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Selective Binding and Inverse Fluorescent Behavior of Magnesium Ion by Podand Possessing Plural Imidazo[4,5-*f*]-1,10-phenanthroline Groups and Its Ru(II) Complex

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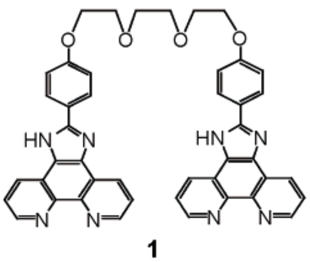

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Two podands, 4,4′-[(ethylenedioxy)bis(ethyleneoxy)]bis[1-(2-imidazo[4,5-*f*]-1,10-phenanthroline)-benzene] (**1**) and [Ru(phen)$_2$]$_2$(**1**)(PF$_6$)$_4$ (**2**) complex, were synthesized from 1,10-phenanthroline. The photophysical behavior and the binding ability of **1** and **2** with some alkali metal and alkaline earth cations were investigated by UV−vis and fluorescence spectrometry and ^{1}H NMR experiments as well as fluorescence lifetime measurements. The complex stability constants (K_S) and Gibbs free energy changes ($\Delta G°$) for the stoichiometric 1:1 complexation of **1** and **2** with the cations were obtained by the fluorimetric titrations. The podands **1** and **2** exhibit different fluorescent behavior in the cations examined, i.e., fluorescence quenching for **1**, and fluorescence enhancement for **2**. In particular, **1** showed responses specific for Mg^{2+}, resulting in readily distinguishable by eye.

Introduction

Fluorescent sensors have drawn increasing attention for their use in fields as diverse as chemistry, biology, medical analysis, and environmental monitoring.[1,2] Of particular interest has been the measurement of concentration of magnesium ion (Mg^{2+}) in biological samples because the alkaline earth metal ion is the most abundant divalent cation in living cells, and plays vital roles in many cellular processes, for example, as an enzyme cofactor, stabilization of DNA conformation, ion transport through the membrane, maintenance of cell shape, and signal transduction.[3] As a result, a great deal of effort has been devoted to the design and synthesis of sensitive and selective fluorescent sensors for Mg^{2+}.[4−8]

It is known that the conformation of noncyclic crown ethers changes drastically from a linear structure to a pseudocyclic structure upon complex formation with

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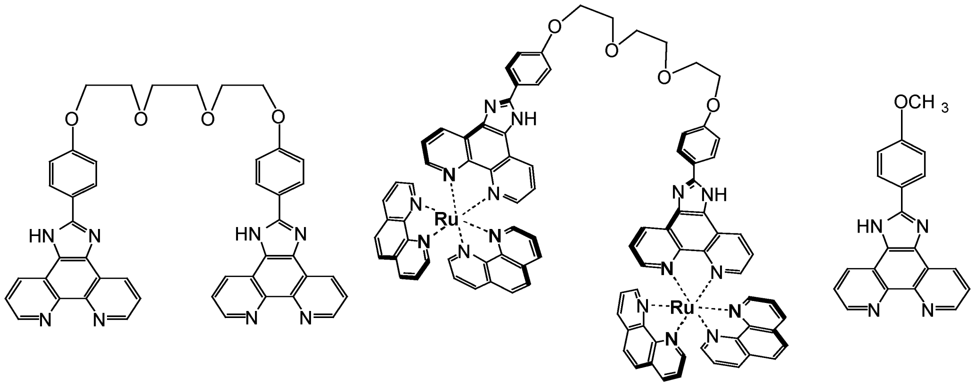
CHART 1. Structures of Compounds 1–3



1 2 3

metal ions. If this conformational change could be converted into physical signs, such as UV absorption and fluorescence, etc., it would be possible to establish more sensitive cation sensors.[8a,9–13] For instance, a water-soluble open-chain compound containing aminonaphthalimide groups displayed high selectivity and sensitivity for Hg^{2+}.[9] A noncyclic polyether dicarboxylic acid ionophore could be used as an extraction reagent to separate Pb^{2+} from weakly acidic aqueous solutions.[12] In addition, because of a unique combination of chemical stability, redox properties, luminescence intensity, and excited-state lifetime, the ruthenium complexes of the polypyridine-type family[14–16] have been used extensively not only as photosensitizers in a variety of intermolecular electron-transfer processes[15] but also to obtain photoinduced energy- or electron-transfer processes in suitably designed supramolecular systems.[16]

