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

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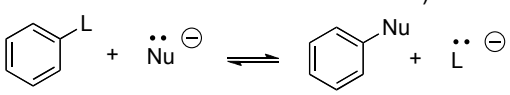
Descriptif du projet

Context: This project is an international collaborative work between CNRS/Aix-Marseille Université, Strasbourg Univ.(JM Lehn), Namur Univ. (G. Berionni, BE), Sherbrooke Univ. (L. MacGillivray, CAN) and Bologna Univ.(P. Ceroni, IT). The doctoral student will work in an international context while learning chemistry. The interdisciplinary project will involve: organic synthesis, organic materials, sulfur and aromatic chemistry, supramolecular chemistry, optoelectronic and chiral properties, and nanoscience (in a collaboration with C. Barth at CINAM).

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 reversibilty 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 in materials science. It could also provide an interface with physics and nanoscience from the dynamic formation of nano-objects in solution or onto surfaces. This project has a general and wide impact in aromatic, supramolecular, materials chemistry and chiral sciences.



Goals of the Project:

1) To delineate the scope of reversible S_NAr in DCC: assessment of important parameters in reversible bond formation with oxygenated and sulfurated arenes and heteroarenes; solvent study, nucleophilicity, steric hindrance, reactivity, scope, chiral ligands, temperature effects, selectivity. Synthetic utility of these DCC processes in macrocyclic, helicene 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 and 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 aromatic systems: an assessment of kinetics vs thermodynamics, mechanistic rationale, regioselectivity, intermediates and side-products is mandatory. Calculations will suggest intermediates and transition states to guide the 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 trigerring molecules and effectors leading to the dynamics? How can we control themodynamics and kinetics toward the assembly of nano-objects, films, self-healing, and responsive materials with sensing or imaging capabilities?

Results: 1) exchange of sulfur components by reversible S_NAr in DCC was demonstrated with a wide scope of arenes; 2) assembly of phosphorescent sulfurated cavitand, macrocycles and dendrimers might proceed by DCC; 3) Luminescent materials with exalted properties can be produced.

Références Bibliographiques

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