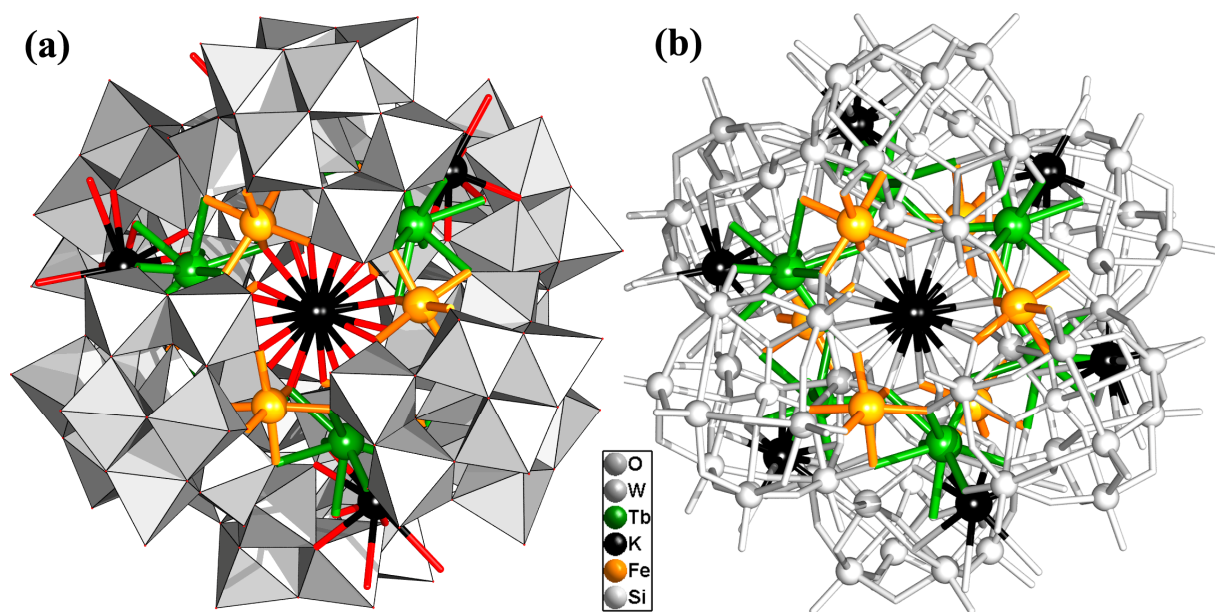


## Supporting Information

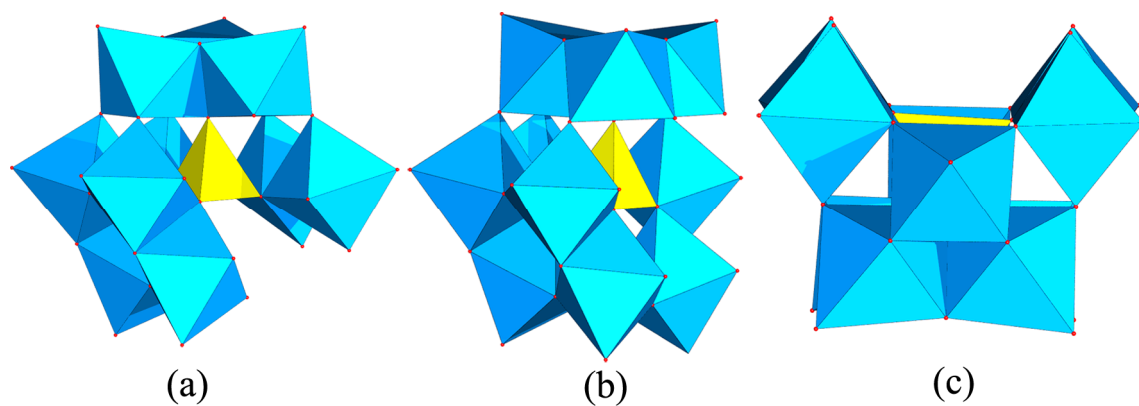
### Hexameric Polyoxometalates Decorated by Six 3d-4f Heterometallic Clusters

