Acid Exfoliation of Imine-linked Covalent Organic Frameworks Enables Solution Processing into Crystalline Thin Films

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Covalent organic frameworks (COFs) are highly modular, porous, crystalline polymers of interest for charge storage devices, nanofiltration membranes, optoelectronic devices, and more. COFs are typically synthesized as microcrystalline powders, a morphology that limits their performance in these applications, and their limited solubility precludes large-scale processing into more useful morphologies and devices. Here, we report a general, scalable method to exfoliate two-dimensional imine-linked COF powders by temporarily protonating their linkages. The resulting suspensions were cast into continuous, crystalline COF films up to 10 cm in diameter. This strategy was successfully applied to three different COF structures, and excellent film thickness control (50 nm to 20 μ m) was achieved by modifying the suspension composition, concentration, and casting protocol. Acid-mediated exfoliation is a promising strategy for solution processing readily accessible imine-linked COF powders into functional devices.

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Acid Exfoliation of Imine-linked Covalent Organic Frameworks Enables Solution Processing into Crystalline Thin Films

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Abstract: Covalent organic frameworks (COFs) are highly modular, porous, crystalline polymers of interest for charge storage devices, nanofiltration membranes, optoelectronic devices, and more. COFs are typically synthesized as microcrystalline powders, a morphology that limits their performance in these applications, and their limited solubility precludes large-scale processing into more useful morphologies and devices. Here, we report a general, scalable method to exfoliate two-dimensional imine-linked COF powders by temporarily protonating their linkages. The resulting suspensions were cast into continuous, crystalline COF films up to 10 cm in diameter. This strategy was successfully applied to three different COF structures, and excellent film thickness control (50 nm to 20 μ m) was achieved by modifying the suspension composition, concentration, and casting protocol. Acid-mediated exfoliation is a promising strategy for solution processing readily accessible imine-linked COF powders into functional devices.

Covalent organic frameworks (COFs) are an emerging class of porous, crystalline polymers constructed from combinations of geometrically compatible monomers capable of polymerizing into two- or three-dimensional networks.^[1-3] These materials have attracted significant attention over the past decade due to their high stability,^[4] accessible pores, and tunable functionality^[5] that demonstrate promise for applications including energy^[6,7] and gas storage,^[8] catalysis,^[9,10] and membranes-based separations.^[11-14] A major challenge to this promise is that most reported syntheses

produce COFs as insoluble microcrystalline powders, a morphology that precludes many of these uses.^[15] Recent efforts have been directed towards fabricating 2D COF thin films, a morphology ideal for applications requiring rapid mass transport through the pores.^[16,17] In particular, large-area films with precisely defined thicknesses and oriented crystalline domains are ideal.^[17]

Three main strategies have been developed to access COF thin films. The first is solvothermal synthesis, in which the COF is grown directly on a solid support.^[17-21] This method produces highly crystalline films, with pores sometimes oriented perpendicular to the substrate.^[18,22] However, these films are difficult to remove from the support, which prevents their use in applications requiring freestanding films. Although these procedures have provided the highest quality films, this approach has numerous disadvantages, including difficult scale-up, lack of generality across substrate types, and the inefficiency of producing powder products in addition to the film.^[16] The second is interfacial polymerization, in which the monomers or catalyst are dissolved separately in two immiscible solvents such that COF formation occurs at the interface.^[11,23,24] This strategy provides freestanding films, but thickness control requires significant reoptimization for every network and films with poor or no crystallinity are often obtained, especially when they are thinner than 50 nm.^[24,25] Finally, a third method, exfoliation and reconstitution of COF powders, has been explored.^[26-29] This strategy is highly desirable because it provides a direct route to the film morphology from abundant microcrystalline powders, which are comparatively simple to synthesize, and the film dimensions can be precisely tuned by changing the suspension concentration and substrate surface area.

Exfoliation strategies developed thus far have made use of intentionally incorporated functional groups that are not generalizable across broad classes of COF networks.^[26,28-30] For example, Banerjee and coworkers demonstrated that an anthracene-based 2D COF powder could be chemically exfoliated via a Diels-Alder reaction between the anthracene units and *N*-hexylmaleimide.^[26] Ma and coworkers synthesized a 2D COF containing cationic viologen units, such that the resulting sheets were easily separated due to electrostatic repulsion.^[28] Alternative mechanical exfoliation methods produce suspensions of low concentrations (~0.2 mg/mL) that are not conducive to large area film fabrication.^[27] Here, we report a general method to exfoliate imine-linked COFs, one of the largest and most structurally diverse COF classes, by temporarily protonating their imine linkages (Figure 1A). These suspensions were deposited onto various substrates to produce crystalline COF films with

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Figure 1. (A) Overview of acid exfoliation and film casting procedures. Protonation of imine-linked COF powders results in electrostatic repulsion between adjacent layers, which induces rapid exfoliation of the powders into thin sheets upon stirring. Suspensions of exfoliated COF sheets were deposited onto substrates and dried into thin, crystalline COF films. (B) Pore structure of the BND-TFB COF.

thicknesses ranging from 50 nm to 20 μm , depending on the suspension composition, concentration, and casting method. Films quickly delaminate from the substrate when submerged in alcohol and can be transferred to any desired support. These results suggest that acid-mediated exfoliation is a powerful alternative to previously reported film fabrication techniques that will enable the synthesis of the next generation of COF materials.

