# Geometric requirements and examples of important structures in the assembly of square building blocks

Mohamed Eddaoudi*, Jaheon Kim*, David Vodak*, Andrea Sudik*, Joseph Wachter*, Michael O'Keeffe[†], and Omar M. Yaghi*[‡]

*Department of Chemistry, University of Michigan, Ann Arbor, MI 48109; and [†]Department of Chemistry, Arizona State University, Tempe, AZ 85287
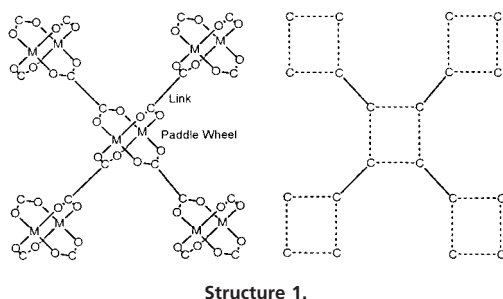
The basic structures for linking squares into polyhedra and networks (reticulation) are enumerated, and corresponding examples are described in which crystals were synthesized by linking paddle wheel (square) units into metal–organic frameworks (MOFs)—named MOF-102 to MOF-112.

The designed construction of chemical structures requires knowledge of the different topological possibilities that might result from linking various molecular shapes (1). It has been our thesis that, for a given shape, only few simple high-symmetry structures (referred to as default structures) are of general importance and that they are most likely to form (2, 3) in the assembly of distinct and well defined molecular building blocks. For example, the polymerization of tetrahedral building blocks generally gives structures based on the cubic diamond network (the most symmetric tetrahedral network). This is despite hundreds of other structures that can, in principle, form by linking tetrahedra in three dimensions. The sodalite network is one such possibility: like cubic diamond, the structure is composed entirely of tetrahedra, although here they are linked into four- and six-membered rings, in contrast to only six-membered rings that make up diamond. Structures based on the sodalite network are rarely observed, especially in the design and synthesis of metal–organic frameworks (MOFs), thus raising the question: can sodalite or other less common networks be designed by the deliberate assembly of molecular building blocks?

To address this question we have recently developed a general conceptual method for the assembly of target networks; in this approach a hierarchy of information is incorporated into building blocks that make them sufficiently unique for the construction of a target network (4). Two essential elements of this approach are: (*i*) knowledge of the possible networks that could form based on a given building block, and (*ii*) determination of the geometric attributes that uniquely define the network targeted for design. This study is focused on delineating *i* and *ii* for the case of linking squares into extended structures and polyhedra.

The paddle wheel structure motif, $M_2(CO_2)_4$, can be considered as a square molecular building block, which has been reticulated with organic links into extended (3) and discrete structures (5). Here, the four carboxylate carbon atoms of each paddle wheel form square units (Structure 1) referred to as a secondary building units (SBUs). In this study, the default structures that are likely to form by reticulating squares are enumerated and crystal structures of corresponding metal–carboxylate examples are described.

It is worth noting that, in principle, addition of an organic link into a reaction that yields the paddle wheel arrangement provides means for the design of linked-square structures. Here we chose nine ditopic organic carboxylate links (Table 1) where the carboxylate functionalities are at a variety of angles, and thus they were expected to provide suitable starting points for reticulating square SBUs into structures other than the planar $4^4$-grid motif (6).

## Synthesis and Characterization of Crystals

All materials were synthesized as single crystals under aerobic conditions. For easy reference, the abbreviations of links and compounds including formulation and crystallography data have been summarized in Table 1 (all data analysis and synthesis details are included as supporting information, which is published on the PNAS web site, www.pnas.org). Compounds are referred to as MOF-*n* (metal–organic framework, where *n* is an integer assigned roughly in chronological order).

Two synthetic routes were used to prepare and crystallize the MOFs reported here: (*i*) For Cu (II) and Fe (II): Equimolar amount of $Cu(NO_3)_2 \cdot 2.5H_2O$ or $FeBr_2$ was dissolved in an alcoholic mixture of either *N,N'*-dimethylformamide (DMF), *N,N'*-diethylformamide (DEF), and *N,N'*-dibutylformamide (DBF), with the acid link and placed in a Pyrex tube (i.d. × o.d. = 8 × 10 mm², 140 mm length), heated to either 80°C (Cu) or 120°C (Fe) for 20 h, then cooled to room temperature at 2°/min. (*ii*) For Zn (II): Equimolar amount of $Zn(NO_3)_2 \cdot 6H_2O$ and the acid link (for MOF-103, anhydrous $ZnCl_2$ was used in double the molar amount) were dissolved in DMF, then an appropriate amine was allowed to diffuse or it was added into the reaction mixture that was placed in a closed container at room-temperature.

