

The Next Chapter in MOF Pillaring Strategies: Trigonal Heterofunctional Ligands To Access Targeted High-Connected Three Dimensional Nets, Isorecticular Platforms

Jarrold F. Eubank,[†] Lukasz Wojtas,[†] Matthew R. Hight,[†] Till Bousquet,[†] Victor Ch. Kravtsov,[‡] and Mohamed Eddaoudi^{*,†,§}

[†]Department of Chemistry, University of South Florida, 4202 East Fowler Avenue (CHE 205), Tampa, Florida 33620, United States

[‡]Institute of Applied Physics of Academy of Sciences of Moldova, Academy str. 5, MD2028 Chisinau, Moldova

[§]KAUST Advanced Membranes and Porous Materials Center, 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

S Supporting Information

ABSTRACT: A new pillaring strategy, based on a ligand-to-axial approach that combines the two previous common techniques, axial-to-axial and ligand-to-ligand, and permits design, access, and construction of higher dimensional MOFs, is introduced and validated. Trigonal heterofunctional ligands, in this case isophthalic acid cores functionalized at the 5-position with N-donor (e.g., pyridyl- or triazolyl-type) moieties, are designed and utilized to pillar pretargeted two-dimensional layers (supermolecular building layers, SBLs). These SBLs, based on edge transitive Kagomé and square lattices, are cross-linked into predicted three-dimensional MOFs with tunable large cavities, resulting in isorecticular platforms.

Metal–organic frameworks (MOFs) is an emerging class of porous solid-state materials with significant contributions in numerous application areas including, but not limited to, catalysis, separations, gas storage, and drug delivery.¹ In this typical class of periodic solids, there has been great progress toward design, due largely to the ability to target specific [molecular] building blocks with given geometry and directionality (e.g., squares, tetrahedra, etc.) prior to the assembly process.² One of the most common examples, likely owing to its ability to form with a large range of metals, is the $M_2(O_2CR)_4A_2$ paddlewheel-like unit (Figure 1).^{2–4} This dinuclear cluster can serve as (i) a simple linear bridge when the carboxylates terminate the dimer (i.e., monocarboxylates) and polytopic ligands coordinate through the axial or apical (A) sites, (ii) a square building unit if the carboxylate C atoms serve as sole points of extension (i.e., terminal axial ligands), and (iii) an octahedral building unit, if all the dimer cluster coordination sites are occupied by polytopic ligands (i.e., saturated).⁴

It is recognized that, for square building units, there are only two edge transitive two-dimensional (2D) nets, square lattice (sql) and Kagomé lattice (kgm).⁵ The predictability and regular formation of the square paddlewheel molecular building block (MBB) has allowed the design and synthesis of several MOFs based on these network topologies where, for example, the MOF layer is composed of $M_2(O_2CR)_4(A)_2$ dimer units bridged by

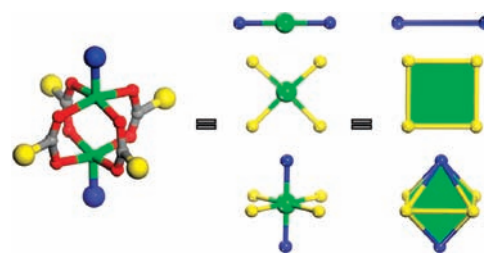


Figure 1. $M_2(O_2CR)_4A_2$ MBB can function as a linear linker, square MBB, or octahedral MBB.

linear or bent dicarboxylate organic ligands (e.g., terephthalate or isophthalate, respectively) (Figure 2) and the layers are separated by terminal axial ligands (A) and/or guest molecules.^{3d,e}

Recently, there has been an increased effort to generate 3D porous MOFs via “pillaring” these layered MOFs.^{6,7} One approach, referred to here as axial-to-axial (A-A) pillaring, takes additional advantage of the auxiliary axial metal sites of the paddlewheel, which are typically occupied by terminal ligands like water or pyridine. In this case, pairs of terminal ligands are replaced by a ditopic (bridging) ligand, typically a nitrogen donor like pyrazine or 4,4'-bipyridine (bipy), that can coordinate the axial positions of two dimer units from neighboring layers (Figure 2), resulting in bridged (i.e., cross-linked or pillared) MOF layers based on six-connected dimer units (i.e., a 6-connected octahedral-based 3D MOF).⁶

