

Hg²⁺-selective fluoroionophoric behavior of pyrene appended diazatetrathia-crown ether

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Abstract—Bis(pyrene) derivative of diazatetrathia-crown ether has been prepared and its Hg²⁺-selective fluoroionophoric properties were investigated. The compound showed a pronounced Hg²⁺-selectivity and other metal ions except for Cu²⁺ showed almost no discernible responses. The Hg²⁺-selectivity of the compound was also confirmed by the competitive experiments performed in the presence of physiologically important metal ions and the detection limit was found to be 1.6×10^{-6} M. The prominent selective and efficient fluorescence quenching behavior could be utilized as a new chemosensing system for the analysis of toxic Hg²⁺ ions in aqueous environment.

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There are a number of ingeniously designed supramolecular systems for the selective chemosensing of chemically and biologically important ionic species.¹ Particularly important is the selective detection of Hg²⁺ ions due to the toxic impacts of this heavy metal ion on our environments.² Among many Hg²⁺-selective chemosensors developed so far, optical detection systems attracted much research interest and are generally derived from the traditional structural skeleton of crown ethers,³ calixarenes,⁴ and other versatile molecular frameworks including proteins, oligonucleotides, and dye-based structures.⁵ The molecular framework of diazatetrathia-crown ether **1** has been utilized as a platform for the construction of supramolecular systems having transition metal ion selectivity.⁶ Crystal structures of Hg²⁺ complexes of a series of cage-annulated sulfur-containing cryptands, especially having diazatetrathia-crown moiety, suggest the stable complex formation of thia-crown ethers with Hg²⁺ ions.⁷ Bipyridine-armed diazatetrathia-crown ether showed a specific binding ability for Cu²⁺ ions in the presence of Ni²⁺, Co²⁺, and Zn²⁺ ions when assisted by a vesicle forming surfactant.⁸ In addition to these, an efficient Hg²⁺-selective fluorescent sensor bearing diazatetra-

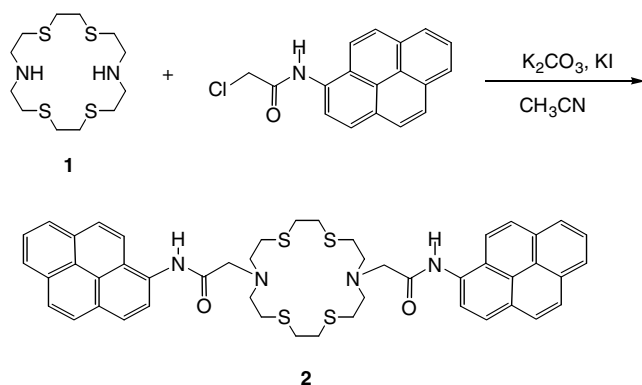
thia-crown moiety on the 1,8-positions of the anthracene ring has been reported.⁹ Fluorescence is a particularly attractive signaling tool for the construction of chemosensors because of its sensitivity and easy of signal detection.¹⁰ Among many fluorophores, pyrene subunits are versatile and frequently employed for the construction of important chemosensors having efficient fluorogenic behavior.¹¹ In this letter, we report a new fluoroionophore derived from diazatetrathia-crown ether having two pyrenylacetamide fluorophore for the sensing of transition metal ions. Designed compound exhibited a highly Hg²⁺-selective and efficient fluorescence quenching behavior in aqueous acetonitrile solution.

The pyrene appended compound **2** was prepared by the reaction of 1,4,10,13-tetrathia-7,16-diazacyclooctadecane **1** with 2-chloro-*N*-pyren-1-yl-acetamide^{4c} (K₂CO₃, KI) in acetonitrile (75% yield) (Scheme 1).¹² The complexation of targeted metal ions by the diazatetrathia-crown moiety could be further assisted by the amide carbonyl groups of the appending side chain in somewhat axial type participation as is frequently observed in lariat ethers.¹³

First, the fluoroionophoric properties of **2** toward representative alkali, alkaline earth, and transition metal ions were investigated in aqueous organic solutions. Among the surveyed systems of common water miscible organic

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Scheme 1. Synthesis of pyrene appended diazatetrathia-crown ether.

solvents, aqueous acetonitrile was found to be relatively well suited for the selective responses of a specific transition metal ion. To have a more optimized condition for a specific metal ion, the effects of water composition on fluorescence behavior were investigated (Fig. 1). As the composition of water increases, the fluorescence intensity of pyrene monomer emission at 387 nm decreases progressively. Similar decreases, but with much larger changes in lower water composition region, were also observed for **2** in the presence of 100 equiv of Hg^{2+} or Cu^{2+} ions. The maximum selectivity toward target metal ions seems to be obtained in relatively lower water composition region between 0% and 20%. Based on this profile the fluorescence measurements were carried out in 90% aqueous acetonitrile solution ($\text{CH}_3\text{CN}-\text{H}_2\text{O} = 90:10$, v/v) where both requirements for the use of aqueous solution in the analysis of real samples and the high selectivity toward Hg^{2+} and Cu^{2+} ions are fulfilled.

