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A "Turn-On" Fluorescent Sensor for Selective Hg(II) Detection in Aqueous Media Based on Metal-Induced Dye Formation

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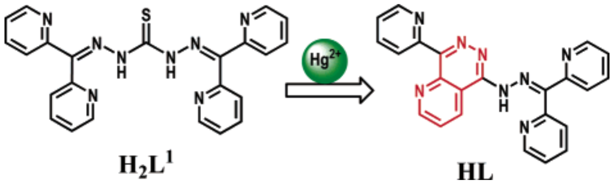
A Hg-promoted desulfurization reaction of a thiocarbazone derivative was introduced in the design of a fluorescent sensor for selective Hg(II) detection. Crystal structural and spectroscopic investigations demonstrated the formation of a triazanaphthalene ring and the "turn-on" responding for Hg(II) in aqueous media.

Recently, the development of selective and sensitive fluorescent imaging tools capable of monitoring heavy- and transition-metal ions has attracted considerable attention because their wide use and subsequent impact on the environment and nature.[1,2] The design of sensors that give fluorescent enhancement (FE) upon Hg(II) binding is a particular challenge because, like many other heavy metals, Hg(II) often causes fluorescent quenching via enhanced spin−orbit coupling associated with the heavy atom effect, which will facilitate the intersystem crossing process.[3,4] Besides, the application of those "turn-on" Hg(II) sensors to an aqueous environment introduces an additional complexity to this problem.[5] To date, a number of selective small-molecular Hg(II) fluorescent sensors have been synthesized through well-designed strategies.[6,7] One of the attractive approaches in this field is to use the Hg-promoted desulfurization reactions, such as hydrolysis,[8] cyclizations,[9] and elimination reactions,[10] to promote the selectivity of sensors. In these reactions, the FE is directly related to the concentration of Hg(II). Here we report a fluorescent sensor for Hg(II) detection by introducing an "off−on" fluorescent response associated with a Hg(II)-promoted cyclization of a thiocarbazone derivative, tetra-2-pyridylthiocarbazone (**H_2L^1**; Scheme 1).

Scheme 1. Hg(II)-Promoted Desulfurization Cyclization



H_2L^1

HL

The ligand **H_2L^1** was prepared according to the literature.[11] The UV−vis absorption spectrum of **H_2L^1** exhibits a $\pi-\pi^*$ transition of the aromatic backbone at 345 nm in a H_2O/CH_3OH (90:10, v/v) solution. In the presence of an equivalent mole ratio of $Hg(NO_3)_2 \cdot 0.5H_2O$, the absorption band red-shifted to 395 nm, with the intensity decreased (Figure 1a). A fluorescence titration of Hg(II) was carried out by using a H_2O/CH_3OH solution of **H_2L^1** (5.0×10^{-5} M) at pH = 7.0. Initially, the fluorescent spectrum of **H_2L^1** showed a very weak band at 530 nm when it was excited at 380 nm ($\Phi < 0.001$). Upon the addition of 1 equiv of $Hg(NO_3)_2 \cdot$

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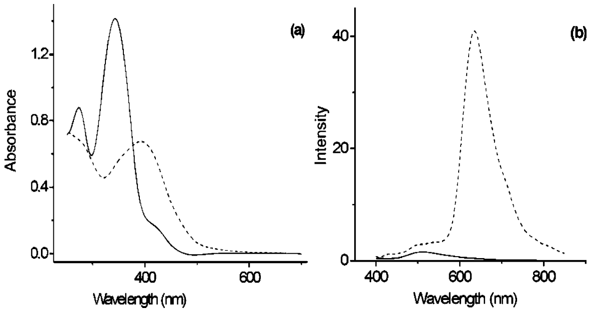

Figure 1. UV−vis spectra (a) and fluorescent spectra (b) (excitation was at 380 nm) for $\mathbf{H_2L^1}$ (5.0×10^{-5} M) in H_2O/CH_3OH (90:10, v/v) without (—) and with (---) the presence of an equivalent mole ratio of $Hg(NO_3)_2 \cdot 0.5H_2O$.

$0.5H_2O$ to the above solution, the fluorescence intensity at 530 nm increased, accompanied by a new strong band at around 635 nm with a ∼100-fold increase in the integrated emission ($\Phi \approx 0.022$; Figure 1b). The saturation behavior of the fluorescence intensity after the addition of 1 equiv of $Hg(NO_3)_2 \cdot 0.5H_2O$ and the linear response to the concentration of Hg(II) (see the Supporting Information) suggested the formation of a new compound from equivalent $\mathbf{H_2L^1}$ and Hg(II).

