Electronic supplementary information (ESI)

Three resorcin[4]arene-based lanthanide-coordination polymers for multifunctional photoluminescence sensing properties

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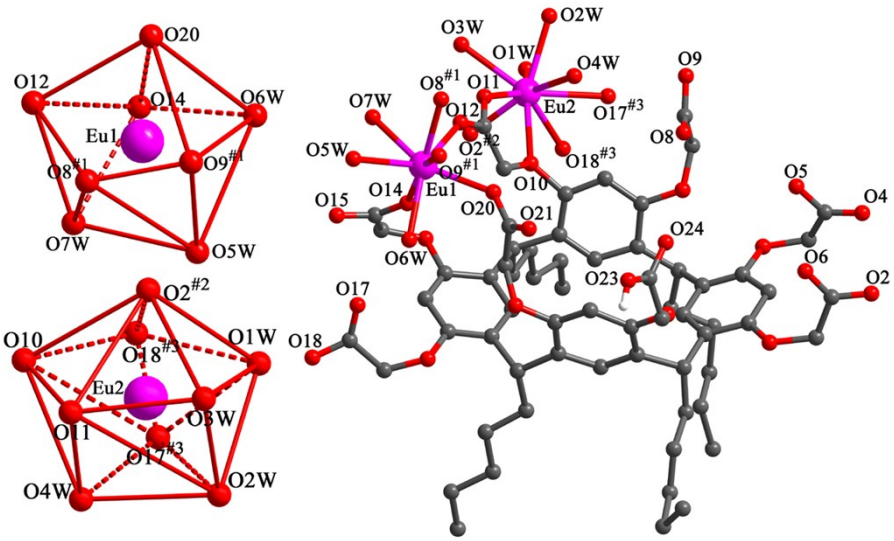
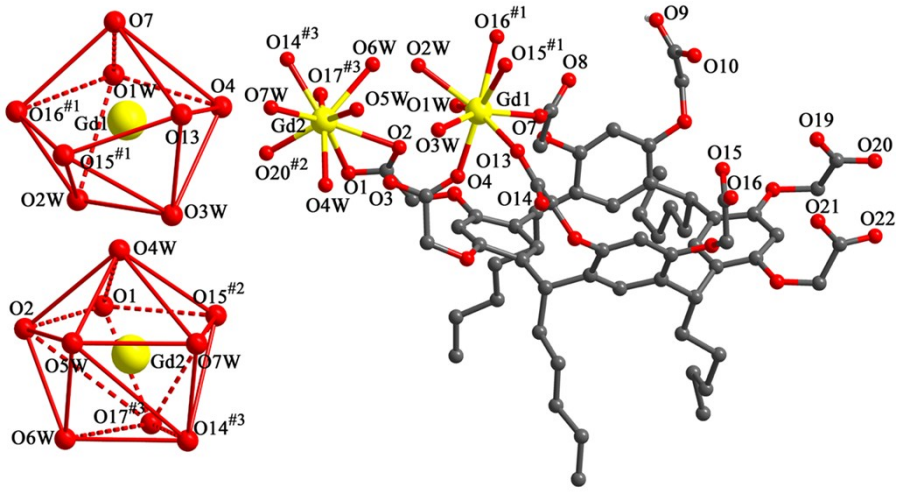


(a)



(b)

Fig. S1. Coordination environments of Ln^{3+} cations in **2** (a) and **3** (b).

