

*Supporting Information for:*

# **Constructing Nanosized Polyanions with Diverse Structures by the Self-Assembly of W/Nb Mixed-Addendum Polyoxometalate and Lanthanide Ion**

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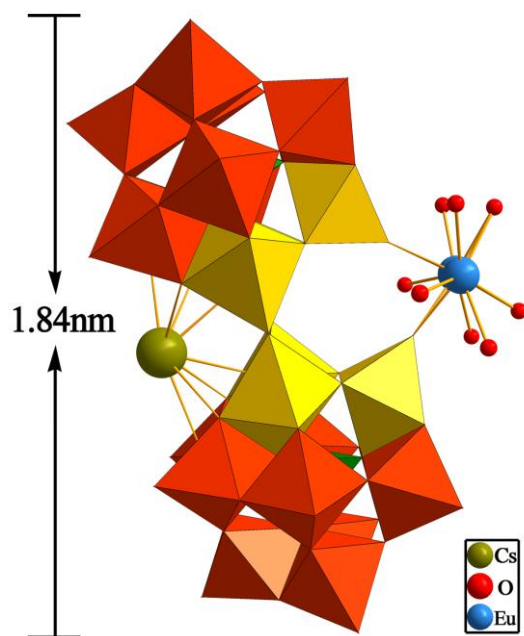
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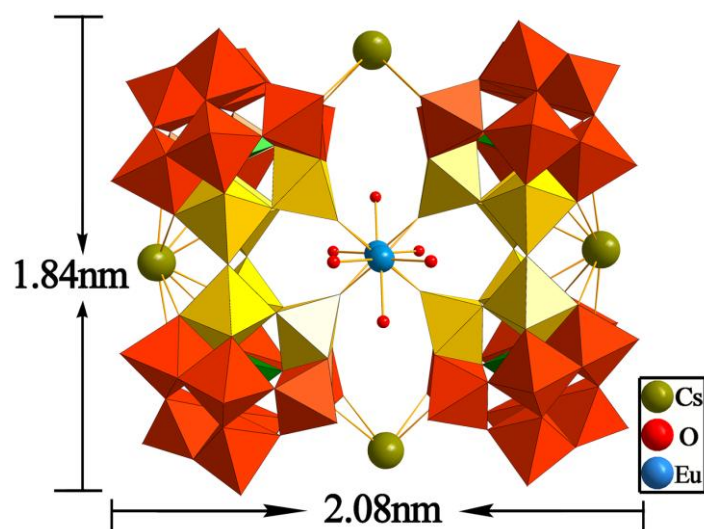
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## S1. Structure figures

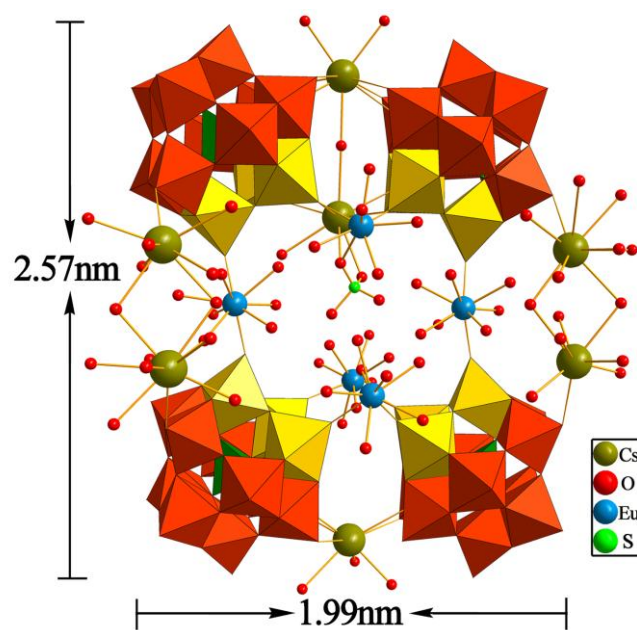
### 1.1 The cesium templating effect for 1a–5a



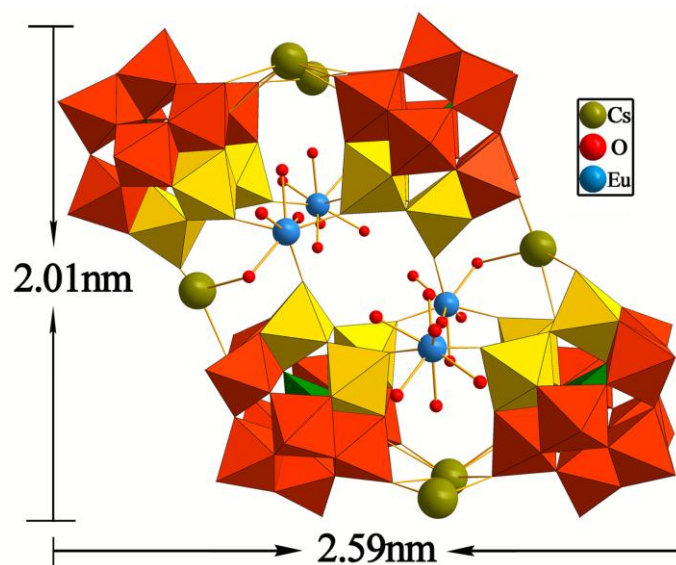
**Fig. S1.1.1** Combined polyhedral/ball-and-stick representation of polyanion **1a**. The WO<sub>6</sub> octahedra are shown in red, GeO<sub>4</sub> tetrahedra (green), NbO<sub>6</sub> octahedra (golden) and the balls represent europium (blue), cesium (dark yellow) and oxygen (red). The aqua ligands on cesium atom have been omitted for clarity.



**Fig. S1.1.2** Combined polyhedral/ball-and-stick representation of polyanion **2a**.  
The color code is the same as in Figure S.1.1.1.

