \times CH_3$), 3.6 (24H, m, $12 \times CH_2$), 7.6 (6H, d, $3 \times$ bipy), 7.75 (6H, d, $3 \times$ bipy), 7.90 (6H, d, $3 \times$ bipy), 9.0 (6H, s, $6 \times NH\#$). #, exchanges with D_2O . δ_C ^{13}C NMR (d_6 -DMSO) 162.9 (CONH, qC), 157.2 (Bpy 2,2', qC), 152.2 (Pyr 6,6'), 152.8 (Bpy 6,6'), 142.2 (Bpy 4,4', qC), 126.2 (Bpy 3,3), 122.4 (Bpy 5,5'), 58.3 (OCH_3), 70.35 (OCH_2), 70.54 (NCH_2). Elemental analysis; $C_{54}H_{70}N_{12}O_{14}RuP_2F_{12}$ requires C, 43.17; H, 4.66; N, 11.20%; Found: C, 43.14; H, 4.35; N, 10.94.

3.2.5. $[Ru(L1)_3](Cl)_2 \cdot 2H_2O$ (**3a**)

The dichloride was obtained using the procedure above with the following modification. After the reaction was completed the reaction mixture was evaporated to dryness, diluted with a small volume of ethanol, and chilled overnight. The precipitated dichloride was collected and dried in vacuo (300 mg, 78%). The metal cation obtained was identical by hplc and NMR to the hexafluorophosphate salt. Elemental analysis; $C_{54}H_{70}N_{12}O_{14}RuCl_2$ requires C, 50.54; H, 5.46; N, 13.10%; Found: C, 50.54; H, 5.20; N, 13.03.

4. Results

4.1. General

All compounds were obtained in analytically pure form by established synthetic methods. It was noticed that phosphate saturated solutions of the hexafluorophosphate salts (especially at high concentrations of the complex) produce a precipitate upon standing overnight. No precipitation was observed when chloride was used as a counter ion. For this reason a set of dichloride analogues **1a** and **3a** were prepared for comparison.

4.2. Emission studies

The effect of the addition of dihydrogenphosphate on the emission properties of dilute acetonitrile solutions (1×10^{-5} M) of complexes **1–3** has been studied. All three compounds show small changes in the emission maximum (Table 1). For all compounds well-defined but relatively small changes in the UV spectra are observed upon addition of the anion. The clearest changes are obtained for **2**. For this compound there is a significant decrease in the absorption maxima at 263 nm upon addition of 2.5 equivalent of dihydrogen phosphate.

Addition of phosphate to **1** shows a 2.6-fold increase in emission intensity upon addition of 2.5 equivalents of $H_2PO_4^-$ (Fig. 2) with no further change thereafter. Under the same conditions the dichloride **1a** shows an increase in the emission intensity by a factor of 1.7. In

Table 1
The effect of the addition of dihydrogenphosphate on the emitting properties of compounds **1–3** in anhydrous CH_3CN

Complex	Lifetime (ns) (λ_{em} (nm))	Lifetime (ns) (λ_{em} (nm)) with phosphate
1a	332(645)	680(649)
1	320(647)	680(650)
2	340(648)	460(639)
3a	448(626)	736(633)
3	480(626)	784(634)

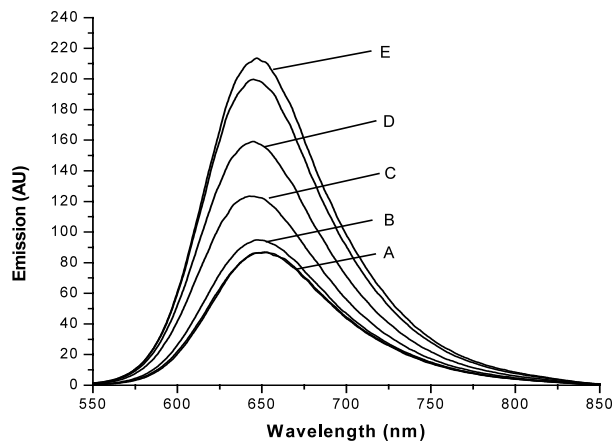


Fig. 2. The effect of the addition of molar equivalents of dihydrogenphosphate on the emission intensity of **1** (1.0×10^{-5} M) in CH₃CN. *A* = 0 eq, *B* = 1.0 eq, *C* = 1.5 eq, *D* = 2.0 eq, *E* = 2.5 eq.

ethanol similar results are obtained but the magnitude of the increase was not as large.

Complex **2** shows a 1.5-fold increase in emission intensity upon addition of 2.5 equivalents of phosphate. At phosphate concentrations greater than this there was no further change in emission intensity. For complex **3** addition of 2.5 equivalents of dihydrogenphosphate caused a 1.6-fold increase in the emission intensity (Fig. 3). However, unlike observed for **1** and **2**, further additions of phosphate caused stepwise reduction in the emission signal, until at 4 equivalents or above, the intensity had dropped to a value slightly below that observed without phosphate. The dichloride analogue **3a** shows a similar trend in emission intensities and maxima as observed for **3**. This compound shows a 1.7-fold increase upon addition of 2.5 equivalents of phosphate, followed again by stepwise quenching.

