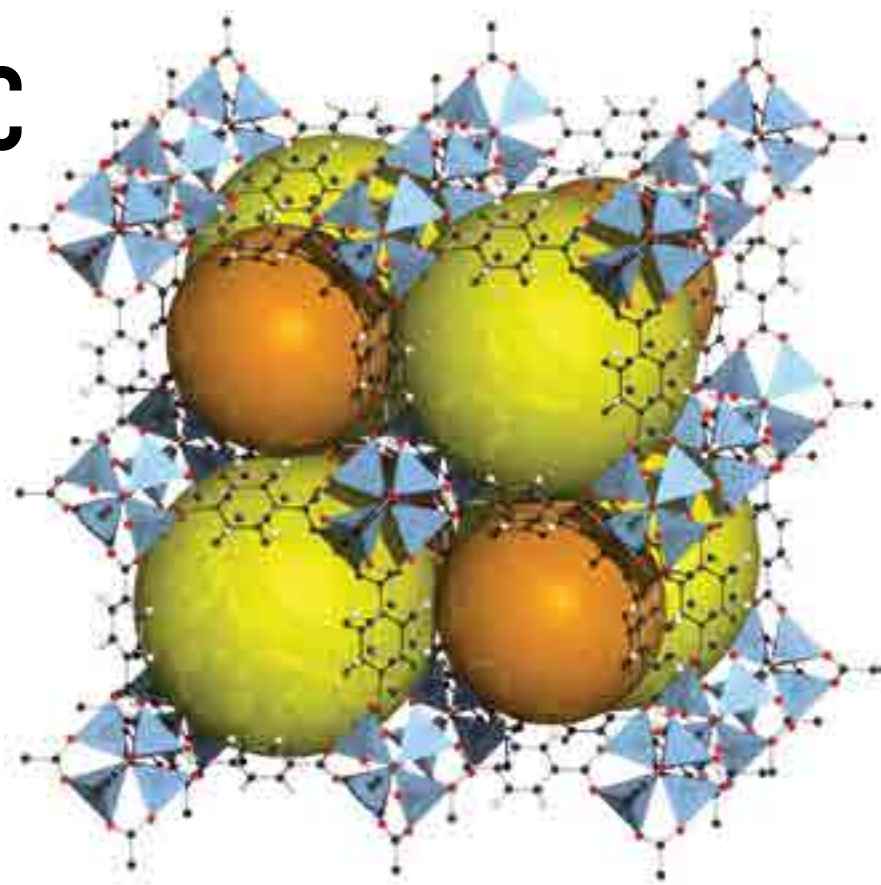


METAL-ORGANIC FRAMEWORKS: THE NEW ALL-ROUNDERS IN CHEMISTRY RESEARCH

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Metal-Organic Frameworks (MOFs) are a newly developed class of materials that allow us to store vast amounts of gases at low pressures in small volumes. Why do these materials matter? How do we use them? This article explores advances in our understanding of MOFs.

In April 2017, collaborators from the University of California, Berkeley and the Massachusetts Institute of Technology (MIT) reported the successful design of the prototype of a device that used sunlight to harvest moisture from the air¹. Listed as one of the year's top ten emerging technologies by the World Economic Forum², this prototype is just one of many applications of a new class of designer crystals (materials with pre-determined structures and properties) called metal-organic frameworks (MOFs).

What are MOFs?

The International Union of Pure and Applied Chemistry (IUPAC) defines Metal-Organic Frameworks (MOFs) as 'coordination networks with organic ligands containing potential voids'³. Simply put, MOFs are a class of crystalline compounds with exceptionally large pores that can bind molecules or ions of different shapes and sizes. First predicted by the chemists Bernard Hoskins and Richard Robson in 1990^{4,5}, the term 'metal-organic framework' was coined in 1995 by Omar Yaghi, a Jordanian-American chemist

working at the University of Michigan, USA. In 1999, two groups headed by Ian Williams and Omar Yaghi, working independent of each other, reported the synthesis of the first MOFs – called HKUST-1 and MOF-5 respectively^{4,6}.

