

# Controlling crystalline structure of imine-linked 3D Covalent Organic Frameworks

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## Supplementary Information

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## I. Materials and instrumentation

**Materials.** All reagents and solvents were purchased from commercial sources and used without further purification.

**Instrumentation.** Nitrogen sorption BET surface area and NLDFT porosity measurements were conducted on a Micromeritics Tristar II 3020 (instrument software version 1.03) with N<sub>2</sub> isotherms collected at 77K. Tabulated BET surface areas were calculated over 0.05 – 0.15 P/P<sub>0</sub>. Powder X-ray diffraction (PXRD) patterns were obtained with a PANalytical X'Pert PRO diffractometer on a low background holder, using a Cu K $\alpha$  source at 45 kV and 40 mA. PXRD and N<sub>2</sub> sorption analysis for all samples were performed immediately following synthesis. Expected PXRD patterns were generated using Mercury software (version 3.9) and reported CIF structures for COF-300<sup>1</sup> and COF-320<sup>2</sup>. Infrared spectroscopy measurements were obtained on a Thermo Nicolet 4700 FT-IR with a solid-state ATR (PIKE Technologies GladiATR). Thermal gravimetric analysis measurements were obtained on a TA Instruments SDT Q600 at a heating rate of 10 °C/min. Scanning electron microscopy was performed on a FEI Quanta-400 ESEM at high-vacuum conditions with an accelerating voltage of 2–3 kV, spot size of 3–4, and a working distance of 3–4 mm, using uncoated samples adsorbed on a silicon wafer.

## II. Experimental protocols

### Procedure for COF-300 synthesis from monophasic conditions

Synthesis developed based upon initial report of COF-300.<sup>3</sup> Tetrakis(4-aminophenyl)methane (TAPM) (20. mg, 0.053 mmol) was fully dissolved in 1,4-dioxane (900  $\mu$ L) in a 1.8 mL GC vial with brief heating. After cooling the solution to room temperature, acetic acid (95  $\mu$ L, 1.7 mmol) and water (455  $\mu$ L, 25.2 mmol) were combined and added to the vial. Terephthaldehyde (PDA) (12 mg, 0.089 mmol, 1.7 equiv.) was separately dissolved in dioxane (0.74 M) and injected into the tetrakis(4-aminophenyl)methane solution. The mixture was kept at 90°C for 48 hours. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (22 mg, 85% yield based on terephthaldehyde)

### Procedure for TAPM-PDA amorphous solid synthesis

Tetrakis(4-aminophenyl)methane (200. mg, 0.526 mmol) was fully dissolved in 1,4-dioxane (9.0 mL) in a 20 mL scintillation vial with brief heating. After cooling the solution to room temperature, acetic acid (0.950 mL, 16.6 mmol) and water (4.55 mL, 252 mmol) were combined and then added to the vial. Terephthaldehyde (120 mg, 0.89 mmol, 1.7 equiv.) was separately dissolved in dioxane (0.74 M) and injected into the tetrakis(4-aminophenyl)methane solution. The mixture was kept at room temperature for 30 minutes. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 15 mL) for 24 hours at room

temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (190 mg, 74% yield based on terephthaldehyde)

#### **Procedure for COF-300 synthesis from amorphous regrowth**

TAPM-PDA amorphous solid (32 mg) was combined in a 1.8 mL GC vial with 1,4-dioxane (1,020  $\mu$ L) acetic acid (95  $\mu$ L, 1.7 mmol), and water (455  $\mu$ L, 25.2 mmol). The mixture was kept at 90°C for 48 hours. The resulting solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (29 mg, 91% yield based on amorphous solid)

#### **Procedure for COF-300 synthesis from biphasic conditions**

Tetrakis(4-aminophenyl)methane (20 mg, 0.053 mmol) was fully dissolved in 1,4-dioxane (600  $\mu$ L) in a 1.8 mL GC vial with brief heating. After cooling the solution to room temperature, toluene (300  $\mu$ L) was added to the vial. Acetic acid (95  $\mu$ L, 1.7 mmol) and water (455  $\mu$ L, 25.2 mmol) were separately combined and added to the vial, resulting in a biphasic mixture. Terephthaldehyde (12 mg, 0.089 mmol, 1.7 equiv.) was separately dissolved in dioxane (0.74 M) and carefully injected into the top layer of the reaction mixture. The mixture was kept at 90°C for 48 hours. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (24 mg, 93% yield based on terephthaldehyde)

#### **Procedure for COF-300 synthesis from agitated biphasic conditions**

COF-300 was prepared identically to synthesis from biphasic conditions, with the exception that the biphasic mixture was shaken vigorously prior to terephthaldehyde addition. (23 mg, 89% yield based on terephthaldehyde)

#### **Procedure for COF-320 synthesis from monophasic conditions**

Synthesis developed based upon initial report of COF-320.<sup>2</sup> Tetrakis(4-aminophenyl)methane (16 mg, 0.042 mmol) was fully dissolved in 1,4-dioxane (900  $\mu$ L) in a 1.8 mL GC vial with brief heating. After cooling the solution to room temperature, acetic acid (95  $\mu$ L, 1.7 mmol) and water (455  $\mu$ L, 25.2 mmol) were combined and added to the vial. 4,4 biphenyldicarboxaldehyde (BPCA) (15 mg, 0.071 mmol, 1.8 equiv) was separately dissolved in dioxane (0.47 M) and injected into the tetrakis(4-aminophenyl)methane solution. The mixture was kept at 90°C for 48 hours. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (19 mg, 73% yield based on 4,4 biphenyldicarboxaldehyde)

#### **Procedure for TAPM-BPCA amorphous solid synthesis**

Tetrakis(4-aminophenyl)methane (160. mg, 0.421 mmol) was fully dissolved in 1,4 dioxane (9.0 mL) in a 20 mL scintillation vial with brief heating. After cooling the solution

to room temperature, acetic acid (0.950 mL, 16.6 mmol) and water (4.55 mL, 252 mmol) were combined and then added to the vial. 4,4 biphenyldicarboxaldehyde (150. mg, 0.714 mmol) was separately dissolved in dioxane (0.47 M) and injected into the tertakis(4-aminophenyl)methane solution. The mixture was kept at room temperature for 30 minutes. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 15 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (220 mg, 85% yield based on 4,4 biphenyldicarboxaldehyde)

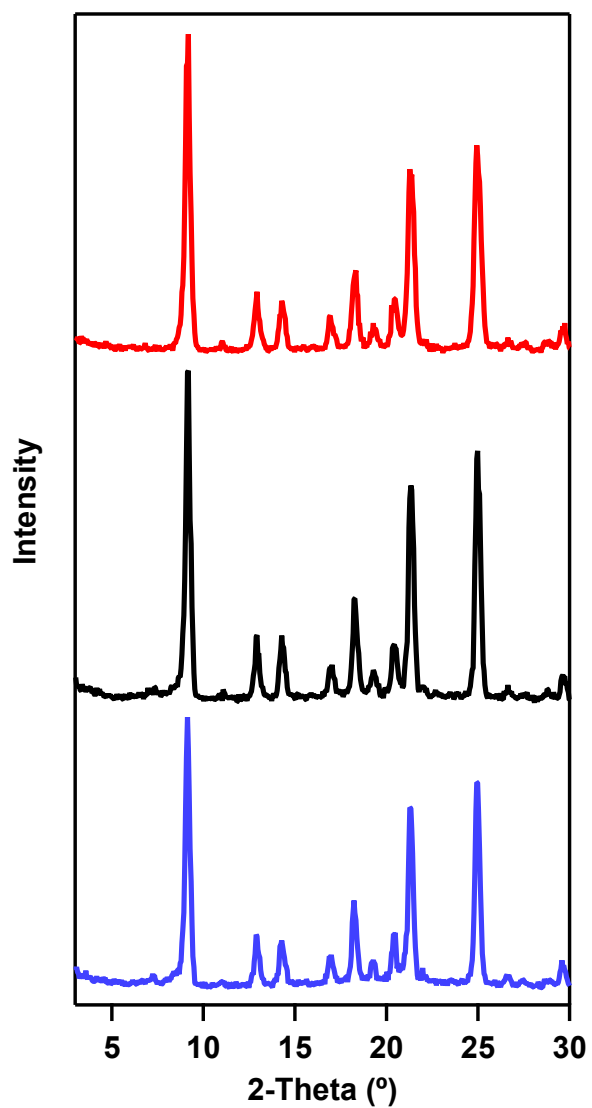
#### **Procedure for COF-320 synthesis from amorphous regrowth**

