

Supporting Information

Boronic acid derivatized lanthanide-polyoxometalates with novel B-OH-Ln and B-O-Nb bridges

Shujun Li, Yue Zhao, Huihui Qi, Yanfang Zhou, Shuxia Liu, Xiaoming Ma, Jie Zhang,^{*} and Xuenian Chen^{*}

Table of Contents

SI-1 Materials and measurement	1
SI-2 Synthesis of the title compounds	1-2
SI-3 X-ray Crystallography	3-4
SI-4 Structure figures	5-8
SI-5 UV-vis-near-IR absorption spectra	15-16
SI-6 Photoluminescence	16-18
SI-7 FTIR Spectroscopy	8-10
SI-8 Thermal analyses	11-13
SI-9 Powder X-ray diffraction patterns	13-15

SI-1 Materials and measurement

All the reagents were readily available from commercial sources and used without further purification. The FTIR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with a VECTOR 22 Bruker spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D& Advance X-ray powder diffractometer with graphite monochromatized Cu $K\alpha$ radiation at 293 K. Elemental analyses for B, P, W, Nb, Er, and Eu were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Elemental analyses for C and N were performed on a Perkin-Elmer 2400 elemental analyzer. The thermal behaviors of compounds were examined by synchronous thermal analyses (TG, Netzsch 449C). The samples were heated to 1000 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{C}/\text{min}$, under a flowing N_2 atmosphere.

SI-2 Synthesis of the title compounds

Synthesis of 1Er: A sample of $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}] \cdot 12\text{H}_2\text{O}^{\text{[1]}}$ (0.20 g, 0.04 mmol) was dissolved in 25 mL of deionized water at 75 $^{\circ}\text{C}$. Solid NaHSO_3 (0.04 g, 0.38 mmol) was added with stirring until the yellow solution became colorless. Then, solid $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.025 g, 0.065 mmol) and 3-PBA (0.01g, 0.081 mmol) were added respectively. The pH of the resulting solution was adjusted to 4.0 with hydrochloric acid (1 M), and further stirred at 75 $^{\circ}\text{C}$ for 40 min. After cooled to room temperature the reaction solution was filtrated and left for evaporation. Colourless clubbed crystal products were obtained within two week. Yield: 0.10 g (46.3% based on $\text{K}_5\text{Na}_4[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{NbO}_2)_3] \cdot 17\text{H}_2\text{O}$). Anal. Calcd (%) for **1Er**: B 0.76, C 4.20, N 0.98, P 1.08, Er 8.77, Nb 4.87, W 48.21; found B 0.79, C 4.25, N 1.02, P 1.13, Er 8.81, Nb 4.78, W 47.96. IR (KBr disks): 1623 (w), 1087 (s), 946 (s), 906 (s), 768 (vs), 598 (m), 526 (m), 460 (m) cm^{-1} .

Synthesis of 2Er: A sample of $\text{K}_8\text{H}[\text{P}_2\text{W}_{15}(\text{NbO}_2)_3\text{O}_{59}] \cdot 12\text{H}_2\text{O}$ (0.20 g, 0.04 mmol) was dissolved in 25 mL of deionized water at 75 $^{\circ}\text{C}$. Solid NaHSO_3 (0.04 g, 0.38 mmol) was added with stirring until the yellow solution became colorless. Then, solid $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.025 g, 0.065 mmol) and 3-PBA (0.01 g, 0.081 mmol) were added respectively. The pH of the resulting clear solution was adjusted to 2.0 with hydrochloric acid (1 M), and further stirred at 75 $^{\circ}\text{C}$ for 40 min. After cooled to room temperature the reaction solution was filtrated and left for evaporation. Colourless virgate crystal products were obtained within one week. Yield: 0.16 g (74.8% based on $\text{K}_5\text{Na}_4[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{NbO}_2)_3] \cdot 17\text{H}_2\text{O}$). Anal. Calcd (%) for **2Er**: B 0.21, C 1.16, N 0.27, P 1.19, Er 6.44, Nb 5.36, W 53.07; found B 0.19, C 1.19, N 0.27, P 1.23, Er 6.38, Nb 5.18, W 52.86. IR (KBr disks): 1623 (m), 1457 (vw), 1400 (vw), 1217 (vw), 1085 (s), 950 (s), 910 (s), 769 (vs), 528 (s), 460 (m) cm^{-1} .

Synthesis of 2Eu: A sample of $K_8H[P_2W_{15}(NbO_2)_3O_{59}] \cdot 12H_2O$ (0.20 g, 0.04 mmol) was dissolved in 25 mL of deionized water at 75°C. Solid $NaHSO_3$ (0.04 g, 0.38 mmol) was added with stirring until the yellow solution became colorless. Then, solid $EuCl_3 \cdot 6H_2O$, (0.025 g, 0.071 mmol) and 3-PBA (0.01g, 0.081 mmol) were added respectively. The pH of the resulting solution was adjusted to 2.0 with hydrochloric acid (1 M), and further stirred at 75 °C for 40 min. After that the reaction solution was filtrated and left for evaporation. Colourless block crystals were obtained within one week. Yield: 0.15 g (73.2% based on $K_5Na_4[P_2W_{15}O_{59}(NbO_2)_3] \cdot 17H_2O$). Anal. Calcd (%) for **2Eu**: B 0.22, C 1.22, N 0.29, P 1.26, Nb 5.67, Eu 6.19, W 56.12; found P 1.06, La 7.54, Ta 10.14, W 50.73. IR (KBr disks): 1623 (w), 1537 (vw), 1456 (vw), 1398 (vw), 1214 (vw), 1087 (s), 951 (s), 908 (s), 769 (vs), 526 (m) cm^{-1} .

