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Growth rates and water stability of 2D boronate ester covalent organic frameworks

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Supporting Information

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I. Materials and Instrumentation

Materials. 2,7-pyrenebis(boronic acid)[1] and 4,4'-diphenylbutadiynebis(boronic acid)[2] were prepared according to literature conditions. All other 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. NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer with a standard 1H/BB switchable Z-PFG probe or a Varian INOVA 600 MHz spectrometer using a standard 1H{13C, 15N} XYZ-PFG probe with a 20 Hz sample spin rate and variable temperature controller. 1H NMR spectra for rate determination were acquired at 500 MHz or 600 MHz with a 3 s acquisition time and a 12 s relaxation delay.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer using 75 mg 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.

UV/Vis/NIR absorbance and turbidity spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer with a mercury lamp. Cuvette temperature and stirring were regulated with a Quantum Northwest Temperature Controller.

Supercritical CO_2 wash was performed with a Baltech critical point drier. Sonication was performed with a Branson 3510 ultrasonic cleaner with a power output of 100W and a frequency of 42 kHz.

II. Experimental Protocols

Homogeneous synthesis of COF-5. 1,4-phenylenebis(boronic acid) (41 mg, 0.25 mmol) and MeOH (0.099 mL, 2.5 mmol) were combined with a dioxane / mesitylene solution (4:1 *v/v*, 16 mL). The mixture was then heated for 3 minutes and then cooled to room temperature. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) (53 mg, 0.16 mmol) was added and the solution was sonicated for 1 minute. The solution was then filtered (0.45 µm PTFE) to remove any trace residual particulate. The solution was heated to 90 ˚C, with stirring, for 20 hours, under atmospheric pressure. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding an off-white powder. (54 mg, 73% yield by mass)

Homogeneous synthesis of COF-10. 4,4'-biphenylbis(boronic acid) (50 mg, 0.21 mmol) and MeOH (0.084 mL, 2.1 mmol) were combined with a dioxane / mesitylene solution (4:1 *v/v*, 14 mL). The mixture was then heated for 3 minutes to fully dissolve the monomers and then cooled to room temperature. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) (45 mg, 0.14 mmol) was added and the solution was sonicated for 1 minute. The solution was then filtered (0.45 µm PTFE) to remove any trace residual particulate. The solution was heated to 90 ˚C, with stirring, for 20 hours, under atmospheric pressure. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding an off-white powder. (66 mg, 82% yield by mass)

Homogeneous synthesis of TP-COF. 2,7-pyrenebis(boronic acid) (8.7 mg, 0.030 mmol) and MeOH (0.012 mL, 0.30 mmol) were combined with a dioxane / mesitylene solution (4:1 *v/v*, 2.0 mL). The mixture was then heated for 3 minutes to fully dissolve the monomers and then cooled to room temperature. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) (6.5 mg, 0.020 mmol) was added and the solution was sonicated for 1 minute. The solution was then filtered (0.45 μm PTFE) to remove any trace residual particulate. The solution was heated to 90 ˚C, with stirring, for 20 hours, under atmospheric pressure. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding an off-white powder. (12 mg, 92% yield by mass)

Homogeneous synthesis of HHTP-DPB COF. 4,4'-diphenylbutadiynebis(boronic acid) (0.013 mg, 0.046 mmol) and MeOH (0.012 mL, 0.46 mmol) were combined with a dioxane / mesitylene solution (4:1 *v/v*, 3.2 mL). The mixture was then heated for 3 minutes to fully dissolve the monomers and then cooled to room temperature. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) (0.010 mg, 0.031 mmol) was added and the solution was sonicated for 1 minute. The solution was then filtered (0.45 μm PTFE) to remove any trace residual particulate. The solution was heated to 90 ˚C, with stirring, for 20 hours, under atmospheric pressure. The COF solid was isolated by filtration, rinsed with toluene, and subsequently dried under vacuum, yielding an off-white powder, which was treated with supercritical CO_2 washing. (8.5 mg, 54% yield by mass) Note: low yields are due primarily to powder loss in the supercritical CO_2 washing sample collection.

III. Additional Characterization

A. Powder X-ray diffraction

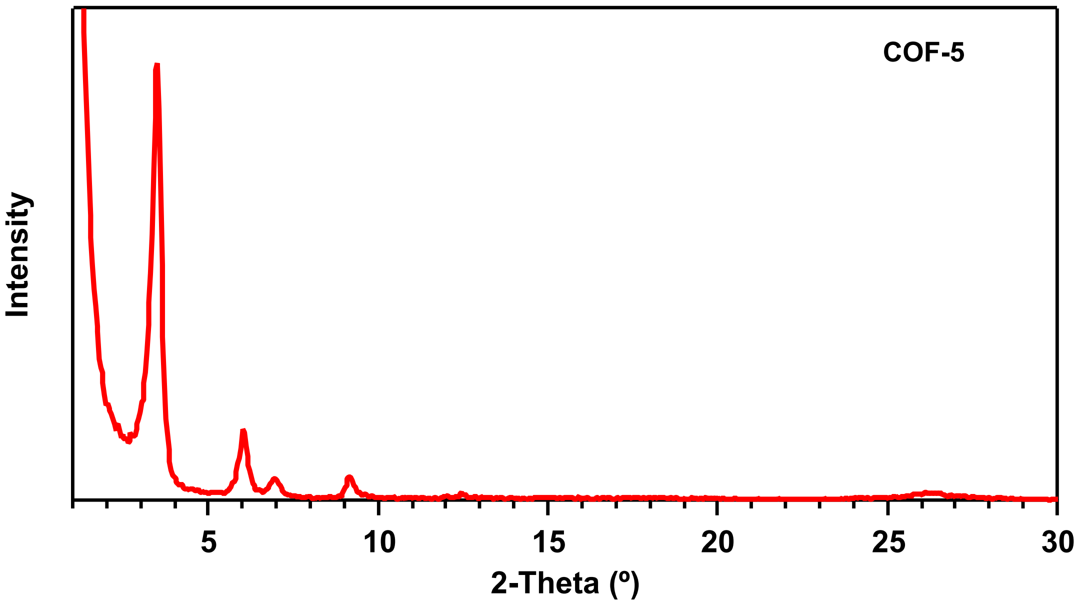


Figure S1. Powder X-ray diffraction of COF-5 prepared from homogeneous conditions. Average in-plane crystallite size is 24 nm.

