



# Spiers Memorial Lecture:

## Progress and prospects of reticular chemistry

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Reticular chemistry, the linking of molecular building units by strong bonds to make crystalline, extended structures such as metal–organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs), and covalent organic frameworks (COFs), is currently one of the most rapidly expanding fields of science. In this contribution, we outline the origins of the field; the key intellectual and practical contributions, which have led to this expansion; and the new directions reticular chemistry is taking that are changing the way we think about making new materials and the manner with which we incorporate chemical information within structures to reach additional levels of functionality. This progress is described in the larger context of chemistry and unexplored, yet important, aspects of this field are presented.

## Overview

In order to appreciate the progress that is being made in reticular chemistry, it is useful to make the following observation: the most important materials of the twentieth century have been either organic (*e.g.* polymers and pharmaceuticals) or inorganic (*e.g.* zeolites, cement, steel, silicon, and alloys), and they function largely in a monolithic manner (*i.e.* one structure for one function). Reticular chemistry advanced the state of materials in three major ways. First, with the synthesis of MOFs and ZIFs, it showed that organic and inorganic building units could be combined through strong bonds to make robust, porous materials, which take advantage of the vast possible variations that could be applied to their constituents. In the case of COFs, the principles of reticular chemistry are used to show how crystalline organic materials could be made to have two- and three-dimensional structures, thus propelling the field of organic chemistry beyond discrete molecules and one-dimensional polymers. Second, reticular chemistry showed how functionality and metrics of extended chemical structures can be altered by virtue of varying building blocks, while maintaining the integrity of their underlying structure. In all other materials, organic or inorganic, altering

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either or both the functionality and metrics of their constituents frequently results in destruction of their original structures and this, prior to reticular chemistry, was an impediment to designing materials with targeted properties. Third, because MOFs, ZIFs, and COFs have open structures with permanent porosity, it became possible to also modify them post-synthetically. The fact that their structures are maintained after such modifications meant that specific chemical environments can be designed into these materials.

Although, the potential for creating highly selective catalysts, and specific binding environments is already being pursued, the biggest impact will emerge from the ability to design sequences of multivariate functionalities and metal combinations to affect properties where the whole performs better than the sum of its parts. It is this latter advance which is beginning to clearly point the way to numerous opportunities for making materials that are multifunctional. We envision such materials to be capable of: (1) operating several functions in parallel, (2) sorting, storing and releasing molecules for specific operations within a larger and more complex system, (3) compartmentalization where spatially defined regions of specific compositions exist within one structure and are intimately linked yet function differently, and (4) combining flexibility and dynamics with resiliency. In this contribution, we highlight, for the purpose of discussion, the milestones in the field and their relationship to the future of reticular chemistry and their essentiality in making materials for the twenty first century.

## Historical perspective

The issue of porosity figures prominently in any discussion of reticular chemistry because most of the materials produced involve the use of multi-atomic building units and this leads to 'open' structures in which ions or molecules fill those openings. Before going further, it is helpful for our discussion to provide a brief history of 'openness' in organic and metal-organic structures. Throughout most

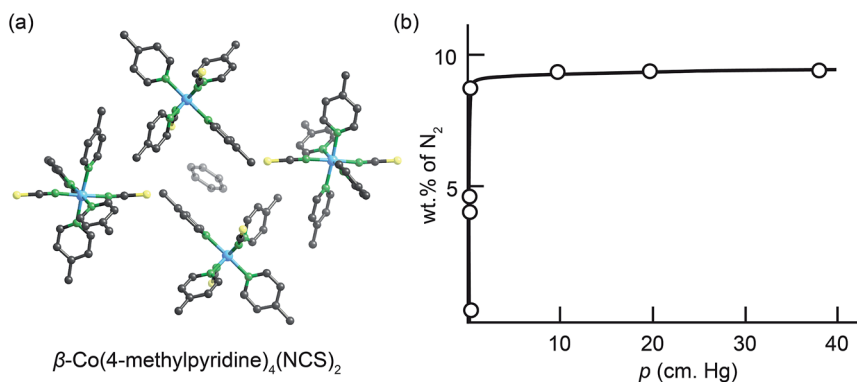


Fig. 1 Inclusion compound of a Werner complex: (a) crystal structure of  $\beta\text{-Co(4-methylpyridine)}_4(\text{NCS})_2$ , NCS = thiocyanate, showing benzene occupying the open spaces between the complexes and (b) N<sub>2</sub> adsorption isotherm of the Werner complex measured at  $-195\text{ }^\circ\text{C}$ .<sup>1</sup> This porosity is gradually lost upon cycling due to the discrete molecular nature of the crystal structure. Atom labeling scheme: C, black; N, green; Co, blue; S; yellow. H atoms are omitted for clarity. (b) was adapted with permission from ref. 1. Copyright 1969 Royal Society of Chemistry.

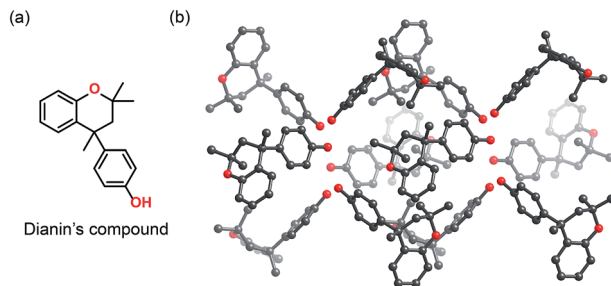


Fig. 2 Inclusion compound of an organic molecule: (a) Dianin's compound and (b) the crystal structure of Dianin's compound where the molecules are held together by hydrogen bonding to form cages.<sup>4</sup> Atom labeling scheme: C, black; O, red. H atoms are omitted for clarity.

of the twentieth century, there were extensive studies performed on molecular, as well as extended, structures with openness observed in their crystal structures. The most notable examples are: (1) crystal structures of some of the discrete transition metal complexes (Werner complexes) showing small openings, which were later found to be porous to gases but did not sustain their porosity because of their discrete molecular nature (Fig. 1),<sup>1</sup> (2) many organic crystals in which large molecules are bound together by weak forces (such as hydrogen bonding) which were shown to absorb and release organic molecules either from crevices within the molecules themselves or from their packing arrangements in the crystal (Fig. 2),<sup>2–6</sup> (3) metal–cyanide frameworks such as Prussian blues and Hofmann clathrates which have openings, typically filled with solvent molecules or ions, where the former was found to take up gases but in general these materials have limited chemistry as the cyanide linker is not amenable to functionalization (Fig. 3),<sup>7–13</sup> and (4) metal–nitrile- and metal–bipyridine-type open frameworks (commonly referred to as coordination polymers) which potentially have a large open space, but were frequently found to have counterions filling the pores or to be too frail to sustain permanent porosity (Fig. 4).<sup>14–22</sup>

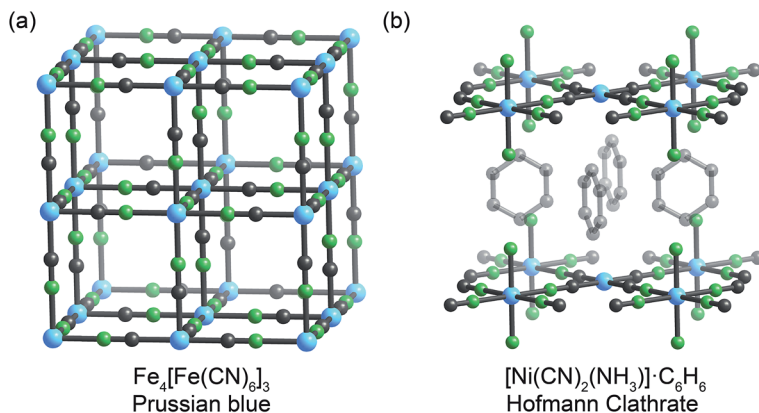


Fig. 3 Metal–cyanide frameworks: (a) Prussian blue and (b) Hofmann clathrates with benzene molecules occupying the space between the layers.<sup>9</sup> Atom labeling scheme: C, black; N, green; metals, blue. H atoms are omitted for clarity.

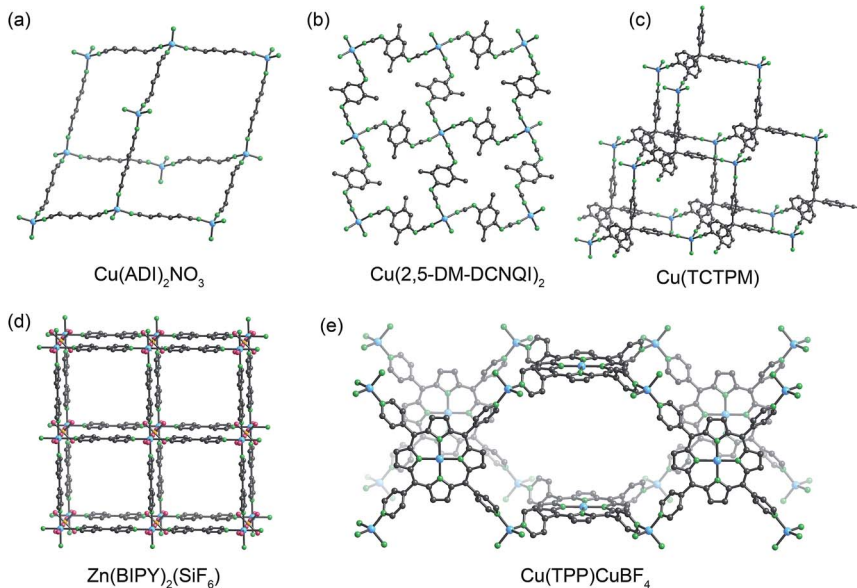


Fig. 4 Coordination polymers of metal–nitrile- and metal–bipyridine-type open frameworks: (a)  $\text{Cu}(\text{ADI})_2\text{NO}_3$ , ADI = adiponitrilo,<sup>15</sup> (b)  $\text{Cu}(\text{2,5-DM-DCNQI})_2$ , 2,5-DM-DCNQI = 2,5-dimethyl-*N,N'*-dicyanoquinonediimine,<sup>17</sup> (c)  $\text{Cu}(\text{TCTPM})$ , TCTPM = 4,4',4'',4'''-tetracyanotetraphenylmethane,<sup>19</sup> (d)  $\text{Zn}(\text{BIPY})_2(\text{SiF}_6)$ , BIPY = 4,4'-bipyridine,<sup>22</sup> and (e)  $\text{Cu}(\text{TPP})\text{CuBF}_4$ , TPP = 5,10,15,20-tetra(4-pyridyl)21*H*,23*H*-porphine.<sup>21</sup> Atom labeling scheme: C, black; N, green; metals, blue; Si, orange; F, purple. H atoms, anions are omitted for clarity, and only one framework is shown for interpenetrating networks (a).

