Electronic Supporting Information

Materials and Methods:

$Al(NO_3)_3.9H_2O$, 2-aminoterephthalic acid and acetic acid were obtained from Sigma Aldrich. Sodium acetate, sodium hydroxide and dimethylformamide were obtained from Merck. All chemicals were used as received.

General:

PXRD data for the *nanorods* and *nanoparticles* was obtained using a Bruker D8 General Area Detector Diffraction System with a graphite monochromator and Cu Kα wavelength of 1.5418 Å (40 kV, 40 mA) and a HI STAR Area Detector with a two dimensional multi wire proportional counter. A double pin-hole collimator used to control the beam size and divergence. Scanning Electron Microscopy (SEM) analysis was performed with a JEOL JSM 6360LA scanning electron microscope (tungsten source) with an accelerating voltage of 5 to 10 kV. Prior to SEM analysis, samples were sputtered with gold using a JEOL JFC-1200 Fine Coater. TEM analysis was performed with a Philips CM300 FEG TEM at 300 kV.

Nanoparticle sizes were obtained by measurement of 200 nanoparticles from their TEM images using Gatan Digital Micrograph and obtaining the average and standard deviation based on these measurements. Aspect ratios of microneedles and nanorods were obtained by measurement of 200 microneedles or nanorods respectively and dividing the length of each particle by its width. The average length of microneedles obtained is 6.2 ± 3.7 µm, average width is 0.32 ± 0.16 µm. For the nanorods, the average length is 107.5 ± 73.3 mm, average width is 15.3 ± 4.5 nm.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed on a Perkin Elmer Spectrometer. Powder samples were ground with KBr and pelletized for FTIR analysis. PXRD measurements were performed in Bragg-Brentano geometry using a Bruker D8-Advance equipped with Cu-Kα source, 2.5° primary and secondary Soller slits, 0.5° divergence slit and a position sensitive detector with opening angle of 6°. The data were collected over an angle range from 5° to 105° with a step width of 0.0167° and scan speed of 2°/min. Sample spinning was used to improve particle statistics. Thermogravimetric analysis was performed using a Perkin Elmer TGA 7 instrument from 100 to 800 °C under air at a rate of 10 °C min^{-1}.

Synthesis of NH_2-MIL-53(Al) Nanoparticles:

2-aminoterephthalic acid (190.2 mg, 1.05 mmol) was added to a 15 mL centrifuge tube. Then, 1.05 mL of 2.0M aq. NaOH solution was added to yield a pale yellow solution. $Al(NO_3)_3.9H_2O$ (393.5 mg, 1.05 mmol) was added to a separate 15 mL centrifuge tube. The volume in each tube was increased to a total of 7.5 mL by addition of H_2O. Both tubes were sonicated for 2 minutes to ensure even dispersion. Then, contents from both tubes were placed in an autoclave, sealed and left to react in an oven at 120 °C. After 3 days, the resulting mixture was collected by centrifugation at 14000 rpm for 5 minutes. The supernatant was decanted leaving yellowish solid. The solid was washed with ethanol and collected by centrifugation twice. The resulting yellowish solid was purified by refluxing in methanol at 90 °C for 6 hrs in a RBF, collected by centrifugation and washed with ethanol twice. The supernatant was decanted leaving beige coloured solid. Resulting product was dried in oven at 85 °C overnight and collected. Yield (124.1 mg).

Synthesis of NH_2-MIL-53(Al) Nano Rods:

2-aminoterephthalic acid (1.1771 g, 6.50 mmol) was added to a 50 mL centrifuge tube. Then sodium acetate (1.7958 g, 21.9 mmol) was added. $Al(NO_3)_3.9H_2O$ (1.6413 g, 4.39 mmol) was added to a separate 50 mL centrifuge tube. The volume in each tube was increased to a total of 31.25 mL by addition of H_2O. Both tubes were sonicated for 2 minutes to ensure even dispersion. Then, contents from both tubes were mixed in a 125 mL Teflon cup-lined autoclave, sealed and left to react in an oven at 120 °C. After 3 days, the resulting mixture was collected by centrifugation at 14000 rpm for 5 minutes. The supernatant was decanted leaving yellowish solid. The solid was washed with acetone and collected by centrifugation twice. The resulting yellowish solid was purified by refluxing in DMF at 120 °C for 6 hrs. The resulting material was collected by centrifugation, washed with ethanol, then centrifuged again. The supernatant was decanted leaving beige coloured solid. Resulting product was dried in oven at 85 °C overnight and collected. Yield (1.1091g).

