



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

Thermodiffraction data of a high-quality Mn(III)-based terephthalate obtained in methanol enabled us to *refine its structure* (Figure 1). Unfortunately, the experiments showed that this MOF does not possess any detectable flexible behavior upon exposure to solvents or CO₂. Multivariate derivatives of this MOF, obtained by direct synthesis involving partial substitution of either the Mn(III) metal center metal (using 10 or 20 mol% of Cr^{III}, Fe^{III} or Al^{III}) or the linker (using variable amounts of 2-nitroterephthalate), were analyzed by thermodiffraction to detect eventual thermally-induced flexibility. Indeed, it has previously been shown that such a strategy can potentially significantly impact the flexible behavior of MOFs [2].

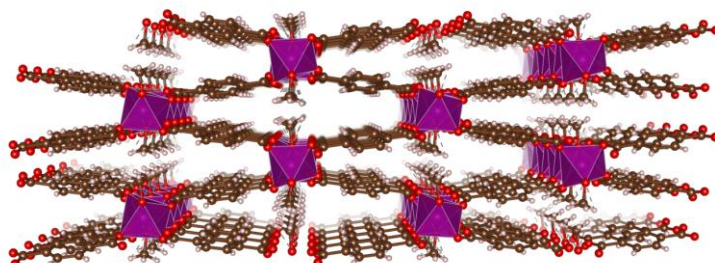


Figure 1. Structure of the MIL-53-like Mn(III)-based MOF with methoxy (OMe) bridging linkers. Color code: purple: Mn, red: O, brown: C, light pink: H.

The multivariate samples with metal substitution did not reveal any substantial peak shifts upon heating, indicating the absence of flexible behaviour. However, the samples with 10, 20, 30, 40, 50 and 60 mol% substitution by 2-nitroterephthalate showed surprising results. Whereas the crystallinity of those samples has been thoroughly checked in our lab one week before the experiment and showed a single phase of the MOF with the expected topology, splitting of diffraction peaks has been observed on the data recorded at SNBL (Figure 2).

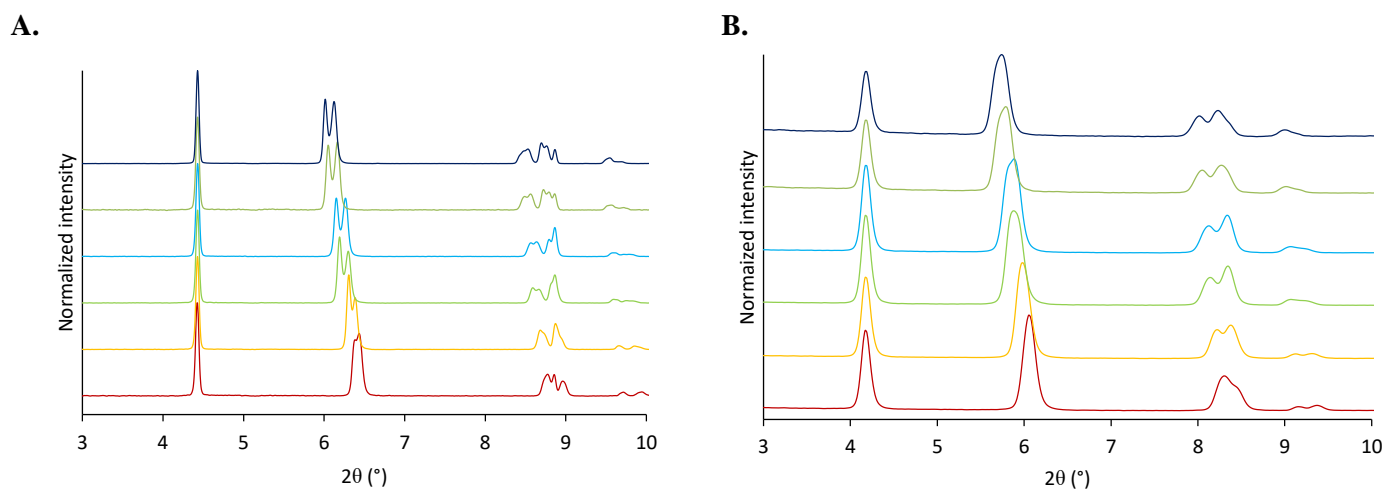


Figure 2. PXRD patterns of the multivariate derivatives of the MIL-53-like Mn(III)-based MOF with increasing amounts of 2-nitroterephthalate substitution (for bottom to top: 10, 20, 30, 40, 50 and 60 mol% nitro derivative used for the synthesis). The synchrotron data (A.) reveals peak splitting, which was undetectable by measurements performed in our lab (B.). Peak shifting is revealing gradual pore opening with increasing amounts of -NO₂ functions.

