Supporting information

Color Tunable and White Light Emitting Tb^{3+} and Eu^{3+} Doped Lanthanide Metal-Organic Framework Materials

Xingtang Rao[†], Qian Huang[†], Xiuli Yang[§], Yuanjing Cui[†], Yu Yang[†], Chuande Wu[§], Banglin Chen[*, †, ‡], Guodong Qian[*, †]

[†] *State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China,* [‡] *Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, United States, and* [§] *Department of Chemistry, Zhejiang University, Hangzhou 310027, China*

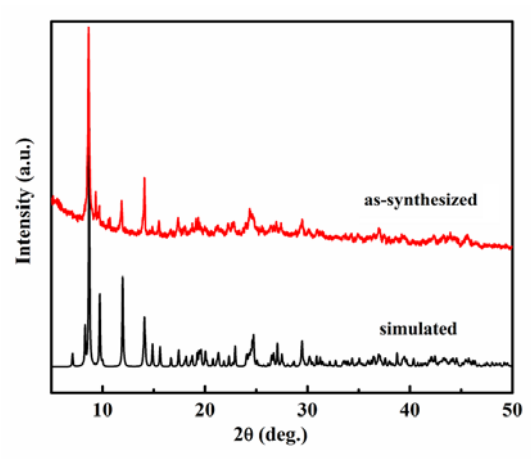

Figure S1. PXRD patterns of **ZJU-1** (calculated, black; as-synthesized, red)

* To whom correspondence should be addressed. G. Q: Fax, (+86) 571-87951234; e-mail, gdqian@zju.edu.cn. B. C.: fax, (210) 458-7428; e-mail, banglin.chen@utsa.edu.

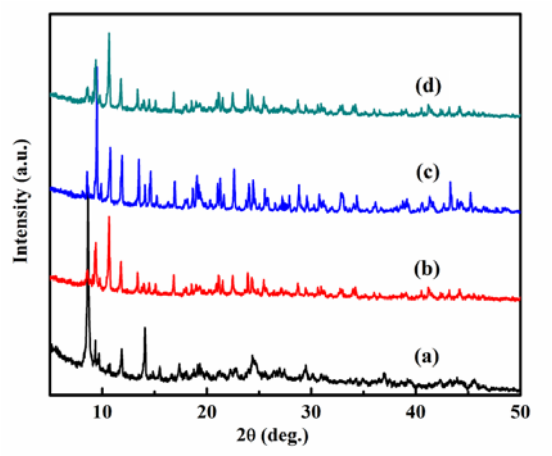

Figure S2. PXRD patterns of the doped samples: (a) **ZJU-1**, (b) **ZJU-1**:5%Tb^{3+}, (c) **ZJU-1**:5%Eu^{3+}, (d) **ZJU-1**:1.0%Tb^{3+}, 2.0%Eu^{3+}.

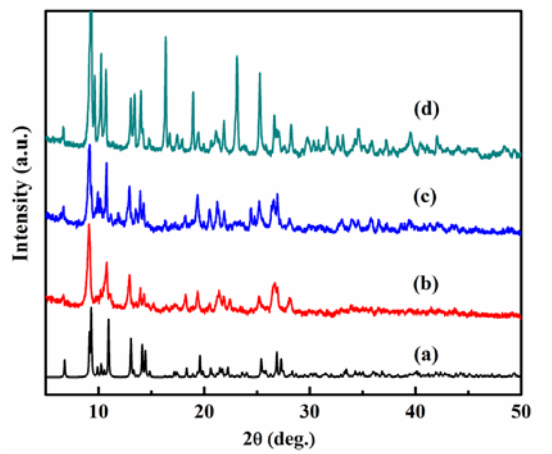

Figure S3. PXRD patterns of the $Na_3[Ln(PDA)_3](H_2O)_x$: (a) simulated XRD pattern using the X-ray structure of $Na_3[Lu(PDA)_3](H_2O)_{12}$ single crystal , (b) $Na_3[Tb(PDA)_3](H_2O)_9$, (c) $Na_3[Eu(PDA)_3](H_2O)_{10}$, (d) $Na_3[La(PDA)_3](H_2O)_{12}$.

