Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

A Single-Ligand-Protected $Eu_{60-n}Gd(Tb)_n$ Cluster: A Reasonable New Approach to Expand Lanthanide Aggregations

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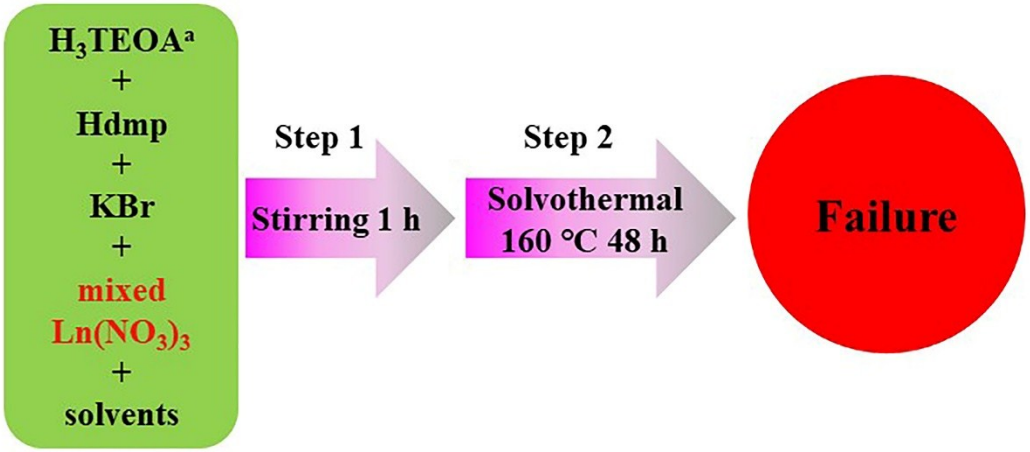
Content

Section 1. Crystal Synthesis

Scheme S1. Wrong Synthetic Route for mixed-Ln_{60}



Synthetic discussion:

The order of mixing procedure is important to successful synthesis. The mixtures (Hdmp, KBr, H_3TEOA, methanol, acetonitrile and deionized water) were stirred 1 h until forming clarifying solution. Then adding the lanthanide salts, and a subsequent solvent-thermal process was performed to finally obtain the target crystal product.

If all reactants were simultaneously mixed and stirred, the crystals will not appear and only clear liquid will produce.

Section 2. Crystal Structures

The morphology of compounds mixed-Ln_{60} and Gd_{60}

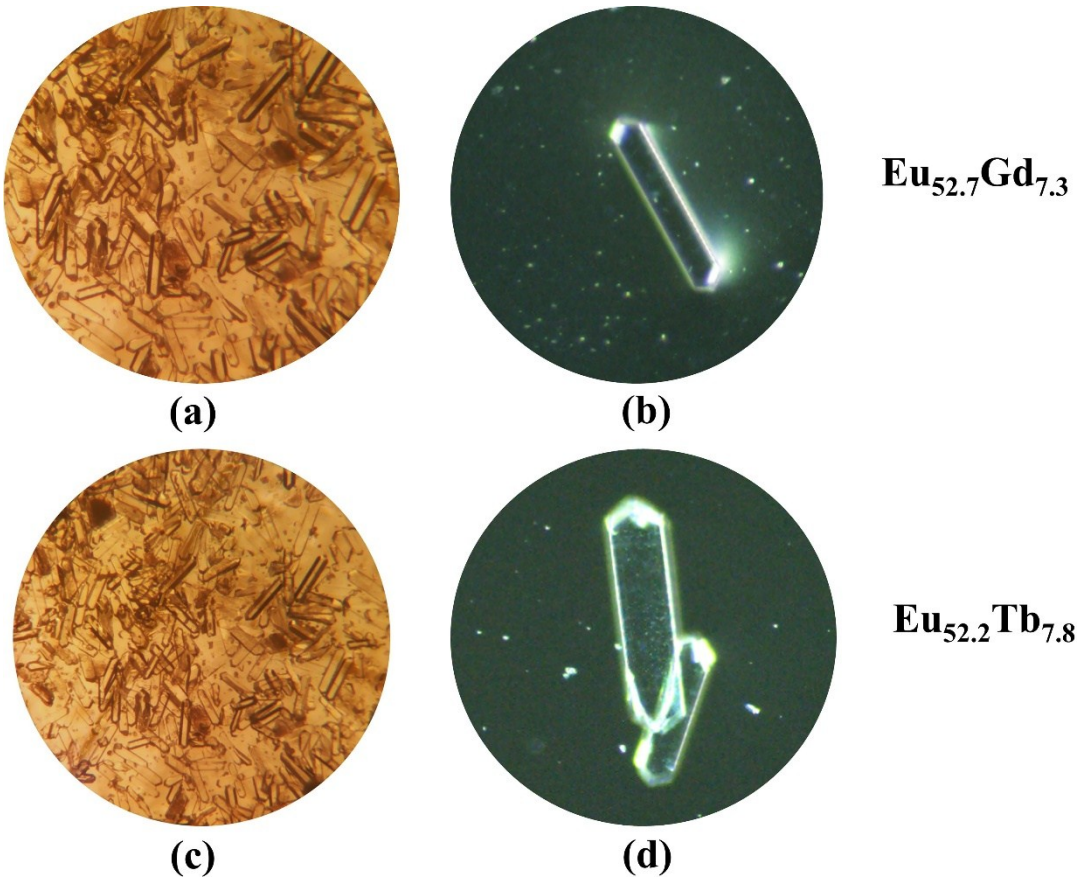


Figure S1. The morphology of compounds $Eu_{52.7}Gd_{7.3}$ (a), (b), and $Eu_{52.2}Tb_{7.8}$ (c), (d).

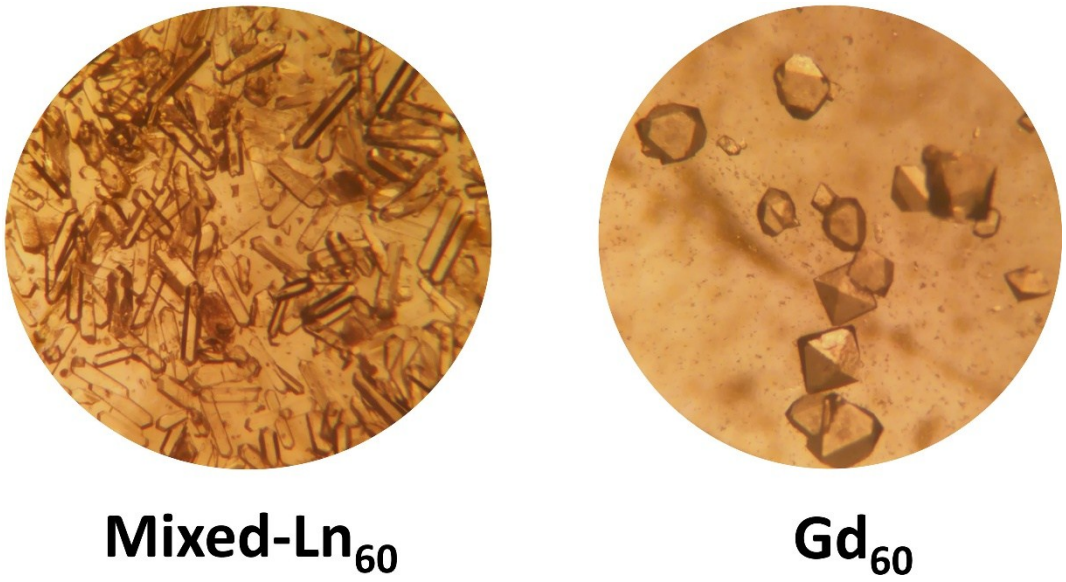


Figure S2. The morphology of compounds **mixed-Ln_{60}** (left) and **Gd_{60}(1)** (right).

Crystal structure figures

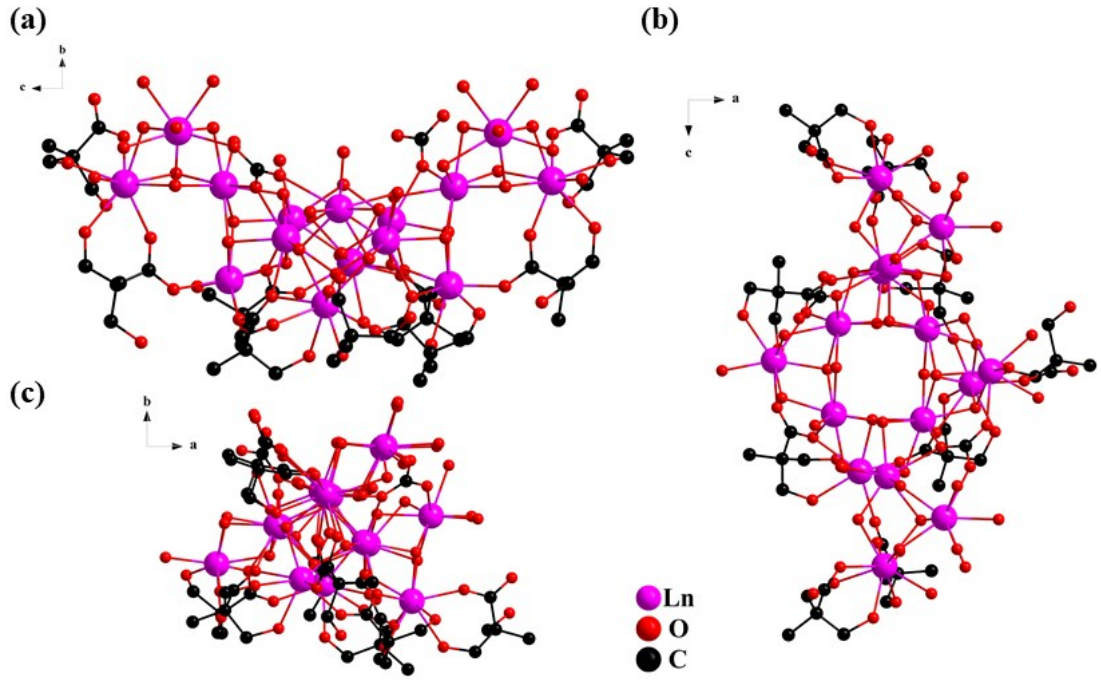


Figure S3. Ball-and-stick view of the asymmetric unit of **mixed-Ln$_{60}$** (a), (b), (c).

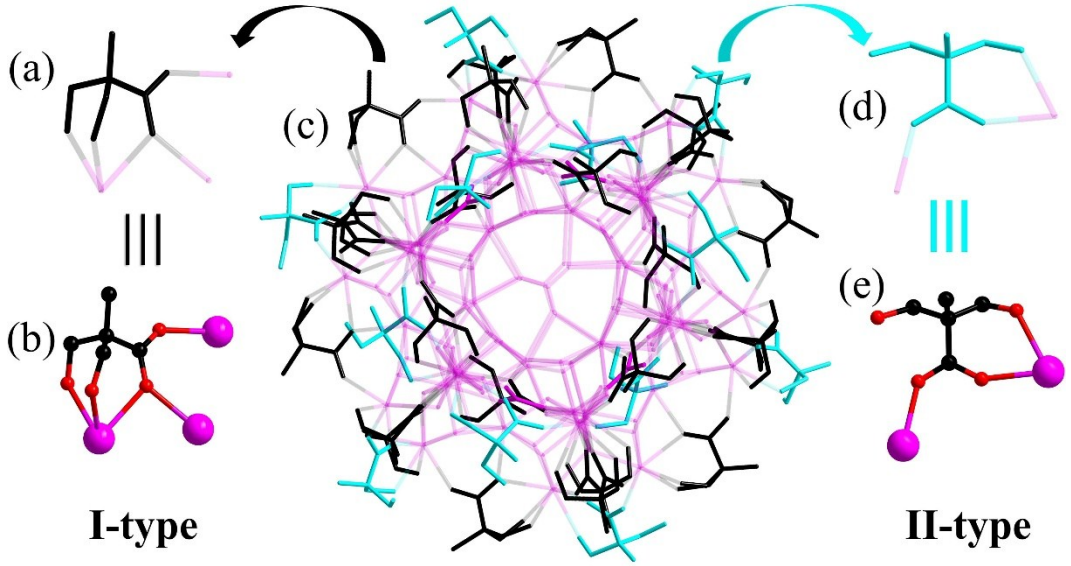


Figure S4. The coordination modes of **L** ligand (a), (b), (d), (e); the unit of compound **mixed-Ln$_{60}$** (c).

