

Electronic Supplementary Information

A Record Ammonia Adsorption of Calcium Chloride Confined in Covalent Organic Frameworks

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Section S1. Materials and methods

2,4,6-Tris(4-amino phenyl)-s-triazine (TAPT) ($\geq 95\%$), 2,5-dimethoxyterephthalaldehyde (DMTA) ($\geq 97\%$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Organic solvents such as O-dichlorobenzene (O-DCB) (extra pure), 1-butanol (BuOH) ($\geq 99.4\%$), acetic acid (99.7+%), tetrahydrofuran (THF) ($\geq 99\%$, AR), anhydrous MeOH ($\geq 99.5\%$), N,N-dimethylformamide (DMF) ($\geq 99.5\%$), acetone ($\geq 99.5\%$), anhydrous CaCl_2 ($\geq 96\%$) and n-hexane ($\geq 99.5\%$) were purchased from Sinopharm chemical reagent Co., Ltd and used without further purification.

Power X-ray diffraction (PXRD) data were obtained with an X' Pert3 powder diffractometer at 40 kV and 40 mA with Cu K α radiation from $2\theta = 2^\circ$ to 40° in 0.05° increment. Fourier transform mid-infrared (FT-MIR) and far-infrared spectra (FIR) of the samples were collected on a Spectrum 400 spectrometer (Perkin-Elmer). Nitrogen adsorption and desorption isotherms were measured at 77 K using a ASiQwin Quantachrome instrument. The samples were treated at 150°C for 8 h before measurements. Specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Pore size distribution data were calculated based on the nonlocal density functional theory (NLDFT) model. Field emission scanning electron microscopy (FE-SEM) observations were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) and energy dispersive X-Ray spectroscopy (EDX) images were obtained on a Tecnai G2 F20 S-TWIN electron microscope. The X-ray photoelectron spectrum (XPS) was recorded on a Thermo Scientific K-Alpha electron energy spectrometer using Al K α (1486.6 eV) radiation as the X-ray excitation source.

NH_3 sorption isotherms were measured at 25.0°C and up to 1 bar of gas pressure using a gas adsorption analyzer (Beishide Instrument 3H-2000PM analyzer). Purity of ammonia gas used in measurements was 99.999% (v/v). Before sorption, approximately 50 mg of sample was loaded in the tube and activated under vacuum at 80.0°C for 10 h. Ammonia breakthrough experiments were performed by a 3P

mixSorb SHP instrument. Typically, approximately 50 mg of sample was activated at 80 °C under N₂ for 3 h and tested at an ammonia challenge content of 9000 ppm (0.9%) in N₂ with a flow rate of 40 mL/min at 50 °C.

Synthesis of TAPT-DMTA COF

A mixture of BuOH/*o*-DCB (2.5 mL/2.5 mL), 2, 4, 6-tris(4-aminophenyl)-s-triazine (141.8 mg, 0.40 mmol), 2,5-dimethoxyterephthalaldehyde (116.5 mg, 0.60 mmol), and an aqueous acetic acid solution (6 M, 0.5 mL) was degassed in a Pyrex tube (10 mL) by three freeze-pump-thaw cycles. The tube was sealed and heated at 120 °C for 3 days. The precipitate was collected by filtration, washed with THF, DMF, acetone, and MeOH, and then dried at 120 °C under vacuum overnight to give TAPT-DMTA COF in 90% yield.

Synthesis of CaCl₂@COF-x hybrids

The CaCl₂@COF-x was synthesized by slight modification of the double solvent method adopted by Xu et al ^[1] and Vaidhyanathan et al ^[2]. Taking CaCl₂@COF-34% as an example, the original COF (60 mg) was dispersed in 30 mL of n-hexane and the mixture was sonicated for about 30 min to result in a yellow dispersion. To this, a clear methanolic solution of CaCl₂ (40 mg in 0.2 mL of MeOH) was added drop by drop under vigorous stirring. The system was stirred for 12h at room temperature. The solid particles were extracted by filtration and then dried at 100 °C under vacuum for 12h. By using similar procedures, the hybrid materials with different calcium chloride loadings were prepared: CaCl₂@COF-6% (3.2 mg of CaCl₂, 60 mg COF); CaCl₂@COF-11% (6.7mg of CaCl₂, 60 mg COF) and CaCl₂@COF-26% (20 mg of CaCl₂, 60mg COF). The Ca content in each hybrid material was estimated by ICP-OES after digesting the as-made samples in H₂SO₄ at 50 °C.

