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NAME OF THE RESEARCH TEAM: NanoSciences Group (GNS)
NAMES OF SUPERVISORS: Claire Kammerer and Gwénaël Rapenne
Email address of the supervisor: kammerer@cemes.fr ; rapenne@cemes.fr

Synthesis of desymmetrized molecular gears with seven teeth

Within the molecular chemistry team of the NanoSciences Group at CEMES, one of the current projects deals with the synthesis of technomimetic molecular machines.[1] We are particularly interested in gear-like molecules that can exploit rotational motion at the nanoscale.[2-3] To achieve this, we need to control several parameters, such as the rotational movement, which must be concentric and bidirectional, the anchoring of the individual gears on the surface, and the interactions between adjacent gear teeth. In this context, we have already synthesized several prototypes[2-3] but until now it has not been possible to transfer rotary motion beyond three molecules.[4] In the proposed project, we aim at synthesizing a new family of molecular gear prototypes with seven teeth based on a desymmetrized heptaarylcycloheptatriene ligand.

We already synthesized the hepta(*p*-fluorophenyl)cycloheptatriene precursor (Figure, left) but to monitor the rotation of consecutive molecules by Scanning Probe Microscopy, the differentiation of one tooth, among the seven, is required. First, a series of desymmetrized heptaarylcycloheptatrienes will be synthesized following our methodology. In a second part, their aromatic derivatives will be prepared and their coordination chemistry explored with Ru^{II} and a tripodal ligand displaying thioether functions, already used in our molecular motors,[5] to anchor the resulting gear prototypes tightly on the surface.

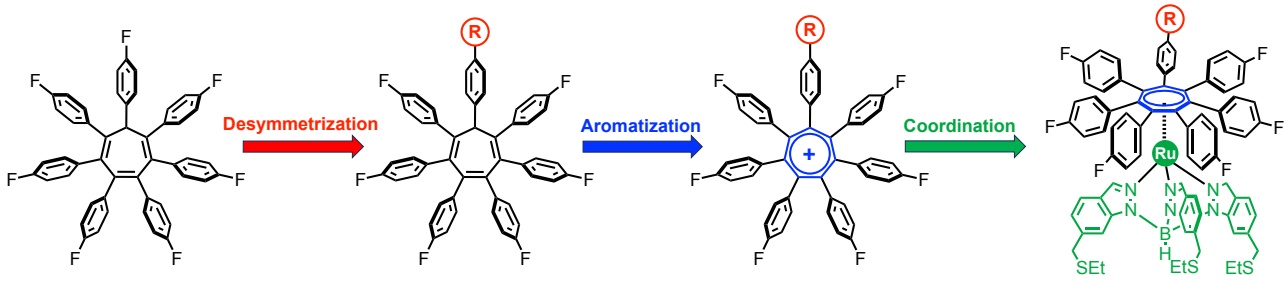

Figure : The already synthesized symmetric hepta(*p*-fluorophenyl)cycloheptatriene (left) and the target molecules.

This project is a synthetic chemistry project involving organic and coordination chemistry. The deposition and rotation studies of the gear prototypes on gold surface will be performed in collaboration with colleagues in USA and Japan.

[1] ***Biomimetic and technomimetic single molecular machines*** C. Kammerer, G. Erbland, Y. Gisbert, T. Nishino, K. Yasuhara, G. Rapenne, *Chem. Lett.* **2019**, *48*, 299-308.
[2] ***Molecular gears from solution to surfaces*** Y. Gisbert, S. Abid, C. Kammerer, G. Rapenne, *Chem. Eur. J.* **2021**, *27*, 12019-12031.
[3] ***Gearing up molecules on surfaces*** T. A. Hector, G. Rapenne, C. Kammerer, *Trends Chem.* **2025**, *7*, 350-353.
[4] ***Transmitting stepwise rotation between three molecular gears on the Au(111) surface.*** K.H. Au-Yeung, T. Kühne, F. Eisenhut, Y. Gisbert, R. Robles, N. Lorente, C. Joachim, G. Rapenne, C. Kammerer, F. Moresco, *J. Phys. Chem. Lett.* **2020**, *11*, 6892-6899.
[5] ***Controlled clockwise and anticlockwise rotational switching of a molecular motor*** U. Perera, F. Ample, H. Kersell, Y. Zhang, G. Vives, J. Echeverria, M. Grisolia, G. Rapenne, C. Joachim, S.-W. Hla, *Nature Nanotech.* **2013**, *8*, 46-51.