Typically, the amine was diluted with the reaction solvent(s) to ensure its slow diffusion. In both synthetic procedures, the resulting crystals were washed with the reaction solvent to give unoptimized yields in the range 20–90%. The homogeneity of the bulk material was confirmed by comparison of the observed powder x-ray diffraction pattern to that simulated using the single crystal x-ray diffraction data. Each compound was formulated based on elemental microanalysis and single-crystal x-ray diffraction.

## Default Structures for Linking Squares

Before describing the structures of MOF-102–112, it is of interest to enumerate the number of distinct ways squares can be linked by equal linkers (i.e., all links related by symmetry).
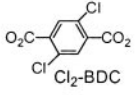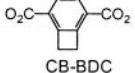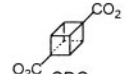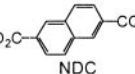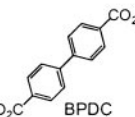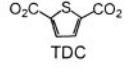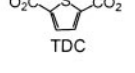
In two dimensions the problem is simple: it turns out that the structures correspond to certain Archimedean plane tilings or



Structure 1.

**Table 1. Summary of links and MOFs including formulations and crystallographic cell parameters**

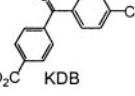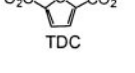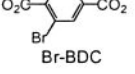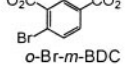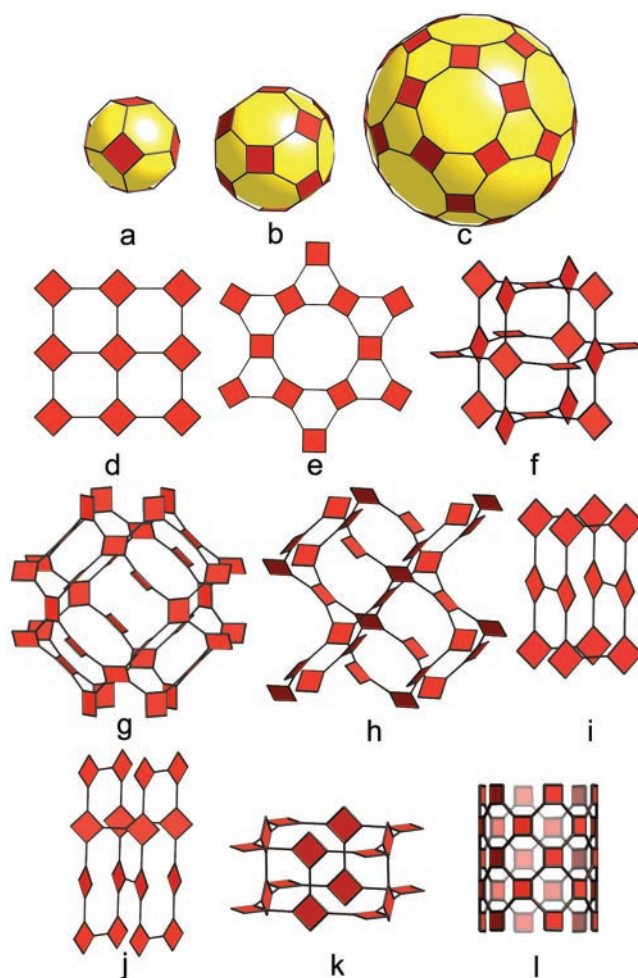| MOF-n | Link and Abbreviation | Chemical Formula Space Group; a, b, c (Å); α, β, γ (°); V (Å³); Z |
|---|---|---|
| MOF-102 | $Cl_2$-BDC | $Cu_2(Cl_2BDC)_2(DMF)_2 \cdot (H_2O)(DMF)_{3.5}$<br>$P$-1; 9.3845, 10.7943, 10.8305; 91.633, 106.243, 112.005; 965.6; 1 |
| MOF-103 | CB-BDC | $Zn_2(CB\text{-}BDC)_2(H_2O)_2 \cdot (H_2O)_3(DMF)_{1.8}$<br>$P2_1/n$; 7.3386, 16.8338, 12.5204; 90.00, 94.714, 90.00; 1541.5; 2 |
| MOF-104 | CDC | $Zn_2(CDC)_2(DMF)_2 \cdot (DMF)_2(ClBz)$<br>$C2/m$; 13.7877, 16.6254, 110.6179; 90.00, 112.364, 90.00; 2250.83; 2 |
| MOF-105 | NDC | $Zn_2(NDC)_2(DMF)_2 \cdot (ClBz)$<br>$P2_1/c$; 8.130, 16.444, 12.807; 90.00, 92.127, 90.00; 1711.1; 2 |
| MOF-106 | BPDC | $Fe_2(BPDC)_2(DMF)_2 \cdot (H_2O)_{0.4}(DMF)_{3.6}$<br>$C2/c$; 27.124, 15.270, 12.0109; 90.00, 94.604, 90.00; 4958.7, 4 |
| MOF-107 | TDC | $Cu_2(TDC)_2(DEF)_2 \cdot (H_2O)(DEF)_3$<br>$P$-1; 11.0318, 18.0673, 18.4528; 104.812, 97.075, 95.206; 3499.9; 2 |
| MOF-108 | TDC | $Cu_2(TDC)_2(CH_3OH)_2 \cdot (DBF)_2$<br>$P2_1/c$; 15.474, 14.514, 14.031; 90.00, 113.63, 90.00; 2887.2, 4 |
| MOF-109 | KDB | $Cu_2(KDB)_2(DMF)_2 \cdot (H_2O)_2(DMF)_8$<br>$P2_1/c$; 23.8801, 16.8339, 18.3890; 90.00, 111.979, 90.00; 6855.0; 4 |
| MOF-110 | TDC | $Cu_2(TDC)_2(DMF)_2 \cdot (H_2O)(DMF)_{3.5}$<br>$R(\text{-}3)m$; 20.0468, 20.0468, 20.7484; 90.00, 90.00, 120.00; 7221.0; 4.5 |
| MOF-111 | Br-BDC | $Cu_2(TDC)_2(DMF)_2 \cdot (H_2O)(DMF)_2$<br>$C2/c$; 10.677, 18.781, 21.052; 90.00, 102.16, 90.00; 4127; 4 |
| MOF-112 | o-Br-m-BDC | $Cu_2(Br\text{-}BDC)_2(DMF)_2 \cdot (H_2O)_2 (DMF)_2$<br>$C2/c$; 29.3240, 21.2972, 18.0688; 90.00, 107.49, 90.00; 10762.7; 12 |



