

Reticular synthesis and the design of new materials

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The long-standing challenge of designing and constructing new crystalline solid-state materials from molecular building blocks is just beginning to be addressed with success. A conceptual approach that requires the use of secondary building units to direct the assembly of ordered frameworks epitomizes this process: we call this approach reticular synthesis. This chemistry has yielded materials designed to have predetermined structures, compositions and properties. In particular, highly porous frameworks held together by strong metal–oxygen–carbon bonds and with exceptionally large surface area and capacity for gas storage have been prepared and their pore metrics systematically varied and functionalized.

Although the synthesis of new materials has long been recognized as the most essential element in advancing technology, it generally remains more of an art than a science—in that the discovery of new compounds has mostly been serendipitous, using methods referred to by critics as ‘shake and bake’, ‘mix and wait’ and ‘heat and beat’. For much of the twentieth century, this worked well for the synthesis of important solid-state materials, and we expect that it will continue to yield interesting compounds. However, it is becoming increasingly urgent to produce materials designed to perform highly specific and cooperative functions^{1,2}.

Recent extensive research into the design and synthesis of metal-organic frameworks (MOFs) has led to numerous practical and conceptual developments in that direction^{3–7}. Specifically, the chemistry of MOFs has provided an extensive class of crystalline materials with high stability, tunable metrics, organic functionality, and porosity. Here we present some of the important developments that have shaped this rapidly growing field and propose a general conceptual framework, which serves as a useful tool in designing materials constructed from molecular building blocks.

Reticular synthesis

General lack of control over the character of solids produced from the traditional synthetic methods is directly related to the fact that the starting entities do not maintain their structure during the reaction, leading to poor correlation between reactants and products. We have shown that the design of an extended network can be realized by starting with well-defined and rigid molecular building blocks that will maintain their structural integrity throughout the construction process^{3,8}. Alternatively, the use of well-defined conditions that lead to the formation of such building blocks *in situ* is an equally viable approach to the design of extended structures and one that has been especially fruitful in MOF chemistry⁸. We have shown^{8,9} that the practice of logical synthesis must begin with knowledge of the target network ‘blueprint’ and identification of the required building blocks for its assembly. This process is central to our ability to achieve true design of solid-state materials: we refer to its implementation as reticular synthesis.

In essence, reticular synthesis can be described as the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding. It is different from retrosynthesis of organic compounds¹⁰, because the structural integrity and rigidity of the building blocks in reticular synthesis remain unaltered

throughout the construction process—an important aspect that could help to realize fully the benefits of design in crystalline solid-state frameworks. Similarly, reticular synthesis should be distinguished from supramolecular assembly¹¹, because in the former, building blocks are linked by strong bonds throughout the crystal.

In this context, it is worth noting that a plethora of extended structures successfully prepared by copolymerization of metal ions with organic links have been reported and reviewed under the rubric of ‘crystal engineering’, a term which has mutated somewhat over the years and which is now rather broadly defined^{12–14}. We use the more precise term reticular synthesis (or chemistry) to describe the logical approach to the synthesis of robust materials with pre-designed building blocks, extended structures, and properties. Thus, it might be considered a subclass of crystal engineering.

Research in the area of MOFs and, to a lesser extent, inorganic frameworks, has recently progressed far enough to provide examples which show the feasibility of the building-block approach and the scope of reticular synthesis. Here we take selected examples to highlight the ideas involved, with emphasis on our own work on MOFs in which structural and thermal stability characterization have been combined with in-depth studies of surface area and gas sorption capacities. The subject of metal-organic frameworks has a long history, however, so we begin by giving some perspectives on the field.

Perspectives and challenges

The Cambridge Structure Database (CSD) documents the crystal structures of more than 11,000 extended metal-organic compounds in which a metal ion or cluster has been linked by an organic moiety in which the linking functionality is a cyanide, pyridyl, phosphate or carboxylate. Of these, nearly 3,000 compounds have three-dimensional (3D) structures and about double that number have 2D structures. MOFs composed of the first-row transition metals and organic links such as cyanide^{15,16}, glutamate¹⁷, formate¹⁸, triazole¹⁹, oxalate²⁰, 1,2,4,5-tetracarboxylates²¹ and squarates²² have long been known. Also, expanded diamond structures based on linking of Cu(I) with ANT²³, DCNQ²⁴ and TCTPM²⁵, and decorated diamond structures based on linking Mn(II) with Ge₄S₁₀⁴⁻ (T2) clusters⁹ (see Box 1 for abbreviations of chemical names and clarification of terms) represent the numerous forerunners of the extended structures constructed from molecular building blocks. Subsequently, other compounds based on linking metal ions with ADC²⁶, ETC²⁷, INT²⁸, BPY^{29,30} and BPCN³¹ have been reported. Tetrahedral building blocks such as HMT³² and

MCP³³ have been linked by metal ions to form decorated diamond structures, while TPY³⁴ and ATC³⁵ are examples of links pre-designed so that their assembly into diamond networks is done by linking through hydrogen bonding.

Consideration of this range of crystal structures, in particular those of MOFs, has led us to identify two critical questions for reticular synthesis. First, of the almost unlimited possible networks, which can be expected to form and how can they be synthesized?

Box 1

Definitions and structures

Here we define some terms and illustrate organic species referred to in the text by abbreviations in the Box 1 figure.

Reticular: (adjective) having the form of a (usually periodic) net.

Isoreticular: Based on the same net (having the same topology).

MOF-*n*: Metal-organic framework (with *n* an integer assigned in roughly chronological order).

IRMOF-*n*: Isoreticular MOF (with *n* an integer referring to a member of the series).