Synthesis of NH_2-MIL-53(Al) Microneedles

2-aminoterephthalic acid (0.565 g, 3.12 mmol) was added to a 50 mL centrifuge tube. Then acetic acid (3.7832 g, 0.063 mol) was added. $Al(NO_3)_3.9H_2O$ (0.7878 g, 2.10 mmol) was added to a separate 50 mL centrifuge tube. The volume in each tube was increased to a total of 15 mL by addition of DMF. Both tubes were sonicated for 2 minutes to ensure even dispersion. Then, contents from both tubes were mixed in a 100 mL autoclavable bottle, sealed and left to react in an oven at 120 °C. After 3 days, the resulting mixture was collected by filtration and washed with acetone. The resulting yellowish solid was purified by refluxing in DMF at 120 °C for 6 hrs. The resulting material was collected by filtration and washed with ethanol giving a pale yellow solid. Resulting product was dried in an oven at 85 °C overnight and collected. Yield (0.3006 g).

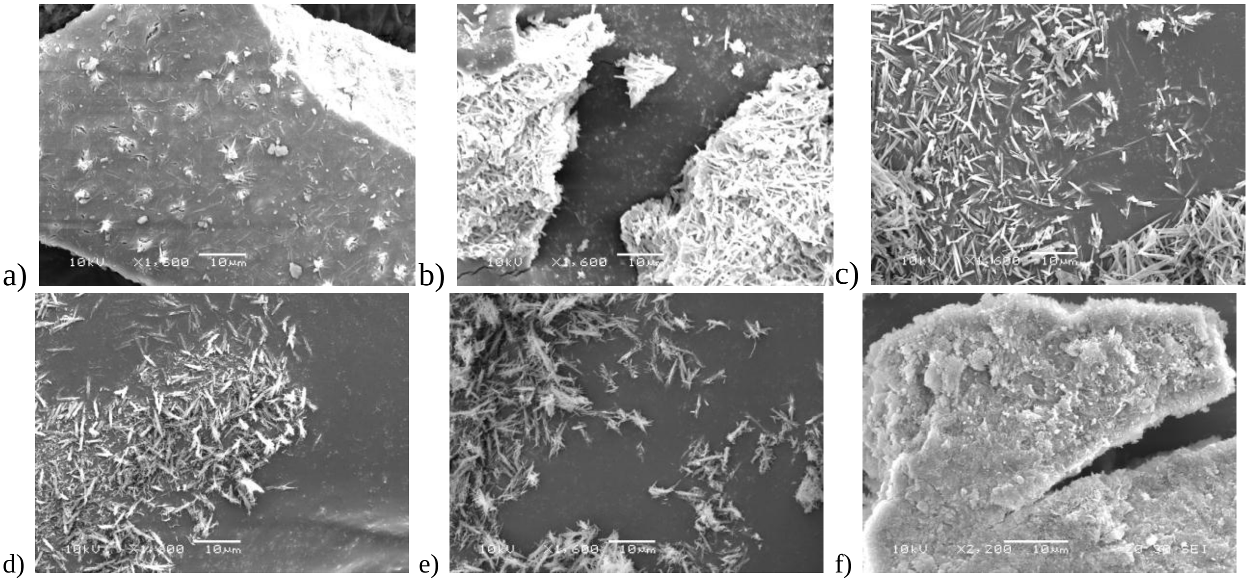

Figure S1. SEM images of NH_2-MIL-53(Al) synthesized with increasing molar ratio of acetic acid to $Al(NO_3)_3.9H_2O$ a) 10 b) 20 c) 30 d) 40 e) 50 f) 60. All 6 syntheses were performed at 120 °C for 3 days in DMF.

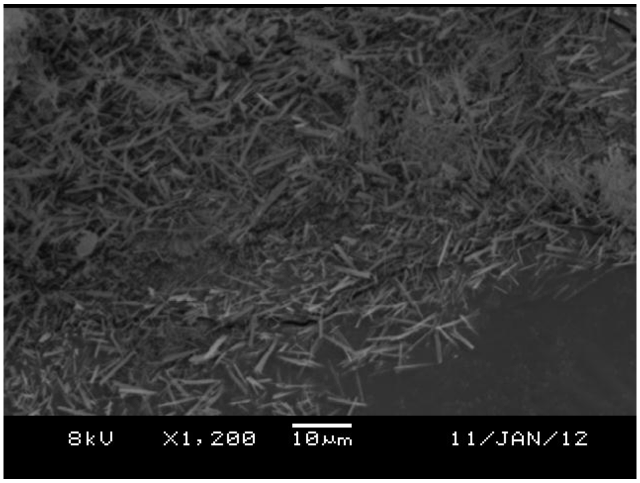

Figure S2. SEM image of NH_2-MIL-53(Al) synthesized with increasing 120 equivalents of acetic acid to $Al(NO_3)_3.9H_2O$ at 120 °C for 3 days in H_2O.

