ATP Recognition Through a Fluorescence Change in a Multicomponent Dinuclear System Containing a $Ru(Tpy)_2^{2+}$ Fluorescent Core and a Cyclam−Cu^{2+} Complex

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The Cu^{2+} complex of the ligand L^1 (L^1 = $[Ru(tpycyclam)(mtpy)]^{2+}$, tpycyclam = 1-[4′-*p*-tolyl-(2,2′:6′,2′′-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane and mtpy = 4′-methyl-2,2′:6′,2′′-terpyridine) is able to display a selective sensing response against anions such as ATP. The L^1–Cu^{2+} system contains a $Ru(tpy)_2^{2+}$ fluorescent core and a cyclam–Cu^{2+} subunit. The fluorescent response of the $Ru(tpy)_2^{2+}$ core in an aqueous environment (acetonitrile/water, 70:30) is governed by the quenching produced by the Cu^{2+} cation. In the presence of anions the L^1–Cu^{2+} system shows a rich emission fluorescent response. Electrochemical studies on the $Cu(cyclam)^{2+}$ complex in propylene carbonate in the presence of certain anions allowed us to conclude that the interaction with the anions sulfate, phosphate, ATP, ADP and GMP is mainly electrostatic whereas chloride and bromide form axial covalent bonds with the copper atom in the $Cu(cyclam)^{2+}$ complex. The addition of anions that coordinate at the axial positions of the square-planar Cu^{2+}–cyclam subunit (such as Cl^-, Br^- and OH^-) produced an enhancement of the emission intensity. This enhancement is attributed to the occupation of the apical positions of copper in the Cu^{2+}–L^1 complex that might reduce the probability of an interaction between the Cu^{2+} ions and the $Ru(tpy)_2^{2+}$ groups reducing the quenching process and, consequently, resulting in an enhancement of the fluorescence. A prediction of the fluorescent behaviour with the anions sulfate, phosphate, ATP, ADP and GMP that give electrostatic interactions with the positively charged cyclam–Cu^{2+} and/or $Ru(tpy)_2^{2+}$ centres is rather difficult. Potentiometric studies on the L^1–Cu^{2+}–H^+–ATP system suggested that the $[Cu(L^1)(ATP)]$ complex is responsible for the quenching observed at basic pH in the presence of ATP. It is noticeable that the quenching of the intensity of the fluorescence due to ATP in the pH range 9 to 10 is selective and no other anion studied is able to quench the emission of the $Ru(tpy)_2^{2+}$ core in this pH range.

Introduction

The development of new sensing molecules based on the application of supramolecular chemistry concepts is an area of current interest.[1,2] It involves the functionalisation of suitable coordination sites with appropriate groups that can switch their state upon guest binding. When the switching process is followed by a change in a macroscopically observable parameter such as redox potential, absorption or emission spectrum etc., then it is simple to get information in relation to molecular events (the presence or not of a certain guest).[3−5] In general, some factors can be straightforwardly controlled to procure selectivity against a target guest: (i) the nature of the binding sites; (ii) the nature of the signalling subunit; and (iii) the solvent in which the receptor−guest interaction takes place. Such is the number of combinations that the search for new, selective signalling receptors seems to be wide open.[6]

Although anion recognition and fluorescent sensing methods are both fields of interest there are very few examples dealing with the use of fluorescent receptors for anion sensing.[7−9] The development of such new receptors involves the linkage of fluorescent groups to anion coordination sites. In this sense, we have recently been involved in the study of $Ru(tpy)_2^{2+}$ as a fluorescent signalling subunit.[10] Additionally, several types of anion coordination sites have been tested, among them polyammonium units have been some of the most widely used. In contrast, transition metal ions have been much less studied as potential binding sites in receptors based on the "binding site-signalling subunit" concept.[11] When metal ions are used as centres for metal−ligand interactions it is possible to construct structurally defined complexes with appropriate metal cations that might impose high barriers for anion discrimination.[11] We report here the fluorescent behaviour of a multicomponent dinuclear system containing $Ru(tpy)_2^{2+}$ as the fluorescent signalling subunit and a cyclam−Cu^{2+} complex in the presence of anions such as chloride, sulfate, phosphate, ATP, ADP and GMP.

