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Large Free Volume in Maximally Interpenetrating Networks: The Role of Secondary Building Units Exemplified by $Tb_2(ADB)_3[(CH_3)_2SO]_4\cdot 16[(CH_3)_2SO]$[1]

Theresa M. Reineke,[†] Mohamed Eddaoudi,[†] David Moler,[†]
M. O'Keeffe,[‡] and O. M. Yaghi*,[†]

Materials Design and Discovery Group
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109
Department of Chemistry and Biochemistry
Arizona State University, Tempe, Arizona 85287

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The rapid growth in the area of metal-organic frameworks (MOFs) continues to provide open structures with interesting compositions, architectures and properties.[2,3] However, this progress, although significant, has not witnessed many discussions on the relationship between porosity and interpenetration of open frameworks; a topic addressed here. We have recently used a synthetic strategy utilizing secondary building units (SBUs) for achieving stable, highly porous, and functionalized open networks.[4−6] Here, the extended 3-D framework of crystalline MOF-9, $Tb_2(ADB)_3[(CH_3)_2SO]_4\cdot 16[(CH_3)_2SO]$, illustrates another aspect of SBUs: namely, their ability to support the existence of large free volume in interpenetrating structures, which thus far have had the propensity to form assemblies containing very little or no free volume.[2]

In an effort to prepare open networks having $Ln_2C_6O_{12}$ core units (already known in molecular clusters)[7] as SBUs, we copolymerized the long dicarboxylate linker ADB with Tb (III) ions:[1b] A mixture of $Tb(NO_3)_3\cdot 5H_2O$ (35 mg, 0.08 mmol) and H_2ADB (32 mg, 0.12 mmol) was dissolved in dimethylsulfoxide (DMSO) (10 mL).[8] Diffusion from a solution mixture containing DMSO (4 mL) and triethylamine (0.15 mL) over 7 d at 25 °C gave crystals of MOF-9 (85 mg, 79.1% yield). A single-crystal X-ray diffraction study confirmed that these synthetic conditions are well-suited for the polymerization of the SBUs into a crystalline 3-D framework structure.[9,10]

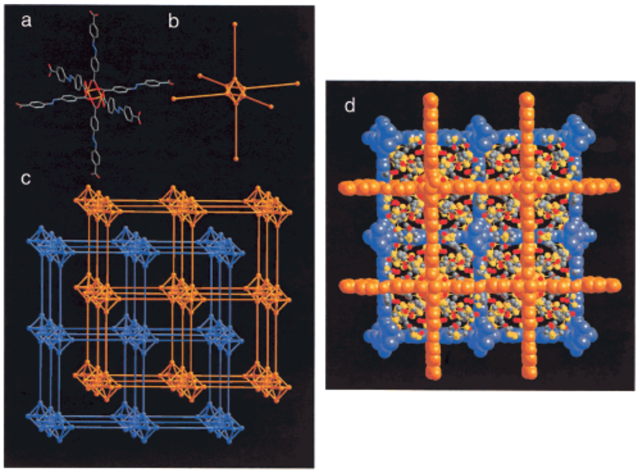

Figure 1. The crystal structure of MOF-9 (shown at 45° from the *ab* plane) constructed from (a) octahedral $Tb_2(ADB)_3(DMSO)_4$ building units (Tb, orange; O, red; C, gray; N, blue) with the DMSO ligands (two on each Tb atom) not shown. A representation of this SBU is shown in (b) with the carboxylate carbon atoms (orange balls) connected by short lines to give an octahedral SBU that is connected to other SBUs by ADB linkers (long orange lines). This gives (c) two interpenetrating networks (colored separately in blue and orange) with large void space (d) which is occupied by a 16 DMSO guests and 4 DMSO ligands (DMSO shown as stick-and-ball, and framework as space filling representation).

The crystal structure of MOF-9 (Figure 1) is constructed from $Tb_2C_6O_{12}$ cluster SBUs where each Tb is bound to five ADB linkers with four coordinated to Tb (III) as di-monodentate and one as bidentate. Two DMSO ligands are also bound to each Tb atom with $Tb{-}OS(CH_3)_2 = 2.40$ (2) and 2.40 (2) Å to give eight coordinate Tb centers. Thus the SBUs, topologically, are considered octahedral C_6 units that are joined by long struts to give a 3-D structure having two identical interpenetrating framework, where each adopts the topology of the boron net in the CaB_6 structure with each C in an SBU replacing B.[11]

Despite the presence of two interpenetrating networks, at least 16 DMSO guest molecules in addition to 4 DMSO ligands per SBU were located by crystallography and confirmed by elemental analysis.[9,10] All DMSO guests and ligands in MOF-9 occupy a complex 3-D intersecting void system of rectangular channels

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[†] University of Michigan.

