Supporting Information

Lanthanide coordination compounds with 1*H*-benzimidazole-2-carboxylic acid: syntheses, structures and spectroscopic properties

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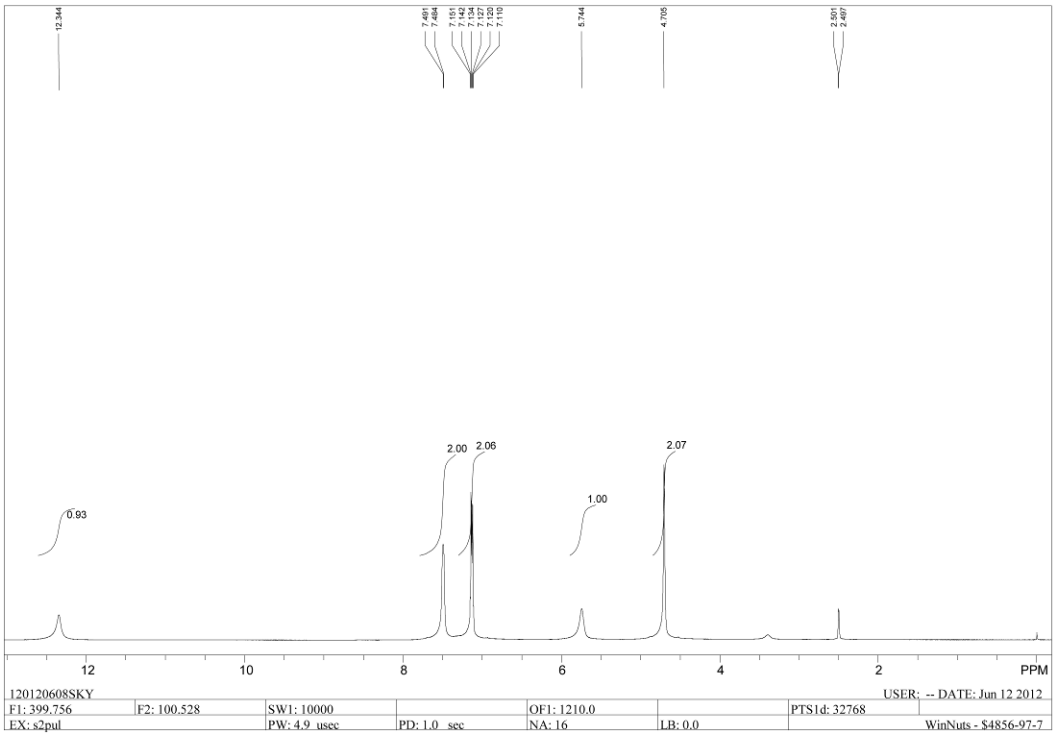

Fig. S1 [1]H NMR of 2-(hydroxymethyl)benzimidazole.