Section S2. Figures S1-11

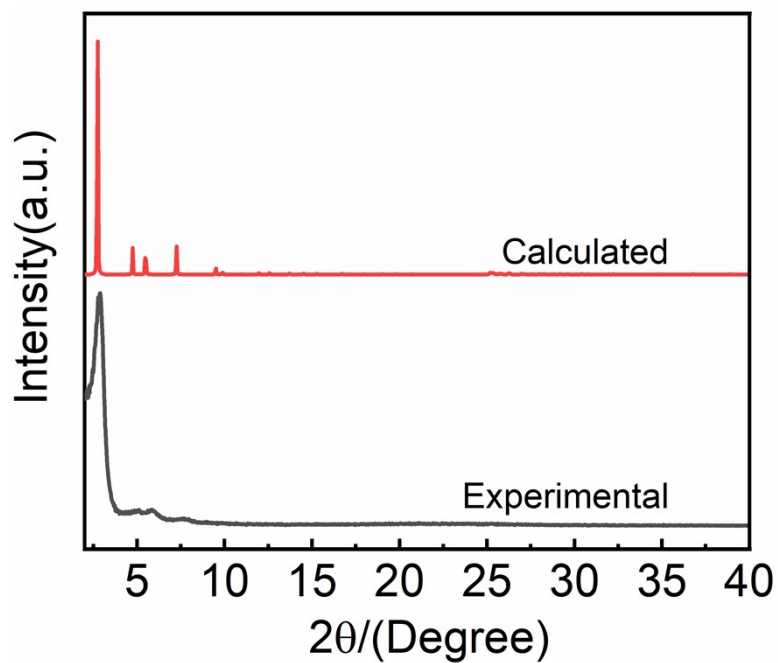


Figure S1. The experimentally observed and calculated PXRD patterns of TAPT-DMTA COF.

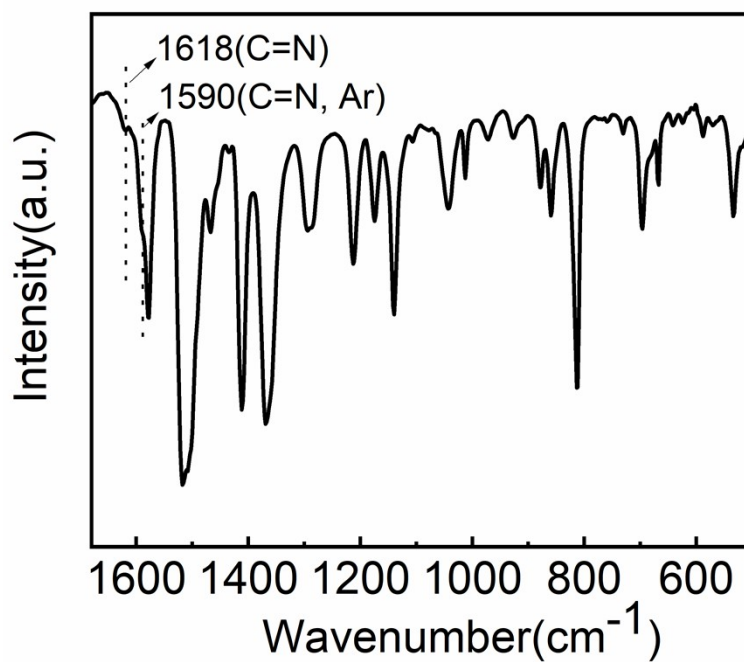


Figure S2. FT-IR spectra of the as-synthesized TAPT-DMTA COF.

