Supporting Information

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

Koji Harano,† Shuichi Hiraoka,†,‡ and Mitsuhiko Shionoya*,†

† Department of Chemistry, Graduate School of Science, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
‡ Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Honcho, Kawaguchi, Saitama 332-0012, Japan

Contents

Preparation of the $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ complex

Synthetic procedure for disk-shaped ligand **1** was previously reported[1]. $Hg(OTf)_2$ (0.9 mg, 1.8 μmol, 1.5 eq) was added to a solution of **1** (1.0 mg, 1.2 μmol) in CD_3CN (0.4 mL), and the mixture was kept standing at room temperature for 5 min. Its ^1H NMR spectrum showed the quantitative formation of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ complex.

^1H NMR (500 MHz, CD_3CN, 293 K) δ 9.00 (s, 12 H), 8.67 (d, *J* = 5.6 Hz, 12H), 8.43 (d, *J* = 7.8 Hz, 12H), 7.95 (dd, *J* = 7.8, 5.6 Hz, 12H), 7.48 (d, *J* = 7.8 Hz, 12H), 7.38 (d, *J* = 7.7 Hz, 12H), 7.19 (d, *J* = 7.8 Hz, 12H), 7.19 (d, *J* = 7.7 Hz, 12H), 6.94 (d, *J* = 7.6 Hz, 12H), 6.89 (d, *J* = 7.3 Hz, 12H), 6.74 (d, *J* = 7.6 Hz, 24H), 6.73 (d, *J* = 7.3 Hz, 24H), 2.00 (s, 36H); ^{19}F NMR (470 MHz, CD_3CN, 293 K) δ 85.3 (s, 36F); ESI-TOF Mass (CD_3CN) *m/z* = 1095.9 $[Hg_6\mathbf{1}_4\cdot(OTf)_7]^{5+}$, 1407.4 $[Hg_6\mathbf{1}_4\cdot(OTf)_8]^{4+}$, 1926.2 $[Hg_6\mathbf{1}_4\cdot(OTf)_9]^{3+}$.

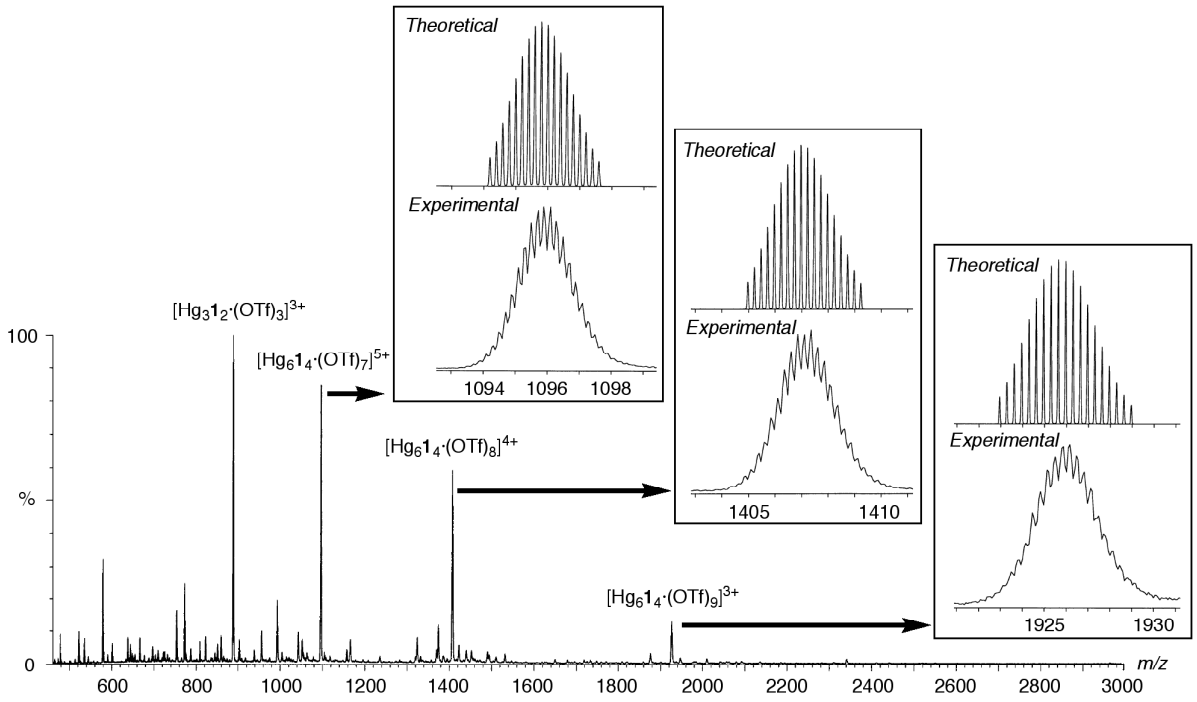

Figure S1. ESI-TOF mass spectrum of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$.