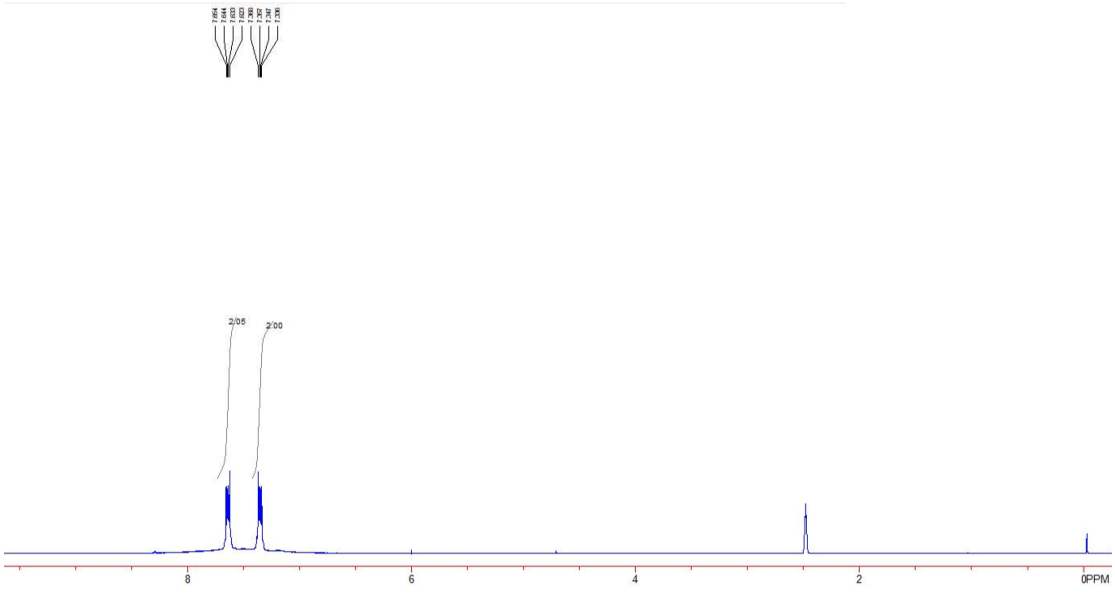

Fig. S2 [1]H NMR of 1*H*-benzimidazole-2-carboxylic acid.

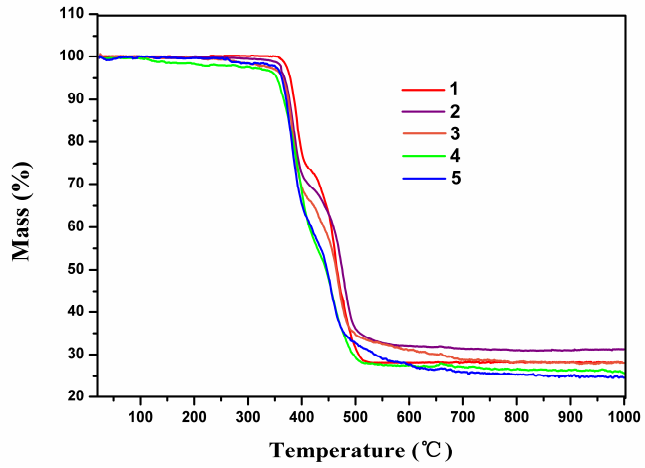

Fig. S3 TG curves of compounds **1-5** with a heating rate of 10 $^{o}C \cdot min^{-1}$.

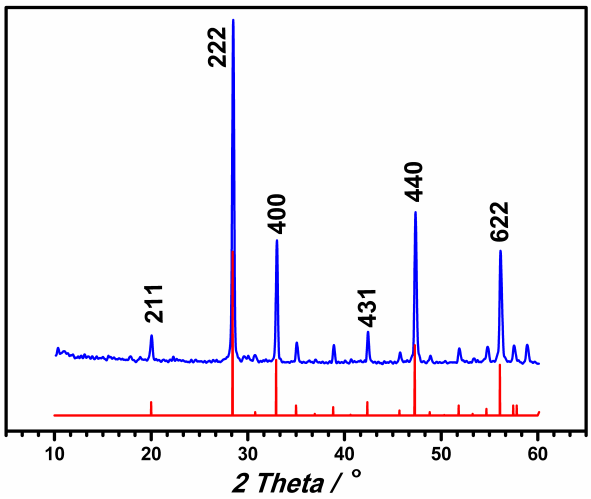

Fig. S4 PXRD pattern for **1** (the red line is the PXRD pattern available in the Powder Diffraction File (JCPDS NO. 34-0392) and the blue line is the experimental data of the end product).

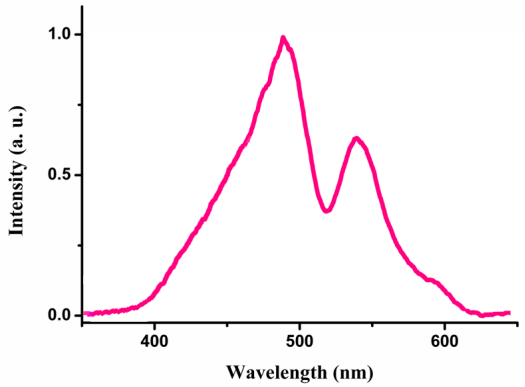

Fig. S5 Phosphorescence spectrum of $[Gd(HBIC)_3]_n$ at 77 K.