TAPM-BPCA amorphous solid (32 mg) was combined in a 1.8 mL GC vial with 1,4 dioxane (1,020  $\mu$ L) acetic acid (95  $\mu$ L, 1.7 mmol), and water (455  $\mu$ L, 25.2 mmol). The mixture was kept at 120°C for 14 days. The resulting solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (28 mg, 88% yield based on amorphous solid)

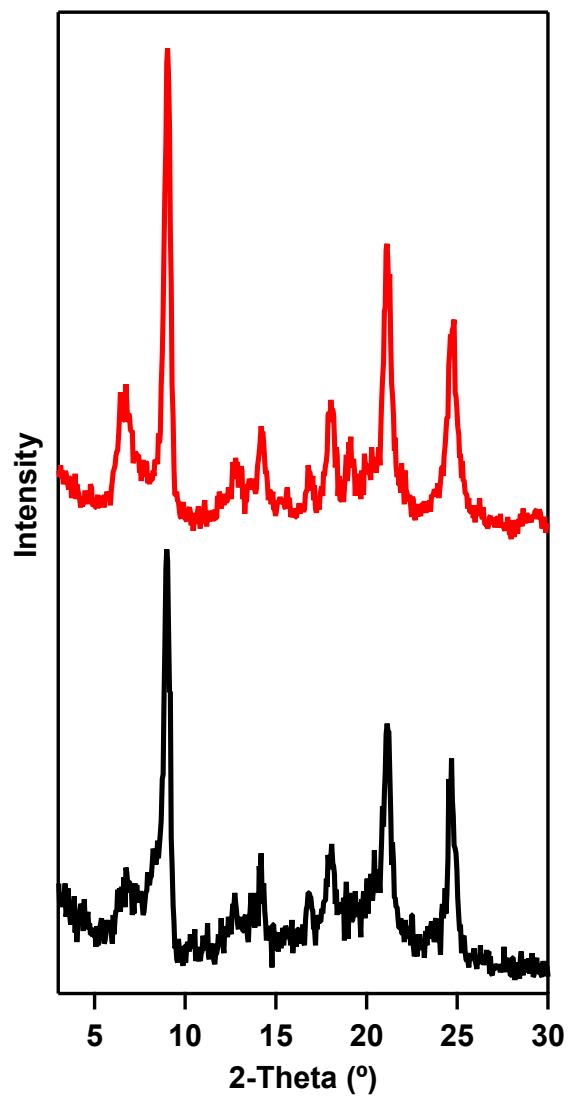
#### **Procedure for COF-320 synthesis from biphasic conditions**

Tetrakis(4-aminophenyl)methane (16 mg, 0.042 mmol) was fully dissolved in 1,4 dioxane (600  $\mu$ L) in a 1.8 mL GC vial with brief heating. After cooling the solution to room temperature, toluene (300  $\mu$ L) was added to the vial. Acetic acid (95  $\mu$ L, 1.7 mmol) and water (455  $\mu$ L, 25.2 mmol) were separately combined and added to the vial, resulting in a biphasic mixture 4,4 biphenyldicarboxaldehyde (BPCA) (15 mg, 0.071 mmol, 1.8 equiv) was separately dissolved in dioxane (0.47 M) and injected into the tertakis(4-aminophenyl)methane solution. The mixture was kept at 90°C for 48 hours. The resulting yellow solid was isolated by vacuum filtration and rinsed with dioxane, followed by additional soaking in dioxane (ca. 10 mL) for 24 hours at room temperature. The solid was then isolated by vacuum filtration and held under vacuum at 50 torr and 120°C for 24 hours. (20 mg, 77% yield based on 4,4 biphenyldicarboxaldehyde)

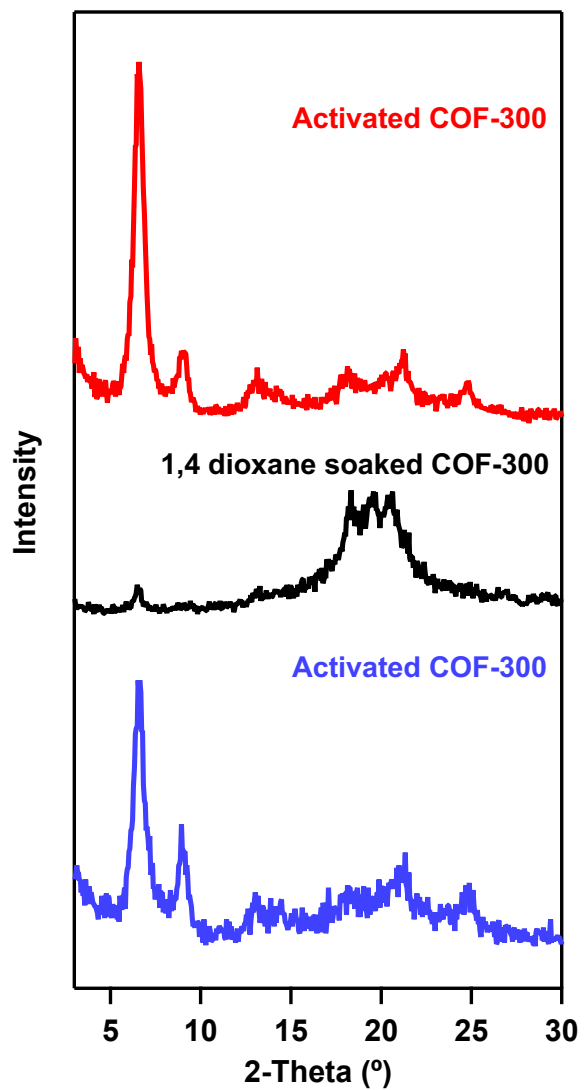
### III. Evacuation studies



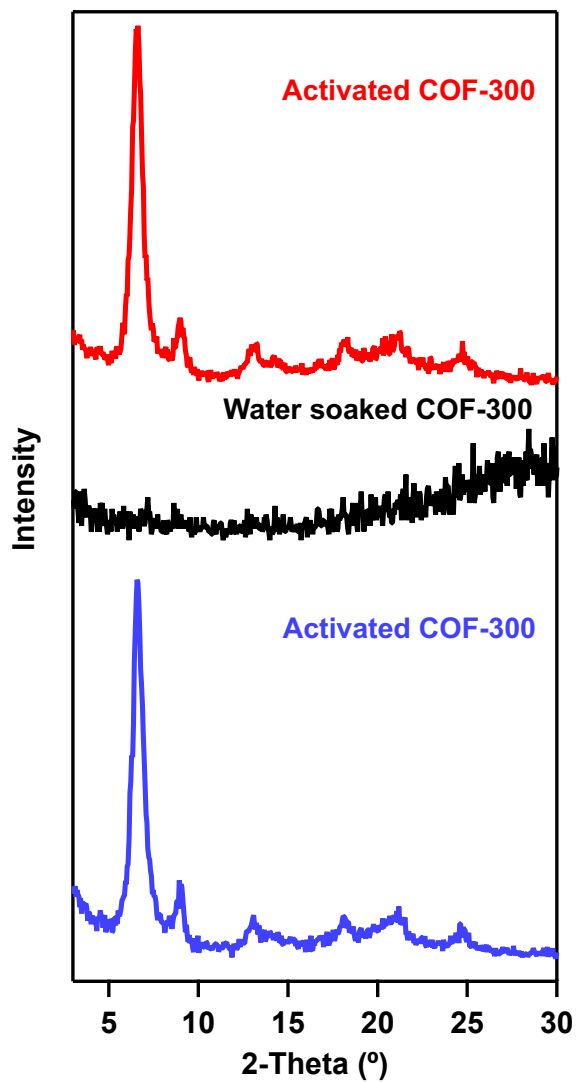
**Figure S1.** Powder X-ray diffraction of collapsed COF-300 sequentially activated at: 90°C and 50 torr for 1 day (red), 160°C and 50 torr for 1 day (black), 23°C and 0.150 torr for 1 day (blue).



