

Supplementary Information for

Microwave-Assisted Solvothermal Synthesis of Zirconium Oxide Based Metal-Organic Frameworks

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EXPERIMENTAL SECTION

Syntheses

Microwave Heating: Microwave syntheses of MIL-140A-MW, MIL-140B-MW and MIL-140A-NH₂-MW were conducted using an Anton Paar Monowave 300 microwave oven. A 30 mL glass microwave vial was charged with 0.25 mmol ZrCl₄ (> 99.9%, Sigma-Aldrich) and 0.5 mmol 1,4-benzenedicarboxylic acid (H₂bdc, 98%, Sigma-Aldrich), 2,6-naphthalenedicarboxylic acid (H₂ndc, 99%, Sigma-Aldrich) or 2-amino-1,4-benzenedicarboxylic acid (H₂abdc, 99%, Sigma-Aldrich). Thereafter, 0.04 mL (0.7 mmol) of acetic acid and 2.5 mL of *N,N'*-dimethylformamide (DMF) were introduced. The mixture was heated with magnetic stirring to 220 °C within 2 min, and held at this temperature for 15 min before cooling to 55 °C within 2 min. The precipitates were vacuum filtered, and repeatedly washed with DMF and acetone. The materials were subsequently solvent exchanged with methanol using a Soxhlet washing procedure for 12 h. The resulting powder was dried in air. Elemental analysis calculated for the newly synthesised framework MIL-140A-NH₂-MW ([ZrO(O₂C-C₆H₅N-CO₂)]): C, 33.54; H, 1.75; N, 4.90 %; experimental: C, 32.16; H, 1.95; N, 4.16 %.

Conventional Electric Heating. MIL-140A-CE, MIL-140B-CE and MIL-140A-NH₂-CE were synthesised solvothermally using similar methods to those reported by Serre and coworkers.¹ Typically, in a 25 mL Teflon-lined steel Parr bomb, 0.5 mmol of H₂bdc, H₂ndc or H₂abdc and 0.25 mmol of ZrCl₄ were dissolved in 2.5 mL of DMF. To this solution, 0.04 mL (0.7 mmol) of acetic acid was added (the synthesis of MIL-140A-NH₂-CE was attempted using three different amounts of acetic acid, namely, 0.04, 0.16 and 0.54 mL). The reaction vessel was sealed and placed in a pre-heated oven at 220 °C for a period of 16 h for MIL-140A-CE, 6 h for MIL-140B-CE, and both 12 and 24 h for MIL-140A-NH₂-CE. The Parr bombs were subsequently cooled to room temperature in the oven within 8 h before the precipitates were isolated by vacuum filtration and washed with DMF and acetone. The materials were subsequently solvent exchanged with methanol using a Soxhlet washing procedure for 12 h. The resulting powder was dried in air.

A summary of the reaction conditions is provided in Tables S1 and S2.

Table S1 Synthesis conditions for the frameworks using microwave heating (MW) and conventional electric heating (CE)

| Phase ^a | ZrCl ₄ ² | Ligand ² | DMF [mL] | Acetic acid [mL] | Heating method ^b | T [°C] | Time [min] | Yield [%] ^c |
|------------------------------|--------------------------------|---------------------|----------|------------------|-----------------------------|--------|------------|------------------------|
| MIL-140A-MW | 0.25 | 0.5 | 2.5 | 0.04 | MW | 220 | 15 | 91.0 |
| MIL-140A-CE | 0.25 | 0.5 | 2.5 | 0.04 | CE | 220 | 960 | 88.9 |
| MIL-140B-MW | 0.25 | 0.5 | 2.5 | 0.04 | MW | 220 | 15 | 90.3 |
| MIL-140B-CE | 0.25 | 0.5 | 2.5 | 0.04 | CE | 220 | 360 | 90.0 |
| MIL-140A-NH ₂ -MW | 0.25 | 0.5 | 2.5 | 0.04 | MW | 220 | 15 | 96.1 |

^a bdc: 1,4-benzenedicarboxylic acid, ndc: 2,6-naphthalenedicarboxylic acid, abdc:

2-amino-1,4-benzenedicarboxylic acid; ^b MW: microwave heating, temperature ramp to 220 °C within 2 min; CE: conventional electric heating, syntheses in a pre-heated oven at 220 °C; ^c based on zirconium.