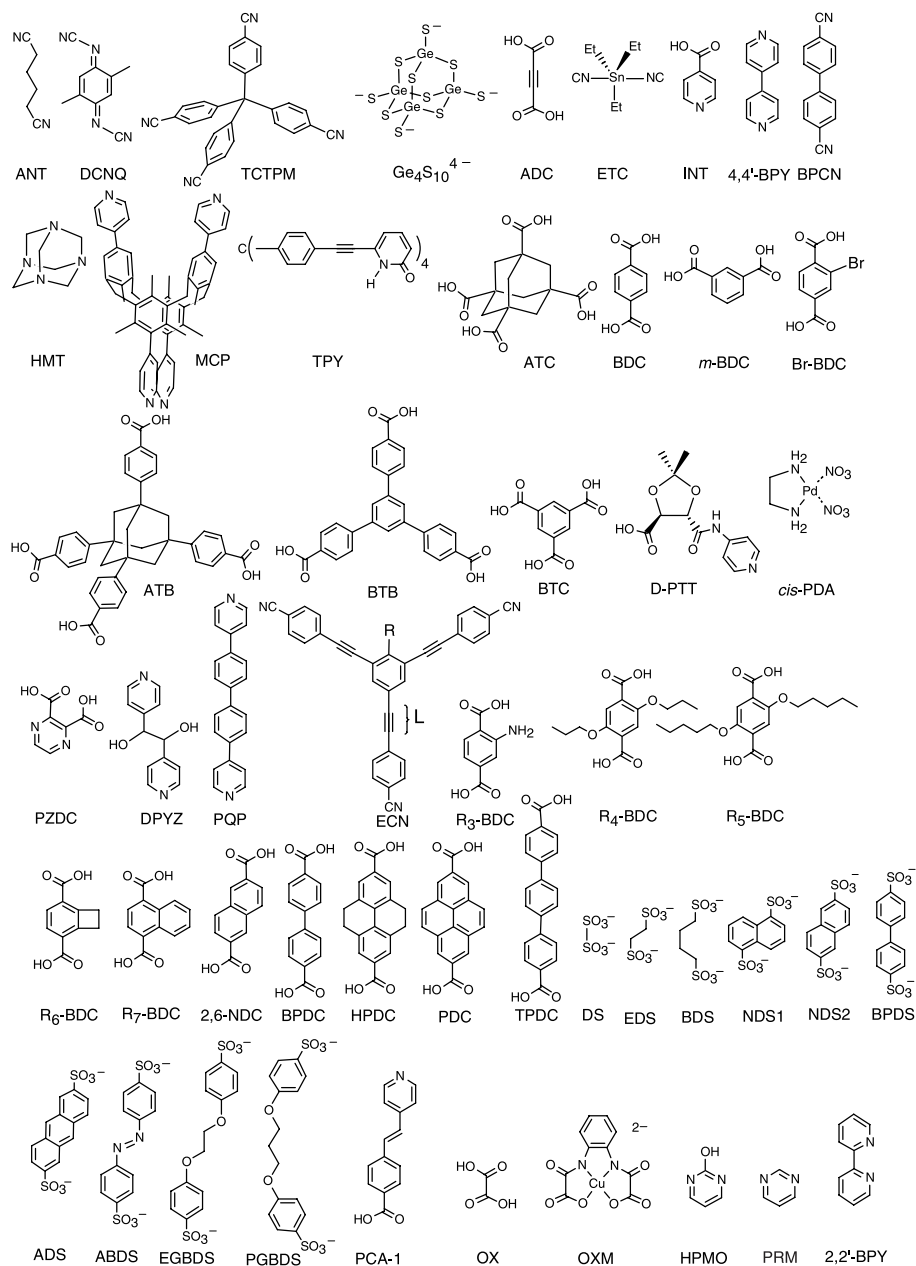
Interpenetration: A term used to describe the mutual intergrowth of two or more networks in a structure where the networks are physically

but not chemically linked. See refs 4 and 8 for reviews on this property.

Expansion: Increasing the spacing between vertices in a network.

Decoration: Replacing a vertex in a net by a group of vertices.

SBU: The term 'secondary building unit' has been used for some time to describe conceptual fragments of zeolites; in the context of reticular chemistry it refers to the geometry of the units defined by the points of extension (such as the carboxylate C atoms in most carboxylate MOFs).



Second, with few exceptions, MOFs based on M-N linkages in which the vertex of the network is just a single atom have a tendency to form structures which collapse upon removal of ‘guest’ atoms from the pores, rendering the structure nonporous. How then can we ensure that our structures will be robust?

Secondary building units

To address these questions it is important to first appreciate that it is difficult (although not impossible) to attempt *a priori* synthesis of structures, such as those presented above, from simple metal ions and organic links because ions hold little directional information. This relative lack of directionality often results in flexibility around the metal ion, a multiplicity of possible structures and a general lack of control—as exemplified by frameworks based on Cu ions and bipyridine and related links^{13,36–42}. We have focused on using the carboxylate functionality to chelate metal ions and lock them into rigid and thus directional metal–oxygen–carbon clusters, with the

points of extension (in this example, carboxylate C atoms) defining geometrical shapes referred to as secondary building units (SBUs)²⁶. The successful design of rigid frameworks based on such SBUs was demonstrated for the first time in MOF-2 (see ref. 43 and below) and MOF-5⁴⁴. The design principles employed for MOF-5 will be discussed here to show that SBUs have intrinsic geometric properties that facilitate network design and help us to address the issues of network synthesis and robustness.

In MOF-5 (Fig. 1a), $\text{Zn}_4\text{O}(\text{CO}_2)_6$ units containing four ZnO_4 tetrahedra with a common vertex and six carboxylate C atoms that define an octahedral SBU are joined together by benzene links. This leads to a cubic network in which the vertices are the octahedral SBUs and the edges are the benzene struts. In practice, this compound was prepared from Zn(II) and BDC acid under conditions pre-determined to yield the octahedral SBU *in situ*. Because the SBU and benzene links are relatively large and rigid entities, the structure produced has exceptional porosity (indicated by its sorption), and stability (indicated by thermal analysis and single crystal X-ray diffraction studies on the completely evacuated framework^{8,44}).

