High-efficiency white light-emitting lanthanide −organic frameworks assembled from 4,4′-oxybis(benzoic acid), 1,10-phenanthroline and oxalate

Dou Ma, Xia Li* and Rui Huo

Department of Chemistry, Capital Normal University, Beijing 100048. Fax: +86 10 68902320*; Tel:* +86 10 68902320*; E-mail:* xiali@mail.cnu.edu.cn

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Experimental Section

S1. Materials and Physical measurement

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

Elemental analyses (C, H and N) were performed on an Elementar Vario EL analyzer. 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 $2°·min^{-1}$ and a step size of 0.02° in 2θ. Infrared (IR) spectra were measured on a Bruker Tensor37 spectrophotometer using the KBr pellets technique. Inductively coupled plasma (ICP) spectroscopy was performed on an Agilent 7500Ce spectrometer. 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, 3** and the doped complex. 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

A mixture of $Ln(NO_3)_3·6H_2O$ (0.1 mmol) (Ln = Eu **1**, Gd **2** and Tb **3**), 4,4′-oxybis(benzoic acid) (0.2 mmol), 1,10-phenanthroline (0.2 mmol), and potassium oxalate monohydrate(0.2 mmol) was placed in a 23 mL Teflon-lined reactor with 10

mL H_2O and an aqueous solution of NaOH (1 mol/L, 0.4 mL). Then the mixture was heated to 170 ºC in 3 days. After slow cooling to room temperature. After filtration, colorless crystals were obtained. The product was washed with distilled water and then dried. Yield: 42% for **1**, 41% for **2**, 45% for **3** based on the Ln(III).For **1**: Anal. Calc. for $C_{27}H_{16}N_2O_7Eu$: C, 51.28; N, 4.43; H, 2.55%.Found: C, 51.03; N, 4.55; H, 2.76%. Selected IR (KBr pellet, cm^{-1}): 3433(vs)、1667(m)、1600(vs)、1558(m)、1532(m)、1401(vs)、1229(m)、1158(w)、1049(w)、875(w)、845(w)、785(w)、730(w)、669(w)、654(w)、 559(w)、420(w). For **2**: Anal. Calc. for $C_{27}H_{16}N_2O_7Gd$: C, 50.86; N, 4.39; H, 2.53%.Found: C,50.54; N, 4.27; H, 2.52%. Selected IR (KBr pellet, cm^{-1}): 3435(vs)、1668(m)、1601(vs)、1560(m)、1534(m)、1402(vs)、1229(m)、1157(w)、1049(w)、875(w)、845(w)、785(w)、730(w)、669(w)、655(w)、559(w)、420(w). For **3**: Anal. Calc. for $C_{27}H_{16}N_2O_7Tb$: C, 50.72; N, 4.38; H, 2.52%.Found: C,50.66; N, 4.25; H, 2.74%. Selected IR (KBr pellet, cm^{-1}): 3435(vs)、1669(m)、1602(vs)、1560(m)、1534(m)、1402(vs)、1229(m)、1157(w)、1049(w)、875(w)、846(w)、786(w)、730(w)、669(w)、654(w)、559(w)、422(w).

The synthetic method of the $Gd_{0.91}Eu_{0.05}Tb_{0.04}$(oba)phen$(ox)_{0.5}$ doped complex is same as mentioned above just by loading the corresponding $Ln(NO_3)_3{\cdot}6H_2O$ as the starting materials in stoichiometric ratios. The lanthanide content for the doped complex was obtained by inductively coupled plasma spectroscopy (ICP). For $Gd_{0.91}Eu_{0.05}Tb_{0.04}$(oba)phen$(ox)_{0.5}$ doped complex, Selected IR (KBr pellet, cm^{-1}): 3434(vs)、1668(m)、1601(vs)、1560(m)、1533(m)、1402(vs)、1229(m)、1157(w)、1049(w)、875(w)、845(w)、786(w)、730(w)、669(w)、654(w)、559(w)、420(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 using the SADABS program.[2] The structures were solved by direct methods and refined by full matrix least squares method on *F*2 using SHELXS 97 and SHELXL 97 programs.[3, 4] The crystallographic data and selected

bond lengths of complexes **1**–**3** are listed in Tables S1 and S2, respectively.

