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Electronic Supplementary Information (ESI)

Eu^{3+}-doped Tb(III)-Zn(II) metal–organic frameworks emitting tunable three primary colors towards white light

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Table S1 Selected bond distances and angles for **1-Eu** and **2-Tb**.

1-Eu			
Eu(1)-O(11)	2.288(3)	Eu(2)-O(12)	2.298(4)
Eu(1)-O(21)	2.320(3)	Eu(2)-O(41)	2.310(3)
Eu(1)-O(52)	2.344(3)	Eu(2)-O(22)	2.330(3)
Eu(1)-O(8W)	2.416(5)	Eu(2)-O(51)	2.362(4)
Eu(1)-O(7W)	2.443(4)	Eu(2)-O(42)#1	2.381(3)
Eu(1)-O(9W)	2.520(4)	Eu(2)-O(32)	2.491(3)
Eu(1)-O(6W)	2.521(4)	Eu(2)-O(31)	2.503(3)
Eu(1)-O(10W)	2.548(4)	Eu(2)-O(11W)	2.562(4)
Eu(3)-O(1W)	2.375(5)	Zn(1)-N(43)#3	1.990(4)
Eu(3)-O(2W)	2.401(8)	Zn(1)-N(32)	1.995(4)
Eu(3)-O(5WA)#2	2.403(8)	Zn(1)-N(11)#4	2.004(4)
Eu(3)-O(3W)	2.407(8)	Zn(1)-N(54)#1	2.005(4)
Eu(3)-O(4W)	2.462(7)	Eu(3)-O(5WB)	2.512(9)

Eu(3)-O(1W)#2	2.492(5)		
O(11)-Eu(1)-O(21)	125.69(12)	O(11)-Eu(1)-O(6W)	143.07(13)
O(11)-Eu(1)-O(52)	80.82(13)	O(21)-Eu(1)-O(6W)	80.21(12)
O(21)-Eu(1)-O(52)	80.05(12)	O(52)-Eu(1)-O(6W)	78.59(13)
O(11)-Eu(1)-O(8W)	75.91(15)	O(8W)-Eu(1)-O(6W)	70.42(14)
O(21)-Eu(1)-O(8W)	146.89(14)	O(7W)-Eu(1)-O(6W)	68.52(14)
O(52)-Eu(1)-O(8W)	79.49(14)	O(9W)-Eu(1)-O(6W)	109.01(14)
O(11)-Eu(1)-O(7W)	135.89(14)	O(11)-Eu(1)-O(10W)	78.03(13)
O(21)-Eu(1)-O(7W)	78.48(13)	O(21)-Eu(1)-O(10W)	72.46(12)
O(52)-Eu(1)-O(7W)	143.17(14)	O(52)-Eu(1)-O(10W)	124.65(12)
O(8W)-Eu(1)-O(7W)	103.63(15)	O(8W)-Eu(1)-O(10W)	140.54(14)
O(11)-Eu(1)-O(9W)	70.93(13)	O(7W)-Eu(1)-O(10W)	75.97(13)
O(21)-Eu(1)-O(9W)	138.04(12)	O(9W)-Eu(1)-O(10W)	75.11(14)
O(52)-Eu(1)-O(9W)	141.38(13)	O(6W)-Eu(1)-O(10W)	138.68(12)
O(8W)-Eu(1)-O(9W)	68.64(15)	O(12)-Eu(2)-O(22)	93.62(14)
O(7W)-Eu(1)-O(9W)	68.30(13)	O(41)-Eu(2)-O(22)	88.83(13)
O(12)-Eu(2)-O(41)	156.45(13)	O(12)-Eu(2)-O(51)	75.43(15)
O(41)-Eu(2)-O(51)	82.88(13)	O(1W)-Eu(3)-O(4W)	84.6(2)
O(22)-Eu(2)-O(51)	73.51(14)	O(2W)-Eu(3)-O(4W)	81.7(3)
O(12)-Eu(2)-O(42)#1	80.73(13)	O(5WA)#2-Eu(3)-O(4W)	111.2(3)
O(41)-Eu(2)-O(42)#1	108.52(12)	O(3W)-Eu(3)-O(4W)	69.2(3)
O(22)-Eu(2)-O(42)#1	148.77(14)	O(1W)-Eu(3)-O(1W)#2	127.79(11)
O(51)-Eu(2)-O(42)#1	132.88(14)	O(2W)-Eu(3)-O(1W)#2	79.9(2)
O(12)-Eu(2)-O(32)	125.54(13)	O(5WA)#2-Eu(3)-O(1W)#2	76.8(3)
O(41)-Eu(2)-O(32)	78.01(11)	O(3W)-Eu(3)-O(1W)#2	82.1(2)
O(22)-Eu(2)-O(32)	83.03(12)	O(4W)-Eu(3)-O(1W)#2	146.7(2)
O(51)-Eu(2)-O(32)	149.93(14)	O(2W)-Eu(3)-O(5WA)#2	152.8(3)
O(42)#1-Eu(2)-O(32)	75.81(12)	O(1W)-Eu(3)-O(3W)	128.7(2)
O(12)-Eu(2)-O(31)	75.36(13)	O(2W)-Eu(3)-O(3W)	86.3(3)