The exceptional stability of MOF-5 can be understood by comparing its basic network, composed of single atom vertices (Fig. 1b), with the actual structure of MOF-5, which has cationic clusters at those vertices (Fig. 1a). The basic network has no resistance to shear if the links are considered to be universal joints. However, in the actual MOF-5 structure, the cationic clusters have a truncated tetrahedral envelope (Fig. 1c), and the rigidly planar $\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2$ linkers have a planar slat envelope. The linkage of these two groups produces an inherently rigid structure held together by mutually perpendicular hinges.

This approach, based on the concept of SBUs, has been useful in rationalizing the topologies of MOF structures²⁶, and more importantly, it has allowed the synthesis and use of a large number of inorganic and organic SBUs with varying geometries (Fig. 2)^{26,43–52}. In many of these cases, identifying the reaction conditions that produce an SBU with a specific geometry *in situ* means that the addition of a rigid organic SBU will result in the formation of a pre-determined network. In other words, with this strategy it is now possible to control the overall coordination number of the inorganic and organic SBUs, and therefore the need to identify the networks that are expected to form from different geometric shapes becomes particularly acute.

Possible framework topologies

Which framework topology can be expected to form is of critical importance because there are a large number of possible structures for each geometrical shape. For example, more than 100 different topologies (in addition to that of diamond)⁵³ are possible for linking tetrahedral building blocks together into structures with just one kind of vertex (that is, all vertices related by symmetry), and the would-be designer must find some criteria for deciding which will be selected.

We have recently argued that in general only a small number of simple, high-symmetry structures will be of overriding general importance, and they would be expected to form most commonly⁵⁴. We call these default structures, in that they would be expected to form if the assembly reaction involved simple building blocks, especially single atoms (ions) joined by flexible linkers. More complicated structures can be targeted by judicious use of appropriately shaped SBUs and linkers (we give examples below). A list of some default structures⁵⁴ and some criteria for their classification^{55–60} are given in Box 2.

We have undertaken a systematic survey⁵⁹ of structures with the goal of design in mind. There are just six three-periodic structures with one kind of vertex, edge and ring—we call these regular and quasi-regular. The next most regular are those with just one kind of link. Their enumeration is mostly straightforward and—together

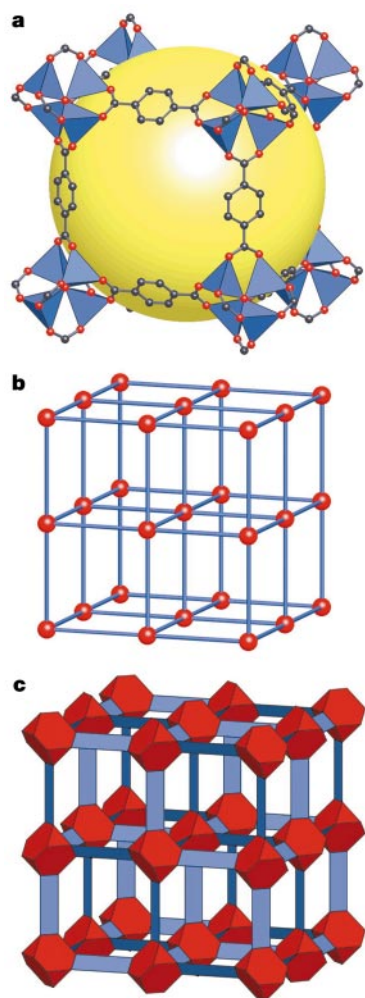


Figure 1 The MOF-5 structure and its topology. **a**, The MOF-5 structure shown as ZnO_4 tetrahedra (blue polyhedra) joined by benzene dicarboxylate linkers (O, red and C, black) to give an extended 3D cubic framework with interconnected pores of 8 Å aperture width and 12 Å pore (yellow sphere) diameter. (Yellow sphere represents the largest sphere that can occupy the pores without coming within the van der Waals size of the framework). **b**, The topology of the structure (primitive cubic net) shown as a ball-and-stick model. **c**, The structure shown as the envelopes of the $(\text{OZn}_4)\text{O}_{12}$ cluster (red truncated tetrahedron) and benzene dicarboxylate (BDC) ion (blue slat). Note that opposing slats are all at 90°.

with the regular structures—they are the most common structures used in reticular chemistry, because one almost always attempts a synthesis with just one kind of linker. As an illustration, we⁴⁸ have enumerated the nine principal ways in which square SBUs can be joined by equal linkers to form polyhedra, rods, layers or three-dimensional nets. In the next section we show how this enumeration allows particular linked-square structures of each different dimensionality to be successfully targeted for synthesis using appropriately shaped linkers.

Design and synthesis of pre-determined frameworks

As we noted above, metal-containing (cationic) SBUs are not isolatable entities, and so it has been essential to establish the exact chemical conditions that will yield a specific SBU *in situ*. On the other hand, organic (anionic) SBUs are pre-assembled

using the considerable sophistication of organic synthetic methods¹⁰—see Box 1 and Fig. 2 for examples. For a given cationic SBU the geometry of the organic unit plays an important role in directing the structure. This is illustrated (Fig. 3) for four structures^{41,61–63} of different dimensionality (periodicity—0-D refers to an object within only point symmetries): a truncated cuboctahedron (0D), a linear rod (1D) the square grid (2D), and the NbO network (3D) based on linkage of paddle-wheel clusters by ditopic linkers. The dihedral angle between the paddle wheels (square SBUs) plays a crucial role in determining which one of these structures will be produced. The reaction conditions that would yield the paddle-wheel clusters were used in the presence of the appropriate link, to give the desired structure—which is in each case the only possible structure given identical linkers of the shape indicated.

