Omar Yaghi's Accomplishments

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Historical Perspective

The design and synthesis of zero-dimensional (organic molecules and metal complexes) and one-dimensional (organic polymers) thrived in the twentieth century and achieved an impressive level of sophistication and precision. The ability to build complex organic molecules and to design organic ligands suitable for coordination to metal ions greatly contributed to this advance and gave rise to the now established fields of organic and inorganic chemistry. In contrast, the use of these chemistries to build infinite two- and three-dimensional extended structures remained undeveloped because of the crystallization challenge. Namely, linking building units (organic or inorganic) together by strong bonds (> ~100 kJ/mol) led to amorphous products, thus precluding their characterization on the molecular level. Consequently, the objective of building up structures from organic molecules and metal complexes into extended structures remained a dream for much of the twentieth century.

Supramolecular chemistry provided means for linking molecular building blocks by weak intermolecular forces (e.g., hydrogen bonding). However, the need for building robust extended structures by linking molecules and metal complexes together with strong bonds remained a formidable challenge. The quest for the synthesis of such robust structures was motivated by their potential to solve problems in clean air, energy, and water, where their repeated use for long periods of time would be required. Additionally, the strong bonds linking well-defined organic molecules and inorganic complexes meant that extended structures could be designed with precision and that they could be post-synthetically modified without destruction of the underlying structural arrangement. Indeed, the successful crystallization of these robust structures promised the synthesis of solid-state materials by design with tremendous impact on societal applications.

Coordination Networks

Extended structures based on metal-organic constituents have been known since the late 1950s; they were referred to as coordination networks (or coordination polymers), in which metal ion nodes are linked by nitrile- or pyridyl-type bridging molecules. The first crystal structure of a coordination network was reported in 1959 (SAITO, Y., et al. *Bull. Chem. Soc. Jpn.*, 1959, 32, 1221-1226) for $Cu(-NCCH_2CH_2CH_2CH_2CN-)_2{\bullet}NO_3$, where Cu(I) nodes are linked by the dinitrile organic bridges to make a 3D extended structure. The nitrate ions fill the pores and serve to balance the charge on the overall structure. The synthesis of such networks based on other transition metal ions and nitrile- as well as pyridyl-type linkers have continued to appear in the literature since that original report. During this period metal-cyanide compounds, known since the nineteenth century, such as Hofmann clathrates (2D) and Prussian blues (3D), reemerged and were studied. In 1965, E. A. Tomic published a report titled “Thermal Stability of Coordination Polymers” where he synthesized and characterized many coordination polymers constructed with different ligands and various metal ions (TOMIC, E.A., *J. Appl. Polym. Sci.* 1965, 9, 3745-3752). However, coordination networks were interesting because of the prospect of using various metal ions at the nodes and chemically modifying the organic linkers to make extended structures by design.

Indeed, A. F. Wells had articulated and popularized the concept of «nodes» and «linkers» to classify and understand the topology of extended structures. He described the original Cu(-$NCCH_2CH_2CH_2CH_2CN$-$)_2$ coordination network along with other such compounds in this context as based on the diamond topology (WELLS, A.F., *Structural Inorganic Chemistry*, 1st–5th Ed., 1945-1984). Reports on the synthesis of such coordination networks continued with numerous examples that used the same synthesis reported in 1959 and Wells's concepts. For example, in 1986 and 1989, two reports (WERNER, H.-P. et al. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 740-741, and ROBSON, R. et al., *J. Am. Chem. Soc.,* 1989, 111, 5962-5964) showed how other coordination networks based on the diamond topology can be made using other nitrile-based organic linkers. By the 1990s, hundreds of crystal structures of such coordination networks (based on nitrile- and pyridyl-type organic linkers) were reported. Since their crystal structures showed openness, the questions from many outside the field (e.g., zeolite scientists) focused on the possible porosity of such coordination networks. Will these compounds have the architectural robustness to sustain permanent porosity?

In 1997, high-pressure room temperature gas uptake measurements were performed on a metal-bipyridyl coordination network (KITAGAWA, S. et al. *Angew. Chem., Int. Ed. Engl.* 1997, 36, 1725-1727). While this study demonstrated that gas can be forced into a coordination network, such measurements did not prove permanent porosity since gases under high pressure will permeate through porous and nonporous materials alike. The IUPAC standard for proving permanent porosity requires measurement of a nitrogen adsorption isotherm at low pressure and low temperature (77K) to reveal the true molecular-based porosity properties of a material as discussed below.

