Supplementary Information

Extended Hybrid Architectures Based on Tetra-Co^{II} Sandwiched Polyoxotungstate

Yu Zhu,[a] Wei-Hui Fang,[a] Qi Wei,[b] and Guo-Yu Yang*[a, b]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China, E-mail: ygy@fjirsm.ac.cn; Fax: (+86) 591-8371-0051

[b] MOE Key Laboratory of Cluster Science, School of Chemistry, Beijing Institute of Technology, Beijing 10008, China. E-mail: ygy@bit.edu.cn; Fax: (+86) 10-6891-8572

The first two authors have equal contributions.

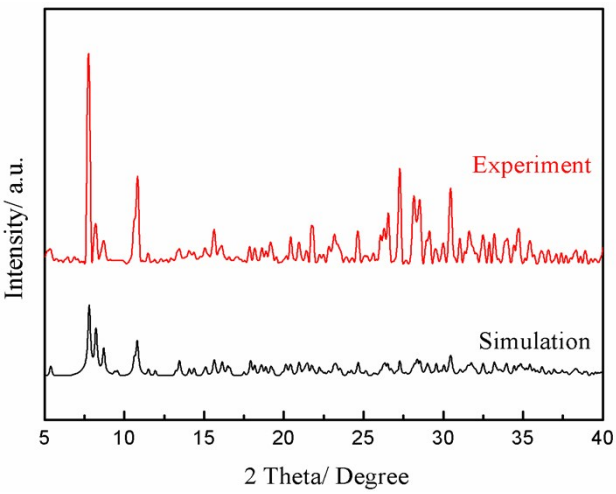

Fig. S1. Powder XRD pattern of compound **1**, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.

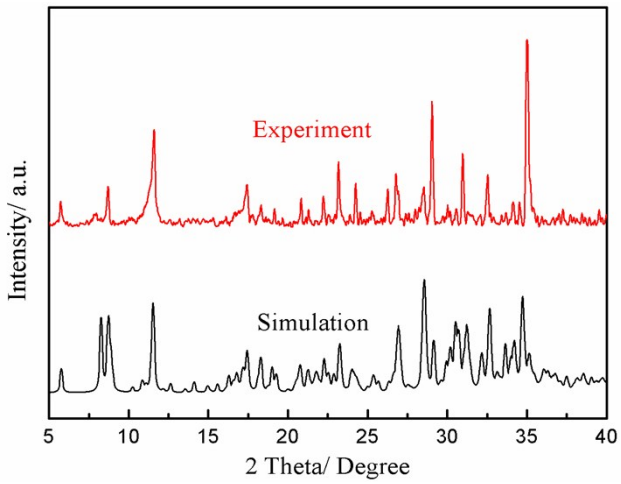

Fig. S2. Powder XRD pattern of compound **2**, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.

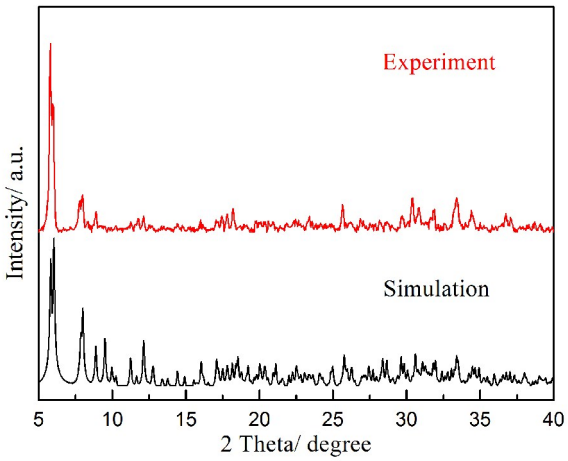

Fig. S3. Powder XRD pattern of compound **3**, showing the bulk product is in good agreement with the calculated pattern based on the result from single-crystal X-ray diffraction.

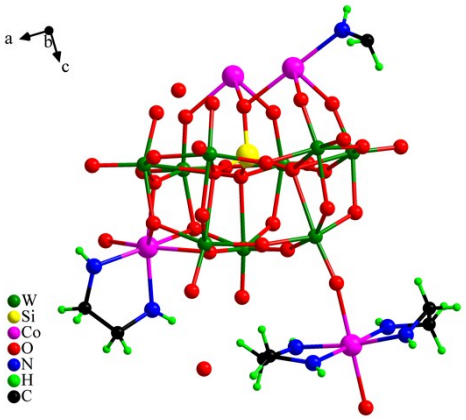

Fig. S4. The asymmetric unit of compound **1**.

