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Colorimetric Sensor and Inverse Fluorescent Behavior of Anions by Calix[4]arene Possessing Imidazo[4,5-*f*]-1,10-phenanthroline Groups and its Ru(II) Complex

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A calix[4]arene derivative (1) possessing imidazo[4,5-*f*]-1,10-phenanthroline groups and its Ru(II) complex (2) have been prepared. The photophysical behavior and the binding ability of 1 and 2 with some anions were investigated by fluorescence spectrometry and ^{1}H NMR experiments. The complex stability constants (K_S) for the stoichiometric 1:1 complexation of 1 and 2 with the anions were obtained by the fluorimetric titrations, indicating that the binding abilities of both hosts for F^- and AcO^- are highest among all anions examined. Interestingly, compound 1 can be used as a colorimetric sensor to F^- and AcO^- due to anion-induced deprotonation of the NH group of the imidazole ring. In contrast, the addition of Cl^-, Br^-, I^- and HSO_4^- to the DMF solution of 2 enhances its relative emission intensity, while the addition of F^- and AcO^- quenches its fluorescence intensity.

Keywords: Calixarene; Colorimetric sensors; Anionic recognition; Ru(II) complex

INTRODUCTION

Anions play a major role in many biological processes and structures. For example, the fluoride ion is a biologically important anion because of its critical role in dental care [1] and the treatment of osteoporosis [2]. Recently, considerable attention has been focused upon the design of receptors that have the ability to selectively bind and sense anions by the naked eye, electrochemical, and optical responses [3–21]. The fluorescent sensor, on account of its simplicity and high sensitivity, is particularly attractive [22]. Although a lot of effort has been made to develop fluorescent sensors for cations and neutral guests [23–32], it has been only a few years since fluorescent sensors for anions have been extensively investigated [33–45]. Therefore, the design of anions fluorescent sensors is challenging.

Calixarenes are macrocyclic molecules with unique three dimensional structures. Because of their custom chemical derivatization and good complexation ability, these compounds have been widely utilized in supramolecular chemistry as building blocks or molecular scaffolds for the construction of various receptors. Calixpyrrole, a colorless macrocycle containing four pyrrole NHs as hydrogen bond donors shows considerable promise in the area of anion sensing [33,46–50]. Meanwhile bearing the amide [17,51–58], urea [59–62], or the thiourea groups [63–65], calixarenes can selectively recognize different anions by the hydrogen binding interactions of NH groups with anions. In addition, because of an unique combination of chemical stability, redox properties, luminescence intensity and excited-state lifetime, the ruthenium complexes of the polypyridine-type family [66–78] have been used extensively not only as photosensitizers in a variety of intermolecular electron-transfer processes [70–73], but also to obtain photoinduced energy- or electron-transfer processes in suitably-designed supramolecular systems [74–78].

In the present study, we wish to report the syntheses and characterization of 11,23-bis(2-imidazo[4,5-*f*]-1,10-phenanthroline)-25,27-dihydroxy-26,28-di-*n*-propoxycalix[4]arene (**1**) and its Ru(II) polypyridine complexes (**2**) (Scheme 1) and also their photophysical behavior upon complexation with anions. Our particular interest is to investigate how Ru(II) coordination with fluorophore affects the

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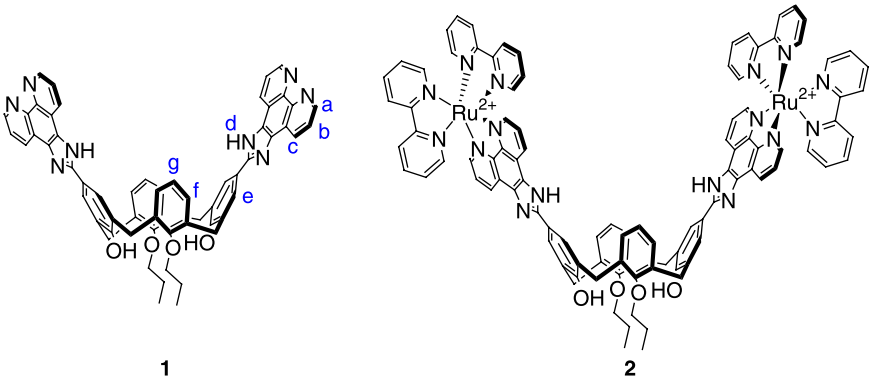

