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Cation-Selective and Anion-Controlled Fluorogenic Behaviors of a Benzothiazole-Attached Macrocycle That Correlate with Structural Coordination Modes

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S Supporting Information

ABSTRACT: We report how the metal cation and its counteranions cooperate in the complexation-based macrocyclic chemosensor to monitor the target metal ion via the specific coordination modes. The benzothiazolyl group bearing NO₂S₂-macrocycle L was synthesized, and its mercury(II) selectivity (for perchlorate salt) as a dual-probe channel (UV–vis and fluorescence) chemosensor exhibiting the largest blue shift and the fluorescence turn-off was observed. In the mercury(II) sensing with different anions, except ClO₄⁻ and NO₃⁻, no responses for mercury(II) were observed with other anions such as Cl⁻, Br⁻, I⁻, SCN⁻, OAc⁻, and SO₄²⁻. A crystallographic approach for the



mononuclear mercury(II) perchlorate complex $[Hg(L)(ClO_4)_2] \cdot 0.67 CH_2 Cl_2$ (1) and polymeric mercury(II) iodide complex $[Hg(L)I_2]_n$ (2) revealed that the observed anion-controlled mercury(II) sensing in the fluorescence mainly stems from the endoand exocoordination modes, depending on the anion coordinating ability, which induces either the Hg-N_{tert} bond formation or not. The detailed complexation process with mercury(II) perchlorate associated with the cation sensing was also monitored with the titration methods by UV-vis, fluorescence spectroscopy, and cold-spray ionization mass spectrometry.

INTRODUCTION

Synthetic receptors for sensing toxic heavy metal ions have been of widespread interest due to the environmental and clinical importance.¹ Thus, many efforts have been devoted to design and construction of the photophysical chemosensors for detecting mercury(II),² lead(II),³ and cadmium(II).⁴ In the category of sensor molecules, dye-attached macrocycles⁵ represent a promising research area, not only in terms of their chromo- or fluorophoric function but also because of their high selectivity for the metal ions of interest, including mercury(II) and other heavy metal species. In particular, some sulfur-containing mixed donor macrocycles have been proposed as excellent mercury(II) selective hosts.⁶

Martínez-Máñez and co-workers⁷ have introduced a phenoxazinone-attached azaoxathia-macrocyclic mercury(II) chemosensor that can be used in the parts per billion level by using either absorption or emission spectroscopy. With the similar parent host, our group has reported several N-azo-coupled chromogenic macrocycles whose mercury(II) selectivity is controlled by anions.^{8,9} However, benzothiazole is an important bicyclic ring system with multiple applications in the biological and luminescent materials. For example, it is known to exhibit a wide range of biological properties including

anticancer and antimicrobial activities.^{10a} In addition, benzothiazole derivatives¹⁰ and their complexes¹¹ have been studied as excellent luminescent materials because of the heterocyclic binding site, generating UV–vis and fluorescent signals as a dual-channel probe.

In this work, we propose a benzothiazole-attached NO_2S_2 macrocycle L and are currently working on its synthesis for the detection of heavy metal ions. In particular, we have undertaken a structure–function relationship as an extension of the anion dependency on the mercury(II) sensing,⁸ with emphasis on the fluorescence-modulation, because no examples of the fluorescence sensor showing the cation-selective and anioncontrolled behaviors have been reported so far. Therefore, as depicted in Chart 1, we assumed that the expected mercury(II) selectivity might be controlled by its anions, and such phenomena are strongly associated with the structures of the respective complexes generated when the events occur.

To examine the proposed hypothesis, we decided to reveal the molecular-level structures of the related species in the solid state that exhibit the anion-controlled functions. We herein



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report the synthesis of the N-benzothiazolyl group attached NO₂S₂-macrocycle L and an in-depth study demonstrating the anion-controlled mercury(II) sensing both in the UV–vis and fluorescence channels. This is the first systematic study of the anion effect on the fluorescence on–off behaviors via structure–function relationship based on the single-crystal X-ray analysis.

RESULTS AND DISCUSSION

Synthesis of Chemosensor L. Three-step reactions involving the coupling cyclization led to the synthesis of the target macrocycle L (Scheme 1). The key macrocyclic precursor 3 was prepared by the coupling cyclization between dichloride 4 and corresponding dithiol as described previously.¹² The target macrocycle L was obtained from the reaction of 3 with 2-aminobenzenthiol in 40% yield.

