

Cluster Organic Frameworks

Deutsche Ausgabe: DOI: 10.1002/ange.201602087
Internationale Ausgabe: DOI: 10.1002/anie.201602087

Designed Assembly of Heterometallic Cluster Organic Frameworks Based on Anderson-Type Polyoxometalate Clusters

Xin-Xiong Li, Yang-Xin Wang, Rui-Hu Wang,* Cai-Yan Cui, Chong-Bin Tian, and Guo-Yu Yang*

Abstract: A new approach to prepare heterometallic cluster organic frameworks has been developed. The method was employed to link Anderson-type polyoxometalate (POM) clusters and transition-metal clusters by using a designed rigid tris(alkoxo) ligand containing a pyridyl group to form a three-fold interpenetrated anionic diamondoid structure and a 2D anionic layer, respectively. This technique facilitates the integration of the unique inherent properties of Anderson-type POM clusters and cuprous iodide clusters into one cluster organic framework.

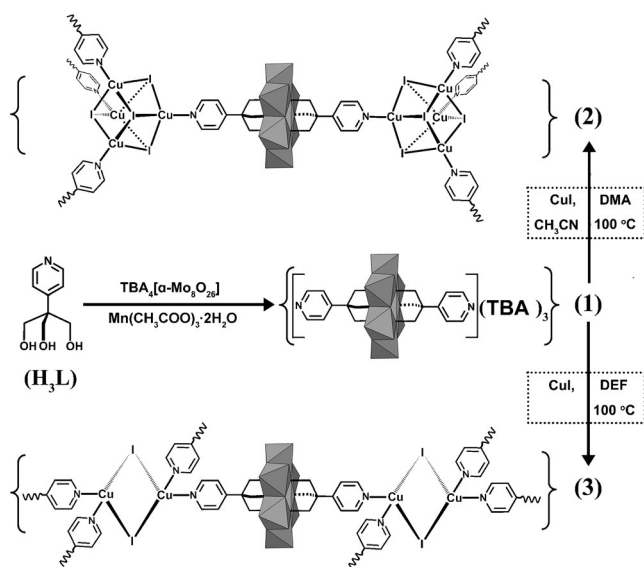
Cluster organic frameworks,^[1] composed of cluster secondary build units (SBUs) and organic linkers, have attracted extensive interest because of their fascinating structures and potential applications.^[2–4] So far, the majority of work in this area has focused on the assembly of transition-metal (TM) cluster organic frameworks, leading to the development of some intriguing framework structures.^[5] However, the design and synthesis of cluster organic frameworks from polyoxometalate (POM) clusters is still in its infancy. POMs are anionic metal oxide clusters with not only versatile applications^[6] but also different shapes, sizes, and compositions, providing a variety of SBUs for assembling novel cluster organic frameworks.^[1] For instance, we have reported a series of cluster organic frameworks based on {Ni₆PW₉} SBUs and multi-carboxylate linkers,^[1a] and Dolbecq et al. have used {Zn₄PMo₁₂O₄₀} SBUs to make porous frameworks.^[1b,c] More recently, Su and co-workers reported two frameworks obtained by linking {Zn₄PMo₁₂O₄₀} SBUs with multicarboxylate ligands.^[1d]

In contrast to the above-mentioned cluster organic frameworks which only contain either POM or TM cluster SBUs, the assembly of heterometallic cluster organic frameworks containing both POM and TM cluster SBUs has been largely unexplored, mainly because POM clusters and TM clusters are two different SBUs with different inherent characteristics. POM clusters usually have large negative charges and

oxygen-rich compositions and preferentially bond to metal cations rather than carboxylate anions or N-donor ligands, whereas TM clusters are only stable in the presence of carboxylate anions or N-donor ligands. Therefore, the search for suitable organic ligands to bridge the gap between POM clusters and TM clusters is an attractive but highly challenging task since heterometallic cluster organic frameworks should combine the physicochemical properties of the two different SBUs and provide the chance to produce multifunctional materials.

In this Communication, we chose 2-(hydroxymethyl)-2-(pyridin-4-yl)-1,3-propanediol (**H₃L**) as the bridging ligand based on the following considerations: 1) it is a rigid bifunctional ligand containing three hydroxy groups and a 4-pyridyl group on opposite sides, enabling the **L** ligand to act as a linear bridge; 2) The hydroxy groups can be easily incorporated into POM clusters (so far, tris(alkoxo) ligand grafted Anderson,^[7] Lindqvist,^[8] Dawson,^[9] and other POMs^[10] have been documented); 3) The 4-pyridyl group may capture and stabilize TM clusters formed in situ.^[11] As a result, extended cluster organic frameworks containing POM and TM clusters might be obtained (Scheme 1).

