Bis(terpyridyl)-Ruthenium(II) Units Attached to Polyazacycloalkanes as Sensing Fluorescent Receptors For Transition Metal Ions

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A synthetic strategy has been devised for the preparation of new compounds in which terpyridyl fragments are linked to 1,4,8,11-tetraazacyclotetradecane (cyclam). Reaction of excess cyclam with 4′-[(4-bromomethyl)phenyl]-2,2′:2″,6′-terpyridine afforded the ligand 1-[4′-*p*-tolyl-(2,2′:6′,2″-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^1) in which the tetraaza macrocycle was covalently attached to one benzyl-terpyridyl fragment. Under similar conditions reaction of cyclam with excess 4′-[(4-bromomethyl)phenyl]-2,2′:2″,6′-terpyridine gave the tetra substituted cyclam derivative 1,4,8,11-[4′-*p*-tolyl-(2,2′:6′,2″-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^2). The multidentate ligand L^2 was crystallographically characterised by single-crystal X-ray diffraction techniques. Reaction of L^1 with $[Ru(mtpy)Cl_3]$ gave the heteroleptic ruthenium(II) complex $[Ru(L^1)(mtpy)][PF_6]_2$ (mtpy = 4′-methyl-2,2′:6′2″-terpyridine). The fluorescent intensity of the metallo-receptor $[Ru(L^1)(mtpy)][PF_6]_2$ was quenched selectively in the presence of copper(II) in an aqueous environment. To gain insight into the nature of this interaction, potentiometric titrations on $[Ru(L^1)(mtpy)]^{2+}$ in the presence of Cu^{2+} were carried out. The quenching of the emission intensity was associated with the presence of the copper $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ complex in solution. The receptor 1-[4′-methyl-(2,2′:6′,2″-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^3), in which the cyclam fragment is separated from the terpyriyl by a methylene group, has also been synthesised by reaction of 4′-bromomethyl-2,2′:2″,6′-terpyridine and cyclam. With L^3 as starting material, the ruthenium complex $[Ru(L^3)(mtpy)]^{2+}$ was prepared in order to evaluate the effect that the nature of the spacer has on the quenching of the fluorescence upon addition of Cu^{2+}.

Introduction

The assembly of oligopyridyl groups with Ru^{II} or some other transition metals ions to yield polymetallic species has been studied for both practical and fundamental reasons.[1,2] Some examples are: (a) the investigation of energy and electron-transfer processes,[3–8] (b) the exploitation of spectroscopic properties for testing the sensing ability of appended groups towards protons, cations and anions[9,10] and (c) the building up of dendritic species comprising several metal centres for light-harvesting and energy-collection purposes.[11,12] The investigation on these area has mainly been concentrated on building covalently linked metal complexes,[3,5,13] with the building of noncovalent links between components being an alternative pathway.[14] Few examples of these metallo-receptors have demonstrated sensor properties.[15]

We have synthesised terpyridine-functionalised cyclam ligands and formed complexes with the photoactive Ru^{II} metal ion. The domains of the macrocyclic cavity could allow for the binding of an appropriate guest that might trigger a change in the luminescence of the appended ruthenium metal centre. One of the best known metallo-fluorophores is the tris(2,2'-bipyridyl)-ruthenium(II) core, however the related bis(2,2':6',2''-terpyridine)-ruthenium(II) group has been much less studied as a luminescent signalling subunit.[9,16] We report here that the incorporation of the Cu^{2+} cation into the macrocyclic cavity appended to a bisterpyridyl ruthenium centre changes the emission properties of the $[Ru(tpy)_2]^{2+}$ core, allowing for access to new potential chemosensors based on the fluorophore–spacer–receptor concept.

Results and Discussion

The attachment of polypyridyl fragments to secondary amines in polyazacycloalkanes can be carried out by the use of a polypyridyl fragment containing a CH_2Br substituent. 4'-[(4-Bromomethyl)phenyl]-2,2':6',2''-terpyridine was synthesised following literature procedures.[17] The terpyridine-functionalised cyclam receptor was readily prepared by reaction of the terpyridine derivative with an excessof cyclam in dichloromethane in the presence of NEt_3 at 30° C for 24 hours and further column chromatography in alumina with a mixture of CH_2Cl_2/MeOH (99:1 v/v) as eluent obtaining a ca. 50% yield of L^1 (see Scheme 1). The ^1H NMR spectrum of L^1 shows pyridyl protons in the range of 7.2–8.8 ppm. The proton signals were fully assigned by using $^1H,^1H$ correlation (COSY) spectroscopy. The spectrum is completed by one singlet at 3.7 ppm of the methyl-

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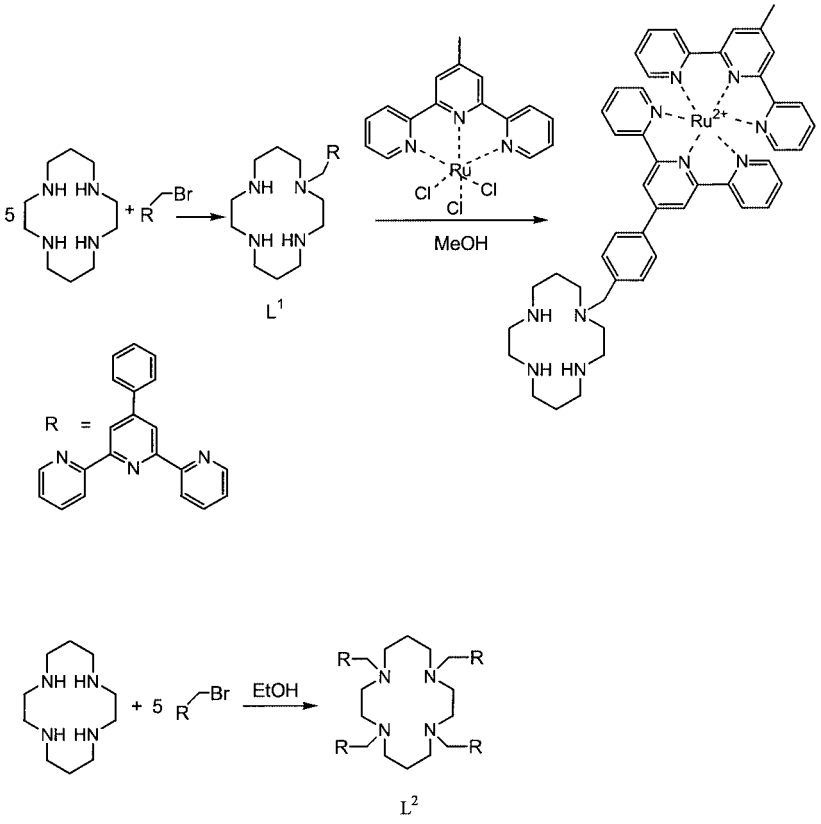


