

A Carbazole-Attached NO_2S_2 -Macrocyclic Exhibiting Hg^{2+} and Cu^{2+} Selectivity

Seul-Gi Lee, Eun-Ju Kang, and Shim Sung Lee*

Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea

*E-mail: sslee@gnu.ac.kr

Received February 4, 2013, Accepted February 13, 2013

A synthesis and cation-induced fluorescent behavior of the carbazole-attached NO_2S_2 -macrocyclic (**L**) is described and structurally characterized by single crystal X-ray analysis. The photoluminescence spectrum of **L** in 80% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ displays a peak maximum at 431 nm (blue emission). In the metal-induced fluorometric experiment, **L** showed a drastic chelation-enhanced fluorescence quenching (CHEQ) effect only with Hg^{2+} and Cu^{2+} . In ESI-mass study, a 1:1 stoichiometry for complexation of **L** with Hg^{2+} was confirmed, suggesting the unique sensing behavior of the proposed ligand **L** due to the selective complexation affinity for Hg^{2+} . The observed results indicate that **L** is a promising turn-off type fluoroionophore for Hg^{2+} and Cu^{2+} detections. Additionally, the Ag^+ complex of the precursor macrocycle was prepared and its solid structure was crystallographically characterized.

Key Words : Carbazole-attached macrocycle, Fluoroionophore, Mercury(II), Copper(II), X-ray crystal structure

Introduction

Chemosensor showing excellent selectivity toward a given analyte is in great demand because of its economic advantage, high throughput capability, and point-of-care monitoring.¹ Therefore, many efforts have been devoted in designing and preparation of photophysical chemosensors such as colorimetric and fluorescent ones.² In particular, the design of new fluoroionophores is an area of intense research works and of tremendous significance to the field of chemosensor and related device fabrication.³ Most of the fluoroionophores are designed as multicomponent systems comprising a recognition unit (receptor) and signaling unit (fluorophore): the two are often separated by a spacer unit.^{2,3}

Owing to their selective metal ion recognition, macrocycle-receptor-based fluoroionophores make them good candidates for the chemosensors for the metal ions.⁴ According to our previous works on the macrocyclic supramolecular complexes, primarily, the dibenzo- NO_2S_2 parent macrocycle has been an adequate candidate toward the soft heavy metal including Hg^{2+} .⁵ Among the fluorophores as a signaling unit, carbazole is highly promising due to its attractive fluorescence and electron donor properties.⁶

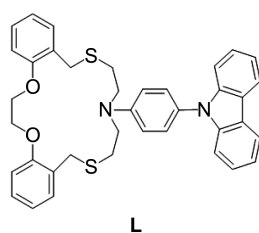
In our continuing program on the design and preparation of new chemosensors for the detection of the environmentally important metal ion species,^{5c,7} we propose here a new fluoroionophore **L** with macrocycle-spacer-fluorophore

format comprising a carbazole moiety attached to the dibenzo- NO_2S_2 macrocycle with a phenyl group spacer. The photoluminescent properties of the complexation phenomena of this new fluoroionophore were investigated in the presence of diverse metal ions including soft heavy metal species.

Experimental

General. All commercial reagents and solvents were of analytical reagent grade where available. The ^1H and ^{13}C NMR spectra were recorded with a Bruker Advance-300 (300 MHz) NMR spectrometer. The FT-IR spectra were measured with a Shimadzu FT-IR 8100 spectrometer. UV-vis spectra were measured with a Scinco S-3150. Fluorescence emission spectra were recorded with a Shimadzu RF-5301-PC instrument. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer.

Synthesis and Characterization of 5. Cesium carbonate (4.64 g, 14.2 mmol) was dissolved in DMF (600 mL) in a 1 L round-bottom flask. And 2,2'-(4-bromophenylazanediyl)-diethanethiol **4**^{5c} (1.01 g, 4.70 mmol) and corresponding dichloride⁸ (1.41 g, 4.75 mmol) were dissolved in DMF (30 mL) and placed in a 50 mL glass syringe. Under a nitrogen atmosphere, the contents of the syringe were added dropwise into the DMF solution at 45–50 °C for 50 h. The mixture was kept for a further 10 h. After cooling to room temperature the reaction mixture was filtered and evaporated. Water (100 mL) was added, and the mixture was extracted. The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed to give colorless oil. Flash column chromatography (SiO_2 , 10% ethyl acetate/*n*-hexane) afforded the product as a white solid in 33% yield. mp 147–148 °C (decomp.). IR (KBr pellet) 3062, 3035, 2922, 2872, 2354, 2208, 1589, 1493, 1450, 1350, 1289, 1247, 1185, 1104,



