

Vietnam Journal of Chemistry, International Edition, **55**(6): 700-707, 2017  
DOI: 10.15625/2525-2321.2017-00529

## A quantum chemical study on the use of complexes between Hg(II) ions and fluorescent ligands for detection of cysteine

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Received 10 August 2016; Accepted for publication 29 December 2017

### Abstract

A benzothiazolium derivative as a fluorescent ligand was studied by the quantum chemical calculations, including research on the synthesis process, characteristics and applications. The calculated results showed that its complex with Hg(II) ions can be used as a fluorescent sensor for detection of cysteine. These findings have opened up opportunities for the use of previously reported complexes as well as new complexes between Hg(II) and fluorescent ligands for detection of cysteine.

**Keywords.** Fluorescence, chemosensor, mercury, complexation, cysteine.

### 1. INTRODUCTION

Thiol biomolecules are important sulfur containing compounds in biological processes. The metabolism and transportation of biothiols, including cysteine (H<sub>2</sub>Cys), homocysteine (Hcy) and glutathione (GSH) are related to the important enzymes and proteins in biological systems. The abnormality of endogenous concentrations of these biothiols are unusual expressions on the functional state of the proteins and enzymes and associated with diseases [1]. For example, diseases such as liver damage, skin lesions, and slowed growth are thought to be related to the abnormality of concentrations of cysteine [2]. The free GSH and its oxidized state play an important role in maintaining the redox environment and greatly affect the biological processes in living cells. The abnormal levels of GSH greatly affect the effectiveness of the process of killing cancer cells by the chemotherapy [3]. The high levels of Hcy in blood serum can cause the high risk of Alzheimer's, cardiovascular, and inflammatory bowel disease [4].

In recent years, the development of fluorescent sensors for detection of analytes has been attracting the attention of scientists. This is because the analytical techniques based on fluorescence are usually high sensitivity and selectivity, easy to implement and less expensive [5].

The announced fluorescent sensors for the detection of biothiols mainly based on the different reactions, such as Michael addition reactions, cleavage reactions of sulfonate ester, sulfonamide, disulfides, and cyclization reactions with aldehydes [6-9]. Recently, the fluorescence techniques based on interactions between biothiols with complexes of metal ions and fluorescent ligands have been strongly developed [10, 11]. This is because these sensors are usually more sensitive. An interesting fact is that these sensors can be dual used for analyzing both biothiols and heavy metal ions such as Hg(II), Cu(II) and Ag(I). Excessive concentrations of these metal ions can cause the negative impacts on the environment, animals, plants and humans.

Until now, many fluorescent sensors for detection of heavy metal ions have been published based on the complexation reactions between heavy metal ions and fluorescent ligands [12-16]. The quantum chemical studies on the use of complexes between heavy metal ions and fluorescent ligands for detection of biothiols are very useful, helping us to develop new sensors as well as use previously announced complexes.

In this work, following the previously reported experimental studies, a fluorescence technique based on complexes between Hg(II) ions and fluorescent

ligands as fluorescent sensors for detection of cysteine was studied by using the quantum chemical calculations, including a benzothiazolium derivative (**L**) [17], a dansyl-diethylenetriamine-thiourea conjugate (**DA**) [12], and a rhodamine-derived Schiff base (**RS**) [13].

## 2. COMPUTATIONAL METHODOLOGY

The single point energy calculations and geometry optimizations of molecules have been carried out by the Gaussian 09 program, with using the B3LYP/LanL2DZ level of theory which has been used successfully for systems involving heavy metal ions [18-20]. The time-dependent density functional theory (TD-DFT) is used for the calculation of excited states, electronic and fluorescent properties of molecules. The variation of enthalpy ( $\Delta H$ ) and variation of Gibbs free energy ( $\Delta G$ ) of reactions are calculated based on the difference between the total energy of the reaction products and the total energy of the reactants. The Polarizable Continuum Model (PCM) was used for calculations of solvent effects. These calculations are performed at the same level of theory as the geometry optimization [21]. All theoretical calculations were performed on a supercomputer operating system with a 32-cores processor and 72-gigabytes memory at the laboratory of computational chemistry and modelling of Quy Nhon University.

