

Azo 8-hydroxyquinoline benzoate as selective chromogenic chemosensor for Hg²⁺ and Cu²⁺

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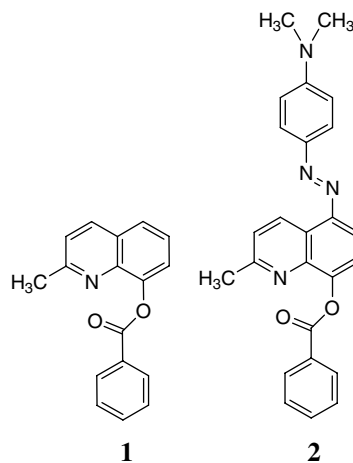
Abstract—Azo 8-hydroxyquinoline benzoate (**2**) was synthesized and studied to detect metal ions. Distinct color change was found for compound **2** in the presence of transition metal ions Hg²⁺ or Cu²⁺ in CH₃CN, respectively, which makes it possible for distinguishing Hg²⁺ and Cu²⁺ from other metal ions by the ‘naked eye’.
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The design and synthesis of new chemosensors for metal ions is an important subject in the field of supramolecular chemistry due to their fundamental role in biological, environmental, and chemical processes.¹ Particularly, the recognition and detection for Hg²⁺ and Cu²⁺ is of growing interest because they are considered as highly noxious elements.² Some examples of chromogenic³ and fluorescent⁴ chemosensors, electrochemical devices,⁵ biosensors,⁶ and sensors based on mass changes⁷ have been reported over the past years. Colorimetric sensors are popular due to their capability for ‘naked eye’ detection without resorting to any expensive instruments. To develop simple-to-use and naked-eye diagnostic tools, a great effort has recently been made for the design and synthesis of selective chromogenic sensors for Hg²⁺ and Cu²⁺.⁸

8-Hydroxyquinoline benzoates have been used as receptors for Hg²⁺.⁹ However, the absorption spectral change in ultraviolet (UV) region restrained their application in practicality. Azo dye is one type of important colorimetric sensor for cations and anions. In the presence of some special ion, the strong receptor–ion interaction causes the absorption band of azo dye shift to visible light region.¹⁰ In this letter, azo group was introduced to 8-hydroxyquinoline benzoate and a new compound

benzoic acid 5-(4-dimethylamino-phenylazo)-2-methylquinolin-8-yl ester (**2**) (Scheme 1) was easily synthesized to detect metal ions. Distinct color change was found for **2** in the presence of transition metal ions Hg²⁺ or Cu²⁺ in CH₃CN.

For comprehensive comparison, benzoic acid 2-methylquinolin-8-yl ester (**1**) was synthesized by a previously reported procedure.⁹ Compound **2** was synthesized by a diazo-reaction of 2-methyl-8-hydroxyquinoline with arylamine, followed by esterification with benzoyl chloride.¹¹ The analogous structures of **1** and **2** were characterized by ¹H NMR, ¹³C NMR spectra, and MS



Scheme 1. Molecular structures of **1** and **2**.

Keywords: Chromogenic chemosensor; Hg²⁺; Cu²⁺.

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(EI) (see ESI).¹² Further structure information of **2** was obtained from single-crystal X-ray diffraction study (see ESI). The CCDC reference number of **2** is 299042.

The UV–vis absorption spectra of **1** and **2** were measured in CH₃CN (2.0×10^{-5} mol L⁻¹) and the corresponding data are shown in ESI. Compound **2** exhibits a maximal absorption band at 445 nm, which is obviously red-shifted compared with that of **1** ($\lambda_{\max} = 276$ nm), indicating that the introduction of azo group improves the chromogenic ability of the 8-hydroxyquinoline benzoate. Moreover, the extinction coefficients are 5.7×10^3 (**1**) and 3.1×10^4 (**2**) mol⁻¹ L cm⁻¹, respectively, revealing that **2** has a stronger ability of absorbing light than **1**.

