

Facile Synthesis of a Highly Crystalline, Covalently Linked Porous Boronate Network

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A covalent organic framework (**COF-18A**) based on poly(boronate ester)s has been successfully synthesized through a facile dehydration process in 85–95% isolated yield. Spectroscopic characterization confirms formation of the intended ester linkages as the key structural motif forming infinite 2D hexagonally porous sheets. Powder X-ray diffraction studies were used to determine the stacking orientation between the ester-linked sheets, such that atoms in adjacent layers lie directly over each other, resulting in a hexagonal array of 1D, 18 Å pores. **COF-18A** exhibits rigid, thermally stable (to 500 °C) pores with high surface area (1260 m²/g) and a micropore volume of 0.29 cm³/g.

Introduction

Porous materials are of great interest for applications in gas storage,¹ catalysis,² and separations.³ Therefore, the ability to generate highly porous, robust materials in an efficient and simple manner is greatly desired.⁴ Self-assembly is one approach to build extended networks.⁵ An entire issue of a recent *Accounts of Chemical Research* was dedicated to the development of “Molecular Architectures” as it relates to the creation of macroscopic structure in self-assembling networks.⁶ In particular, metal-organic coordination networks have been vigorously investigated as a means to generate microporous frameworks.⁷ Many of these metal-organic frameworks (MOFs) are logically constructed from molecular building blocks (reticular synthesis) to yield crystalline

porous materials in which metal ions and clusters are linked by organic units.⁸ While there have been numerous successes using this approach, it would be beneficial to have a means to assemble covalently linked networks for the generation of more structurally stable assemblies. The generation of self-assembling materials based on the interactions between polyboronic acids and poly diol compounds forming boronate ester linked materials represents one method to generate such porous covalent networks. Given the covalent yet reversible nature of the boronate ester linkage, these assemblies form in a highly ordered manner through a simple dehydration process without the need for the addition of catalysts or other reagents.⁹ Compared to other covalently bonded organic materials, boronate-linked networks are assembled with greater ease and with higher efficiency. Furthermore, compared to their noncovalently bonded equivalents, the boronate-linked structures display enhanced stability.

Highly ordered, porous networks based on boronic acid building blocks have been previously described by Wuest and Galoppini.¹⁰ However, these materials assemble through hydrogen bonding to form stable, highly interpenetrating, diamondoid frameworks. Previously, we demonstrated the utility of using boronate ester formation for the creation of linear polymers with self-repairing capabilities⁹ as well as for self-assembling crystalline networks.¹¹ Yaghi and co-workers recently added to this field with the elegant

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description of covalent organic frameworks (COFs) exhibiting persistent porosity based on boronate ester formation.¹² Herein, we have continued to expand upon this assembly motif and present the facile synthesis and characterization of a highly crystalline, covalently linked, microporous extended organic network synthesized in good yields under moderate conditions that is assembled solely with boronate ester linkages (**COF-18Å**, so named because it is a covalent organic framework with 18 Å diameter pores).

Experimental Section

Materials. 1,2,4,5-tetrahydroxybenzene was obtained according to a literature procedure,¹³ as well as 1,3,5-tris(trimethylsilyl)-benzene.¹⁴ All reagents used in their preparation were purchased from Acros and used without further purification, with the exception of boron tribromide which was purchased from Sigma-Aldrich and used as received. All solvents used were obtained from solvent purification systems from Innovative Technologies.

Instrumentation. Solution-phase ¹H NMR spectra were collected on a Varian Mercury/VX 300 MHz spectrometer. Solid-state ¹¹B NMR spectra were collected on a Varian Inova 500 MHz spectrometer with a Doty 4 mm XC-MAS probe. FT-IR spectra were collected on a Thermo Nicolet Nexus 470 FT-IR ESP with polished potassium chloride plates. Thermogravimetric analysis was carried out using a TA Instruments SDT 2960 DTA/TGA. Gas adsorption data were collected on a Quantachrome Autosorb-1 automated adsorption analyzer, using a liquid nitrogen bath, with nitrogen gas as the adsorbate. Powder X-ray diffraction data were collected on a Rigaku DMax 2200 using Cu K α radiation. The sample was mounted in a deep well glass slide. Data were collected from 2 to 70° 2 θ with steps of 0.02° with a count time of 12 s per step. There were no observable diffraction lines beyond 50° 2 θ so this data was not used in the data analysis.