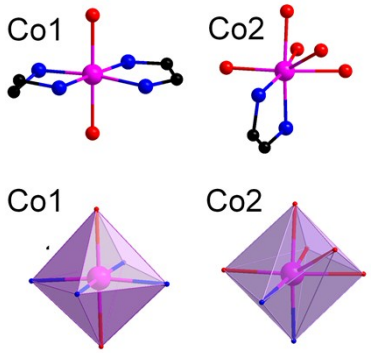

Fig. S5. The coordination environment of the Co1 and Co2 ions in compound **1**.

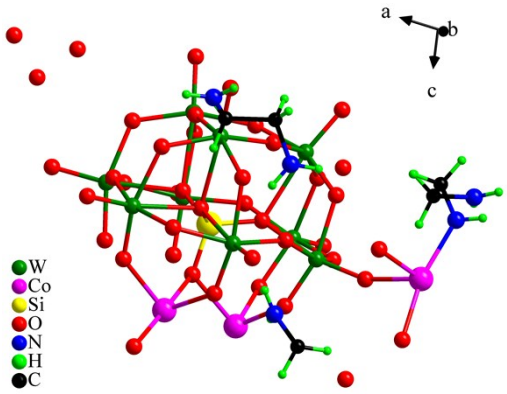

Fig. S6. The asymmetric unit of compound **2**.

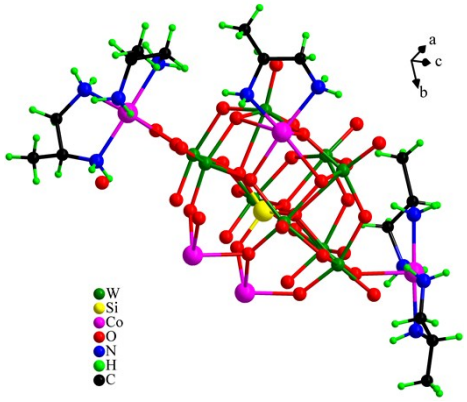

Fig. S7. The asymmetric unit of compound **3**.

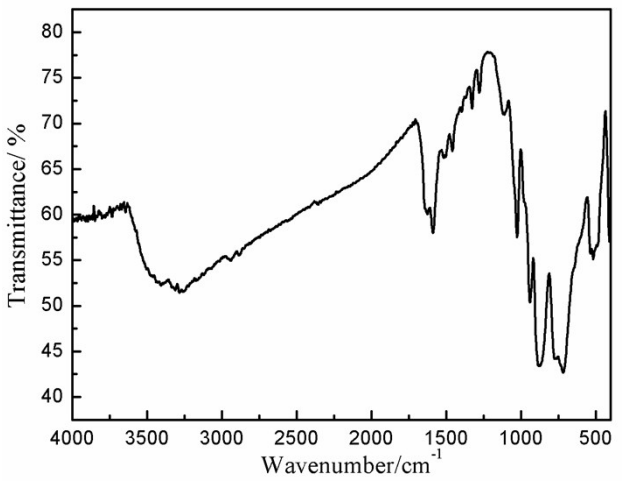

Fig. S8. IR spectrum of compound **1**.

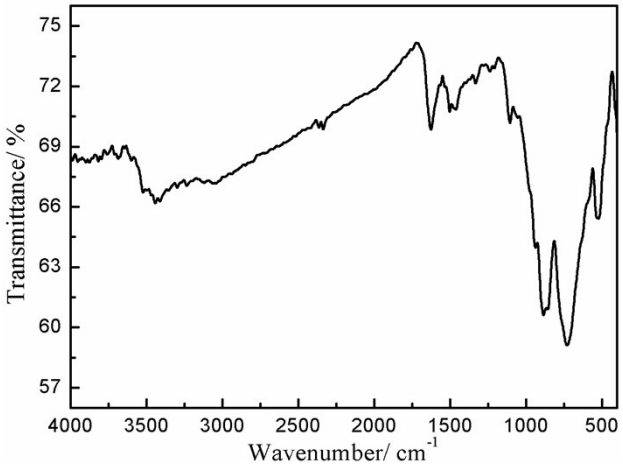

Fig. S9. IR spectrum of compound **2**.

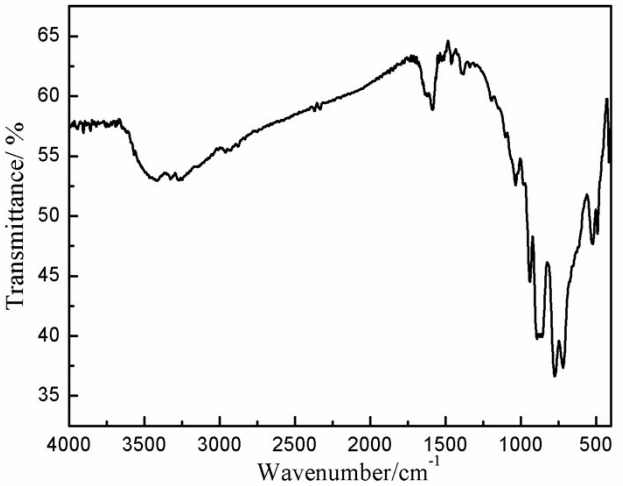

Fig. S10. IR spectrum of compound **3**.