## Permanent porosity

These various classes of materials were studied extensively, and in one case, that of creating open organic molecules, has evolved to what we now know as supramolecular chemistry.<sup>23–25</sup> In contrast, the field of open metal–organic extended structures, although tantalizing for the promise that the porosity of such compounds would enable the functionalization of the pores and hence the ability to perform chemistry within them, was in crisis and being challenged by researchers from the traditional fields of porous materials (zeolites and mesoporous silica). One of us recalls pointed questions and spirited discussions at a zeolite Gordon Conference and an NSF Materials Workshop in the mid-1990s that were centered on the principal issue of whether permanent porosity can be achieved in these compounds. At that time, no one had shown that metal–organic structures in which porosity is sustained could be made. More to the point, the experiment to prove permanent porosity, that of measuring their gas adsorption isotherm at 77 K (for  $\text{N}_2$  as an adsorbate), had not yet been performed.

A coordination polymer was shown to take up gases at high pressures and room temperature (Fig. 5a).<sup>26</sup> This type of measurement, albeit inspiring, does not constitute a proof of permanent porosity, as structure distortions and collapse would not be readily detectable under these conditions. For example, a collapsed pore in a structure may open up under high pressure at room-temperature;



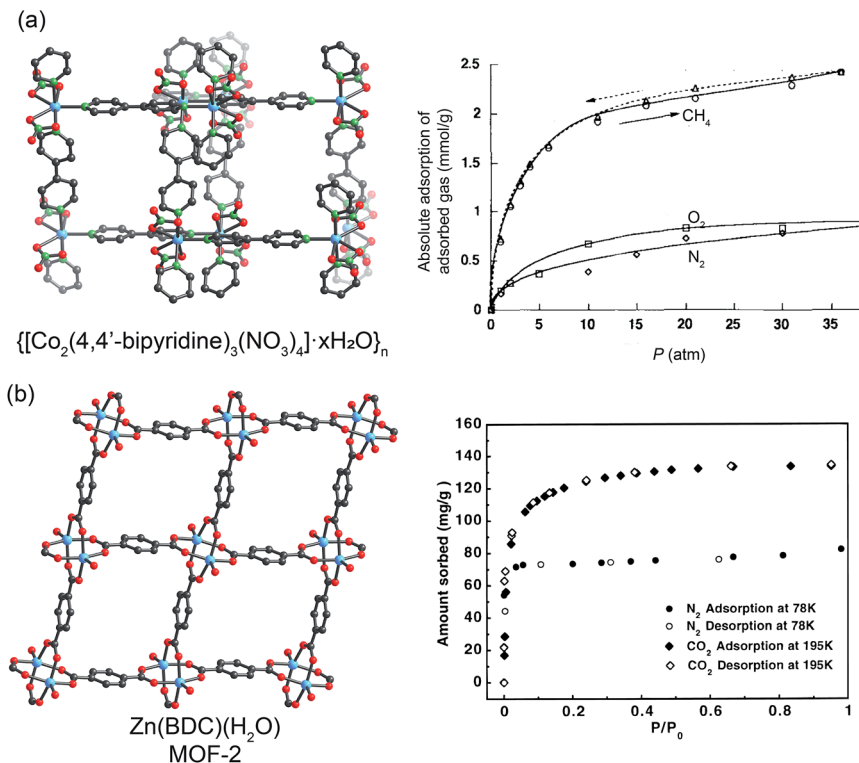


Fig. 5 (a) Crystal structure of  $\{[Co_2(4,4'\text{-bipyridine})_3(NO_3)_4] \cdot xH_2O\}_n$  and its high pressure gas uptake measured at room temperature (top right).<sup>26</sup> (b) Crystal structure of MOF-2 [Zn(BDC); BDC = 1,4-benzenedicarboxylate] and its gas adsorption isotherms (bottom right) measured at the cryogenic temperature of the adsorbates such as nitrogen or carbon dioxide.<sup>29</sup> Atom labeling scheme: C, black; N, green; metals, blue; O, red. H atoms are omitted for clarity. Adapted with permission from ref. 26 and 29. Copyright 1997 John Wiley & Sons Inc. Copyright 1998 American Chemical Society.

however, this does not indicate permanent porosity. A measurement of the gas adsorption isotherm under high pressure at room-temperature will not show evidence of such an event, since these structural distortions are observed in low pressure, low temperature isotherms. Furthermore, there is no widely accepted model to describe the gas adsorption behavior under high pressure conditions, and consequently, important figures of merit such as pore volume and surface area cannot be determined. Accordingly, the standard procedure for determining permanent porosity and surface area recommended by IUPAC is to apply the Brunauer–Emmett–Teller method to the gas adsorption isotherm of a given material obtained in the low pressure region ( $0.05 < p/p_0 < 0.3$ ) and at the boiling point of the adsorbate.<sup>27,28</sup> This is the reason why the measurement of low pressure, low temperature isotherms using nitrogen or argon gases is the gold standard for determining permanent porosity. The reticular chemistry community widely uses low pressure, low temperature gas adsorption isotherms because these measurements give an accurate assessment of permanent porosity, which has had a tremendous impact on the development of useful porous materials.

It was not until linkers based on carboxylates were successfully applied to making MOFs, that robust structures were produced and shown to exhibit permanent porosity as evidenced by their Type I gas adsorption isotherms.<sup>29</sup> Two factors led to permanent porosity in MOFs: the multi-nuclear metal–carboxylate secondary building units (SBUs) were sufficiently rigid to allow for architectural stability and the strong metal–carboxylate bonds ensured thermal and ultimately chemical stability of the resulting frameworks.<sup>30</sup> In contrast, coordination polymers were largely composed of weak M–N (neutral linker) bonds and their construction was based on single metal-ions, which were too ‘wobbly’ for making stable frameworks.<sup>31</sup> Based on the SBU strategy, the discovery of metal–carboxylate MOFs, and the proof of permanent porosity by low pressure, low temperature gas adsorption (Fig. 5b), the field of metal–organic extended structures was beginning to be defined by the post-isotherm era where it quickly experienced a renaissance followed by rapid and intense development which continues until the present.

The pre-isotherm period was useful in bringing forward the concepts of nodes and links in a network. These were articulated long ago by Wells and, later, further developed by many others in making coordination polymers.<sup>15,19,21,22,32</sup> Such original concepts were further applied and important networks were recognized and targeted for synthesis. Above all, the concept of the underlying topology of crystals, long known in chemistry, gained prominence as it became relevant to the analysis of increasingly complex MOFs and also to the prediction of new ones. This work has ultimately led to developing the taxonomy and grammar of design for extended structures, in general, and MOFs, ZIFs, and COFs, in particular. These aspects have been summarized elsewhere and, although important, are beyond the scope of this presentation.<sup>33–36</sup>

## Design principles and crystallization of products

### Metal–organic frameworks (MOFs)

**Secondary building units.** The SBU approach is a powerful concept used in the building of MOFs. Originally, metal–carboxylate clusters, long known in chemistry, were targeted as units to be reticulated with organic linkers leading to MOFs (Fig. 6).<sup>30,37–43</sup> The attributes of these SBUs include rigidity, directionality and, in contrast to single metal ion nodes, they provided one kind of coordination (connectivity) instead of the multiple possible ones for a single metal ion. The fact that SBUs locked down the geometry around the metal ions allowed for making MOFs by design. Since the metal–carboxylate bonds are much stronger than the M–N (neutral linker) bonds, they ensure that the resulting MOFs were architecturally and thermally stable. These properties of SBUs, when taken together, make for ideal building units for targeting and realizing a wide range of MOFs. Similar SBU constructs based on chelating units other than carboxylates have since been employed for expanding the family of MOFs.<sup>44–47</sup> Using this SBU approach one can target MOFs by judicious choice of rigid building blocks and thereby limiting the formation of other possible structures. Subsequent optimizations including change in concentration, solvent polarity, pH and temperature eventually led to the desired phase. After the reaction conditions were established for the generation of an SBU, it was often possible to substitute the organic building blocks with others in possession of the same type of linkage. This aspect gave rise to the

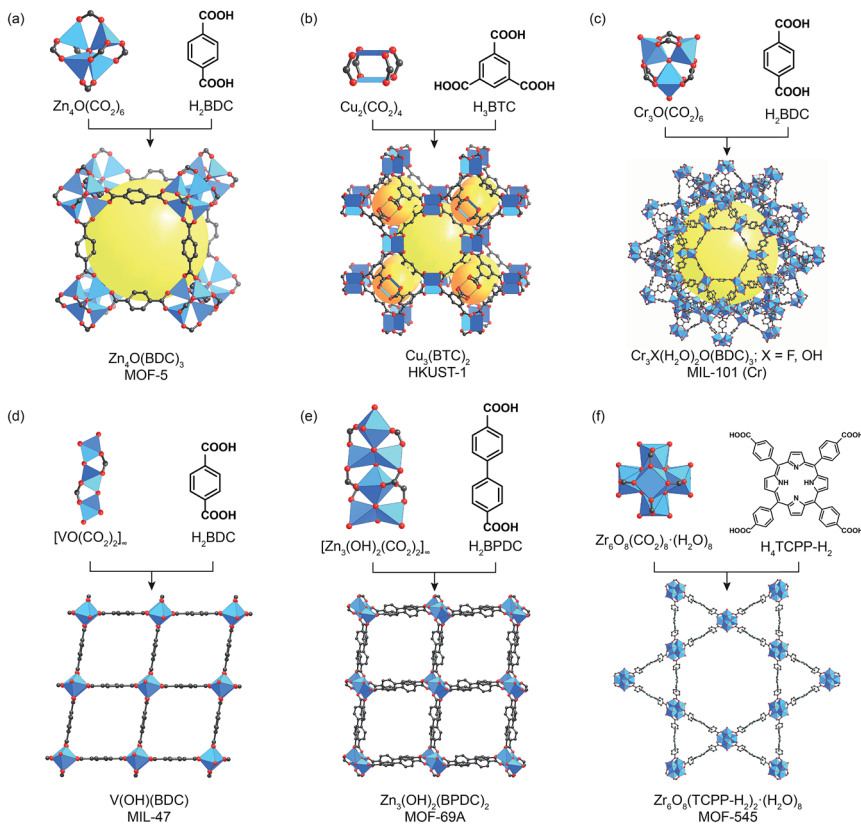


Fig. 6 The SBU approach (the use of multi-nuclear metal clusters as nodes) allowed for the formation of rigid and directional inorganic building blocks which could then react with charged organic linkers to form MOFs. Atom labeling scheme: C, black; O, red; metals, blue polyhedra. H atoms are omitted for clarity. Yellow and orange spheres represent the space in the framework.