In the present study, we report the syntheses and characterization of 4,4′-[(ethylenedioxy)bis(ethyleneoxy)]-bis[1-(2-imidazo[4,5-*f*]1,10-phenanthroline)benzene] (**1**) and its Ru(II) polypyridine complexes (**2**) and also their photophysical behavior upon complexation with alkali/alkaline earth metal ions. Comparison of the photophysical behavior of these podands with that of the parent fluorophore analogue **3** (Chart 1) will further our understanding of the luminescent origin upon complexation with cations. Our particular interest is to investigate how Ru(II) coordination with fluorophore affects the fluorescent behavior and the cation selectivity of the podand upon complexation with these metal ions.

Experimental Section

Materials. *N*,*N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under a reduced pressure prior to use. 1,10-Phenanthroline-5,6-dione,[17] 2-(4′-hydroxyphenyl)imidazo[4,5-*f*]-1,10-phenanthroline (HOP),[18] compound **3**,[19] triethyleneglycol di(toluene-*p*-sulfonate),[20] and $Ru(phen)_2Cl_2$ [21] were prepared according to the literature procedures.

Spectrophotometric Titrations. Fluorescence spectra were measured using a conventional quartz cell (10 × 10 × 45 mm) at 25 °C with the excitation and emission slits of 5 nm width for **1** and 10 nm width for **2**, respectively. The titration solutions were prepared in 10.0 mL volumetric flasks with the guest/host molar ratio ranging from 0 to ca. 200. The sample solutions at a host concentration of approximately 2×10^{-5} mol·dm^{-3} were excited at 350 nm for **1** and 450 nm for **2** to give a strong emission, and the fluorescence intensity at the emission maximum was used to determine the complex stability constants.

The fluorescence quantum yields were determined according to the reported procedure[22] and using quinine sulfate in 5 M H_2SO_4 as the reference standard ($\Phi_F = 0.55$). Fluorescence lifetimes were measured using time-resolved fluorescence spectroscopy. The molecules were excited at 400 nm using the frequency-doubled output of a picosecond-pulse laser with 5 μJ energy. The experimental conditions used were as follows: [host] = 2×10^{-5} M, [Mg^{2+}] = 10 mM, [K^+] = 10 mM. The uncertainty in τ is 5–10% for the biexponential decays.

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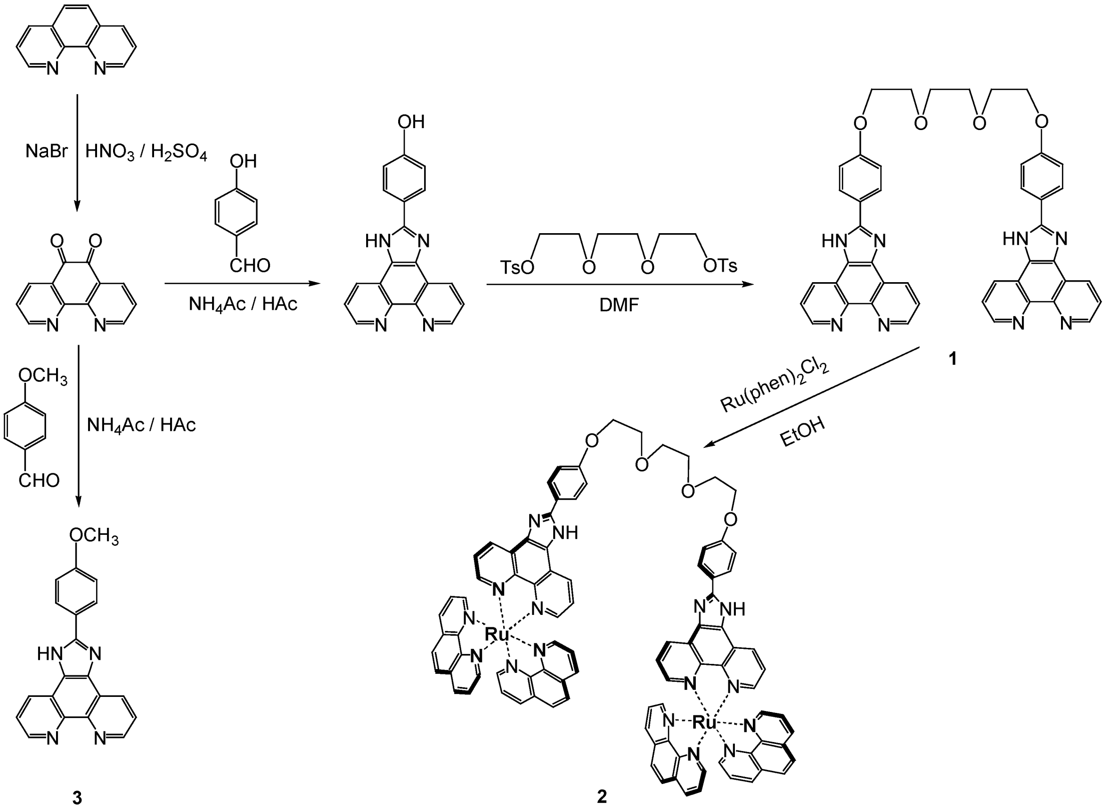
SCHEME 1. Synthesis Routes to Compounds 1−3



