

Electronic Supporting Information

Elucidating White Light-Emitting Emissions in Tm³⁺/Dy³⁺ Codoped Polyoxometalates: a Color-Tunable and Energy Transfer Mechanism Study

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Experimental section

Synthesis of 2

DyCl₃·6H₂O (0.228 g, 0.605 mmol) was dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colourless block crystals at room temperature.

Synthesis of 3 (Tm³⁺:Dy³⁺ = 0.97:0.03)

TmCl₃·6H₂O (0.221 g, 0.576 mmol) and DyCl₃·6H₂O (0.007 g, 0.019 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Synthesis of 4 (Tm³⁺:Dy³⁺ = 0.92:0.08)

TmCl₃·6H₂O (0.210 g, 0.547 mmol) and DyCl₃·6H₂O (0.018 g, 0.048 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Synthesis of 5 (Tm³⁺:Dy³⁺ = 0.90:0.10)

TmCl₃·6H₂O (0.205 g, 0.534 mmol) and DyCl₃·6H₂O (0.023 g, 0.061 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Synthesis of 6 (Tm³⁺:Dy³⁺ = 0.80:0.20)

TmCl₃·6H₂O (0.182 g, 0.475 mmol) and DyCl₃·6H₂O (0.046 g, 0.122 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g,

1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Synthesis of 7 (Tm³⁺:Dy³⁺ = 0.75:0.25)

TmCl₃·6H₂O (0.171 g, 0.446 mmol) and DyCl₃·6H₂O (0.057 g, 0.151 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Synthesis of 8 (Tm³⁺:Dy³⁺ = 0.50:0.50)

TmCl₃·6H₂O (0.114 g, 0.297 mmol) and DyCl₃·6H₂O (0.114 g, 0.302 mmol) were dissolved in 30 mL of deionized water, and then tartaric acid (0.120 g, 0.800 mmol) and precursor K₁₄[P₂W₁₉O₆₉(H₂O)]·24H₂O (2.120 g, 0.465 mmol) were added step by step with stirring. The pH value of mixture solution was adjusted to approximately 3.2 by 3 M KOH solution and heated to 60 °C for 1.5 h. Subsequently, tetramethyl ammonium chloride (TMACl) (0.110 g, 1.000 mmol) was added and stirred for another 30 min. The resulting solution was cooled to room temperature and filtered to evaporate for two weeks to obtain colorless block crystals at room temperature.

Photoluminescence section

The CIE 1931 chromaticity coordinates, color purity, and CCT are important optical parameters in research of PL properties of luminescent complexes. The CCT can be calculated by the following equations (1):

$$n = (x - x_e)/(y_e - y)$$

$$CCT = 499.0n^3 + 3525.0n^2 + 6823.3n + 5520.22 \quad (1)$$

Where $x_e = 0.3320$; $y_e = 0.1858$; x, y are the CIE 1931 chromaticity coordinates.

The lifetime adheres to a double exponential decay mode, which can be fitted with the formulae (2):

$$I(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + A_2 e^{\left(-\frac{t}{\tau_2}\right)} \quad (2)$$

Where $I(t)$ represents the emission intensity at time t , A_1 and A_2 represent weighting parameters; τ_1 and τ_2 represent short time and long time component. The double decay time may be the two emitting Tm³⁺ centres with different coordinated configurations. In generally, the average lifetime τ could be regarded as experimental lifetime value and be calculated by the following formulae (3):

$$\tau^* = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (3)$$

Table S1 The Calculated and Found Analyses of Tm and Dy in 1–8.

Sample	Calcd		Found	
	Tm(%)	Dy(%)	Tm(%)	Dy(%)
1	4.81	0	4.80	
2	0	4.64		4.69
3	4.67	0.14	4.71	0.08
4	4.43	0.37	4.60	0.24
5	4.33	0.46	4.26	0.36
6	3.85	0.93	3.67	0.74
7	3.61	1.16	3.51	1.06
8	2.32	2.41	2.21	2.18

Table S2. Selected bond angles (°) of 1.