Further evidence for this new compound came from the independent synthesis of Hg(II) coordination compound **1** by the reaction of equivalent $Hg(NO_3)_2 \cdot 0.5H_2O$ with $\mathbf{H_2L^1}$ in CH_3OH at room temperature.[12] The X-ray crystal structure study and elemental analysis were clearly indicative of the occurrence of a Hg-triggered desulfurization and the existence of a cyclization product consequently.[13]

Compound **1** was a centrosymmetric-related dimer (Figure 2). The Hg(II) ion was in a five-coordination environment, bonded by a S atom, a N(1) atom of pyridine, an imine N(3) atom, a pyridazine N(5) atom, and a pyridine N(2A) atom from another ligand. The C−N and N−N bond distances in compound **1** were intermediate between the regular single and double bonds, indicating the extensive electron delocalization over the entire molecular skeleton. It is suggested that a new pyridazine ring was formed by the desulfurization of the Hg(II) ion. The decomposed SH^- group was likely to coordinate to the Hg(II) ion as an anionic donor, which was confirmed by the significantly shorter Hg−S bond compared with that shown in relative Hg(II) complexes derived from thiosemicarbazones.[14]

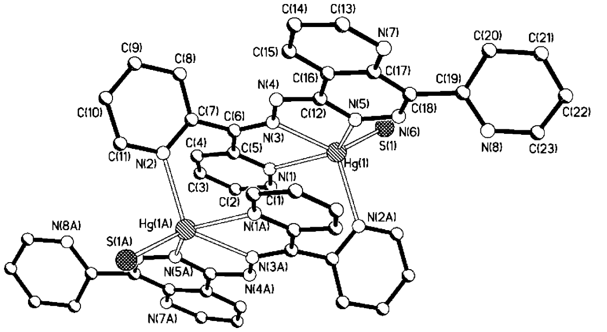

Figure 2. Perspective view of the molecular skeleton of compound **1**. H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg(1)−S(1) 2.414(2), Hg(1)−N(1) 2.459(6), Hg(1)−N(3) 2.372(6), Hg(1)−N(5) 2.338(6), Hg(1)−N(2A) 2.361(7), N(5)−N(6) 1.320(9), N(5)−C(12), 1.328(9), N(6)−C(18) 1.306(10); N(5)−Hg(1)−N(2A) 107.0(2), N(5)−Hg(1)−N(3) 67.9(2), N(2)−Hg(1)−N(3) 125.2(2), N(5)−Hg(1)−S(1) 110.4(2), N(2A)−Hg(1)−S(1) 99.0(2), N(3)−Hg(1)−S(1) 135.0(2), N(5)−Hg(1)−N(1) 135.0(2), N(2)−Hg(1)−N(1) 93.1(2), N(3)−Hg(1)−N(1) 67.6(2), S(1)−Hg(1)−N(1) 105.4(2). Symmetry codes: A, $1 - x$, $1 - y$, $-z$.

This reaction could be employed for Hg(II) detection with a high selectivity. To the H_2O/CH_3OH solution of $\mathbf{H_2L^1}$ (5.0×10^{-5} M) was added 5 equiv of other metal salts, and the fluorescence intensities were monitored by excitation at 380 nm. After 3 h, the solutions of $\mathbf{H_2L^1}$ (5.0×10^{-5} M) containing nitrate salts of Mg(II), Ca(II), Ba(II), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and even Ag(I) and Pb(II) did not show any significant changes in both the wavelengths and intensities of the emission, although most of the metal ions had the potential to form stable 4:4 metal/ligand metallocycles.[15] Upon the addition of Zn(II) and Cd(II), the luminescence intensities at 530 nm increased without any new emission bands appearing. The separation of more than 100 nm between the maximum wavelengths of the emission bands induced by Hg(II) and Zn(II) or Cd(II), respectively, suggested no interference from Zn(II) or Cd(II) in the fluorescent detection of Hg(II) at 635 nm. Because the Hg(II)-promoted cyclization reaction was irreversible and controlled by the reaction kinetics, the presence of Zn(II) or Cd(II) could not have any impact on the detection of Hg(II) in such aqueous media.

