Synthesis of Highly Crystalline Imine-linked Covalent Organic Frameworks via Controlling Monomer Feeding Rates in an Open System

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Contents

1. Experimental Section

Materials: N,N-Dimethylformamide (DMF), dichloromethane (DCM), acetone, 1,2-dichlorobenzene (o-DCB), aqueous acetic acid, 1,4-dioxane, mesitylene, n-hexane, absolute ethanol, methanol were analysis grade and purchased from National Medicines Corporation Ltd. of China. All reagents of analytical grade were utilized without further purification.

Synthesis of TATB-DAPB-COF:

One pot: A mixture of 4,4',4″-(1,3,5-Triazine-2,4,6-Triyl)Tris-Benzaldehyde (TATB) (0.16 mmoL 64 mg) and 4,4″-diamino-p-terphenyl (DAPB) (0.24 mmoL 63 mg), DMF (30 mL) was charged in a 50 mL round-bottom flask and sonicated. Then, 6 mL of 12 M aqueous acetic acid was added to the solution. This mixture was stirred for 12 hours at 30°C and reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane (DCM) for 12 hours and acetone for 12 hours. The damp COF was activated at room temperature for 12 hours under nitrogen flow, yielding a yellow powder. (80 mg, 65%)

20, 40, 80, 120 µL min^{-1}: A 25 mL flask was charged with 4,4',4″- (1,3,5-triazine-2,4,6-triyl), tris-benzaldehyde (TATB) (0.16 mmoL 64 mg) and DMF (20 mL). This mixture was sonicated for 5 min and marked as

Solution A. A 50 mL flask was charged with 4,4″-diamino-p-terphenyl (DAPB) (0.24 mmoL 63 mg) and DMF (10 mL). This mixture was sonicated for 5 min, then 6 mL of 12 M aqueous acetic acid was added to the solution. The obtained mixture was marked as Solution B. Solution A was added dropwise to solution B at different feeding rates by a peristaltic pump at 30°C. Then this mixture was reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane (DCM) for 12 hours and in acetone for 12 hours. The damp COF was activated at room temperature for 12 hours under nitrogen flow. (100 mg, 81%)

Synthesis of PDA-TAPB-COF:

One pot: A mixture of 1,3,5-tris(4-aminophenyl) benzene (TAPB) (0.16 mmoL 56 mg), terephthaldehyde (PDA) (0.24 mmoL 32 mg), 1,4-dioxane (16 mL) and mesitylene (4 mL) was charged in a 50 mL round-bottom flask and sonicated. Then 4 mL of 12 M aqueous acetic acid was added to the solution. This mixture was stirred for 12 hours at 30°C and reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was

immersed in dichloromethane (DCM) for 12 hours and n-hexane for 12 hours. The damp COF was activated at 120°C for 12 hours under nitrogen flow, yielding a yellow powder. (60 mg, 70%)

40, 80, 120 μL min^{-1}: A 25 mL flask was charged with terephthaldehyde (PDA) (0.24 mmoL 32 mg), 1, 4-dioxane (8 mL) and mesitylene (2 mL). This mixture was sonicated for 5 min and marked as Solution A. A 50 mL flask was charged with 1,3,5-tris(4-aminophenyl) benzene (TAPB) (0.16 mmoL 56 mg), 1,4-dioxane (8 mL) and mesitylene (2 mL). This mixture was sonicated for 5 min, then 4 mL of 12 M aqueous acetic acid was added to the solution. The obtained mixture was marked as Solution B. Solution A was added dropwise to solution B at different feeding rates by a peristaltic pump at 30°C. Then this mixture was reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane (DCM) for 12 hours and n-hexane for 12 hours. The damp COF was activated at 120°C for 12 hours under nitrogen flow. (66 mg, 77%)

Synthesis of OMePDA-TAPB-COF:

One pot: A mixture of 1,3,5-tris(4-aminophenyl) benzene (TAPB) (0.16 mmoL 56 mg), 2,5-dimethoxyterephthalaldehyde (OMePDA) (0.24 mmoL

46.6 mg), 1,4-dioxane (16 mL) and mesitylene (4 mL) was charged in a 50 mL round-bottom flask and sonicated. Then 4 mL of 12 M aqueous acetic acid was added to the solution. This mixture was stirred for 12 hours at 30°C and reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane (DCM) for 12 hours and n-hexane for 12 hours. The damp COF was activated at 120°C for 12 hours under nitrogen flow, yielding a yellow powder. (70 mg, 72%)

