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Competitive binding of $Ba^{2+}$and Sr^{2+} to 18-Crown-6 in a Receptor with a 1-Methoxyanthraquinone Analogue as the Other Binding Site

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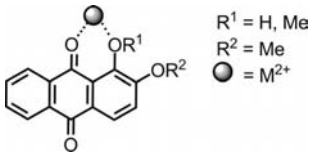
Owing to their immense biological significance, development of sensors for the selective detection of alkaline earth metal ions has attracted vast research interest. In this article we have reported the synthesis, characterisation and ion binding studies of a new Ru^{II}-polypyridyl-crown-anthraquinone complex (**5**). Studies confirm selective binding of Ba^{II}, Sr^{II} and Ca^{II} ions, with $K_{Ba^{2+}} > K_{Sr^{2+}} >> K_{Ca^{2+}}$, over all other metal ions, to the crown ether moiety and not to the methoxy anthraquinone component, the latter being the second binding site available and known for its affinity towards alkaline earth metal ions from one of our previous reports.

Introduction

The role that different alkaline earth metal ions play in various critical biological processes is well acknowledged. Among different alkaline earth metal ions, calcium is perhaps the most important because of the imperative role that it plays in neurotransmitter release, in muscle contraction, in blood clotting and in the electrical conduction system of the heart.[1] Calcium also plays the central role in the development and strengthening of the skeletal system in almost all animal life forms and its deficiency leads to diseases such as rickets and osteoporosis.[1a,1b,2] Strontium being similar to calcium, is incorporated in the bones and is known to aid bone growth and prevent fractures.[3] The $^{87}Sr/^{86}Sr$ ratio in the bones also helps in dating archaeological specimens.[4] Barium, in lower concentrations, acts as a muscle relaxant.[5] However, the presence of Sr^{2+} and Ba^{2+} beyond a threshold concentration is known to have adverse effects causing cardiac and nervous system disorders and even paralysis.[6] Thus, development of suitable sensors for the selective and efficient detection of these ions is of immense interest in current research.

A considerable number of reports exist for selective calcium sensing with different kinds of reporter groups and receptors.[7] Crown ether derivatives have clearly been one of the most popular choices for the design of selective sensors for Ca^{2+}.[8] More recently, a new PET based fluorescent sensor for Ca^{2+} using an aryl anthryl diaza 18-crown-6 derivative has been reported.[9] A number of reports also exist on selective sensing of Ba^{2+}.[10] A recent article reports the utilisation of self assembling processes of fluorophore-crown ether systems for the detection of Ba^{2+} present in micromolar concentrations.[11] Reports on recognition of Sr^{2+} in solution, however, are *extremely* scarce and all the existing reports show a poor selectivity towards Sr^{2+}.[12] Selective sensing of this alkaline earth metal ion has predominantly been achieved using carrier based PVC membrane ion sensitive electrodes.[13] Existing literature reports, therefore, suggest that there is ample opportunity and challenge for designing receptors that show selectivity to these alkaline earth metal ions.

In one of our earlier reports, we have shown that 1,2-dihydroxy- or 1,2-dimethoxy anthraquinone show moderate binding affinity (ca. 10^3 to 10^4 M^{-1} in DMF) towards the different alkaline earth metal ions and the affinities follow the order $K_{Mg^{2+}} >> K_{Ca^{2+}} > K_{Sr^{2+}} >> K_{Ba^{2+}}$.[14] Studies revealed that the O_{OMe} or O_{OH} atoms of one of the two methoxy/hydroxy functionalities and one of the two O_{CO} atoms are actually involved in the coordination to these metal ions (Scheme 1). The affinity of 18-crown-6 derivatives towards the alkaline earth metal ions is also well documented throughout the literature.[15] Such crown ether derivatives bind to the alkaline earth metal ions with moder-



Scheme 1. Binding mode of alkaline earth metal ions to anthraquinone moiety as in ref.[14].

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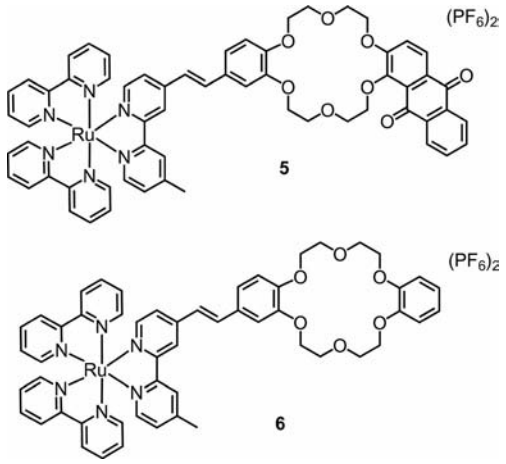
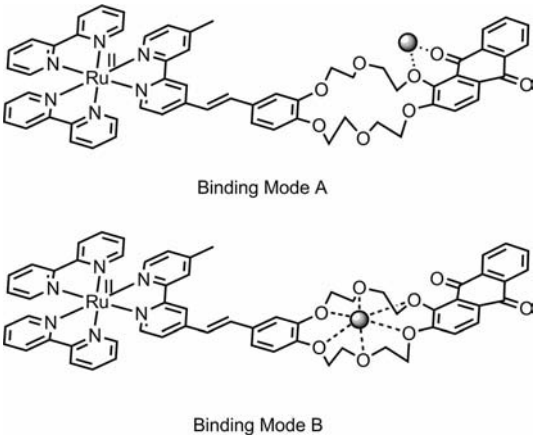
ate binding affinities as well (ca. 10^3 to 10^4 M^{-1} in MeOH).[15j]

M. D. Ward and his coworkers found that Ba^{2+} binds to Re^{I}-phenanthroline-18-crown-6 complex.[16] On the other hand, Finney et al. showed that a more flexible oxa-crown-6 moiety, coupled with a Ru^{II}-polypyridyl core, binds to Ca^{2+}, Mg^{2+} and Pb^{2+} with preference for Pb^{2+}.[17] Erk et al. have prepared anthraquinone 18-crown-6 ethers and have shown that Na^+ and K^+ have appreciable binding affinity with these.[18] Thus, literature reports tend to suggest that with a little change in the flexibility and the electronic environment of the crown ether moiety, preference of binding to metal ions changes.

In order to verify whether, in this process, one can achieve any preference towards any particular metal ion and to study two competitive binding modes for the binding of the alkaline earth metal ion(s), we have synthesised a new receptor molecule **5** in which the 18-crown-6 moiety is coupled to anthraquinone and to the Ru^{II}-polypyridyl unit. This is expected to allow coordination of metal ions to both the probable binding sites, namely the crown ether and the methoxyanthraquinone moiety (Schemes 2 and 3). Furthermore, a new compound **6**, without the anthraquinone moiety, has also been synthesised as the model compound for unambiguous assignment of the binding site. The choice of the Ru^{II}-polypyridyl moiety as the signalling unit is governed by its rich spectroscopic properties.[17b,19]



Scheme 2. Molecular structures of compounds **5** and **6**.



Scheme 3. Possible binding modes of the alkaline earth metal ions to **5**.

Experimental studies reveal a preferential binding of calcium, strontium and barium ions to the crown ether moiety in **5** and not to the methoxyanthraquinone end (see binding mode B in Scheme 3) which marks a self-sorting type of binding behaviour of the ions mentioned.

Results and Discussion

Synthesis

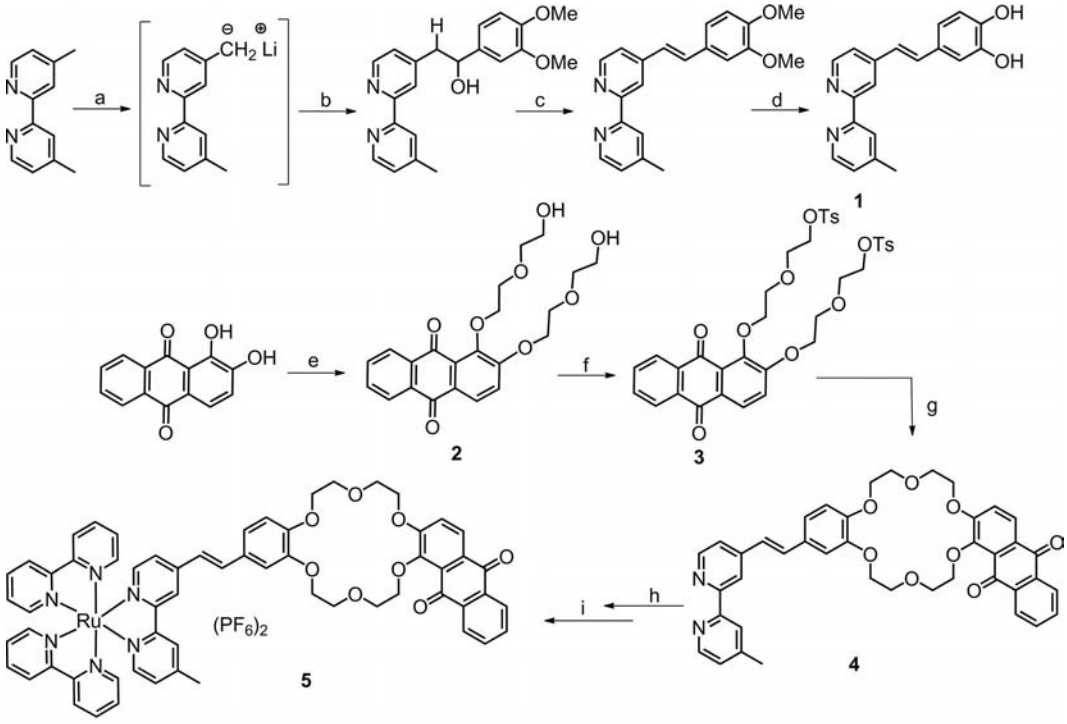
The synthetic methodologies adopted for the synthesis of the bipyridine based ligands **4** and **4a** and the corresponding Ru^{II}-polypyridyl complexes **5** and **6** are outlined in Schemes 4 and 5, respectively.

