A sugar-quinoline fluorescent chemosensor for selective detection of Hg^{2+} ion in natural water†‡

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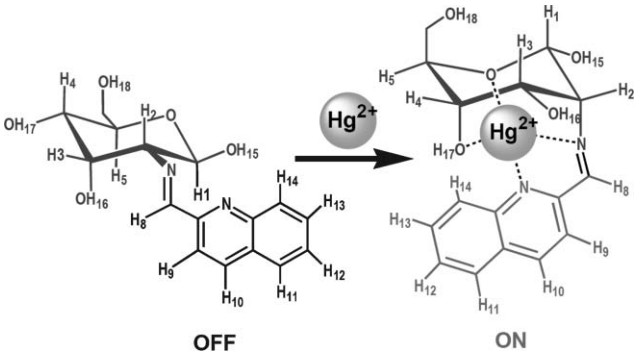
A selective and sensitive fluorescent sensor for detection of Hg^{2+} in natural water was achieved by incorporating the well-known fluorophore quinoline group and a water-soluble D-glucosamine group within one molecule.

Mercury(II) is one of the environmentally most important cations whose toxicity has long been recognized as a ubiquitous environmental problem, still attracting a great deal of public attention today, because marine aquatic organisms convert inorganic mercury Hg^{2+} into neurotoxic methylmercury which bioaccumulates through the food chain.[1,2] Accordingly, the development of new or improved analytical methods for the sensitive and selective determination of Hg^{2+}, which are applicable in a wide range of different sites and environments, is highly desirable. To date, a number of selective small-molecular Hg(II) sensors have been devised utilizing redox,[3] chromogenic[4] or fluorogenic[5,6] changes. Most of these systems display shortcomings in practical use, such as interference from other metal ions, delayed response to Hg^{2+}, and/or lack of water solubility. To circumvent these problems, Rurack *et al.*[7] described a fluorescent probe based on the indoaniline chromophore that exhibited selectivity for Hg^{2+} in water. Lippard *et al.*[8] designed a water soluble turn-on fluoroscein-based sensor that exhibited high selectivity and sensitivity for Hg^{2+}. Here we introduce a new strategy for the design of a selective and sensitive fluorogenic sensor in natural water by incorporating the well-known fluorophore quinoline group and a water-soluble D-glucosamine group within one molecule (Scheme 1).

The reaction of 2-quinolinecarboxaldehyde with D-glucosamine in methanol solution gave the Schiff-base compound **QG**. The UV-*vis* spectrum of **QG** in aqueous solution exhibits a broad band at about 310–320 nm, and the excitation of the solution at 315 nm induces a weak emission band at 480 nm. The low quantum yield (0.005)[9] of the unbonded **QG** compound suggests the presence of a photo-induced electron transfer (PET) quenching process of the emission of the quinoline group by the lone-pair electron of the imine nitrogen atom.[10]

Upon addition of Hg^{2+} ion, the emission band blue-shifts to 415 nm with the luminescent intensity enhanced by an order of magnitude (Fig. 1). The separation of about 70 nm in the maximum emission wavelength from the original **QG** compound, and the enhancement of the luminescence by one magnitude indicates no interference from **QG** in the detection of Hg^{2+} and suggests a photo-induced charge transfer (PCT)[11] signaling mechanism from the deprotonated hydroxyl group to the quinoline fluorophore. The deprotonation increases the electronic density on the quinoline ring, which leads to the charge-transfer state responsible for the luminescence toward higher energy. Meanwhile, the enhancement of luminescence intensity also demonstrates the disruption of the quenching pathway by Hg^{2+} coordination and thus suggests the combined properties of both PCT and PET signaling transductions.



Scheme 1 Potential structural changes of compound **QG** (sugar ring showing the $^4C_1$ conformation) in coordination with Hg^{2+} ion (sugar ring showing the $^1C_4$ conformation).