Bond	Angel	Bond	Angel
O23–Tm1–O29	77.3(11)	O15–Tm2–O40	76.9(8)
O23–Tm1–O36	74.3(10)	O15–Tm2–O74	72.4(10)
O23–Tm1–O46	123.2(10)	O15–Tm2–O86	133.9(10)
O23–Tm1–O81	71.7(10)	O15–Tm2–O88	80.2(12)
O23–Tm1–O83	138.8(11)	O40–Tm2–O74	138.7(9)
O23–Tm1–O85	139.6(11)	O40–Tm2–O86	72.2(9)
O23–Tm1–O89	78.2(10)	O40–Tm2–O88	76.6(12)
O29–Tm1–O36	121.3(12)	O42–Tm2–O15	126.1(11)
O29–Tm1–O46	75.1(10)	O42–Tm2–O40	81.0(9)
O29–Tm1–O81	77.3(11)	O42–Tm2–O43	73.5(10)
O29–Tm1–O83	76.9(13)	O42–Tm2–O74	139.9(9)
O29–Tm1–O89	140.5(11)	O42–Tm2–O86	81.7(11)
O36–Tm1–O46	79.4(10)	O42–Tm2–O87	80.0(12)
O36–Tm1–O81	138.1(10)	O42–Tm2–O88	140.0(12)
O36–Tm1–O83	146.9(12)	O43–Tm2–O15	78.6(10)
O36–Tm1–O89	80.4(11)	O43–Tm2–O40	123.0(10)
O46–Tm1–O81	140.7(10)	O43–Tm2–O74	77.1(10)
O83–Tm1–O46	79.7(12)	O43–Tm2–O86	147.3(11)
O83–Tm1–O81	70.6(12)	O43–Tm2–O87	79.3(12)
O83–Tm1–O89	102.9(12)	O43–Tm2–O88	146.2(12)
O85–Tm1–O29	142.9(12)	O74–Tm2–O88	71.5(12)
O85–Tm1–O36	77.8(11)	O86–Tm2–O74	111.5(11)
O85–Tm1–O46	78.4(11)	O86–Tm2–O88	60.1(13)
O85–Tm1–O81	115.0(12)	O87–Tm2–O15	138.1(11)

O85-Tm1-O83	73.1(12)	O87-Tm2-O40	144.5(10)
O85-Tm1-O89	68.8(12)	O87-Tm2-O74	68.1(12)
O89-Tm1-O46	144.4(10)	O87-Tm2-O86	75.6(12)
O89-Tm1-O81	69.4(11)	O87-Tm2-O88	99.9(14)
W4-O23-Tm1	138.4(15)	W12-O40-Tm2	134.2(11)
W7-O29-Tm1	154.9(18)	W14-O42-Tm2	157.2(16)
W19-O36-Tm1	142.7(18)	W5-O43-Tm2	158.7(16)
W11-O46-Tm1	157.1(14)	W6-O15-Tm2	136.8(14)

Table S3. Selected bond lengths (Å) of **1**.

Bond	Length	Bond	Length
Tm1-O23	2.32(3)	Tm2-O15	2.25(2)
Tm1-O29	2.31(3)	Tm2-O40	2.34(2)
Tm1-O36	2.28(3)	Tm2-O42	2.29(4)
Tm1-O46	2.26(3)	Tm2-O43	2.25(3)
Tm1-O81	2.48(3)	Tm2-O74	2.43(3)
Tm1-O83	2.35(4)	Tm2-O86	2.40(3)
Tm1-O85	2.39(4)	Tm2-O87	2.26(4)
Tm1-O89	2.43(3)	Tm2-O88	2.41(4)

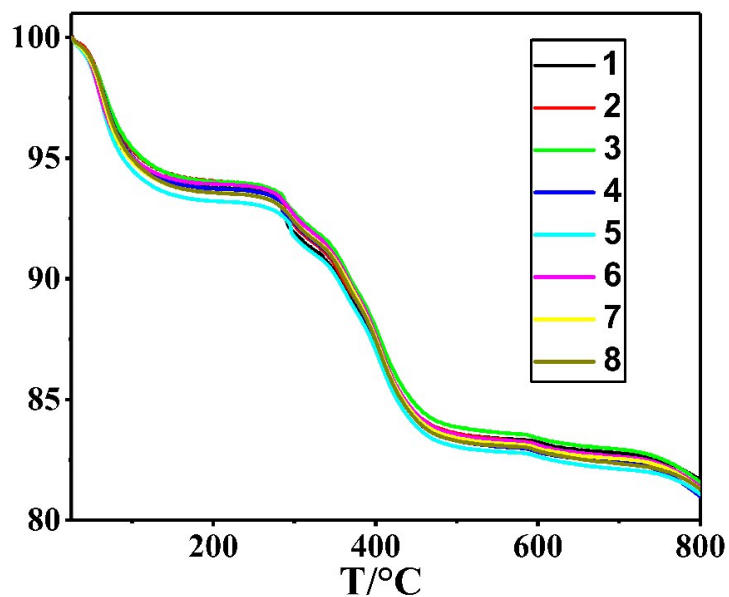


Fig. S1. Thermogravimetric curves of spectra of **1-8**.

