

Supporting Information

A universal solution-phase strategy for bright lanthanide(III) emission: aggregation-induced emission via electronic–vibrational decoupling

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Experimental section

Materials The samarium nitrate ($\text{Sm}(\text{NO}_3)_3$, 99.99%), dysprosium nitrate ($\text{Dy}(\text{NO}_3)_3$, 99.99%), terbium nitrate ($\text{Tb}(\text{NO}_3)_3$, 99.99%) are purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Dimethyl formamide (DMF) is purchased from

Sigma-Aldrich. Deuterated DMF is obtained from J&K Scientific Co., Ltd (Beijing, China). Deionized water is obtained from the laboratory, All the reagents are used as received.

Methods

Preparation of Aqueous Sm(NO₃)₃, Dy(NO₃)₃, and Tb(NO₃)₃ Solutions at Different Concentrations

Weighed amounts of Sm(NO₃)₃·6H₂O (42.2 mg and 422 mg) were separately transferred into 20 mL glass beakers. A minimal volume of deionized (DI) water was added to each beaker to dissolve the solids completely. The resulting solutions were quantitatively transferred into 10 mL volumetric flasks and made up to the mark with DI water, yielding 10 mM and 100 mM aqueous Sm(NO₃)₃ solutions, respectively. Each solution was magnetically stirred for 5 min and subsequently sonicated for 2 min to promote homogeneity. Serial dilutions of the 10 mM Sm(NO₃)₃ solution were then performed with DI water to furnish 1 mM and 0.1 mM working solutions, which were treated under the same stirring and sonication conditions. Aqueous Dy(NO₃)₃ and Tb(NO₃)₃ solutions were prepared following same procedures.

Preparation of Sm(NO₃)₃, Dy(NO₃)₃, and Tb(NO₃)₃ Solutions in Different Solvents

Weighed amounts of Sm(NO₃)₃·6H₂O (422 mg), Dy(NO₃)₃·6H₂O (434 mg), and Tb(NO₃)₃·6H₂O (345 mg) were separately transferred into 20 mL glass vials. Subsequently, 10 mL of solvent—N,N-dimethylformamide (DMF), deuterated DMF (d-DMF), or deionized water (H₂O)—was added to each vial. The mixtures were

magnetically stirred for 5 min and then sonicated for 2 min to promote complete dissolution.

Energy level calculation

The vibrational fundamental energy levels of ligand molecules were estimated from the peak wavenumbers obtained via infrared (IR) spectroscopy, using the following equation:

$$E(eV) = \frac{\nu(cm^{-1})}{8065.5}$$

Specifically, the wavenumbers used in this study are: 3400 cm^{-1} for the O–H stretching mode in H₂O, 2400 cm^{-1} for the O–D stretching mode in D₂O, 1690 cm^{-1} for the C=O stretching mode in DMF, and 2950 cm^{-1} for the C–H stretching mode in the methyl group of DMF. Overtones were estimated as integer multiples of the corresponding fundamental frequencies, while anharmonic effects were neglected in this analysis.^{1,2}

Spectroscopic Measurements

Ultraviolet absorption spectra were recorded on a UV-1900i UV–vis spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra and fluorescence lifetimes at room temperature and 77 K were measured using an FLS1000 fluorescence spectrometer (Edinburgh Instruments, UK). Photoluminescence quantum yields (PLQY) were determined by employing a Quantaurus C11347 integrating sphere system (Hamamatsu, Japan). Infrared spectra were recorded on a Thermo Fisher Nicolet

iS10 spectrometer equipped with an ATR accessory. All solution samples were filtered through a 0.2 μm membrane prior to optical measurements.

