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A benzoxadiazole–thiourea conjugate as a fluorescent chemodosimeter for Hg(II) in aqueous media

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ABSTRACT

A benzoxadiazole–thiourea conjugate (**1**) was synthesized and used for chemodosimetric detection of Hg^{2+} in aqueous media. The compound **1** shows a selective and quantitative fluorescence quenching upon addition of Hg^{2+}. This is promoted via a Hg^{2+}-induced desulfurization of the thiourea moiety, leading to a formation of an imidazoline derivative, **2**. *Ab initio* molecular orbital calculation reveals that the formation of imidazoline moiety by the reaction of **1** with Hg^{2+} promotes a photoinduced electron transfer from the aniline moiety to the excited state benzoxadiazole moiety and results in fluorescence quenching.

1. Introduction

Hg^{2+} is one of the most hazardous components in the environment [1]. The design and development of Hg^{2+}-selective probes that show colorimetric or fluorometric response to Hg^{2+} has therefore attracted a great deal of attention [2]. A large number of Hg^{2+}-selective probes have been proposed so far [3]; however, most of the probes act only in organic media. Hg^{2+} probes that act in aqueous media have also been proposed [4]; however, many of these probes show insufficient selectivity for Hg^{2+}. The design of Hg^{2+} probes with high selectivity in aqueous media is therefore of current focus.

Recently, reaction-based Hg^{2+} probes that are called chemodosimeters have attracted much attention [5], as alternative to the classical chelation-based probes. The irreversible chemical reaction between the chemodosimeter molecules and Hg^{2+} leads to a significant change in absorption or fluorescence spectrum. Several colorimetric or fluorometric chemodosimeters for Hg^{2+} that act in aqueous media have been proposed so far based on the reactions promoted selectively by Hg^{2+}, such as hydrolysis of alkynes, alkenes, or azines [6], desulfurization of sulfide or thiocarbonyl groups [7], and desulfurization of thiocarbonyl group followed by structure rearrangement (formation of oxadiazole, thiazoline, or imidazoline ring) [8–10]. In particular, the desulfurization followed by the formation of imidazoline ring is one of the potential reactions for Hg^{2+} detection [10], because: the chemodosimeter molecules are easily synthesized by an introduction of thiourea moiety; the reaction occurs very rapidly (terminates within 1 min); and, the reaction promotes a significant change in absorption or fluorescence spectrum. However, detailed analysis of the change in electronic configuration of the chemodosimeter molecules, associated with the imidazoline ring formation, has not been carried out.

7-Nitrobenzo-2-oxa-1,3-diazole (NBD) is a fluorescent molecule that has been widely used as a fluorescence labeling reagent and a fluorophore for fluorescent probes because of its long excitation and emission wavelengths [11]. In the present work, a NBD derivative containing a thiourea moiety (**1**, Fig. 1) was synthesized and used as a fluorescent chemodosimeter for Hg^{2+} in aqueous media. The fluorescence of **1** is quenched selectively by Hg^{2+}, and the intensity decreases quantitatively with an increase in the Hg^{2+} amount, enabling selective and quantitative detection of Hg^{2+}. The fluorescence response of **1** is promoted via a Hg^{2+}-induced desulfurization of the thiourea moiety, leading to a formation of an imidazoline derivative (**2**, Fig. 2). The electronic configurations of **1** and **2**, determined by *ab initio* molecular orbital calculation, indicate that the formation of imidazoline moiety promotes a photoinduced electron transfer from the aniline moiety to the excited state benzoxadiazole moiety and results in fluorescence quenching.

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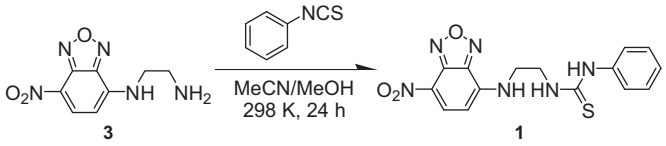


Fig. 1. Synthesis of the chemodosimeter, **1**.

