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Crystal Engineering, Structure-Function Relationships, and the Future of Metal-Organic Frameworks

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Abstract

Metal-Organic Frameworks (MOFs) are a rapidly expanding class of hybrid organic-inorganic materials that can be rationally designed and assembled through crystal engineering. The explosion of interest in this subclass of coordination polymers results from their outstanding properties and myriad possible applications, which include traditional uses of microporous materials, such as gas storage, separations, and catalysis, as well as new realms in biomedicine, electronic devices, and information storage. The objective of this *Highlight* article is to provide the reader with a sense of where the field stands after roughly fifteen years of research. Remarkable progress has been made, but the barriers to practical and commercial advances are also evident. We discuss the basic elements of MOF assembly and present a conceptual hierarchy of structural elements that assists in understanding how unique properties in these materials can be achieved. Structure-function relationships are then discussed; several are now well understood, as a result of the focused efforts of many research groups over the past decade. Prospects for the use of MOFs in membranes, catalysis, biomedicine, and as active components in electronic and photonic devices are also discussed. Finally, we identify the most pressing challenges in our view that must be addressed for these materials to realize their full potential in the marketplace.

I. The advent of MOFs as a new class of materials

It is now 20 years since the first use of the term “Metal-Organic Framework” (MOF) in the literature.[1] Since then, over 7,000 articles involving that search term have been published, 1,300 of which appeared in 2013 alone. Even this very large number is probably an underestimate, as there are terms other than MOF to describe porous crystalline solids comprised of metal ions coordinated to organic groups. “Coordination polymer” is a more general term, but this includes a large body of materials that are not porous. Yaghi et al. identified more than 20,000 structures reported in the past decade as MOFs;[2] however, it is unclear how many of these display permanent porosity. By contrast, there are approximately one thousand zeolites comprising about two hundred topologies.[3] Crystal structures of selected MOFs from the CSD that have had a particularly large impact are presented in **Figure 1**.

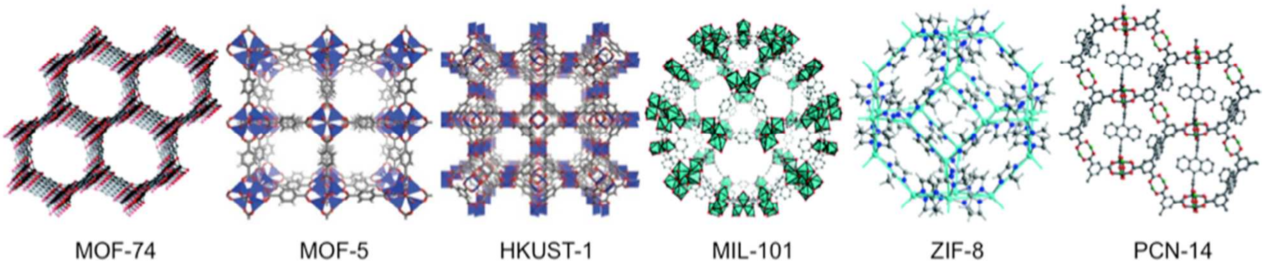


Figure 1. Crystal structures of common MOFs published in the CSD database.

An important early objective in the field of coordination polymers was to synthesize materials with permanent microporosity, using organic or inorganic building blocks that enable rational design in a way not afforded by the inorganic oxide structure zeolites. A major turning point came in 1999 when two key structures were published, HKUST-1[4] and MOF-5.[5] HKUST-1 exhibits nanoscale porosity and high thermal stability, with the potential to chemically functionalize its pores, a significant advance over zeolites. MOF-5 is similar in this regard and set a record for the surface area of a crystalline material. Together, these two canonical structures generated tremendous excitement for applications such as hydrogen storage, where a major quest for improved materials was already underway. Within six years, the number of annual MOF publications increased by more than a factor of ten. Since then, interest expanded far beyond gas storage, to include fields such as drug delivery, sensing, medical imaging, energy storage, and light harvesting, as well as more "traditional" applications of microporous materials, such as separations and catalysis. The breadth of the research is summarized in a large number of excellent reviews, several of which are listed in **Table 1** for individual topics.

Table 1. Selected recent MOF-related review articles by topic.

Topic	Review	Ref.
General	The chemistry and applications of Metal-Organic Frameworks	2
Topologies and Morphologies	Synthesis of Metal-Organic Frameworks (MOFs): routes to various MOF topologies, morphologies, and composites	6
MOF thin films	Metal–Organic Framework thin films: From fundamentals to applications	7
Flexible MOFs	Flexible metal–organic frameworks	8
Crystal engineering	Crystalline metal-organic frameworks (MOFs): synthesis, structure and function	9
MOF assembly	Metal–Organic Frameworks: From molecules/metal ions to crystals to superstructures	10
Template synthesis	Template-directed synthesis of metal-organic materials	11
Luminescent MOFs	Luminescent functional Metal-Organic Frameworks	12
Luminescent MOFs	Engineering metal-based luminescence in coordination polymers and metal-organic frameworks	13
Ferroelectric MOFs	Ferroelectric Metal–Organic Frameworks	14
Magnetic MOFs	Microporous magnets	15
Photocatalysis	Metal-organic frameworks for artificial photosynthesis and photocatalysis	16
Mechanical properties	Mechanical properties of hybrid inorganic-organic framework materials: establishing fundamental structure-property relationships	17
Amorphous MOFs	Amorphous Metal-Organic Frameworks	18
MOF Fabrication	MOF positioning technology and device fabrication	19
MOF Devices	MOF-based electronic and opto-electronic devices	20
MOF membranes	Metal-organic framework membranes: from synthesis to separation application	21
Porphyrin MOFs	Metal-metalloporphyrin frameworks: a resurging class of functional materials	22
Polyoxometalate MOFs	Polyoxometalate based open-frameworks (POM-OFs)	23
MOFs in biomedicine	Metal–Organic Frameworks in biomedicine	24
Drug delivery	Metal-organic frameworks as potential drug delivery systems	25
Nanomedicine	Nanoscale Metal-Organic Frameworks for biomedical imaging and drug delivery	26
Post-synthetic modification	Beyond post-synthesis modification: evolution of metal–organic frameworks *via* building block replacement	27
Catalysis	Metal Organic Framework catalysis: Quo vadis?	28

A number of encouraging developments during the past five years are accelerating the pace of MOF development. Among these is the report by researchers at BASF that at least one MOF can be synthesized in ton-scale quantities.[29] This demonstration of large-scale production feasibility lends confidence that real-world applications are not far off. MOF synthesis is also being facilitated by the commercial availability of many organic "linker" reactants. A few MOFs are now in commercial production in multi-kg amounts, including MIL-53, HKUST-1, and ZIF-8, and small companies are now selling other MOFs or offering custom synthesis services to produce them in quantities up to 1 kg. At least one pilot-scale use of MOFs is underway: the U.S. Dept. of Energy's Hydrogen Storage Engineering Center of Excellence selected MOF-177 as the sorbent in a vehicular hydrogen storage tank.[30] The field as a whole also appears to be solidifying in a professional sense; an international meeting devoted to MOFs will have its fourth meeting in Kobe, Japan in 2014 and there are regular symposia focused on these materials at the annual meetings of major scientific societies. The International Zeolite Association also initiated a MOF Commission in 2013. These events signify that MOFs are recognized as an important new class of materials with the potential to be commercially successful.

This explosion of work suggests that MOFs constitute a new subdiscipline of coordination chemistry. It seems unlikely that the pace of MOF synthesis will slow anytime soon; at current rates, there will be more than 40,000 "MOFs" by 2025, based on a recent calculation.[2] In this Highlight article, therefore, we offer our perspective of the status of this rapidly expanding field. This is a very high-level view and our intention is not to provide a comprehensive "review of reviews." Rather, our purpose is to give the reader a sense of the current maturity of MOF chemistry from our vantage point as developers of MOFs for engineered applications, i.e., ones for which we have been forced to confront many practical issues associated with their use in specific technologies. We first examine the question of whether the MOF field is at a turning point in terms of commercial development: what scientific and engineering barriers impede progress? Following an abbreviated summary of the elements of MOF structure, we discuss some of the important structure-function correlations that now enable crystal engineering of these materials at an unprecedented rate. Next, some of the most promising applications that we expect will drive innovation in the next several years are reviewed. Finally, we summarize some key challenges that must be addressed to enable MOFs to go beyond the laboratory and reach at least the stage of pilot-scale engineering, if not full-scale commercialization.

II. Are MOFs at a turning point?

It is appropriate to ask, after this period of vigorous research, where does the field stand as a whole and in what direction is it, or should it be, headed? A quite different, but highly relevant question is, why are there currently no major commercial applications of these materials? To borrow a term from the software industry, what will be the “killer app” that forms the basis for major industrial production and propels the field forward? Development times for new materials vary, of course, but in general they average around twenty years (**Figure 2**).[31, 32] MOFs therefore appear ripe for entering the marketplace. Although they became commercially available in 2008, only four were sold as specialty chemicals. By contrast, 2013 worldwide production of zeolites is estimated to be around 2.7 Mtons.[33] Cost is often mentioned as a factor inhibiting commercial use of MOFs, but new materials are always expensive initially and once production is increased to an industrial scale, prices drop dramatically. There are other reasons for the relatively slow rate at which MOFs have penetrated the marketplace. Some of these are perceived, rather than actual barriers, but they include concerns about their mechanical robustness, water stability, and properties that are insufficiently superior to warrant replacing an established material with a MOF.

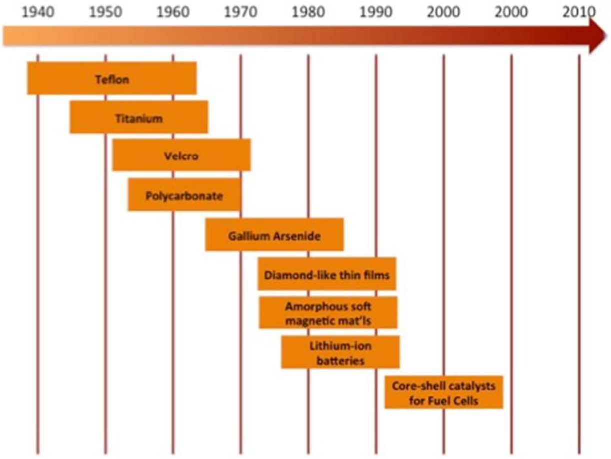


Figure 2. Approximate time-to-market following creation of new materials. Data from Ref. 31 and adapted from Ref. 32.

In addition to these market-driven factors, we recognize several significant technical hurdles that could limit the pace of commercial development. Among these is the fact that, although the number of frameworks is expanding rapidly, relatively few isoreticular MOF series exist. Initially, one of the major selling points for MOFs relative to other microporous materials was their “tunability,” i.e., the ability to modulate their properties by modifying the organic linker or metal ion while maintaining the basic topology. Certainly, there are good examples where this is true: the original IRMOF-n series, which includes MOF-5; the IRMOF-74-n(M) (**Figure 3**) series, in which both metal ion and linker can be varied; and the **nbo** and **rht** paddlewheel topologies. Not all of these can be synthesized *de novo*; some require post-synthetic modification approaches (see below). The vast majority of MOFs are unique, however, which stymies systematic modification. In most cases, the linker is the synthetic entry to analogous structures, since changing the metal ion may affect the coordination geometry and lead to a different structure (although recent work indicates that post-synthetic exchange of one metal cation for another is less of a problem than originally thought[34, 35]). Linker modification can be far from straightforward, however. Multistep organic syntheses are often required, which are complicated by the need to preserve the coordinating functional groups. The orientation of these groups may leave little or no room for additional functional groups and may deactivate open positions on aromatic rings.

