Supporting Information

Synthesis of Vinylene-Linked Covalent Organic Frameworks from Acetonitrile: Combining Cyclotrimerization and Aldol Condensation in One Pot

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Section S1: Materials, instruments and methods:

Materials:

All reagents and solvents used for the synthesis were commercially available and used without further purification. Anhydrous acetonitrile (99.9 %), anhydrous chloroform (99.9 %), anhydrous methanol (99.9 %) and mesitylene (> 98 %) were purchased from Sigma Aldrich Chemicals. The precursors such as 4,4'-biphenyldicarboxaldehyde (BPDA) (TCI chemicals, 99 %) and terepthalaldehyde (TA) (Sigma Aldrich, 99 %), 1,3,5-tris(4-formylphenyl)triazine (TFPT) (Ambinter, 98 %) were purchased and used as received. 1,3,5-tris(4-formylphenylphenyl)benzene (TFPB) was synthesized following a reported procedure.¹

Instruments and methods:

NMR measurements:

Time dependent ¹H NMR experiments were carried on a Bruker Avance II (400 MHz) spectrometer. ¹H and ¹³C NMR of model compound and other small molecules were performed on a Bruker Avance II (200 MHz) spectrometer. Solid state ¹³C cross-polarization total-sideband suppression (CP-TOSS) NMR spectroscopy analyses were performed on JEOL ECZ600 S (600 MHz) spectrometer.

Fourier transform infrared spectroscopy (FT-IR) analyses:

Fourier transform infrared spectroscopy (FTIR) analyses of the samples were carried out on a Varian 640IR spectrometer equipped with an ATR cell.

Thermogravimetric Analysis (TGA):

Thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/DSC1 Star System analyzer under nitrogen atmosphere at a heating rate of $5 \,^{\circ}\text{C}\cdot\text{min}^{-1}$ within the temperature range of $25 - 800 \,^{\circ}\text{C}$.

Powder X-ray diffraction (PXRD) analysis:

Powder X-ray diffraction data was collected on a Bruker D8 Advance diffractometer in reflection geometry operating with a Cu K α anode ($\lambda = 1.54178$ Å) operating at 40 kV and 40 mA. Samples were ground and mounted as loose powders onto a Si sample holder. PXRD patterns were collected from 2 to 60 2 θ degrees, with a step size of 0.02 degree and an exposure time of 2 seconds per step.

Physisorption measurements:

Low pressure nitrogen (N₂) and argon (Ar) physisorption isotherms were measured volumetrically at 77 K and 87 K up to 1 bar using an Autosorb-IQ-MP from Quantachrome equipped with a Quantachrome CryoCooler for temperature regulation. Prior to the measurement, the samples were dried under a dynamic vacuum ($<10^{-3}$ Torr) at room temperature (RT) followed by heating 120 °C for 24 h. Surface areas were calculated from the N₂ isotherms using the Brunauer-Emmett-Teller (BET) method. Isotherm points chosen to calculate the BET surface area were subject to the three consistency criteria detailed by Rouquerol.² The pore size distributions of COF-701 and V-COF-1 were calculated from high-resolution Ar adsorption isotherms by quenched solid density functional theory (QSDFT) using the cylindrical pore for carbon adsorbents.

Scanning electron microscopy:

Scanning electron microscope (SEM) analyses of COF samples were performed on a S-2700 scanning electron microscope (Hitachi, Tokyo, Japan).

Section S2: In-situ NMR study and synthetic procedures

An NMR tube was charged with CD_2Cl_2 (0.10 mL, 15 % v/v) and anhydrous acetonitrile (0.16 mL, 3 mmol) under argon. The mixture was cooled to 0 °C before TfOH (0.5 mL, 6 mmol) was added. The tube was sealed with a rubber cap under argon and a ¹H NMR spectrum was collected every 10 minutes.



Figure S1: ¹H-NMR spectrum of an acetonitrile : TfOH (1 : 2) mixture in CD_2Cl_2 collected at t = 0 min (i.e. NMR spectrum was recorded just after adding TfOH in acetonitrile in CD_2Cl_2).



Figure S2: Yield of formation of protonated TMT-tautomers *in-situ* as a function of time from NMR studies.

Synthesis of 1H,3H-2,4,6-trimethyl-1,3,5-triazinium triflate (TMT-triflate Salt):

Anhydrous acetonitrile (0.16 mL, 3 mmol) and TfOH (0.50 mL, 6 mmol) were mixed under inert atmosphere at 0 °C. The solution was allowed to warm up to room temperature and react for 1 hour. Subsequently, diethyl ether was added and the mixture was stirred until a white precipitate was obtained (Yield ≈ 20 %). The solid was recrystallized from a 1:1 methanol: diethyl ether mixture. IR spectra of the isolated salt matched with the literature report.³



Figure S3: Chemical structure of TMT-triflate salt⁴

Synthesis of 2,4,6-tristyryl-1,3,5-s-triazine (model compound):



Figure S4: Chemical structure of 2,4,6-tristyryl-s-triazine (TST).

