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White light emission by lanthanide doped Sm(III) framework constructed from 4-sulfobenzoate and 1*H*-imidazo[4,5-*f*][1,10]-phenanthroline

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Experimental Section

S1. Materials and Physical measurement

$Eu(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$ were prepared by the corresponding oxide with nitric acid. Other reagents were commercially available and were used without further purification.

Elemental analyses (C, H and N) were performed on an Elementar Vario EL analyzer. Inductively coupled plasma (ICP) spectroscopy was performed on an Agilent 7500Ce spectrometer. Infrared (IR) spectra were measured on a Bruker Tensor37 spectrophotometer using the KBr pellets technique. Thermogravimetric analyses (TGA) were carried out using a HCT-2 thermal analyzer under air from room temperature to 800 °C with a heating rate of 10 °C/min. X-ray diffraction carried out on a PANaytical X'Pert PRO MPD diffractometer for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of $2° \cdot min^{-1}$ and a step size of 0.02° in 2θ. The simulated PXRD patterns were obtained from the single-crystal X-ray diffraction data. Fluorescence spectra were recorded on an FL4500 fluorescence spectrophotometer (Japan Hitachi company) at room temperature. The lifetimes were measured at room temperature on FLS920 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instrument) for complexes **1**, **2** and **4**. The emission quantum yields were measured at room temperature using a Quantum Yield Measurement System Fluorolog®-3 (HORIBA company) with a 450W Xe lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as sample chamber, and an analyzer R928P for signal detection. The Commission International de I'Eclairage (CIE) color coordinates were calculated on the basis of the international CIE standards[1].

S2. Synthesis of the complexes **1-4** and the doped samples

A mixture of $Ln(NO_3)_3 \cdot 6H_2O$ (0.1 mmol) (Ln = Sm **1**, Eu **2**, Gd **3** and Tb **4**), 4-sulfobenzoate (0.15 mmol), 1*H*-imidazo[4,5-*f*][1,10]-phenanthroline) (0.1 mmol), H_2O (8 mL), and an aqueous solution of NaOH (2 mol/L, 0.10 mL) was sealed in a Teflon-lined reactor and heated at 160 °C for 3 days. After slow cooling to room temperature, block crystals of the complexes were obtained. Yield: 44% for **1**, 52% for **2**, 47% for **3** and 56% for **4** based on the Ln(III). For **1**: Anal. Calc. for $C_{40}H_{32}N_8O_{15}S_2Sm_2$: C, 39.07; N, 9.11; H, 2.62%.

Found: C, 38.62; N, 8.71; H, 3.08%. Selected IR (KBr pellet, cm^{-1}): 3421(vs), 1599(s), 1553(s), 1386(s), 1227(m), 1179(s), 1119(w), 1054(w), 1008(w), 816(w), 777(s), 738(m), 639(s), 561(w), 483(w), 418(w). For **2**: Anal. Calc. for $C_{40}H_{32}N_8O_{15}S_2Eu_2$: C, 38.97; N, 9.09; H, 2.62%. Found: C, 38.71; N, 8.83; H, 2.78%. Selected IR (KBr pellet, cm^{-1}): 3409(s), 1598(vs), 1555(vs), 1386(s), 1227(s), 1180(vs), 1119(s), 1055(s), 1008(m), 817(m), 777(s), 739(s), 640(s), 560(m), 484(s), 418(w). For **3**: Anal. Calc. for $C_{40}H_{32}N_8O_{15}S_2Gd_2$: C, 38.64; N, 9.01; H, 2.59%. Found: C, 38.93; N, 9.69; H, 2.84%. Selected IR (KBr pellet, cm^{-1}): 3397(vs), 1595(s), 1554(vs), 1388(s), 1221(m), 1186(m), 1115(m), 1051(s), 1005(s), 816(m), 780(m), 739(s), 643(s), 567(w), 486(m), 415(w). For **4**: Anal. Calc. for $C_{40}H_{32}N_8O_{15}S_2Tb_2$: C, 38.54; N, 8.99; H, 2.59%. Found: C, 39.03; N, 9.29; H, 2.84%. Selected IR (KBr pellet, cm^{-1}): 3413(vs), 1590(s), 1554(vs), 1385(vs), 1221(s), 1182(vs), 1116(s), 1053(s), 1004(s), 817(s), 779(s), 739(m), 642(s), 564(m), 487(m), 418(w).

For isostructural Ln analogies, Eu(III) or Gd(III)/Eu(III) and Tb(III)/Eu(III) codoped into the Sm(III) framework, the synthetic methods are same as mentioned above just by loading the corresponding $Ln(NO_3)_3{\cdot}6H_2O$ as the starting materials in stoichiometric ratios, which is exclusively confirmed by inductively coupled plasma spectroscopy (ICP). For $Sm_{99.83}Eu_{0.17}$, Selected IR (KBr pellet, cm^{-1}): 3428(vs), 1599(m), 1554(m), 1385(m), 1227(m), 1179(m), 1118(w), 1055(w), 1008(w), 816(w), 777(m), 739(w), 639(m), 561(w), 483(w), 419(w). For $Sm_{41.26}Gd_{44.72}Eu_{14.02}$, Selected IR (KBr pellet, cm^{-1}): 3405(m), 1598(s), 1555(s), 1386(s), 1228(s), 1180(vs), 1118(m), 1055(w), 1008(w), 816(w), 778(w), 738(s), 640(s), 562(m), 484(m), 416(w). For $Sm_{27.93}Tb_{53.13}Eu_{18.94}$, Selected IR (KBr pellet, cm^{-1}): 3435(s), 1590(s), 1554(m), 1385(m), 1229(s), 1180(m), 1110(m), 1053(m), 1005(m), 818(w), 784(m), 739(m), 642(w), 563(w), 484(w), 415(w).