Notably, the isostructural analogues of **2Er** and **2Eu** can be synthesized by using other lanthanide ions, such as La^{3+} , Ce^{3+} , Sm^{3+} and Tb^{3+} . But the structure of **1Er** can only be obtained by using Er^{3+} .

SI-3X-ray Crystallography

Single crystal XRD analysis of the three title compounds were recorded on a Super Nova Dual diffractometer using graphite-monochromated Cu $K\alpha$ radiation $\lambda = 1.54184 \text{ \AA}$ for **1Er** and **2Eu** and Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ for **2Er**. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography.^[2] Empirical absorption corrections were applied. The structures were solved by using the direct method and refined through the full matrix least-squares method on F^2 using SHELXS-97.^[3] Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception for a few oxygen atoms. Those hydrogen atoms attached to lattice water molecules were not located. Crystallization water molecules were estimated by thermogravimetry and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. The crystal data and structure refinement results of the five compounds are summarized in Table S1. Further details on the crystal structure investigation scan be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif on quoting the depository numbers CCDC-1581186 (**1Er**), CCDC-1581187 (**2Er**), CCDC-1849594 (**2Eu**).

Table S1. Crystal data and structural refinement for the title compounds.

Compound	1Er	2Er	2Eu
Formula	C ₂₀ H ₁₆ B ₄ Er ₃ N ₄ Nb ₃ O _{104.75} P ₂ W ₁₅	C ₅ H ₄ B ₁ Er ₂ N ₁ Nb ₃ O ₉₄ P ₂ W ₁₅	C ₅ H ₄ B ₁ Eu ₂ N ₁ Nb ₃ O _{85.5} P ₂ W ₁₅
Formula weight (g·mol ⁻¹)	5643.30	5025.84	4859.24
<i>T</i> (K)	100.00(10)	291.29(10)	293(2)
Wavelength (Å)	1.54184	0.7100	1.54184
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2 ₁ /n	P2 ₁ /n
<i>a</i> (Å)	17.8960(3)	23.0950(6)	23.1824(3)
<i>b</i> (Å)	18.9430(3)	14.2098(4)	14.1907(1)
<i>c</i> (Å)	18.9630(3)	28.0704(9)	28.1627(3)
<i>α</i> (°)	72.5180(10)	90	90
<i>β</i> (°)	72.2610(10)	104.388(3)	104.580(1)
<i>γ</i> (°)	87.635(2)	90	90
<i>V</i> (Å ³)	5831.13(17)	8923.1(5)	8966.46(17)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (mg m ⁻³)	3.212	3.741	3.600
<i>μ</i> (mm ⁻¹)	33.933	21.632	48.662
<i>F</i> (000)	4986.0	8788.0	8476.0
Crystalsize (mm)	0.13×0.11×0.09	0.11×0.09×0.08	0.5×0.03×0.01
Goodness-of-fit on <i>F</i> ²	1.079	1.073	1.119
Final <i>R</i> indices	R1 = 0.0376	R ₁ = 0.0400	R ₁ = 0.0896
[<i>I</i> > 2σ(<i>I</i>)] ^[a]	wR2 = 0.0954	wR ₂ = 0.0876	wR ₂ = 0.2595
<i>R</i> indices ^[a]	R1 = 0.0453	R ₁ = 0.0574	R1 = 0.0994
(all data)	wR2 = 0.0988	wR ₂ = 0.0963	wR2 = 0.2767

[a] $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$

SI-4 Structure figures

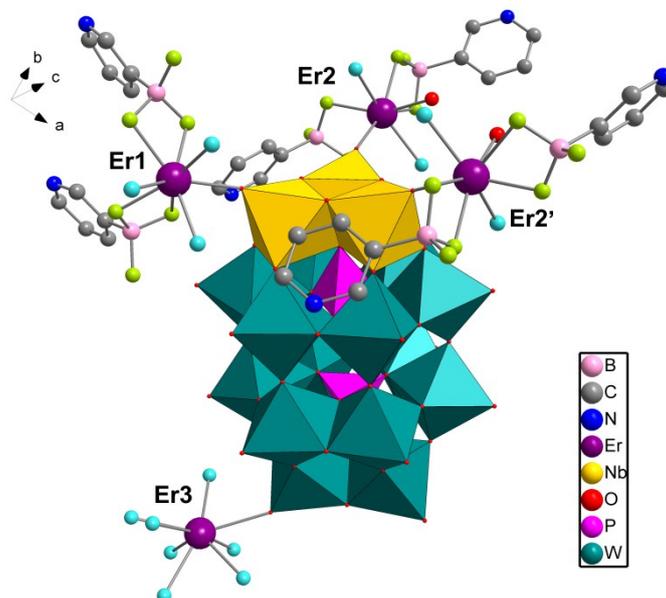


Figure S1. Combined polyhedral/ball-and-stick representation of **1Er**. The lime balls (●) and aqua balls (●) represent OH and H₂O respectively.