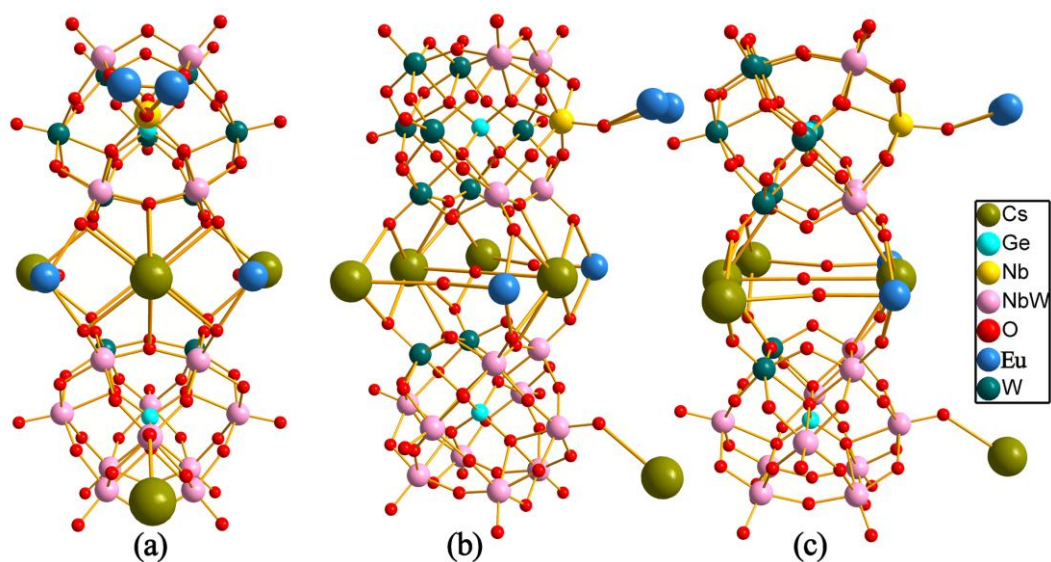


**Fig. 1.1.3** Combined polyhedral/ball-and-stick representation of polyanion **3a**. The color code is the same as in Figure S1.1.1 with only different that the green balls represent sulfur.



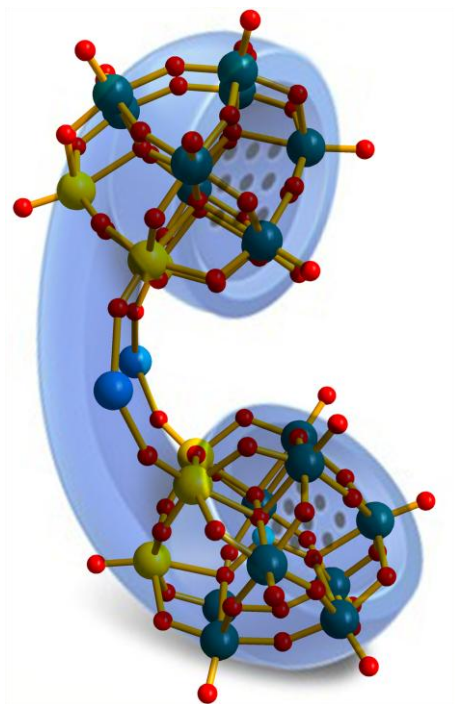
**Fig. S1.1.4** Combined polyhedral/ball-and-stick representation of polyanion **4a**.

The color code is the same as in Figure S1.1.1.

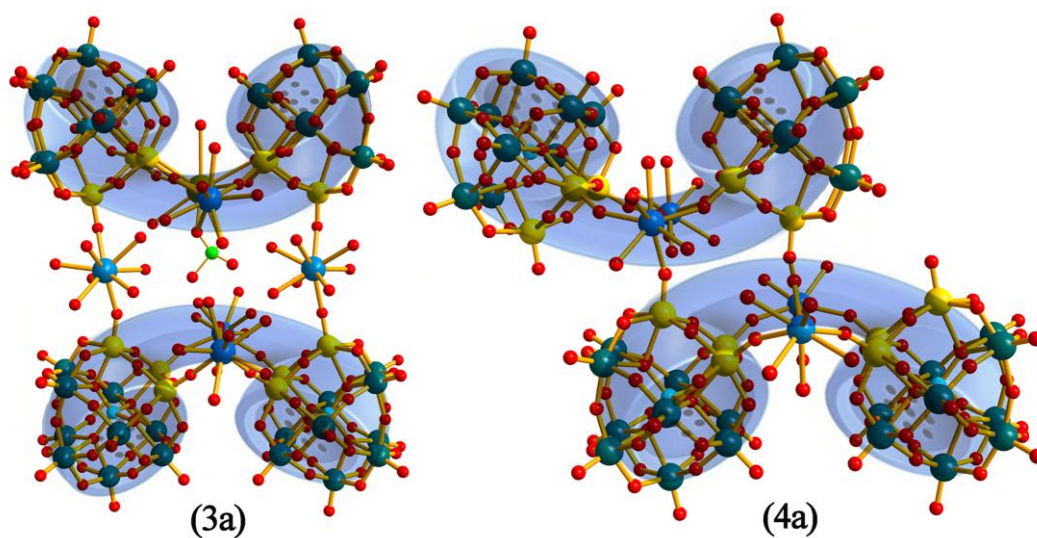


**Fig. S1.1.5** The cesium templating effect in polyanion **5a**, viewing from different orientations. (The aqua ligands on cesium and europium atoms have been omitted for clarity.)

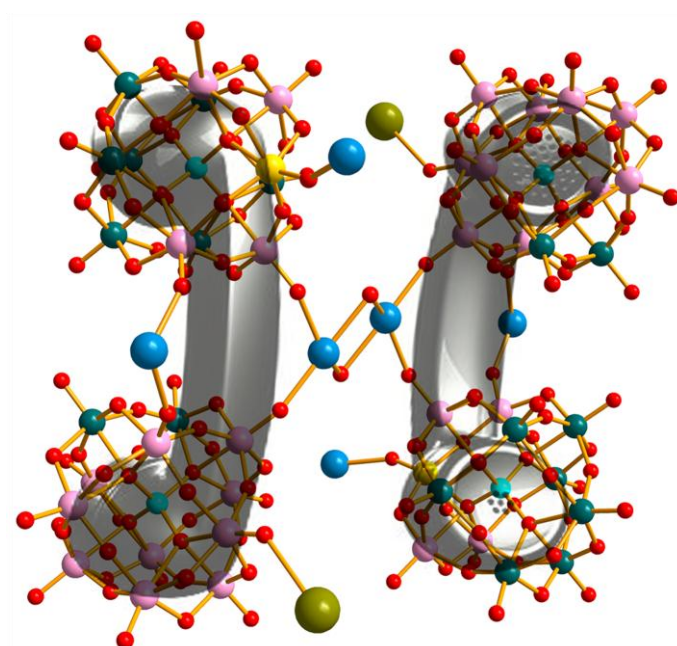
## 1.2 The telephone receiver-like building units in 3a–5a