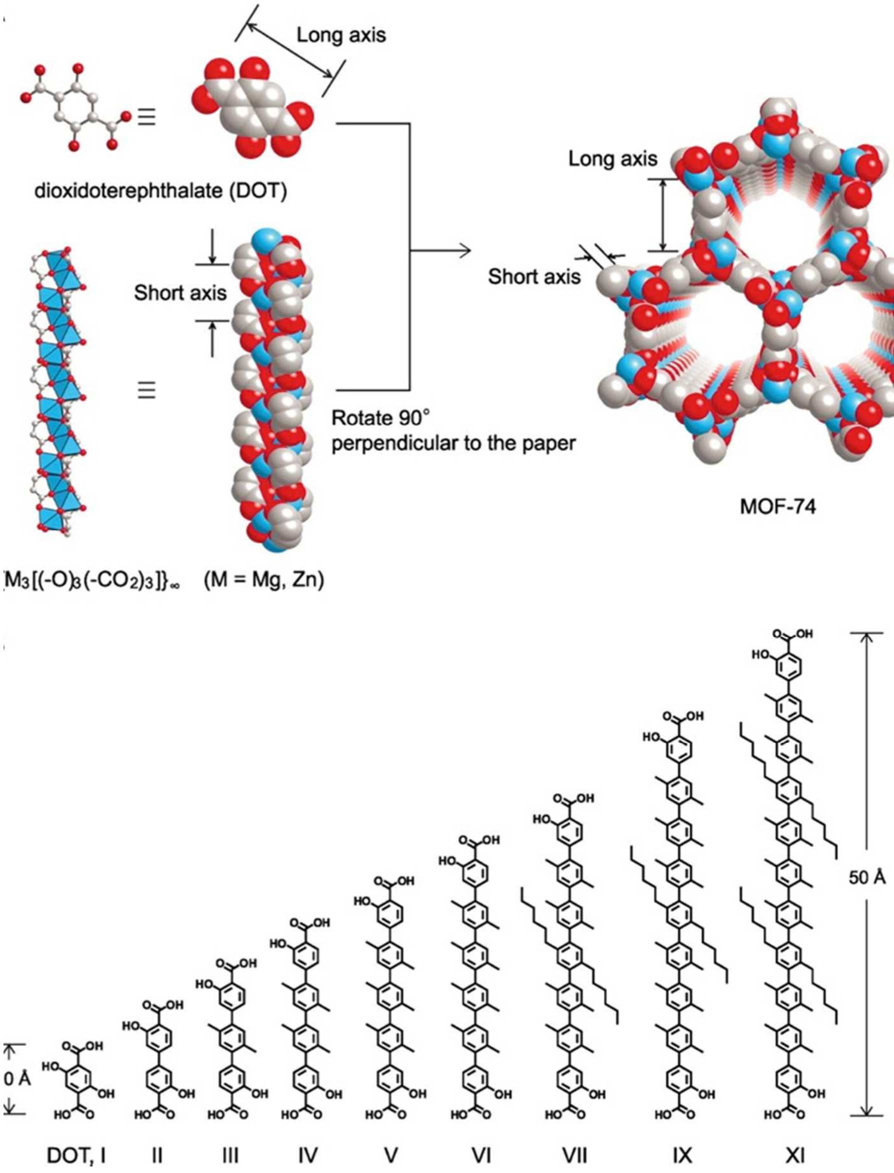


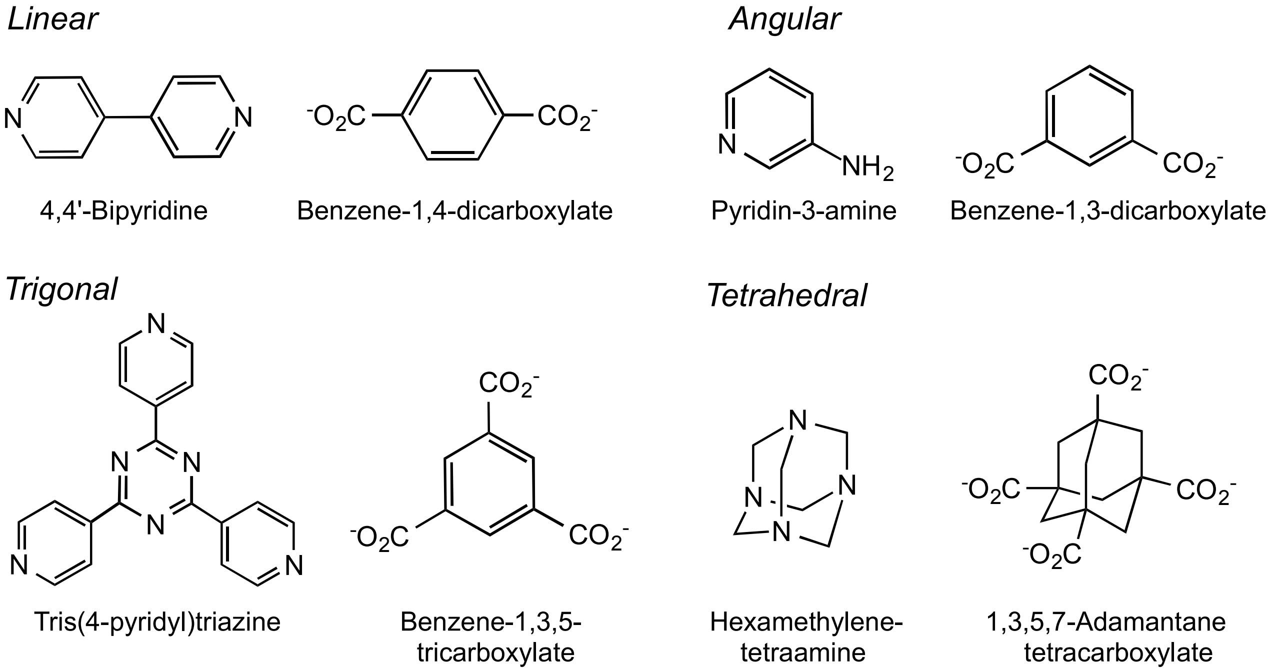
Figure 3. The IRMOF-74(n) series with organic linkers joined by a metal oxide SBU to make the three-dimensional MOF structure with one-dimensional hexagonal channels. Reprinted with permission from Ref. 36.

A related problem is that it is by no means assured that exchanging one linker for another will preserve the original topology. Synthesis of new MOFs can thus be very time consuming. In an effort to shorten development times, automated, high-throughput synthetic methods to quickly sample a range of reaction temperatures, times, and reactant concentrations have been demonstrated.[37] Unfortunately, the cost of the required automated equipment is prohibitive for most researchers. Computational screening provides a partial solution, since the stability of very large numbers of structures can be assessed in a relatively short time. This was illustrated on a truly grand scale by Wilmer *et al.*,[38] who evaluated the stability of nearly 138,000 potential MOFs by assembling a fixed set of linkers and metals using a set of self-assembly rules.[38] Another approach is to impose application-specific criteria that reduce the number of structures that must be synthesized. For example, Sholl and coworkers screened a larger number of MOF structures in the Cambridge Structural Data Base for their gas sorption properties relevant to CO_2 separation[39] and light adsorption of noble gases.[40] Once a set of promising structures is identified (a few dozen to a hundred), these can be assessed for ease of synthesis, and previously reported properties, such as adsorption capacity or selectivity, can be considered to determine if they are consistent with model predictions. The Carbon Capture Materials Database (CCMDB, carboncapturematerials.org) is another comprehensive database focused on crystalline porous materials such as MOFs and zeolites.[41] In addition to the CSD, a few structural databases built from computational screening are now available to assist in this process, including MOF*omics*[42] and Hypothetical Metal-Organic Frameworks Database.[38]

Post-synthetic modification (PSM) offers a second alternative for modifying MOF structures and expanding isoreticular series.[27] One of the best-developed strategies is to modify reactive groups already incorporated into the structure, such as a primary amine on a linker phenyl ring. Cohen and coworkers have developed this approach; their work now provides a suite of tested routes for incorporating new functionalities into existing structures. “Click chemistry” is also proving to be a powerful and selective route to MOF PSM.[43] Recently, however, new and versatile methods for exchanging structural elements without altering the topology are now being demonstrated. Hupp and coworkers developed Solvent Assisted Linker Exchange (SALE),[27] in which ligands are exchanged in solution with an existing structure; the Cohen group is also developing this line of attack.[44] Metal ions can also be substituted by analogous means, although complete substitution is not always feasible. For example, Dincă *et al.* showed that up to 25% of the divalent metal ions in MOF-5 can be substituted with virtually any other first-row transition metal, even ones that are trivalent.[45] The surprising ability to accomplish this is a testament to both the robust nature of many MOFs but also the dynamic nature of these structures in the presence of a promoting solvent. These routes to modifying existing MOFs could dramatically expand the number of available structures and remove a major barrier to property optimization.

III. MOFs and crystal engineering

Crystal engineering provides the basic principles for assembling coordination polymers in general, and MOFs in particular, based on geometrical and topological considerations.[2, 9, 46, 47] As early as 1990, Hoskins and Robson[48] uttered some prophetic words on the feasibility of stable porous coordination polymers with large internal porosity: “Despite Nature’s abhorrence of a vacuum it may be possible to devise rods with sufficient rigidity to support the existence of solids with relatively huge empty cavities. Materials combining good or even high thermal, chemical, and mechanical stability with unusually low density may thereby be afforded.” The node-and-linker approach to building coordination polymers is strictly based on metal and ligand coordination requirements and takes into account the specific shapes and geometrical orientations of the building blocks, which act as “tinker-toys”. The employment of geometrical and coordination requirement principles not only facilitates the description of known MOFs, but also provides a way to predict novel frameworks by altering the chemical connectivity. The 3D assembly of MOFs can be achieved in various crystallographic settings using linear, angular, trigonal or tetrahedral ligands. Typical amine and carboxylate linkers of various angularity used to assemble MOF structures are depicted in **Scheme 1**.



Scheme 1. Representative examples of amine- and carboxylate-based linear, angular, trigonal and tetrahedral linkers used to assemble MOF structures.

The MOF structure conceivably has a higher degree of complexity compared to other inorganic or organic materials. A parallel can be made between the structural complexity of proteins and MOFs with multiple levels of structural hierarchy. Proteins are macromolecules with four different levels of structure: primary, secondary, tertiary and quaternary. The *primary* structure of a protein is given by the aminoacid sequence, with aminoacid residues bound to each other through peptide bonds. The *secondary structure* is defined by stretches or strands of polypeptides that display different local structural conformation, such as α-helices or β-sheets. The *tertiary structure* is given by the overall 3D shape of the protein molecule, which allows for the maximum stability or lowest energy state. Finally, the *quaternary structure* describes how proteins interact with each other to form larger aggregate protein complexes. The *quaternary structure* of proteins is typically achieved through hydrogen bonding, disulfide bridges or electrostatic interactions.

Recently we drew an analogy between the structural complexity of MOFs and proteins.[49] The purpose of this is conceptual; we wish to create an organizational construct that enables one to visualize how various elements of MOF structure relate to one another and, ultimately, to MOF properties. Here, we expand and refine this concept in the context of crystal engineering. One can argue that, similar to proteins, MOF structure is hierarchical and can be divided into several sub-components characterized by different length scales and energetics (**Figure 4**). The *primary* MOF structure can be defined as the coordination bonds between organic linkers (typically carboxylic acids, amines, heterocyclic compounds, etc.) and metal ions (both transition and main group elements). Here, the important length scales are those of coordination bonds (~2 Å) and the size of the linkers themselves, which can range from ~ 5 Å in a linker such as oxalate to > 20 Å in the largest linkers used in IRMOF-74(n)[36] structures or NU-100.[50] The individual components of the MOF *primary structure* can be preselected for their ability to self-assemble, similar to nodes and spacers in "tinker toys." Using the "node-and-spacer" approach, metal ions and polydentate ligands can be assembled in coordination polymers of different dimensionality. For instance, 4,4'-bipyridine can be used to assemble 1D chains, 1D ladders, 2D square grids and 3D diamond nets[51] based on coordination requirements of various transition metal ions. An alternative strategy is to describe the primary structure is to employ the "secondary building units" (SBUs) concept, where SBUs act as building blocks for the MOF structure. This concept originates from zeolite chemistry and was redefined by Yaghi's group[52] to include molecular complexes or metal clusters with well-defined symmetric coordination geometries. One of the most abundant SBU is the so-called paddle wheel unit, which can be constructed from a variety of linkers and metal ions. According to the CSD, MOF paddlewheels based on Cu and Zn are the most common, but examples with other ions such as V, Cr, Mn, Fe, Co, Ni, Mo were also reported.