Design and Synthesis of the First Metal-Organic Frameworks

In the early 1990s, Omar Yaghi proposed using molecular building blocks linked by strong bonds to create crystalline materials. At the time, the scientific community deemed this concept chemically impossible because strong bonding between such molecular building blocks always resulted in ill-defined, amorphous solids. This state of affairs and the prevailing view of the chemistry community changed in 1995 when the successful crystallization of structures composed of metal ions and carboxylate organic linkers appeared for the first time (YAGHI, O., et al. *Nature*, 1995, 378, 703-706). Unlike the neutral organic linkers used to build the coordination networks, the negatively charged 1,3,5-benzene-tricarboxylate linker used in this report provided for much stronger bonding to the metal. This was a major departure from coordination networks, and it was the carboxylate linkers and their strong bonding and chelating ability to metal ions that represented the key advance leading to what we now know as metal-organic frameworks (MOFs). This term was introduced by Yaghi in that same paper and meant to be a descriptive term for extended frameworks containing metal ions and organic linkers. In 1998, he used another carboxylate linker to make a crystalline Cu(1,4-benzene-dicarboxylate)•DMF, whose structure has at its nodes di-zinc units linked by 1,4-benzene-dicraboxylate to give a porous framework with DMF filling the pores (*J. Am. Chem. Soc.*, 1998, 120, 8571-8672).

Using this MOF compound, he measured the gas adsorption isotherm at low pressure, low temperature on the evacuated structure and proved its permanent porosity. This was the first gas adsorption isotherm reported for a metal-organic structure. Performing the gas adsorption measurements at low pressure and low temperature was critically important for several reasons. The shape of the gas adsorption isotherm unveils the porosity properties of the framework. These include the framework's overall architectural stability, pore rigidity, possible pore collapse, pore flexibility, and indeed pore size. Importantly, these measurements are critical to obtaining the pore volume and surface area of the material, noting that all this porosity data and important pore characteristics are unobtainable from high pressure, room temperature gas uptake measurements.

Discovery of Highly Porous Metal-Organic Frameworks

The challenge to making highly porous frameworks capable of permanent porosity is the creation of very open structures, which can withstand extremely strong capillary forces upon evacuation of their pores. In 1999, the synthesis, X-ray single crystal structure, and low-pressure, low-temperature gas adsorption isotherms of the first highly porous MOF, $Zn_4O(1,4\text{-benzene-dicarboxylate})_3 \bullet x\text{DMF}$, termed MOF-5, was reported by Yaghi (*Nature*, 1999, 402, 276-279). This MOF was constructed from tetra-zinc nodes and 1,4-benzene-dicarboxylate linkers to give an extended primitive cubic structure. Extensive studies of gas and vapor sorption measurements on MOF-5 revealed 61% porosity and 2,320 m^2/g BET surface area. These values exceeded those found for the traditional porous materials, zeolites, porous carbon, and mesoporous silicas, and set a high record for porosity. In 2000, BASF scientists, initially thinking this remarkably high surface area was a misprint, reproduced the surface area reported for MOF-5, and in collaboration with Yaghi, proved that its synthesis could be scaled-up to kg quantities. In 2005, BASF constructed a plant for the production of MOFs on a multi-ton scale using simple and high-yielding procedures under ambient conditions. These developments set off an avalanche of research activities worldwide and as of this year, the original paper on the discovery of MOF-5 has received over 8,000 citations.

