AAP Postdoctoral Researcher E4C

Project title	**Metal Phosphide thin film from well-defined single-source precursors for catalytic applications**
PI #1 - Name and laboratory	SCHNEIDER, Nathanaelle, n.schneider@cnrs.fr Institut Photovoltaïque d'Ile-de-France, IPVF, UMR 9006
PI #2 - Name and laboratory	AUFFRANT Audrey, audrey.auffrant@polytechnique.edu Laboratoire de Chimie Moléculaire, LCM, UMR 9168
Research axis	RA1 : Decarbonized energy supply

Detailed description of the project

This project aims to develop **safe and efficient synthetic strategies for the deposition of metal phosphide thin films**. These are emerging as a versatile class of materials combining high chemical and thermal stability, good electrical conductivity, and mechanical robustness. Composed of abundant and low-toxicity elements, it offers a **sustainable alternative for advanced technologies in energy application, energy storage, and catalysis**.[1–4] Hence, the capacity to prepare metal phosphide nanostructures such as nanoparticles or thin films, is critical for applications.

Despite their promising properties, the controlled synthesis of metal phosphide nanostructures —particularly as conformal, ultrathin coatings on complex nanostructures—remains a major challenge. Conventional preparation routes (solid-state, hydrothermal, or gas–solid methods) involve toxic reagents and generally require multiple steps, high temperatures, and offer poor control over thickness and composition. In contrast, Atomic Layer Deposition (ALD) and Chemical Vapor Deposition (CVD) provide unparalleled control and conformality, yet their application is still limited by the lack of suitable, safe, easy-to-handle precursors.

Collaborative research between UMR-IPVF (Nathanaelle Schneider, DR) and LCM (Audrey Auffrant, DR) has led to the development of **an innovative methodology for identifying ALD/CVD precursors**. This approach integrates molecular engineering, thermal analysis, thin film fabrication, and characterization. In particular, these studies have highlighted the pivotal role of auxiliary X ligands (such as Me or NMe_2) in determining the efficiency of ALD precursors, and the relationship between molecular structures and thermogravimetric properties of gallium–amidinate based compounds.[5] It also emphasizes the complexity and uniqueness of surface chemistry compared to behavior in solution-phase environments.[6] Recently the research has focused on **metal complexes featuring phosphorus ligands** and have allowed the identification of ligand structures leading to thermally stable metal precursors from which thin films could be grown by CVD.

The present postdoctoral proposal targets:

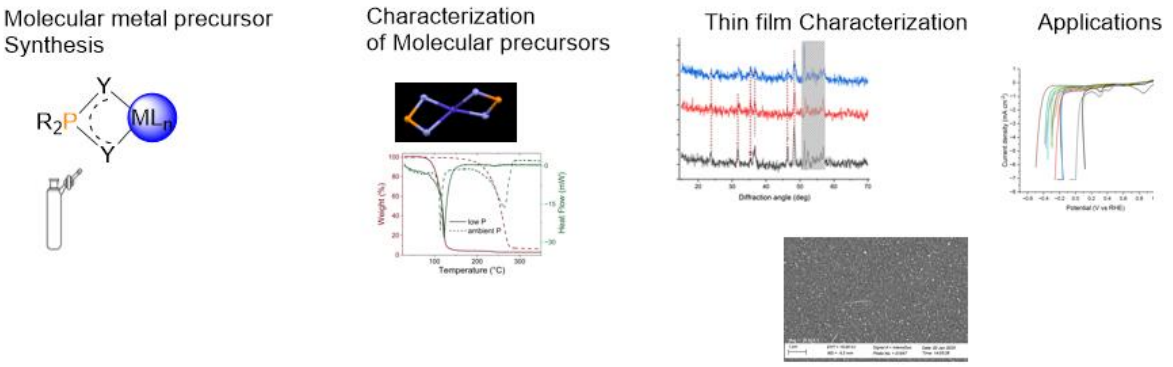
(i) The synthesis of an extended library of single-source metal precursor differing by the nature of of the phosphorus ligand or/and the metal employed in order to better understand the surface chemistry

(ii) Thin film deposition experiments through CVD or ALD and their characterization.

(iii) The exploration of structure–reactivity relationships governing film composition, morphology and phase formation

(iv) The evaluation of the electrochemical functionality of the resulting coatings

By establishing robust and sustainable synthetic routes, this project will pave the way toward scalable integration of metal phosphides in energy conversion and storage devices.



References

(1) Li, G.; Feng, Y.; Yang, Y.; Wu, X.; Song, X.; Tan, L. Recent Advances in Transition Metal Phosphide Materials: Synthesis and Applications in Supercapacitors. *Nano Materials Science* **2024**, *6* (2), 174–192. https://doi.org/10.1016/j.nanoms.2023.03.003.

(2) Wu, W.; Luo, S.; Huang, Y.; He, H.; Shen, P. K.; Zhu, J. Recent Advances in Transition Metal Phosphide-Based Heterostructure Electrocatalysts for the Oxygen Evolution Reaction. *Mater. Chem. Front.* **2024**, *8* (4), 1064–1083. https://doi.org/10.1039/D3QM00793F.

(3) Lu, X.; Yan, K.; Yu, Z.; Wang, J.; Liu, R.; Zhang, R.; Qiao, Y.; Xiong, J. Transition Metal Phosphides: Synthesis Nanoarchitectonics, Catalytic Properties, and Biomass Conversion Applications. *ChemSusChem* **2024**, *17* (10), e202301687. https://doi.org/10.1002/cssc.202301687.

(4) Bhunia, K.; Chandra, M.; Kumar Sharma, S.; Pradhan, D.; Kim, S.-J. A Critical Review on Transition Metal Phosphide Based Catalyst for Electrochemical Hydrogen Evolution Reaction: Gibbs Free Energy, Composition, Stability, and True Identity of Active Site. *Coordination Chemistry Reviews* **2023**, *478*, 214956. https://doi.org/10.1016/j.ccr.2022.214956.

(5) Pavard, P.-A.; Pugliese, E.; Coutancier, D.; Albin, V.; Casaretto, N.; Bourcier, S.; Lair, V.; Ringuede, A.; Auffrant, A.; Schneider, N. Relationship between Molecular Structures and Thermogravimetric Properties of Gallium–Amidinate Based Compounds. *Dalton Trans.* **2025**. https://doi.org/10.1039/D5DT00944H.

(6) Pugliese, E.; Coutancier, D.; Pavard, P.-A.; Hervochon, J.; Linden, B. van der; Casaretto, N.; Bourcier, S.; Pourtois, G.; Bouttemy, M.; Auffrant, A.; Schneider, N. Unveiling Surface Reactivity: The Crucial Role of Auxiliary Ligands in Gallium Amidinate-Based Precursors for Atomic Layer Deposition. *Dalton Trans.* **2025**. https://doi.org/10.1039/D4DT03498H.

IPVF

LCM Laboratoire de Chimie Moléculaire