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Title: A Supramolecular Sensing System for Ag^I at Nanomolar Levels by Formation of Luminescent Ag^I-Tb^{III}-Thiacalix[4]arene Ternary Complex

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1. Materials and Methods

Materials

Tetrasodium salt of thiacalix[4]arene-*p*-tetrasulfonate (TCAS, H_4tcas^{4-}) was prepared as described previously,¹ and was dissolved into water to be stocked (5.0×10^{-3} M). The stock solutions of silver(I) and terbium(III) ions (0.01 M) were prepared by dissolving an appropriate amount of the nitrate (Kanto Chemical Co., Inc., Tokyo) in 0.01 M HNO_3 . The pH buffer 2-morphorinoethanesulfonic acid (MES) was purchased from Dojindo Laboratories, Kumamoto. Buffer solution (0.5 M) was prepared by dissolving the buffer in water, followed by adjustment of the pH by NaOH and made up to appropriate volume by water. Doubly distilled water was used throughout this study.

Detection of Ag^I

Sample solutions were prepared by mixing appropriate amounts of aqueous solutions of silver(I) nitrate, foreign ion if any, terbium(III) nitrate, TCAS, and pH buffer (MES). Before the measurement of luminescent spectra, the sample solution was allowed to stand for 1 h at room temperature to ensure equilibration. The luminescent spectra were measured with a Hitachi F-4500 fluorescent spectrometer.

*ESI-MS measurement of complex $Cd^{II}_2 \cdot Tb^{III}_2 \cdot TCAS_2$ (**3**)*

The stock solution of metal chlorides (0.01 M) prepared by dissolving appropriate amounts of the chlorides (Kanto Chemical Co., Inc., Tokyo) in 0.01 M HCl were used. Sample solution of complex **3** was prepared by mixing appropriate amounts of aqueous solutions of cadmium(II) chloride, terbium(III) chloride, and TCAS, followed by adjustment of pH to 5.8 with NH_3 . ESI-MS experiments were performed using a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer APEX III (Bruker). Mass spectra were simulated with a program iMass for Mac OS X ver. 1.1.²

1) N. Iki, T. Horiuchi, H. Oka, K. Koyama, N. Morohashi, C. Kabuto and S. Miyano, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2219.

2) <http://home.datacomm.ch/marvin/iMass/>

2. Electrospray ionization MS of $\text{Cd}^{\text{II}}\cdot\text{Tb}^{\text{III}}\cdot\text{TCAS}_2$ (**3**)

Figure S1 shows spectra for (a) whole region of the sample and (b) part for complex $\text{Cd}^{\text{II}}\cdot\text{Tb}^{\text{III}}\cdot\text{TCAS}_2$ (**3**), $[\text{2Cd}^{2+} + 2\text{Tb}^{3+} + n\text{Na}^+ + (4-n)\text{H}^+ + 2\text{tcas}^{8-} + \text{H}_2\text{O}]^{2-}$. Figures S2-S6 show expansions of complex **3** part ranging from $n = 0$ to 4 as well as simulation of the isotopomer pattern. In each case, isotopomer pattern of MS spectrum and that of simulation agree well except at the wing showing overlap of unknown minor species (see each caption for the location).

