

Synthesis, Characterisation, Electrochemistry and Ion-Binding Studies of Ruthenium(II) and Rhenium(I) Bipyridine/Crown Ether Receptor Molecules

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A number of molecular receptors containing a ruthenium(II)/rhenium(I) bipyridine moiety as fluorophore and a crown ether, connected to the 4,4'-positions of the bipyridine/phenanthroline unit through >C=O and -HC=N- spacers, as ionophore have been synthesised and characterised. The luminescence and electrochemical properties of these receptors have been studied. The cation-binding properties of these molecules have been investigated with the cations Na⁺, K⁺, Rb⁺, Mg²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Cu²⁺ and the recognition event monitored by ¹H NMR spectroscopy, luminescence, the oxidation potential of the metal ion and UV/Vis absorption studies. The emission intensities of complexes **1–3** are strongly quenched by the addition of Pb²⁺, Cu²⁺, Hg²⁺ and Na⁺, whereas a significant enhancement of the emission intensities is observed for **4** in the presence of Cu²⁺ and Hg²⁺ and for **5** in the presence of Cd²⁺ and Hg²⁺. Luminescence titrations for **1–5** with the above-mentioned metal ions have been carried out. The binding constants (K_s) and stoichiometry of the complexes have been calculated from titration data, with values of K_s ranging from 9.97×10^3 to

$1.28 \times 10^2 \text{ M}^{-1}$ in the decreasing order $\text{Pb}^{2+} > \text{Na}^+ > \text{Cu}^{2+} > \text{Hg}^{2+} > \text{Cd}^{2+}$. The stoichiometries found for **1–3** and **5** are in the range 1.85–2.09 and for **4** 0.99–1.04. A ¹H NMR spectroscopic study with selected metal ions exhibits significant spectral changes for the protons attached to the crown moiety; a few significant changes are also noted in the aromatic region. Among the ions studied, the highest change is observed with Na⁺ and Pb²⁺, whereas K⁺ does not show any significant change. The electrochemical study exhibits a significant cathodic shift of the oxidation potentials of the Ru^{II} centre in the presence of Na⁺ and Pb²⁺, thereby indicating complexation of these ions with the crown moiety. The electronic spectra, however, do not show significant spectral changes with various metal ions except for that of the Re^I complex **6**, which exhibits some change upon addition of Na⁺. The results obtained are presented and discussed in light of selectivity and intramolecular energy-transfer.

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Introduction

The design and synthesis of functional molecules that could serve as molecular devices for selective sensing, switching and signalling is currently an area of intense research activity.^[1] Among various such functional molecules, fluorescent sensors for the detection of ions are of great interest because of their important role in many biological and environmental processes.^[2] Such molecular sensors can be constructed by the combination of an ionophore, designed to bind a specific incoming ion, and a luminescent fragment whose photophysical properties are perturbed during the recognition process to produce a measurable output signal.^[3] Photoactive units attached with a crown ether or its derivatives, which serve as receptors, are generally used for the recognition of alkali, alkaline earth and heavy metal ions.^[4,5] Both organic photoactive molecules

and ruthenium(II)/rhenium(I) polypyridine-based photoactive metal complexes have been used as fluorophores, although the latter are of special interest because of various advantages they have over organic molecules. Thus, besides exhibiting luminescence changes like organic molecules, they also exhibit measurable changes in electrogenerated chemiluminescence and redox properties during the ion-recognition process.^[4–6] The spacers, which connect the fluorophore and ionophore, also play an important role in ensuring electronic communication between the two units. It is desirable to have a short and/or conjugated bridging unit to achieve a strong interaction between the two units. Macrocyclic compounds, which are noted for their remarkable selectivity towards specific cations, have been extensively used as ionophores in cation recognition studies. In this regard, crown ethers are excellent choices as complexing agents for alkali and alkaline earth metal ions.^[5,6c–6d,6f]

A significant amount of work has been done on fluoro-ionophores containing Ru^{II}/Re^I polypyridine-based fluorophore and crown ether-based ionophores. Beer et al., for example, have reported a number of Ru^{II}- and Re^I-based photochemical receptors in which azacrown or benzocrown

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ionophores are connected to a metal chromophore via an amide moiety.^[5a,5b,6c,6e] A fluoroionophore containing a crown ether moiety directly fused with a bipyridine/1,10-phenanthroline unit, which coordinates to a metal ion, have also been reported.^[7,8] Diaza crown ethers, which act as a bridging unit between photoactive metal chromophores, have also been reported as receptors for Ba²⁺ ions.^[9] Ru^{II}-polypyridine based complexes containing an azacrown as ionophore have recently been reported as quadruple-channel sensors for the selective and quantitative analysis of Pb²⁺, Cu²⁺ and Hg²⁺.^[10,11] Upon ion recognition, changes in the UV/Vis/NIR, luminescence and electrochemiluminescence (ECL) spectra occurred for selective metal ions.^[11] A complex containing an azacrown ether connected to Re^I via an alkynyl pyridine has also been reported recently as a light-controlled ion switch for Ba²⁺.^[12]

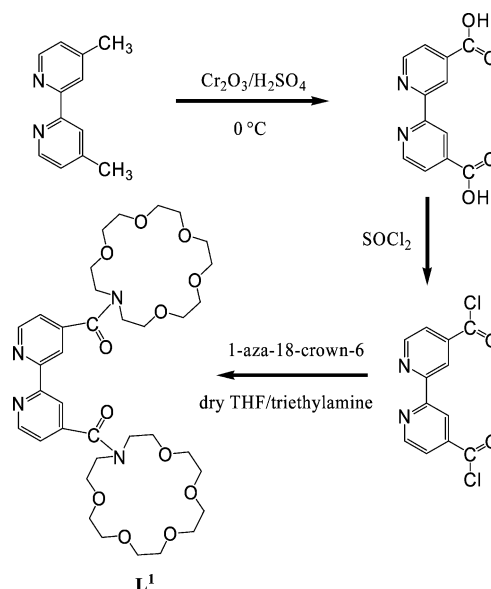
Herein we report the synthesis and characterisation of a series of fluoroionophores containing a Ru^{II}/Re^I-polypyridine based unit as the fluorophore and an azacrown/benzocrown moiety as the ionophore. The macrocyclic unit is connected to the metal-bound bipyridine or 1,10-phenanthroline unit through an amide (>C=O) or imino (-CH=N-) moiety. The electrochemical properties and ion-recognition behaviour of these fluoroionophores with a large number of metal ions are reported. The ion-recognition process is monitored by luminescence, ¹H NMR and UV/Vis spectral changes and also by electrochemical methods. The binding constants and stoichiometry of the complexes formed by the strongly interacting metal ions are reported, along with a detailed discussion of the ion-recognition behaviour and intramolecular energy transfer.

Results and Discussion

Synthesis of Ligands L¹–L³

The route followed for the synthesis of L¹ is shown in Scheme 1. A similar procedure was used for the synthesis of L², with the exception that 4,7-dimethyl-1,10-phenanthroline was used as starting material instead of 4,4'-dimethylbipyridine. L³ was prepared by treating 4'-methyl-2,2'-bipyridine-4-carbaldehyde with 4'-aminobenzo-18-crown-6; the former was synthesised following a published procedure.^[13] Microanalytical (C, H and N), mass spectrometric, IR and ¹H NMR spectroscopic data of all these ligands are given in the Exp. Sect. The microanalytical and mass spectrometric data are in agreement with the calculated values. It should be noted that the *m/z* values for all these compounds correspond to the Na⁺/K⁺ adducts (ligand + Na⁺/K⁺), which is a well known phenomenon when using the LC-MS technique.^[14] In the ¹H NMR spectra, the aromatic regions of L¹ and L² exhibit two doublets and a singlet, as expected for a symmetrically substituted bipyridine/1,10-phenanthroline unit. The high-field doublets (δ = 8.73 ppm for L¹ and δ = 9.23 ppm for L²) are assigned to 6-H and 6'-H of the bpy moiety of L¹ and 2-H and 9-H of the phen moiety of L² (the usual numbering system for the protons in 2,2'-bipyridine and 1,10-phenanthroline is used).

The low-field doublets at δ = 7.40 ppm for L¹ and δ = 7.62 ppm for L² are due to 5-H and 5'-H of the bpy moiety of L¹ and 3-H and 8-H of the phen moiety of L², respectively. The singlets at δ = 8.48 (L¹) and 7.87 ppm (L²) are due to the 3-H and 3'-H protons of bpy and the 5-H and 6-H protons of phen, respectively. The protons attached to the crown moieties appear as multiplets in the region δ = 3.5–4.0 ppm. The NMR spectroscopic data are consistent with the proposed structures shown in Scheme 1 (L¹) and Figure 1 (L²). In the case of L³, four doublets and two singlets, as expected for the unsymmetrically 4,4'-substituted 2,2'-bipyridine unit (Figure 1), are observed in the range δ = 8.78–7.17 ppm (a detailed peak assignment is given in the Exp. Sect.). The protons of the benzocrown unit appear as multiplets at δ = 6.92 (phenyl), 4.20, 3.96 and 3.77–3.70 ppm (crown ether), and the methyl group attached to the bpy moiety appears as a singlet at δ = 2.47 ppm. The molecular structure of L¹ was confirmed by a single-crystal X-ray study (see below).