S3. Thermogravimetric analyses (TGA) of the complexes **1-4** and the doped samples

Thermogravimetric analyses (TGA) were carried out (Fig. S8). The complexes Sm(III) **1** and Eu(III) **2,** Gd(III) **3** and Tb(III) **4** display similar thermal behaviour, respectively. The complexes **1** and **2** display a gradual weight loss between 68-331℃ for **1** and 75-356℃ for **2**. A second weight loss occurs between 441-564 ℃ for **1** and 429- 556 ℃ for **2.** For the complexes **3** and **4**, the first weight loss occurs between 75-146 ℃ for **3** and 84-145 ℃ for **4.** The observed weight loss is 5.17% for **3** and 5.04% for **4**. Complicated decomposition reaction takes place between

323-585℃ for **3** and 319-586℃ for **4**. The final residue weight is 31.89% for **1**, 33.13% for **2**, 32.69% for **3** and 31.66% for **4.** The thermal behaviour of the $Sm_{99.83}Eu_{0.17}$ doped complex is similar to the complexes Sm(III) **1** and Eu(III) **2** while the thermal behaviour of the $Sm_{41.26}Gd_{44.72}Eu_{14.02}$ and $Sm_{27.93}Tb_{53.13}Eu_{18.94}$ doped complexes is similar to the complexes Gd(III) **3** and Tb(III) **4.**

S4. X-ray crystal structure determination

The X-ray single crystal data collections for the four complexes were performed on a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K. Semiempirical absorption correction was applied on the complex using the SADABS program. The structure was solved by direct methods and refined by full matrix least squares method on F^2 using SHELXS 97 and SHELXL 97 programs.[2, 3] All non-hydrogen atoms in the complexes were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. A summary of the crystallographic data and details of the structure refinements are listed in Table S1. Selected bond distances and bond angles are listed in Table S2.

Table S1. Crystal data and structure refinement for complexes **1-4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{40}H_{32}N_8O_{15}S_2Sm_2$	$C_{40}H_{32}N_8O_{15}S_2Eu_2$	$C_{40}H_{32}N_8O_{15}S_2Gd_2$	$C_{40}H_{32}N_8O_{15}S_2Tb_2$
Formula weight	1229.56	1232.78	1243.36	1246.70
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å , °)				
a	6.9200(4)	6.9016(6)	6.8982(4)	6.8766(7)
b	10.1694(6)	10.1652(9)	10.1549(6)	10.1482(10)
c	15.2822(9)	15.2500(13)	15.2233(8)	15.1965(15)
α	83.6210(10)	83.715(2)	83.8120(10)	83.857(2)
β	78.0290(10)	78.047(2)	78.1380(10)	78.023(2)
γ	77.6100(10)	77.496(2)	77.5150(10)	77.275(2)
Volume ($Å^3$)	1025.05(10)	1019.52(15)	1016.71(10)	1009.83(17)
Z	1	1	1	1
Calculated density / $g\cdot cm^{-3}$	1.992	2.008	2.031	2.050
Absorption coefficient/ mm^{-1}	3.023	3.236	3.422	3.663
F(000)	604	606	608	610
Crystal size / mm^3	0.15×0.11×0.08	0.17×0.13×0.06	0.14×0.09×0.03	0.10×0.07×0.02
Θ range for data collection / (°)	2.39-25.25	2.06-25.24	2.55-25.25	2.06-25.25

Limiting indices	-8≦h≦7;	-8≦h≦8;	-5≦h≦8;	-8≦h≦8;
	-12≦k≦12;	-12≦k≦6;	-11≦k≦12;	-12≦k≦11;
	-18≦l≦12	-18≦l≦16	-18≦l≦18	-18≦l≦17
Reflections collected/unique	[R(int)=0.0224]	[R(int)=0.0367]	[R(int)=0.0313]	[R(int)=0.0358]
	5216 / 3668	5233 / 3646	5112 / 3631	5093 / 3617
Data / restraints / parameters	3668 / 0 / 307	3646 / 0 / 307	3631 / 0 / 307	3617 / 0 / 307
Goodness-of-fit on F^2	0.975	1.025	0.916	1.017
Final R indices[I>2sigma(I)]	R1 = 0.0301	R1 = 0.0448	R1 = 0.0232	R1 = 0.0456
	wR2 = 0.0752	wR2 = 0.1017	wR2 = 0.0639	wR2 = 0.0983
R indices(all data)	R1 = 0.0334	R1 = 0.0536	R1 = 0.0252	R1 = 0.0574
	wR2 = 0.0778	wR2 = 0.1066	wR2 = 0.0653	wR2 = 0.1042
Largest difference peak and hole / e.$Å^{-3}$	0.743 and -0.679	0.798 and -0.692	0.724 and -0.741	1.007 and -1.249
CCDC	956199	956197	956198	956200

Table S2. Selected bond lengths [Å] and angles [°] for complexes **1-4**.