[‡] Arizona State University.

(1) (a) Free volume refers to space unoccupied by the metal-organic frameworks. (b) ADB: 4,4′-azodibenzoate, $C_{12}H_8N_2(CO_2)_2$.

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(9) Orange polyhedral single crystals of MOF-9 were analyzed at −97 ± 1 °C: monoclinic, space group *C*2/*c* (No. 15) with $a = 27.0558$ (8) Å, $b = 16.7945$ (5) Å, $c = 28.1386$ (1) Å, $\beta = 102.086$ (1)°, $V = 12502.5$ (4) Å^3, $Z = 4$, $d_{calcd} = 1.426$ g·cm^{-3} and μ_a(Mo K$_\alpha$) = 49.09 cm^{-1}. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo K$_\alpha$ radiation. R_1(unweighted, based on F) = 0.105 and $R_w = 0.111$. The maximum and minimum peaks on the final difference Fourier map corresponded to 4.12 and −4.88 e$^-$/Å^3, respectively, which is due to disorder in the S and C atoms of DMSO.

(10) Anal. Calcd for MOF-9, $Tb_2(ADB)_3[(CH_3)_2SO]_{20}$: C, 36.68; H, 5.41; N, 3.13; S, 23.88. Found: C, 35.68; H, 4.99; N, 4.49; S, 18.07 and C, 36.19; H, 5.79; N, 2.94; S, 24.74. Elemental microanalysis on samples of MOF-9 were largely consistent with the formula assigned, but variations in the level of S content was observed due to the facility with which DMSO guests can leave the pores at room-temperature as evidenced by thermal gravimetric (TG) analysis (see text).

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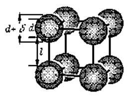
running linearly throughout the structure and having dimensions of 7.54 × 6.65 Å and 7.07 × 5.69 Å.[12a] The free volume is 71% of the crystal volume—a value heretofore unobserved for interpenetrating networks, which generally incorporate either very little (up to 20% of crystal volume) or no free volume.[12b]

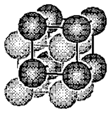
A TG analysis study was performed on a sample (24.87 mg) of as-synthesized material, which showed a weight loss starting at room-temperature and ending at 180 °C to give a total loss of 14.54 mg (58.5%). This is equivalent to the loss of 20 DMSO molecules per formula unit (calcd: 58.2%) and accounting for the liberation of all guests in the channels. In addition, framework stability to reversible exchange of DMSO guests was demonstrated by exchanging DMSO in the as-synthesized material with $CHCl_3$, then using the resulting solid to exchange $CHCl_3$ guests with DMF and also back with DMSO.[13a−c,14]

The unprecedented amount of void space found in MOF-9 despite its interpenetrating structure presented us with two scenarios: (a) the structure is not maximally interpenetrated and thus the presence of large free volume occupied by DMSO molecules, or (b) the size of SBUs is too large to fit in the space remaining after two interpenetrating frameworks form; leading to the large free volume. The latter case was more likely since we and others have observed that the first possibility exists only in the presence of large guests and thus does not apply here.[15] Indeed, the SBUs are too large to allow a third interpenetrating framework to form (compare the *van der Waals* dimensions of the distorted C octahedron of each SBU, 13.05 × 8.65 × 8.59 Å^3, to the cross section of the channels, vide supra).[12c]

Our interest in SBUs and their impact on interpenetrating networks motivated us to examine how these parameters are related to porosity or free volume in crystals. Here, it is instructive to consider a simple geometric argument involving spherical SBUs of diameter d that form a cubic network with linkers of length l, **a**. The cubic cell edge is $a = d + l$. If the van der Waals radius ($\delta/2$) of the atom joining the SBU and linker is considered, then for n frameworks to interpenetrate with centers of their SBUs aligned along a body diagonal (as shown for $n = 2$ in **b**), $n(d + \delta) \le \sqrt{3a}$; thus, $n \le \sqrt{3}(d + l)/(d + \delta)$.



a



b

A composite plot of n as a function of d and l and their relationship to the free volume is shown in Figure 2, which, although purely mathematical, can be used to gain insight into interpenetrating structures. The plot clearly shows that the level of interpenetration is largely determined by the length of linkers, l, while the free volume is dramatically influenced by the size of the SBUs, d. Significantly, for structures having a small degree of interpenetration ($n = 3$ or 2 in the example here), an optimum amount of available free volume can be achieved. Also, due to the use of SBUs, structures having large free volume are possible at an even higher level of interpentration ($n = 4+$). Furthermore, the free volume becomes smaller at high degree of interpenetration (with relatively small SBUs) because now much of the available space is taken up by the linkers. It should be noted that if interpenetration can be hindered (e.g. by the use of large counterions for charged networks)[15,16] this simple analysis would need to be modified.