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

Complex	**1**	**2**	**3**
Empirical formula	$C_{27}H_{16}N_2O_7Eu$	$C_{27}H_{16}N_2O_7Gd$	$C_{27}H_{16}N_2O_7Tb$
Formula weight	632.38	637.67	639.34
Crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a(Å)	10.5419(8)	10.5261(12)	10.4973(9)
b(Å)	10.7871(7)	10.7578(13)	10.7315(9)
c(Å)	11.8223(8)	11.8168(13)	11.7907(11)
α(°)	76.9420(10)	76.911(2)	76.9920(10)
β(°)	83.0650(10)	83.003(2)	83.050(2)
γ(°)	65.9260(10)	65.981(2)	66.0220(10)
Volume (Å^3)	1195.10(14)	1189.8(2)	1181.82(18)
Z	2	2	2
Calculated density / g· cm^{-3}	1.757	1.780	1.797
Absorption coefficient/ mm^{-1}	2.675	2.839	3.044
F(000)	622	624	626
Crystal size / mm^3	0.35x0.15x0.10	0.32x0.10x0.05	0.37x0.14x0.09
θ range for data collection / (°)	1.77 to 25.00	2.11 to 25.00	1.77 to 27.64
Limiting indices	-10≦h≦12; -12≦k≦12; -7≦l≦14	-10≦h≦12; -12≦k≦11; -14≦l≦12	-13≦h≦13; -12≦k≦13; -8≦l≦15
Reflections collected/unique	[R(int)= 0.0263] 5982 / 4161	[R(int)= 0.0527] 5939/4163	[R(int)= 0.0193] 7085 / 5252
Data / restraints / parameters	4161 /0 / 334	4163 /0 / 334	5252 / 0 / 334
Goodness-of-fit on F^2	1.088	0.909	0.880
Final R indices[I>2sigma(I)]	R1 = 0.0363 wR2 = 0.0862	R1 = 0.0548 wR2 = 0.1069	R1 = 0.0299 wR2 = 0.0748
R indices(all data)	R1 = 0.0433 wR2 = 0.1012	R1 = 0.0821 wR2 = 0.1228	R1 = 0.0343 wR2 = 0.0778
Largest difference peak and hole / e.Å^{-3}	0.778 and -0.660	0.821 and -1.389	0.614 and -0.578
CCDC No.	1009125	1009127	1009126

