White light emission based on single component Sm(III) framework and two component Eu(III)- doped Gd(III) framework constructed from 2,2′-diphenyldicarboxylate and 1H-imidazo[4,5-f][1,10]-phenanthroline

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Experimental Section

S1. Materials and Physical measurement

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

Infrared (IR) spectra were measured on a Bruker Tensor37 spectrophotometer using the KBr pellets technique. 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. X-ray diffraction carried out on a PANaytical X'Pert PROMPD diffractometer for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of $2°·min^{-1}$ and a step size of 0.02° in 2θ. The simulated PXRD patterns were obtained from the single-crystal X-ray diffraction data. 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. Solid state fluorescence spectra were recorded on an FL4500 fluorescence spectrophotometer (Japan Hitachi company) at room temperature in identical operating conditions. The lifetimes were measured at room temperature on FLS920 Steady State &Time-resolved Fluorescence Spectrometer (Edinburgh Instrument) for complexes **1** and **2**. 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 and correlated color temperature were calculated on the basis of the international CIE standards.[1]

S2. Synthesis of complexes **1-3**

A mixture of $Ln(NO_3)_3·6H_2O$ (0.1 mmol) (Ln = Sm, Eu, and Gd), 2,2'-diphenyldicarboxylic acid (0.15 mmol), 1H-imidazo[4,5-f][1,10]-phenanthroline (0.1 mmol), H_2O (10 mL), and an aqueous solution of NaOH (1 mol/L, 0.30 mL) was

sealed in a Teflon-lined reactor and heated at 120 °C for 3 days. After slow cooling to room temperature, block crystals of the complexes were obtained. Yield: 62% for **1**, 52% for **2**, and 60% for **3** based on the Ln(III). For **1**: Anal. Calc. for $C_{34}H_{22}SmN_4O_7$: C, 54.52; N, 7.48; H, 2.96%. Found: C, 54.00; N, 7.61; H, 3.17%. Selected IR (KBr pellet, cm^{-1}): 3428(s), 1604(s), 1552(vs), 1450(s), 1415(vs), 1395(vs), 1156(w), 1078(m), 1049(m), 945(w), 860(w), 748(m), 738(m), 671(m), 636(m), 416(w). For **2**: Anal. Calc. for $C_{34}H_{22}EuN_4O_7$: C, 54.41; N, 7.47; H, 2.95%. Found: C, 53.97; N, 7.53; H, 3.14%. Selected IR (KBr pellet, ν/cm^{-1}): 3423(s), 1605(s), 1553(vs), 1452(s), 1415(vs), 1395(vs), 1157(w), 1078(m), 944(w), 860(w), 748(m), 737(m), 671(m), 636(w), 417(w). For **3**: Anal. Calc. for $C_{34}H_{22}GdN_4O_7$: C, 54.03; N, 7.41; H,2.93%. Found: C, 53.75; N, 7.49; H, 3.12%. Selected IR (KBr pellet, cm^{-1}): 3430(s), 1605(s), 1546(vs), 1452(s), 1415(vs), 1156(w), 1078(m), 944(w), 862(m), 754(m), 737(m), 680(m), 637(w), 415(w).

S3. X-ray crystal structure determination

The X-ray single crystal data collections for the three 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.