The complexation abilities of **1** and **2** with Hg²⁺ were investigated by the UV–vis absorption technique. In our present experiments, the mercury source Hg(ClO₄)₂ was gradually added to a solution of **1** and **2** in CH₃CN. Figure 1 shows UV–vis absorption spectra of **2** with various concentrations of Hg²⁺. Notably, upon addition of Hg²⁺, the characteristic strong absorption band at 445 nm decreased, and a new band centered at 518 nm arose, corresponding to a λ_{\max} (abs) red-shift of 73 nm and an isobestic point at 476 nm, which indicated the formation of a new compound. At the same time, an apparent color change from yellow to red in ambient light could be observed by the ‘naked eye’ (see ESI). However, no apparent color change occurred for **1** upon addition of Hg²⁺ in CH₃CN solution because the absorption band red-shifted only in UV region (see ESI). This fact indicated that the presence of azo group improves the chromogenic ability of sensors for Hg²⁺. Furthermore, the red-shift of the absorption band of **1** confirmed the binding of Hg²⁺ to quinoline N together with carbonyl O, which was consistent with the literature.⁹ We believe that **2** recognition of Hg²⁺ proceeds via a similar binding site as that of **1**. By plotting the changes of **2** in the absorbance intensity at 518 nm as a function of Hg²⁺ concentration, sigmoidal curve was obtained and is shown in the inset of Figure 1. The 1:1 binding stoichiometry of **2**–Hg²⁺ was supported by

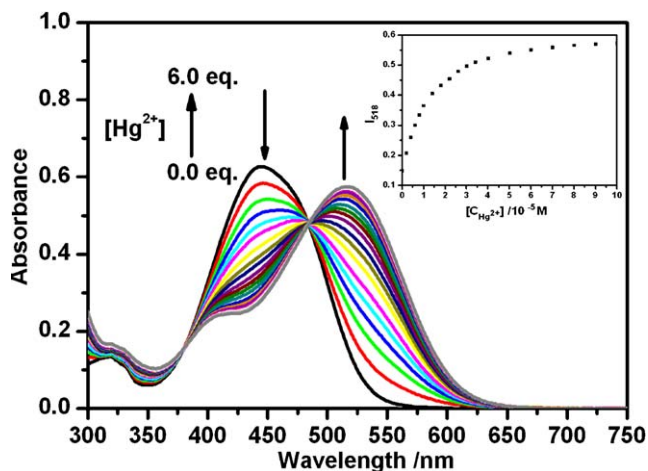


Figure 1. UV–vis absorption spectra of **2** in CH₃CN ($[C] = 2.0 \times 10^{-5}$ mol L⁻¹) with Hg²⁺. Inset: Plot of absorbance intensity at 518 nm as a function of Hg²⁺ concentration.

the nice nonlinear fitting¹³ of the absorption–titration curve, which was also affirmed by the literature.⁹ The binding constant (K) of **2** with Hg²⁺ was calculated to be 4.4×10^5 mol⁻¹ L at 20 °C in CH₃CN. In compound **2**, the 8-hydroxyquinoline benzoate group could be used as an electron donor with weak electron-donating ability. The addition of Hg²⁺ might result in the binding of Hg²⁺ with quinoline N together with carbonyl O,⁹ and then the D– π –D’ structure transformed to D– π –A structure (Fig. 2), which increased the degree of intramolecular charge transition (ICT), resulting in a red-shift of absorption band of **2**.¹⁴