Compound **1** was prepared according to a previously reported procedure and the analytical data matched well with the reported results. Compound **2** was prepared by simple *O*-alkylation of alizarin with 2-(2-chloroethoxy)ethanol in dry and distilled DMF with potassium carbonate as a base in the presence of KI. The crude product was purified by column chromatography to isolate **2** in pure form. This was tosylated with 4-methylbenzenesulfonyl chloride in a THF/acetonitrile mixture in the presence of NaOH. Column chromatography yielded pure **3** which was subsequently treated with **1** in the presence of K_2CO_3 in dried and distilled DMF. The solvent was evaporated and pure **4** was isolated by subsequent precipitation from chloroform using methanol. This was then made to react with $Ru(2,2'\text{-bpy})_2Cl_2\cdot 2H_2O$ in ethanol and the crude compound **5** was isolated as the hexafluorophosphate salt and purified subsequently by column chromatography and recrystallisation.

The synthesis of compound **6** was done following a similar methodology. The analogous tosylation step was, however, carried out in a slightly different manner using Et_3N as the base in dichloromethane in the presence of a catalytic amount of DMAP. The reaction time for this method was only 12 h compared with a 5 d reaction time for the synthesis of **3** from **2**.

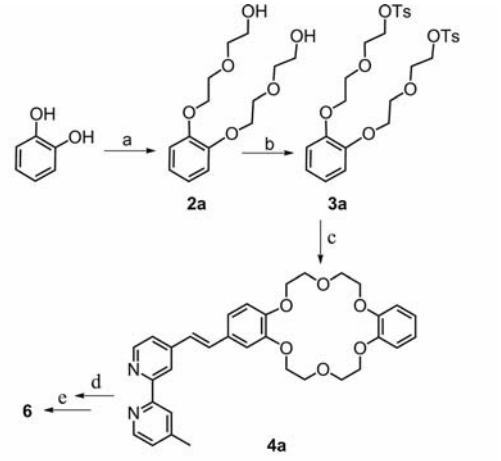
Ion Binding Studies

Figure 1 shows the absorption and the fluorescence spectra of **5** in acetonitrile. The low energy broad absorption peak with maxima at 463 nm arises predominantly due to $d\pi_{Ru}{}^{II} \rightarrow \pi^*_{2,2'\text{-bpy}}$ and $d\pi_{Ru}{}^{II} \rightarrow \pi^*_4$ based MLCT transitions.[20] Literature reports reveal that the $Ru(2,2'\text{-bpy})_3{}^{2+}$ moiety shows MLCT absorption maxima at 452 nm.[21] Shift of the absorption maxima of the MLCT transition to a longer wavelength compared with $Ru(2,2'\text{-bpy})_3{}^{2+}$ is perhaps due to the extended conjugation in the coordinated ligand **4**. This hypothesis is supported by the previous reports from our group.[22] Strong ligand centred π-π* transitions at 288 nm and higher energy MLCT d-π* transitions



a = LDA, THF, 0 °C; b = 3,4-dimethoxybenzaldehyde, THF, –30 °C; c = $POCl_3$, pyridine, r.t.; d = pyridine, HCl, 200 °C; e = 2-(2-chloroethoxy)ethanol, K_2CO_3, KI, DMF, 90 °C; f = TsCl, NaOH, ACN/THF/H_2O, r.t.; g = **1**, K_2CO_3, DMF, 90 °C; h = $Ru(bpy)_2Cl_2 \cdot 2H_2O$, EtOH, reflux; i = satd. aq. NH_4PF_6.

Scheme 4. Synthetic methodology of **5** and its precursors.



a: 2-(2-chloroethoxy)ethanol, K_2CO_3, KI, DMF, 90 °C; b: TsCl, Et_3N, DMAP, DCM, r.t.; c: **1**, K_2CO_3, DMF, 90 °C; d: $Ru(bpy)_2Cl_2 \cdot 2H_2O$, EtOH, reflux; e: satd. aq. NH_4PF_6.

Scheme 5. Synthetic methodology of **6** and its precursors.

at 245 nm could also be observed.[20] The absorption band at 369 nm could be ascribed to an overlap of several transitions, namely, n→π* charge transfer transitions with the crown ether as the donor and the low lying π* orbital involving the phenyl conjugated bipyridine part of **4** as the acceptor, n→π* charge transfer transition with the crown ether moiety as the donor and anthraquinone as the acceptor,[14,23] along with contributions from $\pi_{bpy} \rightarrow \pi^*_4$ and $\pi_{bpy} \rightarrow \pi^*_{bpy}$ based interligand charge transfer transitions.[20,22] The analogous band for the reference compound **6** has a maximum at 357 nm (Figure 1). This difference of 12 nm arises due to the absence of the relatively lower energy anthraquinone based n→π* charge transfer transition as discussed before. A broad ^{3}MLCT emission band (ϕ = 0.0023) with a maxima at 653 nm can be observed upon excitation of **5** at 463 nm.

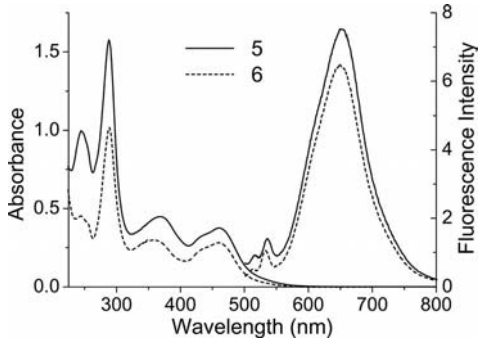


Figure 1. Absorption and fluorescence spectrum (λ_{exc} = 463 nm) of **5** (2.0×10^{-5} M) and **6** (1.33×10^{-5} M) in acetonitrile.

A significant change in the electronic spectral pattern was observed upon addition of Ca^{2+}, Sr^{2+} and Ba^{2+} ions to an acetonitrile solution of **5** (Figure 2). The extent of the observed changes was a little less for Ca^{2+} when compared with Ba^{2+} and Sr^{2+}.

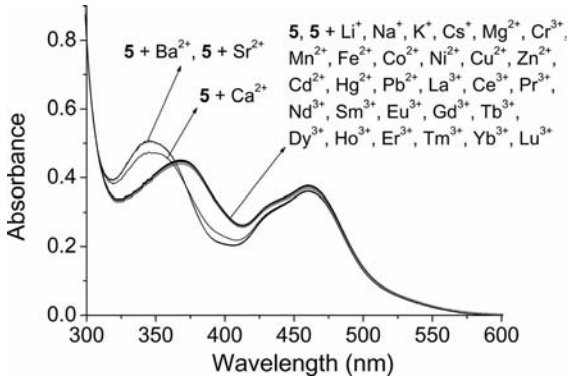


Figure 2. UV/Vis spectrophotometric scan of **5** (2.0×10^{-5} M) in the presence of 100 equiv. of different metal ions in acetonitrile.

No such spectroscopic change was observed upon the addition of any other alkali, alkaline earth, lanthanide or transition metal ions (Figures 2 and 3). On addition of the aforesaid metal ions to an acetonitrile solution of the reference compound **6**, a total loss in the selectivity is observed (Figure S30, Supporting Information). Almost all the metal ions elicit some change in the spectral pattern. However, relatively prominent changes could be obtained for Ba^{2+}, Sr^{2+}, Ca^{2+}, Pb^{2+} and K^+ for which a hypsochromic shift in the absorption band at 357 nm could be observed similar to that for complex **5**. The appearance of the absorption

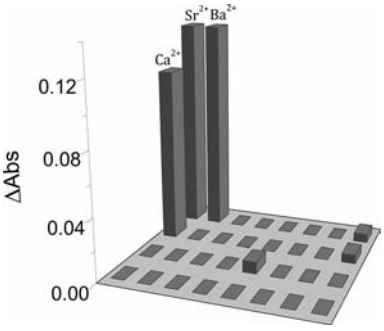


Figure 3. 3D depiction of the binding of Ca^{2+}, Sr^{2+} and Ba^{2+} in the UV/Vis scan of **5** with the metal ions. Changes shown are those at 385 nm. Each of the points in the *xy* plane represents a metal ion, the names of which have been omitted for clarity.

band at 357 nm for complex **6** further supports the contribution of an $n \rightarrow \pi^*$ charge transfer transition, with the crown ether as the donor and the low lying π^* orbital involving the phenyl conjugated bipyridine part of **4** as the acceptor, to the absorption band at 369 nm for complex **5**.