Results

Quenching Studies

The complex L^1 (see below) contains a ruthenium(II) bisterpyridine core covalently anchored to a polyamine unit. We have recently reported studies on the fluorescence beha-

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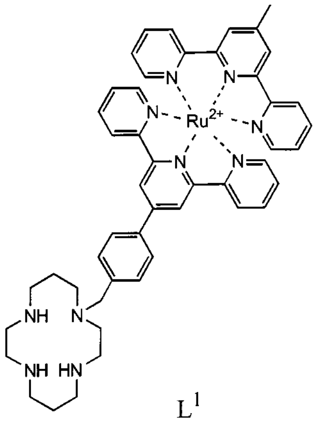
viour of the $Ru(tpy)_2{}^{2+}$ centre in L^1 in the presence of transition metal ions in acetonitrile/water solutions. It was found that in the presence of stoichiometric amounts of Cu^{2+}, the fluorescence of the $Ru(tpy)_2{}^{2+}$ core in L^1 diminished in the pH range of 4−7 (λ_{ex} = 484 nm, λ_{em} = 650 nm). This behaviour is clearly observed in Figure 1, which plots the relative emission intensity for L^1 in the presence of Cu^{2+} at certain pH values ($L^1-Cu^{2+}-H^+$ system). The figure also shows the emission intensity found for L^1 as a function of the pH (L^1-H^+ system). The emission intensity of L^1 is pH-independent: the presence of Cu^{2+} reduces the emission intensity at neutral and acidic pH. Additional solution studies (potentiometric experiments) allowed us to determine that the fall of the fluorescent emission intensity is observed when the complex $[Cu(L^1)]^{4+}$ exists in solution, whereas the protonation of the ligand (to give $[Cu(HL^1)]^{5+}$) at acidic pH, or the formation of hydroxo complexes ($[Cu(L^1)(OH)]^{3+}$ and $[Cu(L^1)(OH)_2]^{2+}$) at basic pH, hinders the quenching mechanism (see below). The $[Cu(L^1)]^{4+}$ complex more likely contains the Cu^{2+} cation coordinated by the cyclam unit in a square-planar environment.[10]



L^1

We complete now these preliminary fluorescent results with new studies on the effect that the presence of certain anions has on the emission behaviour of the $L^1-Cu^{2+}-H^+$ system. In the first step we studied the fluorescent emission behaviour of the $Ru(tpy)_2{}^{2+}$ core as a function of the pH when one equivalent of chloride is added to a solution containing L^1 and Cu^{2+}. It was found that the *I* vs. pH profile of this system ($Cu^{2+}-L^1-H^+-Cl^-$) is very close to that found for the $Cu^{2+}-L^1-H^+$ system (without chloride). However, addition of a second equivalent of chloride induces an enhancement of the fluorescence (decrease of quenching) and an additional excess results in an *I* vs. pH profile close to that found for the L^1-H^+ system (deactivation of the quenching process; see Figure 1). A similar effect to that found for chloride (not shown in Figure 1) is observed when Br^- is added to the $Cu^{2+}-L^1$ system.

The fluorescent behaviour of the $Cu^{2+}-L^1-H^+$ system has also been tested against other anions such as sulfate and phosphate (see Figure 1). Whereas sulfate gave a response between that observed for L^1-H^+ and that of the $Cu^{2+}-L^1-H^+$ system, the presence of phosphate resulted in a similar *I* vs. pH profile to that found for the L^1-H^+ system (see Figure 1).

Of special interest is the study of the effect produced by biological anions such as ATP, ADP and GMP on the fluorescence behaviour of the $Cu^{2+}-L^1-H^+$ system (see Figure 2). The AMP anion is insoluble in acetonitrile/water (70:30 v/v) and could not be studied. It was found that the *I* vs. pH curve of the $L^1-Cu^{2+}-H^+-ATP$ system was quite different to that of $Cu^{2+}-L^1-H^+$. This time the quenching effect is still fully effective but it operates for different pH values, from 6 to 11 (see Figure 2) with a minimum for the fluorescent emission intensity at pH 9.2. GMP also modifies the emission intensity vs. pH curve of the $L^1-Cu^{2+}-H^+$ system and shows a minimum at a pH of