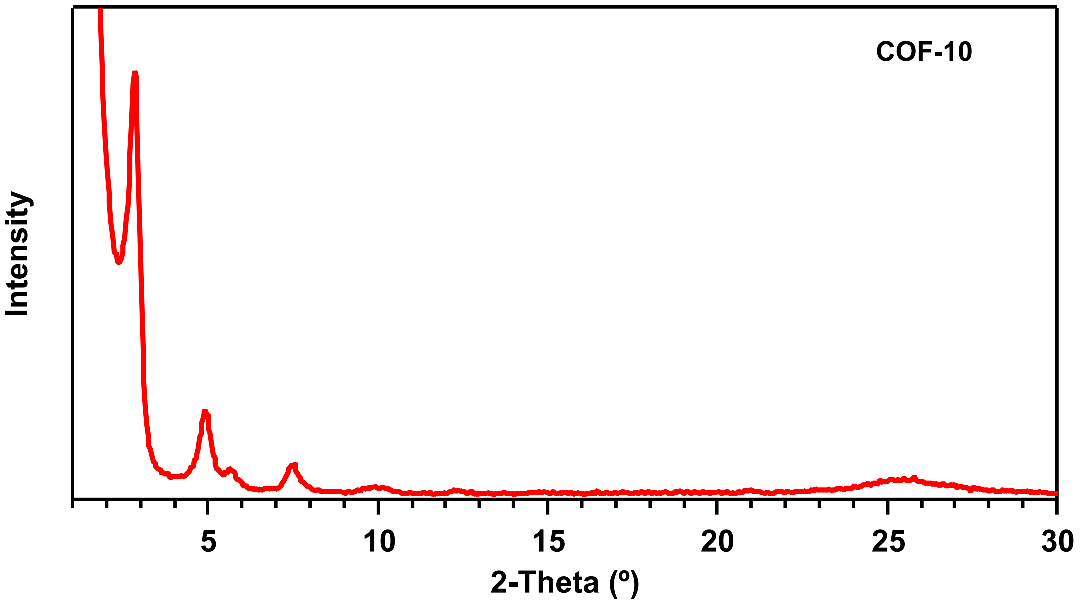


Figure S2. Powder X-ray diffraction of COF-10 prepared from homogeneous conditions. Average in-plane crystallite size is 23 nm.

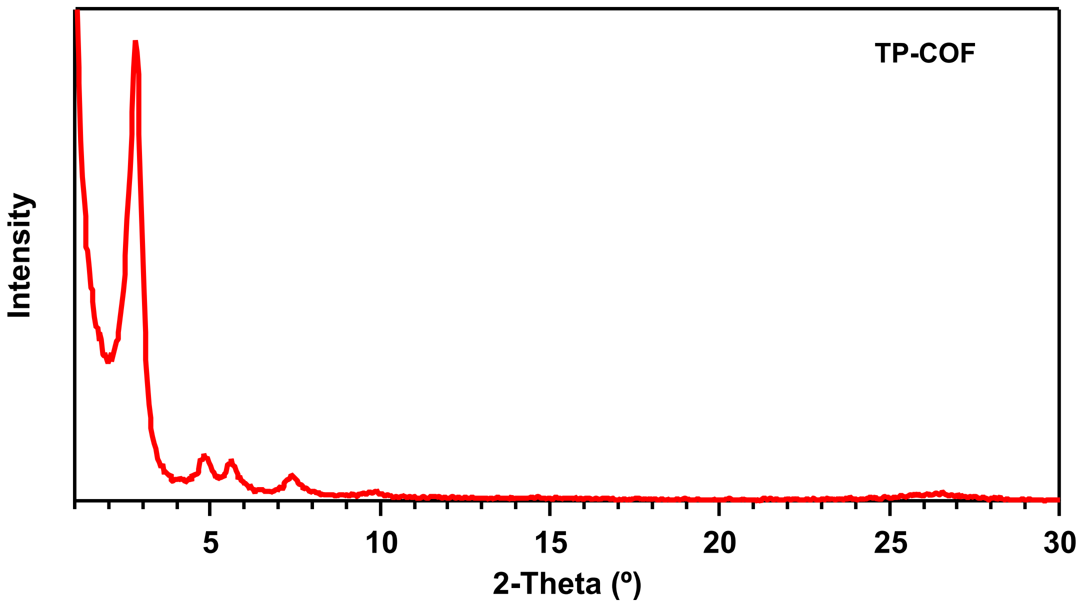


Figure S3. Powder X-ray diffraction of TP-COF prepared from homogeneous conditions. Average in-plane crystallite size is 20 nm.

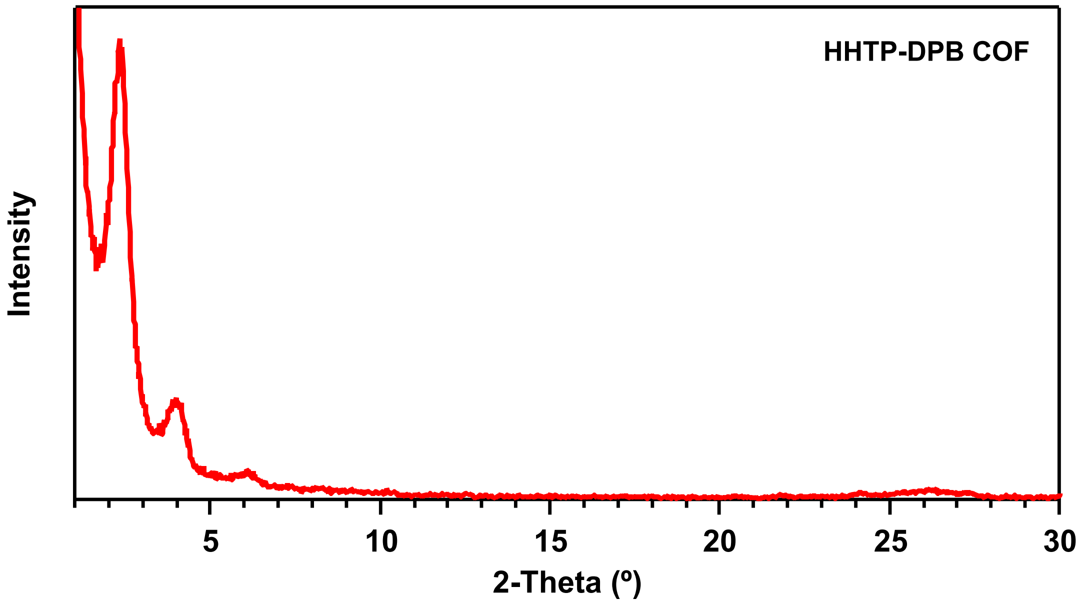
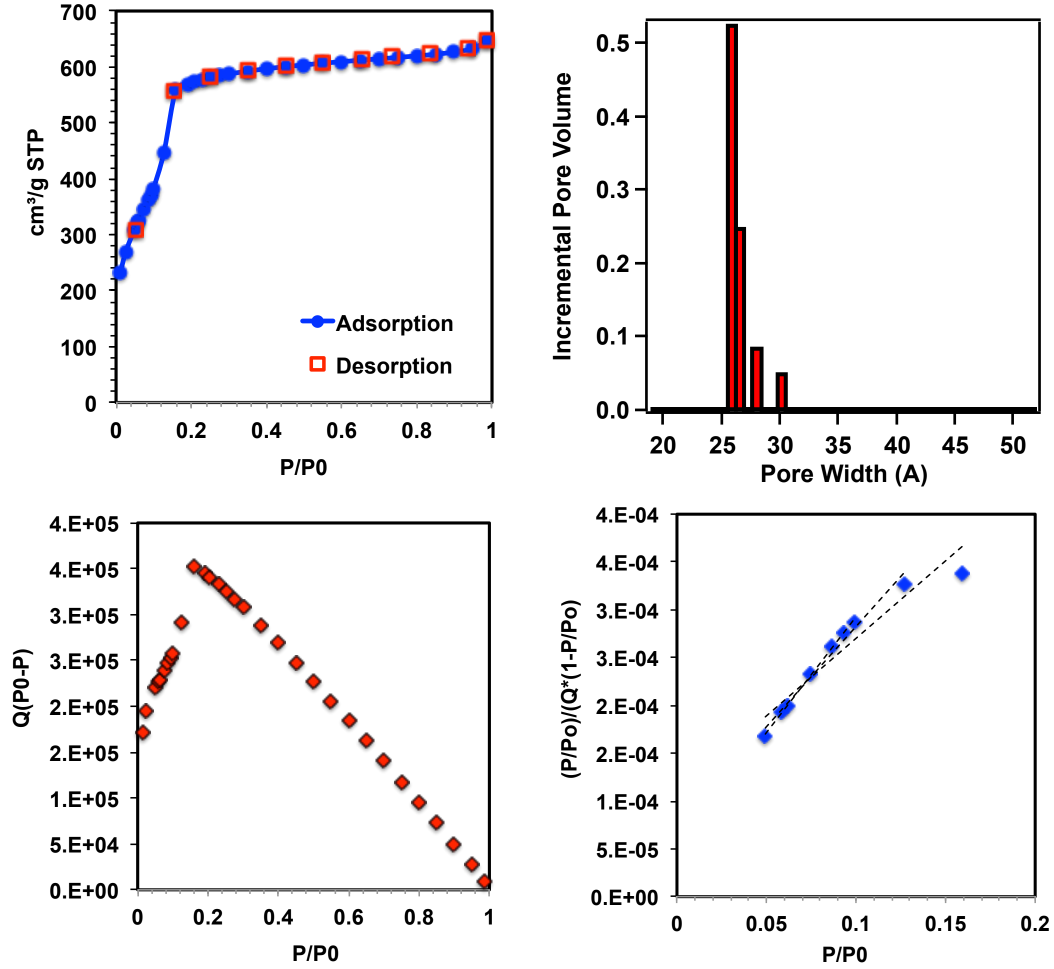