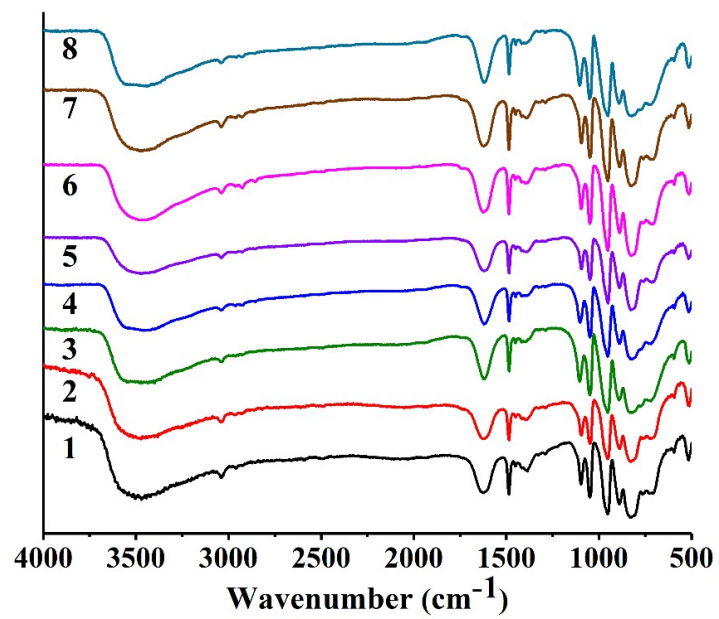


Fig. S2. IR spectra of 1–8.