SCHEME 1 Structures of compounds **1** and **2**.

fluorescent behavior and the anion selectivity of the calixarene derivatives upon complexation with these anions.

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EXPERIMENTAL SECTION

General Procedures

N, *N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under a reduced pressure prior to use. Chloroform was distilled and stored over 4 Å molecular sieves before use. All other reagents and solvents were of reagent grade quality, obtained from commercial suppliers, and used without further purification. 1,10-Phenanthroline-5,6-dione [79], 25,27-dihydroxy-26,28-di-*n*-propoxycalix[4]arene [80], and $Ru(bpy)_2Cl_2$ [81] were prepared according to the literature procedure. All anions were used in the form of their tetrabutylammonium salts.

Measurements

Fluorescence spectra were measured in 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. 100 for **1** and 0 to 40 for **2**. The sample solutions were excited at a host concentration of 1×10^{-5} mol dm^{-3} at 348 nm for **1** and 420 nm at concentration of 1×10^{-4} mol dm^{-3} 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 [82–84] and using quinine sulfate in 5 M H_2SO_4 ($\Phi_F = 0.55$) for **1** and $[Ru(bpy)_3]^{2+}$ in 4:1 ethanol/methanol ($\Phi_F = 0.089$) [85] for **2** as the reference standard at 25°C.

11,23-Diformyl-25,27-dihydroxy-26,28-di-*n*-propoxycalix[4]arene

After 25,27-dihydroxy-26,28-*n*-propoxycalix[4]arene (1.5 mmol) was dissolved in chloroform (25 mL), the solution was cooled to −15°C, and then $SnCl_4$ (4.0 g, 15.4 mmol) and 1,1-dichlorodimethyl ether (0.44 g, 3.9 mmol) were rapidly added. The reaction mixture was then stirred at room temperature for 30 min and quenched with water. The organic layer was separated, washed twice with water, dried ($MgSO_4$) and evaporated. The solid residue was washed with hot methanol, filtered off and dried, giving product as a white solid (0.75 g, 90%), m.p. > 300°C; ^{1}H NMR ($CDC1_3$, 300 MHz, TMS, ppm) δ 9.79 (s, 2H), 9.26 (s, 2H), 7.64 (s, 4H), 6.98 (d, $J = 3.9$ Hz, 4H), 6.80 (t, $J = 7.5$ Hz, 2H) 4.31 (d, $J = 6.6$ Hz, 4H), 4.02 (t, $J = 6.3$ Hz, 4H), 3.53 (d, $J = 6.6$ Hz, 4H), 2.09 (q, $J = 10.0$ Hz, 4H), 1.33 (t, $J = 7.3$ Hz, 6H); ESI -MS m/z 564.3 (M^+).

11,23-Bis(2-imidazo[4,5-*f*]-1,10-phenanthroline)-25,27-dihydroxy-26,28-di-*n*-propoxy- Calix[4]arene (1)