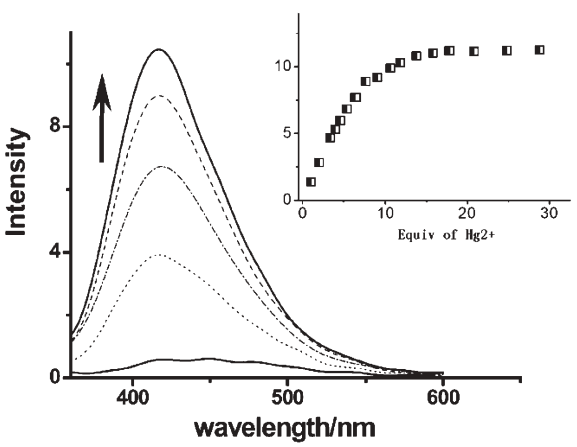


Fig. 1 Changes in emission spectra of an aqueous solution of **QG** (1.0×10^{-5} M) with increasing concentration of Hg(II) excited at 315 nm. The inset shows the fluorescence titration profile at 415 nm.

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† The HTML version of this article has been enhanced with colour images

‡ Electronic supplementary information (ESI) available: Experimental procedures, ESI-MS spectra, fluorescence spectra and ^1H NMR spectra. See DOI: 10.1039/b607287a

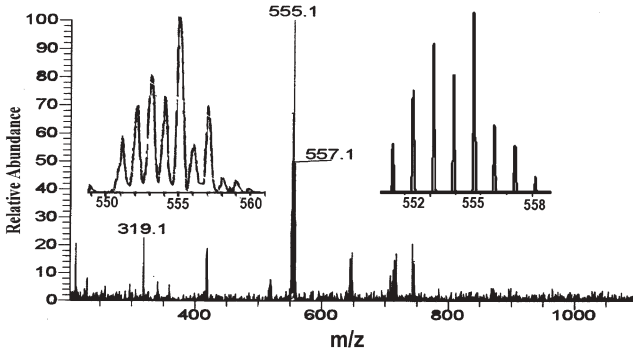

Fig. 2 ESI-MS spectrum of **QG** with Hg^{2+} in aqueous solution, the positive peak of *m*/*z* is assigned to $[Hg(\mathbf{QG})(H_2O)_2]^+$. The left insert picture is the high-resolution spectrum at *m*/*z* 555.1. The right insert picture is the simulation pattern of the $[Hg(QG)(H_2O)_2]^+$ species.

Hg^{2+}-binding titrations indicate that **QG** forms a 1 : 1 complex with Hg^{2+} in water. The association constant is calculated as 7.14×10^4 M^{-1}. The ESI-MS spectrum of the titration solution exhibits a strong peak at *m*/*z* 555.1, which is assigned to the species $[Hg(\mathbf{QG})(H_2O)_2]^+$ in aqueous solution, and confirms the formation of a 1 : 1 Hg^{2+}–**QG** complexed species (Fig. 2). The stability of the +1 charged species indicates that the **QG** sensor loses one of the hydroxyl protons and coordinates to Hg^{2+} as a mononegatively charged multidentate chelator.

To further investigate the potential chelating behavior of the **QG** compound, ^1H NMR titration of the **QG** compound with Hg^{2+} was carried out in D_2O-d_6-DMSO (1 : 1) mixed solution (1.0×10^{-3} M) (Fig. 3). The sensor itself shows a typical β-$^4C_1$ conformation with the chemical shift of H_1 being 4.9 ppm.[12] Upon addition of Hg^{2+}, a $^1C_4$ conformation[13] is stabilized by the coordination of Hg^{2+} ion with the H_1 signal downfield shifted to 6.3 ppm. Such a coordination mode of a sugar ring has been found in several Pt–sugar complexes in which the hemiacetal oxygen atom was helpful in chelating the metal center.[14] Meanwhile, the presence of Hg^{2+} also causes significant downfield shifts of the H_9, H_{10} signals in the quinoline ring, suggesting the participation of the quinoline ring in the coordination of Hg^{2+} ion. Furthermore, the special geometry of the sugar ring makes the special N_2O_2 chelating donors exhibit lower affinities for the six-coordinated first-row transition metals, such as Co^{2+}, Ni^{2+}, Cu^{2+} and even the IIB metals Zn^{2+} and Cd^{2+}.

