Electronic supplementary information

Luminescent cluster-organic frameworks constructed from predesigned supertetrahedral $\{Ln_4Zn_6\}$ secondary building units

Rui Ge[a], Jin-Hua Liu,[a] Xin-Hao Li,[b] Ling-Yun Li,[b] Yan-Qiong Sun,[a] Zhikai Li,[c] Xin-Xiong Li,*[a] and Shou-Tian Zheng*[a]

[a]*State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou, Fujian 350108, China.*

[b]*College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian 350108, China.*

[C] *College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, 518055 China.*

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Section S1 Synthesis and Methods

Materials and General methods: All the reactants and solvents were obtained from commercial sources and used for reactions without further purification. The H_3L ligand was synthesized according to literature procedure.[1] Powder XRD patterns were obtained using a RIGAKU-Miniflex II diffractometer with Cu *Kα* radiation (*λ* = 1.54056 Å). IR spectra were recorded on PerkinElmer Spectrum One FT-IR infrared spectrophotometer with pressed KBr pellets in the range of 4000-500 cm^{-1}. Fluorescence spectra were measured with an Edinburgh FLS980 fluorescence spectrophotometer equipped with an Oxford Instruments liquid nitrogen flow cryostat. ESI-TOF MS was recorded with a Waters Synapt G2-Si mass spectrometer, using solutions of 0.05 mg sample in 1 mL mixture of CH_3OH and DMF for **1-Eu**.

Synthesis of $Eu_4Zn_6(\mu_6\text{-}O)L_4(CH_3COO)_6(NO_3)_4(CH_3OH)_4(H_2O)_2\cdot 4CH_3CN$ (1-Eu): $Eu(NO_3)_3\cdot 6H_2O$ (0.1 mmol, 45 mg), $Zn(CH_3COO)_2\cdot 2H_2O$ (0.1 mmol, 22 mg), and H_3L (0.1 mmol, 18 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (6mL, v:v = 2:4), and then stirred for 1 h at room temperature. Then the solution was sealed in a 25 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless octahedral crystals were obtained. Yield: about 25mg (56.3 % based on $Eu(NO_3)_3\cdot 6H_2O$). IR (KBr pellet, ν/cm^{-1}, Fig. S10): 3216(m), 2925(w), 2865(w), 2819(w), 1704(w), 1557(s), 1413(s), 1320(s), 1231(w), 1173(w), 1088(s), 1043(m), 929(s), 817(w), 741(w), 661(s), 612(w), 562(m).

Synthesis of $Zn_6Eu_4(\mu_6\text{-}O)L_4(CH_3COO)_9(H_2O)_3\cdot$solvent (2-Eu): $Eu(NO_3)_3\cdot 6H_2O$ (0.5 mmol, 225 mg), $Zn(CH_3COO)_2\cdot 2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, yellow cubic crystals were obtained. Yield: about 50 mg (25.8 % based on $Eu(NO_3)_3\cdot 6H_2O$). IR (KBr pellet, ν/cm^{-1}, Fig. S11): 3381(m), 2925(w), 2866(w), 2818(w), 2740(w), 1569(s), 1418(s), 1384(s), 1234(w), 1173(w), 1093(s), 1075(m), 1047(m), 929(m), 874(w), 815(w), 771(w), 741(w), 662(m), 617(w), 566(w).

Synthesis of $Zn_6Tb_4(\mu_6\text{-}O)L_4(CH_3COO)_9(H_2O)_3\cdot$solvent (2-Tb): $Tb(NO_3)_3\cdot 6H_2O$ (0.5 mmol, 227 mg), $Zn(CH_3COO)_2\cdot 2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed

solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 20 mg (10.3 % based on $Tb(NO_3)_3·6H_2O$). IR (KBr pellet, ν/cm^{-1}, Fig. S12): 3328(s), 3224(s), 3137(s), 2923(w), 2873(w), 2734(w), 1697(m), 1550(s),1412(m), 1319(s), 1234(w), 1164(w), 1089(s), 1037(m), 929(s), 815(m), 732(w), 659(s), 615(w), 559(w).

Synthesis of $Zn_6Gd_4(\mu_6\text{-}O)L_4(CH_3COO)_9(H_2O)_3$·solvent (2-Gd): $Gd(NO_3)_3·6H_2O$ (0.5 mmol, 226 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 50 mg (25.8 % based on $Gd(NO_3)_3·6H_2O$). IR (KBr pellet, ν/cm^{-1}, Fig. S13): 3289(s), 3218(s), 3141(s), 2929(m), 2865(m),1700(m), 1554(s), 1407(s), 1319(s), 1236(w), 1166(w), 1087(s), 1022(m), 929(s), 869(w), 817(m), 730(w), 659(m), 615(w), 562(w).

Synthesis of 2-Ln (35%Eu45%Tb20%Gd): $Eu(NO_3)_3·6H_2O$ (0.175 mmol, 80 mg), $Tb(NO_3)_3·6H_2O$ (0.225 mmol, 102 mg), $Gd(NO_3)_3·6H_2O$ (0.1 mmol, 45 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, yellow cubic crystals were obtained. Yield: about 45 mg (23.3 % based on $Zn(CH_3COO)_2·2H_2O$).

Synthesis of 2-Ln (30%Eu30%Tb40%Gd): $Eu(NO_3)_3·6H_2O$ (0.15 mmol, 67 mg), $Tb(NO_3)_3·6H_2O$ (0.15 mmol, 68 mg), $Gd(NO_3)_3·6H_2O$ (0.2 mmol, 91 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, yellow cubic crystals were obtained. Yield: about 35 mg (18.1 % based on $Zn(CH_3COO)_2·2H_2O$).

Synthesis of 2-Ln (20%Eu30%Tb50%Gd): $Eu(NO_3)_3·6H_2O$ (0.1 mmol, 45 mg), $Tb(NO_3)_3·6H_2O$ (0.15 mmol, 68 mg), $Gd(NO_3)_3·6H_2O$ (0.25 mmol, 113 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 40 mg (20.7 % based on $Zn(CH_3COO)_2·2H_2O$).

Synthesis of 2-Ln (15%Eu30%Tb55%Gd): $Eu(NO_3)_3·6H_2O$ (0.075 mmol, 34 mg), $Tb(NO_3)_3·6H_2O$ (0.15 mmol, 68 mg), $Gd(NO_3)_3·6H_2O$ (0.275 mmol, 124 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 30 mg (15.5 % based on $Zn(CH_3COO)_2·2H_2O$).

