

# 3D Anionic Silicate Covalent Organic Framework with srs Topology

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## Section S1. General methods.

Inert reactions were carried out using standard Schlenk technique or in an MBraun glovebox type MB 120 BG.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR were recorded on a Bruker Avance II 400 MHz spectrometer in the given solvent. Data are reported in the following order: chemical shift ( $\delta$ ) in ppm; multiplicities (br for broadened singlet, s for singlet, d for doublet, t for triplet, m for multiplet); coupling constants (J) in Hertz (Hz); number of protons. Elemental analyses were obtained on a Thermo FlashEA 1112 elemental analyzer. 1,2-Dimethoxybenzene (99 %), iron (III) chloride (99 %), boron tribromide (1.0 M in anhydrous dichloromethane), tetramethyl orthosilicate (98 %), methyltrimethoxysilane (98 %) and sodium methoxide (0.5 M in anhydrous methanol) were obtained and used as purchased from Sigma-Aldrich. Silica gel (for chromatography, pore size 60 Å, 230-400 mesh particle size, Sigma-Aldrich) was activated at 100 °C for 12 h under vacuum prior use. Anhydrous grade solvents were used throughout (Sigma-Aldrich and Acros).

**Procedure for ICP-AES analyses:** Between 5 and 20 mg of sample was placed in a 10 mL glass vial and digested with 5 mL 5 %  $\text{HNO}_3$  in distilled water in a microwave at 150 °C. For silicon content measurements 5 mg of sample was digested with 5 mL of diluted aqueous HF solutions in a 20 mL Teflon-lined steel autoclave at 150 °C. The solutions were then further diluted with 45 mL Millipore water. Standard solutions ranging from 5 to 20 ppm of Na and Si were prepared for the calibration curve.

**Activation of samples for gas adsorption measurements.** A 90 mg sample of SiCOF-5 was degassed at room temperature under dynamic vacuum for 12 h. The sample was backfilled with Argon and then transferred to the required vessel for gas adsorption measurements.

## Section S2. Full synthetic procedures.

**2,3,6,7,10,11-hexamethoxytriphenylene.**<sup>1</sup> An oven-dried Schlenk flask was equipped with a magnetic stir bar and charged with FeCl<sub>3</sub> (17.5 g, 108 mmol). The flask was sealed with a rubber septum and then evacuated and backfilled with Argon (this process was repeated a total of 3 times). Anhydrous dichloromethane (200 mL) was then added and 5 mL of 1,2-dimethoxybenzene (5.42 g, 39 mmol) was injected quickly to the suspension. After 2 h of stirring at room temperature, the reaction mixture was quenched with 300 mL of methanol and was allowed to settle overnight in a refrigerator. The solution was filtered and the collected solid was washed with methanol and ethanol to give a light grey powder that was dried at 60 °C overnight (3.5 g, 65 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.78 (s, 6H), 4.13 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 148.9, 123.3, 104.5, 56.2.

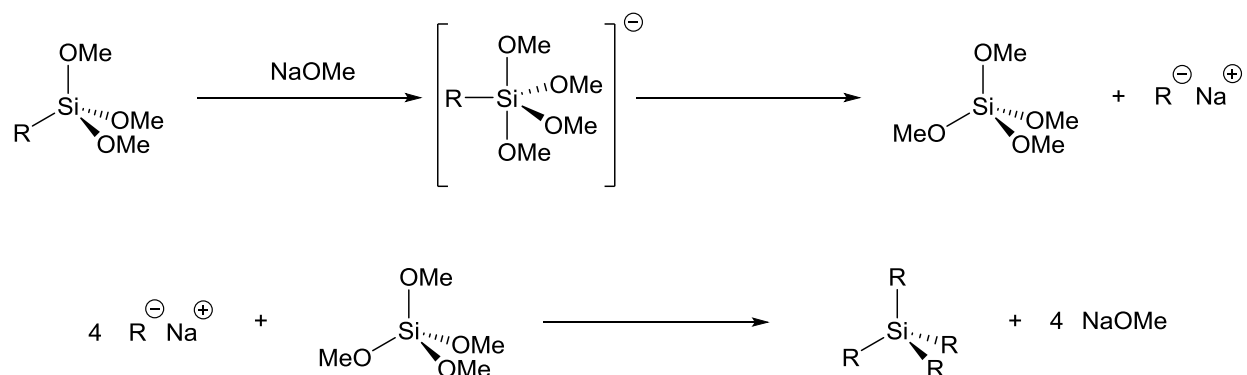
**2,3,6,7,10,11-hexahydroxytriphenylene.** An oven-dried two-neck round-bottom flask equipped with a reflux condenser and a magnetic stir bar was charged with 2,3,6,7,10,11-hexamethoxytriphenylene (1.0 g, 2.45 mmol). The flask was sealed with a rubber septum and then evacuated and backfilled with Argon (this process was repeated a total of 3 times). Anhydrous dichloromethane (40 mL) was then added and 17.2 mL of a 1.0 M boron tribromide solution in anhydrous dichloromethane (4.3 g, 17.2 mmol) was injected quickly to the suspension. After refluxing overnight, the solution was filtered and washed with water to give a light blue powder that was dried at 60 °C overnight (771 mg, 97 %). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 9.30 (s, 6H), 7.60 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 145.2, 121.8, 107.8.

**Synthesis of SiCOF-5.** A 20 mL Teflon-lined steel autoclave was charged under Argon with 2,3,6,7,10,11-hexahydroxytriphenylene (150 mg, 0.46 mmol), anhydrous methanol (7.0 mL), 3.0 mL of a 0.5 M sodium methoxide solution in anhydrous methanol (81 mg, 1.5 mmol) and 0.1 mL of methyltrimethoxysilane (94 mg, 0.69 mmol). The autoclave was sealed and placed in an oven heated at 180 °C for 4 days yielding a light blue powder which was collected by filtration under inert atmosphere, washed with anhydrous acetone and evacuated at room temperature for 12 h (165 mg, 92 %).

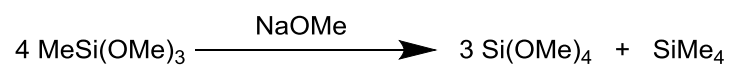
As-synthesized SiCOF-5: Anal. Calcd for C<sub>18</sub>H<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>Si·(MeOH)<sub>2.6</sub>·(Acetone)<sub>0.4</sub>: C, 52.49; H, 3.80; Na, 9.22; Si, 5.63. Found C, 52.46; H, 3.79; Na, 9.11; Si, 5.43. Air-exposed SiCOF-5: Anal. Calcd for C<sub>18</sub>H<sub>6</sub>Na<sub>2</sub>O<sub>6</sub>Si·(H<sub>2</sub>O)<sub>8.15</sub>: C, 40.10; H, 4.17; Na, 8.53; Si, 5.21. Found C, 40.97; H, 5.07; Na, 8.15; Si, 5.04.

