Electronic Supplementary Information for

Water-soluble lanthanide complexes with a helical ligand modified for strong luminescence in a wide pH region

Shuhei Ogata,[a] Tomohito Shimizu,[a] Takashi Ishibashi,[a] Yushi Ishiyone,[a] Mitsuhiro Hanami,[a] Minami Ito,[a] Ayumi Ishii,[a] Shogo Kawaguchi,[b] Kunihisa Sugimoto[b] and Miki Hasegawa*[a]

[a] Collage of Science and Engineering, Aoyama Gakuin University 5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5259, Japan, E-mail: hasemiki@chem.aoyama.ac.jp;

[b] *Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan*

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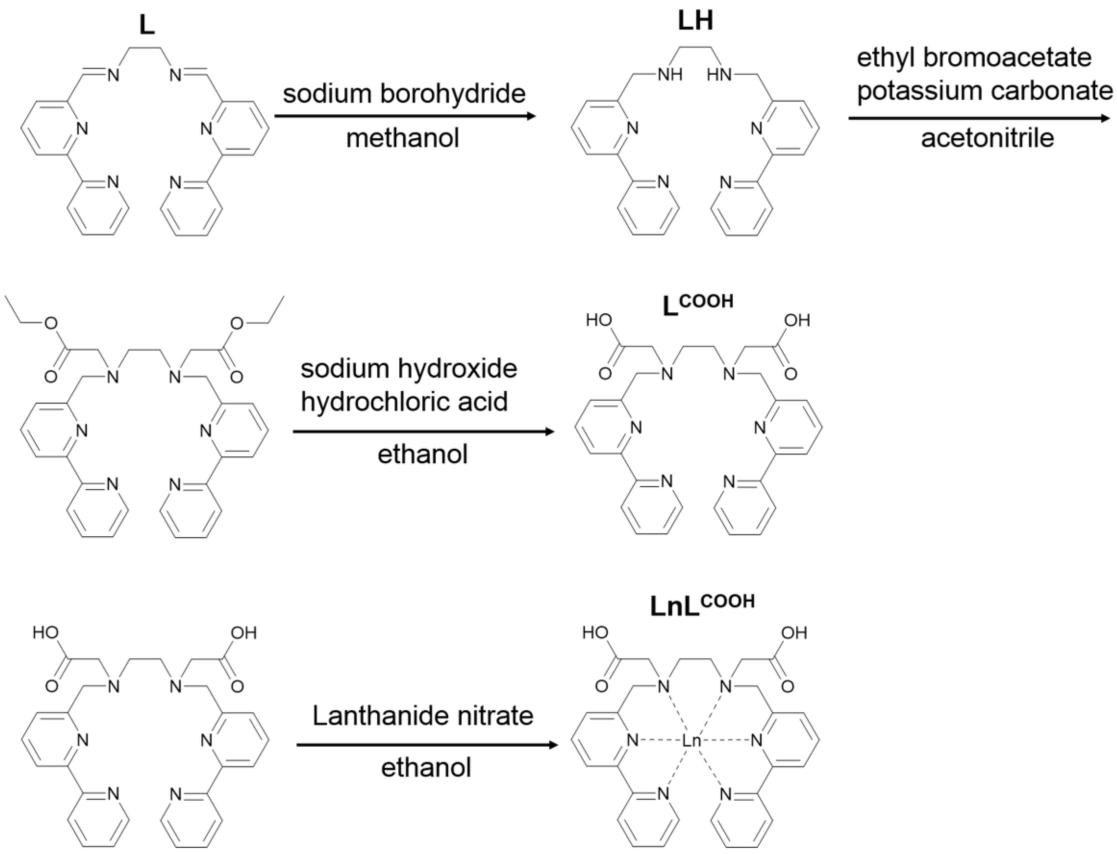

