

Reticular Chemistry and Metal-Organic Frameworks for Clean Energy

Omar M. Yaghi and Qiaowei Li

This article is an edited transcript of the MRS Medal presentation given by Omar Yaghi (University of California, Los Angeles) on November 28, 2007, at the 2007 Materials Research Society Fall Meeting in Boston. Yaghi was awarded the Medal for "his pioneering work on the synthesis, structure, and theory of metal-organic frameworks." The MRS Medal recognizes a specific outstanding recent discovery or advancement that is expected to have a major impact on the progress of any materials-related field.

Abstract

Reticular chemistry concerns the linking of molecular building blocks into predetermined structures using strong bonds. We have been working on creating and developing the conceptual and practical basis of this new area of research. As a result, new classes of crystalline porous materials have been designed and synthesized: metal-organic frameworks, zeolitic imidazolate frameworks, and covalent organic frameworks. Crystals of this type have exceptional surface areas (2,000–6,000 m²/g) and take up voluminous amounts of hydrogen (7.5 wt% at 77 K and $3\text{--}4 \times 10^6$ Pa), methane (50 wt% at 298 K and 2.5×10^6 Pa), and carbon dioxide (140 wt% at 298 K and 3×10^6 Pa). We have driven the basic science all the way to applications without losing sight of our quest for understanding the underlying molecular aspects of this chemistry. The presentation was focused on the design concepts, synthesis, and structure of these materials, with emphasis on their applications to onboard energy storage.

Introduction

I am delighted to be here and I am pleased and honored to receive this award. In this lecture, I will show how one can take a simple idea from basic science and planning through to application. The field of metal-organic frameworks (MOFs)¹ is rapidly expanding; more than 1,000 new MOF structures have been reported each year for the last few years.² This is an unparalleled development—it is the fastest growing field in materials chemistry, and it is also the first time that one has such a diverse class of new materials to investigate.

I call the chemistry I will be discussing today "reticular chemistry." I will describe the basic thinking behind reticular chemistry and the design strategy and show that this chemistry leads to a cornucopia

of new materials. The focus today will be on polyhedral and periodic MOFs, but I will also mention covalent-organic frameworks (COFs)³ and more recent work on zeolitic imidazolate frameworks (ZIFs).⁴ I will then briefly describe the applications of MOFs to clean energy, hydrogen⁵⁻⁷ and methane storage,⁸ and carbon dioxide capture.⁹ Finally, I will describe the mass production of these materials by BASF in collaboration with my group.¹⁰

Reticular Chemistry

The meaning of the word reticular is "net-like." I define reticular chemistry as the chemistry concerned with the linking of molecular building blocks—these can be organic molecules, inorganic clusters, dendrimers, peptides, and proteins—into

predetermined structures in which such units are repeated and are held together by *strong bonds*. The more brief definition is that reticular chemistry is "stitching molecules together by strong bonds." The reason I have emphasized these two terms is because they are the new aspects of this chemistry. For the first time outside molecular chemistry, we are able to conceive of a structure and go to the laboratory and make it. In collaboration with Michael O'Keeffe, we have developed the blueprint for extended structures that go beyond molecules and 1D structures.¹¹ This is a new region of structure space in chemistry, and we want the building blocks to be linked by strong bonds so that we can make robust materials that are useful as catalysts or as storage materials. The ability to do this is the reason for the popularity of this field.

The basic thinking behind reticular chemistry is that all extended structures are composed entirely of joints and links, which correspond to vertices and edges of a net. In each of such structures, there are branching points and links that join them. This way of thinking helps in understanding how one can assemble building blocks into predetermined structures, as I will demonstrate later. This approach covers the entire gamut of compounds in chemistry. Figure 1 shows a number of structures: 0D, nanoparticles; 1D, chains; 2D, sheets; and 3D, networks. Notice that all of these structures are composed of intersections that are square in shape. The only difference between these structures is the angle between the squares. And so, if there is a way first to make molecular squares and second to place them at the required angles to make these shapes, then the synthesis should produce compounds that are based on these blueprints.

This point is illustrated in Figure 2 using a basic structure in inorganic chemistry, copper acetate, in which four carboxylates (--COO^-) are chelating the copper centers (shown in yellow). Of course, the copper acetate structure is terminated with methyl groups to make a discrete molecule. Our strategy was to replace methyl with a ditopic link (a link with two connecting points) and thus link these together into larger and extended structures. If completed, then this structure would act as a square, and, depending on what the link is, squares could be assembled into various shapes. This copper acetate unit is a secondary building unit, and the geometry of the unit is defined by the points of extension (such as the carboxylate C atoms in most carboxylate MOFs). Having an assembly composed of metal-oxygen bonds,

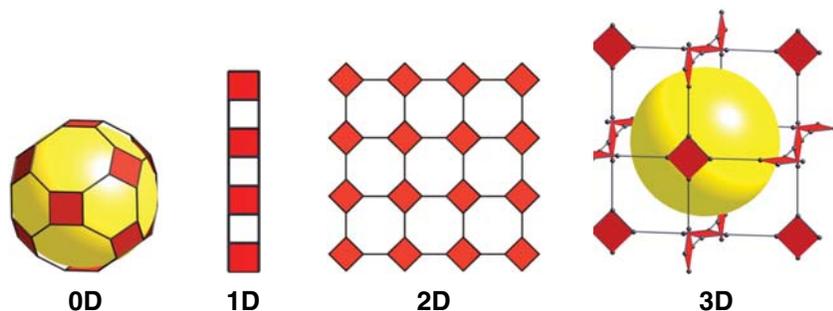


Figure 1. Design of nanoparticles (0D), chains (1D), sheets (2D), and networks (3D). All these structures are composed of intersections that are square in shape (red), which are connected by ditopic linkers (black). The dimensionality of linked square units is controlled by use of precise linker geometry.

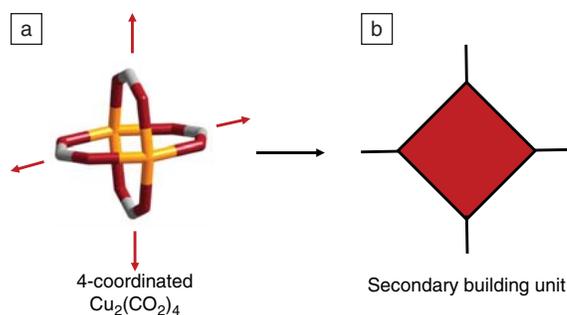


Figure 2. Example of a secondary building unit (SBU). (a) In copper acetate SBU, two copper atoms (yellow) are chelated by four carboxylates (O, red; C, white). The whole SBU is very rigid, because they are constructed by strong bonds. (b) The geometry of SBU is precisely controlled because of the fixed coordination geometry of metals. $\text{Cu}_2(\text{CO}_2)_4$ can be considered as a square (red), which can be linked to four linkers.

oxygen-carbon bonds, and then carbon-carbon bonds, as links, results in robust materials. The fact that the building unit is a chelated entity leads to a rigid unit that can only link as a square and has strong bonds with covalent characters (bond energy is approximately 360 kJ/mol), as strong as carbon-carbon bonds (carbon-carbon single bond energy in alkane is approximately 348 kJ/mol). At the heart of the development of MOFs is that we have found a way to make rigid molecular units of well-defined molecular shapes that can be linked to produce robust extended structures.

