PhD offer at IRIG (CEA, CNRS, Grenoble Alpes Univ.) in the MEM and SyMMES research units.

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Project title: DNP-enhanced NMR to improve the stability of lead-free perovskite nanocrystals capped with bio-inspired ligands for the photoelectrocatalytic CO2 reduction.

A three-year PhD on NMR of perovskite nanocrystals using high-fields, ultra-low temperature MAS and Dynamic Nuclear Polarization is available. This will be a joint PhD between the MEM and SyMMES research units (CEA / CNRS / Univ. Grenoble Alpes).

Starting date between September and December 2024.

Keywords: solid-state NMR, Dynamic Nuclear Polarization, high magnetic field, quantum dots, lead-free perovskite

Background and motivation: In the development of colloidal nanocrystal synthesis, the discovery of $CsPbBr_3$ perovskite nanocrystals (PNCs) in 2015, and their **unique optical and electronic properties** have generated significant research interest.**[1-3]** In addition to their unique light-emitting properties, halogenated PNCs are also envisioned for other types of applications, such as **photocatalysis**. Several examples of the use of PNCs as photosensitizers or co-catalysts for the bio-inspired artificial photosynthesis approaches, such as solar-driven H_2 generation or CO_2 reduction have been reported.**[4,5]**
Currently, **the main issues for their applications for the photo(electro)catalysis are (i) the stability of PNCs in polar media** which are used in photocatalytic reactions, **(ii) the toxicity of lead**, which is still present in most of the PNCs materials, **(iii) the control of the facets termination** of the PNCs and their accessibility for photocatalysis.
Similar to most semiconductor NCs, **ligands are key to control both the growth** (size and shape), and **the colloidal stability of PNCs**. However, the ionic nature of the perovskite core makes them very different from other covalent semiconductor NCs, and particularly prone to degradation from environmental factors as well as in polar solvents. In addition, the defect-rich surface of the PNCs requires thorough passivation to avoid surface traps for the generated excitons. Recently, some strategies have been proposed **to improve their stability and further improve optical properties**, such as for example the use of **zwitterionic ligands**.**[6]** These bio-inspired molecules combine a cationic (such as quaternary ammonium) and anionic (such as phosphates or sulfonates) moieties for the passivation of anionic and cationic PNCs surface defects, respectively. By using a natural phospholipid, soy lecithin, this strategy has recently allowed to significantly improve optical properties and colloidal stability of $CsPbBr_3$ PNCs,**[7]** meanwhile the examples of use of zwitterionic ligands for the Pb-free analogues are extremely scarce.**[8]**

Approach: In this project, we propose to develop an approach **based on the use of Dynamic Nuclear Polarization (DNP) enhanced solid-state NMR**, combined with solution NMR, XRD and TEM to improve our understanding of the **surface structure and passivation of these systems and guide the engineering of improved ligands for photocatalysis**. DNP is an emerging **hyperpolarization approach** that allows enhancing the solid-state NMR sensitivity by several orders of magnitude. DNP has thus the potential for detecting site-specifically the inorganic core and the surface sites (NMR of 133Cs, 207Pb, 109Ag, etc.) of the NCs. More importantly, we are also planning to detect the surface ligands (1H, 13C, 15N, 31P) and their interaction with the NC surface sites. Such information is key to understand the **surface chemistry** of these systems, improve the **controllability of their synthesis** (**monodisperse PNCs in a large size range)**, and perform some **ligand engineering** with the goal to improve **their stability, their photoluminescence quantum yield (PLQY), or their reactivity to CO2** in the case of photocatalysis application.

