Enhancement of crystallinity of imine-linked covalent organic frameworks via aldehyde modulators

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Supporting Information

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Section A. Methods

Supercritical CO₂ drying was conducted on a Leica EM CPD300 Critical Point Dryer.

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

Powder X-ray diffraction (PXRD) data were recorded on a Rigaku SmartLab XRD from $2\theta = 1^{\circ}$ up to 30° with 0.02° increment. 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.

TGA measurements were performed on Q-600 Simultaneous TGA/DSC from TA Instrumentsa Mettler-Toledo model under Ar, by heating to 800 °C at a rate of 10 °C min⁻¹.

Nitrogen sorption measurements were conducted on Quantachrome Autosorb-iQ-MP/Kr BET Surface Analyzer using samples degassed at 120 °C for 12 h and backfilled with N₂. N₂ 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 (ASiQwin version 5.2).

Scanning electron microscopy was performed on a FEI Quanta 400 FESEM operating at 30.00 kV. Samples were prepared by dispersing COF powders in ethanol and dropping on clean aluminum samples holders. After drying for 24 hours, samples were coated with a 10 nm gold using a Denton Desk V Sputter.

Transmission electron microscopy (TEM) of COF powders was performed using a JEOL 2100 Field Emission Gun Transmission Electron Microscope operating at 300 keV equipped with a Gatan (Gatan, Inc., Pleasanton, CA) One View-IS camera (FEG Emission: 15 μ A, spot size 5, 150 μ m CL aperture, exposure time of 0.5 s). All image acquisition was done using the Gatan Microscopy Suite (GMS), Digital Micrograph (Gatan, Inc., Pleasanton, CA).

Solid state NMR test

¹H-¹³C CPMAS spectra were obtained on a Bruker 4.7 T NMR spectrometer previously described in detail1 and with the data acquisition and processing parameters previously described1 (except for the amount of line broadening used in processing the FIDs: 50 Hz). In particular, with the sample spinning at 7.6 kHz, thirteen spectra with contact times ranging from 0.1 ms to 3.75 ms were obtained for each sample in order to study the relative rates of cross polarization for the different carbon environments, with a 5-minute waiting period preceding each experiment to ensure complete relaxation. In addition, at the contact time that appeared optimal for maximizing the intensity of the quaternary carbon signals, a dipolar dephasing experiment was performed for each sample with a 50- μ s dephasing interval in order to provide additional evidence for differentiating proton-bearing from quaternary carbons. The number of scans per spectrum varied: TAPB-PDA COF 0 eq (6208), 1 eq (6320), 3 eq (6272), 6 eq (8736), 9 eq (5200); TAPB-TFPA COF 0 eq (7472), 1 eq (7712), 2 eq (6352), 3 eq (6320), 4 eq (6112).

There was not enough material to fill a standard 4mm rotor for any sample. If sufficient space remained, an upper silicon nitride plug was inserted to confine the material closer to the center of the rotor. When only a very limited amount of material was available, a special 4mm rotor with a thick-bottom was used in order to maximize the amount of material centered in the rf coil region. Sometimes, not even enough material was available to fill a thick-bottom rotor; if sufficient space remained, an upper silicon nitride plug was inserted to confine the material to the center of the rotor.

Reference

 Alemany, L. B.; Verma, M.; Billups, W. E.; Wellington, S. L.; Shammai, M. *Energy Fuels* 2015, **29**, 6317-6329.

Section B. Materials and experimental protocols

I. Materials.

All chemicals were purchased from commercial sources and used without further purification. 1,3,5-tris(4-aminophenyl)benzene was purchased from TCI America. Terephthaldehyde, tris(4-formylphenyl)amine, anhydrous dioxane and mesitylene were purchased from Sigma Aldrich. All other solvents were purchased from VWR.

II. Experimental Protocols

Synthesis of TAPB-PDA COFs with different amounts of benzaldehyde added.

1,3,5-tris(4-aminophenyl)benzene (TAPB, 20.85 mg, 0.059 mmol) and terephthaldehyde (PDA, 12 mg, 0.089 mmol) were dissolved in a mixture of 1.6 mL dioxane and 0.4 mL mesitylene separately. TAPB solution was transferred in a Pyrex tube and then benzaldehyde was added (1 equivalent, 3 equivalents, 6 equivalents and 9 equivalents compared to the amount of TAPB, reaction without benzaldehyde was conducted as comparison). Afterwards, PDA solution was transferred to the mixtures and 0.2 mL 6M acetic acid was added. The Pyrex tube was sealed immediately and heated to 120 °C for 24 hours. The COF solids were isolated by filtration, rinsed with THF, acetone and ethanol respectively, immersed in ethanol overnight and subsequently dried using supercritical point dryer, yielding a yellow powder. The yields for different reaction conditions are listed below. COF powders are kept in glass vials in ambient conditions for further characterizations.

