Electronic Supplementary Information

Thiacalixarene Assembled Heterotrinuclear Lanthanide Clusters Comprising Tb^{III} and Yb^{III} Enabling *f-f* Communication to Enhance the Yb^{III}-centred Luminescence

Ryunosuke KARASHIMADA, Nobuhiko IKI*

* Graduate School of Environmental Studies, Tohoku University
6-6-07 Aramaki-aoba, Aoba-ku, Sendai 980-8579 Japan. E-mail: iki@m.tohoku.ac.jp

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Experimental details

Materials

Thiacalix[4]arene-*p*-tetrasulfonate (TCAS) was synthesized as previously reported[1] and stocked as a 0.005 M aqueous solution. A stock solution of 0.01 M Tb^{III} and Lu^{III} were prepared by dissolving the nitrate hexahydrate for Tb^{III} and the nitrate tetrahydrate for Lu^{III} (99.95% purity, respectively) purchased from Kanto Chemical Company, Inc. (Tokyo) into 0.01 M HNO_3. A stock solution of 0.01 M Yb^{III} was prepared by dissolving the nitrate tetrahydrate (99.9%, Wako Pure Chemical Industries, Ltd., Osaka) in 0.01 M HNO_3. The concentration of the metal ions in the stock solutions was determined using accepted chelatometry. 2-[4-(2-Hydroxyethyl)-1-piperaazinyl]ethanesulfonic acid (HEPES) was purchased from Dojindo Laboratories (Kumamoto). A buffer solution (0.5 M) was prepared by dissolving HEPES in water, by adjusting the pH with NaOH, and then by diluting the solution to an appropriate volume in water.

Equipment

A Hitachi F-7000 spectrofluorophotometer was used to measure excitation and emission spectra for UV-Vis region as well as emission lifetime. A Jobin Yvon FluoroLog®–3 model FL3-11 spectrofluorometer equipped with a 450 W Xe lamp as the excitation source and an InGaAs semiconductor detector (DSS-IGA020L) was used to record excitation and emission spectra for near-infrared region. The pH values were recorded using a TOA HM-25R pH meter with a combined glass electrode. Electro-spray ionization-mass spectrometry was conducted using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer SolariX 9.4T (Bruker). The mass spectra were calculated using the software iMass for Mac OS X ver. 1.1.[2]

Measurement

Aqueous solutions of the $Tb_{3-x}Yb_xTCAS_2$ (x = 0–3) were prepared by simply mixing appropriate amounts of the aqueous solutions of $Tb(NO_3)_3$, $Yb(NO_3)_3$, TCAS, and HEPES buffer (pH 7.4). Prior to measurement of the luminescence spectra, the sample solution was allowed to stand for 24 hours at room temperature. For the $Tb_{3-x}Lu_xTCAS_2$ system, the same procedure was applied. A sample for ESI-MS was prepared by same procedure except using

NH_3 as a buffer.

