Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

One high-nuclearity Eu_{18} nanoring with rapid ratiometric fluorescent response to dipicolinic acid (an anthrax biomarker)

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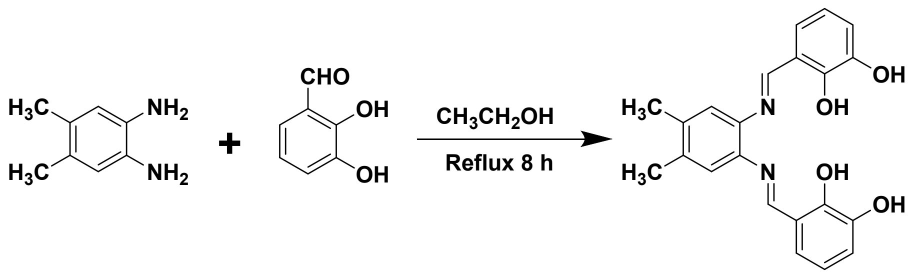
1. General Procedures

All chemical materials and solvents were purchased from commercial sources. The synthesis of lanthanide complexes was carried out using Schlenk techniques. Powder XRD spectra were obtained using a D8 Advance; IR spectra were determined on a FTIR-650 spectrometer; The UV-vis absorbance spectra were measured on an UV-3600 spectrophotometer; The thermogravimetric analyses were carried out on a Perking Elmer Diamond TG-DTA spectrum GX. The sample is under a N_2 flow of 200 mL min^{-1}, and heated from room temperature to 800 °C with a heating rate of 5°C min^{-1}; NMR experiments were performed on a Bruker Avance III NMR spectrometer at 500.13MHz, equipped with a 5 mm room temperature probe (Bruker Instruments Inc., Germany). The experimental conditions are as follows: spectrometer frequency 500.13 MHz, spectral width (SW) 10 ppm, pulse 90°, acquisition time (AQ) 5.40 s, relaxation delay (RD) 2.00 s, and Fourier Transform (FT) size 32K data point; Dynamic light scattering (DLS) measurement was carried out on a Malvern Zetasizer zs90 for 10^{-5} M solution of the Eu(III) nanoring **1** in CH_3CN; The morphology of the sample was analyzed by Nova NanoSEM 200 scanning electron microscope (SEM) and an attached energy-dispersive x-ray spectrometer (EDX). The sample was installed on an aluminum sheet coated with Au.

Photophysical Studies. Visible luminescence spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

2. Synthesis of the ligand H_4L^1 and clusters



Scheme S1. Synthetic approach to H_4L^1.

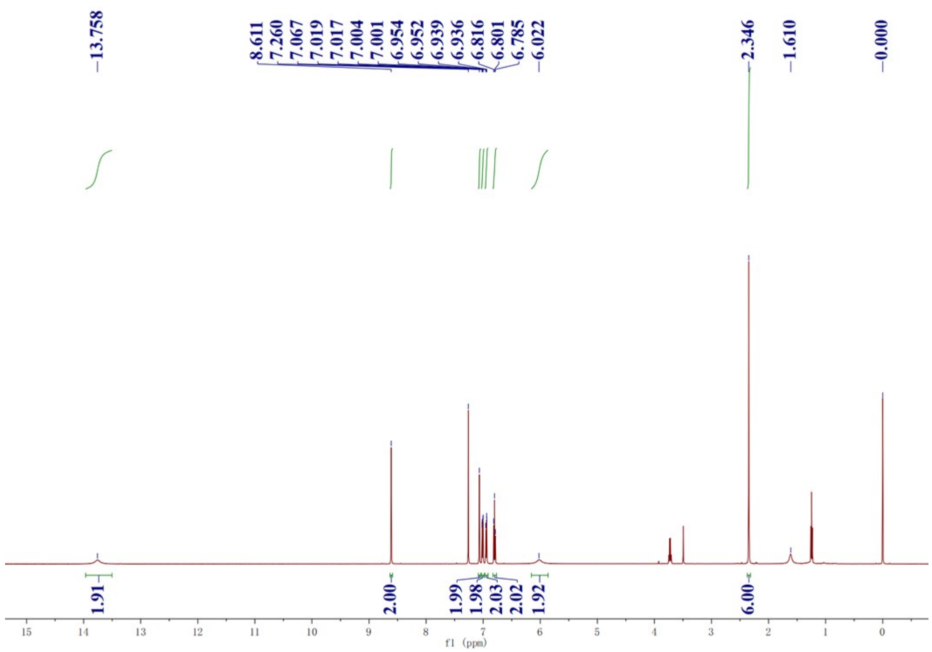
Synthesis of H_4L^1: 2,3-Dihydroxybenzaldehyde (20.0 mmol, 2.7624 g) was dissolved in 30 mL EtOH, and a solution of 4,5-dimethyl-1,2-phenylenediamine (10.0 mmol, 1.3619 g) in 40 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 8 h. It was allowed to cool and was then filtered in vacuum. The solid was washed with EtOH (3 × 5 mL) and then dried under vacuum to give red product. Yield (based on 4,5-Dimethyl-1,2-phenylenediamine): 3.27 g (87%).^{1}H NMR(δ_H, ppm, 500 MHz, $CDCl_3$-d_1): 13.758(s, 2H), 8.611(s, 2H), 7.067(s, 2H), 7.001-7.019(m, 2H) 6.936-6.954 (m, 2H), 6.801 (t, *J*=7.50 Hz, 2H), 2.346 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$-d_1, δ): 162.233, 150.172, 145.403, 138.919, 136.815, 112.935, 120.356, 118.879, 118.486, 117.728, 19.629. IR (KBr, cm^{-1}): 1614(s), 1539(w), 1461(s), 1420(w), 1353(s), 1281 (s), 1214(s), 1158(s), 1017(m), 876(m), 724(s).

Synthesis of $[Eu_{18}(L^1)_8(HL^2)_2(OAc)_{20}(MeOH)_8(EtOH)_6(H_2O)_4]$ (1): At room temperature, $Eu(OAc)_3·6H_2O$ (0.20 mmol, 0.070 g), H_4L^1 (0.20 mmol, 0.0756 g) and H_2L^2 (0.10 mmol, 0.0136 g) were dissolved in 9 mL EtOH, and then triethylamine in MeOH (1.0 mol/L, 1 ml) was added into the solution. The mixture was heated for 30 mins under reflux with stirring, and cooled to room temperature. The clear solution was obtained by filtered, and slow diffusion of diethyl ether into the solution for one week gave the red crystalline product of **1**. Yield (calculated from $Eu(OAc)_3·6H_2O$): 0.0269 g (30%). Elemental analysis: Found: C, 37.12; H, 4.03; N, 2.62 %. Calc. for $[Eu_{18}(L^1)_8(HL^2)_2(OAc)_{20}(MeOH)_8(EtOH)_6(H_2O)_4]·4(MeOH)·15(H_2O)$ ($C_{254}H_{318}N_{16}O_{115}Eu_{18}$): C, 37.34; H, 3.92; N, 2.74 %. IR (KBr, cm^{-1}): 1616 (s), 1539 (s), 1438 (s), 1375 (s), 1321 (m), 1253 (s), 1203 (s), 1180 (s), 1079 (m), 1028 (w), 997 (w), 753 (s), 775 (w), 725 (s). m. p. > 270°C (decompose).