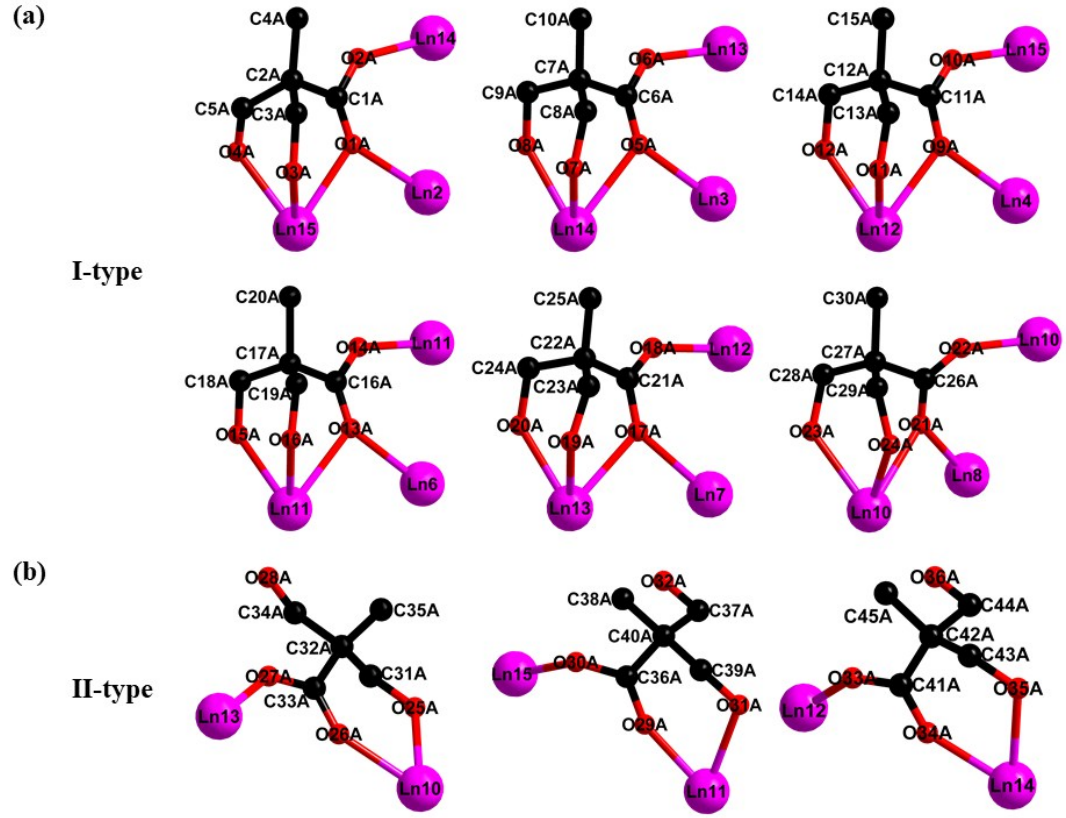


Figure S5. The coordination modes of **L** ligand (a), (b).

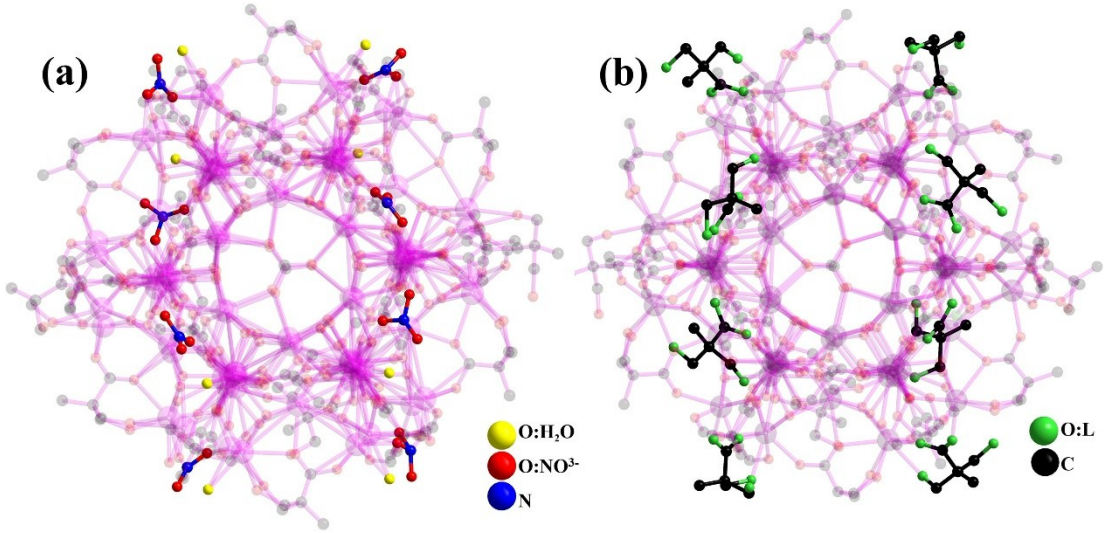


Figure S6. The view of $\mathbf{Gd_{60}(2)}$ (a); $\mathbf{mixed\text{-}Ln_{60}}$ (b).

Section 3. Characterizations

PXRD

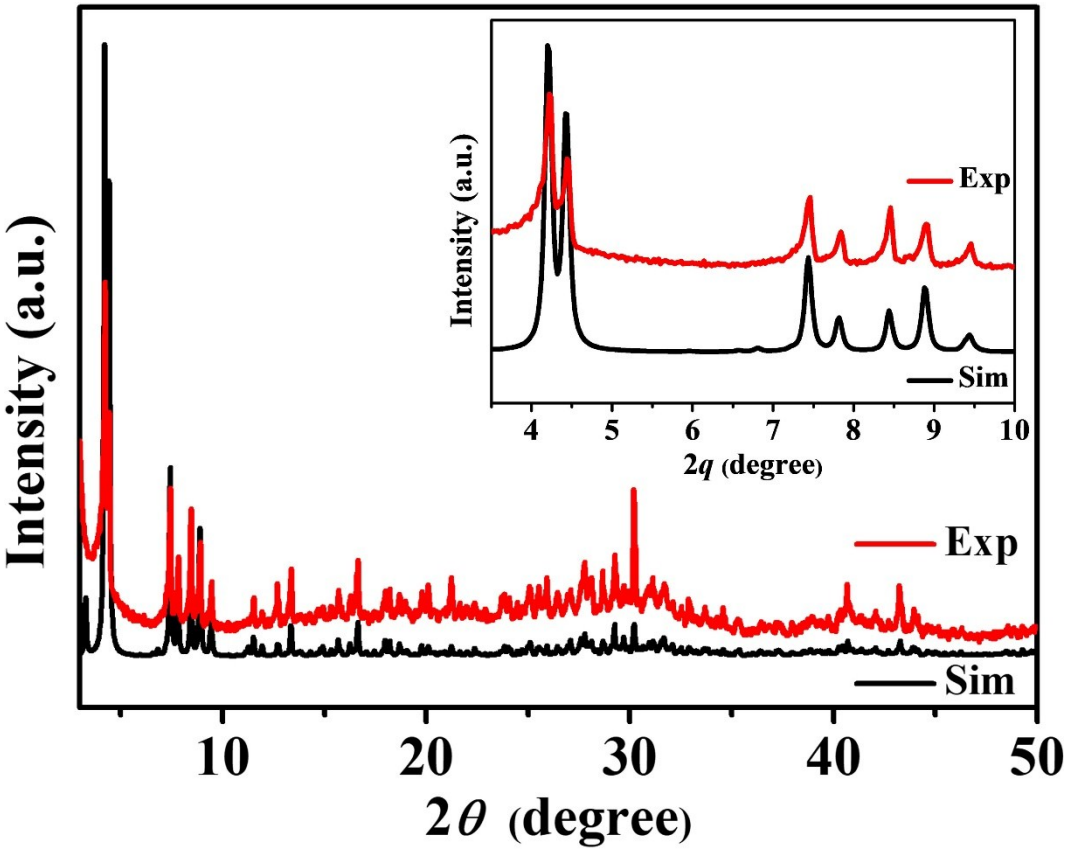


Figure S7. The simulated and experimental PXRD patterns of $Eu_{52.7}Gd_{7.3}$.

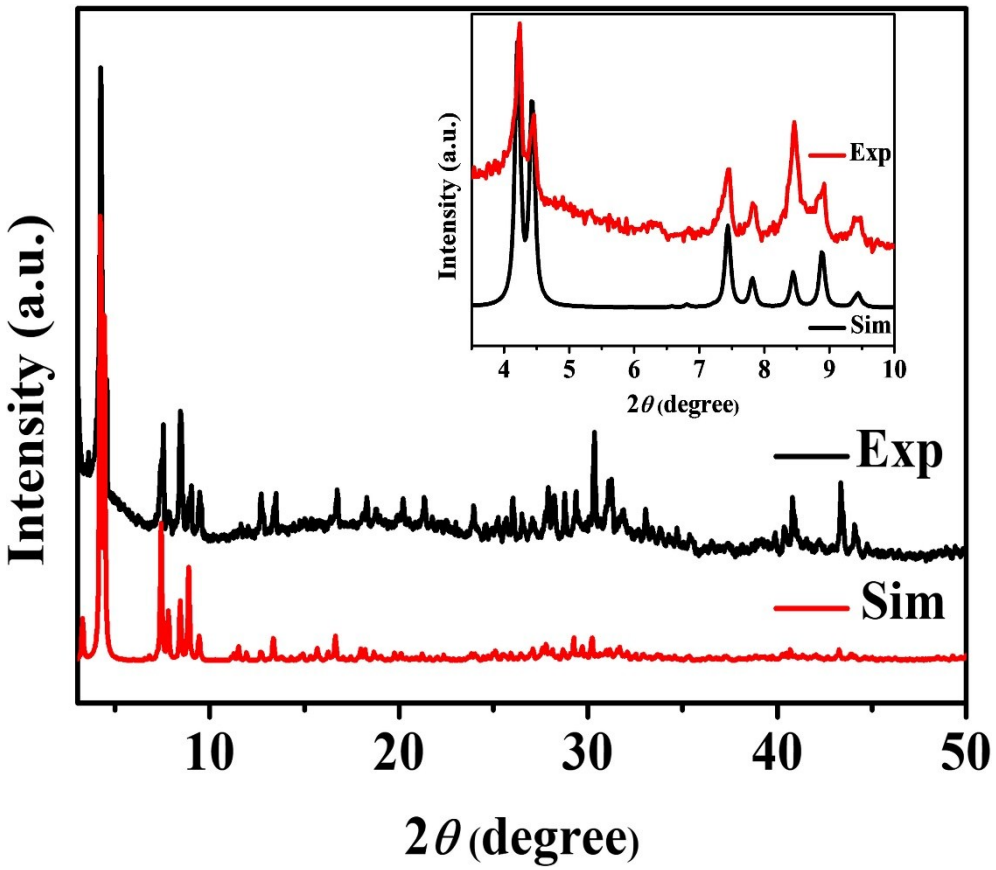


Figure S8. The simulated and experimental PXRD patterns of $Eu_{52.2}Tb_{7.8}$.

