662 **RESEARCH PAPER** NOVEMBER, 662–664 JOURNAL OF CHEMICAL RESEARCH 2013

Synthesis and mercury ion recognition of a novel azobenzene derivative bearing naphthalene units

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A fluorescent probe for selective detection of mercury based on an azobenzene derivative bearing naphthalene units has been synthesised and its cation recognition abilities examined by UV-Vis and fluorescence spectroscopy. The fluorescent probe exhibits a highly selective response of fluorescence enhancement toward mercury in DMF aqueous media (DMF: H_2O, v/v = 1:1).

Keywords: azobenzene, naphthalene, recognition, mercury, UV-Vis spectroscopy, fluorescence spectroscopy

The design of optical sensors for selective recognition and sensing of desired metal ions is an important and contemporary research area. In this regard, metal ions that are known to have detrimental effects on living organisms or the environment are generally more common as target metal ions for such studies.[1,2] Mercury is a prevalent toxic metal in the environment because both elemental and ionic mercury can be converted by bacteria in the environment to methyl mercury, which subsequently bioaccumulates through the food chain. When absorbed in the human body, mercury causes damage to the central nervous, DNA, mitosis, and endocrine systems.[3–5] Therefore, developing new and practical multi-signalling chemosensors for Hg^{2+} is still a challenge.

Azobenzene, as a molecular scaffold for the construction of selective ionophores, has been incorporated into fluorescent ion sensors. A few fluorescent chemosensors based on azobenzene that display selectivity to heavy and transition metal cations have been reported.[6–9] However, since there are only limited reports about recognition of heavy metal cations, such as Hg^{2+},[10,11] there is a need for good sensors and further efforts are required to develop them. Here we describe a new fluorescent chemosensor, based on the azobenzene framework with the azo group as ionophore and naphthyl as fluorophore, which has metal-binding properties and shows a selective and sensitive fluorescence enhancement response to the Hg^{2+} ion.

Results and discussion

The target products were synthesised using a three-step procedure as shown in Scheme 1: (i) synthesis of (*E*)-4,4′-dicarboxyl azobenzene **1** using the reduction reaction of 4-nitrobenzoic acid D-(+)-glucose; (ii) synthesis of the (*E*)-4,4′-bischloroformyl azobenzene **2** by chlorination reaction of **1** with thionyl chloride; (iii) azobenzene derivative **3** was synthesised by nucleophilic addition-elimination reaction of **2** with 1-naphthylamine. The crude product was purified by column chromatography and a pink solid was obtained. The target compound was characterised by elemental analysis, ^1H NMR, ^{13}C NMR, IR, and MS, the spectral data are in agreement with the desired structure.

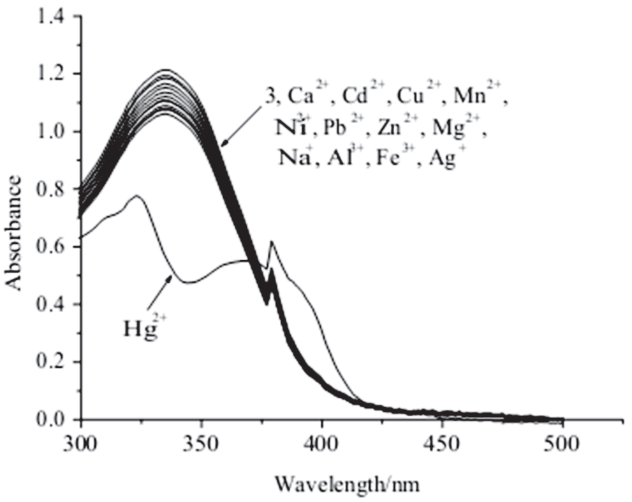
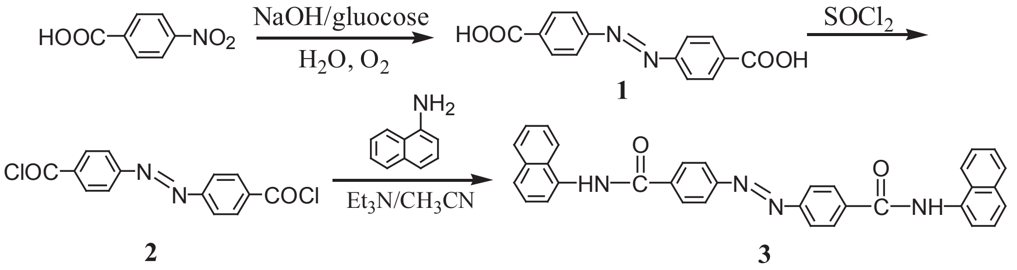


Fig. 1 UV-Vis spectra of compound **3** (10 μM) upon addition of various ions (20 μM) in DMF and H_2O (v/v = 1/1).

