PAPER

A novel water soluble chemosensor based on carboxyl functionalized NDI derivatives for selective detection and facile removal of mercury(II)†

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Mercury(II) (Hg^{2+}) has acute toxicity. It is still a challenge to design and synthesize chemosensors for selective detection and removal of Hg^{2+} in water solutions. By rationally combining the carboxyl group and naphthalene diimide moieties, we obtained a novel water-soluble Hg^{2+} chemosensor (**M2**). Interestingly, the sensor **M2** showed a dramatic fluorescent "turn-on" response for Hg^{2+} in water. Moreover, the sensor **M2** displayed a high specificity for Hg^{2+}, other cations (including Fe^{3+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+}) had no influence on the Hg^{2+} detection process. Moreover, the sensor **M2** showed high sensitivity for Hg^{2+}, with detection limits of 1.18×10^{-6} M. Even more meaningfully, the sensor **M2** can remove Hg^{2+} from water solutions effectively *via* the formation of a **M2**–Hg^{2+} coordination polymer, which can increase the possibility of **M2** being used for practical applications.

Introduction

As we all know, ions play a significant role in life and technological processes.[1–4] Moreover, heavy metal ions pose a big threat to human health and the environment due to their high toxicity and bioaccumulation.[5,6] Among the heavy metals, mercury is one of the most toxic.[7–11] However, large quantities of mercury salts are widely used in industrial chemicals, electricals, apparatus, dental amalgams, and batteries.[12–15] Hence, the rational design and synthesis of efficient sensors to selectively detect and remove Hg^{2+} ions has attracted much attention.[16–18] Moreover, due to most of the biological or environmental procedures being carried out in water systems, it is very important to develop a Hg^{2+} chemosensor, which can detect and remove Hg^{2+} in water.

Thus far, some methods based on organic fluorophores[19] or chromophores,[20] semiconductor nanocrystalline materials,[21] cyclic voltammetry,[22] polymeric materials,[23] and proteins[24] have been established for the detection of Hg^{2+}. However, most of these materials are difficult to be applied in the detection of mercury ions in water solutions due to their poor water solubility. Moreover, these chemosensors cannot remove Hg^{2+} in water simultaneously. Therefore, the search for effective sensing systems in a water environment is still a great challenge. At the same time, various absorbents, such as activated carbon,[25] resins,[26] silica,[27] zeolites[28] and metal sulfides[29] have been applied to remove Hg^{2+} from wastewater; however, these absorbents cannot detect Hg^{2+} in water. The reports on simultaneous detection and removal of Hg^{2+} in water are still very scarce.[30–33] Therefore, the development of water soluble Hg^{2+} chemosensors, which can synchronously detect and remove Hg^{2+} in water is an important task.

In view of this and based on our research in ion recognition,[34,35] we report a water-soluble Hg^{2+} sensor **M2** based on naphthalene diimide derivatives. In order to achieve fluorescent sensing and efficient removal of Hg^{2+} in water, we rationally introduced the carboxyl group into the sensor molecule as a hydrophilic group and Hg^{2+} binding site. Moreover, we introduced a naphthalene diimide moiety as the fluorescent signal group and π–π stacking site. As a result, the sensor **M2** showed good solubility in water and could fluorescently "turn on" when it detected Hg^{2+} with high selectivity and sensitively in water solution. More interestingly, the sensor **M2** could efficiently remove Hg^{2+} in water simultaneously.

The sensor **M2** was synthesized by a simple dehydration condensation procedure (Scheme 1) and was characterized by ^{1}H NMR spectroscopy and ESI-MS (Fig. S1 and S2†). The recognition properties of the chemosensor **M2** towards various metal cations, such as Fe^{3+}, Hg^{2+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ag^+, Cr^{3+}, and Mg^{2+}, were primarily investigated by

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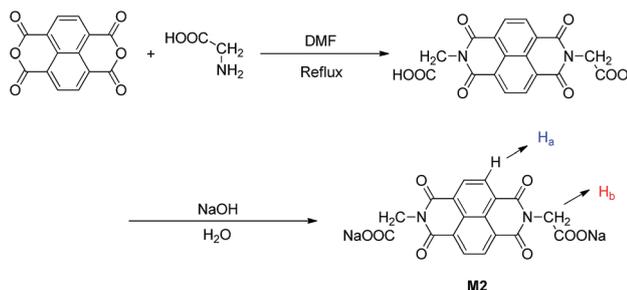
Scheme 1 Synthesis of compound **M2**.

