



Scientific Background to the Nobel Prize in Chemistry 2025

METAL-ORGANIC FRAMEWORKS

The Nobel Committee for Chemistry

Metal–Organic Frameworks

The Royal Swedish Academy of Sciences has decided to award **Susumu Kitagawa**, **Richard Robson**, and **Omar M. Yaghi** the Nobel Prize in Chemistry 2025, for the development of metal–organic frameworks.

Introduction

Over the years, Chemists have developed many methods to control synthesis of structures in “zero” dimensions, *i.e.*, single and discrete compounds, where skilled experimentalists can construct almost any complex molecule imaginable. In contrast, the synthesis of extended structures in one, two, or three dimensions has proven very challenging, and their realisation has been more elusive. For compounds in one dimension (linear structures), many synthetic approaches have been developed, and we now have powerful methods for making certain long-chain structures, such as polymers, with good structural fidelity and control.

Up until the 1990s, the advancement was remarkably limited for the higher dimensions, which prompted Chemistry Laureate *Ronald Hoffmann* to state:¹ ‘But in two or three dimensions, it’s a synthetic wasteland.’ In this case, *Hoffmann* referred specifically to organic structures, but up to that point inorganic, crystalline structures had also been generally grown using a trial-and-error approach.

Not only were the synthetic procedures themselves challenging; so was the prediction of how the structures would look. In 1988, *John Maddox* commented that:² ‘One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition.’ Although the amount of information had grown substantially since crystallography techniques were introduced, it was difficult to actually foresee how specific building blocks would come together to form a periodic solid.

Even more unattainable was the ability to build materials that temporarily could hold smaller substances inside their inner scaffolding. Such materials were of interest, since they would be of use for a variety of applications that had already been demonstrated for other entities, such as zeolites. This would not only involve the establishment of a predictable three-dimensional network, but a structure that contained sizeable holes or cavities that could house the smaller compounds.

From a historical perspective, in this context, several intriguing structures and methods had been known for a long time. A classical structure is the well-known pigment “Prussian blue” or “Berlin

blue”, which was discovered in the 18th century,³ although its relatively complex structure was only deciphered much later.^{4,5} The pigment structure is built from repeated $-\text{Fe}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}-$ sequences, forming a three-dimensional cubic framework, shown in [Figure 1](#). The void space inside the material is typically filled with water molecules and cyanide ions. Thus, this indicated that it, in principle, would be possible to design and produce such cavity-forming structures, and to control the inclusion of smaller entities within them.

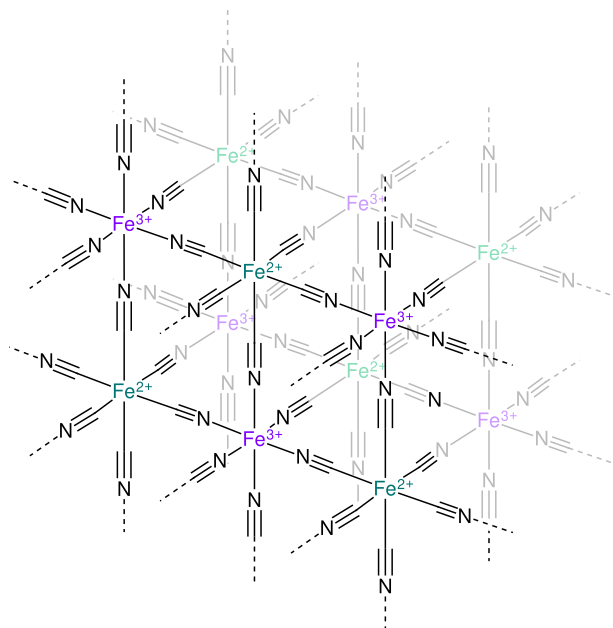


Figure 1: Structure of Prussian blue or Berlin blue.