Terephthalate or benzenedicarboxylate, illustrated in Figure 3, can be thought of as an entity with three angles to control. The carboxylate groups can make a coplanar bend in the middle of the link (θ) by using the meta-carboxylate. It can also twist the carboxylate planes around the linker axis relative to one another (ϕ) or bend the planes of the carboxylates toward each other (ψ). If we can control these three angles, then that link provides metric information or angular informa-

tion that will direct linkage of those squares into the desired structure. As an illustrative example, if we take the meta-benzenedicarboxylate with an θ angle of 120° and carry out the chemistry that produces that square, the copper acetate unit, we obtain the truncated cube octahedron, cuboctahedron,¹² shown in Figure 4. A very simple reaction in *N,N*-dimethylformamide and ethanol at 80°C for 24 hours produces this structure. The planes of linked squares in this structure are at 120° , and the bent links are exactly what were required to bring this to fruition. We can make a polyhedron that is about 3.4 nanometers in external diameter, with 1.5 nanometers in internal diameter.¹² The yellow ball in the picture is there to make the structure clear, but also to indicate the largest molecule that could fit inside the pore without contacting the van der Waals radii of the atoms making up the walls. This is a nanoparticle, in which the positions of all the atoms, and the way they are linked, are known. We know exactly what the bond lengths are, the atoms on the outside, the atoms

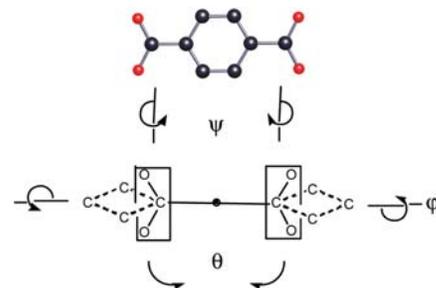


Figure 3. Control angles for metal-organic frameworks constructed from benzenedicarboxylic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$). θ , bending in the middle of the link with carboxylate groups (COO^-) coplanar; ψ , bending of the planes of the carboxylates toward each other; ϕ , twisting of the carboxylate planes about the linker axis relative to one another. C, black; O, red.

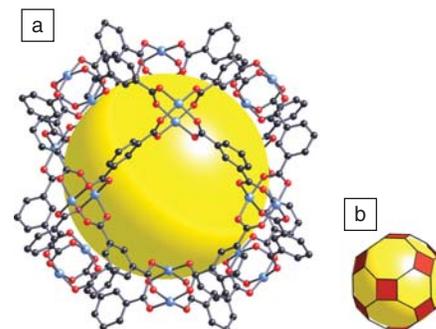


Figure 4. Truncated cuboctahedron. (a) Twelve paddle-wheel units (Cu, blue; O, red; C, black) were linked by 1,3-benzenedicarboxylate (*m*-BDC) to form a large truncated cuboctahedron of 15 angstroms diameter void. The yellow ball in the picture indicates the largest molecule that could fit inside the pore without contacting the van der Waals radii of the atoms making up the walls. Hydrogen atoms have been omitted for clarity. (b) The same structure was illustrated by connecting red squares (paddle-wheel secondary building units) with black rods (organic linkers).

on the inside, the metrics of everything in the structure, and its geometry. Using the conditions that produce this intersection, we can functionalize the phenylene ring (in black) shown in Figure 4, and as long as we do not change the angle of 120° , we can functionalize the surface of this sphere without changing its underlying structure. And thus we are able to create the amino-, -OH, -bromo-, -allyl-, *t*-butyl- and $-\text{OC}_{12}\text{H}_{25}$ functionalized spheres,^{13,14} all based on the same truncated cubocta-

hedron blueprint. This is very important for various applications, such as design of devices, and if their exact structures are known, they can be patterned on surfaces such as graphite.¹³

These copper acetate squares can now be linked in other ways by varying the angles of the linkers. If terephthalate is used, which predisposes the linked squares to be coplanar, a 2D square grid can be made called MOF-2.¹⁵ If we place -bromo in the ortho position of -COO- on the benzene ring, it turns one carboxylate 90° to the other. If we are careful not to heat this reaction mixture, so as not to overcome the rotation barrier to turn two carboxylates coplanar, the squares will be at 90°, thus leading to formation of a 3D extended structure¹⁶ based on a NbO type of net as illustrated in Figure 5.

I have demonstrated how to make 0D, 1D, 2D, and 3D structures using simple chemistry, by taking a link and a metal ion and combining them under mild conditions to produce well-defined materials.¹ Most MOF syntheses are performed at ambient pressure, and the reaction temperatures range from 25 to 200°C. Squares are not the only possible joints. Inorganic chemistry is replete with metal-carboxylate clusters that could be used as secondary building blocks in various shapes. Organic chemistry provides links, which, in themselves, could also have different geometries. These links lead to questions about other structures that could be made from a square and a triangle, a square and a tetrahedron, and so on. The possible structures from such combinations of shapes are almost infinite; only a few are known. Our strategy has not been to enumerate all of the possibilities, but to realize that there are only a limited number of high symmetry structures that will be the most favored structures for synthesis, whether they are based on triangles, squares, tetrahedra, or any other shape.¹⁷ Generally, only a handful of structures need to be considered; in particular, those with just one kind of link are overwhelmingly the ones that are most commonly observed. Most, if not all, structures of this type are known.¹⁷

The structure based on triangles joined by one kind of link is called the SrSi₂ network (the Si substructure in that compound has this topology, and the net is given the symbol srs); for squares joined at right angles by one kind of link, they have the nbo topology named for NbO; similarly, when tetrahedra are linked together, a structure with the diamond topology (dia) is obtained; octahedra linked together form a structure based on the primitive cubic lattice (pcu). These basic structures

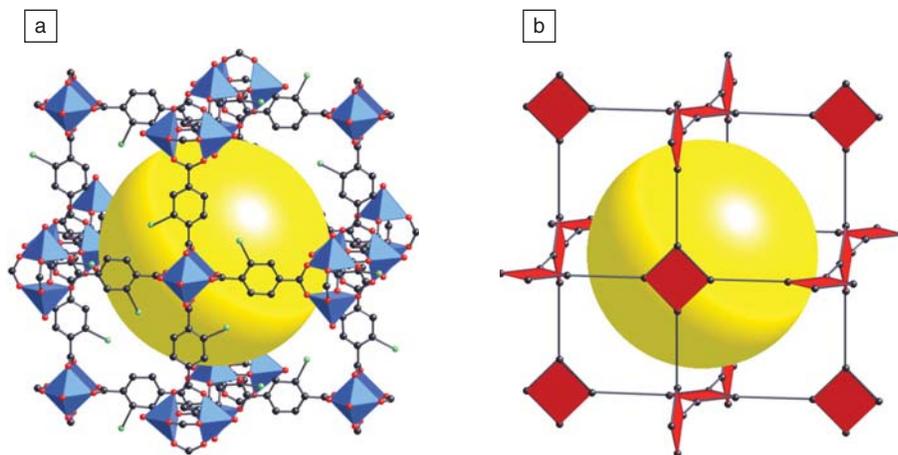


Figure 5. A 3D extended structure based on a NbO type of net. (a) The crystal structure of $\text{Cu}_2[\text{o-Br-C}_6\text{H}_3(\text{CO}_2)_2]_2$ was deliberately designed to have an NbO framework by using reaction conditions that produce the paddle-wheel unit, a square secondary building unit (SBU). Cu, blue square pyramid; O, red spheres; C, black spheres; Br, green spheres. Hydrogen atoms have been omitted for clarity. (b) Schematic illustration of NbO net from red squares (paddle-wheel SBUs) with black rods (organic linkers).