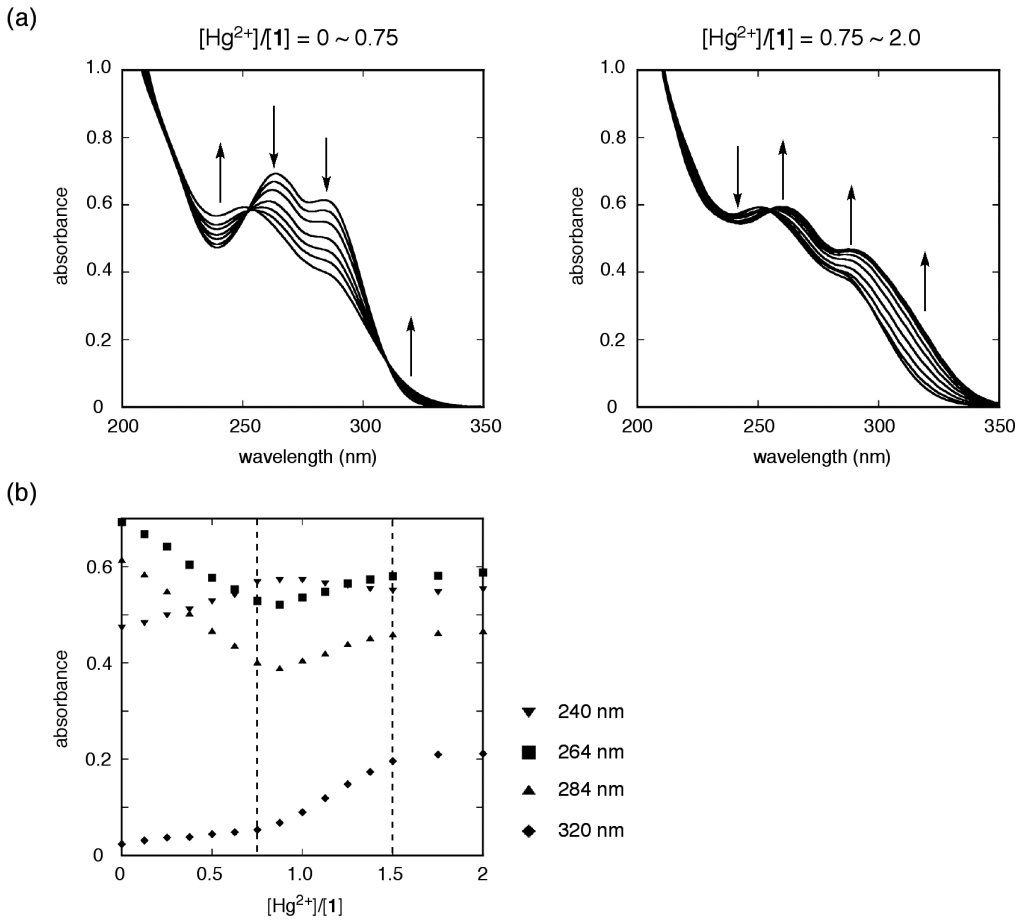

Figure S2. (a) UV absorption changes of **1** at various $[Hg^{2+}]/[\mathbf{1}]$ ratios ([**1**] = 100 μM, *l* = 1 mm, 293 K); $[Hg^{2+}]/[\mathbf{1}]$ = 0 ~ 0.75 (left) and 0.75 ~ 2.0 (right); (b) Plot of absorbance at 240, 264, 284, and 320 nm against the $[Hg^{2+}]/[\mathbf{1}]$ ratio.

