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1 Introduction to reticular chemistry and its applications

1.1 History

If one dives deep into the nuances of the chemical literature, much can be argued about the origins of metal-organic frameworks (MOFs). Many research groups from around the world have laid claim to the earliest discovery of MOFs (ideation or practical conception) and those seminal contributions from Robson [1], Yaghi [2, 3], O’Keeffe [4], Fujita [5], Zaworotko [6] and Kitagawa [7] among others, are worthy of praise. Regardless, the history of the chemical science that underlies MOFs, termed reticular chemistry—the study of linking discrete molecular building blocks (inorganic and/or organic) through strong chemical bonds into extended, crystalline architectures—dates back to the invention of coordination chemistry by Alfred Werner who was awarded the Nobel Prize in Chemistry in 1913 [8]. The result of Werner’s work on understanding the spatial arrangement of atoms in discrete, 0-dimensional (0D) coordination complexes led to conceptual transfer from designing 0D structures to 2D and 3D extended structures in the form of Hofmann clathrates [9, 10]. Advancements were then made in the targeted synthesis of such 2D and 3D coordination compounds in the form of the modulation of distance between layers in the 2D compounds and in the connecting of layers to achieve 3D structures. However, it was at this point that several issues began to spring forth: (i) all compounds reported were purely inorganic with limited chemical functionalization being possible and (ii) although the concept of tuning the metrics of a given Hofmann clathrate was proven possible, precise control over these metrics was yet to be fully realized. Given that the structures were crystalline meant that they were well understood and this provided an opportunity to expand beyond purely inorganic building units to employing organic units that could be chemically functionalized and their metrics precisely controlled. In the 1950s, Saito’s group exploited the use of organic linkers to construct extended, solid-state materials, termed coordination polymers. This group demonstrated the concept of topological design by simply varying the length of the organic linker used in producing a series of bis(alkylnitrilo)-linked Cu^{I} coordination polymers of varying dimensionality [11–13]. Specifically, they demonstrated that they could produce a 1D, 2D or 3D coordination polymer simply by moving from succinonitrile to glutaronitrile and adiponitrile as organic linkers, respectively. In the 1990s, Robson followed this groundbreaking work by designing more complex organic linkers and targeting

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binodal topologies (i. e., having two vertices in the topology), by which the principle of “building blocks” was proven to truly work [1]. Indeed, Robson demonstrated the ability to systematically change the metrics of the building blocks through changing their geometry, size and points of extension (i. e., coordination type and number) to realize materials of diverse structure-type. The groups of Fujita, Yaghi and Zaworotko followed this work in the 1990s by switching from cyano-based coordinating groups to employing organic linkers with the neutrally-charged pyridine-based coordinating group [5, 6, 14]. The solvothermal conditions used with these organic linkers led to the discovery of many coordination polymers and proved useful as the synthetic basis for realizing MOFs to this day.

The work reported up to this point had focused on establishing the geometric design principles for transforming 0D discrete coordination complexes to 1D, 2D and 3D coordination polymers through the proper selection and use of inorganic and organic building blocks. Although conceptually important, all synthesized materials were architecturally, thermally and chemically unstable—properties that prevented their use for practical purposes. Addressing the stability challenge rested solely on the “crystallization challenge,” whereby coordination polymers needed to be constructed from strong, chelating, coordinate covalent bonds. However, when pursued, such compounds precipitated as amorphous materials because microscopic reversibility (i. e., “error-correcting”) could not be established during the crystallization process due to a higher bond energy for M-charged linker bonds (typically up to 400 kJ mol^{-1}) when compared to M-donor bonds (typically up to 200 kJ mol^{-1}). In 1995, Yaghi demonstrated that extended structures could, in fact, be crystallized when charged, chelating linkers were used [2]. The critical discovery here being that the reaction kinetics needed to be slowed down via the slow release of base (in this case pyridine), which slowly deprotonated the carboxylate-based organic linker to establish reversibility. With the synthesis of $\text{Co}(\text{BTC})(\text{Py})_2$ (BTC = benzene-tricarboxylate; Py = pyridine), stronger, charged bonds with bridging and chelating coordination modes were shown to afford more stable extended network materials, now termed MOFs.

