A Crystalline Imine-Linked 3-D Porous Covalent Organic Framework

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Covalent organic frameworks (COFs) are a new class of materials created by linking organic building units into predetermined structures using the principles of reticular chemistry.[1,2] These materials are composed entirely of covalent bonds between light elements (C, Si, B, O, N). It has long been argued that the crystallization of 2- and 3-periodic covalent structures would be very difficult,[3] if not impossible,[4] and a key advance has been overcoming this "crystallization problem". In particular we have shown not only that the synthesis of ordered COFs is possible but also that predesigned structures and properties can be achieved by carefully selecting the building blocks and their conditions for assembly. Thus, the successful design and synthesis of COFs linked by C−B, B−O, C−C, and C−Si have been demonstrated.[2] Here, we describe the preparation and characterization of the first crystalline 3-D framework material constructed solely from C−C and C−N covalent linkages and demonstrate its permanent porosity.

The condensation of aniline **A** with benzaldehyde **B** results in imine bond formation in **C** with elimination of water. Our target in this instance was to design and synthesize a framework based on a net with tetrahedral vertices (4-connected). To effect this, we chose the condensation of the tetrahedral building block tetra-(4-anilyl)methane[5] **D** with the linear linking unit terephthaldehyde **E** to produce a material with an extended 3-D framework structure that we name COF-300. The dehydration of the tetrahedral aniline and the dialdehyde will form the linear bis-imine *N,N′*-[1,4-phenylenebis(methylidene)]-bis(4-aniline) **F**, which will connect together the tetrahedral methane carbons. When tetrahedra are connected together, the default structure is the diamond topology.[6] It has been observed in metal−organic framework chemistry that when such tetrahedral centers are separated by long rod-like links, the resulting structures tend to be interpenetrated.[7] Given that the bis-imine link is *ca.* 19 Å long,[8] a multiply interpenetrated structure was expected and indeed observed here in the case of COF-300.

The synthesis of COF-300 was carried out by solvothermolysis of a suspension of **D** and **E** in a 10:2 (v/v) mixture of 1,4-dioxane and 3 M aqueous acetic acid.[9,10] Thermal gravimetric analysis (N_2) shows that COF-300 is stable up to 490 °C.[10] The material is insoluble in water and common organic solvents such as hexanes, methanol, acetone, tetrahydrofuran, and *N,N*-dimethylformamide. The formation of imine linkages in COF-300 was confirmed by FT-IR and NMR spectroscopies. Studies were performed on the starting materials, the synthesized COF-300, and model compound **C**.[10] The FT-IR spectrum of COF-300 showed the C=N stretching modes characteristic for imines at 1620 and 1202 cm^{-1} (1625 and 1198 cm^{-1} in **C**).

The crystallinity of COF-300 was confirmed by powder X-ray diffraction analysis in which all peaks were indexed on a primitive
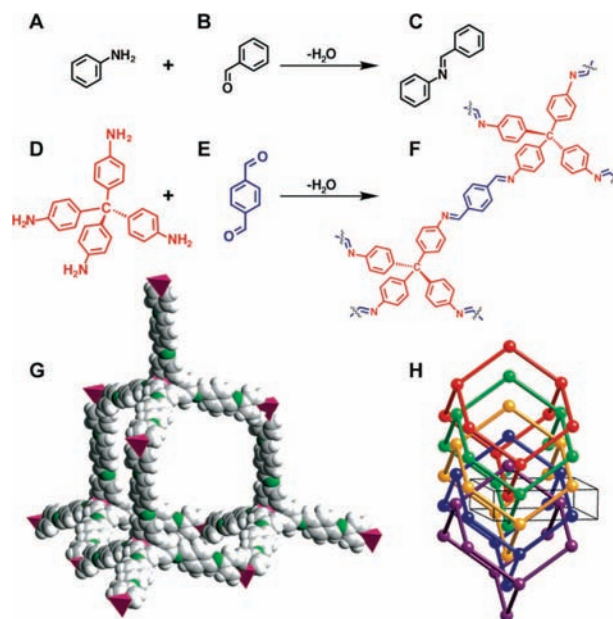

Figure 1. Condensation of aniline **A** with benzaldehyde **B** forms the molecular *N*-benzylidene-aniline **C**. Condensation of divergent **D** with ditopic **E** leads to the rod-like bis-imines **F** which will join together the tetrahedral building blocks to give the diamond structure of COF-300: **G** single framework (space filling, C gray and pink, N green, H white) and **H** representation of the **dia-c5** topology.
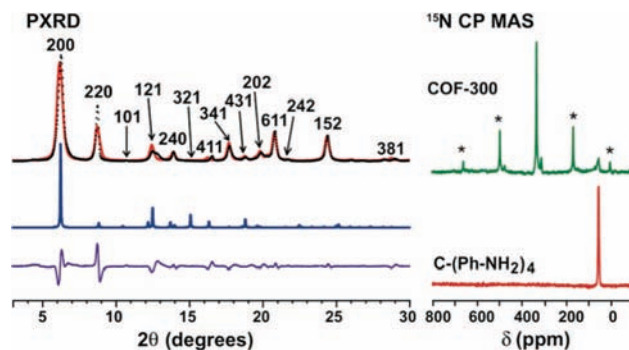

