

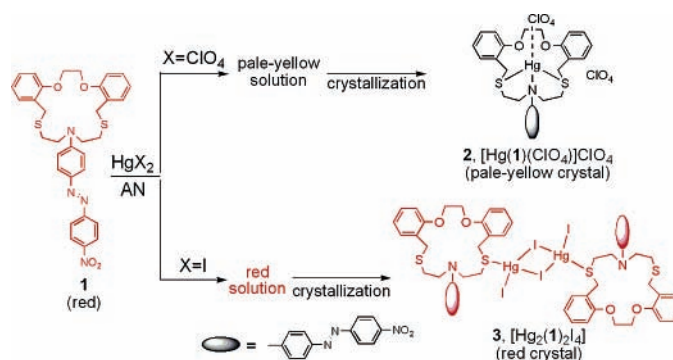
A Chromogenic Macrocycle Exhibiting Cation-Selective and Anion-Controlled Color Change: An Approach to Understanding Structure–Color Relationships

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ABSTRACT



A *N*-azo-coupled macrocycle (1) with a NO₂S₂ donor set was synthesized as a chromiophore and shown to exhibit Hg²⁺ selectivity; anion control of the color of the Hg²⁺ complex was observed. As a first approach, the nature of the color generation process was probed by determining the crystal structures of the two different colored species obtained with perchlorate and iodide anions. The results can be explained in terms of a “Push-n-Pull Process”, which serves to illustrate how the coordinating ability of the anion controls the color change through formation of endo- or exo-metal complexes. The use of “simple” salts to induce color-switching of the above complex species was also reported.

Chromogenic receptors as chemosensors are especially attractive because guest determination can be carried out without the use of instrumentation.^{1–5} Such systems are basically composed of two parts: binding (*recognition*) and

color-changing (*signaling*) units which are covalently linked. *N*-azo-coupled macrocycles,^{1,3,6} the prototypical type in this

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(1) (a) Dix, J. P.; Vögtle, F. *Chem. Ber.* **1980**, *113*, 457. (b) Dix, J. P.; Vögtle, F. *Chem. Ber.* **1981**, *114*, 638.

(2) (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721. (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. (c) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **2001**, *40*, 3118.

(3) Sancenón, F.; Martínez-Máñez, R.; Soto, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1416.

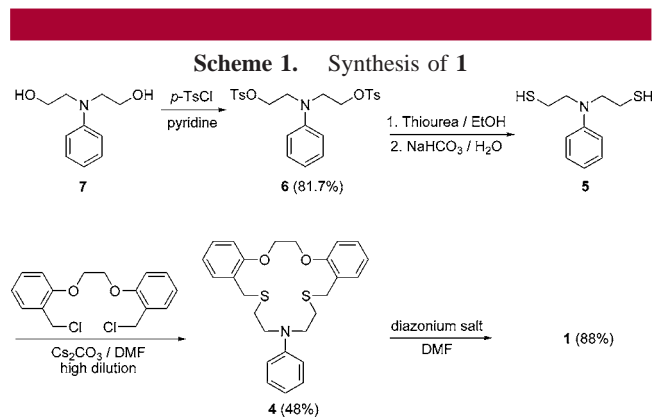
(4) (a) Inoue, Y.; Liu, Y.; Hakushi, T. In *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Dekker: New York, 1990; Chapter 1. (b) Descalzo, A. B.; Martínez-Máñez, R.; Radeglia, R.; Rurack, K.; Soto, J. *J. Am. Chem. Soc.* **2003**, *125*, 3418. (c) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499. (d) Lee, J. Y.; Kim, S. K.; Jung, J. H.; Kim, J. S. *J. Org. Chem.* **2005**, *70*, 1463.

