

A Highly Hg(II)-selective Chemosensor with Unique Diarylethene Fluorophore

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Mercury and its ion are considered as one of dangerous and wide spread global pollutants. Mercury brings about a vast of contamination in our life because of its long term residence in air and its oxidation to water soluble Hg²⁺.¹ Recently the tools used for detecting mercury are atomic spectroscopy, inductively coupled plasma mass spectroscopy, and absorption/emission spectroscopy and so forth.² These methods, however, require expensive and sophisticated instrumentations. These facts provide motivation to develop new and cheap probes for the detection of mercury ion from our environmental samples. Fluorescent chemosensors for monitoring Hg²⁺ have many advantages, such as low cost, simple instrumentations and high selectivity, as compared to other techniques.³ Therefore, the development of chemosensors become attractive subjects to organic/inorganic chemists.

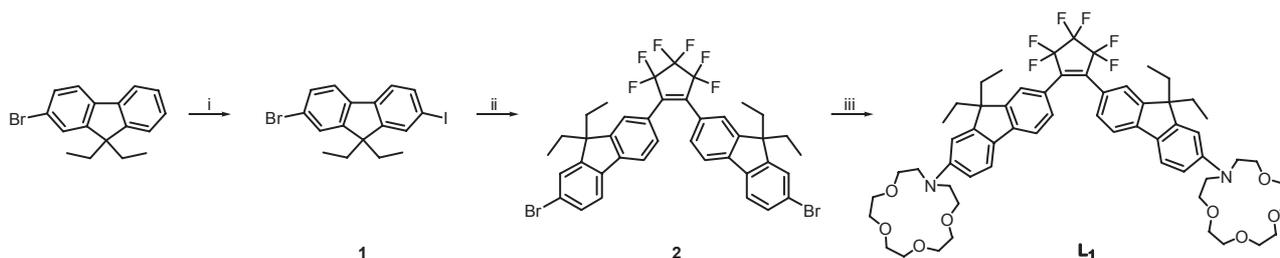
Recently, macrocyclic fluorescent chemosensor based on crown ether have been intensively studied for application in many areas due to their selectivity for transition metals ions.⁴ Due to the softness of mercury ions, Hg²⁺, macrocycles to selective mercury ions mainly are consisted of N-S and/or O-S donor sets in receptor segment.^{3b,5} Macrocycles including NO donor set also show high selectivity to alkali metal ions. Meanwhile, the reports on the selectivity of mercury ions using this kind of donor set can hardly be found.⁶ Fluorophore plays an important role in fluorescent chemosensors since it evolves a detecting signal (fluorescence) upon metal recognition of macrocycles. For this reason, anthracene derivatives with high quantum efficiency are mainly used as fluorophore in fluorescence chemosensors.⁷ In the course of our development on the luminescent materials for use in varied applications,⁸ we found that diaryl-

ethene compounds have shown much higher quantum efficiency than even 9,10-diphenylanthracene ($\Phi_{PL} = 0.95$) due to their molecular rigidity and the presence of varied intermolecular interactions. In this regard, we envisioned that diarylethene composed of azacrownether as a receptor and of two fluorenes, which are linked by perfluorocyclopentene, as a fluorophore would show a unique photophysical properties and metal recognition. Herein, we report our systematic investigation into photophysical and coordinative properties to varied metal ions of 1,2-bis{9,9-diethyl-7-(1,4,7,10-tetraoxa-13-azacyclopentadecane)fluoren-2-yl}-3,3,4,4,5,5-hexafluorocyclopentene (**L**₁).

As shown in Scheme 1, starting materials **1** and **2** were prepared as previously reported.^{8a,9} Details of synthetic procedures of **1** and **2** are described in experimental section. The target ligand **L**₁ was prepared by the reaction of 2-bromo-9,9-diethyl-7-iodofluorene (**2**) and 1-aza-15-crown-5 in the presence of 2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl, Pd₂(dba)₃, and sodium *tert*-butoxide. This ligand was fully characterized by varied spectroscopic methods.

The photophysical properties of **L**₁ were measured in CH₃CN. In emission spectrum of free ligand (Figure 1 inset), a broad emission band was observed at 600 nm (excitation at 383 nm). Interestingly, emission band of **L**₁ is much red shifted as compared to that of compound **2**. Compound **2** exhibits strong emission band with λ_{max} 450 nm, while emission maximum of ligand **L**₁ appears at 600 nm with less intensity (See supporting information). This fact suggests that the introduction of azacrown moiety may have significantly influenced on the electronic transition.

