PhD position - Helicenes for and from magnetochiral effects (HEL-MCH)

Place: Institut des Sciences Chimiques de Rennes (UMR 6226) and Laboratoire National des Champs Magnétiques Intenses

(LNCMI, UPR 3228) **PhD CNRS** (80 Prime) **Duration**: 36 months

Expected starting date: 01.10.2023

Full-time work, with a net monthly salary around 1700 € per month.

Supervisor: Jeanne Crassous (**jeanne.crassous@univ-rennes1.fr**), ISCR UMR 6226 (Rennes, France) **Co-supervisor**: Matteo Atzori (**matteo.atzori@lncmi.cnrs.fr**), LNCMI-CNRS UPR 3228 (Grenoble, France)

The term chirality originates from the Greek word "χειρ" (Kheir) which means "hand". First defined in 1848 by Louis Pasteur as "molecular dissymmetry" during his famous experience of resolution of double tartrates by spontaneous crystallization, it was Lord Kelvin who in 1884 proposed the term chirality to describe any geometric figure or any set of points which cannot be superimposed on its mirror-image (like the right and left hands). Three-dimensional chirality is closely linked to the appearance of life on earth since almost all the essential natural amino acids and constituents of proteins as well as the sugars of DNA and RNA adopt a one and the same configuration! The origin of the homochirality of the living world remains one of the great unresolved scientific enigmas to date.

Pasteur had already noticed this ("The Universe is dissymmetric", 1883) and was the first to attempt to generate an excess of one of the two forms, right and left, of a chiral molecule, by means of an asymmetric force during enantioselective crystallization experiments under a magnetic field. However, for symmetry reasons, the magnetic field alone is not sufficient to generate chirality. For this, it is necessary to associate a light propagating parallel to the magnetic field. This is called the magnetochiral effect (MCh). Observed for the first time in 1997, the magnetochiral effect and the enantioselective magnetochiral photochemistry are a fascinating demonstration of the chiral light-matter interaction. The aim of this interdisciplinary project, at the interface between chemistry and physics, is to better understand the magnetochiral phenomena and to observe magnetochiral dichroism (MChD), which corresponds to the enantioselective absorption of unpolarized light from a chiral system placed under a magnetic field, on helices, and to take advantage of this to generate an excess of enantiomer by magnetochiral photochemistry, in particular to carry out the synthesis of enantioenriched helicenes.

For this purpose, new organometallic precursors will be synthesized at the ISCR in Rennes in the team of Jeanne Crassous (chemist, project leader, specialist in helicenes, chiral molecules with helical topology) while the study and obtention of helices by a magnetochiral force will be studied and implemented at the LNCMI by Matteo Atzori, Cyrille Train and Geert Rikken,. The helicenes will be modified to bind to many ions and in particular rare earths in collaboration with specialists in the field (Fabrice Pointillart, Boris Le Guennic, Olivier Cador, ISCR, Rennes).²

The interests and implications of this project are multiple: i) development of organometallic architectures sensitive to light and magnetic field; ii) improvement of the detection limits of MChD and implementation of photochemistry under a magnetic field; iii) better knowledge of the magnetochiral effect at the molecular and supramolecular levels, in the solid state and in solution; iv) enantioselective synthesis via a fundamental chiral force.

¹ a) Observation of magneto-chiral dichroism. G. L. J. A. Rikken, E. Raupach, Nature **1997**, 390, 493. b) Enantioselective magneto-chiral photochemistry. G. L. J. A. Rikken, E. Raupach, Nature **2000**, 405, 932. Observation of Magneto-Chiral Dichroism. G. L. J. A. Rikken, E. Raupach, Nature **1997**, 390, 493. c) Magneto-Chiral Dichroism: A Playground for Molecular Chemists. M. Atzori, G. L. J. A. Rikken, C. Train, Chem. Eur. J. **2020**, 26, 9784.

² a) Ligand-Centered Helicoidal Chirality Enables Strong Magneto-Chiral Dichroism in an Enantiopure Yb^{III} Paramagnetic Complex. M. Atzori, K. Dhbaibi, H. Douib, M. Grasser, V. Dorcet, I. Breslavetz, K. Paillot, O. Cador, G. L. J. A. Rikken, B. Le Guennic, J. Crassous, F. Pointillart, C. Train, J. Am. Chem. Soc. 2021, 143, 2671. b) Multifunctional Helicene-Based Ytterbium Coordination Polymer Displaying Circularly Polarized Luminescence, Slow Magnetic Relaxation and Room Temperature Magneto-Chiral Dichroism. K. Dhbaibi, M. Grasser, H. Douib, V. Dorcet, O. Cador, N. Vanthuyne, F. Riobé, O. Maury, S. Guy, A. Bensalah-Ledoux, B. Baguenard, G. L. J. A. Rikken, C. Train, B. Le Guennic, M. Atzori, F. Pointillart, J. Crassous, Angew. Chem. Int. Ed. 2023, e202215558.