Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information (ESI)

Alkyl ammonium ion-induced unusual emission enhancement of Eu(*D*-facam)$_3$ in 1-butanol

Haruki Minami, Mayu Miyazato, Ziying Li, Kazuki Nakamura, Norihisa Kobayashi*

Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522 Japan
E-mail: koban@faculty.chiba-u.jp

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1. Experimental

1-1. Reagents

All the chemicals were commercially available and used as received. Europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate] (Eu(*D*-facam)$_3$) was purchased from Sigma-Aldrich, Japan. Ammonium salts [tetramethylammonium chloride (TBACl), tetraethylammonium chloride (TEACl), tetrabutylammonium chloride (TBACl), and tetrapropylammonium chloride (TPACl)] were purchased from Tokyo Chemical Industry Co. Ltd., Japan. 1-Butanol and 1-butanol-d_1 were purchased from Tokyo Chemical Industry Co. Ltd., Japan and used as the solvent.

1-2. Preparation of Eu(*D*-facam)$_3$/alkylammonium solutions

Eu(*D*-facam)$_3$/alkylammonium solutions were prepared by mixing Eu(*D*-facam)$_3$ and each alkylammonium salt (TMACl, TEACl, TBACl, and TPACl) in 1-butanol or 1-butanol-d_1. The molar ratios of Eu(*D*-facam)$_3$ and alkylammonium salts ([Eu(*D*-facam)$_3$]:[alkylammonium salt]) were 1:0, 1:1, 1:3, 1:5, and 1:10. The concentration of Eu(*D*-facam)$_3$ was fixed at 0.1 mmol/L.

1-3. Measurements of optical properties

Oxygen in the Eu(*D*-facam)$_3$/alkylammonium solutions were removed by bubbling nitrogen gas before optical measurements. Absorbance and CD spectra of Eu(*D*-facam)$_3$/TMACl were acquired using a photonic multichannel analyzer (J-1100, JASCO Corporation, Japan). Electrospray ionization-mass spectrometry (ESI-MS) spectra were recorded using Exactive (Thermo Fisher Scientific, United States). FT-IR spectra of Eu(*D*-facam)$_3$/TMACl were acquired using an FTIR 680 spectrophotometer, JASCO Corporation, Japan. Photoluminescence spectra were acquired using a spectrofluorometer (FP-6600, JASCO Corporation, Japan). Emission quantum yields were calculated from the data obtained from an absolute PL quantum yield spectrometer (Quantaurus-QY C11347-01, Hamamatsu photonics K. K., Japan). The emission lifetimes were determined using a time-resolved fluorescence spectrometer (Quantaurus-Tau C11367-21, Hamamatsu photonics K. K., Japan). CPL measurements were conducted using the previously reported system.* This system consists of the following components: 375 nm LED (M365L2, Thorlabs Japan Inc., Japan), LED driver (DC2100, Thorlabs Japan Inc., Japan), photoelastic modulator (PEM-90, Hinds instruments, Inc. United States), photomultiplier tube (H7732-10, Hamamatsu photonics K. K., Japan), linearly polarized cubic prism (200,000:1), photomultiplier tube (H7732-10, Hamamatsu photonics K. K., Japan), and dual phase DSP lock-in amplifier (7265, Signal Recovery Ltd., United Kingdom). The appropriate detection wavelength of the monochromator and the PEM was controlled by a PC.

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* H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.*, 2010, **12**, 2362–2365.

2. Emission change of Eu(*D*-facam)$_3$ upon the addition of TMACl

2-1. Emission spectra of Eu(*D*-facam)$_3$ alone solution

The emission spectrum of Eu(*D*-facam)$_3$ had sharp peaks at 579, 590, and 613 nm corresponding to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively, in Eu(III).