Supporting Figures

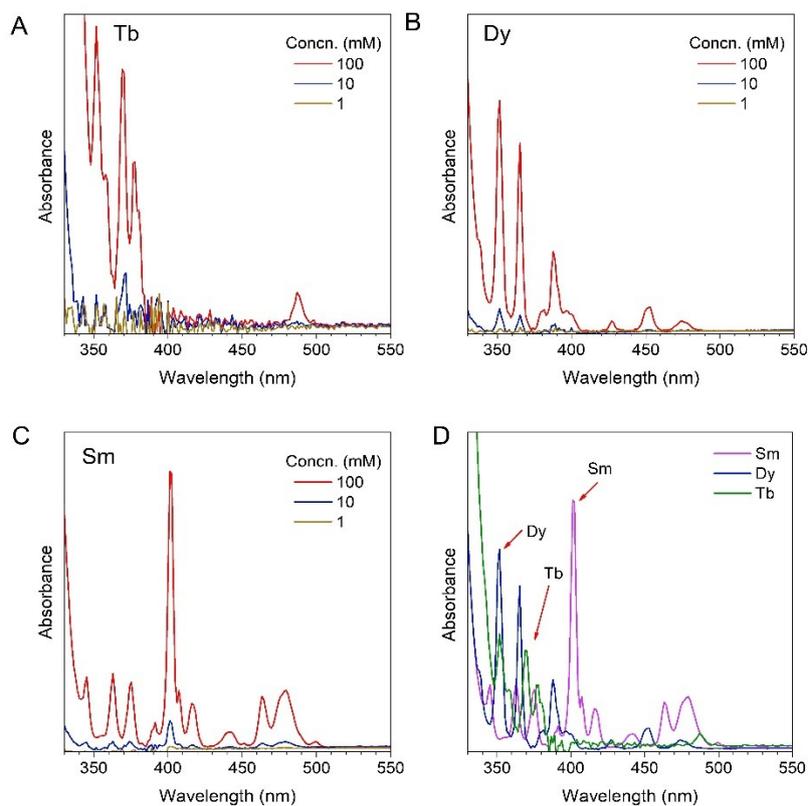


Fig. S1. UV-vis absorption spectra of lanthanide nitrate aqueous solutions. (A–C) UV-vis absorption profiles of $\text{Sm}(\text{NO}_3)_3$, $\text{Dy}(\text{NO}_3)_3$, and $\text{Tb}(\text{NO}_3)_3$ at various concentrations. (D) Selection of excitation wavelengths for different lanthanide solutions.

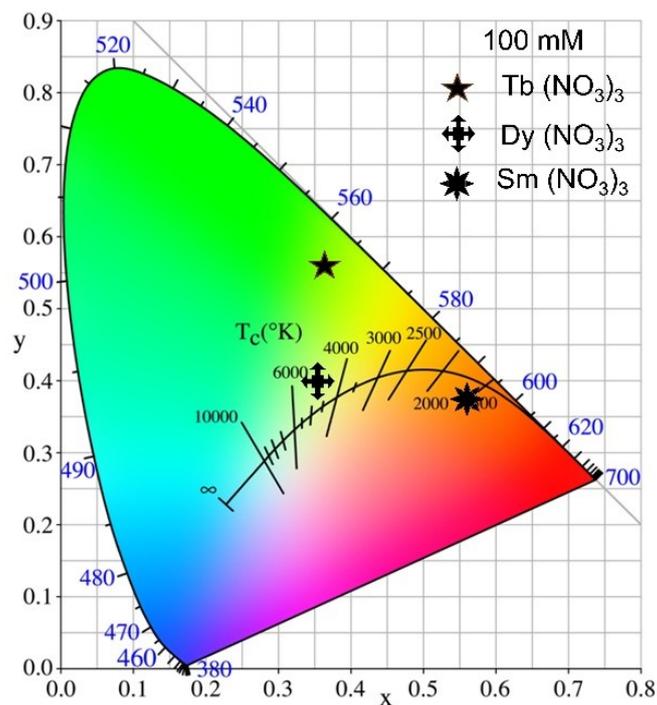


Fig. S2. CIE coordinates of 100 mM lanthanide nitrate aqueous solutions

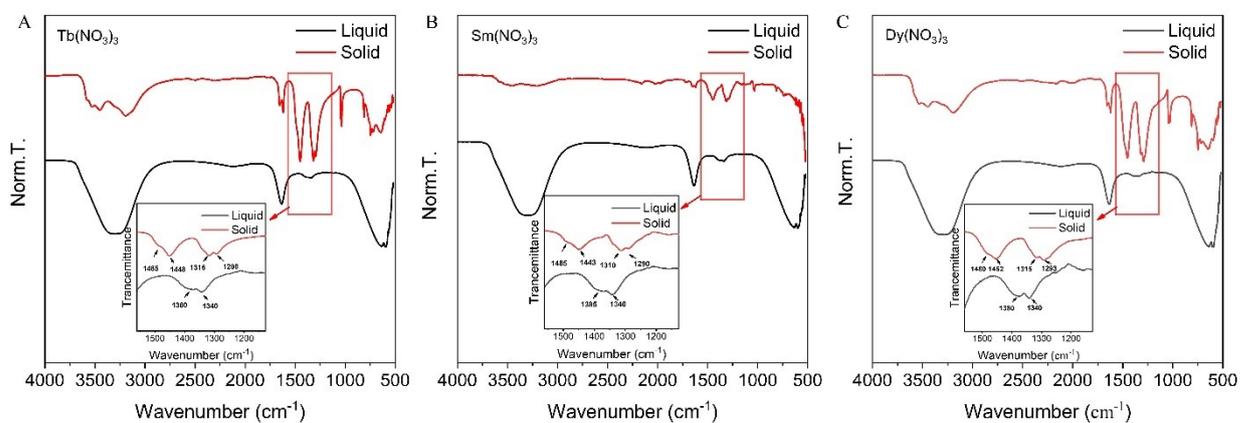


Fig. S3. The infrared spectra of $\text{Ln}(\text{NO}_3)_3$ with different states.