The effect of the addition of dihydrogenphosphate on the emission lifetime of the compounds was also

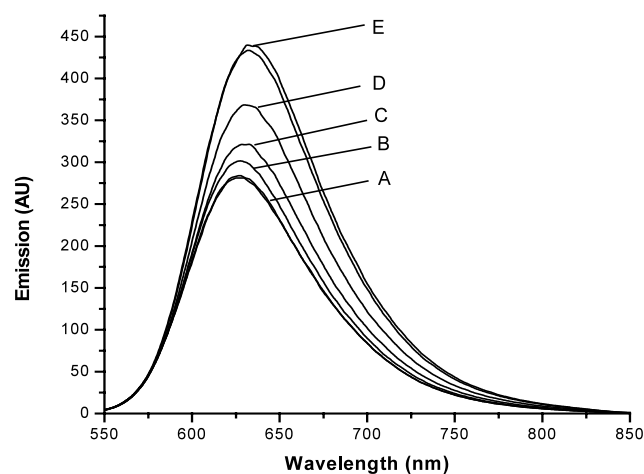


Fig. 3. The effect of the addition of molar equivalents of dihydrogenphosphate on the emission intensity of **3** (1.0×10^{-5} M) in CH₃CN. *A* = 0 eq, *B* = 0.5 eq, *C* = 1.0 eq, *D* = 1.5 eq, *E* = 2.5 eq.

investigated. Table 1 shows lifetimes of the free receptors and the maximum values obtained after phosphate addition. For **1**, **1a** and **2** lifetimes increase up to a maximum at approximately 2.5 equivalents, there after the lifetime stabilised. The lifetimes of complex **3** and **3a** increase up to 2.5 equivalents and then decrease until at approximately 4 equivalents it has returned to the value observed in the absence of phosphate.

Since it is generally accepted that the mechanism responsible for the interaction between receptor and anion is hydrogen bonding, the effect of the water in the emitting behaviour was investigated. The results obtained in a typical example are shown in Fig. 4. In this experiment, phosphate solutions containing different amounts of water are added. The results obtained show that the emission intensity decreases dramatically in the presence of water and that in the presence of 1000 molar equivalents the emission is that observed in the absence of phosphate. In another experiment water was added to a receptor/anion solution to obtain information about the stability of the assembly upon addition of water. These experiments showed that at least 10^6 molar equivalents are needed to disrupt the anion/receptor interaction.

5. Discussion

The application of ruthenium polypyridyl complexes as sensing materials is based on their well-known electronic properties. The parent compound [Ru(bpy)₃]²⁺ has a strong absorbance at about 450 nm, which is MLCT in nature and a relatively long-lived emission with a maximum at about 600 nm. The

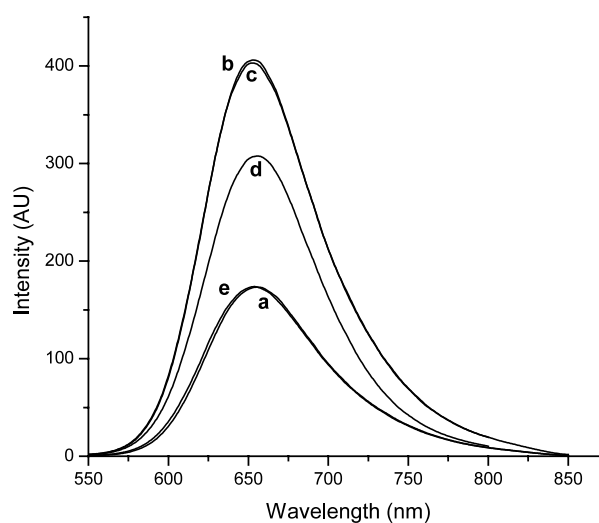


Fig. 4. The effect of the addition of different molar equivalents of water on the emission intensity of **1** (1.0×10^{-5} M) in the presence of phosphate in dry CH₃CN. Curve (a) 0 eq of dihydrogenphosphate and 0 eq of water, (b), (c), (d), and (e), are respectively 2.5 eq of dihydrogenphosphate and 0, 10^2 , 5×10^2 , 10^3 eq of water.

potential sensing properties of the compounds are based on the anion binding properties of **L1** and the effect that this interaction has on the emitting properties of its polypyridyl complex. **L1** has been designed to bind anions such as phosphate via a combination of hydrogen bonding (amide groups) and electrostatic interactions (3,3'-bipyridyl protons) [5]. This is expected to increase the rigidity of the ligand and this would be expected to result in an increase in the emission intensity. If increased rigidity of the complex would be solely responsible for potential emission changes then it would be expected that, because of the number of **L1** ligands present in compounds, **1** and **3** the latter compound would yield an emission increase over a longer concentration range. The expectation that three can bind three anions is confirmed by NMR spectroscopy from chloride binding experiments [5]. Binding of phosphate for both types of compounds is apart from the emission changes observed further confirmed by small but consistent changes in the absorption spectra of the ruthenium compounds in the UV part of the spectrum. This suggests that interaction of the anion with the receptor ligand does affect the electronic levels of the receptor ligand.

