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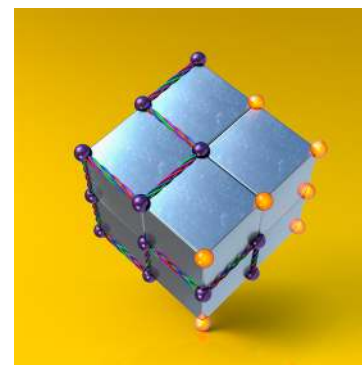
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# Reticular Chemistry in All Dimensions

Chemistry, first and foremost, is concerned with the geometry that atoms and molecules adopt in space. Whether we are pursuing chemical reactions or studying the properties of materials, inevitably we seek to know and understand the geometrical aspects of chemical structures. Indeed, it has been historically the case that no matter how far chemists veer away from this practice, especially when racing toward making materials that “benefit” society, they come back to questions regarding how atoms are linked into molecules and how molecules interact with each other to account for their observations. It has also been our quest, once we acquire this knowledge, to use it for controlling chemical structures and in many ways “bending them to our will”. Chemists have done so for molecules (0D) and to some extent polymers (1D), but beyond these our ability to express control in infinite 2D and 3D remained undeveloped throughout the twentieth century.<sup>1</sup>

Over the last 25 years, reticular chemistry has emerged from this thinking and in its current practice serves to fill the gulf between what we know and can do on the molecular level in 0D and 1D, and what could be possible in 2D and 3D.<sup>2</sup> It started first with linking inorganic clusters into extended porous frameworks, and then linking organic molecules and metal ions into metal–organic frameworks (MOFs), and organic molecules together into covalent organic frameworks (COFs).<sup>3,4</sup> In other words, it opened the way for developing chemistry beyond the molecule. It is now widely accepted that reticular chemistry is the chemistry of linking molecular building blocks by strong bonds to make extended crystalline structures as exemplified by MOFs and COFs. What is in this definition? (i) Molecular building blocks provide control in the construction of frameworks because of their well-defined structure and geometry, (ii) strong bonds impart architectural, thermal, and chemical stability to the resulting frameworks, and (iii) crystallinity, which was the challenge impeding the progress toward realizing such frameworks, ensures that their structures can be definitively characterized by X-ray or electron diffraction techniques. Each of these aspects has been established through the synthesis and study of over eighty thousand MOFs and hundreds of COFs, where it is no longer a major challenge to control matter in 2D and 3D.



As we take stock of the progress made in reticular chemistry, we are struck by how quickly it has developed in employing libraries of organic molecules in the chemistry of reticulating them with metal ions and other organic molecules into a seemingly infinite variety of ways, leading to what can only be imagined to be an infinite structure space. When we add the vast possibilities of functionalizing these structures, the infiniteness of reticular chemistry supported by the exquisite control with which such structures can be made and modified is exceptional. Although I have emphasized the structural aspects of these synthetic creations because they form the foundation onto which further levels of control can be achieved, the vastness of this field requires simplifying concepts with the hope to achieve better understanding of the chemistry.

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## Addressability along All Dimensions

The contributions in [this virtual issue](#) inspired me to present here another important and unifying concept in reticular chemistry. This concerns how one can address molecules linked together into frameworks. The terms “address” and “addressability” will be used in this Editorial to indicate that

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the molecular building units constituting the framework can be reached and manipulated by chemical reactions and/or stimuli to affect a change. Since the framework fixes the molecule in specific orientation, geometry, and spatial arrangement, the change we speak of can be taking place at a specific site (0D), along a certain path (1D), over molecules lying on a “flat” surface (2D), or over the entire crystal (3D). Indeed, addressability in this context represents the next level of control beyond the actual construction of the framework backbone structure. The contributions in this issue clearly tell us that not only do we express structural control in all dimensions (backbone) but that we can address the very molecular building units making up these structures in all dimensions.

### The ‘Molecule Becomes the Framework’ as the ‘Framework Becomes the Molecule’

The result of reticulating discrete molecules into extended structures such as MOFs and COFs is that the molecule becomes the framework, and with the ability to address them in a site-specific manner as one would with discrete molecules, the ‘framework becomes the molecule’.<sup>5</sup> Nowhere else in chemistry has it been possible to carry out a reaction on an extended structure and maintain its order, crystallinity, and porosity. Clearly, the breathtaking success of reticulating molecules and addressing them in the resulting structures has tremendous implications over the design and properties of MOFs and COFs. The addressability takes on different forms in the framework and includes operations such as inducing rotations of specific bonds within linkers to give gate opening effects and highly selective separations, reactions of incoming guest at specific sites resulting in better catalysts, trapping of molecules in well-crafted pockets for water harvesting, placement of linkers as struts for retrofitting an entire framework, and inducing motional dynamics by an electrical stimulus. Not only are the structures built in all dimensions, but the results of addressability are also experienced in all dimensions. Thus, the control of structure also imparts control of a resulting property and its potential localization or propagation in a specific dimension. [This virtual issue](#) is a display of the vast richness that addressability brings to reticular chemistry.

