# Benzothiazole-Based Semisquaraine as Colorimetric Chemosensor for $Hg^{2+}$

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## Abstract

A highly selective colorimetric chemosensor for $Hg^{2+}$ based on the semisquaraine(BSQ) containing benzothiazole moiety was investigated. BSQ showed color change only with $Hg^{2+}$ but it showed no significant changes upon addition of other metal ions such as $Ca^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Ce^{2+}$, $Ba^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Zn^{2+}$, and $Mg^{2+}$. $Hg^{2+}$ ions coordinated to the BSQ forming 1:1 complex. The experimental data and conclusions are rationalized by $DMol^3$ calculation results.

## 1. 서 론

Colorimetric chemosensors are now recognized as the valid analytical method used in the process control, environmental and biomedical monitoring. The detection of heavy metal ions is of particular significance due to the toxic impact on the environment. Heavy metal ion pollution poses severe risks for human health and the environment. The design and synthesis of a $Hg^{2+}$ selective colorimetric chemosensor is popular due to their capability for naked-eye detection without restoring to any expensive instruments. Recently, quinaldine-based semisquaraine has been developed as a dual chromogenic and fluorogenic sensor for $Hg^{2+}$ion. As a part of our study on developing molecular sensing switches, we now demonstrate an benzothiazole-based semisquaraine chemosensor BSQ, that allows the color changes only on addition of $Hg^{2+}$.

## 2. 실 험

$Hg(ClO_4)_2$was gradually added to the solution of BSQ in a $CH_3CN$-water as mercury source, and the coordination abilities of BSQ with $Hg^{2+}$ were investigated by the UV-Vis spectroscopy. Fig. 1 showed the absorption spectral changes of BSQ as a function of the $Hg^{2+}$ concentration in a CH3CN-water solution(10:10, v/v) at room temperature; as the $Hg^{2+}$ concentration increases, the absorbance of BSQ at 530 nm decreases, turning to a color change from red to a colorless solution. However, addition of other metal ions such as $Ca^{2+}$, $Pb^{2+}$, $Al^{3+}$, $Ce^{2+}$, $Ba^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Zn^{2+}$ 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 1:1. The superior selectivity of **BSQ** for $Hg^{2+}$ in $H_2O/CN_3CN$(1/1, v/v) solution is evident from the absorbance response of the metal ions, as illustrated in Fig. 2.

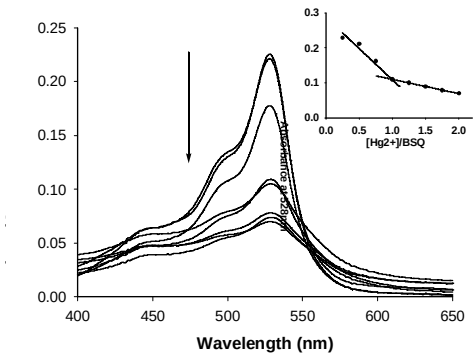



Fig. 1. The changes in the absorption spectra of BSQ(3 x $10^{-5}$ $molL^{-1}$) upon titration with $Hg^{2+}$ in 50%(v/v) water/$CH_3CN$.

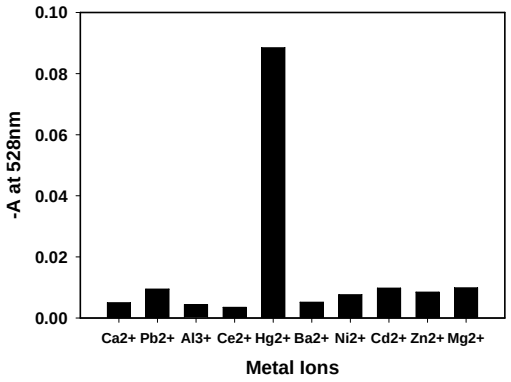
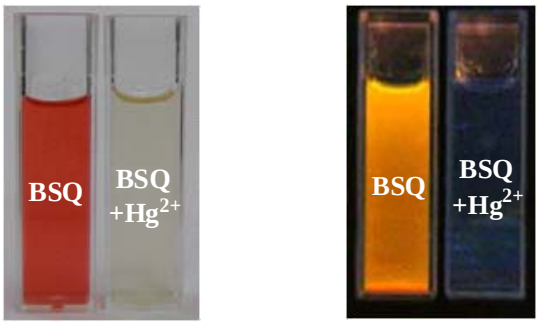



Fig. 2. Responses of 1 in 50%(v/v) water/$CH_3CN$ to representative metal ions (3 x $10^{-5}$ $mol^{-1}$) The concentration of BSQ was 3 x $10^{-5}$ $molL^{-1}$.

## 3. 결 론

Selective complexation can be expected to alter the photophysical properties of the fluorophore, and these can then be used for the detection of metal ions. The above color changes and fluorescence change are shown in Fig. 3. For the interpretation of the complexation and electronic structure of **BSQ** and **BSQ**-$Hg^{2+}$, the quantum chemical $DMol^3$ approach was used. The $Hg^{2+}$ ion is bridged between sulfur atom and carbonyl oxygen atom. As a result, the complexation of the $Hg^{2+}$ to sulfur atom reduces the electron density on the sulphur atom and lowers the electron donating ability of thiazole moiety.




Color change Fluorescence change

Fig. 3. Color change(left) and Fluorescence change(right).

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