		1	
Sm(1)-O(1A)	2.426(3)	Sm(1)-O(3B)	2.431(3)
Sm(1)-O(4C)	2.451(3)	Sm(1)-O(5)	2.397(3)
Sm(1)-O(6)	2.329(3)	Sm(1)-O(6C)	2.357(3)
Sm(1)-N(1)	2.615(4)	Sm(1)-N(2)	2.624(4)
O(6)-Sm(1)-O(6C)	76.81(11)	O(6)-Sm(1)-O(5)	82.23(11)
O(6C)-Sm(1)-O(5)	72.75(11)	O(6)-Sm(1)-O(1A)	146.99(11)
O(6C)-Sm(1)-O(1A)	77.27(11)	O(5)-Sm(1)-O(1A)	108.96(11)
O(6)-Sm(1)-O(3B)	71.38(11)	O(6C)-Sm(1)-O(3B)	138.99(12)
O(5)-Sm(1)-O(3B)	77.84(11)	O(1A)-Sm(1)-O(3B)	140.45(12)
O(6)-Sm(1)-O(4C)	74.45(11)	O(6C)-Sm(1)-O(4C)	76.47(11)
O(5)-Sm(1)-O(4C)	144.82(11)	O(1A)-Sm(1)-O(4C)	79.90(11)
O(3B)-Sm(1)-O(4C)	117.53(11)	O(6)-Sm(1)-N(1)	115.81(11)
O(6C)-Sm(1)-N(1)	145.48(11)	O(5)-Sm(1)-N(1)	138.11(11)
O(1A)-Sm(1)-N(1)	77.04(12)	O(3B)-Sm(1)-N(1)	73.68(12)
O(4C)-Sm(1)-N(1)	76.64(11)	O(6)-Sm(1)-N(2)	140.80(11)
O(6C)-Sm(1)-N(2)	128.32(11)	O(5)-Sm(1)-N(2)	79.12(11)
O(1A)-Sm(1)-N(2)	72.13(11)	O(3B)-Sm(1)-N(2)	71.14(12)
O(4C)-Sm(1)-N(2)	134.72(11)	N(1)-Sm(1)-N(2)	63.01(11)
		2	
Eu(1)-O(1A)	2.413(5)	Eu(1)-O(3B)	2.426(5)
Eu(1)-O(4C)	2.449(5)	Eu(1)-O(5)	2.384(5)
Eu(1)-O(6)	2.307(5)	Eu(1)-O(6C)	2.338(5)
Eu(1)-N(1)	2.609(6)	Eu(1)-N(2)	2.606(6)
O(6)-Eu(1)-O(6C)	76.38(18)	O(6)-Eu(1)-O(5)	82.75(17)
O(6C)-Eu(1)-O(5)	72.70(17)	O(6)-Eu(1)-O(1A)	146.67(18)

O(6C)-Eu(1)-O(1A)	77.26(17)	O(5)-Eu(1)-O(1A)	108.30(18)
O(6)-Eu(1)-O(3B)	71.60(17)	O(6C)-Eu(1)-O(3B)	138.77(17)
O(5)-Eu(1)-O(3B)	78.06(17)	O(1A)-Eu(1)-O(3B)	140.64(18)
O(6)-Eu(1)-O(4C)	74.62(17)	O(6C)-Eu(1)-O(4C)	76.31(17)
O(5)-Eu(1)-O(4C)	145.08(17)	O(1A)-Eu(1)-O(4C)	79.62(18)
O(3B)-Eu(1)-O(4C)	117.88(18)	O(6)-Eu(1)-N(1)	115.63(18)
O(6C)-Eu(1)-N(1)	145.78(18)	O(5)-Eu(1)-N(1)	137.96(17)
O(1A)-Eu(1)-N(1)	77.60(19)	O(3B)-Eu(1)-N(1)	73.46(18)
O(4C)-Eu(1)-N(1)	76.63(17)	O(6)-Eu(1)-N(2)	141.07(17)
O(6C)-Eu(1)-N(2)	128.36(17)	O(5)-Eu(1)-N(2)	78.72(16)
O(1A)-Eu(1)-N(2)	72.16(18)	O(3B)-Eu(1)-N(2)	71.23(17)
O(4C)-Eu(1)-N(2)	134.62(17)	N(1)-Eu(1)-N(2)	63.24(17)
		3	
Gd(1)-O(1A)	2.412(3)	Gd(1)-O(3B)	2.420(3)
Gd(1)-O(4C)	2.423(3)	Gd(1)-O(5)	2.367(3)
Gd(1)-O(6)	2.312(3)	Gd(1)-O(6C)	2.339(3)
Gd(1)-N(1)	2.594(3)	Gd(1)-N(2)	2.603(3)
O(6)-Gd(1)-O(6C)	77.28(9)	O(6)-Gd(1)-O(5)	82.67(9)
O(6C)-Gd(1)-O(5)	72.95(9)	O(6)-Gd(1)-O(1A)	146.72(10)
O(6C)-Gd(1)-O(1A)	76.69(9)	O(5)-Gd(1)-O(1A)	108.83(9)
O(6)-Gd(1)-O(3B)	71.38(9)	O(6C)-Gd(1)-O(3B)	139.18(9)
O(5)-Gd(1)-O(3B)	77.64(9)	O(1A)-Gd(1)-O(3B)	140.72(10)
O(6)-Gd(1)-O(4C)	74.50(9)	O(6C)-Gd(1)-O(4C)	76.74(9)
O(5)-Gd(1)-O(4C)	145.32(9)	O(1A)-Gd(1)-O(4C)	79.62(9)
O(3B)-Gd(1)-O(4C)	117.65(9)	O(6)-Gd(1)-N(1)	114.95(9)
O(6C)-Gd(1)-N(1)	145.44(9)	O(5)-Gd(1)-N(1)	138.13(10)
O(1A)-Gd(1)-N(1)	77.75(10)	O(3B)-Gd(1)-N(1)	73.50(10)
O(4C)-Gd(1)-N(1)	76.09(9)	O(6)-Gd(1)-N(2)	141.00(9)
O(6C)-Gd(1)-N(2)	127.82(9)	O(5)-Gd(1)-N(2)	78.80(9)
O(1A)-Gd(1)-N(2)	72.21(10)	O(3B)-Gd(1)-N(2)	71.27(9)
O(4C)-Gd(1)-N(2)	134.49(9)	N(1)-Gd(1)-N(2)	63.63(9)
		4	
Tb(1)-O(1A)	2.403(5)	Tb(1)-O(3B)	2.406(5)
Tb(1)-O(4C)	2.421(5)	Tb(1)-O(5)	2.354(5)
Tb(1)-O(6)	2.294(5)	Tb(1)-O(6C)	2.323(5)
Tb(1)-N(1)	2.574(6)	Tb(1)-N(2)	2.577(6)
O(6)-Tb(1)-O(6C)	76.73(19)	O(6)-Tb(1)-O(5)	82.60(18)
O(6C)-Tb(1)-O(5)	73.03(18)	O(6)-Tb(1)-O(1A)	146.80(19)
O(6C)-Tb(1)-O(1A)	76.87(18)	O(5)-Tb(1)-O(1A)	108.33(18)
O(6)-Tb(1)-O(3B)	71.66(18)	O(6C)-Tb(1)-O(3B)	139.19(19)
O(5)-Tb(1)-O(3B)	77.84(18)	O(1A)-Tb(1)-O(3B)	140.52(19)
O(6)-Tb(1)-O(4C)	74.94(18)	O(6C)-Tb(1)-O(4C)	76.44(18)

