

Supplementary information for:

High pressure, high temperature electrochemical synthesis of Metal Organic Frameworks: films of MIL-100 (Fe) and HKUST-1 in different morphologies

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S1 Experimental Methods

Synthesis of Cu-BTC (HKUST-1)

The electrolytic copper (99% purity, Testas Belgium) plates were ground and polished before being washed with alcohol and rinsed in diluted sulphuric acid. Then the plate to be used as anode was mounted in a PTFE mask. The mask decreases the edge effect otherwise observed with the bare plates and limits the surface to a well-defined area (6.2 cm^2).

Unless stated otherwise, the electrodeposition was performed from the moment the solution inside the cell reached the desired temperature, the current was switched on at the set conditions and lasted 45 minutes. Two different solutions were used for the syntheses: solution A to synthesize MOF layers and solution B to produce larger amounts of MOF in suspension.

Solution A: 10 g/l 1,3,5-benzenetricarboxylic acid (H_3BTC , 98% purity ABCR Germany) in 67 vol% absolute ethanol (99.9% purity, VWR France) and 33 vol% milliQ water.

Solution B: 20 g/l methyltributylammonium methyl sulfate (MTBS, $\geq 95\%$ purity, Aldrich Germany) and 20 g/l 1,3,5-benzenetricarboxylic acid (H_3BTC , 98% purity ABCR Germany) in 100 vol% of absolute ethanol (99.9% purity, VWR France).

In order to deposit Cu-BTC solution A was used. Following the result reported by Ameloot et al. [2] the current was applied with pulses at 0.5 Hz and a current density of 2.5 mA/cm^2 .

After synthesis the plates were washed, rinsed and dried with a flow of hot air several times. The layers were observed with SEM and the MOF crystals could also be scratched with a spatula and analyzed by XRD. It was observed that the patterns obtained from the MOF filtered from the solution and those obtained scratching the deposited layer are very similar.

Experiments have been run at temperatures from $5 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ and the XRD patterns are reported in Figure S10. SEM pictures of samples synthesized at room temperature and at $200 \text{ }^\circ\text{C}$ are shown in Figure S9.

Synthesis of MIL-100(Fe)

Electrolytic iron (99.99% Sochibo, Japan) plates were mounted in a PTFE mask similar to that used for Cu-BTC synthesis and the same solutions were used.

While in the case of Cu-BTC anode and cathode were both made of the same material, for the synthesis of MIL-100(Fe) a more noble material, namely copper, was chosen as cathode following the suggestion reported in the BASF patent [1]. From XRD patterns (not shown) taken from powders synthesized with different cathodic materials it was concluded that the cathode does not affect the composition of the synthesized MOF. No traces of Cu-BTC could be found in any of the samples synthesized with a copper cathode.

The temperature was varied from $110 \text{ }^\circ\text{C}$ to $190 \text{ }^\circ\text{C}$ and the current density from 0 to 20 mA/cm^2 . All the experiments for electrodeposition were run with the same solution used for Cu-BTC (solution A) while solution B was used to collect powder for XRD analysis.

The pure iron plates used for the experiments have all been ground and polished, rinsed with a diluted sulphuric acid solution and washed with ethanol before the experiments. After synthesis the electrodeposited samples have been washed with ethanol and dried several times with a jet of hot air.

The electrodeposition time was calculated to deposit $1 \text{ }\mu\text{m}$ of MIL-100 (Fe) over the 1.13 cm^2 exposed surface supposing 100% process efficiency with the different current densities used:

53 seconds for 2 mA/ cm², 11 s for 10 mA/ cm² and 5 s for 20 mA/ cm², 10 s for 20 mA/ cm² pulsed current (square waves 0-20 mA/ cm², 0.5 Hz frequency).

Experiments have been run also with solution B at higher current densities. The suspension after synthesis was centrifuged and the precipitate was washed different times with alcohol and water. The powders collected from the suspensions were used for the XRD analysis. The XRD patterns of the powder synthesized with the two solutions are indistinguishable after a proper cleaning. The layers synthesized with solution B are incomplete and not well adherent but the amount of material in suspension (thanks to the higher current applied) is more suitable for XRD analysis where a certain quantity of material is required.

The synthesis reported by Achmann et al. [17] was successfully reproduced. The experimental details were kept as similar as possible to those reported: the same solution reported in the paper (480 mg of MTBS, 480 mg of BTC in 40 cc of methanol), the same time and current density (38 mA/cm² for 55 min), iron anode (1 cm²) and steel cathode, and a temperature just slightly above that reported (40 °C instead of 32 °C). After the current was applied for 55 minutes the solution was transformed to a red suspension. The suspension was then centrifuged and washed with ethanol. The XRD pattern of the obtained powder (Figure S6), is very similar to that reported for commercial Fe-BTC by Dhakshinamoorthy et al.[11]. The pattern shows that the material is not completely crystalline and can therefore be considered as Fe-BTC but not as MIL-100(Fe).

Carbon steel C10 is one of the cheapest and most common construction materials. Polished C10 plates (Acier Crustin, Belgium) have been used for the synthesis of MIL-100(Fe) showing that the production and deposition of the MOF is possible even with cheaper and not completely pure electrodes.

Corrosion deposition of MIL-100

In S4 are reported a digital picture and a micrograph of a layer obtained with the corrosion deposition method. The common carbon steel plate (C10 Acier Crustin, Belgium) with AgSn brazing alloy droplets applied on each corner (in S4 three have been removed for the picture) has been heated up in solution A to 110 °C and then left for 15 minutes at that temperature before cooling down the system again to room temperature. The two conductive materials in contact with each other and with an ion conductive solution, form a galvanic cell. As in every spontaneous corrosion process, the less noble material, in this case iron, will behave as an anode releasing ions in the solution. The release is equivalent to that achievable with an imposed current from outside, only the current source is different.