Herein, we report the designed syntheses and structures of two unprecedented heterometallic cluster organic frameworks (TBA)₆[Cu₄I₄][MnMo₆O₁₈(L)₂]₂·2DMA (**2**) and (TBA)₆[Cu₂I₂][MnMo₆O₁₈(L)₂]₂·4DEF (**3**; TBA = *n*-Bu₄N⁺, DEF = *N,N*-diethylformamide, DMA = *N,N*-dimethylacetamide).



Scheme 1. Synthetic route to cluster organic frameworks 1–3.

[*] Dr. X.-X. Li, Y.-X. Wang, Prof. Dr. R.-H. Wang, C.-Y. Cui, Dr. C.-B. Tian
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: ruihu@fjirsm.ac.cn
Prof. Dr. G.-Y. Yang
MOE Key Laboratory of Cluster Science, School of Chemistry
Beijing Institute of Technology, Beijing 100081 (China)
E-mail: ygy@bit.edu.cn
ygy@fjirsm.ac.cn

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201602087>.

These cluster organic frameworks are based on the combination of Anderson-type POM and cuprous iodide cluster SBUs and were prepared through a two-step strategy (Scheme 1). To date, though a few cluster organic frameworks containing different SBUs have been reported,^[1e–i,12] the direct connection of POM clusters and TM clusters through organic linkers into higher dimensional architectures has been rarely reported. To our knowledge, **2** and **3** represent the first examples of heterometallic cluster organic frameworks based on Anderson-type POMs and cuprous iodide clusters.

The synthetic strategy for the preparation of **2** and **3** is shown in Scheme 1. First, we grafted **L** onto both sides of the Anderson POM and obtained a new **L**-functionalized POM, (TBA)₃[MnMo₆O₁₈L₂]·2CH₃CN (**1**), which was prepared in good yield by heating (TBA)₄[α-Mo₈O₂₆], Mn(CH₃COO)₃·2H₂O, and **H₃L** in dry acetonitrile. The structural analysis revealed that **1** contains three TBA cations, one **L**-grafted Anderson-type cluster [MnMo₆O₁₈L₂]^{3–} (Figure 1a), and two lattice acetonitrile molecules. The [MnMo₆O₁₈L₂]^{3–} can be described as a well-known B-type Anderson cluster [MnMo₆O₂₄]^{3–} capped by two deprotonated **L** ligands on both sides. The length of the Anderson-type cluster is about 1.47 nm (Figure 1a). Second, when **1** is used as a starting material to react with CuI, the free 4-pyridyl groups on both sides of cluster [MnMo₆O₁₈L₂]^{3–} successfully capture and stabilize cuprous iodide clusters formed in situ. As a result, yellow block crystals of **2** (see Figure S1 in the Supporting Information) and lamellar crystals of **3** (Figure S2) were obtained under different conditions.

Single-crystal X-ray diffraction analysis revealed that **2** crystallizes in the tetragonal space group *P*₄₃₂₁₂, and features a 4-connected porous anionic framework containing tetrahe-

dral Cu₄I₄ clusters linked by the linear [MnMo₆O₁₈L₂]^{3–} cluster bridges. The asymmetric unit consists of one [MnMo₆O₁₈L₂]^{3–} anion, two TBA cations, two TBA moieties, and one Cu₄I₄ moiety (Figure S3). As a basic tetrahedral building unit, each Cu₄I₄ cluster in **2** is composed of four tetrahedrally coordinated Cu⁺ ions bonded by four μ₃-I[–] anions (Figure 1b). The Cu⋯Cu distances vary from 2.553 to 2.647 Å. Each Cu₄I₄ cluster is stabilized by four pyridyl nitrogen atoms from different [MnMo₆O₁₈L₂]^{3–} ions (Figure 1c), and the Cu–N bond lengths are 2.019(8) and 1.996(9) Å, which are in agreement with those in the reported Cu₄I₄-based cluster organic framework.^[5f] The [MnMo₆O₁₈L₂]^{3–} ion serves as a linear bridge to link two adjacent Cu₄I₄ clusters, and the distance between Cu₄I₄ clusters is about 1.86 nm. As expected, such connections between Cu₄I₄ and [MnMo₆O₁₈L₂]^{3–} clusters lead to the formation of an open 3D anionic cluster organic framework with diamondoid topology (Figure 1e). The sizes of the channels based on opposite polyhedra are about 2.78 × 2.92 nm, and the diameter of each diamondoid cavity is about 2.88 nm (Figure 1d,e; Figure S4). Such an extremely large cavity induces three-fold interpenetration of three symmetry-related cluster organic frameworks in **2** (Figure 1f; Figures S5,S6). Despite the three-fold interpenetration, the whole structure still shows large 1D irregular channels with the sizes of 1.01 × 1.01 nm² along the *c* axis (Figure 1g), where the bulky TBA cations and disordered solvent molecules are located for balancing the charge and stabilizing the cluster organic framework (Figure S7). PLATON calculations shows that the total empty volume of the anionic cluster organic framework is 14047.4 Å³, corresponding to 69.4 % of the total crystal volume (20253.2 Å³). This value is higher than that in

