delocalized electrons on the linkers between the chains, exhibit very low T_N values (4–10 K). The presence of these π electrons drastically enhances the magnetic characteristics of these solids above the strategic borderline of liquid nitrogen temperature. This renders porous solids magnetic with sufficiently high and available ordering temperatures which could now find applications, for example, in magnetic sorting.

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Infinite Secondary Building Units and Forbidden Catenation in Metal-Organic Frameworks**

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Catenation, in the form of interpenetrating and interweaving,[1] has been a major concern in the design of low-density (porous) structures due to the following widely held beliefs: a) the use of long links for the design of frameworks with large pores results in catenated structures and thus small pores, b) highly catenated frameworks typically have low porosity (<20%), and c) catenation contributes negatively to the structural stability and porosity of open frameworks.[1, 2] We recently found in the chemistry of metal-organic frameworks (MOFs) that *discrete* secondary building units (SBUs) are important for designing structures with attributes that disprove the universality of b) and c); specifically, maximally interpenetrating MOFs have been shown to have highly porous (>65%) structures, and interweaving in open frameworks has been recognized and used for the design of structures with reinforced walls and permanent porosity.[1c–d, 3]

Herein, we introduce the use of *infinite* SBUs toward addressing the point presented in a). Specifically, we show that MOF-69A, $[\text{Zn}_3(\text{OH})_2(\text{bpdc})_2] \cdot 4\,\text{DEF} \cdot 2\,\text{H}_2\text{O}$ (bpdc = 4,4'-biphenyldicarboxylate; DEF = *N,N'*-diethylformamide), and its 2,6-naphthalenedicarboxylate (ndc) analogue MOF-69B have three-dimensional (3D) structures constructed from infinite Zn-O-C SBUs and long bpdc or ndc links that expand the Al net in SrAl_2 and provide a framework where catenation is forbidden.

Infinite Zn-O-C SBUs were produced by subjecting reaction mixtures that typically give MOF-5 to increasing amounts of H_2O_2.[4] These solutions were monitored for the appearance of crystalline solids. A single-crystal X-ray diffraction study[5a] performed on a rodlike colorless crystal of MOF-69A

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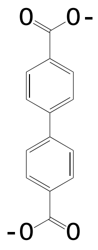

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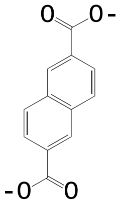

ndc

revealed the presence of a 3D network that is constructed from columns of Zn-O-C units running along the [001] direction (Figure 1a). In the asymmetric unit there are three crystallographically unique Zn atoms that are bridged in a di-monodentate fashion by four carboxylate groups, each from a different bpdc link. The Zn atoms are also bound to two hydroxy groups to give two tetrahedral and one octahedral Zn centers arranged in a coplanar fashion. Assignment of the bridging oxygen atom as a μ_3-hydroxy group was confirmed by comparing the Zn-O(H)-Zn angles (93.7(3), 110.2(5), 110.3(5)°) in MOF-69A to those typically found in the analogous molecular Zn complexes containing μ_3-hydroxy groups (103.3(1), 110.7(2), 112.2(2)°), in which the angles are close to the expected tetrahedral geometry rather than the trigonal-planar one generally observed for μ_3-oxy groups.[6, 7] Interestingly, the Zn-O-C connectivity pattern observed in MOF-69A is identical to the one observed in the structure of discrete basic zinc crotonate, $[Zn_5(OH)_2(O_2CHCHCH_3)_8]$, in which similar μ_3-hydroxy groups are also present.[6b]

The infinite Zn-O-C columns in MOF-69A are stacked in parallel and connected in the [110] direction by the biphenyl links to give one-dimensional (1D) rhombic channels of 12.2 Å along an edge and 16.6 Å along the diagonal[8] (Figure 1b) into which four DEF and two water molecules per formula unit reside as guests. Two DEF molecules were found hydrogen-bonded to μ_3-hydroxy groups (O⋯H⋯OC 2.81 Å for MOF-69A), while the remaining two DEF and two water guests are disordered in the crystal, an aspect that facilitates their liberation from the pores (vide infra).