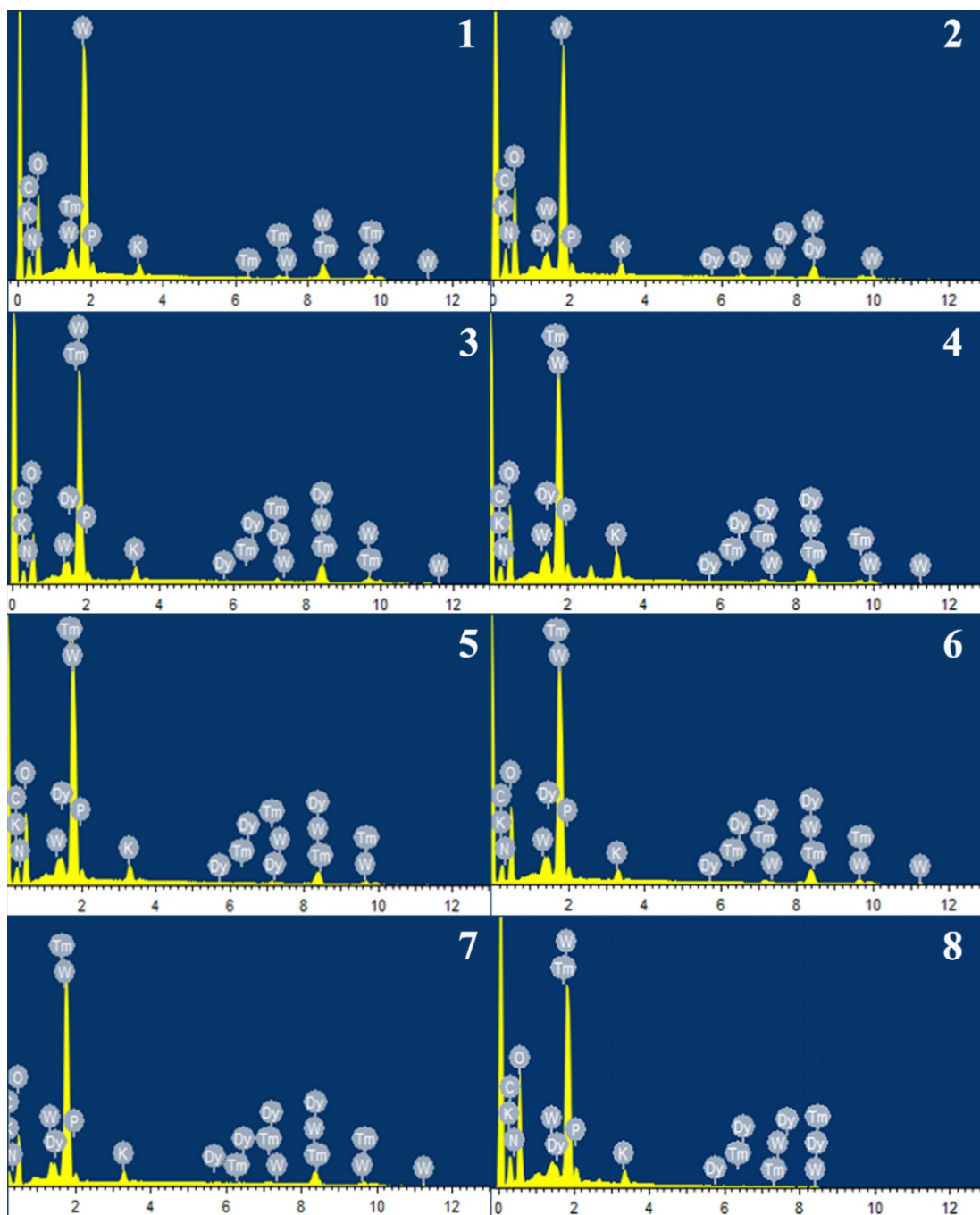


Fig. S3. EDX elemental spectra of **1–8** showing the presence of C, N, O, P, K, W, Tm and Dy element in the lattice. The measured ratios of $\text{Tm}^{3+}/\text{Dy}^{3+}$ ions are almost consistent with nominal ratios.

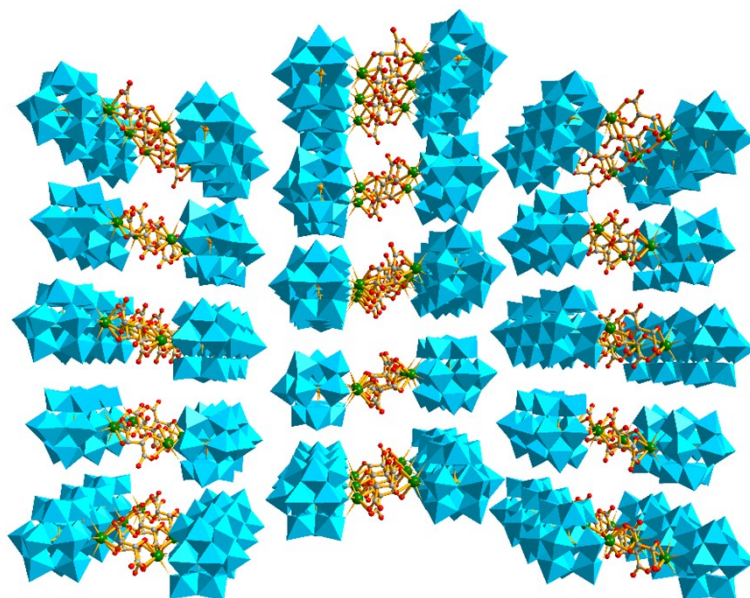


Fig S4. The packing arrangement of polyanions of **1**. (Color code: WO_6 , sky blue; P, pink; Tm, green; O, red; C, gray)

