Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Lanthanide metal–organic frameworks based on a 1,2,3-triazole-containing tricarboxylic acid ligand for luminescence sensing of metal ions and nitroaromatic compounds

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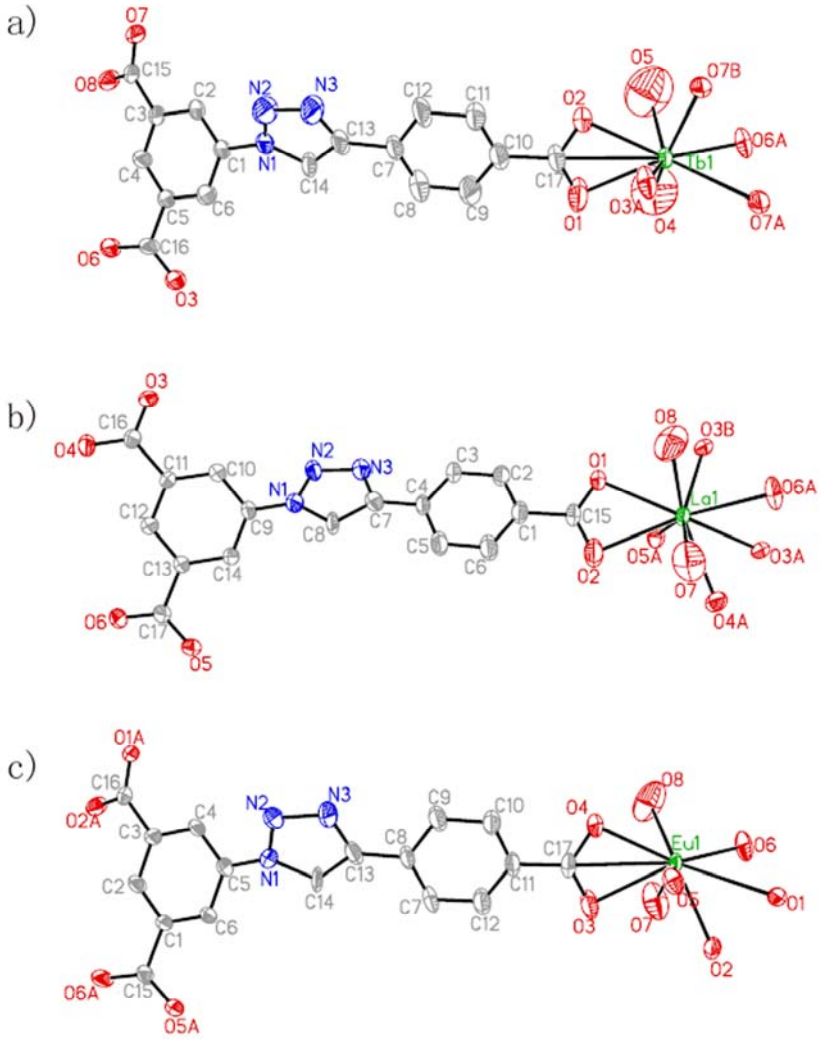

Fig. S1 Representation of the asymmetric unit of **1** (a), **2** (b) and **3** (c) showing ellipsoid at the 50% probability level.

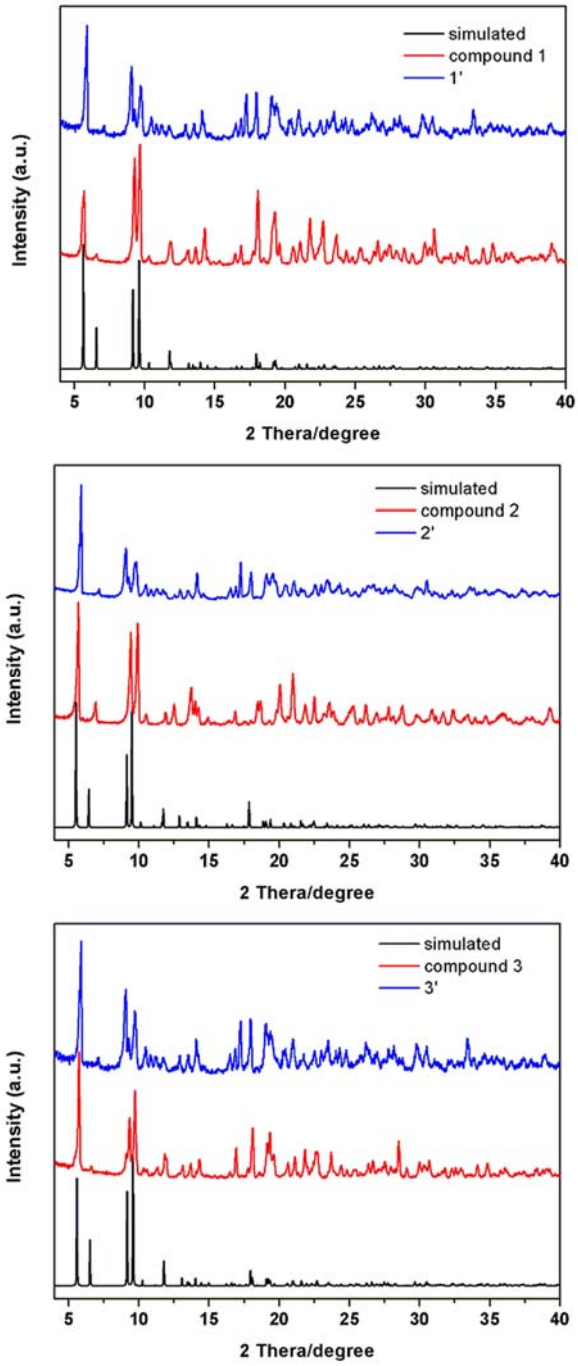

Fig. S2 Powder X-ray diffraction patterns of compounds **1**−**3** and micrometer-sized **1'**−**3'**.