Synthesis of 2-Ln (10%Eu30%Tb60%Gd): $Eu(NO_3)_3·6H_2O$ (0.05 mmol, 22 mg), $Tb(NO_3)_3·6H_2O$ (0.225 mmol, 102 mg), $Gd(NO_3)_3·6H_2O$ (0.3 mmol, 136 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 37 mg (19.1 % based on $Zn(CH_3COO)_2·2H_2O$).

Synthesis of 2-Ln (10%Eu20%Tb70%Gd): $Eu(NO_3)_3·6H_2O$ (0.05 mmol, 22 mg), $Tb(NO_3)_3·6H_2O$ (0.1 mmol, 45 mg), $Gd(NO_3)_3·6H_2O$ (0.35 mmol, 158 mg), $Zn(CH_3COO)_2·2H_2O$ (0.5 mmol, 110 mg), and H_3L (0.5 mmol, 90 mg) were dissolved in a mixed solution of CH_3OH/CH_3CN (27.5mL, v:v = 2.5:25), and then stirred for 1 h at room temperature. Then the solution was sealed in a 100 mL Teflon-lined stainless steel container and heated at 120 °C for 72 h. After the solution cooled to room temperature, colorless cubic crystals were obtained. Yield: about 32 mg (16.5 % based on $Zn(CH_3COO)_2·2H_2O$).

Single-crystal structure analysis: Single-crystal X-ray diffraction data of **1-Eu** was collected on Bruker Apex Duo CCD diffractometer with a graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) operating at 175 K. The structure of **1-Eu** was solved through direct methods and refined by full-matrix least-squares refinements based on F^2 adopting the SHELX-2014 program package. The C(15), C(16), and O1w ions in **1-Eu** were disordered and scattered over two positions. The C(16) and C(17) ions in **2-Eu** were disordered and scattered over three positions. All non-H atoms were located with successive difference Fourier syntheses and refined anisotropically. The H atoms of the free water molecules and coordinated water molecules have not been included in the final refinement. Crystallographic data and structure refinements for **1-Eu** and **2-Eu** are summarized in Table S1. CCDC 2076012 and 2076140 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Section S2 Additional Tables

Table S1 Crystal Data and Structure Refinement for **1-Eu** and **2-Eu**

	1-Eu	**2-Eu**
Empirical formula	$Eu_4Zn_6O_{43}N_{12}C_{60}H_{86}$	$Eu_4Zn_6O_{34}N_4C_{54}H_{73}$
Formula weight	2663.46	2322.22
Crystal system	Tetragonal	Cubic
Space group	$P4_2/n$	$I3d$
a (Å)	13.8705(3)	35.0393(3)
b (Å)	13.8705(3)	35.0393(3)
c (Å)	22.5752(8)	35.0393(3)
V (Å^3)	4343.3(2)	43020(10)
Z	2	16
F(000)	2612	18064
crystal size / mm	0.23 × 0.24 × 0.24	0.21 × 0.21 × 0.22
ϑ range / °	2.326 to 25.044	2.175 to 25.058
limiting indices	-16 ≤ h ≤ 16 -16 ≤ k ≤ 16 -26 ≤ l ≤ 26	-41 ≤ h ≤ 41 -41 ≤ k ≤ 23 -41 ≤ l ≤ 24
ρ_{calcd}(g cm^{-3})	2.037	1.434
Temperature (K)	175(2)	175(2)
$\mu(mm^{-1})$	4.565	3.668
Refl. Collected	38470	53673
Independent relf.	3848	6292
Parameters	213	308
R_{int}	0.0323	0.0929
GOF on F^2	1.073	1.074
Final R indices ($I = 2\sigma(I)$)	R_1= 0.0397, wR_2= 0.1029	R_1= 0.0450, wR_2= 0.0991
R indices (all data)	R_1= 0.0469, wR_2= 0.1081	R_1= 0.0702, wR_2= 0.1097

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/w(F_o)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, where x = 0.0467, y = 44.9876 for **1-Eu**; x = 0.0450, y = 410.1602 for **2-Eu**.

Table S2 CIE chromaticity coordinates of **2-Ln** with different Eu: Tb: Gd ratios.

Samples (Eu:Tb:Gd)	**(x,y)**
35%Eu45%Tb20%Gd	(0.37, 0.34)
30%Eu30%Tb40%Gd	(0.36, 0.31)
20%Eu30%Tb50%Gd	(0.34, 0.32)
15%Eu30%Tb55%Gd	(0.32, 0.33)
10%Eu30%Tb60%Gd	(0.29 ,0.32)
10%Eu20%Tb70%Gd	(0.31, 0.34)

Section S3 Additional Figures

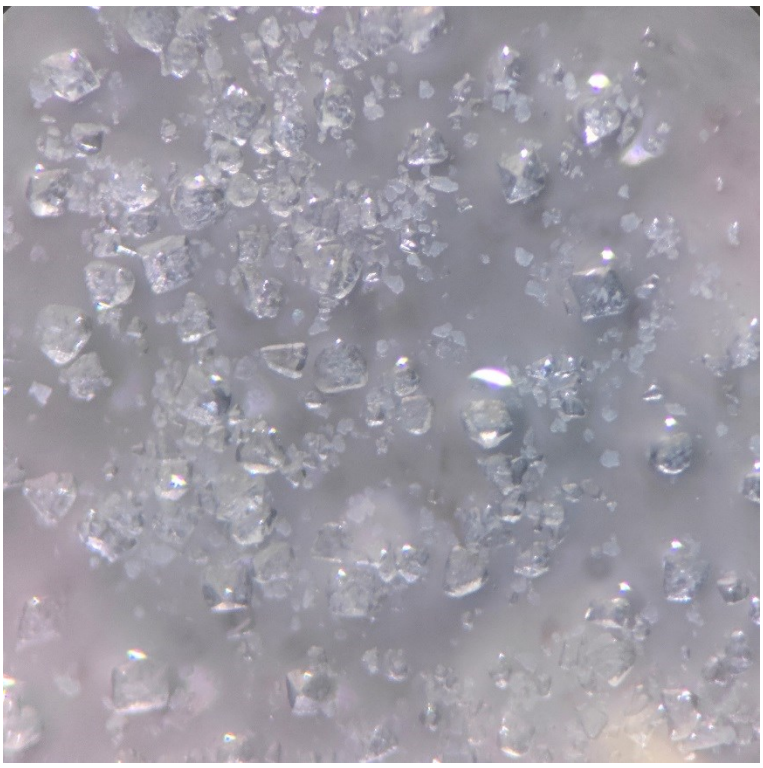

Fig. S1. Optical photograph of **1-Eu**.