Powder X-ray Diffraction Analysis. Unit cell dimensions were first determined in the JADE 7 program for X-ray diffraction pattern processing, identification, and quantification. The analysis suggested a hexagonal crystal system with a unit cell of approximately $a = 20.805$ Å and $c = 3.461$ Å. The observed diffraction lines were then compiled and used for lattice parameter indexing in the Crysfire suite.¹⁵ The indexing program TREOR¹⁶ was used, and a satisfactory indexing was achieved that indicated a primitive hexagonal unit cell, with unit cell dimensions of $a = 20.832$ Å and $c = 3.456$ Å.

As a consequence of the low number of observed lines (seven) in the diffraction pattern, all attempts to determine an appropriate space group inevitably yielded a large number of possible primitive hexagonal space groups. Structural models were developed based on information obtained from single-crystal data¹¹ of the network's structural components to identify the stacking sequence in the phase using the DIAMOND 3¹⁷ software package and, thus, to determine the probable space group. Two likely structural models that differ

in the layer stacking sequence were considered, including an AA arrangement, where each layer of the network lies directly on top of one another, forming a hexagonal array of linear pores as in boron nitride, and an AB sequence, where the layers are staggered in a graphite-like fashion, with the three-connected vertices lying over the center of the rings of neighboring layers. The AA model was built in space group $P6/mmm$ and the AB model was built in space group $P6_3/mmc$ following the protocol established by Yaghi and co-workers.¹² Powder diffraction patterns from these models were generated within the Diamond 3 software package and compared to the diffraction pattern of the sample (see Supporting Information for details).

Gas Adsorption Analysis. A sample of **COF-18Å** was suspended in dry THF for 24 h. Solvent was decanted and the sample was once again suspended in THF for another 24 h and the solvent decanted. This sample was dried under vacuum (1 Torr) for 24 h. The sample was additionally dried under dynamic vacuum (10^{-5} Torr) while being heated at 400 °C for 2.5 h. This sample was used for gas adsorption measurements from 0 to 760 Torr at 77 K. The adsorption profile was reversible and reproducible and showed a very sharp uptake at low partial pressure (P/P_0 from 4×10^{-6} to 0.01), which is indicative of microporous materials. The Brunauer-Emmett-Teller (BET) model was applied to the isotherm for P/P_0 between 0.05 and 0.3, resulting in an apparent surface area of 1260 m²/g and a micropore volume of 0.29 cm³/g.

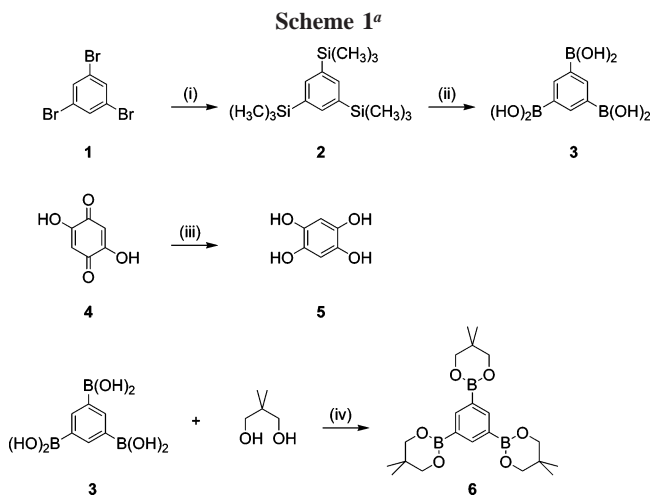
Benzene-1,3,5-triboronic Acid (3).¹⁸ 1,3,5-Tris(trimethylsilyl)-benzene (**2**) (9.82 g, 33.4 mmol) was treated with neat boron tribromide (41.0 g, 0.164 mol) under argon. A condenser was attached that was also charged with argon, and the solution was heated at 100 °C for 4 h. Once cooled, excess boron tribromide was distilled under vacuum (1 Torr) at room temperature. The resulting gray-purple solid was dissolved in dry hexane (50 mL) and cooled to 0 °C with an ice bath. Water was slowly added dropwise while stirring vigorously until the reaction had been fully quenched. The gray solid was collected by filtration and rinsed with water. After drying under vacuum (1 Torr) for 72 h, the product was obtained as the trihydrate in >99% yield. ¹H NMR (300 MHz, 1 M KOH in D₂O): δ 7.33 (s, 3 H). Solid MAS ¹¹B NMR (160.49 MHz, BF₃·Et₂O at 0 ppm as the external reference and solid boric acid as the second reference at 19.3 ppm): δ 25.24. FTIR: 3383, 3232, 1591, 1325, 1165, 1057, and 710 cm⁻¹

(Note: Due to poor solubility and low volatility of this compound, further characterization was obtained by directly capping the boronic acid functionality with neopentyl glycol.)