Table S2 Attempted synthesis conditions for MIL-140A-NH₂ using conventional electric heating (CE)

| Entry | ZrCl ₄ ² | Ligand ² | DMF [mL] | Acetic acid [mL] | T [°C] | Time [min] | Product |
|-------|--------------------------------|---------------------|----------|------------------|--------|------------|--------------------------------------|
| 1 | 0.25 | 0.5 | 2.5 | 0.04 | 220 | 12 | UiO-66-NH ₂ ^{a3} |
| 2 | 0.25 | 0.5 | 2.5 | 0.16 | 220 | 12 | UiO-66-NH ₂ ^a |
| 3 | 0.25 | 0.5 | 2.5 | 0.54 | 220 | 12 | UiO-66-NH ₂ ^a |
| 4 | 0.25 | 0.5 | 2.5 | 0.54 | 220 | 24 | UiO-66-NH ₂ ^a |

^a MIL-140A-NH₂ was not attainable using the conventional electric heating method. The amino-tagged framework UiO-66-NH₂ was the only product obtained from each of the four attempted syntheses.³

Characterisation

Powder X-ray diffraction (PXRD). PXRD measurements were performed on a PANalytical X'pert Pro diffractometer fitted with a solid-state PIXcel detector (40 kV, 30 mA, 1° divergence and anti-scatter slits, and 0.3 mm receiver and detector slits) using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation.

Gas Sorption. N₂ sorption isotherms were measured on an Accelerated Surface Area & Porosimetry System, ASAP 2020 (Micromeritics Instruments Inc.). Prior to analysis, the materials were solvent exchanged with methanol using a Soxhlet washing procedure for 12 h. Approximately 100 mg of the powdered solid was loaded into a glass analysis tube and outgassed for 12 h under vacuum at 120 °C. N₂ adsorption and desorption isotherms were measured at 77 K and data was analysed using Brunauer-Emmett-Teller (BET) analysis models to determine the surface area.

Scanning Electron Microscopy (SEM). Field-emission SEM (FE-SEM) images were obtained using a Zeiss ULTRA plus microscope (working distance 9 mm; acceleration voltage 15 kV). Samples were prepared

by dispersing the powdered solids in ethanol to produce a suspension that was deposited onto a carbon block and dried in air.

Thermogravimetric Analysis (TGA). TGA measurements were carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyser. Approximately 5 mg of sample was placed on a platinum pan which was heated under a flow of N₂ at a rate of 1.5 °C.min⁻¹ up to 800 °C.

Elemental analyses. Elemental analyses were performed at the Chemical Analysis Facility, Macquarie University, Sydney, Australia.

RESULTS

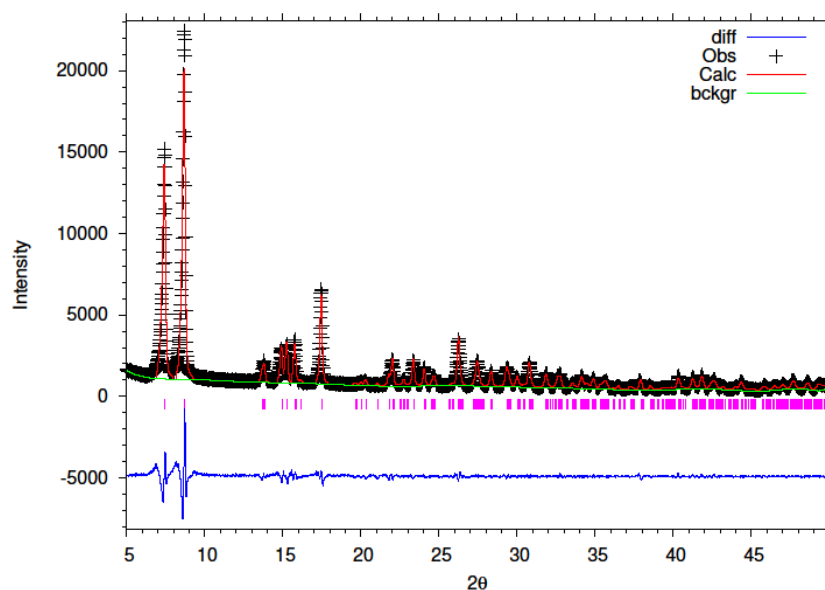


Fig. S1 Le Bail refinement of MIL-140A-MW showing the experimental (black), refined (red), and difference (blue) patterns. The positions of the Bragg peaks are indicated by the pink bars.

