

A benzothiazolium-derived colorimetric and fluorescent chemosensor for detection of Hg²⁺ ions

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Abstract

A benzothiazolium-derived colorimetric and fluorescent chemosensor (**L**) for detection of mercury ions has been prepared. The detection limits of the colorimetric and fluorescent method for mercury ions are 15.3 and 11.8 ppb, respectively, much lower than the reported chemosensors based on similar derivatives of benzothiazolium. The optimized molecular structures, absorption and fluorescence characteristics of the chemosensor and its complex with mercury ions were carried out using the calculations at the B3LYP/LanL2DZ level of theory, combination with Atoms in Molecules and Natural Bond Orbitals analyses.

Keywords. Colorimetric, fluorescent, chemosensor, Hg²⁺ ions, benzothiazolium.

1. INTRODUCTION

Mercury is of great concern in the toxic heavy metals and the least abundant in the crust of the Earth [1]. At the concentration levels of ppb, mercury ions can cause the negative impacts on the environment, animals, plants and humans. Mercury ions are toxic and danger to most living organisms at the higher concentration levels [2,3]. On humans, mercury can cause the changes in the structure of DNA and damage to the brain, gingivitis, stomatitis, digestive system and cause neurological disorders, even death. It is also believed to be associated with spontaneous abortion and congenital malformation [4-8].

The development of analytical methods for heavy metals, especially mercury ions, at ppb levels, has been attracting the attention of scientists [9-10]. In particular, the optical methods, including colorimetric and fluorescence methods, are of particular interest because they are simple, less expensive, as well as imaging methods for using in the fieldwork or in the living cells [11-13]. Until now, a number of colorimetric and fluorescent chemosensors for detection of mercury ions have been reported. However, most of the developed chemosensors have some defects, for instance, low

sensitivity, the effects of competitive metal ions, and working in a large amount of organic solvents. As a result, the scientists are continuing efforts to develop the new chemosensors for detection of mercury ions [14, 15]. Many different dye and fluorescent compounds have been used as the the original substances for design of the colorimetric and fluorescent chemosensors to detect mercury ions, including derivatives of naphthalene [16], rhodamine [17], fluorescein [18], dansyl [19], dimethylaminocinnamaldehyde [20], and benzothiazole [15], etc. However, the fluorescent chemosensors for detection of mercury ions based on benzothiazole derivatives, including benzothiazolium derivatives, are still very little reported until now. The limits of detection for mercury ions of most published chemosensors are still quite high, from 214 to 1767 ppb [15, 21, 22]. In our previous work [23], we reported the design and preparation of a benzothiazolium hemicyanine derivative. Its complex with Hg²⁺ may be used for selective and sensitive sensing of thiol biomolecules through the reversible visual color and fluorescence changes. In this work, a further investigation on this benzothiazolium hemicyanine derivative with the combination of quantum chemical calculations and

experiments is carried out for the purpose of Hg^{2+} detection. It can be used as a colorimetric and fluorescent chemosensor for determination of mercury ions with the significantly low detection limits, 15.3 and 11.8 ppb, respectively.

2. MATERIALS AND METHODS

2.1. Instruments

The experimental UV-Vis and fluorescence properties were investigated by Shimadzu spectrometers, including UV-1800 UV-vis spectrophotometer and RF-5301 PC Series fluorescence spectrometer. All computational investigations were performed at the Laboratory of Computation Science and Modeling of Quy Nhon University (Vietnam), using a Supercomputer Operating System (32-cores processor, 72-gigabytes memory).

2.2. Reagents

2-Methylbenzothiazole, 4-diethylamino-2-hydroxybenzaldehyde, bromopropionic acid, all amino acids, and all perchlorate or chloride salts of metal cations were obtained from Sigma - Aldrich, without further purification. All used solvents were HPLC reagents and surely free of fluorescent impurities.