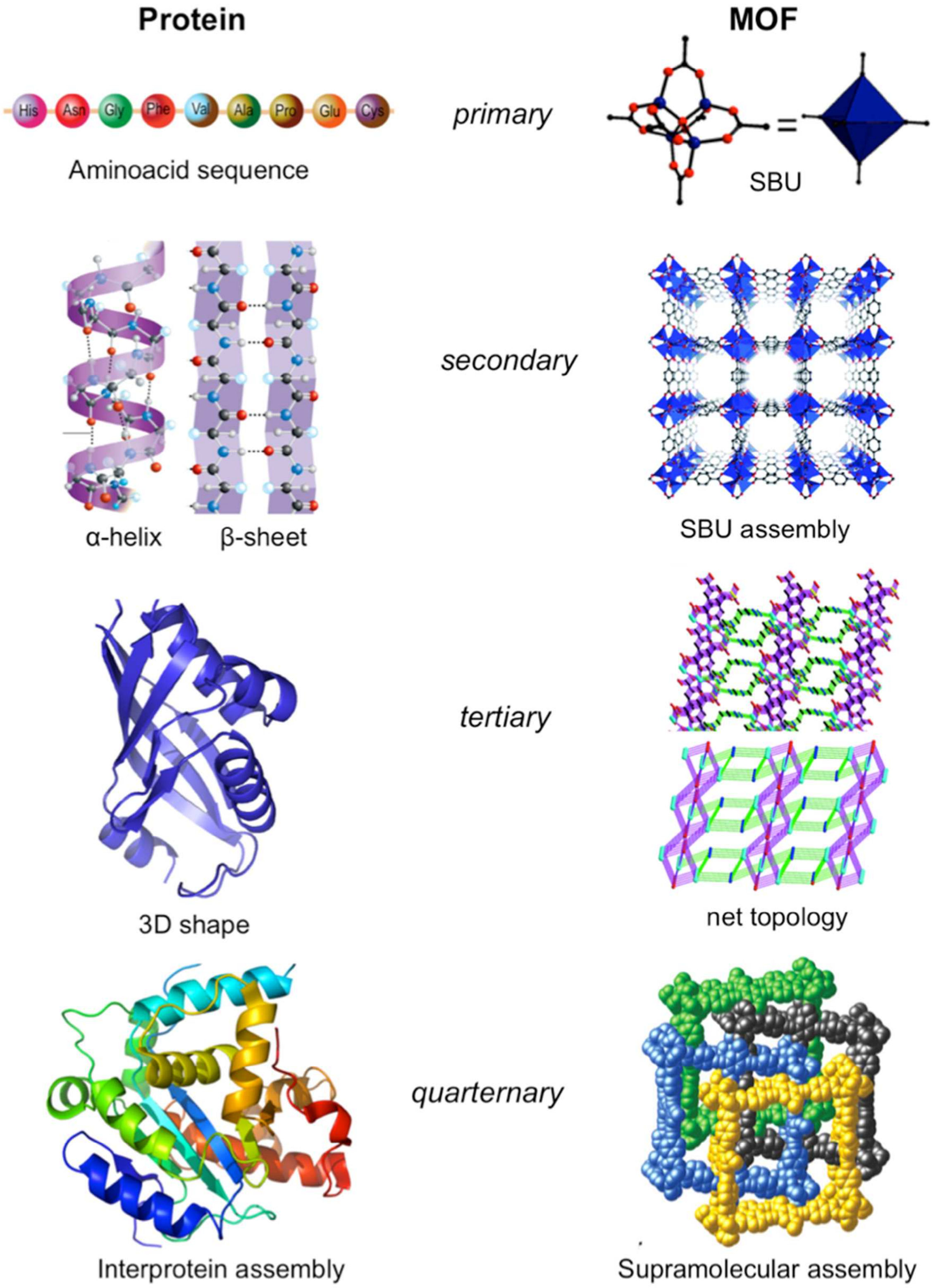


Figure 4. Hierarchical structure of proteins and MOFs.

The *secondary* structure of the MOF is given by the way the SBUs are assembled into a 3D structure. The overall topology of a 3D structure can be described by a net, which is typically assigned by a three-letter symbol (for example *rht*, *soc*, *pts*, *sod*). The Reticular Chemistry Structure Resource (RCSR) is a collection of more than 2,000 different nets [http://rcsr.anu.edu.au]. Two characteristic length scales relevant here are the pore dimensions (pore limiting diameter, PLD, and largest cavity diameter, LCD) and the unit cell dimensions, although the latter can be very large in some cases due to low symmetry. With respect to the energies operative in secondary structure, these are the same as far as the metal-linker bonding is concerned. However, now that the SBUs are assembled to form a supramolecular structure, interactions between SBUs (electronic and/or magnetic) also occur; these can have dramatic effects, particularly in the case of magnetic properties, but they are in general poorly understood. Various types of nets are known, including nets with one type of vertex are called uninodal, (one type of vertex), bimodal (two types of vertices), trimodal (three types of vertices), *etc*. The metal-containing building units produced during synthesis are generally polygonal or polyhedral. Although organic building units have predetermined shape and geometry, their flexibility often determines the final architecture. Hence, it is vital to identify all vertices and edges rather than just identifying the nets. In particular, all types of network structures (organic, inorganic or organic–inorganic hybrid materials) possess inherent nets, and the interest of researchers drives them for topological construction of MOF networks based on rational assembly of building units in different dimensions. The nets can be regarded as examples of blueprints for the construction of MOFs that can be formulated from a diverse range of chemical constituents, and leads to an unprecedented structural diversity, pore size, and geometry. The size of pores can be systematically varied using the versatile concept of “reticular synthesis”,[2, 36, 53, 54] which allows tuning the pore sizes from several angstroms to several nanometers by simply increasing the length of the organic linker.

The nets are capable of further interacting with each other and other structural elements of a MOF in different ways, giving rise to a diverse range of superstructures, which can be classified as the *tertiary* MOF structure. For instance, MOFs are known to display “supramolecular isomerism”, as first recognized by Zaworotko, who defined it as “the existence of more than one type of network superstructure for the same molecular building blocks”.[51] A new subtype of supramolecular isomerism based on polyhedra arrangement was identified by Lah and co-workers,[55] who reported a face-driven corner-linked polyhedron with C_3-symmetric ligands and C_4-symmetric metals, where the truncated octahedron $[Pd_6L_8]^{12+}$ (L= *N*,*N*′,*N*″-tris(3-pyridinyl)-1,3,5-benzenetricarboxamide) displays conformational isomerism and affords two types of MOF pores when crystallized: the *syn*-conformer with a cavity volume *ca.* 1600 Å^3 and the *anti*-conformer with a cavity volume of *ca.* 1900 Å.[55] Along these lines, Lah and Eddaoudi recently introduced the useful concepts of supermolecular building block (SBB) and supermolecular building layer (SBL), which offer some rationale for the judicious construct of desired MOFs based on supramolecular considerations.[56]

Finally, the *quarternary* structure of a MOF can be described as either host-guest interactions or association of multiple individual nets into a single unit (nanoparticle, crystal, thin film, *etc.*) with multiple subunits. In either case, the forces between nets, or between a net and a guest molecule, can alter MOF structure. MOF interpenetration is one example of such quarternary structures. MOF interpenetration occurs when the large voids in one net is filled by another net passing through it.[57] Although the interpenetration reduces the pore sizes of the MOFs, in many cases it enhances the adsorption enthalpy of various molecules by increasing the interactions between the guest molecules and the framework walls. Matryoshka-type single crystals[58, 59] and MOF heterostructured films[60, 61] represents other examples of complex MOF assemblies. We include "guest" molecules as a second example of quarternary structure because in some cases these are essentially permanent residents within the pores, as in the case of strongly coordinated or intercalated solvent molecules. The inherent modular structure of MOFs offers enormous compositional and structural diversity, while crystal engineering allows some control at different structural levels of molecular, topological and supramolecular motifs. Obviously, our analogy between MOFs and proteins should not be taken too literally, as the parallels break down fairly quickly as the chemical bonds and supramolecular arrangements in MOFs are typically very different from proteins. Nevertheless, this construct highlights the complexity of these supramolecular materials and may be useful, particularly to those not familiar with the topological aspects of MOFs, for conceptualizing the relationships between their structure and properties.

IV. Structure-function relationships

There is no doubt that intrinsically, MOFs are well suited to establishing clear structure-function relationships. The fact that they are crystalline means that the position of all atoms are known to a high degree of accuracy (although there are issues here related to structural flexibility). Moreover, as discussed above, the availability of isoreticular series leads to the potential to systematically vary MOF pore size, geometry, and chemical functionality. In the context of this overview, it is useful to summarize the structure-function relationships that have been established thus far, since these demonstrate the extent to which phenomenological understanding is available to guide the synthesis of new MOFs.

Gas sorption. Extensive efforts focused on the uptake of light gases such as hydrogen, methane, the noble gases, and CO_2 has lead to reasonable clarity concerning the factors governing gas sorption by MOFs. In hindsight, some of these are not particularly surprising, given that MOFs resemble zeolites in some aspects and the structure-function relationships have been studied extensively for these materials. Nevertheless, some key structure-function relationships for gas sorption by MOFs are:

- Gas uptake vs. pore size: capacity, Henry's constant (k_H), and isosteric heat of adsorption (Q_{st}) tend to increase with decreasing pore diameter. Modeling and experimental investigations demonstrate that tailoring pore size to be only slightly larger than the kinetic diameter of the gas of interest increases uptake and selectivity.
- Catenation or interpenetration: the generalization is that these lead to higher gas uptake than by non-catenated or interpenetrated structures, but this is highly structure specific since pore size, surface area, and pore volume can be severely affected.
- Hydrogen uptake vs. surface area: hydrogen storage is probably the most extensively studied aspect of MOF chemistry.[62-64] The behavior is complex, but an important generalization is that storage capacity at 77 K is linearly related to surface area at pressures of 10 – 90 bar.[62] Unfortunately, this no longer holds at either at room temperature or lower pressures (1 atm), at which the interaction with the framework is so weak that the sites with the highest adsorption affinity control gas uptake.
- Unsaturated metal coordination sites (also known as "open metal sites"): interactions with these are stronger than typical Van der Waals forces, which can increase heats of adsorption.
- Polarizability of MOF functional groups: capacity, k_H, and Q_{st} increase when linkers are functionalized with highly polarizable groups such as Br or I.