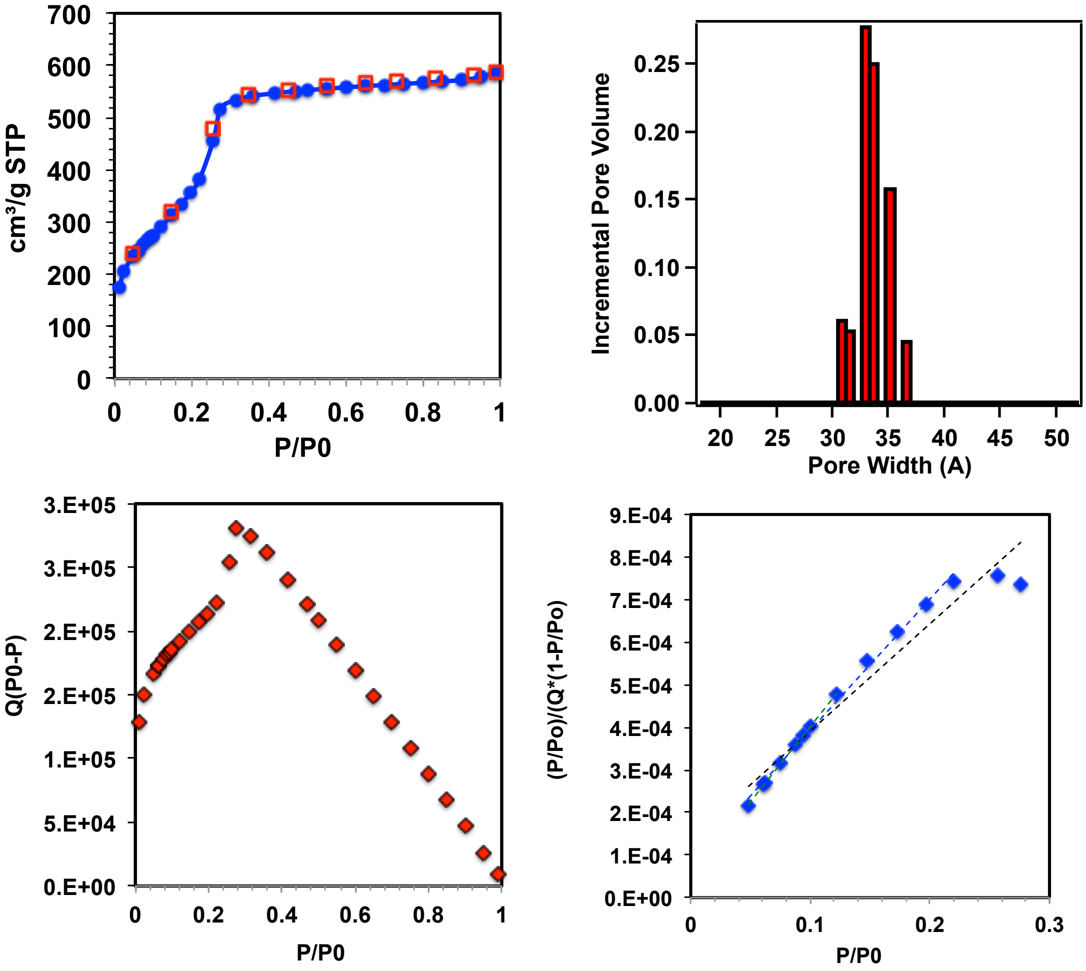
Figure S4. Powder X-ray diffraction of HHTP-DPB COF prepared from homogeneous conditions, after supercritical CO_2 washing. Average in-plane crystallite size is 16 nm.