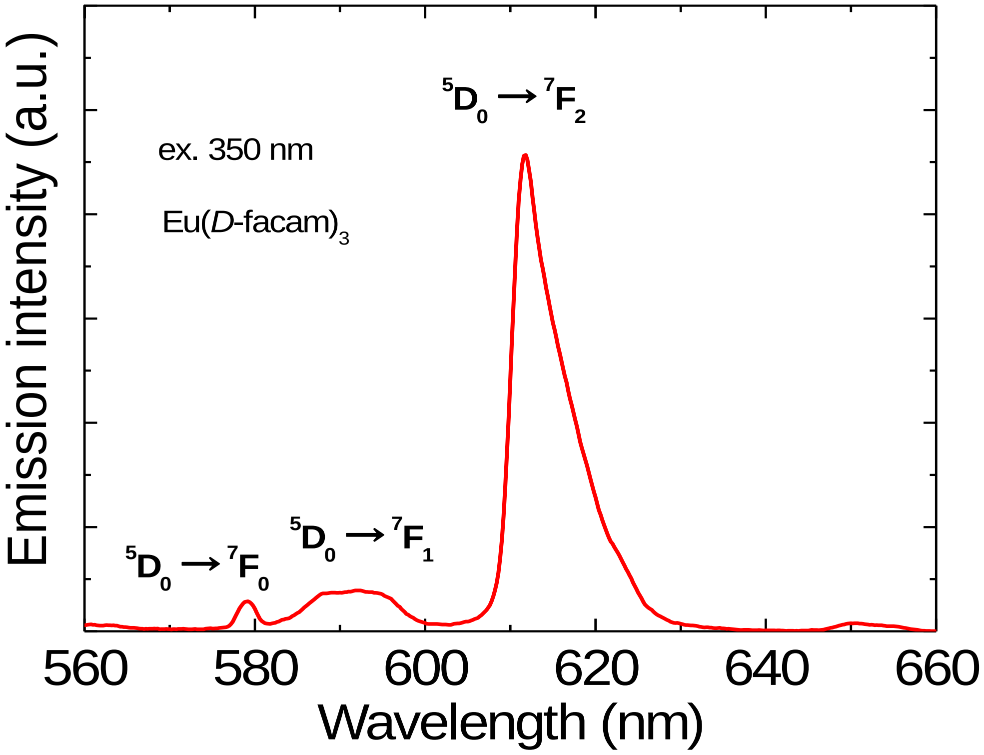


Figure S1. Emission spectrum of Eu(*D*-facam)$_3$ in 1-butanol. Excitation wavelength was 350 nm.

2-2. Saturated emission enhancement

The emission intensity increased with increasing concentrations of TMACl. The intensity saturated at [Eu(*D*-facam)$_3$]:[TMACl] = 1:100 and it was 150 times compared to the original one.

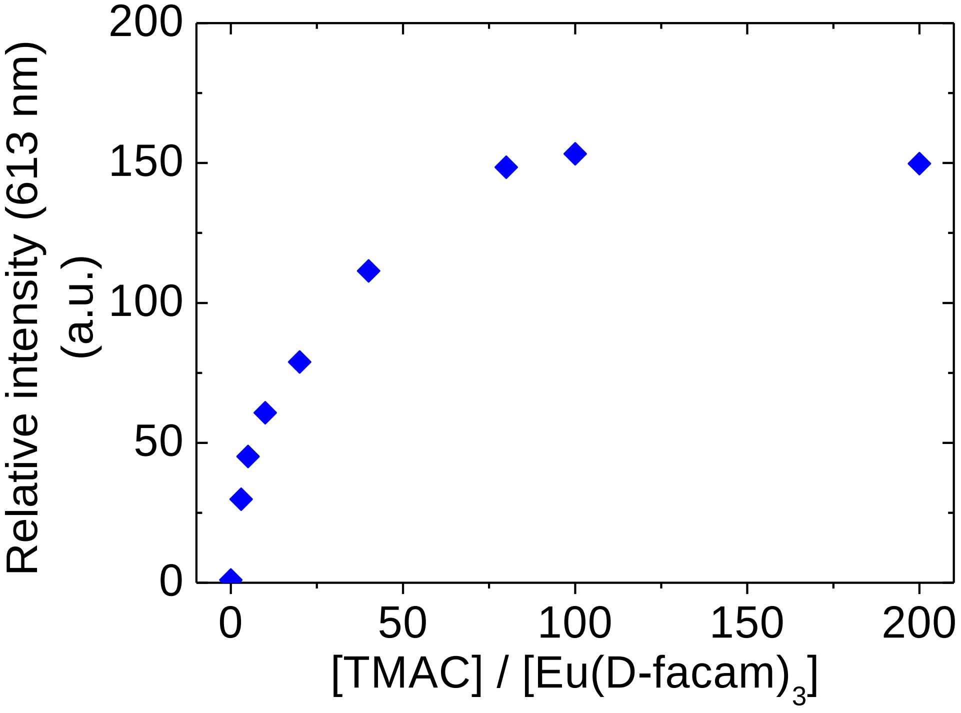


Figure S2. Change in the emission intensity of Eu(*D*-facam)$_3$ at 613 nm with increasing concentrations of TMACl.