A highly attractive pathway to two- or three-dimensional structures is to assemble them using metal coordination of organic ligands. Steps towards this end were taken by the end of the 19th century when *Alfred Werner*, who would be awarded a Nobel Prize in Chemistry for his work in 1913, laid the foundation for coordination chemistry ([Figure 2](#)).⁶ It then became clear that metal coordination to some extent could serve as a relatively predictable joinery method in structural design. Furthermore, while clathrates – a type of solid inclusion compounds – had been discovered in the early 19th century,^{7,8} *Werner's* work inspired the discovery of what would become known as Hofmann clathrates.⁹ *Karl A. Hofmann* thus showed that the diffusion of benzene into a solution of $\text{Ni}(\text{CN})_2$ and ammonia yielded a crystalline material, which was later shown to be composed of layered, extended 2D-networks of nickel–cyanide coordination entities, with benzene molecules between the layers.¹⁰

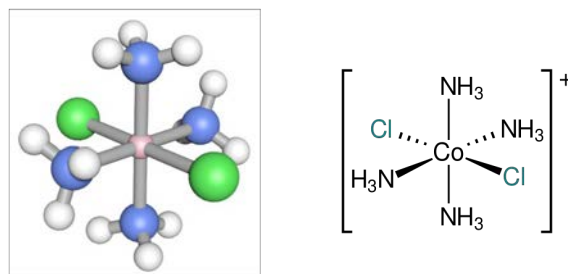


Figure 2: Structure of the *trans*-tetraamminedichlorocobalt(III) ion as established by *Alfred Werner*.

Initial Steps

In the 20th century, following breakthroughs in crystallography and other important structure determination methods, the field of structural chemistry witnessed substantial growth and many new structures were made and analysed. However, as seen by the quotes from Maddox and Hoffmann above, the steps from analysis to prediction and then to controlled synthesis were difficult to take. One of the scientists meeting this formidable challenge was **Richard Robson**. According to a personal statement,¹¹ **Robson** was intrigued by the idea of building extended structures with predictable topologies based on the assembly of selected and well-designed building blocks, a quest he embarked upon by the end of the 1980s. Based on prior knowledge, he reasoned that extended 3D diamondoid structures with sizeable cavities could possibly be accessible through the interactions between a tetranitrile compound with a tetrahedral geometry and a metal ion preferring tetrahedral coordination geometry under the conditions used. To test this, **Robson** chose the cuprous ion (Cu^{I}) as the metal centre and an organic nitrile as the coordinating ligand. This choice was made from a series of assumptions to maximise the probability of obtaining structured networks with less deviating interaction geometries. Cu^{I} was, in this case, assumed to adopt a tetrahedral coordination with nitriles, as, *e.g.*, shown for the tetrakis(acetonitrile) perchlorate complex.¹² Furthermore, to ensure a tetrahedral coordination, **Robson** used a relatively rigid tetranitrile (4',4'',4''',4''''-tetracyanotetraphenylmethane) as the ligand. In this context, other studies could show that $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ represents a diamondoid clathrate structure,¹³ and, with the objective to study cuprous ion dyeing of polyacrylonitrile polymers, that crystalline networks from dinitriles and Cu^{I} could indeed be obtained under certain conditions.¹⁴ The general expectations that **Robson**'s system would work well could be regarded as low, and the prediction was rather that it would more likely yield an amorphous, relatively heterogeneous structure or a highly interpenetrated, cavity-less structure.

However, the opposite turned out to be the case, and a crystalline, diamondoid, extended framework was formed much as predicted ([Figure 3](#)).¹⁵ The framework also contained relatively large

cavities, which were filled with randomly distributed and freely moving solvent molecules (nitrobenzene) and counterions (BF_4^-).