## 3. RESULTS AND DISCUSSION

### 3.1. The survey on the synthesis process of chemosensor **L**

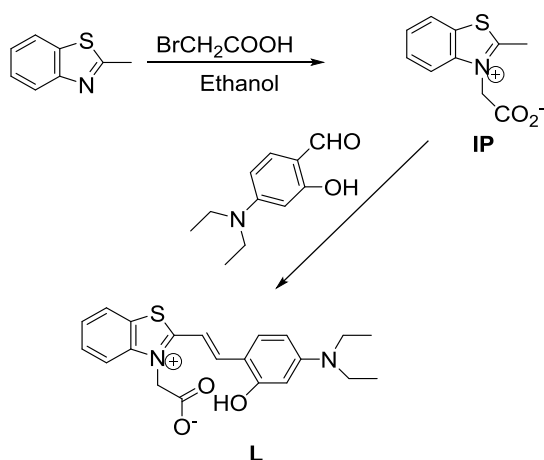


Figure 1: Synthetic route of the chemosensor **L**

The synthetic route of the chemosensor **L** is performed via two stages as shown in Fig.1. First, **IP**

is prepared from 2-methylbenzothiazole and bromoacetic acid. Fig.2 shows that the reaction between 2-methylbenzothiazole and bromoacetic acid can form 5 different products (**IP**, **IP-1**, **IP-2**, **IP-3**, and **IP-4**). The calculated free energies of reactions in different solvents at the B3LYP/LanL2DZ level are listed in table 1.

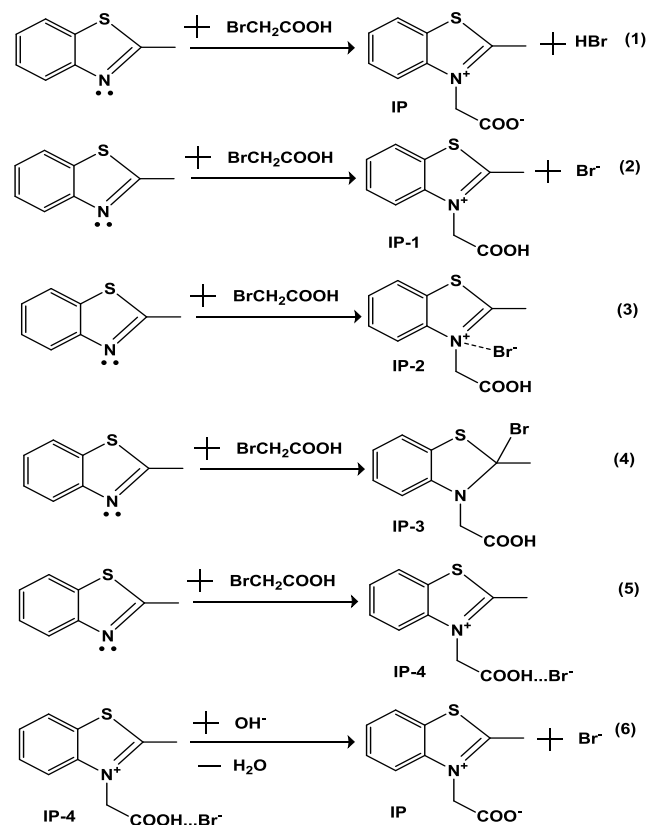


Figure 2: The possible products formed from the reaction between 2-methylbenzothiazole and bromoacetic acid

Table 1: The calculated free energies of reactions between 2-methylbenzothiazole and bromoacetic acid at the B3LYP/LanL2DZ level ( $\text{kcal.mol}^{-1}$ )

