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A stable luminescent zinc-organic framework as dual-sensor towards Cu^{2+} and $Cr_2O_7^{2-}$, and excellent platforms encapsulated Ln^{3+} for systematic color tuning and white-light emission

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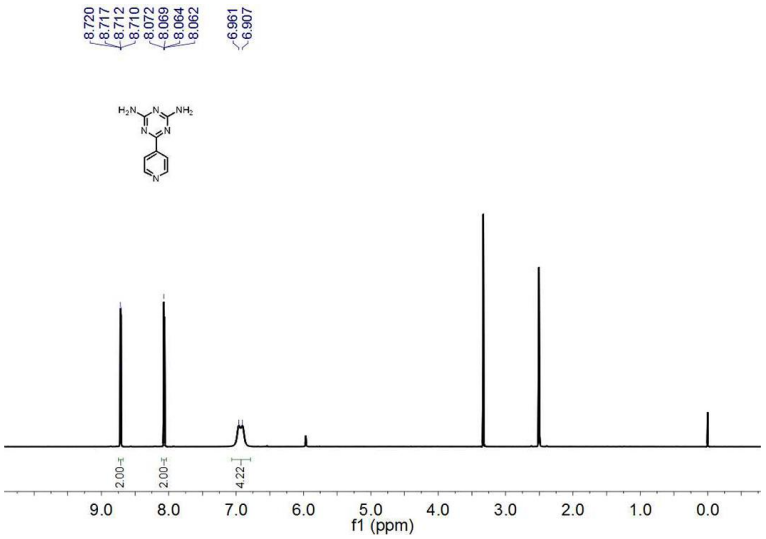


Fig. S1 The ^{1}H NMR spectrum of PTD ligand.

Table S1. Crystallographic data for compound **1**.

Compound	Compound **1**
empirical formula	$C_{36}H_{24}N_6O_{10}Zn$
formula weight	765.99
T [K]	293(2)
crystal system	orthorhombic
space group	*Fdd*2
a [Å]	39.603
b [Å]	43.585
c [Å]	38.789
α [^{o}]	90.00
β [^{o}]	90.00
γ [^{o}]	90.00
V	66953.570
Z	16
ρ_{calcd} [g cm^{-3}]	0.990
μ [mm^{-1}]	0.903
F(000)	20256

reflections collected	45496
independent reflections	29500
GOF	0.977
R_1,[a] $I > 2\sigma(I)$	0.0648
wR_2,[b] $I > 2\sigma(I)$	0.1865

[a] $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$. [b] $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2/\sum w(F_0{}^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (°) for complex **1**.

Zn(1)-O(16)	2.044(7)	Zn(2)-O(2)	2.040(7)	Zn(3)-O(10)#1	2.109(7)
Zn(1)-O(1)	2.047(8)	Zn(2)-O(12)	2.052(8)	Zn(4)-O(20)#2	1.997(8)
Zn(1)-O(11)	2.063(7)	Zn(2)-N(6)#1	2.054(7)	Zn(4)-O(5)#3	2.021(8)
Zn(1)-O(6)	2.079(9)	Zn(3)-O(14)	2.032(7)	Zn(4)-O(9)#1	2.036(8)
Zn(1)-N(1)	2.079(8)	Zn(3)-O(19)#2	2.033(8)	Zn(4)-O(15)	2.066(8)
Zn(2)-O(7)	2.008(8)	Zn(3)-O(4)#3	2.049(8)	Zn(4)-N(12)#4	2.091(8)
Zn(2)-N(17)	2.028(7)	Zn(3)-N(7)	2.074(8)		
O(16)-Zn(1)-O(1)		89.0(3)	O(14)-Zn(3)-O(19)#2		87.6(3)
O(16)-Zn(1)-O(11)		89.9(3)	O(14)-Zn(3)-O(4)#3		158.8(3)
O(1)-Zn(1)-O(11)		154.8(3)	O(19)#2-Zn(3)-O(4)#3		88.6(3)
O(16)-Zn(1)-O(6)		159.3(3)	O(14)-Zn(3)-N(7)		103.3(3)
O(1)-Zn(1)-O(6)		88.4(4)	O(19)#2-Zn(3)-N(7)		102.3(3)
O(11)-Zn(1)-O(6)		84.0(4)	O(4)#3-Zn(3)-N(7)		97.8(3)
O(16)-Zn(1)-N(1)		101.8(3)	O(14)-Zn(3)-O(10)#1		90.0(3)
O(1)-Zn(1)-N(1)		103.1(3)	O(19)#2-Zn(3)-O(10)#1		156.4(3)
O(11)-Zn(1)-N(1)		101.8(3)	O(4)#3-Zn(3)-O(10)#1		85.2(3)
O(6)-Zn(1)-N(1)		98.7(4)	N(7)-Zn(3)-O(10)#1		101.0(3)
O(7)-Zn(2)-O(17)		156.2(3)	O(20)#2-Zn(4)-O(5)#3		88.8(4)
O(7)-Zn(2)-O(2)		91.8(4)	O(20)#2-Zn(4)-O(9)#1		158.9(3)
O(17)-Zn(2)-O(2)		86.5(3)	O(5)#3-Zn(4)-O(9)#1		88.6(4)
O(7)-Zn(2)-O(12)		85.5(4)	O(20)#2-Zn(4)-O(15)		87.2(4)
O(17)-Zn(2)-O(12)		88.8(4)	O(5)#3-Zn(4)-O(15)		157.1(3)
O(2)-Zn(2)-O(12)		161.8(3)	O(9)#1-Zn(4)-O(15)		87.0(4)
O(7)-Zn(2)-N(6)#1		107.2(3)	O(20)#2-Zn(4)-N(12)#4		97.6(3)
O(17)-Zn(2)-N(6)#1		96.5(3)	O(5)#3-Zn(4)-N(12)#4		103.8(4)
O(2)-Zn(2)-N(6)#1		99.1(3)	O(9)#1-Zn(4)-N(12)#4		103.4(4)
O(12)-Zn(2)-N(6)#1		98.9(3)	O(15)-Zn(4)-N(12)#4		99.1(3)