Scheme 1. Synthesis of L^1 and L^2 and the corresponding ruthenium complex of L^1

enic protons of the tolyl spacer, several overlapped signals in the range 2.40–2.90 of CH_2 groups attached to the nitrogen atoms in the macrocycle and two quintuplets at 1.6–1.8 ppm corresponding to the two nonequivalent central CH_2 groups from the propylene chains in the cyclam macrocycle.

Reaction of cyclam with an excess of 4'-[(4-bromomethyl-)phenyl]-2,2':6',2''-terpyridine in ethanol in the presence of NEt_3 gave L^2 as the unique product (see Scheme 1). The ^1H NMR spectrum of L^2 shows pyridyl protons in the range 7.25–8.70 ppm. The protons of the cyclam moiety appear in the range 1.8–2.8 ppm, whereas the benzylic protons give rise to a singlet at 3.52 ppm.

L^2 has also been characterised by single-crystal X-ray diffraction techniques. Suitable crystals for diffraction purposes were obtained by slow diffusion of diethyl ether into a solution of L^2 in dichloromethane. Some selected bond lengths and angles are listed in Table 1. Figure 1 shows the molecular structure of L^2. The structure consists of a cyclam core substituted with four benzyl-terpyridyl groups, giving a multidentate molecule with a promising geometry containing a central tetraaza and four peripheral terpyridine binding sites. Cyclic tetraamines can exist in several conformations depending on the relative position of the *N*-substituted groups with respect to the N4 plane.[18] Of the five possible conformations for a tetra-substituted cyclam derivative, the crystal structure of L^2 shows that the conformation with two substituents above and two below the mean N4 plane is adopted, the two benzyl-terpyridyl groups above the plane being separated by an ethylene chain. The 2,2':6',2''-terpyridine adopts the usual trans–trans conformation through the C–C interannular bond as has been found in related structures.[19] The terpyridine groups adopt a near-planar conformation with dihedral angles between the planes N(2)–C(10) and N(1)–C(5), N(3)–C(11) and N(2)–C(10), N(5)–C(38) and N(4)–C(45), N(6)–C(40) and N(5)–C(38) of 7.2°, 3.4°, 9.6°, and 13.7°, respectively. The angles between the planes C(16)–C(21) and N(2)–C(11), C(29)–C(34) and N(5)–C(38) are 26.6° and 10.5°, respectively.

Table 1. Selected bond lengths and angles[a]

Length			
N(1)–C(5)	1.307(12)	N(7)–C(22)	1.461(11)
N(1)–C(1)	1.321(13)	N(8)–C(28)	1.464(10)
N(8)–C(26)	1.492(10)	N(7)–C(23)	1.461(10)
N(8)–C(27)	1.480(10)	N(7)–C(24)	1.451(10)
C(1)–C(2)	1.38(2)	C(8)–C(16)	1.508(12)
C(2)–C(3)	1.38((2)	C(19)–C(22)	1.502(13)
C(3)–C(4)	1.371(13)	C(24)–C(25)	1.501(11)
C(4)–C(5)	1.369(12)	C(25)–C(26)	1.519(11)
C(5)–C(6)	1.484(13)		
Angles(°)			
C(9)–C(8)–C(16)	121.2(10)	C(24)–C(25)–C(26)	112.9(8)
C(23)–N(7)–C(22)	110.0(8)	N(8)–C(28)–C(29)	111.0(8)
N(7)–C(22)–C(19)	114.8(9)	N(8)–C(26)–C(25)	110.9(8)

[a] Values in parentheses are standard deviations in the last significant figure.

Reaction of equimolar quantities of L^1 with $Ru(mtpy)Cl_3$ [mtpy = 4'-methyl-2,2':6',2''-terpyridine] in methanol with