On addition of Ba^{2+} ions to an acetonitrile solution of **5**, the absorption band at 369 nm was found to decrease with a concomitant increase in the absorption at 344 nm. Occurrence of an isosbestic point at 365 nm during titration with Ba^{2+} ions indicates the presence of two species in equilibrium (Figure 4a). Similar trends were observed for titrations with Sr^{2+} and Ca^{2+} ions with respective isosbestic points at 365 nm and at 361 nm (Figure 4). This change in the absorption spectrum for **5** can be explained if one considers that the aforesaid metal cations bind to the donor, the crown ether moiety – the excited state will therefore be more strongly destabilised by the cation than the ground state, resulting in an hypsochromic shift of the absorption band at 369 nm.[24] The relative affinity of these three ions (Ca^{2+}, Ba^{2+} and Sr^{2+}) towards **5** was evaluated by the comparative change in the absorbance data at λ_{342} nm while varying the concentration of the three metal ions. Binding constants for the formation of the complexes **5**·Ca^{2+}, **5**·Sr^{2+} and **5**·Ba^{2+} were evaluated from the Benesi–Hildebrand plot using Equation (2) (see Exp. Sect.) and were found to be 1.59×10^3 M^{-1}, 5×10^3 M^{-1} and 6.1×10^3 M^{-1}, respectively (Figure 5). The linearity of the plots in Figure 5 indicates the formation of a 1:1 complex for all the three metal ions discussed. Binding constant for the formation of the complex **6**·Ba^{2+} at λ_{344} nm has also been determined for comparison with **5** and was found to be 4.3×10^4 M^{-1}.

Formation of a 1:1 complex for these three metal ions was also ascertained by mass spectrometric analysis of an acetonitrile solution of **5** in the presence of an excess of these metal ions. For 1:1 binding of Ca^{II} with **5**, a prominent peak can be observed at *m*/*z* = 1394.04 ascribed to **5** – $2PF_6$ + Ca + $2ClO_4$ + H_2O + K (Figure S32, Supporting Information). For Sr^{2+}, a 1:1 complexation peak can be observed with the desired isotopic distribution at *m*/*z* = 1323.59, **5** – $2PF_6$ + Sr + ClO_4 + K (Figure S33, Supporting Information), while for Ba^{2+} this peak can be observed at *m*/*z* = 1258.59, **5** – $2PF_6$ + Ba + Na (Figure S34, Supporting Information).

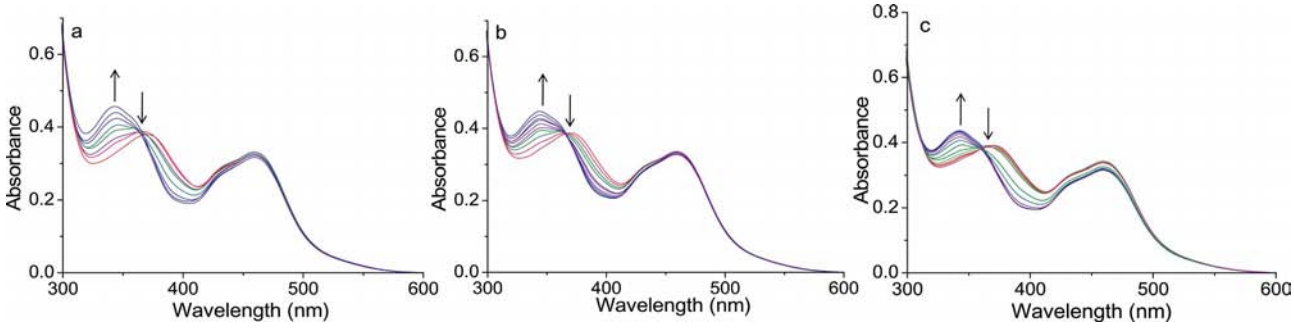


Figure 4. Spectrophotometric titration of (a) **5** (2.11×10^{-5} M) in the presence of (0–12.3) $\times 10^{-4}$ M $Ba(ClO_4)_2$ in acetonitrile, (b) **5** (1.916×10^{-5} M) in the presence of (0–7.44) $\times 10^{-4}$ M $Sr(ClO_4)_2$ in acetonitrile and (c) **5** (1.916×10^{-5} M) in the presence of (0–28.39) $\times 10^{-4}$ M $Ca(ClO_4)_2$ in acetonitrile.

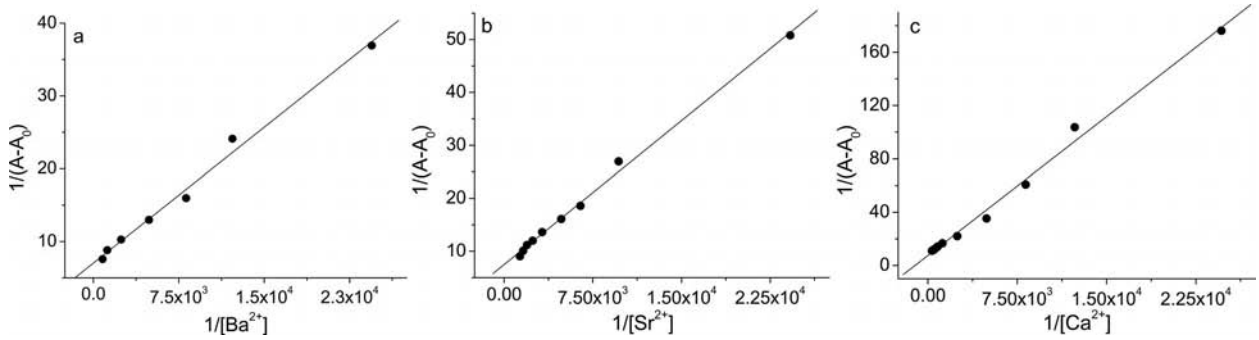


Figure 5. Benesi–Hildebrand plots for binding constant calculation with (a) Ba^{2+}, (b) Sr^{2+} and (c) Ca^{2+} from the specrophotometric titrations for **5**.

Emission spectroscopic studies of **5** in acetonitrile show an enhancement in the emission intensity at 653 nm in the presence of added Ca^{2+}, Ba^{2+} and Sr^{2+} with changes being more prominent for Sr^{2+} and Ba^{2+} than for Ca^{2+} ($\phi = 0.003$, 0.0032 and 0.0032 for **5**·Ca^{2+}, **5**·Sr^{2+} and **5**·Ba^{2+}, respectively) (Figure 6). As was observed in the electronic spectroscopic studies, no change was observed for any other metal ion in the emission spectrum. A similar experiment with compound **6** did not yield any selectivity towards any metal ion. (Figure S35, Supporting Information).

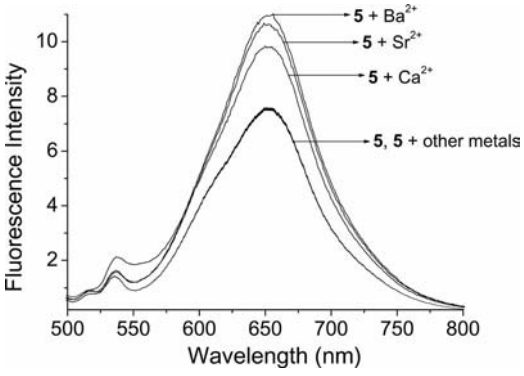


Figure 6. Emission scan of **5** (2×10^{-5} M) in the presence of 100 equiv. of different metal ions in acetonitrile (λ_{exc} = 463 nm).

In the present study, a broad charge transfer emission band appears at 425 nm on excitation of the charge transfer absorption band of **5** at 369 nm.[14] This assignment is further corroborated by the observation that no such emission band could be obtained when an acetonitrile solution of **6** was excited at 357 nm (Figure S36, Supporting Information). No change in the emission profile at 425 nm was observed when an acetonitrile solution of **5** was scanned with the various metal ions, except for Cu^{2+} ion which quenches the fluorescence appreciably (Figure S37, Supporting Information). This response can be attributed to dynamic quenching by Cu^{2+} on the basis of a lifetime titration experiment. The free complex **5** shows monoexponential decay with a lifetime of 1.076 ± 0.009 ns ($\chi^2 = 1.08$) when monitored at 425 nm in acetonitrile using a 340 nm LED as an excitation source. This lifetime of **5** was measured in the presence of varying concentrations of Cu^{2+}. The Stern–Volmer plot i.e., the plot of τ_0/τ, where τ_0 is the lifetime in the absence of Cu^{2+} vs. the concentration of Cu^{II}, shows an increase in the τ_0/τ values with increasing concentrations of Cu^{2+}, i.e., the lifetime decreases steadily as the concentration of Cu^{2+} is increased (Figure S38, Supporting Information). This confirms that no ground state complex is formed between Cu^{2+} and **5** and that the quenching is purely dynamic in nature.[25] No change in the emission profile on the addition of Ca^{II}, Sr^{II} or Ba^{II} ions is probably because of the fact that the rate of excited state decay of the anthraquinone moiety is much less than the rate of repulsion between the cations and the receptor in the excited state. The lifetime of **5** in the presence of Ca^{2+}, Sr^{2+} and Ba^{2+} at 653 nm could not be measured because of the exceedingly low quantum yield of the Ru^{II}-polypyridyl fluorophore at that wavelength.