Symmetry codes: #1: x+1/4, -y+3/4, z-1/4; #2: x+1/2, y+1/2, z; #3: x+1/4, -y+1/4, z+1/4; #4: x-1/4, -y+1/4, z-1/4

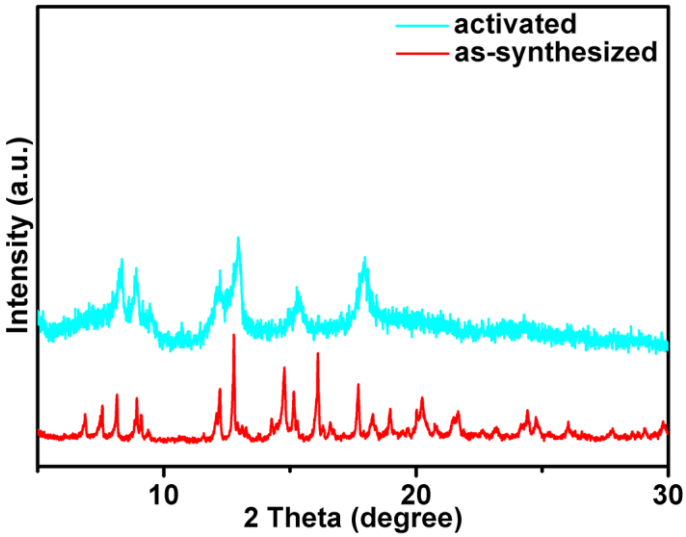


Fig. S2 The PXRD spectra of compound **1** after activated and freshly prepared.

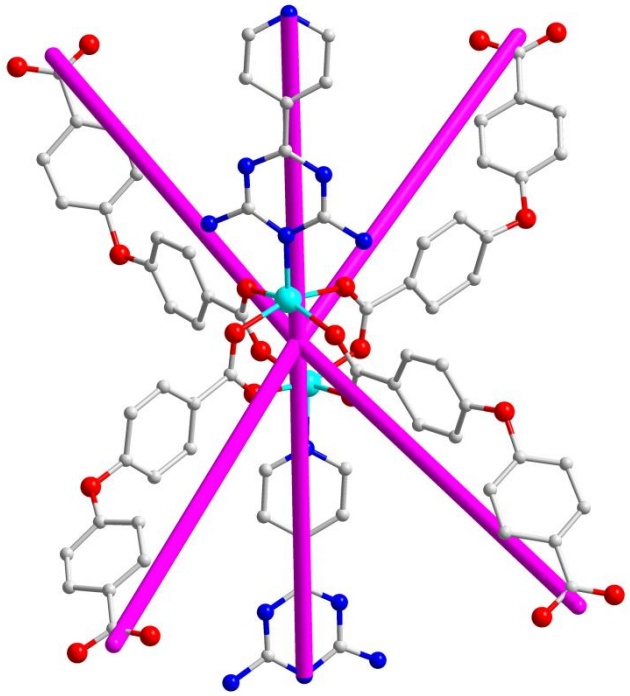


Fig. S3 The $Zn_2O_8N_2$ paddle-wheel SBU and its topological structure.

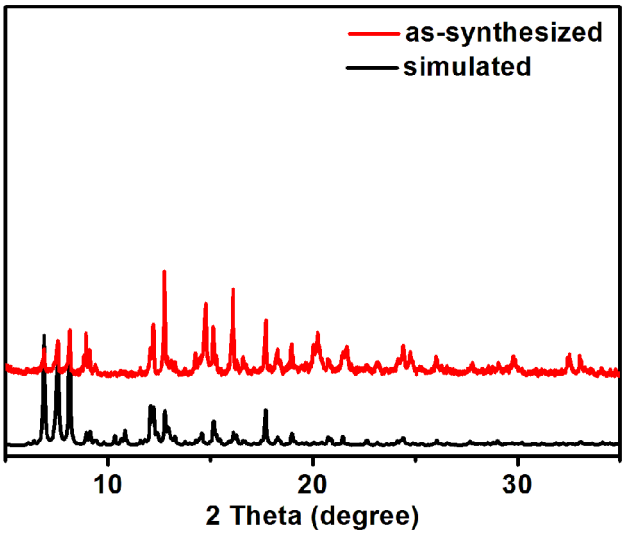


Fig. S4 PXRD spectra of complex **1**.

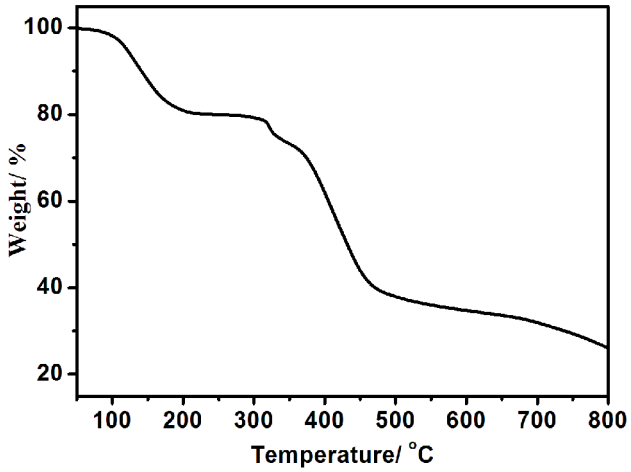


Fig. S5 TGA curve of complex **1**.

