Inorganic Chemistry
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A Selective Colorimetric Hg^{2+} Probe Featuring a Styryl Dithiaazacrown Containing Platinum(II) Terpyridine Complex through Modulation of the Relative Strength of ICT and MLCT Transitions

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S *Supporting Information*

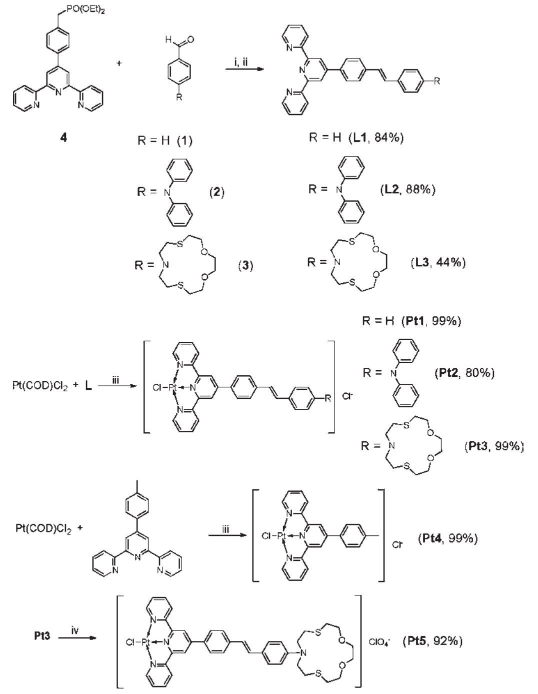
ABSTRACT: A series of platinum(II) terpyridine complexes featuring an aminostilbene donor−acceptor framework was synthesized. The complex with a dithiaazacrown moiety exhibits a highly sensitive and selective colorimetric response to a Hg^{2+} cation through modulation of the relative strength of ICT and MLCT transitions. The results from ^1H NMR titration suggest the existence of a weak $Pt^{II}\cdots Hg^{II}$ metallophilic interaction at low Hg^{2+} concentration.

The toxicity of certain metal ions to human and other living organisms has been a constant cause of environmental concern. The sensitive detection of trace amounts of heavy-metal ions in the environment is of utmost importance.[1] Among these heavy-metal ions, mercury ion (Hg^{2+}) is one of the most troublesome to the environment and living systems because it is highly toxic and easily accumulates in living organisms.[2,3] In recent years, numerous efforts have been directed at the design of chemosensors capable of specifically detecting Hg^{2+}.[4] One of the most common Hg^{2+} binding motifs is the thioether-containing macrocycles, which have been proven to be effective hosts for Hg^{2+} because of the high affinity of Hg^{2+} for a sulfur atom.[5]

Although a number of methods are available for determining the presence of metal ions in the environment, there is a growing need for rapid on-site analysis with chemosensors capable of detecting metal ions on a real-time basis. In this regard, the ability to operate a naked-eye colorimetric response to the analyte is an attractive approach to the design of sensing molecules. Recently, a series of platinum(II) terpyridyl complexes imparted with metal-binding units developed by Yam and co-workers have been reported that display colorimetric and/or luminescent responses toward various protons and cations.[6a−6c] Typically, these metal complexes possess multiple optical transitions such as metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer in the visible region. The binding of protons or cations perturbs the charge density in the binding unit and subsequently induces optical signal switching between different energy states to achieve the desired optical responses. Related proton- or cation-induced excited-state switching in platinum(II) terpyridyl complexes with azacrown moieties has also been reported by Tung et al.[6d]

The design principle here is to integrate two chromophores, platinum(II) terpyridine and dithiaazacrown-functionalized stilbene, with charge-transfer dipoles in opposite directions and optical transitions in different absorption regions. With analyte recognition motifs conjugated to the ligand framework, the recognition event of a specific analyte can be conveniently monitored by analyte-binding-triggered switching of optical transitions by utilizing a transition-metal complex possessing a MLCT transition in conjunction with a ligand-based optical transition such as an internal charge-transfer (ICT) transition to achieve such a dual-channel sensing mode.[5i,7]

Scheme 1. Synthetic Procedures for the Ligands and Complexes[a]



[a] Experimental conditions: (i) NaH, DMF, ice bath, 1 h; (ii) aldehyde, reflux 24 h; (iii) MeOH, reflux 8 h; (iv) Bu_4NClO_4, DMF, reflux 6 h.