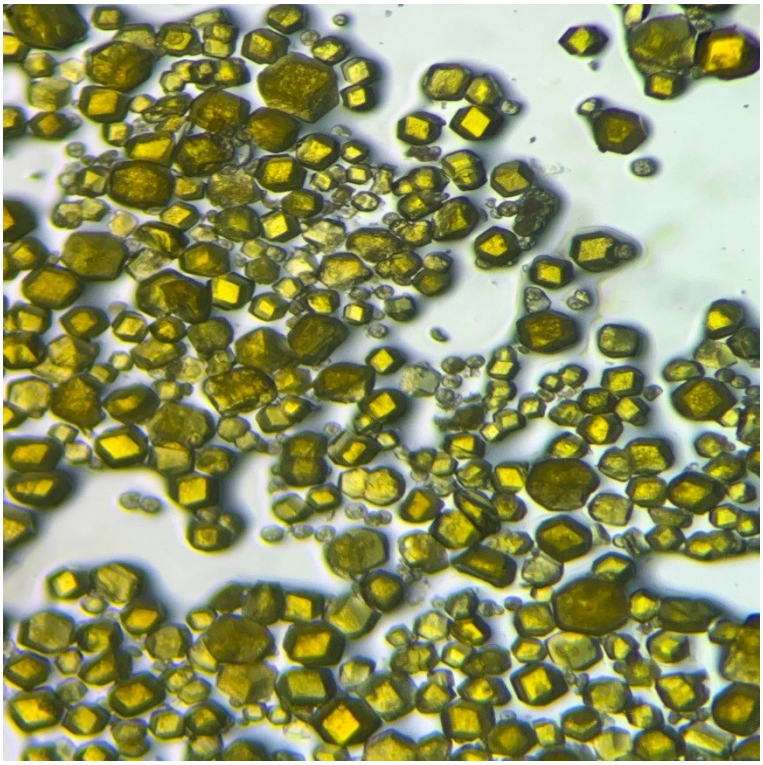

Fig. S2. Optical photograph of **2-Eu**.

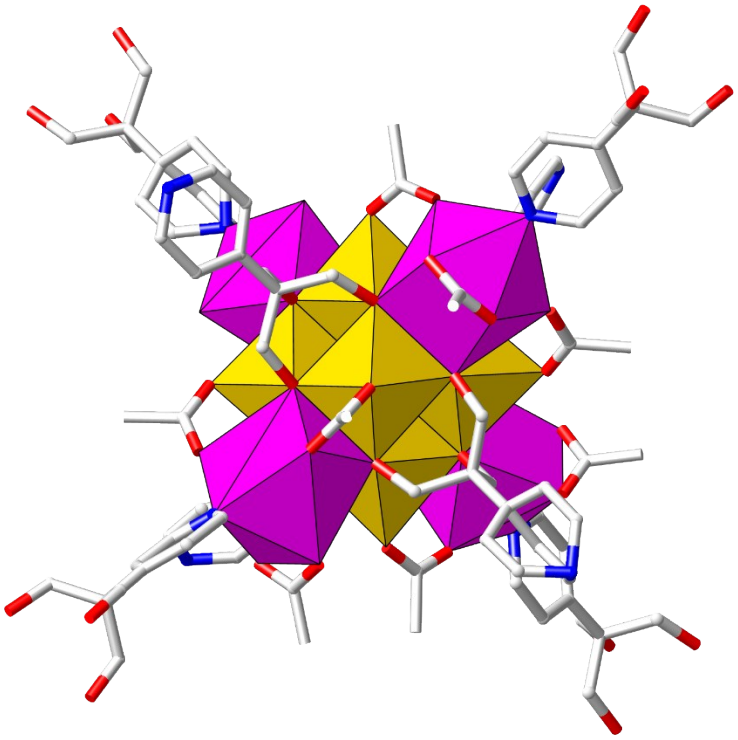

Fig. S3. Polyhedral mode of the SBU in **2-Eu**.

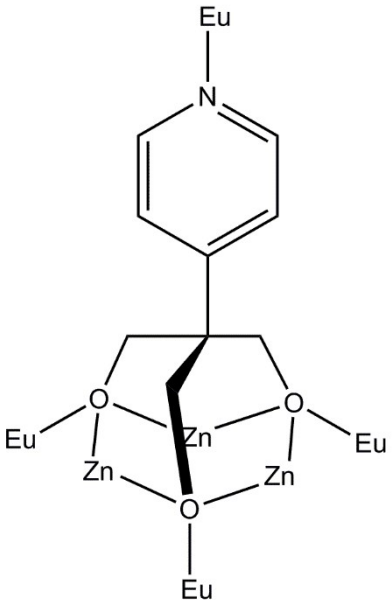

Fig. S4. View of the coordination mode of the L^{3-} ligand in **2-Eu**.

