1,3-Dithiole-2-thione derivatives featuring an anthracene unit: new selective chemodosimeters for Hg(II) ion†

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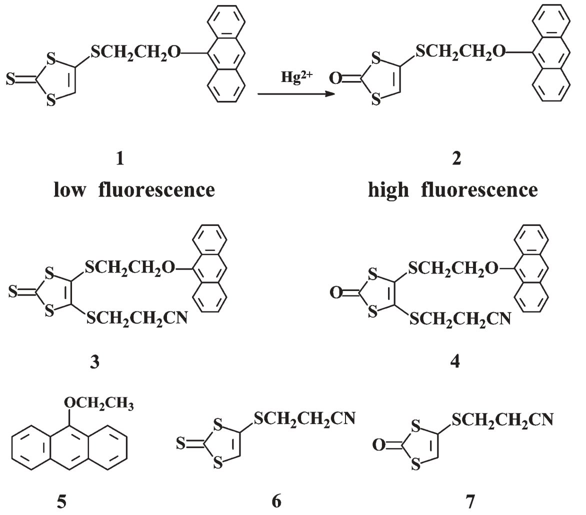
New selective chemodosimeters for Hg(II) ion based on 1,3-dithiole-2-thione derivatives containing an anthracene unit are described.

Mercury contamination is widespread and arises from a variety of natural sources.[1] It is known that, once introduced into the marine environment, bacteria convert inorganic mercury ion into methylmercury, which is neurotoxic and has been implicated as a cause of mercury pollution related diseases.[2] Thus, pollution by mercury ion will have severe effects on human health and the environment. Accordingly, the development of new or improved detecting methods, applicable in a wide range of different sites and environments, is highly desirable.

Most of the ionophores for Hg(II) ion described so far are based on a molecular motif composed of two building units: a receptor unit containing nitrogen/sulfur atoms and a chromophore that signals the absorption/fluorescence alteration upon exposure to Hg(II) ion.[3] In some cases the interference from other metal ions needs to be minimized for these ionophores. Alternative methodologies for detecting Hg(II) ion rely on the chemical transformations involving Hg(II) ion. For instance, Czarnik *et al.* reported that a chemodosimeter based on thioamide substituted anthracene could detect Hg(II) ion.[4] Herein we report that 1,3-dithiole-2-thione derivatives featuring an anthracene unit: 4-[2-(9-anthryloxy)ethyl]thio-1,3-dithiole-2-thione (**1**) and 4-[2-(9-anthryloxy)ethyl]thio-5-(2-cyanoethylthio)-1,3-dithiole-2-thione (**3**), can be used as highly selective chemodosimeters for Hg(II) ion.

We have recently reported the redox fluorescence switch and chemical luminescence as well as selective singlet O_2 detection based on tetrathiafulvalene (TTF) molecules containing anthracene units.[5] One route to TTF molecules is the trialkyl phosphite-mediated coupling of the derivatives of 1,3-dithiol-2-one, which were synthesized by the reaction of the corresponding 1,3-dithiole-2-thione derivatives with Hg(II) ion. During the reaction of compound **1**[6] with Hg(II) ion, TLC analysis was performed. Upon UV light (254 nm) irradiation of the TLC plate, the spot corresponding to 4-[2-(9-anthryloxy)ethyl]thio-1,3-dithiol-2-one (**2**, Scheme 1) is strongly fluorescent, while that corresponding to compound **1** is almost non-fluorescent. This observation prompted us to investigate the photophysical behaviors of compounds **1** and **2**. Fig. 1A shows the fluorescence spectra of compounds **1** and **2**. Obviously, compound **1** shows weak fluorescence with rather low quantum yield (0.010).[7] In contrast, compound **2** shows strong fluorescence with relatively high quantum yield (0.18), which is 18-fold larger than that of compound **1**. The same fluorescence properties are observed for compound **3** and 4-[2-(9-anthryloxy)-ethyl]thio-5-(2-cyanoethylthio)-1,3-dithiol-2-one (**4**) (Scheme 1), the analogues of compounds **1** and **2** (see ESI).



Scheme 1 Transformation of **1** into **2** with Hg^{2+} and structures of reference compounds.

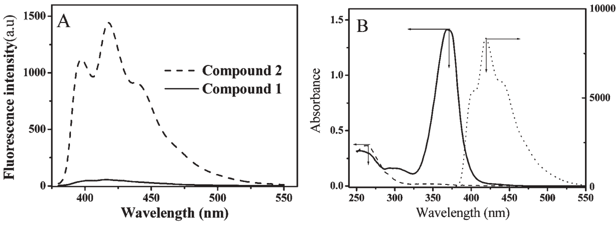


Fig. 1 A) Fluorescence spectra (λ_{ex} = 370 nm): (——) for compound **1** (10 μM) in THF, (————) for compound **2** (10 μM) in THF. B) The absorption spectrum in THF: (—) for compound **6** (0.1 mM), (—) for compound **7** (0.1 mM); fluorescence spectrum (λ_{ex} = 370 nm) for compound **5** (0.1 mM) in THF (…).