Under the same experimental conditions (*i.e.* the same con-



Scheme 1. Synthetic routes of **L**₁ and reagents and experimental conditions: i) I₂, HIO₄, CH₃COOH/H₂O/H₂SO₄, reflux, 10 h. ii) *n*-BuLi/Ether, octafluorocyclopentene, 12 h. iii) 1-aza-15-crown-5, NaO^tBu, Pd₂(dba)₃, C₂₆H₃₆NP/Toluene, reflux, 24 h

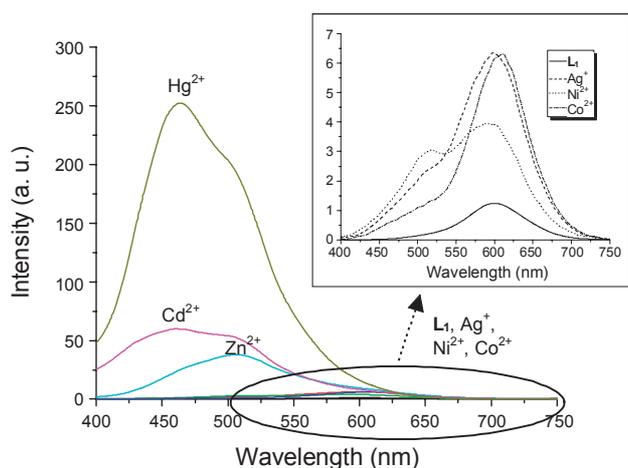


Figure 1. Change in fluorescent emission spectra of L_1 (100 μ M) in CH_3CN in the presence of 50 equiv Hg^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Ag^+ .

centration), the absorption spectrum of L_1 shows the same trend (much red-shifted: *ca.* 70 nm; See supporting information). These absorption and emission observed for L_1 are likely to due to intramolecular charge transfer (lone pair of nitrogen atom on azacrown ether to fluorene). The emission quantum yield of L_1 was determined by using rhodamine 6G (0.94) as reference. This value is 0.035, which is much lower than that of reference. This observation implies that an effective fluorescent quenching of excited state caused by the lone pair electron of receptor moiety, photo-induced electron transfer (PET), occurs prior to metal ion recognition. Figure 1 exhibits fluorescent emission changes of L_1 after addition of 50 equivalent of metal nitrate. It is interesting that the strong intense emission peak was observed in the presence of $Hg(II)$ ion as compared to those of other metal ions.

To investigate the metal-induced fluorescent change of L_1 in the presence of metal ions such as $Ag(I)$, $Ni(II)$, $Co(II)$, $Zn(II)$, $Hg(II)$, and $Cd(II)$, we carried out titration experiments. The fluorescent enhancement effect upon metal complexation was observed for L_1 in the presence of metal ions investigated, but the intensity of this CHEF (Chelating Enhancement of Fluorescence) effect was different in all of them (Figure 1). The most effective enhancement was upon Hg^{2+} complexation, after addition of two equivalents the intensity of emission was reached in 252 [I/I_0] (I/I_0 value is the ratio of fluorescence intensity in the presence (I) and absence (I_0) of metal ions). While after addition of 50 equivalents [I/I_0] values for Ni^{2+} , Ag^+ , Co^{2+} , Zn^{2+} and Cd^{2+} were 4, 6, 6, 38 and 60, respectively. These results suggest a stronger complexation with Hg^{2+} when compared to the other metals. As shown in Figure 2, intensity change is observed that the band at 464 nm reaches a plateau upon the addition of 2 equiv of Hg^{2+} , confirming the formation of a 1:2 ($L_1:M^{2+}$) complex. The binding constant for the interaction of ligand, L_1 , in the presence of Hg^{2+} ion were calculated using absorption spectra (See experimental section).¹⁰ The binding constant for the formation of the $L_1:Hg^{2+}$ (K_{11}) and $L_1:Hg^{2+}$ (K_{12}) complexes are $3.3 \times 10^4 M^{-1}$, and $= 6.2 \times 10^3 M^{-1}$, respectively.