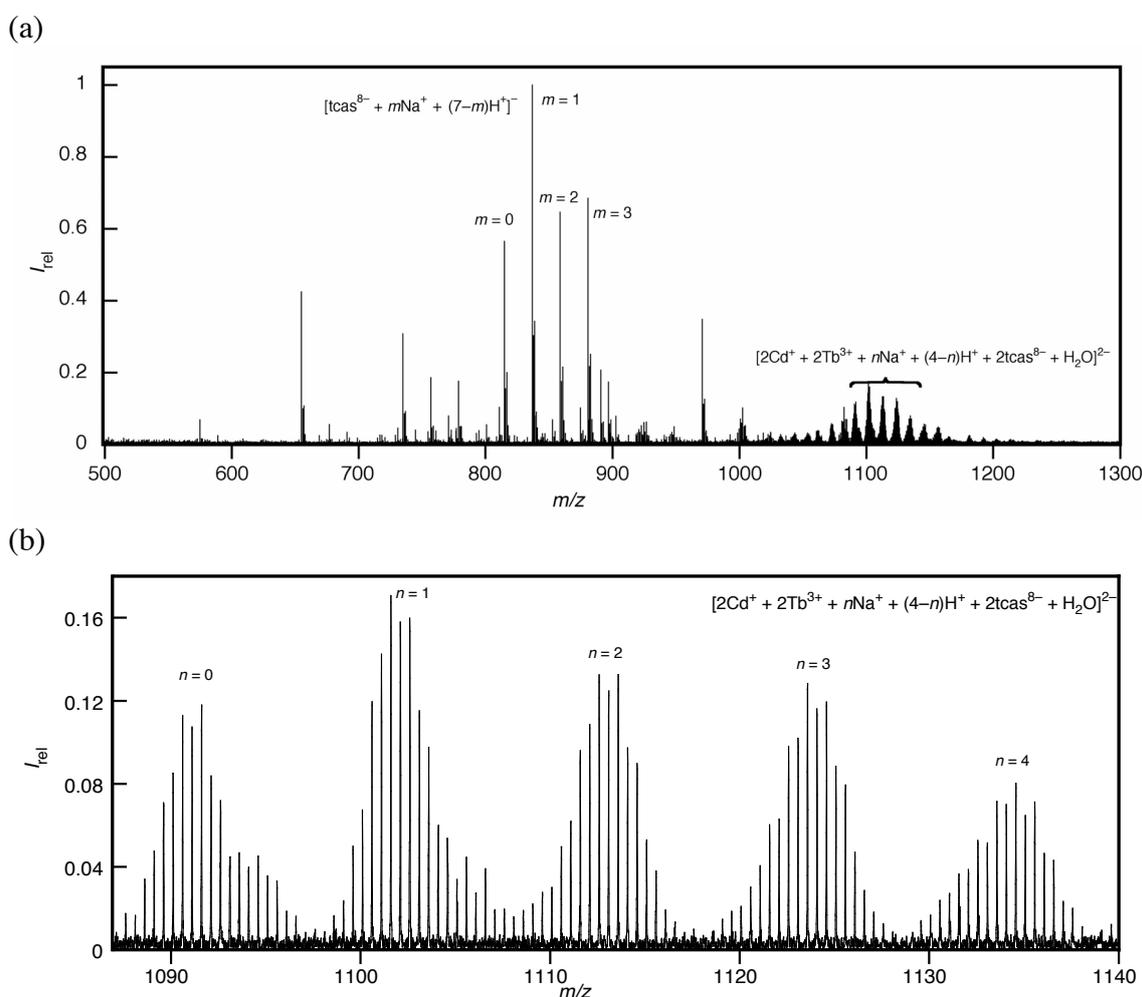
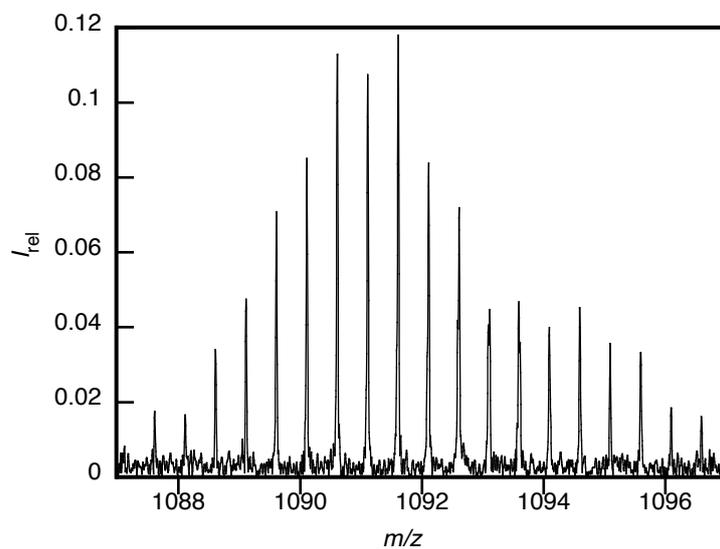