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O(41)-Eu(2)-O(31)	127.15(11)	O(5WA)#2-Eu(3)-O(3W)	76.9(3)
O(22)-Eu(2)-O(31)	70.75(13)	O(1W)-Eu(3)-O(5WB)	62.3(2)
O(51)-Eu(2)-O(31)	131.58(13)	O(2W)-Eu(3)-O(5WB)	72.0(3)
O(42)#1-Eu(2)-O(31)	78.13(12)	O(5WA)#2-Eu(3)-O(5WB)	132.2(3)
O(32)-Eu(2)-O(31)	52.15(10)	O(3W)-Eu(3)-O(5WB)	145.5(3)
O(12)-Eu(2)-O(11W)	86.27(14)	O(4W)-Eu(3)-O(5WB)	81.1(3)
O(41)-Eu(2)-O(11W)	77.00(13)	O(1W)#2-Eu(3)-O(5WB)	118.5(2)
O(22)-Eu(2)-O(11W)	139.93(14)	N(43)#3-Zn(1)-N(32)	112.85(17)
O(51)-Eu(2)-O(11W)	67.70(15)	N(43)#3-Zn(1)-N(11)#4	111.51(16)
O(42)#1-Eu(2)-O(11W)	70.75(14)	N(32)-Zn(1)-N(11)#4	102.83(17)
O(32)-Eu(2)-O(11W)	128.55(12)	N(43)#3-Zn(1)-N(54)#1	99.63(18)
O(31)-Eu(2)-O(11W)	146.01(14)	N(32)-Zn(1)-N(54)#1	120.65(16)
O(1W)-Eu(3)-O(2W)	133.7(2)	N(11)#4-Zn(1)-N(54)#1	109.57(17)
O(1W)-Eu(3)-O(5WA)#2	72.8(2)		

Symmetry codes for **1-Eu**: (#1) –x + 1, –y + 1, –z + 1; (#2) –x, –y + 2, –z + 2; (#3) x – 1, y, z – 1; (#4) x – 1, y – 1, z – 1.

2-Tb			
Tb(1)-O(11)	2.260(7)	Tb(2)-O(42)#3	2.344(6)
Tb(1)-O(21)	2.286(6)	O(11W)-Tb(2)	2.554(8)
Tb(1)-O(52)	2.309(7)	O(12)-Tb(2)	2.272(8)
Tb(1)-O(8W)	2.373(7)	O(22)-Tb(2)	2.314(6)
Tb(1)-O(7W)	2.422(7)	O(31)-Tb(2)	2.484(7)
Tb(1)-O(6W)	2.483(7)	O(32)-Tb(2)	2.469(5)
Tb(1)-O(9W)	2.500(8)	O(51)-Tb(2)	2.340(7)
Tb(1)-O(10W)	2.554(6)	O(41)-Tb(2)	2.276(6)
Tb(3))-O(1W	2.447(9)	Zn(1)-N(11)#1	1.985(8)
Tb(3)-O(2W)	2.379(14)	Zn(1)-N(43)#2	1.990(8)
Tb(3)-O(3W)	2.356(15)	Zn(1)-N(32)	1.994(7)
Tb(3)-O(4W)	2.443(10)	Zn(1)-N(54)#3	1.995(8)