3. Structual analysis of Eu(*D*-facam)$_3$/alkylammonium ions

3-1. Absorption and circular dichroism (CD) measurements

Absorption band at around 310 nm was attributed to the π-π* transition in the *D*-facam ligands. No significant change in the ligand absorption was observed upon the addition of TMACl or TBACl. Although there was no obvious change in the CD signal from the ligand upon the addition of TBACl, absorption maxima in the CD spectra shifted to longer wavelengths with increasing TMACl concentrations. This suggests a structural change in Eu(*D*-facam)$_3$ in the presence of TMACl.

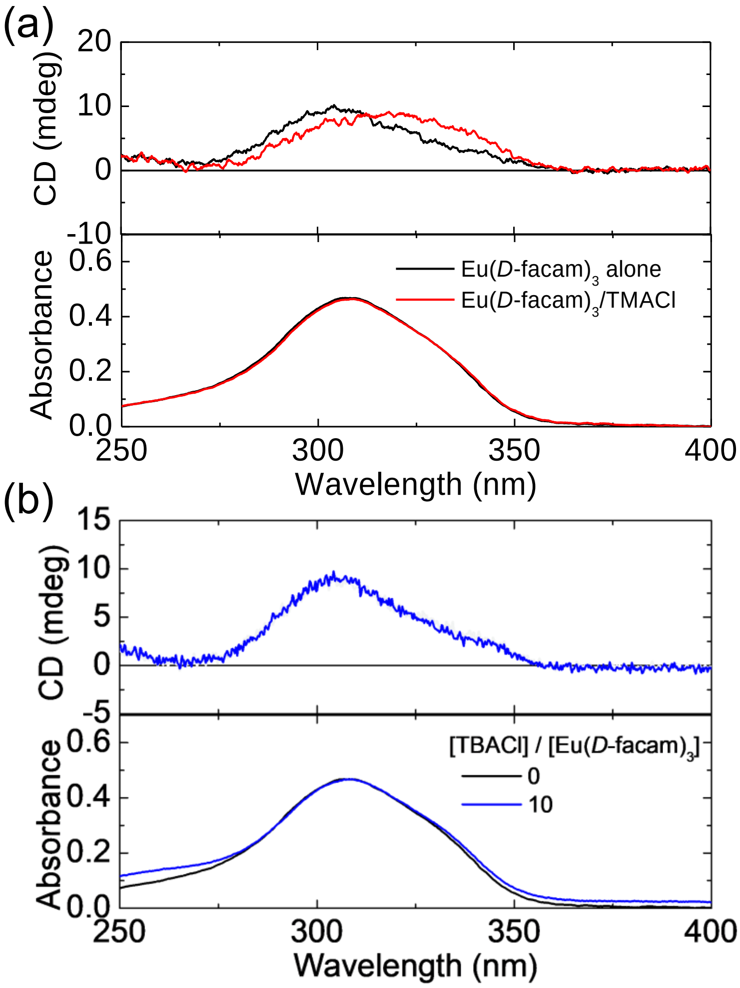


Figure S3. Absorbance (bottom) and CD (top) spectra of Eu(*D*-facam)$_3$/TMACl (a) and Eu(*D*-facam)$_3$/TBACl (b) solutions. The concentration of Eu(*D*-facam)$_3$ was fixed 0.1 mmol/L. Length of light path was set to 1 mm.

3-2. FT-IR spectra of Eu(D-facam)$_3$/TMACl

In the FT-IR spectrum of Eu(*D*-facam)^3, two peaks corresponding to the stretching vibration of conjugated bonds (C═C═C) in β-diketonate were observed at 1500–1600 cm^{-1}. These peaks merged into one broad peak at around 1500 cm^{-1} upon the addition of TMACl. Thus, it is considered that the bond length and/or angle between these bonds changed in the presence of TMACl.