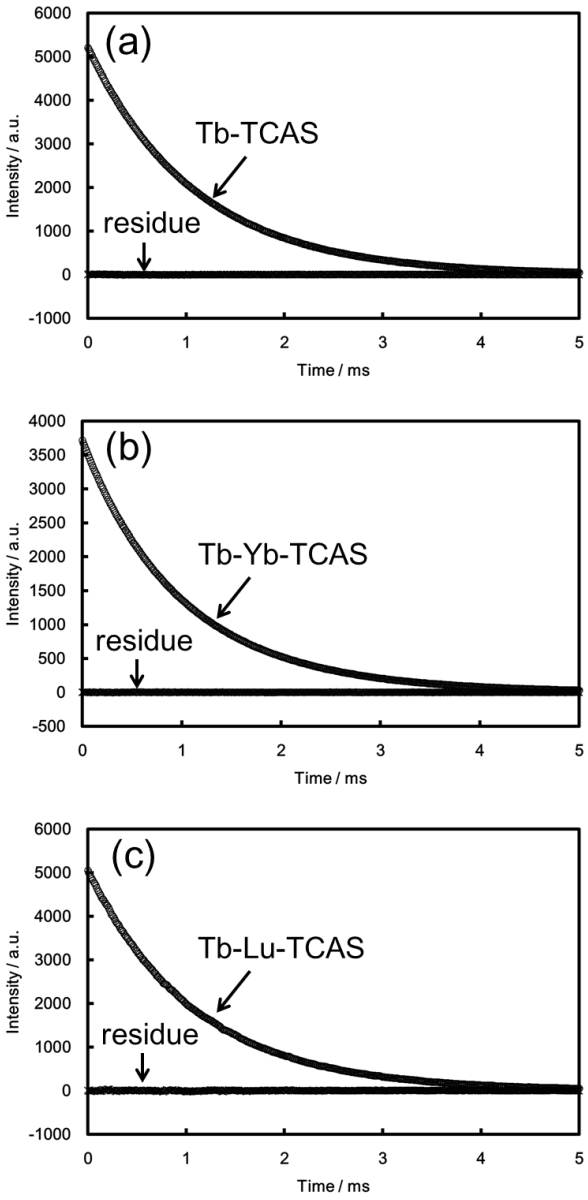

Figure S1 Decay curves for Tb^{III}-centered luminescence at 549 nm in Tb-TCAS binary (a), Tb-Yb-TCAS ternary (b), and Tb-Lu-TCAS ternary systems (c).

(a) Tb-TCAS binary system: [Tb^{III}] = 15 μM, [TCAS] = 10 μM, [HEPES] = 0.01 M, pH 7.4

(b) Tb-Yb-TCAS ternary system: [Tb^{III}] = [Yb^{III}] = 4.5 μM, [TCAS] = 6.0 μM, [HEPES] = 0.01 M, pH 7.4

(c) Tb-Lu-TCAS ternary system: [Tb^{III}] = [Lu^{III}] = 15 μM, [TCAS] = 10 μM, [HEPES] = 0.01 M, pH 7.4

λ_{ex} = 316 nm, λ_{em} = 549 nm.

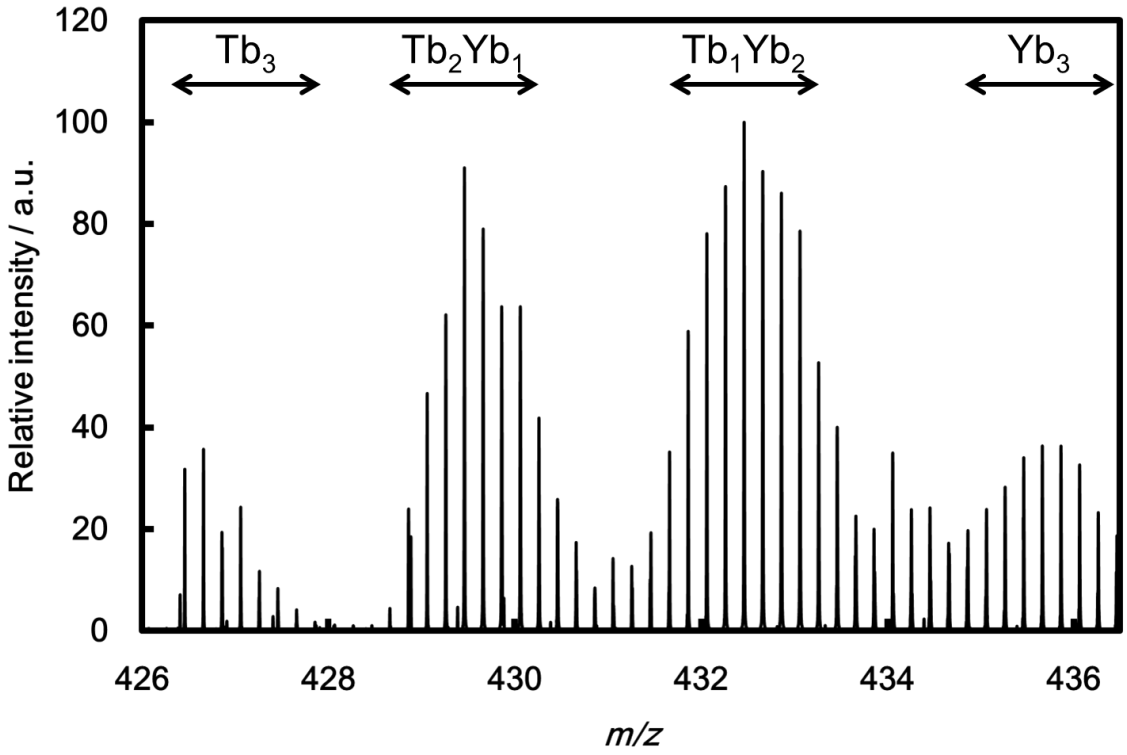

Figure S2 ESI-mass spectra of Tb-Yb-TCAS ternary system.

