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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

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O.-S. Kwon^a; H.-S. Kim^a

^a Department of Applied Chemistry, Kyungpook National University, Daegu, South Korea

To cite this Article Kwon, O.-S. and Kim, H.-S.(2007) 'Fluorescent Sensing Properties of Benzo-18-crown-6 Ethers Containing Thiazoles', *Supramolecular Chemistry*, 19: 4, 277 – 281

To link to this Article: DOI: 10.1080/10610270701416497

URL: <http://dx.doi.org/10.1080/10610270701416497>

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Fluorescent Sensing Properties of Benzo-18-crown-6 Ethers Containing Thiazoles

O.-S. KWON and H.-S. KIM*

Department of Applied Chemistry, Kyungpook National University, Daegu 702-701, South Korea

(Received 15 January 2007; Accepted 24 April 2007)

The binding properties of dibenzo-18-crown-6 ether (BTB, **1**) and naphthobenzo-18-crown-6 ether (NTB, **2**), containing two thiazole units toward mono- and divalent cations, are outlined. The ion-selective properties of **1** and **2** were studied by measuring their fluorescent emission responses to alkali, alkaline earth, and transition metal ions. BTB (**1**) showed the highest binding constant toward Ag^+ over Pb^{2+} , Hg^{2+} , and Cu^{2+} . NTB (**2**) revealed a high selectivity toward Ag^+ over Pb^{2+} , Hg^{2+} , and Cu^{2+} .

Keywords: Crown ether; Thiazole; Fluorescence sensor; Silver ion

INTRODUCTION

The design and synthesis of new chemosensors for metal ions is an important subject in the field of supramolecular chemistry, due to their significance and potential in physiological, environmental, and chemical applications [1–4]. Chemosensors, based on ion-induced changes in fluorescence, appear to be attractive due to the simplicity and high detection limit of the fluorescence. Chemosensors offer many distinct advantages regarding their sensitivity, selectivity, rapid response time, and real-time local imaging by non-invasive techniques [5–11]. Silver (I) is one of the main transition metals used in industries and drug manufacturing. Due to their antibacterial properties, silver derivatives have been used to disinfect potable water, and they have been used for dental and pharmaceutical purposes. Therefore, the design of the Ag^+ -selective ionophore and the construction of Ag^+ -selective chemosensors have attracted much attention regarding environmental and clinical purposes [12,13]. In recent years, considerable attention has been devoted to the

selective and efficient detection of metal ions [14–22]; some examples of fluorescent chemosensors for Ag^+ have been reported [23–28]. Calix[4]arenes [29–31], crown-ether derivatives [32–34], benzene-based tripodal receptors [35,36], and steroidal tweezers [37,38] have been used for the selective detection of Ag^+ by the introduction of soft heteroatoms such as N and S, as an electron donor to metal cations. Recently, we have synthesized new crown ethers **1** and **2** that contain thiazole moieties [39–42]. The ion selective electrodes (ISEs), based on solvent-polymeric membranes (plasticized PVC) doped with these ionophores, exhibited large ammonium ion selectivity [40]. To better understand the cation recognition mechanisms of these compounds, we investigated **1** and **2** for metal-cation binding by fluorescence spectroscopy. An initial UV–vis study of **1** confirmed the absence of ammonium ion selectivity and the presence of silver ion selectivity. This prompted the screening of **1** and related NTB (**2**) by fluorescent emission responses toward a comprehensive range of hard and soft cations.

In this paper, we report on the fluorescent response characteristics of **1** and **2** regarding various mono- and divalent cations (alkali, alkaline earth, and transition metal ions) and the ^1H NMR analysis of **1** with Ag^+ .

RESULTS AND DISCUSSION

Chemosensors **1** and **2** were synthesized by a reaction of 1,2-bis(chloromethylthiazoly)benzene and a corresponding naphthalene derivative, with catechol, as described previously [39,42] (Fig. 1).