Another, albeit more recent, pillaring method involves what we call ligand-to-ligand (L-L) pillaring, where specific ligands are selected to simultaneously contain two bridging ligand moieties (e.g., di-isophthalates, “X”- or “I”-shaped) that pillar adjacent layers through the covalent linkage of the tetracarboxylate ligand (Figure 2). When the 4-connected ligand coordinates to form the 4-connected paddlewheel MBB, the resulting 3D MOF is based on a (4,4)-connected topology (e.g., nbo-MOFs).⁷

Here, we present a new strategy, henceforth referred to as ligand-to-axial (L-A) pillaring. It is expected that a multifunctional ligand simultaneously containing carboxylate and nitrogen

Received: May 12, 2011

Published: June 15, 2011

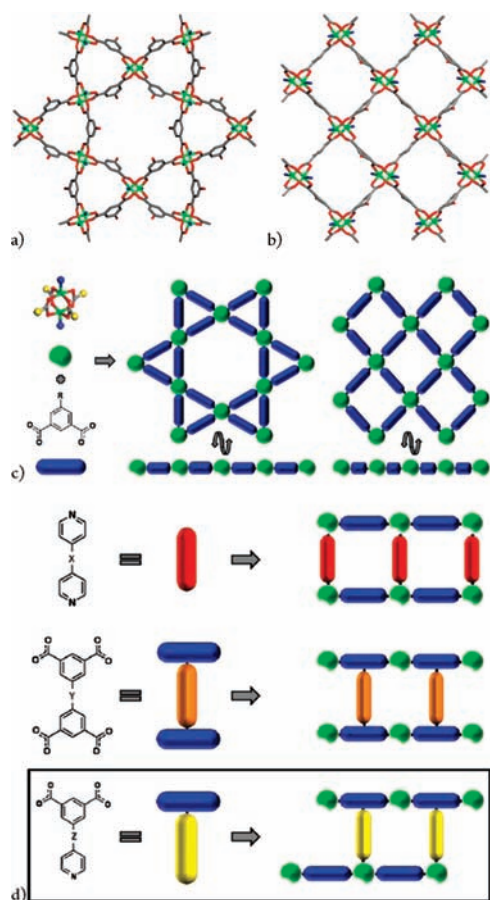


Figure 2. (a) Layer segment of a **kgm**-MOF made from 5-NR_n-1,3-BDC and M₂(O₂CR)₄A₂ MBB. (b) Layer segment of a **sql**-MOF made from 5-NR_n-1,3-BDC and M₂(O₂CR)₄A₂ MBB. (c) Scheme showing the derivation of corresponding nets, Kagomé lattice and square lattice, respectively (overhead and side views). (d) Scheme representing the various layered MOF (side view) pillaring techniques using exemplary ligands; axial-to-axial (red, linear), ligand-to-ligand (blue–orange–blue, “T”-shaped), and ligand-to-axial (blue–yellow, “T”-shaped).

donor (or similar) moieties,⁸ when coordinated with the expected paddlewheel MBB, will lead to a 3D structure. Specifically, each ligand is selected/ designed to be bifunctional and trigonal, containing the ditopic bridging moiety (e.g., 5-substituted isophthalate) that forms the expected 2D MOF having **kgm** or **sql** topology,⁹ a supermolecular building layer (SBL), as well as a second function (e.g., an N-donor group in the 5-position) to coordinate the apical metal site of an inorganic MBB in a neighboring layer. This trigonal (3-connected) pillaring technique will produce an octahedral-like inorganic MBB (6-connected building unit, Figure 1) and thus results in the construction of (3,6)-connected 3D MOFs.¹⁰

