Fluorescent Chemosensors for Heavy Metal Ions Based on Bis(terpyridyl) Ruthenium(II) Complexes Containing Aza-Oxa and Polyaza Macrocycles

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Reactions of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine with 4,10-diaza-15-crown-5 and 1-aza-12-crown-4 in dichloromethane yielded the ligands L^1 and L^3, respectively. Reaction of an excess of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine with 4,10-diaza-15-crown-5 yielded L^2, while treatment of the same terpyridine ligand with 1,4,7,10,13-pentaazacyclopentadecane afforded L^4. Reactions of L^1, L^3, and L^4 with Ru(mtpy)Cl_3 (mtpy = 4′-methyl-2,2′:6′,2′′-terpyridine) in methanol yielded the metallo receptors $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, and $[Ru(L^4)(mtpy)][PF_6]_2$ after precipitation with ammonium hexafluorophosphate and column chromatography. On treating L^3 with $RuCl_3$, the homoleptic ruthenium complex $[Ru(L^3)_2][PF_6]_2$ was obtained. The synthesized metallo receptors contain oxa-aza crown or polyazacycloalkane moieties as recognition sites and $[Ru(tpy)_2]^{2+}$ cores as the signal-generating centre. The electronic spectra of the complexes are as expected for an $Ru(tpy)_2^{2+}$ chromophore, with the main $Ru[d(\pi)] \rightarrow tpy(\pi^*)$ MLCT transition at ca. 484 nm and intense ligand-centred transitions in the UV region. One of the most interesting aspects of these ruthenium complexes is their multicomponent nature, as they contain both coordination sites and fluorescent $Ru(tpy)_2^{2+}$ cores. The cations $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$ display an emission maximum at ca. 650 nm, the intensity of which is pH dependent, showing an enhancement upon protonation. The metallo receptor $[Ru(L^1)(mtpy)]^{2+}$ selectively senses Hg^{2+} in preference to Cu^{2+}, Cd^{2+}, and Pb^{2+}. The emission intensity vs. pH curve for $[Ru(L^2)(mtpy)]^{2+}$ in the presence of Cu^{2+} and Hg^{2+} ions is close to that of the free receptor, but the presence of Cd^{2+} or Pb^{2+} enhances the emission intensity in the range pH 4–6. For the $[Ru(L^3)_2]^{2+}$ complex, Cd^{2+}, Pb^{2+}, and Hg^{2+} induce an enhancement of the fluorescence of the $Ru(tpy)_2^{2+}$ core in the range pH 3.5–7.5. These results are compared with those obtained for the metallo receptor $[Ru(L^4)(mtpy)]^{2+}$ containing a polyazacycloalkane moiety as the binding domain.

Introduction

Ligands with a macrocyclic unit attached to a metal-polypyridyl core are potentially useful in the preparation of luminescent or electrochemical sensors, in which the macroscopic properties of the core are modified by molecular-level interactions between the recognition centre and the substrate.[1−4] The polypyridyl complexes of d^6 metals, with their strong metal-to-ligand charge transfer absorptions and emitting excited states, are good candidates as signalling subunits.[5,6] The metal−polypyridyl complex most widely used as a fluorophore is probably $Ru(bipy)_3^{2+}$.[7,8] In contrast, the ruthenium−terpyridine $Ru(tpy)_2^{2+}$ unit has been less well studied. Although the $Ru(tpy)_2^{2+}$ core is less fluorescent than $Ru(bipy)_3^{2+}$, terpyridine complexes may have some advantages over their bipyridine counterparts. Thus, for instance, it has been reported that the octahedral tpy-type complex has the advantage of being non-chiral (preventing the generation of stereoisomers that may arise with bipy-Ru complexes) and, through functionalization of the ligand at the appropriate position, allows the construction of multicomponent systems with fine control over the geometry of the assembly.[9,10] Additionally, from a practical viewpoint, emission in the visible part of the spectrum (as shown by Ru-tpy complexes) is much more convenient than emission near the UV region, where many other organic fluorophores typically emit.

We have recently reported the functionalization of the $Ru(tpy)_2^{2+}$ unit with cyclam and the use of the resulting compound as a potential sensing receptor for Cu^{2+} ions.[11] Further, we are interested in the development of potential chemosensors for heavy transition metal ions such as Cd^{2+}, Hg^{2+}, and Pb^{2+}. Sensing receptors for toxic heavy metal ions are of interest in areas such as environmental chemistry, where the development of highly selective analytical tools is of importance. In order to direct the sensing ability of $Ru(tpy)_2^{2+}$-based chemosensors towards the selective determination of these metals, we have covalently functionalized the fluorophore core with binding sites that are known to show greater stability constants with large transition metal ions than with smaller ones.[12,13] In fact, it has been established that a combination of O and N donor atoms on such macrocyclic structures promotes the formation of complexes with large-sized transition metal cations as opposed to those with smaller radii.[15] Based on the fact that large stability constants could lead to a high selectiv-

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ity,[17] we report herein on the synthesis of three new oxa-aza functionalized $Ru(tpy)_2^{2+}$ receptors. The main goal of this work has been the quest for new potential chemosensors for toxic heavy metal cations.

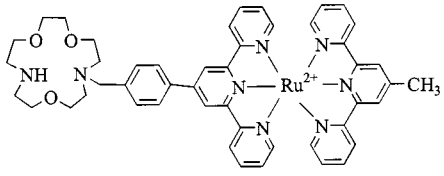
Results and Discussion

Synthesis and Characterization

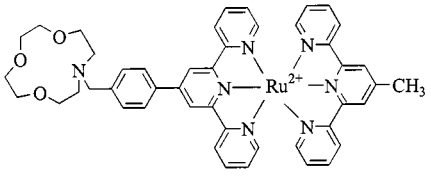
4′-[4-(Bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine (Br-mphtpy) was synthesized according to the procedure of Spahni and Calzaferri.[18] From this derivative, terpyridine-functionalized crowns could be readily prepared by reaction with the appropriate macrocycle in dichloromethane in the presence of Et_3N at 30 °C for 24 h, followed by column chromatography on alumina using a mixture of CH_2Cl_2/MeOH as the eluent. This led to yields of ca. 30% for L^1 and L^2, of 35% for L^3, and of 50% for L^4.