Both photoinduced electron transfer and energy transfer may be responsible for the different fluorescent properties of compounds **1** and **2**: (1) As shown in Fig. 1B, there is overlap between the fluorescence spectrum of the reference compound **5** (9-ethoxyanthracene)[5] and the absorption spectrum of the reference compound **6** (4-(2-cyanoethylthio)-1,3-dithiole-2-thione).[8] Consequently, the FRET from the excited anthracene unit to the

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† Electronic supplementary information (ESI) available: synthesis and characterization of compounds **1**, **3** and **4**; fluorescence spectra of compounds **1** and **3** in the presence of Hg(II) ion and other metal ions; preliminary theoretical calculation results. See http://www.rsc.org/suppdata/cc/b4/b417952h/
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1,3-dithiole-2-thione unit becomes possible, which may be ascribed to the low fluorescence quantum yield of compound **1**. In contrast, there is nearly no spectral overlap between the reference compound **5** and **7** (4-(2-cyanoethylthio)-1,3-dithiol-2-one),[8] and as a result the corresponding energy transfer process within compound **2** is not favorable. Thus, it is understandable to observe the different fluorescent behaviors of compounds **1** and **2**.[9] (2) The reduction potential of compound **5** was measured with differential pulse voltammetry to be −1.89 V, and the oxidation potentials of compounds **6** and **7** were 1.20 V and 1.78 V, respectively.[9] Based on these data, the values of ΔG for the photoinduced electron transfer (PET) reaction between the excited anthracene unit and the 1,3-dithiole-2-thione unit within compound **1** and that between the excited anthracene unit and the 1,3-dithiol-2-one unit within compound **2** were calculated to be −0.17 eV and 0.41 eV,[10] respectively. These results indicate that the corresponding PET reaction within compound **1** is more favorable than that within compound **2**. This may also contribute to the different fluorescent behaviors between compounds **1** and **2**.

In the following experiments, we demonstrate that the different fluorescent behaviors of compounds **1** and **2** enable compound **1** to be suited for use as a selective chemodosimeter for Hg(II) ion. According to previous studies,[11] due to the interaction of Hg(II) ion (soft acid) with sulfur atoms (soft base) of 1,3-dithiole-2-thione, the carbon atom of **C**=S becomes more electrophilic and would be more easily attacked by water, leading to the conversion of compound **1** to compound **2**. Thus, the presence of water is required for the transformation of **1** to **2** with $Hg(ClO_4)_2$. As compound **1** has low solubility in water, a mixture of THF and water (20 : 1, v/v) was used for the fluorescence measurements described below. In order to choose appropriate conditions for recording the fluorescence spectrum of compound **1** in the presence of Hg(II) ion, we studied the conditions for transformation of **1** to **2** at 40 °C by varying reaction times and amounts of Hg(II) ion. In each case, addition of Hg(II) ion resulted in fluorescence enhancement for the solution of compound **1** (10 μM) (Fig. 2). For example, the fluorescence intensity (at 418 nm) of the solution of **1** (10 μM) was increased by 10 times after reaction with 1 equiv. of Hg(II) ion for 30 min at 40 °C. When the amount of Hg(II) ion added to the solution of **1** (10 μM) was fixed, the fluorescence intensity of the solution increased with longer reaction time, and became saturated if the reaction between **1** and Hg(II) ion was conducted for 30 min or more at 40 °C as shown in the inset A of Fig. 2. Accordingly, the reaction of **1** with Hg(II) ion was allowed to proceed for 30 min at 40 °C before recording the fluorescence spectra of **1** in the presence of different amounts of Hg(II) ion. Under these conditions, the fluorescence intensity (at 418 nm) of the solution of **1** was nearly proportional to the amounts of Hg(II) ion added to the solution as shown in the inset B of Fig. 2, where the plot of the fluorescence intensity of the solution *vs.* the amount of Hg(II) ion is displayed. The detection limit for Hg(II) ion with compound **1** was determined to be 5×10^{-8} M under the present conditions. These results indicate that compound **1** can function as a chemodosimeter for Hg(II) ion.

The influences of other metal ions such as Ag^+, Ba^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Fe^{3+} on the fluorescence spectrum of **1** were investigated. As shown in Fig. 3, the reaction of **1** with other metal ions did not lead to large fluorescence enhancement under identical conditions to those for the reaction of **1** with Hg(II) ion. To further explore the utility of **1** as a selective chemodosimeter for Hg(II) ion, the competition experiment was performed for the solution of **1** in the presence of Hg(II) ion mixed with Ag^+, Ba^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} (see ESI). The results show that almost the same fluorescence spectra were obtained for the solution of **1** as those in the presence of only Hg(II) ion under identical reaction conditions, so the interference from these metal ions could be neglected. The interference from other high-oxidation state metal ions such as La^{3+}, Ce^{3+}, Nd^{3+}, Y^{3+} and Gd^{3+}can also be neglected. Therefore, it can be concluded that compound **1** is a new selective chemodosimeter for Hg(II) ion with a remarkably low detection limit. In fact, similar experiments were also conducted with compound **3**, and the results imply that compound **3** is also a good chemodosimeter for Hg(II) ion (see ESI). It should be mentioned that Czarnik *et al.*[4] reported the first chemodosimeter for Hg(II) ion based on the desulfation reaction