A mixture of dialdehyde calix[4]arene (250 mg, 0.425 mmol), 1,10-phenanthroline-5,6-dione (350 mg, 1.7 mmol) and ammonium acetate (2.6 g, 34 mmol) in glacial AcOH (25 mL) was refluxed for 2 h [86]. The reaction was cooled to room temperature and the yellow precipitate was collected by filtration, subsequently washed with AcOH, 10% aq Na_2CO_3 and water and dried under vacuum at 130°C, affording **1** (202 mg, 50%) as a pale white solid, m.p. > 300°C. ^{1}H NMR (300 MHz, DMSO-d_6, TMS, ppm): δ 13.45 (s, 2H, NH), 9.02 (s, 6H), 8.94 (d, $J = 4.0$ Hz, 4H,), 8.13 (s, 4H), 7.84 (s, 4H,), 7.21 (d, $J = 3.9$ Hz, 4H), 6.90 (t, $J = 7.3$ Hz, 2H), 4.35 (d, $J = 6.3$ Hz, 4H, CH_{ax}), 4.06 (s, 4H,), 3.69 (d, $J = 6.6$ Hz, 4H, CH_{eq}), 2.08 (q, $J = 3.0$ Hz, 4H), 1.38 (t, $J = 7.2$ Hz, 6H); ESI-MS: $m/z = 945.6$ (M^+); Anal. Calcd for $C_{60}H_{48}N_8O_4{\cdot}6H_2O$: C, 68.43; H, 5.74; N, 10.64; Found: C, 68.58; H, 5.75; N, 10.68.

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$[Ru(bpy)_2]_2(1)(PF_6)_4$ (2)

A sample of $Ru(bpy)_2Cl_2$ (0.1 mmol) was mixed with **1** (0.025 mmol) in a 100 mL round-bottom flask. About 40 mL of DMF was added, and the solution was refluxed for 8 h. When it was cooled to room temperature, saturated NH_4PF_6 was added. The solution was evaporated, and then 50 ml EtOH was added to wash the residue. The solid was filtered and dried in vacuum. The obtained solid give the final product with a yield of 89% (52.6 mg). M.p. > 300°C; EI-MS: $m/z = 885.0$ $(M\text{-}4PF_4\text{-}2H)^{2+}$, 443.6 $(M\text{-}4PF_4 + 2H)^{4+}$ Anal. Calcd for $C_{100}H_{80}N_{16}O_4P_4F_{24}Ru_2 \cdot 6H_2O$: C, 48.83; H, 3.77; N, 9.11. Found: C, 48.75; H, 4.06; N, 9.28.