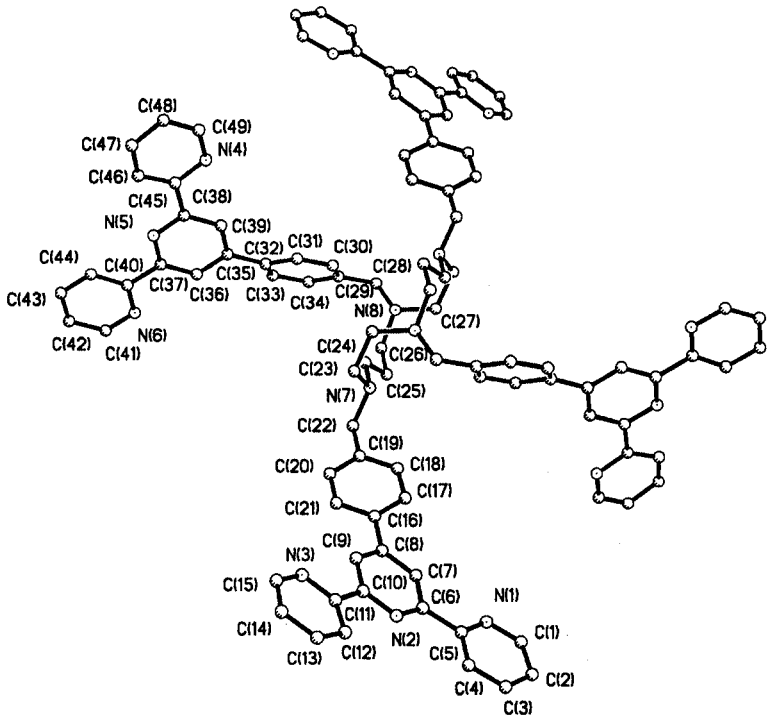


Figure 1. Molecular structure of L^2

the addition of *N*-ethyl-morpholine as mild reductant, afforded the receptor $[Ru(L^1)(mtpy)][PF_6]_2$ after column chromatography in silica using a mixture of acetonitrile/water/saturated aqueous solution of KNO_3 (17:1:2 v/v) as eluent and further precipitation with ammonium hexafluorophosphate (see Scheme 1). The FAB mass spectrum of the bis-terpyridyl ruthenium(II) complex $[Ru(L^1)(mtpy)][PF_6]_2$ showed peaks at *m*/*z* = 1161, 1015 and 869 corresponding to $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^1)(mtpy)][PF_6]^+$ and $Ru(L^1)(mtpy)^{2+}$, respectively. The ^1H NMR spectrum shows the expected signals for the aromatic protons in the range 7.2–9.0 ppm, with two non-equivalent terpyridine groups. The spectrum also contained poorly defined overlapping signals in the 2.8–4 ppm range. The CH_3 of the terminal group appears at 2.93 ppm. Owing to the presence of the acetonitrile signal, the corresponding signal for the central CH_2 groups of the propylene chain in the cyclam cycle were not observed.

The synthesized ruthenium(II) complex contains a polyamine as the "receptor" part of the molecule and a bis(2,2':6',2''-terpyridine)-ruthenium(II) group able to act as signalling subunit. The following study has been carried out mainly to detect the effect that the coordination of the cyclam fragment has on the emission properties of the signalling ruthenium-terpyridine unit. The electronic spectrum of the complexes is as expected for a $[Ru(tpy)_2]^{2+}$ chromophore, with the principal $Ru[d(\pi)] \rightarrow tpy(\pi^*)$ MLCT transition at 484 nm, and the usual intense ligand-centred transitions in the UV region.[20] We have investigated the fluorescence behaviour of acetonitrile/water solutions of the receptor $[Ru(L^1)(mtpy)]^{2+}$ in the presence of transition metal ions M^{2+} (M^{2+} = Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}) as a function of the pH (see Figure 2) by luminescence spectroscopy. The continuous protonation of the poly- amine enhanced the emission intensity of the ruthenium core only slightly, indicating that the photoinduced electron transfer mechanism between the lone pair of the amines and the $Ru(tpy)_2^{2+}$ fluorophore is poor. The presence of the transition metals Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} does not modify the fluorescence versus pH profile of the free receptor. In contrast, the coordination of Cu^{2+} in the macrocyclic cavity is accompanied by substantial quenching of the luminescence intensity with a minimum centred at pH = 6.9 (see Figures 2 and3).

Figure 2. Relative intensity versus pH for the L and $L-M^{2+}$ systems (L = $[Ru(L^1)(mtpy)][PF_6]_2$; M^{2+} = Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}) (λ_{ex} = 484 nm, λ_{em} = 664 nm)

To gain insight into the nature of the interaction of Cu^{2+} with the $Ru(tpy)_2$ fluorophore, two additional studies were carried out: (i) potentiometric titrations on an acetonitrile/water solution of $[Ru(L^1)(mtpy)]^{2+}$ in the presence of Cu^{2+}, and (ii) the synthesis of a parent fluorophore–spacer–receptor multicomponent system where the nature of the spacer was varied.

The protonation and coordination behaviour of L^1 and $[Ru(L^1)(mtpy)]^{2+}$ was studied by potentiometric titrations with KOH of previously acidified solutions in acetonitrile/

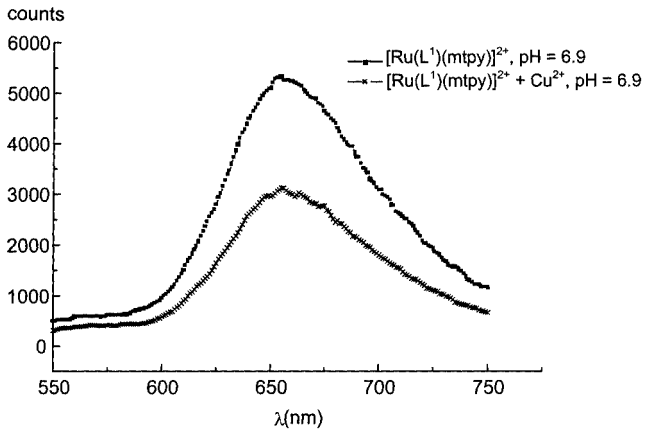


Figure 3. Emission spectra of the $[Ru(L^1)(mtpy)]^{2+}$ cation at pH = 6.9 with and without Cu^{2+}

water (70:30 v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate). Additionally the protonation constants of cyclam in acetonitrile/water were also determined. Table 2 shows that $\log K_2 - \log K_3$ for the cyclam is 7.5, but only 3.85 for L^1 and 3.17 for $[Ru(L^1)(mtpy)]^{2+}$. The need to break a hydrogen bond to enable the third proton to become attached has been suggested as an explanation for the large difference between the values of $\log K_2$ and $\log K_3$ in the cyclam. Similar behaviour for cyclam has been observed in water or in THF/water (70:30 v/v).[21] However, this effect disappears in substituted derivatives such as L^1 and $[Ru(L^1)(mtpy)]^{2+}$. Five protonation steps were determined for L^1: the first two protonations probably took place at the macrocyclic moiety; the last three protonations either took place at the terpyridine or at the cyclam. For the $[Ru(L^1)(mtpy)]^{2+}$ complex and cyclam only three protonation constants were observed, the four being too acidic to be determined. Remarkably the $[Ru(L^1)(mtpy)]^{2+}$ complex does not show