The main drawback of the technique is the impossibility to control the synthesis conditions, in particular the current: the corrosion starts when the plate with the two metals is dipped in solution at room temperature and ends only when the plate is dried with a hot air flow after synthesis. The voltage between the metals and the conductivity of the solution (and therefore the current) are temperature dependent and will vary during the heating and cooling of the system. The crystallization and growth kinetics of MIL-100 are also temperature dependent and will change during the whole process as well.

SEM, XRD and isotherms analyses

Scanning electron microscope images have been taken with a FEI/Philips XL30 FEG microscope. The layers were coated with a thin layer of Pt/Pd (5 - 10 nm) to enhance the conductivity. X-Ray diffraction patterns were taken with a Bruker AXS D8 diffractometer

using Cu-K α radiation (wavenumber $\lambda = 1.5405 \text{ \AA}$) and Ni filter from 0 to 50° in 2 θ with a step of 0.02° and 2 s per step.

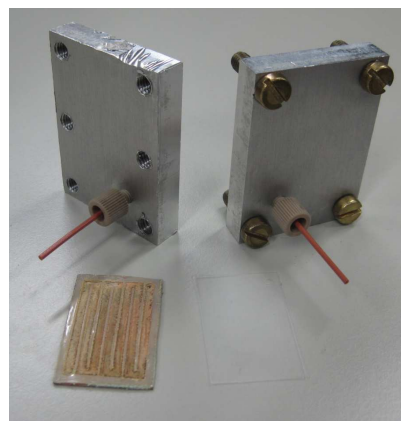
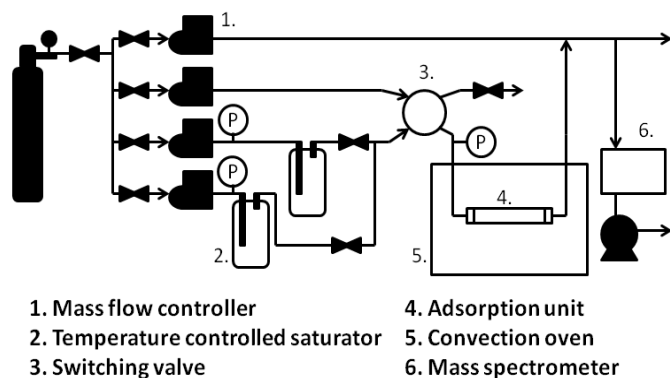
Isotherms were performed with a SGA-100H gravimetric apparatus by VTI corporation. The sample, synthesized with solution B at 130 °C, was activated for 24 h at ca. 50 °C in vacuum before the adsorption with pure methanol (Sigma-Aldrich, $\geq 99.9\%$) in nitrogen carrier gas. The isotherm is reported in Figure S5.

The argon adsorption isotherms of the electrochemically synthesized MIL-100(Fe) and commercial iron-trimesate Basolite F300, S8, were determined with a Quantasorb Autosorb AS-1 (Quantachrome Instruments, USA) at 87 K. About 25 mg of adsorbent powder was activated by gradual heating at a rate of 1 °C/min to 150 °C under high vacuum. The BET-area of an electrochemically synthesized MIL-100(Fe) sample (130 °C, solution A) was calculated to be 1335 m²/g while the Langmuir surface is 2037 m²/g. The pore size distribution of the sample was determined using the Dubinin–Astakhov method, and is shown in S8.

As expected from an electrochemical synthesis [Hartmann, *Langmuir* 24, 2008, 8634] the resulting surface area is lower than that reported with other solvothermal fluorine free syntheses, 1335 m²/g versus 1520-1800 m²/g [Seo, *Micropor Mesopor Mater* 157, 2012, 137]. This difference is in part due to the lower synthesis temperature used in the electrochemical synthesis, and in part to the less efficient purification procedure used by us after synthesis.

S8 also reports the adsorption isotherm of the commercial Fe-BTC with disordered structure. The calculated BET-area, 722 m²/g, is only about half of that of MIL-100(Fe) synthesized electrochemically and is similar to the values reported in literature [Seo, *Micropor. Mesopor. Mater.* 157, 2012, 137].

Breakthrough Curves



This experiment is very similar to that published by some of the authors with an HKUST-1 microdevice [8]. Methanol (>99.9% Sigma-Aldrich, Germany) was evaporated at 15°C in an evaporator, by flowing 3 ml/min N₂ carrier gas through the evaporator. n-hexane (>96% Biosolve, The Netherlands) was evaporated at 25°C in a second evaporator, by flowing 2 ml/min N₂ carrier gas through the evaporator. The two streams were combined and sent through the microdevice. The methanol/n-hexane ratio is approximately 40/60. The outlet of the microdevice was diluted with 100 ml/min N₂ and sent to a mass spectrometer (MS) (QME-125, Balzers). The composition of the outlet streams was monitored at m/z ratios of 31 and 57 for methanol and n-hexane respectively and the concentrations were compared with

the inlet concentrations (C/C_{fed}). The experiment was performed at 40°C (microdevice set in the oven), while all the gas lines were kept at 50°C to avoid vapor condensation.

As can be seen from the pictures above, the microdevice consisted of a single sheet containing a single meandering channel of approximately 24 cm length, 2 mm width and 500 μm depth. The microdevice was made by adhering a patterned 500 μm thick PEEK layer on a copper sheet, followed by electrochemical deposition of iron (Fe) and MIL-100 electrochemical synthesis (solution A, 110 °C) . The microdevice sheet was subsequently clamped and sealed in an aluminum holder.