Tb(3)-O(5WB)	2.535(18)	Tb(3)-O(1W)#4	2.375(10)
Tb(3)-O(5WA)#4	2.354(14)		
O(11)-Tb(1)-O(21)	125.3(2)	O(12)-Tb(2)-O(41)	155.5(2)
O(11)-Tb(1)-O(52)	80.0(3)	O(12)-Tb(2)-O(22)	93.8(3)
O(21)-Tb(1)-O(52)	80.5(2)	O(41)-Tb(2)-O(22)	89.8(2)
O(11)-Tb(1)-O(8W)	76.7(3)	O(12)-Tb(2)-O(51)	75.8(3)
O(21)-Tb(1)-O(8W)	146.5(2)	O(41)-Tb(2)-O(51)	82.1(2)
O(52)-Tb(1)-O(8W)	79.3(3)	O(22)-Tb(2)-O(51)	73.3(3)
O(11)-Tb(1)-O(7W)	135.3(3)	O(12)-Tb(2)-O(42)#3	81.0(3)
O(21)-Tb(1)-O(7W)	78.3(2)	O(41)-Tb(2)-O(42)#3	107.7(2)
O(52)-Tb(1)-O(7W)	144.7(3)	O(22)-Tb(2)-O(42)#3	148.5(2)
O(8W)-Tb(1)-O(7W)	104.2(3)	O(51)-Tb(2)-O(42)#3	133.7(3)
O(11)-Tb(1)-O(6W)	144.2(2)	O(12)-Tb(2)-O(32)	127.2(2)
O(21)-Tb(1)-O(6W)	79.6(2)	O(41)-Tb(2)-O(32)	77.3(2)
O(52)-Tb(1)-O(6W)	79.7(2)	O(22)-Tb(2)-O(32)	82.8(2)
O(8W)-Tb(1)-O(6W)	70.7(2)	O(51)-Tb(2)-O(32)	148.3(3)
O(7W)-Tb(1)-O(6W)	69.0(2)	O(42)#3-Tb(2)-O(32)	76.1(2)
O(11)-Tb(1)-O(9W)	71.0(2)	O(12)-Tb(2)-O(31)	76.5(2)
O(21)-Tb(1)-O(9W)	138.0(2)	O(41)-Tb(2)-O(31)	127.3(2)
O(52)-Tb(1)-O(9W)	140.9(2)	O(22)-Tb(2)-O(31)	70.9(2)
O(8W)-Tb(1)-O(9W)	69.0(3)	O(51)-Tb(2)-O(31)	132.4(2)
O(7W)-Tb(1)-O(9W)	68.1(2)	O(42)#3-Tb(2)-O(31)	77.8(2)
O(6W)-Tb(1)-O(9W)	109.4(2)	O(32)-Tb(2)-O(31)	52.61(19)
O(11)-Tb(1)-O(10W)	77.7(2)	O(12)-Tb(2)-O(11W)	85.5(3)
O(21)-Tb(1)-O(10W)	72.1(2)	O(41)-Tb(2)-O(11W)	76.2(2)
O(52)-Tb(1)-O(10W)	123.8(2)	O(22)-Tb(2)-O(11W)	139.7(2)
O(8W)-Tb(1)-O(10W)	141.3(2)	O(51)-Tb(2)-O(11W)	67.5(3)
O(7W)-Tb(1)-O(10W)	75.2(2)	O(42)#3-Tb(2)-O(11W)	71.3(2)
O(6W)-Tb(1)-O(10W)	137.9(2)	O(32)-Tb(2)-O(11W)	128.6(2)

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O(9W)-Tb(1)-O(10W)	75.4(2)	O(31)-Tb(2)-O(11W)	146.2(3)
O(3W)-Tb(3)-O(5WA)#4	80.4(5)	O(3W)-Tb(3)-O(5WB)	143.2(5)
O(3W)-Tb(3)-O(2W)	82.7(5)	O(5WA)#4-Tb(3)-O(5WB)	129.1(5)
O(5WA)#4-Tb(3)-O(2W)	157.2(6)	O(4W)-Tb(3)-O(5WB)	80.0(4)
O(3W)-Tb(3)-O(1W)#4	84.8(5)	O(1W)-Tb(3)-O(5WB)	59.1(4)
O(5WA)#4-Tb(3)-O(1W)#4	76.0(5)	O(2W)-Tb(3)-O(1W)	131.2(5)
O(2W)-Tb(3)-O(1W)#4	87.2(5)	O(1W)#4-Tb(3)-O(1W)	122.0(2)
O(3W)-Tb(3)-O(4W)	69.9(5)	O(4W)-Tb(3)-O(1W)	82.2(3)
O(5WA)#4-Tb(3)-O(4W)	105.6(5)	N(11)#1-Zn(1)-N(43)#2	111.4(3)
O(2W)-Tb(3)-O(4W)	82.7(4)	N(11)#1-Zn(1)-N(32)	102.8(3)
O(1W)#4-Tb(3)-O(4W)	153.6(3)	N(43)#2-Zn(1)-N(32)	112.3(3)
O(3W)-Tb(3)-O(1W)	133.0(4)	N(11)#1-Zn(1)-N(54)#3	109.7(3)
O(5WA)#4-Tb(3)-O(1W)	71.5(5)	N(43)#2-Zn(1)-N(54)#3	99.3(3)
O(2W)-Tb(3)-O(5WB)	72.8(5)	N(32)-Zn(1)-N(54)#3	121.6(3)
O(1W)#4-Tb(3)-O(5WB)	120.0(4)		

Symmetry codes for **2-Tb**: (#1) x – 1, y – 1, z – 1; (#2) x – 1, y, z – 1; (#3) –x + 1, –y + 1, –z + 1; (#4) –x, –y + 2, –z + 2.

