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Azobenzene-Based Colorimetric Chemosensors for Rapid Naked-Eye Detection of Mercury(II)

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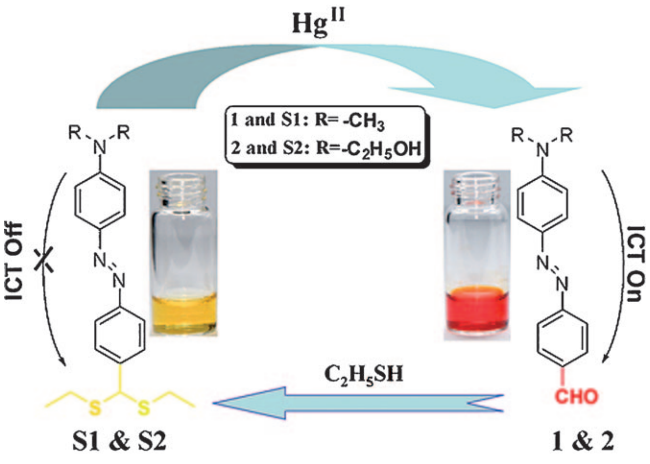
Abstract: Two new highly selective colorimetric chemosensors for Hg^{2+}, based on azobenzene and highly selective Hg^{2+}-promoted deprotection of a dithioacetal have been designed and synthesized. In the presence of as little as 20 μM Hg^{2+}, the sensors change their color from light yellow to deep red, which can easily be observed by the naked eye. The underlying signaling mechanism is intramolecular charge transfer (ICT). The sensors have good selectivity for Hg^{2+} with respect to several common alkali, alkaline earth, and transition metal ions. Furthermore, they can be used for in-the-field measurements by virtue of a dipstick approach without any additional equipment.

Keywords: azo compounds · charge transfer · colorimetry · mercury · sensors

Introduction

Mercury pollution is a global problem and has been receiving much attention.[1] Both human activities, including gold mining, solid-waste incineration, and fossil-fuel combustion,[2] and nonanthropogenic sources, such as volcanic and oceanic emissions and forest fires,[3] have caused rapid increase of Hg^{2+} levels in the environment. Ionic mercury is converted to methylmercury by bacteria when it enters the environment and subsequently bioaccumulated through the food chain. Mercury accumulation in the body can cause various neurological damage.[4] Thus, a convenient and fast method to detect Hg^{2+} is in high demand. Recently, considerable efforts have been made to develop straightforward methods such as fluorescence[5] or electrochemical changes[6] for rapid detection of mercury ions. Among these methods, colorimetric sensors are especially promising because the color change can easily be observed by the naked eyes, thus requiring less labor and no equipment. A large number of colorimetric sensors for Hg^{2+} have been developed.[7] As potential sensing systems, specific chemical reactions with high selectivity for toxic metal ions have drawn great attention. The reaction between the sensor molecule and target species should give a unique spectroscopic change.[8] Because of the strong thiophilicity of Hg^{2+}, many fluorescent chemodosimeters with high selectivity, long-range excitation and emission wavelengths, and high quantum yield have been designed on the basis of the mercury desulfurization reaction.[9]

Here we report two colorimetric chemosensors (**S1** and **S2**) for Hg^{2+} based on azo derivatives and using intramolecular charge transfer (ICT) as signaling mechanism, in which the azobenzene moiety acts as electron donor and the aldehyde group as the electron acceptor. The design of these two sensors took advantage of the well-known azobenzene structure and the highly selective Hg^{2+}-promoted deprotection of the dithioacetal, as we reported previously.[10] Precursors **1** and **2** of **S1** and **S2**, respectively, were synthesized according to previous literature.[11] A straightforward protection reaction between the aldehyde group and ethyl mercaptan gave sensors **S1** and **S2** in high yields (Scheme 1). While the formyl group is electron-withdrawing, after mercaptan



Scheme 1. Hg^{2+}-sensing process of **S1** and **S2**.

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protection, the resulting dithioacetal moiety can be regarded as a weak electron donor. Addition of Hg^{2+} converts the protected aldehyde group back to the original aldehyde, and the D–π–D′ structures in **S1** and **S2** are transformed into D–π–A structures (Scheme 1). This increases the degree of ICT and resulting in an obvious redshift of the absorption bands of the compounds.[12] Addition of Hg^{2+} to dilute solutions of **S1** and **S2** changes the color from light yellow to deep red in a process visible to the naked eye (see Scheme 1). Here we describe the synthesis and the spectroscopic evaluation of both colorimetric chemosensors in detail.