O(5)-Tb(1)-O(4C)	145.44(18)	O(1A)-Tb(1)-O(4C)	79.58(18)
O(3B)-Tb(1)-O(4C)	117.94(18)	O(6)-Tb(1)-N(1)	115.09(18)
O(6C)-Tb(1)-N(1)	145.42(18)	O(5)-Tb(1)-N(1)	138.23(18)
O(1A)-Tb(1)-N(1)	78.03(19)	O(3B)-Tb(1)-N(1)	73.34(19)
O(4C)-Tb(1)-N(1)	75.93(18)	O(6)-Tb(1)-N(2)	140.96(18)
O(6C)-Tb(1)-N(2)	128.26(18)	O(5)-Tb(1)-N(2)	78.73(18)
O(1A)-Tb(1)-N(2)	72.13(19)	O(3B)-Tb(1)-N(2)	71.05(19)
O(4C)-Tb(1)-N(2)	134.30(18)	N(1)-Tb(1)-N(2)	63.74(18)

Symmetry transformations used to generate equivalent atoms: For **1-4**, A: -x+1, -y+1, -z; B: -x, -y+1, -z+2; C:-x+1, -y, -z.

Table S3. Hydrogen bond lengths and bond angles for complexes **1-4**.

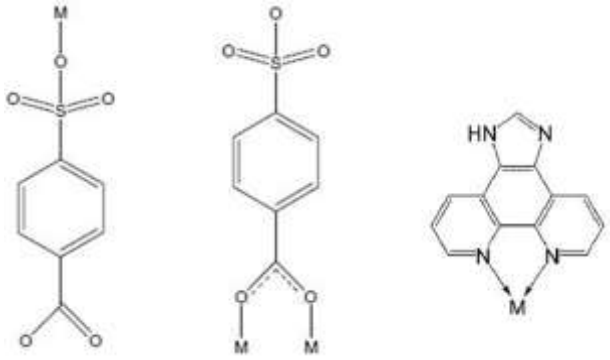
D-H···A	*d*(D-H) / Å	*d*(H···A) / Å	*d*(D···A) / Å	∠DHA / °
		1		
N4-H4···O2#1	0.86	1.92	2.782(5)	176
O1W-H1WB···O6#4	0.85	2.22	2.953(6)	144
O2W-H2WA···N3#5	0.85	1.99	2.834(10)	170
O6-H6A···O1#6	0.86	2.13	2.987(4)	179
		2		
N4-H4···O2#1	0.86	1.93	2.786(8)	175
O1W-H1WB···O6#4	0.85	2.23	2.956(9)	144
O2W-H2WA···N3#5	0.85	2.01	2.846(15)	170
O6-H6A···O1#6	0.85	2.11	2.966(7)	179
		3		
N4-H4···O2#1	0.86	1.92	2.774(5)	176
O1W-H1WB···O6#4	0.85	2.22	2.950(5)	143
O2W-H2WA···N3#5	0.85	1.99	2.833(9)	170
O6-H6A···O1#6	0.85	2.10	2.948(4)	179
		4		
N4-H4···O2#1	0.86	1.93	2.784(9)	176
O1W-H1WB···O6#4	0.85	2.25	2.975(9)	144
O2W-H2WA···N3#5	0.85	2.02	2.858(15)	170
O6-H6A···O1#6	0.85	2.09	2.938(7)	179

Symmetry transformations used to generate equivalent atoms: For **1-4**, #1: x, -1+y, 1+z; #4: 1-x, -y, 1-z; #5: 1-x, 1-y, 1-z; #6: x, -1+y, z.

Table S4. CIE chromaticity coordinates, color rendering index (CRI) and correlated color temperature (CCT) for the doped complexes excited at 340 to 395nm.