Reaction	Ethanol	Acetonitrile	Chloroform	Water
(1)	6.8	6.0	10.6	6.0
(2)	-12.9	-15.2	7.4	-17.3
(3)	-11.9	-13.3	-11.5	-12.9
(4)	-7.7	-9.3	-5.9	-9.1
(5)	-19.4	-20.9	-17.6	-20.6
(6)	-52.1	-52.0	-51.8	-51.6

The obtained results show that the free energy ( $\Delta G^{298}$ ) of reaction (5) is the most negative. Accordingly, **IP-4** is the preferred product of the reaction between 2-methylbenzothiazole and bromoacetic acid. The reaction between **IP-4** and hydroxide ions (reaction (6)) to form the **IP** is energetically favorable because the free energy of reaction is quite negative. The reaction between 2-methylbenzothiazole and bromoacetic acid to directly form **IP** (reaction (1)) does not occur because the free energy is positive. Therefore, the **IP** is formed via the **IP-4**. The calculated results show that the formation of **IP** is a bit different in the common solvents, including ethanol, acetonitrile, chloroform, and water.

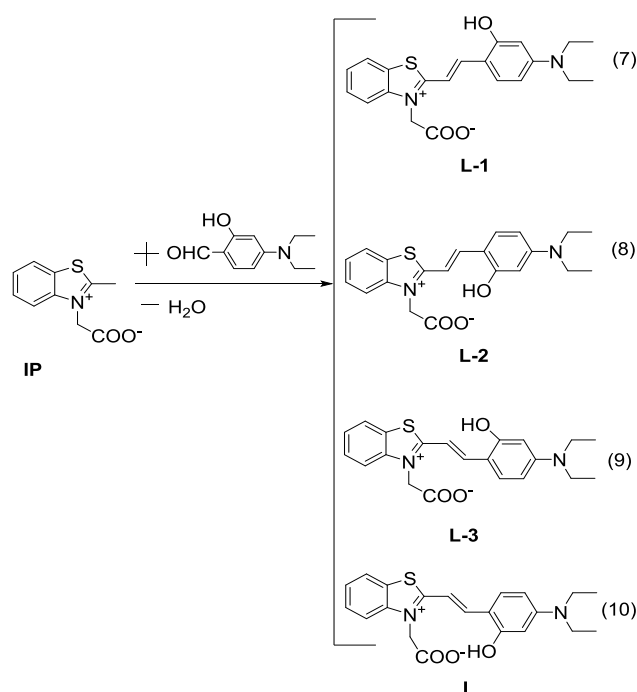


Figure 3: The possible products formed from the reaction between **IP** and 4-diethylamino-2-hydroxybenzaldehyde

Figure 3 shows that the reaction between **IP** and 4-diethylamino-2-hydroxybenzaldehyde can form 4 different products (**L-1**, **L-2**, **L-3**, and **L**). The obtained results about the free energies of reactions in table 2 show that the free energy of reaction (10) is negative. Accordingly, **L** is the preferred product of the reaction between **IP** and 4-diethylamino-2-hydroxybenzaldehyde. The calculated results show that the formation of **L** in the chloroform is the most energetically favorable. In empirical research, ethanol is used because it easily dissolves the **IP** compound.

The experimental studies on the synthesis of **L** were reported in our other publication and were in a

good agreement with the theoretical results [17]. The chemosensor **L** was synthesized from the reaction of 2-methylbenzothiazole and bromoacetic acid, followed by the reaction with 4-diethylamino-2-hydroxybenzaldehyde in ca. 28.5% overall yield. The structures of **IP** and chemosensor **L** were confirmed by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and MS. The structures of **IP** and **L** were obtained as shown in Figs. 2 and 3.