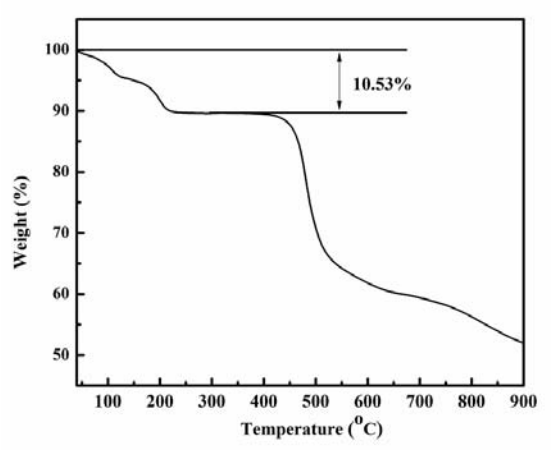

Figure S4. TGA curve for **ZJU-1** under nitrogen.

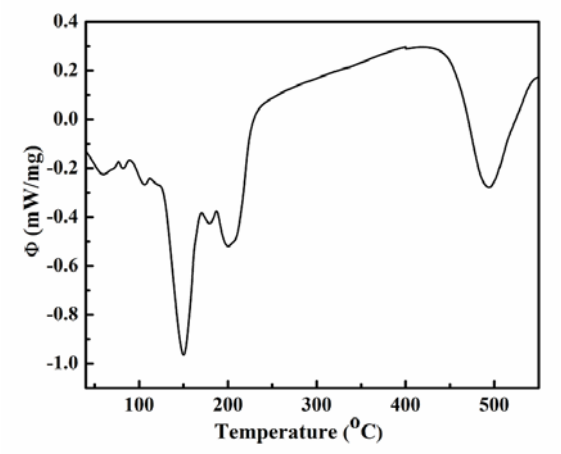

Figure S5. DSC curve for **ZJU-1** under nitrogen.

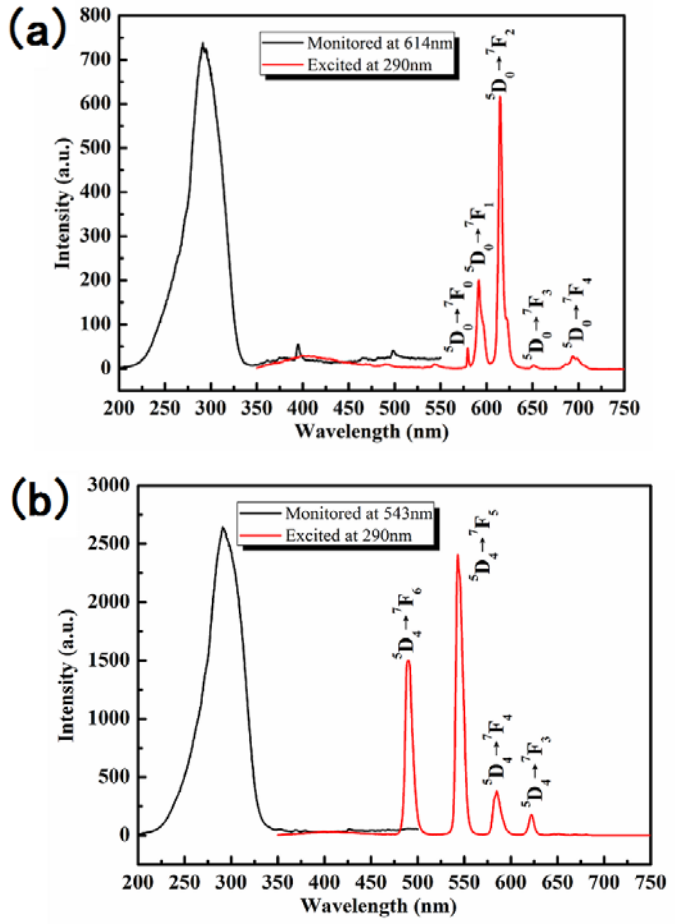

Figure S6. Excitation and emission spectra of **ZJU-1**:1.0%Eu^{3+} (a) and **ZJU-1**:1.0%Tb^{3+} (b), respectively.