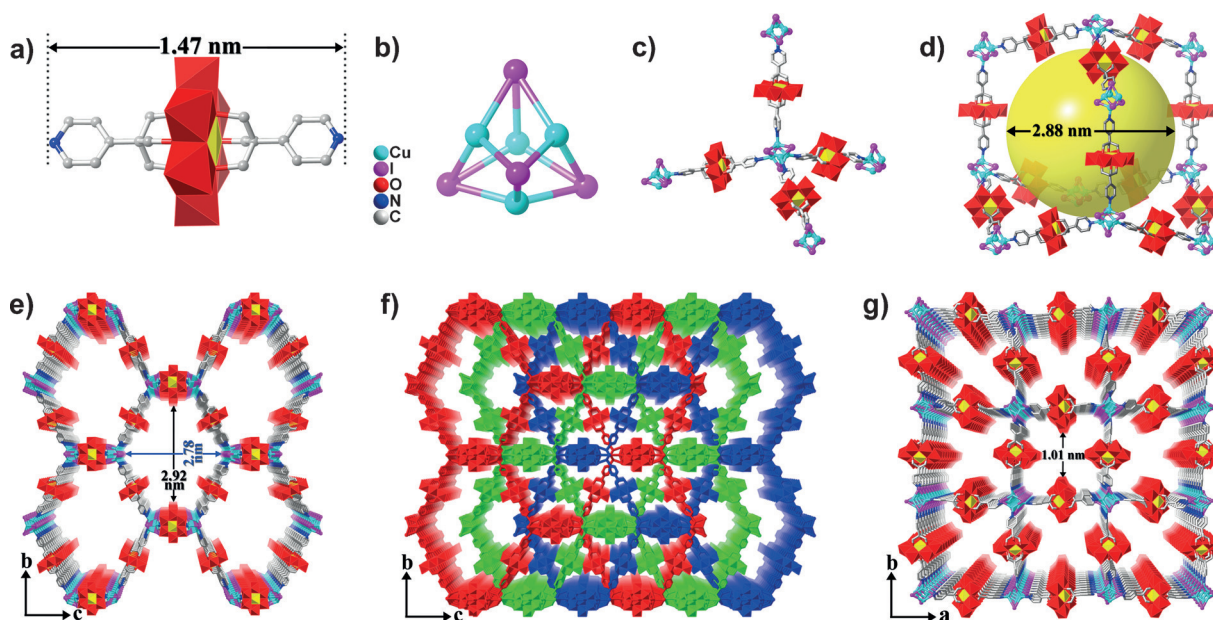


Figure 1. a) Structure of the cluster [MnMo₆O₁₈L₂]^{3–} in **1**; b) Ball and stick representation of the Cu₄I₄ cluster in **2**; c) View of the coordination environment of the Cu₄I₄ cluster in **2**; d) View of the diamondoid cavity consisting of twelve Cu₄I₄ clusters and twelve [MnMo₆O₁₈L₂]^{3–} clusters in **2**; e) View of the 3D anionic cluster organic framework based on Cu₄I₄ clusters and [MnMo₆O₁₈L₂]^{3–} clusters; f) View of the 3-fold interpenetrated cluster organic framework in **2**; g) View of the 3D cluster organic framework of **2** along the *c* axis. Color codes in a), c), d), e), and g): MoO₆ = red; MnO₆ = yellow.

some of the most open zeolites, such as faujasite, in which the free space is 45–50 % of the crystal volume.^[13]

Variation of the reaction conditions led to the formation of another interesting cluster organic framework **3**, which is based on rhombohedral Cu_2I_2 and $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ clusters. The asymmetric unit of **3** contains one Cu_2I_2 moiety and two independent $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ moieties, one TBA cation, and one TBA moiety (Figure S8). As another conventional cuprous iodide cluster, the Cu_2I_2 cluster can be viewed as two tetrahedrally coordinated Cu^+ ions linked by two $\mu_2\text{-I}^-$ anions. The $\text{Cu}\cdots\text{Cu}$ distance in the Cu_2I_2 cluster is 2.582 Å, which is comparable with that in **2**.

