Electronic Supplementary Information

Heterotrilanthanide Cluster Complexes Exhibiting Up-conversion Luminescence in Water

Ryunosuke Karashimada, Koki Musha, Nobuhiko Iki

Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aramaki-aoba, Aoba-ku, Sendai 980-8579 Japan.

Table of Contents

1 Experimental

1-1 Materials

A stock solution of 0.01 M $Ln(NO_3)_3$ (Ln = Yb, Er, Tb) was prepared by dissolving $Ln(NO_3)_3$ with 99.95% purity (Kanto Chemical Company, Inc.) in 0.01 M HNO_3. The concentrations of the metal ions in the stock solutions were determined using commonly accepted chelatometry. Thiacalix[4]arene-*p*-tetrasulfonate (TCAS) was synthesized as previously reported[1] and stocked in a 0.01 M aqueous solution. 2-[4-(2-Hydroxyethyl)-1-pyperadinyl]ethanesulfonic acid (HEPES, Dojindo Laboratories), N-cyclohexyl-3-aminopropanesulfonic acid (CAPS, Dojindo Laboratories), and NH_3 solution (Kanto Chemical Company, Inc.) were used as a buffer solution by adjusting the pH with NaOH, and then diluting the solution in an appropriate water volume. Acetonitrile (CH_3CN, Kanto Chemical Company, Inc.) was used as an eluent by mixing it with pure water. Tetrabutylammonium bromide (TBABr, FUJIFILM Wako Pure Chemical Corporation, Ltd.) was used as an ion-pairing reagent.

1-2 Equipment

High-performance liquid chromatography (HPLC) was performed using a SHIMADZU LC-20AD pump and a SHIMADZU SPD-20A UV-Vis detector equipped with a Mightysil RP-18II column. Electro-spray ionization mass spectrometry (ESI-MS) was conducted using a SolariX 9.4T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer (Bruker). The mass spectra were analyzed using the software iMass for Mac OS X ver. 1.1 (U. Roethlisberger, iMass for Mac OS X to be found http://home.datacomm.ch/marvin/iMass/). The excitation and emission spectra in the near-infrared region were obtained using a FluoroLog–®3 model FL3-11 spectrofluorometer (HORIBA Jobin Yvon Inc.) equipped with a 450 W Xe lamp as the excitation source and an InGaAs semiconductor detector (DSS-IGA020L). A spectrofluorometer F-7000 (Hitachi, Ltd.) combined with a 972 nm NIR laser (LE1166SPOLD, Hamamatsu Photonics) was used to record the UC luminescence in the visible region. The pH values of the sample solutions were measured using a TOA HM-25R pH meter equipped with a glass electrode. The luminescent decay curves were monitored using an LSP-1000 (UNISOKU Co., Ltd.) combined with a pulsed N_2 laser (337.1 nm, 3.5 ns) as the excitation source and fitted using the nonlinear least-squares method.

1-3 Preparation and measurement of sample solution

Solutions of $Ln(NO_3)_3$ (Ln = Yb or Er), TCAS, and HEPES were mixed and stood 24 h at room temperature to prepare homotrinuclear complexes ([Ln] = 2.5 μM, [TCAS] = 5.0 μM, [HEPES] = 10 mM, pH 7.4). Additionally, a mixture of two types of Ln salts (i.e., Er–Yb or Tb–Yb pairs) was used to prepare heterotrinuclear Ln–Ln'–TCAS systems ([Ln] = [Ln'] = 2.5 μM, [TCAS] = 5.0 μM, [HEPES] = 10 mM, pH 7.4). The NH_3 solution was used instead of the HEPES solution and stood 60 °C to prepare a high concentration sample to observe UC luminescence

([Ln] = [Ln'] = 1.5 mM, [TCAS] = 2.0 mM, [NH_3] = 0.1 M, pH 10). The sample solutions were diluted to the optimal conditions for HPLC measurements, ESI mass spectrometry, spectrophotometry, or lifetime analysis. In HPLC measurements, an eluent consisting of 45 wt% CH_3CN in H_2O with 10 mmol/kg HEPES (apparent pH 7.4) and 30 mmol/kg TBABr was used. The flow rate was set to 1.5 mL/min, and 20 μL of the sample solution was injected using a sample loop. In ESI-MS measurements, an appropriate amount of CH_3CN was added to the sample solution, and the mass spectra were acquired in negative ion mode.

2 Estimation of the Yb-centered luminescence intensity

According to Fig. 2, we mainly discussed the ratio of the intensity of the NIR luminescence (Yb-centered luminescence) between Yb–TCAS and Er–Yb–TCAS system based on the concentration of Yb ion. On the other hand, the ratio of that based on the concentration of Ln_3TCAS_2 complex (7.6 times) was additionally written in the manuscript without the detailed calculation. Here, we explain that the estimation of the ratio of the Yb-centered luminescence based on the concentration of Yb_3TCAS_2 complex and $Er_2Yb_1TCAS_2$ complex or $Er_1Yb_2TCAS_2$ complex is as below.