1056, 939, 808, 753 cm^{-1} . Anal. Calcd for $[\text{C}_{26}\text{H}_{28}\text{BrNO}_2\text{S}_2]$: C, 58.86; H, 5.32; N, 2.64. Found: C, 58.49; H, 5.55; N, 2.42%. ^1H NMR (300 MHz, CDCl_3) δ 7.45–6.33 (m, 12H, aromatic), 4.39 (s, 4H, $\text{CH}_2\text{CH}_2\text{O}$), 3.85 (s, 4H, ArCH_2S), 3.50 (t, 4H, $\text{CH}_2\text{CH}_2\text{N}$), 2.57 (t, 4H, $\text{CH}_2\text{CH}_2\text{S}$); ^{13}C NMR (75 MHz, CDCl_3) δ 156.3, 145.7, 131.9, 130.9, 128.2, 127.2, 121.7, 113.5, 111.8, 107.9, 67.5, 52.0, 29.0, 28.1. Mass spectrum m/z (ESI): 529.6 $[\text{S}+\text{H}]^+$.

Synthesis and Characterization of L. Under a nitrogen atmosphere, copper iodide (0.036 g, 0.19 mmol), K_3PO_4 (0.60 g, 2.80 mmol) and carbazole (0.30 g, 1.9 mmol) were dissolved in 1,4-dioxane (150 mL). *N*-Phenylated macrocycle **5** (1.0 g, 1.90 mmol) and (\pm)-trans-1,2-diaminocyclohexane (0.040 g, 0.038 mmol) were dissolved in 1,4-dioxane (20 mL). The mixture was stirred at 110 $^\circ\text{C}$ for 24 h. After cooling to room temperature, the reaction mixture was filtered and evaporated. Water (100 mL) was added, and the mixture was extracted. The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed to give colorless oil. Flash column chromatography (SiO_2 , 5% ethyl acetate/*n*-hexane) afforded the product as a white solid in 15% yield. mp 209–210 $^\circ\text{C}$ (decomp.). IR (KBr, cm^{-1}): 3059, 3038, 2914, 2871, 2350, 2320, 1518, 1487, 1449, 1332, 1229, 1196, 1136, 1103, 930, 816, 752, 726. Anal. Calcd for $[\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{S}_2]$ (%): C, 73.99; H, 5.88; N, 4.54; S, 10.39. Found: C, 73.78; H, 6.00; N, 4.38; S, 10.11. ^1H NMR (300 MHz, CDCl_3) δ 8.14–6.67 (m, 20H, aromatic), 4.43 (s, 4H, $\text{CH}_2\text{CH}_2\text{O}$), 3.92 (s, 4H, ArCH_2S), 3.63 (t, 4H, $\text{CH}_2\text{CH}_2\text{N}$), 2.70 (t, 4H, $\text{CH}_2\text{CH}_2\text{S}$); ^{13}C NMR (75 MHz, CDCl_3) δ 184.2, 156.4, 141.5, 130.9, 128.4, 127.3, 125.7, 122.9, 121.7, 120.1, 119.3, 111.9, 109.8, 67.6, 52.2,

32.3, 29.1, 28.4. Mass spectrum m/z (ESI): 616.92 for $[\text{L}+\text{H}]^+$ (Calcd 617.23).