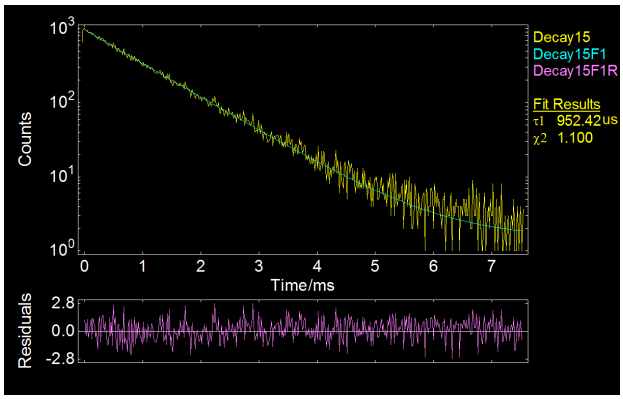

Fig. S6 The ambient temperature $^5D_0$ decay profile for compound **1** (solid state) excited at 394 nm, and monitored at 613 nm.

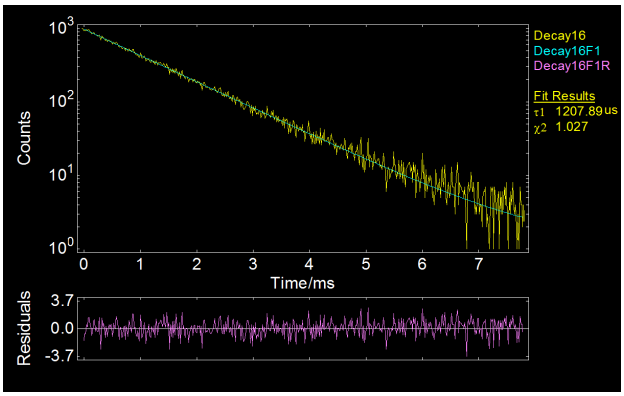

Fig. S7 The ambient temperature $^5D_4$ decay profile for compound **2** (solid state) excited at 333 nm, and monitored at 545 nm.

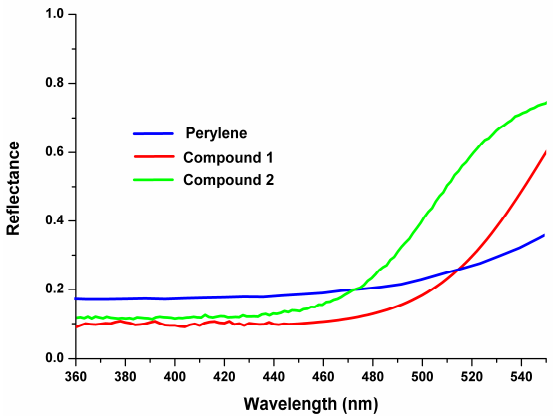

Fig. S8 Diffuse reflectance spectra of compounds **1-2** and the standard phosphor perylene.

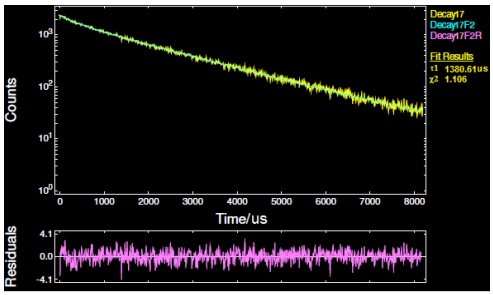

Fig. S9 The low temperature (77 K) $^5D_4$ decay profile for compound **2** excited at 333 nm, and monitored at 545 nm.

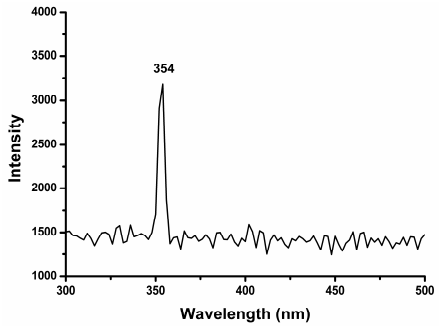

Fig. S10 Solid-state excitation spectrum for **5** monitored at approximately 1060 nm.

