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3 nm-Scale Molecular Switching between Fluorescent Coordination Capsule and Nonfluorescent Cage

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The reversible arrangement of molecular building blocks in self-assembled architectures is a key to the growth strategy for structural and functional molecular switching systems.[1] In metal-assembled systems, a change in coordination number and geometry of metal centers can be triggered by external stimuli, and thereby dynamic structural switching of the entities would take place in association with a notable change in their chemical and physical properties.[2,3] Herein we describe a novel molecular switching system using 3 nm-sized Hg^{2+}-mediated coordination capsules that are formed from trismonodentate ligands **1** and Hg^{2+} ions in a self-assembled manner. In this system, a capsule-shaped, fluorescent $Hg_6\mathbf{1}_8$ complex and a cage-shaped, nonfluorescent $Hg_6\mathbf{1}_4$ complex are quantitatively formed and structurally switchable in response to the Hg^{2+}/**1** ratios in solution (Figure 1). The repeatable interconversion between the two distinct complexes is accompanied by the reversible changes in the coordination mode of Hg^{2+} ion between an octahedral and a linear coordination geometries.

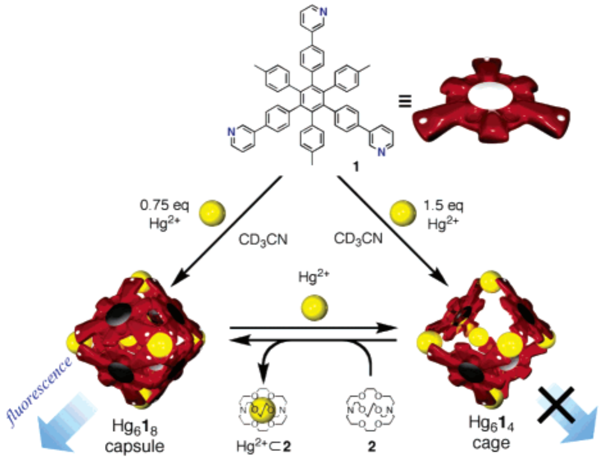

Figure 1. Schematic representation of the quantitative and reversible structural interconversion between a fluorescent $Hg_6\mathbf{1}_8$ capsule complex and a nonfluorescent $Hg_6\mathbf{1}_4$ cage complex formed from trismonodentate ligands **1** and Hg^{2+} ions.

Recently, we reported the isostructural formation of $M_6\mathbf{1}_8$ complexes from ten kinds of divalent d^5-d^{10} metal ions (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), and the tightly packed capsule-shaped structure of $Hg_6\mathbf{1}_8$ complex was determined by ^1H NMR, ESI-TOF mass, and X-ray analyses.[4] In this study, further ^1H NMR study revealed that the $Hg_6\mathbf{1}_8$ capsule complex can be quantitatively converted into an alternative cage-shaped complex, $Hg_6\mathbf{1}_4$.

Specifically, the signals of methyl protons (H_i) and two of the *p*-tolyl protons (H_h) of $Hg_6\mathbf{1}_8$ showed upfield shift compared with those of ligand **1** ($\Delta\delta = -1.3$ ppm for H_i, and -0.8 and -0.4 ppm for H_{h1} and H_{h2}, respectively) (Figure 2a,b), indicating the shielding effects from the neighboring aromatic ligands tightly packed in a capsule-shaped structure of $Hg_6\mathbf{1}_8$ in solution. Upon further addition of Hg^{2+} ions to the solution of $Hg_6\mathbf{1}_8$ in CD_3CN, a new set of signals appeared in its ^1H NMR spectrum with highly symmetrical patterns,[5] and when the Hg^{2+}/**1** ratio reached 3:2, the signals of $Hg_6\mathbf{1}_8$ complex completely disappeared (Figure 2c). The ESI-TOF mass spectrum of a mixed solution of $Hg(OTf)_2$ and **1** (3:2) showed signals at *m*/*z* 1095.9, 1407.4, and 1926.2 assignable to $[Hg_6\mathbf{1}_4\cdot(OTf)_7]^{5+}$, $[Hg_6\mathbf{1}_4\cdot(OTf)_8]^{4+}$, and $[Hg_6\mathbf{1}_4\cdot(OTf)_9]^{3+}$, respectively, without any signals arising from $Hg_6\mathbf{1}_8$ complex.[6] These results demonstrate $Hg_6\mathbf{1}_4$ complex is quantitatively formed in solution when the Hg^{2+}/**1** ratio is 3:2. UV titration experiments also supported the quantitative formation of $Hg_6\mathbf{1}_8$ and $Hg_6\mathbf{1}_4$ complexes in response to the Hg^{2+}/**1** ratios.[6]

