

Vibrational Properties of Boroxine Anhydride and Boronate Ester Materials: Model Systems for the Diagnostic Characterization of Covalent Organic Frameworks

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Supporting Information

ABSTRACT: The vibrational characteristics of 28 different boronic acid, boroxine anhydride, and boronate ester species have been systematically investigated using a combination of experimental infrared (IR) spectroscopy and computational modeling. IR bands characteristic to each boron-containing functionality have been categorized and assigned in conjunction with density functional theory (B3LYP/6-31G(d)), with the aim of better understanding and distinguishing the vibrational characteristics of covalent organic frameworks (COFs) built from boronic acids. In several cases, vibrational assignments differ from those previously reported in the literature on boronic acid-based COFs. Vibrations commonly regarded as diagnostic for one functionality are found in regions of the IR spectrum where other functionalities also show characteristic peaks. The collective experimental and computational results reveal that several alternative bands in the IR region can



be used to more diagnostically distinguish between boronic acid, boroxine anhydride, and boronate ester species. The results presented herein provide the tools for straightforward characterization of boroxine anhydride and boronate ester species using IR spectroscopy. The results can be applied to additional theoretical studies of larger COF-like assemblies as well as the analysis of other boronic-acid-based materials.

■ INTRODUCTION

Boronic acids have long played several central roles in synthetic, bioorganic, and analytical chemistry.¹ They serve as key building blocks for Suzuki-Miyaura cross-coupling reactions, form the basis of myriad saccharide receptors,³ function as selective anion sensors,⁴ and can enhance electrophoretic separations.⁵ Recently, there has been significant and increasing interest in the dynamic covalent assembly⁶ of boronic-acidderived materials.⁷ The dynamically reversible self-condensation of boronic acids to form boroxine anhydrides and the similarly reversible assembly of boronic acids with organic diols to generate boronate esters (Scheme 1) have enabled the facile, thermodynamically driven synthesis of multiple complex molecular and supramolecular compounds, e.g., macrocycles,⁸ capsules,⁹ dendrimers,¹⁰ polymers,¹¹ and mechanically interlocked molecules.¹² Particularly exciting is the recent growth in the area of boronic-acid-based covalent organic frameworks¹³ (COFs). First reported by Yaghi and co-workers¹⁴ in 2005, COFs represent a class of rigid, highly ordered, nanoporous crystalline polymers. Interest in boronic-acid-derived COFs has grown exponentially with several research groups, e.g., Yaghi,¹⁵ Jiang,¹⁶ Dichtel,¹⁷ Lavigne,¹⁸ and others,¹⁹ making significant contributions to the field. Much of the interest in boronic-acidderived COFs is due, in large part, to their outstanding physical properties: strong covalent linkages, low mass densities, high thermal stabilities, and permanent porosity.¹³ Given their Scheme 1. Boronic Acids Are Able to Dynamically Self-Assemble into Boroxine Anhydrides (top) and Boronate Esters (bottom), Which Serve As Fundamental Secondary Building Units (SBUs) for the Design and Synthesis of COFs



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Figure 1. Chemical structures and ideal point group symmetries of (a) boronic acid, (b) boroxine anhydride, and (c) boronate ester species used in the current study.

desireable physical and structural characteristics, COFs have found applications spanning gas uptake and storage, $^{13a,14,15a-c}$ catalysis, 20 charge carrier materials, $^{15d,16e-i}$ and optoelectronic-s. $^{16a-c}$

Unlike most discrete boronate ester and boroxine anhydride materials, boronic-acid-based COFs are, by their very nature, insoluble powders. Two-dimensional, planar COFs tend to stack into multilayered structures, whereas three-dimensional COFs adopt different net topologies. As the range of methods and compounds (secondary building units, SBUs) used to synthesize new COFs has expanded, two techniques-powder X-ray diffraction (PXRD) and infrared (IR) spectroscopyhave emerged as the most prominent means of analyzing these new materials, though solid-state NMR, elemental analysis, and X-ray photoelectron spectroscopy (XPS) have also been used. PXRD is able to provide insight into the long-range 2D and 3D ordering of COFs by comparing experimentally obtained diffraction data to predictions obtained from molecular simulations. PXRD, however, does not provide information regarding chemical composition or connectivity. IR spectroscopy, on the other hand, provides this complementary analysis of chemical functionalities and connectivities while being unable to provide long-range structural information. In reviewing the literature of COFs, ^{13–19} and in conjunction with our own efforts²¹ to synthesize and characterize discrete, soluble COF analogues, we have found that IR spectroscopic analysis and characterization of boronate ester and boroxine anhydride materials can be misleading, as many spectral bands reported as diagnostic for one functionality (i.e., boronic acid, boroxine anhydride, or boronate ester) are also present in others. Many, if not most, of the absorption bands typically reported as characteristic of a particular structure are supportive of, but not diagnostic for, the structures they aim to describe. Few absorption bands have been assigned to specific vibrational modes characteristic of boronic acid, boroxine anhydride, or boronate ester species. Given the many structural similarities among secondary building units used in COF synthesis, it is likely that vibrational bands seemingly correlated with boroxine anhydride and/or boronate ester assemblies are actually attributable to other commonly shared vibrational modes not associated with boron-containing species. As the complexity of boronic-acid-derived COF materials expands it becomes increasingly important to be able to distinguish and assign those vibrational modes that are characteristic of and unique to boronic acid, boroxine anhydride, and boronate ester linkages.

The vibrational mode most commonly cited as being characteristic of both boroxine anhydride and boronate ester formation is a strong absorption band(s) in the region between 1300 and 1400 cm^{-1.13} Given that strong absorptions exist in this region for boronic acids, boroxine anhydrides, and boronate esters, it is generally not possible to characterize the chemical linkages present in boronic-acid-based COFs using only the vibrational absorption bands present between 1300 and 1400 cm⁻¹. Other bands attributed to boroxine anhydride or boronate ester linkages have been also noted in the literature, though less frequently. In particular the regions between 1220 and 1250 cm⁻¹, 1000–1090 cm⁻¹, and 500–750 cm⁻¹ have been assigned to C–O stretches, ^{14,15a,16a–c,e,f,19a,b,d} B–C stretches, ^{14,15a,16a–e,g–i,k,17a,19a,b,d} and out-of-plane vibrations, ^{14,18a,b} respectively. In some cases, however, assignments of C-O and B-C stretches appear switched, with bands in the region between 1100 and 1200 cm⁻¹ being assigned^{16d,g,j,19e} to C–O stretches and those in the region between 1200 and 1270

cm⁻¹ assigned^{14,15a,16d,19e} to B–C stretches. In their study of oligo(dioxaborole)s, Rambo and Lavigne²² critically compared the IR spectra of two discrete bis-boronate esters, one oligo-boronate ester, and one boroxine anhydride and convincingly point out that the fingerprint region provides a more direct means of distinguishing boroxine anhydrides from boronate esters.

We have undertaken a systematic investigation, combining experimental IR spectroscopy and density functional modeling, of the vibrational characteristics of 28 different boronic acid, boroxine anhydride, and boronate ester species (Figure 1). The combination of synthesis, IR spectroscopy, and computational frequency analysis allows us to directly visualize and assign experimental absorption bands to particular vibrational modes. The selection of 28 different individual components and assemblies has allowed us to determine those vibrational modes that are shared between different functionalities and those that are distinct and diagnostic. Theoretical vibrational analysis is then expanded to representative larger COF-like assemblies to further investigate the relationships between IR spectra of such large assemblies and their smaller SBU components. The results presented herein will enable more definitive characterization of boronate ester and boroxine anhydride species by IR spectroscopy, and can be applied to the analysis of other boronate ester and anhydride materials in general.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Materials. Chemicals were obtained from commercial sources and used as purchased. Reagent-grade solvents were used as obtained from commercial sources. Anhydrous solvents were dried using an Innovative Technologies SPS-400–5 solvent purification system.

Instrumentation. ¹H and ¹³C NMR spectra were recorded with a Varian Mercury (300 and 75 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the δ scale and all coupling constants are expressed in Hertz (Hz). Infrared spectroscopic analysis was performed on a PerkinElmer Spectrum BX FT-IR system. CI and LIFDI TOF-MS analysis was carried out at the University of California, Riverside, Mass Spectrometry Facility.