**Fig. S1.2.1** The telephone receiver-like building unit exists in polyanion **3a**, **4a**, and **5a**.



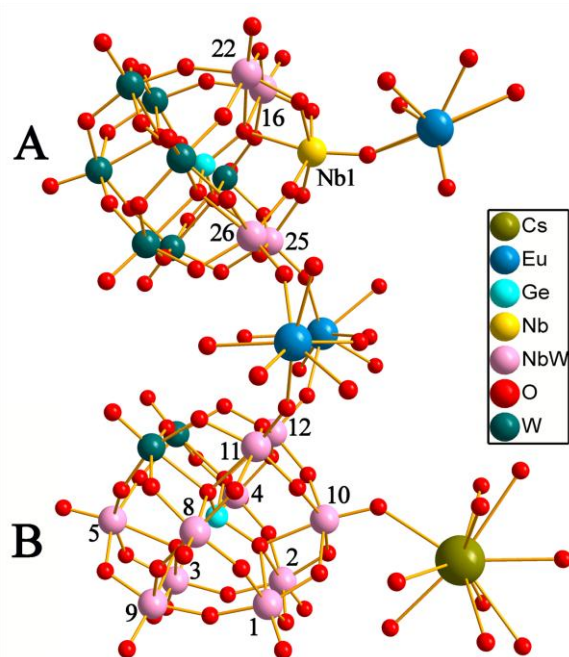
**Fig. S1.2.2** The connection modes of “telephone receiver-like building units” in polyanions **3a** and **4a**.



**Fig. S1.2.3** The connection modes of “telephone receiver-like building units” in the minimal asymmetric unit of polyanion **5a**.



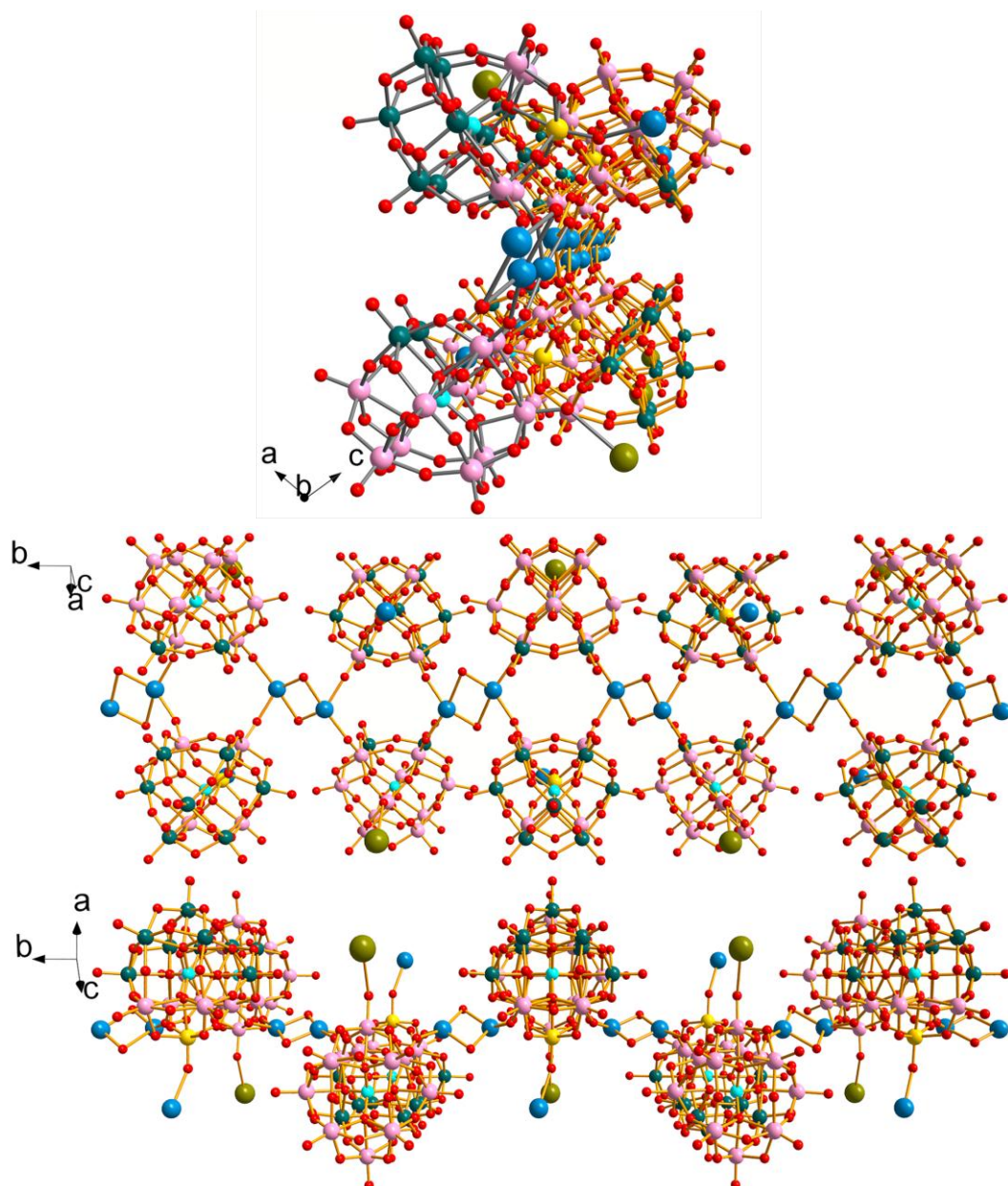
### 1.3 The detailed structures of 5a and 6a



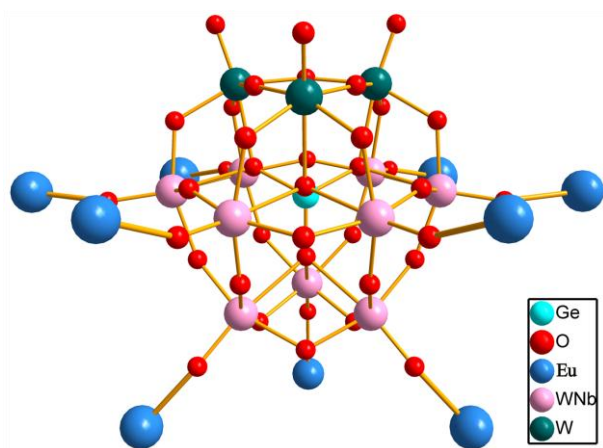
Atom sites	16	22	25	26	11	12	10
Occupancy factor (Nb)	0.25	0.25	0.75	0.75	0.55	0.65	0.55
Atom site	1	2	4	8	3	9	5
Occupancy factor (Nb)	0.15	0.2	0.25	0.15	0.2	0.2	0.1

**Fig. S1.3.1** Ball-and-stick representation of the Telephone unit in polyanion **5a**, and the table shows the occupancy factor of Nb in every Nb/W site.