Scheme 1.

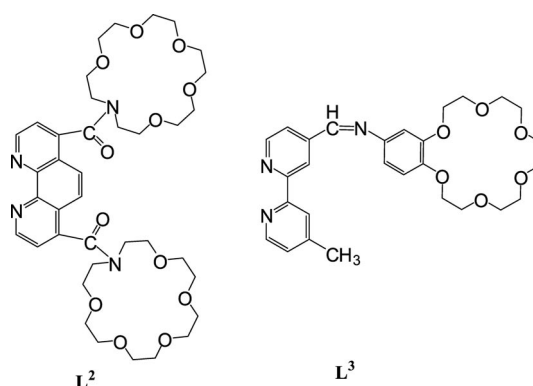


Figure 1. Structural drawings of ligands L² and L³.

Synthesis of Complexes 1–6

The Ru^{II} complexes **1–4** (Figure 2) were synthesised by treating *cis*-[Ru(bpy)₂Cl₂]/*cis*-[Ru(phen)₂Cl₂] with **L**¹/**L**³ in refluxing ethanol/water. They were isolated as their PF₆[−] salts and purified by column chromatography, as described in the Exp. Sect. All these complexes gave satisfactory C, H and N analysis, and their mass spectrometry data are in excellent agreement with the calculated values. It should be noted that, like the ligands, the complexes also exhibit *m/z* values corresponding to the Na⁺ adduct with PF₆[−]. The ¹H NMR spectra of complexes **1–4** were recorded in CD₃CN (see Exp. Sect. for the peak assignment). Peaks were assigned with the aid of COSY spectra recorded in the same solvent. The COSY spectrum of **1** is provided as Supporting Information (Figure S1), and the detailed peak assignment for complex **1** is described below. The most deshielded singlet at δ = 8.58 ppm is due to 3-H and 3'-H of the bpy moiety of **L**¹, the doublet at δ = 8.51 ppm (4 H, *J* = 8.0 Hz) is due to 6-H and 6'-H of the two bpy ligands and the overlapping triplets in the range δ = 8.06–8.10 ppm (4 H) are due to 5-H and 5'-H of the bpy ligand. The doublets at δ = 7.80 (2 H, *J* = 5.5 Hz) and 7.71 ppm (2 H, *J* = 5.5 Hz) are due to 3-H and 3'-H of the bpy units. The other doublets at δ = 7.76 (2 H, *J* = 5.5 Hz) and 7.44 ppm (2 H, *J* = 5.5 Hz) are due to 6-H/6'-H and 5-H/5'-H of the bpy moiety of **L**¹, respectively. The overlapping triplets in the range δ = 7.40–7.45 ppm (4 H) are due to 4-H and 4'-H of the bpy ligand. The signals due to the crown moiety appear as multiplets in the region δ = 3.43–3.72 ppm. Detailed NMR spectroscopic data for **2–4**, along with the peak assignments, are given in the Exp. Sect. and will not be discussed further here.

The Re^I complexes (**5** and **6**) were synthesised by treating [Re(CO)₅Cl] with **L**¹/**L**³ in dry refluxing thf. The crude product was purified by column chromatography. The microanalytical (C, H and N) and mass spectrometric data are

consistent with the proposed composition of the complexes. The ¹H NMR spectrum of **5** exhibits two doublets at δ = 9.03 and 7.64 ppm and a singlet at δ = 8.50 ppm for the aromatic protons. This spectral pattern is similar to that of **L**¹, although a slight upfield shift of the doublets is noted due to coordination of the bpy moiety to the metal ion. In the aliphatic region, the NCH₂ and OCH₂ protons of the azacrown moiety appear at δ = 3.75 and 3.52–3.62 ppm, respectively. The ¹H NMR spectral pattern for complex **6** is similar to that of **L**³ but with slight changes in the chemical shifts; a detailed peak assignment is given in the Exp. Sect. The IR spectra of these complexes exhibit three strong bands at 2021, 1900 and 1894 cm^{−1} for **5** and 2018, 1910 and 1889 cm^{−1} for **6**. These CO stretching frequencies are within the range normally found for a typical “*fac*-Re-(CO)₃” moiety with C_{3v} symmetry (A₁ and E for the one high- and two low-energy bands, respectively).^[15] The CO frequencies therefore suggest a facial arrangement of the carbonyl groups, as shown in the proposed structures (Figure 2).

Crystal Structure of **L**¹

The molecular structure of **L**¹ was determined by single-crystal X-ray crystallography. It crystallises in the monoclinic space group *P*2₁/*n* and possesses a centre of symmetry at the mid-point of the C1–C1a bond of the bipyridine moiety bridging the azacrowns on either side (Figure 3). The two pyridine rings of the 2,2'-bipyridine moiety are planar but with the nitrogen atoms on opposite sides. The symmetrically disposed carbonyl oxygen O1 on either side of the 2,2'-bipyridine moiety is involved in two intermolecular C–H···O interactions with the phenyl hydrogen H4 and the methylene hydrogen H112, which generates a layered network structure (Figure S2, Supporting Information). Several strong intermolecular C–H···O interactions involving

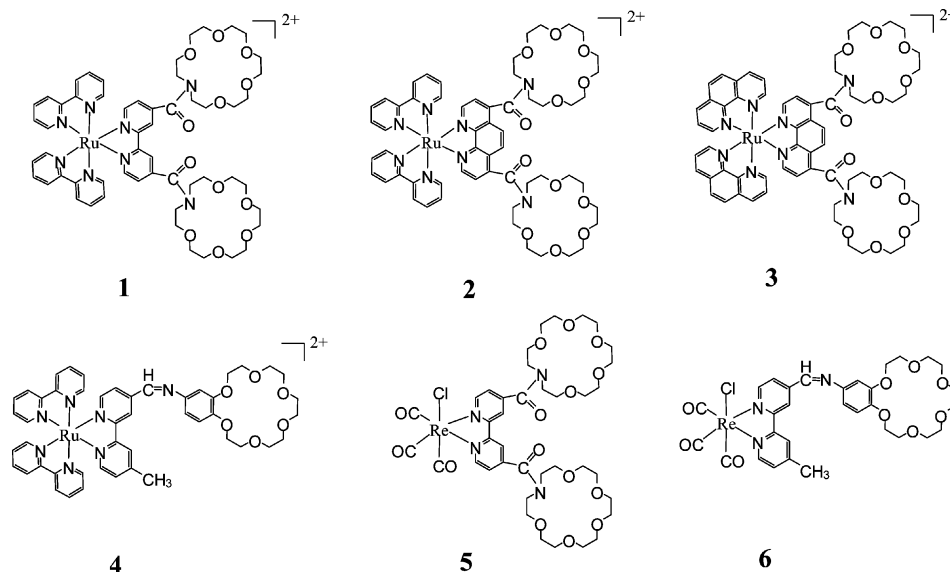


Figure 2. Structural drawings of complexes **1–6**.

the methylene hydrogen atoms on C17 and C18 and oxygen atoms O4, O2 and O3 of the crown moieties also exist. Further details of these pertinent hydrogen-bonding interactions, along with the symmetry codes, are given in Table S1 (Supporting Information).

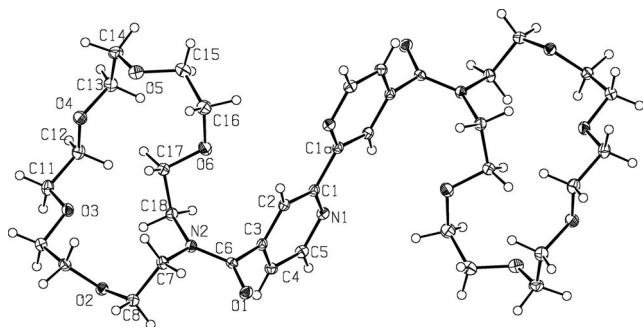


Figure 3. ORTEP diagram of ligand **L**¹ with atom numbering scheme (50% probability factor for the thermal ellipsoids).

Absorption and Luminescence

The absorption and luminescence spectra of all complexes were recorded in acetonitrile and the data are given in the Exp. Sect. The low-energy bands in the region 435–465 nm for Ru^{II} and at 385 and 342 nm for Re^I are due to metal-to-ligand (bpy/phen) charge-transfer (MLCT) transitions ($d\pi \rightarrow \pi^*$).^[16] The high-energy bands, which appear at around 290 and 245 nm, are ligand-centred charge transfer (CT) bands due to $\pi \rightarrow \pi^*$ transitions.^[16] The steady-state emission spectra (λ_{em}) and quantum yield (ϕ) of all complexes were recorded in acetonitrile at room temperature and the data are given in Table 1. All the Ru^{II} complexes exhibit a strong ³MLCT emission band in the region 617–633 nm, whereas the Re^I complexes show only weak emission at 630 and 603 nm for **5** and **6**, respectively.

Electrochemistry

The cyclic voltammograms of all complexes were recorded in acetonitrile and the results are listed in Table 2. The cyclic voltammogram of complex **3** is shown in Figure 4 as an example. All the Ru^{II} complexes exhibit a quasi-reversible redox couple in the potential range 1.43–1.55 V due to Ru^{II}→Ru^{III} oxidation.^[5a,8a,16] They also show three ligand-based redox couples in the potential range –1.03 to –1.72 V, which are assigned to the sequential one-electron reduction of three bpy/phen moieties (bpy/phen→bpy/

Table 2. Electrochemical data for complexes **1–6** in acetonitrile.