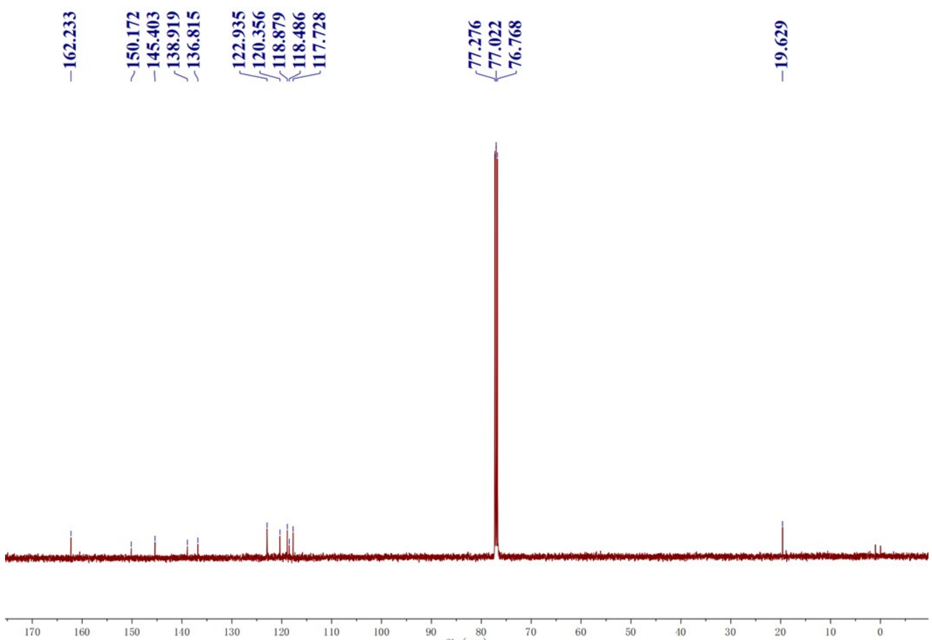
Synthesis of the Tb_{18} analogue: The procedure was the same as that for **1** using $Tb(OAc)_3{\cdot}4H_2O$ (0.20 mmol, 0.067 g), H_4L^1 (0.20 mmol, 0.0756 g) and H_2L^2 (0.10 mmol, 0.0136 g). The yellow crystalline product of the Tb(III) analogue was formed after one week. Yield (based on $Tb(OAc)_2{\cdot}4H_2O$): 0.0289 g (32%). m. p. > 270 ^oC (dec.). Elemental analysis: Found: C, 37.89; H, 3.88; N, 2.65 %. Calc. for $C_{252}H_{290}N_{16}O_{104}Tb_{18}$: C, 37.52; H, 3.62; N, 2.78 %. IR (KBr, cm^{-1}): 1611 (m), 1588 (m), 1540 (s), 1443 (s), 1384 (s), 1205(s), 1178 (s), 1099 (m), 994 (w), 873 (s), 789 (m), 725 (m).

Synthesis of the La_{18} analogue: The procedure was the same as that for **1** using $La(OAc)_3{\cdot}4H_2O$ (0.20 mmol, 0.063 g), H_4L^1 (0.20 mmol, 0.0756 g) and H_2L^2 (0.10 mmol, 0.0136 g). The yellow crystalline product of the La(III) analogue was formed after one week. (based on $La(OAc)_2{\cdot}4H_2O$): 0.0349 g (52%). m. p. > 268 ^oC (dec.). Elemental analysis: Found: C, 39.05; H, 3.93; N, 2.80 %. Calc. for $C_{252}H_{290}N_{16}O_{104}La_{18}$: C, 39.27; H, 3.79; N, 2.91 %. IR (KBr, cm^{-1}): 1613 (m), 1579 (m), 1536 (s), 1445 (s), 1380 (s), 1225(s), 1179 (s), 1090 (m), 992 (w), 870 (s), 772 (m), 723 (m).

3. ^{1}H NMR and ^{13}C NMR spectra of the ligand H_4L^1



(**a**)



(**b**)

Figure S1. (**a**) ^{1}H NMR of the ligand H_4L^1 in $CDCl_3$; (**b**) ^{13}C NMR of the ligand H_4L^1 in $CDCl_3$.

4. IR spectra of the ligand H_4L^1 and 1

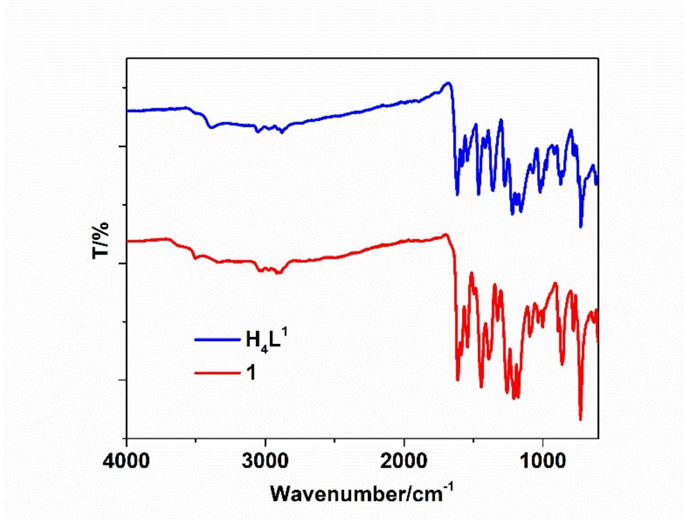


Figure S2. IR spectra of the ligand H_4L^1 and **1**.

5. The coordination modes of Eu(III) ions in 1

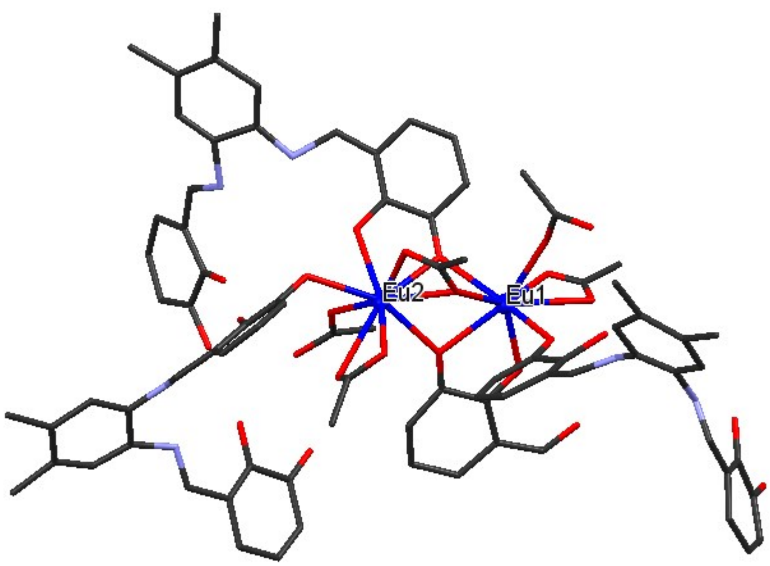


Figure S3. The eight-coordinated Eu(1) and nine-coordinated Eu(2) in the structure of **1**.