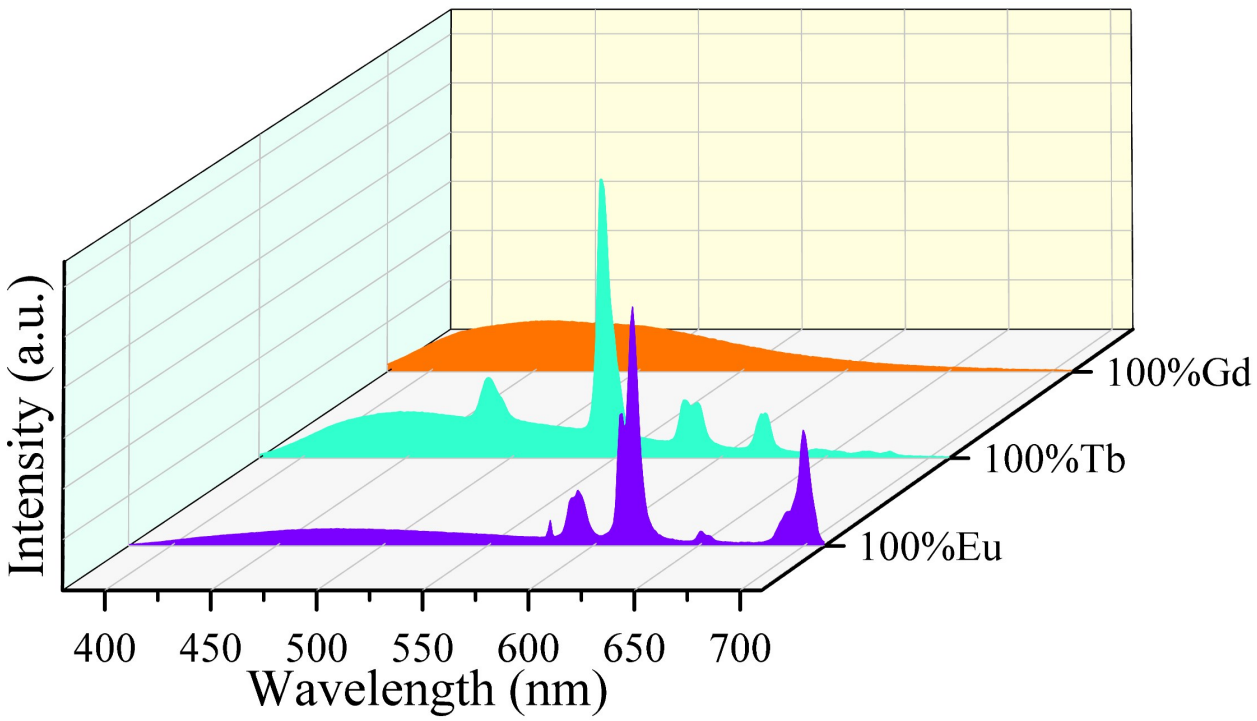

Fig. S5. Emission spectra of **2-Eu**, **2-Tb**, and **2-Gd**.

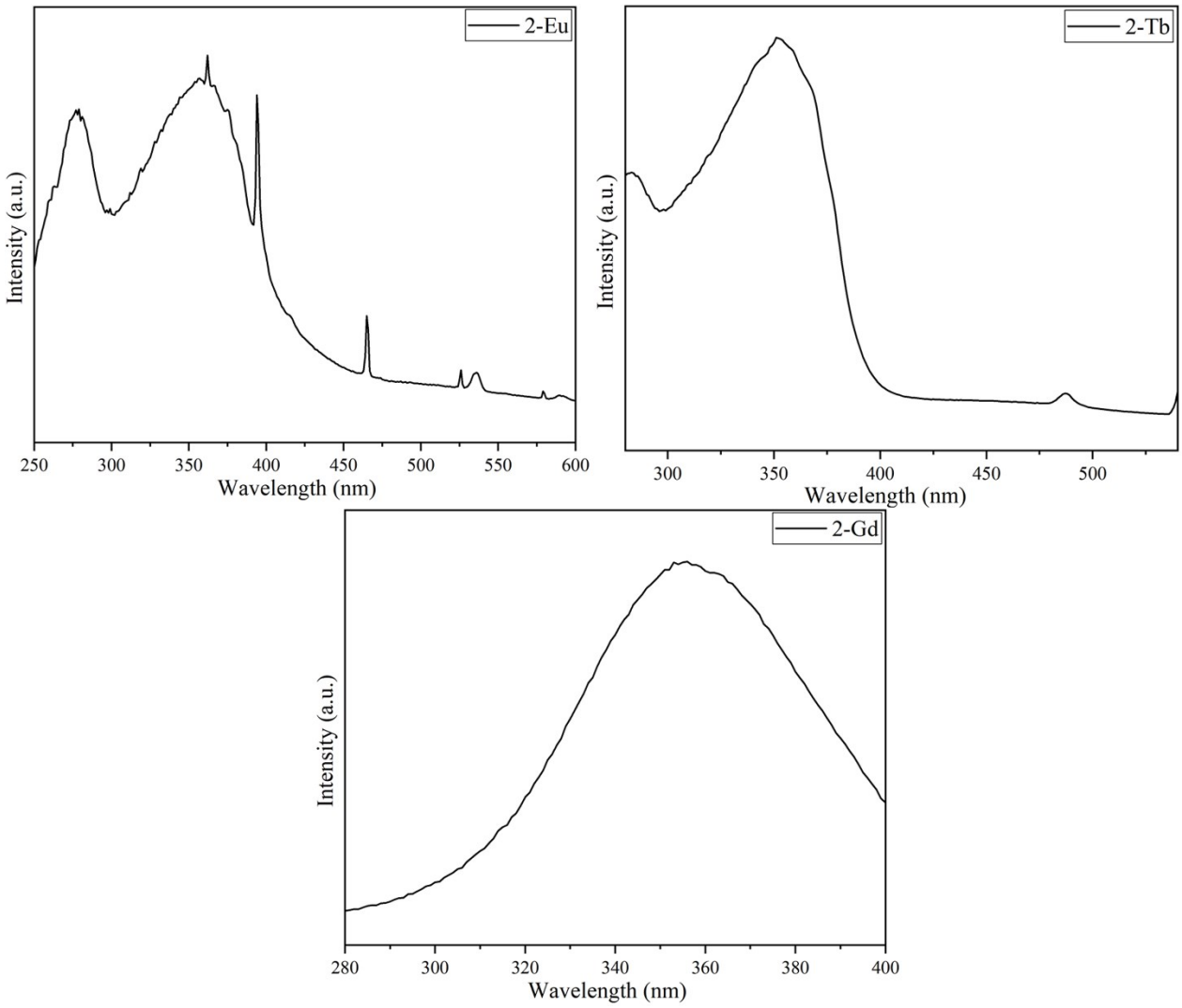

Fig. S6. Excitation spectra of **2-Eu**, **2-Tb**, and **2-Gd**.