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

1			
Eu(1)-O(4)#1	2.315(4)	Eu(1)-O(6)#3	2.425(4)
Eu(1)-O(5)#2	2.322(4)	Eu(1)-O(2)	2.469(4)
Eu(1)-O(7)	2.411(4)	Eu(1)-N(1)	2.562(5)
Sm(1)-N(1)	2.423(4)	Eu(1)-N(2)	2.568(5)
O(4)#1-Eu(1)-O(5)#2	89.33(15)	O(6)#3-Eu(1)-O(2)	132.39(15)
O(4)#1-Eu(1)-O(7)	150.96(15)	O(4)-Eu(1)-N(1)	74.25(15)
O(5)#2-Eu(1)-O(7)	96.72(16)	O(5)#2-Eu(1)-N(1)	88.65(15)
O(4)#1-Eu(1)-O(1)	84.12(15)	O(7)-Eu(1)-N(1)	134.04(15)
O(5)#2-Eu(1)-O(1)	138.86(15)	O(1)-Eu(1)-N(1)	127.70(15)
O(7)-Eu(1)-O(1)	72.66(15)	O(6)#3-Eu(1)-N(1)	70.44(14)
O(4)#1-Eu(1)-O(6)#3	142.28(14)	O(2)-Eu(1)-N(1)	153.73(16)
O(5)#2-Eu(1)-O(6)#3	77.14(15)	O(4)#1-Eu(1)-N(2)	102.75(17)
O(7)-Eu(1)-O(6)#3	66.50(13)	O(5)#2-Eu(1)-N(2)	144.27(16)
O(1)-Eu(1)-O(6)#3	128.54(15)	O(7)-Eu(1)-N(2)	88.75(17)
O(4)#1-Eu(1)-O(2)	80.09(15)	O(1)-Eu(1)-N(2)	76.42(16)
O(5)#2-Eu(1)-O(2)	85.45(14)	O(6)#3-Eu(1)-N(2)	72.83(17)
O(7)-Eu(1)-O(2)	72.16(14)	O(2)-Eu(1)-N(2)	129.42(15)
O(1)-Eu(1)-O(2)	53.40(14)	N(1)-Eu(1)-N(2)	63.43(16)
2			
Gd(1)-O(4)#1	2.289(5)	Gd(1)-O(6)#3	2.424(5)
Gd(1)-O(5)#2	2.315(5)	Gd(1)-O(2)	2.469(4)
Gd(1)-O(7)	2.389(5)	Gd(1)-N(1)	2.556(5)
Gd(1)-O(1)	2.410(5)	Gd(1)-N(2)	2.549(6)
O(4)#1-Gd(1)-O(5)#2	88.90(18)	O(4)#1-Gd(1)-N(1)	74.25(15)
O(4)#1-Gd(1)-O(7)	150.30(17)	O(5)#2-Gd(1)-N(1)	88.65(15)
O(5)#2-Gd(1)-O(7)	97.19(19)	O(4)#1-Gd(1)-N(1)	74.41(18)
O(4)#1-Gd(1)-O(1)	84.31(18)	O(5)#2-Gd(1)-N(1)	88.74(17)
O(5)#2-Gd(1)-O(1)	138.46(16)	O(7)-Gd(1)-N(1)	134.50(17)
O(7)-Gd(1)-O(1)	71.86(18)	O(1)-Gd(1)-N(1)	127.97(18)
O(4)#1-Gd(1)-O(6)#3	142.56(17)	O(6)#3-Gd(1)-N(1)	70.54(17)
O(5)#2-Gd(1)-O(6)#3	77.72(17)	O(2)-Gd(1)-N(1)	153.77(18)
O(7)-Gd(1)-O(6)#3	66.89(16)	O(4)#1-Gd(1)-N(2)	103.21(19)
O(1)-Gd(1)-O(6)#3	128.16(18)	O(5)#2-Gd(1)-N(2)	144.63(18)
O(4)#1-Gd(1)-O(2)	80.03(18)	O(7)-Gd(1)-N(2)	88.49(19)
O(5)#2-Gd(1)-O(2)	84.96(16)	O(1)-Gd(1)-N(2)	76.43(18)
O(7)-Gd(1)-O(2)	71.65(17)	O(6)#3-Gd(1)-N(2)	72.55(19)
O(1)-Gd(1)-O(2)	53.50(16)	O(2)-Gd(1)-N(2)	129.52(18)
O(6)#3-Gd(1)-O(2)	132.16(17)	N(1)-Gd(1)-N(2)	63.69(19)
3			

Tb(1)-O(4)#1	2.275(2)	Tb(1)-O(6)#3	2.407(2)
Tb(1)-O(5)#2	2.288(2)	Tb(1)-O(2)	2.441(2)
Tb(1)-O(7)	2.383(2)	Tb(1)-N(1)	2.539(2)
Tb(1)-O(1)	2.397(2)	Tb(1)- N(2)	2.540(3)
O(4)#1-Tb(1)-O(5)#2	88.67(8)	O(6)#3-Tb(1)-O(2)	132.01(8)
O(4)#1-Tb(1)-O(7)	150.10(8)	O(4)#1-Tb(1)-N(1)	74.22(8)
O(5)#2-Tb(1)-O(7)	97.99(9)	O(5)#2-Tb(1)-N(1)	87.97(8)
O(4)#1-Tb(1)-O(1)	83.84(8)	O(7)-Tb(1)-N(1)	134.81(8)
O(5)#2-Tb(1)-O(1)	138.98(7)	O(1)-Tb(1)-N(1)	127.79(8)
O(7)-Tb(1)-O(1)	72.01(8)	O(6)#3-Tb(1)-N(1)	70.79(8)
O(4)#1-Tb(1)-O(6)#3	142.48(8)	O(2)-Tb(1)-N(1)	153.22(8)
O(5)#2-Tb(1)-O(6)#3	77.09(8)	O(4)#1-Tb(1)-N(2)	103.45(9)
O(7)-Tb(1)-O(6)#3	67.15(7)	O(5)#2-Tb(1)-N(2)	144.69(8)
O(1)-Tb(1)-O(6)#3	128.93(8)	O(7)-Tb(1)-N(2)	87.82(9)
O(4)#1-Tb(1)-O(2)	79.78(8)	O(1)-Tb(1)-N(2)	75.94(8)
O(5)#2-Tb(1)-O(2)	85.11(8)	O(6)#3-Tb(1)-N(2)	73.23(9)
O(7)-Tb(1)-O(2)	71.87(8)	O(2)-Tb(1)-N(2)	129.34(8)
O(1)-Tb(1)-O(2)	53.88(7)	N(1)-Tb(1)-N(2)	64.55(9)