$[Tb^{III}] = [Yb^{III}]$ = 15 μM, [TCAS] = 20 μM, pH 9.3 (adjusted with NH_3)

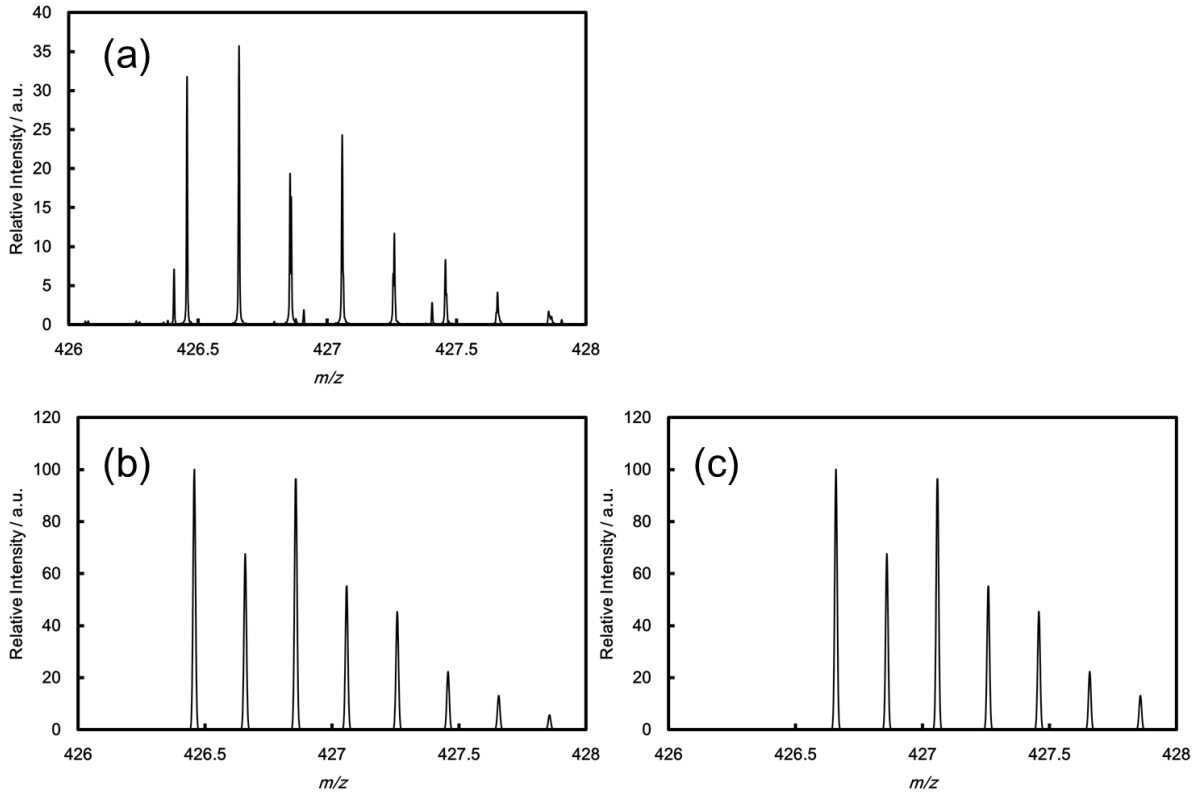

Figure S3 ESI- mass spectra of Tb-Yb-TCAS ternary system for Tb_3TCAS_2 part.

(a) $[Tb^{III}] = [Yb^{III}] = 15$ μM, [TCAS] = 20 μM, pH 9.3 (adjusted with NH_3),

(b) Calculated for $[Tb^{n+} + Tb^{m+} + Tb^{l+} + 2TCAS^{8-} + Na^{+} + H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 4 + 4$),

(c) Calculated for $[Tb^{n+} + Tb^{m+} + Tb^{l+} + 2TCAS^{8-} + Na^{+} + 2H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$).

