A Triple-Probe Channel NO$_2$S$_2$-Macrocycle: Synthesis, Sensing Characteristics and Crystal Structure of Mercury(II) Nitrate Complex

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A triple-probe channel type chemosensor based on an NO$_2$S$_2$-macrocycle functionalized with phenyltricyanovinyl group was synthesized and its sensing characteristics were examined. The pink-red solution of **L** changed selectively to pale yellow upon addition of Hg^{2+}. The selective fluorometric response of **L** to all the tested metal ions was studied. The results showed that a large enhancement of the fluorescence of **L** was observed only in the case of Hg^{2+}. In addition, **L** showed large anodic shift (~ 0.3 V) for the addition of excess Hg^{2+}. Through above three observed results by the different techniques, we confirmed that the proposed chemosensor acts as the multiple-probe channel sensing material. The crystal structure of mercury(II) nitrate complexs of **L** which shows a 1-D polymer network with a formula [Hg$_2$(**L**)$_2$(NO$_3$)$_2$(μ-NO$_3$)$_2$]$_n$ was also reported.

Key Words: NO$_2$S$_2$-Macrocycle, Tricyanovinyl-group, Triple-probe channel, Hg^{2+}-selectivity, Crystal structure

Introduction

One of the most interesting and growing research areas in supramolecular chemistry is related to the management of input/output signals and their relationship with molecular information based on host-guest interactions.[1] Chemosensors have been prepared by coupling binding units (host part) and signaling units for the transduction of the binding event (input signal) into an observable output signal. In chemosensing protocols, color and fluorescence variations together wth an electrochemical signal can be considered as output signals which are related to the presence of certain chemical species as input information. Based on these conditions, three different functional groups have been mainly used as signaling units: fluorescent groups,[2] dyes[3] and redox-active groups.[4] Despite the development of individual chromogenic, fluorogenic and electrochemical sensors, however, there are few examples of the signaling receptors capable of exhibiting two or more output signals, so-called multi-probe channel receptors, upon guest binding.[5] For examples, Martínez-Máñez group[5c] introduced the first triple-channel macrocyclic recptors with NO$_5$ and NO$_2$S$_2$ donor sets by employing tricyanovinyl dye as a singaling unit.

In the view of the host part, a range of mono-, di- and multinuclear complexes of thiaoxa- or thiaoxaaza-macrocycles with supramolecular structures have been reported by us[6-9] and other groups.[10] We reported the synthesis of NO$_2$S$_2$ macrocycles with the dibenzo-subunit[6-9] that show an affinity for Hg^{2+} and bind to this cation in both an exo-[8] or endo-cyclic[9] manner. Therefore, we have been interested in extending these results in the receptor-based approach to develop new chemosensors for thiaphilic heavy metal species such as Ag$^+$ and Hg^{2+}. Based on this consideration, we have investigated the *N*-azo-coupled analogue, which shows Hg^{2+} selectivity; with the color of the Hg^{2+} complex also controlled by the nature of the anion present.[11] More recent-

ly, the synthesis and comparative chromogenic behavior of the *N*-azo-coupled thiaoxaaza-macrocycles incorporating benzene and pyridine subunits are presented.[12] In this case, the benzene derivatives exhibits better Hg^{2+} selectivity and sensitivity than pyridine one because of the coordination of the pyridine nitrogen inhibiting the bond formation between Hg^{2+} and the macrocyclic *tert*-N atom, with the observed induced color being very sensitive to the this effect.

On the other hand, the cyclic and acyclic NO$_2$S$_2$ fluoroionophores with 'receptor-spacer-fluorophore' motif were synthesized, and their photophysical and complexation properties were investigated by us.[13] In this study, the proposed fluoroionophores with cyclic receptor unit exhibited excellent 'TURN-ON' type selectivity toward Ag$^+$ in aqueous media due to the several cooperative factors, such as transduction capacity of anthracene fluorophore, the spacer group contribution and synergic effect of the NS$_2$O$_2$ donors with well-preorganized coordination environment of the cyclic receptor.