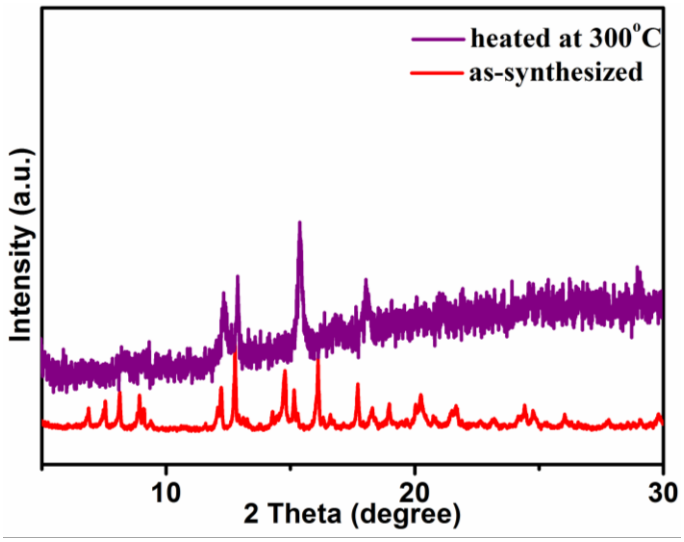


Fig. S6 PXRD spectra of complex **1** after heated for 4 hours at 300°C.

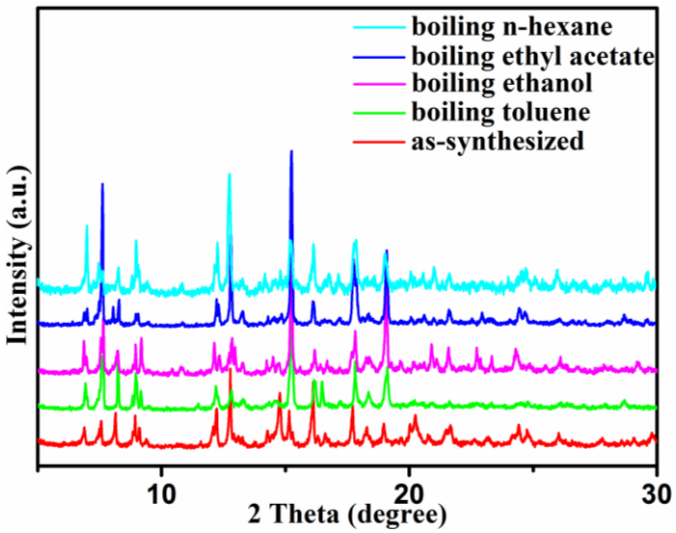
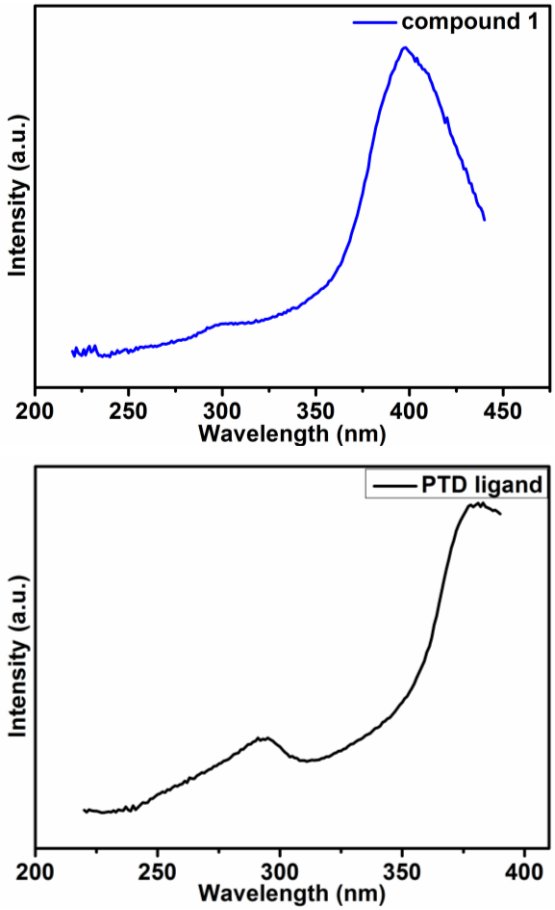


Fig. S7 PXRD spectra of compound **1** after being soaked in various boiling solvents for 36 hours.



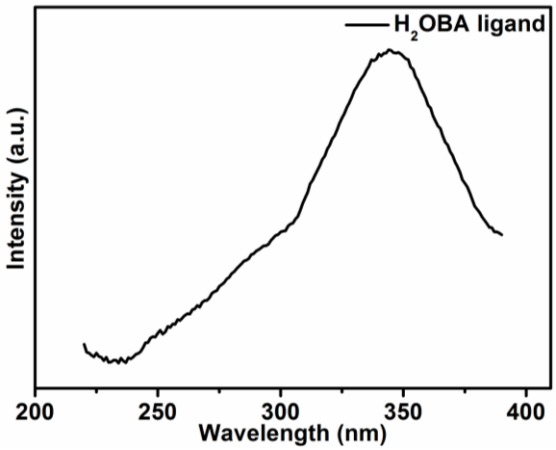


Fig. S8 Solid-state excitation spectra of compound **1**, PTD ligand, and H_2OBA ligand at room temperature.

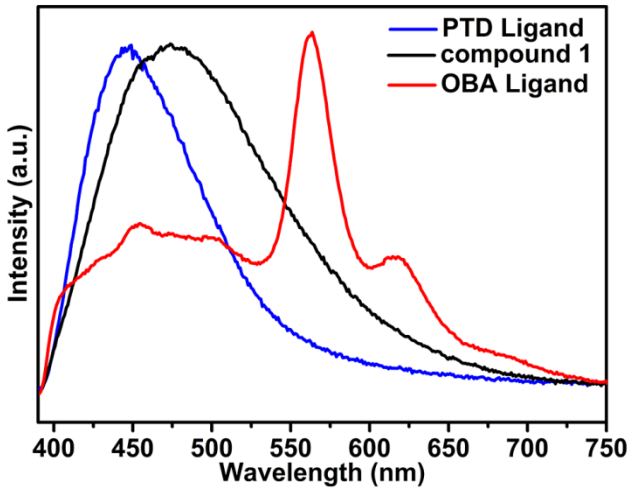


Fig. S9 Solid-state emission spectra of PTD ligand (excited at 375 nm), compound **1** (excited at 380 nm) and OBA ligand (excited at 346 nm) at room temperature.