Ligands L^1 and L^2 show very similar ^1H NMR spectra, the main difference being the appearance of the proton signal of the amine group at δ = 2.5 in the spectrum of L^1, which is not observed in the case of L^2. The pyridyl proton signals are seen in the range δ = 7.3−8.8. The spectra are completed by two groups of signals, one in the range δ = 2.7−3.0, corresponding to the protons of CH_2 groups attached to a nitrogen atom in the crown, and the other in the range δ = 3.6−3.9, attributable to benzylic protons and to the protons of CH_2 groups bonded to oxygen atoms. The ^1H NMR spectrum of L^3 shows signals due to the protons of CH_2 groups bonded to an N atom in the crown at δ = 2.8, and signals due to the protons of the CH_2 groups attached to an O atom as well as those of the benzylic protons in the range δ = 3.4−3.8. The ^1H NMR spectrum of L^4 is also in agreement with the proposed formulation.

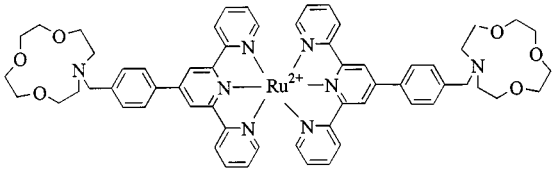
Reactions of equimolar amounts of L^1, L^3, or L^4 with [Ru(mtpy)Cl_3] in methanol in the presence of *N*-ethylmorpholine as a mild reductant yielded the complexes $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, and $[Ru(L^4)(mtpy)][PF_6]_2$, respectively, after precipitation with ammonium hexafluorophosphate and column chromatography on silica using acetonitrile/water/satd. aq. KNO_3 (17:1:2, *v*/*v*) as the eluent. The FAB mass spectra showed peaks at *m*/*z* = 1177, 1033, and 887 for $[Ru(L^1)(mtpy)][PF_6]_2$, at *m*/*z* = 1135, 990, and 845 for $[Ru(L^3)(mtpy)][PF_6]_2$, and at *m*/*z* = 1174, 1030, and 885 for $[Ru(L^4)(mtpy)][PF_6]_2$, corresponding to {$[Ru(L)(mtpy)][PF_6]_2$}, {$[Ru(L)(mtpy)][PF_6]^+$}, and {$[Ru(L)(mtpy)]^{2+}$}, respectively. The ^1H NMR spectra of the ruthenium complexes showed the expected signals due to the aromatic protons in the region δ = 7.1−9.1. They were fully assigned with the assistance of ^1H-^1H correlation spectroscopy (COSY). The spectra also featured signals due to the protons of the terminal CH_3 groups, at δ = 2.93 in each case. The signals due to the protons of the CH_2 groups



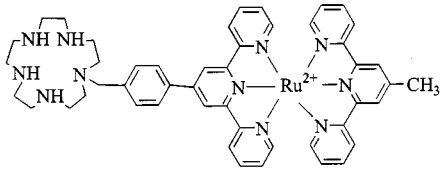
$[Ru(L^1)(mtpy)]^{2+}$



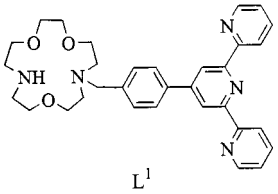
$[Ru(L^3)(mtpy)]^{2+}$



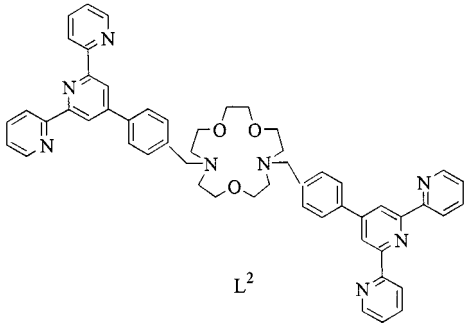
$[Ru(L^3)_2]^{2+}$



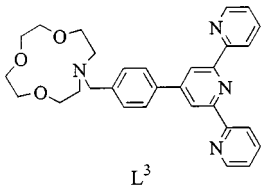
$[Ru(L^4)(mtpy)]^{2+}$



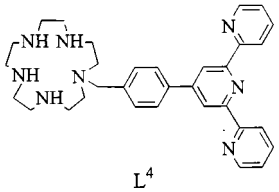
L^1



L^2



L^3



L^4

attached to a nitrogen atom appeared at ca. δ = 3.3, whereas those due to the protons of CH_2 groups bonded to oxygen atoms were seen at δ = 3.6−4.0. The ruthenium complex of L^4 shows signals due to the protons of the polyazacycloalkane ring in the region δ = 2.8−3.2.

The homoleptic complex of L^3 was obtained by treating $RuCl_3$ with two equivalents of L^3 in methanol in the presence of *N*-ethylmorpholine as a mild reductant, followed by precipitation with ammonium hexafluorophosphate and column chromatography. The FAB mass spectrum of $[Ru(L^3)_2][PF_6]_2$ showed peaks at *m*/*z* = 1240, 1094, and 920, corresponding to $\{[Ru(L^3)_2][PF_6]_2\}$, $\{[Ru(L^3)_2][PF_6]^+\}$, and $\{[Ru(L^3)_2]^{2+}\}$, respectively. The ^1H NMR spectrum of the $[Ru(L^3)_2][PF_6]_2$ complex was also in agreement with the proposed formulation.

Photophysical Characterization and pH-Dependence of the Fluorescence

The electronic spectra of the complexes were found to be as expected for an $[Ru(tpy)_2]^{2+}$ chromophore, with the main Ru[d(π)] → tpy(π*) MLCT transition at ca. 484 nm and the usual intense ligand-centred transitions in the UV region.[5,6] It is likely that the absorption band at ca. 484 nm corresponds to a mixture of dπ(Ru) → π(mtpy) and dπ(Ru) → π(L^n) transitions for the heteroleptic $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, and $[Ru(L^4)(mtpy)][PF_6]_2$ complexes and to the transition dπ(Ru) → π(L^3) in the case of the homoleptic $[Ru(L^3)_2][PF_6]_2$ complex, which would otherwise give a narrower absorption band.[19] The photophysical properties of the complexes $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, $[Ru(L^4)(mtpy)][PF_6]_2$, and $[Ru(L^3)_2][PF_6]_2$ in acetonitrile/water (70:30, *v*/*v*) at 298 K are summarized in Table 1.