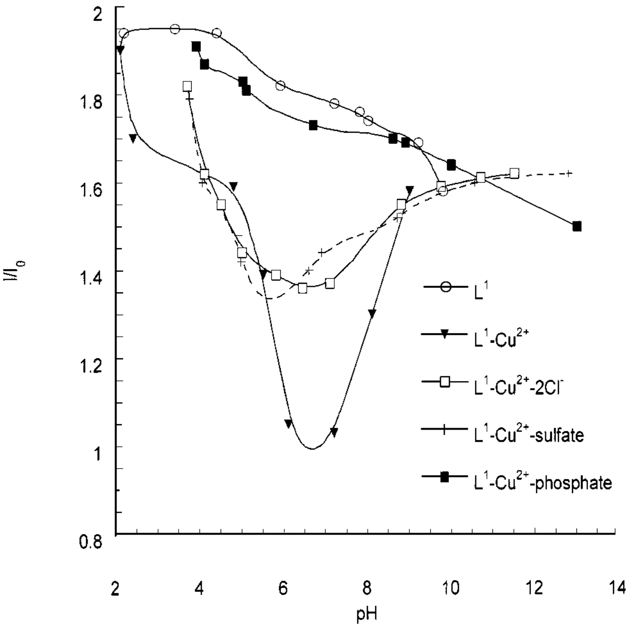


Figure 1. Relative intensity vs. pH for the $L^1-Cu^{2+}-A-H^+$ system, with A = phosphate, sulfate and chloride

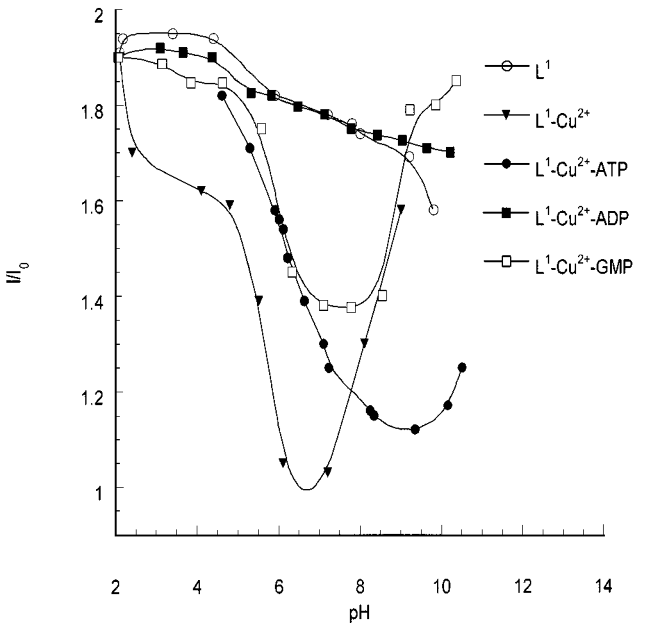


Figure 2. Relative intensity vs. pH for the $L^1-Cu^{2+}-A-H^+$ system, with A = ATP, ADP and GMP

ca. 7.5. In contrast, the ADP anion shows a similar *I* vs. pH profile to that found for the L^1-H^+ system.

In summary, the system containing Cu^{2+} and the ligand L^1 shows a rich fluorescent response in the presence of anions. The most significant feature is that ATP is able to induce quenching of the fluorescent $Ru(tpy)_2{}^{2+}$ subunit at pH 9.2, a pH at which none of the other anions studied (such as phosphate, sulfate, chloride, bromide, ADP or GMP) are able to produce any significant effect on the fluorescent behaviour of the $Cu^{2+}-L^1$ complex. It is also interesting to note that, in general, L^1 is a poor fluorescent chemosensor for anions, whereas it is the presence of Cu^{2+}, as we show in this work, that induces the mentioned changes in the fluorescence behaviour of the Ru-tpy subunit when anions are also present. In order to rationalise the emission fluorescent behaviour described above we have carried out additional electrochemical and potentiometric studies in an attempt to characterise the nature of the species existing in solution in the presence of certain anions.