design of a wide range of MOFs and also led to the use of the isorecticular principle. Here, the length<sup>48–61</sup> (Fig. 7) and functionality<sup>54,59,62</sup> (Fig. 8) of the linker can be varied without changing the underlying topology of the structure provided the linking functionality (linkage) remains the same. Isorecticular MOFs showed, for the first time, that extended solid-state structures can be altered, both metrically and chemically by introducing functionality into them, without changing their underlying topology.

**Crystallization challenge.** It should be noted that the idea of building chemical structures by linking molecular building units through strong bonds into crystalline extended solids was an objective in chemistry throughout the twentieth century. This was realized with the successful synthesis of MOFs. It was taken as an article of faith that linking molecules by strong bonds would lead to amorphous products and therefore ill-defined structures. Indeed, all students of synthetic chemistry know all too well that as the bond strength increases between constituents of structures and as such structures become increasingly larger, the difficulty in obtaining them as crystals increases dramatically.<sup>63</sup> This challenge

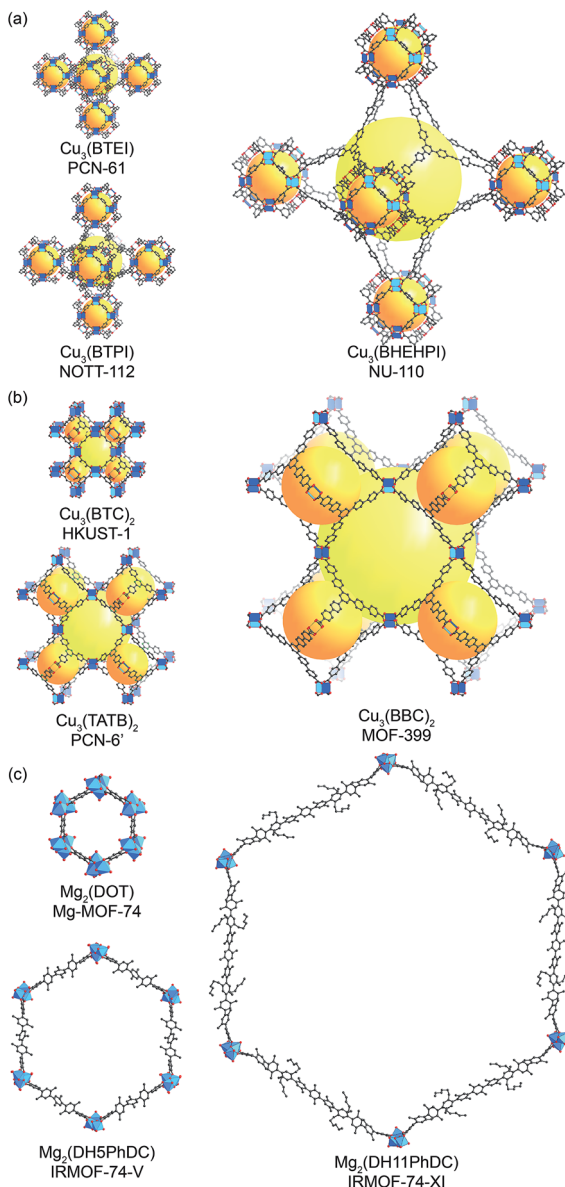


Fig. 7 Isoreticular expansion of MOFs: increasing the pore sizes and pore apertures while retaining the same topology. This is achieved by increasing the length of organic linkers of the same symmetry.  $\text{BTEI}^{6-} = 5,5',5''\text{-(benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))trisophthalate}$ ,  $\text{BTPI}^{6-} = 5,5',5''\text{-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))trisophthalate}$ ,  $\text{BHEHPI}^{6-} = 5,5',5''\text{-(((benzene-1,3,5-triyltris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))-tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))trisophthalate}$ ,  $\text{BTC}^{3-} = \text{benzene-1,3,5-tricarboxylate}$ ,  $\text{TATB}^{3-} = 4,4',4''\text{-(1,3,5-triazine-2,4,6-triyl)tribenzoate}$ ,  $\text{BBC}^{3-} = 4,4',4''\text{-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate}$ , and  $\text{DOT}^{4-} = \text{dioxidoterephthalate}$ .  $\text{DH}_5\text{PhDC}^{4-}$  and  $\text{DH}_{11}\text{PhDC}^{4-}$  are the expanded  $\text{DOT}^{4-}$  with 5 and 11 phenylene units, respectively. Atom labeling scheme: C, black; O, red; N, green; metals, blue polyhedra. H atoms are omitted for clarity. Yellow and orange spheres represent the space in the framework.

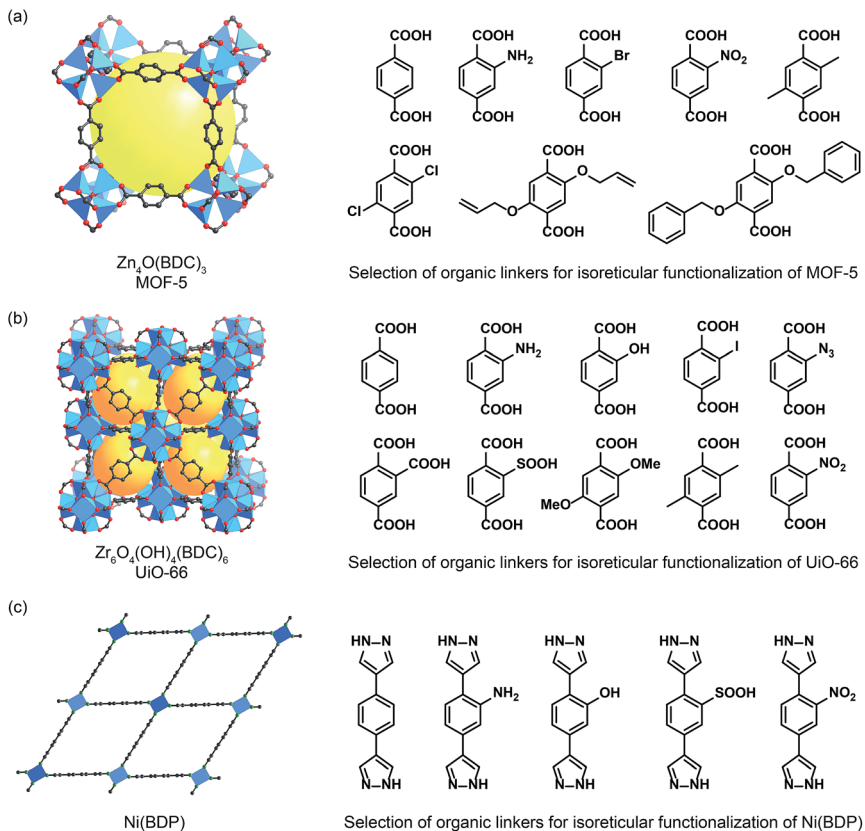
was overcome in MOF chemistry by a simple, yet effective strategy. It involved creating conditions under which it was possible to slowly deprotonate the carboxylic acids of the linker.<sup>29,37</sup> This was the rate-limiting step in the synthesis, and controlling it meant specific conditions could be achieved for MOF crystal nucleation and growth. Several strategies were used involving either dilution of the deprotonating base or allowing the base to be produced from the decomposition of DMF solvent during the solvothermal synthesis of the MOF. In essence, by controlling the strength and the rate of release of the base in the synthesis, one was able to control the crystallization process. Other methods involving the use of terminal carboxylates, such as formate or acetate as ‘modulators’, were later deployed in the crystallization of MOFs.<sup>64–67</sup> The original MOF synthesis conditions remain in use today, being applied with minor modifications. This has contributed significantly to the expansion of the MOF field.

**The question of design.** The question of whether MOFs are achieved by design has arisen in the past.<sup>68</sup> There are plenty of examples where the design of MOFs has been demonstrated.<sup>69–71</sup> They require the use of the isorecticular principle,<sup>48,50,51,56,58,60–62</sup> introduction of geometric constraints on the building units,<sup>72</sup> replacement of specific linkers,<sup>73–77</sup> and control of crystal growth to produce these materials on the nanoscale for preparing colloids<sup>64–67,78–80</sup> and thin films.<sup>81–93</sup> However, it should be mentioned that for cases involving a metal ion previously unused in MOF synthesis, some work is required to fine-tune the conditions for crystallization of the target MOF. Here, the inability to predict the geometry of the SBU introduces a level of uncertainty in targeting a specific MOF structure. However, once the conditions for making that specific SBU are delineated, such conditions are usually sufficiently robust to target a variety of structures by design.