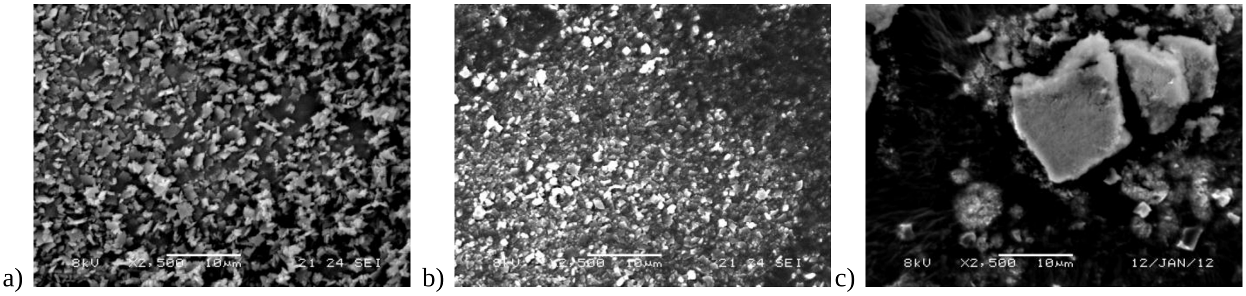

Figure S3. SEM images of NH_2-MIL-53(Al) synthesized with increasing molar ratio of sodium acetate to $Al(NO_3)_3.9H_2O$ ***a***) 0.09 ***b***) 0.18 ***c***) 1. All 3 syntheses were performed at 120 °C for 3 days in H_2O. The crystallites get progressively smaller with increasing equivalents of sodium acetate utilized.

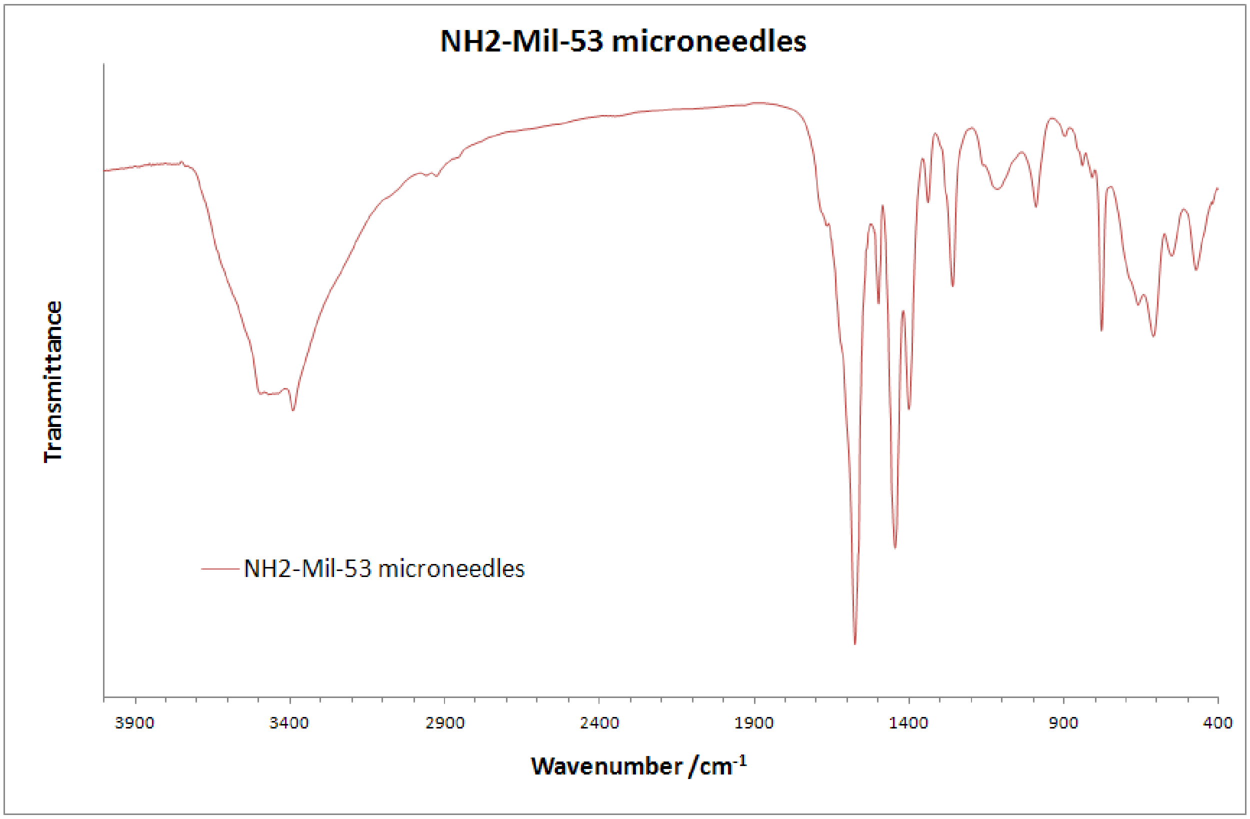

Figure S4. IR spectrum of NH_2-MIL-53(Al) micro-needles. The 2 sharp bands at 3392 cm^{-1} and 3503 cm^{-1} are due to the symmetric and asymmetric N-H vibrations respectively.[1]