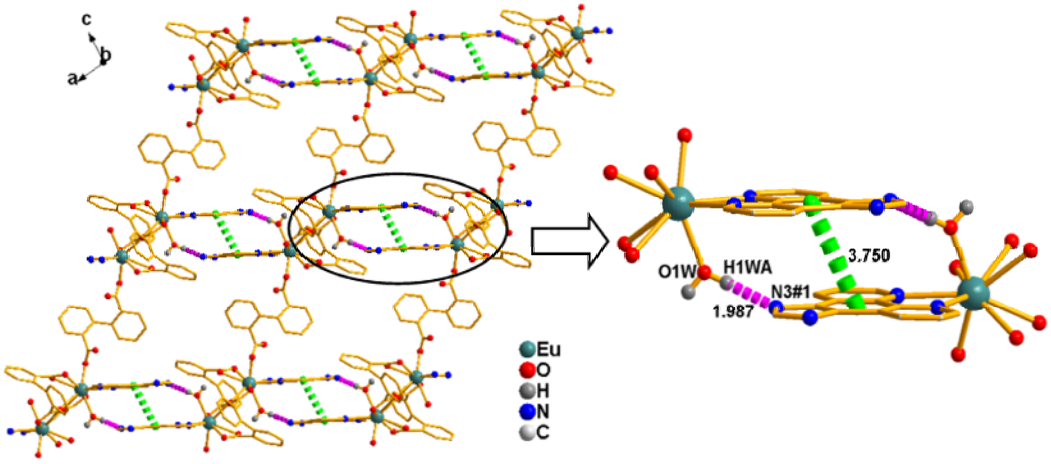


Figure S1. The 2D supramolecular network of complex **2.**

Symmetry code: #1: -x, y, -z+3/2.

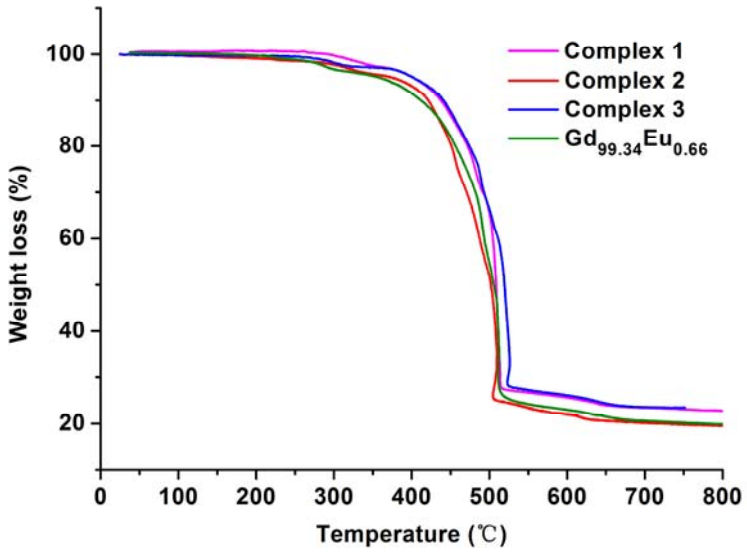


Figure S2. The TGA curves of complexes **1 - 3** and the $Gd_{99.34}Eu_{0.66}$ doped complex

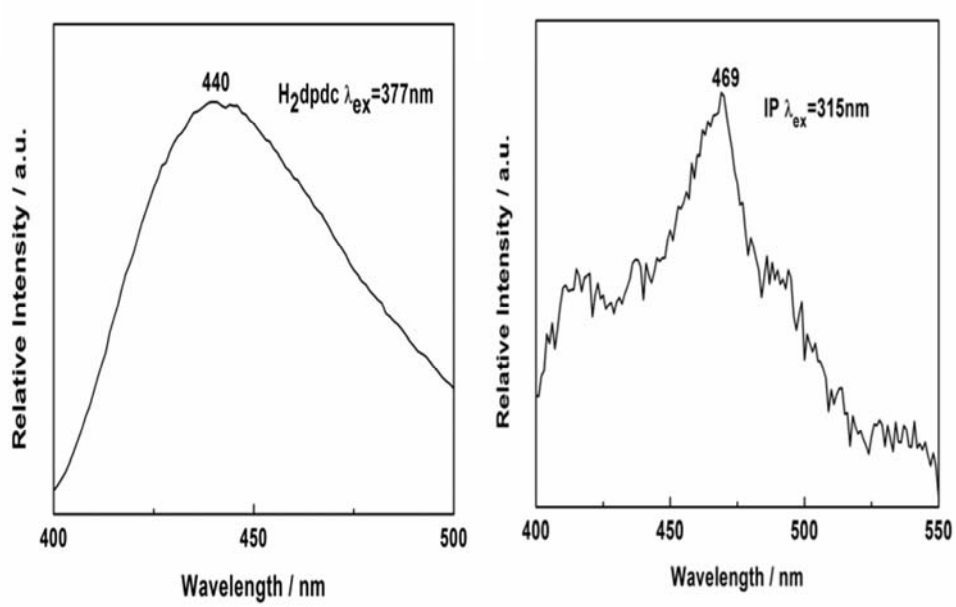


Figure S3. Emission spectra of H_2dpdc and IP in the solid state at room temperature.