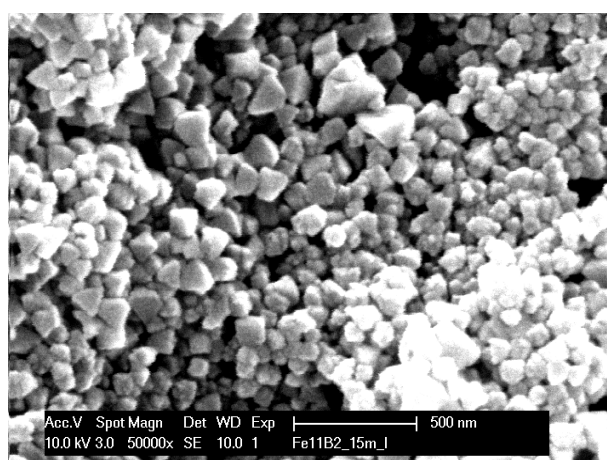
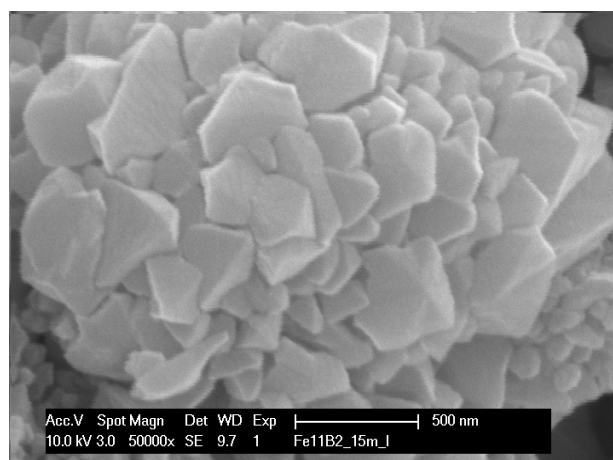
The breakthrough experiment is shown in figure 3. First, no methanol or n-hexane is observed as both vapors are being adsorbed on the MIL-100 layer. After approximately 130 seconds, n-hexane breaks through, resulting in a pure stream of carrier gas and n-hexane. Only 80 seconds later, methanol breaks through as the MIL-100 layer in the microdevice reaches equilibrium with the feed stream. For comparison, a 'blank' measurement was run, without any adsorption device. In that case methanol and n-hexane break through at a similar time (20s), proving that MIL-100 has separation properties for the feed.

As can be seen in figure 3, after the initial steep rise of the breakthrough profile, tails can be noticed at relative concentrations of 0.7 C/C_{fed} and higher. These tails were also noticed in a 'blank' measurement reported previously, and are due to the experimental set-up rather than to an adsorption phenomenon of the MOF layer, in this case MIL-100(Fe) [8].

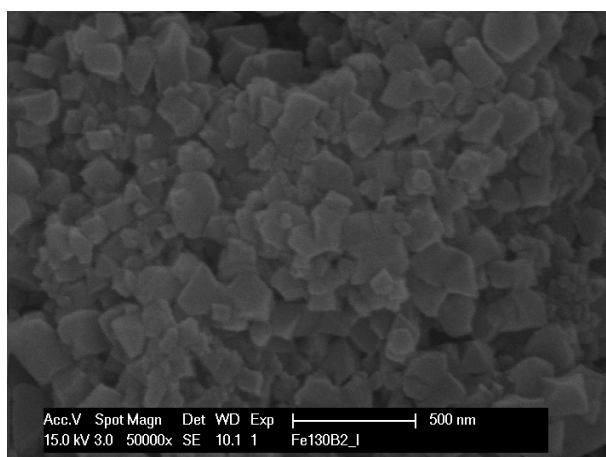
A first order method to calculate the amount of adsorbed compound can be used. This calculation, also reported in the paper quoted above, is based on the comparison between the breakthrough profile data of the microdevice and the 'blank' measurement. With the MIL-100 based device the result is approximately 1.4 mg of methanol and 2.8 mg of n-hexane adsorbed on the microdevice, or 2.91 g/m² and 5.83 g/m² respectively.

