

Supporting Information

Covalent organic framework crystallization using a continuous flow packed-bed reactor

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I. General Information

Reagents

All reagents were purchased from commercial suppliers. 1,3,5-tris(4-aminophenyl)benzene (TAPB) was purchased from Ambeed, Inc. with a 97% purity. 2,5-dihydroxyterephthalaldehyde (OHPDA) was purchased from Ambeed, Inc. with a 95% purity.

Data

All data was plotted using Origin Pro.

Fourier Transform-Infrared Spectroscopy (FT-IR)

Data was collected using a Bruker Invenio X FT-IR in ATR mode on solid powders of the materials. The scanner rate was 10 kHz.

Powder X-ray diffraction data was collected (PXRD)

Data was collected on a Rigaku Smartlab diffractometer with a $\text{CuK}\alpha(1.5406 \text{ \AA})$ X-ray radiation source and was operated at 40 V and 44 mA. The scan speed was $2.0^\circ/\text{min}$.

Raman Spectroscopy

Raman spectra were collected using 514 nm excitation wavelength in a Renishaw inVia Raman microscope. A 50 x objective lens was used to focus the incident laser beam on the samples and the laser power was set to 0.5 mW. Raman spectra were collected from the samples with 40 second acquisition times and 1 acquisition.

UV-Vis Absorption Spectroscopy

Spectra were collected with a Craic microspectrophotometer. The crystalline COF powder was loaded onto a Si/SiO₂ substrate, and a 36x objective lens was used to focus the light from a xenon lamp onto the crystals. A 100 micron sized aperture was used for the measurement and absorbance spectra were collected from the COFs after obtaining a dark scan (with the CCD shutter closed) and reference scan from the Si/SiO₂ substrate.

UV-Photoluminescence Spectroscopy

The same sample substrate that was used for UV-Vis Absorption was used here. Data was collected with a Photon Systems RPL200 deep UV Raman/PL system equipped with a 248.6 nm NeCu laser and a 300 groove/mm diffraction grating. For this measurement, a 40x objective was used to focus the 248.6 nm excitation on the COF crystals and the PL spectrum was acquired by setting the laser frequency and number of pulses to 60 Hz and 200, respectively.

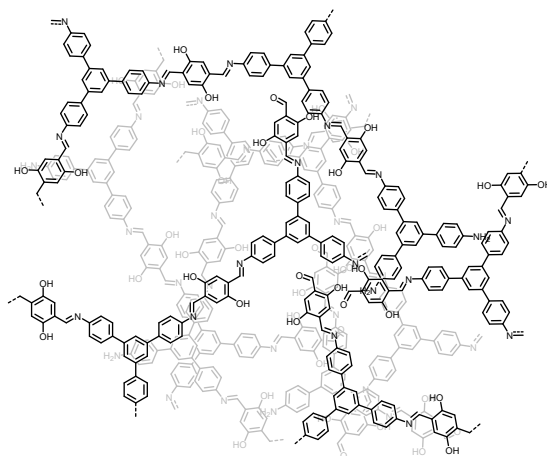
Crystallite Calculation

$D = K\lambda/\beta\cos(\theta)$
D = Crystallite Size
K = Scherrer constant (0.94)
λ = Wavelength of X-ray beam (1.54 Å)
β = Full-width half maximum of $\langle 100 \rangle$ plane peak
θ = Bragg angle of $\langle 100 \rangle$ plane peak

BET Surface Area Analysis

N₂ sorption experiments were carried out using an ASAP 2020. N₂ (99.999% purity) was purchased from Indiana Oxygen Company and used as received. An activated sample (~30 mg) was charged into a sample cell subsequently transferred to the degas unit for degassing and sorption apparatus for measurement at 77K (N₂ isotherm).