Scheme S1 Syntheses of L^{COOH} and LnL^{COOH}

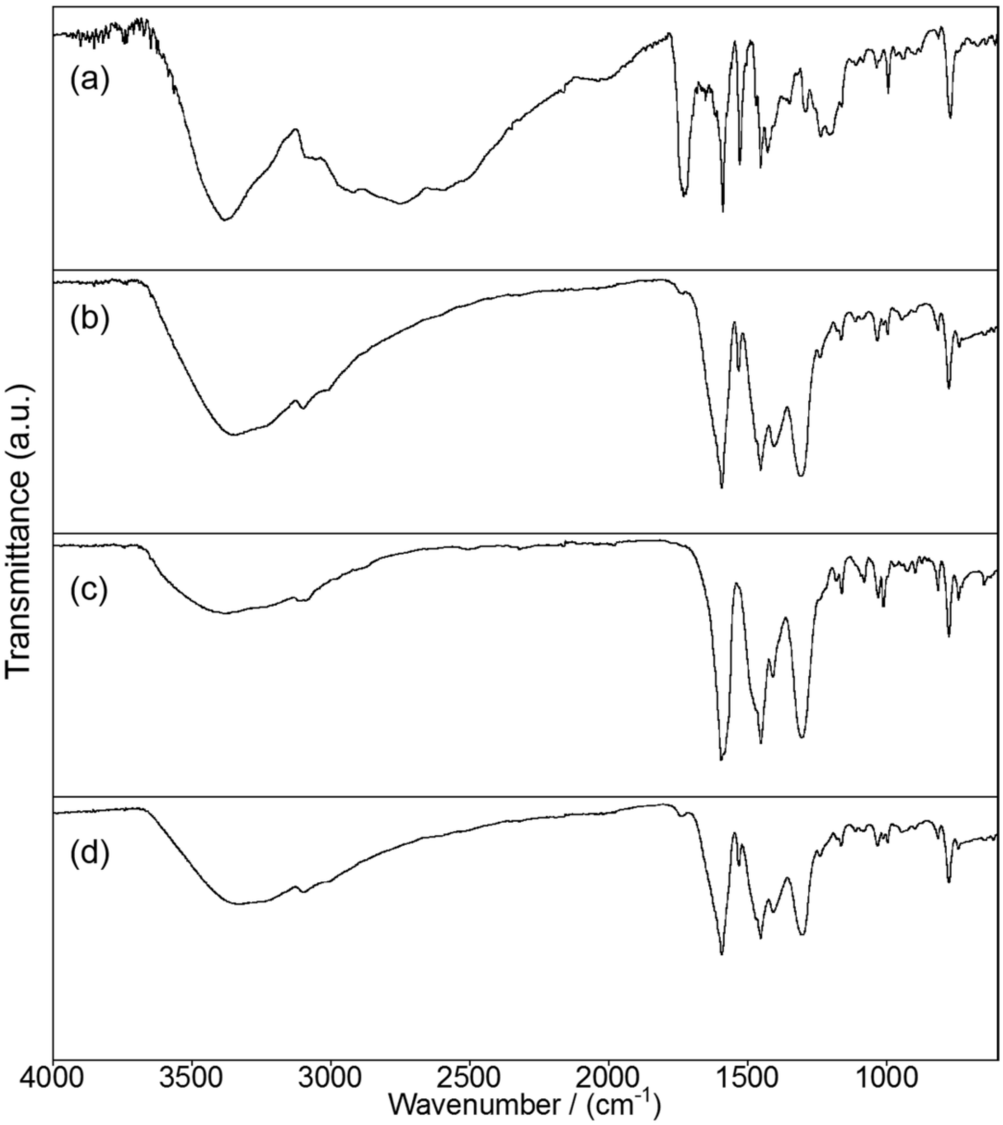

Fig. S1 Attenuated total reflection FT-IR spectra of L^{COOH} (a), EuL^{COOH} (b), GdL^{COOH} (c), and TbL^{COOH} (d).

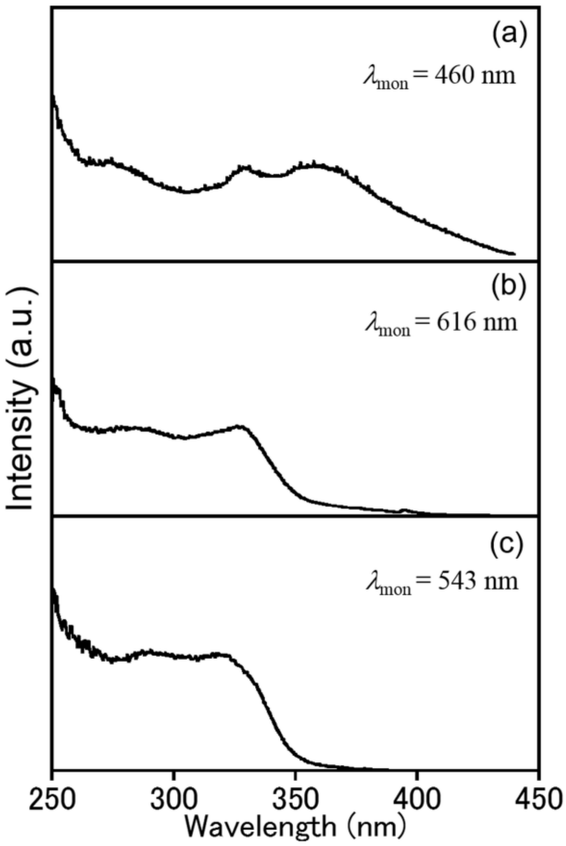

Fig. S2 Excitation spectra of LnL^{COOH} in the solid state. Ln = Gd (a), Eu (b), and Tb (c).

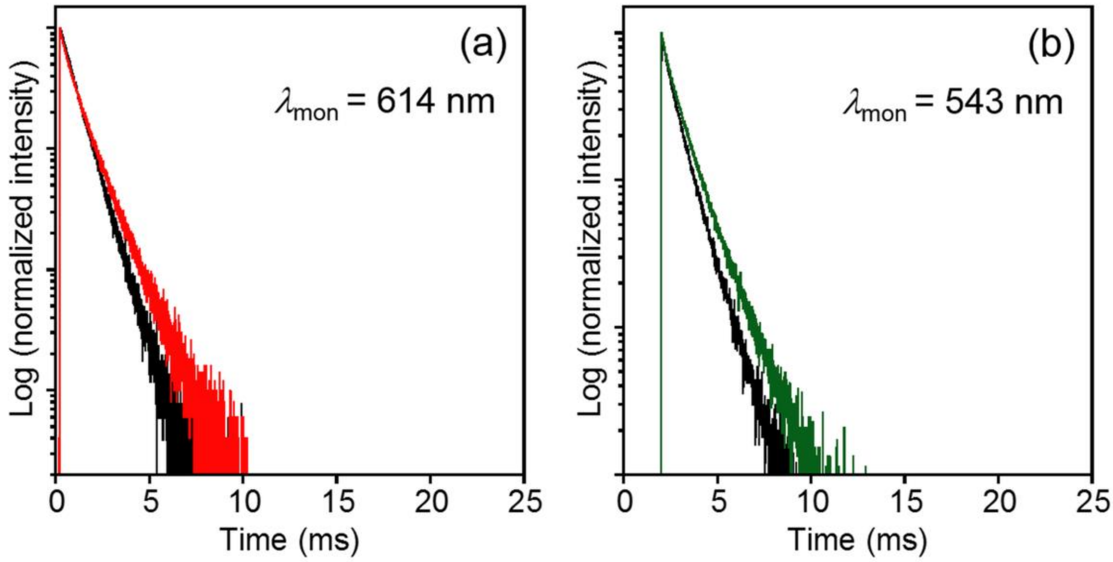

Fig. S3 Decay profiles for ff emission of EuL^{COOH} (a) and TbL^{COOH} (b) in the solid state at rt (black line) and 77 K (colored line). λ_{ex} = 280 nm.