**Figure S2.** Powder X-ray diffraction of collapsed COF-300 activated under standard prep conditions (red), and subsequently activated at 100°C and 0.250 torr (blue).

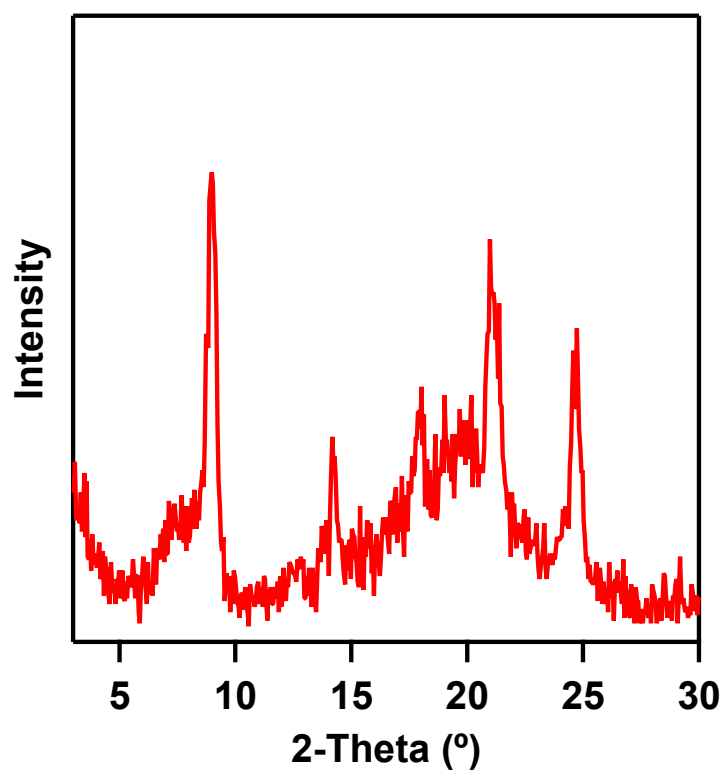


**Figure S3.** Powder X-ray diffraction of porous COF-300 (red), COF-300 treated with 1,4-dioxane (black), COF-300 evacuated at 100°C and 50 torr for 5 minutes (blue).



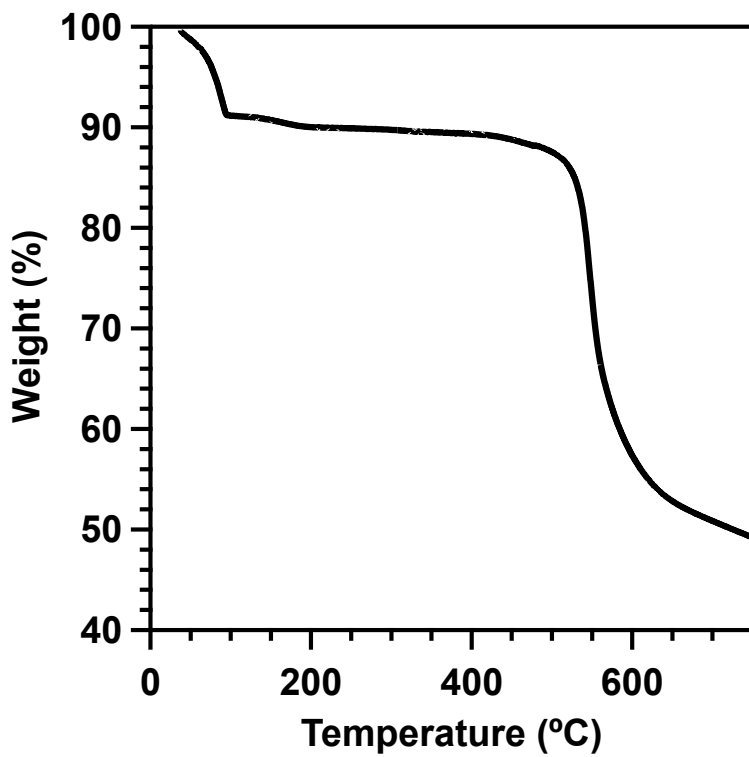
**Figure S4.** Powder X-ray diffraction of activated, porous COF-300 (red), COF-300 treated with water for 5 minutes (black), COF-300 evacuated at 100°C and 50 torr for 5 minutes (blue).





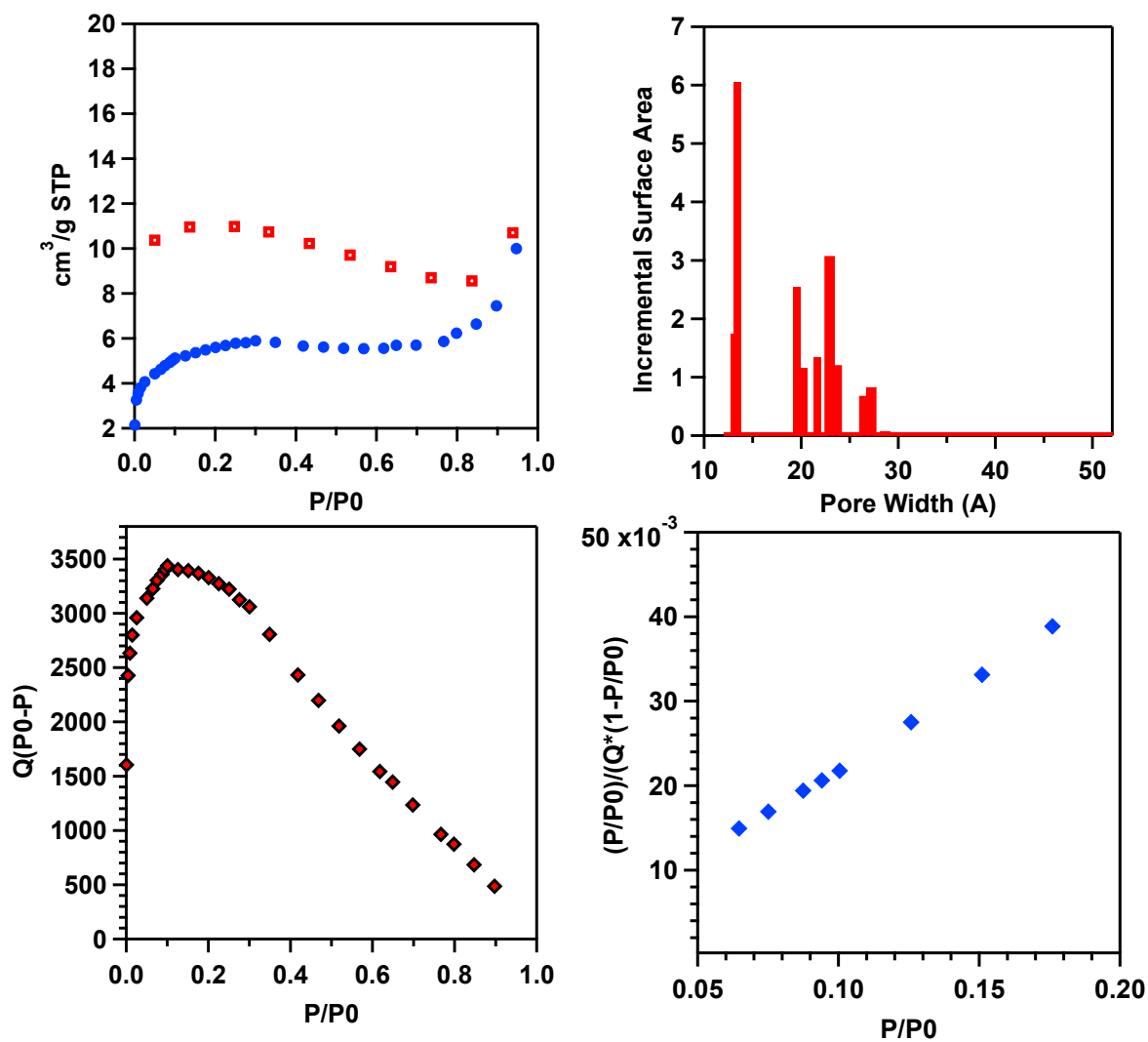
**Figure S5.** Powder X-ray diffraction of COF-300 synthesized from monophasic homogeneous initial conditions, in absence of additional water.