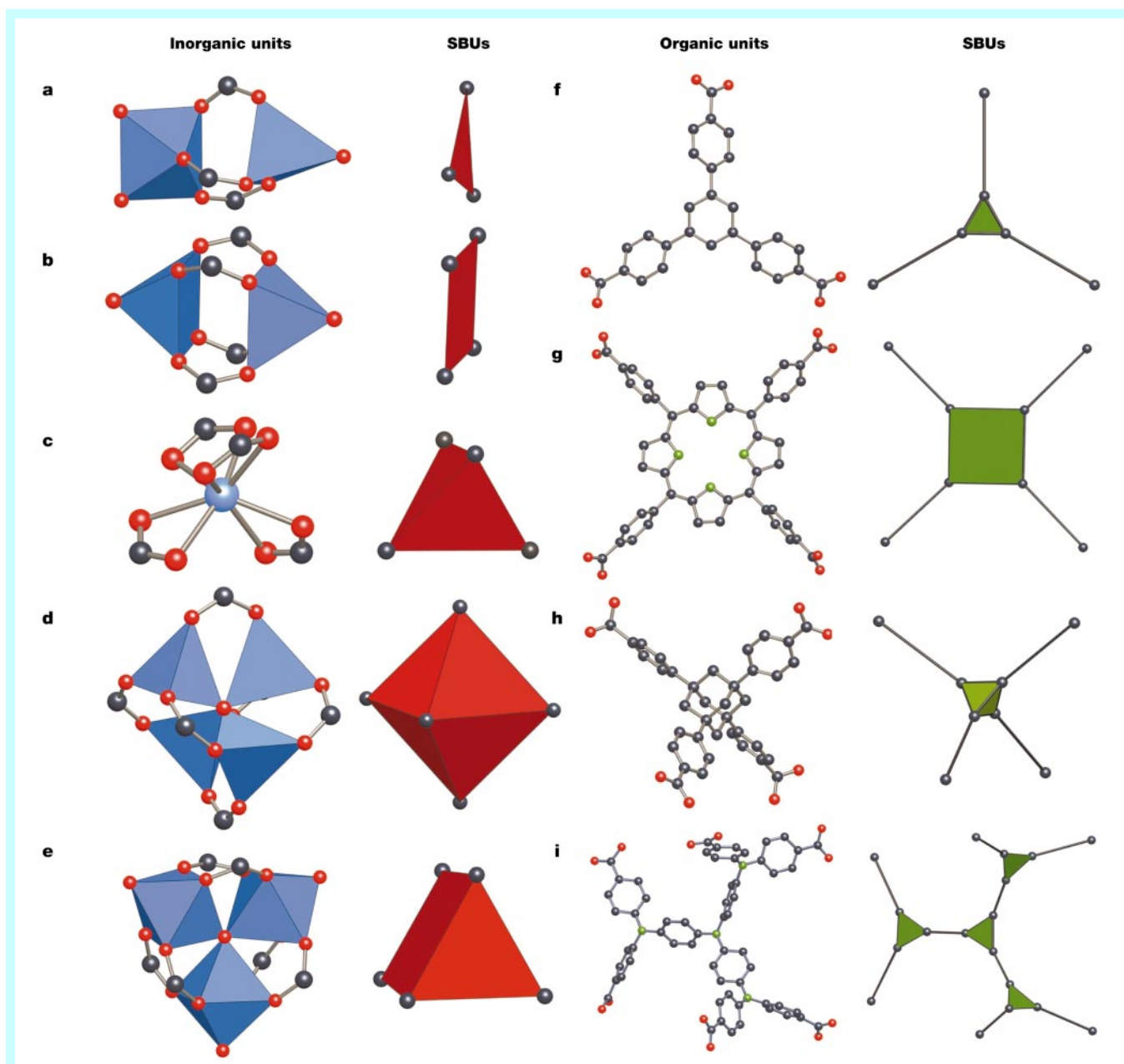


Figure 2 Examples of SBUs from carboxylate MOFs. O, red; N, green; C, black. In inorganic units⁹ metal-oxygen polyhedra are blue, and the polygon or polyhedron defined by carboxylate carbon atoms (SBUs) are red. In organic SBUs the polygons or polyhedra to which linkers (all $-\text{C}_6\text{H}_4-$ units in these examples) are attached are

shown in green. The geometry for **i** is an example of a tertiary building unit⁵² consisting of four SBUs (green triangles). The carboxylate carbons of this unit are at the vertices of a trigonal prism.

This approach can be used in linking together other SBU shapes. For example, the PtS net is the default structure for linking squares (Pt) and tetrahedra (S). Assembly of the paddle wheel with ATC and ATB (tetrahedral SBUs) yields MOF-11⁵¹ and MOF-36²⁶, which are indeed based on the PtS net. There are only two ways of linking square and triangular SBUs—these are the nets named for Pt₃O₄ and ‘twisted boracite’—and they might both be considered default structures⁵⁴ (Box 2). Again, linking a copper-based paddle wheel with triangular SBUs, either BTB or BTC, gives MOF-14⁴⁹ with the Pt₃O₄ topology and HKUST-1⁶⁴ with the twisted boracite topology, respectively. Examination of the parent nets shows that the simpler Pt₃O₄ net requires the more flexible BTB links.

The regular (and hence default) structure for linking triangles is the chiral 3D Si network in SrSi₂, which has been a target of reticular synthesis^{45,65}. Interestingly, it is composed of achiral triangular vertices, which twist with respect to adjacent like vertices by a dihedral angle of 70.5° to make an overall chiral arrangement. This topology was assembled from BTC and Zn(II) under conditions

that give a propeller-shaped binuclear M₂(CO₂)₃ SBU (Fig. 2a)⁴⁵. Here, three carboxylate C atoms of the SBU are twisted with respect to the C atoms on the benzene ring to give chiral crystals although the bulk material is racemic. Recently, it has been demonstrated that an enantiopure MOF can be prepared from a derivative *D*-tartaric acid (*D*-PTT) and Zn(II) to give a triangular SBU, which formed a hexagonal layered network⁶⁶ that was functionalized with pyridine units to allow the pores to be used for chiral catalysis.

It is worth noting that exquisite control over the outcome of reticular synthesis has also been developed using site-blocked metal complexes that express angular information. For example, *cis*-PDA provides 90° binding angles such that with linear ditopic organic links such as BPY⁶⁷, the nitrate ligands are displaced by BPY, leading to molecular squares. On the basis of this approach other metal complexes of various binding angles and a variety of branching and bent organic links have been used in the design of other polygons, platonic and archimedean polyhedra^{61,68–71}.