6. The thermogravimetric analysis of 1

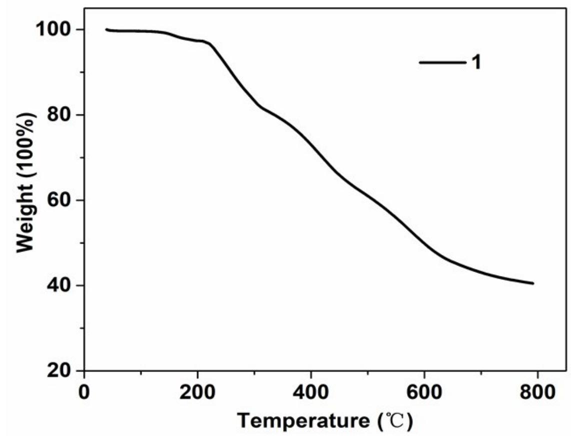


Figure S4. The thermogravimetric analysis of **1**.

7. ^{1}H NMR spectrum of the La_{18} analogue

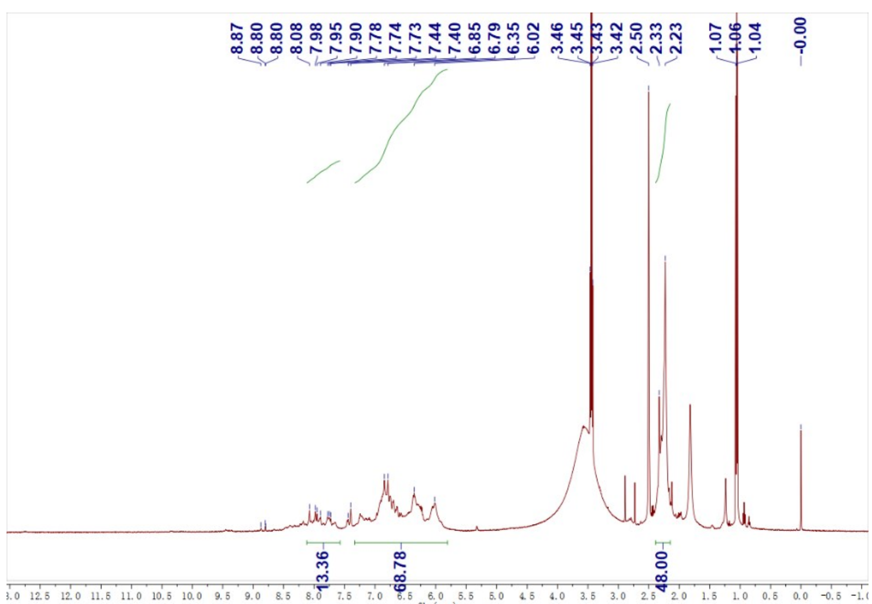


Figure S5. The ^{1}H NMR spectrum of the La_{18} analogue.

8. UV-vis absorption spectra of the ligand H_4L^1 and 1

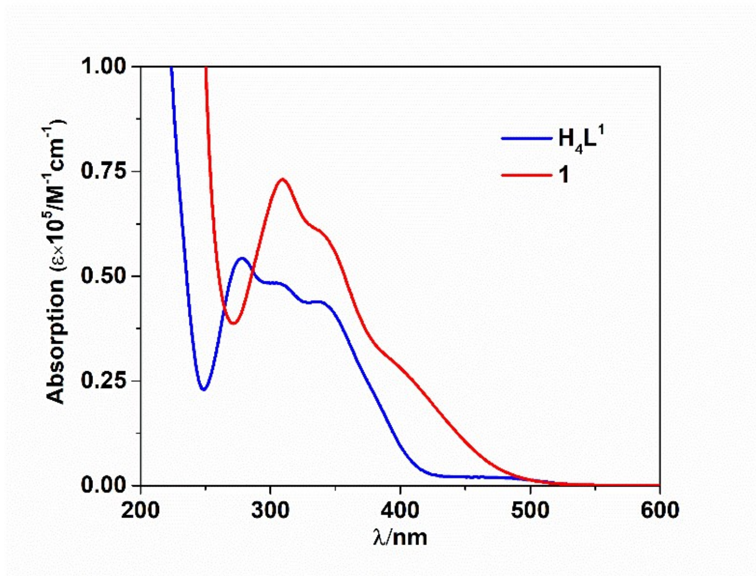
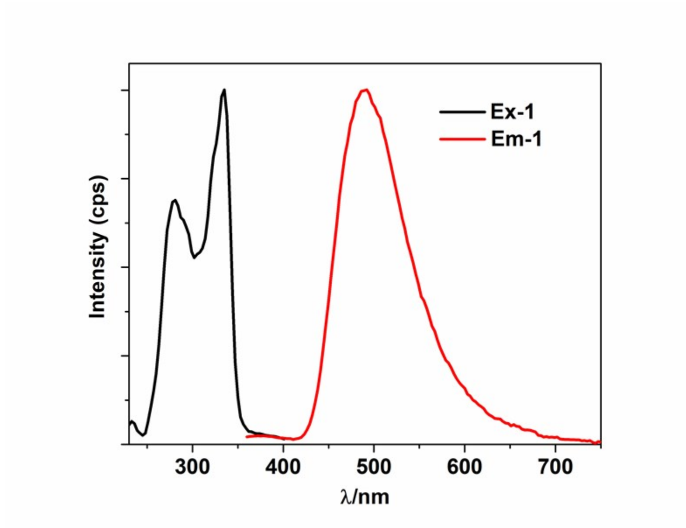
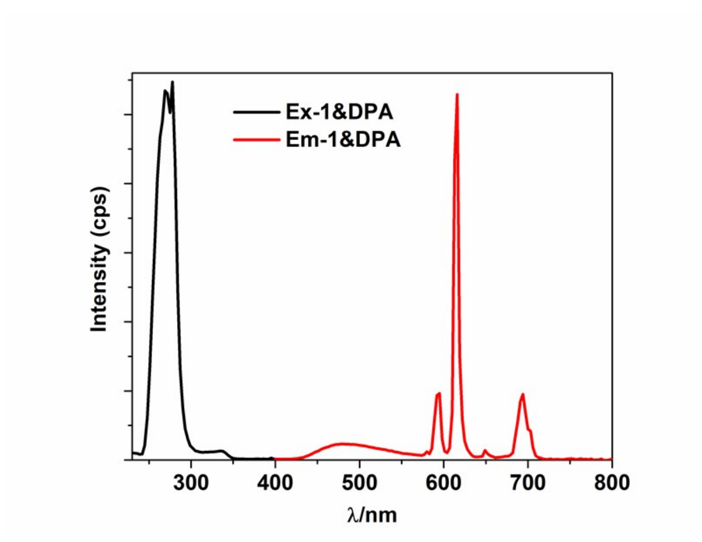


Figure S6. UV-vis absorption spectra of the ligand H_4L^1 and **1** in CH_3CN.

9. The excitation and emission spectra of 1



(a)



(b)

Figure S7. (a) The excitation and emission spectra of **1** (10 μM) without the addition of DPA in CH_3CN; (b) The excitation (λ_{em} = 616 nm) and emission (λ_{ex} = 272 nm) spectra of **1** (10 μM) with the addition of DPA (200 μM) in CH_3CN.