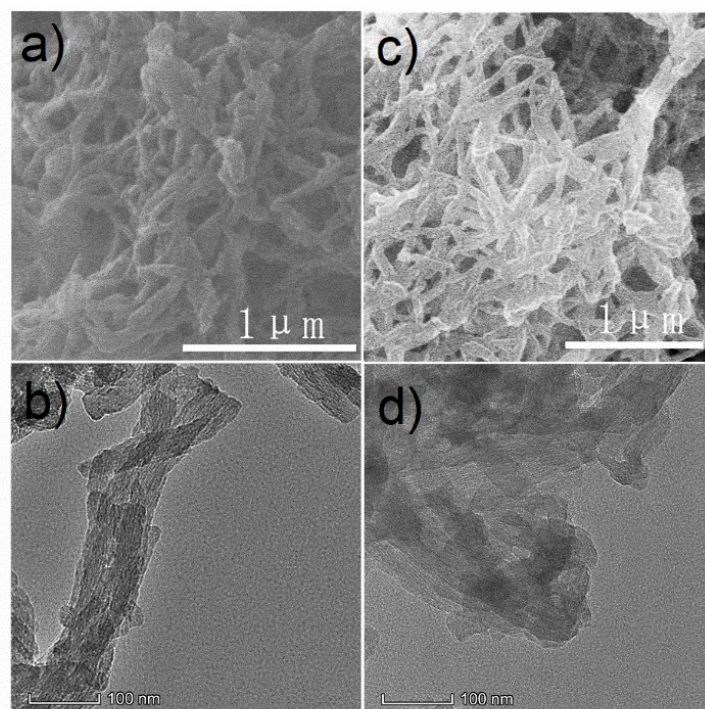


Figure S3. SEM and TEM images of the neat COF and CaCl₂@COF-34%. a) SEM image of the neat COF, b) TEM image of the neat COF, c) SEM image of CaCl₂@COF-34%, and d) TEM image of CaCl₂@COF-34%.

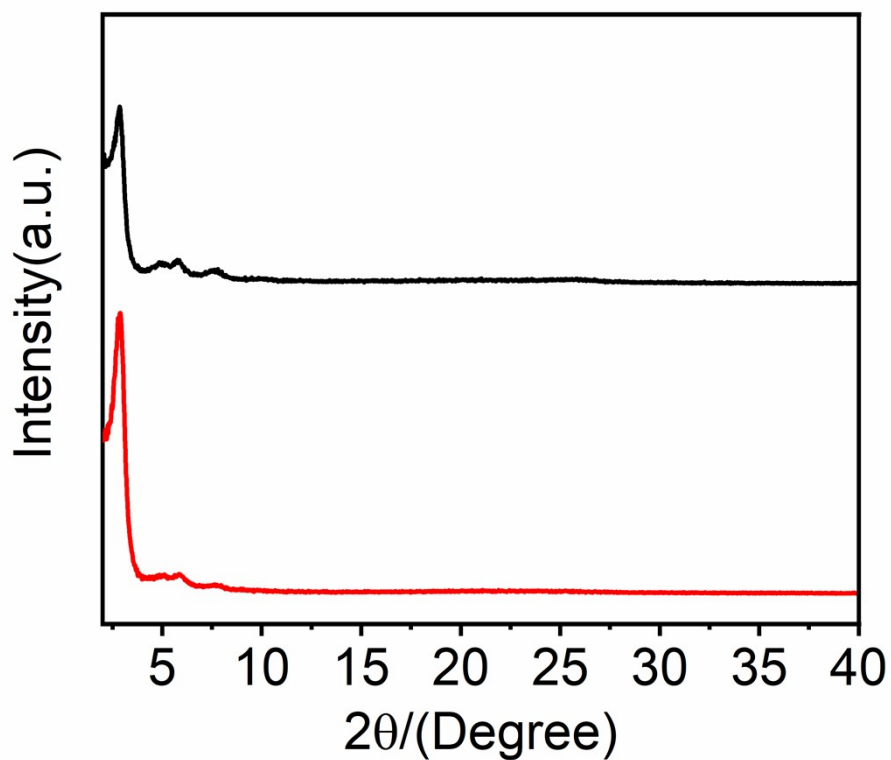


Figure S4. PXRD patterns of CaCl₂@COF-34% (black) after washing with water in comparison with that of the neat COF (red).

