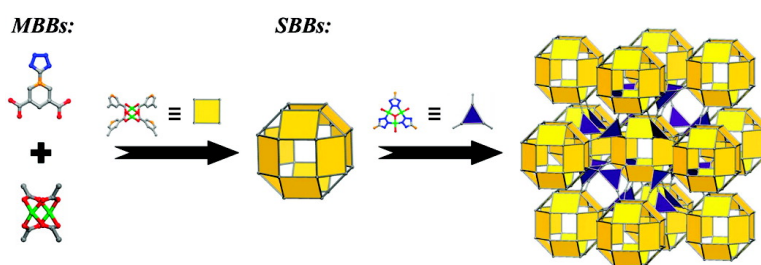Communication

Supermolecular Building Blocks (SBBs) for the Design and Synthesis of Highly Porous Metal-Organic Frameworks

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Supermolecular Building Blocks (SBBs) for the Design and Synthesis of Highly Porous Metal-Organic Frameworks

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The molecular building block (MBB) approach has recently emerged as a powerful strategy for the design and construction of solid-state materials.[1] This is evidenced by the burgeoning academic and industrial[2] interest in the class of materials known as metal-organic frameworks (MOFs), for which desired functionality can be introduced at the molecular level prior to the assembly process.[3] Conventional MBBs (coordination clusters or organic ligands) with varied connectivity and specific geometry and directionality are readily accessible and can be employed to access structures where the points of extension of MBBs define the secondary building units (SBUs) that serve to augment the vertices of a given net;[4] that is, the SBU is the vertex figure of the original vertex. Nevertheless, it is an ongoing challenge to absolutely predict the network topology of the constructed MOF. Accordingly, the ability to target nets that are exclusive for a combination of building blocks[5] presents greater potential toward prediction, design, and synthesis of the resultant framework in crystal chemistry. Here, we demonstrate this strategy by utilizing metal-organic polyhedra (MOP), which can be externally functionalized, as supermolecular building blocks (SBBs) for edge transitive nets that are unique, specifically nets where the vertex figures indicate the need for high connectivity.[6] Indeed, since simple MBBs with connectivity ≥8 are often too intricate to systematically obtain by means of organic ligands or multinuclear clusters, such structures can only be designed by utilizing SBBs with a high degree of symmetry and connectivity; that is, enhanced directional and structural information is already built in. In principle, there is a degree of predictability in such a strategy that is not present with basic MBBs.

Polyhedral SBBs have already been utilized to assemble MOFs,[7] one where the inorganic MBB (metal cluster) serves as a square SBU in the formation of 12-connected cubohemioctahedral SBBs,[7b] which essentially serve as cuboctahedral tertiary building units (TBUs).[8] Square SBUs can generate only two other types of MOPs (owing to the fact that there are only three ways to link squares with one kind of edge into a polyhedron),[9] which could be used as SBBs. Herein we report the use of metal-organic truncated cuboctahedral SBBs (Figure S1),[10] generated in situ, as rhombicuboctahedral TBUs to construct a (24-connected)-based MOF (Figure 1).[11] The SBB consists of 12 copper paddlewheels joined by 24 1,3-BDC linkers so that the 5-position of the bent bridging ligand (120° angle) lies exactly on the vertices of the rhombicuboctahedron, the 24-connected vertex figure for the (3,24)-connected *rht* net.[6b] Thus, functionalization at this 5-position with an organic moiety that permits the formation of a rigid triangular MBB, that is, the SBU is the 3-connected vertex figure, will definitely lead to the assembly of a MOF having the *rht*-like network topology since this (3,24)-connected net is, to the best of our knowledge, the only edge transitive net known for the assembly of 24- and 3-connected vertices.[5]
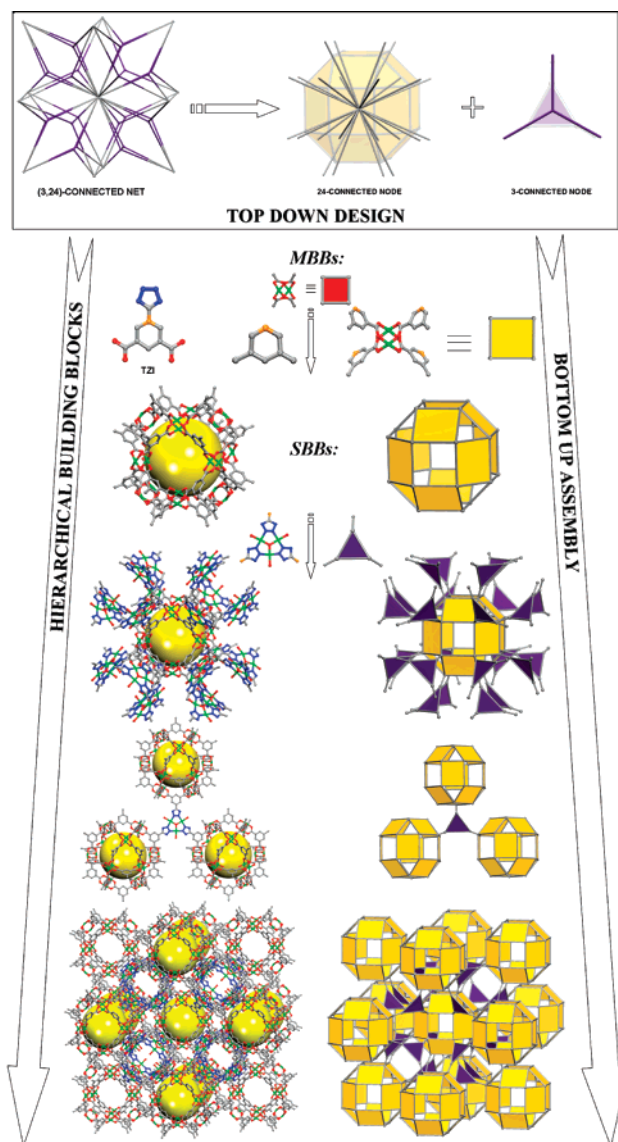