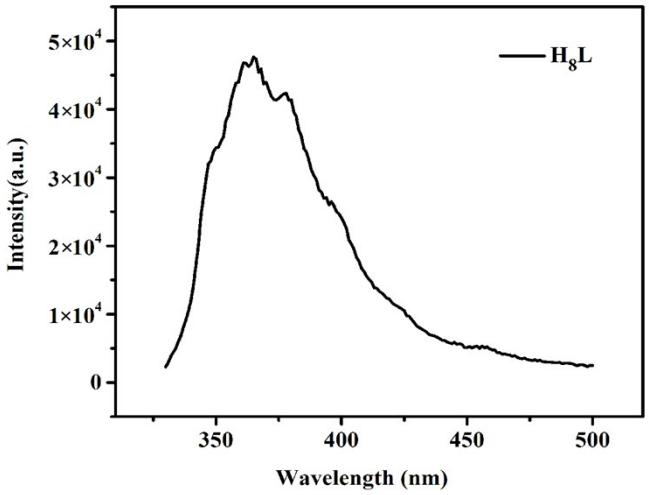


Fig. S2. Solid state emission spectra of H_8L

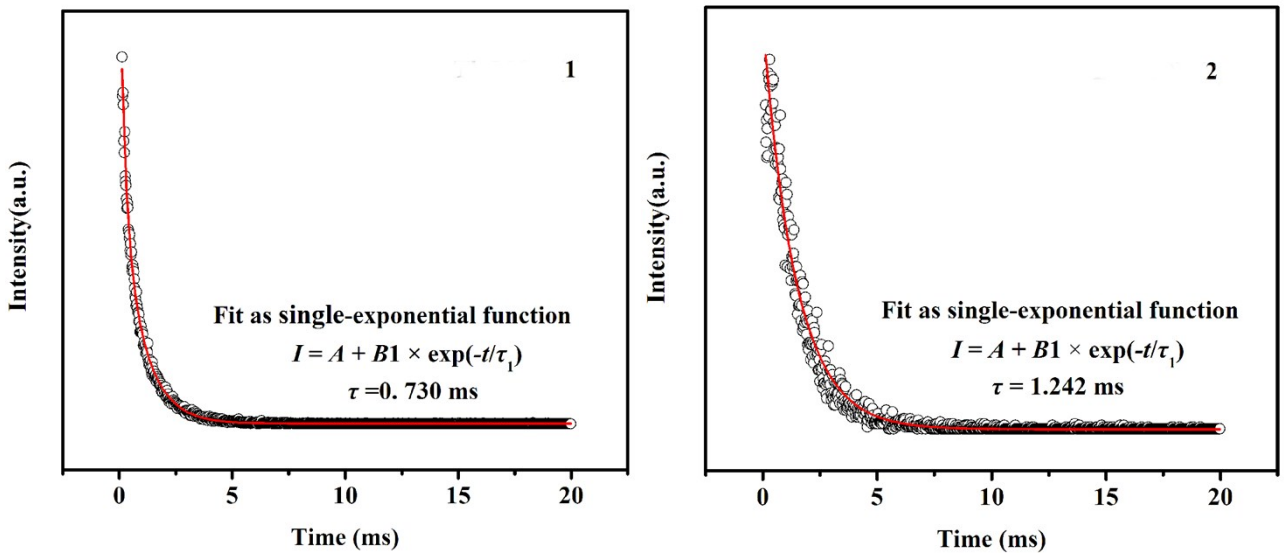
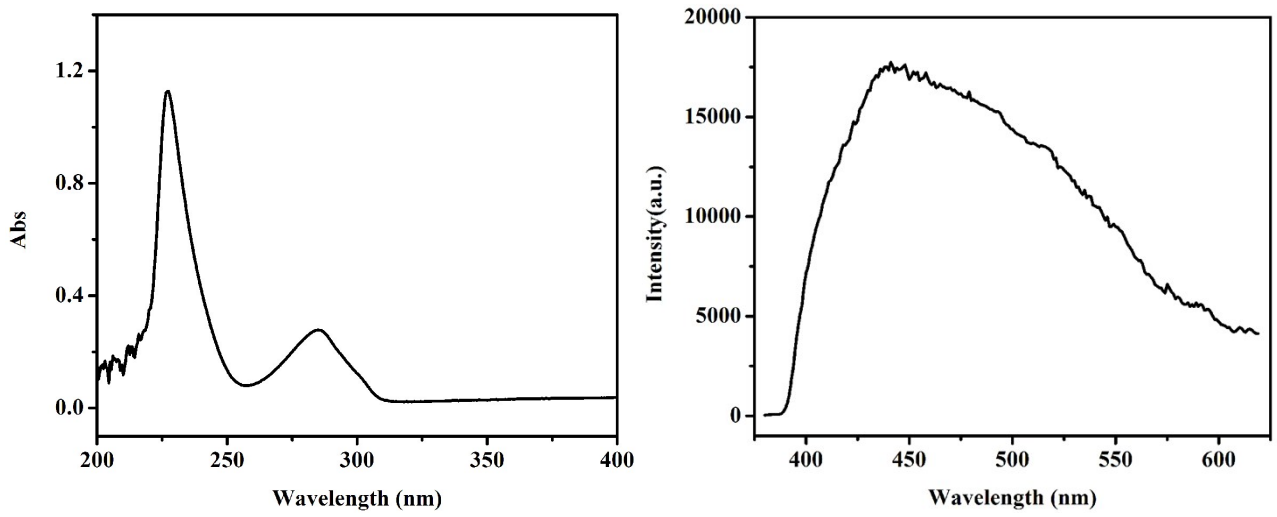


Fig. S3. Decay curves of **1** and **2** recorded at 543 nm for Tb^{3+} and 614 nm for Eu^{3+}.



(a) (b)

Fig. S4. (a) UV-vis absorption spectrum of **3** in methanol solution. (b) Solid state phosphorescent spectrum of **3** at 77 K.

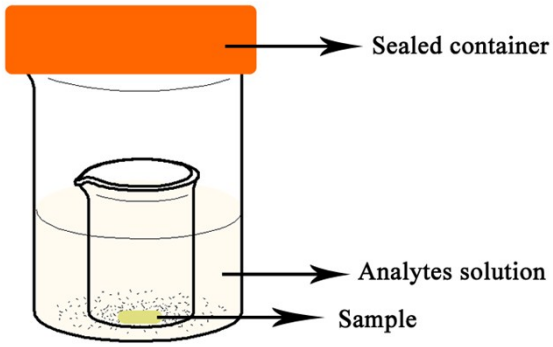
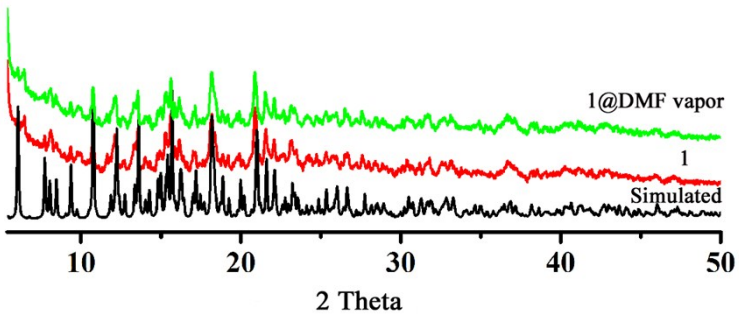
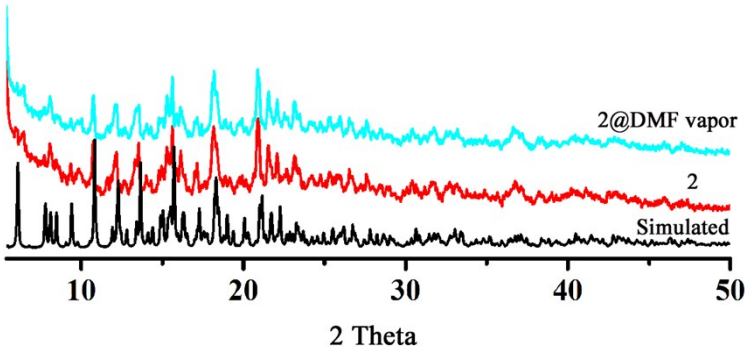


Fig. S5. Diagram showing the gas sensing equipment for DMF vapor.