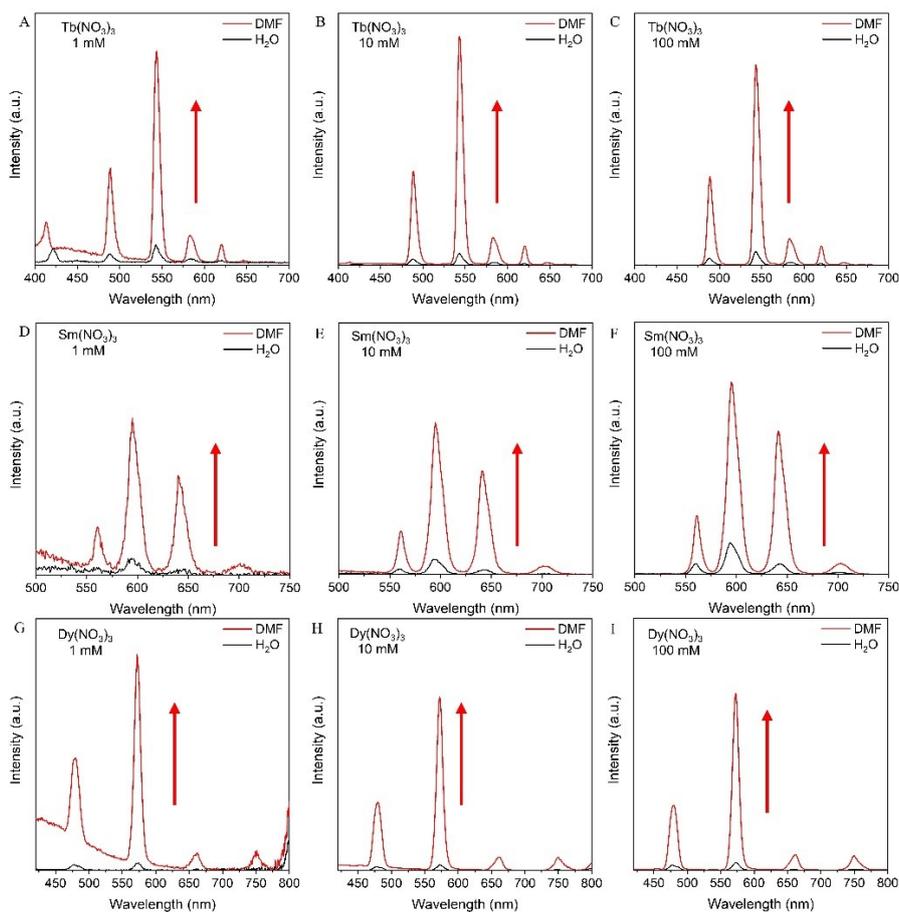


Fig. S4 The EVD strategy is universally applicable in enhancing photophysical properties in Ln^{3+} solutions of varying concentrations. The emission spectrum of (A-C) $\text{Tb}(\text{NO}_3)_3$, (D-F) $\text{Sm}(\text{NO}_3)_3$, (G-I) $\text{Dy}(\text{NO}_3)_3$ in different solvent with different concentration.

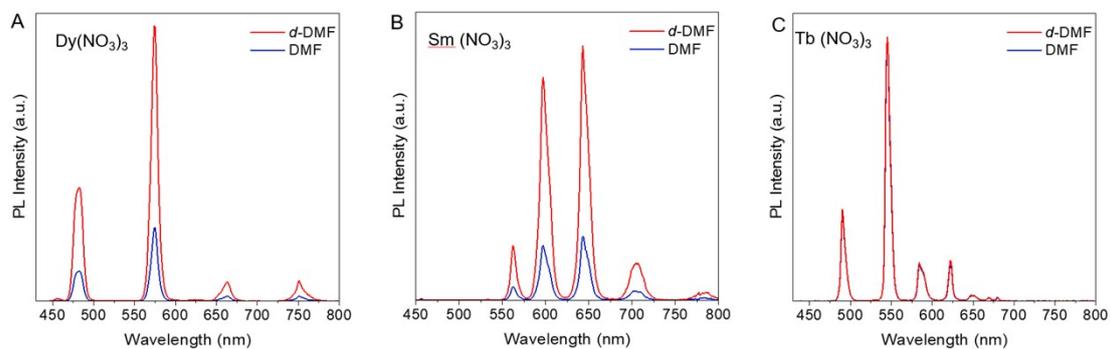


Fig. S5 Emission spectra of 100 mM (A) $\text{Dy}(\text{NO}_3)_3$, (B) $\text{Sm}(\text{NO}_3)_3$, (C) $\text{Tb}(\text{NO}_3)_3$ in DMF and *d*-DMF

references

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2. A. Kuligiewicz, A. Derkowski, M. Szczerba, V. Gionis and G. D. Chryssikos, *Clay Clay Miner*, 2015, **63**, 15-29.