Additionally, peak shifting is observed, which, according to a preliminary data treatment, corresponds to an increase in the *b* parameter and a decrease of the β angle of the unit cell. This indicates that *the pores of the MOF gradually open with increasing amounts of nitro functions* on the linkers. Further refinement of the data is however needed to evaluate the origin of the peak splitting. The structure with the largest pore opening (i.e. using 60 mol% of 2-nitroterephthalate for linker substitution) has been tested for potential flexibility by sorption of CO₂, but unfortunately no significant changes in the diffraction patterns were observed during this experiment, indicating no or only very low uptake of the gas, with no associated structural change. Similarly,

no structural change was observed upon exposure to dimethylformamide (DMF), ethanol or dimethylsulfoxide (DMSO).

A derivative of the Mn(III)-based MOF with *naphthalene-2,6-dicarboxylate as and extended linker* was also synthesized in methanol. A thermodiffraction experiment showed that *the obtained MOF is a new framework with is similar to the previously described MIL-69* (which has previously been reported only with Al, Ga and V metal centers) (Figure 3) [3]. Thermodiffraction of this sample however does not reveal any significant change in diffraction patterns before decomposition, indicating that this MOF does not demonstrate any flexible behavior upon thermal stimulus. This observation is however not surprising as it is in accordance with the properties of the previously described MIL-69 derivatives.

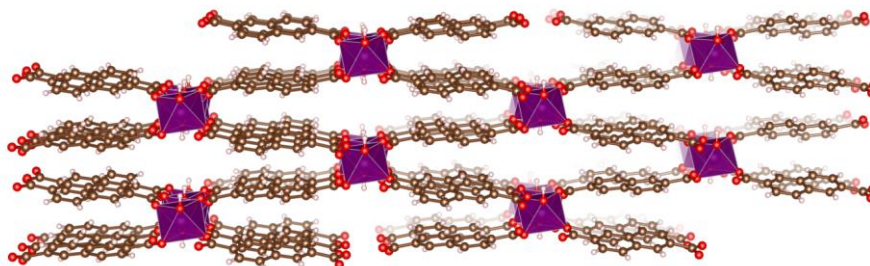


Figure 3. Preliminary structure of the MIL-69-like Mn(III)-based MOF based on the experimental data. Further refinement is needed to determine the presence of methoxy bridging groups (instead of -OH groups in the current model). Color code: purple: Mn, red: O, brown: C, light pink: H.

A terephthalate Mn(III)-based MOF was also obtained by *substituting methanol by ethanol for the synthesis*, with the aim to exchange the bridging -OMe groups by -OEt. This led to a MOF with a diffraction pattern that is significantly different from the MIL-53-type MOF that was obtained in methanol. Preliminary data treatment allowed to solve the *unprecedented structure* of this MOF, which shows *unidimensional porous channels* with a *unique spatial arrangement of Mn atoms in the chain-like secondary building unit* composing the framework, significantly different from the one in MIL-53 (Figure 4).