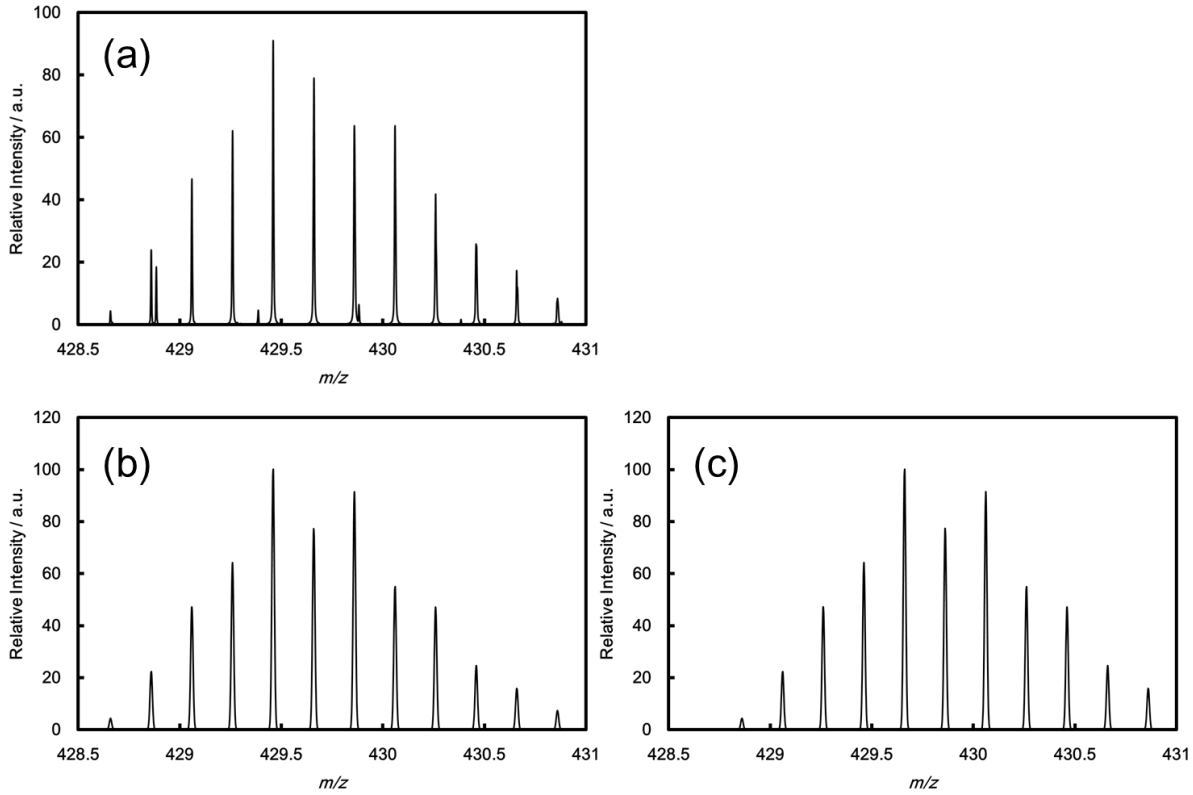

Figure S4 ESI- mass spectra of Tb-Yb-TCAS ternary system for $Tb_2Yb_1TCAS_2$ part.

(a) $[Tb^{III}] = [Yb^{III}] = 15$ μM, [TCAS] = 20 μM, pH 9.3 (adjusted with NH_3),

(b) Calculated for $[Tb^{n+} + Tb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 4 + 4$),

(c) Calculated for $[Tb^{n+} + Tb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + 2H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$).

