EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

	Experiment title: Mimicking antenna systems from Nature: pressure-induced supra-molecular organization in dye-zeolite L hybrids.	**Experiment number**: CH-4262
Beamline: BM01	**Date of experiment**: from: 14/nov/2014 to: 18/nov/2014	**Date of report**: 6 July 2016
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Report:

We have investigated the response to high pressure of dye-zeolite L hybrid composites, where photoactive molecules are organized in one-dimensional nanostructures inside the zeolite channels.

The excellent optical properties and chemical stability of these composites make them key components of artificial antenna systems. We have applied high pressure to induce structural modifications to the system, and, possibly, to improve their functionality and expand their technological applications.

An artificial antenna system is an organized multi-component arrangement in which several chromophores absorb the incident light and channel the excitation energy to a common acceptor component [1-5]. Our artificial antenna systems were built by incorporating fluorenone (FL) dye molecules into the one-dimensional channels of zeolite L (ZL). ZL crystals feature strictly parallel nano-sized channels arranged in an hexagonal symmetry. These channels can be filled with suitable guests. The geometric constraints imposed by the host structure allow achieving supra-molecular organization of photoactive guests [2].

Hybrids formed by ZL and fluorenone have been synthesized at different FL loading (ZL/0.5FL, ZL/1FL, ZL/1.5FL) and characterized by conventional X-ray diffraction, TG and UV-Vis spectroscopy. Their structures at ambient conditions (previously simulated by means of computational studies [6]) have been recently investigated by conventional X-ray powder diffraction [7] (see Figure 1).

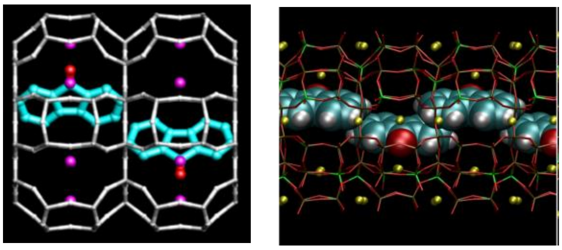

Fig. 1 - Graphical representations of fluorenone molecules inside zeolite L channel from X-ray diffraction experiments (left, projection along *a* axis) and molecular dynamics simulations (right, projection along *b* axis).

The in situ HP X-ray powder diffraction (XRPD) experiments were performed at the SNBL1 (BM01a) beamline at the ESRF with fixed wavelength of 0.72 Å, using a modified Merril-Basset DAC. Two different experiments were performed, using two PMTs. All the sample were studied with silicon oil (s.o.) as the non-penetrating P-transmitting medium and ZL/0.5FL, ZL/1FL also with a mixture of 16:3:1 by volume of methanol/ethanol/water (m.e.w.) used as a penetrating P-transmitting medium. Bidimensional diffraction patterns were recorded on a PILATUS2M-Series detector. One dimensional diffraction patterns were obtained in the 2theta range 0–43 by integrating the two dimensional images with the program FIT 2D. The experiments were performed from Pamb up to 6.0 GPa about for all the samples. Other patterns were measured while decompressing the samples down to room conditions (labeled (rev) in tables and figures). On average, about 15 spectra were collected for each sample with silicon oil and with m.e.w. (Figure 2).