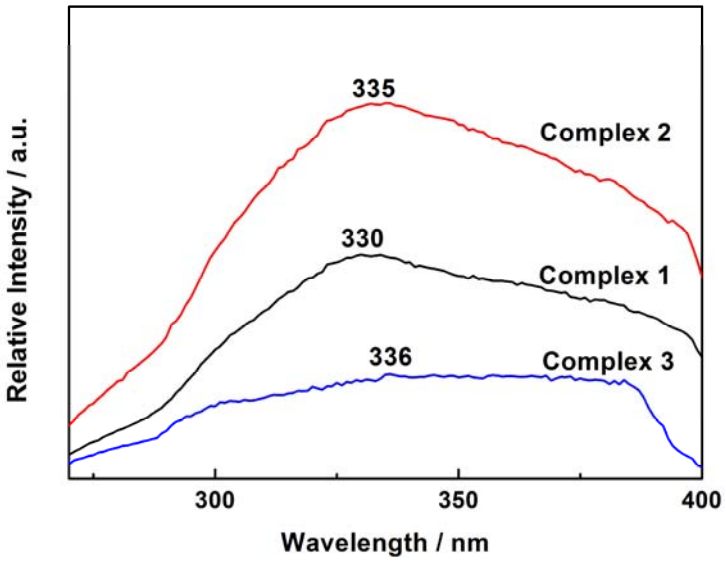
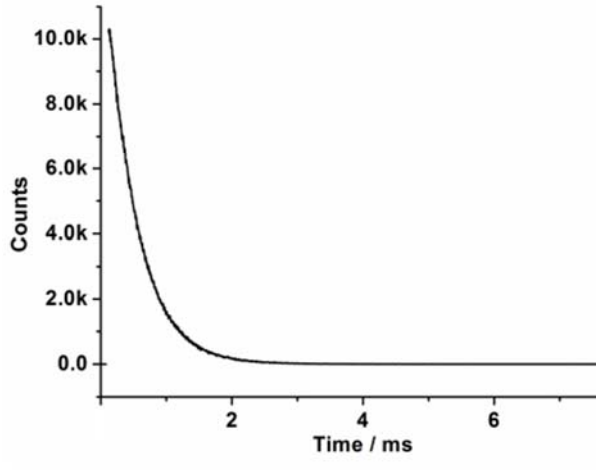
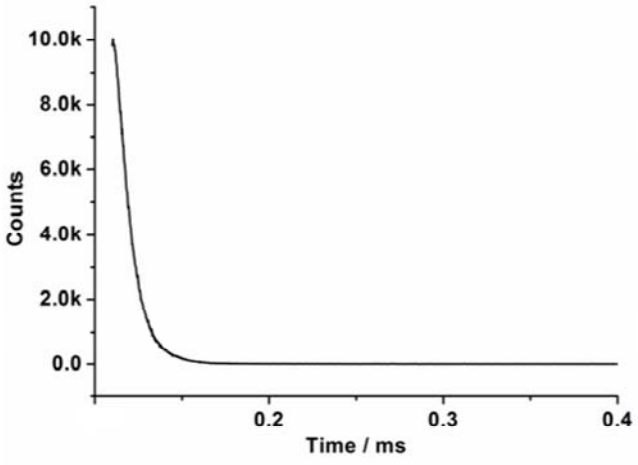


Figure S4. Excitation spectra of complexes **1-3** in the solid state at room temperature.



(a)



(b)

Figure S5. Decay profile of the complexes **2**(a) and **1**(b).