Firstly, under the condition in Fig. 2, the concentration of the Yb_3TCAS_2 for the Yb–TCAS system is approximately 0.833 μM ([Yb] = 2.5 μM, [TCAS] = 5.0 μM). In the Er–Yb–TCAS system, the total concentration of homo- and heterotrinuclear complexes ($[Er_{3-x}Yb_xTCAS_2] = [Er_3TCAS_2] + [Er_2Yb_1TCAS_2] + [Er_1Yb_2TCAS_2] + [Yb_3TCAS_2]$) for Er–Yb–TCAS system is approximately 1.67 μM ([Er] = [Yb] = 2.5 μM, [TCAS] = 5.0 μM). Since these systems contain an excess amount of TCAS, the Ln_3TCAS_2 complex is formed quantitatively. In the Er–Yb–TCAS system, the ratio of $[Er_3TCAS_2]$:$[Er_2Yb_1TCAS_2]$:$[Er_1Yb_2TCAS_2]$:$[Yb_3TCAS_2]$ is 1:3:3:1, based on the binomial distribution. The concentrations of each complex are:

$[Er_3TCAS_2] = 1.67\ \mu M \times 1/8 \approx 0.21\ \mu M$

$[Er_2Yb_1TCAS_2] = 1.67\ \mu M \times 3/8 \approx 0.625\ \mu M$

$[Er_1Yb_2TCAS_2] = 1.67\ \mu M \times 3/8 \approx 0.625\ \mu M$

$[Yb_3TCAS_2] = 1.67\ \mu M \times 1/8 \approx 0.21\ \mu M$

The contribution of the Yb-centered luminescence from Yb_3TCAS_2 in the Er–Yb–TCAS system ($I_{Yb3TCAS2inEr–Yb–TCAS}$) is:

$$I_{Yb3TCAS2inEr–Yb–TCAS} = I_{Yb–TCAS} \times 0.21/0.833 = 2.08 \times 0.21/0.833 = 0.52$$

The net Yb-centered luminescence of $Er_2Yb_1TCAS_2$ and $Er_1Yb_2TCAS_2$ complexes ($I_{ErYbTCAS} = I_{Er2Yb1TCAS} + I_{Er1Yb2TCAS}$) is:

$$I_{ErYbTCAS} = I_{Er\text{-}Yb\text{-}TCAS} - I_{Yb3TCAS2inEr\text{-}Yb\text{-}TCAS} = 0.93 - 0.52 = 0.41$$

$$I_{Er2Yb1TCAS} = I_{Er1Yb2TCAS} = I_{ErYbTCAS} / 2 = 0.41 / 2 = 0.205$$

Finally, since the concentration of the complex for the $I_{Yb\text{-}TCAS}$, $I_{Er2Yb1TCAS}$, and $I_{Er1Yb2TCAS}$ were different, $I_{Yb\text{-}TCAS}$, $I_{Er2Yb1TCAS}$, and $I_{Er1Yb2TCAS}$ are normalized.

$$I_{Yb\text{-}TCAS} / [Yb_3TCAS_2] = 2.08 / 0.833 = 2.496\ \text{a.u.}/\mu M$$

$$I_{Er2Yb1TCAS} / [Er_2Yb_1TCAS_2] = I_{Er1Yb2TCAS} / [Er_1Yb_2TCAS_2]) = 0.205 / 0.625 = 0.328\ \text{a.u.}/\mu M$$

Thus, the ratio of the intensity for the Yb-centered luminescence of the Yb–TCAS system compared with that of the Er–Yb–TCAS system is:

$$2.496 / 0.328 \approx 7.6$$

In conclusion, the intensity of the Yb-centered luminescence for the Yb–TCAS system (Yb_3TCAS_2) was approximately 7.6 times higher than that of the Er–Yb–TCAS system ($Er_2Yb_1TCAS_2$ or $Er_1Yb_2TCAS_2$), which reflect the effect by the Yb→Er energy transfer.

3 Lists of Figures and Tables

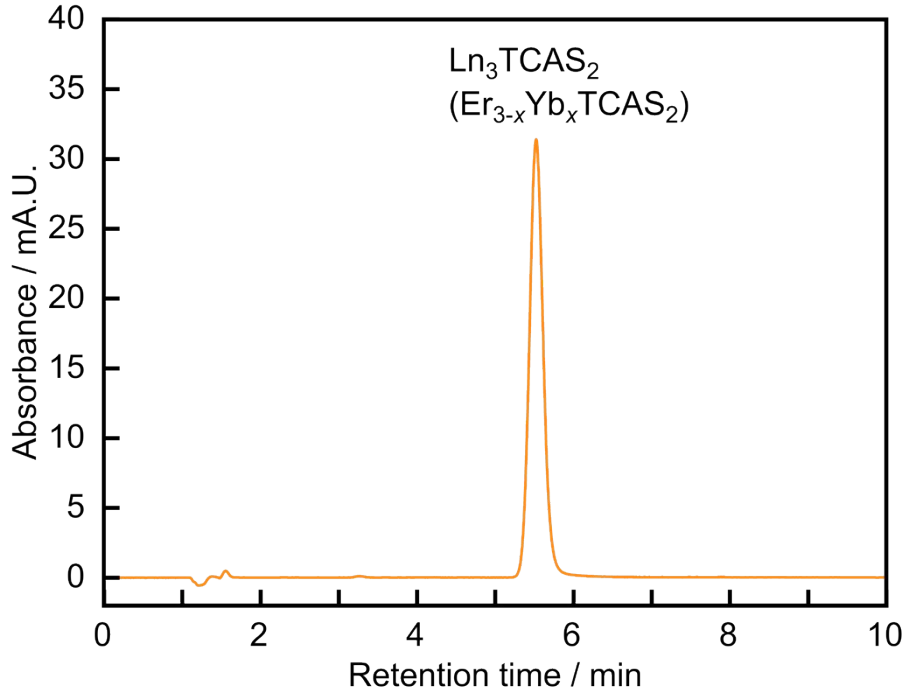

Fig. S1 Chromatogram of Er–Yb–TCAS system. [Er] = [Yb] = 1.5 mM, [TCAS] = 2.0 mM, [NH_3] = 0.1 M, pH 10, λ = 316 nm.

