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PAPER

Mercury(II)-mediated formation of imide-Hg-imide complexes†

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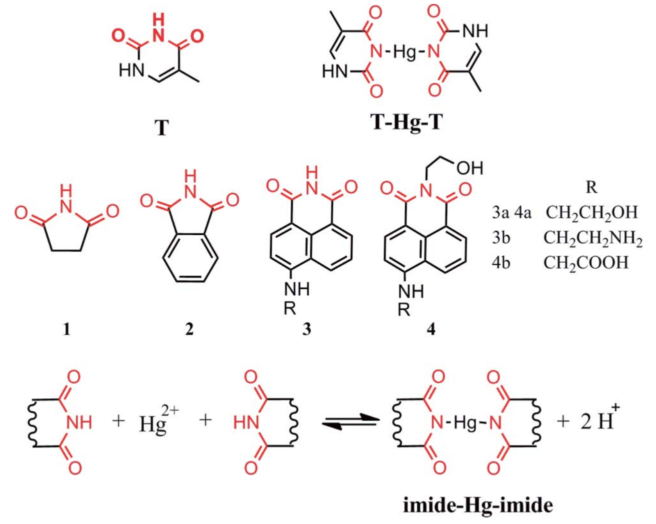
Three different kinds of cyclic imides with imido protons are chosen to interact with Hg(II): succinimide, the simplest cyclic imide (five-membered ring); phthalimide (conjugated five-membered ring); and 1,8-naphthalimide (conjugated six-membered ring). Based on the results of MS, ^{1}H-NMR, XPS, IR spectroscopy and fluorescence response analyses, it is suggested that *N*-unsubstituted cyclic imides react specifically with Hg(II) and form imide-Hg-imide complexes through an imido proton–metal exchange process. The reaction is reversible and occurs rapidly at moderate to high pH. This discovery expands the comprehension of the specific interaction of Hg(II) with the nucleobase thymine, and may open up new possibilities in designing novel ligands for sensing and removing Hg(II) based on cyclic imides.

Introduction

Based on the highly specific interaction of Hg(II) with the nucleobase thymine (T), a variety of T-rich DNA sensors for the selective detection of Hg(II) ions in aqueous solutions have been developed recently.[1,2] It has been demonstrated that Hg(II) binds to two thymine residues and forms a stable neutral T-Hg-T complex (Scheme 1) through an imido proton–metal exchange process.[3] Guided by this theory, thymine-modified polymers and phthalocyanine have also been developed for the selective adsorption and detection of Hg(II).[4,5] Therefore this specific recognition of Hg(II) is regarded as a feature of thymine and has been widely exploited for the construction of Hg(II) sensors and Hg(II) sorbents. However, we recently observed that the highly selective binding to Hg(II) ions was not unique to thymine but also common to *N*-unsubstituted cyclic imides.



Scheme 1 Compounds containing the imide moiety (red), the T-Hg-T complex and the formation of imide-Hg-imide complexes.

To demonstrate this finding, three different kinds of cyclic imides with imido protons were chosen to interact with Hg(II): succinimide (**1**), the simplest cyclic imide (five-membered ring); phthalimide (**2**) (conjugated five-membered ring); and 1,8-naphthalimide (**3**) (conjugated six-membered ring) (Scheme 1). The Hg(II)-mediated formation of imide-Hg-imide complexes was characterized by mass spectrometry (MS), ^{1}H-nuclear magnetic resonance spectroscopy (^{1}H-NMR), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) and luminescence responses.

Experimental

Materials and general procedures

All starting materials were obtained from commercial suppliers and used without further purification. Succinimide (99%) and phthalimide (99%) were purchased from Acros. 4-Bromo-1,8-naphthalic anhydride (98%) was purchased from Liaoning Liangang Dyes Chemical Co. Ltd., China. Ammonia (25%), Ethanolamine (99%), Glycine (99%), 1,2-Diaminoethane (99%) and other reagents were received from Sinopharm Chemical Reagent Co. Ltd., China.