40, 80, 120 μL min^{-1}: A 25 mL flask was charged with 2,5-dimethoxytere-phthalaldehyde (OMePDA) (0.24 mmoL 46.6 mg), 1,4-dioxane (8 mL) and mesitylene (2 mL). This mixture was sonicated for 5 min and marked as Solution A. A 50 mL flask was charged with 1,3,5-tris(4-aminophenyl) benzene (TAPB) (0.16 mmoL 56 mg), 1,4-dioxane (8 mL) and mesitylene (2 mL). This mixture was sonicated for 5 min, then 4 mL of 12 M aqueous acetic acid was added to the solution. The obtained mixture was marked as Solution B. Solution A was added dropwise to solution B at different feeding rates by a peristaltic pump at 30°C. Then this mixture was reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane (DCM) for 12 hours and n-hexane for

12 hours. The damp COF was activated at 120°C for 12 hours under nitrogen flow. (66 mg, 77%)

Synthesis of 3D COF-320:

One pot: A mixture of 4'4-biphenyldicarboxaldehyde (BPDA) (0.238 mmoL 50 mg), tetra(4-anily) methane (TAM) (0.132 mmoL 50 mg), 15 mL 1,4-dioxane was charged in a 50 mL round-bottom flask and sonicated. Then 3 mL of 9 M aqueous acetic acid was added to the solution. This mixture was stirred for 12 hours at 30°C and reacted under 70°C for 72 hours. There was no solid product by this way.

20, 40, 80, 120 μL min^{-1}: A 25 mL flask was charged with 4'4-biphenyldicarboxaldehyde (BPDA) (0.238 mmoL 50 mg) and 10 mL 1,4-dioxane. This mixture was sonicated for 5 min and marked as Solution A. A 50 mL flask was charged with tetra(4-anily) methane (TAM) (0.132 mmoL 50 mg) and 5 mL 1,4-dioxane. This mixture was sonicated for 5 min, then 3 mL of 9 M aqueous acetic acid was added to the solution. The obtained mixture was marked as Solution B. Solution A was added dropwise to solution B at different feeding rates by a peristaltic pump at 30°C. Then this mixture was reacted under 70°C for 72 hours. The yellow precipitate was collected by filtration and washed with methanol. The collected sample was further treated through Soxhlet extraction with methanol for two days. Then the sample was immersed in dichloromethane

(DCM) for 12 hours and acetone for 12 hours. The damp COF was activated at room temperature for 12 hours under nitrogen flow. (60 mg, 70%)

2. Characterization

The formation of imine bond was confirmed by Fourier-transformed infrared (FTIR) spectra in ATR mode with a Bruker Vertex 70 FTIR spectrometer, and solid-state ^{13}C CP/MAS NMR experiments on a WB 400 MHz Bruker Avance II spectrometer with the contact time of 2 ms (ramp 100) and pulse delay of 3 s. Powder X-ray diffraction (XRD) patterns were recorded on the X-ray diffraction instrument (XRD, Philips X' Pert Pro) from $2\theta = 1.5°$ up to 30° and 40° with 0.02° increment using the Cu Kα radiation (40 kV, 40 mA, $\lambda = 1.5418$ Å). The porous structure of COFs was analyzed by using Micromeritics ASAP 2460 surface area and porosity analyzer, and the pore size distribution was calculated by non-local density functional theory (NLDFT) modelling based on N_2 adsorption data. The morphology of COFs was characterized by FEI Sirion 200 field emission scanning electron microscope (FE-SEM). Elemental analysis (EA) measurements were performed on a VarioMicrocube Elemental Analyser (Elementar, Germany). The stability of COFs was tested evaluated using Thermogravimetric analysis (TGA) instrument (Perkin-Elmer Pyrisl) at the rate of 10 °C/min under nitrogen atmosphere up to 800°C.