Crystal Structure of L. The structure of L was also characterized in the solid state by single-crystal X-ray crystallography (Figure 1 and Table S1). Colorless single crystals of L were prepared by slow evaporation of its dichloromethane solution. In the crystal structure, the macrocycle unit adopts a slightly twisted conformation in which two oxygen donors are oriented in an endodentate fashion with a gauche arrangement, while two sulfur donors are positioned exodentate with respect to the ring cavity. The S1 \cdots S2 distance is 7.56 Å, and the macrocyclic ring is flattened with the two torsion angles between S and N donors (S1-C-C-N1-

Scheme 1. Synthesis of L



Figure 1. Crystal structure of L. Displacement ellipsoids were drawn at 30% probability level, and H atoms were omitted for clarity.

 173.2° and $S2-C-C-N1-160.6^{\circ}$), indicating a propensity for each linkage to adopt an anti–anti conformation.

Photophysical Properties of L. The macrocyclic chemosensor L exhibits an intense absorption and fluorescence properties in solution state. As shown in Figure 2a, L presents the absorption and emission spectra in acetonitrile, showing an absorption maximum at 358 nm (pale yellow, $\varepsilon_{max} = 57\ 100$ $M^{-1}\ cm^{-1}$) and a strong emission band centered at 416 nm as a characteristic emission band for the benzothiazole unit.¹³ The absolute quantum yield for L in acetonitrile was determined to be $\Phi = 0.83\ (5.0 \times 10^{-4}\ M\ at 365\ nm)$. As shown in Figure 2b, the single crystals of L exhibit a broad band with weak blue emission maxima at 425 and 450 nm ($\lambda_{ex} = 365\ nm$) arising from the intramolecular charge transfer.^{7,14}

Selectivity for Metal lons. The metal-sensing abilities of L were examined with several metal ions (Ag⁺, Hg²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺) by UV–vis and fluorescence spectroscopy in acetonitrile with respect to the cation-induced spectral changes. Considering the solubility and the influences of counteranions, which are described in the latter part, metal perchlorates were used. Addition of mercury(II) (5.0 equiv) to the solution of L provided noticeable changes in the absorption (Figure 3a) and emission (Figure 3b) spectra. In the UV–vis experiments, for instance, the mercury(II) induced the largest blue shift from 358 nm (27 933 cm⁻¹) to 308 nm (32 468 cm⁻¹) [$\Delta \lambda_{max} = 50$ nm (4535 cm⁻¹)] with the decrease of absorption intensity, changing its solution color from pale yellow to colorless.

In the fluorescence study, L is also highly selective for mercury(II) leading to a drastic change from bright (on) to dark (off) in the emission intensity centered at 416 nm (Figure 3b), while no significant fluorescence spectral changes were observed upon addition of the other metal ions. These observed results in the both ways are quite different from those obtained with other mercury(II) sensor molecules that



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Figure 2. (a) Absorption and fluorescence spectra of L in acetonitrile ($[L] = 1.5 \times 10^{-5} \text{ M}$) and (b) solid-state photoluminescence spectrum of L.



Figure 3. (a) UV-vis and (b) fluorescence spectra of L in the presence of metal perchlorates (5.0 equiv) in acetonitrile ($[L] = 1.5 \times 10^{-5} M$).



Figure 4. (a) UV-vis and (b) fluorescence titrations of L ($[L] = 1.5 \times 10^{-5}$ M) with mercury(II) perchlorate (0-3.0 equiv) in acetonitrile. (insets) Titration curves.

have usually been affected by silver(I) and other heavy metal ions. 15

UV-vis and Fluorescence Titrations. In an attempt to probe the origins of the above photophysical changes related to the mercury(II) selectivity, the characteristics of the mercury(II) complexes were investigated. Since L has multiple binding sites, its mercury(II) complexes could exist in different stoichiometric combinations in solution. So, the interaction of L with mercury(II) perchlorate in acetonitrile was examined by means of UV-vis and fluorescence titrations.

