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Metal–Organic Frameworks

Multicomponent Self-Assembly of a Nested Co_{24}@Co_{48} Metal–Organic Polyhedral Framework**

Shou-Tian Zheng, Tao Wu, Burcin Irfanoglu, Fan Zuo, Pingyun Feng, and Xianhui Bu**

Discrete high-symmetry coordination cages, some of which have recently been called metal–organic polyhedra (MOPs), represent one of the most fascinating classes of coordination compounds because of their intriguing host–guest chemistry associated with high and tunable porosity, as well as their aesthetic appeal.[1–6] Furthermore, their formation can be regarded as a somewhat simplified version of the complex biological self-assembly process and as such they can serve as models for biosystems. More recent advances in the development of 3D metal–organic polyhedral frameworks (MOPFs), loosely defined here as a subset of MOFs constructed with MOPs as building blocks, have revealed an even greater level of complexity in the self-assembly of coordination polymers. These MOPFs have emerged as a growing new class of materials because of their remarkable structural characteristics (e.g., well-defined cavities) and potential applications in areas such as gas storage and separation, drug delivery, and catalysis.[7–12]

Clearly, the evolution from the simple MOPs (e.g., a small Platonic cage with just one type of metal ion and one type of ligand) to MOPs and MOPFs with complexity approaching that of biological systems would encompass different types of assemblies with various degrees of hierarchy and sophistication. The complexity in such self-assembly can come from the nature of building blocks (e.g., more than one type of metal ion/cluster and/or ligand) or geometrical features (e.g., larger cages or nested cages). In this context, we have been interested in a type of 3D porous framework in which two (and perhaps more) polyhedral cages of different types form nested configurations with multiple covalent bonds interconnecting the outer and inner cages.[13] In such nested structures, either the outer cage or the inner cage can theoretically be a discrete MOP or form a 3D MOPF, leading to four general architectural styles, including 0D–0D MOP@MOP, 3D–0D MOPF@MOP, 0D–3D MOP@MOPF,[13] or 3D–3D MOPF@MOPF, the last one being the topic of this work. Such nested cage-based structures are very rare and should be distinguished from structures containing different side-by-side polyhedral cages, the latter being more common, because with a very limited number of exceptions such as cube and truncated octahedron (also called sodalite or β-cage), most polyhedral cages (e.g., 16 out of 18 Platonic and Archimedean cages) are non-space-filling, and their 3D packing would naturally leave polyhedral gaps of different types (e.g., tetrahedral gaps as a result of 3D packing of octahedra, and vice versa). Such side-by-side arrangement of heterogeneous polyhedral cages is in fact also present in the structure reported herein, but only as a side feature.

Being among the fundamental building blocks of 3D space and highly symmetrical, 13 Archimedean solids are of extraordinary interest for constructing 3D porous frameworks. While the coordination chemistry involved in the formation of such cages has been extensively studied with many examples known,[1–6] few nested cage-based assemblies (either 0D or 3D such as MOP@MOPF or MOPF@MOPF) are known, and the successful development of this family of nested materials would require the conceptual development of a generalized mechanism for establishing the radial intercage connectivity and for establishing the intercage communication so that the initial formation of a cage can dictate the growth of either the inner or outer cage based on the structural features of the initially formed cage.

We present herein an elegant material that reveals the feasibility of just such a general mechanism. In this material, the carboxy functional group emanating from each edge center of the inner Archimedean cage defines a complete set of vertex positions that form the basis for the growth of the outer Archimedean cage. Thus, at least a subfamily of nested cages in which the number of edges of one cage equals the number of vertices of another cage (e.g., cuboctahedron with 24 edges and rhombicuboctahedron with 24 vertices, or rhombicuboctahedron with 48 edges and great rhombicuboctahedron with 48 vertices) can be conceivably developed. In addition to providing insights into the mechanistic aspects of complex self-assembly processes, one practical consideration in pursuing such nested assemblies is the exquisite control that such architectures might offer in terms of partitioning of the pore space and pore size for optimum fit with adsorbate molecules.