B. N_2 Isotherm and BET surface area determination



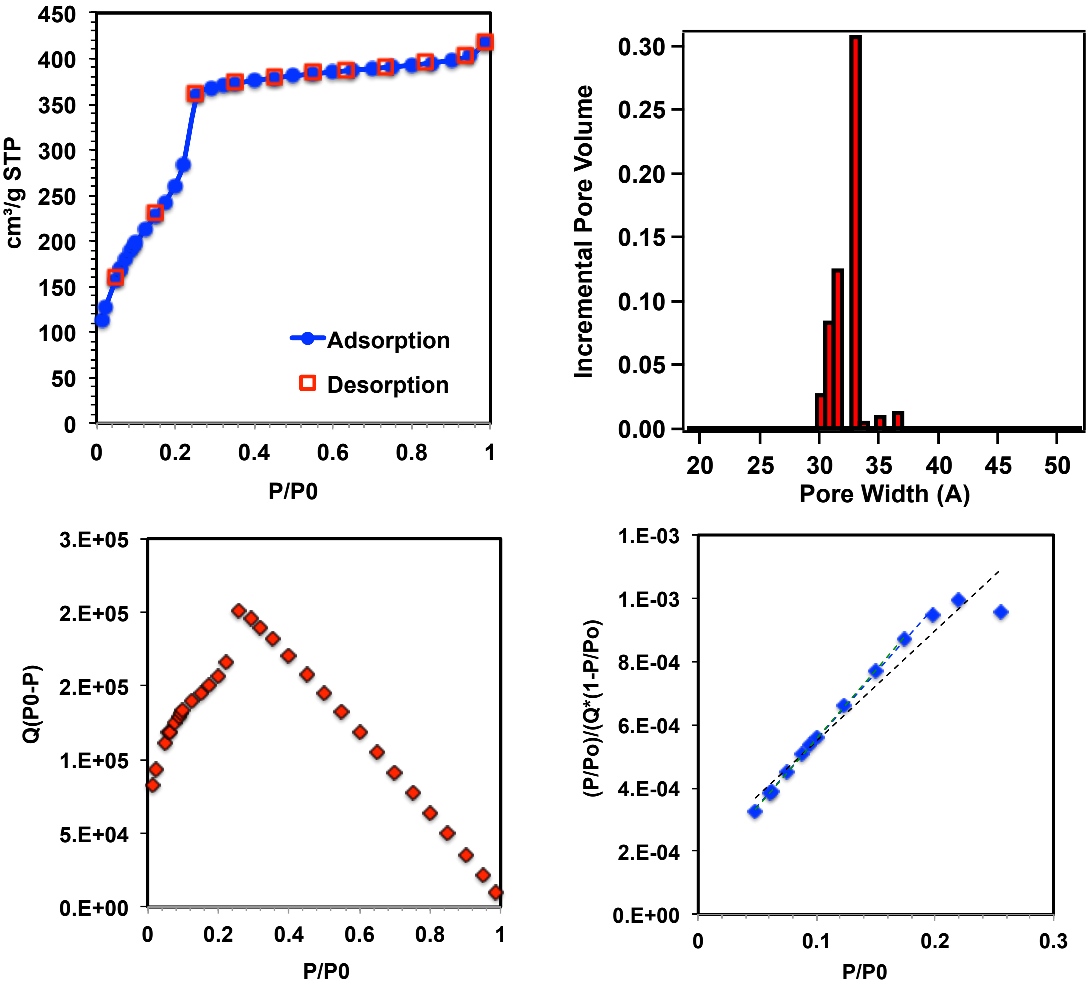
P/P_0	BET Surface Area ($m^2 g^{-1}$)	R^2
0.05 – 0.10	1760	0.998
0.05 – 0.12	2006	0.978
0.05 – 0.15	2515	0.918

Figure S5. N_2 adsorption isotherm (77 K) and surface area data analysis of COF-5 synthesized from homogeneous conditions



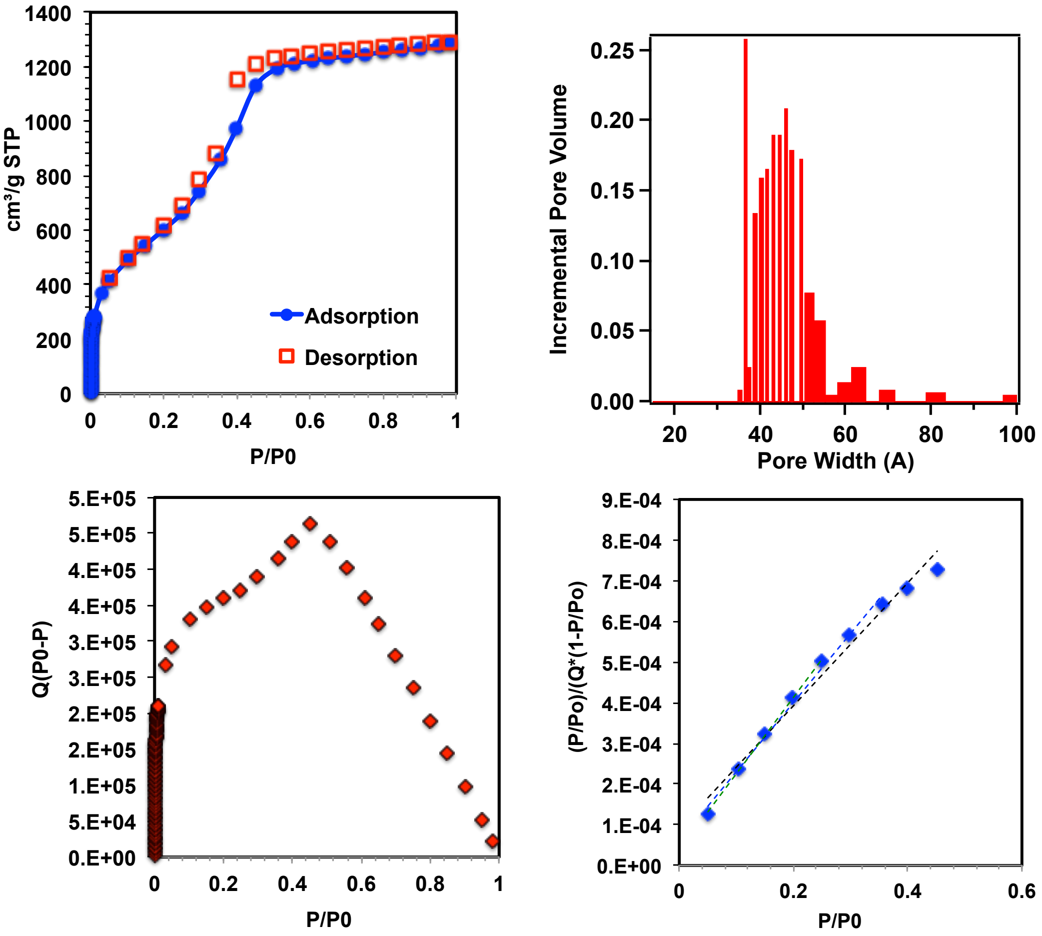
P/P_0	BET Surface Area ($m^2\,g^{-1}$)	R^2
0.05 – 0.12	1217	0.999
0.05 – 0.22	1375	0.995
0.05 – 0.27	1637	0.950

Figure S6. N_2 adsorption isotherm (77 K) and surface area data analysis of COF-10 synthesized from homogeneous conditions



P/P_0	BET Surface Area ($m^2\,g^{-1}$)	R^2
0.05 – 0.17	976	0.999
0.05 – 0.20	1001	0.998
0.05 – 0.25	1179	0.951

Figure S7. N_2 adsorption isotherm (77 K) and surface area data analysis of TP-COF synthesized from homogeneous conditions



P/P_0	BET Surface Area ($m^2\ g^{-1}$)	R^2
0.05 – 0.25	2270	0.999
0.05 – 0.35	2471	0.993
0.05 – 0.45	2717	0.981

Figure S8. N_2 adsorption isotherm (77 K) and surface area data analysis of HHTP-DPB COF synthesized from homogeneous conditions, after supercritical CO_2 washing

C. UV-vis spectroscopy

Turbidity characterization of COF growth. Homogeneous precursor solutions of identical concentration were prepared using the techniques described above (10 mM HHTP, 1.5 equiv. xBBA, 15 equiv. MeOH, in 4:1 dioxane:mesitylene). A septum-sealed, screw-capped cuvette of COF homogeneous precursor solution (1.5 mL) was heated to the appropriate temperature and turbidity was monitored at 1310 nm (1 cm path length). The solution was rapidly and constantly stirred throughout the measurement to prevent precipitate settling and maintain uniform distribution. Rates were calculated from the maximum slope of the plotted turbidity versus time. Calibration of turbidity to percent yield was determined from suspensions of known concentration prepared with COF samples synthesized independently.