Most of these generalizations were derived from studies of weakly interacting gases such as hydrogen. When larger molecules are considered, however, three important caveats must be mentioned. First, MOF pore sizes and geometry are in most cases far from uniform. There are examples where this is not the case, such as the IRMOF-74 series. In many structures, the geometry of the linker and the coordination topology can lead to a distribution of pore sizes (although these tend to be discrete, rather than broad as are found in amorphous microporous materials). Pore sizes obtained from crystallographic data, microporosimetry, or codes such as HOLE often give conflicting results. We recently found, however, that the Zeo++ program, which uses an algorithm that accounts for the multidimensional nature of MOF pores (unlike the HOLE code, for example, which requires the user to define a trajectory through the pore) yields results consistent with experiment.[65] Second, and more troubling, rotatable groups on MOF linkers and the ability of some MOF structures to "breathe" leads to variable pore dimensions that are inconsistent with those determined by any of the methods mentioned above. For example, uptake of molecules larger than the apparent pore dimensions is reported in a number of cases, such as alkane uptake in ZIF-7[66, 67] or alkanes/alkenes uptake in $Zn_2(bpdc)_2(bpee)$ (bpdc = 4,4'-biphenyldicarboxylate; bpee = 1,2- bipyriylethylene), also known as RPM3-Zn.[68] This feature of MOF structures is not present in rigid inorganic materials such as zeolites and is particularly problematic from the point of view of modeling. Almost all force fields used to model gas uptake by MOFs fix the locations of the framework atoms. The question then becomes, what atomic coordinates should be adopted to simulate the adsorption isotherm? Those obtained at the low-temperatures used for x-ray diffraction may not be appropriate for modeling gas sorption at room temperature. Optimized structures from quantum calculations have also been used as initial configuration for force field simulations.[69] There are a few examples of flexible force fields, but the bonded terms are not transferrable to other MOFs, thus inhibiting their use for screening large numbers of structures.[69-74] One way around this is to use a hybrid simulation approach combining gas adsorption with framework flexibility, but this requires validated force fields for each MOF (or class of MOF). Consequently, this remains an unresolved problem.

Luminescent MOFs. This is possibly the largest category of MOFs designed with a specific functionality outside of those intended for gas storage. General reviews list hundreds of articles on this topic[12, 75] and more specialized reviews focused on topics such as luminescent lanthanide frameworks[76] and metal-based luminescence[13] provide insight into structure-function relationships for these materials. Most reports describing luminescent frameworks are not systematic investigations designed to develop structure-function correlations. Cumulatively, however, this body of work provides considerable insight into how MOF luminescence is influenced by aspects of its structure. Luminescence can be broken down into several basic categories related to the structural component from which it originates (**Figure 5**): linker-localized, charge transfer (metal-to-ligand or ligand-to-metal) metal ion – lanthanide; metal ion – transition metal (typically d^{10} metals); metal ion – main group; metal ion – mixed-metal; and guest-induced luminescence. By far the largest categories are the first two; there are very few luminescent MOFs involving open *d*-shell transition metals because unpaired electrons in these metals quench luminescence. Consequently, the most common of these are composed of Cu(I), Ag(I), Zn(II), and Cd(II) ions. Luminescent main-group MOFs are also rare because the heavy-metal effect results in efficient quenching.[77]

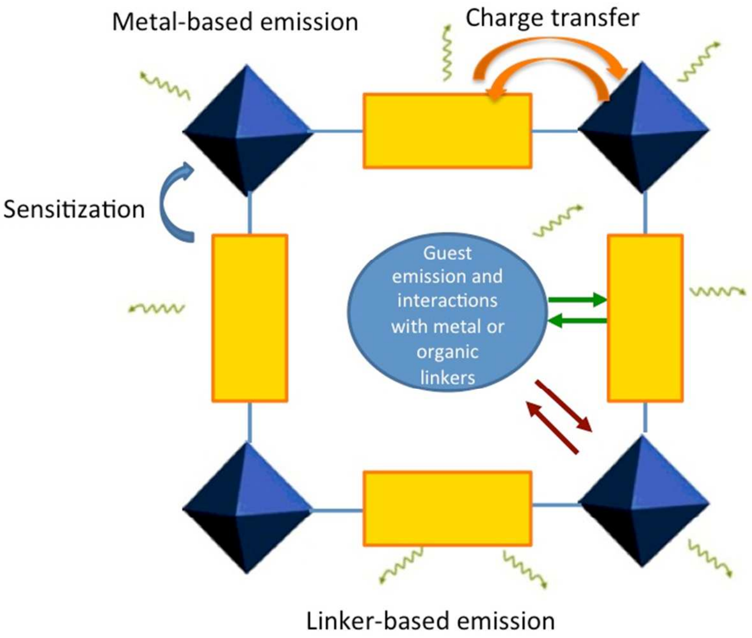


Figure 5. Luminescence mechanisms in MOFs (adapted from Ref. 75).

Linker-based luminescence in MOFs is probably the best understood of these subcategories, in part because of the large number of structures and the availability of isoreticular series that enable systematic variation. Moreover, since the influence of the metal on the luminescent properties is either minor or non-existent in these systems, electronic structure calculations often focus on the linker only. In fact, for MOFs that are not interpenetrated or are structures that bring the linkers into close contact (< 4 Å) with each other, the luminescence typically resembles that of the linker in dilute solution.[49, 78] However, in cases where the structure enables charge transfer to occur between linkers, either by formation of a ground-state complex or an exciton, new luminescence appears that is not characteristic of the isolated linkers.[79-84] Some basic relationships between MOF structure and luminescence are listed below. We developed these design guidelines to maximize light output from the organic linkers, which is particularly important for MOF-based scintillators, but is also relevant to other types of sensing using luminescent MOFs:

- Use only closed-shell metal ions to minimize luminescence quenching and ligand-to-metal charge transfer and limit emission to that of the linker.
- Select framework topologies that isolate the linkers from one another to prevent inter-linker interactions that reduces the emission quantum yield.
- Utilize strategies that control interpenetration[57] to avoid unpredictable inter-framework interactions.

- Choose rigid frameworks that cannot undergo dramatic structural changes, such as MOFs with “breathing” modes or that expand or contract upon removal or uptake of guest molecules, as the luminescence will likely be conformation dependent. Similarly, employ rigid linkers with limited potential for internal rotation are advantageous, as ligand rotational freedom or an ability to adopt multiple conformations leads to less predictable luminescent properties as well as reduced control over MOF structure.

Luminescence induced by the presence of guest molecules is a promising area of MOF research, as it relates directly to both sensing applications and the use of MOFs as light harvesters.[85-90] The luminescence can be due to a guest molecule, such as a fluorescent dye that acts as a reporter for uptake of other molecules or changes in solvent polarity.[80, 91] Alternatively, sequestered electron donor or acceptor molecules, such as thiophenes, fullerenes, [92] or lanthanide complexes,[93] can serve as antennae molecules to enhance light absorption or transmit energy via the Fluorescence Resonance Energy Transfer (FRET). Here, the expected correlation between overlap of the antennae emission and emitter absorption spectra is observed. Another powerful concept for sensing is the use of structurally flexible MOFs that can form ground-state charge transfer complexes between the MOF linker and the guest.[79, 81] Here, the luminescence produced by the complex is highly dependent on the electron donating ability of the guest; the emission maximum gradually shifts to the red as the ionization potential of the guest decreases.[81] This phenomenon can also be used to gauge solvent polarity.[79] It should be noted, however, that the role of impurities in MOF-based luminescence is in general poorly understood; these can produce significant luminescence that complicates interpretation of spectra. For example, we found that the formation of ZnO nanoparticles can produce luminescence that is similar to the luminescence of MOF-5 synthesized under high-temperature conditions. In addition, trapped solvent molecules such as dimethylformamide can also be fluorescent.[94]

Water stability and pore hydrophobicity. The stability of MOFs with respect to water became a prominent issue in ~ 2007, when a few authors described experiments and modeling showing that a variety of effects can occur when MOFs are exposed to either liquid or gas-phase water. The instability of the IRMOFs was known colloquially for some time, but rigorous documentation was lacking. Molecular dynamics simulations using a flexible force field predicted that MOF-5 undergoes catastrophic collapse when the amount of water in the pores exceeds 3.9% by weight.[95] Later, Long and coworkers showed that MOF-5 undergoes a phase transition to non-porous MOF-69C upon exposure to water vapor.[96] The extent to which this occurs is related to the synthetic method and can lead to wildly varying surface areas. Interestingly, the effects of water on MOF-5 could be reversed under some conditions. Water adsorption isotherms for some MOFs have been successfully measured; this work was recently reviewed.[97] Although MOF-5 and the isoreticular IRMOF structures are among the most water-reactive of MOFs, due in large part to the presence of the Zn_4O moiety in their structure, this early work raised an important question, namely, what is the meaning of “unstable” in the context of MOFs? The most strenuous criterion is that the material is unchanged in any way, *i.e.*, crystal structure, pore volume, and surface area are invariant. An argument can be made, however, that a MOF is not “unstable” if the changes induced by water are reversible. This can be turned to practical advantage by using a MOF as a drying agent; a recent study by Matzger and coworkers showed that several MOFs have higher total capacity than alumina, a standard industrial sorbent.[98] The issue of water stability in MOFs must be placed in the context of the intended use, an aspect of their chemistry that is not a problem for zeolites and many other microporous materials.

In 2009, variations of known MOF structures began to appear in which linkers were modified to make the MOF hydrophobic and/or water resistant. Interest in the field increased dramatically starting in 2012, most likely because the practical implications. Walton and coworkers[99, 100] are conducting systematic investigations and identified three important criteria: 1) accessibility of the metal ion; 2) pK_a of the linker; and 3) concatenation. Briefly, facile access to the metal ion contributes greatly to water reactivity. Moreover, more basic linkers lead to stronger metal-linker bonds, thereby reducing reactivity. The reasons for the greater stability of catenated structures are less obvious, but are related to the smaller pore volumes available to accommodate water and the higher stability of these structures in general as a result of increased linker-linker interactions.[72, 73] There are, of course, many subtleties that are not encompassed by these generalizations, which are summarized in the review article by these authors.[97] Consequently, the issue of MOF stability with respect to water (and by implication, exposure to atmosphere) remains far from resolved.

Mechanical properties. These are among the most poorly understood and least explored aspects of MOFs, in spite of their importance for many practical applications. Considering hybrid framework materials in general, which encompass both dense and porous materials as defined by Tan and Cheetham in their recent review, there is virtually no work reported prior to 2005. This reflects the fact that few people working in the field have the necessary technical background or equipment such as a nanoindentor to conduct such work. Nevertheless, understanding the mechanical properties of MOFs will have obvious implications for applications in which MOFs encounter abrasive conditions, such as fluidized beds using MOFs for catalysis or separations. The friability of zeolites leads to considerable loss of material under these conditions. Since MOFs are softer than many zeolites, one might expect that the problems would be considerably magnified. However, MOFs are also more ductile than zeolites, which could reduce their susceptibility to abrasion. Long-term durability studies have not been performed for any MOFs, however, fundamental studies of this kind will be of considerable value. Such large-scale industrial applications are not the only reason to understand MOF mechanical properties. For example, the formation of optically transparent monoliths is necessary if MOFs are to be used in many optical applications (e.g., radiation detection); this will likely require knowledge of phenomena such as creep, plasticity, and bulk-phase diffusion, not to mention microstructural properties concerning defects and grain boundaries. New MOF behaviors such as piezoelectricity are intimately connected with the mechanical properties of the materials and development of the relevant structure-function relationships is essential if the full potential of rational design in MOFs is to be realized.

The Cheetham group at Cambridge has measured the elastic moduli and Poisson's ratio of a large number of MOFs and applied theoretical tools to predict these properties. Fundamental structure-property relationships are beginning to emerge, which are summarized in their review. An example of these is shown in **Figure 6**, which reveals that the bulk modulus of MOFs is in a region of intersection among foams with macroscale pores, organic polymers, and inorganic ceramics (including some zeolites), having lower density than many of these materials while retaining their stiffness. The diversity of MOF structures and the variety of chemical bonds within them make establishing such relationships difficult and correlations between experiment and theory are not always conclusive. DFT calculations often overpredict the elastic moduli, due in all likelihood to deficiencies in the theoretical models and the fact that measurements are made at finite temperatures rather than 0 K of the calculations. An important general principle is that mechanical properties can be tailored through the rigidity of the linkers and the strength of the metal-linker bonds. Nanoindentation measurements on lanthanide MOFs involving carboxylate linkers yields the interesting result that the structure is less rigid on crystallographic planes with a strong M-O-M component These bonds are weaker than the covalent bonds of the linkers. This result highlights an important aspect of mechanical properties, namely, that they are highly orientation dependent. Design of MOFs to resist forces in specific directions must therefore take this into account. Moreover, these measurements reveal a structure-property correlation useful for crystal engineering: MOFs with growth planes containing primarily covalent bonds should be selected when seeking high elastic stiffness (*i.e.*, high Young's modulus) in a particular direction.