II. Synthetic Methods and Continuous Flow Set Up



Synthesis of Amorphous TAPB-OHPDA Polymer

A 98 mL solution was prepared by mixing 1,4-dioxane (76 mL) and mesitylene (22 mL) in an Erlenmeyer flask. Then 1 equivalent of 1,3,5-tris(4-aminophenyl)benzene (TAPB) (600 mg, 1.7 mmol) and 1.5 equivalents of 2,5-dihydroxyterephthalaldehyde (OHPDA) (425 mg, 2.6 mmol) was added. Next, glacial acetic acid (11 mL) was added to the reaction and swirled to mix. The reaction mixture was then periodically swirled over 15 minutes. Orange solid precipitate could be observed forming during this time. After 15 minutes, the reaction was filtered using a filter paper and Buchner funnel. To remove excess starting material, the orange precipitate was then washed with methanol and acetone until the filtrate was clear. The precipitate was collected and stored in acetone until usage. Drying this material to completion under high vacuum results in pore collapse which prevents any subsequent crystallization steps from taking place. Therefore, prior to characterization, the precipitate was only briefly placed under vacuum to partially dry and did not undergo any activation steps.

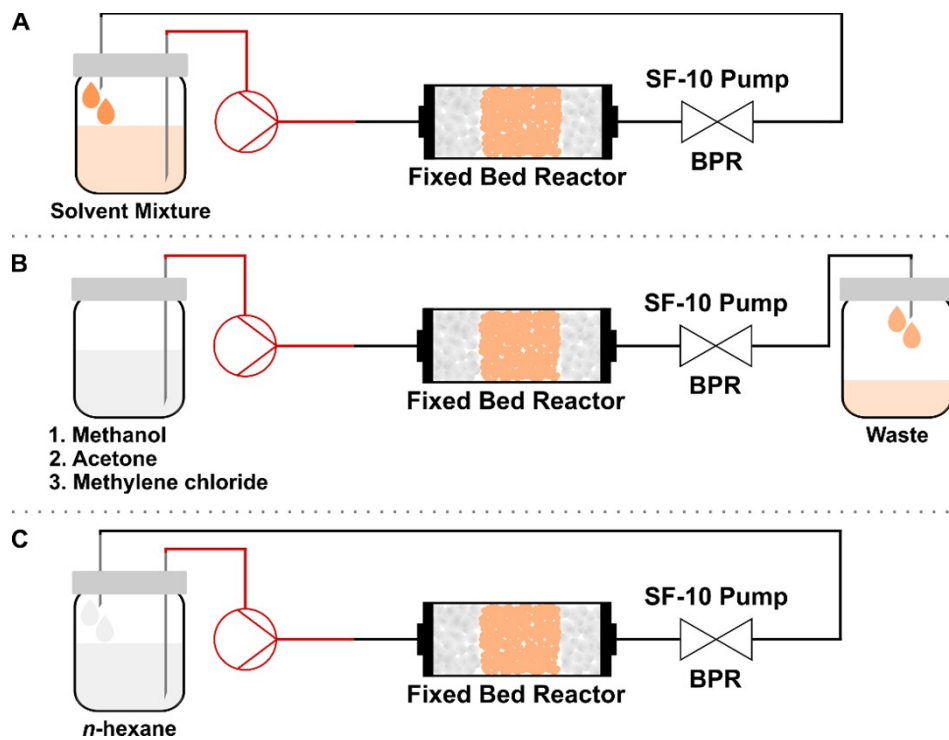
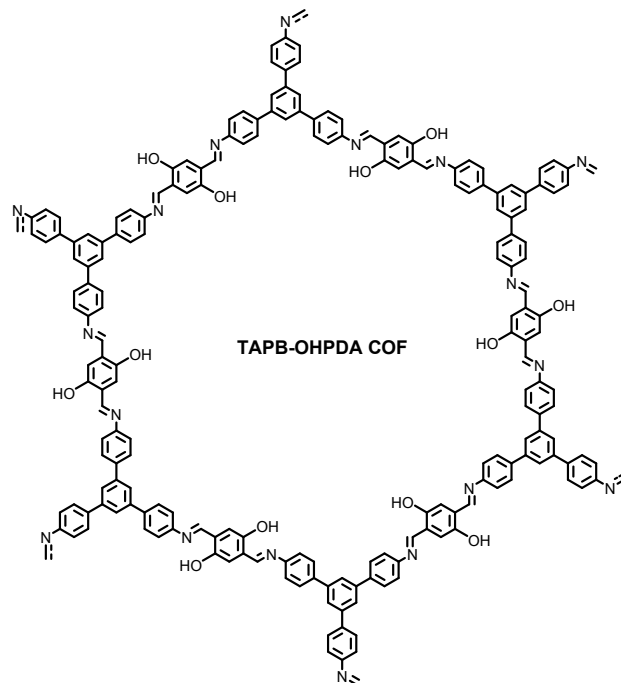