2. Experimental

2.1. General

Fluorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer [12]. Absorption spectra were measured on a UV–Vis photodiode-array spectrophotometer (Shimadzu; Multispec-1500) [13]. The spectra were measured in an aerated condition at 298 ± 1 K using a 10-mm path length quartz cell. Perchlorate (Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Mn^{2+}, and Fe^{2+}), nitrate (Ni^{2+} and Co^{2+}), and tetrafluoroborate salts (Ag^{+}) were used as the metal cation source. ^1H and ^{13}C NMR spectra were obtained by a JEOL JNM-GSX270 Excalibur. EI-MS chart was obtained by a JEOL JMS-700 Mass Spectrometer.

2.1.1. Synthesis of *1*

Compound **3** (83.4 mg, 0.37 mmol) [14] and phenyl isothiocyanate (0.70 mL, 5.9 mmol) were stirred in a mixture of MeCN (10 mL) and MeOH (10 mL) at 298 K for 24 h. The resultant was concentrated by evaporation. The crude product was purified by a silica gel column chromatography with CH_2Cl_2/ethyl acetate (10/1, v/v). The eluent was concentrated by evaporation and dried in vacuo, affording **1** as a yellow solid (47.1 mg, 36%). ^1H NMR (CD_3CN, 270 MHz, TMS): δ (ppm) = 8.50 (d, J = 8.74 Hz, 1H), 8.20 (s, 1H), 7.90 (s, 1H), 7.32–7.39 (m, 2H), 7.21–7.26 (m, 3H), 6.83 (s, 1H), 6.41 (d, J = 8.74 Hz, 1H), 3.94 (q, J = 5.88 Hz, 2H), and 3.73 (q, J = 5.72 Hz, 2H). ^{13}C NMR (DMSO-d_6, 68 MHz, TMS): δ (ppm) = 180.4, 145.2, 144.2, 143.9, 138.4, 137.5, 128.6, 124.5, 123.5, 120.8, 99.3, 42.7, and 42.1. EI-MS: Calcd for $C_{15}H_{14}N_6O_3S$: 358.1, found: m/z 358.4 $[M]^+$. HRMS (EI^+) m/z calcd for $C_{15}H_{14}N_6O_3S$ $[M]^+$ 358.0848, found 358.0853. ^1H, ^{13}C NMR, and EI-MS charts are summarized in AppendixBFigs. S1-S3 (Supplementary material).

2.1.2. Synthesis of *2*

1 (50.3 mg, 0.14 mmol) and $Hg(ClO_4)_2{\cdot}6H_2O$ (71.6 mg, 0.14 mmol) were stirred in MeCN (20 mL) at room temperature for 10 min. The resultant was concentrated by evaporation. The crude product was purified by a silica gel column chromatography with CH_2Cl_2/ethyl acetate (5/1, v/v). The eluent was dried in vacuo, affording **2** as an orange solid (23.6 mg, 52%). ^1H NMR (CD_3CN, 270 MHz, TMS): δ (ppm) = 8.73 (d, J = 8.74 Hz, 1H), 8.59 (d, J = 8.57 Hz, 1H), 7.39 (t, J = 7.92 Hz, 2H), 7.15 (t, J = 7.50 Hz, 1H), 7.08 (d, J = 8.24 Hz, 2H), 4.67 (t, J = 7.83 Hz, 2H), and 3.64 (t, J = 7.91 Hz, 2H). ^{13}C NMR (acetone-d_6, 68 MHz, TMS): δ (ppm) = 152.5, 149.7, 147.2, 144.9, 139.3, 135.1, 129.8, 124.9, 123.2, 122.9, 113.1, 50.9, and 40.9. EI-MS: Calcd for $C_{15}H_{12}N_6O_3$: 324.1, found: m/z 324.0 $[M]^+$. HRMS (EI^+) m/z calcd for $C_{15}H_{12}N_6O_3$ $[M]^+$ 324.0971, found 324.0954. ^1H, ^{13}C NMR, and EI-MS charts are summarized in AppendixBFigs. S4-S6 (Supplementary material).