Excitation wavelength λ_{ex} / nm	$Sm_{99.83}Eu_{0.17}$			$Sm_{41.26}Gd_{44.72}Eu_{14.02}$			$Sm_{27.93}Tb_{53.13}Eu_{18.94}$		
	CIE chromaticity coordinates (x, y)	CRI	CCT (K)	CIE chromaticity coordinates (x, y)	CRI	CCT (K)	CIE chromaticity coordinates (x, y)	CRI	CCT (K)
340	(0.356, 0.325)	66.9	4478	(0.345, 0.355)	83.9	4992	(0.349, 0.359)	88.1	4867

350	(0.345, 0.321)	66.3	4911	(0.347, 0.350)	82.6	4902	(0.350, 0.353)	87.2	4824
360	(0.345, 0.319)	65.6	4870	(0.347, 0.344)	81.3	4891	(0.349, 0.348)	87.0	4851
370	**(0.337, 0.316) A**	**66.6**	**5259**	(0.345, 0.338)	80.6	4963	(0.342, 0.341)	86.1	5090
375	(0.328, 0.316)	68.3	5713	(0.342, 0.335)	80.2	5070	(0.339, 0.337)	86.0	5218
380	(0.314, 0.318)	72.1	6505	(0.340, 0.333)	79.7	5142	(0.336, 0.335)	85.9	5319
385	(0.289, 0.322)	78.1	8006	(0.336, 0.331)	80.5	5328	**(0.330, 0.333) C**	**85.9**	**5595**
390	(0.257, 0.323)	78.7	10404	**(0.332, 0.330) B**	**81.2**	**5523**	(0.309, 0.319)	86.6	6818
395	(0.230, 0.326)	66.6	12563	(0.321, 0.328)	84.7	6032	(0.285, 0.315)	87.7	8478



Scheme S1. The coordination modes of the ligands in complexes **1-4**.

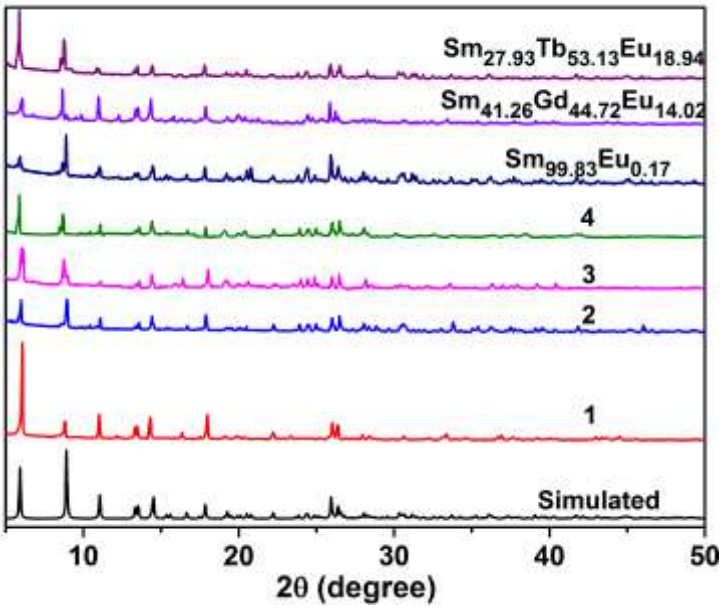


Fig. S1 The PXRD patterns for complexes **1-4** and the doped complexes.

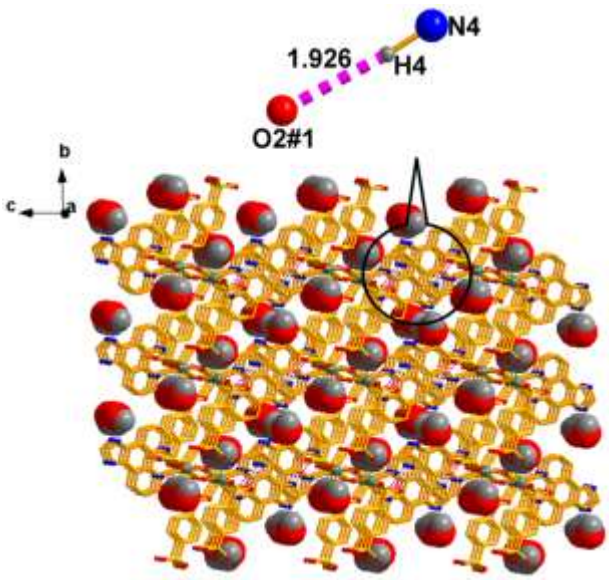


Fig. S2 3D porous structure by hydrogen bonds for complex **4**, free water molecules present in the cavity. Symmetry codes: #1: x, -1+y, 1+z.

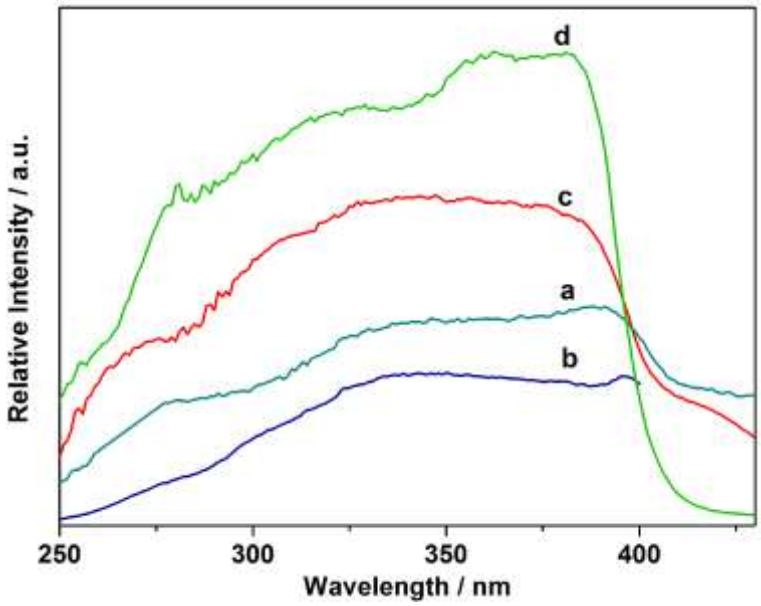


Fig. S3 Excitation spectra of complexes **3** (a), **1** (b), **2** (c) and **4** (d) in the solid state at room temperature.