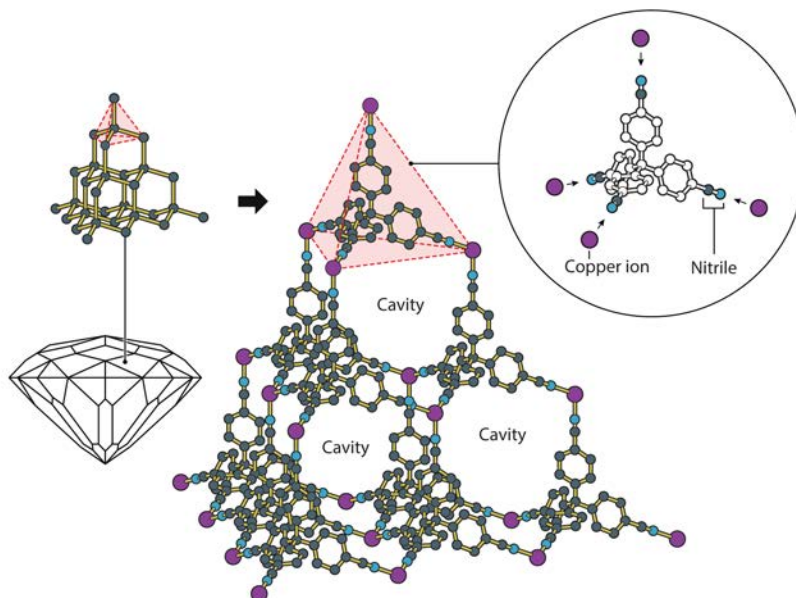


Figure 3: 3D diamondoid framework based on Cu^{I} and (4',4'',4''',4''''-tetracyanotetraphenylmethane)^{15,16}

This success led **Robson** to further predict, and to some extent demonstrate, several important features of these frameworks.¹⁶ He foresaw that diffusion of molecular or ionic species could take place throughout the structures, thereby leading to materials acting as molecular sieves or having ion-exchange properties; he suggested that post-modification of the resulting framework could be achievable; he reasoned that it would be possible to design and produce frameworks based on components that would persist vacuum-treatment and removal of inclusions, and that would have good physicochemical stability; and he opened up the possibility of integrating catalytic sites within the frameworks and the generation of efficient heterogeneous catalysts. To illustrate these features, he demonstrated the ion exchange properties of the diamondoid framework (exchange of BF_4^- for PF_6^-) without collapse of the structure.

These studies had explosive impact on the area of coordination networks and the subsequent development of MOFs, and **Robson's** group continued to use the principles to produce other frameworks. For example, structures with PtS and rutile topologies were produced.^{17–19}

Robson's work using coordination of organic ligands to metal ion centres represented a substantial development within the field of coordination networks or frameworks and porous structures.

As a consequence, the field witnessed high activity during the first half of the 1990s, and a multitude of structures were developed and characterised. For example, **Susumu Kitagawa** described an extended two-dimensional network, based on Cu^{I} coordinated with pyrazine and acetonitrile,²⁰ containing cavities that accommodated loosely bound acetone molecules, and **Omar M. Yaghi** demonstrated the use of 1,3,5-benzenetricarboxylate (BTC) together with $\text{Co}(\text{NO}_3)_2$ and pyridine to produce neutral 2D-frameworks with pyridine molecules acting as spacers and guests.²¹ The Co–BTC frameworks were thermally stable up to 350 °C, even after removal of included guest molecules, which could be selectively readsorbed.

Other examples of studies during this time include the formation of a two-dimensional network built from Cd^{II} and 4,4'-bipyridine, in the cavities of which catalytic cyanosilylation of aldehydes could be achieved,²² three-dimensional coordination networks resulting from cross-linking of square grids,²³ and coordination networks with predicted auxetic behaviour (materials that expand in the transverse direction when stretched and contract when compressed).²⁴

However, while the term 'coordination polymer' had been in use since 1916,²⁵ no established definition of this field existed at the time. Therefore, different terminology was being used to describe similar structures while the area matured. For example, 'infinite polymeric frameworks', 'coordination networks', or 'network structures' were used in addition to coordination polymer. The wildly popular term 'metal–organic framework' and its abbreviation 'MOF' appeared in the second half of the 1990s,^{21,26} while the alternative phrase 'porous coordination polymer' ('PCP') was introduced in the early 2000s.²⁷ For clarity, the currently recommended terminology from IUPAC distinguishes the following structures:²⁸ a coordination polymer is 'A coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.'; a coordination network is 'A coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions.'; and a metal–organic framework is 'A metal–organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids.' Within this classification system, MOFs constitute a subset of coordination networks, which in turn constitute a subset of the overall group of coordination polymers.