The synthetic procedures for the terpyridyl ligands and their platinum(II) complexes are depicted in Scheme 1. Terpyridyl ligands **L1**−**L3** were synthesized in *N*,*N*-dimethylformamide (DMF) via a standard Hornet−Emmons reaction with moderate-to-excellent yields.[8] Complexes **Pt1**−**Pt3** were obtained by the reaction of

Received: September 17, 2010
Published: January 26, 2011

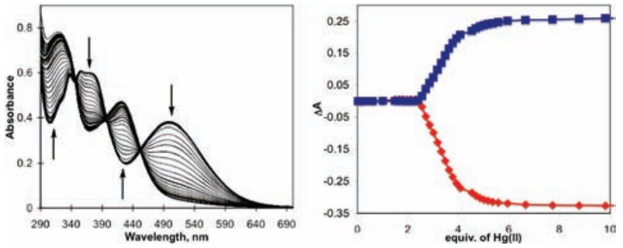


Figure 1. Left: Absorption spectral changes of **Pt3** (2.0×10^{-5} M) upon the addition of $Hg(ClO_4)_2$ [$(0-1.4) \times 10^{-3}$ M] in DMF. Right: Changes of absorbance at 500 nm (red curve) and 422 nm (blue curve) versus equivalents of Hg^{2+} addition.

$Pt(COD)Cl_2$ (COD = 1,5-cyclooctadiene) and terpyridyl ligands **L1**−**L3** in MeOH. Complexes **Pt4** and **Pt5** were also synthesized to serve as model compounds.

The UV−visible spectra of **L2** and **L3** in a CH_3CN solution showed intense bands centered at 388 and 394 nm, respectively. These low-energy bands showed great solvatochromic effects and are assigned as ICT [diphenylamine (π) to terpyridine (π^*) for **L2** and thiaazacrown (π) to terpyridine (π^*) for **L3**] transitions. Dissolution of **Pt2** and **Pt3** in DMF gave pinkish solutions that consisted of intense absorption bands at 300−400 nm and broad low-energy bands at 464 and 500 nm for **Pt2** and **Pt3**, respectively (Figures S1−S3 in the Supporting Information, SI). By comparison to the spectra of **Pt1** and **Pt4** and relevant platinum(II) complexes in the literature,[9] the high-energy absorption bands are assigned to ligand-localized $\pi-\pi^*$ transitions, whereas the low-energy absorption is assigned to an ICT transition overlapping with a MLCT ($Pt_{d\pi}-tpy_{\pi^*}$) transition for **Pt2** and **Pt3**. All three terpyridyl ligands are highly emissive at room temperature. However, **Pt1** and **Pt2** are only luminescent in the solid state at 77 K, and **Pt3** is nonluminescent even at 77 K. The photophysical properties are summarized in Table S1 in the SI.

Figure 1 illustrates the absorption spectral changes of **Pt3** upon the addition of $Hg(ClO_4)_2$ in a DMF solution. The absorbance of the ICT band at 500 nm gradually diminished, accompanied by an increase of the MLCT band centered at 422 nm. The original absorption profile of **Pt3** can be restored by extracting the mixture with excess ethylenediaminetetraacetic acid. The addition of other biologically and/or environmentally important metal cations (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+}) to a DMF solution of **Pt3** resulted in no apparent spectral and solution color changes. No luminescence was detected with the addition of Hg^{2+} ions. The specific colorimetric responses clearly demonstrated that **Pt3** is highly selective toward a Hg^{2+} ion. The control experiments carried out by titration of Hg^{2+} to a DMF solution of either **Pt2** or **Pt1** resulted in only very minor spectral responses under the same conditions. **Pt5** as the perchlorate salt of **Pt3** was titrated with Hg^{2+} to access the counterion effect. The titration profile of the absorption spectra (Figures S4 and S5 in the SI) is essentially identical with the one shown in Figure 1 that excludes the possible interference between Hg^{2+} and Cl^- during titration.

