Supporting Information

Microwave-assisted Synthesis of the Flexible Iron-based MIL-88B Metal-Organic Framework for Advanced Energetic Systems

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➢ Structure of MIL-88B(Fe) SBU:

The overall structure of the iron-based flexible MIL-88B metal-organic framework is shown in the main text in Fig. 1. However, its secondary building unit, the smallest building block in the framework, is not fully illustrated. As explained, in the MIL-88B(Fe) structure, the trinuclear metal μ_3-oxo cluster is formed at the reported reaction conditions, whereby the three metal centers are connected through a central oxygen atom (Fig. S1).[1] Each metal ion forms an octahedral complex with the four connecting linkers around the central ion in its square plane. At the outer vertex of the complex, a solvent molecule bonds to the metal center through an oxygen atom or an individual halide anion present from the initial precursors.[2, 3]

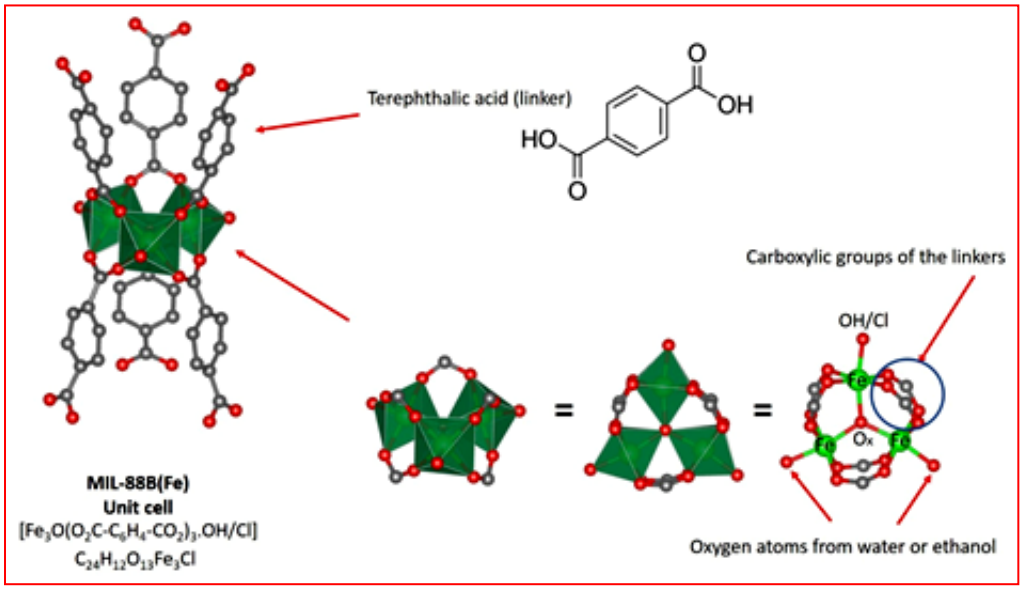

Figure S1. The trimetallic μ_3-O cluster of the MIL-88B(Fe) metal-organic framework.

➢ **Microwave synthesis of MIL-88B(Fe):[4, 5]**

- Model: Microwave Synthesis Reactor Monowave 400.
- Company: Anton Paar (Canada).
- Vial type: Glass vial G30.
- Vial volume: 30 ml. - Filled volume: 15 ml.
- Temperature control: Ruby thermometer + IR sensor

Table S1. The applied method for the microwave-assisted synthesis of MIL-88B(Fe)

Step	Program	Temp. (°C)	Time (hh:mm:ss)	Actual step time (hh:mm:ss)	Power (W) [limit]	Cooling	Stirrer speed (rpm)
1	Heat as fast as possible	150	----	00:00:55	850	Off	500
2	Hold	150	00:15:00	00:15:00	850	Off	500
3	Cool down	55	----	00:04:05	----	On	500

