

Intitulé du Sujet de Thèse : Reversible Nucleophilic Aromatic Substitutions in Dynamic Covalent Chemistry With Arenes and Heteroarenes

Laboratoire : CINAM, UMR CNRS 7325, Aix-Marseille Université

Equipe : Marc GINGRAS

Directeur de thèse : Pr. Marc GINGRAS

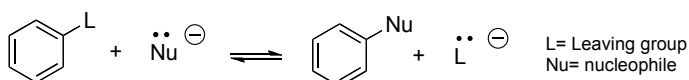
Co-encadrant (éventuellement) : Pr. Corinne MOUSTROU

Email : marc.gingras@univ-amu.fr

Contexte de l'étude: This project is an international collaborative work between CNRS/Aix-Marseille Université, Strasbourg University and the University of Bologna. The doctoral student will work in an international context for learning chemistry. The interdisciplinary project will involve in the following order: organic synthesis, organic materials, sulfur and aromatic chemistry, supramolecular chemistry, optoelectronic properties, chirality and (bio)nanoscience.

Descriptif du projet

Abstract: Nucleophilic aromatic substitutions (S_NAr) are among the most useful reactions in organic chemistry. In spite of countless S_NAr reactions since



1854, there are still several debates about the substitution mechanisms involved. Recent work and reviews even propose a concerted S_NAr . In spite of such debates, the reversibility of S_NAr reactions has been largely overlooked and only a few articles with specialized substrates are mentioned. The impact of reversibility is fundamental in science and we would like to emphasize it as a new avenue in dynamic covalent chemistry (DCC). In this area, several potent applications can be foreseen in chemistry, in life and materials science. It could also provide an interface with physics and nanoscience from the dynamic formation of nano-objects in solution or onto surfaces. As a model study of dynamic S_NAr , we propose to use oxygenated and sulfurated arenes and heteroarenes as templates in DCC.

Goals of the Project:

- 1) To delineate the scope of reversible S_NAr in DCC: assessment of important parameters in the reversible covalent bond formation with oxygenated and sulfurated arenes and heteroarenes; in particular, a solvent study, nucleophilicity, steric hindrance, reactivity, scope, chiral ligands, temperature effects, selectivity. Synthetic utility of these DCC processes in macrocyclic and aromatic chemistry.
- 2) To define structural, electronic, and photophysical properties: conformers, XRD data and electronic density (aromaticity), in a comparison to other polyarenes, are essential to better evaluate and to predict their reactivity and mechanisms toward electrophiles, or nucleophiles in substitution mechanisms. A better photophysical understanding of luminescence and REDOX is required, toward optimized structure-property relationships.
- 3) To propose some mechanistic hypotheses in these reversible formation of these arenes and heteroarenes : An assessment of kinetics vs thermodynamics, rate-determining step, mechanistic rationale, regioselectivity, intermediates and side-products is mandatory. Calculations will suggest intermediates and transition states to guide experiments.
- 4) To delineate the best DCC templates: Which rules govern oxygenated and sulfurated component exchanges and rates with arenes and heteroarenes? What could be the triggering molecules and effectors leading to the dynamics? How can we control thermodynamics and kinetics toward the assembly of nano-objects, films, self-healing, and responsive materials with sensing or imaging capabilities?

Preliminary results: 1) exchange of sulfur components by reversible S_NAr in DCC has been demonstrated with a wide scope of substrates of thioarenes and thioheteroarenes; 2) assembly of a phosphorescent phenylene sulfide cavitand and dendrimers might proceed by DCC; 3) Luminescent materials with exalted properties can be produced.

Références Bibliographiques

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