

Design of MOFs and intellectual content in reticular chemistry: a personal view†

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This article gives a personal perspective on the ideas leading to the development of reticular chemistry. The feasibility of achieving targeted materials with predetermined metrics and functionality by designed synthesis is defended.



Michael O’Keeffe was born in Bury St Edmunds, England in 1934 and attended the University of Bristol (BSc 1954, PhD 1958, DSc 1976). He is Regents’ Professor of Chemistry at Arizona State University where he has been since 1963. His research has ranged over many areas of solid state chemistry. Recent efforts have been devoted particularly to development of the theory of periodic nets and tilings and its application to materials synthesis by design.

Michael O’Keeffe

When I was asked to write an account of our work on the taxonomy of nets for this themed issue, I reluctantly declined as I felt there was little I could add at this time to an article we (Olaf Delgado-Friedrichs, Omar Yaghi, and I) recently published in another RSC journal.¹ Instead, with the editors’ permission, I would like to touch on the topics of that paper and other aspects of the development of MOF chemistry, particularly as they affected me with the vantage point of a front-row seat. I refer mainly to work in which I was personally involved so it certainly is not a comprehensive review.

I use the term ‘MOF’ in the narrow sense of materials with frameworks built by linking polyatomic clusters (secondary building units or SBUs) entirely by strong covalent bonds and thus not including coordination polymers, which have some generally weaker bonds and lower stability, as described elsewhere in this issue.² This seems to be now widely accepted although originally the term ‘MOF’ was applied to coordination polymers and some still apply the term ‘coordination polymer’ to MOFs, but I think the distinction is usefully made.

What has been most remarkable to me in MOF chemistry over the years was the constant Greek chorus saying that ‘it can’t be done’. (I could have titled this essay “The Power of Negative Thinking”). But subsequent history has been an illustration of the truism “never say ‘never’”; naysayers can only be proved wrong.

First there was the long-held belief that it was impossible to synthesize materials with three-periodic

frameworks composed of atoms linked by directional covalent bonds. This is the famous ‘crystallization problem’. Roald Hoffmann described it well (but Roald was far too astute to say ‘never’): ³

Organic chemists are masterful at exercising control in zero dimensions...One subculture of organic chemists has learned to exercise control in one dimension. These are polymer chemists, the chain builders...

But in two or three dimensions, it's a synthetic wasteland. The methodology for exercising control so that one can make unstable but persistent extended structures on demand is nearly absent. Or to put it in a positive way—this is a certain growth point of the chemistry of the future.

An early example of a MOF with a two-periodic net formed of strong bonds was a zinc-benzenedicarboxylate (now known as MOF-2) from the Yaghi group.⁴ In this compound, square ‘paddle wheels’ containing two Zn atoms were linked in a periodic square array. Microporosity and high surface area was evidenced by the ability to adsorb gases at *low pressures* and show Type I isotherm behavior.

To me the first MOF with a 3-periodic framework of covalent bonds is the zinc-benzenetricarboxylate (now known as MOF-4) again from Yaghi and co-workers.⁵ Again there were Zn₂ paddle wheels, but now triangular. The net was the beautiful chiral cubic net that we know as **srs**. In that paper the design and rationale of a strategy for effecting crystallization were carefully delineated.

Those who went to conferences where such materials were discussed a decade ago heard the chorus: “they won’t be stable” (they were), “the frameworks will collapse when solvent is removed” (they didn’t), “they won’t be porous” (they were—they adsorbed gases at *low pressures* and had “permanent” porosity) and so it continued.

Omar Yaghi and I were colleagues at Arizona State University at that time and I recall my response when he showed me the structures of MOF-2 and MOF-3: “there are simply too many atoms”.⁶ I came from the austere world of metal-oxide chemistry and found structures with benzene rings and C–H bonds far too baroque for my taste. No doubt with tongue in cheek, Omar thanked me in the MOF-2 paper for my “interest”.

But the now-iconic MOF-5 which came shortly thereafter changed everything. This had truly unprecedented surface area, porosity, and stability. The zinc carboxylate cluster with the six carboxylate carbons forming a regular octahedron but with tetrahedral (T_d) symmetry was elegantly beautiful especially when linked in such regular arrays (by, yes, those benzene rings) like terracotta warriors, and I jumped aboard the bandwagon.⁷ I undertook the task of drawing the structure by hand as good crystal drawing programs were not yet generally available. I found that the clarity of the picture was greatly enhanced by placing a yellow ball (a giant ‘atom’) in the cavity of the structure (see table of contents graphic). I believe this was the first ‘yellow ball’ illustration, and perhaps my most significant contribution to MOF chemistry.

What is startling in retrospect is that the zinc cluster—the secondary structure building unit (SBU)—had been known in basic zinc acetate for some 40 years and was illustrated in widely-read texts such as Wells’ *Structural Inorganic Chemistry*.⁸ Had really no one before Yaghi thought of replacing the acetic acid by terephthalic acid (or some other ditopic linker)? And if they had, were they deterred by knowledge of the crystallization problem?

MOF-5 changed the way we thought about such materials. Omar realized that the same inorganic SBU could be linked by different ditopic linkers to produce a variety of materials with the same structural topology (an *isoreticular series*) with predetermined cavity size and functionalization.⁹ *I.e.* crystalline materials could be made by design; we called that process *reticular chemistry*.¹⁰

This leads me to the next negative attitude that I wish to comment on; this is the widespread belief that even if one could link SBUs into periodic frameworks we had no knowledge of what structure to expect. This point of view was epitomized in an often-cited paper by John Maddox (then the editor of *Nature*) which began:¹¹

One of the continuing scandals in physical sciences is that it remains in general impossible to predict the structure of even the simplest crystallographic solids from knowledge of their chemical composition.