Box 2

Framework topologies

The topology underlying periodic structures is that of a periodic net. Crystal chemists, particularly Wells¹⁵, have laboured to enumerate, describe and classify such nets. We⁵⁸ find the approach based on tiling to be particularly fruitful^{55,66}. The tiles are generalized polyhedra (cages) which generate the entire structure when packed together. For each periodic net there is a unique ‘natural’ tiling⁵⁸; examples are shown in Fig. 5. The adamantane unit with ten vertices is the natural tile of the diamond net. Its four faces are six-membered rings, which we symbolize as [6⁴]. The natural tiling of the lonsdaleite net has equal numbers of two tiles that are [6³] and [6⁵] (Fig. 5).

To classify nets we make use of the transitivity of the structure⁵⁷. If there are *p* kinds of vertex, *q* kinds of edge (link), *r* kinds of ring (faces of tiles) and *s* kinds of tile, the transitivity is *pqrs*. It turns out⁵⁸ that the five structures whose natural tilings have transitivity 1111 have coordination figures that are regular polygons or polyhedra and we call them ‘regular’ (see Table 1). Their importance in reticular synthesis is comparable to that of the five platonic solids in other areas of chemistry. Structures 1112 are called ‘quasiregular’ and structures 11rs are ‘semiregular’. These are the structures that are most likely to form with one kind of SBU joined by one kind of link. They can be enumerated fairly easily and there are only about twenty

of them (the exact number depends on some subtle details of what we consider to be allowable structures). There are another twenty or so structures with two vertices and one edge. Structures with just one kind of edge (edge transitive) are the most reasonable targets of designed reticular synthesis, and thus the most important from that point of view. Even these approximately 50 structures can quickly be reduced to a smaller number. For example, there are seven edge-transitive nets with tetrahedral vertices (examples are given in Table 1) but the diamond net is the most regular, and thus the default net for tetrahedral coordination.

Of course less regular nets can be forced by low-symmetry SBUs. For example, 5-coordinated SBUs cannot be linked by just one kind (that is, symmetry equivalent) of link. Two simple examples are given in Table 1. There is only one 3-coordinated 3D net with symmetry that requires the coordination figure to be an equilateral triangle (that of SrSi₂—see Table 1). The use of 3-coordinated SBUs with a T or Y shape can accordingly lead to a lower-symmetry net such as that of Si in ThSi₂ (also listed). The formation of the rutile net instead of the more symmetrical pyrite net in (6,3)-coordinated structures is often ascribable to similar causes.

Table 1 Some important nets and their natural tilings

CN	LC	Name	Vertex figure	Transitivity	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	cl	Body-centred cubic	Cube	1111	[4 ⁴]
12	cF	Face-centred cubic	Cuboctahedron	1112	2[3 ⁴] + [3 ⁸]
3		ThSi ₂	T or Y	1211	[10 ⁴]
4		CdSO ₄	Square	1221	[6 ² , 8 ²]
4	W*	Sodalite	Tetrahedron	1121	[4 ⁸ , 6 ⁸]
4	Q	Quartz	Tetrahedron	1121	[6 ² , 8 ²]
4		Lonsdaleite	Tetrahedron	1222	[6 ³] + [6 ⁵]
6	E		Trigonal prism	1122	2[4 ³] + [4 ³ , 6 ²]
5		CaB ₆	Square pyramid	1222	[3 ⁷] + [3 ² , 4 ⁹]
5		BN	Trigonal bipyramid	1221	[4 ⁵ , 6 ²]
6		Polybenzene	Hexagon	1121	[4 ⁸ , 6 ⁴]
4,8		Fluorite (CaF ₂)	Tetrahedron, cube	2111	[4 ¹²]
3,6		Pyrite (FeS ₂)	Triangle, octahedron	2112	2[6 ³] + [6 ⁶]
3,6		Rutile (TiO ₂)	T or Y, octahedron	2232	2[4, 6 ²] + [6 ² , 8 ²]
3,4		Pt ₃ O ₄	Triangle, square	2122	3[8 ⁴] + 2[8 ⁸]
3,4		Boracite	Triangle, tetrahedron	2122	[6 ⁷] + [6 ² , 8 ⁶]
4,4		PtS	Square, tetrahedron	2122	[4 ² , 8 ²] + [8 ⁴]
6,6		NiAs	Prism, octahedron	2122	[4 ³] + [4 ⁹]

CN is the coordination number of the vertices. LC refers to the symbol for invariant lattice complexes⁵⁹. The transitivity is defined in the text, and the entries under ‘tiles’ are the face symbols of the tiles. The first six rows are the five regular and one quasi-regular tilings. For illustrations of these nets see refs 54 and 60.

A new class of porous materials

We have just argued that the rigidity and directionality of SBUs provide a means for the logical synthesis of a wide variety of frameworks. An important aspect of this approach is that the large sizes of SBUs inevitably lead to there being spaces within these structures where solvent and/or counter-ion guests reside. In many cases, such solids are interchangeably referred to as “porous” and “open-framework”, without definitive proof of porosity⁷². We prefer to categorize them according to the mobility of the species occupying their cavities. It is inaccurate to use the term ‘open framework’ to refer to any low-density or large-scale structure, because ‘open’ implies allowing passage. We note that in many cases this property is absent (or at least undetermined in the structure in question) because passage is hindered by solvent molecules that form strong interactions with the framework; as a result, such solvent molecules are necessary to maintain the crystal architecture.

Thus we consider that ‘porous’ implies having pores, and pores

are, in the Oxford English Dictionary definition, a “minute... opening... through which fluids or gases can pass”. In addition, demonstration of porosity through gas sorption isotherms is necessary to prove permanent porosity. Indeed, we find that MOFs having structures based on inorganic SBUs are exceptionally porous with pore diameters and volumes which exceed those of the most porous and useful zeolites as shown in Fig. 4^{73–84}.