Protonation of the 2D imine-linked BND-TFB COF (Figure 1B) with excess trifluoroacetic acid (TFA) enables its dispersion in organic solvents and degrades its apparent crystallinity and

porosity, yet preserves its imine linkages. After stirring in a mixture of acetonitrile, tetrahydrofuran, and TFA (7:3:2 v/v/v) overnight, the COF powder was broken up into a polydisperse suspension composed of a wide range of particle sizes, including both thin sheets and some aggregates visible to the naked eye. The color of the powder also changed from bright orange to red upon acid addition, which is consistent with protonation of the imine linkages. An analogous color change was previously observed upon protonation of imine-linked macrocycles.^[31] The exfoliated solids were isolated by centrifugation, washed, and dried under vacuum overnight prior to characterization. Powder X-ray diffraction (PXRD) and nitrogen adsorption data (Figure 2A-B, purple and orange traces) indicate that the excellent crystallinity and surface area of the starting COF powder ($S_{\text{BET}} = 2120 \text{ m}^2/\text{g}$) are mostly lost after acid exfoliation ($S_{\text{BET}} = 5 \text{ m}^2/\text{g}$). However, the Fourier-transform infrared (FT-IR) spectra of both the initial powder and the exfoliated solids (Figure 2C, purple and orange traces) are nearly identical, and both contain a sharp imine peak at $\sim 1620 \text{ cm}^{-1}$, indicating that the imine-linked network is preserved. We hypothesize that the reduction in crystallinity and surface area are due to disordered stacking of the protonated COF sheets after acid treatment. The sheets may stack in a disorganized fashion rather than the usual eclipsed orientation to minimize electrostatic repulsion. This disordered arrangement is also consistent with the reduced porosity of the framework. A similar disrupted stacking model was recently validated by Medina and coworkers, who observed a reduction in the crystallinity and porosity of several imine-linked COF powders upon exposure to certain solvents.^[32]

High-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) images of drop-cast BND-TFB COF suspensions provide further evidence that the exfoliated sheets maintain their integrity and periodicity during acid exfoliation (Figure 3). HRTEM imaging revealed the presence of thin, large ($>300 \text{ nm}$ diameter) sheets of crystalline

Figure 2. Characterization of BND-TFB COF powder prior to exfoliation (BND-TFB COF, purple) and after exfoliation (Exfoliated, orange). (A) PXRD patterns indicate a significant loss of crystallinity upon exfoliation. (B) Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) indicate that the porosity of the as-synthesized BND-TFB COF is lost after treatment with acid. (C) FT-IR spectra of each material suggest that the imine-linked network is largely conserved during this process.

Figure 3. (A) HRTEM image of an exfoliated BND-TFB COF sheet. (B) Two regions of interest at higher magnification corresponding to the blue and green boxed regions of the sheet in (A). Inset: FFTs of the two high-magnification images from the two color-coded regions of interest in (B) show the predominant diffraction feature (~ 22 Å). (C) AFM images of exfoliated COF particles deposited onto freshly cleaved HOPG reveal a distribution of particle sizes.

COF with lattice fringes extending throughout the structures (Figures 3A, S4). A fast Fourier transform (FFT) was applied to two regions of the image shown in Figure 3A, both of which reveal uniform six-fold symmetry with lattice spacings of ~ 22 Å, which closely match d_{100} of BND-TFB COF powder (Figure 3B). It is worth mentioning that other particles without lattice fringes were also observed, which may be attributed to aggregates too thick to analyze by TEM, particles that were damaged by the electron beam, or other weakly crystalline or amorphous structures produced as a byproduct of the exfoliation method. To measure the dimensions of the dispersed particles, an aliquot of unfiltered BND-TFB COF suspension was deposited onto a freshly cleaved HOPG substrate and imaged by AFM. These images revealed the presence of a wide distribution of particle sizes, the smallest of which are approximately 5 nm thick and 50 nm in diameter (Figure 3C). Particles with 50 nm thickness and >1 μm diameter were also observed, with still larger aggregates visible to the naked eye, indicating a broad size distribution. To ensure that these particle sizes observed by AFM are indicative of the sizes in solution rather than aggregates formed during the drying process, a BND-TFB COF suspension was passed through a 5 μm PTFE syringe filter to remove the largest aggregates and analyzed by dynamic light scattering (DLS) (Figure S5). These data reveal an average particle diameter of 170 nm, which is in agreement with the sizes observed by AFM. Collectively, these results suggest that acid treatment disperses 2D imine-linked COF powder into a polydisperse suspension while preserving its porous, periodic structure.

When the exfoliated BND-TFB COF suspension is deposited onto a silicon wafer and allowed to evaporate in air, it dries into a uniform, continuous thin film that retains some of the crystallinity and porosity of the pristine COF powder. Immediately after deposition, the suspension exhibited a bright red color and contained visible aggregates, but became more uniform and yellow before finally drying into a bright red film. The resulting film (400 nm thick) was imaged by AFM, which revealed an array of