fluorescence emission spectra in water solution (buffered with HEPES, pH = 7.2). The compound **M2** alone displayed no fluorescence when it was excited at 365 nm (Fig. 1). However, when 10 equiv. of Hg^{2+} was added to the water solution of **M2** (2.0×10^{-4} M), the solution emitted bright blue fluorescence emission. Simultaneously, in the fluorescence spectrum, an emission peak at 425 nm could be observed (Fig. S3†). To validate the selectivity of sensor **M2** for Hg^{2+}, the same tests were carried out for other cations (including Fe^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ag^+, and Mg^{2+}); however, these cations could not induce any significant fluorescent changes in the fluorescence spectrum (Fig. 1). These results indicate that the sensor **M2** can selectively fluorescently "turn-on" when sensing Hg^{2+} in water solution.

To further investigate the interaction between sensor **M2** and Hg^{2+}, the fluorescence emission spectral variation of sensor **M2** (2.0×10^{-4} M) in water (buffered with HEPES, pH = 7.2) was recorded during titrations with different concentrations of Hg^{2+}. As shown in Fig. 2, with the addition of increasing

concentrations of Hg^{2+} from 0 to 3.26 equiv., the emission peak at 425 nm gradually enhanced. Furthermore, in order to determine the detection limits of **M2** for Hg^{2+}, the fluorescence spectra of blank tests were measured 20 times and the standard deviation of the blank measurements was determined (Fig. S4†). The fluorescence quantum yield (Φ) of sensor **M2** in water is 0.03 with quinine hemisulfate salt as a reference while the Φ increased to 0.32 when sensor **M2** reacts with Hg^{2+} (see ESI†). The linear fitting was performed according to the titration curves, and the mean intensity was calculated to determine the slope. The limit of detection (LOD) was determined from the equation LOD = $K \times \sigma/S$,[36] where $K = 3$, σ is the standard deviation of the emission intensity of **M2** in the presence of Hg^{2+}, and S is the slope of the calibration curve of the fluorescence emission. The detection limit of the fluorescence spectrum was 1.18×10^{-6} M. This data indicate that the sensor can detect Hg^{2+} at very low concentrations in the environment (Fig. S5†). Moreover, the binding constant (K) derived from the fluorescence titration data was found to be 2.65×10^9 M (see ESI†) using a Benesi–Hildebrand plot,[37] which indicates a high detection sensitivity.

Then, the competition experiments were also measured by the addition of 10 equiv. of Hg^{2+} to the water solution of **M2** in the presence of 10 equiv. of other metal ions, such as Fe^{3+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Ag^+ and Mg^{2+}. As shown in Fig. 3, the effect on emission intensity of **M2** upon the addition of higher concentrations of various cations was almost negligible. These results revealed that **M2** had a remarkable selectivity towards Hg^{2+} over competitive ions, and moreover, the detection of Hg^{2+} by **M2** was hardly affected by these common coexisting cations in water (buffered with HEPES, pH = 7.2). Moreover, in order to investigate the influence of coexisting anions on the Hg^{2+} sensing process, the competition experiments were also carried out by adding various anions into the **M2**–Hg^{2+} water solution (Fig. 4). As a result, coexisting anion ions, such as F^-, Cl^-, Br^-, I^-, Ac^-, $H_2PO_4^-$, HSO_4^-, $HClO_4^-$, SCN^- and CN^-, could not interfere in the Hg^{2+} sensing process of **M2**.
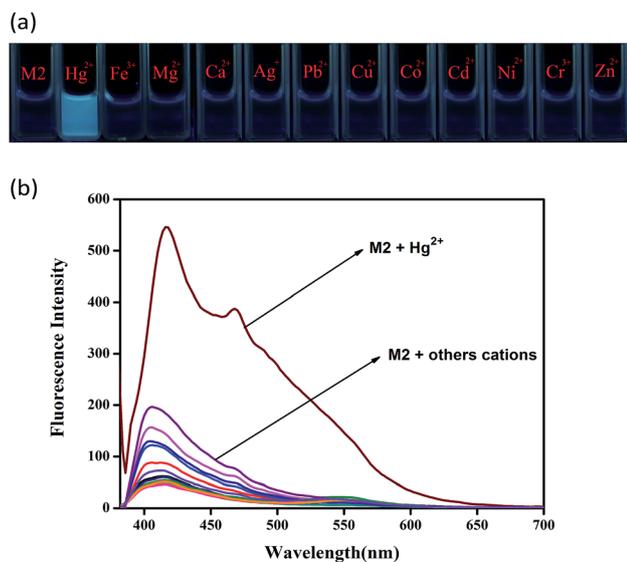