Neopentyl Glycol Ester of 3 (6). 1,3,5-Tris(trimethylsilyl)-benzene (**2**) (395 mg, 1.34 mmol) was treated with neat boron tribromide (1.83 g, 7.32 mmol) under argon. A condenser was attached that was also charged with argon, and the solution was heated at 100 °C for 4 h. Once cooled, excess boron tribromide was distilled off under vacuum (1 Torr) at room temperature. The resulting gray-purple solid was dissolved in dry hexane (10 mL) and cooled to 0 °C with an ice bath. Water was slowly added dropwise while stirring vigorously until the reaction had been fully quenched. Neopentyl glycol (513 mg, 4.93 mmol) and methanol (3 mL) were added and the mixture was evaporated under reduced pressure at 40 °C to dryness. Excess glycol was removed by sublimation (90 °C/1 Torr), yielding the pure product (570 mg). Yield: >99%. ¹H NMR (300 MHz, CDCl₃): δ 1.00 (s, 18 H), 3.76 (s, 12 H), 8.33 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃): δ 22.1, 32.1, 72.5, 142.1. Solid MAS ¹¹B NMR (160.49 MHz, BF₃·Et₂O at 0 ppm as the external reference and solid boric acid as the second

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^a Conditions: (i) Mg, (CH₃)₃SiCl; (ii) (a) BBr₃, 100 °C, 4 h; (b) H₂O; (iii) Sn, HCl, THF; (iv) CH₃OH.

reference at 19.3 ppm): δ 24.59. HRMS calcd for C₂₁H₃₃B₃O₆: 414.2567; found: m/z 414.2555.

COF-18Å. Benzene-1,3,5-triboronic acid (**3**) (2.34 g, 8.86 mmol) and 1,2,4,5-tetrahydroxybenzene (**5**) (2.96 g, 20.8 mmol) were dissolved in THF (98 mL) and methanol (2 mL). The solution was refluxed under constant flow of nitrogen for 3 days. The reaction mixture was cooled to room temperature and the fine suspension that had formed was collected by filtration. The solid was rinsed with THF (100 mL) and dried in a vacuum oven (70 °C/1 Torr) for 72 h, yielding 2.63 g of a fine white powder. Yield: 96%. ¹H NMR (hydrolyzed/degraded **COF-18Å**) (300 MHz, 1 M KOH in D₂O): δ 6.42 (s, 2 H), 6.71 (s, 1 H), 7.33 (s, 3 H). Solid MAS ¹¹B NMR (160.49 MHz, BF₃·Et₂O at 0 ppm as the external reference and solid boric acid as the second reference at 19.3 ppm): δ 29.89. FTIR: 3400, 1601, 1471, 1425, 1345, 1306, 1140, 887, 841, 704, and 640.

Results and Discussion

Synthesis and Characterization of Monomers. The preparation of **COF-18Å** was initiated by the synthesis of monomers **3** and **5** as depicted in Scheme 1. Monomer **5**, 1,2,4,5-tetrahydroxybenzene, was obtained in good yield using the procedure published by Hegedus and co-workers.¹³ It is important that this material be recrystallized numerous times to remove all trace of the tin reducing agent; otherwise, the material will decompose upon standing in air. We found that recrystallizing this bis-diol from THF at least three times afforded material that could be stored at ambient temperature without exhaustive regard for the exclusion of moisture or oxygen for at least 3 years.¹⁹

