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Review

Metal–organic frameworks: a new class of porous materials

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Abstract

A review of the synthesis, structure, and properties of metal–organic frameworks (MOFs) is presented, highlighting the important advances in their research over the past decade. This new class of porous materials is attracting attention due to demonstrations of their large pore sizes, high apparent surface areas, selective uptake of small molecules, and optical or magnetic responses to the inclusion of guests. More importantly, their synthesis from molecular building blocks holds the potential for directed tailoring of these properties.
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Contents

1. Introduction

Traditionally, solids with outstanding properties such as high porosity have been produced by discovery-based synthetic chemistry. A logical and seemingly simple way to circumvent combinatorial searching for novel mate-rials is to link together molecular building blocks exhibiting the desired property. To produce a robust porous material one could envision constructing the equivalent of a "molecular scaffold" by connecting rigid rod-like organic moieties with inflexible inorganic clusters that act as joints. The size, and more importantly the chemical environment of the resulting void spaces are defined by the length and functionalities of the organic units. Accordingly, tailoring of the material's properties would be realized by the appropriate choice

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of starting materials. Employment of this strategy has yielded materials that not only exhibit selective adsorption of small molecules [1], but also inclusion of large molecules such as C_{60} [2]. Their construction has also highlighted another important consideration: it is not only the building blocks that are important, but the way in which they are connected. By studying how the building units reticulate (form a network), principles have been established that provide materials designers with a level of predictive capability [3].

2. Terminology

Over the past few decades a myriad of solids have been described that contain metal ions linked by molecular species. This collection of compounds has been variously termed metal–organic frameworks, coordination polymers, hybrid organic–inorganic materials and organic zeolite analogues with unavoidable overlap [4–8]. Each term carries its own connotation regarding which compounds it encompasses, and some attempts have been made in the literature to elucidate their definitions [9,10]. Some distinction may be drawn based on composition; solids constructed from large inorganic clusters connected with short ligands are often distinguished from compounds with isolated metal cations linked by elaborately designed organics. The term *coordination polymer* is undoubtedly the most nebulous, as it simply signifies the extended connection of metal and ligand monomers through coordination bonds with no regard towards the final structure or morphology.

For a solid to be labelled a *metal–organic framework*, it should display the inherent attributes that this term implies: strong bonding providing robustness, linking units that are available for modification by organic synthesis, and a geometrically well-defined structure. The latter property further implies that these solids should be highly crystalline, an important criterion for the precise establishment of structure–property relationships. One exciting result of this ever-increasing collection of crystal structures is the opportunity to deconstruct their often bewildering complexity and search for trends in connectivity [11–14]. In turn, this has lead to the identification of principles that govern the design and assembly of target frameworks (a strategy termed *reticular synthesis* [3], see below), demonstrations of which are largely non-existent outside of the MOF literature.

Similar to the synthesis of organic copolymers, the building blocks of a MOF are carefully chosen such that their properties are retained and exhibited by the product material. Whereas the nature and concentration of the monomers in an organic polymer determine its processability, physical and optical characteristics, it is the network connectivity of the building units that largely determines the properties of a MOF. These may include magnetic exchange, acentricity for non-linear optical (NLO) applications, or the definition of large channels available for the passage of molecules. The inclusion of chiral centers or reactive sites within an open framework are also active goals for generating functional materials. Consequently, MOF synthesis not only requires the selection and/or preparation of desired modules, but also some foresight as to how they will be assembled in the final solid. In order to aid the process of structure prediction, the concept of secondary building units (SBUs) as structural entities was adopted from zeolite structure analysis [15]. These are simple geometric figures representing the inorganic clusters or coordination spheres that are linked together by the (typically linear) organic components to form the product framework. Examples of some SBUs that are commonly encountered in metal carboxylate MOFs are illustrated in Fig. 1. Although many of these units have been observed in molecular species [16,17], they are generally not introduced directly, but are formed in situ under specific synthetic conditions. Conversely, branched organic links with greater than two coordinating functionalities constitute preformed SBUs. The success of an SBU in the design of open frameworks relies both on its rigidity and directionality of bonding, which must be reliably maintained during the assembly process.