(a)



(b)

Fig. S6. PXRD patterns of **1** (a) and **2** (b) treated in DMF vapor.

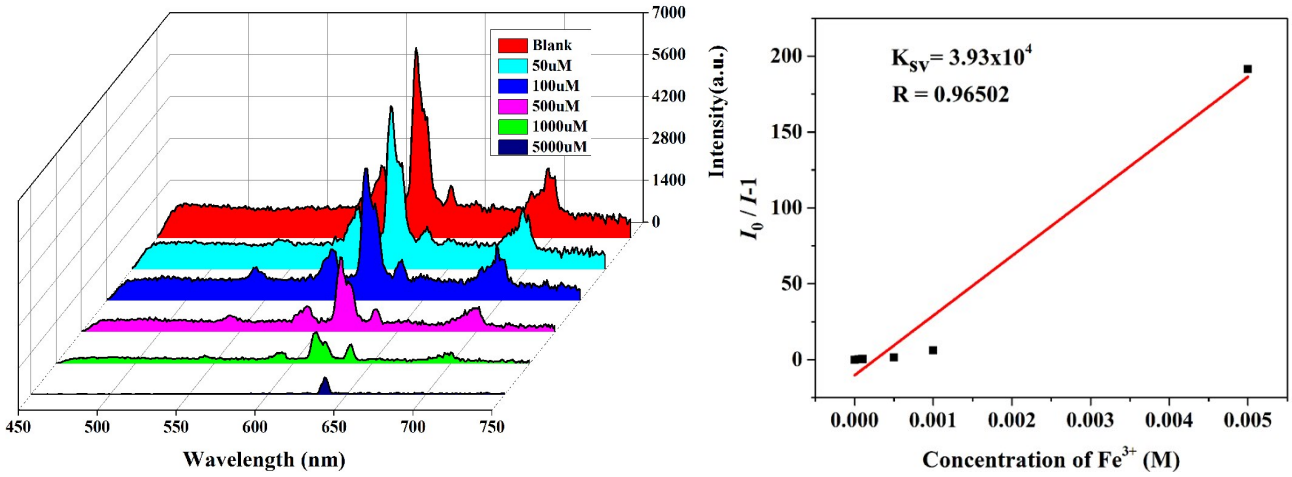


Fig. S7. Emission spectra and linear relationship for **2** in aqueous solution of different concentrations of Fe^{3+}

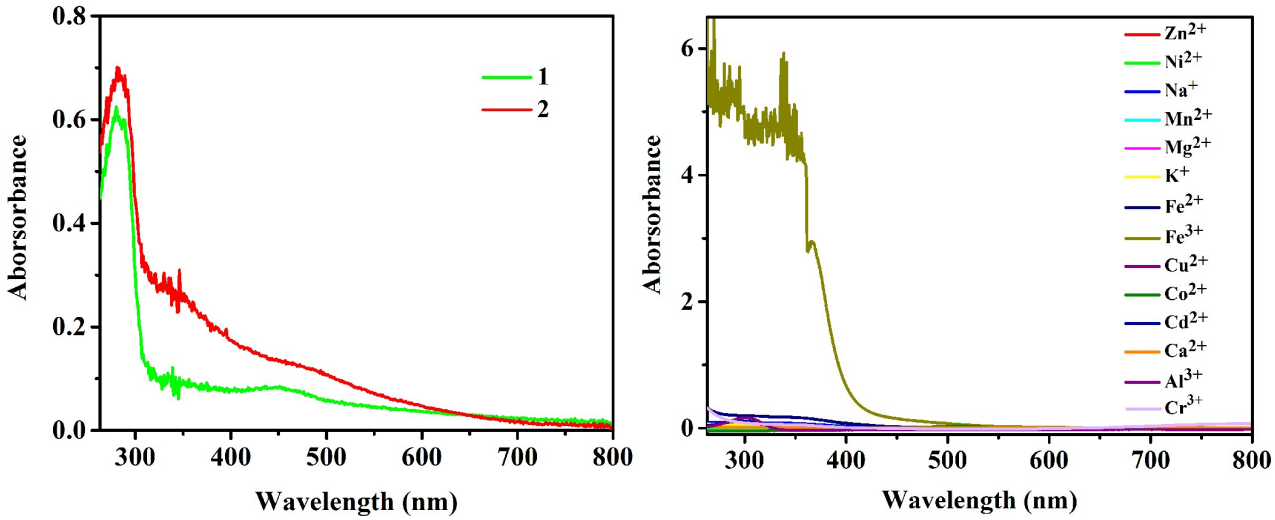


Fig. S8. UV-Vis absorption spectra of **1**, **2** and various metal cations in aqueous solutions.