discrete, circular particles piled into an extended structure, as expected for an assembly of 2D polymer sheets (Figure 4A). A portion of the COF film was submerged in reagent alcohol (90% ethanol, 5% methanol, 5% isopropanol) immediately after drying, and its color rapidly changed from red to yellow, which we attribute to the deprotonation of its iminium ions back to neutral imines.^[31] Notably, the film also delaminated from the substrate, providing a freestanding COF film (Figure 4B) that could be transferred to any desired support. To evaluate the crystallinity of these freestanding films, a BND-TFB COF film (variable thickness of 2-5 μm across the film) was packed into a capillary while wet with reagent alcohol and analyzed by synchrotron wide-angle X-ray scattering (WAXS) measurements. The film exhibited sharp diffraction peaks at the same positions as the starting COF powder, with crystalline domain sizes of 34 nm and 33 nm calculated by the Scherrer equation for the powder and film, respectively (Figure 4C). Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements of a substrate-bound COF film confirmed that these crystalline domains exhibit no preferential orientation (Figure S7). Two additional freestanding BND-TFB COF thick films were activated by supercritical CO_2 drying and interrogated by nitrogen adsorption measurements to determine their porosity (Figure 4D). This study revealed that the films ($S_{\text{BET}} = 510 \text{ m}^2/\text{g}$) retained some of the porosity of the parent powder ($S_{\text{BET}} = 1580 \text{ m}^2/\text{g}$). This reduction in surface area may arise from the disordered stacking of COF sheets, or regions of amorphous imine-linked polymer produced as a byproduct of the exfoliation and film casting processes.

Film thickness can be precisely controlled by modifying both the concentration of the exfoliated COF suspension and the casting technique. Suspensions ranging in concentration from 2-10 mg/mL COF were spin coated onto silicon wafers at various spin speeds to access continuous thin films ranging from 50-150 nm thick (Table S1, Figure S10). Meanwhile, films ranging from

Figure 4. Characterization of BND-TFB COF films. (a) AFM image of the edge of a 400 nm thick film. (b) Photographs of film before and after reagent alcohol delamination. (c) Wide-angle X-ray scattering patterns of BND-TFB COF powder (blue) and a film prepared via acid exfoliation of that powder (red), both normalized at the (100) peak. (d) Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) of COF powder (blue) and a corresponding COF film (red).

400 nm–5 μm thick were prepared by drop casting suspensions of equivalent concentrations (Figures 4A, S11). Such fine control of film thickness has not been achieved by interfacial polymerization and solvothermal synthetic methods,^[11,18,24] making this approach ideal for fabricating membranes for chemical separation applications, where the film thickness and pore size define the performance of the material.^[33–35]

The acid exfoliation methodology enabled the rapid fabrication of crystalline films from two additional imine-linked COF powders (TAPB-PDA COF, Methyl COF, Schemes S2–3), establishing the generality of the procedure. In each case, the pristine COF powder was exfoliated via stirring and sonication in the presence of TFA (see SI for detailed procedure). Notably, when the exfoliated TAPB-PDA and Methyl COF solids were isolated by centrifugation and purified by Soxhlet extraction and supercritical CO₂ drying, high surface areas (Figures S14, S27) and crystallinity (Figures S12, S25) were still observed. In these cases, the iminium ions were deprotonated upon exposure to large volumes of methanol during the Soxhlet extraction, as indicated by a color change from red to bright yellow during the workup.^[31] HRTEM images of exfoliated TAPB-PDA and Methyl COF particles both contained lattice fringes with spacings of ~32 Å, which corresponds to d_{100} of both structures (Figures S20, S33). Exfoliated suspensions of both COFs were then drop cast onto silicon wafers, and the resulting films were delaminated from the substrates according to the aforementioned procedure. Both exhibited WAXS signals consistent with the corresponding COF powders, indicating that this method can be applied to a variety of imine-linked structures with different pore sizes (Figures S24, S37).

By modifying the exfoliating solvent composition, solutions with COF contents as high as 25 mg/mL were prepared, providing access to large-area crystalline films up to 20 μm in thickness. As previously noted, suspended COF aggregates gradually dissolve after being deposited onto a substrate, forming a clear yellow solution prior to drying. The mixture likely absorbs some moisture from the air during the evaporation process, so the effect of added H₂O on COF solubility was examined. Notably, when the standard exfoliating solvent (7:3:2 acetonitrile/tetrahydrofuran/TFA) was modified to contain 5% v/v H₂O, 50 mg of TAPB-PDA COF powder (Figure S38A) dissolved completely after stirring for 4 hours (Figure S38B). With less H₂O, well-dispersed COF aggregates formed a flocculent solid instead of completely dissolving. When the acetonitrile/tetrahydrofuran portion of the solvent mixture was removed, 50 mg of imine COF powder could be completely dissolved in 2 mL of TFA (5% v/v H₂O) in under 30 minutes to form a transparent, red solution (Figure S38C). Films up to 50 mg in mass and ~10–20 μm in thickness were cast from TFA/H₂O solutions in glass or aluminum dishes. To efficiently neutralize all iminium ions, it was necessary to wash these thicker films with alcohol followed by base (see SI). After supercritical CO₂ drying, the films (Figure S38D) exhibited PXRD patterns equivalent to the pristine powder (Figures S39). Furthermore, they retained up to 80% of the powder surface area as confirmed by nitrogen adsorption measurements (Figure S40), as well as the characteristic imine stretch at ~1620 cm^{−1} as determined by FT-IR spectroscopy (Figure S43).