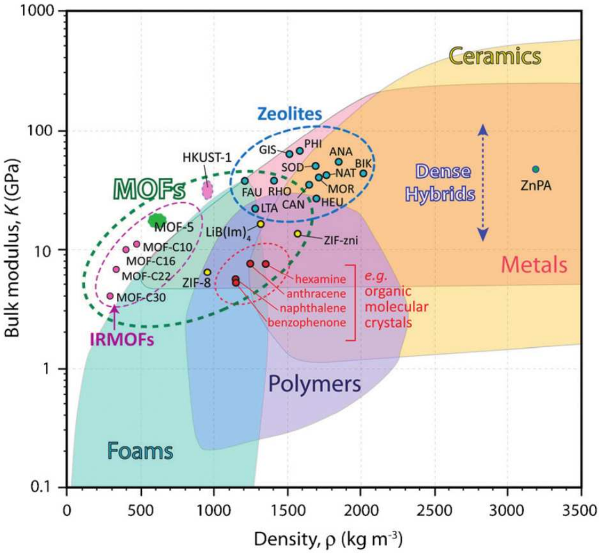


Figure 6. Correlation between bulk modulus and density. Used with permission from Ref. 17.

ZIFs are among the better-investigated MOF categories, since they provide a convenient method of systematic structural variation within a constant topology. Tan et al. demonstrated, for example, that sterically bulky linkers increase the elastic modulus (greater stiffness) due to increased short-range interlinker interactions. Non-linear scaling of the elastic moduli was observed as a function of density, with the moduli increasing substantially with increasing density. Hardness also increases with density. Elasticity can also be guest dependent, as shown by comparison of desolvated vs. solvated ZIF-8.[101]

V. Future prospects: a selection of promising applications

As discussed above, MOFs are being considered for a growing number of applications. In this section, we highlight a few that in our estimation are particularly promising. Some of these, such as gas storage, are very advanced in their development, whereas the potential of others, such as electronics and photonics, is only beginning to be explored.

Gas storage and separation. The large surface areas, adaptable pore sizes, and tailorable pore environments, coupled with good chemical and thermal stability, made MOFs attractive for these applications from the outset. This is the application that is the most advanced with respect to commercialization; MOF-based hydrogen[102] and methane[103] storage tanks for research vehicles have already been demonstrated. Gas storage in MOFs has been widely explored in the past decade and many groups are actively involved in seeking suitable frameworks to efficiently store various molecules,[63, 64, 89, 104-109] with the most intensively studied gases being hydrogen,[62, 64, 110] methane,[38, 54, 111-113] and carbon dioxide.[107, 108, 114, 115] Some critical requirements for MOFs as gas storage media include: 1) high volumetric/gravimetric uptake capacity; 2) fast sorption and desorption kinetics at practical temperatures and pressures; 3) high tolerance to impurities; and 4) extended cycling. Although there are now hundreds, if not thousands, of MOFs for which there are reported gas adsorption isotherms, many reported frameworks that appear to be porous, based on their crystal structure, in fact may not be. The terms “porous” and “open framework” imply the existence of porosity; in reality, this must be experimentally demonstrated rather than graphically inferred from crystallographic data.[52-54]

MOFs are also being considered for gas separations, including purification or collection of hydrogen,[116] hydrocarbons,[117-121] oxygen,[122] nitrogen,[108] CO_2,[37, 39, 73, 114, 123] NO,[124] iodine,[125, 126] and noble gases.[127] Efficient gas separations in MOFs can be based on molecular sieving,[128, 129] kinetic[130, 131] or thermodynamic mechanisms,[65, 127] or the quantum sieving effect for He/H_2 and H_2/D_2 separations.[116, 132] In principle, MOFs offer several advantages over other porous materials such as zeolites, which could be exploited in industrial gas separations. For instance, MOF structures with acute angles in their pore walls are possible, whereas zeolite pores are always obtuse, decreasing their ability to distinguish between isomers of various hydrocarbons. Long *et al*. demonstrated that the triangular channels in the MOF $Fe_2(bdp)_3$ (bdp^{2-} = 1,4-benzenedipyrazolate) can efficiently separate 5 hexane isomers by their ability to wedge along the triangular corners of the pores, with the more branched isomers passing faster through the membrane (**Figure 7**).[133] Zaworotko *et al.* also reported a series of MOFs assembled from metal-pyrazine cations and hexafluorosilicate $[SiF_6]^{2-}$ anions, in which the 90° pore angles enable a near-perfect fit for CO_2, producing record-high CO_2/N_2, CO_2/H_2 and CO_2/CH_4 selectivities.[123] Although many MOFs are promising materials for these applications, major hurdles include meager knowledge of the effects of impurities and water vapor, and the lack of economical membrane fabrication processes.[134] A significant development was recently reported by Nair *et al.*, who demonstrated a hollow fiber membrane concept based on poly(amide-imide) polymers coated with ZIF-8 inside the 100 μm fibers.[135] Such MOF/polymer fibers display separation factors as high as 370 for H_2/propane and 12 for propene/propane. These impressive figures single out MOFs as having particularly strong potential for high-efficiency industrial-scale separations, if practical issues can be addressed.

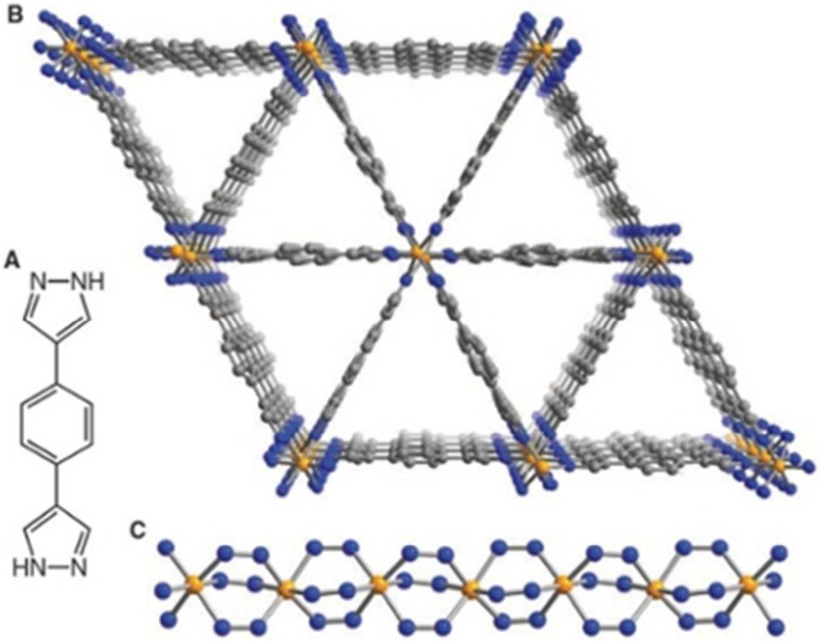


Figure 7. A) H_2bdp linker; B) triangular pore geometry in $Fe_2(bdp)_3$; C) coordination environment of Fe and a fragment of the polymeric structure. Orange, blue and grey spheres represent Fe, N, and C atoms. Reproduced with permission from Ref. [133].

Heterogeneous catalysis. MOF pore sizes are well suited to hosting small-molecule chemical reactions. Since MOFs feature ordered structures with well-defined pores, they also provide opportunities for encapsulating metal nanoparticles or for tethering molecular catalysts. Moreover, the pores can be modified to incorporate catalytic functionalities, effectively serving as "nanoreactors."[136, 137] There are now many reports of MOF-based catalysis for a variety of reaction types, including hydrogenation,[138, 139] oxidation,[140, 141] alkylation,[142, 143] arylation,[144, 145] transesterification,[146, 147] cyanosylilation,[148, 149] various reductions[150, 151] and condensations.[152, 153] Although this progress is highly encouraging, in most cases these results can be considered as "proof of concept," rather than demonstration of an industrially relevant catalyst. Aside from economic issues associated with large-scale production, critical data concerning their mechanical durability and long-term stability are still lacking. In addition to these practical challenges, fundamental aspects of MOF catalysis remain largely uncharacterized. There are almost no detailed mechanistic studies of MOF-catalyzed reactions.[28, 141] To take advantage of the full potential of MOFs for catalysis and to achieve reaction selectivities and turnover rates that are competitive with established microporous catalysts such as zeolites, it will be necessary to understand the connection between the design of the active site and its catalytic behavior.

Sensors. The factors that make MOFs so attractive as molecular recognition chemistries for sensing go beyond their tailorable pore structure. Unlike other classes of nanoporous materials, such as porous carbon, silica aerogels, and zeolites, a multitude of transduction mechanisms are possible. These include mass uptake,[60] interferometry,[154] acoustic,[155] magnetic,[156] luminescence,[12, 85] and mechanical strain[157] responses to the chemical environment. Several review articles appeared in recent years covering various aspects of MOFs for chemical sensing.[20, 90, 158] Our group first introduced chemical detection using MOF-coated micro-electro-mechanical systems (MEMS).[155, 157, 159-161] $Cu_3(btc)_2$-coated microcantilevers were shown to also respond to various molecules, including water, methanol, ethanol, acetone, chloroform and toluene. The concentration range of the analytes that can be detected by this technique varies over a wide range, from tens to thousands of ppm. $Cu_3(btc)_2$-coated surface acoustic wave (SAW) sensors exhibiting sensitivity to water vapor from 0.28 to 14,800 ppmv, are competitive with many commercial sensors.[155] Fischer's group recently demonstrated selective absorption of methanol, 1,3,5-trimethylbenzene and 1,3,5-triisopropylbenzene on a SURMOF bilayer composed of heteroepitaxial $[Cu_3(btc)_2]$ grown on top of $[Cu_2(ndc)_2(dabco)]$.[162] As with most of the other applications discussed here, the results are highly encouraging, but a great deal of engineering development remains to be done. Raising the technical readiness level (TRL) of these devices will require investigators to evaluate sensor operation in realistic environments, determine cross sensitivities, optimize film thickness to improve response times, and characterize sensor drift and reproducibility. Practical fabrication techniques also need to be developed.[90] An important advance in this direction was the discovery of patterning techniques, for example ink-jet printing of MOF coatings (**Figure 8**).[163]

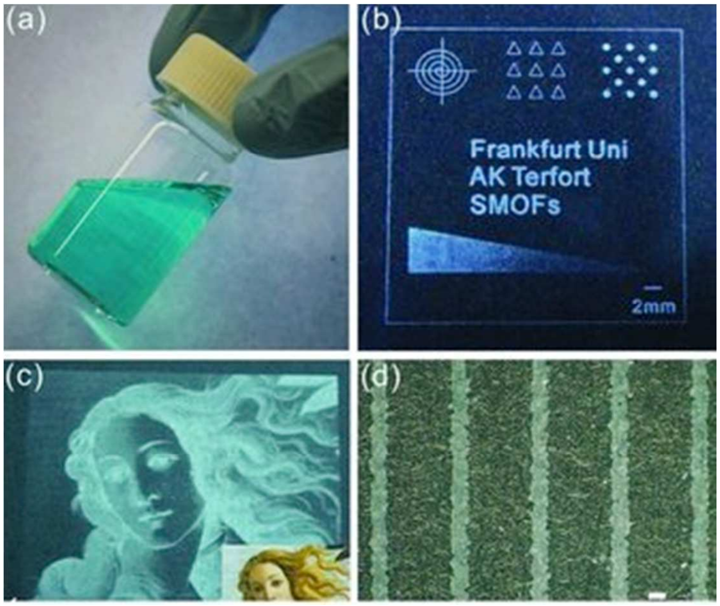


Figure 8. a) HKUST-1 ink solution; b) various patterns, letters, and a gradient wedge; c) Botticelli's “Venus” printed in HKUST-1 (the inset shows the original image); d) a line array of printed MOF. Reprinted with permission from Ref. [163].

