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A Luminescent Chemosensor with Specific Response for Mg^{2+}

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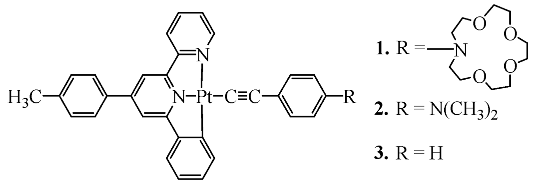
A novel chemosensor, a cyclometalated platinum(II) bipyridyl acetylide complex containing a monoazacrown moiety in the acetylide ligand, which can signal Mg^{2+} specifically and display large changes both in color and in luminescence intensity upon complexation with Mg^{2+}, is described.

Metal ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Zn^{2+} play an important role in biological processes. However, investigation of their function in biological systems can be challenging because these metal ions lack intense visible absorption and emission for easy detection. Chemosensors for these ions provide an approach to such investigation and have received considerable attention.[1] A number of "chromophore−spacer−receptor" systems that can selectively recognize specific guest ions at their receptor site and produce measurable color and/or luminescence changes have been described.[2−8] However, the performance accuracy of these sensors is still limited, and there needs to be improved specific response, in particular, in recognition selectivity for Mg^{2+} over other alkaline earth and alkali metal ions.[9,10] This issue necessitates the development of sensor molecules that can adequately discriminate Mg^{2+} from other metal ions.

Chart 1 Structure of Complexes **1**−**3**



In this Communication, we report a new chemosensor, a cyclometalated platinum(II) bipyridyl acetylide complex containing a monoazacrown moiety in the acetylide ligand (Chart 1, complex **1**), which can signal Mg^{2+} specifically. The azacrown in this complex serves as metal ion receptor. In the absence of cations, complex **1** is nonemissive and its lowest energy absorption arises from ligand-to-ligand charge transfer (LLCT) transition. However, upon complexation of a metal ion, this transition is shifted above the metal-to-ligand charge transfer (MLCT) transition in energy. For complexation with Mg^{2+}, bright luminescence from the ^{3}MLCT state is observed. Thus, complex **1** can be utilized as a chemosensor specific for detection of Mg^{2+} by monitoring the changes both in luminescence and color.

The preparation and analysis data of complexes **1**−**3** are given in Supporting Information. The UV−vis spectrum of **1** in acetonitrile is shown in Figure 1 (the top curve of the long wavelength band). Complex **2** exhibits a similar absorption spectrum. The solutions of these complexes are red and exhibit an absorption band at 390−470 nm (centered at ca. 435 nm, $\epsilon = 7310$ dm^3 mol^{-1} cm^{-1}) and a more intense band at 470−630 nm (λ_{max} at ca. 500 nm with $\epsilon = 8370$ dm^3 mol^{-1} cm^{-1}). The absorption spectrum properties were found to follow Beer's Law below a concentration of 1×10^{-3} M, suggesting the absence of significant complex aggregation. With reference to previous spectroscopic work on cyclometalated platinum(II) 6-phenyl-2,2′-bipyridyl complexes,[11,12] the absorption band at 390−470 nm is ascribed to the $d\pi(Pt) \rightarrow p^*(C\text{^}N\text{^}N)$ MLCT transition. The absorption band at 500 nm is tentatively assigned to the LLCT transition from the amine-substituted acetylide ligand to the (C^N^N) acceptor (see Supporting Information). The LLCT transitions have been reported for the platinum(II) complexes containing

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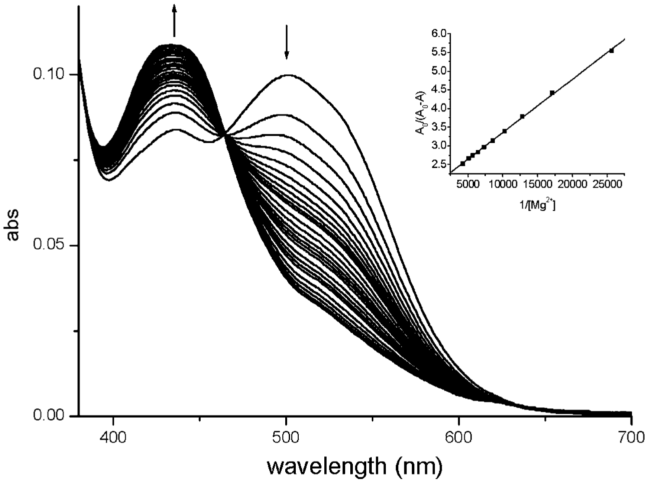

Figure 1. The changes in absorption spectrum of **1** (1.2×10^{-5} M) in acetonitrile upon addition of Mg^{2+}. The insert shows the plot of $A_0/(A_0 - A)$ vs $[Mg^{2+}]^{-1}$. See text for details.