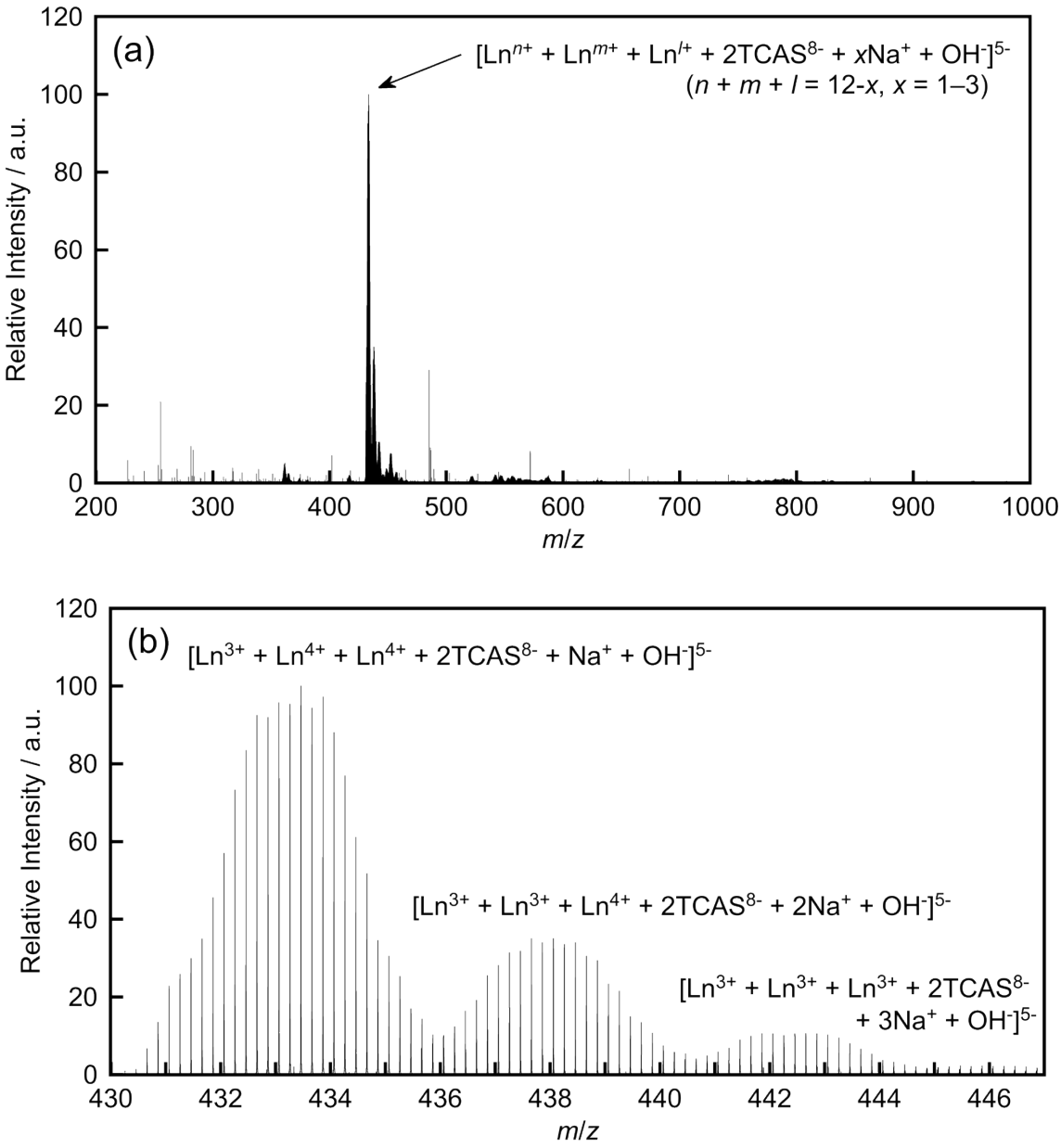

Fig. S2 ESI mass spectra of the Er–Yb–TCAS system. [Er] = [Yb] = 1.5 mM, [TCAS] = 2.0 mM, [NH_3] = 0,1 M, pH 10. (a) observed isotopic distribution m/z 200–1000 and (b) expanded observed isotopic distribution m/z 430–447.