Although, there has been discussion about design in MOF chemistry, most of it has centered around a strict definition of design. This has not been useful in the context of inspiring the synthesis of new structures, and very little of it has taken into account the reproducible nature of the SBUs in the presence of a variety of organic linkers. We advocate a definition for design that is derived from experience, where a plan is made and followed in the making of a specific structure. The result may or may not be what has been targeted but it represents a useful step in understanding what the next step should be towards achieving the targeted design. As Thomas Edison once remarked “I have not failed. I have just found the 10 000 ways it won’t work”.<sup>94</sup> In my own laboratory when a student comes to me and says “it didn’t work” my response is usually “it will not work unless you make it work”. Thus, the synthesis of entirely new MOFs based on new metal ions or linkers, especially in the case of those not typically used in this chemistry, is an exercise in optimism, strong will, and faith in the expectation that while the original plan may not lead you to the targeted MOF, a modified one will. We are always thrilled by discovery, and the fact that MOFs sometimes do not entirely submit to design has provided the community with the ability to learn from Mother Nature and tease out her unimaginable discoveries.

### **Zeolitic imidazolate frameworks (ZIFs)**

The design aspect is also interesting to consider in the chemistry of zeolitic imidazolate frameworks (ZIFs), where tetrahedral metal ions are linked by imidazolates to make porous frameworks based on tetrahedral topologies, including



**Fig. 8** Isorecticular functionalization of MOFs: the introduction of functionalities on the organic linkers of the MOFs with retention of the topology of the parent MOF. Shown are examples of MOFs and the corresponding organic linkers for making their isorecticular structures. Atom labeling scheme: C, black; O, red; N, green; metals, blue polyhedra. H atoms are omitted for clarity. Yellow and orange spheres represent the space in the framework.

those of zeolites (Fig. 9).<sup>95,96</sup> These geometric parameters favor the construction of frameworks with small pore apertures; an aspect that caused a problem in the early days when imidazolate-based extended structures were of dense phases (non-porous).<sup>97–101</sup> It was then realized that tuning the steric hindrance by functionalization of the imidazolate linkers is a powerful strategy to open up the structures to yield permanently porous materials.<sup>102</sup> Soon after this discovery, the general solvothermal synthesis of ZIFs was established and a large number of porous ZIF structures were reported.<sup>103</sup> In the chemistry of ZIFs, it has been possible to direct the synthesis toward making tetrahedral structures but not toward a specific tetrahedral topology. However, design principles based on the employed linkers and the size of the functionalities attached to them, have recently emerged as powerful intellectual and practical tools for targeting ZIFs with specific pore openings and internal pore sizes.<sup>104,105</sup> In these structures, permanent porosity was discovered in spite of a single metal ion at the vertex,



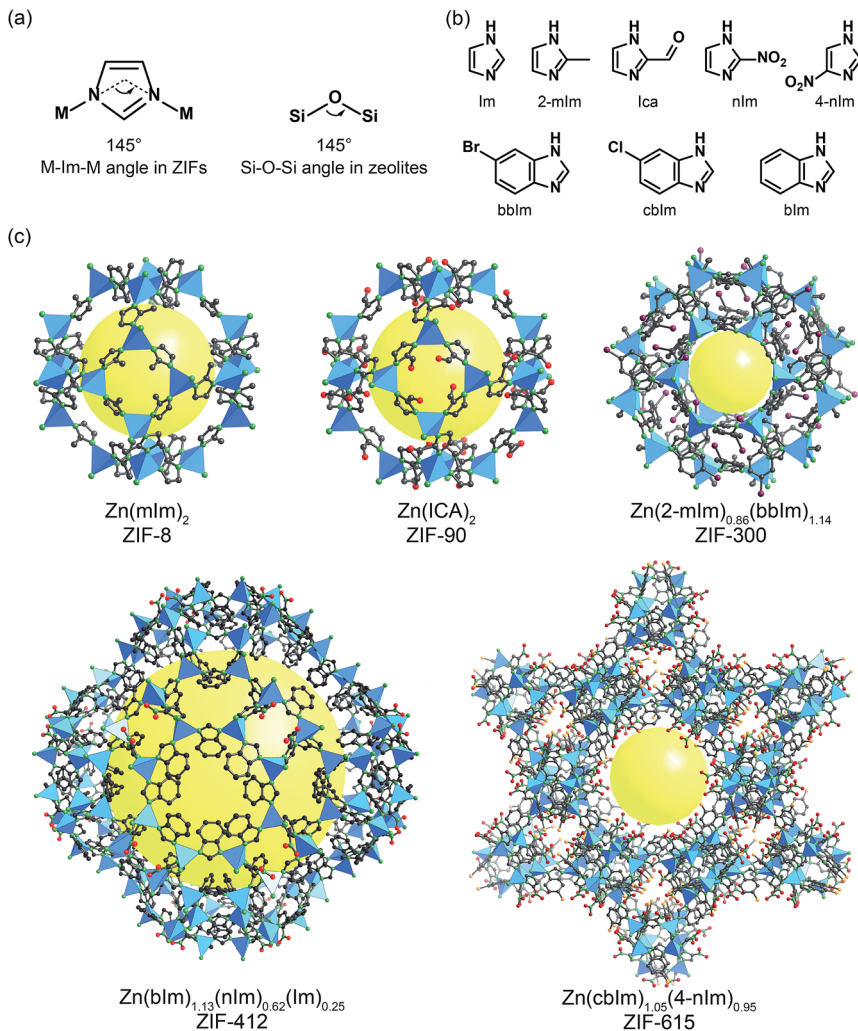


Fig. 9 Zeolitic imidazolate frameworks: (a) design of ZIFs using tetrahedral metals and imidazolates to give tetrahedral topologies typically found in zeolites, (b) selection of imidazolate linkers used in the synthesis of ZIFs, and (c) crystal structures of ZIFs with diverse pore sizes and pore openings. Atom labeling scheme: C, black; O, red; N, green; Br, purple; Cl, orange; Zn, blue polyhedra. H atoms are omitted for clarity. Yellow spheres represent the space in the framework.

because the strength of the M–N (charged linker) bond in imidazolate and its short length impart architectural and thermal stability to ZIFs.

### Covalent organic frameworks (COFs)

In his 1916 paper titled “The Atom and the Molecule”, Gilbert N. Lewis introduced the idea of covalent bonding between atoms to form molecules.<sup>106</sup> This fundamental concept has since been at the very core of organic chemistry and has been applied to the synthesis of increasingly complex structures, which has resulted in natural products for use in the pharmaceutical industry and organic performance



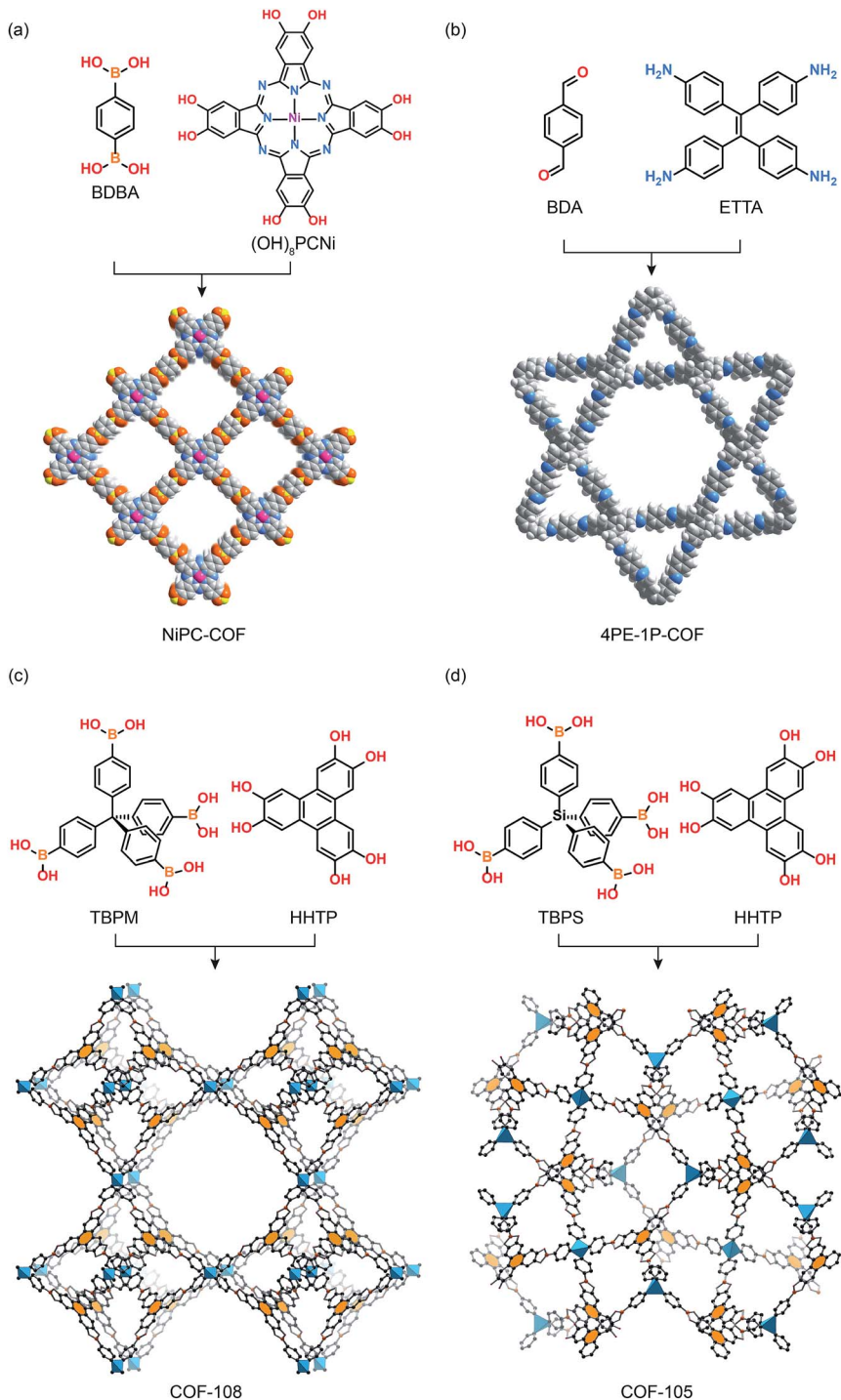
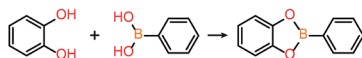


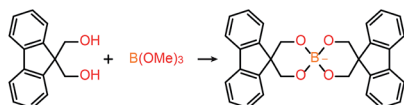
Fig. 10 Synthesis of covalent organic frameworks. A desired network can be targeted by deconstructing it into its fundamental organic building blocks with appropriate length and geometry.