Preparation of 6, $[\text{Ag}(\text{5})]\text{PF}_6\cdot 2\text{CH}_3\text{OH}$. Silver(I) hexafluorophosphate (9.53 mg, 0.038 mmol) dissolved in methanol (2 mL) was added to a solution of the precursor macrocycle **5** (20.0 mg, 0.038 mmol) in dichloromethane (2 mL). Vapor diffusion of diethyl ether into a DMF solution of this product afforded **6** as a crystalline product suitable for X-ray analysis (30%). mp 163–164 $^\circ\text{C}$ (decomp.). IR (KBr pellet) 3066, 2932, 2876, 2405, 2250, 1587, 1492, 1452, 1295, 1243, 1187, 1134, 1108, 1048, 941, 841 (PF_6^-), 752, 557, 494 cm^{-1} . Anal. Calcd for $[\text{C}_{26}\text{H}_{28}\text{AgBrF}_6\text{NO}_2\text{PS}_2]$: C, 39.86; H, 3.60; N, 1.79. Found: C, 39.83; H, 4.10; N, 2.12%. Mass spectrum m/z (ESI): 635.4 $[\text{Ag}(\text{5})]^+$.

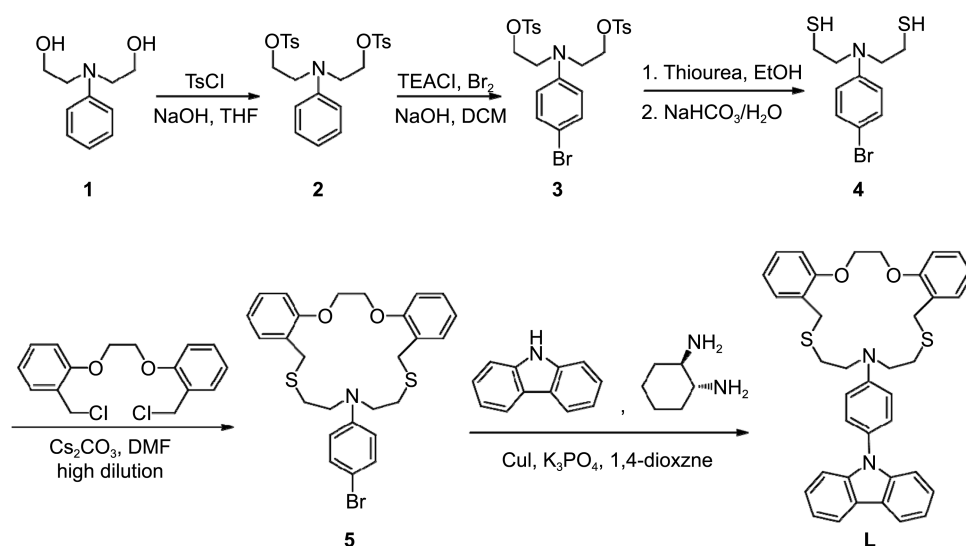
X-Ray Crystallographic Analysis. The diffraction data were measured at 173 K on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program.⁹ The intensity data were processed using the SAINT Plus program.⁹ All of the calculations for the structure determination were carried out using the SHELXTL package.¹⁰ Absorption corrections were applied using XPREP and SADABS.¹¹ Relevant crystal data collection and refinement data for the crystal structures are summarized in Table 1.

Results and Discussion

Synthesis of L. Compounds **1–4** were prepared using known procedures.¹² As a key precursor, *N*-phenylated macro-

Table 1. Crystal and Experimental Data

	5	L	6
Formula	$\text{C}_{26}\text{H}_{28}\text{BrNO}_2\text{S}_2$	$\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{S}_2$	$\text{C}_{28}\text{H}_{36}\text{AgBrF}_6\text{NO}_4\text{PS}_2$
Formula weight	530.52	616.81	847.45
Temperature	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	8	4
<i>a</i> (Å)	4.9678(4)	31.697(3)	17.829 (1)
<i>b</i> (Å)	15.746(1)	16.844 (2)	8.5265(5)
<i>c</i> (Å)	16.033(1)	12.007 (1)	21.620(1)
α ($^\circ$)	69.665(1)	90	90
β ($^\circ$)	89.484(2)	90.591(2)	95.503(1)
γ ($^\circ$)	88.467(2)	90	90
<i>V</i> (Å ³)	1175.5 (2)	6411(1)	3273.1(3)
<i>D</i> _{calc} (g/cm ³)	1.499	1.278	1.720
$2\theta_{\text{max}}$ ($^\circ$)	52.00	52.00	52.00
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0289, 0.0593	0.1073, 0.2008	0.0635, 0.1624
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0354, 0.0644	0.1750, 0.2267	0.1179, 0.2099
No. of reflection used [<i>I</i> > 2 σ (<i>I</i>)]	4516 [<i>R</i> _{int} = 0.0189]	6280 [<i>R</i> _{int} = 0.0825]	6429 [<i>R</i> _{int} = 0.0875]
GOF	1.122	1.089	1.062
Structure determination	SHELXTL	SHELXTL	SHELXTL
Refinement	full-matrix	full-matrix	full-matrix