Table 2. Stepwise protonation constants (log K) of L^1, $[Ru(L^1)(mtpy)]^{2+}$ and cyclam in acetonitrile/water (70:30 v/v, 0.1 mol dm^{-3} of $[n\text{-}Bu_4N][ClO_4]$

Reaction	L^1	$[Ru(L^1)(mtpy)]$	cyclam
$L + H^+ \rightleftarrows (HL)^+$	10.88(4)[a]	10.33(1)	11.6(2)
$L + 2H^+ \rightleftarrows (H_2L)^{2+}$	19.34(4)	19.08(1)	21.09(1)
$L + 3H^+ \rightleftarrows (H_3L)^{3+}$	23.95(3)	24.66(1)	23.1(2)
$L + 4H^+ \rightleftarrows (H_4L)^{4+}$	26.89(3)		
$L + 5H^+ \rightleftarrows (H_5L)^{5+}$	29.51(2)		
$L + H^+ \rightleftarrows (HL)^+$	10.88	10.33	11.6
$(HL)^+ + H^+ \rightleftarrows (H_2L)^{2+}$	8.46	8.75	9.49
$(H_2L)^{2+} + H^+ \rightleftarrows (H_3L)^{3+}$	4.61	5.58	2.01
$(H_3L)^{3+} + H^+ \rightleftarrows (H_4L)^{4+}$	2.94		
$(H_4L)^{4+} + H^+ \rightleftarrows (H_5L)^{5+}$	2.62		

[a] Values in parentheses are standard deviations in the last significant figure.

substantial basicity difference from L^1 for the first three protonation constants, despite the existence of a positively charged $Ru(tpy)_2^{2+}$ core.

Table 3 shows the stability constants for the formation of Cu^{2+} complexes of $[Ru(L^1)(mtpy)]^{2+}$ in acetonitrile/water (70:30 v/v). The distribution diagram of the $[Ru(L^1)(mtpy)]^{2+}$–H^+–Cu^{2+} is depicted in Figure 4. The receptor $[Ru(L^1)(mtpy)]^{2+}$ forms the complex $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ existing in the neutral pH range. These species undergo two protonation processes upon lowering of the pH, whereas two additional hydroxo complexes were found to exist at basic pH. The logarithm of the stability constant for the formation of the complex $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ is 13.30. This value can be compared with that found for the formation of $[Cu(tmfcyclam)]^{2+}$ ($\log K = 19.06$)[22] (where tmfcyclam = 1,4,8,11-tetrakis(ferrocenylmethyl)-tetraazacyclotetradecane), or with that of $[Cu(cyRubipy)]^{10+}$ ($\log K = 6.01$)[23] (where cyRubipy stand for a tetramethyl-$Ru(bipy)_3$-substituted cyclam). In the latter, the Cu^{2+} cation is brought within the range of the electrostatic repulsion from all four of the pendent $[Ru(bipy)_3]^{2+}$ groups while in $Cu[Ru(L^1)(mtpy)]^{4+}$ the Cu^{2+} cation only experiences the electrostatic repulsion of one tolyl-distanced $[Ru(tpy)_2]\}^{2+}$ core. The above could explain the difference in the stability constants of $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ and $\{Cu[cyRu(bipy)_3]\}^{10+}$ ($\log K$ of $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ – logK of $\{Cu[cyRu(bipy)_3]\}^{10+}$ = 7.29). Effects of the electrostatic repulsion could also be observed when comparing the stability constants for the formation of the complexes $[Cu(tmfcyclam)]^{2+}$ and

Table 3. Stability constants (log K) for the formation of copper(II) complexes of $[Ru(L^1)(mtpy)]^{2+}$

Reaction	logK
$Cu^{2+} + 2H^+ + L^{2+} \rightleftarrows [Cu(H^2L)]^{6+}$	24.84(5)[a]
$Cu^{2+} + H^+ + L^{2+} \rightleftarrows [Cu(HL)]^{5+}$	19.77(8)
$Cu^{2+} + L^{2+} \rightleftarrows [Cu(L)]^{4+}$	13.30(7)
$Cu^{2+} + L^{2+} + H_2O \rightleftarrows [Cu(L)(OH)]^{3+} + H^+$	4.89(10)
$Cu^{2+} + L^{2+} + 2H_2O \rightleftarrows [Cu(L)(OH)_2]^{2+} + 2H^+$	–4.36(9)

[a] Values in parentheses are standard deviations in the last significant figure.

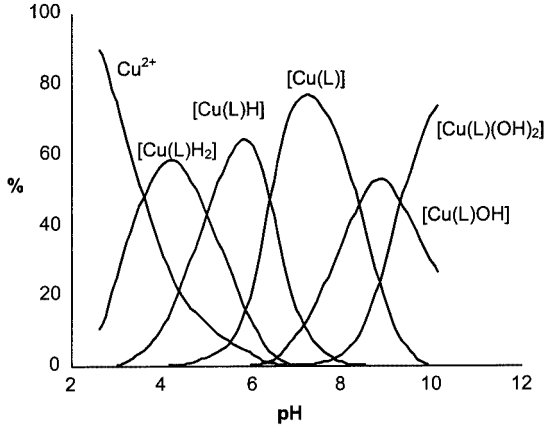


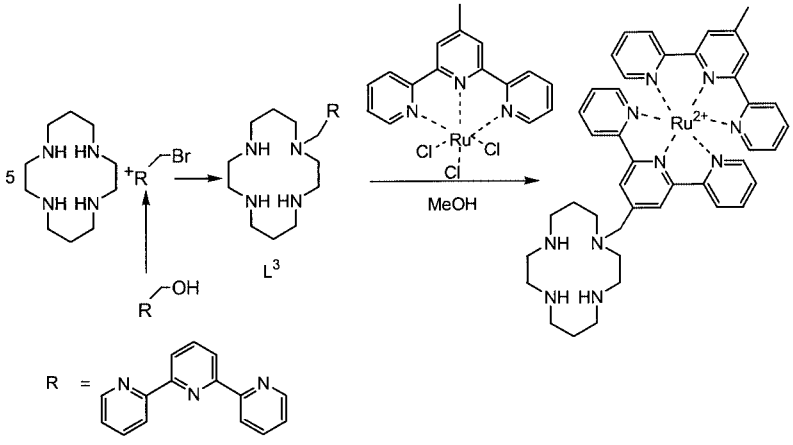
Figure 4. Distribution diagram of the species for the system $[Ru(L^1)(mtpy)]$–Cu^{2+}–H^+