Herein, we report a nested 3D–3D MOPF@MOPF cobalt–organic framework $[(CH_3)_2NH_2]_{10}[Co_2(IN)_4(Ac)_2]$-$[Co_2(BTC)_2(H_2O)]_4[Co_2(OH)(IN)_3]_4 \cdot 4H_2O$ (CPM-24, CPM = crystalline porous materials, H_3BTC = 1,3,5-benzenetricarboxylic acid, HIN = isonicotinic acid). The four components enclosed in square brackets above represent extraframework charge-balancing cations, the dimeric Co–Co paddlewheel connector between inner cages, the inner cage itself

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[*] Dr. S.-T. Zheng, B. Irfanoglu, Prof. Dr. X. Bu
Department of Chemistry and Biochemistry
California State University, Long Beach, CA 90840 (USA)
E-mail: xbu@csulb.edu
T. Wu, F. Zuo, Prof. Dr. P. Feng
Department of Chemistry
University of California, Riverside, CA 92521 (USA)
E-mail: pingyun.feng@ucr.edu

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(cuboctahedron with each vertex occupied by a Co–Co paddlewheel), and the outer cage (rhombicuboctahedron with each vertex occupied by a V-shaped Co-OH-Co dimer), respectively.

As expected from the high symmetry of Archimedean cages, CPM-24 crystallizes in a highly symmetric cubic space group $F\bar{4}3c$ with a large unit cell (ca. 165 000 Å^3). As shown in Figure 1, it is constructed from two kinds of cobalt dimeric secondary building units (SBUs; paddlewheel $[Co_2(O_2C)_4]$ and hydroxy-bridged $[Co_2(OH)]^{3+}$) and two kinds of organic linkers (BTC^{3-} and IN^-), thus creating a fascinating MOPF@MOPF in which a large Archimedean cage $\{Co_{48}(IN)_{48}\}$ (rhombicuboctahedral cage, denoted as Co_{48}) encapsulates a small Archimedean-type cage $\{Co_{24}(BTC)_{24}\}$ (cuboctahedral cage, Co_{24}-A). The presence of two different Co dimers is in distinct contrast with the mixed indium monomeric $[In(O_2CR)_4]^-$ and trimeric $[In_3(O)(O_2CR)_6]^+$ units found in In_{12}@In_{24} MOP@MOPF in CPM-5 and CPM-6.[13] CPM-24 is also different and more sophisticated because it is based on two types of linkers (BTC^{3-} and IN^-), whereas CPM-5 and CPM-6 are based on only one type of linker (BTC^{3-}).

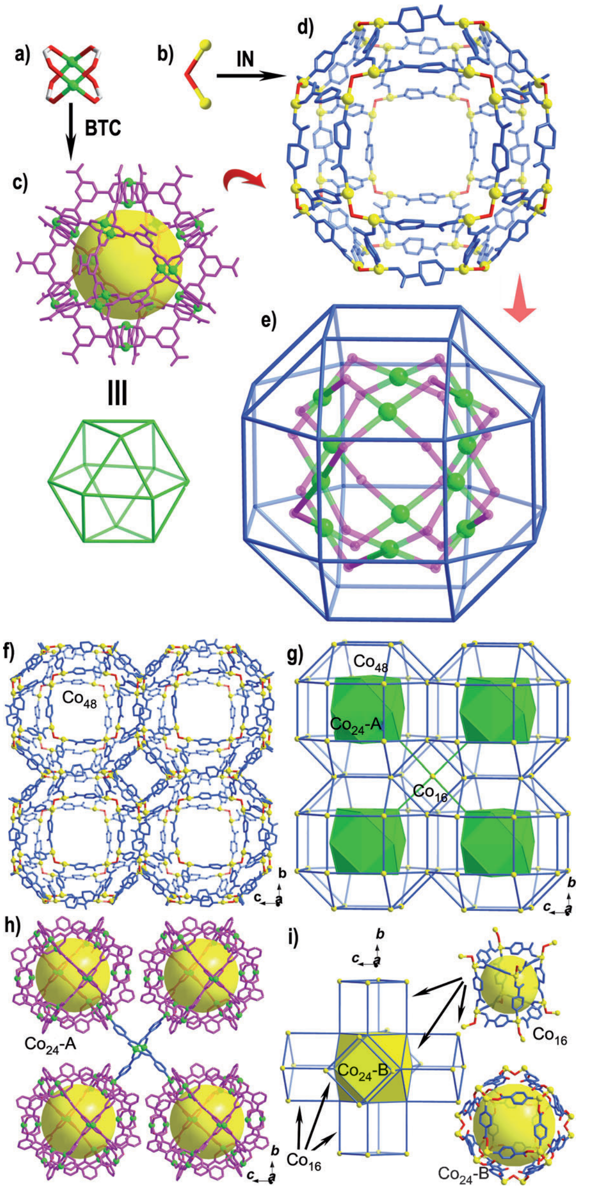

Figure 1. a) $\{Co_2(O_2C)_4\}$ dimer (Co green, O red, C gray), b) $\{Co_2(OH)\}$ dimer (Co yellow, O red), c) Co_{24}-A cage (BTC^{3-} pink, Co green), d) Co_{48} cage (IN^- blue, OH^- red, Co yellow), e) nested Co_{24}@Co_{48}, f) outer 3D MOP-based framework, g) nested MOP-based framework, h) inner 3D MOP-based framework. The CO_2^- groups serving as bridges between the inner and outer cages are omitted for clarity. i) View of Co_{16} and Co_{24}-B and their relative positions.