Designed Porosity

After the discovery of MOF-5, Yaghi showed that a large family of MOFs with the same MOF-5 topology can be produced using the same Zn_4O nodes and variously functionalized and expanded carboxylate organic linkers (*Science*, 2002, 295, 469-472). The importance of the development of these so-called isoreticular MOFs, or IRMOFs, was threefold. First, it demonstrated for the first time that the functionality and metrics of the pores within an extended structure can be varied without altering its underlying topology, thus opening an unlimited potential for making MOFs by design. This led Yaghi to report a MOF with the largest pores (10 nm in diameter) of any porous crystal and showed its utility in binding proteins (*Science*, 2012, 336,1018-1023). Second, it showed how the pores could be precisely designed and systematically varied for capturing and storing gases such as hydrogen, methane, and carbon dioxide. Yaghi went on to pioneer the utility of MOFs in these applications (*Science*, 2003, *300*, 1127-1129; *Science*, 2002, 295, 469-472; *J. Am. Chem. Soc.*, 2005, 127, 17998-17999). Third, these IRMOFs illustrated how control of the connectivity within the tetra-zinc nodes and its overall coordination in the final MOF structure leads to an unlimited potential for making new MOFs by joining the same nodes, or others like it, with multitopic linkers. This third development later led Yaghi to report MOFs with 90% porosity and 6,500 m^2/g BET surface area (*Science*, 2010, 239, 424-428).

Emergence of Reticular Chemistry

At this point in the development of the field, the term «MOF» became synonymous with extended metal-organic structures for which permanent porosity has been proven using the low-pressure, low-temperature gas adsorption isotherm method first introduced in the field by Yaghi. In contrast to coordination networks (coordination polymers) whose nodes have single metal ions and thus lead to frail structures, the multi-metallic units of MOFs ensured architectural robustness, and their strong bonds (M-carboxylate) ensured thermal and chemical stability. Therefore, these and similar MOFs based on the strong bond, multi-metallic approach became the ones of wide interest since they can be used for various catalytic reactions, post-synthetic modifications, and gas storage and separation applications without collapse of the framework. The extensive area of MOFs we are witnessing today, including the overwhelming majority of MOFs synthesized and studied, originate from Yaghi's strong bond, multi-metallic approach. In 2003, Yaghi published a review article (*Nature*, 2003, 423, 705-714) on MOFs and introduced the term «reticular chemistry» defining it as the «linking of molecular building units by strong bonds into crystalline extended structures». This definition and chemistry encompassed three important developments: the use of the building block approach to make materials led to frameworks by design; the strong bond led to robust structures having permanent porosity; and crystallinity led to the characterization of these structures on the atomic scale. On the fundamental level, Yaghi's development of reticular chemistry through his work on MOFs extended the chemistry of metal-complexes to infinite 2D and 3D with profound implications on how we view, make, and use materials.

Development of Covalent Organic Frameworks

Continuing his strong bond approach to building extended structures, Yaghi developed in parallel to MOFs the chemistry of covalent organic frameworks (COFs). These are crystalline, porous organic 2D and 3D extended structures constructed from light elements (B, C-H, N, and O) held together entirely by strong covalent bonds. To appreciate this development, it is helpful to point out that, in a *Scientific American* article published in 1993, Nobel laureate Roald Hoffmann stated that the field of synthetic organic chemistry with structures that extend infinitely into 2D and 3D was non-existent and indeed a «synthetic wasteland». Yaghi changed this state-of-affairs by (again) overcoming the crystallization challenge, which attends anyone attempting to link molecules by strong bonds into extended structures. His strategy was to choose reversible organic reactions to create robust linkages between organic building blocks. He reported the first 2D and 3D COFs respectively in 2005 and 2007 (*Science*, 2005, 310, 1166-1170, and *Science*, 2007, 316, 268-272).

In these two reports, Yaghi showed how boroxine and boroester linkages can be used to join organic building blocks together into crystalline extended structures. The reaction conditions he devised are widely used as the basis for making and crystallizing COFs today. Since these first reports, he went on to develop the chemistry and design principles for constructing COFs with borosilicate, imine, hydrazone, urea, and olefin linkages (*J. Am. Chem. Soc.*, 2008, 130, 11872-11873; 2009, 131, 4570-4571; 2011, 133, 11478-11481; 2018, 140, 16438-16441; 2019, 141, 6848-6852).