Figure S1. Flow Chemistry Schematic A) General set up for Conversion of Amorphous to Crystalline TAPB-OHPDA COF in Flow, B) Washing in flow with methanol, acetone, and methylene chloride, C) Washing in flow with *n*-hexane



Conversion of Amorphous to Crystalline TAPB-OHPDA COF in Flow

Flow conversion was done using a Vapourtec R-Series Modular Flow Chemistry System (Fig. S1A) with a fixed bed reactor (6.6 mm I.D.). Amorphous COF material (~80 mg) was placed into the fixed bed reactor and packed with glass beads (1 mm O.D.) on both sides. Additionally the fixed bed reactor was fitted with 30 μm polytetrafluoroethylene (PTFE) frits on both ends. The reagent mixture of dioxane, mesitylene, and 10 M acetic acid (6.7:1.7:1, v/v, 8 mL) was flowed through 1 mm bore perfluoroalkoxy (PFA) tubing using a R2 S+ peristaltic pump. A SF-10 peristaltic pump was used as a backpressure regular (BPR), and positioned after the fixed bed reactor and set to 5 bar to prevent solvent from boiling at elevated temperatures. A temperature probe was placed onto the fixed bed reactor and the temperature was increased by 20 $^{\circ}\text{C}$ intervals every 10 minutes until the bed reactor reached the desired reaction temperature.

Standard Washing and Heating

The material was removed from the fixed bed reactor and placed into a scintillation vial. It was washed with methanol (20 mL) followed by acetone (20 mL) to remove any small molecules that might have redissolved into solution. Then dichloromethane (8 mL) was added and it was left to stand still at RT for 30 min. The solvent was decanted and this step was repeated two more times. Immediately following, n-hexane (8 mL) was added and it was left to stand still at RT overnight. Finally, this solvent was decanted and the material was placed under N_2 flow at room temperature for 30 minutes. It was then heated stepwise to 50 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, and 150 $^{\circ}\text{C}$ (30 minutes each) under N_2 flow.¹

Washing in Flow and Standard Heating

The reaction was cooled down to RT and then the reagent outlet was connected to waste. Methanol (20 mL) was flowed through the inlet at 2.0 mL/min followed by acetone (20 mL). Then, dichloromethane was slowly flowed through at 0.27 mL/min for 90 minutes (24 mL total). Then, the inlet and outlet reagent lines (Fig. S1B) were added to the same vial containing *n*-hexane (8 mL). The solvent was recycled through at 0.27 mL/min overnight (Fig. S1C). From visual inspection, no material was lost during the washing step.

The material was then subjected to the standard heating conditions described above.

III. Powder X-Ray Diffraction (PXRD) Data

Table S1. Raw PXRD Data for All Flow and Batch Conversions

Starting Material/Amorphous Polymer				110 °C (Flow)			
Hours	FWHM	Peak Position	Crystallite Size	Hours	FWHM	Peak Position	Crystallite Size
0	0.60	3.10	13.9	2	0.51	2.92	16.2
70 °C (Batch)				7 (Sample 1)	0.35	2.75	23.8
Hours	FWHM	Peak Position	Crystallite Size	7 (Sample 2)	0.42	2.83	20.0
2	0.52	2.96	16.0	17	0.51	2.79	16.3
5	0.57	3.03	14.5	20	0.46	2.82	18.0
17	0.51	2.91	16.3	140 °C (Flow)			
22	0.48	2.92	17.3	Hours	FWHM	Peak Position	Crystallite Size
46	0.47	2.86	17.8	0.5	0.43	2.82	19.3
72	0.46	2.90	17.9	2 (Sample 1)	0.40	2.78	20.6
70 °C (Flow)				2 (Sample 2)	0.48	2.80	17.2
Hours	FWHM	Peak Position	Crystallite Size	7	0.41	2.84	20.4
2	0.53	2.93	15.6	20	0.38	2.80	21.6
7	0.45	2.84	18.4	140 °C (Wash In Flow)			
17	0.50	2.93	16.7	Hours	FWHM	Peak Position	Crystallite Size
20	0.46	2.83	18.1	2	0.43	2.75	19.5
46	0.41	2.82	20.0	TAPB-OHPDA COF <100> Peak Position: 2.82			

