Electronic Supplementary Information for Dalton Transactions

Supporting Information

Combination of POMs and Deliberate Designed Macrocations: a Rational Approach for Synthesis of POM-Pillared Metal-Organic Framework

Ya-Qian Lan, Shun-Li Li, Kui-Zhan Shao, Xin-Long Wang, Xiang-Rong Hao and Zhong-Min Su*

Institute of Functional Material Chemistry; Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China.

E-mail: zmsu@nenu.edu.cn;
Tel: +86 431 85099108

The bond valence sum calculations for compound 1:

The bond valence sums (BVS)[1] are 5.967, 6.064, 6.071, 5.036, 5.969, 5.767, 5.788, 5.668, 5.879, 6.039, 6.020 and 6.139 for twelve independent molybdenum atoms (Mo1-Mo12) in **1**, respectively. The average value of 5.867 is in good agreement with the expected bond valence of 5.833 calculated from the composition of $Mo^{V}_{2}Mo^{VI}_{10}$. The calculated results reveal that, in the structure of the polyanion of **1**, two out of the twelve Mo centers are in the +5 oxidation state. Such mixed-valence Mo atoms have been found in two-electron-reduced $[Co(phen)_3]_{1.5}[PMo^{VI}_{10}Mo^{V}_{2}O_{40}Co(phen)_2(H_2O)]\cdot 0.5H_2O$ and $(NH_4)[Cu_{24}I_{10}L_{12}][PMo^{VI}_{10}Mo^{V}_{2}O_{40}]_3$.[2,3] The values of BVS for Cu1, Cu2, Cu3 and Cu4 centers are 1.890, 1.875, 1.785 and 1.017, respectively, suggesting that the Cu1, Cu2 and Cu3 atoms exhibit an oxidation state of +2, and Cu4 has an oxidation state of +1.

The bond valence sum calculations for compound 2:

The bond valence sums (BVS)[1] for four independent molybdenum atoms (Mo1-Mo4) in **2** suggest that all Mo atoms exhibit an oxidation state of +6. The values of BVS for three independent vanadium atoms (V1-V3) are 4.585, 4.425 and 4.467, respectively. The average value of 4.493 is in good agreement with the expected bond valence of 4.500 calculated from the composition of $V^{V}_{3}V^{IV}_{3}$. The calculated results reveal that, in the structure of the polyanion of **2**, three out of the six V centers are in the +4 oxidation state. The values of BVS for Cu1 and Cu2 centers are 1.884 and 0.971, respectively, suggesting that the Cu1 atoms exhibit an oxidation state of +2, and Cu2 has an oxidation state of +1.

1 The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February 1993, written by C. Hormillosa, with assistance from S. Healy, distributed by I. D. Brown.

2 Y. Xu, J. Q. Xu, K. L. Zhang, Y. Zhang and X. Z. You, *Chem. Commun.*, 2000, 153.

3 X. L. Wang, C. Qin, E. B. Wang, Z. M. Su, Y. G. Li and L. Xu, *Angew. Chem., Int. Ed.*, 2006, **45**, 7411.

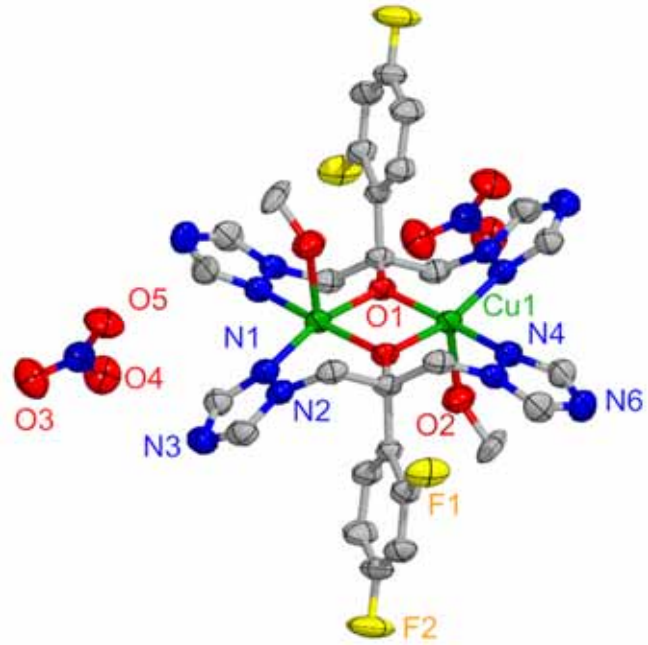


Fig. S1 ORTEP diagram showing the coordination environments for Cu atoms in the dimer with thermal ellipsoids at the 30% probability displacement, only parts of atoms are labeled and all the hydrogen atoms are omitted for clarity.

