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Reticular Synthesis of Covalent Organic Borosilicate Frameworks

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Linking molecular building blocks into extended structures by strong covalent bonds (reticular chemistry) is now commonly practiced in the synthesis of metal−organic frameworks wherein transition metal−oxide bonds (e.g., Zn−O) join organic units to make highly robust, porous structures.[1] Recently, we showed that this chemistry can be extended to linking organic units by covalent bonds of small, light atoms (C−C, C−B, and B−O) to give a new class of solids termed covalent organic frameworks (COFs) whose members have the least dense crystals known to date.[2,3] Overcoming the "crystallization problem" has been the key fundamental advance since it provides for definitive characterization and specific control over the topology and functionality of the resulting structure. In this report, we further demonstrate the generality of this approach by linking organic units with the strong covalent bonds found in Pyrex (borosilicate glass, B−O and Si−O) to give a porous covalent organic borosilicate framework designated as COF-202.[4] Our strategy for designing COF-202 borrows from the chemistry of molecular borosilicate clusters (Figure 1A through C) where it is known that the condensation of *tert*-butylsilane triol[5] **A** with monotopic boronic acid **B** forms a high symmetry borosilicate cage **C**.[6] We used the same condensation reaction with a divergent organic tetraboronic acid unit to articulate the borosilicate cage in a covalently linked organic framework (Figure 1E and F).

The synthesis of crystalline COF-202 was carried out by combining a 1:2 v/v dioxane/toluene solution mixture of *tert*-butylsilane triol, ^{t}BuSi(OH)$_3$, and tetra(4-dihydroxyboryl-phenyl)methane,[7] C{C$_6$H$_4$[B(OH)$_2$]}$_4$, (**A** and **D**, respectively) in a sealed glass tube. This solution was heated to 120 °C for 3 days to yield a white microcrystalline powder whose composition coincided well with the expected formula of $C_{107}H_{120}B_{12}O_{24}Si_8 \equiv [C(C_6H_4)_4]_3[B_3O_6(^tBuSi)_2]_4$.[8,9]

The building units in this framework are geometrically analogous to those employed in the design of boroxine based 3D COFs (e.g., COF-102) where planar triangular rings and tetrahedra are connected to yield extended structures.[2,3] In COF-202 the boron atoms of the borosilicate cages and the divergent boronic acids constitute the triangular and tetrahedral building units, respectively. We previously demonstrated that connecting triangles with tetrahedra results in the formation of the most highly symmetrical topologies: carbon nitride (**ctn**, $I\bar{4}3d$) or boracite (**bor**, $P\bar{4}3m$).[10] Based on this principle we constructed models of the structures engendered from these two topologies and calculated their expected powder X-ray (Cu Kα) diffraction (PXRD) patterns. The experimental PXRD patterns obtained from microcrystalline samples of COF-202 show an excellent agreement with the peak positions and intensities of the calculated pattern for the carbon nitride structure (Figure 2). The PXRD pattern was subjected to a model-biased Le Bail refinement to extract F_{obs}. The **ctn** model constructed in Cerius[2] was used as a starting point, where refined unit cell parameters closely matched those of the model.[11] This result as well as the ready convergence and low residuals ($R_p = 10.31$, $wR_p = 14.16$) from Le Bail extraction strongly supports our structural assignments.[12] We note that peak broadening in the observed pattern is primarily the result of the small particle size of the polycrystalline product (100−500 nm).[9]

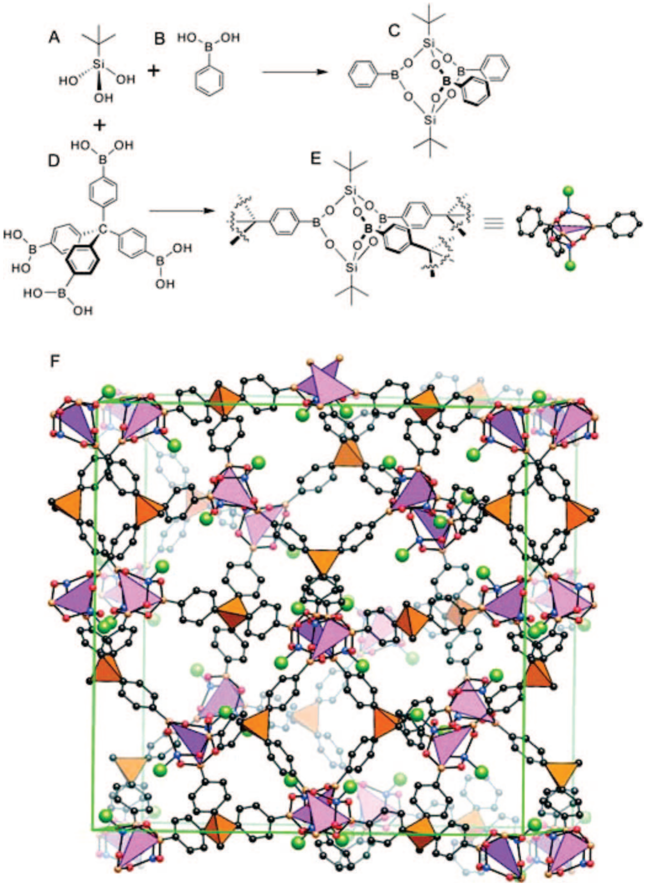

Figure 1. Condensation of *tert*-butylsilane triol **A** with monotopic boronic acid **B** forms the molecular borosilicate cage **C**. Condensation of **A** with divergent boronic acid **D** leads to the building unit **E** in which the boron atoms occupy the vertices of a triangle and join together the tetrahedral building blocks **D** to give COF-202 **F**. Coloring Scheme: C, black; Si, blue; O, red; B, yellow (H atoms have been omitted and *tert*-butyl groups are represented as green spheres for clarity).

