

Reticular Chemistry—Construction, Properties, and Precision Reactions of Frameworks

Reticular chemistry, the chemistry of linking molecular building blocks by strong bonds to make crystalline open frameworks, has significantly expanded the scope of chemical compounds and useful materials. Metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) exemplify the manner in which this chemistry is practiced and epitomize the molecular-level control being exercised over matter. Typically, MOFs are constructed from metal–oxide units joined by organic linkers through strong metal–carboxyl bond linkages, where it is possible to widely vary the combination of metal ions and organic linkers to achieve the desired framework composition and structure. COFs are constructed from organic building units to make two- and three-dimensional crystalline open organic frameworks with backbone structures that are entirely composed of light elements (e.g., B, C, N, O) and joined throughout by strong covalent bonds. The early work leading to MOFs and COFs required that the linking reactions be designed to overcome the “crystallization problem” and thus give crystalline products whose structure can be definitively characterized using X-ray and electron diffraction techniques. MOFs and COFs would have been considered as only beautiful “sculptures” with nothing else to offer, in terms of properties and reactivity, had it not been for another early advance, namely, that pertaining to their architectural stability and proof of their permanent porosity (i.e., demonstration of gases moving in and out of the pores without deformation or destruction of the framework). The gold standard to show this property is measurement of the $N_{2(g)}$ or $Ar_{(g)}$ adsorption isotherm at 77 K, as originally reported for MOF-2 and MOF-5. The crystallinity of these MOF/COF compounds and their permanent porosity were the properties needed to develop this chemistry beyond mere beauty. Today, members of the MOF and COF compound families have been designed and made to have ultrahigh porosity (500–10 000 m^2/g), high thermal stability (300–500 $^{\circ}C$), and exceptional chemical stability in organic and aqueous media, acids, and bases. In the long line of progress in using covalent chemistry to build organic molecules and inorganic chemistry to build metal complexes, simple and complex alike, the chemistry of MOFs and COFs extends this precision molecular chemistry to frameworks. This framework chemistry would not be possible if not for the fact that metal complexation and covalent organic reactions can be carried out on MOF and COF structures, respectively, with preservation of framework crystallinity and porosity—giving rise to the “chemistry of the framework”. Thus, the stage is set for study of the physical properties and chemical reactivity of MOFs and COFs, and indeed their development in a myriad of applications.

This *ACS Select* collection highlights advances in the (a) sophistication in how MOFs and COFs can be constructed and their components varied to target specific structures, (b) precision with which their interior can be functionalized (including exposed metal ions) to make them suitable catalysts

both as bulk frameworks and as nanocrystals, (c) capability of these frameworks to be dynamic and thus select gases on the basis of gating effects, (d) flexibility in choosing organic linkers with light-emissive properties and others that absorb light to give long-lived charge-separated states, and (e) extension of reticular chemistry to linking of large proteins into 3D biological frameworks.

Most of the known MOFs and COFs have been based on one or two kinds of building blocks; thus, from a structural point of view, these materials are relatively “simple”. Introducing complexity into frameworks is expected to give properties where the whole performs better than the sum of the parts. An interesting strategy by Li and co-workers shows how this goal is accomplished by employing only one kind of linker, pyrazolecarboxylate, but with two metal ions of Cu and Zn.¹ This combination gives rise to three distinct metal-containing secondary building units (SBUs) and geometries that can be arranged to make a mesoporous MOF having four different cages. As a result, tracing a molecule diffusing through the pores of this MOF reveals a sequence of organic linker and metal ion coordination variations previously unknown in MOF chemistry.

It has generally been one of the operating principles in MOF chemistry that the most symmetric networks are the most likely to result from the synthesis, especially when highly symmetric building units are used. This guideline holds for the majority of MOFs. Three contributions in this *ACS Select* collection show how topological complexity can be achieved by producing frameworks belonging to networks of lower symmetry by increasing the complexity of the building blocks. A team led by Zhou and Lan shows how trigonal-prismatic building units can be linked into a lonsdaleite-type network.² Inge, O’Keeffe, Stock, and co-workers report a MOF with unprecedented complexity in that it has 54 unique nodes and 135 edges.³ They attribute this complexity to the presence of aperiodic helical rod SBUs. The ultimate expression of design in reticular chemistry is found in the contribution by Eddaoudi, Trikalitis, and colleagues, where they are successful in making a zirconium MOF incorporating the polybenzene network, which was predicted for carbon about 70 years ago.⁴ Here, judicious selection of the prerequisite hexagonal building units and six connected organic and inorganic building blocks allowed the formation of this rare network. It is found to have one of the highest methane storage capacities observed to date.

Examples of complexity highlighted thus far produce backbone structures of multiple building units or of less symmetric networks. Researchers led by Rosi show how it is also possible to introduce complexity by exchange of linkers with others that are more elaborately functionalized, producing a more complex MOF construct having orthogonal ternary functionalization.⁵ Bein and colleagues use modulators to enhance the crystallinity of COFs and at the same time

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demonstrate how the outer surfaces of these frameworks can be functionalized to have sites amenable to post-synthetic covalent reactions.⁶ The authors report elegant experiments that stain the functionalization sites to show their position on the external surface. **Zhao** and co-workers achieve complexity in the variety of pores they create.⁷ They report a strategy for using mixed linkers to produce new COFs with three different kinds of pore by condensing D_{2h} -symmetric tetraamine and two C_2 -symmetric dialdehyde organic linkers of different lengths.