are called *default structures* (Table I); they are in a way “the platonic networks” for extended structures,¹⁸ and they play a role analogous to that of platonic solids in molecular chemistry. We have identified the most symmetric possibilities for linking trigonal prisms, hexagons, etc., into 3D structures.^{18,19} We also have identified the key ways of linking different shapes such as cubes and tetrahedra, squares and triangles, tetrahedra and triangles, tetrahedra and squares, squares and hexagons, and octahedra and triangles.²⁰ We have analyzed the thousands of MOFs in the literature, and their topologies are generally the symmetric structures I have described.¹⁷

Some Examples of MOFs

The next few examples illustrate the way this chemistry works. Figure 6 shows a structure based on the linking of trigonal prisms, which is made from a famous cluster in inorganic chemistry, composed of three octahedral metals linked to two sets of three carboxylates, arranged in a trigonal prismatic geometry.²¹ This is named the acs net after Andrea C. Sudik, the student who discovered this compound having this underlying net topology.

Figure 7 shows a structure linking the paddle-wheel copper acetate structure with adamantane tetracarboxylate, which makes the pts type of net, so named after PtS.²² The same thing can be done by replacing adamantane with carbon and four benzene rings, and the pts net also is obtained.²³

The result of linking octahedra together would be a primitive cubic structure.

Table I: Default Structures from Each Building Block Geometries and One Kind of Linker.¹⁷

Building Block Geometry	Default Structure
Trigonal	srs
Tetrahedral	dia
Square	nbo
Trigonal bipyramidal	bnn
Octahedral	pcu

Figure 8 shows an octahedral cluster, which is a basic zinc acetate structure, with an oxide and four zinc centers that are tetrahedral, bridged by six carboxylates. This is a robust and rigid intersection. When it is linked with terephthalate, it forms the cubic structure based on the pcu net called MOF-5.²⁴ If we have the reaction conditions that produce this intersection, then we can add any desired link to change the functionality of the structure and the metrics. The thermal stability of these materials is quite high. Once the molecules filling the pores are removed by heat, the structure has a large stability range, up to about 500°C. In this case, the solvent molecules in the pores of the as-synthesized material can be exchanged with chloroform to remove unreacted links, metal salts, and original solvent molecules in the pores. Chloroform is then evacuated, and the resulting framework

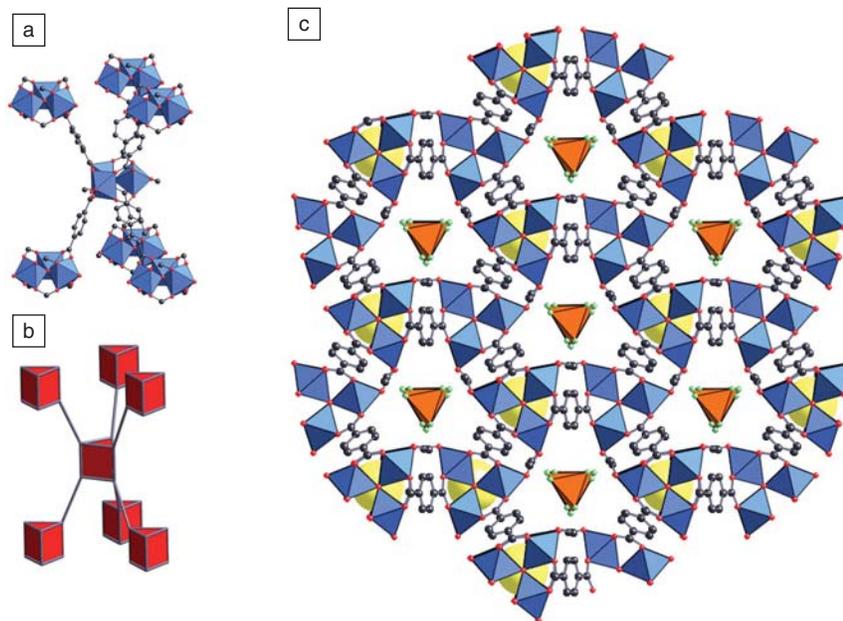


Figure 6. Structures linking triangular prisms composed of three octahedral metals and two sets of three carboxylates arranged in a trigonal prismatic geometry. (a) Fe_3O clusters and terephthalate (1,4-BDC) are reticulated into decorated and expanded versions of the acs net, a hexagonal ABA array of trigonal prisms. Fe, blue; O, red; C, black. (b) Topological view of this acs net, based on trigonal prismatic secondary building units (red) and ditopic links (gray). (c) Single-crystal x-ray structure of $[\text{Fe}_3\text{O}(1,4\text{-BDC})_3][\text{FeCl}_4]$ (MOF-235) composed of oxo-centered iron trimers and benzenedicarboxylate links (views down z-axis). Fe, blue octahedra; O, red spheres; C, black spheres; $[\text{FeCl}_4]^-$, orange tetrahedra. Axial coordinating ligands and hydrogen atoms have been omitted for clarity.

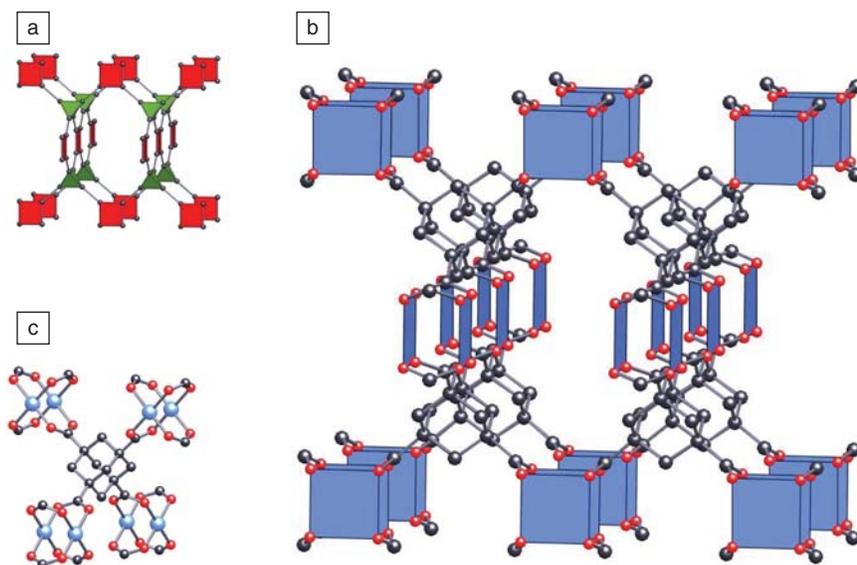


Figure 7. MOF-12, $\text{Cu}_2(\text{adamantane tetracarboxylate})$, an example of the PtS structure (pts-a). pts-a is the augmented net of pts, in which the vertices of the original net are replaced by a group of vertices with the shape of the original coordination figure of the vertex. (a) Squares (red) and tetrahedra (green) assemble to adopt the pts net. (b) $\text{Cu}_2(\text{OCO})_4$ cluster and adamantane cluster were chosen because of their square and tetrahedral geometry, respectively. Cu, blue; O, red; C, black. (c) Vertices in pts net were occupied by the clusters to form a decorated pts framework. Cu, blue squares; O, red spheres; C, black spheres.

does not lose any weight even when heated up to 400–500°C.