To make a MOF, you need a metal salt and an organic compound (ligand) capable of forming multiple covalent bonds with the metal ion. The relative arrangement of the ligand and metal ion can generate structures that are porous and highly crystalline. For example, MOF-5 is synthesized (refer Fig. 1) by combining zinc nitrate (metal salt) with 1, 4-benzenedicarboxylic acid

Box 1. Adsorption: refers to the capacity of external or internal surfaces of solids to attract and bind ions or molecules of gases, liquids or dissolved solids they are in contact with. Solids with this capacity are called adsorbents, and the gases or solutions they bind are called adsorbates. When a gas or fluid is adsorbed, it does not permeate the solid (as it would if it were absorbed) – it accumulates as a film on the surface of the solid.

(terephthalic acid). As long as a linker can form multiple coordinate bonds, a MOF can be made using it. Thousands of new MOFs have been synthesised in this way in the last decade. The most famous among them are HKUST-1, a copper MOF developed by Hong Kong University of Science and Technology; UiO-66, a zirconium based MOF from University of Oslo, Norway; MIL-101, a chromium MOF reported by Institute Lavoisier, France; and the zinc-based MOFs ZIF-8 and MOF-74 developed by Omar Yaghi⁷. Unlike the water-sensitive MOF-5, most modern MOFs remain quite stable on exposure to air, water and many common solvents. However, they can be destroyed by exposure to acids or bases (with some exceptions), and at temperatures high enough to burn their organic ligands to CO₂ and water.

Applications of MOF's

(a) Gas Sorption

MOFs are known for their high capacity to trap gases. Gas molecules are held together by weak intermolecular forces. Consequently, packing large amounts of gas into small volumes is possible only under conditions of high pressure – an energy-intensive requirement. Using MOFs allows us to bypass this requirement – like activated charcoal, MOFs bind gas molecules through adsorption (refer Box 1). Unlike activated charcoal, MOFs offer variety – a wide range of them can be synthesised using different elements and methods.

A MOF's ability to trap gases stems from its high surface area, ranging from 2500-5000 m²/g of mass. Some MOFs, such as NU-109E, have surface areas as high as 7000 m²/g. To give an analogy, a gram of NU-109E would have the size of a sugar crystal but an internal surface area equal to that of 27 tennis courts⁸! Since every bit of its internal surface area can adsorb gas molecules, MOFs can be used to pack large amounts of gas into a small volume. Each MOF can be reused multiple times, with slight heating or application of a vacuum to remove (desorb) trapped gases.

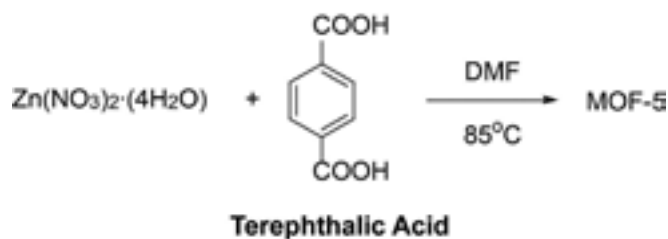


Fig. 1a. How to make MOF-5.
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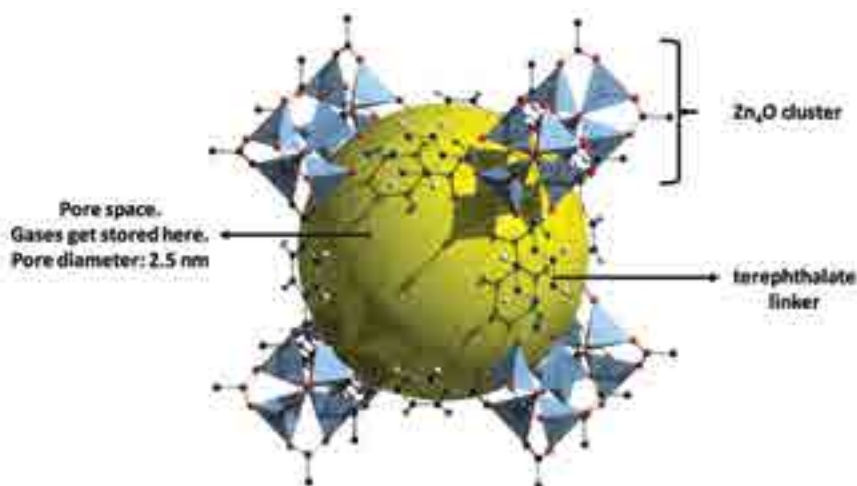


Fig. 1b. The structure of MOF-5. Notice that all the zinc atoms (represented by blue tetrahedra) are attached to a central oxygen atom (in red) to form a Zn₄O cluster, derived from zinc nitrate. The Zn atoms are also attached to oxygen atoms in terephthalic acid. Each molecule of terephthalic acid links a couple of Zn₄O clusters, forming a pore (represented by the yellow sphere) where gases are trapped.