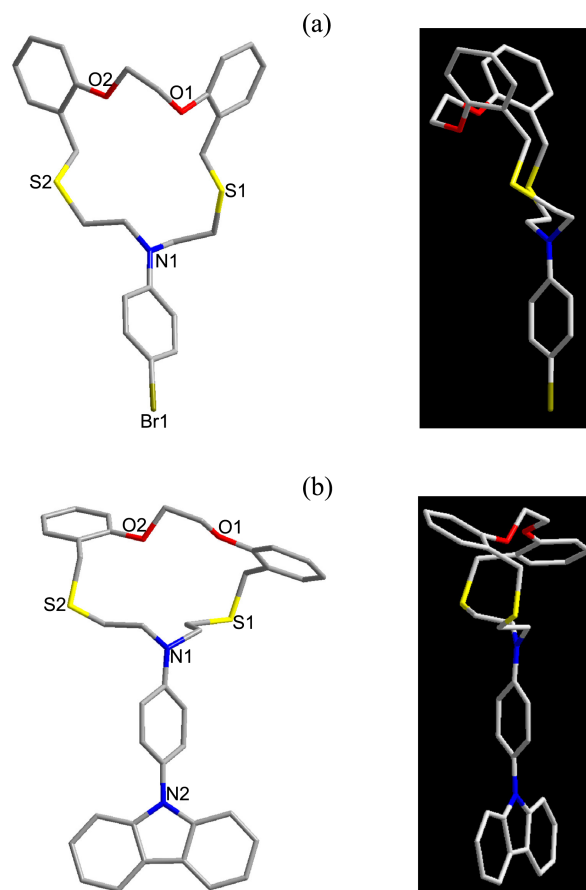
Scheme 1. Synthesis of **L**.

cycle **5** was prepared by coupling reaction between dithiol **4**^{5c} and corresponding dichloride⁸, employing Cs_2CO_3 under high dilution (Scheme 1). The carbazole-attached macrocycle **L** was synthesized by means of a Buchwald procedure.¹³ The ^1H and ^{13}C NMR spectra together with elemental analysis and mass spectra were clearly in agreement with the proposed structures.

Crystal Structures of 5 and L. The structures of the precursor macrocycle **5** and target **L** were also characterized by single crystal X-ray analysis (Figure 1). Both of the colorless single crystals of **5** and **L** suitable for X-ray analysis were obtained by slow evaporation of each dichloromethane solution. In crystal, the macrocyclic ring in **5** is slightly folded (Figure 1(a)), while that in **L** is twisted (Figure 1(b)). In both cases, two oxygen atoms are oriented endodentate, but two sulfur donors are arranged exodentate with respect to the ring cavity. The S...S distances in **5** and **L** is 5.831 and 7.384 Å, respectively. In **L**, the dihedral angle between the *N*-phenyl ring and the carbazole terminal unit is $54.0(2)^\circ$.

Solid-state photoluminescence spectrum of **L** was observed at room temperature (Figure 2). The colorless single crystal of **L** exhibits a broad band with a blue emission maxima at 397 nm ($\lambda_{\text{ex}} = 365$ nm) arising from the intermolecular charge transfer (ICT) states between the *N*-phenylated macrocyclic unit and excited carbazole terminal group.⁶

Metal-Induced Fluorescence Changes. As a preliminary tool, the cation sensing as a fluorescence sensor toward diverse metal ions (10 equivalents) was examined for **L** (excitation at 365 nm). The fluorescent responses to the diverse metal ions as perchlorate salts under the same conditions are shown in Figure 3. Free **L** exhibits a blue photoluminescence at 431 nm in 80% acetonitrile/dichloromethane. Notably, a drastic chelation-enhanced fluorescence quenching (CHEQ) effect is observed upon addition of Cu^{2+} and Hg^{2+} , although a relatively small CHEQ effect ($\sim 15\%$ decrease of the peak intensity) is observed with Ag^+ . The group IA, IIA, and *d*-block transition metal ions (Na^+ , Ba^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+}), however, showed either no or only a small

Figure 1. Crystal structures of (a) **5** and (b) **L**: (left) front views and (right) side views.

influence on the fluorescence intensity. The observed results suggest that **L** is a selective *turn-off* type fluorescence sensor candidate for detecting Hg^{2+} or Cu^{2+} .