Gas Adsorption

One of the most important applications of porous materials takes advantage of their ability to act as sorbents and reservoirs of small guest molecules, such as gases. Porous materials, such as zeolites and activated carbon, have thus found extensive large-scale industrial use in, *e.g.*, in natural gas processing and gas purification. In the case of coordination polymer frameworks, gas adsorption was also soon demonstrated. To avoid undesired disruption of the frameworks upon adsorption/desorption, as well as non-optimal encumbrance of the cavities in the materials, neutral

frameworks devoid of loose anionic counterions were sought after. One option to achieve this is to directly use anionic organic ligands, such as carboxylic acids,^{21,29,30} or to use the counterions themselves as metal coordination ligands.³¹ An important contribution in this context was made by **Kitagawa** and coworkers, who in 1997 demonstrated adsorption of small gases (CH_4 , N_2 , O_2) at room temperature in a “tongue-and-groove” framework based on Co^{II} , 4,4'-bipyridine, and nitrate (**Figure 4**).³¹ The framework displayed a geometry where protruding ridges (tongues) fit into adjacent grooves within the material. The cavities of the structure were initially filled with water, but the framework could be shown to adsorb and release the gas substances in the dry state. In a later study,³² it was further revealed that the framework showed type-I adsorption isotherms (reversible adsorption isotherm concave to the p/p° axis and approaching a limiting value as $p/p^\circ \rightarrow 1$).³³ for N_2 and CO_2 under low-temperature conditions.

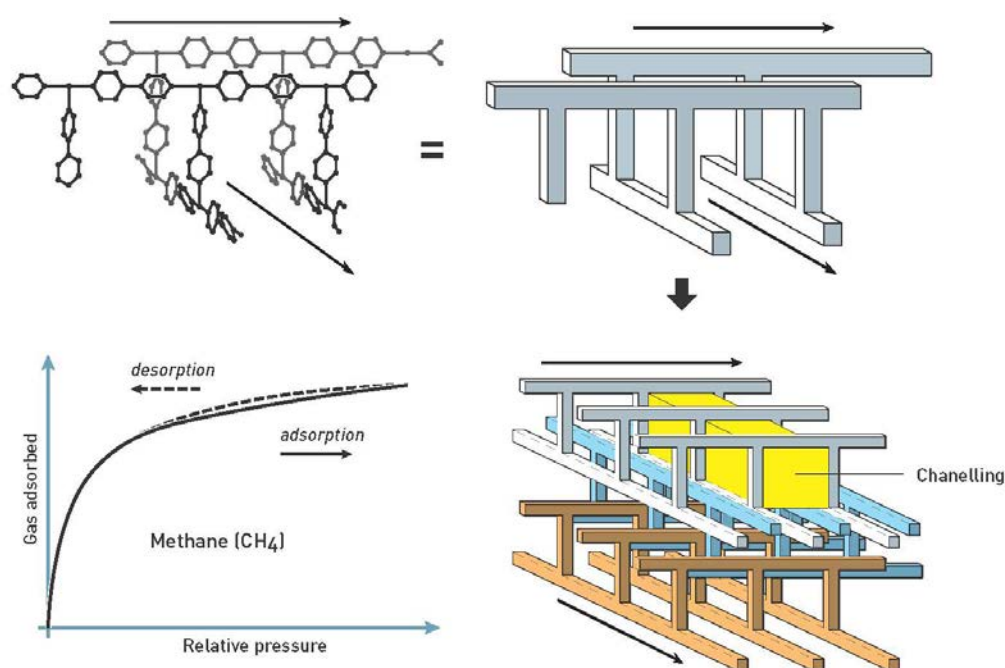


Figure 4: “Tongue-and-groove” framework based on Co^{II} , 4,4'-bipyridine, and nitrate; and adsorption isotherms for CH_4 at ambient temperature.³¹

This Co^{II} framework indicated that the metal–organic frameworks displayed the desired gas-adsorption properties, but was also found to possess other intriguing features. Later studies on this and related frameworks,^{32,34,35} would thus show that these tongue-and-groove structures are locally flexible porous frameworks.

