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A Novel Colorimetric and Fluorescent Anion Chemosensor Based on the Flavone Quasi-crown Ether–Metal Complex

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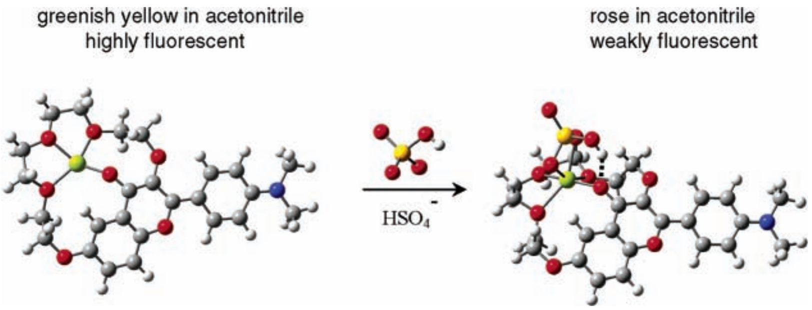
ABSTRACT



The metal–ligand complex 1 ([Mg (L)] $^{2+}$) (or 2 ([Ca (L)] $^{2+}$)) was demonstrated to selectively bind HSO_4^- (or $H_2PO_4^-$) over other anions by using UV–vis absorption and fluorescence spectroscopy. The studied complex exhibits the remarkable color change and fluorescence quenching upon introducing HSO_4^- (or $H_2PO_4^-$) anion in acetonitrile. Both the mechanism and structure of the secondary complex of complex 1 with anion were proposed on the basis of theoretical computation.

Anions play numerous indispensable roles in biological system.[1] For instance, phosphate and sulfate binding proteins are important biomolecular species in transport systems.[2] The importance of anions in biological systems has attracted much attention on anion recognition.[3] Efforts have been taken to design new chemosensors for detection of anions.[1c,4] The metal–ligand coordinative interaction displays its superiorities to hydrogen bonding and electrostatic interaction in a polar environment.[5] Therefore, the metal–ligand complexes

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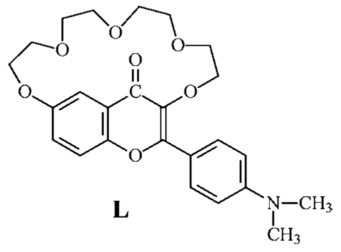

Figure 1. Structure of the ligand **L**.

have been reported for effective and selective recognition of anions.[6] However, most work was focused on the transition-metal ions, such as Cu (II), Zn (II), and Hg (II).[5,6] In this paper, we demonstrate that the alkaline earth metal ions can serve as coordinative centers as well for anion recognition.

Chromogenic sensors have attracted much attention due to their capability to detect analytes by the naked eye without resorting to any expensive instruments.[7] For example, Soto and co-workers used a Hg(II)−ligand complex to monitor nitrate concentrations via color change in acetonitrile.[6b] Fluorescence is also popular for its in-real-time detection and sensitivity.[1b,5c,8] However, such colorimetric and fluorescent sensors for anionic substrates are relatively few.[1c,8] Our study shows that alkaline earth metal−ligand complexes function as unique colorimetric and fluorescent chemosensors, with high sensitivity and selectivity to HSO_4^- (or $H_2PO_4^-$).

We previously reported that ligand **L** (Figure 1), characteristic of a hard base, prefers to bind alkali metal and alkaline earth metal cations, rather than transition-metal ions such as Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Fe^{3+}.[9] No changes were observed in the UV−vis absorption and fluorescence spectra of ligand **L** in acetonitrile upon addition of 10 equiv of Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, and Fe^{3+}. The addition of the alkali metal ions, such as Li^+, Na^+, and K^+ did not significantly effect on the electronic transitions of ligand **L**. However, the UV−vis absorption peak of ligand **L** shifted from 375 to 402 nm upon introducing Mg^{2+} and Ca^{2+}, concomitant with the color change of the solution from green to greenish yellow, and the fluorescence intensity of lignad **L** was quenched. These observed electronic transition changes might be interpreted with the enhancement of the intramolecular charge transfer. As assumed, the oxygen of carbonyl group of ligand **L** bound to cations enhances the efficiency of intramolecular charge transfer, resulting in the red shift of maximal absorbance and the fluorescence quenching. Moreover, the titration of ligand **L** with Mg^{2+} or Ca^{2+} indicated the formation of stable 1:1 ligand-to-metal complex.[9]