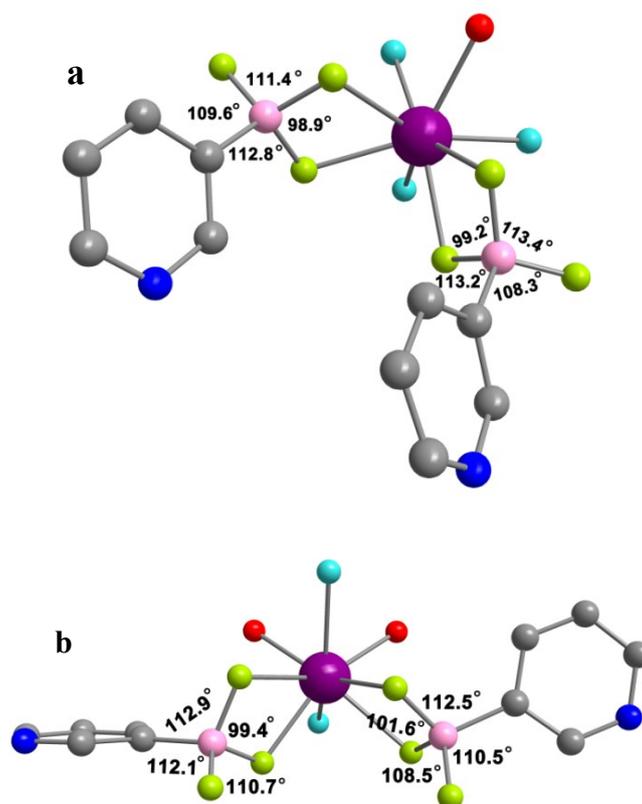


Figure S2. The coordination configuration of Er and boronic acids in **1Er**.

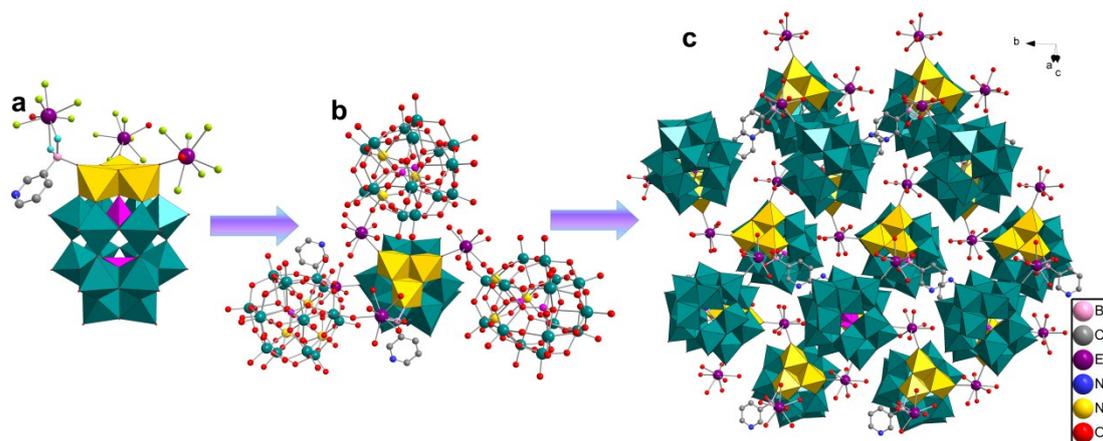


Figure S3. The smallest asymmetric unit in **2Er** (a), the Coordination environment (b) and the extended structure of **2Er** (c, viewed from different direction with that in Fig. 2b).

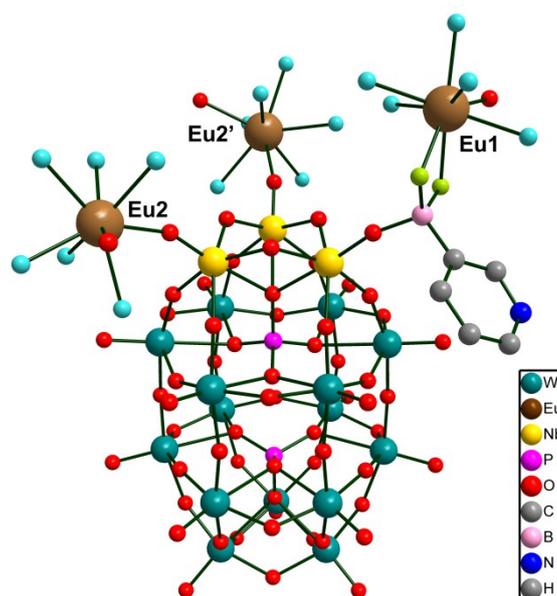


Figure S4. Ball-and-stick representation of the smallest asymmetric unit in **2Eu**.