The formation of the nested cages and frameworks is first and foremost attributed to the dual roles (cage forming and intercage cross-linking) of the tritopic BTC^{3-} ligand. Furthermore, the charge and shape complementarity between two different dimeric Co clusters and two ligands (BTC^{3-} vs. IN^-) also contributes to the highly cooperative co-assembly of nested Archimedean cages and the 3D–3D MOPF@MOPF structure. In CPM-24, the inner cage framework has an overall neutral charge, whereas the outer cage framework exhibits an overall negative charge, in contrast with CPM-5, which has a positive@negative In_{12}@In_{24} inner–outer charge distribution (Figure S1 in the Supporting Information).

The outer Co_{48} cage (ca. 3.3 nm in diameter) is built from 24 hydroxy-bridged $\{Co_2(OH)\}$ dimers linked together by 48 linear ligands IN^-, while the inner Co_{24}-A cage (ca. 2.1 nm in diameter) is formed by 12 paddlewheel $\{Co_2(O_2C)_4\}$ dimers bridged by 24 tritopic BTC^{3-} ligands. In forming the inner Co_{24}-A cage, each BTC^{3-} ligand just uses two of its three carboxylic groups. The third carboxylic group of each BTC^{3-} ligand emanates from the edge center of the Co_{24}-A cage and serves to connect the inner Co_{24}-A cage with the outer Co_{48} cage.

Unlike CPM-5 and CPM-6, in which the outer truncated octahedron is a space-filling polyhedron, CPM-24 is more complex, because the 3D packing of non-space-filling rhombicuboctahedral Co_{48} cages generates two additional types of polyhedral cages in gaps of Co_{48} cages. Quite interestingly and perhaps not coincidentally, one such side cage (denoted Co_{24}-B) belongs to the same type of Archimedean solid as the Co_{24}-A inner cage. This finding is somewhat surprising, considering that Co_{24}-A is different from Co_{24}-B in both metal clusters and cross-linking ligands. The Co_{24}-B cage is made up of 12 $\{Co_2(OH)\}$ dimers and 24 IN^- ligands, whereas Co_{24}-A consists of Co_2 paddlewheels and BTC^{3-} ligands.

In CPM-24, the outer 3D MOPF can be viewed as a simple cubic packing of rhombicuboctahedral Co_{48} cages sharing square windows (*reo-e* net, Figure 1 f and Figure S2 in the Supporting Information). The non-space-filling character of the Co_{48} cage leaves large gaps that form the basis of one Platonic cage and one Archimedean cage: a small cubic $\{Co_{16}(IN)_8\}$ cage (Co_{16}, Figure 1 i) and a large cuboctahedral $\{Co_{24}(IN)_{24}\}$ cage (Co_{24}-B). Each cubic Co_{16} cage (ca. 1.6 nm in diameter; defined by eight $\{Co_2(OH)\}$ dimers and eight IN^- ligands) is located at the face-center position of cubic arrays of Co_{48} cages (Figure 1 g), while each Co_{24}-B cage (ca. 2.2 nm in diameter) is at the body-center position and therefore is surrounded by six cubic Co_{16} cages (Figure 1 i, S2). Interestingly, one additional paddlewheel $[Co_2(IN)_4]$ dimer resides inside every cubic Co_{16} cage and serves to bridge four adjacent Co_{24}-A cages though four IN^- ligands (Figure 1 g,h). In turn, every Co_{24}-A cage is connected to twelve $[Co_2(IN)_4]$ paddlewheel dimers, leading to the formation of a "hidden" inner MOPF.