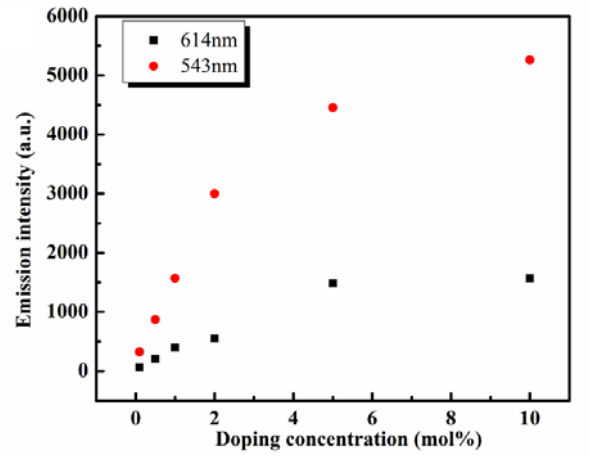

Figure S7. Data comparison for emission spectra of **ZJU-1**:*x*%Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) and **ZJU-1**:*x*%$Tb^{3+}$ ($^5D_4 \rightarrow {}^7F_5$) excitation at 312 nm.

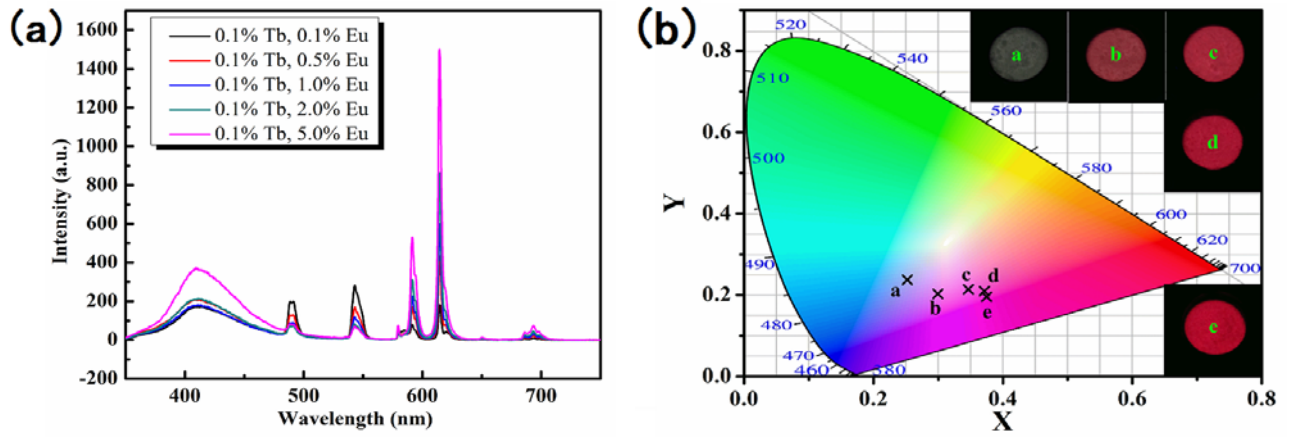

Figure S8. (a) Emission spectra; (b) CIE chromaticity coordinates and photographs of **ZJU-1**:0.1%Tb^{3+}, *x*%Eu^{3+} (*x* =0.1, 0.5, 1.0, 2.0, 5.0) under 312 nm excitation.

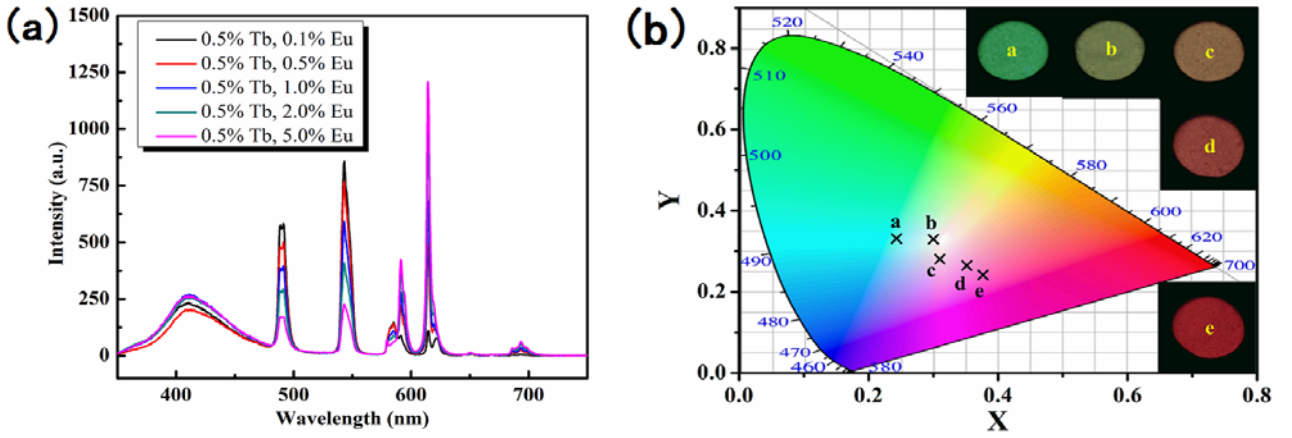

Figure S9. (a) Emission spectra; (b) CIE chromaticity coordinates and photographs of **ZJU-1**:0.5%Tb^{3+}, *x*%Eu^{3+} (*x* =0.1, 0.5, 1.0, 2.0, 5.0) under 312 nm excitation.