As shown in Figure 2a, each Cu_2I_2 cluster in **3** is ligated by four pyridyl groups from four $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ bridges with Cu-N bond lengths of 2.042(5) and 2.050(5) Å. Four symmetry-related nitrogen atoms bound to the Cu_2I_2 unit are coplanar, with a N-Cu-N bond angle of 111.5(1)°, leading to the formation of an unprecedented 2D cluster organic framework (Figure 2b). In each layer, the coordination connectivity between Cu_2I_2 clusters and $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ anions generates giant parallelogram-shaped rings with sizes of $2.46 \times 3.05 \text{ nm}^2$ (measured between opposite atoms). Each ring is circumscribed by four Cu_2I_2 and four $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ clusters. The 2D layers are stacked in parallel along the *a* axis, and each layer is slightly shifted with respect to the next one (Figure S9). The distance between the adjacent layers is about 4.877 Å. Such stacking of the layers gives rise to 1D channels

with decreased sizes of $2.30 \times 2.45 \text{ nm}^2$ along the *a* axis (Figure 2c), in which the charge-compensated TBA cations and guest solvent molecules are located (Figure S10). After the removal of TBA cations and solvent molecules, the total potential accessible volume of **3** is 71.4 %, based on PLATON calculations, which is slightly higher than that in **2**.

Bond valence sum (BVS) calculations^[14] based on bond lengths revealed that the oxidation states of Mo and Mn ions in **1–3** are +6 and +3, respectively (Table S2). The average BVS values for Cu ions in **2** and **3** are 1.155 and 1.042, respectively, suggesting Cu ions are in the +1 oxidation state. These results are consistent with the charge-balanced requirement of the anions and the frameworks. **2** and **3** are stable in air and the good agreement between powder X-ray diffraction (PXRD) patterns for the as-synthesized samples and the simulated ones based on single-crystal data indicate the phase purities of **2** and **3** (Figure S11, S12). Thermogravimetric analyses (TGA) of **2** and **3** (Figure S13) show weight losses of 3.88 % and 8.43 % in 30–240 °C and 30–190 °C, respectively, corresponding to the removal of free DMA (calculated as 3.52 % for **2**) and DEF molecules (calculated as 8.92 % for **3**), respectively. As shown in Figure S11, in situ variable-temperature PXRD patterns indicate that the anionic framework of **2** remains intact up to 250 °C, whereas the thermal stability of **3** is lower than that of **2**. **3** is only stable at temperatures lower than 220 °C, as evidenced by the variable-temperature PXRD patterns (Figure S12), which further confirms that the framework with the diamondoid topology is more stable than the 2D structure. In the IR spectra of **1–3** (Figure S14), the characteristic vibrational bands of Anderson-type anions for the terminal Mo=O units and the bridging Mo-O-Mo groups are located at 840–980 cm^{-1} and 620–730 cm^{-1} ,^[7g] respectively. The bands at 1366–1460 and 3025–2815 cm^{-1} are ascribed to the stretching vibrations of TBA cations.^[15] These results are consistent with their single-crystal structural analyses.

The variable-temperature photoluminescent properties of the as-synthesized framework **2** were studied in the temperature range of 77–350 K (Figure 3). Upon excitation at $\lambda = 327 \text{ nm}$ at 77 K, **2** exhibits a remarkable emission band with a maximum around $\lambda = 656 \text{ nm}$. The emission may be attributed to a “cluster-centered” triplet excited state that involves both Cu_4 and I_4 tetrahedral units and has mixed iodide-to-metal charge transfer and “metal-cluster-centered” ($d^{10} \text{ Cu} \rightarrow d^9 s^1 \text{ Cu}$) character.^[16] As the temperature increases, the emission intensities sharply decrease without an obvious shift of the emission maximum, and the emission is nearly quenched at room temperature. Such emission variation may be attributed to the quenching effects caused by the solvent molecules or other components gradually become stronger as the temperature increases.^[17] The UV/Vis diffuse reflectance spectra (Figure S15) of the polycrystalline samples showed that the band gaps of **2** and **3** can be calculated as 2.20 and 1.96 eV, respectively. Pure inorganic POMs are usually insulators,^[18] however, the interactions between organic ligands and the POM clusters can affect energy levels near the Fermi level to make such hybrid POMs as potential semiconductors.^[19] The magnetic susceptibility of **2** was measured under an applied magnetic field of 1 kOe in the temperature range from 300 to 2 K (Figure S16). At 300 K,