The competition measurements were carried out by the subsequent addition of other metal ions (5-fold excess), including alkali [Li(I), Na(I), and K(I)], alkaline-earth [Mg(II), Ba(II), and Ca(II)], and transition- and heavy-metal [Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), and even Pb(II) and Ag(I)] ions (Figure 3), to the solution of Hg(II). The results of neither the new emission band nor the enhancement in the fluorescence intensity associated with the addition of Hg(II) were obviously influenced, which is consistent with the hypothesis of the reaction mechanism. The only exception is the case of Cu(II), in which the

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(12) Compound **1** was synthesized as follows: $\mathbf{H_2L}$ (0.10 g, 0.23 mmol) and $Hg(NO_3)_2 \cdot 0.5H_2O$ (0.08 g, 0.23 mmol) were mixed and stirred in 20 mL of CH_3OH for 2 h at room temperature, with a red solution forming. After careful evaporation of the solution in air for a few days, orange crystals with a prism shape were formed. Anal. Calcd for $Hg_2C_{47}H_{40}N_{18}O_8S_2$: C, 38.93; H, 2.78; N, 17.38. Found: C, 39.34; H, 2.92; N, 17.03.

(13) Crystal data for compound **1**: $C_{48}H_{48}Hg_2N_{18}O_{12}S_2$, $M_r = 1534.34$, monoclinic, space group $P2_1/n$, $a = 7.676(5)$ Å, $b = 16.301(10)$ Å, $c = 22.599(14)$ Å, $\beta = 91.42(1)°$, $V = 2827(3)$ Å^3, $\rho_{cald} = 1.802$ Mg m^{-3}, $\mu = 5.574$ mm^{-1}, $Z = 2$, $T = 293$ K, R1 = 0.0579, wR2 = 0.1574. The intensities of compound **1** were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) using the *SMART* and *SAINT* programs; 4929 unique reflections were collected for 3388 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with *SHELXTL* version 5.1. All of the non−H atoms were refined anisotropically.

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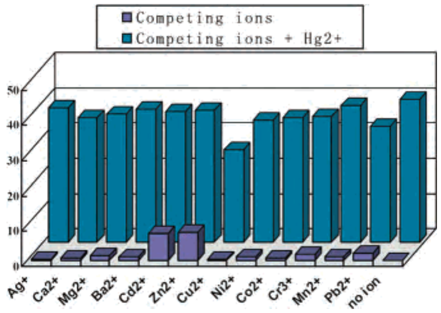

Figure 3. Fluorescence intensity change profiles of 50 μM of $\mathbf{H_2L^1}$ in H_2O/CH_3OH (90:10, v/v) in the presence of selected metal ions. The excitation wavelength was 380 nm, and the emission was monitored at 635 nm.

luminescent signal was quenched obviously. So, $\mathbf{H_2L^1}$ exhibited a selectivity for fluorescent detection of Hg(II) in an aqueous solution.

Furthermore, the reaction of $HgCl_2$ and $\mathbf{H_2L^1}$ also gave a mononuclear Hg(II) coordination compound **2**, with the thiocarbazone group being desulfurized (Figure 4).[16] As shown in Figure 4, the Hg(II) center in compound **2** was coordinated by two Cl ions, an imine N(3) atom, a pyridazine N(1), and a pyridine N(5) atom. It is clearly shown that the Hg-promoted cyclization of the $\mathbf{H_2L^1}$ ligand will not be influenced by the presence of different anions.

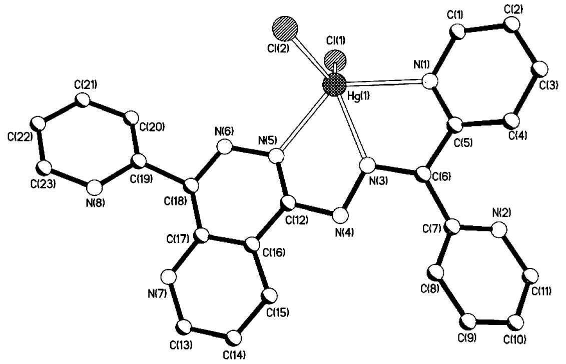

Figure 4. Perspective view of the molecular skeleton of compound **2**. H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Hg(1)−N(1) 2.414(5), Hg(1)−N(3) 2.342(4), Hg(1)−N(5) 2.360(5), Hg(1)−Cl(1) 2.438(1), Hg(1)−Cl(2) 2.437(1), N(5)−N(6) 1.382(7), N(5)−C(12), 1.356(6), N(6)−C(18) 1.346(6); N(5)−Hg(1)−N(1) 130.3(2), N(1)−Hg(1)−N(3) 67.6(1), N(5)−Hg(1)−N(3) 63.6(2), N(1)−Hg(1)−Cl(1) 98.9(1), N(5)−Hg(1)−Cl(1) 102.2(1), N(3)−Hg(1)−Cl(1) 126.1(1), Cl(1)−Hg(1)−Cl(2) 120.41(4).