The experimental phenomenon was different from that of Hg²⁺ when Cu²⁺ was added to **2** in CH₃CN. The sensing process consisted of two processes, as shown in Figure 3. At less than 1.0 equiv of Cu²⁺ addition, the characteristic strong absorption band at 445 nm decreased and a very weak absorption appeared at 500 nm with an isobestic point at 515 nm (Fig. 3A). The color of **2** changed from yellow to pale red. This fact indicated that Cu²⁺ could coordinate weakly with 8-hydroxyquinoline benzoate in the first process. As more than 1.0 equiv of Cu²⁺ was added, the absorption band of **2** at 445 nm further decreased. However, a new band centered at 383 nm appeared and increased, corresponding to a λ_{\max} (abs) blue-shift of 62 nm and an isobestic point at 396 nm (Fig. 3B). Correspondingly, the color of **2** changed from pale red back to colorless (see ESI). This hypsochromic shift might be ascribed to the complexation of Cu²⁺ at –N=N–C₆H₆–N(CH₃)₂ site as the second process,^{15,16} which diminished the degree of the ICT. The whole color change process could be detected by the ‘naked eye’. However, only slight spectral change was found for **1** in CH₃CN solution upon addition of Cu²⁺ (see ESI). Therefore, the introduction of azo group makes **2** a chromogenic chemosensor for Hg²⁺ and Cu²⁺.

For an excellent chemosensor, high selectivity is a matter of necessity. Analysis of UV–vis absorption spectra of **2** with other metal ions has been employed, which gave out the chromogenic ability in the following order: Hg²⁺ > Cu²⁺ > Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺, Cr²⁺, Pb²⁺, Ca²⁺, Na⁺, K⁺, Ag⁺ in CH₃CN (Fig. 4).

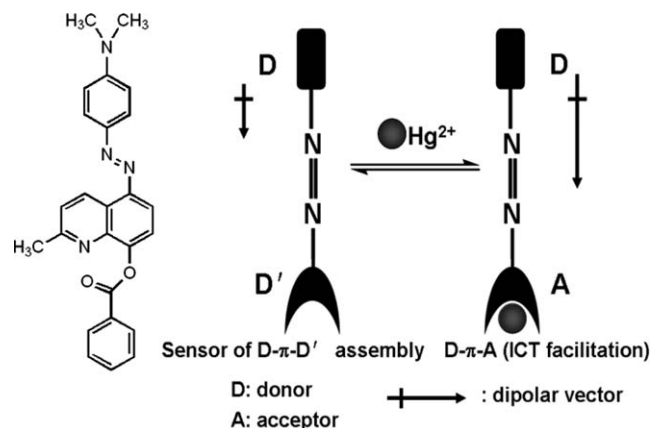


Figure 2. The sensing process of **2** with Hg²⁺.

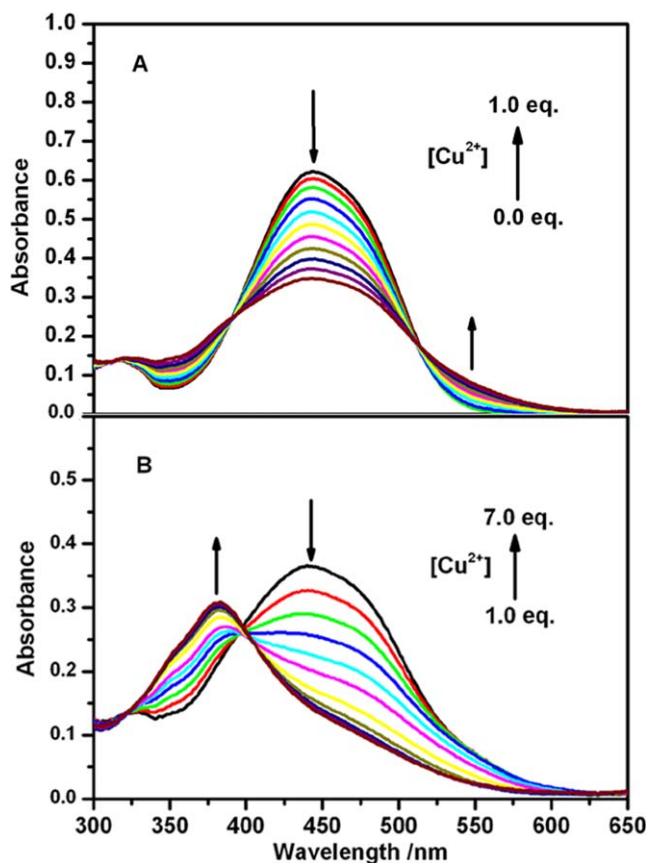


Figure 3. UV-vis absorption spectra of **2** in CH_3CN ($[\text{C}] = 2.0 \times 10^{-5} \text{ mol L}^{-1}$) with Cu^{2+} before 1.0 equiv (A) and after 1.0 equiv (B).