All ^{1}H-NMR spectra were measured in DMSO-d_6 or CD_3OD on a Bruker AVANCE-400 NMR spectrometer (400 MHz) with TMS as an internal reference. X-Ray photoelectron spectroscopy data were obtained using an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The base pressure was about 3×10^{-9} mbar. Binding energies were referenced

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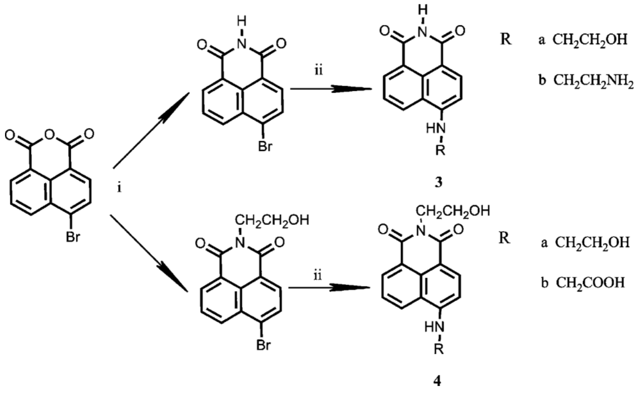
to the C1s line at 284.8 eV of adventitious carbon. FTIR spectra were measured with a Bruker Tensor27 spectrometer using KBr discs. All the fluorescence measurements were acquired on a SpectraMax M5 instrument (Molecular Devices Corporation, USA).

Syntheses

The syntheses of compounds 3 and 4.

General. The syntheses of **3** and **4** were achieved in a two-step procedure (Scheme 2). Firstly, the intermediates were synthesized by reacting 10 equiv. of ammonia or ethanolamine in refluxing ethanol with 4-bromo-1,8-naphthalic anhydride.[6] The second step involved stirring the intermediates with the corresponding amine in DMSO at 90 °C for 10 h under N_2, then washing with water and DCM to yield the product as a yellow solid after purification by column chromatography on silica (ethyl acetate–MeOH 90–80%).[7]



Scheme 2 The synthesis of the 1,8-naphthalic derivatives: (i) ammonia or ethanolamine, reflux in ethanol, 2 h; (ii) K_2CO_3, Cu_2O, DMSO, 90 °C, 10 h.

4-Bromo-1,8-naphthalimide. 4-Bromo-1,8-naphthalic anhydride (2.7 g, 10 mmol) was suspended in 300 mL of absolute ethanol and the solution heated at 85 °C under stirring. Ammonia (5 mL) was then dropped into the flask. After 1 h of reflux, the mixture was cooled to room temperature. Then, the solid was filtered and washed with absolute ethanol, and dried under vacuum at 40 °C. EI-MS m/z 275 (M). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 7.94 (t, J = 7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 8.48 (m, 2H), 11.80 (s, 1H).

*4-Bromo-*N*-(2-hydroxyethyl)-1,8-naphthalimide.* 4-Bromo-1,8-naphthalic anhydride (0.56 g, 2 mmol) was suspended in 50 mL of absolute ethanol and the solution heated at 85 °C under stirring. Ethanolamine (3.6 mL) was then dropped into the flask. After 1 h of reflux, the mixture was cooled to room temperature. Then, the solid was filtered and washed with absolute ethanol, and dried under vacuum at 40 °C. EI-MS m/z 319 (M). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.60 (q, J = 6.0 Hz, 2H), 4.13 (t, J = 6.4 Hz, 2H), 4.78 (t, J = 6.0 Hz, 1H), 7.98 (t, J = 7.6 Hz, 2H), 8.20 (d, J = 7.6 Hz, 1H), 8.32 (d, J = 7.6 Hz, 1H), 8.55 (t, 2H). ^{13}C-NMR (400 MHz, DMSO-d_6) (δ, ppm): 42.4, 58.2, 122.2, 123.1, 128.5, 129.1, 130.0, 130.1, 131.3, 131.7, 131.9, 132.9, 163.38, 163.43.