**Fig. 1.** Default structures for linking squares into polyhedra and networks. See also Table 2.

polyhedra (tilings of a sphere), and these are all well known (7) with examples in chemical structures (6, 8, 9). We find that there are three polyhedral cases and two plane nets (Fig. 1 **a–e**). In addition, cylindrical (tubular) structures are possible with the same connectivity as plane figures, and with variable diameter. An example with the only topology having all equivalent links is shown (Fig. 1, **l**). We do not discuss cylindrical structure further here, but, of course, they are potentially of great interest.

In three dimensions the squares together with the links form three-connected networks. If the edge lengths of the squares and the links are made equal, the network is that of three-coordinated sphere packing, and a convenient source to find possible structures has been compiled (10). From this source, and from a separate independent enumeration (11), we find that there are three such structures with just one kind of link between squares (Fig. 1 **f–h**). One of these, **f**, is obtained by replacing the vertices of the familiar NbO network (7, 12) by squares, a process we call augmentation (2). The other two, **g** and **h**, are possible targets for synthesis, but we have not yet found crystal examples of linked squares with these topologies. However, we name **g** and **h** as RHOS and augmented UCR-1, because they form the basis of the tetrahedral frameworks of zeolite RHO (13) and a recently reported cadmium indium sulfide framework (14), respectively.

In the specific example of paddle wheels linked by dicarboxylate linkers, the particular structure favored will depend on the geometry of the linker. We choose as our reference structure that of the planar 1,4-benzenedicarboxylate (BDC); paddle wheels linked by this link will be coplanar and at 90° to the BDC link. There are three principal modes of distortion from this reference geometry (Structure 2): bending in the middle of the link by an angle $\theta$ with the two-carboxylate groups remaining coplanar; bending of the planes of the carboxylates toward each other by an angle $\psi$; and twisting of the planes of the carboxylates about the linker axis relative to each other by an angle $\varphi$.