#### IV. Thermogravimetric analysis



**Figure S6.** TGA of collapsed COF-300 heated from room temperature to 650°C at 10°C/min.

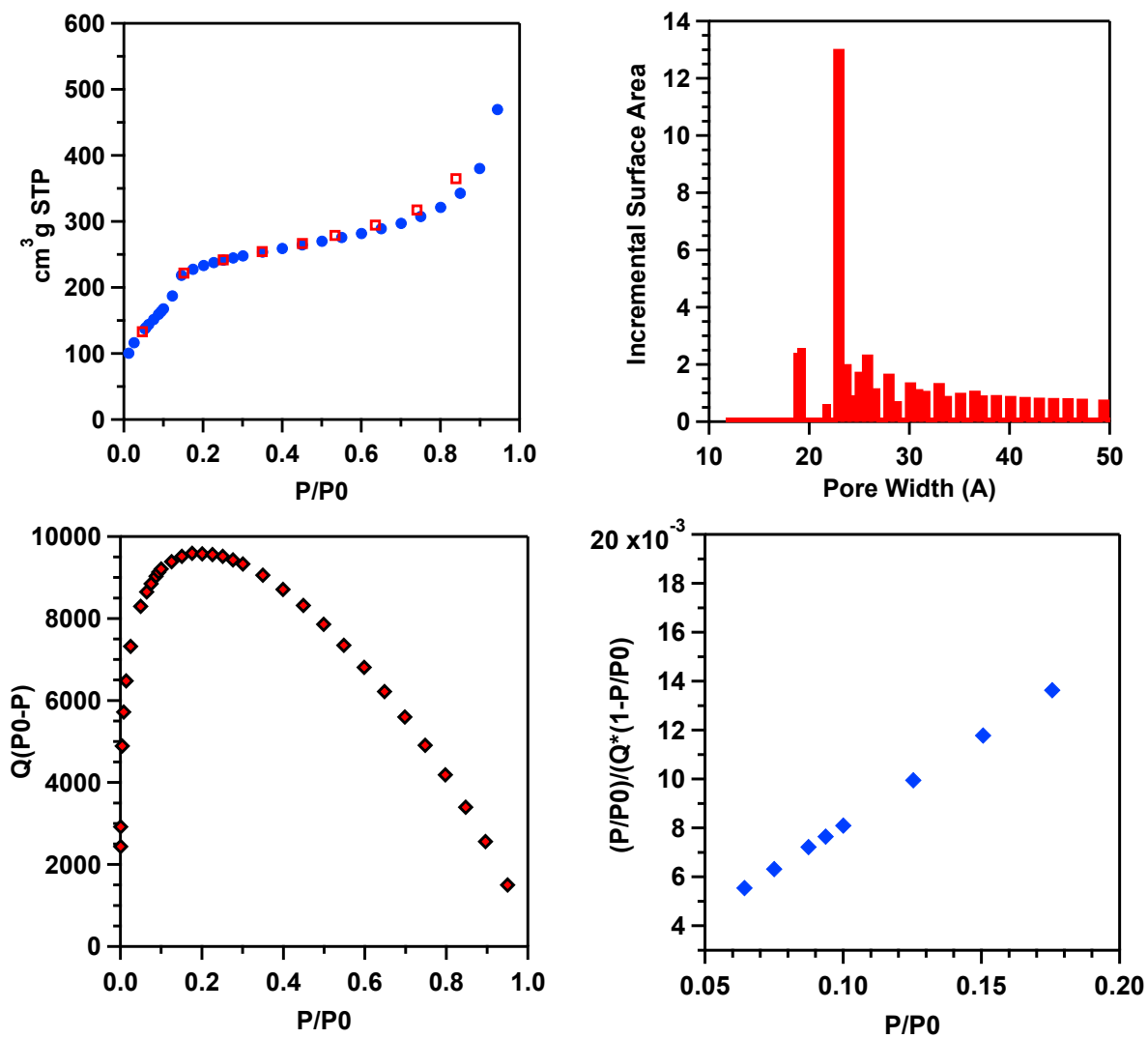
## V. BET surface area and porosity determination



### BET Surface Area

P/P <sub>0</sub>	m <sup>2</sup> /g	R <sup>2</sup>
0.05-0.10	22	0.999
0.05-0.15	21	0.998
0.05-0.20	20	0.999

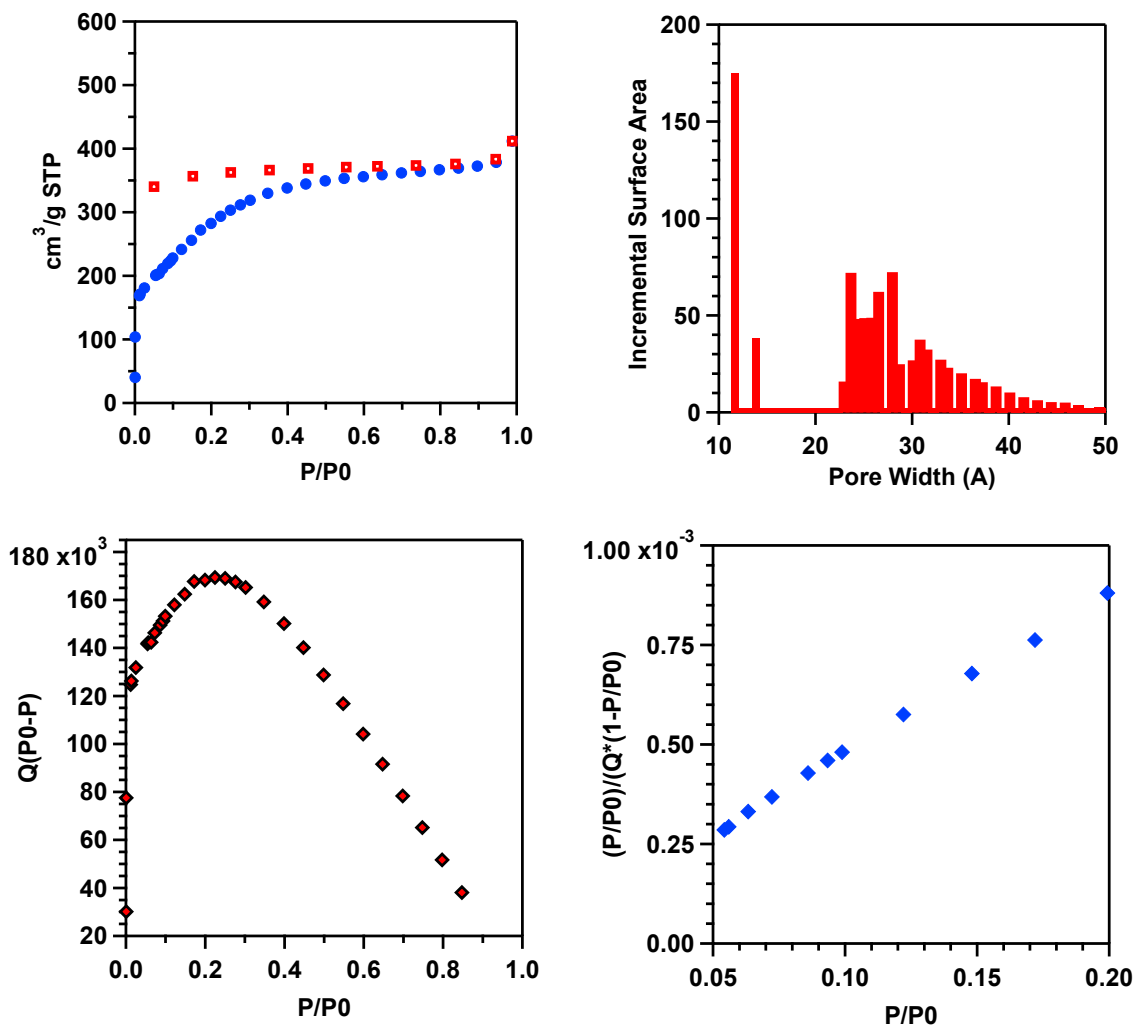
**Figure S7.** N<sub>2</sub> adsorption isotherm (77 K) and surface area data analysis of COF-300 synthesized from homogeneous monophasic conditions.



