PhD in INGEGNERIA DEI MATERIALI / MATERIALS ENGINEERING - 41st cycle

BORSE TEF Research Field: EXPLORING THE INCLUSION AND STRUCTURAL ELUCIDATION OF CO2 IN AMORPHOUS M12L8 INTERLOCKED METAL-ORGANIC CAGES USING IN SITU HIGH-RESOLUTION POWDER XRD SYNCHROTRON DATA

Monthly net income of PhDscholarship (max 36 months)
1800.0 In case of a change of the welfare rates during the three-year period, the amount could be modified.

Context of the research activity	
Motivation and objectives of the research in this field	Polycatenanes formed of selfassembled metalorganic cages (MOCs) are a relatively new class of materials and unexplored (from a functional point of view) that are very appealing both for their interesting topology and for their potential dynamic behaviour. The focus of this project is on polycatenanes of large icosahedral M12L8 interlocked nanocages self-assembled from tris-pyridyl benzene (TPB) (L) and zinc metal salt (M) (1). While the synthesis and the single crystal X-ray diffraction (SC-XRD) structure of 1 in solution has been investigated, some structural aspects of the product obtained using mechanochemical methods remain still to be understood. This is because the solid-state product is amorphous (a1). The grinding synthesis gives a short-range order amorphous phase that was demonstrated to be the catenane chains because undergo an amorphous-to-crystalline transformation upon guest inclusion, with the crystalline phase matching that of the interlocked structure of 1. The structure of 1 is unique as does not have direct channels but isolated voids with internal volumes of ca. 2600 Å3. However, 1 can undergo guest exchange reactions due to the dynamic behavior of the pyridine rings and the good host-guest affinity. In the amorphous phase, the dynamic behaviour and flexibility of the interlocked cages of a1 allows the guest inclusion of aromatic compounds, which give enough energy through templating effect for the chains to stack together into a stable crystalline phase.

	When non-aromatic solvents (e.g. methanol or chloroform) are used, there is still this transformation, but the product is not stable, and the evaporation of the guest makes the structure collapse and returning to the amorphous form after some time. The aim of this project is to investigate better this amorphous phase, including the isostructural counterparts using $ZnCl_2$ and ZnI_2 metal halides, trying to understand the topology and evolution in real time during the phase transformations. So far, the reported studies explored the inclusion of liquid solvents as templating agents. An interesting aspect that we would like to observe is the potential gas uptake, in particular CO_2. It would be significant to see if CO_2 can also induce this transformation and where it is located inside the cages to study the host-guest interactions.
Methods and techniques that will be developed and used to carry out the research	Powder X-ray diffraction (PXRD) laboratory experiments proved the evolution between amorphous to crystalline and then back to amorphous phase when small molecules like methanol or ethanol are used as templating agents. It is reasonable to think that CO_2 can have a very similar behaviour, and with the presence of CO_2 inside the cages could help to reconstruct the crystalline phase. However, this depends on the stability of CO_2 molecules trapped in the cages, and the ability to keep the crystalline phase for the duration of the powder XRD measurements. For this reason, it is hard to get a powder XRD pattern of the intermediate crystalline phase using ex situ laboratory diffractometers. However, using in situ high-resolution powder XRD synchrotron measurements, it could be possible to detect it due to the high intensity of the radiation and fast measurements. If the CO_2 inclusion yields a crystalline phase, we might be able to perform the structure solution and locate the position of the CO_2 molecules within the cage, as it is possible to index the unit cell using data from SC-XRD data. Moreover, we could monitor the entire evolution of the diffractograms from amorphous to crystalline as a function of time. From these powder XRD synchrotron experiments we expect to confirm the inclusion of CO_2 inside the cages, the transformation from amorphous to crystalline upon guest inclusion, and to elucidate the nature and topology

	of the interlocked material in the powder form. Studying the host-guest interactions occurring within the cages can help to select the best molecules to be trapped inside the material. Thus, the need for synchrotron beamtime is essential to allow the in situ high-resolution measurements that cannot be performed using laboratory instruments. The results from this proposal could contribute to the understanding of the solid-state host-guest chemistry of polycatenanes self-assembled from MOCs as potential candidates for molecular recognition and gas adsorption. Moreover, structural data is very important to carry out theoretical DFT calculations that can corroborate the experimental outcomes form high resolution synchrotron data.
Educational objectives	This PhD project is oriented to give the student a critical view of a given research field that can be later applied also at industrial level projects. The PhD student will learn how to independently approach and solve challenging research projects in the field of Chemistry and Materials Science. Finally, the ability to use experimental techniques (X-rays), writing articles and research proposals will be important in the PhD project.
Job opportunities	With the skills learned during the PhD program, the student will be well positioned to apply to both academic and industrial job opportunities. Given the topic addressed in the PhD project, jobs related to the CO2 mitigation will be of interest and highly demanded worldwide and especially at the European level. The portal of the European Research Council can be a place to check. https://erc.europa.eu/about-erc/work-with-us.
Composition of the research group	0 Full Professors 2 Associated Professors 0 Assistant Professors 1 PhD Students
Name of the research directors	Prof. Javier Martí Rujas

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ricerca/organicscm_lab/

Additional support - Financial aid per PhD student per year (gross amount)	
Housing - Foreign Students	--
Housing - Out-of-town residents	--

Scholarship Increase for a period abroad	
Amount monthly	900.0 €
By number of months	6

Additional information: educational activity, teaching assistantship, computer availability, desk availability, any other information

Confidentiality: since this is a thematic scholarship, the management of Confidential Information, Results and their publication should be subordinated to restrictions. Upon acceptance of the scholarship, the beneficiary may sign a specific commitment.

Educational activities (funding for participation in courses, summer schools, workshops and conferences) - financial aid per PhD student per year:
1st year: around 2.400 euros
2nd year: around 2.400 euros
3rd year: around 2.400 euros

Teaching assistantship: availability of funding in recognition of supporting teaching activities by the PhD student: There are various forms of financial of for activities of support to the teaching practice. The PhD student is encouraged to take part in these activities within the limits allowed by the regulation.