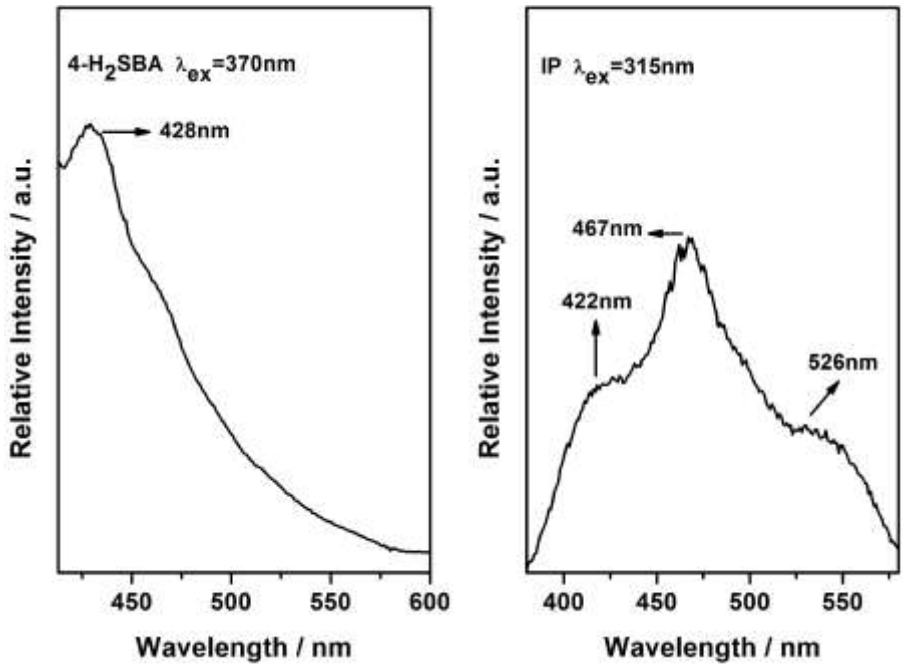
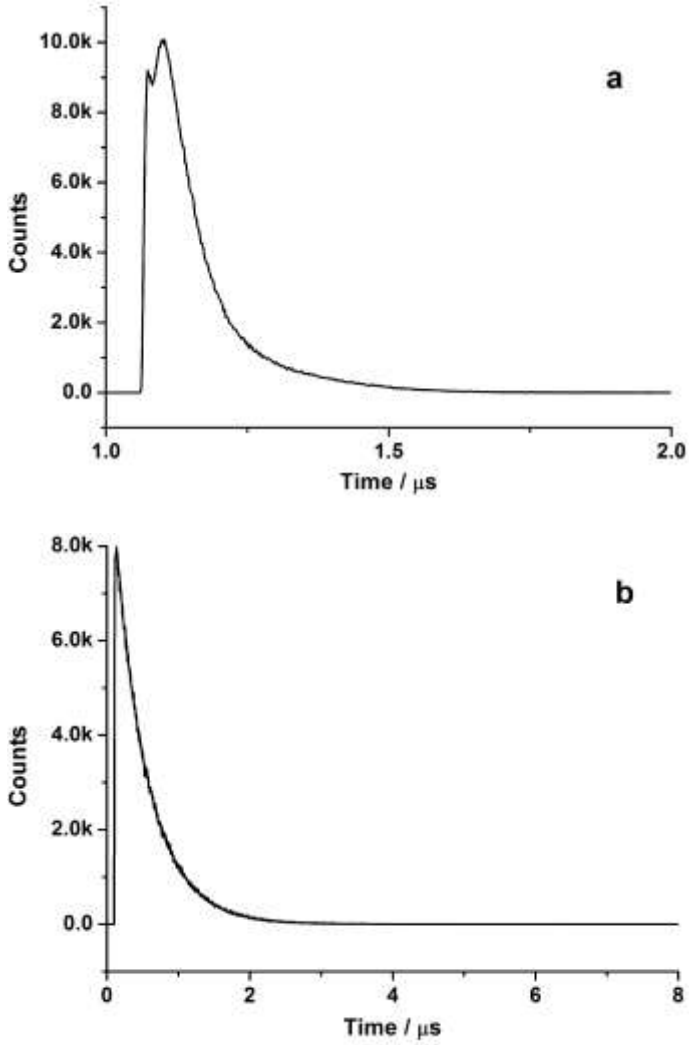


Fig. S4 Emission spectra of 4-H_2SBA and IP.