#### BET Surface Area

P/P <sub>0</sub>	m <sup>2</sup> /g	R <sup>2</sup>
0.05-0.10	60	0.999
0.05-0.15	59	1.000
0.05-0.20	59	0.999

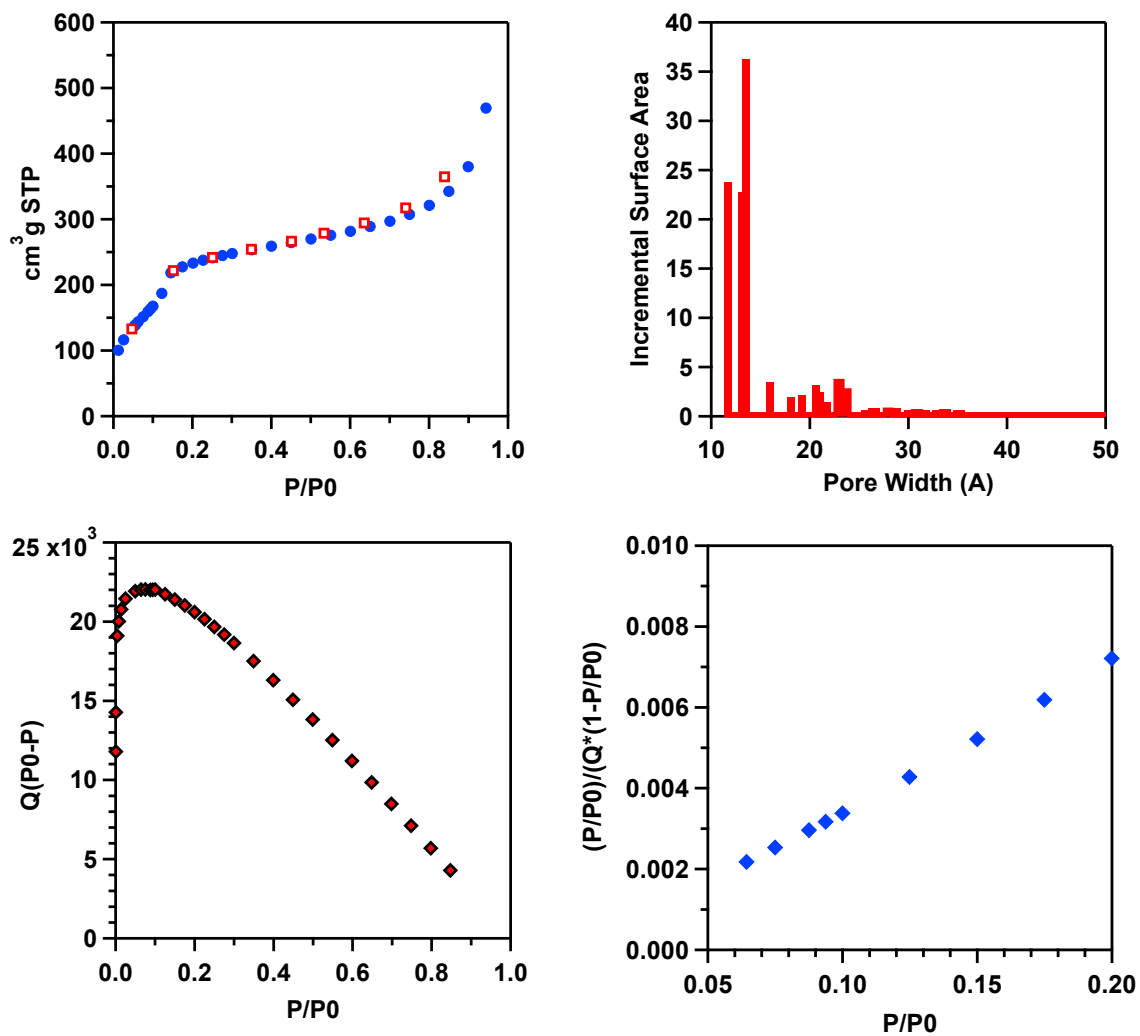
**Figure S8.** N<sub>2</sub> adsorption isotherm (77 K) and surface area data analysis of TAPM-PDA amorphous solid synthesized from homogeneous monophasic conditions.



#### BET Surface Area

P/P <sub>0</sub>	m <sup>2</sup> /g	R <sup>2</sup>
0.05-0.10	981	0.998
0.05-0.15	1023	0.999
0.05-0.20	1053	0.999

