Ecole Doctorale des Sciences Fondamentales

Title of the thesis: Study of supramolecular assemblies in homogeneous and heterogeneous phases

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Summary :

For various applications, including the development of "intelligent" materials and biosensors, thin films made of monolayers organized on surfaces are developed. Adsorbates then attach themselves to a solid surface (adsorbent) by various processes that may involve different types of bonds (physisorption or chemisorption).

The formation of inclusion complexes on a surface by supramolecular chemistry allows the immobilization of many molecules on surfaces. The most commonly used host or receptor molecules are macrocycles modified by the introduction of thiol groups. They can then be assembled on a gold surface to form a monolayer. We have recently focused on the thermodynamics of supramolecular structures immobilized on a surface. By calculating using molecular simulation techniques, the free energy profile along the reaction coordinates between host and guest during the association process, thermodynamic association quantities can be obtained in the heterogeneous phase (the host and/or guest are grafted onto a surface) and compared with those obtained in the homogeneous phase (species are free in solution). This heterogeneous systems simulation methodology has recently been used on model systems (the inclusion complexes of b-cyclodextrine and calixarenesulfonate and 4-aminoazobenzene) for which we were able to explain the differences between the homogeneous and heterogeneous phase association. This study has allowed a better understanding of the association process in the particular case of the inclusion of 4-aminoazobenzene.

In order to complete this study and rationalize these self-assemblage processes, we aim to study the grafting cucurbiturils on different types of surfaces, in order to compare the affinities and selectivity of the different hydrophobic cages in the heterogeneous phase. Indeed, in the homogeneous phase cucurbiturils associate better than cyclodextrins and calixarenes. We will study this trend in the heterogeneous phase. The effect of the nature of the surface will also be examined. Thus, carbon nanotubes with their exceptional electrical, mechanical and thermal properties offer many applications in the field of biosensors. Different types of covalent or non-covalent functionalization based on compound adsorption are possible to allow protein anchoring.

Finally, we propose to focus on these systems using a multi-scale approach. Indeed, for various applications in biomedicine or biotechnology, it is necessary to immobilize biomolecules such as proteins, enzymes, DNA on surfaces. To study these complex "biomaterials" type systems, a new simulation methodology will be developed. Indeed, their sizes require the use of "coarse-grained" descriptions of the material.

The objective of this thesis is therefore to better understand the behaviour and molecular interactions at interfaces. In order to validate the parameters of our simulations, this work will be combined with measurements of XPS (grafting surface density), pulsed field gradient NMR (dynamics of the systems studied) and X-ray diffraction (structure factor). The experimental measurements will be carried out at the Institute of Physics in Rennes.