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A benzothiazole-based semisquarylium dye suitable for highly selective Hg^{2+} sensing in aqueous media

Jin-Seok Bae [a], Seon-Yeong Gwon [a], Young-A. Son [b], Sung-Hoon Kim [a,*]

[a] Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea
[b] School of Chemical and Biological Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

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ABSTRACT

A novel semisquarylium dye was synthesized by the reaction between 3,4-dibutoxy-3-cyclobutene-1,2-dione and a benzothiazolium salt and its metal ion sensing properties were investigated using absorption and emission spectroscopy. These misquarylium exhibited high selectivity for Hg^{2+} ions, as compared with Ca^{2+}, Pb^{2+}, Al^{3+}, Ce^{2+}, Ba^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Mg^{2+} ions in DMSO/H_2O (9:1, v/v), which was attributed to the formation of a 2:1 BSQ:Hg^{2+} coordination complex, the formation of which was supported by the calculated geometry of the complex.

1. Introduction

Heavy metal ion contamination may pose significant risks to the environment. Mercury in particular is regarded as a highly toxic and widespread pollutant. Once mercury is introduced into the food chains as a result of bioaccumulation, this environmental cycle causes serious threat to the human health and ecology [1,2]. Despite the great efforts for the reduction of its industrial use, mercury pollution still continues through a variety of natural and anthropogenic sources [1–3]. To date, a number of Hg^{2+} ion detection methods have been examined and include colorimetric strategies [4–7] and fluroionophores [3,8–11]. We have previously reported the synthesis and metal ion detection properties of squarylium dyes [12–14] and have also described the aggregation properties of unsymmetrical squarylium dyes [15]. On the basis of these previous reports, we are currently exploring the synthesis and properties of new derivatives of squarylium dyes, which can potentially yield a new class of chromogens for the selective and quantitative detection of metal ions, both for biological and environmental applications. In the present paper, we report the Hg^{2+}-selective chemosensing properties of a simple chemosensor based on semisquarylium containing benzothiazolium species where the sulfur atom provides the mercury-coordinating element.

2. Experimental

2.1. Materials and characterization

2-Methylbenzothiazole [ed. Note: harmful; irritant] bromoacetic acid and 3,4-dibutoxy-3-cyclobutene-1,2-dione were purchased from Aldrich. The other chemicals were of the highest grade available and were used without further purification. All employed solvents were analytically pure and were employed without any further drying or purification. Compound **1**, 3-(carboxymethyl)-2-methylbenzothiazolium bromide, was synthesized according to the literature method [6]. Melting points were determined using an Electrothermal IA900 and are uncorrected. FAB mass spectra were recorded using JMS700. ^{1}H NMR spectra were recorded on Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard.

2.2. Synthesis of semisquarylium (BSQ)

A mixture of benzothiazolium bromide **1** (0.25 g, 0.886 mmol) and 3,4-dibutoxy-3-cyclobutene-1,2-dione **2** (0.3 g, 1.33 mmol) in anhydrous ethanol (5 ml) was heated under reflux for 1 h in the presence of triethylamine (0.3 ml). The reaction mixture was

* Corresponding author. Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

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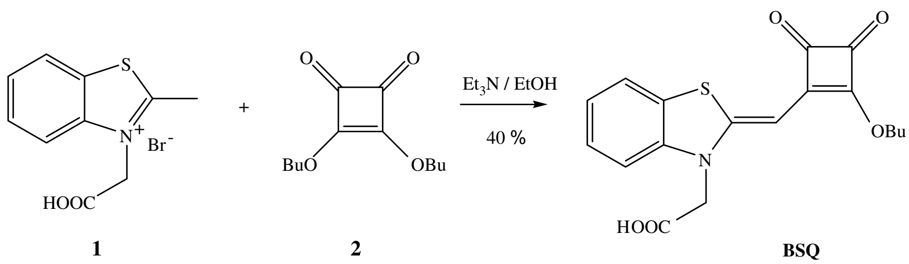

Fig. 1. Synthesis of **BSQ**.