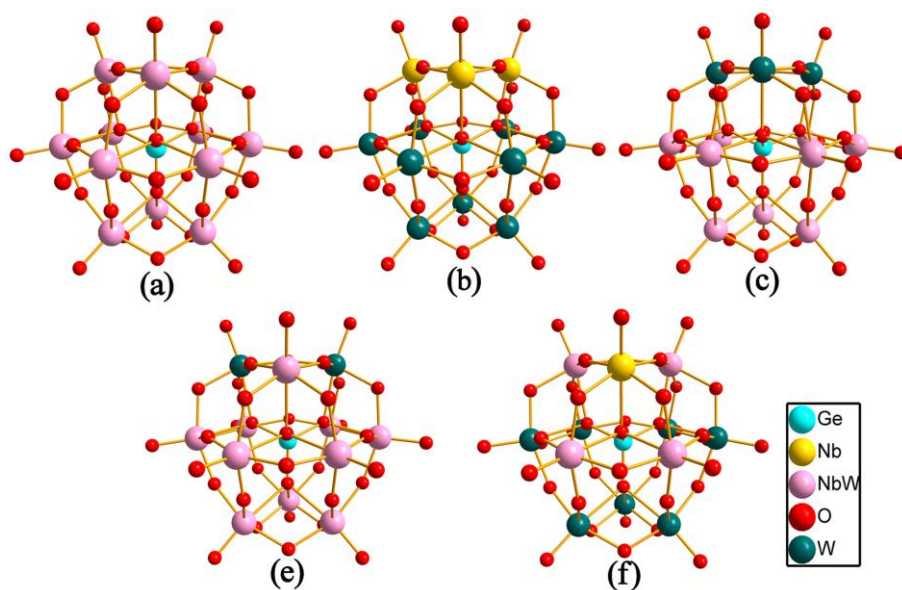
As determined from the Difference-Fourier map and approved by elemental analysis, the positions of Nb<sub>3</sub>O<sub>13</sub> clusters in the {GeW<sub>9</sub>Nb<sub>3</sub>O<sub>40</sub>} possess 2.5 Nb atoms in Keggin A (Nb/W25, Nb/W26, and Nb1), and 1.75 Nb atoms in Keggin B (Nb/W10, Nb/W11, and Nb/W12), respectively. Other 0.5 and 1.25 Nb atoms distribute on two and seven metal locations of Keggin A and Keggin B. The terminal O atoms of the Nb1 and Nb/W10 are bonded to a disordered Eu<sup>3+</sup> and Cs<sup>+</sup> respectively. The Telephone units in **5a** are linked to a 1D chain because the Eu<sup>3+</sup> atoms of adjacent Telephone units share aqua ligands (as shown in Figure S1.3.2).



**Fig. S1.3.2** Ball-and-stick representation of 1-D chain structure in polyanion **5a** (viewing from three different orientations).



**Fig. S1.3.3** Ball-and-stick representation of the minimal asymmetric unit in polyanion **6a**. All the nine  $O_t(\text{Nb}/\text{W})$  are bonded to  $\text{Eu}^{\text{III}}$ .



**Fig. S1.3.4** Five isomers of Keggin-type  $\{\text{GeW}_9\text{Nb}_3\text{O}_{40}\}$  segments in  $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9\text{Nb}_3\text{O}_{40}]$  (a), in compounds **1–4** (b), in compound **6** (c) and in compound **5** (d-e). The rate of Nb:W for the pink ball is 1:3 for (a) and 1:2 for (c). The rate for (d) and (e) are shown in Figure S4.3.1.













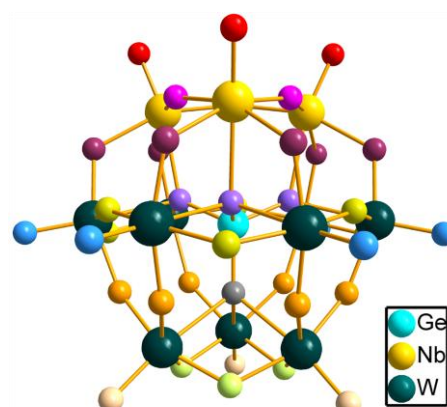
## S2. Density Functional Theory (DFT) Calculations

The geometry optimization of  $[\text{GeW}_9\text{Nb}_3\text{O}_{40}]^{7-}$  anion has been carried out using DFT methodology with Amsterdam Density Functional (ADF) 2009 program.<sup>1</sup> The zero-order regular approximation (ZORA) relativistic correction was adopted to account for the scalar relativistic effects.<sup>2,3</sup> The generalized-gradient approximation (GGA) was employed by using the Beck<sup>4</sup> and Perdew<sup>5</sup> (BP86) exchange-correlation (XC) functional. The basis functions for describing the valence electrons of each atom are triple- $\xi$  plus polarization Slater-type orbitals, which are standard TZP basis sets in the ADF package. The frozen cores (O.1s, Ge.3p, W.4d, Nb.3d) were described by single Slater functions in this work. Besides, the solvent effects were employed in the calculation of geometry optimization by means of the conductor-like screening model (COSMO).<sup>6-9</sup> The solute dielectric constant was set to 78.39 (water), and the suitable van der Waals radii are 1.40, 2.15, 2.10 and 2.07 Å for O, Ge, W and Nb, respectively.

1. Amsterdam Density Functional (ADF) Code 2009.01, Release (Vrije Universiteit, Amsterdam, The Netherlands 2009).
2. van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.*, **1993**, *99*, 4597-4610.
3. van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.*, **1999**, *110*, 8943-8953.
4. Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.*, **1988**, *38*, 3098-3100.
5. Perdew, J. P. *Phys. Rev. B: Condens. Matter*, **1986**, *33*, 8822-8824.
6. Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 799-805.
7. Klamt, A. *J. Phys. Chem.*, **1995**, *99*, 2224-2235.
8. Klamt, A.; Jonas, V. *J. Chem. Phys.*, **1996**, *105*, 9972-9981.
9. Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.*, **1999**, *101*, 396-408.

**Table S1.** Mulliken charge computed for the  $[\text{GeW}_9\text{Nb}_3]^{7-}$  anion. The O atoms at different locations of the keggin anion are shown in different colors (right).