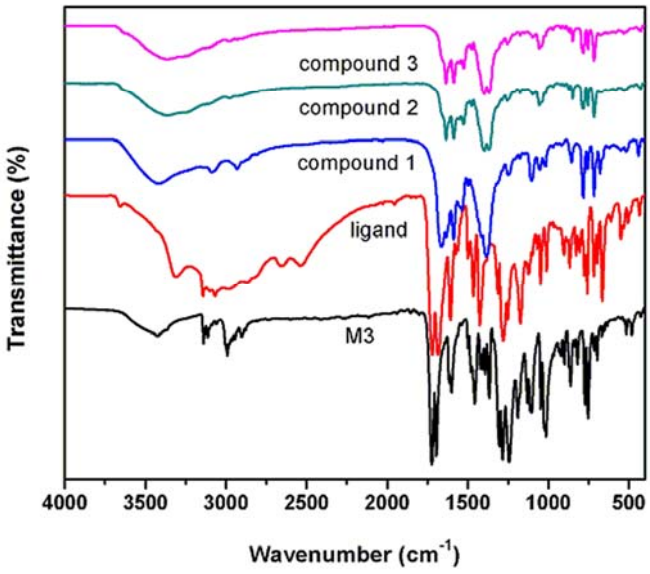

Fig. S3 Infra-red spectra of M3, ligand and compounds **1**−**3**.

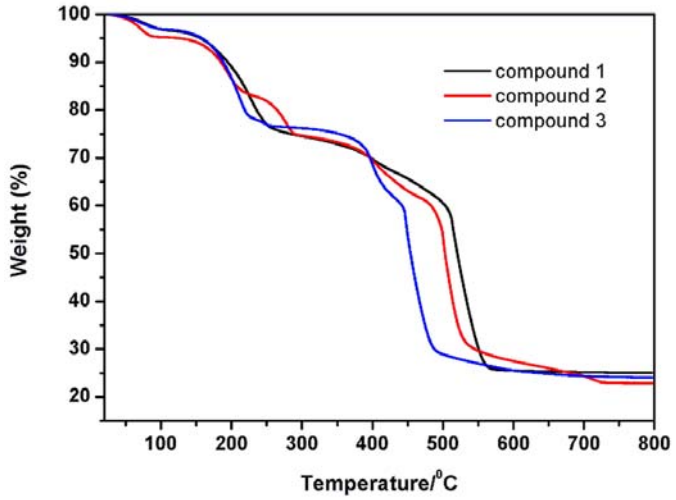

Fig. S4 TGA curves of compounds **1**−**3**.

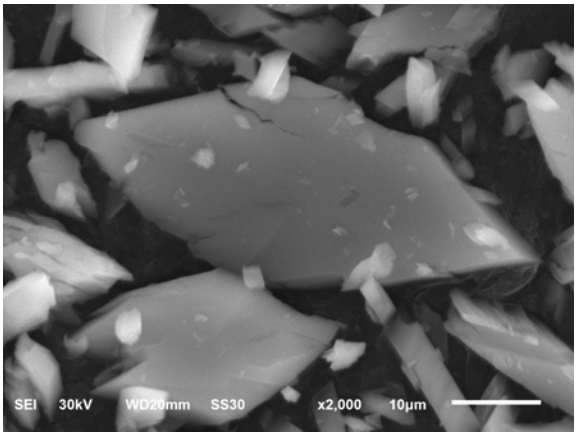

Fig. S5 SEM image of micrometer **1**'.

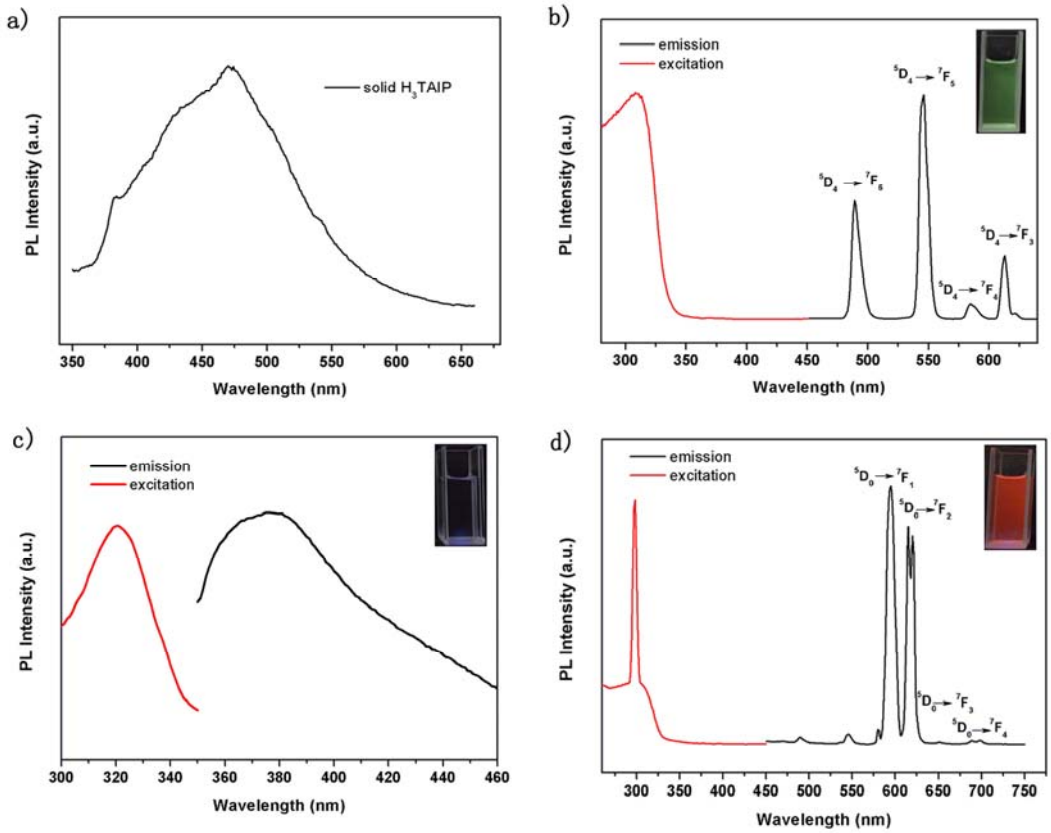

Fig. S6 Luminescent spectra of H_3TAIP in the solid state (a, λ_{ex} = 340 nm). Excitation and emission spectra of **1'** (b, λ_{ex} = 305 nm), **2'** (c, λ_{ex} = 321 nm) and **3'** (d, λ_{ex} = 297 nm) in ethanol suspensions (Inset: photographs of micrometer-sized **1'**, **2'** and **3'** under UV-light of 254 nm.).