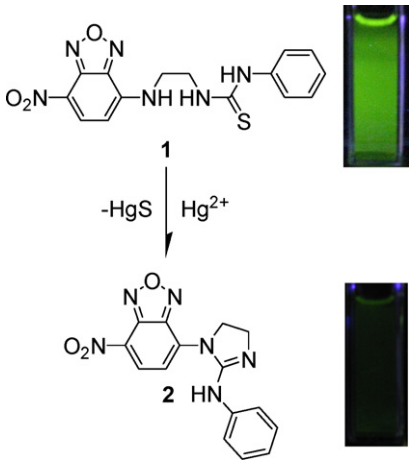


Fig. 2. Structure change of **1** via the reaction with Hg^{2+}, and the change in fluorescence color of the solution.

2.2. Calculation details

Preliminary geometry optimizations were performed using the WinMOPAC version 3.0 software (Fujitsu Inc.) at the semiempirical PM3 level [15]. The obtained structures were fully optimized with tight convergence criteria at the DFT level with the Gaussian 03 package [16], using the B3LYP/6-31G* basis set. The excitation energies and the oscillator strengths of each structure were calculated by the time-dependent density-functional response theory (TD-DFT) [17] at the same level of optimization using the polarizable continuum model (PCM) [18] with water as a solvent. Cartesian coordinates for the calculated structure are summarized in Supplementary material.

3. Results and discussion

3.1. Synthesis and spectral properties

The synthesis procedure of the compound **1** is summarized in Fig. 1. The reaction of a NBD derivative, **3**, with phenyl isothiocyanate in a mixture of MeCN and MeOH at 298 K gives rise to **1** as a yellow solid with 36% yield. The purity of **1** was confirmed by ^1H, ^{13}C NMR and EI-MS analysis, as summarized in AppendixBFigs. S1-S3 (Supplementary material).

Fig. 3a shows the fluorescence spectra (λ_{ex} = 468 nm) of **1** (10 μM) measured in a buffered MeCN/water mixture (9/1, v/v; HEPES 10 mM; pH 7.0) with 1 equiv. of respective metal cations. Without metal cation, **1** shows a distinctive fluorescence band at 480–650 nm, assigned to the NBD fluorescence [19], where the fluorescence quantum yield (Φ_F) is determined to be 0.01 [20]. Addition of Hg^{2+}, however, leads to a significant decrease in the fluorescence intensity (Φ_F < 0.001). As shown in Fig. 2, a bright yellow-green fluorescence of **1** almost disappears upon Hg^{2+} addition. In contrast, addition of other metal cations to **1** shows almost the same fluorescence spectra as that obtained without metal cation. This indicates that **1** undergoes selective fluorescence quenching via the interaction with Hg^{2+}. The thiophilic Ag^{+} and Cu^{2+} cations often interfere the Hg^{2+} sensing by the sulfur-containing probes [21]. However, as shown in AppendixBFig. S7 (Supplementary Material), the fluorescence response of **1** to Hg^{2+} is unaffected by the addition of these cations, indicating that **1** enables selective Hg^{2+} sensing even in the presence of these cations. It must be noted that the decrease in fluorescence intensity terminates within 1 min (AppendixBSupplementary Material, Fig. S8). These data clearly indicate that **1** enables rapid and selective fluorometric detection of Hg^{2+} in aqueous media. It must also be noted that **1** is tolerant for Hg^{2+} detection in larger water content solutions. Fig. 4 shows the effect of water content on the fluorescence intensity of **1** measured without and with 1 equiv. of Hg^{2+}. The fluorescence of **1** is successfully quenched by the addition of Hg^{2+} even in the presence of 10–90% water. The fluorescence intensity of **1** obtained without Hg^{2+} decreases with an increase in water content, although the intensity obtained with