RESULTS AND DISCUSSION

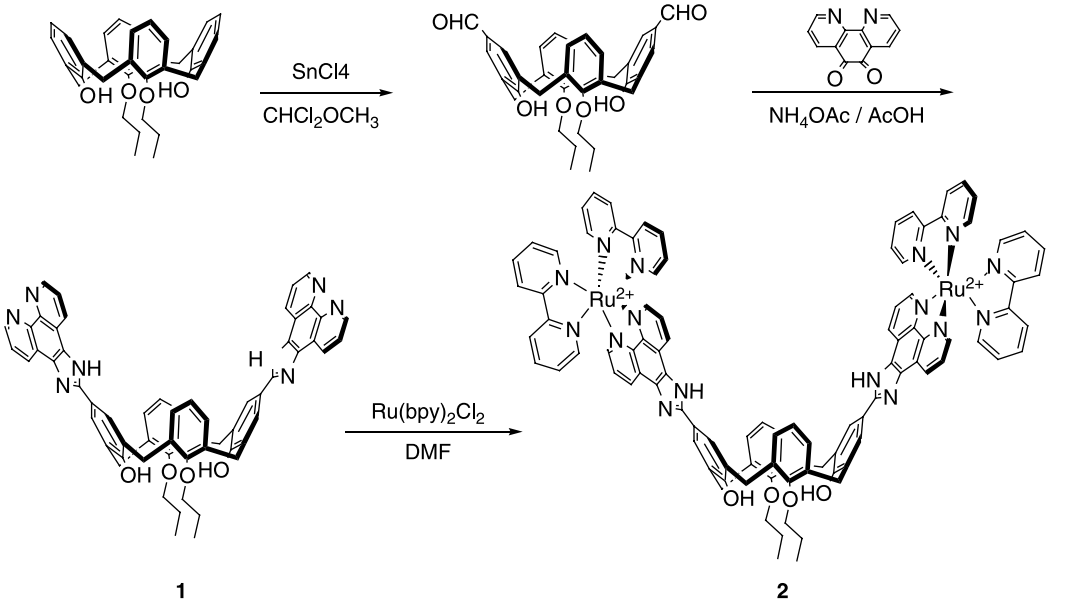
Synthesis

The intermediates 1,10-phenanthroline-5,6-dione and 25,27-dihydroxy-26,28-*n*-propoxycalix[4]arene as well as 11,23-diformyl-25,27-dihydroxy-26,28-di-*n*-propoxycalix[4]arene (dialdehyde calix[4]arene) were prepared according to the literature procedure [80]. Reaction of dialdehyde calix[4]arene with 1,10-phenanthroline-5,6-dione in the presence of ammonium acetate afforded **1** in 50% yield, and then complex **2** was synthesized in 89% yield by the coordination reaction of **1** with $Ru(bpy)_2Cl_2$ in DMF (Scheme 2). 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 shown in Fig. 1, when excesses equivalent anions were added to the DMF solution of **1**, different fluorescence behaviors were observed. Upon the addition of F^-, the unique peak at 537 nm appeared and the relative emission intensity at 460 nm quenched. Meanwhile, a distinct isoemissive point at 510 nm was also observed (Fig. 2), which implies that a 1:1 complex is formed. In the case of AcO^-, a new peak at 525 nm appeared, and accompanied an isoemissive point at 515 nm. In contrast, no new fluorescence peaks were observed in the presence of Cl^-, Br^-, I^-, and HSO_4^-, and the relative emission intensity of **1** just decreased at 460 nm accompanied with slight red shift. These new peaks at 537 nm for F^- and 525 nm for AcO^- should be attributed to the deprotonated process of the imidazo [4,5-*f*]-1,10-phenanthroline group in **1**, which was confirmed by the Brønsted acid-base reaction of adding strong base $[Me_4N]OH$. When the NH groups of the imidazole moieties are deprotonated, charge redistribution takes place within the molecule and causes the fluorescence red shift. The results allow **1**·F^- and **1**·AcO^- to be readily detected by eye, as shown in Fig. 3.

It is significantly noted that, the addition of Cl^-, Br^-, I^- and HSO_4^- to the DMF solution of **2** enhanced its relative emission intensity under comparable conditions, while the addition of F^- and AcO^- quenched its relative emission intensity, but no shift was observed, as illustrated in Fig. 4. One possible explanation for the enhancement of emission intensity is that those free anions neutralize partially the positive charge of Ru(II), decreasing the PET effect from the nitrogen lone pairs to the Ru(II)



SCHEME 2 Synthesis routes to compounds **1** and **2**.

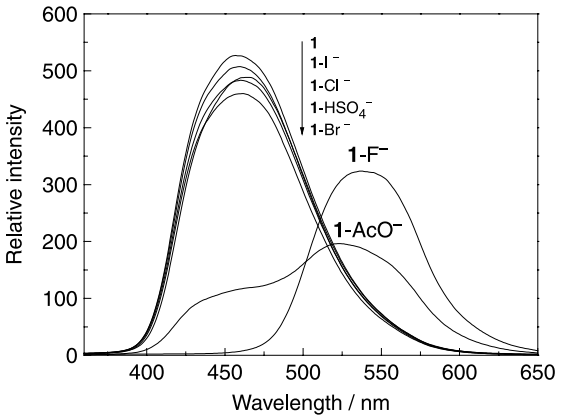


FIGURE 1 Fluorescence spectra of **1** (1.0×10^{-5} M) in the absence and in the presence of I^- (1.0×10^{-3} M), Br^- (1.0×10^{-3} M), Cl^- (1.0×10^{-3} M), HSO_4^- (1.0×10^{-3} M), AcO^- (1.0×10^{-3} M), F^- (1.0×10^{-3} M), in DMF at 25°C. Excitation wavelength: 348 nm. Band width (Ex): 5 nm; Band width (Em): 5 nm.