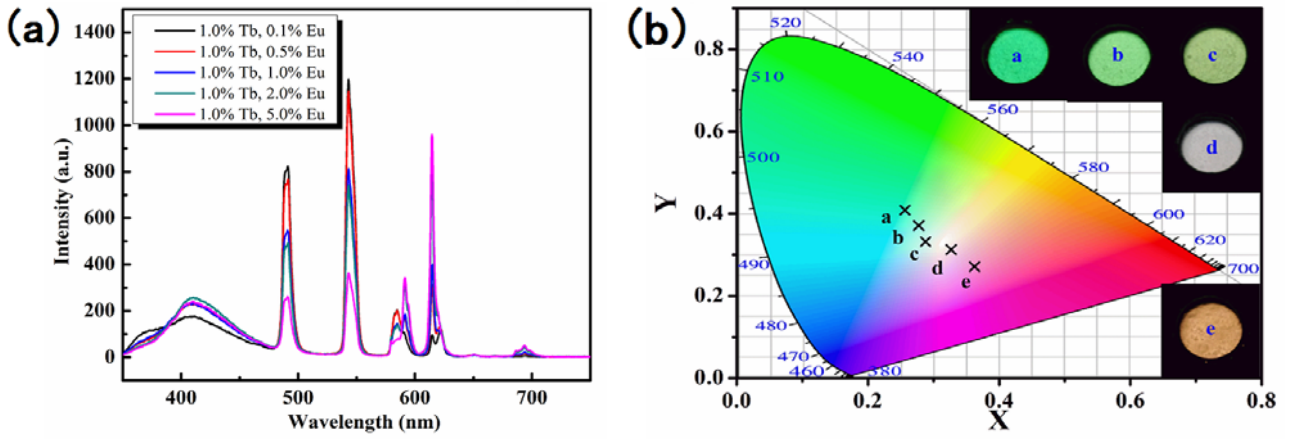

Figure S10. (a) Emission spectra; (b) CIE chromaticity coordinates and photographs of **ZJU-1**:1.0%Tb^{3+}, x%Eu^{3+} (x =0.1, 0.5, 1.0, 2.0, 5.0) under 312 nm excitation.