4,4′-[(Ethylenedioxy)bis(ethyleneoxy)]bis[1-(2-imidazo-[4,5-*f*]1,10-phenanthroline)benzene] (1). To a solution of 2-(4′-hydroxyphenyl)imidazo-[4,5-f]1,10-phenanthroline (HOP) (312 mg, 1 mmol) in DMF (10 mL) was added anhydrous K_2CO_3 (0.15 g, 1 mmol). The mixture was stirred for 2 h at room temperature under nitrogen, to which triethylene glycol ditosylate (0.48 mmol) in dry DMF (10 mL) was added dropwise with stirring, and then the whole solution was heated to 80 °C for 24 h. The resultant solution was evaporated under reduced pressure to give a deep-brown ropy solid, and then the solid was washed several times with water, chloroform, and ethanol, respectively. The obtained solid was dried in vacuo to give pure brown powder **1** in 45% yield: mp 248−251 °C; FAB-MS *m/z* 739.5 (M^+), calcd 738.8; ^1H NMR (DMSO-d_6, TMS, ppm) δ 3.63 (s, 4H), 3.82−3.85 (t, 4H), 4.21−4.23 (t, 4H), 7.18−7.21 (d, 4H), 7.78−7.83 (m, 4H), 8.20−8.22 (d, 4H), 8.86−8.93 (d, 4H), 9.00−9.02 (m, 4H), 13.6 (s, 2H); IR (KBr) ν/cm^{-1} 3332, 3054, 2871, 1891, 1733, 1652, 1611, 1563, 1521, 1481, 1450, 1395, 1352, 1293, 1252, 1180, 1122, 1068, 1033, 950, 838, 807, 741, 693, 652, 623, 550, 526, 471, 410; UV−vis (H_2O) λ_{max} (ϵ/M^{-1} cm^{-1}) 281 (55800), 310 nm (37500). Anal. Calcd for $C_{44}H_{34}O_4N_8$: C, 71.53; H, 4.64; N, 15.17. Found: C, 71.25; H, 4.45; N, 14.81.