*Note: attempts to crystallize SiCOF-5 from commercially available HHTP (TCI) were not successful.*

**Reaction mechanism of Si-C bond cleavage and methyltrimethoxysilane disproportionation under basic condition.**



Overall reaction equilibrium with methyltrimethoxysilane:



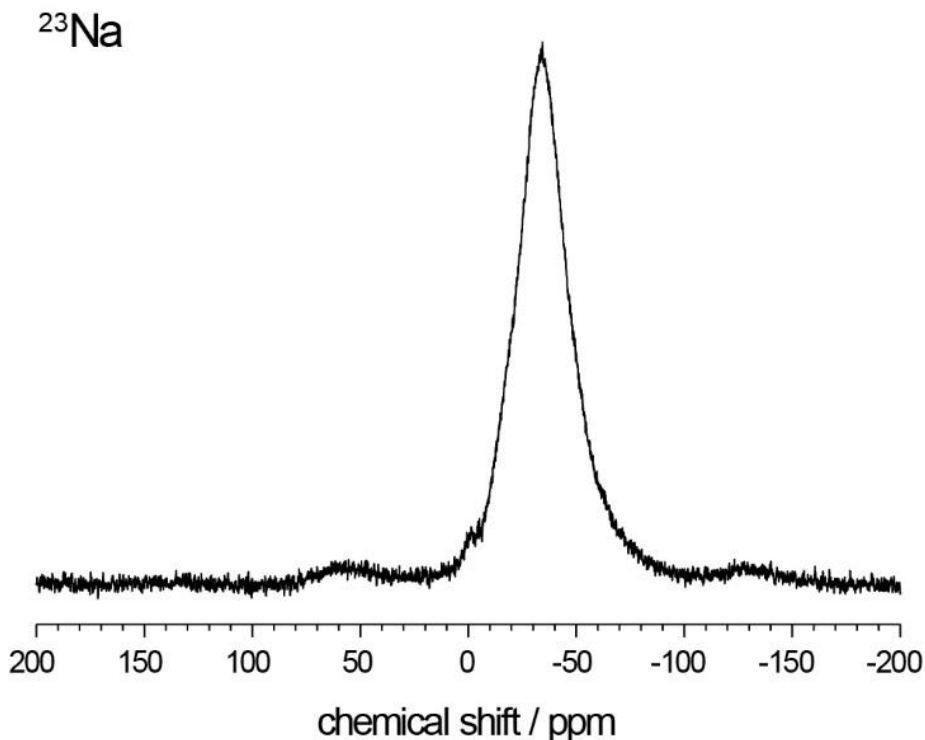
### Section S3. Nuclear Magnetic Resonance (NMR) spectroscopy.

Solid state NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 100.56 MHz for  $^{13}\text{C}$ , 79.44 MHz for  $^{29}\text{Si}$ , 105.77 MHz for  $^{23}\text{Na}$  and 399.88 MHz for  $^1\text{H}$ .  $^1\text{H}$ - $^{13}\text{C}$  and  $^1\text{H}$ - $^{29}\text{Si}$  cross polarization magic angle spinning (CP-MAS) NMR experiments were carried out at a MAS rate of 10 kHz using 4 mm MAS HX double resonance probe. The  $^1\text{H}$   $\pi/2$  pulse length was 3.1  $\mu\text{s}$  and two pulse phase modulation (TPPM) heteronuclear dipolar decoupling was used during acquisition. The spectra were measured using contact time of 2.0 ms and a recycle delay of 2 s.

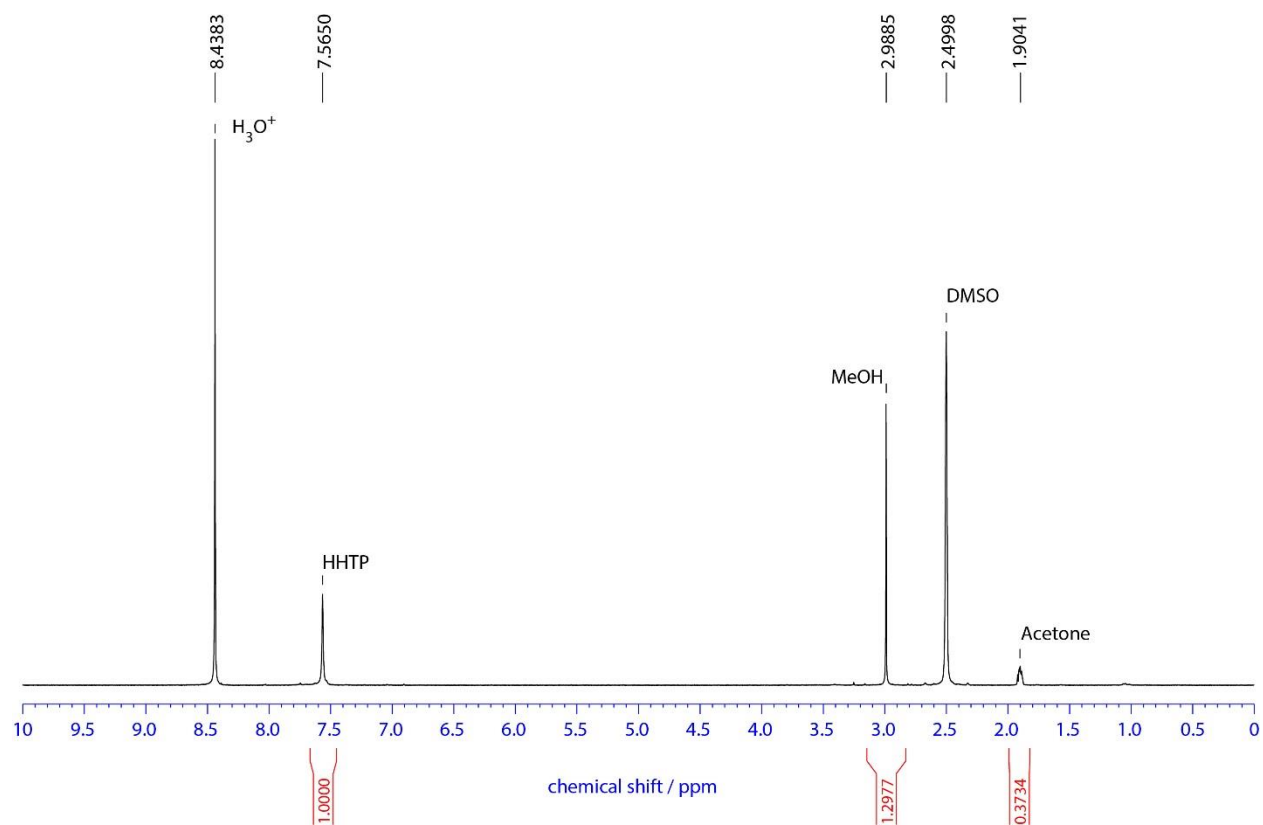
$^{23}\text{Na}$  MAS single pulse spectra were recorded using the same probe head and MAS frequency using TPPM decoupling. The  $^{23}\text{Na}$   $\pi/2$  pulse length was 2  $\mu\text{s}$  and a recycle delay of 5 s was used in acquisition.

All  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra are referenced to external tetramethylsilane (TMS) at 0 ppm for  $^{13}\text{C}$  and for  $^{29}\text{Si}$  using adamantane and tetrakis(trimethylsilyl)silane (TKS) as secondary references, respectively. All  $^{23}\text{Na}$  spectra are referenced to a 1 M aqueous solution of NaCl at 0 ppm using solid NaCl as a secondary reference.