Site	Charge	Number	Atom color
O <sub>t</sub> (Nb)	-0.9214	3	
O <sub>t</sub> (W)	-0.8433	6	
O <sub>t</sub> (W)	-0.8362	3	
O <sub>b</sub> (Nb <sub>2</sub> )	-1.0170	3	
O <sub>b</sub> (W <sub>2</sub> )	-0.9832	6	
O <sub>b</sub> (W <sub>2</sub> )	-0.9747	6	
O <sub>b</sub> (W <sub>2</sub> )	-1.0019	3	
O <sub>b</sub> (NbW)	-0.9872	6	
O <sub>c</sub> (W <sub>3</sub> )	-1.2067	1	
O <sub>c</sub> (NbW <sub>2</sub> )	-1.2234	3	

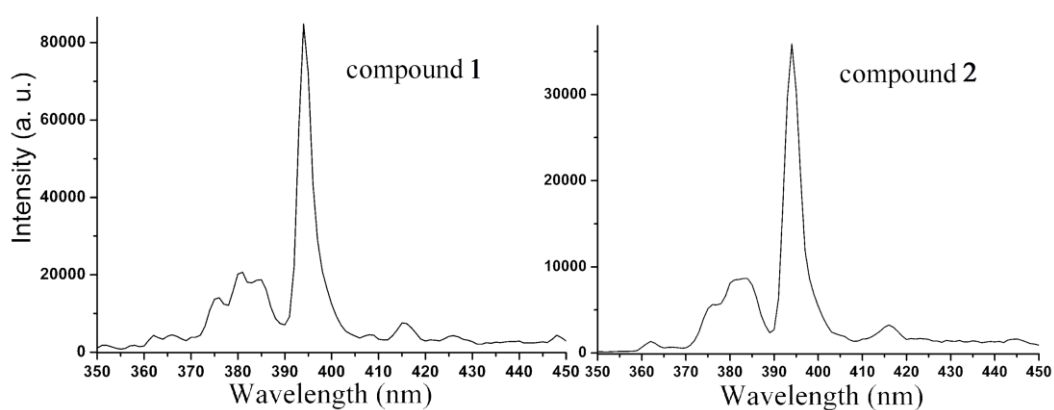


**Table S2.** Cartesian Coordinates of the  $[\text{GeW}_9\text{Nb}_3\text{O}_{40}]^{7-}$  ( $C_{3v}$  symmetry)

W	3.163329	1.689764	-0.324928	O	4.481160	2.797663	-0.013587
W	-0.118286	-3.584406	-0.324928	O	-4.663427	-2.481967	-0.013587
W	-0.118286	3.584406	-0.324928	O	-0.779716	-1.350508	3.558859
W	-3.045043	1.894641	-0.324928	O	0.000000	0.000000	1.541507
W	0.981363	-1.699771	2.761608	O	1.618520	-2.803359	3.961002
W	-3.045043	-1.894641	-0.324928	O	0.798448	-1.382953	-3.443339
W	0.981363	1.699771	2.761608	O	-0.832827	1.442499	-0.814766
W	-1.962727	0.000000	2.761608	O	1.665654	0.000000	-0.814766
W	3.163329	-1.689764	-0.324928	O	2.425387	-1.577914	1.519993
Ge	0.000000	0.000000	-0.233714	O	-2.904668	-2.206779	-2.170067
O	2.425387	1.577914	1.519993	O	3.363461	-1.412127	-2.170067
O	1.688615	2.924767	-0.603307	O	1.618520	2.803359	3.961002
O	0.798448	1.382953	-3.443339	O	4.481160	-2.797663	-0.013587
O	-1.524379	2.640302	-4.750464	O	-1.596897	0.000000	-3.443339
O	1.688615	-2.924767	-0.603307	O	-1.524379	-2.640302	-4.750464
O	-0.458793	-3.618906	-2.170067	O	-0.832827	-1.442499	-0.814766

O	0.153820	-2.889403	1.519993	O	4.076314	0.000000	0.055629
O	-2.038157	-3.530192	0.055629	O	-0.458793	3.618906	-2.170067
O	0.182267	-5.279630	-0.013587	O	-2.904668	2.206779	-2.170067
O	0.153820	2.889403	1.519993	O	-2.038157	3.530192	0.055629
O	-2.579207	1.311489	1.519993	O	0.182267	5.279630	-0.013587
O	-4.663427	2.481967	-0.013587	O	1.559433	0.000000	3.558859
O	-3.377230	0.000000	-0.603307	O	3.048758	0.000000	-4.750464
O	-2.579207	-1.311489	1.519993	Nb	-1.090035	1.887996	-3.192755
O	-0.779716	1.350508	3.558859	Nb	-1.090035	-1.887996	-3.192755
O	3.363461	1.412127	-2.170067	Nb	2.180070	0.000000	-3.192755
O	-3.237040	0.000000	3.961002				

### S3. Photoluminescence properties



**Fig. S3.1** Excitation spectra of solid samples **1** (left) and **2** (right).

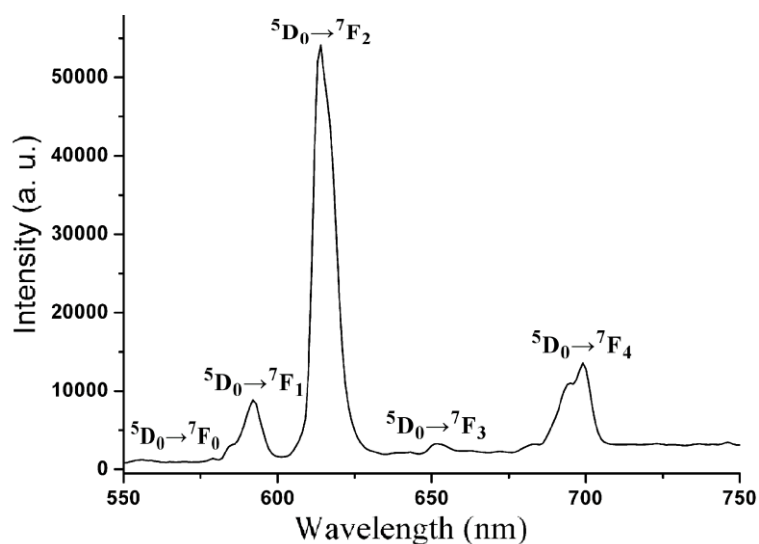


Fig. S3.2 Emission spectrum ( $\lambda_{\text{ex}} = 394$  nm) of solid sample 2.