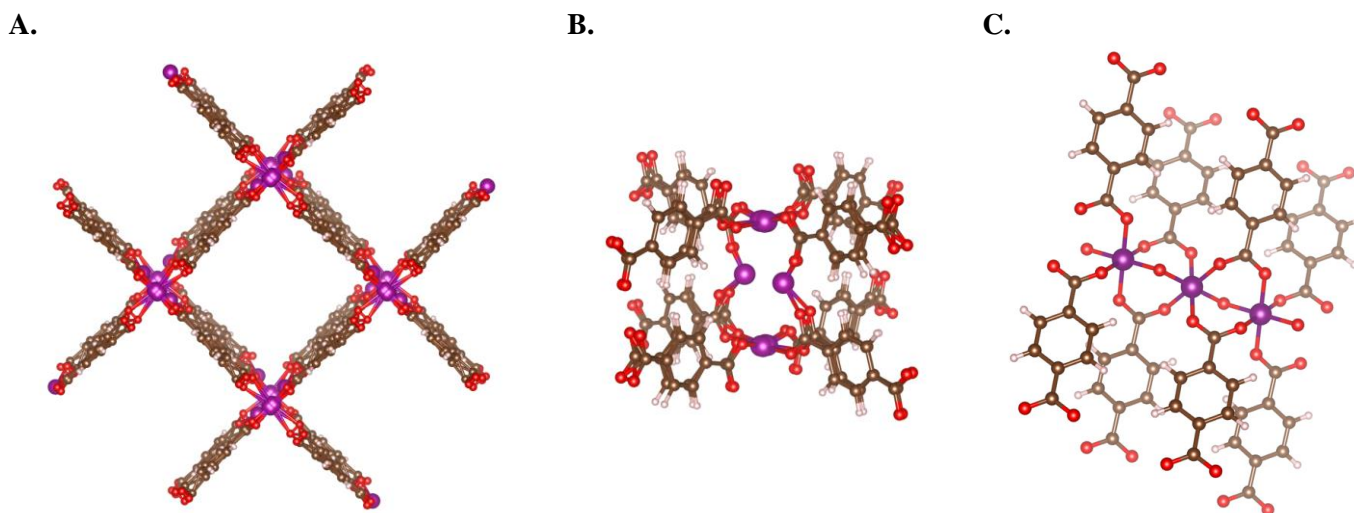


Figure 4. (A.) Preliminary structure of the terephthalate Mn(III)-based MOF obtained in ethanol along the porous channels with (B.) detail of the connectivity of the chain-like secondary building unit, compared to the one in the MIL-53-like derivative (C.). Further refinement is ongoing to determine the presence of alkoxy bridging groups and/or guest molecules. Color code: purple: Mn, red: O, brown: C, light pink: H.

This new MOF shows interesting behaviour upon exposure to various solvents molecules, as indicated by the thermodiffraction data collected on samples upon exposure to acetone, dichloromethane, DMF, DMSO, ethanol and acetonitrile. Surprisingly, *exposure to DMF leads to amorphization of the structure, which was shown to be perfectly reversible upon exchange with ethanol*, leading to recovery of a highly crystalline phase of the structure

displayed in Figure 4. This might be an example of recently described “*frustrated flexibility*” [4], as the reversibility observed during the experiments indicates that the connectivity, and thus the functionality, of the framework is maintained although crystallinity decreases. Upon *charging with DMSO*, the sample shows the presence of three different crystalline phases upon heating before decomposition (structures still to be solved), indicating a *complex breathing process upon thermally-induced DMSO guest removal*. Trials of charging CO₂ into the structure were shown unsuccessful, as no significant changes were observed using low pressure (0.5 bar) and amorphization occurred upon a test under higher pressure (40 bar). However, this might be due to inefficient activation of the MOF due to the fact that its properties are not yet fully understood.

Supplementary results (investigation of other samples taking advantage of remaining beam time)

Given the efficiency with which the experiments were performed, advantage of remaining beam time (last two shifts) has been taken to study several other interesting systems. This includes several MOFs, porous materials, hydrogen storage materials and composites for solid-state electrolyte applications.

Magnesium gallate is a MOF that is known for its interaction with several gases, and has been shown particularly useful for adsorption of CO₂, due to the particular S-shaped isotherms occurring during sorption of this gas in this particular framework [5]. Although this MOF has been studied with various gases and shows the best affinity with CO₂, no *in situ* structural studies have been performed on this framework up to now. Furthermore, in our lab we showed, by measuring gas sorption isotherms, that this MOF also possesses a very good interaction with N₂O, which is a greenhouse gas with a heat trapping ability 265 times higher than CO₂ and is currently the atmospheric gas that is the most implicated in destruction of the ozone layer. During our beam time, we were able to follow the thermally-induced activation process of this MOF under atmospheric pressure and under vacuum. Our results indicates that, unlike previously suggested by ex-situ measurements, activation of the framework to the dehydrated phase can be performed without applying vacuum (280°C under air), and the structural thermal stability of Mg gallate was shown to be particularly high. Thermodiffraction under CO₂ and N₂O loading was performed to determine the nature of the adsorption sites with both gases. The (high quality) data obtained during these experiments is currently being processed and refined.