To fully appreciate the structure of MOF-69A and how its topology is a prototype for frameworks that *will not* catenate, it is instructive to connect all the points-of-extension (the carboxylate C atoms) in the structure. This gives a tetrahedral net with the C atoms at the vertices (Figure 1c). Closer examination of this net shows that the Zn-O-C columns become square ribbons, corresponding to the infinite SBUs, and the biphenyl units represent the lines that connect the SBUs together. This topology is identical to that of the Al net in $SrAl_2$.[9] However, unlike $SrAl_2$, MOF-69A has an open structure due to expansion of the Al net with Zn–O links (within the SBUs) and C_6H_4–C_6H_4 links (between the SBUs). Such an arrangement provides two important distances that impact catenation: a short distance between carboxylate C atoms along the [001] direction (5.839(3) Å and 6.237(3) Å), and a longer one in the [110] direction (between the SBUs) (10.069(4) Å). The first distance allows the long links to come closer together such that the phenyl rings of each bpdc linker have a torsion angle of 28.9(1)° and, more significantly, form close mutual CH⋯π interactions (3.73 Å) to adjacent links resulting in an impenetrable wall of bpdc units (Figure 1d). For this structure to catenate, an additional bpdc would have to fit between adjacent links which is metrically impossible and thus results in a structure that forbids catenation.[10]

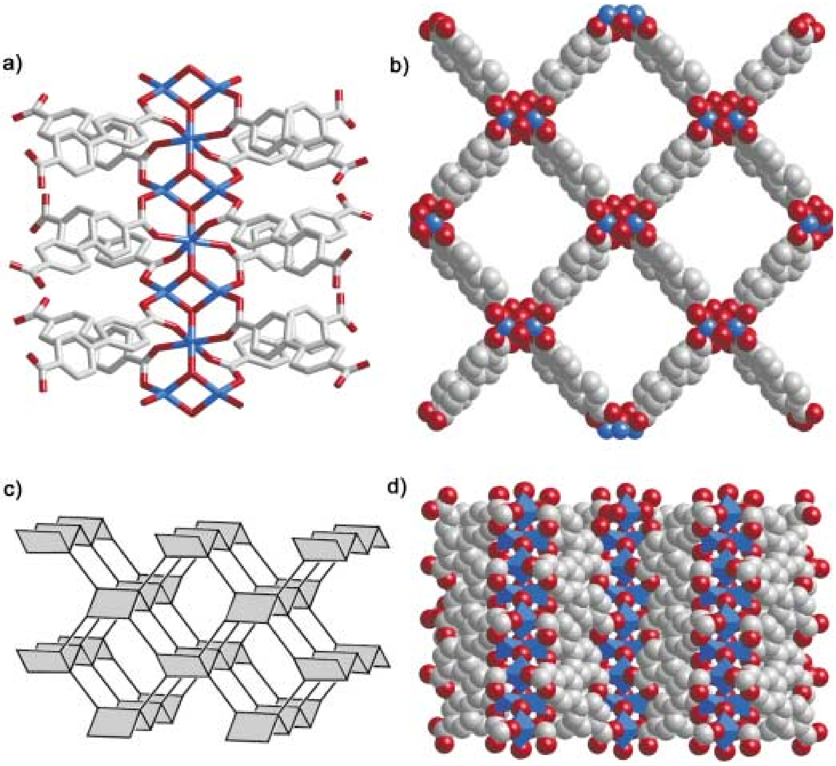

Figure 1. The crystal structure of MOF-69A, $[Zn_3(OH)_2(bpdc)_2]\cdot 4DEF\cdot 2H_2O$, containing a) infinite Zn-O-C SBUs that are linked together by bpdc links to form b) a 3D network with large channels running along the [001] direction (as shown) where the four DEF and two water guests per formula unit reside. c) This framework has the topology of the Al net in $SrAl_2$, which creates a structural arrangement where d) the walls of the channels are impenetrable as a result of close biphenyl–biphenyl CH⋯π interactions leading to a structure motif that will not catenate regardless of the linker's length.

The implication of this finding is that linkers of longer lengths than bpdc and the same width (one benzene ring) can be employed in identical syntheses to produce the same framework but with correspondingly larger pores. As a first step in this direction, we have demonstrated that the infinite SBUs present in MOF-69A can be reproduced with ndc to give the isostructural compound formulated as $[Zn_3(OH)_2(ndc)_2]\cdot 4DEF\cdot 2H_2O$ (MOF-69B).[5b]