In the dimer, two deprotonated fcz^- ligands coordinate to two Cu^{2+} cations to generate the dimer. Two NO_3^- groups act as counterions. Cu^{2+} shows a square pyramidal geometry, which is surrounded by two position-2 nitrogen atoms and two oxygen atoms from different fcz^- ligands, and one methanol molecule.

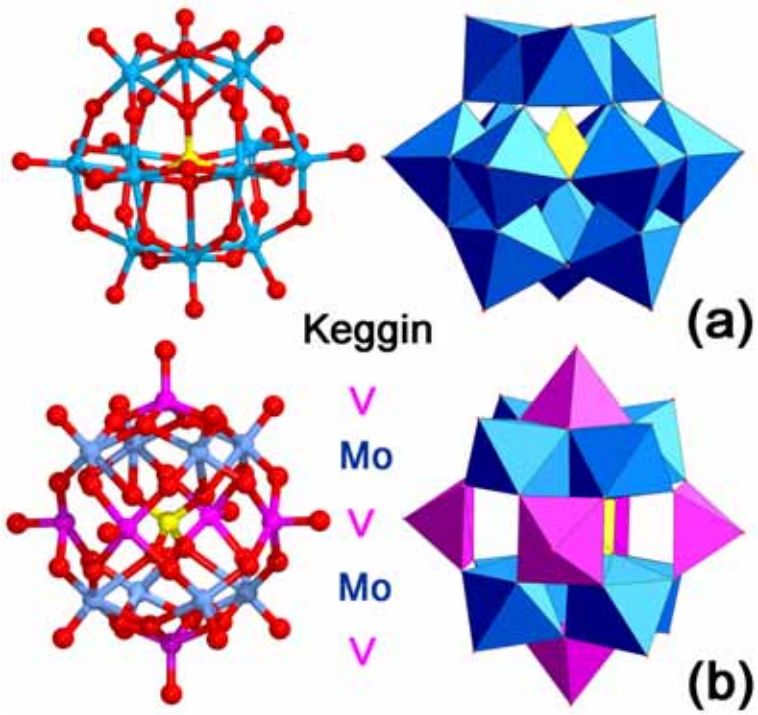


Fig. S2 Ball-and-stick (left) and simplified (right) views of the Keggin-type $(PMo^{VI}_{10}Mo^{V}_{2}O_{40})^{5-}$ cluster in compound **1** (a) and the $(PMo_8V_6O_{42})^{4-}$ cluster in compound **2** (b).