3a. 4-Bromo-1,8-naphthalimide (4 mM, 1 equiv.), Cu_2O (0.2 equiv.), potassium carbonate (0.5 equiv.), ethanolamine (10 equiv.) and DMSO (30 mL) were added to a flask. The flask was then sealed after filling with N_2 and the mixture heated to 90 °C. After stirring at this temperature for 10 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was washed three times with water and dichloromethane, then directly filtered through a pad of silica gel and concentrated to yield the product, which was purified by silica gel chromatography (4 : 1 ethyl acetate–MeOH) to yield **3a** as a yellow solid. EI-MS m/z 256 (M). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.47 (q, J = 5.6 Hz, 2H), 3.70 (q, J = 5.2 Hz, 2H), 4.87 (t, J = 5.2 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 7.66 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 7.2 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H), 11.22 (s, 1H). ^{13}C-NMR (400 MHz, DMSO-d_6) (δ, ppm): 46.6, 59.9, 104.7, 109.2, 121.6, 123.5, 124.9, 129.6, 131.0, 131.9, 134.4, 151.9, 164.8, 165.6.

3b. 4-Bromo-1,8-naphthalimide (4 mM, 1 equiv.), Cu_2O (0.2 equiv.), potassium carbonate (0.5 equiv.), 1,2-diaminoethane (10 equiv.) and DMSO (30 mL) were added to a flask. The flask was then sealed after filling with N_2 and the mixture heated to 90 °C. After stirring at this temperature for 10 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was washed three times with water and dichloromethane, then directly filtered through a pad of silica gel and concentrated to yield the product, which was purified by silica gel chromatography (4 : 1 ethyl acetate–MeOH) to yield **3b** as a yellow solid. EI-MS m/z 255 (M). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 2.86 (t, J = 6.4 Hz, 2H), 3.38 (t, J = 6.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 1H), 7.66 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 7.2 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-d_6) (δ, ppm): 46.1, 62.6, 104.2, 108.6, 121.0, 122.8, 124.7, 129.2, 130.5, 131.2, 133.9, 151.3, 164.3, 165.0.

4a. 4-Bromo-*N*-(2-hydroxyethyl)-1,8-naphthalimide (0.6 mM, 1 equiv.), Cu_2O (0.2 equiv.), potassium carbonate (0.5 equiv.), ethanolamine (10 equiv.) and DMSO (6 mL) were added to a flask. The flask was then sealed after filling with N_2 and the mixture heated to 90 °C. After stirring at this temperature for 10 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was washed three times with water and dichloromethane, then directly filtered through a pad of silica gel and concentrated to yield the product, which was purified by silica gel chromatography (4 : 1 ethyl acetate–MeOH) to yield **4a** as a yellow solid. ESI-MS m/z 301.2 (M + H), 323.1 (M + Na), 339.1 (M + K). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.45 (q, J = 5.6 Hz, 2H), 3.57 (q, J = 6.4 Hz, 2H), 3.68 (q, J = 5.6 Hz, 2H), 4.10 (t, J = 6.4 Hz, 2H), 4.76 (t, J = 5.6 Hz, 1H), 4.86 (t, J = 5.6 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 7.66 (m, 2H), 8.25 (d, J = 8.4 Hz, 1H), 8.42 (d, J = 7.2 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H).^{13}C-NMR (400 MHz, DMSO-d_6) (δ, ppm): 41.9, 46.0, 58.5, 59.3, 104.3, 108.2, 120.6, 122.4, 124.7, 129.0, 130.0, 131.1, 134.7, 151.3, 163.6, 164.4.