Given that infinite SBUs heretofore have not been recognized and used in the context of design and construction of MOFs, we sought to probe the structural stability of MOF-69A and the mobility of the guests within its pores. Calculation of the pore space in MOF-69A reveals that about 67% (66% for MOF-69B) of the structure is occupied by guest molecules.[11] Thermal gravimetric analysis (TGA) performed on a sample of the as-synthesized MOF-69A showed one sharp weight loss of 37.1% in the range 25–150 °C that continued slowly until 400 °C which is equivalent to the loss of four DEF and two water molecules per formula unit (calcd: 38.2%). For MOF-69B, two distinct weight loss steps were observed: 21.2% in the range 40–150 °C and an additional 19.1% in the range 150–400 °C, which correspond to the consecutive loss of two DEF and two water (calcd: 21.7%), and two DEF (18.4%) molecules, respectively. Presumably, the latter weight loss is due to the two strongly hydrogen-bonded DEF guests in the crystal structure of MOF-69B. This was unobserved as a distinct weight loss in MOF-69A perhaps due to weaker hydrogen-bonded interactions. It appears that the hydrogen-bonded DEF molecules are crucial to the stability of MOF-69, as illustrated by a variable-temperature X-ray powder diffraction (XRPD) study performed on both MOF-69A or B between 50 and 300 °C in 50 °C increments. Comparison of the XRPD patterns at these temperatures to those of the as-synthesized samples of MOF-69A and B showed that MOF-69A maintains its crystallinity up to 150 °C, while for MOF-69B a more complex behavior is observed: a new phase begins to emerge at 150 °C, which results from the loss of the non-hydrogen-bonded DEF and water guests. The original phase can be regained by introduction of DEF into solids of MOF-69B that have been heated up to 250 °C. For both MOF-69A and B heating above 150 °C and 250 °C, respectively, leads to an irreversible loss of crystallinity; specifically, attempts to regain crystallinity of the heated solids by reintroduction of DEF were unsuccessful, pointing to the importance of hydrogen-bonded DEF guests to the integrity of the structure.

MOF-69A and B are quite stable to exchange of guests in solution. Immersion of as-synthesized samples into benzene, chloroform, isopropanol, tetrahydrofuran, and toluene, typically overnight with three cycles of supernatant removal followed by fresh solvent addition, showed complete exchange of DEF.[12] The exchange process does not result in destruction of the framework as evidenced by XRPD, where the exchanged solids showed sharp XRPD lines albeit some shifts of the lines from their original position were observed. Preliminary evidence suggests that the shifts can be related to slight contraction of the framework in the [100] direction accompanied by corresponding elongation in the [011] direction. Further work is underway to quantitatively characterize these distortions. Nevertheless, the exchange process is fully reversible in that reintroduction of DEF into the channels gives an XRPD pattern identical to that of the starting MOF-69 material.

Encouraged by the solution–guest exchange and thermal stability, we attempted to evaluate the rigidity of the MOF-69A and MOF-69B frameworks. The samples were evacuated in a CAHN C1000 microbalance under reduced pressure (1×10^{-5} Torr) until no more weight loss was observed. The evacuated sample was exposed to different gas and organic vapor sorbates using published protocol.[13] No sorption of N_2 or Ar was observed, possibly due to the flexibility of the framework. Nevertheless, we observed that benzene can be sorbed into the pores of MOF-69B: exposure of an evacuated sample to near saturated benzene vapor pressure (65.7 Torr) resulted in 1.04 benzene molecules sorbed per formula unit.

We have demonstrated a strategy for realizing frameworks with large pores as exemplified by MOF-69 where a direct dependence is established between long links and the achievement of large pores, without the complications commonly observed due to catenation. Consideration of infinite SBUs in MOF-69 as rods or cylinders points to establishing design strategies based on rod packing for the synthesis of mesoscopic MOFs.

Experimental Section

MOF-69A: A solid mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (24.6 mg, 0.083 mmol) and H_2bpdc (10 mg, 0.041 mmol) was dissolved in a vial containing DEF (12 mL), 30% H_2O_2 (0.40 mL), and $MeNH_2$ (0.20 mL, 51.4 mM in DMF). The mixture was allowed to stand in a capped vial for seven days at room temperature. Colorless crystals of MOF-69A were collected and air-dried (21 mg, 86.1% yield). This compound is insoluble in water and common organic solvents. Elemental analysis calcd (%) for $[Zn_3(OH)_2(bpdc)_2] \cdot 4DEF \cdot 2H_2O$: C 50.08, H 5.78, N 4.87, Zn 17.04; found: C 50.81, H 5.48, N 5.16, Zn 16.13.

MOF-69B: A solid mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (24.6 mg, 0.083 mmol) and H_2ndc (8.9 mg, 0.041 mmol) was dissolved in a vial containing DEF (12 mL), 30% H_2O_2 (0.40 mL), and $MeNH_2$ (0.20 mL, 51.4 mM in DMF). The mixture was allowed to stand in a capped vial for seven days at room temperature. Colorless crystals of MOF-69B were collected and air-dried (18 mg, 80.4% yield). This compound is insoluble in water and common organic solvents. Elemental analysis calcd for MOF-69B, $[Zn_3(OH)_2(ndc)_2] \cdot 4DEF \cdot 2H_2O$: C 48.08, H 5.69, N 5.10, Zn 17.85; found: C 48.28, H 5.13, N 5.02, Zn 17.76.