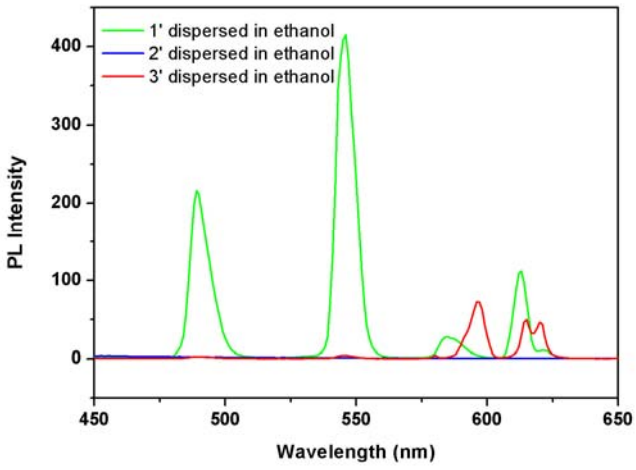

Fig. S7 Comparison of **e**mission intensities for micrometer-sized **1'**, **2'** and **3'** in ethanol suspensions (0.25 mg/mL).

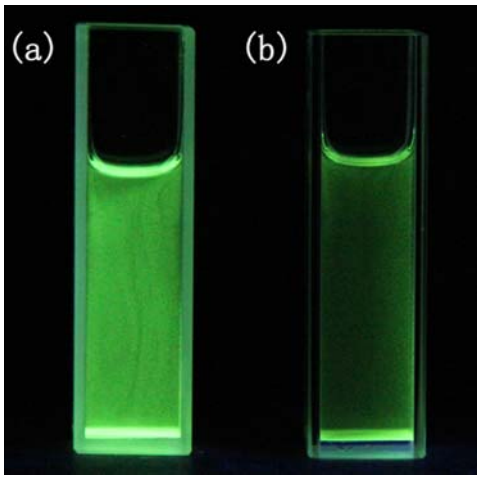

Fig. S8 The photographs of micrometer-sized **1'** before (a) and after (b) adding Fe^{3+} under the UV-light of 254 nm.

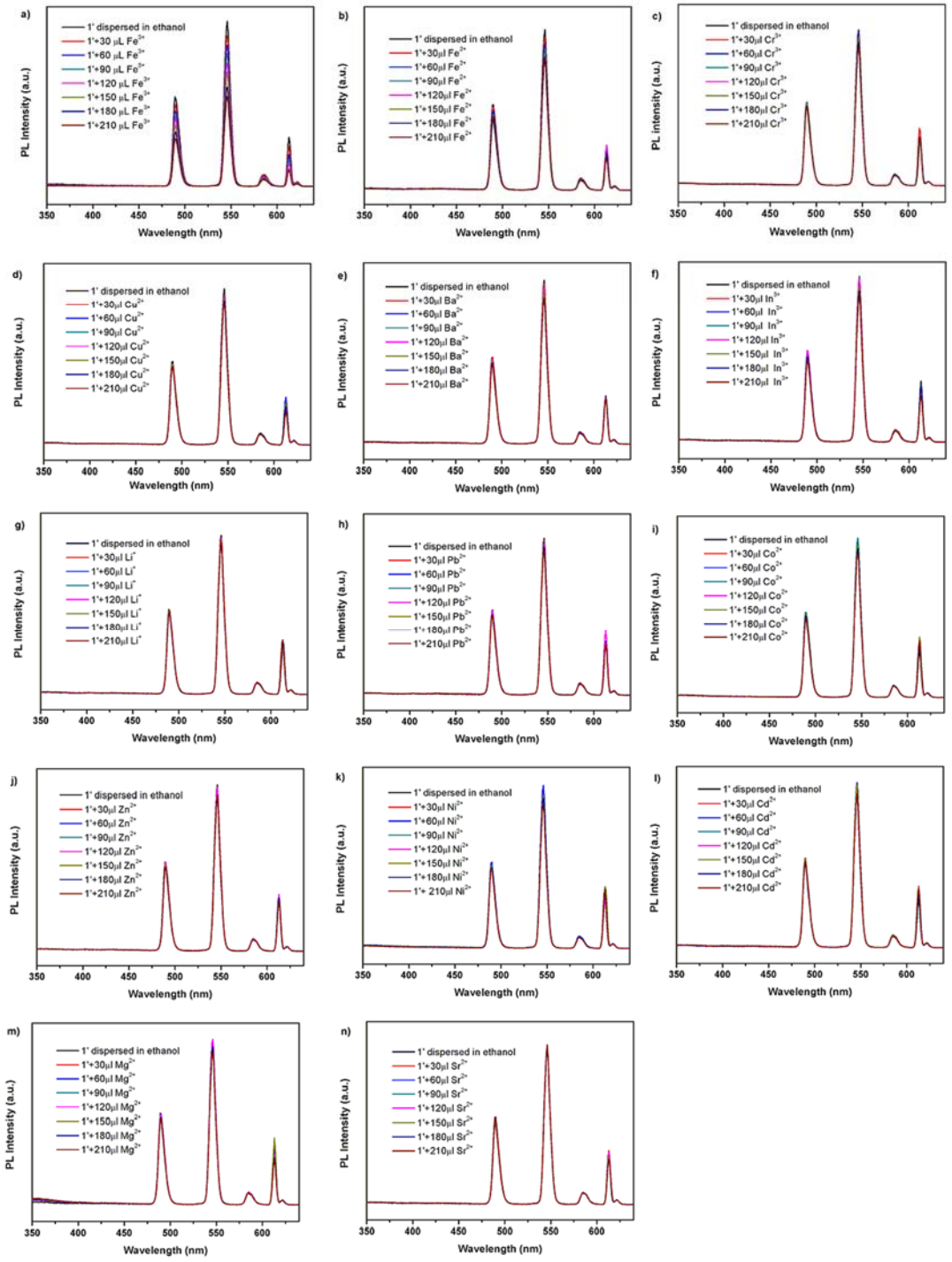

Fig. S9 Fluorescent titrations of 0.5 mg **1'** dispersed in 2 mL ethanol solution with the addition of different volume of 0.001 M solution of a) Fe^{3+}, b) Fe^{2+}, c) Cr^{3+}, d) Cu^{2+} e) Ba^{2+}, f) In^{3+}, g) Li^{+}, h) Pb^{2+}, i) Co^{2+}, j) Zn^{2+}, k) Ni^{2+}, l) Cd^{2+},m) Mg^{2+} and n) Sr^{2+} in ethanol. The fluorescent emission spectra were recorded from 350 nm to 640 nm upon the excitation at 305 nm. The slit width for excitation and emission is 1.5 nm and 3.0 nm, respectively.