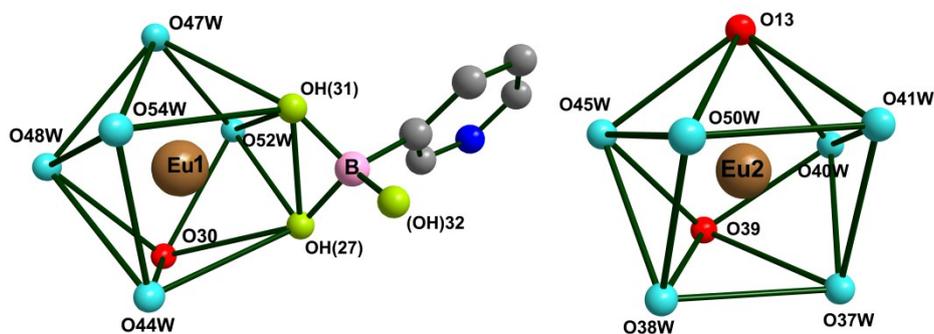


Figure S5. The coordination configuration of Eu1 and Eu2 in compound **2Eu**.

SI-5 UV-vis-near-IR absorption spectra

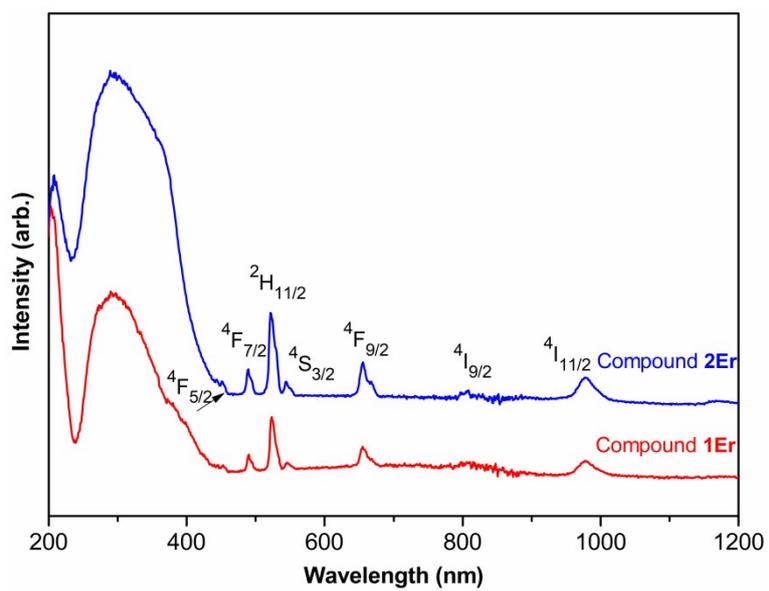


Figure S6. UV-vis-near-IR absorption spectra of **1Er**, and **2Er**.

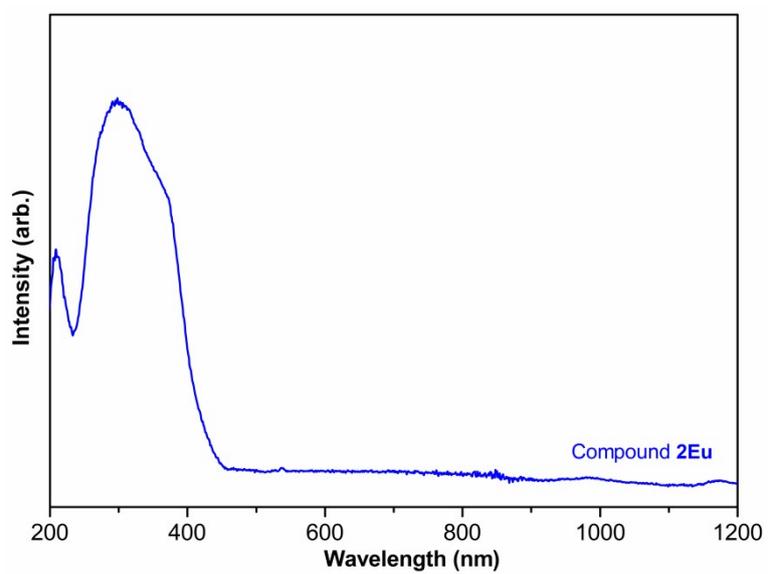


Figure S7. UV-vis-near-IR absorption spectrum of **2Eu**.