Photoluminescence Titrations. In order to probe the origins of the above observed CHEQ effect, the solution behaviors of the complexes of **L** were investigated by photoluminescence titrations of **L** with mercury(II) and copper(II)

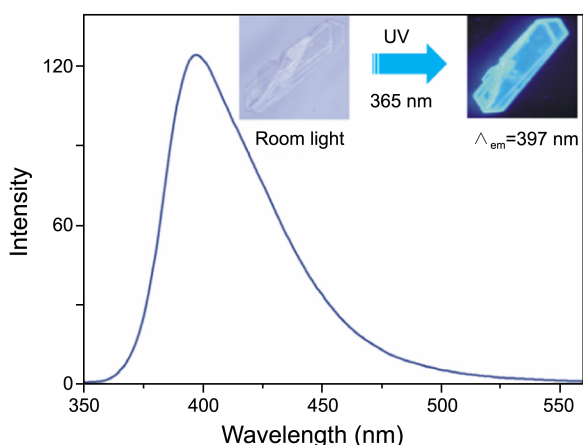


Figure 2. Solid-state photoluminescence spectrum of **L** at room temperature (excitation at 365 nm).

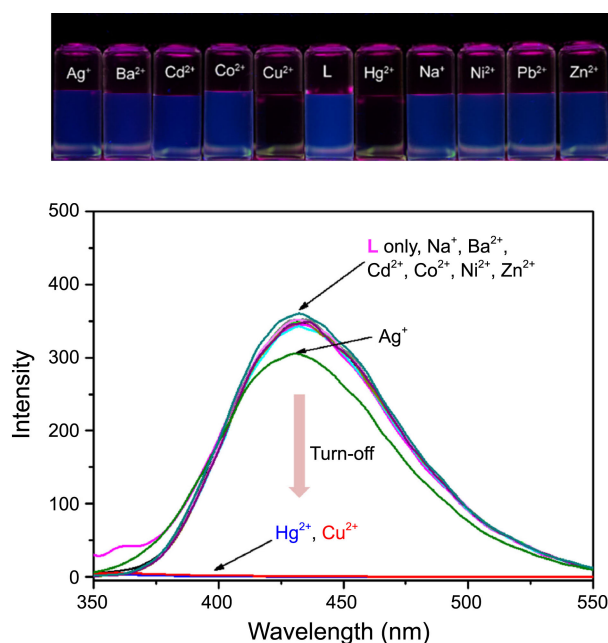


Figure 3. Photoluminescence spectral change of **L** (5.0×10^{-5} M) in the presence of metal perchlorate (10 equiv) in 80% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$.

perchlorates (Figure 4). Upon complexation titrations, the changes of λ_{max} for each metal ion were negligible indicating that none of both metal ions influence the HOMO and LUMO levels of the ligand. The titration plots (insets of Figures 4a and 4b) show that, in the initial addition stage, Cu^{2+} causes a sharper decrease in the fluorescence intensity than that of Hg^{2+} . Overall, the intensity decreases in both cases occur similarly until the addition of 10 equivalents of each metal ion and then the intensity decreases almost to the baseline (*turn-off*). The CHEQ effect can be attributed to an intersystem crossing mechanism due to the heavy atom effect.¹⁴

ESI-Mass Study for Hg(II) Complex. The relationship between structure and properties is the critical issue in functional supramolecular system including the chemosensor