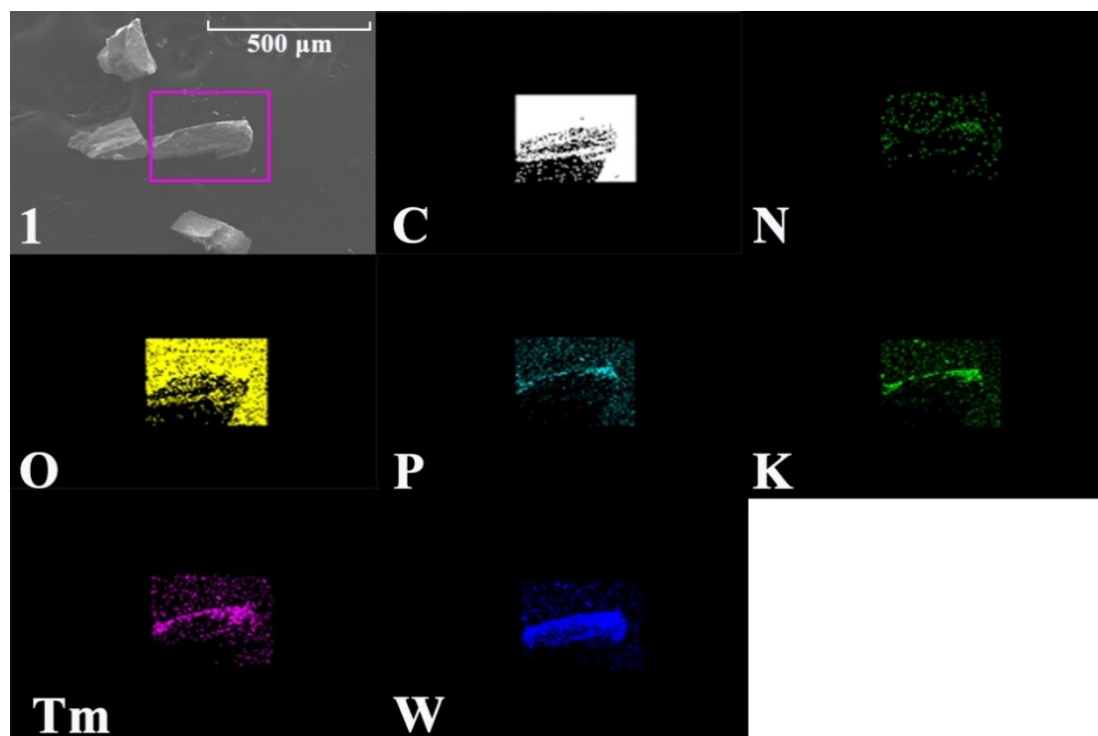


Fig. S5. STEM-EDX element maps of **1**.

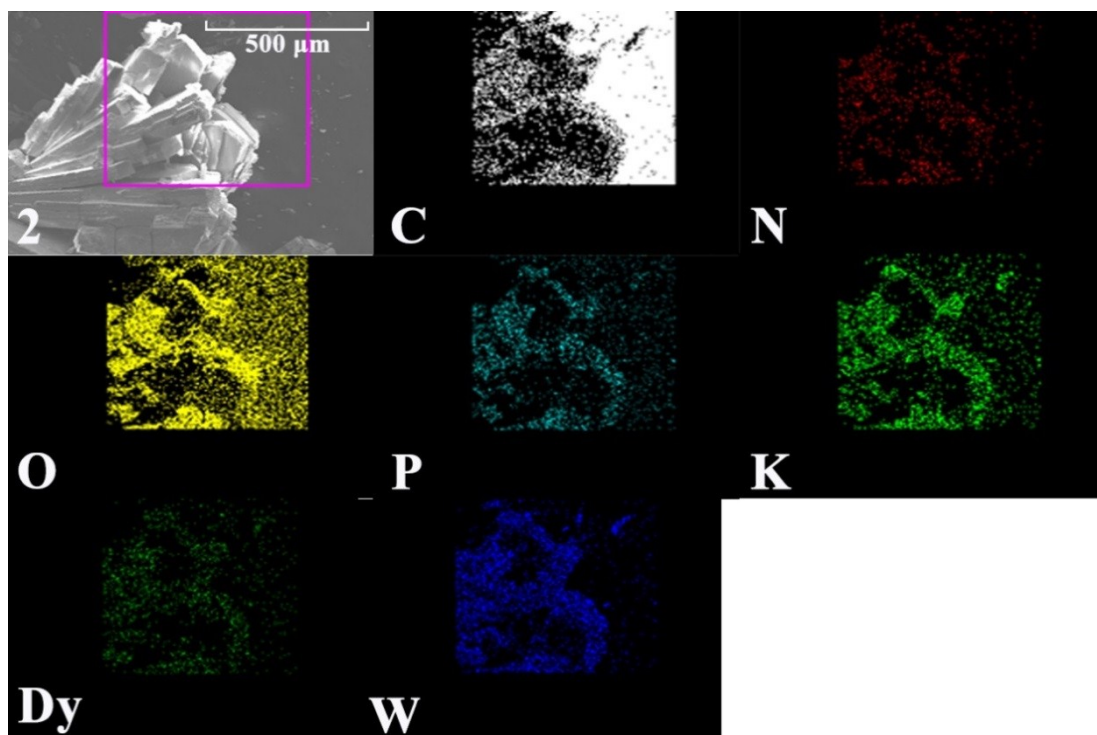


Fig. S6. STEM-EDX element maps of **2**.