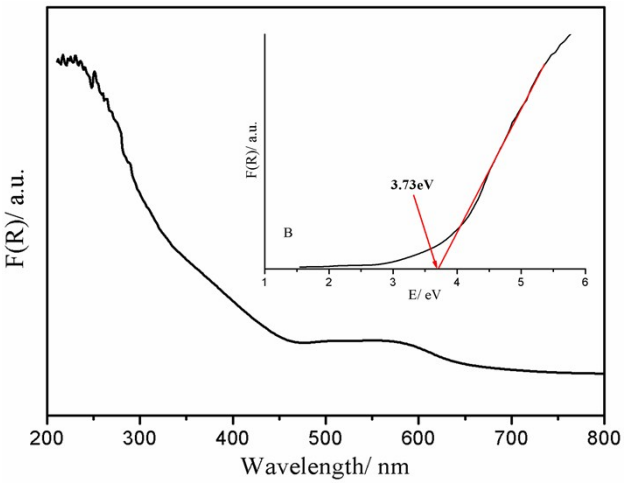

Fig. S11. UV-vis diffuse reflectance spectrum of **1**.

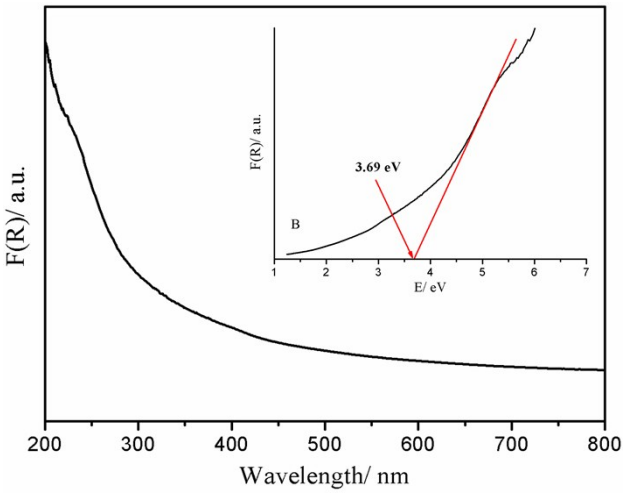

Fig. S12. UV-vis diffuse reflectance spectrum of **2**.

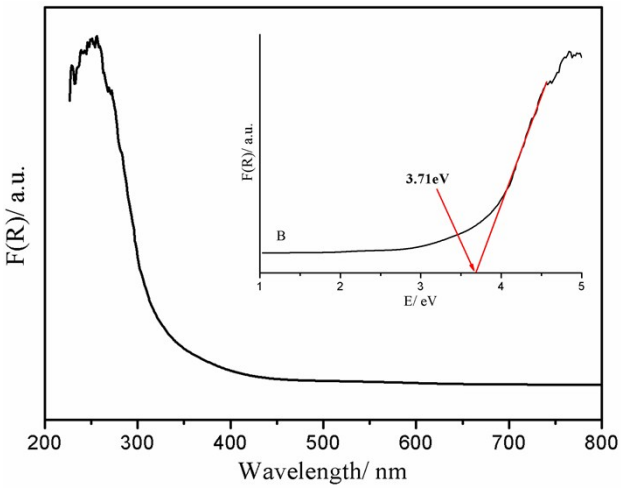

Fig. S13. UV-vis diffuse reflectance spectrum of **3**.

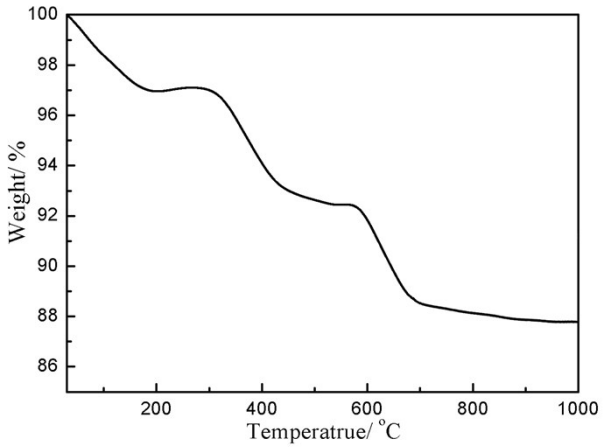

Fig. S14. TG curve of compound **1**.