The behaviour of $[\text{Ru}(\text{L})_2(\text{L1})]^{2+}$ and $[\text{Ru}(\text{L1})_3]^{2+}$ type complexes is very similar up to 2.5 molar equivalents of anion. Above that concentration however, their behaviour is very different. After complexation of 2.5 equivalents of phosphate to **1**, no further changes in the emitting properties occur. This observation is very different from the behaviour observed by Beer et al. who observed a decrease in the emission intensity when increasing the dihydrogenphosphate concentration from 0 to 20 molar equivalent range [6]. For **3** a slow decrease in the emission intensity is observed for higher anion concentrations. For this latter compound there is clearly still interaction with incoming additional phosphate and the emission is affected, as is also observed for the chloride anion from NMR [5]. It is clear however that this interaction does not lead to a further increase in emission intensity. The reasons for the decrease observed are at present not understood but may be related to the overall charge of the complex formed upon binding of the anion.

The results obtained for the hexafluorophosphate and chloride salts are very similar, indicating the formation of precipitates with the PF_6^- compounds at higher phosphate concentrations does not affect the results. It was however observed that the emission increase observed is less for the chlorides. For **1**, the intensity increases 2.5-fold, while for the dichloride **1a** a 1.7-fold increase is observed. In the case of **3** the difference between the behaviour of the two salts is not as marked. This suggests that the counter chloride anions are interacting with the modified ligand cavity in solution prior to the addition of phosphate. The difference

between **3** and **3a** is less than between **1** and **1a** since in **3a** a free site is available for incoming phosphate ions while in **1a** the one recognition site available will most likely already contain chloride. The binding of chloride has been reported before [5].

The ultimate purpose of studies of this type is the development of novel sensing devices based on the interaction between receptor and anion. An important potential application is the measurement of phosphate ions in water. It is therefore important to consider the impact of water upon the measurement. Early in this study it was observed that the results obtained varied considerably when the source of phosphate was a home made solution of the tetrabutylammonium dihydrogenphosphate salt in acetonitrile. For example, using this solution the maximum emission intensity for **1** occurred after the addition of approximately 1 equivalent of dihydrogenphosphate. However, when the same measurements were made using as an anion source, a 0.4 M solution of the phosphate salt in anhydrous acetonitrile, (Aldrich Sureseal) the results were those presented here. This is attributed to the presence of small amounts of water, which are inadvertently introduced while preparing the phosphate solution in acetonitrile. This was investigated in a more systematic manner as shown in Fig. 4. In this experiment known amounts of water are added to the anion solution before it is combined with the receptor and as a result the emission increase is much reduced. The addition of water after interaction between receptor an anion has taken place is much less effective and the water concentrations needed to significantly reducing the emission response is a factor of thousand higher. This indicates that the anions are mostly preferentially solvated by water and that as a result hydrogen bond formation is much less effective with the receptor after formation.

6. Conclusions

The results obtained in this study indicate that ruthenium polypyridyl complexes containing **L1**, are capable of recognising phosphate anions in acetonitrile. The similar behaviour observed for compounds **1** and **2** shows that the nature of the non-receptor polypyridyl ligand is not an important factor for the luminescent behaviour of the compounds. This is probably not that surprising as the excited state properties of bpy and phen are similar and since the emitting state is most likely based on the receptor ligand. However, the analytical application of the systems studied is very limited. In acetonitrile an analytically useful signal can only be obtained for dihydrogenphosphate concentrations of about 2.5×10^{-5} M in solutions containing 10^{-5} M of the receptor molecule. It was initially thought that it would be possible to extend this short

linear range by introducing additional receptor ligands. However, the results obtained for compound **3** show that this is not the case. The emission increase observed for this compound upon addition of phosphate anions occurs over the same range as observed for compounds **1** and **2** so no increase in the analytically useful concentration range is obtained. In addition, at higher anion concentrations further additions of dihydrogen phosphate leads to a decrease in the emission intensity. This precludes the application of **3** in sensing devices. Furthermore, the extreme sensitivity of the interaction between receptor and anion to traces of water prevents real life application of these systems. The results obtained show that in the presence of water the efficiency of hydrogen bonding based interaction between the receptor group and the anion is greatly reduced. This sensitivity to traces of water is such that when experiments are carried out with the hygroscopic tetrabutylammonium dihydrogenphosphate salt it is very difficult to obtain meaningful results. Since this salt has been widely used in the literature as a source for phosphate, data reported for phosphate sensors should be interpreted with great care.

Acknowledgements

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