Table 1. Photophysical properties of the complexes $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, $[Ru(L^4)(mtpy)][PF_6]_2$, and $[Ru(L^3)_2][PF_6]_2$ in acetonitrile/water (70:30, *v*/*v*) at 298 K

	abs. (298 K)		em. (298 K)
	λ [nm]	ε [M^{-1} cm^{-1}]	λ [nm]
$[Ru[L^1](mtpy)][PF_6]_2$	480	17500	652
$[Ru(L^3)(mtpy)][PF_6]_2$	483	17700	650
$[Ru(L^4)(mtpy)][PF_6]_2$	484	17000	650
$[Ru(L^3)_2][PF_6]_2$	482	16800	652

One of the most attractive features of these complexes is their multicomponent nature as they contain sites suitable for coordinating metal ions in the vicinity of a fluorescent $Ru(tpy)_2^{2+}$ group. It is known that, compared to acyclic structures, macrocyclic receptors generally display more selective complexation. Additionally, the introduction of central oxygen donor atoms in macrocycles has been used to achieve selectivity for large metal ions as opposed to small ones.[15] The presence of aza-oxa macrocycles in the metallo receptors $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, and $[Ru(L^3)_2][PF_6]_2$ thus makes them good candidates as fluorescent signalling systems for toxic heavy metal ions in solution.

The fluorescence behaviour of the complexes $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, $[Ru(L^4)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$ was investigated in acetonitrile/water mixtures as a function of the pH, in the absence and presence of transition metal ions M^{2+} (M^{2+} = Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) {see Figure 1 (a) for $[Ru(L^1)(mtpy)]^{2+}$, Figure 1 (b) for $[Ru(L^3)(mtpy)]^{2+}$, Figure 1 (c) for $[Ru(L^3)_2]^{2+}$, and Figure 1 (d) for $[Ru(L^4)(mtpy)]^{2+}$}.

The complexes $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$ display an emission maximum at ca. 650 nm, the intensity of which is seen to be pH-dependent. In the case of $[Ru(L^1)(mtpy)]^{2+}$, an enhancement of the luminescence of ca. 60% is observed upon protonation, which is close to the enhancement seen for the $[Ru(L^3)(mtpy)]^{2+}$ complex. Remarkably, the enhancement in the emission intensity of $[Ru(L^3)_2]^{2+}$ upon protonation is ca. twice that observed for the heteroleptic complexes. In contrast, the emission intensity of the $[Ru(L^4)(mtpy)]^{2+}$ complex is seen to be almost pH-independent, showing only a slight increase at acidic pH. This suggests that the electron- or energy-transfer path from the amine to the $Ru(tpy)_2^{2+}$ fluorophore is more effective in aza-oxa derivatives than in the polyazacycloalkane. In fact, negligible pH-dependence was also found for the ruthenium(II) complex [Ru(cyphtpy)(mtpy)]$^{2+}$ {cyphtpy = 1-[4′-(*p*-tolyl)-2,2′:6′,2′′-terpyridyl]-1,4,8,11-tetraazacyclotetradecane}, which contains a cyclic tetraamine unit anchored to the ruthenium(II) bis(terpyridine) centre.[11]

Typical quantum yields for these complexes are around $5 \cdot 10^{-5}$, comparable to those reported for similar ruthenium bis(terpyridyl) complexes.[19] Unfortunately, these low quantum yields prevent further studies on the lifetimes of the excited states. As stated above, the intensities of the emission maxima (or quantum yields) of the $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$ complexes are pH-dependent. In order to gain a better understanding of the pH-dependent fluorescent behaviour seen for the aza-oxa-functionalized bis(terpyridyl) ruthenium(II) complexes, further studies were carried out on the $[Ru(L^1)(mtpy)]^{2+}$ complex. Two possible mechanisms may be invoked to account for the fluorescence quenching of the $Ru(tpy)_2^{2+}$ signalling unit,[19] i.e. electron transfer and energy transfer. The occurrence or otherwise of an electron-transfer mechanism can be assessed on the basis of electrochemical and photophysical data. For instance, the free energy associated with the electron-transfer process $[Ru(tpy)_2^{2+}*-amine] \rightarrow [Ru(tpy)_2^{+}-amine^{+}]$, where an electron from the lone pair of the amine is transferred to an orbital of the fluorophore leading to a quenching process, can be calculated from the equation: $\Delta G = -(hcN_A/\lambda) + F[E^0_{amine+/amine} - E^0_{fl/fl-}]$ (fl = fluorophore), where $E^0_{amine+/amine}$ and $E^0_{fl/fl-}$ are the redox potentials associated with the redox processes 'amine$^+$ + 1 e^- → amine' and 'fl + 1 e^- → fl$^-$', respectively, and λ relates to the so-called spectroscopic energy that can be obtained from the emission fluorescence spectrum. Redox potentials were measured in dry acetonitrile (containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate) at 25 °C. Cyclic voltammograms