The conceptual approach by which a metal–organic framework is designed and assembled is termed reticular synthesis and is based upon identification of how building blocks come together to form a net, or reticulate. It is hypothesized, and indeed observed for a large number of compounds, that the various network topologies adopted by MOFs are represented by only a small number of simple, high symmetry structures [13]. These have been likened to the nets underlying simple inorganic compounds, such as diamond, graphite, $SrSi_2$, and PtS. Foreknowledge as to which topology will be adopted by a given set of building blocks is particularly relevant to the development of porous materials, as it is precisely the expansion of these simple nets by the organic links that defines voids within the solid. Knowledge may also be gleaned about the likelihood of *catenation*, where two or more identical frameworks are intergrown at the expense of pore volume. This may take the form of *interpenetration* [18], where the networks are maximally displaced from each other, or *interweaving*, where they are minimally displaced and exhibit close contacts that may result in mutual reinforcement [19]. The former is commonly cited as one of the major obstacles that must be overcome in the development of a porous MOF. The possibility of either of these events is directly dependent on the network topology [20] or distortions thereof [21].
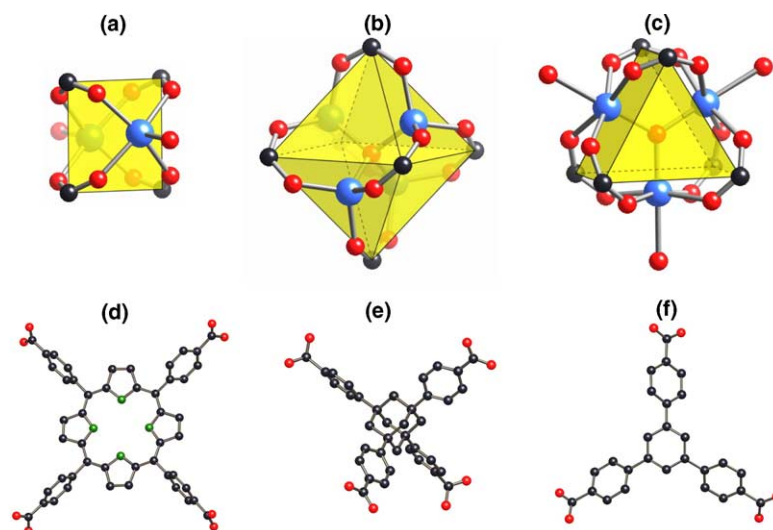
Fig. 1. Inorganic secondary building units (SBUs) commonly occurring in metal carboxylates include (a) the square ''paddlewheel'', with two terminal ligand sites, (b) the octahedral ''basic zinc acetate'' cluster, and (c) the trigonal prismatic oxo-centered trimer, with three terminal ligand sites. The SBUs are reticulated into metal–organic frameworks by linking the carboxylate carbons with organic units, but may also be linked by replacement of the terminal ligands. Examples of organic SBUs include the conjugate bases of (d) square tetrakis(4-carboxyphenyl)porphyrin, (e) tetrahedral adamantane-1,3,5,7-tetracarboxylic acid, and (f) trigonal 1,3,5-tris(4-carboxyphenyl)benzene. Metals are shown as blue spheres, carbon as black spheres, oxygen as red spheres, nitrogen as green spheres. [1]

Finally, a note must be made concerning the terminology used to describe porosity, which is often assumed in metal–organic frameworks. The adjective *porous* often appears in reports of newly synthesized MOFs that have solely been characterized by crystallographic analysis. This is clearly inappropriate for frameworks in which the included solvent molecules cannot be removed or exchanged without loss of framework integrity. The term *open framework* has generally been conceded as an adequate description of materials containing highly disordered, unbound solvent molecules that appear to flow freely through the void spaces of the well-defined framework, although it is essential that their facile exit from the MOF be tested. The most common method for examining the stability of a MOF in the absence of its original guests is a powder X-ray diffraction (PXRD) analysis of the bulk material after heating and/or evacuation, referenced to the calculated pattern of the host structure. This is then correlated with thermogravimetric analysis (TGA), in which framework stability is indicated by negligible weight loss between the temperatures of guest desorption and framework decomposition. Importantly, neither method of analysis is sufficient on its own to demonstrate the ''openness'' of a material. In addition, corroborating evidence should be presented in the form of changes in elemental composition (M, C, H, N, etc.), and infrared (IR) and/or nuclear magnetic resonance (NMR) spectra. In some cases, the integrity of single crystal specimens has been main-

tained during guest desorption [22–36] and the differences in structure refinements provide striking proof of the obtainment of an open framework. Even in these instances, however, care must be taken during interpretation of the data, and loss of diffraction quality due to increased crystal mosaic structure must be accounted for when scrutinizing extra-framework electron density difference peaks.

Aside from these preliminary analyses, the establishment of a material as *porous* requires studies evidencing the reversible flow of guests into and out of the void volume. One method is fluid exchange by immersion, which requires monitoring of the crystal morphology to ensure that a dissolution mechanism is not at work, followed by elemental analysis (EA) and spectroscopy. Unfortunately, this method does not prove that the framework exhibits *permanent porosity*; i.e. stability in the fully evacuated state. This is best evidenced by traditional techniques such as the isothermal sorption of gases or mercury porosimetry [37,38]. Moreover, these are the only techniques that allow the quantification of framework porosity, and it is the remarkable results obtained by these studies that have lead to the current excitement surrounding MOF research.