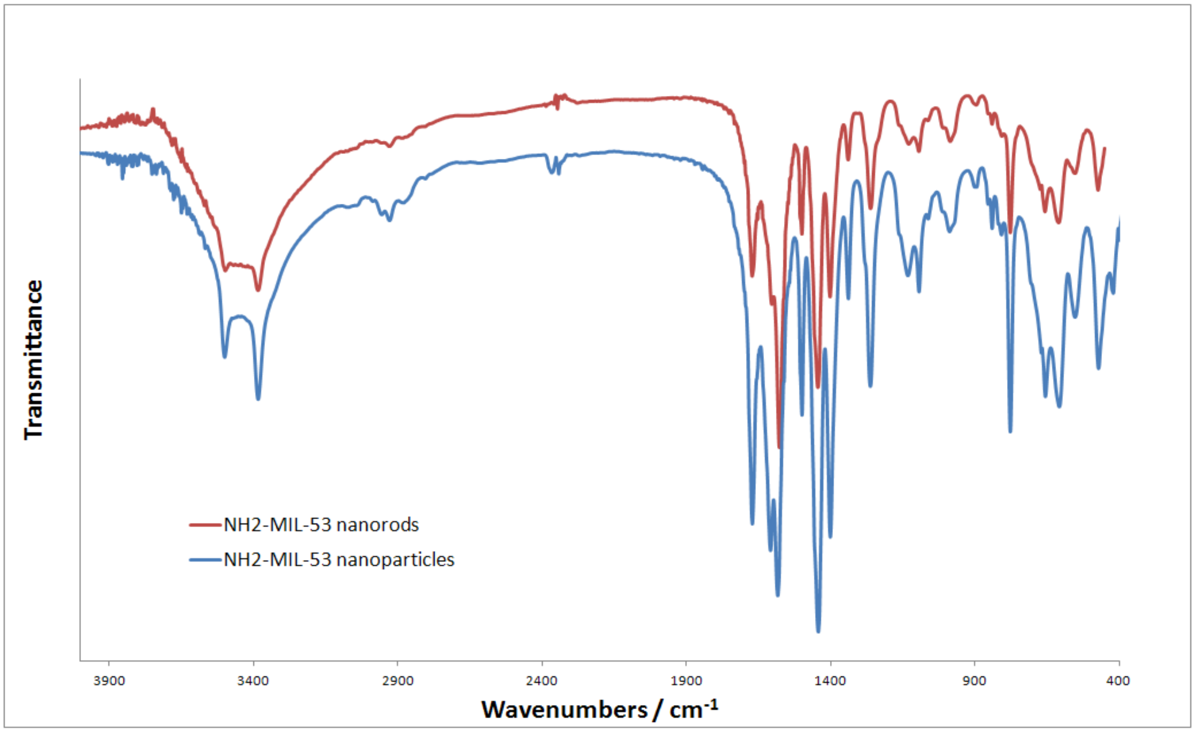

Figure S5. IR spectrum of NH_2-MIL-53(Al) nanoparticles and nanorods.