Electronics and photonics. MOFs display a remarkable variety of electronic and photonic properties. For example, there are MOFs displaying promising low-*k* dielectric properties and ferroelectric, ferromagnetic, antiferromagnetic, luminescent, and non-linear optical behaviors.[20, 90] When combined with their porosity, they become a truly unique category of optoelectronic materials. Unfortunately, most MOFs are electrical insulators;[164] however, a few semiconducting frameworks are known.[165, 166] Dincă and coworkers recently reported a MOF analogue of graphene with an electrical conductivity of 2 S/cm in pelletized form and as high as 40 S/cm in thin-film geometry,[167] as well as two other frameworks that have high charge mobility.[168, 169] Clearly, the porous structure of MOFs distinguishes them from traditional inorganic and organic conductors. This allows guest species (molecules, clusters, nanoparticles) to be introduced that can alter the native MOF functionality. For example, we recently demonstrated that doping intrinsically insulating HKUST-1 with TCNQ renders the resulting TCNQ@HKUST-1 material electrically conductive.[170] The fact that electrical conductivity can be achieved in MOFs is highly intriguing, as their crystallinity and hybrid inorganic-organic nature suggest the potential to have the best of two worlds: traditional semiconductors, with their highly ordered, low-defect structure, and organic conductors, with their tailorable properties and low-cost fabrication. It remains to be seen whether MOFs can achieve this technical Valhalla; mobility and conductivity must both be improved substantially. Perhaps more importantly, generality beyond a few unique structural cases must be demonstrated before these materials attract the kind of widespread attention that conducting organic polymers received several decades ago.

Ion-conducting membranes. The possibility of incorporating functional groups at desired locations within the MOF pore structure makes them promising for ion- and proton-conducting membrane applications. Nafion is the state-of-the-art Proton Exchange Membrane (PEM) in various fuel cells. However, it loses its proton conductivity above 100 °C; elevated temperatures are often desirable for fuel cell operation to increase the reaction rate at the cathode. MOF-based membranes generally display lower proton conductivities compared to Nafion; however, some are conducting at temperatures as high as 150 °C, even in the absence of water.[171, 172] Unlike disordered polymers like Nafion, for which the conduction mechanisms and nano- and microstructure are still the subject of debate, the crystalline structure of MOFs enables structural determination with sub-angstrom resolution, allowing for a better understanding of the ion transport mechanisms. Based on this knowledge, modifications to the MOF structure, either by PSM or introduction of guest molecules, can be performed to improve the performance of the material. For example, Shimizu and coworkers[172] isolated Na_3(2,4,6-trihydroxybenzenetrisulfonate (β-PCMOF2), a 3D honeycomb structure made up of hexagonal sheets of the organic linker cross-linked via Na atoms to form 1D channels of approx. 0.6 nm in diameter. The as-synthesized framework has a rather low proton conductivity of $<10^{-8}$ S/cm above 70 °C. However, upon infiltration of 1,2,4 triazole within the 1D pores, the proton conductivity reached 5×10^{-4} S/cm at 150 °C. Initial results indicate that MOFs are robust enough to be incorporated into membranes for Li-ion batteries[173] and PEM fuel cells,[171, 174] as they are thermally and chemically stable and are good electronic insulators.[171] Metal sulfonates[172] and phosphonates[175] are the most commonly used MOF-based proton conductors; however, other classes of MOFs are also being investigated for ionic membrane applications.[171, 174]

Biomedical applications. The efficacy of new therapeutics could be improved by more precise delivery to targeted cells or portions of the body. This strongly motivates ongoing research to develop MOFs for biomedical applications that include drug delivery and bioimaging,[24-26, 176] where full advantage can be taken of their structural and chemical versatility. Controlled release of drugs, antibiotics, and small molecules such as NO[177, 178] has been reported. For example, Horcajada *et al*. investigated the utility of MIL-100 and MIL-101 for the delivery of ibuprofen and achieved a loading of 0.35 g/g MIL-100 and 1.4 g / g MIL-101.[179] An anionic MOF composed of Zn(II), adenine, and para-diphenyl-dicarboxylic acid was shown to incorporate and slowly release procainamide hydrochloride.[180] Several Fe(III)-based MILs (MIL-53, MIL-88A, MIL-89, MIL-100 and MIL-101-NH2) were found to be promising delivery vehicles for anti-cancer and anti-AIDS drugs, including bisulfan, caffeine, doxorubicin, azidothymidine triphosphate, and cidofovir, with loadings from 2.6 to 42 wt%.[181] Delivery of gases can also be achieved; Cohen *et al.*[177] and Morris *et al.*[178] employed a series of MOFs for controlled release of NO, an important bioactive molecule produced in the human body by nitric oxide synthases. MOFs have been also investigated as contrast agents for MRI[182] and optical imaging.[183] Little is known about the toxicity of MOFs, although the few early studies at the preclinical level suggest that at least some MOFs are biocompatible.[24, 26, 176, 184]

VI. Moving forward: key challenges

The previous discussion points to several problems that must be addressed before MOFs can achieve the status of other porous materials used extensively in industry. Among the most critical are the following:

- Robustness in manufacturing environments remains a largely unaddressed challenge. MOF mechanical properties and long-term durability are, in general, very poorly understood. There are also very few reports describing consolidation into pellets and other solid bodies. This contrasts with promising results showing MOF stability in hostile chemical environments and water vapor can be achieved. Researchers with expertise in materials science and engineering therefore have an important role to play in the future success of MOFs.
- The perception that MOFs are high-cost materials and are therefore not economical for large-scale use is a major stumbling block. The field would benefit tremendously if the number of frameworks commercially available in reasonable quantities (say 1 kg or more) increased beyond the current handful.
- The ability of computational modeling to guide synthesis is limited by the shear number of structures that are known. Although accuracy and understanding are both improving, the field is losing ground. With the potential for new topologies on the horizon and variations on existing themes, the number of conceivable structures reaches into the millions. New computational approaches are critically needed that can accurately capture trends so that the scope of a synthetic effort can be quickly narrowed.
- Defects in MOF crystals have been largely ignored, yet their influence on properties is likely to be substantial.
- A daunting problem for enabling MOFs to be considered for electronic device applications is achieving control over their electronic properties. The fundamental principles governing charge mobility in these materials must be elucidated so that rational design can proceed.
- Integrating MOFs with substrates of all kinds is far from mature. Reliable thin film growth over large areas (wafer- or membrane-scale), with control over nucleation, crystallographic orientation, and surface roughness, is lacking. A related issue is the need for patterning techniques with the spatial resolution needed for state-of-the-art device architectures.

- MOF biocompatibility requires much more investigation before they become a serious competitor to other materials under development for nanomedicine.

VII. Conclusions

In many ways, the advent of MOFs represents a triumph for the field of crystal engineering. The concept of rational materials design has possibly been realized to a greater extent in MOFs than by any other class of materials: because one can know and predict structure so accurately in MOFs, it is also possible to predict and achieve desirable properties. Although much of the work during the last decade was motivated by traditional uses of porous materials, such as gas storage, separations, and heterogeneous catalysis, several important discoveries in the last few years are opening new and significant opportunities for MOFs beyond the aforementioned. It is now recognized, and in some cases demonstrated, that MOFs could have an impact on areas as technically diverse as microelectronics, energy harvesting and storage, sensing, defense and security, and human health. Thus, the potential exists to create new industries and revolutionize existing ones, which in turn could have enormous and long-lasting economic impact. As we pointed out earlier, new materials typically require, on average, about twenty years to be incorporated into commercial products. We can predict, therefore, that it will not be long before MOFs achieve this. Based on the accumulated investment of research funding, a product related to gas storage is perhaps the most likely, but it would not come as a complete surprise if a completely different application emerges. The discussion here highlights an important point, however: the barriers hindering the rapid practical implementation of MOFs necessitate the involvement of disciplines outside synthetic chemistry. Perhaps, then, the most important challenge is to engage the rest of the scientific community and kindle their enthusiasm for these remarkable materials.

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References

1. O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703.
2. H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**.
3. S. Yang, M. Lach-hab, I. I. Vaisman, E. Blaisten-Barojas, X. Li and V. L. Karen, *J. Phys. Chem. Ref. Data*, 2010, **39**.
4. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.
5. H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
6. N. Stock and S. Biswas, *Chem. Rev.*, 2011, **112**, 933.
7. A. Bétard and R. A. Fischer, *Chem. Rev.*, 2011, **112**, 1055.
8. A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062.
9. C. Dey, T. Kundu, B. P. Biswal, A. Mallick and R. Banerjee, *Acta Cryst. B*, 2014, **70**, 3.
10. A. Carné-Sánchez, I. Imaz, K. C. Stylianou and D. Maspoch, *Chem. Eur. J.*, 2014, **20**, 5192.
11. Z. Zhang and M. J. Zaworotko, *Chem. Soc. Rev.*, 2014, **43**, 5444.
12. Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126.
13. J. Heine and K. Muller-Buschbaum, *Chem. Soc. Rev.*, 2013, **42**, 9232.
14. W. Zhang and R.-G. Xiong, *Chem. Rev.*, 2011, **112**, 1163.
15. P. Dechambenoit and J. R. Long, *Chem. Soc. Rev.*, 2011, **40**, 3249.
16. T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982.
17. J. C. Tan and A. K. Cheetham, *Chem. Soc. Rev.*, 2011, **40**, 1059.
18. T. D. Bennett and A. K. Cheetham, *Acc. Chem. Res.*, 2014, **47**, 1555.
19. P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill and M. J. Styles, *Chem. Soc. Rev.*, 2014, **43**, 5513.
20. V. Stavila, A. A. Talin and M. D. Allendorf, *Chem. Soc. Rev.*, 2014, **43**, 5994.
21. S. Qiu, M. Xue and G. Zhu, *Chem. Soc. Rev.*, 2014, **43**, 6116.
22. W.-Y. Gao, M. Chrzanowski and S. Ma, *Chem. Soc. Rev.*, 2014, **43**, 5841.
23. H. N. Miras, L. Vila-Nadal and L. Cronin, *Chem. Soc. Rev.*, 2014, **43**, 5679.
24. P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2011, **112**, 1232.
25. C.-Y. Sun, C. Qin, X.-L. Wang and Z.-M. Su, *Expert Opin. Drug Deliv.*, 2013, **10**, 89.
26. J. Della Rocca, D. Liu and W. Lin, *Acc. Chem. Res.*, 2011, **44**, 957.
27. P. Deria, J. E. Mondloch, O. Karagiaridi, W. Bury, J. T. Hupp and O. K. Farha, *Chem. Soc. Rev.*, 2014, **43**, 5896.
28. J. Gascon, A. Corma, F. Kapteijn and F. X. Llabrés i Xamena, *ACS Catal.*, 2013, **4**, 361.
29. M. Gaab, N. Trukhan, S. Maurer, R. Gummaraju and U. Muller, *Microporous Mesoporous Mater.*, 2012, **157**, 131.
30. http://hsecoe.org, *The Hydrogen Storage Engineering Center of Excellence (HSECoE)*.
31. T. W. Eagar, *Technol. Rev.*, 1995, **98**, 43.
32. C. Wadia, http://www.whitehouse.gov/mgi, Accessed June 14, 2014.
33. R. L. Virta, *Zeolites Statistics and Information*, http://minerals.usgs.gov/minerals/pubs/commodity/zeolites/, Accessed June 14, 2014.
34. C. K. Brozek and M. Dincă, *Chem. Soc. Rev.*, 2014, **43**, 5456.
35. Y. Han, J.-R. Li, Y. Xie and G. Guo, *Chem. Soc. Rev.*, 2014, **43**, 5952.
36. H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**, 1018.

37. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.
38. C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, *Nat. Chem.*, 2012, **4**, 83.
39. E. Haldoupis, S. Nair and D. S. Sholl, *J. Amer. Chem. Soc.*, 2012, **134**, 4313.
40. T. Van Heest, S. L. Teich-McGoldrick, J. A. Greathouse, M. D. Allendorf and D. S. Sholl, *J. Phys. Chem. C*, 2012, **116**, 13183.
41. L.-C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhown, M. W. Deem, M. Haranczyk and B. Smit, *Nat. Mater.*, 2012, **11**, 633-641.
42. E. L. First and C. A. Floudas, *Microporous Mesoporous Mater.*, 2013, **165**, 32.
43. M. Savonnet, A. Camarata, J. Canivet, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel and D. Farrusseng, *Dalton Trans.*, 2012, **41**, 3945.
44. Z. Wang and S. M. Cohen, *Chem. Soc. Rev.*, 2009, **38**, 1315.
45. C. K. Brozek and M. Dincă, *J. Amer. Chem. Soc.*, 2013, **135**, 12886.
46. S. Furukawa, J. Reboul, S. Diring, K. Sumida and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5700.
47. M. O’Keeffe and O. M. Yaghi, *Chem. Rev.*, 2011, **112**, 675.
48. B. F. Hoskins and R. Robson, *J. Amer. Chem. Soc.*, 1990, **112**, 1546.
49. J. J. Perry, P. L. Feng, S. T. Meek, K. Leong, F. P. Doty and M. D. Allendorf, *J. Mater. Chem.*, 2012, **22**, 10235.
50. O. K. Farha, A. Özgür Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944.
51. B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
52. M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
53. O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.
54. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
55. D. Moon, S. Kang, J. Park, K. Lee, R. P. John, H. Won, G. H. Seong, Y. S. Kim, G. H. Kim, H. Rhee and M. S. Lah, *J. Amer. Chem. Soc.*, 2006, **128**, 3530.
56. V. Guillerm, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, *Chem. Soc. Rev.*, 2014, **43**, 6141.
57. H. L. Jiang, T. A. Makal and H. C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232.
58. K. Koh, A. G. Wong-Foy and A. J. Matzger, *Chem. Comm.*, 2009, 6162.
59. S. Furukawa, K. Hirai, K. Nakagawa, Y. Takashima, R. Matsuda, T. Tsuruoka, M. Kondo, R. Haruki, D. Tanaka, H. Sakamoto, S. Shimomura, O. Sakata and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2009, **48**, 1766.
60. M. Meilikhov, S. Furukawa, K. Hirai, R. A. Fischer and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2013, **52**, 341.
61. F. M. Hinterholzinger, A. Ranft, J. M. Feckl, B. Ruhle, T. Bein and B. V. Lötsch, *J. Mater. Chem.*, 2012, **22**, 10356.
62. Y. H. Hu and L. Zhang, *Adv. Mater.*, 2010, **22**, E117.
63. A. Uzun and S. Keskin, *Prog. Surf. Sci.*, 2014, **89**, 56.
64. J. Sculley, D. Yuan and H.-C. Zhou, *En. Environ. Sci.*, 2011, **4**, 2721.
65. J. J. Perry, S. L. Teich-McGoldrick, S. T. Meek, J. A. Greathouse, M. Haranczyk and M. D. Allendorf, *J. Phys. Chem. C*, 2014, **118**, 11685.

66. C. Gücüyener, J. van den Bergh, J. Gascon and F. Kapteijn, *J. Amer. Chem. Soc.*, 2010, **132**, 17704.
67. J. van den Bergh, C. Gücüyener, E. A. Pidko, E. J. M. Hensen, J. Gascon and F. Kapteijn, *Chem. Eur. J.*, 2011, **17**, 8753.
68. N. Nijem, H. Wu, P. Canepa, A. Marti, K. J. Balkus, T. Thonhauser, J. Li and Y. J. Chabal, *J. Am. Chem. Soc.*, 2012, **134**, 15201-15204.
69. M. V. Parkes, H. Demir, S. L. Teich-McGoldrick, D. S. Sholl, J. A. Greathouse and M. D. Allendorf, *Microporous Mesoporous Mater.*, 2014, **194**, 190.
70. D. Dubbeldam, K. S. Walton, D. E. Ellis and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2007, **46**, 4496.
71. D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons and T. Duren, *J. Amer. Chem. Soc.*, 2011, **133**, 8900.
72. J. A. Greathouse, N. W. Ockwig, L. J. Criscenti, T. R. Guilinger, P. Pohl and M. D. Allendorf, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12621.
73. E. Haldoupis, T. Watanabe, S. Nair and D. S. Sholl, *ChemPhysChem*, 2012, **13**, 3449.
74. B. L. Huang, A. J. H. McGaughey and M. Kaviany, *Int. J. Heat Mass Transfer*, 2007, **50**, 393.
75. M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330.
76. J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926.
77. J. R. Lakowicz, *Principles of fluorescence spectroscopy*, 3rd edn., Springer, New York, 2006.
78. C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Amer. Chem. Soc.*, 2007, **129**, 7136.
79. P. L. Feng, K. Leong and M. D. Allendorf, *Dalton Trans.*, 2012, **41**, 8869.
80. R. Grunker, V. Bon, A. Heerwig, N. Klein, P. Muller, U. Stoeck, I. A. Baburin, U. Mueller, I. Senkovska and S. Kaskel, *Chem. Eur. J.*, 2012, **18**, 13299.
81. Y. Takashima, V. Martinez Martinez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto and S. Kitagawa, *Nat. Comm.*, 2011, **2**, 168.
82. O. M. Yaghi and H. L. Li, *J. Amer. Chem. Soc.*, 1995, **117**, 10401.
83. Q.-B. Bo, H.-T. Zhang, H.-Y. Wang, J.-L. Miao and Z.-W. Zhang, *Chem. Eur. J.*, 2014, **20**, 3712.
84. Y. Liu, M. Pan, Q.-Y. Yang, L. Fu, K. Li, S.-C. Wei and C.-Y. Su, *Chem. Mater.*, 2012, **24**, 1954.
85. Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273**, 76.
86. X.-L. Tong, H.-L. Lin, J.-H. Xin, F. Liu, M. Li and X.-P. Zhu, *J. Nanomater.*, 2013, 616501.
87. J. Heine and K. Mueller-Buschbaum, *Chemical Society Reviews*, 2013, **42**, 9232-9242.
88. O. Shekhah, J. Liu, R. A. Fischer and C. Wöll, *Chem. Soc. Rev.*, 2011, **40**, 1081.
89. S. T. Meek, J. A. Greathouse and M. D. Allendorf, *Adv. Mater.*, 2011, **23**, 249.
90. M. D. Allendorf, A. Schwartzberg, V. Stavila and A. A. Talin, *Chem. Eur. J.*, 2011, **17**, 11372.
91. N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura and S. Kitagawa, *Nat. Mater.*, 2011, **10**, 787.
92. K. Leong, M. E. Foster, B. M. Wong, E. D. Spoerke, D. V. Gough, J. C. Deaton and M. D. Allendorf, *J. Mater. Chem. A*, 2014, **2**, 3389.
93. H. C. Streit, M. Adlung, O. Shekhah, X. Stammer, H. K. Arslan, O. Zybaylo, T. Ladnorg, H. Gliemann, M. Franzreb, C. Wöll and C. Wickleder, *ChemPhysChem*, 2012, **13**, 2699.
94. P. L. Feng, J. J. Perry, S. Nikodemski, B. W. Jacobs, S. T. Meek and M. D. Allendorf, *J. Amer. Chem. Soc.*, 2010, **132**, 15487.
95. J. A. Greathouse and M. D. Allendorf, *J. Amer. Chem. Soc.*, 2006, **128**, 10678.
96. S. S. Kaye, A. Dailly, O. M. Yaghi and J. R. Long, *J. Amer. Chem. Soc.*, 2007, **129**, 14176.
97. N. C. Burtch, H. Jasuja and K. S. Walton, *Chem. Rev.*, 2014, accepted for publication.

98. P. Guo, A. G. Wong-Foy and A. J. Matzger, *Langmuir*, 2014, **30**, 1921.
99. H. Jasuja and K. S. Walton, *Dalton Trans.*, 2013, **42**, 15421.
100. S. Han, Y. Huang, T. Watanabe, S. Nair, K. S. Walton, D. S. Sholl and J. C. Meredith, *Microporous Mesoporous Mater.*, 2013, **173**, 86.
101. J. C. Tan, T. D. Bennett and A. K. Cheetham, *Proc. Nat. Acad. Sci. USA*, 2010, **107**, 9938.
102. *Mercedes-Benz F125*, http://www.emercedesbenz.com/autos/mercedes-benz/concept-vehicles/mercedes-benz-f125-research-vehicle-technology.
103. *BASF press release*, 2013, http://www.basf.com/group/corporate/us/en/news-and-media-relations/news-releases/news-releases-usa/P-13-452.
104. H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 974-+.
105. S. Chaemchuen, N. A. Kabir, K. Zhou and F. Verpoort, *Chem. Soc. Rev.*, 2013, **42**, 9304-9332.
106. D. Zhao, D. J. Timmons, D. Yuan and H.-C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123.
107. Y.-S. Bae and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2011, **50**, 11586.
108. J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477.
109. A. J. Fletcher, K. M. Thomas and M. J. Rosseinsky, *J. Sol. State Chem.*, 2005, **178**, 2491.
110. M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782.
111. D. A. Gomez-Gualdron, C. E. Wilmer, O. K. Farha, J. T. Hupp and R. Q. Snurr, *J. Phys. Chem. C*, 2014, **118**, 6941.
112. F. Gandara, H. Furukawa, S. Lee and O. M. Yaghi, *J. Amer. Chem. Soc.*, 2014, **136**, 5271.
113. Z. Wang, B. Zheng, H. Liu, X. Lin, X. Yu, P. Yi and R. Yun, *Cryst. Growth Des.*, 2013, **13**, 5001.
114. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
115. S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. Mark Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710.
116. H. Oh, I. Savchenko, A. Mavrandonakis, T. Heine and M. Hirscher, *ACS Nano*, 2013, **8**, 761.
117. H. Kim and Y. Jung, *J. Phys. Chem. Lett.*, 2014, **5**, 440.
118. P. Verma, X. Xu and D. G. Truhlar, *J. Phys. Chem. C*, 2013, **117**, 12648.
119. H. Kim, J. Park and Y. Jung, *Phys. Chem. Chem. Phys.*, 2013, **15**, 19644.
120. T. K. Trung, N. A. Ramsahye, P. Trens, N. Tanchoux, C. Serre, F. Fajula and G. Ferey, *Microporous Mesoporous Mater.*, 2010, **134**, 134.
121. T. K. Trung, P. Trens, N. Tanchoux, S. Bourrelly, P. L. Llewellyn, S. Loera-Serna, C. Serre, T. Loiseau, F. Fajula and G. Ferey, *J. Amer. Chem. Soc.*, 2008, **130**, 16926.
122. W. Wang, J. Yang, L. Li and J. Li, *Funct. Mater. Lett.*, 2013, **06**, 1350004.
123. P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.
124. S. R. Miller, E. Alvarez, L. Fradcourt, T. Devic, S. Wuttke, P. S. Wheatley, N. Steunou, C. Bonhomme, C. Gervais, D. Laurencin, R. E. Morris, A. Vimont, M. Daturi, P. Horcajada and C. Serre, *Chem. Comm.*, 2013, **49**, 7773.
125. D. F. Sava, T. J. Garino, T. M. Nenoff, K. W. Chapman and P. J. Chupas, *Trans. Amer. Nucl. Soc.*, 2012, **106**, 191.
126. K. W. Chapman, D. F. Sava, G. J. Halder, P. J. Chupas and T. M. Nenoff, *J. Amer. Chem. Soc.*, 2011, **133**, 18583.
127. S. T. Meek, S. L. Teich-McGoldrick, J. J. Perry, J. A. Greathouse and M. D. Allendorf, *J. Phys. Chem. C*, 2012, **116**, 19765.
128. B. Li, H. Wang and B. Chen, *Chem. Asian J.*, 2014, **9**, 1474.
129. N. Chang and X.-P. Yan, *J. Chromatog. A*, 2012, **1257**, 116.