Results and Discussion

Synthesis and structural characterization: Compounds **S1** and **S2** were prepared by the protection reaction between ethyl mercaptan and aldehydes **1** and **2** (Scheme 1), in accordance with our previous report.[10] The synthetic route is simple and purification easy.

Compounds **S1** and **S2** exhibit good solubility in common organic solvents such as DMF, CH_3Cl_3, CH_3CN, and THF. They were characterized by spectroscopic methods, and both gave satisfactory spectral data (see Experimental Section). The signal of the aldehyde proton at $\delta = 10.04$ ppm in the ^1H NMR spectrum of **2** (see Figure S1 in the Supporting Information) disappeared in the spectrum of **S2**. In the FTIR spectrum of **S2** (see Figure S2 in the Supporting Information) the strong band at 1685 cm^{-1} ascribed to C=O stretching of the aldehyde group disappeared owing to the protection reaction between ethyl mercaptan and **2**. The absorption maximum centered at about 460 nm in the UV/Vis spectrum of **2** (see Figure S3 in the Supporting Information) shifted to 420 nm in dithioacetal **S2**. The above results confirm conversion of aldehyde **2** to dithioacetal **S2**.

Hg^{2+}-sensing properties: As shown in Scheme 1 and Figure 1, compound **1** is deep red with maximum absorption wavelength centered at about 455 nm in its UV/Vis spectrum, corresponding to the ICT character of the chromophore due to the pull–push effect. After reaction with ethanethiol, the resulting dithioacetal **S1** showed a light yellow color with maximum absorption wavelength centered at about 420 nm, due to a change in the electronic property and hence different ICT efficiency. On adding Hg^{2+} ions to a dilute solution of **S1** in CH_3CN, the absorption maximum shifted from 420 to 455 nm, with an isosbestic point at about 440 nm, indicating formation of aldehyde **1**. Surprisingly, with increasing concentrations of Hg^{2+} ions, not only did the absorption maximum further shift from 455 to 515 nm with an isosbestic point at about 470 nm, but also the new band at 515 nm showed a larger molar absorption coefficient than the original one. The intensities at 420 and 515 nm are compared in Figure S4 (see the Supporting Information), which shows that intensity change almost linearly with the concentration of Hg^{2+} ions. The different colors before and after addition of Hg^{2+} ions could be easily distinguished by the naked eye (Scheme 1 and Figure 1), and this validates our design of colorimetric chemosensors for Hg^{2+} ions based on the ITC mechanism and the Hg^{2+}-promoted deprotection of dithioacetals.

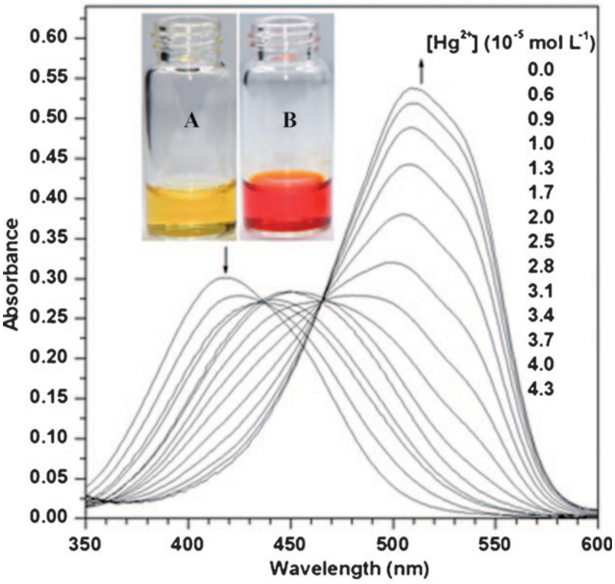


Figure 1. UV/Vis spectra of **S1** (10 μм, CH_3CN) in the presence of increasing concentration of Hg^{2+}. Inset: Photograph of **S1** (A) and **S1**+Hg^{2+} (B, 50 μм).

We studied the influence of traces of water in the Hg^{2+} solution on the sensing process (see Figure S5 in the Supporting Information). The absorption decreased only to a very limited degree, even when 100 μL of H_2O was introduced, which would not affect the results of the titration experiment (Figure 2, inset V). Thus, the Hg^{2+}-promoted deprotection reaction of dithioacetal **S1** occurred as expected, and the color change was observed.