*Corresponding author. E-mail: kimhs@knu.ac.kr

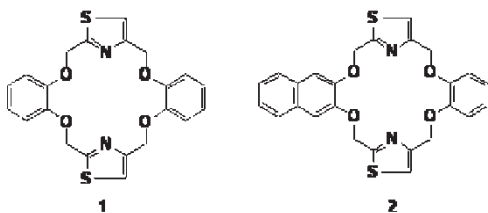
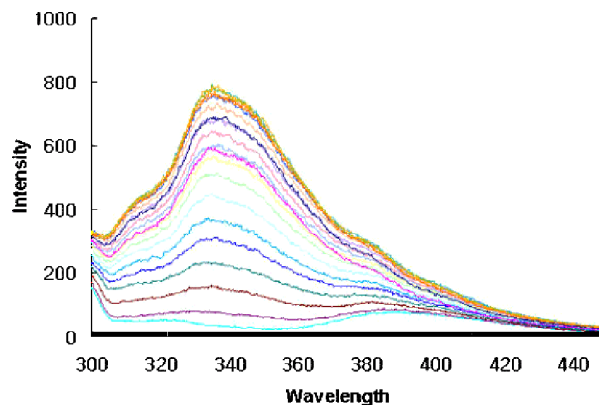


FIGURE 1 Structure of BTB (1) and NTB (2).

The binding ability of **1** and **2** toward selected cations was measured by fluorescent emission responses in DMSO. The absorption-fluorescent correlated 3D-spectrum of **1** showed that a maximum fluorescent emission response appeared with an excitation at 295 nm. Thus, the fluorescent spectra of **1** (1 μM), with a 20 equiv. of metal ions (Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Al^{3+} , Cu^{2+} , Ag^+ , Hg^{2+} , Pb^{2+}), were examined on an excitation at 295 nm, and the results are summarized in Table I. All cations were used in the form of perchlorate (ClO_4^-) salts.

Upon the addition of Ag^+ , the fluorescent intensity ($\lambda_{\text{em}} = 335 \text{ nm}$) of **1** increases continuously, and the position of the emission maximum moves to a longer wavelength ($\Delta\lambda = 10 \text{ nm}$) (Fig. 2). These results implicate that the binding of **1** with Ag^+ induces an enhanced fluorescent intensity and a 10 nm red shift operated by strong coordination of Ag^+ to fluorophoric thiazole and benzene rings. A close interaction of Ag^+ with sulfur and nitrogen in the thiazole enhances the electron withdrawing character of sulfur and nitrogen, and consequently stabilize more the excited state of the complex between **1** and Ag^+ than that of **1** itself, so that which leads to red-shift in the emission [3].

Similar types of behavior were observed upon the addition of Pb^{2+} and Hg^{2+} , but the fluorescent enhancement in the intensity was smaller than that of Ag^+ : the measurements are in the order of Ag^+ ($I/I_0 = 14.5$), Pb^{2+} ($I/I_0 = 9.2$), and Hg^{2+} ($I/I_0 = 7.2$) (Fig. 3). In contrast to the above metals (Ag^+ , Pb^{2+} , and Hg^{2+}), the addition of Cu^{2+} to **1** quenches the

FIGURE 2 Emission responses of **1** (1 μM), upon the addition of Ag^+ (as ClO_4^- , 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.74, 1.0, 1.23, 1.48, 1.96, 2.44, 2.91, 3.38, 4.76, 9.09, 13.04, 16.67, 20.00, 33.33, 50.00 equiv from the bottom); $\lambda_{\text{ex}} = 295 \text{ nm}$.

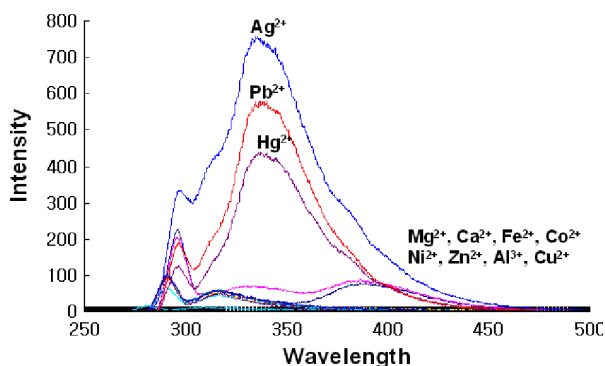
fluorescence ($I/I_0 = 0.1$). It is remarkable that the other metal ions such as Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Al^{3+} do not show any relevant influence on the fluorescent intensity. NH_4^+ ions, even at a high concentration, show almost negligible effects [43]. Compound **1** can bind ammonium ions through hydrogen bonds with N and O in the crown cavity [41], but complexation is not signaled by a change in fluorescent intensity.