[Ru(phen)$_2$]$_2$(1)(PF$_6$)$_4$ (2). A sample of $Ru(phen)_2Cl_2$ (0.25 mmol) was mixed with **1** (0.25 mmol) in a 250 mL round-bottom flask. About 100 mL of absolute ethanol was added, and the solution was refluxed for ca. 5 h. It was then filtered to remove unreacted reagents. The solution was diluted with water to about 200 mL, and saturated NH_4PF_6 was added to precipitate a brown solid. The solid was filtered, washed with ether (3 × 15 mL), and then dried in a vacuum oven. The resulting rude product was dissolved in methanol and reprecipitated in ether. The obtained solid was then dried in vacuo to give the final product with a yield of 75%: mp > 300 °C; ^1H NMR (DMSO-d_6, TMS, ppm) δ 3.69(s, 4H), 3.83−3.85 (t, 4H), 4.35−4.37 (t, 4H), 6.91−6.95 (m, 8H), 7.10(d, 4H), 7.25 (d, 8H), 7.69−7.76 (m, 4H), 7.94−7.97 (m, 4H), 8.08−8.13 (m, 4H), 8.19−8.22 (d, 4H), 8.63−8.66 (d, 4H), 9.19−9.21 (m, 8H), 9.59−9.61 (d, 4H); IR (KBr) ν/cm^{-1} 3381, 3065, 2922, 1970, 1733, 1651, 1611, 1578, 1507, 1480, 1453, 1429, 1365, 1292, 1252, 1233, 1181, 1111, 1041, 949, 847, 776, 740, 722, 656, 558, 528, 404; UV−vis (H_2O) λ_{max} (ϵ/M^{-1}cm^{-1}) 268.0 (137805), 289.5 (102146), 431 (25610), 460 nm (26780). Anal. Calcd for $C_{92}H_{66}O_4N_{16}P_4F_{24}Ru_2\cdot 4H_2O$: C, 48.72; H, 3.67; N, 9.28. Found: C, 48.98; H, 3.86; N, 9.13.

Results and Discussion

Synthesis. Our synthesis began with 1,10-phenanthroline. The intermediates 1,10-phenanthroline-5,6-dione and 2-(4′-hydroxyphenyl)imidazo[4,5-*f*]1,10-phenanthroline (HOP) as well as compound **3** were prepared according to the literature procedure. Treating HOP with triethyleneglycol di(toluene-*p*-sulfonate) in DMF afforded **1** in 45% yield. Then, complex **2** was synthesized in 75% yield by the coordination reaction of **1** with $Ru(phen)_2Cl_2$ (Scheme 1). For the complexes **2**, two diastereoisomers are formed as a result of the chirality of the octahedral coordination around the ruthenium center. No efforts were made to separate these isomers.

Fluorescence Behaviors. As can be seen from Figure 1, when excesses equivalent alkali metal and alkaline earth metal cations were added to the DMF solution of **1**, the relative emission intensity of **1** decreased along with different red shifts of the emission spectra. The replacement of podand **1** by compound **3** did not result in any significant changes upon the addition of these cations in the same conditions, suggesting that the formation of complexes be as a result of the interaction between oxyethylene moiety in **1** and the metal ions. In that case, the oxygen atoms attached to the benzene rings

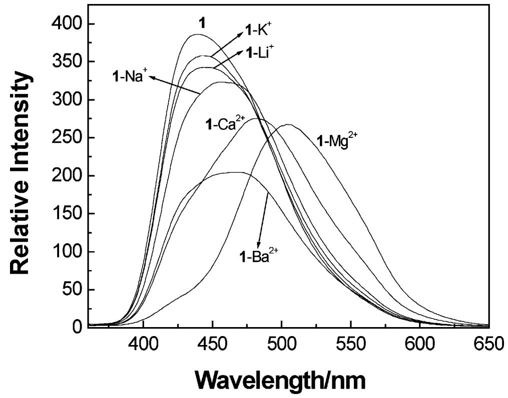


FIGURE 1. Fluorescence spectra of **1** (2.6×10^{-5} M) in the absence and in the presence of Li^+ (1.09×10^{-2} M), Na^+ (1.20×10^{-2} M), K^+ (1.17×10^{-2} M), Mg^{2+} (1.00×10^{-2} M), Ca^{2+} (1.01×10^{-2} M), and Ba^{2+} (1.03×10^{-2} M) in DMF at 25 °C. Excitation wavelength: 350 nm. Bandwidth (E_x): 5 nm. Bandwidth (E_m): 5 nm.