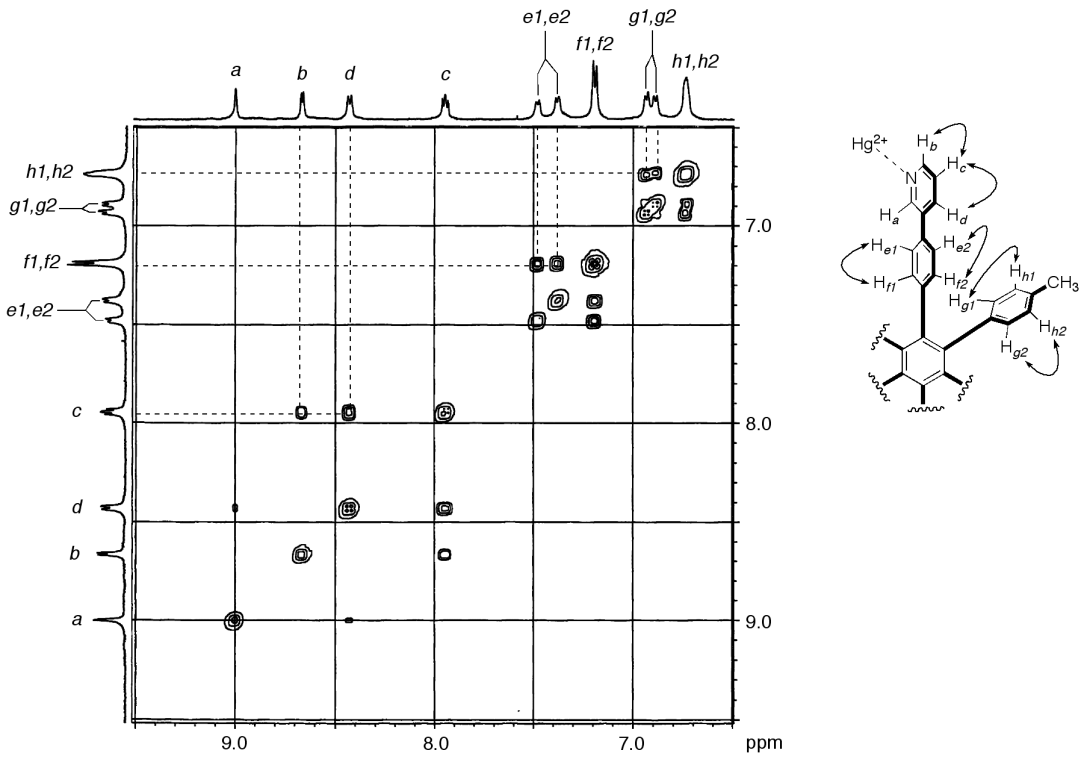

Figure S3. ^{1}H-^{1}H COSY spectrum of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ (aromatic region only, 500 MHz, CD_3CN, 293 K)