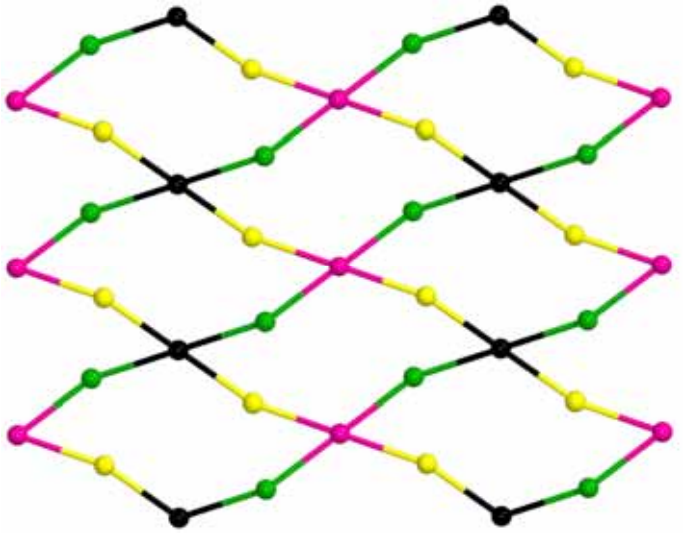
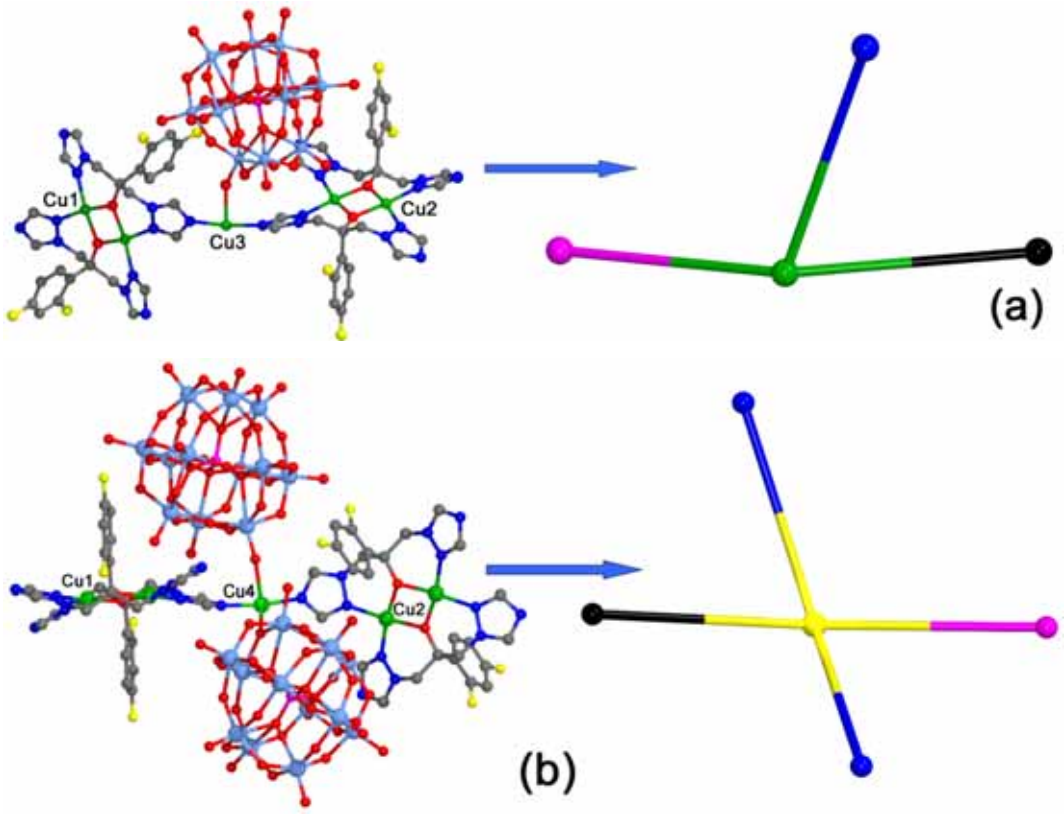


Fig. S3 Schematic view of the wavelike cationic sheet with (4, 4) topology along the *a*,*b* plane in **1** and **2**.