3. FTIR spectra

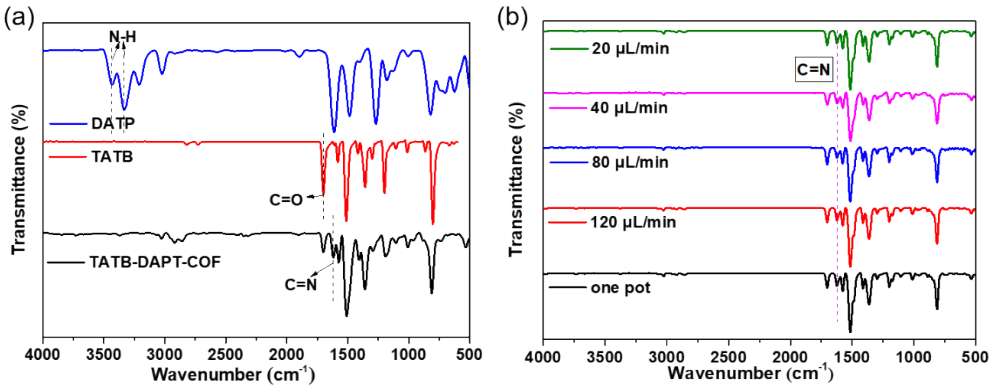

Figure S1. (a) FTIR spectra of TATB-DATP-COF (black), monomers DATP (blue) and TATB (red), (b) FTIR spectra of TATB-DATP-COF samples synthesized under different feeding rates.

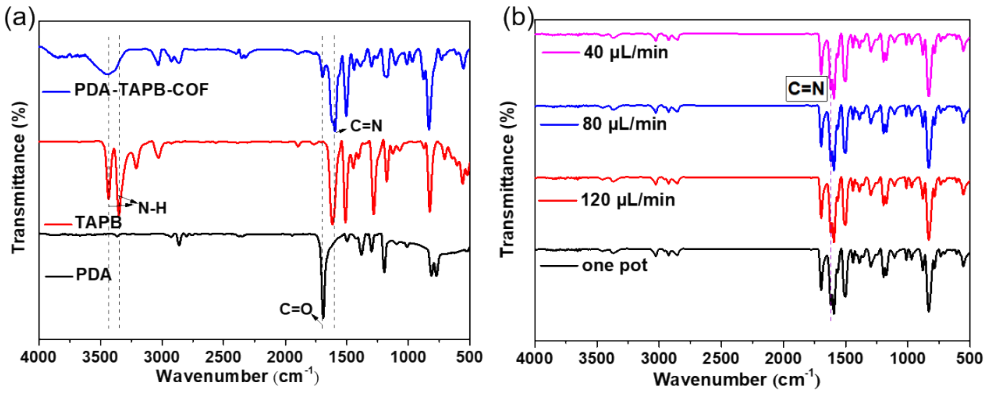

Figure S2. (a) FTIR spectra of PDA-TAPB-COF (blue), TAPB (red) and PDA (black), (b) FTIR spectra of PDA-TAPB-COF samples synthesized under different feeding rates.

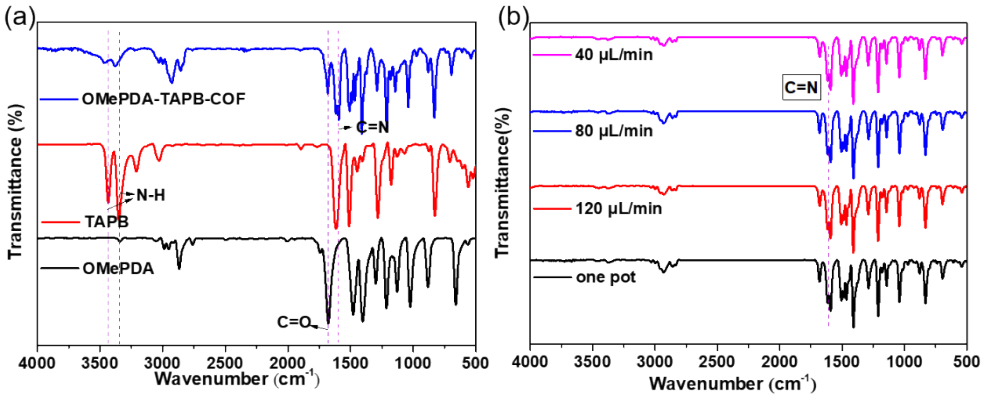

Figure S3. (a) FTIR spectra of OMePDA-TAPB-COF (blue), TAPB (red) and OMePDA (black), (b) FTIR spectra of OMePDA-TAPB-COF samples synthesized under different feeding rates.