## Paper

## B-O bond formation

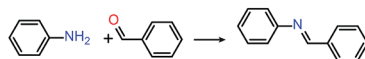


boronate ester

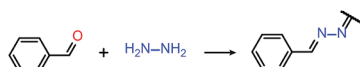


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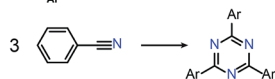
## C=N bond formation



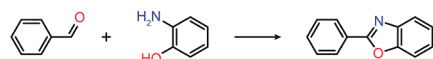
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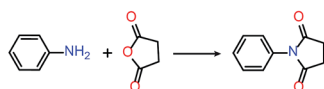
C=N<sub>Ar</sub> bond formation

triazine

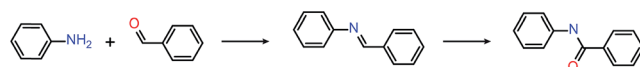


oxazole

## C-N bond formation

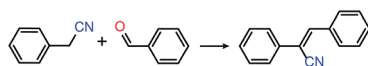


imide

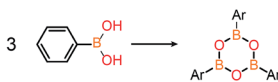


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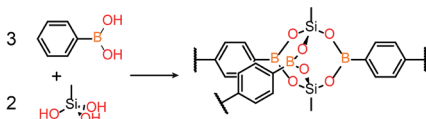
## C=C bond formation



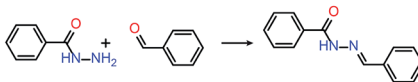
alkene



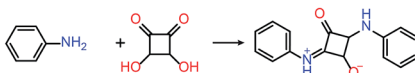
boroxine



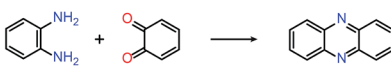
borosilicate



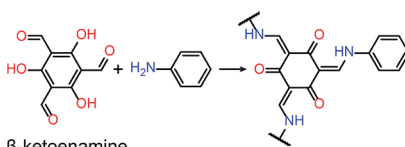
hydrazone



squaraine



phenazine



β-ketoenamine

## B=N bond formation



borazine

Fig. 11 A range of linkages reported in the synthesis of COFs.

materials such as polymers. However, up until recently, this chemistry was limited to discrete molecules and linear (1D) polymers, as highlighted by Roald Hoffmann in a 1993 article: "Organic chemists are masterful at exercising control in zero dimensions. One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders... But in two or three dimensions, it's a synthetic wasteland".<sup>107</sup> The long-standing challenge of expanding organic chemistry to two- and three-dimensions was overcome with the first reports of 2D and 3D COFs in 2005 and 2007, respectively.<sup>108,109</sup> In the chemistry of COFs the uncertainty of design in the synthesis is no longer present because the structures of the organic building units are maintained throughout the linking and crystallization processes. Although, the crystallization challenge still exists for COFs, their production in crystalline form has already been achieved.<sup>110-114</sup> Beyond the original boroxine and boronate linked COFs, this chemistry has expanded to include over 10 linkage types and has produced over 200 different COF structures (Fig. 10 and 11).<sup>108,110,115-126</sup> In COF chemistry, a specific network is targeted, then molecular building units (linkers) corresponding to the connections in that network are identified and placed on those connections. This notion has been very useful in designing COF materials as the configurations of building blocks are preserved throughout the reactions.<sup>122,127</sup> A powder X-ray diffraction (PXRD) pattern is calculated for that expected chemical structure, and then this pattern is matched to the one obtained experimentally from analysis of the product of the synthesis. More often than not, the structure predicted is the one obtained. Thus, COFs are

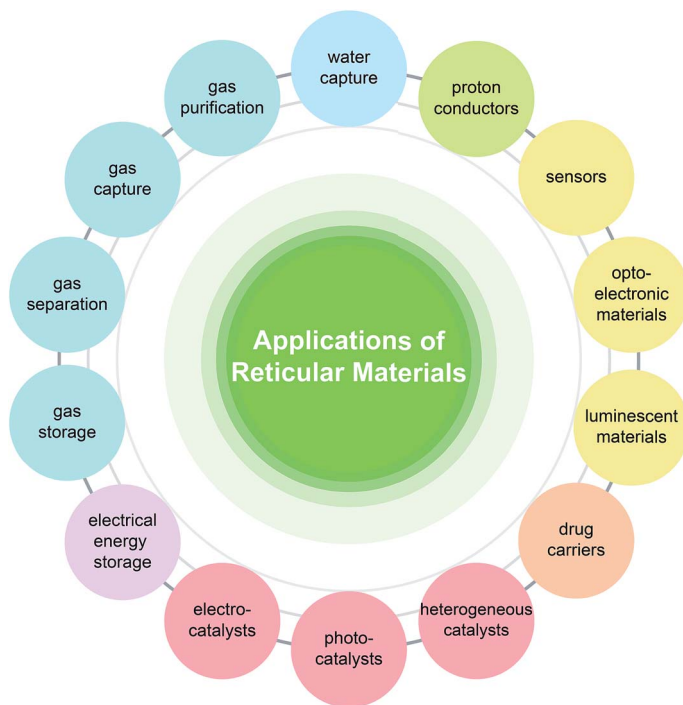


Fig. 12 Reticular materials are being developed in many areas ranging from energy storage, gas separation, water capture, and catalysis to biomedical applications.

generally made by design, as without prediction it would be difficult, if not impossible, to confirm their crystal structure from the PXRD pattern. Recently, it was possible to determine the structure of several COFs using single crystal electron diffraction and PXRD data.<sup>128,129</sup>

## Scope of applications

The now large community of scientists and engineers working in the field of reticular chemistry is using these principles and methods to expand the field into applications (Fig. 12). Certainly, the SBU and isorecticular principles when combined with the ability to crystallize new structures constitute a powerful mix, which has led to the synthesis of the largest class of porous crystalline materials ever made (Fig. 13). These reticular materials (MOFs, ZIFs and COFs) have provided access to crystalline structures with exceptional surface areas,<sup>60,109,112,130–132</sup> pore openings<sup>61,112,133</sup> and pore sizes.<sup>41,134–137</sup> Knowledge of the location of adsorptive sites within the pores has been critical to the design of MOFs with ultra-high porosity and to crafting the sterics and electronics of such sites for various applications.<sup>138,139</sup> It is now possible to make materials capable of the highest storage capacity for gases such as methane,<sup>140–146</sup> the most selective gas separations especially carbon dioxide from water,<sup>147–151</sup> and harvesting water from air.<sup>152–160</sup> High surface area and the capability to tune the metrics and composition in reticular materials allow for precisely designed catalysts for highly selective transformations and small molecule activation.<sup>161–170</sup> Such tunability is also advantageous in discovering conductive materials.<sup>120,171–179</sup> With accumulated fundamental understanding of charge transport in porous materials, the conductivities in MOFs and COFs have been significantly improved and found applications that require both porosity and conductivity such as capacitors<sup>180–182</sup> and electrocatalysts.<sup>183–186</sup> The ability to make these materials as nanocrystals made it possible to process them into large thin films and membranes for gas separation applications<sup>87–89,187–191</sup> and to synthesize colloidal materials for biomedical applications.<sup>79,192–196</sup> The fact that the crystal structures of

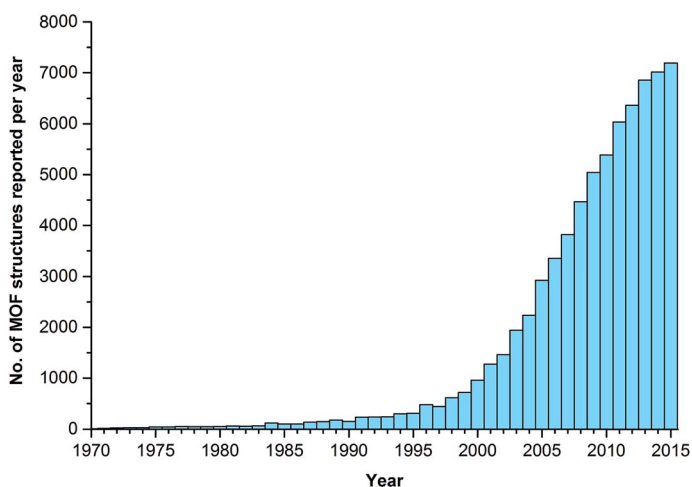


Fig. 13 Metal–organic framework structures (1D, 2D, and 3D) reported in the Cambridge Structural Database (CSD) from 1970 to 2015.

the bulk forms are known also facilitates knowledge of the chemical composition and structure of their corresponding nanocrystals. This, in turn, plays a key role in modulating the reactivity and selectivity of metal nanocatalysts when embedded in nanocrystals of reticular materials.<sup>197–202</sup> There is no doubt that the development of modelling and theory of the frameworks will become increasingly important for material discovery and understanding various properties.<sup>150,203–209</sup>

BASF is now scaling up MOFs to multi-ton quantities and over a dozen start-up companies are pursuing MOF applications. This is in addition to a large number of research programs at major chemical and automobile companies worldwide focusing on the development of reticular materials.<sup>210–212</sup>

## Precision chemistry within the framework and related applications

Another area of development in reticular chemistry is using frameworks as a starting point to target specific and synergistic functions. Here, MOFs, ZIFs and COFs were either interfaced with other materials<sup>213–216</sup> or subjected to post-synthetic reactions<sup>74,76,124,217–226</sup> to install desired functionalities. Such control of matter in space allowed for the synthesis of materials with unique properties enumerated here. (1) Open metal sites, a vacant site on the SBU that is available for the coordination of molecules.<sup>227</sup> One example involves the placement of amines in a row using the open metal sites in the pore of MOFs where a chain

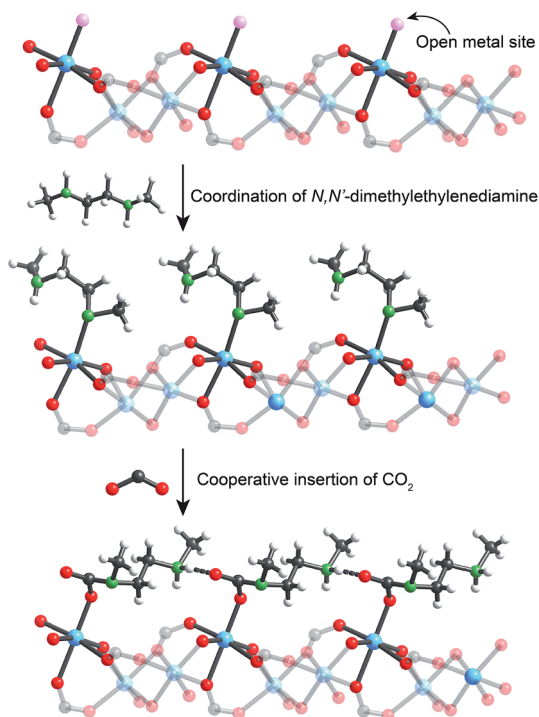


Fig. 14 Open metal sites in MOFs were used to align *N,N'*-dimethylethylenediamine molecules in one-dimensional pores facilitating a concerted CO<sub>2</sub> capture process. Atom labeling scheme: C, black; O, red; N, green; Mn, blue.