130. N. Nijem, H. Wu, P. Canepa, A. Marti, K. J. Balkus, Jr., T. Thonhauser, J. Li and Y. J. Chabal, *J. Amer. Chem. Soc.*, 2012, **134**, 15201.
131. B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115.
132. S. A. FitzGerald, C. J. Pierce, J. L. C. Rowsell, E. D. Bloch and J. A. Mason, *J. Amer. Chem. Soc.*, 2013, **135**, 9458.
133. Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna and J. R. Long, *Science*, 2013, **340**, 960.
134. M. Shah, M. C. McCarthy, S. Sachdeva, A. K. Lee and H.-K. Jeong, *Indust. Eng. Chem. Res.*, 2011, **51**, 2179.
135. A. J. Brown, N. A. Brunelli, K. Eum, F. Rashidi, J. R. Johnson, W. J. Koros, C. W. Jones and S. Nair, *Science*, 2014, **345**, 72.
136. A. Carne, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, **40**, 291.
137. V. Stavila, R. K. Bhakta, T. M. Alam, E. H. Majzoub and M. D. Allendorf, *ACS Nano*, 2012, **6**, 9807.
138. Z. Guo, C. Xiao, R. V. Maligal-Ganesh, L. Zhou, T. W. Goh, X. Li, D. Tesfagaber, A. Thiel and W. Huang, *ACS Catal.*, 2014, **4**, 1340.
139. O. Kozachuk, I. Luz, F. X. Llabrés i Xamena, H. Noei, M. Kauer, H. B. Albada, E. D. Bloch, B. Marler, Y. Wang, M. Muhler and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2014, **53**, 7058.
140. H. Noei, S. Amirjalayer, M. Müller, X. Zhang, R. Schmid, M. Muhler, R. A. Fischer and Y. Wang, *ChemCatChem*, 2012, **4**, 755.
141. H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer and S. M. Cohen, *J. Amer. Chem. Soc.*, 2014, **136**, 4965.
142. P. V. Dau and S. M. Cohen, *Chem. Comm.*, 2013, **49**, 6128.
143. A. M. Rasero-Almansa, A. Corma, M. Iglesias and F. Sánchez, *ChemCatChem*, 2014, **6**, 1794.
144. T. Maity, D. Saha and S. Koner, *ChemCatChem*, 2014, 2373.
145. N. T. S. Phan, C. K. Nguyen, T. T. Nguyen and T. Truong, *Catal. Sci. Technol.*, 2014, **4**, 369.
146. J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982.
147. C. Chizallet, S. Lazare, D. Bazer-Bachi, F. Bonnier, V. Lecocq, E. Soyer, A.-A. Quoineaud and N. Bats, *J. Amer. Chem. Soc.*, 2010, **132**, 12365.
148. O. R. Evans, H. L. Ngo and W. Lin, *J. Amer. Chem. Soc.*, 2001, **123**, 10395.
149. A. Henschel, K. Gedrich, R. Kraehnert and S. Kaskel, *Chem. Comm.*, 2008, 4192.
150. R. F. D'Vries, M. Iglesias, N. Snejko, S. Alvarez-Garcia, E. Gutierrez-Puebla and M. A. Monge, *J. Mater. Chem.*, 2012, **22**, 1191.
151. M. Yadav and Q. Xu, *Chem. Comm.*, 2013, **49**, 3327.
152. S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa, *J. Amer. Chem. Soc.*, 2007, **129**, 2607.
153. A. Dhakshinamoorthy, M. Opanasenko, J. Čejka and H. Garcia, *Adv. Synth. Catal.*, 2013, **355**, 247.
154. G. Lu and J. T. Hupp, *J. Amer. Chem. Soc.*, 2010, **132**, 7832.
155. A. L. Robinson, V. Stavila, T. R. Zeitler, M. I. White, S. M. Thornberg, J. A. Greathouse and M. D. Allendorf, *Anal. Chem.*, 2012, **84**, 7043.
156. M. Ohba, K. Yoneda and S. Kitagawa, *CrystEngComm*, 2010, **12**, 159.
157. M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall and P. J. Hesketh, *J. Amer. Chem. Soc.*, 2008, **130**, 14404.
158. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2011, **112**, 1105.
159. I. Ellern, A. Venkatasubramanian, J.-H. Lee, P. Hesketh, V. Stavila, A. Robinson and M. Allendorf, *Micro Nano Lett.*, 2013, **8**, 766.

160. A. Venkatasubramanian, J.-H. Lee, V. Stavila, A. Robinson, M. D. Allendorf and P. J. Hesketh, *Sens. Act. B*, 2012, **168**, 256.
161. V. Stavila, J. Volponi, A. M. Katzenmeyer, M. C. Dixon and M. D. Allendorf, *Chem. Sci.*, 2012, **3**, 1531.
162. M. Tu and R. A. Fischer, *J. Mater. Chem. A*, 2014, **2**, 2018.
163. J.-L. Zhuang, D. Ar, X.-J. Yu, J.-X. Liu and A. Terfort, *Adv. Mater.*, 2013, **25**, 4631.
164. S. Eslava, L. Zhang, S. Esconjauregui, J. Yang, K. Vanstreels, M. R. Baklanov and E. Saiz, *Chem. Mater.*, 2012, **25**, 27.
165. Y. Kobayashi, B. Jacobs, M. D. Allendorf and J. R. Long, *Chem. Mater.*, 2010, **22**, 4120.
166. S. Takaishi, M. Hosoda, T. Kajiwara, H. Miyasaka, M. Yamashita, Y. Nakanishi, Y. Kitagawa, K. Yamaguchi, A. Kobayashi and H. Kitagawa, *Inorg. Chem.*, 2008, **48**, 9048.
167. D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik and M. Dincă, *J. Amer. Chem. Soc.*, 2014, **136**, 8859.
168. T. C. Narayan, T. Miyakai, S. Seki and M. Dincă, *J. Amer. Chem. Soc.*, 2012, **134**, 12932.
169. L. Sun, T. Miyakai, S. Seki and M. Dincă, *J. Amer. Chem. Soc.*, 2013, **135**, 8185.
170. A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Léonard and M. D. Allendorf, *Science*, 2014, **343**, 66.
171. P. Ramaswamy, N. E. Wong and G. K. H. Shimizu, *Chem. Soc. Rev.*, 2014, **43**, 5913.
172. J. A. Hurd, R. Vaidhyanathan, V. Thangadurai, C. I. Ratcliffe, I. L. Moudrakovski and G. K. H. Shimizu, *Nat. Chem.*, 2009, **1**, 705.
173. R. Ameloot, M. Aubrey, B. M. Wiers, A. P. Gómora-Figueroa, S. N. Patel, N. P. Balsara and J. R. Long, *Chem. Eur. J.*, 2013, **19**, 5533.
174. H. Kitagawa, *Nat. Chem.*, 2009, **1**, 689.
175. J. Wegener, A. Kaltbeitzel, R. Graf, M. Klapper and K. Müllen, *ChemSusChem*, 2014, **7**, 1148.
176. S. Keskin and S. Kizilel, *Indust. Eng. Chem. Res.*, 2011, **50**, 1799.
177. J. G. Nguyen, K. K. Tanabe and S. M. Cohen, *CrystEngComm*, 2010, **12**, 2335.
178. A. C. McKinlay, B. Xiao, D. S. Wragg, P. S. Wheatley, I. L. Megson and R. E. Morris, *J. Amer. Chem. Soc.*, 2008, **130**, 10440.
179. P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle and G. Férey, *Angew. Chem. Int. Ed.*, 2006, **45**, 5974.
180. J. An, S. J. Geib and N. L. Rosi, *J. Amer. Chem. Soc.*, 2009, **131**, 8376.
181. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172.
182. A. Carne-Sanchez, C. S. Bonnet, I. Imaz, J. Lorenzo, E. Toth and D. Maspoch, *J. Amer. Chem. Soc.*, 2013, **135**, 17711.
183. D. Liu, K. Lu, C. Poon and W. Lin, *Inorg. Chem.*, 2014, **53**, 1916.
184. M. Hanke, H. K. Arslan, S. Bauer, O. Zybaylo, C. Christophis, H. Gliemann, A. Rosenhahn and C. Wöll, *Langmuir*, 2012, **28**, 6877.

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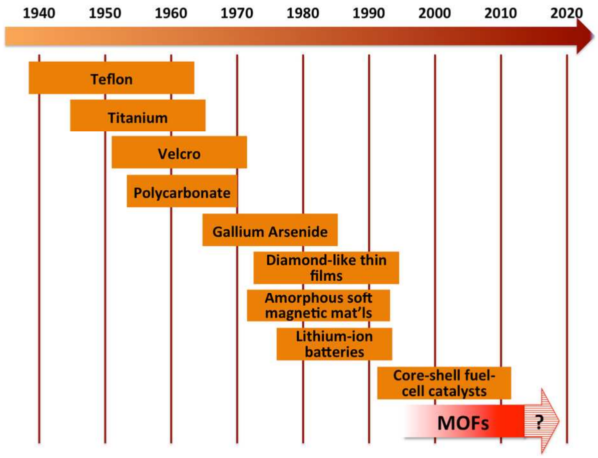
Table of contents image and text



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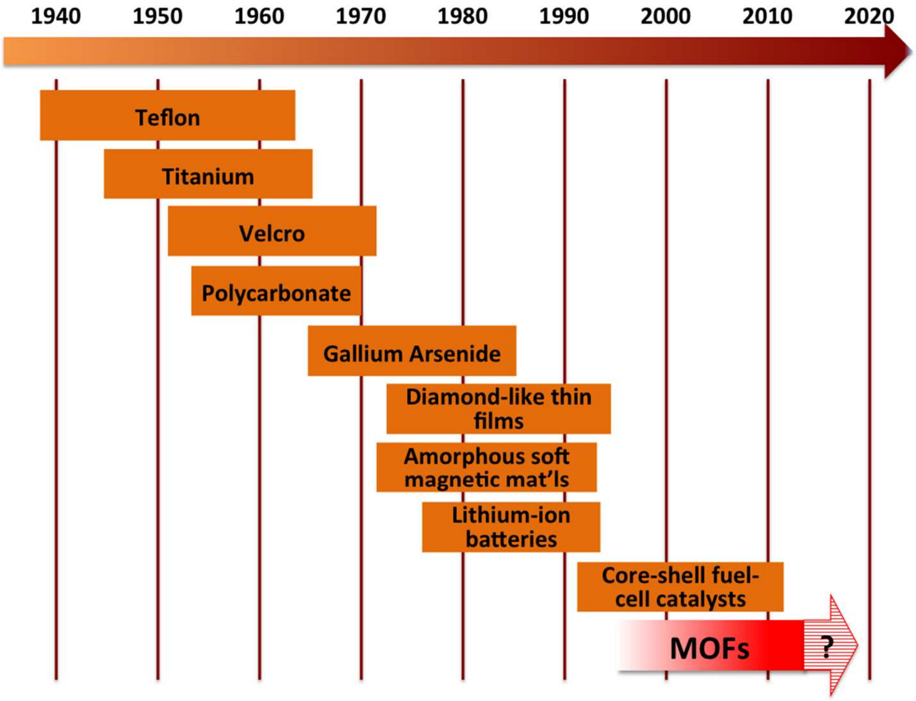

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