(5) (a) Sancenón, F.; Descalzo, A. B.; Martínez-Máñez, R.; Miranda, M. A.; Soto, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2640. (b) Kim Y.-H.; Hong, J.-I. *Angew. Chem., Int. Ed.* **2002**, *41*, 2947. (c) Lee, D. H.; Im, J. H.; Son, S. U.; Chung, Y. K.; Hong, J.-I. *J. Am. Chem. Soc.* **2003**, *125*, 7752.

category, have been extensively investigated for the detection of cations,^{2,3} anions,^{4,5} and organic species.^{2b,5c} In this category of chromophore, photoexcitation causes a net electronic charge transfer from the donor end (bridgehead nitrogen) to the acceptor end within the chromophore. However, contrary to our expectation, neither the preparation nor crystal structure of an *N*-azo-coupled macrocyclic complex has been reported previously in relation to their chromophoric function. Further, the complexity of such chromophoric systems frequently results in the co-occurrence of multiple phenomena, some of which may involve both cations and anions.^{3,6}

We recently reported two NO₂S₂ macrocycles⁷ showing affinity for Hg²⁺, with the latter being bound in an exo-⁸ or endo-coordination manner. More recently, we synthesized the *N*-azo-coupled analogue **1**, which shows Hg²⁺ selectivity; the color of the Hg²⁺ complex is controlled by anions as outlined in the Abstract. This result prompted a structure–function analysis in terms of the use of **1** for sensing. From this approach, we were able to elucidate the nature of the color-generation process. As a first approach, the latter was probed in two ways. The crystal structures of the two different colored species were obtained and simple salt-induced color-switching in solution was investigated.

Ligand **1** (see Abstract) was synthesized by the reaction of the diazonium salt of *p*-nitroaniline with the *N*-phenylated macrocycle **4** (Schemes 1 and S1 (Supporting Information)).



First, the binding properties of **1** were examined with respect to color changes (Figure 1a). Species **1** exhibits an intense absorption at 480 nm (red, ϵ 29 700). Interestingly, the large cation-induced hypochromic shift for Hg²⁺ ($\Delta\lambda$ = 133 nm) and Cu²⁺ or Fe³⁺ ($\Delta\lambda$ = 74 nm) (all as nitrates) resulted in

(6) Kim, J. S.; Shon, O. J.; Lee, J. K.; Lee, S. H.; Kim, J. Y.; Park, K.-M.; Lee, S. S. *J. Org. Chem.* **2002**, *67*, 1372.

(7) 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.

(8) (a) Hill, S. E.; Feller, D. *J. Phys. Chem. A* **2000**, *104*, 652. (b) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328. (c) 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. (d) Park, K.-M.; Yoon, I.; Seo, J.; Lee, J.-E.; Kim, J.; Choi, K. S.; Jung, O.-S.; Lee, S. S. *Cryst. Growth Des.* **2005**, *5*, 1707. (e) Seo, J.; Yoon, I.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Park, S. H.; Kim, T. H.; Park, K.-M.; Kim, B. G.; Lee, S. S. *Inorg. Chem. Commun.* **2005**, *8*, 916.

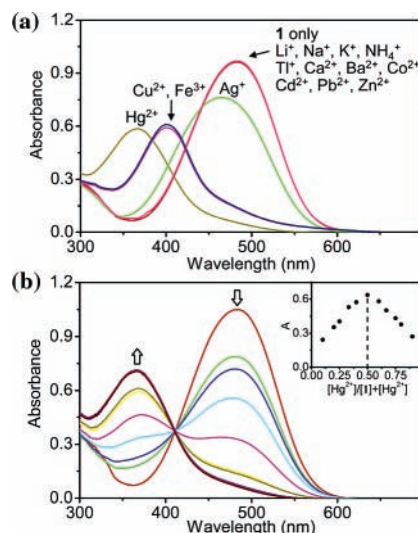


Figure 1. (a) UV/vis spectra of **1** (0.30 mM) in the presence of metal nitrates (5.0 equiv) in acetonitrile and (b) UV/vis titrations of **1** (0.30 mM) with Hg(NO₃)₂ (0–5.0 equiv) in acetonitrile; (inset) Job's plot.