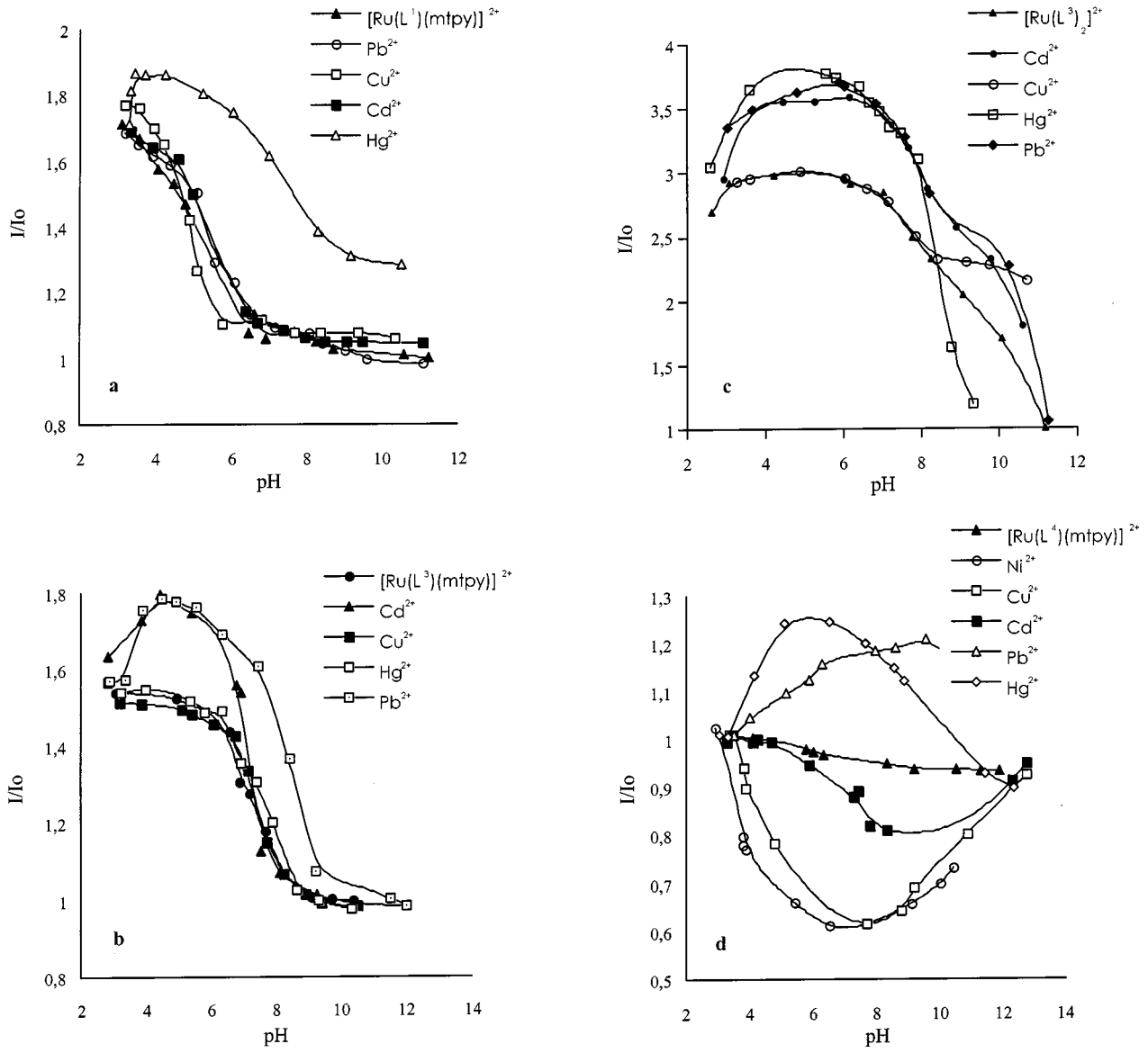


Figure 1. Relative emission intensity versus pH for the L and L−M^{2+} systems: (a) L = $[Ru(L^1)(mtpy)][PF_6]_2$, M^{2+} = Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}; (b) L = $[Ru(L^3)(mtpy)][PF_6]_2$, M^{2+} = Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}; (c) L = $[Ru(L^3)_2][PF_6]_2$, M^{2+} = Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}; (d) L = $[Ru(L^4)(mtpy)][PF_6]_2$, M^{2+} = Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}

of the ruthenium complex $[Ru(L^1)(mtpy)]^{2+}$ show two oxidation processes, at 1.05 V and 1.23 V. The first of these is irreversible and can be ascribed to the oxidation of the 4,10-diaza-15-crown-5, whereas the second corresponds to the oxidation of the Ru^{II} centre. The complex $[Ru(L^1)(mtpy)]^{2+}$ also displays two quasi-reversible reduction processes at −1.25 and −1.52 V, attributable to the formal reduction of the $Ru(tpy)_2^{2+}$ core. Taking these data into account, the ΔG value obtained is ca. −6.5 kcal/mol. This negative value suggests that a photoinduced electron-transfer process from the amine to the $Ru(tpy)_2^{2+}$ fluorophore is possible. This is probably the mechanism that is operative under conditions of basic pH (where the amine is not protonated). When the pH is decreased, the amine groups are protonated, and the oxidation of the amine becomes more difficult, thus making ΔG positive. A positive value of the free energy reduces the probability of electron-transfer processes and therefore an increase in the emission intensity would be expected at acidic pH, as is indeed observed (Figure 1).

Sensing Response towards Transition Metal Ions

The I/I_0 vs. pH curve for the free receptor $[Ru(L^1)(mtpy)]^{2+}$ remains essentially unchanged in the presence of the transition metal ions Cu^{2+}, Cd^{2+}, and Pb^{2+} (see Figure 1). In contrast, in the presence of Hg^{2+}, a different I/I_0 vs. pH profile is seen over a wide pH range. The presence of Hg^{2+} led to an enhancement of the emission intensity by as much as 60% at pH 6.5, with some enhancement even being observed at lower pH. This intensity increase may be attributed to the formation of $[Ru(L^1)(mtpy)]^{2+}-Hg^{2+}$ species, in which the lone pair of the nitrogen atom would no longer be available for the photoinduced electron-transfer process owing to its involvement in the coordinative interaction. At this point it is interesting to note that the 4,10-

diaza-15-crown-5 cycle has also been *N*-functionalized with the organic anthrylmethyl fluorophore.[20] Whereas the metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} had no modifying effect on the fluorescence intensity vs. pH profile of the anthryl derivative, the presence of Hg^{2+} enhanced the emission intensity in the range pH 5−9. This result is similar to that found for the $[Ru(L^1)(mtpy)]^{2+}$ complex in the presence of metal ions, suggesting that both fluorophores, i.e. the $Ru(tpy)_2^{2+}$ and the anthryl signalling subunits, are able to selectively detect the presence of Hg^{2+} through a combination of coordination to an appropriate binding site (the 4,10-diaza-15-crown-5 cycle) and enhancement of the fluorescence.

To gain insight into the interaction of Hg^{2+} with $[Ru(L^1)(mtpy)]^{2+}$, protonation and coordination studies were carried out by means of potentiometric titrations of previously acidified solutions of the ruthenium(II) complex in acetonitrile/water (70:30, *v*/*v*, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) with KOH. Protonation constants are given in Table 2, while stability constants for the formation of Hg^{2+} complexes with $[Ru(L^1)(mtpy)]^{2+}$ are given in Table 3. The $[Ru(L^1)(mtpy)]^{2+}$ complex displays two protonation process with basicity constants of $\log K = 9.47$ and $\log K = 7.67$. These values are close to those found for the analogous ferrocenylmethyl-functionalized derivative 7,13-ferrocenylmethyl-7,13-diaza-15-crown-5 ($\log K = 8.49$ and $\log K = 6.69$ in dioxane/water, 70:30, *v*/*v*).[21]

Table 2. Stepwise protonation constants in acetonitrile/water (70:30, *v*/*v*, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) for $[Ru(L^1)(mtpy)]^{2+}$

Reaction	log *K*[a]
$[Ru(L^1)(mtpy)]^{2+} + H^+ \rightleftarrows [Ru(HL^1)(mtpy)]^{3+}$	9.47(1)
$[Ru(L^1)(mtpy)]^{2+} + 2\ H^+ \rightleftarrows [Ru(H_2L^1)(mtpy)]^{4+}$	17.14(2)

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

Table 3. Stability constants (log *K*) for the formation of the Hg^{2+} complexes of $[Ru(L^1)(mtpy)]^{2+}$ in acetonitrile/water (70:30, *v*/*v*, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) at 25 °C