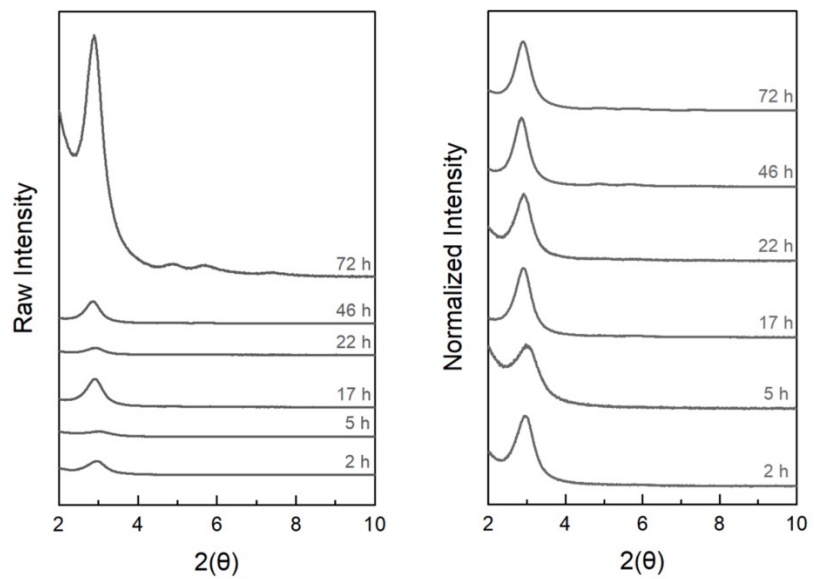


Figure S2. Raw and Normalized PXRD for Batch Conversion at 70°C

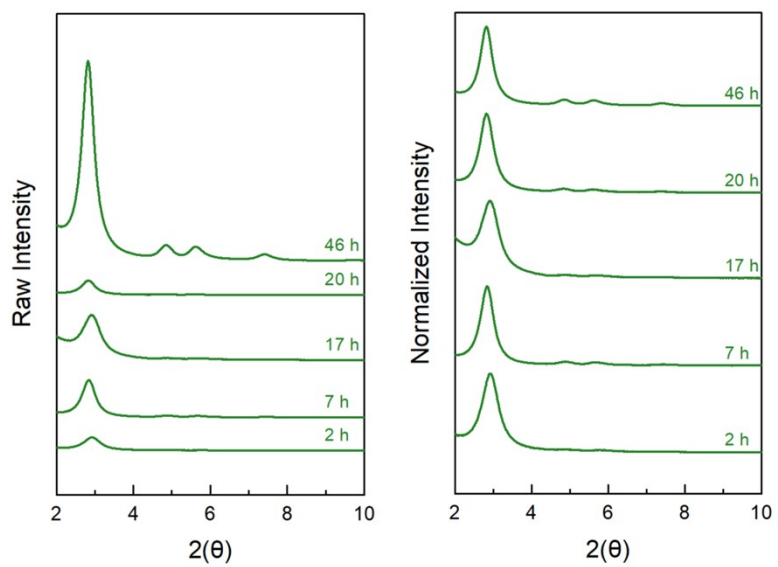


Figure S3. Raw and Normalized PXRD for Flow Packed-Bed Conversion at 70°C

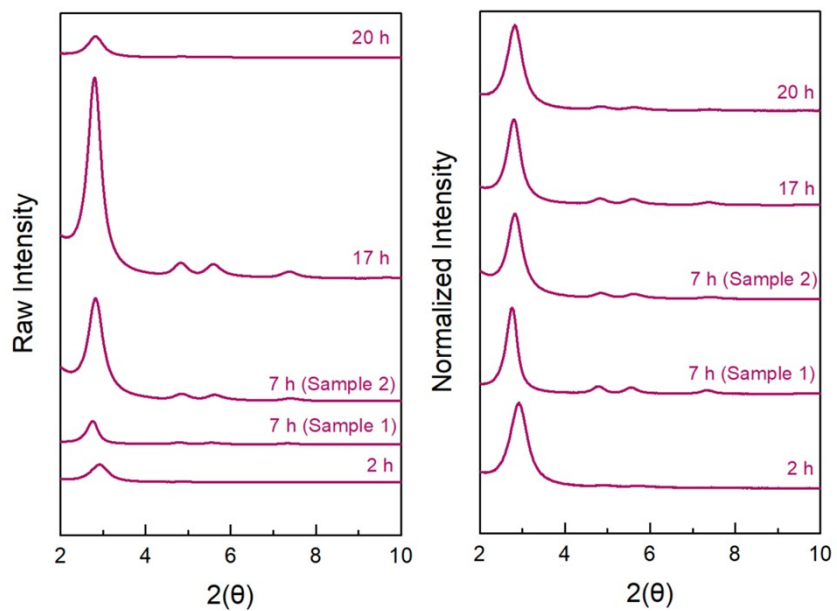


Figure S4. Raw and Normalized PXRD for Flow Packed-Bed Conversion at 110°C