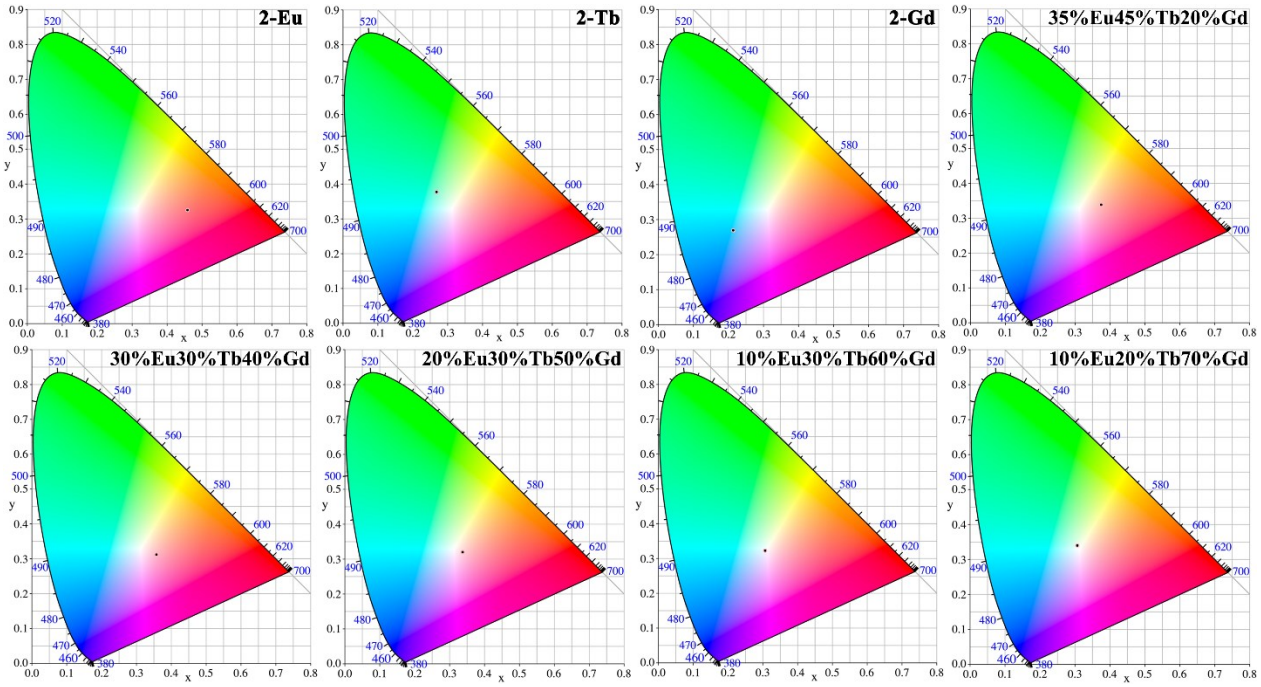

Fig. S7. CIE chromaticity diagrams of **2-Eu**, **2-Tb**, **2-Gd**, and tri-doped **2-Ln**.

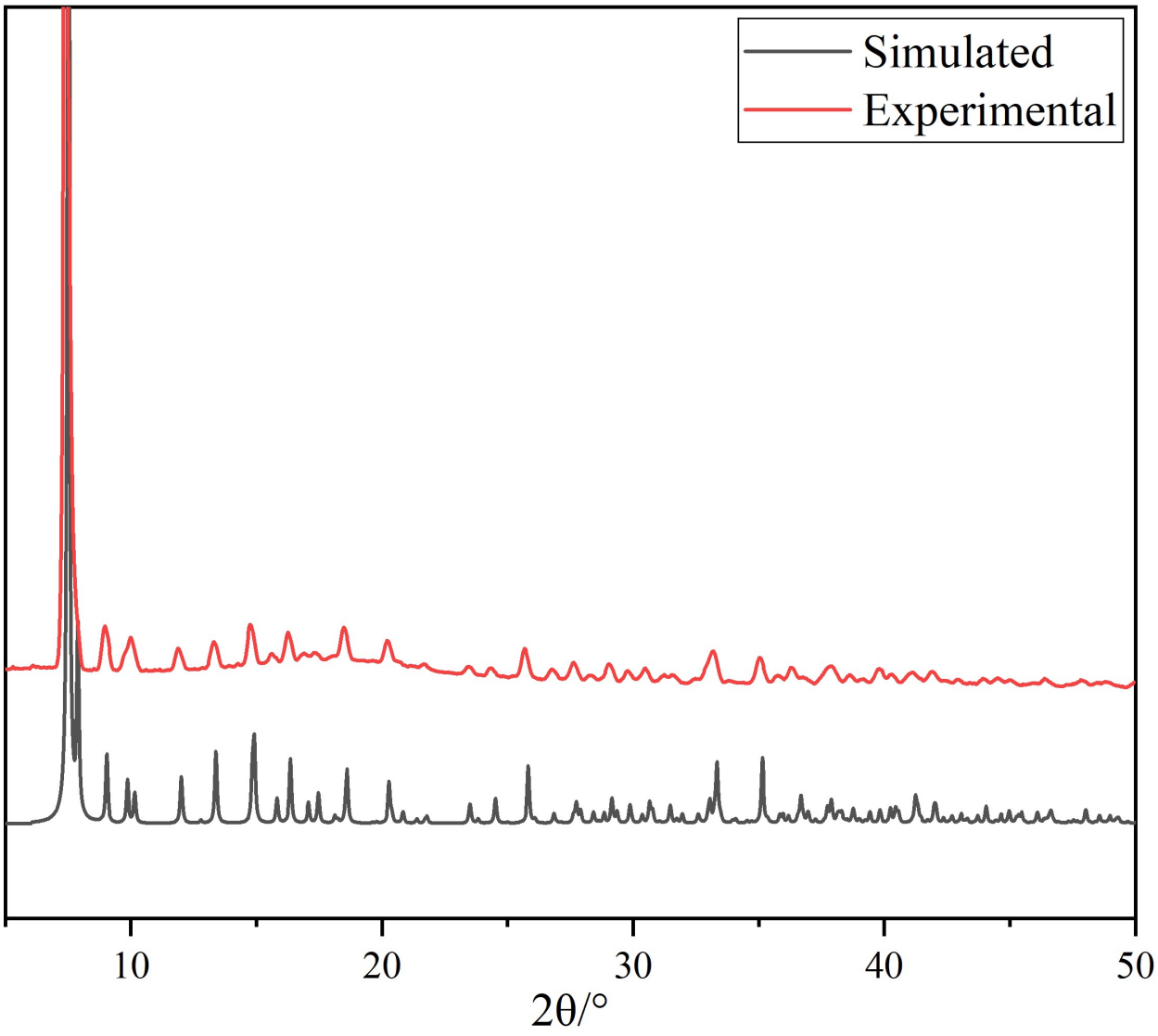

Fig. S8. Simulated and experimental PXRD patterns of **1-Eu**.

