

Supporting Information

Syntheses, crystal structures and properties of a series of isostructural Lanthanide Organic Frameworks

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1. Materials and Characterization

1.1 Materials

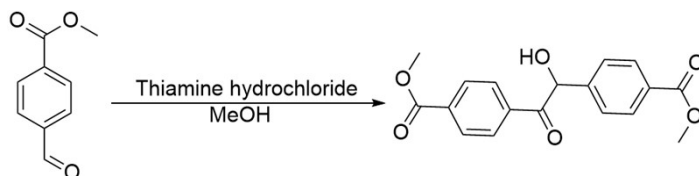
All reagents were purchased commercially and used without further purification. Gadolinium(III) Nitrate Hydrate, Samarium(III) nitrate hexahydrate, Holmium(III) Nitrate Pentahydrate, Praseodymium(III) Nitrate Hexahydrate, Europium(III) Nitrate Pentahydrate, Dysprosium(III) Nitrate Hydrate, Neodymium(III) Nitrate Hydrate, Terbium(III) Nitrate Hexahydrate, Methyl 4-Formylbenzoate, Thiamine Hydrochloride and Lithium hydroxide monohydrate was purchased from Adamas-beta. Methanol (MeOH), Ethanol (EtOH), sodium borohydride (NaBH₄), tetrahydrofuran (THF), hydrochloric acid (HCl), N, N-dimethylformamide (DMF) and N, N-diethylformamide (DEF), dichloromethane (DCM), chloroform, acetone, 1, 4-dioxane, dimethyl sulfoxide (DMSO), cyclohexane (CYH) and acetonitrile (ACN) were purchased from Sinopharm Group Co., Ltd. (China).

1.2 Characterization

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of 5-50 ° with a scanning rate of 5 °/min. Thermogravimetric analysis (TGA) data were carried out in an N₂ atmosphere with a heating rate of 10 °C/min on a STA 449F3 integration thermal analyzer. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III spectrometer (400 MHz and 101 MHz, respectively) or a JEOL ECZ600S spectrometer (600 MHz and 151 MHz, respectively). The UV-vis diffuse reflection data were recorded at room temperature using a powder sample with BaSO₄ as a standard (100% reflectance) on a Perkin Elmer Lamda-950 UV spectrophotometer and scanned at 200-1200 nm. Fourier transform infrared (FT-IR) spectra were recorded with a Spectrum One FT-IR Spectrometer in the 400-4000 cm⁻¹ range. Element analyses (C, H) were measured with an Elemental Vairo EL III analyzer. Fluorescence spectra for the solid samples were performed on an Edinburgh Analytical instrument FLS920.

2. Synthesis and Characterization

2.1 Synthesis of 4, 4'-(1, 2-dihydroxyethane-1, 2-diyl)dibenzoic acid



Scheme S1. The synthesis method of dimethyl 4, 4'-(1-hydroxy-2-oxoethane-1, 2-diyl)dibenzoate.

Synthesis of dimethyl 4, 4'-(1-hydroxy-2-oxoethane-1, 2-diyl)dibenzoate (Hdydb) was synthesized according to the literature.¹ Thiamine hydrochloride (1.80 g, 5.35 mmol) was dissolved in a 20 mL of 1:3 water/methanol mixture solution, and then, cooled down to 0 °C using an ice bath. After that, a solution of NaOH (2 M, 5 mL) was added dropwise over a period of 10 min. Subsequently, 4-formyl benzoate (14.9 g, 91 mmol) was added to the solution, the resulting mixture was heated to 60 °C for 15 min and then refluxed at 80 °C for 1 h. After cooling to room temperature, the white solid was filtered off, washed with water, methanol and ethyl ether, and then air-dried to afford the title compound. Yield: 12.7 g (84%).

¹H NMR (400 MHz, Chloroform-d) δ 8.05 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 6.01 (d, J = 5.8 Hz, 0H), 4.54 (d, J = 5.9 Hz, 0H), 3.89 (d, J = 15.7 Hz, 2H).

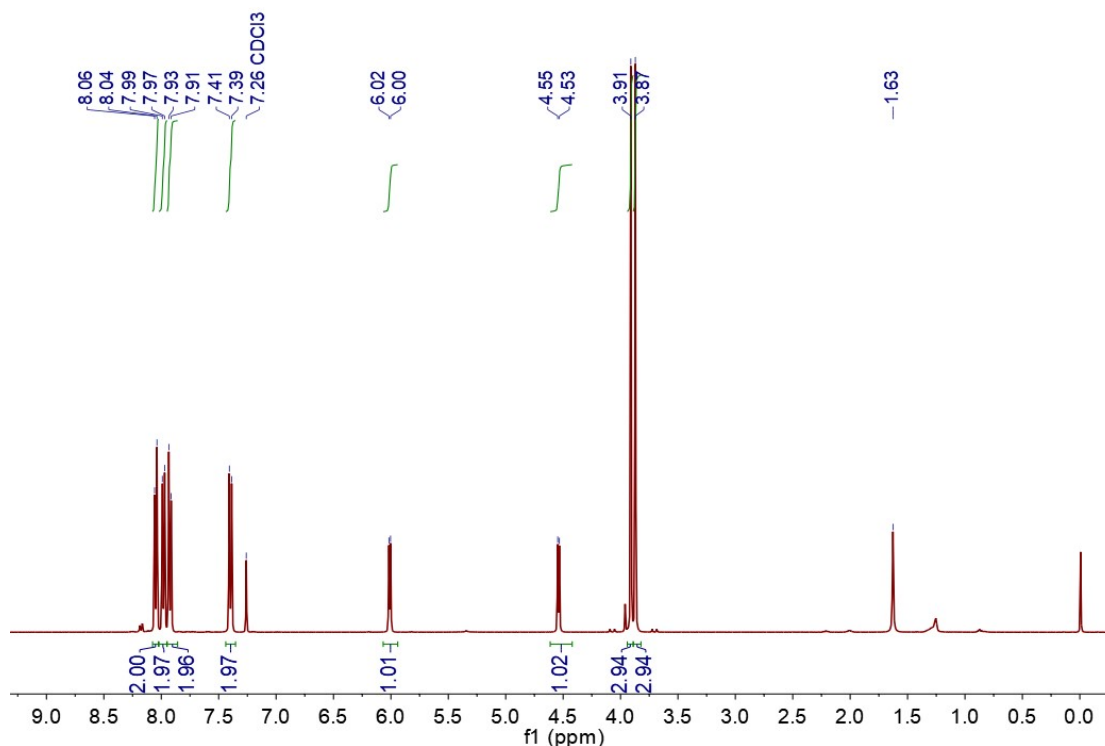
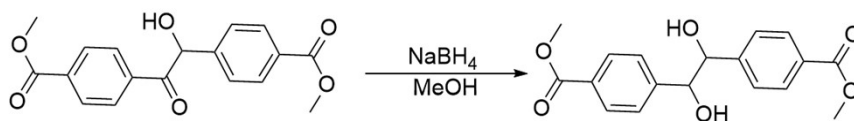


Figure S1. 400 MHz ¹H NMR spectrum of Hdydb in Chloroform-d.



Scheme S2. The synthesis method of dimethyl 4, 4'-(1-hydroxy-2-oxoethane-1, 2-diyl)dibenzoate.

Synthesis of dimethyl 4, 4'-(1,2-dihydroxyethane-1, 2-diyl)dibenzoate (H₂dydb): A mixture of compound H₂dydb (4.98 g, 15 mmol) and sodium borohydride (0.6g, 15 mmol) was placed in 150 mL methanol and stirred at room temperature for 30 minutes. After cooling to room temperature, the white solid was filtered off, washed with water and methanol, and then air-dried to afford the title compound. Yield: 3.8 g (76%).

¹H NMR (400 MHz, DMSO-d₆) δ 7.84 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 5.55 (s, 0H), 4.68 (s, 0H), 3.83 (s, 2H).

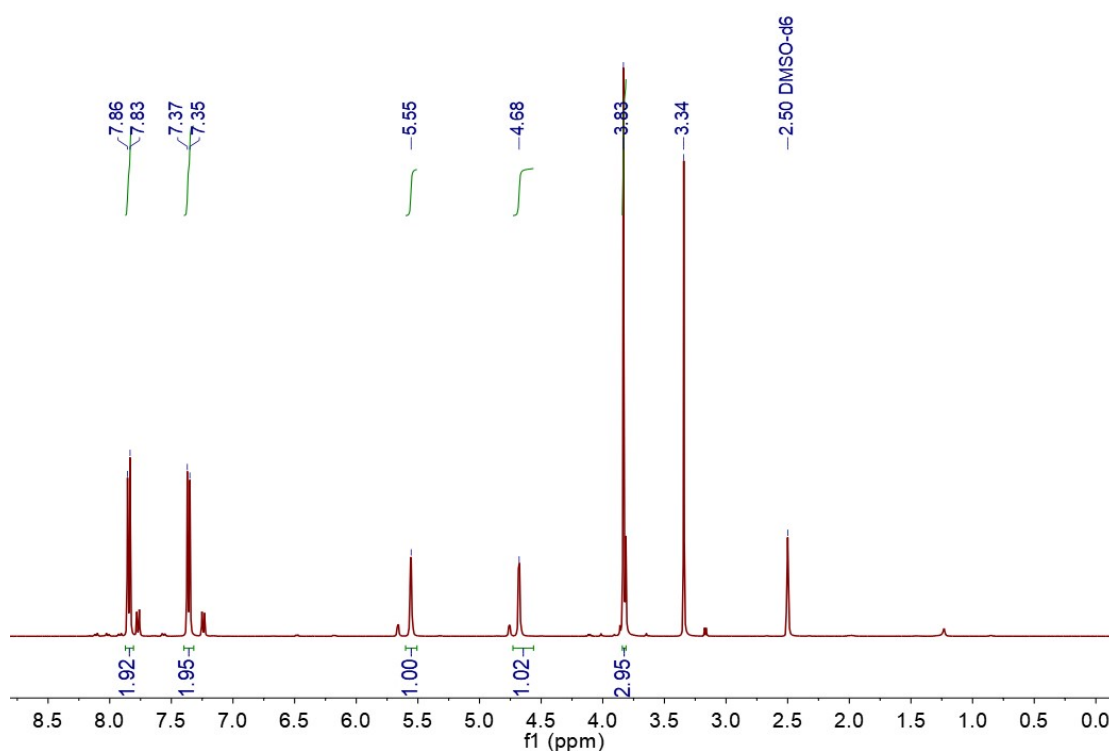
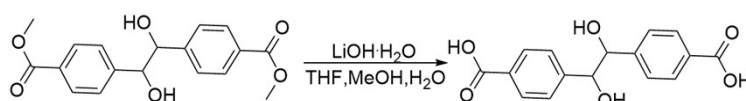


Figure S2. 400 MHz ¹H NMR spectrum of H₂dydb in DMSO-D₆.



