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Molecule-Constructed Microporous Materials: Long under Our Noses, Increasingly on Our Tongues, and Now in Our Bellies

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Crystalline, microporous materials—that is, exhibiting permanent/accessible pores of molecular (< 2 nm) dimensions—constructed from molecular components have been under our noses now for over four decades. Historical examples arose from the study of crystalline clathrates (e.g., Dianin's compound, Werner clathrates) that were discovered to be formally porous. Increasingly, however, molecule-constructed microporous materials are on our tongues in the context of materials design, as the power of synthetic chemistry is progressively being brought to bear on materials related issues. Indeed, science continues to challenge truths related to our current inability to formally predict the crystalline structure—or, therefore, the properties—of molecular materials from a simple knowledge of their building blocks. While Maddox's famous, two-decade old assertion[1] regarding the problem of crystal structure prediction resonates nearly as true today, most contemporary efforts in the synthesis of molecule-constructed materials circumvent the issue of structure prediction by employing empirical strategies that attempt to exploit known, reproducible, structural building blocks.

The empirical approach has been particularly fruitful in the development of new microporous materials. Efforts in crystal engineering have led to molecular crystals that exhibit microposority,[2] "porosity without pores",[3] or other important properties (e.g. reactivity, polarity). Moreover, in recent years it has become almost routine to connect multi-topic organic ligand struts by inorganic coordination clusters to give crystalline coordination polymers or metal–organic frameworks (MOFs) that, through judicious choice of components, can often be expected to exhibit microporosity.[4] Similarly, crystalline covalent organic frameworks (COFs) are now possible through the reversible condensation of rigid, symmetrical molecular precursors. And if one eschews the issue of crystallinity, polymers of intrinsic microporosity (PIMs) are available by the condensation of rigid molecular units that are unable to close-pack. Many of these approaches are buoyed by coincident advances in the fields of supramolecular chemistry, self-assembly, and coordination chemistry and, while an appreciable level of structural design is possible in certain chemical systems—for example, through the reticular approach[5]—the role of serendipity in materials synthesis remains an important one. Two recent articles by Stoddart, Yaghi and co-workers[6,7] illustrate the roles of design and serendipity at the crossroads of emerging applications for molecule-constructed microporous materials.

At a rudimentary level, crystal microporosity permits an influence on the dynamic behavior of atoms and molecules—for example, rotation/translation, uptake/release, sampling/recognition, switching, reaction—within ordered, three-dimensional nanoenvironments. It is no wonder then that porosity is coupled to technologically useful properties such as ion exchange, separations, storage, heterogeneous catalysis, etc. In an effort to couple the addressable dynamics of mechanically interlocked molecules with the tunable crystalline arrangements afforded by MOFs, a strategy that has been described as robust dynamics,[8] the Stoddart and Yaghi groups have for the first time successfully anchored a molecular catenane within a three-dimensional (3D) MOF (Figure 1).[6] Possessing unresolved chirality, ethynyl moieties, cationic charge, counteranions, high surface area, and exceptional length (3.3 nm!), the catenated ligand (±)-$[H_2\mathbf{L}][PF_6]_4$ presents a significant challenge to a reticular design strategy.

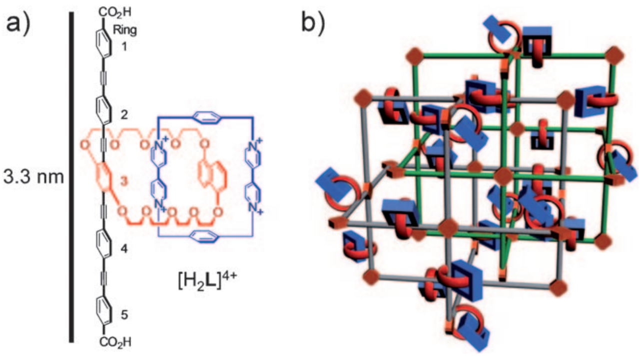

Figure 1. MOF-1030, a three-dimensional coordination polymer constructed from an exceptionally long, catenated ligand. a) The 3.3 nm ligand strut, $[H_2\mathbf{L}][PF_6]_4$. b) The ***nbo*** framework structure of MOF-1030.

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Thus, it is probably fair to suggest that the structural particulars of the exemplary MOF-1030 (e.g. **nbo** topology) were not part of the original blueprint. Regardless, there was/is a reasonable expectation that (±)-$[H_2\mathbf{L}][PF_6]_4$ and emerging ligands would/will assemble with metal ions into open 3D frameworks under some set of synthetic conditions. These ligands are therefore likely to provide new opportunities in the robust dynamic regime. Further progress can be expected and the next step, clearly, is to incorporate dissymmetric catenanes whose bistable states can be addressed by external stimuli. No doubt, it is only a matter of time before even these complex ligands can be reticulated into MOFs with a reasonable degree of confidence in terms of the structure design.