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

Table S3. CIE chromaticity coordinates for the $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex excited at 330 to 390nm.

$Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$	
Excitation wavelength λex / nm	CIE chromaticity coordinates (x, y)
330	(0.506, 0.403)B
340	(0.498, 0.402)
350	(0.471, 0.397)
360	(0.415, 0.382)C
370	**(0.333, 0.335)A**
380	(0.294, 0.301)
390	(0.275, 0.270)

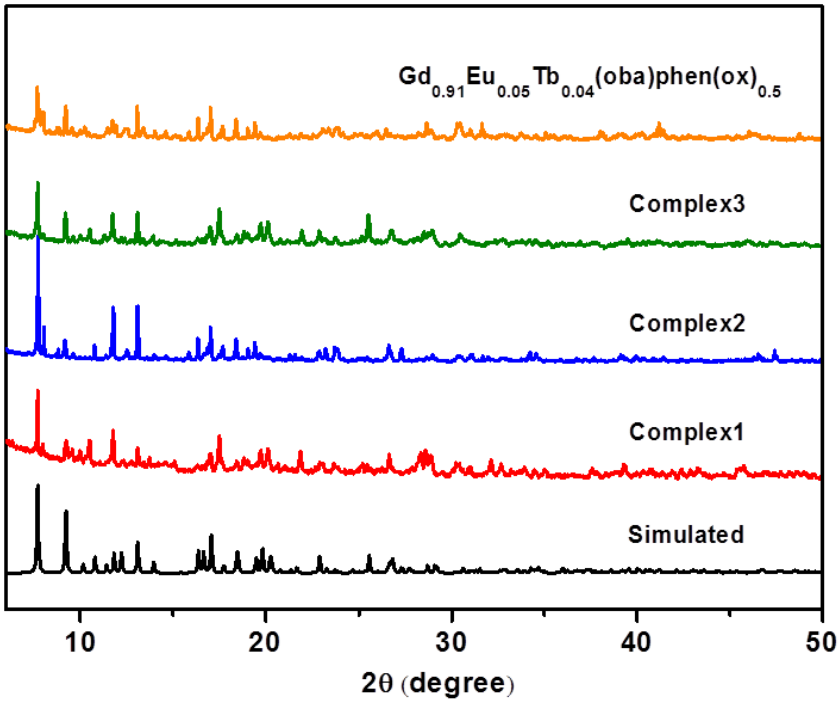


Fig. S1 The PXRD patterns for complexes **1-3** and the $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex.