### Stimuli Induced Dynamics

Barbour, Zhou, Zhang, and Ma et al.<sup>6</sup> take full advantage of the concept of addressable components to visualize how guest binding (carbon dioxide) transforms a MOF under high pressure. The high crystallinity of this MOF allowed for observation of the many states of transformation before and after carbon dioxide adsorption using *in situ*

single-crystal X-ray diffraction studies. Indeed, the adsorptive sites for carbon dioxide were identified, and more to the point, the molecular basis for how this transformation takes place was also determined and found to involve a switch between two states in the dihedral angle of the organic linker. Using high pressure of carbon dioxide “controls” this dihedral angle, which in turn determines whether the 1D pores are open or closed to carbon dioxide.

Ghoufi et al.<sup>7</sup> uses advanced molecular simulations to study how an electric field can lead to breathing in a MOF. Here, contractions and expansions across 1D channels running along a crystallographic axis, perpendicular to the pores, are predicted to be responsive to electrical stimuli. It is intriguing to imagine the possibility that variations in the applied current would lead to structural switching for highly selective separations, and eventually to giving rise to electrical swing adsorption. An elegant approach to addressing specific molecular units is given by Schmid et al.<sup>8</sup> They introduce rotatable groups or other types of mechanical motion within the organic linkers. These motions are believed to be driven by electric fields. In this theoretical study, they demonstrate how the electric response of MOFs can be realized by rotatable dipolar linkers to generate structures capable of dielectric behavior in 1D and paraelectric behavior in 2D.

### Site-Specific Designs within Frameworks

MOFs commonly have rigid structures, and this ensures repeatable uptake and release of guests without stressing and breaking the strong bonds making up the backbone structure. The rigidity also allows one to address the steric and electronic environment of the pores within metrically defined pockets in order to be able to separate molecules that are difficult to separate. This is illustrated in the study by Dai and Sun et al.<sup>9</sup> where they report a new copper MOF with 1D pore structure in which a pocket is identified to trap propylene from a mixture with ethylene. Initial experiments show binding of propylene in this unfunctionalized MOF but not sufficient to affect reasonable separation. To enhance the selectivity to propylene, other isorecticular (having the same connectivity) MOFs were made by employing the same organic linkers but with strategically placed functionality that decorates the binding pocket. In so doing, the electronic and steric environments of the pockets are optimized as evidenced by the observed excellent separation of propylene.

Dincă et al.<sup>10</sup> in their study of water uptake use a mesoporous MOF with open metal sites for optimal water adsorption. The open metal sites serve as nucleation points for the first water molecules to enter the pore onto which

other incoming water will bind to fill the pores. Since the pore diameter is designed to be above the critical dimension needed for water capillary action, this MOF has one of the highest capacities for water uptake at low humidity. This research is directly applicable to solving the water stress facing the world.

Open metal sites are also important in many heterogeneous applications. Dincă et al.<sup>11</sup> critically review the wide diversity of MOF structures and how the precise control of the electronic structure of their pores including open metal sites is a key feature of their chemistry. They discuss the opportunities and challenges in realizing the exceptional number of potential applications in gas separation, electrical conductivity, and catalysis. Another sample of what is possible in MOF chemistry is highlighted by Zhou et al.<sup>12</sup> who review the extraordinary stability of MOFs made from group 4 metals. These Outlooks clearly indicate that catalysis is an important direction for reticular chemistry. The fact that MOFs are routinely obtained as single crystals and therefore can be characterized by X-ray diffraction techniques has played an important role in developing the computational aspects of reticulated structures.

Such an approach is presented by Gagliardi et al.<sup>13</sup> who use computational design as a tool for introducing catalytic sites at the inorganic nodes of those MOFs deemed ideally suited for highly selective chemical transformations. The community has come to rely on computational modeling as an indispensable tool to, in the words of the authors, support, rationalize, and guide experimental studies, especially in the field of MOF catalysis. Needless to say, the fact that the catalytic sites are an integral part of the MOF nodes, which are separated from each other by organic linkers in 3D periodic fashion, prevents them from sintering thus making MOFs excellent candidates for both computational and experimental studies. [This virtual issue](#) includes several beautiful examples of strategies for the design of catalytic sites within MOF structures.