3. Synthesis

Several factors must be borne in mind when approaching the synthesis of a new metal–organic framework, aside from the geometric principles that are considered during its design. By far the most important

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[1] For interpretation of colour in the figures, the reader is referred to the web version of this article.

is the maintenance of the integrity of the building blocks. Quite often a great deal of effort has been expended on the synthesis of a novel organic link and conditions must be found that are mild enough to maintain the functionality and conformation of this moiety, yet reactive enough to establish the metal–organic bonds. Where a desired SBU is to be generated in situ, the required synthetic conditions (which may occupy only a small range of composition space) must be compatible with the mobilization and preservation of the linking units. Typically, this is performed by precipitation of the product from a solution of the precursors. This is not to imply that solubility is a necessary attribute of the building blocks, as this limitation is quite often circumvented by using solvothermal techniques.

Traditionally, the overriding goal of MOF synthesis has been to obtain high quality single crystals for structural analysis. Before a sufficient knowledge base was established to begin elucidating the conceptual roots of reticular synthesis, the majority of studies were exploratory. It is not surprising, therefore, that early attempts involved simple, highly soluble precursors, and labile metal ions of the late transition series. The assembly process of a MOF is akin to organic polymerizations in that an insoluble entity is quickly formed that precludes recrystallization. Fortunately, it differs in the degree of reversibility of the bond formation event, allowing detachment of incoherently matched monomers followed by reattachment with continued defect-free crystal growth. Regardless, the framework assembly occurs as a single synthetic step, and thus all of the desired attributes of the target material must be carried by the building blocks. The reader should bear in mind that the MOF designer is always at the mercy of intermolecular forces that limit predictability, and some effort must be made to identify and modify synthetic conditions that allow the assembly of the building units in the intended fashion. This often requires a combinatorial approach, and it has often been observed that subtle changes in concentration, solvent polarity, pH, or temperature lead to poorer quality crystals, reduced yields or the formation of entirely new phases. Fortunately, once these conditions are elucidated, most high yielding syntheses share the attributes of low energy expenditure (temperatures typically range between room temperature and 200 °C), reasonable time scale (hours to days), possibility of solvent recycling, and facile quality control monitoring by PXRD or microscopy. There are already examples of highly porous MOFs that have been prepared in amounts far greater than the laboratory scale [39,40].

Early efforts to produce highly crystalline MOFs involved a variety of techniques previously used to grow crystals of simple inorganic salts. These generally involved the slow introduction of the building blocks to reduce the rate of crystallite nucleation. Methods included slow evaporation of a solution of the precursors, layering of solutions, or slow diffusion of one component solution into another through a membrane or an immobilizing gel. Where a ligand needed to be deprotonated prior to coordination (such as a carboxylic acid), a volatile amine was gradually added via vapor diffusion. Just as for many of the polar solvents used, adroit choice of base was necessary to avoid competitive coordination with the organic links for the available metal sites. While in some cases, blocking of metal coordination sites is necessary for the formation of a particular SBU, this occurrence has generally been regarded as leading to low-dimensional structures that are less likely to define an open framework.

As the need for more robust frameworks was recognized, greater difficulties in crystal growth were encountered. The inverse relationship between metal–organic bond strength and reversible formation is directly responsible for this obstacle. Fortunately, solvothermal techniques were found to be a convenient solution to this dilemma and have largely supplanted the older, often time-consuming methods involving slow coupling of the coordinating species. The precursors are typically combined as dilute solutions in polar solvents such as water, alcohols, acetone or acetonitrile and heated in sealed vessels such as Teflon-lined stainless steel bombs or glass tubes, generating autogenous pressure. Mixed solvent systems are often used to tune the solution polarity and the kinetics of solvent-ligand exchange, effecting enhanced crystal growth. Exposing the growing framework to a variety of space-filling solvent molecules may also be an effective way to stabilize its defect-free construction as they efficiently pack within the defined channels. In cases where deprotonation of the linking molecule is necessary, gradual neutralization of a solution can be effected by thermal decomposition of an amide co-solvent. Fluids such as alkyl formamides and pyrrolidinones have been particularly useful to this end, as they are also excellent solubilizing agents. An alternative method is to slowly generate the desired link in situ, for example, by hydrolyzing nitriles or esters to yield carboxylates. Finally, it should be mentioned that if high yield is desired over crystal quality, reaction times can be greatly reduced by increased concentration and agitation of the solution. Quite often microcrystalline, rather than amorphous, materials are formed under these conditions, as evidenced by electron microscopy and PXRD.