Another solid proof of the Hg(II)-promoted desulfurization and cyclization came from the isolation of neat Hg(II)-free cyclization product **HL**.[17] As expected, compound **HL** itself exhibited a bright emission band at about 670 nm in a dimethyl sulfoxide (DMSO) solution. Upon the addition of 1 equiv of $Hg(NO_3)_2 \cdot 0.5H_2O$, the fluorescence intensity at 670 nm increased dramatically. However, the presence of other metal ions did not induce any obvious luminescence changes of the cyclization product **HL** in a DMSO solution, which confirmed the involvement of a specific interaction between Hg(II) and **HL**. Titration tests (see the Supporting information) of **HL** with Hg(II) exhibited that compound **HL** could also act as a highly sensitive fluorescent sensor for Hg(II) in a luminescence enhancement signaling behavior.

In summary, an ion-selective fluorescent sensor $\mathbf{H_2L^1}$ was prepared for detecting Hg(II) in aqueous media through Hg-promoted intramolecular cyclization. The irreversible response of the desulfurization reaction allows this sensor to have the potential of being a fluorescent chemodosimeter.

Acknowledgment. This work is supported by the National Natural Science Foundation of China.

Supporting Information Available: CIF files of the Hg(II)-containing compounds **1** and **2**, general notes and procedures, UV−vis and fluorescent titrations for $\mathbf{H_2L^1}$ with the addition of Zn(II)/Cd(II), ^{1}H NMR spectrum of **HL**, and fluorescent titration of **HL** with the addition of Hg(II). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) For compound **2**. Elem anal. Calcd for $HgC_{25}H_{24}N_8O_2Cl_2$: C, 40.58; H, 3.27; N, 15.14. Found: C, 40.12; H, 2.98; N, 15.37. Crystal data of compound **2**: $HgC_{23}H_{16}Cl_2N_8$, $M_r = 675.93$, monoclinic, space group $P2_1/n$, $a = 10.5580(10)$ Å, $b = 14.5870(10)$ Å, $c = 15.3600(10)$ Å, $\beta = 107.090(10)°$, $V = 2261.1(3)$ Å^3, $\rho_{cald} = 1.986$ Mg m^{-3}, $\mu = 7.074$ mm^{-1}, $Z = 4$, $T = 298$ K. A total of 4379 unique reflections were collected on a Siemens SMART CCD system, R1 = 0.0462, and wR2 = 0.0858 for 3145 reflections with $I > 2\sigma(I)$.

(17) The compound **HL** was synthesized as follows: The mixture of $\mathbf{H_2L^1}$ (0.44 g, 1 mmol) and $Hg(NO_3)_2 \cdot 0.5H_2O$ (0.33 g, 1 mmol) in 40 mL of CH_3OH were refluxed for 6 h. Upon the addition of 1.2 mL of NH_4S (8% aqueous solution) and further stirring for 4 h, a dark precipitate formed and was filtered off. The crude product that was obtained by evaporating the filtration under reduced pressure was chromatographed on silica gel with a CH_2Cl_2/MeOH (1:1) solution as the eluent. Yield: 0.18 g, 45%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35−9.37 (H, d, $J = 6.8$ Hz), 9.26−9.28 (H, d, $J = 8.8$ Hz), 8.96−9.00 (H, t, $J = 8.0$ Hz), 8.83−8.84 (H, d, $J = 4.8$ Hz), 8.77−8.79 (H, d, $J = 4.8$ Hz), 8.72−8.74 (H, d, $J = 8.0$ Hz), 8.59−8.60 (H, d, $J = 4.4$ Hz), 8.39−8.43 (H, t, $J = 7.2$ Hz), 8.13−8.16 (H, t, $J = 6.8$ Hz), 8.144 (H, s, NH), 8.08−8.12 (H, t, $J = 8.8$ Hz), 8.00−8.02 (H, d, $J = 8.0$ Hz), 7.75−7.77 (H, d, $J = 8.0$ Hz), 7.67−7.70 (H, t, $J = 6.4$ Hz), 7.64−7.70 (H, t, $J = 6.4$ Hz), 7.56−7.59 (H, t, $J = 6.0$ Hz).