The enhancement in the emission intensity of the ^{3}MLCT emission band at 653 nm on binding to the aforesaid metal ions is suggestive of a photoinduced electron transfer process being operational. Binding to these metal ions to the oxygen atoms of the crown ether moiety interrupts the photoinduced electron transfer process and an enhancement in the Ru^{II}-polypyridyl based emission results.[24b,26] Binding constants were evaluated from systematic fluorescence titrations using Equation (3) (see Exp. Sect.) and were found to be 2.63×10^3 M^{-1}, 6.08×10^3 M^{-1} and 7.76×10^3 M^{-1}, respectively, for Ca^{2+}, Sr^{2+} and Ba^{2+} (Figure 7). This was found to corroborate nicely with the binding constants calculated from the spectrophotometric titrations. The binding constants therefore obey the order $K_{Ba^{2+}} > K_{Sr^{2+}} >> K_{Ca^{2+}}$. The binding constant for the formation of the complex **6**·Ba^{2+} has also been determined from a similar spectrophotometric titration as carried out for **5** and was found to be 1.8×10^4 M^{-1} (Figure S39, Supporting Information). The relatively lower binding constant for **5**·Ba^{2+} compared with that for **6**·Ba^{2+} might be due to the presence of the electron withdrawing anthraquinone fragment in **5** which reduces the basicity of the O_{Crown} atoms – especially that of the two O_{Crown} atoms that are in conjugation with the anthraquinone fragment.

Literature reports on the binding of the alkaline earth metals to 18-crown-6 moiety are plentiful.[15] On the other hand, we, in one of our previous reports, have explored 1,2-

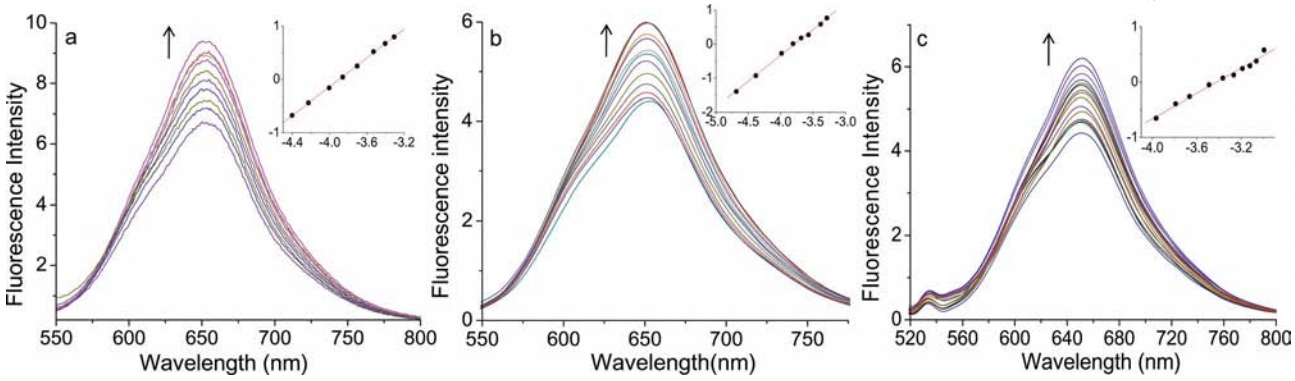


Figure 7. Emission titration of **5** (1.988×10^{-5} M) in presence of (a) $(0–5.9) \times 10^{-4}$ M Ba^{2+}, (b) $(0–6.2) \times 10^{-4}$ M Sr^{2+} and (c) $(0–14.2) \times 10^{-4}$ M Ca^{2+}in acetonitrile. Respective logarithmic plots ($\log[F_0 - F]/[F - F_\infty]$ as the ordinate and $\log[M^{2+}]$ as the abscissa) for the calculation of binding constants are shown as insets.

dimethoxy anthraquinone as a sensor for the alkaline earth metal ions.[14] In that study, spectrophotometric, fluorescence and theoretical calculations confirmed binding of the metal ions to the ether and the carbonyl oxygen atom (Scheme 1).

Both of the aforesaid binding sites have been combined in **5** in order to establish the relative binding affinity of the alkaline earth metal ions towards these two binding sites. Studies corroborate preferential binding of Ca^{2+}, Sr^{2+} and Ba^{2+} ions to the crown ether and not to the methoxyanthraquinone moiety. This is confirmed from an analysis of the infrared spectrum of **5** in absence and in the presence of these ions. Free complex **5** shows carbonyl stretching frequencies at 1653 cm^{-1} (C1) and 1635 cm^{-1} (C2) (Figure S23, Supporting Information). On addition of an excess of Ca^{2+}, the peak at 1635 cm^{-1} does not shift much but the 1653 cm^{-1} peak shifts to 1665 cm^{-1}. Addition of an excess Sr^{2+} and Ba^{2+} shifts these peaks to 1707 cm^{-1}, 1669 cm^{-1} and to 1709 cm^{-1}, 1669 cm^{-1}, respectively (Figure 8). In our earlier report, for binding of Mg^{2+} to one of the ether and the carbonyl oxygen atoms (Scheme 1), a shift of the carbonyl stretching frequency in the FTIR spectrum to lower energy was observed.[14] In the present study, however, the carbonyl stretching frequencies are found to shift to higher energies. The shifting of the ν(C=O) values to higher energies is because of the metal ions binding to the crown ether moiety which draws electron density from the carbonyl oxygen atoms towards the anthraquinone ring system making the carbonyl bond stronger. For Sr^{2+} and Ba^{2+}, the shifts are more pronounced indicating stronger binding of these metal ions than calcium. This inference corroborates our results obtained from the spectrophotometric and fluorescence measurements.

^{1}H NMR titrations were carried out in the presence of the aforesaid ions and the results support our ideas of the ions binding to the crown ether part. The signals arising from almost all of the hydrogens of the crown ether moiety were found to shift downfield on addition of either of these metal ions indicating binding to the ethereal oxygen atoms. However, for H^9, H^{10}, H^{11} and H^{12} protons, i.e. the protons corresponding to the centre of the crown ether, the effects

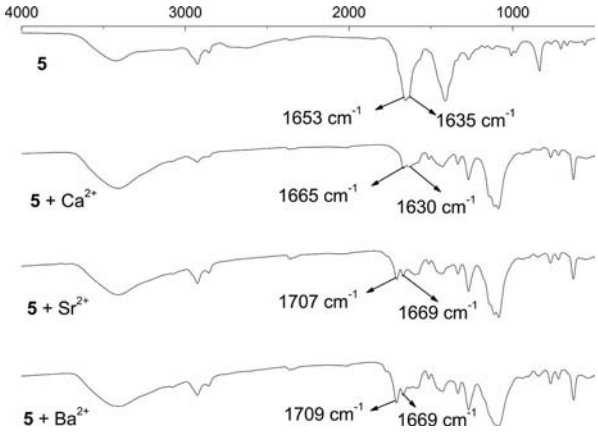


Figure 8. Changes in the IR spectroscopic pattern upon addition of the metal ions.

are most prominent. Addition of Ba^{2+} ions to an acetonitrile solution of **5** causes the spectrum to become very broad which may be due to a very fast relaxation of the complex formed. Similar broadening has been observed by other groups as well.[26,27] For Ba^{2+}, a set of new complexation peaks could be observed at δ = 4.96 and 4.84 ppm (Figure 9).

The appearance of a new complexation peak is reminiscent of slow exchange in the NMR time scale which is expected in the case of strong binding of Ba^{2+} ions.[27,28] For Ca^{2+} and Sr^{2+} respectively, the set of eight protons i.e., H^9, H^{10}, H^{11} and H^{12}, at δ = 4.29–4.2 ppm, were found to shift to δ = 4.38–4.29 ppm and δ = 4.58–4.41 ppm (see Figures 10 and S40, the latter in the Supporting Information).

A final confirmation comes from the ^{13}C NMR studies in acetone. ^{13}C NMR spectra of **5** were recorded for each metal ion when present in equivalent amounts and in excess. Acetone was used in order to prevent interference from the signals arising from acetonitrile itself in the aromatic region of the spectrum. Though **5** was less soluble in acetone, the solubility increased on the addition of the metal ions indicating complex formation of **5** with the metal ions.[15c,29] For **5**, the carbonyl carbons appear at δ = 182.5 and

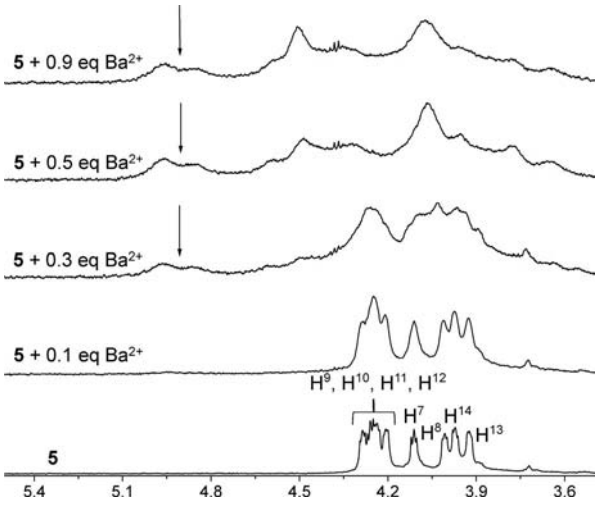


Figure 9. Changes in the ^{1}H NMR spectrum on addition of increasing equivalents of Ba^{2+} in acetonitrile. The appearance of complexation peaks at δ = 4.96 and 4.84 ppm is marked with arrows.