As shown on Fig. S7-8, the PXRD of the samples have the same pattern as those of the simulated based on structural information, indicating that those compounds are pure materials.

IR

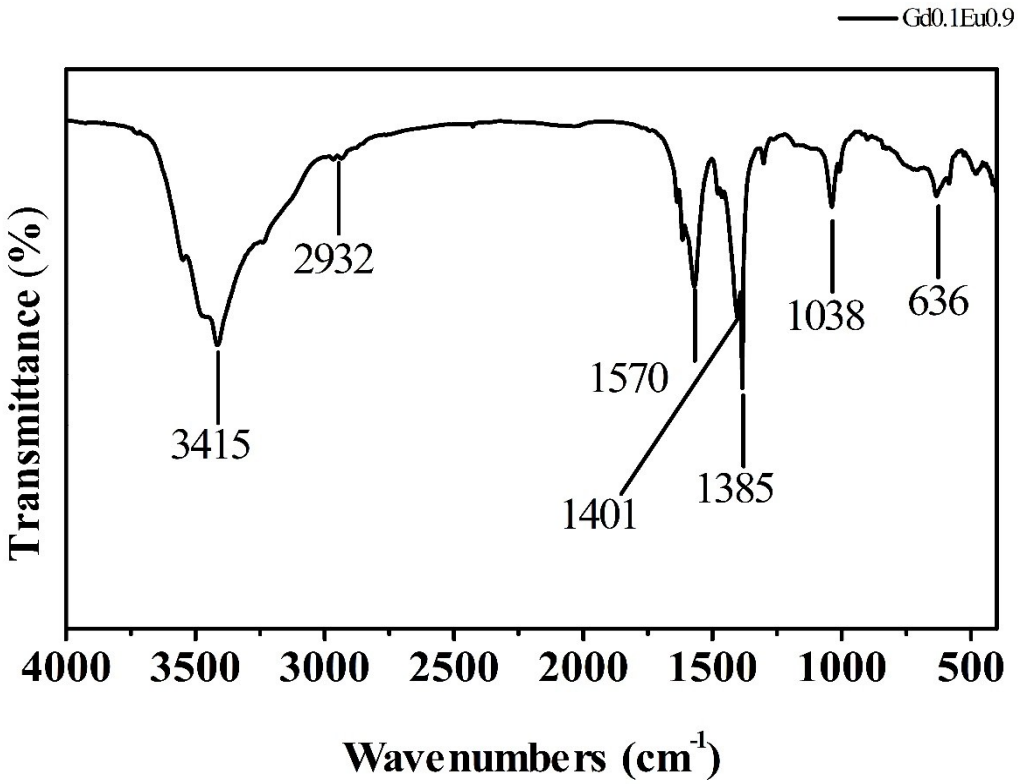


Figure S9. FT-IR spectra of $\mathbf{Eu_{52.7}Gd_{7.3}}$.

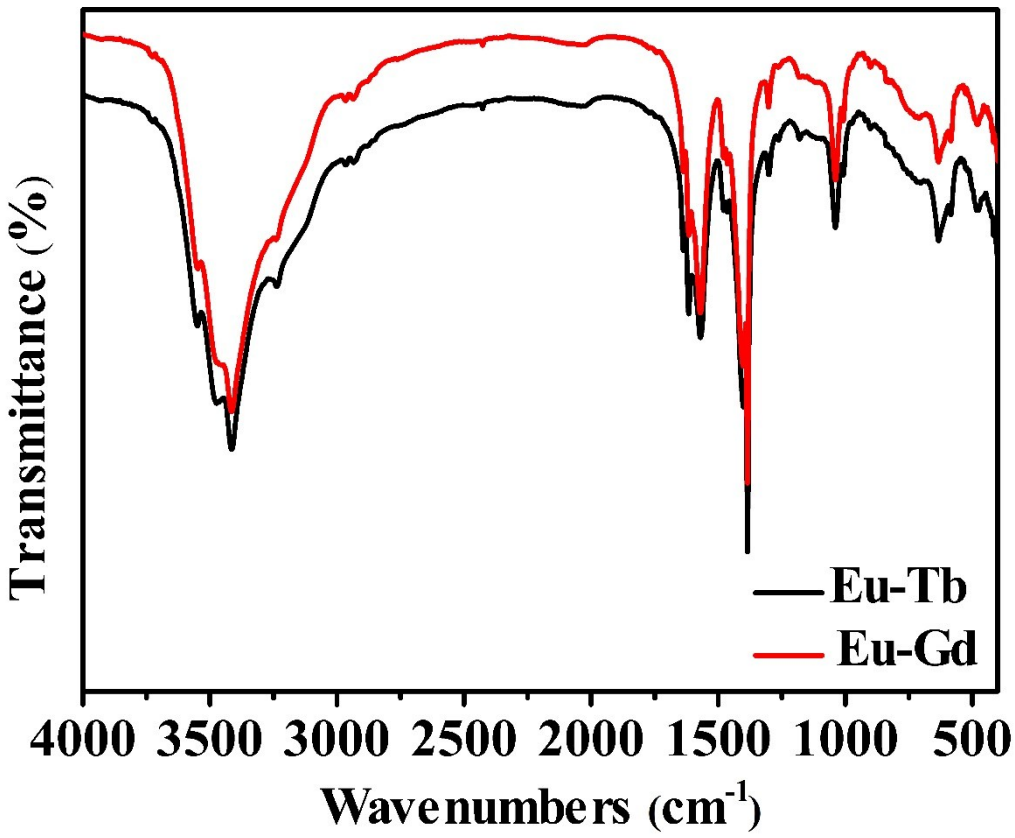


Figure S10. FT-IR spectra of $Eu_{52.7}Gd_{7.3}$ and $Eu_{52.2}Tb_{7.8}$.

TGA

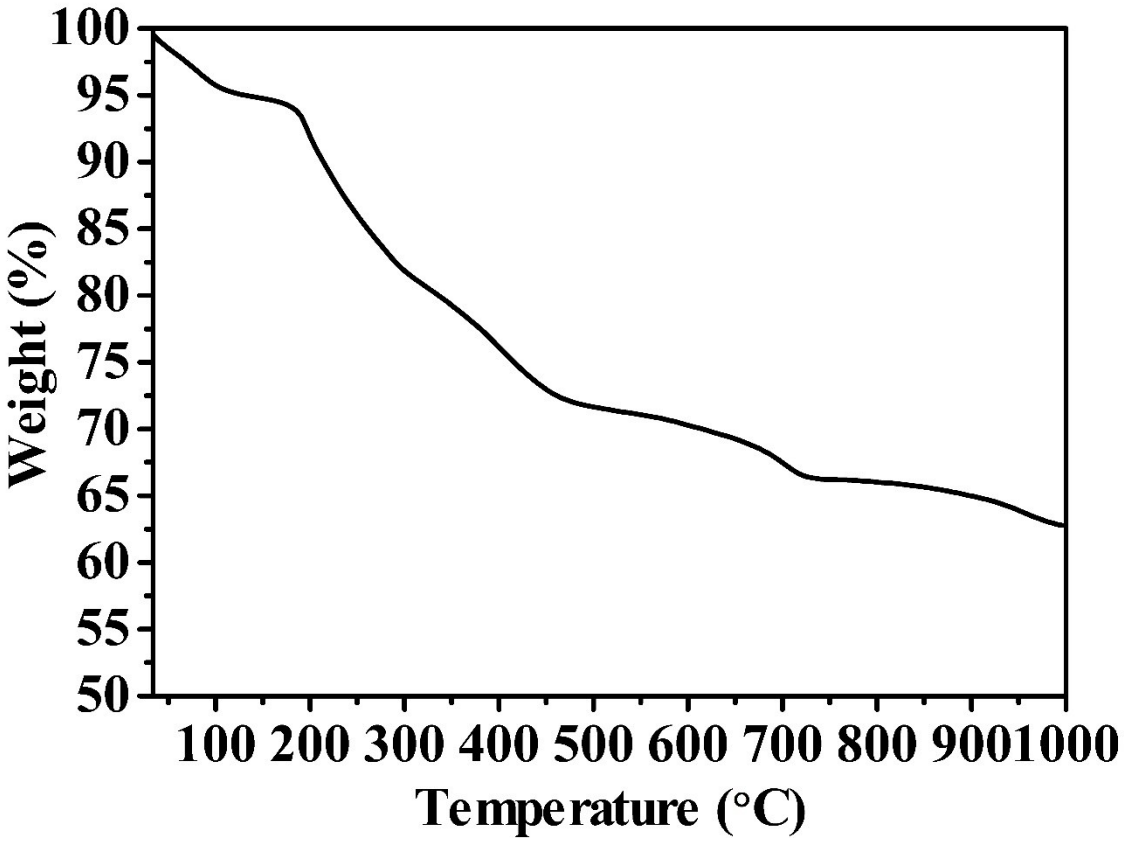


Figure S11. The TG measurement of $Eu_{52.7}Gd_{7.3}$.

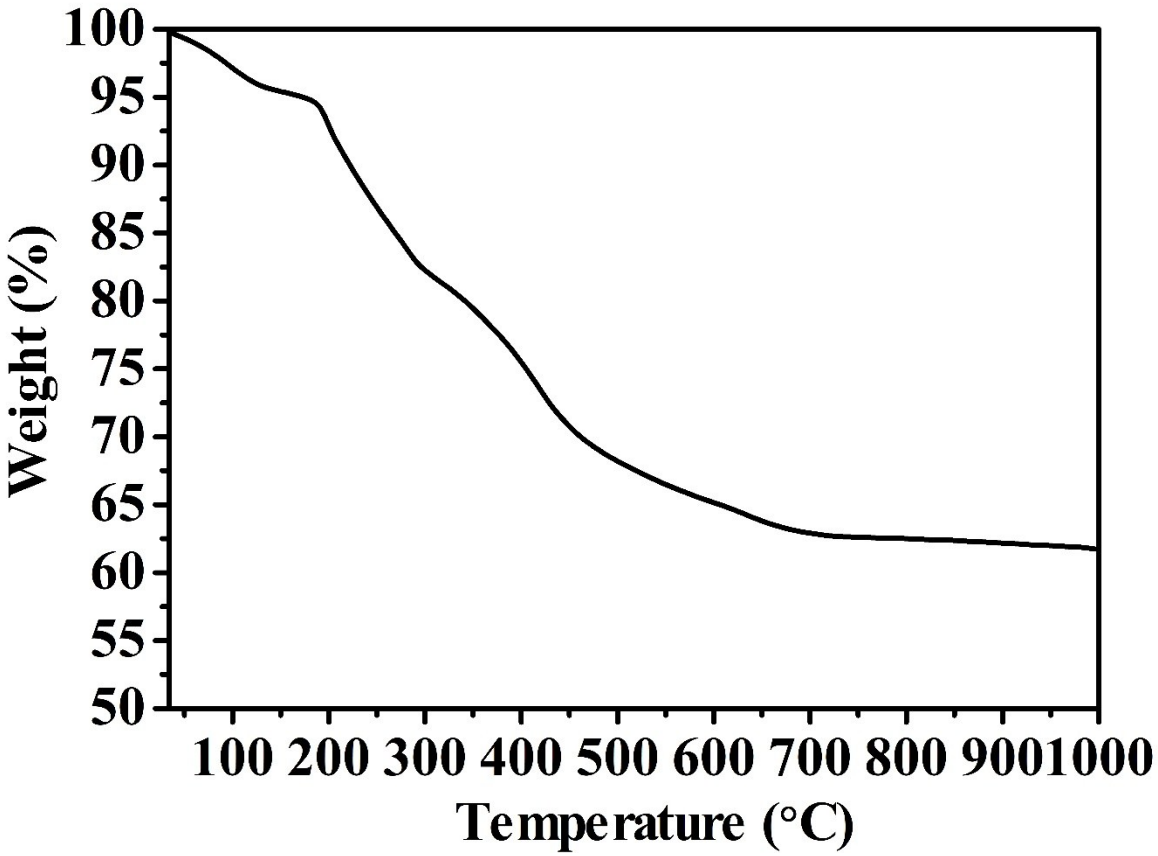


Figure S12. The TG measurement of $\mathbf{Eu_{52.2}Tb_{7.8}}$.