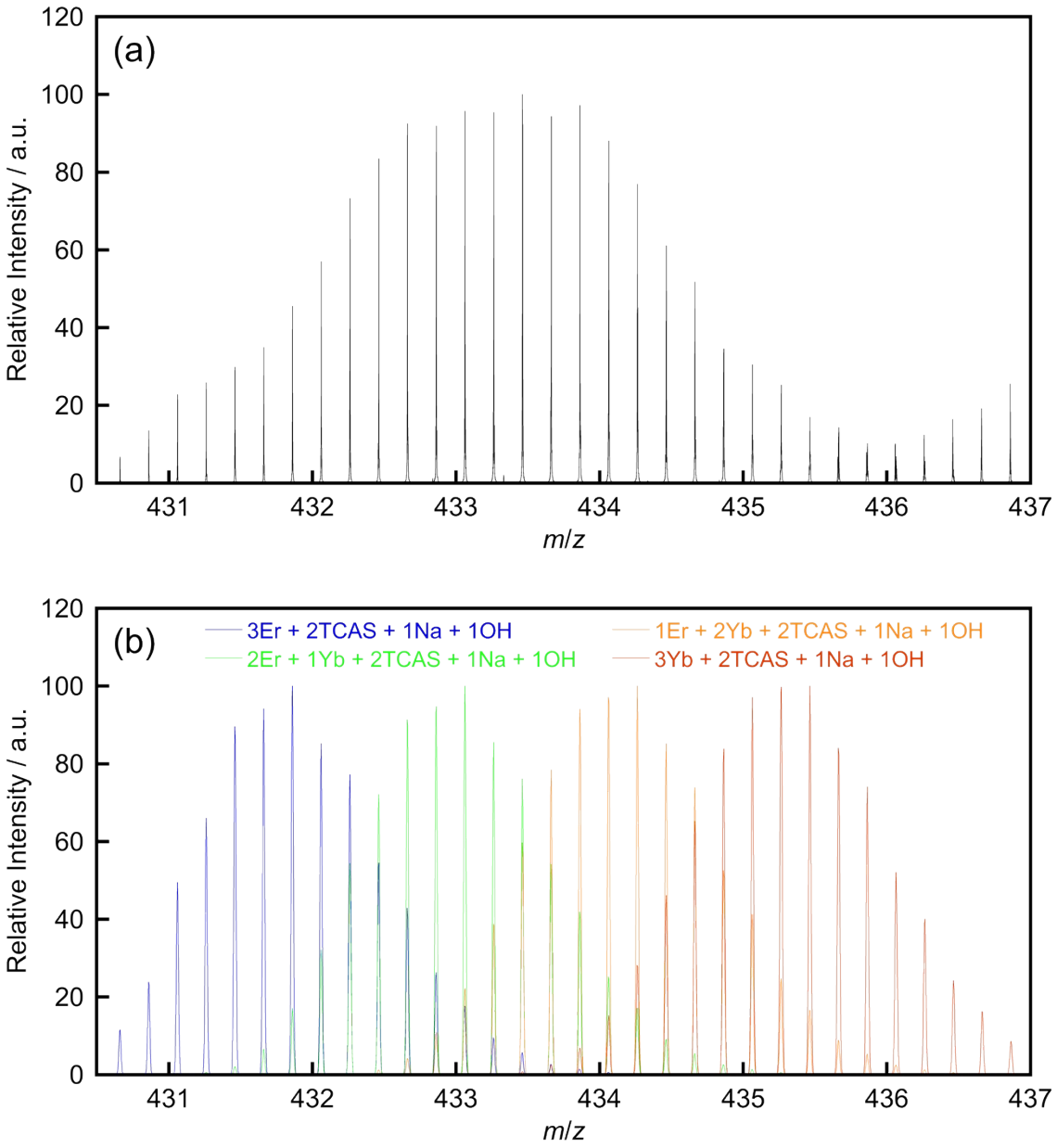

Fig. S3 ESI mass spectra of the Er–Yb–TCAS system. (a) Observed isotopic distribution around *m*/*z* 430.5–437 and (b) Calculated isotopic distribution for $\{[Er_{3-x}Yb_xTCAS_2]^{5-} + 1Na^+ + 1OH^-\}^{5-}$ (x = 0–3).

Table S1 The assignment of the observed peaks around *m*/*z* 430.5–437.

Observed *m*/*z*	Calculation *m*/*z*	Assignment	difference / ppm
431.8618	431.8624	$[Er_3TCAS_2]^{5-} + 1Na^+ + 1OH^-$	–1.28
433.0633	433.0634	$[Er_2Yb_1TCAS_2]^{5-} + 1Na^+ + 1OH^-$	–0.25
434.2647	434.2633	$[Er_1Yb_2TCAS_2]^{5-} + 1Na^+ + 1OH^-$	3.29
435.4661	435.4651	$[Yb_3TCAS_2]^{5-} + 1Na^+ + 1OH^-$	2.30