Porosity of MOFs

The porosity of MOFs is greater than that of any other porous material, double the record for porous carbon. The surface area of MOF-5 was initially reported at 2,900 m^2/g ,²⁴ but now MOF-5 can be activated to obtain 3,800 m^2/g .²⁵ In such a material, 60% is open space, into which gases and organic molecules can be introduced.

To demonstrate the possibilities of finding materials with higher surface areas than MOF-5, it is useful to examine the calculated surface area of a hypothetical layer of graphite (Figure 9a). The calculated surface area on both sides of this sheet approaches 3,000 m^2/g . However, if we strip this sheet into different shapes (Figure 9b–9d), we see a dramatic increase in the surface area. The reason for this is that, in addition to the faces being exposed to incoming gas molecules, the edges are also exposed. The edge of a six-member ring is about 3.7 angstroms, onto which gas molecules can bind. We know this from x-ray diffraction studies on gas molecules in the pores, and we know exactly where they bind in these structures.²⁶

To make those high surface area materials, we added a tritopic triangular carboxylate linker to combine with the octahedral secondary building unit, which is the MOF-5 cluster, to make MOF-177 (Figure 10).²⁷ MOF-177 is replete with exposed faces and exposed edges, and it should have the high surface area that we would have predicted from those calculations. Unlike other porous materials, MOFs have pores without walls; they are made entirely of struts and intersections. They are open scaffolds, where the struts or the intersections are sites for gas molecules to enter. That is the reason they have very high surface area, and this is the optimal way to create high surface area materials. MOF-177 had a surface area of 4,500 m^2/g when we first reported it,²⁷ and now we can obtain 5,500 m^2/g ⁵ by evacuating the pores completely. These are previously unheard of surface areas. Seven years ago, we had to be content with zeolite surface areas of 500 m^2/g , mesoporous materials of 1,000 m^2/g , and porous carbon, which is amorphous with 1,500 m^2/g surface area (2,000 m^2/g with some expensive processing). Now, using simple chemistry, we can obtain 5,500 m^2/g .

In addition to discrete metal oxide units and intersections, it is also possible to use rod-like metal oxides as infinite clusters and then link those rods with organics (Figure 11).²⁸ This unit is nothing more

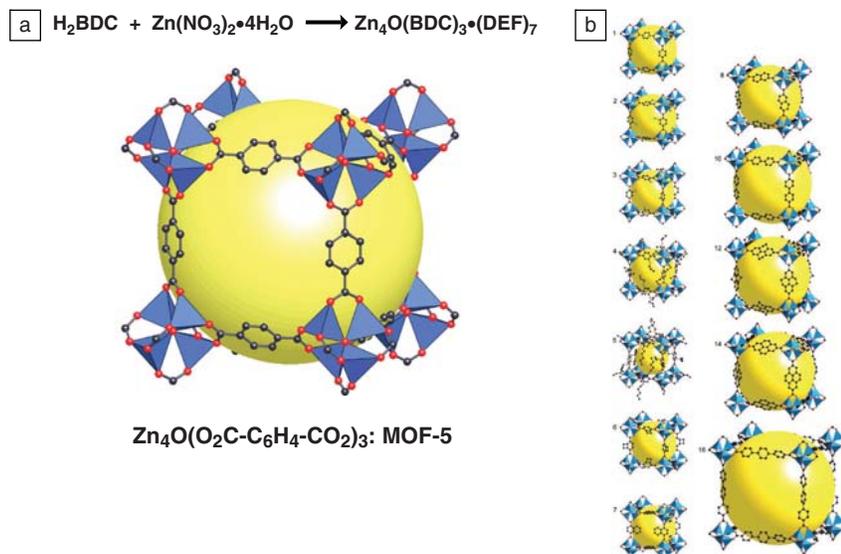


Figure 8. Isoreticular metal-organic frameworks (IRMOFs). (a) MOF-5 was synthesized from terephthalic acid (H_2BDC) and zinc nitrate in *N,N*-diethylformamide (DEF). One of the cavities in the MOF-5 framework is shown. Eight clusters constitute a unit cell and enclose a large cavity. Each octahedral cluster, which is a basic zinc acetate unit, contains an oxide and four zinc centers that are tetrahedral, and these clusters are bridged by six carboxylates. (b) Structures of IRMOF-*n* (*n* = 1 through 7, 8, 10, 12, 14, and 16), labeled respectively. ZnO_4 , blue polyhedra; O, red spheres; C, black spheres. The large yellow spheres represent the largest van der Waals spheres that would fit in the cavities without touching the frameworks. All hydrogen atoms have been omitted, and only one orientation of disordered atoms is shown for clarity.

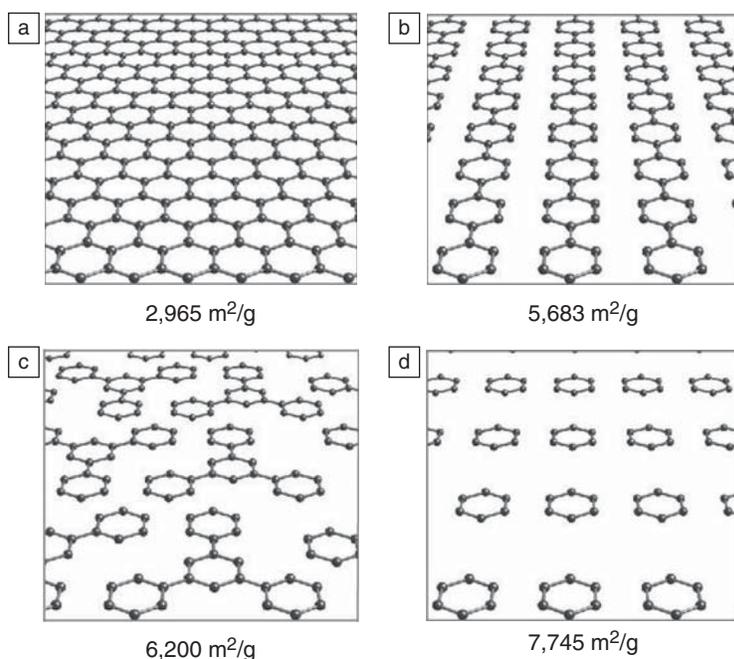


Figure 9. (a) Calculated surface area of a hypothetical layer of graphite. The calculated surface area on both sides of this sheet approaches 3,000 m^2/g . When the sheet is stripped into different shapes (b)–(d), a dramatic increase is seen in the surface area. When the graphene sheet is fully decomposed into isolated six-member rings, the surface area reaches a maximum of 7,745 m^2/g .

than zinc oxide, with zinc in blue and oxygen in red, forming a rod intersection. These rods can then be linked with organics to make porous materials that are very robust. We have identified the most symmetric blueprints that could result from linking rods (Figure 12).²⁹ In the case of bnn net, these rods are going into the page to make a hexagonal pattern. The rods are at an angle to each other; the green rods are at an angle to the red rods and are linked by organics.

