







Master 2 internship available at the University of Rennes (France)

" Synthesis of Möbius hexaphyrin-cyclodextrin hybrids"



Context: Möbius aromatic molecules were unambiguously identified only 14 years ago.¹ This major breakthrough was achieved with a [28]hexaphyrin macrocycle, the six-pyrrole counterpart of a porphyrin featuring a singly twisted 28π -conjugated system. Besides, Möbius hexaphyrins are inherently chiral, conformationally dynamic, and exhibit unusual coordination properties, making them attractive as a platform to design multi-functional devices.² Currently, a considerable challenge consists in the preparation of stable Möbius antiaromatic compounds,³ as their unusual electronic properties may lead to innovative functionalities. In this context, we have developed hybrid macrocyclic structures associating a hexaphyrin with one or two cyclodextrins, affording capped

or sandwiched architectures.⁴ Remarkable properties emerge from this particular coupling (three-type chiralities, (anti)aromaticity, multiple planar/twisted conformations, coupled confined environments...) that can be tuned by protonation, coordination or molecular recognition.⁵ Building on these achievements, this project, funded by the French National Research Agency and in collaboration with the team of Dr. Mickaël Ménand (Sorbonne University, Paris), will focus on <u>molecular engineering of optically active metal complexes</u> <u>of Möbius hexaphyrin-cyclodextrin hybrids</u>, aiming at a redox control of their (anti)aromatic character and chiroptical properties. Ultimately, challenging Möbius hybrids featuring a dual electronic circuit or being part of an oligomeric chain will be targeted.

Laboratory: the internship will be conducted at the *Institut des Sciences Chimiques de Rennes*, in the team *Organometallics: Materials and Catalysis*, under the supervision of Dr. Stéphane Le Gac (https://iscr.univ-rennes1.fr/stephane-le-gac).

Candidate profile: The candidate, holder of a Master 1 in molecular chemistry, should have solid knowledge in general chemistry and more particularly in organic synthesis and NMR spectroscopy. The synthesis and characterization of macrocyclic ligands in solution will be an important part of this internship. Strong practical skills as well as personal investment will be required. Interested persons will kindly send (stephane.legac@univ-rennes1.fr) a CV, a cover letter, the contact details of two people who can recommend the candidate as well as the transcript justifying the Master 1.

General information: the city of Rennes is located in the west part of France, 1^{1/2}h from Paris by train. It has a strong local culture and welcomes a large student population. Rennes is undoubtedly one of the most livable city in France.

¹ Osuka, A. et al. J. Am. Chem. Soc. 2008, 130, 13568.

² Reviews: (a) Osuka, A. et al. Chem. Rev. 2017, 117, 2584. (b) Latos-Grażyński, L. et al. Chem. Rev. 2017, 117, 2839.

³ (a) Osuka, A. et al. Angew. Chem. Int. Ed. 2010, 49, 4950. (b) Osuka, A. et al. Angew. Chem. Int. Ed. 2012, 51, 13105.

⁴ (a) Ménand, M.; Sollogoub, M.; Boitrel, B.; Le Gac, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 297. (b) Le Gac, S.; Boitrel, B.; Sollogoub, M.; Ménand, M. *Chem. Commun.* **2016**, *52*, 9347. (c) Ménand, M.; Sollogoub, M.; Boitrel, B.; Le Gac, S. *Chem. Eur. J.* **2018**, *24*, 5804. (d) Benchouaia, R.; Cissé, N.; Boitrel, B.; Sollogoub, M.; Le Gac, S.; Ménand, M. *J. Am. Chem. Soc.* **2019**, *141*, 11583. (e) Robert, F.; Boitrel, B.; Ménand, M.; Le Gac, S. *J. Porphyrins Phthalocyanines* **2021**, *25*, 1022.

 ⁵ See also : (a) Ruffin, H.; Nyame Mendendy Boussambe, G.; Roisnel, T.; Dorcet, V.; Boitrel, B.; Le Gac, S. J. Am. Chem. Soc.
2017, 139, 13847. (b) Le Gac, S.; Caytan, E.; Dorcet, V.; Boitrel, B. Org. Biomol. Chem. 2019, 17, 3718. (c) Boitrel, B.; Le Gac, S. Chem. Commun. 2020, 56, 9166. (d) Boitrel, B.; Le Gac, S. Chem. Commun. 2021, 57, 3559. (e) Ruffin, H.; Fihey, A.; Boitrel, B.; Le Gac, S. Angew. Chem. Int. Ed. 2022, 61, e202113844.