a change from red to pale-yellow (Figures 1a and S1 (Supporting Information)), whereas no significant color change was observed upon addition of other selected metal ions. The titration of **1** with Hg(NO₃)₂ resulted in the 480 nm absorption gradually decreasing whereas the 368 nm absorption gradually increased to give an isosbestic point at 407 nm (Figure 1b). In addition, a 1:1 (**1** to Hg²⁺) stoichiometry for complexation was demonstrated by means of a Job's plot. From the titration data the log *K* values for the (1:1) complexes were calculated to be 6.02, 5.12, and 5.08 for Hg²⁺, Cu²⁺, and Fe³⁺, respectively (Figures S2 and S3, Supporting Information). Thus **1** forms its strongest complex with Hg²⁺ among the metal ions investigated.

More interestingly, we found that the color change for **1** with Hg²⁺ may change with the anion. For instance, the addition of NO₃[−] or ClO₄[−] resulted in hypochromic shifts to 367 and 350 nm (pale-yellow), respectively (Figures 2 and S4 (Supporting Information)). However, no color changes were observed upon addition of Cl[−], Br[−], I[−], CH₃COO[−], SCN[−], or SO₄^{2−}. This is attributed to the

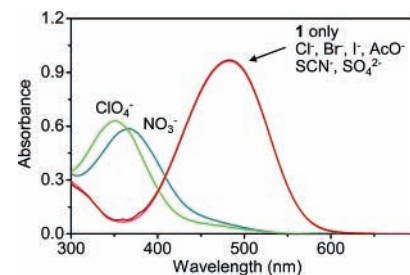


Figure 2. Anion-dependent shift in the spectrum of **1** for mercury(II) salts in acetonitrile.

significant coordinating ability of these latter anions to the Hg^{2+} ion. The results indicate that **1** cannot only be useful as an efficient chromogenic reagent for cation sensing, but it also shows promise as a reagent for ClO_4^- and NO_3^- sensing in the presence of a range of other anions.

The behavior observed undoubtedly reflects the structures of the respective complexes generated. Thus, we decided to undertake the preparation and crystal structure of each colored species. We have successfully isolated pale-yellow (**2**) and red (**3**) complexes as single crystals suitable for X-ray analysis from solutions of **1** with $\text{Hg}(\text{ClO}_4)_2$ and HgI_2 , respectively.

The crystal structure of pale-yellow **2** revealed a 1:1 complex of formula $[\text{Hg}(\mathbf{1})_2(\text{ClO}_4)]\text{ClO}_4$ (Figure 3). Hg^{2+} is

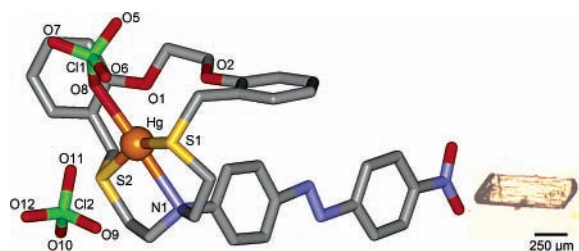
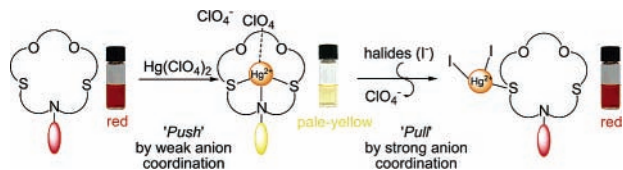


Figure 3. Endo-coordinated structure of **2**, $[\text{Hg}(\mathbf{1})(\text{ClO}_4)]\text{ClO}_4$ (pale-yellow crystals).