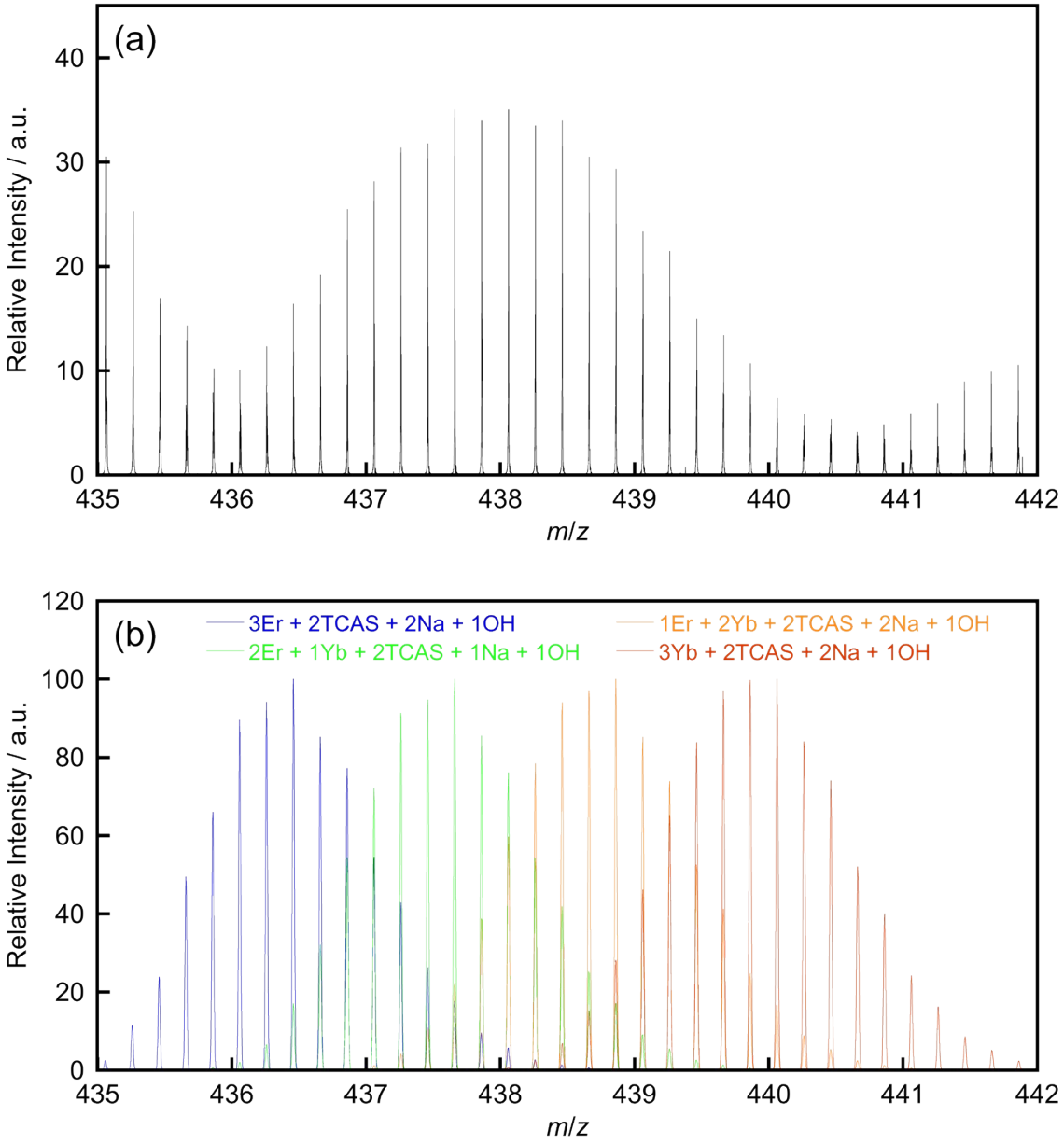

Fig. S4 ESI mass spectra of the Er–Yb–TCAS system. (a) Observed isotopic distribution around *m*/*z* 435–442 and (b) Calculated isotopic distribution for $\{[Er_{3-x}Yb_xTCAS_2]^{6-} + 2Na^+ + 1OH^-\}^{5-}$ (x = 0–3).

Table S2 The assignment of the observed peaks around *m*/*z* 435–442.

Observed *m*/*z*	Calculation *m*/*z*	Assignment	difference / ppm
436.4599	436.4604	$[Er_3TCAS_2]^{6-} + 2Na^+ + 1OH^-$	–1.12
437.6633	437.6614	$[Er_2Yb_1TCAS_2]^{6-} + 2Na^+ + 1OH^-$	4.23
438.8627	438.8612	$[Er_1Yb_2TCAS_2]^{6-} + 2Na^+ + 1OH^-$	3.32
440.0640	440.0630	$[Yb_3TCAS_2]^{6-} + 2Na^+ + 1OH^-$	2.18

