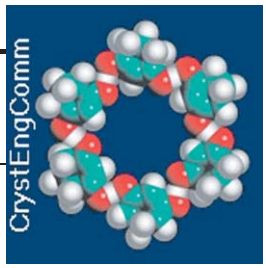

Highlight

Advances in the chemistry of metal–organic frameworks†

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An extensive body of research results currently exists from the synthesis of metal–organic frameworks (MOFs), an area that has attracted widespread attention due to the facility with which well-defined molecular building blocks can be assembled into periodic frameworks and the promise that such a process holds for the logical design of materials. The synthesis of MOFs generally involves the copolymerization of organic links and metal ions in a polar solvent under mild temperatures (up to 200 °C) and autogenous pressures (up to 100 atm). Since most products can be considered kinetically driven and lie on local thermodynamic minima, factors such as solubility of the organic link and metal salt, solvent polarity, ionic strength of the medium, temperature and pressure play critical roles in determining the character of products. Indeed, slight perturbations in synthetic parameters have been the basis for the preparation of what seems to be a flood of new MOF compounds.

In the spirit of this discussion we advance the following ideas and developments that we believe contribute to the maturity of the field: (I) a conceptual framework that unifies the processes involved in the designed synthesis of MOFs, and which can be extended to other materials with extended structures; (II) a thesis concerning the possible structures that may form from building blocks with various shapes; (III) important considerations for achieving the design and synthesis of frameworks in which it is possible to change chemical functionality and metrics without changing the underlying framework topology; (IV) the inevitability of porosity for designed structures and some factors affecting framework stability; (V) insights on catenation: interpenetration *versus* interweaving, forbidden catenation, and duals. These points will be presented to an extent that will stimulate discussion—it is not an attempt to be comprehensive or to give a thorough treatment of this rich field.

I. Bottom up synthesis by top down design (reticular synthesis)

The significance of top down design logic and its impact on the course of design can be captured using as examples two basic networks, namely, cubic and hexagonal diamond (lonsdaleite).[1,2] The simplest deconstruction scheme yields tetrahedral building blocks in both cases. Thus the assembly of molecules with tetrahedral shape would be expected to yield at least one of these two possible arrangements. However, in practice most structures obtained from simple tetrahedral building blocks are based on the cubic diamond network and in fact reticulations based on the lonsdaleite topology are very rare. Why is this?

The diamond network corresponds to the simplest, highest-symmetry structure (it is the only *regular* tetrahedral structure) and unless the building blocks contain information to the contrary, it is the default reticulation (see Section II). To obtain the less common hexagonal form it is necessary to deconstruct

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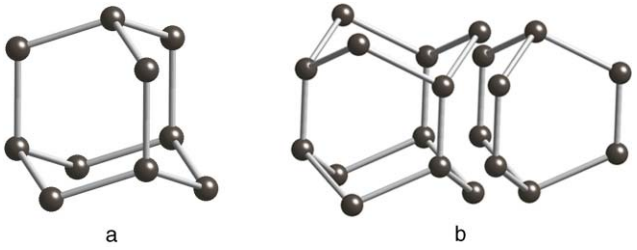

Fig. 1 Basic units (tiles) for (a) diamond and (b) lonsdaleite.

its structure into more elaborate building blocks that express structural features unique to that structure. Although the two structures are composed of fused 6-membered rings, all such rings in diamond have the chair conformation (Fig. 1a) while those in the hexagonal form assume both chair and boat conformations (Fig. 1b). Thus it seems reasonable to suggest that in order to make frameworks based on lonsdaleite, the net should be deconstructed into building blocks of fused chair *and* boat rings rather than of individual tetrahedra. In this way, the assembly of the corresponding molecules would yield exclusively the target network. It should be noted that the foregoing discussion does not preclude the possibility of achieving lonsdaleite from smaller building blocks but they would certainly have to be less regular in nature.

This treatment can be universally applied to the design of crystalline molecular arrays of any dimensionality. However, it is important to emphasize that the achievement of complex low-symmetry topologies *by design* requires the construction of complex building blocks (or inclusion of other components such as templates into the synthesis) coded specifically for that reticulation.