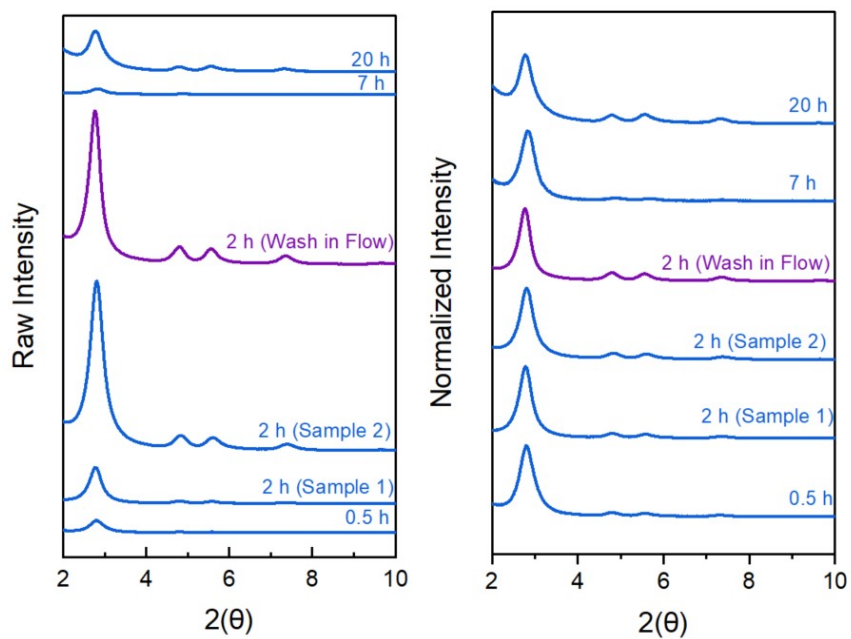


Figure S5. Raw and Normalized PXRD for Flow Packed-Bed Conversion at 140°C

IV. Spectroscopy Data

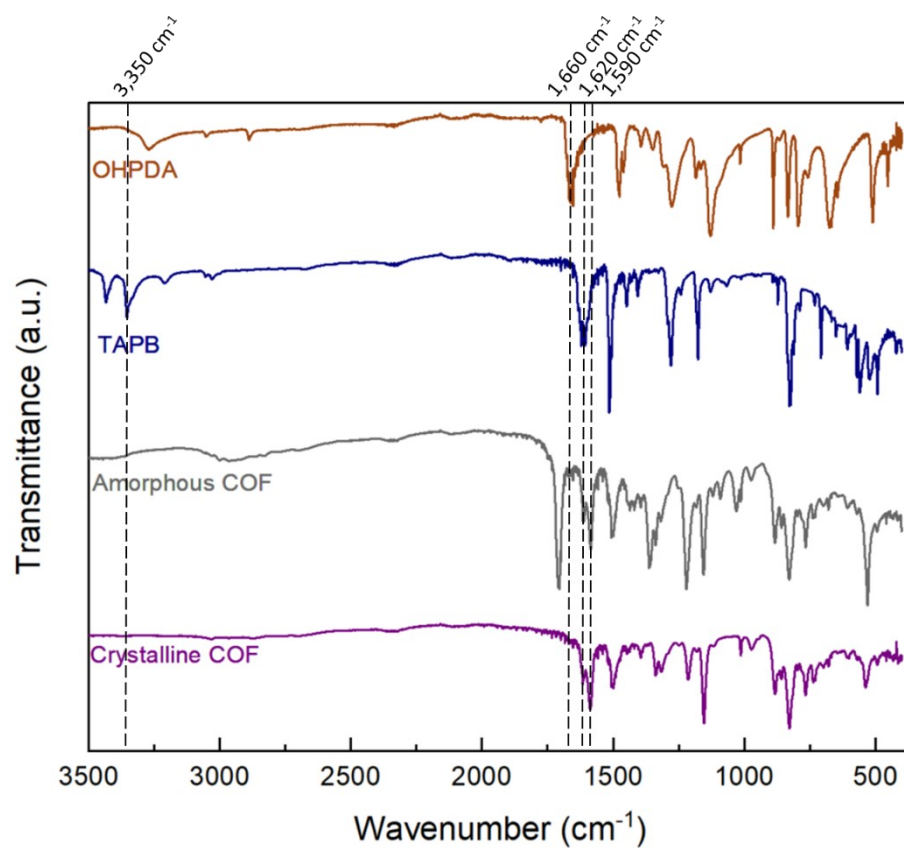


Figure S6. FT-IR Spectroscopy of Starting Materials, Amorphous COF, and COF Crystallized in Flow (140°C/2 h)