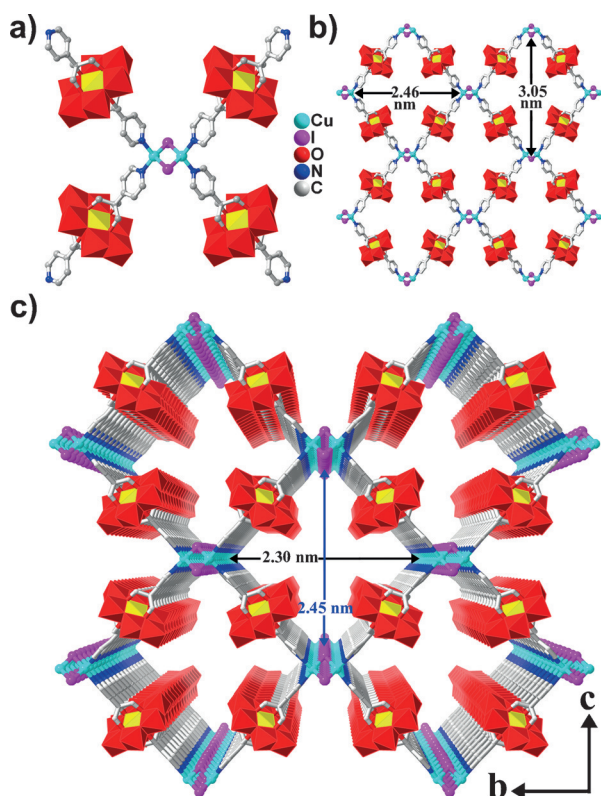


Figure 2. a) View of the coordination environment of the Cu_2I_2 cluster in **3**; b) View of the 2D layer based on Cu_2I_2 and $[\text{MnMo}_6\text{O}_{18}\text{L}_2]^{3-}$ clusters in **3**; c) View of the 3D stacking style of 2D layers, showing 1D channels along the *a* axis.

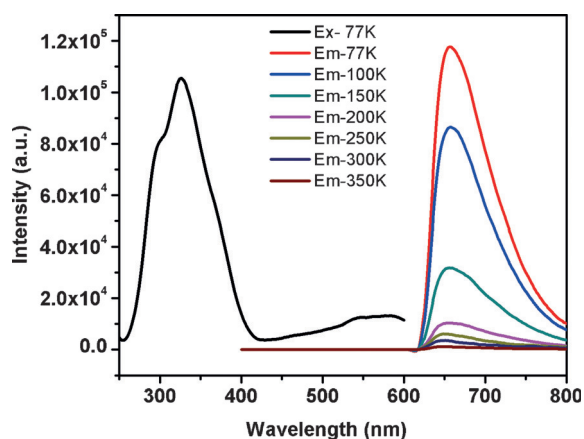


Figure 3. Variable-temperature photoluminescence spectra of **2** in the solid state. For the excitation (ex) spectrum, $\lambda_{\text{ex}} = 327$ nm; for the emission (em) spectra, $\lambda_{\text{em}} = 656$ nm.

the $\chi_m T$ value is $2.91 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, which is very close to the value of $3.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for an isolated Mn^{III} ion with $g = 2.0$. Upon cooling, the $\chi_m T$ value remains constant to about 35 K; subsequently, it decreases abruptly to a minimum value of $2.20 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. Such magnetic behavior is typical for a high-spin Mn^{III} compound.^[20] The decrease of the $\chi_m T$ value at low temperature should be attributed to the zero-field splitting of Mn^{III} ions rather than antiferromagnetic intermolecular interactions. The absence of antiferromagnetic intermolecular interactions was confirmed by the very small and negative Weiss constant $\theta = -0.47$ K, obtained based on $1/\chi_m$ versus T plots in the temperature range of 2–300 K according to the Curie–Weiss law (Figure S16).

The catalytic performance of **2** was initially investigated by its application in a Cu^{I} -catalyzed three-component azide–alkyne cycloaddition reaction at 25°C . As shown in Figure S17, the one-pot reaction between benzyl bromide, sodium azide, and phenylacetylene in the presence of **2** provided the target product in a quantitative yield in 5 h. In control experiments, CuI only afforded a 39% conversion of benzyl bromide, and no target product was detected when **1** was used as a catalyst. Notably, the mixture of **1** and CuI showed a higher catalytic activity before 3 h than **2**, which is probably ascribed to the shorter induction period in the reaction. After 4 h, the catalytic activity of the mixture was inferior to that of **2** and achieved a 90% conversion in 5 h. These results suggested that the integration of Cu_4I_4 clusters and **1** containing POM clusters to form a cluster organic framework was greatly favorable for the catalytic reaction. In addition, the catalytic system shows good generality (Table S3). When different types of terminal alkynes, such as a phenylacetylene bearing an electron-donating group or a heteroaromatic acetylene and alkylacetylene, were used as substrates under the same conditions (Table S3, entries 1–4), the corresponding products were obtained in excellent yields (as determined by GC). Similarly, the reactions of other benzyl bromides also proceeded smoothly regardless of their electronic and steric nature (Table S3, entries 5–9).