The plot of the changes in the induced fluorescence emission of **1** versus the metal ion concentration level provided titration curves with complexes corresponding to the formation of 1:1 (Fig. 4). During titration, there were no other observable changes in the emission spectra. In most cases, the titration curves satisfactorily fitted to a 1:1 stoichiometry.

Furthermore, the stoichiometry of the complexation was confirmed by measuring the Job plot of **1** with Ag^+ by a ^1H NMR experiment (Fig. 5). The binding constants of **1** were obtained using the ENZFITTER program [44,45], based on the response of the emission spectra of **1** (1 μM), upon the addition

TABLE I Emission responses of **1** (1 μM) upon the addition of various metal ions (20 eq) at $\lambda_{\text{ex}} = 295 \text{ nm}$

Metal ions	BTB (1)		
	λ_{ex} (nm)	λ_{em} (nm)	I/I_0
Ion-free	295	325	1.0
Mg^{2+}	295	325	1.0
Ca^{2+}	295	325	1.0
Fe^{2+}	295	325	0.7
Co^{2+}	295	325	1.0
Ni^{2+}	295	326	1.0
Zn^{2+}	295	326	1.0
Al^{3+}	295	326	1.1
Cu^{2+}	295	336	0.1
Ag^+	295	335	14.5
Hg^{2+}	295	335	7.2
Pb^{2+}	295	335	9.2

FIGURE 3 Emission responses of **1** (1 μM), with various metal ions (20 eq); $\lambda_{\text{ex}} = 295 \text{ nm}$.

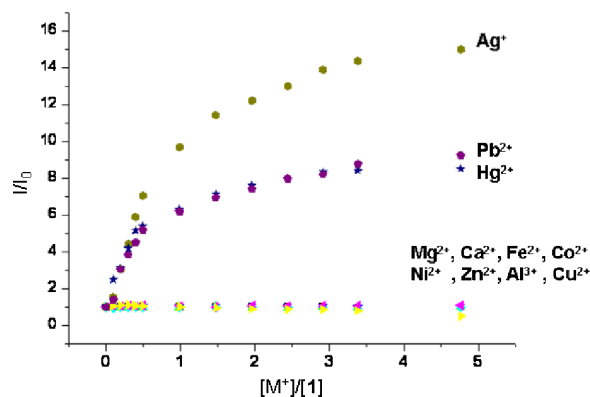


FIGURE 4 Relative fluorescence intensity of **1** ($1\ \mu\text{M}$), with various metal ions; $\lambda_{\text{ex}} = 295\ \text{nm}$.

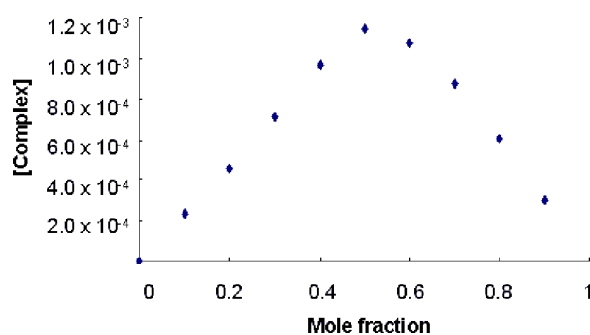


FIGURE 5 ^1H NMR-based Job plot of **1** with Ag^+ in $\text{DMSO-}d_6$, $[\text{H}]_0 = [\text{G}]_0 = 4.5\ \text{mM}$.

of metal ions, as shown in Fig. 4. The results are summarized in Table II.

