NANO LETTERS

pubs.acs.org/NanoLett

VIEWPOINT

The Reticular Chemist

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Cite This: https://dx.doi.org/10.1021/acs.nanolett.0c04327

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A new chemist is emerging to extend chemistry from the atom and the molecule to the framework and to meet the new intellectual and practical challenges of the 21st century.

I was recently asked by a science reporter whether I am an organic or inorganic chemist. I found myself saying that I am a reticular chemist. The reporter responded: I really like that but I am not sure whether my editor would accept it. As the reporter pressed me further to put myself in one of those categories, I stated that inorganic chemists consider me a materials scientist and organic chemists think of me as an inorganic chemist, and further complicating this view is that material scientists working on nanomaterials think of me as an organic supramolecular chemist and not really a polymer chemist. Given that my research led to metal−organic frameworks (MOFs) and covalent organic frameworks (COFs), and that these are made using basic inorganic and organic chemistry reactions, I wondered why is it that generally chemists are slow to embrace new emerging chemistries unless they fit in the mold of what many think are the "legitimate" divisions of chemistry. I am writing this Viewpoint to introduce the reader to reticular chemistry, the chemistry behind MOFs and COFs and one that concerns itself with *linking molecular building units by strong bonds into crystalline extended structures.*[1,2] I wish to make the case that it not only originates in both basic organic and inorganic chemistry, and its pursuit has expanded the scope and intellectual basis of those chemistries, but that it is quite distinct from supramolecular and polymer chemistry. I hope this introduction of reticular chemistry, done through answering the question asked by the reporter, will serve as a helpful guide to those interested in this topic and care about what we communicate to our emerging scholars who represent the future of chemistry. I will argue that I and my colleagues across the country and the world are reticular chemists and that we routinely and by necessity cross the traditional divisions of chemistry and that the question of how such a chemist may or may not fit in those divisions does not add meaningfully to the discourse of chemistry. I will also outline in this contribution some important future scientific directions worthy of consideration by the reticular chemist.

Chemists are a unique brand of scientist because we are concerned with the art and science of building chemical structures, figuring out their structures using atomically precise techniques, and studying their reactivity. Our focus in the 20th century was on discrete molecular objects, but when it came to linking these molecules with strong bonds into extended structures, especially in infinite 2D and 3D, it was taken as an article of faith that such activity is far more difficult to master because of the crystallization problem. What I mean is that as structures become larger and as the strength of bonding interactions between their components increases so does the difficulty in attaining them as crystals. Since chemists are interested in not just making structures but also modifying them, such crystallizations necessarily have to be carried out under sufficiently mild conditions to allow for the character of the starting molecular building blocks to be preserved and therefore translated into the resulting crystals. Certainly, one can crystallize inorganic oxides and other solids at high temperatures, but the chemistry of the resulting structures is not amenable to the precision commonly practiced in molecular organic and inorganic chemistries. Thus, it fell upon the future reticular chemists to show how one can extend the exquisite control achieved in molecular chemistry to infinite 2D and 3D.

It all started in 1995, when it was shown that metal ions can be linked with charged organic linkers (carboxylates) to make crystalline 2D structures (coined at that time as MOFs), and in 1998 the ability of such carboxylates to make multimetallic units (called secondary building units, SBUs) was used to make 2D porous MOFs (MOF-2).[3,4] The usefulness of the SBUs in providing directionality and rigidity very quickly became apparent when the permanent porosity of MOF-2 was proven by gas adsorption isotherms, performed for the first time on a metal−organic structure.[4] These measurements also meant that the SBUs can maintain the architectural robustness of the MOF in the absence of guests and that the strong bonds afforded by the metal ion to charged linker "linkages" meant that the MOF will be thermally stable. In 1999, the SBU approach was used to demonstrate the construction of a primitive cubic MOF in which tetra-zinc oxide SBUs were linked by terephthalate to make a 3D extended structure termed MOF-5 whose porosity of 2900 m^2 g^{-1} exceeded all previous porosities.[5] These reports were later followed by linking organic molecules by strong covalent bonds into 2D and 3D COFs in 2005 and 2007, respectively.[6,7] COFs have entirely organic structures, which served as first examples in the extension of organic chemistry to infinite 2D and 3D. The fact that the MOF and COF structures are not only architecturally and thermally robust but also chemically stable meant that postsynthetic covalent modifications[8] could be implemented on their frameworks without altering their underlying connectivity or crystallinity. In other words, the concept of using MOF and COF "crystals as molecules" became real, thereby opening the way for crafting the pores to be ideally suited for gas separation, catalysis, and a plethora of other applications.[9,10]

There was an additional development that would further distinguish these reticular structures from anything witnessed in molecular chemistry, and this was the design of multivariate functionality and mixed metals into their structures.[11−15] The incorporation of many different functional groups or many different kinds of metal ions into a reticular structure provided a unique control handle on their chemistry and ultimately on their properties. Their pores can now have designed complexity while maintaining the order of the framework's backbone. Indeed, this is viewed as "heterogeneity within order" and it served as the basis for the decipherment of sequences within the pores of MOFs and COFs.[16,17] It was the first time outside biology that the concept of sequences was realized. The frameworks holding sequence information have properties that far exceed the sum of their components (i.e., the whole is performing better than the sum of the parts).