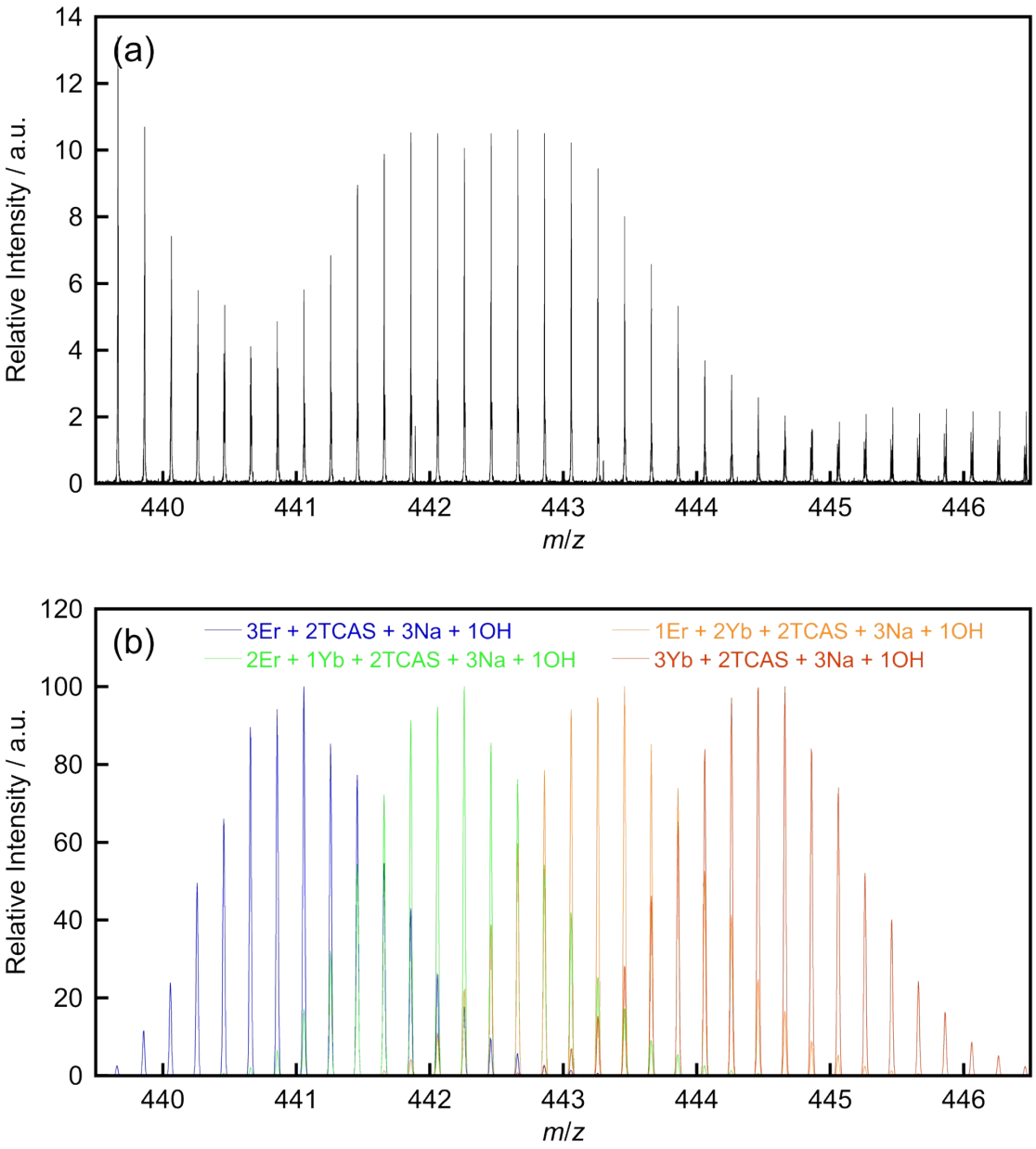

Fig. S5 ESI mass spectra of the Er–Yb–TCAS system. (a) Observed isotopic distribution around *m/z* 439–447 and (b) Calculated isotopic distribution for $\{[Er_{3-x}Yb_xTCAS_2]^{7-} + 3Na^+ + 1OH^-\}^{5-}$ (x = 0–3).

Table S3 The assignment of the observed peaks around *m/z* 439–447.

Observed *m/z*	Calculation *m/z*	Assignment	difference / ppm
441.0581	441.0583	$[Er_3TCAS_2]^{7-} + 3Na^+ + 1OH^-$	–0.40
442.2598	442.2593	$[Er_2Yb_1TCAS_2]^{7-} + 3Na^+ + 1OH^-$	1.09
443.4610	443.4592	$[Er_1Yb_2TCAS_2]^{7-} + 3Na^+ + 1OH^-$	4.09
444.6627	444.6610	$[Yb_3TCAS_2]^{7-} + 3Na^+ + 1OH^-$	3.84