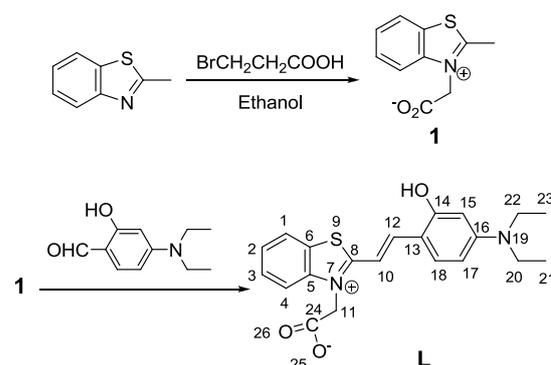
2.3. Computational methods

Geometry optimizations of molecules were calculated by applying the B3LYP density functional theory with the LanL2DZ basis set [24, 25], using the Gaussian 09 program [26]. The excited states and other time-dependent factors were carried out using the time-dependent density functional theory (TD-DFT) [27]. The chemical bonding and electronic properties of molecules were evaluated based on the interaction energies ($E^{(2)}$) between the donor of a natural bond orbital (NBO) and acceptor of a NBO, obtained from the NBO analysis, using NBO 3.1 program implemented in Gaussian 09 [28].

3. RESULTS AND DISCUSSION

A benzothiazolium-derived chemosensor **L** was synthesized from the reaction of the 2-methylbenzothiazole and bromoacetic acid, followed by the condensation reaction with 4-diethylamino-2-hydroxybenzaldehyde in *ca.* 60% overall yield. The structures of intermediate and final products were confirmed by ^1H NMR, ^{13}C NMR, and mass spectra

[23]. The synthetic route was showed at scheme 1.



Scheme 1: The synthetic route to chemosensor **L**

Figure 1a shows that the free **L** exhibits a characteristic absorption band peaked at 540 nm in an ethanol/water solution (7/3, v/v). The molar extinction coefficient of free **L** is determined and very high (*ca.* $10^4 \text{ M}^{-1}\cdot\text{cm}^{-1}$ at 540 nm, in an ethanol/HEPES solution). Upon the addition of Hg^{2+} ions to the **L** solution, there is an increasing intensity in a new absorption band at 460 nm, whereas there is a gradually decreasing signal at 540 nm. The color of the solution is changed gradually from pink ($\lambda_{\text{max}} = 540 \text{ nm}$) to orange ($\lambda_{\text{max}} = 460 \text{ nm}$). Furthermore, an isosbestic point is obviously observed at 490 nm. These results indicate that there is a concentration conversion of the light-absorbing compounds in the solution.

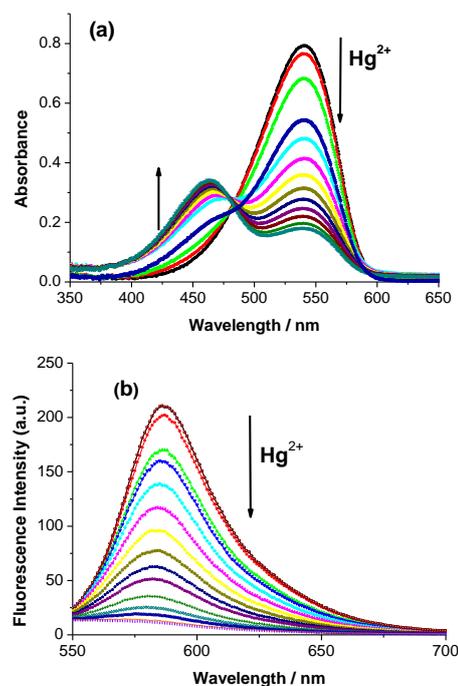


Figure 1: Absorbance (a) and Fluorescence (b) titration spectrum of **L** (3.10^{-6} M) with Hg^{2+} (0-1.5 equiv) in EtOH/ H_2O (7/3, v/v)

In contrast, the free **L** shows a red emission at 585 nm in solution with a fluorescence quantum yield of 0.175 based on rhodamine B solution as a reference. The fluorescence intensity of **L** solution is gradually quenched when Hg^{2+} ions are added. It is almost completely quenched (about 95 %) upon the addition of one equivalent of Hg^{2+} ions, and then no more change in the fluorescence intensity is observed when Hg^{2+} ions are more added (figure 1b). These results indicate that Hg^{2+} ions reacted with **L** in 1:1 stoichiometry. Upon the addition of 1 equiv of Cysteine to the solution resulted from the reaction between 1 equiv of Hg^{2+} and 1 equiv of **L**, the fluorescence intensity is restored to the original value of free **L**. It indicates that Hg^{2+} ions reversibly react with **L**.