A survey of the RCSR database⁵ reveals 20 possible (3,6)-connected nets,¹¹ only six of which (i.e., **anh**, **ant**, **apo**, **brk**, **pyr**, **rtl**), to our knowledge, can be deconstructed into 2D layers of octahedra linked by triangles (“Y”- or “T”-shaped). As such, these networks would be regarded as the most plausible targets using our strategy, since the 2D layers in each correspond to the edge transitive **sql** network, and edge transitive nets are the most appropriate targets in crystal chemistry.¹² It should be noted, there are no (3,6)-connected nets in the RCSR database composed of triangle-linked edge transitive **kgm** 2D sheets, which would

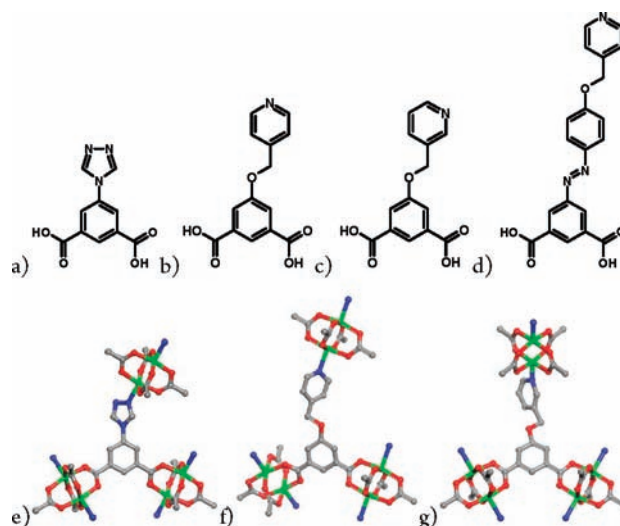


Figure 3. (a–d) Bifunctional trigonal ligands used in this study; H₂L1, H₂L2, H₂L3, and H₂L4, of lengths ~8.4, ~11.3, ~11.3, and ~18 Å, respectively. (e–g) Example of the coordination mode of the L1, L2, and L3 ligands, respectively, when coordinated to the M₂(O₂CR)₄A₂ MBB.

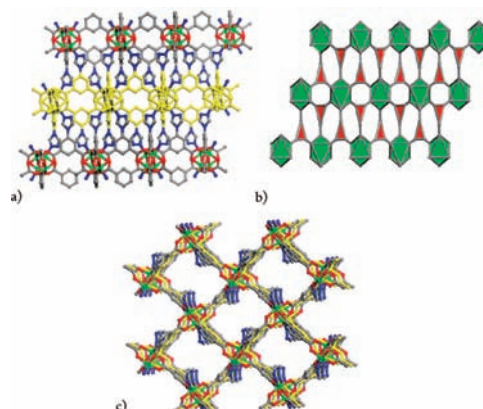


Figure 4. (a) Crystal structure of **1** reveal pillared square grid layers. (b) Polyhedral representation of this net shows the layers of octahedra (green, inorganic MBB) pillared by triangles (red, ligand). (c) Layers stack in a staggered fashion. C = gray, O = red, N = blue, Cu = green; H atoms omitted and one layer shown yellow for clarity.

be essential to determine the corresponding pillared **kgm**-MOF. However, to our knowledge there has been only one such (3,6)-connected net, ScD_{0.33} (46032),¹³ reported in the TOPOS Topological Database (TTD), which should serve as a suitable target. As expected, reactions between selected hetero-, bifunctional trigonal ligands (Figure 3) and various metal salts have afforded the predicted 3D MOFs based on pillaring of the 2D edge transitive nets, **sql** and **kgm**.

According to O’Keeffe, et al.,^{10b} the rutile net (**rtl**) is likely the “easiest target for a designed synthesis” for combining triangles and octahedra, which is supported by its relatively large occurrence in MOFs compared to other (triangle, octahedra)-based (3,6)-connected topologies.^{4,13} In addition, the **rtl** net is one of the nets that can be regarded as square grids (**sql**) pillared by triangular (3-connected) nodes. Thus, the **rtl** net is a suitable target for constructing 3D MOFs from our triangular ligands when combined with the paddlewheel octahedral building unit.