S2 SEM of MIL-100 synthesized at different temperatures

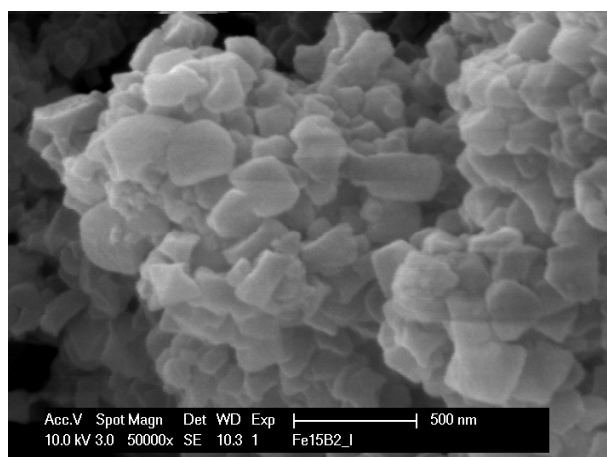
Current density: 2 mA/cm²



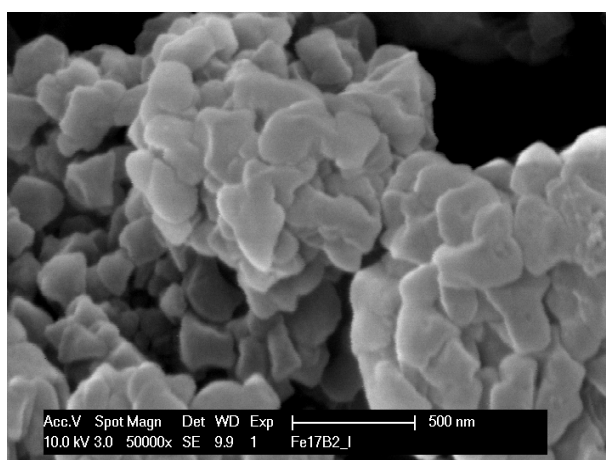
110 °C Large and small crystals



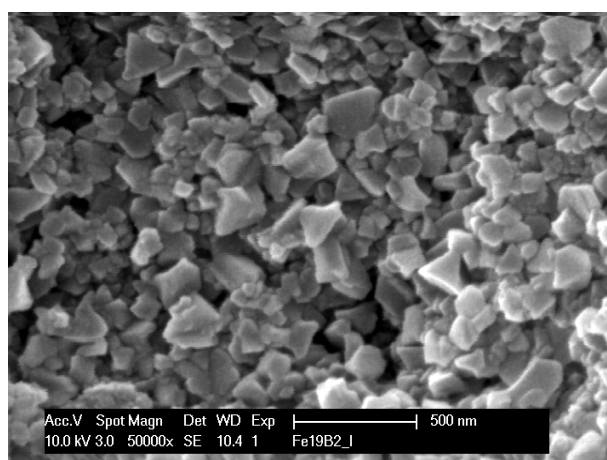
130 °C



150 °C

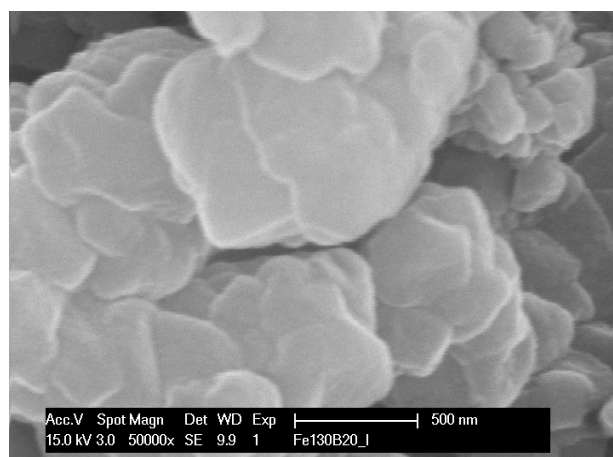


170 °C

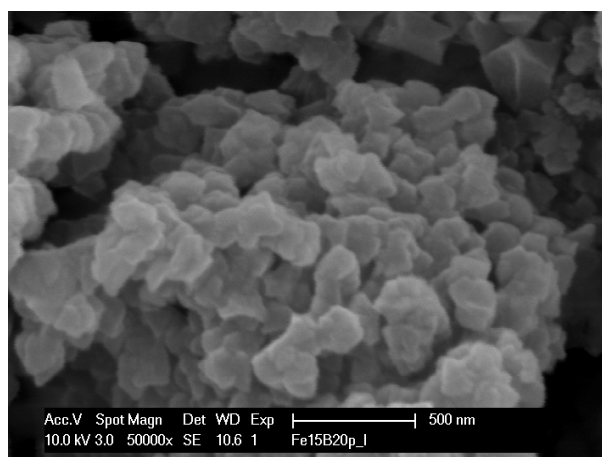


190 °C

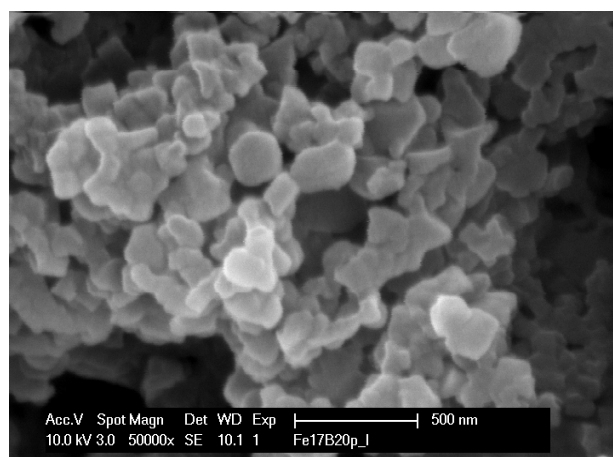
Current density: 20 mA/cm²



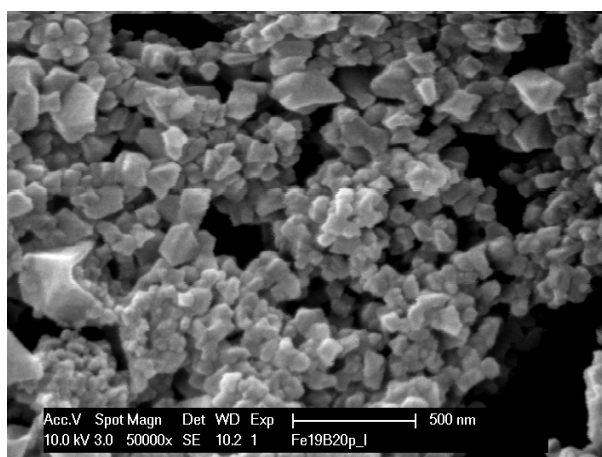
130 °C



150 °C

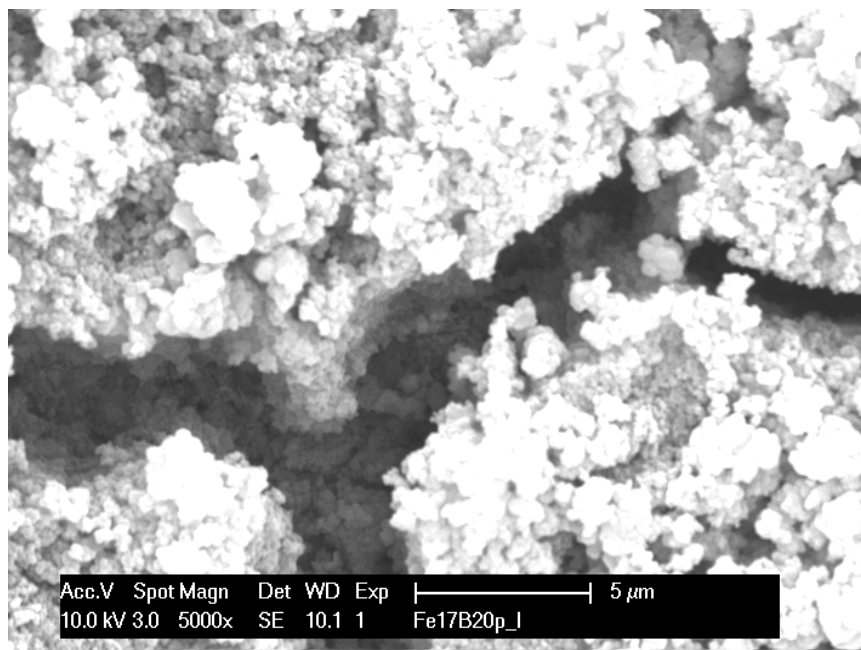


170 °C



