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Control over Catenation in Metal−Organic Frameworks via Rational Design of the Organic Building Block

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Metal−Organic Frameworks (MOFs) are a novel class of hybrid materials made from metals and organic compounds with numerous potential applications.[1] MOFs are one of the most significant breakthroughs in solid-state science and have garnered significant attention from a number of researchers in chemistry, physics, materials science, and biology. These fascinating materials are characterized by large internal surface areas, ultralow densities, and uniformly structured pores and channels. Among the many applications that may capitalize on these extraordinary properties are gas and chemical storage,[2] chemical separations,[3] sensing,[4] selective catalysis,[5] ion exchange,[6] and drug delivery.[7]

Most of the applications mentioned above require pure-phase materials that retain their full porosities after guest removal. It is also imperative that pore cavities in MOFs have the largest void volume possible. Indeed, we have recently proposed a solution to circumvent a typical MOF collapse scenario upon thermal activation by introducing a supercritical treatment method.[8] We have also developed a method that allows for the separation of different MOF phases based on density differences.[9] Although density-based separation is a powerful technique, it does not address the principal problem that results in the formation of multiphased products: catenation (i.e., interpenetration or interweaving of two or more identical and independent frameworks). Obtaining a single network (noncatenated) MOF product, which is a direct route to the highest porosity, has proven to be problematic in the majority of cases, especially when the strut (ligand) used to construct the framework is large. Catenation imposes a severe limitation on efforts to expand surface area and/or decrease density by employing lengthier ligands for the framework structures. High degrees of catenation overall tend to diminish the porosity. While 2- and 3-fold catenation are routinely encountered in MOF structures,[10] examples of significantly higher degrees of catenation are also known.[11] Noncatenated systems should have larger channels and pores than their catenated counterparts, a feature of value in certain catalysis applications. (On the other hand, catenation can be useful for precise pore sizes, essential for separations.)

In their ground breaking work on the IRMOF (isoreticular metal-organic framework) homologous series,[12] Yaghi and co-workers were the first to show the systematic assembly of MOFs without changing the topology. In order to produce a reasonable quantity of a noncatenated version of IRMOFs, however, very high dilutions are required. Still, the well-known IRMOF-1 (MOF-5) can be contaminated with its doubly catenated counterpart,[13] thus complicating the study of its properties such as surface area and gas sorption. Thus, dilution did not prove itself as a general method to completely avoid interpenetration. For example, IRMOF-0 (acetylenedicarboxylic acid is used as ligand) could only be made in its 2-fold catenated version.[14] Ma and co-workers utilized an alternative strategy, based on templating agents (oxalic acid), to produce noninterpenetrated materials.[15] To date, only a single example has been reported, and no apparent generality demonstrated for this method.

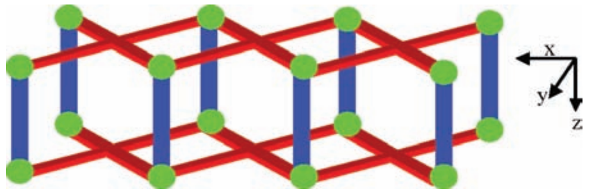
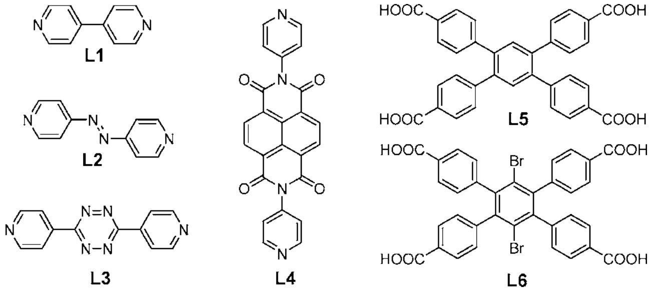


Figure 1. Cartoon representation of the 2D sheet formation by the tetraacid ligand (red) pillared by a dipyridal strut (blue). The green corners are the zinc paddlewheel nodes.

More recently, Shekhah and co-workers have shown that they can suppress catenation by using “liquid-phase epitaxy” on an organic template[16] and then employing a step-by-step growth method.[17] This elegant work demonstrated that the paddlewheel compound, MOF-508, could be synthesized as a noncatenated material in contrast to the solvothermal method, which always generates two networks.[18] Unfortunately, liquid-phase epitaxy is only applicable for small-scale MOF fabrication, limiting the use of this method to surface-related applications only. Yet there are numerous cases where bulk quantities of these materials are required. Currently, a versatile method that can produce large quantities of both the catenated and noncatenated versions under the same condition is nonexistent.