To further enhance the stability of MOFs, Yaghi pursued the replacement of single metal ion building blocks that had been predominant in all extended structures reported thus far with polynuclear clusters, termed secondary building units (SBUs). The motivation was that SBUs realized through charged linkers could provide MOF structures with more architectural rigidity and stability. Indeed, in 1998, Yaghi published the first MOF, termed MOF-2 [$\text{Zn}(\text{BDC})(\text{H}_2\text{O})$], whose internal free space (i. e., pores) could be completely evacuated without the overall structure collapsing [3]. Establishing permanent porosity for such structures demonstrated the almost endless potential of designing 2D and 3D MOFs by combining different SBUs with different charged organic linkers. Indeed, the discovery of the fundamental geometric design principles for realizing extended structures in combination with the use of charged linkers and SBUs ushered in a new era in synthetic inorganic chemistry.

1.2 Reticular chemistry as a field of study

Expanding the scope of the charged organic linker and SBU approach in synthesizing more and more MOF materials, such as the iconic MOF-5, provided further proof that the stability challenge had been overcome [4]. This led to a new field of study being invented—a field called reticular chemistry. By definition, the word “reticular” means to resemble a net in appearance or construction or to be net-like, and when combined with “chemistry,” the field is defined as the study of logically constructed chemical structures that are held together by strong bonds [15, 16]. This field of study has not only led to the flourishing of MOFs, but has also brought into existence many other class of materials including, zeolitic imidazolate frameworks (ZIFs—metal-organic analogues of zeolites), covalent organic frameworks (COFs—extended structures made entirely of light atoms), metal triazolates (METs), metal catecholate frameworks (CATs), metal phosphonate and sulfonate frameworks, hybrid extended structures, among others [16–21].

Although the number of original research articles, reviews and textbooks (technical and educational) has exponentially grown since the first MOF report and from when the term reticular chemistry came into our scientific lexicon, it is our belief that this edited book is comprised of the most up-to-date contributions from a diverse cast of renown scholars from all over the world on the topic of reticular chemistry. The scope of this monograph picks up from that first report of MOF-2 and extends through the maturing science underlying the design, synthesis, characterization and post-synthetic modification of MOFs to their applications in gas capture, storage and separation, renewable energy and catalysis, and water, among others. Accordingly, based on almost 30 years of research having been reported on the chemistry and applications of MOFs, it is our intention for this monograph to detail the most important knowledge and know-how available to help any reader embarking on a project based on MOFs such that this work will serve as a reference for those old and new reticular chemists alike. The book is divided practically in multiple parts, which are ordered in a manner that the reader experiences a natural progression in the knowledge and understanding being presented.

1.3 Understanding the fundamentals of reticular chemistry and its applications

The first part (Chapters 1–4) showcases the hallmarks of MOFs and the reason they have attracted so much interest in research laboratories across the world. The aesthetic beauty of MOF structures is derived from their order, periodicity and symmetry. These elements are, in turn, derived from the geometry principles that underly their construction. In reticular chemistry, one can either rationally design (*a priori*)

a targeted structure or reverse-engineer a structure that was serendipitously discovered to understand its constituent parts. In their chapter, Yuan and El-Sayed touch on these ideas with prominent examples being provided. To realize one's design of a new MOF in the laboratory requires a fundamental appreciation of the different synthetic conditions and techniques that can be used to practically and tangibly achieve a designed architecture. Yuan and El-Sayed deliver a master course on all of the synthetic approaches, variables and conditions that have been reported—from conventional solvothermal synthesis that includes many different liquid- and solid-phase methods to the state-of-the-art sustainable (green) synthesis techniques. Along the way, the authors provide all necessary information for a new reticular chemist to leave with a fundamental understanding of the different reaction conditions (and their effect) on MOF synthesis including, the effect of solvent, pH, temperature, molar ratio of reactants and other parameters.