Complex	$E_{1/2}^{ox}$ [V] (ΔE_p [mV])	$E_{1/2}^{red1}$ [V] (ΔE_p [mV])	$E_{1/2}^{red2}$ [V] (ΔE_p [mV])	$E_{1/2}^{red3}$ [V] (ΔE_p [mV])
1	1.55 (170)	–1.06 (120)	–1.34 (140)	–1.60 (155)
2	1.55 (170)	–1.03 (110)	–1.29 (200)	–1.60 (172)
3	1.43 (170)	–1.14 (78)	–1.38 (146)	–1.66 (135)
4	1.52 (127)	–1.21 (110)	–1.44 (110)	–1.72 (200)
5	1.53 (85)	–1.05 (90)	–	–
6	1.57 (140)	–1.28 (180)	–	–

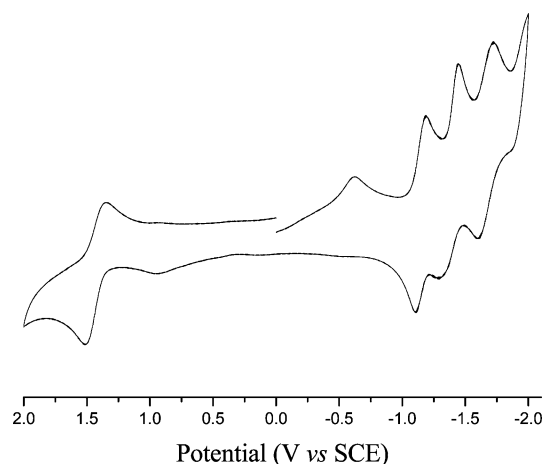


Figure 4. Cyclic voltammogram of **3** recorded in acetonitrile.

Table 1. Luminescence data, binding constant (K_s) and stoichiometry of complex formation for the ionophores.

	λ_{em}	Quantum yield (ϕ)	Metal ion	Binding constant $K_s \times 10^{-2} \text{ M}^{-1}$	$n^{[a]}$
1	633	0.0555	Pb ²⁺	21.80	1.95
			Hg ²⁺	1.99	1.86
			Cu ²⁺	4.95	1.92
			Na ⁺	7.12	2.03
2	627	0.0628	Pb ²⁺	49.15	1.98
			Hg ²⁺	2.69	2.09
			Cu ²⁺	5.90	1.96
			Na ⁺	9.95	1.91
3	617	0.0578	Pb ²⁺	99.72	1.90
			Hg ²⁺	4.19	1.88
			Cu ²⁺	8.81	2.03
			Na ⁺	12.12	1.96
4	624	0.0086	Hg ²⁺	26.63	1.04
			Cu ²⁺	45.99	0.99
5	630	0.0030	Hg ²⁺	34.88	1.85
			Cd ²⁺	1.28	1.93
6	603	0.0149	–	–	–

[a] Complex/guest metal ion ratio.

phen⁻) coordinated to the metal ion.^[5a,8a,16] For the Re^I complexes, a quasi-reversible metal-based oxidation wave (Re^I → Re^{II}) appears at 1.53 and 1.57 V for **5** and **6**, respectively.^[9a,17] The ligand (bpy)-based single electron reduction for these complexes occurs at -1.05 and -1.28 V for **5** and **6**, respectively.

Binding of Ionophores with Metal Ions

The binding of a number of metal ions (Na⁺, K⁺, Rb⁺, Mg²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Cu²⁺) with the ionophores **1–6** has been investigated. The host–guest interactions were monitored by means of luminescence, ¹H NMR and UV/Vis spectral changes and also by an electrochemical study of the oxidation potential of the metal ion.

The photoluminescence of all six ionophores (**1–6**) in the presence of various metal ions in acetonitrile has been investigated. For complexes **1–3**, the characteristic luminescence from the ³MLCT state was found to decrease in intensity in the presence of certain metal ions. Thus, the emission intensities were quenched by 75–85% upon addition of Pb²⁺ (100 equiv.) and 90–97% in the presence of Cu²⁺ (500 equiv.) for all three complexes. The emission maxima for all three complexes were red-shifted by 13 nm upon addition of Pb²⁺, although no shift of the emission maxima was observed with Cu²⁺. The addition of Na⁺ and Hg²⁺ (approx. 500 equiv.) resulted in a 25–40% reduction of the emission intensities for **1–3** and a small red shift (4–5 nm) of the emission maxima. Among the other metal ions studied, Cd²⁺ produced some quenching but the others did not show significant changes in emission intensities (Figure S3, Supporting Information). The changes in luminescence intensities for **1**, **2** and **3** upon addition of increasing concentrations of Pb²⁺, Cu²⁺ and Na⁺, respectively, are shown in Figures 5, 6 and 7. Interestingly, the emission intensity of complex **4** was enhanced by 140% and 124% upon addition of Cu²⁺ and Hg²⁺ (100 equiv.), respectively, and a substantial red-shift (47 nm) of the emission maxima (λ_{em}) was noted for both metal ions. Upon addition of Na⁺, the emission intensity enhancement was about 20%, whereas some initial intensity enhancement was observed with Pb²⁺, although it soon started to decrease. No further detailed studies were undertaken. The enhancement of luminescence intensity for **4** upon addition of increasing concentrations of Hg²⁺ is shown in Figure 8.

The Re^I complex of **L**¹ (**5**), which shows weak emission in acetonitrile ($\phi = 0.003$), underwent a 17- and 20-fold enhancement of its emission intensity, with a hypsochromic shift of the emission wavelength (λ_{em}) of 57 and 55 nm, upon addition of Cd²⁺ and Hg²⁺, respectively. The change in luminescence intensity for **5** upon addition of increasing concentrations of Cd²⁺ and Hg²⁺ is illustrated in Figures 9 and 10, respectively. The other metal ions did not induce significant changes in the emission intensity. Complex **6** did not show a significant change in its emission spectra upon addition of any metal ion.

The binding constants of strongly interacting metal ions for **1–5** were calculated from the emission titration data fol-

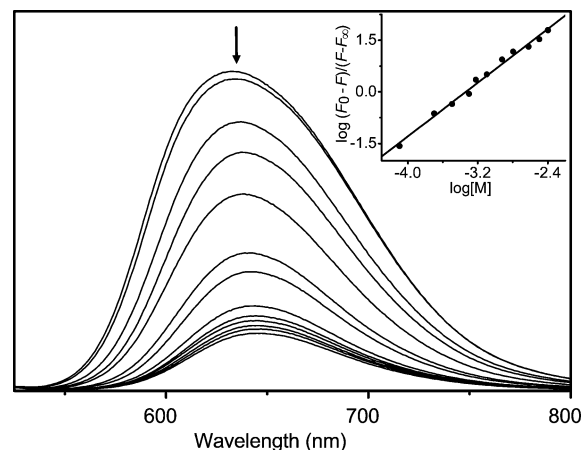


Figure 5. Emission spectral changes of **1** (2×10^{-5} M) upon addition of increasing concentrations of Pb(ClO₄)₂. Excitation wavelength: 454 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

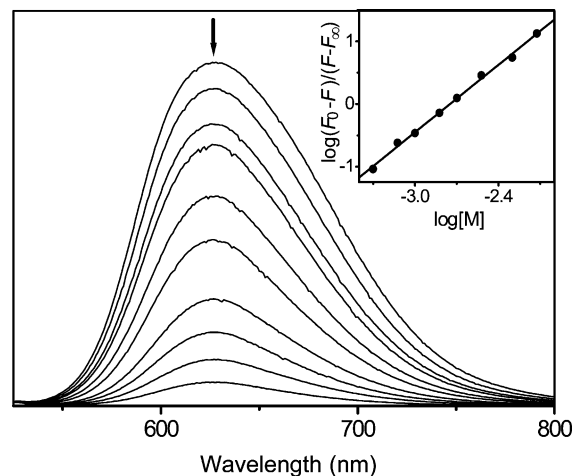


Figure 6. Emission spectral changes of **2** (2×10^{-5} M) upon addition of increasing concentrations of Cu(ClO₄)₂. Excitation wavelength: 445 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

lowing a literature procedure.^[18] According to this procedure, the fluorescence intensity (F) scales with the metal ion concentration ($[M]$) according to the formula $(F_0 - F)/(F - F_\infty) = ([M]/K_{\text{diss}})^n$. The binding constant (K_s) is obtained by plotting $\log[(F_0 - F)/(F - F_\infty)]$ vs. $\log[M]$, where F_0 and F_∞ are the relative fluorescence intensities of the complex without addition of guest metal ion and with maximum concentration of metal ion (when no further change in emission intensity takes place), respectively. The slope of the plot obtained from the experimental data gives the value of n , the number of metal ions bound to each complex, whereas the value of $\log[M]$ at $\log[(F_0 - F)/(F - F_\infty)] = 0$ gives the value of $\log(K_{\text{diss}})$, the reciprocal of which is the binding constant (K_s). The $\log[(F_0 - F)/(F - F_\infty)]$ vs. $\log[M]$ plots are shown as insets in Figures 5, 6, 7, 8, 9, and 10. The titration data showed a nice linear fit ($R^2 = 0.99$) with the above equation. The binding constants and values

