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Insight Into the Crystallization of Amorphous Imine-Linked Polymer Networks to 2D Covalent Organic Frameworks

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I. Materials and Instrumentation

Materials. Reagents were purchased from commercial sources and used without further purification. MeOH and toluene were purchased from commercial sources and purified using a custom-built alumina-column based solvent purification system. Other solvents were purchased from commercial sources and dried over activated 3Å molecular sieves.

Instrumentation. Infrared spectra of solid samples were recorded using a ThermoNicolet iS10 FT-IR spectrometer with a diamond ATR attachment and are uncorrected.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer using samples degassed at 90 °C for 24 h and backfilled with N_2. N_2 isotherms were generated by incremental exposure to ultra high purity nitrogen up to 1 atm in a liquid nitrogen (77 K) bath and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00).

Powder X-ray diffraction (PXRD) patterns were obtained on a Scintag Theta-Theta Powder X-Ray Diffractometer in reflectance Bragg-Brentano geometry employing Cu Kα line focused radiation at 2200 W (40 kV, 40 mA) power and equipped with a Ge crystal detector fitted with a 0.3 mm radiation entrance slit. Samples were mounted on zero background sample holders by dropping powders from a spatula and then leveling the sample surface with a glass microscope slide. No sample grinding or sieving was used prior to analysis. Crystallite size was determined by applying the Scherrer equation to the powder patterns using MDI JADE.

Scanning electron microscopy was performed on a LEO 1550 FESEM (Keck SEM) operating at 2.00 kV and a working distance of 3 – 4 mm with an aperture size of 20 µm. Samples were prepared by adsorption onto a silicon wafer, which was then attached to a flat aluminum platform sample holder. The sample was then placed directly into the instrument. No metal coating was applied.

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

The Accelrys Materials Studio (version 5.5) program suite was used to simulate the powder diffraction. The structures were optimized using the Geometry Optimization routine including energy minimization with cell parameters optimization, using the parameters from the Universal Force Field. The PXRD was calculated for the optimized structures with the Reflex Plus module.

II. Experimental Protocols

General conditions for homogeneous synthesis of TAPB-PDA COF. 1,3,5-tris(4-aminophenyl)benzene (55 mg, 0.16 mmol) and terephthaldehyde (31 mg, 0.23 mmol) were combined in a scintillation vial with a dioxane / mesitylene solution (4:1 *v/v*, 6.3 mL). The solution was heated to 70 ˚C for 3 minutes to ensure dissolution and then cooled to room temperature. Distilled H_2O (1.2 mL) was added to the solution, followed by glacial CH_3CO_2H (1.8 mL). The resulting suspension was sealed and heated to 70 ˚C for 72 hrs. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding a yellow powder. (66 mg, 85 % yield)

Conditional survey of acetic acid and water for TAPB-PDA COF synthesis. A stock solution of the monomers in dioxane / mesitylene solution (4:1 *v/v*) was prepared as described above. Various mixtures of distilled H_2O, glacial CH_3CO_2H, and additional dioxane / mesitylene were added to the stock solution (1.0 mL) to obtain a final volume of 1.7 mL for each experiment (0.015 M [TAPB], 0–0.3 mL water, 0–0.4 mL glacial acetic acid). Each reaction mixture was heated to 70 ˚C for 3 days, after which the COF or amorphous polymer precipitates were isolated as described above and subsequently characterized by PXRD.

Homogeneous synthesis of TAPB-PDA amorphous network. 1,3,5-tris(4-aminophenyl)benzene (100 mg, 0.28 mmol) and terephthaldehyde (57 mg, 0.43 mmol) were combined in a scintillation vial with dioxane / mesitylene solution (4:1 *v*/*v*, 11.4 mL), and heated to 70 ˚C for 3 min to ensure dissolution and then cooled to room temperature. Distilled H_2O (2.3 mL) was added to the solution, followed by glacial CH_3CO_2H (3.4 mL). The resulting solid was isolated by filtration after 15 min, rinsed with toluene, and subsequently dried under vacuum, yielding a yellow powder. (0.41 mg, 95 % yield)