Responses of **2** in CH_3CN to 3.0 equiv of cations are shown in Figure 5. Compared to the response (bathochromic shift) of **2** with Hg^{2+} , a contrary shift change (hypsochromic shift) was observed when Cu^{2+} was added to a solution of **2** in CH_3CN , while no obvious color was observed upon addition of Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , etc., indicating that **2** shows high selectivity for Hg^{2+} and Cu^{2+} upon other metal ions.

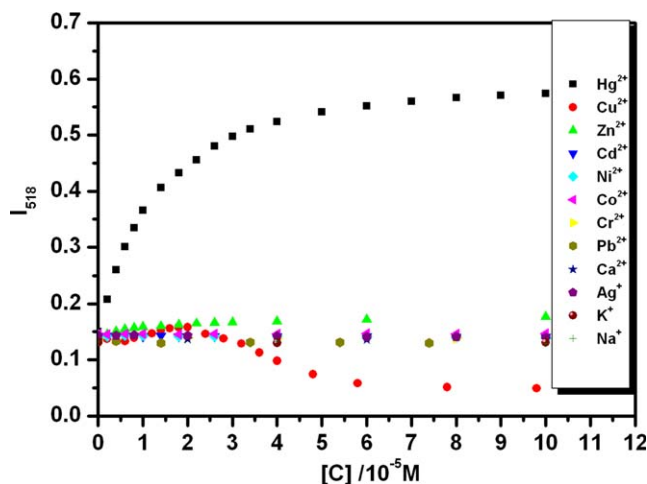


Figure 4. Titration profile of **2** ($[\text{C}] = 2.0 \times 10^{-5} \text{ mol L}^{-1}$) on the band of 518 nm with representative metal ions.

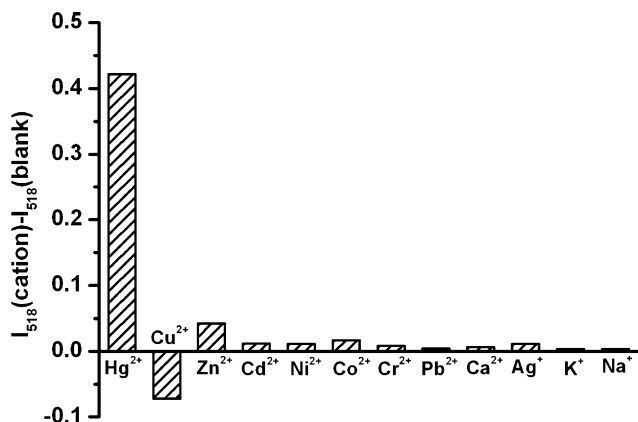


Figure 5. Responses of **2** in CH_3CN to representative metal ions ($6.0 \times 10^{-5} \text{ mol L}^{-1}$, χ -axis markers). The absorbance was at 518 nm. The concentration of **2** was $2.0 \times 10^{-5} \text{ mol L}^{-1}$.

To explore the practical applicability of **2** as a Hg^{2+} - and Cu^{2+} -selective sensor, competition experiments were also performed in 5.0 equiv of Hg^{2+} or Cu^{2+} mixed with 5.0 equiv of background metal cations such as Zn^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Cr^{2+} , and Pb^{2+} . The $\Delta I(I(\text{cation}) - I(\text{blank}))$ containing both background and Hg^{2+} or Cu^{2+} showed similar variation compared with that only containing Hg^{2+} or Cu^{2+} (see ESI).

