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COMMUNICATION

Assembly of super-supertetrahedral metal-organic clusters into a hierarchical porous cubic framework^{†‡}

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A porous framework comprising a super-supertetrahedral metalorganic cluster building block has been synthesized. Its cubic framework represents a multi-level hierarchical architecture and also possesses an interesting magnetic property.

The use of molecular building blocks is a powerful method for the synthesis of solid state materials.^{1,2} In the areas of metal–organic frameworks (MOFs) and metal–organic polyhedra (MOPs), the "node and spacer" approach involving molecular building blocks of various combinations is very successful in constructing the targeted open architectures. Compared to traditional dense solid state materials, molecular building blocks such as organic linkers and metal clusters exhibit a much greater diversity and provide new opportunities for generating materials with high porosity.

More recently, supramolecular building blocks have been found to be a potent way for achieving hierarchical assemblies that allow a new level of control over structural properties and pore structures. This method, as highlighted by the use of MOPs as building units, beautifully demonstrates the self-assembly on a supramolecular scale by larger and more sophisticated aggregates of multi-metal nodes and organic linkers.² Compared to molecular building blocks, these supramolecular cages or clusters can dramatically scale up the pore architecture, and very often they also possess well-defined coordination geometry, which bestows a certain degree of predictability in the synthetic design.^{3,4} On the other hand, so far there are much fewer examples of supramolecular building units, compared to molecular building units. Hence creating new rationally designed supramolecular building blocks is of increasing importance.

Most interesting to us is the fact that even among supramolecular building units, it is possible to have multiple levels of hierarchies. For example, in metal chalcogenide chemistry,⁵ four InS₄ molecular tetrahedra can form an In₄S₁₀ supertetrahedral cluster (known as T2) by corner sharing. Such T2 clusters, by themselves, can form 3D porous frameworks with zeolite-like topologies such as sodalite.^{6a} Yet, it is also known that four T2 clusters can form a closed supersupertetrahedral cluster with the same T2 configuration, $In_{16}S_{34}$ (known as super-supertetrahedral T2,2 cluster).^{6a} Similar formation of hierarchical superstructures is also known for larger clusters (e.g., the assembly of four T4 Cd₄In₁₆S₃₅ clusters into the T2 configuration of Cd₁₆In₆₄S₁₃₄, denoted T4,2 cluster).^{6b} In comparison, while supramolecular tetrahedral building units are also found in MOFs, as exemplified by [(Cr₃O)₄(BTC)₄] and [(Cr₃O)₄(BDC)₆] cages in MIL-100 and MIL-101, as well as dense clusters like $Cu_5(btz)_6(L)_4$ and $Co_5(btz)_6(L)_4$;^{7,8} a higher level of assembly into a super-supertetrahedron-like cluster has so far remained elusive in MOFs.

Herein, we report a multi-hierarchical MOF structure constructed by a super-supertetrahedral metal-ligand cluster with twenty metal sites. It has a cubic unit cell with the formula of $[Mn_5(TBA)_3(HCOO)_3(OH)(H_2O)_2]_4 \cdot 6DMF$ (denoted CPF-5, CPF = Crystalline Porous Framework; $H_2TBA = 4$ -tetrazole-benzoic acid).§

In CPF-5, each tetrazolate uses three of its four N-donors to assemble five metal ions into a supertetrahedral T2-like cluster (Fig. 1a). Within the T2 cluster, three tetrazolate groups are arranged on three adjacent edges of the tetrahedron that share the same corner Mn, while the other three edges are occupied by formate groups, forming the $Mn_3(HCOO)_3$ 3-ring. One O site of the formate group is bonded to only one Mn^{2+} site of the triangle, while the other O site bridges one Mn^{2+} site of the triangle with the core Mn^{2+} site. Thus, the core Mn is 6-coordinated, to three N atoms of three different tetrazolate groups and three O atoms of different formate groups (Fig. 1a).

Four T2 clusters are joined together by using two carboxyl groups and one DMF O donor to bridge two Mn^{2+} sites from two adjacent Mn-formate triangles, leading to a T2,2 cluster (Fig. 1b). Within the T2,2 cluster, the Mn^{2+} sites in the Mn-formate triangle have a 5-coordinate environment. However, the four Mn atoms at the corner of the T2,2 cluster possess 6-coordination by also bonding to three O atoms with an average bond length of 2.25 Å.

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Fig. 1 (left) Five Mn atoms are aggregated into a [Mn₅(TBA)₃(HCOO)₃] supertetrahedral T2-like cluster. Six edges of the T2 cluster are occupied by 3 TBA and 3 formate groups. (right) Four T2 clusters are further linked to a super-supertetrahedral T2,2 cluster by carboxylate groups and DMF oxygen. Orange: Mn; red: O; blue: N; grey: C.

This hierarchical self-assembly of the T2 cluster into the T2,2 cluster drastically scales up the size of the building block. Interestingly, in CPF-5, T2,2 clusters are further assembled together through a special type of quadruple edge-to-edge connection (Fig. 2) into a 3D simple cubic topology (Fig. 3), which leads to the 4th-order of structural hierarchy (the 1st-order being the MnL_5 and MnL_6 complexes). This is highly unusual, not only because the overall framework involves four levels of hierarchical constructions, but also because the total connections



Fig. 2 Two T2,2 clusters are connected together by a total of 4 ligands. Each TBA ligand runs from the edge center of one T2,2 cluster to the edge center of one T2 cluster within the other T2,2 cluster. Orange: Mn; red: O; blue: N; grey: C.