**Structure 2.**

In two structures (**c** and **h**) a combination of distortions is required, and as the different distortions do not commute, and as the synthesis of these structures solely by design of linkers is much less likely, we do not specify those angles here.

It is important to recognize that the listed topologies do not necessarily require the ideal linker geometry to be formed, because all of the structures have a degree of flexibility. In particular, factors such as solvent templating, temperature, and metal ion solvation may play a decisive role in deciding which structure is found. Nevertheless, the design principles are generally sound, as evidenced by the fact that the predicted result has been found in a number of instances.

Other linkages of squares that might be reasonable targets of synthesis are known, and again, can be derived by augmenting simple four-connected networks. In particular there are known two such networks with one kind of vertex (i.e., all vertices related by symmetry) and now two kinds of links (15). The first of these networks, **i**, is named for $CdSO_4$ as it represents the topology of the Cd–O–S linkages in that compound, and the second, **j**, is named the "quartz dual" network, formerly called "dense" network (7). These nets are particularly simple topologically as they have only two and three vertices, respectively, in the repeat unit. The network of MOF-112, **k** (also described below), is the next simplest of this family; it has two kinds of vertexes and two kinds of links but only three vertices in the repeat unit.

### Description of Crystal Structures

**General Features of MOF-102–112.** We have described examples corresponding to some of the ideal networks. Table 2 summa-

rizes the ideal networks and the relevant corresponding references and all examples that we have prepared thus far, including MOF-102–112.

Each of MOF-102–112 structures is composed of paddle wheel units that are linked by the respective link (Table 1). The square secondary building units (SBUs) in each structure are nearly regular with edges and angles ranging between 3.347 and 3.826 Å and 88.3 and 90.0°, respectively. Also, each paddle wheel unit shows M–M distances (Cu, 2.617–2.665 Å; Zn, 2.919–3.001 Å; and Fe–Fe, 2.802 Å) consistent with those observed in molecular analogues (ref. 16, and references therein). The angles between the squares are directly related to those relating the carboxylates within each link.

**MOF-102–110 (Two-Dimensional Networks).** MOF-102–109 have the $4^4$-network default topology. It is similar to that of MOF-2 BDC structure (6), in which the benzene rings and the squares are coplanar. In MOF-102 (Fig. 2, **a**), the presence of Cl on two ortho positions in $Cl_2$-BDC brings the benzene ring out of the plane of the squares without changing the essential angles between the squares. The use of CB-BDC results in $\varphi$ of 26.1°, thereby giving the sheets corrugated conformation in the amount of $\varphi$. Similar corrugation of the $4^4$ sheets is observed in the case of CDC and 2,6-NDC compounds; however, now with $\varphi$ being 7.0° and 25.2°, respectively.

Although BPDC is expected to be a linear link, the structure of MOF-106 reveals that it is significantly bent ($\theta = 167°$) with only a small dihedral angle between the squares ($\varphi = 2.8°$). In this case, corrugation of the sheets is mainly due to the bending of BPDC, because the squares lie within the plane of the squares. Progressively larger corrugation of the sheets is observed for MOF-107–109 with links TDC and KDB having increasingly lower $\theta$ (158.0°, 153.0°, and 123.7°) and higher $\varphi$ (6.3°, 26.0°, and 50.8°) angles.

It is worth noting that bent links adapt to the $4^4$-grid topology by bending alternately above and below the plane of the grids; a conformation that is favored for its centro-symmetric nature and the fact that it relieves strain within the plane.