The complexation properties of compound **3** were investigated toward various heavy and transition metal cations (Ca^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Na^+, Al^{3+}, Fe^{3+}, Ag^+) by UV-Vis spectroscopy. As show in Fig. 1, the UV-Vis absorption band of compound **3** was observed at 337 nm. When Hg^{2+} was added, the original peak decreased and new absorption bands at 324 nm and 379 nm were formed, whereas negligible changes were observed with the other metal ions. Thus, it may be concluded that compound **3** has special selectivity and sensitivity to Hg^{2+}.



Scheme 1 Synthesis of azobenzene derivative **3**.

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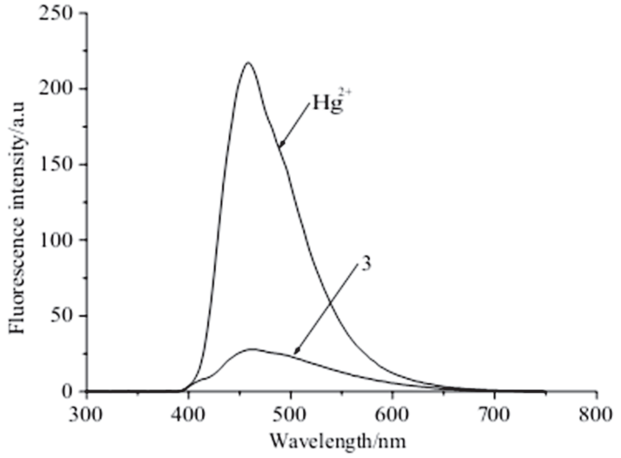

Fig. 2 Fluorescence emission spectra of compound **3** (10 μM) upon addition of Hg^{2+} and Cu^{2+} (20 μM) in DMF and H_2O (v/v = 1/1).

The fluorescence enhancement effects of Hg^{2+} ion on compound **3** in DMF aqueous media were investigated, as shown in Fig. 2.

In the fluorescence spectrum, compound **3** exhibited weak fluorescence emission at 461 nm in DMF/aqueous media. When Hg^{2+} was added to compound **3**, the fluorescence intensity was enhanced nine-fold. The fluorescence enhancement observed for **3** is attributed to the formation of the **3**–Hg^{2+} complex, as a result of which the PET from nitrogen atoms to the naphthalene moiety is suppressed, resulting in the fluorescent enhancement.

The titration of compound **3** by Hg^{2+} with an excitation at $\lambda_{ex} = 396$ nm, given in Fig. 3 as an example, exhibited an increase of its emission intensity at 461 nm. From the titrations, we determined the association constant of compound **3** for Hg^{2+} ($Ka = 1.25 \times 10^6\ M^{-2}$).

Using the changes in the fluorescence spectra of compound **3** with Hg^{2+} ions, we applied the method of continuous variation (Job's plot) to prove the complexation ratio between compound **3** and Hg^{2+} ions. As shown in Fig. 4, the maximum point at the mole fraction of 0.67 indicates the complexation ratio of compound **3** and Hg^{2+} is 1:2.

In conclusion, we have synthesised a novel azobenzene derivative bearing naphthalene units **3**. The structure of the target compound was clearly identified by ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis. The UV and fluorescence spectra data indicate that compound **3** could recognise Hg^{2+} and a 1:2 stoichiometric complex was formed between the receptor and cation.

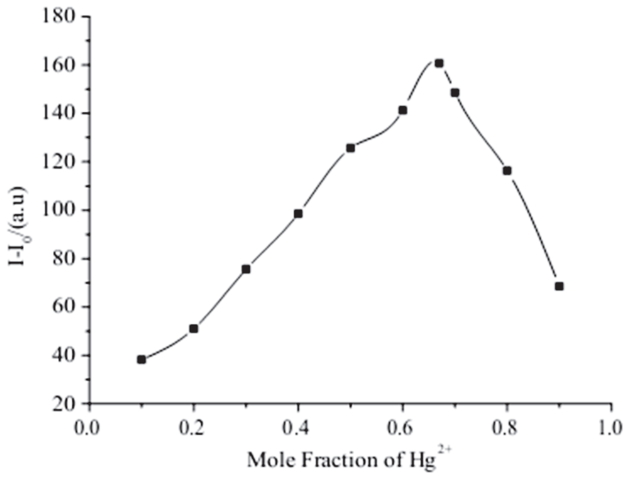

Fig. 4 Job's plot for determining the stoichiometry of receptor **3** and Hg^{2+} ion in DMF and H_2O(v/v = 1/1), I and I_0 are the fluorescence intensity of **3** in the presence and absence of Hg^{2+}, respectively; the total concentration of **3** and Hg^{2+} ion is 0.1 mM ($\lambda_{ex} = 396$ nm).