Scheme S3. The synthesis method of 4, 4'-(1,2-dihydroxyethane-1, 2-diyl)dibenzoic acid.

Synthesis of 4, 4'-(1, 2-dihydroxyethane-1, 2-diyl)dibenzoic acid (H₄dhdba): The mixture of compound H₂dydb (5 g, 15mmol) and lithium hydroxide monohydrate (0.6g, 15mmol) was placed in a mixture of 60ml tetrahydrofuran, 40mL methanol and 20ml water and stirred overnight at room temperature. Dissolve in water and then spin steam to remove tetrahydrofuran and methanol. Adding 50 mmol concentrated hydrochloric acid to the solution, white solid was precipitated. After cooling to room temperature, the white solid was filtered off, washed with water and methanol, and then air-dried to afford the title compound. Yield: 3.2 g (71%).

¹H NMR (400 MHz, DMSO-d₆) δ 7.83 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 5.51 (s, 0H), 4.66 (s, 1H).

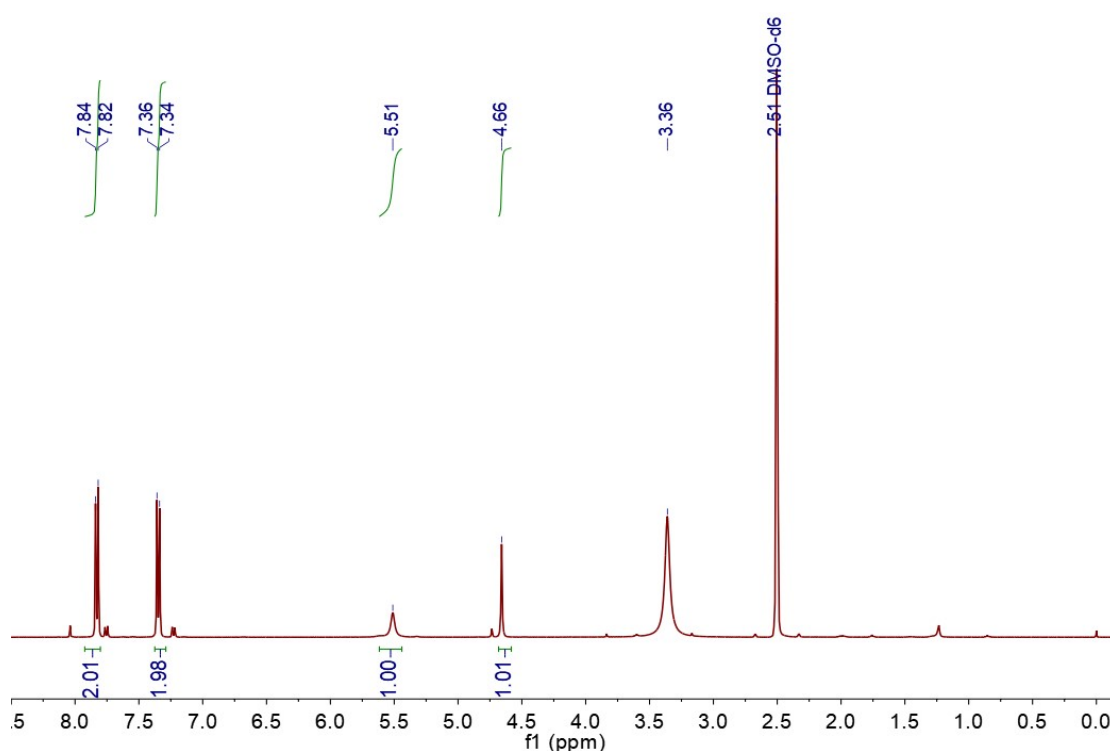


Figure S3. 400 MHz ¹H NMR spectrum of H₄dhdba in DMSO-D₆.

2.2 Synthesis of MOFs

General synthesis of compounds 1-9: Synthesis of Ln(L)_{1.5}(H₂O)₂•H₂O (Ln = Ce³⁺, Dy³⁺, Eu³⁺, Gd³⁺, Ho³⁺, Nd³⁺, Pr³⁺, Sm³⁺, Tb³⁺). The mixture of rare earth salt Ln(NO₃)₃•xH₂O (0.1 mmol) and H₄dhdba (0.1 mmol) in DEF/H₂O (2:1, 3 mL) was placed in screw-capped glass vial and heated at 100 °C for 1 day. Colorless crystals were collected and washed by N, N-Dimethylformamide (DMF).

Colorless prismatic crystals of 1-Ce were obtained (yield 56% based on Ce(NO₃)₃•6H₂O). Elemental analysis calcd (%) for C₂₄H₂₄CeO₁₂ (644.55): C 44.78, H 3.72; found: C 44.83, H 3.62.

IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 2-Dy were obtained (yield 76% based on $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{DyO}_{12}$ (666.93): C 43.28, H 3.52; found: C 43.29, H 3.52. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 3-Eu were obtained (yield 73% based on $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{EuO}_{12}$ (656.39): C 40.94, H 3.36; found: C 40.49, H 3.35. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 4-Gd were obtained (yield 65% based on $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{GdO}_{12}$ (616.30): C 43.78, H 3.58; found: C 43.83, H 3.62. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 5-Ho were obtained (yield 54% based on $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{HoO}_{12}$ (669.36): C 43.18, H 3.58; found: C 43.13, H 3.56. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 6-Nd were obtained (yield 60% based on $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{NdO}_{12}$ (648.67): C 44.75, H 3.70; found: C 44.66, H 3.77. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 7-Pr were obtained (yield 75% based on $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{PrO}_{12}$ (645.34): C 44.99, H 3.64; found: C 44.65, H 3.85. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 8-Sm were obtained (yield 68% based on $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{SmO}_{12}$ (654.78): C 44.54, H 3.65; found: C 44.38, H 3.64. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

Colorless prismatic crystals of 9-Tb were obtained (yield 77% based on $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{24}\text{TbO}_{12}$ (654.78): C 44.54, H 3.65; found: C 44.07, H 3.61. IR (KBr pellet cm^{-1}): 3375 w, 3309 w, 2898 w, 1624 m, 1589 s, 1550 s, 417 s, 1275 w, 1387 s, 1029 m, 1012 m, 773 s, 709 m, 531 m, 498 m.

2.3 X-Ray Crystallography

2.3.1 Single crystal structure determination

Data collections were collected at 100.00 K - 110.00 K on a ROD, Synergy Custom system, HyPix diffractometer equipped with Ga K α radiation ($\lambda = 1.3405 \text{ \AA}$) using a HyPix CCD detector. Nonhydrogen atoms were refined anisotropically, and all hydrogen atoms were generated geometrically. Absorption corrections were applied by using the multi-scan program. The structures were solved and refined using Full-matrix least-squares based on F2 with program SHELXS-2015² and SHELXL-2015 within Olex2.³ Crystallographic data and other pertinent information for 1–9 are summarized in Table 1. Selected bond distances and angles for these compounds are listed in Table S1, Supporting Information. CCDC numbers for coordination polymers 1–9 are 2303379–2303387, respectively.

Table S1. Crystal data and structure refinement for Crystals.

Compound ds	1-Ce	2-Dy	3-Eu	4-Gd	5-Ho	6-Nd	7-Pr	8-Sm	9-Tb
Empirical formula	C ₂₄ H ₂₄ C eO ₁₂	C ₂₄ H ₂₄ D yO ₁₂	C ₂₄ H ₂₄ E uO ₁₂	C ₂₄ H ₂₄ G dO ₁₂	C ₂₄ H ₂₄ H oO ₁₂	C ₂₄ H ₂₄ N dO ₁₂	C ₂₄ H ₂₄ Pr O ₁₂	C ₂₄ H ₂₄ S mO ₁₂	C ₂₄ H ₂₄ T bO ₁₂
Crystal system	monoclin ic	monoclin ic	monoclin ic	monoclin ic	monoclin ic	monoclin ic	monoclin ic	monoclin ic	monoclin ic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
a/ \AA	17.3426(3)	17.2906(7)	17.2995(3)	17.2951(5)	17.2596(3)	17.4259(3)	17.4448(4)	17.3836(3)	17.3235(7)
b/ \AA	9.36730(10)	9.22220(2)	9.31930(10)	9.2984(2)	9.20850(10)	9.27290(10)	9.26860(2)	9.24400(10)	9.2270(3)
c/ \AA	15.5652(3)	15.3769(6)	15.4902(2)	15.4981(4)	15.3367(3)	15.4800(3)	15.5561(5)	15.4813(3)	15.4275(6)
β / $^\circ$	110.316(2)	112.651(4)	111.900(2)	111.988(3)	112.653(2)	112.308(2)	112.084(3)	112.620(2)	112.661(5)
Volume/ \AA^3	2371.32(7)	2262.83(15)	2317.10(6)	2311.07(11)	2249.49(7)	2314.18(7)	2330.71(11)	2296.38(7)	2275.62(17)