In conclusion, we demonstrated that addition of acid to 2D imine-linked COF powders enables their dispersion in organic solvents by temporarily weakening their interlayer stacking through electrostatic repulsions. The exfoliated COF suspensions were characterized by PXRD, nitrogen adsorption measurements, IR spectroscopy, and TEM, all which suggest that the structural integrity of the COF sheets are largely maintained upon protonation. Furthermore, we prepared freestanding, crystalline films from three different COF powders by casting acid exfoliated COF suspensions, and demonstrated excellent thickness control based on suspension composition, concentration, and casting technique. These results suggest that acid exfoliation can be leveraged as a powerful strategy to solution process abundant imine-linked COF powders into functional devices, opening up a wealth of potential applications for this class of materials that were previously inaccessible.

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Supplementary Information

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A. Materials and Instrumentation.

Materials.

Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. Anhydrous solvents (tetrahydrofuran, acetonitrile, dimethylformamide) were obtained from a solvent purification system (JC Myer System).

Instrumentation.

Infrared Spectroscopy. Infrared spectra were collected using a Nicolet iS10 FT-IR spectrometer equipped with a ZnSe ATR attachment and are uncorrected.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) patterns were obtained at room temperature on a STOE-STADIMP or STOE-STADIP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK α 1 radiation, $\lambda = 1.54056 \text{ \AA}$) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The as-obtained powder samples were held between two acetate foils (polymer sample with neither Bragg reflections nor broad peaks above $10^\circ 2\theta$) mounted in flat plates with a disc opening diameter of 3 mm, and measured in transmission geometry in a rotating holder. The patterns were recorded in the 2θ range of $0 - 33^\circ$ for an overall exposure time of 23 minutes. The instrument was calibrated against a NIST Silicon standard (640d) prior to the measurement.

Gas Adsorption. Gas adsorption isotherms were collected using a Micromeritics ASAP 2420 Accelerated Surface Area and Porosity Analyzer. Typically, 15-40 mg samples were transferred to dried and tared analysis tubes equipped with filler rods and capped with a Transeal. The samples were heated to 40°C at a rate of $1^\circ\text{C}/\text{min}$ and evacuated at 40°C for 20 min, then heated to 100°C at a rate of $1^\circ\text{C}/\text{min}$ heat, and evacuated at 100°C until the outgas rate was $\leq 0.4 \mu\text{mHg}/\text{min}$, at which point the tube was weighed again to determine the mass of the activated sample. The tube was then transferred to the analysis port of the instrument. UHP-grade (99.999% purity) N_2 was used for all adsorption measurements. N_2 isotherms were generated by incremental exposure to nitrogen up to 760 mmHg (1 atm) in a liquid nitrogen (77 K) bath. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements. Brunauer-Emmett-Teller (BET) surface areas were calculated from the linear region of the N_2 isotherm at 77 K within the pressure range P/P_0 of 0.05 – 0.15.

Atomic Force Microscopy. Atomic force microscopy (AFM) images were collected using a Bruker Dimension Fastscan AFM in tapping mode.

Profilometry. Profilometry measurements were performed using a Veeco Dektak 150 Surface Profiler.

Transmission Electron Microscopy. TEM images in **Figure 3** were collected with a Hitachi (Hitachi, Ltd., Tokyo, Japan) HT-7700 Biological S/TEM equipped with a Gatan (Gatan, Inc., Pleasanton, CA) Orius 4k x 2.67k bottom mounted digital camera with an acceleration voltage of

120 kV. TEM images in **Figures S4, S20, and S33** were collected using a JEOL (JEOL USA, Inc., Peabody, MA) ARM300F GrandARM TEM operating at 300 keV with a Gatan (Gatan, Inc., Pleasanton, CA) K3-IS “direct electron” detector (FEG Emission: 15 μ A, spot size 5, 150 μ m CL aperture). The ARM300F was aligned for low-dose imaging, measuring the dose rate on the K3 detector through vacuum (no grid inserted). All image acquisition was done using the Gatan Microscopy Suite (GMS), Digital Micrograph (Gatan, Inc., Pleasanton, CA).

Dynamic Light Scattering. Dynamic Light Scattering (DLS) data were collected using a Malvern Zetasizer equipped with a 633 nm He-Ne 5 mW laser at room temperature in a quartz cuvette with a 10 mm pathlength. Measurements were performed using a standard operating procedure for acetonitrile, since this was the primary component of the suspensions. Data was analyzed using the proprietary Zetasizer software.

Wide-Angle X-Ray Scattering. Wide-angle X-ray scattering (WAXS) measurements were performed at Sectors 5-ID-D (beam energy = 13.3 keV) and 12-ID-D (beam energy = 12 keV) of the Advanced Photon Source (APS) at Argonne National Laboratory in capillary transmission geometry. Linear diffraction patterns were each obtained by collecting 10 one-second frames on a Pilatus 2D detector, which were then averaged and radially integrated using proprietary software available at the APS. Samples were packed into borosilicate capillaries (1.5 mm diameter, 0.01 mm wall thickness) purchased from Charles Supper. All patterns presented herein have been baseline corrected and normalized at the (100) diffraction peak.

Grazing Incidence Wide-Angle X-Ray Scattering. Grazing-Incidence Wide-Angle X-Ray Scattering (GIWAXS) measurements were performed at Sector 8-ID-E (beam energy = 11 keV) of the Advanced Photon Source at Argonne National Laboratory. Samples were placed under vacuum and aligned to provide an incident angle of $\sim 0.14^\circ$. Diffraction patterns were collected using a Pilatus 2D detector.