Two important attributes of porous MOFs account for their structural stability and high porosity. First, they are essentially scaffoldings with all or most atoms on internal surfaces, which lead to the highest known surface areas ($2,900\text{ m}^2\text{ g}^{-1}$) and pore volumes ($1\text{--}2\text{ cm}^3\text{ g}^{-1}$). In other porous solids such as zeolites and molecular sieves the interior of the pores is largely composed of walls leading to relatively lower specific capacity for sorption.

Second, in contrast to frameworks of the metal bipyridine type, which are known to collapse upon removal of guests, MOFs constructed with oxide SBUs are far more robust, owing to the

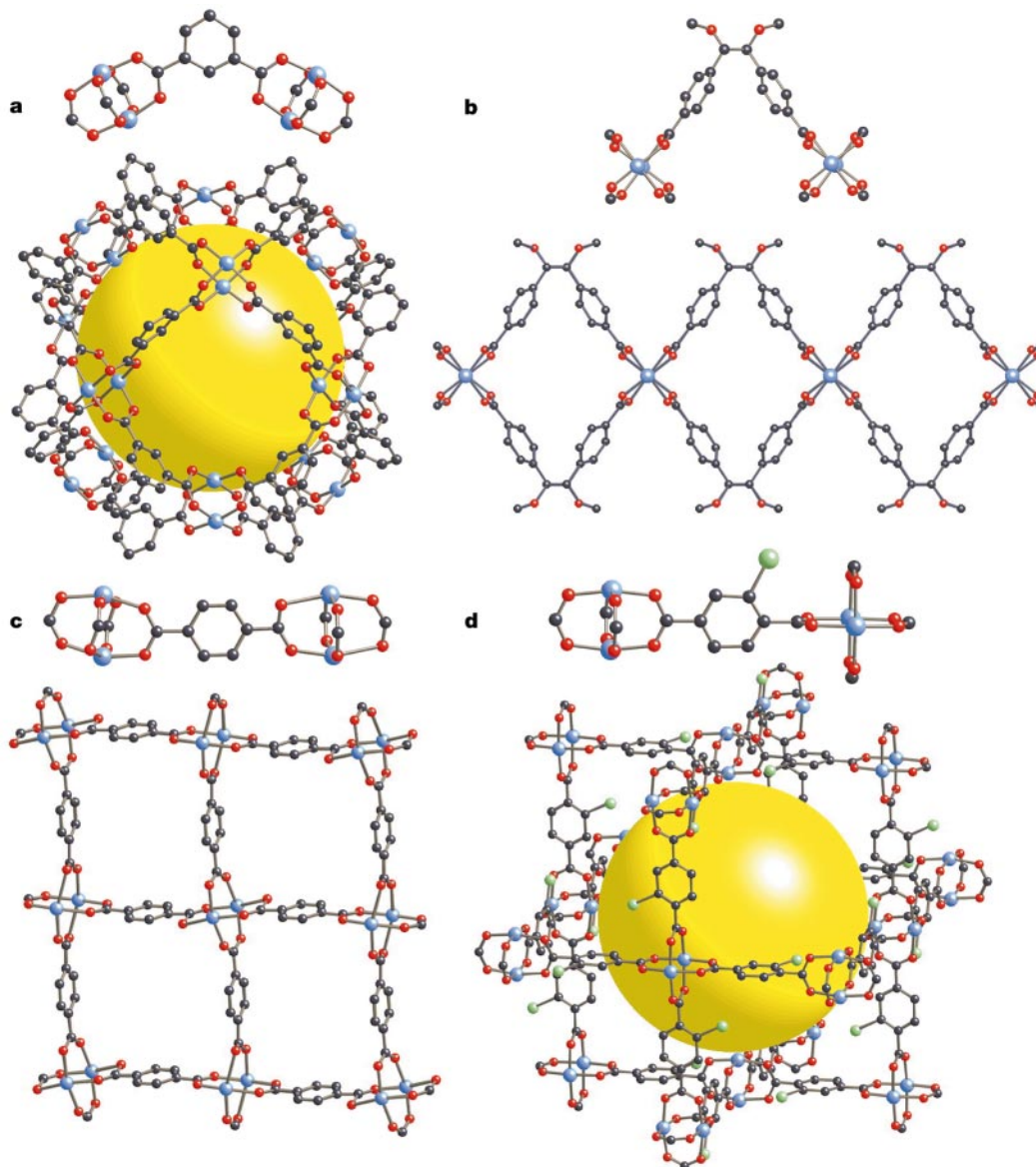


Figure 3 The control of dimensionality of linked paddle-wheel units by use of precise linker geometry. Shown are fragments of the assembled structures of MOP-1⁶¹ (a), MOF-222 (Chae, H.K., Rowsell, J.R., O’Keeffe, M., Yaghi, O.M., to be published) (b),

MOF-242 (c) and MOF-101⁶³ (d). C, black; O, red; Br, green; metal, blue. Above each structure, one linker is shown joined to two paddle-wheel units. The yellow spheres are at the centres of large cavities in the structures of MOP-1 and MOF-101.

presence of strong metal–oxygen bonds. For example, in MOF-5 each link to an octahedral SBU involves two Zn–O bonds with energy of 360 kJ mol^{-1} per pair (based on the heat of formation of ZnO)⁸⁵ comparable to the C–C bond energy of 358 kJ mol^{-1} in diamond. The corresponding energy for two Cu–O bonds (as in linked paddle wheels) is 372 kJ mol^{-1} . In contrast, we estimate from the heats of formation of ammoniates such as $\text{CuCl}\cdot 3\text{NH}_3$ and $\text{CuCl}_2\cdot 2\text{NH}_3$ that the energy of the Cu(I)–N coordination bond is about 55 kJ mol^{-1} and the Cu(II)–N bond is about 90 kJ mol^{-1} : very much weaker, and indeed the weak link in metal-bipyridine type frameworks.