4. TGA

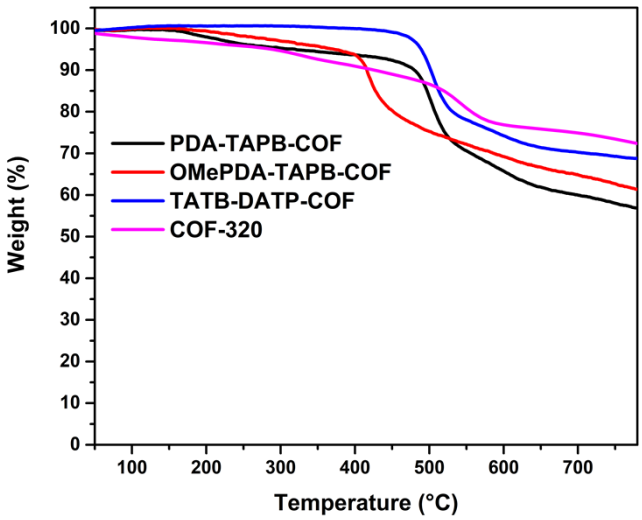

Figure S4. TGA curves of TATB-DATP-COF (blue), PDA-TAPB-COF (black), OMePDA-TAPB-COF (red) and COF-320 (purple).

5. HR-TEM, BET and SEM

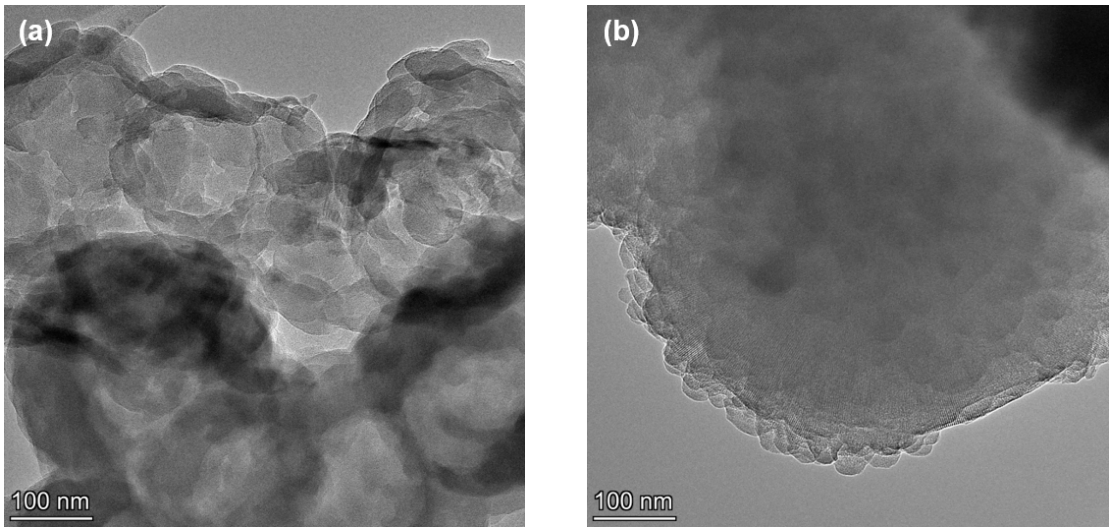

Figure S5. HR-TEM images of (a) PDA-TAPB-COF and (b) OMePDA-TAPB-COF.