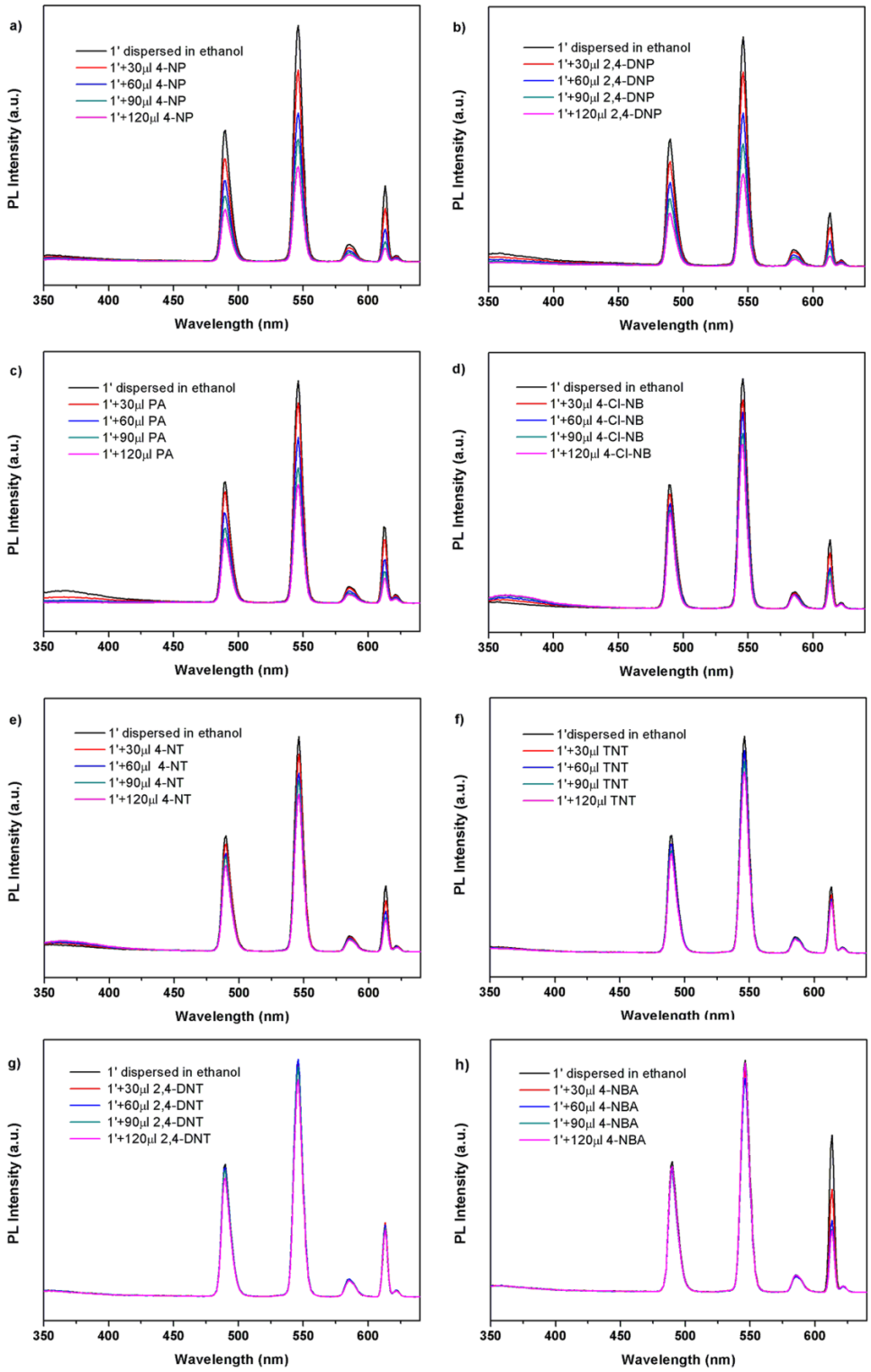

Fig. S10 Fluorescent titrations of 0.5 mg **1'** dispersed in 2 mL ethanol solution with the addition of different volume of 0.001 M solution of a) 4-nitrophenol (4-NP), b) 2, 4-dinitrophenol (2,4-DNP), c) Picric acid (PA), d) 4-chloronitrobenzene (4-Cl-NB) e) 4-nitrotoluene (4-NT), f) 2,4,6-trinitrotoluene (TNT), g) 2,4-dinitrotoluene (2,4-DNT), and h) 4-nitrobenzaldehyde (4-NBA) in ethanol. The fluorescent emission spectra were recorded from 350 nm to 640 nm upon the excitation at 305 nm. The slit width for excitation and emission is 1.5 nm and 3.0 nm, respectively.

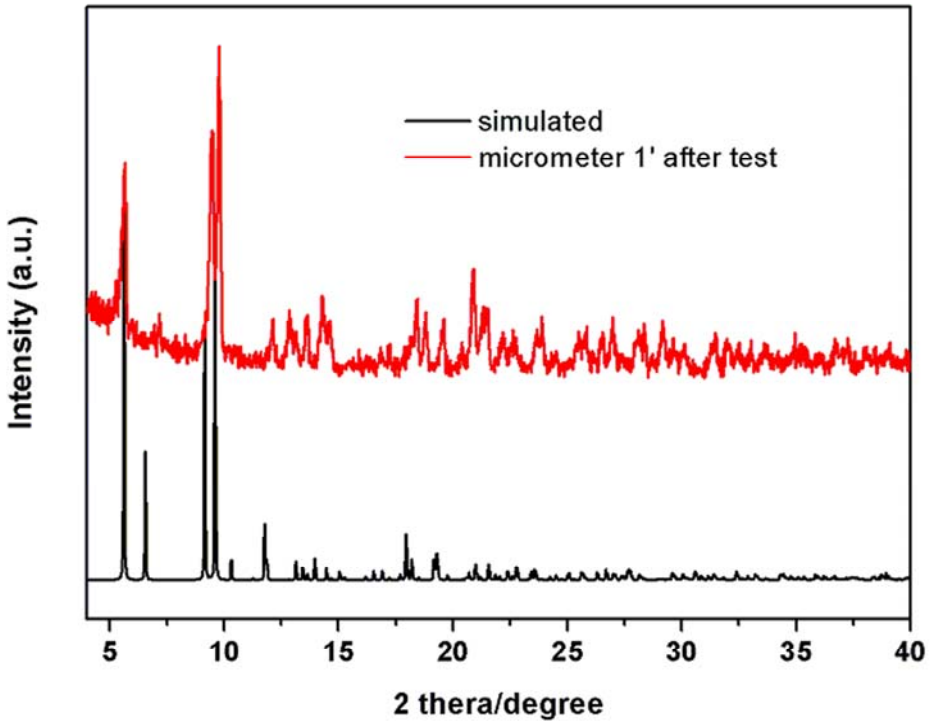

Fig. S11 Powder X-ray diffraction patterns of simulated and micrometer-size phase **1'** after test.