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Table S2 Selected hydrogen-bonding geometries for **1-Eu** and **2-Tb**.

D-H···A	D-H/Å	H···A/Å	D···A/Å	∠D-H···A/º
1-Eu				
O6W-H6WA···N53_$1	0.85(3)	2.12(3)	2.879(6)	149(3)
O7W-H7WA···N22_$2	0.86(3)	1.84(3)	2.689(7)	172(3)
O8W-H8WB···N52_$1	0.84(3)	2.39(4)	2.838(8)	114(3)
O9W-H9WB···N31_$3	0.84(2)	2.21(3)	2.934(6)	145(4)
O10W-H10B···N21_$2	0.86(3)	2.34(3)	3.127(7)	153(3)
2-Tb				
O6W-H6WB···N53_$1	0.82(4)	2.03(4)	2.852(12)	176(3)
O7W-H7WA···N22_$2	0.81(3)	1.89(4)	2.667(12)	160(4)
O8W-H8WA···N12_$1	0.82(5)	2.07(5)	2.885(12)	168(4)
O8W-H8WA···N13_$3	0.82(5)	2.54(5)	3.200(13)	138(3)
O8W-H8WB···N52_$3	0.82(4)	2.28(7)	2.806(14)	122(7)
O9W-H9WB···N31_$2	0.82(4)	2.15(4)	2.900(11)	151(7)
O10W-H10B···N21_$4	0.83(4)	2.57(5)	3.052(11)	119(4)

Symmetry codes for **1-Eu**: $1 2 – x, 1 – y, 2 – z; $2 – x, – y, 1 – z; $3 –x, 1 – y, –z; **2-Tb**: $1 – x, –y, 1 – z; $2 2 – x,1 – y, 2 – z; $3 1 – x, 2 – y, 2 – z; $4 –x, 1 – y, 1 – z.

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Table S3 Corresponding CIE coordinates and CRI values of **1-Eu**, **2-Tb** and Eu^{3+}-doped **2-Tb** with different molar ratios excited at 330 nm.

Sample	**2-Tb**	**0.1%**	**0.3%**	**0.4%**	**0.5%**	**0.6%**	**0.7%**
CIE (x,y)	(0.271, 0.398)	(0.302, 0.409)	(0.340, 0.391)	(0.326, 0.344)	(0.331, 0.328)	(0.352, 0.350)	(0.354, 0.358)
CCT	7886	6573	5272	5781	5562	4714	4681
CRI	43.7	54.5	73.6	80.4	81.7	84.5	85.4
Sample	**1.0%**	**1.5%**	**8.0%**	**20.0%**	**40.0%**	**1-Eu**	
CIE (x,y)	(0.352, 0.334)	(0.391, 0.281)	(0.422, 0.252)	(0.487, 0.266)	(0.580, 0.309)	(0.617, 0.334)	
CCT	4051	2490	3679	10453	11884	10040	
CRI	85.5	70.1	47.9	57.1	58.2	45.3	

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Fig. S1 Powdered X-ray diffraction (PXRD) patterns of **1-Eu**, **2-Tb**, and x%-Eu^{3+}-doped **2-Tb**.