Fig. S1. ESI-mass spectra of $\text{Cd}^{\text{II}}\text{-Tb}^{\text{III}}\text{-TCAS}$ ternary system. Sample solution: $[\text{TCAS}]_{\text{T}} = [\text{Cd}^{\text{II}}]_{\text{T}} = [\text{Tb}^{\text{III}}]_{\text{T}} = 2.5 \times 10^{-5}$ M, $[\text{HCl}]_{\text{T}} = 5 \times 10^{-5}$ M, pH 5.82 (adjusted with NH_3). (a) Whole region, (b) expansion for $[\text{2Cd}^{2+} + 2\text{Tb}^{3+} + n\text{Na}^+ + (4-n)\text{H}^+ + 2\text{tcas}^{8-} + \text{H}_2\text{O}]^{2-}$ ($n = 0 - 4$).

(a)



(b)

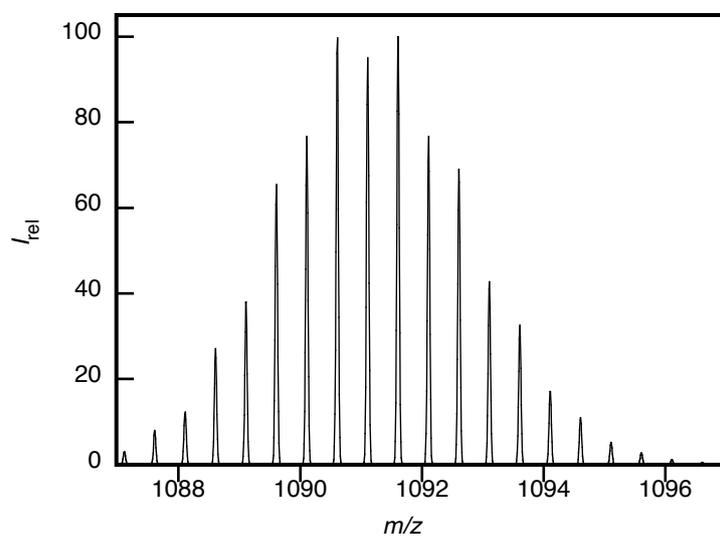
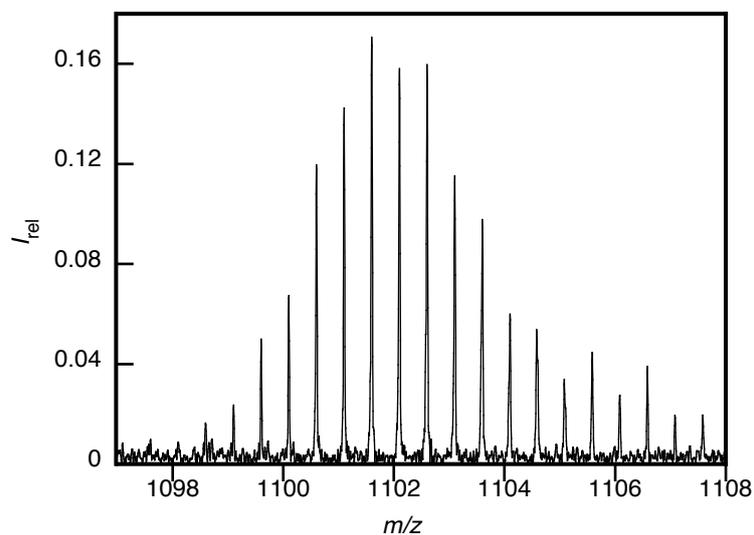


Fig. S2 Isotopomer pattern for $[2Cd^{2+} + 2Tb^{3+} + 4H^+ + 2tcas^{8-} + H_2O]^{2-}$ obtained with (a) ESI-MS and (b) simulation. Overlap of peaks from minor species can be seen in the region $m/z > 1093$.