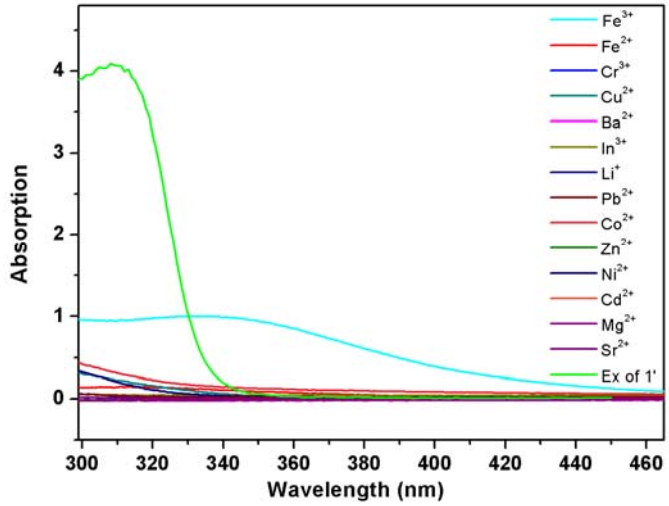

Fig. S12 UV-Vis adsorption spectrum of $M(NO_3)_X$ aqueous solution and the excitation spectrum of micrometer-size phase **1'**.