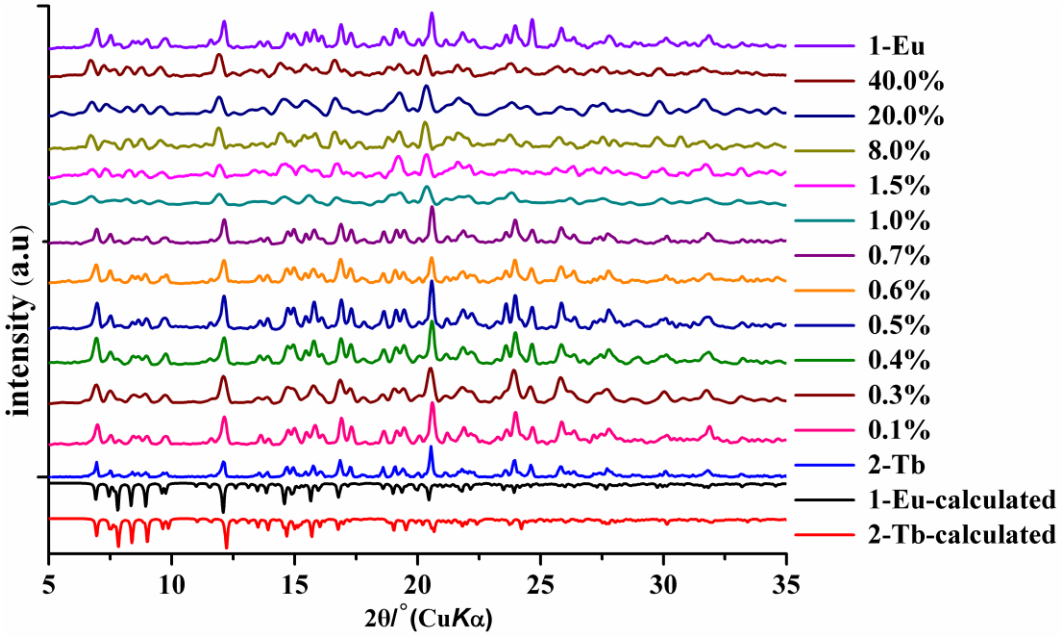

Fig. S2 TG curves of **1-Eu**, **2-Tb**, 0.5% and 40.0% Eu^{3+}-doped **2-Tb**.

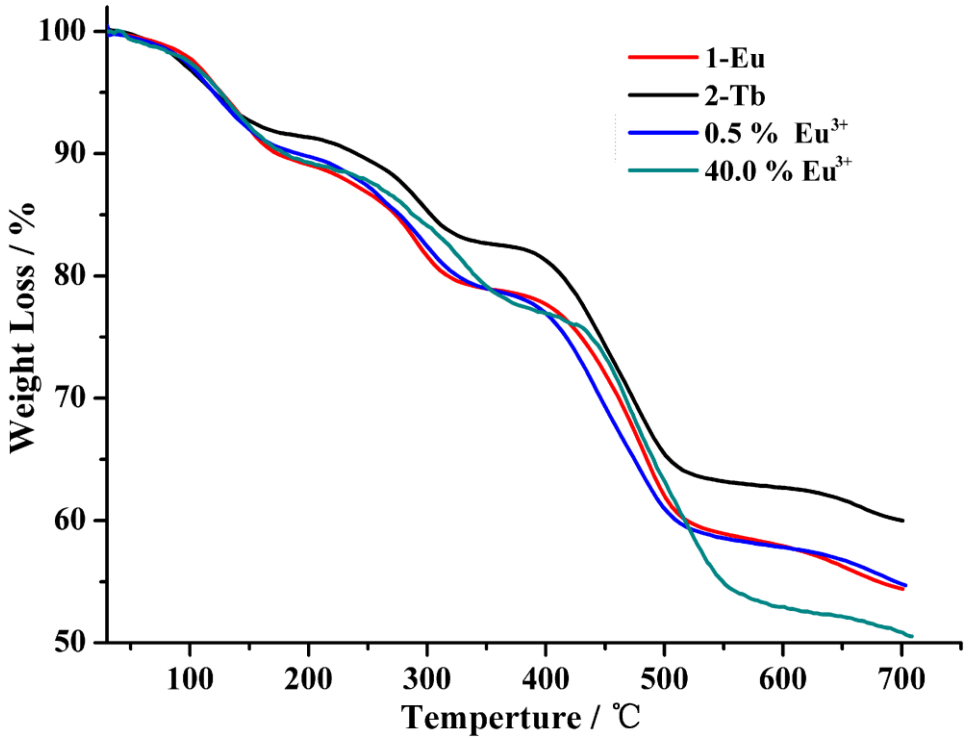

Fig. S3 Schematic representation the tetranuclear cluster unit [$Eu_4(\mu_2$-$COO)_8$] in the 2-D framework of **1-Eu**.