Structures based on assembly of rod-like units have been discussed little in the literature, but we have recognized their importance, and we have identified them as the prime structures that could result from linking such building blocks together;²⁹ the basic rods can be trigonal helical or square helical, or they could resemble ladders. We have made a number of MOFs based on these blueprints.^{28,29}

So far, I have discussed a wide range of materials and have covered a significant part of the periodic table with the organic links. My goal is to make a MOF of every single element in the periodic table and to ensure that it is porous and that its properties are studied.

MOFs can be made from simple starting materials: terephthalic acid, which is used for MOF-5, is a main component of plastics; zinc oxide, which is a source of zinc that can be used in MOF synthesis, is used in sun cream. The possibilities are endless, and this can be translated to real chemistry, with nice structures, highly porous materials, and record-breaking surface areas.

BASF is one company dedicated to the production of MOFs, which is being scaled up to produce materials in ton scale. MOFs can be shaped for various applications, including catalysis and gas separation. The price of the raw materials for manganese MOFs based on organic links is approximately four dollars per kilo.

Clean Energy Applications

So far this article has covered ways to think about the chemistry, how the structures are assembled, and the way they are characterized. Now I will describe a new program to address applications for clean energy. A new source of renewable energy has not been found; instead, we are trying to work on issues that can be related to the production of clean energy. Crystals of MOF-5 are well-defined materials, with entire scaffolding; they have no walls, only struts and intersections. Our idea is to take gases that could occupy large volumes and compact them inside an MOF without requiring high pressure or low

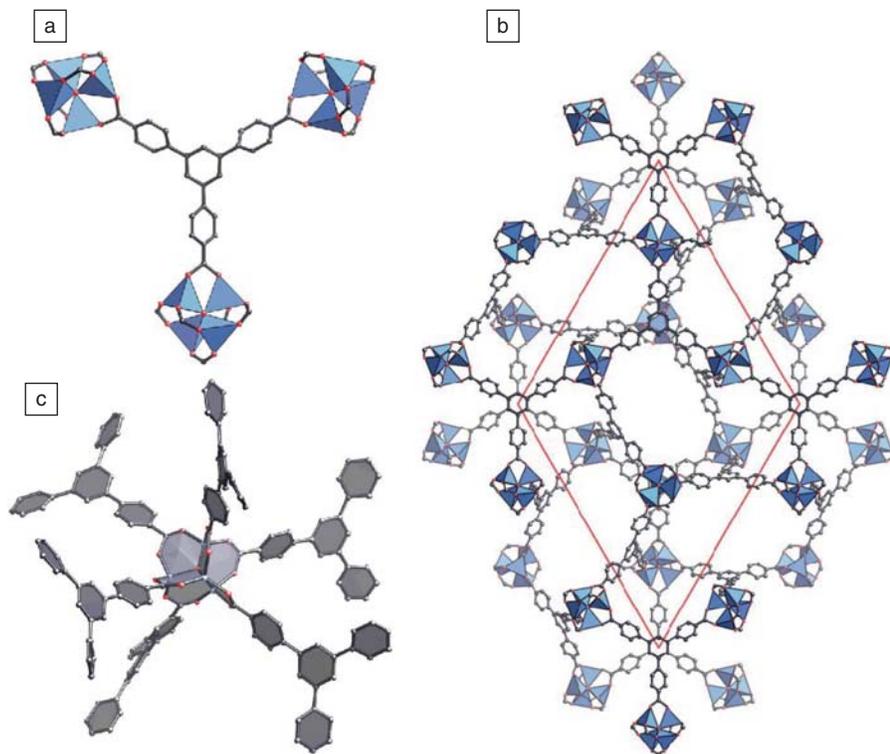


Figure 10. MOF-177 is replete with exposed faces and edges and has a high surface area. (a) A 1,3,5-benzenetricarboxylate (BTB) unit linked to three Zn_4O units (H atoms are omitted). Zn_4O blue tetrahedra; O, red spheres; C, black spheres. (b) The structure projected down [001]. Only half of the *c*-axis repeat unit is shown. Colors as for (a). (c) A fragment of the structure radiating from a central Zn_4O : six-member rings are shown as grey hexagons, O atoms as red spheres, and Zn atoms as blue spheres.

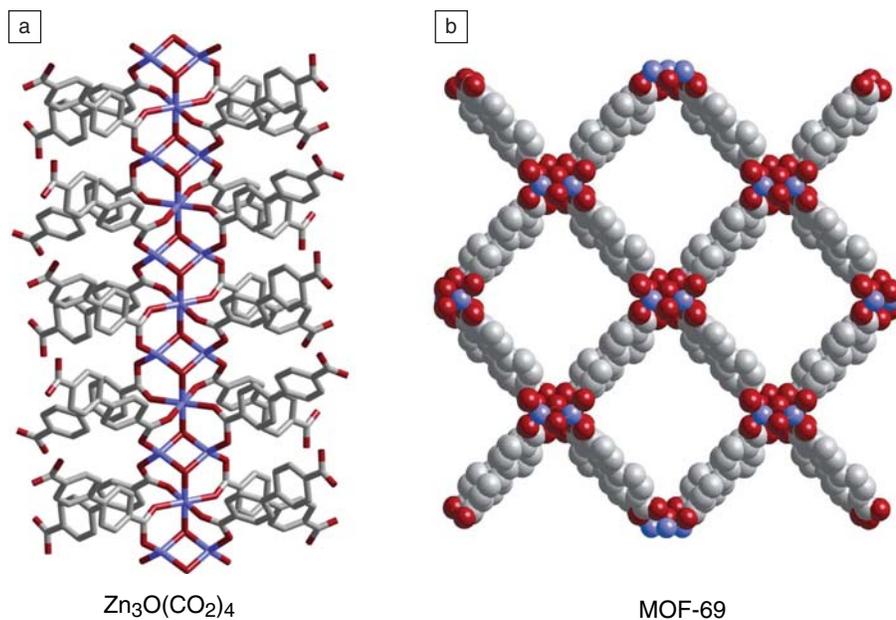


Figure 11. MOF-69A: An example of metal-organic frameworks from zinc oxide structures with rod intersections. (a) Infinite Zn-O-C secondary building units are linked together by 4,4'-biphenyldicarboxylate links. (b) A 3D network was formed with large channels running along the [001] direction. Zn, blue; O, red; C, grey.

temperature. This has now been realized for methane⁸ and carbon dioxide.⁹ It also has been realized for hydrogen at 77 K,⁵ and we are investigating ways of compacting hydrogen inside MOFs at room temperature.^{25,30}

The Department of Energy (DOE) requirement for hydrogen to be used in automobile fueling is that 6% by weight of the fuel tank should be hydrogen, or 45 grams of hydrogen for each liter. MOFs have great advantages over other potential materials since they have well-defined, known, and tunable structures. They need to have an adsorption energy of about 15–20 kJ/mol; that is essentially binding enthalpy of hydrogen molecules into the pores of the material.⁷ MOFs also have high surface area and facile diffusion in and out of the pores. Some MOFs have pore sizes of 7 to 8 angstroms; we can vary the composition and structure; and we can fine tune the electronic character of the adsorption sites. After about six years of study on hydrogen, we have concluded that it is possible to store hydrogen in MOF-177 at 7.5% by weight at 77 K, and the total amount of hydrogen deposited would be 12% by weight.³¹ We have therefore achieved the first goal of the DOE, but at 77 K. This is important, because it demonstrates that we can store sufficient hydrogen in MOFs for them to be useful for storage. Now we need to work on the adsorption energy at the surface. However, hydrogen can go into a pore, or leave the pore, with great facility. If MOF-177 were in the fuel tank of a vehicle, the fueling time would be about two and a half minutes, because hydrogen is held through polarizing or weak forces into the framework.