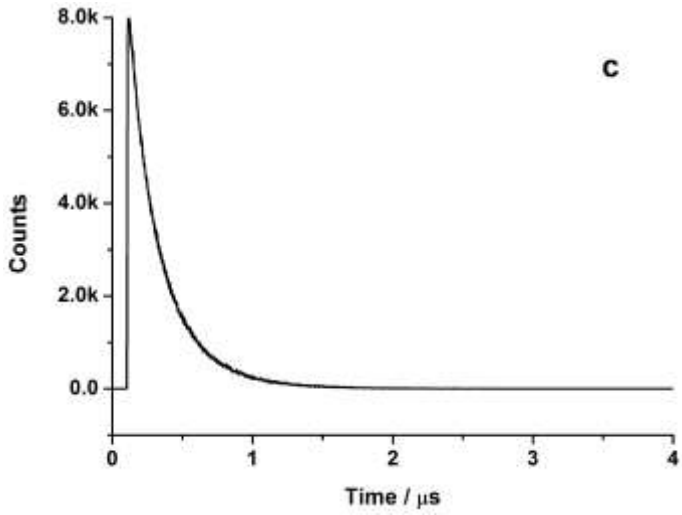
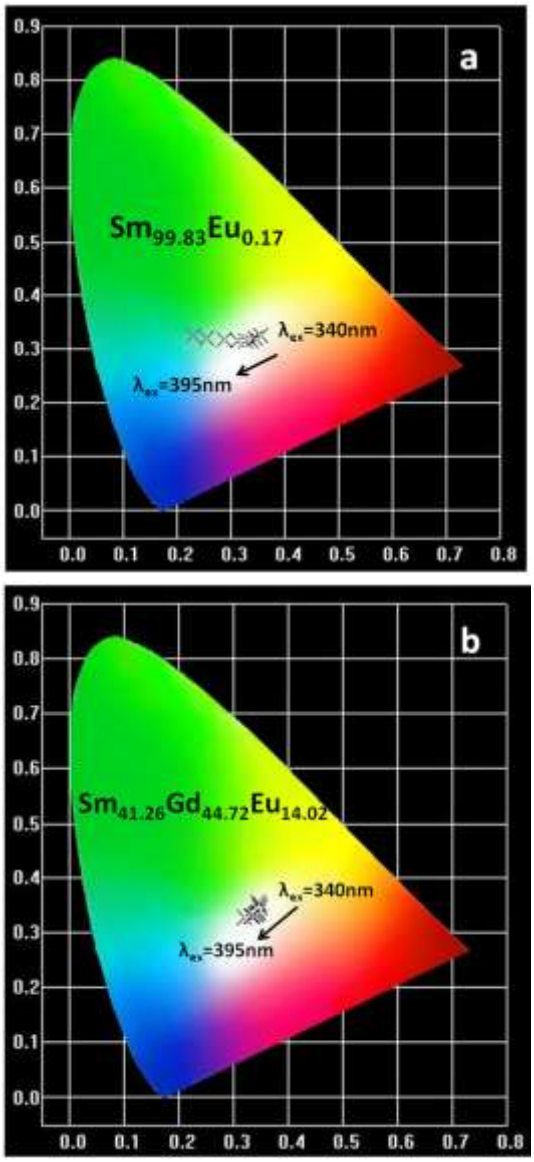


Fig. S5 Decay profile of complexes **1**(a), **2**(b) and **4**(c).



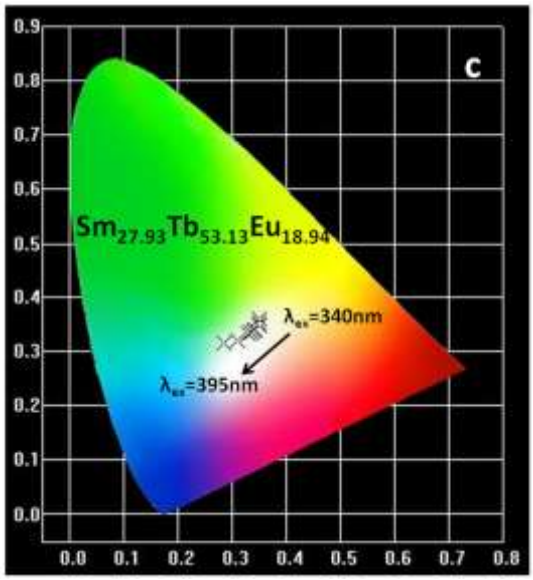
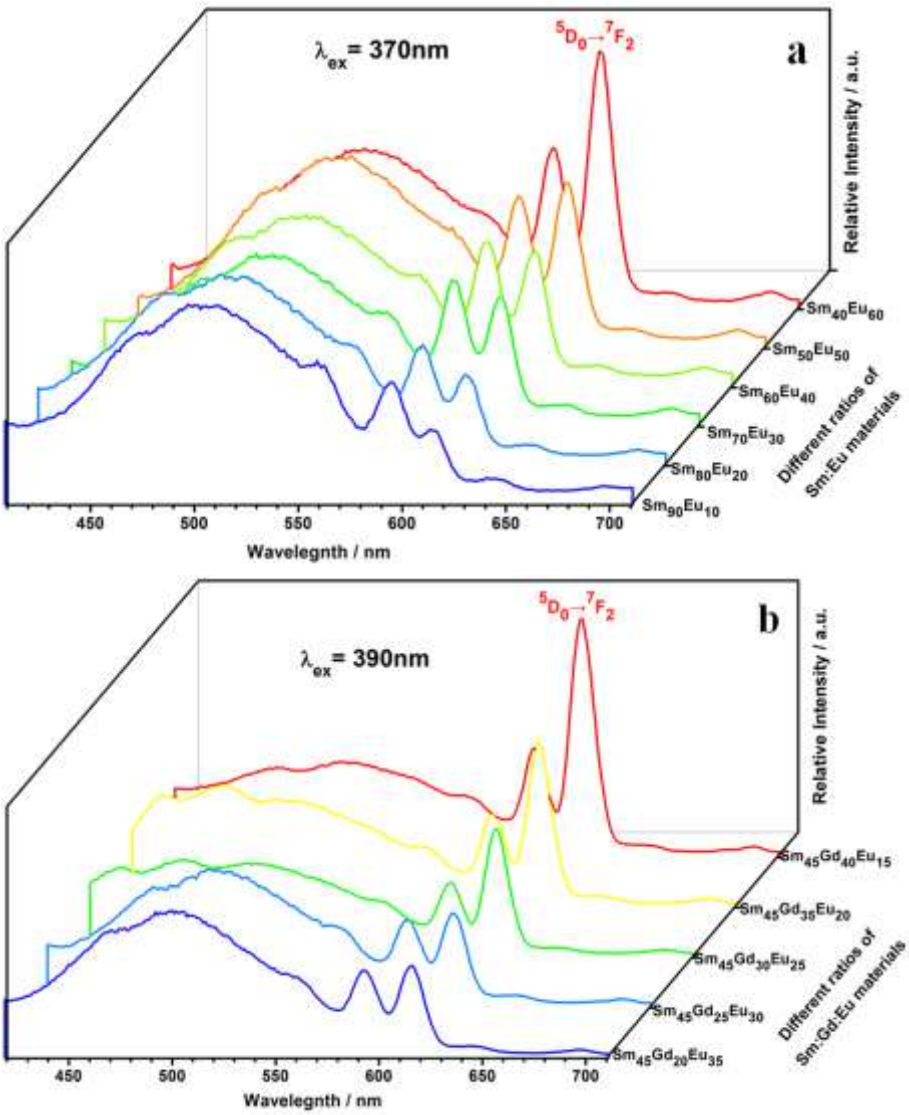