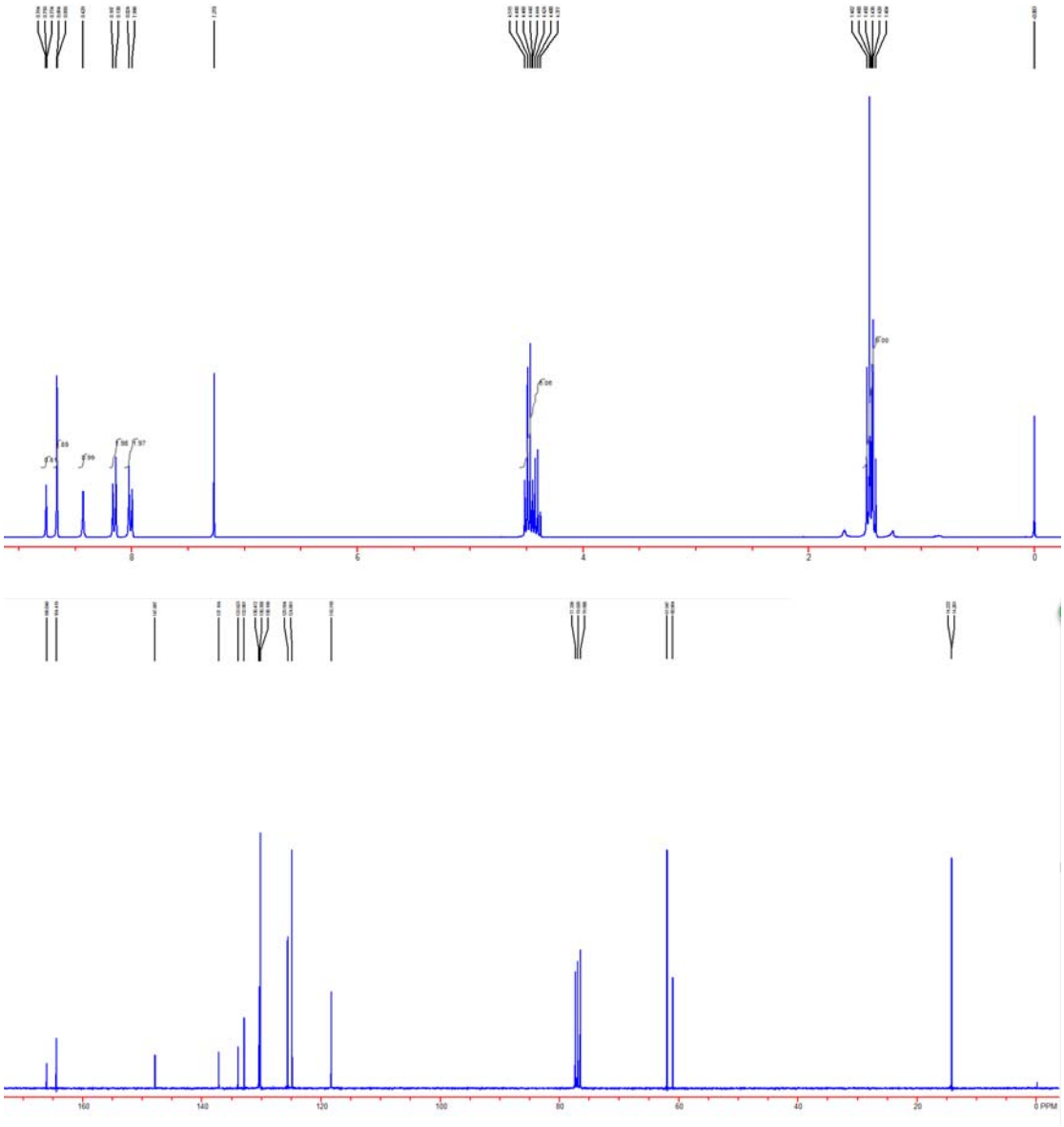

Fig. S13 The ^{1}H and ^{13}C NMR spectra of **M3**

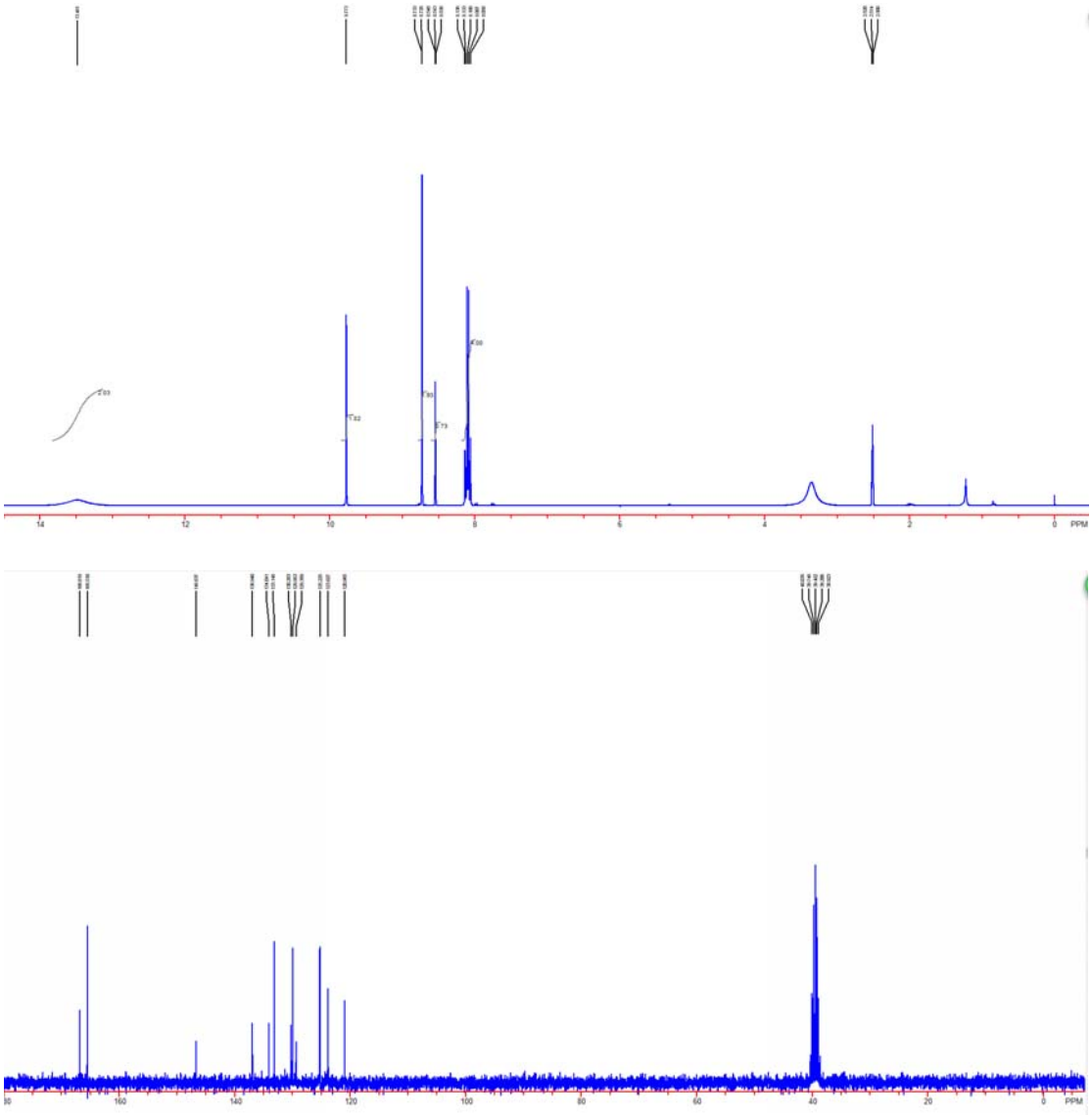

Fig. S14 The ^{1}H and ^{13}C NMR spectra of H_3TAIP.

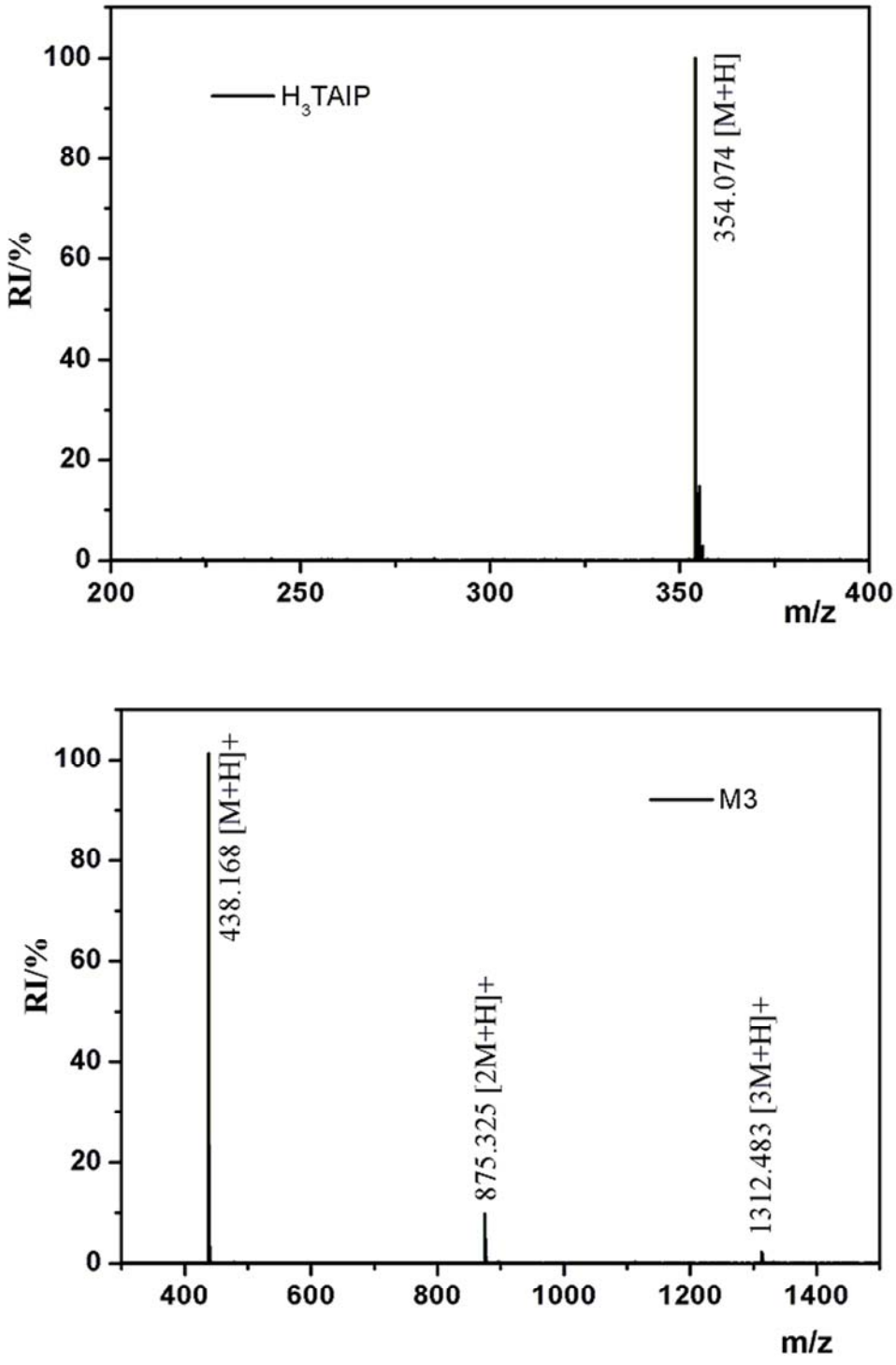

Fig. S15 MS of H_3TAIP and **M3**.