$\{Cu[Ru(L^1)(mtpy)]\}^{4+}$. Despite the existence of the constraints imposed by the tmfcyclam ligand in their interaction with Cu^{2+}, the formation constant for $[Cu(tmfcyclam)]^{2+}$ is larger that that found for $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ (logK of $[Cu(tmfcyclam)]^{2+}$ – logK of $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ = 5.76), indicative of the electro-

static repulsion induced by the $[Ru(tpy)_2]^{2+}$ core on the macrocyclic cavity.

Comparison between the distribution diagram in Figure 4 and the I vs. pH curve in Figure 2 provides information about the stoichiometry and the nature of the complexes existing in the pH range where the luminescence is decreased. The quenching of the emission of the $Ru(tpy)_2^{2+}$ fluorophore is related to the presence of the $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ complex in solution, whereas further coordination of OH^- to the copper metal ion, or protonation of the amine groups in cyclam hinder the quenching.

In order to evaluate the role played by the spacer groups we have also synthesised a parent cyclam terpyridine ligand containing a CH_2 group as spacer instead of a tolyl one as in the case of L^1. For this purpose, the synthesis of the 4'-bromomethyl-2,2':6',2''-terpyridine using the 4'-methyl-2,2':6',2''-terpyridine as starting material was tested using two different routes: (i) by simple bromination of the methyl groups with *N*-bromosuccinimide, or (ii) reaction of CBr_4 with 4'-hydroxymethyl-2,2':6',2''-terpyridine obtained from the methyl derivative. When *N*-bromosuccinimide and catalytic amounts of dibenzoyl peroxide react with 4'-methyl-2,2':6',2''-terpyridine, three products were obtained: monobrominated, dibrominated and starting material. However, the mixture is not amenable to chromatographic separation. In our hands, silica or alumina did not give a very satisfactory separation of the products. The second procedure involves the reaction of 4'-(hydroxymethyl)-2,2':6',2''-terpyridine (OHmtpy) with carbon tetrabromide and triphenylphosphane to give 4'-bromomethyl-2,2':6',2''-terpyridine as the only product in 40% yield (see Scheme 2). 4'-Methyl-2,2':6',2''-terpyridine was reacted with selenium dioxide to give 4'-carbaldehyde-2,2':6',2''-terpyridine which was reduced with $NaBH_4$ to yield the corresponding 4'-(hydroxymethyl)-2,2':6',2''-terpyridine. OHmtpy has been mentioned, but to the best of our knowledge, full experimental information has not been given for its synthesis, so details are included in this paper.



Scheme 2. Synthesis of L^3 and the corresponding ruthenium complex

Reaction of the 4'-bromomethyl-2,2':6',2''-terpyridine with excess cyclam afforded the corresponding L^3 molecule in a 50% yield (see Scheme 2). As expected, the ^1H NMR spectrum of L^3 is very similar to the one of L^1 showing the pyridyl protons in the range 7.2–8.65 ppm. The spectrum is completed by one singlet at 3.62 ppm of the methylenic protons of the spacer, several overlapped signals in the range 2.40–3.10 ppm for the CH_2 groups attached to the nitrogen atoms in the macrocycle and two quintuplets at 1.8–1.95 ppm corresponding to the two nonequivalent central CH_2 groups of the propylenic chains in the cyclam macrocycle. Synthesis of $[Ru(L^3)(mtpy)][PF_6]_2$ ruthenium(II) complex was carried out by a similar method to that used in the synthesis of $[Ru(L^1)(mtpy)][PF_6]_2$ (see Scheme 2). The FAB spectrum of this complex shows peaks at m/z = 1085, 940 and 794, corresponding to $\{[Ru(L^3)(mtpy)]_2[PF_6]\}$, $\{[Ru(L^3)(mtpy)][PF_6]\}^+$ and $\{Ru(L^3)(mtpy)\}^{2+}$, respectively. The ^1H NMR spectrum shows the expected signals for the aromatic protons in the range of 7.2–8.7 ppm with two nonequivalent terpyridine groups. The spectrum also contains poorly defined overlapping signals in the 2.9–3.9 ppm range. The CH_3 of the terminal group appears at 2.93 ppm. As in the spectrum of $[Ru(L^1)(mtpy)]^{2+}$, the presence of the acetonitrile signal hampers the observation of the corresponding signal for the central CH_2 groups of the propylenic chain in the cyclam cycle.

The fluorescence behaviour of acetonitrile/water solutions of the receptor $[Ru(L^3)(mtpy)]^{2+}$ in the presence of transition metal ions M^{2+} (M^{2+} = Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}) as a function of the pH has also been studied. The behaviour of the ruthenium complex containing L^3 as ligand is similar to the behaviour observed for the ruthenium complex of L^1. There is a poor enhancement of the emission intensity of the ruthenium core upon protonation of the polyaza macrocycle and whereas the presence of Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} does not modify the fluorescence versus pH profile of the free receptor, the coordination of Cu^{2+} quenches the luminescence intensity with a minimum centred at pH = 6.2 (see Figure 5). However, despite the shorter spacer between the cyclam and the $Ru(tpy)_2^{2+}$ core in complex $[Ru(L^3)(mtpy)]^{2+}$ than in $[Ru(L^1)(mtpy)]^{2+}$, a larger quenching is observed for the latter than for the former in the presence of Cu^{2+}.