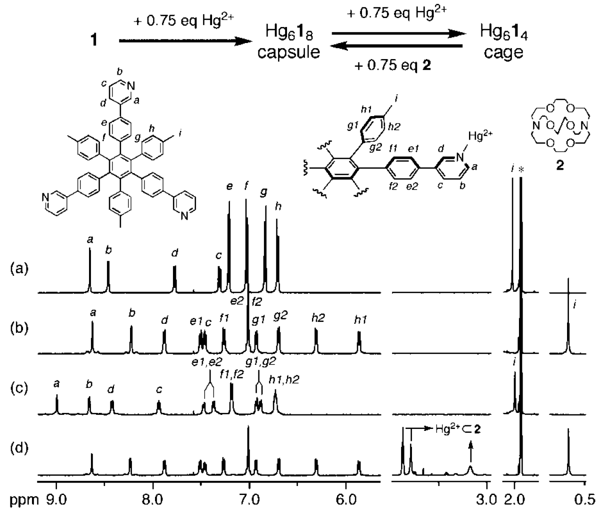

Figure 2. ^1H NMR spectra (500 MHz, CD_3CN, 293 K): (a) ligand **1** only ([**1**] = 4.2 mM), (b) $Hg_6\mathbf{1}_8$ capsule ($[Hg^{2+}]$ = 3.1 mM, [**1**] = 4.2 mM, $[Hg^{2+}]$/[**1**] = 3:4), (c) $Hg_6\mathbf{1}_4$ cage ($[Hg^{2+}]$ = 6.3 mM, [**1**] = 4.2 mM, $[Hg^{2+}]$/[**1**] = 3:2), (d) after addition of cryptand **2** (0.75 equiv) to the sample of trace c; signals with an asterisk (*) represent residual peaks of CD_3CN.

The ^1H NMR spectrum of $Hg_6\mathbf{1}_4$ showed eight doublets for aromatic protons of *p*-tolyl and *p*-phenylene groups, as observed with $Hg_6\mathbf{1}_8$, suggesting that the disk-shaped ligand **1** should face the internal and external areas of the metal-assembled cagelike molecule. However, upfield chemical shifts observed for some of the protons of $Hg_6\mathbf{1}_8$ were no longer observed with $Hg_6\mathbf{1}_4$. This result suggests a remarkable change in the Hg^{2+} complex from a densely closed to a partly closed structure. Diffusion-ordered NMR spectroscopy (DOSY)[7] of this newly generated $Hg_6\mathbf{1}_4$ complex in CD_3CN showed a set of signals with a diffusion coefficient of 3.9

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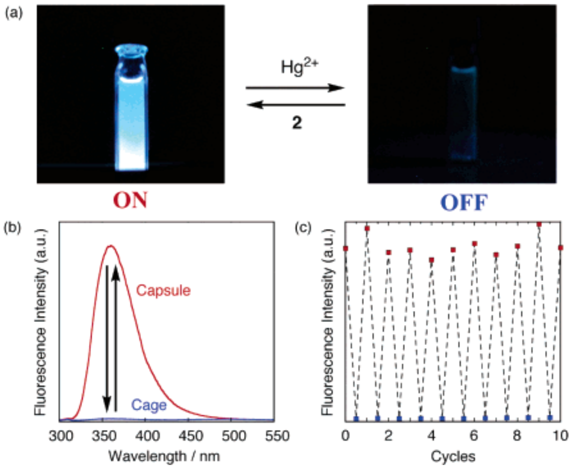