poured into diethyl ether (30 ml) and resulting product was filtered and washed with diethyl ether (100 ml) to give **BSQ** as a red solid. Yield 40%: mp 238–240 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.98 (t, $J = 7.3$ Hz, 3H), 1.48 (sextet, $J = 7.3$ Hz, 2H), 1.82 (quintet, $J = 7.3$ Hz, 2H), 4.56 (s, 2H), 4.76 (t, $J = 6.5$ Hz, 2H), 5.45 (s, 1H), 7.06 (d, $J = 8.3$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 8.3$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 12.8 (s, 1H). ^{13}C NMR(DMSO, 100 MHz): δ 9.08, 14.06, 19.04, 32.42, 46.53, 48.55, 56.79, 73.87, 101.01, 111.59, 122.12, 124.04, 126.68, 127.42, 141.68, 160.75, 169.71, 186.04. FAB-MS: calcd. for $C_{18}H_{17}NO_5S$ m/z (M^+) 359.4; Found m/z ($M + H^+$) 360.4. Anal. Calcd. for $C_{18}H_{17}NO_5S$: C, 60.16; H, 4.73; N, 3.89. Found: C, 60.19; H, 4.68; N, 3.85.

3. Results and discussion

This present work is aimed at the design and synthesis of a benzothiazole-based semisquarylium (**BSQ**) to detect the presence of Hg^{2+} against competing analytes. The structures and synthesis of **BSQ** are shown in Fig. 1.

BSQ was synthesized by condensation of 3-(carboxymethyl)-2-methylbenzothiazolium bromide **1** with 3,4-dibuthoxy-3-cyclobutene-1,2-dione **2** in the presence of triethylamine (40%). **BSQ** was fully characterized using ^{1}H, ^{13}C and FAB mass spectrometry. The peak for the acidic proton was observed at low field region of 12.8 ppm. And the methylene adjacent to the thiazole ring was observed at 5.45 ppm. In our present experiments, $Hg(ClO_4)_2$ was gradually added to the solution of **BSQ** in DMSO/H_2O (9:1, v/v) as mercury source, and the coordination abilities of BSQ with Hg^{2+} were investigated by UV–Vis spectroscopy. Fig. 2 showed the absorption spectral changes of **BSQ** as a function of the Hg^{2+} concentration in DMSO/H_2O (9:1, v/v) at room temperature; as the Hg^{2+} concentration increases, the absorbance of **BSQ** at 446 nm decreases, the solution changing from yellow to colourless solution. However, addition of other metal ions such as Ca^{2+}, Pb^{2+}, Al^{3+},

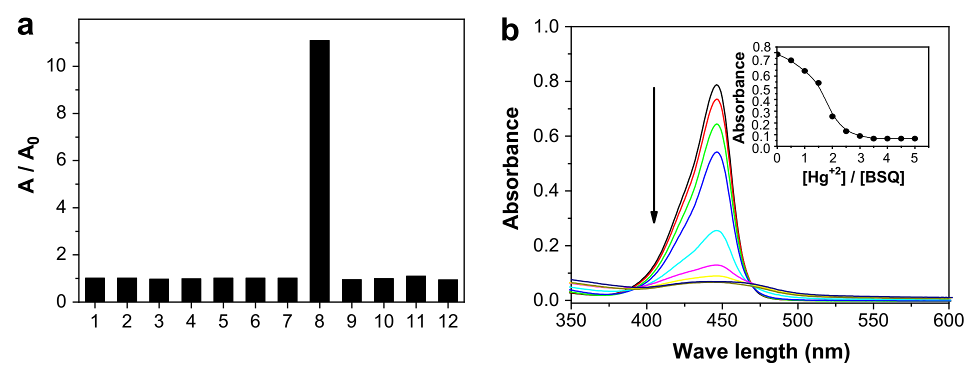

Fig. 2. (a) Absorption responses of **BSQ** (30 μM) in DMSO/H_2O (9:1, v/v) solution to addition of 4 eqiv of (1) $Al(ClO_4)_3$, (2) $Ca(ClO_4)_2$, (3) $Cd(ClO_4)_2$, (4) $Cr(NO_3)_3$, (5) $Cu(ClO_4)_2$, (6) $Fe(ClO_4)_2$, (7) $Fe(NO_3)_3$, (8) $Hg(ClO_4)_2$, (9) $LiClO_4$, (10) $Ni(ClO_4)_2$, (11) $Pb(ClO_4)_2$ and (12) $Zn(ClO_4)_2$ ($\lambda = 446$ nm). (b) Absorption spectral variation of **BSQ** (30 μM) upon addition of Hg^{2+} in DMSO/H_2O (9:1, v/v) solution from 0 to 40 μM. Inset shows the plot of absorbance vs the ratio of Hg^{2+} to **BSQ**.