Scheme 1. Representation of Structures of Struts and Starting Materials



Herein we demonstrate an approach to suppress catenation through careful ligand design that controls network growth. We have previously reported a tetracarboxylic acid ligand (4,4′,4″,4‴-

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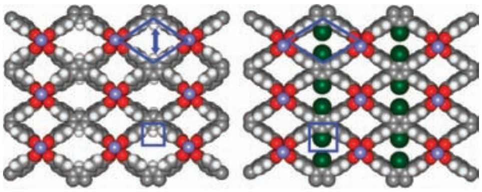
benzene-1,2,4,5-tetrayl-tetrabenzoic acid, **L5**; Scheme 1).[19] We envisioned that the deprotonated **L5** would favor the formation of comparatively large cavities that resist the formation of catenated MOFs. Also, we rationalized the use of a tetratopic building block to produce robust frameworks, which is desirable for MOF applications. Indeed, the solvothermal reaction of **L5** and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF (Dimethylformamide) at 80 °C for 24 h afforded in high yield a noncatenated MOF.[19] Then we examined the use of **L5** to form pillared paddlewheel MOFs, which we have previously described based upon mixed-ligand Zn(II) coordination to linear dicarboxylates and dipyridyls.[18a] We reasoned that ligand **L5** would form a 2D sheet within the *xy*-plane, which could be pillared by a dipyridyl ligand (see Figure 1). The 2D sheets can function as *scaffolds* for dipyridyl ligands. This allows for diverse functionalities to be incorporated into new functional MOFs. MOF materials that were made in this fashion produced several examples of noncatenated[5a,20] as well as catenated structures.[21] We noticed that in the instances where noncatenated MOFs formed, we used either a sterically demanding (porphyrin-based or trimethylsilane-protected struts) or a hydrogen-bonding capable (diol-containing) dipyridyl ligand. On the other hand, the linear dipyridyl ligand *N*,*N*′-di-(4-pyridyl)-1,4,5,8-naphthalenetetracarboxydiimide produced a pillared paddlewheel structure that is catenated where the dipyridal strut resides directly in the middle of the diamond-shaped cavities formed by two of the **L5** ligands (see Scheme 2). From this structure, we concluded that the sterics of the dipyridyl moiety plays a significant role in the control of catenation.

Scheme 2. Crystallographically derived space-filled *ab*-plane looking down the *c*-channel using **L5** (left) and **L6** (right) (yellow = Zn, red = O, green = Br, blue = N, gray = C, white = H).



We therefore redesigned ligand **L5**, expecting to suppress catenation by introducing additional steric blockage in the *xy*-plane. We reasoned that ligand **L6**, bearing two large bromine atoms instead of hydrogen atoms (as in **L5**), would suppress the formation of interpenetrated structures. To verify our hypothesis, we constructed paddlewheel MOFs using **L6** with the same dipyridyl moieties used to create paddlewheel structures with **L5**. Indeed, the approach using **L6** produced only noncatenated materials, where under the identical conditions **L5** produced 2-fold catenated structures. Overall, a rational comparison between a total of eight materials, four with ligand **L5** (2-fold catenated; **1**, **3**, **5** and **7**) and four with ligand **L6** (noncatenated; **2**, **4**, **6** and **8**), supports this hypothesis. The only variable in the synthesis is the identity of the tetra-acid (**L5** or **L6**). Thus a change from aryl-H moieties to aryl-Br furnished on the tetraacid ligand is sufficient to suppress an undesired catenation by contracting the diamond shaped opening (Scheme 2). The general method to assemble these materials via static heating of L_{bp} (**L1**, **L2**, **L3**, or **L4**), L_{ta} (**L5** or **L6**), and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF and one drop of concentrated HCl at 80 °C for 24 h resulted in single crystals suitable for X-ray diffraction (bp = bipyridal; ta = tetraacid). Analysis of the single crystal data reveals a framework formula of $Zn_2(L_{bp})(L_{ta})$ with either noncatenated or 2-fold catenated networks (Figure 2). L_{ta} bridges the Zn(II) dimers and forms flat two-dimensional sheets that can be pillared by L_{pb}. Thermogravimetric analysis (TGA) of **1**−**8** revealed significant mass loss between 115 and 175 °C depending on the material. This is assigned to DMF molecules, and no further mass loss was observed until 300 or 400 °C, conditional on the material. Materials **2**, **4**, **6**, and **8** show greater solvent loss than **1**, **3**, **5**, and **7**, which is expected going from a 2-fold catenated material to noncatenated material (see Figure 3a and Figures SI9−11). The purities of the samples were determined by powder X-ray diffraction (PXRD) (see Figures SI1−8).