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The utility of strategically placing catalytically active molecular entities in the pores of MOFs is revealed in the report by Dincă and Román-Leshkov et al.,<sup>14</sup> where an organometallic complex is introduced into the pores postsynthetically. The cooperativity between the weakly bound organometallic complex guest and a site-isolated Lewis acidic metal ion, strongly coordinated within the

secondary building unit (SBU) in MOF backbone, is believed to be essential in the use of this MOF as a heterogeneous catalyst. It is effective in catalyzing ring-expansion carbonylation of epoxides to  $\beta$ -lactones.

Jiang, Huang, and Zhou et al.<sup>15</sup> report a 3D MOF having highly sought after titanium–zirconium oxo-cluster nodes. The incorporation of titanium in this construct is not very much unlike having titanium dioxide nanoparticles separated by designable organic linkers serving as antenna chromophores. This structure is desirable for solar energy conversion. The authors go on to make a family of isorecticular MOFs, which are porous, chemically stable, and photoresponsive, leading to good activity toward photocatalytic hydrogen evolution reactions. Catalytically active alloyed nanoparticles can also be incorporated as highly dispersed and ultrafine guests into the pores of MOFs as Shen and Li et al.<sup>16</sup> report. These materials exhibit excellent activity for the homocoupling reaction of phenylacetylene under base- and additive-free conditions and at room temperature.

### Steadying Frameworks under Pressure

In our own work (Yaghi et al.),<sup>17</sup> we demonstrate how very specific sites in a MOF can be addressed in order to retrofit its framework structure. An aluminum MOF is reported to be mechanically unstable when subjected to high pressure in a diamond anvil. Precise placement of biphenylene units in the backbone structure in only the *ab* plane, done postsynthetically, affords a mechanically robust framework. The high crystallinity of the MOF before and after application of pressure showed clearly that the added biphenylene units act as “girders” of the right size and shape to make the MOF structure withstand pressure up to 5.5 gigapascal.

Smit et al.<sup>18</sup> have studied through computations the relationship between mechanical stability of a subclass of MOFs, zeolitic imidazolate frameworks (ZIFs), and the functionality attached to the imidazolate linker. Remarkably, they find that the functional groups can either enhance the mechanical stability of the ZIF structure through the formation of a secondary network of linker–linker interactions or soften the material by destabilizing the strong bonds making up the backbone of the ZIF.

### Detecting Pollutants and Trapping Lead Ions from Water

Dincă et al.<sup>19</sup> report a 2D electrically conductive MOF, which they use to demonstrate carbon dioxide sensing for indoor atmosphere monitoring. The sensitivity of the sensor is obtained by incorporating imino-semiquinonate moieties in the MOF backbone. They attribute the observed high

sensing performance under humid conditions partly to hydrated adsorption sites in the MOF.

An interesting approach to making sensors uses ZIFs as “templates” for metal oxide interfaces. Kim et al.<sup>20</sup> show that, by controlling the ratio of water and ethanol in the reaction mixture of ZIFs, it was possible to control the morphological evolution of ZIF rods, sheets, and polyhedra particles. These were calcined to give 1D  $\text{Co}_3\text{O}_4$  rods immobilized onto 2D ZnO sheets with n-type ZnO/p-type  $\text{Co}_3\text{O}_4$  heterogeneous interfaces. These unique structures are found to have exceptional sensing performance for organics.

Water contamination with lead remains a major problem worldwide. Queen et al.<sup>21</sup> report an elegant, inexpensive method for selective binding of lead. They use a MOF with exposed iron ion sites, which, when treated with dopamine, undergoes spontaneous polymerization to polydopamine. This composite removes 99.9% lead(II) from a 1 ppm solution, yielding drinkable water—a performance maintained in river and seawater samples spiked with lead. This attests to the power of using sites within MOFs to incorporate and distribute highly selective metal binding units.

### Covalent Organic Frameworks

Linking organic molecules together by covalent bonds to give crystalline covalent organic frameworks is a maturing major field of reticular chemistry. These covalent bonds offer new advantages compared to MOFs in addition to porosity and crystallinity of 2D and 3D networks—their versatile organic chemistry and relationship to polymers bode well for developing various processing strategies for materials applications. The field has developed rapidly since the initial discovery of 2D and 3D COFs in 2005 and 2007.<sup>22,23</sup> This progress is almost entirely due to two factors: (i) the ability to use different linkage chemistries, especially for linkages originally thought to be less reversible, and (ii) the success of making their reticulated structures in crystalline form. This has been a dream come true for organic chemists since no such organic structures existed prior to 2005. Thus far, extensive research efforts have gone into figuring out the linkage chemistry, the conditions under which to crystallize these COFs, and study of their gas storage, catalytic, and electronic properties. The Outlook by Dichtel et al.<sup>24</sup> summarizes the recent progress made in these areas and highlights the need for better methods to process COFs into materials and devices.