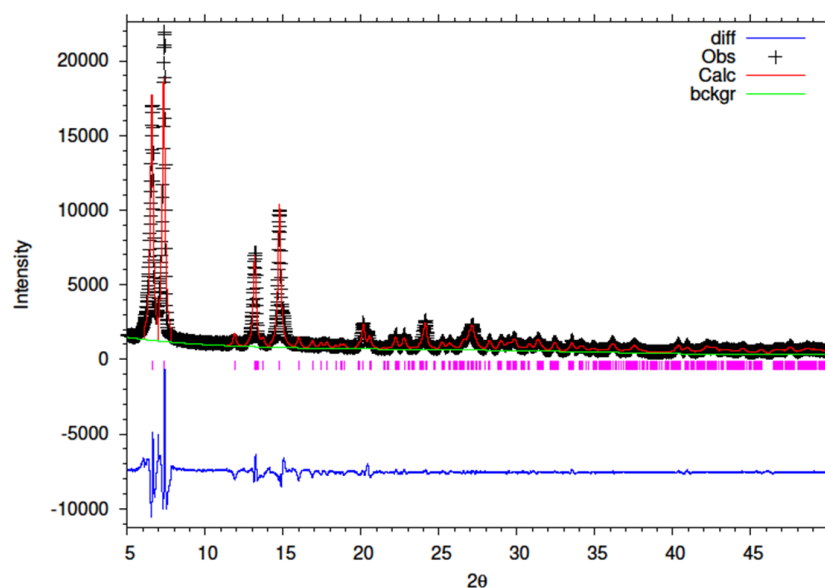


Fig. S2 Le Bail refinement of MIL-140B-MW showing the experimental (black), refined (red), and difference (blue) patterns. The positions of the Bragg peaks are indicated by the pink bars.

Table S3 Experimental and simulated Le Bail cell parameters for MIL-140A-MW and MIL-140B-MW

| Phase | Space group | a (Å) | b (Å) | c (Å) | β (Å) | V (Å ³) |
|-------------------------|-------------|-----------|-----------|----------|-------------|---------------------|
| MIL-140A _{sim} | C2/c | 24.53 | 11.24 | 7.87 | 97.71 | 2150.4 |
| MIL-140A-MW | C2/c | 24.420(1) | 11.211(1) | 7.836(1) | 103.98(1) | 2081.7(1) |
| MIL-140B _{sim} | C c | 27.65 | 13.41 | 7.85 | 90.13 | 2909.9 |
| MIL-140B-MW | C c | 26.865(1) | 13.424(1) | 7.820(1) | 93.669(1) | 2814.7(1) |

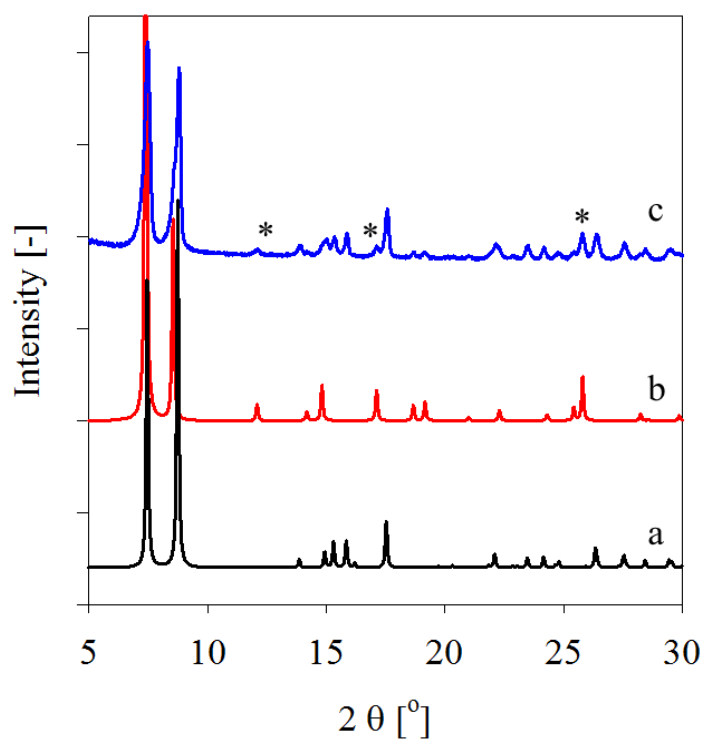


Fig. S3 Simulated PXRD patterns for (a) MIL-140A and (b) UiO-66; Experimental PXRD patterns for (c) MIL-140A-CE (target temperature: 220 °C, hold-time: 16 h, peaks marked with an asterisk indicate the UiO-66 impurity).