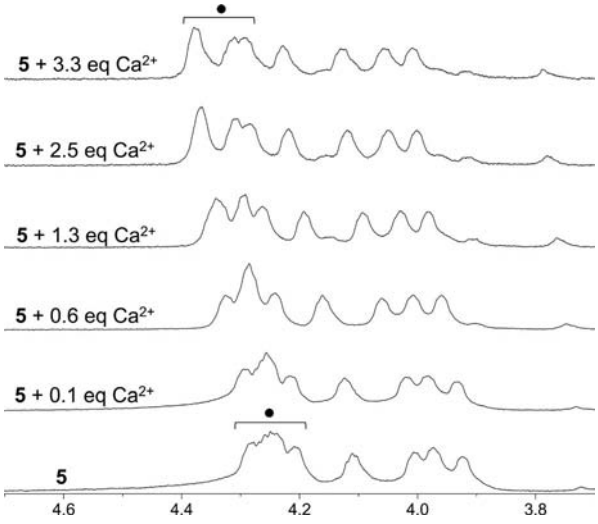


Figure 10. Changes in the ^{1}H NMR spectrum on addition of increasing equivalents of Ca^{2+} in acetonitrile. The initial and the final positions of the H^9, H^{10}, H^{11} and H^{12} protons are marked with the black dot.

182.1 ppm. In case of a possibility of the metal ions interacting with the carbonyl oxygen, one of the aforesaid signals would be expected to shift downfield. No such shift was observed for any of the metal ions when present in either equivalent amounts or in excess (Figure 11).

The signals arising from the carbons of the crown ether moiety in the region δ = 73.59–69.2 are instead seen to become affected in every case which confirms our proposition of the metal ions binding to the crown ether moiety (Figures S41 and S42, Supporting Information).

UV/Vis and emission titrations reveal a binding constant an order of magnitude higher for Ba^{2+} binding to **6** (ca. 10^4 M^{-1}) than to **5** (ca. 10^3 M^{-1}) in acetonitrile. For Ba^{2+} binding separately to the methoxyanthraquinone moiety

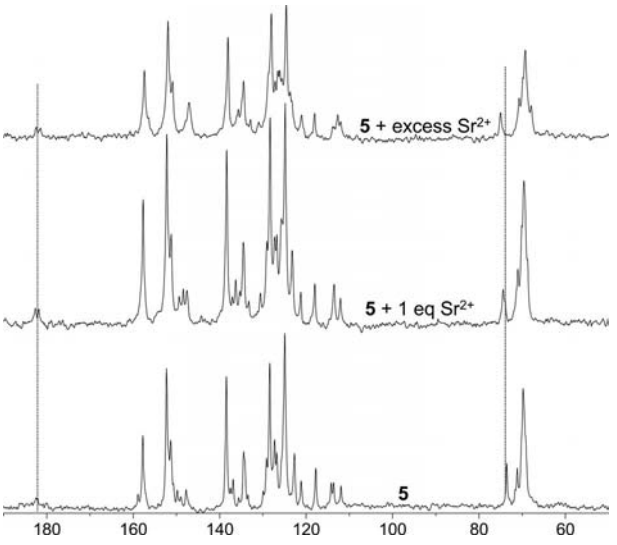


Figure 11. ^{13}C NMR spectrum of **5** in the presence of 1 equiv. and excess of Sr^{2+} in [D_6]acetone. The peaks due to the carbonyl carbon atoms (δ = 182.5 and 182.1 ppm) are not seen to shift. The C signals of the crown ether moiety can, however, be seen to become deshielded.

(Scheme 1), the binding constant value is reported to be equal to 0.6×10^3 M^{-1} in DMF.[14] Although the solvent plays a dominant role in the binding phenomena, the relatively higher binding affinity of the aforesaid alkaline earth metal ions to the crown ether moiety compared with the methoxyanthraquinone part is apparently, therefore, the possible reason for the selective binding to the crown ether in **5**.

Conclusions

We have synthesised and characterised a new Ru^{II}-polypyridyl/anthraquinone-based molecule **5** with two probable binding sites for the binding of metal ions, an 18-crown-6 ether and a methoxyanthraquinone moiety. Compound **5** was found to bind selectively with Ca^{2+}, Sr^{2+} and Ba^{2+} ions in acetonitrile over all other alkali, alkaline earth, transition and lanthanide metal ions and the binding phenomena have been probed by spectrophotometric, fluorimetric and mass spectrometric measurements. ^{1}H, ^{13}C and IR spectroscopic studies prove binding of the aforesaid metal ions selectively to the crown ether part and not to the methoxyanthraquinone moiety.

Experimental Section

Materials and Methods: $RuCl_3 \cdot xH_2O$, 4,4′-dimethyl-2,2′-bipyridine, *n*-butyllithium, 3,4-dimethoxybenzaldehyde, 2,2′-bipyridine, 4-methoxybenzaldehyde, alizarin, 2-(2-chloroethoxy)ethanol, 4-methylbenzenesulfonyl chloride, ammonium hexafluorophosphate, 4-(dimethyamino)pyridine, $LiClO_4$, $NaClO_4$, $KClO_4$, $CsClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2 \cdot 4H_2O$, $Sr(ClO_4)_2 \cdot xH_2O$, $Ba(ClO_4)_2$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Mn(ClO_4)_2$, $Fe(ClO_4)_2 \cdot xH_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Cd(ClO_4)_2 \cdot H_2O$, $Hg(ClO_4)_2 \cdot xH_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, $La(NO_3)_3 \cdot 6H_2O$,

$Ce(NO_3)_3{\cdot}6H_2O$, $Pr(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}5H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Tb(NO_3)_3{\cdot}5H_2O$, $Dy(NO_3)_3{\cdot}xH_2O$, $Ho(NO_3)_3{\cdot}5H_2O$, $Er(NO_3)_3{\cdot}5H_2O$, $Tm(NO_3)_3{\cdot}5H_2O$, $Yb(NO_3)_3{\cdot}5H_2O$ and $Lu(NO_3)_3{\cdot}xH_2O$ were purchased from the Sigma–Aldrich Chemical Co. and were used as received. Diisopropylamine, triethylamine, $POCl_3$, pyridine, HCl, K_2CO_3, KI, NaOH, $MgSO_4$ and all other chemicals (AR grade) were purchased from S. D. Fine Chemicals (India) and were used without any further purification. Dimethyl formamide (DMF), dichloromethane (DCM), tetrahydrofuran (THF) and pyridine, used for synthesis, were dried and distilled before use according to standard procedures.[30] All other solvents used (AR grade) were purchased from S. D. Fine Chemicals (India). Spectroscopic grade solvents were used for all spectroscopic and photophysical studies. $Ru(2,2'\text{-bpy})_2Cl_2{\cdot}2H_2O$ was prepared following a previously reported procedure.[31]

^1H and ^{13}C NMR spectra were recorded with either a Bruker 200 MHz FT NMR (model: Avance-DPX 200) or a Bruker 500 MHz FT NMR (model: Avance-DPX 500) spectrometer at room temperature (r.t., 25 °C). Tetramethylsilane (TMS) was used as an internal standard for all ^1H NMR spectroscopic studies. ESI-MS measurements were carried out with a Waters QTof-Micro instrument. Microanalyses (C, H, N) were performed by using a Perkin–Elmer 4100 elemental analyser. Infrared spectra were recorded as KBr pellets by using a Perkin–Elmer Spectra GX 2000 spectrometer. HRMS measurements were done using a micromass Q-Tof micro™ instrument. UV/Vis spectra were obtained by using either a Shimadzu UV-3101 PC or a Cary 500 Scan UV/Vis/NIR spectrophotometer. Room-temperature steady state emission spectra were obtained by using either a Fluorolog (Horiba Jobinyvon) or an Edinburgh Instruments Xe 900 luminescence spectrofluorimeter. Time-resolved fluorescence measurements were carried out using Horiba Jobinyvon FluoroHub spectrofluorimeter. The instrument works on the principle of the time-correlated single-photon counting technique (TCSPC). The fluorescence quantum yields (ϕ_f) were estimated using Equation (1) in acetonitrile by using the integrated emission intensity of $Ru(bpy)_3(PF_6)_2$ (ϕ_f = 0.062 in acetonitrile at r.t.) as a reference.[21]

$$\phi_f = \phi_f' \, (I_{sample}/I_{std})(A_{std}/A_{sample})(\eta^2_{sample}/\eta^2_{std}) \quad (1)$$

ϕ_f' is the absolute quantum yield for the $Ru(bpy)_3(PF_6)_2$ used as reference, I_{sample} and I_{std} are the integrated emission intensities, A_{sample} and A_{std} are the absorbances at the excitation wavelength, and η_{sample} and η_{std} are the respective refractive indices.

Binding constants were calculated from the UV titrations by using the Benesi–Hildebrand Equation (2).[32]

$$\frac{1}{A-A_0} = \frac{1}{K(A_{max}-A_0)[M^{x+}]^n} + \frac{1}{A_{max}-A_0} \quad (2)$$

A_0 is the absorbance of **5/6** in the absence of any metal ion M^{x+}, A is the absorbance in the presence of the metal ion, A_{max} is the absorbance in presence of added $[M^{x+}]_{max}$ and K is the association constant. This association constant (K) could be determined from the slope of the linear plot of $1/(A-A_0)$ vs. $1/[M^{x+}]$.