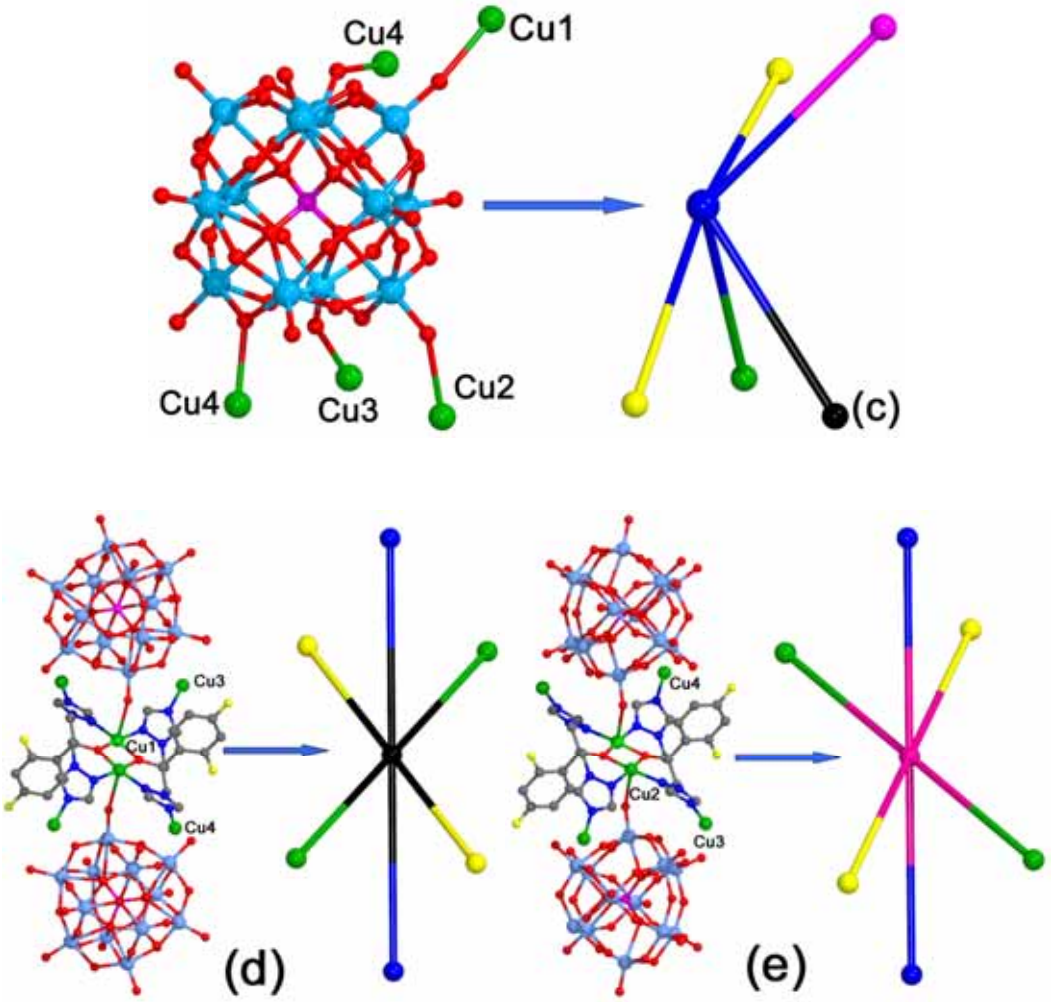
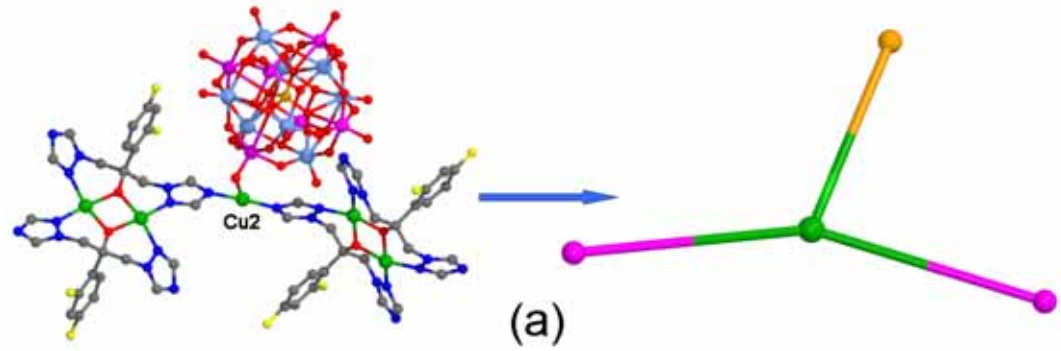


Fig. S4 Ball-and-stick (left) and simplified (right) views of the (3,4,5,6)-connected nodes in compound **1**, the 3-connected nodes are Cu3 atoms (a), 4-connected ones are Cu4 atoms (b), 5-connected ones are $(PMo^{VI}_{10}Mo^{V}_{2}O_{40})^{5-}$ anions (c), and 6-connected ones are two kinds of macrocations (d, e) (green, yellow, blue, pink and dark balls representations of three, four, five and two kinds of six-connected nodes).