Computational Details. All calculations were performed with the Gaussian09 suite of programs.²³ Prior to geometry optimization, dihedral scans were performed at a low level of theory (HF/3-21G) to approximate the global energy minimum conformation of molecular species containing easily rotating torsion angles. Ground-state geometries were then optimized to full convergence at the B3LYP/ 6-31G(d) level of theory.²⁴ Vibrational analyses were carried out at the same level and the resulting frequencies were used to aid in assigning IR absorption bands observed experimentally. Calculated frequencies were scaled by a factor of 0.960.²⁵ Several studies have demonstrated^{21,26–28} that geometry optimization and frequency analysis of polycyclic aromatic molecules performed at the B3LYP/ 6-31(d) level provides results that are in good agreement with experimental vibrational frequencies and intensities. Indeed, in the current study, frequencies obtained theoretically at the B3LYP/6-31G(d) level were observed to have a mean absolute deviation (MAD) of ± 8 cm⁻¹ relative to experimental frequencies (see the Supporting Information).

General Procedure for Boroxine Anhydrides 10–15. Boronic acids 1–6 were suspended in chloroform (0.5 M) in a round-bottom flask and ethyl acetate was added dropwise until a homogeneous solution was obtained. Each solution was then allowed to stir open to atmosphere and at room temperature for 30 min. A small amount of anhydrous $MgSO_4$ was then added to each flask and the resulting suspensions were allowed to continue stirring for 3 h. After this time the suspensions were filtered and the solvents were removed under

reduced pressure to afford boroxine anhydrides 11–16. No attempts were made to optimize the synthetic yields of anhydrides 11–16. Emphasis was instead placed on isolating each assembly in its purest form to limit the possibility of obtaining IR spectra convoluted by incompletely assembled anhydride species and/or residual boronic acid.

11: Reaction scale. Boronic acid **1** (100 mg, 0.820 mmol). Yield: 75 mg, 0.241 mmol (88%). Boroxine anhydride **11** was isolated as a white solid. Mp > 200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.27 (dd, *J* = 7.9, 1.2 Hz, 6H), 7.60–7.65 (m, 3H), 7.53 (t, *J* = 7.0 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 135.6, 132.7, 128.0 ppm. Characterization matched reported analysis.²⁹

12: Reaction scale. Boronic acid 2 (222 mg, 1.25 mmol). Yield: 182 mg, 0.387 mmol (91%). Boroxine anhydride 12 was isolated as a white solid. Mp = 174–179 °C. TOF MS FD⁺ (m/z) [M]⁺ calcd for C₃₀H₃₉¹¹B₃O₃, 480.3173; found 480.3195. ¹H NMR (CDCl₃, 300 MHz): δ 8.21 (d, J = 8.1 Hz, 6H), 7.58 (d, J = 8.4 Hz, 6H), 1.42 (s, 27H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 172.1, 150.3, 102.1, 54.5, 54.0 ppm.

13: Reaction scale. Boronic acid **3** (250 mg, 1.79 mmol). Yield: 215 mg, 1.79 mmol (99%). Boroxine anhydride **13** was isolated as a white solid. Mp > 200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.20–8.25 (m, 6H), 7.17–7.23 (m, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 130.1, 130.1, 138.0, 115.4, 115.2 ppm. Characterization matched reported analysis.²⁹

14: Reaction scale. Boronic acid 4 (250 mg, 1.64 mmol). Yield: 119 mg, 0.297 mmol (54%). Boroxine anhydride 14 was isolated as a white solid. Mp > 200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.17 (d, *J* = 8.8 Hz, 6H), 7.02 (d, *J* = 8.8 Hz, 6H), 3.89 (s, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 163.1, 137.5, 113.5, 55.1 ppm. Characterization matched reported analysis.³⁰

15: Reaction scale. Boronic acid **5** (250 mg, 1.39 mmol). Yield: 216 mg, 0.445 mmol (96%). Boroxine anhydride **15** was isolated as a white solid. Mp = >200 °C. ¹H NMR (CDCl₃, 300 MHz): *δ* 8.33 (d, *J* = 8.2 Hz, 6H), 8.19 (d, *J* = 8.2 Hz, 6H), 3.99 (s, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 193.42, 135.61, 133.49, 128.92, 53.73 ppm. Characterization matched reported analysis.³¹

16: Reaction scale. Boronic acid **6** (100 mg, 0.681 mmol). Yield: 66 mg, 0.504 mmol (74%). Boroxine anhydride **16** was isolated as a white solid. Mp > 200 °C. TOF MS FD⁺ (m/z) [M]⁺ calculated for C₂₁H₁₂¹¹B₃N₃O₃, 387.1152; found 387.1168. ¹H NMR (CDCl₃, 300 MHz): δ 8.32 (d, J = 8.1 Hz, 6H), 7.82 (d, J = 8.4 Hz, 6H) ppm. Solubility precluded collection of a ¹³C NMR spectrum.

General Procedure for Boronate Esters 17-28. Three general methods were used to assemble discrete boronate ester species. No attempts were made to optimize the synthetic yields of esters 17-28. Method A: To a suspension of boronic acid in dichloromethane (0.3 M) was added the appropriate organic catechol. Ethyl acetate was added dropwise until a homogeneous solution was obtained and the resulting mixture was stirred at room temperature overnight. The reaction solution was dried over anhydrous MgSO4, filtered, concentrated under reduced pressure, and purified via column chromatography eluting with a solution of hexanes:dichloromethane. Method B: To a suspension of boronic acid in chloroform (0.1 M) was added catechol (1.0 equiv. per boronic acid) and DOWEX (1 equiv by mass with respect to the boronic acid). The resulting suspension was stirred at 50 $^\circ\text{C}$ for 3 h, allowed to cool down to room temperature, dried over anhydrous MgSO4, filtered, and concentrated under reduced pressure to afford pure boronate ester product. Method C: To a suspension of boronic acid in dichloromethane (0.3 M) was added the appropriate organic catechol. Ethyl acetate was added dropwise until a homogeneous solution was obtained and the resulting mixture was stirred at room temperature overnight. The reaction solution was dried over anhydrous MgSO4, filtered, and allowed to slowly evaporate leaving clear crystals on the sides of the flask. When the solution had been reduced to approximately one-third of its original volume the remaining solvent was removed by pipet and the resulting crystals washed thoroughly with hexanes to afford pure boronate ester product.

17: Synthesized by Method A. Reaction scale. Boronic acid 1 (1.0 g, 8.20 mmol) and catechol (1.4 g, 12.3 mmol). Crude boronate ester 17 was subjected to column chromatography, eluting with 1:1 hexanes:dichloromethane, to afford 1.3 g (6.63 mmol, 81%) of a white solid product. This resulting solid was further purified by slow evaporation from a dilute solution of dichloromethane, yielding clear crystals that were isolated and washed thoroughly with hexanes. Mp = 104–105 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.58–7.63 (m, 1H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.31–7.36 (m, 2H), 7.12–7.18 (m, 2H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.5, 135.0, 132.4, 128.2, 122.8, 112.5 ppm. Spectroscopic analysis of pure 17 matched that reported in the literature.³²

18: Synthesized by Method B. Reaction scale. Boronic acid 2 (100 mg, 0.562 mmol) and catechol (62 mg, 0.562 mmol). Yield: 122 mg, 0.484 mmol (87%). The product was isolated as a white solid. Mp = 74–75 °C. TOF MS CI⁺ (*m*/*z*) [MH]⁺ calcd for C₁₆H₁₈¹¹BO₂, 253.1394; found 253.1389. ¹H NMR (CDCl₃, 300 MHz): δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.34–7.31 (m, 2H), 7.14.7.11 (m, 2H), 1.38 (s, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 156.0, 148.8, 135.2, 125.5, 122.9, 112.8, 35.3, 31.4 ppm.