It is intuitive to rationalize the spectral response of **Pt3** upon the addition of Hg^{2+} to be simply the result of encapsulation of Hg^{2+} to the dithiaazacrown moiety via $Hg^{II}-S,N$ bonding, which suppressed the ICT process (diminishing of the ICT band at 500 nm) but enhanced the MLCT transition (increasing of the MLCT band at 422 nm). However, careful scrutiny of the plot of the absorbance changes as a function of the addition of Hg^{2+} equivalents reveals that there was no apparent optical response until an addition of Hg^{2+} of over 2 equiv. Indeed, the intensity of the ICT band at 500 nm was slightly increased between the addition of 1 and 2 equiv of Hg^{2+} before diminishing with higher concentrations of Hg^{2+} (Figure S6 in the SI). A similar minor increase of absorbance was observed upon titration of Hg^{2+} to a DMF solution of **Pt2** (Figure S7 in the SI). The possibility of displacing Pt^{2+} by Hg^{2+} during titration is excluded by comparing the model complex **L3**$HgCl_2$ with the titration spectra between **Pt3** and Hg^{2+} (Figure S8 in the SI). Furthermore, Job's plot did not show the expected 1:1 stoichiometry but yielded a complicated pattern (Figure S9 in the SI), which indicates the existence of possible multiple equilibria between Hg^{2+} and **Pt3**.

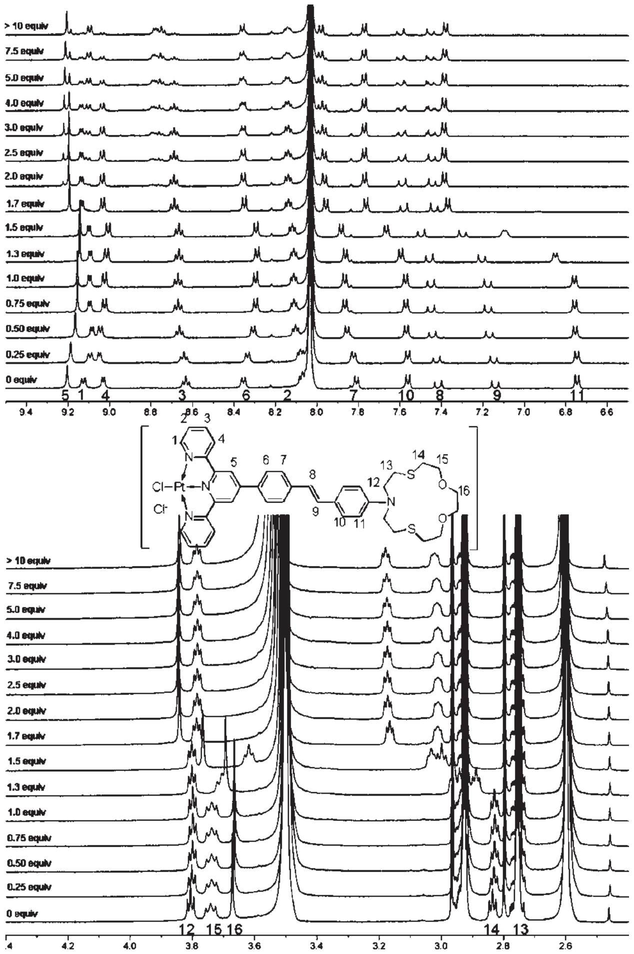


Figure 2. Plots of ^1H NMR spectra of **Pt3** (26.3 mM) showing aromatic (top) and aliphatic (bottom) regions upon the addition of $Hg(ClO_4)_2$ in DMF-d_7.

A ^1H NMR titration experiment was performed with the aim to gaining a further understanding of the interaction between the complex **Pt3** and Hg^{2+} cation. Figure 2 shows the ^1H NMR spectra for titration of a DMF-d_7 solution of **Pt3** with Hg^{2+}. It is surprising to see that, upon the addition of Hg^{2+} of up to 1 equiv, the proton signals of the expected interacting dithiaazacrown virtually did not shift at all, but only the protons in the region between 8.2 and 9.3 ppm associated with the terpyridine moiety (H_1-H_7) showed a slight shift. After the addition of Hg^{2+} of over 1 equiv, the proton signals from dithiaazacrown (H_{13} and H_{14}) became broad and started to shift in the downfield direction. Control experiments carried out by titration of Hg^{2+}

