-Supplementary info file-

Live encapsulation of a Keggin polyanion in NH$_2$-MIL-101(Al) observed by *in-situ* time resolved X-ray scattering

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1.- Experimental procedures

Time resolved SAXS-WAXS experiments were performed at the beamline BM16 of the European Synchrotron Radiation Facility, ESRF (Grenoble, France), equipped with Roper Scientific CCD camera PI SCX90-1300 mounted on a Newport RV240PE goniometer, and X-Ray Research marCCD detector for WAXS and SAXS measurements, respectively. A complete description of the beamline is reported elsewhere. [1]

With the high-intensity synchrotron radiation and position-sensitive detectors, SAXS and WAXS patterns could be collected simultaneously with an excellent signal to noise ratio every twenty seconds at different points of the crystallization cell. The data were normalized for the intensity of the X-ray beam, sample transmission and corrected for detector sensitivity prior to background correction. The background scattering from the solvent (DMF or water) at the given reaction temperature was subtracted.
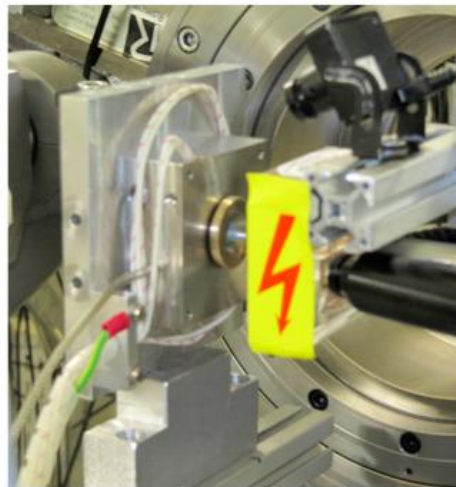

Figure S1.- Crystallization cell: a) top view; b) "at work"

A home-made synthesis cell was used for the experiments (Figure 1). In this cell the synthesis solution is loaded between two diamond or mica windows (10 mm diameter) separated by PTFE spacers (1.5 mm height). Heating was provided by four electrical resistance cartridges and temperature was controlled at the external wall of the PTFE inserts.

2.- MOF synthesis:

NH_2-MIL-101(Al) and HPA-NH_2-MIL-101(Al) were synthesized solvothermally with N,N-dimethylformamide (DMF) as solvent. Starting reactants are aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, Sigma Aldrich, 99%, 0.051 g), 2-amino terephthalic acid (HO_2C-$C_6H_3NH_2$-CO_2H, Sigma Aldrich, 99%, 0.056 g), and N,N-dimethylformamide (($CH_3)_2NCHO$, Sigma Aldrich, >99.9%, 3 ml). Phosphotungstic acid hydrate ($H_3PW_{12}O_{40} \cdot H_2O$, 99.995%, 0.08 g) was added in the HPA-NH_2-MIL-101(Al) synthesis. After vigorous stirring for 5 min, 0.1 ml aliquot was transferred to the in situ cell.

3.- Kinetic modelling

Analysis of the kinetic profiles was performed using the model developed by Gualtieri [2] and applied by Millange et al. [3] for the formation of several prototypical MOFs. This model is based on decoupling the nucleation and crystal growth processes. In such a way, the extent of crystallization (C) with time (t) can be simulated according to the following equation:

$$C = \left[\frac{1}{1 + \exp\left(-\left(\frac{t-a}{b}\right)\right)} \left(1 - \exp\left(-(k_g t)^n\right)\right) \right]$$

Fitting a kinetic curve with this expression yields the parametrization of a, b and k_g (growth rate constant) and indirectly the nucleation rate constant, $k_n = 1/a$. In this work, as suggested earlier by Millange et al., [3] it is assumed that MOF crystals grow in three dimensions ($n=3$) and that nucleation is heterogeneous ($b = 15$).

Table S1. Crystal growth and nucleation rate constants for NH_2-MIL-101(Al) and HPA-NH_2-MIL-101(Al) crystallization estimated from the fitting of experimental profiles recorded at different temperatures.