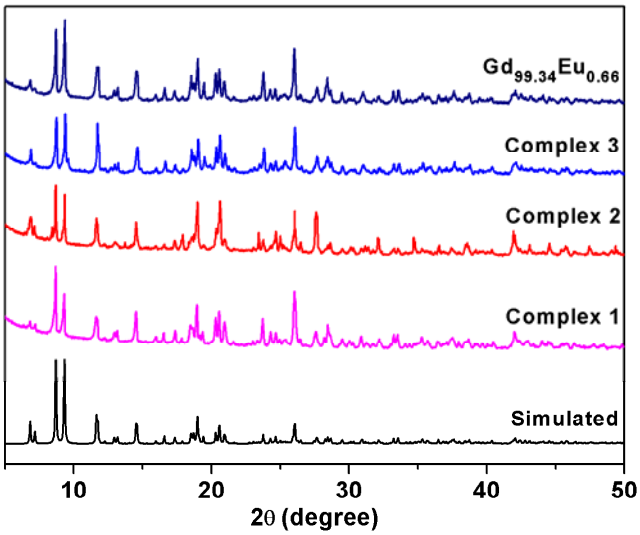
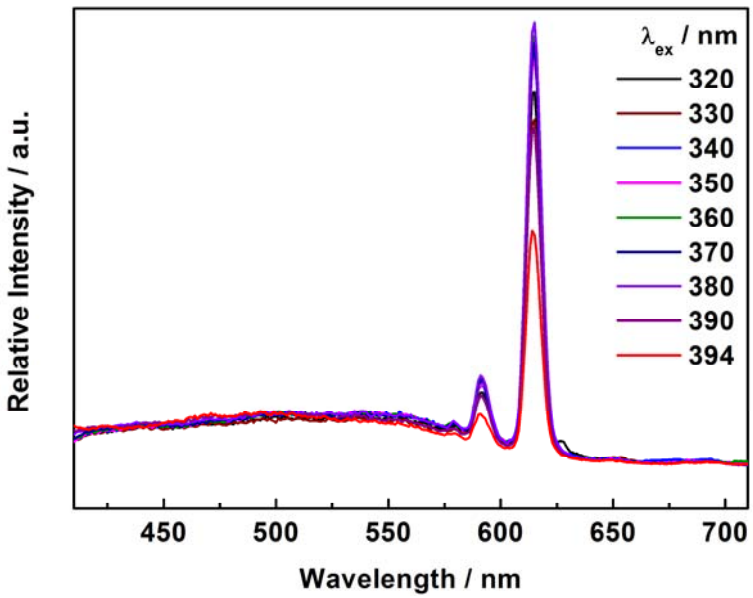
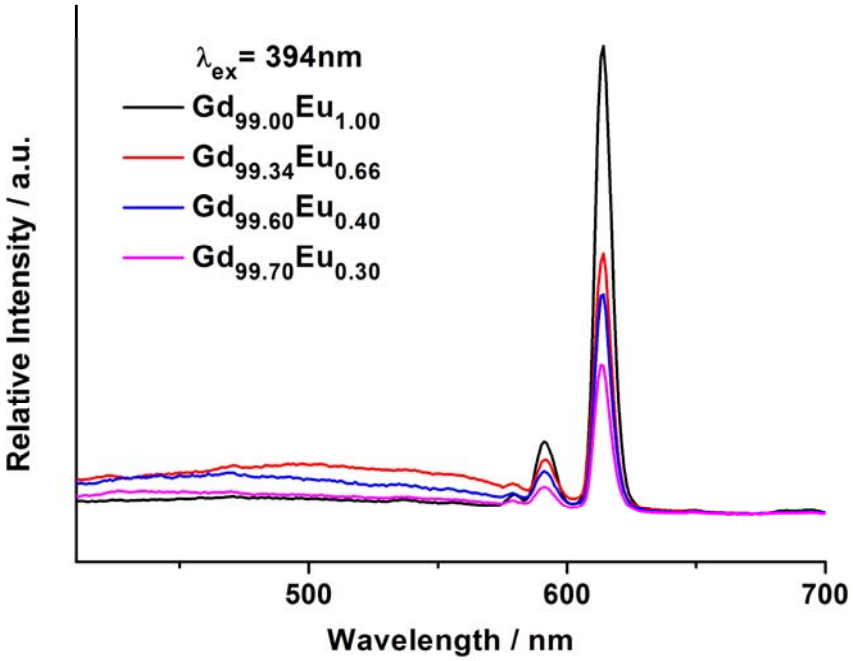
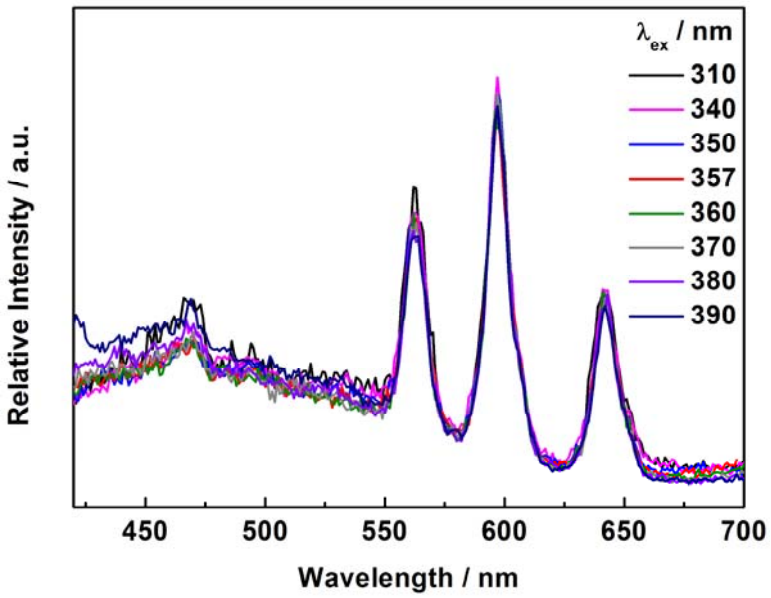