Frameworks with adjustable metrics and properties

An important step forward has been the use of expanded links such as ECN which can be linked into MOF structures in which the pores can be functionalized by modifying R⁸⁶, and expanded by lengthening L (see Box 1). When assembled with Ag(I) this link gives networks based on the Si network in ThSi_2 (Box 2). It is interesting to note that the unfunctionalized (R = H) link also gives the same network. This finding indicates that the presence of functional groups (R) does not alter the course of reticulation. In other words, all frameworks produced by this method are isorecticular (having the same network topology). These compounds have not been shown to have permanent porosity or rigid frameworks, which is not surprising as they are not based on vertices of clusters (SBUs), but rather on single Ag ion vertices, which do not provide for the prerequisite rigidity.

On the other hand, frameworks isorecticular with MOF-5 have been synthesized with functionalized structures and shown to have permanent porosity. Employing each of the links: *o*-Br-BDC, R₃-BDC, R₄-BDC, R₅-BDC, R₆-BDC, R₇-BDC, 2,6-NDC, BPDC, HPDC, PDC and TPDC instead of BDC yielded IRMOF-2 to IRMOF-16, including the non-interpenetrating structures of BPDC, HPDC, PDC and TPDC. Each member of the IRMOF series has been isolated and characterized by single-crystal X-ray

diffraction studies⁸². The key element in synthesizing this series was to use the acid form of the link under reaction conditions known to form the octahedral SBU. In this series, the per cent free volume in crystals varies in small increments (1 to 5%) starting from 55.8% (R₅-BDC) to an exceptional 91.1% (TPDC).

It is worth noting that the lowest per cent free volume obtained in this series exceeds that found in some of the most open zeolites (Fig. 4) in which the free space is 45–50% of the crystal volume. In fact, the fraction of free space in crystals of the most expanded member (TPDC) of this series has only been achievable in non-crystalline porous systems such as SiO_2 xerogels and aerogels⁸⁷. Furthermore, the calculated crystal densities (in the absence of guests) of these materials also vary in small increments (around 0.1) in the range 1.00 g cm^{-3} (R₅-BDC) to 0.21 g cm^{-3} (TPDC) having densities, which are the lowest reported for any crystalline material. In comparison, the density of Li metal is 0.56 g cm^{-3} . The ability to control and incrementally vary the metrics in this series has important technological implications. It has already been shown that the specific uptake of fuel gases such as methane in one member (R₆-BDC) of the series is the highest known at present and comes close to meeting Department of Energy guidelines for use of natural gas in mobile applications.

In cognate work an isorecticular series based on lamellar G and S (guanidine-sulphonate) hydrogen-bonded materials has been achieved by varying the sulphonate functionality from DS-PGBDS (Box 1). Although these frameworks do not have permanent porosity as in MOFs, they provide advantages for selective crystallization-based separations⁸⁸.

In addition to providing rigidity and structure information, SBUs can also impart physical properties to the framework. In the examples based on the paddle wheel and other binuclear clusters, the axial ligands are weakly bound to the porous framework, allowing their removal by heating or evacuation. The resulting open metal sites act as molecular imprints and site-isolated units⁵¹, exhibiting highly selective binding of organic molecules and, in the case of Tb(III), luminescent behaviour that has formed a basis for sensing small molecules⁷⁴.

Although porosity is almost an inevitable outcome of the SBU approach, other MOFs that have not been examined for their porosity have shown other interesting properties. Acentric SBUs can be assembled into MOFs having nonlinear optical properties, as illustrated for PCA-1⁸⁹. Here, a triangular SBU is linked by PCA-1 to give a decorated honeycomb-type framework. Similar frameworks have been designed using paramagnetic metal ions to produce ferromagnetic MOFs: links such as OX and OXM serve as magnetic coupling bridges in 2D ferromagnetic frameworks^{90,91}. Recently, 3D magnetic frameworks have also been targeted using Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Cr(III) metal ions and CN^{92} , $\text{C}(\text{CN})_3^{93}$ and $\text{Re}_6\text{S}_8(\text{CN})_6^{94}$ links to produce rutile and Prussian-blue type solids. A mixed-valence conductive framework based on BDC has been constructed from V(III/IV)⁸⁰, in which infinite vanadium oxide SBUs lead to the same SrAl_2 topology found for MOF-69⁹⁵.

Logic of synthesis by design

On the conceptual level, the underlying process for logical synthesis of MOFs starts with the designer choosing a specific target network, which is then deconstructed into its component geometric units. Molecular building blocks with the same geometry as those of the units are then assembled into a MOF structure that has the target network topology. The value of this approach is not limited to its utility in accessing a vast number of materials with predetermined structures: it also allows the designer to develop a deconstruction strategy for a target network. Such a deconstruction strategy becomes indispensable when designing non-default networks. This aspect is also addressed by reticular synthesis as shown in Fig. 5 for two basic networks; diamond and lonsdaleite ('hexagonal diamond')^{54,60}.

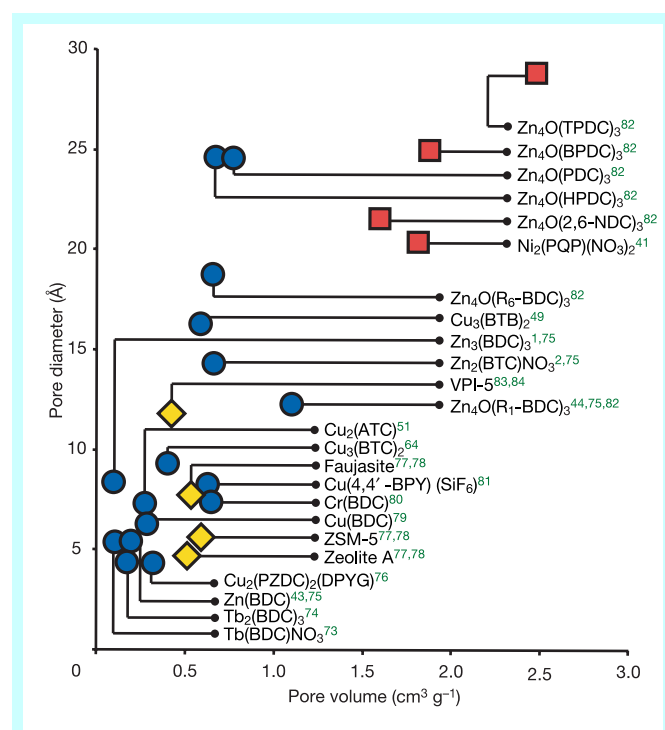


Figure 4 The porosity of MOFs compared to zeolites. Blue circles, sorption and crystal MOF structures; red squares, crystal MOF structures; yellow diamonds, some typical zeolites. Reference numbers (superscripted) are shown in green.