Figure 2. Left: Indexed experimental (black) and calculated (blue) PXRD patterns for COF-300 including the Le Bail fitting (red) and the difference plot (purple). Right: ^{15}N cross-polarization with magic angle spinning (CP-MAS) NMR spectra of nitrogen-15 isotopically enriched COF-300 (green) and starting material **D** (red). Asterisks denote spinning side bands.[10]

tetragonal unit cell with parameters $a = 20.0044$ Å, $c = 8.8530$ Å (TREOR figures of merit $M_{16} = 22$, $F_{16} = 20$). In particular no diffraction peaks from starting materials were observed.[10] We remark that the peaks could equally be indexed on a body-centered

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Table 1. Crystallographic Data for the Ideal Geometry of *N*-Fold Interpenetrated Diamond Nets

N^a	crystal system	space group	a^b	c^b	a/c
1	cubic	$Fd\bar{3}m$	$4/\sqrt{3}$	a	1
2	cubic	$Pn\bar{3}m$	$2/\sqrt{3}$	a	1
$2n+1$	tetragonal	$I4_1/amd$	$\sqrt{8}/\sqrt{3}$	$4/\sqrt{3}N$	$N/\sqrt{2}$
$4n$	tetragonal	$P4/nbm$	$2/\sqrt{3}$	$4/\sqrt{3}N$	$N/2$
$4n+2$	tetragonal	$P4_2/nnm$	$2/\sqrt{3}$	$4/\sqrt{3}N$	$N/2$

^{a} N = Interpenetration number, n is any integer > 1. ^{b} Cell parameters are in units of the edge length (distance between linked vertices).

tetragonal cell with $a' = \sqrt{2}a$, $c' = c$. Interpenetrated diamond nets most naturally form with the individual nets being related by a translation parallel to one of the original cubic axes.[11] The topology of the *N*-fold interpenetrated structures is designated with RCSR symbol **dia-c***N*.[12] The maximum symmetry and ideal unit cell dimensions are determined by the degree of interpenetration and length of the links between the tetrahedral nodes (Table 1). For the ideal structure, $a = 1.15$ times the length of the link between tetrahedra, so we expect $a \approx 21.8$ Å, sufficiently close to the observed value to confirm the expected **dia** topology. Again for the ideal case, the degree of interpenetration can be determined from $N = 2a/c$.[13] In the present instance $2a/c = 4.52$ suggesting 4- or 5-fold interpenetration. We then used the *Cerius*^{2} chemical structure-modeling software suite[14] to simulate the crystal structures from the **dia-c4** and **dia-c5** topologies and the experimental unit cell parameters. From these, simulated powder patterns were calculated and compared to the experimental, obtaining a perfect match in peak position from the **-c5** topology. Differences in the intensity between the experimental PXRD and the simulated pattern can be explained by the fact that the predicted structures were modeled without guests. The presence of guests in COF-300 samples as indicated by the slight variation in elemental analysis results, higher measured density, and lower than expected surface area, can account for the differences in observed peak intensities.[10] To verify the assignment of the **dia-c5** structure, the experimental PXRD data were subjected to a model-biased Le Bail full pattern decomposition where the model was used as a starting point to extract F_{obs} (Figure 2). The resulting refined unit cell parameters [$a = 28.127(13)$ Å, $c = 8.879(26)$ Å, $Rp = 0.121$ $wRp = 0.195$, $\chi^2 = 11.9$] corresponded closely with those of the model. This agreement along with the low convergence in the Le Bail parameters and the excellent correlation in peak positions support the proposed structure.[10] Note that as a unit cell contains exactly the same number of atoms for any degree of interpenetration, the calculated density (0.54 g cm^{-3}) using the experimental unit cell dimensions is the same for any value of N. The measured density is 0.66 g cm^{-3}, corroborating the presence of guests within the pores.[10]

The permanent porosity of COF-300 was demonstrated by measuring argon adsorption at 87 K. The isotherm (Figure 3) shows a sharp uptake below $P/P_0 = 0.10$. The application of the Brunauer–Emmett–Teller (BET) model results in a surface area of $S_{BET} = 1360$ m^2 g^{-1}. The total pore volume was calculated for $P/P_0 = 0.80$ to be $V_p = 0.72$ cm^3 g^{-1}. The Ar isotherm was fit with nonlinear density functional theory models[15] from which the pore size distribution was calculated, resulting in a value of 7.2 Å, which is close to the values observed in the crystal model (7.8 Å). The observed hysteresis may be attributed to the dynamic response of the framework: higher gas pressures should be required to activate the pores as observed in other frameworks.[16]
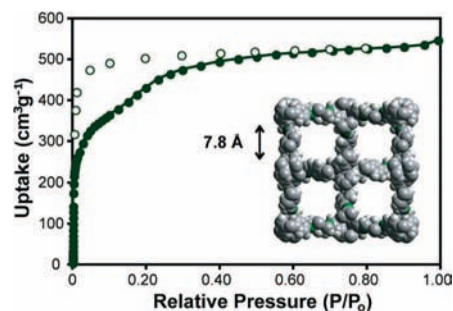

Figure 3. Argon adsorption (filled symbol) and desorption (open symbol) isotherm for COF-300 measured at 87 K. Inset: space-filling model of COF-300 (**dia-c5**) along the 001 direction showing the size of the channels.

We have demonstrated that covalent organic frameworks can be designed and synthesized in crystalline form from organic building units linked by C=N bonds.

Supporting Information Available: Detailed synthetic procedures, PXRD patterns, modeling techniques and atomic coordinates, FT-IR and MAS NMR spectra, SEM images, TGA traces, gas adsorption, and density measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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