For COFs made from linkages that are less reversible, Yaghi also devised post-synthetic reactions, linker exchange methods, and multistep conversion reactions to achieve COFs with amide, oxazole, thiazole, dioxin, and aryl linkages (*J. Am. Chem. Soc.*, 2016, 138, 15519-15522; 2018, 140, 9099-9103; 2018, 140, 12715-12719; 2024, 146, 89-94). With these developments, COFs can be made from many common organic linkages, thus vastly expanding the scope of organic chemistry beyond 0D and 1D to 2D and 3D. The development of COFs added further support to his reticular chemistry approach and in effect extended organic chemistry to completely new arenas, namely, precision chemistry and design in infinite 2D and 3D space. It is worth mentioning that another unique outcome of his reticular chemistry approach led him to devise methods of linking molecules covalently to make molecularly woven COFs for the first time. His **molecular weaving** (*Science*, 2016, 351, 365-369) has yielded new materials in which the porosity and robustness of frameworks are combined with dynamics, thus having the potential to revolutionize the way we make flexible, yet resilient materials (*Science*, 2024, 383, 1337-1343).

Environment and Sustainability Applications

Hydrogen, methane, carbon dioxide, and water are four molecules that have the highest impact on clean energy and environment, and thus the sustainability of life on our planet. Hydrogen is the cleanest fuel, but it is difficult to use for transportation because extreme temperatures and pressures are required for its storage in sufficient amounts to make it a viable fuel. Methane is a major greenhouse gas, yet it is a desirable transitional fuel since it is cleaner than petroleum. It represents two-thirds of the fossil fuels on earth. Carbon dioxide, which is being emitted freely from power plants and automobiles, is detrimental to our planet since it causes climate change and acidifies the oceans. Water is essential to life, yet one-third of the people on our planet have limited access to fresh water, and by 2050 two-thirds will live in water-stressed regions.

MOFs and COFs, the two classes of porous frameworks Yaghi discovered and developed, have provided important new opportunities to achieve solutions previously unimagined and have already led to many technologies and startup companies commercializing products based on his materials. The precision of his chemistry and his strong bond approach has led to materials having high thermal and chemical stability, and that can consequently be used and cycled for many years of operation. The record high porosities that are an order of magnitude higher than those found for traditional porous materials has contributed to opening the way for their use in the storage technologies of these important molecules, with the added advantage of high capacity, efficiency, and lower costs. Yaghi has demonstrated these applications as described below.

For **hydrogen storage**, in a tank filled with MOF, it is possible to store double the amount of hydrogen, compared to a tank without MOF. This means that the storage capacity of hydrogen can be doubled at 77K without applying high pressure or further lowering the temperature. This is especially important since 20 Gt of hydrogen are being transported at 77K all over the world. He continues to work on room-temperature storage of hydrogen for automobile fueling.

The challenge of **capturing and storing methane** and using it for automobile fueling has been addressed by Yaghi in collaboration with BASF. Currently, a fuel tank filled with MOF can store triple the amount of methane, compared to a tank without MOF. This makes it possible for automobiles to travel triple the distance without refueling. Test automobiles have been running for several years with numerous cycles. The cycling stability is due to the robustness of the MOF material, thus allowing its use for the entire lifetime of the automobile.

Currently, **carbon dioxide capture** is done using monoethanolamine water solutions. These solutions are toxic, corrosive, and break down after cycling, further exacerbating the environmental challenge. They must also be heated to high temperatures (>120 ºC) to release captured carbon dioxide. The energy expended on such a carbon capture process could cost a power plant up to 30-40% of its energy output. Yaghi has shown that the interior of the pores within MOFs and COFs can be chemically modified to selectively capture carbon dioxide from combustion gases and without adverse interference from water. Heating these solids to remove carbon dioxide is far more energy-efficient because of their low heat capacity compared to that of monoethanolamine solutions. Yaghi has pioneered the use of MOFs and COFs for direct air capture and carbon capture from point sources. In 2005, he opened the door to carbon dioxide capture and storage using MOFs when he demonstrated for the first time that MOFs have an exceptionally high capacity for trapping carbon dioxide (*J. Am. Chem. Soc.*, 2005, 127, 17998-17999). He showed that at room temperature carbon dioxide storage capability could be increased 18-fold simply by adding one of his MOFs. In two high-profile papers of 2008 published by the Yaghi research group, they created MOFs with the largest pores of any crystalline material chemically designed at the time to capture carbon dioxide (*Nature*, 2008, 453, 207-211), and used robotics for high-throughput production and discovery of MOFs that exhibit unusual selectivity for CO2 capture (*Science*, 2008, 319, 939-943). Yaghi has also shown that the interior of the pores within MOFs and COFs can be chemically modified to selectively capture carbon dioxide from combustion gases and without interference from water (*J. Am. Chem. Soc.*, 2014, 136, 8863-8866).