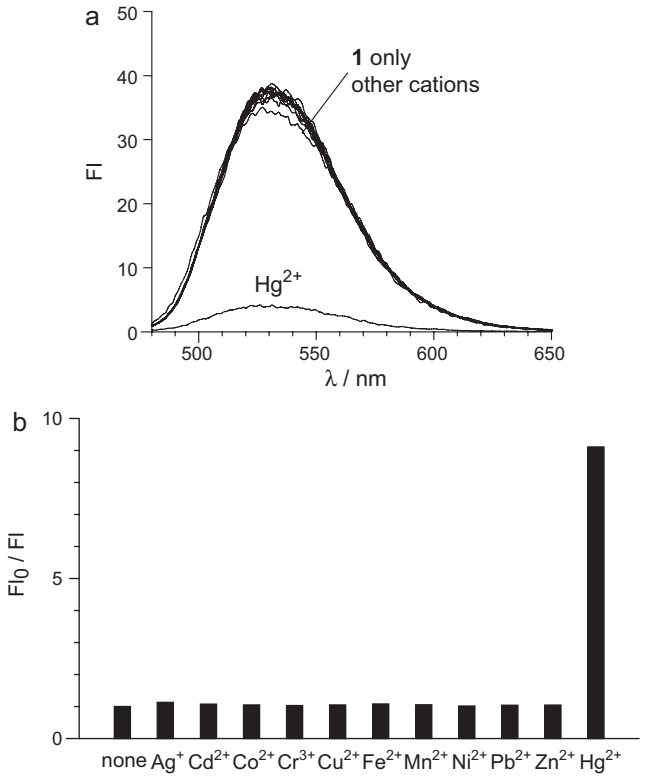


Fig. 3. (a) Fluorescence spectra (λ_{ex} = 468 nm) of **1** (10 μM) measured in a buffered MeCN/water mixture (9/1, v/v; HEPES 10 mM; pH 7.0) with respective metal cations (1 equiv.) at 298 K. The spectra were measured after stirring the solution for 1 min after addition of respective metal cations. (b) The ratio of the fluorescence intensity (FI_0/FI) of 1 (λ_{em} = 531 nm), where FI_0 and FI are the intensity measured without and with cations.

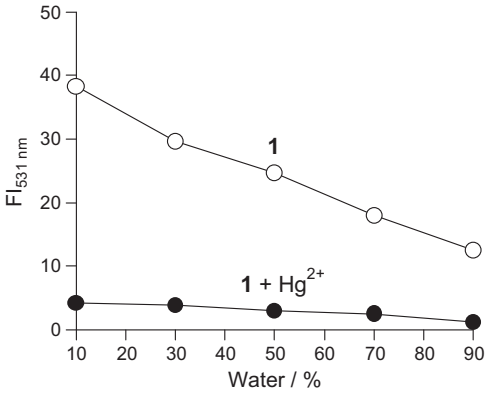


Fig. 4. Effect of water content in the MeCN solution (HEPES 10 mM; pH 7.0) on the fluorescence intensity (λ_{ex} = 468 nm; λ_{em} = 531 nm) of **1** (10 μM) measured without and with 1 equiv. of Hg^{2+}.

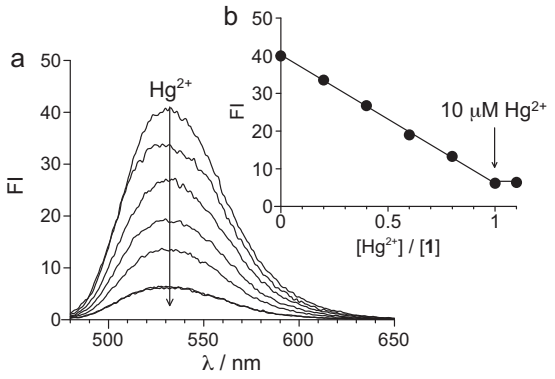


Fig. 5. (a) Change in fluorescence spectra (λ_{ex} = 468 nm) of **1** (10 μM) measured in a buffered MeCN/water mixture (9/1, v/v; HEPES 10 mM; pH 7.0) upon addition of Hg^{2+}. (b) Change in the fluorescence intensity monitored at 531 nm.