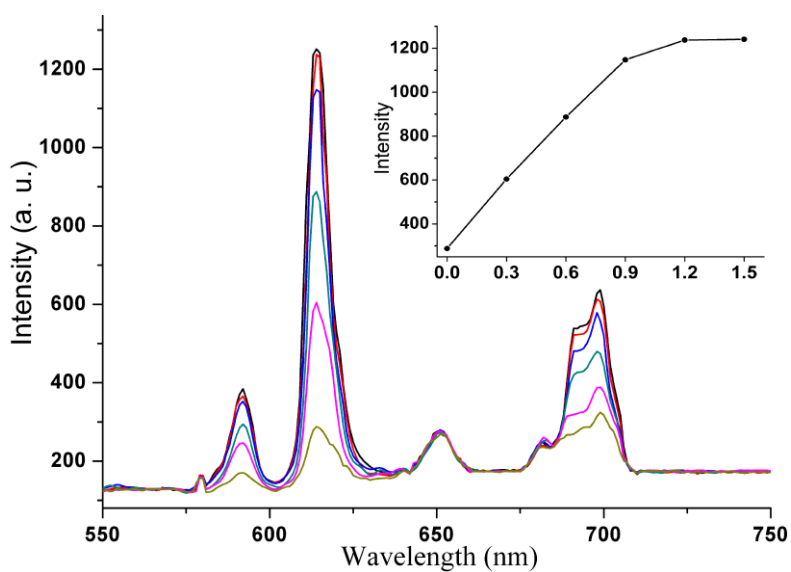
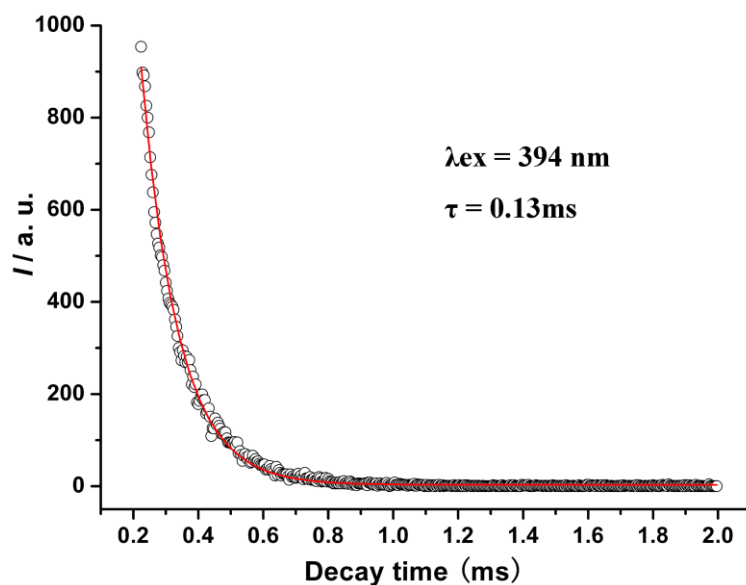
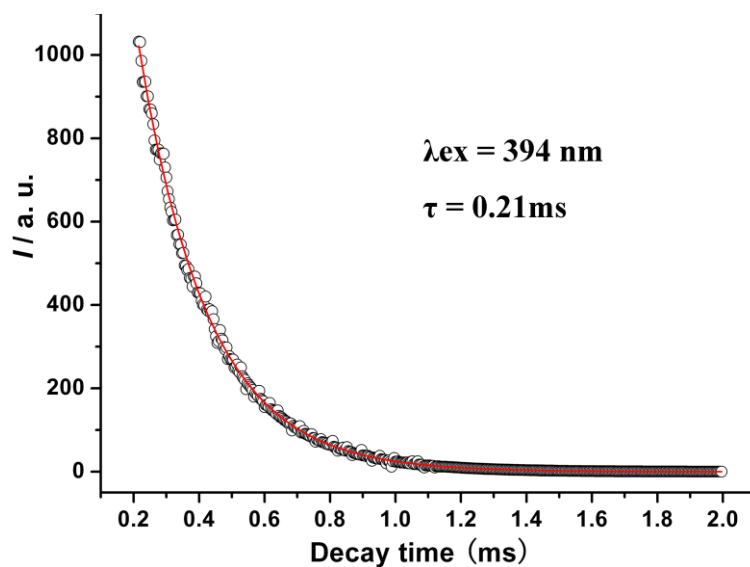


Fig. S3.3 The changes in the emission of **1** ( $1.0 \times 10^{-3}$  M, in 0.5M HCl solution) at the present of different concentration of malonic acid (0 equal, 0.3 equal, 0.6 equal, 0.9 equal, 1.2 equal and 1.5 equal). Insert: variation of the emission intensity (614 nm) for **1** as a function of the concentration of malonic acid.

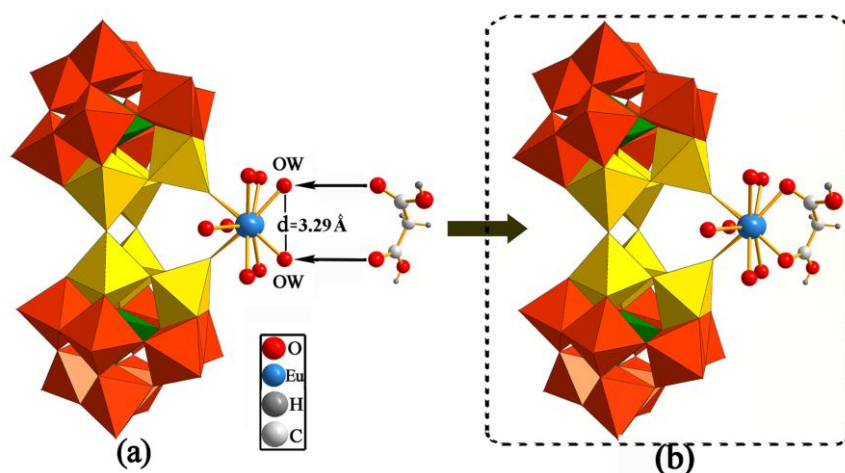




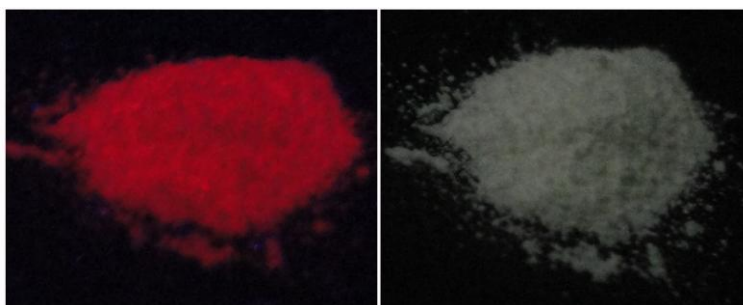
**Fig. S3.4** Luminescence decay curves of the 614 nm emission of compounds **1** ( $1.0 \times 10^{-3} \text{ M}$ , in 0.5M HCl solution) under  $\lambda_{ex} = 394 \text{ nm}$ . The black circles represent experimental data, and the solid red lines represent fitting results. The curve can be well fitted into a single-exponential function.