Binding constants from the fluorescence titrations were calculated using Equation (3).[33]

$$\frac{F_0-F}{F-F_\infty} = \left[\frac{[M^{x+}]}{K_d}\right]^n \quad (3)$$

K_d is the dissociation constant, n is the number of metal ions bound to each complex, F_0 is the fluorescence intensity of the complex in the absence of any metal ion, F_∞ is the fluorescence intensity at the maximum concentration of the metal ion i.e., when the emission intensity does not change any more. We plotted $\log[(F_0 - F)/(F - F_\infty)]$ against $\log[M^{x+}]$. The value of $\log[M^{x+}]$ at $\log[(F_0 - F)/(F - F_\infty)] = 0$ gives K_d, the reciprocal of which is the binding constant.

Synthesis

4-[2-(4′-Methyl-2,2′-bipyridinyl-4-yl)vinyl]benzene-1,2-diol (1): This compound was prepared following a literature procedure.[34] ESI-MS (*m*/*z*): calcd. for $C_{19}H_{16}N_2O_2$ 304.34; found 305.22 $[M + 1]^+$. ^1H NMR (500 MHz, CD_3OD): δ = 8.54 [d, J = 5.5 Hz, 1 H, $H^{6'}$ (bpy)], 8.52 [d, J = 5 Hz, 1 H, H^6 (bpy)], 8.34 [s, 1 H, $H^{3'}$ (bpy)], 8.13 [s, 1 H, H^3 (bpy)], 7.53 [dd, J = 4, 1 Hz, 1 H, $H^{5'}$ (bpy)], 7.43 [d, J = 16 Hz, 1 H, H (ethenyl)], 7.32 [dd, J = 4, 1 Hz, 1 H, H^5 (bpy)], 7.11 [d, J = 1.5 Hz, 1 H, H^2 (phenyl)], 7.02–6.98 [m, 2 H, H (ethenyl) and H^6 (phenyl)], 6.79 [d, J = 8 Hz, 1 H, H^5 (phenyl)], 2.49 (s, 3 H, bpy-CH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3238 [ν (OH)], 1590 [ν(C=C)] cm^{-1}. $C_{19}H_{16}N_2O_2$ (304.35): calcd. C 74.98, H 5.30, N 9.20; found C 74.6, H 5.28, N 9.16.

1,2-Bis[2-(2-hydroxyethoxy)ethoxy]anthraquinone (2): Alizarin (2.5 g, 0.01 mol) was dissolved in pre-dried and distilled DMF (80 mL). Anhydrous K_2CO_3 (4.83 g, 0.035 mol) was ground and added in a powdered form to this solution with constant stirring under an inert atmosphere (oxygen- and moisture-free argon gas blanket). The reaction mixture was heated to 90 °C. 2-(2-Chloroethoxy)ethanol (3.2 mL, 0.03 mol) was dissolved in dry DMF (10 mL) and was added in a dropwise manner to the resultant solution. When the addition was complete, anhydrous KI (5.81 g, 0.035 mol) was added and the reaction mixture was stirred at 100 °C for 6 d in the inert atmosphere. The solvent was evaporated thereafter and solvent extraction was carried out with the crude mixture. Undesired inorganic salts were removed in the aqueous phase and the organic (chloroform) layer was collected. This was dried with anhydrous magnesium sulfate before chloroform was finally removed under reduced pressure to obtain the crude product. This crude solid was subjected to column chromatography using silica as the stationary phase and $CHCl_3$/MeOH solvent mixture as the eluent. The major fraction was eluted as the second band to yield the desired compound **2** in pure form; yield 1.3 g, 30%. ESI-MS (*m*/*z*): calcd. for $C_{22}H_{24}O_8$ 416.42; found 417.52 $[M + 1]^+$, 439.52 $[M + Na]^+$. ^1H NMR (500 MHz, CD_3OD): δ = 8.29 (d, J = 8 Hz, 1 H, H_1), 8.22–8.18 (m, 1 H, H^2), 8.08 (d, J = 8.5 Hz, 1 H, H^3), 7.75–7.71 (d, J = 8.5 Hz, 1 H, H^4), 7.73 (m, 1 H, H^5), 7.25–7.22 (m, 1 H, H^6), 4.37–4.35 [m, 4 H, H^7 (two protons), H^8 (two protons)], 4.30 (t, J = 4.5 Hz, 2 H), 4.12 (t, J = 4.5 Hz, 2 H), 4.09 (t, J = 4.5 Hz, 2 H), 3.96 (t, J = 4.5 Hz, 2 H), 3.76 (t, J = 4.5 Hz, 2 H), 3.69 (t, J = 4.5 Hz, 2 H) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3406, 3259 [ν(OH)], 1672 [ν(C=O)] cm^{-1}. $C_{22}H_{24}O_8$ (416.43): calcd. C 63.45, H 5.81; found C 63.38, H 5.76.

2,2′-{2,2′-[1,2-Phenylenebis(oxy)]bis(ethane-2,1-diyl)}bis(oxy)diethanol (2a): Catechol (1.65 g, 0.015 mol) was dissolved in pre-dried and distilled DMF (80 mL). Anhydrous K_2CO_3 (5 g, 0.036 mol) was ground and added in a powdered form to this solution with constant stirring under an inert atmosphere. The reaction mixture was heated to 90 °C. 2-(2-Chloroethoxy)ethanol (4.7 mL, 0.045 mol) was dissolved in dry DMF (10 mL) and was added in a dropwise manner to the resultant solution. When the addition was complete, anhydrous KI (6 g, 0.036 mol) was added and the reaction mixture was stirred at 100 °C for 6 d in the inert atmosphere. The solvent was evaporated thereafter and solvent extraction was carried out with the crude mixture. Undesired inorganic salts were

removed in the aqueous phase and the organic (chloroform) layer was collected. This was dried with anhydrous magnesium sulfate before chloroform was finally removed under reduced pressure to obtain the crude product. This crude solid was subjected to column chromatography using silica as the stationary phase and $CHCl_3$/MeOH solvent mixture as the eluent. The major fraction was eluted as the second band to yield the desired compound **2a** in pure form; yield 3.67 g (85.5%). ESI-MS (*m*/*z*): calcd. for $C_{14}H_{22}O_6$ 286.32; found 287.84 $[M + 1]^+$, 309.82 $[M + Na]^+$, 325.8 $[M + K]^+$. ^1H NMR (500 MHz, CD_3OD): δ = 6.98–6.96 (m, 2 H, $H^{2'}$ and $H^{3'}$), 6.91–6.89 (m, 2 H, $H^{1'}$ and $H^{4'}$), 4.13 [t, J = 4 Hz, 4 H, $H^{5'}$ (two protons) and $H^{6'}$ (two protons)], 3.82 [t, J = 4.5 Hz, 4 H, $H^{7'}$ (two protons) and $H^{8'}$ (two protons)], 3.69 [t, J = 4.5 Hz, 4 H, $H^{9'}$ (two protons) and $H^{10'}$ (two protons)], 3.63 [t, J = 4.5 Hz, 4 H, $H^{11'}$ (two protons) and $H^{12'}$ (two protons)] ppm. IR (KBr pellet): $\tilde{\nu}$ = 3397 [ν(OH)] cm^{-1}. $C_{14}H_{22}O_6$ (286.32): calcd. C 58.73, H 7.74; found C 58.78, H 7.70.

{[(9,10-Dioxo-9,10-dihydroanthracene-1,2-diyl)bis(oxy)bis(ethane-2,1-diyl)]bis(oxy)}bis(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (3): 2 (1.15 g, 2.76 mmol) was dissolved in THF/CH_3CN mixture (95:5, v/v) and the temperature was lowered to 0 °C. Aqueous NaOH (1.104 M, 11.04 mmol, 10 mL) was added to it with constant stirring. 4-Methylbenzenesulfonyl chloride (2.1 g, 11.04 mmol) was dissolved in THF (20 mL) and was added in a dropwise manner to the resultant solution under ice cold conditions. The reaction mixture was then allowed to attain room temperature and was stirred for 6 d. The solvent was then evaporated and the crude product was redissolved in chloroform and the undesired water soluble ionic impurities were discarded in the aqueous phase following a solvent extraction process. The organic layer was collected, dried with anhydrous magnesium sulfate and was evaporated to dryness to obtain the crude desired compound (**3**). This was further purified and isolated by column chromatography using silica as the stationary phase and $CHCl_3$/hexane solvent mixture as the eluent; yield 790 mg (39.5%). ESI-MS (*m*/*z*): calcd. for $C_{36}H_{36}O_{12}S_2$ 724.79; found 747.10 $[M + Na]^+$. ^1H NMR (500 MHz, CD_3OD): δ = 8.26–8.25 (m, 1 H, H^1), 8.24–8.22 (m, 1 H, H^2), 8.13 (d, J = 8.5 Hz, 1 H, H^3), 7.79 [m, 3 H, H_a (two protons), H^4], 7.77 [m, 2 H, H_b (two protons)], 7.75 (m, 1 H, H^5), 7.32 [d, J = 8 Hz, 4 H, H_c (four protons)], 7.25 (d, J = 8.5 Hz, 1 H, H^6), 4.235 [m, 4 H, H^7 (two protons), H^8 (two protons)], 4.20–4.16 [m, 4 H, H^9 (two protons), H^{10} (two protons)], 3.936 [t, J = 4.5 Hz, 2 H, H^{11} (two protons) or H^{12} (two protons)], 3.9 [t, J = 4.5 Hz, 2 H, H^{11} (two protons) or H^{12} (two protons)], 3.81 [t, J = 4.5 Hz, 4 H, H^{13} (two protons), H^{14} (two protons)], 3.09 [s, 3 H, H_d (two protons)], 3.02 [s, 3 H, H_e (two protons)] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1674 [ν(C=O)], 1283 [ν(S=O)] cm^{-1}. $C_{36}H_{36}O_{12}S_2$ (724.79): calcd. C 59.66, H 5.01; found C 59.70, H 4.97.