T / K	k_g / 10^4 s^{-1}	k_n / 10^4 s^{-1}
NH_2-MIL-101(Al)		
393	2.3	5.8
403	6.3	14
413	9.3	20
HPA- NH_2-MIL-101(Al)		
403	1.9	5.3
413	8.2	17

4.- SAXS analysis

Figures S2 and S3 show a selection of the first log Q - log $I(Q)$ scattering profiles measured at the beginning of the crystallization experiments at 403 K for both NH_2-MIL-101(Al) and HPA-NH_2-MIL-101(Al) before the onset of crystallization together with the development of the scattering intensity plotted vs. time for different Q values.
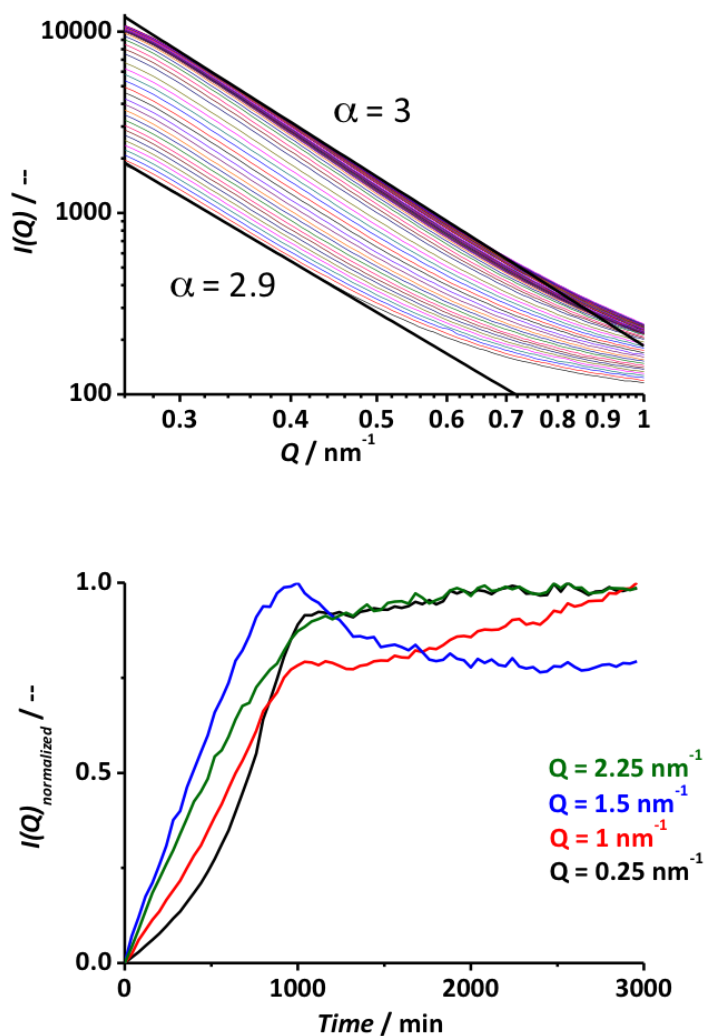

Figure S.2.- NH_2-MIL-101(Al) @ 403K: Selected $I(Q)$ profiles starting at time 0 and covering until the beginning of the crystallization in log-log representation. Black lines illustrate the $Q^{-\alpha}$

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decay (*top*). Development of the X-ray scattering at different Q values during the MOF synthesis, intensities are normalized (*bottom*).
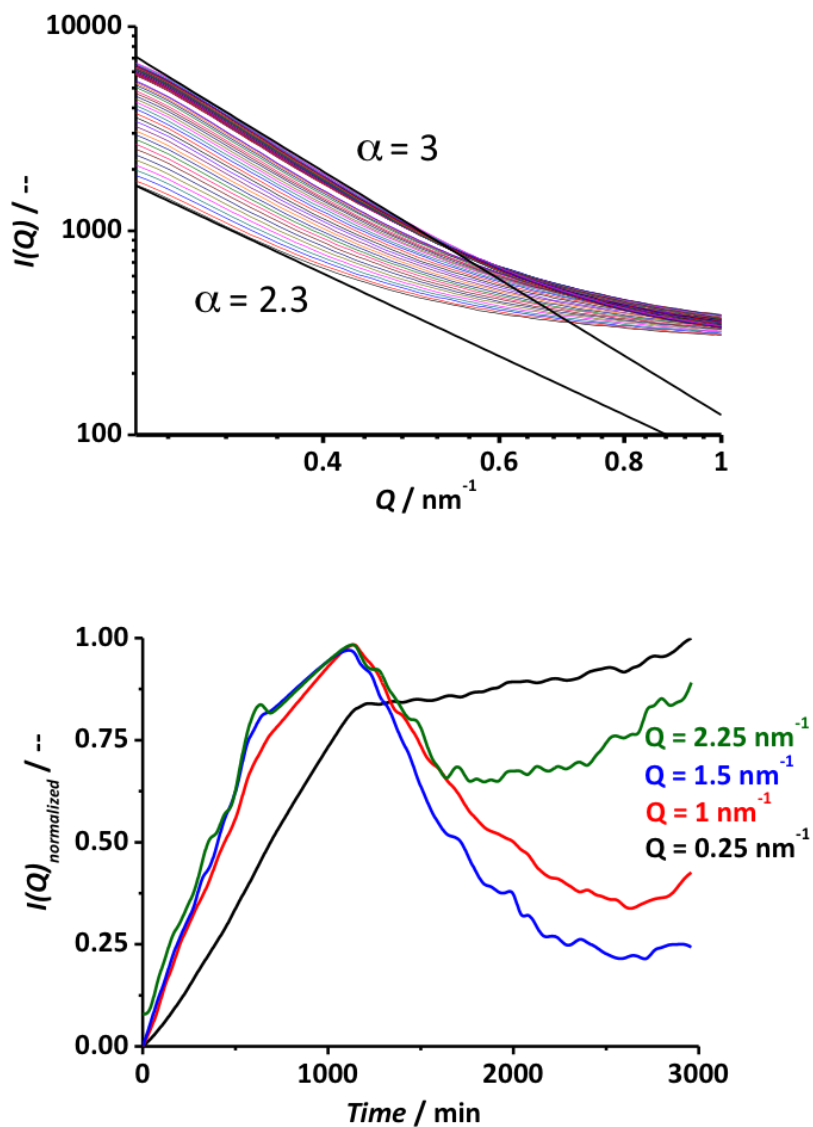