Final indexes	$R_1=0.0275,$	$R_1=0.0262,$	$R_1=0.0337,$	$R_1=0.0308,$	$R_1=0.0374,$	$R_1=0.0446,$	$R_1=0.0325,$	$R_1=0.0286,$	$R_1=0.0263,$
[$I \geq 2\sigma$]	$wR_2=0.0684$	$wR_2=0.0599$	$wR_2=0.0873$	$wR_2=0.0670$	$wR_2=0.0976$	$wR_2=0.1$	$wR_2=0.0$	$wR_2=0.0$	$wR_2=0.0$
(I)	319	829	686	555					
CCDC	2303379	2303380	2303381	2303382	2303383	2303384	2303385	2303386	2303387

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \frac{[\sum (|F_o|^2 - |F_c|^2)] / \sum |F_o|^2}{1/2}$$

2.3.2 Powder X-ray diffraction analysis

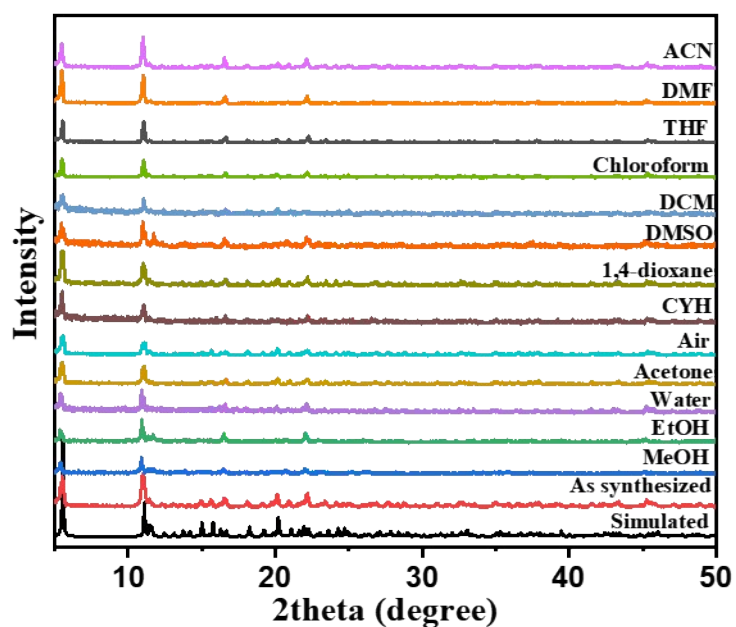


Figure S4. Powder XRD (PXRD) patterns of Dy under different conditions for 7 days at room temperature.

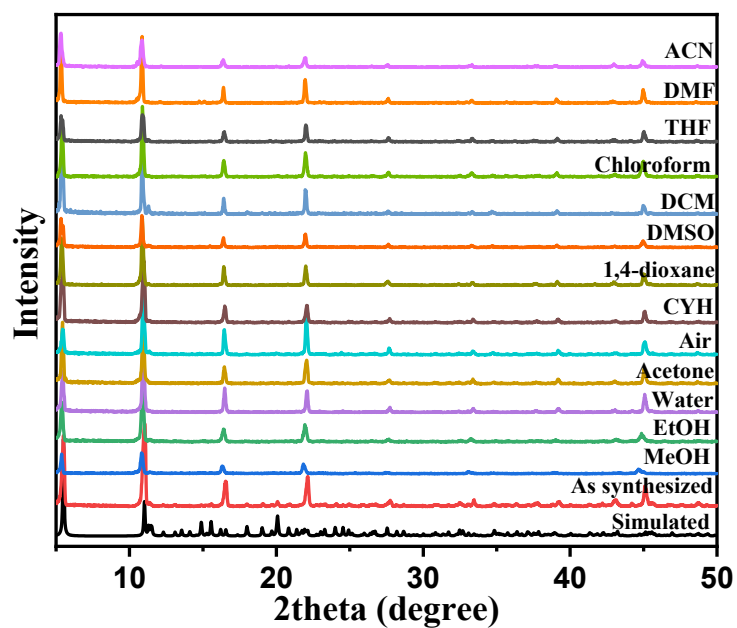


Figure S5. Powder XRD (PXRD) patterns of Eu under different conditions for 7 days at room temperature.

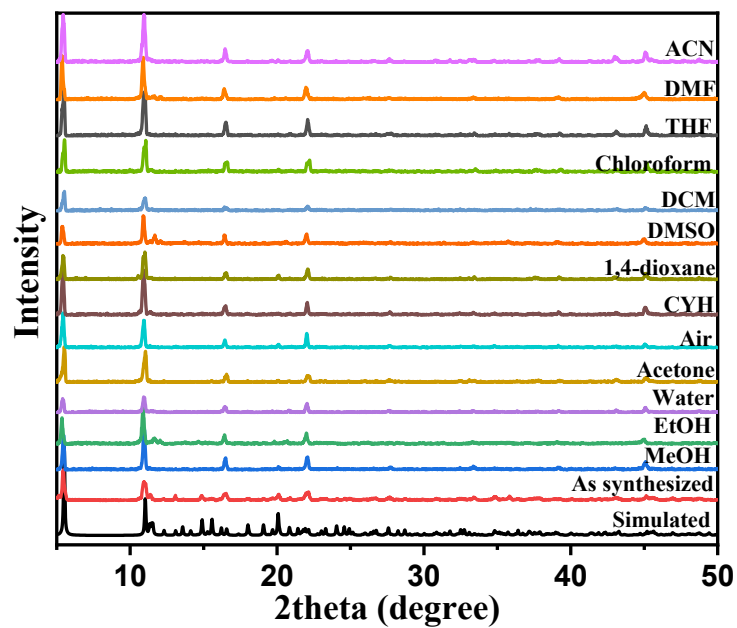


Figure S6. Powder XRD (PXRD) patterns of Gd under different conditions for 7 days at room temperature.

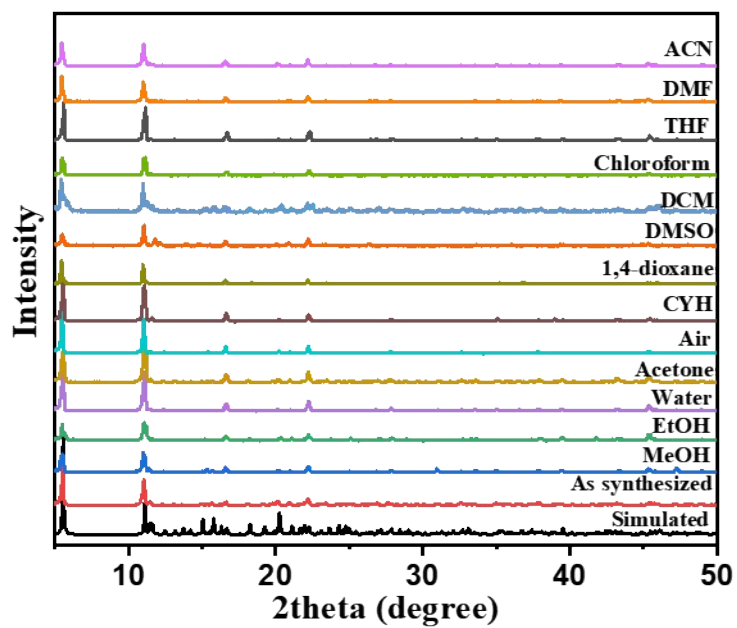


Figure S7. Powder XRD (PXRD) patterns of Ho under different conditions for 7 days at room temperature.

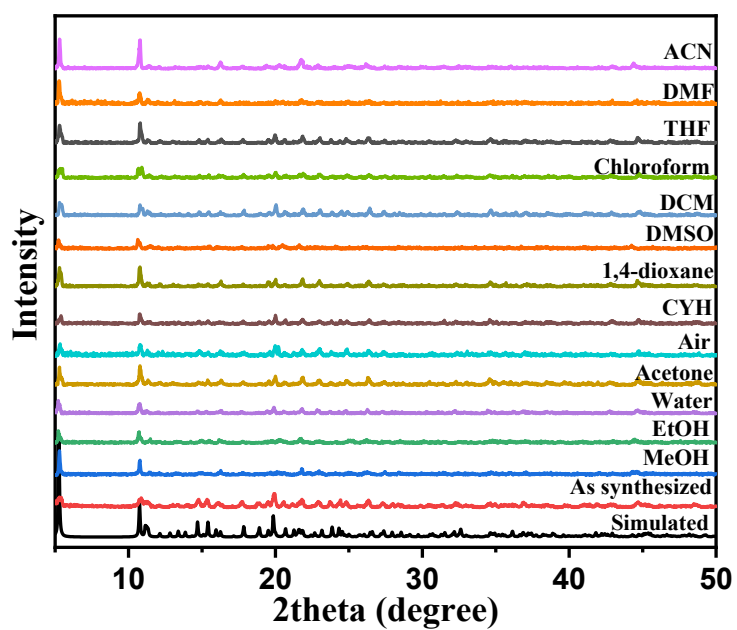


Figure S8. Powder XRD (PXRD) patterns of Nd under different conditions for 7 days at room temperature.

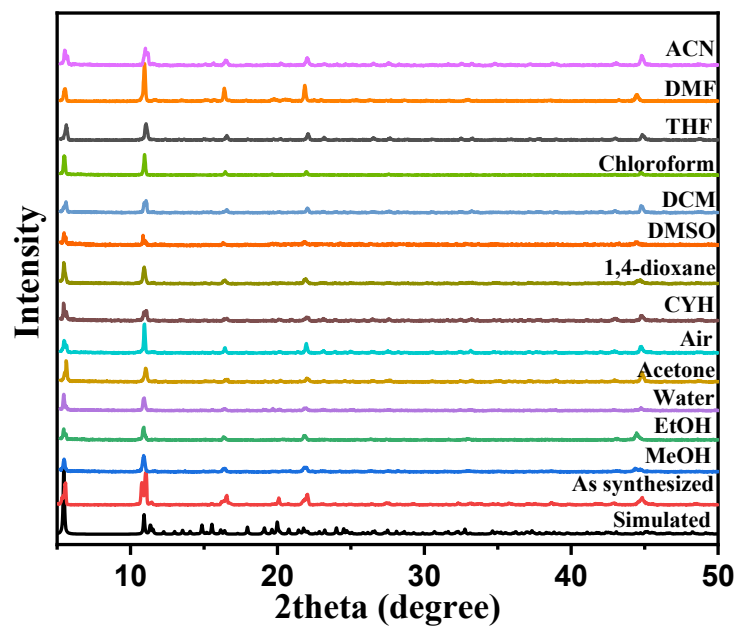


Figure S9. Powder XRD (PXRD) patterns of Pr under different conditions for 7 days at room temperature.

