Synthesis of Polycarboxylate Rh(II)-Metal-Organic Polyhedra and their use as Building Blocks for Highly-Connected Metal-Organic Frameworks

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Abstract: Use of preformed metal-organic polyhedra (MOPs) as supermolecular building blocks (SBBs) for the synthesis of metal-organic frameworks (MOFs) remains underexplored due to lack of robust functionalized MOPs. Herein we report the use of polycarboxylate cuboctahedral Rh(II)-MOPs for constructing highly-connected MOFs. Cuboctahedral MOPs were functionalized with carboxylic acid groups on their 12 vertices or 24 edges through coordinative or covalent post-synthetic routes, respectively. We then used each isolated polycarboxylate Rh(II)-MOP as 12-c cuboctahedral or 24-c rhombicuboctahedral SBBs that, upon linkage with metallic secondary building units (SBUs), afford bimetallic highly-connected MOFs. The assembly of a pre-synthesized 12-c SBB with a 4-c paddle-wheel SBU, and a 24-c SBB with a 3-c triangular Cu(II) SBU gave rise to bimetallic MOFs having **ftw** (4,12-c) or **rht** (3,24-c) topologies, respectively.

Metal-organic polyhedra (MOPs) have emerged as powerful building blocks for the creation of extended porous solids as they are intrinsically porous and exhibit high symmetry, connectivity and well-defined peripheral points of extension.[1-3] These characteristics have been recently exploited for the synthesis of porous amorphous soft materials, wherein MOPs are connected through flexible N,N'-based linkers using the peripheral axial positions of their constituent paddle-wheel units.[4] Additionally, porous crystalline salts have been assembled from the electrostatic interaction of oppositely charged MOPs.[5] In metal-organic frameworks (MOFs), MOPs are used for the rational construction of highly-connected nets following the well-known supermolecular building block (SBB) approach.[6,7] In this approach, the in-situ assembly of the MOP is traditionally harnessed to guide formation of a targeted MOF with a given topology.[8-13]

An alternative, but far less-explored, route for the formation of MOFs is the use of pre-synthesized, isolated MOPs as SBBs. Zhou and Chun first showed the feasibility of this route. They applied a similar approach to that used for the synthesis of MOP-based soft materials but, instead of flexible N,N'-based

linkers, they used the rigid 4,4'-bipyridine (bipy) and 1,4-diazabicyclo[2.2.2]octane linkers to bridge Cu(II)- and Zn(II)-based octahedral and cuboctahedral MOPs and form 6-connected (6-c) **pcu** and 12-c **fcu** MOFs, respectively.[14,15] Later, two more 12-c **fcu** MOFs made from the assembly of cuboctahedral MOPs with bipy were reported.[16,17] However, no one has yet demonstrated the ability to chemically control the formation and isolation of MOPs with multiple peripheral coordinating sites (e.g. carboxylic acid groups), and then use them as SBBs for the synthesis of MOFs. This is mainly due to the difficulty of controlling the formation of the MOP, rather than extended coordination networks, when the precursor MOP linkers are functionalized with additional coordinating groups; the challenge of preventing any cross-linking reactions between MOPs that are functionalized with available coordinating sites;[18,19] and the lack of stability and solubility of the isolated MOPs under the conditions commonly used for MOF synthesis.[20]