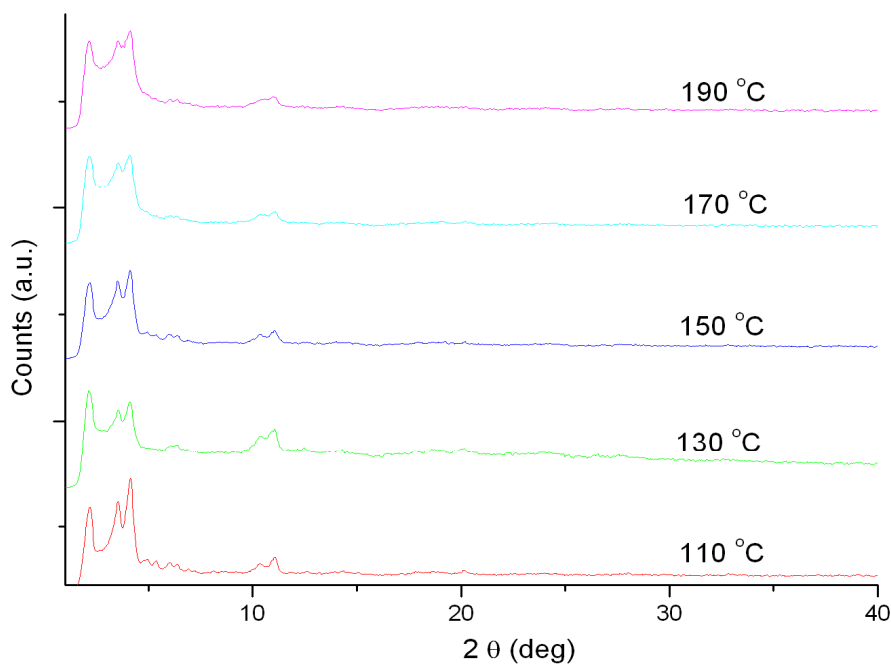
190 °C

Cracks

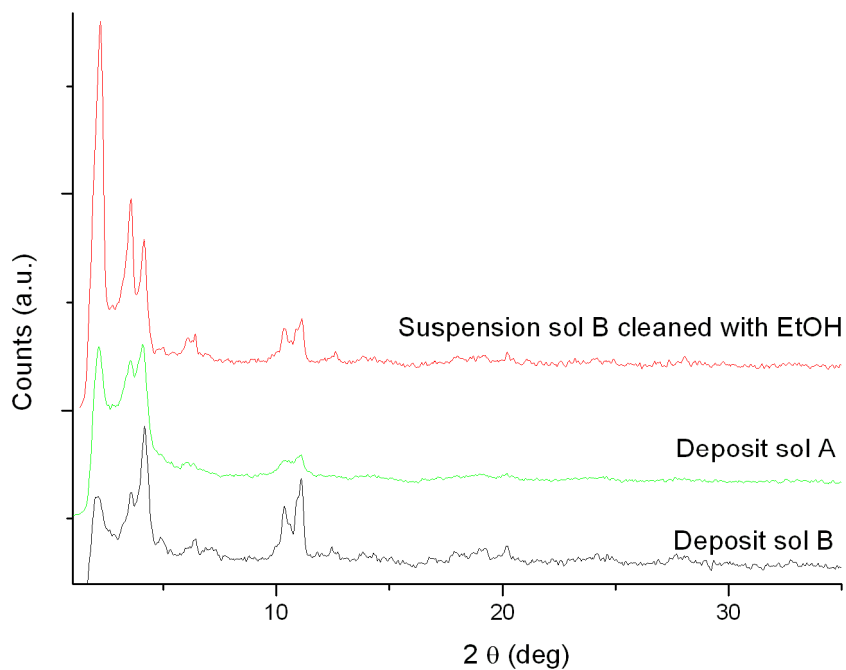


SEM picture of MIL-100(Fe) layer synthesized at 170 °C on top of an iron plate. At the bottom of the cracks, one can see more MOF crystals rather than the bare metal.

S3 XRD of Fe-BTC MIL-100 synthesized at different temperatures

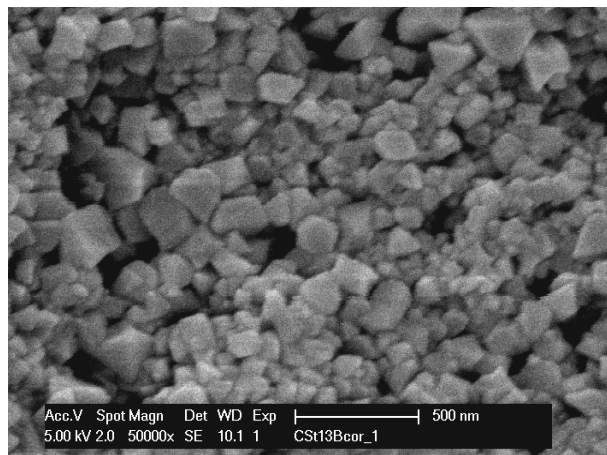


Fe-BTC MIL-100(Fe) synthesized at different temperatures with solution B. The peaks of MIL-100 synthesized at lower temperature are sharper than those of the same material synthesized at higher.