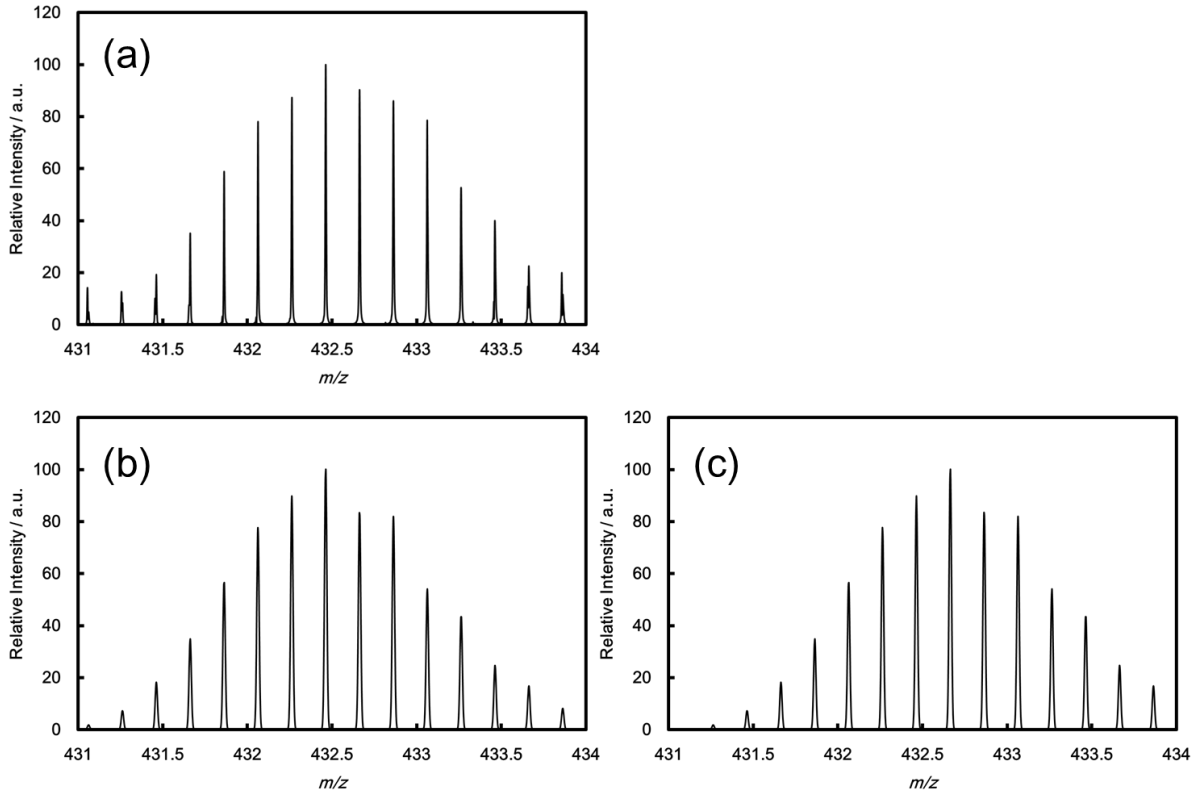

Figure S5 ESI-mass spectra of Tb-Yb-TCAS ternary system for $Tb_1Yb_2TCAS_2$ part.

(a) $[Tb^{III}] = [Yb^{III}] = 15$ μM, [TCAS] = 20 μM, pH 9.3 (adjusted with NH_3),

(b) Calculated for $[Tb^{n+} + Yb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 4 + 4$),

(c) Calculated for $[Tb^{n+} + Yb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + 2H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$).

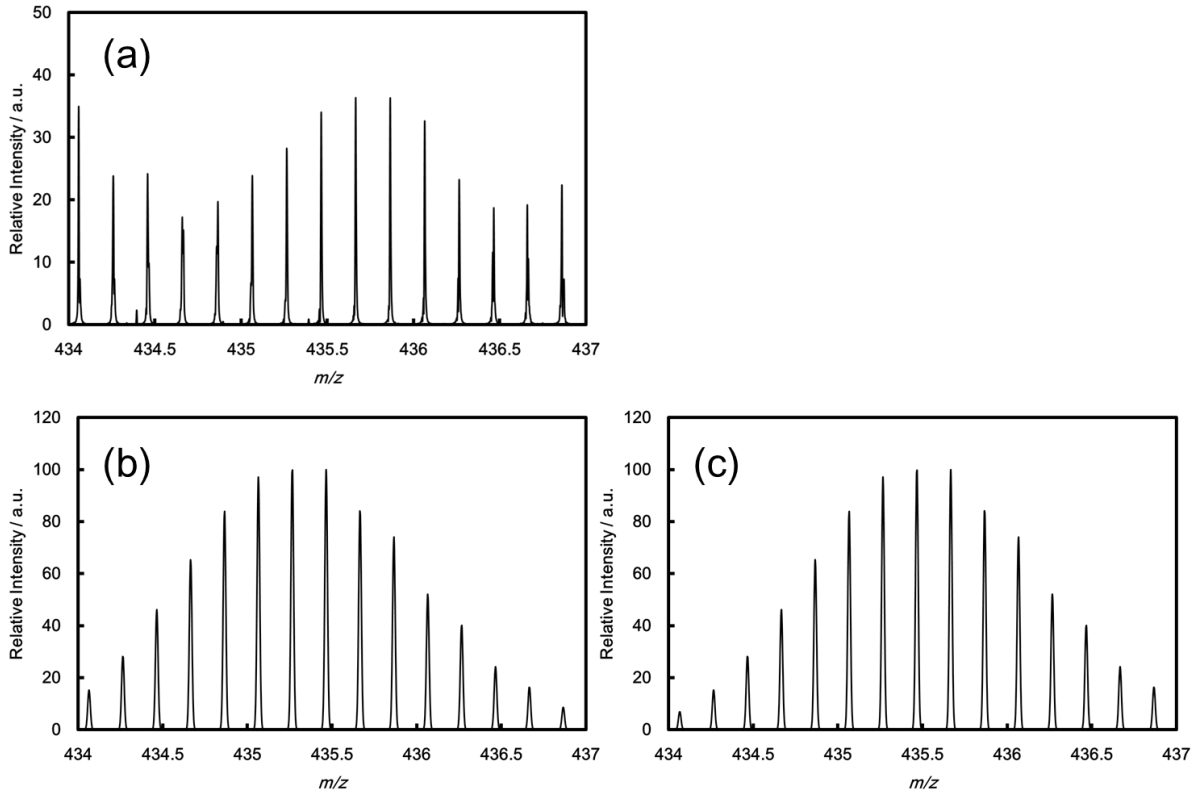

Figure S6 ESI- mass spectra of Tb-Yb-TCAS ternary system for Yb_3TCAS_2 part.