Herein we report the design, synthesis and isolation of two types of polycarboxylate MOPs, and their subsequent use as SBBs to build highly-connected bimetallic MOFs. We chose cuboctahedral Rh(II)-based MOP as our platform for poly-carboxylate MOPs owing to its high stability, symmetry, and multiple sites for functionalization with carboxylic acid groups.[21,22] We began by synthesizing the two polycarboxylate MOPs, each of which by a different route (Figure 1). Firstly, we synthesized a cuboctahedral MOP functionalized with twelve carboxylic acid groups by using a coordinative route, in which the twelve vertices of the cuboctahedron are functionalized by coordination of isonicotinic acid (HINA) in each peripheral axial position of the twelve constituent Rh(II) paddle-wheel units (Figure 1, top). Next, we prepared a cuboctahedral MOP functionalized with 24 carboxylic acid groups, using a covalent route based on selective carboxylic group protection.[23] In it, the 24 edges of the cuboctahedron are functionalized with carboxylic acid groups using a protective synthetic strategy (Figure 1, bottom).[24] We anticipated that the different number and location of carboxylic acid groups on the periphery of both Rh(II)-MOPs, which define a 12-c cuboctahedral SBB and a 24-c rhombicuboctahedral SBB, could be used to anticipate their structural outcome upon assembly with metallic secondary building units (SBUs). To demonstrate the utility of these SBBs for constructing MOFs, we combined both a 12-c SBB with a paddle-wheel 4-c SBU, and a 24-c SBB with a triangular 3-c Cu(II) SBU to construct atomically-precise bimetallic MOFs having (4,12-c) **ftw** and (3,24-c) **rht** topologies, respectively.

-Figure 1-

We began with the coordinative synthesis of the 12-c cub-octahedral SBB. To this end, we first prepared the cuboctahedral Rh(II)-MOP with formula $[Rh_2(OH-bdc)_2(H_2O)(DMA)]_{12}$ (hereafter named OH-RhMOP; where OH-bdc is 5-hydroxy-1,3-benzenedicarboxylate and DMA is N,N-dimethylacetamide) following a previously reported protocol.[21] Then, the twelve DMA linkers coordinating each peripheral axial position of their twelve paddle-wheel units were substituted with HINA linkers, through addition of 12 mol. eq. of HINA to a DMF/methanol solution of OH-RhMOP. This reaction generated $[Rh_2(OH-bdc)_2(H_2O)(HINA)]_{12}$ (here-after named OH-RhMOP(HINA)$_{12}$), as determined by UV–Vis spectroscopy and single-crystal X-ray diffraction (SCXRD) (Figures S1-S2a and Figure 1,top). Note that, to prepare this SBB, instead of using an N,N'-based linker that would connect the MOPs to form an amorphous soft material[4] or a MOF with **fcu** topology,[25] we selected HINA because it bears both pyri-dine and carboxylic acid groups. These coordinating groups enable HINA to coordinate to the peripheral axial positions of each paddle-wheel unit through its pyridine moiety, while leaving the carboxylic acid group free, as it cannot replace either the Rh(II)-pyridine or the Rh(II)-(OH-bdc) coordination bonds. Topologically, OH-RhMOP(HINA)$_{12}$ forms a cuboctahedral SBB with twelve available carboxylic acid groups (Figure 1,top).

Next, we synthesized the 24-c rhombicuboctahedral SBB via the covalent route. We began by preparing the Rh(II)-MOP with formula $[Rh_2(COOH\text{-}bdc)_2(H_2O)(DMF)]_{12}$ (hereafter named COOH-RhMOP), following our own previously reported protocol entailing the use of stoichiometric protecting groups.[24] Crystals of COOH-RhMOP suitable for SCXRD were obtained by slow diffusion of diethyl ether vapors into a DMF solution of this MOP. Formation of the cuboctahedral Rh(II)-MOP functionalized with 24 free carboxylic acid groups on its edges was confirmed by SCXRD. Topologically, COOH-RhMOP can be considered as a rhombicuboctahedral SBB with 24 available carboxylic acid groups (Figure 1,bottom).