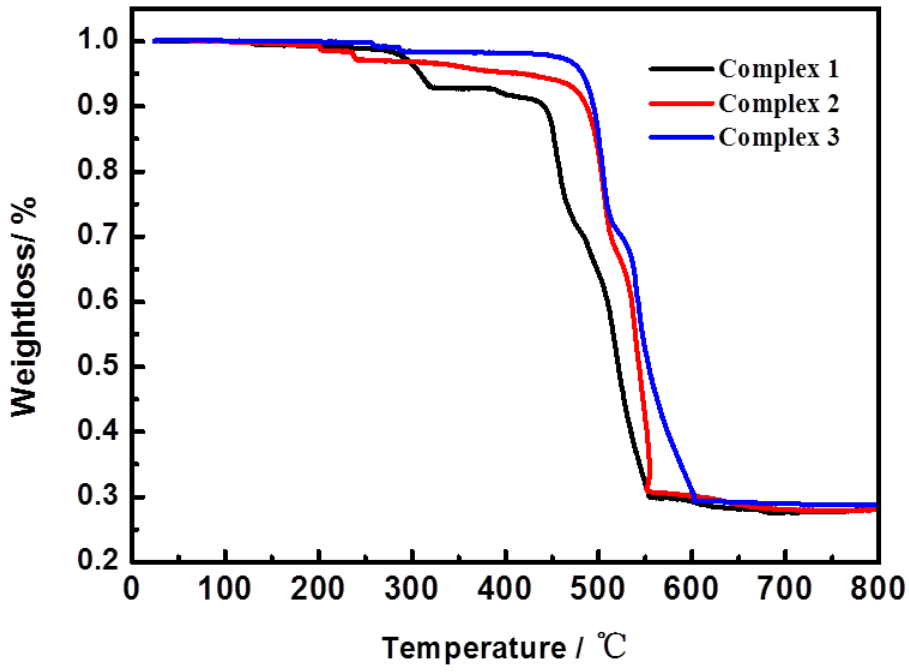


Fig. S2 The TGA curves of complexes **1-3.**

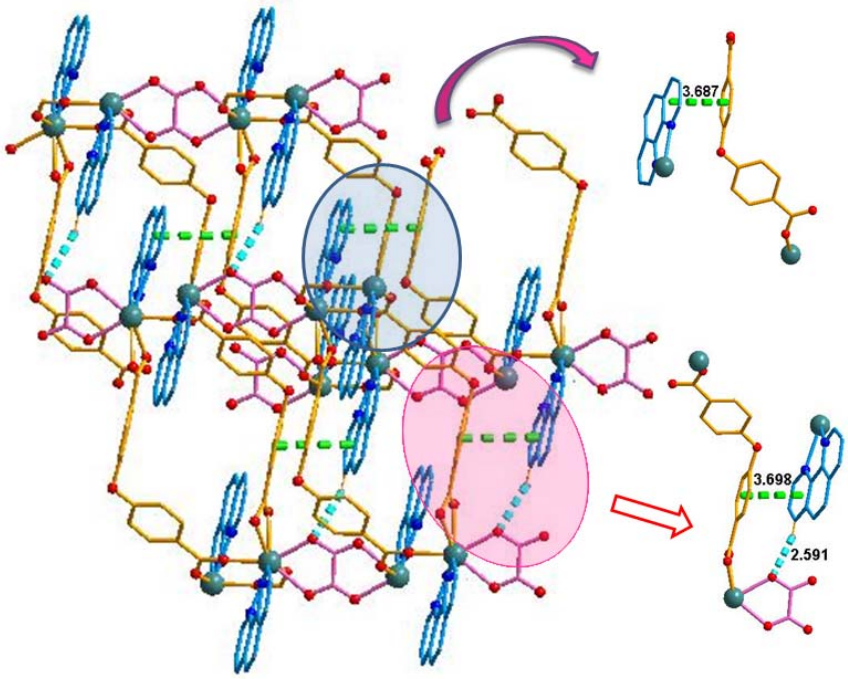


Fig. S3 3D structure by the hydrogen bonds and π…π stacking interactions.