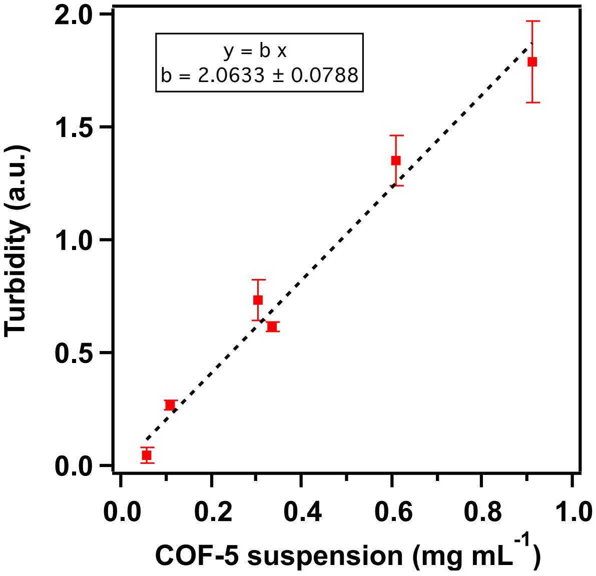


Figure S9. Calibration of suspension turbidity at 1310 nm as a function of COF-5 suspension concentration (mg COF /mL solvent). Markers are the average of at least three separate solutions, with the error bars indicating the standard deviation.

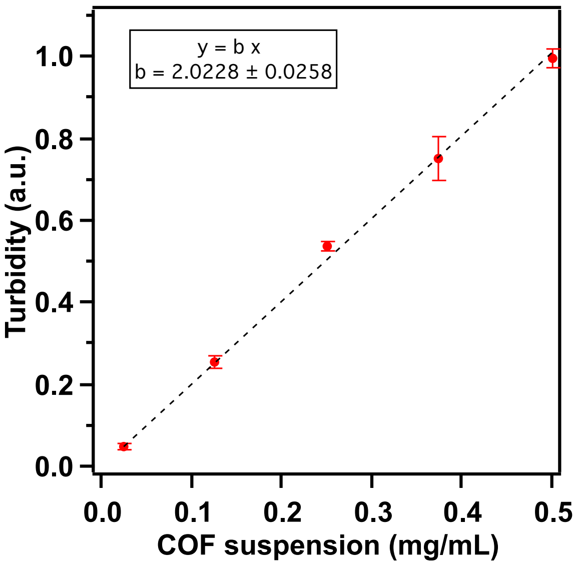


Figure S10. Calibration of suspension turbidity at 1310 nm as a function of COF-10 suspension concentration (mg COF /mL solvent). Markers are the average of at least two separate solutions, with the error bars indicating the standard deviation.

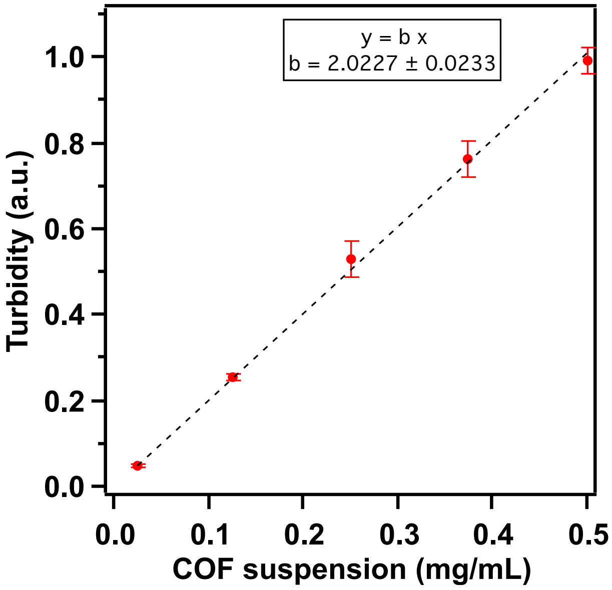


Figure S11. Calibration of suspension turbidity at 1310 nm as a function of TP-COF suspension concentration (mg COF /mL solvent). Markers are the average of at least two separate solutions, with the error bars indicating the standard deviation.

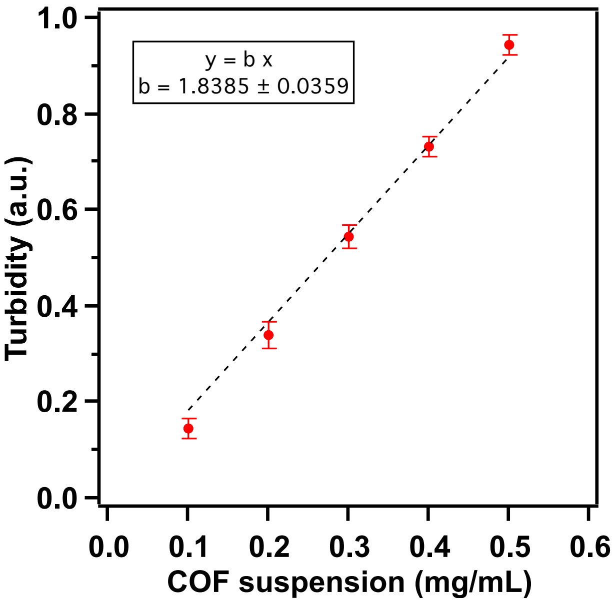


Figure S12. Calibration of suspension turbidity at 1310 nm as a function of HHTP-DPB COF suspension concentration (mg COF /mL solvent). Markers are the average of at least two separate solutions, with the error bars indicating the standard deviation.