EDS

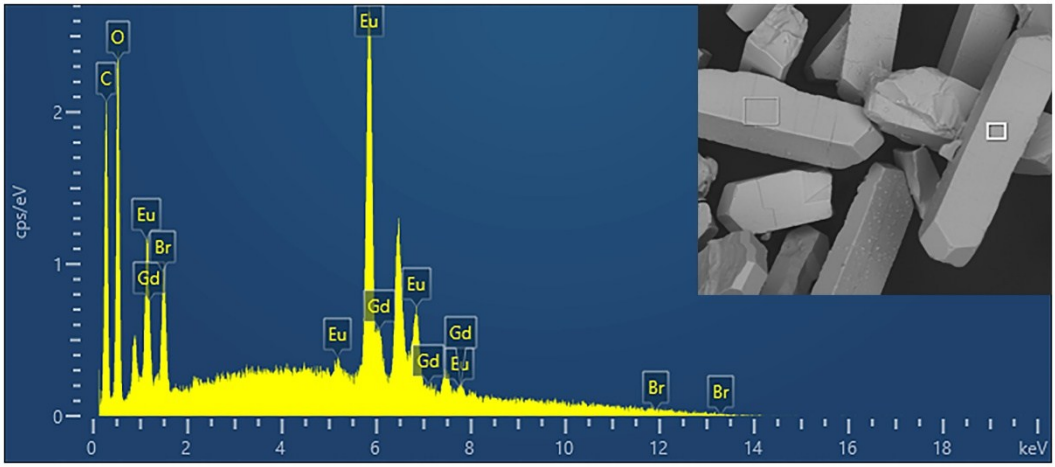


Figure S13. The EDS measurement of $\mathbf{Eu_{52.7}Gd_{7.3}}$.

Table S1. The C, N, O, Br, Eu and Gd components of $\mathbf{Eu_{52.7}Gd_{7.3}}$ recorded from the EDX quantitative analyses.

Element	Percentage by weight / %
C	13.96
Br	5.25
O	32.59
Eu	42.49
Gd	6.28

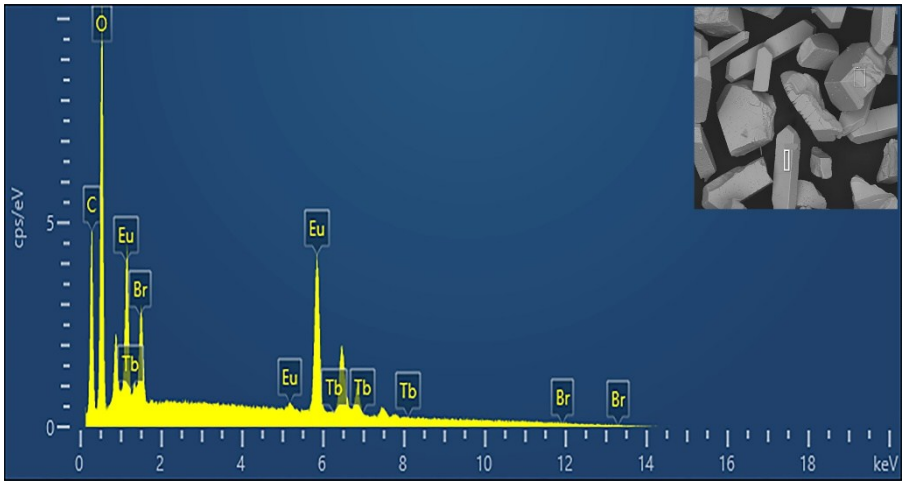


Figure S14. The EDS measurement of $\mathbf{Eu_{52.2}Tb_{7.8}}$.

Table S2. The C, N, O, Br, Eu and Tb components of $\mathbf{Eu_{52.2}Tb_{7.8}}$ recorded from the EDX quantitative analyses.

Element	Percentage by weight / %
C	13.96
Br	6.98
O	29.47
Eu	42.35
Tb	7.24

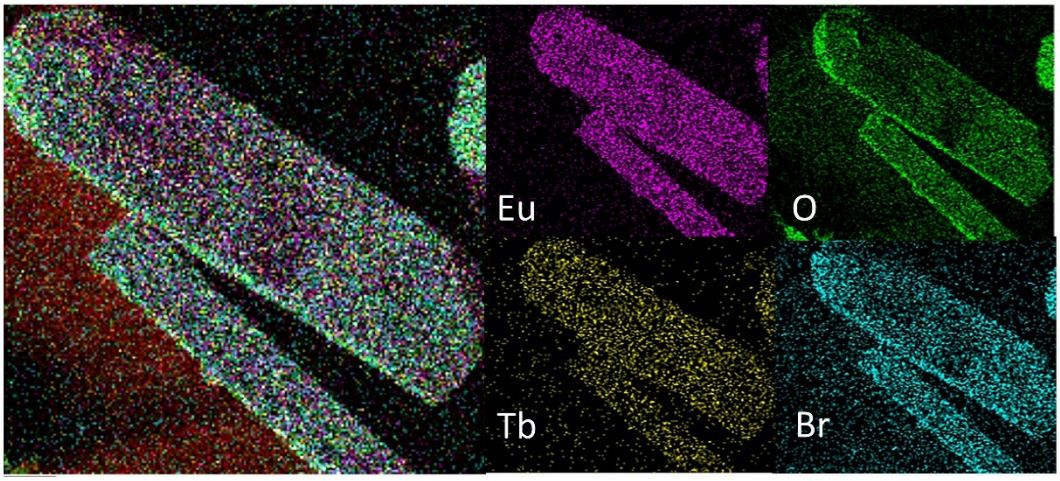


Figure S15. The SEM-EDS mapping of compounds $\mathbf{Eu_{52.2}Tb_{7.8}}$.

XRF

Table S3. The C, N, O, Br, Eu and Gd components of $\mathbf{Eu_{52.7}Gd_{7.3}}$ recorded from the XRF quantitative analyses.

Component	mass %	LOD (limit of detection)	intensity
C	13.2854	0.10524	12.6033
N	0.7155	0.50248	0.0565
O	31.4430	0.93224	0.5591
Br	5.2397	0.00605	287.5566
Eu	43.0461	0.0328	185.0066
Gd	6.2703	0.03189	28.2619

Table S4. The C, N, O, Br, Eu and Tb components of $\mathbf{Eu_{52.2}Tb_{7.8}}$ recorded from the XRF quantitative analyses.

Component	mass %	LOD (limit of detection)	intensity
C	12.1272	0.10184	11.9055
N	0.5049	0.47353	0.087
O	30.5844	0.87293	0.5161
Br	6.3886	0.00548	339.6892
Eu	43.1428	0.05777	184.7422
Tb	7.1462	0.03495	41.8983

ICP

Table S5. The Eu and Gd components of $\mathbf{Eu_{52.7}Gd_{7.3}}$ recorded from the ICP quantitative analyses.

Compound	Eu (ppm)	Gd (ppm)	Eu (μmol / mL)	Gd (μmol / mL)	Eu Percentage by weight / %	Gd Percentage by weight / %	Gd:Eu (mol %)
Eu_xGd_{60-x}	7.73	1.11	5.09×10^{-2}	7.05×10^{-3}	42.7	6.13	13.85

Table S6. The Eu and Tb components of $\mathbf{Eu_{52.2}Tb_{7.8}}$ recorded from the ICP quantitative analyses.

Compound	Eu (ppm)	Tb (ppm)	Eu (μmol / mL)	Tb (μmol / mL)	Eu Percentage by weight / %	Tb Percentage by weight / %	Tb:Eu (mol %)
Eu_xGd_{60-x}	7.40	1.16	4.87×10^{-2}	7.30×10^{-3}	42.53	6.67	14.99

Section 4. Luminescence properties

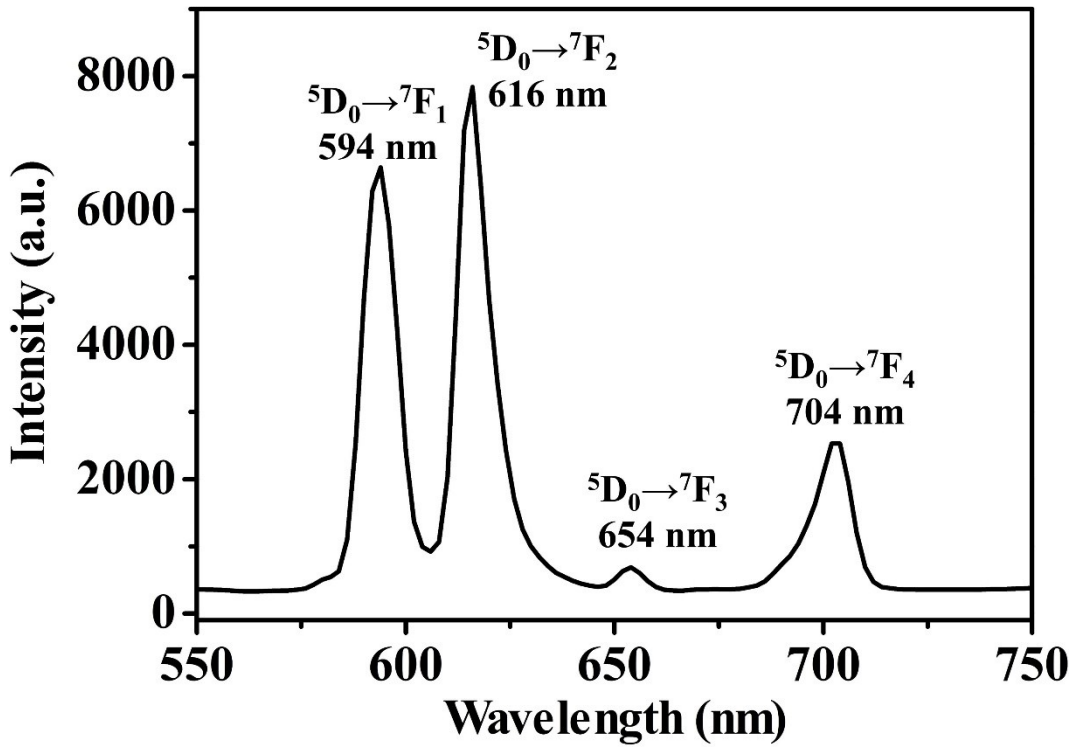


Figure S16. Emission spectra of compound $Eu_{52.7}Gd_{7.3}$.