As an extension of our previous studies,[11a] we are currently working on the development of multiple-signaling macrocyclic receptors for the selective detection of heavy metal ions. We herein report the synthesis and characterization of an NO$_2$S$_2$ macrocycle **L** containing tricyanovinyl dye,[5c] which shows good selectivity for Hg^{2+} sensing *via* the desired triple-probe channel: the tricyanovinyl unit is a redox-active group and chromo/fluorophore and seemed ideal for incorporation in a multi-probe sensor (Scheme 1).

Results and Discussion

The *N*-phenylated macrocycle **4** was obtained by a coupling reaction of dibenzo-dichloride with the *N*-phenylated dithiol as described by us previously.[11a] The multi-channel probe macrocycle **L** was synthesized as a dark-reddish glassy solid by
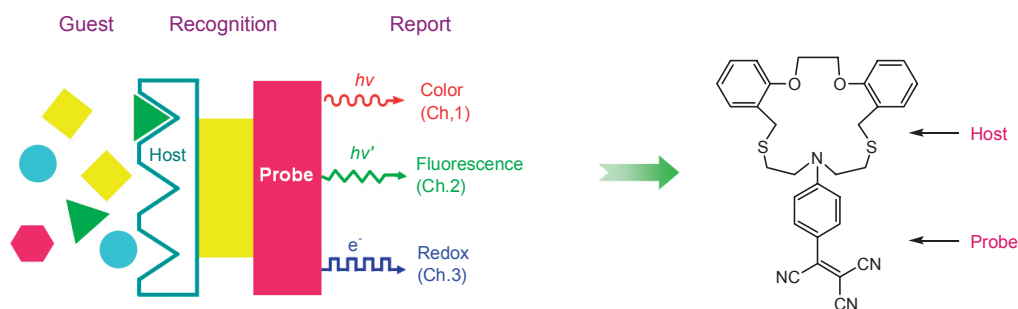
Scheme 1. Principle of the triple-channel probe receptor (left) and proposed macrocyclic receptor **L** in this work (right).
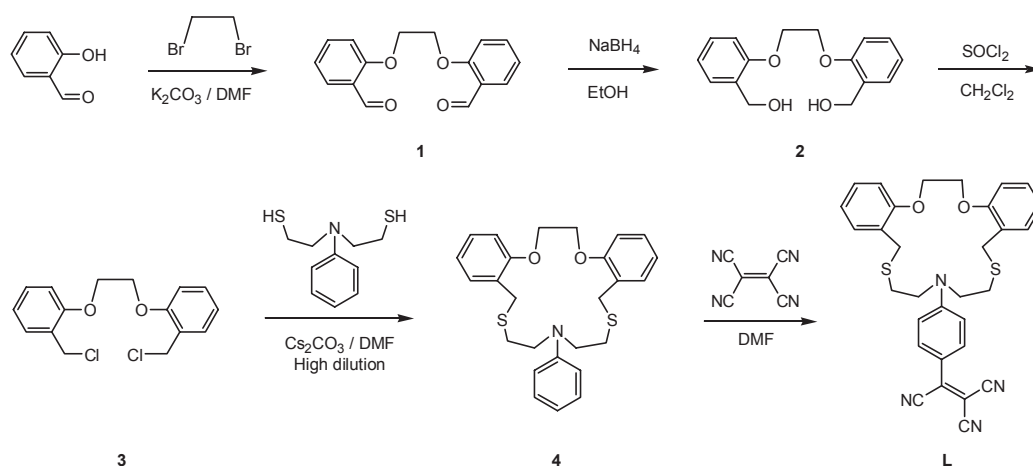
Scheme 2. Synthesis of the multi-channel probe macrocycle **L**.

the reaction of **4** with tetracyanoethylene in warm DMF.