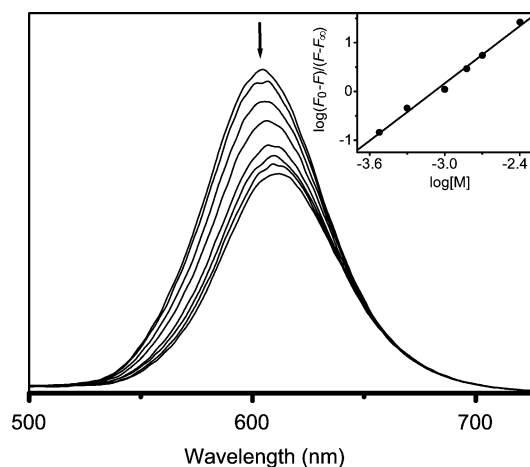


Figure 7. Emission spectral changes of **3** (2×10^{-5} M) upon addition of increasing concentrations of NaClO_4 . Excitation wavelength: 435 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

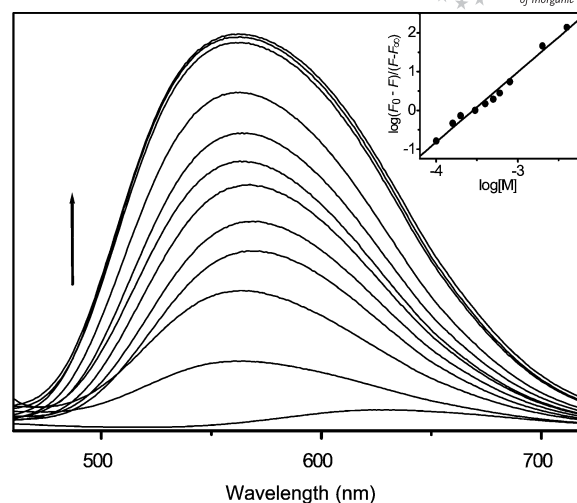


Figure 9. Emission spectral changes of **5** (2×10^{-5} M) upon addition of increasing concentrations of $\text{Hg}(\text{ClO}_4)_2$. Excitation wavelength: 385 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

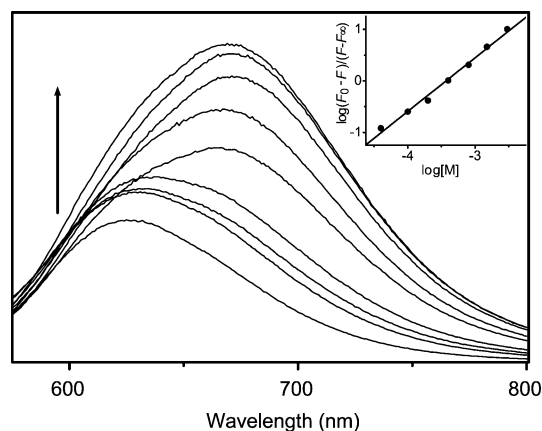


Figure 8. Emission spectral changes of **4** (2×10^{-5} M) upon addition of increasing concentrations of $\text{Hg}(\text{ClO}_4)_2$. Inset: Excitation wavelength: 465 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

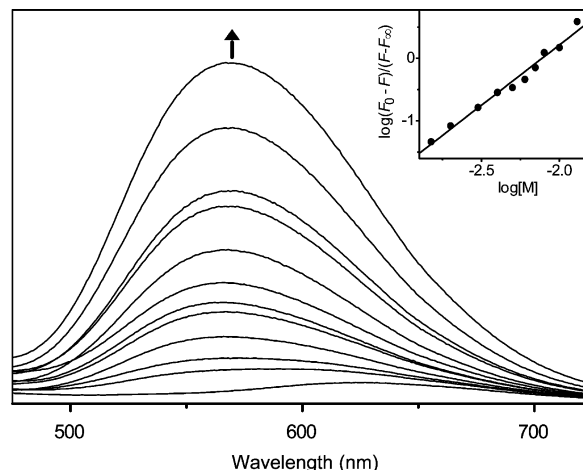


Figure 10. Emission spectral changes of **5** (2×10^{-5} M) upon addition of increasing concentrations of $\text{Cd}(\text{ClO}_4)_2$. Excitation wavelength: 385 nm. Inset: linear regression fit (double-logarithmic plot) of the titration data as a function of metal ion concentration.

of n for all complexes are summarised in Table 1. The values of n for **1–3** and **5** with all metal ions studied are in the range 1.85–2.09, which suggests 1:2 complex formation and therefore that both crown cavities are occupied by the guest metal ions. The n values of 0.99 and 1.04 for complex **4** indicate 1:1 complex formation.

Analysis of the data (Table 1) showed that the binding constants (K_s) for complexes **1–3** follow the order $\text{Pb}^{2+} > \text{Na}^+ > \text{Cu}^{2+} > \text{Hg}^{2+}$; complex **4** also follows a similar order ($\text{Cu}^{2+} > \text{Hg}^{2+}$; K_s for Na^+ was not calculated because of only small changes in the emission intensity). For **5**, the binding constant with Hg^{2+} is significantly higher than that with Cd^{2+} . The complexing ability of macrocyclic ionophores such as crown ethers with various metal ions depends on the size of the macrocyclic cavity and the diameter of the metal ion (size matching), the conformation of the macrocycles and the type of donor atoms. The diameter of the 18-crown-6 moiety used in this study is in the range 2.6–

3.2 Å, which matches very well with the ionic diameter of K^+ (2.66 Å), therefore this ion expected to form stable complexes with these ionophores.^[19] However, both fluorescence and NMR studies (see below) suggest a poor complexing ability of these ionophores with K^+ . The ionic diameter of those metal ions which form stable complexes ($\text{Pb}^{2+} = 2.34$, $\text{Na}^+ = 1.96$, $\text{Hg}^{2+} = 1.86$, $\text{Cu}^{2+} = 1.84$ and $\text{Cd}^{2+} = 1.84$ Å) are less than that of K^+ (2.66 Å).^[19b] A ^1H NMR study of ligand **L**¹ in the presence of K^+ indicates that it forms a complex with this ion (see below). The above results therefore suggest that the crown rings in these complexes are twisted rather than planar and that the effective cavity size of the crown moiety available for incoming metal ions is less than that observed for a planar conformation. This means that metal ions with an ionic diameter greater or equal to that of K^+ will not form stable complexes with

these ionophores. This non-planarity of the crown moiety might be due to steric hindrance and/or intra-/intermolecular interactions.

The emission quantum yield (ϕ , approx. 0.06) and complexation properties of complexes **1–3** with guest metal ions are similar, which suggests that the significant emission quenching of these ionophores in the presence of the above-mentioned metal ions is probably related to the orientation of the complexed crown moiety with respect to the attached bpy/phen unit. The crown moieties attached to bpy/phen are flexible and these units, together with the amide ($>\text{C}=\text{O}$), are involved in intra- and intermolecular hydrogen-bonding interactions. After complexation of the crown units, these interactions are expected to change or break to minimize steric hindrance. This effect changes the orientation and conformation of the complexed crown moieties, as indicated by NMR spectroscopic and electrochemical studies (see below), and the change of orientation with respect to the coordination sphere of Ru^{II} probably promotes non-radiative decay processes.^[6a,6e,20] The enhancement of emission intensity observed in **4** and **5** is probably due to blocking of the intramolecular electron-transfer quenching process as coordination of a metal ion in the crown cavity reduces the ability of the donor atoms of the crown moiety to quench the emissive $^3\text{MLCT}$ state by photoinduced electron transfer.^[6c,7a,21] It should be noted that **4** contains only one crown moiety (L^3) and **5** is the Re^{I} complex containing CO and Cl, instead of bpy, as ligand, therefore the steric crowding and intra-/intermolecular interactions of these two complexes are expected to be different from those of **1–3**. Enhancement and quenching of the emission intensity of the same/similar complexes in the presence of different ions is well documented.^[6a,6e,7a,11,20]

The ^1H NMR spectra of selected complexes were recorded in the presence of various metal ions. A typical spectrum of **1** and those in the presence of Na^+ , K^+ and Pb^{2+} ions are shown in Figure 11. It should be noted that the spectra recorded in the presence of Na^+ and Pb^{2+} ions exhibit significant changes in both the aliphatic and aromatic regions compared to **1** whereas the spectrum recorded in the presence of K^+ does not show a significant change except for a slight upfield shift of the signals due to the protons attached to the crown moiety and the 4,4'-H signals of two bpy moieties. Upon addition of Na^+ and Pb^{2+} ions, the signals of the crown moiety are deshielded, with a significant change in their splitting pattern indicating complex formation between the crown moiety and the guest metal ion. This complexation results in changes in the chemical environment of the coordination sphere, which, in turn, affects the chemical shift of some of the protons of the bipyridine ligand (Figure 11). Similar changes in the ^1H NMR spectra of complexes **2** and **3** in the presence of Na^+ and Pb^{2+} ions were observed in both the aliphatic and aromatic regions (see Figure 12 for **2**). It should be noted that the splitting pattern and the change in chemical shifts of the signals due to the crown moiety are significantly different for Na^+ and Pb^{2+} (cf. Figures 11 and 12) for any particular receptor molecule. This difference is due to the different

ionic size and charge of the metal ions ($\text{Na}^+ = 1.96 \text{ \AA}$; $\text{Pb}^{2+} = 2.34 \text{ \AA}$) – coordination of these metal ions in the same crown cavity results in a different chemical environment for the CH_2 protons of the crown moiety. Similar ^1H NMR spectral changes are observed in the aliphatic region for Re^{I} complexes in the presence of Na^+ and Pb^{2+} ions. Like Ru^{II} , the Re^{I} complexes also exhibit minor spectral changes in the presence of K^+ even though the ionic diameter of K^+ matches the cavity size of the crown very well. To understand this finding better, the ^1H NMR spectrum of **L**¹ in the presence of K^+ (20 equiv) was recorded. The spectrum shows a significant change in the region of the crown moiety (Figure S4, Supporting Information), thereby indicating stable complex formation. Taken together, these observations therefore suggest that the crown moiety in the Ru^{II} / Re^{I} complexes is not planar and that the effective cavity size is smaller than that of a free crown moiety, consistent with the observations noted in the fluorescence study.