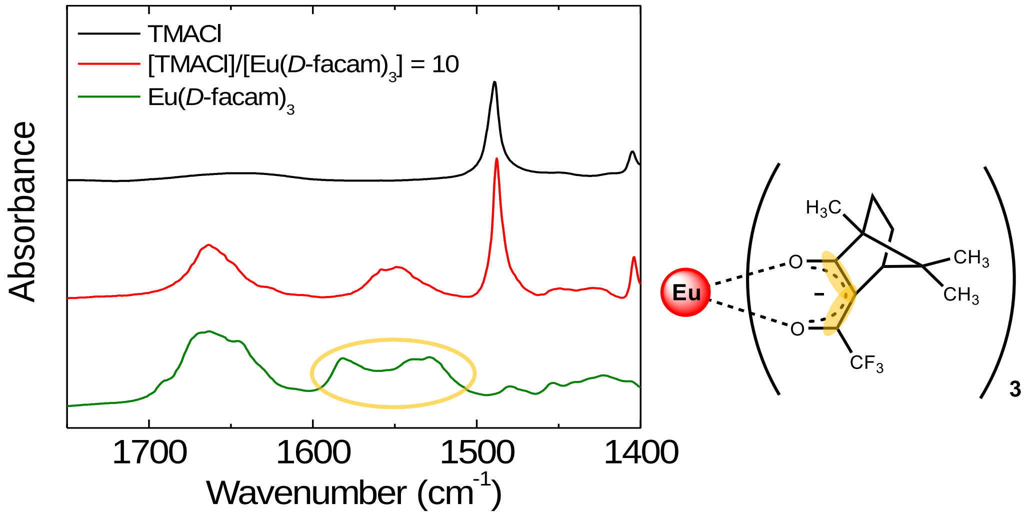
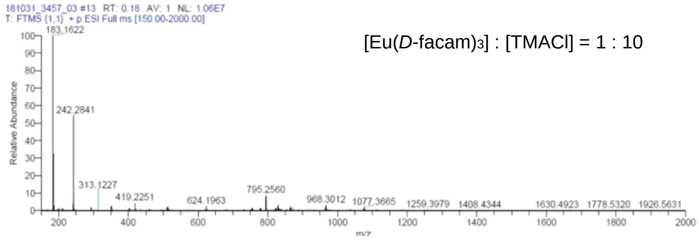


Figure S4. FT-IR spectra of Eu(*D*-facam)$_3$ and TMACl and Eu(*D*-facam)$_3$/TMACl.

3-3. ESI-MS analysis

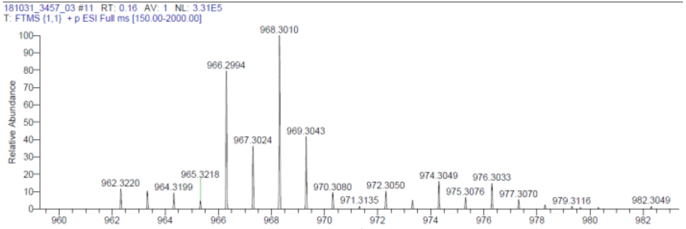
For the Eu(*D*-facam)$_3$/TMACl solution, m/z peaks corresponding to [Eu(*D*-facam)$_3$·TMA]$^+$ and [Eu(*D*-facam)$_3$·2TMA·Cl]$^+$ were observed. This suggested that Eu(*D*-facam)$_3$ and TMA$^+$ formed an associated structure in 1-butanol. No m/z peak due to the association of Eu(*D*-facam)$_3$ and TBA$^+$ was observed in the Eu(*D*-facam)$_3$/TBACl solution.