Reaction	log *K*[a]
$Hg^{2+} + [Ru(HL^1)(mtpy)]^{3+} \rightleftarrows \{Hg[Ru(HL^1)(mtpy)]\}^{5+}$	14.24(3)
$Hg^{2+} + [Ru(L^1)(mtpy)]^{2+} \rightleftarrows \{Hg[Ru(L^1)(mtpy)]\}^{4+}$	6.23(3)
$Hg^{2+} + [Ru(L^1)(mtpy)]^{2+} + H_2O \rightleftarrows \{Hg(OH)[Ru(L^1)(mtpy)]\}^{3+} + H^+$	−3.57(4)
$Hg^{2+} + [Ru(L^1)(mtpy)]^{2+} + 2\ H_2O \rightleftarrows \{Hg(OH)_2[Ru(L^1)(mtpy)]\}^{2+} + 2\ H^+$	−13.27(3)

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

The coordination behaviour of the receptor $[Ru(L^1)(mtpy)]^{2+}$ towards Hg^{2+} has been studied. Our aim was to explore the coordination ability of the aza-oxa cycle and the effect of the presence of a bulky, charged $Ru(tpy)_2^{2+}$ group on the coordination of metal ions. Hg^{2+} was chosen because of the selective fluorescence response seen in the presence of this cation. An exhaustive and detailed coordination study was beyond the scope of this article, mainly due to the relatively low yields achieved in the synthesis of the complex $[Ru(L^1)(mtpy)][PF_6]_2$ and of the related complexes mentioned in this paper.

From the refinement of the potentiometric data in the range pH 2−10.5 in the presence of Hg^{2+}, the species $\{Hg[Ru(HL^1)(mtpy)]\}^{5+}$, $\{Hg[Ru(L^1)(mtpy)]\}^{4+}$, $\{Hg(OH)[Ru(L^1)(mtpy)]\}^{3+}$, and $\{Hg(OH)_2[Ru(L^1)(mtpy)]\}^{3+}$ were found. The stability constant for the equilibrium $Hg^{2+} + [Ru(L^1)(mtpy)]^{2+} \rightleftarrows \{Hg[Ru(L^1)(mtpy)]\}^{4+}$ was evaluated as $\log K = 6.23$. We have recently studied the interaction of Hg^{2+} with the ferrocene-functionalized ligand 7,13-ferrocenylmethyl-7,13-diaza-15-crown-5. In this case, the logarithm of the formation stability constant of the ligand with Hg^{2+} was measured as $\log K = 8.79$ in dioxane/water (70:30, *v*/*v*).[21] Although a different solvent system has been used for the study of the interaction between Hg^{2+} and the aforementioned $Ru(tpy)_2^{2+}$- and ferrocene-functionalized receptors, it seems that the presence of the positively charged, bulky $Ru(tpy)_2^{2+}$ signalling subunit might impose some constraints on the coordination of Hg^{2+} by the aza-oxa macrocycle and makes the stability constant with $[Ru(L^1)(mtpy)]^{2+}$ lower than that with the analogous ferrocene-functionalized derivative. Figure 2 shows the distribution diagram for the $[Ru(L^1)(mtpy)]^{2+}-Hg^{2+}-H^+$ system.

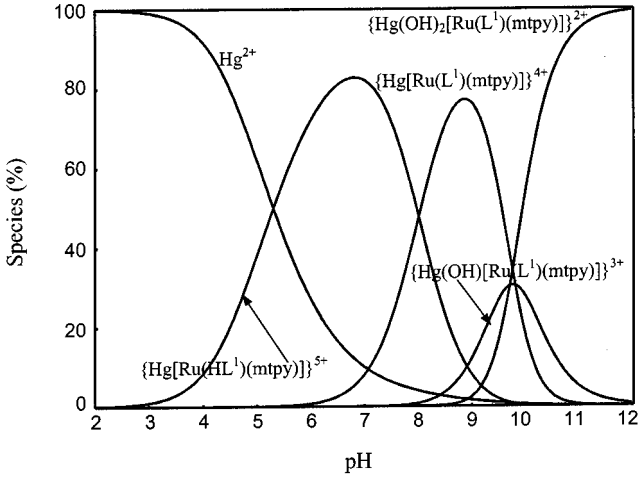


Figure 2. Distribution diagram of the species for the system $[Ru(L^1)(mtpy)]-Hg^{2+}-H^+$

Figure 1b shows the I/I_0 vs. pH curves for the $[Ru(L^3)(mtpy)]^{2+}$ complex in the presence of metal ions. The I/I_0 vs. pH profiles for this complex are similar with Cu^{2+} and Hg^{2+}, but in the presence of Cd^{2+} and Pb^{2+} an enhancement of the emission intensity of the order of 30% is observed in the range pH 4−6. The 1,4,7-trioxa-10-azacyclododecane unit has also been *N*-functionalized with anthryl groups as fluorescent signalling subunits.[20] In contrast to the fluorescent behaviour of the $[Ru(L^3)(mtpy)]^{2+}$ complex, the anthracene-containing derivative does not show any response in the presence of the metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, or Hg^{2+}. The signalling fluores-

cence behaviour of the ruthenium and anthrylazamacrocycle compounds in the presence of metal ions is quite different, highlighting the active role that the signalling subunit might play in the selectivity of the sensing event.

The fluorescence response of the $[Ru(L^3)_2]^{2+}$ complex has also been studied in acetonitrile/water (70:30, *v*/*v*) as a function of pH in the presence of two equivalents of Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. This receptor contains two peripheral aza-oxa units, rather than just one as in the analogous $[Ru(L^3)(mtpy)]^{2+}$ complex. The *I* vs. pH curve for $[Ru(L^3)_2]^{2+}$ does not change in the presence of Cu^{2+}, but the presence of Cd^{2+}, Pb^{2+}, or Hg^{2+} induces an enhancement in the luminescence of the $Ru(tpy)_2^{2+}$ core in the range pH 3.5−7.5 (see Figure 1c). The behaviour observed for the $[Ru(L^3)_2]^{2+}$ complex is quite similar to that seen for $[Ru(L^3)(mtpy)]^{2+}$, the only difference being the sensing of Hg^{2+} by the homoleptic complex, which is not observed for the heteroleptic one. This behaviour is not easy to rationalize, but it nevertheless seems to highlight the importance of slight structural modifications of the receptor in determining the final fluorescent behaviour. It is noteworthy that the $[Ru(L^3)(mtpy)]^{2+}$ receptor is able to sense the presence of all three toxic heavy metal ions Cd^{2+}, Pb^{2+}, and Hg^{2+} in an aqueous environment (acetonitrile/water) at the commonly encountered neutral pH in preference to smaller metal ions such as Cu^{2+}.