Table 2: The calculated results of free energies of reactions between **IP** and 4-diethylamino-2-hydroxybenzaldehyde at the B3LYP/LanL2DZ level ( $\text{kcal.mol}^{-1}$ )

Reaction	Ethanol	Acetonitrile	Chloroform	Water
(7)	5.0	6.4	7.1	3.6
(8)	3.0	4.5	1.4	3.0
(9)	7.1	8.5	7.6	6.3
(10)	-2.6	-1.1	-12.5	-2.9

### 3.2. The survey on the characterization of chemosensor **L**

The optimized geometries of **IP**, 4-diethylamino-2-hydroxybenzaldehyde, **L** with the numbering scheme of the atoms are identified at the B3LYP/LanL2DZ level of theory and are shown in Fig. 4.

The obtained results show that the majority of the atoms in **L** are distributed on two planes, one of them is **IP** moiety, and the other is 4-diethylamino-2-hydroxybenzaldehyde moiety. The dihedral angle of these two planes is  $22.0^\circ$ . The structures of **IP** moiety and 4-diethylamino-2-hydroxybenzaldehyde moiety in **L** are virtually unchanged compared to the free **IP** and 4-diethylamino-2-hydroxybenzaldehyde compounds, but the (C11, C24, O25, O26) plane in **L** is turned 60 degrees around the C11–C24 axis, compared with the free **IP**. This leads to the formation of internal hydrogen bondings in **L**, between H47 and O25, H33 and O25. Evidence is that the contact distances between H47 and O26, H33 and O25 are 1.522 Å and 1.961 Å, significantly smaller than the sum of the van der Waals radii of the H and O (2.720 Å). The formation of internal hydrogen bonding may cause the process of **L** formation to be thermodynamically favorable as

analyzed above.

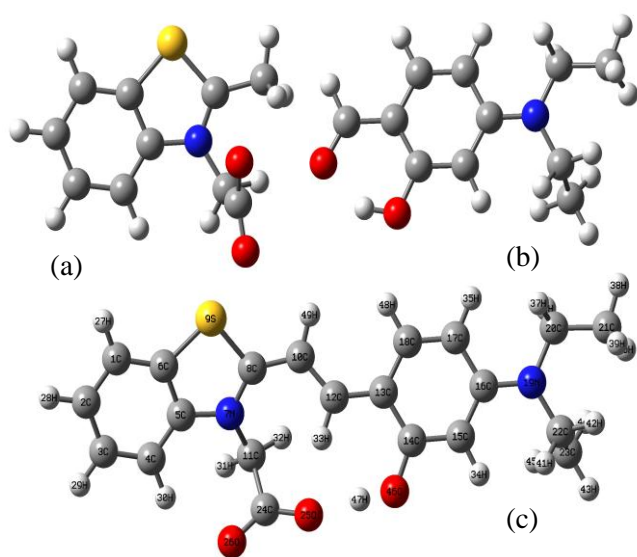


Figure 4: The optimized geometry of IP (a), 4-diethylamino-2-hydroxybenzaldehyde (b), L (c) with the numbering scheme of the atoms at the B3LYP/LanL2DZ level of theory

The theoretical absorption and fluorescence properties of chemosensor **L** were investigated by using TD-DFT at the B3LYP/LanL2DZ level of theory, combining with the NBO analysis. The calculated results show that the theoretical absorption spectrum of **L** exhibits a band at 569.7 nm, and **L** is a fluorescent compound. These results are in a good agreement with the previously published experimental investigations. The free **L** exhibits a strong absorption band peaked at 540 nm and shows a red emission at 585 nm in an ethanol/water solution [17].

### 3.3. The complex between Hg(II) and L

The obtained experimental results indicated that when Hg(II) ions were added to the **L** solution, the color of the solution was changed gradually from pink to orange, along with that, the red emission at 585 nm of the solution was gradually quenched. As a result, **L** can be used as a colorimetric and fluorescent chemosensor for selective detection of Hg(II) ions. Hg(II) ions reacted with **L** in 1:1 stoichiometry and changed the UV-Vis and fluorescence spectra of **L**. The most stable structure of complex between Hg(II) ion and **L** in 1:1 stoichiometry was identified and shown in Fig. 5.