Conversion of amorphous network to TAPB-PDA COF. The TAPB-PDA amorphous network (80 mg) was added to a scintillation vial with dioxane / mesitylene solution (4:1 *v/v*, 6.4 mL). Distilled H_2O (1.3 mL) was added to the solution, followed by glacial CH_3CO_2H (1.9 mL). The resulting suspension was heated to 70 ˚C for 48 hours, under atmospheric pressure. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding a yellow powder. (60 mg, 75% yield)

III. Additional Characterization

A. Powder X-ray diffraction

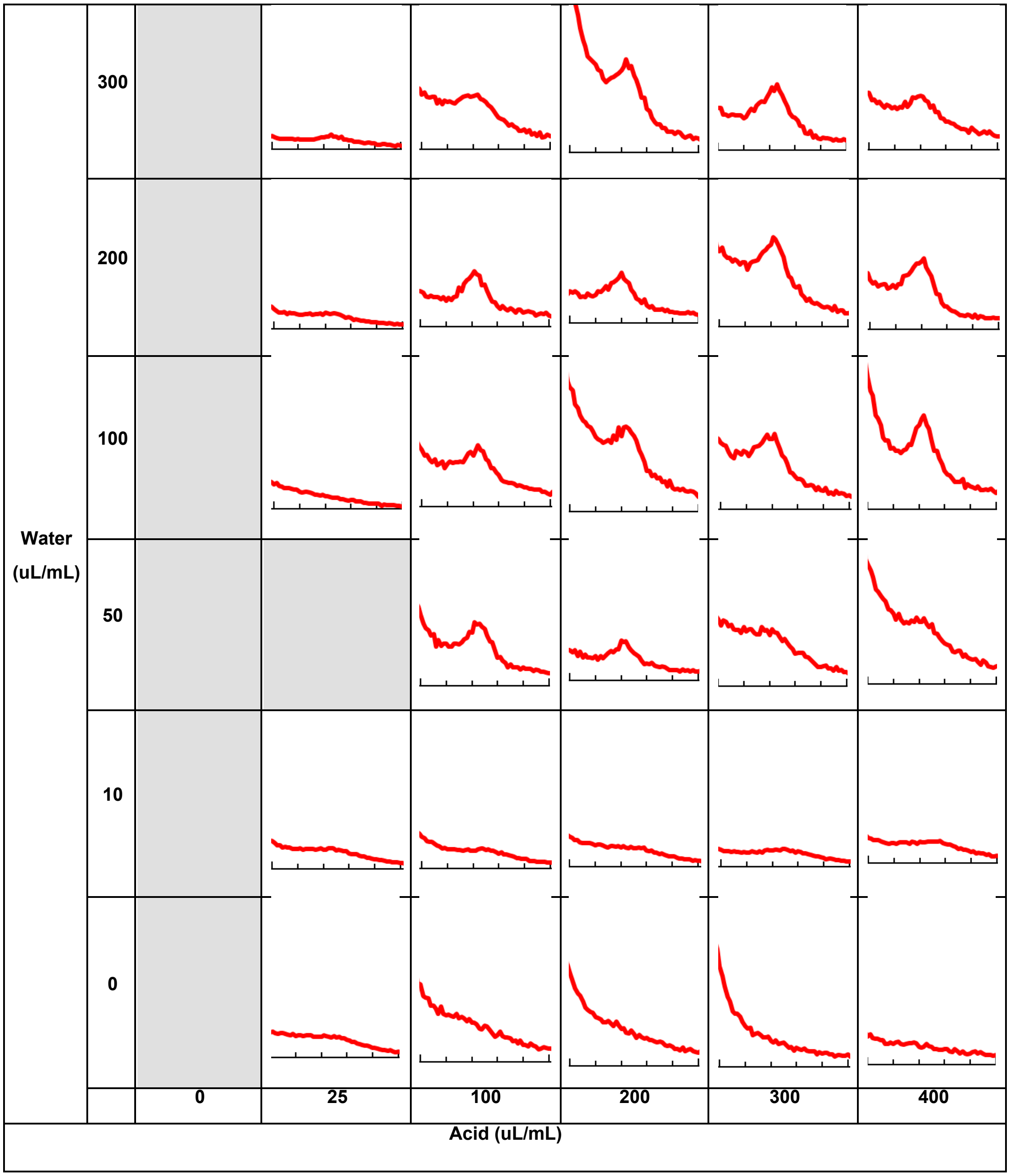


Figure S1. Partial powder X-ray diffraction (2θ 2–4˚) of TAPB-PDA COF synthesized in the presence of water and/or glacial acetic acid, added to 1 mL of stock (final concentration normalized to 0.015 M [TAPB]).
Reaction conditions: 70 ˚C, 72 h. Conditions in gray yielded no solid.