Figure 1 shows the structure of COF-202 **F** where the three planar boron atoms of the prismatic borosilicate cages **E** form a triangle. A desirable feature of this structure is that the chemically mutable sites on the apical silicon atoms, in this case *tert*-butyl, are directed into the pores of the framework providing ample space to accommodate a wide variety of functionalities.

Formation of the anticipated B−O−Si linkage was confirmed by Fourier Transform infrared (FT-IR) and multiple-quantum magic angle spinning nuclear magnetic resonance (MQ-MAS) spectroscopies. The FT-IR spectrum of COF-202 indicates the presence of the B−O−Si stretch at 1310 cm^{-1} and expected decrease of

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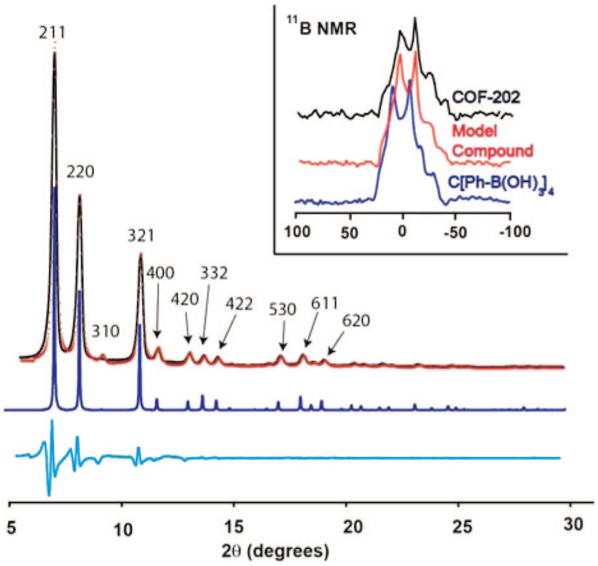

Figure 2. Experimental (black) and calculated (blue) PXRD patterns for COF-202 including Le Bail fitting (red) and the difference plot (turquoise). ^{11}B NMR traces of COF-202, model compound **C**, and starting material are shown in the inset.

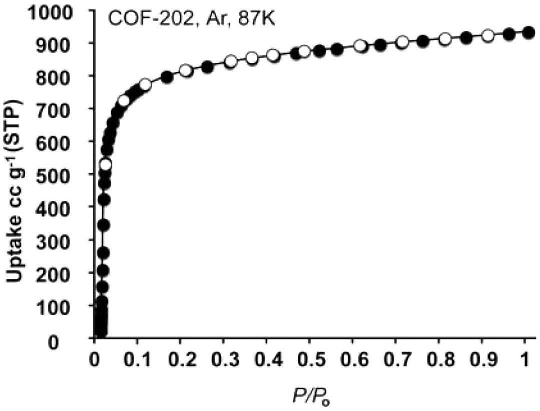

Figure 3. Gas adsorption isotherm for COF-202 with adsorption desorption points represented by closed circles and open circles, respectively.

the hydroxyl stretching band at 3400 cm^{-1}. ^{11}B MQ-MAS NMR data of COF-202 and the discrete molecular model compound **C** showed matching peak shapes and positions (see Figure 2 inset) confirming that the respective boron atoms have identical chemical environments. Additionally, ^{29}Si and ^{13}C MAS NMR experimental data were congruent with the formation of COF-202.[9]

Thermogravimetric analysis shows that COF-202 is stable up to 450 °C and is insoluble in common organic solvents such as alkanes, tetrahydrofuran (THF), alcohols, acetone, and *N*,*N*-dimethylformamide. Moreover, samples of COF-202 maintain both porosity and crystallinity after exposure to air for 24 h.[9]

Immersion of COF-202 in anhydrous THF and subsequent evacuation under vacuum at 85 °C for 16 h remove all volatile guests from the pores and activate the material for gas adsorption experiments. The porosity of COF-202 was measured by running an argon low pressure isotherm at 87 K from 0 to 760 Torr (Figure 3). The observed classic type I isotherm indicates that COF-202 is a microporous material. Furthermore, Brunauer−Emmet−Teller (BET) and Langmuir models yielded high surface area values of 2690 m^2 g^{-1} and 3214 m^2 g^{-1}, respectively.

The pore volume determined by the Dubinin−Radushkevich equation for COF-202 is 1.09 cm^3 g^{-1}, while the pore size distribution determined from density functional theory calculations equates to 11 Å which fits well with the expected pore size of 10 to 12 Å based on the Cerius^2 model.[13]

We have demonstrated the use of reticular chemistry principles in the design and synthesis of a new robust covalent organic framework constructed from borosilicate linkages (B−O−Si) that possesses comparably high porosity and thermal stability to those of previously reported 3D COF materials.[2b] In addition to the stability and high permanent porosity of COF-202, the apical silicon sites of the borosilicate cages may be functionalized to afford materials with a wide variety of applications. We are currently pursuing the synthesis of such functionalized borosilicate COF materials.

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Supporting Information Available: Synthetic procedure, modeling techniques, PXRD patterns, atomic coordinates, MAS NMR and FT-IR spectra, SEM images, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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