Figure 3. Fluorescence switching between $Hg_6\mathbf{1}_8$ capsule and $Hg_6\mathbf{1}_4$ cage; (a) emission of $Hg_6\mathbf{1}_8$ capsule (left) and $Hg_6\mathbf{1}_4$ cage (right) under UV irradiation ($[\mathbf{1}] = 1$ mM), (b) fluorescence spectra of capsule (red) and cage (blue) complexes ($[\mathbf{1}] = 10\ \mu$M, CH_3CN, 293 K, $\lambda_{ex} = 284$ nm), and (c) reversible switching cycles of fluorescence intensity ($\lambda_{em} = 360$ nm) by alternate addition of Hg^{2+} ions and cryptand **2**.

$\times 10^{-10}$ $m^2\ s^{-1}$, which is almost the same as that of $Hg_6\mathbf{1}_8$ capsule (3.7×10^{-10} $m^2\ s^{-1}$).[6] These results indicate that the $Hg_6\mathbf{1}_4$ complex is similar in size and shape to the $Hg_6\mathbf{1}_8$ capsule in solution. In other words, Hg^{2+} ions in $Hg_6\mathbf{1}_4$ occupy the six apexes of the octahedron with the Hg···Hg distance of approximately 18 Å as confirmed for $Hg_6\mathbf{1}_8$,[4] but only four of the eight faces are occupied by the ligand molecules with high symmetry. While some proton signals of $Hg_6\mathbf{1}_8$ upfield-shifted in the ^1H NMR spectrum, those of $Hg_6\mathbf{1}_4$ did not show any shift, suggesting that the structure of the $Hg_6\mathbf{1}_4$ complex is cagelike and lacunal. To be more exact, this structural change from the $Hg_6\mathbf{1}_8$ capsule to the $Hg_6\mathbf{1}_4$ cage can be depicted as elimination of four ligand panels from the closely packed octahedron.

This structural switching is accompanied by a change in coordination geometry of Hg^{2+} from an octahedral six-coordinate geometry to a linear two-coordinate geometry. ^{19}F NMR spectrum of $Hg_6\mathbf{1}_4$ complex showed only one signal as a sharp singlet at δ 85.3, whereas that of $Hg_6\mathbf{1}_8$ complex exhibited two signals at δ 85.2 and 86.1 owing to the separation of TfO^- anions into inside and outside the capsule. This result suggests that only two pyridine N donors coordinate to the Hg^{2+} centers of the $Hg_6\mathbf{1}_4$ cage, considering that Hg^{2+} ions prefer a two-coordinate geometry,[8] and that the rate of exchange between the inner and the outer anions of the $Hg_6\mathbf{1}_4$ cage is faster than the NMR time scale owing to the presence of the large openings in the cage-shaped structure.

The formation of the $Hg_6\mathbf{1}_8$ capsule and the $Hg_6\mathbf{1}_4$ cage fully depends on the relative concentration between Hg^{2+} ions and ligand **1** in solution, and the structural interconversion between the capsule and the cage can be further repeated by reversibly changing the available concentration of Hg^{2+} ions using strong Hg^{2+}-chelating reagents such as [2.2.2]-cryptand **2**. Upon addition of 0.75 equiv of $Hg(OTf)_2$ (to **1**) to the $Hg_6\mathbf{1}_8$ solution, the capsule structure quickly and quantitatively switched to the $Hg_6\mathbf{1}_4$ cage structure (Figure 2c). When 0.75 equiv of cryptand **2** was further added to the $Hg_6\mathbf{1}_4$ solution to trap exactly half of Hg^{2+} ions in solution as an Hg^{2+}-cryptate ($Hg^{2+} \subset \mathbf{2}$) inclusion complex, the $Hg_6\mathbf{1}_8$ capsule was simultaneously and quantitatively regenerated (Figure 2d). Each conversion step was brought to completion within a few minutes.