Zhi-Ming Zhang,<sup>a</sup> Yang-Guang Li,<sup>\*a</sup> Shuang Yao,<sup>a</sup> and En-Bo Wang<sup>\*a</sup>

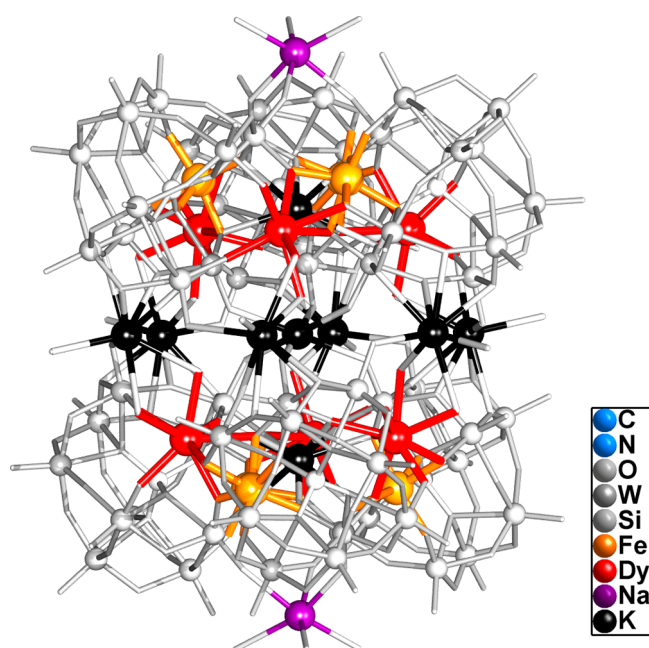
## 1. Supplementary Structural Figures of Compounds 1-2



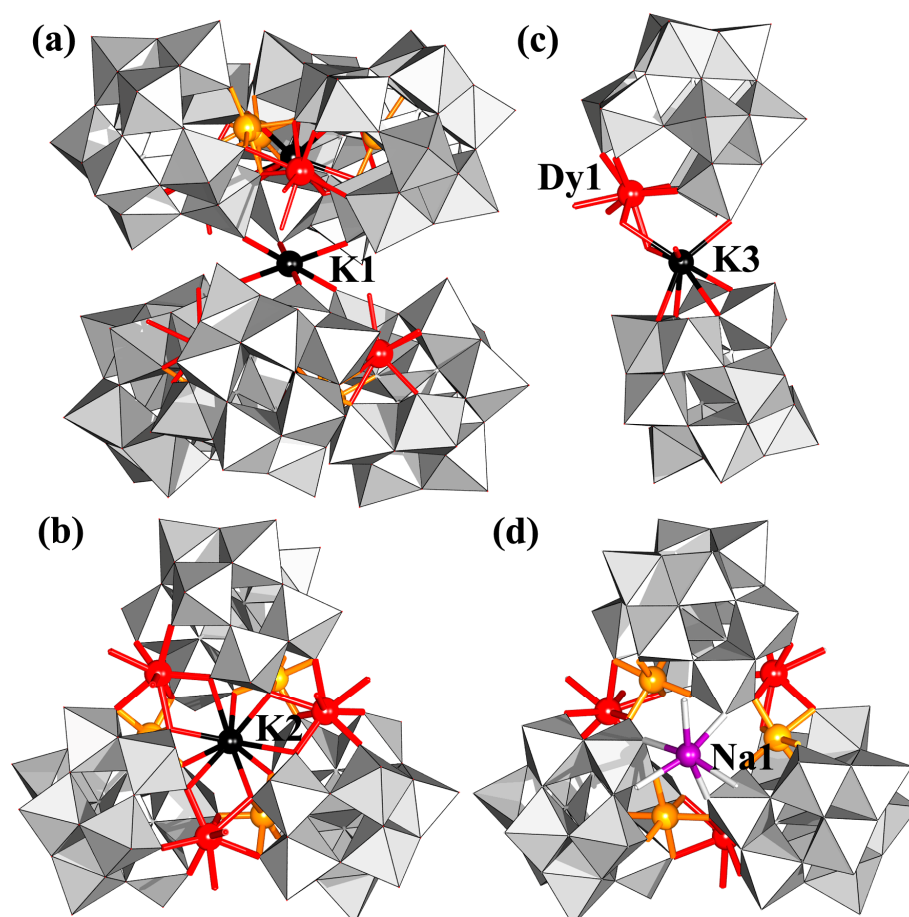
**Fig. S1.** (a) Polyhedral and ball-and-stick representation of polyoxoanion 2; (b) ball-and-stick representation of polyoxoanion 2.