With regard to the quenching mechanism, preliminary results suggest that the quenching of the fluorescence of the

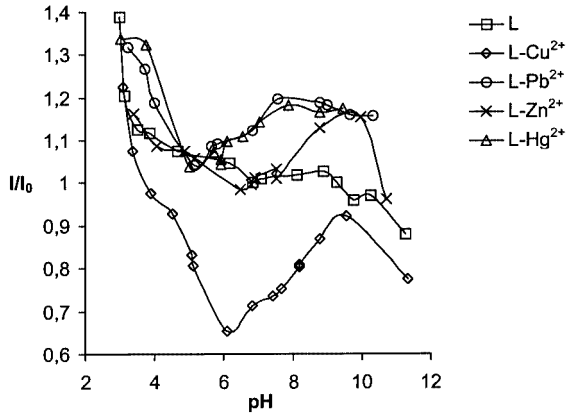


Figure 5. Relative intensity versus pH for the L and L–M^{2+} systems (L = $[Ru(L^3)(mtpy)][PF_6]_2$; M^{2+} = Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}) (λ_{ex} = 484 nm, λ_{em} = 625 nm)

$[Ru(L^1)(mtpy)]^{2+}$ and $[Ru(L^3)(mtpy)]^{2+}$ metallo-receptors upon Cu^{2+} binding most likely occurs predominantly by means of an energy transfer, bearing in mind that the electron transfer is unlikely due to the difficulty of oxidation or reduction of $[Cu(cyclam)]^{2+}$.[24] We have calculated the free energy associated with an electron-transfer mechanism by using the emission band intensity, the Ru^{II}/Ru^{III} oxidation potential of the ruthenium bis-terpyridine core ($E_{Ru(III)/Ru(II)}$ = + 1.3 V and the reduction potential for the Cu^{II}/Cu^{I} process ($E_{Cu(II)/Cu(I)}$ = – 1.05 V) in the cyclam environment, and have found a thermodynamically unfavourable ΔG value of +0.45 V for an electron transfer process. Energy-transfer mechanisms would require a close proximity between the fluorophore and the copper metal ion. In this sense, it is remarkable that the quenching is more pronounced in $[Ru(L^1)(mtpy)]^{2+}$ than in $[Ru(L^3)(mtpy)]^{2+}$. In $[Ru(L^1)(mtpy)]^{2+}$, the $Ru(tpy)_2^{2+}$ is separated by a tolyl spacer from the macrocyclic cavity, while in L^3 the spacer is a CH_2 group. The tolyl spacer in L^1 probably favours the movement of the Cu-cyclam core in search of a better overlap between the metal cation in the tetraamine and the $Ru(tpy)_2^{2+}$ fluorophore while in L^3 the CH_2 spacer diminishes this possibility.

Conclusion

We have developed new cyclam receptors functionalised with fluorescent $Ru(tpy)^{2+}$ signalling subunits and have demonstrated that the presence of copper(II) selectively quenches the fluorescence of the ruthenium(II) core more than other common metal ions in an aqueous environment at neutral pH. We have determined that the $\{Cu[Ru(L^1)(mtpy)]\}^{4+}$ complex is responsible for the quenching of the emission of the $[Ru(tpy)_2]^{2+}$ core, whereas further amine protonation or OH^- coordination to the complex hinders the quenching process. Additionally the $[Ru(L^3)(mtpy)]^{2+}$ receptor has also been synthesised and confirmed that Cu^{2+} produces a smaller decrease in fluorescence. An energy-transfer mechanism is suggested. We are currently extending our approach by attaching several macrocyclic structures to ruthenium-terpyridine units and continuing our study on the multireceptor L^2 to obtain dendritic species with several metal centres in order to construct assemblies with tuneable luminescence properties.

Experimental Section

General Remarks: The complexes $[Ru(mtpy)Cl_3]$, 4'-[4-(bromomethyl)phenyl]-2,2':6'.2''-terpyridine (Brmphtpy),[17] 4'-(4-methylphenyl)-2,2':6'.2''-terpyridine (mphtpy) and 2,2':6'.2''-terpyridinyl-4'-carboxaldehyde (CHOtpy), [25] were prepared according to published methods; all other reagents were commercially available and used as received. Photochemical data were obtained with a FS900CDT steady state T-Geometry Fluorometer, Edinburgh Analytical Instruments. All solutions for photophysical studies were rigorously degassed. Concentration of the ligand and metal ion was *ca.* 1.0×10^{-4} mol dm^{-3}. ^1H NMR spectra were recorded with a Varian Gemini spectrometer. Potentiometric titrations were carried out in acetonitrile/water (70:30 v/v, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) using a water-thermostatted reaction vessel at 25.0 ± 0.1 °C under nitrogen. The titrant was added by a Crison microburette 2031. Experimental potentiometric details have been published previously.[26] The concentration of the metals ions was determined using standard methods. The computer program SUPERQUAD[27] 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 2.5–10.2, concentration of the ligand and metal ion 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.

Synthesis of 4'-(Hydroxymethyl)-2,2':6'.2''-terpyridine (OHmtpy): To a mixture of CHOtpy (1.0 g, 3.8 mmol) in THF (10 mL) was added $NaBH_4$ (200 mg, 5.3 mmol) and the resulting mixture was stirred for 15 min at 0 °C. The reaction mixture was extracted with EtOAc (70 mL), and washed with water (3 × 3 mL) and brine (3 mL). The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel. Yield 841 mg, 85%.

Synthesis of 4'-(Bromomethyl)-2,2':6'.2''-terpyridine (Brmtpy): To a mixture of OHmtpy (1 mmol) and carbon tetrabromide (2 mmol) in CH_2Cl_2 (5 mL) was added triphenylphosphane (1.1 mmol) at 0 °C in several portions over 15 min. The mixture was stirred for 0.5 h at the same temperature and for 0.5 h at room temperature. In order to remove triphenylphosphane oxide, the mixture was passed through a short silica gel column (10 g) and eluted with CH_2Cl_2. Compound Brmtpy was obtained as a yellow oil that solidified on prolonged drying. Yield 130 mg, 40%. – ^1H NMR (300 MHz, $CDCl_3$): δ = 4.48 (s, 2 H, CH_2Br), 7.29–7.31 [2 H, tpy H(5, 5'')], 7.78–7.81 [2 H, tpy H(4, 4'')], 8.42 [s, 2 H, tpy H(3', 5')], 8.54–8.56 [2 H, tpy H(6, 6'')] and 8.63–8.66 [2 H, tpy H(3, 3'')]. – $C_{16}H_{12}N_3Br.CH_2Cl_2$: calcd. C 49.8, H 3.4, N 10.3; found C 49.6, H 3.1, N 10.3. – FAB-MS: *m/z* (%): 327(30), 325(65), 247(80).