In acetonitrile, the multi-channel probe macrocycle **L** exhibited an intense absorption at 520 nm (pink-red, $\varepsilon_{max} = 32,000$ dm^3 mol^{-1} cm^{-1}) due to a charge transfer process from the donor nitrogen atom of the aniline group to the accepter tricyanovinyl moiety. The metal-induced color changes of the ligand in acetonitrile were investigated by addition of Group I and II (Li$^+$, Na$^+$, K$^+$, and Ba^{2+}) as well as transition and heavy (Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Ag$^+$, Hg^{2+}, Cd^{2+}, and Pb^{2+}) metal ions. Figure 1 shows

the spectral changes of **L** after addition of 5 equiv of the respective metal nitrates. Interestingly, a cation-induced hypochromic shift from 520 nm to 440 nm for Hg^{2+} ($\Delta\lambda = 80$ nm) occurred resulting in a change from a pink-red to pale yellow solution. In contrast, no significant color changes were observed upon addition of the other metal ions listed above.

In order to assess the potential of this chromogenic Hg^{2+} chemosensor for selective colorimetric detection, a UV-vis titration was carried out and the results are shown in Figure 2. Clear
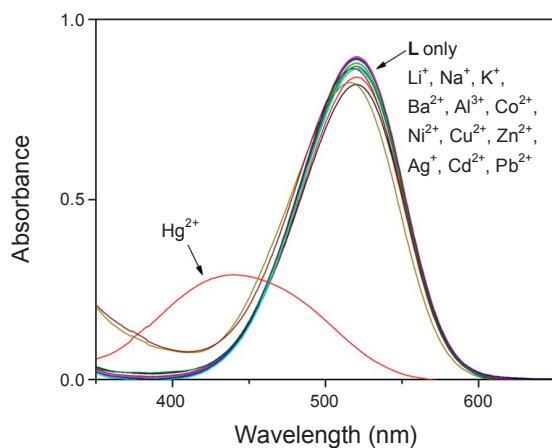

Figure 1. Changes in the UV-vis spectrum of **L** on addition of metal nitrates (ligand concentration: 0.02 mM in CH$_3$CN, added metal ion: 5.0 equiv).
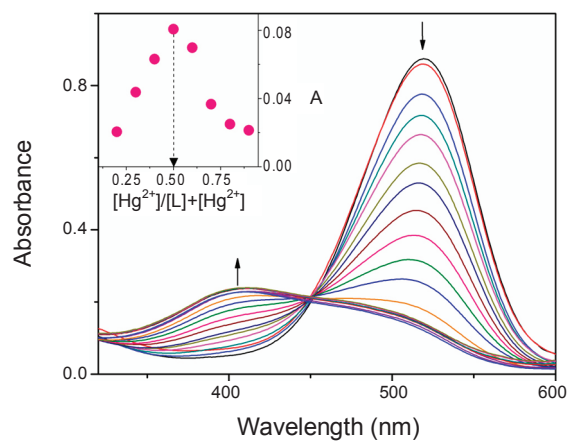