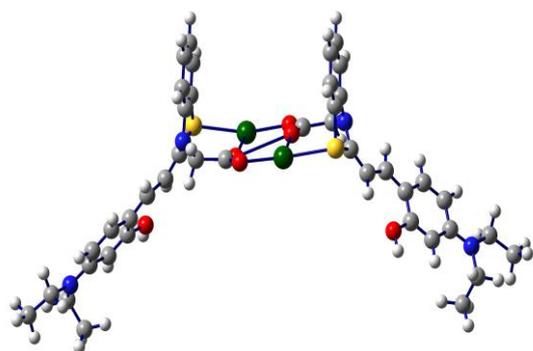


Figure 2: The optimized geometry of Hg_2L_2 at the B3LYP/LanL2DZ level of theory

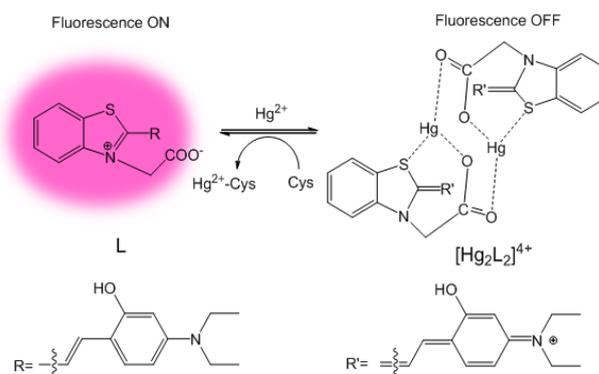
The most stable structure of the 1:1 interaction

Table 1: Calculated excitation energy (E), wavelength (λ), and oscillator strength (f) for low-lying singlet state of **L** and Hg_2L_2

Compound	Main orbital transition	TD-DFT/B3LYP/LanL2DZ				
		CIC ^a	E (eV)	λ (nm)	f	
L	$S_0 \rightarrow S_1$	HOMO-1 \rightarrow LUMO	0.62576	2.05	604.7	0.0043
		HOMO \rightarrow LUMO	-0.32210			
	$S_0 \rightarrow S_2$	HOMO-2 \rightarrow LUMO	-0.26505	2.18	569.7	0.1044
		HOMO-1 \rightarrow LUMO	0.28864			
	$S_0 \rightarrow S_3$	HOMO \rightarrow LUMO	0.58734			
		HOMO-3 \rightarrow LUMO	0.40392	2.33	533.0	0.0282
		HOMO-2 \rightarrow LUMO	0.53836			
		HOMO-1 \rightarrow LUMO	0.13894			
Hg₂L₂	$S_0 \rightarrow S_1$	HOMO-1 \rightarrow LUMO	-0.12571	1.31	948.3	0.1026
		HOMO \rightarrow LUMO	0.43803			
		HOMO \rightarrow LUMO+1	0.53118			
	$S_0 \rightarrow S_2$	HOMO-1 \rightarrow LUMO	0.12116	1.40	888.0	0.6065
		HOMO-1 \rightarrow LUMO+1	-0.13429			
		HOMO \rightarrow LUMO	0.54547			
	$S_0 \rightarrow S_3$	HOMO \rightarrow LUMO+1	-0.40365			
		HOMO-1 \rightarrow LUMO	0.49543	1.59	778.0	0.1175
		HOMO-1 \rightarrow LUMO+1	0.47484			

^aCIC expansion coefficients for the main orbital transitions.

between Hg^{2+} and **L** is identified at the B3LYP/LanL2DZ level of theory and is shown in figure 2. The proposed interaction mechanism between **L** and Hg^{2+} ions is presented in scheme 2.