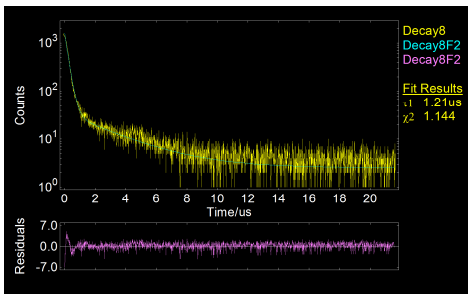

Fig. S11 The room temperature $^4F_{3/2}$ decay profile for compound **5** excited at 354 nm.

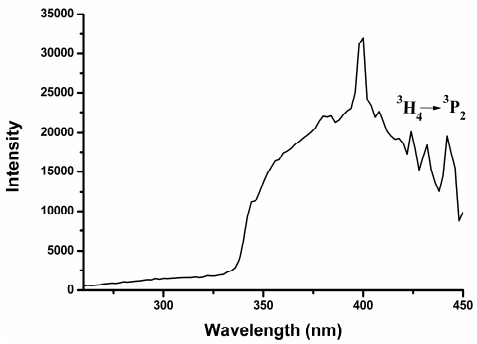

Fig. S12 Solid-state excitation spectrum for **4** at approximately 499 nm.

Table S1 Selected bond lengths (Å) and bond angles (°) for **1-5**.

[Eu(HBIC)$_3$]$_n$ (1)					
		bond			
Eu(1)-O(4)#1	2.338(3)	Eu(1)-O(6)#2	2.396(3)	Eu(1)-O(1)	2.413(3)
Eu(1)-O(3)	2.443(3)	Eu(1)-O(5)	2.487(3)	Eu(1)-N(5)	2.519(3)
Eu(1)-N(1)	2.563(3)	Eu(1)-N(3)	2.567(3)		
		angle			
O(4)#1-Eu(1)-O(6)#2	81.55(9)	O(4)#1-Eu(1)-O(3)	81.59(9)	O(4)#1-Eu(1)-O(5)	139.40(9)
O(4)#1-Eu(1)-O(1)	79.23(9)	O(6)#2-Eu(1)-O(3)	157.00(10)	O(6)#2-Eu(1)-O(5)	70.63(9)
O(6)#2-Eu(1)-O(1)	119.27(9)	O(1)-Eu(1)-O(3)	72.45(9)	O(1)-Eu(1)-O(5)	140.23(9)
O(3)-Eu(1)-O(5)	114.28(9)	O(4)#1-Eu(1)-N(5)	84.97(11)	O(6)#2-Eu(1)-N(5)	96.91(10)
O(1)-Eu(1)-N(5)	137.28(10)	O(4)#1-Eu(1)-N(1)	152.20(10)	O(3)-Eu(1)-N(1)	72.41(10)
O(3)-Eu(1)-N(5)	66.09(10)	O(6)#2-Eu(1)-N(1)	126.12(9)	O(5)-Eu(1)-N(1)	63.63(9)
O(5)-Eu(1)-N(5)	70.18(10)	O(1)-Eu(1)-N(1)	83.62(10)	O(4)#1-Eu(1)-N(3)	119.79(10)
O(6)#2-Eu(1)-N(3)	76.53(10)	O(1)-Eu(1)-N(3)	65.13(10)	O(3)-Eu(1)-N(3)	125.76(10)
O(5)-Eu(1)-N(3)	82.36(10)	N(5)-Eu(1)-N(1)	93.17(11)	N(5)-Eu(1)-N(3)	152.32(11)
N(1)-Eu(1)-N(3)	70.80(11)				
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+1/2 #2 -x+3/2,y-1/2,-z+1/2					
[Tb(HBIC)$_3$]$_n$ (2)					
		bond			
Tb(1)-O(4)#1	2.318(4)	Tb(1)-O(1)	2.386(4)	Tb(1)-O(5)	2.467(4)
Tb(1)-O(6)#2	2.379(4)	Tb(1)-O(3)	2.424(4)	Tb(1)-N(5)	2.493(6)
Tb(1)-N(1)	2.541(5)	Tb(1)-N(3)	2.546(5)		
		angle			
O(4)#1-Tb(1)-O(6)#2	81.33(15)	O(6)#2-Tb(1)-O(1)	119.35(15)	O(6)#2-Tb(1)-O(3)	157.36(16)
O(4)#1-Tb(1)-O(1)	78.89(15)	O(4)#1-Tb(1)-O(3)	82.02(16)	O(1)-Tb(1)-O(3)	71.93(15)
O(4)#1-Tb(1)-O(5)	139.08(15)	O(6)#2-Tb(1)-O(5)	70.36(15)	O(1)-Tb(1)-O(5)	140.82(15)
O(3)-Tb(1)-O(5)	114.56(15)	O(3)-Tb(1)-N(5)	66.58(16)	O(4)#1-Tb(1)-N(1)	119.57(17)
O(4)#1-Tb(1)-N(5)	84.76(18)	O(5)-Tb(1)-N(5)	70.35(16)	O(6)#2-Tb(1)-N(1)	76.50(16)
O(6)#2-Tb(1)-N(5)	96.65(17)	O(1)-Tb(1)-N(1)	65.52(15)	O(5)-Tb(1)-N(1)	82.40(16)
O(1)-Tb(1)-N(5)	137.04(16)	O(3)-Tb(1)-N(1)	125.41(16)	O(5)-Tb(1)-N(3)	63.99(16)
O(4)#1-Tb(1)-N(3)	152.26(16)	O(1)-Tb(1)-N(3)	83.88(17)	O(3)-Tb(1)-N(3)	72.00(17)
O(6)#2-Tb(1)-N(3)	126.28(16)	N(5)-Tb(1)-N(1)	152.56(18)	N(5)-Tb(1)-N(3)	93.46(19)
N(1)-Tb(1)-N(3)	71.00(18)				
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+1/2 #2 -x+3/2,y-1/2,-z+1/2					
[Gd(HBIC)$_3$]$_n$ (3)					
		bond			
Gd(1)-O(2)	2.403(4)	Gd(1)-O(3)	2.480(4)	Gd(1)-O(4)#2	2.390(4)
Gd(1)-O(5)	2.430(4)	Gd(1)-O(6)#1	2.326(4)	Gd(1)-N(1)	2.514(5)
Gd(1)-N(3)	2.554(4)	Gd(1)-N(5)	2.557(5)		
		angle			
O(6)#1-Gd(1)-O(4)#2	81.09(12)	O(6)#1-Gd(1)-O(5)	81.80(13)	O(6)#1-Gd(1)-O(3)	138.97(13)
O(6)#1-Gd(1)-O(2)	79.20(13)	O(4)#2-Gd(1)-O(5)	156.80(14)	O(4)#2-Gd(1)-O(3)	70.70(12)