D. Boronate ester COF growth activation energy data

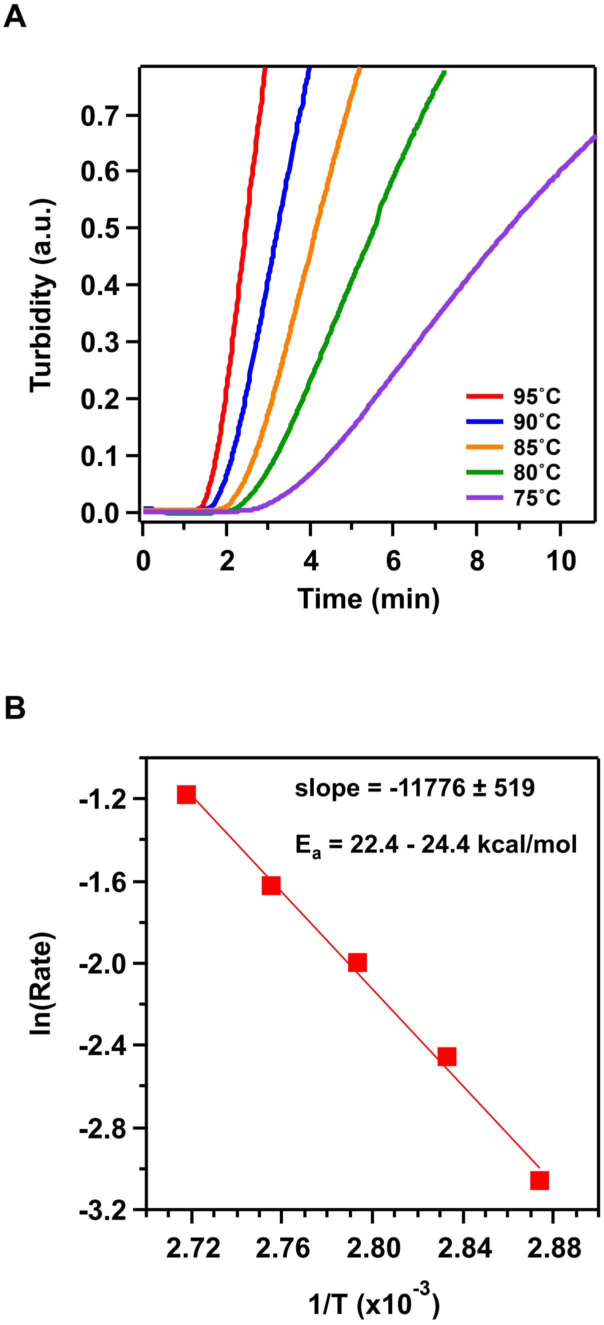


Figure S13. (A) Turbidity due to COF-5 synthesis as a function of time at various temperatures (10 mM HHTP, 1.5 equiv. **1**, 15 equiv. MeOH, 4:1 dioxane mesitylene). (B) Arrhenius plot of the initial rate of COF-5 formation.

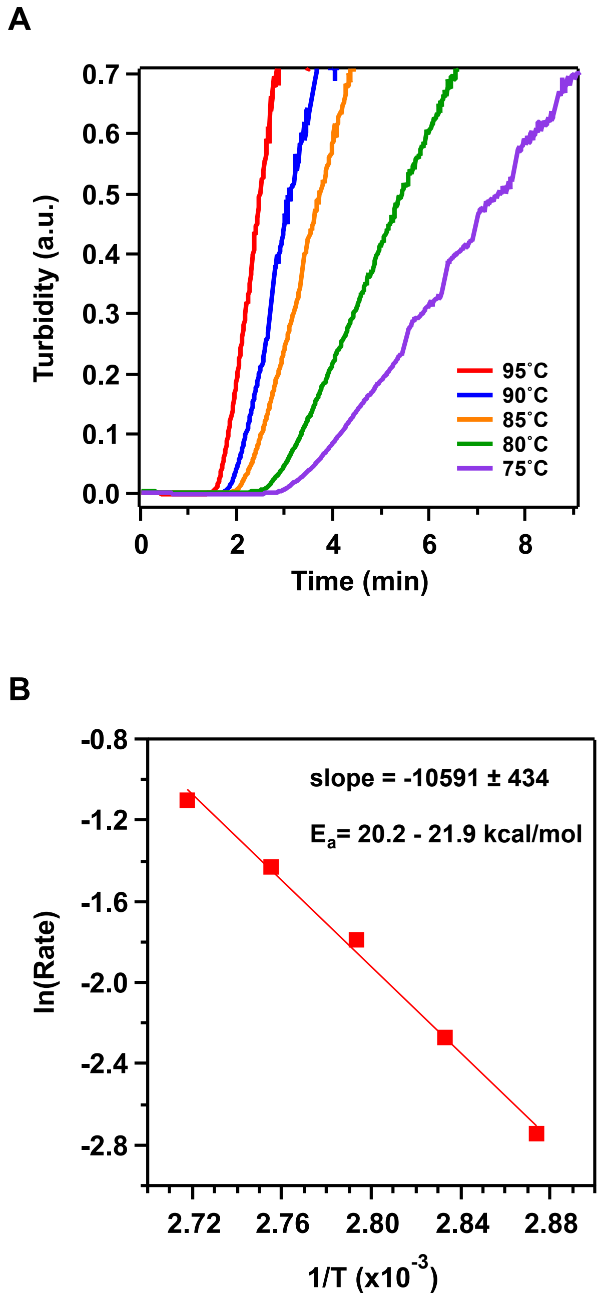


Figure S14. (A) Turbidity due to COF-10 synthesis as a function of time at various temperatures (10 mM HHTP, 1.5 equiv. **2**, 15 equiv. MeOH, 4:1 dioxane mesitylene). (B) Arrhenius plot of the initial rate of COF-10 formation.

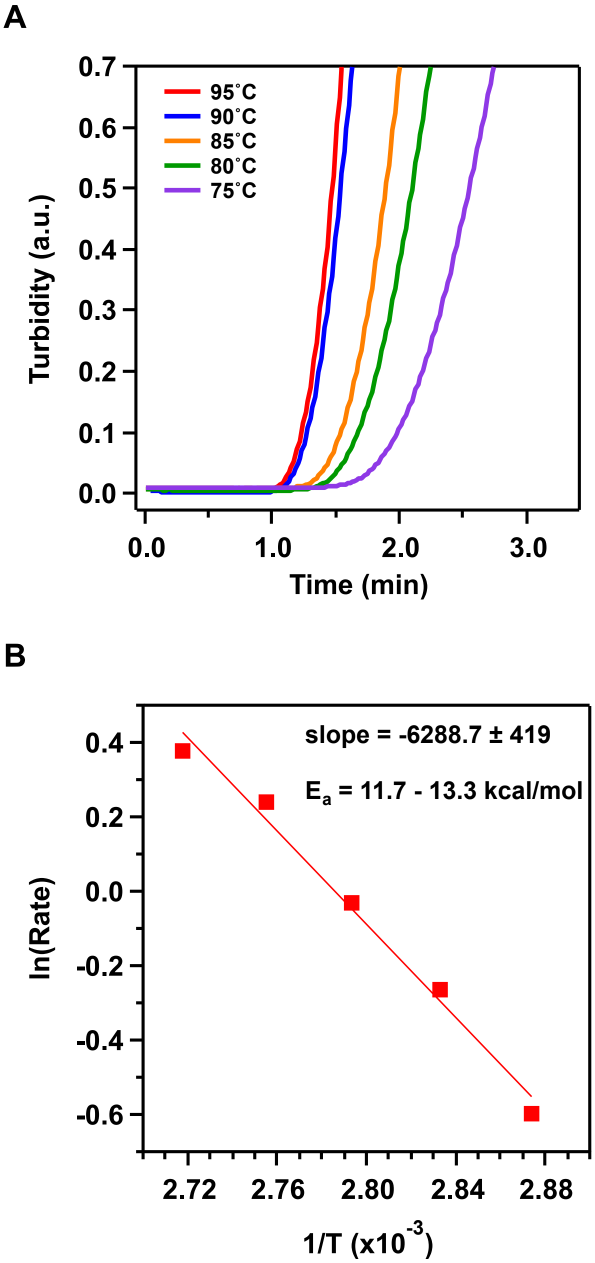


Figure S15. (A) Turbidity due to TP-COF synthesis as a function of time at various temperatures (10 mM HHTP, 1.5 equiv. **3**, 15 equiv. MeOH, 4:1 dioxane mesitylene). (B) Arrhenius plot of the initial rate of TP-COF formation.