19: Synthesized by Method C. Reaction scale. Boronic acid **3** (250 mg, 1.79 mmol) and catechol (217 mg, 1.97 mmol). Yield: 133 mg, 0.622 mmol (35%). The product was isolated as a white solid. Mp = 90–91 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.07–8.12 (m, 2H), 7.30–7.35 (m, 2H), 7.11–7.23 (m, 4H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 167.4, 164.0, 148.5, 137.2, 122.8, 115.7, 112.5 ppm. Spectroscopic analysis matched literature values.³³

20: Synthesized by Method B. Reaction *Scale*: Boronic acid **4** (100 mg, 0.658 mmol) and catechol (72 mg, 0.658 mmol). Yield: 132 mg, 0.584 mmol (89%). The product was isolated as a white solid. Mp = 104–105 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.29–7.32 (m, 2H), 7.10–7.13 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.6, 136.8, 122.6, 113.9, 112.4, 55.2 ppm. Spectroscopic analysis matched literature values.³⁴

21: Synthesized by Method B. Reaction scale. Boronic acid **5** (100 mg, 0.556 mmol) and catechol (61 mg, 0.556 mmol). Yield: 92 mg, 0.362 mmol (65%). The product was isolated as a white solid. Mp = 176–177 °C. TOF MS CI⁺ (m/z) [MH]⁺ calculated for C₁₄H₁₂⁻¹¹BO₄, 255.0823; found 255.0824. ¹H NMR (CDCl₃, 300 MHz): δ 8.15–8.14 (m, 4H), 7.35–7.31 (m, 2H), 7.16–7.13 (m, 2H), 3.95 (s, 3H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 167.1, 148.6, 135.1, 133.5, 129.3, 123.3, 113.0, 52.6 ppm.

22: Synthesized by Method B. Reaction scale. Boronic acid **6** (100 mg, 0.681 mmol) and catechol (75 mg, 0.681 mmol). Yield: 108 mg, 0.489 mmol (72%). The product was isolated as a white solid. Mp = 164–165 °C. TOF MS CI⁺ (m/z) [MH]⁺ calculated for C₁₃H₉¹¹BNO₂, 222.0721; found 222.073. ¹H NMR (CDCl₃, 300 MHz): δ 8.19 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.36–7.32 (m, 2H), 7.18–7.15 (m, 2H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.5, 135.5, 131.9, 123.5, 118.7, 115.9, 113.1 ppm.

23: Synthesized by a modified Method C wherein pentane was used as the primary solvent with ethyl acetate added dropwise until all starting materials dissolved, and MgSO₄ was added to the reactants prior to stirring overnight. Reaction scale. Boronic acid 7 (200 mg, 1.33 mmol) and catechol (147 mg, 1.33 mmol). Yield 189 mg, 0.844 mmol (63%). The product was isolated as a waxy off-white solid. Mp = 67–68 °C. TOF MS Cl⁺ (*m*/*z*) [MH]⁺ calculated for C₁₄H₁₄¹¹BO₂, 225.1081; found 225.1085.¹H NMR (CDCl₃, 300 MHz): δ 7.34–7.31 (m, 2H), 7.17–7.01 (m, 5H), 2.47 (s, 6H) ppm. ¹³C NMR (CD₃COCD₃, 75 MHz): 148.3, 144.1, 131.0, 127.4, 123.2, 120.8, 112.7, 22.4 ppm.

24: Synthesized by Method C. Reaction scale. Boronic acid 1 (258 mg, 2.11 mmol) and 1,2,4,5-tetrahydroxybenzene (143 mg, 1.01 mmol). Yield: 30 mg, 0.096 mmol (9%). The product was isolated as a white solid. Mp = >200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.09 (dd, J = 6.9, 1.5 Hz, 4H), 7.57–7.62 (m, 2H), 7.48–7.53 (m, 4H), 7.33–7.35 (m, 2H) ppm. Solubility precluded collection of a satisfactory ¹³C NMR spectrum. Spectroscopic analysis matched literature values.²²



Figure 2. Depictions of the six vibrational modes involving the $B(OH)_2$ functionality that were found to be conserved across boronic acids 1–10. Symmetries are assigned based on the $C_{2\nu}$ symmetry of phenylboronic acid (1). Relative intensities (weak, medium, or strong) and maximum, minimum, and average frequencies (in wavenumbers, cm⁻¹) were obtained from theoretical frequency analysis of optimized structures. At the bottom is a visual representation of the relative location, average (black dashed line), and span of each $B(OH)_2$ vibrational mode within the IR region from 450 to 1450 cm⁻¹.

25: Synthesized by modified Method C. Reaction scale: Boronic acid **8** (100 mg, 0.603 mmol) and catechol (133 mg, 1.21 mmol). Yield: 68 mg, 0.217 mmol (36%). The product was isolated as a pinkish-white solid. Mp > 200 °C. ¹H NMR (CDCl₃, 300 MHz): δ 8.21 (s, 4H), 7.34–7.36 (m, 4H), 7.16–7.18 (m, 4H) ppm. Solubility precluded collection of a ¹³C NMR spectrum. Spectroscopic analysis matched literature values.³⁵

26: Synthesized by Method C. Reaction scale: Boronic acid **9** (106 mg, 0.640 mmol) and catechol (148 mg, 1.34 mmol). Yield: 136 mg, 0.433 mmol (68%). The product was isolated as a white solid. Mp = >200 °C. TOF MS FD⁺ (m/z) [M]⁺ calculated for C₁₈H₁₂¹¹B₂O₄, 314.0916; found 314.0931. ¹H NMR (CDCl₃, 300 MHz): δ 8.84 (s, 1H), 8.28 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.36–7.32 (m, 4H), 7.18–7.13 (m, 4H) ppm. Solubility precluded collection of a ¹³C NMR spectrum.

27: To a freshly prepared suspension of 1,3,5-benzenetriboronic acid **10** (585 mg, 2.79 mmol) in hexanes (20 mL) and water (5 mL) was added catechol (952 mg, 8.65 mmol). Catalytic methanol (0.5 mL) and ethyl acetate (3 mL) were added to increase solubility of the inhomogeneous mixture, which was then stirred for 30 min at room temperature. Following removal of the solvent under reduced pressure the resulting residue was taken up ethyl acetate, dried over anhydrous MgSO₄, filtered, and concentrated to afford a gray powder, which was washed with ethyl acetate and dichloromethane to give pure ester **27**. Yield: 376 mg, 0.871 mmol (31%). Mp = >200 °C. TOF MS FD⁺ (m/z) [M]⁺ calculated for C₂₄H₁₅¹¹B₃O₆, 432.1142; found 432.1137.¹H NMR (CDCl₃, 300 MHz): δ 9.02 (s, 3H), 7.38–7.36 (m, 6H), 7.19–7.15 (m, 6H) ppm. Solubility precluded collection of a ¹³C NMR spectrum.

28: A mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (140 mg, 0.431 mmol) and phenylboronic acid **1** (158 mg, 1.29 mmol) was suspended in 1:1 solution of mesitylene:dioxane (8.6 mL) in a 3 dram screw cap vial. The suspension was sonicated for 30 min and then heated in a convection oven at 100 °C overnight. The resulting suspension was filtered and the solids were washed with acetone. The crude material was then resuspended in anhydrous acetonitrile for 90 min, filtered, and the solid was washed with acetone to afford 124 mg (0.213 mmol, 52% yield) of **28** as a lavender solid. Mp > 200 °C. TOF

MS FD⁺ (m/z) [M]⁺ calcd for C₃₆H₂₁¹¹B₃O₆, 582.1612; found 582.1639. ¹H NMR (CDCl₃, 300 MHz): δ 8.46 (s, 6H), 8.20 (d, J = 8.4 Hz, 6H), 7.73–7.56 (m, 9H) ppm. Solubility precluded collection of a ¹³C NMR spectrum.