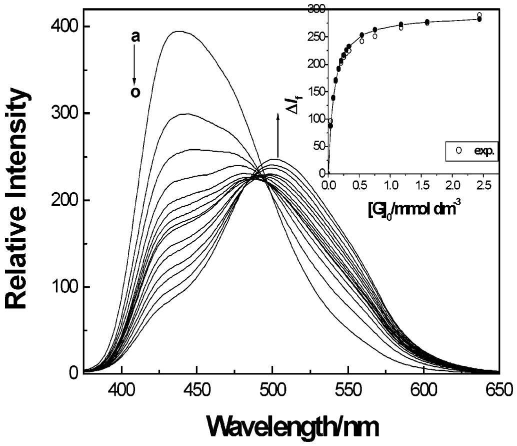


FIGURE 2. Fluorescence spectral changes of **1** (2.6×10^{-5} M) and the nonlinear least-squares analysis (inset) of the differential intensity (ΔI_f) to calculate the complex stability constants (K_s) upon addition of magnesium perchlorate (0−3.28×10^{-3} M, a−o) in DMF at 25 °C, excitation wavelength (λ_{ex}) 350 nm. Bandwidth (E_x): 5 nm. Bandwidth (E_m): 5 nm.

in **1** served as the donor for coordination with cations, which reduced the electron-donating character of these oxygen atoms, making them conversely change into "the acceptor" compared with the amino group in imidazole. Consequently, upon excitation by light, intramolecular charge transfers from the donor (amino group in imidazole) to "the acceptor" (oxygen atom attached to the benzene ring) would lead to a red shift of the emission spectrum of **1**.[1a]

Different from other cations, not only a large decrease of the monomer emission was shown in the fluorescent spectra of **1** upon binding of Mg^{2+} but also a corresponding increase of the intramolecular excimer emission was observed at 503 nm (Figure 2). The result allows **1**·Mg^{2+} to be readily distinguished by eye, as shown in Figure 3. One reasonable explanation for this observation is that the mutual distance of two imidazo[4,5-*f*]-1,10-phenanthroline fluorophores in **1** decreased due to binding of Mg^{2+} to oxyethylene moiety, leading to the formation of the intramolecular excimer.[9,11]

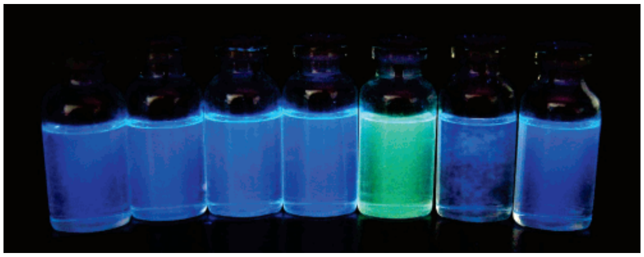


FIGURE 3. Visible emission observed from samples of **1** and various alkali metal and alkaline earth cations. Left to right: no metal, **1** + Li^+, **1** + Na^+, **1** + K^+, **1** + Mg^{2+}, **1** + Ca^{2+}, and **1** + Ba^{2+}.

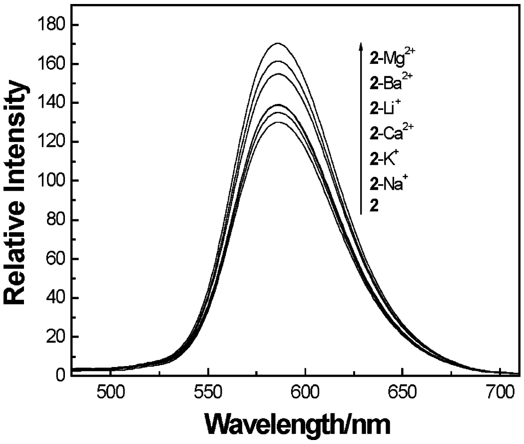


FIGURE 4. Fluorescence spectra of **2** (2.1×10^{-5} mol/L) in the absence and in the presence of Li^+ (1.05×10^{-2} mol/L), Na^+ (1.01×10^{-2} mol/L), K^+ (1.01×10^{-2} mol/L), Mg^{2+} (0.99×10^{-2} mol/L), Ca^{2+} (0.99×10^{-2} mol/L), and Ba^{2+} (1.01×10^{-2} mol/L) in DMF at 25 °C. Excitation wavelength: 450 nm. Bandwidth (E_x): 10 nm. Bandwidth (E_m): 10 nm.