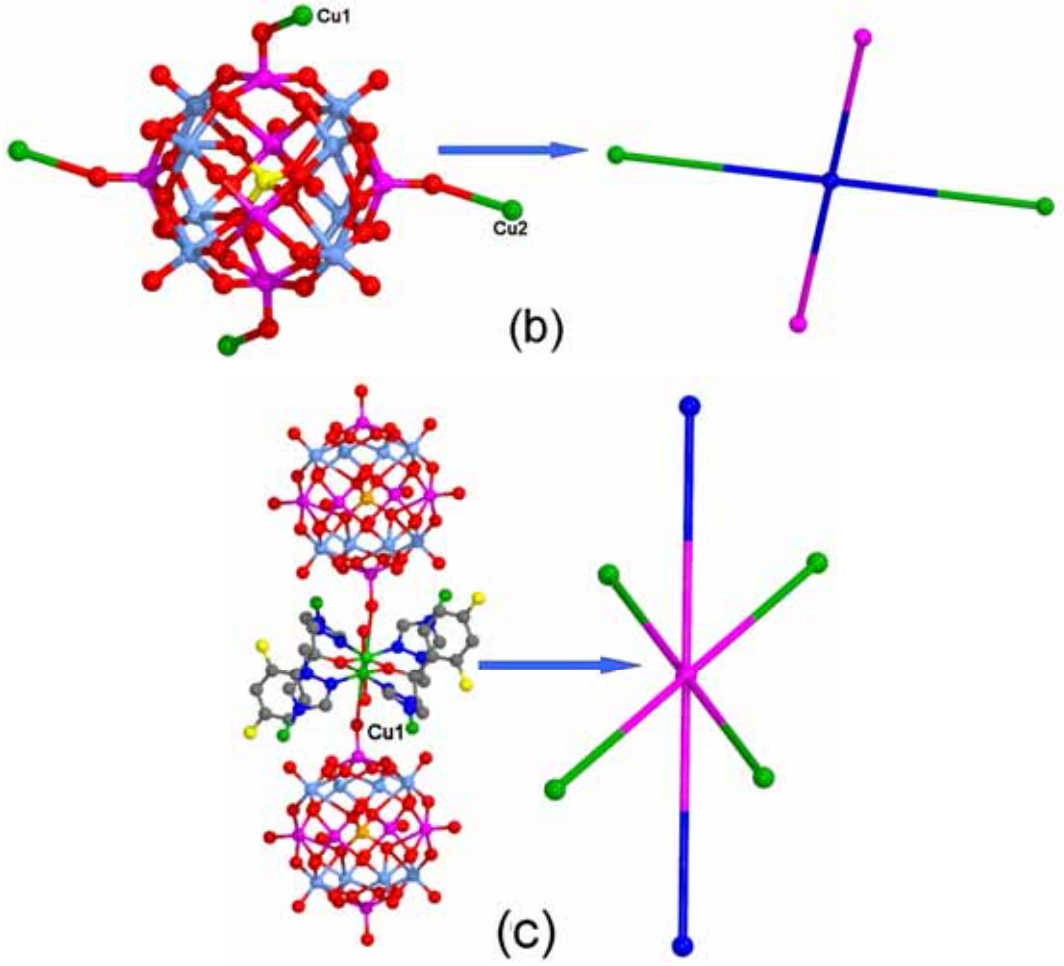
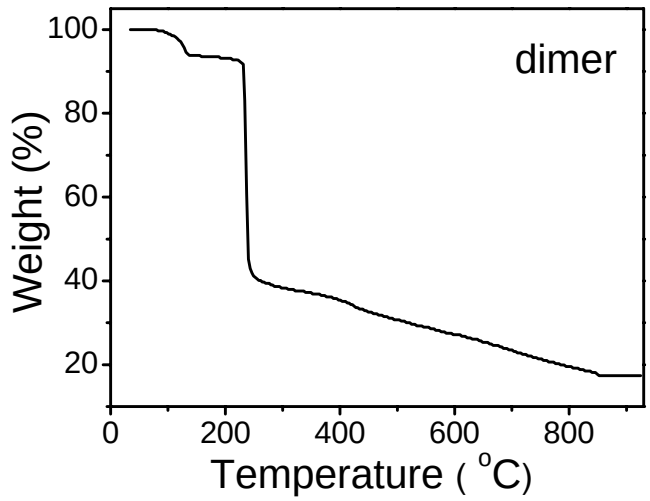
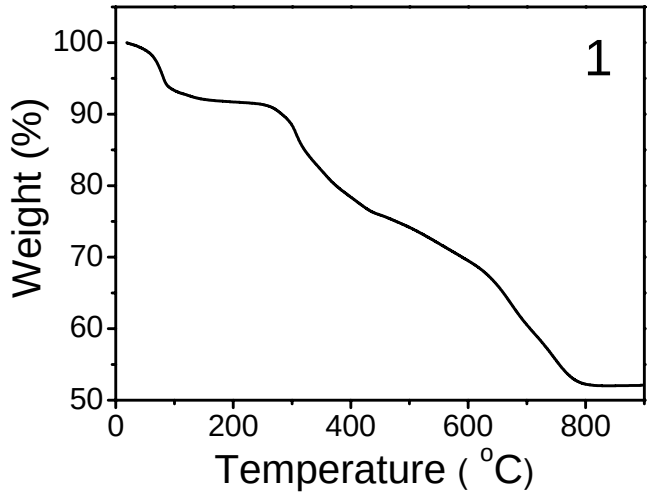