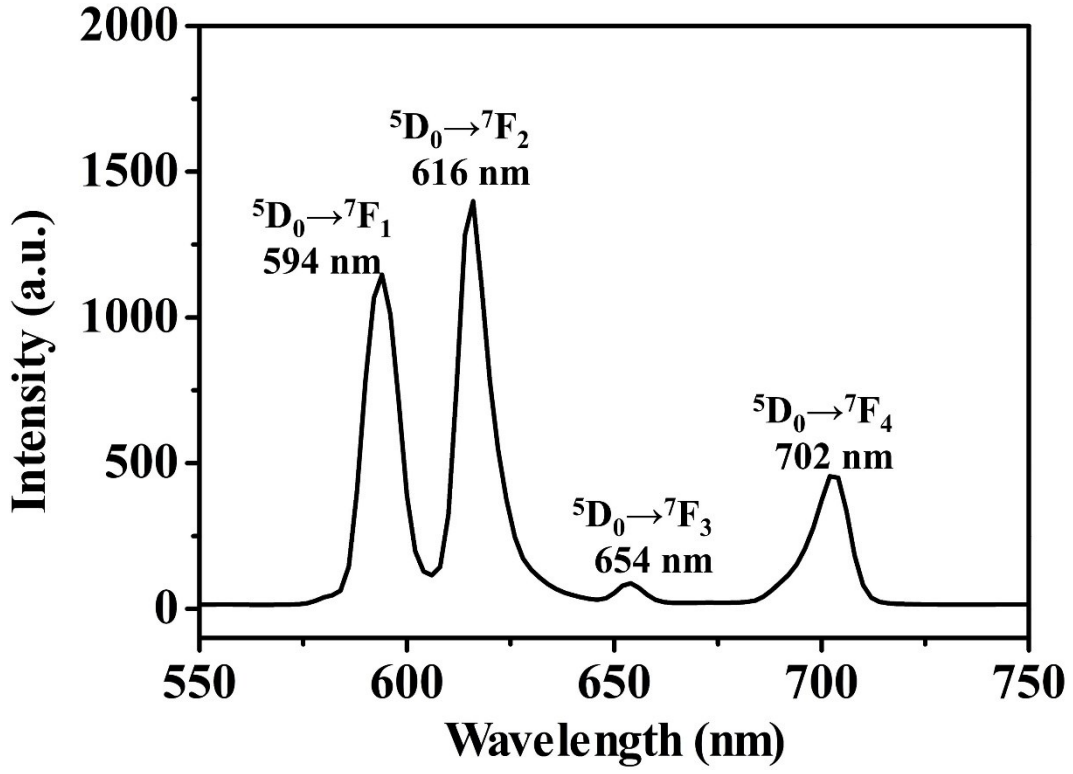
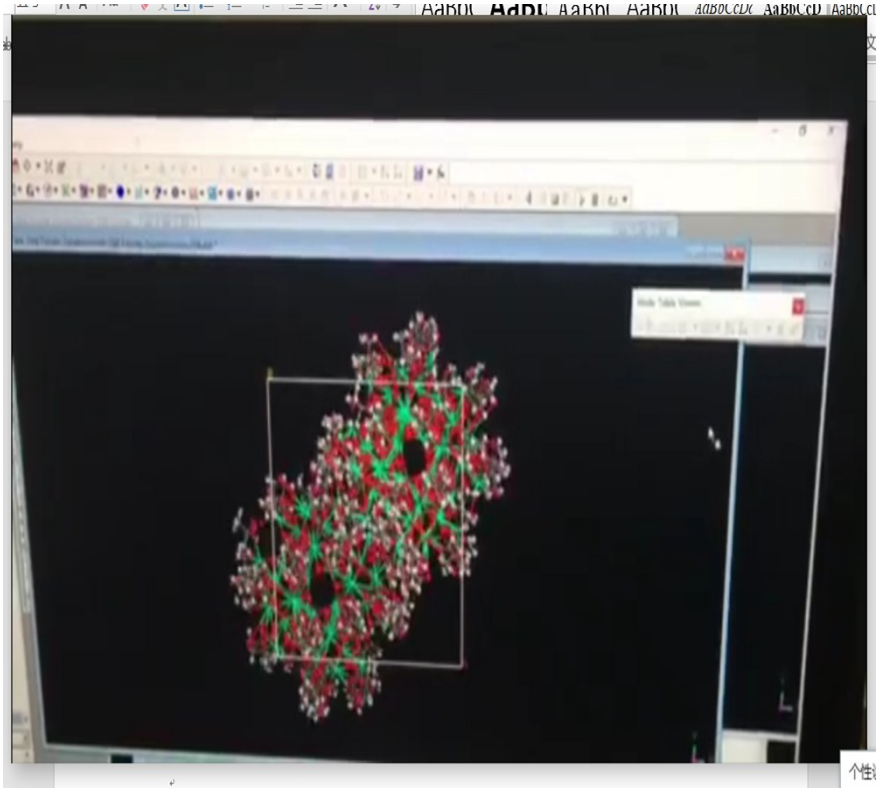


Figure S17. Emission spectra of compound $Eu_{52.2}Tb_{7.8}$.

Due to the excellent luminescent properties of Eu^{III}, herein compounds **$Eu_{52.7}Gd_{7.3}$** and **$Eu_{52.2}Tb_{7.8}$** were investigated. The luminescence spectra of compounds **$Eu_{52.7}Gd_{7.3}$** and **$Eu_{52.2}Tb_{7.8}$** are shown in Fig. S16-17. Here only compound **$Eu_{52.7}Gd_{7.3}$** was discussed in detail, owing to similar luminescent properties of **$Eu_{52.7}Gd_{7.3}$** and **$Eu_{52.2}Tb_{7.8}$**.

The luminescent property of **$Eu_{52.7}Gd_{7.3}$** was measured with the characteristic f−f transition of an Eu^{III} ion on excitation at 394 nm (Fig. S16).[1-3] Major emission peaks at 594, 616, 654, 704 nm are ascribed to characteristic emissions arising from the $^5D_0 \rightarrow {}^7F_j$ (j = 1,2,3,4) transition. The strongest intensity at 616 nm corresponds to electric dipolar $^5D_0 \rightarrow {}^7F_2$. Correspondingly, the medium intensity peak at 592 nm is due to magnetic dipolar $^5D_0 \rightarrow {}^7F_1$, which hardly varies with the coordination environment. The remaining two peaks at 653 and 696 nm pertain to the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively.[1-3]

Section 5. The calculated energy of compound $Eu_{52.7}Gd_{7.3}$.



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---- Initial structure ----

Total enthalpy                    :  24.007637 kcal/mol
  External pressure term          :  0.000000 kcal/mol

Total energy                      :            24.007637 kcal/mol

Contributions to total energy (kcal/mol):
  Valence energy (diag. terms)    :            11.821
    Bond                          :             2.416
    Angle                         :            12.096
    Torsion                       :            -2.691
    Inversion                     :             0.000
  Valence energy (cross terms)    :            -0.940
    Stretch-Stretch               :             0.080
    Stretch-Bend-Stretch          :             0.174
    Stretch-Torsion-Stretch       :            -0.494
    Separated-Stretch-Stretch     :             0.000
    Torsion-Stretch               :             0.385
    Bend-Bend                     :             0.004
    Torsion-Bend-Bend             :            -0.513
    Bend-Torsion-Bend             :            -0.576
  Non-bond energy                 :            13.127
    van der Waals                 :            13.128
    Long range correction         :            -0.001
    Electrostatic                 :             0.000
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Figure S18. The calculated energy of compound $Eu_{52.7}Gd_{7.3}$.

Section 6. Stability

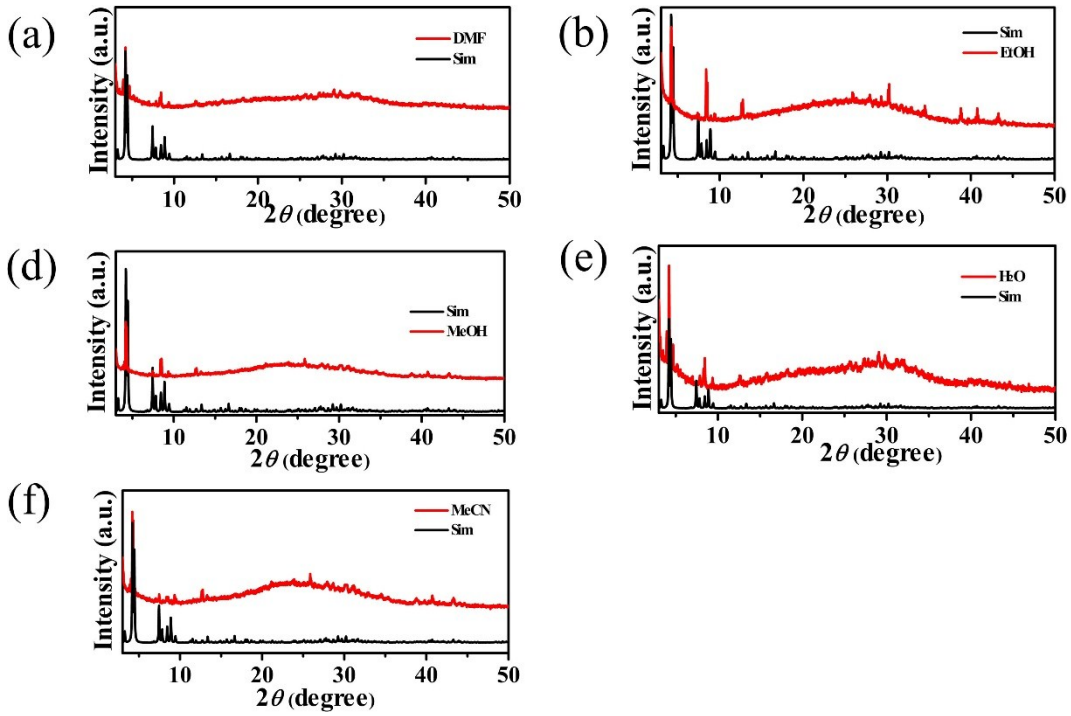

Figure S19. Stability of as-synthesized compound $\mathbf{Eu_{52.7}Gd_{7.3}}$ in different solvent checked by PXRD.

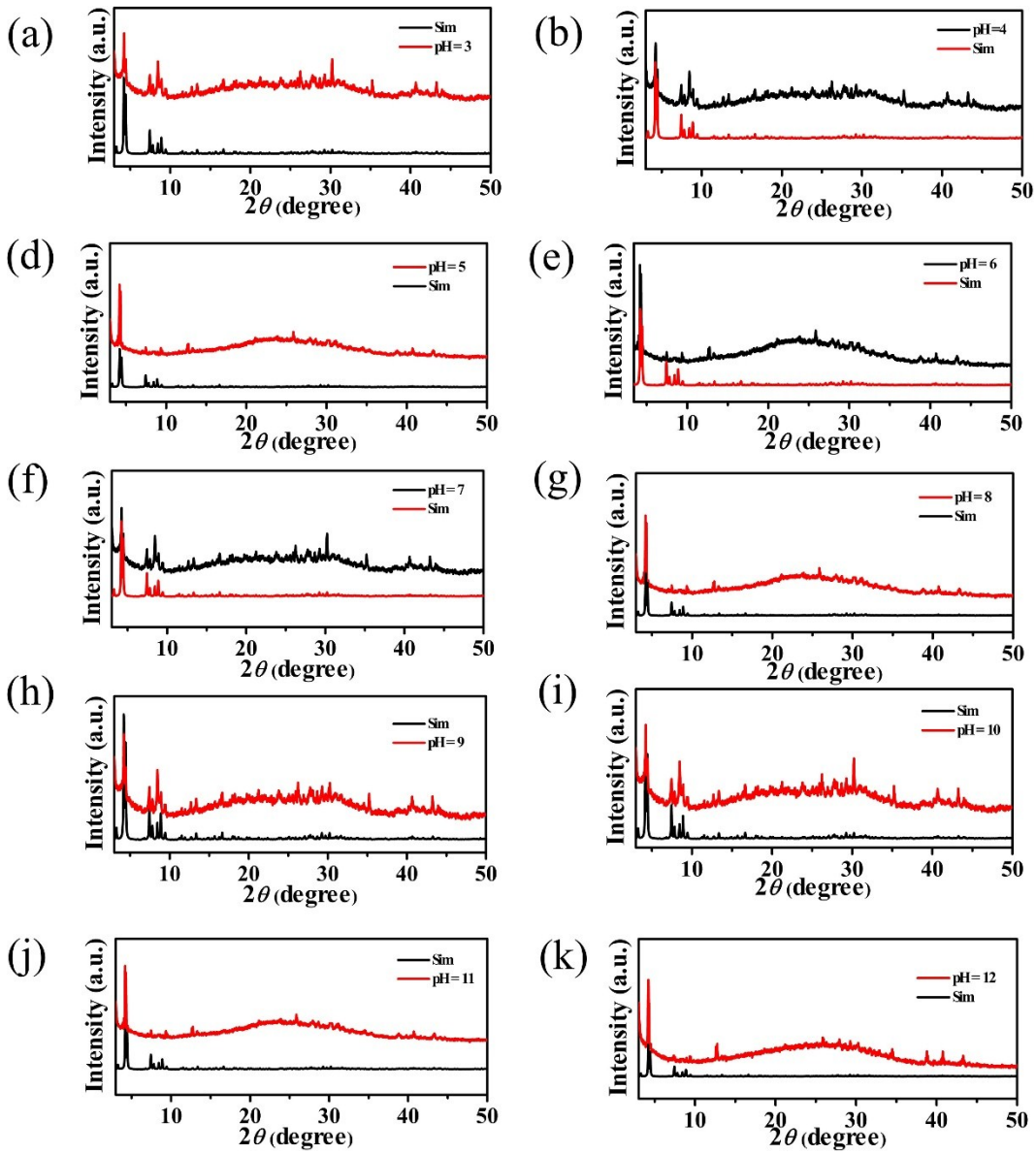

Figure S20. Variable-pH PXRD of compound $\mathbf{Eu_{52.7}Gd_{7.3}}$.