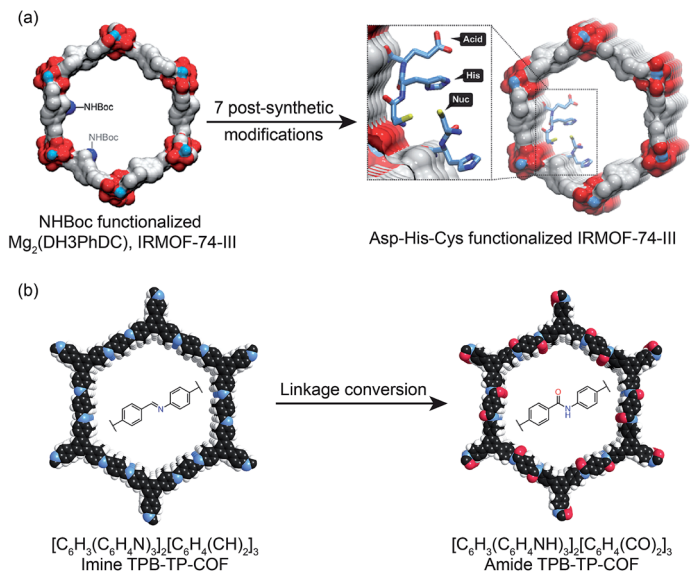


Fig. 15 (a) Amine functional groups in functionalized IRMOF-74-III were post-synthetically functionalized with amino acids leading to catalytic sites similar to TEV endoprotease.  $\text{DH}_3\text{PhDC}^{4-} = 3,3''\text{-dihydroxy-(1,1':4',1''-terphenyl)-4,4''-dicarboxylate}$ .<sup>228</sup> (b) Imine linkages in COFs were selectively transformed into amide linkages while preserving the structural integrity and bypassing the crystallization problem.<sup>124</sup> Adapted with permission from ref. 124 and 228. Copyright 2016 American Chemical Society.

reaction of  $\text{CO}_2$  capture could be obtained leading to a sharp  $\text{CO}_2$  uptake over a narrow pressure range (Fig. 14).<sup>150</sup> (2) Post-synthetic functionalization of frameworks.<sup>217</sup> This chemistry has become very useful to access the pore metrics and chemical environment, which could not be incorporated during the synthesis of the frameworks due to interference with crystal growth. As demonstrated recently, MOFs were post-synthetically covalently functionalized with primary amines to show, for the first time, the capture of carbon dioxide in the presence of water.<sup>148</sup> This same MOF with the covalently appended primary amine was further

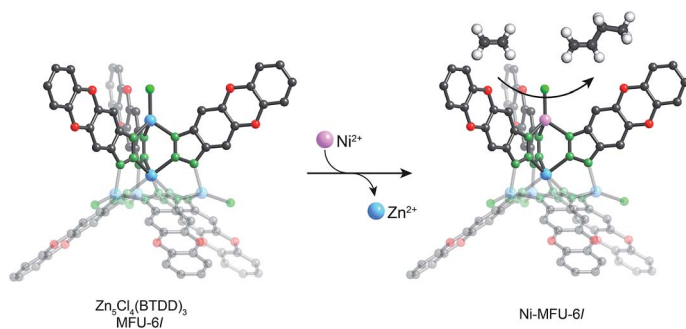


Fig. 16 Metals in the SBUs of the MOF were partially exchanged to produce the isolated active sites for ethylene dimerization.  $\text{H}_2\text{BTDD} = \text{bis}(1\text{H}-1,2,3\text{-triazolo}[4,5\text{-}b],[4',5'\text{-}i])\text{dibenzo}[1,4]\text{dioxin}$ . Atom labeling scheme: C, black; O, red; N, green.



modified with amino acids resulting in a material with catalytic selectivity similar to that of the TEV enzyme (Fig. 15a).<sup>228</sup> This concept has also appeared in COFs where the linkage in imine-based COFs could be selectively converted to amide COFs yielding materials with high chemical stability in basic and acidic media (Fig. 15b).<sup>124</sup> (3) Post-synthetic metal and ligand exchange, substitutions of metals, linkers, or capping molecules of the original frameworks.<sup>74,220</sup> It has been shown that metals in the SBUs can be partially substituted with catalytically active metals to produce site-isolated active sites for ethylene dimerization resulting in high catalytic activity and selectivity surpassing that of current homogeneous catalysts used in industry (Fig. 16).<sup>169</sup> Such isolated active nodes in the framework are crucial as they prohibit dimerization of catalysts, a common cause for catalyst deactivation. (4) Nanocrystals of reticular materials, the size regime compatible for interfacing with inorganic nanomaterials to yield well-defined interfaces.<sup>214–216</sup> As an example, Pt nanocrystals were sandwiched within MOFs where open metal sites are positioned over the entire nanocrystal, thereby interacting with substrates during catalysis (Fig. 17).<sup>202</sup> As a result, selective hydrogenations towards carbonyl over carbon–carbon double bonds in  $\alpha,\beta$ -unsaturated aldehydes were achieved. This example also signifies the reciprocity resulting from the combination of different classes of materials.

## The current state put in the larger context of chemistry

The field of reticular chemistry has overcome the long-standing challenge of achieving crystalline materials from linking of molecular building units through

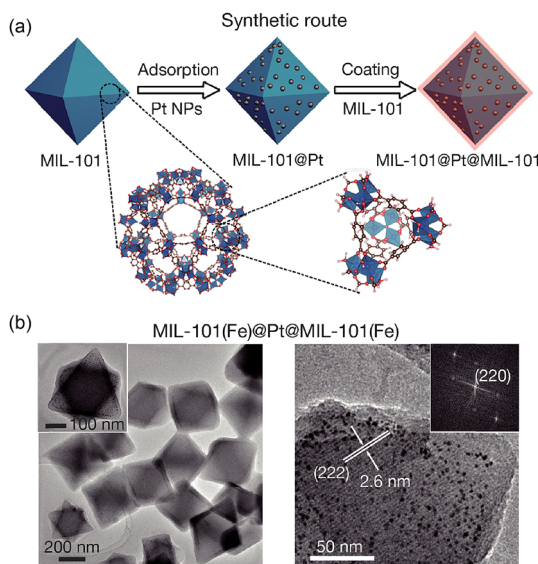


Fig. 17 Pt NCs were sandwiched between the MOFs which regulate the hydrogenation selectivity. Shown are the synthetic route (a) and TEM images (b) of the sandwich nanostructure. Adapted with permission from ref. 202. Copyright 2016 Nature Publishing Group.



strong bonds. The flexibility with which the resulting structures can be varied in their composition, metrics and chemical environment of the pores has, without a doubt, changed the very foundation of how we imagine and make new materials. This has led to a rapid growth of the field. In the context of chemistry as a whole, the field of MOFs and ZIFs has brought together two areas of chemistry – organic and inorganic – typically thought of as separate and indeed taught as separate disciplines, into one area where it is possible to make structures by design and to target specific properties. On the other hand, the field of COFs has propelled organic chemistry into two- and three-dimensions, and provided clear methods for how cross-linked organic polymers may be crystallized. Definitely, the attainment of these reticular materials in crystalline form not only strengthens our knowledge of their interworking but also provides a platform for pinpointing, within confined space, sites onto which specific reactions and chemical events can take place in a controlled fashion. The ability to carry out post-synthetic modification on reticular structures while still maintaining their porosity and long-range order, takes this field back into the realm of molecular chemistry. Here, organic reactions and inorganic complex reactions can be performed within enclosed space on a well-defined framework backbone while maintaining the definitive nature of molecular chemistry due to the knowledge of the crystal structure of the MOF/ZIF/COF. In other words, crystals are being used as molecules, and the frameworks making up these crystals are now endowed with chemistry that goes beyond that of molecules.<sup>63</sup> This has been referred to as ‘framework chemistry’, which indeed brings extended structures for the first time under the precision and control that molecular organic and inorganic chemists are accustomed to practicing. We remark that with the achievement of framework

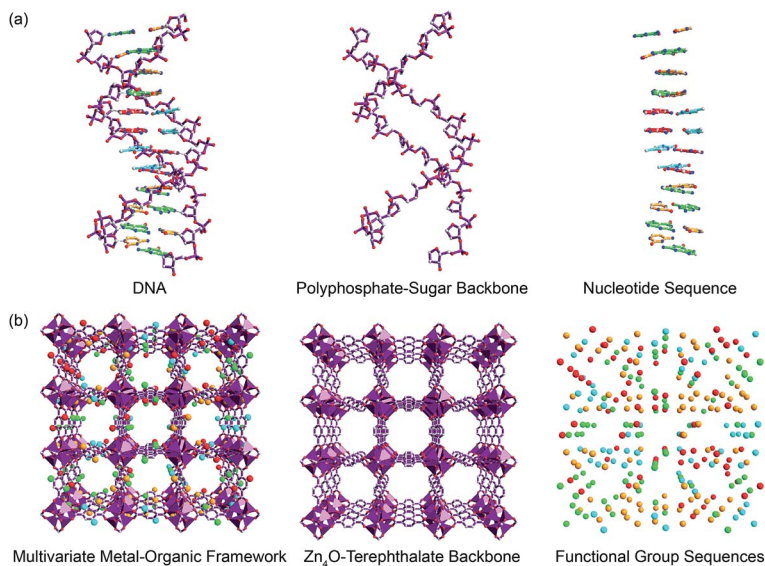


Fig. 18 MOFs can be envisaged as a backbone akin to the polyphosphate–sugar backbone of DNA (a) where functional groups can be incorporated to form multivariate MOFs (b). The arrangement of these functional group sequences can encode specific properties. Adapted with permission from ref. 229. Copyright 2017 American Chemical Society.

chemistry, there is still a lot to be done in the realms already mentioned. However, we wish to ask the following questions: what comes next that goes beyond what we have already discussed? Have we figured out all this precision chemistry, just to pursue applications such as the ones we see today? Or are there larger and far more reaching implications of this sophisticated chemistry that would impact materials made in this century? What is the unexplored landscape of reticular chemistry? We attempt to address these questions in the remaining sections of this contribution.