4. Structures

It is impractical to pursue a discussion of the over 13 000 crystalline extended metal-containing compounds that are presently catalogued in the Cambridge Structure Database. Instead, a selected few will be described

to illustrate the conceptual evolution of MOF design and preparation. It will be noted that only a few of these demonstrate properties associated with an open framework material, and these will be discussed further in the next section. All references to cavity or channel sizes have been measured by taking the van der Waals radii of the surrounding atoms into account [41]. There is also some debate about the minimum dimensionality that is necessary to constitute a MOF, as chain or sheet structures do not quite fit the connotation of the term "framework". Nonetheless, some of these structures have shown sorption properties and others have been integral in the development of design strategies. Discussion of discrete (zero-periodic) structures, known variously as molecular squares, polygons, or polyhedra, has been avoided for brevity [42–46]. A very large body of work involves frameworks linked by cyanides, small cyano-derivatives, and oxalates, many of which were pivotal in the recognition of MOFs as simple nets. The short length of these links generally does not lead to the definition of extra-large pores (>10 Å, [47]); further, they do not contain centers available for organic modification, therefore, discussion of these compounds will be limited. Regardless, they are very effective in facilitating spin correlation between paramagnetic metals and have been intensely studied as molecular magnetic materials [10].

One early example of a structure that demonstrates some of the concepts described above is the MOF formed when Cu^+ is tetrahedrally bound by the linear dinitrile adiponitrile [48]. Analysis of the connectivity of these copper ions shows that they lie in the same arrangement as the carbon atoms of the diamond structure, albeit with lower symmetry. The adiponitrile moieties replace the short C–C bonds of this net, leading to an impressive expansion that defines adamantanoid cavities with an interior diameter of 12 Å. In the crystal, the compound consists of six individual diamondoid networks, which interpenetrate to efficiently pack the potential void space surrounding the nitrate counterions. Since the discovery of this compound, a plethora of other diamond nets has been reported, the majority of which also suffer from interpenetration [49–57]. One of these was constructed by what is perhaps the first example of an organic SBU, the tetrahedral $4,4',4'',4'''$-tetracyanotetraphenylmethane molecule, which forms a diamond net with 10.5 Å pores when linked to Cu^+ [58]. Here, the tetrahedral vertices are replaced in alternating fashion by Cu^+ and the center of the linking tetranitrile. No interpenetration occurred for this compound, and IR spectroscopy showed that the guest BF_4^- ions could be readily exchanged by PF_6^-.

Widespread use of neutral nitrogen-donor ligands soon followed. The majority of these links contained rigid linear, trigonal, or square backbones terminated by pyridyl or cyano groups. In particular, $4,4'$-bipyridine (BPY) has been used extensively, giving rise to a vast array of structure types, including square [59,60] and hexagonal grids [61,62], diamond nets [53–55], molecular ladders [62,63], railroads [64,65], bilayers [66], three-dimensional frameworks [67–70], and helices [71]. The structure type adopted by a particular metal–BPY combination depends primarily on the typical coordination geometry of the metal and the number of sites blocked by terminal ligands. Due to the general unpredictability of these factors, structure prediction was only acknowledged for a few compounds. In addition, several shortcomings of these frameworks were noted early on: inclusion of a counterion was necessary, interpenetration was common, and thermal stability was often low (the large majority decomposing below 250 °C), especially upon guest removal. The latter failing has been attributed to the flexibility of transition metal coordination modes and low metal–nitrogen bond strengths [3]. Attempts to increase the thermal stability of pyridyl-based MOFs have included the use of chelating ligands such as 1,4,5,8,9,12-hexaazatriphenylene, which produces a framework that exchanges guest solvent molecules with atmospheric water when bound to Ag^+ [72]. Regardless of their weaknesses, some of these nitrogen-donor MOFs were shown to have novel solvent or ion exchange properties, and promoted the notion that molecular zeolite analogues could indeed be synthesized.

From the beginning, it was clear that the path to robust, truly porous MOFs must begin with the adroit choice of organic linking agent. The subsequent success of employing anionic, polydentate links is a testament to the power of reticular synthetic precepts. Early use of rigid carboxylates such as benzene-1,3,5-tricarboxylate [1,73–78] and benzene-1,4-dicarboxylate [4,22,79–81] yielded neutral, non-interpenetrated networks that were shown to maintain (or at least regain) crystallinity during desorption and resorption of guest molecules. Decomposition temperatures for many of these frameworks (as observed by TGA) are in the range of 300–500 °C, leaving an impressive window of stability above the temperatures required for guest removal. The strength of these frameworks arises from the inherent attributes of metal–carboxylate bonds: first, that their energy is comparatively large due to enhanced electrostatic attraction, and second, the size of the carboxylate functionality permits bridging and/or chelation of metal cations to produce rigid, geometrically defined clusters. Furthermore, these clusters are characteristic of the metal employed—typically having been previously identified in molecular species—and are often reproducibly formed under specific synthetic conditions. It is here that the chemist's arsenal of SBUs can be expanded to include new shapes that are dependably integrated into a desired net.