A pyrex tube was charged with anhydrous acetonitrile (0.16 mL, 3 mmol) under argon flow and cooled to 0 °C. TfOH (0.5 mL, 6 mmol) was added in the tube at 0 °C and the reaction mixture was allowed to warm up to room temperature and react for 1 hour. Benzaldehyde (6 eq, 0.12 mL, based on acetonitrile trimerization yield) and a 1 : 1 methanol : acetonitrile mixture (1.5 mL) were added. After 3 freeze-pump thaw cycles, the tube was cut maintaining a length of approximately 10 cm and kept in an oven at 120 °C for 1 day. After 1 day, crystalline precipitate appeared in the side of the tube walls. The tube was cooled down to room temperature and the reaction mixture was added to an ice-water : ammonia solution to neutralize the excess acid. The off-white precipitate was recovered and washed with cold methanol and then dried under air. Purification by column chromatography (hexane / DCM, 1/4) allowed to isolate the pure compound as a white solid (isolated yield: 80 %, based on acetonitrile trimerization yield).

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.30 (d, J = 15.9 Hz, 3H), 7.73–7.68 (m, 6H), 7.48–7.37 (m, 9H), 7.19 (d, J = 15.9 Hz, 3H)

¹³C NMR (100 MHz, CDCl₃): δ [ppm] = 171.0, 142.2, 135.4, 130.06, 128.9, 128.2, 125.8

Note: Reactions with TfOH are exothermic; therefore, addition of TfOH is generally performed after cooling the reaction mixture to 0 °C.

Possible mechanism of the acid catalyzed trimerization and subsequent aldol condensation:



Scheme S1: Illustration of the possible reaction mechanism of cyclotrimerization of acetonitrile and subsequent Aldol condensation with an aryl aldehyde under acidic condition.

Synthesis of COF-701: A pyrex tube was charged with anhydrous acetonitrile (0.16 mL, 3 mmol) under argon flow and cooled to 0 °C. TfOH (0.5 mL, 6 mmol) was added in the tube at 0 °C and the reaction mixture was allowed to warm up to room temperature and react for 1 hour. 4,4'-biphenyldicarboxaldehyde (BPDA) (1.5 eq, 0.3 mmol, 63 mg; calculated based on a 20 % acetonitrile trimerization yield which corresponds to the formation of 0.2 mmol of protonated TMT tautomers) and a 1 : 1 methanol : acetonitrile mixture (1.5 mL) were added. After 3 freeze-pump thaw cycle, the tube was cut maintaining a length of approximately 10 cm and kept in an oven at 120 °C for 3 days. The collected dark red solid solid was filtered and washed with acetone and methanol before a neutralization step with a dilute ammonia solution (5 %) during which the powder turned yellow. After Soxhlet extraction with methanol overnight and vacuum drying at 100 °C, COF-701 was obtained as fluffy yellow powder.

Isolated yield: 91 %, Elemental analysis for C_9H_6N : Calcd. C 84.35 %, H 4.72 %, N 10.93 %, Found C 79.24 %, H 4.64 %, N 12.23 %, reported⁵ 78.95 %, H 5.42 %, N 11.00 %.

Entry No.	Solvents	Temp	Time (days)	Observation
		(0)	(uays)	
COF-701-1	Mesitylene/ dioxane (1:1)	150	3	Amorphous black residue
COF-701-2	Mesitylene/ dioxane (1:1)	120	3	Amorphous brown residue
COF-701-3	Mesitylene	150	3	Amorphous black residue
COF-701-4	o-dichlorobenzene	150	3	Amorphous brown residue
COF-701-5	<i>o</i> -dichlorobenzene/ dioxane (1.1)	150	3	Amorphous black residue
COF-701-6	Dioxane	150	3	Amorphous black residue
COF-701-7	Dioxane	40	3	Amorphous red precipitate
COF-701-8	Mesitylene: THF (1:1)	RT	1	THF polymerizes
COF-701-9	Chloroform	RT	1	Amorphous red polymer
COF-701-10	DCM	RT	3	Amorphous red polymer
COF-701-12	МеОН	RT	3	Amorphous red polymer
COF-701-13	МеОН	40	3	Amorphous red polymer
COF-701-14	MeOH	100	1	Weakly crystalline powders
COF-701-15	MeOH	120	3	Weakly crystalline powders
COF-701-16	MeOH/ Mesitylene (1:1)	120	3	Weak crystalline powders
COF-701-17	MeOH/ Mesitylene (1:1)	150	3	Weak crystalline powders
COF-701-18	Acetonitrile	120	3	Weak crystalline powders
COF-701-19	MeOH/ acetonitrile (1:1)	100	3	Weak crystalline powders
COF-701-20	MeOH/ acetonitrile (1:1)	120	3	Crystalline powder
COF-701-21	MeOH/ acetonitrile (1:1)	150	3	Weak crystalline powder
COF-701-22	MeOH/ acetonitrile/mesitylene (1:1:1)	120	3	Weak crystalline powder
COF-701-23	MeOH/ acetonitrile/mesitylene (1:1:1)	120	3	Weak crystalline powder