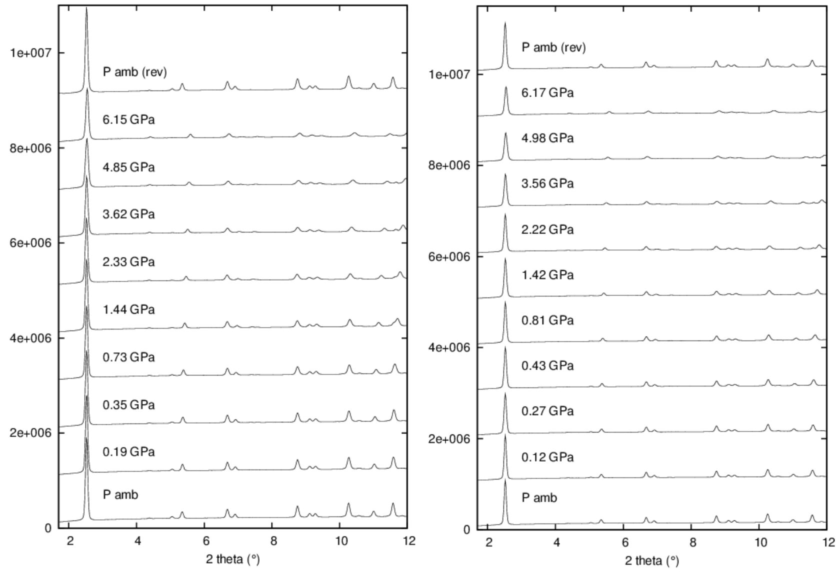

Fig. 2. Selected integrated powder patterns of ZL/0.5FL (left) ZL/1.0FL(right) as a function of pressure, reported in the 2theta range 3–12. The powder patterns at the top of the P amb (rev) collected during decompression.

Unit cell parameters of all the three samples were determined by Rietveld profile fitting up to 6 GPa both in s.o. and m.e.w. (Figure 3). The quality of the powder data collected allowed the structural refinement of the ZL/0.5FL, ZL/1FL composites successfully for the experiments at 2 GPa and 0.8 GPa and upon decompression (Pamb (rev)) in s.o. and m.e.w. respectively. The complexity of the ZL/1.5FL sample whereas allowed us to refine only the cell parameters up to the highest pressure, 6GPa in s.o. In general the analysis of the observed diffraction patters did not show any phase transition.

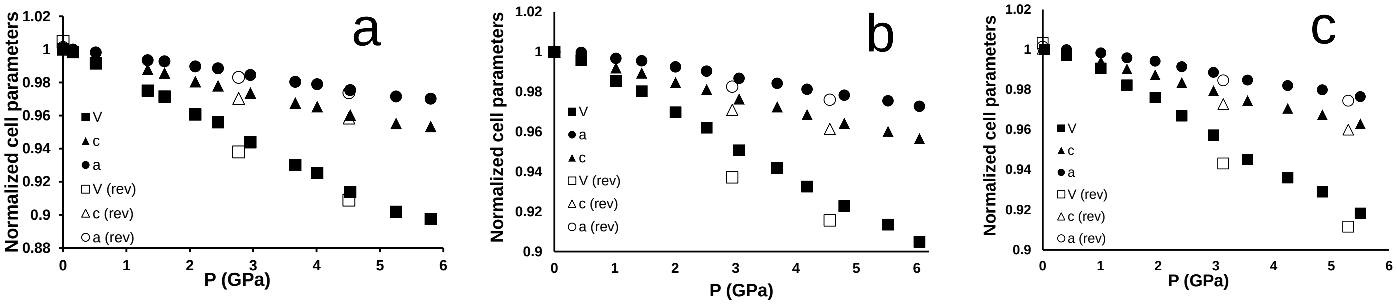

Fig. 3 Variations of ZL/0.5FL (a), ZL/1FL (b), ZL/1.5FL (c) normalized lattice parameters as a function of P. Open symbols are associated to the lattice values determined during decompression.

For ZL/0.5FL and ZL/1FL the structural refinements - still in progress - were carried out in the space group P/6mmm, using the GSAS package with EXPGUI interface.

References

[1] G. Calzaferri et al.(2003) Angew. Chem. Int. Ed., 42, 3732-3758.
[2] G. Calzaferri, K. Lutkouskaya (2008) Photochem. Photobiol. Sci., 7, 879 – 910.
[3] G. Calzaferri, et al. (2011) Chem Phys Chem., 12, 580-594.
[4] G. Calzaferri, A. Devaux (2011) in Supramol. Photochem.; Controlling Photochemical Processes. Eds. V. Ramamurthy, Y. Inoue, John Wiley & Sons, N. J., US, Chapter 9, p. 285-387.
[5] G. Calzaferri (2012) Langmuir, 28, 6216.
[6] E. Fois, et al. (2010) J. Phys. Chem. C, 114, 10572–10579.
[7] L. Gigli, R. Arletti,G. Tabacchi, E. Fois, J. G. Vitillo, G. Martra, G. Agostini, S. Quartieri, G. Vezzalini (2014) Phys. Chem C, 118, 15732-15743