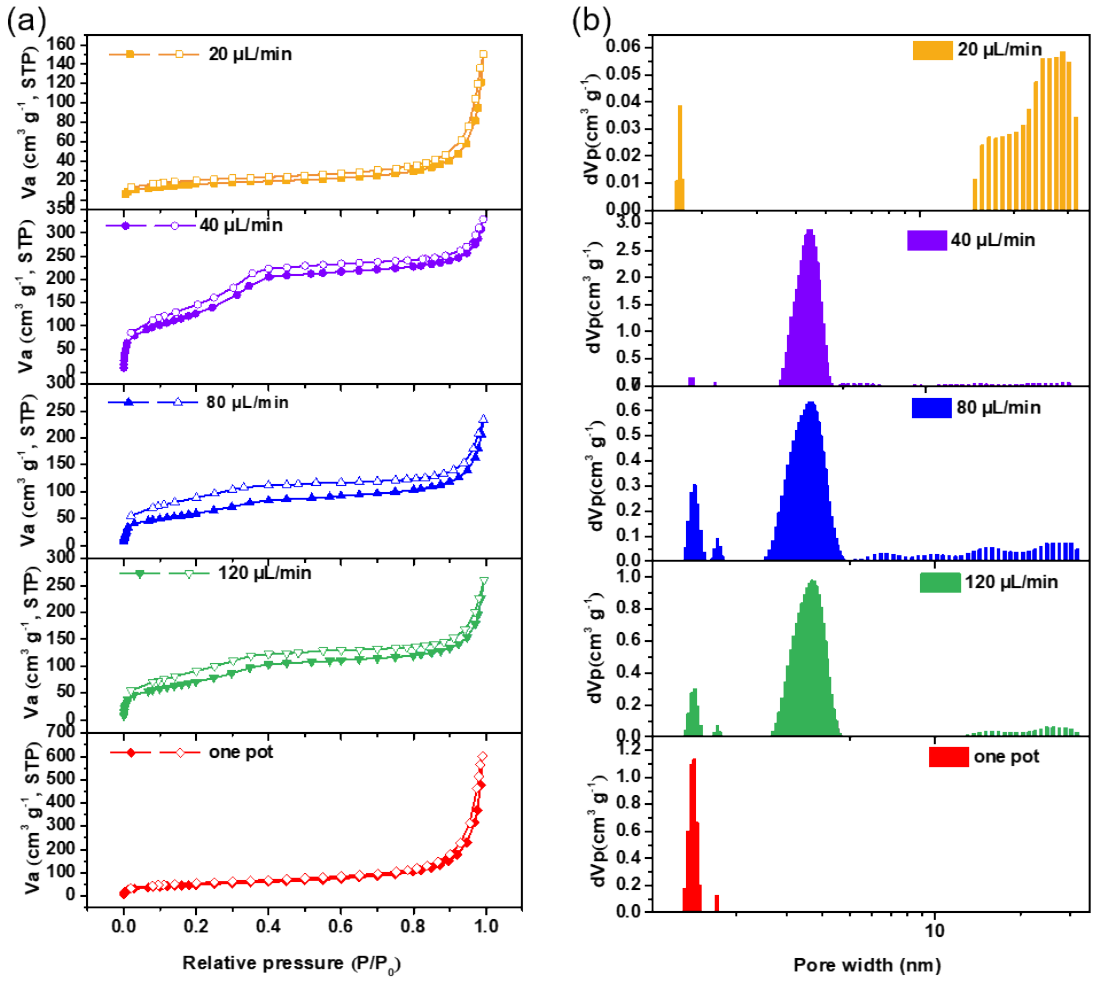

Figure S6. (a) N_2 adsorption isotherm (77 K) and (b) pore size distribution

of TATB-DATP-COF sample synthesized under different feeding rates. The BET surface area of the COF sample synthesized by 20, 40, 80, 120 μL min^{-1} and one pot were 60 m^2 g^{-1}, 455 m^2 g^{-1}, 267 m^2 g^{-1}, 217 m^2 g^{-1} and 177 m^2 g^{-1}, respectively.