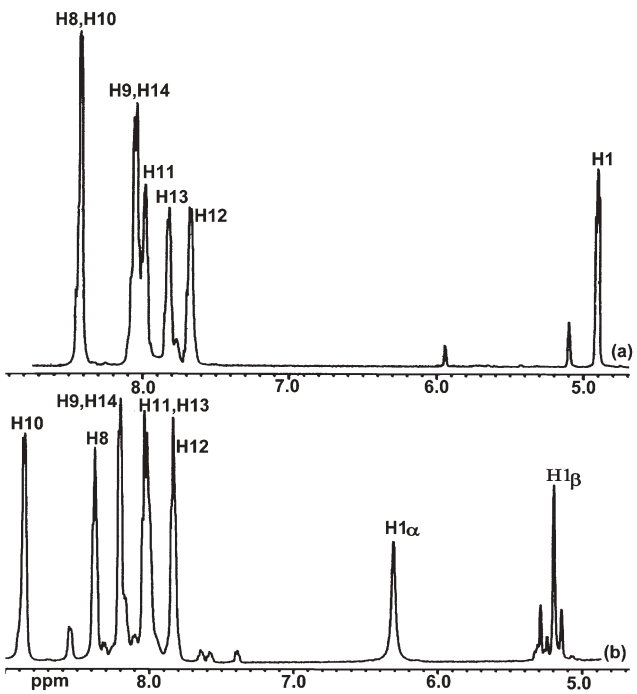

Fig. 3 ^1H NMR Spectra of compound **QG** and in the presence of 1 mole ratio of Hg^{2+} in D_2O solution (1.0×10^{-3} M).

The fluorescence response of **QG** to various cations and its selectivity for Hg^{2+} are illustrated in Fig. 4. Clearly, the presence of alkali-, alkaline earth- and transition metals such as Ag^+, Fe^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} do not cause any significant luminescence changes with the **QG** sensor in aqueous solution (Fig. 4). The presence of a 10 mole ratio of Zn^{2+} increases the luminescent intensity about 15%. The competing experiments reveal that the luminescence for Hg^{2+} is unaffected in a background of 10 equivalents mole ratio of alkali- and alkaline earth-metals. The presence of 5 equivalent mole ratio excess of transition metal ions such as Pb^{2+}, Ag^+, Fe^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} do not influence obviously the detection of Hg^{2+} in water, except Cu^{2+} ion, which quenches the luminescent intensity about 20%. The moderate binding strength of the −1 charged N_2O_2 chelating unit with a special coordination geometry not only prevents the interference of alkali and alkaline earth metals in environmentally relevant concentrations, but also retains or improves selectivity for Hg^{2+} over the first-row transition metals. Therefore, **QG** type fluorescent sensors may become a new type of efficient probe in distinguishing Hg^{2+} over competing cations in natural water.

To further investigate the potential application of the **QG** as a fluorescent sensor for Hg^{2+} in natural water, pH-dependent emission measurements of **QG** in the presence and absence of Hg^{2+} were also displayed in the pH range from 4.5 to 8 (Fig. 5). Clearly, **QG** can selectively respond to Hg^{2+} through an "off–on" type in the pH range from 5.0 to 7.5. When the pH value is lower

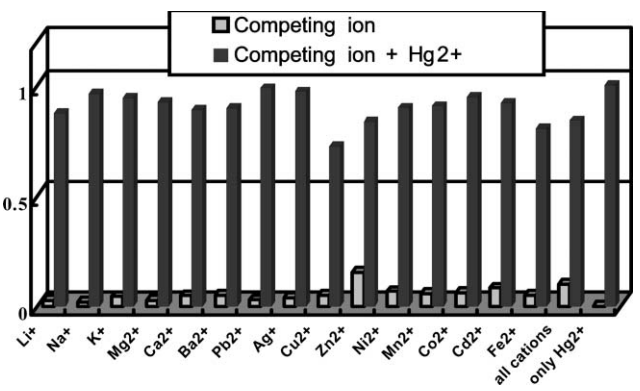

Fig. 4 The fluorescence intensity change profiles of **QG** (1.0×10^{-5} M) in water in the presence of selected metal ions. The light bars represent the emission of **QG** in the presence of the selected cations (1.0×10^{-4} M). The dark bars represent the change in integrated emission that occurs upon subsequent addition of Hg^{2+} (2.0×10^{-5} M) to the above mentioned solutions, respectively. Excitation wavelength was 315 nm, and emission intensities were monitored at 415 nm.