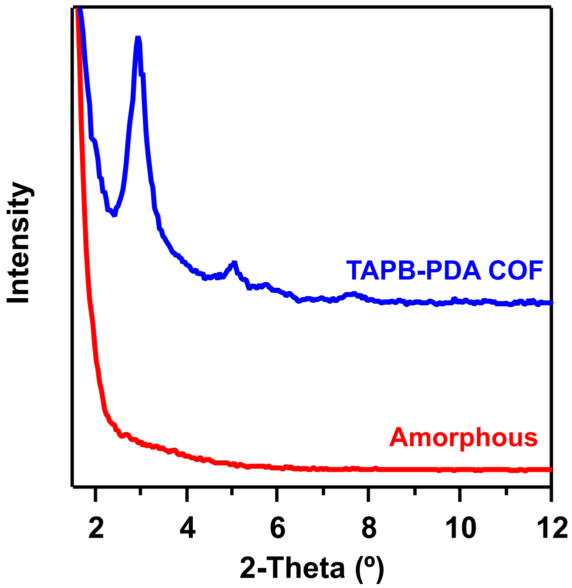


Figure S2. Powder X-ray diffraction of initial amorphous imine network and TAPB-PDA COF after resubjection to the reaction conditions (70 ˚C, 48 h).

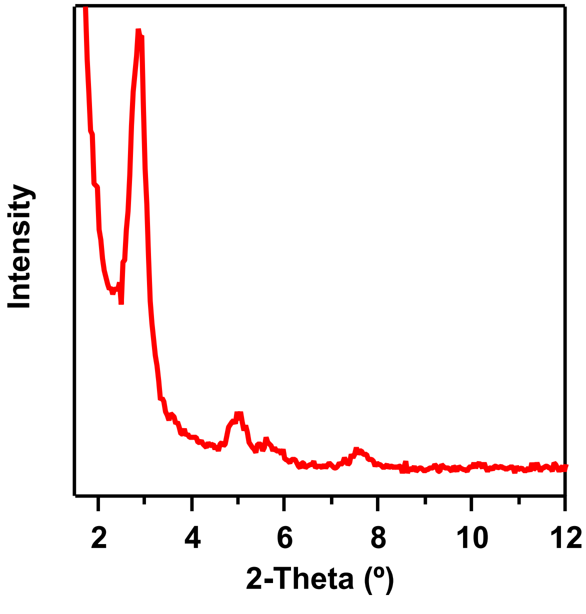
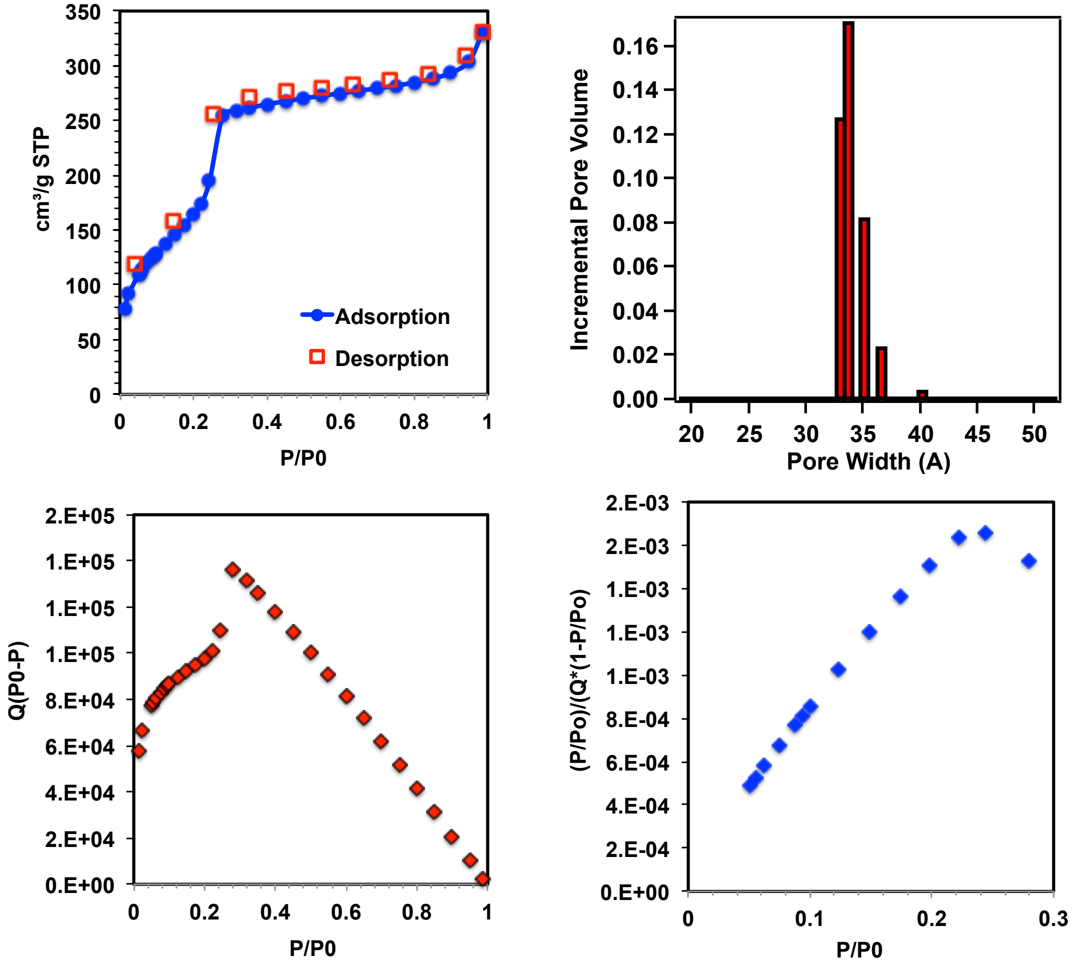