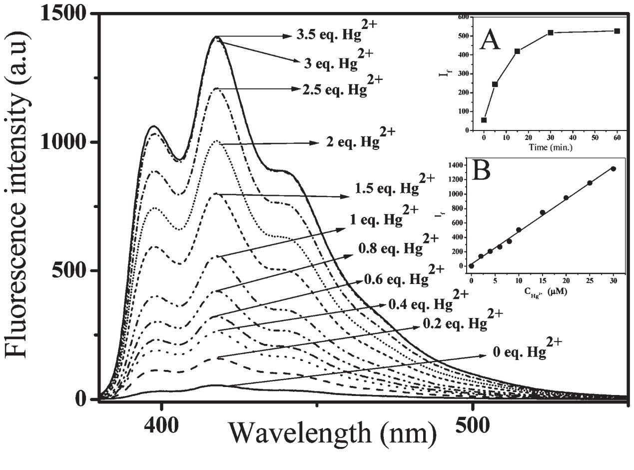

Fig. 2 Fluorescence spectra (λ_{ex} = 370 nm) of compound **1** (10 μM) in the presence of different amounts of Hg^{2+} in a mixture of THF–water (20 : 1, v/v). Inset **A**: Fluorescence intensity at 418 nm (λ_{ex} = 370 nm) *vs.* reaction time in the presence of 1 equiv. Hg^{2+}. Inset **B**: Fluorescence intensity at 418 nm *vs.* amounts of Hg^{2+} added to the solution.

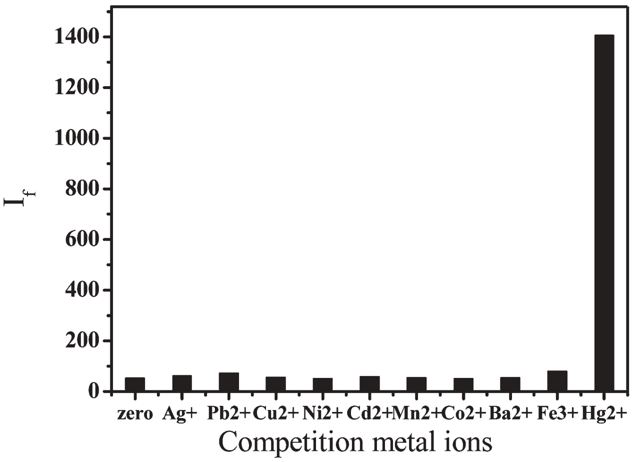

Fig. 3 The fluorescence intensity at 418 nm (λ_{ex} = 370 nm) change profile of **1** (10 μM) in THF–water (20 : 1, v/v) in the presence of several relevant metal ions (50 μM for each metal ion); the reaction time in each case is 30 min at 40 °C.

involving Hg(II) ion in 1992, but this chemodosimeter also senses Ag(I) ion besides Hg(II) ion.

In summary, we discover that compound **1** is weakly fluorescent, while compound **2** is strongly fluorescent. As a result, the transformation of **1** to **2** with Hg(II) ion is accompanied by fluorescence change. Such a unique property enables compound **1** to be a good chemodosimeter for Hg(II) ion. Interference from relevant metal ions is negligible. Similar experiments were also performed with compound **3** and results indicate that compound **3** is also a selective chemodosimeter for Hg(II) ion. This finding may not only enlarge the arsenal for detecting Hg(II) ion, but also add new merits to the chemistry of 1,3-dithiole-2-thione (-one), which are usually used as the precursors of tetrathiafulvalene derivatives. Further investigations include design and synthesis of analogues of **1** with improved solubility in water, with a view to developing new chemodosimeters for Hg(II) ion suitable for use in aqueous solution.

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6 The synthesis and characterization of compounds **1**, **3** and **4** are described in the Electronic Supplementary Information.

7 The fluorescence quantum yields were determined by using 9,10-diphenylanthracene in THF as a reference.

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9 The results of the preliminary theoretical calculation with compounds **6** and **7** (see ESI) indicate that compound **6** shows strong absorption at longer wavelength compared with compound **7**. Moreover, the calculation results also show that the HOMO energy of compound **6** is higher than that of compound **7**, which is in agreement with the fact that compound **6** shows lower oxidation potential than compound **7**.

10 They were calculated with the Rehm–Weller equation: $\Delta G_{\mathrm{PET}} = E(\mathrm{ex.}) - E(\mathrm{red.}) + E(\mathrm{ox.}) - e^2/\varepsilon r$, with $E(\mathrm{ox.}) = 1.20$ eV, 1.78 eV respectively; $E(\mathrm{red.}) = -1.89$ eV, $\lambda(\mathrm{ex.}) = 370$ nm, and $e^2/\varepsilon r = -0.1$ eV. see (*a*) D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259; (*b*) Z. R. Grabowski and J. Dobkowski, *Pure Appl. Chem.*, 1983, **55**, 245.

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