In silico techniques are finding a prominent place in reticular chemistry due to the era of big data and the treasure trove of structures and properties of MOFs reported. In their chapter, Sarikas, Fanourgakis and Froudakis present the expediency of computational screening and how machine learning can significantly accelerate the discovery process even with a relatively small amount of data. The authors begin their contribution with a tutorial of the machine learning landscape, touching on the fundamental differences of supervised versus unsupervised and reinforcement learning. Furthermore, they demonstrate a general overview for how to build a machine learning pipeline by defining the critical aspects that must be considered during data collection and algorithm selection (e. g., decision trees, neural networks). In machine learning, the combination of multiple algorithms creates a stronger one and for this, examples are given in random forest and gradient boosted trees. Finally, Froudakis et al. focus the latter half of their chapter to applying machine learning to MOF research. Detailed examples are provided for using such approaches in screening and predicting MOFs for gas storage and separation. As the authors state so succinctly in their conclusion, "...this chapter serves as an introduction for material science researchers to the world of machine learning. The basic terminology, techniques and workflow were presented, allowing new practitioners to familiarize with the field of machine learning in an easy and comprehensive manner."

MOFs are crystalline solids—a property that works toward a reticular chemist's advantage; with crystalline solids as a product means that one of the most powerful structural characterization techniques can be used to elucidate the atomic structures, X-ray diffraction. In their chapter, Infas and Huang delineate the crystal growth and crystallization process of MOFs highlighting key synthetic elements to pay attention to while describing the key characteristics of a single crystal suitable for X-ray diffraction analysis. They then administer a brief course on the fundamentals of X-ray diffraction with context emphasis being placed on how such fundamentals are applied to the structure determination, refinement and solution of MOF crystals. Wisely, the authors describe, in detail, this process from both a single-crystal and powder X-ray diffraction

perspective. To demonstrate how far X-ray diffraction, as a technique, has been applied to the study of MOFs, the chapter details advanced studies on the crystallization mechanisms of MOFs through time-resolved *in situ* measurements. Infas and Huang end their substantive chapter on what has become widely seen as the future of structure solution in reticular chemistry: electron diffraction. The rate-limiting step in reticular chemistry has always been obtaining MOF crystals of suitable size. With evolving electron diffraction techniques, single crystals that are too small for X-ray diffraction are now capable of providing structural information at the atomic level. In a rather insightful final portion of the chapter, the authors present the principles and protocols of electron diffraction and lay out the structure determination process from data processing and structure solution to structure refinement and further applications in the study of MOFs.

The second part (Chapters 5–9) highlights the potential usefulness of MOFs for solving some of the world's most vexing challenges pertaining to gases. In a chapter whose depth matches its breadth of coverage, Assen details MOFs' applicability to the challenging air separation, light hydrocarbons separation and noble gas purification processes by correlating structural properties to the physical properties and demands of those specific gas separations. Representative examples are presented throughout, which provide benchmarks for newcomers to the field to assess their own compound's performance. Maythality and Lau expand upon Assen's chapter by demonstrating the effectiveness of processing MOFs into pure membranes or mixing them with polymers to form mixed-matrix membranes. The fabrication strategies presented provide a real tutorial for those pursuing this topic leaving the reader with a solid footing in starting or expanding upon their own membrane research program. Understanding how to fabricate MOF-based membranes is important, but not without the context for which they are applied. Maythality and Lau then take a deep dive into the versatility by which membranes can be utilized for both gas separations and water purification. Similar to Assen before them, they provide benchmark data for the membranes and their separation performances.