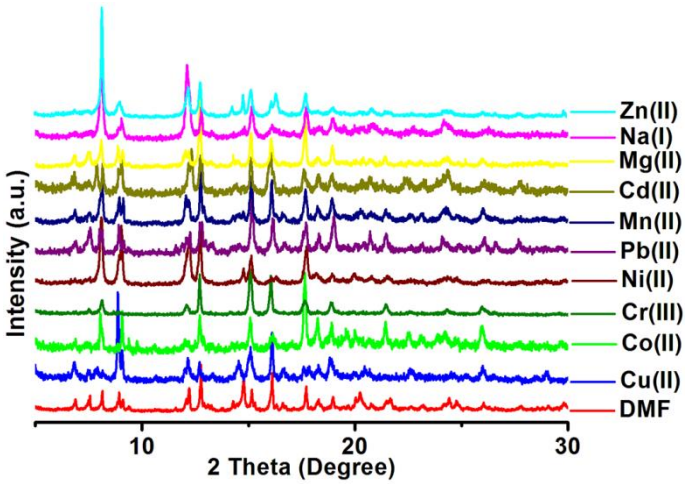


Fig. S10 PXRD patterns of as-synthesized compound **1** and metal ions-incorporated samples.

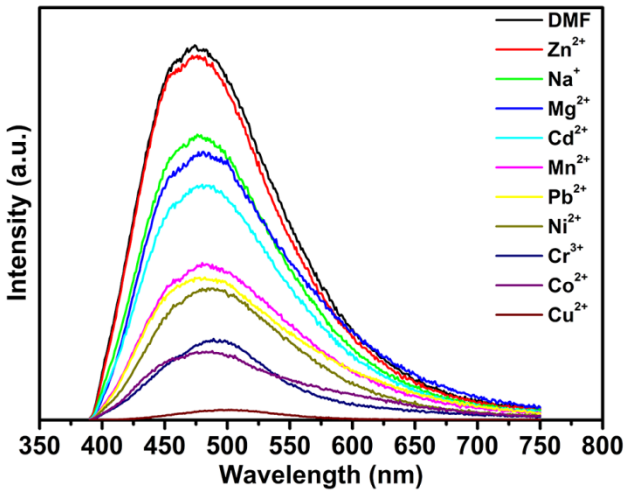


Fig. S11 Luminescence spectra of solid compound **1** treated with 10 mM various cations in DMF solutions for 24 hours.

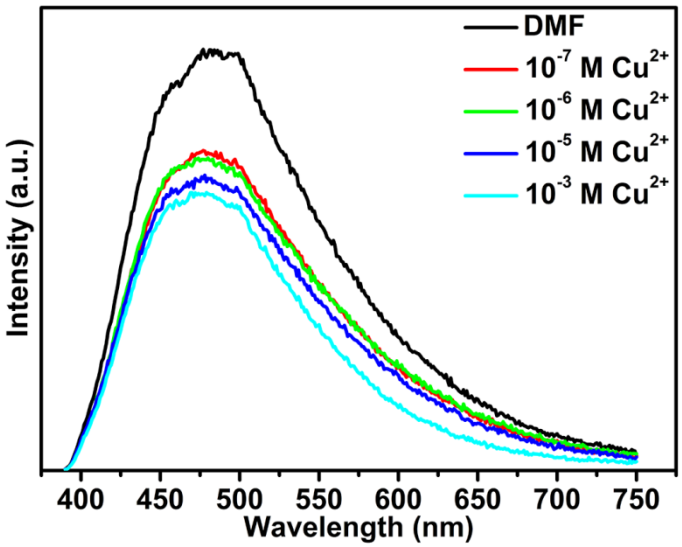


Fig. S12 Luminescence spectra of solid compound **1** treated with Cu^{2+} ions at various concentrations in 10 mL DMF solutions for 24 hours.

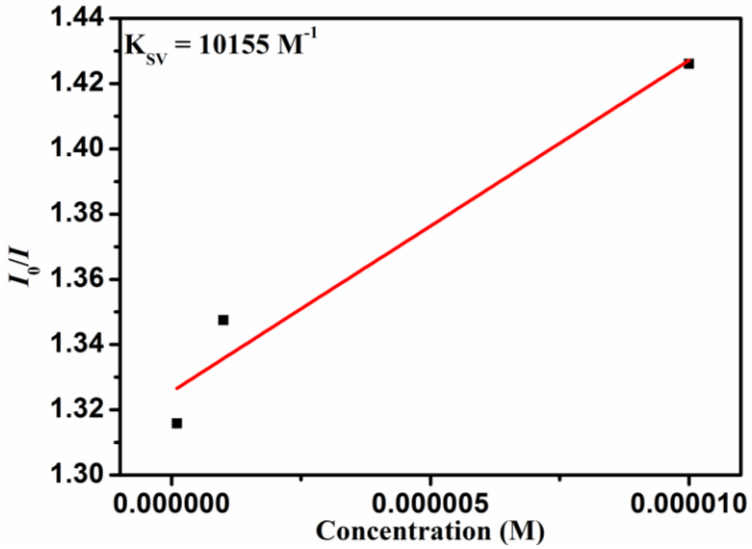


Fig. S13 Stern-Volmer plot of I_0/I vs. the concentration of Cu^{2+} ions in DMF.

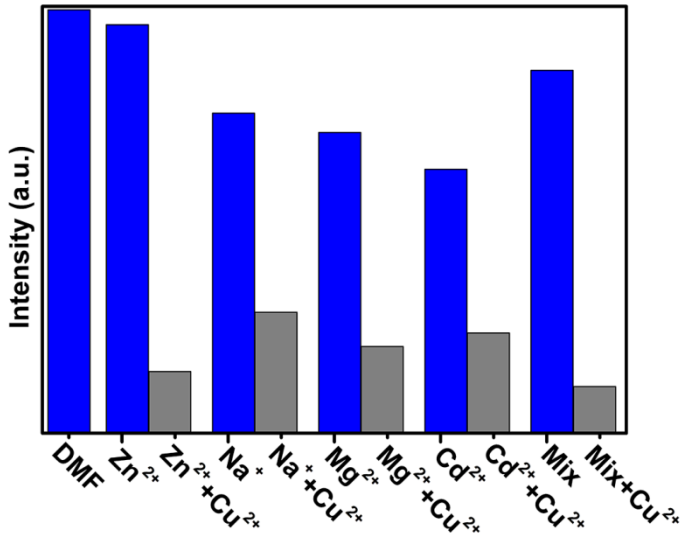


Fig. S14 The comparisons of luminescent intensities of compound **1** treated with 10 mM various cations in 10 mL DMF solutions for 24 hours. Mix: mixture of Zn^{2+}, Na^{+}, Mg^{2+} and Cd^{2+}.