## Next generation of concepts and materials in reticular chemistry

The future of reticular chemistry can be best described by first considering the framework as composed of three general components: the backbone, the functionality, and the space that these two parts encompass.<sup>229</sup> The backbone provides the structure onto which functionalities could be covalently attached (Fig. 18). When multiple functionalities or metal ions are introduced into a single framework, a multivariable system results. The case of functionalities is not too dissimilar in concept from the constructs of most biologically important molecules. In DNA, a polyphosphate sugar backbone provides for DNA's overall structure, while the nucleotides, which are covalently attached to the backbone, provide the multivariable but unique sequences. Another way to introduce multivariable units is by using many different building units as part of the structure backbone. This is exemplified by many amino acid sequences making up protein structures. In synthetic materials, the introduction of a large number of building units as part of the backbone is much harder to do because of the problems caused by phase separation and disorder in the resulting structure. However, in general, the two scenarios represent ways of introducing diverse complexity into chemical structures. Until the advent of reticular materials, attempts to employ multiple functionalities or multiple building units in materials has resulted in amorphous, ill-defined products. It would be desirable to find strategies for transferring the diversity concepts that are so common in biology to synthetic systems. How such diversity manifests itself in synthetic materials and in particular reticular materials is a fascinating question worth addressing in future research. It becomes useful in the context of how one might use the space encompassed by such chemical diversity. Below we outline several examples as potentially rich and rewarding directions for the introduction and use of this diversity.

## Sequence-dependent materials

It is now possible to introduce up to eight different functional groups into one MOF structure.<sup>62</sup> We have shown how the spatial arrangements of such functionalities can potentially form sequences, which may very well be the basis for encoding properties. The kinds of functionality introduced into such sequences and their ratios can be controlled and detected, however the spatial arrangement within the pores is not as well defined because they occupy the same crystallographic position and are therefore disordered. The questions to be answered

center around whether these functionalities form unique sequences, which is very likely the case, but to prove it requires the development of new physical techniques capable of deciphering the spatial arrangements of the functionalities. Recently, in MOFs containing two and three different functionalities, it was shown using solid-state NMR that, depending on the nature of functionality and concentration in the MOF, apportionment of functionalities as large or small clusters, random distribution, or highly mixed arrangement on the nanometer scale was possible (Fig. 19a).<sup>230</sup> This means that even with a binary functionality system one can design regions within a MOF crystal to have intermingled regimes bearing different functionalities and therefore different intrinsic properties.

Recently, it was also possible to create MOFs with many different metals incorporated within the same framework (Fig. 19b).<sup>231</sup> Depending on the topology of the structure containing these multiple metals, it was possible to determine their distribution using combined spectroscopic techniques. It is worth noting that these systems stand out in terms of their exceptional performance in gas adsorption or small molecule activation compared to the unmixed systems. In the future, as we learn how to characterize the chemical diversity of these multivariable materials, it should be possible to design unique sequences that will direct incoming molecules into energetically favorable binding states or, when anisotropy is included throughout the pores, it will be possible for substrates to travel along specific circuitry of pathways defined by the uniqueness of the sequences lining the pores.<sup>232,233</sup>

The importance of sequence-dependent materials to catalysis cannot be overestimated. The great gulf separating heterogeneous and homogenous catalysis (including enzymes) can be bridged by the materials we propose here. In particular, the robustness of heterogeneous catalysts can be combined with the high selectivity that is so characteristic of enzymes and possible in other molecular-based catalysts. Recent preliminary results showed that a MOF, which has undergone seven post-synthetic modification steps to introduce a short peptide in its interior, is capable of catalyzing a selective bond breaking reaction, previously only observed for a specific enzyme.<sup>228</sup> We note that since the post-synthetic steps are not all quantitative, the system is highly multivariable and this diversity may very well be the key to achieving the observed unique reactivity.

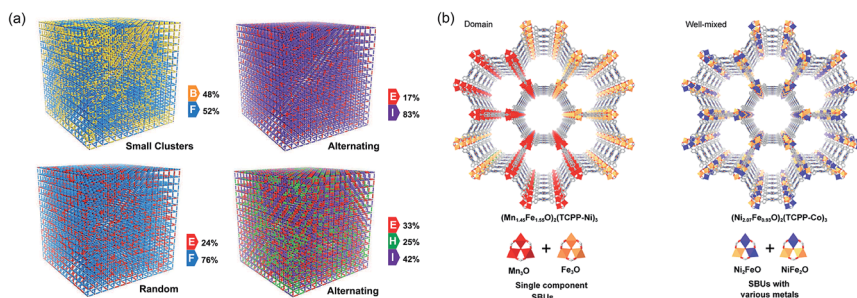


Fig. 19 (a) Apportionments of functionalities in MOFs mapped by solid-state nuclear magnetic resonance measurements.<sup>230</sup> (b) Spatial arrangement of metals in the SBUs decoded by combined spectroscopic analyses.<sup>231</sup> Reproduced with permission from ref. 230 and 231. Copyright 2013 American Association for the Advancement of Science. Copyright 2016 American Chemistry Society.

It is useful to think of multivariable systems such as these MOFs as encapsulating a very large number of states (specific but unknown regions within the pores of variable steric and electronic characters) and therefore a substrate passing through the pore would be ‘sampling’ these states. The success achieved here opens many opportunities to using reticular materials as catalysts that are both thermally and chemically stable, yet have the selectivity characteristic of enzymes and other discrete catalysts.

## Dynamic, yet resilient materials

It has been a long-standing challenge to find means of creating extended structures, which might undergo fluxional behavior while preserving their structure. Certainly, we have learned from biology that dynamics are a necessary component of function, and that for reticular materials or synthetic materials in general to take a leap forward in their function, strategies for introducing dynamics are to be developed. Thus far, dynamics in reticular materials have been focused on using flexible linkers or finding extended structure, which can flex in a similar manner to that of an accordion<sup>45,143,234–239</sup> (Fig. 20) or shift with respect to each other.<sup>240–243</sup> Although, these systems show interesting gated gas uptake and release behavior, the fact that covalent or coordinative bonds are inevitably broken, and thus likely to cause framework collapse upon repeated cycling, is a major limitation. Better ways of creating dynamics should be developed if we are to make reticular systems that take advantage of sequence information and function similar to biological molecules.

A few years ago, we proposed ‘robust dynamics’ as a way to overcome the fidelity issue faced by fluxional frameworks.<sup>244</sup> Our concept relies on introducing components within the organic linkers which are mechanically interlocked and therefore capable of dynamics without the risk of breaking the bonds making up the backbone. Recent reports showed how implementation of this concept could be done in a MOF material (Fig. 21).<sup>245–249</sup> These systems are ideal for stimuli responsive mechanical motions and represent a novel direction in robust dynamics.

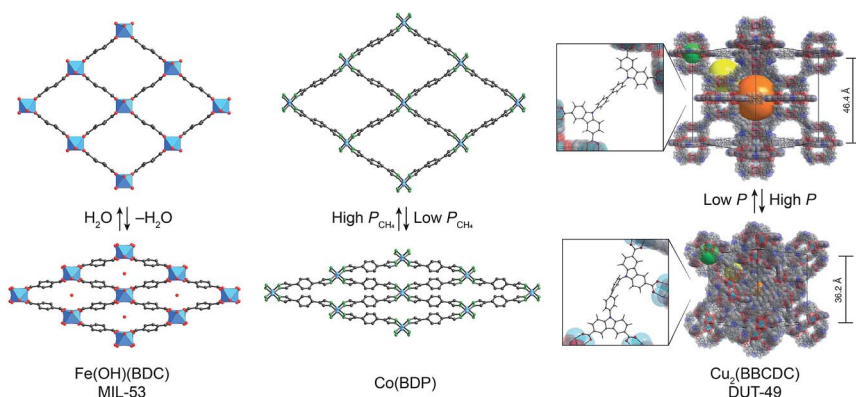


Fig. 20 Flexible frameworks whose movements originate from the change in bond angles due to external stimuli.  $\text{BBCDC}^{4-} = 9,9' - ([1,1' - \text{biphenyl}] - 4,4' - \text{diyl})\text{bis}(9H - \text{carbazole} - 3,6 - \text{dicarboxylate})$ . Adapted with permission from ref. 237. Copyright 2016 Nature Publishing Group.

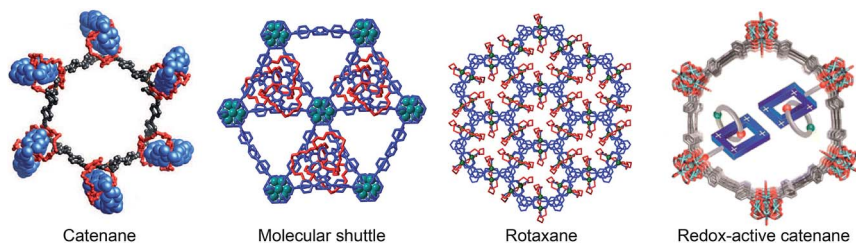


Fig. 21 Robust dynamics: mechanically interlocked molecules carrying the movement without compromising the framework integrity. Adapted with permission from ref. 245 and 247–249. Copyright 2010 John Wiley & Sons Inc. Copyright 2012 and 2015 Nature Publishing Group. Copyright 2016 American Chemical Society.