Amounts of benzaldehyde	Isolated COF mass	Yield
0 eq.	22.6 mg	76.33%
1eq.	20.4 mg	68.67%
3eq.	14.9 mg	50.33%
6eq.	11.8 mg	40.00%
9eq.	4.4 mg	14.68%

Synthesis of TAPB-TFPA COFs with different amounts of benzaldehyde added.

1,3,5-tris(4-aminophenyl)benzene (TAPB, 17 mg, 0.048 mmol) and tris(4-formylphenyl)amine (TFPA, 15.94 mg, 0.048 mmol) were dissolved in a mixture of 2 mL solution of dioxane/mesitylene (v:v, 1:1) separately. TAPB solution was transferred in a Pyrex tube and then benzaldehyde was added (1 equivalent, 2 equivalents, 3 equivalents and 4 equivalents compared to the amount of TFPA, reaction without benzaldehyde was conducted as comparison). Afterwards, TFPA solution was transferred to the mixtures and 0.2 mL 6M acetic acid was added. The Pyrex tube was sealed immediately and heated to 120 °C for 24 hours. The COF solids were isolated by filtration, rinsed with THF, acetone and ethanol respectively, immersed in ethanol overnight and subsequently dried using supercritical point dryer, yielding a yellow powder. The yields for different reaction conditions are listed below. COF powders are kept in glass vials in ambient conditions for further characterizations.

Amounts of benzaldehyde	Isolated COF mass	Yield
0 eq.	27.3mg	86.9%
1eq.	25.3mg	80.6%

2eq.	20.2mg	64.3%
3eq.	17.5mg	55.7%
4eq.	15.9mg	50.6%

Section C. Infrared spectroscopy (FTIR)



Figure S1 Infrared spectra of TAPB, PDA monomers and TAPB-PDA COFs synthesized with different equivalents of benzaldehyde added from $1800 \sim 500 \text{ cm}^{-1}$



Figure S2 Infrared spectra of TAPB, PDA monomers and TAPB-PDA COFs synthesized with different equivalents of benzaldehyde added from $4000 \sim 500 \text{ cm}^{-1}$



Figure S3 Time-dependent infrared spectra of TAPB-PDA COFs synthesized (a) without benzaldehyde added (b) with 3 eq. benzaldehyde added from $1800 \sim 500 \text{ cm}^{-1}$



Figure S4 Infrared spectra of TAPB, TFPA monomers and TAPB-TFPA COFs synthesized with different equivalents of benzaldehyde added from 1800~500 cm⁻¹



Figure S5 Infrared spectra of TAPB, TFPA monomers and TAPB-TFPA COFs synthesized with different equivalents of benzaldehyde added from 4000~500 cm⁻¹

D. Solid state ¹³C NMR spectroscopy



Figure S6 Solid state ¹³C NMR spectra for TAPB-PDA COFs synthesized with different equivalents of benzaldehyde added (black: without benzaldehyde; red: with 1 eq. benzaldehyde; green: with 3 eq. benzaldehyde; blue: with 6 eq. benzaldehyde; magenta: with 9 eq. benzaldehyde)



Figure S7 Solid state ¹³C NMR spectra for TAPB-TFPA COFs synthesized with different equivalents of benzaldehyde added (black: without benzaldehyde; red: with 1 eq. benzaldehyde; green: with 2 eq. benzaldehyde; blue: with 3 eq. benzaldehyde; magenta: with 4 eq. benzaldehyde)





Figure S8 BET plots for TAPB-PDA COFs synthesized with different equivalents of benzaldehyde (a) without benzaldehyde; (b) with 1 eq. benzaldehyde; (c) with 3 eq. benzaldehyde; (d) with 6 eq. benzaldehyde; (e) with 9 eq. benzaldehyde



Figure S9 BET plots for TAPB-TFPA COFs synthesized with different equivalents of benzaldehyde (a) without benzaldehyde; (b) with 1 eq. benzaldehyde; (c) with 2 eq. benzaldehyde; (d) with 3 eq. benzaldehyde; (e) with 4 eq. benzaldehyde

Section F. SEM characterizations



Figure S10 SEM of TAPB-PDA-COFs with different equivalents of benzaldehyde added. (a) without benzaldehyde; (b) 1eq. benzaldehyde; (c) 3eq. benzaldehyde; (d) 6eq. benzaldehyde; (e) 9eq. benzaldehyde. Scale bar is 4 μ m.