in a square planar environment with its coordination sites occupied by two S and one N atom from **1** arranged in an endo-fashion. One ClO_4^- is weakly bound to Hg^{2+} at a fourth binding site while the other is not coordinated. The presence of direct $\text{Hg}-\text{N}$ [2.672(11) Å] bond formation appears to be reflected by the color change to pale-yellow. That is, it suggests that the presence of the less coordinating ClO_4^- allows (“Push”, see Scheme 2) the Hg^{2+} to engage the N

Scheme 2. Push-n-Pull Process of Anion-Induced Color Change



lone pair and thereby results in direct $\text{Hg}-\text{N}$ bonding in the endo-mode, resulting in the observed color change. This also agrees with the results from the UV/vis experiments.

X-ray analysis of **3** confirms that this red product has a dimeric structure with a formula of $[\text{Hg}_2(\mathbf{1})_2\text{I}_4]$ (Figure 4). The structure contains a rhomboidal $\text{Hg}-\text{I}_2-\text{Hg}$ core bridging two macrocycles through $\text{Hg}-\text{S}$ bonds. The Hg^{2+} is four-coordinated with one S and three I^- in an exo-fashion. It unequivocally shows that the N donor of **1** is not bound to Hg^{2+} , and hence the Hg^{2+} is located outside of the cavity.

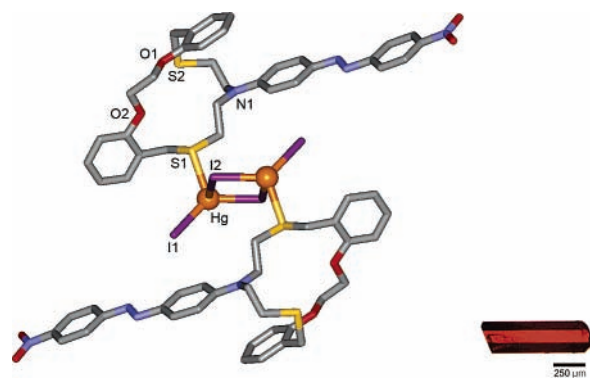
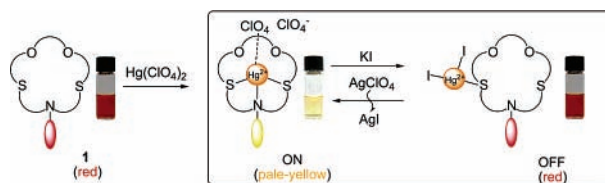


Figure 4. Exo-coordinated dimer structure of **3**, $[\text{Hg}_2(\mathbf{1})_2\text{I}_4]$ (red crystals).

This result can be explained in terms of the strong coordination (“Pull”, see Scheme 2) of the iodides acting to prevent $\text{Hg}-\text{N}$ bond formation, resulting in no color change. Once again, the “Push-n-Pull Process” serves to illustrate how the coordinating ability of anions can control the color change through formation of endo- or exo-metal complexes.

On the basis of the crystal structures of **2** and **3**, we anticipated that the anion-induced color change might also be switchable by the addition of simple salts. In fact, the pale-yellow solution of **1** in the presence of $\text{Hg}(\text{ClO}_4)_2$ returns to its original red color upon addition of KI or NaCl (Scheme 3). A reversible color change from red to pale-yellow occurs

Scheme 3. Color-Switching of **1** by Addition of Salts in Acetonitrile



on addition of AgClO_4 (a precipitate of AgI is formed). Such phenomena correspond to “ON–OFF” switching of the chromogenic system driven by the Push-n-Pull process illustrated and involve simple addition of the chosen cation and anion pair.

In this study, conclusive evidence for cation-selective and anion-controlled color changes for the *N*-azo-coupled host system **1** are presented. The investigation corresponds to the first systematic study of the relationship between structure and color change for chromogenic host molecules.

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Supporting Information Available: Syntheses of **1**, **2** and **3**; UV/vis titrations, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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