2,2′-{2,2′-[1,2-Phenylenebis(oxy)]bis(ethane-2,1-diyl)}bis(oxy)bis-(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (3a): 2a (3 g, 0.01 mol) was dissolved in dry DCM (50 mL) and dry triethylamine (7 mL, 0.05 mol) was added to it. 4-(Dimethylamino)pyridine (20 mg, 0.1637 mmol) was then added to the reaction mixture. The temperature was lowered to 0 °C and the reaction mixture was stirred as such for 0.5 h under an inert argon atmosphere. 4-Methylbenzenesulfonyl chloride (3.813 g, 0.02 mol) was dissolved in dry DCM (20 mL) and was added in a dropwise manner to the aforesaid solution under ice cold conditions. The reaction mixture was then allowed to attain room temperature and was stirred for 12 h. After 12 h, the reaction mixture was evaporated to dryness and loaded for column chromatography on silica gel and eluted with MeOH/$CHCl_3$ to yield the pure desired compound **2a** as the second band; yield 2.81 g (45%). ESI-MS (*m*/*z*): calcd. for $C_{28}H_{34}O_{10}S_2$ 594.69; found 617.45 $[M + Na]^+$. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.75 [d, J = 8.2 Hz, 4 H, $H^{a'}$ (four protons)], 7.26 [d, J = 8 Hz, 4 H, $H^{b'}$ (four protons)], 6.87–6.86 (m, 4 H, $H^{1'}$, $H^{2'}$, $H^{3'}$ and $H^{4'}$), 4.15 [t, J = 4 Hz, 4 H, $H^{5'}$ (two protons) and $H^{6'}$ (two protons)], 4.03 [t, J = 4.4 Hz, 4 H, $H^{7'}$ (two protons) and $H^{8'}$ (two protons)], 3.76–3.70 [m, 8 H, $H^{9'}$ (two protons), $H^{10'}$ (two protons), $H^{11'}$ (two protons), $H^{12'}$ (two protons)], 2.37 [s, 6 H, $H^{c'}$ (six protons)] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1179 [ν(S=O)] cm^{-1}. $C_{28}H_{34}O_{10}S_2$ (594.69): calcd. C 56.55, H 5.76; found C 56.58, H 5.75.

3-{2-[4′-Methyl-(2,2′-bipyridin)-4-yl]vinyl}-6,7,9,10,21,22,24,25-octahydroanthra[1,2-*b*]benzo[*k*][1,4,7,10,13,16]hexaoxacyclooctadecine-14,19-dione (4): 1 (331 mg, 1.09 mmol) was dissolved in dry DMF (50 mL). To this was added K_2CO_3 (527 mg, 3.815 mmol) and the mixture stirred at 90 °C for 30 min. Compound **3** (790 mg, 1.09 mmol) was dissolved in dry DMF (30 mL) and was added dropwise to the resultant solution over a period of 30 min. The reaction was then stirred under argon atmosphere at 100 °C for 5 d. After this time the DMF was evaporated from the reaction mixture. The desired organic compounds were removed by repeated solvent extractions with chloroform which was then dried with anhydrous magnesium sulfate and the solvents evaporated to dryness. The residue so obtained was dissolved in a minimum volume of chloroform and methanol was added dropwise to it which precipitated **4** as a deep yellow solid. This was kept in a refrigerator for half an hour to ensure complete precipitation and was later filtered through a grade-4 sintered glass crucible, washed with cold methanol and dried in a vacuum desiccator to yield pure compound **4**; yield 400 mg (54%). ESI-MS (*m*/*z*): calcd. for $C_{41}H_{36}N_2O_8$ 684.73; found 685.89 $[M + 1]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 5 Hz, 1 H, H^{25}), 8.58 (d, J = 4.5 Hz, 1 H, H^{21}), 8.50 (s, 1 H, H^{23}), 8.27–8.25 (m, 3 H, H^1, H^2, H^{22}), 8.15 (d, J = 8.5 Hz, 1 H, H^{17}), 7.78–7.73 (m, 2 H, H^3, H^4), 7.41 (d, J = 16 Hz, 1 H, H^{19}), 7.36 (d, J = 4.5 Hz, 1 H, H^{24}), 7.17 (d, J = 4.5 Hz, 1 H, H^{20}), 7.15–7.11 (m, 3 H, H^5, H^6, H^{16}), 6.99 (d, J = 16 Hz, 1 H, H^{18}), 6.91 (d, J = 8 Hz, 1 H, H^{15}), 4.38 [t, J = 4 Hz, 2 H, H^7 (two protons)], 4.29 [t, J = 4.5 Hz, 6 H, H^9 (two protons), H^{10} (two protons), H^{12} (two protons)], 4.21–4.16 [m, 4 H, H^8 (two protons), H^{11} (two protons)], 4.14–4.12 [m, 2 H, H^{14} (two protons)], 4.07–4.04 [m, 2 H, H^{13} (two protons)], 2.47 [s, 3 H, H^{26} (three protons)] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1670 [ν(C=O)], 1586 [ν(C=C)] cm^{-1}. $C_{41}H_{36}N_2O_8$ (684.74): calcd. C 71.92, H 5.30, N 4.09; found C 71.96, H 5.24, N 4.12.

4-Methyl-4′-(2-(6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin-2-yl)vinyl)-2,2′-bipyridine (4a): 1 (100 mg, 0.329 mmol) was dissolved in dry DMF (40 mL). To this was added K_2CO_3 (159 mg, 1.1515 mmol) and the mixture was stirred at 90 °C for 30 min. **3a** (196 mg, 0.329 mmol) was dissolved in dry DMF (20 mL) and was added dropwise to the resultant solution over a period of 30 min. The reaction was then stirred under argon atmosphere at 100 °C for 6 d. After this time the DMF was evaporated from the reaction mixture. The desired organic compounds were removed by repeated solvent extractions with chloroform which was then dried with anhydrous magnesium sulfate and the solvents evaporated to dryness. The residue so obtained was dissolved in a minimum volume of chloroform and was added dropwise to diethyl ether (30 mL) which precipitated **4a** as a deep yellow solid. This was kept in a refrigerator for half an hour to ensure complete precipitation and was later filtered through a grade 4 sintered glass crucible, washed with cold ether and dried in a vacuum desiccator to yield pure compound **4a**; yield 101 mg (55.4%). ESI-MS (*m*/*z*): calcd. for $C_{33}H_{34}N_2O_6$ 554.63; found 577.25 $[M + Na]^+$, 593.23 $[M + K]^+$. ^1H NMR (500 MHz, CD_2Cl_2): δ = 8.58 (d, J = 5 Hz, 1 H, $H^{23'}$), 8.53 (m, 2 H, $H^{19'}$ and $H^{21'}$), 8.29 (s, 1 H, $H^{20'}$), 7.42–7.38 (m, 2 H, $H^{15'}$ and $H^{17'}$), 7.17 (d, J =

4.5 Hz, 1 H, $H^{22'}$), 7.13–7.11 (m, 2 H, $H^{13'}$ and $H^{18'}$), 7.03 (d, J = 16 Hz, 1 H, $H^{16'}$), 6.91–6.85 (m, 5 H, $H^{1'}$, $H^{2'}$, $H^{3'}$, $H^{4'}$ and $H^{14'}$), 4.25–4.20 [m, 2 H, $H^{12'}$ (two protons)], 4.19–4.16 [m, 2 H, $H^{11'}$ (two protons)], 4.16–4.11 [m, 4 H, $H^{9'}$ (two protons), $H^{10'}$ (two protons)], 4.03–3.93 [m, 8 H, $H^{5'}$ (two protons), $H^{6'}$ (two protons), $H^{7'}$ (two protons) and $H^{8'}$ (two protons)], 2.45 [s, 3 H, $H^{24'}$ (three protons)] ppm. IR (KBr pellet): $\tilde{\nu}$ = 1589 [ν(C=C)] cm^{-1}. $C_{33}H_{34}N_2O_6$ (554.64): calcd. C 71.46, H 6.18, N 5.05; found C 71.48, H 6.18, N 5.02.