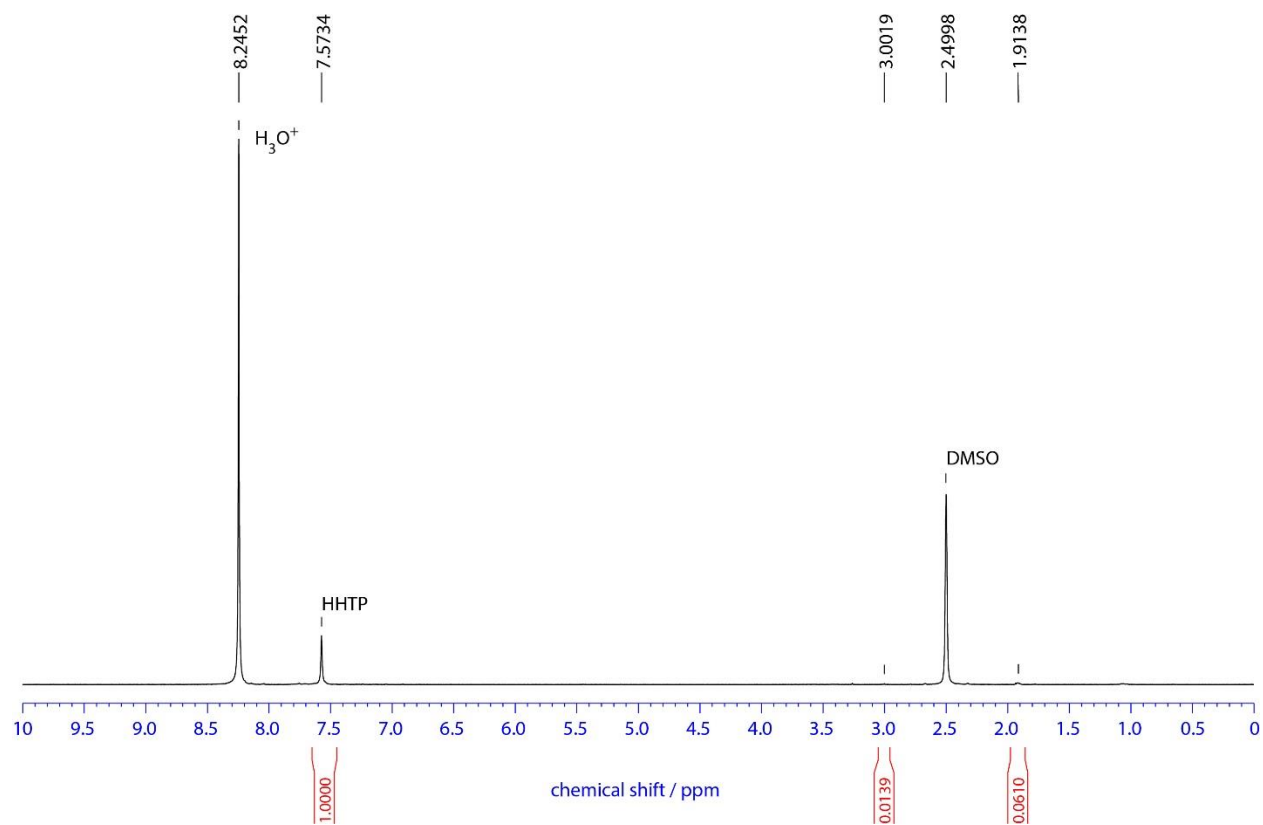
**Figure S1.**  $^{23}\text{Na}$  MAS NMR spectrum of SiCOF-5.



**Figure S2.**  $^1\text{H}$  NMR spectrum of acid digested as-synthesized SiCOF-5.



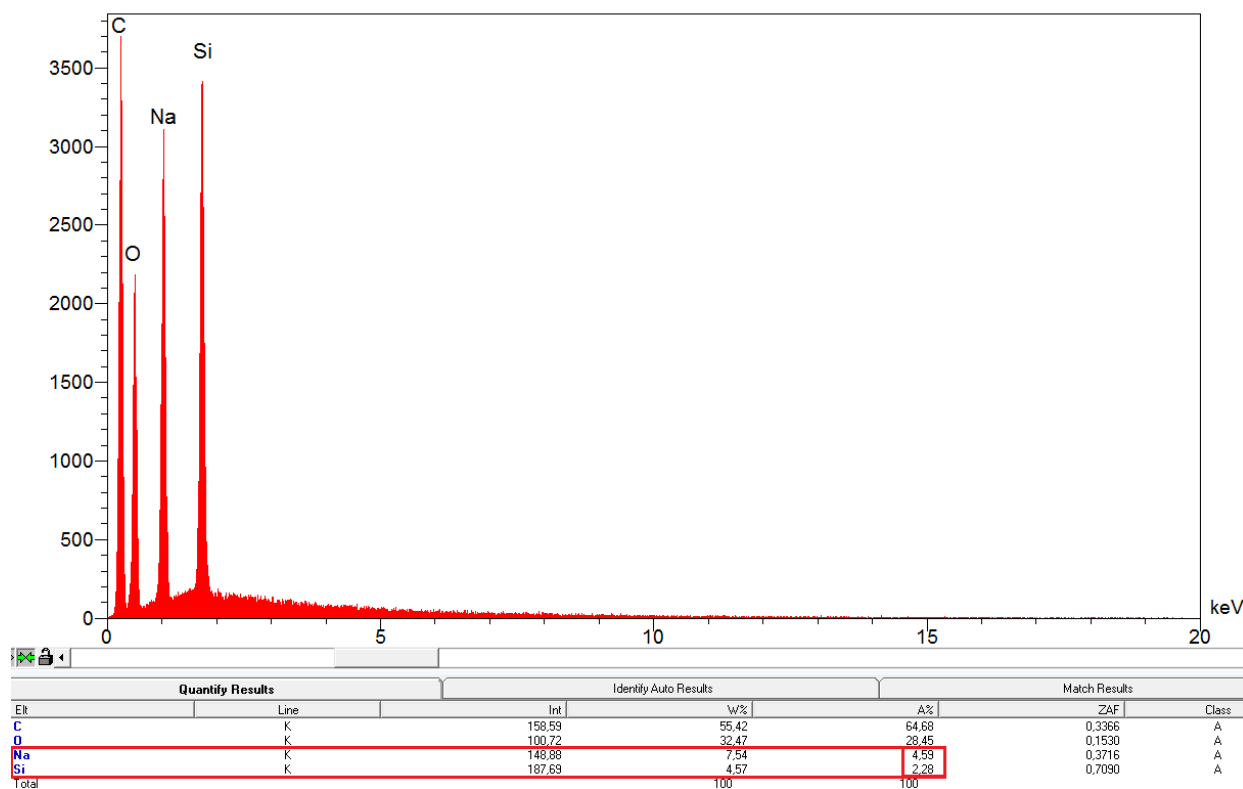
**Figure S3.**  $^1\text{H}$  NMR spectrum of acid digested air-exposed SiCOF-5.