The obtained calculation results show that the interaction of Hg(II) with **L** to form Hg<sub>2</sub>L<sub>2</sub> is

energetically favorable with a  $\Delta H^{298}$  value of -436.1 kcal.mol<sup>-1</sup> and a  $\Delta G^{298}$  value of -410.2 kcal.mol<sup>-1</sup>.

The quenching of fluorescence intensity in Hg<sub>2</sub>L<sub>2</sub> complex has been clarified by using TD-DFT to study the excited states, with a combination of NBO analysis. Accordingly, the formed complex led to break the  $\pi$ -electron conjugated system in ligands and quenched the fluorescence of complex [17].

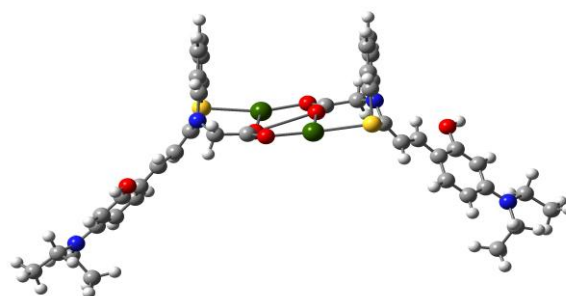


Figure 5: The optimized geometry of Hg<sub>2</sub>L<sub>2</sub> at the B3LYP/LanL2DZ level of theory

### 3.4. The survey on the use of Hg<sub>2</sub>L<sub>2</sub> complex for detection of biothiols

To consider the possibility of using the Hg<sub>2</sub>L<sub>2</sub> complex for detection of biothiols, the interactions between Hg(II) with Cysteine (H<sub>2</sub>Cys) are investigated.

The stable geometric structures of H<sub>2</sub>Cys and its possible complexes with Hg(II) are identified at the B3LYP/LanL2DZ level of theory and shown in Fig.6. Accordingly, 6 stable geometric structures of complex between Hg(II) and H<sub>2</sub>Cys have been identified, including [Hg(Cys)<sub>2</sub>]<sup>2-</sup> (2 coordination type), [Hg(Cys)<sub>2</sub>]<sup>2-</sup> (4 coordination type), [Hg(Cys)<sub>3</sub>]<sup>4-</sup>, [Hg(Cys)<sub>4</sub>]<sup>6-</sup>, [Hg(HCys)<sub>2</sub>]<sup>-</sup> (2 coordination type), and [Hg(HCys)<sub>3</sub>]<sup>1-</sup>.

The reactions to form the complexes are shown in Fig. 7. The variation of enthalpy ( $\Delta H$ ) and variation of Gibbs free energy ( $\Delta G$ ) of reactions were calculated and presented in table 3.

The results show that the variation of enthalpies ( $\Delta H^{298}$ ) and free energy ( $\Delta G^{298}$ ) of reaction (12) are the most negative, with a  $\Delta H^{298}$  value of -841.8 kcal.mol<sup>-1</sup> and a  $\Delta G^{298}$  value of -821.6 kcal.mol<sup>-1</sup>. Accordingly, [Hg(Cys)<sub>2</sub>]<sup>2-</sup> (4 coordination type) is the preferred product of the reaction between Hg(II) and H<sub>2</sub>Cys. It is consistent with previously announced experimental results [22]. These findings indicate that to be able to use the complexes of metal ions with the fluorescent ligands for detection of cysteine based on the complexation/decomplexation interactions, the value of the free energy variation of