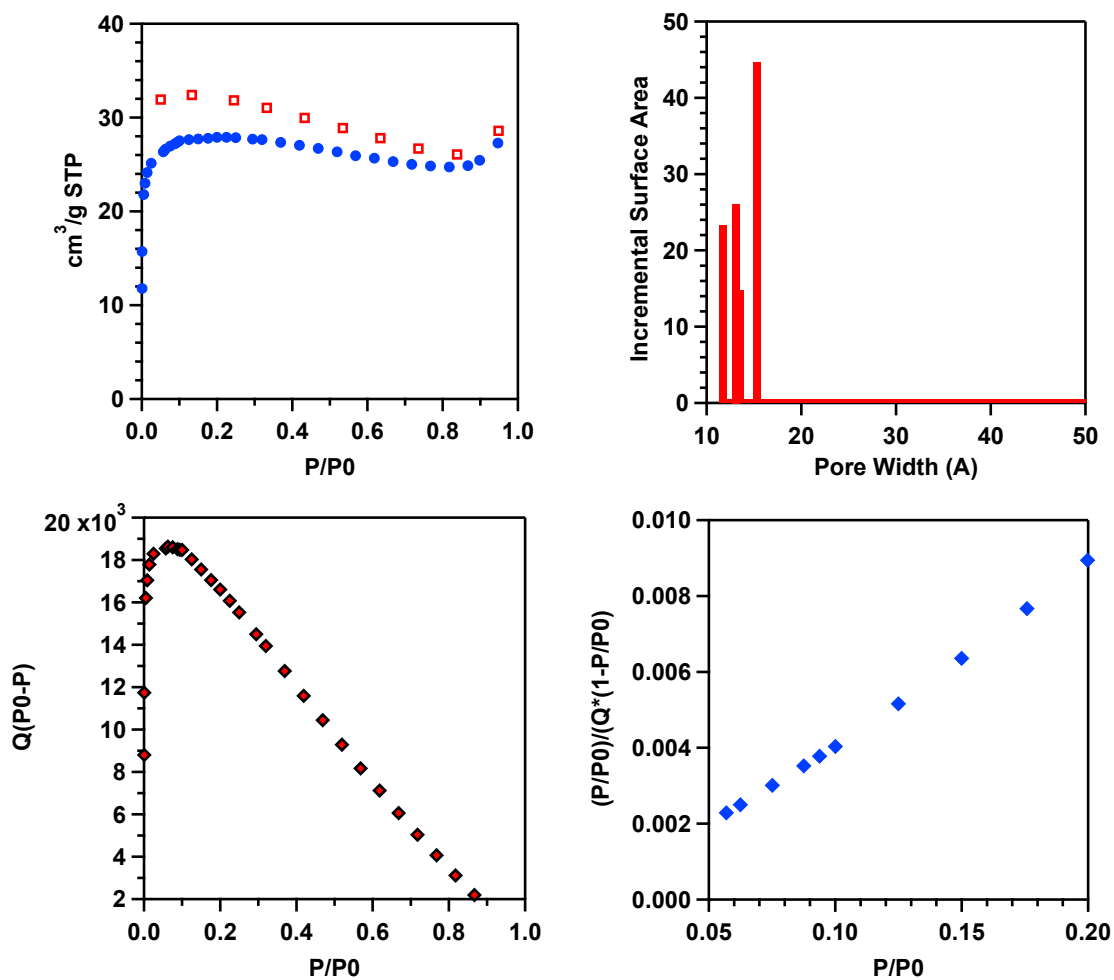
**Figure S9.** N<sub>2</sub> adsorption isotherm (77 K) and surface area data analysis of COF-300 synthesized from monophasic regrowth of TAPM-PDA amorphous solid.



#### BET Surface Area

$P/P_0$	$m^2/g$	$R^2$
0.05-0.10	129	1.000
0.05-0.15	124	0.999
0.05-0.20	119	0.999

**Figure S10.** N<sub>2</sub> adsorption isotherm (77 K) and surface area data analysis of COF-300 synthesized from biphasic conditions.

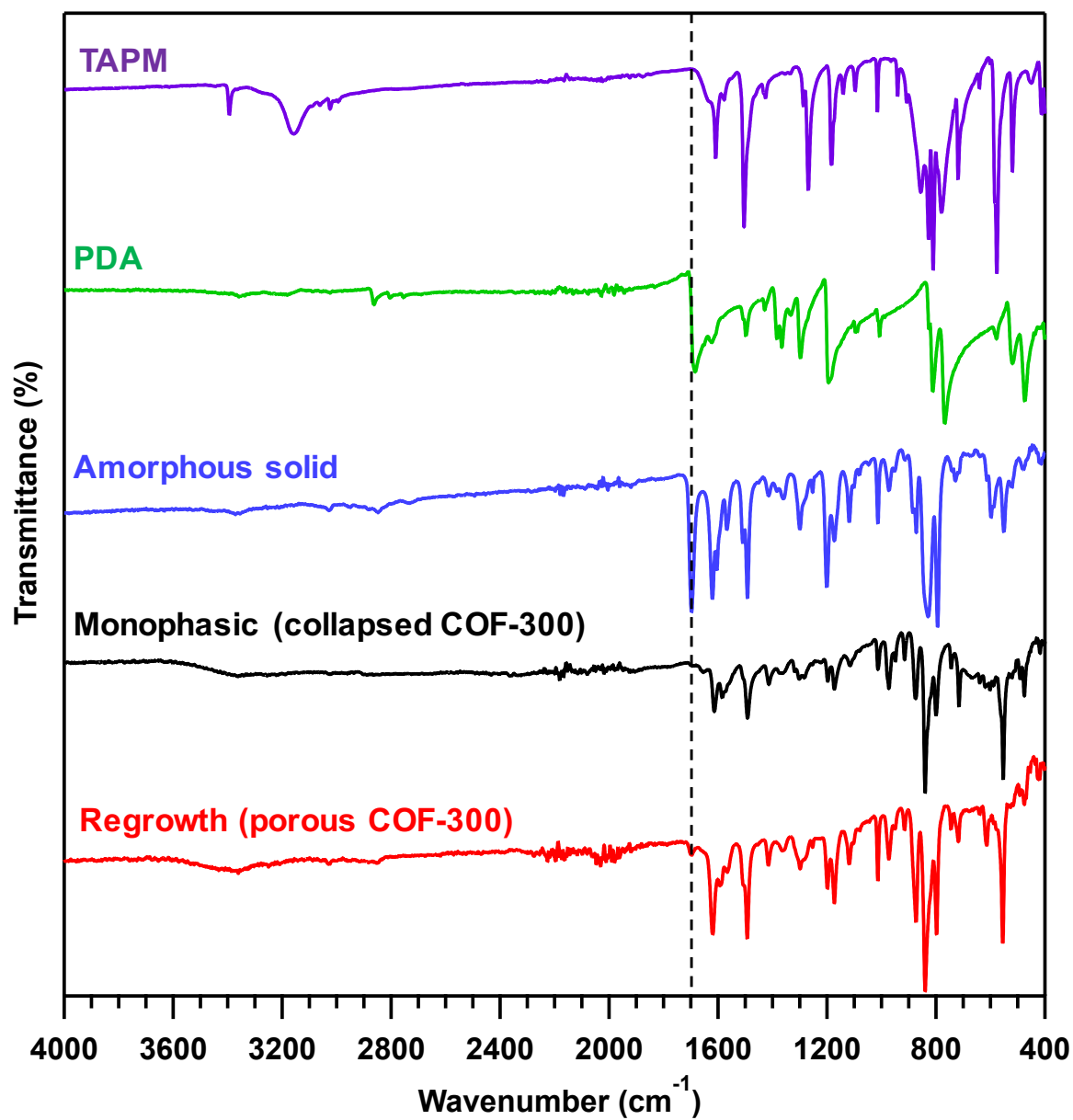


#### BET Surface Area

P/P <sub>0</sub>	m <sup>2</sup> /g	R <sup>2</sup>
0.05-0.10	107	1.000
0.05-0.15	100	0.998
0.05-0.20	95	0.998

**Figure S11.** N<sub>2</sub> adsorption isotherm (77 K) and surface area data analysis of COF-300 synthesized from agitated biphasic conditions.