Electrochemical Studies

Electrochemical studies on the $Cu(cyclam)^{2+}$ complex in the presence of anions can give information about the kind of interaction between the anion and the Cu^{2+}-cyclam centre. For instance, the axial coordination of anions to Cu^{2+} in a cyclam environment could be studied electrochemically and it is expected that strong axial coordination would reduce significantly the oxidation potential of the process $Cu^{2+} \rightarrow Cu^{3+} + 1e^-$. Electrochemical studies on $Cu(cyclam)^{2+}$ in the presence of phosphate, sulfate, ADP, chloride and bromide in propylene carbonate as solvent (0.1 mol dm^{-3} tetrabutylammonium perchlorate) have been carried out. Other solvents such as acetonitrile/water were discarded because the oxidation potential of Cu^{2+} in $Cu(cyclam)^{2+}$ is poorly defined probably due to the oxidation of water. Attempts to carry out studies in acetonitrile were also unsuccessful as phosphate and sulfate gave insoluble precipitates with the $Cu(cyclam)^{2+}$ complex.

In propylene carbonate, the $Cu(cyclam)^{2+}$ complex gave an irreversible oxidation process at 1.3 V vs. SCE. In the presence of chloride there is a cathodic oxidation potential shift up to 170 mV, whereas in the presence of sulfate and phosphate the electrochemical shift is only of 50 and 90 mV, respectively. The presence of ADP does not induce any significant oxidation potential shift of the Cu^{2+}/Cu^{3+} couple (less than 20 mV). Additionally, the presence of chloride produces a change of colour in the complex $Cu(cyclam)^{2+}$ that is not observed upon addition of sulfate, phosphate, or ADP anions. All these results appear to suggest that the interaction of the anions sulfate, phosphate, ADP and also probably ATP and GMP with the $Cu(cyclam)^{2+}$ unit is mainly electrostatic whereas chloride and also probably bromide and OH^- form covalent bonds with $Cu(cyclam)^{2+}$ in axial positions.

Stability Constants

Taking into account the difficulty of characterising the $L^1-Cu^{2+}-H^+-$anion systems at a molecular level we have accomplished potentiometric studies in an attempt to characterise some of these systems thermodynamically. Bearing in mind the selectivity found for ATP at basic pH (see Figure 2) we have carried out titration experiments in the presence of this biologically important anion in acetonitrile/water (70:30 v/v) solutions. Figure 3 shows the distribution diagram of the $L^1-Cu^{2+}-H^+-ATP$ system.

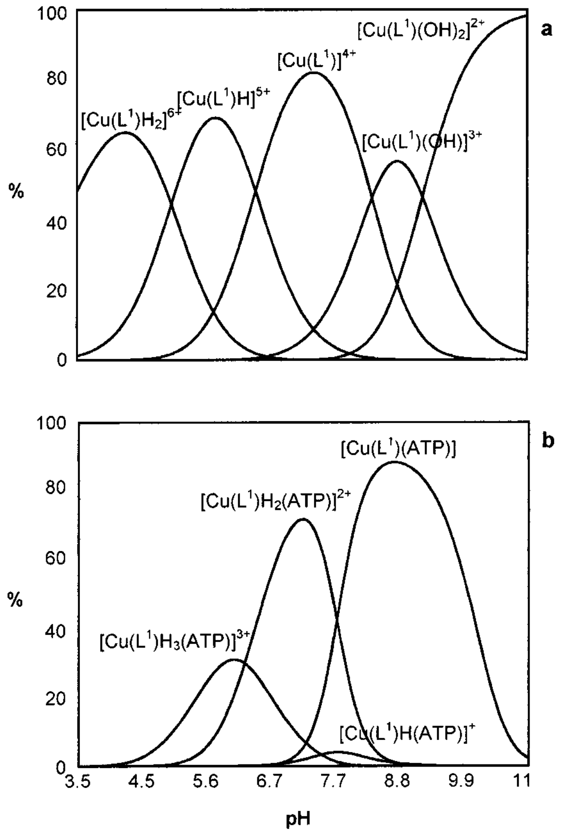


Figure 3. Distribution diagrams for the systems: a) $L^1-Cu^{2+}-H^+$; b) $L^1-Cu^{2+}-ATP-H^+$; in the presence of anions only the ligand−copper−anion species have been plotted