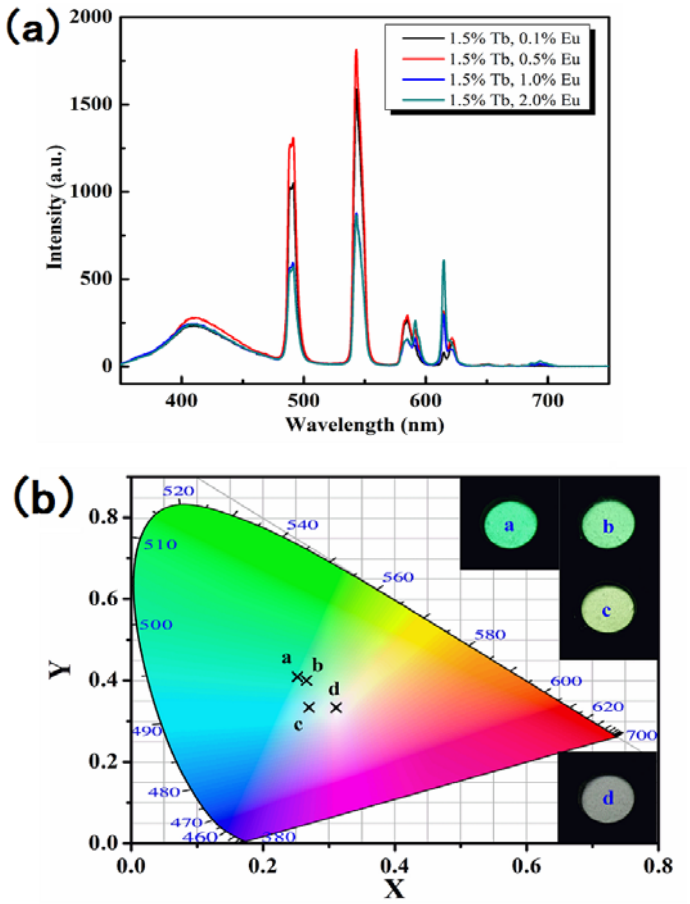

Figure S11. (a) Emission spectra; (b) CIE chromaticity coordinates and photographs of **ZJU-1**:1.5%Tb^{3+}, x%Eu^{3+} (x =0.1, 0.5, 1.0, 2.0) under 312 nm excitation.

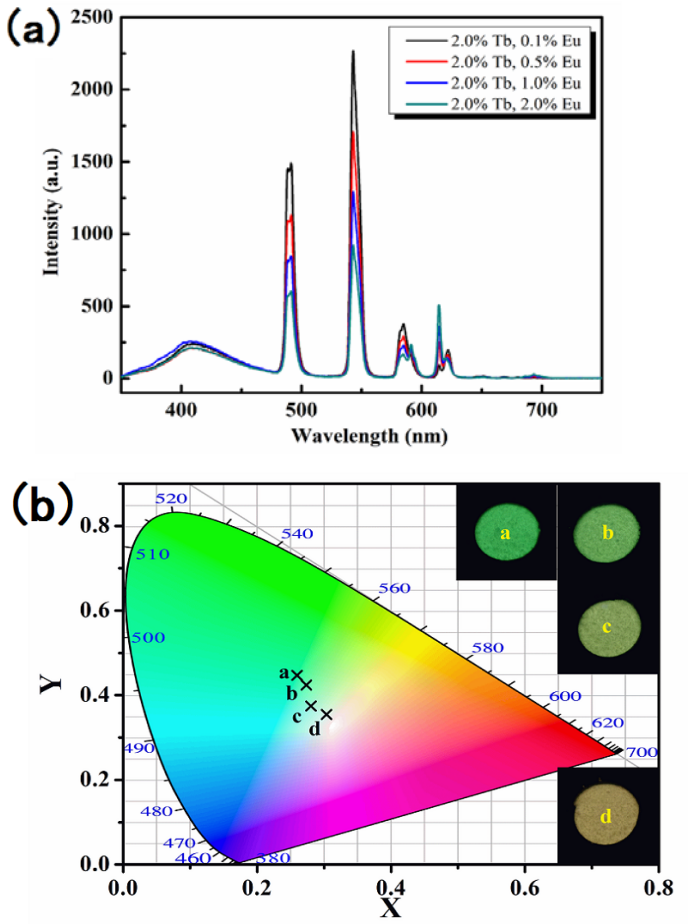

Figure S12. (a) Emission spectra; (b) CIE chromaticity coordinates and photographs of **ZJU-1**:2.0%Tb^{3+}, x%Eu^{3+} (x =0.1, 0.5, 1.0, 2.0) under 312 nm excitation.