While MOFs and COFs have fruitfully used basic inorganic and organic reactions, they have extended those chemistries into infinite 2D and 3D. On the fundamental level, a molecule to an atom is the same as the framework to a molecule: The molecule fixes the atom in specific geometry, connectivity, and spatial arrangement, whereas the framework fixes the molecule in specific geometry, connectivity, and spatial arrangement. Except additionally, the framework encompasses space within which matter can be further manipulated and controlled. Indeed when sequences are designed into the pores of the framework, coding of their function becomes an exciting prospect. So, you see the reticular chemist is a chemist par excellence and must work intimately with inorganic, organic, and materials chemistry without being hindered by divisions. Since reticular chemistry is about the control of the strong bonds, which are so necessary for the desirable properties of the framework, it should not be confused with supramolecular chemistry, defined as the chemistry of assembling constituents by weak bonds.[18] One final note on the topic of terminology and intellectual distinctions: Both MOFs and COFs are crystalline, infinite structures and should not be referred to as polymers, which are large molecules whose crystals (when accessible) are intrinsically molecular in that many linear or branched polymer *molecules* interact through weak forces to make the crystal. In contrast, reticular compounds have structures in which strong bonds (metal-charged ligand for MOFs or covalent for COFs) hold their constituents together in either 2D or 3D *throughout* the crystal.

Thus, a reticular chemist is just a chemist: A scientist working across the more established areas with a new approach and thinking about the very thing chemists enjoy doing, that is, crafting matter on the atomic and molecular levels and now the framework level.

Where is reticular chemistry heading? The precise control over framework chemistry is beginning to translate into the impact on society. The future extent of this can be best appreciated by stepping back and considering the materials that served humanity so well and helped build our modern civilizations. Many would agree that these include wood, steel, aluminum, silicon, cement, polymers, pharmaceuticals, paper, fabric, and petroleum. The 21st century comes with its own set of challenges dealing with access to clean energy, environment, and water, as well as responsible use of natural resources and sustainable development. Each one of these challenges demands solutions in which not only are we able to understand the problem on the molecular level but also meet the challenge with materials designed and crafted on the molecular level. Could the skills of the reticular chemists and the outcome of their labors, thus far articulated in MOF and COF chemistry and materials, be the answer and that these infinite creations are the 21st century materials? If the current progress being made, for example, in carbon capture and harvesting water from desert air is any indication,[19,20] I would say "yes", provided that we can build ecosystems around these materials as was done around each one of the traditional materials enumerated above. There is a lot of work to be done and it is not for the faint-of-heart, just like the initial path taken for developing reticular chemistry and materials.

In order to begin to develop these ecosystems, the reticular chemist needs to have no hesitation in venturing into new intellectual endeavors and continue to ask hard questions. For example, the vast possibilities that MOFs and COFs give us in new composition, structure, properties, and applications, create infiniteness that challenges traditional means of addressing chemical problems. How do we harness this infinite space? How do we continue to grow the intellectual basis of reticular chemistry, while at the same time focus on the applications and uses of our materials? How do we introduce tools for emerging scholars to plug in and contribute to this evolving field? I believe that the approaches to answering these questions will ultimately require a diversity of thinking and tools, but I am convinced that developing digital reticular chemistry is one of the most promising directions.[21] Development of artificial intelligence tools (robotics[22] and machine learning[23−25]) to be used routinely in exploring the infinite chemical space and identifying the "star" structures for specific applications will be a fertile direction. The ability to use these tools to work out the sequences of information embedded in multivariate MOFs and COFs constitutes another important direction for making sophisticated structures capable of sorting and counting, operating in parallel, having open compartments that are linked yet function differently, replicating and translating information, and ultimately metabolizing substances, all within a MOF or COF "system". There is a lot to be done and the reticular chemist having indiscriminately and productively worked in and across the traditional divisions of chemistry must continue to rise to the occasion and bring in computer science tools and concept transfer from biology to survive the exciting future and hopefully thrive in it.

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https://pubs.acs.org/10.1021/acs.nanolett.0c04327

Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

The author appreciates the interest expressed and critique of this article by Prof. Dr. Stefan Wuttke, Basque Center for Materials, Applications and Nanostructures, Leioa, Spain.

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