



	Experiment title: Functional Microcrystalline Layered Lanthanide-Organic Frameworks	Experiment number: CH-2489
Beamline: ID31	Date of experiment: from: 19 – Apr. – 2008 to: 21 – Apr. – 2008	Date of report: 23 – Feb. – 2012
Shifts: 6	Local contact(s): Dr. Irene Margiolaki (E-mail: irene.margiolaki@esrf.fr)	<i>Received at ESRF:</i>
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Introduction e Summary of the Results:

In recent years our research group has been highly active in the synthesis and structural characterization of novel metal-organic frameworks (MOFs) in which lanthanide centers are coordinated to highly flexible phosphonate-based organic linkers.^[1-5] The main core of our research started in 2007 when we first described the two-dimensional (2D) lanthanide-organic materials formulated as $[\text{Ln}(\text{H}_3\text{nmp})] \cdot 1.5(\text{H}_2\text{O})$ [where $\text{Ln}^{3+} = \text{La}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}$ or Eu^{3+} ; $\text{H}_3\text{nmp}^{3-}$ is a residue of nitrilotris(methylenephosphonic acid)], whose crystalline structure could only be unveiled using *ab initio* methods based on high-resolution powder X-ray diffraction data collected at ID31.^[5] More recently, with the same organic linker, we have reported the layered $[\text{La}(\text{H}_3\text{nmp})]$ compound which undergoes a micro-crystal-to-micro-crystal phase transformation above 300 °C into a 2D network formulated as $[\text{La}(L)]$ (where $L^{3-} = [-(\text{PO}_3\text{CH}_2)_2(\text{NH})(\text{CH}_2\text{PO}_2)-]_n^{3n-}$).^[1]

This proposal (CH-2489) was performed in parallel with the experiment with reference CH-2533 (the research team is identical) and, prior to this visit to ID31, a considerable amount of powder data was already collected in September 2007 at BM01a. In this context, many of the results that were expected to be collected in this experiment were gathered in a previous visit to the ESRF. This resulted from a management of the allocated time: only 6 shifts were given to this proposal and, because many samples were important to be analyzed, the team decided to start collecting data at the BM01a beam line. In short, many of the results presented in the report for experiment CH-2533 are also of significant relevance to the present report and we encourage the reader to consult that same document.

During the course of the present experiment (CH-2489), high-resolution data were collected for a novel one-dimensional (1D) hybrid material with molybdenum that resulted in a good impact publication in which Dr Irene Margiolaki (our local contact) is a co-author. In addition, we completed some structural studies that

could not be completed in September 2007 at the experiment in the BM01a beam line concerning the post-catalysis structural features of the $[\text{Y}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$ material.

Results and Discussion:

The experiment started with a summary of the samples to be studied and our personal aim towards this experiment, to our local contact Dr Irene Margiolaki. It was decided that, taking into account previous investigations using similar materials but under different experimental conditions, hard X-rays were needed so to avoid radiation damage. After a wavelength change and the concomitant calibration of the ID31 machine the experiment started by collecting data for a short number of selected compounds.

$\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$

A significant portion of the shifts allocated to the execution of this experiment (CH-2489) was solely dedicated to the data acquisition of a high signal-to-noise powder pattern for a material which was ultimately formulated as $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$.^[6] The compound was systematically isolated as microcrystalline powders using either hydrothermal synthesis, an open reflux system or in a microwave reactor. A complete elucidation of the crystal structure was only possible by employing *ab initio* methods based on high-resolution synchrotron powder data (Figure 1). The structure is composed of two distinct