{Bis(2,2′-bpy)-(3-(2-(4′-methyl-[2,2′-bipyridin]-4-yl)vinyl)-6,7,9,10,21,22,24,25-octahydroanthra[1,2-*b*]benzo[*k*][1,4,7,10,13,16]hexaoxacyclooctadecine-14,19-dione)}ruthenium(II) Hexafluorophosphate (5): $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (100 mg, 0.192 mmol) and **4** (131.5 mg, 0.192 mmol) were heated to reflux in ethanol for 12 h with continuous stirring. The solvent was then evaporated and the product was dissolved in a minimum volume of water. Saturated aqueous NH_4PF_6 (10 mol equiv.) was added to the resultant solution to precipitate the desired Ru^{II}-polypyridyl complex as the hexafluorophosphate salt. This was kept as such for 4–5 h in a refrigerator to ensure complete precipitation after which it was filtered, washed with cold water and dried in a desiccator. The crude compound so obtained was purified by column chromatography over neutral Al_2O_3 (Grade I) using acetonitrile/toluene as the eluent. The first fraction was collected and the solvent was removed to isolate **5** which was further purified by recrystallisation carried out by diffusion of diethyl ether vapour into an acetonitrile solution of **5**. The recrystallised compound was found to be pure enough to carry out further studies; yield 120 mg (50%). HRMS (*m*/*z*): calcd. for $C_{61}H_{52}N_6O_8PF_6Ru$ 1243.2532 [M – PF_6^-]$^+$; found 1243.2532 [M – PF_6^-]$^+$. ^{1}H NMR (500 MHz, CD_3CN): δ = 8.56 [s, 1 H, H^3 (bpy) or $H^{3'}$ (bpy)], 8.49 [d, J = 8 Hz, 3 H, H^3 (bpy) and $H^{3'}$ (bpy) (three protons)], 8.47 (s, 1 H, H^{23}), 8.19 [d, J = 7.5 Hz, 1 H, H^6 (bpy) or $H^{6'}$ (bpy)], 8.16 [d, J = 7.5 Hz, 1 H, H^6 (bpy) or $H^{6'}$ (bpy)], 8.08–8.03 [m, 6 H, H^4 (bpy), $H^{4'}$ (bpy), H^6 (bpy), $H^{6'}$ (bpy), H^1, H^2], 7.82–7.8 (m, 2 H, H^4, H^{22}), 7.78 [d, J = 7 Hz, 1 H, H^4 (bpy) or $H^{4'}$ (bpy)], 7.75 (d, J = 6 Hz, 1 H, H^{25}), 7.73 (d, J = 5 Hz, 2 H, H^3, H^{21}), 7.61 (d, J = 16.5 Hz, 1 H, H^{19}), 7.57 (d, J = 6 Hz, 1 H, H^{24}), 7.54 (d, J = 5.5 Hz, 1 H, H^{20}), 7.42–7.37 [m, 6 H, H^4 (bpy) or $H^{4'}$ (bpy), H^5 (bpy, two protons), $H^{5'}$ (bpy, two protons), H^{16}], 7.26–7.24 (m, 2 H, H^5, H^6), 7.18 (d, J = 7.5 Hz, 1 H, H^{17}), 7.13 (d, J = 16 Hz, 1 H, H^{18}), 6.98 (d, J = 8 Hz, 1 H, H^{15}), 4.29–4.28 [m, 2 H, H^9 (two protons)], 4.27–4.23 [m, 4 H, H^{10} (two protons), H^{12} (two protons)], 4.21–4.2 [m, 2 H, H^{11} (two protons)], 4.11 [t, J = 5 Hz, 2 H, H^7 (two protons)], 4.01 [t, J = 4 Hz, 2 H, H^8 (two protons)], 3.98–3.96 [m, 2 H, H^{14} (two protons)], 3.93–3.92 [m, 2 H, H^{13} (two protons)], 2.56 [s, 3 H, H^{26} (three protons)] ppm. ^{13}C NMR [200 MHz, $(CD_3)_2CO$]: δ = 182.5, 182.1, 158.9, 157.8, 152.3, 151.3, 150.7, 149.8, 149, 147.8, 138.4, 137.5, 136.9, 135.6, 134.4, 134.1, 133.5, 129.9, 129.2, 128.4, 127.3, 126.8, 125.7, 124.9, 122.7, 121.2, 117.8, 114.2, 113.6, 111.9, 73.59, 71.6, 71.1, 70.2, 69.8, 69.2, 20.8 ppm. IR (KBr pellet): $\tilde{\nu}$ = 1653 [ν(C1=O)], 1635 [ν(C2=O)], 835 [$\nu(PF_6)$] cm^{-1}. $C_{61}H_{52}F_{12}N_6O_8P_2Ru$ (1388.11): calcd. C 52.78, H 3.78, N 6.05; found C 52.8, H 3.8, N 6.02.

{Bis(2,2′-bpy)-(4-methyl-4′-(2-(6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin-2-yl)vinyl)-2,2′-bipyridine)}ruthenium(II) Hexafluorophosphate (6): $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (22.5 mg, 0.0432 mmol) and **4a** (20 mg, 0.036 mmol) were heated to reflux in ethanol for 5 h with continuous stirring. The solvent was then evaporated and the product dissolved in a minimum volume of water. Saturated aqueous NH_4PF_6 (10 mol equiv.) was added to the resultant solution to precipitate the desired Ru^{II}-polypyridyl complex as the hexafluorophosphate salt. This was kept as such for 4–5 h in a refrigerator to ensure complete precipitation after which it was filtered, washed with cold water and dried in a desiccator. The crude compound so obtained was purified by column chromatography over neutral Al_2O_3 (Grade I) using acetonitrile/toluene as the eluent. The first fraction was collected and the solvent was removed to isolate **6**; yield 20 mg (36.7%). ESI-MS (*m*/*z*): calcd. for $C_{53}H_{50}F_6N_6O_6PRu$ 1113.03 [M – PF_6^-]$^+$; found 1113.98 [M – PF_6^-]$^+$. ^{1}H NMR (200 MHz, CD_3CN): δ = 8.56 [s, 1 H, H^3 (bpy) or $H^{3'}$ (bpy)]; 8.49 [d, J = 8 Hz, 4 H, H^3 (bpy) and $H^{3'}$ (bpy) (three protons), H^6 (bpy) or $H^{6'}$ (bpy)], 8.12–8.01 [m, 4 H, H^6 (bpy) and $H^{6'}$ (bpy) (two protons), $H^{21'}$ and $H^{23'}$], 7.85 (d, J = 5.6 Hz, 1 H, $H^{19'}$), 7.75–7.66 [m, 4 H, H^4 (bpy, two protons) and $H^{4'}$ (bpy, two protons)], 7.57 (d, J = 6 Hz, 1 H, $H^{22'}$), 7.50 [d, J = 8.4 Hz, 1 H, H^5 (bpy) or $H^{5'}$ (bpy)], 7.44–7.35 [m, 4 H, H^5 (bpy) and $H^{5'}$ (bpy) (three protons), H^6 (bpy) or $H^{6'}$ (bpy)], 7.30–7.20 (m, 3 H, $H^{17'}$, $H^{18'}$ and $H^{20'}$), 7.16 (d, J = 5.4 Hz, 1 H, $H^{15'}$), 7.05 (m, 2 H, $H^{14'}$ and $H^{16'}$), 6.98–6.85 (m, 4 H, $H^{1'}$, $H^{2'}$, $H^{3'}$ and $H^{4'}$), 6.84 (d, J = 6 Hz, 1 H, $H^{13'}$), 4.25–4.18 [m, 2 H, $H^{12'}$ (two protons)], 4.16–4.03 [m, 6 H, $H^{9'}$ (two protons), $H^{10'}$ (two protons) and $H^{11'}$ (two protons)], 3.97–3.77 [m, 8 H, $H^{5'}$ (two protons), $H^{6'}$ (two protons), $H^{7'}$ (two protons) and $H^{8'}$ (two protons)], 2.56 [s, 3 H, $H^{24'}$ (three protons)] ppm. ^{13}C NMR [200 MHz, $(CD_3)_2CO$]: δ = 157.6, 157.2, 156.8, 151.8, 150.9, 148.3, 147.3, 147, 138.1, 136.1, 135.5, 129.5, 128.1, 127, 124.4, 121.7, 120.9, 120.3, 119.8, 111.7, 111.1, 110.6, 101.4, 100.9, 100.2, 68.9, 68.8, 68.5, 68.1, 67.8, 20.4 ppm. IR (KBr pellet): $\tilde{\nu}$ = 1582 [ν(C=C)], 842 [$\nu(PF_6)$] cm^{-1}. $C_{53}H_{50}F_{12}N_6O_6P_2Ru$ (1258.01): calcd. C 50.60, H 4.01, N 6.68; found C 50.9, H 3.96, N 6.66.

Supporting Information (see footnote on the first page of this article): ESI-MS, FTIR and FTNMR spectra of **5** and **6** and their precursors, HRMS spectrum of **5**, ESI-MS spectrum of **5** in presence of Ca^{2+}, Sr^{2+} and Ba^{2+}, spectrophotometric and fluorescence scan of **6** with different metal ions, fluorescence scan of **5** with different metal ions (λ_{ex} = 369 nm), spectrophotometric and fluorescence titration of **6** with Ba^{2+}, Stern–Volmer plot for lifetime titration of **5** with Cu^{2+}, changes in the ^{1}H NMR spectrum of **5** on addition of Sr^{2+}, changes in the ^{13}C NMR spectrum of **5** on addition of Ca^{2+}, changes in the ^{13}C NMR spectrum of **5** on addition of Ba^{2+}.

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