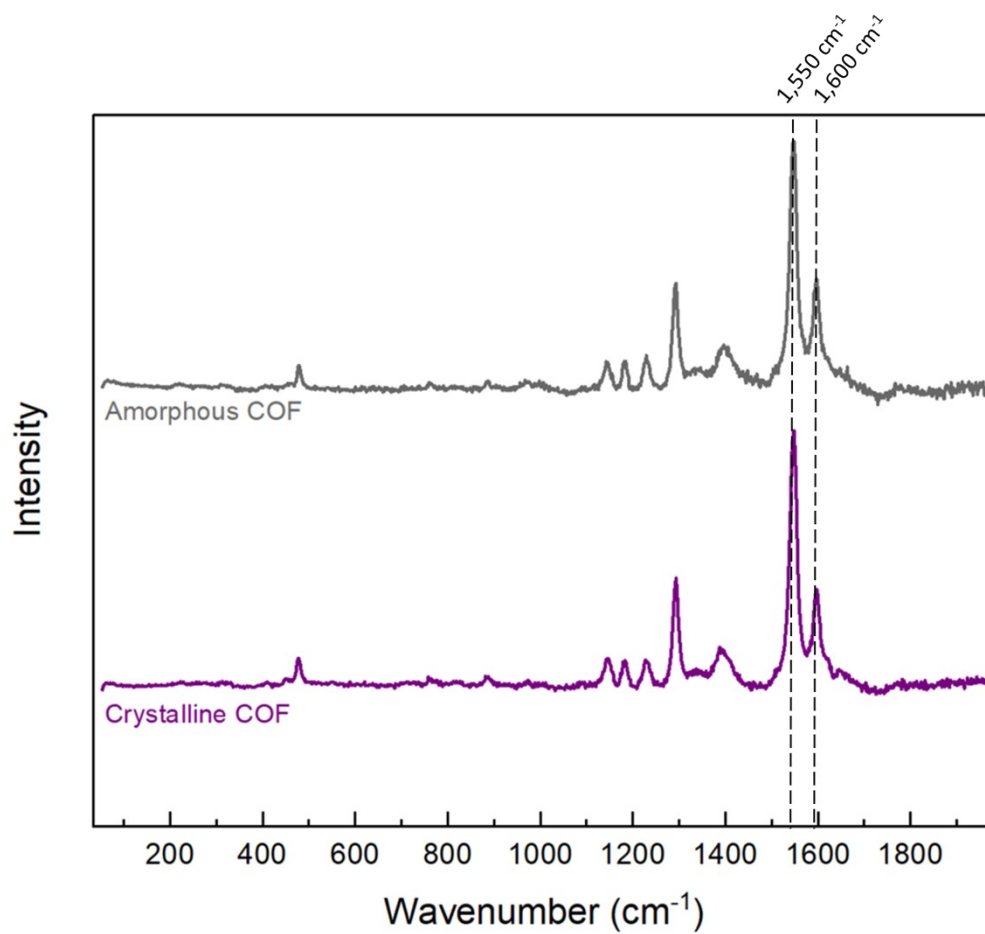


Figure S7. Amorphous Polymer Network and COF Crystallized in Flow (140°C/2 h)