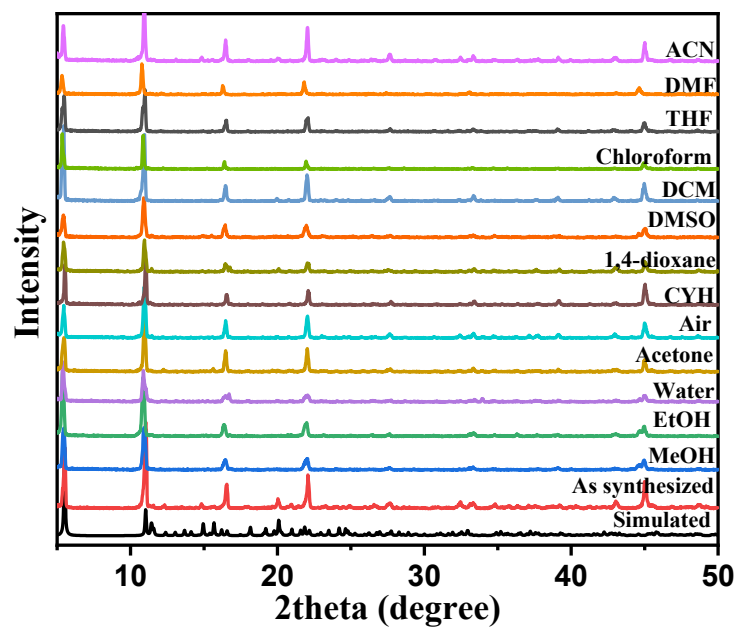


Figure S10. Powder XRD (PXRD) patterns of Sm under different conditions for 7 days at room temperature.

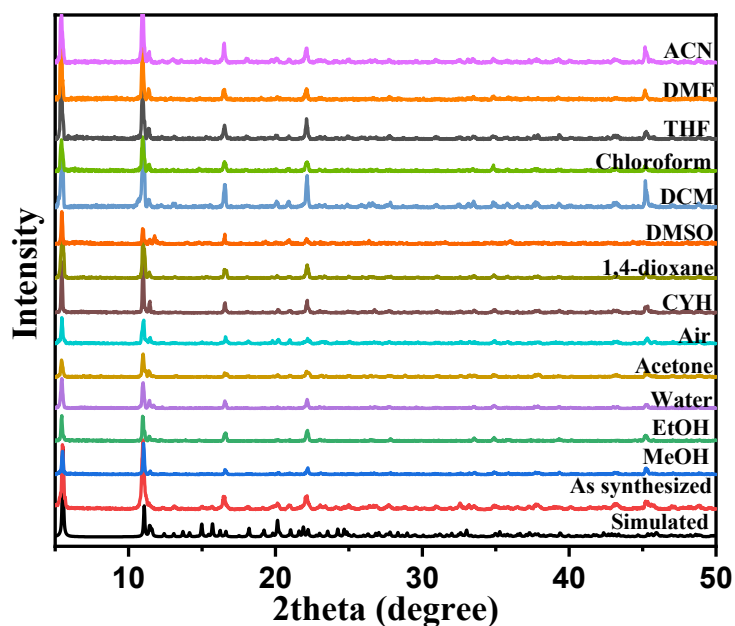


Figure S11. Powder XRD (PXRD) patterns of Tb under different conditions for 7 days at room temperature.

2.4 Morphological characteristics of crystals

The stability of nine compounds were further characterized through scanning electron microscope (SEM). Taking 1-Ce as example, the initial sample was a prismatic crystal with a smooth surface (Figure S12). After soaking in the solvent for a week (Figure S13), the crystal maintained its original transparent prismatic shape and the surface is still relatively smooth. Similar result was also observed after soaking 1-Ce in boiling water for 1 weeks (Figure S14). These results prove that they have good solvent stability.

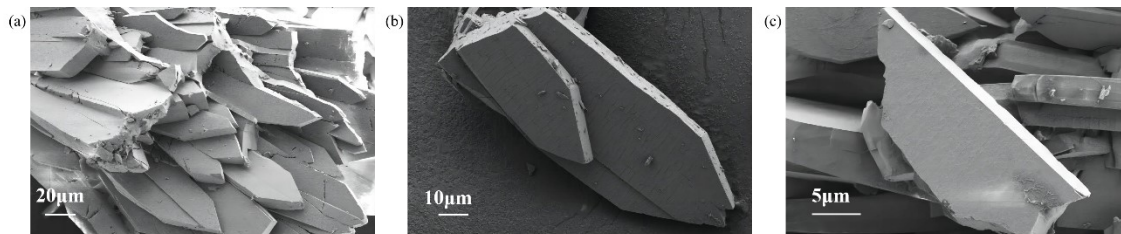


Figure S12 SEM images of the initial 1-Ce at different scales.

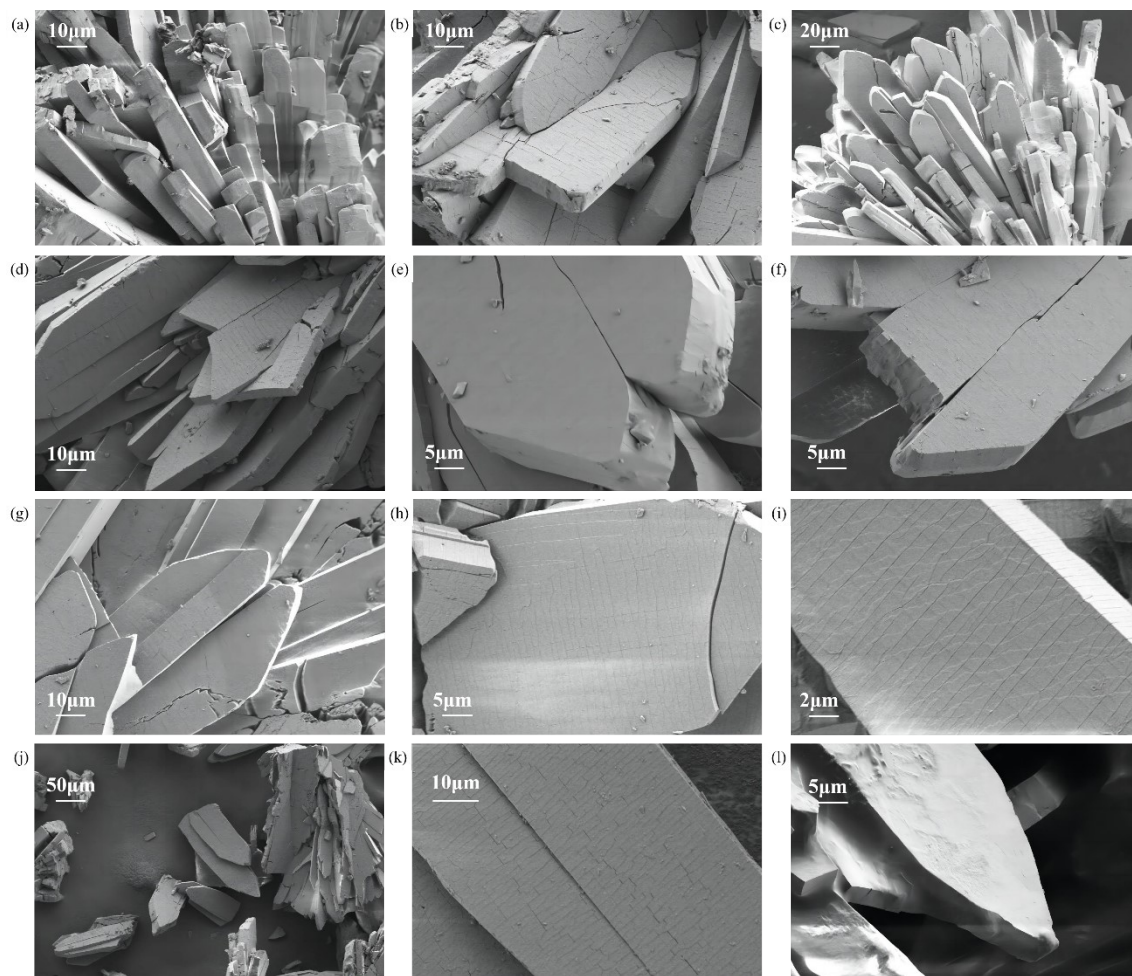


Figure S13 SEM image of the initial 1-Ce after solvent treatment (a) MeOH (b) EtOH (c) H₂O (d) acetone (e)

CYH (f) DMSO (g) 1, 4-dioxane (h) DCM (i) chloroform (j) THF (k) DMF (l) acetonitrile.

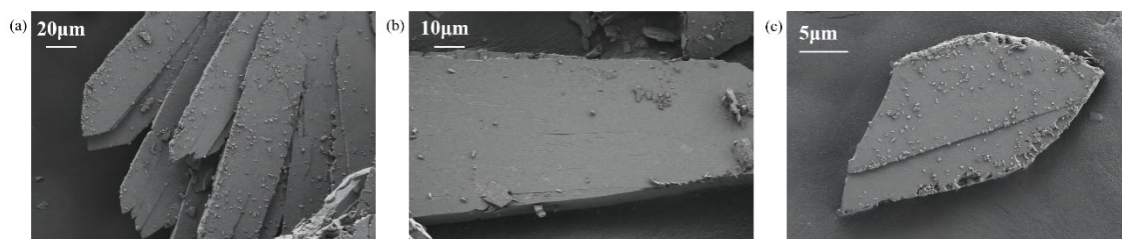


Figure S14 SEM image of the initial 1-Ce in boiling water for a week.