4b. 4-Bromo-*N*-(2-hydroxyethyl)-1,8-naphthalimide (0.4 mM, 1 equiv.), Cu_2O (0.2 equiv.), potassium carbonate (0.5 equiv.), glycine (10 equiv.) and DMSO (4 mL) were added to a flask. The flask was then sealed after filling with N_2 and the mixture heated to 90 °C. After stirring at this temperature for 10 h, the heterogeneous mixture was cooled to room temperature and diluted with dichloromethane. The resulting solution was washed three times with water and dichloromethane, then directly filtered through a pad of silica gel and concentrated to yield the product, which was purified by silica gel chromatography (4 : 1 ethyl acetate–MeOH) to yield **4b** as a yellow solid. ESI-MS *m/z* 313.1 (M − H). ^{1}H-NMR (400 MHz, DMSO-d_6) (δ, ppm): 3.57 (q, J = 6.0 Hz, 2H), 4.10 (t, J = 6.4 Hz, 2H), 4.16 (d, J = 5.6 Hz, 2H), 4.76 (t, J = 5.6 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 7.6 Hz, 1H), 8.03 (t, J = 5.6 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 7.2 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 12.40 (s, 1H). ^{13}C-NMR (400 MHz, DMSO-d_6) (δ, ppm): 40.8, 41.9, 58.5, 104.8, 109.2, 120.6, 122.5, 125.1, 128.8, 129.8, 131.2, 134.4, 150.9, 163.6, 164.4, 171.8.

Synthesis of imide-Hg-imides[8]

1-Hg-1. The complex was prepared by adding $HgCl_2$ salt (0.5 equiv. in water) to a solution of **1** (1 mmol, 2 mL basic water solution). The resulting solid was washed with water and methanol, and dried under vacuum (130 mg, 65%).

2-Hg-2. **2** (0.5 mmol) was dissolved in 6 mL methanol–DMF. Triethylamine (TEA) (1 equiv.) and a $HgCl_2$ solution (0.5 equiv. in methanol) were then added. The resulting solid was washed with water and methanol, and dried under vacuum (83 mg, 67%).

3a-Hg-3a. **3a** (0.13 mmol) was dissolved in 2 mL DMSO. Then, TEA (1 equiv.) and a $HgCl_2$ solution (0.5 equiv. in methanol) were added. The resulting solid was washed with DMSO and methanol, and dried under vacuum (35 mg, 75%).

Results and discussion

Mass spectrometry

The electrospray ionization-MS (ESI-MS) analysis of the precipitates of Hg(II) with **1**, **2** and **3a** exhibited a [2(**1** − H) + Hg + Na] peak at *m/z* 421.0, a [2(**2** − H) + Hg + Na] peak at *m/z* 517.1 and a [2(**3a** − H) + Hg + H] peak at *m/z* 713.5, respectively. The electron impact-MS (EI-MS) analysis of the complexes of Hg(II) with **1** and **2** also exhibited molecular ion peaks at *m/z* 398 [2(**1** − H) + Hg] and 494 [2(**2** − H) + Hg] (Fig. 1, S1†), respectively[9] The isotopic pattern of these peaks supports the presence of Hg in the molecular ions. The MS data suggest the formation of 1 : 2 complexes of Hg with the imides.

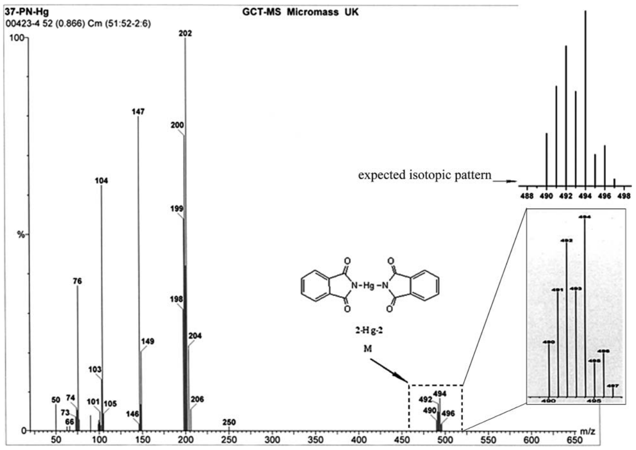


Fig. 1 The EI-MS of complex **2**-Hg-**2**.