According to the UV-vis titration in Figure 4a, there are three distinct regions of the titration curve. In the region 1 (up to 0.5 equiv), the absorption at 358 nm shows no significant changes, suggesting the formation of a 1:2 (metal-to-ligand)

complex that has no spectral difference with the free L. In the region 2 (between 0.5 and 2.0 equiv), the ligand peak gradually decreased, whereas the absorption for the complexed species gradually increased showing an isosbestic point at 335 nm until 1.0 equiv. After this no more free ligand peak exists, and the complex peak shifts toward shorter wavelength (308 nm), most likely indicating the formation of a 1:1 species and its gradual conversion to a 2:1 species. In the region 3 (after 2.0 equiv), the absorption at 308 nm corresponding to the complexed species shows no significant changes, indicating the stable formation of the 2:1 species, and no other species with higher stoichiometry are formed.

As shown in Figure 4b, the fluorescence titration of L with mercury(II) perchlorate demonstrates the cation-induced

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quenching behaviors, and the unusual shape of the titration curve also suggests the coexistence of more than one complexed species in solution. Upon addition of mercury(II), the peak intensity at 416 nm shows no significant changes until 0.5 equiv. In the range of 0.5-2.0 equiv, the fluorescence intensity of L gradually decreases without peak shift. Above the 2.0 equiv, no longer emissions were observed, indicating the formation of the nonemissive product. The observed fluorescence titration curve also reflects the stepwise equilibria involving the complexed species with 1:2, 1:1, and 2:1 stoichiometries.

Comparative Cold-Spray Ionization Mass Spectrometry. Cold-spray ionization (CSI) mass spectrometry is effective for detection of the labile supramolecules in solution.¹⁶ So the CSI mass experiments were performed by varying the mercury(II) content (0–2.5 equiv) in the presence of L, and the formation of the complexes with different stoichiometries were confirmed (Figure 5). The mass spectrum of the free



Figure 5. CSI-mass spectra of L $(5.0 \times 10^{-4} \text{ M})$ in the presence of different mole ratios of mercury(II) perchlorate in acetonitrile: (a) 0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, and (f) 2.5 equiv.

ligand L shows the presence of some univalent monomer and dimer ligand species due to the protonation or interactions with the abundant alkali metal ions (Figure 5a). The mass spectra of L with 0.5 equiv (Figure 5b) and 1.0 equiv (Figure 5c) of mercury(II) were dominated by peaks for the 1:1 complexes (Hg^{2+}/L) such as $[HgL(CH_3CN)(OH)]^+$, $[HgL(ClO_4)]^+$, and $[HgL(CH_3CN)(H_2O)(ClO_4)]^+$. Additions of 1.5 to 2.5 equiv of mercury(II) led to a new set of peaks in accord with the formation of the 2:1 species such as $[Hg_2L(ClO_4)(OH)]^{2+}$ and $[Hg_2L(ClO_4)_2(OH)]^+$ (Figure 5d-f). Once again, this observation suggests that L forms 1:2 (HgL₂), 1:1 (HgL), and 2:1 (Hg₂L) complexes and that these species coexist with different composition depending on the mole ratios (Figure 6a).

The Equilibria of the Hg²⁺ Complexation. As observed from the experiments by UV-vis, fluorescence spectroscopy, and CSI mass spectrometry, the complexation equilibria between mercury(II) and L could not be described using one or two species binding model. Therefore, the fitting of the UVvis titration data to determine the stability constants of the mercury(II) complexation was performed with HyperSpec software¹⁷ by employing the multiple binding model including 1:2, 1:1, and 2:1 ratios (Figure 6a), and a good fit of the data was obtained (Figure 6b). In the distribution curves for the complexation equilibria shown in Figure 6a, the HgL₂ content is predominant around 0.5 equiv of mercury(II). Around 1.0 equiv, similar amounts of the three complexed species coexist, and when the mercury(II) is in excess, the data are consistent with the formation of a Hg₂L species, presumably involving two mercury(II) binding to one L. As listed in Table 1, the fitting yields the log K values of 7.21 \pm 0.03 (log K_{11}), 13.14 \pm 0.06 $(\log K_{12})$, and 14.06 ± 0.03 $(\log K_{21})$ between L and Hg(II). The proposed complexation process for these Hg₂L, HgL, and HgL_2 species together with the stepwise log K values between two species are given in Scheme 2.