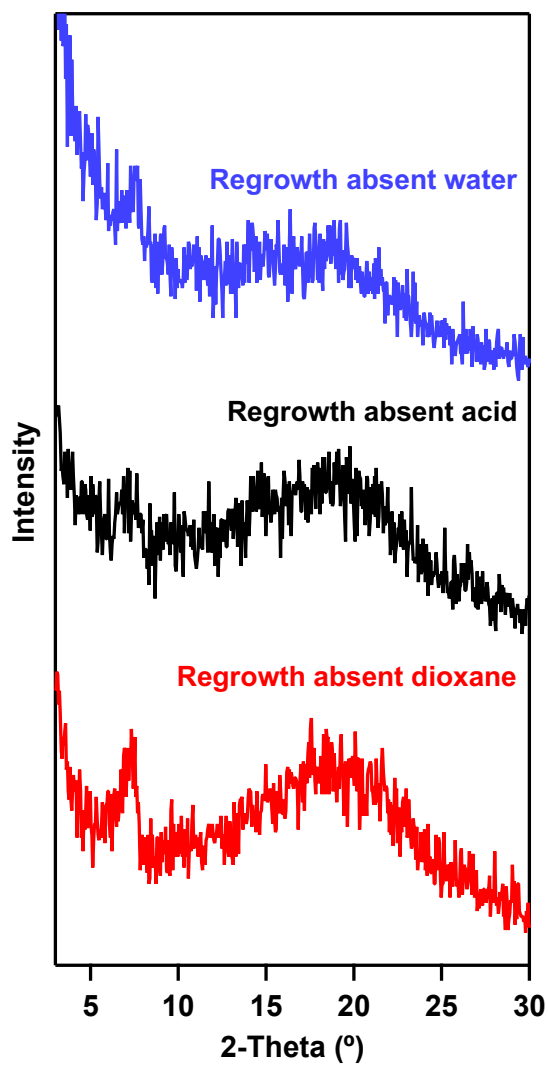
## VI. Infrared spectroscopy



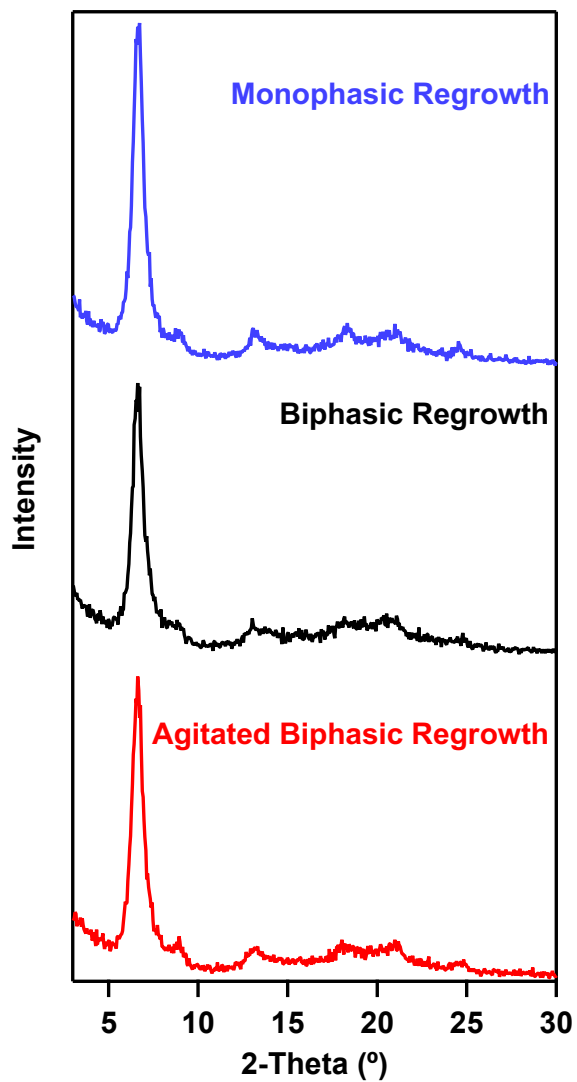
**Figure S12.** IR spectra of COF-300 synthesized from different growth methods and related monomers, with a dashed line highlighting 1698  $\text{cm}^{-1}$ .



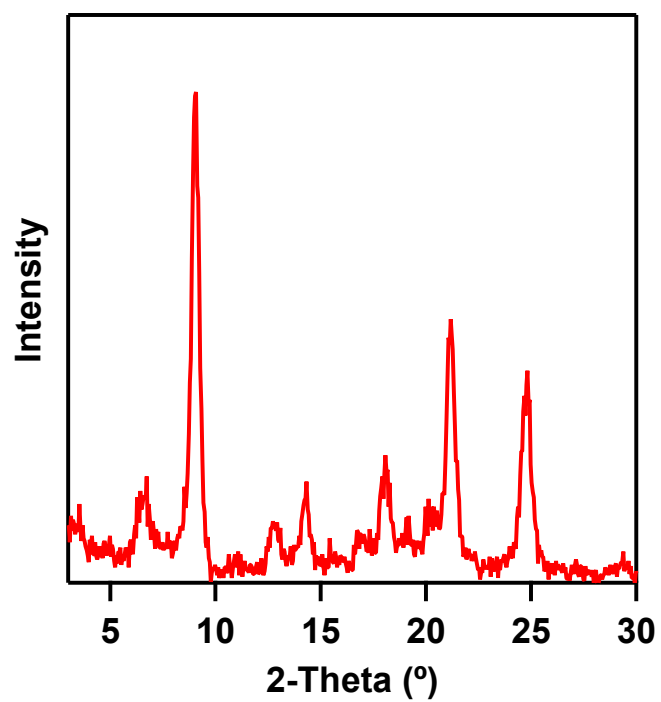
## VII. Regrowth studies



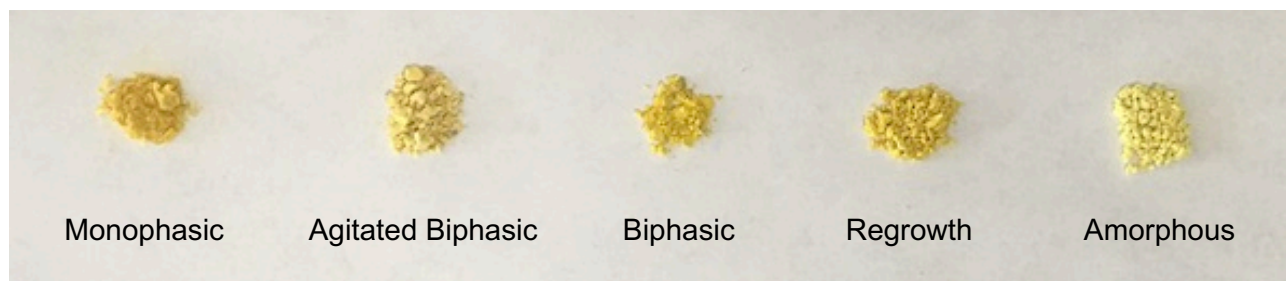
**Figure S13.** Powder X-ray diffraction of control regrowth attempts of TAPM-PDA amorphous solid under standard conditions, absent water (blue), acetic acid (black) and 1,4-dioxane (red).



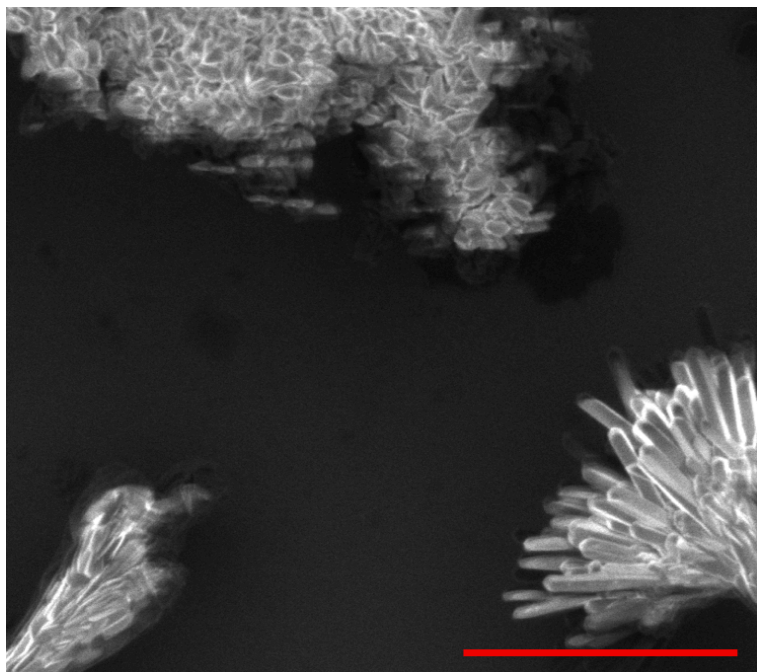
**Figure S14.** Powder X-ray diffraction of COF-300 synthesized by regrowth of TAPM-PDA amorphous solid under monophasic conditions (blue), biphasic conditions (black), and agitated biphasic conditions (red).