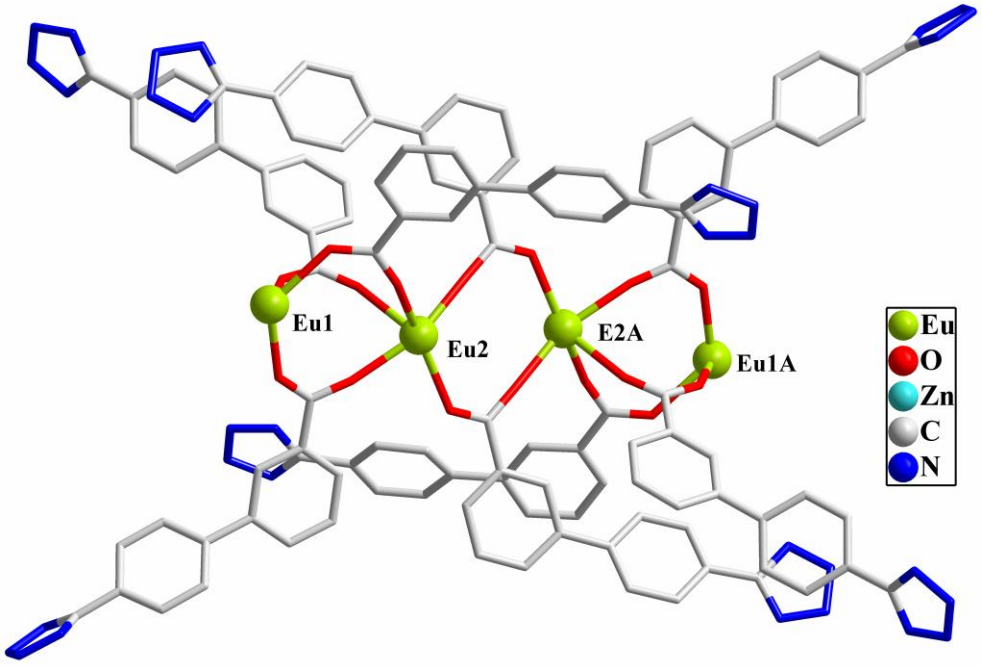

Fig. S4 Schematic representation of the connection between the Zn(II) atom and tetranuclear cluster units [$Eu_4(\mu_2$-$COO)_8$] by four 4-tbca^{2-} ligand.

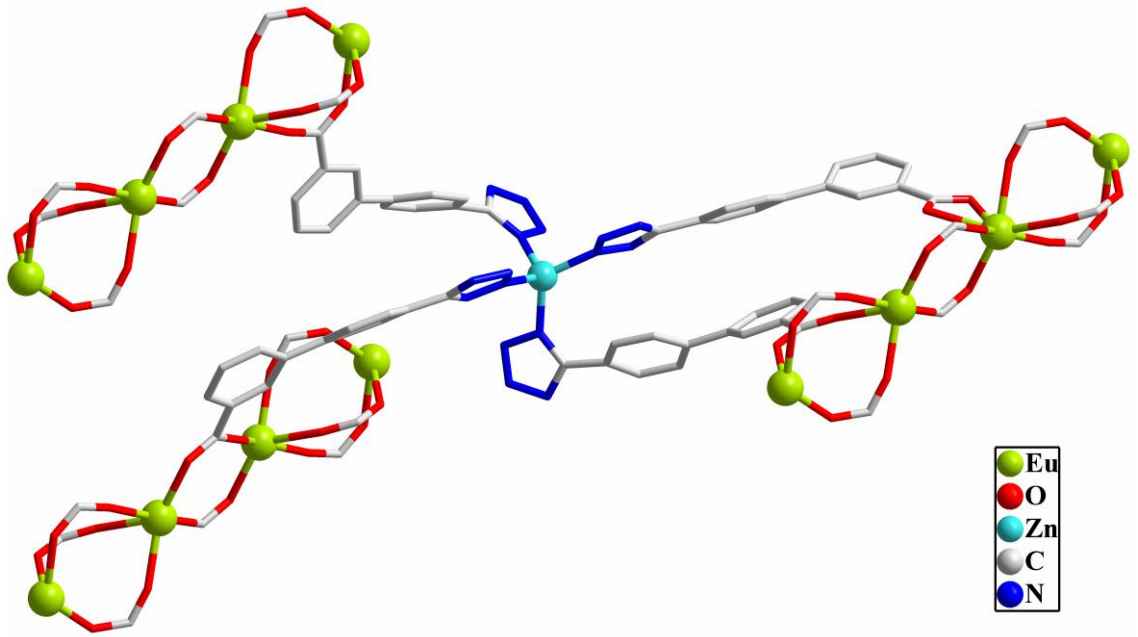

Fig. S5 (a) Schematic representation of 3D supramolecular framework of **1-Eu** viewed along the *c* axis. The $[EuOH(H_2O)_6]^{2+}$ units are shown as space-filling models with lattice H_2O molecules omitted for clarity. (b) 1-D channel in the 3D supramolecular framework of **1-Eu**.