At this point, it almost goes without saying, that the world is facing a serious challenge in addressing climate change. A recognized critical step is to prevent further emissions of harmful greenhouse gases, like carbon dioxide, from entering the atmosphere. Carbon capture is where MOFs, and related materials, stand the best chance to make an impact. Nguyen and Kegere describe in great detail the differences that exist between conventional materials used in carbon capture and MOFs. From their discussion, it was made abundantly clear the advantages that MOFs have in terms of structure and performance over zeolites, activated carbons and aqueous alkanolamine absorbents. The authors then take the reader on a tour-de-force through the approaches taken for applying MOFs toward carbon dioxide capture—from structural properties and performance and the processes of carbon dioxide capture to the key design elements that must be considered for future MOF construction. The question that is always posed once carbon dioxide is captured is, what should be done with it? Nguyen

and Kegere dedicate a large portion of their chapter to enumerating MOFs for conversion, whether that be via photocatalysis, electrocatalysis or photo-electrochemical conversion.

In parallel with carbon dioxide emission reduction, it is widely recognized that society has to wean itself off the use of petroleum-based fuels. Natural gas is a transition fuel source that is cleaner than petroleum and hydrogen is the cleanest fuel as upon combustion it produces no greenhouse gases. MOFs are once again well positioned to support this transition through their high-porosity and ultrahigh uptake capacities. Tu et al. tackle this topic by starting their chapter with the fundamentals of adsorption before detailing MOFs for onboard natural gas storage. Similar to the previous chapters, Tu et al. present the key metrics for the highest performing MOFs and detail strategies for improving upon these achievements with a particular focus on structural properties such as coordinatively unsaturated metal sites, porosity, pore volume, functionalization and pore metrics. Critical to realizing MOFs for onboard natural gas storage is to understand and then design structures that balance volumetric and gravimetric working capacities. Indeed, Tu et al. do a masterful job at delineating the important points for this. Attention is then turned in the second half of their chapter to MOFs for onboard hydrogen storage. The authors once again cover the important fundamentals, present the benchmark materials with their performance metrics and illustrate the structural features that are most important to consider when pursuing MOFs for this application.

From cost, environmental and energy viewpoints, the production of specialty chemicals is exigent. In the conventional processes, several metal-based reagents have been developed that can selectively and efficiently drive the necessary transformations. However, the requirement of stoichiometric amounts of the metal catalysts and accumulation of a considerable amount of waste remain inevitable. One solution to this challenge is to employ heterogeneous catalysts. As a result of their inherent structural flexibility, MOFs bear similar catalytic features as zeolites, including porosity and diversity in pore sizes and shapes, yet have the distinct advantage of containing functionalizable organic linkers. Functionalization is possible either by pre-MOF synthesis linker design or through post-synthetic modification on the framework. Furthermore, the large surface areas, structured internal pore environment and high density of accessible active sites facilitate both reactivity and selectivity. One theory of higher efficiency in catalysis is the formation of a “near attack conformation,” which means the substrate molecules are forced to come into close proximity with catalytic sites (similar to what is proposed to occur in MOF pores), therefore, increasing the rate by many folds. In their chapter, Hmadeh et al. take the reader on a journey to show them the advantages of using the metal nodes as site-selective catalytic sites, functionalized linkers as site-selective active sites and how post-synthetic modification can introduce new sites as well as exploiting synergistic effects between the metal nodes and organic linkers. The authors end their riveting chapter with pre-

senting strategies for creating composites where the “whole is greater than the sum of its parts.”

The final part of the monograph (Chapters 10–13) focuses itself on emerging applications of MOFs—applications that are less mature than the previous section but represent exciting hope and potential. Alkordi and colleagues set the scene of their chapter on MOFs for energy conversion and storage via water electrolysis by presenting the current status and challenges in moving from fossil fuel-based energy to renewables. The authors then provide fundamental concepts of the water splitting reactions such that reader has the context from which to understand the applicability of MOFs. They then detail, at great length, the different roles that MOFs play in the hydrogen evolution reaction (e. g., pristine MOF electrocatalysts, porous scaffolds/supports and sacrificial precursors) and follow this with a similar approach for MOFs in the oxygen-evolution reaction. Alkordi et al. conclude their chapter with a clear statement that this is a burgeoning application—one in which the rich chemistry of MOFs is well positioned to advance for years to come.