Another recent paper by Stoddart and co-workers pushes the emerging applications envelope in a different direction. The construction of MOFs from biologically compatible and/or renewable components is rare. In a remarkable finding, the structures of seemingly simple alkali metal salt complexes of the C_8-symmetric γ-cyclodextrin (γ-CD, Figure 2)—so-called CD-MOFs of composition $[(\gamma\text{-CD})(MX)_2]_n$ ($M^+ = Na$, K, Rb, Cs; $X^- = OH^-$, halides, RCO_2^-, etc.)—were established and demonstrated to be microporous.[7] Scarcely does a discovery emerge at the confluence of so many topical branches of chemistry—green chemistry; food chemistry; materials: molecular, low-density, homochiral, microporous; host–guest chemistry; nanoscience, etc. Perhaps foremost, the CD-MOFs are the quintessential "green" materials. They are synthesized under benign conditions from renewable, food-grade components, they are edible, and are seemingly poised to find application in food science or biological (e.g. drug) delivery.

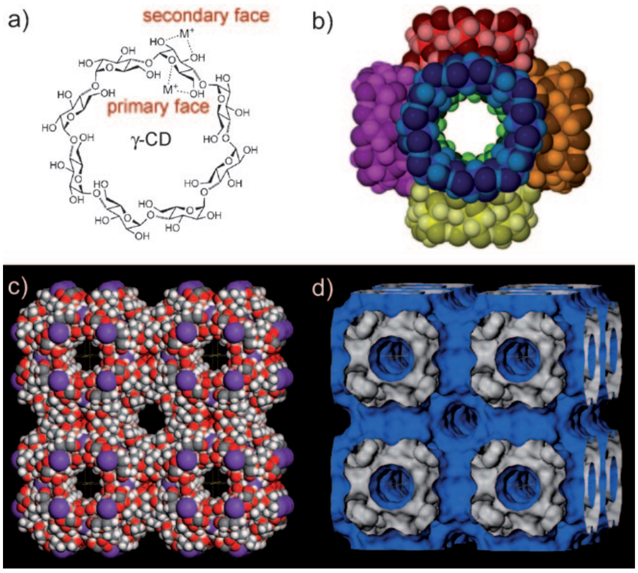

Figure 2. Edible CD-MOFs derived from γ-CD: a,b) Edge-connection of six γ-CDs generates a large central cavity. c) Model of the cubic CD-MOF frameworks and d) their solvent accessible pores.

From the perspective of structure, it is remarkable that the CD-MOFs are cubic; most CD materials are columnar. A cubic structure effectively requires an open topology as the γ-CDs do not possess the three-fold symmetry required of cubic systems. Crystal symmetry appears to trump packing efficiency in these materials, facilitated by the eight-coordinate chelation of the alkali metals ions by four γ-CDs—two chelating to the metal through primary hydroxy groups and glycosidic oxygen atoms, and two chelating through the secondary hydroxy groups. In this sense, the C_8 symmetry of the γ-CD may be key, as it is compatible with the fourfold symmetry requirements of the faces of a cubic unit cell. Edge connection of the primary faces of six γ-CD tori generates large, open (ca. 18 Å diameter) cages that are connected to adjacent cages by face-shared secondary faces. The resulting low-density, cubic packing is reminiscent of that adopted by some other recent porous molecular crystals—e.g., porous phthalocyanine crystals.[2]

From the perspective of properties, the crowded coordination sphere of the metals and extensive hydrogen bonding between adjacent γ-CDs appears to impart rigidity to the CD-MOFs, allowing the extraction of included solvents without collapse of the structure. Thus, CD-MOFs derived from Na^+ are low-density and possess large pore volumes, a feature that bodes well for storage applications. The CD-MOFs are also homochiral, a feature that provides obvious advantages over traditional, achiral inorganic microporous materials. Lastly, it seems to be significant that the CD-MOFs are constructed from components that may be exploited in terms of their host–guest chemistry. An emerging means of introducing functionality (e.g. separations, selective catalysis) into MOFs is their construction from selective complexation agents. Our own modest contribution in this regard involves the synthesis of coordination polymers from container molecules.[9]

It should be credited that a material isostructural to the CD-MOFs was earlier reported by Gatteschi and co-workers.[10] Due to crystal quality issues, however, elucidation of the crystal structure and hence the exact composition of this material was not possible. Moreover, these authors did not demonstrate the porosity of the CD-MOF. Nonetheless, the cubic phase was used to confine maghemite ($\gamma\text{-}Fe_2O_3$) nanoparticles with a rather uniform dispersity (18 Å, $\sigma = 0.19$). The structure determinations of the cubic CD-MOFs by the Stoddart group now make it apparent that the $\gamma\text{-}Fe_2O_3$ nanoparticles of Gatteschi and co-workers were confined within the large, 18 Å diameter cages of the $[(\gamma\text{-CD})(NaOH)_2]_n$ structure, and were capped by the primary faces of six γ-CD tori. So, nanoscience applications of the CD-MOFs are already a reality.

Considering the possibilities for synthetic modification of the CDs, it will be interesting to discover the extent to which functional group manipulations will be compatible with CD-MOF microporosity. Remarkably, nearly 120 years after the discovery of the CDs, surprises continue to unfold and the new CD-MOFs are poised to develop into a broad family of useful molecule-constructed materials.

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