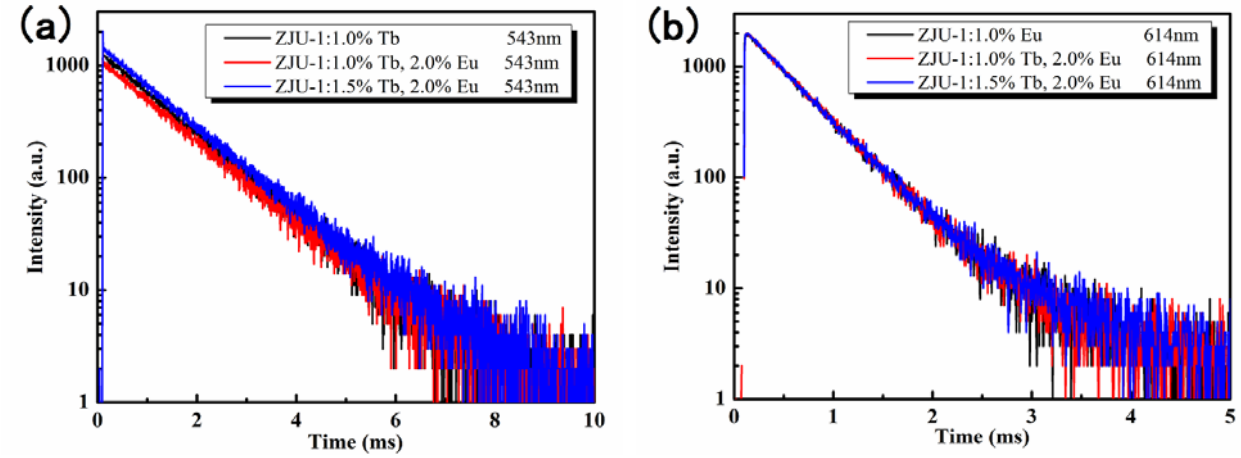

Figure S13. PL decay curves of **ZJU-1**:x%Tb^{3+}, y%Eu^{3+} under 312 nm excitation. (Monitored: (a) 543 nm, (b) 614 nm)

Table S1. Distance (Å) and Angles (deg) of Hydrogen Bonds for **ZJU-1**

D-H···A	Distance (D-H)	Distance (H···A)	Distance (D···A)	Angle (D-H···A)
O(13)-H(13A)-O(5)#2	0.858	2.088	2.694	127.16
O(13)-H(13A)-O(6) #2	0.858	2.451	3.191	145.02

O(13)-H(13B)-O(8) #3	0.852	2.313	3.055	145.65
O(14)-H(14A)-O(1) #1	0.845	1.848	2.693	179.64
O(14)-H(14B)-O(8) #3	0.850	1.905	2.756	179.56
O(15)-H(15A)-O(15) #2	0.815	2.142	2.920	160.01
O(15)-H(15B)-O(11) #2	0.856	2.292	2.748	113.50
O(16)-H(16A)-O(10) #1	0.863	2.060	2.830	148.23
O(16)-H(16B)-O(12) #4	0.851	2.079	2.898	161.26

Symmetry transformations used to generate equivalent atoms: #1,-x, -y, -z; #2, -x, -y, -z+1; #3, -x, -y-1, -z+1; #4, x, y-1, z.

Table S2. Selected Bond lengths (angstroms) and Angles (degrees) for **ZJU-1**

Distances					
La(1)-O(1)	2.504(6)	La(1)-N(1)	2.637(7)	La(2)-O(4)	2.595(6)
La(1)-O(13)	2.520(6)	La(1)-N(3)	2.740(6)	La(2)-O(7)#3	2.601(6)
La(1)-O(9)	2.579(5)	La(1)-O(10)#1	2.972(6)	La(2)-O(7)	2.606(5)
La(1)-O(11)	2.588(5)	La(2)-O(12)#2	2.541(5)	La(2)-O(3)	2.665(5)
La(1)-O(9)#1	2.593(5)	La(2)-O(5)	2.549(5)	La(2)-N(2)	2.695(6)
La(1)-O(14)	2.599(5)	La(2)-O(15)	2.564(6)	La(2)-O(8)#3	2.877(6)
La(1)-O(3)	2.610(4)	La(2)-O(16)	2.584(6)		
Angles					
O(1)-La(1)-O(13)	144.70(18)	O(9)-La(1)-N(3)	59.24(16)	O(12)#2-La(2)-O(7)	82.78(17)
O(1)-La(1)-O(9)	78.97(17)	O(11)-La(1)-N(3)	59.01(17)	O(5)-La(2)-O(7)	118.17(17)
O(13)-La(1)-O(9)	92.28(19)	O(9)#1-La(1)-N(3)	114.09(16)	O(15)-La(2)-O(7)	147.8(2)
O(1)-La(1)-O(11)	82.79(18)	O(14)-La(1)-N(3)	114.9(2)	O(16)-La(2)-O(7)	66.79(17)
O(13)-La(1)-O(11)	71.3(2)	O(3)-La(1)-N(3)	134.59(17)	O(4)-La(2)-O(7)	101.59(19)
O(9)-La(1)-O(11)	118.22(15)	N(1)-La(1)-N(3)	114.18(19)	O(7)#3-La(2)-O(7)	59.8(2)
O(1)-La(1)-O(9)#1	72.44(16)	O(1)-La(1)-O(10)#1	95.98(17)	O(12)#2-La(2)-O(3)	143.41(16)
O(13)-La(1)-O(9)#1	132.70(18)	O(13)-La(1)-O(10)#1	119.30(17)	O(5)-La(2)-O(3)	86.12(16)
O(9)-La(1)-O(9)#1	61.59(19)	O(9)-La(1)-O(10)#1	104.40(14)	O(15)-La(2)-O(3)	73.89(19)
O(11)-La(1)-O(9)#1	154.89(18)	O(11)-La(1)-O(10)#1	136.05(16)	O(16)-La(2)-O(3)	69.48(16)
O(1)-La(1)-O(14)	138.05(16)	O(9)#1-La(1)-O(10)#1	46.06(14)	O(4)-La(2)-O(3)	49.59(16)
O(13)-La(1)-O(14)	66.62(19)	O(14)-La(1)-O(10)#1	65.01(19)	O(7)#3-La(2)-O(3)	120.64(15)