(a)



(b)

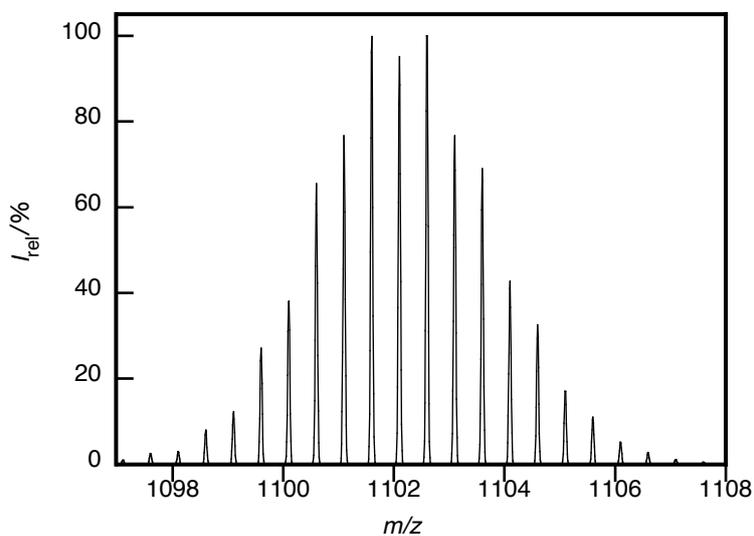


Fig. S3 Isotopomer pattern for $[2\text{Cd}^{2+} + 2\text{Tb}^{3+} + \text{Na}^+ + 3\text{H}^+ + 2\text{tcas}^{8-} + \text{H}_2\text{O}]^{2-}$ obtained with (a) ESI-MS and (b) simulation. Overlap of peaks from minor species can be seen in the region $m/z > 1105$.