Figure S6. The PXRD patterns for complexes **1 -3** and the $Gd_{99.34}Eu_{0.66}$ doped complex.



(a)





(b)

Figure S7. Emission spectra of $Gd_{99.34}Eu_{0.66}$ doped complex excited at 320 - 394 nm (a) and complex **1** excited at 310 - 390 nm (b).

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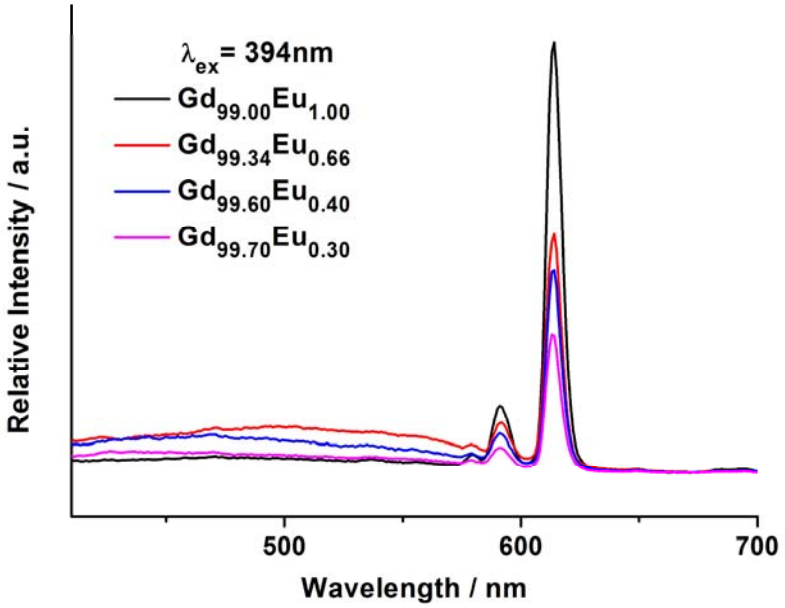

Figure S8. Emission spectra of Gd:Eu doped complexes excited at 394 nm.