Our best result is 62 grams of hydrogen per liter at 77 K, which is more than two-thirds of that obtained from liquid hydrogen at 20 K.³¹ This is very exciting, because it means that a container filled with MOF-177, or another MOF not discussed here, can hold 50 percent more hydrogen than one without MOF. That is very interesting for people who want to store hydrogen cryogenically for stationary applications. Our goal is to obtain the same hydrogen uptake numbers at room temperature. Current hydrogen adsorption record for MOF at room temperature is $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$ (H_3BTT = benzene-1,3,5-tris(1*H*-tetrazole)), from Jeffery Long's group, which achieved 12.1 g/L hydrogen uptake at 9×10^6 Pa and 298 K.⁶ In order to reach the goal, we are collaborating with Bill Goddard at Caltech. He has calculated the effect of doping MOFs containing aromatic linkers with lithium so that each six-member ring would have a lithium atom.

Lithium associated with the aromatic rings provides strong stabilization of molecular H_2 . Using this concept, he predicted that MOFs could achieve five percent hydrogen uptake at close to room temperature.³⁰ This is an important development, and the community is now moving toward making MOFs impregnated with lithium or other metals.

Obviously companies such as BASF are not going to make these materials in large quantities due to the sophisticated organic link synthesis and expense, but we can consider structures that would be

equivalent to this. We are currently examining covalent organic frameworks (COFs). Structures that are entirely composed of six-member rings could easily be made by taking tetrahedral units that have boronates, as illustrated in Figure 13. These structures can be either self-condensed to make extended structures that are entirely composed of carbon-carbon bonds, carbon-boron bonds, and boron-oxygen bonds.^{3,32} These are all strong bonds based on small atoms, so they are robust. We can either self-condense or co-condense or co-polymerize

to make extended structures, and we know what those structures would be.³² We have characterized them using x-ray diffraction and found it is possible to make COFs that represent the least dense materials known to date in crystalline form.³² Figure 14 shows COF-108,³² with a density of 0.17 grams per cubic centimeter; the surface area is 4,700 m^2/g , and Goddard's calculations predict that COF-108 is going to have an uptake of hydrogen at about 18.9 wt% at 77 K.³³ Goddard's calculations have independently matched every experimental value that we have achieved in MOFs,³⁴ so I am optimistic about obtaining room-temperature storage.

Methane is a cleaner fuel than petrol or coal, and it represents two-thirds of our global natural energy resources; however, half of the available methane is a stranded gas that is difficult to transport. Methane is currently being transported at $-50^\circ C$; if we could store methane at room temperature, it would be a great development. COF-102 takes up about 250 milligrams of methane for each gram of material at 298 K, at a very reasonable pressure of $6-8 \times 10^6$ Pa.³⁵ That is an exciting prospect, since a tank filled with MOF or COF under these conditions will hold twice the methane as one without those materials. This would double the range for automobiles that run on natural gas. A coalition of about 20 compa-

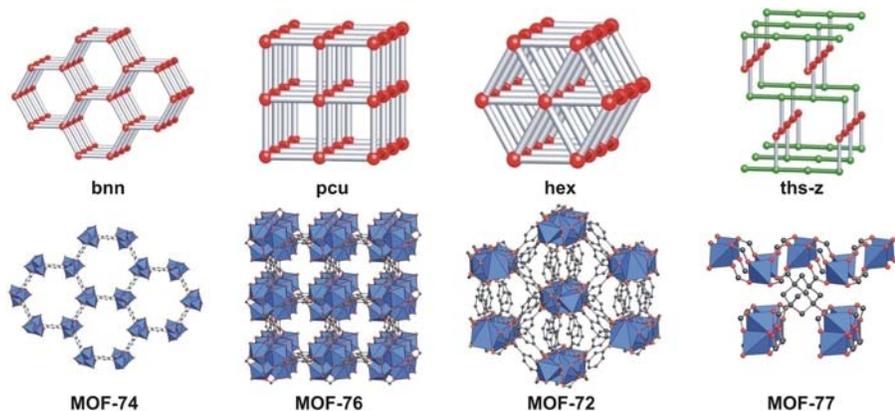


Figure 12. Metal-organic framework (MOF) examples of blueprints based on rod building blocks. The rods are at an angle to each other; the green rods are at an angle to the red rods and are linked by organics. A three-letter symbol system was developed to describe these invariant rod packings. pcu, primitive cube lattice; bnn, boron nitride net; hex, hexagonal lattice; ths-z, $ThSi_2$. MOFs illustration: metal, blue polyhedra; oxygen, red spheres; carbon, black spheres.

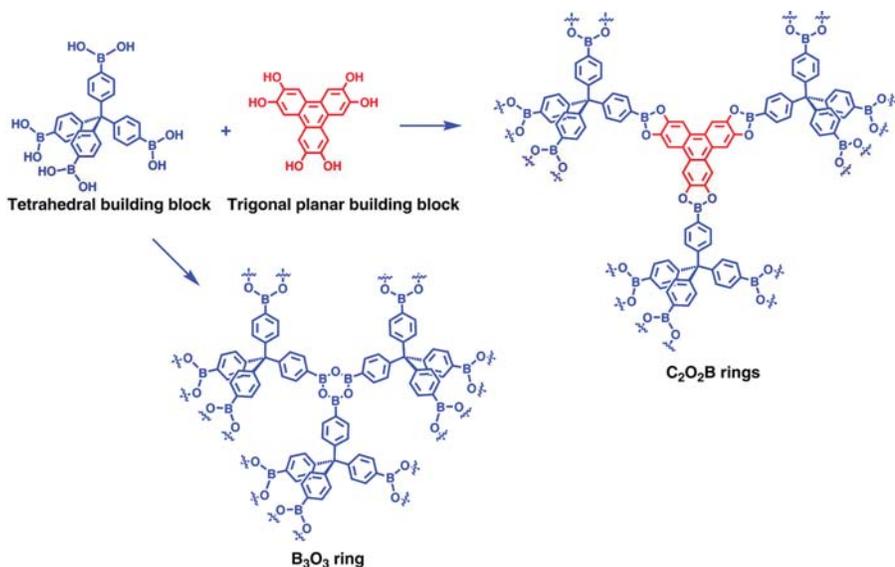


Figure 13. Representative condensation routes to 3D covalent-organic frameworks. Boronic acids (blue) can undergo self-condensation to form B_3O_3 rings or form C_2O_2B rings upon condensation with hexahydroxytriphenylene (red), a planar triangular unit.