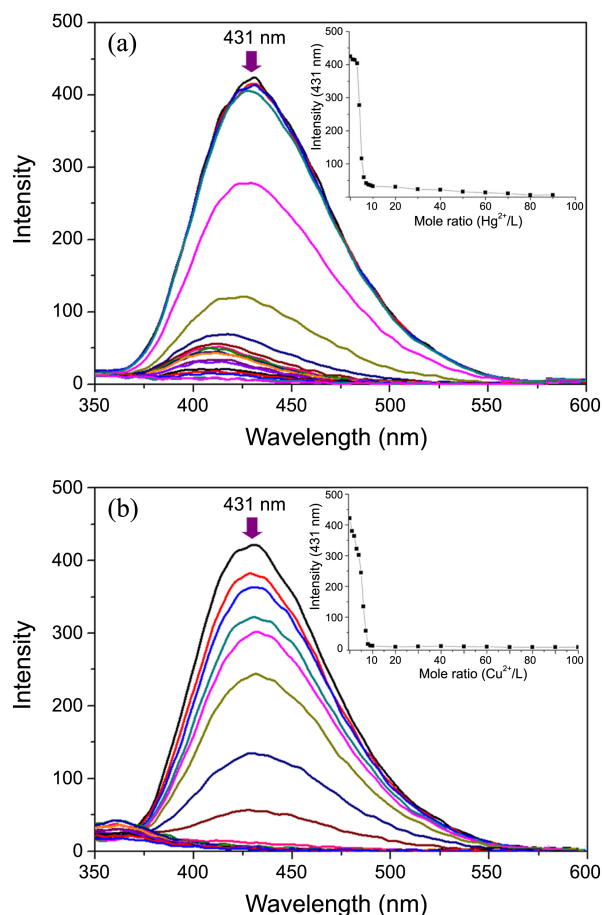


Figure 4. Photoluminescence titrations of **L** (5.0×10^{-5} M) with (a) $\text{Hg}(\text{ClO}_4)_2$ and (b) $\text{Cu}(\text{ClO}_4)_2$ in 80% $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$. Inset: titration curves.

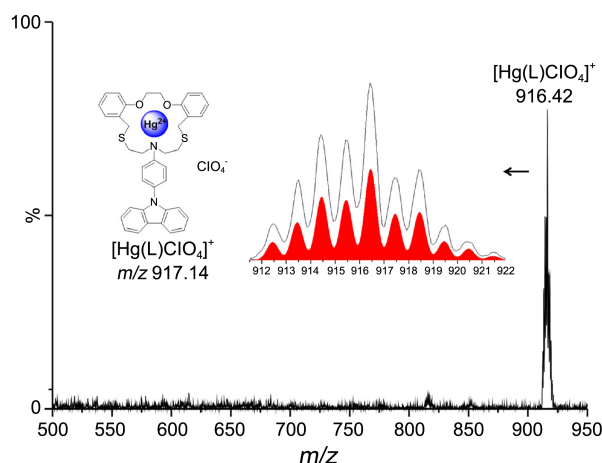


Figure 5. ESI-Mass spectrum of **L** in the presence of $\text{Hg}(\text{ClO}_4)_2$ in acetonitrile.

area. However, our repeated effort to obtain the crystal structures of the corresponding complexes was not successful. Instead, the complexation behavior of the ligand toward Hg^{2+} was further investigated by ESI-mass technique (Figure 5). The observed 1:1 stoichiometry for complexation of **L** with Hg^{2+} was confirmed, which correspond to the species

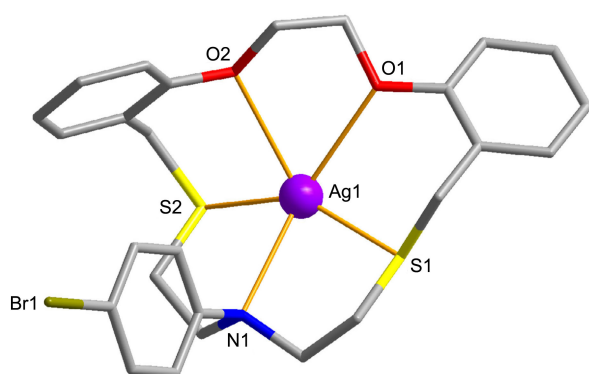


Figure 6. Crystal structure of **6**, [Ag(**5**)]PF₆·2CH₃OH. Non-coordinating anion and solvent molecules are omitted.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for **6**