10. The fluorescent response of 1 to DPA and interferents

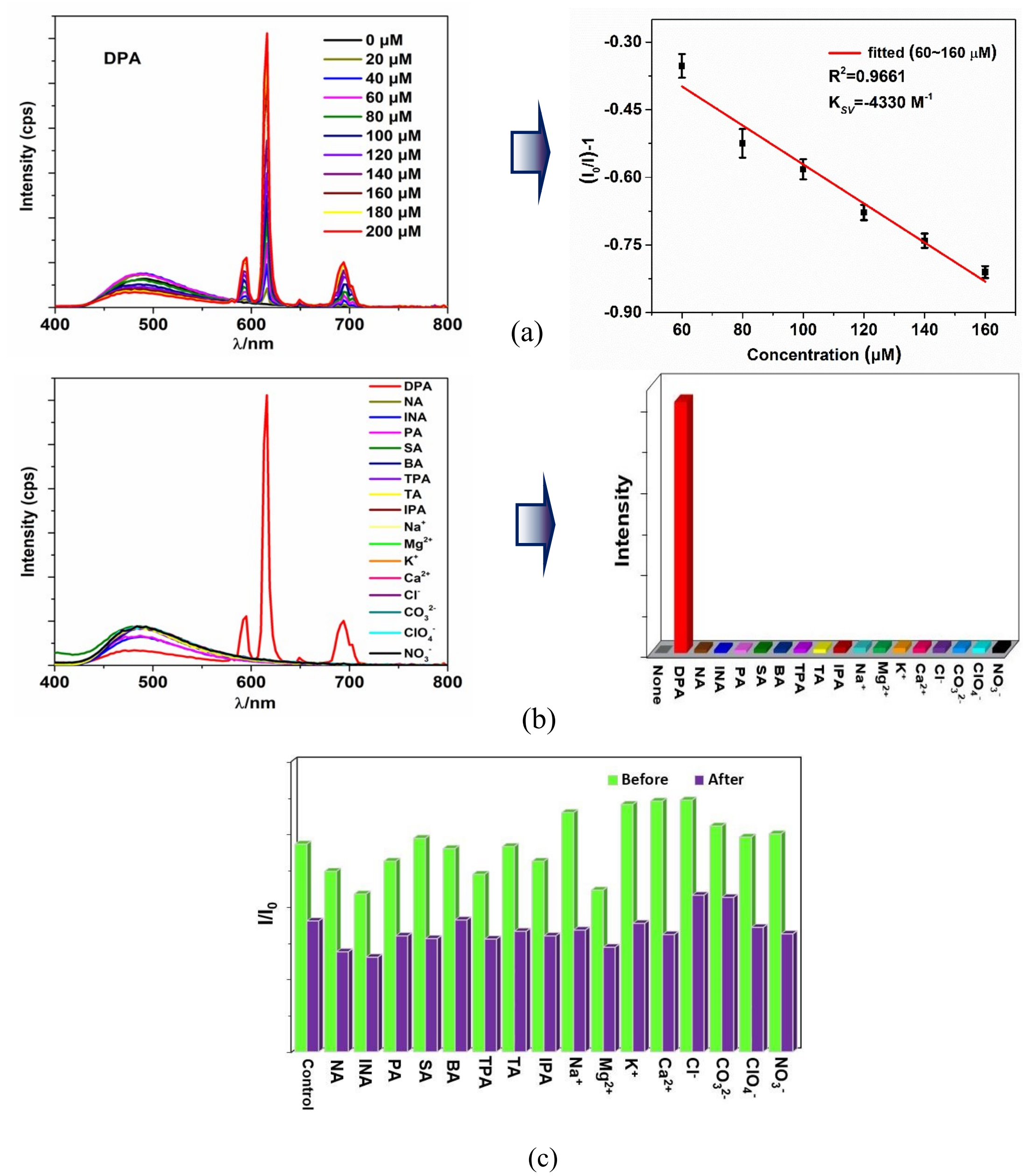
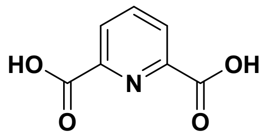
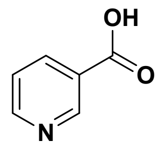
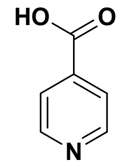


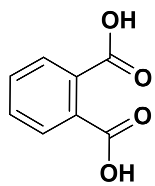
Figure S8. (a) The emission response and K_{sv} of **1** (10 μM) to the addition of DPA with different concentrations in CH_3CN (λ_{ex} = 272 nm). (b) The emission response of **1** (10 μM) to DPA and various carboxylic acids and ions (200 μM) in CH_3CN (λ_{ex} = 272 nm); (c) The ligand-centered emission (490 nm) quenching of **1** (10 μM) before and after the addition of DPA (200 μM) in the presence of other interferents (200 μM).

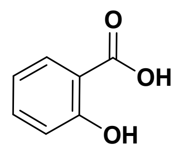
11. Chemical structures of DPA and carboxylic acids

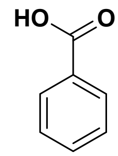

Dipicolinic acid **DPA**

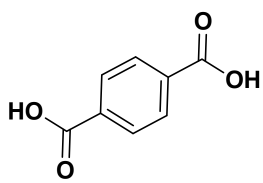

Nicotinic acid **NA**

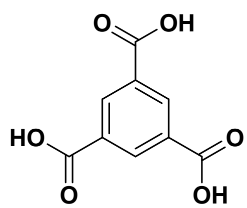

Isonicotinic acid **INA**

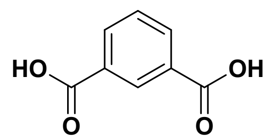

Phthalic acid **PA**


Salicylic acid **SA**


Benzoic acid **BA**


terephthalic acid **TPA**


Trimesic acid **TA**


Isophthalic acid **IPA**

Scheme S2. Chemical structures of various carboxylic acids.

12. The luminescent response of the Tb_{18} analogue to DPA and interferents

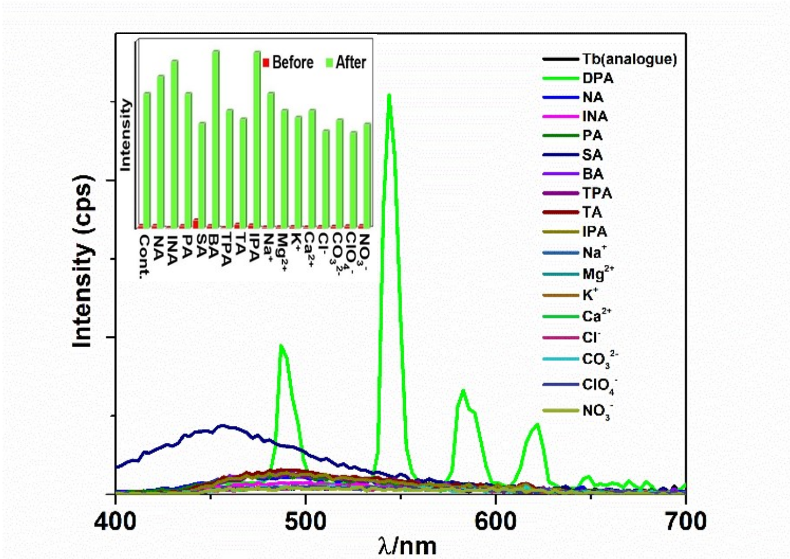


Figure S9. The emission response of the Tb_{18} analogue (10 μM) to DPA and various carboxylic acids and ions (30 μM) in CH_3CN (λ_{ex} = 272 nm); Insert: The luminescence intensities of the Tb_{18} analogue (10 μM) at 544 nm before and after the addition of DPA (30 μM) in the presence of other interferents (30 μM).