Figure 2. UV-vis titration spectra of **L** (0.050 mM) on stepwise addition of Hg(NO$_3$)$_2$ (0-5.0 equiv) in acetonitrile; (inset) Job plot showing 1:1 (M:**L**) complexation of **L** with Hg^{2+}.
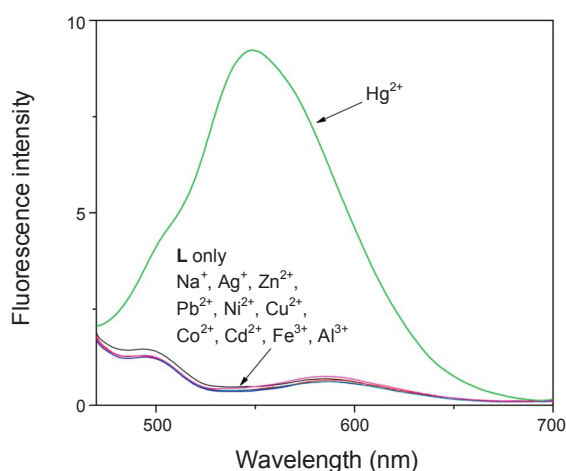
Figure 3. Fluorescence spectra of **L** on addition of metal nitrates (ligand concentration: 0.05 mM in CH_3CN, added metal ion: 5.0 equiv).
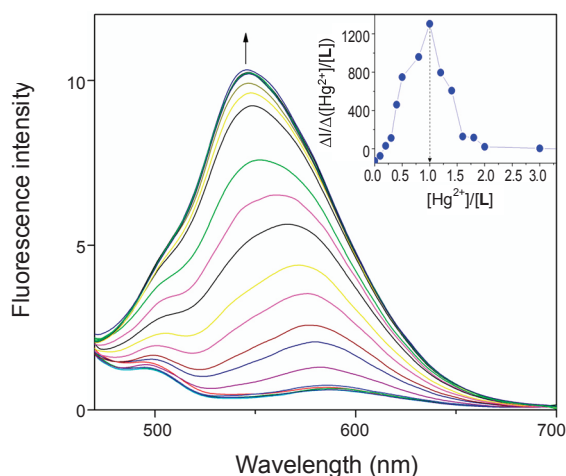

Figure 4. Fluorescence titration spectra of **L** (0.050 mM) on stepwise addition of $Hg(NO_3)_2$ (0 - 3.0 equiv) in acetonitrile; (inset) the first derivative titration plot.
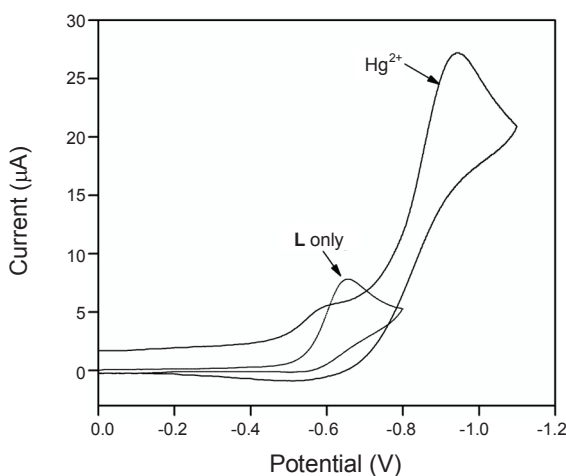

Figure 5. Cyclic voltammograms of **L** and **L**+Hg^{2+} in acetonitrile with Bu_4NPF_6 (0.1M). Scan rate: 50 mVs^{-1}, Working electrode: Pt, Reference elecectrode: Ag/AgCl.
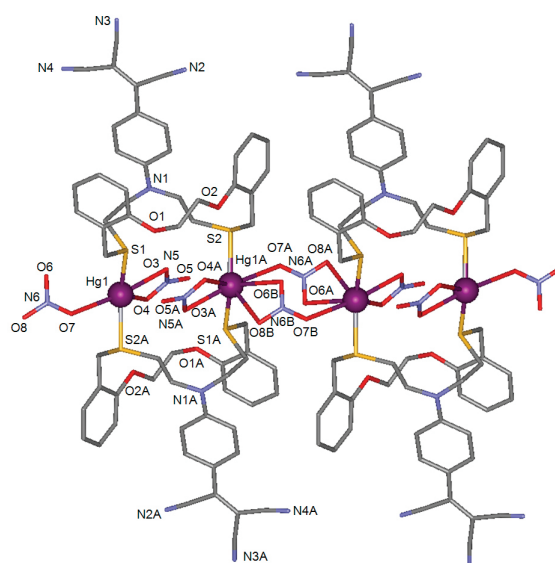