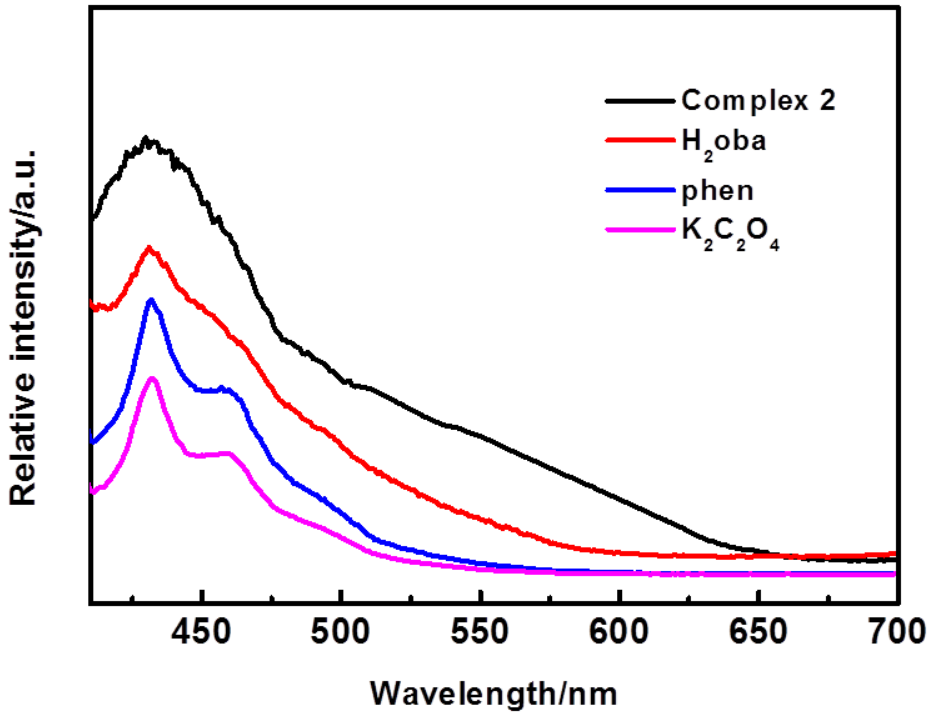
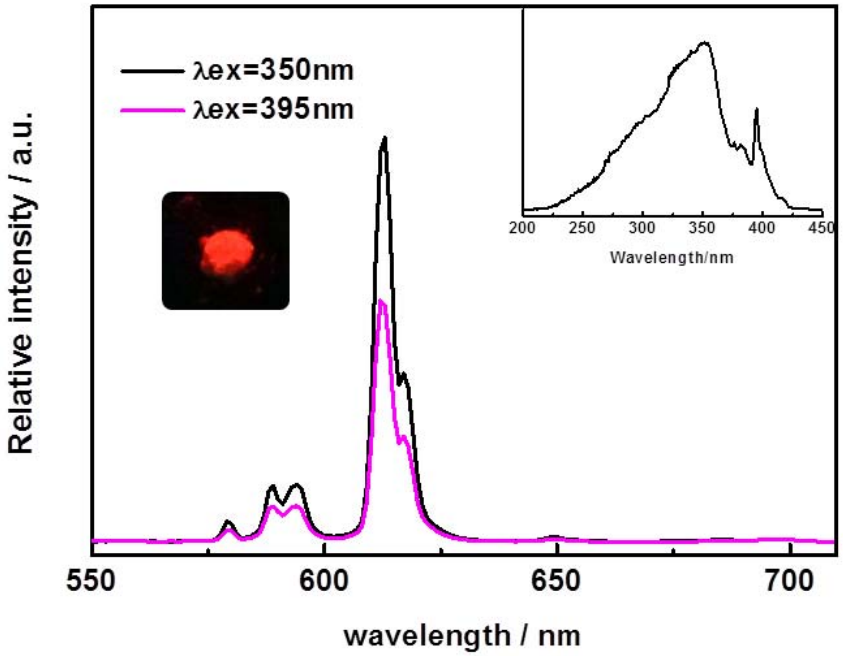
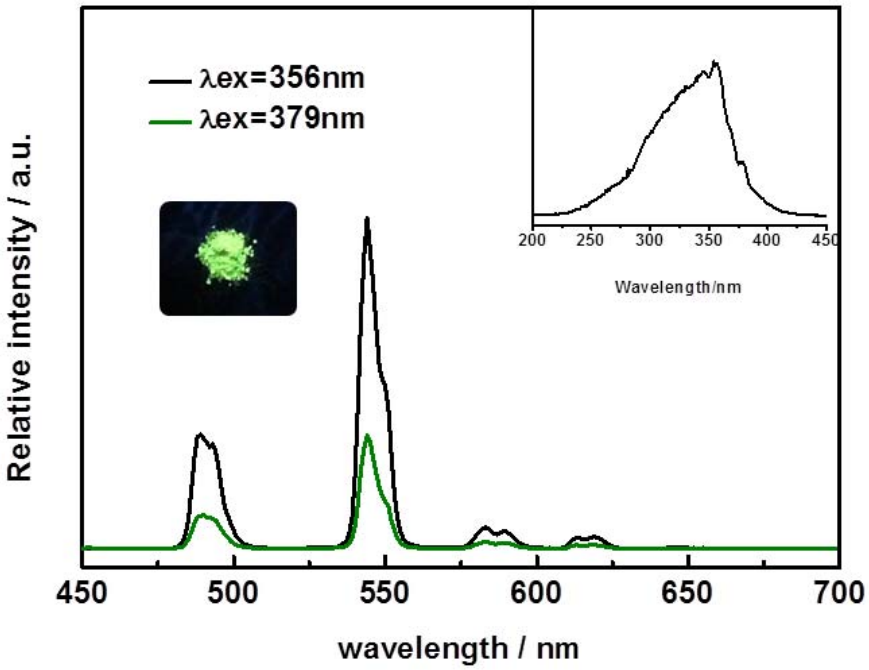