13. Powder XRD pattern of 1

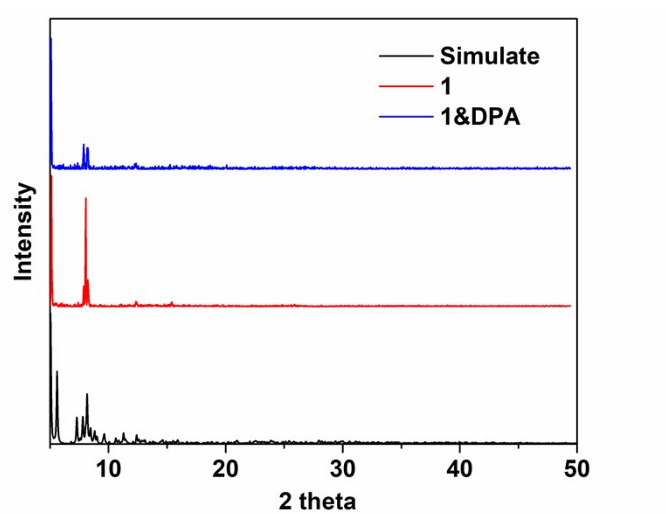


Figure S10. Powder XRD patterns of **1** before (red) and after (blue) the addition of DPA.

14. UV-vis titration of 1 to the addition of DPA

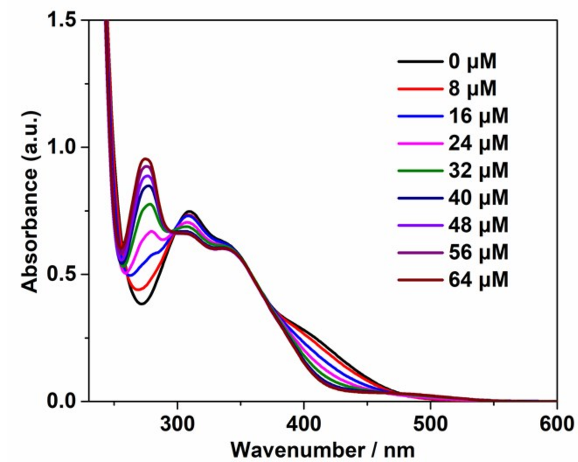


Figure S11. UV-vis titration of **1** (10 μM) with the addition of DPA in CH_3CN.

15. UV-vis absorption spectra of the PDA and carboxylic acids

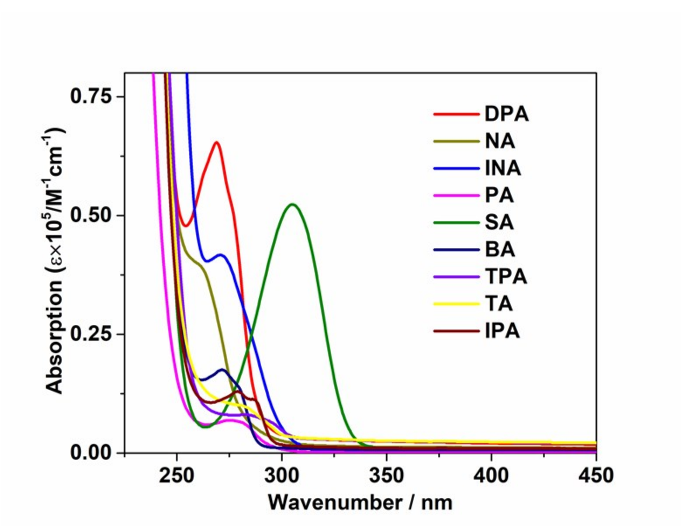


Figure S12. UV-vis absorption spectra of the carboxylic acids in CH_3CN (c = 10 μM).

16. The emission spectra of 1 with the addition of DPA

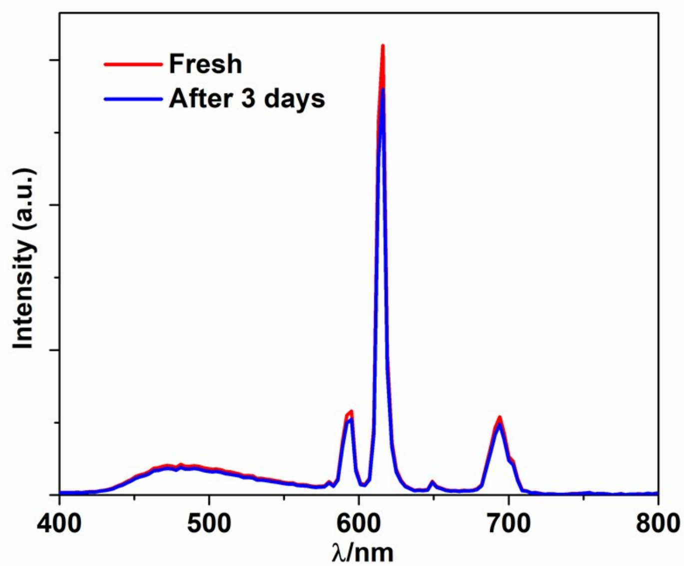


Figure S13. The emission spectra of **1** (10 μM) with the addition of DPA (200 μM).

17. X-Ray Crystallography

X-ray data of **1** were collected on a Smart APEX CCD diffractometer in the θ–2θ mode with monochromated Mo Kα radiation at 190 K. The structures were solved by direct method using SHELX 97 program.[1] An empirical absorption correction was applied using SADABS program. The non-hydrogen atoms in the structures were refined anisotropically. All hydrogen atoms were calculated by geometrical methods and refined isotropically. The data can be obtained from www.ccdc.cam.ac.uk/data_request/cif (CCDC numbers: 2043018). The structure refinements of **1** are listed in Table S1, and selected bond lengths and angles are shown in Table S2.

Ref. (1) G. H. Sheldrick, SHELX 97, *A software package for the solution and refinement of X-ray data*; University of Göttingen: Göttingen, Germany, **1997**.

Table S1. Crystal data and structure refinements for **1**.

	1
Formula	$C_{250}H_{264}N_{16}O_{107}Eu_{18}$
Fw	7940.05
Crystal system	Triclinic
Space group	P-1
a [Å]	21.689(2)
b [Å]	23.580(2)
c [Å]	24.848(3)
α [deg]	97.165(2)
β [deg]	110.855(2)
γ [deg]	115.142 (2)
V / [Å^3]	10162.0(18)
d / [g/cm^3]	1.297
Z	1
T [K]	190(1)
F(000)	3866
μ, mm^{-1}	2.795
θ rang, deg	0.93-25.00
reflns meads	39951
reflns used	35275
params	1765
R1^a, wR2^a [$I > 2\sigma(I)$]	0.0804, 0.1712
R1, wR2 (all data)	0.1441, 0.2159
Quality of fit	1.163

^{a} R1 = $\Sigma|F_o| - |F_c|\Sigma|F_o|$. wR2 = $[\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. w=1/[$\sigma^2(F_o^2)$+(0.075P)^2], where P = [max(F_o^2,0)+2F_c^2]/3.

Table S2. Selected Bond Lengths (Å) and angles (◦) for **1**.