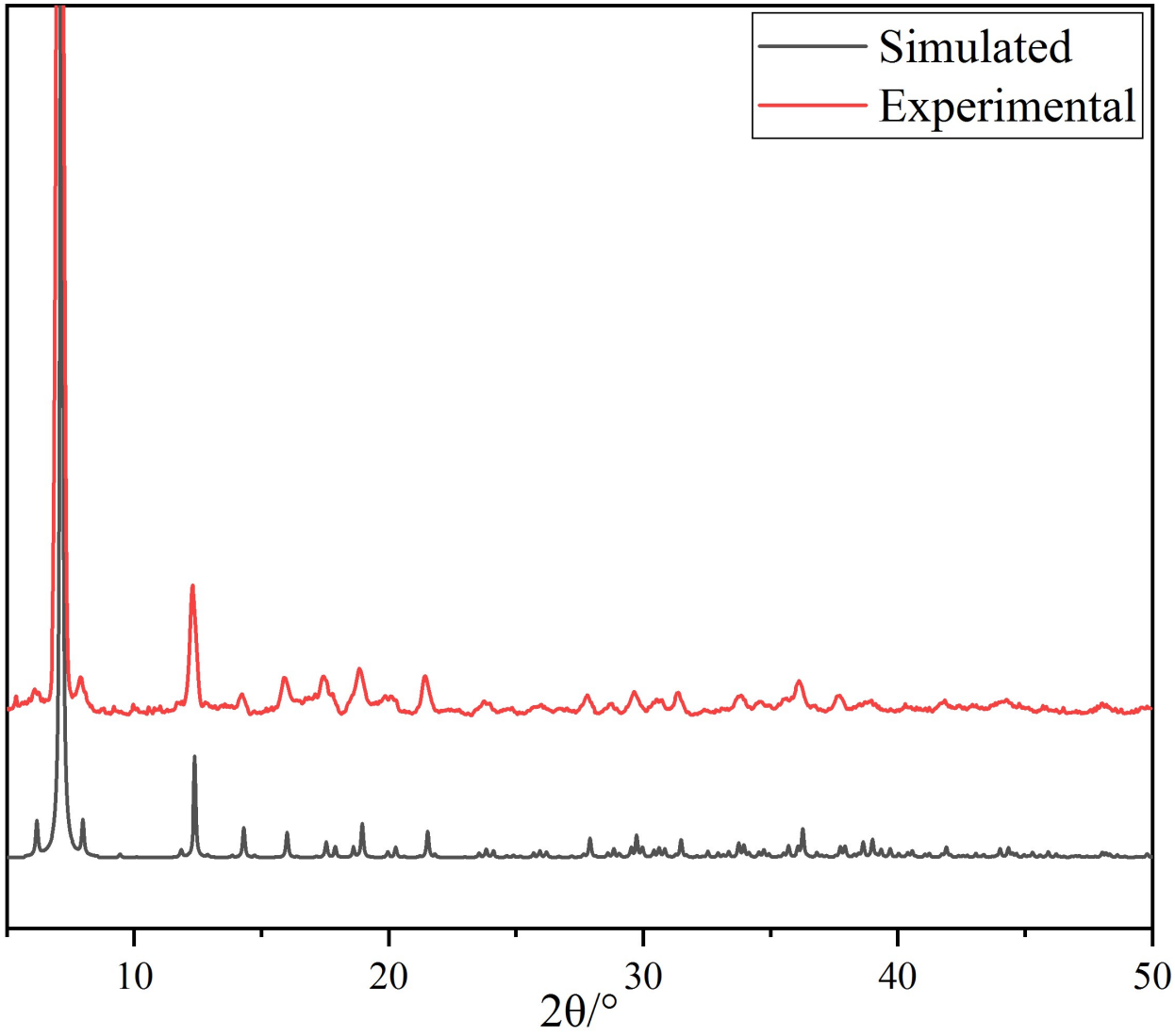

Fig. S9. Simulated and experimental PXRD patterns of **2-Eu**.

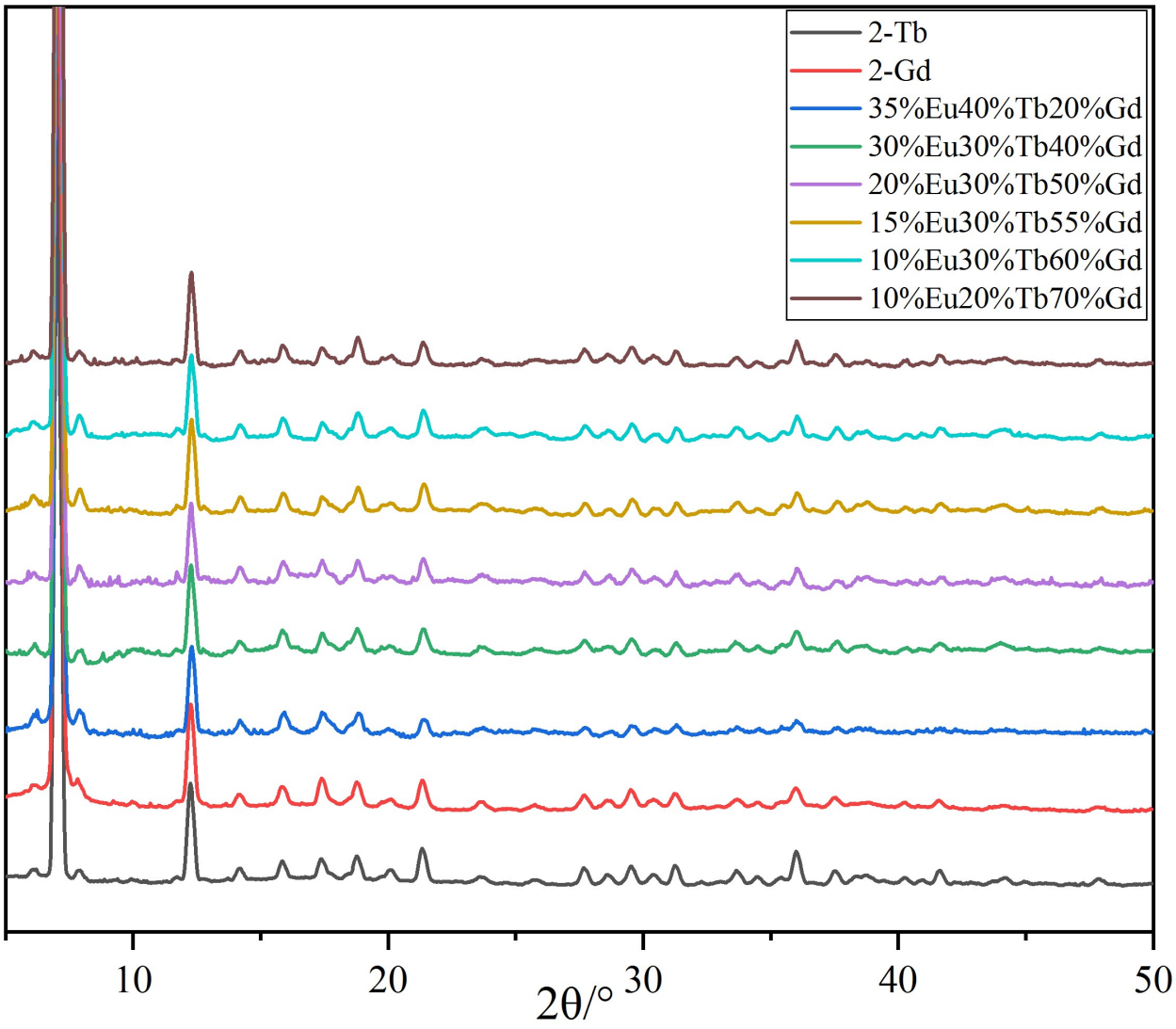

Fig. S10. Simulated and experimental PXRD patterns of **2-Tb**, **2-Gd**, and tri-doped samples.