Caluculation of luminescence rate constants and efficiency of EuL^{COOH}.

The total emission quantum yield of Eu sensitized by the ligand L^{COOH} ($\phi_{L\text{-}Ln}$) is determined by the triplet yield of the ligand (ϕ_{ISC}), the efficiency of energy trasfer (η_{EnT}) and the efficiency of metal-centerd luminescence (ϕ_{Ln}) as following equation.[1]

$\phi_{L\text{-}Ln} = \phi_{ISC} \times \eta_{EnT} \times \phi_{Ln}$ (1)

The value of ϕ_{ISC} can be approximately 1, because of the nπ* character of the ligand and the high spin-orbit coupling constant of the lanthanid ion.[2,3] $\phi_{Ln\text{-}Ln}$ can be calculated from radiative rate constat (k_R) and non-radiative rate constant (k_{NR}) the following equation.

$\phi_{Ln\text{-}Ln} = k_R / k_R \times k_{NR} = k_R \times \tau_{obs}$ (2)

The radiativ rate constat can be calculated from equation (3).[4,5]

$k_R = A_{MD} \times n^3 \times (I_{tot} / I_{MD})$ (3)

Where, A_{MD} is the spontaneous emission probability of the $^5D_0 \rightarrow {}^7F_1$ transiton of Eu ion in vacuo, n is the refractive index, I_{tot} / I_{MD} represents the ratio of the total integrated intensity of the corrected Eu luminescence spectrum to the integrated intensity of the magnetic-dipole transition.

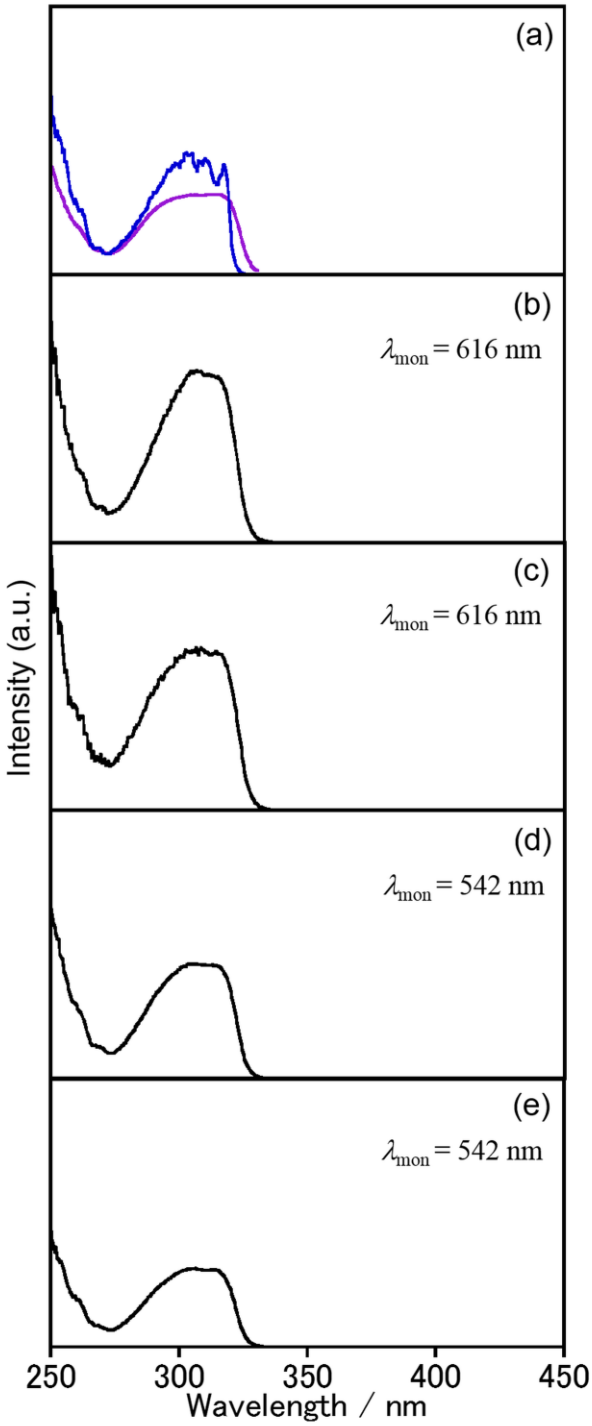

Fig. S4 Excitation spectra of LnL^{COOH}. Ln = Gd (a), Eu (b and c), and Tb (e and f). The solvent is H_2O (a, b and d) and D_2O (b and d). Excitation spectra monitored ad fluorescence (λ_{mon} = 336 nm) and phosphorescence band (λ_{mon} = 438 nm) of GdL^{COOH} are shown in purple and blue, respectively.