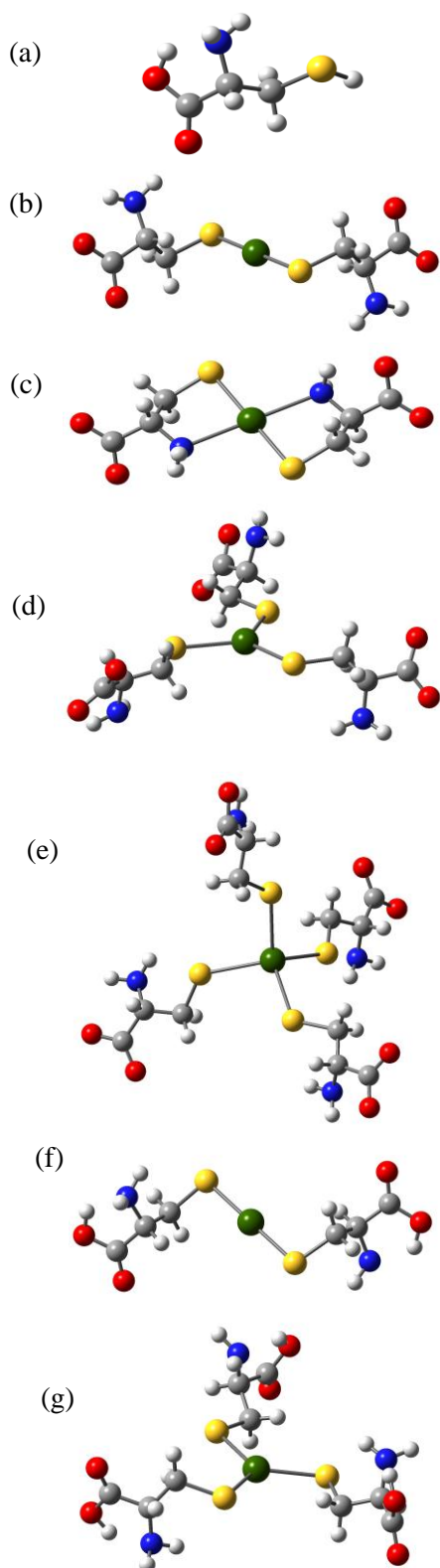


Figure 6: The stable geometric structures of H<sub>2</sub>Cys (a) and its possible complexes with Hg(II): (b) [Hg(Cys)<sub>2</sub>]<sup>2-</sup> (2 coordination type), (c) [Hg(Cys)<sub>2</sub>]<sup>2-</sup> (4 coordination type), (d) [Hg(Cys)<sub>3</sub>]<sup>4+</sup>, (e) [Hg(Cys)<sub>4</sub>]<sup>6-</sup>, (f) [Hg(HCys)<sub>2</sub>] (2 coordination type), and (g) [Hg(HCys)<sub>3</sub>]<sup>1-</sup> at the LanL2DZ level of theory

reaction to form complex between metal ions and the fluorescent ligands must be less negative than -821.6 kcal.mol<sup>-1</sup>.

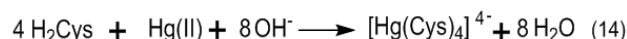
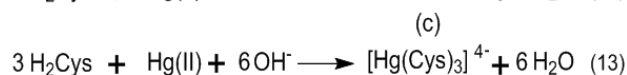
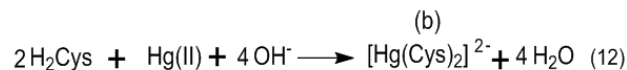
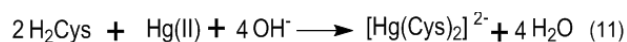


Figure 7: The reactions to form the complexes between H<sub>2</sub>Cys with Hg(II)

Table 3: The enthalpy ( $\Delta H^{298}$ ) and Gibbs free energy ( $\Delta G^{298}$ ) of complex formation between Hg(II) with H<sub>2</sub>Cys at the B3LYP/LanL2DZ level (kcal.mol<sup>-1</sup>)