Figure 2. A_{515}/A_{420} change profile of **S1** (10 μм, CH_3CN) in the presence of various metal ions (40 μм). Inset: Photograph of **S1** in the presence of various metal ions (50 μм). A: **1** (1 mM); B: **S1** (100 μм); C–V: **S1**+Hg^{2+}, Ba^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, K^+, Na^+, Ag^+, Li^+, Al^{3+}, Fe^{3+}, Cr^{3+}, H_2O (100 μL).

To assess the specificity of our sensor towards Hg^{2+}, various ions were examined in parallel under the same conditions. As shown in Figure 2 and Figure S6 of the Supporting Information, the reaction of **S1** with Hg^{2+} resulted in strong absorbance, whereas Ba^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, K^+, Na^+, and Ag^+ showed no change, and Fe^{3+}, Al^{3+}, and Cr^{3+} negligible changes. Therefore, **S1** has much higher selectivity for Hg^{2+} than the other ions examined here. This unique property enabled Hg^{2+} to be detected directly by the naked eye over other species (Figure 2). In our previous report on fluorescent sensors,[10] Ag^+ could also promote conversion of dithioacetal to aldehyde to some degree, similar to Hg^{2+}. However, Ag^+ did not induce any apparent absorption change even at a concentration of 50 μM (Figures 2 and S6d in the Supporting Information), that is, by adjusting the chemical structure, better selectivity of this kind of chemosensors towards Hg^{2+} could be achieved.

To improve the solubility of **S1** in water, **S2** bearing two hydroxyl groups was synthesized (Scheme 1). Compound **S2** exhibited a similar absorption profile to **S1**, owing to the similar structure. Surprisingly, **S2** displayed much better Hg^{2+}-sensing performance than **S1**. As shown in Figure 3, a change in absorption occurred even on addition of as little as 2 μM Hg^{2+}. With increasing concentrations of Hg^{2+}, the typical strong absorption band of **S2** at 420 nm gradually decreased, and a new absorption band centered at 515 nm with a larger molar absorption coefficient than **S1** appeared. This 515 nm absorption was responsible for the color change and can be observed by the naked eye. The UV/Vis spectra of dithioacetal **S2** before and after the addition of Hg^{2+} also support this transformation (see Figure S7 in the Supporting Information).

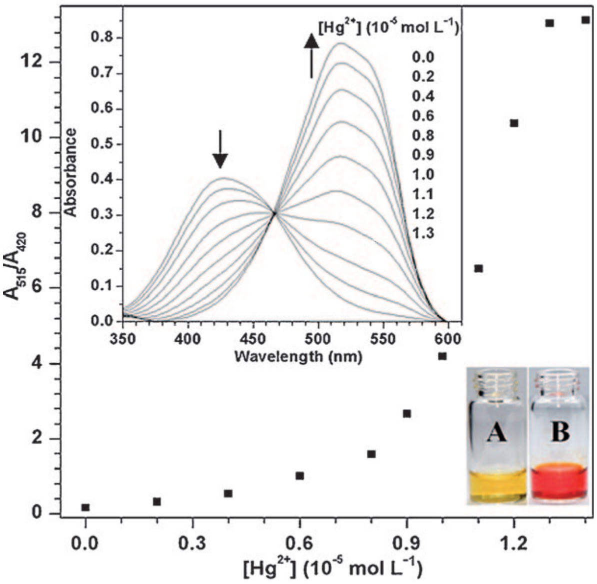


Figure 3. Ratiometric calibration curve A_{515}/A_{420} of **S2** (10 μM, CH_3CN) as a function of the concentration of Hg^{2+}. Inset: UV/Vis spectra of **S2** (10 μM, CH_3CN) in the presence of increasing concentration of Hg^{2+}, and photograph of **S2** (A) and **S2**+Hg^{2+} (B, 50 μM).

Like **S1**, **S2** also shows good selectivity towards Hg^{2+}. Traces of water and metal ions caused almost no apparent absorption change (see Figures S8–S10 in the Supporting Information). In Figure 3 and Figure S8 in the Supporting Information, the A_{515}/A_{420} ratio of **S2** in CH_3CN was almost 12-fold for Hg^{2+}, while the values for the other metal ions were less than 0.5-fold. The sensing process could also be observed visually (see Charts S1 and S2 in the Supporting Information). These results indicate that **S2** is an Hg^{2+}-specific colorimetric sensor.