Table 1 shows the formation stability constants for the $L^1-Cu^{2+}-H^+-ATP$ system. In the presence of ATP the complexes $[Cu(L^1)H_3(ATP)]^{3+}$, $[Cu(L^1)H_2(ATP)]^{2+}$, $[Cu(L^1)H(ATP)]^+$ and $[Cu(L^1)(ATP)]$ have been detected. Whereas the nature of protonated complexes is not easy to determine bearing in mind that both the ATP anion and the $[Cu(L^1)]^{4+}$ cation can be protonated, we can probably ascribe the formation of the $[Cu(L^1)(ATP)]$ complex to the interaction between the cation $[Cu(L^1)]^{4+}$ and the anion ATP^{4-}. Thus, the logarithm of the stability constant for the equilibrium $[Cu(L^1)]^{4+} + ATP^{4-} \rightleftarrows [Cu(L^1)(ATP)]$ is 6.10. The most interesting feature arises when comparing the distribution diagrams in Figure 3 and the plot of the emission intensity vs. pH for the $L^1-Cu^{2+}-H^+$- ATP system in Figure 2: the agreement between the pH range where the quenching is observed and the pH range of existence of the $[Cu(L^1)(ATP)]$ complex is noticeable.

Table 1. Logarithms of the stability constants for the $L^1-Cu^{2+}-ATP-H^+$ systems in acetonitrile/water (70:30 v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) at 25 °C

Reaction	$\log K$[a][b]
$L^1 + Cu^{2+} + ATP + 3H^+ \rightleftarrows [Cu(L^1)H_3(ATP)]$[c]	41.26(4)[d]
$L^1 + Cu^{2+} + ATP + 2H^+ \rightleftarrows [Cu(L^1)H_2(ATP)]$	35·00(4)
$L^1 + Cu^{2+} + ATP + H^+ \rightleftarrows [Cu(L^1)H(ATP)]$	26.18(4)
$L^1 + Cu^{2+} + ATP \rightleftarrows [Cu(L^1)(ATP)]$	19.40(5)

[a] Stability constants for the $L^1-Cu^{2+}-H^+$ system from ref.[10] are the following: $(L^1)^{2+} + Cu^{2+} + 2H^+ \rightleftarrows [Cu(H_2L^1)]^{6+}$, $\log K = 24.84(5)$; $(L^1)^{2+} + Cu^{2+} + H^+ \rightleftarrows [Cu(HL^1)]^{5+}$, $\log K = 19.77(8)$; $(L^1)^{2+} + Cu^{2+} \rightleftarrows [Cu(L^1)]^{4+}$, $\log K = 13.30(7)$; $(L^1)^{2+} + Cu^{2+} + H_2O \rightleftarrows [Cu(L^1)(OH)]^{3+} + H^+$, $\log K = 4.89(10)$; $(L^1)^{2+} + Cu^{2+} + 2H_2O \rightleftarrows [Cu(L^1)(OH)_2]^{2+} + 2H^+$, $\log K = -4.36(9)$. – [b] The formation stability constants for the $L^1-ATP-H^+$ system from ref.[13] are the following: $(L^1)^{2+} + ATP^{4-} + 2H^+ \rightleftarrows [L^1H_2ATP]$, $\log K = 27.82(6)$; $(L^1)^{2+} + ATP^{4-} + 3H^+ \rightleftarrows [L^1H_3ATP]^+$, $\log K = 36.75(6)$; $(L^1)^{2+} + ATP^{4-} + 4H^+ \rightleftarrows [L^1H_4ATP]^{2+}$, $\log K = 43.75(6)$; $(L^1)^{2+} + ATP^{4-} + 5H^+ \rightleftarrows [L^1H_5ATP]^{3+}$, $\log K = 48.02(10)$; $(L^1)^{2+} + ATP^{4-} + 6H^+ \rightleftarrows [L^1H_6ATP]^{4+}$, $\log K = 52.10(6)$. – [c] Charges have been omitted for clarity. – [d] Values in parentheses are standard deviations on the last significant figure.