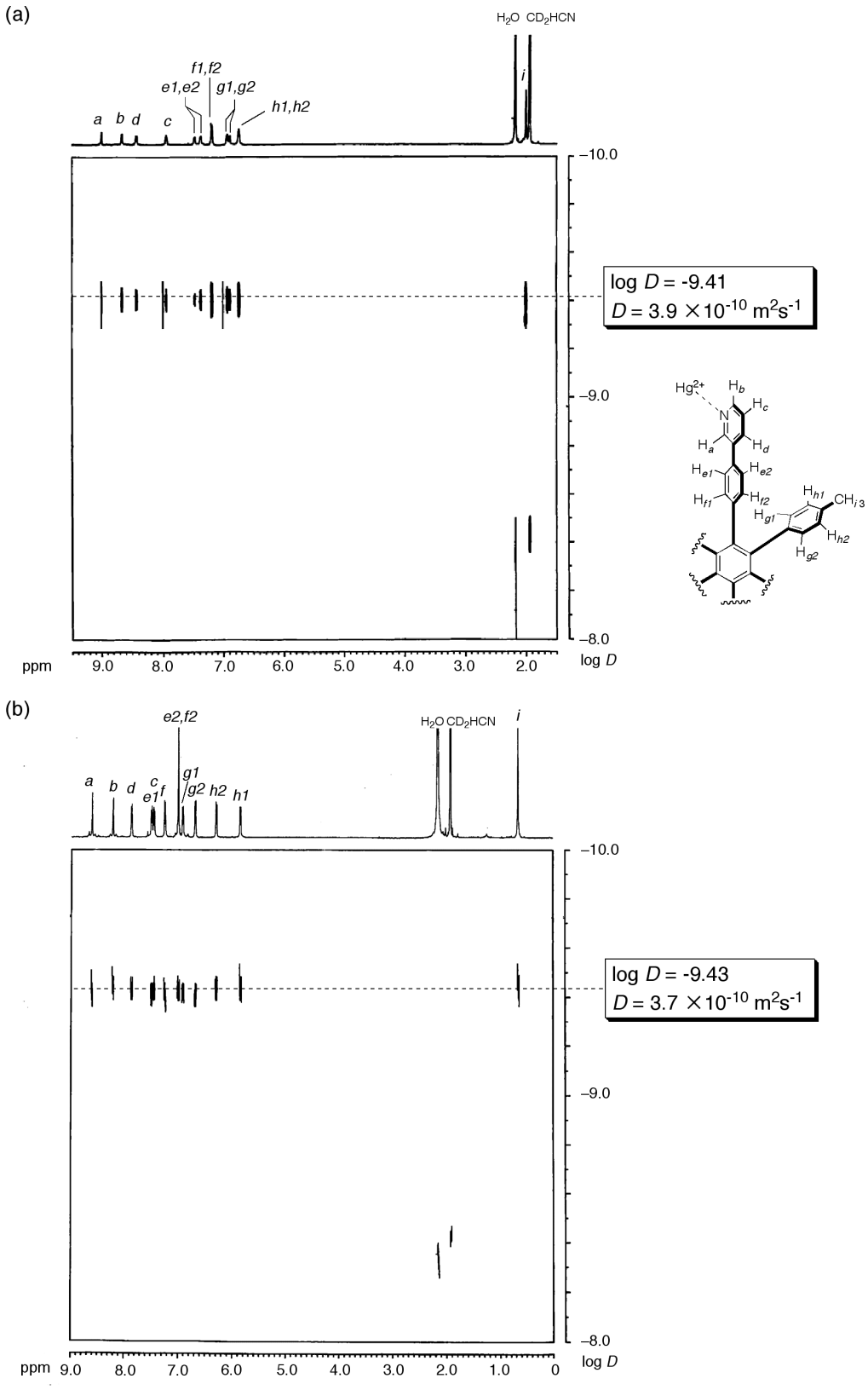

Figure S4. ^{1}H DOSY spectra (500 MHz, CD_3CN, 293 K); (a) $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ cage; (b) $Hg_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule.

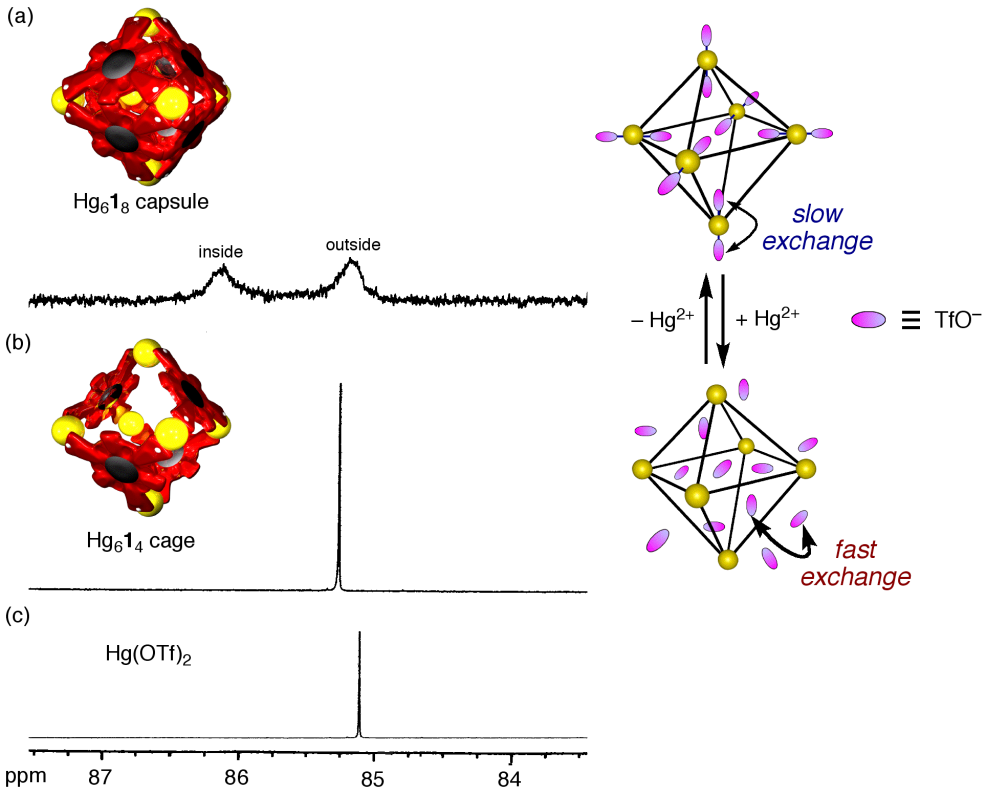

Figure S5. ^{19}F NMR spectra of Hg^{2+} complexes (470 MHz, CD_3CN, 293 K, C_6F_6 as internal standard); (a) $Hg_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule; (b) $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ cage; (c) $Hg(OTf)_2$.