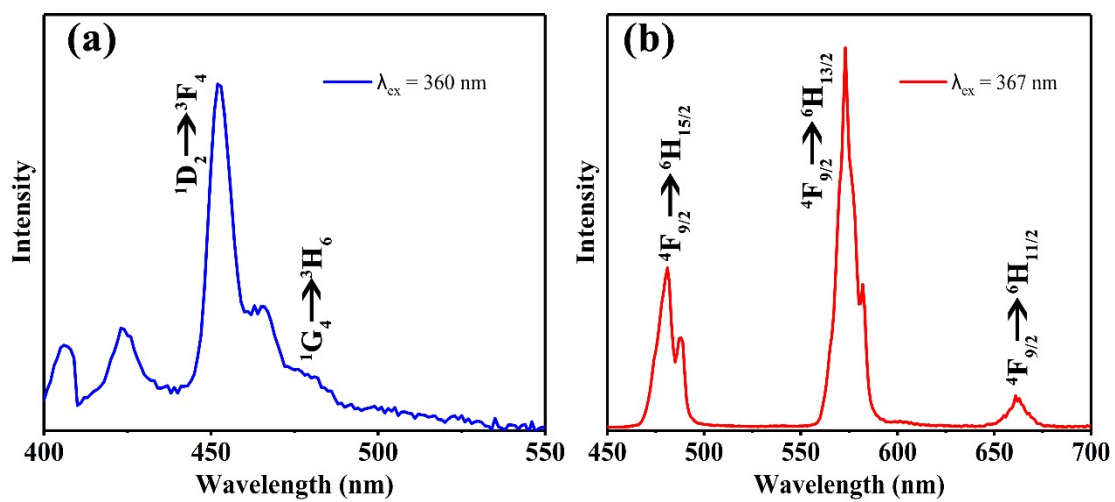


Fig. S7. (a) The PL emission spectra of **1** ($\lambda_{\text{ex}} = 360$ nm); (b) the PL emission spectra of **2** ($\lambda_{\text{ex}} = 367$ nm).

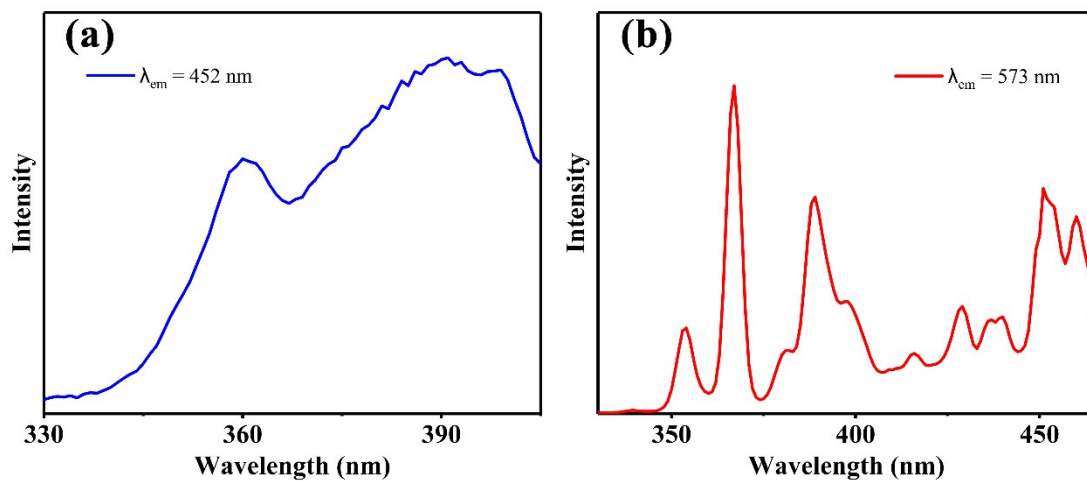


Fig S8. (a) The PL excitation spectra of **1** ($\lambda_{em} = 452$ nm); (b) the PL excitation spectra of **2** ($\lambda_{em} = 573$ nm).