Another important property of such materials is their porosity. In 1998, using porosimetry analyses at low temperatures, **Yaghi** and coworkers showed that a framework based on Zn^{II} and 1,4-benzenedicarboxylate (BDC) ($\text{Zn}(\text{BDC})\cdot(\text{DMF})(\text{H}_2\text{O})$) displayed type-I isotherms for N_2 and CO_2 , indicative of permanent microporosity.³⁰ The specific surface areas and the pore volumes in these cases were measured to approximately $300 \text{ m}^2/\text{g}$ (Langmuir adsorption model) and $0.1 \text{ cm}^3/\text{g}$ for N_2 or CO_2 .

Building on the positive results with the $\text{Zn}(\text{BDC})$ framework, and inspired by metal carboxylate cluster chemistry,³⁶ **Yaghi** and coworkers then went on to produce the iconic structure that essentially became a paragon and showcase of the entire field.²⁶ In 1999, by choosing conditions that led to the formation of Zn_4O -carboxylate clusters as secondary building units (SBUs),³⁷ a highly stable framework - denoted MOF-5 - could thus be obtained ([Figure 5](#)).

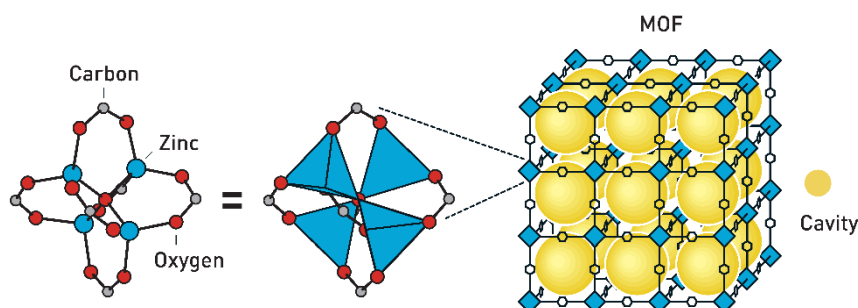


Figure 5: The iconic framework MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$), indicating the secondary building unit (left) and the large cavities (yellow, right).²⁶

The MOF-5 structure showed permanent porosity, with the crystal structure intact upon evacuation of guest molecules, and high thermal stability. A Langmuir surface area of $2900 \text{ m}^2/\text{g}$ could also be estimated (using N_2), and an associated pore volume of approximately $0.6 \text{ cm}^3/\text{mL}$. For comparison, zeolites have typical surface areas of several hundred square meters per gram, while activated carbon materials can reach higher values. These values demonstrated that the frameworks had properties similar to commonly used, commercial sorbents, which also resulted in increased interest from industry.

Another notable contribution in this context is the highly stable 3D-framework HKUST-1 ($[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$),³⁸ based on Cu^{II} -carboxylic acid paddlewheels³⁹ as secondary building units. The framework was shown to be stable up to 240°C and to possess channels with a pore size of 1 nm . Porosimetry studies (using N_2) revealed that the material had a surface area of approximately $690 \text{ m}^2/\text{g}$ (Brunauer-Emmett-Teller (BET) adsorption model) or $920 \text{ m}^2/\text{g}$ (Langmuir model) with a pore volume of circa $0.3 \text{ cm}^3/\text{g}$.

Concepts

An intriguing aspect of these materials is their potential flexibility and structural dynamics. Following the gas adsorption studies, **Kitagawa** predicted in 1998 that this would lead to fundamentally new properties of the frameworks, also representing a new paradigm of solid state chemistry (**Figure 6**).⁴⁰ He thus introduced the notion of three “generations” of frameworks, where the first generation represents porous structures that are unstable upon removal of the inclusions; the second generation includes stable frameworks capable of reversibly releasing and readsorbing guest species while maintaining their phase and morphology; and the third generation encompasses dynamic frameworks that can change their morphology in response to external stimuli (pressure, temperature, light, etc.). **Kitagawa** later on expanded on this classification with the introduction of the term ‘soft porous crystals’ for the third generation frameworks.⁴¹ Several structures were soon demonstrated to have third-generation properties.^{42–46} Furthermore, the Co^{II} tongue-and-groove structure used to demonstrate gas adsorption,³¹ was later found to also belong to this class of frameworks.³²