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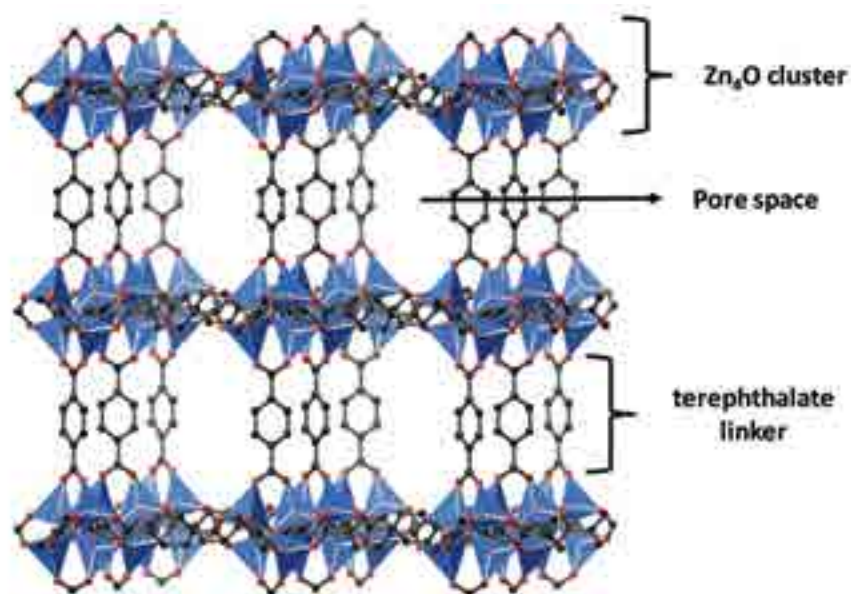


Fig. 1c. The extended crystal structure of MOF-5.
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Box 2. Catalysis: refers to the process of accelerating a chemical reaction using a catalyst. It is of two broad kinds, called homogenous and heterogeneous catalysis. In homogenous catalysis, the reactants and the catalyst are dissolved in the same solvent. Thus, once the reaction is complete, additional chemicals and energy need to be invested in separating the catalyst from the reaction mixture. Since heterogeneous catalysis uses insoluble, high surface area materials to catalyse reactions, the catalyst is separated from the reaction mixture by simple filtration. Consequently, most industries prefer using heterogeneous catalysts for chemical synthesis. Examples include the use of vanadium pentoxide with platinum (for sulfuric acid production) or finely powdered iron (in Haber's process for ammonia production).

The ability of MOFs to adsorb gases has found many interesting applications. One example of this comes from the automobile industry. The German chemical company BASF (Badische Anilin und Soda Fabrik) has developed MOF-containing cylinders to store CNG (Compressed Natural Gas) in vehicles like the truck model Ford F-550⁹. Since MOFs increase the amount of CNG stored to twice or thrice that of a conventional cylinder, they reduce the frequency at which the cylinder needs to be refilled. While this is seen as a significant advantage, MOF-containing vehicles are yet to be made available on

sale. The sudden drop in international crude oil prices in 2014 has made CNG much cheaper and reduced the economic incentive to commercialise such vehicles¹⁰. In another example, companies such as NuMat Technologies have developed MOF-containing cylinders (called ION-X7) to store toxic gases such as arsine (AsH₃), phosphine (PH₃) or boron trifluoride (BF₃). While these gases have important applications in the semiconductor industry, they are highly toxic and can cause severe damage when inhaled. MOF-containing cylinders can store these gases at sub-atmospheric (below atmospheric)

pressures. Given that gases flow from areas of high pressure to lower pressure, this decreases the chances of their leakage, even from improperly sealed cylinders¹⁰.

(b) Catalysis

Gas sorption is not the only feature typical of MOFs – their high surface areas make them ideal for catalysis (refer Box 2) of chemical reactions.

MOF-based catalysis can involve one of three strategies. In the first strategy, metal nanoparticles are adsorbed onto the pores of MOFs. Reactants diffusing into the MOF pore interact with the adsorbed nanoparticles achieving catalysis (refer Fig. 2a). This is used for the hydrogenation of alkenes and the synthesis of epoxides, hydrogen

Box 3. Aldol reaction: involves the combination of two carbonyl compounds (compounds containing a carbon-oxygen double bond) to form a product called an aldol.