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

Complex	**1**	**2**	**3**
Empirical formula	$C_{34}H_{22}SmN_4O_7$	$C_{34}H_{22}EuN_4O_7$	$C_{34}H_{22}GdN_4O_7$
Formula weight	748.91	750.52	755.81
Crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
Unit cell dimensions (Å , °)			
a	24.778(12)	24.8251(13)	24.833(6)
b	15.194(8)	15.1782(8)	15.143(3)
c	15.200(7)	15.1878(9)	15.160(3)
β	97.601(12)	97.7670(10)	97.889(6)
Volume ($Å^3$)	5672(5)	5670.3(5)	5647(2)
Z	8	8	8
Calculated density / g· cm^{-3}	1.754	1.758	1.778
Absorption coefficient/ mm^{-1}	2.131	2.273	2.410
F(000)	2976	2984	2992
Crystal size / mm^3	0.06x0.04x0.03	0.16x0.09x0.07	0.20x0.10x0.05
θ range for data collection / (°)	1.66 to 25.00	2.00 to 25.00	1.58 to 25.00
Limiting indices	-29≦h≦29;	-29≦h≦21;	-29<=h<=27;
	-18≦k≦18;	-17≦k≦18;	-18<=k<=17;
	-18≦l≦14	-18≦l≦16	-18<=l<=16
Reflections collected/unique	[R(int)= 0.2037]	[R(int)= 0.0433]	[R(int)= 0.1634]
	13848 / 5000	13749 / 5003	13689 / 4974
Data / restraints / parameters	5000 / 14 / 421	5003 / 2 / 421	4974 / 0 / 415
Goodness-of-fit on F^2	0.930	1.027	0.943

Final R indices[I>2sigma(I)]	R1 = 0.0736	R1 = 0.0351	R1 = 0.0678
	wR2 =0.1048	wR2 =0.0769	wR2 =0.1143
R indices(all data)	R1 = 0.1810	R1 = 0.0516	R1 = 0.1569
	wR2 = 0.1421	wR2 = 0.0843	wR2 = 0.1512
Largest difference	0.961 and -0.879	2.047 and -0.842	1.388 and - 1.039
peak and hole / e.Å^{-3}			
CCDC No.	948899	948900	948901

Table S2. Selected bond lengths [Å] and angles [°] for complexes **1- 3**

		1	
Sm(1)-O(5)	2.331(9)	Sm(1)-O(1W)	2.415(10)
Sm(1)-O(4)#1	2.465(8)	Sm(1)-O(2)	2.489(8)
Sm(1)-O(3)#1	2.548(7)	Sm(1)-N(2)	2.605(10)
Sm(1)-O(1)#1	2.606(10)	Sm(1)-N(1)	2.626(9)
Sm(1)-O(1)	2.661(9)		
O(5)-Sm(1)-O(1W)	146.8(3)	O(5)-Sm(1)-O(4)#1	84.1(3)
O(1W)-Sm(1)-O(4)#1	123.8(3)	O(5)-Sm(1)-O(2)	78.4(3)
O(1W)-Sm(1)-O(2)	83.6(3)	O(4)#1-Sm(1)-O(2)	146.9(3)
O(5)-Sm(1)-O(3)#1	75.1(3)	O(1W)-Sm(1)-O(3)#1	134.9(3)
O(4)#1-Sm(1)-O(3)#1	51.9(3)	O(2)-Sm(1)-O(3)#1	96.1(3)
O(5)-Sm(1)-N(2)	100.2(3)	O(1W)-Sm(1)-N(2)	74.6(3)
O(4)#1-Sm(1)-N(2)	73.8(3)	O(2)-Sm(1)-N(2)	136.7(3)
O(3)#1-Sm(1)-N(2)	125.7(3)	O(5)-Sm(1)-O(1)#1	143.2(3)
O(1W)-Sm(1)-O(1)#1	69.2(3)	O(4)#1-Sm(1)-O(1)#1	70.7(3)
O(2)-Sm(1)-O(1)#1	108.5(3)	O(3)#1-Sm(1)-O(1)#1	68.2(3)
N(2)-Sm(1)-O(1)#1	98.2(3)	O(5)-Sm(1)-N(1)	75.9(3)
O(1W)-Sm(1)-N(1)	72.8(3)	O(4)#1-Sm(1)-N(1)	126.6(3)
O(2)-Sm(1)-N(1)	75.8(3)	O(3)#1-Sm(1)-N(1)	150.9(3)
N(2)-Sm(1)-N(1)	62.2(3)	O(1)#1-Sm(1)-N(1)	140.9(3)
O(5)-Sm(1)-O(1)	109.7(3)	O(1W)-Sm(1)-O(1)	77.2(3)
O(4)#1-Sm(1)-O(1)	114.1(3)	O(2)-Sm(1)-O(1)	48.9(3)
O(3)#1-Sm(1)-O(1)	69.6(3)	N(2)-Sm(1)-O(1)	149.6(3)
O(1)#1-Sm(1)-O(1)	60.8(3)	N(1)-Sm(1)-O(1)	119.2(3)
		2	
Eu(1)-O(5)	2.317(4)	Eu(1)-O(1W)	2.401(4)
Eu(1)-O(4)#1	2.443(3)	Eu(1)-O(2)	2.466(4)
Eu(1)-O(3)#1	2.547(3)	Eu(1)-N(1)	2.622(4)
Eu(1)-O(1)	2.688(3)	Eu(1)-N(2)	2.596(4)
Eu(1)-O(1)#1	2.560(3)		
O(5)-Eu(1)-O(1W)	146.27(14)	O(5)-Eu(1)-O(4)#1	83.23(13)
O(1W)-Eu(1)-O(4)#1	124.37(13)	O(5)-Eu(1)-O(2)	79.08(14)