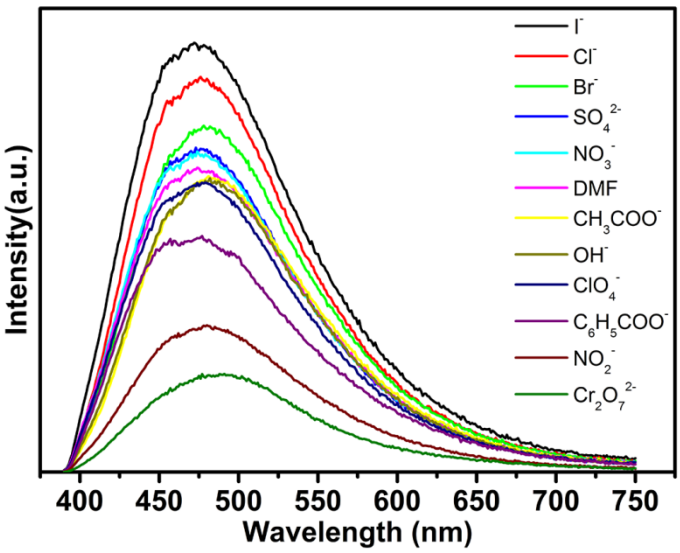


Fig. S15 Luminescence spectra of solid compound **1** treated with 10 mM various anions in DMF solutions for 24 hours.

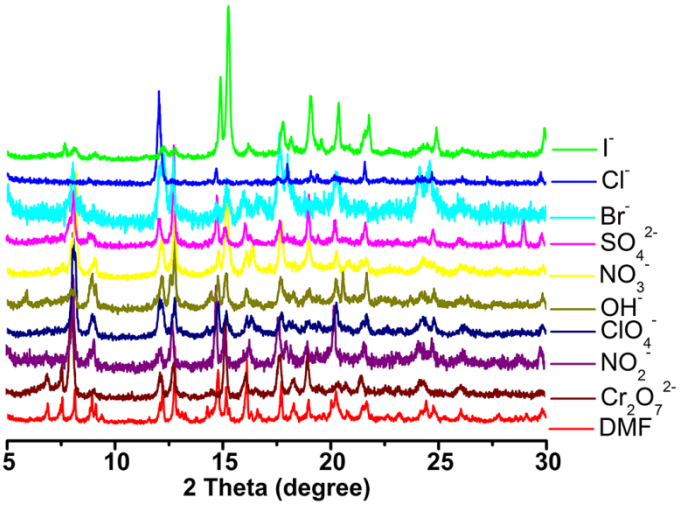


Fig. S16 PXRD patterns of as-synthesized compound **1** (DMF) and some anions-incorporated samples.

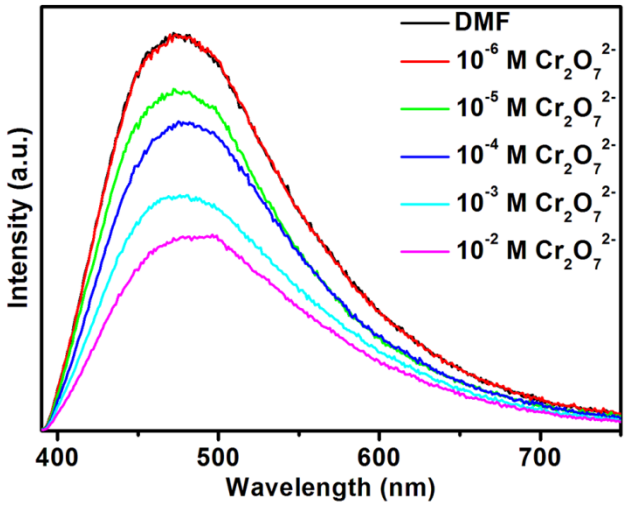


Fig. S17 Luminescence spectra of solid compound **1** treated with $Cr_2O_7^{2-}$ ions at various concentrations in 10 mL DMF solutions for 24 hours.

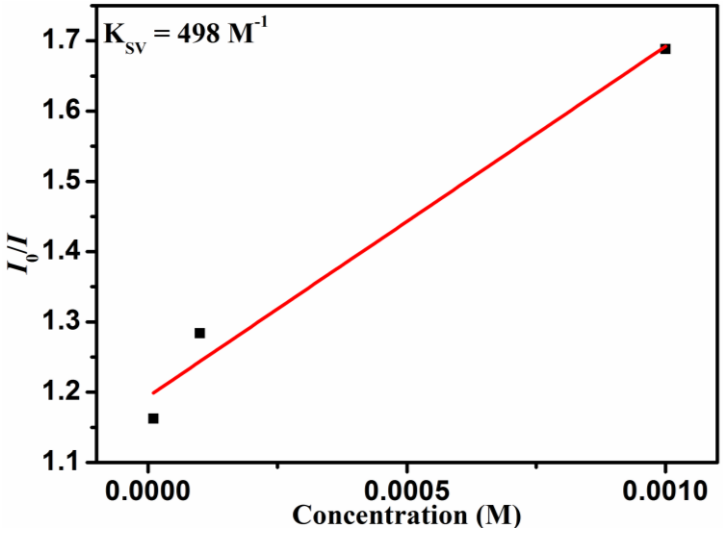


Fig. S18 Stern-Volmer plot of I_0/I vs. the concentration of $Cr_2O_7^{2-}$ ions in DMF.