Figure 1. (Top) The (3,24)-connected *rht* net and the two vertices and corresponding vertex figures when augmented. (Left) Select fragments from the crystal structure of **1**. C = gray, N = blue, O = red, Cu = green; the 5-position of the 1,3-BDC ligand is highlighted in orange; the yellow spheres indicate the cavity of truncated cuboctahedra; some spheres, all solvent molecules, and all hydrogen atoms have been omitted for clarity. (Right) Schematic showing the corresponding strategy from MBBs to SBBs (generated all together in situ) to MOF.

Indeed, solvothermal reaction between 5-tetrazolylisophthalic acid (H_3TZI)[12] and $Cu(NO_3)_2 \cdot 2.5H_2O$ in an *N,N*-dimethylformamide/ethanol solution yields a homogeneous crystalline material,
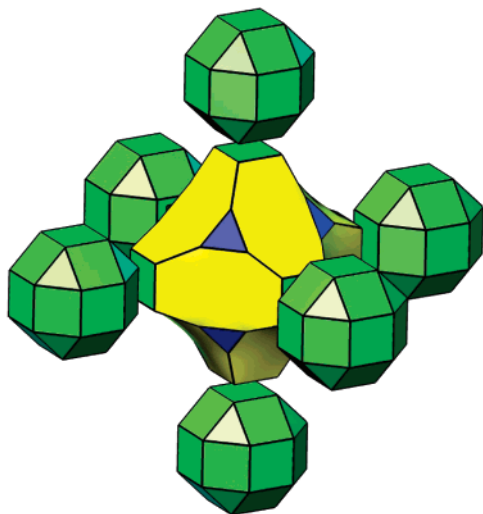
Figure 2. Illustration of the *rht* framework using tile presentation. The largest cage (yellow) is surrounded by six rhombicuboctahedral TBUs (green). The blue triangles delimiting the yellow cage represent the trigonal $Cu_3O(N_4CR)_3$ trimers, and the green squares represent the quadrangular $Cu_2(O_2CR)_4$ paddlewheel MBBs.