The designer of a material having these topologies would recognize that 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 (discussed above) obtained from simple tetrahedral building blocks are based on the cubic diamond network (Fig. 5a), which corresponds to the simplest, highest-symmetry structure (it is the only regular tetrahedral net) and unless the molecular building blocks contain information to the contrary, it is the default reticulation. Reticulations based on the lonsdaleite topology are rare.

We therefore investigated how reticular synthesis could be used to access non-default structures such as lonsdaleite. It is necessary to deconstruct its structure into more elaborate units that express structural features unique to its structure. Although the two structures are composed of fused six-membered rings, all such rings in diamond have the 'chair' conformation, whereas those in the hexagonal form assume both chair and 'boat' conformations as illustrated in Fig. 5. Thus it seems reasonable that to make frameworks based on lonsdaleite, the network should be deconstructed into units of fused chair and boat rings rather than of individual tetrahedra. In this way, the assembly of the corresponding molecular building blocks would yield exclusively the target network. We note that the above discussion does not preclude the possibility of achieving lonsdaleite from smaller units, if the structure formation were driven by the templating effect of included guest molecules⁹⁶ as described in the next section.

This treatment can be universally applied to the design of crystalline molecular arrays of any dimensionality. We emphasize that the achievement of complex low-symmetry topologies by design requires the construction of complex molecular building blocks coded specifically for those topologies.

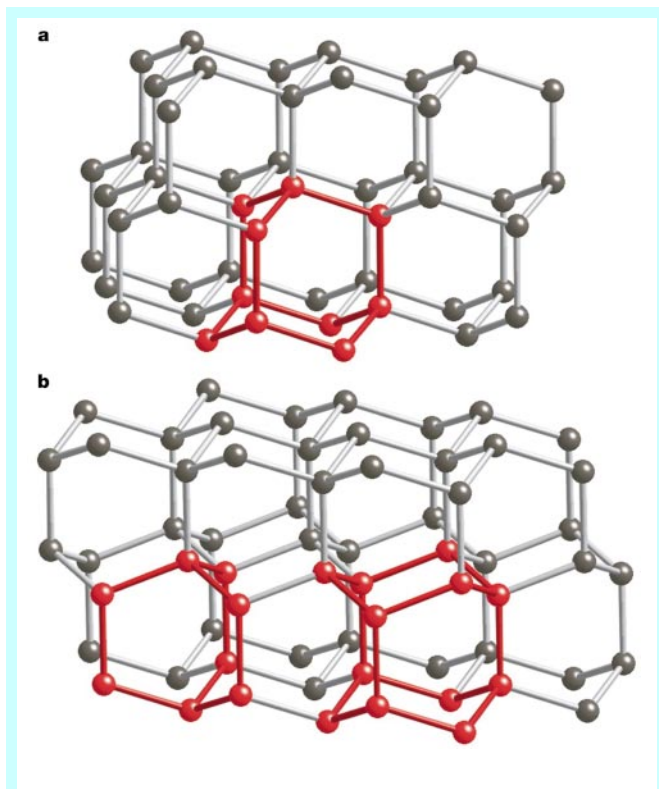


Figure 5 The deconstruction of diamond and lonsdaleite. **a**, diamond; **b**, lonsdaleite ('hexagonal diamond'). The units outlined in red are the natural tiles for these structures.

Complexity and non-default structures

The discussion so far has been limited to the design of frameworks in which the geometry of the links and/or vertices largely determines the outcome. In the formation of neutral frameworks, such as those of metal carboxylates, the role of the solvent in default structures is largely a space-filling one, although their function as structure-directing agents (templates) becomes more important in the design of networks where the building blocks have more than one possible default structure⁹⁶.

In particular, assembly of charged frameworks with counter ions requires careful matching of the charge, size and volume of counter ion to the charge per unit area of the target framework. This was illustrated in the assembly of T3 and T4 indium sulphide super-tetrahedra, whose tetrahedral symmetry leads not only to the default diamond-like frameworks⁹⁷, but also to the slightly less symmetric structures such as that of sodalite and the boron network in CrB_4 ⁹⁸. Here it is important to consider both the size and volume of the organic ammonium cations and the charge they provide per unit area of the prospective charged framework. We expect that similar factors must be considered to explain the formation of sodalite, feldspar and quartz MOF networks from tetrahedral Cu(I) and HPMO⁹⁹, PRM¹⁰⁰ and 2,2'-bpy³⁹, respectively. This analysis indicates that for some target non-default networks, elaborate units similar to those suggested for the reticular synthesis of lonsdaleite may not be the only option for their design.

Future prospects

Even with only the structures that are based on default networks, the immense wealth and scope of reticular chemistry has become apparent. In particular, design of the structural skeleton coupled with the ability to control its chemical functionalization and adjustment of its metric dimensions present exciting prospects. We have described here a conceptual approach to this subject, which we believe has proved useful, and which will continue to guide the designer.

Specific future challenges include the ability to design sophisticated molecular building blocks that would act as carriers of structural and functional information to be expressed in a specific target material. This will be of great benefit to many emerging technologies involving molecular electronics, miniature fuel cells, chiral catalysis and materials with hybrid properties. □

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