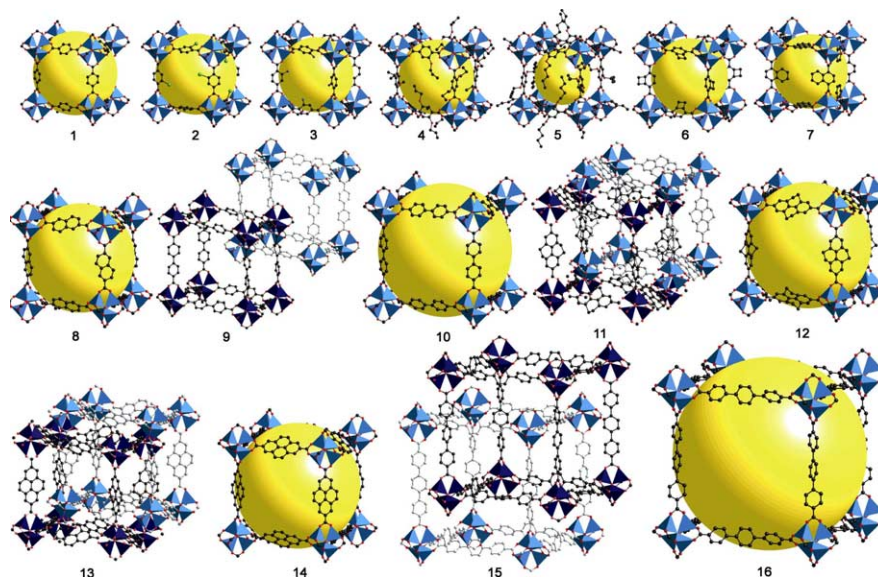No other series of compounds exemplifies these attributes better than those sharing the formula

Fig. 2. A large series of isoreticular metal–organic frameworks (IRMOFs) has been produced in which each member shares the same cubic topology. Each compound is synthesized by employing the corresponding organic link in the solvothermal conditions established for formation of the octahedral secondary building unit (SBU). The links differ both in functionality of the pendant groups (IRMOF-1 to -7) and in length (IRMOF-8 to -16). While expansion of the links increases the internal void space (represented by yellow spheres), it also allows the formation of catenated phases (IRMOF-9, -11, -13 and -15) [83].

$Zn_4O(L)_3$, where L is a rigid linear dicarboxylate. These materials have the same cubic topology as prototypical MOF-5 [22], the framework generated when octahedral $Zn_4O(CO_2)_6$ clusters (the core of the basic zinc acetate structure [82]) are linked along orthogonal axes by phenylene rings (see Fig. 2). This structure is synthesized from a solution of Zn^{2+} and benzene-1,4-dicarboxylic acid under conditions that generate the tetrazinc cluster in situ. The highly crystalline material is incredibly stable, up to 400 °C as measured by TGA, and remarkably, evacuated single crystals maintain their diffraction quality after heating to 300 °C. A simple structural analysis reveals it is the reinforced connectivity within the octahedral SBUs that is responsible for this enhanced stability. Compared to the simple cubic net formed when single octahedral metal centers are linked through monodentate ligands (as in Ref. [68], Prussian blue is another classic example), the MOF-5 components have sizeable girth. The tetrazinc cluster defines a truncated tetrahedral envelope, while the conjugated aromatic carboxylate can be geometrically described as a planar "slat". Opposing slats connected at the SBU are perpendicularly disposed, providing resistance to shear. Conversely, the fewer (and weaker) bonds of the simple cubic network are susceptible to distortion.

After identification of the synthetic conditions necessary for the generation of the "basic zinc acetate SBU", tailoring of this network became feasible. A series of 16 *isoreticular* (of the same net) metal–organic frameworks (IRMOFs) were produced in crystalline form, differing in the polarity, reactivity, and bulk of the pendant groups on the aromatic link [83]. Expansion of

the network was achieved by substituting benzene-1,4-dicarboxylate by naphthalene-2,6-dicarboxylate, biphenyl-4,4'-dicarboxylate, pyrene-2,7-dicarboxylate, or terphenyl-4,4''-dicarboxylate, giving rise to a series of structures with calculated pore sizes up to 28.8 Å, and fractional free volumes up to 91.1% (see Fig. 2). As expected, the properties of these materials differ in discernible ways. Although one of the commonly quoted assets of metal–organic frameworks is their potential for chemical modification of the organic link, this series of compounds is one of the only instances where this level of control has been exerted in molecular-based solids [84,85]. More recently, trigonal links such as 4,4',4''-tricarboxytriphenylamine [86] and 1,3,5-tris(4-carboxyphenyl)benzene and the trigonal prismatic dendrimer 4,4',4''-tris(N,N-bis(4-carboxyphenyl)amino)triphenylamine [87] have also been employed to connect the tetrazinc SBUs, one giving rise to a material with the highest surface area recorded to date [2].

