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 of 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.

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0.5H₂O 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 (Φ ≈ 0.022; Figure 1b). The saturation behavior of the fluorescence intensity after the addition of 1 equiv of Hg(NO₃)₂·0.5H₂O and the linear response to the concentration of Hg(II) (see the Supporting Information) suggested the formation of a new compound from equivalent H₂L¹ 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(NO₃)₂·0.5H₂O with H₂L¹ in CH₃OH at room temperature. 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.

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.

This reaction could be employed for Hg(II) detection with a high selectivity. To the H₂O/CH₃OH solution of H₂L¹ (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 H₂L¹ (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. 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: H₂L¹ (0.10 g, 0.23 mmol) and Hg(NO₃)₂·0.5H₂O (0.08 g, 0.23 mmol) were mixed and stirred in 20 mL of CH₃OH 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 Hg₄C₁₅H₂₆N₁₅O₂₆S₂: 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: Ca₄H₂Hg₂N₄O₂S₂, Mᵣ = 1534.34, monoclinic, space group P2₁/n, a = 7.676(5) Å, b = 16.301(10) Å, c = 22.599(14) Å, β = 91.42(1)°, V = 2827(3) Å³, μ = 1.802 mg 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 Kr (λ = 0.71073 Å) using the SMART and SADABS programs; 4929 unique reflections were collected for 3388 reflections with I > 2σ(I). The structure was solved by direct methods and refined on F² by full-matrix least-squares methods with SHELXTL version 5.1. All of the non–H atoms were refined anisotropically.


Hg-promoted cyclization of the N(1), and a pyridine N(5) atom. It is clearly shown that the coordinated by two Cl ions, an imine N(3) atom, a pyridazine shown in Figure 4, the Hg(II) center in compound 2 and cyclization came from the isolation of neat Hg(II)-free influenced by the presence of different anions.

Furthermore, the reaction of HgCl₂ and H₃L₁ also gave a mononuclear Hg(II) coordination compound 2, with the thiocarbazone group being desulfurized (Figure 4).² 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 H₃L₁ ligand will not be influenced by the presence of different anions.

Another solid proof of the Hg(II)-promoted desulfurization and cyclization came from the isolation of neat Hg(II)-free

(16) For compound 2. Elemen anal. Calcd for HgC₃₂H₳₇N₄O₂Cl₂: C, 40.58; H, 3.27; N, 15.14. Found: C, 40.12; H, 2.98; N, 15.37. Crystal data of compound 2: Hg₂C₃₂H₳₇N₄O₂Cl₂·H₂O, Mf = 675.93, monoclinic, space group P2₁/a, a = 10.5580(10) Å, b = 14.5870(10) Å, c = 15.3600(10) Å, β = 107.09010(10)°, V = 2261.1(3) Å³, ρcalc = 1.986 Mg m⁻³, μ = 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 l > 2σ(l).

(17) The compound HL was synthesized as follows: The mixture of H₃L₁ (0.44 g, 1 mmol) and Hg(NO₃)₂·0.5H₂O (0.33 g, 1 mmol) in 40 mL of CH₃OH were refluxed for 6 h. Upon the addition of 1.2 mL of NH₂S (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 CH₃Cl/MeOH (1:1) solution as the eluent. Yield: 0.18 g, 45%. ¹H NMR (400 MHz, DMSO-d₆): 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).

In summary, an ion-selective fluorescent sensor H₃L₁ 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.

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Supporting Information Available: CIF files of the Hg(II)-containing compounds 1 and 2, general notes and procedures, UV−vis and fluorescent titrations for H₃L₁ with the addition of Zn(II)/Cd(II), ¹H 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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