^{1}H-nuclear magnetic resonance

The ^{1}H-NMR spectra of the complex of Hg(II) with **3a** show a complete disappearance of the imido proton peak (11.2 ppm), considerable downfield shifts of the two naphthyl proton peaks (8.2 and 8.4 ppm) ($\Delta\delta \approx 0.1$ ppm), and moderate downfield shifts of the other naphthyl protons and aromatic N–H peaks compared to the spectrum of **3a** (Fig. 2). Similar changes were also found in the ^{1}H-NMR spectra of the complex of Hg(II) with **1** (loss of imido proton peak and considerable downshift of the methylene protons) (Fig. S2†). These ^{1}H-NMR data suggest that the imido protons of compounds **3a** and **1** are displaced by Hg(II).

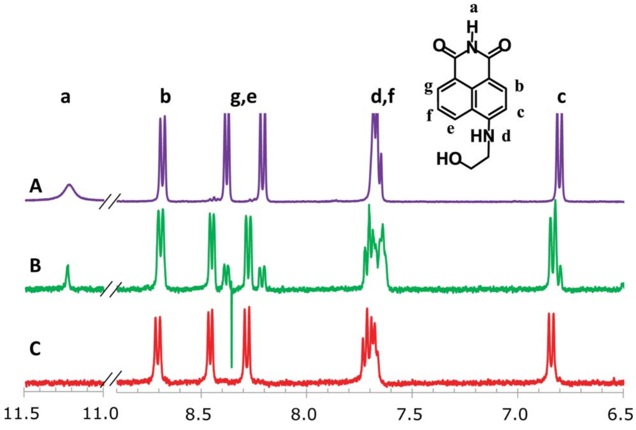


Fig. 2 ^{1}H-NMR spectra (400 MHz, DMSO-d_6) of **3a** (A), coexisted **3a** and **3a**-Hg-**3a** (B); **3a**-Hg-**3a** (C).

X-ray photoelectron spectroscopy

The XPS survey spectra of complexes of Hg(II) with **3a** and **2** exhibit four characteristic peaks corresponding to C1s, O1s, N1s and Hg 4f (Fig. 3, S3†). No signals attributed to Cl2p are found. The measured atom ratios of C : O : N : Hg are 28.00 : 5.77 : 3.89 : 0.93 and 15.73 : 1.89 : 4.00 : 1.15 for the two complexes, which are in good agreement with the theoretical ratios of complexes **3a**-Hg-**3a** (28 : 6 : 4 : 1) and **2**-Hg-**2** (16 : 2 : 4 : 1) respectively (Table S1†). The high-resolution N1s XPS spectra show that the N1s binding energy

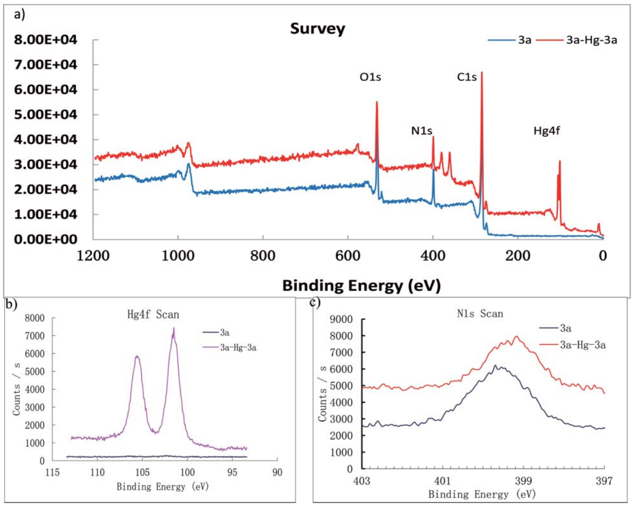


Fig. 3 XPS spectrum of **3a** (blue) and **3a**-Hg-**3a** (red) (a: survey spectrum; b: high resolution Hg 4f spectrum; c: high resolution N 1 s spectrum).

of these complexes shifts mildly towards a lower value than that of **3a** (from 399.7 to 399.3 eV) and **2** (from 400.0 to 399.4 eV) (Fig. S3†), which is consistent with a smaller Pauling electronegativity for Hg (2.00) than for H (2.20).[10] The XPS results suggest Hg–N bond formation and a 2 : 1 stoichiometry of ligand/Hg.