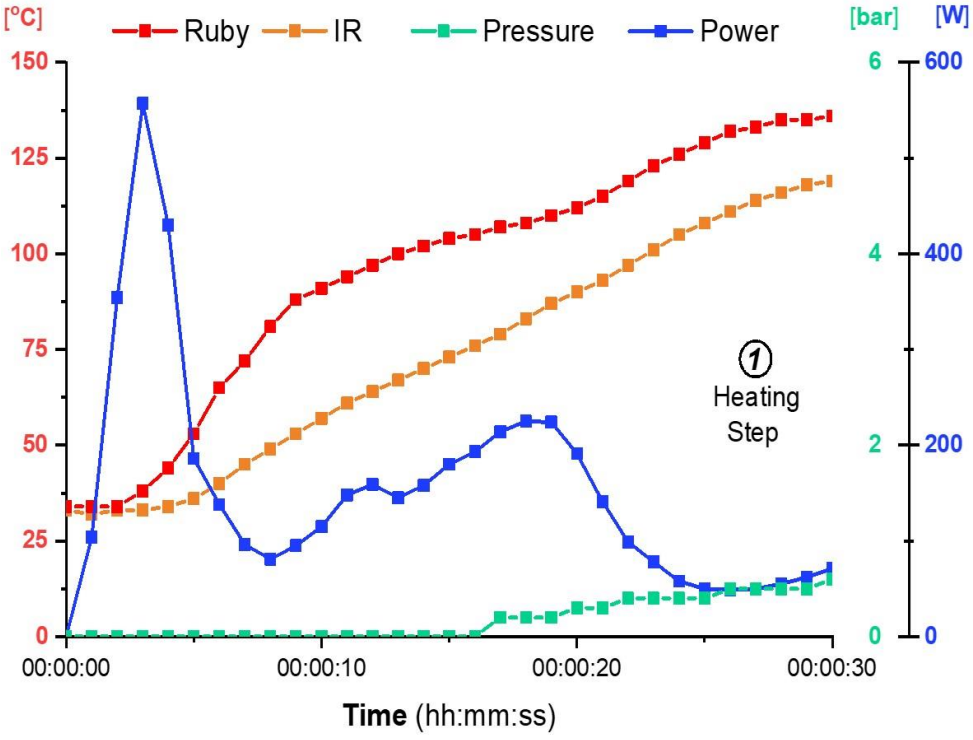

Figure S2. Detailed demonstration of the initial heating step during the MIL-88B(Fe) preparation.

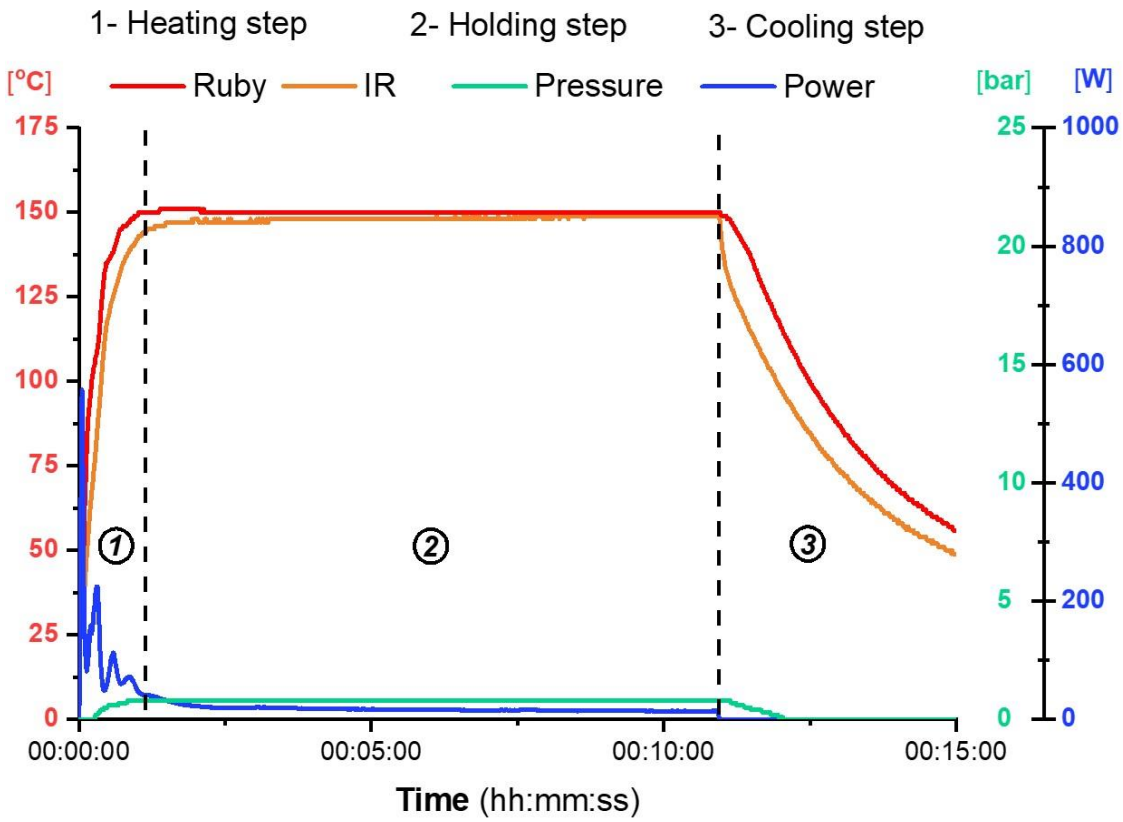

Figure S3. Graphical representation of the reactor conditions at each step during the MW synthesis process for MIL-88B(Fe).