The use of DMF instead of DEF and DBF with TDC yields MOF-110 (Fig. 2, **b**), which represents the first example of a MOF having the 4.6.12 tiling structure. The TDC link here has $\theta = 152.8°$ and $\varphi = 0.0°$. However, in order for three squares to make a triangle, the carboxylates bend toward each other to

**Table 2. Default structures for linking squares into polyhedra and networks, including reference to examples prepared thus far in paddle wheel carboxylate chemistry**

| Structure type | Symmetry | Site symmetry | Ideal link geometry: $\theta, \psi, \varphi$ (°) | Ideal Fig. | Example (ref.) |
|---|---|---|---|---|---|
| Truncated octahedron | $O_h$ | $C_{4v}$ | 90, 180, 0 | **1a** | Unknown |
| Truncated cuboctahedron | $O_h$ | $C_{2v}$ | 120, 180, 0 | **1b** | (8, 9) |
| Truncated icosidodecahedron | $I_h$ | $C_2$ | Complex | **1c** | Unknown |
| Augmented square lattice | P4/mmm | $D_{4h}$ | 180, 180, 0 | **1d** | (6) |
| Tiling 4.6.12 | P6/mmm | $D_{2h}$ | 180, 150, 0 | **1e** | MOF-110 (this work) |
| Augmented NbO | Im$\bar{3}$m | $D_{4h}$ | 180, 180, 90 | **1f** | (12) |
| RHOS | Im$\bar{3}$m | $C_{2v}$ | 180, 180, 60 | **1g** | Unknown |
| Augmented UCR-1 | I4$_1$/amd | $C_{2h}$ | Complex | **1h** | Unknown |
| Augmented $CdSO_4$ | P4$_2$/mmc | $D_{2h}$ | 1) 180, 180, 90 | **1i** | MOF-111 (this work) |
| | | | 2) 180, 180, 0 | | |
| Augmented quartz dual | P6$_2$22 | $D_2$ | 1) 180, 180, 60 | **1j** | Unknown |
| | | | 2) 180, 180, 0 | | |
| MOF-112 | P4/mmm | 1) $D_{4h}$ | 1) 180, 0, 90 | **1k** | MOF-112 (this work) |
| | | 2) $D_{2h}$ | 2) 180, 180, 0 | | |

Crystallographic data for edge-transitive three-dimensional nets. NbO, $a$ = 2.0, vertices in 6 *b*: 0.5, 0.5, 0. Augmented NbO, $a$ = 4.828, vertices in 24 g: 0.1465, 0, 0.5. RHOS parent, $a$ = 3.4640, vertices in 24 *h*: 0, 0.3333, 0.3333. RHOS, $a$ = 8.2928, vertices in 96 *l*: 0.3701, 0.2848, 0.0603. UCR-1, $a$ = $c$ = 2.3090, vertices in 8 *c*: 0, 0, 0. Augmented UCR-1, $a$ = 5.6241, $c$ = 5.3289, vertices in 32 *i*: 0.0889, 0.4393, 0.9315.
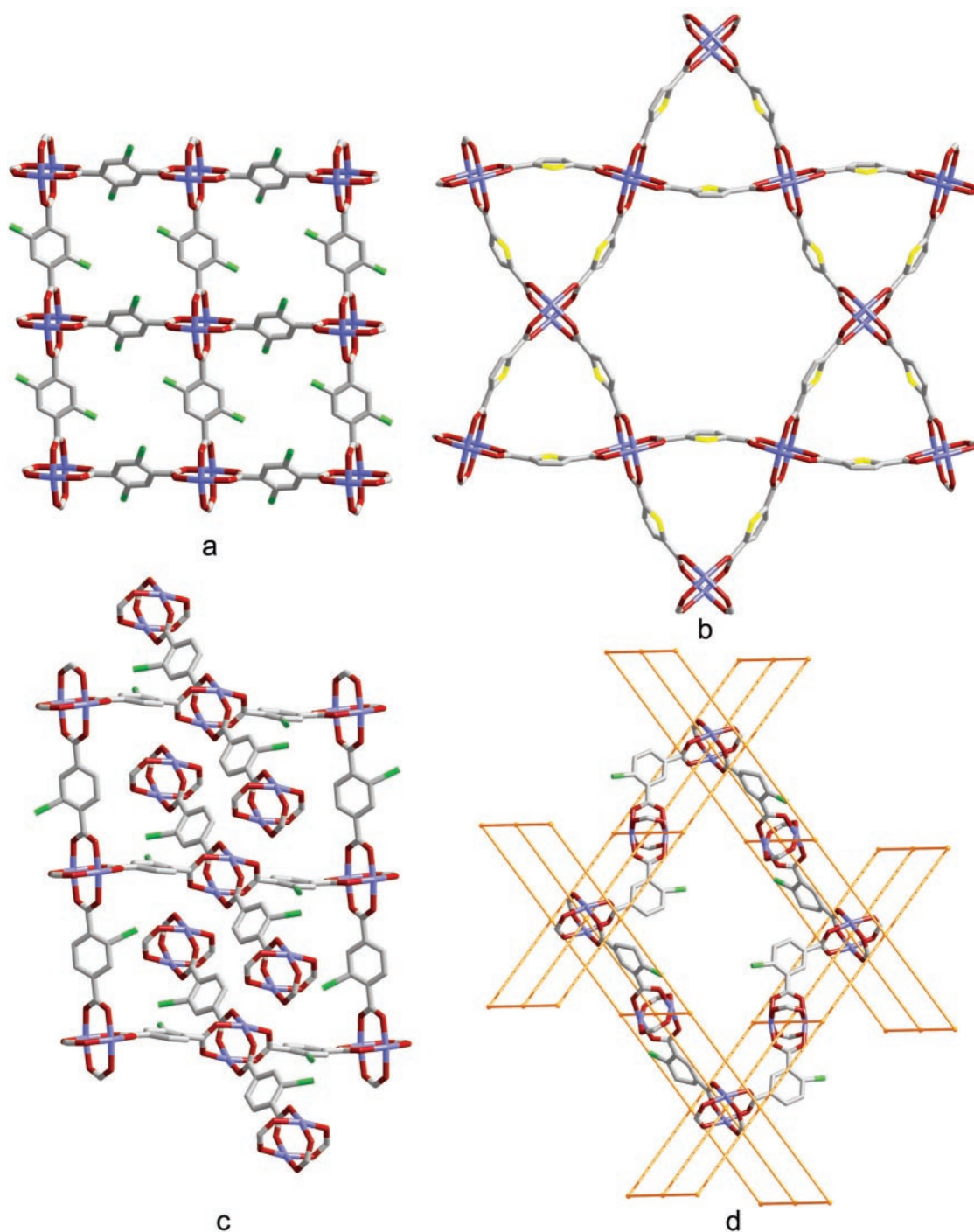
**Fig. 2.** Crystal structure of (**a**) MOF-102 (also adopted by MOF-103–109), (**b**) MOF-110, (**c**) MOF-111, and (**d**) MOF-112—drawn using single-crystal x-ray diffraction data