O(9)-La(1)-O(14)	71.15(16)	O(3)-La(1)-O(10)#1	65.24(15)	O(7)-La(2)-O(3)	133.79(17)
O(11)-La(1)-O(14)	137.34(19)	N(1)-La(1)-O(10)#1	68.80(17)	O(12)#2-La(2)-N(2)	75.3(2)
O(9)#1-La(1)-O(14)	67.70(17)	N(3)-La(1)-O(10)#1	159.79(16)	O(5)-La(2)-N(2)	60.37(18)
O(1)-La(1)-O(3)	123.09(17)	O(12)#2-La(2)-O(5)	73.97(18)	O(15)-La(2)-N(2)	127.87(19)
O(13)-La(1)-O(3)	75.61(18)	O(12)#2-La(2)-O(15)	71.01(18)	O(16)-La(2)-N(2)	103.7(2)
O(9)-La(1)-O(3)	155.27(16)	O(5)-La(2)-O(15)	72.7(2)	O(4)-La(2)-N(2)	72.12(19)
O(11)-La(1)-O(3)	78.74(15)	O(12)#2-La(2)-O(16)	143.00(18)	O(7)#3-La(2)-N(2)	112.29(18)
O(9)#1-La(1)-O(3)	111.26(15)	O(5)-La(2)-O(16)	138.6(2)	O(7)-La(2)-N(2)	58.51(18)
O(14)-La(1)-O(3)	84.20(16)	O(15)-La(2)-O(16)	127.0(2)	O(3)-La(2)-N(2)	120.95(19)
O(1)-La(1)-N(1)	61.53(18)	O(12)#2-La(2)-O(4)	137.92(18)	O(12)#2-La(2)-O(8)#3	97.79(18)
O(13)-La(1)-N(1)	127.92(19)	O(5)-La(2)-O(4)	67.1(2)	O(5)-La(2)-O(8)#3	137.79(17)
O(9)-La(1)-N(1)	138.08(18)	O(15)-La(2)-O(4)	110.3(2)	O(15)-La(2)-O(8)#3	65.63(19)
O(11)-La(1)-N(1)	72.38(19)	O(16)-La(2)-O(4)	71.6(2)	O(16)-La(2)-O(8)#3	69.6(2)
O(9)#1-La(1)-N(1)	91.76(18)	O(12)#2-La(2)-O(7)#3	72.15(17)	O(4)-La(2)-O(8)#3	121.65(17)
O(14)-La(1)-N(1)	130.87(19)	O(5)-La(2)-O(7)#3	146.03(18)	O(7)#3-La(2)-O(8)#3	46.88(15)
O(3)-La(1)-N(1)	61.60(18)	O(15)-La(2)-O(7)#3	93.7(2)	O(7)-La(2)-O(8)#3	101.10(16)
O(1)-La(1)-N(3)	70.42(19)	O(16)-La(2)-O(7)#3	74.4(2)	O(3)-La(2)-O(8)#3	76.56(16)
O(13)-La(1)-N(3)	75.71(19)	O(4)-La(2)-O(7)#3	145.72(18)	N(2)-La(2)-O(8)#3	158.79(18)

Symmetry transformations used to generate equivalent atoms: #1,-x, -y, -z; #2, -x, -y, -z+1; #3, -x, -y-1, -z+1; #4, -x-1, -y+1, -z.