Section 7. Tables

Table S7. The selected bond lengths (Å) and bond angles (°) for $\mathbf{Eu_{52.7}Gd_{7.3}}$.

Eu(1)-O(5)	2.323(8)	Eu(11)-O(22)	2.428(8)
Eu(1)-O(3)	2.361(7)	Eu(11)-O(15A)	2.449(9)
Eu(1)-O(1)	2.371(7)	Eu(11)-O(16A)	2.451(9)
Eu(1)-O(6)	2.382(8)	Eu(11)-O(13A)	2.572(9)
Eu(1)-O(4)	2.393(8)	Eu(11)-O(31A)	2.584(16)
Eu(1)-O(2)	2.421(8)	Eu(12)-O(33A)#1	2.312(9)
Eu(1)-O(1B)#1	2.647(8)	Eu(12)-O(18A)	2.353(9)
Eu(1)-O(2B)	2.669(8)	Eu(12)-O(15)	2.378(8)
Eu(2)-O(9)	2.362(8)	Eu(12)-O(9A)	2.528(9)
Eu(2)-O(10)	2.370(8)	Eu(13)-O(27A)	2.340(9)
Eu(2)-O(12)	2.403(8)	Eu(13)-O(6A)	2.351(8)
Eu(2)-O(8)	2.406(8)	Eu(13)-O(6)	2.381(8)
Eu(2)-O(11)	2.409(8)	Eu(13)-O(14)	2.391(8)
Eu(2)-O(7)	2.412(8)	Eu(13)-O(3)	2.422(7)
Eu(2)-O(1A)	2.435(9)	Eu(13)-O(19A)	2.430(9)
Eu(2)-O(4B)#2	2.501(8)	Eu(13)-O(20A)	2.460(9)
Eu(3)-O(8)	2.365(8)	Eu(14)-O(10)	2.424(8)
Eu(3)-O(13)	2.372(7)	Eu(14)-O(7A)	2.454(8)
Eu(3)-O(14)	2.403(8)	Eu(14)-O(8A)	2.464(9)
Eu(3)-O(3)	2.406(8)	Eu(14)-O(9)	2.476(8)
Eu(3)-O(10)	2.413(8)	Eu(14)-O(35A)	2.532(9)
Eu(3)-O(5A)	2.415(8)	Eu(14)-O(5A)	2.623(9)
Eu(3)-O(2B)	2.454(8)	Eu(15)-O(30A)	2.231(13)
Eu(3)-O(4)	2.460(8)	Eu(15)-O(10A)	2.355(10)
Eu(4)-O(18)	2.359(8)	Eu(15)-O(18)	2.437(8)
Eu(4)-O(16)#1	2.375(7)	Eu(15)-O(4A)	2.462(11)
Eu(4)-O(7)	2.384(8)	Eu(15)-O(1A)	2.533(9)
Eu(4)-O(17)	2.394(8)	Gd(1)-O(5)	2.323(8)
Eu(4)-O(12)	2.412(8)	Gd(1)-O(3)	2.361(7)
Eu(4)-O(15)	2.425(8)	Gd(1)-O(1)	2.371(7)
Eu(4)-O(9A)	2.451(8)	Gd(1)-O(6)	2.382(8)
Eu(4)-O(6B)	2.456(8)	Gd(1)-O(4)	2.393(8)
Eu(5)-O(16)	2.374(8)	Gd(2)-O(9)	2.362(8)

Eu(5)-O(15)#2	2.377(8)	Gd(2)-O(10)	2.370(8)
Eu(5)-O(8)	2.390(8)	Gd(2)-O(12)	2.403(8)
Eu(5)-O(4B)#2	2.648(8)	Gd(2)-O(8)	2.406(8)
Eu(5)-O(3B)	2.686(8)	Gd(2)-O(11)	2.409(8)
Eu(6)-O(20)	2.371(8)	Gd(2)-O(1A)	2.435(9)
Eu(6)-O(23)	2.376(8)	Gd(2)-O(4B)#2	2.501(8)
Eu(6)-O(20)#1	2.446(8)	Gd(3)-O(8)	2.365(8)
Eu(6)-O(5B)#2	2.501(8)	Gd(3)-O(13)	2.372(7)
Eu(7)-O(4)	2.352(8)	Gd(3)-O(2B)	2.454(8)
Eu(7)-O(6)	2.367(8)	Gd(3)-O(4)	2.460(8)
Eu(7)-O(16)#1	2.429(7)	Gd(4)-O(18)	2.359(8)
Eu(7)-O(17A)	2.429(8)	Gd(4)-O(16)#1	2.375(7)
Eu(7)-O(3B)#1	2.508(8)	Gd(4)-O(7)	2.384(8)
Eu(8)-O(1)	2.358(7)	Gd(4)-O(15)	2.425(8)
Eu(8)-O(5)#2	2.367(8)	Gd(4)-O(9A)	2.451(8)
Eu(8)-O(2)	2.372(8)	Gd(4)-O(6B)	2.456(8)
Eu(8)-O(1B)	2.565(8)	Gd(5)-O(19)	2.351(8)
Eu(9)-O(22)	2.348(8)	Gd(5)-O(16)	2.374(8)
Eu(9)-O(21)	2.349(8)	Gd(5)-O(15)#2	2.377(8)
Eu(9)-O(18)	2.358(8)	Gd(5)-O(8)	2.390(8)
Eu(9)-O(12)	2.376(8)	Gd(5)-O(4B)#2	2.648(8)
Eu(9)-O(11)	2.380(8)	Gd(5)-O(3B)	2.686(8)
Eu(9)-O(5B)#2	2.638(8)	Gd(6)-O(20)	2.371(8)
Eu(9)-O(6B)	2.712(8)	Gd(6)-O(23)	2.376(8)
Eu(10)-O(5)	2.335(8)	Gd(6)-O(22)	2.384(8)
Eu(10)-O(22A)#2	2.378(9)	Gd(6)-O(21)#2	2.399(8)
Eu(10)-O(26A)	2.405(9)	Gd(6)-O(23)#2	2.412(8)
Eu(10)-O(24)#1	2.433(8)	Gd(6)-O(13A)#2	2.442(8)
Eu(10)-O(23A)	2.458(8)	Gd(6)-O(20)#1	2.446(8)
Eu(10)-O(24A)	2.465(9)	Gd(6)-O(5B)#2	2.501(8)
Eu(10)-O(21A)	2.664(9)	Gd(7)-O(4)	2.352(8)
Eu(11)-O(29A)	2.385(18)	Gd(7)-O(6)	2.367(8)
Eu(11)-O(21)	2.397(8)	Gd(7)-O(17)	2.379(7)
Eu(11)-O(23)	2.398(8)	Gd(7)-O(19)#1	2.382(8)
Eu(11)-O(14A)#2	2.404(9)	Gd(7)-O(14)	2.412(7)
Gd(11)-O(14A)#2	2.404(9)	Gd(7)-O(16)#1	2.429(7)
Gd(11)-O(22)	2.428(8)	Gd(7)-O(17A)	2.429(8)
Gd(11)-O(15A)	2.449(9)	Gd(7)-O(3B)#1	2.508(8)

Gd(11)-O(31A)	2.584(16)	Gd(8)-O(1)	2.358(7)
Gd(12)-O(33A)#1	2.312(9)	Gd(8)-O(5)#2	2.367(8)
Gd(12)-O(18A)	2.353(9)	Gd(8)-O(2)	2.372(8)
Gd(12)-O(15)	2.378(8)	Gd(8)-O(24)#1	2.384(8)
Gd(12)-O(17)	2.387(8)	Gd(8)-O(24)	2.423(7)
Gd(12)-O(12A)	2.387(11)	Gd(8)-O(21A)#2	2.429(9)
Gd(12)-O(19)#1	2.415(8)	Gd(8)-O(1)#2	2.460(7)
Gd(12)-O(11A)	2.417(10)	Gd(8)-O(1B)	2.565(8)
Gd(13)-O(27A)	2.340(9)	Gd(9)-O(22)	2.348(8)
Gd(13)-O(6A)	2.351(8)	Gd(9)-O(21)	2.349(8)
Gd(13)-O(6)	2.381(8)	Gd(9)-O(18)	2.358(8)
Gd(13)-O(14)	2.391(8)	Gd(9)-O(12)	2.376(8)
Gd(13)-O(3)	2.422(7)	Gd(9)-O(11)	2.380(8)
Gd(13)-O(19A)	2.430(9)	Gd(9)-O(20)#1	2.386(8)
Gd(13)-O(20A)	2.460(9)	Gd(9)-O(5B)#2	2.638(8)
Gd(13)-O(17A)	2.526(8)	Gd(9)-O(6B)	2.712(8)
Gd(14)-O(2A)	2.378(10)	Gd(10)-O(5)	2.335(8)
Gd(14)-O(13)	2.394(8)	Gd(10)-O(22A)#2	2.378(9)
Gd(14)-O(10)	2.424(8)	Gd(10)-O(26A)	2.405(9)
Gd(14)-O(7A)	2.454(8)	Gd(10)-O(24)#1	2.433(8)
Gd(14)-O(8A)	2.464(9)	Gd(10)-O(23A)	2.458(8)
Gd(14)-O(9)	2.476(8)	Gd(10)-O(24A)	2.465(9)
Gd(14)-O(35A)	2.532(9)	Gd(10)-O(25A)	2.520(9)
Gd(14)-O(5A)	2.623(9)	Gd(10)-O(2)	2.531(8)
Gd(15)-O(30A)	2.231(13)	Gd(10)-O(21A)	2.664(9)
Gd(15)-O(10A)	2.355(10)	Gd(11)-O(29A)	2.385(18)