Fig. 1 (a) Photograph of **M2** upon adding 10 equiv. of various cations in, which was taken under an UV-lamp (365 nm) at room temperature. (b) Fluorescence spectra responses in water solution (buffered with HEPES, pH = 7.2) of **M2** (2.0×10^{-4} M) upon addition of different cations (10 equiv.).
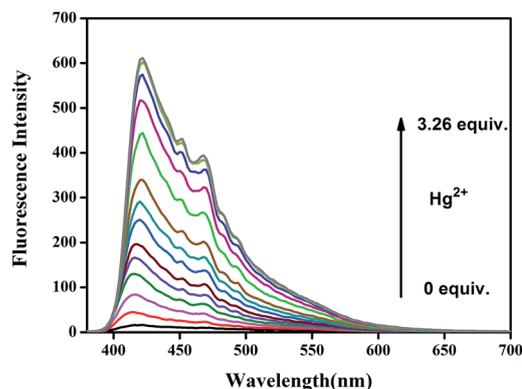

Fig. 2 Fluorescence titration spectra of Hg^{2+} in water solution (buffered with HEPES, pH = 7.2) upon addition of increasing concentration of Hg^{2+}.

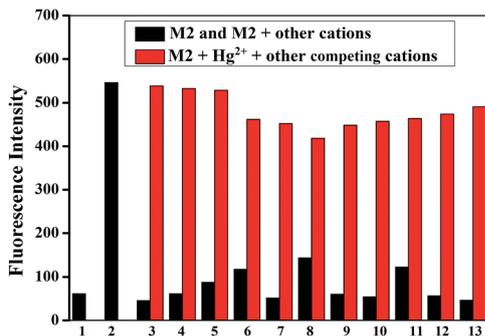**Fig. 3** Fluorescent emission ($\lambda_{ex} = 365$ nm) spectra of **M2** (2×10^{-4} M) to Hg^{2+} (10 equiv.) in the presence of various competing cations in water (buffered with HEPES, pH = 7.2). Form 1 to 12: **M2**, **M2** + Hg^{2+}, **M2** + Hg^{2+} + Fe^{3+}, **M2** + Hg^{2+} + Ca^{2+}, **M2** + Hg^{2+} + Cu^{2+}, **M2** + Hg^{2+} + Co^{2+}, **M2** + Hg^{2+} + Ni^{2+}, **M2** + Hg^{2+} + Cd^{2+}, **M2** + Hg^{2+} + Pb^{2+}, **M2** + Hg^{2+} + Zn^{2+}, **M2** + Hg^{2+} + Ag^{+}, **M2** + Hg^{2+} + Cr^{3+}, **M2** + Hg^{2+} + Mg^{2+}.

As we all know, the pH has a strong influence on the coordination properties of ligands and metal ions. Therefore, the effects of pH on the Hg^{2+} sensing process were also investigated (Fig. 5). Over the tested pH range, sensor **M2** alone had no fluorescence and was stable in the pH range 4.0–13.0. However, the **M2**–Hg^{2+} complex showed a significant fluorescence response between pH 4.0 and 8.0. These results indicate that Hg^{2+} could be clearly detected by the fluorescence spectral measurement using **M2** over a pH range from 4.0 to 8.0. In acidic conditions, carboxylate groups in **M2** changed to carboxylic acids, whereas, in alkaline conditions, the Hg^{2+} could form $Hg(OH)_2$. In either case, the coordination abilities of **M2** and Hg^{2+} were restrained. Moreover, in strongly acidic (pH < 1) or strongly alkaline conditions (pH > 13), the sensor **M2** showed unusual fluorescence, which indicated the **M2** is unstable in these conditions.