RESULTS AND DISCUSSION

Symmetry plays a central role in the synthetic design of infinitely repeating 2D and 3D COFs. Symmetry also plays a fundamental role in determining which vibrational modes of COFs, and their component secondary building units, are IR active versus Raman active. As such, the compounds selected for this study were chosen to maintain, in general, a high degree of symmetry across both secondary building units (boronic acid and catechol derivatives) and the discrete COF-like assemblies built from them. With a few exceptions, the starting materials and assemblies investigated herein (Figure 1) are members of the point groups $C_{2\nu}$, C_{2h} , D_{2h} , or D_{3h} . This intentional utilization of symmetry serves as a starting point from which a more thorough understanding of the IR active spectroscopic modes characteristic of boronic acids, boroxine anhydrides, and boronate esters can be developed. The series of compounds chosen also provides a means of investigating the effects of aromatic substitution on the vibrational characteristics of each species. Specifically, boronic acids 2-6 bear electron-donating (alkyl, fluoro, methoxy) and electron-withdrawing groups (ester, cyano) at their para position, allowing a means of investigating the influence of electronic effects on vibrational spectra. Similarly, ortho-dimethyl phenylboronic acid (8) provides a means of investigating the influence of sterics on vibrational modes.

The relationships between individual vibrational modes of simple discrete assemblies and those of fully assembled COFs may be better determined by combining experimental and computational analyses while systematically progressing from simple to more complex systems. For example, as discrete COF-like analogues progress from simple monoesters (e.g., 17) to more complex diesters (e.g., 26) and triesters (e.g., 28) the number of related yet symmetrically distinct vibrational modes increases. Experimentally, such closely related yet distinct vibrational modes can lead to broadening of IR absorption bands. Furthermore, the specific symmetry of each individual vibrational mode will determine the magnitude of its dipole vector and, thus, intensity. With computational frequency analysis, all symmetrically similar yet vibrationally distinct vibrational modes can be more directly "resolved" and analyzed individually.

The following three sections are divided according to the different boron-containing functionalities involved in boronicacid-based COF formation: boronic acids, boroxine anhydrides, and boronate esters. Vibrational modes characteristic of each boron-containing functionality have been assigned according to their symmetry and intensity as well as the maximum, minimum, and average frequency observed across the range of compounds investigated within each group. Once all modes characteristic of each boron-containing functionality are explored it becomes possible to distinguish which modes are diagnostic, rather than simply supportive, of the different functionalities. When appropriate, absorption bands within each region that are conserved across several boronate esters and/or boroxine anhydrides but do not arise from boronspecific chemical linkages are also discussed as potential "red herrings." The results are then applied to the theoretical study of larger COF-like assemblies to investigate how knowledge of small molecule analogues relates to larger systems, which is key to diagnostic IR analysis of "infinite" 2D and 3D COFs. Overall, the results provide a straightforward means of evaluating the IR spectra of myriad new boronic-acid-based COF materials and allow significantly more definitive vibrational assignments to be made

Boronic Acids 1–10. Shown in Figure 2 are the six vibrational modes that directly involve the boronic acid $B(OH)_2$ moiety and are conserved across the ten boronic acids studied. Arrows or (+)/(-) symbols are provided to highlight the atomic displacements that characterize each different mode. Also provided in Figure 2 are the symmetry and relative intensity of each mode as well as the maximum, minimum, and average frequency found computationally for boronic acids 1-10. Phenyl boronic acid (1), the simplest aryl boronic acid in the series, is used as a representative example for all compounds in the series. For complete results detailing the symmetry, frequencies, and intensities specific to each individual boronic acid see Table S1 in the Supporting Information. It should be noted that only computational results are provided for acids 1-10 as it is not possible to obtain experimental IR spectra of purely discrete boronic acids given their propensity to undergo spontaneous self-assembly into boroxine anhydrides, the presence of which convolute experimental results.

Theoretical calculations predict that the hydroxyl stretching frequencies of boronic acids 1-10 (not shown in Figure 2) all fall within the narrow range of 3629-3634 cm⁻¹. Symmetric O–H stretching modes were predicted to occur at higher frequencies and higher intensities than asymmetric modes for all compounds investigated. The attenuation of hydroxyl stretching modes in experimental IR spectra of COFs is often cited¹³⁻¹⁹ as evidence for the formation of boroxine anhydride or boronate ester functionalities. Hydroxyl peaks do not disappear entirely for even well-formed COFs because their

leading edges will inevitably be composed of hydroxyl units from either unassembled boronic acids or organic catechol derivatives. Although it can be instructive to note where O-Hstretches of boronic acids 1-10 occur, in practice it is unlikely that the specific range of O-H frequencies will aid in the characterization of COF materials. This conclusion is drawn from the fact that O-H frequencies are well-known to be broad and their intensities are often variable. Few definitive conclusions can be drawn from subtle changes in peak location and intensity. It should be noted, however, that all boroxine anhydride and boronate ester assemblies in the current study are discrete species with no terminal hydroxyl functions.

Two distinct vibrational modes are calculated in the region extending from 1306 to 1353 cm⁻¹ for boronic acids **1–10**. These two vibrations correspond to an asymmetric B–O stretching mode (Figure 2a) and a symmetric B–C stretching mode (Figure 2b). The intensities of both vibrational modes in the 1300 cm⁻¹ region are strong. For most boronic acids the B–O stretching mode was observed to occur at a higher frequency than the B–C stretching mode. The separation between the B–O and B–C modes for any given boronic acid **1–10**, however, was found to average 12 cm⁻¹. Although the two vibrational modes are easily distinguished by computational frequency analysis, it is less likely that experimental IR spectroscopic analysis of "bulk" samples would resolve the two bands.

The region from 900 to 1000 cm⁻¹ also contains two welldefined and distinct IR active modes that are conserved across boronic acids 1-10. Figure 2c shows a representative example of the higher-frequency vibrational mode consisting of a coupled B-O stretch and O-H in-plane bend. For the ten boronic acids investigated this coupled mode spans a region of ca. 24 cm⁻¹. In general the intensity of this coupled B-O stretch and O-H in-plane bending mode is predicted to be strong with the exception of triboronic acid 10, which is predicted to display a medium intensity peak in this region due to the smaller dipole change associated with asymmetric stretching in such 1,3,5-substituted systems. The lower frequency mode in this region (Figure 2d) is more tightly focused between 907 and 920 cm⁻¹ and consists solely of symmetric, in-plane O-H bending. The intensity of this mode centered at 910 cm⁻¹ was also found to be high for all boronic acids. Both modes in the 900-1000 cm⁻¹ region are characteristic of boronic acids and distinct from the O-H inplane bending modes typical of catechol derivatives (e.g., catechol, 1,2,4,5-tetrahydroxybenzene, and 2,3,6,7,10,11-hexahydroxytriphenylene), which are typically observed between 1120 and 1180 cm⁻¹. For the series of compounds studied the coupled B-O stretch/O-H in-plane bending mode does not have an analogue outside boronic acids. Given that both boronic acid vibrational modes in the 900-1000 cm⁻¹ region are sharper and more distinct than hydroxyl stretches around 3600 cm^{-1} , we propose that their attenuation will provide a better means of evaluating the self-assembly of COF materials than the attenuation of hydroxyl O-H stretching bands. Indeed, a survey of several IR spectra of boroxine anhydride and boronate ester COFs reported in the literatur- $e^{14,15a,b,d,16a,c,i-k,17a,c-h,18,19}$ reveal a general lack 36 of mediumor high-intensity peaks centered around 974 or 909 cm⁻¹.