Sonication. Sonication was performed using a Branson 3510 ultrasonic cleaner with a power output of 100 W and a frequency of 42 kHz.

Critical Point Dryer. Supercritical CO₂ drying was performed using a Leica EM CPD300 critical point dryer equipped with bone dry grade CO₂ (99.8% purity). Samples were first loaded into the drying chamber, which was cooled to 15 $^\circ$ C and filled with liquid CO₂. The CO₂ within the chamber was then exchanged 80 times, after which the temperature was raised to 45 $^\circ$ C to generate supercritical CO₂. The chamber was then vented to provide the activated samples.

Glow Discharge. Silicon wafers were plasma cleaned in air using a PELCO easiGlow Glow Discharge Cleaning System. All cleaning cycles (20 second glow) were performed at a pressure of 0.26 mbar and current of 15 mA.

B. Synthesis of Covalent Organic Framework Monomers

***N*-Aryl Benzophenone Imine of Benzidine**

This monomer was synthesized according to a literature procedure.^[1] The ¹H NMR spectrum matched that reported in the literature.

2,5-dimethylterephthalaldehyde

This monomer was synthesized according to a literature procedure.^[2] The ¹H NMR spectrum matched that reported in the literature.

C. Synthesis of Covalent Organic Framework Powders

Scheme S1. BND-TFB COF Synthesis

BND-TFB COF powder was synthesized according to literature precedent.^[1]

Scheme S2. TAPB-PDA COF Synthesis

The synthesis of TAPB-PDA COF powder was adapted from a literature procedure.^[3] Terephthalaldehyde (80 mg, 0.60 mmol) and 1,3,5-tris(4-aminophenyl)benzene (144 mg, 0.41 mmol) were added to a 40 mL scintillation vial along with a 1,4-dioxane/mesitylene mixture (4:1 v/v, 16 mL). This mixture was heated to 70 °C for 5 minutes to ensure that all solids had dissolved, then cooled back down to room temperature. Scandium(III) trifluoromethanesulfonate (12 mg, 0.024 mmol) was added to the monomer solution, and the resulting reaction mixture was capped and sonicated for 10 seconds. The reaction was then left to stand (no stirring) for 2.5 hours, at which point the solid precipitate was transferred to a teabag. The vial was rinsed with additional 4:1 1,4-dioxane/mesitylene to ensure that all solids had been transferred. The powder was then washed with methanol in a Soxhlet extractor overnight and activated by supercritical CO₂ drying. This yielded the desired TAPB-PDA COF powder as a yellow solid (187 mg, 83% yield).

Scheme S3. Methyl COF Synthesis

2,5-dimethylterephthalaldehyde (75 mg, 0.46 mmol) and 1,3,5-tris(4-aminophenyl)benzene (110 mg, 0.31 mmol) were mixed in a scintillation vial along with a 1,4-dioxane/mesitylene mixture (4:1 v/v, 12.6 mL). This solution was heated to 70 °C for 3 minutes to ensure that all monomers had dissolved, at which point some COF powder began to precipitate. The mixture was then cooled to room temperature, and water (2.4 mL) and glacial acetic acid (3.6 mL) were added. The vial was shaken to mix the reagents, and subsequently heated at 70 °C for 3 days (no stirring). The resulting solids were then transferred to a tea bag while wet, purified with methanol in a Soxhlet extractor overnight, and activated by supercritical CO₂ drying. This afforded the desired Methyl COF powder as a yellow solid (112 mg, 61% yield).

D. Exfoliation, Film Casting, and Sample Preparation Methods

General COF Exfoliation Protocol in 7:3:2 MeCN/THF/TFA

To a 20 mL scintillation vial were added imine-linked COF powder (20 mg) and an acetonitrile/tetrahydrofuran mixture (7:3 v/v, 10 mL). Both solvents were obtained from a dry solvent system to ensure that no water was present. Next, trifluoroacetic acid (2 mL) was added to the COF mixture while stirring at 300 rpm. The vial was then capped, and the mixture was stirred at 700 rpm overnight at room temperature to provide the desired 2 mg/mL COF suspension. Note that the TAPB-PDA COF and Methyl COF suspensions were further dispersed via sonication for 60 minutes after stirring. To prepare 10 mg/mL suspensions, 60 mg of imine-linked COF powder were stirred in 6 mL of the 7:3:2 MeCN/THF/TFA solvent mixture overnight as described above. This strategy was used for all experiments reported herein unless otherwise noted.

Silicon Wafer Cleaning Protocol

1. Wipe the wafer with a Kimwipe to remove particulates
2. Sonicate in acetone for 15 min
3. Sonicate in isopropanol for 15 min
4. Sonicate in soapy DI water for 20 min
5. Sonicate in fresh DI water for 20 min ($\times 2$)
6. Rinse the substrates one more time with fresh DI water (no sonication)
7. Sonicate in acetone for 15 min
8. Sonicate in isopropanol for 15 min
9. Store the substrates in fresh isopropanol to keep them clean prior to use.

Note: Prior to casting TAPB-PDA COF films, the substrates were dried with compressed air and cleaned via glow discharge to improve the wettability of the surface.