The redox behaviour of the Ru^{II} centre in **1–3** in the presence of Na^+ , K^+ and Pb^{2+} ions was also investigated. Upon addition of these ions (50 equiv.), the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation potential of **1** is shifted cathodically by 88 and 128 mV for Na^+ and Pb^{2+} , respectively (Figure 13), whereas with K^+ only a very small shift ($<50 \text{ mV}$) is observed. Similar changes were also noted for **2** and **3**. However, **4** and the Re^{I} complexes **5** and **6** do not show significant changes in the presence of these metal ions. Generally, an anodic shift of the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation wave is noted upon complexation of a crown moiety with a metal ion.^[10,11] However, in most of these cases the crown moiety is directly attached to a bipyridine unit, and in those cases where a $>\text{C}=\text{O}$ or $-\text{HN}-\text{C}=\text{O}$ type spacer connects the crown and bipyridine units the Ru^{II} -based oxidation potential does not show a significant change.^[5a] It should be noted that the redox potentials of the metal centres of complexes **1–3** are rather high (1.55–1.65 V) compared to those found in other similar systems (1.01–1.07 V) containing an azacrown connected to the 5,5'-position of a bipyridine unit through a $>\text{C}=\text{O}$ or an amide moiety.^[5a] This difference is probably related to strong H-bonding between $>\text{C}=\text{O}$ and the hydrogen atoms attached to the 3,3'-positions of the bipyridine unit and the 5,6-positions of the 1,10-phenanthroline moiety. The $>\text{C}=\text{O}$ moieties of complexes **1–3** are attached at the 4,4'-positions of the bpy/phen unit, which means that the oxygen atom of the $>\text{C}=\text{O}$ unit is in a favourable position to form a $>\text{C}=\text{O} \cdots \text{H}$ interaction with the hydrogen atoms at the 3,3'-position of the bipyridine unit and generate a five-membered ring, as shown in Figure 14. The strong electron withdrawing effect of the $>\text{C}=\text{O}$ units through the hydrogen atoms makes the bipyridine moiety more electron deficient, which results in an anodic shift of the oxidation potential of the metal centre. The orientation of the complexed crown moiety changes upon complexation, which results in a loss of this $>\text{C}=\text{O} \cdots \text{H}$ interaction and, in turn, reduces the electron-withdrawing ability of the amide moiety and causes a cathodic shift of the oxidation potential of the metal ion. Evidence to support this argument is provided by the NMR spectra. Upon complexation of **L**¹

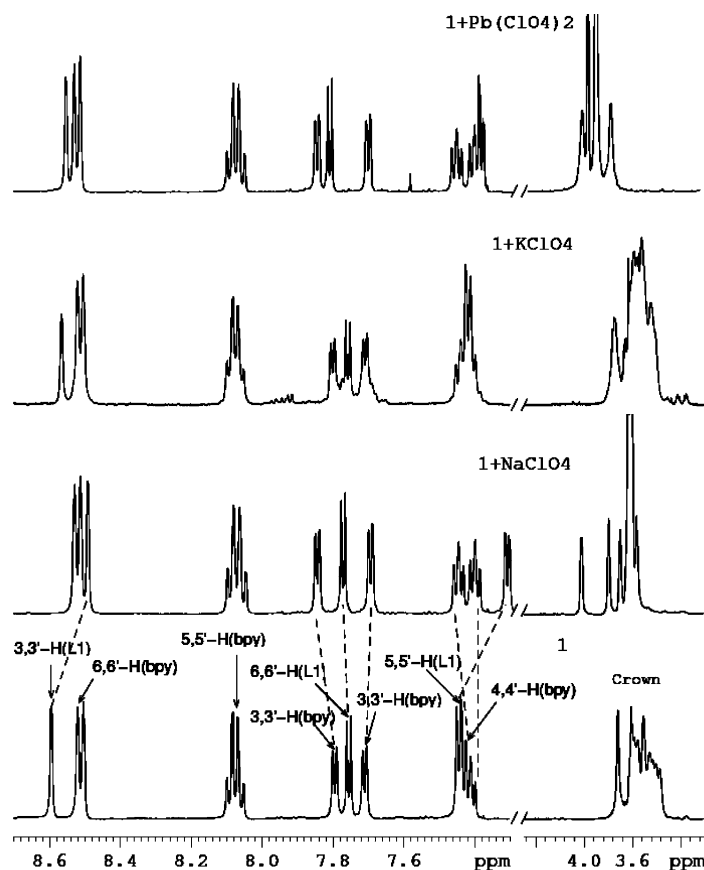


Figure 11. Selected portion of the ^1H NMR spectra of **1**, **1** + NaClO_4 , **1** + KClO_4 and **1** + $\text{Pb}(\text{ClO}_4)_2$, recorded in CD_3CN at room temperature.

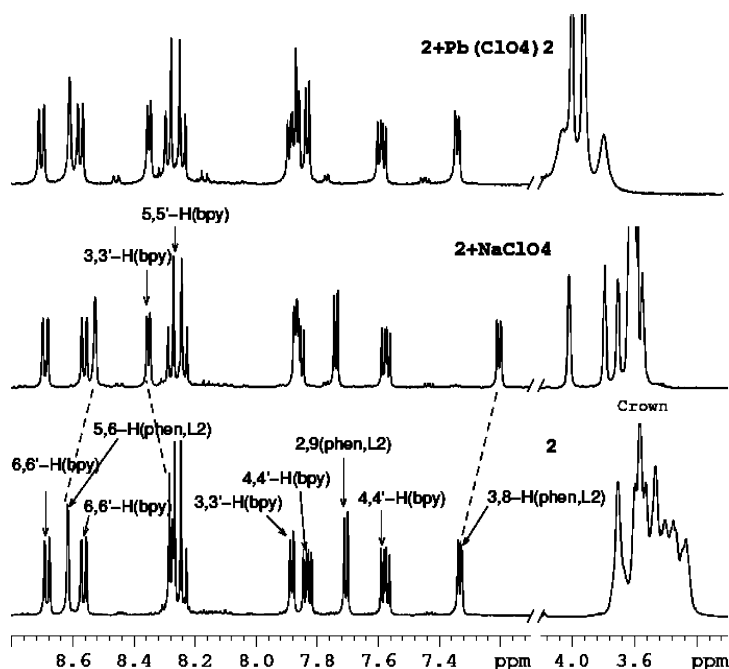


Figure 12. Selected portion of the ^1H NMR spectra of **2**, **2** + NaClO_4 and **2** + $\text{Pb}(\text{ClO}_4)_2$, recorded in CD_3CN at room temperature.

with the $\text{Ru}(\text{bpy})_2$ unit, the chemical shift of the protons attached to the 6,6'-positions of the bipyridine unit of **L**¹ are substantially shielded ($\Delta\delta = 0.98$ ppm), whereas the pro-

tons attached to the 3,3'-positions are deshielded ($\Delta\delta = 0.12$ ppm). Shielding of the adjacent protons (6,6') is expected upon coordination through nitrogen, although there

is no obvious explanation for the deshielding of the protons attached to the 3,3'-positions other than their involvement in some kind of H-bonding interaction. Again, after complexation of the crown moiety with a metal ion ($\text{Na}^+/\text{Pb}^{2+}$), the deshielding effect on these protons is lost and the protons at the 3,3'-positions shift to their original positions found in the ligand ($\delta = 8.48$ ppm), whereas the chemical shift of the protons at the 6,6'-positions remains unchanged (Figures 11 and 12). This observation is consistent with that noted in the electrochemical study.

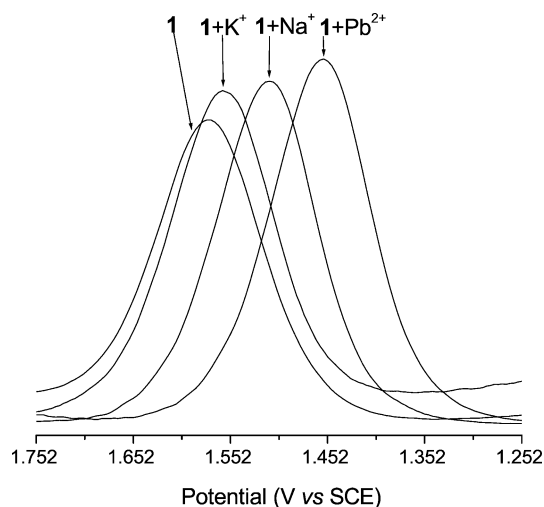


Figure 13. Oxidation potential (DPV) of the Ru^{II} centre of **1** and in the presence of K⁺, Na⁺ and Pb²⁺ (50 equiv.) in acetonitrile.