Capturing and storing the carbon dioxide produced by humans is essential for reducing greenhouse gases in the atmosphere and mitigating global warming. Current carbon capture technologies are more effective for concentrated sources like power plant emissions, but the scientific community struggles to efficiently capture CO2 from ambient air, where levels are significantly lower. Direct air capture (DAC) is seen as crucial for reversing the increase in CO2 levels, which have now reached 426 parts per million (ppm)—50% above pre-Industrial Revolution levels. The Intergovernmental Panel on Climate Change warns that without DAC, achieving the goal of limiting global warming to 1.5 °C (2.7 °F) above historical averages will be impossible. The Yaghi group has recently developed a new absorbing material that may help the world achieve negative emissions. This porous COF, COF-999, effectively and rapidly captures CO2 from ambient air while resisting degradation from water and other contaminants, thus addressing a key limitation of current DAC technologies (*Nature*, 2004, 10.1038/s41586-024-08080-x). This COF-999 has a strong chemically and thermally stable backbone, it requires less energy, and it has been shown to withstand at least 100 cycles with no loss of capacity. No other material has been shown to perform like that, and it is basically the best material available for direct air capture today.

Yaghi also applied the ability of MOFs to seek out specific molecules and store them into the pores to tackling another long-standing challenge: **Harvesting water from desert air.** The majority of the world’s population lives in water-stressed regions where access to fresh, clean water is limited. Nevertheless, our atmosphere contains ~13,000 trillion liters of water vapor at any given time. Although many solutions have been proposed for harvesting water from fog and high humidity climates, to date no efficient technology exists for harvesting water from arid regions of the world, where it is most needed. In a groundbreaking report of 2014, Yaghi showed that MOFs can be tailored to harvest drinking water from desert air (*J. Am. Chem. Soc.*, 2014, 136, 4369-4381) with no energy requirement aside from ambient sunlight (*Science*, 2017, 356, 430-434). The power of MOFs for harvesting water from air was demonstrated when Prof. Yaghi’s group collected drinkable amounts of water in the Arizona desert during the hottest and driest time of the year using essentially only MOFs and two plastic boxes – with no external power source (*Science Advances*, 2018, 4, eaat3198).

The key advance towards addressing the water challenge occurred when Yaghi discovered that members of the MOF family exhibited a voluminous uptake of water at very low relative humidity (5-20%). His MOFs can work not only in the arid regions of the world but also in the more humid areas where access to clean water is a challenge. Further physical characterization revealed that the high-water affinity of these MOF materials is due to water binding to their pores in exactly the same way as water molecules bind in ice. In essence, inside these MOFs, one has solid water (i.e., ice fragments) in hot weather. To get the water out, as the goal is liquid water, one simply heats the materials to a mere 45 ºC. This provides enough energy to release the water from the pores to make clean water. This is the first and only material to date that is capable of rapidly extracting water from air even at very low humidity (hence the desert air) and, at the same time, that is able to release the water for collection in an energy-efficient way.

Based on those initial findings, Yaghi quickly realized the need to demonstrate this water harvesting technology outside the laboratory, in the desert. His research group designed several generations of prototypes employing kilograms of MOFs and showed that these water harvesters work well in some of the driest deserts in the world (*ACS Cent. Sci.*, 2020, 6, 1348-1354). He and his group members tested the MOF water harvesters in the Arizona and the Mojavi deserts and found that significant amounts of water can be harvested from air (*Science*, 2017, 356, 430-434; *Science Advances*, 2018, 4, eaat3198; *ACS Cent. Sci.*, 2019, 5, 1699-1706). The productivity and efficiency of each generation of his water harvesters has gradually and significantly increased. The latest development from the Yaghi group showcased an extreme-weather proven, hand-held MOF-based device that can extract water from thin air repeatedly in the hottest and driest desert in North America, Death Valley, using only ambient sunlight as its energy source (*Nat. Water*, 2023, 1, 626-634). Remarkably, his MOF water harvesters have been tested in over 30,000 cycles and have been found to maintain their optimal performance. The MOF material remains in the harvester for the lifetime of the device (up to 10 years), and at the end of its performance life, the MOF is then reversibly disassembled and reassembled into its original state using a zero discharge, recyclable process. The water harvested has been shown to be ultra-pure, exceeding FDA and EPA standards for drinking water. His technology not only works in the deserts, but anywhere in the world and anytime of the year.