A small series of other microporous MOFs was characterized by thermodiffraction under air to determine their structural thermal stability, as thermogravimetric analysis of the measured samples does not enable this due to difficult guest removal. The knowledge of the thermal stability of the measured samples will enable the optimization of activation processes for hydrogen storage purposes.

Thermodiffraction data of a (rare case of) porous cocrystal was also recorded, to complement laboratory data obtained on a single crystal. The aim of this experiment was to determine the structural integrity of the sample under the conditions used in the lab for gas sorption, to elucidate remaining questions about the properties of this sample.

A porous dodecaborate, namely (Me₄N)₂B₁₂H₁₂, was recently obtained by us and revealed the presence of isolated pores. Recent experiments showed that, although those pores are isolated one from another, gas sorption is possible (as demonstrated by sorption isotherms). Therefore, this material was subjected to an *in situ* experiment consisting of CO₂ loading under a fixed pressure and temperature. The results showed an important change in diffraction patterns upon exposure to the gas, which is promising in further understanding of the sorption processes in this material.

Four samples of candidate solid-state chemical hydrogen storage materials were also characterized by thermodiffraction. This will enable to evaluate the structure of intermediates that are formed during the dehydrogenation of the studied solids.

A last series of samples, composed of zeolites impregnated with hydrides (solid-state electrolytes materials) was measured by thermodiffraction. This enabled to determine the thermal stability of those composites.

We also measured nice single crystals data on two complicated cases within our collaboration with UNamur.

Conclusions and Perspectives

The experiments enabled the following about the Mn(III)-based MOFs:

- The structure of the terephthalate-based MOF obtained in methanol could be refined on a high quality sample;
- We showed that the terephthalate-based MOF obtained in methanol and its multivariate derivatives are rare examples of MIL-53 analogues that do not demonstrate any breathing behaviour upon heating, exposure to gases or solvents;
- Partial substitution of terephthalate by 2-nitro terephthalate in the Mn(III)-based MIL-53 derivative leads to partial pore opening;
- A new MIL-69 type MOF has been obtained with Mn(III) as metals center, but presents no flexibility upon heating;
- The structure of a new Mn(III) MOF composed of terephthalate units was obtained and its reversible (frustrated) flexible behavior was demonstrated by thermodiffraction data.

The above described results are currently being complemented with supplementary analyses to prepare a manuscript for publication. Further in-depth interpretation of the obtained diffraction data will also be performed to finalise the refinement and localise light elements in the pores, including guests and alkoxy groups which may have been overlooked by the preliminary data treatment (for example in the MIL-69 derivatives, since bridging -OMe groups were found in the MIL-53 derivative and synthesis conditions were highly similar for both MOFs). Further gas loading experiments on the flexible terephthalate Mn(III) MOF obtained in ethanol will be performed in our lab to evaluate the potential functional porosity of the material upon gas exposure, despite loss of crystallinity.

Data obtained during the other experiments will also be subject of upcoming publications, dealing with among other things:

- The activation process and sorption mechanisms of CO₂ and N₂O in Mg gallate;
- The synthesis and porous properties of a rare case of porous cocrystal;
- The synthesis and gas sorption properties of (Me₄N)₂B₁₂H₁₂;
- The dehydrogenation intermediates of new hydrogen storage materials;
- The structural stability of solid-state electrolytes based on zeolite-hydride composites

References

- [1] Millange F., Walton R.I., *Isr. J. Chem.*, **2018**, 58, 1019.
- [2] Bitzer J., Teubnerová M., Kleist W., *Chem. Eur. J.*, **2020**, 27 (5), 1724-1735.
- [3] Loiseau T., Mellot-Draznieks C., Muguerra H., Férey G., Haouas M., Taulelle F., *Comptes Rendus Chimie*, **2005**, 8 (3-4), 765-772.
- [4] Pallach R., Keupp J., Terlinden K., Frenzel-Beyme L., Kloß M., Machalica A., Kotschy J., Vasa S. K., Chater P. A., Sternemann C., Wharmby M. T., Linser R., Schmid R., Henke S., *Nature Communications*, **2021**, 4097.
- [5] Heymans N., Bourrelly S., Normand P., Bloch E., Mkhadder H., Cooper L., Gorman M, Bouzidi I., Guillou N., De Weireld G., Devic T., *J. Phys. Chem. C*, **2020**, 124 (5), 3188-3195.