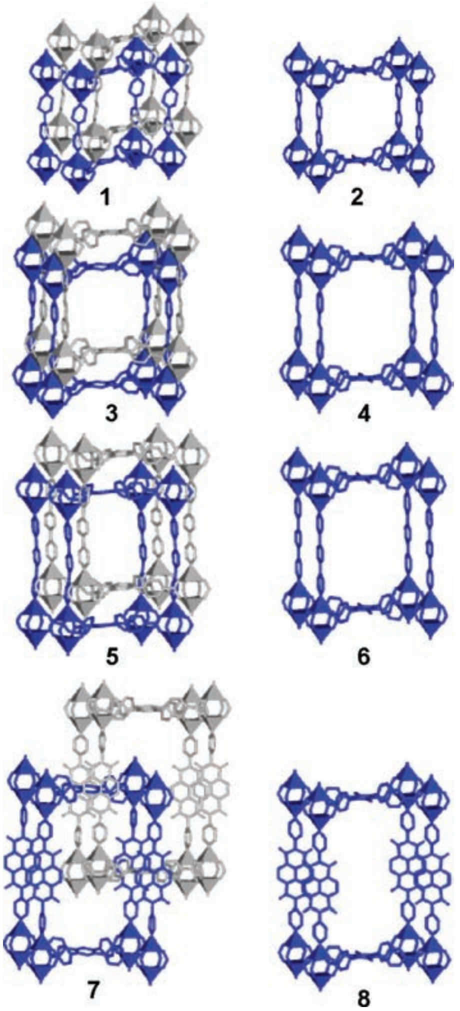


Figure 2. Single crystal X-ray structures: 2-fold catenated structure with building block **L5** (left) and noncatenated structures with building block **L6** (right).

Unlike most pillared paddlewheel MOF structures, those of **1**, **3**, **5**, and **7** are inter*penetrated* as opposed to inter*woven*, such that the networks are maximally displaced from one another.[1] All have L_{bp} pillars that reside directly in the center of the diamond-shaped cavities formed by two of the L_{ta} ligands. Compound **7** has a unique structure in that it is interpenetrated instead of interwoven with respect to the *x*,*y*-plane as well as the *z*-direction. The other three (**1**, **3**, and **5**) are only interpenetrated in the *z*-direction and interwoven in the *x*,*y*-plane.

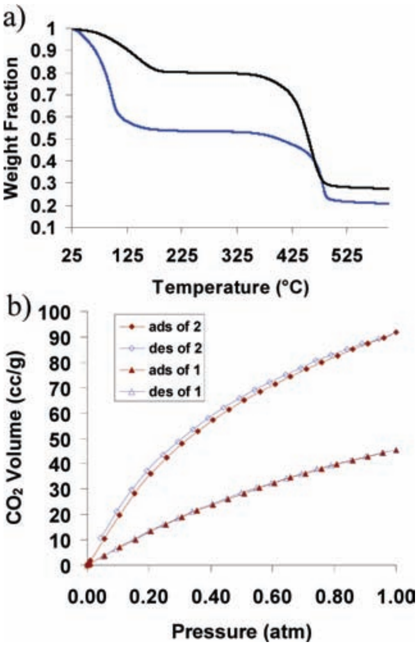


Figure 3. (a) TGA traces of **1** (top) and **2** (bottom) and (b) CO_2 isotherm at 273 K of **1** and **2**.

The porosity of **1**−**8** was examined using CO_2 at 273 K. Based on the TGA (thermogravimetric analysis), pore evacuation/ "activation" was performed for 24 h at 90 and 100 °C for the noncatenated and catenated, respectively. The only exception was compound **L5**, which was activated using supercritical CO_2[8] because heating and low-boiling-solvent exchange gave a very low surface area. Based on nonlocal density functional theory (NLDFT) analysis (see Table SI-1), all of these compounds have moderate surface areas. For example, compounds **1** and **2** gave CO_2 accessible surface areas of 535 and 980 m^2/g respectively (see Figure 3b). This shows that porosity and sorption properties can be different for the two cases. Furthermore, the step in the isotherm at $P/P_o \approx 0.022$ in **7**, attributed to the potential dynamic structural behavior upon activation and guest adsorption,[21] disappears in **8** when the catenation is suppressed. This illustrates the importance of studying the properties of both catenated and noncatenated structures to completely elucidate their behavior.

In conclusion, we have demonstrated that by appropriate design of organic building blocks (robust tetratopic carboxylates), the degree of catenation of MOFs can be controlled. These MOFs can now be designated as scaffolds on which to incorporate features needed for effective catalysis, gas sorption, and chemical separation, i.e., tunable porosities. We are currently investigating other MOF systems to ascertain the extent to which this method can be further generalized.

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Supporting Information Available: Experimental procedures, X-ray crystallographic files in CIF format, PXRD, TGA, and sorption isotherm data. This material is available free of charge via the Internet at http:// pubs.acs.org.

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