

Summary

The research described in this thesis is focused on the combination of orthogonal supramolecular interactions for functional monolayer architectures on surfaces. The term “orthogonal supramolecular interactions” refers to non-covalent interactions that do not influence each other's assembly properties when applied in the same system. Orthogonal self-assembly allows extended control over the self-assembly process and promotes new materials properties. Individual noncovalent interactions (e.g. hydrogen bonding, metal coordination, electrostatic or host-guest interactions) have been employed in many studies. However, the combination of different supramolecular interactions in the same system can improve the properties of the materials. The research described in this thesis aims to develop hybrid, multifunctional monolayers by using orthogonal supramolecular interactions, enabling the control over the monolayer composition and functionality. Orthogonal host-guest and lanthanide-ligand coordination interaction motifs have been employed to create supramolecular luminescent monolayers in the first part of the thesis (Chapters 3 to 5). The second part of the thesis (Chapters 6 and 7) deals with the fabrication of functional monolayers on silicon and gold substrates for applications in electronics.

A general introduction has been given in Chapter 1 which addresses the importance of non-covalent interactions for the fabrication of functional surfaces.

A literature overview has been given in Chapter 2 on the use of supramolecular interactions for the generation of hybrid assemblies and materials. Supramolecular chemistry and molecular self-assembly including hydrogen bonding, metal coordination, electrostatic and host-guest interactions to direct the immobilization of functional systems on surfaces are

discussed in detail. Special attention is given to the combination of different supramolecular interaction types for the generation of functional monolayer architectures.

Chapter 3 describes the assembly of a guest-functionalized naphthalene antenna and a Eu^{3+} -complexed EDTA-based ligand molecule onto a receptor surface by combining the orthogonal host-guest and metal-ligand coordination motifs. Local fluorescence emission spectra of the immobilized complex demonstrated the occurrence of sensitized Eu^{3+} luminescence. The energy transfer efficiency between the antenna and the Eu^{3+} complex was determined by time-resolved fluorescence measurements and found to be about 35%. The stoichiometry of complexation between antenna and Eu^{3+} complex was investigated by the very first Job plot analysis at a surface and found to be 1:1 by examining the sensitized luminescence of the surface-immobilized complex at different antenna- Eu^{3+} complex ratios.

In Chapter 4, the same lanthanide complex system was used for the ratiometric detection of dipicolinic acid (DPA), which is a unique biomarker for anthrax bacterial spores, with high sensitivity and selectivity on a supramolecular monolayer surface. The fluorescence intensity ratio of the lanthanide-based surface receptor system upon addition of different concentrations of DPA showed that the recovery of the naphthalene emission is practically complete in the presence of only 200 nM DPA. The intensity ratio of the Eu^{3+} -based sensing platform as a function of time upon addition of 200 nM DPA indicated that the sensing response is complete within 10 min. The detection limit of the system was also investigated and found to be about 25 nM of DPA. To exhibit the selectivity of the supramolecular sensing surface, fluorescence changes upon addition of different competitive aromatic ligands were investigated. The negligible changes demonstrated the excellent selectivity of the system for DPA.

Chapter 5 has introduced a supramolecular sensing platform on a microchip surface that allows the detection of biologically relevant phosphate anions and aromatic carboxylic

acids in a high-throughput format. The Eu^{3+} -based supramolecular sensing system was implemented on the surface of a multichannel chip. The sensing layer on the microchip surface is an ensemble of the antenna and Eu^{3+} -complexed ligand. When an anionic guest was added to the ensemble, it displaced the antenna, and triggered a fluorescence decrease upon binding to the Eu^{3+} center. ATP and pyrophosphate among various phosphate anions, and the anthrax biomarker DPA among various aromatic carboxylic acids showed a strong response to the sensitized Eu^{3+} luminescence-based microchip surface.

Chapter 6 describes the local doping of oxide-free silicon using nanoimprint lithography (NIL) and molecular monolayers. Covalently bonded Si-C monolayer patterns with feature sizes ranging from 100 nm to 100 μm were created via a local hydrosilylation reaction on NIL-patterned resist areas. These patterns were characterized by XPS, AFM, and TOF-SIMS measurements. Monolayer patterns with 100- μm features were fabricated to enable pattern characterization by XPS. Elemental mapping spectra showed that the patterned monolayers were created by hydrosilylation. To fabricate the nanoscale features, a nickel-plated mold containing a square array of 150 nm pillars was used and the resulting structures were visualized by AFM. Results showed that clearly defined patterns were obtained. Using a phosphorus-containing organic precursor, highly-doped and patterned (μm scale) regions in nearly intrinsic silicon were successfully fabricated. These patterned regions were characterized by TOF-SIMS for imaging and depth profiling. The dopant surface dose on a doped area measured $(2.3 \pm 0.1) \times 10^{19}$ P atoms. cm^{-3} corresponding to an areal dose on a doped area of $5.6 \pm 0.1 \times 10^{13}$ P atoms. cm^{-2} . Electrical characterizations were performed by Hall and sheet-resistance measurements. An average sheet carrier density was determined and found to be $1.9 \pm 0.1 \times 10^{13}$ cm^{-2} at 300K and $9.4 \pm 0.1 \times 10^{12}$ cm^{-2} at 150K in case of patterned samples. More importantly, the resistance measured on line-patterned substrates along the

line direction was significantly lower than when measured perpendicular to the pattern direction.

Chapter 7 describes the fabrication of monolayers of organic molecules with unpaired spins on a thin gold film. Nitroxyl 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) radicals and terpyridinyl-cobalt complexes were used in this study. The existence of unpaired spins in self-assembled monolayers was investigated by XPS, and CV measurements. XPS measurements identified the cobalt ions in the monolayer. The two main peaks occurred at 781.3 and 796.3 eV, corresponding to the $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ states, respectively. The CVs of cobalt complexes on gold substrate showed a typical reversible electrochemical reaction, with an oxidation peak at 0.22 V corresponding to the $\text{Co}^{3+/2+}$ process. The CVs of TEMPO radicals exhibited a symmetrical reversible one electron redox process. The redox potentials were +0.72 V and +0.68 V vs Ag/AgCl, respectively. Electrical transport measurements of terpyridinyl-cobalt complexes showed an increase of the sheet resistance of gold layers covered with a SAM of magnetic and non-magnetic molecules when the temperature was decreased. Electrical transport measurements of TEMPO radicals were carried out and no significant difference in resistance between the bare gold and the gold covered with the monolayer was observed.

The results presented in this thesis illustrate the power of relatively weak supramolecular interactions to direct the immobilization of functional systems on surfaces. The work on the combination of host-guest and lanthanide-ligand coordination interaction motifs on surfaces demonstrates that hybrid, multifunctional supramolecular monolayers can be fabricated by integrating different non-covalent interactions in the same system. Hence, the combination of different supramolecular interactions opens up new avenues for the fabrication of complex hybrid organic-inorganic materials and stimuli-responsive surfaces.