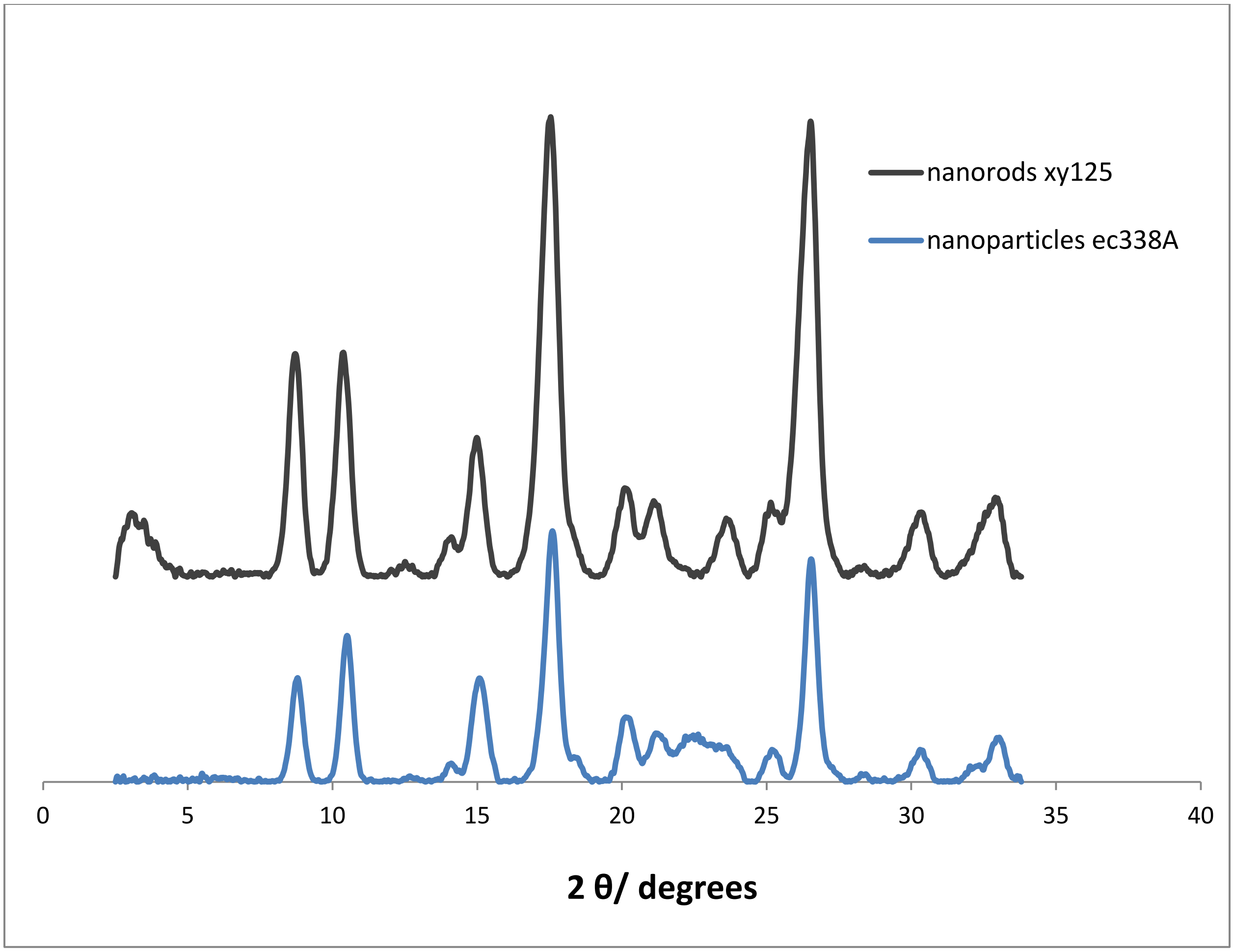

Figure S6. Powder x-ray diffraction of NH_2-MIL-53(Al) nanorods and nanoparticles using GADDS