Figure 6. The exo-coordinated 1-D polymer structure $[Hg_2(\mathbf{L})_2(NO_3)_2$ $(\mu_3\text{-}NO_3)_2]_n$ (red color). Hydrogen atoms are omitted for clarity.

complex formation of **L** was observed on titration with Hg^{2+}. The addition of Hg^{2+} causes the ligand absorption (520 nm) gradually to decrease whereas the complex absorption (440 nm) increases to give a clear isosbestic point at 468 nm. The spectral changes in Figure 2 are consistent with 1:1 (M:**L**) binding between ligand and Hg^{2+}. Support of the 1:1 binding ratio was also demonstrated by means of a Job plot experiment (inset in Figure 2). Once again, it should be noted that the unique behavior observed reflects the uniquely selective complexation affinity of **L** for Hg^{2+}.

The binding properties of **L** were also examined with respect to fluorescence. **L** in acetonitrile shows a fluorescence emission band at 550 nm. Changes in the fluorescence emission intensity upon addition of 5 equiv of the corresponding metal ions are shown in Figure 3. **L** is highly selective for Hg^{2+} leading to an enhancement of the emission intensity of 8-fold for this ion. The titration of **L** with Hg^{2+} shows gradual enhancement in fluorescence between 0 - 1.0 equiv of Hg^{2+} and then achieves a plateau (Figure 3). The first derivative titration plot shows 1:1 **L**-Hg^{2+} complexation in solution (inset in Figure 4).

The binding property of **L** was also examined with respect to its redox properties (Figure 5). The electrochemical behavior of the tricyanovinyl receptor was studied in acetonitrile with platinum as working electrode and Bu_4NPF_6 as supporting electrolyte. This family of receptors has been shown to undergo a one-electron reversible reduction process at about −0.65 V *vs*. Ag/AgCl attributed to the reduction of the tricyanovinyl group.[5c,14] There is a remarkable anodic shift of 300 mV of the reduction wave observed for **L** in the presence of Hg^{2+}. This observation suggests the binding of the Hg^{2+} at the NO_2S_2 receptor site of **L** inductively withdraws electronic charge *via* the conjugated bond linkages away from the tricyanovinyl redox-active moiety.

In an extension of the chemosensor studies for **L** in solution, the preparation of its solid complex with a mercury(II) salt and

the structural investigation were undertaken. Red crystals of the complex were obtained after adding a small amount of toluene to a dichloromethane solution of **L** then layering this with a acetonitrile solution of $Hg(NO_3)_2$ and allowing the resulting two phase system to stand. X-ray analysis confirms that the complex has a unique 1-D poly(cyclic dimer) structure with a formula $[Hg_2(\mathbf{L})_2(NO_3)_2(\mu_3\text{-}NO_3)_2]_n$ (Figure 6). The basic cyclic dimer unit contains two bridging Hg atoms and two macrocycles *via* the Hg-S bonds. Each seven-coordinated Hg atom that lies outside the macrocyclic cavity bridges two S atoms from two different macrocycles in a bent fasion. Each cyclic dimer unit is further held together *via* Hg-$(O_2NO)_2$-Hg linkages, leading to the 1-D poly(cyclic dimer) array. Each Hg atom is essentially seven coordinate, being coordinated by two S atoms from two **L**, two nitrato ligands in bidentate manner and one nitrato ligand in monodentate manner. The two Hg-S bond lengths [Hg1-S1 2.456(2)Å, Hg1-S2A 2.453(2) Å] in the complex are comparable to those in other Hg(II) complexes of thiamacrocycles [2.450−2.627 Å].[12-16] The structure unequivocally shows that the bridgehead N_{tert} donor of **L** is not bound to Hg^{2+}. Instead, the Hg^{2+} locates outside the macrocyclic cavity (exo-coordinated), binding to the nitrato ligands. This result can be explained in terms of the strong coordination of the nitrato ligands, acting to prevent Hg-N_{tert} bond formation and, as a consequence no color change was observed.