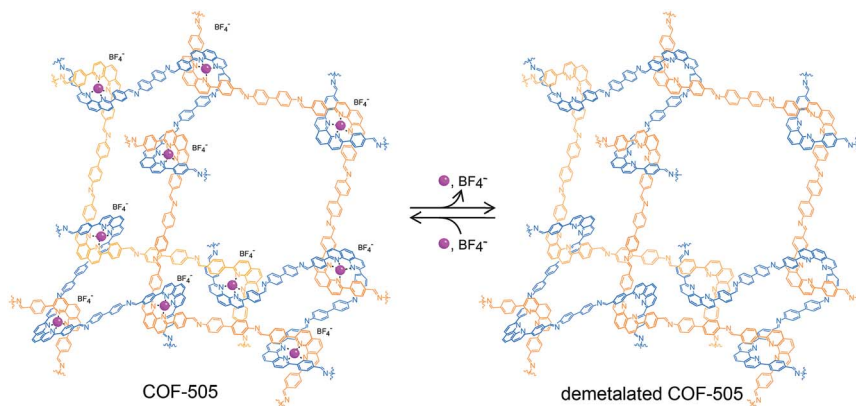


Fig. 22 Molecular weaving of COFs. Adapted with permission from ref. 128. Copyright 2016 American Association for the Advancement of Science.

Last year, we reported ‘molecular weaving’ of covalent organic frameworks whereby the interlacing of threads, made by linking organic molecules, was demonstrated in a crystalline COF structure (Fig. 22).<sup>128</sup> The key feature of the formation of this construct is that metal-binding sites, designed to be at regular intervals of the threads, serve as points of registry to bring the threads together in an interlacing fashion. Initially, a ‘metalated’ COF forms which can then be demetalated leaving behind a woven organic structure. The metal ions can be reintroduced and removed at will without unzipping the threads. This woven construct can be thought of as a molecular cloth where it is possible for it to be highly fluxional because of the threads’ increased motional degrees of freedom. In this arrangement, only mechanical bonds are used for the dynamics, leaving the covalent threads intact.

## Concluding remarks

Up to now, we have learned how to design the framework’s backbone structure and functionalize it without losing porosity and long-range order, thereby achieving framework chemistry as an extension of molecular chemistry. These reticular materials will continue to be important in various applications and offer properties



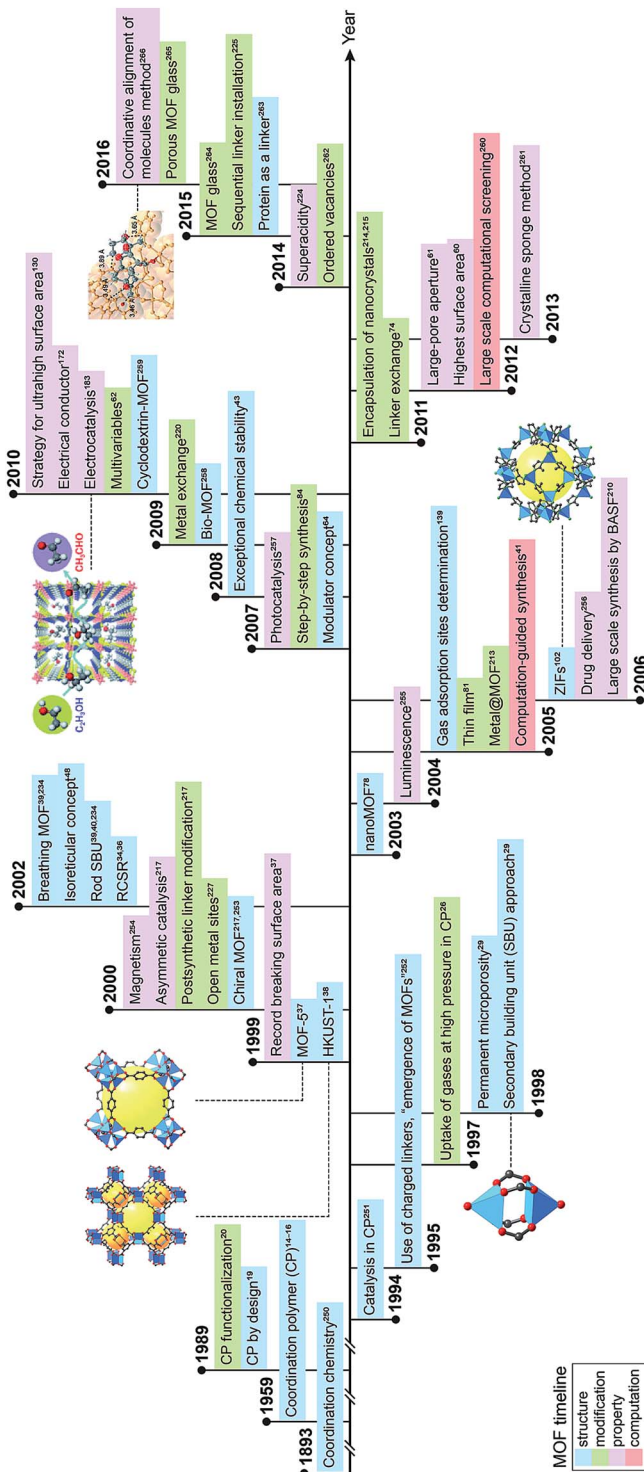


Fig. 23 Chronology of first reports of contributions in the field of metal–organic frameworks (MOFs). The history of the field could be traced back to the time where the structures of coordination complexes were described in 1893, subsequently leading to the discovery of many other molecular complexes and crystalline extended structures. The use of charged organic linkers and metal clusters (SBUs) to form crystalline extended structures with permanent porosity marked the beginning of the field of MOFs. If not otherwise noted, we refer to MOFs as crystalline and porous materials made from strong bonds. Figures in the chronology were adapted with permission from ref. 183 and 266. Copyright 2010 John Wiley & Sons Inc. Copyright 2016 American Association for the Advancement of Science.

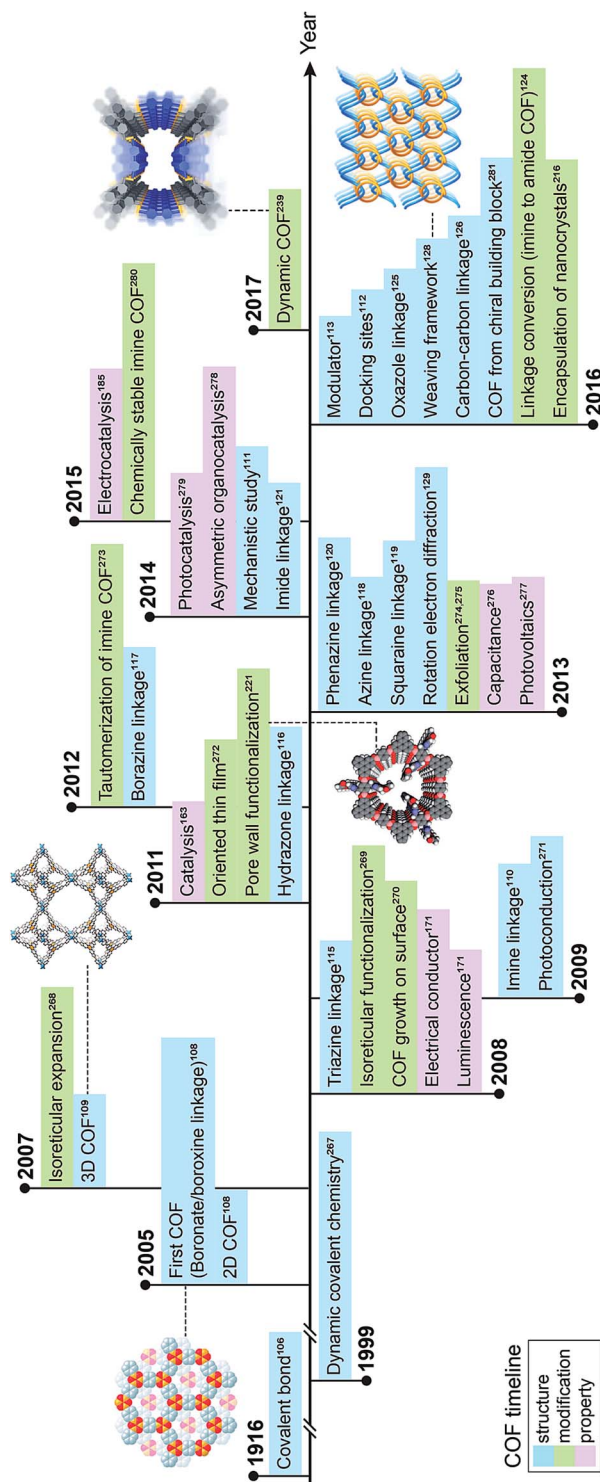


Fig. 24 Chronology of first reports of contributions in the field of covalent organic frameworks (COFs). Extension of 1D organic molecules to crystalline 2D and 3D frameworks gave rise to the field of covalent organic frameworks. Figures in the chronology were adapted with permission from ref. 128, 221 and 239. Copyright 2011 Nature Publishing Group. Copyright 2016 American Association for the Advancement of Science. Copyright 2017 American Chemical Society.



not possible by their molecular components alone. However, the future of reticular chemistry belongs to the domain of controlling the spatial arrangement of functional units and metal ions in multivariable systems. Once we figure out how to characterize the diverse arrangement that is covalently linked to the framework backbone, then we will be in a position to truly craft the space encompassed by the backbone and control matter within a complex environment. These aspects are not offered by today's materials but reticular materials offer a rich platform for achieving these complex, diverse yet highly ordered systems. We have provided timelines for the development of reticular chemistry, MOFs, ZIFs and COFs, (Fig. 23 and 24). The authors hope that these timelines will guide the readers and give them a launching point to this vast and rapidly growing field of compounds and properties, and to hopefully occasionally pause to appreciate their beautiful facets (the timelines include, in addition to those already cited, ref. 250–281).

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