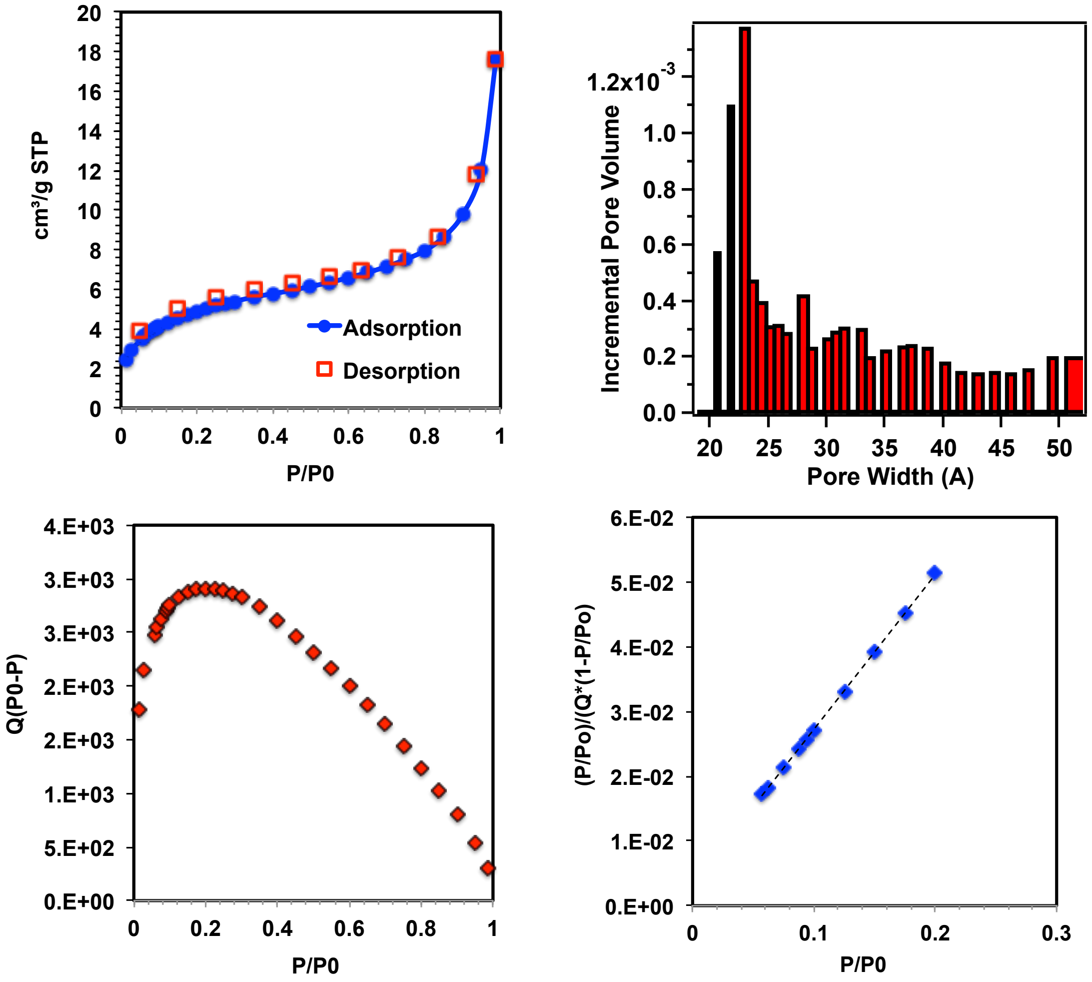
Figure S3. Powder X-ray diffraction of initial amorphous imine network after resubjection to the reaction conditions (room temperature, 6 days).