(a) MS spectrum of Eu(*D*-facam)$_3$/TMACl (measured values)

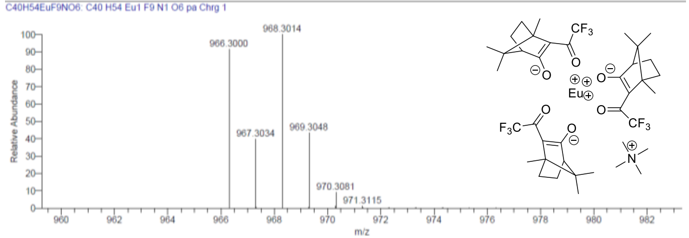


[Eu(*D*-facam)$_3$] : [TMACl] = 1 : 10

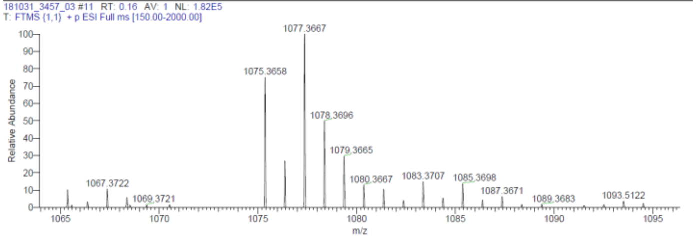
(b) Expended MS spectrum of Eu(*D*-facam)$_3$/TMACl (measured values)



(c) Calculated MS spectrum of [Eu(*D*-facam)$_3$·TMA]$^+$



(d) Expended spectrum of Eu(*D*-facam)$_3$/TMACl (measured values)



(e) Calculated MS spectrum of [Eu(*D*-facam)$_3$·2TMA·Cl]$^+$

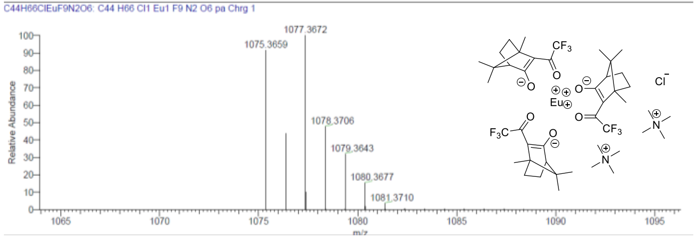
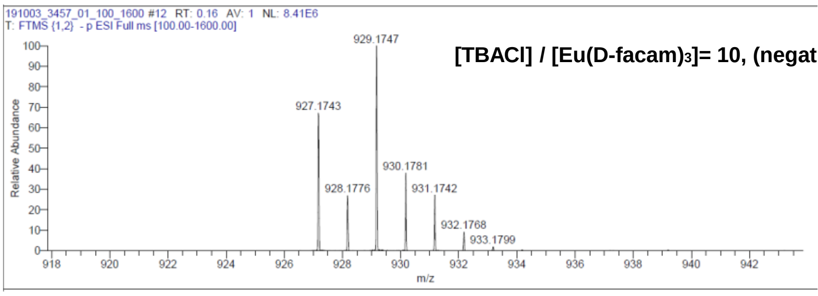
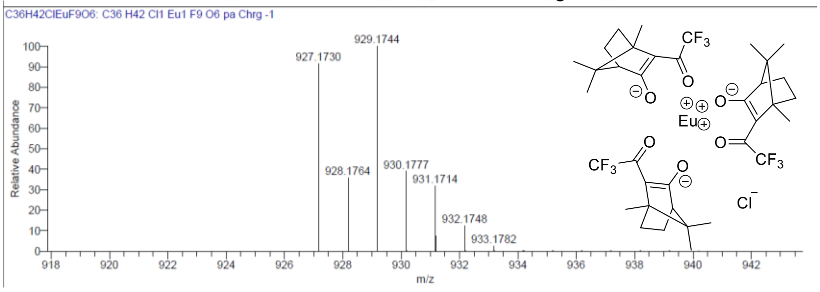


Figure S5. MS spectra of Eu(*D*-facam)$_3$/TMACl (a, b, d) and calculated MS spectrum of [Eu(D-facam)$_3$·TMA]$^+$ (c) and [Eu(D-facam)$_3$·2TMA·Cl]$^+$ (e).