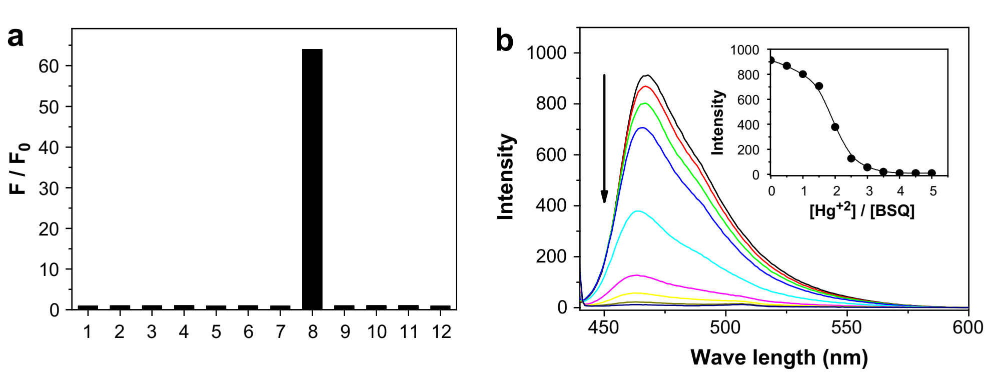

Fig. 3. (a) Fluorescence responses of **BSQ** (30 μM) in DMSO/H_2O (9:1, v/v) solution to addition of 4 eqiv of (1) $Al(ClO_4)_3$, (2) $Ca(ClO_4)_2$, (3) $Cd(ClO_4)_2$, (4) $Cr(NO_3)_3$, (5) $Cu(ClO_4)_2$, (6) $Fe(ClO_4)_2$, (7) $Fe(NO_3)_3$, (8) $Hg(ClO_4)_2$, (9) $LiClO_4$, (10) $Ni(ClO_4)_2$, (11) $Pb(ClO_4)_2$ and (12) $Zn(ClO_4)_2$ ($\lambda_{ex} = 420$ nm, $\lambda_{em} = 468$ nm). (b) Fluorescence spectral variation of **BSQ** (30 μM) upon addition of Hg^{2+} in DMSO/H_2O (9:1, v/v) solution from 0 to 40 μM excited at 420 nm. Inset shows the plot of absorbance vs. the ratio of Hg^{2+} to **BSQ**.

Ce^{2+}, Ba^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+} and Mg^{2+} under similar condition does not have any significant effect on the absorption spectrum of **BSQ**. From the titration to a solution of **BSQ**, we notice the stoichiometry of the **BSQ**-Hg^{2+} complex is 2:1, Fig. 2 (b) inset.

The superior selectivity of **BSQ** for Hg^{2+} in DMSO/H_2O (9:1, v/v) solution is evident from the absorbance response of the metal ions, as illustrated in Fig. 2(a).

The fluorescence intensity of **BSQ** also decreases markedly upon the Hg^{2+} (Fig. 3). Other metal ions did not have any significant effects on the fluorescence intensity of **BSQ**. Selective complexation can be expected to alter the photophysical properties of the flurophore, and these can then be used for the detection of Hg^{2+}.