➢ Surface area measurement:

The specific surface area of the obtained MIL-88 crystals was calculated using the BET method, at a relative pressure between 0.05 and 0.15 [6], expressing a specific surface area of 47 m^2 g^{-1}. The fitting for the data obtained within this range matched perfectly with the BET fitting (Figure S4). Nevertheless, the low SSA reported for the MIL-88B framework has been reported to be highly dependent on the adsorbed solvent.[7-11]

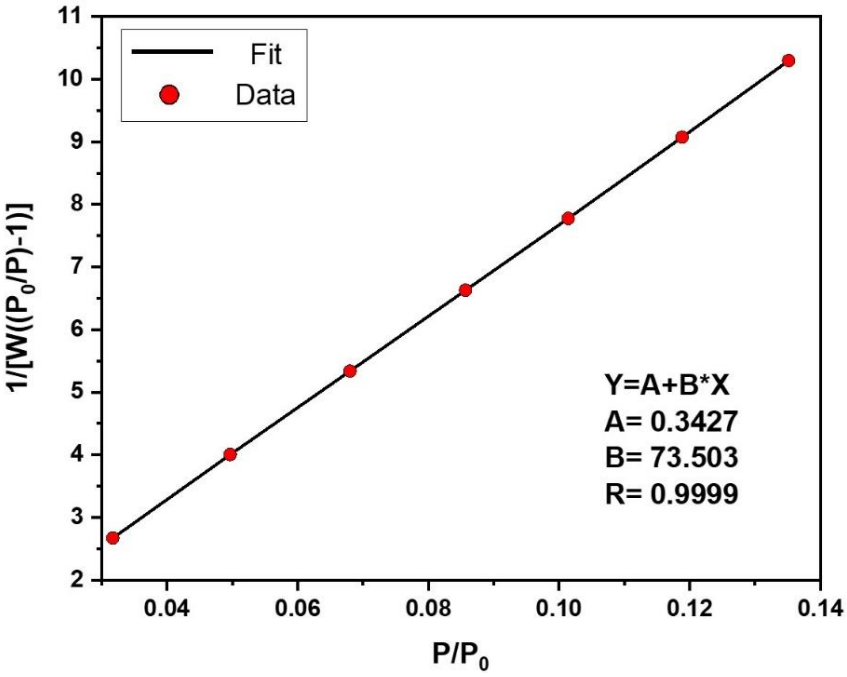

Figure S4. BET fit for the adsorption isotherm of MIL-88B(Fe).

We dug deeper to find the reason behind the low SSA measured for the MIL-88 framework. The MIL-88 framework possesses a flexible structure similar to that of the framework isomer MIL-53. They are both built from the trivalent metal ions and the ditopic H_2BDC linker. However, their breathing character comes as a result of different stimuli. The MIL-53 structure comprises infinite chains of metal oxo-clusters. These chains are corner linked to each other through the BDC linker. In the as-synthesized form MIL-53-as (cell volume = 1440 $Å^3$), the tunnels are occupied by structurally disordered molecules of neutral terephthalic acid. They leave the structure by heating at 300 °C and create the structure MIL-53-ht, with empty tunnels (cell volume = 1486 $Å^3$). By cooling in air, the structure reabsorbs water, which leads to the third form MIL-53lt (cell volume = 1012 $Å^3$).[12] Hence, thermal treatment would make the framework swell, and adsorbing polar molecules would make it shrink again. During SSA measurement of the MIL-53 framework via nitrogen sorption, the powders are degassed at high temperatures, and high SSA is measured due to the structure expansion.

Unlike MIL-53, evacuating the pores of the as-synthesized MIL-88 framework forces the structure to shrink, and the original space group is preserved. As a result, a drastic increase in the length between the two non-equatorial trimers of the framework's cages is observed, correlated with a decrease in the distance between the equatorial ones. Upon solvent adsorption, the bipyramidal cages flatten, increasing the cell volume, resulting in the framework swelling.[12]

Hence, the dry (solvent-free) MIL-88 has small pores, while MIL-53ht has expanded ones. Moreover, the swelling of the MIL-88 structure is highly dependent on the type of adsorbate and the steric hindrance of the terminal ligands.[7, 8, 13] Its low affinity towards nitrogen adsorption (very minute swelling) also contributes to the measured SSA. In addition, the adsorption kinetics is to be considered, in which the time taken by the structure to express its flexing character varies from seconds to hours or days depending on the incorporated solvent. All these reasons interpret why the reported SSA for the MIL-88 framework is usually low compared to the very high SSA known for MOFs.[7-11]

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