

SURFACE ENGINEERING ON THE NANOMETER SCALE WITH SUPRAMOLECULAR COMPLEX SPECIES

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INTRODUCTION: Bio-macromolecules, such as proteins, are synthesized by nature one-by-one with accurate distributions of monomers (amino-acids) in polypeptide chains. Responsible biochemical reactions make use of molecular templates and molecular recognition. The proteins formed are organized on various levels of molecular assembly and fulfill structural and functional roles in living organisms. Relevant aspects of the corresponding biochemical processes and structural organization include non-covalent (supra-molecular) interactions, molecular templates, and recognition on the single-molecule level. Structural organization by “self” assembly eventually results in complex hierarchical structures.

In contrast, most synthetic (industrial) chemical processes are performed in organic solvents, by mixing large bulk amounts of reactants, compared to nature in a crude way. It has been one of the main objectives of science and technology to mimic nature also in man-controlled synthesis, molecular fabrication, and assembly of structures. Recent breakthrough discoveries in supra-molecular chemistry, spatial and temporal confinement of individual molecules, and achievements in applications of various scanning probe techniques have laid the foundations of molecular nanotechnology. This is regarded as the first step to realize bottom-up molecular nanochemistry. The term “nanochemistry” is specifically used here to describe manipulation, structural modification, and spatial and temporal characterization of localized, individual atomic, and/or molecular systems, or their clusters (aggregates) consisting of a small number of elementary units. Interactions with such nanoobjects in nanotechnology must either occur via other nanoobjects directly (single molecule probing), or via mediation by using macro-microobjects (e.g. using scanning force microscopes with contact definition of ultra sharp probes on the nanoscale).

Self-assembled monolayers (SAMs) of thiols, sulfides and disulfides on Au can be used to construct templates for attaching confined, isolated molecules. They can also serve to modify surface properties, or as reactive platforms in surface engineering. Cyclodextrins can act as hosts for the binding of a variety of small, organic guest functionalities in water through hydrophobic interactions [1]. These receptor molecules can be immobilized on Au in SAMs using derivatives with sulfide linkages. These “molecular printboards” [1 (b)] have specific recognition sites, e.g. molecular

cavities, to which molecules can be anchored via specific and directional supramolecular interactions.

METHODS: SAMs were assembled on Au using standard procedures. Corresponding monolayers were used as reference (or reactive) templates and to immobilize isolated molecules (e.g. at SAM defect sites). Atomic force microscopy (AFM) was used to image molecular lattices and isolated molecules.

AFM tips were functionalized to tune molecular interactions between tip and templates for force spectroscopy, and for in-situ kinetic studies of surface reactions. Guest molecules were attached to AFM tips in mixed SAMs at different surface concentrations to study guest-host specific binding on the single molecule level.

RESULTS AND DISCUSSION: First the use of AFM will be illustrated to image the head group lattices of SAMs and to locate and image single macromolecules (dendrimers), and their assemblies [1,2]. A discussion on molecular interactions and recognition will follow, based on guest-host chemistry of surface-immobilized β -cyclodextrin receptors and apolar guests in aqueous environments [3]. Single-molecule force spectroscopy was used in the latter case to study individual supramolecular interactions utilizing SFM. Complexes interacting via self-complementary quadruple hydrogen bonds for surface molecular recognition is the next case to be discussed [4]. The complex stability can be controlled in these molecular assemblies by a proper choice of temperature and solvent, which enables us to tackle transitions from non-equilibrium to equilibrium guest-host kinetics in single-molecule force spectroscopy. These complexes also serve as model systems of pyrimidone-based supramolecular polymers at surfaces and interfaces. In the next example, chemistry on individual molecules will be illustrated by a study of surface-confined dendrimers and their attachment (on single molecule level) into self-assembled thiol monolayers on gold [2]. As last example, monitoring surface reactions will be discussed using SAMs with a near-to-molecular resolution [5]. This approach – which we named “inverted chemical force microscopy” – allows us to follow reaction kinetics in real time. As examples ester hydrolysis and aminolysis of SAMs, the latter using “bioreactive” 11,11'-dithio bis(*N*-hydroxy-succinimidy) undecanoate, will be presented.

CONCLUSIONS: By the examples shown in this presentation, including molecular visualization, single molecule force spectroscopy, molecular recognition, and in-situ reaction kinetics studies, we

demonstrate progress in molecular nanochemistry inspired by nature.

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