Boronic acids 1-10 also display two characteristic out-ofplane bending modes in the fingerprint region of their IR spectra. These last two vibrational modes are shown in Figure 2e, f. The first, centered around 622 ± 17 cm⁻¹ corresponds to



Figure 3. Representative examples of the 6 vibrational modes involving the B_3O_3 functionality found to be conserved across boroxine anhydrides **11–16**. Symmetries are assigned based on the D_{3h} symmetry of anhydride **11**. Relative intensities (weak, medium, or strong) are based on experimental FTIR data. Maximum, minimum, and average frequencies obtained experimentally (black text) and computationally (blue text) are given in wavenumbers (cm⁻¹). Modes shown in d and e involve symmetric displacements of all aryl C–H, though only five are shown for simplicity. At the bottom is a visual representation of the relative location, average (black dashed line), and span of each B_3O_3 vibrational mode within the IR region from 450 to 1450 cm⁻¹.

the out-of-plane bending of boron atoms syn with out-of-plane bending of aryl hydrogen atoms (Ar-H). This mode was found to be of medium to high intensity for the ten acids investigated. A significantly less intense mode was also observed for out-ofplane displacements of boron and aryl hydrogen atoms anti to each other. The anti relationship of out-of-plane displacements results in a very minor dipole change and, consequently, a very weak IR absorption. The anti out-of-plane mode was, therefore, not included in the discussion of characteristic boronic acid vibrational modes. Shown in Figure 2f is the second prominent vibrational mode in the fingerprint region, which corresponds to out-of-plane displacements of hydroxyl hydrogen atoms. The out-of-plane bending of hydroxyl hydrogens was found to average 520 cm⁻¹ for the ten boronic acids studied computationally and its intensity is predicted to be strong. Several other out-of-plane and in-plane bending modes are present in the fingerprint region of boronic acids 1-10. The intensities of these modes were predicted to be less than half, and typically less than a quarter, of the intensities of the boronic acid specific modes shown in Figure 2e, f. Furthermore, the out-of-plane

modes specific to boronic acids were separated by a minimum of 8 cm⁻¹ and an average of 45 cm⁻¹ from all other out-of-plane and in-plane bending modes in the region. Given the medium– strong intensities, narrow range of frequencies, and general separation from other modes in the region it is expected that the boronic acid specific modes around 622 and 520 cm⁻¹ can be distinguished from other vibrations in the fingerprint region.

It should be reiterated that this discussion of boronic acid vibrational modes is based solely on computational frequency analysis, not experimental IR spectra. However, we²¹ and others^{26–28} have found good agreement ($\pm 8 \text{ cm}^{-1}$) between scaled B3LYP/6-31G(d) frequencies and experimental IR frequencies as well as reasonable agreement between the intensities of theoretically predicted and experimentally determined IR modes. Conclusions regarding the vibrational characteristics of boronic acids that have been drawn from computational analysis of compounds 1–10 are therefore expected to be applicable across a range of aryl boronic acids.

Boroxine Anhydrides 11–16. Figure 3 outlines the six vibrational modes characteristic to the central B_3O_3 ring of



Figure 4. Representations of the five vibrational modes that involve displacements of atoms within the C_2O_2B ring systems of compounds 17–28. Symmetries are assigned based on the $C_{2\nu}$ symmetry of ester 17. Relative intensities (weak, medium, or strong) are based on experimental FTIR data. Maximum, minimum, and average frequencies obtained experimentally (black text) and computationally (blue text) are given in wavenumbers (cm⁻¹). At the bottom is a visual representation of the relative location, average (black dashed line), and span of each C_2O_2B vibrational mode within the IR region from 450 to 1450 cm⁻¹. The outlying C–O vibration of ester 24 is indicated by a dashed blue line.

boroxine anhydrides 11–16. The symmetry, relative intensity, range, and average frequency of each boroxine anhydride mode are also given in Figure 3. Experimental frequency results are given in black text while computational results are in blue text. Assignments of vibrational modes in Figure 3 were based on comparisons of experimental IR spectra and computational frequency analysis. The boroxine anhydride formed upon self-condensation of phenyl boronic acid, 11, is shown in Figure 3 as a representative example for purposes of visualizing each vibrational mode. As before, complete details regarding the symmetry, frequencies, and intensities specific to boroxine anhydrides 11–16 can be found in Table S2 in the Supporting Information.

Three distinct vibrational modes of boroxine anhydrides 11-16 were found to involve stretching of the B-C(aryl) bond (Figure 3a-c). Figure 3a shows a representative example of the highest frequency B-C stretching mode, which was observed to range from 1332 to 1344 cm⁻¹ and to involve a combination of B-C stretching coincident with stretching of the two B-O bonds oriented parallel to the B-C stretch. The intensity of this vibrational mode was strong for all boroxine anhydrides 11-16. Vibrational modes depicted in Figures 3b, c both involve displacements of boron atoms not involved in the dominant B-C stretch. Where they differ is in their relative displacements with respect to the aryl carbon atoms they are covalently attached to: the higher frequency mode (1298-1310 cm⁻¹, Figure 3b) involves displacement of aryl carbon atoms in the opposite direction of boron displacements, while in the lower frequency mode (1242-1259 cm⁻¹, Figure 3c) displacements of aryl carbon atoms and their covalently linked boron atoms are oriented in the same direction. Intensities of these two modes were found to be variable. The high-frequency B-C stretching mode shown in Figure 3b was found to be strong for all but methoxy-substituted anhydride 14. The B-C stretch shown in Figure 3c was found, both experimentally and

theoretically, to be either weak or strong but in no cases was it medium in intensity. Interestingly, anhydrides of D_{3h} symmetry (11, 13, 16) displayed weak intensity for this mode while C_{3h} anhydrides (12, 14, 15) were observed to have strong intensity. A greater range of anhydrides would be necessary to determine whether this trend applies more broadly, but within the current set of structures this observation again highlights the importance of symmetry in influencing the IR spectra of boroxine anhydrides. No correlation was found between vibrational frequencies and the electron withdrawing or electron donating nature of substituents at the para position of aryl rings of boroxine anhydrides 11-16. There have been reports^{14,16b,22} of boroxine anhydride IR

There have been reports^{14,16b,22} of boroxine anhydride IR peaks in the regions between 1000 and 1100 cm⁻¹ that have been assigned as B–C stretching modes. Indeed boroxine anhydrides **11–16** all show absorption bands of medium to high intensity within these two regions. Computational simulations of the vibrational frequencies of anhydrides **11–16** indicate that none of the vibrational modes between 1000 and 1100 cm⁻¹ involve the displacement of boron or oxygen atoms of their central B_3O_3 rings. IR bands in this region instead arise from aryl C–H in-plane bending modes of varying symmetry.

The next two modes found to involve displacements of atoms in the central B_3O_3 ring of anhydrides **11-16** are shown in Figure 3d, e. Both modes involve out-of-plane displacements of boron atoms. Interestingly, the three oxygen atoms of the central B_3O_3 moiety were observed to be relatively stationary, which is in contrast to the out-of-plane vibrations of boronic acids **1–10** (Figure 2e) where oxygen atoms of $B(OH)_2$ moieties are prominently displaced in the opposite direction of the boron atom. The two modes shown in Figure 3d and 3e differ in the displacements of central boron atoms relative to aryl hydrogen atoms. The higher frequency mode, ranging from 736 to 762 cm⁻¹, involves boron displacements that are anti to

the displacements of aryl hydrogen atoms. The lower frequency out-of-plane vibrational mode (677-696 cm⁻¹) involves displacements of boron atoms syn to the displacements of aryl hydrogen atoms. The intensity of this lower band was observed to be strong for all anhydrides 11-16, likely because of the greater dipole change that occurs when boron and aryl hydrogen atoms are all displaced in the same out-of-plane direction. Both out-of-plane vibrational modes of boroxine anhydrides 11-16 are observed at higher frequencies than the out-of-plane vibrations of their component boronic acids (604-649 cm⁻¹, Figure 2e), likely providing a convenient means of distinguishing between boronic acid and boroxine anhydride species.

The last distinct vibrational mode characteristic of boroxine anhydrides **11–16** is a sharp peak of medium-strong intensity observed between 500 and 628 cm⁻¹ (Figure 3f). This vibrational mode involves the "squeezing" of the central B_3O_3 ring in a manner analogous to the v_{6b} mode³⁷ of unsubstituted benzene. The range of this vibrational mode overlaps significantly with the out-of-plane vibration of hydroxyl hydrogen atoms of boronic acids **1-10** (492–548 cm⁻¹, Figure 2f). The two out-of-plane boroxine anhydride vibrational modes shown in Figures 3d, *e*, which do not overlap with modes characteristic to boronic acids, are therefore expected to be more useful for distinguishing between condensed boroxine anhydride species and their boronic acid components.

Boronate Esters 17–28. Twelve boronate esters (17–28) were investigated experimentally and computationally. Figure 4 outlines the five vibrational modes that were found to be conserved across the 12 esters studied. Boronate ester 17 is used in Figure 4 as a representative example for the purposes of graphically displaying the displacements involved in each vibrational mode. The symmetry, relative intensity, range, and average frequency of each vibrational mode as obtained experimentally (black text) and assigned by computational frequency analysis (blue text) are also given in Figure 4. Complete analysis of the symmetry, frequencies, and intensities specific to boronate esters 17–28 can be found in Table S3 of the Supporting Information.