Fig. S6 The CIE chromaticity diagram for the doped complexes $Sm_{99.83}Eu_{0.17}$(a), $Sm_{41.26}Gd_{44.72}Eu_{14.02}$(b) and $Sm_{27.93}Tb_{53.13}Eu_{18.94}$(c).



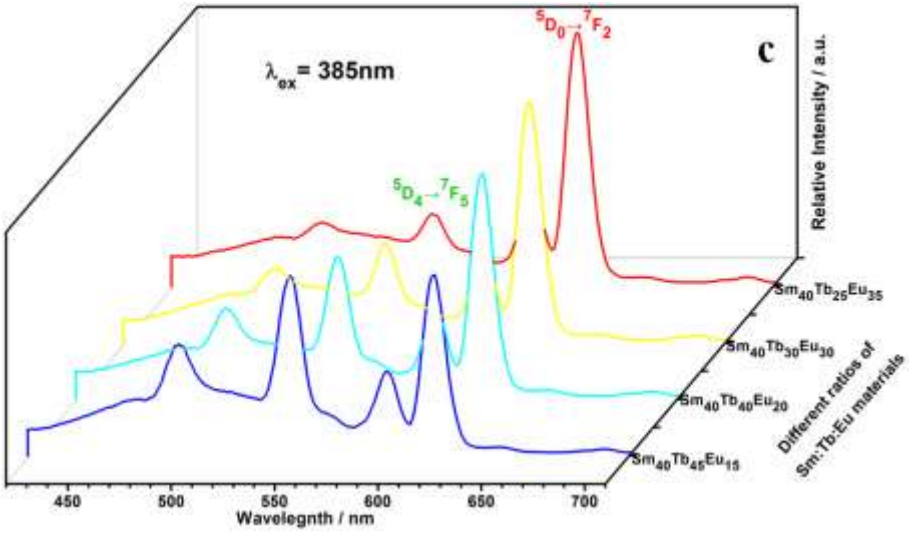


Fig. S7 Emission spectra of the doped complexes Sm:Eu (a), Sm:Gd,Eu (b) and Sm:Tb,Eu (c).

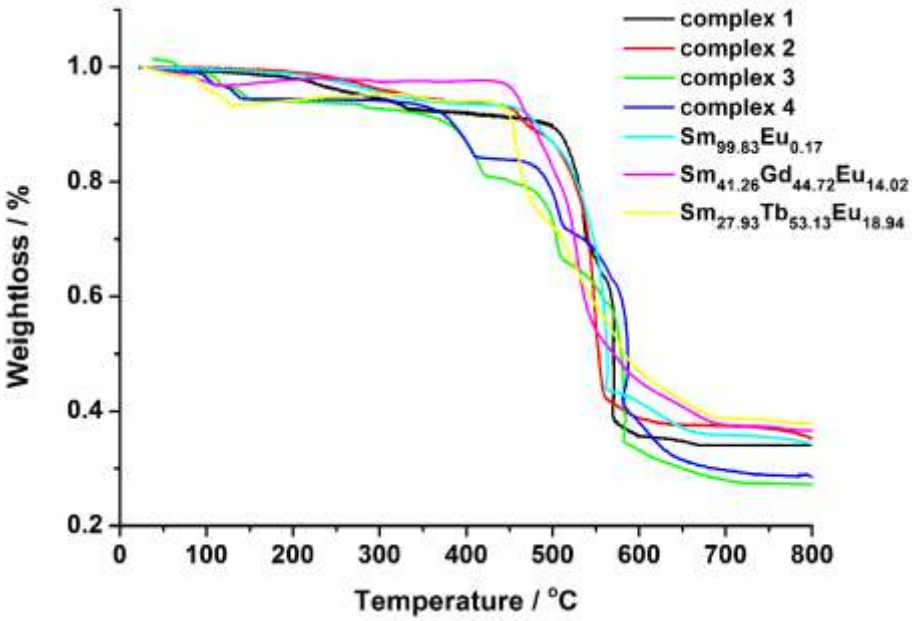


Fig. S8 TGA curve of the complexes **1**-**4** and the doped complexes.

References:

1. T. Smith; J. Guild, *Trans Opt. Soc.* 1931, ***33***, 73.

2. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Refinement, University of Göttingen (1997).

3. G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Solution, University of Göttingen (1997).