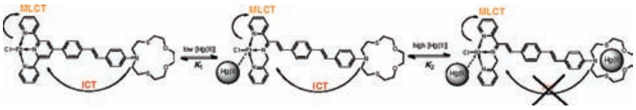


Figure 3. Proposed mechanism for Hg^{II} sensing by probe **Pt3**.

into a DMF-d_7 solution of **Pt1** or **Pt2** resulted in a similar upfield shift of the proton signals associated with the terpyridine moiety (Figures S10 and S11 in the SI). Apparently, the Hg^{2+} ion interacted with the platinum terpyridyl moiety first, followed by encapsulation of Hg^{2+} to the dithiaazacrown moiety. Although attempts to grow good quality single crystals of a Hg^{2+}-**Pt3** adduct were not successful, the results from ^{1}H NMR titration hint at a possible $Pt^{II}-Hg^{II}$ interaction. In addition, a peak cluster at m/z 1657.7 corresponding to a formula of $[2(\mathbf{Pt3} - Cl)^+ + 4Hg^{2+} + 7ClO_4^- + Cl^-]^{2+}$ (calculated m/z 1657.9) was observed in the electrospray ionization mass spectrum (Figure S12 in the SI).

Recent studies have suggested that the dispersive forces responsible for the formation of metallophilic interactions between closed-shell atoms would be magnified by relativistic effects, especially when these interactions involve a Hg^{2+} ion.[10] Examples of metallophilic interactions of $Hg^{II}\cdots Au^{I}$,[11] $Hg^{II}\cdots Pt^{II}$,[12] and $Hg^{II}\cdots Pd^{II}$[13] bonds have been well documented. ^{195}Pt NMR spectra of **Pt3** and **Pt3** upon the addition of 1 equiv of Hg^{2+} were separately recorded. Although the low solubility of **Pt3** in DMF-d_7 precluded the observation of ^{199}Hg satellites, the 10 ppm upfield shift of the ^{195}Pt signal of **Pt3** in the presence of 1 equiv of Hg^{2+} indicates the existence of a weak metallophilic interaction between Pt^{2+} and Hg^{2+} (Figures S13 and S14 in the SI). Thus, we tentatively suggest that the initial interaction of **Pt3** and the incoming Hg^{2+} involves the formation of a weak $Pt^{II}\cdots Hg^{II}$ metallophilic interaction, followed by Hg^{II}—dithiaazacrown interaction.

Beyond the relativistic effect, the strong ICT effect from dithiaazacrown to terpyridine may reinforce the possible donor (Pt^{2+}) to acceptor (Hg^{2+}) interaction. The mechanism of optical response of **Pt3** upon the addition of Hg^{2+} is summarized in Figure 3. It is expected to observe a minor enhancement of the ICT transition upon formation of the $Pt^{II}\cdots Hg^{II}$ interaction at low Hg^{2+} concentration. Indeed, both **Pt2** and **Pt3** exhibited such an enhancement in the absorption spectra with the initial addition of a Hg^{2+} ion. Upon the addition of more than 1 equiv of Hg^{2+}, encapsulation of Hg^{2+} to the dithiaazacrown moiety occurred, which shuts down ICT absorption and turns on the optical output from MLCT absorption. The binding constants based on the two-step equilibrium shown in Figure 3 were calculated to be 1.33×10^4 M^{-1} (K_1) and 1.64×10^3 M^{-1} (K_2), and the detection limit for Hg^{II} is estimated to be on the order of micromolar concentration.

In conclusion, we have designed a simple yet highly selective optical probe for Hg^{2+}. The optical output can be modulated by switching off the ICT transition upon Hg^{2+} binding and converted to a colorimetric response from MLCT transition. The possible dispersive $Pt^{II}\cdots Hg^{II}$ interaction is proposed to rationalize the observed unusual spectral properties at low concentrations of Hg^{2+} in solution. This result may contribute not only to the design of new Hg^{II} probes but also to the development of the model system to explore the metallophilic interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures, characterization data, and titration spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank the National Science Council of Taiwan and Academia Sinica for support of this research.

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