Going beyond structure to physical properties, the reticulation of organic building units into frameworks to make COFs can overcome quenching caused by aggregation, which is the most common emission quenching mechanism. **Jiang** and co-workers report a highly emissive COF based on a novel aggregation-induced emission, employing organic polygons as vertices.⁸ This structure modification yields crystalline porous COFs with periodic π -stacked columnar arrays, which dominate the luminescence of the COF and achieve exceptional quantum yield by a synergistic structural locking effect of intralayer covalent bonding and interlayer non-covalent π - π interactions. **Huang** and co-workers use zeolitic imidazolate frameworks (a subclass of MOFs) to achieve an exceptionally long-lived charged-separated state with implications for photocatalytic applications of frameworks.⁹

Frameworks of mechanical flexibility are intriguing for their potential as selective systems. **Matsuda**, **Kitagawa**, and colleagues find that they can use gating effects to discriminate between adsorbates such as carbon dioxide and acetylene.¹⁰ The material they report shows gate-opening type adsorption for acetylene but not for carbon dioxide. **Sholl** and co-workers deploy computational tools to measure the hopping rates of many different molecules within the archetypical ZIF-8.¹¹ Here, umbrella sampling and dynamical correction calculations include flexibility, which is found to be critical in accurately describing molecular diffusion in this material.

Chirality can be introduced into frameworks, and **Coudert** and co-workers report on a process of chiral induction in frameworks by non-chiral guest adsorption in MOF-5.¹² Their results show that the molecular size and chemical nature of *N*-methyl-2-pyrrolidone give rise to chiral transformation in MOF-5, which does not occur with other guest molecules, such as *N,N*-dimethylformamide. Enantiopure peptide-functionalized MOFs are reported by **Canivet** and co-workers.¹³ They use microwave-assisted post-synthetic methods to give enantiopure peptides anchored inside MOF cavities of Al-MIL-101-NH₂, In-MIL-68-NH₂, and Zr-UiO-66-NH₂ for asymmetric catalysis.

MOFs are increasingly being used as platforms to control matter by positioning magnetic and catalytic entities on their internal surface. **Wriedt** and co-workers apply this concept to single-molecule magnets (SMMs) by incorporating Mn₁₂O₁₂-(O₂CCH₃)₁₆(OH₂)₄ clusters under mild conditions into a highly porous MOF.¹⁴ The incorporated clusters exhibit significantly enhanced stability as well as location- and direction-specific loading of the SMM. **Grzybowski** and co-workers show how incorporating nanocrystals in MOFs renders them photoconductive when charge transport occurs via tunneling between spatially separated nanocrystals within a small percent of the MOFs' accessible pores.¹⁵

The flexibility with which MOFs' composition, structure, and pore metrics can be varied lends itself to their application as catalysts. Several approaches are reported in this ACS *Select* collection. **Gagliardi**, **Hupp**, **Marks**, **Cramer**, **Delferro**, **Farha**, and co-workers use MOFs (Hf-Nu-1000) to embed a single-site

organozirconium catalyst, which is found to be promising for ethylene and stereoregular 1-hexene polymerization.¹⁶ **Lin** and colleagues show how MOF nodes can be utilized as single-site magnesium-alkyl catalysts for hydroboration and hydroamination reactions.¹⁷ This MOF displays very high turnover numbers for ketone hydroboration. **Dincă** and co-workers also report single-site MOF catalysts for olefin polymerization.¹⁸ Here, metal ion exchange of zinc in the MOF with more reactive metals leads to high selectivity for polyethylene with controlled molecular weight and morphology. A creative approach to building biocatalytic MOFs is reported by a team led by **Shieh**, **Wu**, and **Tsung**, who embed enzymes into microcrystalline MOFs.¹⁹ The researchers demonstrate that 10 nm catalase molecules are incorporated in 2 μ m single crystals and show activity in hydrogen peroxide degradation, even in the presence of protease proteinase K.

Work is underway to determine how thin-film growth of MOFs can be accomplished for various device applications. **Terfort** and co-workers show how layer-by-layer growth of a surface-attached MOF can be achieved and studied by various surface characterization techniques.²⁰ **Gianneschi** and co-workers grow MOFs in a liquid cell for transmission electron microscopy studies that will enable direct observations of solution-phase nanoscale MOFs.²¹ The team shows that, by controlling the liquid cell membrane surface chemistry and electron beam conditions, the dynamics and growth of MOFs can be observed despite of their sensitivity to electron beams.

Researchers led by **Tezcan** describe an extension of reticular chemistry to protein-based frameworks.²² They report a three-dimensional, porous, crystalline framework formed by linking spherical protein nodes. The octahedral iron storage enzyme, ferritin, is engineered in its C_3 -symmetric pores with tripodal zinc coordination sites. Crystallographic studies show that this Zn-ferritin construct could assemble into the desired bcc-type crystals upon coordination of a ditopic linker bearing hydroxamic acid functional groups. This example is the first protein-based MOF, which is believed to be the earliest member of a large family of such frameworks.

This ACS *Select* collection exhibits contributions representing only a small fraction of the large body of publications in the *Journal of the American Chemical Society*. The specific work highlighted here shows the richness of the chemistry of frameworks: from backbone design and variation to using the internal space to further control matter on the molecular level and achieve interesting properties which otherwise are not possible. The chemistry of frameworks retains at its core the fact that, when molecules are linked into frameworks, they become fixed in a specific geometry and spatial arrangement—much like how molecules fix atoms in place with specific geometry and spatial arrangement. In other words, the molecule to the atom is what the framework is to the molecule, with the added advantage that the framework provides pores in which matter can be further manipulated and controlled. In a recent JACS Perspective titled “Covalent Chemistry beyond Molecules”, **Yaghi** and his co-authors summarize how the chemistry of linking molecular building blocks into frameworks and their further covalent modification represents a natural progression of molecular chemistry to extended structure regimes.²³ A companion virtual issue covering several ACS journals and highlighting the various emerging applications of MOFs and COFs²⁴ is appearing alongside this ACS *Select*.

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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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