Reaction	$\Delta H^{298}$	$\Delta G^{298}$
(11)	-821.6	-806.2
(12)	-841.8	-821.6
(13)	-782.4	-758.2
(14)	-569.3	-536.2
(15)	-707.3	-688.5
(16)	-836.7	-808.9

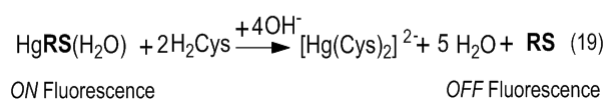
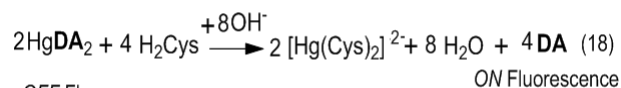
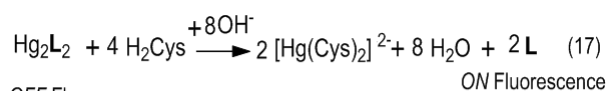


Figure 8: The reaction between H<sub>2</sub>Cys and complexes of metal ions with fluorescent ligands

As shown above, the variation of free energy of reaction to form Hg<sub>2</sub>L<sub>2</sub> from Hg(II) ions and chemosensor L is -410.2 kcal.mol<sup>-1</sup>, less negative than -821.6 kcal.mol<sup>-1</sup>. Therefore, the reaction between Hg<sub>2</sub>L<sub>2</sub> and H<sub>2</sub>Cys to form free L (reaction

(17)) is energetically favorable, with a  $\Delta G^{298}$  value of  $-1232 \text{ kcal.mol}^{-1}$ . As a result,  $\text{Hg}_2\text{L}_2$  can be used as an *OFF-ON* fluorescent chemosensor for detection of cysteine. Once again, the calculation results completely agree with the experimental investigations.

### 3.5. The survey on the use of some complexes between Hg(II) and other fluorescent ligands for detection of biothiols

In our previously published work, a Dansyl-diethylenetriamine-Thiourea conjugate (**DA**) as a fluorescent ligand was presented. The free **DA** shows a characteristic absorption wavelength at 380 nm and an extensive emission centered at 510 nm with the fluorescence quantum yield of 0.25 (in EtOH/H<sub>2</sub>O solution, 1/9, v/v). The reaction between Hg(II) ions and **DA** to form  $\text{HgDA}_2$  complex has resulted in fluorescence quenching of **DA** solution. As a result, **DA** can be used as a fluorescent chemosensor for detection of Hg(II) ions. The calculated  $\Delta G^{298}$  value of reaction between Hg(II) and **DA** to form  $\text{HgDA}_2$  at the B3LYP/LanL2DZ level is  $-303.7 \text{ kcal.mol}^{-1}$ . The  $\Delta G^{298}$  value of reaction between  $\text{HgDA}_2$  and H<sub>2</sub>Cys to form free **DA** is  $-1125 \text{ kcal.mol}^{-1}$  (reaction (18)). It suggests that the complex between Hg(II) and **DA** can be used for detection of cysteine as an *OFF-ON* fluorescent chemosensor [12,21].

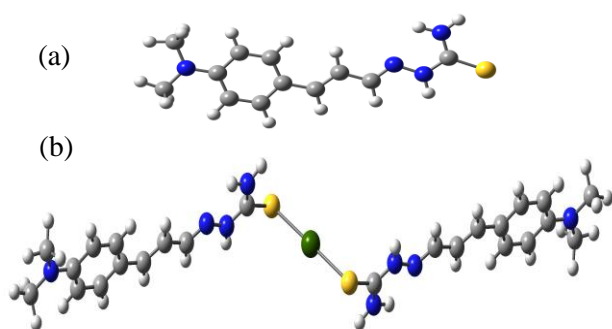


Figure 9: The stable geometric structures of **DA** (a) and  $\text{HgDA}_2$  (b) at the B3LYP/LanL2DZ level of theory