make a $\psi = 151.1°$, thereby relieving the strain of having three squares in a triangle and providing the necessary angle for 4.6.12 tiling. The direction of sulfur alternates above and below the plane of the resulting hexagonal arrangement of squares to give a corrugated sheet structure. This hexagonal arrangement of triangles of squares is a required ring motif for the design of the as yet unknown truncated icosidodecahedral cluster (Fig. 1**c**); however, it is unlikely that TDC link would lead to this polyhedron because it would be required to have different angles and noncorrugated ring conformation.

**MOF-111 and -112 (Three-Dimensional Networks).** In an earlier study, we used the ortho-substituted link *o*-Br-BDC in designing the NbO-type network, in which squares are at right angles (13). Indeed, reactions performed at room temperature allowed the carboxylate not to overcome the barrier of rotation and thus form the NbO-type network. Heating such reactions lowers the barrier to rotation of carboxylates and yields MOF-111 and -112 (Fig. 2 **c** and **d**) having structure based on CdSO$_4$ and the so-called MOF-112 network (Table 2), respectively. The links *o*-Br-BDC in MOF-111 and *o*-Br-*m*-BDC in MOF-112 provide,

as required, two distinct sets of angles: MOF-111 has 180°, 179.0°, 59°, and 180°, 180°, 0°; whereas MOF-112 has more complex angles because of a bent link and a pronounced carboxylate plane bending angles (113°, 87°, 55° and 113°, 57°, 25°).

Many of the compounds reported here exhibit interesting pore structures and inclusion chemistry, an aspect that we intend to report in future publications.

## Summary

The present study introduces the basic networks that are likely to form as a result of linking molecular squares into zero-dimensional, two-dimensional, and three-dimensional structures. It is clear that for the construction of frameworks by design, rigid links must be designed first as exemplified in the case of NbO-type MOF-101 structure; however, we note that for most of the common networks, there is a great deal of flexibility in the angles that a link may provide as illustrated in MOF-102–112. [All crystal structures may be viewed and manipulated at http://www.umich.edu/~yaghigrp/structures.html.]

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