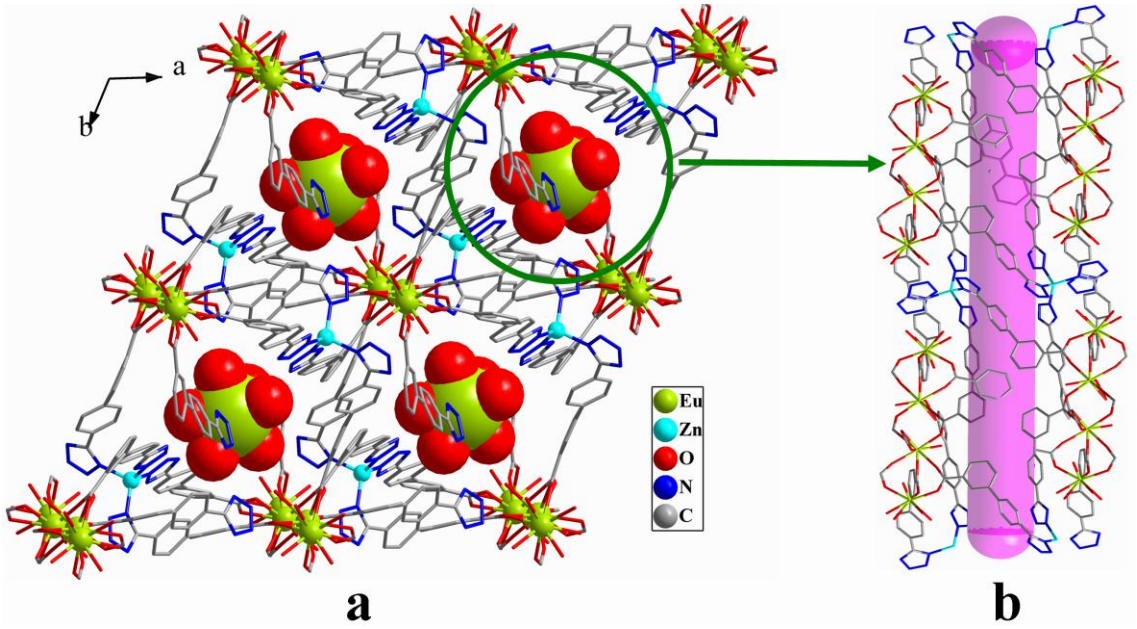

Fig. S6 Excitation spectra of 4-H_2tbca, **1-Eu** and **2-Tb**.

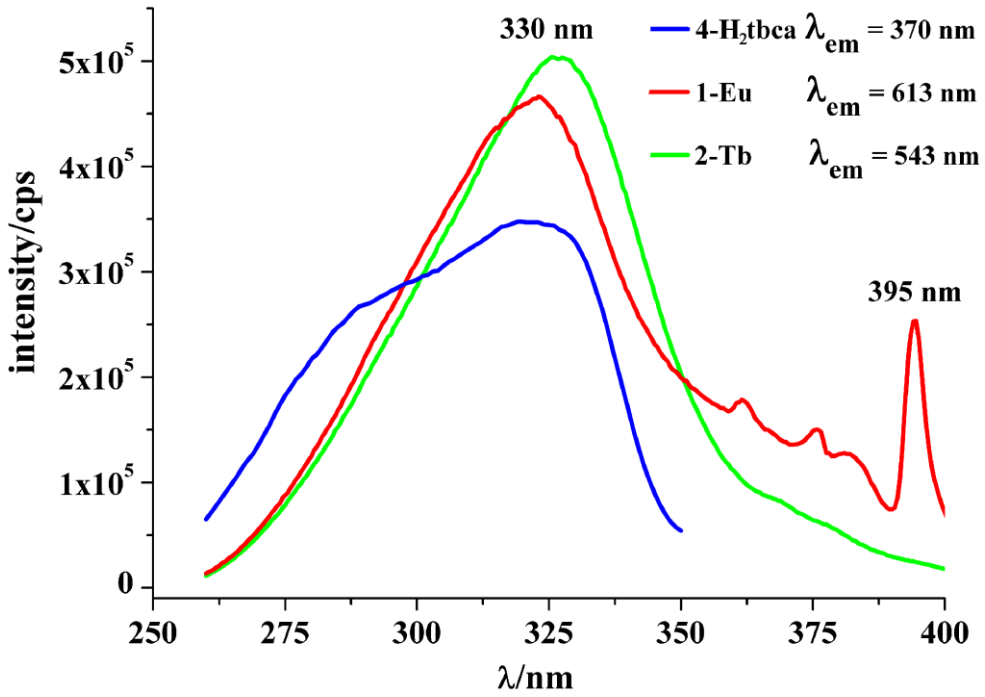

Fig. S7 Luminescent decay curves of **1-Eu, 2-Tb**, 0.5% and 2.0% Eu^{3+}-doped **2-Tb**.