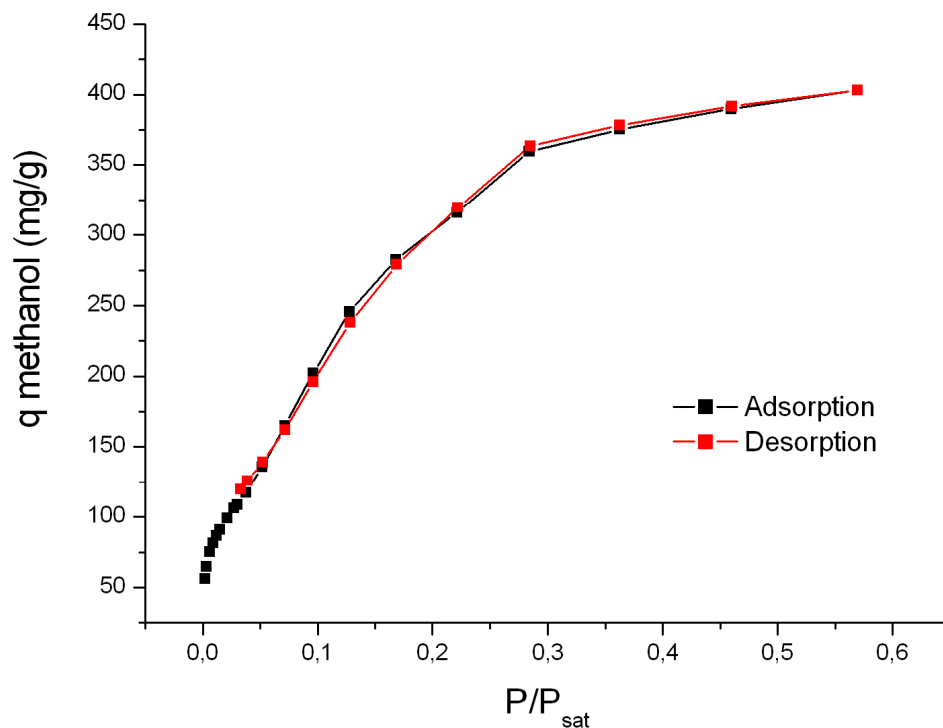
From the bottom, XRD patterns of MIL-100 synthesized at 170 °C: scratched from a deposited layer synthesized with solution B, scratched from deposited layer synthesized with solution A, and the suspension filtered from the experiment with solution B after several washes with warm ethanol.

S4 Corrosion deposition of MIL-100 (Fe)



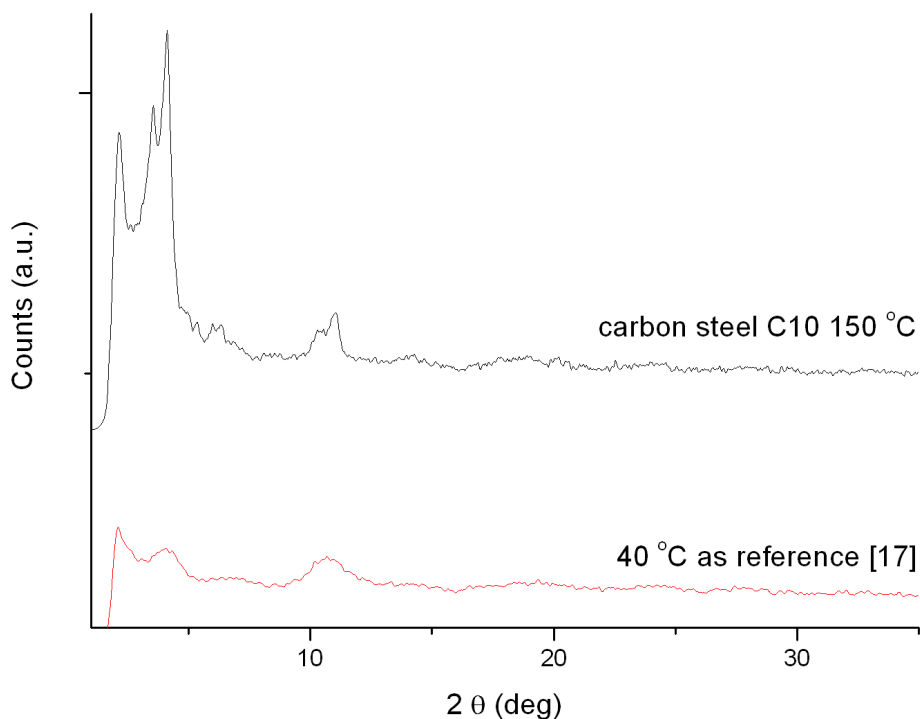
Layer obtained with the corrosion deposition method. On the left a digital picture of the plate and on the right an SEM picture of the obtained layer.