IR characterization of essentially all reported COFs that contain boronate esters note one or two strong IR absorption bands in the 1300 cm⁻¹ region.¹³ Most reported boronate ester-based COFs assign^{14,15a,b,16a,c-k,17a,d,f,19,22} these IR bands to B– O stretches within the C₂O₂B ring. Indeed, both experimental and computational analyses of boronate esters 17-28 revealed two distinct vibrational modes in the 1300 cm^{-1} region (Figure 4a, b); however, analysis of these modes reveals that they involve stretching of the B-C bond rather than the B-O bonds. The two modes differ in the relationship between the B–C and C=C stretches within the 5-member boronate ester ring. In the higher frequency mode, which spans from 1355 to 1422 cm⁻¹ (Figure 4a), the boronate ester B-C bond lengthens as the C=C bond shortens and vise versa. This results in a net shrinking and subsequent expansion of the boronate ester 5-member ring that can be likened to a "breathing" motion within the C2O2B ring. The second vibrational mode in this region (Figure 4b) ranges between 1272 and 1342 cm^{-1} for the 12 boronate esters investigated. In this mode the B-C and C=C bonds shorten and lengthen in unison. For all 12 boronate esters investigated the B-C stretching mode shown in Figure 4a was observed at a higher frequency than the B-C stretching mode shown in Figure 4b, with the intensity of both modes being strong. It should be

noted that the peaks associated with B–C stretching modes in the IR spectra of nonlinear boronate esters 26-28 are broad relative to those of linear boronate esters 17-25. It is believed, based on computational frequency analysis, that this broadening results from symmetric and asymmetric B–C stretching modes that are of similar frequency but slightly different intensity.

Two additional stretching modes (Figure 4c, d) were found to be characteristic of boronate ester C2O2B rings. The higher frequency mode, found between 1138 and 1241 cm⁻¹ (Figure 4c) for boronate esters 17-28, corresponds to symmetric stretching of both C–O bonds in the 5-member boronate ester ring. For nine of the 12 boronate esters investigated, this symmetric C-O stretching mode was observed to be more intense than either B-C stretching mode in the 1300 cm⁻¹ region and, in fact, the most intense IR band above 800 cm^{-1} . The three exceptions to this observation were diesters 24 and 26, which both had medium intensity absorptions in this region, and triester 27, for which the intensity of this C-O stretch was nearly equal to stretches in the 1300 cm⁻¹ region. Compound 24, at 1138 cm⁻¹, is particularly interesting as it is the only ester studied for which this mode falls outside the narrow range of 1219-1241 cm⁻¹. This notably low frequency is observed for 24 because the C-O vibrations are coordinated through the adjoining aromatic ring. Given the typically high intensity of the C-O stretching mode of boronate esters, and the general lack of other intense peaks in this region, it is believed that C-O stretch can be considered more diagnostic of boronate ester compounds than the often cited B-C stretches in the 1300 cm^{-1} region.

Shown in Figure 4d is the fourth stretching mode characteristic of boronate esters, which involves symmetric stretching of both B-O bonds of the 5-member boronate ester ring. As stated previously, much of the literature of boronate ester COFs assigns bands in this region to B-C stretching rather than what we have found to be B-O stretching. The intensity of the B–O stretching mode, which was more variable than the intensities of higher frequency modes shown in Figure 4a-c, ranged between medium to strong. While the range of B–O stretching frequencies is listed as spanning from 1033 to 1080 cm⁻¹, it should be noted that all but one of the 12 boronate esters displayed B-O stretching frequencies between a much tighter range of 1064-1080 cm⁻¹. The one ester that lies outside this range is ortho-dimethyl boronate ester 23 for which experimental IR spectra shows (and computational frequency analysis supports) a B-O stretching frequency of 1032 cm⁻¹. The B-O stretching mode for esters 17-22 and 24-28 is coupled with in-plane bending of aryl hydrogen atoms at the ortho and meta positions of the boron-linked aryl ring. In the case of ortho-dimethyl ester 23, however, ortho positions are occupied by methyl groups rather than hydrogen atoms. These methyl groups do not undergo any displacement in conjunction with the B-O stretch, resulting in a lower vibrational frequency. Apart from this outlier, the B-O stretching frequency is especially diagnostic for boronate esters, with most compounds falling between a narrow range centered at 1072 cm^{-1} and spanning only 16 cm^{-1} .

The last vibrational mode found to be conserved across the 12 boronate esters investigated involves the out-of-plane displacement of the boron and oxygen atoms of the boronate ester ring (Figure 4e). As shown, out-of-plane displacements of the boron atom are coupled with out-of-plane displacements of aryl hydrogen atoms (Ar–H), most prominently those at the 3

and 5 positions of monoesters 17-23. Boronate ester oxygen atoms are displaced in the opposite direction of boron and Ar– H motions. The out-of-plane vibrations of boronate esters were observed to fall between 633 and 658 cm⁻¹ and were all strong intensity. The B_3O_3 out-of-plane modes of boroxine anhydrides 11–16 were observed in the ranges 736–762 and 677–714 cm⁻¹ (Figure 3d, e), showing no overlap with the out-of-plane vibrations of boronate esters. There is, however, overlap between the out-of-plane vibrations of boronate esters (633– 636 cm⁻¹) and boronic acids (604–649 cm⁻¹, Figure 2e). Consideration of a combination of vibrational modes, however, does allow a more definitive distinction between acids and boronate esters.

Larger COF Analogues. As stated above, it is instructive to investigate whether trends observed for simple model systems (e.g., acid 1, anhydride 11, and ester 17) carry over to larger, more complex assemblies. To help answer this question we computationally investigated the vibrational modes of three larger COF-like assemblies: boroxine anhydride assembly 29 and boronate ester assemblies 30 and 31 (Figure 5). Investigations of 29–31 were limited to computational frequency analysis, as it is not currently possible to prepare perfectly monodisperse, discrete COFs experimentally.



Figure 5. Space filling representations of COF-like boroxine anhydride (29) and boronate ester (30, 31) assemblies investigated computationally (gray = C, red = O, green = B, white = H). Anhydride 29 can be envisioned as a "second generation" analogue of anhydride 11, whereas esters 30 and 31 can be envisioned as "second generation" analogues of esters 27 and 28, respectively.

Listed in Tables 1 and 2 are the relevant vibrational frequencies of second generation COF-like assemblies **29–31**. Also provided in Tables 1 and 2 are vibrational frequencies computed for boroxine anhydride and boronate ester assemblies that can be considered small subunits of second generation assemblies **29–31** as well as the average frequencies of all boroxine anhydrides and boronate esters studied. Finally, Tables 1 and 2 include FTIR data from as-synthesized COFs that are the most closely related "infinite" analogues of computationally investigated COF-like assemblies; COF-1, COF-6, and COF-5 can be considered larger, periodically repeating analogues of **29**, **30**, and **31**, respectively.

Each second generation assembly is predicted to have a multiple IR-active vibrations in the $1300-1400 \text{ cm}^{-1}$ region. This greater number of distinct vibrational modes results from the increased number of symmetric and asymmetric modes that exist for each fundamental vibration shown in Figures 3 and 4. Differences in the symmetries of each vibrational mode result in significant differences in their IR intensities such that only one, or a limited few, of each type of vibration is expected to rise significantly above the baseline. Unless otherwise noted, Tables 1 and 2 list those vibrations that are predicted to be of medium-

Table 1. Ca	lculated V	<i>ibrational</i>	Frequencie	es for 2nd	
Generation	COF-like	Boroxine	Anhydride	Assembly 2	29^a

boroxine anhydrides									
mode	29	11	COF-1	avg					
3a	1345	1331	1342	1331					
3b	1281	1292	1301	1296					
3c	1252	1250	1260	1252					
3d	766 ^b	762	762 ^c	743					
3e	695	691	711	683					
3f	632	566	665	542					

"Key vibrational modes involving atoms within the B_3O_3 ring are categorized according to their designations in Figure 3a–f. The vibrational frequencies calculated for anhydride 11 (a smaller analogue of 29), experimentally reported vibrational frequencies of COF-1 (an "infinite" analogue of 29), and average calculated frequencies for anhydrides 11–16 are also provided for comparison. Data are given in cm⁻¹. ^bThe intensity of this mode, on account of its symmetry, is very weak and likely would not be distinguishable from the baseline. ^cThis peak at 762 cm⁻¹ is reported¹⁴ for COF-1; however, its intensity is nearly at the baseline, in agreement with computational modeling of COF-like assembly 766.

strong intensity and that relate directly to fundamental vibrations already discussed.