The recognition mechanism of the sensor **M2** with Hg^{2+} was primarily investigated by IR spectroscopy. In the IR spectrum of

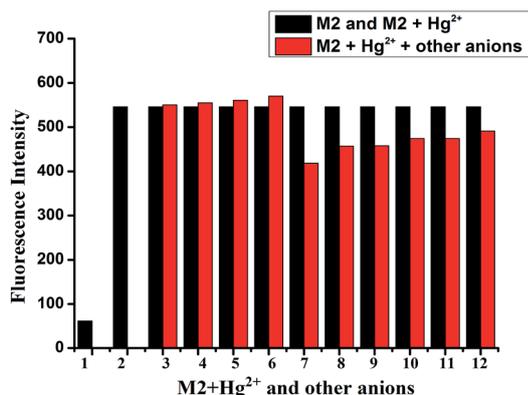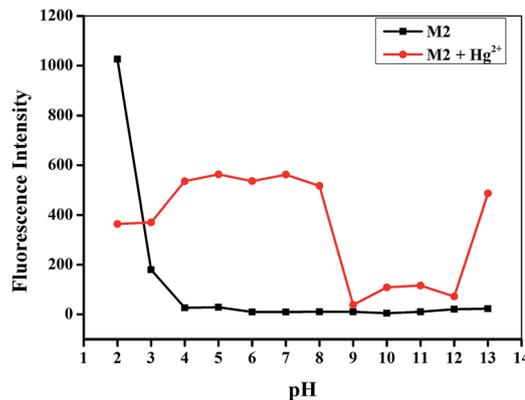**Fig. 5** Effect of pH on the fluorescence spectra of **M2** (20 μM) in response to Hg^{2+} (10 equiv.) from pH 2.0 to 13.0 in water solution.

M2 (Fig. 6), the carboxyl groups show the stretching vibrations absorption peak at 1715 cm^{-1}. However, after the addition of Hg^{2+}, this peak shifts to 1663 cm^{-1}, which indicates that **M2** bonds to Hg^{2+} *via* carboxyl groups. In addition, the mass spectroscopy results also supported this presumption. The ion peak at m/z 582.60 demonstrated the presence of [**M2** + Hg^{2+}] (Fig. S7†).

The recognition mechanism of the sensor **M2** with Hg^{2+} was also investigated by ^{1}H NMR titration. As shown in Fig. 7, sensor **M2** shows two single peaks at 8.55 and 4.58 ppm in D_2O solution, which correspond to the protons of the naphthalene rings (H_a) and –CH_2 (H_b), respectively. With the addition of Hg^{2+}, the signal of –CH_2 (H_b) showed a slight upfield shift, indicating that **M2** combined with Hg^{2+} *via* the carboxyl group. Moreover, the signal of the naphthalene rings (H_a) also showed a slight upfield shift, indicating that the π–π stacking interactions between the naphthalene rings were involved in the detection process.[38] Moreover, the XRD patterns (Fig. S6†) of the **M2**–Hg^{2+} complex showed a peak at $2\theta = 25.67°$ corresponding to d spacings of 3.53 Å, which also suggested that π–π stacking existed in the naphthyl groups.[39] Interestingly, after adding 2.0 equiv. Hg^{2+}, all the ^{1}H NMR signal disappeared. According to these ^{1}H NMR, XRD and IR experiments, we presumed that **M2** formed