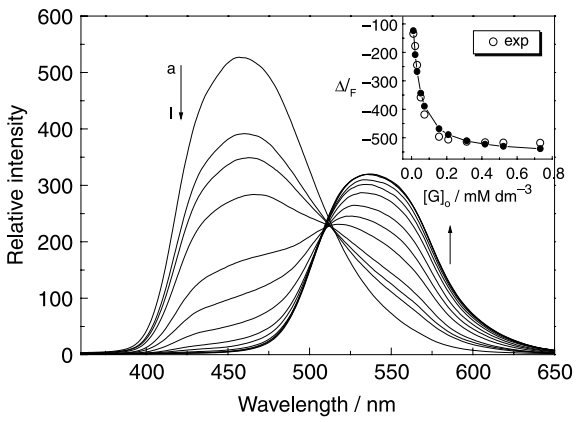


FIGURE 2 Fluorescence spectral changes of **1** (1.0×10^{-5} M) and the nonlinear least-squares analysis (inset) of the differential intensity (ΔI_f) to calculate the complex stability constants (K_s) upon addition of F^- (0–1.0×10^{-3} M from a to l) in DMF at 25°C, excitation wavelength (λ_{ex}) 348 nm. Band width (E_x): 5 nm. Band width (E_m): 5 nm.

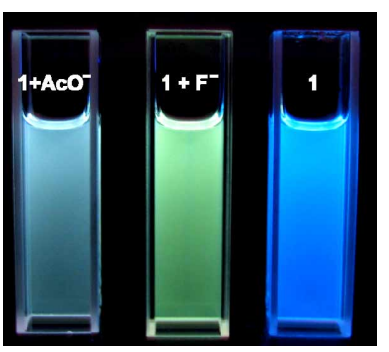


FIGURE 3 Visible emission observed from samples of **1** (1.0×10^{-5} M) in the absence and the presence of F^- (1.0×10^{-4} M) or AcO^- (1.0×10^{-4} M).

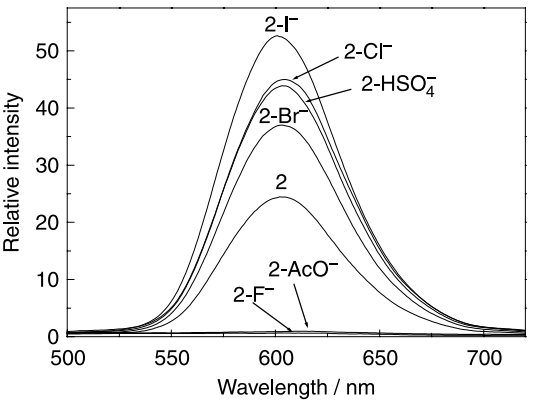


FIGURE 4 Fluorescence spectra of **2** (1.0×10^{-4} M) in the absence and in the presence of F^- (0.01 M), Cl^- (0.01 M), Br^- (0.01 M), I^- (0.01 M), AcO^- (0.01 M), and HSO_4^- (0.01 M) in DMF at 25°C. Excitation wavelength: 420 nm. Band width (E_x): 10 nm. Band width (E_m): 10 nm.

center. However, for the latter spectral phenomenon, the deprotonated imidazo[4,5-*f*]-1,10-phenanthroline group is favorable for the intramolecular PET, resulting in the fluorescence quenching.

The fluorescence quantum yields (Φ_F) of **1**, **2** and their complexes with anions were determined using the literature procedure [82–84]. The emission quantum yields were then calculated using Eq. (1).

$$\Phi_x = (A_{std}/A_x)(I_x/I_{std})\Phi_{std} \quad (1)$$

where Φ_x and Φ_{std} refer to the emission quantum yields of the sample and the standard, and A_{std} and A_x represent the absorbance of the standard and the sample, respectively, while I_{std} and I_x are the integrals of the emission envelope of the standard and the sample, respectively. The obtained quantum yields of **1**, **2** and their complexes with anions are listed in Table I.