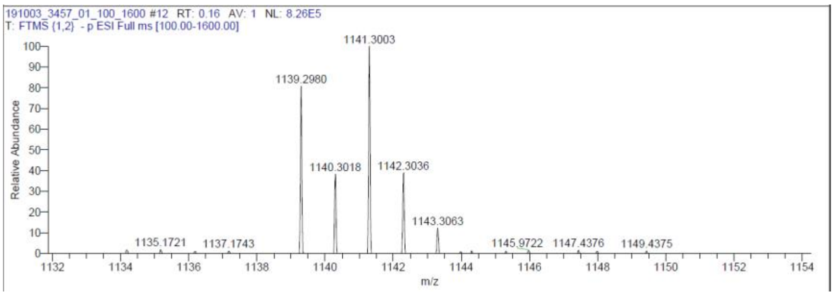
(a) Expended MS spectrum of Eu(*D*-facam)$_3$/TBACl (measured values)



(b) Calculated MS spectrum of [Eu(*D*-facam)$_3$·Cl]$^-$



(c) Expended MS spectrum of Eu(*D*-facam)$_3$/TBACl (measured values)



(d) Calculated MS spectrum of [Eu(*D*-facam)$_4$]$^-$

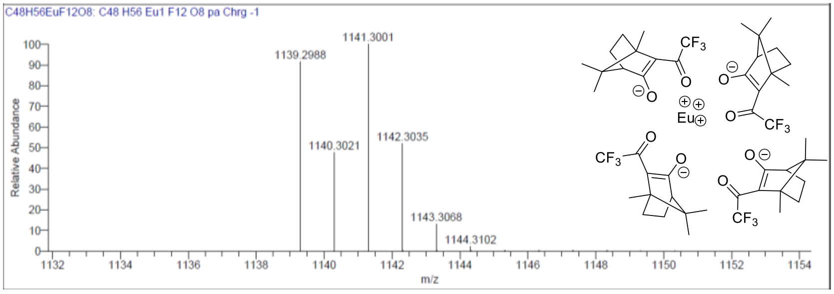
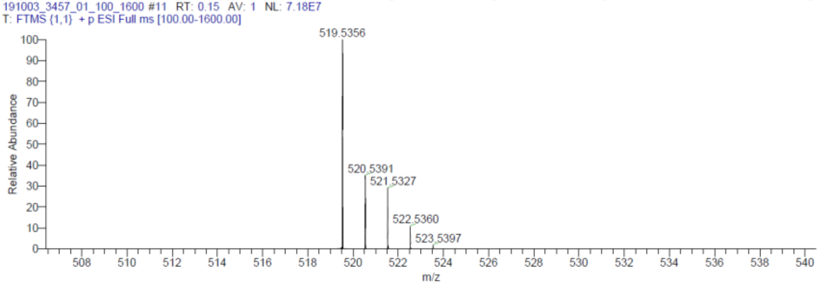
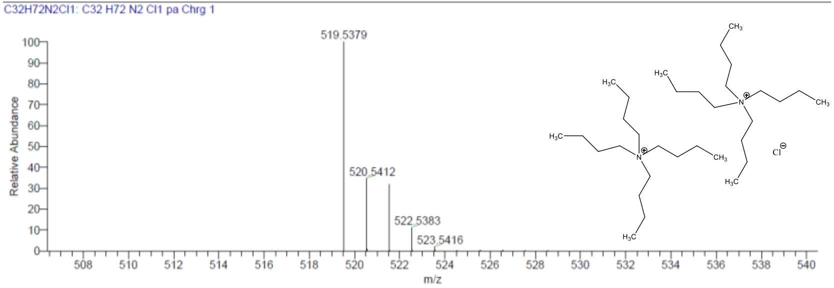


Figure S6. MS spectra of Eu(*D*-facam)$_3$/TBACl (a, c) and calculated MS spectrum of Eu(*D*-facam)$_3$·Cl]$^-$ (b) and [Eu(*D*-facam)$_4$]$^-$ (d).