Anion Effect on the Mercury(II) Sensing. While investigating the metal-sensing and the related complexation equilibria for L discussed above, a spectral dependence on the anion employed was observed. In this work, we found that the observed mercury(II) selectivity of L as the UV-vis probe was effective in ClO_4^- or NO_3^- anion system: for instance, the blue shift from 358 nm $(27\,933 \text{ cm}^{-1})$ to 308 nm $(32\,468 \text{ cm}^{-1})$ $[\Delta \lambda_{\text{max}} = 50 \text{ nm } (4535 \text{ cm}^{-1})]$ for perchlorate ion or to 320 nm $(31\,250 \text{ cm}^{-1}) [\Delta \lambda_{\text{max}} = 30 \text{ nm} (3317 \text{ cm}^{-1})]$ for nitrate ion were observed (Figure 7a). However, no significant spectral changes were observed for the other anions. In the fluorescence study for the anion effect on the mercury(II) sensing, addition of mercury(II) perchlorate or nitrate to the solution of L displays the cation binding interaction with L, leading to the drastic fluorescence quenching (Figure 7b). However, the addition of mercury(II) salts with the other anions such as Cl⁻, Br⁻, I⁻, OAc⁻, SCN⁻, or SO₄²⁻ shows no responses to the mercury(II), leading to almost no spectral change. Consequently, no anions gave a meaningful quenching except ClO_4^{-} or NO_3^{-} in the fluorescence experiments.

Crystallographic Study on the Mercury(II) Complexes. As mentioned above, the observed anion-controlled behaviors in both probes (UV–vis and fluorescence) are assumed to be associated with the structures of the respective complexes generated in the corresponding solution state. Previously, we reported the anion-controlled endo/exocyclic coordination behaviors of the silver(I) complexes with S₂O₃-macrocycle in the solid state.¹⁸

To gain further insight for the complexation-based and anion-controlled mercury(II)-sensing fluorescence, we thus decided to reveal the crystal structures of the related complex species because no anion-controlled cation-sensing fluorescence system has been reported so far. On complexation of L with mercury(II) salts, it was possible to isolate a perchlorate complex 1 and an iodo complex 2 from the nonemissive and emissive solutions, respectively, as single crystals suitable for Xray analysis.

The X-ray analysis revealed that the perchlorate complex 1 is a mononuclear species with the formula of $[Hg(L)(ClO_4)_2]$. 0.67CH₂Cl₂ (Figure 8 and Table S2). In the asymmetric unit of 1, three crystallographically different mononuclear species exist, but their structures and coordination environments are not

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Figure 6. Fitting of UV-vis titration data to determine the stability constants of the mercury(II)-L complexation with HyperSpec software by employing the multiple binding model including 1:2, 1:1, and 2:1 ratios: (a) species distribution diagram for L and its mercury(II) complexes as a function of the mole ratio (Hg²⁺/L) and (b) HyperSpec output (\Box : experimental points, solid line: theoretical fit).

Table 1. Stability Constants for the Complexations of L with Mercury(II) Perchlorate in Acetonitrile^{*a*}

reactions	products	stability constants		PL switching
$Hg^{2+} + 2 L$	HgL ₂	log K ₁₂	13.14 ± 0.06	on
$Hg^{2+} + L$	HgL	$\log K_{11}$	7.21 ± 0.03	weak
$2 \text{ Hg}^{2+} + L$	Hg_2L	$\log K_{21}$	14.06 ± 0.03	off
^a UV-vis titration method at 25 °C using the HyperSpec software. ¹⁷				

Scheme 2. Proposed Complexation Process of L and Related Fluorescence Behaviors



significantly different (Figures S1 and S2). Above all, each Hg(II) atom in 1 resides inside the macrocyclic cavity to form a 1:1 (metal-to-ligand) stoichiometric complex. For example, the endocyclic Hg1 atom in 1 is seven-coordinate being bound to all donors from the macrocycle in a bent conformation adopting a "tight" conformation. The coordination sphere is completed by two perchlorate O atoms (O3 and O9). The coordination geometry can be best described as a distorted pentagonal bipyramid (Figure 8b). The Hg1-S bond distances [Hg1-S1 2.423(2), Hg1-S2 2.422(2) Å] in 1 are typical. Those of Hg1-O_{ether} bonds [Hg1-O1 2.660(6), Hg1-O2 2.580(6) Å] are also within the normal literature range.¹⁹ And two monodentate perchlorate ions show different Hg1-O_{perchlorate} bond strengths [Hg1-O3 2.593(6), Hg1-O9 3.161(6) Å]. Notably, the Hg–N_{tert} bond distance [Hg1–N1 2.671(6) Å] in 1 falls into the longer end of the normal range (2.02-2.74 Å).²⁰ The preferred endocyclic coordination of the complex 1 is mainly due to the relatively weak coordination affinity of ClO₄⁻ toward the metal center. From this result, it is found that the Hg-N_{tert} bond formation by the endocoordination reflects the mercury(II) sensing via the fluorescent quenching in the presence of ClO_4^- as shown in Figure 7b. The details for the structure-function relationship for the anioncontrolled mercury(II) sensing from the crystal structures with different anions are discussed in the later part.