In our other published study, a Rhodamine-derived Schiff base (**RS**) was used as a fluorescent chemosensor for detection of Hg(II) ions in water media. The free **RS** is non-fluorescent compound. The reaction between Hg(II) ions and **RS** to form  $\text{HgRS(H}_2\text{O)}$  complex led to the ring-opening of spirolactam in **RS** and gave rise to an obviously enhanced fluorescence peaked at 556 nm (*OFF-ON*) as well as visual change from colorless to pink. The

$\Delta G^{298}$  value of reaction between Hg(II), **RS**, and H<sub>2</sub>O to form  $\text{HgRS(H}_2\text{O)}$  at the B3LYP/LanL2DZ level is  $-256.8 \text{ kcal.mol}^{-1}$ . The  $\Delta G^{298}$  value of reaction between  $\text{HgRS(H}_2\text{O)}$  and H<sub>2</sub>Cys to form free **RS** is  $-1078 \text{ kcal.mol}^{-1}$  (reaction (19)). It shows that the  $\text{HgRS(H}_2\text{O)}$  complex can be used as an *ON-OFF* fluorescent chemosensor for detection of cysteine [13].

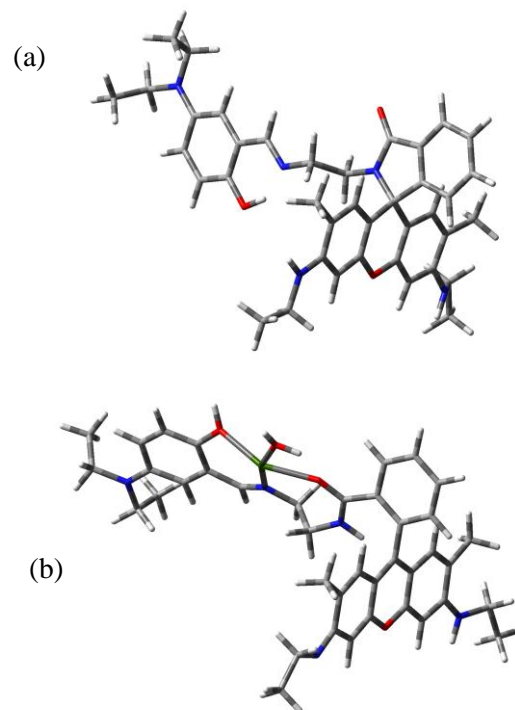


Figure 10: The stable geometric structures of **RS** (a) and  $\text{HgRS(H}_2\text{O)}$  (b) at the B3LYP/LanL2DZ level of theory

## 4. CONCLUSIONS

A benzothiazolium derivative as a fluorescent ligand (**L**) was studied by the quantum chemical calculations, including the research on the synthesis process, characteristics and applications. The  $\Delta G$  of reaction to form complex between Hg(II) ions and the fluorescent ligand (**L**) is less negative than the  $\Delta G$  of reaction to form complex between Hg(II) ions and cysteine. As a result, the complex between Hg(II) ions and fluorescent ligand (**L**) can be used as an *OFF-ON* fluorescent chemosensor for detection of cysteine. Similarly, the  $\Delta G$  of reactions to form complexes between Hg(II) ions and the other fluorescent ligands (**DA**, **RS**) are also less negative than  $\Delta G$  of reaction to form complex between Hg(II) ions and cysteine. As a result, if  $\Delta G$  of reaction to form complex between a fluorescent ligand and Hg(II) ions is less negative than  $\Delta G$  of reaction to form complex between cysteine and Hg(II) ions, the

complex of this fluorescent ligand can be expectedly used as a fluorescent sensor for detection of cysteine. These findings have opened up opportunities for the use of many previously announced complexes between Hg(II) and fluorescent ligands for detection of cysteine, as well as established a basis for the development of new complexes between Hg(II) and fluorescent ligands for detection of cysteine.

**Acknowledgment.** *This research was funded by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.04-2014.35 (DTQ).*

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