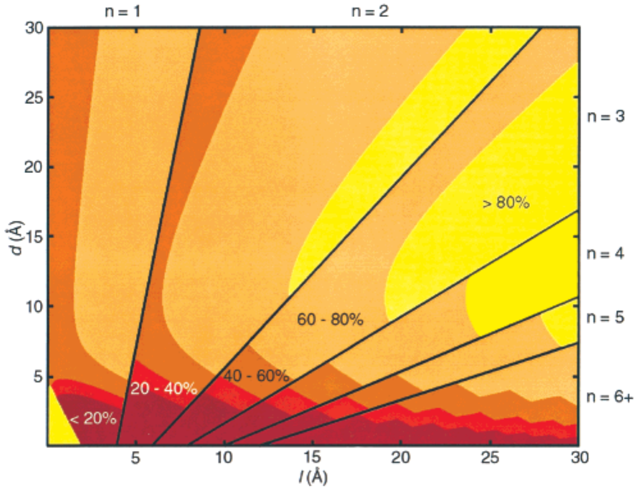


Figure 2. A *dlnv* plot for a cubic system having spherical SBUs and cylinder shaped rods: n is plotted (total number of frameworks in a structure) as a function of d (diameter of an SBU) and l (length of linker) with the corresponding free volume expressed as percent of crystal volume shown in decreasing shades of darkness (darkest: <20 to lightest: >80%). The solid dark lines for $n = 1$ to $n = 6+$ were obtained according to the equation for n (see text) and assuming a C connector with $\delta = 3.4$ Å (van der Waals diameter of a C atom) and linkers with negligibly small diameter. For the volume calculation the SBUs diameter was considered d and the volume of the linker was based on a cylinder of a diameter ($2r$) equivalent to that of a benzene ring (5 Å) and a length l. Thus, the free volume was calculated based on the following: Volume of the cell $= (d + l)^3$; volume occupied by SBUs/cell $= n(\pi/6)d^3$; and volume of the linkers/cell $= 3n[(\pi r^2)]l$.

The case of MOF-9 can be considered here, albeit it is not strictly cubic: We find that $d = 9.65$ Å and $l = 11.88$ Å, which lies in the region of $n = 2$ with void volume of 60−80%. Note that if d was less by only 2 Å, then the possibility of a structure having three interpenetrating frameworks with less free volume (40%) would have been achieved. Thus, Tb−O−C cluster served as an optimal SBU for ADB, allowing MOF-9 to just miss a third interpenetrating framework.[17]

The *dlnv* plot produced here for an ideal cubic system and demonstrated qualitatively for MOF-9, provides a useful view across the landscape of porous SBU-based frameworks. Elaboration of this theme toward other common topologies such as diamond, $ThSi_2$, and $SrSi_2$ is currently being pursued.

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Supporting Information Available: Crystallographic data for MOF-9: crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles, including solvent exchange data (PDF). This material is available free of charge at http://pubs.acs.org.

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(12) Van der Waals radii of C (1.7 Å), O (1.4 Å), and H (1.1 Å) were used in the calculation of (a) pore dimensions, (b) percent volume occupied by the frameworks (CERIUS program was used, where crevices of less than 1 Å diameter were not included as free volume), and (c) SBU axial and equatorial lengths.

(13) (a) Anal. Calcd for $Tb_2(ADB)_3[(CH_3)_2SO]_2[CHCl_3]_3$: C, 35.95; H, 2.40; N, 5.13; S, 3.92. Found: C, 35.00; H, 2.55; N, 5.10; S, 4.03. (b) Anal. Calcd for regenerated $Tb_2(ADB)_3[(CH_3)_2SO]_{20}$: C, 36.68; H, 5.41; N, 3.13; S, 23.88. Found: C, 36.31; H, 5.55; N, 3.01; S, 23.67. Anal. Calcd for $Tb_2(ADB)_3[(CH_3)_2SO][DMF]_{20}$: C, 46.92; H, 6.44; N, 13.68; S, 1.20. Found: C, 46.93; H, 6.17; N, 13.37; S, 1.14.

(14) Attempts to examine gas sorption isotherm for the evacuated solid using N_2 and organic solvents such as $CHCl_3$, CH_2Cl_2, and C_6H_6 were not successful; however, small amount of $CO_{2(g)}$ (56 mg/g) was found to permeate the framework with an estimated surface area of 127 m^2/g. These observations coupled to the clean weight loss obtained in the TG experiment point to a flexible evacuated framework, perhaps due to the flexible nature of ADB.

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(17) Assuming that the octahedron approximates a sphere with d being the longest C···C distance (9.65 Å) in the SBU and l is the distance between the carboxylate C atoms (11.88 Å) within an ADB linker.