Triboronic acid **3** has been previously reported by Tour and co-workers.²⁰ This documented synthesis uses a one-step nickel-catalyzed process, starting with the commercially available 1,3,5-tribromobenzene, to introduce the boronic acids followed by an oftentimes difficult and tedious

purification process resulting in a modest yield (~40–50%). The route outlined in Scheme 1, while requiring a two-step procedure, introduces the boronic acid in near quantitative yield with no need for further purification. The first step involves conversion of 1,3,5-tribromobenzene (**1**) to the 1,3,5-tris(trimethylsilyl)benzene (**2**) by generation of the Grignard reagent in the presence of chlorotrimethylsilane.¹⁴ This sequence produces modest yields (45–50%) of the desired product but the purification is readily accomplished via column chromatography using hexanes as the eluent or via fractional distillation. Treatment of the tris-TMS product (**2**) with boron tribromide followed by an aqueous workup results in quantitative conversion to the triboronic acid **3**. While the overall yields are similar to the route reported by Tour and co-workers, the ease of purification is notably more facile and reaction conditions are more convenient.

Isolation of analytically pure triboronic acid **3** was problematic. Upon workup, water was always included in the recorded mass of the triboronic acid. When efforts were taken to remove this water, anhydride or semi-anhydride formation resulted, leading to lower than expected mass values. Elemental analysis is notoriously poor at evaluating exact mass for boronic acid containing compounds; therefore, ¹H NMR analysis was used to quantify the amount of water in the initial product. The synthetic route described above consistently produces the hydrated product with three water molecules per triboronic acid (one water molecule per boron atom). To confirm the efficiency of the boronylation reaction, triboronic acid **3** was directly converted to the triboronate ester, **6**. Compound **3** was treated with 3.3 equiv of neopentyl glycol in methanol and the solvent evaporated under reduced pressure. Removal of excess neopentyl glycol via sublimation resulted in greater than 99% yield of the tri-ester in greater than 99% purity as assessed by ¹H NMR. The ease and high conversion with which this tri-ester was formed supports the proposed facile formation of covalently linked porous networks using this approach.

Synthesis and Characterization of COF-18Å. The covalent organic framework, **COF-18Å**, was readily obtained through the condensation reaction between benzene-1,3,5-triboronic acid (**3**) and 1,2,4,5-tetrahydroxybenzene (**5**) in 2% methanol/THF by refluxing under a constant flow of nitrogen for 72 h (Figure 1). After cooling to room temperature, the resulting fine solid was collected by filtration, washed with copious amounts of THF, and dried under vacuum (1 Torr) at 70 °C for 24 h to afford 85–95% yield²¹ of **COF-18Å**. Note, if all starting materials were fully dissolved at the beginning of the reaction (~40 mL of solvent per mmol of reactants), networks were formed but yields were greatly reduced (25–30%). Optimal yields were obtained when the starting materials were suspended in solvent with the solvent to monomer ratio near 12 mL of solvent per mmol of monomer. Excess bis-diol was used in the reaction (up to 2.5 equiv) to ensure that no boron anhydride (boroxine) was formed and thereby limit corrup-

(19) A sample of 1,2,4,5-tetrahydroxybenzene prepared in the spring of 2003 has been stored in a glass, push-top vial on a bench in lab without any regard for protection from moisture, oxygen, or light. No discoloration has occurred and ¹H NMR analysis shows material of consistent purity with that upon initial synthesis in 2003.

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(21) The range in yield is included to cover subtle changes in hydration state. If the trihydrate form of the boronic acid (based on NMR) is used to calculate yield, 95% is obtained. If the boroxine form is the assumed starting material, 85% yield is isolated.