Finally, the emission properties of the $[Ru(L^4)(mtpy)]^{2+}$ complex in the presence of Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} were monitored as a function of pH. This receptor contains a polyazacycloalkane unit covalently attached to the $Ru(tpy)_2^{2+}$ fluorophore rather than an aza-oxa macrocycle as in $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$. This is reflected in the observation of a quite different response towards metal ions. All five metals induce a change in the fluorescence response of the $[Ru(L^4)(mtpy)]^{2+}$ receptor, as shown in Figure 1d. Ni^{2+}, Cu^{2+}, and Cd^{2+} quench the fluorescence intensity of the free receptor over a wide pH range. In contrast, Pb^{2+} and Hg^{2+} enhance the fluorescence of the receptor. The fluorescent response as a function of the pH in the presence of Cu^{2+} resembles that found with the receptor $[Ru(cyphtpy)(mtpy)]^{2+}$, which contains a cyclic tetraamine moiety anchored to the ruthenium(II) bis(terpyridine) centre.[11] It is interesting to note that there seems to be a close relationship between the emission intensity and the radii of the metal cations; large metal ions enhance the fluorescence of the $Ru(tpy)_2^{2+}$ core, whereas smaller ones have a quenching effect. This represents rather unusual behaviour, which, to the best of our knowledge, has not been reported previously. In Figure 3, the relative fluorescence at pH 7.5 found in the presence of Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions is plotted as a function of the cationic radius. A linear response between emission intensity and cation size can be seen.

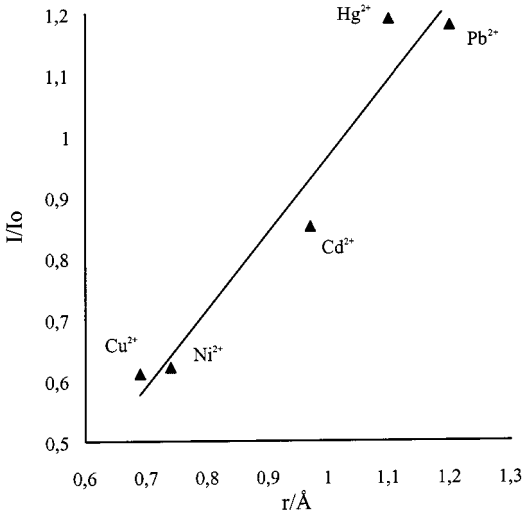


Figure 3. Relative fluorescence at pH 7.5 found for the interaction of Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} ions with $[Ru(L^4)(mtpy)][PF_6]_2$ as a function of the cationic radius

Conclusions

New terpyridine derivatives attached to aza-oxa macrocycles have been synthesized and their homoleptic or heteroleptic ruthenium(II) complexes have been prepared. One of the most interesting features of these metallo receptors is their multicomponent nature, in that they consist of an $Ru(tpy)_2^{2+}$ core capable of acting as a fluorescent signalling subunit and an aza-oxa macrocycle unit that acts as a cation binding site. Studies have been mainly carried out with a view to achieving discrimination between toxic heavy metal ions by means of fluorescence techniques. The receptors $[Ru(L^1)(mtpy)]^{2+}$, $[Ru(L^3)(mtpy)]^{2+}$, and $[Ru(L^3)_2]^{2+}$ are capable of transforming a coordination event occurring at the molecular level into a measurable macroscopic signal, thus allowing the sensing of heavy metal ions such as Cd^{2+}, Pb^{2+}, and especially of Hg^{2+} in water/acetonitrile (70:30, *v*/*v*) mixtures. The $[Ru(L^4)(mtpy)]^{2+}$ receptor, containing a polyazacycloalkane moiety as a binding site, shows a quite different response with the fluorescence of the $Ru(tpy)_2^{2+}$ core being enhanced by large metal ions and quenched by smaller ones. A linear response between emission intensity and cation size was found for this metallo receptor.

Experimental Section

General Remarks: $[Ru(mtpy)Cl_3]$[22] and 4′-[4-(bromomethyl)-phenyl]-2,2′:6′,2′′-terpyridine (Br-mphtpy)[18] were prepared according to the published methods; all other reagents were obtained from commercial sources and were used as received.

Preparations

Synthesis of L^1 and L^3: A solution of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine (Br-mphtpy) (200 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 4,10-diaza-15-crown-5 (545 mg, 2.5 mmol) in order to obtain L^1, or to a solution of 1-aza-12-crown-4 (438 mg, 2.5 mmol) in CH_2Cl_2 (20 mL) in order to afford L^3. The respective solutions were treated with 5 drops of Et_3N and then heated at 30 °C for 24 h. Each reaction mixture was washed with water (3 × 3 mL). The organic phases were dried with $MgSO_4$ and concentrated under reduced pressure. The residues

were purified by column chromatography on alumina using CH_2Cl_2/CH_3OH (99:1, *v*/*v*) as the eluent. A yellow oil was obtained, which solidified on keeping the flask under reduced pressure. Yields: 81 mg, 30% for L^1; 87 mg, 35% for L^3.

L^1: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.4 (1 H, NH), 2.70−2.85 (8 H, CH_2N), 3.5−3.7 (12 H, CH_2O and 2 H, CH_2Ph), 7.28−7.32 (2 H, tpy 5-,5′′-H), 7.42−7.48 (2 H, Ph), 7.75−7.85 (2 H, tpy 4-,4′′-H and 2 H, Ph), 8.55−8.60 (2 H, tpy 6-,6′′-H), 8.65−8.70 (2 H, tpy 3-,3′′-H and 2 H, tpy 3′-,5′-H). − ^{13}C NMR ($CDCl_3$): δ = 48.8 (CH_2), 54.3 (CH_2), 60.1 (CH_2), 69.0−71.0 (CH_2), 118.8 (CH, tpy), 121.3 (CH, tpy), 123.8 (CH, tpy), 127.2 (CH, tolyl), 129.4 (CH, tolyl), 149.1 (CH, tpy), 155.9 (C, tpy), 156.1 (C, tpy). − $C_{32}H_{37}N_5O_3{\cdot}CH_2Cl_2$ (624.6): found C 64.0, H 6.0, N 10.8; L^1 requires C 63.5, H 6.2, N 11.2. − FAB MS: *m*/*z* (%) = 540 (60), 461 (35), 401 (30), 327 (65), 281 (50), 221 (55).