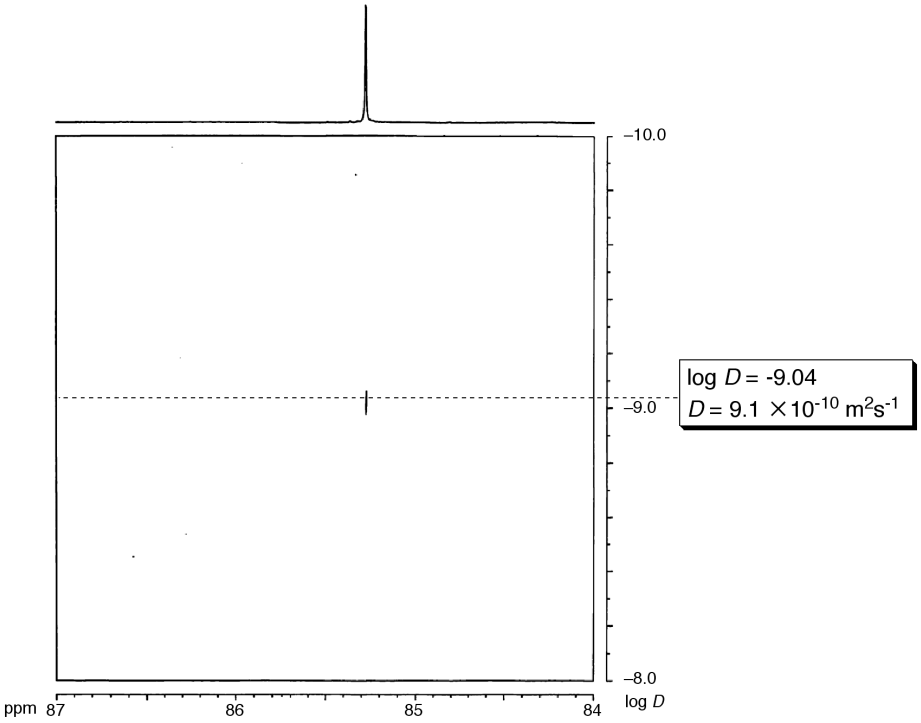

Figure S6. ^{19}F DOSY spectrum of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ (470 MHz, CD_3CN, 293 K).

Solution behavior of TfO^- anions in $Hg_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule

Firstly, an ^{19}F DOSY measurement of the $Hg_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule was conducted at 293 K, but the diffusion coefficient of the TfO^- anions could not be determined due to the fast of exchange between two signals compared to the DOSY NMR timescale. By lowering temperature (243K or 263 K) to slow down the exchange rate, the TfO^- signals became sharpened, nevertheless any signals were not observed in ^{19}F DOSY spectra.

However, the diffusion coefficients of counter anions in the $Zn_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule, which is structurally equivalent to the $Hg_6\mathbf{1}_8\cdot(OTf)_{12}$ capsule, could be determined by ^{19}F DOSY measurement due to the slower exchange between inside and outside TfO^- (Figure S7). The diffusion coefficient (D) of the TfO^- signal at the lower field (δ 85.9 ppm) was determined to be 2.8×10^{-10} m^2s^{-1}, which is comparable to the $Zn_6\mathbf{1}_8$ capsule ($D = 4.2 \times 10^{-10}$ m^2s^{-1}). This suggests that the signal at the lower field is assignable to the inner TfO^- anions, which are strongly bound to the capsule framework. In contrast, the diffusion coefficient of the signal at the upper field (δ 85.1 ppm) was 1.2×10^{-9} m^2s^{-1}, which is a meaningfully larger value than the signal at the lower field. Therefore, this signal is assignable to the outer TfO^- anions, indicative of intermolecular anion exchange with neighboring Zn-capsules in solution. In light of the structural similarity between the $Hg_6\mathbf{1}_8$ and $Zn_6\mathbf{1}_8$ capsules, the TfO^- anions of the $Hg_6\mathbf{1}_8$ capsule would show similar solution behavior.