purity confirmed by similarities between simulated and experimental X-ray powder diffraction (XRPD) patterns (Figure S3). The as-synthesized compound, characterized by single-crystal X-ray diffraction as $[Cu_6O(TZI)_3(H_2O)_9(NO_3)]_n \cdot (H_2O)_{15}$ (**1**),[13] reveals a crystal structure consisting of truncated cuboctahedra (24 functionalized isophthalate ligands connected by 12 copper dimer centers, $Cu_2(O_2CR)_4$ paddlewheels) connected to trigonal $Cu_3O(N_4CR)_3$ trimers through each tetrazolate (N_4CR) moiety, which is unprecedented for tetrazolate ligands.[14] Each inorganic paddlewheel MBB is dinuclear and consists of two copper ions with the expected square pyramidal geometry, each coordinated to four oxygen atoms of four carboxylates and one axial water molecule, CuO_5. Both carboxylate moieties of the triply deprotonated TZI ligand coordinate in a bis-monodentate fashion to two copper atoms to form the $Cu_2(O_2CR)_4$ MBBs, which combine in a *cis* fashion to form the finite truncated cuboctahedron. Each tetrazolate moiety also coordinates in a bis-monodentate fashion to two copper atoms of the $Cu_3O(N_4CR)_3$ trimer. Each copper atom of the trimer is coordinated to two nitrogen atoms (one from each of two tetrazolates), an oxygen (oxo) core, one oxygen atom of an equatorial water molecule, and one oxygen atom of an axial disordered water molecule to give square pyramidal geometry, CuN_2O_3. The formation of the oxo trimer with the tetrazolate portion of the TZI ligands results in a 24-connected rhombicuboctahedral TBU, formed via the isophthalate portion, linked to 12 neighboring TBUs through 24 3-connected trigonal SBUs (metal-tetrazolate trimers). This results in a (3,24)-connected MOF having *rht*-like topology (Figure 2) that has only recently been depicted by Delgado-Friedrichs and O'Keeffe as the sole edge transitive net for the assembly of rhombicuboctahedral and trigonal building units.[6b]

It should be noted that the present framework can also be interpreted topologically as a novel three-dimensional (3,3,4)-connected ternary net (i.e., trinodal), based on the assembly of three different basic SBUs (Figure S4).[5] The first MBB, copper paddlewheel $Cu_2(CO_2)_4$, decorates the 4-connected vertex; the second is the trigonal $Cu_3O(N_4CR)_3$ trimer that decorates the first 3-connected vertex; and the third, the tritopic ligand that was designed to be bifunctional to accommodate two types of metal clusters at each of the two types of coordination functionalities (tetrazolate and carboxylate) decorates the second 3-connected vertex. The SBB
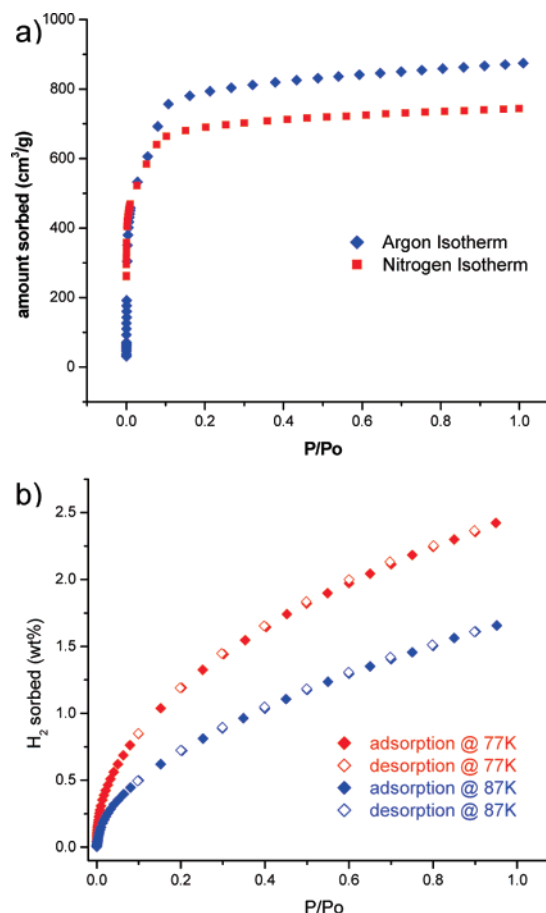
Figure 3. (a) Nitrogen and argon sorption isotherms at 78 and 87 K, respectively. (b) Hydrogen sorption isotherms at 77 and 87 K.

approach involving multifunctional ligands is a suitable pathway to design and construct ternary nets in MOFs.[15] In fact, the trinodal topology of **1** has not been encountered in MOF chemistry nor experimentally/theoretically predicted. It is also important to mention that the connectivity in **1** can be alternatively interpreted to be related to inorganic zeolite A with *lta* topology (Figure S5).[5,16]