Scheme 2: The proposed interaction mechanism between **L** and Hg^{2+}

The changes in UV-Vis and fluorescence spectra of the **L** and Hg_2L_2 complex were elucidated by theoretical investigations. The TD-DFT method was used at the same level optimized structure to calculate the excited states of **L** and Hg_2L_2 complex. The calculated results were listed in table 1. Table 1 shows that the singlet electronic transitions from ground states (S_0) to excited states (S_i) in the **L** and Hg_2L_2 complex are mainly contributed by the $S_0 \rightarrow S_2$ transitions because the oscillator strength (f) of these transitions are much stronger than that of the other transitions.

In **L**, the $S_0 \rightarrow S_2$ transition energy is 2.18 eV (569.7 nm). This transition resulted in the maximum absorption peak at 560 nm in the UV-Vis spectra of **L**. In three main orbital transitions of the $S_0 \rightarrow S_2$ transition, including the HOMO-2 \rightarrow LUMO, HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO transition, the HOMO \rightarrow LUMO is transition between two continuous MOs, therefore the PET process does not occur, and this transition gave rise to a red emission at 585 nm.

In the Hg_2L_2 , the complexation leads to a significant transfer of electron density from ligands to the metal ions, resulting in the small energy gap of HOMO and LUMO, about 1.39 eV. The excitation and emission wavelengths will be shifted to longer wavelength than 888 nm. As a result, there is no significant strong peak in absorbance and fluorescence spectra. It could be the cause of fluorescence quenching in the complex.

Table 2: Significant second-order interaction energies ($E^{(2)}$) between donor and acceptor orbitals in benzothiazolium moieties of **L** and Hg_2L_2 (in kcal.mol⁻¹, at the B3LYP/LanL2DZ level of theory)

Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$	Donor NBO (i)	Acceptor NBO (j)	$E^{(2)}$
L			Hg₂L₂		
$\pi(C1-C2)$	$\pi^*(C3-C4)$	19.44	$\pi(C1-C2)$	$\pi^*(C3-C4)$	21.64
$\pi^*(C1-C2)$	$\pi^*(C3-C4)$	226.02	$\pi^*(C5-C6)$	$\pi^*(C1-C2)$	71.76
$\pi(C1-C2)$	$\pi^*(C5-C6)$	22.30	$\pi(C1-C2)$	$\pi^*(C5-C6)$	24.93
$\pi(C3-C4)$	$\pi^*(C1-C2)$	22.02	$\pi(C3-C4)$	$\pi^*(C1-C2)$	19.39
$\pi(C3-C4)$	$\pi^*(C5-C6)$	25.33	$\pi(C3-C4)$	$\pi^*(C5-C6)$	30.17
$\pi(C5-C6)$	$\pi^*(C1-C2)$	19.66	$\pi(C5-C6)$	$\pi^*(C1-C2)$	19.34
$\pi^*(C5-C6)$	$\pi^*(C1-C2)$	136.44	$\pi^*(C5-C6)$	$\pi^*(C3-C4)$	77.75
$\pi(C5-C6)$	$\pi^*(C3-C4)$	16.45	LP(N7)	$\pi^*(C5-C6)$	20.97
$\pi^*(C5-C6)$	$\pi^*(C3-C4)$	97.79	LP(N7)	$\sigma^*(C8-S9)$	12.65
$\pi(N7-C8)$	$\pi^*(C5-C6)$	12.95	LP(N7)	$\pi^*(C8-C10)$	16.63
$\pi^*(N7-C8)$	$\pi^*(C5-C6)$	25.51	$\pi(C5-C6)$	$\pi^*(C3-C4)$	14.77
LP(S9)	$\pi^*(C5-C6)$	14.60	$\sigma^*(C8-S9)$	$\sigma^*(C6-S9)$	11.42
LP(S9)	$\pi^*(N7-C8)$	28.44	LP(O25)	$\sigma^*(C11-C24)$	11.81
LP(O25)	$\sigma^*(C11-C24)$	17.13	LP(O25)	LP*(C24)	139.46
LP(O25)	$\sigma^*(C24-O26)$	17.88	LP(O26)	$\sigma^*(C11-C24)$	14.84
LP(O25)	$\sigma^*(C24-O25)$	19.90	LP(O26)	$\sigma^*(C24-C25)$	19.31
LP(O25)	$\pi^*(C24-O26)$	115.15	LP(O26)	LP*(C24)	176.95
LP(O26)	$\sigma^*(C11-C24)$	20.81	LP(O25)	LP*(Hg(a))	31.61
LP(O26)	$\sigma^*(C24-O25)$	18.95	LP(S9)	LP*(Hg(b))	51.90
			LP(O26)	LP*(Hg(b))	10.96