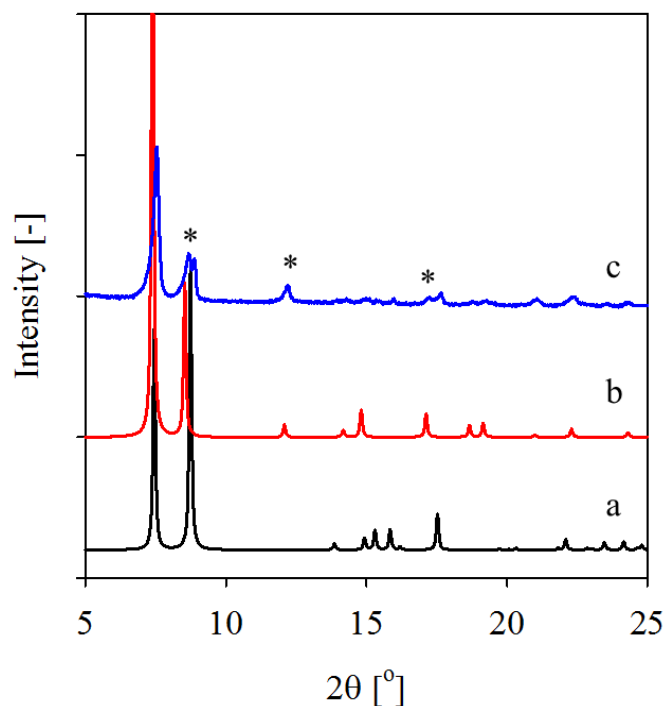


Fig. S4 Simulated PXRD patterns for (a) MIL-140A and (b) UiO-66; Experimental PXRD patterns for MIL-140A-CEa (target temperature: 220 °C, hold-time: 18 h). Peaks marked with an asterisk indicate the UiO-66 impurity which is maintained, despite the increased reaction time compared with the data presented in Fig. S3.

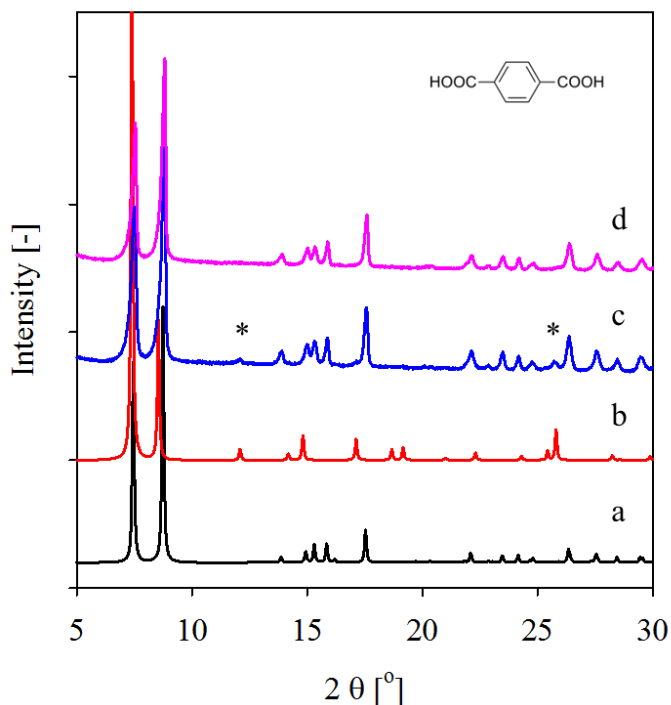


Fig. S5 Simulated PXRD patterns for (a) MIL-140A, (b) UiO-66, (c) MIL-140A-MW synthesized with a slow ramp rate (1 h to 220 °C and 15 min hold-time) in the microwave oven (peaks marked with an asterisk indicate the UiO-66 impurity) and (d) phase pure MIL-140A-MW synthesized with a fast ramp rate (2 min to 220 °C and 15 min hold-time) in the microwave oven.

