CREAM

Chemical rections in macromolecules: a joint theoretical and experimental study

Blanc + 2009

PI: Manuel F. Ruiz-Lopez, CNRS Research Director at SRSMC, University of Lorraine, Nancy. The team is composed of theoretical, physical and organic chemists from the same lab.

Aims

• The CREAM project focuses on cyclodextrin (CD) applications as molecular reactors. The aims are: 1) development of more efficient theoretical tools to study chemical processes in macromolecules, 2) understanding environment effects in such reaction media and 3) synthesize of a new class of potential catalysts.

• Models of increasing complexity have been implemented and applied to theoretically investigate prototypical reaction mechanisms. Then a collaborative work between theoreticians and experimentalists has been carried out to synthesize and evaluate the catalytic properties of aza-crown β–CD derivatives (Figure 1) that are expected to selectively complex transition metals.

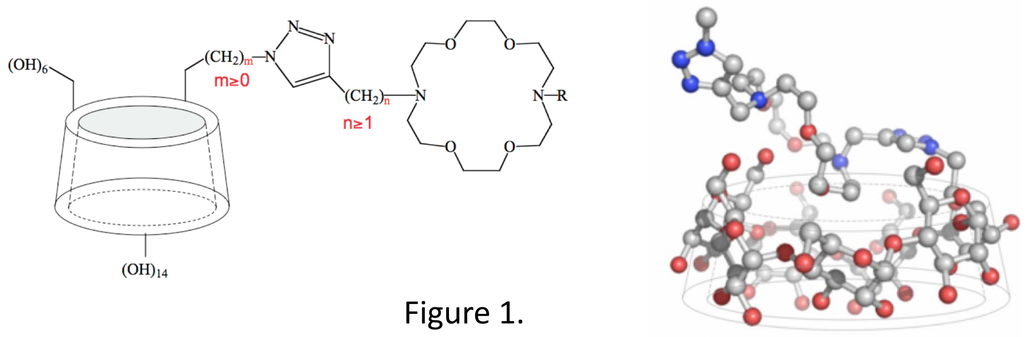

Figure 1.

Simulation, solvation effects in CD's

A large computational effort has been devoted to better understand how the properties of the guest (and then its reactivity) are modified under host-guest complex formation in aqueous solution. This has led us to: 1) evaluate the effective dielectric constant inside a β-CD, 2) analyze solvation effects at water/hydrophobic interfaces, 3) rationalize the observed effects on reaction rates (ester hydrolysis, Figure 2).

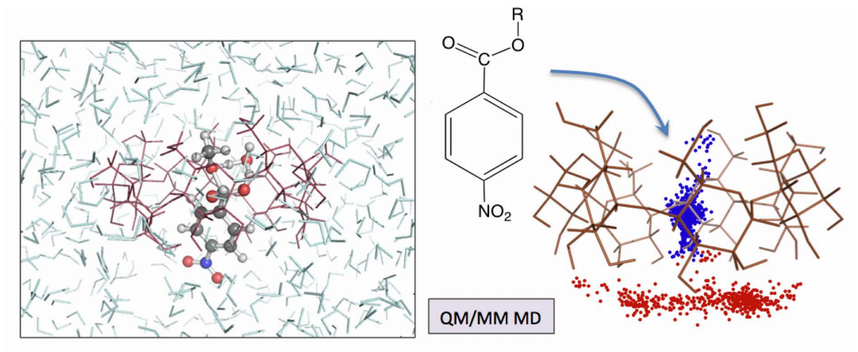

Figure 2.

Synthesis, evaluation

The Huisgen Cu(I)-catalysed reaction has been chosen because of its high flexibility to synthesize cyclic and acyclic ligands. Then, 1:1 complexes with Cu^{2+}, Ni^{2+}, Zn^{2+} have been investigated (Figure 3); the metal is axially or equatorially coordinated by the triazole groups and it displays penta-, hexa- or hepta-coordination. Cu^{2+} complexes exhibit catalytic activity towards catechol oxidation, with acyclic systems being more efficient. This activity is not modified by the presence of the CD.

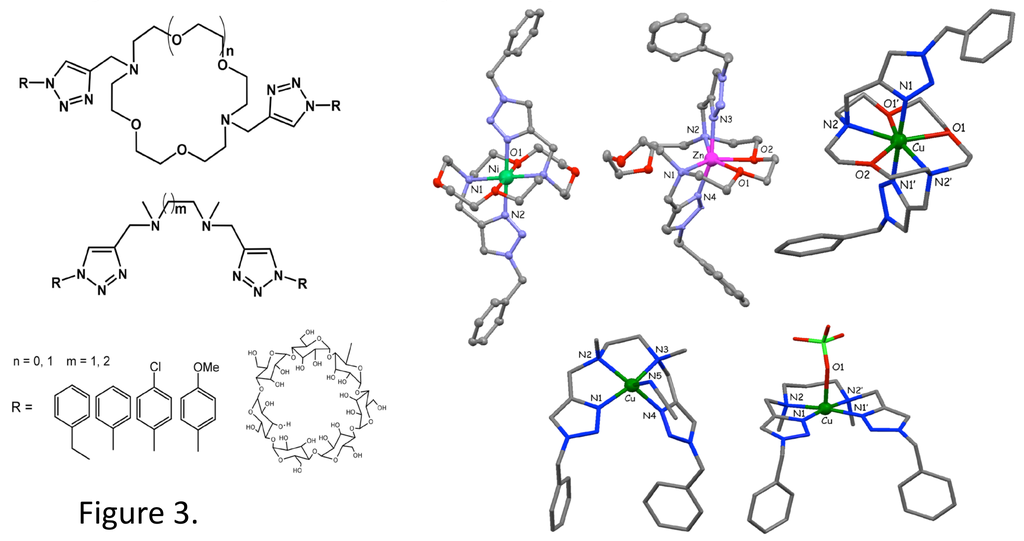

Figure 3.

From water to supercritical CO_2

Supercritical CO_2 has attracted much attention as a green solvent. We have investigated the properties of CD's in this medium + their ability to form host-guest complexes (in collaboration with Prof. A. Marsura, SRSMC, and Dr. D. Barth, ENSIC-Nancy). The open/close dynamics of peracetylated CDs in $scCO_2$ has been described through Molecular Dynamics simulations (Figure 4). The results encourage us to continue further work in this direction.

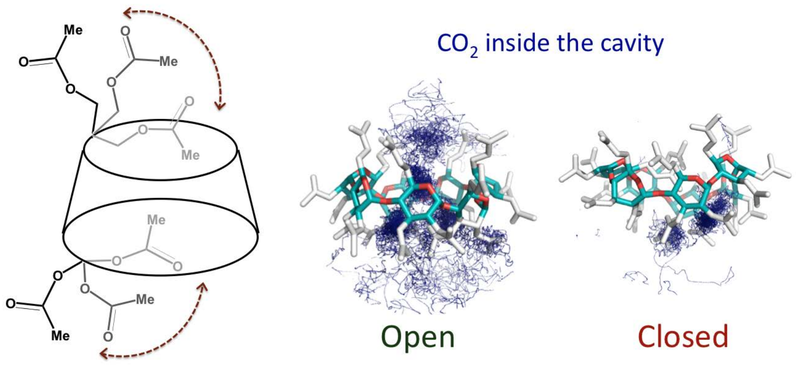

Figure 4.

CONTACT :

Dr. Manuel Ruiz-Lopez, SRSMC, University of Lorraine, Nancy Manuel.Ruiz@univ-lorraine.fr