Reticular synthesis is different from retrosynthesis,[3] used in the synthesis of organic compounds, since the structural integrity and rigidity of the building blocks in reticular synthesis remain unaltered throughout the construction process—an important aspect that is a prerequisite to fully realizing the benefits of design in crystalline solid state frameworks. Similarly, reticular synthesis should be distinguished from supramolecular assembly,[4] because in the former, building blocks are linked by strong covalent bonds throughout the crystal.

II. Default structures

It is our thesis that in the assembly of molecular shapes only a few simple high-symmetry topologies (default structures) are of paramount importance, and they would be expected to form from symmetric building blocks.[5] In practice building blocks that hold little complexity (highly symmetric) are expected to form, depending on their shape, one of the corresponding default structures listed in Table 1.

To examine the universality of this thesis and its application to MOF chemistry, it was important to control the geometry of the metal ion and the link during assembly of the MOF structure. Since the geometry around metal ions is difficult to control (especially in the case of metal–bipyridine MOFs), we have developed the chemistry of carboxylate links with metal ions where metal–carboxylate (M–O–C) clusters (named secondary building units, SBUs) fix the metal ion position and impart rigidity to the resulting MOF structure.[6] Since most SBUs are not isolable entities, it is important to determine the conditions that would yield a specific SBU. For example, we have identified the reaction conditions that yield the paddle wheel (square SBU) and the basic zinc acetate (octahedral SBU) structures.[7,8] Thus addition of the organic links adamantane tetracarboxylate (tetrahedron) and benzene tribenzoate (triangle) to reactions that give the paddle wheel resulted into the corresponding default structures, PtS and Pt_3O_4, respectively.[9,10]

Benzenedicarboxylate illustrates the dramatic influence of the organic link geometry on the dimensionality of the resulting framework. Here, 1,4-benzenedicarboxylate (a linear link) places the paddle wheel units at 180° to each other and gives MOF-2 having the 4^4 square grid structure (Fig. 2a).[7,11] 1,3-benzenedicarboxylate (a bent link) results in having the paddle wheel units at 120° to each other and thus gives the discrete truncated cuboctahedron structure of MOP-1 (MOP = metal–organic polyhedron) (Fig. 2b).[12,13] 2-Bromo-1,4-benzenedicarboxylate, a link that places the paddle wheel units at 90° angles, gives MOF-101 having the expected NbO network (Fig. 2c).[14] We note that all the resulting structures from the paddle wheel motif fall into the class of default structures, since no complexity was incorporated into the building blocks or the synthesis.[11]

III. Functionalization and control of metrics

The insolubility of MOFs necessitates that their assembly be accomplished in only a single step. Thus, in order to design a target extended structure with the same precision practiced in organic synthesis, (i) the starting building blocks should have the relevant attributes necessary to assemble into the skeleton of the desired structure, and (ii) the synthesis has to be adaptable to using derivatives of those building blocks to produce structures with the same skeleton but different

Table 1 Default structures

CN[a]	LC[b]	Name	Vertex figure	Transitivity[c]	Tiles
3	^+Y*	$SrSi_2$	triangle	<1111>	$[10^3]$
4	*J**	NbO	square	<1111>	$[6^8]$
4	*D*	diamond	tetrahedron	<1111>	$[6^4]$
6	*cP*	primitive cubic	octahedron	<1111>	$[4^6]$
8	*cI*	body-centered cubic	cube	<1111>	$[4^4]$
12	*cF*	face-centered cubic	cuboctahedron	<1112>	$2[3^4] + [3^8]$
6	*E*		trigonal prism	<1122>	$2[4^3] + [4^3.6^2]$
4,8		fluorite (CaF_2)	tetrahedron, cube	<2111>	$[4^{12}]$
3,6		pyrite (FeS_2)	triangle, octahedron	<2112>	$2[6^3] + [6^6]$
3,4		Pt_3O_4	triangle, square	<2122>	$3[8^4] + 2[8^6]$
3,4		boracite	triangle, tetrahedron	<2122>	$[6^4] + [6^4.8^6]$
4,4		PtS	square, tetrahedron	<2122>	$[4^2.8^2] + [8^4]$
6,6		NiAs	prism, octahedron	<2122>	$[4^3] + [4^9]$

[a]CN = coordination number. [b]LC = lattice complex. [c]Transitivity ⟨*pqrs*⟩ refers to the tilings that carry the vertex figure and have *p* kinds of vertex, *q* kinds of edge (link), *r* kinds of face (ring) and *s* kinds of tile. The smaller the transitivity, the more regular the net.