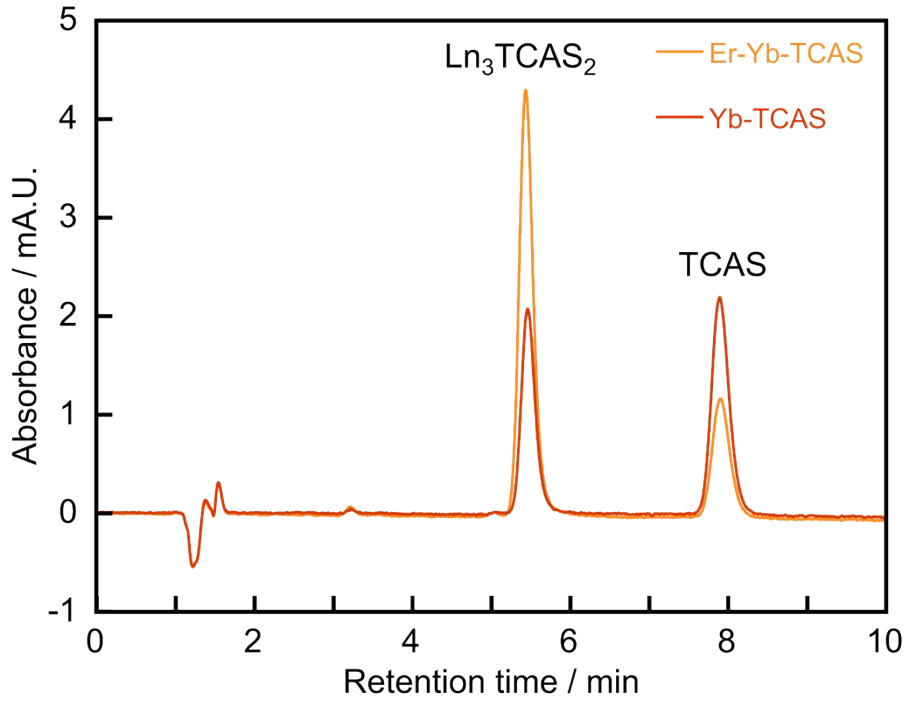

Fig. S6 Chromatograms of Er–Yb–TCAS and Yb–TCAS systems. Er–Yb–TCAS system: [Er] = [Yb] = 2.5 μM, , [TCAS] = 5.0 μM, [HEPES] = 10 mM, pH 7.4, λ = 316 nm, Yb–TCAS system: [Yb] = 2.5 μM, [TCAS] = 5.0 μM, [HEPES] = 10 mM, pH 7.4, λ = 316 nm.

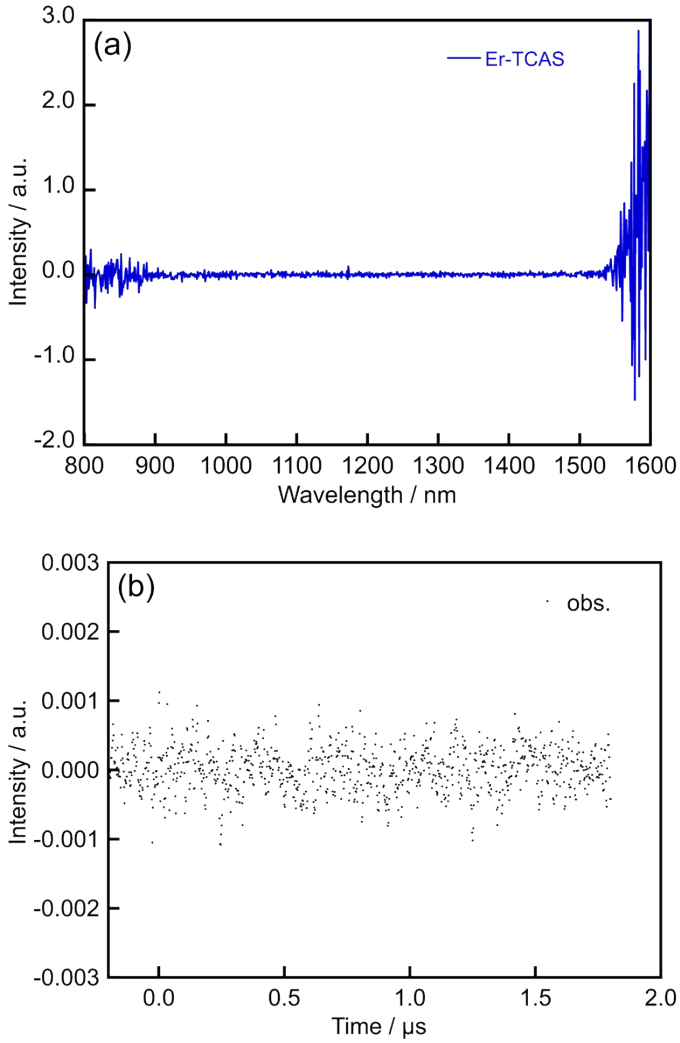

Fig. S7 (a) Emission spectra and (b) decay curve of the Er–TCAS system. [Er] = 30 μM, [TCAS] = 20 μM, [HEPES] = 10 mM, pH 7.4, λ_{ex} = 313 nm for (a), and 337.1 nm for (b).

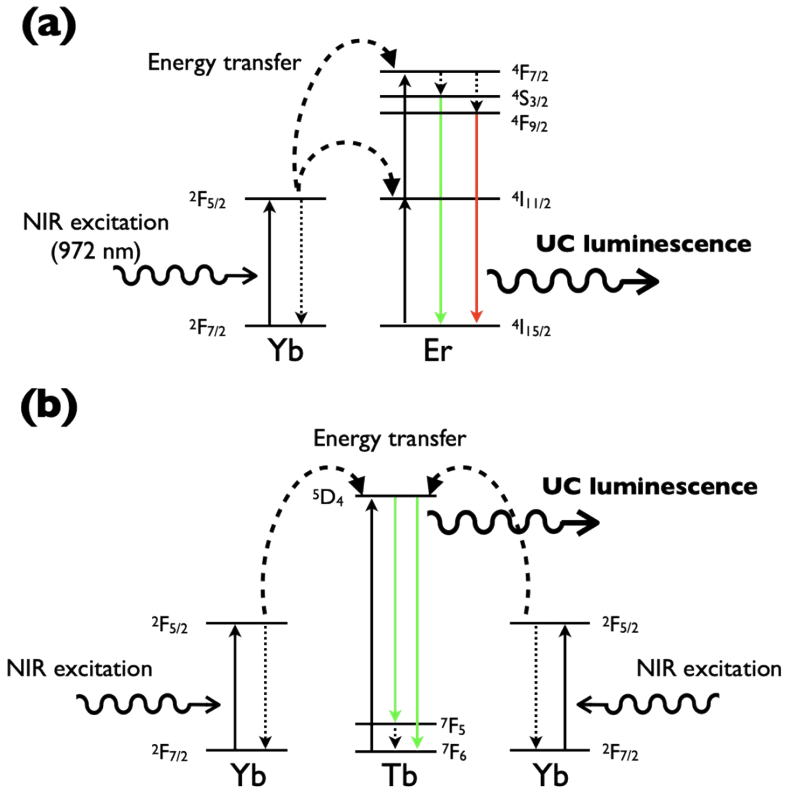

Fig. S8 Energy diagrams and proposed energy transfer paths for UC luminescence in (a) Er–Yb–TCAS and (b) Tb–Yb–TCAS systems.