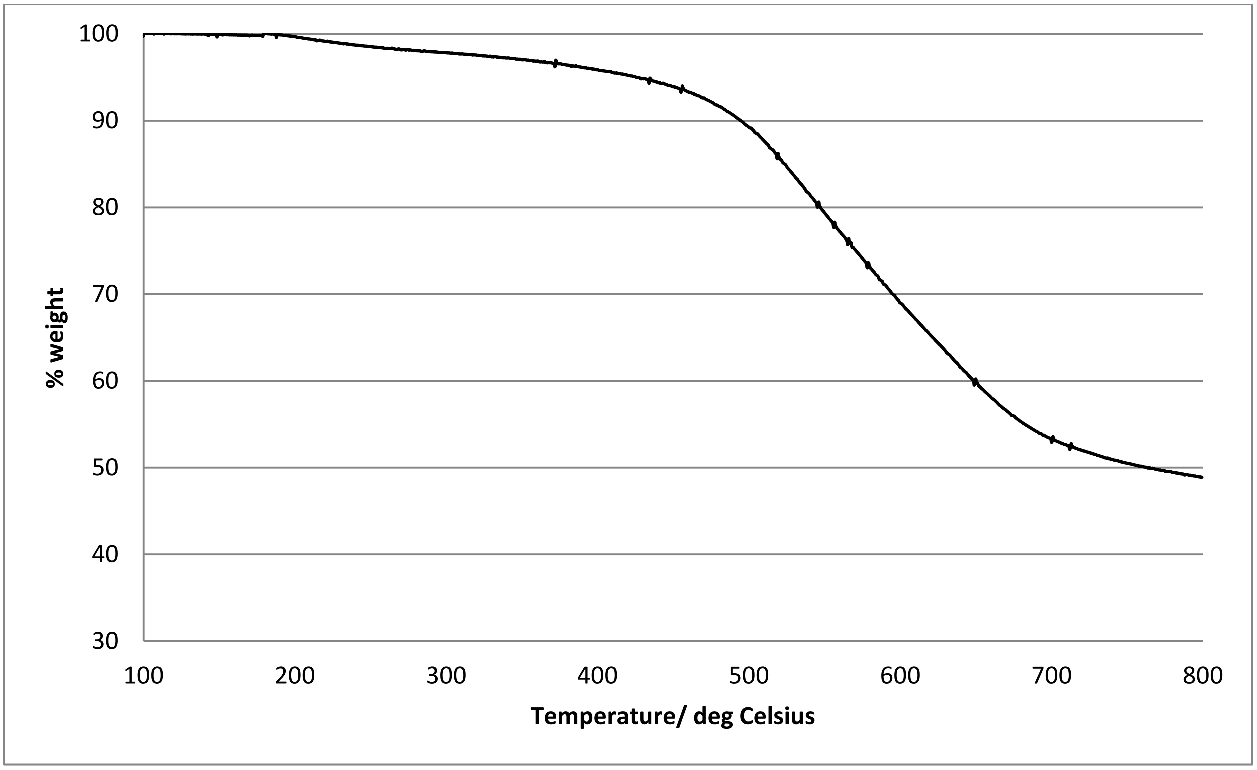

Figure S7. Thermogravimetric analysis of NH_2-MIL-53 microneedles. Needles were purified by refluxing in MeOH overnight and then placing at 120 °C *in vacuo* over 1 day prior to analysis.

Determination of preferred orientation using PXRD

Sample preparation and measurement:

The sample powder was packed into a back-loading sample holder. PXRD-measurements were performed in Bragg-Brentano geometry using a Bruker D8-Advance equipped with Cu-Kα source, 2.5° primary and secondary Soller slits, 0.5° divergence slit and a position sensitive detector with opening angle of 6°. The data were collected over an angle range from 2° to 105° with a step width of 0.0167° and scan speed of 2°/min. Sample spinning was used to improve particle statistics. A variable counting time scheme[2] was employed to improve the counting statistics at high angles. The measurement was divided into 6 ranges; 2-11°, 11-20°, 20-29°, 29-47°, 47-65° and 65-105° which were measured with counting times of 0.25 s, 0.36 s, 0.63 s, 1.07 s, 2.64 s and 5.21 s per step. Subsequently, all ranges were normalized to 0.25 s per step and this combined dataset was used for the data evaluation.

Data evaluation:

All refinements described below were conducted using the fundamental parameter approach[3] for instrumental and microstructure broadening as implemented in Topas version 4.2.[4]

Qualitative analysis confirmed that most observed reflections in both samples are consistent with the orthorhombic I-centered phase of Mil-53(Al). However, several reflections remained unidentified. Pawley fits[5] gave considerably improved fit if the structures is transformed to C2/c (with a = 17.448 Å, b = 11.739 Å, c = 6.633 Å and β = 111.0°) as seen in Figure S8. In this fit a reflection at 22.36° is still unexplained.

Further improvement can be obtained by assuming that the channels are unequally filled in a checkerboard fashion. This leads to a superstructure which can be described in P2/c with a = 18.685 Å, b = 11.730 Å, c = 6.643 Å and β = 90.9 °. The resulting refinement is shown in Figure S9.

A transformation to P1 with finally gives the nearly perfect Pawley shown in Figure S10. This unit cell was consequently the basis for structure refinement.

In order to limit the degrees of freedom all molecules (NH_2-terephthalate and water) were treated as rigid bodies. Additionally suitable minimum distances for the atoms in question were introduced to prevent implausible inter-atomic distances. At first a filling with 2 water molecules per formula unit was assumed. Accordingly 16 water molecules were added into the unit cell. Their position was subjected to simulated annealing. Due to the crystallites needle shape strong preferred orientation was expected as well. To account for this in an unbiased manner a spherical harmonics function was used as described by Whitfield et al.[6] A subsequent refinement of the overall water occupancies led to the assumption that four more water molecule were needed. Structure solution was followed by Rietveld refinement. In order to determine the direction of preferred orientation now the March-Dollase function was used. Several refinement cycles where alternately water, terephthalate and Al positions were refined followed. The final structure model is provided in the attached cif. The preferred orientations found were [1 0 0] and [1 1 0] which clearly indicates [0 0 1] as growth direction.