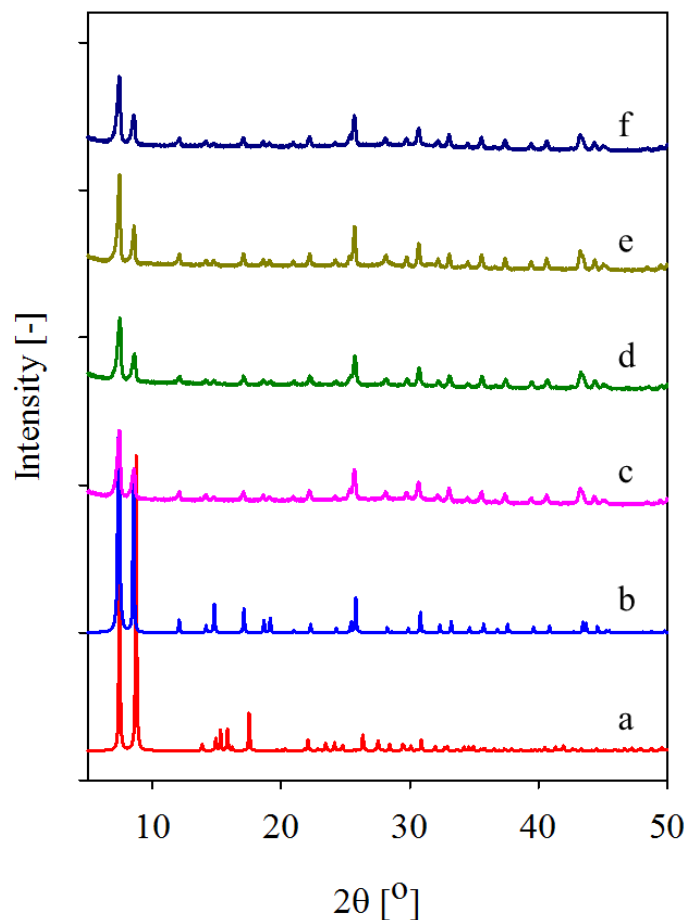
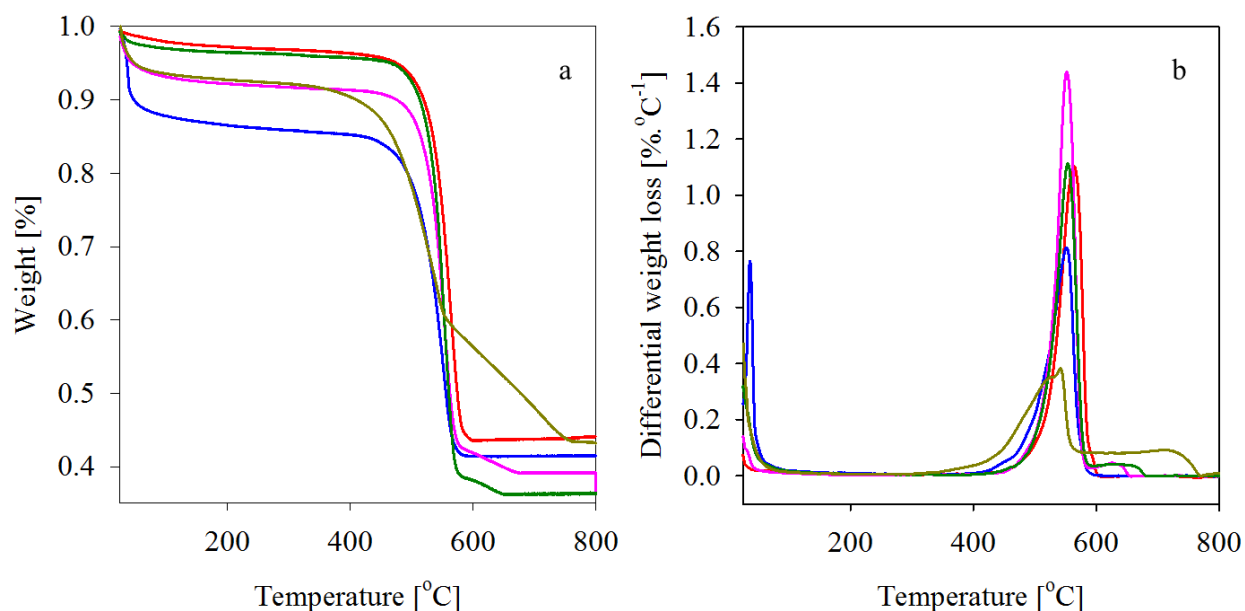