Such a structural interconversion system could trigger a remarkable change in chemical and physical properties between the two states. This system actually allowed fluorescence switching in conjunction with the structural interconversion.[9] Upon excitation at 284 nm, the $Hg_6\mathbf{1}_8$ capsule showed violet-light emission at 360 nm in CH_3CN at 293 K. In contrast, the $Hg_6\mathbf{1}_4$ cage exhibited almost no emission (Figure 3a,b).[10] In a cycle, when 0.75 equiv of Hg^{2+} ions and [2.2.2]-cryptand were added in this order to the initial solution of $Hg_6\mathbf{1}_8$ capsule, the violet-fluorescence disappeared and again appeared in association with the interconversion between the two Hg^{2+} complexes. This ON/OFF switching process could be repeated at least ten times without any loss of fluorescent efficiency (Figure 3c).

In conclusion, we demonstrated the quantitative self-assembly of the positively charged $Hg_6\mathbf{1}_4$ cage complex and its reversible interconversion with the structurally distinct, neutral $Hg_6\mathbf{1}_8$ capsule complex in response to $Hg^{2+}/\mathbf{1}$ ratios. These dynamic structural changes were found to associate with fluorescence switching between the fluorescent capsule and the nonfluorescent cage. The present molecular system design would allow structurally as well as electrostatically controlled molecular capturing in association with an external stimulus-triggered response.

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Supporting Information Available: Experimental procedures and spectral data of $Hg_6\mathbf{1}_4$ complex. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391.

(2) (a) Balboiu, M.; Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 5201−5206. (b) Marquis, A.; Kintzinger, J.-P.; Graff, R.; Baxter, P. N. W.; Lehn, J.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2760−2764. (c) Balboiu, M.; Prodi, L.; Montalti, M.; Zaccheroni, N.; Kyritsakas, N.; Lehn, J.-M. *Chem.—Eur. J.* **2004**, *10*, 2953−2959. (d) Umemoto, K.; Yamaguchi, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 7150−7151. (e) Jiménez-Molero, M. C.; Dietrich-Buchecker, C.; Sauvage, J.-P. *Chem. Commun.* **2003**, 1613−1616. (f) Yamamoto, T.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 12309−12317. (g) Sun, S.-S.; Stern, C. L.; Nguyen, S.-B. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2004**, *126*, 6314−6326. (h) Albrecht, M.; Janser, I.; Runsink, J.; Raabe, G.; Weis, P.; Fröhlich, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6662−6666. (i) Brown, A. M.; Ovchinnikov, M. V.; Stern, C. L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2004**, *126*, 14316−14317.

(3) (a) Hiraoka, S.; Yi, T.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2002**, *124*, 14510−14511. (b) Hiraoka, S.; Harano, K.; Shiro, M.; Shionoya, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 2727−2731.

(4) Hiraoka, S.; Harano, K.; Shiro, M.; Ozawa, Y.; Yasuda, N.; Toriumi, K.; Shionoya, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6488−6491.

(5) The amount of $Hg_6\mathbf{1}_4$ increased linearly with an increase in the $Hg^{2+}/\mathbf{1}$ ratio. For example, when the ratio reached 9:8, the integral ratio of $Hg_6\mathbf{1}_8$ and $Hg_6\mathbf{1}_4$ became approximately 1:1 in the ^1H NMR spectrum.

(6) See Supporting Information.

(7) Morris, K. F.; Johnson, C. S., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 3141−3142.

(8) ^{19}F DOSY measurement of the $Hg_6\mathbf{1}_4 \cdot (OTf)_{12}$ cage complex showed that the diffusion coefficient of the TfO^- anions is 9.1×10^{-10} $m^2\ s^{-1}$, which is much larger than that of the cationic part of the cage complex. This result suggests that the TfO^- anions do not bind to the Hg^{2+} centers in $Hg_6\mathbf{1}_4$.

(9) Fluorescence of ligand **1** and its metal complexes arises from 4-(3-pyridyl)-phenyl moieties. See: Sarkar, A.; Chakravorti, S. J. *J. Lumin.* **1995**, *65*, 163−168.

(10) The difference in the fluorescence properties of the two Hg^{2+} complexes is probably due to that in the extent of the heavy atom effect of Hg^{2+} associated with the changes in their coordination geometry and to that in the structural flexibilities of the ligands. See Supporting Information.

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