More than 50 % of the world’s population lives in water-stressed areas. Water resources are being depleted faster than can be replenished, drinking water is quickly becoming scarce, and climate change is only exacerbating the problem. MOFs have emerged as viable candidates for addressing a wide-ranging assortment of water issues. In their chapter, Howarth and colleagues demonstrate absolute knowledge of the diverse challenges facing the water security and finesse a brilliant study on the various MOFs used in the adsorption and removal of contaminants or pollutants (e. g., organic, inorganic, and dual removal of organic and inorganic compounds) in water systems. Where adsorption is not feasible, the authors detail how catalytic MOFs can be used to degrade the pollutants. As an emerging field with few examples reported, Howarth wisely presents desalination as a potential application showcasing how much work remains to be done in order to progress this science. Finally, the authors turn their attention to water adsorption in MOFs showcasing the application of atmospheric water harvesting that has received enormous attention as of late. Atmospheric water harvesting represents the promise of MOFs for achieving absolute water security and independence for anyone, anywhere, at any time [22].

The final chapter of the monograph situates itself on addressing and optimizing the structural properties of MOFs for use in biomedical applications. Latif et al. tackle this topic through a deep understanding and illustrating of guest molecules’ interactions with the frameworks of MOFs—guest molecules that span from biomolecules (e. g., proteins, enzymes, peptides, carbohydrates, DNA, nucleic acids and/or lipids). Once a solid understanding of those interactions is gleaned, the authors dive into how the resulting systems can be exploited for use in targeted delivery and demonstrate how computational techniques can ease and structure the synthetic work that is needed to realize such systems. From a combination of experimental and computational studies, Latif et al. describe, in great detail, the many factors that affect host-guest interactions in MOFs—from the effect of cage and pore size, functionalization

of the linkers and coordinatively unsaturated metal sites, to diffusivity and loading capacity. It is a remarkable chapter with much to learn and apply to new research programs.

At a fundamental level, reticular chemistry offers an intellectually stimulating journey through discovery, rational design, structural characterization and technology-driven properties. The breadth of science, techniques and applications experienced through reticular chemistry is unseen in other fields. Through this monograph, readers will come to appreciate the importance of this experience as each chapter showcases a wide variety of topics and highlights the endless impacts that MOFs have been proven to deliver. It is our hope that readers will find this contribution valuable to their pursuit of knowledge in the field of reticular chemistry. With this, we would like to extend our deepest appreciation to all of the expert contributors for their outstanding work and we wish all of the readers nothing but success in their own research pursuits.

Bibliography

- [1] Hoskins BF, Robson R. Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$ structures and the synthesis and structure of the diamond-related frameworks $[\text{N}(\text{CH}_3)_4][\text{Cu}^{\text{I}}\text{Zn}^{\text{II}}(\text{CN})_4]$ and $\text{Cu}^{\text{I}}[4,4',4'',4''']\text{-tetracyanotetraphenylmethane}]\text{BF}_4 \cdot x\text{C}_6\text{H}_5\text{NO}_2$. *J Am Chem Soc.* 1990;112:1546–54.
- [2] Yaghi OM, Li G, Li H. Selective binding and removal of guests in a microporous metal-organic framework. *Nature.* 1995;378:703–6.
- [3] Li H, Eddaoudi M, Groy TL, Yaghi OM. Establishing microporosity in open metal-organic frameworks: Gas sorption isotherms for $\text{Zn}(\text{BDC})$ ($\text{BDC} = 1,4\text{-Benzenedicarboxylate}$). *J Am Chem Soc.* 1998;120:8571–2.
- [4] Li H, Eddaoudi M, O’Keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature.* 1999;402:276–9.
- [5] Fujita M, Kwon YJ, Washizu S, Ogura K. Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium(II) and 4,4'-bipyridine. *J Am Chem Soc.* 1994;116:1151–2.
- [6] Subramanian S, Zaworotko M. Porous solids by design: $[\text{Zn}(4,4'\text{-bpy})_2(\text{SiF}_6)]_n \cdot x\text{DMF}$, a single framework octahedral coordination polymer with large square channels. *Angew Chem Int Ed.* 1995;34:2127–9.
- [7] Kondo M, Yoshitomi T, Matsuzaka H, Kitagawa S, Seki K. Three-dimensional framework with channeling cavities for small molecules: $\{[\text{M}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4] \cdot x\text{H}_2\text{O}\}_n$ ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}$). *Angew Chem Int Ed.* 1997;36:1725–7.
- [8] Werner A. 1,2-Dichloro-tetrammin-*kbaltisalze*. (*Ammoniak-violeosalze*). *Eur J Inorg Chem.* 1907;40:4817–25.
- [9] Hofmann K, Kuspert F. Verbindungen von kohlenwasserstoffen mit metallsalzen. *Zeit Anorg Chem.* 1897;15:204–7.
- [10] Powell HM. The structure of molecular compounds. Part IV. Clathrate compounds. *J Chem Soc.* 1948:61–73.