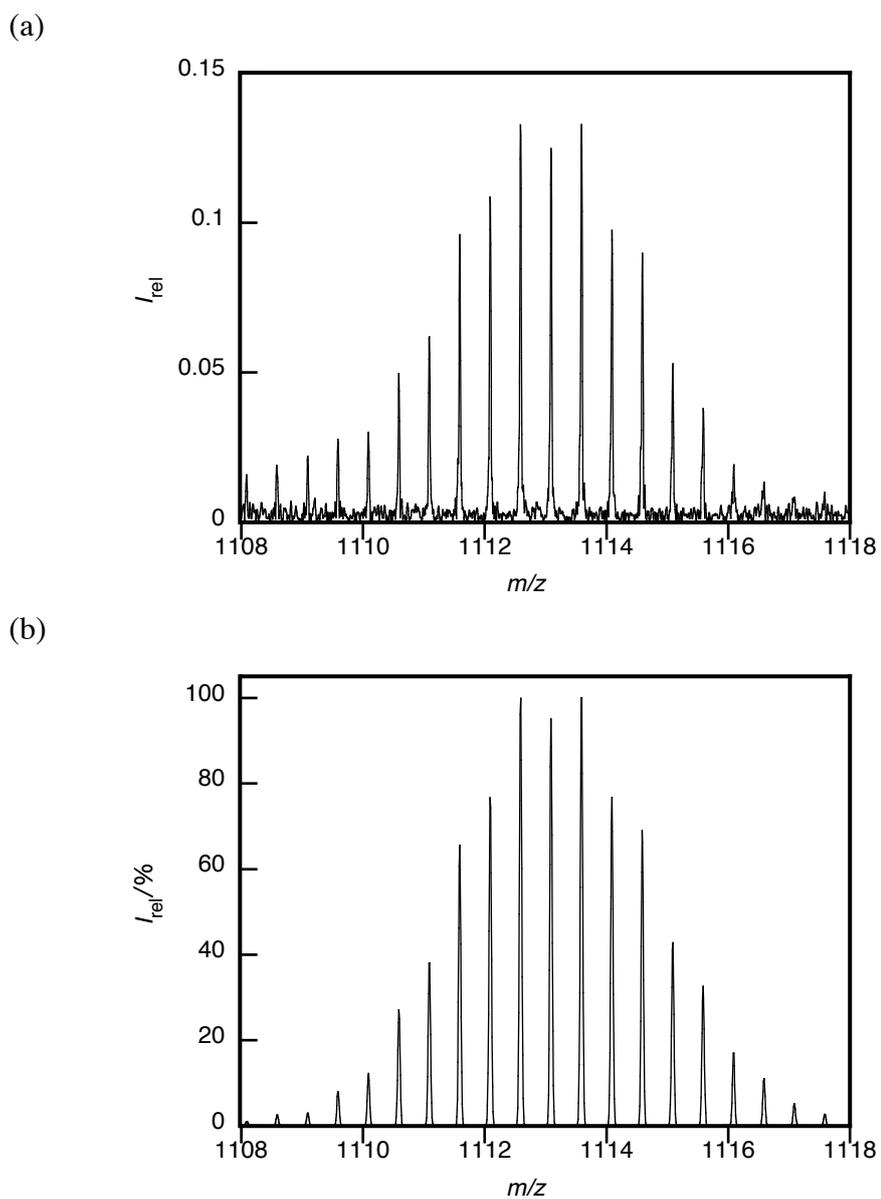


Fig. S4 Isotopomer pattern for $[2\text{Cd}^{2+} + 2\text{Tb}^{3+} + 2\text{Na}^+ + 2\text{H}^+ + 2\text{tcas}^{8-} + \text{H}_2\text{O}]^{2-}$ obtained with (a) ESI-MS and (b) simulation. Overlap of peaks from minor species can be seen in the region $m/z < 1110$.

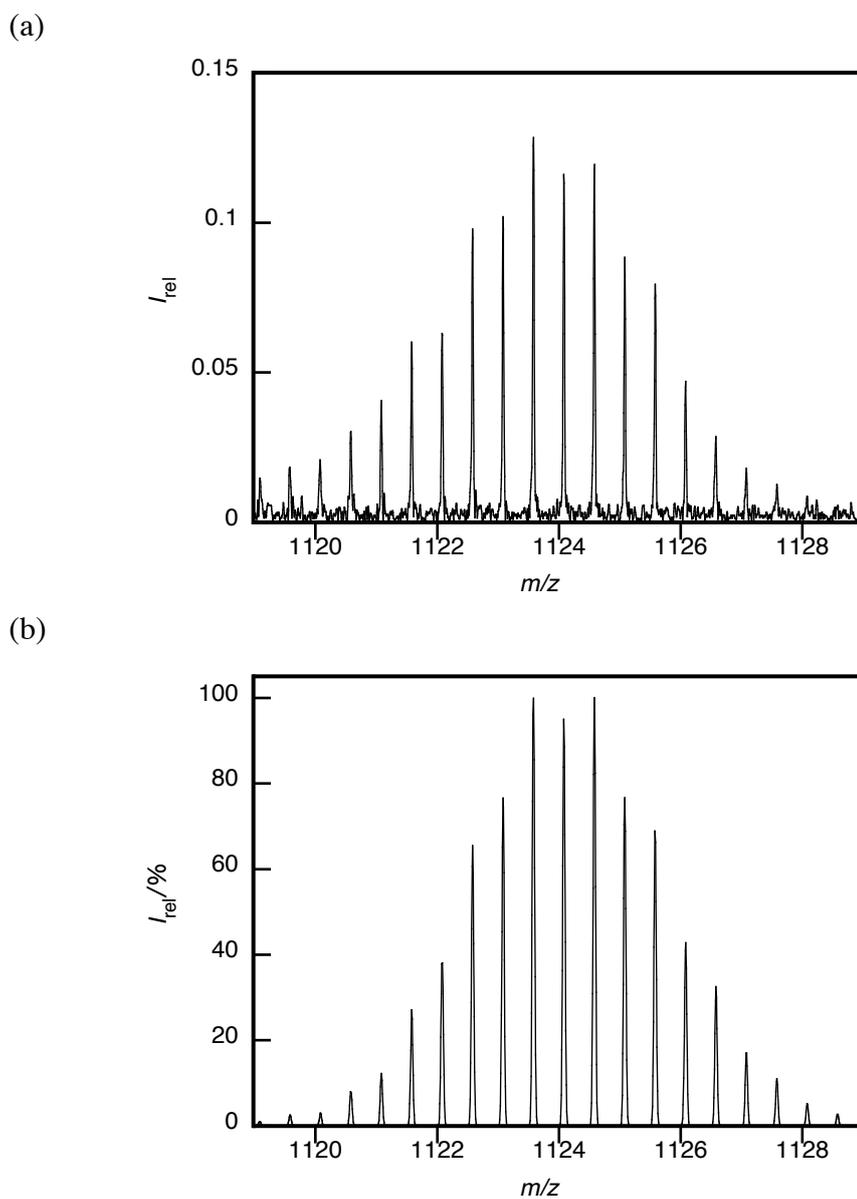
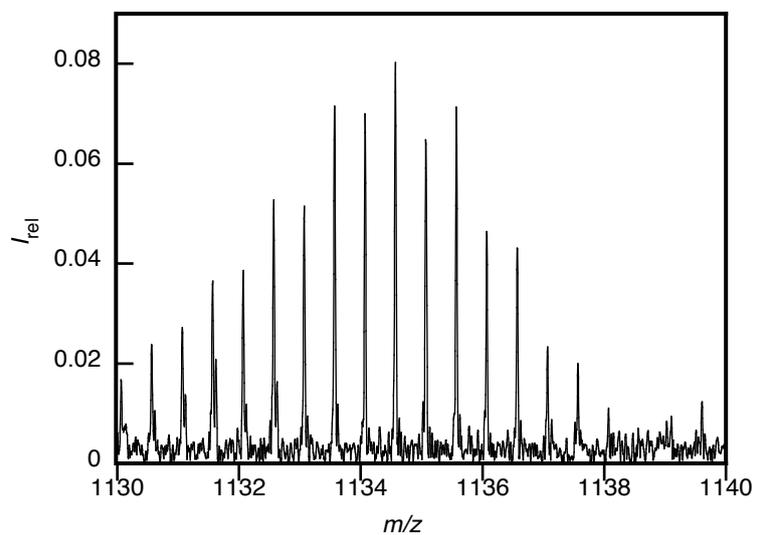