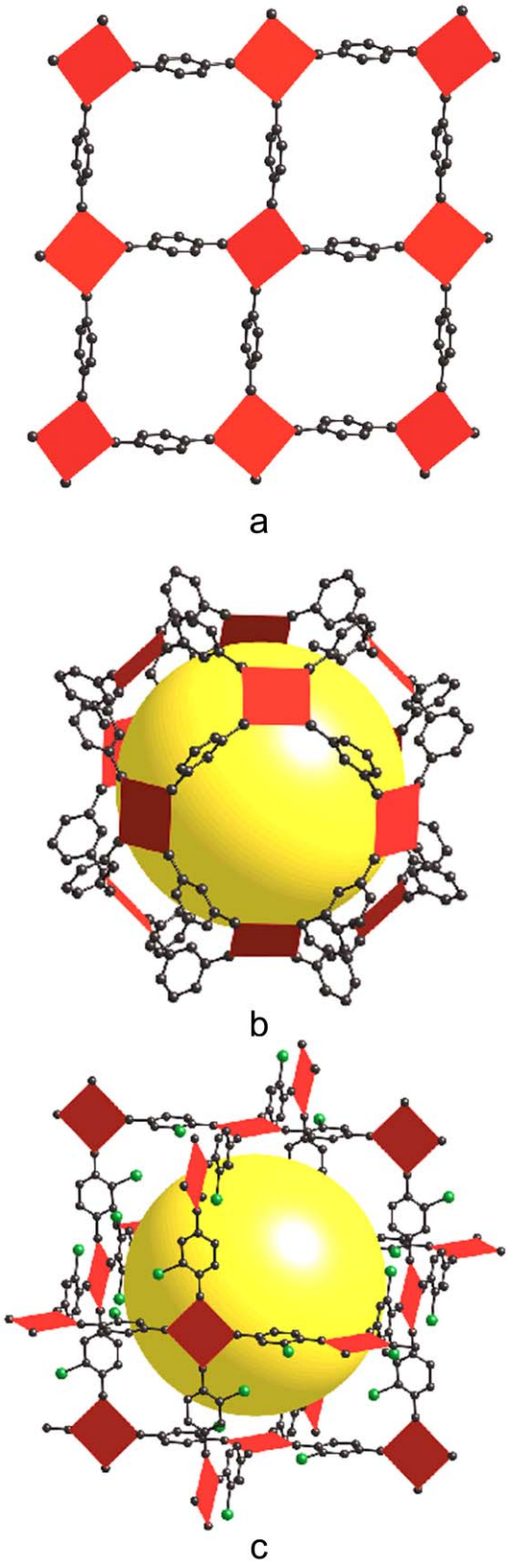

Fig. 2 (a) MOF-2, (b) MOP-1, (c) MOF-101.

functionalities and dimensions. The first point was addressed in the preceding section. Recently the second point was addressed by linking the octahedral zinc acetate SBU with dicarboxylate links of varying length and ring substituents. Sixteen isoreticular structures (having the same network topology) have been synthesized using exactly the same synthetic parameters except for the addition of the desired link (Fig. 3).[15]