The ultimate goal of this research is to develop naked-eye colorimetric sensors. Compound **S2** has better sensitivity and lower detection limit and potentially it can be used for direct naked-eye sensing of Hg^{2+}. Figure 4 shows the results of adding various amounts of Hg^{2+} to a 100 μM solution of **S2** in CH_3CN. Although not as sensitive as measurements by UV/Vis spectrometer, we could easily distinguish color changes at concentrations as low as 20 μM of Hg^{2+}.

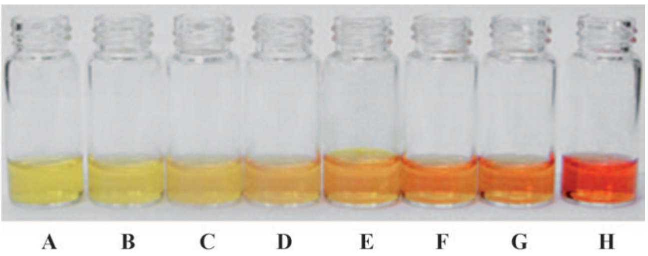


Figure 4. Photograph of **S2** (10 μM, CH_3CN) in the presence of increasing concentrations of Hg^{2+}. A–H): 0, 1, 1.5, 2, 2.5, 3, 4, and 5×10^{-5} mol L^{-1}.

Taking advantage of the two hydroxyl group in **S2**, we attempted to conduct the sensing process in in H_2O/CH_3CN (1/9) at pH 7.0 maintained with HEPES buffer (20 mM). As shown in Figure 5, the absorption maximum wavelength of **S2** shifted from 420 to 460 nm, with an isosbestic point at about 440 nm, indicating formation of aldehyde **2**. The transformation was confirmed by UV/Vis spectra (see Figure S11 in the Supporting Information) with that of aldehyde **2** for comparison. The inset of Figure 5 shows a good linear relationship between the A_{460}/A_{420} ratio and the concentration of Hg^{2+} in the range of 0–12 μM. A linear regression curve was simulated, and the point at which it crossed the abscissa was taken as the detection limit (ca. 0.4 μM).[13] As shown in Figure S12 of the Supporting Information, dithioacetal **S2** can also function in H_2O/CH_3CN (2/8), but the sensing behavior is not as good as in organic solvents and solvent mixtures with less H_2O (H_2O/CH_3CN 1/9). One reason could be the poor solubility of **S2** in the mixed solvents. Further research to develop water-soluble sensors by utilizing this idea is ongoing. The specificity of **S2** towards Hg^{2+} in H_2O/CH_3CN solution was also investigated, but the performance was not as good as in pure CH_3CN (see Figures S8 and S13 in the Supporting Information).

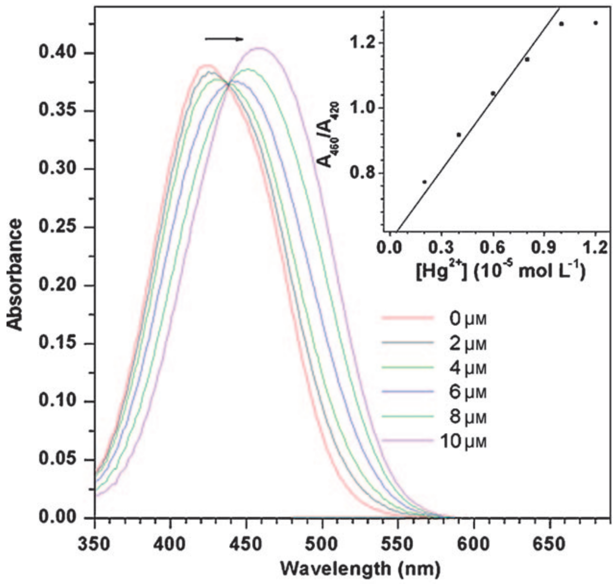
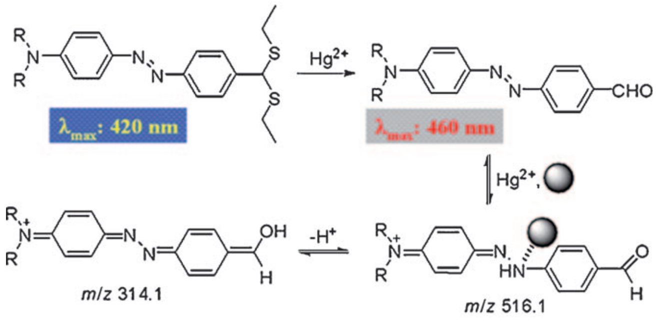