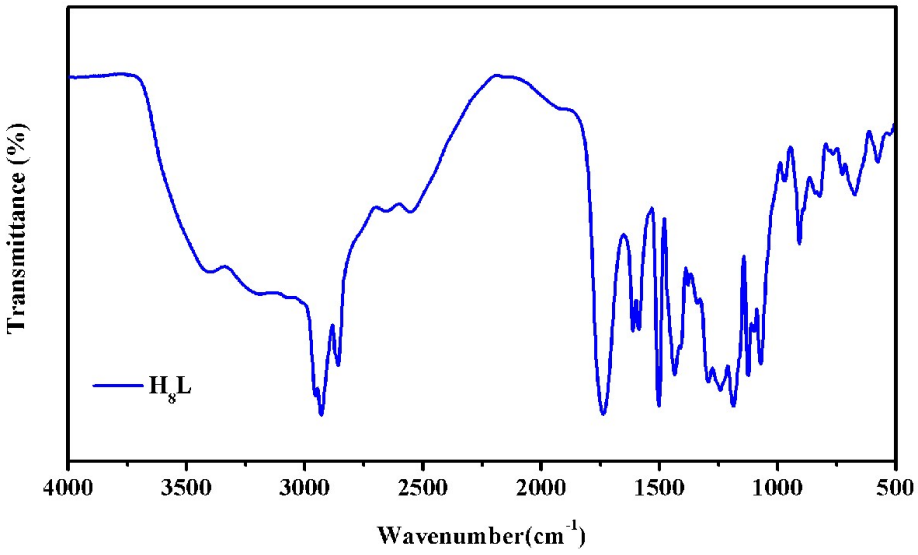


Fig. S9. FT-IR spectrum of H_8L.

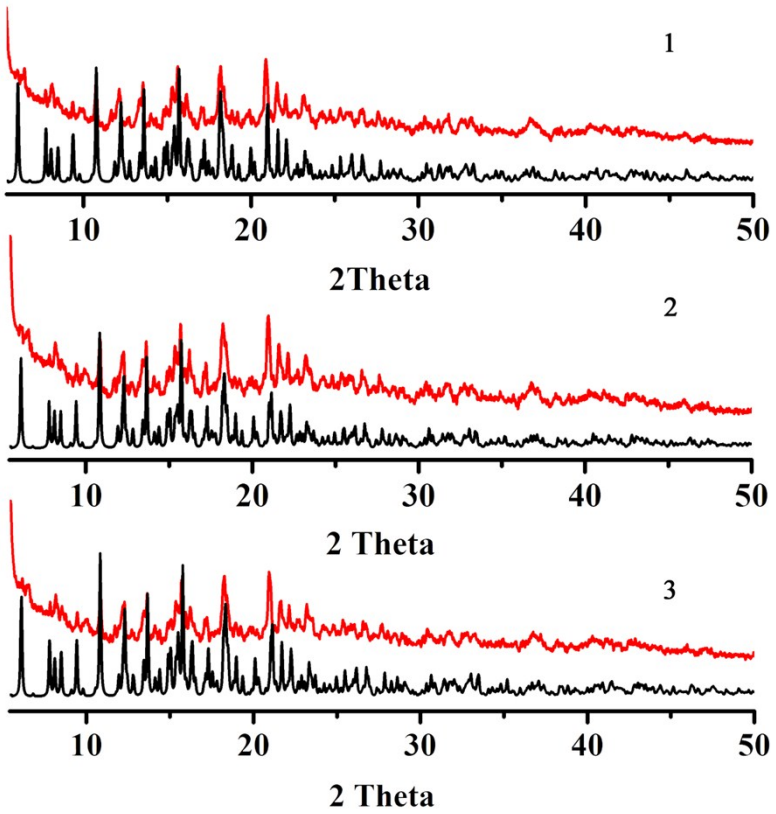
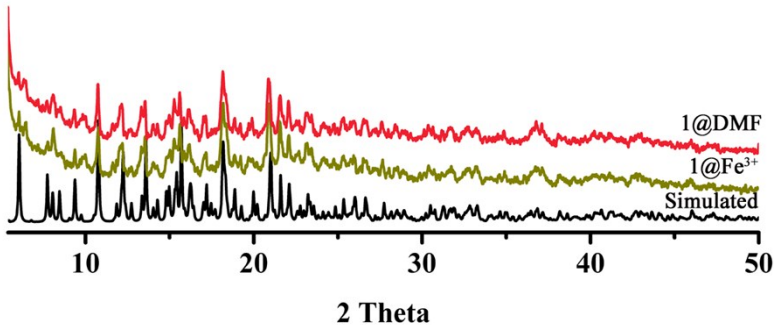
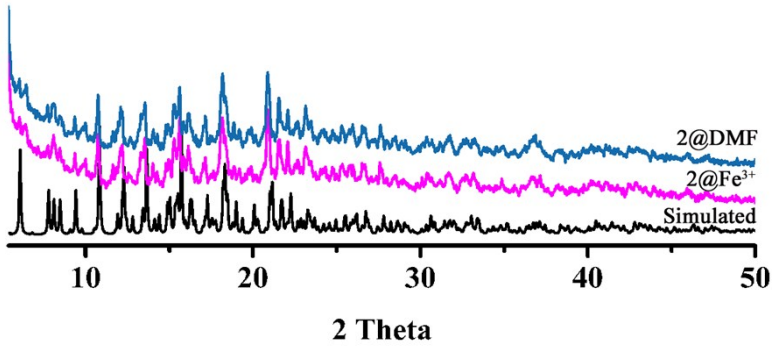


Fig. S10. Simulated and experimental PXRD patterns of **1-3**.