2.5 Thermogravimetric analyses

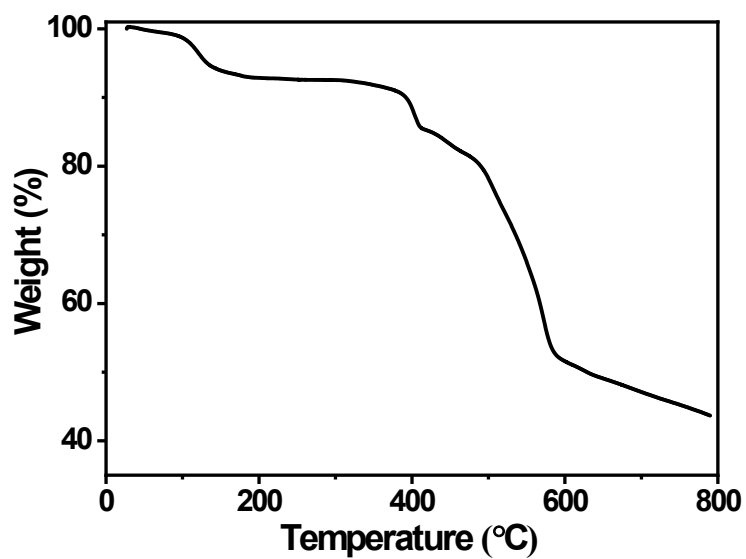


Figure S15. The TG plots of 1-Ce.

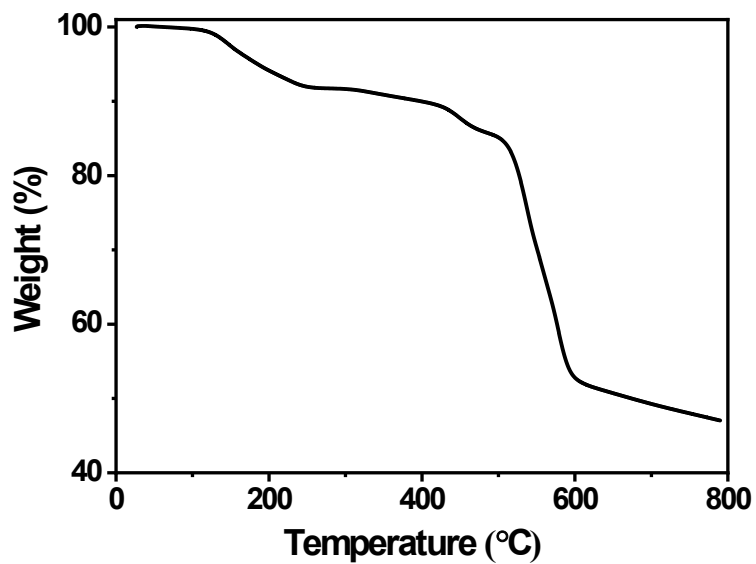


Figure S16. The TG plots of 2-Dy.

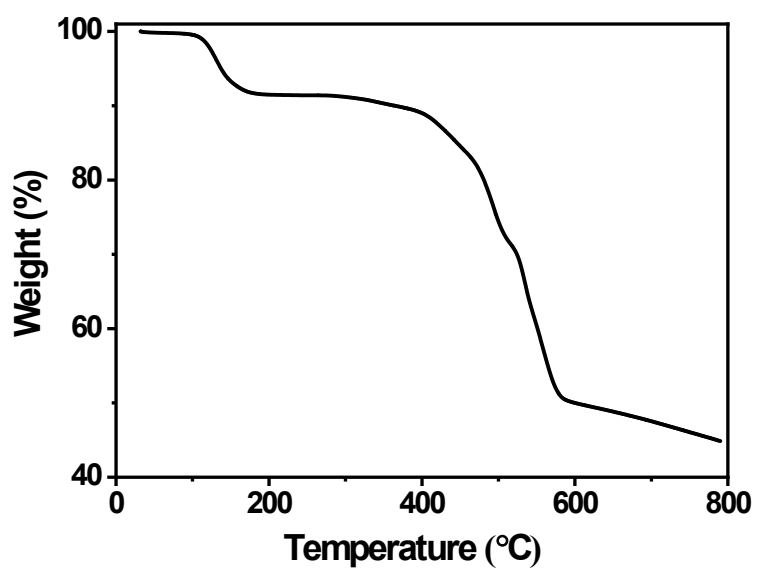


Figure S17. The TG plots of 3-Eu.

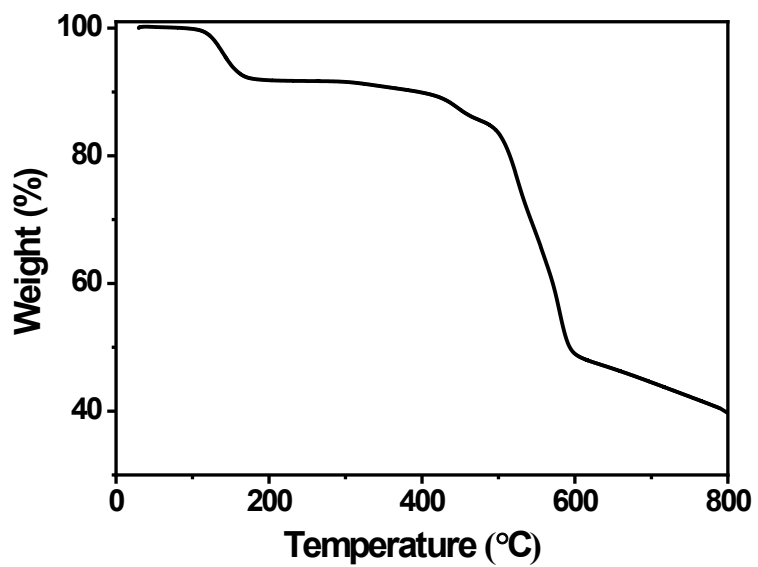


Figure S18. The TG plots of 4-Gd.

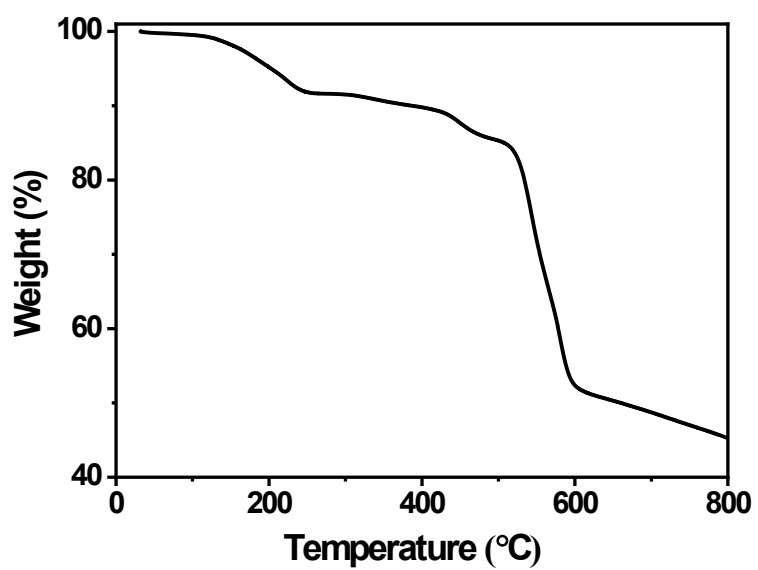


Figure S19. The TG plots of 5-Ho.

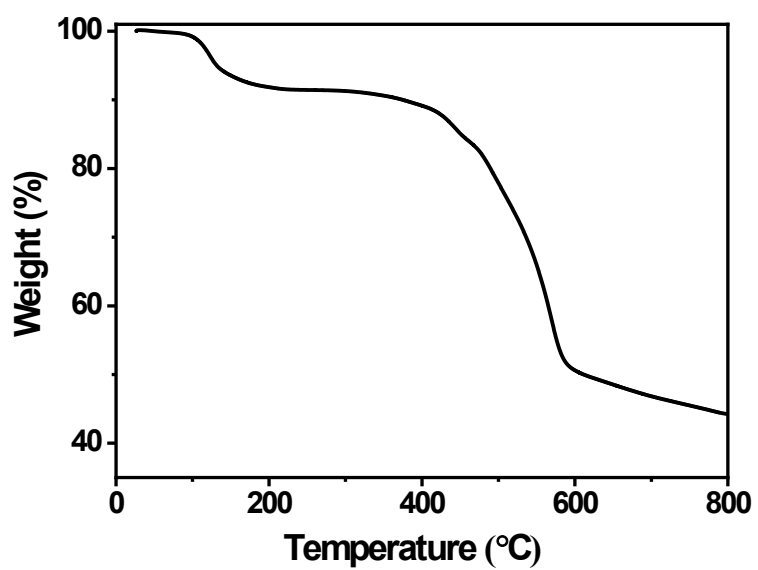


Figure S20. The TG plots of 6-Nd.

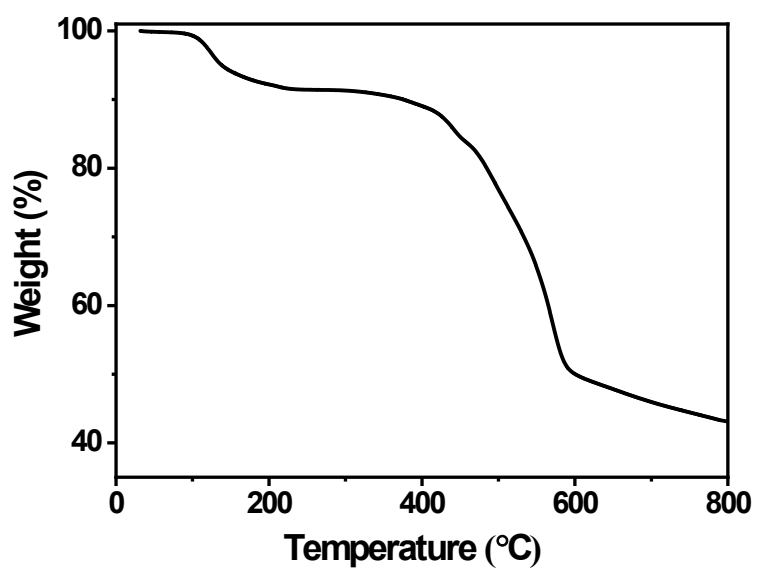


Figure S21. The TG plots of 7-Pr.