In recent related negativity, several distinguished chemists have called into question whether one could, or should, even use the term ‘design’ in connection with MOF synthesis. These critics use ‘design’ in the narrow sense of the activity of a couturier designing ladies’ dresses, or of a designer of teapots(!)

and state that one can't design molecules or crystals in this way. And perhaps in that very narrow sense they are right; but what is really being done is to design experiments to produce materials of predetermined topology and pore size and functionality. In any event, one is on very shaky ground trying to narrowly define the meaning of an English word. The *Shorter Oxford Dictionary* on my desk gives six meanings for the noun 'design'. The first of which is "a plan or scheme conceived in the mind...". *Merriam Webster's Collegiate Dictionary* (also highly regarded as authoritative) gives eight meanings, of which the first is "deliberate purposive planning...", and another is (I quote exactly) "a plan or protocol for carrying out or accomplishing something (such as a scientific experiment)". This sounds to me very much like what goes on in the Yaghi laboratory and elsewhere. Not every design is successful—engineers sometimes design bridges that fall down (Tacoma Narrows!)—but that doesn't mean that design is impossible. In fact good designs often evolve from lessons learned from earlier less-successful efforts.

But do we really know what structures to expect, or do we, as is sometimes claimed, have to resort to computer simulations to find those that are energetically more favorable? I maintain that, in properly designed experiments, we do indeed know what structures to expect and it is a matter of geometry not energetics. There are a limited number of *default* structures for linking simple geometrical structures together and we early gave an empirical account of them (drawing of course on a substantial body of earlier work) with the subtitle *Geometric Design Principles*.¹²

At the time I am talking of (late '90s) Omar Yaghi had attracted some exceptionally talented associates at A. S. U., notably Hailian Li, Mohamed Eddaoudi, and Theresa Reineke (these last two now lead distinguished groups of their own). Another key player who joined me at that time was Olaf Delgado-Friedrichs. Olaf is a mathematician from the group of Andreas Dress in Bielefeld whose group developed the general combinatorial theory of periodic tilings of space. Working with Olaf we realized that tiling theory provided the basis of a taxonomy of periodic nets and allowed a classification of our default nets as *regular, semiregular etc.*¹ Our default nets were, when possible, nets with one kind of link (in the jargon *edge transitive*) and our recognition of this fact was, I think, a significant step forward. In one of many beautiful applications of tiling theory Olaf showed that an essentially complete enumeration of edge-transitive nets of a certain kind (essentially omitting nets that did not admit tilings) could be completed.¹³

A simple application of the importance of edge-transitive structures is to the design of metal-organic polyhedra (MOPs). There is an infinity of polyhedra with one kind of vertex or one kind of face, but, marvellously, only seven convex polyhedra with one kind of edge. These polyhedra form the basis for the structures of MOPs that one might reasonably expect to produce by design.¹⁴

Another example of the importance of knowing edge-transitive structures was to be found in the synthesis of the first 3-periodic covalent organic frameworks (COFs).¹⁵ In this work, organic SBUs with tetrahedral and triangular shapes were linked together by condensation reactions. Nicely-crystalline materials were obtained which provided good powder diffraction data, but the large cell and paucity of peaks precluded direct structure solution. However there are just two edge-transitive structures possible; these have distinctive cubic symmetries and the materials could be assigned unambiguously to one or the other structure type.

I can't resist adding that there are also just two 3-periodic edge-transitive ways of linking triangles and squares. The justly-famous HKUST-1¹⁶ is based on one of these and the equally-lovely MOF-14¹⁷ is based on the other.

Other examples of successful design abound. We have considered the edge-transitive ways of linking squares by ditopic linkers. These can be 0-periodic (MOPs), 1-periodic (rods), 2-periodic (layers) and 3-periodic, and the design of linker shape appropriate to select one particular structure has been described.¹⁸ In most cases the synthesis has been successfully implemented. To demonstrate the generality of the approach, the successful synthesis of many materials with the same framework topologies (*isoreticular*) of different dimensionalities were subsequently described.¹⁹

A nice example demonstrating that *local* geometry alone may be sufficient to predict the crystal structure is provided by MOFs with giant cells that are built from tetrahedral SBUs sharing corners and with the corners on straight lines joining the centers of adjacent tetrahedron centers (*i.e.* linked TX₄ tetrahedra with 180° T-X-T angles). Adjacent tetrahedra may be staggered or eclipsed as dictated by the nature of the SBU but in either case the observed structure is predicted.²⁰

I could go on with many more examples, but I won't. As Voltaire put it "le secret d'ennuyer est celui de tout dire". I hope I have made my point that the development of MOF chemistry, and more generally of reticular chemistry, was not a random development produced by a horde of monkeys in lab coats.

Rather it required a linear sequence of logical steps, and for successful practice requires considerable theoretical knowledge and cerebral input.

I close by calling attention to the Reticular Chemistry Structure Resource (RCSR)—a searchable database of theoretical topologies designed to help those who would embark on new designed syntheses (there's that D word again and again!).²¹

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Footnote

† Part of the metal–organic frameworks themed issue.