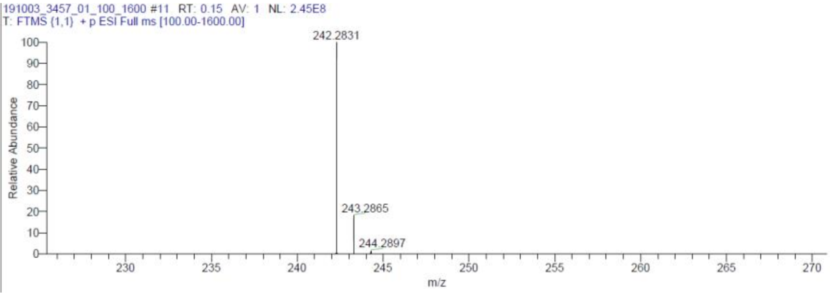
(a) Expended MS spectrum of Eu(*D*-facam)$_3$/TBACl (measured values)



(b) Calculated MS spectrum of [2TBA·Cl]$^+$



(c) Expended MS spectrum of Eu(*D*-facam)$_3$/TBACl (measured values)



(d) Calculated MS spectrum of [TBA]$^+$

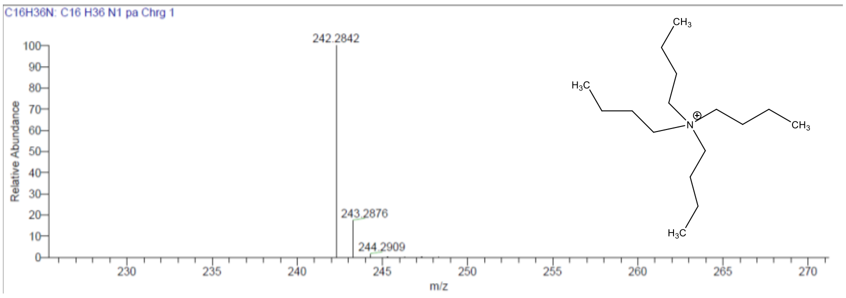


Figure S7. MS spectra of Eu(*D*-facam)$_3$/TBACl (a, c) and calculated MS spectrum of [2TBA·Cl]$^+$ (b) and [TBA]$^+$ (d).

4. Change in emission decay of Eu(*D*-facam)$_3$ solution upon the addition of TMACl.

In solution of Eu(D-facam)$_3$ alone, two components of emission lifetime were observed. The shorter component was ca. 30 μs (70 %) and longer one was ca. 220 μs (30 %) for the Eu(*D*-facam)$_3$ alone solution. The existence of multi components in the Eu(*D*-facam)$_3$ alone solution suggested presence of different states of the complex. For example, number of coordinated water may affect emission lifetime of complexes. By addition of TMACl, the shorter lifetime component disappeared and decay curves of almost single component with lifetime of ~250 μs were observed. This result indicated that interaction between TMACl and Eu(*D*-facam)$_3$ eliminated lower emissive state (shorter lifetime state) of Eu(*D*-facam)$_3$. In main text, we adopted averaged lifetime to calculate photophysical parameters of Eu(*D*-facam)$_3$ alone solution. Average emission lifetime was calculated by using the relation $\tau_{\text{ave}} = (\sum_{i=1}^{n} \tau_i^2 A_i)/(\sum_{i=1}^{n} \tau_i A_i)$, where τ_i is emission lifetime and A_i is amplitude of each component. In case of other solution with TMACl, fitting for single component were employed.