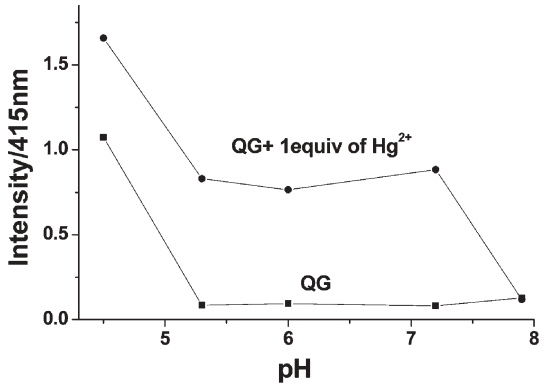

Fig. 5 pH dependent fluorescence response of **QG** (2.0×10^{-6} M) in aqueous solution upon addition of Hg^{2+} at 415 nm (excitation at 315 nm).

than 4.0, both the **QG** sensor and **QG**–Hg^{2+} species exhibit strong luminescence, but the difference in emission intensities is small with poor affinity and sensitivity for Hg^{2+}. When the pH value is larger than 8.0, the luminescent intensities of **QG** and **QG**–Hg^{2+} species are quenched. Furthermore, **QG** can still respond to Hg^{2+} when the concentration of Hg^{2+} is 5.0×10^{-7} M with the luminescent intensity increasing 40% of the free **QG** sensor.

In summary, we present here a new strategy to design water-soluble fluorescence sensors for Hg^{2+}, and obtain a highly selective and sensitive sensor in natural water with the low concentration limit being 0.5 μM. The **QG** sensor responds to Hg^{2+} through a combined signaling of both PET and PCT mechanisms. The $^1C_4$ conformation of the sugar constrains the N_2O_2 chelating donor in a tetrahedral geometry from which high selectivity over transition metals is achieved.§¶

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Notes and references

§ *Synthesis of sensor* ***QG*** Quinolinecarboxaldehyde (0.34 g, 2 mmol) was dissolved in 20 ml methanol. To this solution D-glucosamine·HCl (0.43 g, 2 mmol) and 0.3 ml Et_3N were added. The mixture was refluxed for 90 min and then cooled to room temperature. A pale yellow precipitate was separated and washed with methanol and ether. Yield 66%. Elemental Analysis: calcd(%) for $C_{16}H_{18}N_2O_5$: C 60.35, H 5.70, N 8.80; Found (%): C 60.56 H 5.82 N 8.58. ESI-MS positive peak at *m/z* 319.1 indicated [H(QG)]$^+$. 1H NMR in d_6-DMSO: δ 8.42 (*d*, 1H), 8.35(*s*, 1H), 8.07(*d*, 2H), 8.06(*d*, 1H), 7.81(*t*, 1H), 7.65(*t*, 1H), 6.63(*d*, 1H), 5.50(*d*, 1H), 4.92(*d*, 1H), 4.78(*t*, 1H), 4.57(*t*, 1H), 3.71(*m*, 1H), 3.48(*m*, 2H), 3.26(*m*, 1H), 3.19(*m*, 1H), 3.01(*t*, 1H).

¶ *Competing experiments* The selectivity of **QG** for Hg(II) against a background of various alkali-, alkaline earth- and transition metal ions were investigated using fluorescence spectroscopy. Aqueous solutions of Li(I), Na(I), K(I), Ag(I), Mg(II),Ca(II), Cu(II), Ba(II), Pb(II), Mn(II), Co(II), Ni(II), Cd(II), Zn(II) and Hg(II) were prepared from the nitrate salts. Fe(II) sulfate in aqueous solution was freshly prepared before use. A general procedure was 10 equiv. mole ratio of competing cation was first added to the **QG** aqueous solution and the fluorescence measured. Then 2 equiv. mole ratio of Hg^{2+} was added and the fluorescence change measured.

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