

 MILESTONE 22

Porous by design

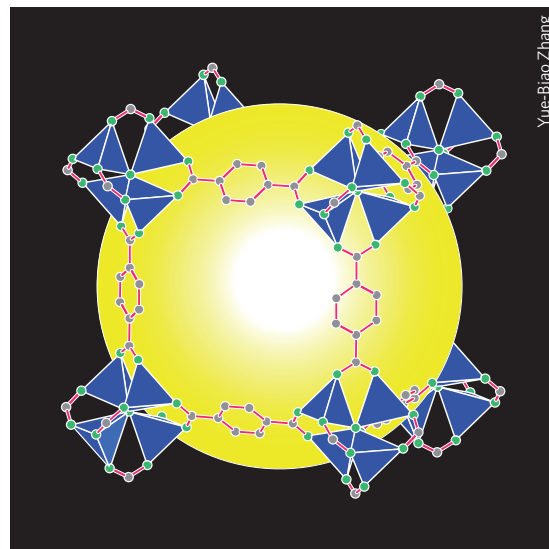
For most of the twentieth century, serendipity was a key ingredient in the synthesis of crystalline solids. The construction of materials with precise architectures was a formidable challenge, but through a subtle combination of chemistry and crystallography, ‘designer’ crystals — materials with predetermined structures and properties — slowly began to emerge. At the forefront of these endeavours was the field of porous crystals.

Porous crystals have nanometre-sized holes that can selectively trap molecules and ions of different shapes and sizes. The archetypal porous crystals are zeolites: aluminosilicates that form naturally in environments such as volcanic rocks. Reports on creating zeolites in the laboratory appeared as far back as the 1860s, but it was the work of Richard Barrer in the 1940s that kick-started the era of synthetic zeolites.

In 1948, Barrer reported the preparation of a zeolite with no natural counterpart and of a synthetic analogue of the zeolite mordenite. In both cases, X-ray powder diffraction provided the key characterization data. Later, following fundamental work by Robert Milton and Donald Breck, the Union Carbide Corporation commercialized synthetic zeolites. The materials were at first used to dry refrigerant and natural gas, but subsequently found widespread use as hydrocarbon cracking catalysts and as ion exchangers in detergents.

Zeolites are entirely inorganic materials, and despite their industrial significance, their chemistry and composition affords only limited control over the final product. To obtain a greater degree of flexibility, chemists have turned to the use of both organic and inorganic components in the preparation of porous crystals. In particular, since the 1990s, there has been an explosion of research interest in crystals known as metal–organic frameworks (MOFs). These materials form ordered networks by connecting metal units through organic linkers; by adjusting these two building blocks, the size and chemical environment of the crystal pores can, in principle, be tailored for a given application.

A number of MOFs were reported throughout the early 1990s and the term ‘metal–organic framework’ itself was introduced by Omar Yaghi’s group in 1995. It was, however, in 1999 that two key papers appeared. In the February, Ian Williams and colleagues reported a MOF known as HKUST-1, a structure made from copper-based clusters and benzene tricarboxylate linkers; in November, Yaghi and colleagues reported MOF-5, a structure made from zinc-based clusters and benzene dicarboxylate linkers. Notably, these robust materials were found to



The unit cell of MOF-5 forms a cavity represented here by a yellow sphere.

have high surface areas and pore volumes, and, in the case of MOF-5, the values were considerably higher than most zeolites.

Today, tens of thousands of different MOF structures have been synthesized, which have a range of intriguing properties. For example, the porous structure and chemical diversity of MOFs make them attractive for catalysis, an application first explored by Makoto Fujita and colleagues in 1994. Alternatively, MOFs are of potential use in drug delivery, can be used to store hydrogen, and can reversibly adsorb carbon dioxide.

Despite the flurry of research activity and range of potential applications, MOFs are yet to have a commercial impact, and concerns regarding their cost and stability remain. But given their versatility and potential to be built by design, it seems likely that MOFs will, at some point, follow zeolites into the world of practical applications.

Owain Vaughan, Senior Editor, Nature Nanotechnology

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