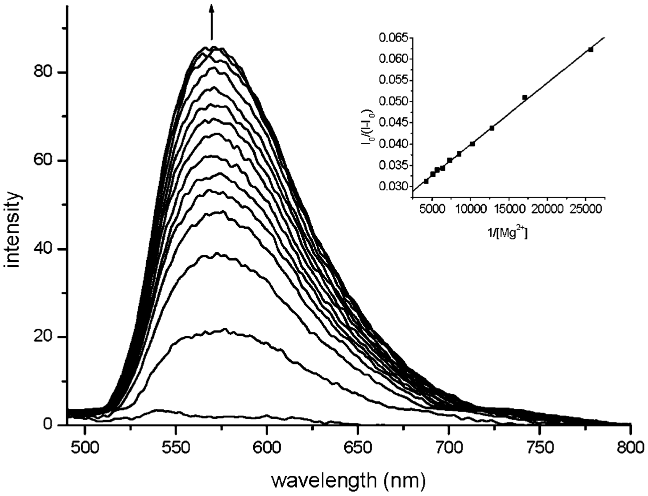

Figure 2. Luminescence spectra of **1** (1.2×10^{-5} M) in acetonitrile in the presence of Mg^{2+}. The insert shows the plot of $I_0/(I - I_0)$ vs $[Mg^{2+}]^{-1}$. Excitation was at 465 nm.

diimine and dithiolate ligands[13−16] and for the platinum(II) diimine bis-acetylide complex containing $-N(CH_3)_2$ groups in the acetylide ligands.[17]

Alkali and alkaline earth metal cations have profound effects on the absorption spectrum of **1**. Addition of Li^+, Na^+, K^+, Ba^{2+}, Ca^{2+}, or Mg^{2+}, available as perchlorate salts, to the solution of **1** in acetonitrile leads to dramatic changes in the absorption spectrum. Figure 1 presents the changes in the UV−vis spectrum of **1** upon addition of Mg^{2+}. The LLCT transition band at 500 nm decreases monotonically throughout the addition, while the MLCT band at 390−470 nm concomitantly grows in with increasing Mg^{2+} concentration. A well-defined isosbestic point at 465 nm is clearly shown. At the end of the titration, the solution becomes yellow, and the absorption spectrum is nearly identical to that of complex **3**. This observation evidently arises from the complexation of the cation with the azacrown ether receptor in the acetylide ligand, which decreases the electron-donation ability of the acetylide ligand. Thus, the LLCT transition from the aza-crown-containing acetylide ligand to the (C^N^N) acceptor shifts to high energy, and the MLCT transition becomes the lowest energy absorption. Indeed, control experiments with the crown-free analogues, complex **2,** showed no such absorption spectrum changes upon addition of the cation under identical conditions. Similar results were observed upon addition of other cations to the solution of **1**. The insert in Figure 1 shows the plot of $A_0/(A_0 - A)$ versus $[Mg^{2+}]^{-1}$, where A and A_0 refer to the absorbance at 500 nm for complex **1** in the presence and absence of Mg^{2+}, respectively. The straight line suggests that the complexation of the ion to the crown ether is in a 1:1 ratio. Bonding constants (log K's), determined from such plots for the cations, are Na^+(2.95), Li^+(3.11), Mg^{2+}(4.17), Ba^{2+}(4.38), and Ca^{2+}(4.99), and their absolute values are very similar to those of other aza-15-crown-5 ionophores reported in the literature.[18] Yam and co-workers reported that the platinum(II) terpyridyl acetylide-crown ether complex, [Pt(terpy)(C≡C-benzo-15-crown-5)]PF_6, exhibits a blue shift in its MLCT absorption band upon addition of alkali metal cations to its solution.[19] This blue shift of the MLCT band is caused by the reduction of electron-donation ability of the acetylide upon ion binding.

The luminescence response of complex **1** to Mg^{2+} is unique. In the absence of cations, complexes **1** and **2** are nonemissive. The lack of emission is probably due to the rapid internal conversion from the MLCT to the LLCT state and the facile nonradiative deactivation of the low-lying LLCT state. In other words, the LLCT state provides a path for rapid radiationless decay of the MLCT state. However, upon addition of Mg^{2+} to the solution of **1** in acetonitrile, a structureless emission band centered at ca. 570 nm is observed. Figure 2 shows the changes in the emission spectrum of **1** as a function of Mg^{2+} concentration. Throughout the titration, the excitation wavelength corresponds to the isosbestic point at 465 nm in Figure 1. The emission intensity is noticeably enhanced upon increasing Mg^{2+} concentration, while the shape and energy of the emission band are not changed. With reference to the previous work on the emission of platinum(II) 6-phenyl-2,2′-bipyridyl complexes,[11,12] this emission is assigned as derived from the ^{3}MLCT excited state. Control experiments with crown-free complex **2** under the same conditions showed no change in the emission character upon addition of Mg^{2+}. Evidently, the appearance of the emission for complex **1** upon addition of Mg^{2+} originates from the complexation of Mg^{2+} with the azacrown receptor. As mentioned above, upon complexation of the azacrown with a cation, the MLCT state of **1** becomes the lowest energy state, which would decay primarily by "normal" radiative and nonradiative decay paths. As a result, the MLCT state becomes emissive. The insert in Figure 2