SI-6 Photoluminescence

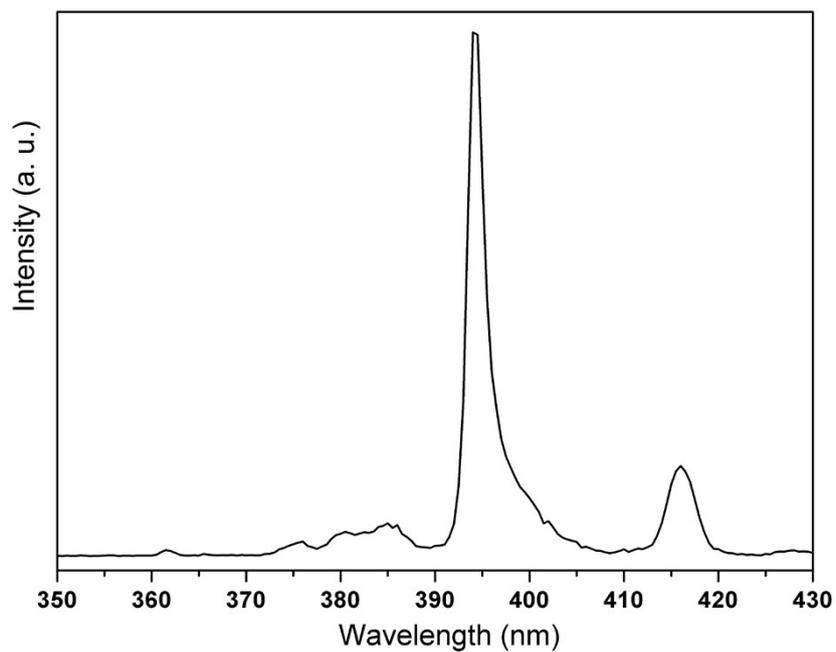


Figure S8. Excitation spectrum of 3Eu.

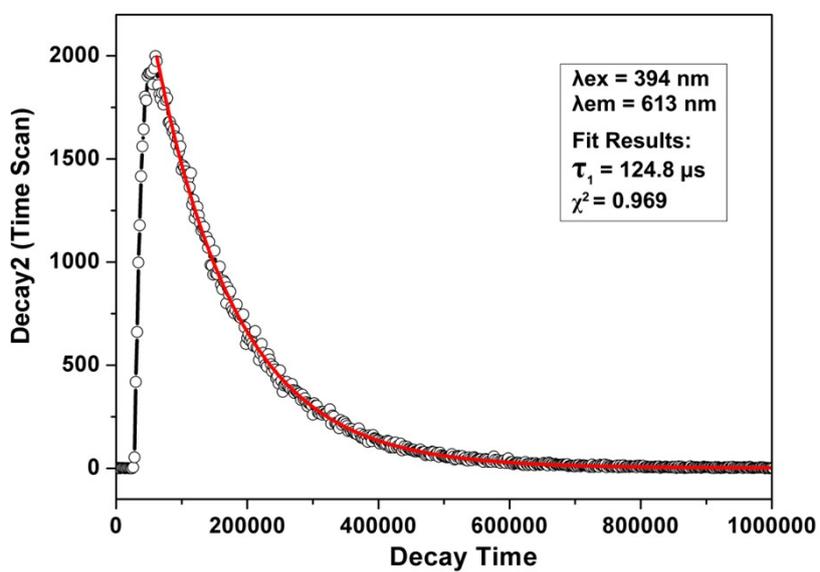


Figure S9. Decay curve of 2Eu monitored under the excitation at 394 nm and emission at 613 nm.

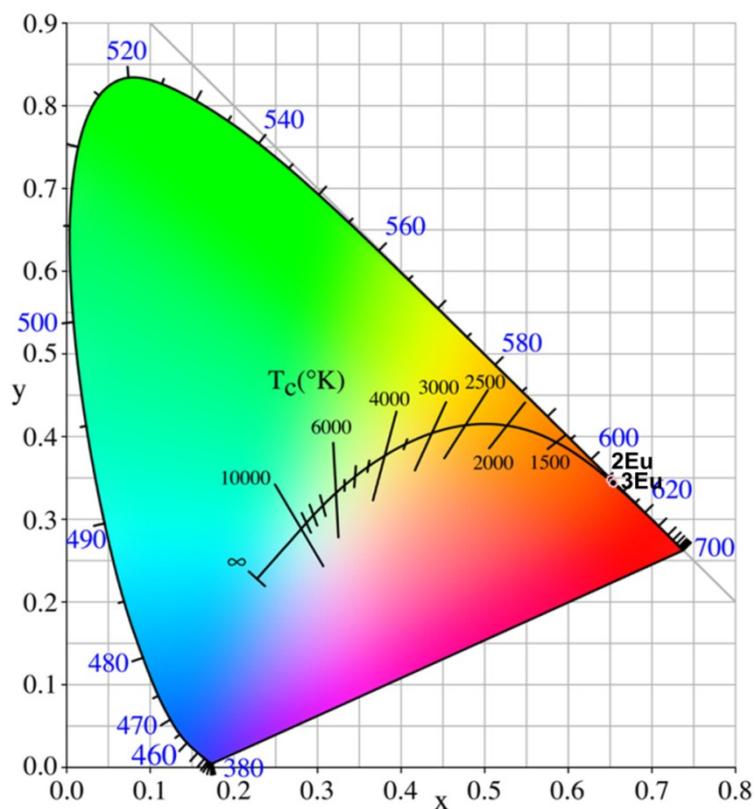


Figure S10. The CIE chromaticity coordinates diagram for compounds **2Eu** and **3Eu**.