Synthesis of 1-[4'-*p*-Tolyl-(2,2':6',2''-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^1): A mixture of 4'-[4-(bromomethyl)phenyl]-2,2':6'.2''-terpyridine (0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of cyclam (500 mg, 2.5 mmol) in CH_2Cl_2 (20 mL). Et_3N (5 drops) was added, and the solution was heated at 30°C for 24 h. The reaction mixture was washed with water (3

× 3 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on alumina with CH_2Cl_2/CH_3OH (99:1 v/v) as eluent. A pale yellow oil was obtained which solidified on scratching. Yield: 130 mg, 50%. – **L^1**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.80 (4 H, $CH_2CH_2CH_2$), 2.3–2.9 (16 H, CH_2–N), 3.52 (2 H, Cy–CH_2-tpy), 7.20–7.22 [2 H, tpy H(5, 5'')], 7.34–7.36[2 H, Ph H_m), 7.70–7.72 [2 H, tpy H(4, 4'')], 7.73–7.73 (2 H, Ph H_o), 8.54–8.56 [2 H, tpy H(6, 6'')], 8.57–8.59 [2 H, tpy H(3, 3'')], and 8.62 [s, 2 H, tpy H(3', 5')]. – ^{13}C NMR ($CDCl_3$): δ = 26.17 (CH_2), 28.60 (CH_2), 46–60 (8 CH_2), 71.53 (CH_2), 118.53 (CH, tpy), 121.2 (CH, tpy), 123.64 (CH, tpy), 126.91 (CH, C_6H_4), 129.55 (CH, C_6H_4), 136.82 (CH, tpy), 140.4 (C, tpy), 148.96 (CH, tpy), 149.92 (CH, tpy), 155.8 (C, tpy), 156.14 (C, tpy). – $C_{32}H_{39}N_7.CH_2Cl_2.H_2O$: calcd. C 63.5, H 6.9, N 15.7; found C, 63.0; H, 6.9; N, 15.4. – FAB-MS: *m/z* (%): 522 (100), 323 (40), 212 (50).

Synthesis of 1,4,8,11-[4'-*p*-Tolyl-(2,2':6',2''-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^2): A mixture of Brmphtpy (650 mg, 1.6 mmol) and cyclam (54 mg, 0.27 mmol) in ethanol (50 mL) and in the presence of Et_3N was heated at reflux for 24 h. Yellow crystals were obtained. The residue was purified by column chromatography on alumina using CH_2Cl_2/CH_3OH (97:3 v/v) as eluent. Yield: 70 mg, 20%. **L^2:**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (2 H, $CH_2CH_2CH_2$), 2.62 (8 H, CH_2–N), 2.71 (8 H, CH_2–N), 3.52 (8 H, Cy–CH_2-phtpy),7.25–7.30 [8 H, tpy H(5, 5'')], 7.45–7.50 [8 H, ph), 7.73–7.74 [8 H, ph), 7.75 [8 H, tpy H(4, 4'')], 8.59 [8 H, tpy H(6, 6'')], 8.63–8.66 [8 H, tpy H(3, 3'')] and 8.66 [s, 8 H, tpy H(3', 5')]. – ^{13}C NMR ($CDCl_3$): δ 30.5 (CH_2), 50.5 (4 CH_2), 51.6 (4 CH_2), 59.0 (4 CH_2), 118.8 (CH, tpy), 121.3 (CH, tpy), 123.8 (CH, tpy), 127.0 (CH, C_6H_4), 129.5 (CH, C_6H_4), 136.8 (CH, tpy), 149.0 (CH, tpy), 155.72 (C, tpy), 156.3 (C, tpy). – $C_{98}H_{84}N_{16}{\cdot}2CH_2Cl_2{\cdot}H_2O$: calcd. C 72.5, H 5.3, N 13.5; found C 72.3, H 5.1, N 12.9. – FAB-MS: *m/z* (%): 1487 (100), 1164 (45).

Synthesis of 1-[4'-Methyl-(2,2':6',2''-terpyridyl)]-1,4,8,11-tetraazacyclotetradecane (L^3): L^3 was prepared in the same manner as L^1, by the reaction of cyclam and 4'-(bromomethyl)-2,2':6'.2''-terpyridine. Yield: 110 mg, 50%. **L^3:** ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.82–1.97 (4 H, $CH_2CH_2CH_2$), 2.4–3.1 (16 H, CH_2–N), 3.62 (2 H, Cy–CH_2-tpy), 7.22–7.24 [2 H, tpy H(5, 5'')], 7.78–7.80 [2 H, tpy H(4, 4'')], 8.40 [s, 2 H, tpy H(3', 5')], 8.53–8.56 [2 H, tpy H(6, 6'')] and 8.60–8.63 [2 H, tpy H(3, 3'')]. – ^{13}C NMR ($CDCl_3$): δ 23.9 (CH_2), 24.2 (CH_2), 45–59 (8 CH_2), 72.38 (CH_2), 121.2 (2 CH, tpy), 123.9 (CH, tpy), 136.9 (CH, tpy), 148.0 (CH, tpy), 150.1 (C, tpy), 155.5 (2 C, tpy). – $C_{26}H_{35}N_7.CH_2Cl_2.H_2O$: calcd. C 59.1, H 7.1, N 17.9; found C 60.0, H 6.9, N 17.4. – FAB-MS: *m/z* (%): 446 (35), 247 (80), 213 (80).