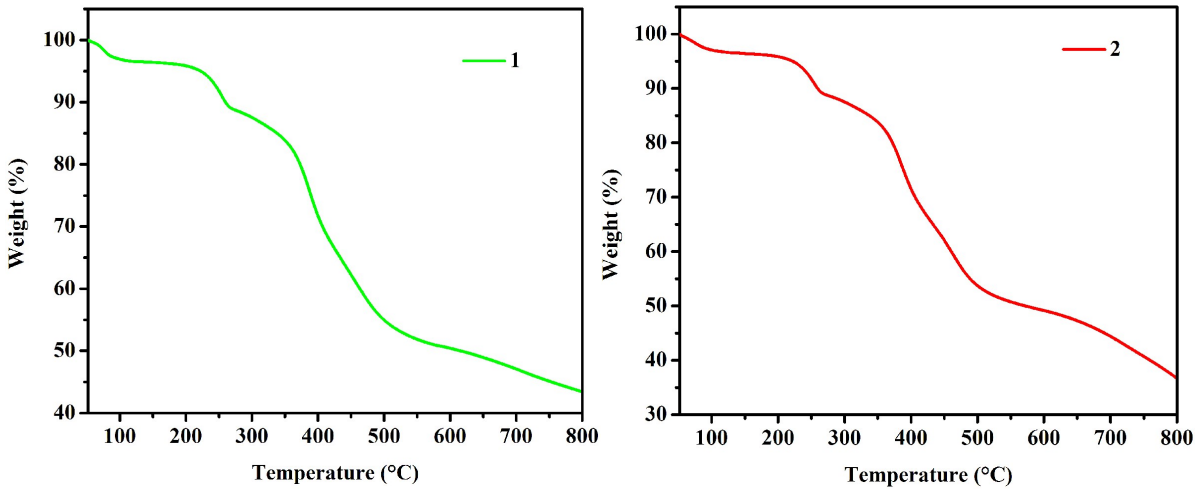


(a)



(b)

Fig. S12. PXRD patterns of **1** (a) and **2** (b) treated in DMF and Fe^{3+} solution.



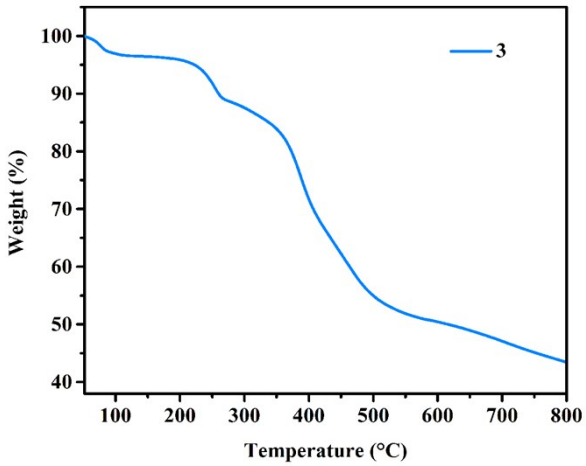


Fig. S13. TG curves of **1**-**3**. The weight loss, corresponding to the $(CH_3)_2NH_2^+$ cation and waters, is observed before 275 °C for **1 (**found: 11.31%, calcd: 11.91%), 279 °C for **2 (**found: 11.50%, calcd: 12.01%), and 280 °C for **3 (**found: 11.36%, calcd: 11.94%), thereafter, the frameworks begain to decompose.

Table S1 Crystal data and structure refinements for **1-3**.

	1	**2**	**3**
Formula	$C_{66}H_{94}Tb_2NO_{33}$	$C_{66}H_{94}Eu_2NO_{33}$	$C_{66}H_{94}Gd_2NO_{33}$
*M*r	1747.26	1733.34	1743.92
Space group	*P*-1	*P*-1	*P*-1
a/Å	11.6240(5)	11.6030(7)	11.573(5)
b/Å	14.8640(9)	14.7990(10)	14.796(5)
c/Å	22.1860(16)	22.0270(14)	22.058(5)
α/°	97.698(5)	97.853(6)	97.762(5)
ß/°	92.368(5)	92.450(5)	92.518(5)
γ/°	98.312(4)	98.272(6)	98.243(5)
V/Å^3	3751.6(4)	3700.3(4)	3696(2)

Z	2	2	2
D_c(g/cm^3)	1.547	1.556	1.567
GOF on F^2	1.107	1.113	1.073
$R1^a$ [I>2σ(I)]	0.1461	0.1390	0.1594
$wR2^b$ (all data)	0.3284	0.2958	0.3434
R_{int}	0.0856	0.0850	0.1271

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for **1**.