The complexation and interaction in solution with $Hg(II)$

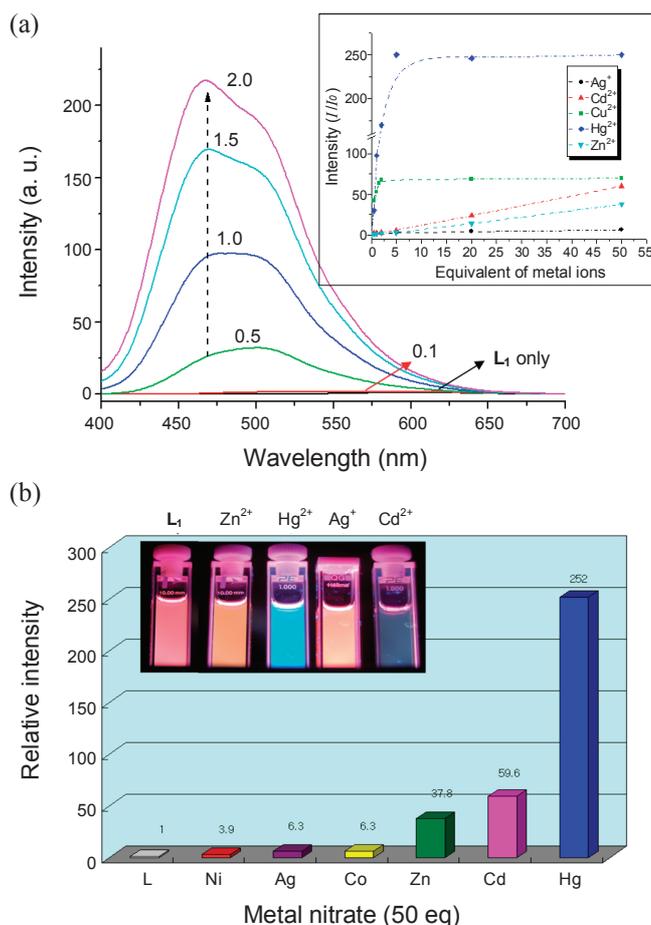


Figure 2. (a) Fluorescent intensity of L_1 in CH_3CN upon addition of Hg^{2+} (0.1 ~ 2.0 equiv.). Inset: I/I_0 vs equivalent of metal (Hg^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , and Ag^+) ions curve. (b) Fluorescent response of L_1 in the presence of various metal ions (50 equiv.) in CH_3CN .

ion were investigated by 1H -NMR, because ligand L_1 was the most effective and selective for this metal ion. Therefore, excess $Hg(NO_3)_2$ in CD_3OD were added to a 0.05 M solution of L_1 in the same solvent. The 1H -NMR spectra of the resulting solutions measured at ambient temperature, 15 min after addition of $Hg(II)$. As shown in Figure 3, well resolved peaks originated from the alkyl and aryl group of L_1 were observed. An increase in the mercury ion concentration gradually downfield-shifted the proton resonance of H9(H9') and H10(H10') from the azacrownether segment, the former being the most affected. This observation strongly suggests that $Hg(II)$ is coordinated *via* the nitrogen atom as well as oxygen atoms. The spectrum resolution of azacrownether region decreases in the presence of metal ion, implying that a fluxional conformation were formed and/or the fast equilibrium between 1:1 ($L_1:M^{2+}$) and 1:2 ($L_1:M^{2+}$) complexes occurs in solution.

Additional evidence of coordination modes is to investigate fluorescence change of L_1 in the presence of H^+ ion. If the nitrogen atoms in azacrownether were still strongly coupled to the metal ions in the excited state, then one would expect the fluorescence of $L_1:2M^{2+}$ to be very similar to that of $L_1:2H^+$. The emission spectrum of the protonated L_1 resembles that of L_1 at high [Hg^{2+}], where a large fraction of the 1:2 ($L_1:Hg^{2+}$)