Infrared spectroscopy

The IR spectra of the complexes of Hg(II) with **1**, **2** and **3a** also exhibit changes compared with those of ligands **1**, **2** and **3a** alone (Fig. 4, S4†). The peaks in the range 3250–3050 cm^{-1} ($\nu_{\text{N–H}}$) disappear, which may be due to the displacement of the imido protons. The strong absorption bands of $\nu_{\text{C=O}}$ (imide I, 1650–1750 cm^{-1})[11] shift to a lower wavenumber by *ca.* 70 cm^{-1}, which is consistent with that reported for platinum-imide complexes.[11] The absorption bands of $\nu_{\text{C–N–C}}$ (imide III, 1050–1200 cm^{-1})[11] shift to a higher wavenumber by *ca.* 50 cm^{-1}. These changes in the IR spectra suggest that the formation of the N–Hg bond may result in a reduced bond order of the C=O bond and an enhanced bond order of the N–C bond.

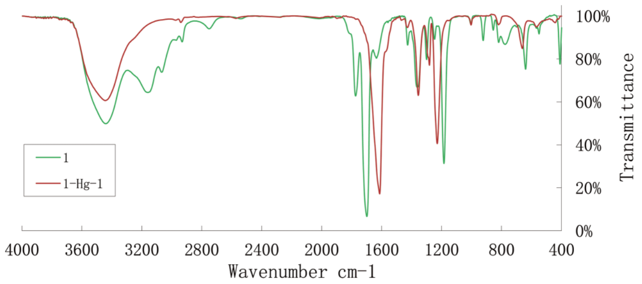


Fig. 4 IR spectra of **1** (green) and **1**-Hg-**1** (red).

The above results demonstrate that Hg(II) substitutes the imido proton to form a stable neutral imide-Hg(II)-imide complex, as shown in Scheme 1. Since crystals of these complexes for X-ray analysis have not been obtained yet, we cannot confirm whether there are any interactions between the carbonyl oxygen and Hg atoms. As far as we know, only one cyclic imide, 3,3-dimethylglutarimidato (six-membered ring, unconjugated)[12] has been report to form a two-coordinate imide-Hg-imide complex besides two thymine derivatives: 1-methylthymine[3d] and thymidine.[13] The reported crystal data[3d,12] show no interaction between the carbonyl oxygen and Hg atoms. Based on all the information we have, it can be deduced that the formation of a two-coordinate imide-Hg-imide complex is common to all *N*-unsubstituted cyclic imides.

The fluorescence properties of 3a and 4a

1,8-Naphthalimide derivatives are well-known fluorescent dyes with a strong fluorescence, high photostability and a large Stokes shift. Therefore, they have been widely used for the development of fluorescence sensors.[14–16] Complex formation of Hg^{2+} with **3a** was found to quench the fluorescence of 1,8-naphthalimides in aqueous solution (Fig. 5a), which provides an easy way to further understand the interactions between Hg^{2+} and imides. Three naphthalimides, **3b**, **4a** and **4b**, were synthesized for further investigation. Hg(II) was able to quench the fluorescence of **3a** and **3b** by up to 90% but did not quench the fluorescence of *N*-substituted naphthalimides **4a** and **4b** (Fig. S5 and S6†), which suggests that the fluorescence quenching is the result of the binding of Hg(II) to the imide N-atom through imido proton–Hg exchange, but not to other groups on the naphthalimides. The quenched fluorescence could be restored by adding Na$_2$S or HCl (Fig. S7†), indicating that the reaction of Hg(II) with imides is reversible.