On reaction with HgI_2 , L forms a pale yellow crystalline product 2. Unlike the endocyclic mononuclear perchlorato



Figure 7. Hg²⁺-induced (a) UV-vis and (b) fluorescence spectral changes of L by varying anions in acetonitrile ($[L] = 1.5 \times 10^{-5}$ M; added mercury(II) salt, 5.0 equiv).



Figure 8. Crystal structure of the mercury(II) perchlorate complex $[Hg(L)(ClO_4)_2] \cdot 0.67CH_2Cl_2$ (1): (a) an endocyclic mononuclear structure showing an Hg1–N1 bond [2.671(6) Å] and (b) a distorted octahedral coordination environment of Hg1 atom. Noncoordinated solvent molecule is omitted. Displacement ellipsoids were drawn at 30% probability level, and H atoms were omitted for clarity.



Figure 9. Crystal structure of the mercury(II) iodide complex $[Hg(L)I_2]_n$ (2): (a) basic coordination unit showing the Hg atom bound from outside the macrocyclic cavity (exocoordination mode) and no interaction between Hg atom and N_{tert} donor (Hg1…N1 5.38 Å) and (b) 1D polymeric chain structure of **2.** Displacement ellipsoids were drawn at 30% probability level, and H atoms were omitted for clarity.

complex 1, this iodo complex 2 adopts a one-dimensional (1D) polymeric arrangement with the formula of $[Hg(L)I_2]_n$ (Figure 9 and Table S3). Asymmetric unit of 2 contains one mercury(II) atom and two iodide ions. Notably, the Hg1 atom in 2 is outside the macrocyclic cavity in a tetrahedral arrangement and links macrocycles via Hg-S bonds [Hg1-S1 2.780(1), Hg1-S2A 2.802(1) Å] forming an "L-Hg-L-Hg" zigzag 1D pattern. The exocyclic Hg1 atom in 2 is fourcoordinate, being bound by two S donors from different macrocycles, and the coordination sites are completed by two terminal iodide atoms. Accordingly, the distance between exocyclic Hg1 atom and N1 atom in 2 is 5.38 Å, which means no interaction and much longer than that of the endocyclic Hg1-N1 distance [2.671(6) Å] in 1. Unlike 1, the preferred exocyclic coordination in the iodo complex 2 is mainly due to the stronger affinity of the iodide ion with soft base nature toward the soft mercury(II) center. Clearly, this situation appears in the solution state as shown in Figure 7 where the inactive mercury(II) sensing in the presence of iodide ion and other anions with the stronger coordination affinity occurs.

Role of Anions in the Mercury(II) Fluorescence Sensing and the Structure–Function Relationship. As mentioned, the perchlorato complex 1 is an endocyclic species in which the central Hg atom is seven-coordinate, being bound to all five donors in the macrocycle including the regular Hg– N_{tert} bond. The coordination environment in 1 is completed by two perchlorate O atoms via the weak Hg–O bond. In marked contrast to the endocoordination mode in the perchlorato complex 1, the iodo complex 2 shows a 1D chain polymeric structure via the exocoordination. The preferred exocyclic structure in 2 is mainly due to the strong coordination of Γ ion, which inhibits the metal ion from locating inside the cavity. Instead the exocoordination mode induces the bond formation of the S1–Hg1–S2A linkage between two adjacent macrocycles outside the cavity, leaving the N_{tert} atom, which regulates the fluorescence uncoordinated (Hg1…N_{tert} 5.38 Å). This result could be the evidence for the no fluorescence change from free L upon addition of the mercury(II) salts shown in Figure 7b and Scheme 3. The comparison of the coordination modes between the endotype in 1 and the exotype in 2 supports the understanding of the anion-controlled cation-sensing system by showing the structure–function relation.