B. N_2 Isotherm and BET surface area determination



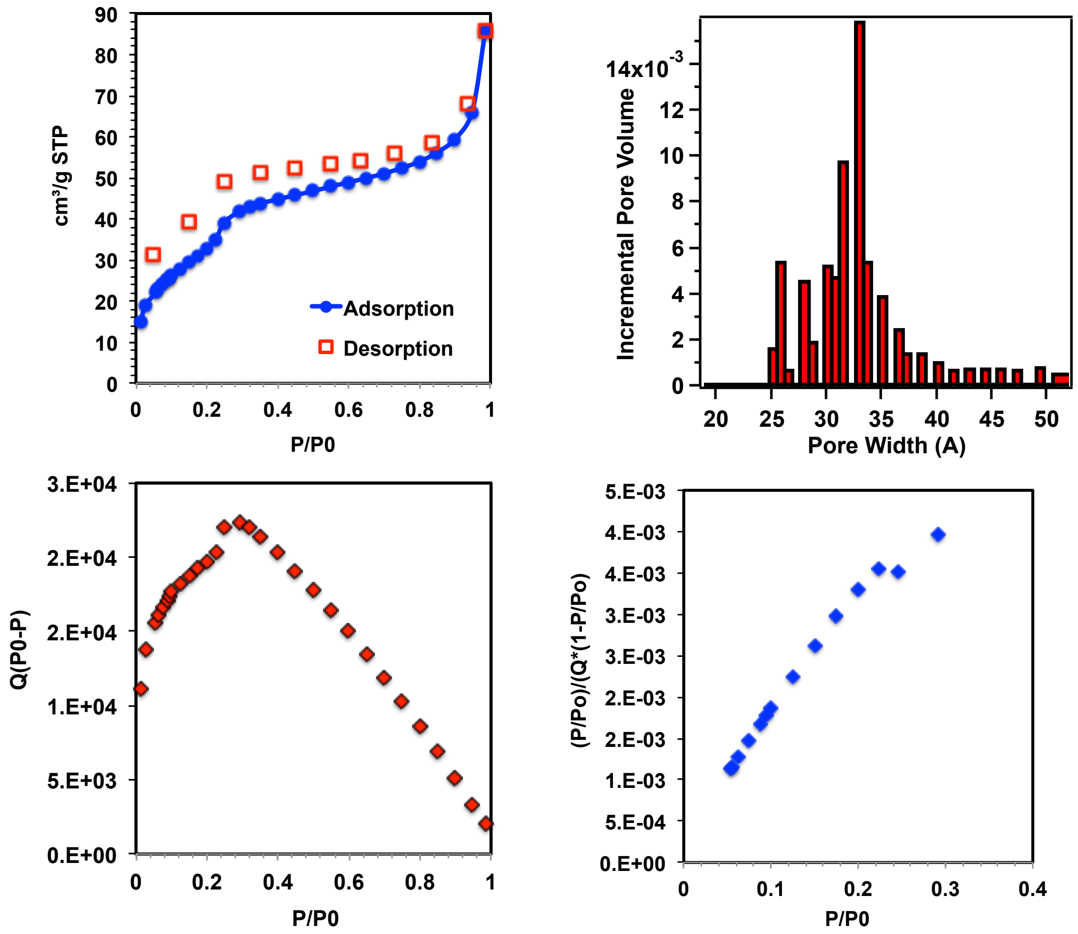
P/P_0	BET Surface Area ($m^2\ g^{-1}$)	R^2
0.05 – 0.20	610	0.999
0.05 – 0.22	625	0.997
0.05 – 0.24	657	0.990
0.05 – 0.27	750	0.931

