

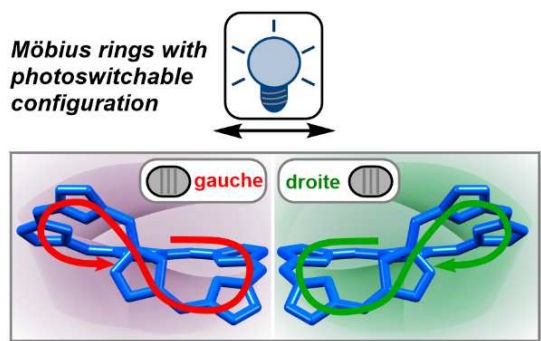
PhD position available at the University of Rennes 1

Title : Möbius rings with photoswitchable configuration

Keywords : hexaphyrin, Möbius topology, chirality, aromaticity, coordination, photoswitch

General information: The thesis will be carried out in the team Macrocyclus 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-macrocyclus-exotic-coordination-and-adaptative-systems>). Period: Oct. 2022-Sept. 2025. Rough salary: ~2000 €/month. This work received financial support under the EUR LUMOMAT project and the Investments for the Future program ANR-18-EURE-0012 (<https://www.lumomat.fr/>).

Description:



Möbius rings are inherently chiral objects, mirror images being generated by twisting the Möbius band according to a right or a left screw sense.[1] Compared to other sources of chirality, Möbius chirality has been scarcely investigated at the molecular level and thus constitutes an innovative stereogenic element. Chirality is an important added value to conjugated π -systems opening to a wide range of functions with potential technological applications. Considering the importance of molecular switches in many fields of science, designing Möbius rings with switchable configuration is of great interest.

Currently, a major obstacle remains the asymmetric preparation of Möbius compounds. Focusing on a [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 $P \leftrightarrow M$ equilibrium in solution, thus exhibiting a dynamic Möbius chirality. This feature enables transfer of chirality under thermodynamic control, useful to build up adaptive systems. Recently, we have investigated Möbius Zn(II)-hexaphyrins bearing a chiral coordinating arm, and demonstrated a chiroptical switch featuring P/M twist inversion controlled by achiral effectors, which is unprecedented.[3e]

Based on this expertise, this project aims at using a non-invasive and non-destructive trigger such as light (further allowing spatial and temporal control) to switch the P/M configuration of Möbius hexaphyrins. This is a challenge that no one has tackled yet! Achievement of this project will undoubtedly stimulate new explorations in many areas related to chirality. The work of the PhD student will thus consist in (1) the design and synthesis of Möbius hexaphyrins functionalized with chiral coordinating arms, (2) the complexation of zinc and the further binding of photoswitchable ligands, (3) light irradiation experiments to photoswitch the Möbius configuration. These systems will be mainly investigated by NMR, UV-vis absorption and circular dichroism analysis.

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 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 a copy of their Master diploma (stephane.legac@univ-rennes1.fr).

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 Bousambe, 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.