Compared to CPM-5 and CPM-6 (0D–3D MOP@MOPF nesting), in which two nested Archimedean cages are based on 8-faced (truncated tetrahedron) and 14-faced (truncated octahedron) polyhedra, this work, in which two nested Archimedean cages are based on 14-faced (cuboctahedron) and 26-faced (rhombicuboctahedron) polyhedra, demonstrates a new level of polyhedral hierarchy in the self-assembly process. Also in distinct contrast with CPM-5 and CPM-6, in which the interconnecting third carboxy group of each BTC^{3-} ligand (the "hook" that joins together the inner and outer cages) converges from the outer cage towards the inner cage (Figure S3 in the Supporting Information), in CPM-24, 24 hooks radiate from the inner cage towards the 24 vertices of the outer cage. It is clear that mechanistically these 24 hooks serve to define the positions of $Co_2(OH)$ dimers that form the vertices of the outer cage.

Thermal gravimetric analysis of CPM-24 shows that the removal of solvents occurs in the temperature range of 40–300 °C (Figure S4 in the Supporting Information). Powder X-ray diffraction further confirms that the desolvated sample retains its crystallinity up to about 300 °C (Figure S5 in the Supporting Information). CPM-24 was activated by heating the crystals at reflux in a saturated methanol solution of NH_4Cl for 72 h to exchange solvents and cations and then degassed at 100 °C for 12 h under vacuum prior to gas adsorption measurements. As shown in Figure 2, the N_2 sorption of CPM-24 at 77 K exhibits a type I isotherm typical of materials with permanent microporosity. The Langmuir and BET surface areas are 296 and 186 $m^2 g^{-1}$, respectively. A micropore volume of 0.100 $cm^3 g^{-1}$ (using the Horvath–Kawazoe method) and a median pore size of 12.68 Å were calculated. CPM-24 exhibits a high uptake of CO_2 at 273 K and 1 atm (68.4 $cm^3 g^{-1}$, 89.3 $L L^{-1}$), which is comparable to the behavior of the highly porous framework ZIF-69 (70 $cm^3 g^{-1}$, 83 $L L^{-1}$) under the same conditions.[9b] Further N_2 sorption measurement of CPM-24 at 273 K indicates little uptake over the entire pressure range (1.08 $cm^3 g^{-1}$ at 1 atm).

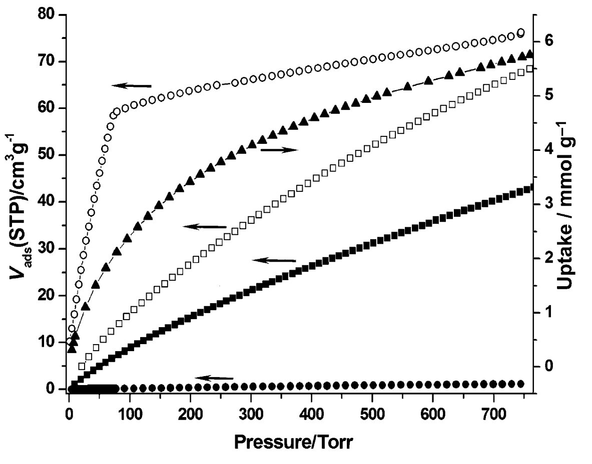

Figure 2. N_2 (77 K, ○), N_2 (273 K, ●), CO_2 (273 K, □), CO_2 (298 K, ■), and H_2 (77 K, ▲) adsorption isotherms of CPM-24.

The selectivity of CO_2/N_2 at 273 K is calculated to be 106:1 at 0.16 atm and 63:1 at 1 atm by volume (or 166:1 at 0.16 atm and 99:1 at 1 atm based on weight). These values, lying in the upper range of reported MOFs,[14] show that CPM-24 has a high CO_2/N_2 selective adsorption. Additionally, CPM-24 can also adsorb a considerable amount of H_2 at 77 K and 1 atm (5.76 mmol g^{-1}, 1.15 wt %).

In summary, the multicomponent co-assembly of two types of cobalt dimers (Co_2 paddlewheel and V-shaped $Co_2(OH)$) and two types of crosslinking ligands (BTC^{3-} and IN^{-}) leads to an extraordinary nested cage-in-cage and framework-in-framework porous material in which a large Archimedean polyhedron (rhombicuboctahedron, Co_{48} cage) encapsulates a small Archimedean polyhedron (cuboctahedron, Co_{24}-A cage). The success of this work offers a tantalizing hope that it might be possible to use even larger Archimedean cages for the construction of nested porous materials. The self-assembly mechanism revealed herein, which is centered on the dual roles (i.e., cage forming and intercage cross-linking) of multitopic ligands may be generally applicable to other ligands and metal clusters and could lead to an exciting family of nested metal–organic polyhedral frameworks.

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