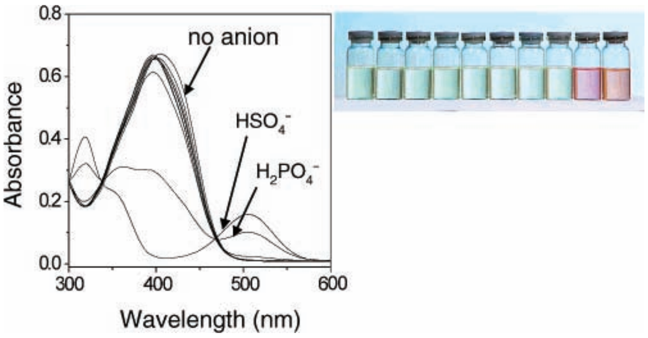

Figure 2. Absorption spectra of complex **1** in acetonitrile (3.0×10^{-5} M) after the addition of 4 equiv of anions (no anion, F^-, Cl^-, Br^-, I^- , AcO^-, NO_3^-, HCO_3^-, HSO_4^-, $H_2PO_4^-$). The photograph shows the color changes of complex **1** in acetonitrile (3.0×10^{-5} M) after the addition of 4 equiv of anion (from left to right: no anion, F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, HCO_3^-, HSO_4^-, and $H_2PO_4^-$).

In this continuous work, complex **1** ($[Mg(\mathbf{L})]^{2+}$) or **2** ($[Ca(\mathbf{L})]^{2+}$) is used as a chemosensor for the detection of different anions. Our results show that these two complexes exhibit quite similar behavior in the presence of studied anions. In the following sections, we present our studies on complex **1** ($[Mg(\mathbf{L})]^{2+}$) in acetonitrile at room temperature.

Figure 2 displays the UV−vis absorption spectra and the photograph of the complex **1** upon addition of 4 equiv of diverse anions (4 equiv are enough for complete color conversion). As shown in Figure 2, the spectral feature of complex **1** displays absorption maximum at 402 nm in acetonitrile. Upon addition of HSO_4^- or $H_2PO_4^-$, the absorption maximum shifts even further to 502 nm, affording a rose-colored solution. However, little response in absorption spectra, upon addition of other anions, is observed even at high concentration. These results indicate that complex **1** exhibits high selective complexation with tetrahedron oxoanions, especially HSO_4^-, whereas it does not bind spherical halides such as F^-, Cl^-, Br^-, and I^- and planar oxoanions such as HCO_3^-, AcO^- , and NO_3^-. This indicates that complex **1** is selective toward the recognition of HSO_4^- or $H_2PO_4^-$ over other anions including HCO_3^-.

Figure 3 shows the UV−vis absorption spectra of complex **1** with various concentrations of HSO_4^- and $H_2PO_4^-$, respectively. The addition of HSO_4^- (Figure 3A) or $H_2PO_4^-$ (Figure 3B) to complex **1**, results in substantial decrease of optical density at 402 nm and gradual increase at 315 and 502 nm. These spectral changes give rise to two clear isosbestic points, localized at 340 and 470 nm in absorption spectra. These electronic transition changes imply the formation of new chromophore which is possibly due to the formation of the secondary complex between complex **1** and HSO_4^- (or $H_2PO_4^-$).

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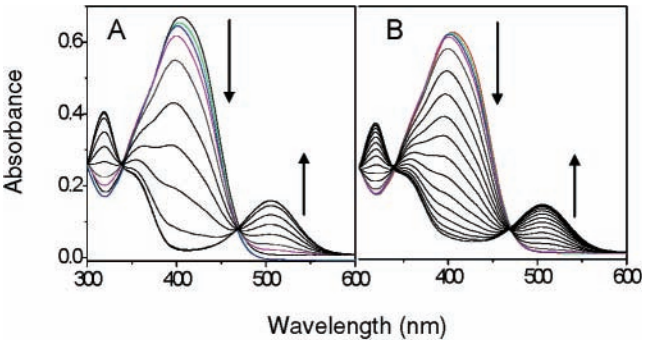

Figure 3. UV−vis absorption spectra of complex **1** (3×10^{-5} M) with different concentrations of (A) HSO_4^- anion (corrected concentrations: 0, 2, 5, 7, 10, 15, 20, 25, 30, and 35 μM) and (B) $H_2PO_4^-$ anion (corrected concentrations: 0, 2, 5, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, and 70 μM).