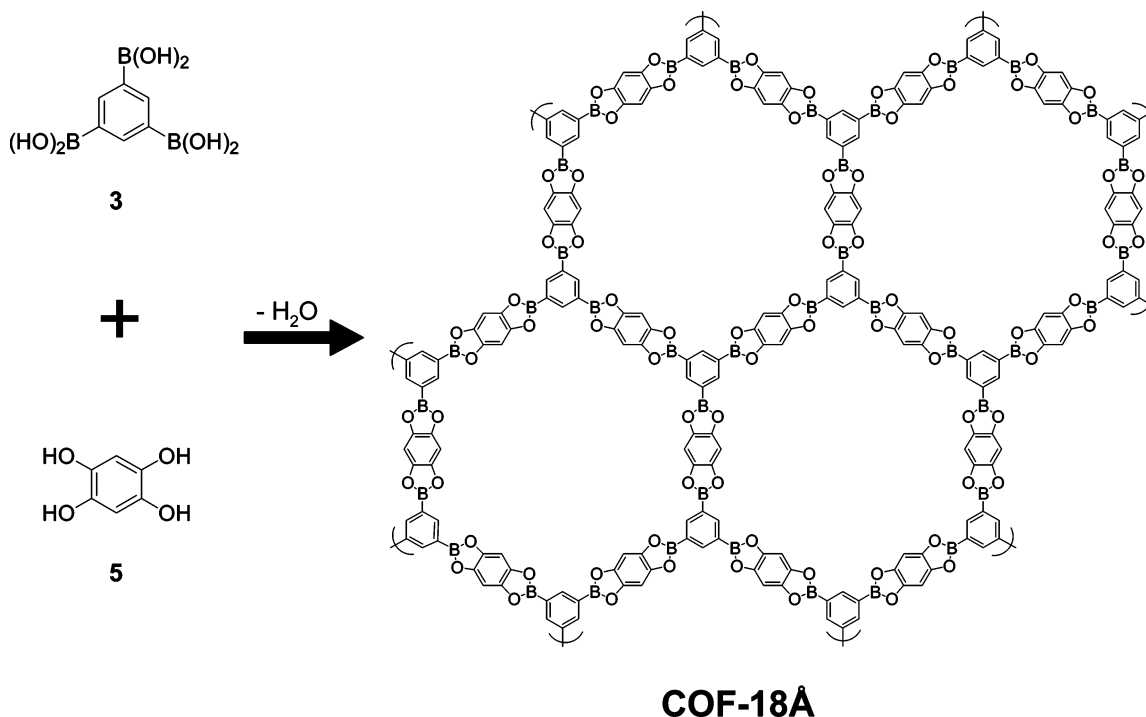


Figure 1. Synthetic scheme and proposed structure for **COF-18Å**.

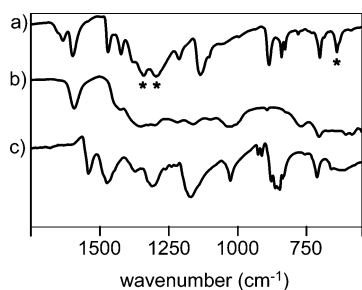


Figure 2. FT infrared spectra for (a) the poly(boronate ester) **COF-18Å**, (b) benzene-1,3,5-triboronic acid (**3**), and (c) 1,2,4,5-tetrahydroxybenzene (**5**). Asterisks (*) indicate signals in the **COF-18Å** spectrum that correspond to the formation of the boronate ester linkage.

tion of the network uniformity. Varying the excess of bis-diol monomer (1.5–2.5 equiv) had no apparent effect on the isolated yield (90–95%) or purity (as assessed by PXRD) of the isolated product. Previous studies from our group⁹ have demonstrated that the reversibility and thermodynamic driving force of the boronate ester formation reaction is such that linear polymers are formed independently of the diol to boronic acid ratio. The one previous synthesis of related material¹² used sealed, pressurized reaction vessels at elevated temperatures (~ 120 °C). The route described herein uses ambient pressure and modest temperatures (~ 60 °C) to obtain networks in higher yields with purities similar to those previously reported. The covalent organic framework, **COF-18Å**, was characterized using FTIR and ^{11}B and ^1H NMR to confirm that the expected building blocks were indeed present in the assembly and that the desired bonds were formed.

Consistent with FTIR analysis of related materials,¹² **COF-18Å** showed modest attenuation of the hydroxyl stretch compared to the starting materials (see Supporting Information). The existing hydroxyl stretch intensity resulted from the hydroxyl groups on the bis-diol units at the network termini. More indicative of network formation were the two

intense peaks (of similar intensity) around 1300 and 1345 cm^{-1} , signifying that the boronate ester functionality is present as does the presence of a new peak appearing at ~ 640 cm^{-1} (Figure 2, all marked with *). Peaks indicative of boron anhydride (boroxine) formation, namely, a broad, intense peak at 1350 and a sharp peak at 580 cm^{-1} , were absent.

Solid-state ^{11}B NMR analysis confirmed the presence of trigonal planar boron centers, revealing a single peak at 30 ppm^{11b,22} compared to the starting boronic acid monomer which appears at 25 ppm. To verify that both monomers were incorporated into the network, ^1H NMR analysis was performed using 1 M KOH in D_2O as the solvent. Under these basic conditions the boronate-linked material is hydrolyzed, providing a simple quantitative method to measure the network composition in solution. Comparison of the spectra for the hydrolyzed/degraded network against starting materials confirms the presence of both monomers in the network. Integration verifies that the bis-diol (**5**) and triboronic acid (**3**) are present in the expected 3:2 ratio.