In the back-titration experiments, the evidence for the proposed anion-controlled cation sensing was also observed. For example, after mercury(II) perchlorate was added (0-3 equiv) to L, then iodide (0-3 equiv), as tetramethylammonium salt) was titrated. Because of the solubility problem of tetramethylammonium iodide, a mixture of methanol/acetoni-trile (1:1) was used as a solvent. In this case, the decreased absorption for free L (360 nm) by mercury(II) perchlorate sharply increased, and finally its absorption intensity was recovered by excess amount of the titrated iodide ion (Figure S3). In the fluorescence (Figure S4), similar to the UV-vis results, the mercury(II) perchlorate-induced quenching (430 nm) was recovered by excess amount of the titrated iodide ion. The observed back-titration results also reflect the anion-



controlled cation-sensing behaviors. In addition, the titrations of L in the presence of iodide (5 equiv, as tetramethylammonium salt) were also performed both in absorption and emission modes (Figures S5 and S6). The titrated mercury(II) perchlorate to the solution of L containing an excess amount (5 equiv) of iodide ion showed no absorption decrease or fluorescence quenching. Once again, these results suggest that the iodide acts as a strong coordinating anion, which inhibits the endocyclic coordination of the mercury(II) with the macrocycle L.

Consequently, it was found that the $Hg-N_{tert}$ bond formation is controlled by the anions that push the metal ion inside the cavity to allow the bond formation when the anion coordinating ability is weaker. Oppositely, the anions with the stronger coordinating ability tend to pull out the metal ion outside the cavity to inhibit the $Hg-N_{tert}$ bond formation.

CONCLUSION

The proposed benzothiazolyl group bearing NO₂S₂-macrocycle L showed the mercury(II) selectivity as a dual-probe channel (UV-vis and fluorescence) chemosensor, but its sensing behaviors work only in the presence of ClO₄⁻ or NO₃⁻. To understand the observed anion-controlled mercury(II)-sensing, especially in the fluorescence, we assumed that it requires the structural information in the solid state. This approach enabled us to isolate the single crystals from the corresponding solutions of the mixtures of L and mercury(II) salts with different anions. In the crystal structures, the perchlorato complex 1 and the iodo complex 2 showed very distinct structures mainly due to the coordination modes, specifically, the endocoordinated complex 1 with the discrete form and the exocoordinated complex 2 with the continuous form. The observed solid structures clearly support the structure-function hypothesis because the anion-controlled fluorescence phenomena mainly stem from the complexation via either the Hg-N_{tert} bond formation or not. In another word, the less coordinating $\text{ClO}_4^{\ -}$ allows the mercury(II) engage the N_{tert} lone pair and thereby results in the direct Hg–N_{tert} bonding in the endocyclic fashion, leading the fluorescence quenching (from ON to OFF), while the stronger coordinating I^- , which participates in the coordination sphere, induces the metal ion outside the cavity showing no influence to the fluorescence change because of no interaction between mercury(II) and N_{tert} atom. This

result can also be explained by the covalent character of the bonds between mercury(II) and some nucleophilic anions (halides including I^-) that show higher affinity to the metal center. The present study corresponds to the first systematic work on the relationship between the structure and the fluorescence change for the macrocyclic receptor.

EXPERIMENTAL SECTION

General. All chemicals and solvents employed in the syntheses were of reagent grade and were used without further purification. Mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. CSI mass spectra were measured on a JEOL AccuTOF (JMS-T100CS) mass spectrometer with ESI ion source. NMR spectra were recorded on a Bruker DRX 300 spectrometer. FT-IR spectra were measured with a ThermoFisher Scientific Nicolet *is* 10 FT-IR spectrometer. The elemental analysis was performed on a Thermo-Fisher Scientific Flash 2000 elemental analyzer. *Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.*