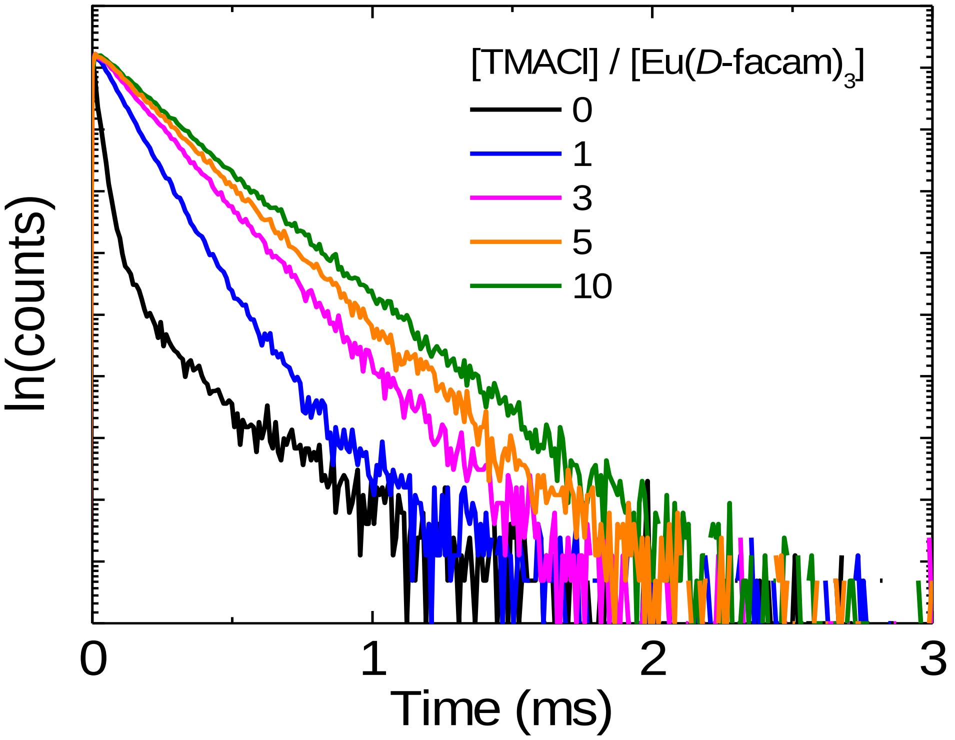


Figure S8. Emission decay curves of Eu(*D*-facam)$_3$/TMACl solutions with various concentration ratio. Excitation wavelength was 405 nm and emission were detected at 613 nm.

5. Effect of TMACl on the T_1 level of *D*-facam in Eu(*D*-facam)$_3$.

Broad phosphorescence bands due to *D*-facam were observed at 400–500 nm; their intensity decreased with increasing TMACl concentration. When [Eu(*D*-facam)$_3$]:[TMACl] = 1:10, the phosphorescence from *D*-facam was almost quenched, indicating that the addition of TMACl improved the efficiency of energy transfer (η_{sens}) from *D*-facam to Eu(III) in Eu(*D*-facam)$_3$. On the other hand, the shapes and onset wavelength of the phosphorescence spectra were not changed by the presence of TMACl, indicating that the T_1 level of *D*-facam was unperturbed.

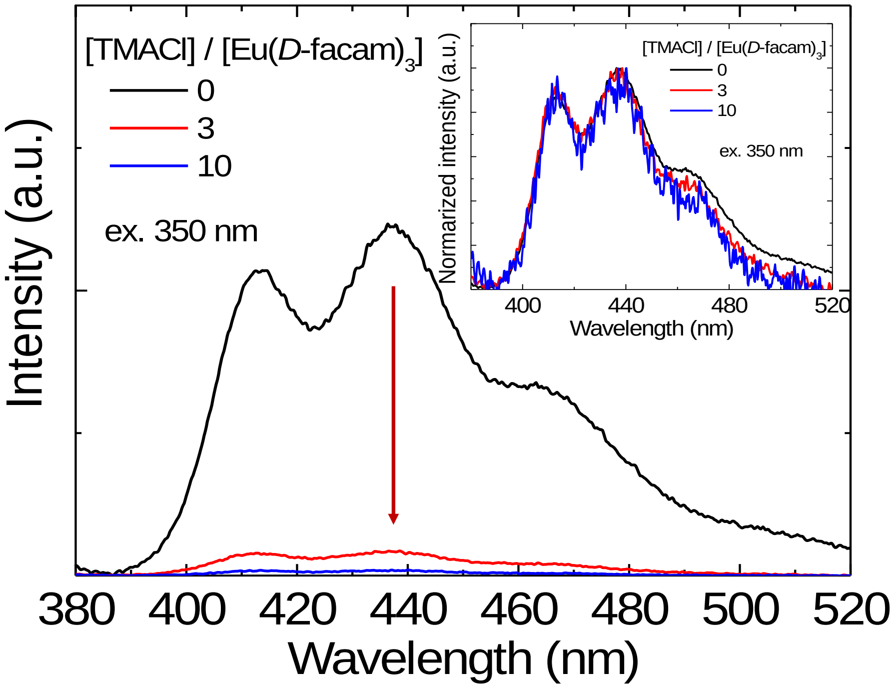


Figure S9. Phosphorescence spectra of Eu(*D*-facam)$_3$ solutions in the presence of various concentrations of TMACl at 77 K.