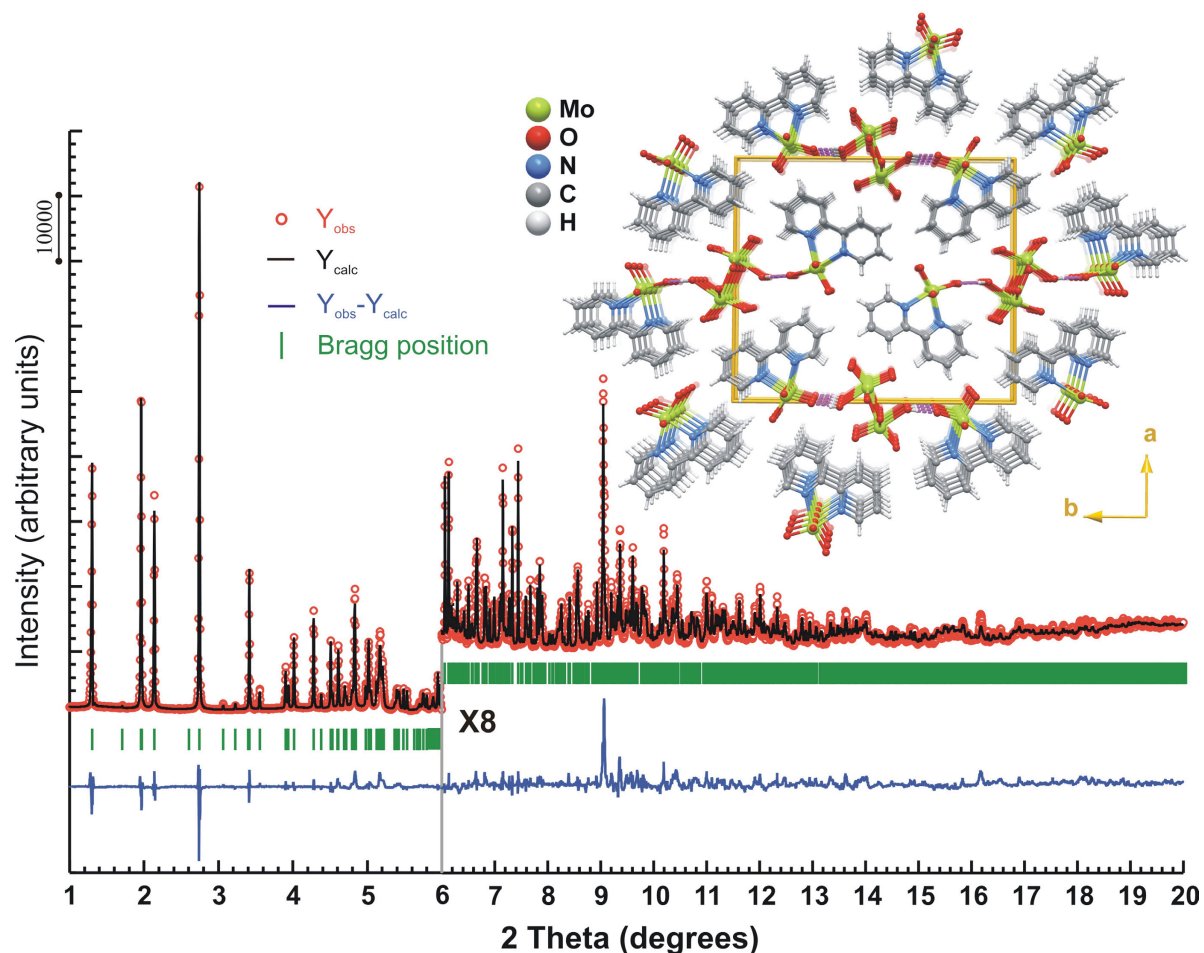


Figure 1. Final Rietveld plot of $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$. Observed data points are indicated as red circles; the best fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The inset shows a ball-and-stick crystal packing representation viewed down the $[001]$ crystallographic direction.

neutral one-dimensional polymers: an organic-inorganic polymer, $[\text{MoO}_3(\text{bipy})]_n$, and a purely inorganic chain, $[\text{MoO}_3(\text{H}_2\text{O})]_n$, both based on Mo^{VI} metal centers as unequivocally confirmed by bond valence calculations. The two polymers are linked in the compound by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding interactions in which the coordinated water molecule of $[\text{MoO}_3(\text{H}_2\text{O})]_n$ donates the two hydrogen atoms to neighboring oxygen atoms of the terminal $\text{Mo}=\text{O}$ oxide groups of the adjacent $[\text{MoO}_3(\text{bipy})]_n$ polymer.

Due to the highly collaborative nature of this work, in particular the studies focused at the catalytic activity of the material, the full set of results were only published in 2010 in *Inorganic Chemistry*.^[6] It is also important to emphasize that this particular work was awarded the prize for best poster in Chemistry by the IUCr in the last General Assembly of the International Union of Crystallography in Madrid (August 2011) – see Figure 2.