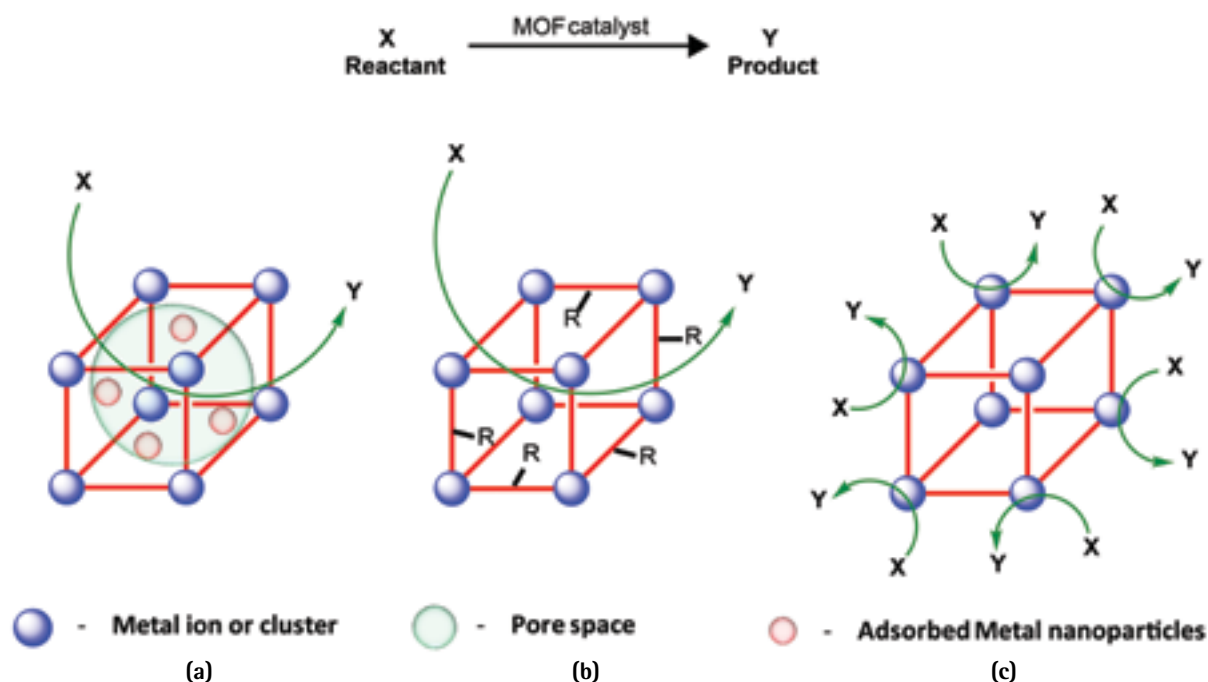


Fig. 2. Strategies for achieving MOF-based catalysis. X and Y represent reactant and product respectively. MOFs are represented as cubes. Organic linkers are represented by red lines which form the sides of the cube, and the blue spheres are the metal ions or clusters. (a) Using the MOF pore space as a catalyst support for metal nanoparticles. (b) Functionalising the organic linkers with catalytic groups (represented by R). (c) Using the metal ion or cluster for catalysis.

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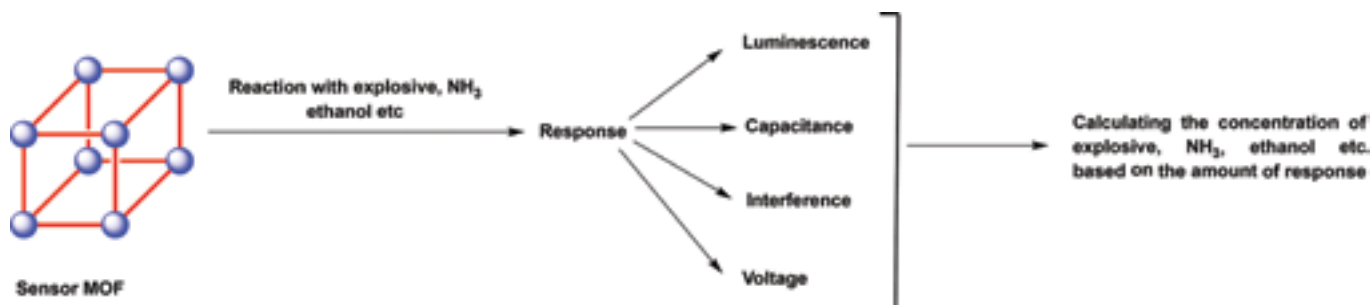


Fig. 3. A general scheme for using a MOF as a chemical sensor.