- [11] Kinoshita Y, Matsubara I, Saito Y. The crystal structure of bis(succinonitrilo)copper(I) nitrate. *Bull Chem Soc Jpn.* 1959;32:741–7.
- [12] Kinoshita Y, Matsubara I, Saito Y. The crystal structure of bis(glutaronitrilo)copper(I) nitrate. *Bull Chem Soc Jpn.* 1959;32:1216–21.
- [13] Kinoshita Y, Matsubara I, Higuchi T, Saito Y. The crystal structure of bis(adiponitrilo)copper(I) nitrate. *Bull Chem Soc.* 1959;32:1221–6.
- [14] Yaghi OM, Li H. Hydrothermal synthesis of a metal-organic framework containing large rectangular channels. *J Am Chem Soc.* 1995;117:10401–2.
- [15] Yaghi OM, O’Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. Reticular synthesis and the design of new materials. *Nature.* 2003;423:705–14.
- [16] Furukawa H, Cordova KE, O’Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. *Science.* 2013;341:1230444.
- [17] Zha X, Li X, Al-Omari AA, Liang CC, Al-Ghourani A, Abdellatif M, Yang J, Nguyen HL, Al-Maythalyon B, Shi Z, Cordova KE, Zhang YB. Zeolite NPO-type azolate frameworks. *Angew Chem Int Ed.* 2022;e202207467.
- [18] Nguyen NTT, Furukawa H, Gandara F, Nguyen HT, Cordova KE, Yaghi OM. Selective capture of carbon dioxide under humid conditions by hydrophobic chabazite-type zeolitic imidazolate frameworks. *Angew Chem Int Ed.* 2014;40:10821–4.
- [19] Nguyen NTT, Lo TNH, Nguyen HTD, Le TB, Cordova KE, Furukawa H. Mixed-metal zeolitic imidazolate frameworks and their selective capture of wet carbon dioxide over methane. *Inorg Chem.* 2016;55:6201–7.
- [20] Nguyen NTT, Furukawa H, Gandara F, Trickett CA, Jeong HM, Cordova KE, Yaghi OM. Three-dimensional metal-catecholate frameworks and their ultrahigh proton conductivity. *J Am Chem Soc.* 2015;137:15394–7.
- [21] Nguyen HL, Gandara F, Furukawa H, Doan TLH, Cordova KE, Yaghi OM. A titanium-organic framework as an exemplar of combining the chemistry of metal- and covalent-organic frameworks. *J Am Chem Soc.* 2016;138:4330–3.
- [22] Almassad HA, Abaza RI, Siwwan L, Al-Maythalyon B, Cordova KE. Environmentally adaptive MOF-based device enables continuous self-optimizing atmospheric water harvesting. *Nat Commun.* 2022;13:4873.