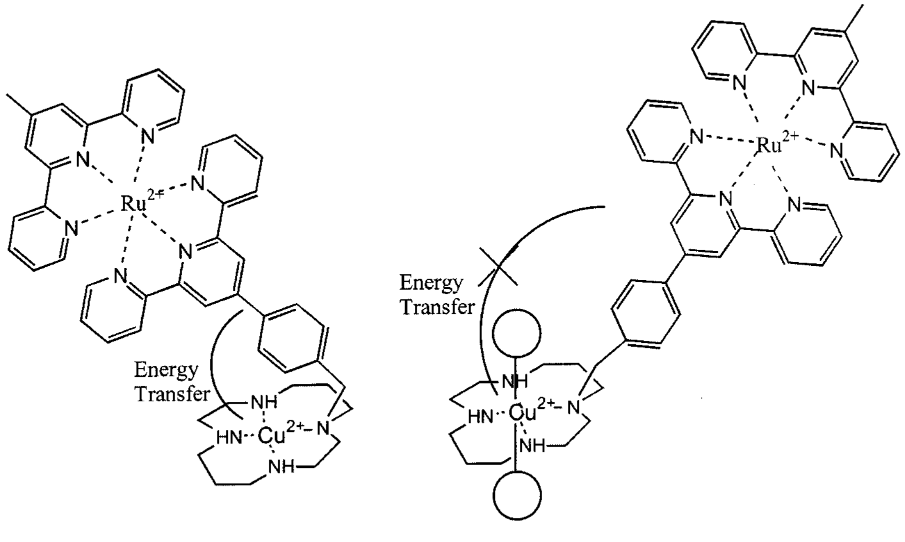
Discussion

Coordinating vs. Noncoordinating Anions

The $[Cu(L^1)]^{4+}$ cation can interact with anions in two different manners: (i) by covalent bonds when anions are able to coordinate the axial positions of the square-planar cyclam$-Cu^{2+}$ unit, or (ii) through electrostatic interactions when anions interact by coulombic forces with the positively charged cyclam$-Cu^{2+}$ and/or $Ru(tpy)_2{}^{2+}$ centres. As the electrochemical experiments suggest, the anions ATP, ADP, GMP sulfate and phosphate give electrostatic interactions with the $Cu^{2+}-L^1$ species, whereas chloride, bromide and OH^- give axial covalent coordination with the copper centre of the cyclam$-Cu^{2+}$ subunit.

We have recently reported that the quenching of the fluorescence observed for the $[Cu(L^1)]^{4+}$ complex most likely occurs by means of an energy-transfer mechanism.[10] Such a mechanism requires a close proximity between the fluorophore and the copper metal ion, as occurs when copper is in a square planar coordination inside the cyclam polyamine (see Scheme 1a). In the presence of chloride, the occupation of the apical positions might significantly reduce the probability of interaction between Cu^{2+} ions and $Ru(tpy)_2{}^{2+}$ groups, thus reducing the quenching process (see Scheme 1b) and, consequently, resulting in an enhancement of the fluorescence upon chloride binding. A similar effect is observed when Br^- is added to a $Cu^{2+}-L^1$ system and, in general, the same effect would be expected with anions able to give strong interactions with Cu^{2+} ions through the axial positions (in fact, the OH^- anions also eliminate the Cu^{2+} quenching effect).

Prediction of the fluorescence response of the $L^1-Cu^{2+}-H^+$ system in the presence of anions able to give mainly coulombic interactions (sulfate, phosphate, ATP, ADP and GMP) is rather difficult. The quenching mechanism in Scheme 1 is operative for chloride (and also for bromide and OH^-) but is not valid for sulfate, phosphate, ATP, ADP or GMP. One would expect that the anions able to give mainly coulombic interactions with the $Cu^{2+}-L^1$ complex may impose geometrical constraints that could modulate the distance between the Cu^{2+} and the $Ru(tpy)_2{}^{2+}$ core and therefore induce changes in the emission behaviour of the $Cu^{2+}-L^1$ system. However, whether the interaction would enhance or reduce the emission intensity is not easy to specify. Nevertheless, the interaction of the $Cu^{2+}-L^1$ complexes with those anions has proved



(a) (b)

Scheme 1

to produce a rich fluorescent response, as shown in Figure 1 and 2.