Figure S4. N_2 adsorption isotherm (77 K) and surface area data analysis of TAPB-PDA COF synthesized from homogeneous conditions.



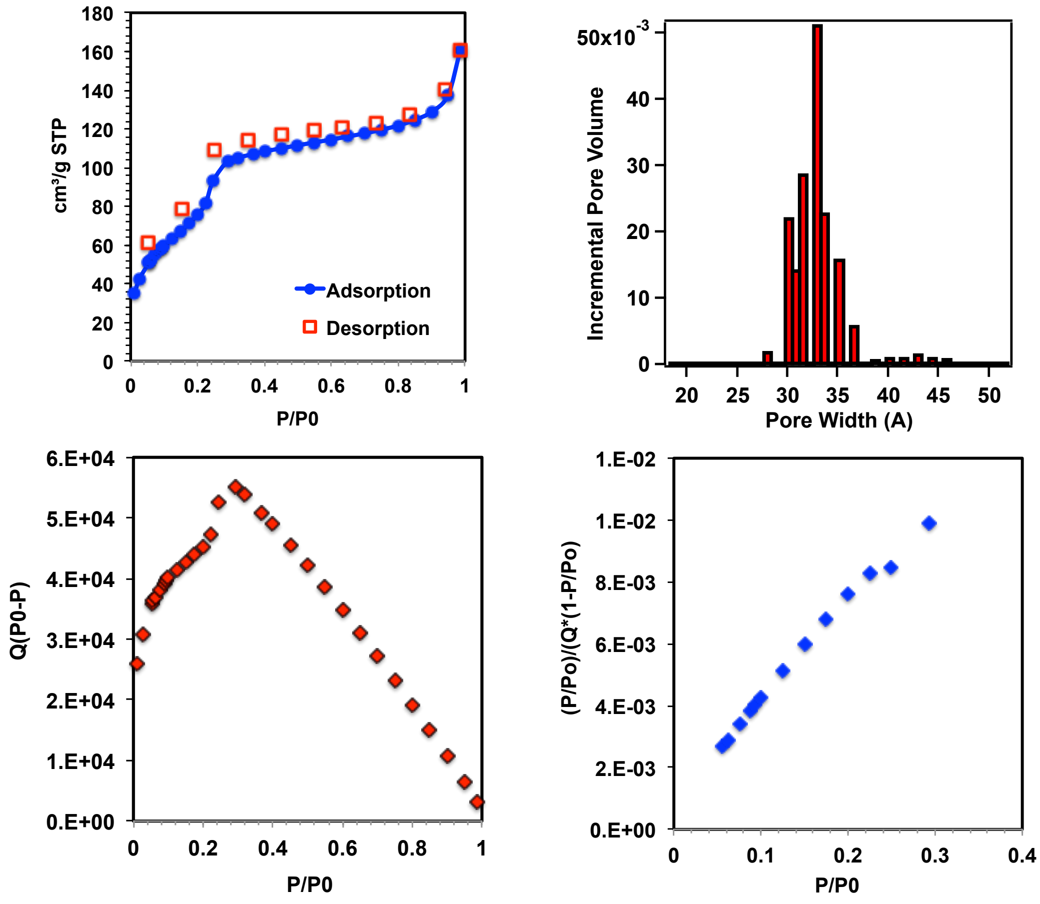
P/P_0	BET Surface Area (m^2 g^{-1})	R^2
0.05 – 0.20	18	0.999

Figure S5. N_2 adsorption isotherm (77 K) and surface area data analysis of amorphous TAPB-PDA synthesized at room temperature from homogeneous conditions.



