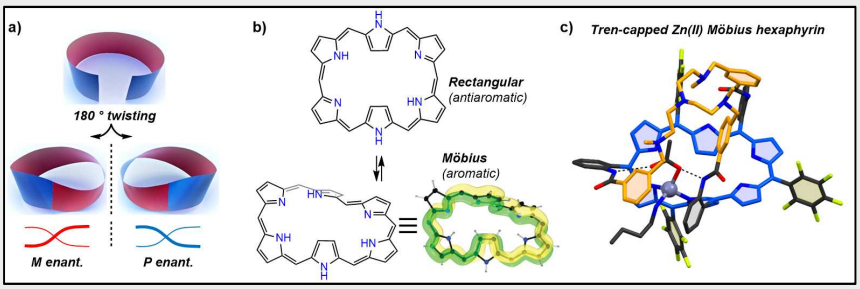
PhD position available at the University of Rennes

Title : Hexaphyrin-Based Networked Multicomponent Systems (HEXANET)
Keywords : hexaphyrin, topology, chirality, aromaticity, coordination, recognition, system chemistry
General information: the thesis will be carried out in the team *Macrocycles Pyrroliques et Processus Bio-Inspirés*, under the supervision of Dr. Stéphane Le Gac, at the *Institut des Sciences Chimiques de Rennes* (UMR CNRS 6226; https://iscr.univ-rennes1.fr/pyrrolic-macrocycles-exotic-coordination-and-adaptative-systems). Period: Oct. 2025-Sept. 2028. Gross salary: ~2300 €/month (financial support from the University of Rennes).

Description: biological systems can be seen as vast ensembles of molecules in which complex interactions between many components, as well as chemical transformations operating in a network, allow the emergence of sophisticated functions essential to life. Being able to understand and control complex behaviors involving several molecular Möbius rings (which our laboratory specializes in),[1] would constitute an interesting starting point for new developments in the chemistry of complex systems, in adaptable materials or in switchable catalytic machines. Focusing on the Möbius [28]hexaphyrin scaffold,[2] our group has investigated an original approach for chirality induction taking advantage of the dynamic character of the twisted π-system.[3] Recently, we designed a pair of hexaphyrin ligands with opposite designs, in order to study mixtures rather than isolated molecules. This novel strategy led to a remarkable networked transformation system, operating through chemical effectors, allowing multiple modulation of the chiroptical activity of the ensemble. This work opens up interesting perspectives, and we wish to extend this research theme to multicomponent systems that can be operated by non-invasive and orthogonal stimuli (*e.g.* light, redox processes, etc.). In the medium term, allosteric metallo-receptors/catalysts that can work in a network and respond selectively to multiple stimuli could thus emerge. This exploratory project aims at pushing to the extreme the adaptive properties of the hexaphyrin macrocycle in a context encompassing molecular recognition, coordination chemistry, chirality and aromaticity. The candidate will have to synthesize highly functionalized hexaphyrins, characterize them by NMR spectroscopy, study their conformational and coordination properties, as well as the modulation of their stereochemistry. He/she will then have to define the best partners capable of forming multicomponent systems and study the behavior of such sets.

Profile of applicant: the candidate, with a Master 2 degree in molecular chemistry, must have a solid knowledge in general chemistry and more particularly in organic synthesis and NMR spectroscopy. The synthesis and characterization in solution of dynamic macrocyclic ligands and zinc complexes will constitute an important part of this thesis. A strong practical aptitude as well as a significant personal investment will be necessary. People interested will kindly send a CV, a motivation letter, the contact details of two people who can recommend the candidate as well as their Master's transcript and diploma (stephane.legac@univ-rennes.fr).



Key features: (a) The two enantiomers of a Möbius ring.[1] (b) Rectangular and Möbius conformers of a [28]hexaphyrin.[2] (c) Bio-inspired Möbius-type metallo-receptor.[3a]

References:

[1] R. Herges, *Chem. Rev.* **2006**, *106*, 4820-4842. [2] T. Tanaka, A. Osuka, *Chem. Rev.* **2017**, *117*, 2584-2640. [3] a) H. Ruffin, G. Nyame Mendendy Boussambe, T. Roisnel, V. Dorcet, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.* **2017**, *139*, 13847-13857; b) R. Benchouaia, N. Cissé, B. Boitrel, M. Sollogoub, S. Le Gac, M. Ménand, *J. Am. Chem. Soc.* **2019**, *141*, 11583-11593; c) B. Boitrel, S. Le Gac, *Chem. Commun.* **2020**, *56*, 9166-9169; d) B. Boitrel, S. Le Gac, *Chem. Commun.* **2021**, *57*, 3559-3562; e) H. Ruffin, A. Fihey, B. Boitrel, S. Le Gac, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113844; f) T. Nédellec, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.* **2023**, *145*, 27067-27079.