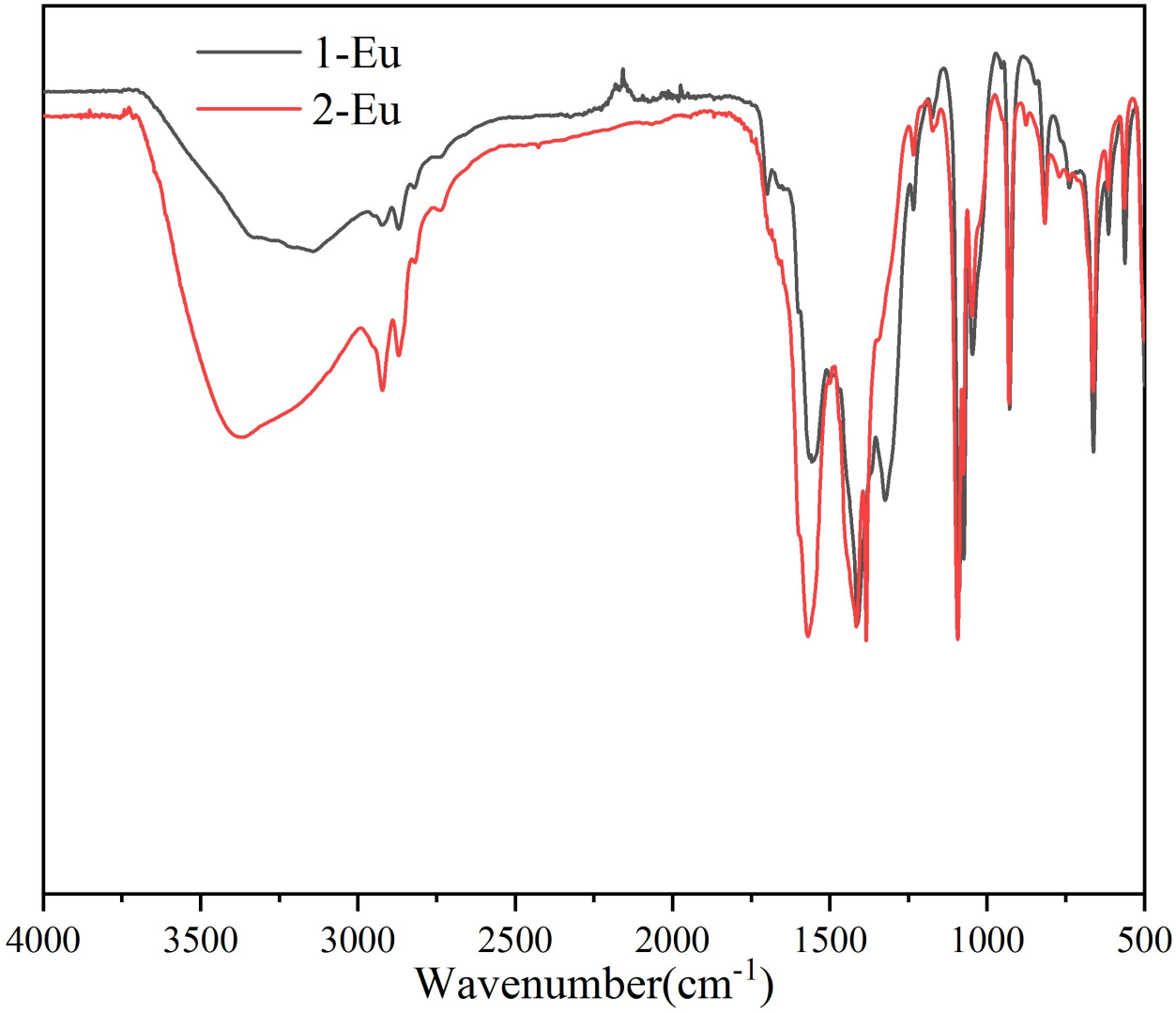

Fig. S11. IR spectra of **1-Eu** and **2-Eu**.