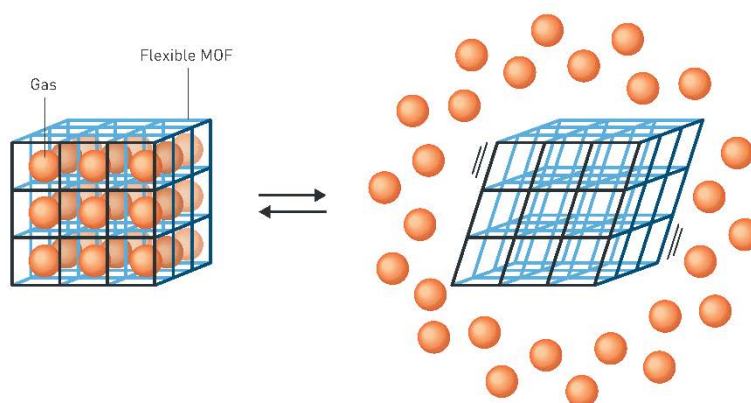


Figure 6: Flexible, third generation framework, subjective to structural change upon addition/removal of guests or exposure to stimuli.

To further conceptualise the design and construction process of the frameworks, **Yaghi** endeavoured to introduce a more distinct terminology in the field. After having started using the phrase ‘metal–organic framework’,²¹ later abbreviated ‘MOF’,²⁶ he and his coworkers thus initially adopted ‘modular chemistry’⁴⁷ for the construction process,^{48,49} and emphasised, together with others, the use of the term ‘secondary building unit’ (SBU) as utilised in the zeolite field. Shortly after, in 2002–2003, **Yaghi** and coworkers introduced the new term ‘reticular synthesis’ (or ‘reticular chemistry’), which was described as ‘...the process of assembling judiciously designed rigid

molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding.^{50,51} This conceptual description of the process was deemed more precise than, *e.g.*, the broader ‘crystal engineering’.

As described and recognised in particular by *Alexander F. Wells*,⁵² the topologies of periodic structures can be considered as nets with vertices (nodes), corresponding to atoms, and edges (links) representing bonds. To build on this, **Yaghi** and coworkers expanded on the concept of reticular chemistry with ‘isorecticular’ to describe structure families with the same underlying net and topology (**Figure 7**).⁵⁰ Thus, by using the same SBU but varying the organic linker unit, series of frameworks with the same net structure could be devised, where the cavity sizes and linker functionalities could be tailored.

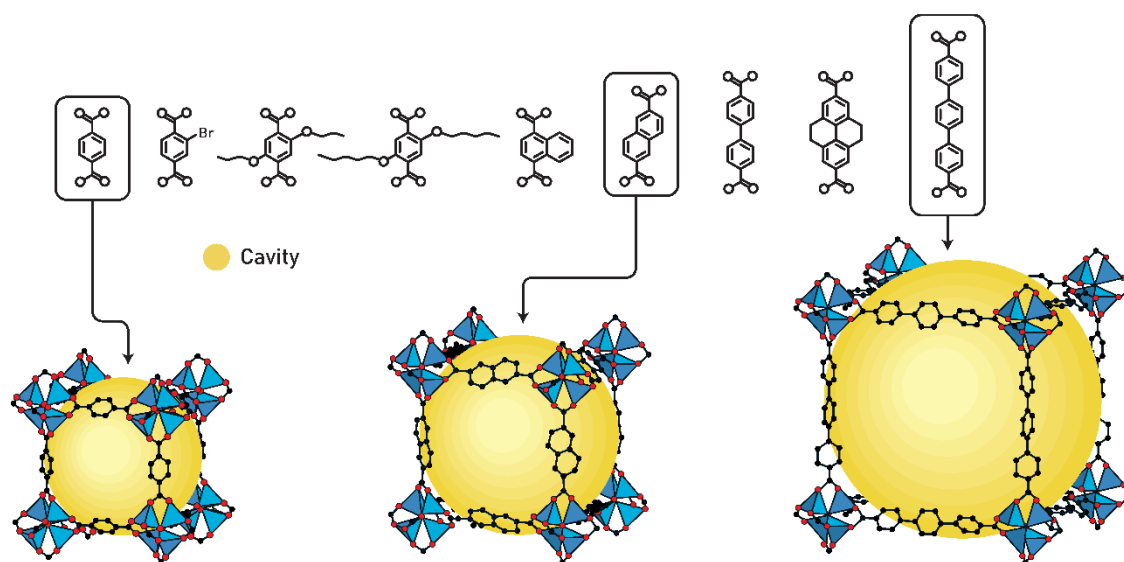


Figure 7: Isorecticular frameworks with the same **pcu** topology/net and the same SBU, but with different linkers and cavity volumes.⁵⁰