Fig. 4 Fluorescent emission ($\lambda_{ex} = 365$ nm) spectra of **M2** (2×10^{-4} M) to Hg^{2+} (10 equiv.) in the presence of various anion ions (10 equiv.) in water (buffered with HEPES, pH = 7.2). Form 1 to 12: **M2**, **M2** + Hg^{2+}, **M2** + Hg^{2+} + F^{-}, **M2** + Hg^{2+} + Cl^{-}, **M2** + Hg^{2+} + Br^{-}, **M2** + Hg^{2+} + I^{-}, **M2** + Hg^{2+} + Ac^{-}, **M2** + Hg^{2+} + $H_2PO_4^{-}$, **M2** + Hg^{2+} + HSO_4^{-}, **M2** + Hg^{2+} + ClO_4^{-}, **M2** + Hg^{2+} + SCN^{-}, **M2** + Hg^{2+} + CN^{-}.
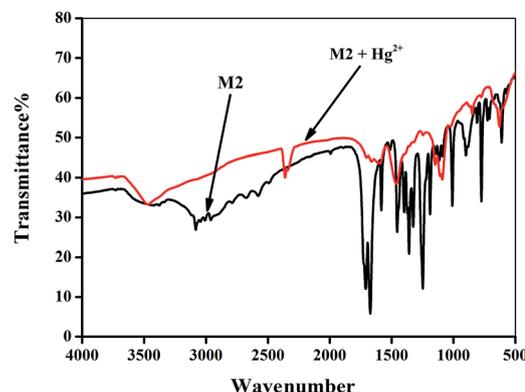

Fig. 6 IR spectra of compound **M2** and **M2**–Hg^{2+} in KBr disks.
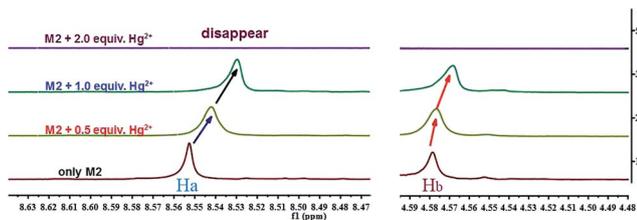
Fig. 7 Partial ^{1}H NMR spectra (600 MHz, D-H$_2$O) of free M2 (0.1 M) and in the different concentration of Hg^{2+} respectively.
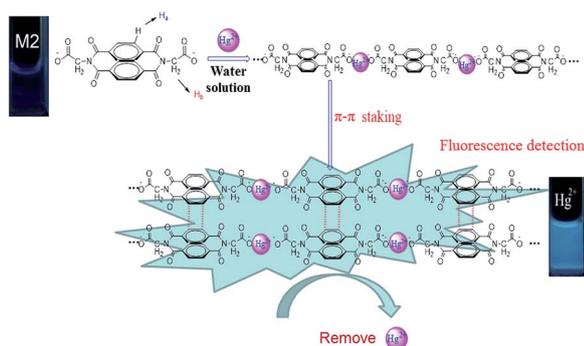
Scheme 2 Possible mechanism for the sensing and removal of Hg^{2+} by the sensor M2 in water.

a coordination polymer with Hg^{2+} and, simultaneously, each coordination polymer chain stacked together through the π–π interactions (Scheme 2).

Then, we further measured the capacity of the removal of Hg^{2+} by sensor M2 *via* inductively coupled plasma (ICP) analysis in aqueous solution (see ESI†). The ICP analysis identified an efficient removal of Hg^{2+}. In order to assess the ingestion capacity of the sensor for Hg^{2+} in water for potential practical applications, M2 (0.19 mg) was suspended in a dilute aqueous solution of Hg(ClO$_4$)$_2$ (0.20 mg in 5.0 mL), and precipitation was found to occur. We separated the precipitate by centrifugation (20 min) and gained the supernatant liquor (5 mL). The ICP analysis verified that the concentration of the residual Hg^{2+} in water was less than 0.2 ppm, indicating that over 98% of Hg^{2+} could be effectively removed. This data indicated that Hg^{2+} could be effectively removed even in extremely dilute solutions.

In summary, a novel water-soluble Hg^{2+} sensor M2 was designed and synthesized *via* an easy to make method. The sensor M2 employs carboxyl groups as hydrophilic groups and Hg^{2+} binding sites, while NDI moieties act as signal groups and π–π stacking sites. Interestingly, the sensor M2 could fluorescently "turn-on" when it detected Hg^{2+} in water with high selectivity and sensitivity. Moreover and more meaningfully, the sensor M2 can remove Hg^{2+} from a water solution effectively *via* the formation of a M2–Hg^{2+} coordination polymer. Therefore, the sensor M2 can be used as an easy to make and efficient sensor for fluorescence detection as well as for the removal of Hg^{2+} in water.

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