(a) $[Tb^{III}] = [Yb^{III}] = 15$ μM, [TCAS] = 20 μM, pH 9.3 (adjusted with NH_3),

(b) Calculated for $[Yb^{n+} + Yb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 4 + 4$),

(c) Calculated for $[Yb^{n+} + Yb^{m+} + Yb^{l+} + 2TCAS^{8-} + Na^{+} + 2H^{+} + O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$).

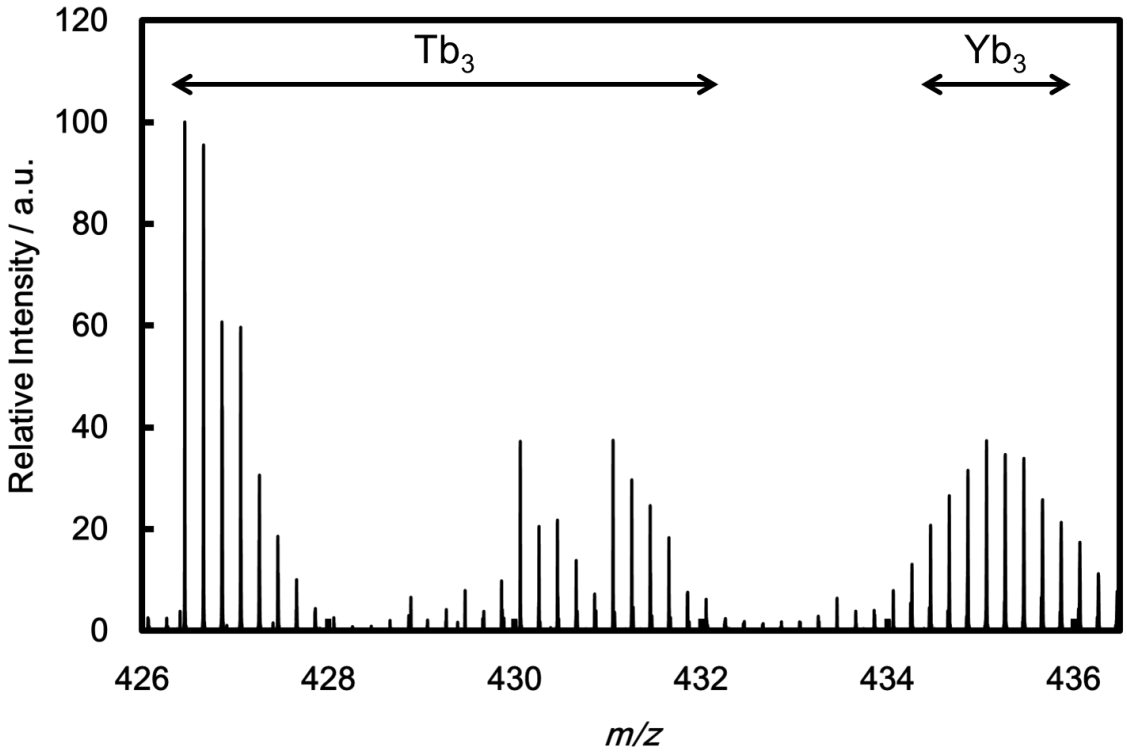

Figure S7 ESI- mass spectra of mixture of Tb_3TCAS_2 and Yb_3TCAS_2 binary systems after mixing immediately.

$[Tb^{III}] = [Yb^{III}]$ = 30 μM, [TCAS] = 40 μM, (as $[Tb_3TCAS_2] = [Yb_3TCAS_2]$ = 10 μM), pH 9.3 (adjusted with NH_3).