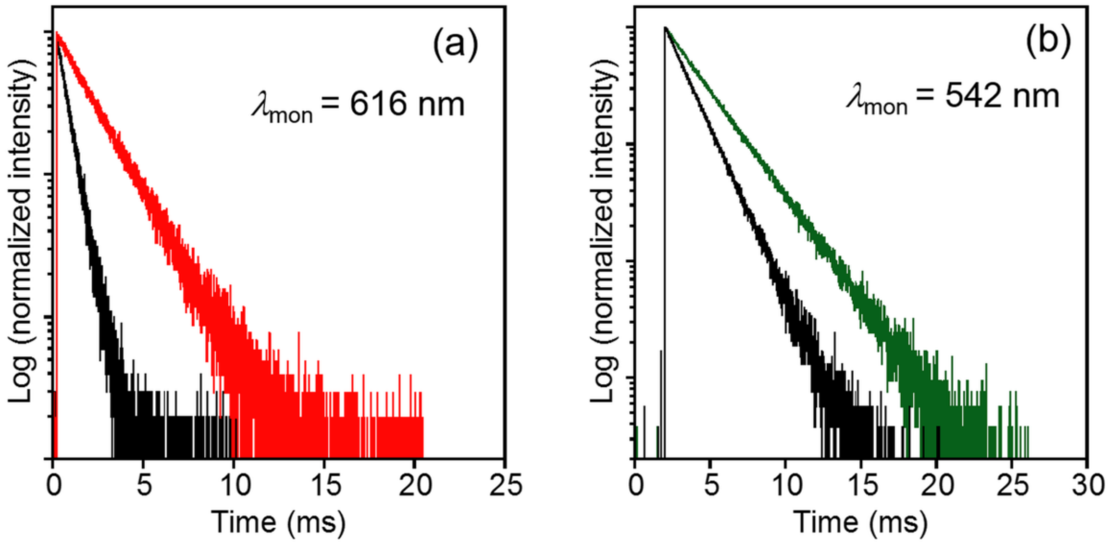

Fig. S5 Decay profiles for ff emissions of EuL^{COOH} (a) and TbL^{COOH} (b) in H_2O (black line) and D_2O (colored line). λ_{ex} = 280 nm.

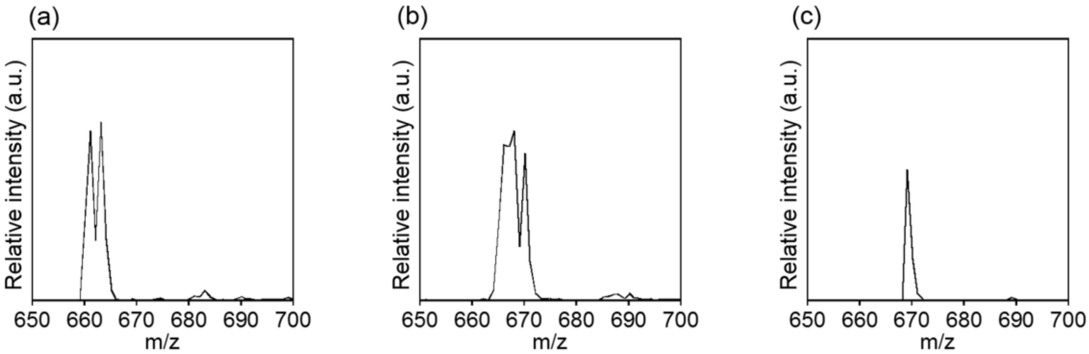

Fig. S6. ESI(+)-MS for the signals related to EuL^{COOH} (a), GdL^{COOH} (b), and TbL^{COOH} (c) in aqueous solutions

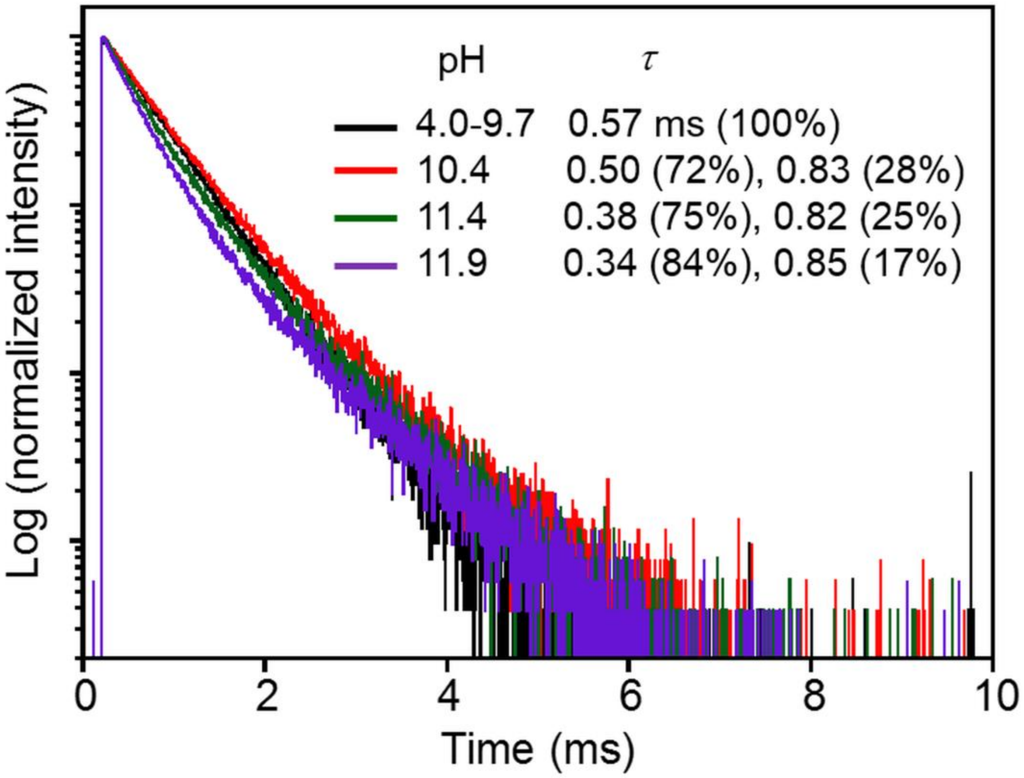

Fig. S7. Decay profiles of EuL^{COOH} in aqueous solution at various pH values. λ_{ex} = 280 nm. λ_{mon} = 616 nm.