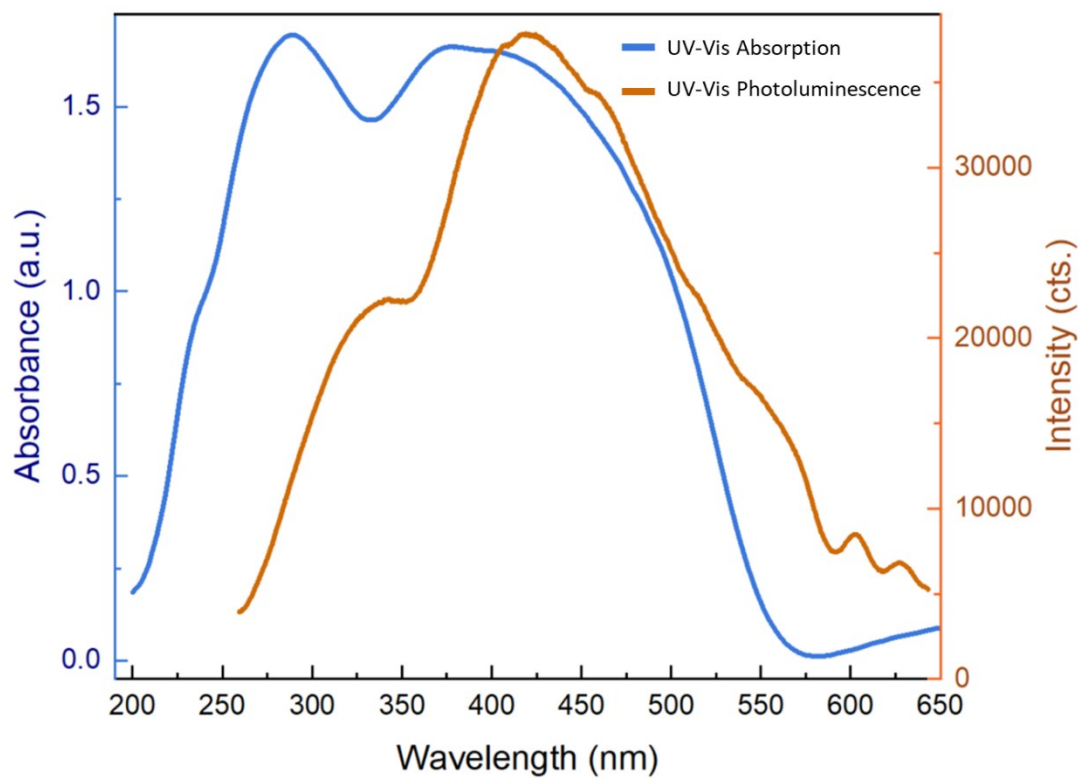


Figure S8. UV-Vis Absorption (blue) and UV-PL (red) Spectra from Flow Conversion (140 °C/2h)