Expansion

Following this development, the field grew rapidly and many new framework structures and applications were reported (see examples in **Figure 8**). The very intriguing results on gas adsorption spurred especially high interest, both in academia and industry, and new structures were developed and evaluated for this purpose. For example, methane adsorption was further targeted,^{50,53} with the aluminium framework Al-soc-MOF-1 reaching very high capacities that surpassed the strict criteria set by the US Department of Energy.⁵⁴ The MOF-5 framework, and the

isorecticular IRMOF-6 and IRMOF-8 structures, showed potential for H₂ adsorption at low temperature,⁵⁵ where further development demonstrated related framework MOF-177 as possessing high capacity for hydrogen even at ambient temperature and moderate pressures.^{56,57} For carbon dioxide, MOF-177 again proved to have high potential,⁵⁸ and later related frameworks MOF-200 and MOF-210 showed a CO₂ uptake of 2400 mg/g.⁵⁹ More recently, the stable CALF-20 framework was shown to have high and selective capacity for CO₂,⁶⁰ which prompted its application for carbon capture on an industrial scale.⁶¹

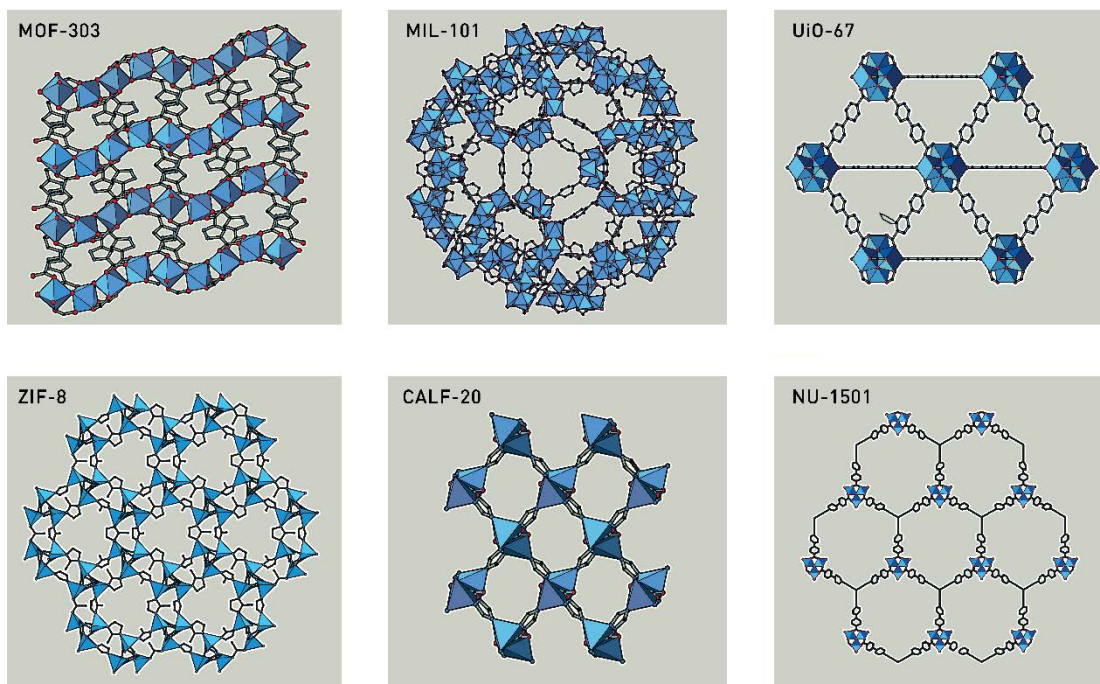


Figure 8: Examples of framework structures: MOF-303 has been applied in water adsorption from low-humidity air;⁶² MIL-101 has large cavities and has been used in catalysis and in storage of H₂ and CO₂;^{63–65} UiO-67 has been used to absorb PFAS from water;^{66,67} ZIF-8 has been evaluated for mining rare-earth metals from wastewater;^{68–70} CALF-20 can capture CO₂;⁶⁰ NU-1501 has been developed to store H₂.⁷¹