## Section S4. Energy Dispersive X-ray (EDX) analysis and Scanning Electron Microscopy (SEM).

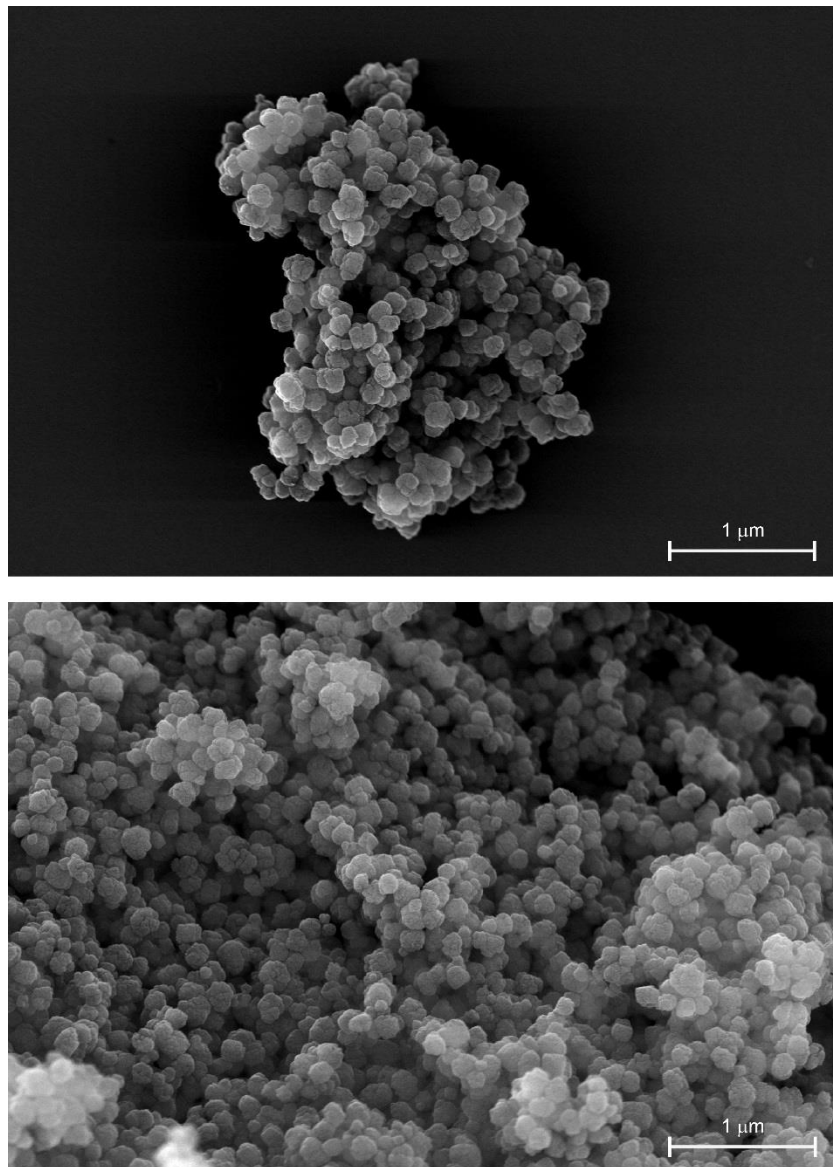
SEM images and EDX analysis were carried out on a Zeiss DSM 982 GEMINI Field and on a Hitachi S-4000 Emission Scanning Electron Microscopes (FE-SEM) equipped with an EDAX EDX-detector (Apollo XPP 10 mm<sup>2</sup>) and a SAMx EDX-detector (eumeX 30 mm<sup>2</sup> Si(Li)), respectively, which was operated in high vacuum mode using 5 to 20 kV accelerating voltage. Materials were dispersed over a sticky carbon surface adhered to a flat aluminum platform sample holder and then sputtered with gold (5 or 25 nm) in an argon atmosphere. EDX analysis was carried out without the sputtering step.

**Figure S4.** EDX analysis of SiCOF-5. The atomic percentages highlighted in red demonstrate the 2/1 Na/Si ratio.





**Figure S5.** SEM images of SiCOF-5.



## Section S5. Powder X-Ray Diffraction (PXRD) analysis and structure simulations.

Powder X-ray diffraction data was collected on a Bruker D8 Advance diffractometer at TU Berlin in reflection geometry operating with a Cu K $\alpha$  anode ( $\lambda = 1.54178 \text{ \AA}$ ) operating at 40 kV 40 mA. Samples were ground and mounted as loose powders onto a Si sample holder. PXRD patterns were collected from 3 to 40 2-theta degrees with a step size of 0.002 degrees and an exposure time of 2 seconds per step.

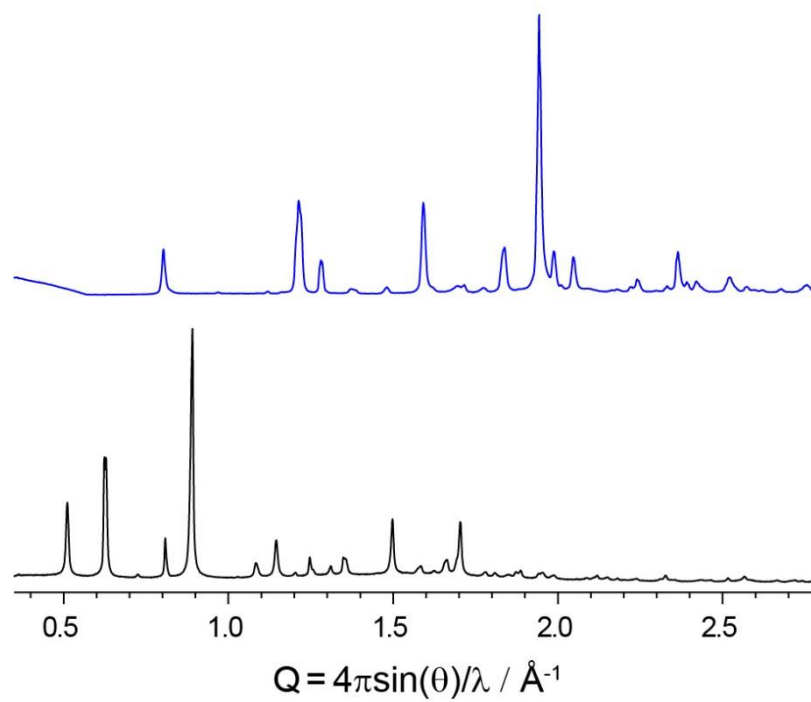
Synchrotron X-ray diffraction experiments were carried out at the high-resolution powder diffraction beamline (ID22) of the European Synchrotron Radiation Facility (ESRF). The samples were sealed in 1.0 mm thin-walled glass capillaries. High-resolution patterns were measured at a wavelength of  $0.399911(2) \text{ \AA}$  (31 keV) at room temperature and at a spinning rate of 787 rpm to ensure good sample homogeneity. Series of continuous scans -5 – 30 degrees were recorded at 10 degrees per minute, using the 9-channel Si-111 multianalyser stage, measuring data every 3 ms. 11 scans were normalized together and rebinned into steps of  $q$ .