In summary, we have successfully constructed two unprecedented heterometallic cluster organic frameworks through

directly linking Anderson-type POM clusters with different cuprous iodide clusters. The deliberate choice of the rigid bifunctional tris(alkoxo) ligand containing a pyridyl group is crucial for designing and developing these frameworks. **2** exhibits a combination of the photoluminescence and magnetic properties as well as the catalytic activity derived from the integration of both cuprous iodide clusters and POM clusters within one cluster organic framework. The interesting properties of these novel cluster organic frameworks testify that the linkage of different types of clusters with distinct properties is an effective method in the exploration of multifunctional materials. This work not only provides a new perspective towards the development of heterometallic cluster organic frameworks, but also confirms the potential for developing new classes of multifunctional materials by using various TM clusters, such as $\text{Zn}_4\text{O}(\text{CO}_2)_6$,^[5a] $\text{Cu}_2(\text{OH})_2(\text{CO}_2)_4$,^[5b] $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$,^[5c] $\text{Cr}_3\text{O}_4(\text{CO}_2)_6$,^[5d] $\text{In}_3\text{O}(\text{CO}_2)_3$,^[5e] WS_4Cu_4 ,^[5g] Cu_4OCl_6 ,^[5h] and $\text{Re}_6(\mu_3\text{-Se})_8$,^[5i] together with POM clusters with different shapes as SBUs.

Acknowledgements

This work was supported by the 973 Program (no. 2011CBA00502), the NSFC (nos. 21273239, 21401195, and 21571016) and the NSF for Young Scholars of Fujian Province (no. 2015J05041).

Keywords: cluster organic frameworks · copper · heterometallic structures · luminescence · polyoxometalates

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 6462–6466
Angew. Chem. **2016**, *128*, 6572–6576

- [1] a) S.-T. Zheng, J. Zhang, G.-Y. Yang, *Angew. Chem. Int. Ed.* **2008**, *47*, 3909–3913; *Angew. Chem.* **2008**, *120*, 3973–3977; b) L. Marleny Rodriguez-Albelo, A. R. Ruiz-Salvador, A. Sampieri, D. W. Lewis, A. Gómez, B. Nohra, P. Mialane, J. Marrot, F. Sécheresse, C. Mellot-Draznieks, R. Ngo Biboum, B. Keita, L. Nadjó, A. Dolbecq, *J. Am. Chem. Soc.* **2009**, *131*, 16078–16087; c) B. Nohra, H. El Moll, L. M. Rodriguez Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O’Keeffe, R. Ngo Biboum, J. Lemaire, B. Keita, L. Nadjó, A. Dolbecq, *J. Am. Chem. Soc.* **2011**, *133*, 13363–13374; d) J.-S. Qin, D.-Y. Du, W. Guan, X.-J. Bo, Y.-F. Li, L.-P. Guo, Z.-M. Su, Y.-Y. Wang, Y.-Q. Lan, H.-C. Zhou, *J. Am. Chem. Soc.* **2015**, *137*, 7169–7177; e) J.-W. Cheng, J. Zhang, S.-T. Zheng, M.-B. Zhang, G.-Y. Yang, *Angew. Chem. Int. Ed.* **2006**, *45*, 73–77; *Angew. Chem.* **2006**, *118*, 79–83; f) F.-W. Fang, L. Zhang, J. Zhang, G.-Y. Yang, *Chem. Eur. J.* **2015**, *21*, 15511–15515; g) F.-W. Fang, J.-W. Cheng, G.-Y. Yang, *Chem. Eur. J.* **2014**, *20*, 2704–2711; h) W.-F. Fang, G.-Y. Yang, *Inorg. Chem.* **2014**, *53*, 5631–5636; i) W.-F. Fang, C. Cheng, L. Huang, G.-Y. Yang, *Inorg. Chem.* **2013**, *52*, 6–8.
- [2] a) C. Wang, O. Volotskova, K. Lu, M. Ahmad, C. Sun, L. Xing, W.-B. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 6171–6174; b) B.-B. Tu, Q.-Q. Pang, E. Ning, W.-Q. Yan, Y. Qi, D.-F. Wu, Q.-W. Li, *J. Am. Chem. Soc.* **2015**, *137*, 13456–13459.
- [3] a) H. He, G.-J. Cao, S.-T. Zheng, G.-Y. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 15588–15589; b) N. M. Padial, E. Quartapelle Procopio, C. Montoro, E. López, J. E. Oltra, V. Colombo, A. Maspero, N. Masciocchi, S. Galli, I. Senkova, S. Kaskel, E. Barea, J. A. R. Navarro, *Angew. Chem. Int. Ed.* **2013**, *52*, 8290–8294; *Angew. Chem.* **2013**, *125*, 8448–8452.