Given that gas adsorption is dependent on the porosity characteristic of the materials, intense efforts were also made to develop frameworks with high surface areas and pore sizes. For example, the MOF-177 framework displayed a Langmuir surface area of 4500 m²/g,⁷² while framework MOF-210 showed values of >10,000 m²/g (Langmuir) or 6240 m²/g (BET).⁵⁹ A similar high BET surface area (6143 m²/g) was recorded for framework NU-100,⁷³ which also showed high storage capacities for hydrogen (164 mg/g) and carbon dioxide (2315 mg/g), and related framework NU-110 with a longer linker showed an even higher value (7140 m²/g, BET).⁷⁴ Very high surface areas

were also recorded for framework DUT-60, which showed a BET surface area of 7839 m²/g; with an accessible pore volume of 5.0 cm³/g.⁷⁵

For the pore sizes, mesoporous frameworks with pore sizes of 2.8 nm were reported for framework IRMOF-16,⁵⁰ and very large pores (apertures of up to 9.8 nm) were reported for the framework IRMOF-74-XI, having the same topology as MOF-74, but being based on very long linker units.⁷⁶ The pores of related members in this family were large enough to accommodate proteins, such as myoglobin or green-fluorescent protein (GFP).

Many other notable developments were also made that advanced the field. A few examples include: framework thin films on surfaces,⁷⁷ surface-modified frameworks,⁷⁸ hybridised frameworks (MOF-on-MOF/PCP-on-PCP) and core-shell structures,⁷⁹ coordination modulation to control the framework extension,⁸⁰ structures with glass-forming characteristics,^{81–83} polymerisation within the frameworks,⁸⁴ frameworks involving mechanically-interlocked molecules,^{85–87} and frameworks displaying proton conductivity.⁸⁸

Applications

The many desirable properties of the frameworks have led to a large variety of applications. In addition to gas storage, as mentioned above, application areas include: analytical chemistry and (bio)sensors, batteries and fuel cell technology, separation science, synthesis and catalysis, harvesting of water from dry (low humidity) air, water purification and environmental remediation, capture/destruction of harmful agents, energy conversion and storage, hydrogen generation, food safety, drug delivery and diagnostics/therapy, etc. Industry has played a continuous and active role in both the discovery of these frameworks and the expansion of their applications. Participation has not been limited to established corporations; many new companies have also emerged, specifically focused on their discovery and commercialisation across all these fields. These endeavours have also shown that framework materials can be produced that display high chemical and thermal stability, and that the production can be cost effective and scalable. The materials also have the added advantage of being recyclable.

Summary and Outlook

To conclude, the field of metal–organic frameworks has expanded rapidly over the past decades. Although scattered examples of related structures have long been known, the ability to predictably design and synthesise such entities was essentially absent until the end of the 20th century. This expansion was to a large extent due to seminal work by **Susumu Kitagawa**, **Richard Robson**, and **Omar M. Yaghi**, who made a range of important contributions that promoted this development. These contributions not only include a multitude of impressive examples of different structures and applications, but also a framework of concepts that has furthered the establishment of

the entire area. Not only has this development led a deepened understanding of predictive synthesis of periodic, extended structures, but it has fundamentally revised our perception of the solid state.

These frameworks hold many attractive properties, and their high surface area, tuneable pore sizes, and versatile chemical functionality make them highly attractive for a wide variety of applications. Continuous advancements have improved their stability, scalability, and cost-effectiveness, leading to their utility in industrial-scale processes. Furthermore, the integration of MOFs with other materials to form composite structures is opening new avenues for enhanced performance in existing applications and the development of novel technologies. The continued exploration of MOFs is expected to yield more significant breakthroughs, positioning them as a cornerstone in the development of advanced materials.

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