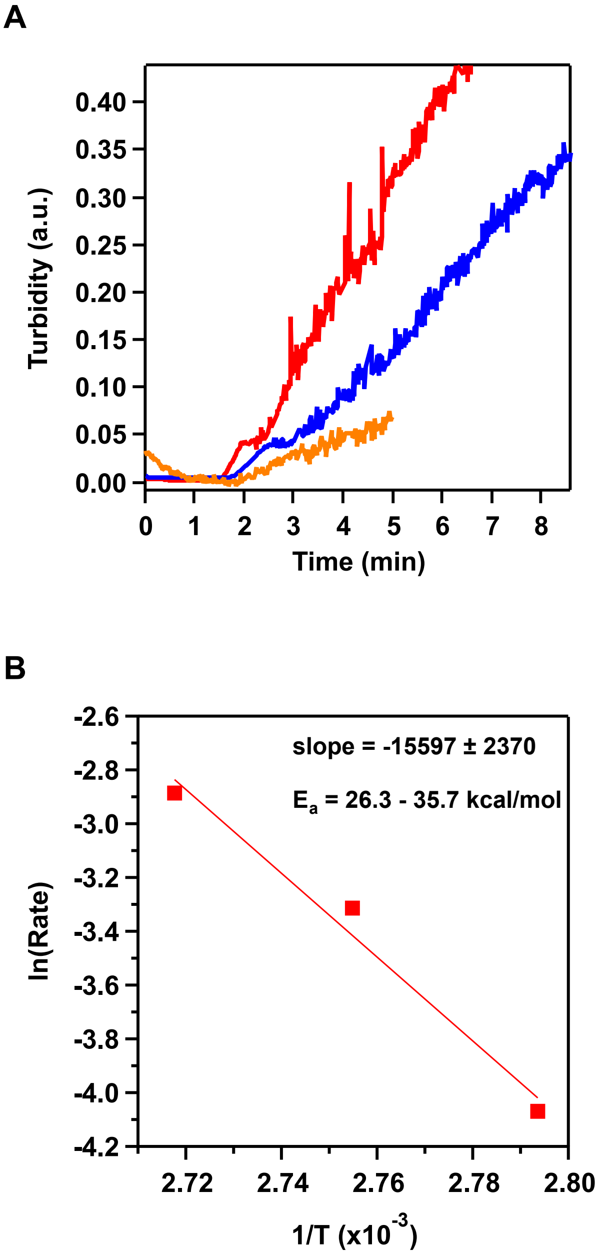


Figure S16. (A) Turbidity due to HHTP-DPB COF synthesis as a function of time at various temperatures (10 mM HHTP, 1.5 equiv. **4**, 15 equiv. MeOH, 4:1 dioxane mesitylene). The measurement noise is due to imperfect stirring and distribution of the COF precipitate. (B) Arrhenius plot of the initial rate of HHTP-DPB COF formation.

E. Boronate ester TCAT activation energy data

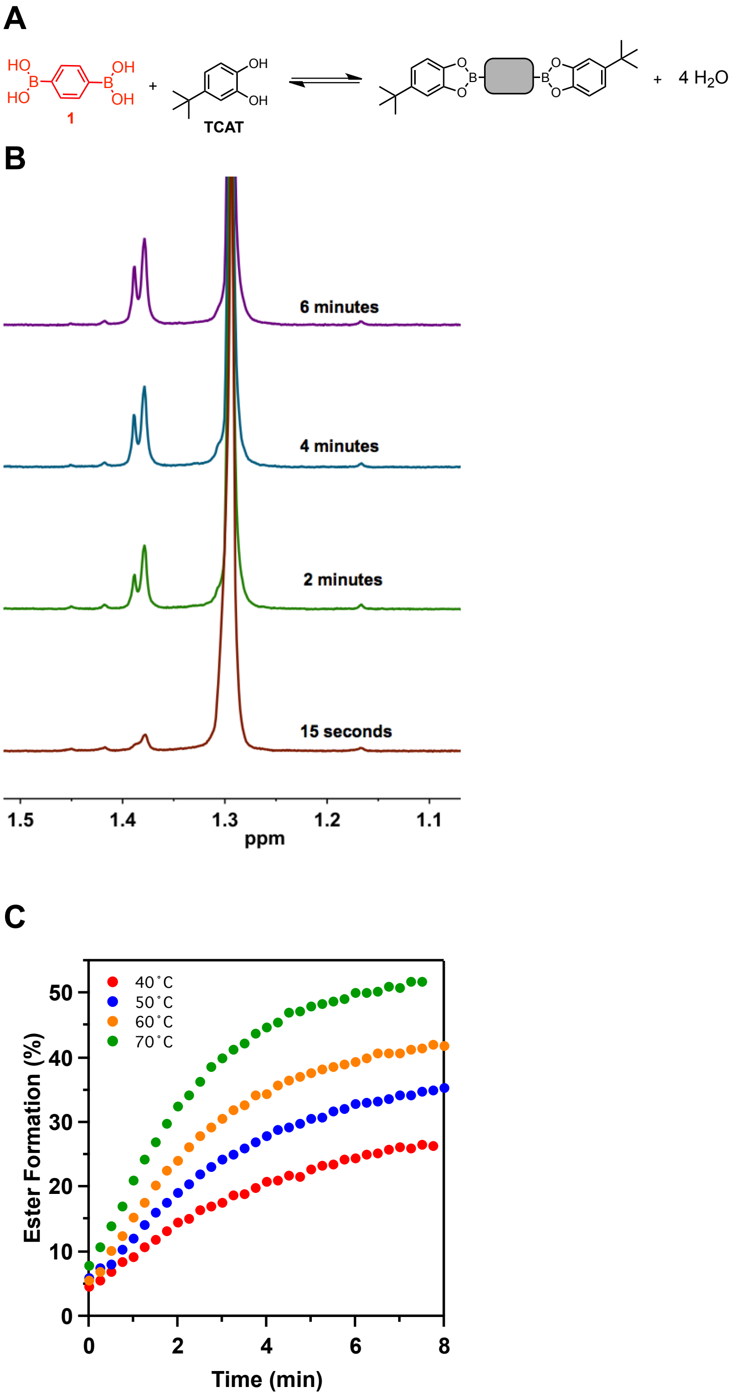


Figure S17. (A) Equilibrium esterification of TCAT and **1**. (B) Partial ^{1}H NMR spectra monitoring the t-butyl signature of the formation of boronate ester (12 mM **1**, 6 equiv. TCAT, 19 equiv. MeOH, 4:1 1,4-dioxane-d8:mesitylene-d12). (C) Boronate ester formation over time at various temperatures.