COF Film Drop Casting Procedure for 7:3:2 MeCN/THF/TFA Suspensions

A clean silicon wafer was first removed from the isopropanol and dried using compressed air. Next, the as-synthesized exfoliated COF suspension was deposited onto the surface of the substrate using a glass pipette. The suspension was then allowed to evaporate to dryness in air. Notably, the suspension became more uniform and viscous over time, and ultimately dried into a bright red film. Shortly after drying, the film was submerged in reagent alcohol (90% ethanol, 5% methanol, 5% isopropanol) upon which the film turned bright yellow. The film was left to rest in the alcohol for a few minutes, at which point the film began to peel off the substrate. If the film did not peel directly off the substrate, the edge of the film was first scratched with a pair of tweezers, and the film was peeled back from the position of the scratch. This drop casting procedure was used for all experiments reported herein unless otherwise noted.

COF Film Spin Coating Procedure

A clean silicon wafer was first removed from the isopropanol and dried using compressed air. Next, the as-synthesized exfoliated COF suspension (200-300 μ L) was deposited onto the surface of the substrate using a micropipette. The solution was then allowed to evaporate in air until it became homogeneous and viscous. At this point, the spin program was activated (see details in **Table S1** below) to provide the desired COF thin film. In most cases, a two-segment spin coater program was employed (spin speed 1 followed by spin speed 2) to achieve the desired film

thickness, in which a first slow segment spread the suspension over the substrate, and a second fast cycle rapidly dried the film. Note that slower spin speeds tend to produce films with lower uniformity in thickness across the substrate. Films thinner than 50 nm thick were not continuous.

Table S1. Spin Coater Programs for Controlling BND-TFB COF Film Thickness

Suspension Concentration	Spin Speed 1	Time at Spin Speed 1	Spin Speed 2	Time at Spin Speed 2	Film Thickness
2 mg/mL	500 rpm	30 sec	1000 rpm	15 sec	50 nm
2 mg/mL	300 rpm	2 min	N/A	N/A	75 nm
10 mg/mL	500 rpm	20 sec	1000 rpm	30 sec	150 nm

General COF Exfoliation Protocol in TFA/H₂O (25 mg/mL solution)

To a 20 mL scintillation vial were added imine-linked COF powder (50 mg) and TFA containing 5% v/v H₂O (2 mL). The vial was then capped, and the mixture was stirred at room temperature for 30 minutes to provide the desired transparent, dark red solution. This strategy was only used where specifically noted.

COF Film Drop Casting Procedure for TFA/H₂O Solutions

The as-synthesized COF solution in TFA/H₂O was deposited onto a glass petri dish (5-10 cm diameter) and allowed to evaporate to produce a solid black/green film. Immediately afterwards, the film (still in the dish) was placed in ethanol for 10 minutes to remove excess TFA. This wash procedure was repeated two more times with fresh ethanol, at which point the film color changed from black/green to red. Next, the film was placed into a sodium hydroxide solution (1 g NaOH in 200 mL H₂O) for ~30 minutes, after which the film color had changed from red to yellow. The film was then transferred to water for 10 minutes, followed by ethanol for 30 minutes. Subsequent activation by supercritical CO₂ drying provided the desired dry COF film, which was characterized by PXRD, IR spectroscopy, and nitrogen adsorption measurements. Films were also prepared in smooth aluminum pans using the same procedure, except the sodium hydroxide wash was replaced with a triethylamine/ethanol wash. This drop casting procedure was only used where specifically noted.

AFM Sample Preparation

Exfoliated COF particles were prepared for AFM imaging by depositing a drop of as-synthesized exfoliated COF suspension (2 mg/mL) onto a freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate (either through drop casting or dip coating) and allowing the droplet to evaporate to dryness in air. COF films were imaged on silicon wafers immediately after drop casting and prior to deprotonation or delamination.

TEM Sample Preparation

To prepare exfoliated BND-TFB COF specimens for TEM analysis, the as-synthesized COF suspension (2 mg/mL) was stirred for an additional 24 hours at room temperature. The resulting suspension was filtered through a 5 µm PTFE syringe filter (Whatman Puradisc) to remove the largest aggregates and drop cast (~4 µL using a micropipette) onto the lacey-carbon substrate (Cu, 400 mesh) TEM grids (Ted Pella, Redding, CA). The droplets were allowed to sit on the grids in

ambient conditions for ~10 seconds and were then wicked dry with filter paper. The same procedure was applied to the TAPB-PDA and Methyl COF suspensions, except that they were not stirred for an additional 24 hours prior to filtration.

DLS Sample Preparation

The as-synthesized COF suspension (2 mg/mL) was filtered through a 5 μ m PTFE syringe filter (Whatman Puradisc) to remove the largest aggregates. This filtered suspension was subjected to DLS analysis.

IR Sample Preparation

All COF powders were analyzed by IR spectroscopy in their as-synthesized state without any additional workup. All COF films were soaked in reagent alcohol for a minimum of 12 hours to ensure complete deprotonation of the imine linkages and activated by supercritical CO₂ drying prior to IR spectroscopy measurements unless otherwise noted.

WAXS Sample Preparation

All COF powders were analyzed by synchrotron WAXS in their as-synthesized state. All COF films were delaminated and soaked in reagent alcohol for a minimum of 12 hours to ensure complete deprotonation of the imine linkages. Films were then packed into the borosilicate capillaries while wet, and WAXS patterns were collected immediately afterwards.