The PXRD patterns were indexed by using the X-cell algorithm included in the *Reflex* module of *Materials Studio* v8.0.1 (Dassault Systèmes, 2014). The pattern of the as-synthesized SiCOF-5 is compatible with a cubic unit cell with a lattice constant of  $a = 17.2703 \text{ \AA}$  and the most likely extinction classes were  $P4_332$  (No. 212),  $P2_13$  (No. 198) and  $P23$  (No. 195), however, the reflection conditions are also compatible with the space group  $Pa\bar{3}$ . A structural model in the space group  $P4_332$  corresponds to a single, non-interpenetrated net and could be excluded (see Fig. S9) due to the mismatch between the experimental and simulated X-ray powder pattern. In order to construct two consistent models for both the as-synthesized and air-exposed sample which are as structurally related as possible,  $Pa\bar{3}$  would be a good candidate. However, due to the additional solvent molecules that have to be taken into account the trigonal space group  $R\bar{3}$  (No. 148) (rhombohedral representation with pseudo-cubic metric) is the more appropriate choice with more structural degrees of freedom to account for the additional electron density of the solvents molecules. After geometry optimization using the *Forcite* module implemented in *Materials Studio* employing the Universal force field (UFF)<sup>2</sup> the 16 sodium counter ions per unit cell were placed at the following positions: 1 Na at (0,0,0), Wyckoff 1a (origin, corners of the unit cells), 3 Na at ( $\frac{1}{2},0,0$ ), ( $0,\frac{1}{2},0$ ), and ( $0,0,\frac{1}{2}$ ), Wyckoff 3d (center of edges of the unit cell), 1 Na at ( $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ ), Wyckoff 1b (center of the cell), 2 Na at ( $x,x,x$ ) and ( $-x,-x,-x$ ) with  $x = 0.2943$ , Wyckoff 2c, (along the space diagonal of the cell), 6 Na at (0.2050, 0.7775, 0.2653), Wyckoff 6f (general position), and 3 Na at ( $0,\frac{1}{2},\frac{1}{2}$ ), ( $\frac{1}{2},0,\frac{1}{2}$ ), and ( $\frac{1}{2},\frac{1}{2},0$ ), Wyckoff 3e (center of faces of the cell). This last position allows to construct a model without disorder; all other positions would imply disordered positions with site occupation factors (SOF) < 1).

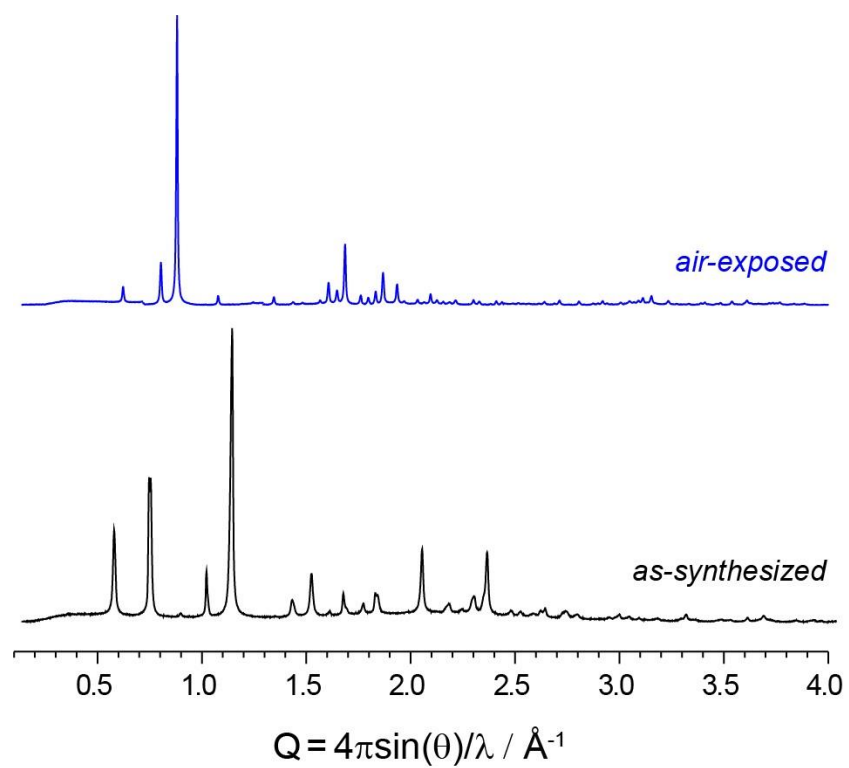
It is plausible to assume that most of the sodium ions are coordinated either tetrahedrally or octahedrally by oxygen atoms (either from the open faces of the  $\text{SiO}_6$  octahedra and/or from solvent molecules). With the exception of the sodium ions at Wyckoff position 3e, which are located right in the center between two co-planar linker moieties (assuming  $\pi$ -cation- $\pi$  interactions), this was accomplished by placing additional 20 methanol molecules at the appropriate positions. Finally, to account for the compositional analysis an additional acetone molecule was placed at the remaining void (the location was evaluated using the PLATON tool<sup>3</sup> at a general position (Wyckoff 6f) and the SOF was set to 0.5 giving 3 acetone molecules per unit cell. In total the cell content amounts to  $\text{Na}_{16}[\text{Si}_8(\text{HHTP})_8] \cdot 20 \text{ MeOH} \cdot 3 \text{ Acetone}$ .

The PXRD pattern of the air-exposed SiCOF-5 could be successfully indexed assuming the space group  $P\bar{a}3$  (No. 205) with lattice parameter  $a = 17.449 \text{ \AA}$ . The structure model was, in principle, analogously generated as described for the as-synthesized SiCOF-5 model. The sodium ion locations are as follows: 4 Na at (0,0,0), ( $\frac{1}{2}$ ,0, $\frac{1}{2}$ ), (0, $\frac{1}{2}$ , $\frac{1}{2}$ ), and ( $\frac{1}{2}$ , $\frac{1}{2}$ ,0), Wyckoff 4a, (corners and center of all faces of the cell), 4 Na at ( $\frac{1}{2}$ , $\frac{1}{2}$ , $\frac{1}{2}$ ), (0,  $\frac{1}{2}$ ,0), ( $\frac{1}{2}$ ,0, 0), and (0, 0, $\frac{1}{2}$ ), Wyckoff 4b, (center of the cell and center of the edges), and 8 Na at ( $x,x,x$ ) with  $x = 0.2733$  and symmetry-related positions, Wyckoff 8c. 48 oxygen atoms (representing 48 water molecules; H atoms were not taken into account) were placed at locations to either complete tetrahedrally or octahedrally oxygen coordination environments for the sodium ions. Additional 24 oxygen atoms were placed at a reasonable remaining void at a general position. The total unit cell content is  $\text{Na}_{16}[\text{Si}_8(\text{HHTP})_8] \cdot 72 \text{ H}_2\text{O}$ .