Fig. S4 Emission spectra of H_2oba, phen, ox and complex **2**.

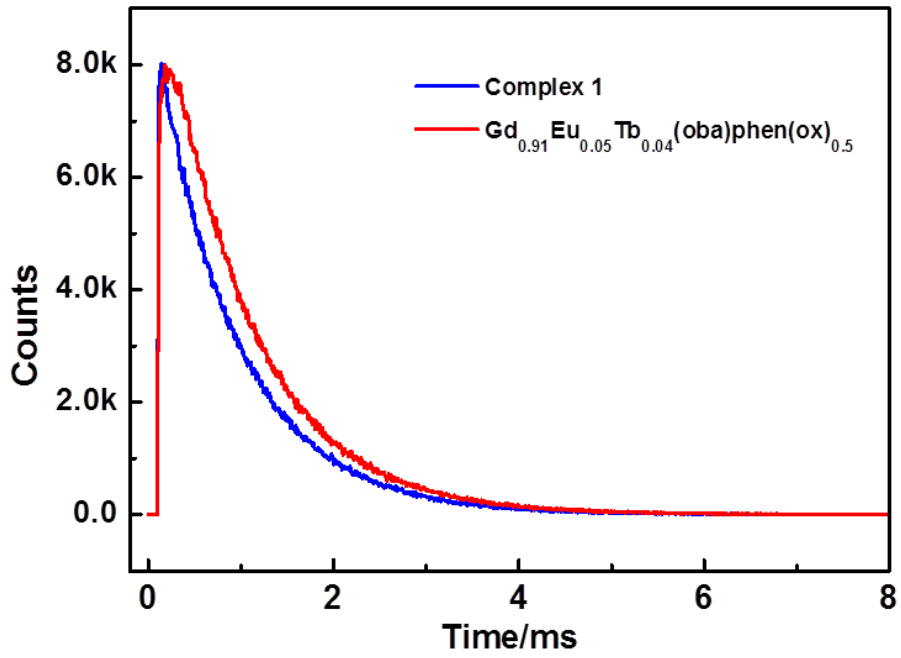


(a)