Tb(1)-O(3)	2.306(16)	Tb(1)-O(7)	2.303(13)
Tb(1)-O(2)	2.355(12)	Tb(1)-O(14)$^{\#1}$	2.386(13)
Tb(1)-O(3W)	2.428(14)	Tb(1)-O(1W)	2.401(16)
Tb(1)-O(2W)	2.481(12)	Tb(1)-O(15)$^{\#1}$	2.501(12)
Tb(2)-O(11)	2.300(14)	Tb(2)-O(1)$^{\#2}$	2.358(13)
Tb(2)-O(6)$^{\#3}$	2.392(15)	Tb(2)-O(4W)	2.401(13)
Tb(2)-O(6W)	2.439(15)	Tb(2)-O(7W)	2.439(15)
Tb(2)-O(5W)	2.491(12)	Tb(2)-O(17)$^{\#2}$	2.607(12)
Tb(2)-O(5)$^{\#3}$	2.648(17)	O(3)-Tb(1)-O(7)	94.0(5)
O(3)-Tb(1)-O(2)	78.7(5)	O(7)-Tb(1)-O(2)	78.1(4)
O(3)-Tb(1)-O(14)$^{\#1}$	149.2(5)	O(7)-Tb(1)-O(14)$^{\#1}$	93.0(5)
O(2)-Tb(1)-O(14)$^{\#1}$	73.5(5)	O(3)-Tb(1)-O(3W)	76.1(5)
O(7)-Tb(1)-O(3W)	79.3(4)	O(2)-Tb(1)-O(3W)	144.6(5)
O(14)$^{\#1}$-Tb(1)-O(3W)	134.7(4)	O(3)-Tb(1)-O(1W)	76.1(5)
O(7)-Tb(1)-O(1W)	147.3(5)	O(2)-Tb(1)-O(1W)	69.5(5)
O(14)$^{\#1}$-Tb(1)-O(1W)	81.9(5)	O(3W)-Tb(1)-O(1W)	126.3(5)
O(3)-Tb(1)-O(2W)	107.9(5)	O(7)-Tb(1)-O(2W)	140.3(4)
O(2)-Tb(1)-O(2W)	137.5(4)	O(14)$^{\#1}$-Tb(1)-O(2W)	84.8(5)
O(3W)-Tb(1)-O(2W)	74.7(4)	O(1W)-Tb(1)-O(2W)	71.6(5)
O(3)-Tb(1)-O(15)$^{\#1}$	157.3(5)	O(7)-Tb(1)-O(15)$^{\#1}$	78.5(5)
O(2)-Tb(1)-O(15)$^{\#1}$	119.7(4)	O(14)$^{\#1}$-Tb(1)-O(15)$^{\#1}$	53.3(4)

O(3W)-Tb(1)-O(15)$^{\#1}$	81.5(4)	O(1W)-Tb(1)-O(15)$^{\#1}$	121.2(5)
O(2W)-Tb(1)-O(15)$^{\#1}$	68.6(4)	O(11)-Tb(2)-O(1)$^{\#2}$	83.7(5)
O(11)-Tb(2)-O(6)$^{\#3}$	75.2(5)	O(1)$^{\#2}$-Tb(2)-O(6)$^{\#3}$	130.2(5)
O(11)-Tb(2)-O(4W)	147.5(5)	O(1)$^{\#2}$-Tb(2)-O(4W)	71.3(5)
O(6)$^{\#3}$-Tb(2)-O(4W)	105.2(5)	O(11)-Tb(2)-O(6W)	138.2(5)
O(1)$^{\#2}$-Tb(2)-O(6W)	103.9(5)	O(6)$^{\#3}$-Tb(2)-O(6W)	121.9(5)
O(4W)-Tb(2)-O(6W)	70.1(5)	O(11)-Tb(2)-O(7W)	78.9(5)
O(1)$^{\#2}$-Tb(2)-O(7W)	145.7(5)	O(6)$^{\#3}$-Tb(2)-O(7W)	73.6(5)
O(4W)-Tb(2)-O(7W)	133.1(5)	O(6W)-Tb(2)-O(7W)	71.7(5)
O(11)-Tb(2)-O(5W)	74.6(5)	O(1)$^{\#2}$-Tb(2)-O(5W)	67.9(4)
O(6)$^{\#3}$-Tb(2)-O(5W)	142.0(4)	O(4W)-Tb(2)-O(5W)	112.7(5)
O(6W)-Tb(2)-O(5W)	70.8(4)	O(7W)-Tb(2)-O(5W)	78.4(5)
O(17)$^{\#2}$-Tb(2)-O(5)$^{\#3}$	93.5(4)	O(11)-Tb(2)-O(17)$^{\#2}$	76.7(5)
O(1)$^{\#2}$-Tb(2)-O(17)$^{\#2}$	61.9(4)	O(6)$^{\#3}$-Tb(2)-O(17)$^{\#2}$	69.5(4)
O(4W)-Tb(2)-O(17)$^{\#2}$	73.3(4)	O(6W)-Tb(2)-O(17)$^{\#2}$	143.4(4)
O(7W)-Tb(2)-O(17)$^{\#2}$	139.8(5)	O(5W)-Tb(2)-O(17)$^{\#2}$	124.0(4)
O(5W)-Tb(2)-O(5)$^{\#3}$	143.4(4)	O(11)-Tb(2)-O(5)$^{\#3}$	126.1(5)
O(1)$^{\#2}$-Tb(2)-O(5)$^{\#3}$	137.6(4)	O(6)$^{\#3}$-Tb(2)-O(5)$^{\#3}$	52.3(4)
O(4W)-Tb(2)-O(5)$^{\#3}$	68.6(5)	O(6W)-Tb(2)-O(5)$^{\#3}$	74.7(5)
O(7W)-Tb(2)-O(5)$^{\#3}$	75.9(5)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -*x*+1, -*y*+2, -*z*; $^{\#2}$ *x*, *y*-1, *z*; $^{\#3}$ *x*+1, *y*-1, *z*.

Table S3. Selected bond distances (Å) and angles (°) for **2**.

Eu(1)-O(20)	2.316(12)	Eu(1)-O(14)	2.321(15)
Eu(1)-O(12)	2.361(10)	Eu(1)-O(8)$^{\#1}$	2.381(13)
Eu(1)-O(7W)	2.425(15)	Eu(1)-O(6W)	2.429(11)
Eu(1)-O(9)$^{\#1}$	2.498(12)	Eu(1)-O(5W)	2.525(13)
Eu(2)-O(2)$^{\#2}$	2.311(14)	Eu(2)-O(11)	2.403(12)
Eu(2)-O(18)$^{\#3}$	2.407(12)	Eu(2)-O(2W)	2.460(13)
Eu(2)-O(4W)	2.464(15)	Eu(2)-O(1W)	2.473(14)
Eu(2)-O(3W)	2.494(12)	Eu(2)-O(17)$^{\#3}$	2.601(14)
Eu(2)-O(10)	2.605(11)	O(20)-Eu(1)-O(14)	94.7(5)
O(20)-Eu(1)-O(12)	78.1(4)	O(14)-Eu(1)-O(12)	79.4(5)
O(20)-Eu(1)-O(8)$^{\#1}$	92.7(4)	O(14)-Eu(1)-O(8)$^{\#1}$	150.1(5)