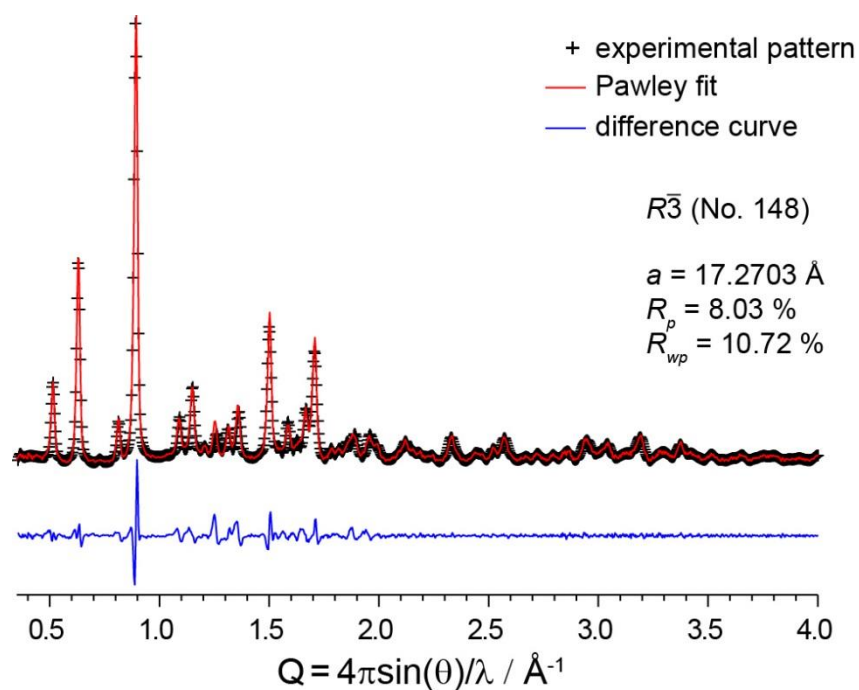
**Figure S6.** Experimental PXRD patterns of as-synthesized SiCOF-5 (black curve) and HHTP (blue curve).



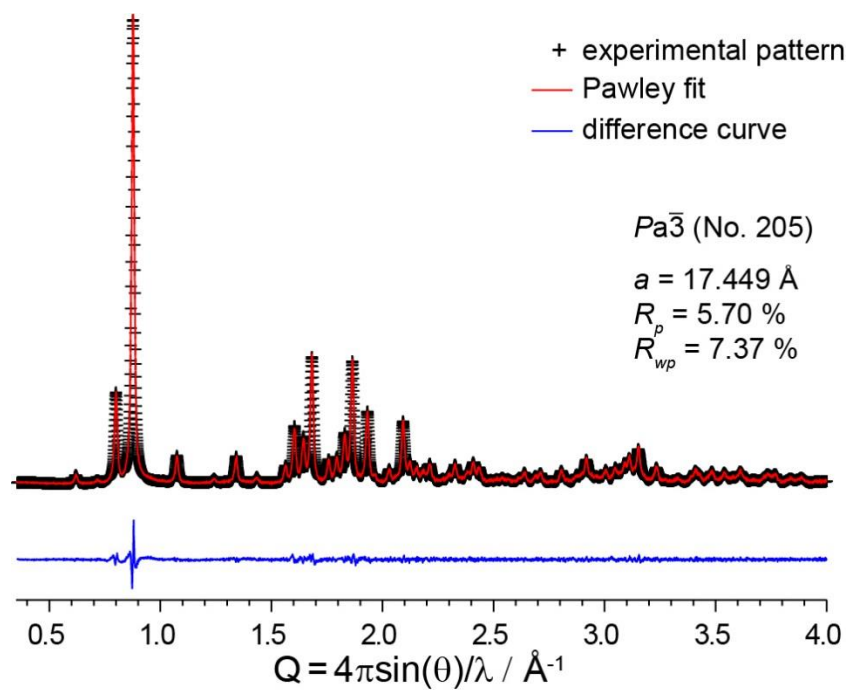
**Figure S7.** PXRD patterns of as-synthesized (black curve) and air-exposed (blue curve) SiCOF-5 showing the phase change of the framework after air exposure.



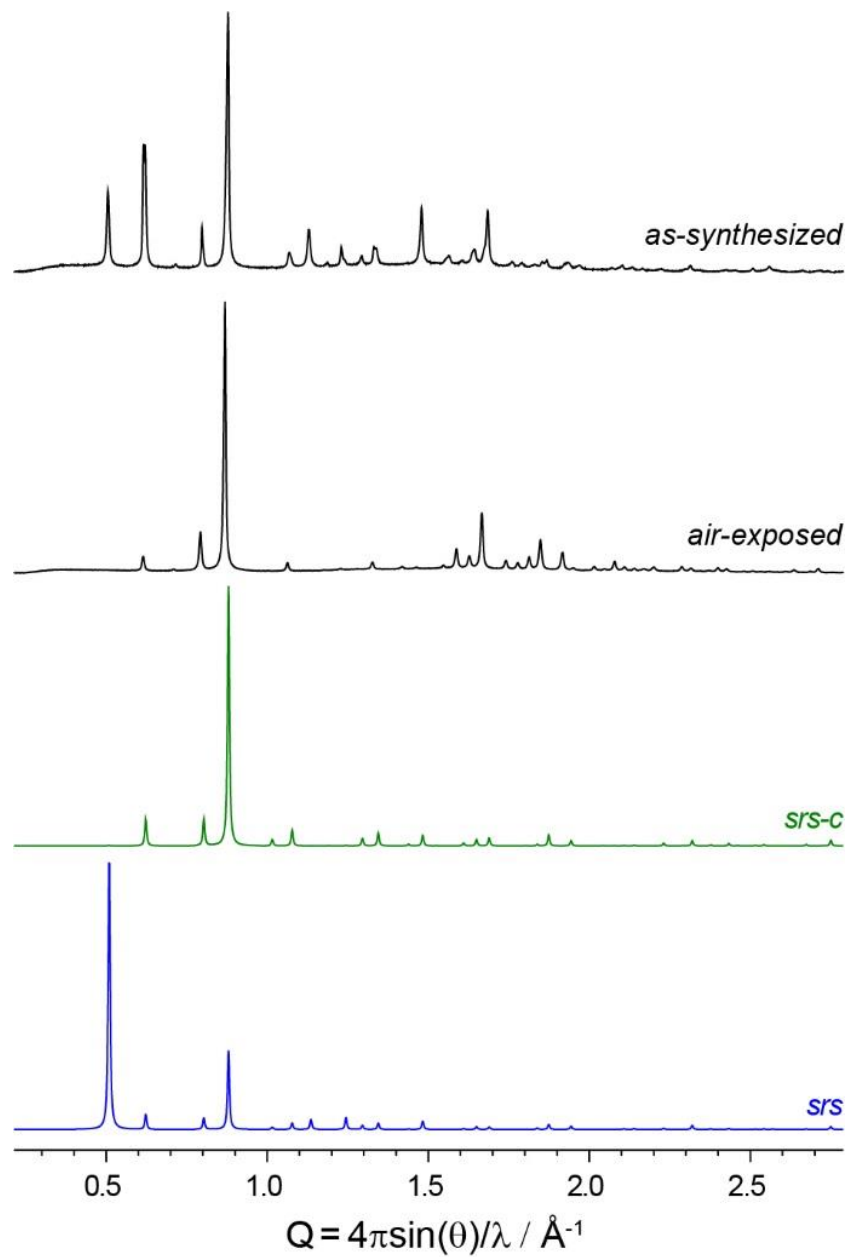
**Figure S8.** Experimental (black) and Pawley refined (red) PXRD patterns of as-synthesized SiCOF-5, the difference plot is provided in blue.