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[5] X-ray structure data: Siemens SMART CCD diffractometer, ω scans, graphite-monochromated $Mo_{K\alpha}$ radiation, SAINT for data integration, SADABS for absorption correction, XPREP for correction of Lorentz and polarization effects, and structure solution with direct methods (teXsan[17] for MOF-69A, SHELX-TL[18] for MOF-69B). a) Data collection for MOF-69A: A colorless columnar crystal was analyzed: approximate dimensions: $0.30 \times 0.090 \times 0.080$ mm at -120 °C, monoclinic, space group *C2/c* (no. 15) with $a = 23.1179(11)$, $b = 20.9192(5)$, $c = 12.0021(5)$ Å, $\beta = 111.627(2)°$, $V = 5395.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.417$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 13.90$ cm^{-1}, $F(000) = 2400$, 3530 unique reflections within $2\theta_{max} = 43.9°$, $T_{max} = 0.87$, $T_{min} = 0.57$. The zinc atoms were refined anisotropically, while the rest were refined

isotropically. Hydrogen atoms were included in predicted positions for the ligand and the ordered DEF molecule but not refined. The final cycle of full-matrix least-squares refinement was based on 1339 observed reflections ($I > 2.50\sigma(I)$) and 171 variable parameters and refined to convergence $R_1 = 0.060$ and R_w (all data) = 0.066. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.64 and -0.55 e$^-$ Å^{-3}, respectively. While a hydrogen-bonded DEF molecule was defined well, the other DEF guest molecule was not modeled suitably due to the severe disorder around a mirror plane. b) Data collection for MOF-69B: A colorless needle crystal was analyzed: approximate dimensions: $0.12 \times 0.020 \times 0.020$ mm at -115 °C, monoclinic, space group *C2/c* (no. 15) with $a = 20.1658(15)$, $b = 18.5518(14)$, $c = 12.1580(9)$ Å, $\beta = 95.331(1)^\circ$, $V = 4528.8(6)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.612$ g cm^{-3}, and $\mu(\text{Mo}_{\text{K}\alpha}) = 16.54$ cm^{-1}, $F(000) = 2288$, 4647 unique reflections within $2\theta_{\text{max}} = 52.86^\circ$, $T_{\text{max}} = 0.97$, $T_{\text{min}} = 0.75$. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ndc ligand and the six methyl hydrogen atoms in a DEF molecule were generated with idealized geometries. The hydrogen atoms in both the hydroxy group and the DEF molecule were found in the electron density map and their positional parameters were refined. The final cycle of full-matrix least-squares refinement was based on 2282 observed reflections ($I > 2.00\sigma(I)$) and 294 variable parameters and refined to convergence $R_1 = 0.0587$ and $R_w = 0.1855$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.854 and -0.761 e$^-$ Å^{-3}, respectively. c) All crystal structures in this report may be viewed and manipulated on the web: http://www.umich.edu/~yaghigrp/structures.html Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-170965 (MOF-69A) and CCDC-170966 (MOF-69B). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] Other structures types such as the B net in CaB_6 can be adapted to the same strategy. Here, linking octahedral SBUs with both short and long links, of the proper length ratio, that have been designed to lie along perpendicular planes would yield frameworks that do not catenate. This is well-represented in the structure of $[\text{Zn}(4,4'\text{-bpy})_2(\text{SiF}_6)_n]_n \cdot x\,\text{DMF}$ (4,4'-bpy = 4,4'-bipyridine: S. Subramanian, M. Zaworotko, *Angew. Chem.* **1995**, *107*, 2295–2297; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127–2129.

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[12] Elemental analysis for the exchange products of $[\text{Zn}_3(\text{OH})_2(\text{bpdc})_2] \cdot (\text{G})_g$; G = guest. Guests: $(\text{C}_6\text{H}_6)_{3.5}$: calcd: C 59.81, H 3.99, N 0.00; found: C 60.16, H 3.76, N 0.00. $(\text{CHCl}_3)_{3.5}$: calcd: C 33.53, H 1.92, N 0.00; found: C 33.35, H 1.78, N 0.00. $(i\text{C}_3\text{H}_7\text{OH})_{0.5}$: calcd: C 44.48, H 2.63, N 0.00; found: C 44.78, H 2.56, N 0.00. $(\text{C}_4\text{H}_8\text{O})_2$: calcd: C 47.88, H 3.77, N 0.00; found: C 48.01, H 3.73, N 0.00. $(\text{CH}_3\text{C}_6\text{H}_5)_{3.75}$: calcd: C 61.70, H 4.58, N 0.00; found: C 61.69, H 4.70, N 0.00. Similar results were obtained with MOF-69B.

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