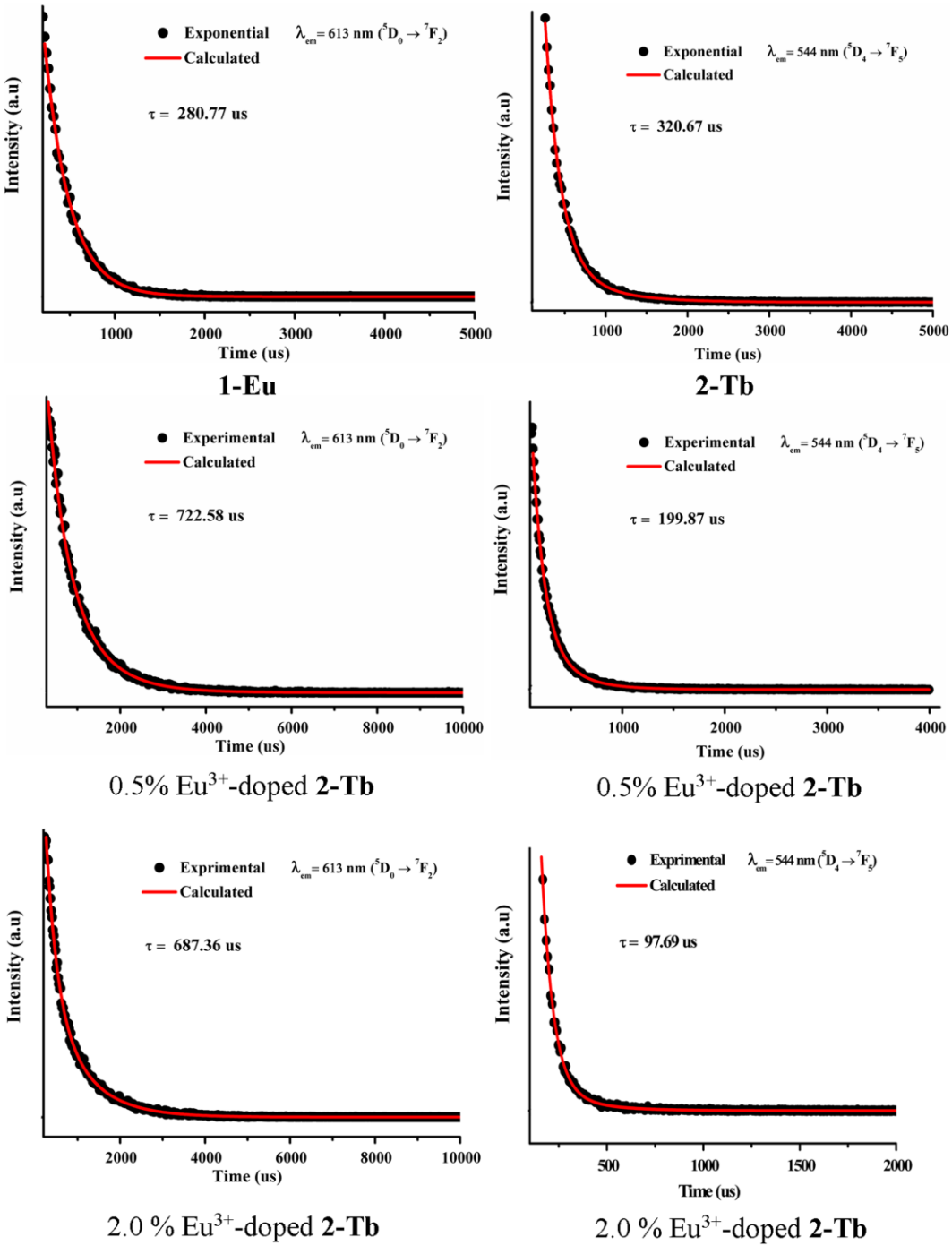

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Fig. S8 Excitation and emission spectra of 0.5% Eu^{3+}-doped **2-Tb**.