As can be seen from Table I, upon complexation with F^- and AcO^-, the corresponding quantum yields for **1** show an obvious decrease, while those with other anions just slightly lower. For **2**, the corresponding quantum yields dramatically decrease upon complexation with F^- and AcO^-, but significantly enhance upon complexation with other anions, which is consistent with the fluorescence spectra feature. These observations suggest that the complexation between host **1**/**2** and F^-/AcO^- should be stronger than that of them with other anions.

Binding Constants

Quantitative investigations of the binding behavior of compounds **1**–**2** have been performed with anions 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 Cl^-, Br^-, I^- and

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TABLE I Fluorescence quantum yields (Φ_F) of **1**, **2** and their complexes in DMF

	Ligand	Complexes					
		F^-	Cl^-	Br^-	I^-	HSO_4^-	AcO^-
1	0.142	0.045	0.135	0.127	0.140	0.136	0.058
2	0.0118	$<10^{-3}$	0.0177	0.0141	0.0193	0.0150	$<10^{-3}$

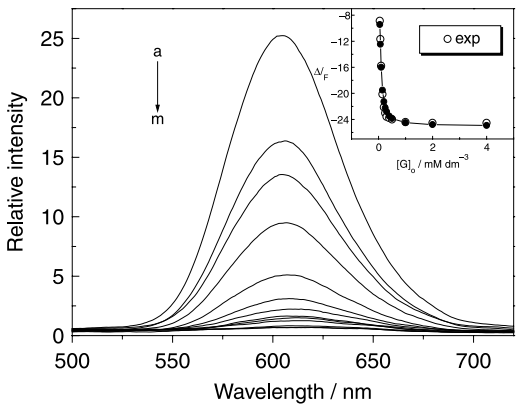

FIGURE 5 Fluorescence spectral changes of **2** (1.0×10^{-4} M) and the nonlinear least-squares analysis (inset) of the differential intensity (ΔI_f) to calculate the complex stability constants (K_s) upon addition of F^- ($0–4.0 \times 10^{-3}$ M from a to m) in DMF at 25°C, excitation wavelength (λ_{ex}) 420 nm. Band width (E_x): 10 nm. Band width (E_m): 10 nm.

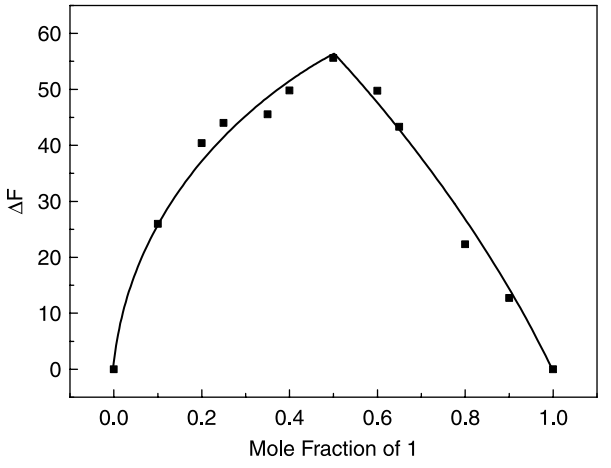

FIGURE 6 Job's plots for the binding of AcO^- anion with **1**.

HSO_4^- concentration, but decreased with increasing AcO^- and F^- (Fig. 5). In contrast, the fluorescence intensity of **1** decreased with an obvious bathochromic shift, as shown in Fig. 2. To determine the stoichiometry of the anion complexation, the Job plots were constructed from the fluorimetric titration data. The formation of the 1:1 complexes was clearly confirmed (Fig. 6). The K_S values of complex were calculated by using the nonlinear least-squares method, and the results are listed in Table II.