SI-7 FTIR Spectroscopy

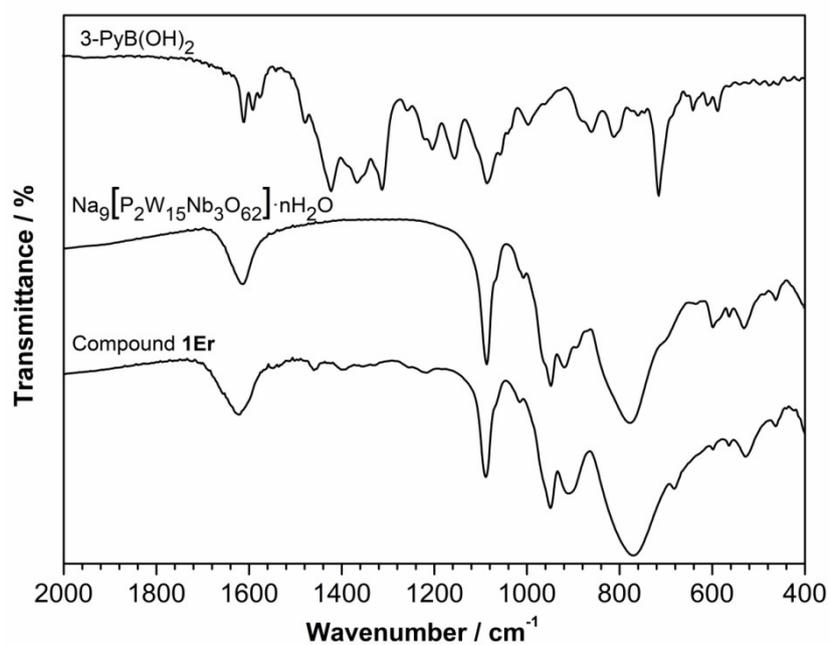


Figure S11. IR spectra of compound **1Er**.

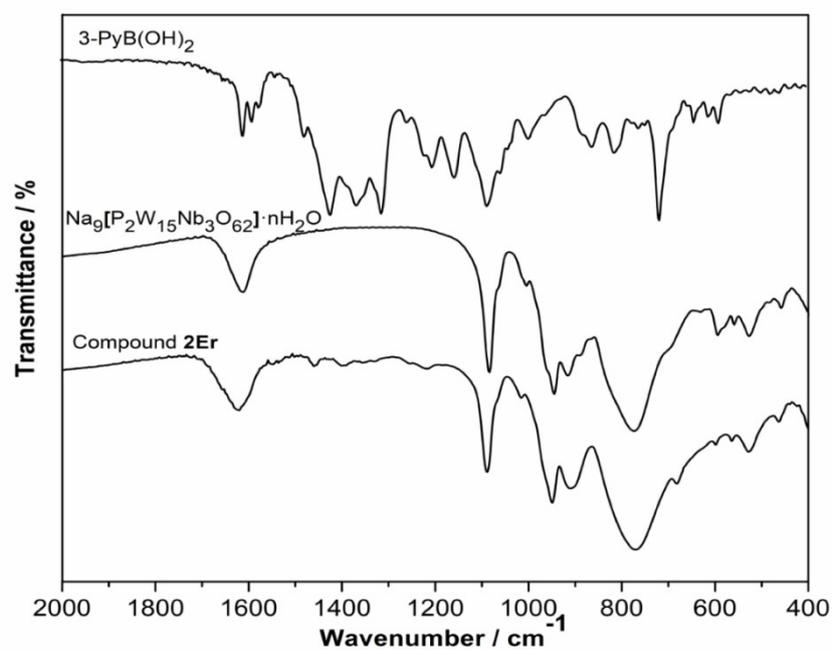


Figure S12. IR spectra of compound 2Er.

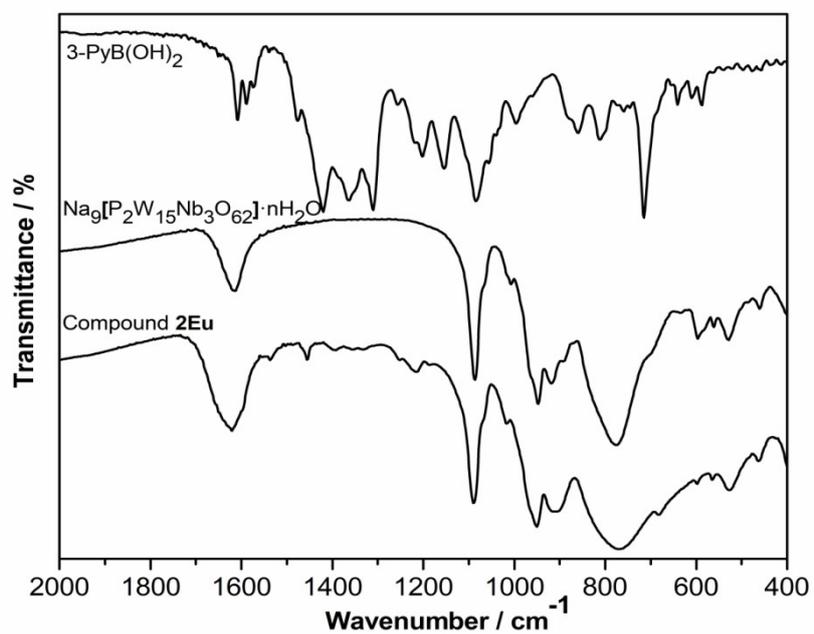


Figure S13. IR spectra of compound 2Eu.