Figure 5. UV/Vis spectra of **S2** (10 μM) in the presence of increasing concentrations of Hg^{2+} in CH_3CN/H_2O (9/1, 20 mM HEPES, pH 7.0). Inset: Ratiometric calibration curve A_{460}/A_{420} as a function of the concentration of Hg^{2+}.

On addition of Hg^{2+} ions to a solution of **S2** in pure CH_3CN, the absorption maximum of **S2** changed by approximately 95 nm (from 420 to 515 nm), with an obvious color change. However, after addition of Hg^{2+} ions to a solution in CH_3CN/H_2O, the absorption profile only changed a little (from 420 to 460 nm). To confirm the formation of the resulting products and gain insight into the sensing mechanism, control experiments were conducted. Dithioacetal **S2** was treated with Hg^{2+} ions and the reaction product (complex I) isolated, and aldehyde **2** was mixed with Hg^{2+} ions to give complex II. Partial ^1H NMR spectra of complexes I and II are shown in Figure 6 with those of **S2** and **2** for comparison. The resonance of the aldehyde proton appeared at $\delta = 10.04$ ppm. Both the aldehyde proton and the phenyl protons of complex I displayed small upfield shift compared to aldehyde **2**, indicating a mutual effect between the resultant aldehyde and Hg^{2+}. In addition, the ^1H NMR spectra of complex I was the same as that of complex II. An absorption peak centered at about 1605 cm^{-1} in the IR spectrum of **2** (see Figure S14 in the Supporting Information) indicated the presence of −N=N− groups. After addition of Hg^{2+} ions, a new broad peak at 1635 cm^{-1} appeared as the result of a reaction between **2** and Hg^{2+} ions to form an N-bound Hg^{2+} complex (Scheme 2). ESI mass spectra (see Figure S15 in the Supporting Information) revealed a main peak at 314.4 after Hg^{2+} ions were added to **2**, corresponding to $[\mathbf{2}-H]^+$ (calcd *m/z* 314.1). A weak peak at about 515.9 was assigned to traces of $[\mathbf{2}+Hg-H]^{2+}$ (calcd *m/z* 516.1), which leads to changes in the absorption spectra and a color change. UV/Vis titrations in CH_3CN supported the formation of a complex on treatment of **2** with Hg^{2+} (see Figures S16 and S17 in the Supporting Information), consistent with a previous report.[14] In CH_3CN/H_2O, smaller changes in the absorption spectra of the sensors may be due to interference of water in the reaction between **2** and Hg^{2+}. Although the above results were unexpected, they are beneficial to sensors due to the much more apparent color changes before and after the addition of the analytes, which led to a much larger red shift (95 nm) in absorption and much more pronounced color change.



Scheme 2. Postulated response process of **2** towards Hg^{2+}.

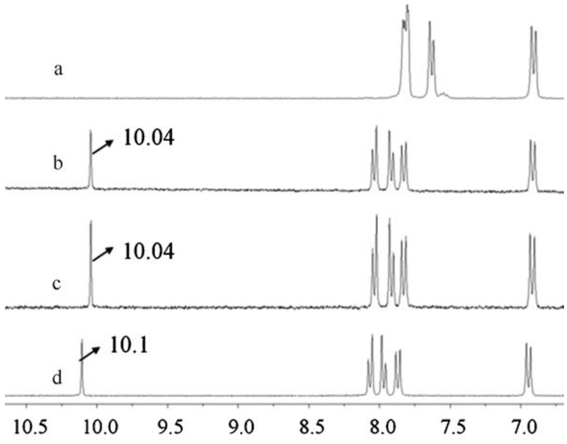


Figure 6. ^1H NMR spectra of **S2** (a), complex I (b), complex II (c), and aldehyde **2** (d) in [D_6]acetone.