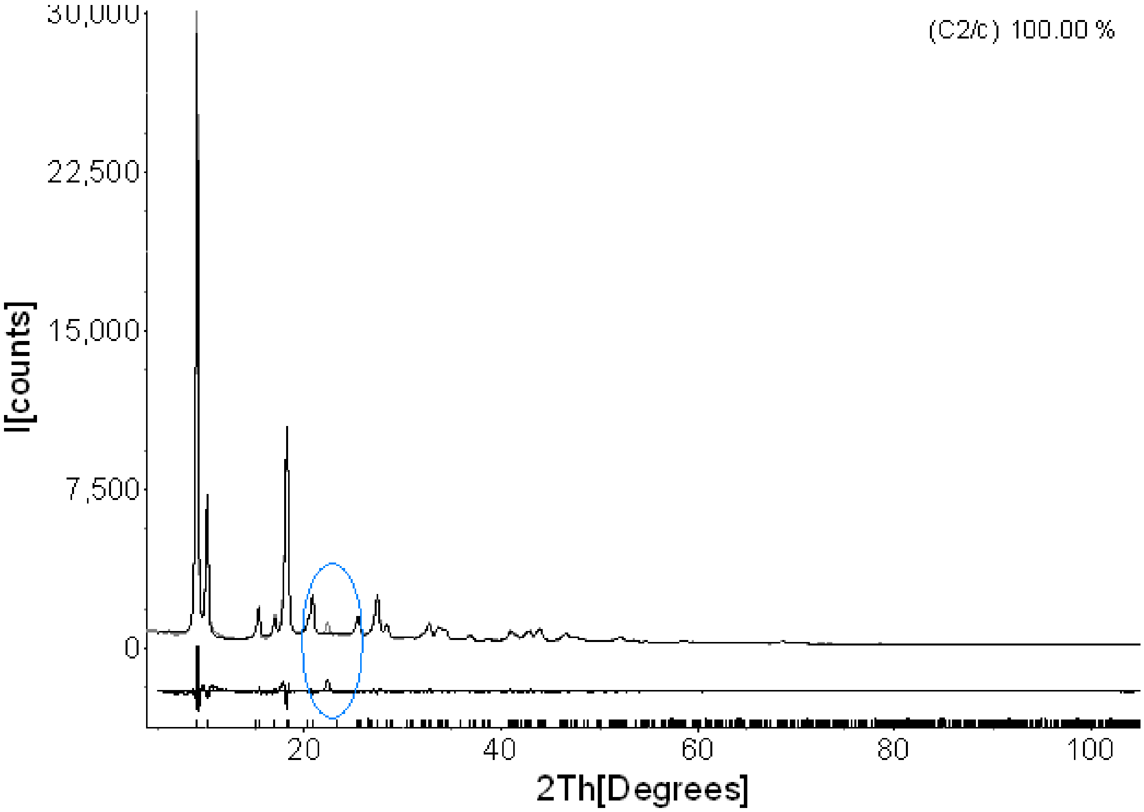

Figure S8. Pawley fit of the diffractogram of NH_2-MIL-53(Al) in C2/c.Note the unindexed reflection at 22.36°.

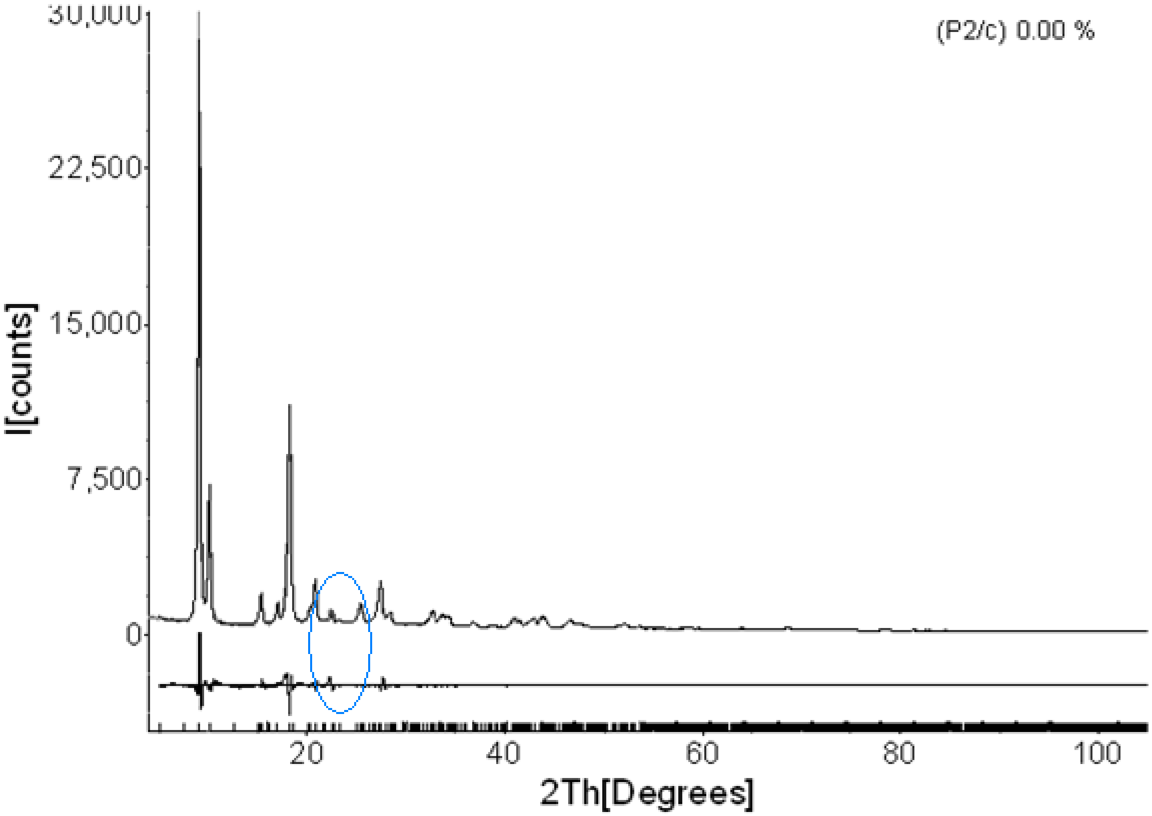

Figure S9. Pawley fit of the diffractogram of NH_2-MIL-53(Al) in P2/c. Note, the previously unindexed reflection at 22.36° is now partly explained.