Hg^{2+} is kept very weak at the entire water content range. This indicates that the sensitivity of **1** to Hg^{2+} decreases with the water content increase, and the lower water content solution allows more sensitive Hg^{2+} detection.

The compound **1** shows a stoichiometrical fluorescence response to the Hg^{2+} amount. Fig. 5 shows the result of fluorescence titration of **1** with Hg^{2+}. The stepwise Hg^{2+} addition to **1** leads to a decrease in the fluorescence intensity, and the spectral change almost stops upon addition of 1 equiv. of Hg^{2+}. This indicates that **1** interacts with Hg^{2+} in a 1:1 stoichiometry. Addition of EDTA (1 equiv.) to the resulting solution does not show further spectral change (AppendixBSupplementary Material, Fig. S9), indicating that **1** reacts with Hg^{2+} irreversibly. As shown in Fig. 5b, a linear relationship is observed between the fluorescence intensity and the Hg^{2+} amount at the range of 0–1 equiv. of Hg^{2+}, which corresponds to 0–10 μM Hg^{2+}. This suggests that **1** enables quantitative Hg^{2+} detection. The detection limit (DL) can be calculated with the equation, DL = $3S_0/m$ [22], where m is the calibration sensitivity of the fluorescence intensity change ($\Delta FI = FI_0 - FI$) *versus* the Hg^{2+} concentration, and S_0 is the standard deviation of the blank FI_0 signal obtained without Hg^{2+}. The m value is determined to be 3.39 at the range of 0–10 μM Hg^{2+} (R^2 = 0.999), and the S_0 value is calculated by ten replicate blank sample measurements to be 0.677. The detection limit is therefore determined to be 0.60 μM, which is the value similar to that of the early reported chemodosimeters based on the imidazoline ring formation [10].

Table 1
Calculated excitation energy (E), wavelength (λ), and oscillator strength (f) for low-laying singlet state (S_n) of **1** and **2**.

Compound		Main orbital transition	CIC[a]	E (eV)	λ (nm)	f
1	$S_0 \rightarrow S_1$	HOMO−2 → LUMO	0.20789	2.8619	433.23	0.0059
		HOMO−1 → LUMO	0.66451			
	$S_0 \rightarrow S_2$	HOMO−1 → LUMO	0.12636	2.9053	426.74	0.2906
		HOMO → LUMO	0.60112			
		HOMO → LUMO+1	0.15959			
	$S_0 \rightarrow S_3$	HOMO−2 → LUMO	0.66632	3.0439	407.32	0.0148
		HOMO−1 → LUMO	−0.18883			
2	$S_0 \rightarrow S_1$	HOMO−1 → LUMO	0.22500	2.3373	530.45	0.0397
		HOMO → LUMO	0.65715			
	$S_0 \rightarrow S_2$	HOMO−1 → LUMO	0.61252	2.7998	442.83	0.3337
		HOMO → LUMO	−0.16362			
	$S_0 \rightarrow S_3$	HOMO−2 → LUMO	0.70548	3.2546	380.95	0.0018

[a] CI expansion coefficients for the main orbital transitions.