Experimental

(E)-4,4’-bischloroformyl azobenzene[12] was prepared according to procedures described in the literature; other reactants and chemicals were purchased from Aladdin. Solvents were of analytical grade. NMR spectra were recorded at room temperature on a Bruker Avance-500 NMR spectrometer. DMSO-d6 and $CDCl_3$ were used as solvents and tetramethylsilane (TMS) as internal standard. Mass spectral data were obtained on an Agilent 1100 LC/MS instrument. IR spectra were obtained with a Perkin Elmer spectrophotometer. Elemental analyses were made with a CHN analyser. (Thermo Finnigan Company). UV-Vis absorption spectra were recorded at room temperature using a Lambda-900 spectrometer. The fluorescence emission spectra were measured using a LS-55 spectrometer.

Synthesis of compound ***3****; general procedure*

(E)-4,4′-bischloroformyl azobenzene **2** (0.98 mmol) was added to a mixture of 1-naphthylamine (1.96 mmol), Et_3N (1.98 mmol) in $ClCH_2Cl$ (20 mL) and the mixture was stirred for 8 h at room temperature. The resulting solid was filtered and the crude product was purified on a silica gel column using petroleum: the product was obtained as salmon pink powder. Yield 69%; m.p. >300 °C; IR (KBr, cm^{-1}): 3283, 3063, 2945, 1646, 1597, 1529, 1439, 1344, 1147, 858, 763; ^{1}H NMR (500 MHz, DMSO-d6): δ 10.693(s, 1H, NH), 10.679(s, 1H, NH), 8.366 (t, 3H, $J = 8.5$, PhH), 8.205 (d, 1H, $J = 8.5$, PhH), 8.153 (m, 2H, PhH), 8.066

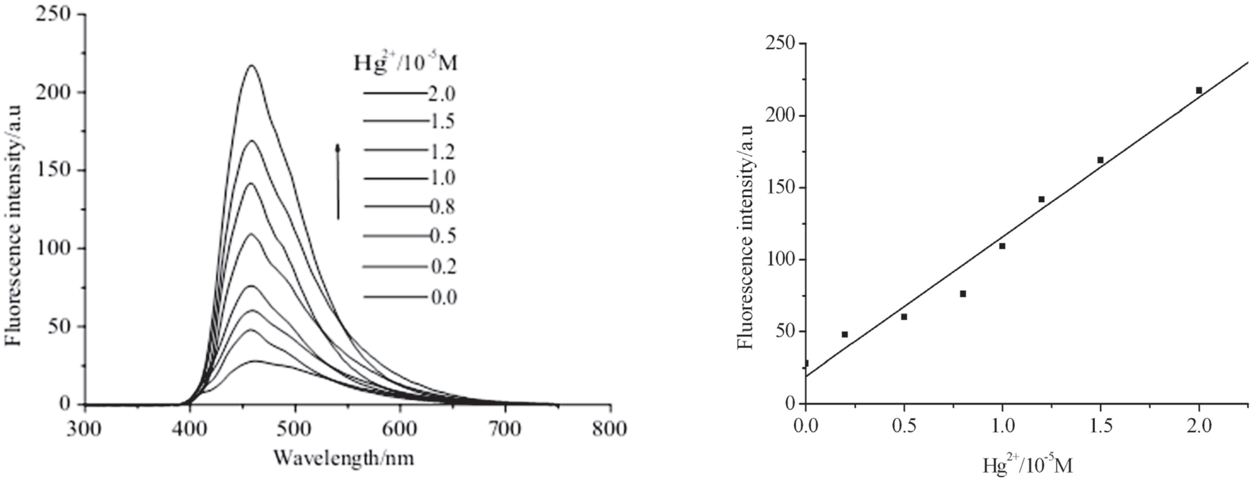

Fig. 3 Fluorescence emission spectra of compound **3** (10 μM) for Hg^{2+} ion: titration in a mixture of DMF/H_2O (v/v = 1/1) ($\lambda_{ex} = 396$ nm).

(m, 4H, PhH and naphthalene-H), 8.016 (m, 2H, naphthalene-H), 7.918 (d, 2H, $J = 8.0$, naphthalene-H), 7.672 (m, 2H, naphthalene-H), 7.610 (m, 6H, naphthalene-H); ^{13}C NMR (500 MHz, DMSO-d6): δ_C (ppm) 167.10, 165.90, 154.74, 154.05, 137.58, 134.28, 134.16, 133.78, 131.17, 129.74, 128.58, 126.93, 126.60, 126.04, 124.39, 123.81, 123.27; MS, *m/z*: 521(M + H$^+$); Anal. Calcd for $C_{34}H_{24}N_4O_2$: C 78.44, H 4.65, N 10.76. Found: C 78.40, H 4.67, N 10.80%.

We acknowledge the financial support of the Key Laboratory Project (2008S127) and the Initial Fund for Young Teachers of Liaoning University of Science and Technology (008131).

Received 9 July 2013; accepted 9 August 2013
Paper 1302054 doi: 10.3184/174751913X13795955735210

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