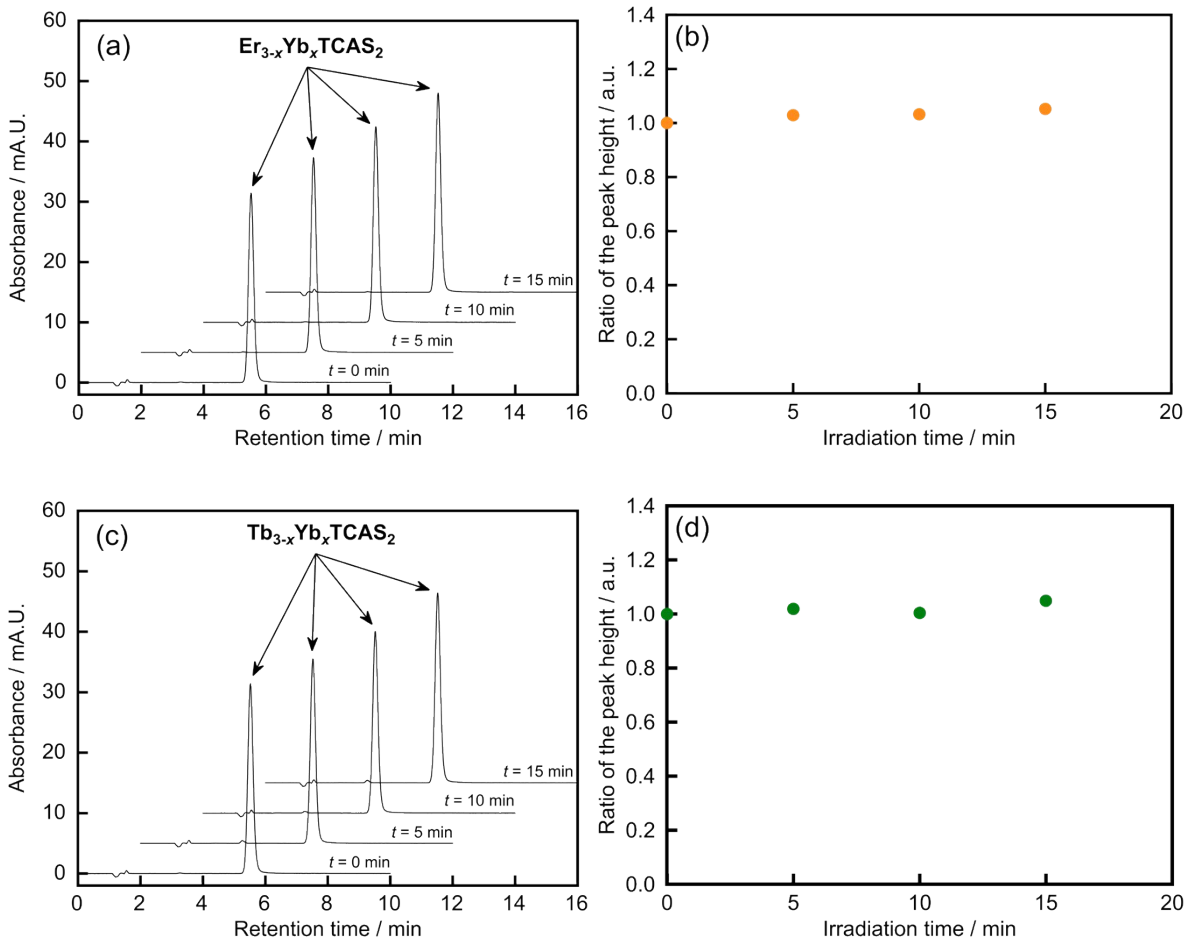

Fig. S9 The stability against NIR laser irradiation (λ = 972 nm, P = 2.2 W). Time-dependence of chromatograms (a) and of the normalized peak height for $Er_{3-x}Yb_xTCAS_2$ (x = 0–3) (b) in the Er–Yb–TCAS system. [Er] = [Yb] = 1.5 mM, [TCAS] = 2.0 mM, [NH_3] = 0.1 M, pH 10, λ = 316 nm, irradiation time t = 0–15 min. Time-dependence of chromatograms (c) and of the normalized peak height for $Tb_{3-x}Yb_xTCAS_2$ (x = 0–3) (d) in the Tb–Yb–TCAS system. [Tb] = [Yb] = 1.5 mM, [TCAS] = 2.0 mM, [NH_3] = 0.1 M, pH 10, λ = 316 nm, irradiation time t = 0–15 min.