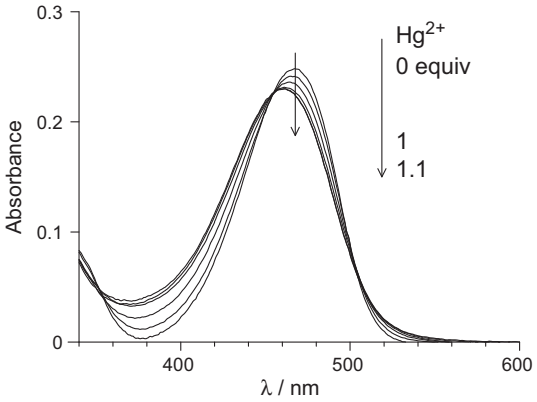


Fig. 6. Change in absorption spectra of **1** (10 μM) measured in a buffered MeCN/water mixture (9/1, v/v; HEPES 10 mM; pH 7.0) upon addition of Hg^{2+}.

Fig. 6 shows the results of absorption titration of **1** with Hg^{2+}. Without cation, **1** shows a distinctive absorption band centered at 468 nm, assigned to the NBD moiety [23]. The Hg^{2+} addition leads to a decrease in this absorption band with a slight blue shift. The spectral change almost stops upon addition of 1 equiv. of Hg^{2+}, which is consistent with the change in fluorescence spectra (Fig. 5). The result again suggests that **1** reacts with Hg^{2+} in a 1:1 stoichiometry. The clear isosbestic points at 455 and 504 nm indicate that the reaction of **1** with Hg^{2+} produces a single component.

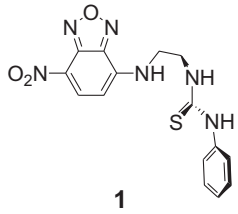
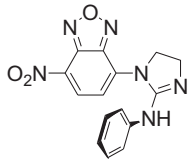
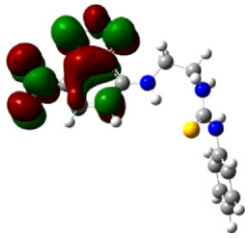
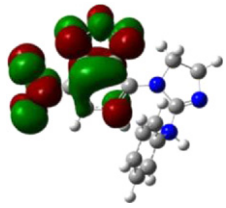
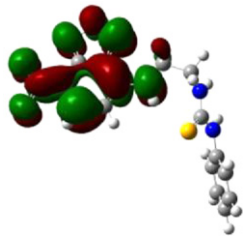
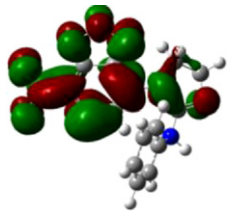
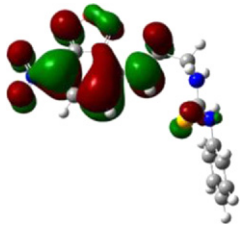
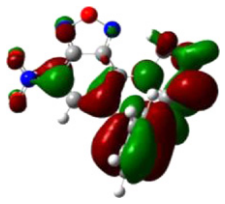
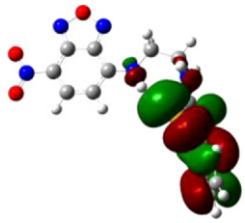
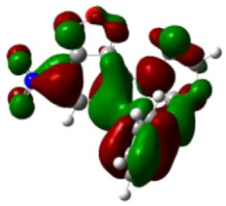
3.2. Mechanism of Hg^{2+}-promoted fluorescence quenching

As shown in Fig. 2, the fluorescence quenching of **1** upon Hg^{2+} addition is due to the Hg^{2+}-promoted desulfurization of the thiocarbonyl moiety of **1** followed by cyclization [10], leading to the formation of an imidazoline derivative, **2**. To clarify this, **1** was treated with $Hg(ClO_4)_2$ in MeCN at room temperature. The obtained product was purified by a silica gel column chromatography and analyzed by ^1H, ^{13}C NMR, and EI-MS analysis (see Section 2). All of the characterization data (AppendixBSupplementary material, Figs. S4-S6) fully confirm the formation of the imidazoline derivative, **2**.

