

Chirality at surfaces: a close up

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Chiral molecules play an important role in numerous industrial (catalysis) and biological processes (e.g. as drugs). Often, the interaction of chiral molecules with surfaces is crucial to bestow these with new functional properties. Chirality abounds in natural and synthetic systems, and also it is therefore not surprising that it is manifested in self-assembled monolayers at the liquid-solid interface, although observing it directly has been virtually impossible until relatively recently. Using non-optical microscopy techniques, such as scanning tunneling microscopy, the ordering of molecules on atomically flat conductive surfaces can be probed on the nanometer scale with near atomic resolution. Chirality on surfaces is both expressed at the level of the molecular organization and at the relation of this molecular organization with respect to the symmetry of the substrate underneath (when the latter is crystalline). It is actually hard not to induce chirality on surfaces by adsorption of molecules, even for achiral molecules. The research group is very active in this domain (partner of two European projects dedicated to chirality on surfaces) and proposes the following topics in this area:

(I) **ordering of chiral molecules on surfaces**: using scanning tunneling microscopy (STM), we will investigate how chiral molecules order on surfaces, and more specifically, we will probe the eventual separation of a racemic mixture into enantiopure domains. The target is to unravel the factors which play a role in what is called conglomerate formation (spontaneous separation of enantiomers in enantiopure two-dimensional crystalline domains: i.e. 2D analogue of the famous Pasteur experiment). It is actually found that in contrast to 3D crystals, in monolayers most racemic mixtures separate into enantiopure 2D domains.

(II) **induced separation of enantiomers**: some time ago, the research groups discovered a chiral system which does not show separation of the enantiomers in domains. By using an external perturbation of the system (physical (e.g. magnetic fields) or chemical (e.g. chiral solvent)), we will try to affect the self-assembly process and to induce separation of the enantiomers in enantiopure domains.

(III) **achiral molecules and chirality**: An intriguing observation is the fact that most achiral molecules form chiral two-dimensional domains on surfaces. However, two types of domains are formed which are each other's mirror image. As equal amounts of both domains are formed, on a macroscopic scale the surfaces are still achiral. We try now to affect this balance and to induce macroscopic homochirality, even for achiral systems. How to do that? Recently, we discovered that by inducing self-assembly at the interface between some chiral solvents and the substrate, homochirality can be obtained. We now intend to explore this fascinating phenomenon by investigating new combinations of achiral molecules and chiral inducers, in order to unravel the mechanism leading to this effect.

(IV) **chiral monolayer templates in chiral separation**: obviously, separation of mixtures of enantiomers into their pure components is of crucial importance in the pharmaceutical industry. We will probe in real space the formation of preferred diastereomeric complexes by adding chiral diamines to surface-confined carboxylic acid derivatives.

Two-dimensional nanoporous structures and templating

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Self-assembly of nanometer-sized building blocks at surfaces and interfaces is of increasing interest for nanotechnology research. Recently surface-confined two-dimensional (2D) molecular networks, especially those with void spaces, so-called “2D porous networks”, attract a lot of interest. One class of molecules which give rise to these 2D porous networks are macrocycles which intrinsically contain a pore. Self-assembly of these molecules into regular 2D lattices gives rise to 2D nanoporous networks. Another conceptual approach is the self-assembly of smaller molecules which according to their design order into 2D porous structures. These porous networks are typically sustained via hydrogen bonds, metal-ligand coordination or even van der Waals interactions. Cavity sizes ranging from 1 nm up to 5 nm have been reported for single or multi-component molecular systems and scanning tunneling microscopy at the liquid/solid interface is the preferred tool to reveal these surface-confined structures with submolecular resolution. These 2D porous networks are used as hosts to immobilize functional units as guest molecules in a repetitive and spatially ordered arrangement. The interplay of molecule-molecule and molecule-substrate interactions is crucial for the outcome of surface-confined self-assembling processes. Other factors such as temperature and the nature of the solvent play an important role too.

2D crystal engineering: A major issue is to develop a set of design rules to direct molecules to assemble into nanoporous structures. In collaboration with the group of Prof. Tobe (Osaka University) and Prof. Höger (University of Bonn), different systems are being explored.

Concentration control: The formation of 2D porous structures based upon the self-assembly of intrinsically non-porous molecules appears to be concentration dependent. Depending on the specific design of the molecules, only at very low concentrations 2D nanoporous structures are observed. Typically, these molecules show polymorphism (one compound, different 2D crystals). This effect will be explored in detail for systems giving rise to exotic ‘Kagome’-lattices.

Host-guest chemistry: Upon formation of the two-dimensional porous structures, their host-guest chemistry is probed. Do these 2D pores show guest selectivity? Can they be made structurally flexible in order to respond to the shape of guest molecules? Can they host several guest molecules at once? Can they be used as templates to induce reactivity in confined spaces.

