







## Doctoral fellowship of the doctoral school: "Physique et Chimie des Matériaux", Sorbonne University (ED 397)

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The colors of sea urchin spines towards the synthesis of bio-inspired hybrid colorants

**Topic**: Chemistry of materials, Biochemistry, Bio-inspiration, Colors

Keywords: organic-inorganic hybrid colorants, CaCO<sub>3</sub> synthesis, biomineralization, bio-coloration, sea urchin spines

Host Institution: Sorbonne University, "Laboratoire Chimie de la Matière Condensée de Paris", France

**Supervisors/Contact**: Marie Albéric and Thierry Azaïs

Research webpage: https://lcmcp.upmc.fr/site/biomineralization-biocolors/

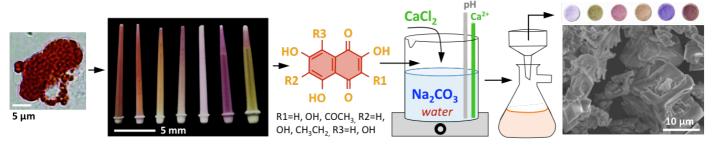
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Starting date: October 2020

Project description: Sea urchin spines show intense and diverse colors (from purple to green) that are due to a family of organic molecules, the polyhydroxylated-naphthoquinone (PHNQ) [1]. Although the majority of synthetic organic pigments hardly disperse in the medium to be colored and fade rapidly under sunlight, PHNQ molecules mass-color and provide long-lasting colors to sea urchin spines. These remarkable properties are likely due to the encapsulation of the PHNQ molecules within the crystalline biogenic calcite, which protects the organic pigments from the external environment [2]. This encapsulation occurs during the coupled pigmentation and biomineralization processes: the PHNQ molecules are first biosynthesized in the red-spherule cells and then incorporated within the calcite via the formation of an amorphous calcium carbonate (ACC) phase [3]. The growing mineral becomes first light pink and then takes different hues according to sea urchins and the biomineralization stages. However, the mechanisms at the origin of the color and its variations are unknown. Therefore, the objectives of this PhD is to 1) identify the physico-chemical mechanisms at the origin of the colors of sea urchin spines and 2) synthetize bioinspired colored hybrid CaCO<sub>3</sub> based materials.

The PHNQ molecules will be first extracted from the spines of different colors and from the red-spherule cells and identified by UV-visible spectroscopy, <sup>1</sup>H solution state NMR and HPLC/LC-MS. Second, bio-inspired synthesis will be performed in order to produce colored CaCO<sub>3</sub> crystals from an ACC precursor in the presence of the PHNQ. The "amorphous structure" of the different ACCs will be determined by pair distribution function analyses in the lab and using X-rays synchrotron radiation. The composition, the morphology and the structure of the colored bio-inspired crystals will be characterized by TGA-DSC, optical microscopy, SEM and TEM. In addition, the molecular interactions between the PHNQ molecules and the mineral phases (amorphous and crystalline) will be studied by solid-state NMR and high-resolution XRD experiments [4]. On its whole, the structural and chemical study as well as the colorimetric characterization of the biogenic samples and the synthetized colored CaCO<sub>3</sub> phases will contribute to a better understanding of the color origin in sea urchins and offer sustainable bio-based colorants that will further be tested for their potential use in the color industry.

- [1] Hou, Y. et al., Royal Society of Chemistry Advances (2018) 8, 32637.
- [2] Sanchez, C. et al., Journal of Materials Chemistry (2005) 15 3559.
- [3] Politi, Y. et al., Science (2004) 306(5699) 1161.
- [4] Albéric, M. et al., Crystal growth and Design (2018) 18 2189.



Required skills: The candidate should have experience in research and a good academic track record. She/He should have background in (bio)chemistry, materials science, synthesis and characterization. In particular, experiences in the analytical techniques cited above will be considered and an interest in multidisciplinary work as well as in biology will be appreciated. She/He should have a good level of English (written and spoken).

Application modalities: Candidate should provide a CV, a report of their last grades, the name and email address of two references and a cover letter before the 1<sup>st</sup> of May 2020.