O(1W)-Eu(1)-O(2)	83.85(14)	O(4)#1-Eu(1)-O(2)	146.36(12)
O(5)-Eu(1)-O(3)#1	75.43(12)	O(1W)-Eu(1)-O(3)#1	135.44(12)
O(4)#1-Eu(1)-O(3)#1	52.28(11)	O(2)-Eu(1)-O(3)#1	95.36(12)
O(5)-Eu(1)-O(1)#1	143.78(12)	O(1W)-Eu(1)-O(1)#1	69.50(12)
O(4)#1-Eu(1)-O(1)#1	71.04(11)	O(2)-Eu(1)-O(1)#1	108.79(11)
O(3)#1-Eu(1)-O(1)#1	68.73(11)	O(5)-Eu(1)-N(2)	98.70(13)
O(1W)-Eu(1)-N(2)	74.69(12)	O(4)#1-Eu(1)-N(2)	73.78(11)
O(2)-Eu(1)-N(2)	136.98(12)	O(3)#1-Eu(1)-N(2)	126.03(11)
O(1)#1-Eu(1)-N(2)	98.05(11)	O(5)-Eu(1)-N(1)	75.16(13)
O(1W)-Eu(1)-N(1)	72.52(13)	O(4)#1-Eu(1)-N(1)	126.69(12)
O(2)-Eu(1)-N(1)	75.68(13)	O(3)#1-Eu(1)-N(1)	150.38(12)
O(1)#1-Eu(1)-N(1)	140.87(12)	N(2)-Eu(1)-N(1)	62.54(13)
O(5)-Eu(1)-O(1)	111.47(12)	O(1W)-Eu(1)-O(1)	77.27(11)
O(4)#1-Eu(1)-O(1)	113.70(10)	O(2)-Eu(1)-O(1)	49.71(11)
O(3)#1-Eu(1)-O(1)	69.12(10)	O(1)#1-Eu(1)-O(1)	60.24(13)
N(2)-Eu(1)-O(1)	149.39(11)	N(1)-Eu(1)-O(1)	119.51(12)
		3	
Gd(1)-O(5)	2.301(7)	Gd(1)-O(1W)	2.386(7)
Gd(1)-O(4)#1	2.423(6)	Gd(1)-O(1)#1	2.545(7)
Gd(1)-O(3)#1	2.555(6)	Gd(1)-N(1)	2.602(7)
Gd(1)-O(1)	2.688(7)	Gd(1)-N(2)	2.580(8)
Gd(1)-O(2)	2.439(6)		
O(5)-Gd(1)-O(1W)	146.2(2)	O(5)-Gd(1)-O(4)#1	82.5(2)
O(1W)-Gd(1)-O(4)#1	124.6(2)	O(5)-Gd(1)-O(2)	79.6(2)
O(1W)-Gd(1)-O(2)	84.7(2)	O(4)#1-Gd(1)-O(2)	145.3(2)
O(5)-Gd(1)-O(3)#1	75.9(2)	O(1W)-Gd(1)-O(3)#1	135.3(2)
O(4)#1-Gd(1)-O(3)#1	52.2(2)	O(2)-Gd(1)-O(3)#1	94.4(2)
O(5)-Gd(1)-O(1)#1	143.8(2)	O(1W)-Gd(1)-O(1)#1	69.8(2)
O(4)#1-Gd(1)-O(1)#1	71.0(2)	O(2)-Gd(1)-O(1)#1	108.7(2)
O(3)#1-Gd(1)-O(1)#1	68.4(2)	O(5)-Gd(1)-N(2)	97.3(2)
O(1W)-Gd(1)-N(2)	75.0(2)	O(4)#1-Gd(1)-N(2)	73.9(2)
O(2)-Gd(1)-N(2)	137.7(2)	O(3)#1-Gd(1)-N(2)	126.0(2)
O(1)#1-Gd(1)-N(2)	98.5(2)	O(5)-Gd(1)-N(1)	74.7(2)
O(1W)-Gd(1)-N(1)	72.6(2)	O(4)#1-Gd(1)-N(1)	126.9(2)
O(2)-Gd(1)-N(1)	76.1(2)	O(3)#1-Gd(1)-N(1)	150.3(2)
O(1)#1-Gd(1)-N(1)	141.3(2)	N(2)-Gd(1)-N(1)	62.7(2)
O(5)-Gd(1)-O(1)	113.0(2)	O(1W)-Gd(1)-O(1)	76.8(2)
O(4)#1-Gd(1)-O(1)	113.8(2)	O(2)-Gd(1)-O(1)	49.6(2)
O(3)#1-Gd(1)-O(1)	69.3(2)	O(1)#1-Gd(1)-O(1)	60.0(2)
N(2)-Gd(1)-O(1)	149.3(2)	N(1)-Gd(1)-O(1)	119.2(2)