Supramolecular pattern formation of molecules on surfaces under potential control: ordering and reactivity

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In view of several nanotechnological applications, surface chemistry and surface physics play an important role. One of the challenges is the controlled structuring of surfaces, for instance based upon the self-assembly of molecules on these surfaces. On the one hand, one of the main characteristics of self-assembly is the exploration of the complete conformational space to form the thermodynamically most stable supramolecular structures. On the other hand, molecule-substrate interactions must be strong enough to stabilize the surface-confined supramolecular structures. An elegant way to tune the interaction strength between molecules and surfaces is by electrochemical control. To get insight in the way molecules respond (ordering and reactivity) to electrified interfaces, molecular resolution imaging is very helpful: it provides detail information in real space. To that end, a scanning tunneling microscope has been combined with an electrochemical cell, allowing the visualisation of surfaces at different potentials.

Ordering: A major activity is the investigation of the potential induced ordering of molecules on these electrified surfaces. Especially, complex multicomponent systems are of interest, for instance combining charged and non-charged systems.

Reactivity: Obviously, electrified interfaces are ideal to induce redox reactions. One of the research activities is in the field of *corrosion*. By using electrochemical scanning tunneling microscopy, we explore the effect of self-assembled molecular protection layers on the oxidation of metal surfaces (e.g. Cu) and reveal the mechanism at the nanometer scale (even atomic scale) by the direct visualization of the processes involved.

Structural nanobiology of HIV-1 integration: an atomic force microscopy study

Contact: Prof. Steven De Feyter

The integration of the retroviral cDNA in the human genome is a crucial step in the replication cycle of the HIV virus. The current knowledge on the structure and dynamics of the functional complex of HIV-1 integrase HIV-IN with DNA is still rather limited. The team of Debyser (KULeuven, Department of Molecular and Cellular Medicine) demonstrated in 2003 that the p75 isostructure of the Lens Epithelium Derived Growth Factor (LEDGF/p75), a human protein, binds directly with HIV-1 IN. This is promising for the rational design of a new generation of drugs. Using in situ atomic force microscopy (AFM) we study protein and nucleoprotein-DNA complexes. Important research themes are: the structure of DNA at the interface between a buffer and a solid substrate; the multimerization of HIV-IN and LEDGF/p75; the binding between HIV-IN and LEDGF/p75; the binding of the proteins with different DNA-substrates and their impact on the structure of DNA (morphology and topology); the influence of buffer conditions on the (supra)molecular structures. You will aim at addressing one or several of these issues by analyzing the behavior of individual biomolecules with AFM.

Visualisation and study of the interaction and reactivity of synthetic DNA probes at the level of individual DNA molecules

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Polypyridyl complexes of Ru(II) are important DNA-probes. Upon illumination, a number of these complexes can remove an electron from a guanine base leading to a cleavage of the DNA strand. In addition, a covalent adduct can be formed between the complex and the guanine base. Both reaction types modify DNA, which leads to interesting applications in vivo (e.g. dynamic phototherapy) and in vitro (synthetic restriction enzymes, DNA footprinting agents, ...). Only limited information is available yet on the effect of complex intercalation on the DNA structure. Such knowledge is of crucial importance though in view of the eventual applications, and the rational design of improved photo-active DNA probes. Using a non-optical microscopy technique (atomic force microscopy (AFM)), the effect of DNA probe binding and the photo reaction at the level of individual DNA molecules will be investigated.

Characterization and spectroscopy of organic quantum dots.

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It can be expected that block copolymers of conjugated polymers consisting of sections with hydrophobic and sections with hydrophilic side chains form in aqueous medium a micelle with a core of hydrophobic side chains and a shell of hydrophilic side chains. This prompts questions on possible aggregation of the chromophores, the occurrence of energy hopping and the possibility to form a single quantum dot. In the latter case a safe (no cadmium) and flexibly adaptable alternative for inorganic quantum dots would exist for in medic-diagnostic applications as a research tool in molecular biology. We will try to answer the questions mentioned above using stationary and time-resolved fluorescence spectroscopy on bulk samples and single micelles. The polymers will be obtained through the division of "Moleculaire Design and Synthesis" of K.U.Leuven, or through of UHasselt, or the "Max Planck Institut für Polymerforschung" in Mainz. For structural characterization of them micelles collaboration with the UCL is possible.

Charge and exciton transport in disordered organic layers doped with semiconductor nanoparticles.

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Electron hole recombination in organic materials yields a ratio 1:3 of singlet and triplet excited states. The latter species, which are non-emitting, can be recuperated for luminescence by the incorporation of intensely luminescent and highly photostable semiconductor nanoparticles. Furthermore in combination with other suitable polymers these quantum dots will yield efficient and stable charge separation. Several matrices, available through collaboration with IMEC, the Lebedev Institute and the "Max Planck Institut für Polymerforschung", will be combined with CdS- or CdSe-nanoparticles (2 tot 6 nm) in thin spin-coated films. The electron and hole mobility will be analyzed in the presence and absence of the nanoparticles in the framework of existing models for the field and temperature dependence of the mobility. In collaboration with the physics department of the K.U.Leuven and with the Université de Mons Hainaut it will be attempted to elucidate the physical meaning of the transport parameters.