Yaghi's water harvesting technology has been showcased at the 2017 World Economic Forum as one of the top ten emerging technologies to change the world. IUPAC in 2019 also named his MOF water harvesters one of the top ten breakthroughs in chemistry. Yaghi has called for «personalized water», which is his vision of having water off the grid in the future, where a family can have a device at home running on ambient sunlight, delivering the water that satisfies the needs of the household. Yaghi has teamed up with a startup and General Electric Company to build sophisticated MOF water harvesters capable of delivering 1,000 L per day in an energy-efficient and economical manner.

Yaghi has taken his discoveries of MOF materials from basic science research to applications that address the water stresses we face on our planet. His MOF water harvesters generate clean water from desert air in an energy-efficient manner. They are unrivaled by any other materials or water harvesting technologies. His technology is truly a modern-day transformation with extraordinary social implications, and it will impact billions of people around the world. As freshwater resources are becoming increasingly scarce, it is important to establish access to clean water as a basic human right that must be guaranteed to every person on Earth, as Yaghi has advocated. In a time when water is becoming industrialized, privatized, and controlled by corporations, the availability of such a technology obviates ownership, and provides from nature and from the ocean-freshwater continuum a base supply directly to individuals.

AI Discovery Cycle

Yaghi has been at the forefront of employing LLMs, data science, and machine learning to the discovery of MOFs and COFs. This AI discovery cycle is intended to speed up the discovery of new materials for sustainability and the environment. Generative AI has shown immense potential across multiple disciplines, and LLMs have garnered particular interest within the chemistry community. These models stand out for their advanced natural language processing abilities, integration of extensive chemical knowledge, and versatility in tool utilization. Yaghi has reported how LLMs can now facilitate the customizable extraction of chemical data from literature, automate synthesis processes on robotic platforms, and support chemists in tackling pressing societal challenges related to climate change, clean energy, pollution, and public health. Additionally, he has shown how these models streamline routine laboratory tasks, bringing newfound efficiency to workflows.

Yaghi's work leverages LLMs for text mining (*J. Am. Chem. Soc.*, 2023, 145, 18048-18062), where vast amounts of chemical literature are analyzed, uncovering critical insights and patterns that would be challenging to capture manually. His team has also pioneered the use of LLMs in image mining, enabling the extraction of structural and mechanistic details from scientific imagery, which enhances the understanding and application of molecular frameworks (*Angew. Chem. Int. Ed.*, 2023, 62, e2023119). Through this innovative integration, Yaghi's research group has demonstrated how AI can transform traditional chemistry methodologies, empowering researchers to expand their knowledge base more rapidly and make data-driven decisions with unprecedented accuracy (*ACS Cent. Sci.*, 2023, 9, 2161-2170; *J. Am. Chem. Soc.*, 2023, 145, 28284-28295; *Digital Discovery*, 2024, 3, 491-501; *J. Chem. Theory Comput.*, 2024, 20, 9128-9137).

Yet, as this field continues to evolve, chemists often face challenges when attempting to configure LLM agents for specific tasks or to optimize their performance within existing workflows. For chemists without extensive AI experience, identifying suitable LLMs and integrating them effectively can be a complex and sometimes daunting process. Dr. Yaghi's contributions here are invaluable, as they lay a foundation that enables his group and the broader chemistry community to adapt and harness the power of LLMs, thereby pushing the boundaries of scientific discovery.

Closing Remarks

Reticular chemistry has opened the door to an infinite number of possible MOFs and COFs, and a plethora of societal applications, thereby turning the chemists' dream of constructing extended structures from molecular building blocks into reality. The structures resulting from this chemistry encompass pore space within which matter can be further manipulated and controlled, thereby creating in solid structures a chemical environment unavailable for molecules in solution. These factors have contributed to the chain reaction we are witnessing in academia and industry worldwide, where chemists are extending organic and inorganic chemistry to infinite 2D and 3D regimes.