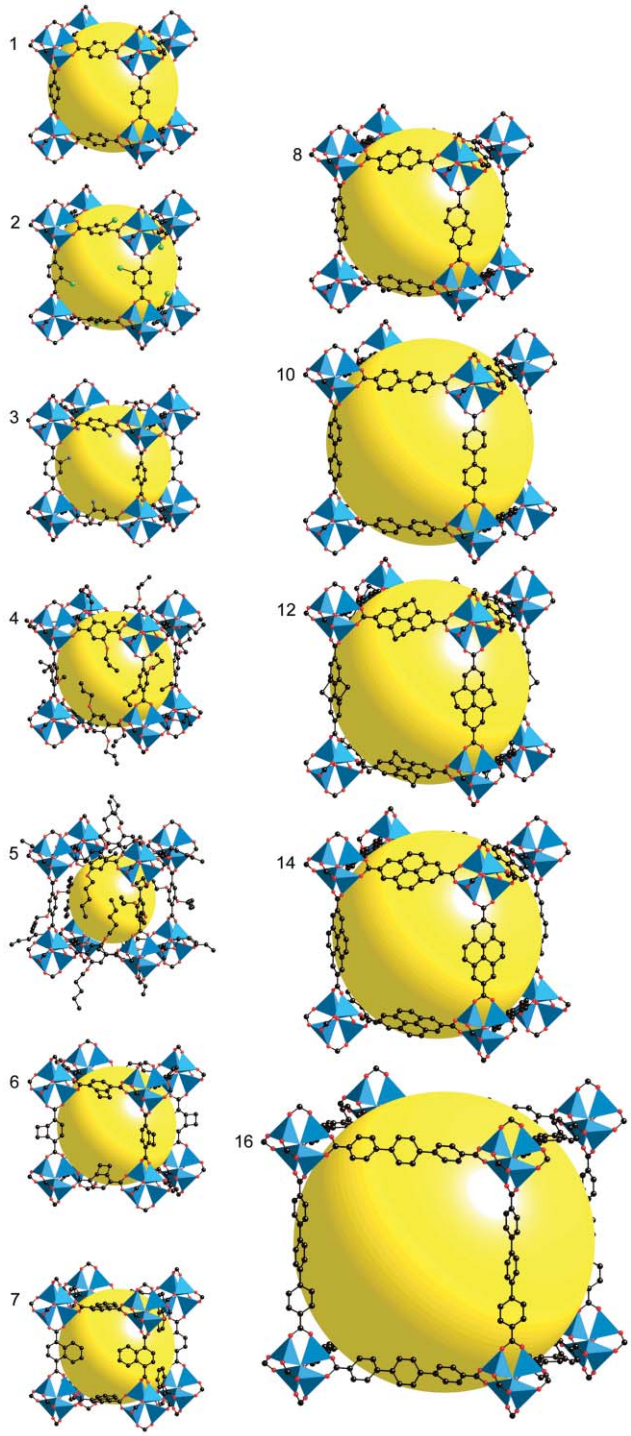

Fig. 3 Isoreticular MOF-1–16.

IV. Porosity

It was clear to us as we moved away from using nitrogen-containing links (such as bipyridine) to carboxylates that rigid metal carboxylate building blocks (SBUs) when combined with rigid organic links yield frameworks that maintain their porosity in the absence of guests. Indeed, MOF-2 was one of the earliest examples,[7] where removal of DMF guests from the pores gave a network that was shown to have permanent porosity. Since then we and others have prepared and reported at least ten MOF structures that exhibit similar porosity. Recently, we reported the single crystal structure of an evacuated framework that had been heated up to 300 °C in air to show no degradation of the MOF structure.[8] Porous MOFs are intrinsically different than traditional porous