Table S3. Elemental analysis for $Na_3[Ln(PDA)_3](H_2O)_x$

Ln (x)	Wt% C Calcd (Found)	Wt% H Calcd (Found)	Wt% N Calcd (Found)
La (x = 12)	27.43 (27.78)	3.63 (3.32)	4.57 (5.00)
Eu (x = 10)	28.14 (27.78)	3.27 (3.15)	4.69 (4.62)
Tb (x = 9)	28.49 (28.12)	3.08 (3.04)	4.75 (4.70)

Table S4. The corresponding CIE coordinates of the **ZJU-1**: *x*% Tb, *y*% Eu excited at 312 nm

CIE / Sample (Tb: Eu)	X, Y	CIE / Sample (Tb: Eu)	X, Y	CIE / Sample (Tb: Eu)	X, Y
0.001:0.001	0.2522, 0.2373	**0.005:0.001**	0.2432, 0.3314	**0.01:0.001**	0.2566, 0.4084
0.001:0.005	0.2993, 0.2029	**0.005:0.005**	0.3002, 0.3300	**0.01:0.005**	0.2773, 0.3710
0.001:0.01	0.3467, 0.2140	**0.005:0.01**	0.3101, 0.2810	**0.01:0.01**	0.2880, 0.3318
0.001:0.02	0.3715, 0.2096	**0.005:0.02**	0.3519, 0.2650	**0.01:0.02**	0.3269, 0.3123
0.001:0.05	0.3747, 0.1957	**0.005:0.05**	0.3766, 0.2419	**0.01:0.05**	0.3626, 0.2711
0.015:0.001	0.2521, 0.4087	**0.015:0.02**	0.3109, 0.3332	**0.02:0.01**	0.2806, 0.3746
0.015:0.005	0.2661, 0.3996	**0.02:0.001**	0.2596, 0.4471	**0.02:0.02**	0.3037, 0.3547
0.015:0.01	0.2697, 0.3337	**0.02:0.005**	0.2736, 0.4239		

Table S5. The unit cell parameters of the **ZJU-1**: *x*%Tb^{3+}, *y*%Eu^{3+} calculated from the PXRD patterns

Unit cell parameters	**ZJU-1**: 5.0%Tb^{3+}	**ZJU-1**: 5.0%Eu^{3+}	**ZJU-1**: 1.0%Tb^{3+}, 2.0%Eu^{3+}
a (Å)	10.4105	10.4217	10.4155
b (Å)	10.9079	10.8997	10.9013
c (Å)	13.0748	13.0768	13.0746
α (º)	77.66	77.61	77.73
β (º)	77.48	77.39	77.45
γ (º)	86.64	86.61	86.7
V ($Å^3$)	1415.8	1415.75	1415.8

Table S6. Lifetimes and quantum yields of **ZJU-1**:*x*%Tb^{3+},*y*%Eu^{3+}

sample	lifetime (τ) at 543nm (μs)	lifetime (τ) at 614nm (μs)	Quantum yield Φ (%)
ZJU-1:1.0%Tb^{3+}	1184.50±0.3		4.75
ZJU-1:1.0%Eu^{3+}		475.95±0.2	2.77
ZJU-1:1.0%Tb^{3+},2.0%Eu^{3+}	1181.38±0.4	477.65±0.4	6.11
ZJU-1:1.5%Tb^{3+},2.0%Eu^{3+}	1185.57±0.5	476.26±0.5	6.80

Quantum yield measurements

The quantum yield (Φ) was determined by employing the method developed by Bril et al,[1] for which the Φ value for a given samples can be calculated by a direct comparison with standard phosphors whose Φ values were previously determined by absolute measurements. The quantum yield Φ_x of a sample can thus be determined by:

$$\Phi_x = \left(\frac{1-R_{ST}}{1-R_x}\right)\left(\frac{\Delta\phi_x}{\Delta\phi_{ST}}\right)\Phi_{ST} \quad (1)$$

Where R_{ST} and R_x are the amount of exciting radiation reflected by the standard and by the sample, respectively, and Φ_{ST} is the quantum yield of the standard phosphor. The terms $\Delta\phi_x$ and $\Delta\phi_{ST}$ correspond to the respective integrate photon flux (photo·s^{-1}) for the sample and the standard phosphor, respectively. As standard phosphor we used sodium salicylate (Merck PA), whose Φ_{ST} is 55% at room temperature as reported by Malta and co-workers.[2]

Reference

1. A. Bril and A. W. D. Jagerveenis, *J. Res. Nat. Bureau Stand.,* 1976, **80A**, 401-407.

2. O. L. Malta, H. F. Brito, J. F. S. Menezes, F. R. Gonc¸alves e Silva, C. de Mello Donega and S. Alves Jr., *Chem. Phys. Lett.*, 1998, **282**, 233-238.