Synthesis of $[Ru(L^1)(mtpy)][PF_6]_2$ and $[Ru(L^3)(mtpy)][PF_6]_2$: These ruthenium complexes were prepared in the same way. A mixture of the appropriate ligand (L^1 105 mg, L^3 89 mg; 0.2 mmol), with $[Ru(mtpy)Cl_3]$ (90 mg, 0.2 mmol) and three drops of *N*-ethylmorpholine as a mild reductor in MeOH (20 mL) was heated at reflux with stirring for 1 h. The resulting deep-red solution was filtered through celite to remove any unchanged $[Ru(mtpy)Cl_3]$ and excess methanolic ammonium hexafluorophosphate was added to the filtrate to precipitate the ligand complexes. Further purification was achieved by chromatography over silica using 17:2:1 acetonitrile/water/saturated aqueous KNO_3 solution. The complexes were isolated as their PF_6^- salts.

$[Ru(L^1)(mtpy)]PF_6]_2$:. Yield: 40 mg, 20%. – ^{1}H NMR (300 MHz, CD_3CN): δ = 2.90 (s, 3 H, CH_3), 3.0–3.5 (16 H, CH_2–N), 3.78–3.82 (2 H, tpy–CH_2–Cy), 7.18–7.20[4 H, tpy H(5,5'')^{1,2}], 7.37–7.39[2 H, tpy H(6,6'')^1], 7.42–7.44[2 H, tpy H(6,6'')^2], 7.74–7.76 (2 H, ph H_m), 7.94–7.96 [4 H, tpy H(4, 4'')^{1,2}], 8.20–8.22 (2 H, ph H_o), 8.48–8.50 [2 H, tpy H(3, 3'')^1], 8.68–8.70 [2 H, tpy H(3, 3'')^2] 8.70 [s, 2 H, tpy H(3', 5')^1] and 9.01 [s, 2 H, tpy H(3', 5')^2].^{1} = mtpy; ^{2} = Cy–spacer–tpy (spacer = tolyl). – $C_{48}H_{52}N_{10}Ru(PF_6)_2.2CH_2Cl_2$: calcd. C 45.1, H 4.2, N 10.5; found C 45.3, H 3.8, N 10.3. – FAB-MS: *m/z* (%): 1161 (8), 1015 (20), 869 (45), 327 (60), 281 (100). – **$[Ru(L^1)(mtpy)]PF_6]_2$:** Yield 30 mg, 15%. – ^{1}H NMR (300 MHz, CD_3CN): δ = 2.97 (s, 3 H, CH_3), 3.0–3.3 (16 H, CH_2–N), 3.7–3.9(2 H, tpy–CH_2–Cy), 7.16–7.18[2 H, tpy H(5,5'')^1], 7.22–7.24 [2 H, tpy H(5, 5'')^2], 7.24–7.26[2 H, tpy H(6,6'')^2], 7.37–7.39[2 H, tpy H(6,6'')^1], 7.92–7.94 [4 H, tpy H(4, 4'')^{1,2}], 8.44–8.46 [2 H, tpy H(3, 3'')^2], 8.50–8.52 [2 H, tpy H(3, 3'')^1] 8.66 [s, 2 H, tpy H(3', 5')^2] and 8.68 [s, 2 H, tpy H(3', 5')^1].^{1} = mtpy; ^{2} = Cy–spacer–tpy (spacer = methylene) – FAB-MS: *m/z* (%): 1085 (20), 939 (26), 793 (45), 595 (60).

X-ray Crystallographic Study: $C_{106}H_{104}N_{16}O_5$, M = 1682.05, triclinic, space group $P\bar{1}$, a = 12.303(4), b = 13.440(5), c = 15.618(6) Å, α = 106.60(3), β = 90.71(3), γ = 101.96(3), Z = 1, U = 2414(2) Å^3, Dc = 1.157 g cm^{-3}, λ(Mo-K_α) = 0.71069 Å, T = 296(2) K, μ(Mo-K_α) = 0.073 mm^{-1}. Measurements were made using a Siemens P4 diffractometer with graphite monochromated Mo-K_α radiation on a yellow crystal of L^2, of dimensions 0.26 × 0.20 × 0.23 mm. A total of 6429 reflections were collected, of which 6090 were unique (R_{int} = 0.0551). Lorentz, polarisation and semi-empirical from psi-scan absorption (Max. and min. transmission 0.4322 and 0.2287) corrections were applied. The structure was solved by direct methods (SHELXTL)[28] and refined by full-matrix least-squared analysis on *F2* (SHELXTL). The refinement converged at R_1 = 0.1077 ($F > 4\sigma(F)$) and wR_2 = 0.3120 (all data). Largest peak and hole in the final difference map +0.44, –0.35 e Å^{-3}. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132890. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+ 44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

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Bis(terpyridyl)-Ruthenium(II) Units Attached to Polyazacycloalkanes as Sensing Fluorescent Receptors For Transition Metal Ions

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Figure 2 on page 743 of the PDF version is missing; it is provided on this additional page.

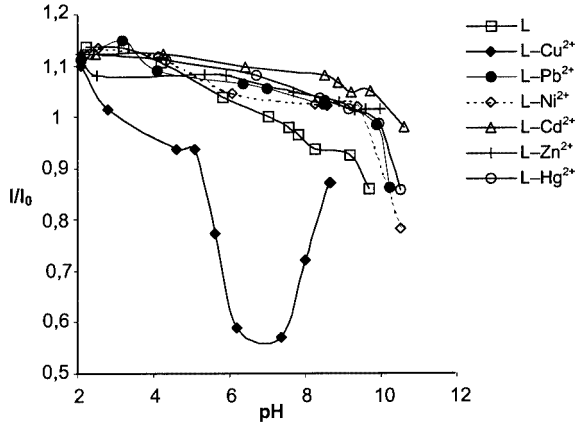

Figure 2. Relative intensity versus pH for the L and L−M^{2+} systems (L = $[Ru(L^1)(mtpy)][PF_6]_2$; M^{2+} = Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}) (λ_{ex} = 484 nm, λ_{em} = 664 nm)