V. Synthesis and Flow Conversion of TAPB-PDA COF Data

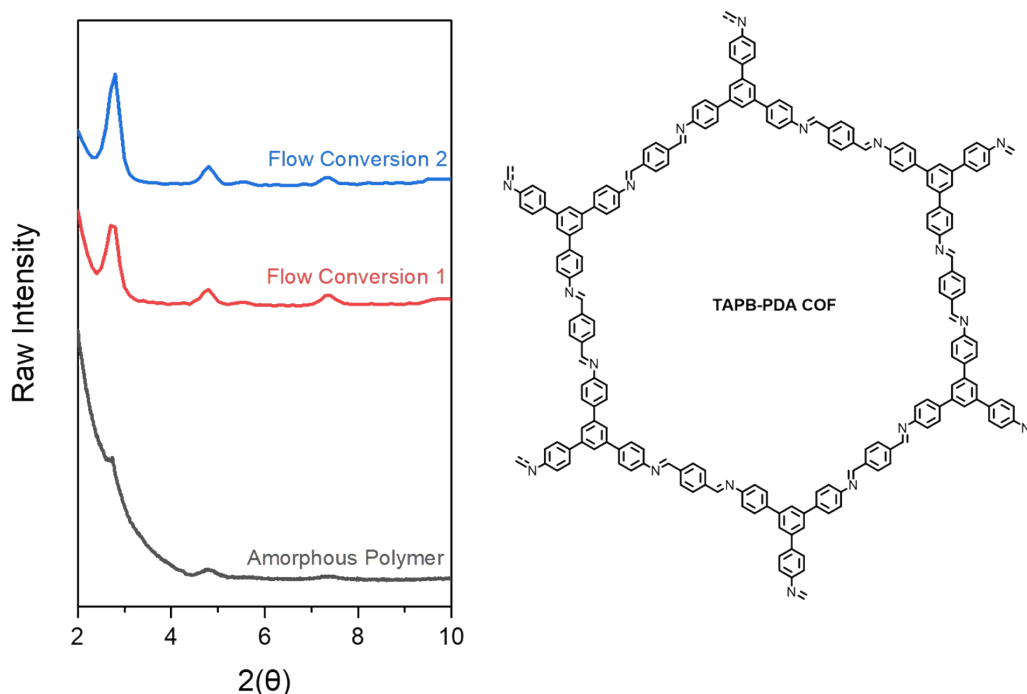


Figure S9. Raw PXRD for amorphous precursor and flow converted TAPB-PDA COF

Synthesis of Amorphous TAPB-PDA Polymer

Amorphous polymer was synthesized under the same conditions used to synthesize amorphous TAPB-OHPDA Polymer.

Conversion of Amorphous to Crystalline TAPB-OHPDA COF in Flow

Flow Conversion 1 - The reagent mixture of dioxane, mesitylene, and 10 M acetic acid (6.7:1.7:1, v/v, 5 mL) was used for the conversion. A SF-10 peristaltic pump was used as a backpressure regular (BPR), and positioned after the fixed bed reactor and set to 0.5 bar. The flow rate was set to 0.0 mL/min and the temperature was ramped to 70 °C. The conversion was left for 24 hours. COF was removed, washed and analyzed with PXRD. The structure of TAPB-PDA COF was confirmed with by the presence of peaks at 2.8, 4.7, and 5.6 2θ corresponding to the <100>, <110>, and <200> planes.¹

Flow Conversion 2 - The reagent mixture of dioxane, mesitylene, and 10 M acetic acid (6.7:1.7:1, v/v, 10 mL) was used for the conversion. A SF-10 peristaltic pump was used as a backpressure regular (BPR), and positioned after the fixed bed reactor and set to 0.5 bar. The flow rate was set to 0.2 mL/min and the temperature was ramped to 70 °C. The conversion was left for 24 hours. COF was removed, washed and analyzed with PXRD. The structure was confirmed as described above.

VI. References

- 1 B. J. Smith, A. C. Overholts, N. Hwang and W. R. Dichtel, *Chem. Commun.*, 2016, **52**, 3690–3693.
- 2 S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma and R. Banerjee, *Nat Commun*, 2015, **6**, 6786.