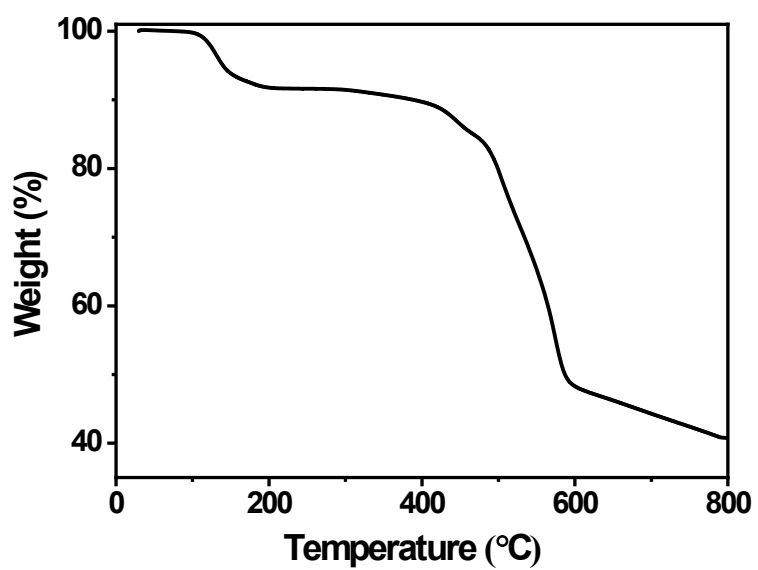


Figure S22. The TG plots of 8-Sm.

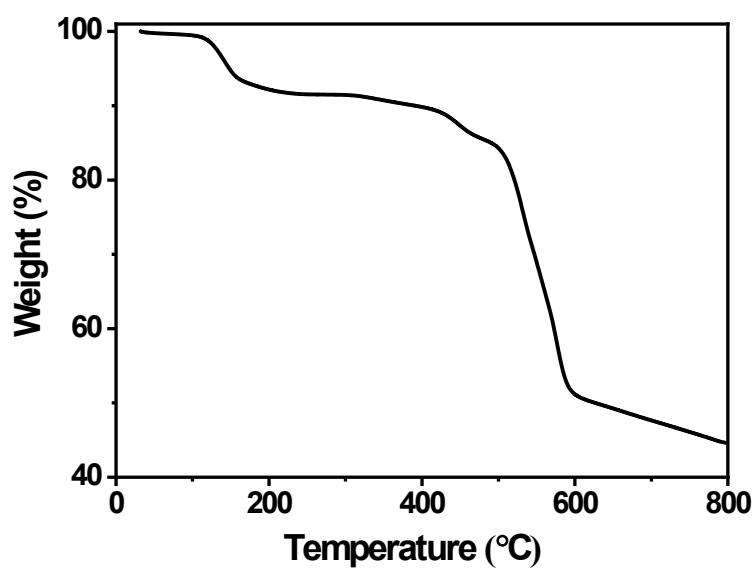


Figure S23 The TG plots of 9-Tb.

2.6 luminescent properties

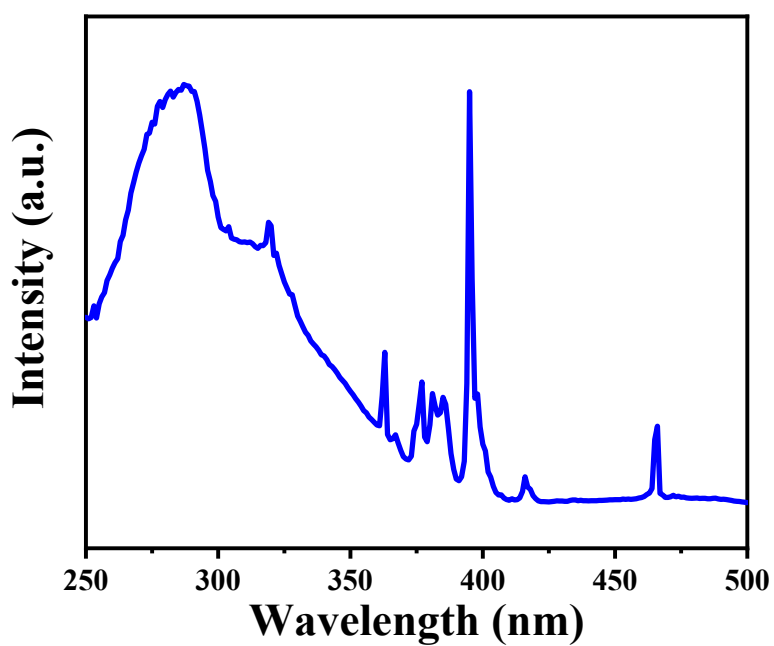


Figure S24 Solid-state excitation spectra for 3-Eu at room temperature.

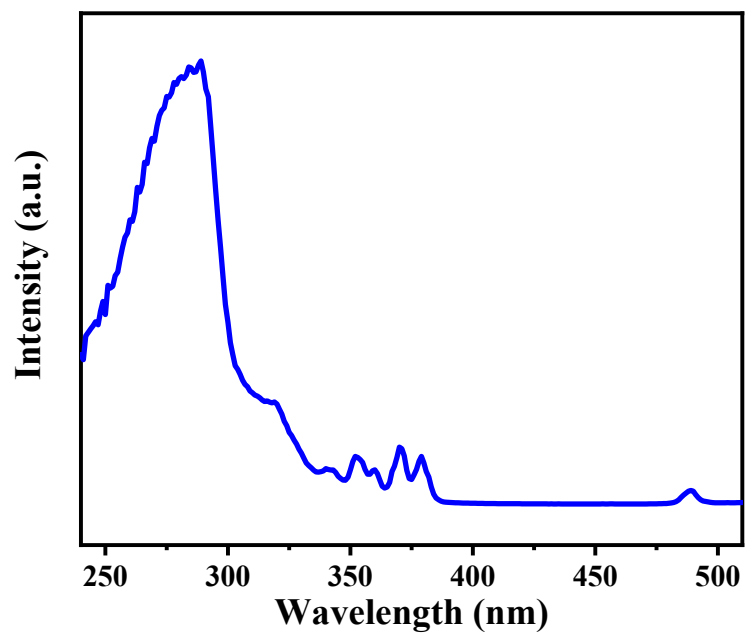


Figure S25 Solid-state excitation spectra for 9-Tb at room temperature.

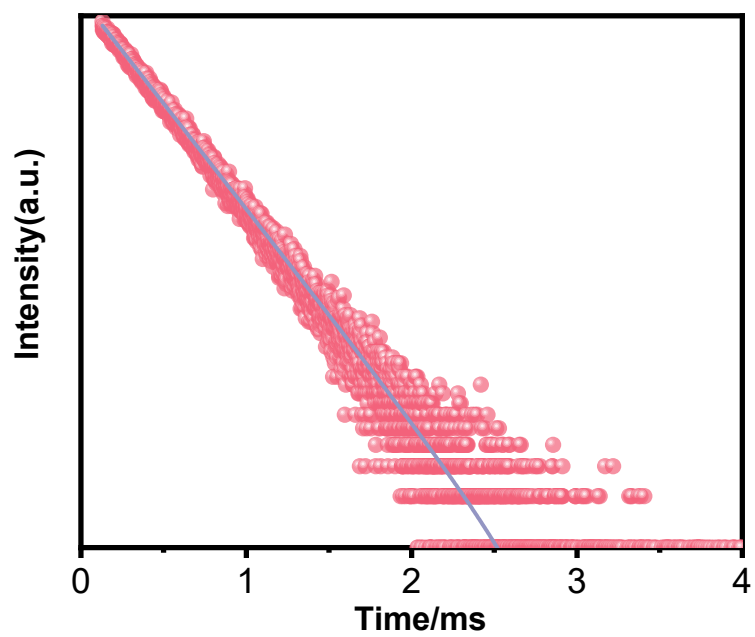


Figure S26 The luminescence decay curves for 3-Eu.

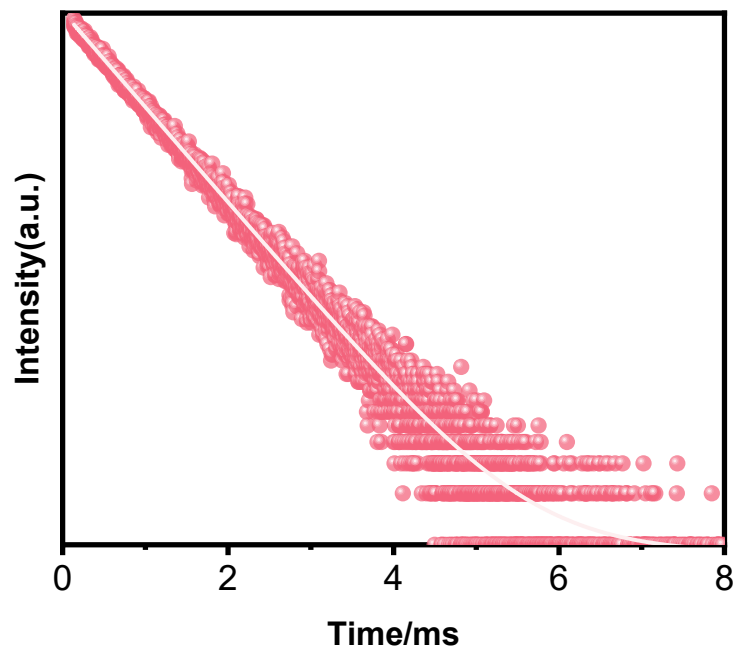


Figure S27 The luminescence decay curves for 9-Tb.