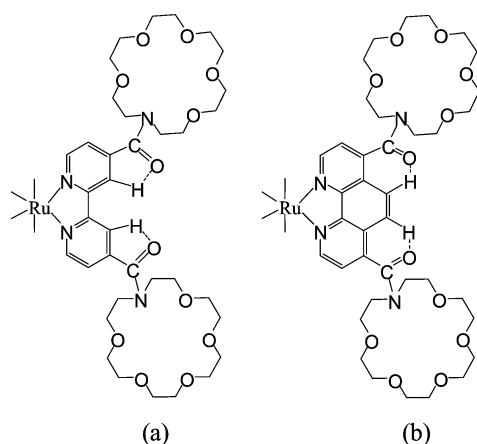


Figure 14. Partial drawing of complexes **1** and **2** showing the H-bonding interactions between the oxygen atom of C=O and the hydrogen atoms at the 3,3'-positions of bpy and the 5,6-positions of the phen moieties.

The UV/Vis spectra of ionophores **1–6** were recorded in acetonitrile in the presence of a 100-fold excess of the various metal ions. No significant change was noted except for complex **6**, where a spectral change observed upon addition of increasing concentrations of Na⁺ ion resulted in a shift of the ³MLCT band from 342 to 360 nm and a slight increase in absorption intensity, with an isosbestic point at 246 nm (Figure S5, Supporting Information).

Conclusions

A series of luminophores containing a ruthenium(II)/rhenium(I) bipyridine moiety as fluorophore and a crown ether as ionophore have been synthesised and characterised. The cation-binding properties of these receptor molecules have been investigated for a large number of cations by means of fluorescence, ¹H NMR, electrochemistry and UV/Vis spectral studies. The receptors **1–3** experience strong quenching of their emission intensity in the presence of Pb²⁺, Cu²⁺, Hg²⁺ and Na⁺, whereas **4** and **5** show a substantial increase of emission intensity in the presence of Hg²⁺ and Cu⁺/Cd²⁺. Coordination of the metal ion with the crown moiety blocks the intramolecular photoinduced reductive electron-transfer process, which results in an enhancement of the emission intensity. The stoichiometry and binding constants for strongly interacting metal ions with **1–5** have been calculated from fluorescence titration data. The complexes containing ligands **L¹** and **L²** form 1:2 complexes encapsulating metal ions in both the crown cavities, whereas complexes containing **L³** form 1:1 complexes. The binding constants for **1–5** decrease in the order Pb²⁺ > Na⁺ > Cu²⁺ > Hg²⁺ > Cd²⁺, with the size of the cation playing an important role in the formation of stable complexes. The effective size of the crown cavity in the complexes is less than that of the free crown ring, which means that K⁺ does not form stable complexes. Steric crowding and intramolecular interactions are probably responsible for twisting the crown moiety. Strong complex formation with Pb²⁺ and Na⁺ has also been demonstrated by ¹H NMR spectroscopy, with significant spectral changes being observed in the presence of these metal ions. The electrochemical oxidation of Ru^{II} in the absence and presence of metal ions also suggests a strong interaction between the ionophores and Pb²⁺ and Na⁺. The >C=O spacer apparently plays a significant role in the intramolecular interactions by promoting electronic communication between the fluorophore and ionophore, as evident from electrochemical studies and the ¹H NMR spectral changes.

Experimental Section

Methods: Elemental analyses (C, H and N) were performed with a model 2400 Perkin–Elmer elemental analyzer. NMR spectra were recorded with DPX 200 and Avance II 500 MHz Bruker FT-NMR instruments. Infrared spectra were recorded with a Perkin–Elmer Spectrum GX FT-IR system. Mass spectra were recorded with a Q-ToF microTM LC-MS instrument. The UV/Vis spectra were recorded with a CARY 500 scan Varian spectrophotometer. Luminescence spectra were recorded with a Perkin–Elmer LS-50B spectrofluorimeter. Quantum yields were measured for optically dilute solution following the literature procedure, with [Ru(bpy)₃]²⁺ ($\phi = 0.062$) as reference emitter.^[22a] Electrochemical measurements were made using a CHI 660A electrochemical workstation equipment. Cyclic and DPV studies were carried in a three-electrode cell consisting of a glassy-carbon working electrode, a platinum-wire auxiliary electrode and an SCE reference electrode. Solutions of the complexes in purified acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte were deaerated

by bubbling nitrogen for 15 min prior to each experiment. The cyclic voltammogram of $[\text{Ru}(\text{bpy})_3]^{2+}$ was recorded first for calibration of the instrument. Single crystal structures were determined using a Bruker SMART 1000 (CCD) diffractometer.

Reagents: The complexes $\text{cis-}[\text{Ru}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ and $\text{cis-}[\text{Ru}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ were prepared following the literature procedure.^[22b] Hydrated ruthenium trichloride was purchased from Arora Matthey. All other starting materials and reagents used in this study were purchased from Aldrich and S. D. Fine Chemicals. All solvents were analytical grade and were purified by standard procedures before use.^[23]

Synthesis of L^1 : A mixture of 2,2'-bipyridine-4,4'-dicarboxylic acid (0.244 g, 1 mmol), which was prepared following a published procedure,^[24] and thionyl chloride (10 mL) was refluxed under nitrogen at 80 °C for 20 h. Excess thionyl chloride was then removed by rotary evaporation and the yellowish solid mass thus obtained was used directly in the next step. In the second step, 1-aza-18-crown-6 (0.50 g, 1.90 mmol) was dissolved in dry thf (50 mL) and triethylamine (2 mL) was added to this solution. The thf solution (10 mL) of the acid chloride obtained in the previous step was added dropwise to the reaction mixture over a period of 0.5 h and the solution was stirred at room temperature for 24 h. The product, which separated during stirring, was isolated by filtration and the solid mass was dissolved in dichloromethane (50 mL) and extracted with water (50 mL, 3 times) to remove triethylamine hydrochloride. The organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated to dryness. The crude product was purified by column chromatography on silica gel (100–200 mesh) with dichloromethane containing 5% methanol as eluent. Yield 0.40 g (54%). ^1H NMR (200 MHz, CDCl_3): δ = 8.73 (d, J = 4.4 Hz, 2 H, 6-H and 6'-H of bpy), 8.48 (s, 2 H, 3-H and 3'-H of bpy), 7.40 (d, J = 4.4 Hz, 2 H, 5-H and 5'-H of bpy), 3.83 (s br, 8 H, $-\text{CH}_2\text{N}$ of crown ether), 3.67–3.58 (m, 40 H, $-\text{CH}_2\text{O}$ of crown ether) ppm. LC-MS: m/z (%) 773.63 (31) [$\text{L}^1 + \text{K}^+$] (calcd. 773.47), 757.57 (94) [$\text{L}^1 + \text{Na}^+$] (calcd. 757.36), 735.68 (18) [$\text{L}^1 + \text{H}^+$] (calcd. 735.38). IR (KBr pellets): $\tilde{\nu}$ = 1619 cm^{-1} (C=O). $\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_{12}$ (734.37): calcd. C 58.85, H 7.35, N 7.63; found C 58.42, H 7.39, N 7.51.

Synthesis of L^2 : This compound was synthesised following a similar method to that described for L^1 . The required intermediates 1,10-phenanthroline-4,7-dicarboxaldehyde and 1,10-phenanthroline-4,7-dicarboxylic acid were synthesised following published procedures.^[24] The corresponding acid chloride and ligand L^2 were synthesised following the method mentioned above for L^1 . Yield 0.15 g (53%, with respect to the dicarboxylic acid derivative). ^1H NMR (200 MHz, CDCl_3): δ = 9.23 (d, J = 4.4 Hz, 2 H, 2-H and 9-H of phen), 7.87 (s, 2 H, 5-H and 6-H of phen), 7.62 (d, J = 4.4 Hz, 2 H, 3-H and 8-H of phen), 4.00–3.93 (m, 8 H, $-\text{CH}_2\text{N}$ of crown ether), 3.76–3.42 (m, 40 H, $-\text{CH}_2\text{O}$ of crown ether) ppm. LC-MS: m/z (%) 781.45 (100) [$\text{L}^2 + \text{Na}^+$] (calcd. 781.84), 759.49 (44) [$\text{L}^2 + \text{H}^+$] (calcd. 759.86). IR (KBr pellets): $\tilde{\nu}$ = 1617 cm^{-1} (C=O). $\text{C}_{38}\text{H}_{54}\text{N}_4\text{O}_{12}$ (758.85): calcd. C 60.14, H 7.17, N 7.38; found C 59.82, H 7.30, N 7.31.