O(4)#2-Gd(1)-O(2)	119.13(13)	O(2)-Gd(1)-O(5)	72.49(13)	O(2)-Gd(1)-O(3)	140.63(12)
O(5)-Gd(1)-O(3)	114.31(13)	O(6)#1-Gd(1)-N(1)	84.71(15)	O(6)#1-Gd(1)-N(3)	152.23(13)
O(5)-Gd(1)-N(1)	66.21(14)	O(4)#2-Gd(1)-N(1)	96.65(14)	O(4)#2-Gd(1)-N(3)	126.55(13)
O(3)-Gd(1)-N(1)	70.14(14)	O(2)-Gd(1)-N(1)	137.32(14)	O(2)-Gd(1)-N(3)	83.56(14)
O(5)-Gd(1)-N(3)	72.28(14)	O(3)-Gd(1)-N(3)	64.09(13)	O(6)#1-Gd(1)-N(5)	119.76(15)
O(4)#2-Gd(1)-N(5)	76.83(14)	O(2)-Gd(1)-N(5)	65.09(13)	O(3)-Gd(1)-N(5)	82.61(14)
O(5)-Gd(1)-N(5)	125.61(14)	N(1)-Gd(1)-N(3)	93.60(16)	N(1)-Gd(1)-N(5)	152.53(15)
N(3)-Gd(1)-N(5)	70.67(16)				

Symmetry transformations used to generate equivalent atoms: #1 -x-1/2,y-1/2,-z+1/2 #2 -x+1/2,y-1/2,-z+1/2