The binding constants of **1** showed 1.08×10^6 , 7.53×10^5 , 5.76×10^5 , and $3.46 \times 10^4\ \text{M}^{-1}$ for the binding of Ag^+ , Hg^{2+} , Pb^{2+} , and Cu^{2+} , respectively. Chemosensor **1** showed the highest binding constant for Ag^+ and modest binding with Hg^{2+} and Pb^{2+} . In the DMSO, compound **1** was found to be moderately selective for Ag^+ (i.e., the selectivity expressed as the ratio of the binding constants is 1.4 for $\text{Ag}^+/\text{Hg}^{2+}$, 1.9 for $\text{Ag}^+/\text{Pb}^{2+}$, and 31.2 for $\text{Ag}^+/\text{Cu}^{2+}$). The selectivity of **1** for Ag^+ over Pb^{2+} and Hg^{2+} is particularly important because Hg^{2+} and Pb^{2+} are metal ions that frequently interfere with Ag^+ analysis.

For comparison, fluorescence emission studies of NTB (**2**), with four metal ions such as Ag^+ , Hg^{2+} , Pb^{2+} , and Cu^{2+} , were carried out under the same conditions. The titration curves of **2** with metals are shown in Fig. 6. The binding constants of **2** revealed

TABLE II Binding constants (K_a) of **1** and **2** with metal ions in DMSO at $\lambda_{\text{ex}} = 295\ \text{nm}$

Metal	Ag^+	Hg^{2+}	Pb^{2+}	Cu^{2+}
1 (K_a in M^{-1})	1.08×10^6	7.53×10^5	5.76×10^5	3.46×10^4
2 (K_a in M^{-1})	8.31×10^5	9.53×10^4	1.70×10^4	1.77×10^0

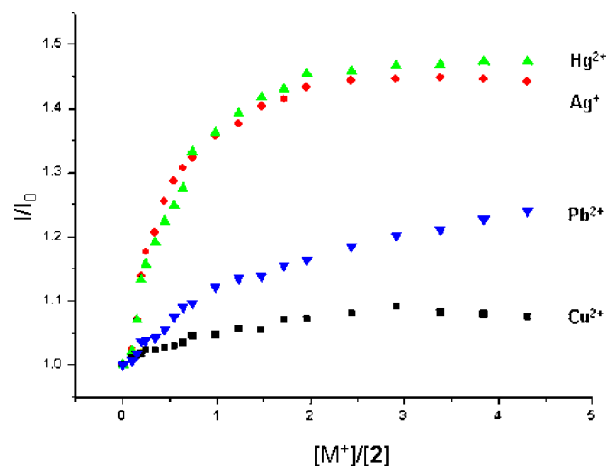


FIGURE 6 Relative fluorescence intensity of **2** ($1\ \mu\text{M}$), with four metal cations in DMSO; $\lambda_{\text{ex}} = 295\ \text{nm}$.

8.31×10^5 , 9.53×10^4 , 1.70×10^4 , and $1.77 \times 10^0\ \text{M}^{-1}$ for the binding of Ag^+ , Hg^{2+} , Pb^{2+} , and Cu^{2+} , respectively. The binding constants of **2** were smaller than those of **1** for Ag^+ , Hg^{2+} , and Pb^{2+} , but the selectivity levels were superior to those of **1**. The selectivity expressed as the ratio of the binding constants is 8.7 for $\text{Ag}^+/\text{Hg}^{2+}$, and 48.8 for $\text{Ag}^+/\text{Pb}^{2+}$, and 4.7×10^5 for $\text{Ag}^+/\text{Cu}^{2+}$. These results implicate that introducing naphthalene ring into the crown ether, (by changing benzene to naphthalene), enhances selectivity. The higher selectivity of Ag^+ over Hg^{2+} can be explained by cation- π interaction with aromatic ring. Furthermore participation of π electrons of naphthalene ring in the formation of Ag^+ complex through cation- π coordination enhances selectivity of **2** toward Ag^+ over Hg^{2+} [46–48].

To get further insight regarding the nature of the Ag^+ complexation, we also evaluated cation recognition using ^1H NMR in DMSO- d_6 . A partial ^1H NMR spectrum of **1**, upon the addition of Ag^+ , is shown in Fig. 7; each peak was assigned based on the 2D-COSY spectrum. As expected, we observed ^1H NMR spectral changes upon the addition of Ag^+ , while no spectral changes were observed upon the addition of Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , or Zn^{2+}