O(5)-Eu(1)-O(3)	115.1(3)	O(9)-Eu(2)-O(4B)#2	72.4(3)
O(5)-Eu(1)-O(1)	78.4(3)	O(10)-Eu(2)-O(4B)#2	127.8(3)
O(3)-Eu(1)-O(1)	147.0(3)	O(12)-Eu(2)-O(4B)#2	83.1(3)
O(5)-Eu(1)-O(6)	79.6(3)	O(8)-Eu(2)-O(4B)#2	69.5(3)
O(3)-Eu(1)-O(6)	70.4(3)	O(11)-Eu(2)-O(4B)#2	84.8(3)
O(1)-Eu(1)-O(6)	142.5(3)	O(7)-Eu(2)-O(4B)#2	149.3(3)
O(5)-Eu(1)-O(4)	142.5(3)	O(1A)-Eu(2)-O(4B)#2	125.3(3)
O(3)-Eu(1)-O(4)	78.7(3)	O(9)-Eu(2)-Eu(5)	41.59(19)
O(1)-Eu(1)-O(4)	109.6(3)	O(10)-Eu(2)-Eu(5)	79.64(19)
O(6)-Eu(1)-O(4)	72.6(3)	O(12)-Eu(2)-Eu(5)	110.95(19)
O(5)-Eu(1)-O(2)	71.6(3)	O(8)-Eu(2)-Eu(5)	42.32(19)

O(3)-Eu(1)-O(2)	82.4(3)	O(11)-Eu(2)-Eu(5)	129.91(19)
O(1)-Eu(1)-O(2)	73.4(3)	O(7)-Eu(2)-Eu(5)	154.57(19)
O(6)-Eu(1)-O(2)	126.6(3)	O(1A)-Eu(2)-Eu(5)	121.1(2)
O(4)-Eu(1)-O(2)	145.8(3)	O(4B)#2-Eu(2)-Eu(5)	48.37(18)
O(5)-Eu(1)-O(1B)#1	66.2(3)	O(9)-Eu(2)-Eu(15)	122.41(19)
O(3)-Eu(1)-O(1B)#1	146.0(2)	O(10)-Eu(2)-Eu(15)	105.05(19)
O(1)-Eu(1)-O(1B)#1	66.6(2)	O(12)-Eu(2)-Eu(15)	83.07(19)
O(6)-Eu(1)-O(1B)#1	76.8(3)	O(8)-Eu(2)-Eu(15)	156.18(19)
O(4)-Eu(1)-O(1B)#1	83.1(3)	O(11)-Eu(2)-Eu(15)	40.69(19)
O(2)-Eu(1)-O(1B)#1	126.0(3)	O(7)-Eu(2)-Eu(15)	41.03(19)
O(5)-Eu(1)-O(2B)	150.5(3)	O(1A)-Eu(2)-Eu(15)	44.2(2)
O(3)-Eu(1)-O(2B)	69.9(3)	O(4B)#2-Eu(2)-Eu(15)	125.45(18)
O(1)-Eu(1)-O(2B)	84.1(2)	Eu(5)-Eu(2)-Eu(15)	161.41(2)
O(6)-Eu(1)-O(2B)	126.8(3)	O(9)-Eu(2)-Eu(9)	140.03(19)
O(4)-Eu(1)-O(2B)	66.1(3)	O(10)-Eu(2)-Eu(9)	150.08(19)
O(2)-Eu(1)-O(2B)	80.8(3)	O(12)-Eu(2)-Eu(9)	37.19(19)
O(1B)#1-Eu(1)-O(2B)	127.2(3)	O(8)-Eu(2)-Eu(9)	110.54(19)
O(5)-Eu(1)-Eu(3)	155.80(19)	O(11)-Eu(2)-Eu(9)	37.33(19)
O(3)-Eu(1)-Eu(3)	41.89(19)	O(7)-Eu(2)-Eu(9)	75.49(19)
O(1)-Eu(1)-Eu(3)	124.71(18)	O(1A)-Eu(2)-Eu(9)	102.4(2)
O(6)-Eu(1)-Eu(3)	83.58(19)	O(4B)#2-Eu(2)-Eu(9)	74.54(18)
O(4)-Eu(1)-Eu(3)	43.28(18)	Eu(5)-Eu(2)-Eu(9)	120.80(2)
O(2)-Eu(1)-Eu(3)	105.8(2)	Eu(15)-Eu(2)-Eu(9)	63.140(18)
O(1B)#1-Eu(1)-Eu(3)	126.33(17)	O(9)-Eu(2)-Eu(3)	76.5(2)
O(2B)-Eu(1)-Eu(3)	43.33(17)	O(10)-Eu(2)-Eu(3)	35.11(19)
O(5)-Eu(1)-Eu(8)#1	39.95(19)	O(12)-Eu(2)-Eu(3)	95.6(2)
O(3)-Eu(1)-Eu(8)#1	153.88(19)	O(8)-Eu(2)-Eu(3)	34.20(18)
O(1)-Eu(1)-Eu(8)#1	42.42(18)	O(11)-Eu(2)-Eu(3)	166.3(2)
O(6)-Eu(1)-Eu(8)#1	104.29(19)	O(7)-Eu(2)-Eu(3)	93.72(19)
O(4)-Eu(1)-Eu(8)#1	125.19(18)	O(1A)-Eu(2)-Eu(3)	116.2(2)
O(2)-Eu(1)-Eu(8)#1	80.93(19)	O(4B)#2-Eu(2)-Eu(3)	101.70(18)
O(1B)#1-Eu(1)-Eu(8)#1	45.09(17)	Eu(5)-Eu(2)-Eu(3)	60.851(16)
O(2B)-Eu(1)-Eu(8)#1	126.42(17)	Eu(15)-Eu(2)-Eu(3)	132.03(2)
Eu(3)-Eu(1)-Eu(8)#1	163.98(2)	Eu(9)-Eu(2)-Eu(3)	132.56(2)
O(5)-Eu(1)-Eu(8)	81.6(2)	O(8)-Eu(3)-O(13)	72.4(3)
O(3)-Eu(1)-Eu(8)	111.64(18)	O(8)-Eu(3)-O(14)	115.2(3)
O(1)-Eu(1)-Eu(8)	37.64(18)	O(13)-Eu(3)-O(14)	143.2(3)
O(6)-Eu(1)-Eu(8)	159.8(2)	O(8)-Eu(3)-O(3)	152.0(3)

O(4)-Eu(1)-Eu(8)	127.63(18)	O(13)-Eu(3)-O(3)	120.9(3)
O(2)-Eu(1)-Eu(8)	38.28(18)	O(14)-Eu(3)-O(3)	70.4(3)
O(1B)#1-Eu(1)-Eu(8)	102.26(17)	O(8)-Eu(3)-O(10)	68.4(3)
O(2B)-Eu(1)-Eu(8)	70.13(17)	O(13)-Eu(3)-O(10)	73.1(3)
Eu(3)-Eu(1)-Eu(8)	111.74(2)	O(14)-Eu(3)-O(10)	76.9(3)
Eu(8)#1-Eu(1)-Eu(8)	64.50(2)	O(3)-Eu(3)-O(10)	137.0(3)
O(5)-Eu(1)-Eu(7)	108.7(2)	O(8)-Eu(3)-O(5A)	128.5(3)
O(3)-Eu(1)-Eu(7)	78.48(18)	O(13)-Eu(3)-O(5A)	69.2(3)
O(1)-Eu(1)-Eu(7)	127.65(18)	O(14)-Eu(3)-O(5A)	80.3(3)
O(6)-Eu(1)-Eu(7)	37.15(19)	O(3)-Eu(3)-O(5A)	79.0(3)
O(4)-Eu(1)-Eu(7)	36.84(18)	O(10)-Eu(3)-O(5A)	68.5(3)
O(2)-Eu(1)-Eu(7)	158.91(18)	O(8)-Eu(3)-O(2B)	83.9(3)
O(1B)#1-Eu(1)-Eu(7)	69.80(17)	O(13)-Eu(3)-O(2B)	87.1(3)
O(2B)-Eu(1)-Eu(7)	100.76(18)	O(14)-Eu(3)-O(2B)	128.6(3)
Eu(3)-Eu(1)-Eu(7)	64.775(17)	O(3)-Eu(3)-O(2B)	73.0(3)
Eu(8)#1-Eu(1)-Eu(7)	113.37(2)	O(10)-Eu(3)-O(2B)	149.5(3)
Eu(8)-Eu(1)-Eu(7)	161.48(2)	O(5A)-Eu(3)-O(2B)	126.0(3)
O(9)-Eu(2)-O(10)	69.9(3)	O(8)-Eu(3)-O(4)	80.4(3)
O(9)-Eu(2)-O(12)	151.9(3)	O(13)-Eu(3)-O(4)	145.2(3)
O(10)-Eu(2)-O(12)	118.2(3)	O(14)-Eu(3)-O(4)	68.6(3)
O(9)-Eu(2)-O(8)	78.0(3)	O(3)-Eu(3)-O(4)	76.5(3)
O(10)-Eu(2)-O(8)	68.4(3)	O(10)-Eu(3)-O(4)	116.5(3)
O(12)-Eu(2)-O(8)	80.6(3)	O(5A)-Eu(3)-O(4)	145.4(3)
O(9)-Eu(2)-O(11)	117.1(3)	O(2B)-Eu(3)-O(4)	68.6(3)
O(10)-Eu(2)-O(11)	144.9(3)	O(5)-Gd(1)-O(3)	115.1(3)
O(12)-Eu(2)-O(11)	73.0(3)	O(5)-Gd(1)-O(1)	78.4(3)
O(8)-Eu(2)-O(11)	145.2(3)	O(3)-Gd(1)-O(1)	147.0(3)
O(9)-Eu(2)-O(7)	137.6(3)	O(5)-Gd(1)-O(6)	79.6(3)
O(10)-Eu(2)-O(7)	78.6(3)	O(3)-Gd(1)-O(6)	70.4(3)
O(12)-Eu(2)-O(7)	69.0(3)	O(1)-Gd(1)-O(6)	142.5(3)
O(8)-Eu(2)-O(7)	116.1(3)	O(5)-Gd(1)-O(4)	142.5(3)
O(11)-Eu(2)-O(7)	75.2(3)	O(3)-Gd(1)-O(4)	78.7(3)
O(7)-Eu(2)-O(1A)	68.0(3)	O(6)-Gd(1)-O(2)	126.6(3)

Table S8. The selected bond lengths (Å) and bond angles (°) for $\mathbf{Eu_{52.8}Tb_{7.2}}$.