Computational studies of second generation assemblies 20-31 lend further support to the conclusion that B-O and B-C IR bands in the 1300-1400 cm⁻¹ region are less diagnostic for boroxine anhydrides and boronate esters than bands in other regions of the spectrum. Considerably more variation is observed for IR bands between 1300 and 1400 cm⁻¹ for both boroxine anhydrides and boronate esters, and bands of boroxine anhydrides and boronate esters in this region overlap. This result is observed in both theoretically modeled and experimentally measured systems. Both this increased variability and general overlap of frequencies that can be assigned to anhydrides and esters precludes the diagnostic characterization of such assemblies based solely on bands in this region. Other regions of the IR spectrum, particulary the fingerprint region, are notably more diagnostic as will be discussed in the following section.

Despite the general difficulty of assigning IR bands in the 1300–1400 cm⁻¹ region, the results in Tables 1 and 2 suggest that simple, discrete boroxine anhydride and boronate ester assemblies can, when appropriately chosen, serve as valuable model systems for understanding the vibrational properties of related COFs. Care must be taken, however, in determining what small analogue(s) will serve as appropriate models for infinitely repeating structures. The boronate ester C-O vibrations (Figure 4c) of second-generation assembly 30 provides a good example. Assembly 30 contains boronate esters built from 1,2,4,5-tetrahydroxybenzene, which are analogous to bis-ester 24. As mentioned earlier, assembly 24 was shown experimentally and computationally to have C-O vibrations well outside the range of 1219-1241 cm⁻¹ found for all other boronate esters investigated. Assembly 24, however, is the simplest discrete analogue that accurately represents (Table 2) the C-O frequency of second generation COF 30 and its "infinite" analogue, COF-6. Other closely related assemblies 17, 26, and 27 do not possess bis-ester functions joined by 1,2,4,5tetrahydroxybenzene and therefore do not accurately³⁸ model assembly 30. Discrete systems used as models for related COFs should therefore be chosen carefully to accurately capture all relevant functionalities present in the larger COF. As the

	Table 2. Calculated	Vibrational Fre	auencies for 2	and Generation	COF-like	Boronate	Ester Assemblies	30 and 31^a
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horonate esters											
boonde esters											
mode	30	17	24	26	27	COF-6	31	25	28	COF-5	avg
											0
4a	1336	1360	1346	1361	1351	1311	1309	1356	1332	1347	1361
4b	1277	1317	1310	1292	1284	1245	1295	1306	1309	1332	1309
40	1127	1230	1124	1228	1228	1164	1232	1228	1234	1245	1221
τc	112/	1250	1127	1220	1220	1104	1202	1220	1234	1245	1221
4d	1068 ^b	1054	1049	1065	1069	с	1062	1064	1055	1082	1052
1.0	620	642	640	624	620	611	610	650	641	665	640
40	028	042	040	054	029	044	048	030	041	005	040

"Key vibrational modes involving atoms within the C_2O_2B ring are categorized according to their designations in Figure 4a-e. The vibrational frequencies calculated for smaller analogues of each ester (compounds 17 and 24–28), experimentally reported vibrational frequencies of COF-6 and COF-5 ("infinite" analogues of 30 and 31, respectively), and average calculated frequencies for boronate esters 17–28 are also provided for comparison. Data are given in cm⁻¹. ^bThe intensity of this mode, on account of its symmetry, is very weak and likely would not be distinguishable from the baseline. ^cNo peaks were observed^{15b,18a} in this region for COF-6, which is in agreement with computational modeling that indicates weak intensity of the 4d mode of COF-like assembly 30.



Figure 6. Summary of IR active vibrational modes that involve displacements of the boron-containing functionalities of boronic acids 1-10 (a, highlighted in orange), boroxine anhydrides 11-16 (b, highlighted in purple), and boronate esters 17-28 (c, highlighted in blue). Dotted black lines represent the average observed vibrational frequency within each range. Areas shaded in gray highlight regions of the IR spectrum where vibrational modes that do not involve the boron-containing moiety of compounds 1-28 are commonly found that may be mistaken as characteristic of alternative structures.

complexity, functionality, and size of SBUs used to prepare COFs continue to increase, such systems can be broken into several discrete species that are each more straightforward to investigate. Alternatively, modeling of a second generation assembly such as 29-31 can provide a wealth of highly useful and diagnostic vibrational information, provided such structures are computationally feasible.

Distinguishing Boron-Containing Functionalities by IR Spectroscopy. Taken together, the above experimental and computational results provide the background necessary to more definitively distinguish between boronic acid, boroxine anhydride, and boronate ester species based on their IR spectra. Figure 6 plots the collective spectral ranges of IR active modes characteristic to the boron-containing functionalities of compounds 1–28. Highlighted in gray in Figure 6 are vibrations that (i) are conserved across boroxine anhydride or boronate ester species, (ii) do not involve boron-containing functionalities, and (iii) appear in regions of the spectrum that are characteristic of other boron-containing functionalities. These gray areas play a prominent role in the diagnostic characterization of boroxine anhydride and boronate ester materials as they highlight regions of the IR spectrum where other common vibrational modes may be misinterpreted or provide false positives of boroxine anhydride or boronate ester formation. The data provides a convenient means of distinguishing which vibrational modes are diagnostic for, rather than simply supportive of, each functionality. Although the results presented in Figure 6 are based on a set of only 28 different compounds, we expect that they can be applied to a broad range of boronic acid, boroxine anhydride, and boronate ester species used in COF synthesis.

Article

Rambo and Lavigne²² have previously cautioned against considering bands in the 1300 cm⁻¹ region of IR spectra to be diagnostic for boroxine anhydrides or boronate esters, given that boronic acids, boroxine anhydrides, and boronate esters all display prominent peaks in this region. Bands in this region are most often attributed to B–O stretches. The data presented in Figure 6 partially corroborates this conclusion, clearly showing the spectral overlap of boronic acid, boroxine anhydride, and boronate ester peaks in the 1300 cm⁻¹ region. Where the current results and previous reports differ is in the assignment of these vibrational modes. Some boronic acid and boroxine anhydride peaks in the 1300 cm⁻¹ region do correspond to B– O stretches (e.g., those shown in Figures 2a and 3a), however most are predominantly B–C stretches (e.g., Figures 2b, 3b, c, and 4a, b) as assigned computationally. Regardless, the current study also recommends that peaks in the 1300 cm⁻¹ region not be considered diagnostic for a particular boron-containing functionality given the overlap of strong vibrational modes between 1300 and 1400 cm⁻¹. Several studies^{14,15a,b,16a,c-k,18a,19} have indicated the presence

of one or more sharp, intense bands between 1000 and 1050 cm⁻¹ that can be attributed to boronate ester formation. The results of this current study suggest that, indeed, boronate esters 17-28 display a sharp, medium-to-strong intensity B-O stretching mode (Figure 3c) in this region. Despite how characteristic this mode is for B-O stretching of boronate esters, it is believed that care should be taken when attempting to distinguish between boroxine anhydride and boronate ester assemblies based upon IR bands in the 1000 cm⁻¹ region. The reason for caution extends from the fact that B-O stretching modes in this region are generally of the same intensity as neighboring peaks, most of which are different variations of symmetric and asymmetric C-H in-plane bending modes that are observed for all species (acids, anhydrides, and esters). Often, these in-plane Ar-H bending modes are difficult to distinguish from each other and can be mistaken for boronate ester B-O stretches. IR bands in this region have also been previously attributed to the formation of B₃O₃ rings, however no IR active B₃O₃ vibrational modes between 1000 and 1180 cm⁻¹ were found for compounds 11-16. In-plane C-H bending modes, rather, dominate this region.