**Fig. S2.** Polyhedral representation of (a)  $\alpha$ -, (b)  $\beta$ -, (c)  $\gamma$ - $\{\text{SiW}_{10}\text{O}_{38}\}$  polyoxoanions.



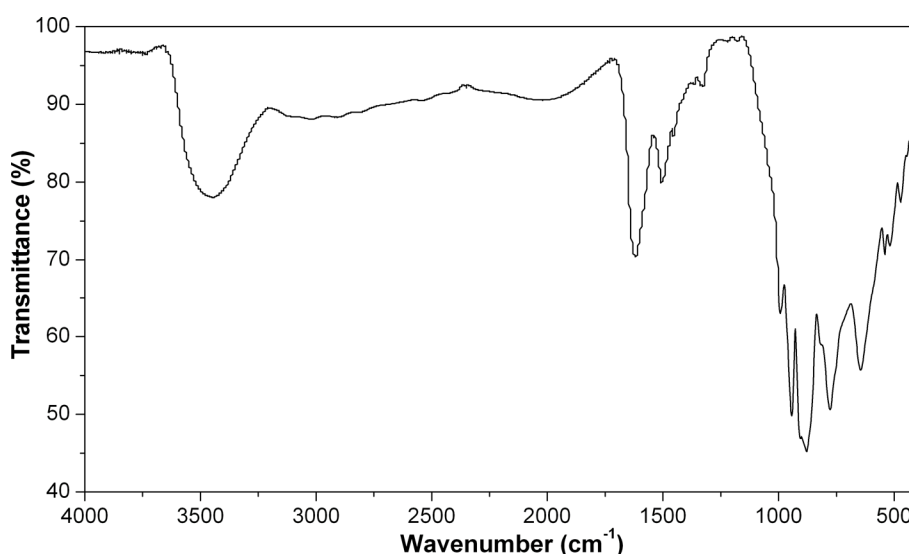
**Fig. S3.** Ball-and-stick representation of bicapped polyoxoanion in **1**.



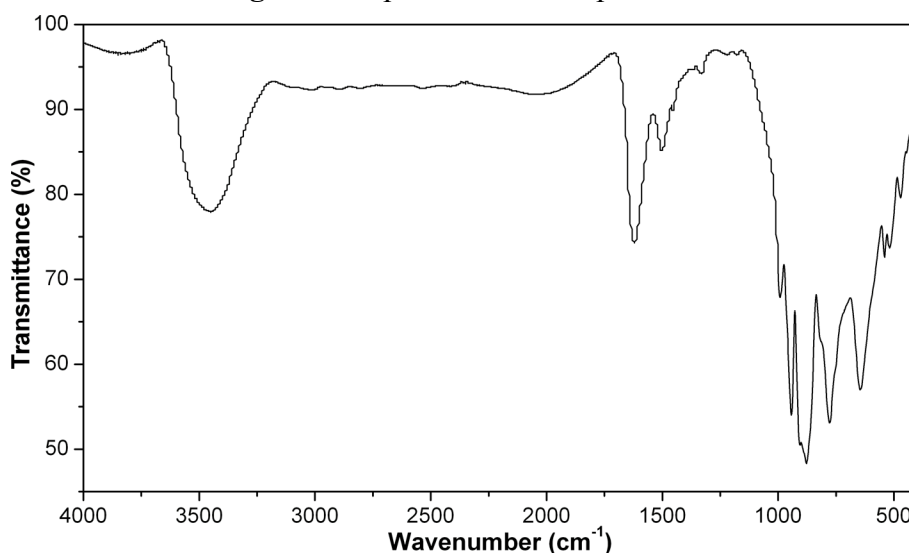
**Fig. S4.** View of the coordination modes of three types of  $K^+$  ions and  $Na^+$  ion in **1**.