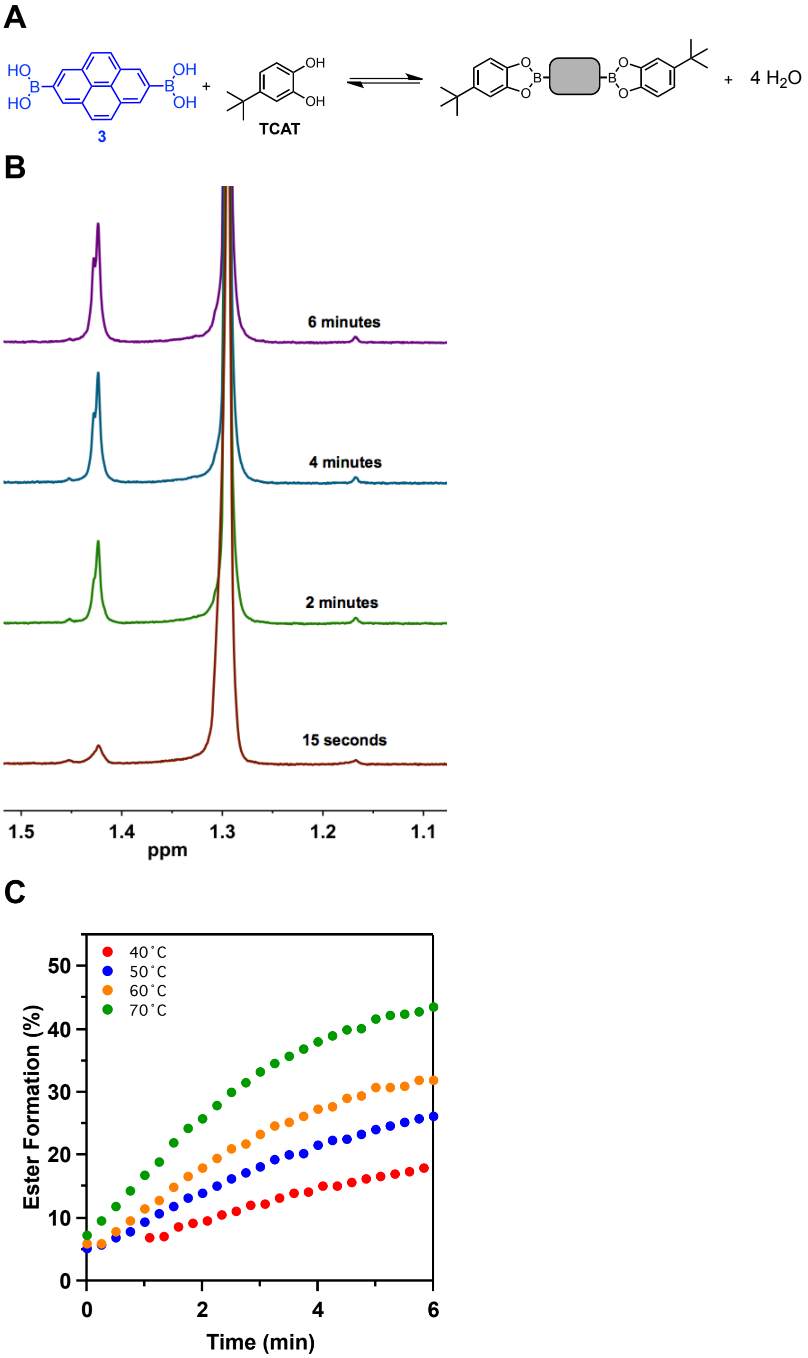


Figure S18. (A) Equilibrium esterification of TCAT and **3**. (B) Partial ^{1}H NMR spectra monitoring the t-butyl signature of the formation of boronate ester (12 mM **3**, 6 equiv. TCAT, 19 equiv. MeOH, 4:1 1,4-dioxane-d8:mesitylene-d12). (C) Boronate ester formation over time at various temperatures.

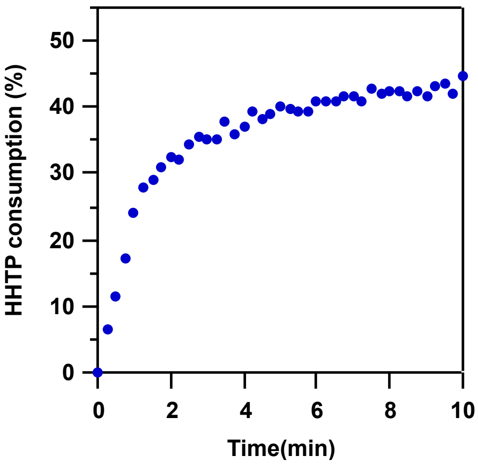


Figure S19. Initial consumption of HHTP in the formation of TP-COF, monitored by NMR of the disappearance of the HHTP peak at 7.78 ppm, referenced to mestiylene and normalized at *t*=0. (8 mM HHTP, 1.5 equiv. **3**, 15 equiv. MeOH, 4:1 1,4-dioxane-d8:mesitylene-d12, 60˚C).

F. COF aqueous digestion

Turbidity characterization of COF digestion. A septum-sealed, screw-capped cuvette of COF suspension in 4:1 dioxane:mesitylene (1.5 mL) was monitored at 1310 nm (1 cm path length). The solution was rapidly and constantly stirred throughout the measurement to prevent precipitate settling and maintain uniform distribution. H_2O (19 uL, 0.7 M final) was introduced via syringe. Rates were calculated from the maximum slope of the plotted turbidity versus time.

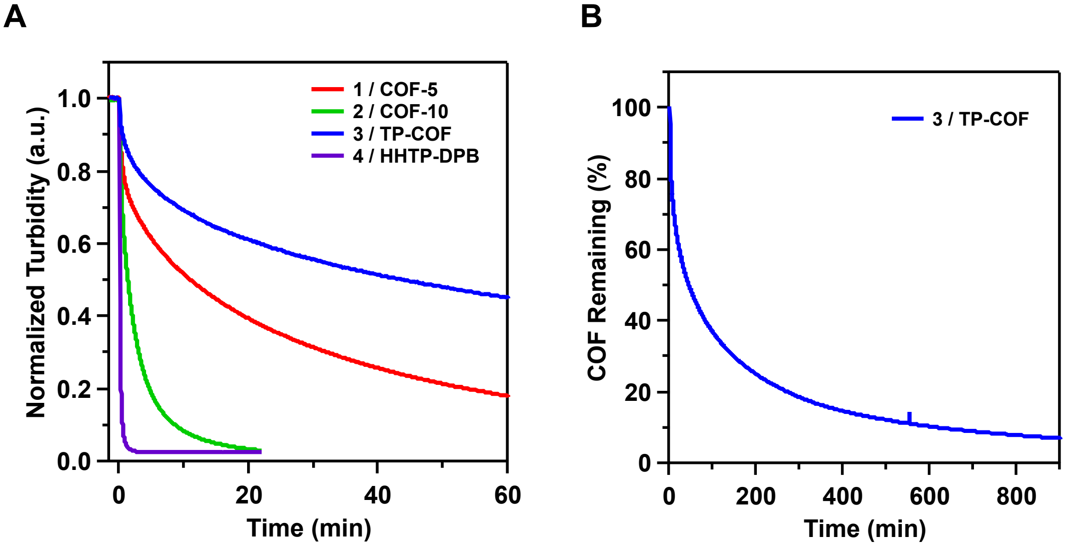


Figure S20. Hydrolytic digestion of COF suspensions at 25˚C, monitored by turbidity, at long time scales. Water added is at t = 0 min (final [H2O] = 0.7M in 4:1 dioxane:mesitylene, ~700 equiv. relative to HHTP present)

References

1 S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem. Int. Ed.*, 2008, 47, 8826–8830.

2 E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, 133, 19416–19421.