Another metal carboxylate cluster that has been successfully used in the synthesis of porous networks is the bimetallic "paddlewheel". This square SBU is generated in situ by the combination of four carboxylates with two cations such as Cu^{2+}, Zn^{2+}, Fe^{2+}, Mo^{2+}, Rh^{2+}, or $Ru^{2+,3+}$, each capped by a labile solvent molecule (see Fig. 1). A variety of link geometries, such as linear [4,20,88], bent [35,89–91], trigonal [19,77], or tetrahedral [25,92] have adjoined these clusters, often producing networks with simple and predictable topologies. Compounds in this class have provided nice examples of reticular synthetic principles, and have allowed the design of metal–organic backbones ranging from zero- to

three-periodic [3]. Several important structural features have been identified in these materials: single crystals of MOF-11 were desolvated and shown by diffraction analysis to contain a periodic array of open metal sites [25], inter-ligand attractions serve to reinforce the nets of MOF-14 via interweaving (versus interpenetration, see above) [19], arrangement of dicopper clusters on the vertices of the Kagome lattice lead to magnetic spin frustration [93], chiral links yield 1-D ribbons with retention of chirality [91], and perpendicular ordering of the squares in MOF-101 gives rise to a structure that geometrically discourages interpenetration [20]. In all cases, these attributes were made possible by the use of appropriate links.

Further mastery in ligand employment has been demonstrated by attaching an additional pair of linear links to the square paddlewheel SBU, transforming it into an octahedral unit. The synthesis involves two stages: first, two-dimensional square grids are prepared by linking dicopper SBUs with a linear dicarboxylate, then these sheets are pillared by replacing the axial solvent ligands with a linear diamine such as 1,4-diazabicyclo[2.2.2]octane (DABCO, or triethylenediamine, TED), or 4,4′-bipyridine to yield a three-dimensional framework [94,95]. Although no single crystal structure analyses have been performed for these isoreticular compounds, powder diffraction patterns calculated using models of the proposed structures show agreement with the measured patterns. Just as for the cubic IRMOFs described above, expansion of the linker is demonstrated, but leads to catenation. Whereas the BPY compound is interpenetrated (as is a related compound where a "three-blade paddlewheel" is formed [96]), the DABCO compounds are not, as this link's shorter length allows the dicarboxylates to define impenetrable walls around the square channels. The same topology is observed when the short SiF_6^{2-} and long BPY links connect Zn^{2+} [68] or Cu^{2+} [97], and interpenetration is again precluded.

Other periodic arrays of large channels can be formed when linear links are used to connect infinite inorganic rods. Quite often, an auxiliary bridging moiety such as hydroxide is present in the backbone of these "infinite SBUs". If these rods are aligned in parallel, the organic crosslinks can be closely spaced, yielding walls that disallow catenation [98–100]. Isoreticular compounds with expanded links (such as biphenyl-4,4′-dicarboxylate) can then be synthesized, with channels over 10 Å in diameter.

More recently, vanadium fluoride/hydroxide layers have been linked [101], yielding pillared galleries where guest water molecules reside. This arrangement is reminiscent of the well-known metal bisphosphonates [102]. Although periodic micropores in these lamellar compounds are rare [103], their research provides some

important early examples of reticular synthesis by augmentation of the organic link [104,105]. Interpenetration is obviously not an issue here, but close spacing of the crosslinks is a problem, as they fill the interlayer region. This has been addressed by attempts to incorporate more small bridging ligands, such as hydrogen phosphate. Already we note this is a step backwards from the original strategy to create porosity in MOFs: the separation of the individual vertices of a net (single metals or SBUs) by long rigid links. It might be expected then, that a material with a three-dimensional inorganic backbone linked with organics would typically be dense as well, but a recent report of a nickel succinate hydroxide hydrate shows this is not the case. The structure of this clathrate material consists of a skeleton of edge- and corner-shared NiO_6 octahedra buttressed by coordinated succinate links [106]. The roles of the inorganic and organic moieties appear to have been reversed; alone, the expansive inorganic frame would certainly be too frail to exist, however, the linked material remains crystalline to 400 °C.

The true strength of metal–organic frameworks is not their thermal stability. In this aspect, they simply cannot compete with traditional aluminosilicate zeolites. Their real advantage springs directly from the modular process by which they are constructed. By imparting functionality unto the organic building block—such as chirality, reactive groups or redox centers—a desired attribute can be realized, in a periodic manner, throughout the bulk material. This property can also be generated as a cooperative effect, such as magnetic coupling of paramagnetic metal centers, or the alignment of asymmetric links. The latter characteristic has been accomplished by linking Zn^{2+} or Cd^{2+} with bifunctional ligands such isonicotinoate, pyridylacrylates and pyridylbenzoates. Non-centrosymmetric diamond net, square grid, and chain connectivities result from the approximately tetrahedral coordination of each metal by two pyridyl and two carboxylate donor groups [107]. As expected, the acentric arrangement of the electronically asymmetric links gives rise to non-linear optical behaviour, and second harmonic generation has been measured for many of these compounds. Unfortunately, only a few of these materials contain removable guests [108].