**Fig. S3.5** Luminescence decay curves of the 614 nm emission of compounds **1** ( $1.0 \times 10^{-3} \text{ M}$ , in 0.5M HCl solution) in the present of 1.2 equal malonic acid, under  $\lambda_{ex} = 394 \text{ nm}$ . The black circles represent experimental data, and the solid red lines represent fitting results. The curve can be well fitted into a single-exponential function.



**Fig. S3.6** The suited dimension of malonic acid and anion **1a** (a), and the possible substituent production (b). The O–O distance in **1a** (d) is 3.29 Å in **1a** and is 3.20 Å in the freely malonic acid.



**Fig. S3.7** Digital photographs of **1** under room light (right) and UV irradiation (365nm) (left).

#### S4. IR spectra

The major bands of **1** and **2** in the FTIR spectra are very similar. There are obvious shifts comparing them with that of  $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9\text{Nb}_3\text{O}_{40}]$ . The characteristic vibrations of Nb-O-Nb (in the region of  $670 - 710 \text{ cm}^{-1}$ ) appear at  $671 \text{ cm}^{-1}$  for both **1** and **2**. These values are markedly different from the Nb-O-Nb vibrations in the tetrameric polyanion  $[(\text{GeW}_9\text{Nb}_3\text{O}_{40})_4\text{Nb}_4\text{O}_6]^{20-}$  ( $703 \text{ cm}^{-1}$ ) and dimeric polyanion  $[\text{Ge}_4\text{W}_{36}\text{Nb}_{16}\text{O}_{166}]^{20-}$  [3]. The IR spectra of **3–6** exhibit similar characters without Nb-O-Nb vibrations. The characteristic peaks at  $1109 \text{ cm}^{-1}$  for **3** is attributed to the sulfate.

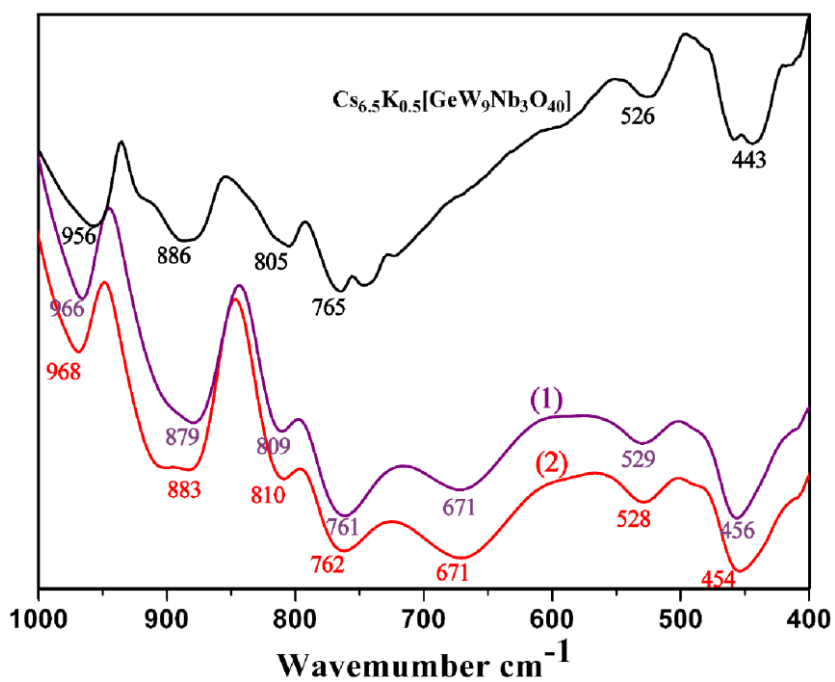


Fig. S4.1 The IR spectra of precursor  $\text{Cs}_{6.5}\text{K}_{0.5}[\text{GeW}_9\text{Nb}_3\text{O}_{40}]$ , compounds 1 and 2.

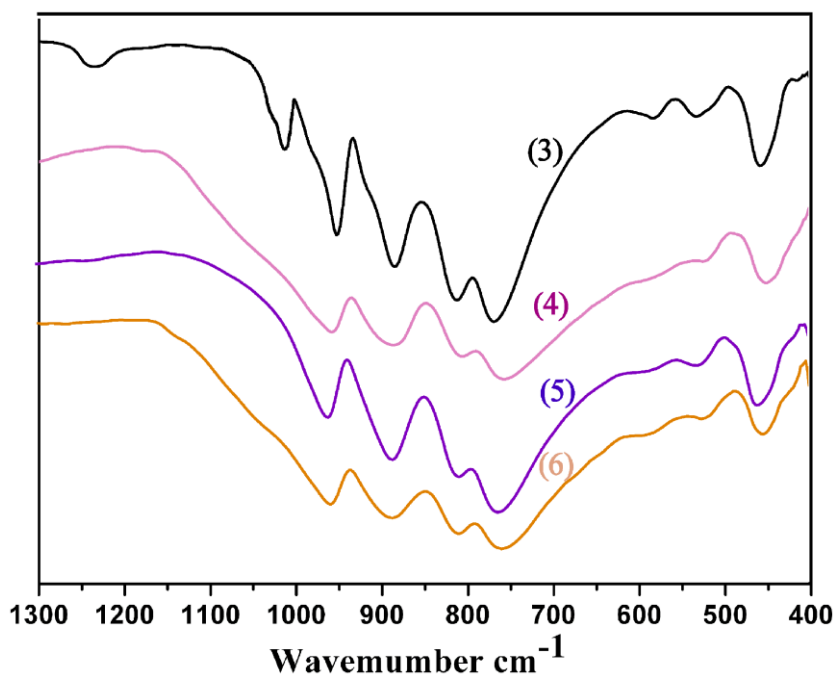
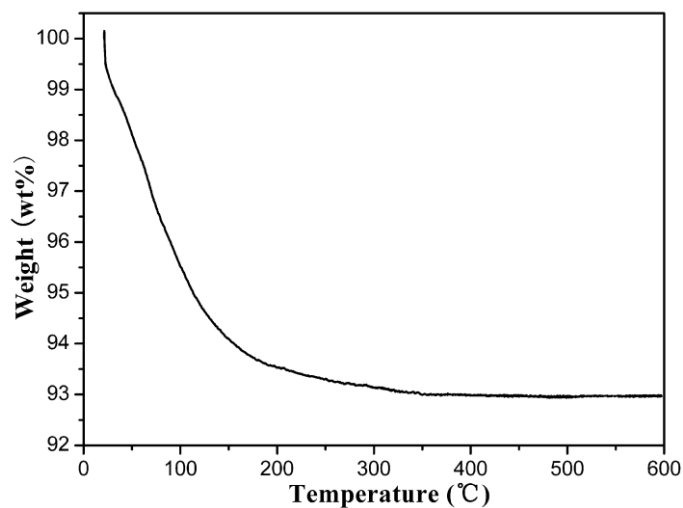
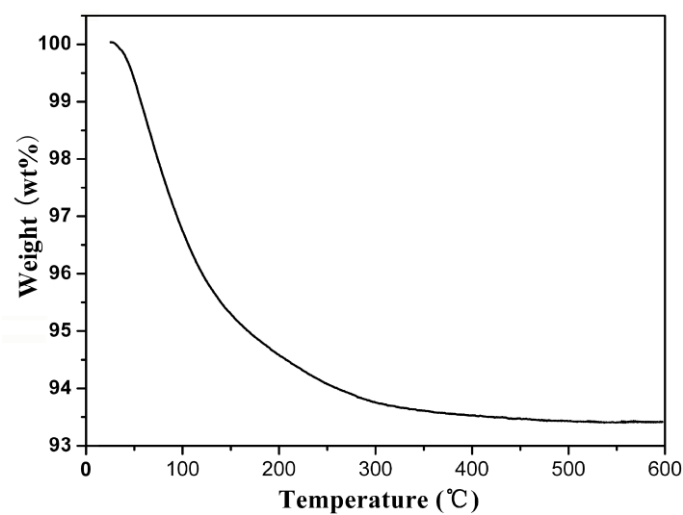