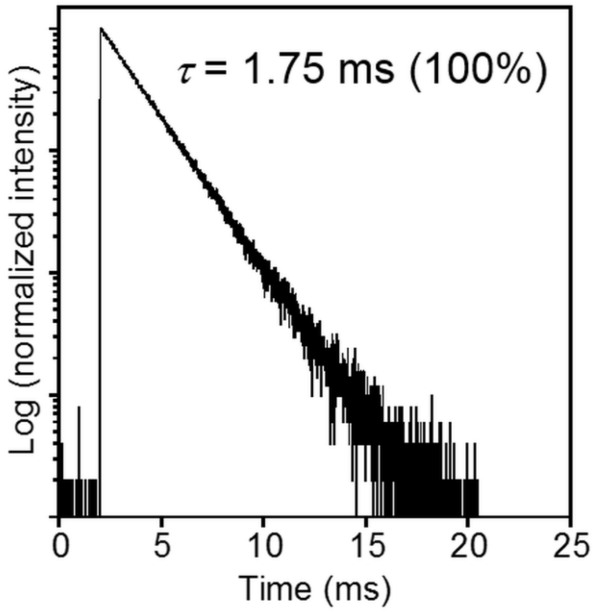

Fig. S8. Decay profiles of EuL^{COOH} in D_2O at basic condition. λ_{ex} = 280 nm. λ_{mon} = 616 nm.

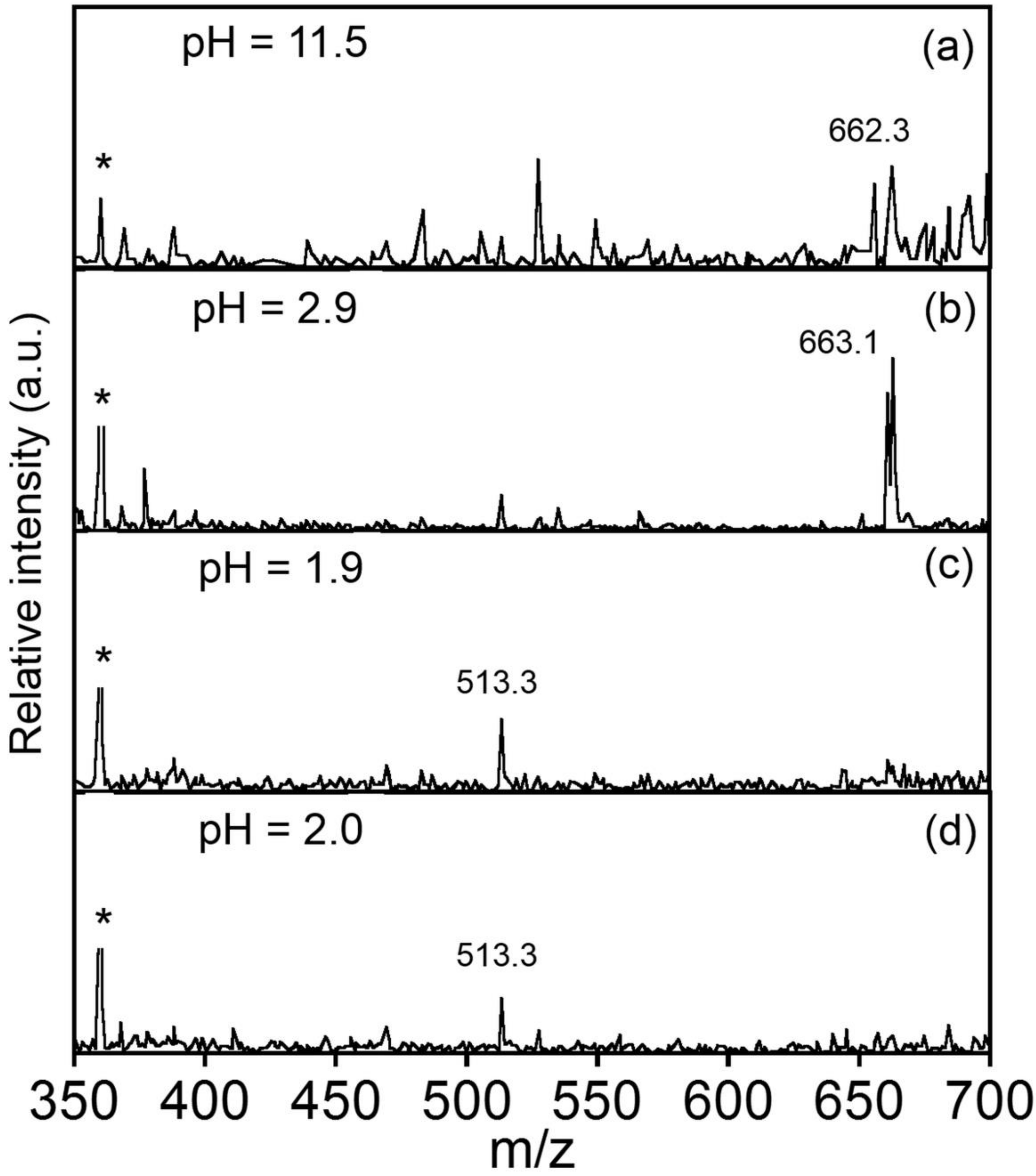

Fig. S9 ESI(+)-MS for the signals related to EuL^{COOH} in aqueous solution at various pH values. L^{COOH} in aqueous solution at pH 2.0 is shown in (d). * is due to a fragment.