The resolution of chiral molecular sieves for enantioselective sorption and catalysis remains challenging, as simple polyhedral oxide building blocks have no propensity for a particular handedness in their condensation. The use of chiral template molecules is one option for preparing such inorganic frameworks, however, the host and template must be intimately related for this to occur, most likely leading to framework collapse during template removal. The generation of homochiral MOFs is much more straightforward: one simply needs to employ an enantiomerically pure link

[84]. A layered open framework with large channels was synthesized by linking Zn^{2+} with the mixed-donor ligand (4R,5R)-2,2-dimethyl-5-[(4-pyridinyl amino)carbonyl]-1,3-dioxolane-4-carboxylic acid or its enantiomer [109]. In this structure, trigonal prismatic SBUs are generated by linking oxo-centered zinc trimers with six carboxylates groups. Three of the six pyridyl donors link to neighbouring SBUs through the axial positions of their zinc ions, while the remaining three dangle into trigonal channels, leaving an aperture of 8.5 Å bounded by available Lewis bases. Recently, phosphonate, carboxylate, and pyridyl links with binapthyl stereocenters have been used to generate a variety of homochiral structures ranging from zero- to three-periodic, some containing removable guest molecules [91,110–114]. Finally, the handedness of the doubly interpenetrated three-connected net displayed by $Ni_3(BTC)_2(pyridine)_6(1,2-propanediol)_3$ was found to be controlled by using enantiomerically pure 1,2-propanediol [115]. This molecule is not a link within the MOF, instead it chelates the Ni^{2+} centers and directs the dihedral angle between neighbouring BTC links via hydrogen bonds, resolving one enantiomer of the net. This is a rare example where a desired property of the framework is determined by a terminal ligand, rather than either the metal or link.

Other functional links that have been utilized are those based on porphyrin. This module is attractive due to its large size, rigid square shape, and the promise of catalytic or chromophoric activity based on metal binding at its center. Both tetrapyridyl [116–121] and tetracarboxy [122–124] derivatives have been used in the synthesis of MOFs. As expected, simple topologies incorporating square vertices are generated, with the final net type determined by the geometry of the inorganic SBU. Still, the underlying topology can be pleasantly surprising [121]. Linkage of distorted octahedral tricobalt SBUs with tetrakis(4-carboxyphenyl)porphyrin (TCPP) yields the three-dimensional open framework PIZA-1, which has large 7×9 Å and 7×14 Å intersecting channels [123]. Use of BPY as a pillaring agent has also been successfully used to connect sheets of Na[ZnTCPP], creating large galleries with channel dimensions of 8×10 Å and 8×12 Å [122]. Both of these materials show stability upon guest removal, and extensive guest uptake studies have been performed for the former, demonstrating selectivity based on size and polarity.

In addition to the progress of incorporating functionality into the body of the organic link, new coordination groups are being explored. While these generally involve weaker metal–ligand interactions, novel frameworks have been constructed that also show thermal stability. For instance, a Ag^+ triphosphine has been recently reported with a layered honeycomb structure defining channels with a free diameter of 16 Å [125]. The dichloromethane-activated structure remains intact after heating in vacuo to 170 °C to remove the guests. Sulfonates have also been explored as coordinating groups, with the impetus that they may behave as softer analogues to phosphonates. Materials reported thus far show few similarities, however, a robust layered barium sulfonate has been prepared with the aid of reinforcing chelation by the linker's catechol functionality [126]. Of much interest is the ability of some frameworks to undergo major rearrangements to afford selective uptake of small molecules [127,128].

5. Properties

From the very beginnings of MOF research, it was recognized that not only would the framework components be alterable, but also the contents of the cavities they would define. To provide evidence of the accessibility of these void regions, ion [58,64,67,70] and solvent molecule [72,129,130] exchanges were studied. These analyses are useful as a preliminary demonstration of the integrity of an open framework when coupled with PXRD, so long as the crystallite integrity and composition of the exchange solvent are monitored to exclude the possibility of a dissolution/recrystallization mechanism. Quantitative exchange studies with a variety of small molecules have also identified MOFs with specificity towards guest shape or functionality [1,73,74,123, 127,128,131]. These observations have inspired beliefs that with proper tailoring, MOFs may be produced to act as highly selective molecular sieves, sensors, or catalysts. Sensor capabilities become realizable when the optical, electronic, or magnetic properties of the framework are altered by guest interactions. This phenomenon has been demonstrated in MOFs containing luminescent lanthanides [81,132] or paramagnetic transition metals [34,133]. Catalytic behaviour has been reported in only a few instances [60,109,110,134–137] and this area deserves much more attention.