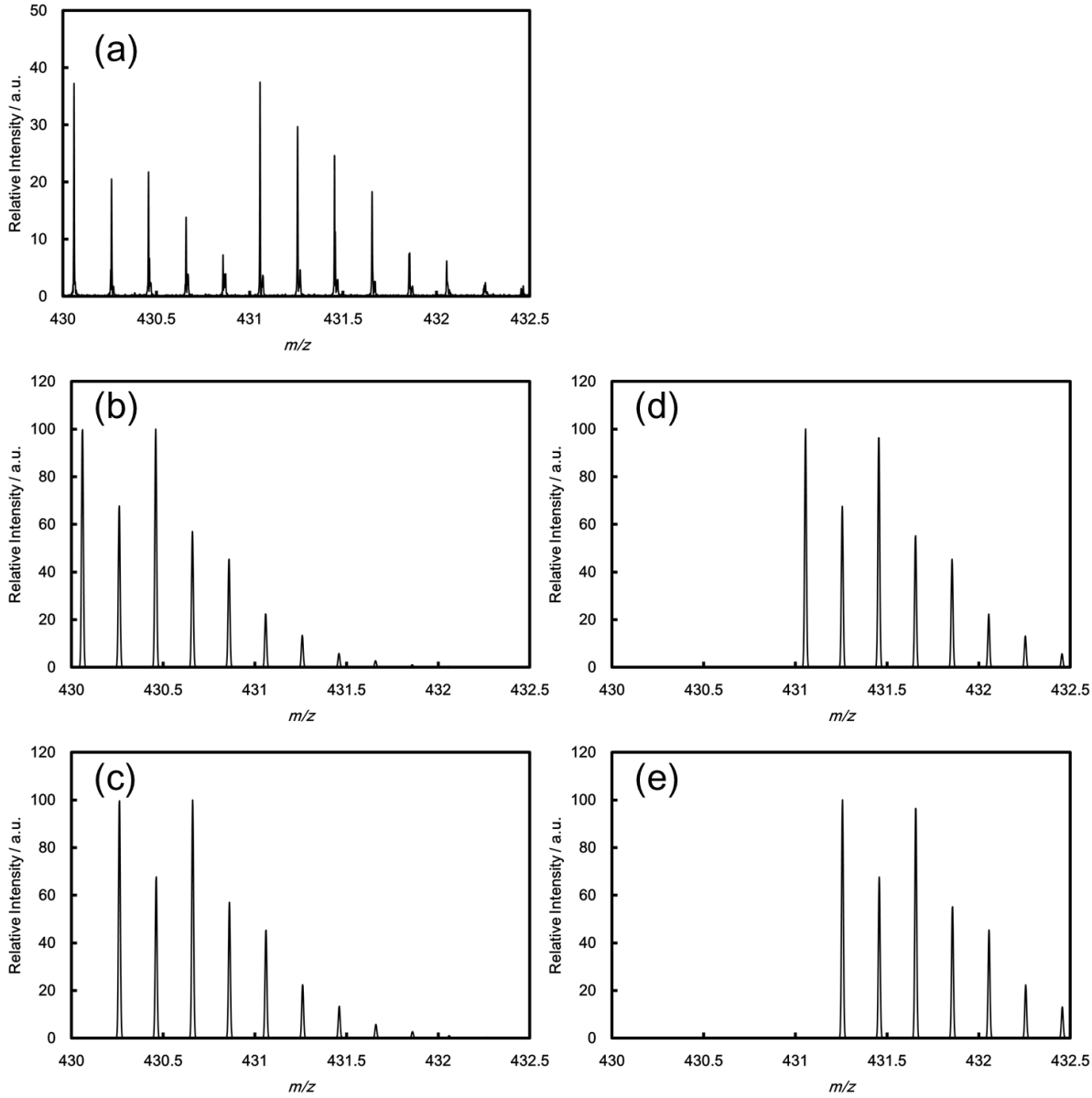

Figure S8 ESI- mass spectra of mixture of Tb_3TCAS_2 and Yb_3TCAS_2 binary systems after mixing immediately for 430–432.5 regions.

(a) $[Tb^{III}] = [Yb^{III}] = 30$ μM, [TCAS] = 40 μM, (as $[Tb_3TCAS_2] = [Yb_3TCAS_2] = 10$ μM), pH 9.3 (adjusted with NH_3),

(b) Calculated for $[Tb^{n+} + Tb^{m+} + Tb^{l+} + 2TCAS^{8-} + Na^+ + 3H^+ + 2O^{2-}]^{5-}$ ($n + m + l = 3 + 4 + 4$),

(c) Calculated for $[Tb^{n+} + Tb^{m+} + Tb^{l+} + 2TCAS^{8-} + Na^+ + 4H^+ + 2O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$),

(d) Calculated for $[Tb^{n+} + Tb^{m+} + Tb^{l+} + 2TCAS^{8-} + 2Na^+ + H^+ + O^{2-}]^{5-}$ ($n + m + l = 3 + 3 + 4$),

(d) Calculated for $[3Tb^{3+} + 2TCAS^{8-} + 2Na^+ + 2H^+ + O^{2-}]^{5-}$.