Figure S11 SEM of TAPB-TFPA-COFs with different equivalents of benzaldehyde added. (a) without benzaldehyde; (b) 1eq. benzaldehyde; (c) 2eq. benzaldehyde; (d) 3eq. benzaldehyde; (e) 4eq. benzaldehyde. Scale bar is $10 \mu m$.



Section G. Thermo-gravimetric Analysis (TGA)

Figure S12 Thermo-gravimetric analysis of TAPB-PDA COFs with different equivalents of benzaldehyde added. (a) without benzaldehyde; (b) 1 eq. benzaldehyde; (c) 3 eq. benzaldehyde; (d) 6 eq. benzaldehyde; (e) 9 eq. benzaldehyde.



Figure S13 Thermo-gravimetric analysis of TAPB-TFPA COFs with different equivalents of benzaldehyde added. (a) without benzaldehyde; (b) 1 eq. benzaldehyde; (c) 2 eq. benzaldehyde; (d) 3 eq. benzaldehyde; (e) 4 eq. benzaldehyde.

Section H. Statistics of FWHM for both TAPB-PDA COFs and TAPB-TFPA COFs

Samples	FWHM (deg)	Samples	FWHM (deg)
TAPB-PDA 0 eq.	0.34	TAPB-TFPA 0 eq	0.28
TAPB-PDA 1 eq.	0.30	TAPB-TFPA 1 eq	0.26
TAPB-PDA 3 eq.	0.25	TAPB-TFPA 2 eq	0.24
TAPB-PDA 6 eq.	0.23	TAPB-TFPA 3 eq	0.23
TAPB-PDA 9 eq.	0.19	TAPB-TFPA 4 eq	0.22

Table S1 FWHM (100 peak) of TAPB-PDA COFs and TAPB-TFPA COFs

Section I. Atomistic coordinates

Atomistic coordinates for TAPB-PDA COF. Space group: *P*6/M; a = 37.4627Å, b = 37.4627Å, and c = 3.6567Å. $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$.

Atom	x/a	y/b	z/c
Н	0.75892	0.44265	0
Н	0.76753	0.33184	0
Н	0.83448	0.48392	0
Н	0.84166	0.37282	0
Н	0.40934	0.70905	0
Н	0.41298	0.5098	0
Н	0.52951	0.57624	0
Н	0.42397	0.45402	0
С	0.77643	0.42661	0
С	0.7813	0.36524	0
С	0.81913	0.45035	0
С	0.82395	0.3887	0
С	0.75597	0.38322	0
С	0.84407	0.43213	0
С	0.35263	0.71033	0
С	0.37596	0.69046	0

С	0.4461	0.53349	0
С	0.51714	0.543	0
С	0.47402	0.51709	0
С	0.45746	0.47399	0
Ν	0.45913	0.57251	0

Atomistic coordinates for TAPB-TFPA COF. Space group: *P3; a* = 23.4887Å, *b* = 23.4887Å, and c = 3.8004Å. $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$.

Atom	x/a	y/b	z/c
С	0.29959	0.70131	0.92363
С	0.26383	0.63236	0.92412
С	0.40551	0.8087	0.93211
С	0.37572	0.53114	0.78608
С	0.40866	0.49588	0.80121
С	0.47047	0.52217	0.96531
С	0.49904	0.58639	0.10411
С	0.46577	0.62129	0.08886
С	0.54897	0.49538	0.16388
С	0.57806	0.4534	0.16589
С	0.54703	0.39111	0.00422
С	0.57583	0.35217	0.00714
С	0.6372	0.37348	0.1702
С	0.66814	0.43571	0.33162
С	0.63896	0.47455	0.33046
Ν	0.49842	0.48177	0.97204
Н	0.27308	0.72837	0.92577
Н	0.32873	0.51017	0.6488

Н	0.38779	0.44721	0.68279
Н	0.54701	0.6088	0.23168
Н	0.48776	0.66978	0.21059
Н	0.57309	0.53892	0.33698
Н	0.50016	0.37467	0.87216
Н	0.55061	0.30408	0.88364
Н	0.7156	0.45373	0.45707
Н	0.66341	0.5221	0.46379
N	0.66667	0.33333	0.17031