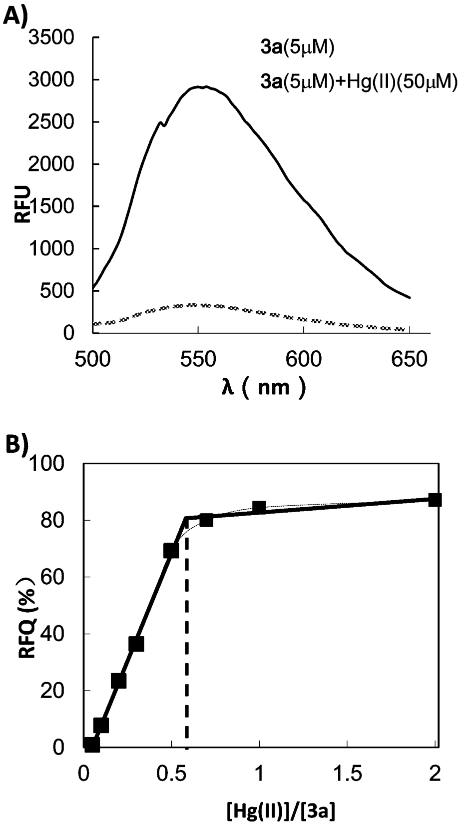


Fig. 5 (A) The emission spectra (excitation at 440 nm) of **3a** and **3a** + Hg(II) in phosphate buffer at pH 7.50; (B) the fluorescence titration of **3a** (5 μM) with Hg(II). RFQ = relative fluorescence quenching.

The fluorescence titration curve of **3a** with Hg(II) (Fig. 5b) shows that the level of fluorescence quenching of **3a** reached plateau with the addition of about $\frac{1}{2}$ equiv. of Hg(II) and that excess Hg(II) did not increase the quenching any further. This result implies that a complex of 2 : 1 stoichiometry (**3a**-Hg(II)) was formed. When 5.0 μM of **3a** was employed in water or phosphate buffer, its fluorescence intensity decreased linearly with the concentration of Hg(II) between 0.25 and 2.5 μM ($R^2 = 0.9985$) (Fig. S8†), implying that **3a** can be used as a fluorescence sensor for Hg(II).

Since two protons are released when the **3a**-Hg-**3a** complex forms, the effect of pH on the formation of the **3a**-Hg-**3a** complex is worth investigating. In the absence of Hg^{2+}, the fluorescence intensity of **3a** remains constant in the pH range 2.9–11.4 (Fig. S9†). As shown in Fig. 6, upon adding Hg(II), the fluorescence of **3a** was quenched quickly at pH values higher than 4.5, and no significant change of fluorescence was observed at pH values lower than 4.05. At pH 4.25, the fluorescence intensity of **3a** decreased gradually over time and reached an equilibrium after 800 min. The reaction equilibrium constant can be calculated as:

$$K = [\mathrm{H}^+]^2[\mathbf{3a}\text{-Hg-}\mathbf{3a}]/([\mathbf{3a}]^2[\mathrm{Hg}^{2+}]).$$

At equilibrium, the fluorescence decrease is about $\frac{2}{3}$ of the maximum quenching observed; therefore [**3a**-Hg-**3a**] should equal

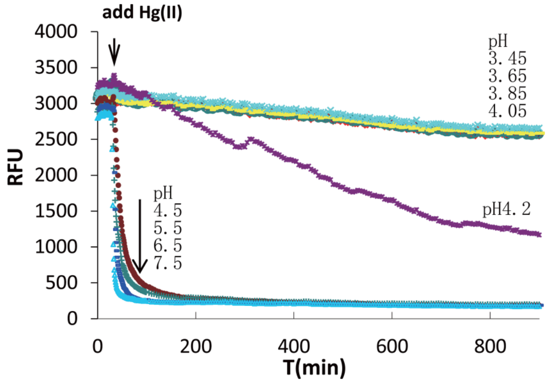


Fig. 6 Fluorescence decay curves of **3a** in the presence of Hg(II) at different pH values (5 µM **3a**, 50 µM Hg(II) in 20 mM phosphate buffer).