In conclusion, we developed a selective chromogenic chemosensor for Hg^{2+} and Cu^{2+} . The presence of azo group significantly improved the chromogenic ability of the receptor. The recognition of Hg^{2+} of **2** gave rise to the obvious color change from yellow to red upon complexation. The recognition process of Cu^{2+} consisted of two processes and the color changed from yellow to pale red, then back to colorless. Such a design strategy would be of great interest in the development of other chemosensors for metal ions.

Acknowledgments

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Supplementary data

Supplementary data associated with this article (Crystallographic information (CIF) of compound **2**, ^1H NMR, ^{13}C NMR data, and absorption spectra) can be found in the online version at doi:10.1016/j.tetlet.2006.06.125.

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11. The synthesis of benzoic acid 5-(4-dimethylamino-phenylazo)-2-methyl-quinolin-8-yl ester (**2**): *p*-Amino dimethyl aniline (0.136 g, 1 mmol) was suspended in 30.0 mL of distilled water at the temperature of 0–5 °C. Then 1.0 mL of 6.0 mol L⁻¹ hydrochloric acid solution was added to the mixture. After 15 min, 10.0 mL aqueous solution of sodium nitrite (0.076 g, 1.1 mmol) was added, followed by acetonitrile solution of 2-methyl-8-hydroxyquinoline (0.159 g, 1 mmol), then pH was adjusted to 8–9 with 2.0 mol L⁻¹ NaOH solution. After stirring for 2 h, the solution was neutralized with 1.0 mol L⁻¹ HCl solution. The produced precipitate was filtered and washed with deionized water several times and dried under vacuum. Then the product (0.05 g) was refluxed with benzoyl chloride (0.057 g, 0.4 mmol) in CH₂Cl₂ (10 mL) for 6 h. The crude product was purified by silica column chromatography (petroleum ether (bp 60–90 °C)-chloroform, 1:4, v/v). Product **2** was obtained in a yield of 46%.
12. Benzoic acid 2-methyl-quinolin-8-yl ester (**1**): ¹H NMR (400 MHz, CDCl₃, rt): δ 8.37 (d, *J* = 7.2 Hz, 2H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH), 7.72–7.65 (m, 2H, ArH), 7.58–7.50 (m, 4H, ArH), 7.30–7.26 (t, 1H, ArH), 2.64 (s, 3H, CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆, rt): δ 165.44, 159.74, 147.30, 140.72, 136.94, 134.61, 130.60, 129.82, 129.69, 128.16, 126.61, 126.11, 123.55, 122.37, 26.98. MS (EI): *m/z* = 263.2 [M⁺]. Anal. Calcd for C₁₇H₁₃NO₂ (263.09): C, 77.55; H, 4.98; N, 5.32. Found: C, 77.46; H, 4.92; N, 5.37.
- Benzoic acid 5-(4-dimethylamino-phenylazo)-2-methyl-quinolin-8-yl ester (**2**): ¹H NMR (500 MHz, CDCl₃, rt): δ 9.16 (d, *J* = 8.6 Hz, 1H, ArH), 8.38 (d, *J* = 7.2 Hz, 2H, ArH), 8.00 (d, *J* = 8.6 Hz, 2H, ArH), 7.86 (d, *J* = 8.6 Hz, 1H, ArH), 7.69–7.66 (t, 1H, ArH), 7.59–7.55 (m, 3H, ArH), 7.41 (d, *J* = 8.6 Hz, 1H, ArH), 6.81 (d, *J* = 8.6 Hz, 2H, ArH), 3.13 (s, 6H, CH₃), 2.67 (s, 3H, CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆, rt): δ 165.26, 159.23, 154.32, 151.81, 143.80, 142.23, 137.96, 135.28, 134.02, 130.35, 128.71, 123.97, 122.92, 122.61, 121.39, 114.68, 112.43, 40.38, 25.26. MS (EI): *m/z* = 410.3 [M⁺]. Anal. Calcd for C₂₅H₂₂N₄O₂ (410.17): C, 73.15; H, 5.40; N, 13.65. Found: C, 73.10; H, 5.35; N, 13.69.
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