Conclusion

A multi-channel probe NO_2S_2 macrocycle **L** was obtained by reaction of the *N*-phenylated NS_2O_2-donor macrocyclic precursor with tetracyanoethylene. **L** in acetonitrile showed an intense pink-red color due to a band centered at 520 nm ($\varepsilon = 35,000$ L mol^{-1} cm^{-1}) in its visible spectrum. Interestingly, upon addition of Hg^{2+}, the pink-red solution of **L** changed to pale yellow (with a λ_{max} shift from 520 to 440 nm). The UV-vis titration for this Hg^{2+}-**L** system showed clear formation of a 1:1 ligand-to-metal complex. In a fluorescence study, **L** exhibits a highly selective CHEF effect (8-fold) in the presence of Hg^{2+}. The fluorescence titration for the Hg^{2+}-**L** system also showed the formation of a 1:1 ligand-to-metal complex. In a redox study, **L** gave a reversible one-electron reduction wave at −0.65 V *vs* Ag/AgCl, which can be ascribed to the reduction of the cyanovinyl group. A remarkably large anodic shift of 300 mV was found in the presence of Hg^{2+}. The mercury(II) nitrate complex of **L** was prepared and structurally characterized by the X-ray anlaysis. The structure of the Hg(II) nitrate complex (red) reveals that strong coordination of the nitrate anion to the Hg(II) center prevents the Hg-N_{tert} bond formation, as a consequence no color change was observed.

Experimental Section

General methods. All commercial reagents including solvents were of analytical reagent grade where available. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) and the mass spectra were obtained on a JEOL JMS-700 spectrometer at the Central Laboratory of Gyeongsang National University, respectively. The UV-vis absorption spec-

Table 1. Crystal data and structure refinement of $[Hg_2(\mathbf{L})_2(NO_3)_2(\mu_3\text{-}NO_3)_2]_n$

Formula	$C_{62}H_{58}\,Hg_2N_{12}O_{17}S_4$
Formula weight	1772.62
T/K	173(2)
Crystal system	Triclinic
Space group	*P*-1
a/Å	8.7334(8)
b/Å	10.5673(9)
c/Å	19.3996(16)
α/°	102.169(2)
β/°	97.112(2)
γ/°	102.565(2)
V/Å^3	1681.0(3)
Z	1
D_{calc} (g/cm^3)	1.751
μ/mm^{-1}	4.763
F(000)	874
Crystal size/mm	$0.20 \times 0.10 \times 0.10$
Reflection collected	9565
Independent reflections	6463 [R(int) = 0.0487]
Completeness to theta	97.9
Data / Restrains / Parameters	6463 / 18 / 451
Goodness-of-fit on F^2	1.054
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, w$R_2 = 0.0887$
R indices (all data)	$R_1 = 0.0959$, w$R_2 = 0.1195$

Table 2. Selected bond lengths(Å), bond angles(°) and torsion angles(°) for $[Hg_2(\mathbf{L})_2(NO_3)_2(\mu_3\text{-}NO_3)_2]_n$

Hg1-S1	2.456(2)	Hg1-S2A	2.453(2)
Hg1-O3	2.734(9)	Hg1-O4	2.624(9)
Hg1-O7	2.798(8)	Hg1A-O6B	2.774(8)
Hg1A-O8B	2.824(9)		
S1-Hg1-S2A	149.1(1)	S2 -Hg1A- O6B	86.9(2)
S1-Hg1-O3	80.3(2)	S2 -Hg1A- O8B	117.3(3)
S1-Hg1A-O4	112.3(2)	S2A -Hg1- O3	91.3(2)
S1-Hg1A-O7	75.3(2)	S2A -Hg1- O4	80.3(3)
S1A-Hg1A-O6B	84.3(3)	S2A -Hg1- O7	91.3(2)
S1A-Hg1A-O8B	122.5(3)	O3-Hg1-O4	45.9(3)
O3-Hg1-O7	141.9(3)	O4-Hg1-O7	171.6(3)
O3A-Hg1A-O6B	129.9(3)	O3A-Hg1A-O8B	127.5(3)
O4A-Hg1A-O6B	138.6(3)	O4A-Hg1A-O8B	161.4(4)
O7B-Hg1A-O8B	19.1(3)	O6B-Hg1A-O7B	36.77(2)
O6B-Hg1A-O8B	26.0(2)		