TABLE 1. Fluorescence Quantum Yields (Φ_F) of 1, 2, and Their Complexes in DMF

		complexes					
	ligand	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
1	0.067	0.070	0.068	0.069	0.045	0.061	0.044
2	0.0017	0.0019	0.0017	0.0017	0.0021	0.0017	0.0020

In sharp contrast, the addition of alkali metal and alkaline earth metal ions to the DMF solution of **2** enhanced its relative emission intensity under comparable conditions, but no shift was observed, as illustrated in Figure 4. On one hand, the coordination of Ru^{2+} enlarges the size of terminal group, making it difficult to form the intramolecular excimer. On the other hand, the metal complexation suppresses the intramolecular photoinduced electron transfer (PET) from the oxygen lone pairs to the Ru (II) center, resulting in the fluorescence enhancement.[1a] Herein, the largest enhancement was still given upon binding of Mg^{2+}, indicating that **2** was more sensitive and selective for this cation.

We also determined the fluorescence quantum yields (Φ_F) of **1**, **2**, and their complexes with cations. As can be seen from Table 1, the quantum yields of both **1** and **2** are low (0.067 for **1**, and 0.0017 for **2**). One possible reason for the observations is that the flexibility of the oxyethylene moiety allows two terminal groups to come into close contact, resulting in the fluorescent self-

TABLE 2. Spectral Data and Fluorescence Lifetimes (τ) of 1 and 2 in the Absence and Presence of $Mg(ClO_4)_2$ or $KClO_4$ in DMF at 25 °C

host	guest	λ_{abs}/nm	ϵ/$M^{-1}cm^{-1}$	λ_{ex}/nm	τ_s/ns (f_s/%)[a]	τ_L/ns (f_L/%)
1	none	281	55800	440	1.9 (52.6)	10.0 (47.4)
	K^+	282	56726	443	1.9 (49.5)	10.1 (50.5)
	Mg^{2+}	285	54874	503	1.3 (50.7)	23.6 (49.3)
2	none	460	26780	587	2.9 (21.7)	104.3 (78.3)
		289	102146			
	K^+	460	27219	586	7.1 (24.9)	132.4 (75.1)
		289	103539			
	Mg^{2+}	460	29780	586	22.1 (32.0)	129.6 (68.0)
		288	113240			

[a] f_s is the fractional intensity corresponding to the decay time τ_s.

TABLE 3. Stability Constants (K_S) for Stoichiometric 1:1 Complexation of 1 and 2 with Alkali Metal and Alkaline Earth Metal Ions in DMF at 25 °C

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
1	887 ± 20	271 ± 10	335 ± 10	12600 ± 300	1230 ± 50	338 ± 10
2	*a*	583 ± 20	325 ± 10	2410 ± 50	*a*	747 ± 20

[a] The ΔF values of the fluorescence intensity were too small to measure.

quenching. It is noted that, upon complexation with alkali metal cations, the corresponding quantum yields hardly change, while those upon complexation with alkaline earth cations show an obvious decrease for **1**, which is consistent with the fluorescence spectra feature. These observations suggest that the complexation between host **1**/**2** and alkaline earth cations should be stronger than that of them with alkali metal cations.

Time-resolved fluorescence decay measurements provided us useful information about the excited-state dynamics of the fluorophores. When fitting the obtained fluorescence decay data to the equation