L^3: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.8 (4 H, CH_2N), 3.65−3.75 (12 H, CH_2O and 2 H, CH_2Ph), 7.33−7.36 (2 H, tpy 5-,5′′-H), 7.52−7.54 (2 H, Ph), 7.85−7.87 (2 H, tpy 4-,4′′-H and 2 H, Ph), 8.69−8.72 (2 H, tpy 6-,6′′-H), 8.72−8.73 (2 H, tpy 3-,3′′-H), 8.74 (s, 2 H, tpy 3′-,5′-H). − ^{13}C NMR ($CDCl_3$): δ = 54.9 (CH_2), 60.6 (CH_2), 70.2 (CH_2), 70.5 (CH_2), 71.3 (CH_2), 119.7 (CH, tpy), 121.3 (CH, tpy), 123.7 (CH, tpy), 127.1 (CH, tolyl), 129.5 (CH, tolyl), 136.8 (CH, tpy), 149.1 (CH, tpy), 150.7 (C, tolyl), 155.8 (C, tpy), 156.1 (C, tpy). − $C_{30}H_{32}N_4O_3{\cdot}CH_2Cl_2$ (581.5): found C 65.0, H 6.0, N 9.8; L^3 requires C 64.0, H 5.8, N 9.6. − FAB MS: *m*/*z* (%) = 497 (100), 322 (45), 193 (15).

Synthesis of L^2: A solution of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine (Br-mphtpy) (200 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 4,10-diaza-15-crown-5 (54.5 mg, 0.25 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was treated with 5 drops of Et_3N and then heated at 30 °C for 24 h. It was subsequently washed with water (3 × 3 mL). The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on alumina using CH_2Cl_2/CH_3OH (99:1, *v*/*v*) as the eluent. A yellow oil was obtained, which solidified on keeping the flask under reduced pressure. Yield: 63 mg, 30%.

L^2: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.7−2.85 (8 H, CH_2N), 3.40−3.70 (12 H, CH_2O), 4.5 (4 H, CH_2Ph), 7.2−7.3 (4 H, tpy 5-,5′′-H), 7.38−7.44 (4 H, Ph), 7.80−7.90 (4 H, tpy 4-,4′′-H and 4 H, Ph), 8.60−8.62 (2 H, tpy 6-,6′′-H), 8.66−8.72 (4 H, tpy 3-,3′′-H and 4 H, tpy 3′-,5′-H). − ^{13}C NMR ($CDCl_3$): δ = 54.4 (CH_2), 60.1 (CH_2), 69.5 (CH_2), 70.7 (CH_2), 118.1 (CH, tpy), 121.3 (CH, tpy), 123.8 (CH, tpy), 127.1 (CH, tolyl), 129.4 (CH, tolyl), 136.8 (CH, tpy), 149.1 (CH, tpy), 155.9 (C, tpy), 156.1 (C, tpy). − $C_{54}H_{52}N_8O_3{\cdot}CH_2Cl_2$ (946.0): found C 69.0, H 6.0, N 10.8; L^2 requires C 69.8, H 5.7, N 11.8. − FAB MS: *m*/*z* (%) = 861 (40), 322 (90), 281 (45), 207 (60).

Synthesis of L^4: A solution of 4′-[4-(bromomethyl)phenyl]-2,2′:6′,2′′-terpyridine (Br-mphtpy) (200 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of 1,4,7,10,13-pentaazacyclopentadecane (500 mg, 2.5 mmol). The resulting mixture was treated with 5 drops of Et_3N and then heated at 30 °C for 24 h. It was subsequently washed with water (3 × 3 mL). The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on alumina using CH_2Cl_2/CH_3OH (99:1, *v*/*v*) as the eluent. A yellow oil was obtained, which solidified on keeping the flask under reduced pressure. Yield: 120 mg, 50%.

L^4: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.5−2.9 (20 H, CH_2), 3.6 (2 H, CH_2Ph), 7.25−7.28 (2 H, tpy 5-,5′′-H), 7.40−7.42 (2 H, Ph), 7.70−7.80 (2 H, tpy 4-,4′′-H and 2 H, Ph), 8.55−8.60 (2 H, tpy 6-,6′′-H), 8.65−8.70 (2 H, tpy 3-,3′′-H and 2 H, tpy 3′-,5′-H). − ^{13}C NMR ($CDCl_3$): δ = 48.8 (CH_2), 56.3 (CH_2), 60.1 (CH_2), 68.5−71.0 (CH_2), 118.7 (CH, tpy), 121.2 (CH, tpy), 123.8 (CH, tpy), 127.2 (CH, tolyl), 129.4 (CH, tolyl), 148.9 (CH, tpy), 155.8 (C, tpy), 156.3 (C, tpy). − $C_{32}H_{40}N_8$ (536.7): found C 71.2, H 7.8, N 20.8; L^4 requires C 71.6, H 7.5, N 20.9. − FAB MS: *m*/*z* (%) = 537 (100), 323 (100), 281 (35), 237 (35).

Synthesis of $[Ru(L^1)(mtpy)][PF_6]_2$, $[Ru(L^3)(mtpy)][PF_6]_2$, and $[Ru(L^4)(mtpy)][PF_6]_2$: These ruthenium complexes were all prepared in the same way. A mixture of the appropriate ligand (L^1 108 mg, L^3 99.4 mg, L^4 107 mg; 0.2 mmol), $[Ru(mtpy)Cl_3]$ (90 mg, 0.2 mmol), and 3 drops of *N*-ethylmorpholine, as a mild reductant, in MeOH (20 mL) was heated to reflux under stirring for 1 h. The resulting deep-red solution was then filtered through Celite to remove any unchanged $[Ru(mtpy)Cl_3]$. Further purification was accomplished by chromatography on silica using acetonitrile/water/satd. aq. KNO_3 solution (17:2:1) as the eluent. The complexes were isolated as their hexafluorophosphate salts.