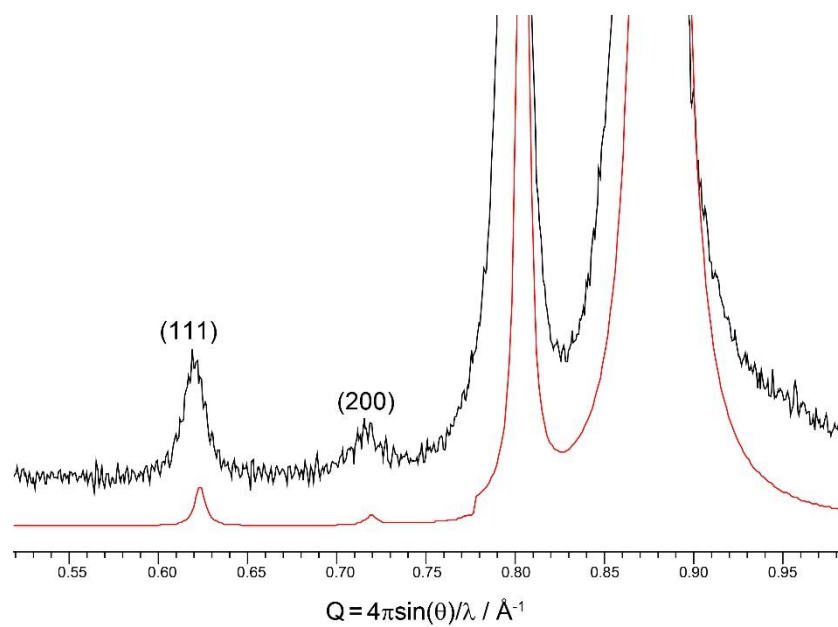
**Figure S9.** Experimental (black) and Pawley refined (red) PXRD patterns of air-exposed SiCOF-5, the difference plot is provided in blue.



**Figure S10.** Simulated X-ray diffraction patterns for the generated guest-free **srs** (blue curve) and **srs-c** (green curve) cubic models compared to the experimentally obtained patterns of as-synthesized and air-exposed SiCOF-5 (black curves).



**Figure S11.** Magnified view onto the  $Q < 1 \text{ \AA}^{-1}$  region to show the good positional and intensity ratio between the simulated and experimentally observed (111) and (200) reflections of air-exposed SiCOF-5.

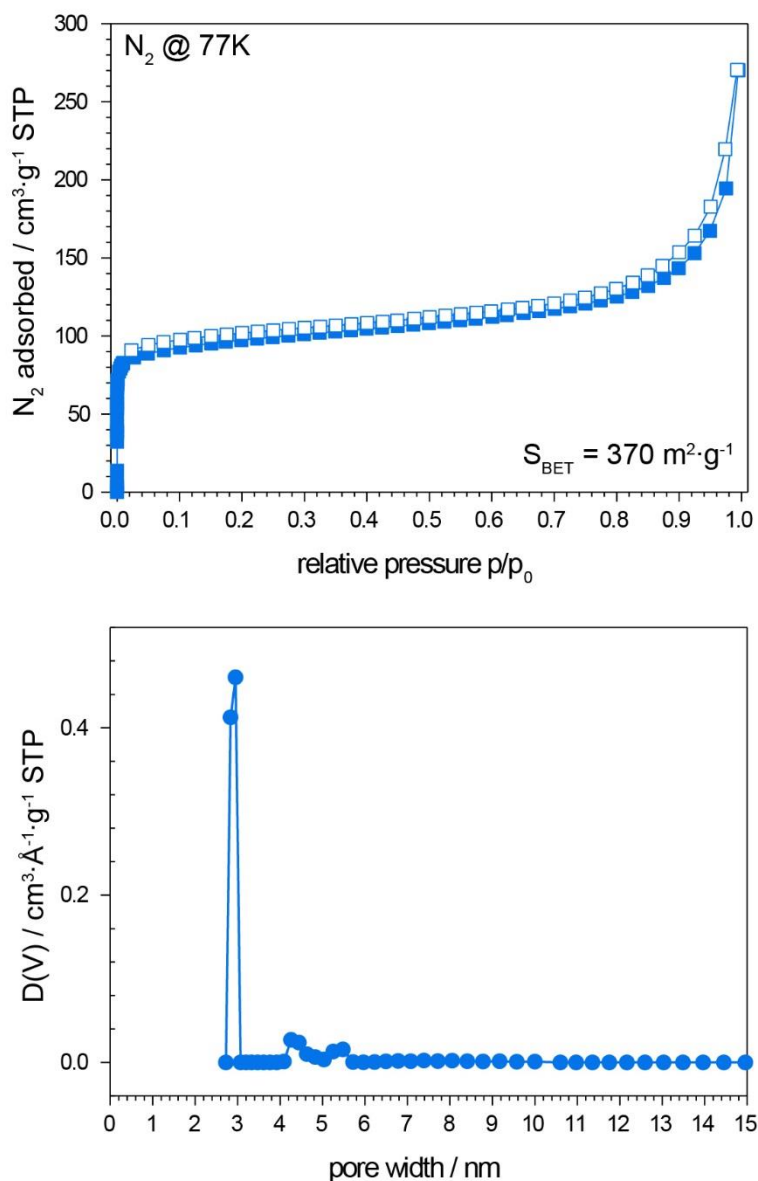




## Section S6. Low pressure gas sorption measurements.

Low pressure nitrogen 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. Isotherm points chosen to calculate the BET surface area were subject to the three consistency criteria detailed by Rouquerol.<sup>4</sup> The pore size distributions were calculated from the adsorption isotherms by quenched solid state density functional theory (QSDFT) using the slit/cylindrical pores QSDFT model for carbon adsorbents.

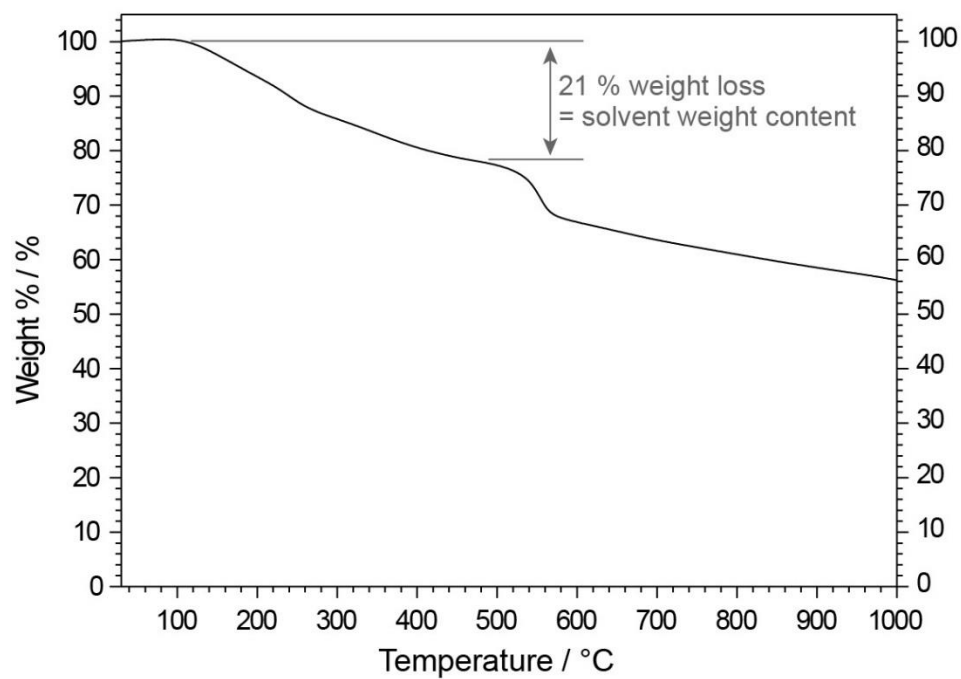
**Figure S12.** N<sub>2</sub> sorption isotherm measured at 77 K (top) and the corresponding pore size distribution profile (bottom) of SiCOF-5.