In addition to the above discussion, several overall conclusions can be drawn from the vibrational summary presented in Figure 6:

- 1 The consumption of boronic acid functionalities can be best evaluated by the attenuation of IR bands between 900 and 1000 cm⁻¹. As stated above, B–O stretching and O-H wagging frequencies observed in this region (Figure 2) are sharper, more distinct, and more diagnostic than O-H stretches in the 3000 cm⁻¹ region. It should be noted that most of boroxine anhydrides 11-16 display C–H out of plane bending vibrations between 940 and 960 cm⁻¹, however their intensities are weak to very weak. All boroxine anhydrides in the current study show medium intensity in-plane bending of Ar-H bonds between 1010 and 1040 cm⁻¹. Given the relatively weaker intensities of these boroxine anhydride vibrational modes and their general separation from the strong intensity modes specific to boronic acids, it is not expected that these boroxine anhydride bands will be confused for boronic acids.
- 2 The fingerprint region is especially valuable for distinguishing between boroxine anhydride and boronate ester species, as has been noted previously by Lavigne and co-workers.²² Two areas of the fingerprint region are particularly notable: the region from 677 to 714 cm⁻¹ is diagnostic for boroxine anhydrides while the region between 633 and 658 cm⁻¹ is diagnostic for boronate esters. Both vibrational modes involve out-of-plane displacements of aryl hydrogen atoms. These out-of-plane vibrations are especially diagnostic in 2D COF and COF-like assemblies because their intensity is not dependent on the overall in-plane symmetry of the assembly. Furthermore, the fundamental differences in

connectivity between six-member boroxine anhydride and five-member boronate ester moieties underlie differences in their out-of-plane vibrations. Specifically, the strong intensity out-of-plane vibrations of boroxine anhydrides (Figure 3e) involve symmetric displacement of three boron atoms within each B₃O₃ ring while the boroxine anhydride oxygen atoms remain relatively stationary. The out-of-plane vibrations characteristic of boronate esters (Figure 4e) involve the displacement of only one boron atom per C₂O₂B ring rather than three, and the two oxygen atoms of the boronate ester moiety are more prominently displaced in the opposite direction of the boron atom. These fundamental differences between out-of-plane vibrational modes of boroxine anhydride and boronate ester assemblies ensure the two modes appear in two distinct ranges of the IR fingerprint region. It is also important to note that as COF-like assemblies grow in size (e.g., ester series $17 \rightarrow 24 \rightarrow 28$ \rightarrow 31) asymmetric out-of-plane vibrations of multiple boroxine anhydride or boronate ester moieties decrease in relative intensity as their net dipole change becomes negligible. By contrast, the single, fully symmetric out-ofplane vibration of large assemblies increases in intensity such that it becomes increasingly distinct and diagnostic. For these reasons, it is believed that the symmetric outof-plane vibrations of boroxine anhydride and boronate esters are especially valuable for distinguishing between the two assemblies.

Two additional conclusions about vibrations in the fingerprint region can be drawn from the summary presented in Figure 6. First, the higher frequency, lower intensity out-of-plane vibrational mode of boroxine anhydrides (Figure 3d), while conserved across anhydrides 11-16, is not a reliably diagnostic mode. Out-ofplane Ar-H displacements of hydrogen atoms in catechol and oligocatechol derivatives also appear in this region for both boroxine anhydrides and boronate esters, and they are of medium to strong intensity. It is also important to note that this higher frequency mode involves out-of-plane boron displacements that are anti to out of plane Ar-H displacements. In larger assemblies, such as structure 29, the intensity of such anti out-of-plane vibrations drops essentially to the baseline. Second, the lowest-frequency vibration of boroxine anhydrides (Figure 4f) is also not reliably diagnostic for boroxine anhydrides. This low-frequency mode is observed to have variable intensity, span wide range of frequencies $(500-628 \text{ cm}^{-1})$, and overlap with strong intensity low-frequency modes characteristic of boronic acids.

3 A strong C–O stretching mode between ~1220–1240 cm⁻¹ (Figure 4c) is highly characteristic of boronate ester formation. This vibrational mode was observed to have the strongest intensity of all vibrations outside the fingerprint region for all but one of the 12 boronate esters investigated. Related C–O stretches of unassembled catechol and oligocatechol derivatives, while strong, occur at frequencies above 1250 cm⁻¹. No analogue of this mode exists for boroxine anhydrides as they simply do not contain the same C–O functionality. Boroxine anhydrides do share a common vibrational mode (Figure 3c) at frequencies just above the boronate ester C–O vibration. This boroxine anhydride mode,

however, is often overshadowed by other stronger intensity boroxine anhydride modes above 1300 cm⁻¹ and is quite easily distinguished from the boronate ester C-O vibration. The only boronate ester observed to have a C-O stretch outside of 1220-1240 cm⁻¹ was compound 24, which is assembled from 1,2,4,5tetrahydroxybenzene. The C-O stretches of boronate esters based on this tetraol, including theoretically investigated second generation assembly 30 and synthetically prepared COF-6, are observed at much lower frequencies around 1130-1160 cm⁻¹ (dashed blue line in Figure 6) for reasons discussed earlier. Overall, the sharpness and very high intensity of boronate ester C–O stretches in the 1220-1240 cm⁻¹ region of the IR spectrum render these bands to be some of the most diagnostic of boronate ester formation, especially when further supported by out-of-plane vibrations in the fingerprint region.

CONCLUSION

Boronic-acid-derived COFs exhibit a variety of useful, unique, and structure-dependent materials properties. Proper characterization of the structures and chemical connectivity of such COFs is therefore of significant importance. IR spectroscopy has arisen as one of the most prominent means of analyzing and characterizing COFs, however a survey of the literature has revealed that the vibrational characteristics of boronic acid derived COFs are often inconsistently assigned and generally not well catagorized. The results presented herein provide a systematic investigation of the vibrational properties of a series of 28 different bonoric acid, boroxine anhydride, and boronate ester species. IR bands observed experimentally have been assigned computationally. The collective data has allowed IR active vibrations conserved across the B(OH)2, B3O3, and C₂O₂B functionalities of boronic acids, boroxine anhydrides, and boronate esters, respectively, to be clarified and classified. IR bands present in one boron-containing functionality that may be mistaken as diagnostic for another have also been assigned through the combination of experimental and computational analysis. The results caution against using the commonly cited 1300-1400 cm⁻¹ as confirmation of boroxine anhydride or boronate ester species as strong bands are present in this region for all three boron-containing functionalities. Other regions of the IR spectrum are shown to be significantly more diagnostic for specific boron-containing functionalities. The collective results provide a straightforward means of determining which boron-containing functionalities are present in dynamically assembled 2D and 3D COFs and other boronic acid-derived materials. Although the series of 28 structures investigated cannot encompass the increasingly wide variety of secondary building units used in COF synthesis, the fact that vibrational modes characteristic of boronic acids, boroxine anhydrides, and boronate esters each fall within generally welldefined regions of the IR spectrum suggests that the conclusions presented herein can be applied broadly. Simple guidelines are also provided for the design of appropriate model systems to computationally investigate the vibrational properties of alternative COF structures. We anticipate the results and guidelines presented in this study will help provide greater clarity and consistency in the characterization of COFs and other boronic-acid-derived materials.

ASSOCIATED CONTENT

S Supporting Information

Experimental IR spectra, mass spectra of all newly reported compounds, Cartesian coordinates of all stationary points reported in this manuscript, tabulated vibrational frequencies for compounds 1-28, and the full author list for ref 23. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(38) Calculations predict assembly **30** to have two distinct frequencies for C–O vibrations: the one at 1127 cm⁻¹ mentioned in the text and another at 1229 cm⁻¹. The lower-frequency mode corresponds to C–O vibrations within the hexagonal ring of **30** while the higher frequency mode corresponds to C–O vibrations of the six phenyl boronate esters that line the periphery of the assembly. The significant difference between the *endo* and *exo* boronate ester C–O vibrational frequencies again highlights the influence of 1,2,4,5-tetrahydroxybenzene moiety.