Once isolated the 12-c and 24-c polycarboxylate Rh(II)-MOPs, we then evaluated their use as SBBs in the construction of highly-connected bimetallic nets, by reacting them with Cu(II)-based SBUs. We considered that 24-c SBB geometry/connectivity is not compatible with square planar nodes (4-c Cu paddle-wheel clusters) to form a (4,24)-c net, as the only binodal topology comprising 24-c nodes of rhombicuboctahedra directionality is the edge-transitive, (3,24)-c **rht** net. It is known that, in presence of geometry mismatch,[26] certain clusters have tendency to undergo structural changes and form unprecedented clusters, including Cu(II). Therefore, we confidently challenged the classical paddle-wheel formation in the presence of our COOH-MOP, aiming for the discovery of a novel 3-c node comprising 3 carboxylates, distinct from the tetrazolate based trimer commonly used for the formation of rht-MOFs.[11] Thus, following this SBB principle, we first assessed our polycarboxylate 24-c rhombicuboctahedral MOP for the formation of a bimetallic RhCu-**rht**-MOF. Solvothermal reaction of COOH-RhMOP with copper(II) nitrate in DMF/ethanol (3:1) at 85 °C for 24 h afforded RhCu-**rht**-MOF, in which each Rh(II)-MOP is linked through an in-situ-synthesized triangular 3-c Cu(II) SBU (Figure 2). This SBU of formula $Cu_3O(OOC)_3$ comprises three Cu(II) ions that are interconnected through three bridging bidentate carboxylate moieties and one central oxygen atom (Figure 2a and S3).

Ideally, the structure of RhCu-**rht**-MOF is a MOP-based three-dimensional (3D) framework in which each Rh(II)-MOP unit is connected to twelve neighboring polyhedra through the 24 available carboxylate groups (Figures 2 and S4). With this connectivity, we would expect a Rh/Cu ratio of 1:1, meaning that a positively charged (+12) framework should be formed. However, EDX analysis indicated a Rh/Cu molar ratio of 1:0.3. Remarkably, the amount of Cu(II) in these crystals increased after 1 week of incubation in a concentrated solution of copper(II) acetate in DMF/EtOH. Afterwards, both EDX and the copper occupancy factor number (extracted from the SCXRD structure) revealed a Rh/Cu molar ratio of 1:0.75 (Figure S10), which is identical to the molar ratio for the bulk sample that we had synthesized in water (Figures S11-15). Altogether these values suggested that only eighteen carboxylic acid groups from each Rh-MOP SBB were coordinating to Cu(II) ions to afford neutrality to the framework, leading to charge-induced Cu(II) defects in the overall structure and giving a formula for RhCu-**rht**-MOF of $[Rh_{24}(btc)_{24}Cu_{18}O_6]$.

-Figure 2-

The overall framework of RhCu-**rht**-MOF comprises three different types of microporous cages (A-C, Figure S5). Cage A is a cuboctahedron composed of 24 isophthalate units from btc linkers and twelve Rh_2 paddle-wheels, with an inner sphere diameter of ca. 15.0 Å (Figure S6). Each triangular window in cage A is shared with another cage, which can be defined as a truncated tetrahedron (t-Td, Cage B). Cage B is formed by four Cu_3O trimers (one in each face of the t-Td) and twelve Rh_2 paddle-wheels, and has an inner sphere diameter of ca. 12.0 Å (Figure S7). Finally, cage A connects with 6 truncated octahedra (t-Oh, cage C) through its square-shaped windows. Cage C comprises eight Cu_3O trimers (one in each face of the t-

Oh) and 24 Rh$_2$ paddle-wheels and has an inner sphere diameter of ca. 16.8 Å (Figure S8). Thus, the overall network in RhCu-**rht**-MOF is constructed by the packing of cages A, B and C at a ratio of 1:2:1, respectively. This generates an open framework in which the total accessible volume is 71 %.[27]