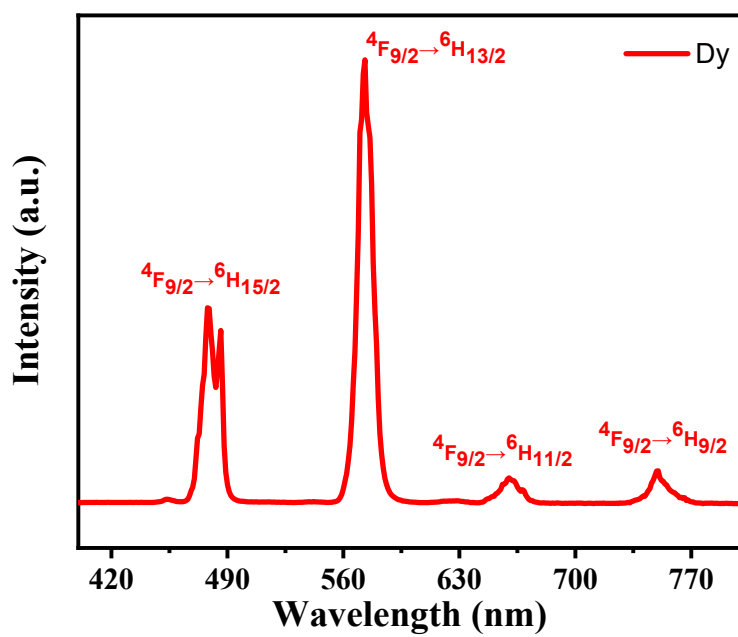


Figure S28 Solid-state emission spectra for 2-Dy at room temperature.

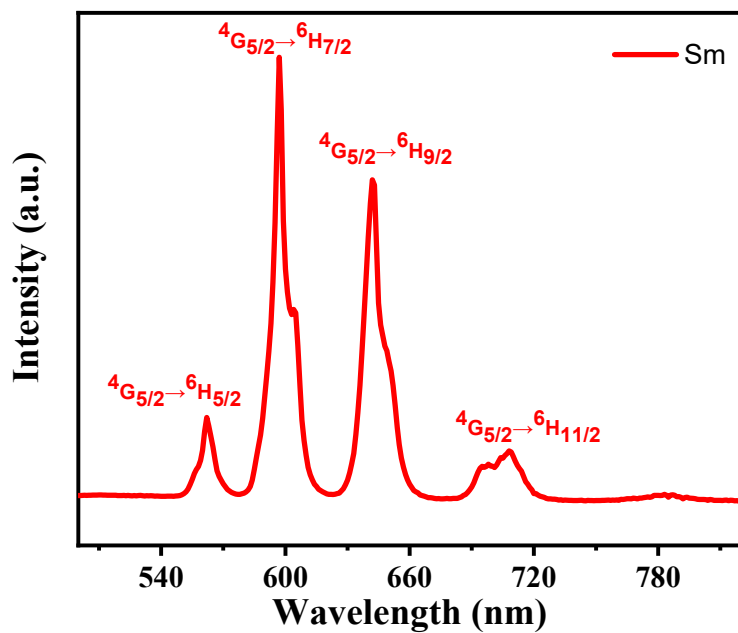


Figure S29 Solid-state emission spectra for 8-Sm at room temperature.

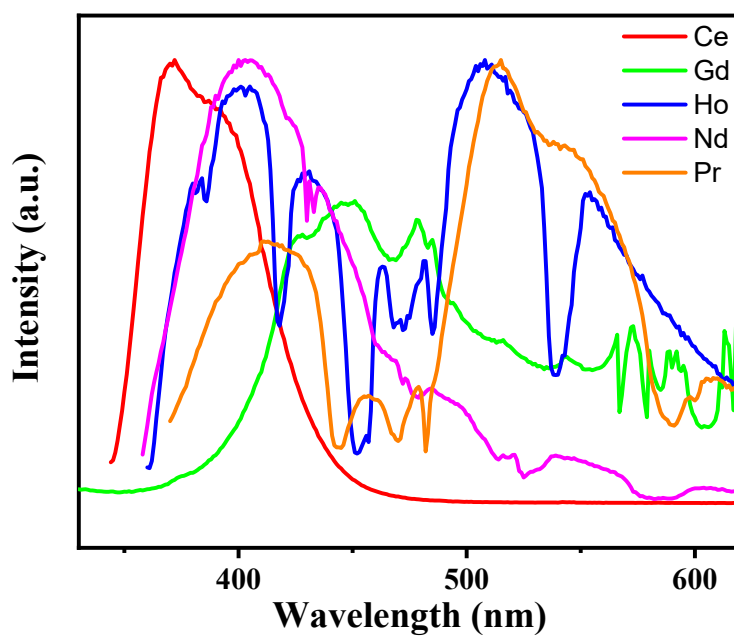


Figure S30 Solid-state emission spectra for 1, 4, 5, 6 and 7 at room temperature.

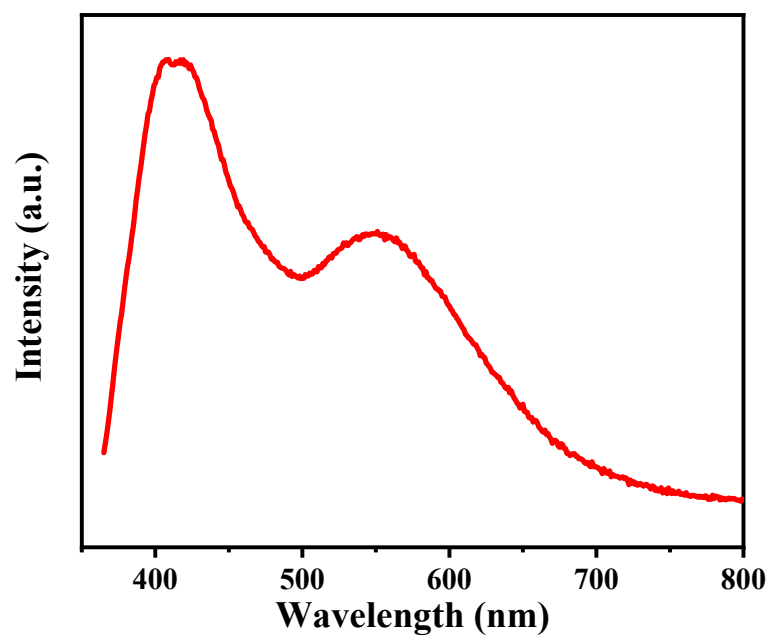


Figure S31 Solid-state emission spectra for H₄dhdba at room temperature.

2.7 Magnetic Properties.

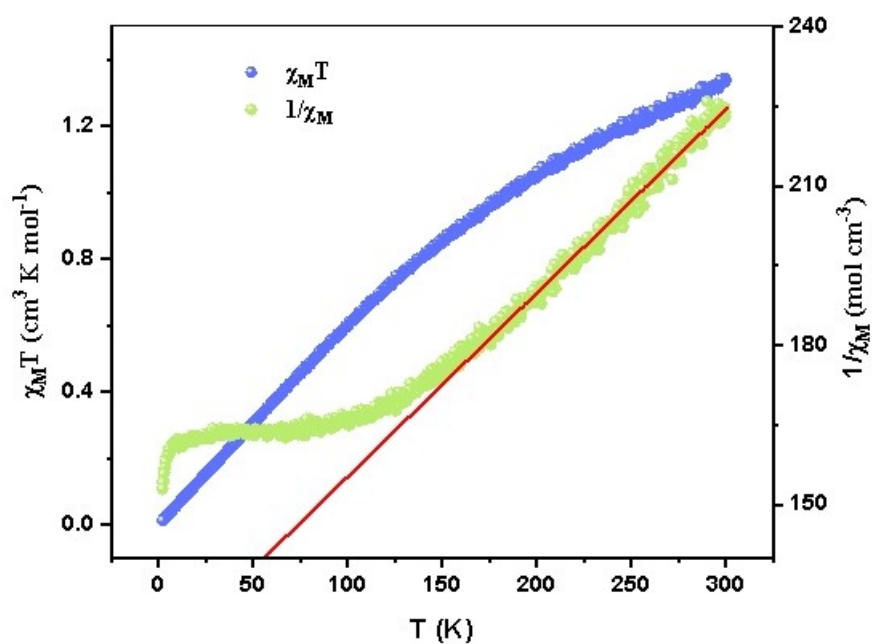


Figure S32 Temperature dependence of $\chi_M T$ and χ_M values for 1-Ce.

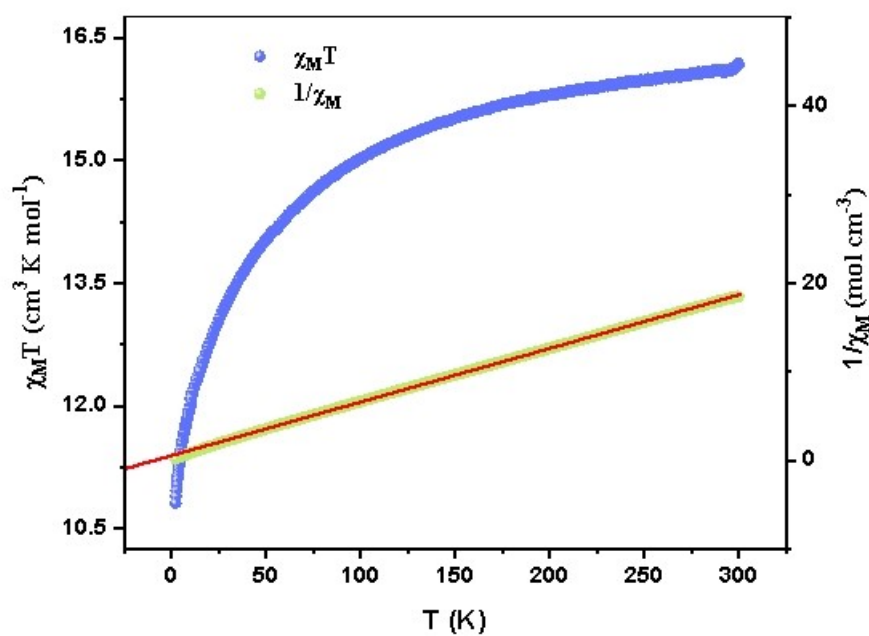


Figure S33 Temperature dependence of $\chi_M T$ and χ_M values for 3-Eu.