One of the most promising applications of metal–organic frameworks is gas storage. To establish the attainment of permanent porosity after guest removal, the measurement of gas isotherms has been indispensable [2,4,19,22,25,77,80,81,83,87,95,99,100,138–142]. The isotherm shapes, typically Type I with little or no hysteresis, demonstrate that resilient microporous structures exist under reversible physisorption of small molecules. Isobars have also been measured, providing insight into the strength of the physisorptive interaction [143–147]. Sorption isotherms of organic vapors such as chloroform, benzene, or cyclohexane have also aided in the estimation of pore volumes and aperture sizes of rigid frameworks [22]. The measurement of nitrogen or argon isotherms has allowed the apparent surface areas of these materials to be quantified, typically assuming Langmuir-type monolayer coverage [38]. As shown in
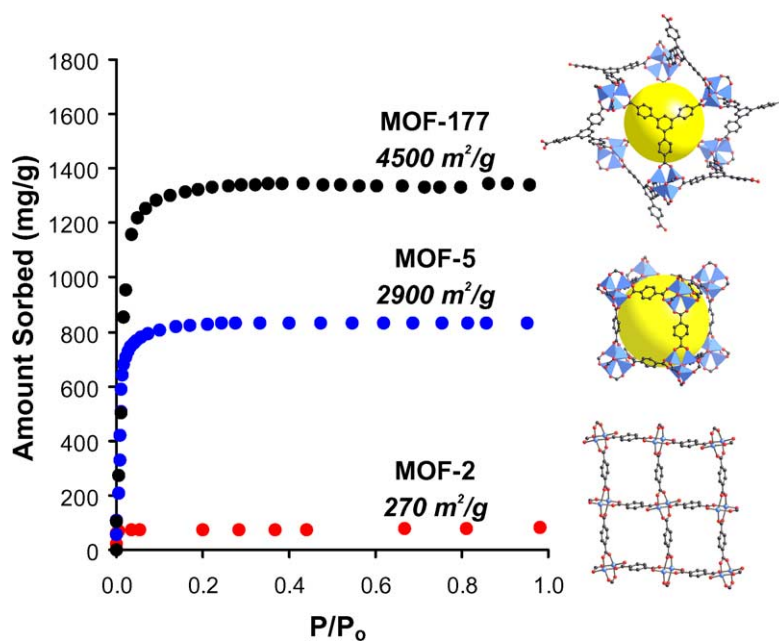
Fig. 3. New MOFs have displayed impressive increases in their apparent surface areas since the measurement of the first low temperature isotherm for these materials [2,4,22]. The nitrogen sorption isotherms were measured at 77 K and display Type I behaviour, as expected for compounds with uniform micropores.

Fig. 3, considerable increases in these values have been obtained in just a few years. The surface area calculated from the nitrogen isotherm of MOF-177 is particularly notable: it is the largest of any reported material.

Novel isotherm shapes have been reported for some compounds that appear to demonstrate activated sorption above a threshold pressure [148–152]. The frameworks apparently possess a degree of flexibility, perhaps stemming from minor disruption of their pyridyl linkages or inter-ligand interactions. To probe this effect, X-ray diffraction studies have been performed to characterize the framework shifts upon guest incorporation [153]. In more rigid frameworks, size exclusion of gas molecules has been observed, promoting the potential of these materials for molecular sieving [154,155]. Differences in the host–guest interaction for closely related sorbates, such as ethane and ethylene, has also been shown by the measurement of gas isotherms [39].

Interest in the gas sorption properties of MOFs is now focused on increasing their uptake of fuel gases such as methane [83,94,95,156–159] and hydrogen [160,161]. The low carbon content and large chemical energies of these molecules make them highly attractive as replacements for fossil fuels. One of the obstacles to their widespread use is storage, especially for mobile applications. Host materials must satisfy a set of criteria including high gravimetric and volumetric uptake, facile gas release and reproducible cycling, in addition to being economically produced. Due to their large and reversible uptake of other gases, MOFs have been proposed as promising materials for this application. Reports have demonstrated that by changing the link in isoreticular

materials, increases in their capacities for methane and hydrogen have been realized [83,95,160].

6. Outlook

In the past the tailoring of a solid state compound's properties has been accomplished by a few general methods: atomic doping or substitution, particle size control, and surface modification, each within the stability limits of the underlying structure type. Metal–organic frameworks are a class of solids that allows greater chemical alteration *on a periodic scale*, since the methodology for organic transformations is well-established. While subtle changes to the coordinating organic links often leads to new framework topologies, certain framework types are amenable to marked modification of the metrics and chemical nature of these moieties. Thus, precise structure–property trends can be established, and optimization of a material may be performed in a rational manner. It has already been demonstrated that the gas sorption properties of a family of MOFs can be improved by augmentation of the link. As new applications for these versatile materials are identified, a greater understanding of the subtleties in the reticulation process will be achieved.

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