Fig. S5 Isotopomer pattern for $[2\text{Cd}^{2+} + 2\text{Tb}^{3+} + 3\text{Na}^+ + \text{H}^+ + 2\text{tcas}^{8-} + \text{H}_2\text{O}]^{2-}$ obtained with (a) ESI-MS and (b) simulation. Overlap of peaks from minor species can be seen in the region $m/z < 1121$.

(a)



(b)

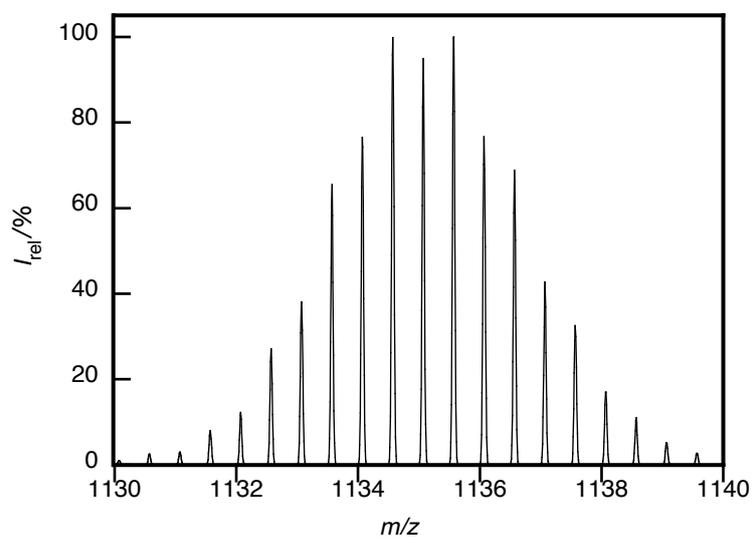


Fig. S6 Isotopomer pattern for $[2\text{Cd}^{2+} + 2\text{Tb}^{3+} + 4\text{Na}^{+} + 2\text{cas}^{8-} + \text{H}_2\text{O}]^{2-}$ obtained with (a) ESI-MS and (b) simulation. Overlap of peaks from minor species can be seen in the region $m/z < 1134$.