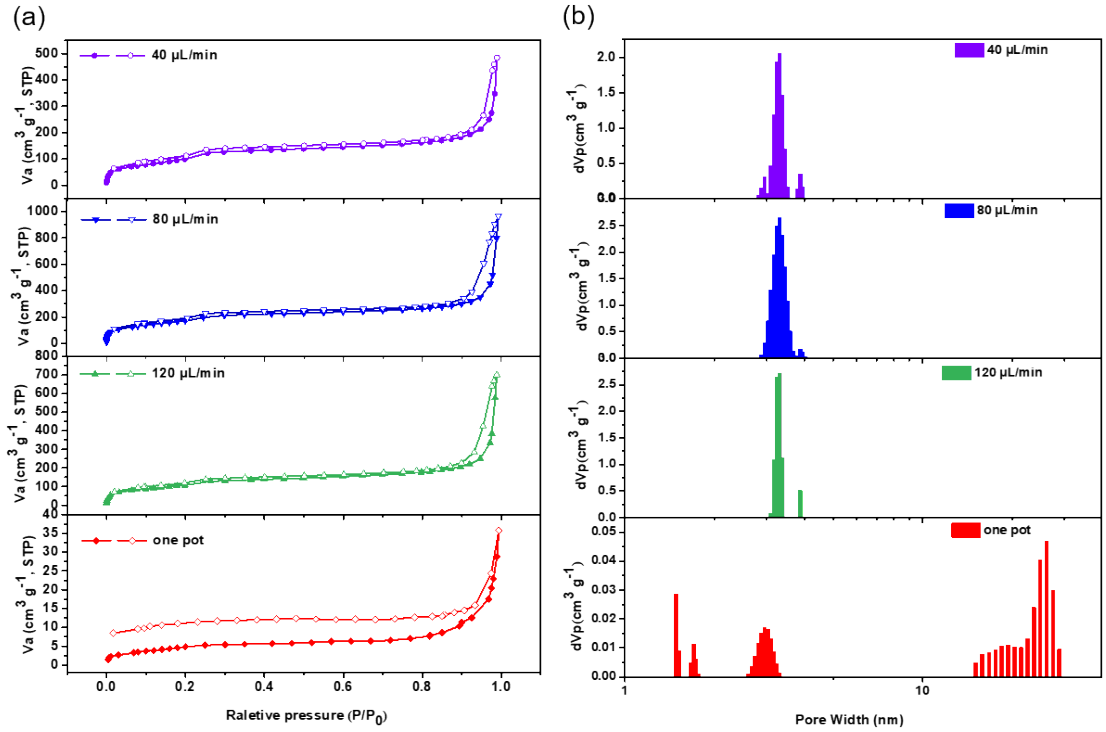

Figure S7. (a) N_2 adsorption isotherm (77 K) and (b) pore size distribution of PDA-TAPB-COF samples synthesized under different feeding rates. The BET surface area of the COF sample synthesized by 40, 80, 120 μL min^{-1} and one pot were 317 m^2 g^{-1}, 655 m^2 g^{-1}, 407 m^2 g^{-1} and 20 m^2 g^{-1}, respectively.