Eu(1)-O(20)	2.360(9)	Tb(4)-O(4)	2.384(10)
Eu(1)-O(7)	2.360(9)	Tb(4)-O(8)	2.394(9)
Eu(1)-O(18)	2.374(9)	Tb(4)-O(23)	2.417(9)
Eu(1)-O(8)	2.391(9)	Tb(4)-O(11)	2.421(10)
Eu(1)-O(2)	2.405(9)	Tb(4)-O(1B)	2.458(9)
Eu(1)-O(16)	2.418(9)	Tb(4)-O(19A)	2.466(10)
Eu(1)-O(11A)	2.444(10)	Tb(5)-O(6)#2	2.362(9)
Eu(1)-O(6B)	2.515(10)	Tb(5)-O(20)	2.370(9)
Eu(2)-O(12)	2.311(9)	Tb(5)-O(19)	2.373(10)
Eu(2)-O(17)	2.357(9)	Tb(5)-O(11)	2.373(10)
Eu(2)-O(5)#1	2.366(9)	Tb(5)-O(16)	2.383(9)
Eu(2)-O(7)	2.367(10)	Tb(5)-O(3B)	2.647(9)
Eu(2)-O(18)	2.375(10)	Tb(5)-O(6B)	2.709(10)
Eu(2)-O(1)#1	2.417(9)	Tb(5)-Tb(13)	3.8976(11)
Eu(2)-O(5B)	2.645(10)	Tb(6)-O(5)	2.362(9)
Eu(2)-O(4B)	2.656(10)	Tb(6)-O(1)	2.373(9)
Eu(3)-O(9)	2.372(9)	Tb(6)-O(24)	2.377(9)
Eu(3)-O(21)#1	2.380(10)	Tb(6)-O(12)	2.380(9)
Eu(3)-O(14)	2.406(10)	Tb(6)-O(24)#1	2.408(9)
Eu(3)-O(23)	2.410(9)	Tb(6)-O(3A)	2.420(10)
Eu(3)-O(4)	2.423(10)	Tb(6)-O(5)#1	2.465(10)
Eu(3)-O(19)#1	2.426(9)	Tb(6)-O(5B)	2.577(10)
Eu(3)-O(21A)	2.454(10)	Tb(7)-O(15)	2.381(10)
Eu(3)-O(3B)#1	2.504(9)	Tb(7)-O(13)	2.381(10)
Eu(4)-O(22)	2.340(10)	Tb(7)-O(3)	2.385(9)
Eu(4)-O(16)	2.378(9)	Tb(7)-O(13)#1	2.429(10)
Eu(4)-O(4)	2.384(10)	Tb(7)-O(3)#2	2.442(9)
Eu(4)-O(8)	2.394(9)	Tb(7)-O(7A)	2.460(9)
Eu(4)-O(23)	2.417(9)	Tb(7)-O(2B)	2.517(10)
Eu(4)-O(11)	2.421(10)	Tb(8)-O(2)	2.388(9)
Eu(4)-O(1B)	2.458(9)	Tb(8)-O(17)	2.405(9)
Eu(4)-O(19A)	2.466(10)	Tb(8)-O(9)	2.417(9)
Eu(5)-O(21)	2.362(9)	Tb(8)-O(15A)	2.419(10)
Eu(5)-O(6)#2	2.362(9)	Tb(8)-O(7)	2.457(10)
Eu(5)-O(20)	2.370(9)	Tb(8)-O(4B)	2.464(9)
Eu(5)-O(19)	2.373(10)	Tb(9)-O(28A)	2.400(11)

Eu(5)-O(11)	2.373(10)	Tb(9)-O(24)#1	2.431(9)
Eu(5)-O(16)	2.383(9)	Tb(9)-O(2A)	2.458(11)
Eu(5)-O(3B)	2.647(9)	Tb(9)-O(1A)	2.474(11)
Eu(5)-O(6B)	2.709(10)	Tb(9)-O(25A)	2.511(11)
Eu(6)-O(5)	2.362(9)	Tb(9)-O(1)#1	2.532(10)
Eu(6)-O(1)	2.373(9)	Tb(9)-O(3A)	2.659(10)
Eu(6)-O(24)	2.377(9)	Tb(10)-O(22)	2.349(11)
Eu(6)-O(12)	2.380(9)	Tb(10)-O(10)	2.353(9)
Eu(6)-O(24)#1	2.408(9)	Tb(10)-O(15)	2.357(10)
Eu(6)-O(3A)	2.420(10)	Tb(10)-O(23)	2.370(9)
Eu(6)-O(5)#1	2.465(10)	Tb(10)-O(14)	2.373(9)
Eu(6)-O(5B)	2.577(10)	Tb(10)-O(3)	2.392(10)
Eu(7)-O(15)	2.381(10)	Tb(10)-O(2B)#1	2.647(11)
Eu(7)-O(13)	2.381(10)	Tb(10)-O(1B)	2.743(9)
Eu(7)-O(3)	2.385(9)	Tb(11)-O(8A)	2.396(11)
Eu(7)-O(13)#1	2.429(10)	Tb(11)-O(13)#1	2.398(10)
Eu(7)-O(3)#2	2.442(9)	Tb(11)-O(15)	2.401(10)
Eu(7)-O(7A)	2.460(9)	Tb(11)-O(10)	2.428(9)
Eu(7)-O(2B)	2.517(10)	Tb(11)-O(6A)	2.430(11)
Eu(8)-O(19)#1	2.352(10)	Tb(11)-O(5A)	2.463(11)
Eu(8)-O(6)	2.383(9)	Tb(11)-O(36A)	2.574(17)
Eu(8)-O(2)	2.388(9)	Tb(11)-O(7A)	2.577(11)
Eu(8)-O(17)	2.405(9)	Tb(12)-O(31A)	2.360(11)
Eu(8)-O(9)	2.417(9)	Tb(12)-O(23A)	2.381(13)
Eu(8)-O(15A)	2.419(10)	Tb(12)-O(6)	2.412(9)
Eu(8)-O(7)	2.457(10)	Tb(12)-O(9)	2.416(9)
Eu(8)-O(4B)	2.464(9)	Tb(12)-O(13A)	2.463(10)
Eu(8)-Eu(12)	3.6811(10)	Tb(12)-O(14A)	2.463(11)
Eu(8)-Eu(14)	3.8939(10)	Tb(12)-O(21)#1	2.479(10)
Eu(9)-O(12)	2.336(9)	Tb(12)-O(30A)	2.530(11)
Eu(9)-O(4A)	2.373(10)	Tb(12)-O(15A)	2.634(11)
Eu(9)-O(28A)	2.400(11)	Tb(13)-O(29A)	2.325(11)
Eu(9)-O(24)#1	2.431(9)	Tb(13)-O(12A)	2.373(11)
Eu(9)-O(2A)	2.458(11)	Tb(13)-O(11)	2.380(10)
Eu(9)-O(1A)	2.474(11)	Tb(13)-O(8)	2.389(9)
Eu(9)-O(25A)	2.511(11)	Tb(13)-O(18A)	2.416(14)
Eu(9)-O(1)#1	2.532(10)	Tb(13)-O(20)	2.429(10)
Eu(9)-O(3A)	2.659(10)	Tb(13)-O(17A)	2.436(12)

Eu(14)-O(2)	2.390(9)	Tb(13)-O(19A)	2.530(11)
Eu(14)-O(9A)	2.418(11)	Tb(14)-O(27A)	2.341(11)
Eu(14)-O(17)	2.420(9)	Tb(14)-O(16A)	2.365(11)
Eu(14)-O(10A)	2.462(12)	Tb(14)-O(18)	2.382(9)
Eu(14)-O(11A)	2.533(10)	Tb(14)-O(2)	2.390(9)
Eu(15)-O(33A)	2.210(17)	Tb(14)-O(9A)	2.418(11)
Eu(15)-O(20A)	2.361(12)	Tb(14)-O(17)	2.420(9)
Eu(15)-O(14)	2.369(10)	Tb(14)-O(10A)	2.462(12)
Eu(15)-O(4)	2.404(10)	Tb(14)-O(11A)	2.533(10)
Eu(15)-O(24A)	2.409(16)	Tb(15)-O(33A)	2.210(17)
Eu(15)-O(22)	2.446(11)	Tb(15)-O(20A)	2.361(12)
Eu(15)-O(22A)	2.488(13)	Tb(15)-O(14)	2.369(10)
Eu(15)-O(21A)	2.532(11)	Tb(15)-O(4)	2.404(10)
Tb(1)-O(20)	2.360(9)	Tb(15)-O(24A)	2.409(16)
Tb(1)-O(7)	2.360(9)	Tb(15)-O(22)	2.446(11)
Tb(1)-O(18)	2.374(9)	Tb(15)-O(22A)	2.488(13)
Tb(1)-O(8)	2.391(9)	Tb(15)-O(21A)	2.532(11)

O(20)-Eu(1)-O(7)	152.7(3)	O(4)-Tb(3)-O(3B)#1	149.4(3)
O(20)-Eu(1)-O(18)	118.2(3)	O(19)#1-Tb(3)-O(3B)#1	69.5(3)
O(7)-Eu(1)-O(18)	72.8(3)	O(21A)-Tb(3)-O(3B)#1	125.7(4)
O(20)-Eu(1)-O(8)	70.2(3)	O(22)-Tb(4)-O(16)	150.7(3)
O(7)-Eu(1)-O(8)	117.4(3)	O(22)-Tb(4)-O(4)	70.6(3)
O(18)-Eu(1)-O(8)	143.1(3)	O(16)-Tb(4)-O(4)	117.2(3)
O(20)-Eu(1)-O(2)	135.8(3)	O(22)-Tb(4)-O(8)	137.1(3)
O(7)-Eu(1)-O(2)	69.6(3)	O(16)-Tb(4)-O(8)	69.6(3)
O(18)-Eu(1)-O(2)	74.9(3)	O(4)-Tb(4)-O(8)	75.6(3)
O(8)-Eu(1)-O(2)	76.4(3)	O(22)-Tb(4)-O(23)	76.0(3)
O(20)-Eu(1)-O(16)	77.2(3)	O(16)-Tb(4)-O(23)	80.7(3)
O(7)-Eu(1)-O(16)	81.5(3)	O(4)-Tb(4)-O(23)	69.6(3)
O(18)-Eu(1)-O(16)	146.0(3)	O(8)-Tb(4)-O(23)	115.8(3)
O(8)-Eu(1)-O(16)	69.0(3)	O(22)-Tb(4)-O(11)	119.9(3)
O(2)-Eu(1)-O(16)	116.7(3)	O(16)-Tb(4)-O(11)	72.6(3)
O(20)-Eu(1)-O(11A)	78.2(3)	O(4)-Tb(4)-O(11)	142.4(3)
O(7)-Eu(1)-O(11A)	128.1(3)	O(8)-Tb(4)-O(11)	74.8(3)
O(18)-Eu(1)-O(11A)	68.5(3)	O(23)-Tb(4)-O(11)	145.6(3)
O(8)-Eu(1)-O(11A)	79.5(3)	O(22)-Tb(4)-O(1B)	73.0(3)
O(2)-Eu(1)-O(11A)	67.9(3)	O(16)-Tb(4)-O(1B)	82.6(3)
O(16)-Eu(1)-O(11A)	145.0(3)	O(4)-Tb(4)-O(1B)	130.7(3)
O(20)-Eu(1)-O(6B)	73.8(3)	O(8)-Tb(4)-O(1B)	149.4(3)
O(7)-Eu(1)-O(6B)	83.1(3)	O(23)-Tb(4)-O(1B)	70.1(3)

O(18)-Eu(1)-O(6B)	84.5(3)	O(11)-Tb(4)-O(1B)	85.1(3)
O(8)-Eu(1)-O(6B)	130.3(3)	O(22)-Tb(4)-O(19A)	80.6(4)
O(2)-Eu(1)-O(6B)	149.6(3)	O(16)-Tb(4)-O(19A)	127.8(3)
O(16)-Eu(1)-O(6B)	70.4(3)	O(4)-Tb(4)-O(19A)	78.9(3)
O(11A)-Eu(1)-O(6B)	124.9(3)	O(8)-Tb(4)-O(19A)	67.5(3)
O(12)-Eu(2)-O(17)	115.0(3)	O(23)-Tb(4)-O(19A)	145.5(3)
O(12)-Eu(2)-O(5)#1	78.6(3)	O(11)-Tb(4)-O(19A)	68.6(3)
O(17)-Eu(2)-O(5)#1	147.2(3)	O(1B)-Tb(4)-O(19A)	126.0(4)
O(12)-Eu(2)-O(7)	142.7(3)	O(21)-Tb(5)-O(6)#2	72.6(3)
O(17)-Eu(2)-O(7)	78.4(3)	O(21)-Tb(5)-O(20)	114.6(3)
O(5)#1-Eu(2)-O(7)	109.6(3)	O(6)#2-Tb(5)-O(20)	82.8(3)
O(12)-Eu(2)-O(18)	79.5(3)	O(21)-Tb(5)-O(19)	78.9(3)
O(17)-Eu(2)-O(18)	70.2(3)	O(6)#2-Tb(5)-O(19)	72.0(3)
O(5)#1-Eu(2)-O(18)	142.5(3)	O(20)-Tb(5)-O(19)	146.6(3)
O(7)-Eu(2)-O(18)	72.6(3)	O(21)-Tb(5)-O(11)	81.9(4)

Supplementary References

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