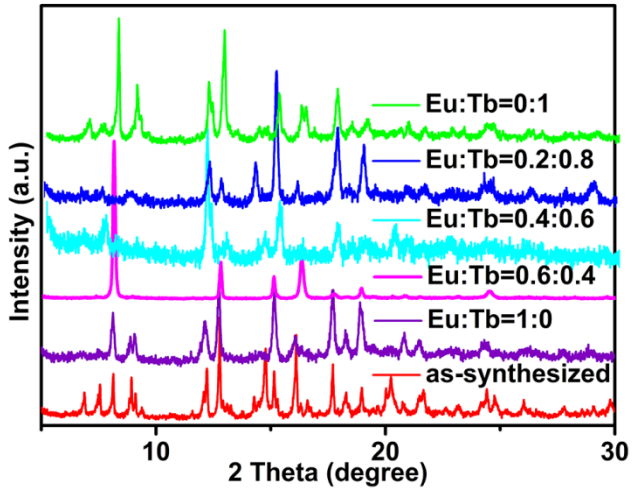


Fig. S19 PXRD patterns of as-synthesized compound **1** and some lanthanide-doped

samples.

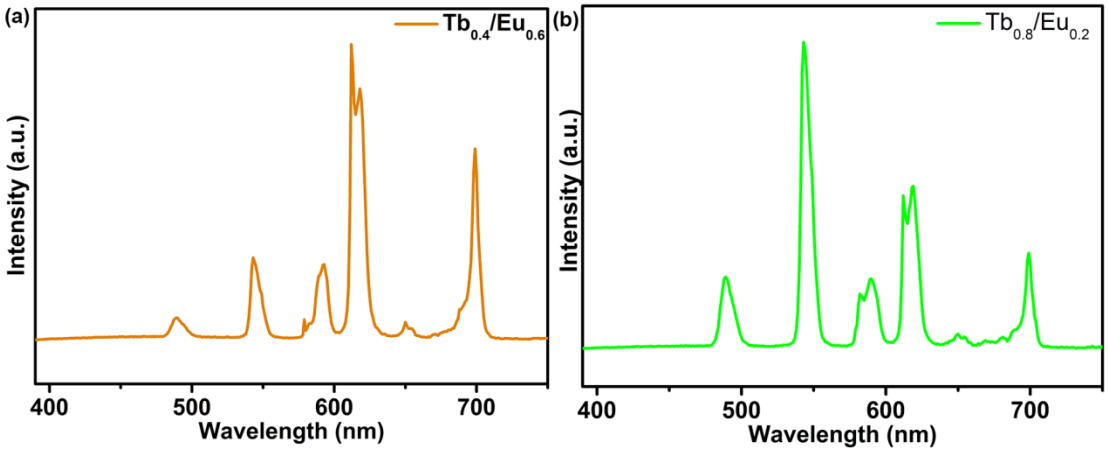


Fig. S20 The emission spectra (λ = 283 nm) of $Tb_{0.4}/Eu_{0.6}$ (a) and $Tb_{0.8}/Eu_{0.2}$ (b) doped compound **1**.