Fluorescence spectra of **2** in aqueous acetonitrile solution comprised of two prominent emissions due to the pyrene moiety: that is characteristic monomer emissions around 370–440 nm and a broad excimer emission centered around 480 nm (Fig. 2). Upon interaction with varying alkali (Na^+ , K^+), alkaline earth (Mg^{2+} , Ca^{2+}),

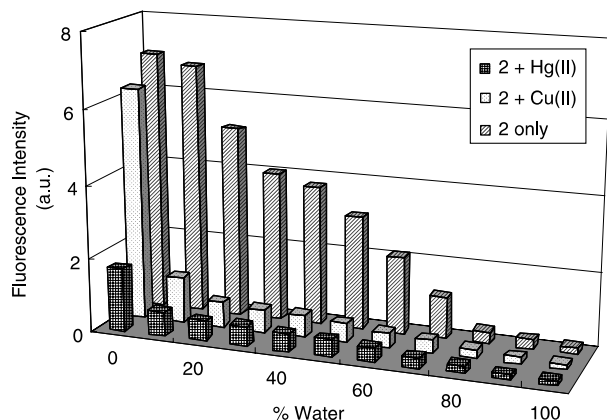


Figure 1. Changes in fluorescence intensity of **2**, **2**- Hg^{2+} , and **2**- Cu^{2+} systems as a function of water composition in aqueous acetonitrile. $[\mathbf{2}] = 5.0 \times 10^{-6}$ M. $[\text{Hg}^{2+}$ or $\text{Cu}^{2+}] = 5.0 \times 10^{-4}$ M as perchlorate salt. $\lambda_{\text{ex}} = 340$ nm and fluorescence intensities were measured at 387 nm. Buffered at pH 4.8 with acetate buffer (10^{-2} M).

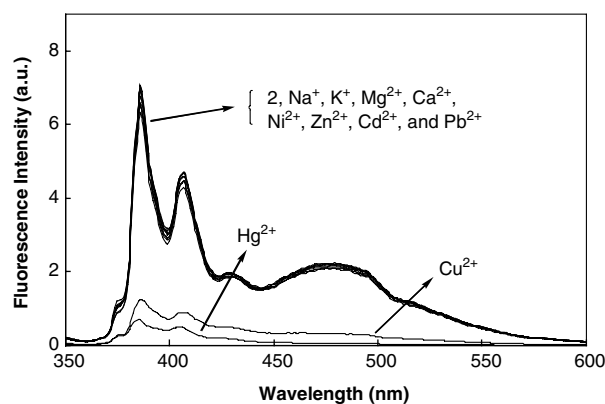


Figure 2. Fluorescence spectra of **2** in the presence of varying metal ions in aqueous acetonitrile. $[\mathbf{2}] = 5.0 \times 10^{-6}$ M. $[\text{M}^{n+}] = 5.0 \times 10^{-4}$ M as perchlorate salts. $\lambda_{\text{ex}} = 340$ nm in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (90:10, v/v) buffered at pH 4.8 with acetate buffer (10^{-2} M).

and transition metal (Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+}) ions, the fluorescence of **2** was selectively quenched only with Hg^{2+} and Cu^{2+} ions. The pronounced Hg^{2+} - and Cu^{2+} -selectivities are not unexpected with reference to the other systems based on the azathia-crown ethers.^{7–9,14} Generally, the azamacrocycles having appended pyrene moiety signal the complexation event by the mechanism of PET (photoinduced electron transfer) type fluorescence enhancements.¹⁵ In the present case, the fluorescence quenching effect induced by the complexed Hg^{2+} and Cu^{2+} ions having intrinsic quenching nature was operative more pronouncedly than the PET type complexation-induced fluorescence enhancements.

The quenching efficiency expressed by I_0/I (I_0 and I denote the fluorescence intensity of **2** in the absence and the presence of metal ions, respectively) was larger than 9.7 for Hg^{2+} ions and 5.1 for Cu^{2+} ions in monomer emission region at 387 nm. The degree of fluorescence quenching in excimer emission region (measured at 480 nm) was more dramatic for Hg^{2+} ions ($I_0/I = 38$ for Hg^{2+} and 6.4 for Cu^{2+} ions). All the other metal ions surveyed revealed relatively constant I_0/I values of 0.93–1.02. The effective fluorescence quenching of **2** might be due to the intrinsic quenching nature of the selectively complexed Hg^{2+} ions as described earlier.¹⁶ In this case, the excimer emissions are also completely disappeared, which might be originated from the conformational changes of the ionophore upon complex formation leading to the separation of the two nearby situated pyrene moieties for the excimer emission.¹⁷ That is the metal ions are nested at the center of the macrocycle with further ligations with amide carbonyl groups of the appended pyrene moiety in somewhat axial type mode, which resulted in the extended conformation of **2** with two divergent pyrene fluorophores. Under this situation, the fluorescences of pyrene excimer as well as monomer region would be effectively quenched with complexed Hg^{2+} ions. Fluorescence quenching was also observed with another intrinsic quenching Cu^{2+} ions,¹⁶ however, in this case the quenching behavior was less effective in monomer region as well as in exci-

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