PROPOSITION DE SUJET DE THESE
Campagne 2018/2019

Cible : étudiants Chinois à des thèses à l'ENS de Lyon
Diffusion : en Chine, via la plateforme du CSC

ECOLE DOCTORALE : Doctoral School of Chemistry in Lyon (ED 206, Chemical Processes, Environment)

TITRE DU SUJET DE RECHERCHE : Synthesis of Cryptophanes with Fully Hydrocarbonated skeleton: Applications to Molecular Receptors with Enhanced Affinity toward Methane and Xenon

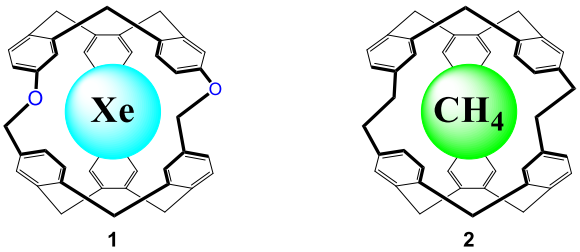
Research team/Equipe de recherche : Supramolecular Chemistry and Chemical Biology Axis – http://www.ens-lyon.fr/CHIMIE/recherche/Teams/Chimie_Organique_et_Materiaux_Nanostructures

Supervisor/Directeur de thèse: De Rycke Nicolas, Brotin Thierry – University of Lyon – ENS Lyon, France – nicolas.de-rycke@ens-lyon.fr; thierry.brotin@ens-lyon.fr

Lab Language/ Langue de travail: English or french
Abstract/Présentation du sujet :

Keywords: multistep organic synthesis, artificial sensor, supramolecular chemistry, gas storage and separation, ^{129}Xe NMR.

The design of artificial receptors for selective gas recognition and separation is a fundamental issue of great importance in medical science and environment. Among the noble gases, Xenon-129 nuclei has recently garnered a great attention because of its promising potential as a magnetic resonance imaging contrast agent.[1] In addition, separation of bulk gas mixtures containing methane and carbon dioxide remains an important goal in the chemical industry.[2] In this context, cryptophanes are chiral molecular cages that exhibit very interesting supramolecular interactions thanks to an easy tuning of their substituents and their internal volumes. Our group and others have demonstrated that such receptors can encapsulate efficiently small organic molecules and cations in water, depending on the nature of the substituents attached on the benzene groups.[3] A recent theoretical study has predicted that cryptophanes with partially or fully hydrocarbonated skeleton would exhibit enhanced affinity towards methane and xenon.[4] These molecular cages would have a great potential as molecular receptors to promote gas storage and separation. Host-guest complexes with strong association constants would be obtained because of an increase of dispersion forces and conformational changes. However the synthesis of such molecules has never been published yet and represents a very important challenge in synthetic organic chemistry (figure 1).



1 2

Figure 1. Challenging design of C_3-symmetric hydrocarbonated cryptophanes **1** and **2** for efficient methane and xenon encapsulation studies.

The aim of this PhD thesis is the design and the study of a series of partially or fully hydrocarbonated cryptophanes and the study of their binding properties with methane and xenon. Particular attention will be paid on the characterization of empty hosts and complex derivatives (^{1}H, ^{13}C and ^{129}Xe NMR for xenon-complexes, isothermal titration calorimetry, X-ray structures, polarimetry, electronic circular dichroism). The most potent molecular receptors will be incorporated in molecular devices for gas recognition, storage and separation. This experience will allow the PhD candidate to develop strong skills, knowledge and autonomy in several disciplinary fields such as organic synthesis, supramolecular chemistry, spectroscopic characterization and analysis.

References:

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[4] Demissie, T.B.; Ruud, K.; Hansen, J.H. *J. Phys. Chem. A* **2017**, *Just accepted*.

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Direction des Affaires internationales : international.strategy@ens-lyon.fr