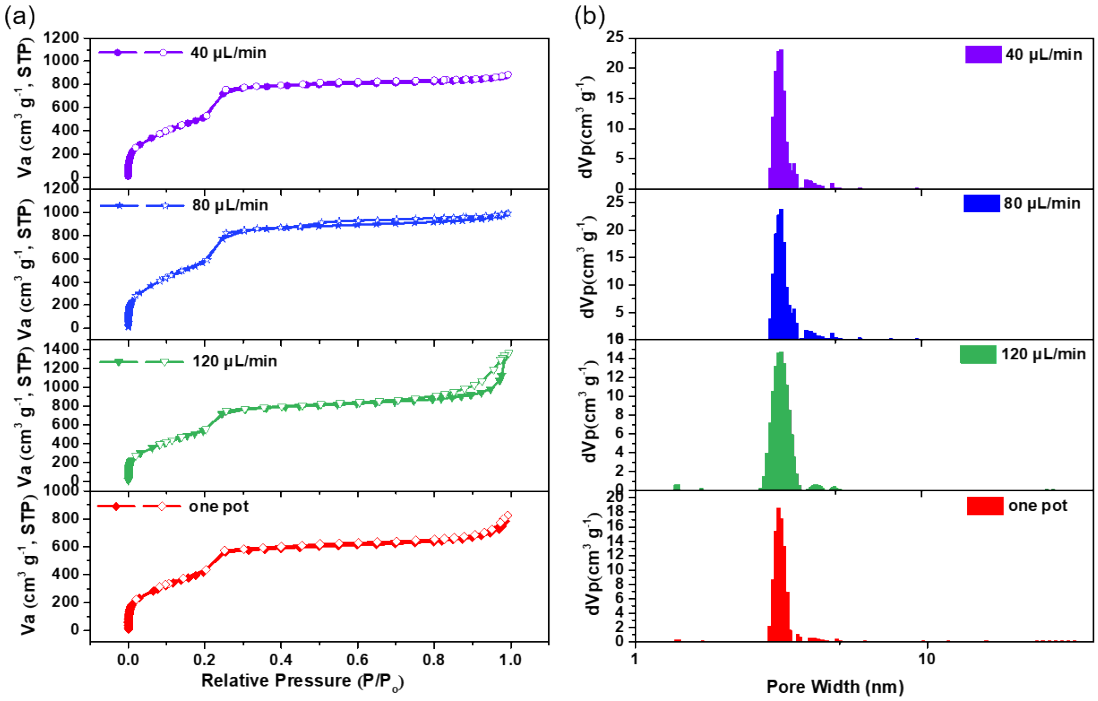

Figure S8. (a) N_2 adsorption isotherm (77 K) and (b) pore size distribution of OMePDA-TAPB-COF samples synthesized under different feeding rates. The BET surface area of the COF sample synthesized by 40, 80, 120 μL min^{-1} and one pot were 2002 m^2 g^{-1}, 2226 m^2 g^{-1}, 2037 m^2 g^{-1}, and 1552 m2 g^{-1}, respectively.

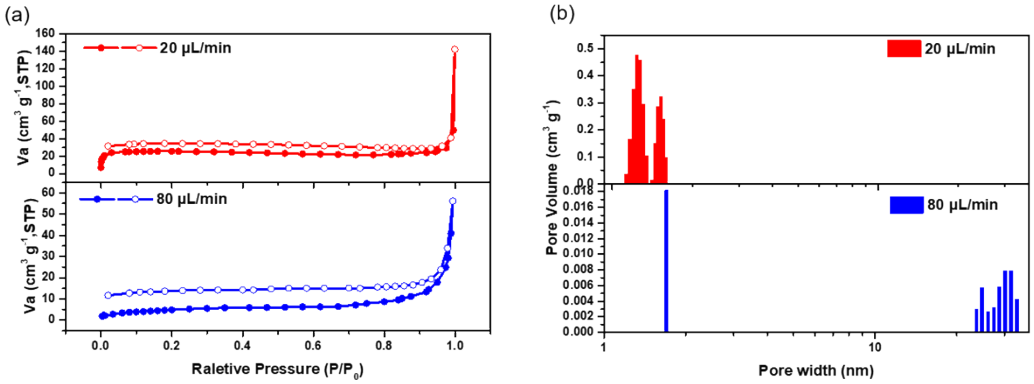

Figure S9. (a) N_2 adsorption isotherm (77 K) and (b) pore size distribution of COF-320 samples synthesized under different feeding rates. The BET

surface area of the COF samples synthesized by 20 and 80 μL min^{-1} were determined to be 100 m^2 g^{-1} and 17 m^2 g^{-1}.

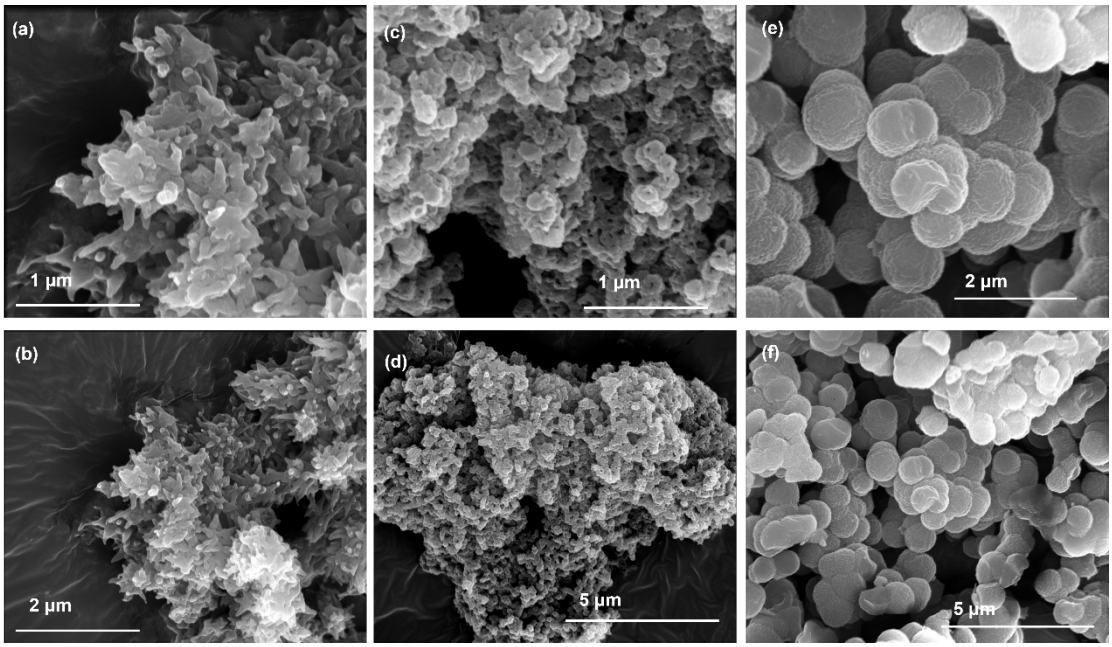

Figure S10. SEM images of (a) and (b)TATB-DATP-COF sample, (c) and (d) PDA-TAPB-COF, (e) and (f) OMePDA-TAPB-COF sample.