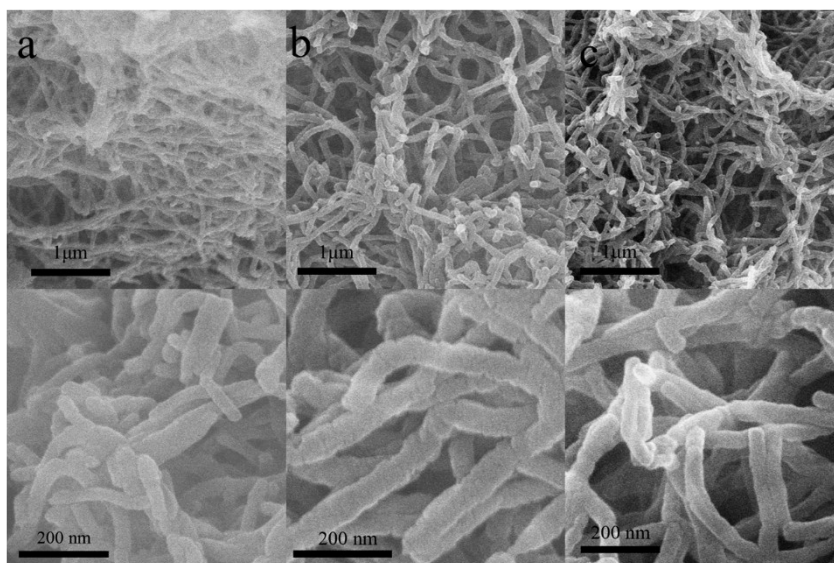


Figure S5. SEM images of the hybrid COF. a) CaCl₂@COF-6%, b) CaCl₂@COF-11%, and c) CaCl₂@COF-26%.

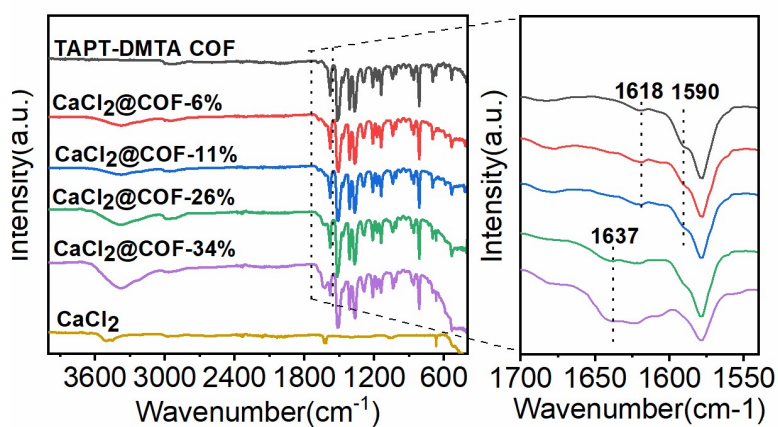


Figure S6. Mid-IR spectra of CaCl₂@COF-x (x=0, 6%, 11%, 26%, 34%, 100%).

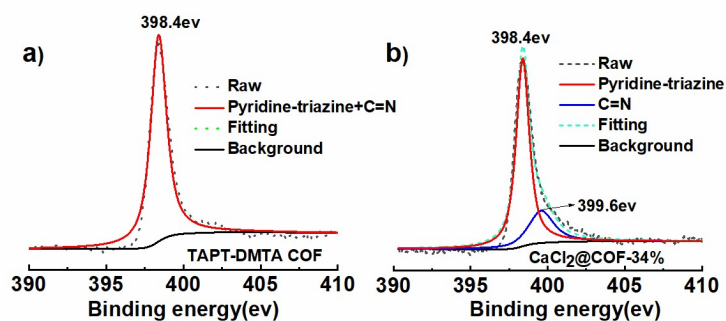


Figure S7. XPS spectra of N 1s for the neat COF and CaCl₂@COF-34%. a) neat COF, b) CaCl₂@COF-34%.