Fluorescent techniques have been widely used to investigate the receptor−substrate interactions due to their high sensitivity.[10] In this work, the complexation behavior of complex **1** toward various anions was also assessed by fluorescence titration in acetonitrile. In contrast to the absorption method, the anions at low concentration (2 ppm) can be monitored by the fluorescence method. No change is observed in the fluorescence spectra when F^-, Cl^-, Br^-, I^-, HCO_3^-, AcO^-, and NO_3^- anions are added into complex **1** solution. However, the fluorescence of complex **1** is significantly quenched by HSO_4^- or $H_2PO_4^-$. Figure 4 shows the fluorescence spectra of complex **1** with various concentrations of HSO_4^- (Figure 4A) and $H_2PO_4^-$ (Figure 4B), respectively. The fluorescence intensity is decreased upon the increase of HSO_4^- or $H_2PO_4^-$ concentrations. These results are consistent with the electronic transition changes in the absorption titration.

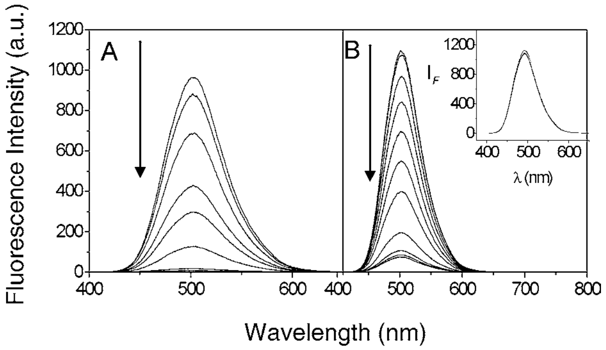

Figure 4. Fluorescence spectra of compound **1** (1×10^{-5} M) with different concentrations of (A) HSO_4^- anion (corrected concentrations: 0, 2, 5, 7, 10, 15, 20, 25, and 30 μM) and (B) $H_2PO_4^-$ anion (corrected concentrations: 0, 2, 5, 7, 10, 15, 20, 25, 30, 35, and 40 μM). Inset is the fluorescence spectra of complex **1** with different concentrations of F^- anion.

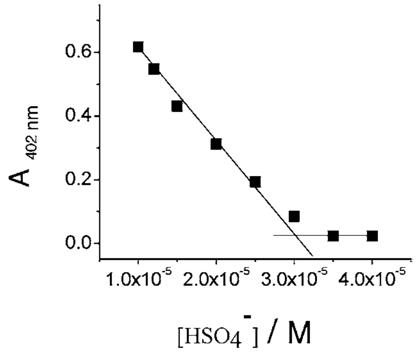

Figure 5. Variation in absorbance of complex **1** in acetonitrile as a function of HSO_4^- concentration (concentration of $[Mg (L)]^{2+}$: 3.0×10^{-5} M).

The variation of optical densities in UV−vis absorption spectra has been utilized to determine the stoichiometry and stability constant of the complex.[11] Figure 5 displays the plot of optical density at 402 nm versus HSO_4^- concentration in acetonitrile. As shown in Figure 5, an approximate plateau is observed at a 1:1 molar ratio of complex **1** to anion guest, indicative of the formation of a 1:1 stoichiometrical complex in solution. On the basis of nonlinear least-squares analysis, the stability constant (log *K* value) was calculated to be 5.75.[10c]

To further verify the affinity to preferred anions arising from complex **1** instead of ligand **L**, the control experiment was performed using ligand **L**. The UV−vis absorption spectrum of ligand **L** does not show any absorbance at 502 nm, after adding the excess of HSO_4^- (or $H_2PO_4^-$) anion in acetonitrile. This clearly demonstrates that the electronic transition of 502 nm peak (seen in Figure 3) is not from ligand **L** perturbated by added anions, but possible from electronic perturbation on complex **1**. Moreover, the suspects about the protonation of complex **1** can be ruled out since no color change is observed upon adding strong acids, such as HCl in acetonitrile.