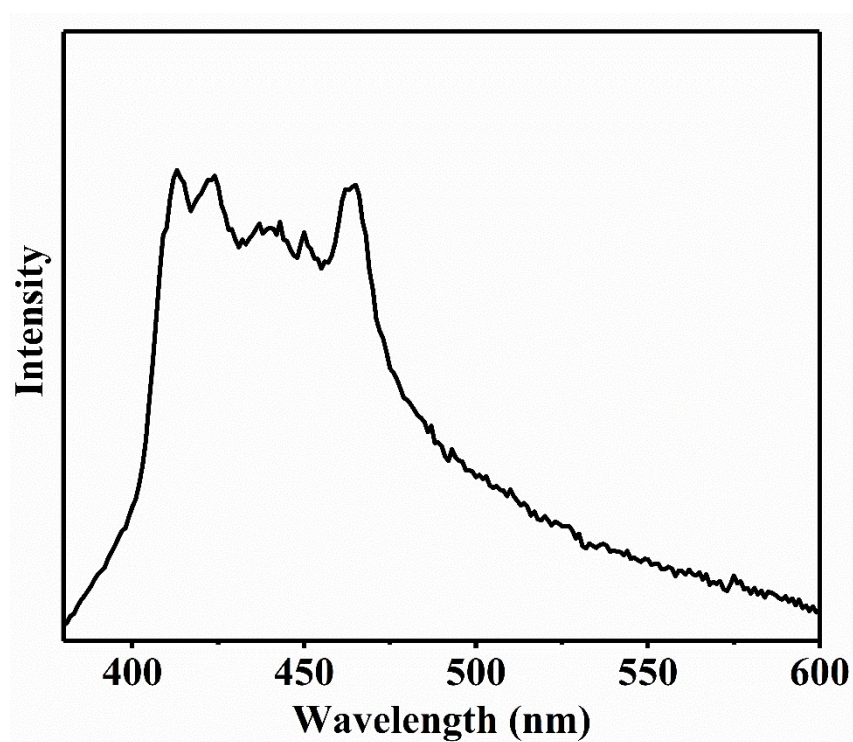


Fig S9. The PL emission spectra of $K_{14}[P_2W_{19}O_{69}(H_2O)] \cdot 24H_2O$ ($\lambda_{ex} = 360$ nm).

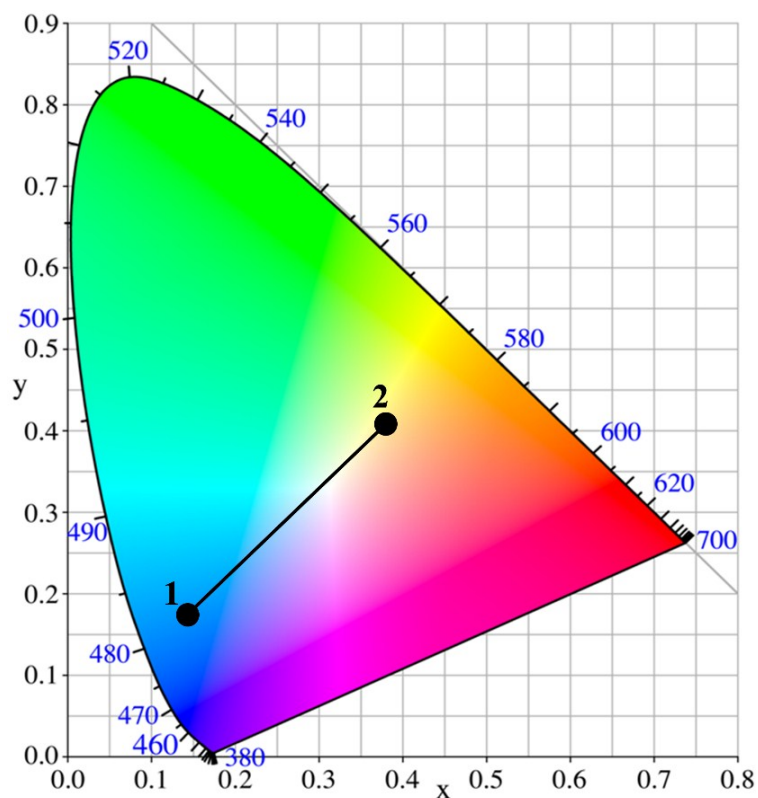


Fig S10. CIE chromaticity diagram of **1** and **2**.