[Pr(HBIC)$_3$]$_n$ (4)

			bond		
Pr(1)-O(5)#1	2.376(3)	Pr(1)-O(3)	2.463(3)	Pr(1)-O(1)	2.524(3)
Pr(1)-O(6)#2	2.433(2)	Pr(1)-O(2)	2.480(3)	Pr(1)-N(3)	2.593(3)
Pr(1)-N(5)	2.613(3)	Pr(1)-N(1)	2.631(3)		
			angle		
O(5)#1-Pr(1)-O(6)#2	82.24(9)	O(5)#1-Pr(1)-O(2)	81.55(9)	O(5)#1-Pr(1)-O(1)	140.20(9)
O(5)#1-Pr(1)-O(3)	79.54(9)	O(6)#2-Pr(1)-O(2)	157.05(9)	O(6)#2-Pr(1)-O(1)	70.64(8)
O(6)#2-Pr(1)-O(3)	119.24(9)	O(3)-Pr(1)-O(2)	73.39(9)	O(3)-Pr(1)-O(1)	139.12(8)
O(2)-Pr(1)-O(1)	113.61(9)	O(5)#1-Pr(1)-N(5)	119.56(10)	O(5)#1-Pr(1)-N(3)	86.68(10)
O(2)-Pr(1)-N(3)	64.94(9)	O(6)#2-Pr(1)-N(5)	76.49(10)	O(6)#2-Pr(1)-N(3)	98.00(10)
O(1)-Pr(1)-N(3)	69.51(9)	O(3)-Pr(1)-N(5)	64.19(9)	O(3)-Pr(1)-N(3)	137.57(9)
O(2)-Pr(1)-N(5)	125.92(10)	O(5)#1-Pr(1)-N(1)	152.29(9)	O(3)-Pr(1)-N(1)	82.86(9)
O(1)-Pr(1)-N(5)	82.39(9)	O(6)#2-Pr(1)-N(1)	125.24(9)	O(2)-Pr(1)-N(1)	72.96(9)
O(1)-Pr(1)-N(1)	63.14(9)	N(3)-Pr(1)-N(5)	151.46(10)	N(3)-Pr(1)-N(1)	92.12(10)
N(5)-Pr(1)-N(1)	70.02(10)				

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y+1/2,-z+1/2 #2 -x+3/2,y+1/2,-z+1/2

[Nd(HBIC)$_3$]$_n$ (5)

			bond		
Nd(1)-O(2)#1	2.370(5)	Nd(1)-O(5)	2.454(6)	Nd(1)-O(4)	2.522(5)
Nd(1)-O(3)#2	2.432(5)	Nd(1)-O(1)	2.477(6)	Nd(1)-N(2)	2.586(7)
Nd(1)-N(3)	2.614(7)	Nd(1)-N(5)	2.656(7)		
			angle		
O(2)#1-Nd(1)-O(3)#2	82.36(19)	O(2)#1-Nd(1)-O(1)	81.5(2)	O(2)#1-Nd(1)-O(4)	140.14(19)
O(2)#1-Nd(1)-O(5)	79.37(19)	O(3)#2-Nd(1)-O(1)	157.2(2)	O(3)#2-Nd(1)-O(4)	70.48(19)
O(3)#2-Nd(1)-O(5)	119.5(2)	O(5)-Nd(1)-O(1)	72.93(18)	O(5)-Nd(1)-O(4)	139.39(18)
O(1)-Nd(1)-O(4)	113.78(19)	O(5)-Nd(1)-N(2)	137.3(2)	O(2)#1-Nd(1)-N(2)	86.4(2)
O(4)-Nd(1)-N(2)	69.7(2)	O(1)-Nd(1)-N(2)	65.22(19)	O(3)#2-Nd(1)-N(2)	97.8(2)
O(2)#1-Nd(1)-N(3)	119.4(2)	O(5)-Nd(1)-N(3)	64.6(2)	O(2)#1-Nd(1)-N(5)	152.5(2)
O(3)#2-Nd(1)-N(3)	76.2(2)	O(1)-Nd(1)-N(3)	126.0(2)	O(3)#2-Nd(1)-N(5)	124.9(2)
O(4)-Nd(1)-N(3)	82.5(2)	O(5)-Nd(1)-N(5)	83.1(2)	O(4)-Nd(1)-N(5)	62.97(19)
O(1)-Nd(1)-N(5)	73.2(2)	N(2)-Nd(1)-N(3)	151.7(2)	N(2)-Nd(1)-N(5)	92.4(2)
N(3)-Nd(1)-N(5)	70.2(2)				