[**3a**] at this point. Since the amount of added Hg(II) is in a large excess, [Hg^{2+}] is approximately equal to its initial concentration. Considering all of the above, we can calculate the apparent equilibrium constant to be:

$$K_{app} = (10^{-4.25})^2 \times (\tfrac{1}{3} \times 5 \times 10^{-6})/((\tfrac{1}{3} \times 5 \times 10^{-6})^2 \times (50 \times 10^{-6})) \\ = 1.2 \times 10^2.$$

Although this equilibrium constant is not high enough, the concentration of **3a**-Hg-**3a** is inversely proportional to the square of the concentration of H^+ according to the equation:

$$[\mathbf{3a}\text{-Hg-}\mathbf{3a}] = K[\mathbf{3a}]^2[Hg^{2+}]/[H^+]^2.$$

This means that the formation of **3a**-Hg-**3a** can be greatly increased by increasing the pH of the solution.

The specificity of the formation of imide-Hg-imide was investigated by measuring the fluorescence of **3a** in the presence of cations such as Pb(II), Cu(II), Ge(II), Co(II), Mn(II), Fe(II), Zn(II), Ni(II), Ba(II), Mg(II), Ca(II), Ce(III), Fe(III), NH_4^+, Ag(I) and K(I). As shown in Fig. 7, only Hg(II) quenches the fluorescence of **3a**, and the other cations have no significant effect on the fluorescence intensity of **3a**. These results indicate that **3a** has a remarkable selectivity for Hg(II), which is consistent with the highly specific interaction between Hg(II) and thymine.[17]

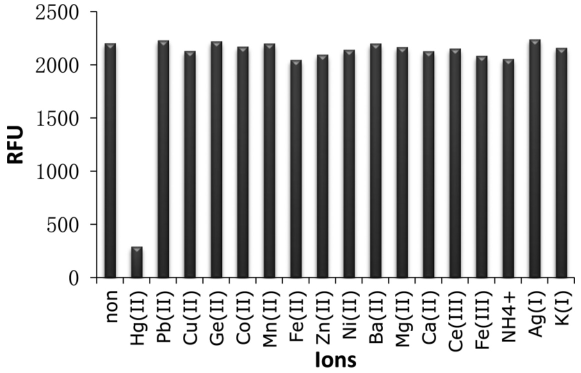


Fig. 7 The selectivity of the reaction of **3a** and Hg(II) (**3a**, 5 µM; Hg(II) 10 µM; other cations >25 µM).

The fluorescence response of **3a** and **4a** to Hg(II) suggests that the reaction of Hg(II) with unsubstituted cyclic imides is rapid, selective and complete at moderate to high pH values. These features would enable the design of various unsubstituted cyclic imides for the specific sensing and chelating of Hg(II). **3a** and **3b** exhibit a fluorescence turn-off property upon binding to Hg(II), which may limit their practical utility in highly sensitive detection. It is feasible to design highly sensitive sensors by combining cyclic imides with other fluorescence molecules (for example pyrene), polymers or nanomaterials, in which imides are only used as the recognition unit. Cyclic imides may also be used as ligands for preparing a sorbent for Hg(II) removal. This sorbent can possess high selectivity and be regenerated by acidic solutions.

Conclusions

In summary, besides the nucleobase thymine (T), other *N*-unsubstituted cyclic imides have been found to react specifically with Hg(II) to form imide-Hg-imide complexes through an imido proton–metal exchange process. This specific reaction is reversible and occurs rapidly at moderate to high pH values. Given that the toxicity of mercury is well documented, and that Hg(II) is a main and stable form of mercury pollutants in the environment,[1,2] the discovery of this highly specific binding feature of *N*-unsubstituted imides to Hg(II) expands the comprehension of T-Hg-T interactions, opening up new possibilities in designing novel and potent ligands for sensing and chelating Hg(II) based on cyclic imides.

Acknowledgements

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