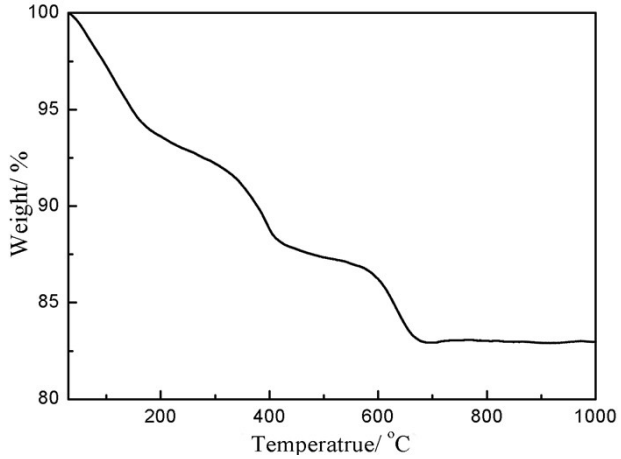

Fig. S15. TG curve of compound **2**.

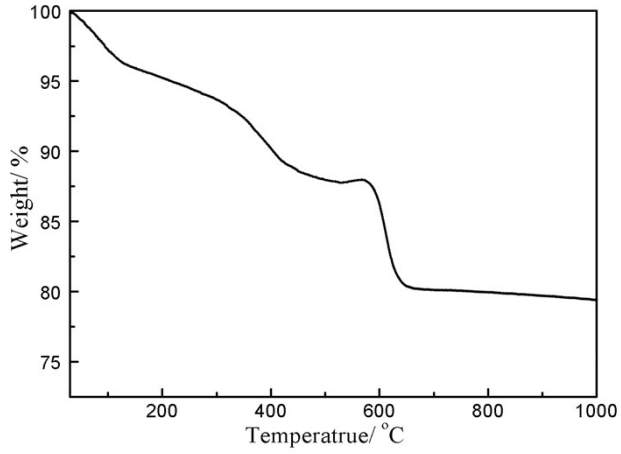

Fig. S16. TG curve of compound **3**.

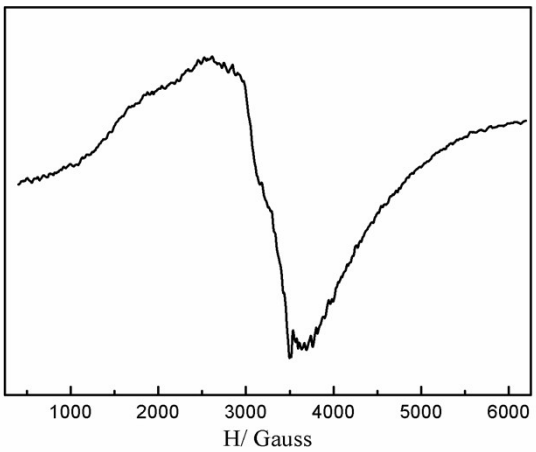

Fig. S17. The X-band EPR spectrum of compound **2**.

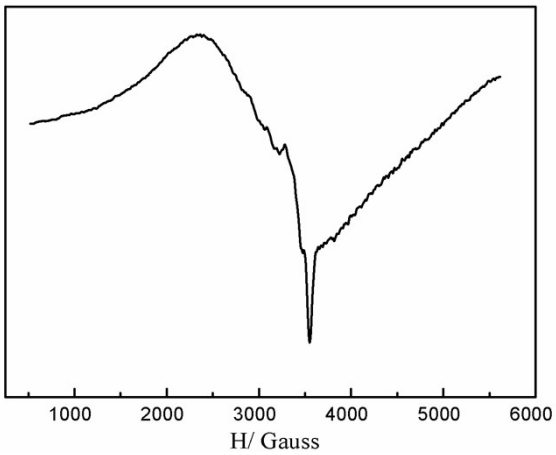

Fig. S18. The X-band EPR spectrum of compound **3**.

Table S1. The BVS values of all the W and O atoms from the asymmetrical unit of compound **1-3.**

Compoud **1**:

Atom	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**
W1	6.110	W2	6.167	W3	6.182	W4	6.112
W5	6.266	W6	6.209	W7	6.077	W8	6.227
W9	6.099	Co1	2.160	Co2	2.017	Co3	2.379
Co4	2.268						

Compoud **2**:

Atom	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**
W1	6.158	W2	6.214	W3	6.225	W4	6.190
W5	6.261	W6	6.139	W7	6.397	W8	6.185
W9	6.197	Co1	2.062	Co2	2.056	Co3	1.879

Compound **3**:

Atom	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**
W1	6.213	W2	6.154	W3	6.218	W4	6.222
W5	6.124	W6	6.135	W7	6.133	W8	6.049
W9	6.183	Co1	1.973	Co2	1.987	Co3	2.035
Co4	2.454	Co5	2.300				