Table S1 Crystal Data and Structure Refinement for **1.**[a]

Empirical formula	C_{23} H_{22} N_5 O_8 Tb
Formula weight	655.20
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 31.6491(17) Å α = 90° b = 14.9143(9) Å β = 96.4660(10)° c = 13.2656(7) Å γ = 90°
Volume	6221.9(6) $Å^3$
Z	8
Absorption coefficient	2.317 mm^{-1}
F (000)	2416
Theta range for data collection	1.51 to 28.30°
Limiting indices	-38≤h≤42, -19≤k≤18, -16≤l≤17
Reflections collected / unique	22674 / 7738
R_{int}	0.0624
Completeness to theta =28.30	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.6805 and 0.6296
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7738 / 214 / 256
Goodness-of-fit on F^2	1.066
Final R indices [I>2 σ (I)][b]	R_1 = 0.0664, wR_2 = 0.1969
R indices (all data)	R_1 = 0.0997, wR_2 = 0.2234
Largest diff. peak and hole	3.327 and -1.540 e.$Å^{-3}$

Table S2. Bond lengths [Å] and angles [deg] for **1.**

Bond lengths		Bond lengths	
Tb(1)-O(7)#1	2.340(4)	Tb(1)-O(6)#2	2.362(4)
Tb(1)-O(3)#3	2.363(4)	Tb(1)-O(5)	2.379(8)
Tb(1)-O(2)	2.406(5)	Tb(1)-O(4)	2.410(7)
Tb(1)-O(8)#4	2.421(4)	Tb(1)-O(1)	2.481(5)
Tb(1)-O(7)#4	2.767(4)	O(7)-Tb(1)#6	2.767(4)
O(3)-Tb(1)#3	2.363(4)	O(8)-Tb(1)#6	2.421(4)
O(6)-Tb(1)#5	2.362(4)	O(7)-Tb(1)#1	2.340(4)

Bond angels		Bond angels	
O(7)#1-Tb(1)-O(6)#2	79.92(13)	O(7)#1-Tb(1)-O(3)#3	74.34(13)
O(6)#2-Tb(1)-O(3)#3	131.35(12)	O(7)#1-Tb(1)-O(5)	79.9(3)
O(6)#2-Tb(1)-O(5)	74.7(3)	O(3)#3-Tb(1)-O(5)	137.4(3)
O(7)#1-Tb(1)-O(2)	81.59(14)	O(6)#2-Tb(1)-O(2)	143.75(15)
O(3)#3-Tb(1)-O(2)	71.48(15)	O(5)-Tb(1)-O(2)	71.6(3)
O(7)#1-Tb(1)-O(4)	146.9(2)	O(6)#2-Tb(1)-O(4)	74.5(2)
O(3)#3-Tb(1)-O(4)	138.7(2)	O(5)-Tb(1)-O(4)	73.4(4)
O(2)-Tb(1)-O(4)	107.4(2)	O(7)#1-Tb(1)-O(8)#4	123.73(12)
O(6)#2-Tb(1)-O(8)#4	85.81(13)	O(3)#3-Tb(1)-O(8)#4	75.71(13)
O(5)-Tb(1)-O(8)#4	146.4(3)	O(2)-Tb(1)-O(8)#4	130.22(15)
O(4)-Tb(1)-O(8)#4	75.3(2)	O(7)#1-Tb(1)-O(1)	131.28(14)
O(6)#2-Tb(1)-O(1)	146.13(14)	O(3)#3-Tb(1)-O(1)	77.30(14)
O(5)-Tb(1)-O(1)	95.9(3)	O(2)-Tb(1)-O(1)	51.92(15)
O(4)-Tb(1)-O(1)	71.7(3)	O(8)#4-Tb(1)-O(1)	85.23(14)
O(7)#1-Tb(1)-O(7)#4	75.39(13)	O(6)#2-Tb(1)-O(7)#4	66.25(12)
O(3)#3-Tb(1)-O(7)#4	67.64(12)	O(5)-Tb(1)-O(7)#4	136.5(3)
O(2)-Tb(1)-O(7)#4	137.06(14)	O(4)-Tb(1)-O(7)#4	111.7(2)
O(8)#4-Tb(1)-O(7)#4	49.29(11)	O(1)-Tb(1)-O(7)#4	127.19(14)

Table S3. Crystal Data and Structure Refinement for **2.**[a]

Empirical formula	$C_{49}H_{51}La_2N_{11}O_{17}$
Formula weight	1343.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 32.118(3) Å α = 90° b = 15.2133(17) Å β = 95.256(2)° c = 13.1789(14) Å γ = 90°
Volume	6412.4(12) $Å^3$
Z	4
Absorption coefficient	1.381 mm^{-1}
F (000)	2484
Theta range for data collection	1.48 to 28.34°
Limiting indices	-42≤h≤36, -18≤k≤20, -13≤l≤17
Reflections collected / unique	23110 / 7987
R_{int}	0.0628
Completeness to theta =28.34	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.7892 and 0.7603
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7987 / 268 / 412
Goodness-of-fit on F^2	1.007
Final R indices [I>2 σ (I)][b]	R_1 = 0.0582, wR_2 = 0.1634
R indices (all data)	R_1 = 0.0947, wR_2 = 0.1886
Largest diff. peak and hole	1.739 and -1.781 e.$Å^{-3}$

Table S4. Bond lengths [Å] and angles [deg] for **2.**

Bond lengths		Bond lengths	
La(1)-O(3)#1	2.482(4)	La(1)-O(6)#2	2.491(5)
La(1)-O(5)#3	2.497(4)	La(1)-O(7)	2.517(6)
La(1)-O(8)	2.524(7)	La(1)-O(1)	2.534(5)
La(1)-O(4)#4	2.538(5)	La(1)-O(2)	2.593(5)
La(1)-O(3)#4	2.831(4)	O(3)-La(1)#1	2.482(4)
O(3)-La(1)#6	2.831(4)	O(4)-La(1)#6	2.538(5)
O(5)-La(1)#3	2.497(4)	O(6)-La(1)#7	2.491(5)