Figure S.3.- HPA-NH$_2$-MIL-101(Al) @ 403K: Selected $I(Q)$ profiles starting at time 0 and covering until the beginning of the crystallization in log-log representation. Black lines illustrate the $Q^{-\alpha}$ decay (*top*). Development of the X-ray scattering at different Q values during the MOF synthesis, intensities are normalized (*bottom*).

5.- Formation of MOF-235

Figure S.4. shows the formation of pure phase MOF-235 during the experiment performed at 393 K in the presence of HPA (top) and the formation of the same phase during the first reaction minutes (low temperature) previous to the formation of NH_2-MIL-101(Al) at 393 K.
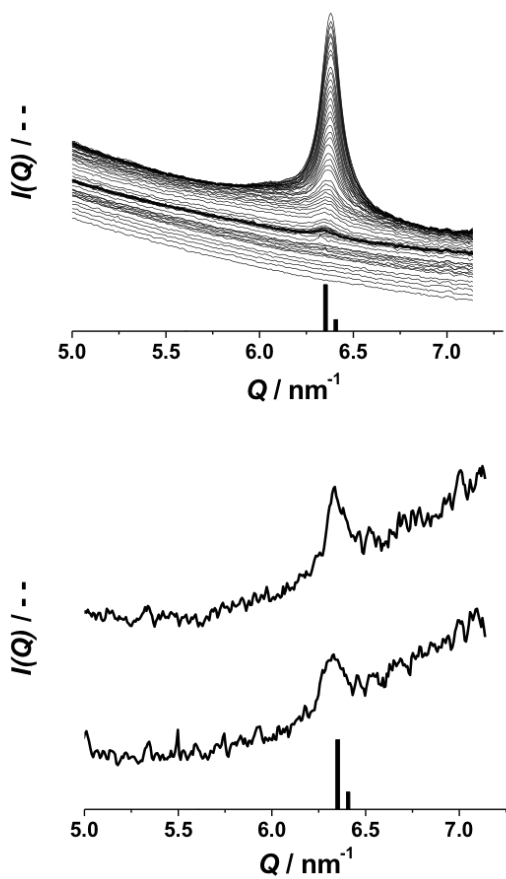
Figure S.4.- HPA-NH$_2$-MOF-235(Al) formation @ 393K: development of the Bragg peak illustrating evolution of the MOF structure (*top*). Spectra taken during the first synthesis minutes of NH$_2$-MIL-101(Al) (*bottom*). Solid bars represent the simulated XRD pattern of MOF-235.

References

[1]   J. Juanhuix, A. Labrador, D. Beltran, J. F. Herranz, P. Carpentier, J. Bordas, *Rev. Sci. Instrum.* **2005**, *76*, 086103-086104.
[2]   A. F. Gualtieri, *Phys. Chem. Miner.* **2001**, *28*, 719-728.
[3]   F. Millange, R. El Osta, M. E. Medina, R. I. Walton, *CrystEngComm* **2011**, *13*, 103-108.