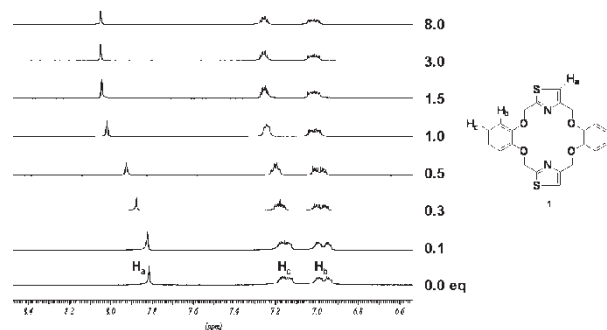


FIGURE 7 Partial ^1H NMR spectra of **1**, with increasing the Ag^+ concentration in DMSO- d_6 , $[\text{H}]_0 = 4.5\ \text{mM}$.

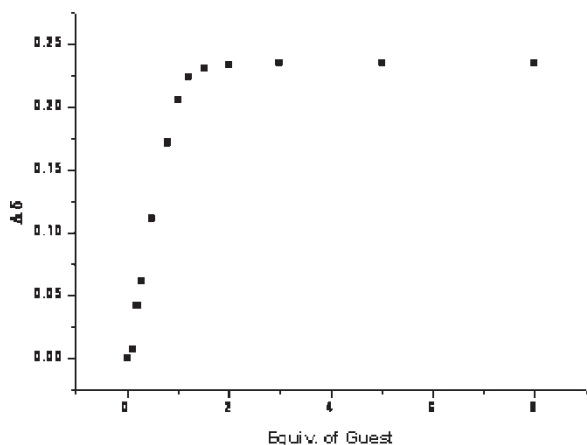


FIGURE 8 ^1H NMR titration curves of **1** with Ag^+ in $\text{DMSO-}d_6$.

under the same conditions. Notably, when 1 equiv. of Ag^+ was added, the signal of H_a shifted downfield from 7.81 ppm to 8.02 ppm ($\Delta\delta = 0.21$ ppm), indicating that nitrogen and sulfur in thiazole moiety interact with Ag^+ . Moreover, the H_c proton showed a downfield shift ($\Delta\delta = 0.11$ ppm), from which we presume that π electrons of benzene also participates in the complexation with Ag^+ through cation- π coordination [46–48]. Changes in the chemical shift of H_a are shown in Fig. 8, as a function of the equivalent of Ag^+ . The ^1H NMR-based Job plot indicated that **1** formed a complex with Ag^+ in a 1:1 ratio [49,50] (Fig. 5). From the linear curve fitting of the EQ NMR program, binding constant K_a of $1.09 \times 10^4 \text{ M}^{-1}$ was determined [51].

Thus, chemosensor **1** showed a high binding affinity toward Ag^+ over other metal ions by coordination with S and N in the thiazole, and by additional coordination with π electrons in aromatic ring enhanced selectivity toward Ag^+ over Hg^{2+} , Pb^{2+} , and Cu^{2+} .

EXPERIMENT

Fluorescence spectra were measured on a Hitachi F-4500 Fluorescence spectrophotometer. Binding constants from fluorescence were obtained using the ENZFITTER program [44,45]. NMR titrations were run with a Bruker AM-400 FT-NMR spectrometer (400 MHz) at concentration levels of 45 mM, with aliquots of a 0.25 M MClO_4 solution added. The non-linear curve fittings program (EQ-NMR) was used for curve fittings [51]. BTB (**1**) and NTB (**2**) were prepared by procedures outlined in literature [39,42].

CONCLUSION

Studies of fluorescent emission spectra clearly showed that both **1** and **2** exhibited substantial

responses to Ag^+ , Hg^{2+} , Pb^{2+} , and Cu^{2+} ions, but there is almost no response to any other transition metal ions examined (Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Al^{3+}). The fluorescent chemosensor **1** exhibited a high binding affinity for Ag^+ over Pb^{2+} , Hg^{2+} , and Cu^{2+} . Chemosensor **2** also showed a high selectivity for Ag^+ over Pb^{2+} , Hg^{2+} , and Cu^{2+} . The ^1H NMR titration and Job plot showed that the Ag^+ ions bound with S and N in the thiazole, and π electrons of benzene in **1** to form a complex in a 1:1 ratio.

Acknowledgements

This work was supported by a Grant from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE) (No. RT104-03-02).

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