Bond angels		Bond angels	
O(3)#1-La(1)-O(6)#2	78.56(16)	O(3)#1-La(1)-O(5)#3	73.68(16)
O(6)#2-La(1)-O(5)#3	130.35(16)	O(3)#1-La(1)-O(7)	148.1(2)
O(6)#2-La(1)-O(7)	75.20(19)	O(5)#3-La(1)-O(7)	137.9(2)
O(3)#1-La(1)-O(8)	80.4(2)	O(6)#2-La(1)-O(8)	72.6(2)
O(5)#3-La(1)-O(8)	138.8(2)	O(7)-La(1)-O(8)	74.7(3)
O(3)#1-La(1)-O(1)	78.73(16)	O(6)#2-La(1)-O(1)	141.37(18)
O(5)#3-La(1)-O(1)	70.81(17)	O(7)-La(1)-O(1)	111.9(2)
O(8)-La(1)-O(1)	73.1(2)	O(3)#1-La(1)-O(4)#4	122.45(14)
O(6)#2-La(1)-O(4)#4	87.71(18)	O(5)#3-La(1)-O(4)#4	74.24(16)
O(7)-La(1)-O(4)#4	74.4(2)	O(8)-La(1)-O(4)#4	146.7(2)
O(1)-La(1)-O(4)#4	130.91(17)	O(3)#1-La(1)-O(2)	129.21(15)
O(6)#2-La(1)-O(2)	146.15(18)	O(5)#3-La(1)-O(2)	81.07(19)
O(7)-La(1)-O(2)	71.8(2)	O(8)-La(1)-O(2)	91.6(2)
O(1)-La(1)-O(2)	51.27(16)	O(4)#4-La(1)-O(2)	90.41(17)
O(3)#1-La(1)-O(3)#4	76.02(14)	O(6)#2-La(1)-O(3)#4	66.14(15)
O(5)#3-La(1)-O(3)#4	67.65(14)	O(7)-La(1)-O(3)#4	108.69(19)
O(8)-La(1)-O(3)#4	135.5(2)	O(1)-La(1)-O(3)#4	135.86(17)
O(4)#4-La(1)-O(3)#4	47.79(13)	O(2)-La(1)-O(3)#4	132.33(18)

Table S5. Bond lengths [Å] and angles [deg] for **3.**[a]

Empirical formula	C_{23} H_{22} Eu N_5 O_{87}
Formula weight	648.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	a = 31.810(6) Å α = 90° b = 14.993(3) Å β = 96.01(3)° c = 13.220(3) Å γ = 90°
Volume	6271(2) $Å^3$
Z	8
Absorption coefficient	2.044 mm^{-1}
F (000)	2400
Theta range for data collection	3.01 to 27.48°
Limiting indices	-41≤h≤41, -19≤k≤18, -15≤l≤17
Reflections collected / unique	29600 / 7152
R_{int}	0.0828
Completeness to theta =27.48	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. Transmission	0.6974 and 0.6507
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7152 / 224 / 289
Goodness-of-fit on F^2	1.092
Final R indices [I>2 σ (I)][b]	R_1 = 0.0596, wR_2 = 0.1638
R indices (all data)	R_1 = 0.0842, wR_2 = 0.1852
Largest diff. peak and hole	1.875 and -1.245 e.$Å^{-3}$

Table S6. Bond lengths [Å] and angles [deg] for **3.**

Bond lengths		Bond lengths	
Eu(1)-O(1)#3	2.379(2)	Eu(1)-O(6)	2.397(3)
Eu(1)-O(5)	2.406(3)	Eu(1)-O(7)	2.422(3)
Eu(1)-O(8)	2.429(4)	Eu(1)-O(2)	2.437(3)
Eu(1)-O(4)	2.443(3)	Eu(1)-O(3)	2.514(3)
Eu(1)-O(1)	2.774(3)	O(1)-Eu(1)#3	2.379(2)

Bond angels		Bond angels	
O(6)-Eu(1)-O(5)	131.49(9)	O(1)#3-Eu(1)-O(7)	146.04(12)
O(6)-Eu(1)-O(7)	73.94(12)	O(5)-Eu(1)-O(7)	139.24(12)
O(1)#3-Eu(1)-O(8)	78.93(14)	O(6)-Eu(1)-O(8)	72.52(13)
O(5)-Eu(1)-O(8)	138.53(14)	O(7)-Eu(1)-O(8)	72.92(16)
O(1)#3-Eu(1)-O(2)	124.19(9)	O(6)-Eu(1)-O(2)	86.25(10)
O(5)-Eu(1)-O(2)	75.47(9)	O(7)-Eu(1)-O(2)	75.60(12)
O(8)-Eu(1)-O(2)	145.78(14)	O(1)#3-Eu(1)-O(4)	80.50(10)
O(6)-Eu(1)-O(4)	142.75(11)	O(5)-Eu(1)-O(4)	71.69(10)
O(7)-Eu(1)-O(4)	108.16(12)	O(8)-Eu(1)-O(4)	72.84(14)
O(2)-Eu(1)-O(4)	130.84(11)	O(1)#3-Eu(1)-O(3)	130.82(9)
O(6)-Eu(1)-O(3)	146.05(10)	O(5)-Eu(1)-O(3)	77.75(11)
O(7)-Eu(1)-O(3)	72.11(12)	O(8)-Eu(1)-O(3)	96.83(14)
O(2)-Eu(1)-O(3)	85.89(10)	O(4)-Eu(1)-O(3)	52.26(10)
O(1)#3-Eu(1)-O(1)	75.99(9)	O(6)-Eu(1)-O(1)	66.10(9)
O(5)-Eu(1)-O(1)	68.01(9)	O(7)-Eu(1)-O(1)	111.28(10)
O(8)-Eu(1)-O(1)	134.48(13)	O(2)-Eu(1)-O(1)	49.25(8)
O(4)-Eu(1)-O(1)	137.32(9)	O(3)-Eu(1)-O(1)	128.21(10)
O(1)#3-Eu(1)-O(5)	74.70(9)		

[a]Date based on *PLATON/SQUEEZE* mode.

[b]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$. $wR_2=[\sum[\ w\ (F_o^2-F_c^2)^2]\ /\ \sum[\ w\ (F_o^2)^2]]^{1/2}$.