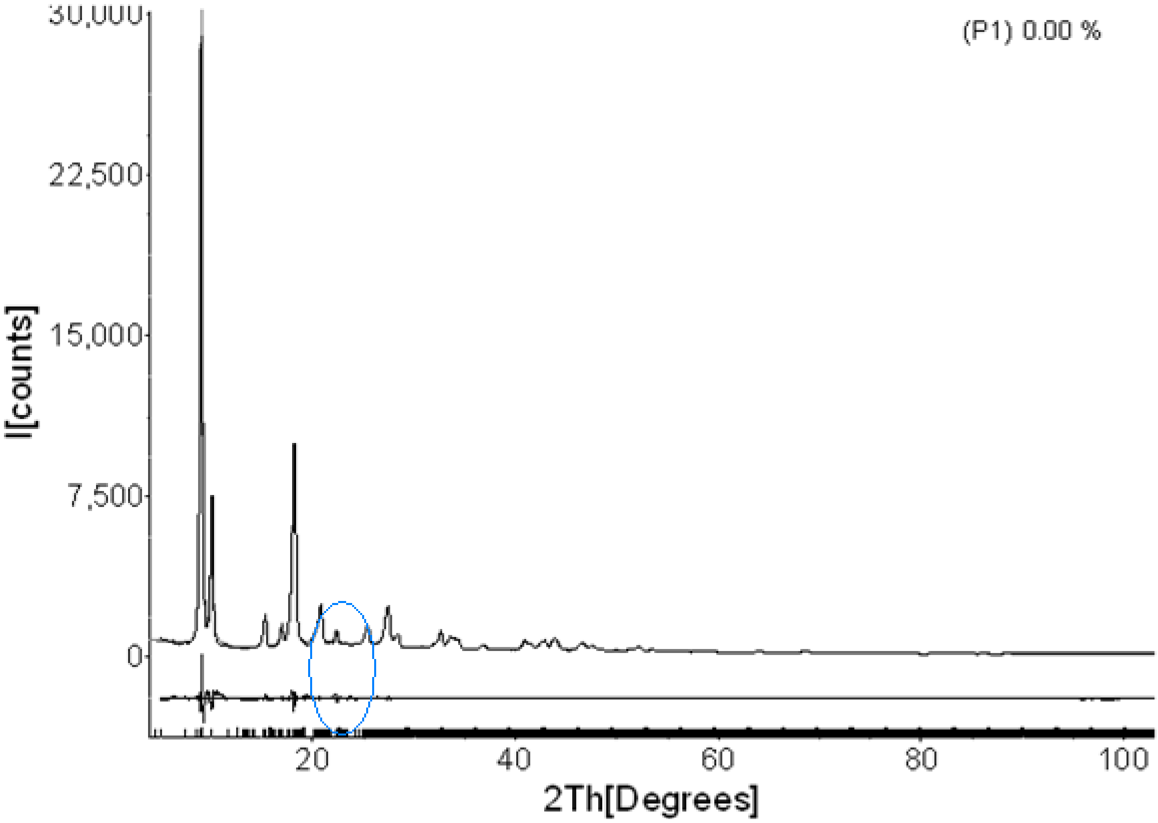

Figure S10. Pawley fit of the diffractogram of NH_2-MIL-53(Al) in P1.

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[1] E. Stavitski, E.A. Pidko, S. Couck, T. Remy, E.J.M. Hensen, B.M. Weckhuysen, J. Denayer, J. Gascon, and F. Kapteijn, *Langmuir*, 2011, **27**, 3970.

[2] I. C. Madsen and R. J. Hill, *J. Appl. Cryst.*, 1994, **27**, 385.

[3] a)R. W. Cheary and a. Coelho, *J. Appl. Cryst.*, 1992, **25**, 109. b) R. W. Cheary and A. A. Coelho, *J. Appl. Cryst.*, 1998, **31**, 862.

[4] A. A. Coelho and Bruker-AXS GmbH, 2009

[5] G. S. Pawley, *J. Appl. Cryst.*, 1981, **14**, 357.

[6] P. S. Whitfield, *J. Appl. Cryst.*, 2008, **42**, 134.