Test strips, prepared by immersing filter paper into a solution of dithioacetal **S2** in CH_3CN (1×10^{-3} mol L^{-1}) and drying in air, were used to determine the suitability of a dipstick method for detection of Hg^{2+}, similar to that commonly used for pH measurements. When the test strips coated with **S2** were immersed into aqueous solutions of Hg^{2+} ions with different concentrations, immediate color change from yellow to pink was observed (Figure 7). The detection limit of the test strips was relatively low (10^{-4} mol L^{-}). Development of such an approach is attractive for in-the-field measurements that would not require any additional equipment.

Conclusion

New naked-eye colorimetric chemosensors **S1** and **S2** were developed by coupling aldehyde protection/Hg^{2+}-promoted

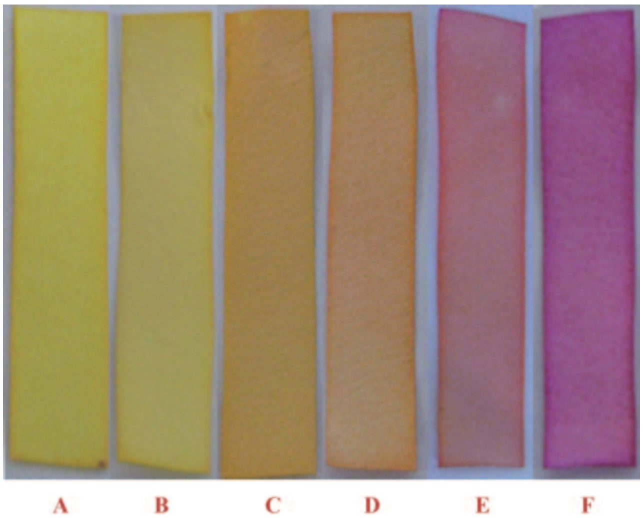


Figure 7. Photographs of test strips of **S2** (A), **S2**+Hg^{2+} (10^{-5} mol L^{-1}, B), **S2**+Hg^{2+} (10^{-4} mol L^{-1}, C), **S2**+Hg^{2+} (5×10^{-4} mol L^{-1}, D), **S2**+Hg^{2+} (10^{-3} mol L^{-1}, E), and **S2**+Hg^{2+}(5×10^{-3} mol L^{-1}, F).

deprotection with the ICT mechanism, and the sensing properties were studied. Both probes displayed high sensitivity and selectivity for Hg^{2+} with respect to several common alkali, alkaline earth, and transition metal ions. In addition, **S1** and **S2** could serve as practical colorimetric sensors for in-the-field measurements that would not require any additional equipment by virtue of a dipstick approach.

Experimental Section

Materials and instrumentation: Dichloromethane was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. All reagents were of analytical-reagent grade and used without further purification. Doubly distilled water was used in all experiments. The ^{1}H and ^{13}C NMR spectra were measured on Varian Mercury300 spectrometer with tetramethylsilane (TMS; $\delta=0$ ppm) as internal standard. FTIR spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on NaCl pellets. The ESI mass spectra were measured on a Finnigan LCQ advantage mass spectrometer. UV/Vis spectra were obtained with a Shimadzu UV-2550 spectrometer, and the pH values were determined by using a DELTA 320 PH dollar. The thermometer used for measurement of melting points was uncorrected.

Synthesis of compound S1: Under dry argon, **1** (71 mg, 0.28 mmol) and ethanethiol (0.052 mL, 0.7 mmol) were dissolved in dry dichloromethane (10 mL) with BF_3•Et_2O (0.1 mL, 0.84 mmol) as Lewis acid. After stirring at 0 °C for 3 h, 0.1 mol L^{-1} aqueous $NaHCO_3$ was added to adjust the pH value of the resultant mixture to 8–9. The resultant mixture was extracted with diethyl ether several times, the organic layers were combined, and the product was recrystallized from dichloromethane to afford **S1** as a yellow solid (90.5 mg, 90 %). M.p. 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.79$–7.81 (d, $J=6.0$ Hz, 2 H), 7.72–7.74 (d, $J=6.0$ Hz, 2 H), 7.46–7.49 (d, $J=9.0$ Hz, 2 H), 6.67–6.70 (d, $J=9.0$ Hz, 2 H), 4.91 (s, 1 H), 3.02 (s, 6 H), 2.44–2.58 (m, 4 H), 1.14–1.18 ppm (t, $J=6.0$ Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.81$, 141.00, 128.34, 124.95, 122.27, 111.43, 52.06, 40.22, 26.18, 14.27 ppm; UV/Vis (CH_3CN): $\lambda_{max}=420$ nm; MS (ESI): *m/z* 360.39 [M^+], calcd 359.55.