S5 Methanol isotherm

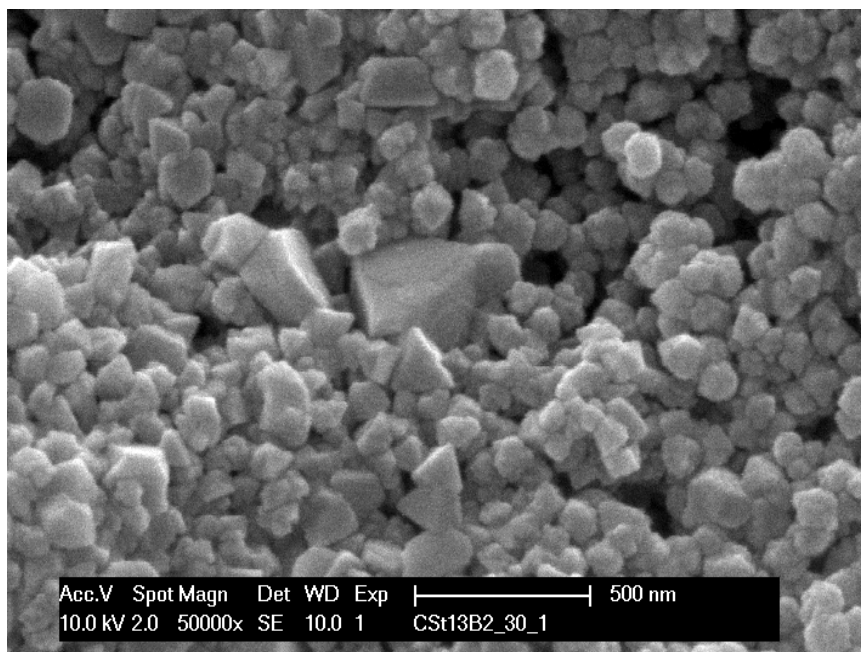


Methanol isotherm at 50 °C of MIL-100(Fe) synthesized at 130 °C. The material can adsorb and desorb up to 40 wt% of methanol.

S6 Fe-BTC and MIL-100 (Fe) on carbon steel

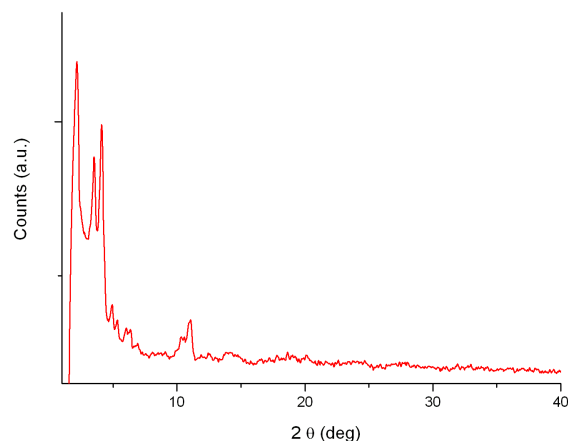


XRD pattern of MOF powder synthesized with a C10 carbon steel anode and solution A. Below, XRD pattern of non-crystalline Fe-BTC synthesized following the procedure reported in reference [17] at 40 °C.



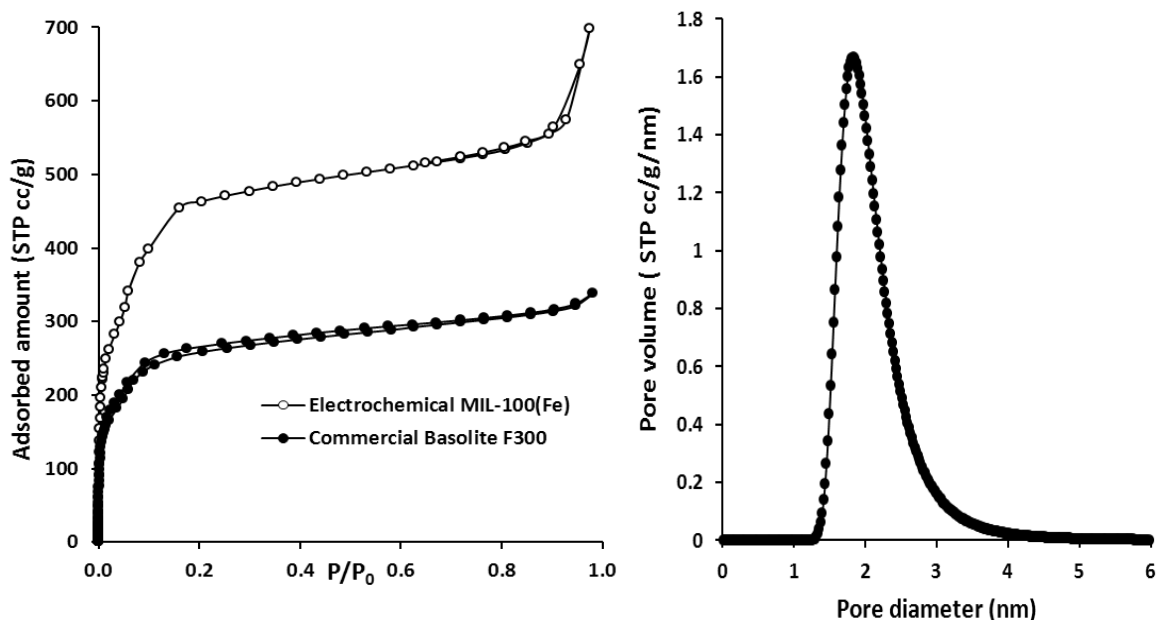
SEM picture of MIL-100(Fe) on top of carbon steel, synthesized with solution A at 130 °C.