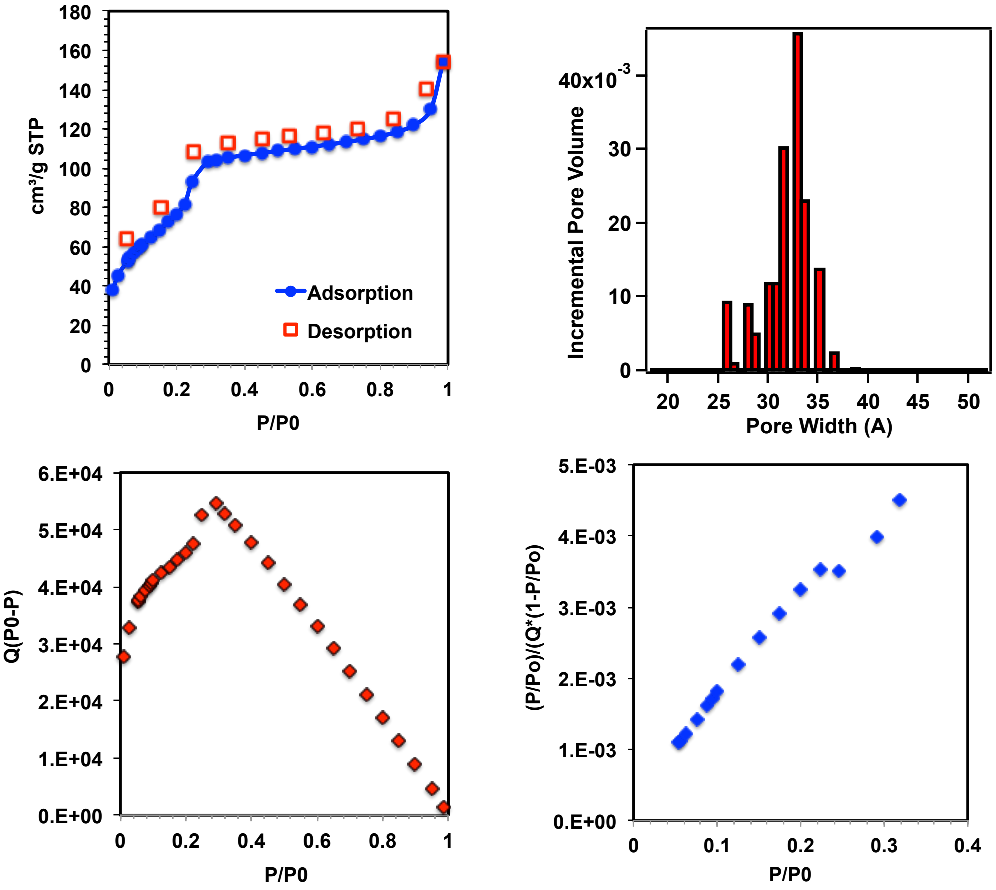
P/P_0	BET Surface Area (m^2 g^{-1})	R^2
0.05 – 0.22	126	0.999
0.05 – 0.24	132	0.991
0.05 – 0.29	136	0.992

Figure S6. N_2 adsorption isotherm (77 K) and surface area data analysis of amorphous TAPB-PDA resubjection to the reaction conditions (70 ˚C, 24 h).



P/P_0	BET Surface Area ($m^2\,g^{-1}$)	R^2
0.05 – 0.20	283	0.999
0.05 – 0.22	291	0.997
0.05 – 0.24	311	0.983
0.05 – 0.29	330	0.977

Figure S7. N_2 adsorption isotherm (77 K) and surface area data analysis of amorphous TAPB-PDA resubjection to the reaction conditions (70 ˚C, 48 h).