O(12)-Eu(1)-O(8)$^{\#1}$	73.9(4)	O(20)-Eu(1)-O(7W)	147.7(5)
O(14)-Eu(1)-O(7W)	77.0(5)	O(12)-Eu(1)-O(7W)	69.7(5)
O(8)$^{\#1}$-Eu(1)-O(7W)	81.3(5)	O(20)-Eu(1)-O(6W)	79.0(4)
O(14)-Eu(1)-O(6W)	75.0(4)	O(12)-Eu(1)-O(6W)	143.9(4)
O(8)$^{\#1}$-Eu(1)-O(6W)	134.8(4)	O(7W)-Eu(1)-O(6W)	126.9(4)
O(20)-Eu(1)-O(9)$^{\#1}$	77.7(4)	O(14)-Eu(1)-O(9)$^{\#1}$	156.8(4)
O(12)-Eu(1)-O(9)$^{\#1}$	119.4(4)	O(8)$^{\#1}$-Eu(1)-O(9)$^{\#1}$	52.9(4)
O(7W)-Eu(1)-O(9)$^{\#1}$	120.6(5)	O(6W)-Eu(1)-O(9)$^{\#1}$	82.0(4)
O(20)-Eu(1)-O(5W)	141.7(4)	O(14)-Eu(1)-O(5W)	107.3(5)
O(12)-Eu(1)-O(5W)	135.7(4)	O(8)$^{\#1}$-Eu(1)-O(5W)	83.6(4)
O(7W)-Eu(1)-O(5W)	69.5(5)	O(6W)-Eu(1)-O(5W)	77.1(4)
O(9)$^{\#1}$-Eu(1)-O(5W)	69.7(4)	O(2)$^{\#2}$-Eu(2)-O(11)	82.8(5)
O(2)$^{\#2}$-Eu(2)-O(18)$^{\#3}$	76.1(5)	O(11)-Eu(2)-O(18)$^{\#3}$	130.6(4)
O(2)$^{\#2}$-Eu(2)-O(2W)	136.1(5)	O(11)-Eu(2)-O(2W)	104.1(4)
O(18)$^{\#3}$-Eu(2)-O(2W)	122.1(4)	O(2)$^{\#2}$-Eu(2)-O(4W)	147.9(5)
O(11)-Eu(2)-O(4W)	71.5(5)	O(18)$^{\#3}$-Eu(2)-O(4W)	106.3(5)
O(2W)-Eu(2)-O(4W)	70.7(5)	O(2)$^{\#2}$-Eu(2)-O(1W)	78.4(5)
O(11)-Eu(2)-O(1W)	144.5(5)	O(18)$^{\#3}$-Eu(2)-O(1W)	73.1(5)
O(2W)-Eu(2)-O(1W)	71.4(5)	O(4W)-Eu(2)-O(1W)	133.5(5)
O(2)$^{\#2}$-Eu(2)-O(3W)	73.1(5)	O(11)-Eu(2)-O(3W)	67.8(4)
O(18)$^{\#3}$-Eu(2)-O(3W)	141.1(4)	O(2W)-Eu(2)-O(3W)	70.1(4)
O(4W)-Eu(2)-O(3W)	112.4(5)	O(1W)-Eu(2)-O(3W)	78.0(5)
O(2)$^{\#2}$-Eu(2)-O(17)$^{\#3}$	126.5(5)	O(11)-Eu(2)-O(17)$^{\#3}$	138.5(5)
O(18)$^{\#3}$-Eu(2)-O(17)$^{\#3}$	51.8(4)	O(2W)-Eu(2)-O(17)$^{\#3}$	75.9(4)
O(4W)-Eu(2)-O(17)$^{\#3}$	69.6(5)	O(1W)-Eu(2)-O(17)$^{\#3}$	75.9(4)
O(3W)-Eu(2)-O(17)$^{\#3}$	142.2(4)	O(2)$^{\#2}$-Eu(2)-O(10)	77.1(4)
O(11)-Eu(2)-O(10)	61.6(4)	O(18)$^{\#3}$-Eu(2)-O(10)	70.4(4)
O(2W)-Eu(2)-O(10)	144.6(4)	O(4W)-Eu(2)-O(10)	73.9(4)
O(1W)-Eu(2)-O(10)	139.8(5)	O(3W)-Eu(2)-O(10)	123.4(4)
O(17)$^{\#3}$-Eu(2)-O(10)	93.9(4)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+2, -y, -z+1$; $^{\#2}$ $x, y+1, z$; $^{\#3}$ $x+1, y, z$.