## 2. IR spectra of compounds **1** and **2**.

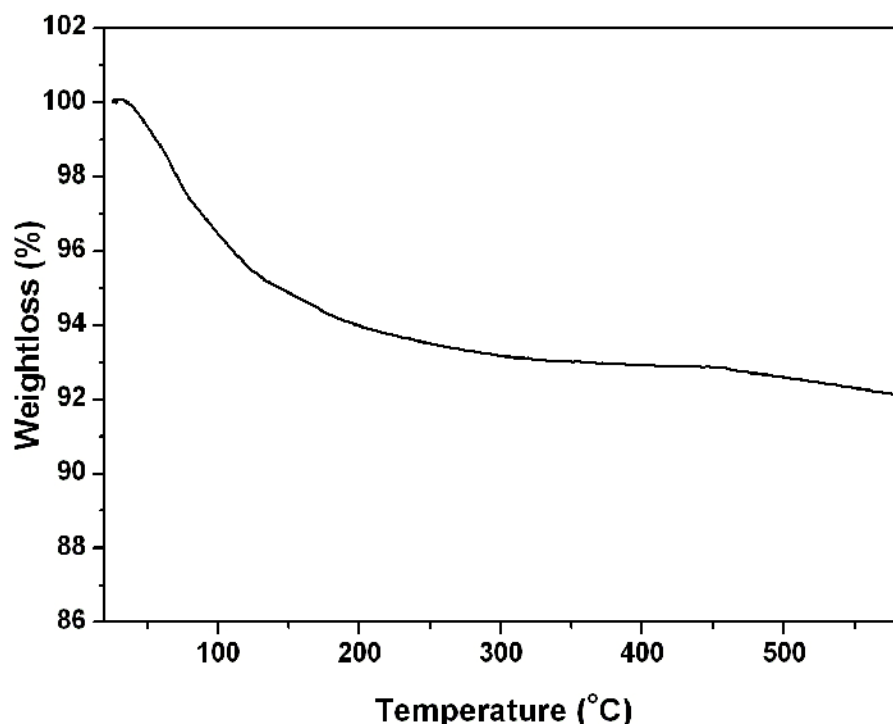
In the IR spectrum of **1** (Fig. S5), the features at 993(m), 943(s), 879(s), 777(s)  $\text{cm}^{-1}$  can be attributed to  $\nu$  (Si–Oa),  $\nu$  (W–Od),  $\nu$  (W–Ob–W), and  $\nu$  (W–Oc–W) in polyoxoanion framework. The broad band at 3442  $\text{cm}^{-1}$  and mild peak at 1617  $\text{cm}^{-1}$  can be regarded as features of the lattice and coordinated water molecules. The stretching vibration of en ligands can be observed at 1506 (m), 1451(w), 1321(w), 1216(w), 1177(w). The IR spectrum of **2** is similar to that of **1**.



**Fig. S5.** IR spectrum for compound **1**.



**Fig. S6.** IR spectrum for compound **2**.



**Fig. S6.** The thermal gravimetric (TG) curve for compound **1**. The TG curve of **1** shows a weight loss of 6.91% steps from 33 - 316°C, which corresponds to the loss of all lattice water molecules, coordinated water molecules and noncoordinated en ligands (calculated value of 6.65%).