Eu(1)-O(30)	2.330(11)	Eu(6)-O(40)	2.712(12)
Eu(1)-O(1)	2.337(11)	Eu(7)-O(10)	2.357(10)
Eu(1)-O(13)	2.338(11)	Eu(7)-O(11)	2.402(12)
Eu(1)-O(22)	2.385(11)	Eu(7)-O(15)	2.499(9)
Eu(1)-O(25)	2.400(9)	Eu(7)-O(16)	2.496(10)
Eu(1)-O(24)	2.428(8)	Eu(7)-O(44)	2.551(4)
Eu(1)-O(31)	2.505(10)	Eu(7)-O(45)	2.610(12)
Eu(1)-O(23)	2.686(11)	Eu(7)-O(48)	2.623(11)
Eu(2)-O(26)	2.399(11)	Eu(7)-N(6)	2.690(13)
Eu(2)-O(31)	2.413(11)	Eu(7)-N(5)	2.688(13)
Eu(2)-O(32)	2.432(11)	Eu(8)-O(15)#1	2.335(12)
Eu(2)-O(5)	2.440(11)	Eu(8)-O(17)	2.426(10)
Eu(2)-O(1)	2.446(8)	Eu(8)-O(14)	2.471(12)
Eu(2)-O(2)	2.457(9)	Eu(8)-O(18)	2.468(11)
Eu(2)-O(27)	2.563(9)	Eu(8)-O(11)#1	2.526(10)
Eu(2)-O(28)	2.579(10)	Eu(8)-O(47)	2.567(9)
Eu(2)-O(25)	2.600(12)	Eu(8)-N(8)	2.634(7)
Eu(3)-O(3)	2.325(11)	Eu(8)-N(7)	2.708(12)
Eu(3)-O(5)	2.375(10)	Eu(8)-O(12)	2.717(9)
Eu(3)-O(46)	2.382(8)	Eu(9)-O(17)	2.295(12)
Eu(3)-O(2)	2.404(11)	Eu(9)-O(14)	2.400(7)
Eu(3)-O(34)	2.555(7)	Eu(9)-O(21)	2.455(12)
Eu(3)-O(6)	2.578(9)	Eu(9)-O(23)	2.482(10)
Eu(3)-N(2)	2.578(12)	Eu(9)-O(20)	2.501(7)
Eu(3)-O(32)	2.649(11)	Eu(9)-O(13)	2.512(10)
Eu(3)-N(1)	2.727(11)	Eu(9)-O(19)	2.559(10)
Eu(4)-O(7)	2.295(11)	Eu(9)-O(47)	2.632(11)
Eu(4)-O(6)	2.339(11)	Eu(9)-O(22)	2.816(12)
Eu(4)-O(4)	2.344(9)	O(30)-Eu(1)-O(1)	119.7(4)
Eu(4)-O(35)	2.445(12)	O(30)-Eu(1)-O(13)	84.0(4)
Eu(4)-O(36)	2.477(12)	O(1)-Eu(1)-O(13)	146.6(3)
Eu(4)-O(3)	2.557(10)	O(30)-Eu(1)-O(22)	139.9(4)
Eu(4)-O(33)	2.651(10)	O(1)-Eu(1)-O(22)	93.2(4)
Eu(4)-N(3)	2.688(12)	O(13)-Eu(1)-O(22)	78.3(4)
Eu(4)-N(4)	2.747(11)	O(30)-Eu(1)-O(25)	132.1(3)
Eu(5)-O(8)	2.392(11)	O(1)-Eu(1)-O(25)	66.5(3)
Eu(5)-O(9)	2.419(12)	O(13)-Eu(1)-O(25)	80.2(4)
Eu(5)-O(33)	2.422(10)	O(22)-Eu(1)-O(25)	79.8(3)
Eu(5)-O(4)	2.425(11)	O(30)-Eu(1)-O(24)	78.8(3)
Eu(5)-O(7)	2.492(8)	O(1)-Eu(1)-O(24)	87.8(3)
Eu(5)-O(39)	2.550(10)	O(13)-Eu(1)-O(24)	121.7(4)
Eu(5)-O(40)	2.562(10)	O(22)-Eu(1)-O(24)	80.6(3)
Eu(5)-O(37)	2.615(11)	O(25)-Eu(1)-O(24)	146.5(4)
Eu(5)-O(38)	2.678(9)	O(30)-Eu(1)-O(31)	67.5(4)
Eu(6)-O(16)	2.327(12)	O(1)-Eu(1)-O(31)	68.7(3)
Eu(6)-O(38)	2.363(13)	O(13)-Eu(1)-O(31)	104.7(3)
Eu(6)-O(43)	2.402(11)	O(22)-Eu(1)-O(31)	151.9(3)
Eu(6)-O(9)	2.454(8)	O(25)-Eu(1)-O(31)	73.4(3)
Eu(6)-O(10)	2.478(10)	O(24)-Eu(1)-O(31)	118.3(3)
Eu(6)-O(42)	2.521(10)	O(30)-Eu(1)-O(23)	73.9(3)
Eu(6)-O(45)	2.564(11)	O(1)-Eu(1)-O(23)	136.8(3)
Eu(6)-O(41)	2.580(9)	O(13)-Eu(1)-O(23)	69.0(3)