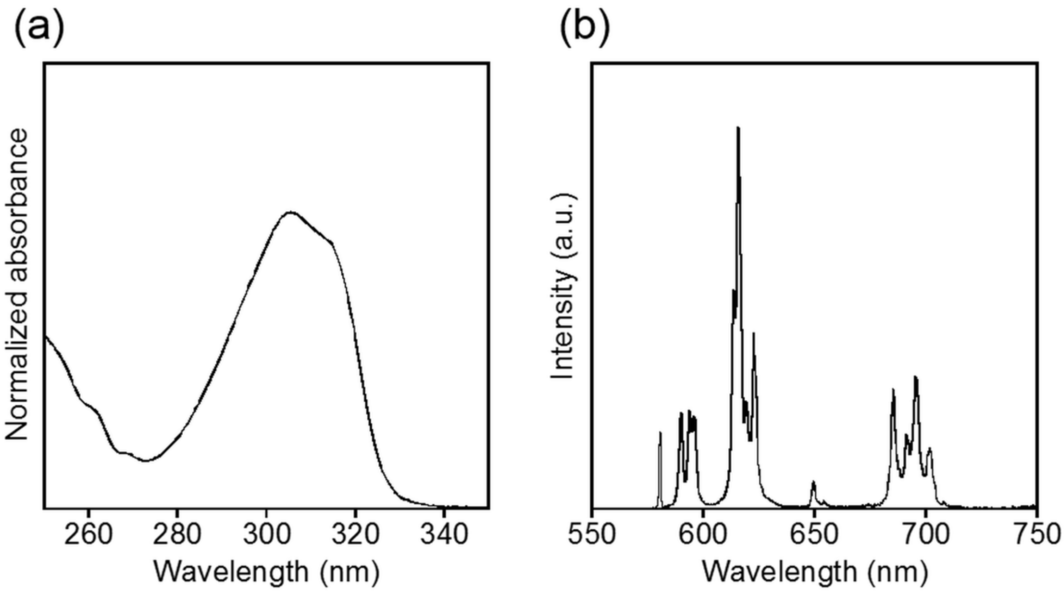

Fig. S10 Electronic absorption (a) and luminescence spectrum (b) of EuL^{COOH} at pH 3.5 after adjustment by hydrochloric acid from pH 11.9. λ_{ex} = 315 nm.

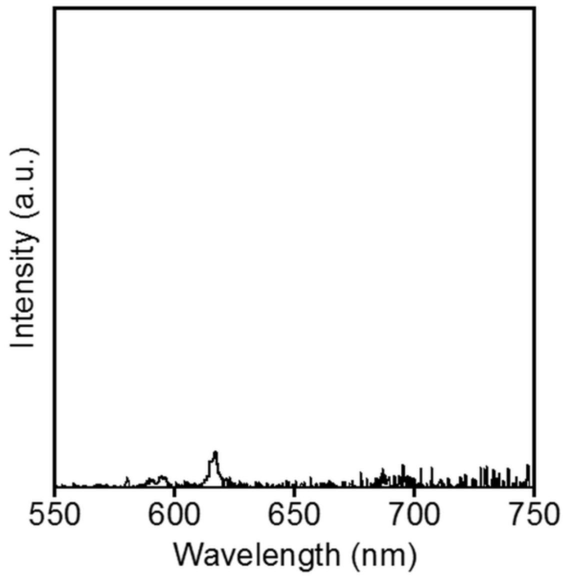

Fig. S11 Luminescence spectrum of EuL^{COOH} in aqueous solution at pH 2.1. λ_{ex} = 315 nm.

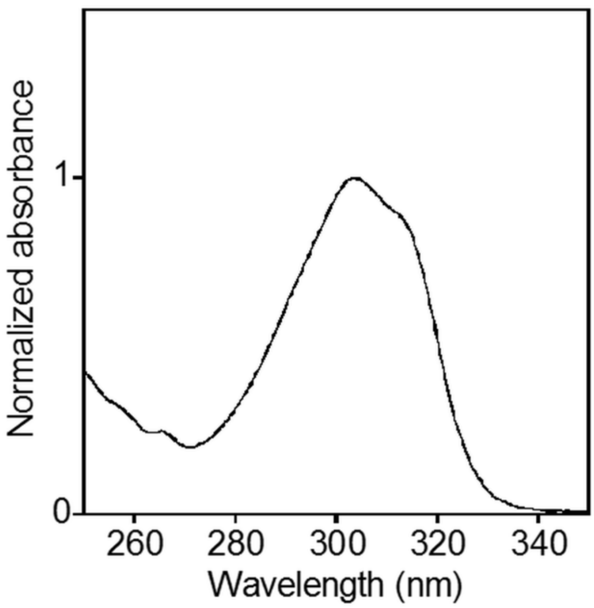

Fig. S12 Electronic absorption spectrum of L^{COOH} in water at acidic condition.