To understand the possible secondary complex, we simulated the interaction between complex **1** and anion with theoretical computation. The general procedures are: the possible secondary complex was first optimized using G98 program at the HF/6-31G level; and then the single point energy were computed at the B3LYP/6-31G* level based on the optimized configuration. The optimized configuration is shown in Figure 6. As seen in Figure 6, two of the conjugated oxygen atoms of HSO_4^- or $H_2PO_4^-$ with negative charge approach to the positively charged metal center. This facilitates to configure the formation of hydrogen bonding

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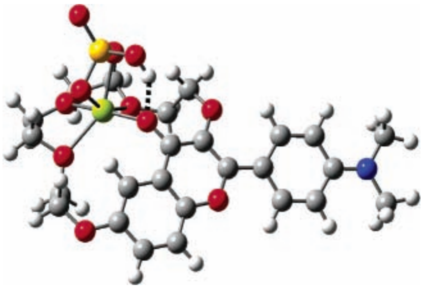

Figure 6. Model structure depicting the association between HSO_4^- and complex **1** ([Mg (**L**)] $^{2+}$). The structure was determined using the G98W program at the HF/6-31G level.

between the hydroxy group in HSO_4^- or $H_2PO_4^-$ and the carbonyl group of ligand **L**. The calculated results show that the charge density of oxygen atom in carbonyl group is increased significantly and that of oxygen atom in ether group at flavone moiety is slightly enhanced. Combined the single point energy calculation results with the optimized configuration, we can conclude that the center-metal assisted hydrogen bonding between anion and carbonyl group of flavone moiety are possibly the major contributor to the observed electronic transition change in the absorption and the fluorescence quenching.

This picture of the secondary complex between complex **1** and anion is illustrated in ^1H NMR spectroscopy. The ^1H NMR spectra of complex **1** were conducted on 300 MHz NMR spectrometer in CD_3CN. Compared to complex **1**, the chemical shifts of protons in flavone moiety shift to the downfield upon adding HSO_4^- anion. The degree of these shifts varied considerably from 0.52 to 0.06 ppm. Analogous to the explanation for the vibration frequency changes of carbonyl in ligand **L** upon complexation with metallic ions,[9] these downfield chemical shifts of protons in complex **1** upon addition of anions can be interpreted as the further electron withdrawing from carbonyl group. It is plausible to deduce that this further electron withdrawal comes from the center-metal-assisted hydrogen bonding between the anion and the carbonyl group of complex **1**.

The specific sensitivity and selectivity of complex **1** to HSO_4^- or $H_2PO_4^-$ can be rationalized on the basis of the structures of preferred anions. The complementary structures are very important for noncovalent interactions, which leads to effective and selective recognition. Here, the tetrahedral structures of HSO_4^- or $H_2PO_4^-$ provide suitable conjugated oxygen atoms with negative charge for ligating to the metal center, which assist the formation of hydrogen bonding between anion and carbonyl group of complex **1**.

In conclusion, complex **1** or **2** has been exhibited a perspective reagent for anion HSO_4^- or $H_2PO_4^-$ recognition in UV−vis absorption and fluorescence spectroscopic studies. The anion HSO_4^- or $H_2PO_4^-$ recognition can be ascribed to the formation of a secondary complex between complex **1** and HSO_4^- or $H_2PO_4^-$ anion via center-metal-assisted hydrogen bonding, which was demonstrated with the simulation of theoretical computation and the illustration of ^1H NMR spectra. To the best of our knowledge, this is the first case of an alkaline earth metal−ligand complex being used for anion recognition, which provides a new concept for developing novel chemsensors for anion recognition.

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Supporting Information Available: Experimental procedures and full characterization for ligand **L**. This material is available free of charge via the Internet at http://pubs.acs.org.

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