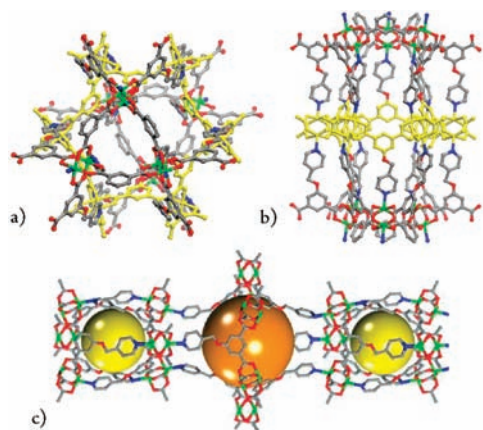


Figure 5. Analysis of the crystal structure of **2** reveals (a,b) pillared Kagomé layers (one layer in yellow), resulting in (c) hourglass-shaped channels with two primary types of cavities (represented as yellow and orange spheres). C = gray, O = red, N = blue, Cu = green; H atoms are omitted for clarity.

Indeed, 5-(4H-1,2,4-triazol-4-yl)isophthalic acid (H_2L1) reacts with copper nitrate to form a L-A pillared **sql**-MOF, $Cu(L1) \cdot x\text{solv}$ (**1**), based on nonequilateral triangles pillaring 2D layers of octahedra (Figure 4). This ligand-to-axial pillared **sql**-MOF also can be viewed as a 3D MOF, where L1 serves as a 3-connected node and the paddlewheel cluster as a 6-connected octahedral node. Topological analysis of the resultant (3,6)-connected net reveals **1** is the expected **rtl**-MOF.⁵

The 1,3-BDC moieties form **sql**-MOF sheets in 1,2-alternate fashion,¹⁴ where a pair of adjacent benzenes in any given four-membered ring point up, while the other adjacent pair point down. This orientation results in the alignment of quadrangular windows of each 2D **sql**-MOF sheet, exposing channels ($\sim 6.2 \text{ \AA} \times 9.6 \text{ \AA}$) running along the *c*-axis (Figure S2, SI). The calculated total potential solvent accessible volume for the as-synthesized **1**, upon removal of guest solvent molecules, was estimated at 970.7 \AA^3 per unit cell volume (1764.0 \AA^3) or 55.0% v/v.

Reaction between copper nitrate and 5-(4-pyridinylmethoxy)-isophthalic acid (H_2L2) results in the expected L-A pillared **kgm**-MOF, $Cu(L2) \cdot x\text{solv}$ (**2**) (Figure 5), which can also be viewed as a 3D MOF, where L2 serves as a 3-connected node and the paddlewheel cluster as a 6-connected octahedral node. Topological analysis⁵ reveals that **2** is consistent with the anticipated $ScD_{0.33}$ (46032),¹³ a novel network in MOF chemistry.

The **kgm**-MOF sheets in **2** are pillared in an arrangement where pairs of three-membered ring windows of neighboring sheets are separated by six-membered ring windows (i.e., 3, 3, 6, 3, 3) to give repeating hourglass-shaped channels (Figure 5c). These hourglass-shaped channels result in two types of cavities ($\sim 7.8 \text{ \AA}$ and 12.6 \AA diameters), one between neighboring three-membered rings and one in the hexagonal windows between neighboring three-membered ring windows, as shown in Figure 5c. The calculated total potential solvent accessible volume for the as-synthesized **2**, upon removal of guest solvent molecules, was estimated at 6969.1 \AA^3 per unit cell volume (11888.4 \AA^3) or 58.6%.