- [4] a) X.-C. Shan, F.-L. Jiang, D.-Q. Yuan, H.-B. Zhang, M.-Y. Wu, L. Chen, J. Wei, S.-Q. Zhang, J. Pan, M.-C. Hong, *Chem. Sci.* **2013**, *4*, 1484–1489; b) J. J. Perry IV, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417.
- [5] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; b) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148–1150; c) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851; d) G. Férey, C. Mellot-Drazniewski, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040–2042; e) S.-T. Zheng, X. Zhao, S. Lau, A. Fuhr, P. Feng, X. Bu, *J. Am. Chem. Soc.* **2013**, *135*, 10270–10273; f) Y. Kang, F. Wang, J. Zhang, X.-H. Bu, *J. Am. Chem. Soc.* **2012**, *134*, 17881–17884; g) K. Liang, H. Zheng, Y. Song, M. F. Lappert, Y. Li, X. Xin, Z. Huang, J. Chen, S. Lu, *Angew. Chem. Int. Ed.* **2004**, *43*, 5776–5779; *Angew. Chem.* **2004**, *116*, 5900–5903; h) A. K. Mishra, S. Verma, *Inorg. Chem.* **2010**, *49*, 3691–3693; i) H. D. Selby, B. K. Roland, Z. P. Zheng, *Acc. Chem. Res.* **2003**, *36*, 933–944.
- [6] a) D.-L. Long, R. Tsunashima, L. Cronin, *Angew. Chem. Int. Ed.* **2010**, *49*, 1736–1758; *Angew. Chem.* **2010**, *122*, 1780–1803; b) S.-T. Zheng, G.-Y. Yang, *Chem. Soc. Rev.* **2012**, *41*, 7623–7646; c) O. Oms, A. Dolbecq, P. Mialane, *Chem. Soc. Rev.* **2012**, *41*, 7497–7536; d) S.-S. Wang, G.-Y. Yang, *Chem. Rev.* **2015**, *115*, 4893–4962.
- [7] a) J. Thiel, D. Yang, M. H. Rosnes, X. Liu, C. Yvon, S. E. Kelly, Y.-F. Song, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* **2011**, *50*, 8871–8875; *Angew. Chem.* **2011**, *123*, 9033–9037; b) C. Yvon, A. J. Surman, M. Hutin, J. Alex, B. O. Smith, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* **2014**, *53*, 3336–3341; *Angew. Chem.* **2014**, *126*, 3404–3409; c) S. Favette, B. Hasenknopf, J. Vaissermann, P. Gouzerh, C. C. Roux, *Chem. Commun.* **2003**, 2664; d) Y. F. Song, N. McMillan, D. L. Long, J. Thiel, Y. Ding, H. Chen, N. Gadegaard, L. Cronin, *Chem. Eur. J.* **2008**, *14*, 2349–2354; e) C. Yvon, A. Macdonell, S. Buchwald, A. J. Surman, N. Follet, J. Alex, D.-L. Long, L. Cronin, *Chem. Sci.* **2013**, *4*, 3810–3817; f) P. R. Marcoux, B. Hasenknopf, J. Vaissermann, P. Gouzerh, *Eur. J. Inorg. Chem.* **2003**, 2406–2412; g) B. Hasenknopf, R. Delmont, P. Herson, P. Gouzerh, *Eur. J. Inorg. Chem.* **2002**, 1081–1087; h) A. Macdonell, N. A. B. Johnson, A. J. Surman, L. Cronin, *J. Am. Chem. Soc.* **2015**, *137*, 5662–5665.
- [8] a) P.-F. Wu, Z.-C. Xiao, J. Zhang, J. Hao, J.-K. Chen, P.-C. Yin, Y.-G. Wei, *Chem. Commun.* **2011**, 47, 5557–5559; b) L. J. Batchelor, R. Shaw, S. J. Markey, M. Helliwell, E. J. L. McInnes, *Chem. Eur. J.* **2010**, *16*, 5554–5557; c) D. Li, J. Song, P. Yin, S. Simotwo, A. J. Bassler, Y. Aung, J. E. Roberts, K. I. Hardcastle, C. L. Hill, T.-B. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 14010–14016; d) S. She, S.-T. Bian, J. Hao, J.-W. Zhang, J. Zhang, Y.-G. Wei, *Chem. Eur. J.* **2014**, *20*, 16987–16994.