Symmetry operation: A) $-x + 1$, $-y + 2$, $-z + 2$. B) $-x + 3$, $y + 1/2$, $-z + 2$.

tra were recorded either with a Varian Cary 5E or Scinco S-3100 spectrophotometer. Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer. Melting points are uncorrected.

Synthesis of multi-channel probe macrocycle (L). *N*-Phenyl macrocycle **4** and tetracyanoethylene were dissolved in dry DMF and heated at 60 °C for 90 min. The crude reaction mixture was concentrated in vacuo to dryness and purified by column chromatography on silica with dichloromethane as eluent to give **L** as a reddish solid. Yield: 65%. mp 120-121 °C. ^{1}H-

NMR (300 MHz, CDCl$_3$) δ 2.62 (t, 4H, SC*H₂*CH$_2$), 3.72 (t, 4H, NCH$_2$), 3.83 (s, 4H, ArCH$_2$), 4.37 (s, 4H, CH$_2$O), δ 7.93-6.47 (m, 12H, Ar). IR (KBr, cm^{-1}) 3424, 2923, 2641, 2356, 2213, 1602, 1500, 1450, 1410, 1339, 1185, 941, 753. HRMS (*m/z*) calcd. For C$_{31}$H$_{28}$N$_4$O$_2$S$_2$: 552.1654; found: 552.1654.

Preparation of mercury(II) nitrate complex. An acetonitrile solution (3 mL) of the required Hg(II) nitrate (41.6 mmol) was layered above a dichloromathane solution (3 mL) of **L** (20 mg, 41.6 mmol). On standing for a week at room temperature crystalline complexes suitable for X-ray analysis were obtained.

Hg(II) complex. [Hg$_2$(**L**)$_2$(NO$_3$)$_2$(μ-NO$_3$)$_2$]$_n$ mp 189 - 190 °C. IR (KBr, cm^{-1}) 3421, 1601, 1514, 1452, 1385 (s, NO$_3^-$), 1339, 1244, 1132, 1105, 955, 858, 756. FAB-mass (*m/z*) 816 ([Hg (**L**)NO$_3$]$^+$).

Crystallograpy. A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 6463 frames of two-dimensional diffraction images were collected, each of which was measured for 20 sec. The frame data were processed to give structure factors by the program SAINT.[15] The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL,[16] and refined using a full matrix least square against F^2 for all data. All the non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1.

Supplementary Material. Supplementary crystallographic data associated to **L** has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 768491. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically *via* www.ccdc.cam.ac.uk/data_request/cif