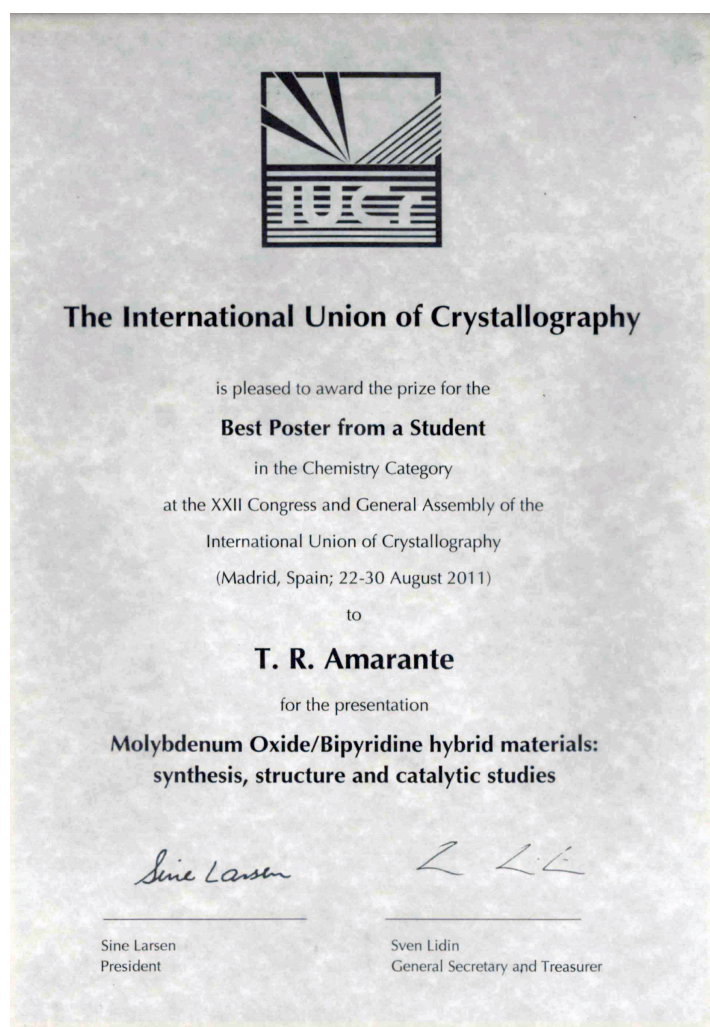


Figure 2. Copy of the award in the Chemistry Category given by the IUCr, and presented in the last General Assembly in Madrid (August 2011) to the poster reporting the structural studies on the $\{[\text{MoO}_3(\text{bipy})][\text{MoO}_3(\text{H}_2\text{O})]\}_n$ material.

Catalytic Studies on $[\text{Y}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$

The $[\text{Y}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$ material (where H_5cmp stands for *N*-(carboxymethyl)iminodi(methylphosphonic acid)) was tested as a heterogeneous catalyst in the cyclodehydration of xylose to furfural (see report for experiment CH-2533 for details on the crystal elucidation of this family of compounds). During the current experiment at ID31, high-resolution powder data were collected for the regenerated materials using either a calcination or a washing method. Figure 3 summarizes the powder data for two selected samples. From the

undertaken studies at ID31 it was possible to unequivocally conclude that calcination destroyed to a significant extent the crystalline structure of the catalyst while washing with appropriate solvents.