As shown in Table II, **1** shows the highest binding ability toward F^- among four spherical anions examined (F^-, Cl^-, Br^- and HSO_4^-, in which HSO_4^- is an aprx-spherical anion), and the relative selectivity for F^- is over 34 of Cl^- or any other spherical anions. Meanwhile, the strong binding ability is also observed for complexation of **1** with the triangular anion AcO^-. To prove that the added F^- do not bind two hydroxyl protons of calix[4]arene moieties in **1**, 2-(4′-methoxyphenyl)imidazo[4,5-*f*]1,10-phenanthroline (MOP) was used. The complexation of the anion with MOP shows the same spectral tendency as that of **1** (Fig. S3). Therefore, it can be concluded that F^- prefers to bind to the NH group [87]. It is noted that the coordination of Ru^{2+} to **1**, affording complex **2**, enhances the binding ability for F^-, Cl^- and Br^-, but lowers the K_S for AcO^- for **2**. The reversed binding behavior for different shape anions could be attributed to the guest basicity and the complex structure upon side arm ligation of **2** to the anions, although we do not have any direct evidence such as crystallographic structure in support of this possibility.

^{1}H NMR Spectra

To understand the above binding and fluorescence behaviors between the host molecule and anions, we carried out ^{1}H NMR experiments in DMSO-*d6* at room temperature. Upon addition of 1 equivalent F^- and AcO^-, the proton signal of H_d in **1** becomes invisible, suggesting that there are strong hydrogen bonding interactions between both anions and two N—H groups of the imidazole at the upper rim of the calix[4]arene. In the meanwhile, aromatic proton signals shift downfield or upfield upon the complexation of **1** with the anions. As can be seen from Fig. 7, upon the addition of 10 equivalent F^- to **1**, H_b H_c H_g show a significant peak shifted upfield

TABLE II Stability constants (K_S, M^{-1}) for stoichiometric 1:1 complexation of **1** and **2** with anions in DMF at 25°C

	F^-	Cl^-	Br^-	I^-	HSO_4^-	AcO^-
1	35400 ± 2000	1040 ± 40	440 ± 20	†	530 ± 20	63600 ± 2400
2	46650 ± 1150	4420 ± 140	1940 ± 100	1710 ± 110	470 ± 20	19950 ± 1250

† Fluorescence changes were too small to measure.

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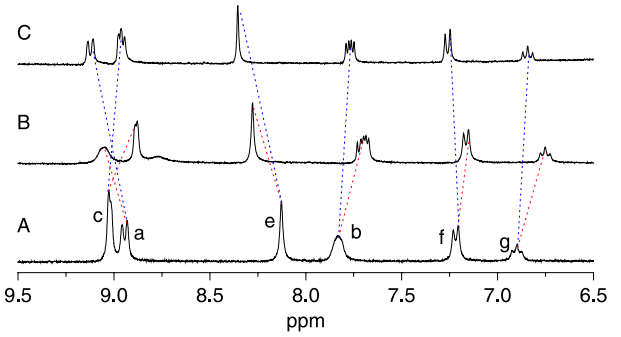

FIGURE 7 Partial ^{1}H NMR of **1** (5×10^{-3} M) in DMSO-d_6 at room temperature: (A) compound **1** only; (B) **1** + 10 equiv of F^-; (C) **1** + 10 equiv of AcO^-.

by $\Delta\delta = -0.13$ ppm, -0.15 ppm and -0.15 ppm, respectively, whereas slight upfield shift is observed for H_f of $\Delta\delta = -0.05$ ppm. However, the signals of H_a and H_e show large downfield shift of $\Delta\delta = 0.12$ ppm and 0.14 ppm, respectively. The upfield shift of H_b and H_c adjacent to imidazole ring should be due to the increasing electron density on the phenyl ring owing to through-bond effects. This indicates the deprotonation of the NH group of the imidazole ring [88–92]. The downfield shift of H_e can be attributed to the through-space effects, the polarization C—H bond in proximity to the hydrogen bond and the hydrogen bonding interaction between anions and the proton [93], but that of H_a is unexpected. One reasonable explanation for the downfield shift of H_a is that two phenanthroline groups in **1** approach each other and then stack partially, making these protons reside in a downshielding environment. Hence, the anion should locate between the two imidazole planes, and interacts simultaneously with four H_e protons. The possible bind mode is shown in Fig. 8a.