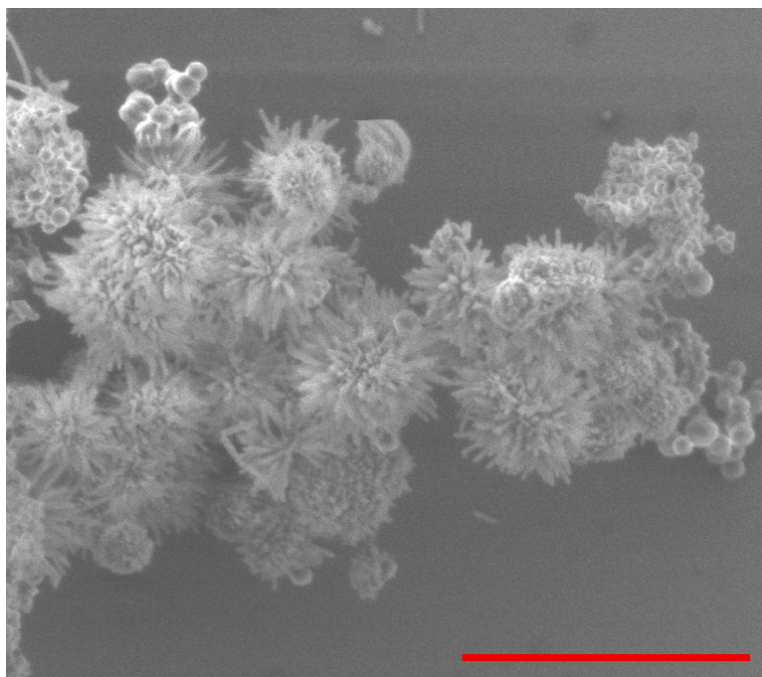
**Figure S15.** Powder X-ray diffraction of COF-300 synthesized from biphasic conditions with constant stirring.



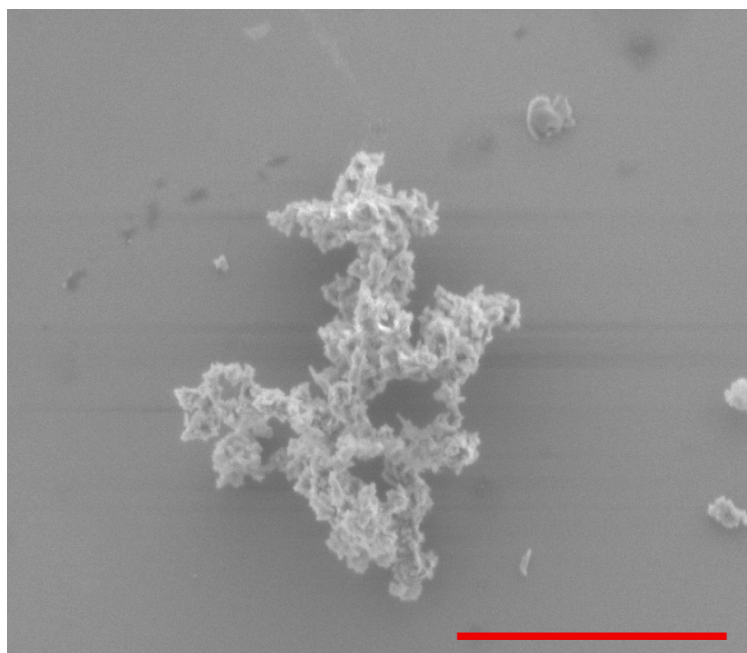
**Figure S16.** Photo of the COF-300 and amorphous solid powders.



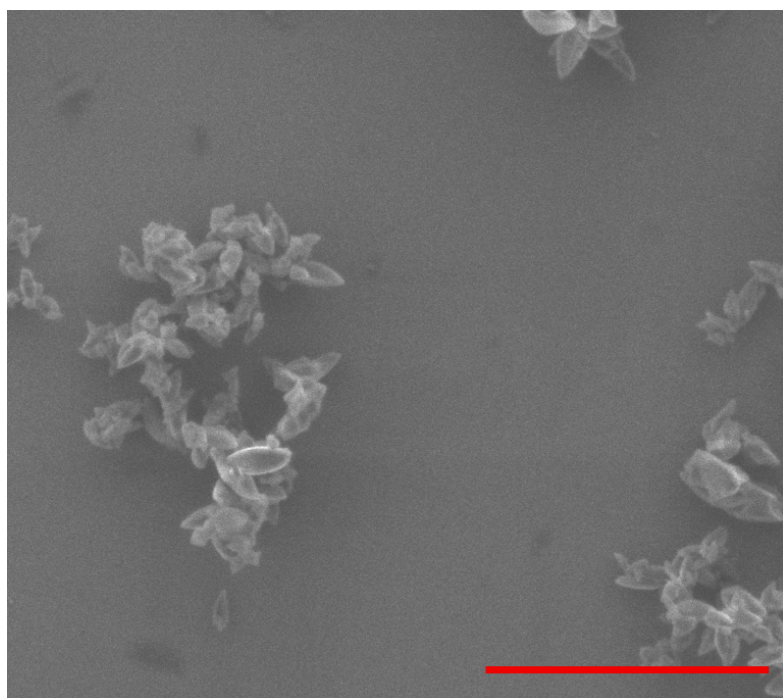
**Figure S17.** SEM of COF-300 synthesized from monophasic conditions. Scale bar is 10  $\mu\text{m}$



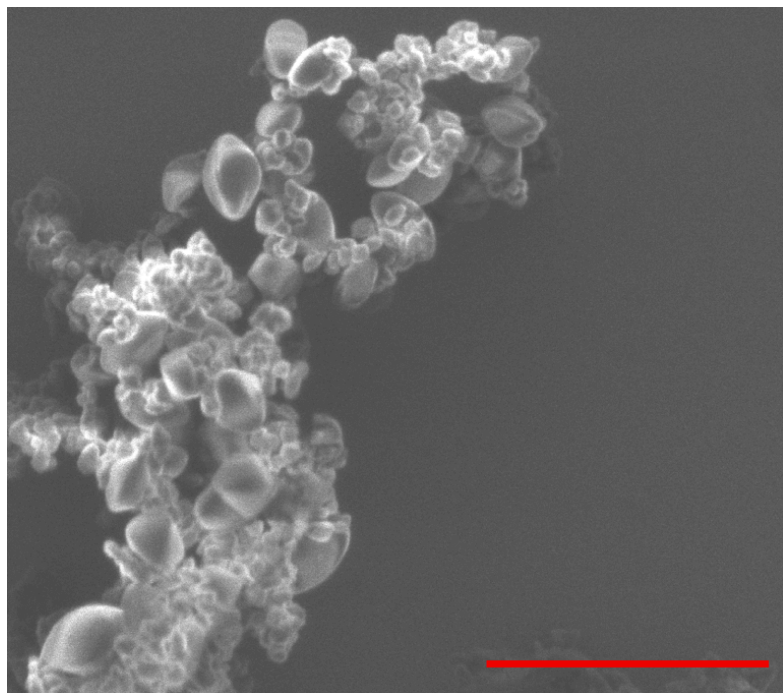
**Figure S18.** SEM of TAPM-PDA amorphous solid synthesized from monophasic conditions. Scale bar is 10  $\mu\text{m}$



**Figure S19.** SEM of COF-300 synthesized from regrowth conditions. Scale bar is 10  $\mu\text{m}$



**Figure S20.** SEM of COF-300 synthesized from biphasic conditions. Scale bar is 10  $\mu\text{m}$



**Figure S21.** SEM of COF-300 synthesized from agitated biphasic conditions. Scale bar is 10  $\mu\text{m}$

### References

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- 3 F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klöck, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, 131, 4570–4571.