This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A highly stable face-extended diamondoid cluster-organic framework incorporating infinite inorganic guests

Wei-Hui Fang,"a" Lei Zhang,"a" Jian Zhang,"a" and Guo-Yu Yang*"a,b

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A highly stable face-extended cluster-organic framework incorporating infinite inorganic guests is hydrothermally made, in which the tetrahedral O-centred Cu$_4$O cluster is firstly found as the face-extended structure building unit to further make diamondoid cluster-organic framework with high thermal and structural stability.

The metal-organic frameworks (MOFs) have a history of nearly two decades from their origins to the present day.1 As the term suggests, MOFs are porous crystalline solids assembled by inorganic structural building units (nodes) with organic ligands (linkers). Their architectures can be tailored with rational design methodology, not only allowing the customization of materials to yield desired physical and chemical properties,2,3 but also forming cationic, neutral and anionic MOFs. Generally, the guests are isolated inorganic anions in cationic MOFs,5,6 while the infinite anionic chain guests in cationic MOFs is rare and unprecedented. Despite the organic linkers can be amenably controlled in the synthesis of new MOFs, the formation of the inorganic nodes still seems "wild" to us. Till now, the most frequently used highly symmetrical inorganic nodes include the paddle-wheel,7 the triangle cornerstone shape cluster,8 the tetrahedron,9 and the octahedron,10 etc.

To a tetrahedron, there are four vertices, six edges and four faces. Theoretically, the tetrahedron can be extended via three ways: vertices, edges and faces. Of which the edge-extended linkage has firstly been observed in MOF-5 in 19997 and well demonstrated in IMOF-1-16.5 Six carboxylates ride on six edges of tetrahedral Zn$_4$O cluster to form an octahedral six-connected Zn$_4$O(CO)$_3$$_2$ node (Scheme 1) in MOF-5. Apart from six edges, if tetrahedral cluster units are extended by vertices and faces, 4-connected zeolite-like frameworks will be constructed. Recently, a vertex-extended linkage of Cu$_4$I$_4$ cluster leads to the formation of a MTN-type zeolitic cluster-organic framework (COZ-1).11 However, it still remains a great challenge to make cluster-organic frameworks via the face-extended linkages.

Our efforts focus on the design and synthesis of cluster-organic frameworks.2-4,12-14 Here, we report a highly stable cluster-organic framework based on tetrahedral O-centred Cu$_4$O clusters, [Cu$_4$O$_3$(µ$_3$-O)I$_4$][Cu$_3$Br$_6$] (1, HL = 4-pyridin-4-yl-benzoic acid), in which the face-extended tetrahedral Cu$_4$O cluster is successfully realized and further connects each other to form a 4-connected diamondoid 3-D cluster-organic framework. In the tetrahedral Cu$_4$O cluster, three Cu atoms located on each triangle face are fixed by one pyridyl nitrogen (N$_{Py}$) and two carboxylate oxygen (O$_{CO}$) atoms from two L ligands with reverse orientations (Scheme 1, right). Interestingly, the 1-D rhombic channels of the host framework are filled by the shape-matching inorganic chain guests.
runs along the $a$-axis with a separated distance from one net to another of 8.0 Å (Fig. S4). Despite the existence of interpenetration, the framework is still open (porosity 31.0%) and exists rhombic channels (cross-section $14.3 \times 14.3$ Å$^2$) along the $a$-axis. Also it represents the minimum number of interpenetrating dia net linked by L ligands till now (Table S1). The decrease of interpenetration degree may be attributed to the size increase of the inorganic nodes.

In guest motif, four Cu$\{2\text{–}5\}$ atoms are all on crystallographic C2 sites with half-occupied and bridged by Br atoms to form a chain: of which Cu(2) and Cu(3) centers are bridged by µ6-Br to further link each other to form 16D Cu6Br chain based motif are $0.95$, $0.96$, $0.94$ and $0.97$, indicating that the valences for Cu(1–5) atoms are $2$, $1$, $1$, $1$, $1$, respectively (Table S2).

The most striking structural feature of I is the shape-matching combination of hybrid host framework and inorganic chain-like guests (Fig. 1c, S5). The rhombic channel around the guests matches the shape of the chain-like guest, which is unique and different from that of known porous MOFs templated by amines. In the structure, the infinite inorganic guests interact with the hybrid host framework via C–H...Br hydrogen bonding interactions (Fig. S6, Table S3).

In addition to the structural novelty, I also shows high thermal and water stability. The thermogravimetric analysis carried out in air atmosphere from 30 to 1000 °C showed one onset weight loss. I does not decompose until 400°C, which indicates the high thermal stability of its 3D cluster-organic framework (Fig. S7). In comparison with MOF-5 that is sensitive to moisture and water, the semiconductive (band gap = 2.32 eV, Fig. S8) crystalline samples of I exhibit highly stability. Its structure can be retained even after being exposed in air or soaked in water for months (Fig. S9).

To reveal the flexibility between the host and guest motifs, the thermal expansion properties of I were studied. From 100 to 500 K, the unit-cell parameters show approximately linear changes and the unit-cell volume expand about 2.6% (Fig. 2, Table S4). The thermal expansion coefficients of $a$ and $b$-axis are $49\times10^{-6}$ K$^{-1}$ and $65\times10^{-6}$ K$^{-1}$, respectively, which are in agreement with the thermal expansion law. However, the length of $c$-axis ($-49\times10^{-6}$ K$^{-1}$) reduces when increasing temperatures, resulting in a negative thermal expansion coefficient of $-49\times10^{-6}$ K$^{-1}$. In order to analyze the structural origin of the thermal expansion of I, its single-crystal structures measured at 100 K and 298 K were compared (Table S5) and found that the changes were small in coordination bond lengths ($<0.026$ Å) but large in the angles (max = $1.3^\circ$) (Table S6). Consequently, the 4-connected Cu$_8$O$_2$Br$_4$ “rhombus grid” was distorted (Fig. S10), with two interior angles change approximately $1.1^\circ$ and $0.5^\circ$. The positive/negative thermal expansion coefficients of I are not significant compared with typical thermal expansion materials, indicating that the expansion of the host framework is restricted by the inorganic guests.

In view of the robust architecture of I, TEM images were studied to visualize its pores as those reported for IRMOF-74-VII and IRMOF-74-IX. However, the attempts to observe the arrangement of the channels of I were unsuccessful due to its sensitivity to the electron beam. Instead, spherical and uniform nanoparticles (NPs, $<5$ nm) are found (Fig. 3a). Fast Fourier transform (FFT) analysis was performed on the centered square areas in the HRTEM images (Fig. 3b). Six reflection spots...
corresponding to the 110 reflections were resolved from the FFT patterns. The interlayer distance of the selected area is calculated to be 0.201 nm, which agrees well with the (110) lattice planes of hexagonal phase CuBr (PDF#06-0700). Considering the compositions of the Cu$_2$Br$_2$-based chains in 1, it is reasonable to conclude that the formation of these CuBr NPs should be attributed to the decomposition and rearrangement of these Cu$_2$Br$_2$-based chains.

In summary, a highly stable face-extended cluster organic framework incorporating infinite inorganic chains has been successfully made under hydrothermal conditions. The key points of the synthetic procedures have been well established. It represents a rare example in the face-extended linkages, which makes it different from other cluster organic frameworks with vertex/edge-extended linkages. This study may open up possibilities for making novel frameworks constructed from the face-extended cluster building units. Further work is in progress.

This work was supported by the NSFC (nos. 21401191, 973 Program (nos. 2014CB932501), and the NSFC for Distinguished Young Scholars (no. 20725101).

Notes and references