Table S1: Brief summary of tested synthetic conditions for the formation of COF-701 in a pyrex tube.

Note 1: Reactions in methanol under solvothermal conditions at higher temperature in sealed pyrex tubes should be performed carefully. Therefore, reactions at 150 °C were carried out after the sealed tube was put inside an autoclave and partially filling the autoclave with methanol to balance the pressure.

Note 2: Methanol as a solvent plays an important role in avoiding that the trimerization reaction continues further as well as for inducing crystallinity in the polymers. Therefore, addition of methanol in optimum amount is required in order to observe the well-defined COF.

Synthesis of V-COF-1, V-COF-2 and V-COF-3 : Syntheses of V-COF-1, V-COF-2 and V-COF-3 were performed by following the procedure optimized for COF-701. V-COF-1, V-COF-2 and V-COF-3 were reticulated with terepthalaldehyde (TA) (0.3 mmol, 40 mg), 1,3,5-tri(4-formylphenyl) benzene (TFPB) (0.2 mmol, 78 mg) and 1,3,5-tri(4-formylphenyl) triazine (TFPT) (0.2 mmol, 81 mg) respectively.

Isolated yields: 87 % (V-COF-1), 87 % (V-COF-2), 83 % (V-COF-3).

Section S3: PXRD analysis of COF-701



Figure S5: Simulated PXRD patterns for the generated **hcb** models with eclipsed (blue) and staggered (red) stacking mode compared to the experimentally obtained pattern of COF-701 (black).

Section S4: Porosity analysis of COF-701



Figure S6: Pore size distribution profile of COF-701.

Section S5: Thermogravimetric analysis (TGA) of COF-701



Figure S7: Thermogravimetric analysis (TGA) of the COF-701 under N_2 flow. After an initial weight loss of approximately 2 wt% assigned to residual solvent molecules trapped within the framework, the framework remains thermally stable up to 400 °C.

Section S6: Scanning electron microscopy (SEM) of COF-701



Figure S8: Representative SEM image of COF-701.

Section S7: Structural analysis of V-COF-1



Figure S9: Stack plot comparing the FT-IR spectra of V-COF-1 (black trace), the TST model compound (red trace) and terepthalaldehyde (TA) (blue trace).



Figure S10: ¹³C CP-TOSS NMR spectrum of V-COF-1. Vinylene carbon signals are located at $\delta \sim 138.1$ ppm and 132.1 ppm. The presence of two distinct aromatic *s*-triazine carbon signals at $\delta \sim 170$ ppm and 176 ppm reveals the partial [2+2]-cycloaddition of vinylene linkages within the 2D-layers of COF-701, further corroborated by the presence of a broad signal at $\delta \sim 42$ ppm attributed to the cyclobutane moieties.

Section S8: Gas sorption analysis of V-COF-1



Figure S11: N₂ sorption isotherm of V-COF-1 measured at 77 K.



Figure S12: Pore size distribution (PSD) profile of V-COF-1.





Figure S13: Synthetic scheme and corresponding PXRD pattern of V-COF-2 and V-COF-3, revealing their predominant amorphous nature.

Section S10: FT-IR analyses of V-COF-2 and V-COF-3



Figure S14. Stack plot comparing the FT-IR spectra of V-COF-2 (black trace) and V-COF-3 (red trace). The presence of -C=C stretching band at 1630 cm⁻¹ and 1626 cm⁻¹ confirms the formation of vinylene-linkage. Furthermore a characteristic -C-N- (aromatic) stretching band, at 1507 cm⁻¹ and 1367 cm⁻¹ respectively, indicates the presence of s-triazine moieties in the framework.



Figure S15: N₂ sorption isotherms of V-COF-2 and V-COF-3 reflect the less-ordered nature of the polymer frameworks. The broad hysteresis and non-closure of the desorption curves at low pressure can be attributed to the flexibility and swelling of the organic polymers, typically seen in microporous polymer networks.^{6,7}



Figure S16: PSD profiles of V-COF-2 and V-COF-3 from N_2 sorption isotherms measured at 77 K.

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