So far, the most promising perovskite systems for CO2 reduction are Bi-based Cs3Bi2X9 **[9,10]** and Cs2AgBiX6 PNCs**[11]**These materials have been used for photocatalytic reduction of CO2 on the gas-solid interface with good efficiency and reasonable stability. **However, the examples of solution photocatalysis are still lacking due to the instability of the NCs in the solvents used.** So, we are planning to address this by performing some ligand engineering guided by the information provided by DNP. We are planning to develop **bio-inspired ligands**, such as soy lecithin, which is a mass-produced phospholipid, or some derivatives of phosphocholines. We expect that their **zwitterionic nature** will **(i) help passivating cationic and anionic surface defects**, and **(ii)** provide stronger bidentate surface binding **to improve both optical properties and the stability**. Since we envision photocatalytic applications, we will also integrate to the ligand **some functional groups such as amine, hydroxyl, carboxylic acid**, etc. in order to favor the affinity of CO2 towards the perovskite surface. We anticipate that improving the understanding of PNC surface passivation should help accelerating the development of lower toxicity, Pb-free PNCs alternatives.

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The candidate: We seek application from national and international students who have graduated in chemistry, physics or materials science, preferably with a background in NMR spectroscopy. The PhD will focus in **innovative NC synthesis** and also the development and application of an emerging hyperpolarization technique: high-magnetic field MAS-DNP (**Magic Angle Spinning Dynamic Nuclear Polarization**). Since the potential of this technique to study the surface chemistry of nanomaterials is beginning to be realized, the aim of this PhD is to further develop the methodology and use it to guide the synthesis of **lead-free perovskite nanocrystals**.

The PhD student chosen for this PhD will ideally have a strong background in chemistry and physical chemistry, and an interest in the development of **functional nanomaterials** as well **as advanced characterization techniques**. The PhD student will play a central role in this project, taking charge of all stages. He or she will have to master the synthesis of NCs and a basic understanding of all the physico-chemical characterizations that are typically performed on such systems (optical spectroscopies, DRX, electron microscopies, solution-state NMR). The PhD student will be able to interact with experts present in the IRIG institute for each of the techniques mentioned above. He/she will also become an expert in solid-state NMR and Dynamic Nuclear Polarization in order to conduct DNP-NMR experiments on the systems to be synthetized. This will also involve spin dynamic simulation and data analysis when needed. The project is designed so that the student develops **multidisciplinary skills** in **chemistry and physical chemistry**. More specifically, the PhD candidate will follow diverse trainings, encompassing chemistry, material synthesis and exposure to a broad range of (advanced) spectroscopies and analytical techniques. The PhD student's role will be to learn to master both facets of the project, to become a specialist in each aspect and to be the driving force behind this collaboration. His or her role will be to bring together the very different expertise of the supervisors, and to be proactive in his or her research and progress meetings. The gained knowledge and awareness will provide the candidate with the best springboard for a future career.

Hosts and research infrastructure: The project is at the frontier between the Emergence Core component and the Bio-inspired axis of the labex Arcane (https://arcane.univ-grenoble-alpes.fr/) since it involves the development of advanced characterization and nanomaterials for the activation of small molecules stabilized by bio-inspired ligands. It will benefit from the complementary expertise of the principal investigators, Gaël De Paëpe (MEM/RM - https://nmr-dnp-grenoble.net/) and Dmitry Aldakov (SyMMES/STEP).

GDP is advancing the field of **Dynamic Nuclear Polarization** and **solid-state NMR** applied to the study of challenging **functional material and complex biomolecular systems**. More specifically, the RM team actively develops advanced instrumentation and innovative NMR-based methods: from the design of improved pulse sequences to the introduction of new polarizing agents for DNP. Such advances enable the development of new applications in the field of materials science and biomolecular NMR. Key applications are related to biosourced materials, protein-ligand interaction, catalysis, energy generation and storage, and semiconductor nanocrystals.

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DA is working in the field of **chemical synthesis and study of colloidal nanocrystals**. The major motivation is to use the **safer-by-design materials** and replace toxic heavy metals by more eco-friendly elements. He then studies these nanomaterials using a variety of methods to understand their structure, surface termination, optical properties, composition etc. He is active in the field of colloidal semiconductor nanocrystals and lead-free halogenated perovskite materials. These (nano)materials are then applied in the field of solar cells, photo(electro)catalysis for H2 generation or CO2 reduction, photodetectors in the infra-red etc.

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