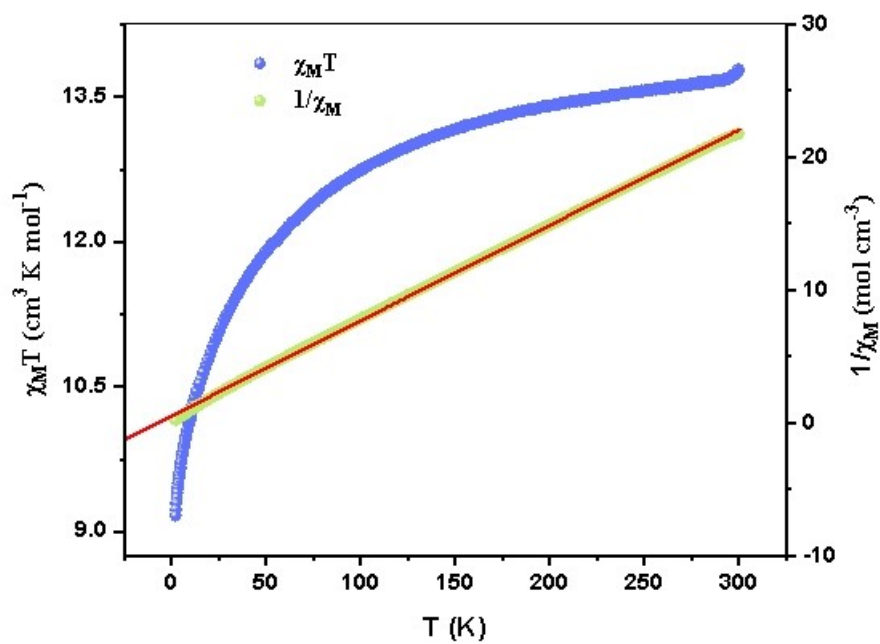


Figure S34 Temperature dependence of $\chi_M T$ and χ_M values for 5-Ho.

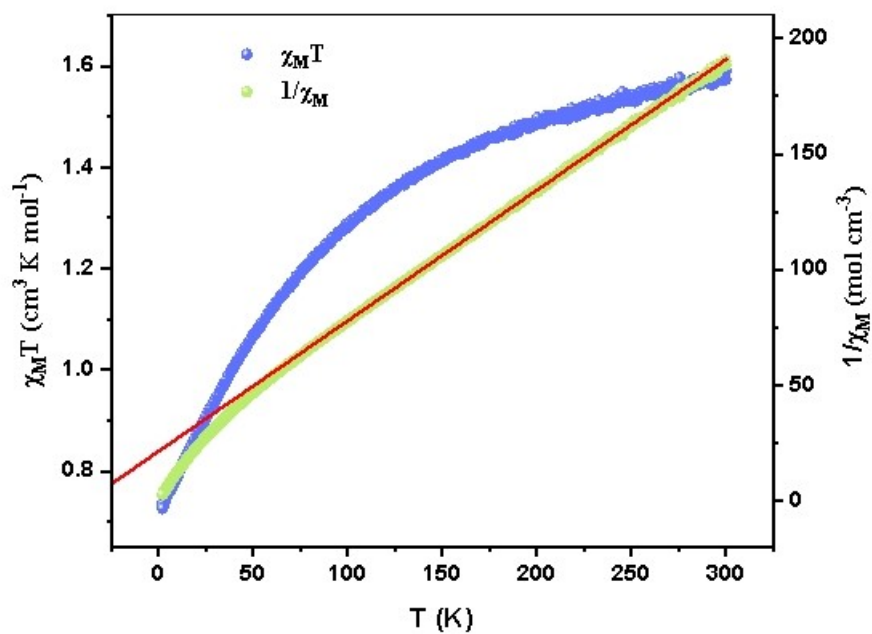


Figure S35 Temperature dependence of $\chi_M T$ and χ_M values for 6-Nd.

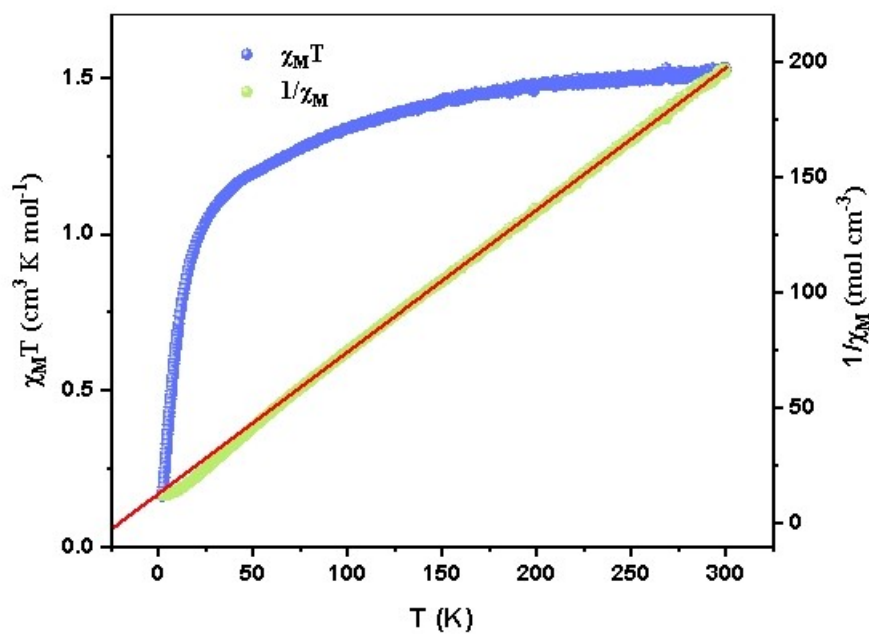


Figure S36 Temperature dependence of $\chi_M T$ and χ_M values for 7-Pr.

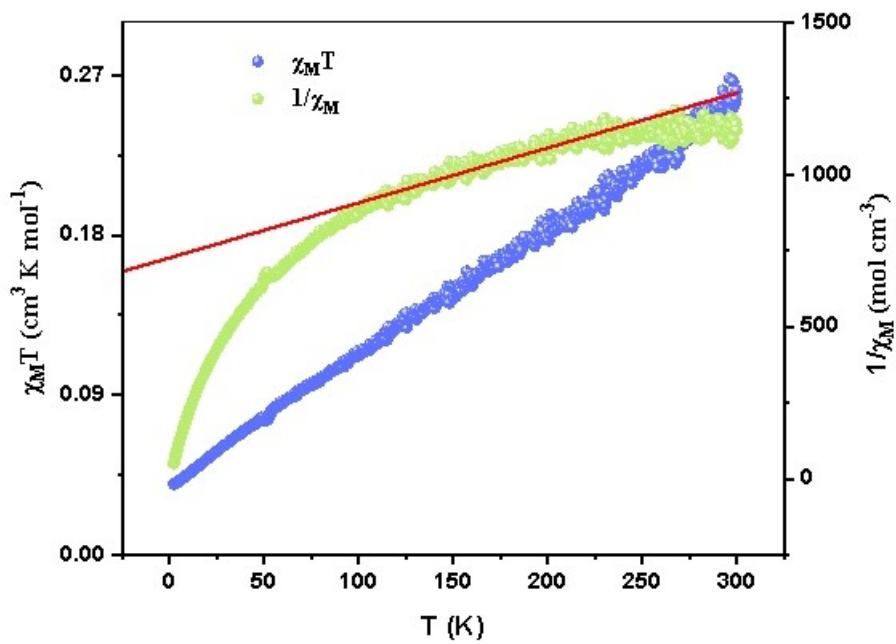


Figure S37 Temperature dependence of $\chi_M T$ and χ_M values for 8-Sm.

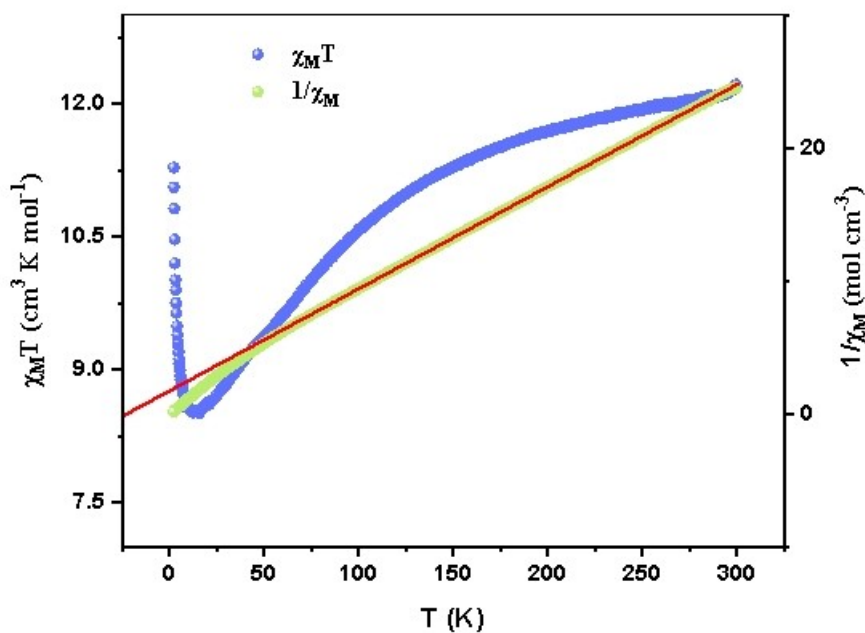


Figure S38 Temperature dependence of $\chi_M T$ and χ_M values for 9-Tb.

References

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