Suggested Mechanism for ATP Quenching

For the $L^1-Cu^{2+}-H^+$ and $L^1-Cu^{2+}-H^+-ATP$ systems we have carried out both potentiometric titrations and fluorescent emission studies. Potentiometry allowed us to characterise the nature of the complexes existing in solution (see Figure 3 for the distribution diagrams), whereas fluorescent studies permitted us to determine the emission response as a function of the pH (see Figure 2). By a combination of both techniques it might be possible to determine which species are responsible for a particular change in the emission fluorescence intensity at a certain pH. Thus, for the $L^1-Cu^{2+}-H^+$ system the quenching of the emission behaviour is observed when the $[Cu(L^1)]^{4+}$ complex exists. In fact, there is a close relation between the intensity vs. pH curve for the $L^1-Cu^{2+}-H^+$ system in Figure 1 and the pH range of existence of the $[Cu(L^1)]^{4+}$ complex (see Figure 3). This quenching is related to the existence of Cu^{2+} in a square-planar environment. In a similar manner, the quenching for the $L^1-Cu^{2+}-ATP-H^+$ system in the 6−11 pH range appears to be directly related to the presence in solution of the $[Cu(L^1)(ATP)]$ complex. As stated above this anion-cation complex is probably formed by electrostatic interaction between the species $[Cu(L^1)]^{4+}$ and ATP^{4-}. Additionally, as the presence of ATP probably doesn't induce any change in the coordination mode of the Cu^{2+} inside the cyclam unit, it might be concluded that in the 6−11 pH range the quenching is related to the presence of the "$[Cu(L^1)]^{4+}$" unit (in the $[Cu(L^1)(ATP)]$ complex) which contains Cu^{2+} in a square-planar environment. In this case ATP seems to be able to modulate the pH zone where the Cu^{2+}−cyclam square-planar unit responsible for the quenching exists by binding to the $L^1-Cu^{2+}-H^+$ system. In other words, ATP is able to modify the pK_a value for complex protonation and/or formation of hydroxo derivatives. However, it cannot be completely ruled out that the quenching observed could be produced by the nucleotide moiety rather than by the Cu^{2+} cation. It is noticeable that the quenching of the intensity of the fluorescence due to ATP in the pH range 9 to 10 is selective and no other anion studied is able to quench the emission of the $Ru(tpy)_2{}^{2+}$ core at this pH range. Thus, coordination of ATP with the L^1-Cu^{2+} system results in a selective sensing of the anion through a fluorescent-signalling event.

Conclusions

In conclusion, we have studied a multicomponent system able to display a selective sensing response against target anions such as ATP. The receptor L^1 contains a $Ru(tpy)_2{}^{2+}$ fluorescent core and a covalently attached cyclam unit. This receptor was reported to show a poor fluorescence response in the presence of anions. In contrast, the formation of the Cu^{2+} complex of L^1 produces a very rich fluorescence response. The $Cu^{2+}-L^1$ fluorescence emission in an aqueous environment is governed by the quenching produced between the Cu^{2+}−cyclam subunit and the $Ru(tpy)_2{}^{2+}$ fluorescent core. The maximum effectiveness for the quenching process takes place when the complex $[Cu(L^1)]^{2+}$ is present. Addition of anions that could coordinate axial positions of the square-planar cyclam−Cu^{2+} unit produces an enhancement of the fluorescence. ATP is selectively recognised through a selective quenching by the $Cu^{2+}-L^1$ system.

Experimental Section

Synthesis: The L^1 complex was prepared following published methods[12] by reaction of $[Ru(mtpy)Cl_3]$ (mtpy = 4′-methyl-2,2′:6′,2′′-terpyridine) and 1-[4′-*p*-tolyl-(2,2′:6′,2′′-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane in the presence of *N*-ethylmorpholine as a mild reductant. The Cu^{2+} complex of L^1 was prepared in situ by addition of stoichiometric amounts of copper(II) perchlorate to an acetonitrile/water (70:30 v/v) solution of L^1. This solution was used for the fluorescent and potentiometric studies in the presence of anions.

Physical Measurement and Instrumentation: Photochemical data were obtained with a FS900CDT steady state T-Geometry Fluorometer, Edinburgh Analytical Instruments. All solutions for photophysical studies were degassed. The concentration of the $Cu^{2+}-L^1$ complex and the concentration of the anions was ca. 1.0×10^{-3} mol dm^{-3}. Potentiometric titrations were carried out in acetonitrile/water (70:30 v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) using a reaction vessel water-thermostatted at 25.0 ± 0.1 °C under nitrogen. The titrant was added with a Crison microburette 2031. Experimental potentiometric details have been published previously.[13] The computer program SUPERQUAD[14] was used to calculate the protonation and stability constants. The titration curves for each system (ca. 250 experimental points corresponding to at least three titration curves, pH range investigated 2.0−10.5, concentration of the ligand and anion was ca. 1.0×10^{-3} mol dm^{-3}) were treated either as a single set or as separate entities without significant variations in the values of the stability constants. Finally the sets of data were merged together and treated simultaneously to give the stability constants.

Acknowledgments

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