P/P_0	BET Surface Area ($m^2\,g^{-1}$)	R^2
0.05 – 0.20	284	0.999
0.05 – 0.22	291	0.998
0.05 – 0.24	310	0.986
0.05 – 0.29	330	0.981

Figure S8. N_2 adsorption isotherm (77 K) and surface area data analysis of amorphous TAPB-PDA resubjection to the reaction conditions (room temperature, 6 days).

C. SEM characterization

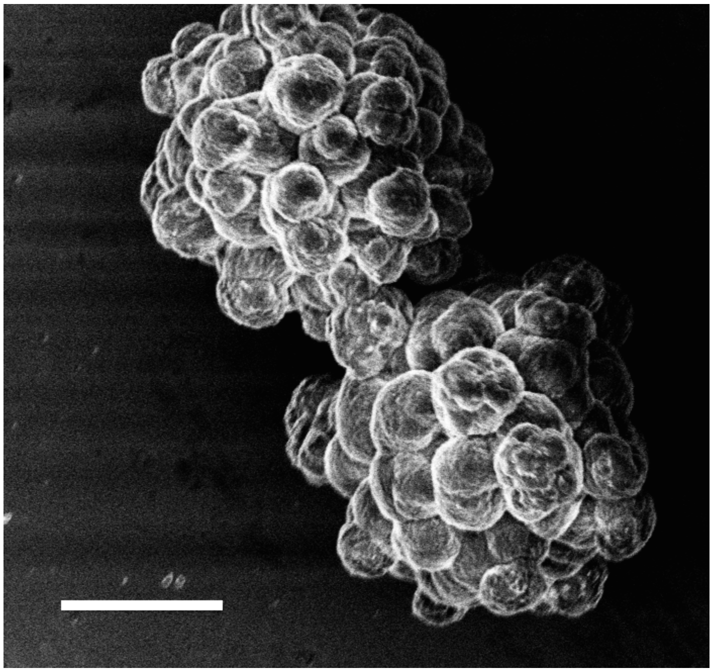


Figure S9. SEM of amorphous TAPB-PDA. Scale bar is 2 μm.

Figure S10. SEM of TAPB-PDA COF. Scale bar is 2 μm.

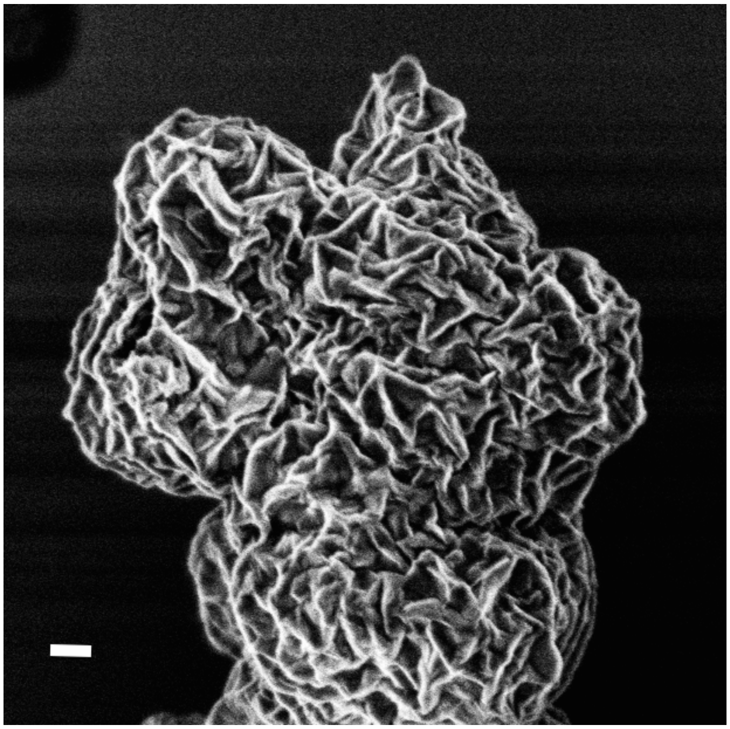


Figure S11. SEM of TAPB-PDA COF. Scale bar is 200 nm.