A similar result is also observed upon addition of 10 equivalent AcO^- to **1** in solution of DMSO-d_6. The signals of H_a and H_e show downfield shift of $\Delta\delta = 0.18$ ppm and 0.22 ppm, respectively, and H_b H_c H_g shows upfield shift of $\Delta\delta = -0.06$ ppm, -0.07 ppm and -0.06 ppm respectively. The bigger downfield shift of H_a should be attributed to the closer distance between two phenanthroline groups. However, the H_f proton shifts downfield rather than upfield like F^-, which may be due to the larger AcO^- interacting with the proton by hydrogen bonding, as illustrated in Fig. 8b. These bind modes assumed by NMR are in good agreement with the conclusion from the fluorescence spectra.

CONCLUSIONS

In summary, a new calix[4]arene derivative (**1**) possessing imidazo[4,5-*f*]-1,10- phenanthroline groups and its Ru(II) complex (**2**) have been synthesized. The addition of anions to their DMF solution leads to different photophysical behaviors. The compound **1** can be used as colorimetric and sensor to F^- and AcO^- without response to other anions. On the other hand, the addition of Cl^-, Br^-,

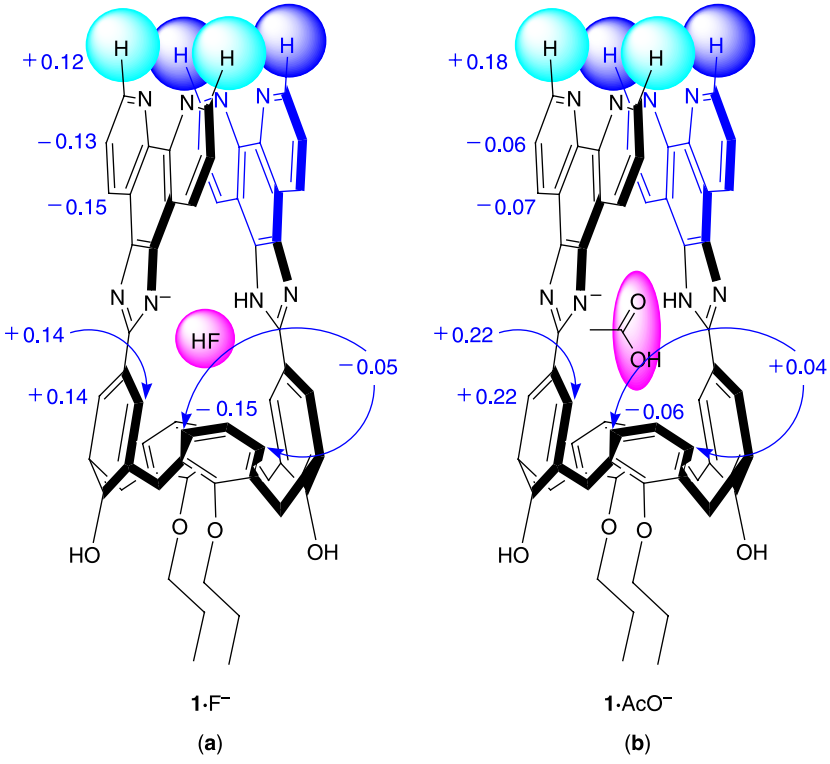

FIGURE 8 Possible structures of complexes (a) **1**·F^-, and (b) **1**·AcO^-. The data represent the chemical shift changes after binding anions.

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I^- and HSO_4^- to the DMF solution of **2** significantly enhances its relative emission intensity, while the addition of F^- and AcO^- quenches its fluorescence intensity. The results provide an approach for the design to fluorescent sensors mediated by anions.

Acknowledgements

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