Once stable polycarboxylate MOPs are isolated, then they can rationally be connected to other well-known metallic SBUs as a strategy to increase the variety of accessible hierarchical highly-connected nets. Accordingly, we sought to connect our 12-c OH-RhMOP(HINA)$_{12}$ with a 4-c paddle-wheel SBU to guide the formation of an edge-transitive net exhibiting an underlying (4,12-c) **ftw** topology (Figure 3). To this end, we slowly diffused DMF/methanol solutions of stoichiometric amounts of HINA-OHRhMOP and Cu(NO$_3$)$_2$ in an H-shaped tube standing at RT for 3 weeks. This yielded a homogenous crystalline sample suitable for SCXRD analysis. In this structure, hereafter called RhCu-**ftw**-MOF-1, each Rh(II)-MOP is linked through 4-c Cu(II) paddle-wheel SBUs to eighteen other neighboring Rh(II)-MOPs, adopting the expected (4,12)-c **ftw** underlying topology (Figures 3 and S16). Note that the topology can be alternately regarded as the (4,5)-c **xae** net, considering the two types of paddle-wheels (Rh, 5-c and Cu, 4-c) SBUs as nodes. RhCu-**ftw**-MOF-1 shows three different types of cages (D-F). Cage D is a cuboctahedron composed of 24 isophthalate units from OH-bdc linkers and twelve Rh$_2$ paddle-wheels, with an inner sphere diameter of ca. 15.0 Å (Figure S18). Each triangular window in cage D is shared with cage E, which can be defined as a rhombicuboctahedron. Cage E is formed by six Cu$_2$(OOC-py)$_4$ and 24 Rh$_2$ paddle-wheel units, and has an inner sphere diameter of ca. 18.4 Å (Figure S19). Each square window in cage D is connected with six prismatic cages (cage F) that fill the gaps between cages D and E. Cage F is formed by eight Rh$_2$ paddle-wheels and has an inner sphere diameter of ca. 11 Å (Figure S20). This structure leads to an open framework in which the total accessible volume is 72 %.[27]

Interestingly, the larger cages E of RhCu-**ftw**-MOF-1 are decorated with the outer OH groups of the initial OH-RhMOP(HINA)$_{12}$ SBB (Figure 3d). This feature paves the way to using the external functionalization of isolated MOP SBBs to modulate the pore functionalization of the resulting MOFs. We proved this concept by synthesizing an identical SBB in which we substituted the outer OH groups of the OH-RhMOP(HINA)$_{12}$ with H atoms. Accordingly, we followed the aforementioned coordinative route except that the Rh(II)-MOP was prepared with bdc instead OH-bdc (see SI). Then, by combining the new SBB with Cu(II) ions, we prepared the isostructural RhCu-**ftw**-MOF-2, in which we decorated the E cages with H atoms instead of OH groups (Figures S22, S27-28, S31-32).

The three MOFs that we have presented here exhibit reversible transformations between crystalline and amorphous states upon solvent guest removal and upon immersion in either water (for RhCu-**rht**-MOF; Figure S15) or methanol (for both RhCu-**ftw**-MOFs; Figures S23-24).[28] However, unlike most flexible MOFs and coordination polymers, which lose their porosity upon activation-triggered amorphization, amorphous RhCu-**rht**-MOF and both RhCu-**ftw**-MOFs exhibit permanent porosity. We attributed this feature to the fact that, similarly to the case of previously reported amorphous soft porous materials,[29] amorphization does not entail collapse of the Rh(II)-MOPs that remain accessible upon activation. Indeed, gas-sorption measurements revealed that all three MOFs are microporous to N$_2$, showing BET areas (A$_{BET}$) of 700 m^2/g (RhCu-**rht**-MOF), 400 m^2/g (RhCu-**ftw**-MOF-1) and 680 m^2/g (RhCu-**ftw**-MOF-2) (Figures S33, S35-36). Moreover, CO$_2$ uptakes at 1 bar and 298 k were 2.5 (RhCu-**rht**-MOF) 1.1 (RhCu-**ftw**-MOF-1) and 1.3 mmol/g (RhCu-**ftw**-MOF-2) (Figures S34, S37).