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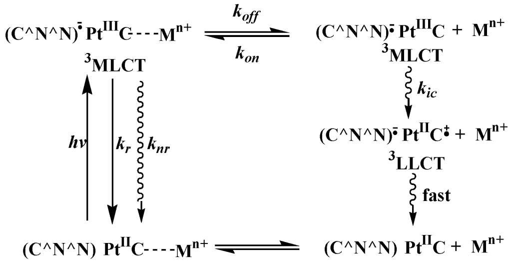
Scheme 1



shows the plot of $I_0/(I - I_0)$ versus $[\mathrm{Mg}^{2+}]^{-1}$, where I_0 and I represent the emission intensity at 570 nm in the absence and presence of Mg^{2+}, respectively. The yielded straight line further confirms that the complexation of Mg^{2+} into the azacrown is in a 1:1 ratio, and the determined log K value of 4.21 is consistent with that obtained from the absorption measurements.

In contrast, Li^+, Na^+, K^+, Ca^{2+}, and Ba^{2+} do not cause the change in the luminescence character of complex **1**, despite complexation of these ions with the azacrown receptor as reflected in the absorption spectrum changes. The solutions of **1** in acetonitrile in the presence of excess of M^{n+} are nonemissive. To account for these observations, we invoke the kinetic model presented in Scheme 1, as proposed by Schanze for interpretation of ion effects on the photophysics of a Re(I) complex.[18] In the scheme, (C^N^N) and C represent, respectively, the bipyridyl ligand and the acetylide containing the azacrown in complex **1**. Excitation of **1**···M^{n+} complex results in the ^{1}MLCT state, which undergoes intersystem crossing to the ^{3}MLCT state. The metal center in **1** in MLCT states ($\mathrm{Pt^{III}}$) is more positive than in the ground state ($\mathrm{Pt^{II}}$), leading to a decrease of the charge density on the amino group in MLCT state. This in turn would lower the binding ability of the azacrown, and M^{n+} can be released from the azacrown during the lifetime of the MLCT state.[20,21] Thus, in addition to the normal radiative and nonradiative pathways the ^{3}MLCT state also can decay via a nonradiative path involving the dissociation of the crowned cation (k_{off}) followed by the rapid internal conversion to the ^{3}LLCT state (k_{ic}). One can expect that k_{off} would depend on the identity of the metal ions. It is known[9] that the charge densities of the metal ions increase in following order: K^+ (0.05) < Na^+ (0.10) < Ba^{2+} (0.13) < Ca^{2+}(0.24) < Li^+(0.33) < Mg^{2+}(0.75). Mg^{2+} has the highest charge density in the series of metal ions, and its value is considerably larger than those of the other cations. As a result, the interaction between Mg^{2+} and the crown nitrogen would be strongest among the **1**···M^{n+} complexes. Cation dissociation is not important for **1**···Mg^{2+}, and its ^{3}MLCT state would decay via normal radiative and nonradiative paths. On the other hand, for other cation complexes with **1**, cation dissociation dominates the decay pathways of the ^{3}MLCT state; hence, no emission could be detected. Protonated **1** and **2** in acetonitrile exhibit strong emission, and the shape and energy of the emission spectra are nearly identical with those of **1**···Mg^{2+}. The lifetime (τ_1) of the protonated **2** can be used to estimate the "normal" ^{3}MLCT state decay rate $[1/(k_{\mathrm{r}} + k_{\mathrm{nr}})]$ (assuming that its deprotonation is not competitive with the normal decay rate), and then k_{off} can be estimated from the lifetime (τ_2) of the ^{3}MLCT state of the **1**···M^{n+} complexes.

$$k_{\mathrm{off}} = 1/\tau_2 - 1/\tau_1 \qquad (1)$$

The emission quantum yields and lifetimes were measured to be 0.023 and 180 ns for **1**···Mg^{2+}, and 0.049 and 330 ns for protonated **2**. The limited value for the lifetime measurements in our instruments is >0.2 ns; thus, τ_2 for the complexes of **1** with other cations must be smaller than 0.2 ns. The k_{off} values obtained from eq 1 are ca. $2.5 \times 10^6\ \mathrm{s}^{-1}$ for **1**···Mg^{2+}, and $>5 \times 10^9\ \mathrm{s}^{-1}$ for other cation complexes.

It is of particular interest that complex **1** can signal Mg^{2+} specifically even in the presence of alkali and alkaline earth metal ions in high concentrations. For example, addition of Mg^{2+} into the solution of **1** in acetonitrile with 1×10^{-3} M $\mathrm{LiClO_4}$ results in bright luminescence from the excited **1**···Mg^{2+} complex. Evidently, complex **1** can remarkably discriminate Mg^{2+} from other alkaline earth and alkali metal ions.

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Supporting Information Available: Synthesis procedure, ^{1}H NMR spectroscopy data, HR-MS spectrometry data, as well as elemental analysis of complexes **1**−**3** and support for the assignment of LLCT excited states in **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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