Synthesis of compound S2: Under dry argon, compound **2** (88 mg, 0.28 mmol) and ethanethiol (0.052 mL, 0.7 mmol) were dissolved in dry dichloromethane (10 mL) with BF_3•Et_2O (0.1 mL, 0.84 mmol) as Lewis acid. After stirring at 0 °C for 2 h, 0.1 mol L^{-} aqueous $NaHCO_3$ was added to adjust the pH of the mixture to 8–9. The resultant mixture was extracted with diethyl ether several times, the organic layers were combined, and the product was purified by column chromatography with ethyl acetate/methanol (11/1) as eluent to afford **S2** as an orange solid (110 mg, 94 %). M.p. 87–88 °C; ^{1} H NMR (300 MHz, $CDCl_3$): $\delta=7.79$–7.87 (m, 4 H), 7.54–7.57 (d, $J=9.0$ Hz, 2 H), 6.75–6.78 (d, $J=9.0$ Hz, 2 H), 4.98 (s, 1 H), 3.95 (s, 2 H), 3.72 (s, 2 H), 3.07 (s, 2 H), 2.55–2.62 (m, 4 H), 1.21–1.26 ppm (t, $J=7.5$ Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=152.75$, 150.53, 144.15, 142.19, 128.68, 125.27, 122.63, 112.20, 60.66, 55.45, 52.35, 26.50 ppm; UV/Vis (in CH_3CN): $\lambda_{max}=420$ nm; MS (ESI) *m/z* 420.54 [M^+], calcd 419.60.

Preparation of solutions of metal ions: 1 mmol of each inorganic salt ($NaNO_3$, KNO_3, LiCl, $Ba(NO_3)_2$, $AgNO_3$, $Cr(NO_3)_3$•$9H_2O$, $CoCl_2$·$6H_2O$, $Ca(NO_3)_2$•$4H_2O$, $Pb(NO_3)_2$, $Ni(NO_3)_2$•$6H_2O$, $Zn(NO_3)_2$•$6H_2O$, $Cu(NO_3)_2$•$3H_2O$, $Al(NO_3)_3$•$9H_2O$, $Fe(NO_3)_3$•$9H_2O$, $MnSO_4$•$2H_2O$, $Cd(SO_4)$•$8H_2O$, $(NH_4)_2Fe(SO_4)_2$·$6H_2O$, $MgSO_4$, and $Hg(ClO_4)_2$•$3H_2O$) was dissolved in distilled water (10 mL) to afford a 1×10^{-1} mol L^{-} aqueous solution. The stock solutions were diluted to desired concentrations with water when needed.

UV absorption changes of S1 due to Hg^{2+} ions: A solution of **S1** (1.0×10^{-5} mol L^{-}) was prepared in CH_3CN. A solution of Hg^{2+} (1×10^{-3} mol L^{-}) was prepared in distilled water. A solution of **S1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the absorption spectrum recorded. The Hg^{2+} solution was introduced in portions and absorption changes were recorded at room temperature each time.

UV absorption changes of S1 due to different metal ions: A solution of **S1** (1×10^{-5} mol L^{-}) was prepared in CH_3CN. The solutions of metal ions (1×10^{-1} mol L^{-}) were prepared in distilled water. A solution of **S1** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the absorption spectrum was recorded. Different ion solutions were introduced and the changes in absorption were recorded at room temperature each time.

UV absorption changes of S2 due to Hg^{2+} ions: Solutions of **S2** (1.0×10^{-5} mol/L) were prepared in CH_3CN and CH_3CN/H_2O (9/1, 20 mM HEPES, pH 7.0). A solution of Hg^{2+} (1×10^{-3} mol/L) was prepared in distilled water. A solution of **S2** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the absorption spectrum was recorded. The Hg^{2+} ion solution was introduced in portions and absorption changes were recorded at room temperature each time.

UV absorption changes of S2 due to different metal ions: A solution of **S2** (1×10^{-5} mol L^{-}) was prepared in CH_3CN. Solutions of metal ions (1×10^{-1} mol L^{-}) were prepared in distilled water. The solution of **S2** (3.0 mL) was placed in a quartz cell (10.0 mm width) and the absorption spectrum was recorded. Different ion solutions were introduced and the changes of the absorption changes were recorded at room temperature each time.

Acknowledgements

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