An example along these lines is reported by Gianneschi and Dichtel et al.<sup>25</sup> where the size of nanoparticles of a COF in solution is monitored and quantified using *in situ*

variable-temperature liquid cell transmission electron microscopy techniques. A solution containing these nanoparticles can be cast into transparent COF films, retaining crystallinity and porosity. COF chemists have borrowed many such concepts and techniques from the more established MOF field. Chen, Ma, and Zhang et al.<sup>26</sup> report another approach for making processable COFs. Here, the interior of 2D COFs is used to introduce small monomers, which are then polymerized to produce so-called polyCOFs. One can think of the COF particle as a substituent onto the 1D polymer. This construct can be triggered by vapor to carry out collective motional dynamics (“sit-ups”). In terms of better processability, Cooper et al.<sup>27</sup> discuss in their Outlook discrete molecules with pores (fragments of COFs). These are not very much unlike the traditional calixarenes or cyclophanes in their ability to incorporate guests and their processability into porous molecular solids.

### Multivariable Frameworks

The ability to functionalize the pores of these frameworks is at the heart of addressability and the resulting unique properties, as displayed above. There is however another level of variation, which can be exerted onto the interior of MOFs and COFs: that is, functionalization of the pores with multiple functionalities.<sup>28</sup> This provides opportunities for making “complex” interiors capable of operations that the unfunctionalized or monofunctionalized counterparts are not. The functional groups are introduced *de novo* or postsynthetically. In both cases, a multivariable system of functional groups decorates the pores, where the nature and ratio of functionalities are known, but their spatial sequence arrangements are more challenging to decipher. Efforts are being applied to solving the sequences of these functionalities in the hope that they can be designed to code for specific properties.<sup>29</sup> These qualities are clearly present in the contributions of Wang and Zhou et al.<sup>30</sup> who report a new approach to making multivariable arrangements of not just functionalities but also MOF-on-MOF constructs. This approach results in one MOF surrounded by a different MOF, where each MOF can indeed have multivariable functionalities. In a couple of contributions by Yuan and Zhu et al.<sup>31</sup> and Zhu et al.<sup>32</sup> the multivariable approach to functionalizing the pores of COFs is reviewed, and an example of how this is used to coordinate different metal sites to a COF backbone is given and shown to result in unusually high affinity for ammonia guests.

### Sequence-Dependent MOFs and COFs?

I have just presented an array of research activities in reticular chemistry that go beyond the backbone structure of

the framework and used addressability as a unifying theme. In the past, this field was concerned with making frameworks, both MOFs and COFs, with architectural, thermal, and chemical stability. This virtual issue shows how useful it is to work with robust structures for carrying out sophisticated operations, which were collated under the rubric of ‘addressability in all dimensions’. However, this progress has generated many new questions. Those concerned with the organization of functionalities in the pores are considered here. This is best illustrated when multiple organic functionalities are introduced into the pores or also when such functionalities are metalated by multiple metal ions. The inevitable outcome of these activities is what was already referred to as multivariable functionality. It is multivariable in its spatial arrangement and heterogeneous in the different compositions decorating the interior of the framework. This heterogeneity, at first glance, is discouraging especially to us chemists, because we are used to equating it with mixtures and impurities—an undesirable outcome of chemical reactions.

What makes reticular heterogeneity different and useful is that it is superimposed onto an ordered backbone, ‘heterogeneity within order’. Thus, the distance between the functionalities is known, especially when they are strongly bound to the backbone. Conceptually, this framework’s backbone is similar to the sugar-polyphosphate backbone of DNA onto which nucleotides are covalently bound. It is the spatial arrangements of the nucleotides that gives DNA its coding capability. Although it is a crude analogy, it is tantalizing to imagine that our strongly bound multivariable functionalities can play a role in frameworks similar to that of nucleotides in DNA. Already we and others have observed exceptional enhancement in properties of the multivariable heterogeneous functionality systems compared to the “simpler” counterparts with fewer functionalities. Given the versatility, diversity, and multiplicity of these reticular structures and the precision with which their chemistry is being practiced, implementing the vision of making sequence-dependent MOFs and COFs may very well be within our grasp.<sup>33</sup> Finally, Yaghi et al.<sup>5,34</sup> point out in their reviews that MOFs and COFs have expanded both coordination chemistry and organic chemistry from 0D and 1D to infinite 2D and 3D with a potential for diversity and multiplicity previously unknown in chemistry.

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#### Notes

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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