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Box 4. Michael addition: occurs when a C-C unsaturated carbonyl compound reacts with a nucleophile (a compound that can donate a pair of electrons). The C-C unsaturation should occur between the carbon atoms next to the carbonyl carbon.

peroxide and methanol (refer Fig. 2b). In another strategy, functional groups with catalytic activity (such as guanidine, phenylalanine, proline, imidazole etc.) are linked to the organic ligands of MOFs. Such MOFs can be used to catalyse some fundamental organic transformations such as Aldol reactions (refer Box 3), Michael additions (refer Box 4) etc. In a third strategy, catalysis occurs at the metal clusters of the MOFs (refer Fig. 2c). For example, titanium-based MOFs have been used to catalyse the famous Zeigler-Natta reaction (polymerisation of ethylene to polyethylene). MOFs containing metal clusters of noble metals (such as rhodium, platinum, ruthenium or palladium) have proven to be effective catalysts for hydrogenation reactions. Ongoing research is aimed at making more efficient and more stable MOFs, capable of catalysing more than one kind of reaction¹¹.

(c) Luminescence

MOFs can be made luminescent (refer Box 5) if luminescent materials like lanthanide elements (e.g. europium, dysprosium etc.) or organic compounds (e.g. porphyrins, dyes) are used to make them^{12,13}. MOFs offer the advantage of

Box 5. Luminescence: is the emission of light by a substance when any form of energy (other than heat) is applied to it. This energy can be in the form of incident photons (photoluminescence), mechanical forces (mechanoluminescence), electricity (electroluminescence), or sound (sonoluminescence). A luminescent substance absorbs this energy and emits light of lower energy. Examples of such substances include glow sticks, 'glow in the dark' watch dials, road signs etc.

being able to achieve luminescence in any desired colour. For example, the ability of MOFs to generate pure white light has important applications in the lighting industry¹⁴.

(d) Chemical Sensors

The most common class of MOF sensors (refer Box 6) are based on their ability to produce measurable changes in luminescence. For example, MOFs with tetraphenylene linkers or lanthanides have been used to sense explosives and heavy metal ions. A change in luminescence is caused by the formation of hydrogen bonds between the nitro (NO_2) groups in explosives and linkers in MOFs. Another class of MOF sensors are based on their ability to cause changes in capacitance. Some of these, for example, have been reported to sense ammonia at concentrations as low as 25 ppb (parts per billion)¹⁵. A third class of MOF sensors are used to detect measurable changes in the interference

Box 6. Chemical sensors: are molecules which react with other molecules to produce a measurable change in voltage, capacitance, luminescence or other physical attributes. They find applications in a variety of devices including glucose meters (for measuring blood glucose levels) and breath-analysers (for measuring alcohol in breath).

of ethanol, propane, and water (refer Fig. 3)¹⁶.

Current research on using MOFs as chemical sensors is aimed at making simpler devices with higher specificity. Synthesizing MOFs which respond to only one specific analyte has proven to be particularly difficult and is an active area of research.

To conclude

The field of MOF chemistry has expanded considerably in the last two decades. Beginning from the first few MOFs to be synthesised in 1999, today structures of at least 6000 new MOFs are published every year. Research has helped refine their use in a range of applications – from gas sorption and catalysis, to luminescence and chemical sensors. It has also opened up new applications – from the use of MOFs for the heating and cooling of buildings and the production of anti-microbial coatings for healthcare products, to the capture of moisture from air and carbon dioxide from power

plant emissions¹⁰. These advancements have fuelled the synthesis of the next generation of porous materials – called COFs (Covalent Organic Frameworks¹⁷) and HUMs (Hybrid Ultramicroporous

Materials¹⁸). The biggest challenge that MOFs face today is their high production costs due to the special methods and skills required for the production of organic linkers. With the

first few MOF-based products hitting open markets in 2016¹⁰, there is hope that this may not remain a challenge for much longer.



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