E. Description of COF Powder Exfoliation Experiments

BND-TFB COF Powder Exfoliation Experiment

Three BND-TFB COF suspensions (12 mL each, containing 20 mg COF) were prepared as described in **Section D**. All of these suspensions were centrifuged (7830 rpm for 10 minutes), and the supernatant was discarded from each. Methanol (3 mL) was added to each of the three solid samples, and the resulting mixtures were shaken briefly to disperse the COF in the added solvent. These mixtures were then centrifuged (7830 rpm for 5 minutes), and the solvent was discarded. The solids were then dried under vacuum (60 °C, ~20 mTorr) overnight, after which they were characterized by PXRD, nitrogen adsorption measurements, and IR spectroscopy (labeled “Exfoliated,” yield = 81%).

TAPB-PDA COF and Methyl COF Powder Exfoliation Experiments

Two COF suspensions (12 mL each, containing 20 mg COF) were prepared as described in **Section D**. These suspensions were centrifuged (7830 rpm for 40 minutes), and the excess liquid was decanted. Immediately afterwards, methanol (~3 mL) was added to the residual solids, and this mixture was poured into a dialysis bag (Fisherbrand). The solids were then washed with methanol in a Soxhlet extractor overnight and activated by supercritical CO₂ drying the following day (labeled “Exfoliated,” TAPB-PDA COF yield = 44%, Methyl COF yield = 65%).

F. Additional BND-TFB COF Suspension and Film Characterization

Additional Suspension Characterization

Figure S1. Pore size distributions for BND-TFB COF powder prior to exfoliation (BND-TFB COF, purple) and after exfoliation (Exfoliated, orange).

Figure S2. BET plots for BND-TFB COF powder prior to exfoliation (BND-TFB COF, purple) and after exfoliation (Exfoliated, orange).

Figure S3. Photograph of an as-synthesized exfoliated BND-TFB COF suspension in 7:3:2 MeCN/THF/TFA after filtration through a 5 μ M PTFE syringe filter (left) and an equivalently prepared mixture of BND-TFB COF and 7:3 MeCN/THF with no added acid after filtration (right). The COF is more effectively dispersed in acid, resulting in a suspension of small COF particles upon filtration, as indicated by the Tyndall effect. When no acid is added, the COF powder is not efficiently exfoliated, and all solids are all removed by the 5 μ M syringe filter.

Figure S4. (A) Lattice-resolution HRTEM image of an exfoliated BND-TFB COF sheet. Cumulative dose per image: $\sim 5.6 \text{ e}^- \text{ \AA}^{-2}$. Inset: FFT of the pink boxed region shows the predominant diffraction feature ($\sim 24 \text{ \AA}$). (B) Region of interest at higher magnification corresponding to the pink boxed region of the sheet in (A). (C) Line profile of the FFT inset in (A) showing the distance between the spots.

Figure S5. DLS trace of an exfoliated BND-TFB COF suspension filtered through a $5 \mu\text{m}$ PTFE syringe filter. These data correspond to a Z_{avg} particle size of 170 nm and a PDI of 0.173, which is consistent with the particle sizes observed by AFM.

Additional Film Characterization

Figure S6. Fourier-transform infrared spectra of BND-TFB COF powder (blue) and a film prepared through acid exfoliation of that powder (red).

Figure S7. GIWAXS pattern for a drop casted BND-TFB COF film (1.3 μm thick) indicates that the crystallites exhibit no preferential orientation within the film. Note that this film was not submerged in reagent alcohol or deprotonated prior to this measurement.

Figure S8. Pore size distributions for BND-TFB COF powder (blue) and a film prepared through acid exfoliation of that powder (red).

Figure S9. BET plots for BND-TFB COF powder (blue) and a film prepared through acid exfoliation of that powder (red).

Film Thickness Control

Figure S10. AFM images of BND-TFB COF films prepared by spin coating a (A) 2 mg/mL suspension and (B) 10 mg/mL suspension onto a silicon wafer. The inset in each image is a photograph of the corresponding film. In each case, the film was scratched with a razor blade and imaged at the edge of the scratch to determine its thickness. These data indicate that by varying the spin program (described in **Table S1**) and suspension concentration, films with thicknesses between 50 nm and 150 nm can be prepared.

Figure S11. Profilometry data for a BND-TFB COF film (4 μm thick) prepared by drop casting a 10 mg/mL suspension onto a silicon wafer. The surface of the film was scratched with a razor blade, and a height profile was acquired by scanning across the scratch.

G. Characterization of TAPB-PDA COF Suspensions and Films

Figure S12. PXRD data for TAPB-PDA COF powder prior to exfoliation (TAPB-PDA COF, purple) and after exfoliation (Exfoliated, orange). Each pattern was normalized at the (100) peak. Note that excellent crystallinity is likely observed for the exfoliated sample because the powder was deprotonated by methanol *in situ* during the Soxhlet extraction.

Figure S13. Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) for pristine TAPB-PDA COF powder.

Figure S14. Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) for TAPB-PDA COF powder after acid exfoliation. Note that the exfoliated sample likely exhibits a high surface area because it was deprotonated by methanol *in situ* during the Soxhlet extraction.

Figure S15. Pore size distribution for pristine TAPB-PDA COF powder.

Figure S16. Pore size distribution for TAPB-PDA COF powder after acid exfoliation.

Figure S17. BET plot for pristine TAPB-PDA COF powder.

Figure S18. BET plot for TAPB-PDA COF powder after acid exfoliation.