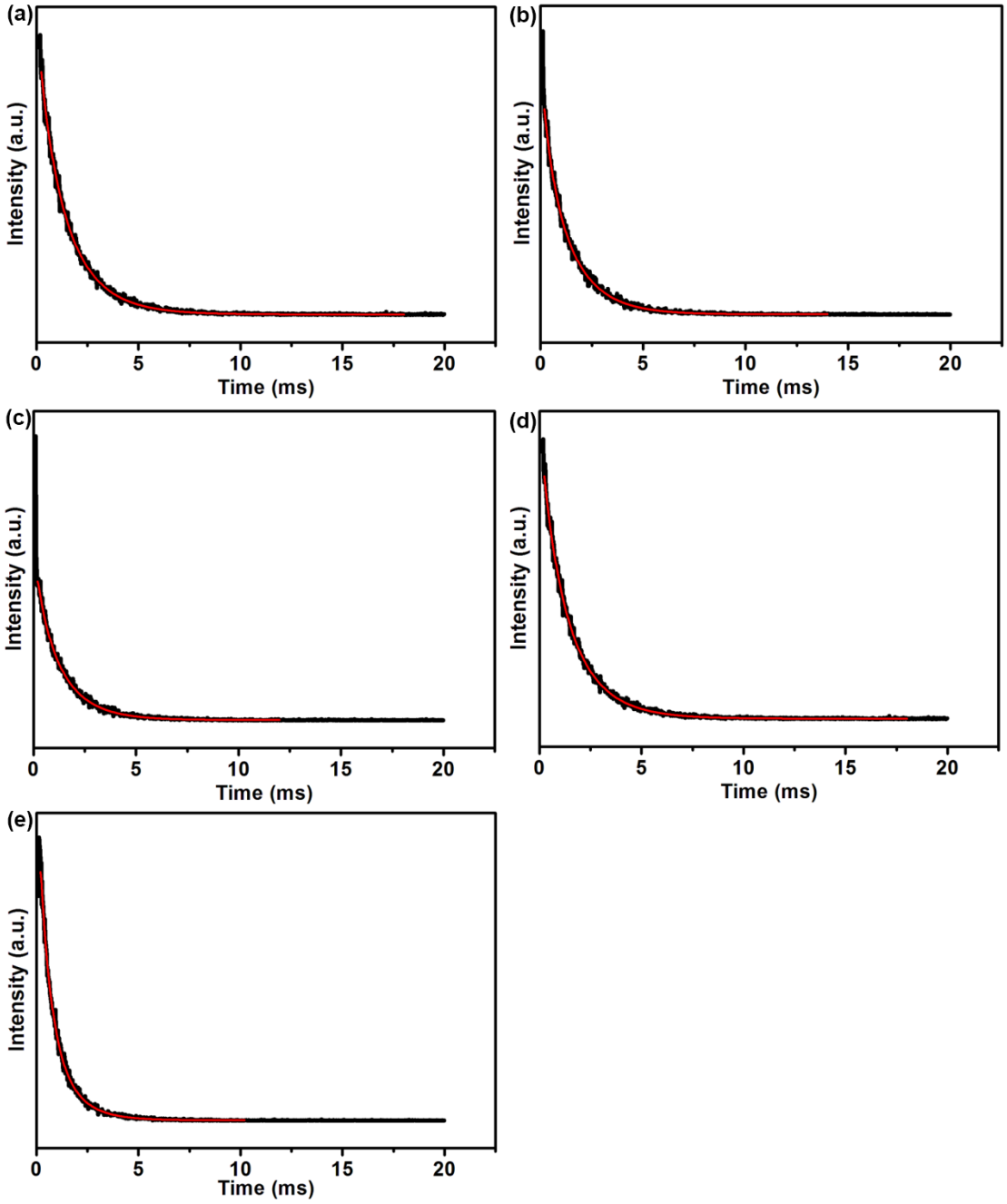


Fig. S21 Luminescence decay curves. (a) τ_1 = 813.8381 and τ_2 = 1673.1261 μs for Tb_1/Eu_0. (b) τ_1 = 532.2680 and τ_2 = 1500.8012 μs for $Tb_{0.8}/Eu_{0.2}$. (c) τ_1 = 612.6855 and τ_2 = 1428.0812 μs for $Tb_{0.6}/Eu_{0.4}$. (d) τ_1 = 488.5423 and τ_2 = 1372.6250 μs for $Tb_{0.4}/Eu_{0.6}$. (e) τ_1 = 530.6851 and τ_2 = 1221.9450 μs for Tb_0/Eu_1.

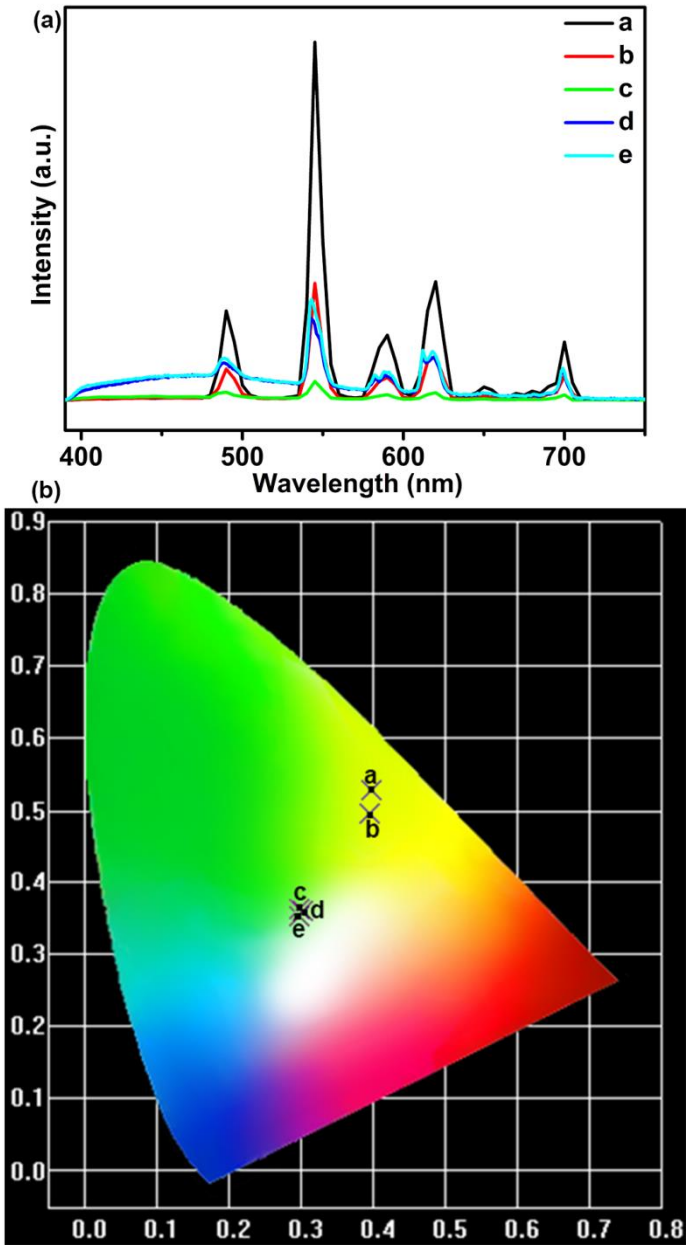


Fig. S22 The Emission spectra (a) and CIE chromaticity diagram (b) of compound **1** incorporated by lanthanide ions upon excitation at 283 nm. The samples were prepared by doping 50 mg as-synthesized compound **1** with different molar mass Ln^{3+} (Eu^{3+}/Tb^{3+}) in 10 mL DMF. a: 5×10^{-1} mmol with Eu^{3+}/Tb^{3+} (1/4); b: 5×10^{-2} mmol with Eu^{3+}/Tb^{3+} (1/4); c: 5×10^{-5} mmol with Eu^{3+}/Tb^{3+} (1/4); d: 5×10^{-5} mmol with Eu^{3+}/Tb^{3+} (1/3); e: 5×10^{-5} mmol with Eu^{3+}/Tb^{3+} (3/7).

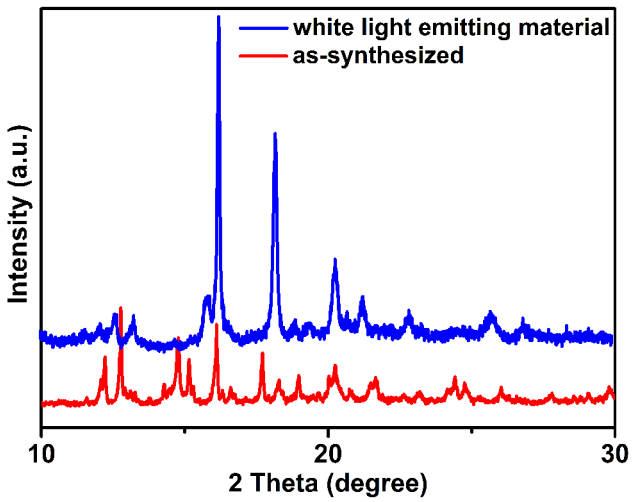


Fig. S23 The PXRD patterns of as-synthesized compound **1** and white-light emission compound **1** with Ln^{3+}-doped.