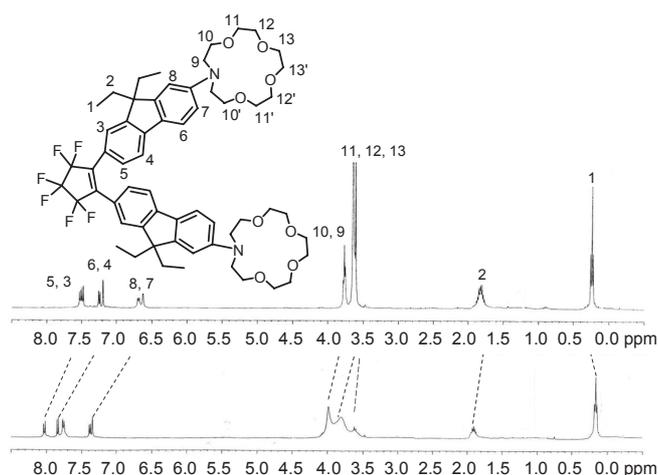


Figure 3. Change of $^1\text{H-NMR}$ spectra for ligand L_1 (top) and after adding excess Hg^{2+} ion in CD_3OD (400 MHz).

complex is present (See supporting information).

The similarity of the spectra of L_1 in the protonated form and in the 1:2 complex with Hg^{2+} is consistent with the nitrogen lone pair not interacting significantly with the π -system upon ion binding. Such similarities in the absorption and emission spectra of the ion-bound form of the aza-crown chromophores and the protonated dye or a modified dye in which the crown is replaced by a hydrogen have been observed for other aza-crown ether substituted systems.¹¹ Thus, it appears two different experiments, NMR and fluorescence measurement, may have concluded that the complex was formed by the strong coordination of O-N-O donor set in azacrown ether moiety and metal ion. In summary, a novel fluorene and perfluorocyclopentene based ligand L_1 with NO_4 donor set was synthesized and was evaluated as fluorimetric sensor for Ni^{2+} , Ag^+ , Co^{2+} , Zn^{2+} , Cd^{2+} , and Hg^{2+} . This ligand exhibits enhanced fluorescence intensity upon addition of all metal ions through the CHEF effect and the formation of 1:2 complexes. In particular, ligand L_1 has been demonstrated highly selectivity and sensitivity for the Hg^{2+} ion due to the strong interactions between NO donor set and metal ion. It is highly recommended to put consistent effort in the development of derivatives of this kind, because starting material, compound **2**, has high photoluminescence quantum efficiency and characteristic for ease of varied receptors introduced into fluorene segments.

Experimental Section

General consideration. All reagents were purchased from commercial sources and without further purification unless otherwise noted. All solvent were freshly distilled from appropriate drying agents prior to use. Conventional schlenk techniques were used, and reactions were carried out under dry nitrogen atmosphere. $^1\text{H-NMR}$ Spectra were recorded with a Bruker advance 300 MHz or 400 MHz spectrometer instrument. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. 2-Bromo-9,9-diethyl-7-iodofluorene (**1**) was prepared according to literature

procedures⁹ as follows: Bromination of 9,9-diethylfluorene was conducted using *N*-bromo succinimide (NBS), and the resulting 2-bromo-9,9-diethylfluorene intermediate was treated with acetic acid, water, concentrated sulfuric acid, iodine, and iodic acid in carbon tetrachloride to afford 2-bromo-9,9-diethyl-7-iodofluorene.

Binding constant determination. The binding constant of L_1 for $\text{Hg}(\text{II})$ was determined by using previous method.¹² The following equations describe the equilibrium constants for the formation of 1:1 ($\text{L}_1:\text{Hg}$) and 1:2 ($\text{L}_1:\text{Hg}_2$) complexes,



where L is the ligand, M is the metal ion, LM and LM_2 are the complexes, and K_{11} and K_{12} is the binding constant. K_{11} and K_{12} can be determined from measurements of absorbance as a function of ion concentration using the following equation

$$\Delta A/L = \{[\text{L}_1]K_{11}\Delta\epsilon_{11}[\text{M}]\}/\{1 + K_{11}[\text{M}]\} \quad (3)$$

$$\Delta A/L = \{[\text{L}_1](K_{11}\Delta\epsilon_{11}[\text{M}] + K_{11}K_{12}\Delta\epsilon_{12}[\text{M}]^2)\}/\{1 + K_{11}[\text{M}] + K_{11}K_{12}[\text{M}]^2\} \quad (4)$$

In equation 3, ΔA is the difference in absorbance at a particular wavelength between the pure dye solution and the solution of dye and metal ion ($A_0 - A$), L is the path length, $[\text{L}_1]$ is the total ligand concentration, $[\text{M}]$ is the concentration of the free metal, and $\Delta\epsilon_{11}$ is the change in extinction coefficient at the measurement wavelength between the ligand and the L:metal complex ($\epsilon_L - \epsilon_{\text{LM}}$). In equation 4, $\Delta\epsilon_{12}$ is the change in extinction coefficient at the measurement wavelength between the ligand and the 1:2 (L:metal) complex ($\epsilon_L - \epsilon_{\text{LM}_2}$). These consideration and treatment are valid if the free metal ion concentration is not significantly altered by binding.