The results obtained from NBO analysis as listed in table 2 show that the π -electron conjugated system of benzothiazolium moiety (as a fluorophore) in free **L** extends throughout from C1 to C8 (see Scheme 1 for numbering scheme), as evidenced by

the existence of π bonds with significantly large degree of interaction energies ($E^{(2)}$), including $\pi(C1-C2)$, $\pi(C3-C4)$, $\pi(C5-C6)$, and $\pi(N7-C8)$ bonds. These findings confirm that the free **L** is a fluorescent compound with properties similar to

those of the benzothiazolium derivatives.

The NBO analysis results also confirm that the complexation of Hg_2L_2 is due to the contributions of these metal-ligand interactions, including $\text{O}25\cdots\text{Hg}(a)$, $\text{S}9\cdots\text{Hg}(b)$, $\text{O}26\cdots\text{Hg}(b)$, with interaction energies ($E^{(2)}$) for these interactions being 31.61, 51.90 and 10.96 $\text{kcal}\cdot\text{mol}^{-1}$, respectively. The presence of these new interactions leads to break the $\pi(\text{N}7-\text{C}8)$ bond and creates the new $\pi(\text{C}8-\text{C}10)$ bond. As a result, the π -electron conjugated system of fluorophore (benzothiazolium moiety) is broken at the N7 atom. This is important cause leading to fluorescence quenching in the complex.

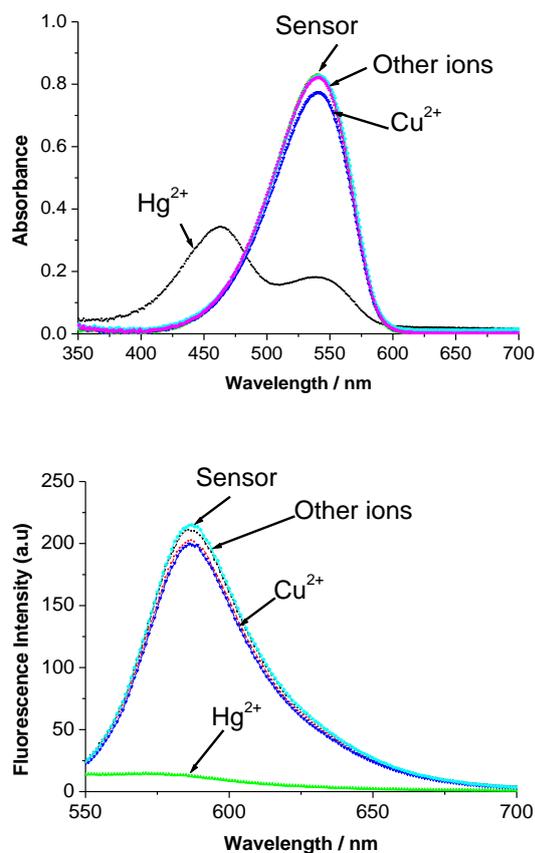


Figure 3: Absorbance (a) and fluorescence (b) spectra of L (3.10^{-6} M) with different metal ions (5 equiv each) in $\text{EtOH}/\text{H}_2\text{O}$ (7/3, v/v) [Hg^{2+} , Cd^{2+} , Fe^{2+} , Co^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ca^{2+} , Na^+ , K^+]

The selectivity of L for Hg^{2+} ions in the presence of other metal ions is also surveyed. Figure 3 shows that there is no significant changes in the absorption spectra and fluorescence spectra when 5 equiv of competing metal ions is added to the L solution, including Cd^{2+} , Fe^{2+} , Co^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ca^{2+} , Na^+ and K^+ ions. These results indicate that the L can be used as a colorimetric and fluorescent chemosensor for selective detection of Hg^{2+} ions in the presence of surveyed competing metal ions.