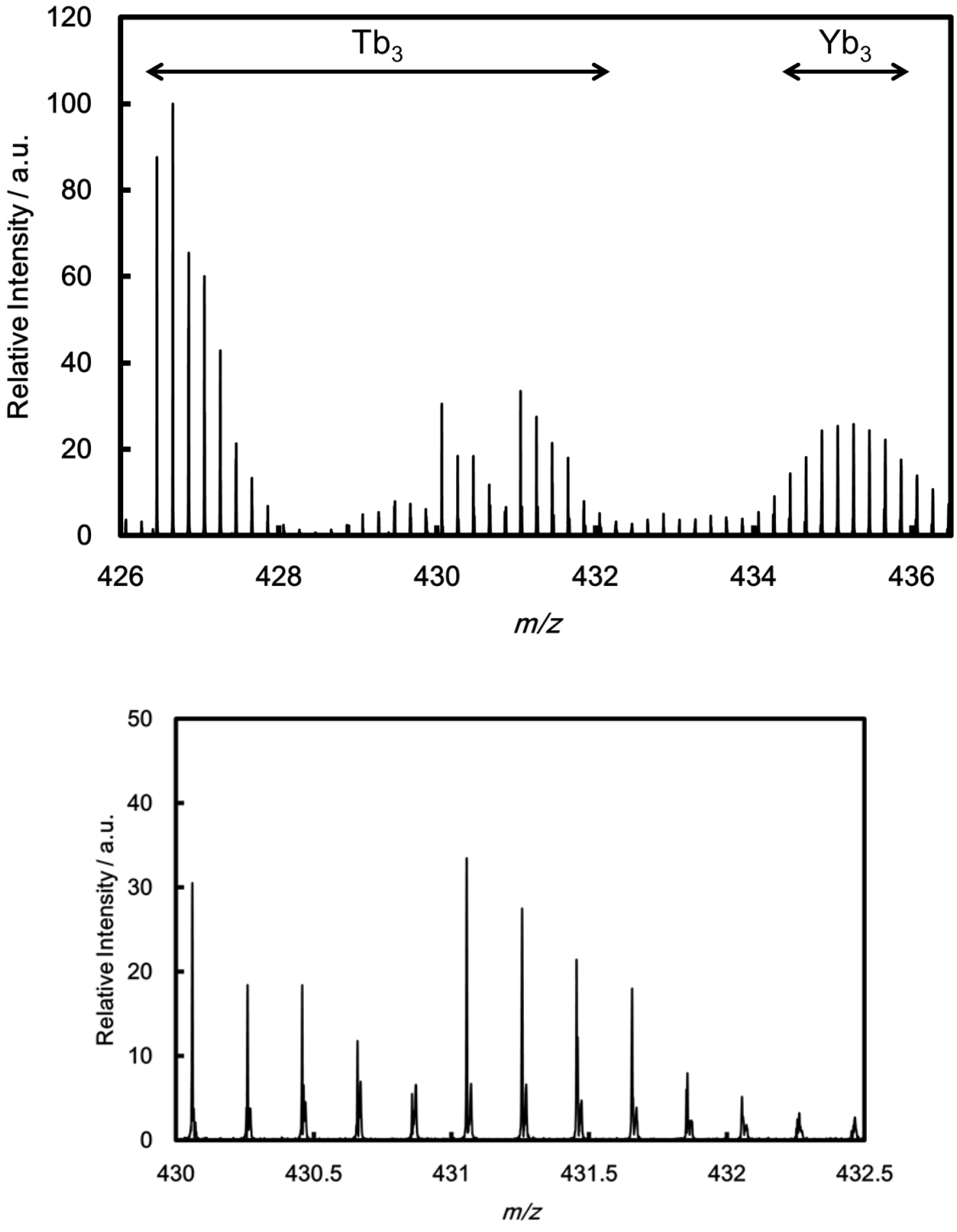

Figure S9 ESI- mass spectra of mixture of Tb_3TCAS_2 and Yb_3TCAS_2 binary systems after mixing after 7 days (up: *m*/*z* = 426–436.5, bottom: *m*/*z* = 430–432.5).
$[Tb^{III}] = [Yb^{III}]$ = 30 μM, [TCAS] = 40 μM, (as $[Tb_3TCAS_2] = [Yb_3TCAS_2]$ = 10 μM), pH 9.3 (adjusted with NH_3).

Reference

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

2 U. Roethlisberger, *iMass for Mac OS X*, **2002**.