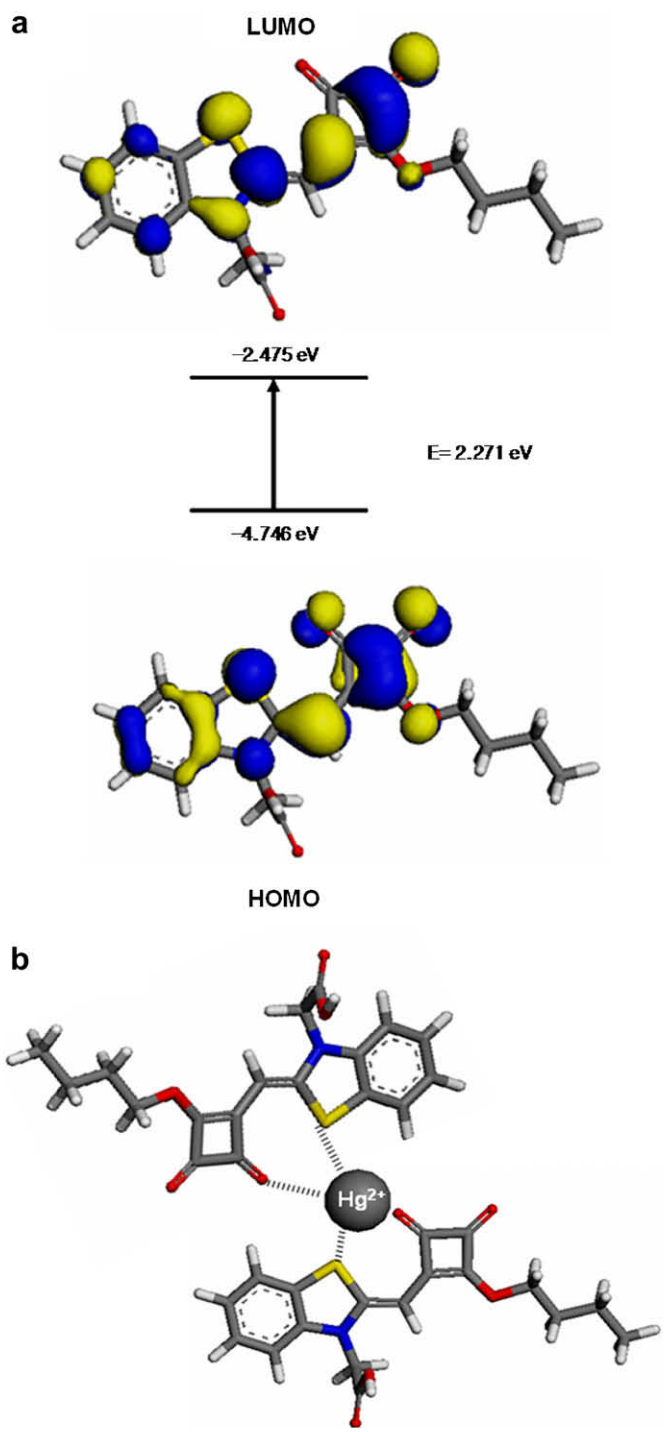

Fig. 4. (a) Electron distribution of the HOMO and LUMO energy levels of **BSQ**. (b) Optimized structure of the **BSQ**–Hg^{2+} complex.

For the interpretation of the complexation and electronic structure of **BSQ** and **BSQ**–Hg^{2+}, the quantum chemical $DMol^3$ approach was used. All the theoretical calculations were performed by $DMol^3$ program in the Materials Studio 4.4 package [16,17] which is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof (PBE) function of generalized gradient approximation (GGA) level [18] with double numeric polarization basis set was used to calculate the energy level of the frontier molecular orbital.

Fig. 4(a) shows the calculated molecular structure of **BSQ** and the electron distribution of its HOMO and LUMO. Comparison of the electron distribution in the frontier MOs reveals that HOMO-LUMO excitation moved the electron distribution from the thiazole moiety to the cyclobutene moiety, which reflect a strong migration of intramolecular charge-transfer character of **BSQ**. Therefore, the sulfur atom of the benzothiazole moiety in the HOMO energy level is important for effective complexation with Hg^{2+} in this system. As a result, the complexation of the Hg^{2+} to the sulfur atom reduces the electron density on the sulfur atom and lowers the electron donating ability of thiazole moiety. The optimized **BSQ**-Hg^{2+} bidentate structure is shown in Fig. 4; the Hg^{2+} ion is bridged between sulfur atom and carbonyl oxygen atom.

4. Conclusion

In conclusion, a benzothiazole-based semisquarylium (**BSQ**) has been synthesized in 40% yield by the condensation reaction between 3-(carboxymethyl)-2-methylbenzo- thiazolium bromide **1** and 3,4-dibuthoxy-3-cyclobutene-1,2-dione **2**, and their properties examined toward various guest metal ions, using visible and fluorescence techniques. **BSQ** showed an extremely high selectivity for Hg^{2+} over a wide range of metal ions. The recognition event has also been studied by DFT calculations. **BSQ** exhibit potential and useful application for the development of efficient chemosensor for the detection of Hg^{2+} in aqueous media.

Acknowledgements

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