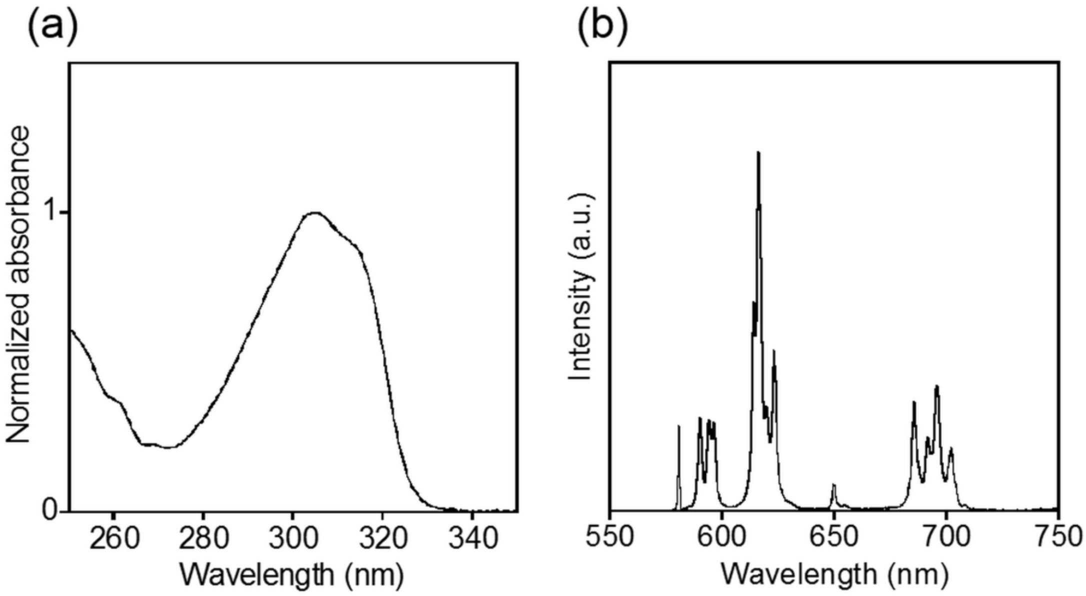

Fig. S13 Electronic absorption (a) and luminescence spectrum (b) of EuL^{COOH} at pH 6.3 after adjustment by NaOH aq. from pH 1.9. λ_{ex} = 315 nm.

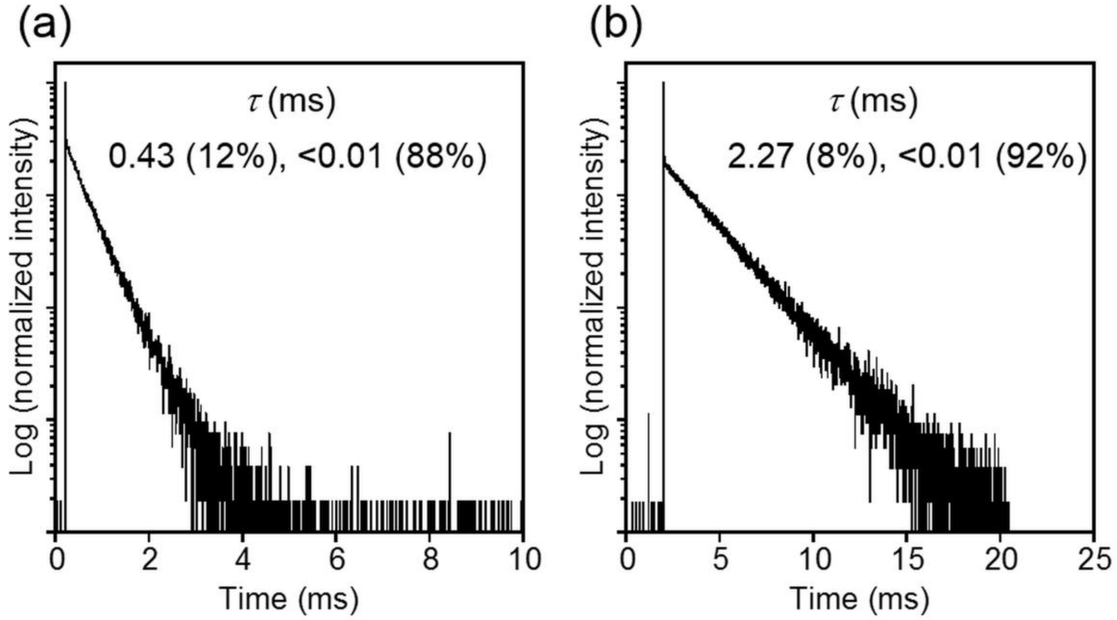

Fig. S14 Decay profiles of EuL^{COOH} in H_2O (a) and D_2O (b) at acidic condition. λ_{ex} = 280 nm. λ_{mon} = 616 nm.