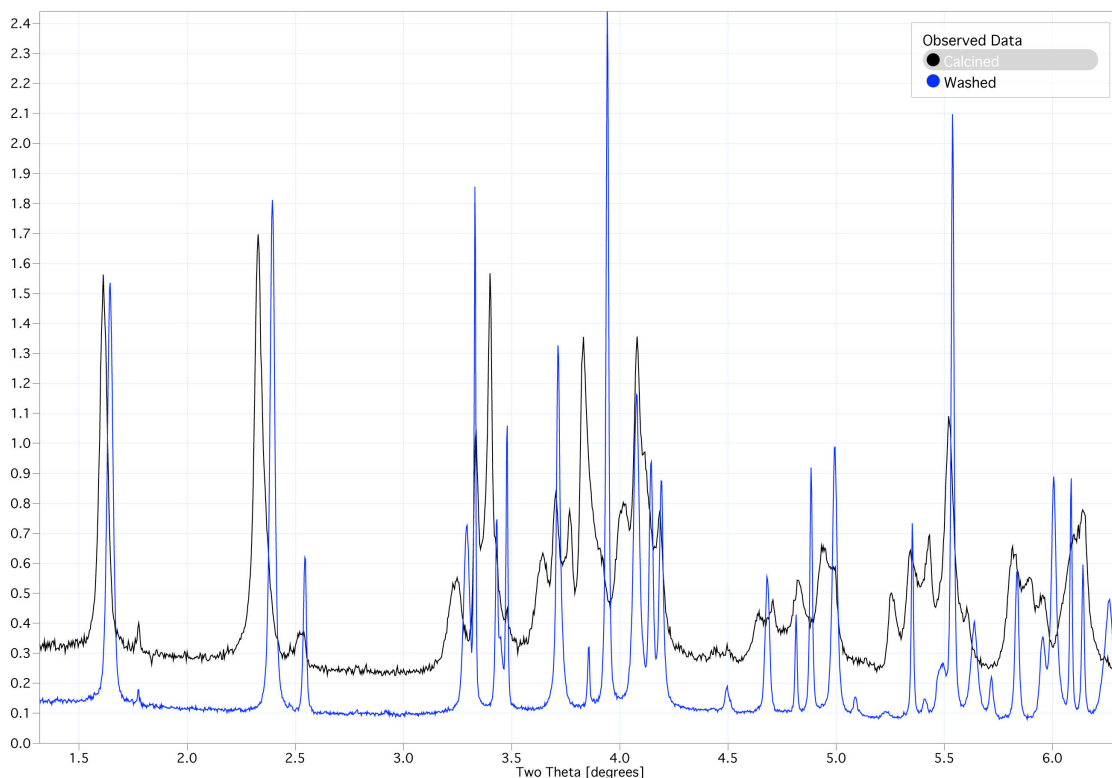


Figure 3. Comparison of the powder X-ray diffraction patterns of the regenerated $[Y(H_2cmp)(H_2O)]$ heterogeneous catalyst after washing with an appropriate solvent and after calcination.

Conclusions:

Despite the short period allocated to perform the experiment, the combination with other visits to the ESRF allowed the research team to manage the available machine time and collect useful data that culminated with the publication of a total of 5 publications (between this, CH-2489, and the experiment at BM01a, CH-2533). In particular, for this experiment, a good impact publication in *Inorganic Chemistry* resulted in collaboration with Dr Irene Margiolaki, in which the structure of the completely unprecedented $\{[MoO_3(bipy)][MoO_3(H_2O)]\}_n$ hybrid polymer was derived from powder X-ray diffraction data. The worldwide relevance of this work was recently internationally confirmed at the General Assembly of the International Union of Crystallography in Madrid (August 2011) where these results were awarded the prize for best poster in the Chemistry Category by the IUCr. During the present experiment important powder data were also collected to complement our previous studies on the structural features and integrity of the layered $[Y(H_2cmp)(H_2O)]$ material.

In summary, we believe that very short visits like this one can indeed produce very interesting results (such as those reported in the previous paragraphs) but, to fully take advantage of the great potentiality and facilities of the ID31 beamline, longer experiments (at least 3 days) are strongly advisable, especially if a wavelength is required in the beginning of the experiment.

Acknowledgements

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References

- [1] P. Silva, F. Vieira, A. C. Gomes, D. Ananias, J. A. Fernandes, S. M. Bruno, R. Soares, A. A. Valente, J. Rocha, F. A. A. Paz, *J. Am. Chem. Soc.* **2011**, *133*, 15120-15138.
- [2] L. Cunha-Silva, S. Lima, D. Ananias, P. Silva, L. Mafra, L. D. Carlos, M. Pillinger, A. A. Valente, F. A. A. Paz, J. Rocha, *J. Mater. Chem.* **2009**, *19*, 2618-2632.
- [3] L. Cunha-Silva, D. Ananias, L. D. Carlos, F. A. A. Paz, J. Rocha, *Z. Kristall.* **2009**, *224*, 261-272.
- [4] F. N. Shi, L. Cunha-Silva, R. A. S. Ferreira, L. Mafra, T. Trindade, L. D. Carlos, F. A. A. Paz, J. Rocha, *J. Am. Chem. Soc.* **2008**, *130*, 150-167.
- [5] L. Cunha-Silva, L. Mafra, D. Ananias, L. D. Carlos, J. Rocha, F. A. A. Paz, *Chem. Mat.* **2007**, *19*, 3527-3538.
- [6] M. Abrantes, T. R. Amarante, M. M. Antunes, S. Gago, F. A. A. Paz, I. Margiolaki, A. E. Rodrigues, M. Pillinger, A. A. Valente, I. S. Goncalves, *Inorg. Chem.* **2010**, *49*, 6865-6873.