Structural Characterization of COF-18Å. Powder X-ray diffraction (PXRD) analysis proved the formation of a highly crystalline network (Figure 3a). To evaluate the structure of the network formed, the possible assemblies were modeled using Macromodel.²³ The proposed network contains pores with a diameter of approximately 18 Å (therefore, the name **COF-18Å**). In conjunction with crystallographic data for analogous model compounds,¹¹ Diamond software¹⁷ was used

(22) (a) In solution, tetrahedral boron exhibits a chemical shift of 0 ppm with respect to $\text{BF}_3\text{-OEt}_2$ (defined as 0 ppm), and trigonal boron displays shifts closer to 30 ppm. Magic angle spinning, solid-state analysis used boric acid as a solid reference at 19.3 ppm based on its solution analysis referenced to $\text{BF}_3\text{-OEt}_2$ at 0 ppm. (b) Noth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Vol. 14; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978.

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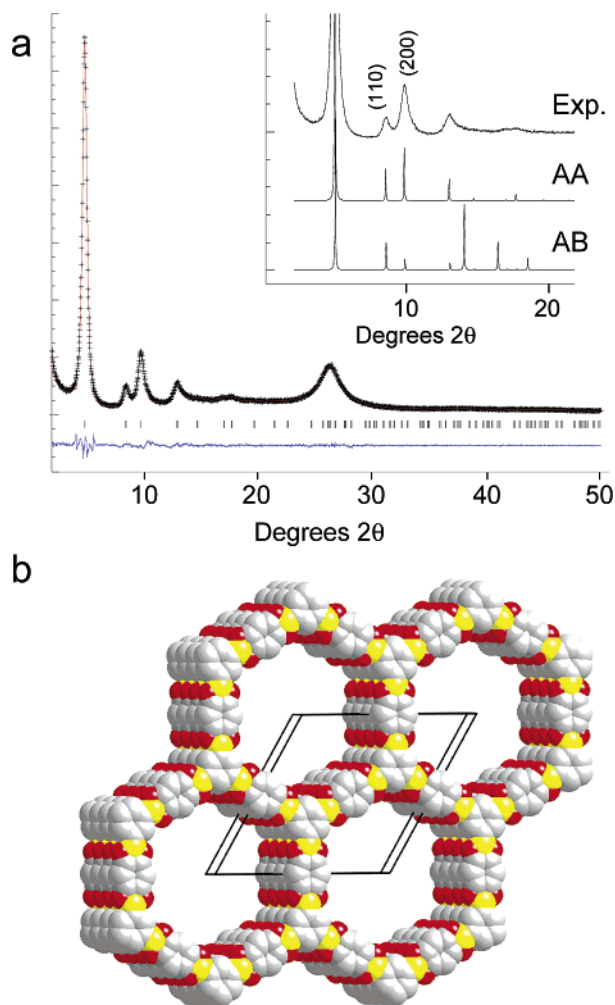


Figure 3. (a) LeBail method fit to PXRD data for **COF-18Å** in space group $P6/mmm$. Black cross hatches are collected data and the red solid line is the refined profile. Differences between observed and calculated intensities are shown in blue. Vertical marks indicate allowed peak positions. *Inset:* X-ray diffraction patterns calculated for the two proposed models, *AA* and *AB*, are shown for comparison to the experimental data. (b) Proposed structure and stacking for **COF-18Å** based on PXRD analysis.

to define a unit cell with the origin located in the center of the pore. Based on these lattice parameters, expected powder diffraction patterns were generated assuming that the tri-boronic acid and bis-diol building blocks assembled as proposed. Planar two-dimensional sheets were expected and the manner in which these sheets can stack is limited. With use of the paradigm established by Yaghi and co-workers, the most likely crystal packing allows the sheets to assemble in a registered *AA* manner where atoms in adjacent sheets lie directly over each other, leaving a hexagonal array of 1D, 18 Å pores. Alternatively, the sheets could assemble in a staggered *AB* arrangement, where the sheets offset by $1/2$, $1/2$, placing the phenyl rings in every other layer in registry while partially blocking the pore of the intermediate layer. Although both models have primitive hexagonal symmetry, they would display distinct diffraction patterns (Figure 3a, inset).