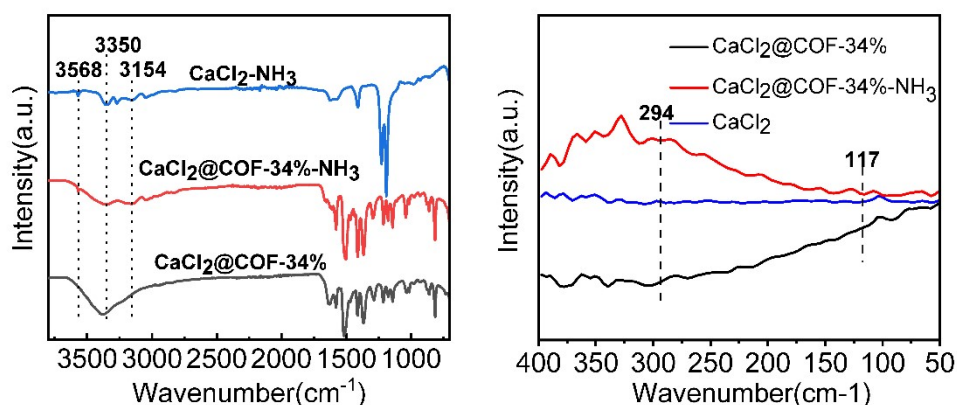


Figure S8. MIR and FIR spectra of $\text{CaCl}_2@COF-34\%$ before and after NH_3 absorption.

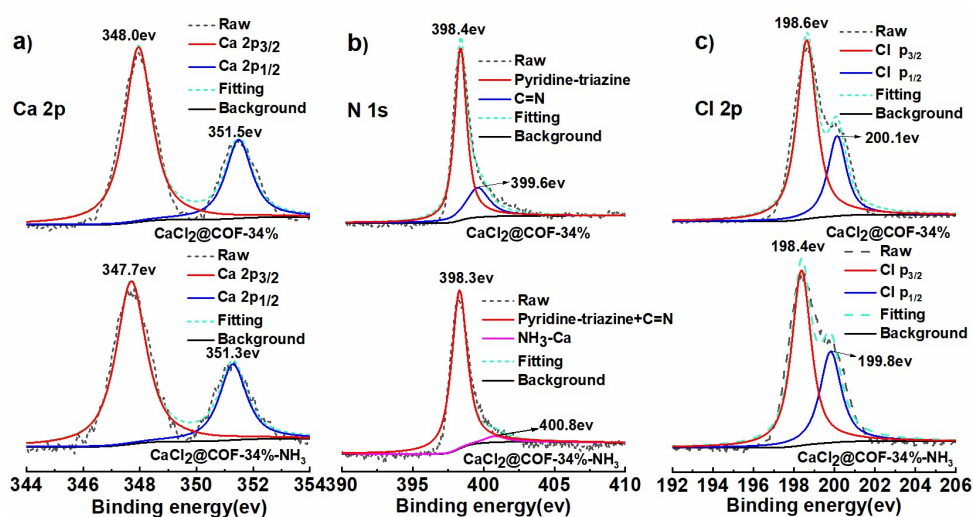


Figure S9. XPS spectra of Ca 2p, N 1s, and Cl 2p for $\text{CaCl}_2@COF-34\%$ before and after adsorption of NH_3 . a) Ca 2p, b) N 1s, and c) Cl 2p.

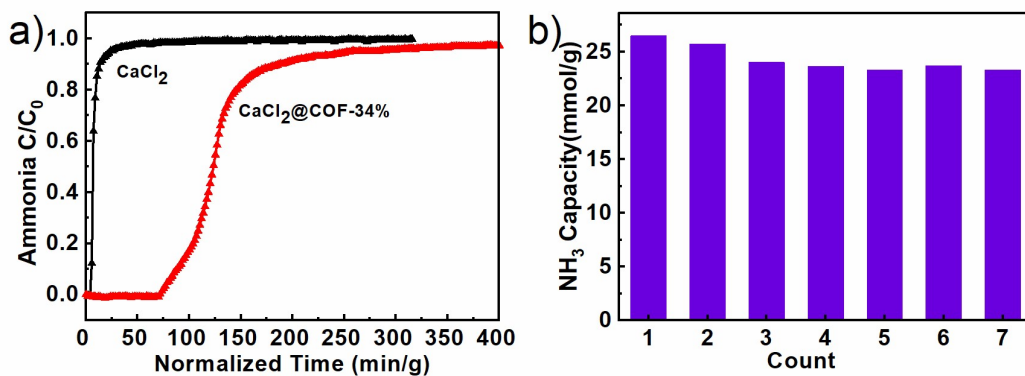


Figure S10 a). Ammonia breakthrough curves at 50 °C for CaCl₂ (black) and CaCl₂@COF-34% (red) under the NH₃ concentration of 9000 ppm with a flow rate of 40 mL/min. b). Regeneration of CaCl₂@COF-34% after NH₃ capture.