Synthesis of L^3 : A mixture of 4'-methyl-2,2'-bipyridine-4-carbaldehyde (0.20 g, 1.01 mmol), which was prepared following a published procedure,^[13] and 4'-aminobenzo-18-crown-6 (0.33 g, 1.0 mmol) was refluxed in ethanol (20 mL) for 8 h. After refluxing, the dark red solution was kept at room temperature overnight, during which time a brown microcrystalline compound precipitated. This compound was isolated by filtration, washed with diethyl ether and dried. Yield 0.425 g (83%). ^1H NMR (200 MHz, CDCl_3): δ = 8.78 (d, J = 5.2 Hz, 1 H, 6-H or 6'-H of bpy), 8.75 (s, 1 H, CH=N), 8.58 (s, 1 H, 3-H or 3'-H of bpy), 8.57 (d, J = 5.2 Hz, 1

H, 6'-H or 6-H of bpy), 8.28 (s, 1 H, 3'-H or 3-H of bpy), 7.85 (d, J = 4.8 Hz, 1 H, 5-H or 5'-H of bpy), 7.17 (d, J = 4.8 Hz, 1 H, 5'-H or 5-H of bpy), 6.92 (m, 3 H, phenyl), 4.20 (m, 4 H, $-\text{CH}_2\text{O}$ crown ether), 3.96 (m, 4 H, $-\text{CH}_2\text{O}$ crown ether), 3.77–3.70 (m, 12 H, $-\text{CH}_2\text{O}$ crown ether), 2.47 (s, 3 H, CH_3) ppm. LC-MS: m/z (%) 530.70 (16) [$\text{L}^3 + \text{Na}^+$] (calcd. 530.57), 508.74 (11) [$\text{L}^3 + \text{H}^+$] (calcd. 508.59). IR (KBr pellets): $\tilde{\nu}$ = 1594 cm^{-1} (C=N). $\text{C}_{28}\text{H}_{33}\text{N}_3\text{O}_6$ (507.58): calcd. for C 66.26, H 6.55, N 8.28; found C 66.10, H 6.84, N 8.24.

General Procedure for the Synthesis of $[\text{Ru}(\text{bpy})_2(\text{L}^1)][\text{PF}_6]_2\cdot 2\text{H}_2\text{O}$ (1), $[\text{Ru}(\text{bpy})_2(\text{L}^2)][\text{PF}_6]_2\cdot 2\text{H}_2\text{O}$ (2), $[\text{Ru}(\text{phen})_2(\text{L}^2)][\text{PF}_6]_2\cdot 2\text{H}_2\text{O}$ (3) and $[\text{Ru}(\text{bpy})_2(\text{L}^3)][\text{PF}_6]_2\cdot 2\text{H}_2\text{O}$ (4): A mixture of $\text{cis-}[\text{Ru}(\text{bpy})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}/\text{cis-}[\text{Ru}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ (0.2 mmol) and the appropriate ligand ($\text{L}^1/\text{L}^2/\text{L}^3$, 0.2 mmol) in ethanol/water (1:1, 50 mL) was refluxed for 12 h. The volume of the reaction mixture was then reduced to around 20 mL by rotary evaporation, filtered and an aqueous solution of NH_4PF_6 (0.20 g, 1.3 mmol) added to the filtrate. The precipitate was filtered off and washed with water and diethyl ether. The compound was purified by column chromatography on neutral alumina, with acetonitrile/toluene (3:2) as eluent. The solvent was removed from the desired fraction on a rotary evaporator and the compound washed with diethyl ether and vacuum dried. Yield 0.2 g (72%) for 1, 0.19 g (66%) for 2, 0.14 g (53%) for 3 and 0.12 g (54%) for 4.

Complex 1: ^1H NMR (500 MHz, CD_3CN): δ = 8.58 (s, 2 H, 3-H and 3'-H of bpy of L^1), 8.51 (d, J = 8.0 Hz, 4 H, 6-H and 6'-H of bpy), 8.06–8.10 (overlapped triplets, 4 H, 5-H and 5'-H of bpy), 7.80 (d, J = 5.5 Hz, 2 H, 3-H and 3'-H of bpy), 7.76 (d, J = 5.5 Hz, 2 H, 6-H and 6'-H of bpy of L^1), 7.71 (d, J = 5.5 Hz, 2 H, 3-H and 3'-H of bpy), 7.44 (d, J = 5.5 Hz, 2 H, 5-H and 5'-H of bpy of L^1), 7.40–7.45 (overlapped triplets, 4 H, 4-H and 4'-H of bpy), 3.43–3.72 (m, 48 H, $-\text{CH}_2\text{O}$ of crown ether) ppm. LC-MS: m/z (%) 1461.69 (31) [$\text{1} + \text{Na}^+$] (calcd. 1461.33), 1293.62 (94) [$\text{1} - \text{PF}_6^-$] (calcd. 1293.24), 1147.62 (18) [$\text{1} - \text{H}^+ - 2\text{PF}_6^-$] (calcd. 1147.27). IR (KBr pellets): $\tilde{\nu}$ = 1634 (C=O), 840 cm^{-1} (PF_6^-). UV/Vis (CH_3CN): λ (e) = 454 (1.28×10^4), 288 nm ($6.31 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{56}\text{H}_{74}\text{F}_{12}\text{N}_8\text{O}_{14}\text{P}_2\text{Ru}$ (1474.2): calcd. for C 45.62, H 5.02, N 7.60; found C 45.49, H 4.84, N 7.43.

Complex 2: ^1H NMR (500 MHz, CD_3CN): δ = 8.68 (d, J = 8.0 Hz, 2 H, 6-H and 6'-H of bpy), 8.61 (s, 2 H, 5-H and 6-H of phen of L^2), 8.56 (d, J = 8.0 Hz, 2 H, 6-H and 6'-H of bpy), 8.28 (d, J = 5.5 Hz, 2 H, 3-H and 3'-H of bpy), 8.23–8.28 (overlapped triplets, 4 H, 5-H and 5'-H of bpy), 7.88 (d, J = 5.5 Hz, 2 H, 3-H and 3'-H of bpy), 7.83 (dd, J_1 = 8.0, J_2 = 5.5 Hz, 2 H, 4-H and 4'-H of bpy), 7.70 (d, J = 6.0 Hz, 2 H, 2-H and 9-H of phen of L^2), 7.57 (dd, J_1 = 8.0, J_2 = 5.5 Hz, 2 H, 4-H and 4'-H of bpy), 7.33 (dd, J_1 = 6.0, J_2 = 1.5 Hz, 2 H, 3-H and 8-H of phen of L^2), 3.35–3.70 (m, 48 H, $-\text{CH}_2\text{O}$ of crown ether) ppm. LC-MS: m/z (%) 1341.92 (38) [$2 - \text{H}^+ - \text{PF}_6^- + \text{Na}^+$] (calcd. 1341.25). IR (KBr pellets): $\tilde{\nu}$ = 1632 (C=O), 840 cm^{-1} (PF_6^-). UV/Vis (CH_3CN): λ (e) = 445 (1.62×10^4), 262 ($7.66 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{58}\text{H}_{74}\text{F}_{12}\text{N}_8\text{O}_{14}\text{P}_2\text{Ru}$ (1498.3): calcd. for C 46.50, H 5.00, N 7.48; found C 46.28, H 5.14, N 7.3.

Complex 3: ^1H NMR (200 MHz, CD_3CN): δ = 8.63 (d, J = 5.0 Hz, 2 H, 2-H and 9-H of phen), 8.59 (d, J = 5.0 Hz, 2 H, 2-H and 9-H of phen), 8.25 (s, 4 H, 5-H and 6-H of phen), 8.13 (s, 2 H, 5-H and 6-H of phen of L^2), 7.99–8.08 (m, 6 H, 4-H and 7-H of phen; and 2-H and 9-H of phen of L^2), 7.60–7.71 (m, 6 H, 3-H and 8-H of phen including L^2), 3.47–3.84 (m, 48 H, $-\text{CH}_2\text{O}$ of crown ether) ppm. LC-MS: m/z (%) 1532.09 (5) [$3 + \text{Na}^+$] (calcd. 1533.25), 1364.74 (30) [$3 - \text{PF}_6^-$] (calcd. 1365.30). IR (KBr pellets): $\tilde{\nu}$ = 1633 (C=O), 841 cm^{-1} (PF_6^-). UV/Vis (CH_3CN): λ (e) = 435 (1.54×10^4), 263 nm ($8.22 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{62}\text{H}_{74}\text{F}_{12}\text{N}_8\text{O}_{14}\text{P}_2\text{Ru}$ (1546.3): calcd. for C 48.15, H 4.82, N 7.24; found C 47.86, H 4.96, N 7.10.