O(22)-Eu(1)-O(23)	66.2(4)
O(25)-Eu(1)-O(23)	137.6(3)
O(24)-Eu(1)-O(23)	52.8(4)
O(31)-Eu(1)-O(23)	141.4(3)
O(26)-Eu(2)-O(31)	122.7(4)
O(26)-Eu(2)-O(32)	146.2(4)
O(31)-Eu(2)-O(32)	89.8(4)
O(26)-Eu(2)-O(5)	78.4(4)
O(31)-Eu(2)-O(5)	155.4(3)
O(32)-Eu(2)-O(5)	72.7(3)
O(26)-Eu(2)-O(1)	87.5(3)
O(31)-Eu(2)-O(1)	68.5(3)
O(32)-Eu(2)-O(1)	97.5(3)
O(5)-Eu(2)-O(1)	129.7(3)
O(26)-Eu(2)-O(2)	84.8(3)
O(31)-Eu(2)-O(2)	126.6(3)
O(32)-Eu(2)-O(2)	66.6(3)
O(5)-Eu(2)-O(2)	62.5(3)
O(1)-Eu(2)-O(2)	68.3(3)
O(26)-Eu(2)-O(27)	76.2(3)
O(31)-Eu(2)-O(27)	83.7(3)
O(32)-Eu(2)-O(27)	120.3(3)
O(5)-Eu(2)-O(27)	90.2(3)
O(1)-Eu(2)-O(27)	133.0(4)
O(2)-Eu(2)-O(27)	149.6(3)
O(26)-Eu(2)-O(28)	122.2(3)
O(31)-Eu(2)-O(28)	78.5(3)
O(32)-Eu(2)-O(28)	69.1(3)
O(5)-Eu(2)-O(28)	79.1(3)
O(1)-Eu(2)-O(28)	144.6(3)
O(2)-Eu(2)-O(28)	127.7(4)
O(27)-Eu(2)-O(28)	51.4(3)
O(26)-Eu(2)-O(25)	51.5(4)
O(31)-Eu(2)-O(25)	71.5(4)
O(32)-Eu(2)-O(25)	155.8(3)
O(5)-Eu(2)-O(25)	129.5(3)
O(1)-Eu(2)-O(25)	61.9(3)
O(2)-Eu(2)-O(25)	112.2(3)
O(27)-Eu(2)-O(25)	73.9(3)
O(28)-Eu(2)-O(25)	119.6(3)
O(3)-Eu(3)-O(5)	127.2(3)
O(3)-Eu(3)-O(46)	98.3(3)
O(5)-Eu(3)-O(46)	76.2(3)
O(3)-Eu(3)-O(2)	145.1(3)
O(5)-Eu(3)-O(2)	64.3(3)
O(46)-Eu(3)-O(2)	116.6(3)
O(3)-Eu(3)-O(34)	72.5(3)
O(5)-Eu(3)-O(34)	136.9(3)
O(46)-Eu(3)-O(34)	144.6(3)
O(2)-Eu(3)-O(34)	79.5(3)
O(3)-Eu(3)-O(6)	62.8(3)
O(5)-Eu(3)-O(6)	65.1(3)
O(46)-Eu(3)-O(6)	75.5(3)
O(2)-Eu(3)-O(6)	122.0(3)
O(34)-Eu(3)-O(6)	124.5(3)
O(3)-Eu(3)-N(2)	69.6(4)
O(5)-Eu(3)-N(2)	143.1(3)
O(46)-Eu(3)-N(2)	68.3(3)
O(2)-Eu(3)-N(2)	123.7(3)
O(34)-Eu(3)-N(2)	76.6(3)
O(6)-Eu(3)-N(2)	113.6(3)
O(3)-Eu(3)-O(32)	88.0(4)
O(5)-Eu(3)-O(32)	69.9(3)
O(46)-Eu(3)-O(32)	141.4(3)
O(2)-Eu(3)-O(32)	63.9(3)
O(34)-Eu(3)-O(32)	73.6(3)
O(6)-Eu(3)-O(32)	73.7(3)
N(2)-Eu(3)-O(32)	147.0(3)
O(3)-Eu(3)-N(1)	128.0(4)
O(5)-Eu(3)-N(1)	102.6(3)
O(46)-Eu(3)-N(1)	77.7(3)
O(2)-Eu(3)-N(1)	66.0(4)
O(34)-Eu(3)-N(1)	81.7(3)
O(6)-Eu(3)-N(1)	152.5(3)
N(2)-Eu(3)-N(1)	60.6(4)
O(32)-Eu(3)-N(1)	127.1(3)
O(7)-Eu(4)-O(6)	146.4(4)
O(7)-Eu(4)-O(4)	66.4(4)
O(6)-Eu(4)-O(4)	128.1(3)
O(7)-Eu(4)-O(35)	78.0(4)
O(6)-Eu(4)-O(35)	74.5(4)
O(4)-Eu(4)-O(35)	139.2(4)
O(7)-Eu(4)-O(36)	116.9(4)
O(6)-Eu(4)-O(36)	96.7(4)
O(4)-Eu(4)-O(36)	74.1(3)
O(35)-Eu(4)-O(36)	143.4(3)
O(7)-Eu(4)-O(3)	123.8(3)
O(6)-Eu(4)-O(3)	62.9(3)
O(4)-Eu(4)-O(3)	65.4(3)
O(35)-Eu(4)-O(3)	127.0(4)
O(36)-Eu(4)-O(3)	74.6(3)
O(7)-Eu(4)-O(33)	60.1(3)
O(6)-Eu(4)-O(33)	95.4(3)
O(4)-Eu(4)-O(33)	66.9(4)
O(35)-Eu(4)-O(33)	78.6(3)
O(36)-Eu(4)-O(33)	138.0(3)
O(3)-Eu(4)-O(33)	75.6(3)
O(7)-Eu(4)-N(3)	125.3(4)
O(6)-Eu(4)-N(3)	65.2(4)
O(4)-Eu(4)-N(3)	142.0(5)
O(35)-Eu(4)-N(3)	75.5(4)
O(36)-Eu(4)-N(3)	68.7(4)
O(3)-Eu(4)-N(3)	110.3(4)
O(33)-Eu(4)-N(3)	151.0(4)
O(7)-Eu(4)-N(4)	65.1(3)
O(6)-Eu(4)-N(4)	125.2(3)
O(4)-Eu(4)-N(4)	103.7(4)
O(35)-Eu(4)-N(4)	77.1(4)

O(36)-Eu(4)-N(4)	79.9(4)
O(3)-Eu(4)-N(4)	154.1(4)
O(33)-Eu(4)-N(4)	123.3(3)
N(3)-Eu(4)-N(4)	62.8(4)
O(8)-Eu(5)-O(9)	93.5(4)
O(8)-Eu(5)-O(33)	88.3(4)
O(9)-Eu(5)-O(33)	150.2(3)
O(8)-Eu(5)-O(4)	128.9(3)
O(9)-Eu(5)-O(4)	86.6(4)
O(33)-Eu(5)-O(4)	69.5(4)
O(8)-Eu(5)-O(7)	66.7(3)
O(9)-Eu(5)-O(7)	92.5(3)
O(33)-Eu(5)-O(7)	61.0(3)
O(4)-Eu(5)-O(7)	62.2(3)
O(8)-Eu(5)-O(39)	145.0(4)
O(9)-Eu(5)-O(39)	116.4(4)
O(33)-Eu(5)-O(39)	74.9(3)
O(4)-Eu(5)-O(39)	73.8(3)
O(7)-Eu(5)-O(39)	125.4(3)
O(8)-Eu(5)-O(40)	139.4(3)
O(9)-Eu(5)-O(40)	70.2(3)
O(33)-Eu(5)-O(40)	124.4(3)
O(4)-Eu(5)-O(40)	88.3(3)
O(7)-Eu(5)-O(40)	147.1(4)
O(39)-Eu(5)-O(40)	49.8(3)
O(8)-Eu(5)-O(37)	75.4(3)
O(9)-Eu(5)-O(37)	118.0(3)
O(33)-Eu(5)-O(37)	91.3(3)
O(4)-Eu(5)-O(37)	146.4(3)
O(7)-Eu(5)-O(37)	132.6(4)
O(39)-Eu(5)-O(37)	74.6(3)
O(40)-Eu(5)-O(37)	80.1(3)
O(8)-Eu(5)-O(38)	79.3(3)
O(9)-Eu(5)-O(38)	67.7(3)
O(33)-Eu(5)-O(38)	141.4(4)
O(4)-Eu(5)-O(38)	144.1(4)
O(7)-Eu(5)-O(38)	139.6(3)
O(39)-Eu(5)-O(38)	94.9(3)
O(40)-Eu(5)-O(38)	60.2(4)
O(37)-Eu(5)-O(38)	50.3(4)
O(16)-Eu(6)-O(38)	143.8(4)
O(16)-Eu(6)-O(43)	78.7(4)
O(38)-Eu(6)-O(43)	134.9(4)
O(16)-Eu(6)-O(9)	130.7(4)
O(38)-Eu(6)-O(9)	72.4(3)
O(43)-Eu(6)-O(9)	89.1(3)
O(16)-Eu(6)-O(10)	64.7(3)
O(38)-Eu(6)-O(10)	124.7(3)
O(43)-Eu(6)-O(10)	79.9(4)
O(9)-Eu(6)-O(10)	66.2(3)
O(16)-Eu(6)-O(42)	75.6(4)
O(38)-Eu(6)-O(42)	75.0(4)
O(43)-Eu(6)-O(42)	119.1(3)
O(9)-Eu(6)-O(42)	146.8(4)
O(10)-Eu(6)-O(42)	131.6(4)
O(16)-Eu(6)-O(45)	68.6(4)
O(38)-Eu(6)-O(45)	83.1(4)
O(43)-Eu(6)-O(45)	140.6(4)
O(9)-Eu(6)-O(45)	95.8(3)
O(10)-Eu(6)-O(45)	66.8(4)
O(42)-Eu(6)-O(45)	73.8(3)
O(16)-Eu(6)-O(41)	86.3(4)
O(38)-Eu(6)-O(41)	91.7(4)
O(43)-Eu(6)-O(41)	72.8(4)
O(9)-Eu(6)-O(41)	135.3(4)
O(10)-Eu(6)-O(41)	143.5(4)
O(42)-Eu(6)-O(41)	51.5(4)
O(45)-Eu(6)-O(41)	124.2(3)
O(16)-Eu(6)-O(40)	146.4(4)
O(38)-Eu(6)-O(40)	62.0(4)
O(43)-Eu(6)-O(40)	73.0(4)
O(9)-Eu(6)-O(40)	67.2(3)
O(10)-Eu(6)-O(40)	125.7(3)
O(42)-Eu(6)-O(40)	102.7(3)
O(45)-Eu(6)-O(40)	144.1(4)
O(41)-Eu(6)-O(40)	68.4(3)
O(10)-Eu(7)-O(11)	147.5(4)
O(10)-Eu(7)-O(15)	127.7(3)
O(11)-Eu(7)-O(15)	63.2(3)
O(10)-Eu(7)-O(16)	64.0(3)
O(11)-Eu(7)-O(16)	128.4(3)
O(15)-Eu(7)-O(16)	67.2(3)
O(10)-Eu(7)-O(44)	79.1(3)
O(11)-Eu(7)-O(44)	71.8(3)
O(15)-Eu(7)-O(44)	124.2(3)
O(16)-Eu(7)-O(44)	131.5(3)
O(10)-Eu(7)-O(45)	67.8(4)
O(11)-Eu(7)-O(45)	89.4(4)
O(15)-Eu(7)-O(45)	76.0(3)
O(16)-Eu(7)-O(45)	65.5(4)
O(44)-Eu(7)-O(45)	72.3(2)
O(10)-Eu(7)-O(48)	110.8(4)
O(11)-Eu(7)-O(48)	101.7(4)
O(15)-Eu(7)-O(48)	74.7(4)
O(16)-Eu(7)-O(48)	77.4(4)
O(44)-Eu(7)-O(48)	148.4(3)
O(45)-Eu(7)-O(48)	139.3(3)
O(10)-Eu(7)-N(6)	122.9(4)
O(11)-Eu(7)-N(6)	65.7(4)
O(15)-Eu(7)-N(6)	108.2(4)
O(16)-Eu(7)-N(6)	147.1(4)
O(44)-Eu(7)-N(6)	79.3(3)
O(45)-Eu(7)-N(6)	147.1(4)
O(48)-Eu(7)-N(6)	70.2(4)
O(10)-Eu(7)-N(5)	66.3(4)
O(11)-Eu(7)-N(5)	124.9(4)
O(15)-Eu(7)-N(5)	145.6(4)
O(16)-Eu(7)-N(5)	103.9(4)