Synthesis of 1,2-bis(7-bromo-9,9-diethylfluoren-2-yl)-3,3,4,4,5,5-hexafluorocyclopentene (2). A solution of *n*-BuLi (2.34 mmol, 1.6 M in hexane) was added slowly to the 2-bromo-9,9-diethyl-7-iodofluorene (1 g, 2.34 mmol) in THF (100 mL) at -78°C and stirred for 60 min. To this solution was added octafluorocyclopentene (0.56 mL, 1.4 mmol). Upon addition of octafluorocyclopentene to the lithiated solutions, the color changed rapidly from pale yellow to brown. The reaction mixture was warmed slowly to ambient temperature and stirred overnight. The reaction mixture was poured into water and repeatedly extracted with CH_2Cl_2 (30 - 50 mL). The combined organic layer was dried over MgSO_4 , filtered, and concentrated under reduced pressure. The pure corresponding compounds were isolated by chromatographic workup (silica). Yield: 41% (eluent: hexane, $R_f = 0.6$); MS (EI): m/z 774 $[\text{M}]^+$. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 7.52-7.20 (12H, m), 1.73 (8H, q, $J = 7.4$ Hz), 0.17 (12H, t, $J = 7.2$ Hz). Anal. Calcd for $\text{C}_{39}\text{H}_{32}\text{Br}_2\text{F}_6$: C, 60.48; H, 4.16. Found: C, 60.22; H, 4.05.

Synthesis of 1,2-bis{9,9-diethyl-7-(1,4,7,10-tetraoxa-13-azacyclopentadecane)fluoren-2-yl}-3,3,4,4,5,5-hexafluoro-

cyclopentene (L₁). The mixture of compound **2** (0.3 g, 0.41 mmol), 1-aza-15-crown-5 (0.2 g, 0.9 mmol), 2-dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl (0.019 g, 0.05 mmol), Pd₂(dba)₃ (0.008 g, 0.008 mmol), and sodium *tert*-butoxide (0.11 g, 1.1 mmol) was placed in a dried Schlenk tube and dissolved in toluene (5 mL). The reaction mixture was heated at 80 °C with stirring for 24 h. The reaction mixture was then cooled to room temperature, taken up in dichloromethane (60 mL), filtered through Celite, and concentrated in a vacuum. The crude product was purified by flash column chromatography on alumina (neutral) using ethyl acetate and hexane as an eluting solvent. Yield: 25% (eluent: ethylacetate/hexane (4/1), *R_f* = 0.53); ¹H-NMR (CDCl₃, 300 MHz) δ 6.47-7.41 (12H, m), 3.74 (8H, m), 3.57 (32H, m), 1.7 (8H, q, *J* = 6.8 Hz), 0.21 (12H, t, *J* = 7.2 Hz). ¹³C-NMR (CDCl₃, 75 MHz) δ 150.9, 150.5, 149.5, 149.0, 141.6, 140.8, 140.2, 128.4, 128.0, 127.0, 126.5, 123.9, 122.9, 120.1, 114.8, 114.1, 71.2, 70.1, 69.8, 69.5, 56.5, 33.2, 8.9. Anal. Calcd for C₅₉H₇₂F₆N₂O₈: C, 67.47; H, 6.90. Found: C, 67.13; H, 6.76.

Supporting Information. Emission spectra of compound **2** and L₁; photo of emission change for L₁; Free L₁ in the presence of Hg²⁺ and H⁺; fluorescent intensity change of L₁ in the presence of Cd²⁺ and Ag⁺ (0 ~ 5.0 eq); fluorescent intensity change of L₁ in the presence of Zn²⁺, Ni²⁺, and Co²⁺ (0 ~ 5.0 eq or 0 ~ 2 eq); absorption spectra of L₁ and L₁:Hg²⁺ in CH₃CN are available on request from the correspondence author (E-mail: kangy@kangwon.ac.kr; Fax: 82-33-242-9598).

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