References

1. Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Lehn, J.-M., Eds.; *Comprehensive Supramolecular Chemistry*; Pergamon/ Elsevier: Oxford, UK, 1996; Vol. 1, pp 635-669.
2. (a) Czarnik, A. W., Ed.; *Fluorescent Chemosensors for Ion and Molecule Recognition*; American Chemical Society: Washington, D.C., 1992. (b) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41.
3. (a) Dix, J. P.; Vögtle, F. *Chem. Ber.* **1980**, *113*, 457. (b) *Chemosensors for Ion and Molecular Recognition*; Desvergne, J. P., Czarnik, A. W., Eds.; Kluwer: Dordrecht, 1997. (c) Sancenón, F.; Martínez-Máñez, R.; Soto, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1416.
4. (a) Beer, P. D.; Cadman, J. *Coord. Chem. Rev.* **2000**, *205*, 131. (b) Lloris, J. M.; Martínez-Máñez, R.; Pardo, T.; Soto, J.; Padilla-Tosta, M. E. *J. Chem. Soc., Dalton Trans.* **1998**, 2635.
5. (a) Boiocchi, M.; Fabbrizzi, L.; Licchelli, M.; Sacchi, D.; Vázquez, M.; Zampa, C. *Chem. Commun.* **2003**, 1812. (b) Caballero, A.; Martínez- Máñez, R.; Lloveras, V.; Ratera, I.; Vidal-Gancedo, J.; Wurst, K.; Tárraga, A.; Molina, P.; Veciana, J. *J. Am. Chem. Soc.* **2005**, *127*, 15666. (c) Jiménez, D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J. *Tetrahedron Lett.* **2004**, *45*, 1257.
6. (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) Yoon, I.; Seo, J.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Choi, K. S.; Jung, O.-S.; Park, K.-M.; Lee, S. S. *Dalton Trans.* **2005**, 2352.
7. (a) Yoon, I.; Seo, J.; Lee, J.-E.; Park, K.-M.; Kim, J. S.; Lah, M. S.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 3487. (b) Seo, J.; Song, M. R.; Lee, J.-E.; Lee, S. Y.; Yoon, I.; Park, K.-M.; Kim, J.; Jung, J. H.; Park, S. B.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 952.
8. (a) Lee, S. Y.; Park, S.; Kim, H. J.; Jung, J. H.; Lee, S. S. *Inorg. Chem.* **2008**, *47*, 1913. (b) Sultana, K. F.; Lee, S. Y.; Lee, J. Y.; Park, K.-M.; Lee, S. S. *Bull. Korean Chem. Soc.* **2008**, *29*, 241. (c) 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.
9. (a) Seo, J.; Lee, S. S.; Gong, W.-T.; Hiratani, K. *Tetrahedron Lett.* **2008**, *49*, 3770. (b) Choi, K. S.; Kang, D.; Lee, J.-E.; Seo, J.; Lee, S. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 747.
10. (a) Janzen, D. E.; Mahne, L. F.; VanDerveer, D. G.; Grant, G. *J. Inorg. Chem.* **2005**, *44*, 8182. (b) Vetrichelvan, M.; Lai, Y.-H.; Mok, K. F. *Eur. J. Inorg. Chem.* **2004**, 2086. (c) Contu, F.; Dermartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Salis, A.; Verani, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4401. (d) Watzky, M. A.; Waknine, D.; Heeg, M. J.; Endicott, J. F.; Ochrymowyzc, L. A. *Inorg. Chem.* **1993**, *32*, 4882. (e) Blake, A. J.; Halcrow, M. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2803.
11. (a) Lee, S. J.; Jung, J. H.; Seo, J.; Yoon, I.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Org. Lett.* **2006**, *8*, 1641. (b) Lee, H. G.; Lee, J.-E.; Choi, K. S. *Inorg. Chem. Commun.* **2006**, *9*, 582.
12. Lee, H.; Lee, S. S. *Org. Lett.* **2009**, *11*, 1393.
13. Park, C. S.; Lee, J. Y.; Kang, E.-J.; Lee, J.-E.; Lee, S. S. *Tetrahedron Lett.* **2009**, *50*, 671.
14. Raposo, M. M. M.; Sousa, A. M. R. C.; Kirsch, G.; Ferreira, F.; Belsley, M.; de M.Gomes, E.; Maurício A.; Fonseca, C. *Tetrahedron* **2005**, *61*, 11991.
15. Bruker, SMART and SAINT: *Area Detector Control and Integration Software Ver. 5.0*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.
16. Bruker, SHELXTL: *Structure Determination Programs Ver. 5.16*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.