SI-8 Thermal analyses

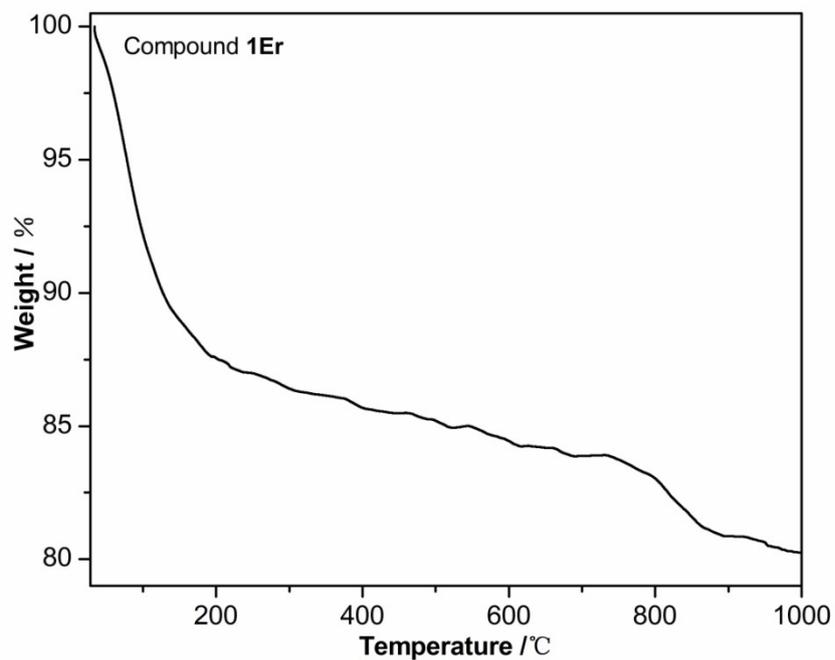


Figure S14. TG curve of compound 1Er.

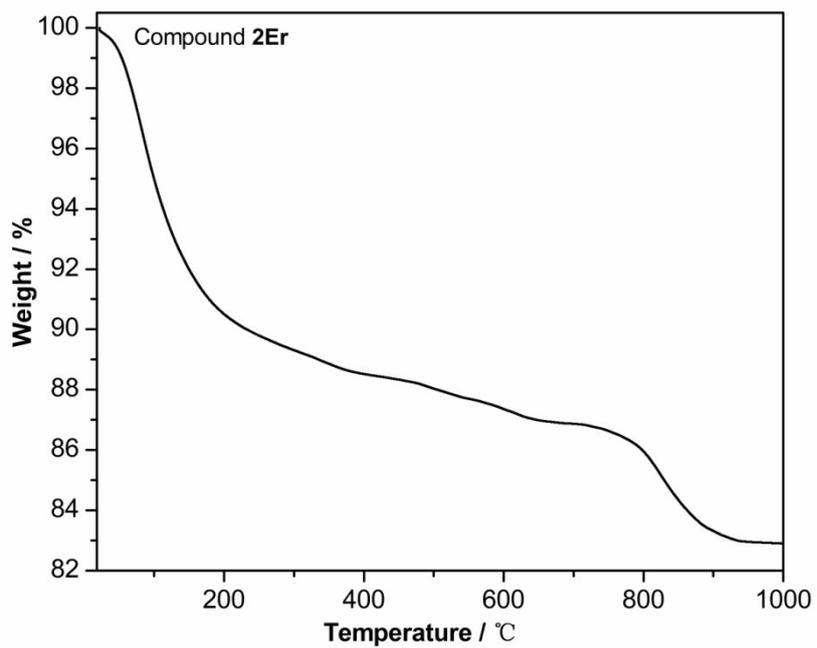


Figure S15. TG curve of compound 2Er.

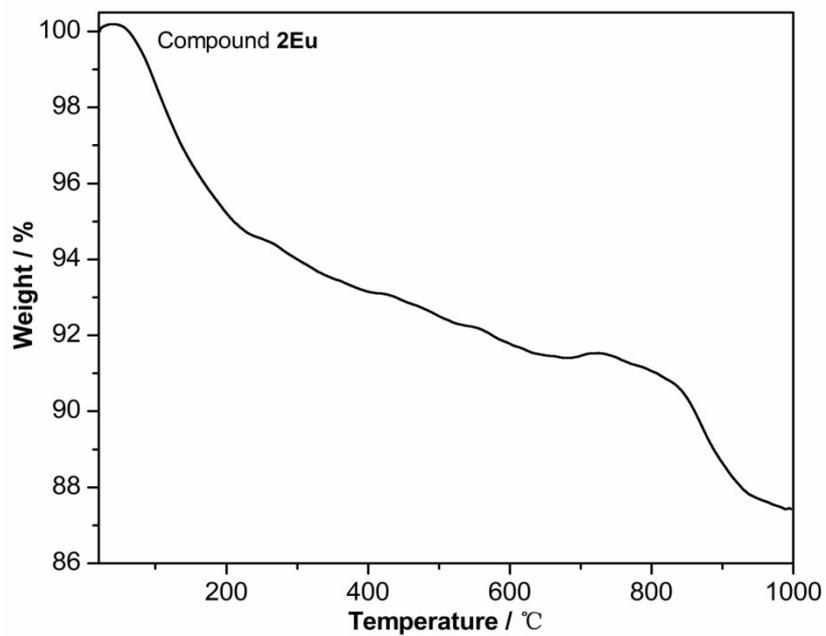


Figure S16. TG curve of compound **2Eu**.