Table S4. Selected bond distances (Å) and angles (°) for **3.**

Gd(1)-O(7)	2.291(15)	Gd(1)-O(4)	2.309(17)

Gd(1)-O(13)	2.361(14)	Gd(1)-O(15)$^{\#1}$	2.370(15)
Gd(1)-O(3W)	2.397(18)	Gd(1)-O(1W)	2.432(16)
Gd(1)-O(2W)	2.481(15)	Gd(1)-O(16)$^{\#1}$	2.511(14)
Gd(2)-O(20)$^{\#2}$	2.301(15)	Gd(2)-O(14)$^{\#3}$	2.378(15)
Gd(2)-O(1)	2.386(16)	Gd(2)-O(4W)	2.420(16)
Gd(2)-O(5W)	2.436(18)	Gd(2)-O(6W)	2.444(18)
Gd(2)-O(7W)	2.466(14)	Gd(2)-O(17)$^{\#3}$	2.581(13)
Gd(2)-O(2)	2.629(19)	O(7)-Gd(1)-O(4)	94.4(6)
O(7)-Gd(1)-O(13)	78.1(5)	O(4)-Gd(1)-O(13)	78.9(6)
O(7)-Gd(1)-O(15)$^{\#1}$	93.2(6)	O(4)-Gd(1)-O(15)$^{\#1}$	147.6(6)
O(13)-Gd(1)-O(15)$^{\#1}$	73.6(6)	O(7)-Gd(1)-O(3W)	147.7(5)
O(4)-Gd(1)-O(3W)	78.0(6)	O(13)-Gd(1)-O(3W)	69.6(6)
O(15)$^{\#1}$-Gd(1)-O(3W)	79.7(6)	O(7)-Gd(1)-O(1W)	79.1(5)
O(4)-Gd(1)-O(1W)	75.0(5)	O(13)-Gd(1)-O(1W)	143.7(6)
O(15)$^{\#1}$-Gd(1)-O(1W)	135.7(5)	O(3W)-Gd(1)-O(1W)	127.3(6)
O(7)-Gd(1)-O(2W)	140.2(5)	O(4)-Gd(1)-O(2W)	108.7(5)
O(13)-Gd(1)-O(2W)	136.8(5)	O(15)$^{\#1}$-Gd(1)-O(2W)	83.2(6)
O(3W)-Gd(1)-O(2W)	70.8(6)	O(1W)-Gd(1)-O(2W)	76.4(5)
O(7)-Gd(1)-O(16)$^{\#1}$	78.3(5)	O(4)-Gd(1)-O(16)$^{\#1}$	157.3(5)
O(13)-Gd(1)-O(16)$^{\#1}$	119.7(5)	O(15)$^{\#1}$-Gd(1)-O(16)$^{\#1}$	53.4(5)
O(3W)-Gd(1)-O(16)$^{\#1}$	119.3(6)	O(1W)-Gd(1)-O(16)$^{\#1}$	82.4(5)
O(2W)-Gd(1)-O(16)$^{\#1}$	67.8(5)	O(20)$^{\#2}$-Gd(2)-O(14)$^{\#3}$	84.8(6)
O(20)$^{\#2}$-Gd(2)-O(1)	75.0(6)	O(14)$^{\#3}$-Gd(2)-O(1)	131.5(5)
O(20)$^{\#2}$-Gd(2)-O(4W)	78.2(6)	O(14)$^{\#3}$-Gd(2)-O(4W)	145.7(5)
O(1)-Gd(2)-O(4W)	72.1(6)	O(20)$^{\#2}$-Gd(2)-O(5W)	137.2(5)
O(14)$^{\#3}$-Gd(2)-O(5W)	104.6(6)	O(1)-Gd(2)-O(5W)	120.3(5)
O(4W)-Gd(2)-O(5W)	70.9(6)	O(20)$^{\#2}$-Gd(2)-O(6W)	148.5(6)
O(14)$^{\#3}$-Gd(2)-O(6W)	71.5(6)	O(1)-Gd(2)-O(6W)	105.4(6)
O(4W)-Gd(2)-O(6W)	132.6(6)	O(5W)-Gd(2)-O(6W)	70.7(5)
O(20)$^{\#2}$-Gd(2)-O(7W)	74.6(5)	O(14)$^{\#3}$-Gd(2)-O(6W)	71.5(6)
O(1)-Gd(2)-O(6W)	105.4(6)	O(4W)-Gd(2)-O(6W)	132.6(6)
O(5W)-Gd(2)-O(6W)	70.7(5)	O(20)$^{\#2}$-Gd(2)-O(7W)	74.6(5)
O(14)$^{\#3}$-Gd(2)-O(7W)	67.3(5)	O(1)-Gd(2)-O(7W)	141.8(6)
O(4W)-Gd(2)-O(7W)	79.4(5)	O(5W)-Gd(2)-O(7W)	71.2(5)
O(6W)-Gd(2)-O(7W)	112.7(6)	O(20)$^{\#2}$-Gd(2)-O(17)$^{\#3}$	77.9(5)

O(14)$^{\#3}$-Gd(2)-O(17)$^{\#3}$	62.1(5)	O(1)-Gd(2)-O(17)$^{\#3}$	70.7(5)
O(4W)-Gd(2)-O(17)$^{\#3}$	139.8(5)	O(5W)-Gd(2)-O(17)$^{\#3}$	143.5(5)
O(6W)-Gd(2)-O(17)$^{\#3}$	72.8(5)	O(7W)-Gd(2)-O(17)$^{\#3}$	123.8(4)
O(20)$^{\#2}$-Gd(2)-O(2)	125.9(6)	O(14)$^{\#3}$-Gd(2)-O(2)	137.5(6)
O(1)-Gd(2)-O(2)	52.3(5)	O(4W)-Gd(2)-O(2)	75.3(5)
O(5W)-Gd(2)-O(2)	73.9(5)	O(6W)-Gd(2)-O(2)	68.1(6)
O(7W)-Gd(2)-O(2)	142.0(5)	O(17)$^{\#3}$-Gd(2)-O(2)	93.4(5)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -*x*-1, -*y*+1, -*z*+1; $^{\#2}$ *x*+1, *y*-1, *z*; $^{\#3}$ *x*+1, *y*, *z*.