$$F(t) = \sum A_i \exp(-t/\tau_i)\ (i = 1, 2, ...)$$

it was observed that the decay curve for **1** and **2** in the presence and absence of cations could not be fitted to a single-exponential function but could be fitted well to a linear combination of two exponential functions. The fluorescence lifetimes (τ_i) for **1** and **2** in the presence and absence of $Mg(ClO_4)_2$ or $KClO_4$ in DMF are summarized in Table 2. The two-component decay observed for **1** or **2** in the presence and absence of cations indicates that there should be an intramolecular equilibrium between the two different conformations in excited singlet states, one of which might be the species having a molecular conformation of a extended type where two terminal groups fall apart and the other pseudocyclic, and also that the interconversion of the two species is much slower than the fluorescence decay, which occurs on the nanosecond time scale. It is reasonable that two ensembles of the conformations should contain a number of related structures but differing in the orientation of the end groups, although we do not have any direct evidence. For **1**, the longer lifetime corresponds to the emissions of the pseudocyclic conformation, and the shorter lifetime corresponds to that of the extended type conformation. Upon complexation with Mg^{2+}, the longer lifetime of **1** increased from 10.0 to 23.6 ns companying with a slight enhancement of the fractional intensity, which could be attributed to the good matching sizes between its pseudocyclic and Mg^{2+} resulting in the further close contact of the two fluorophore terminal groups. It is interesting to note that the longer lifetime of **2** increased only 24% upon complexation with Mg^{2+}, while its shorter lifetime enhanced 7.6 times. Therefore, one might deduce reasonably that the longer lifetime of **2** should be due to the emissions of the extended type conformation, and the shorter lifetimes should correspond to that of the pseudocyclic conformation.

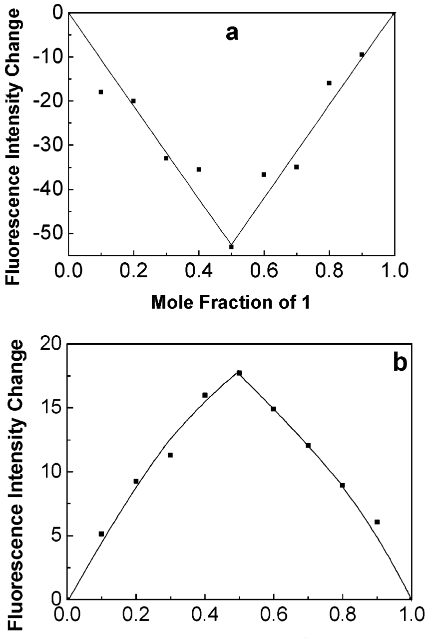


FIGURE 5. Job's plots for the binding of Mg^{2+} ion with (a) **1** and (b) **2**.

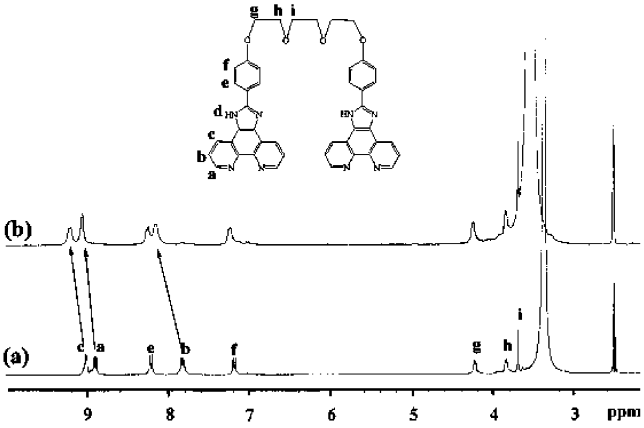


FIGURE 6. ^1H NMR spectra of podand **1** before (a) and after (b) the addition of magnesium perchlorate in DMSO-d_6 at room temperature.

Binding Constants. Quantitative investigations of the binding behavior of **1** and **2** have been performed with alkali/alkaline earth cations in DMF by means of titration fluorimetry to give the complex stability constants (K_S). In the fluorimetric titration experiments, the fluorescence intensity of **2** gradually increased with increasing guest concentration, while that of **1** decreased with an obvious bathochromic shift, as shown in Figure 1. The fluores-

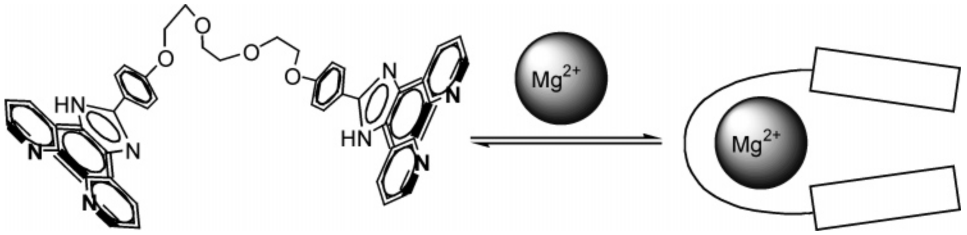


FIGURE 7. Proposed conformational changes of **1** before and after complex formation.

cence emission peak of **3** was too weak to determine signals in the absence and/or upon the addition of cations at same experimental conditions, indicating that coordinating effect of nitrogen atoms in phenanthroline group with these cations is neglectable. In addition, the Job's plots (Figure 5) confirmed the formation of 1:1 complex of cations with **1** and **2**. The K_S values of complex were calculated by using the nonlinear least-squares method, and the results are listed in Table 3.