$[Ru(L^1)(mtpy)][PF_6]_2$: Yield 48 mg, 20%. − ^{1}H NMR (300 MHz, CD_3CN): δ = 2.98 (s, 3 H, CH_3), 3.3−3.4 (4 H, CH_2N), 3.60−3.65 (4 H, CH_2N), 3.7−3.9 (12 H, CH_2O and 2 H, CH_2Ph), 7.15−7.20 (4 H, tpy 5-,5′′-$H^{1,2}$), 7.40−7.45 (4 H, tpy 6-,6′′-$H^{1,2}$), 7.90−8.00 (2 H, Ph and 2 H, tpy 4-,4′′-$H^{1,2}$), 8.30−8.32 (2 H, Ph), 8.48−8.50 (2 H, tpy 3-,3′′-H^1), 8.68−8.70 (2 H, tpy 3-,3′′-H^2), 8.70 (s, 2 H, tpy 3′-,5′-H^1), 9.08 (s, 2 H, tpy 3′-,5′-H^2); 1 = mtpy; 2 = Phtpy. − $C_{48}H_{50}F_{12}N_8O_3P_2Ru{\cdot}CH_2Cl_2$ (1262.5): found C 45.9, H 3.8, N 9.3; $[Ru(L^1)(mtpy)][PF_6]_2$ requires C 46.4, H 4.1, N 8.8. − FAB MS: *m*/*z* (%) = 1177 (25), 1033 (65), 887 (100), 671 (10).

$[Ru(L^3)(mtpy)][PF_6]_2$: Yield 45 mg, 20%. − ^{1}H NMR (300 MHz, CD_3CN): δ = 2.97 (s, 3 H, CH_3), 3.5 (4 H, CH_2N), 3.7−3.8 (8 H, CH_2O), 3.95−4.0 (4 H, CH_2O), 4.52 (2 H, CH_2Ph), 7.15−7.25 (4 H, tpy 5-,5′′-$H^{1,2}$), 7.40−7.45 (4 H, tpy 6-,6′′-$H^{1,2}$), 7.84 (2 H, Ph), 7.95 (4 H, tpy 4-,4′′-$H^{1,2}$), 8.3 (2 H, Ph), 8.46−8.48 (2 H, tpy 3-,3′′-H^2), 8.66−8.68 (2 H, tpy 3-,3′′-H^1), 8.71 (s, 2 H, tpy 3′-,5′-H^2), 9.01 (s, 2 H, tpy 3′-,5′-H^1); 1 = mtpy; 2 = Phtpy. − $C_{46}H_{45}F_{12}N_7O_3P_2Ru{\cdot}2H_2O$ (1170.9): found C 47.3, H 3.9, N 8.3; $[Ru(L^3)(mtpy)][PF_6]_2$ requires C 47.2, H 4.2, N 8.4. − FAB MS: *m*/*z* (%) = 1135 (20), 990 (55), 845 (100), 671 (10).

$[Ru(L^4)(mtpy)][PF_6]_2$: Yield 52 mg, 20%. − ^{1}H NMR (300 MHz, CD_3CN): δ = 2.8−3.2 (20 H, CH_2), 2.98 (s, 3 H, CH_3), 3.95 (2 H, CH_2Ph), 7.15−7.20 (4 H, tpy 5-,5′′-$H^{1,2}$), 7.40−7.45 (4 H, tpy 6-,6′′-$H^{1,2}$), 7.70−7.72 (2 H, Ph^2), 7.9−7.94 (4 H, tpy 4-,4′′-$H^{1,2}$), 8.25−8.28 (2 H, Ph), 8.50−8.52 (2 H, tpy 3-,3′′-H^1), 8.68−8.70 (2 H, tpy 3-,3′′-H^2), 8.70 (s, 2 H, tpy 3′-,5′-H^1), 9.08 (s, 2 H, tpy 3′-,5′-H^2); 1 = mtpy; 2 = Phtpy. − $C_{48}H_{50}F_{12}N_8O_3P_2Ru{\cdot}2H_2O$ (1214.0): found C 54.5, H 5.5, N 14.8; $[Ru(L^4)(mtpy)][PF_6]_2$ requires C 54.0, H 5.3, N 14.5. − FAB MS: *m*/*z* (%) = 1174 (20), 1030 (30), 885 (40), 670 (65).

Synthesis of $[Ru(L^3)_2][PF_6]_2$: The homoleptic ruthenium complex of L^3 was prepared by reacting L^3 (200 mg, 0.4 mmol) with $RuCl_3 3H_2O$ (52.3 mg, 0.2 mmol), in the presence of 3 drops of *N*-ethylmorpholine as a mild reductant, in MeOH (20 mL). The mixture was heated to reflux under stirring for 2 h. The resulting deep-red solution was filtered through Celite to remove any unchanged $RuCl_3$. Further purification was accomplished by chromatography on silica using acetonitrile/water/satd. aq. KNO_3 solution (17:2:1) as the eluent. The complex was isolated as its hexafluorophosphate salt.

$[Ru(L^3)_2][PF_6]_2$: Yield 28 mg, 19%. − ^{1}H NMR (300 MHz, CD_3CN): δ = 3.5−3.6 (8 H, CH_2N), 3.6−4.1 (12 H, CH_2O), 4.55

(4 H, CH_2Ph), 7.22−7.26 (4 H, tpy 5-,5′′-H), 7.56−7.58 (4 H, tpy 6-,6′′-H), 7.86−7.90 (4 H, Ph), 7.98−8.02 (4 H, tpy 4-,4′′-H), 8.34−8.38 (4 H, Ph), 8.70−8.76 (4 H, tpy 3-,3′′-H), 9.08 (4 H, tpy 3′-,5′-H). − $C_{60}H_{64}F_{12}N_8O_6P_2Ru{\cdot}CH_2Cl_2$ (1468): found C 49.0, H 3.9, N 8.3; $[Ru(L^3)_2][PF_6]_2$ requires C 49.9, H 4.5, N 7.6. − FAB MS: *m*/*z* (%) = 1240 (20), 1094 (25), 920 (35).

Physical Measurements and Instrumentation

Photochemical data were obtained with an FS900CDT steady-state T-Geometry Fluorometer from Edinburgh Analytical Instruments. All solutions for photophysical studies were rigorously degassed. The concentrations of the ligand and of the metal ion were ca. $1.0{\cdot}10^{-4}$ mol dm^{-3}. ^1H NMR spectra were recorded on a Varian Gemini spectrometer. Potentiometric titrations were carried out in acetonitrile/water (70:30, *v*/*v*, 0.1 mol dm^{-3} tetrabutylammonium perchlorate) under nitrogen using a vessel water-thermostatted at 25.0 ± 0.1 °C. The titrant was added by means of a Crison microburette 2031. Further details of the potentiometric experiments have been published previously.[23] The concentrations of the metal ions were determined using standard methods. The computer program SUPERQUAD[24] 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; ligand and metal ion concentrations ca. $1.0{\cdot}10^{-3}$ mol dm^{-3}) could be treated either as a single set or as separate entities without significant variation in the values of the stability constants. Finally, the sets of data were merged together and treated simultaneously to give the quoted stability constants.

Acknowledgments

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