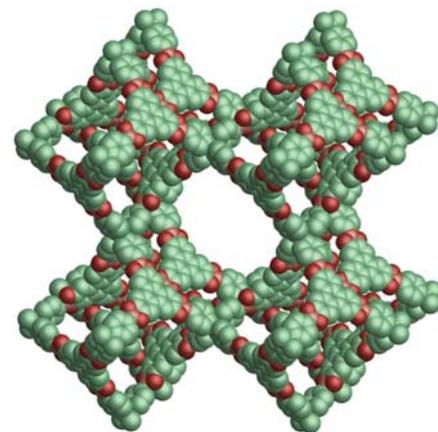


Figure 14. Space-filling illustration of COF-108, with a bor blueprints (the same as boracite). COF-108 was obtained from tetrahedral *tetra*(4-dihydroxyborylphenyl)methane and triangular hexahydroxytriphenylene. Density = 0.17 g/cm^3 ; surface area = 4,700 m^2/g . Hydrogen atoms are omitted for clarity. Carbon, boron, and oxygen atoms are represented as green, brown, and pink spheres, respectively.

nies have undertaken a project to convince the world that a wide distribution of tanks containing MOFs impregnated with methane can be useful in transportation.^{36,37} A prototype car, with an MOF fuel tank, has been successfully driven through five continents.³⁶ According to BASF, fuel tanks of this type may be widely distributed in the near future.

Carbon dioxide emission is an important environmental issue. The world produces more than four tons of carbon dioxide per capita every year. Carbon dioxide emitted from coal or natural gas power plants contains many other gases besides carbon dioxide. At present, in order to meet the EPA levels of emission, the gas is passed through a membrane to separate carbon dioxide from the exhaust gas mixture, and then carbon dioxide is bubbled into an amine solution. This amine solution is heated and carbon dioxide is evolved, and then it is piped into geologic formations under the ground for various purposes. This process costs each power plant a large percentage of its power output.

If we had a material that stored carbon dioxide, we could simply place it in the stacks and pipe carbon dioxide under the ground directly after it is released from the stacks. About 33.5 millimols of carbon dioxide can be stored in every one gram of MOF-177 at room temperature at very acceptable pressures.⁹ A tank filled with MOF can store nine times more carbon dioxide than one without MOFs.

This is not the complete answer, however, because we need materials that can selectively extract carbon dioxide from the exhaust flue gas. We have developed zeolitic imidazolate frameworks (ZIFs) for this purpose.^{4,38,39}

Zeolite structures arise from the characteristic Si-O-Si angle of about 145 degrees. In ZIFs, we have replaced silicon with transition metals with tetrahedral geometries, such as Zn or Co, and oxygen is replaced with imidazolate. The link still has two connecting points, such as oxygen, and the metals are tetrahedral; the linking angle of metal-imidazolate-metal is the same as Si-O-Si in zeolite, so we have a zeolite-like structure that is made of transition metals and organics. One of my students, Kyosung Park succeeded in making the first ZIF, ZIF-8,⁴ which is based on a sodalite (sodium aluminum silicate chloride) net, and it is composed of zinc or cobalt tetrahedra and entirely methylimidazolate links. This work has essentially addressed two holy grails in zeolite chemistry: to develop a material with a high concentration of transition metals and a material with organics in its backbone. Pore environments in ZIFs can

be tailored by different functionalities in organic backbones, and a high concentration of transition metals provides opportunities in various applications, such as catalysis.⁴⁰

ZIFs are thermally very stable up to 500°C, with absolutely no weight loss. Furthermore, unlike other porous materials and some MOFs, they are also chemically stable. We have boiled ZIF-8 in benzene, methanol, water, and sodium hydroxide for periods up to a week, and the material remains crystalline.⁴ X-ray diffraction experiments show there is no change to the framework. It is easy to imagine the different applications in selective gas capture and heterogeneous catalysis for materials with this robust chemical stability. Park delivered approximately a dozen of these materials within three months, based on different zeolite structures, and not just methylimidazolate can be used but also imidazolate and other functionalized imidazolates. This is a beautiful result because these are delocalized π -systems, whose electronic structure could be changed and tailored by the functionality that is introduced on those rings, such that they are highly selective to various gases.

Figure 15 illustrates two ZIFs, the “papa of ZIFs,” ZIF-95 (Figure 15a shows POZ B cage in ZIF-95) and ZIF-100 with “MOZ” cage, the “mother of ZIFs” (Figure 15b). They are both built from tetrahedra, and the MOZ cage is the largest known in chemistry. These are

exceptional structures, in terms of their sheer size. The POZ B cage in ZIF-95 is 30.1×20.0 angstroms in inner diameter, and the size of the MOZ cage in ZIF-100 is 35.6 angstroms in inner diameter.³⁹ ZIF-100 has a Langmuir surface area of 780 m²/g, but what makes it unique is that the MOZ cage has a very nice slit into which carbon dioxide can pass. Once it has entered the pores, it interacts with the imidazolate rings and accumulates there, just as in a reservoir.

We have performed competitive studies on gases containing carbon dioxide, methane, and other power plant flue gases.^{38,39} First, we started with a material that has nothing in the pores and then exposed it to a mixture of nitrogen and carbon dioxide. The carbon dioxide was entirely retained in the pores, while nitrogen passed right through it. ZIFs are thus selective materials for carbon dioxide, and they are twice as efficient as BPL carbon (a commercially available carbon product of Calgon), which is the “state of the art” material.

Summary

In summary, I have described a number of new materials, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and zeolitic imidazolate frameworks (ZIFs), with controlled composition and structure. Within each of these classes, there are subclasses, and each subclass has hundreds of structures. The ways in which we can take molecules

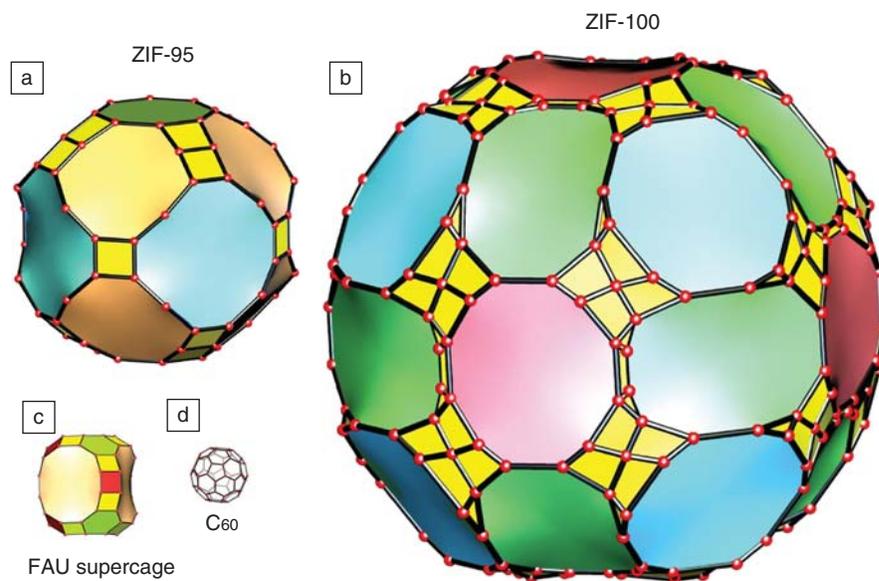


Figure 15. Size comparison of (a) POZ B in ZIF-95, (b) MOZ in ZIF-100, (c) super cage in faujasite (FAU), and (d) C₆₀. The MOZ cage has a 35.6 angstroms inner sphere diameter. All the cages are shown in ball and stick diagrams (Zn, red spheres in (a) and (b); Si/Al, red spheres in (c); C, red spheres in (d)). Different tilings are shown in different colors.

and link them together into structures, for any desired application, are seemingly limitless. The applications are mainly being exploited for catalysis at present, but also for gas storage, carbon dioxide separation, and other areas.