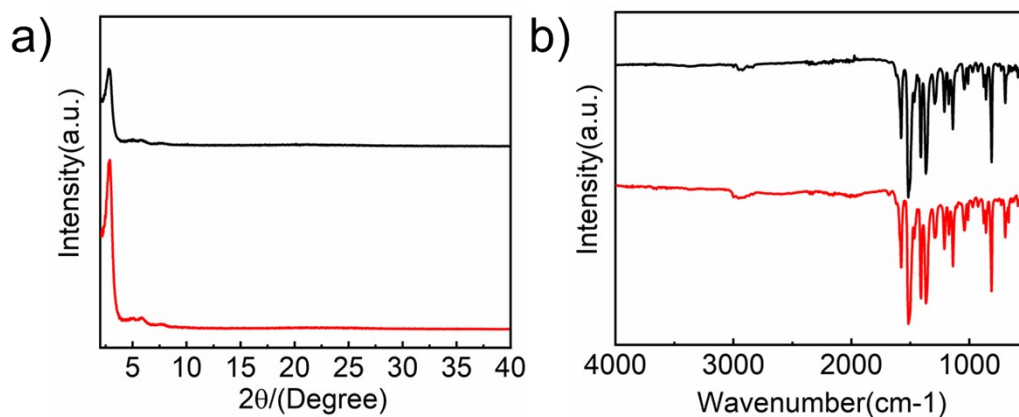


Figure S11. a) PXRD patterns and b) IR spectra of the pristine and recovered TAPT-DMTA COF. The recovered COF was obtained by washing CaCl₂@COF-34% (after 7 absorption-desorption cycles of CaCl₂@TAPT-DMTA-34% at 25 °C and 1bar) with methanol to remove CaCl₂. The black curve is for COF after washing with methanol, and the red curve is for pristine COF.

Section S3. Tables S1-3

Table S1. The Ca content, NH₃ uptake capacity at 25 °C and 1 bar, and ratio of $n(\text{CaCl}_2)$ to $n(\text{NH}_3)$ for the hybrid COFs

Sample	ICP/%	NH ₃ uptake/mmol/g	$n(\text{CaCl}_2): n(\text{NH}_3)$
CaCl ₂ @COF-6%	6.3	6.2	1/5.97
CaCl ₂ @COF-11%	11.3	8.7	1/5.93
CaCl ₂ @COF-26%	26.0	17.2	1/6.39
CaCl ₂ @COF-34%	34.2	26.5	1/7.96

$n(\text{CaCl}_2): n(\text{NH}_3) = [1000 \cdot w / M(\text{CaCl}_2)]: [\text{NH}_3 \text{ capacity (hybrid COF)} - \text{NH}_3 \text{ capacity (neat COF)} \cdot (1-w)]$, w is the mass fraction of CaCl₂ loaded in the COF.

Table S2. The BET surface area and pore volume of hybrid COFs

Sample	BET surface area/m ² /g	pore volume/cm ³ /g
CaCl ₂ @COF-6%	2127	1.864
CaCl ₂ @COF-11%	1717	1.414
CaCl ₂ @COF-26%	963	1.091
CaCl ₂ @COF-34%	240	0.654

Table S3. Summary of the top performing porous materials

Material	Material type	Capacity /mmol g ⁻¹	NH ₃ packing density /g cm ⁻³	Reference
CaCl ₂ @TAPT-DMTA-34%	Covalent organic framework composite	26.5	0.689	This work
[BOHmim][Zn ₂ C _{l₅]@MIL-101(Cr)}	Metal organic framework composite	24.12	-	3
Mg ₂ (dobpdc)	Metal organic framework	23.9	0.564	4

CoHCC	Porous dye	21.9	0.471	5
Co ₂ Cl ₂ BBTA	Metal organic framework	18.0	0.610	6
COF-10	Covalent organic framework	15.0	0.315	7
MFM-300(Al)	Metal organic framework	13.9	0.622	8
Amberlyst 15	Ion-exchange resin	11.3	0.480	9
13X zeolite	Zeolite	9.30	0.465	9
MCM-41	Mesoporous silica	7.90	0.134	9

Section S4. References

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