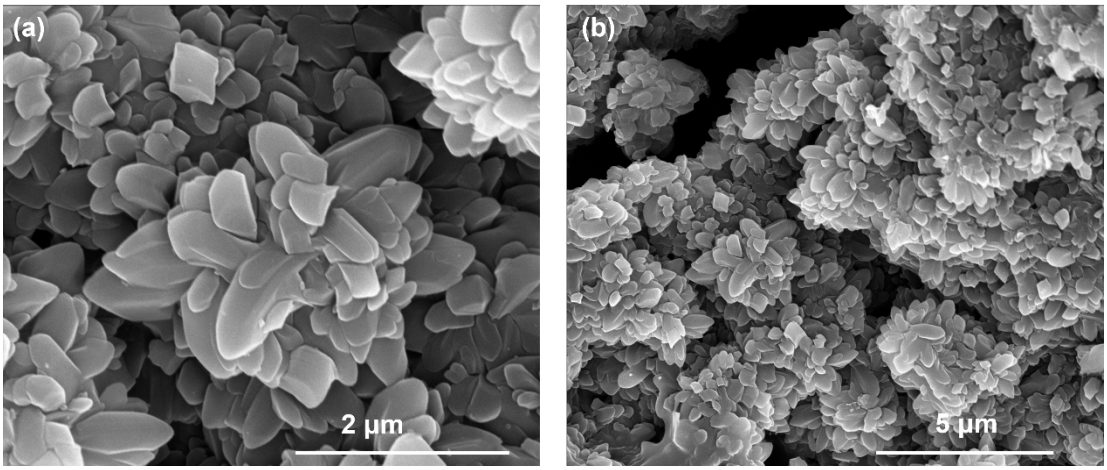

Figure S11. SEM images of 3D COF-320.

6. Supporting Tables

Table S1 Elemental analysis of COFs

Sample	N [wt.%]		C [wt.%]		H [wt.%]		O [wt.%]	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
TATB-DATP-COF	11.52	10.99	83.95	82.16	4.53	4.45	-	-
PDA-TAPB-COF	8.43	8.03	86.75	84.22	4.82	4.36	-	-
OMePDA-TAPB-COF	7.14	7.11	79.59	79.49	5.11	4.38	8.16	7.51
COF-320	17.72	17.36	77.85	77.26	4.43	4.24		

Table S2 Comparison of surface areas of reported COFs and as-synthesized COFs.

Feeding rate	TATB-DATP-COF	PDA-TAPB-COF	OMePDA-TAPB-COF	COF-320
20	60 $m^2 g^{-1}$	-	-	100 $m^2 g^{-1}$
40	455 $m^2 g^{-1}$	317 $m^2 g^{-1}$	2002 $m^2 g^{-1}$	566 $m^2 g^{-1}$
80	267 $m^2 g^{-1}$	655 $m^2 g^{-1}$	2226 $m^2 g^{-1}$	17 $m^2 g^{-1}$
120	217 $m^2 g^{-1}$	407 $m^2 g^{-1}$	2037 $m^2 g^{-1}$	-
One pot	177 $m^2 g^{-1}$	20 $m^2 g^{-1}$	1552 $m^2 g^{-1}$	-
literature	-	600 $m^2 g^{-1}$ [a]	2105 $m^2 g^{-1}$ [b]	1410 $m^2 g^{-1}$ [c]

[a] B. J. Smith, A. C. Overholts, N. Hwang, W. R. Dichtel, *Chem. Commun.* 2016, **52**, 3690.

[b] H. Xu, J. Gao, D. Jiang, *Nat. Chem.* 2015, **7**, 905.

[c] Z. Li, X. Ding, Y. Feng, W. Feng, B. Han, *Macromolecules* 2019, **52**, 1257.