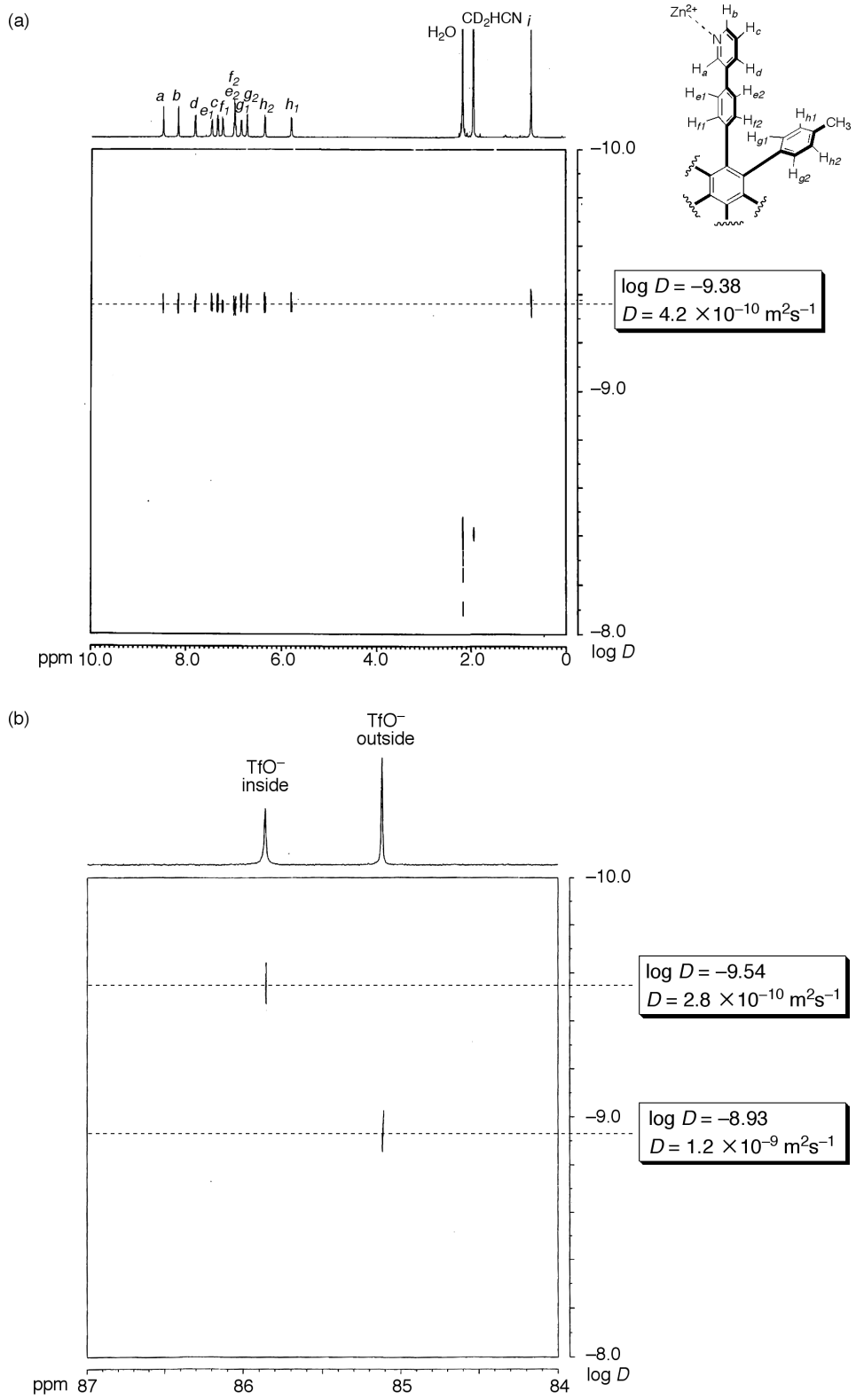

Figure S7. DOSY spectra of the $Zn_6\mathbf{1}_8{\cdot}(OTf)_{12}$ capsule; (a) an ^{1}H DOSY spectrum (500 MHz, CD_3CN, 293 K); (b) an ^{19}F DOSY spectrum (470 MHz, CD_3CN, 293 K).

Experimental details of the interconversion between $Hg_6\mathbf{1}_8$ and $Hg_6\mathbf{1}_4$

To a solution of $Hg_6\mathbf{1}_8{\cdot}(OTf)_{12}$ capsule complex (10 μM) in CH_3CN (3.5 mL) in a quartz cell, a solution (26.7 μL) of $Hg(OTf)_2$ (982 μM) in CH_3CN was added. After stirring the solution at room temperature for 5 min, its fluorescence spectrum was recorded. A solution of [2.2.2]-cryptand (1.29 mM) in CH_3CN (20.3 μL) was added to this solution and stirred for 5 min. And then, its fluorescence spectrum was recorded again. This cycle was repeated ten times. Reversible switching of fluorescence intensity during the interconversion is shown in Figure 3.

Comparison of coordination geometries of Hg^{2+} ions in $Hg_6\mathbf{1}_4$ cage complexes

To clarify that the Hg^{2+} centers in $Hg_6\mathbf{1}_4$ cage are two-coordinate and coordinated by only two pyridine N donors, following NMR experiments were conducted.

(i) ^{19}F DOSY measurement of $Hg_6\mathbf{1}_4{\cdot}(OTf)_{12}$ showed that the diffusion coefficient of the TfO^- anions is 9.1×10^{-10} m^2s^{-1}, which is much larger than that of $Hg_6\mathbf{1}_4$ cage obtained from the ^1H DOSY measurement ($D = 3.9 \times 10^{-10}$ m^2s^{-1}). This result excludes the possibility of the coordination of the counteranions (TfO^-) to the Hg^{2+} centers in $Hg_6\mathbf{1}_4$.

(ii) $Hg_6\mathbf{1}_4$ capsule was prepared in non-deuterated CH_3CN and the solvent was removed under reduced pressure, and then $Hg_6\mathbf{1}_4$ complex was redissolved in CD_3CN. Its ^1H NMR spectrum showed the absence of the CH_3CN signal (Figure S7), indicating that CH_3CN molecules do not coordinate to the Hg^{2+} centers in $Hg_6\mathbf{1}_4$ and therefore could be removed by evaporation.