In summary, we have reported the synthesis and structure of two types of robust polycarboxylate Rh-MOPs, each by a different route. We demonstrated that once isolated, these MOPs can be used as SBBs

to build highly-connected MOFs through coordination of their available peripheral carboxylate groups towards metallic SBUs. The well-located and highly-directional carboxylate groups in Rh-MOPs allow to predict their assembly by means of reticular chemistry. It also allows introducing with atomic precision the elusive Rh(II) paddle-wheel into highly connected MOF structures. We believe that the results here presented will enrich the repertoire of strategies for synthesis of MOFs, including those incorporating inert metal ions.[30]

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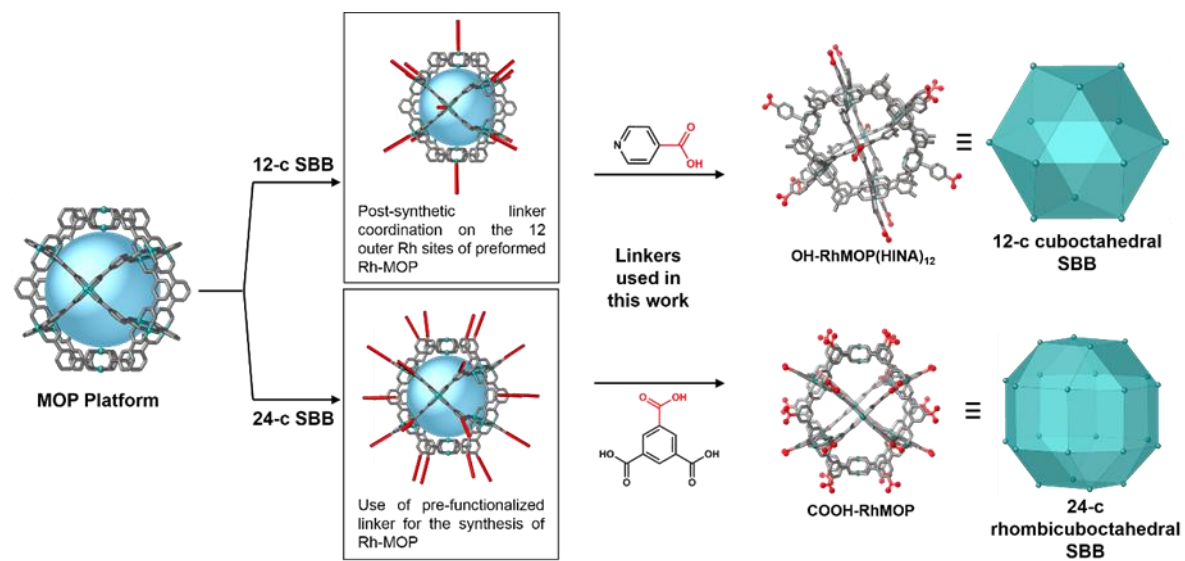
Figure 1. Schematic illustration showing both coordinative (top) and covalent (bottom) routes to polycarboxylate Rh-MOP SBBs. CCDC numbers of OH-RhMOP(HINA)$_{12}$ and COOH-RhMOP can be found in the Supporting Information.