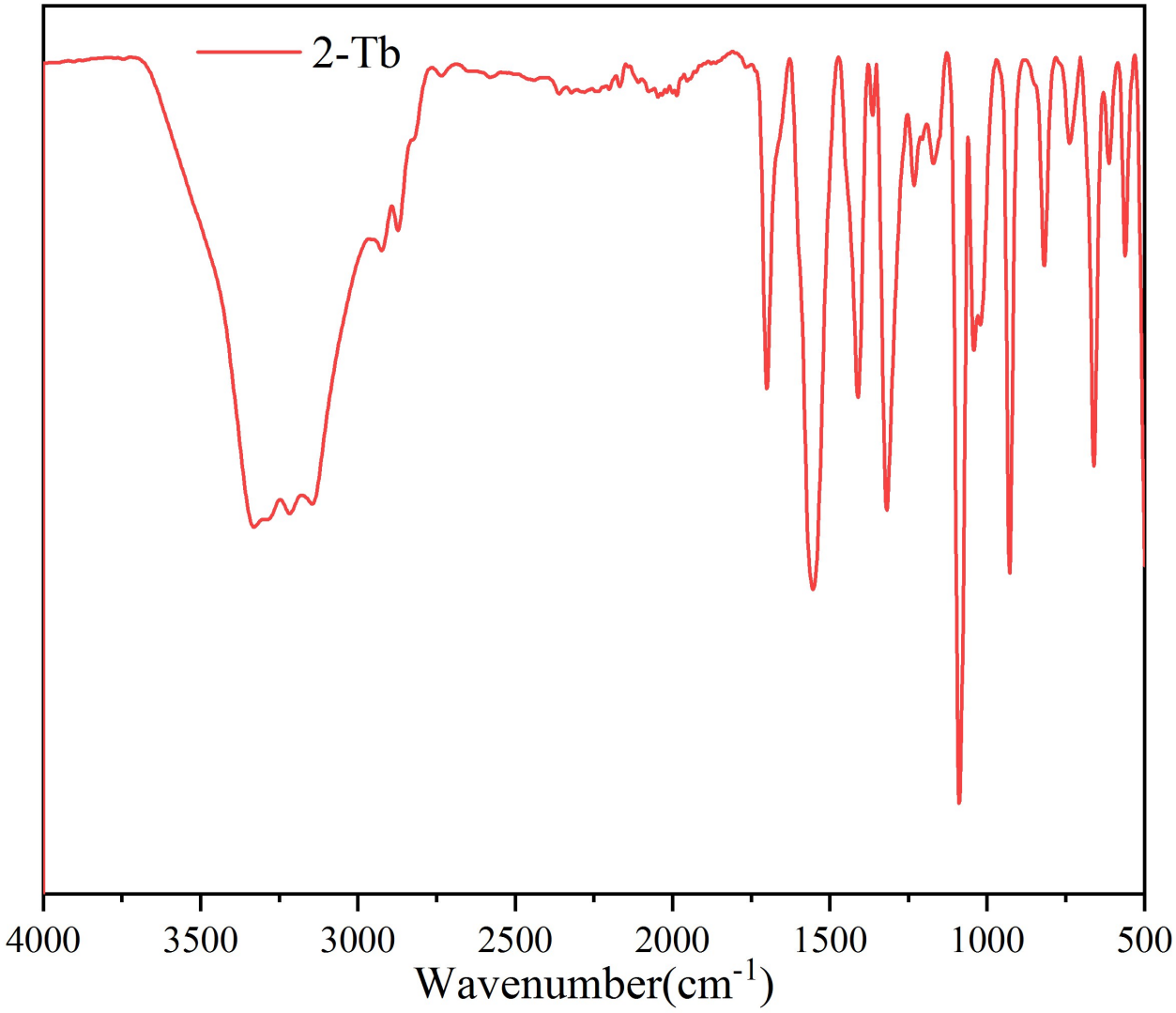

Fig. S12. IR spectra of **2-Tb**.

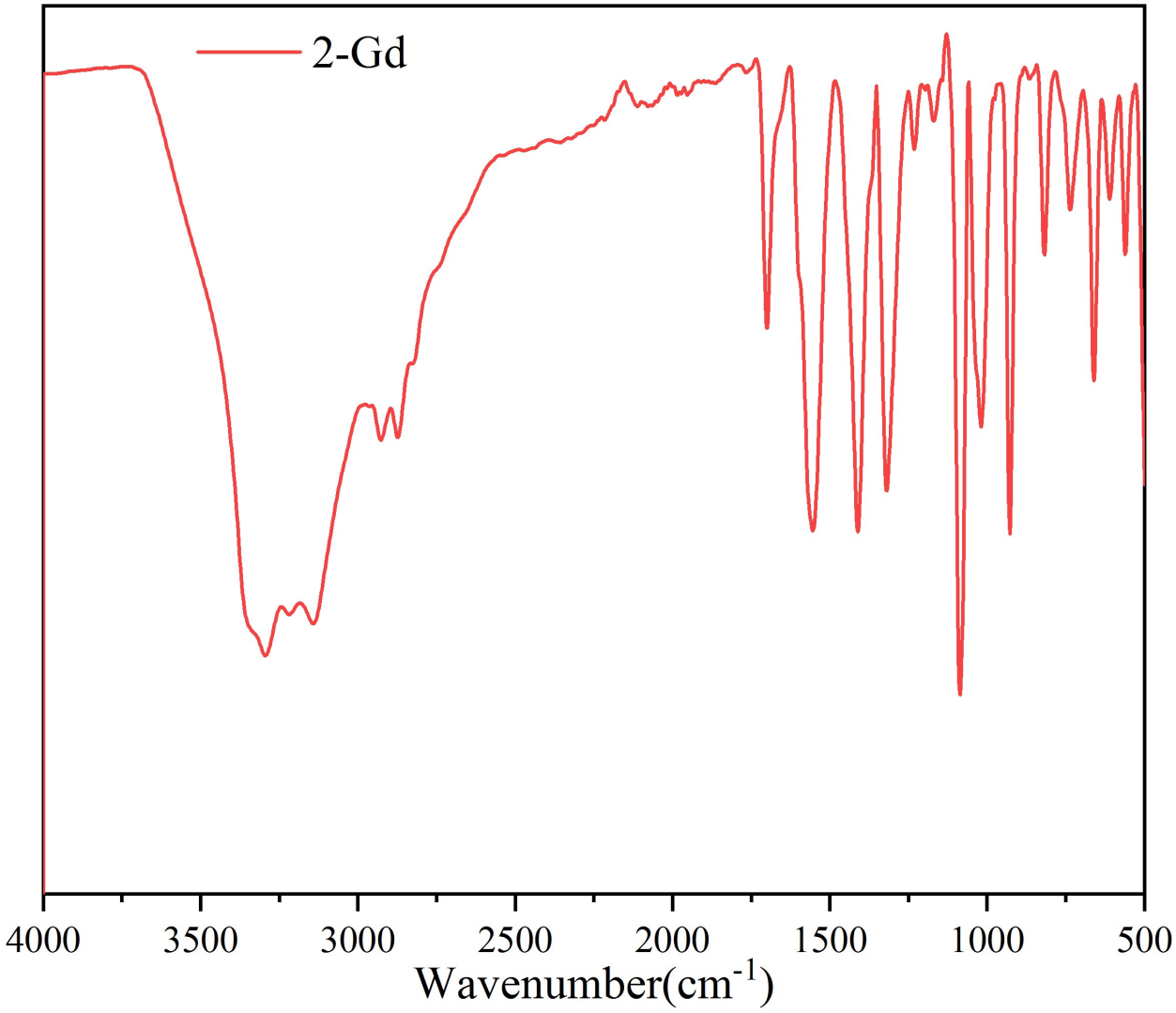

Fig. S13. IR spectra of **2-Gd**.

Section S4 References

[1] D. Menozzi, E. Biavardi, C. Massera, F.-P. Schmidtchen, A. Cornia, E. Dalcanale, Supramolecular Chemistry, 22 (2010) 768-775.