As expected, reaction between copper nitrate and the L2 isomer, 5-(3-pyridinylmethoxy)-isophthalic acid (H_2L3), results in an analogous L-A pillared **kgm**-MOF, $Cu(L3) \cdot x\text{solv}$ (**3**) (Figure S4, SI). The orientation of the ligands results in slight changes in cavity shape and size ($\sim 8.3 \text{ \AA}$ and 12.0 \AA diameters). The calculated total potential solvent accessible volume for the

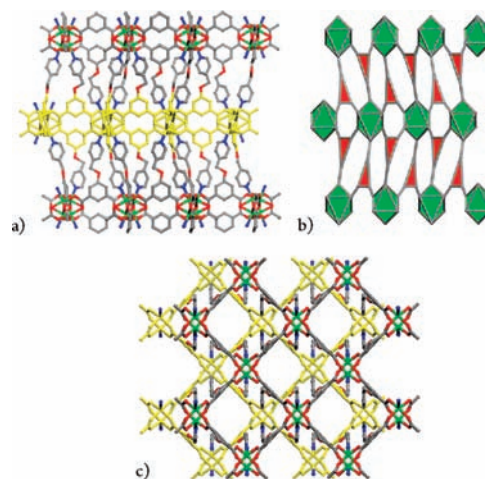


Figure 6. (a) Crystal structure of **4** reveals pillared square grid layers. (b) Polyhedral representation of this net shows the layers of octahedra (green, inorganic MBB) pillared by triangles (red, ligand). (c) Layers stack in a staggered fashion. C = gray, O = red, N = blue, Cu = green; H atoms are omitted, and one layer is shown in yellow for clarity.

as-synthesized **3**, upon removal of guest solvent molecules, was estimated at 5471.2 \AA^3 per unit cell volume (10204.0 \AA^3) or 53.6% v/v.

There are five other (3,6)-connected nets based on the assembly of triangles linking 2D layers of octahedra. Accordingly, just as the parent mineral TiO_2 adopts several (3,6)-connected polymorphic forms (e.g., **ant**, **apo**, **brk**, and **rtl**), multiple rutile-like (i.e., trigonal-pillared **sql**) polymorphs should be anticipated here. A ligand lower in symmetry and flexible in nature should allow for the formation of these less regular nets.

Slight modification of the reaction conditions between copper nitrate and H_2L2 results in another type of pillared **sql**-MOF, $Cu(L2) \cdot x\text{solv}$ (**4**). Adding a small amount of water to the reaction conditions resulted in a mixture of crystals of **2** and **4**, but the addition of a structure-directing agent, in this case 1-iodo-4-nitrobenzene, leads to pure **4**. This ligand-to-axial pillared **sql**-MOF also can be viewed as a 3D MOF, where the L2 ligand serves as a 3-connected node and the paddlewheel cluster as a 6-connected octahedral node (Figure 6). Topological analysis of the resultant (3,6)-connected net reveals that **4** is one of the expected structures, an **apo**-MOF;⁵ to our knowledge, this is the first example of successfully targeting such frameworks.

As in the previous L-A pillared **sql**-MOF, the **sql** sheets are formed via the 1,3-BDC moiety (1,2-alternate fashion¹⁴) of the ligand, L2, and the nitrogen (pyridinyl) moiety (of L2) coordinates to the axial positions of the metal–carboxylate paddlewheel clusters (Figure 6). However, in this case the orientation results in the quadrangular windows ($\sim 8.4 \text{ \AA} \times 9.8 \text{ \AA}$) of each 2D **sql**-MOF sheet being staggered between neighboring sheets, exposing zigzag channels ($\sim 6.8 \text{ \AA} \times 6.8 \text{ \AA}$) running along the *c*-axis (Figure S5, SI). The calculated total potential solvent accessible volume for the as-synthesized **4**, upon removal of guest solvent molecules, was estimated at 2715.5 \AA^3 per unit cell volume (4634.0 \AA^3) or 58.6% v/v.

The unique nature of these nets and the resultant cavities makes them amenable to isorecticular chemistry, allowing the design and synthesis of expanded (3,6)-connected MOFs from an infinite number of trigonal ligands (e.g., interlayer distance of $\sim 10.884 \text{ \AA}$ in **1** vs $\sim 13.663 \text{ \AA}$ in **4**, and $\sim 12.8 \text{ \AA}$ in **2** vs $\sim 11.8 \text{ \AA}$