The overall cationic framework, where one NO_3^- per three Cu cations balances the charge, consists of three different types of open cages (Figure S6) with the largest, having a 23.287 Å diameter (20.247 Å including van der Waals (vdw) radii), delimited by 8 $Cu_3O(N_4CR)_3$ trimers and 24 $Cu_2(O_2CR)_4$ paddlewheel MBBs, and therefore surrounded by 6 truncated cuboctahedra (Figure 2) and 8 tetrahedral-like cages. The tetrahedral-like cage, with a diameter of 22.013 Å (height) × 22.624 Å (edge) (12.088 Å vdw sphere), is delimited by 4 $Cu_3O(N_4CR)_3$ trimers and 12 $Cu_2(O_2CR)_4$ paddlewheel MBBs, each is, as a result, surrounded by four truncated cuboctahedra and four of the largest cages; the truncated cuboctahedra with a diameter of 15.877 Å (13.077 Å vdw sphere) are delimited by 12 $Cu_2(O_2CR)_4$ paddlewheel MBBs, surrounded by 6 of the largest cages and 8 of the tetrahedral-like cages. The total solvent-accessible volume for **1** was estimated to be ∼75% by summing voxels more than 1.2 Å away from the framework using PLATON software.[17] Combined with a low calculated density for the fully evacuated framework (0.702 g/cm³), the large accessible windows, open cavities, and charged nature make this framework seemingly prospective for gas storage, specifically H_2.

In order to assess the sorption properties of **1**, the guests were exchanged with ethanol. The crystalline material was allowed to air dry before being loaded into the sample cell, where it was

outgassed first at room temperature and then 85 °C for 6 h. Argon and nitrogen isotherms can be regarded as pseudo-type I isotherms (Figure 3a), and the apparent surface area was estimated using Langmuir and BET methods (N_2: 3223 and 2847 m^2/g, respectively); the total pore volume was found to be 1.01 cm^3/g (N_2). An interesting feature of the isotherms can be observed for pressures between 0.01 to 0.1 atm, where a second slope appears. This phenomenon is attributed to the three different cage diameters, where the largest cages approach mesoporous range; the smallest cages are first to be covered, the largest are subsequently covered at higher pressure (Figure S7).

Hydrogen capacity was assessed for **1**, measured at 77 and 87 K at atmospheric pressures (Figure 3b), with up to 2.4 wt % at 77 K. The isosteric heat of sorption has an estimated value of 9.5 kJ/mol at the lowest coverage. This indicates the higher strength of H_2 interactions compared to that of previous MOFs.[18] Nevertheless, the isosteric heat falls to 4.7 kJ/mol at higher loadings, which is in accordance with the large size of the cavities filled at higher loading (Figure S7). With a combined large surface area and accessible free volume, **1** offers great potential for higher H_2 uptake at 77 K and higher pressures (estimated up to 6%).

The uniqueness of the *rht* network is beneficial to the practice of isoreticular chemistry, where higher surface areas and larger free pore volumes can be easily achieved through expansion of the bifunctional organic linker. Here, we present a novel approach to construct highly porous MOFs based on the hierarchical bottom-up assembly of SBBs. This represents a new pathway for the assembly of predetermined highly coordinated building blocks based on supermolecules, as well as an alternate route to construct multinodal nets based on predesigned heterofunctional ligands and metal clusters. Work is in progress to construct isoreticular MOFs based on *rht* topology from various bifunctional ligands, as well as tritopic hexacarboxylate ligands, containing three 1,3-BDC moieties analogous to the trigonal 1,3-BDC units generated from the Cu-oxo trimer. Studies are underway to analyze and correlate the framework dihydrogen interactions among the isoreticular MOFs. In addition, we are attempting to utilize other SBBs to target new open MOFs, and using similar heterofunctional ligands may lead to the construction of myriad novel MOFs, especially binary and ternary nets. Perhaps, even higher coordination and more complex nets (e.g., quaternary) are capable of being achieved using this SBB approach.

Supporting Information Available: Nitrogen isotherm, heat of sorption for hydrogen, supporting figures, and XRPD, NMR, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) It should be noted that in this manuscript we define an MBB as the chemical unit of construction (i.e., metal(s) and/or metal cluster(s) and ligand(s)), whereas the SBU is the geometric figure generated by linking the points of extension of the MBB. Here, the MBBs collectively generate the SBB, in situ. Since the MBB is portrayed as a secondary building unit, it is only fitting that the building unit derived from the SBB is depicted as a tertiary building unit.

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