Starting a new field is exciting and rewarding. It has been stated that Shakespeare "only" strung words together to make beautiful sentences. I hope I demonstrated how, in the field of reticular chemistry, we have "only" strung molecules together to make crystals that are not just of wondrous beauty but of unparalleled diversity and utility.

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I would like to acknowledge the help of my colleagues and group members. I am fortunate to have had many students and postdoctoral fellows in my group. I also had the pleasure of working with a number of dedicated collaborators who cared about reticular chemistry, especially Michael O'Keeffe (Arizona State University), Ulrich Mueller (BASF, Ludwigshafen), and Ronald Allain, a retired VP of R&D at NALCO Chemical Company. I also had the pleasure of working with many other colleagues around the world who now stand as leaders in the field of metal-organic frameworks and reticular chemistry. I am also grateful for the support of NSF for a lot of the basic work of reticular chemistry over the past 14 years; the DOE for funding the studies of gas separations and hydrogen storage; BASF for financial support and independence; DOD for funding, and the Defense Threat Reduction Agency for various applications related to personal protection.

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Omar M. Yaghi received his PhD degree from the University of Illinois-Urbana in 1990 with Professor Walter G. Klemperer. He was an NSF postdoctoral fellow at Harvard University (1990–1992) with Professor Richard H. Holm. Yaghi also has been on the faculties of Arizona State University (1992–1998) and the University of Michigan (1999–2006). His current position is the Irving and Jean Stone Chair in Physical Sciences at UCLA. His early accomplishments in the design and synthesis of new materials have been honored by the Solid State Chemistry Award of the American Chemical Society and Exxon Co. (1998) and the Sacconi Medal of the Italian Chemical Society (2004). His work on hydrogen storage was recognized by Popular Science Magazine, which listed him among the "Brilliant 10" scientists and engineers in the United States (2006). He received the U.S. Department of Energy Hydrogen Program Award for outstanding contributions to hydrogen storage (2007) and was the sole recipient of the Materials Research Society Medal (2007) for pioneering work in the theory, design, synthesis, and applications of metal-organic frameworks. He also won the AAAS Newcomb Cleveland Prize for the best paper published in Science (2007), and he is the recipient of the American Chemical Society Chemistry of Materials Award (2009). His work encompasses the synthesis, structure and properties of inorganic compounds and the design and construction of new crystalline materials. He has published more than 130 papers, which have received more than 180 citations per paper. He is listed among the top 10 most highly cited chemists worldwide (1998–2008).

Yaghi can be reached by phone at 310-206-0398 or e-mail at yaghi@chem.ucla.edu.



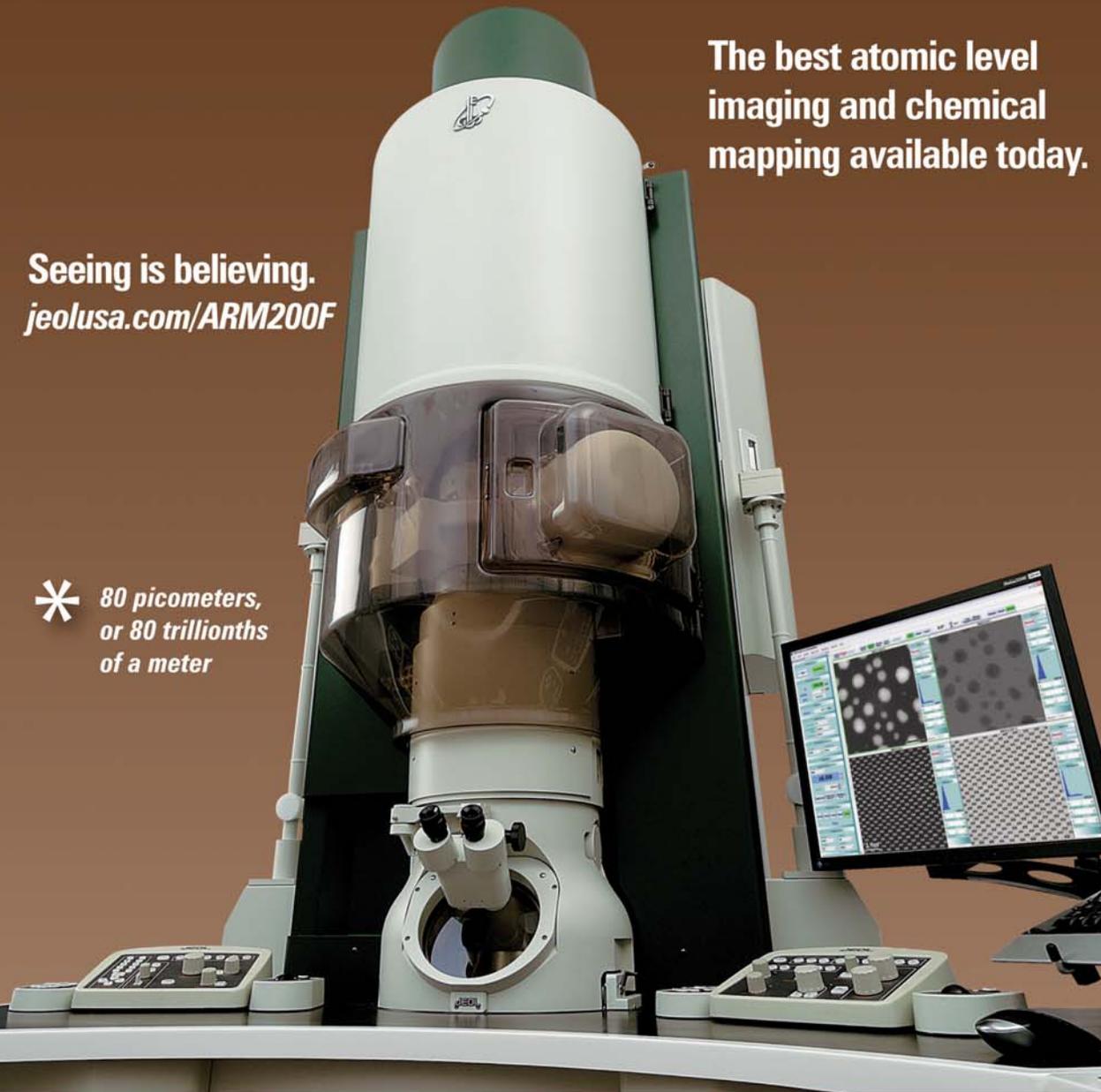
Qiaowei Li received his BS (2004) in applied chemistry from the University of Science and Technology of China and his MS in chemistry from the University of Michigan (2006). He is currently a PhD student at the University of California-Los Angeles, working with Professor Omar M. Yaghi. His current research interests include designing and constructing extended solid structures with complexities and the use of new porous crystalline materials for chemical applications. Li can be reached by e-mail at qqli@chem.ucla.edu.

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