Complex 4: ^1H NMR (200 MHz, CD_3CN): δ = 8.91 (s, 1 H, $-\text{CH}=\text{N}$), 8.74 (s, 1 H, benzocrown-ArH), 8.50 (d, J = 8.0 Hz, 4 H, 6-H and 6'-H of bpy), 8.06 (t, J = 8.0 Hz, 4 H, 5-H and 5'-H of bpy), 7.81 (m, 2 H, 6-H and 6'-H of bpy of L^3), 7.73 (d, J = 5.6 Hz, 4 H, 3-H and 3'-H of bpy), 7.56 (d, J = 6.0 Hz, 1 H, 5-H or 5'-H of bpy of L^3), 7.37–7.44 (m, 4 H, 4-H and 4'-H of bpy), 7.27 (d, J = 6.0 Hz, 1 H, 5'-H or 5-H of bpy of L^3), 7.02–7.06 (m, 3 H, Ar-H of benzocrown), 4.20 (m, 4 H, $-\text{CH}_2\text{O}$ of crown ether), 3.78 (m, 4 H, $-\text{CH}_2\text{O}$ of crown ether), 3.56–3.60 (m, 12 H, $-\text{CH}_2\text{O}$ of crown ether), 2.57 (s, 3 H, CH_3) ppm. LC-MS: m/z (%) 1234.29 (4) [$4 + \text{Na}^+$] (calcd. 1233.93), 1066.29 (100) [$4 - \text{PF}_6^-$] (calcd. 1065.98), 920.31 (10) [$4 - \text{H}^+ - 2\text{PF}_6^-$] (calcd. 920.02). IR (KBr pellets): $\tilde{\nu}$ = 1621 (C=N), 842 cm^{-1} (PF_6^-). UV/Vis (CH_3CN): λ (e) = 465 (1.92×10^4), 288 nm ($5.92 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{48}\text{H}_{53}\text{F}_{12}\text{N}_7\text{O}_8\text{P}_2\text{Ru}$ (1246.97): calcd. for C 46.23, H 4.28, N 7.86; found C 45.92, H 4.32, N 7.78.

Synthesis of $[\text{Re}(\text{L}^1)(\text{CO})_3\text{Cl}]\cdot\text{THF}$ (5) and $[\text{Re}(\text{L}^3)(\text{CO})_3\text{Cl}]\cdot\text{THF}$ (6): A mixture of $[\text{Re}(\text{CO})_5\text{Cl}]$ (0.10 g, 0.275 mmol) and the appropriate ligand (L^1/L^3 , 0.275 mmol) was refluxed in dry thf (30 mL) under nitrogen for 15 h. The solution was then cooled to room temperature and the solvent removed on a rotary evaporator. The residue thus obtained was dissolved in dichloromethane (10 mL) and added dropwise to n-hexane (50 mL) with stirring. The precipitate thus obtained was isolated by filtration and purified by column chromatography packed with neutral alumina using acetonitrile/toluene (1:1) as eluent. The solvent was removed from the desired fraction by evaporation. Yield 0.13 g (47%) for **5** and 0.1 g (40%) for **6**.

Complex 5: ^1H NMR (200 MHz, CDCl_3): δ = 9.03 (d, J = 5.6 Hz, 2 H, 6-H and 6' of bpy), 8.50 (s, 2 H, 3-H and 3'-H of bpy), 7.64 (d, J = 5.6 Hz, 2 H, 5-H and 5'-H of bpy), 3.75 (s, 8 H, $-\text{CH}_2\text{N}$ of crown ether), 3.52–3.62 (m, 40 H, $-\text{CH}_2\text{O}$ of crown ether and $-\text{CH}_2\text{O}$ of thf), 1.92 (m, 4 H, $-\text{CH}_2$ of thf) ppm. LC-MS: m/z (%) 1063.52 (100) [$5 + \text{Na}^+$] (calcd. 1063.51). IR (KBr pellets): ν_{CO} = 2021 (A_1), 1900 and 1894 (E) cm^{-1} . UV/Vis (CH_3CN): λ (e) = 385 (4.13×10^3), 297 nm ($1.77 \times 10^3 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{43}\text{H}_{62}\text{ClN}_4\text{O}_{16}\text{Re}$ (1112.6): calcd. for C 46.42, H 5.62, N 5.04; found C 46.19, H 5.98, N 4.97.

Complex 6: ^1H NMR (200 MHz, CDCl_3): δ = 9.07 (d, J = 5.6 Hz, 1 H, 6-H or 6'-H of bpy), 8.87 (d, J = 5.6 Hz, 1 H, 6'-H or 6-H of bpy), 8.66 (s, 1 H, 3-H or 3'-H of bpy), 8.34 (s, 1 H, 3'-H or 3-H of bpy), 8.16 (s, 1 H, $-\text{CH}=\text{N}$), 7.84 (dd, J_1 = 5.8, J_2 = 1.4 Hz, 1 H, 5-H or 5'-H of bpy), 7.47 (d, J = 5.8 Hz, 1 H, 5'-H or 5-H of bpy), 7.38 (s, 1 H, benzocrown-Ph-H), 7.21–7.25 (m, 2 H, benzocrown-Ph-H), 4.33 (m, 4 H, $-\text{CH}_2\text{O}$ of crown ether), 3.84 (m, 4 H, $-\text{CH}_2\text{O}$ of crown ether), 3.55–3.70 (m, 16 H, $-\text{CH}_2\text{O}$ of crown ether and $-\text{CH}_2\text{O}$ of thf), 2.54 (s, 3 H, CH_3), 1.94 (m, 4 H, $-\text{CH}_2$ of thf) ppm. LC-MS: m/z (%) 907.7 (50) [$6 + \text{Na}^+$] (calcd. 908.36). IR (KBr pellets): ν_{CO} = 2018 (A_1), 1910 and 1889 (E) cm^{-1} . UV/Vis (CH_3CN): λ (e) = 342 (1.37×10^4), 292 nm ($2.04 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$). $\text{C}_{35}\text{H}_{41}\text{ClN}_3\text{O}_{10}\text{Re}$ (885.37): calcd. for C 47.48, H 4.68, N 4.75; found C 47.13, H 4.84, N 4.35.

X-ray Crystallography for L^1 : The crystallographic data and details of data collection are given in Table 3. A crystal of suitable size was selected from the mother liquor, mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystal were collected at 100 K using Mo-K_α (λ = 0.71073 Å) radiation on a Bruker SMART APEX diffractometer equipped with a CCD area detector. The data integration and reduction were processed with SAINT software.^[25] An empirical absorption correction was applied to the collected reflections with SADABS using XPREP.^[25,26] The structure was solved by direct methods using SHELXTL and refined on F^2 by the full-matrix least-squares technique using the

SHELXL-97 program package.^[27,28] Graphics for the packing diagram were generated using PLATON.^[29] All non-hydrogen atoms were refined anisotropically until convergence. Hydrogen atoms attached to the ligand moieties were either located from the difference Fourier map or stereochemically fixed.

Table 3. Crystal, data collection and refinement details for L^1 .

Formula	$\text{C}_{36}\text{H}_{54}\text{N}_4\text{O}_{12}$
Molecular weight	734.83
Crystal colour	yellow
Crystal size [mm]	$0.23 \times 0.16 \times 0.06$
T [K]	293
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	10.5750(7)
b [Å]	10.4136(7)
c [Å]	16.8608(11)
α [°]	90
β [°]	107.1990(10)
γ [°]	90
Z	2
V [Å ³]	1773.7(2)
ρ [g cm ⁻³]	1.376
Absorption coefficient [mm ⁻¹]	0.103
$F(000)$	788
Reflections collected	10193
Independent reflections	4079 [$R(\text{int})$ = 0.0171]
Number of parameters	343
GOF on F^2	1.240
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0552/0.1230
$wR1$, $wR2$ (all data)	0.0566/0.1238

Ion-Binding Study: Stock solutions of the complexes ($4 \times 10^{-5} \text{ M}$) and the perchlorate salts ($4 \times 10^{-3} \text{ M}$) of various cations were prepared in freshly purified acetonitrile. Then, 5 mL of complex stock solution and 5 mL of metal salt stock solution were placed in a 10-mL volumetric flask such that the effective concentration of the complex is $2 \times 10^{-5} \text{ M}$ and that of the metal ions $2 \times 10^{-3} \text{ M}$ (100-fold excess). The luminescence spectra of the resulting solutions were recorded with excitation at the absorption maxima (λ_{max}) of the MLCT band – 454, 445, 435, 465 nm for **1–4**, respectively, and 385 nm for **5**. For the emission titration study, the same complex stock solutions were used and the metal perchlorate solutions of desired concentration were prepared by diluting the concentrated standard solution ($4 \times 10^{-2} \text{ M}$). Then, 5 mL of each solution was mixed in a 10-mL volumetric flask and the luminescence spectra of the resulting solutions were recorded. The binding constant and stoichiometry of complex formation were calculated following the literature procedure described in the Results and Discussion section. The same solutions were also used to study UV/Vis spectral changes. For the NMR study, 5 mg of the complex was dissolved in 0.5 mL of $[\text{D}_3]\text{acetonitrile}$ and the ^1H NMR spectrum of the resulting solution was recorded. The solid perchlorate salt of the metal ion (50 equiv.) was added to the solution and the spectra of the resultant solutions were re-recorded after 30 min. The electrochemical studies were also carried out in dry acetonitrile – the DPV of the complexes in the region 1.2 to 1.8 V for metal oxidation was recorded first and then solid metal salt (Na^+ , K^+ and Pb^{2+} , 50 equiv.) was added to the solution and the DPV of the same region recorded.

Supporting Information (see also the footnote on the first page of this article): COSY NMR spectra of **1** (Figure S1); packing diagram of L^1 (Figure S2); luminescence spectra of **1** in the presence of various metal ions (Figure S3); ^1H NMR spectra of L^1 with

and without KClO₄ (Figure S4); UV/Vis spectral change of **6** upon addition of increasing concentrations of NaClO₄ (Figure S5); and details of the hydrogen-bonding interaction in **L**¹ with symmetry code (Table S1).

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