Ag1-O1	2.767(5)	Ag1-O2	2.818(5)
Ag1-S1	2.459(2)	Ag1-S2	2.443(2)
Ag1-N1	2.759(7)	S1...S2	4.672(3)
S1-Ag1-S2	144.75(7)	S2-Ag1-N1	79.5(1)
S1-Ag1-N1	78.3(1)	S2-Ag1-O1	133.8(1)
S1-Ag1-O1	79.4(1)	N1-Ag1-O1	138.9(2)
S2-Ag1-O2	80.7(1)	S1-Ag1-O2	134.0(1)
N1-Ag1-O2	116.4(2)	O1-Ag1-O2	60.9(2)

[Hg(**L**)ClO₄]⁺ (*m/z* 916.42). This peak is also verified by comparison of the relative abundance of its isotope patterns between the observed peaks and the corresponding theoretical simulation (smaller and red peak in Figure 5). Again, it is noted that the unique behavior of the proposed ligand system can be thus attributed to its selective complexation affinity for Hg²⁺.

Preparation and Crystal Structure of Silver(I) Complex of the Precursor Macrocycle (5). As shown in Figure 1(a), we have characterized the crystal structure of the precursor macrocycle **5**. In extension, single crystals of its Ag⁺ complex **6** were isolated from the reaction of **5** with AgPF₆ in methanol/dichloromethane. X-ray analysis revealed that **6** is a typical endocyclic mononuclear complex of formula [Ag(**5**)]PF₆·2CH₃OH, in which no anion and solvent molecules are presented in the coordination sphere (Figure 6). The selected geometric parameters are presented in Table 2. The Ag atom accommodated in the center of the ring cavity is effectively five-coordinated by NO₂S₂ donors of the macrocyclic ring, in which that macrocycle folds such that an unsymmetrical but apparently favorable cavity is formed. Upon Ag⁺ binding, **5** undergoes considerable conformational rearrangement of sulfur donors from exo- to endo-orientation. Accordingly, the S...S distance in **6** (4.672 Å) is shorter than that in **5** (5.831 Å).

Conclusion

A new macrocyclic fluoroionophore with a 'receptor-

spacer-fluorophore' motif was synthesized and its photo-physical properties were investigated. The proposed fluoro-ionophore shows Hg²⁺ and Cu²⁺ selectivity through a strong CHEQ effect. From the results, it is concluded that the unique selectivity for Hg²⁺ and Cu²⁺ are due to the several cooperative factors, the spacer group contribution and synergic effect of the NO₂S₂ donors with well-preorganized coordination environment of the cyclic receptor.

Acknowledgments. This work was supported by NRF (2010-0022499 and 2011-0011064).

Supporting Information Available. ¹H and ¹³C NMR spectra of compound **5** and **L**. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC 920491(**5**), 920492(**L**), and 920493 (**6**).