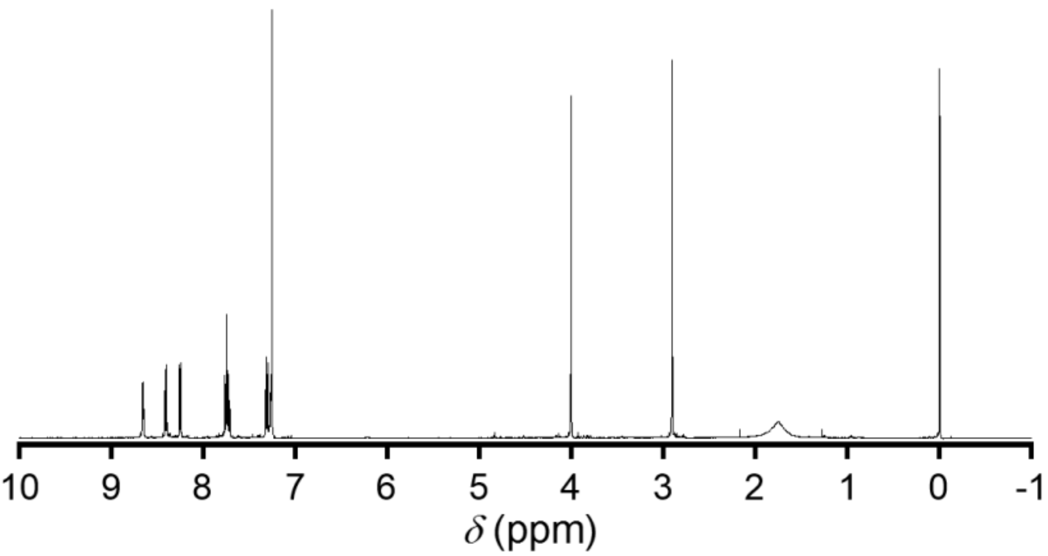

Fig. S15 [1]H-NMR of LH in $CDCl_3$ (TMS).

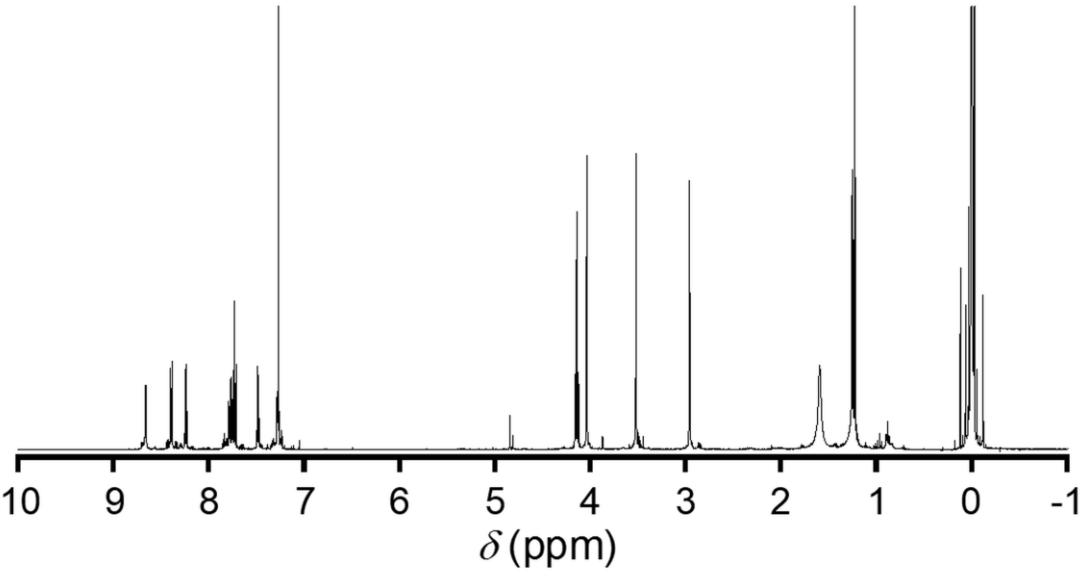

Fig. S16 ^{1}H-NMR of L^{COOEt} in $CDCl_3$ (TMS).

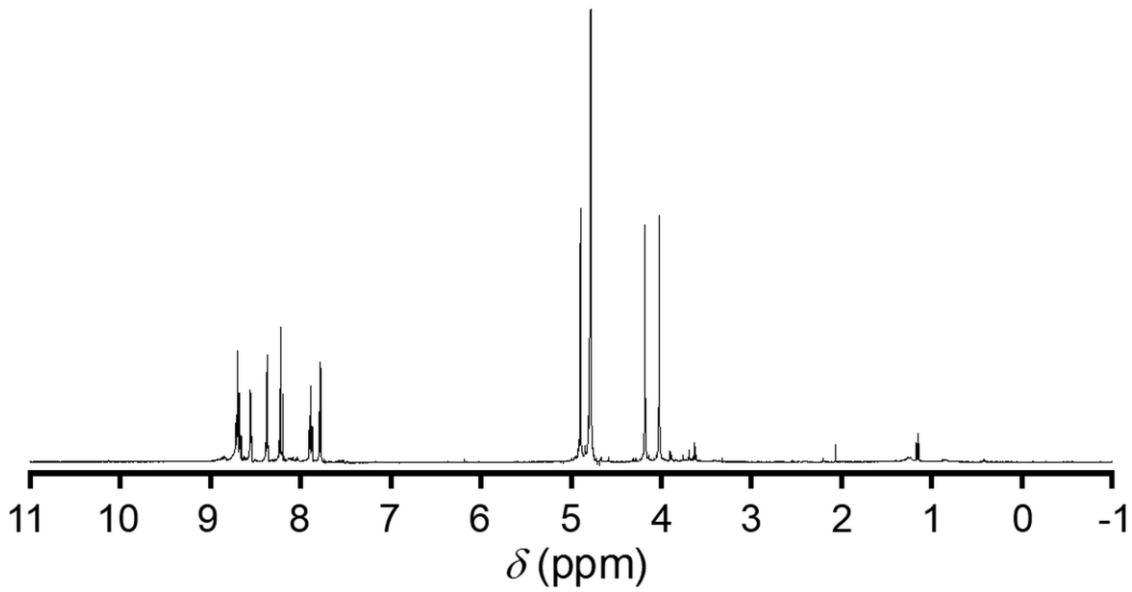

Fig. S17 ^{1}H-NMR of L^{COOH} in methanol-d_4.

References

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