Fig. S24 The photograph of Ln^{3+}-doped compound **1** with white-light emission.

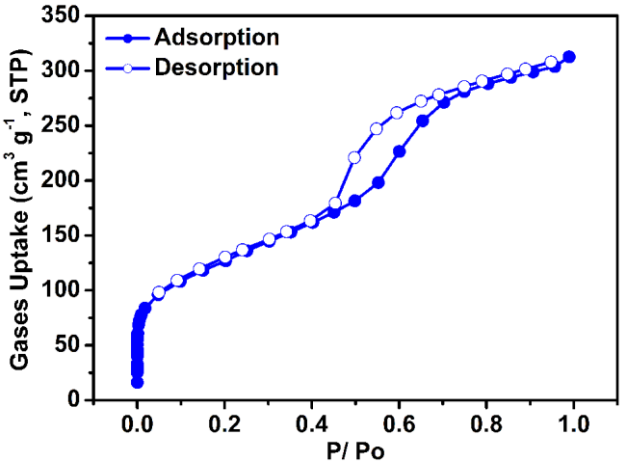


Fig. S25 The N_2 sorption isotherms for compound **1**, outgas temperature is 180°C under vacuum.

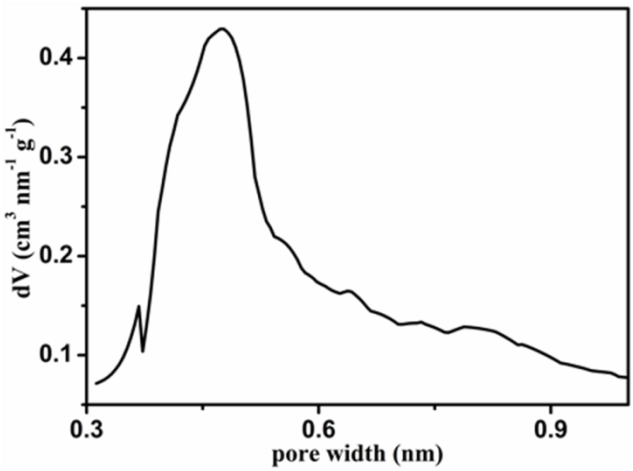


Fig. S26 The pore size distributions of compound **1**.

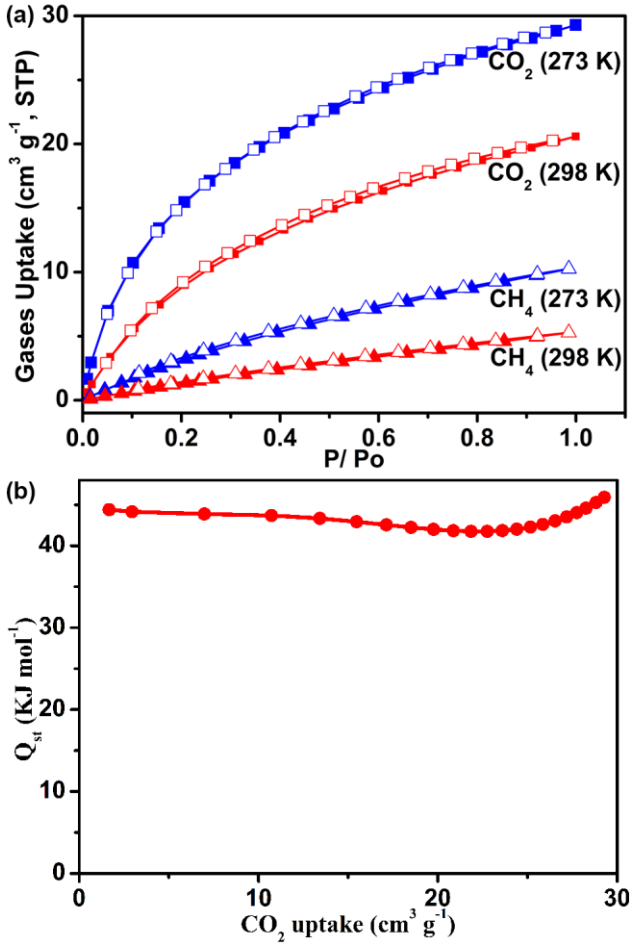


Fig. S27 (a) Gas adsorption isotherms of CO_2 and CH_4 for compound **1** at 273 K and 298 K; (b) Isosteric heat of CO_2 adsorption for compound **1** estimated by the virial equation from the adsorption isotherms at 273 K and 298 K.

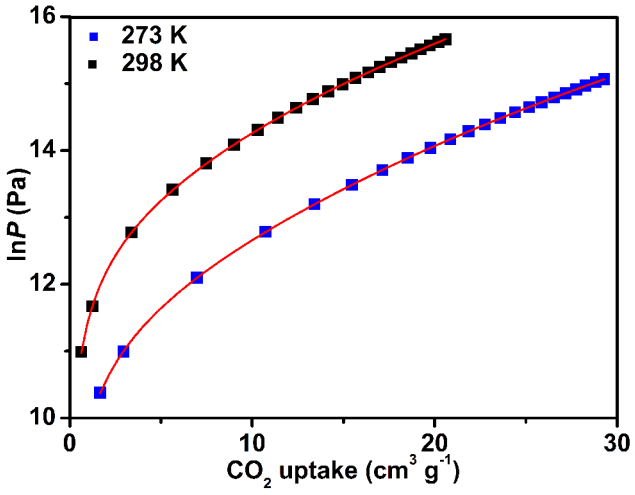


Fig. S28 Virial analysis of the CO_2 adsorption data at 273 and 298 K for compound **1**. Fitting results: a_0 = -9.4742, a_1 = 0.02258, a_2 = 0.00252, a_3 = -0.00008, a_4 = 7.4482E-7, Chi^2 = 0.00003, R^2 = 0.99998.