As shown in Table 3, **1** showed the highest binding ability toward Mg^{2+} among six cations examined, and the relative selectivity for Mg^{2+} is over 10 of Ca^{2+} or any other alkali/alkaline earth metal ions. It is considered that the ethylenedioxy bis(ethyleneoxy) tether in **1** can induce the most favorable conformation for the size-matched Li^+ (ionic diameter 1.36 Å) or Mg^{2+} (1.32 Å), while the difference between charge densities (1.47 qÅ^{-1} for Li^+, and 3.03 qÅ^{-1} for Mg^{2+}) leads to the large affinity only for Mg^{2+}. It is noted that the coordination of Ru^{2+} to **1**, affording complex **2**, alters not only the original photophysical behavior of **1**, but also the cation binding ability and relative cation selectivity. The extra coordination does not greatly affect the K_S for Na^+, K^+ and Ba^{2+} but significantly lowers the K_S for Mg^{2+} for **2**. It could be attributed to the enlarging terminal groups to be unfavorable for the conformation change of the oxyethylene for binding of Mg^{2+}.

^{1}H NMR spectra. To further clarify the structures of complexes in solution, ^{1}H NMR experiments were carried out in both absence and presence of magnesium perchlorate in DMSO-d_6 at room temperature. Addition of $Mg(ClO_4)_2$ to **3** did not show any change in the NMR spectrum, indicating no interaction between Mg^{2+} and **3**, which is in agreement with the emission spectral studies. After the addition of an equivalent amount of $Mg(ClO_4)_2$, the well-resolved resonance signals of the phenanthroline protons in **1** became broad and shifted toward downfield from 9.01 ppm (protons in c position), 8.89 ppm (protons in a position), and 7.81 ppm (protons in b position) to 9.21, 9.05, and 8.14 ppm, respectively, while those which correspond to the aromatic protons in the separated benzene ring and methylene ones in the tether slightly shifted toward downfield, as shown in Figure 6. These observations were somewhat unexpected. One reasonable explanation for the chemical shifts is that the terminal groups in **1** approached each other and then stacked, leading to obvious deshielding effect for the phenanthroline protons; on the other hand, intramolecular charge transfers from the amino group in imidazole to the oxygen atoms attached to the benzene ring would cancel the influence arising from binding of Mg^{2+}, decreasing the changes of the chemical shifts of methylene protons. The obvious downfield shift for the phenanthroline protons (a, b and c) as well as the slight downfield shift for the protons e and f suggests that these protons reside in a downshieding environment, that is to say, the plane of one end group in **1** should be located over the other, but the distance of the two phenanthroline rings is closer than that of the two benzene rings, like a "Clam". In consideration of the ^{1}H NMR spectra, fluorescence behavior and the Job's plots, it is reasonable to deduce the conformational change of **1** before and after the addition of Mg^{2+}, as illustrated in Figure 7.

Conclusions

In summary, a new podand possessing plural imidazo-[4,5-*f*]-1,10-phenanthroline groups at both terminals and its Ru(II) complex have been synthesized. The addition of alkali metal and alkaline earth metal ions to their DMF solution leads to different photophysical behaviors, i.e., fluorescence quenching for the podand and fluorescence enhancement for its Ru(II) complex. Because of good complementarity between the pseudocavity of the podand and the ionic radii of Mg^{2+}, the compound showed the responses specific for Mg^{2+}, resulting in readily distinguished by eye. These new observations not only provide an example of switchable fluorescent sensors mediated by metal ion coordination but also make it possible to visualize ions species on the basis of the cation recognition.

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