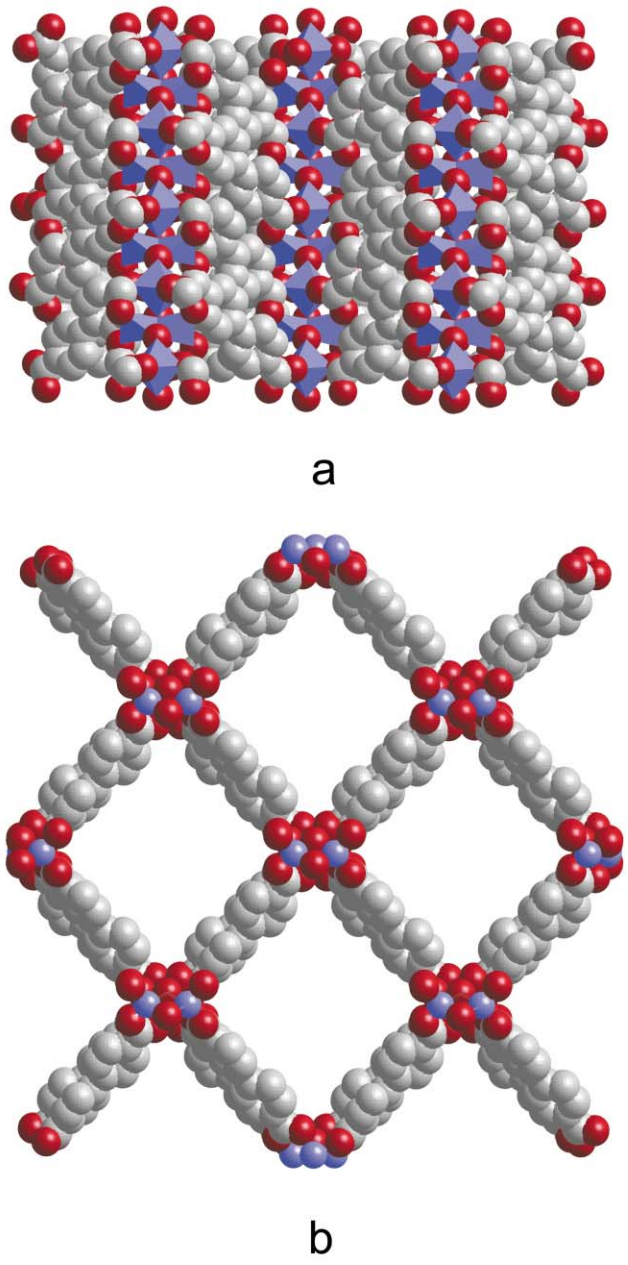

Fig. 4 (a) Impenetrable walls of MOF-69, [100] direction, (b) open channels of MOF-69, [001] direction.

crystalline materials such as zeolites and other molecular sieves, in that MOFs have no walls, so their internal volume is instead based on connected columns (scaffolds), an aspect that provides for remarkably high surface areas and pore volumes in excess of double those found in zeolites. These attributes coupled to our ability to functionalize the pores are ideally suited for facile diffusion in catalysis and also in the high capacity storage of fuel gases such as methane and hydrogen.

V. Catenation

Catenation, in the form of interpenetrating and interweaving, has been discussed in the literature as detrimental to the synthesis of low density (porous) structures due to the following: (a) the use of long links for the design of frameworks with large pores results in highly catenated frameworks and thus small pores, (b) highly catenated frameworks typically have low porosity ($<20\%$), and (c) catenation negatively impacts the structural stability and porosity of open frameworks. We recently found that *discrete* secondary building units (SBUs) are important for designing structures with attributes that disprove the universality of (b) and (c). Specifically, maximally interpenetrating MOFs have been shown to have highly porous ($>65\%$) structures, and interweaving in open frameworks has been recognized and used for the design of structures with reinforced walls and permanent porosity.[10,16] In more recent studies, we point out that (a) appears to be dependent on the intrinsic topology of the network such that certain frameworks are found to be well suited for use of expanded links due to either forbidden catenation resulting from steric factors or to a different coordination geometry of the dual structure.[14,17] MOF-69 (Fig. 4) is a representative framework wherein steric factors prohibit catenation. In this structure, the infinite Zn–O–C columns (Fig. 4a) arrange the 4,4′-biphenyldicarboxylate (BPDC) linkers close together in the [001] direction, resulting in an impenetrable wall glued together with close CH$\cdots\pi$ interactions between the BPDC links. For this structure to catenate, an additional BPDC would have to fit between adjacent links, which is metrically impossible and thus results in a structure that both forbids catenation and exhibits large 1-D channels in the [100] direction (Fig. 4b).

Acknowledgements

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