The fluorescence quenching of **2** is due to the promotion of an intramolecular photoinduced electron transfer (PET) from the aniline moiety to the excited state NBD moiety, as is observed in the intermolecular aniline–NBD system [24]. The electronic excitation energy ($E_{0\text{-}0}{}^{NBD}$) and the redox potential of the NBD moiety [E(NBD/NBD$^-$)] are 2.52 eV and −0.64 V (*vs.* SCE in MeCN), respectively [25], and the redox potential of the aniline moiety [E(aniline$^+$/aniline)] is +0.9 V (*vs.* SCE in MeCN) [26]. Therefore, the free energy change of the PET process, $\Delta G_{PET(aniline \rightarrow NBD^*)}$ (=$-[E_{0\text{-}0}{}^{NBD} + eE(NBD/NBD^-) - eE(aniline^+/aniline)]$) [27], has a negative value (−0.98 eV). This indicates that the PET process is thermodynamically favorable.

Both compounds **1** and **2** contain aniline and NBD moieties; however, the fluorescence quenching occurs strongly in **2**. To clarify this difference, *ab initio* calculations for **1** and **2** were performed within the Gaussian 03 program. Table 1 summarizes the main orbital transitions of the compounds. The singlet electronic transitions of **1** and **2** are mainly contributed by HOMO → LUMO ($S_0 \rightarrow S_2$) and HOMO−1 → LUMO ($S_0 \rightarrow S_2$) transitions, respectively. The $S_0 \rightarrow S_2$ transition energy of **1** is 2.91 eV (427 nm), which is similar to that of **2** (2.80 eV, 443 nm). These calculated energies are similar to the observed absorption maxima (**1**, 468 nm; **2**, 462 nm). Table 2 summarizes the interfacial plots of molecular orbitals of **1** and **2**. The electron density of HOMO and LUMO orbitals of **1** is located on the NBD moiety, where π-electrons on the aniline moiety exist at lower energy level orbitals (HOMO−1 and HOMO−2). This suggests that the PET process from the aniline moiety to the excited state NBD moiety does not occur in the compound **1**. This is probably because the lone pair electrons of the aniline nitrogen are associated with the thiocarbonyl π* orbital, and the charge density is transferred to the thiocarbonyl moiety [28]. This lowers the energy level of the aniline moiety than that of the NBD moiety and, hence, suppresses the PET process in **1**.

Table 2
Interface plots of some molecular orbitals of **1** and **2**.[a]

Orbital	**1**	**2**
		
LUMO+1		
LUMO		
HOMO		
HOMO−1		
HOMO−2		

[a] The gray, blue, red, yellow, and white atoms denote C, N, O, S, and H atoms, respectively.

The compound **2** has a different electronic configuration. As shown in Table 2, HOMO−1 and LUMO orbitals of **2** have an electron density on the NBD moiety, indicating that the electronic excitation of **2** has a NBD $\pi\pi^*$ electronic character, as does **1**. However, the electron densities located on the aniline moiety are observed in the HOMO and HOMO−1 orbitals. This clearly indicates that the PET process from the aniline moiety to the excited state NBD moiety indeed occurs in the compound **2**. This is probably because the removal of thiocarbonyl moiety leads to an increase in the energy level of aniline moiety. The above findings indicate the desulfurization by Hg^{2+} promotes the intramolecular PET process and, hence, results in fluorescence quenching.

4. Conclusion

We found that a NBD–thiourea conjugate (**1**) behaves as a fluorescent chemodosimeter for selective Hg^{2+} detection in aqueous media. **1** shows a quantitative fluorescence quenching with the Hg^{2+} amount. The fluorescence response occurs within 1 min and enables quantitative detection at >0.60 μM Hg^{2+}. The fluorescence response of **1** is due to the Hg^{2+}-promoted desulfurization of the thiocarbonyl moiety. This promotes the intramolecular PET from the aniline moiety to the excited state NBD moiety and results in fluorescence quenching.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data (Figs. S1–S9 and Cartesian coordinates for compounds **1** and **2**) associated with this article can be found in the online version, at doi:10.1016/j.jphotochem.2011.02.005.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.02.005.

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