Fig. 3 Eight T2,2 clusters aggregate into simple cubic packing. Each tetrahedron in this graph represents a T2 supertetrahedral cluster containing 5 Mn atoms. The four ligands connecting neighboring clusters are simplified as purple rods. Orange: Mn; red: O; blue: N; grey: C.

between each T2,2 cluster and its six adjacent T2,2 clusters involve as many as 24 ligands.

While the overall framework topology resembles the wellknown 6-connected MOF-5 structure, the 6-connected node in CPF-5 is far more complicated. In comparison with MOF-5 with only four tetrahedral Zn atoms in its 6-connected node, the 6-connected node in CPF-5 has a total of 20 metal sites, organized into three levels of hierarchies with an accompanying hydrophilic cavity partially occupied by framework-bonded DMF molecules. A much larger void results from the cubic assembly of T2,2 clusters. The 3D interconnecting porous channels possess a hydrophilic central void of 14 Å in diameter with aperture of 11 Å. PLATON calculation indicates that the solvent accessible void space occupies a total of 56% of the crystal volume.

Thermogravimetric analysis shows that CPF-5 lost 15% of its weight at around 100 °C due to the loss of uncoordinated solvent molecules, and continued to gradually lose weight until 210 °C under a N₂ atmosphere. Various degassing temperatures were tested and 100 °C was found to provide the maximum adsorption uptake. Permanent porosity was confirmed by N₂ adsorption performed on a Micromeritics ASAP 2020. N2 adsorption behavior of CPF-5 shows a small step before reaching the saturation and then followed by a hysteresis loop in the higher relative pressure region. The small step is quite typical for the materials with both micro- and meso-apertures. It likely resulted from the multi-layer adsorption of N₂ molecules in the larger channels and the hysteresis loop further confirmed that there is capillary condensation in the larger pores even though the effect of the inter-particle pore near 1 atm is evident. From the isotherm, Langmuir and BET surface areas were calculated to be 262.9 $\text{m}^2 \text{g}^{-1}$ and 161.3 $\text{m}^2 \text{g}^{-1}$, respectively. This material also shows good adsorption ability for carbon dioxide (31.6 cm³ g⁻¹ at 273.15 K and 760 mmHg) and hydrogen $(4.82 \text{ mg g}^{-1} \text{ at } 77 \text{ K and } 760 \text{ mmHg})$ (Fig. S7 and S8, ESI \ddagger).

The three distinct regions, especially evident on the desorption branch (Fig. 4), represent three types of cavity: the octahedral cavity surrounded by the supramolecular Mn_5 -tetrahedra, the large channel built by cubic packing of super-supertetrahedral Mn_{20} -T2,2 clusters, and macropores from macroscale particle packing. The presence of these multi-scale pores clearly demonstrates that by applying super-supramolecular clusters as building blocks, one could scale up the molecular architecture from the atomic scale to the meso-scale.

One advantage of using supramolecular clusters as the building block is the opportunity for incorporating other properties into the structure. A more densely aggregated metal-ligand cluster could offer desirable interactions such as magnetic exchange or other interactions that do not occur when the metal centers are separated significantly. The magnetic property measurement is carried out on a Quantum Design XL7SQUID magnetometer on a degassed sample. The temperature dependent magnetic inverse susceptibility of CPF-5 is given in Fig. 5. Above 20 K, the data follow Curie-Weiss behavior with an effective magnetic moment (μ_{eff}) of 5.4 μ_{B} per magnetic ion and a Weiss temperature (θ) of -23.7 K. This 5.4 $\mu_{\rm B}$ per magnetic ion was derived by treating the mass of the crystal as the weight of the framework only. It is slightly smaller compared to the 5.9 $\mu_{\rm B}$ of the Mn(II) ion, which indicates that there is approximately 9% of the free solvent by weight still left in the open framework



Fig. 4 N_2 adsorption-desorption isotherm and different sized pore windows of CPF-5 at 77 K and 760 mmHg.



Fig. 5 The inverse molar susceptibility (χ^{-1}) versus temperature (*T*) for CPF-5. Below 20 K, the inverse susceptibility descends faster than the Curie–Weiss relation.

under this degassing condition. A maximum is not observed in the susceptibility, indicating the absence of long-range order down to the lowest measured temperature of 2 K. The negative Weiss temperature is an indication that the magnetic moments have an antiparallel coupling as with an antiferro- (AFM) or ferri- magnet (fM). If this system does order, its transition temperature is at least an order of magnitude less than the Weiss temperature, implying that a significant amount of magnetic frustration may be present. Whether the cause for the frustration comes from competing interactions or geometry (or both) requires further investigation.

In conclusion, this work shows that by utilizing supertetrahedral clusters as a sub-building unit, one could push up the architectural scale from molecular to meso-scale with much larger void space. Moreover, once the magnetically active atoms are introduced into the framework, a more densely aggregated structural building block would result in interesting magnetic exchange such as magnetic frustration observed in this case. This work further demonstrates the feasibility of constructing porous frameworks or discrete supramolecular aggregates based on higher-order supertetrahedral metal–organic clusters. Considering there are many orders of supertetrahedral clusters, it is intriguing to speculate that other porous MOFs with multi-level hierarchical ordering may be produced.

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Notes and references

§ Crystallographic data for CPF-5 (CCDC 869709), [Mn₅(C₈H₄N₄O₂)₃-(HCO₂)₃(OH)(H₂O)₂]₄(DMF)₆, cubic *F*43*c*, *a* = 39.6914(12) Å, *V* = 62 530(3) Å³, *Z* = 8, Mo Kα, *T* = 296 K, $2\theta_{max}$ = 41.58°, *R*(*F*) = 4.99% for 183 parameters and 2287 reflections with *I* > 2*σ*(*I*).

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