Fig. S4.2 The IR spectra of compounds 3, 4, 5 and 6 (from the top to the bottom).

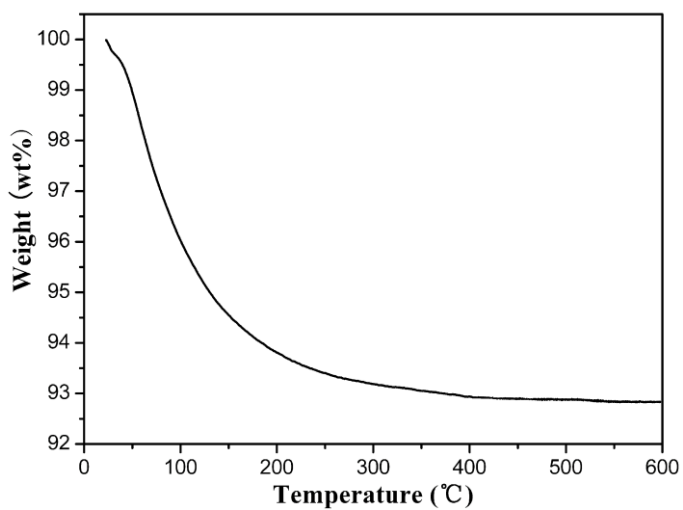
## S5. Thermogravimetry (TG) curves



**Fig. S5.1** Thermogravimetry (TG) curve of compound **1**.

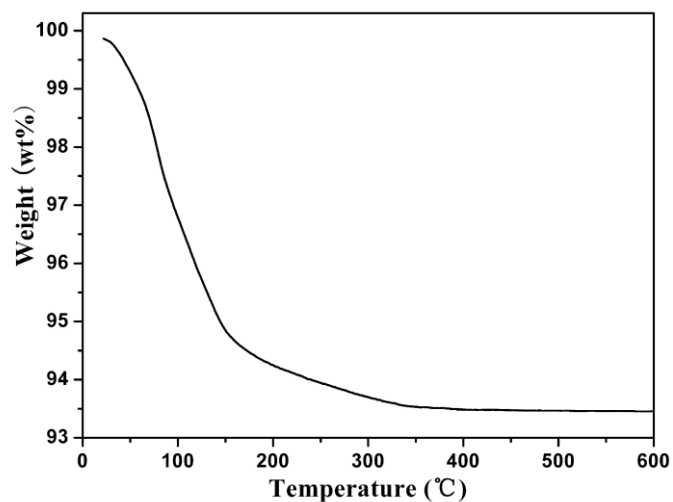


**Fig. S5.2** Thermogravimetry (TG) curve of compound **2**.

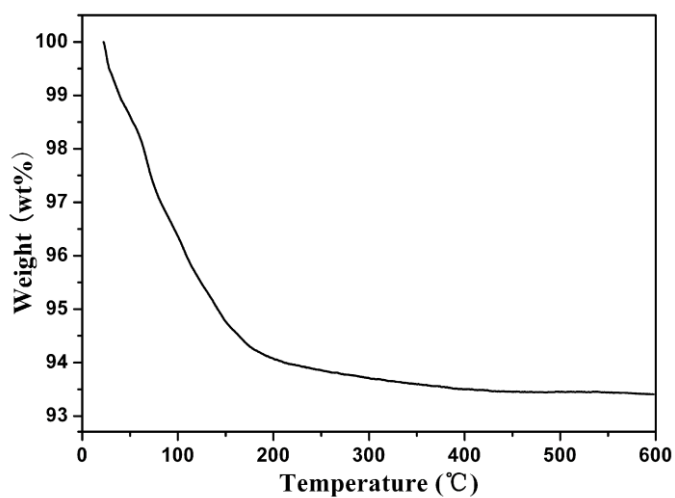


**Fig. S5.3** Thermogravimetry (TG) curve of compound **3**.

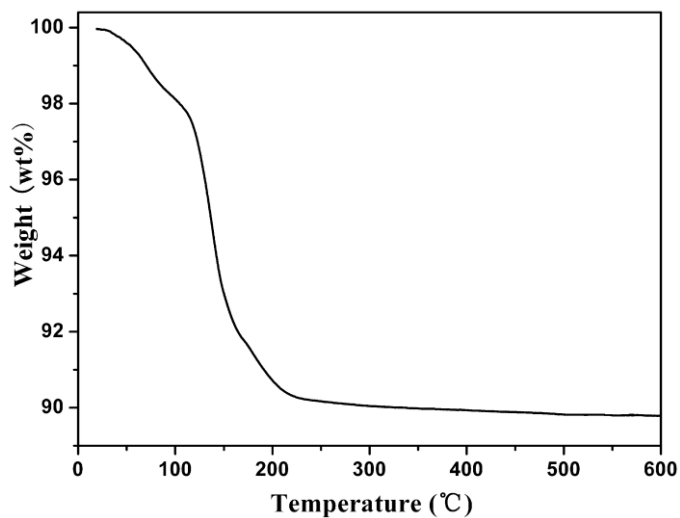




**Fig. S5.4** Thermogravimetry (TG) curve of compound **4**.



**Fig. S5.5** Thermogravimetry (TG) curve of compound **5**.



**Fig. S5.6** Thermogravimetry (TG) curve of compound **6**.