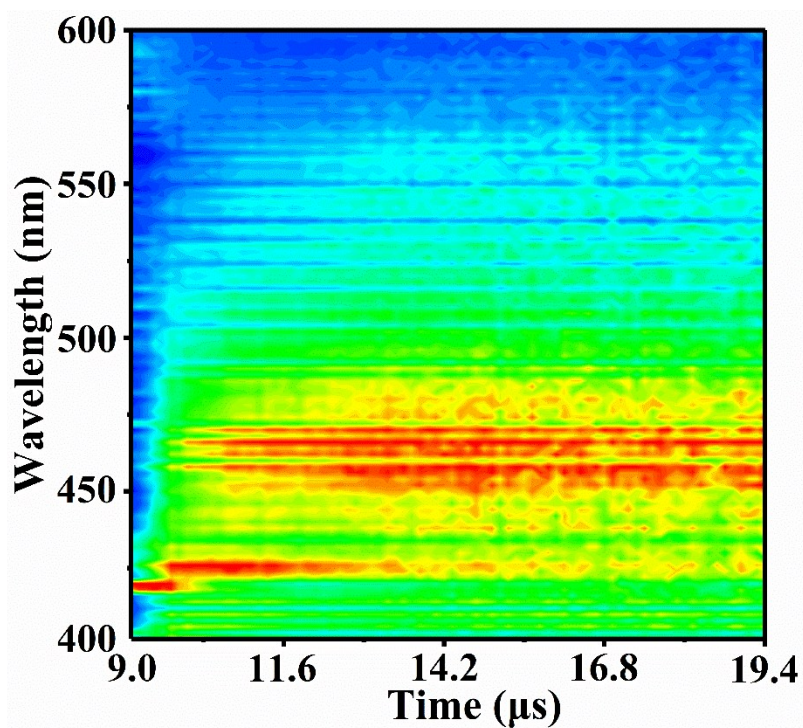


Fig S11. The time resolved emission spectroscopy of **1** ($\lambda_{\text{ex}} = 360$ nm).

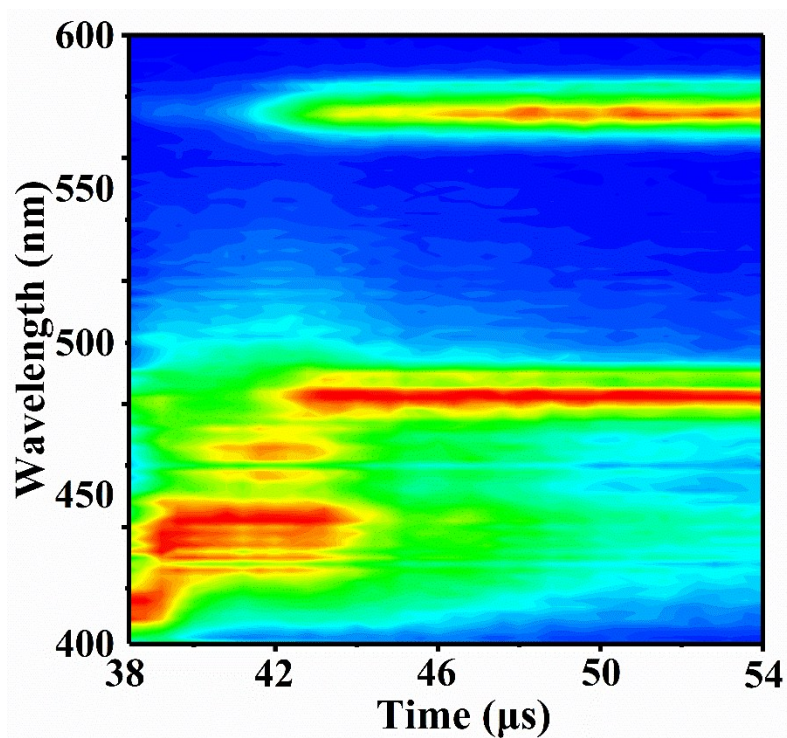


Fig S12. The time resolved emission spectroscopy of **2** ($\lambda_{\text{ex}} = 360$ nm).

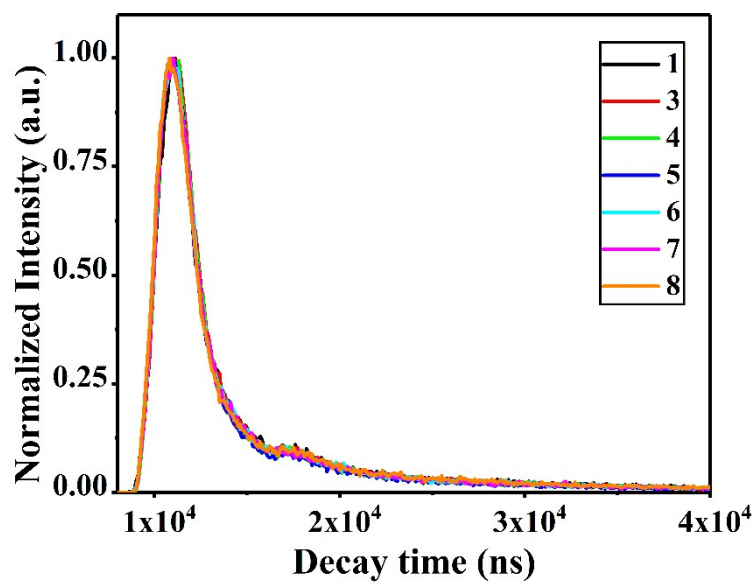


Fig S13. The PL decay curve of Tm^{3+} centre in **1, 3-8** ($\lambda_{\text{ex}} = 360$ nm, $\lambda_{\text{em}} = 452$ nm).