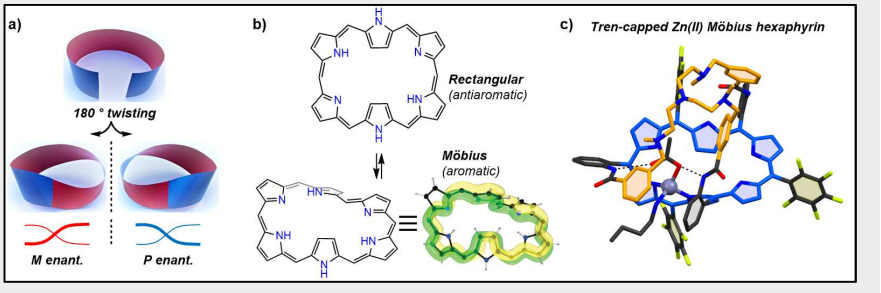
PhD position available at the University of Rennes

Title : Time-Programmable Möbius-Hexaphyrin Winding for Information Encoding (TIMOCO)
Keywords : hexaphyrin, topology, chirality, aromaticity, coordination, recognition, dissipative systems
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 EUR LUMOMAT).

Description: data-storage is undoubtedly a major concern of our modern societies requiring new approaches for information storage and processing. In this context, our group has been investigating for almost a decade various Möbius hexaphyrin architectures for recognition and sensing purposes. Möbius rings are inherently chiral objects (topological chirality),[1] mirror images being generated by twisting the Möbius band according to a right or a left screw sense (respectively *P* and *M* configurations). Compared to other sources of chirality, Möbius chirality has been scarcely investigated at the molecular level and thus constitutes an innovative stereogenic element. 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] Indeed, this conformationally flexible scaffold undergoes rapid *P* ↔ *M* equilibrium in solution, thus exhibiting a dynamic Möbius chirality. This feature enables a transfer of chirality from an exogenous stereogenic source under thermodynamic control, useful to build up adaptive or switchable molecular systems. Recently, we have investigated Möbius Zn(II)-hexaphyrins bearing NH_2 or COOH chiral coordinating arms, and demonstrated unprecedented chiroptical switches controlled by achiral effectors in complex networked systems. Our idea is now to move one-step further, by merging this dynamic chirality induction with out-of-equilibrium (dissipative) processes. Based on our expertise, this project aims at the development of so-called "time-programmable" Möbius-hexaphyrin winding, so that a chiroptical signature (readout) could be produced with a defined lifetime. Such an approach requires a fuel to trigger chirality induction at the level of the Möbius π-system, which will be cancelled when the fuel is consumed. By tuning the experimental conditions, specific lifetime and decay of the chiroptical readout can be set up, allowing a specific encoding of an information (similarly to Morse code with short and long pulses). These dissipative systems will be investigated by NMR and circular dichroism spectroscopies, with which the lab is well experienced, aiming at defining the best criterion yielding to robust systems.

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.