Synthesis and Characterization of L. The mixed ethanol (96%) solution (200 mL) of 3 (2.3 g, 6.47 mmol), 2-aminobenzenethiol (1.1 g, 8.79 mmol), and a drop of acetic acid was refluxed with stirring for 12 h. After the reaction, the mixture was first concentrated, and 250 mL of water was added. The solution was extracted with CH₂Cl₂. The extract was dried over NaSO4, and solvent was evaporated in vacuo. The residue was purified with recrystallization using *n*-hexane, which led to the isolation of L as a crystalline product in a 40% yield. mp 127 °C. IR (KBr pellet): 2882, 1605, 1527, 1477, 1426, 1353, 1281, 1183, 1129, 1102, 1075, 821, 763, and 732 cm⁻¹. Anal. Calcd for C23H28N2O2S3: C, 59.97; H, 6.13; N, 6.08; S, 20.88. Found: C, 59.73; H, 6.12; N, 6.05; S, 20.84%. ¹H NMR (300 MHz, CDCl₃, δ, see Figure S7a, Supporting Information): 7.98 (d, J = 8.3 Hz, 1H, Ar), 7.94 (d, J = 8.9 Hz, 2H, Ar), 7.84 (d, J = 7.9 Hz, 1H, Ar), 7.43 (dd, J = 8.3 Hz, 1H, Ar), 7.30 (dd, J = 7.1 Hz, 1H, Ar), 6.69 (d, J = 8.9 Hz, 2H, Ar), 3.82 (t, J = 5.1 Hz, 4H, SCH₂CH₂N), 3.71 (t, J = 8.1 Hz, 4H, OCH₂CH₂S), 3.65 (s, 4H, OCH₂CH₂O), 2.93 (t, J = 8.1 Hz, 4H, OCH_2CH_2S), 2.77 (t, J = 5.1 Hz, 4H, SCH_2CH_2N). ¹³C NMR (75 MHz, CDCl₃) 168.5, 154.4, 149.1, 134.6, 129.2, 126.0, 124.2, 122.3, 121.6, 121.4, 111.6, 74.3, 70.7, 51.9, 31.3, 29.5. CSI-mass spectrum m/ *z*: 461.08064 [L+H]⁺.

Preparation of 1, [Hg(L)(ClO₄)₂]·0.67CH₂Cl₂. Mercury(II) perchlorate hydrate (11.0 mg, 0.022 mmol) in acetone (2 mL) was added to a solution of L (10.0 mg, 0.022 mmol) in dichloromethane (2 mL). The solution was stirred at room temperature. A fine powder, which precipitated from the solution, was filtered off. Slow evaporation of the solution afforded a pale yellow crystalline product 1 suitable for X-ray analysis. For the elemental analysis and melting point measurement, the sample was dried under vacuum (70 °C, 12 h). mp 162 °C. IR (KBr pellet): 2989, 2946, 2875, 1605, 1480, 1457, 1437, 1412, 1314, 1172, 1116, 1037, 1022, 917, 762, 727, and 621 cm⁻¹. Anal. Calcd for C₂₃H₂₈N₂O₁₀S₃HgCl₂: C, 32.12; H, 3.28; N, 3.26; S, 11.18 Found: C, 32.10; H, 3.25; N, 3.05; S, 11.53%.

Preparation of 2, [Hg(L)I₂]_n. Mercury(II) iodide (9.9 mg, 0.022 mmol) in acetone (2 mL) was added to a solution of L (10.0 mg, 0.022 mmol) in chloroform (2 mL). The solution was stirred at room temperature. Slow evaporation of the solution afforded a pale yellow crystalline product 2 suitable for X-ray analysis. mp 164 °C. IR (KBr pellet): 2888, 2855, 1604, 1557, 1526, 1477, 1427, 1390, 1342, 1232, 1191, 1099, 1004, 963, 816, 754, and 724 cm⁻¹. Anal. Calcd for $C_{23}H_{28}HgI_2N_2O_2S_3$: C, 30.19; H, 3.08; N, 3.06; S, 10.51 Found: C, 30.02; H, 3.02; N, 2.84; S, 10.63%.

Crystallographic Structure Determinations. All data were collected on a Bruker Smart Apex2 Ultra diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. Data collection, data reduction, and semiempirical absorption correction were performed using the software package APEX2.²¹ All of the calculations for the structure determination were performed using the SHELXTL package.²² Relevant crystal data collection and refinement data for the crystal structures are

summarized in Table S1. CCDC reference numbers 1457993 (L), 1457994 (1), and 1457995 (2).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00690.

Crystal data, geometric parameters, crystal structures, and titration data. (PDF)

X-ray crystallographic information. (CIF)

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Notes

The authors declare no competing financial interest.

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