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

Table S3. CIE chromaticity coordinates **(x, y)** and correlated color temperature **(CCT)** for the $Gd_{99.34}Eu_{0.66}$ doped complex and complex **1**.

λex / nm	**$Gd_{99.34}Eu_{0.66}$ (x, y)**	CCT / K	λex / nm	**Complex 1 (x, y)**	CCT / K
320	(0.387,0.351)	3613	310	(0.341,0.347)	5167
330	(0.371,0.348)	4013	340	(0.335,0.341)	5324
340	(0.372,0.350)	4030	**350**	**(0.336,0.337)**	**5320**
350	(0.373,0.349)	4014	**357**	**(0.333,0.332)**	**5442**
360	(0.373,0.347)	3982	**360**	**(0.334,0.331)**	**5416**
370	(0.372,0.344)	3994	**370**	**(0.331,0.327)**	**5580**
380	(0.373,0.341)	3950	380	(0.325,0.319)	5901
390	(0.363,0.341)	4250	390	(0.312,0.310)	6702
394	**(0.332,0.334)**	**5491**			

Table S4. CIE chromaticity coordinates **(x, y)** for the Gd:Eu doped complexes.

λex / nm	**$Gd_{99.00}Eu_{1.00}$ (x, y)**	**$Gd_{99.60}Eu_{0.40}$ (x, y)**	**$Gd_{99.70}Eu_{0.30}$ (x, y)**
320	(0.522,0.331)	(0.346,0.319)	(0.355,0.316)
330	(0.528,0.332)	(0.350,0.317)	(0.360,0.317)
340	(0.530,0.334)	(0.354,0.319)	(0.364,0.317)
350	(0.532,0.333)	(0.355,0.319)	(0.365,0.317)
360	(0.535,0.332)	(0.356,0.316)	(0.365,0.314)
370	(0.534,0.331)	(0.353,0.310)	(0.364,0.311)
380	(0.535,0.330)	(0.353,0.305)	(0.363,0.309)
390	(0.521,0.329)	(0.347,0.301)	(0.360,0.305)
394	(0.501,0.329)	(0.337,0.302)	(0.352,0.304)

References:

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