References

- (a) Czarnik, A. W. *Fluorescent Chemosensors for Ion and Molecule Recognition*; American Chemical Society: Washington, DC, 1993. (b) Desvergne, J. P.; Czarnik, A. W. *Chemosensors of Ion and Molecular Recognition*; NATO ASI Series; Kluwer: Dordrecht, The Netherlands, 1997. (c) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: New York, 2001.
- (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Hudson, Z. M.; Wang, S. *Acc. Chem. Res.* **2009**, *42*, 1584. (c) Quang, D. T.; Kim, J. S. *Chem. Rev.* **2010**, *110*, 6280.
- (a) Hirano, T.; Kikuchi, K.; Urano, Y.; Higuchi, T.; Nagano, T. *Angew. Chem. Int. Ed.* **2000**, *39*, 1052. (b) Sancenón, F.; Martínez-Máñez, R.; Soto, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 1416. (c) Park, C. S.; Lee, J. Y.; Kang, E.-J.; Lee, J.-E.; Lee, S. S. *Tetrahedron Lett.* **2009**, *50*, 671.
- (a) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (c) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41. (d) Amendola, V.; Rabbizzi, L.; Lincchelli, M.; Mangano, C.; Pallavicini, P.; Parodi, L.; Poggi, A. *Coord. Chem. Rev.* **1999**, *190*, 649.
- (a) Jin, Y.; Yoon, I.; Seo, J.; Lee, J.-E.; Moon, S.-T.; Kim, J.; Han, S. W.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Dalton Trans.* **2005**, 788. (b) Lee, J.-E.; Jin, Y.; Seo, J.; Yoon, I.; Song, M. R.; Lee, S. Y.; Park, K. M.; Lee, S. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 203. (c) Lee, S. J.; Jung, J. H.; Seo, J.; Yoon, I.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Org. Lett.* **2006**, *8*, 1641. (d) Lee, S. J.; Lee, J.-E.; Seo, J.; Jeong, I. Y.; Lee, S. S.; Jung, J. H. *Adv. Funct. Mater.* **2007**, *17*, 3441.
- (a) Grabchev, I.; Chovelon, J.-M.; Bojinov, V. *Polym. Adv. Technol.* **2004**, *15*, 382. (b) Zou, Y.; Wan, M.; Sang, G.; Ye, M.; Li, Y. *Adv. Funct. Mater.* **2008**, *18*, 2724. (c) Güney, O.; Cebeci, F. Ç. *J. Appl. Polym. Sci.* **2010**, *117*, 2373. (d) Danjou, P.-E.; Lyskawa, J.; Delattre, F.; Becuwe, M.; Woisel, P.; Ruellan, S.; Fourmentin, S.; Cazier-Dennin, F. *Sens. Actuators, B* **2012**, *171*, 1022.
- (a) Lee, S. J.; Lee, S. S.; Lee, J. Y.; Jung, J. H. *Chem. Mater.* **2006**, *18*, 4713. (b) Lee, S. J.; Lee, S. S.; Jeong, I. Y.; Lee, J. Y.; Jung, J. H. *Tetrahedron Lett.* **2007**, *48*, 393. (c) Kang, Y.; Moon, S.-T.; Park, S.; Kim, J.; Lee, S. S.; Park, K.-M. *Bull. Korean Chem. Soc.* **2007**, *28*, 873. (d) Lee, H.; Lee, S. S. *Org. Lett.* **2009**, *11*, 1393.
- (a) Lee, Y. H.; Lee, S. S. *J. Incl. Phenom.* **2001**, *39*, 235. (b) Kim, H. J.; Song, M. R.; Lee, S. Y.; Lee, J. Y.; Lee, S. S. *Eur. J. Inorg. Chem.* **2008**, 3532.
- Bruker, *SMART and SAINT, Area Detector Control and Integ-*

- ration Software version 6.22; Bruker AXS Inc.: Madison, WI, 2001.
10. Bruker, *SHELXTL-PC version 6.22: Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc.: Madison, Wisconsin, U.S.A. 2008.
11. Bruker, *SADABS version 6.10: Empirical Absorption and Correction Software*; Bruker AXS Inc.: Madison, Wisconsin, U.S.A. 1999.
12. (a) Gervat, S.; Léonel, E.; Barraud, J.-Y.; Ratovelomanana, V. *Tetrahedron Lett.* **1993**, 34, 2115. (b) Yoon, S.; Albers, A. E.; Wong, A. P.; Chang, C. J. *J. Am. Chem. Soc.* **2005**, 127, 16030. (c) de Groot, B.; Loeb, S. J.; Shimizu, G. K. H. *Inorg. Chem.* **1994**, 33, 2663. (d) Constable, E. C.; King, A. C.; Raithby, P. R. *Polyhedron* **1998**, 17, 4275.
13. (a) Klapars, A.; Antilla, J. C.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, 123, 7727. (b) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc.* **2006**, 128, 4101.
14. (a) Kavarnos, G.; Cole, T.; Scribe, P.; Dalton, J. C.; Turro, N. J. *J. Am. Chem. Soc.* **1971**, 93, 1032. (b) Basu, G.; Kubasik, M.; Anglos, D.; Secor, G.; Kuki, A. *J. Am. Chem. Soc.* **1990**, 112, 9410. (c) Basu, G.; Kubasik, M.; Anglos, D.; Kuki, A. *J. Phys. Chem.* **1993**, 97, 3956. (d) Lee, S. Y.; Park, S.; Kim, H. J.; Jung, J. H.; Lee, S. S. *Inorg. Chem.* **2008**, 47, 1913.
-