O(44)-Eu(7)-N(5)	87.3(3)	N(8)-Eu(8)-O(12)	75.7(3)
O(45)-Eu(7)-N(5)	132.4(3)	N(7)-Eu(8)-O(12)	81.1(4)
O(48)-Eu(7)-N(5)	71.0(3)	O(17)-Eu(9)-O(14)	64.7(3)
N(6)-Eu(7)-N(5)	60.5(4)	O(17)-Eu(9)-O(21)	82.8(4)
O(15)#1-Eu(8)-O(17)	129.5(3)	O(14)-Eu(9)-O(21)	84.5(3)
O(15)#1-Eu(8)-O(14)	148.4(4)	O(17)-Eu(9)-O(23)	153.9(3)
O(17)-Eu(8)-O(14)	61.7(3)	O(14)-Eu(9)-O(23)	135.1(3)
O(15)#1-Eu(8)-O(18)	103.7(4)	O(21)-Eu(9)-O(23)	112.4(4)
O(17)-Eu(8)-O(18)	72.5(4)	O(17)-Eu(9)-O(20)	87.4(3)
O(14)-Eu(8)-O(18)	107.8(4)	O(14)-Eu(9)-O(20)	146.6(3)
O(15)#1-Eu(8)-O(11)#1	63.6(3)	O(21)-Eu(9)-O(20)	73.6(3)
O(17)-Eu(8)-O(11)#1	66.9(4)	O(23)-Eu(9)-O(20)	77.5(3)
O(14)-Eu(8)-O(11)#1	123.9(3)	O(17)-Eu(9)-O(13)	131.5(3)
O(18)-Eu(8)-O(11)#1	75.5(3)	O(14)-Eu(9)-O(13)	67.0(3)
O(15)#1-Eu(8)-O(47)	87.8(4)	O(21)-Eu(9)-O(13)	96.7(4)
O(17)-Eu(8)-O(47)	70.0(3)	O(23)-Eu(9)-O(13)	69.9(3)
O(14)-Eu(8)-O(47)	67.8(3)	O(20)-Eu(9)-O(13)	139.3(3)
O(18)-Eu(8)-O(47)	138.9(3)	O(17)-Eu(9)-O(19)	76.8(3)
O(11)#1-Eu(8)-O(47)	74.9(3)	O(14)-Eu(9)-O(19)	129.0(4)
O(15)#1-Eu(8)-N(8)	122.5(3)	O(21)-Eu(9)-O(19)	123.4(3)
O(17)-Eu(8)-N(8)	106.2(3)	O(23)-Eu(9)-O(19)	77.1(3)
O(14)-Eu(8)-N(8)	66.5(2)	O(20)-Eu(9)-O(19)	53.5(3)
O(18)-Eu(8)-N(8)	77.6(3)	O(13)-Eu(9)-O(19)	135.6(3)
O(11)#1-Eu(8)-N(8)	153.0(3)	O(17)-Eu(9)-O(47)	70.7(4)
O(47)-Eu(8)-N(8)	128.9(3)	O(14)-Eu(9)-O(47)	67.8(3)
O(15)#1-Eu(8)-N(7)	68.7(4)	O(21)-Eu(9)-O(47)	147.7(3)
O(17)-Eu(8)-N(7)	141.4(4)	O(23)-Eu(9)-O(47)	99.2(3)
O(14)-Eu(8)-N(7)	123.7(4)	O(20)-Eu(9)-O(47)	121.7(3)
O(18)-Eu(8)-N(7)	69.7(4)	O(13)-Eu(9)-O(47)	87.7(3)
O(11)#1-Eu(8)-N(7)	110.1(4)	O(19)-Eu(9)-O(47)	68.9(3)
O(47)-Eu(8)-N(7)	148.5(4)	O(17)-Eu(9)-O(22)	133.9(4)
N(8)-Eu(8)-N(7)	57.9(3)	O(14)-Eu(9)-O(22)	109.5(3)
O(15)#1-Eu(8)-O(12)	76.5(4)	O(21)-Eu(9)-O(22)	51.4(3)
O(17)-Eu(8)-O(12)	132.4(4)	O(23)-Eu(9)-O(22)	63.0(3)
O(14)-Eu(8)-O(12)	77.3(3)	O(20)-Eu(9)-O(22)	76.1(3)
O(18)-Eu(8)-O(12)	147.9(3)	O(13)-Eu(9)-O(22)	67.8(3)
O(11)#1-Eu(8)-O(12)	129.0(3)	O(19)-Eu(9)-O(22)	121.2(3)
O(47)-Eu(8)-O(12)	72.9(3)	O(47)-Eu(9)-O(22)	153.1(3)