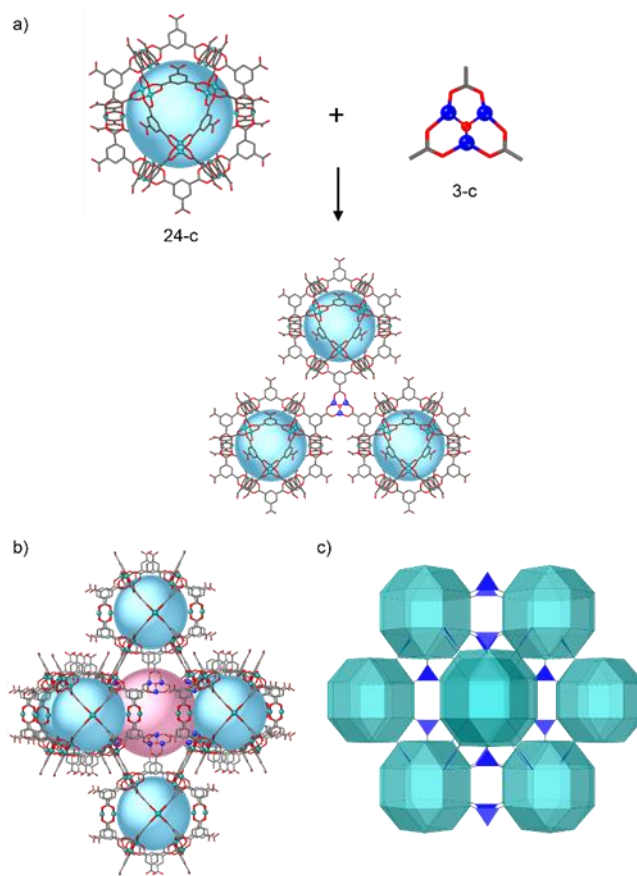
Figure 2. a) Fragments of the structure of RhCu-**rht**-MOF, highlighting the connectivity of COOH-RhMOPs (24-c SBB) through 3-c Cu_3 unit. b) Structure of RhCu-**rht**-MOF, highlighting the inner cavity of COOH-RhMOP (blue) and the cavity C (pink). c) Augmented representation of the **rht** topology. CCDC number of RhCu-rht-MOF can be found in the Supporting Information.
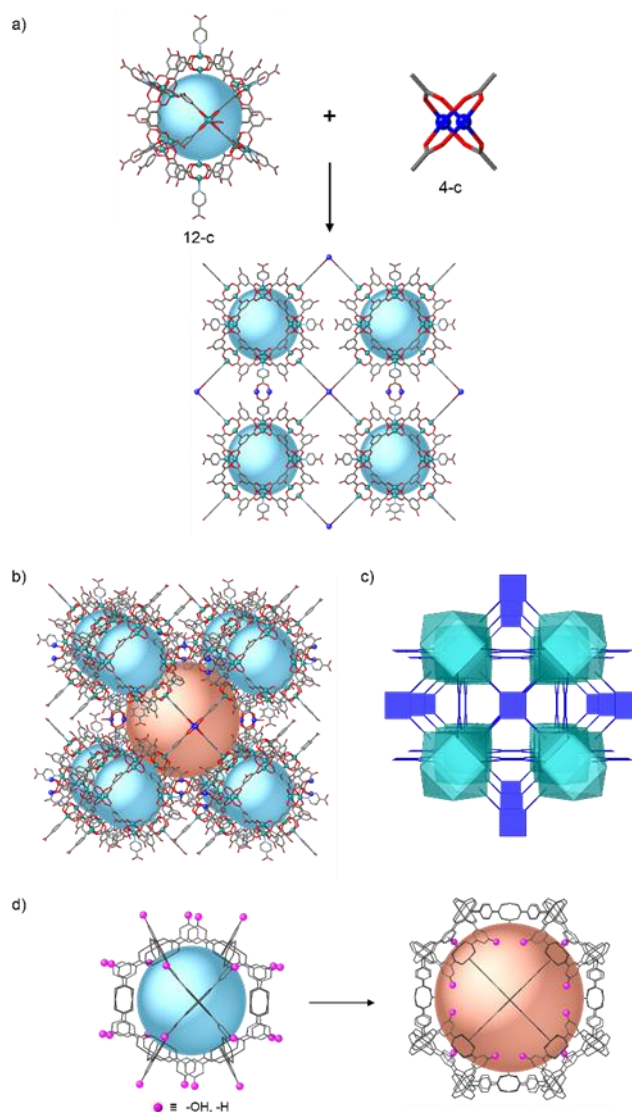
Figure 3. a) Fragments of the structure of RhCu-**ftw**-MOF-1, highlighting the connectivity of OH-RhMOP(HINA)$_{12}$ (12-c SBB) through 4-c Cu$_2$ paddle-wheel unit. b) Structure of RhCu-**ftw**-MOF-1, highlighting the inner cavity of HINA-OHRhMOP (blue) and the cavity E (orange). c) Illustration of the **ftw** topology. d) Outer functionalization of the starting Rh-MOP (pink spheres) decorates the inner surface of cage E in the resulting MOF. CCDC number of RhCu-**ftw**-MOF-1 can be found in the Supporting Information.