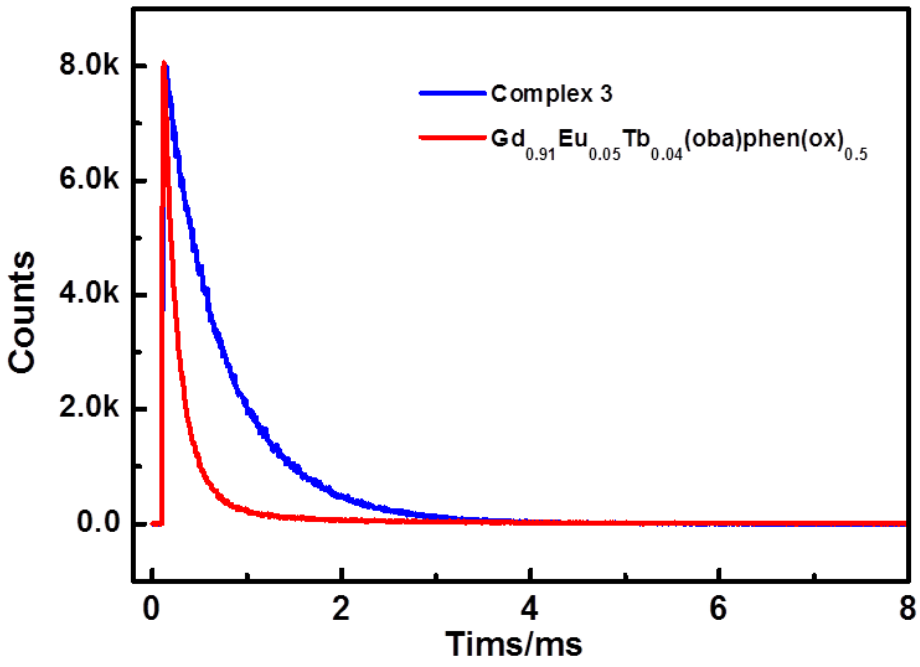


(b)

Fig. S5 Emission spectra of complexes **1 (a)** and **3** (b). Iinsert: excitation spectra, image of **1** and **3** by 365 nm light.



(a)



(b)

Fig. S6 Decay profile of Eu(III) (a), Tb(III) (b) in complexes **1**, **3** and the $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex. For Eu(III), λ_{ex}= 350 nm and λ_{em}= 613 nm. For Tb(III), λ_{ex}= 356 nm and λ_{em}= 544 nm.

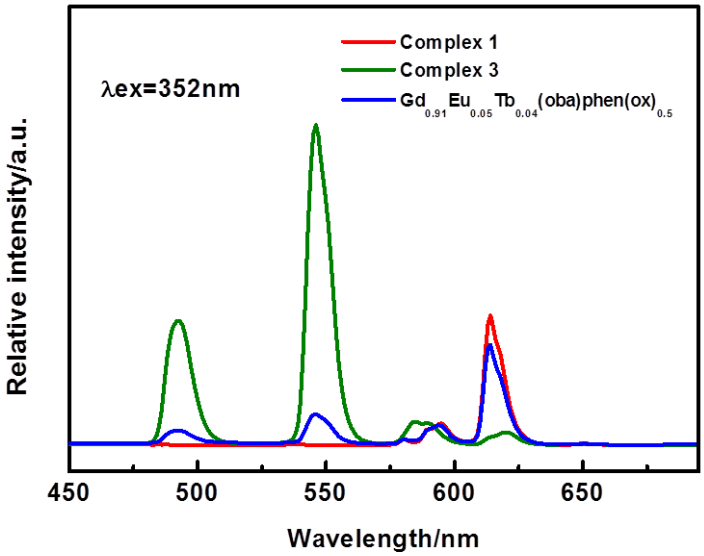


Fig. S7 Emission spectra of complexes **1**, **3** and the $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex.

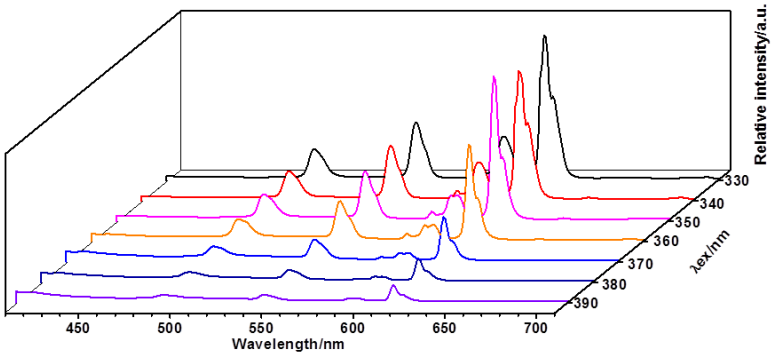


Fig. S8 Emission spectra of the $Gd_{0.91}Eu_{0.05}Tb_{0.04}(oba)phen(ox)_{0.5}$ doped complex excited at 330 - 390 nm.

References:

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