There are too few peaks observed in the PXRD of **COF-18Å** to use the Rietveld method to refine atomic positions; however, the LeBail routine can be used to compare calculated and experimental PXRD patterns to determine the most probable structural motif. The calculated diffraction

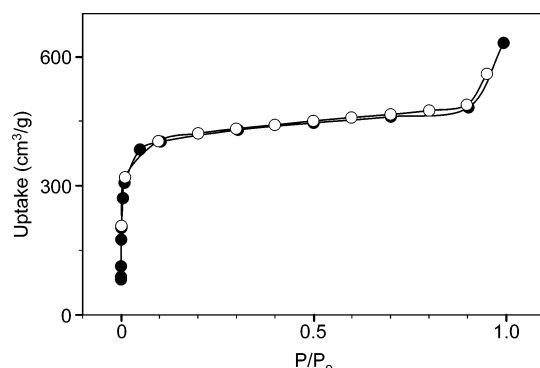


Figure 4. Nitrogen gas adsorption isotherm for **COF-18Å**.

patterns (calculated from PowderCell²⁴) using the atomic positions determined from Diamond for both models along with the experimental diffraction pattern of the sample are shown in Figure 3a, inset. The *AA* model was built in space group $P6/mmm$ and the *AB* model was built in space group $P6_3/mmc$.¹²

There is substantial correlation between the expected peak position and intensities for the registered *AA* model and the experimental data, whereas the projected pattern for the staggered *AB* arrangement does not fit experimental data. In particular, the mismatch in the relative intensity of the 110 and 200 peaks, as well as the presence of calculated intensity in the range of 14° – 19° 2θ for the *AB* model that is lacking in the experimental data, tends to rule out this orientation. Consistent with the modeled structure, the PXRD supports the presence of 18 Å micropores, arranged in a hexagonal orientation (Figure 3b). The interlayer spacing between sheets from modeling versus that found from the PXRD analysis agree well (3.597 Å calculated versus 3.385 Å experimental).

The porosity and pore stability of **COF-18Å** were evaluated by measuring the N_2 gas adsorption. This material exhibits thermal stability to temperatures of more than 500 °C, as shown by thermogravimetric analysis. As such, a sample of **COF-18Å** was evacuated under dynamic vacuum (10^{-5} Torr) while heated at 400 °C for 2.5 h. This sample was used for gas adsorption measurements from 0 to 760 Torr at 77 K. The adsorption profile was reversible and reproducible and showed a very sharp uptake at low partial pressure (P/P_0 from 4×10^{-6} to 0.01), which is indicative of microporous material (Figure 4). With use of the BET model, applied to the isotherm for P/P_0 between 0.05 and 0.3, the apparent surface area was determined to be 1260 m^2/g , corresponding to a micropore volume of 0.29 cm^3/g .

These values are consistent with reported values for the first reported mesoporous polyboronate network (surface area = 1590 m^2/g , pore volume = 0.998 cm^3/g)¹² and similar to the highest reported surface area for macroporous silica (1300 m^2/g).²⁵ As a further comparison, the popular Mobile Crystalline Material 41 (MCM-41) has an apparent surface

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area of 680 m²/g, nearly half that observed for **COF-18Å**, and a pore volume of 0.26 cm³/g.²⁶

Conclusions

In summary, we report on the facile, high-yielding synthesis and characterization of a microporous, covalently linked, polyboronate network with persistent pores. Building blocks synthesized in our labs invert the linkage orientation as compared to previous reports. Spectral characterization has confirmed the bonding motif to generate infinite 2D porous sheets while PXRD was used to provide evidence for the long-range ordering of these sheets, such that atoms in adjacent layers lie directly over each other, resulting in a hexagonal array of 1D, 18 Å pores. The resulting covalent organic framework (**COF-18Å**) is thermally stable to 500

°C and maintains a higher surface area than most known porous materials. Future efforts will focus on the creation of networks based on functional building blocks to tailor the interior of the cavities to controllably alter the adsorption and inclusion phenomena of these materials. Given the enhanced stability, high surface area, and small micropore volume, this **COF** appears ideally suited to serve as a matrix for gas adsorption.

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Supporting Information Available: Complete FTIR characterization; TGA, BET, and crystallographic data and analysis protocols. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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