Fig. S5 Ball-and-stick (left) and simplified (right) views of the (3,4,6)-connected nodes in compound **2,** the 3-connected nodes are Cu2 atoms (a), 4-connected ones are are $(PMo^{VI}_{8}V^{V}_{3}V^{IV}_{3}O_{42})^{4-}$ anions (b), and 6-connected ones are macrocations (c) (green, blue and pink balls representations of three, four and six-connected nodes).



(a)



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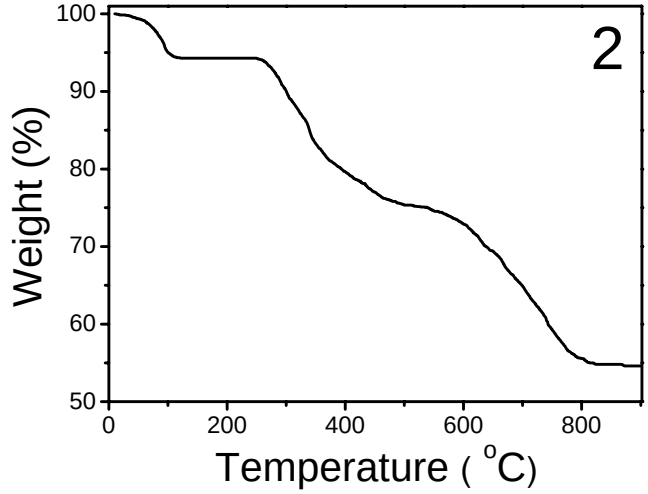

(c)

Fig. S6 TGA curves of dimer (a), **1** (b) and **2** (c).

For dimer, the weight loss corresponding to the release of two methanol molecules is observed from room temperature to 137 °C (obsd 6.9%, calcd 6.7%). The anhydrous composition begins to decompose at 235 °C and ends above 854 °C. The weight loss (found: 82.6%) corresponds to the loss of NO_3^- and organic components (calcd 82.8%). The remaining weight of 17.4% corresponds to the percentage (17.2%) of Cu and O components, indicating that the final product is CuO. The TGA curve of **1** shows a weight loss of 7.2% from room temperature to 108 °C, corresponding to the release of eleven lattice and coordinated water molecules (calcd 6.9%). No weight loss was

observed from 108 to 257 °C, and the framework started to decompose at higher temperatures. The TGA curve of **2** shows a weight loss of 5.4 % from room temperature to 112 °C, corresponding to the release of eight lattice and coordinated water molecules (calcd 5.2%). No weight loss was observed from 112 to 247 °C, and the framework started to decompose at higher temperatures.