SI-9 Powder X-ray diffraction patterns

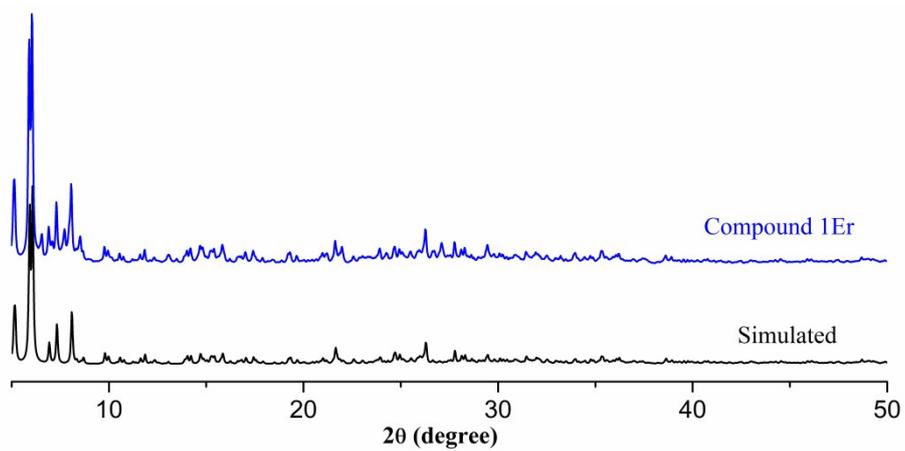


Figure S17. Powder X-ray diffraction patterns of compound **1Er** and the simulated patterns for **1Er**.

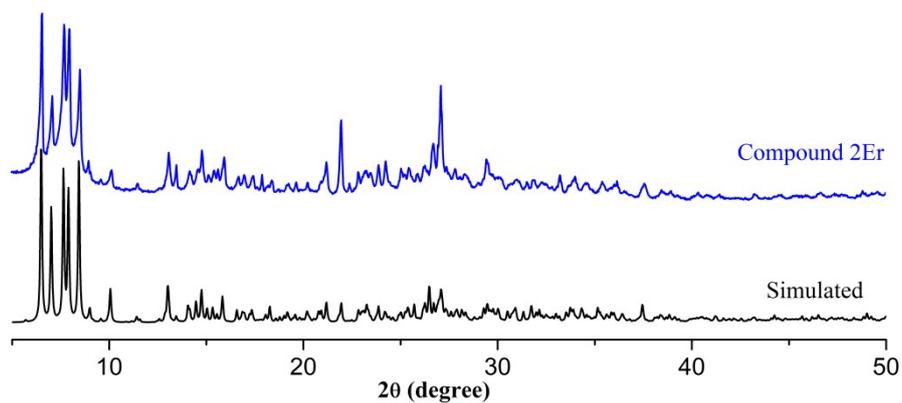


Figure S18. Powder X-ray diffraction patterns of compound **2Er** and the simulated patterns for **2Er**.

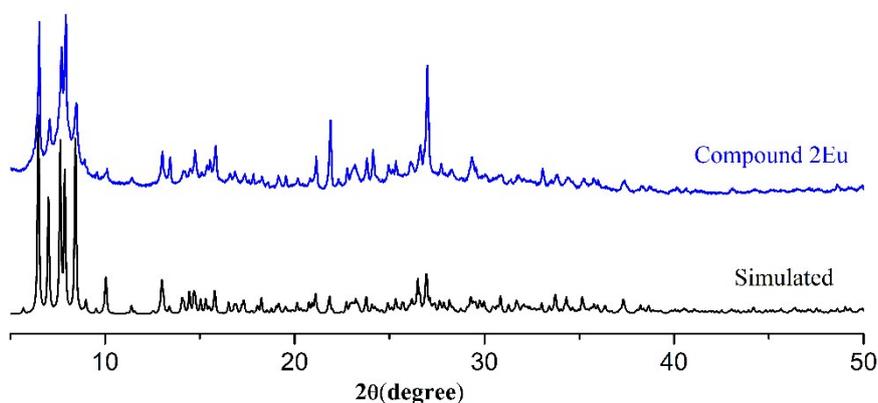


Figure S19. Powder X-ray diffraction patterns of compound **2Eu** and the simulated patterns for **2Eu**.

References

- [1] J. Gong, Y.-G. Chen, L.-Y. Qu, Q. Liu, *Polyhedron*, 1996, **15**, 2273–2277.
- [2] International Tables for X-ray Crystallography (Eds.: N. F. M. Henry, K. Lonsdale), Kynoch Press, Birmingham (1952).
- [3] G. M. Sheldrick, SHELXS-97: Programs for Crystal Structure Solution, University of Göttingen, Göttingen Germany (1997).