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+1/2 #2 -x+3/2,y-1/2,-z+1/2

Table S2 Hydrogen bonding interactions in $H_2BIC \cdot 2H_2O$ and **1**-**5**.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	<DHA (°)
$H_2BIC \cdot 2H_2O$				
N(1)-H(1A)...O(3)	0.86	1.86	2.714(3)	170.2
N(2)-H(2)...O(1)#1	0.86	1.86	2.669(3)	155.6
O(3)-H(3B)...O(2)#2	0.85	2.38	2.855(3)	116.0
O(4)-H(4A)...O(2)	0.85	2.52	3.157(4)	132.9
O(4)-H(4B)...O(2)#2	0.85	2.47	3.242(4)	152.3
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z #2 -x+1,y-1/2,-z+1/2				
$[Eu(HBIC)_3]_n$ (1)				
N(2)-H(2N)...O(5)#1	0.86	1.91	2.718(4)	154.8
N(6)-H(6N)...O(1)#2	0.86	1.94	2.782(4)	166.6
N(4)-H(4)...O(2)#3	0.86	2	2.824(5)	159.5
Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y+1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2 #3 -x+1,-y+1,-z				
$[Tb(HBIC)_3]_n$ (2)				
N(2)-H(2)...O(2)#1	0.86	2.02	2.839(7)	159.6
N(4)-H(4A)...O(5)#2	0.86	1.90	2.697(7)	153.0
O(6)-H(6A)...O(1)#3	0.86	1.93	2.774(7)	165.4
Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z #2 -x+3/2, y+1/2, -z+1/2 #3 -x+1/2, y+1/2, -z+1/2				
$[Gd(HBIC)_3]_n$ (3)				
N(6)-H(6N)...O(1)#1	0.86	2.00	2.827(6)	160.1
N(4)-H(4)...O(3)#2	0.86	1.91	2.710(6)	154.4
N(2)-H(2)...O(2)#3	0.86	1.94	2.781(6)	166.3
Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z #2 -x+1/2,y+1/2,-z+1/2 #3 -x-1/2,y+1/2,-z+1/2				
$[Pr(HBIC)_3]_n$ (4)				
N(4)-H(4N)...O(3)#1	0.86	1.96	2.803(4)	167.1
N(2)-H(2A)...O(1)#2	0.86(4)	1.91(4)	2.739(4)	162(4)
N(6)-H(6)...O(4)#3	0.86	1.98	2.807(4)	159.8
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+1/2 #2 -x+3/2,y-1/2,-z+1/2 #3 -x+1,-y+2,-z				
$[Nd(HBIC)_3]_n$ (5)				
N(1)-H(1)...O(5)#1	0.86	1.95	2.795(9)	167.2
N(4)-H(4)...O(6)#2	0.86	2.00	2.826(9)	159.5
N(6)-H(6)...O(4)#3	0.86	1.94	2.745(8)	155.7
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y+1/2,-z+1/2 #2 -x+1,-y+1,-z #3 -x+3/2,y+1/2,-z+1/2				

Table S3 The photoluminescence properties (τ_{obs}, Φ_{Ln} and $\Phi_{overall}$) of some monomeric Ln-MOFs.