- [9] a) C. P. Pradeep, D.-L. Long, G. N. Newton, Y.-F. Song, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 4388–4391; *Angew. Chem.* **2008**, *120*, 4460–4463; b) C. P. Pradeep, M. F. Misrahi, F. Y. Li, J. Zhang, L. Xu, D. L. Long, T. Liu, L. Cronin, *Angew. Chem. Int. Ed.* **2009**, *48*, 8309–8313; *Angew. Chem.* **2009**, *121*, 8459–8463.
- [10] a) M. I. Khan, Q. Chen, J. Zubietta, *J. Chem. Soc. Chem. Commun.* **1992**, 305–306; b) M. I. Khan, Q. Chen, D. P. Goshorn, J. Zubietta, *Inorg. Chem.* **1993**, *32*, 672–680; c) M. I. Khan, Q. Chen, H. Hope, S. Parkin, C. J. O’Connor, J. Zubietta, *Inorg. Chem.* **1993**, *32*, 2929–2937.
- [11] a) Z. Liu, M. F. Qayyum, C. Wu, M. T. Whited, P. I. Djurovich, K. O. Hodgson, B. Hedman, E. I. Solomon, M. E. Thompson, *J. Am. Chem. Soc.* **2011**, *133*, 3700–3703; b) X. Wang, X. Tian, Q. Zhang, P. Sun, J. Wu, H. Zhou, B. Jin, J. Yang, S. Zhang, C. Wang, X. Tao, M. Jiang, Y. Tian, *Chem. Mater.* **2012**, *24*, 954–961.
- [12] a) J.-J. Qian, F.-L. Jiang, K.-Z. Su, J. Pan, Z.-Z. Xue, L.-F. Liang, P. P. Bag, M.-C. Hong, *Chem. Commun.* **2014**, 50, 15224–15227; b) X.-L. Wang, C. Qin, E.-B. Wang, Z.-M. Su, Y.-G. Li, L. Xu, *Angew. Chem. Int. Ed.* **2006**, *45*, 7411–7414; *Angew. Chem.* **2006**, *118*, 7571–7574.
- [13] C. Baerlocher, L. B. McCusker, D. H. Olson in *Atlas of Zeolite Framework Types*, 6th ed. (Eds.: C. Baerlocher, L. B. M. H. Olson), Elsevier Science B.V., Amsterdam, **2007**, pp. 140–141.
- [14] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247.
- [15] H. Fu, C. Qin, Y. Lu, Z.-M. Zhang, Y.-G. Li, Z.-M. Su, W.-L. Li, E.-B. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7985–7989; *Angew. Chem.* **2012**, *124*, 8109–8113.
- [16] a) M. M. Siddiqui, S. M. Mobin, I. Senkovska, S. Kaskel, M. S. Balakrishna, *Chem. Commun.* **2014**, 50, 12273–12276; b) T. H. Kim, Y. W. Shin, J. H. Jung, J. S. Kim, J. Kim, *Angew. Chem. Int. Ed.* **2008**, *47*, 685–688; *Angew. Chem.* **2008**, *120*, 697–700; c) S. Cho, Y. Jeon, S. Lee, J. Kim, T. H. Kim, *Chem. Eur. J.* **2015**, *21*, 1439–1443; d) P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625–3648; e) M.-H. Bi, G. H. Li, Y. C. Zou, Z. Shi, S. H. Feng, *Inorg. Chem.* **2007**, *46*, 604–606.
- [17] a) N. P. Rath, E. M. Holt, K. Tanimura, *Inorg. Chem.* **1985**, *24*, 3934–3938; b) G. Hu, G. J. Mains, E. M. Holt, *Inorg. Chim. Acta* **1995**, *240*, 559–565; c) K.-C. Chang, J.-L. Lin, Y.-T. Shen, C.-Y. Hung, C.-Y. Chen, S.-S. Sun, *Chem. Eur. J.* **2012**, *18*, 1312–1321.
- [18] E. B. Stokes, State-of-the-Art Program on Compound Semiconductors XXXVIII and Wide Bandgap Semiconductors for Photonic and Electronic Devices and Sensors III: Proceedings of the International Symposia; Electronics Division and Sensor Division, Electrochemical Society, **2003**.
- [19] K. I. Abishek, C. P. Sebastian, *Inorg. Chem.* **2014**, *53*, 653–660.
- [20] a) R. Ishikawa, R. Miyamoto, H. Nojiri, B. K. Breedlove, M. Yamashita, *Inorg. Chem.* **2013**, *52*, 8300–8302; b) B. J. Kennedy, K. S. Murray, *Inorg. Chem.* **1985**, *24*, 1552–1557.

Received: February 29, 2016

Published online: April 9, 2016