## Section S7. Thermogravimetric analysis (TGA).

Thermogravimetric analyses (TGA) data were obtained with a Mettler Toledo TGA 1 Star<sup>®</sup> thermal analyzer at a heating rate of 10 K·min<sup>-1</sup> under nitrogen flow.

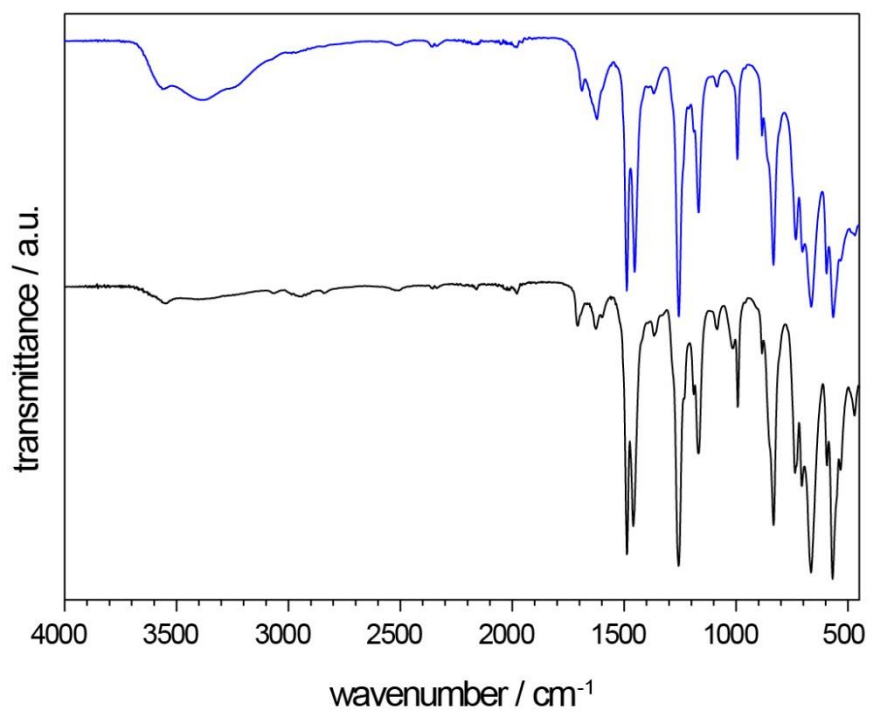
**Figure S13.** TGA trace for as-synthesized SiCOF-5.



## Section S8. Fourier Transform Infrared Spectroscopy (FTIR).

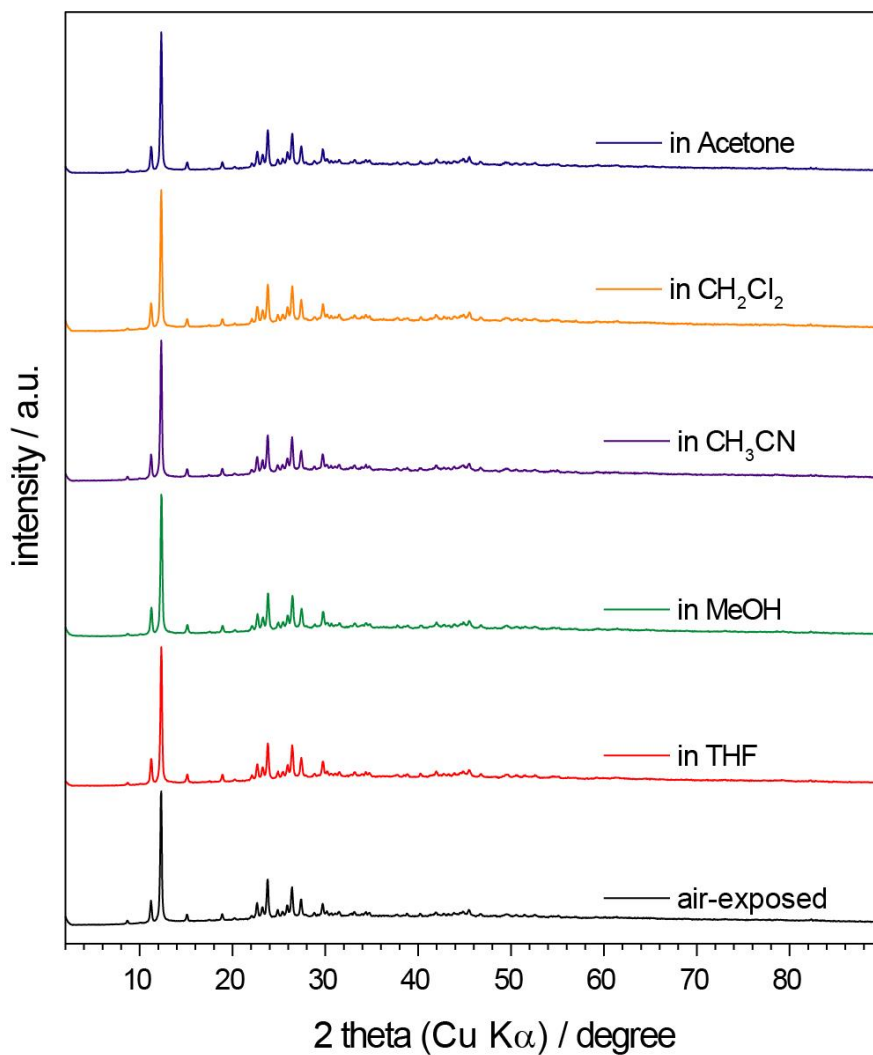
FT-IR spectra were obtained as KBr pellets or with an attenuated total reflectance (ATR) setup using a Varian 640-IR spectrometer.

**Figure S14.** Stack plot comparing the FT-IR spectra of as-synthesized (black curve) and air-exposed (blue curve) SiCOF-5.



## Section S9. Chemical stability.

**Figure S15.** The chemical stability of air-exposed SiCOF-5 was examined by immersing the sample in acetonitrile, methanol, tetrahydrofuran, acetone and dichloromethane at room temperature for 1 day. The PXRD patterns collected for these samples demonstrate that SiCOF-5 retains its crystallinity in all solvents tested.



## Section S10. References.

1. Voisin, E.;Williams, V. E., Do Catechol Derivatives Electropolymerize? *Macromolecules* **2008**, *41* (9), 2994-2997.
2. Rappe, A. K.;Casewit, C. J.;Colwell, K. S.;Goddard, W. A.;Skiff, W. M., UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, *114* (25), 10024-10035.
3. Spek, A., Structure validation in chemical crystallography. *Acta Crystallogr. Sect. D. Biol. Crystallogr.* **2009**, *65* (2), 148-155.
4. Rouquerol, J.;Rouquerol, F.;Llewellyn, P.;Maurin, G.;Sing, K. S. W., *Adsorption by Powders and Porous Solids (Second Edition)*. Academic Press, Oxford: 2014.