S7 Biofilm-inhibiting



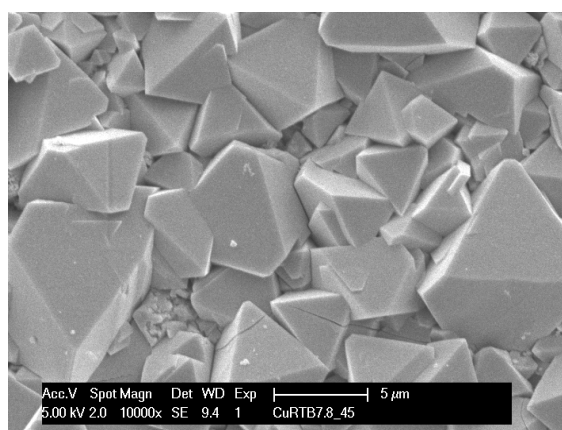
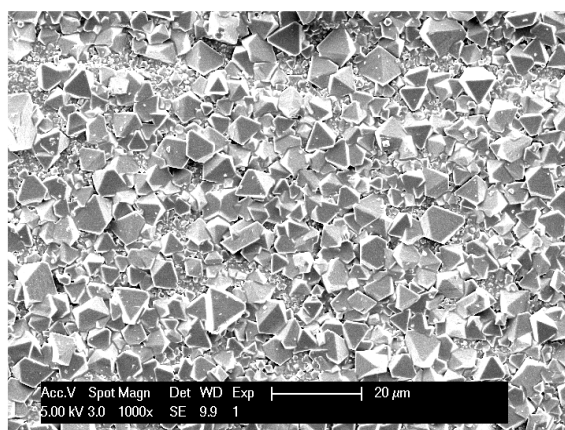
Picture and XRD pattern of a MIL-100(Fe) layer on carbon steel (130 °C, Sol A, 2 mA/cm², 1 min) after loading with the antifouling component and leaving in water for 24 hours. The picture (left) shows that the MIL-100 layer is still present on the carbon steel as confirmed by the XRD pattern (right).

S8 Argon porosimetry

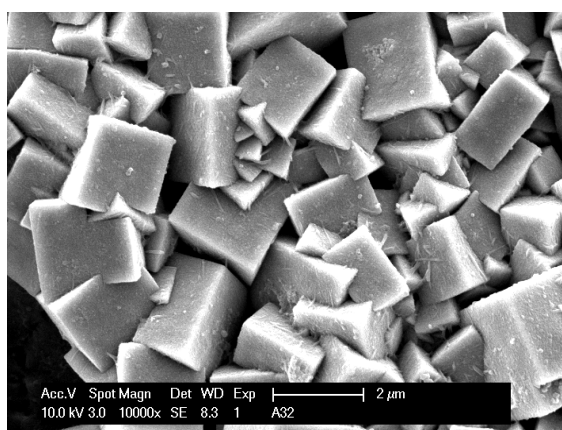
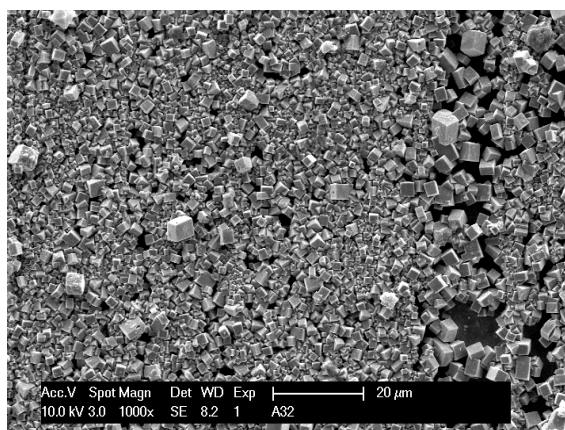


Left: Argon porosimetry isotherms at 87 K measured on electrochemically synthesized MIL-100(Fe) and commercial FeBTC (Basolite F300). Right: Pore size distribution of electrochemically synthesized MIL-100(Fe).

S9 SEM of Cu-BTC layers formed at different temperatures

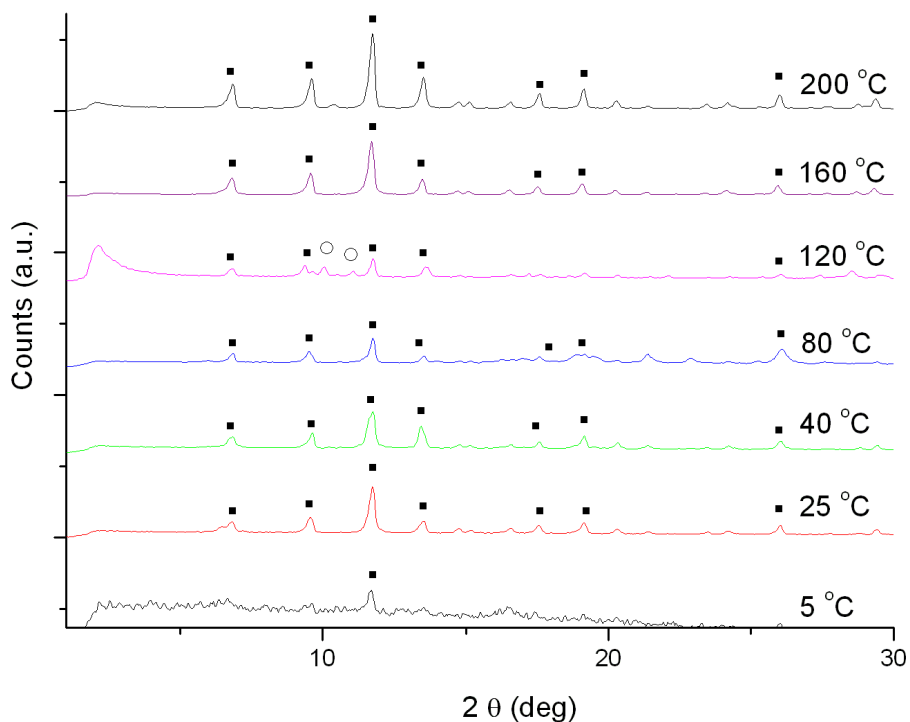


HKUST-1 layers synthesized at 20 °C with solution A



HKUST-1 layers synthesized at 200 °C with solution A

S10 XRD of Cu-BTC layers formed at different temperatures



XRD patterns of Cu-BTC, filtered from suspensions synthesized with solution A at different temperatures. At low temperatures the patterns correspond to the HKUST-1 Cu-BTC phase (■), while upon increasing the temperature also the reflections of the HT phase $\text{Cu}_2(\text{BTC})(\text{OH})(\text{H}_2)$ (○) already reported by Schlesinger [23] appear. At 200 °C the pattern is again that of HKUST-1 with minor reflections of the secondary phase.