(iii) $Hg_6\mathbf{1}_4$ capsule was prepared in CD_3CN dried over molecular sieves 3A (H_2O content ≈ 80 ppm, ca. 1.6 H_2O molecules per Hg^{2+}), and its NMR spectrum did not show any change compared to the spectrum of $Hg_6\mathbf{1}_4$ in wet CD_3CN (H_2O content ≈ 0.16%) (Figure S8). This result indicates that $Hg_6\mathbf{1}_4$ cage can be formed even under the condition that there are less than two H_2O molecules per Hg^{2+} ions. It is thus concluded that H_2O molecules do not coordinate to the Hg^{2+} centers.

In light of these experimental results, no ligand other than two pyridyl groups coordinates to the Hg^{2+} ion in the cage complex and the Hg^{2+} centers may adopt a linear two-coordinate geometry.

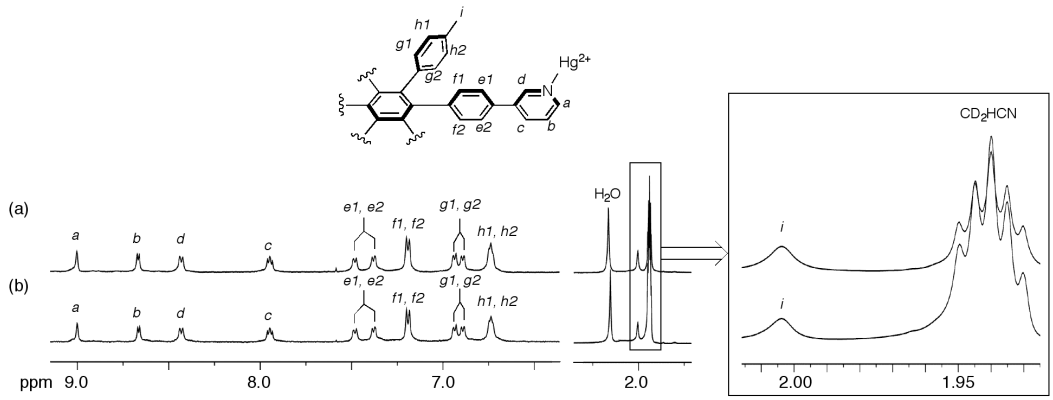

Figure S8. ^{1}H NMR spectra of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ ([**1**] = 3.0 mM, 500 MHz, CD_3CN, 293 K); (a) the sample directly prepared in CD_3CN; (b) the sample prepared in CH_3CN and redissolved in CD_3CN after evaporation of CH_3CN. No signal of CH_3CN (δ 1.96) was observed.

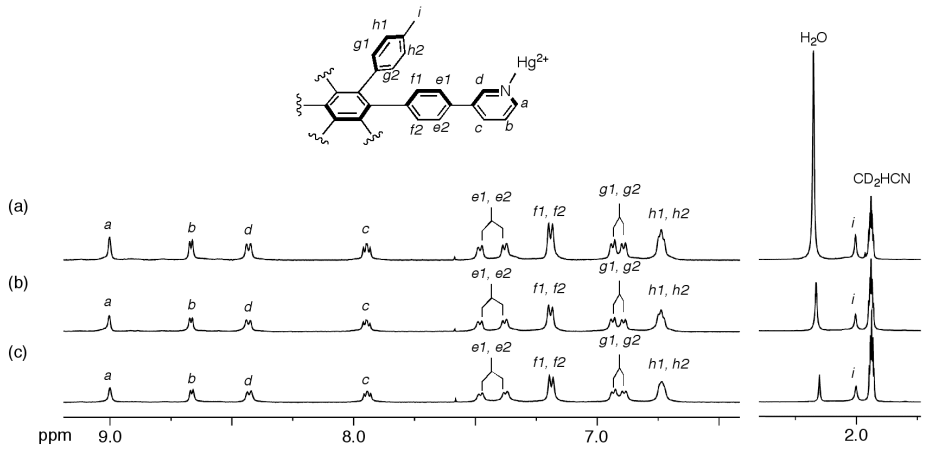

Figure S9. ^{1}H NMR spectra of $Hg_6\mathbf{1}_4\cdot(OTf)_{12}$ ([**1**] = 3.0 mM, 500 MHz, CD_3CN, 293 K); H_2O content in CD_3CN: (a) 0.16% (32.7 H_2O per Hg^{2+}); (b) 630 ppm (12.7 H_2O per Hg^{2+}); (c) 80 ppm (1.6 H_2O per Hg^{2+}). The spectra became slightly broadened with decreasing the H_2O content, which is ascribed to slightly excess Hg^{2+} in solution. When the amount of H_2O is decreased, hydration to the excess Hg^{2+} would become less effective, and thereby the $Hg_6\mathbf{1}_4$ cage would interact with the Hg^{2+} ions.

