Job offer – PhD in coordination chemistry
(*For non-French scientists only*)

Research Project Short Title as Submitted to CEFIPRA: "Non Noble Metal Stereogenicity in Asymmetric Photoredox Catalysis**"**
Principal Investigator contact (Name and email id): "Eric Manoury, Laboratoire de Chimie de Coordination (LCC), University of Tolouse, eric.manoury@lcc-toulouse.fr"
Reference Number of the Job Offer: IFI_CEF_25_16

Project description

- **Keywords:** Asymmetric Catalysis, Photoredox catalysis, Non-noble metals, Chirality at metal, Chiral metal complexes, Chiral at metal only complexes

- **Context:** Although asymmetric catalysis with chiral-at metal complexes has largely and successfully been practiced for noble metals, the use of non-noble metals has been scarce. Because of the fast depletion of noble metal resources worldwide, it is very important to develop new methods based on inexpensive and abundant base metals. This project therefore favours the use of iron, cobalt, and manganese complexes.

- **Abstract of the Research Project:** The aim of this project is to find novel strategies to synthesize chiral-at-metal complexes, thereby extending the boundaries of asymmetric catalysis beyond main-group element-based molecules. While remarkable strides have been made in synthesizing carbon-based chiral compounds through asymmetric catalysis over the past few decades, the catalytic synthesis of chiral-at-metal or chiral-only-at-metal complexes, particularly those involving earth-abundant metals, remains largely unexplored.
  This project focuses on three key objectives:
  1. Isolation of diastereomerically pure, chiral-at-non-noble-metal complexes. This involves creating complexes of metals such as cobalt and nickel through carbon-hydrogen bond activation using chiral ligands, specifically targeting configurations like [L*, Λ-(M)] or [L*, Δ-(M)] where L* represents a chiral ligand.
  2. Chiral Resolution of earth-abundant first-row late-transition-metal complexes. This aims to resolve chiral-only-at-metal complexes, specifically for metals such as iron, cobalt, and manganese, using transiently bound chiral ligands, resulting in configurations like [Λ-(M)] or [Δ-(M)].
  This project also aims to leverage the synthesized complexes as chiral catalysts for unconventional asymmetric catalytic reactions, including:
  (a) asymmetric reductive coupling of two electrophiles under dual photoredox/chiral-only-at-metal catalytic systems; (b) asymmetric mechanophotoredox catalysis; (c) asymmetric C-H bond activation in conjunction with photocatalysts; (d) asymmetric borrowing hydrogen chemistry.
  By advancing the synthesis and application of promising chiral-at-metal complexes, this project is poised to revolutionize our understanding of metal complex synthesis and catalysis. It aims to propel significant advancements in asymmetric catalysis, mechanophotoredox catalysis, and energy transfer catalysis. Grounded in classical coordination chemistry, asymmetric catalysis, photochemistry, and chiral resolution, this proposal embodies a multidisciplinary approach, bringing together diverse experts in one cohesive team. Success in this endeavour promises to catalyse the transition to a more sustainable society, offering transformative benefits across various scientific and industrial domains.

- **Scientific Objectives of the Project:** The scientific objectives of this project are the development of new chiral catalysts with earth-abundant and inexpensive base metals for application in asymmetric catalysis. The use of chiral-at-metal complexes of abundant metals like iron, cobalt or manganese is largely unexplored and the development of such chiral at metal complexes presents tremendous opportunities for major advances and must be highly impactful. For iron, cobalt or manganese, the first aim of our team in the consortium will be to provide robust and efficient methods to obtain diastereoisomerically and enantiomerically pure metal complexes bearing enantiomerically pure ligands and with a configurationally stable chirality at the metal, but also chiral-only-at-metal complexes with, of course, a configurationally

stable chirality at metal. Another aspect will be the mechanistic investigations, both experimentally and computational, of the best catalytic systems developed by our Indian partner.

- **Methodology and Timeline of the Project:** The project will start with the synthesis and characterization of chiral-at-metal complexes of base metals such as cobalt, iron and manganese. We plan to isolate diastereomerically pure chiral-at-metal complexes bearing enantiomerically pure ligands, specifically targeting configurations like [L*, Λ-(M)] or [L*, Δ-(M)], where L* represents a chiral enantiomerically pure ligand (bis-chelates or tetradentate chelators). After separation of the diastereomeric metal complexes, we will remove the chiral auxiliary in order to obtain chiral-only-at-metal complexes, namely complexes of configurations [Λ-(M)] or [Δ-(M)]. We will also isolate such chiral-only-at-metal complexes via resolution using transiently bound chiral ligands.
  As soon as we will have enantiomerically pure chiral-at-metal complexes of iron, cobalt or manganese in hand, our Indian partner will investigate their potential as catalysts for asymmetric catalysis, in combination with photocatalysts or not, for C-H bond functionalization, asymmetric C-H bond amidation, asymmetric C-C and C-X bond formation, asymmetric transfer hydrogenation and dehydrogenation reactions and asymmetric photo-mechanochemical transformations. Our group will focus on the mechanistic aspects, both experimentally and computationally, of the best catalytic systems developed by our Indian partner.

Candidate profile

- Candidates can be of all nationalities except French. In case of double nationality (French and another one), the candidate is not eligible. Indian candidates are preferred.
- Applicants must have an MSc degree or a degree equivalent to a French Master's degree at the time of the deadline of the call.
- No French language skills are required.
- Candidate competences: theoretical training and coordination chemistry, stereochemistry, homogeneous catalysis; basic knowledge of theoretical chemistry, though not mandatory, is also appreciated.
- Candidate know-how: practical experience in the synthesis and characterization of coordination compounds.
- Expected starting date: 01-10-2025.
- Expected duration: 36 months.

How to apply?

Documents to be provided:

i. A cover letter (reasons for the application, professional project …) max 2 pages
ii. A copy of the master's degree or a proof of the program followed (and expected date of end) OR A copy of the PhD degree or a proof of the PhD program followed (and expected date of defense) max 1 page
iii. A copy of results for previous scholarship (max 3 pages)
iv. International curriculum vitae (max 2 pages)
v. Two letters of recommendation: one from any Indian institution and one from the French institution planned to host the candidate –mandatory- (max 2 pages)
vi. All should be submitted within 1 pdf file of no more than 10 pages.

Applications should be submitted to the following email address: msi@ifindia.in mentioning the reference number of the Job offer clearly.

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Candidates are requested to contact the French scientific principal investigator of the project before submission. A recommendation letter from the scientific principal investigator is mandatory.

Benefits:

- Monthly allowance of 1790 euros for PhD
- Travel allowance
- University fee
- Carte de séjour fee
- Campus France management fee
- Registration to the French social security scheme

Selection process:

Selection is made by a dedicated selection committee of at least 4 persons. Decisions will be transmitted by the Embassy of France to CEFIPRA. **No consideration will be given for candidates with no recommendation letter from the French institution.**

Criteria for applicants' selection:

Academic excellence

- Excellence of the Academic background, Academic records, Honors, Letters of support, Participation to international research projects, exchange programmes and conferences.

Motivation and qualities

- Academic maturity: appropriation of the thesis project (stakes and contexts) • Quality of the presentation (oral expression, skills for synthesis, English level) • Maturity of the professional project: capacity to project her/himself within five years in terms of career development.

About CEFIPRA:
Indo-French Center for the Promotion of Advanced Research (CEFIPRA/IFCPAR) is an Indian body which promotes scientific cooperation between France and India in advanced fields of Science and Technology. It is supported by the Department of Science and Technology, Government of India and the Ministry of Europe and Foreign Affairs of the French government