The possibility of using L as a colorimetric and fluorescent chemosensor for quantitative detection of Hg^{2+} ions is also surveyed.

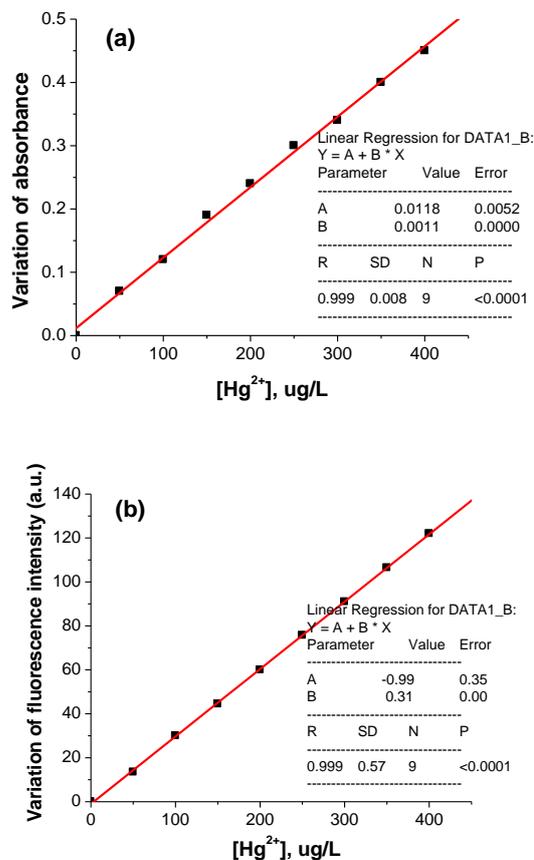


Figure 4: Variation of absorbance at 540 nm (a) and variation of fluorescence intensity at 585 nm (b) of L (3.10^{-6} M) in $\text{EtOH}/\text{H}_2\text{O}$ (7/3, v/v) vs the concentration of Hg^{2+} ions (0-400 $\mu\text{g}/\text{L}$)

Figure 4a shows that there is a good linear relationship between the variation of absorbance of L solution and the concentration of Hg^{2+} ions. In the concentration range of Hg^{2+} ions from 0 to 400 $\mu\text{g}/\text{L}$, the following equation was found from calibration curves: $\Delta A_{540} = (0.01 \pm 0.01) + (0.0011 \pm 0.0000) \times [\text{Hg}^{2+}]$, $R = 0.999$. It indicates that L can be used as a colorimetric chemosensor for quantification of Hg^{2+} ions. The limit of detection and limit of quantification for Hg^{2+} ions are 15.3 $\mu\text{g}/\text{L}$ and 51.2 $\mu\text{g}/\text{L}$, respectively.

Figure 4b also indicates that the fluorescent chemosensor L can be used to detect quantitatively Hg^{2+} ions. With concentrations of Hg^{2+} ions ranging from 0 to 400 $\mu\text{g}/\text{L}$, a good linear relationship was recorded between variation of fluorescence intensity of L and concentration of Hg^{2+} to lead a calibration curve: $\Delta I_{585} = (-1.0 \pm 0.4) + (0.3 \pm 0.0) \times [\text{Hg}^{2+}]$, $R = 0.999$. The limit of detection and limit of

quantification for Hg^{2+} ions are 11.8 $\mu\text{g/L}$ and 39.3 $\mu\text{g/L}$, respectively.

4. CONCLUSION

In summary, a benzothiazolium derivative-based colorimetric and fluorescent chemosensor has been presented. It can be used for selective detection of mercury ions in presence of competing metal ions, including Cd^{2+} , Fe^{2+} , Co^{3+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ca^{2+} , Na^+ and K^+ ions. The detection limits of the colorimetric and fluorescent method for mercury ions are 15.3 and 11.8 ppb, respectively. The formation of Hg_2L_2 complex between **L** and Hg^{2+} ions led to a significant transfer of electron density from ligands to the metal ions, and broke the π -electron conjugated system. This is important cause leading to fluorescence quenching and color change in the complex.

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