Figure S19. Fourier-transform infrared spectra of TAPB-PDA COF powder prior to exfoliation (TAPB-PDA COF, purple) and after exfoliation (Exfoliated, orange). In both cases, the imine peak is present at $\sim 1620\text{ cm}^{-1}$, indicating that the imine linkages are preserved throughout the exfoliation process.

Figure S20. (A) Lattice-resolution HRTEM image of an exfoliated TAPB-PDA COF sheet. Cumulative dose per image: $\sim 54.7 \text{ e}^- \text{ \AA}^{-2}$. (B) Boxed regions of interest in (A) at higher magnification. (C) FFTs of the boxed regions show the predominant diffraction feature ($\sim 32 \text{ \AA}$).

Figure S21. AFM image of exfoliated TAPB-PDA COF particles (100 nm thick) deposited onto a freshly cleaved HOPG substrate.

Figure S22. AFM image of a TAPB-PDA COF film (250 nm thick) prepared through acid exfoliation of TAPB-PDA COF powder. Note that the film was imaged prior to treatment with reagent alcohol. Inset: photograph of the film.

Figure S23. Fourier-transform infrared spectra of TAPB-PDA COF powder (blue) and a film prepared through acid exfoliation of that powder (red).

Figure S24. Synchrotron wide-angle X-ray scattering data for TAPB-PDA COF powder (blue) and a film prepared through acid exfoliation of that powder (red). Both patterns are normalized at the (100) peak.

H. Characterization of Methyl COF Suspensions and Films

Figure S25. PXRD data for Methyl COF powder prior to exfoliation (Methyl COF, purple) and after exfoliation (Exfoliated, orange). Both patterns were normalized at the (100) peak. Note that excellent crystallinity is likely observed for the exfoliated sample because the powder was deprotonated by methanol *in situ* during the Soxhlet extraction.

Figure S26. Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) for pristine Methyl COF powder.

Figure S27. Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) for Methyl COF powder after acid exfoliation. Note that the exfoliated sample likely exhibits a high surface area because it was deprotonated by methanol *in situ* during the Soxhlet extraction.

Figure S28. Pore size distribution for pristine Methyl COF powder.

Figure S29. Pore size distribution for Methyl COF powder after acid exfoliation.

Figure S30. BET plot for pristine Methyl COF powder.

Figure S31. BET plot for Methyl COF powder after acid exfoliation.

Figure S32. Fourier-transform infrared spectra of Methyl COF powder prior to exfoliation (Methyl COF, purple) and after exfoliation (Exfoliated, orange). In both cases, the imine peak is present at $\sim 1620\text{ cm}^{-1}$, indicating that the imine linkages are preserved throughout the exfoliation process.

Figure S33. (A) Lattice-resolution HRTEM image of an exfoliated Methyl COF sheet. Cumulative dose per image: $\sim 54.7 \text{ e}^- \text{ \AA}^{-2}$. (B) Boxed regions of interest in (A) at higher magnification. (C) FFTs of the boxed regions show the predominant diffraction feature ($\sim 32 \text{ \AA}$).

Figure S34. AFM image of exfoliated Methyl COF particles ($\sim 100 \text{ nm}$ thick) deposited onto a freshly cleaved HOPG substrate.

Figure S35. AFM image of a Methyl COF film (500 nm thick) prepared through acid exfoliation of Methyl COF powder. Note that the film was imaged prior to treatment with reagent alcohol. Inset: photograph of the film.

Figure S36. Fourier-transform infrared spectra of Methyl COF powder (blue) and a film prepared through acid exfoliation of that powder (red).

Figure S37. Synchrotron wide-angle X-ray scattering data for Methyl COF powder (blue) and a film prepared through acid exfoliation of that powder (red). Both patterns are normalized at the (100) peak.

I. Alternative Solvent Mixtures for COF Exfoliation

Figure S38. (A) As-synthesized TAPB-PDA COF powder. (B) 50 mg of TAPB-PDA COF powder fully dissolved in 12 mL of a 7:3:2 acetonitrile/tetrahydrofuran/TFA mixture containing 5% v/v H₂O. (C) 50 mg of TAPB-PDA COF powder fully dissolved in 2 mL of TFA containing 5% v/v H₂O. (D) Fragments of a TAPB-PDA COF film prepared by casting the COF solution shown in (C).

Figure S39. PXRD patterns of TAPB-PDA COF powder (blue) and a film prepared from a solution of that powder (red) in trifluoroacetic acid containing 5% v/v H₂O.

Figure S40. Nitrogen adsorption (circles) and desorption (triangles) isotherms (77 K) of TAPB-PDA COF powder (blue) and a TAPB-PDA COF film (red) prepared from a solution of that powder in trifluoroacetic acid containing 5% v/v H_2O .

Figure S41. Pore size distributions for TAPB-PDA COF powder (blue) and a TAPB-PDA COF film (red) prepared from a solution of that powder in trifluoroacetic acid containing 5% v/v H_2O .

Figure S42. BET plots for TAPB-PDA COF powder (blue) and a TAPB-PDA COF film (red) prepared from a solution of that powder in trifluoroacetic acid containing 5% v/v H₂O.

Figure S43. Fourier-transform infrared spectra of TAPB-PDA COF powder (blue) and a film prepared through acid exfoliation of that powder (red) in trifluoroacetic acid containing 5% v/v H₂O.

J. References

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2019_08_ChemRxiv_Burke_COFexfoliation_SI.pdf (4.54 MiB)

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Traditionally
Insoluble

Acid-exfoliated
Suspension