Compounds	τ_{obs}(μs)	Φ_{Ln}(%)	$\Phi_{overall}$(%)	References
$Eu(tta)_3dmbipy$	670	45	23	1. Inorg. Chim. Acta 2007, 360, 3543–3552
$Eu(tta)_3dmphen$	690	45	34	
$Eu(btfac)_3dmbipy$	750	49	18	
$Eu(hfac)_3dmbipy(H_2O)$	330	21	48	
$Eu(hfac)_3(dmphen)(EtOH)$	650	19	39	
$Tb(fod)_3(phen)$	230	28	14.5	2. J. Phys. Chem. A 2010, 114, 7928–7936
$Eu(fod)_3(phen)$	850	40	20.4	
$Eu(fod)_3(H_2O)_2$	620	42	11	
$Eu(fod)_3$(phen-*N*-O)	370	51	15	
$Eu(L_1)_3(ClO_4)_3$	1950	34	34.5	3. Inorg. Chem. 2010, 49, 4657–4664
$Eu(L_4)_2(ClO_4)_3(H_2O)$	530	14	15.5	
$Eu(L_4)_2(CF_3SO_3)_3$	1450	42	29	
$Eu(L_{5a})_2(CF_3SO_3)_3$	43	1.2	1.4	
$Eu(L_{5b})_2(CF_3SO_3)_3$	13	0.36	0.37	
$Eu(L_{5c})_2(CF_3SO_3)_3$	74	2.2	1.2	
$Eu(L_{5d})_2(CF_3SO_3)_3$	33	8.9	3.8	
$Eu(L_6)_2(CF_3SO_3)_3$	9.3	0.034	0.003	
$Eu_2Na_2(L_1)_6(OH)_2{\cdot}2C_2H_5OH{\cdot}2CHCl_3$	870	60	15	4. Dalton Trans. 2009, 7359–7367
$Eu(L_1)_3(phen)$	990	56	30	
$Eu_2Na_2(L_1)_6(L_2)_2(OH)_2{\cdot}8CHCl_3$	950	60	23	
$Eu(PBI)_3\ C_2H_5OH\ H_2O$	250	26	2.2	5. Inorg. Chem. 2006, 45, 10651-10660
$Eu(PBI)_3$ bpy	978	68	15	
$Eu(PBI)_3$ dmbpy	1181	72	18	
$Eu(PBI)_3$ phen	1025	57	11	
$Eu(PBI)_3$ bath	1010	71	15	
$Eu(PBI)_3(DPEPO)$	1060	59	30	6. Cryst. Growth Des. 2009, 9, 3562–3569
$Eu(PBI)_3(EtOH)(H_2O)$	250	26	2	
$Eu(PBI)_3(phen)$	1025	57	11	
$Tb(PBI)_3(DPEPO)$	168	18	0.5	
$Tb(PBI)_3(H_2O)_2$	400	49	11	
$Eu(TTA)_3Phen$	710	51	48	7. Inorg. Chem. 2011, 50, 5417–5429
$Eu(TTA)_2$(Br-TTA)Phen	610	45	43	
$Eu(BrC8\text{-}TTA)_3Phen$	550	41	41	
$Eu(Br\text{-}TTA)_3Phen$	500	36	36	
$Eu(NO_3)_3phen_2$	995	21		8. Eur. J. Inorg. Chem. 2011, 637–646
$Eu(NO_3)_3$(5-nitro-phen)$_2$	996	9		
$Eu(NO_3)_3$(5-methyl-phen)$_2$	1071	26		
$Eu(NO_3)_3$(4-methyl-phen)$_2$	985	27		
$Eu(NO_3)_3$(5-chlorophen)$_2$	995	22		
$Eu(TTA)_3PhoA$		30		9. New J. Chem. 2010, 34, 487–494

$Eu(TTA)_3PhoB$		40		
$Eu(TTA)_3PhoC$		42		
Eu(TTA)3BpoA		16		
Eu(TTA)3BpoB		22		
Eu(TTA)3BpoC		26		
$Tb(DBM)_3TPTZ$		3.4		10. Polyhedron 2007, 26, 1229–1238
$Eu(DBM)_3TPTZ$		17.4		
$Eu(BA)_3TPTZ$		15.5		
$Eu(TTA)_3TPTZ$		40.2		
$Eu(BTFA)_3TPTZ$		69.7		
$Eu(tta)_3$ phen	700	31		11. J. Phys. Chem. B 2005, 109, 15278-15287
$Eu(btfa)_3$ phen	210	50		12. Coord. Chem. Rev. 2000, 196, 165-195
$Eu(NTA)_3$ phen	662	40		13. J. Lumin. 2005, 113, 50-63.
$Eu(NTA)_3$ bpy	620	51		14. J. Mater. Chem. 2005, 15, 3117-3125
$Eu(THA)_3Phen$	678			15. Chem. Commun. 2011, 47, 12467–12469
$Eu(TPD)_3Phen$		28		16. J. Lumin. 2007, 124, 51–57
$Eu(tta)_3(L)$	660			17. Inorg. Chem. 2011, 50, 4851–4856