Fig. S6 Simulated PXRD patterns for (a) MIL-140A and (b) UiO-66. Experimental PXRD patterns for the products obtained from the attempted synthesis of MIL-140A-NH₂ using CE heating (different acetic acid dosage and reaction time): (a) 0.04 mL acetic acid and 12 h at 220 °C, (b) 0.16 mL acetic acid and 12 h at 220 °C, (c) 0.54 mL acetic acid and 12 h at 220 °C and (d) 0.54 mL acetic acid and 24 h at 220 °C. In each case, the product was identifiable as the UiO-66 phase.



— MIL-140A-MW — MIL-140A-CE — MIL-140B-MW — MIL-140B-CE — MIL-140A-NH₂-MW

Fig. S7 Thermogravimetric analysis (N₂ environment) showing the weight loss (a) and differential weight loss (b) for MIL-140A-MW, MIL-140A-CE, MIL-140B-MW, MIL-140B-CE and MIL-140A-NH₂-MW after solvent exchange with methanol as described in the experimental section.

Table S4 Comparison of experimental and theoretical weight losses for the series of frameworks.

| Phase | Theoretical Weight loss [%] ^a | Experimental Weight loss [%] | Reported Weight loss [%] ¹ | Decomposition Temperature [°] |
|------------------------------|--|------------------------------|---------------------------------------|-------------------------------|
| MIL-140A-MW | 54.5 | 55.8 | - | 563.9 |
| MIL-140A-CE | 54.5 | 53.0 | 51.3 | 551.9 |
| MIL-140B-MW | 61.6 | 60.1 | - | 551.9 |
| MIL-140B-CE | 61.6 | 57.9 | 58.6 | 554.0 |
| MIL-140A-NH ₂ -MW | 56.9 | 55.7 | - | 541.6 |

^a calculated from the formula for the framework.

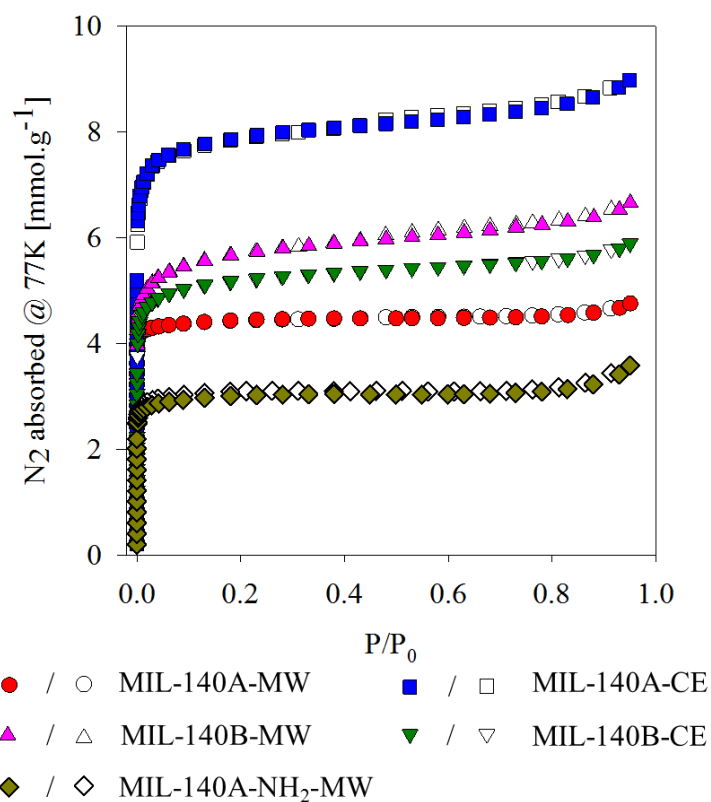


Fig. S8 N₂ adsorption (filled symbols) and desorption (open symbols) isotherms for MIL-140A-MW, MIL-140A-CE, MIL-140B-MW, MIL-140B-CE and MIL-140A-NH₂-MW at 77 K (P₀ = 1 atm., the activation procedure is described in the experimental section).

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