Stabilities of $Hg_6\mathbf{1}_8$ capsule and $Hg_6\mathbf{1}_4$ cage complexes in dilute solution

Dilution experiments were performed for $Hg_6\mathbf{1}_8$ capsule and $Hg_6\mathbf{1}_4$ cage to survey their stability in CH_3CN solution. Judging from UV absorption change upon dilution, $Hg_6\mathbf{1}_8$ capsule were quantitatively formed when the concentration of **1** was higher than 20 μM, and under this concentration, partial dissociation of the capsule complex was observed. In the case of $Hg_6\mathbf{1}_4$ cage, quantitative formation was confirmed when the concentration of **1** was higher than 5 μM.

To evaluate fluorescence quantum yields of the Hg^{2+} complexes, highly dilute conditions are required to suppress the effect of self-absorption (generally, absorbance of the sample solution is set to be < 0.1). Actually, it is rather difficult to determine the fluorescence quantum yields because of effects of concentration-dependent self-absorption. In addition, the complexes are not stable at very low concentrations where the self-absorption is negligible.

Origins of the difference in fluorescence intensity of $Hg_6\mathbf{1}_8$ capsule and $Hg_6\mathbf{1}_4$ cage complexes

The fluorescence of ligand **1** is originated from 4-(3-pyridyl)phenyl moieties, and complexation with Hg^{2+} ions causes quenching of its emission, likely due to the heavy atom effect of Hg^{2+} ions. The quenching effect by the coordination of Hg^{2+} ions are supposed to be strengthened along with the increase of the [Hg^{2+}]/[**1**] ratios. Unexpectedly, however, the fluorescence is strongly suppressed in $Hg_6\mathbf{1}_4$ cage so that almost no emission is observed, and this behavior cannot be explained simply by the change of the [Hg^{2+}]/[**1**] ratios. The strong fluorescence quenching observed only in $Hg_6\mathbf{1}_4$ cage can be considered as the result of the dramatic change in coordination geometry of the Hg^{2+} ions (octahedral six-coordinate to linear two-coordinate), but detailed mechanism is not clear yet.

The difference in the flexibilities of the Hg^{2+} complexes also may account for the fluorescence switching phenomena. $Hg_6\mathbf{1}_8$ capsule has a highly rigid structure due to the close contacts of neighboring ligands, which suppresses radiationless deactivation *via* internal molecular motions. Actually, the fluorescence of $Zn_6\mathbf{1}_8$ capsule, in which the Zn^{2+} ions have no heavy atom effect, is more intense than that of free ligand **1** or $Hg_6\mathbf{1}_8$ capsule (Figure S9). In contrast, $Hg_6\mathbf{1}_4$ cage, which has four large openings, is more flexible and the fluorescence quenching by radiationless deactivation may be dominated. These results indicate the change of rigidity of ligand **1** by the interconversion between the capsule- and cage-shaped structures could effectively contribute for the fluorescence switching.

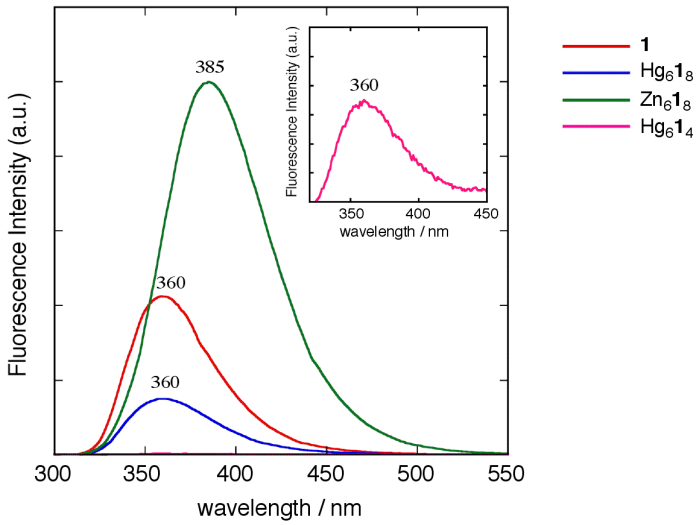

Figure S10. Fluorescence spectra ([**1**] = 10 μM, CH_3CN, 293 K, λ_{ex} = 284 nm) of **1** (red), Hg_6**1**$_8$ capsule (blue), Zn_6**1**$_8$ capsule (green), and Hg_6**1**$_4$ cage (pink). A magnified spectrum of the Hg_6**1**$_4$ cage is shown in an inset. Numbers above each spectrum represent their absorption maxima (nm).

Reference

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