

Summary

Molecular level visualization, sensing (by force), manipulation, and control of supramolecular assemblies and polymeric materials have been explored in this Thesis on the nanoscale using self-assembled monolayers (SAMs) and atomic force microscopy (AFM)-based platforms. Molecular forces in synthetic supramolecular host-guest and H-bonding complexes, direct detection of supramolecular H-bonded polymers, as well as mechanical properties of stimuli-responsive organometallic polymer chains have been studied by AFM-based single molecule force spectroscopy (SMFS). Under thermodynamic quasi-equilibrium conditions, rupture forces of individual host-guest complexes between β -cyclodextrin (β -CD) and various apolar guest molecules have been found to correlate with the corresponding complexation constants. Transitions from non-equilibrium to quasi-equilibrium states controlled by temperature in synthetic H-bonding (ureidopyrimidinone) systems have been observed on a single molecule level for the first time. The probing of reversible supramolecular H-bonding polymers, and the investigation of mechanical properties of stimuli-responsive poly(ferrocenylsilane) (PFS) macromolecules as a model system to realize an electrochemically powered molecular motor by SMFS have also been presented in the Thesis.

With the emergence of nanoscience and nanotechnology, many established fields have been integrated to tackle new scientific and technological challenges. In Chapter 2, a brief account has been given regarding structure, property, fabrication and function of bottom-up controlled molecular objects, including biological systems and synthetic supramolecular complexes. The combination of emerging SMFS experiments with new theories describing single molecular forces is anticipated to provide a solid foundation for the *nanoscience* of molecular forces and their dependence on approach and withdrawal rates. Molecular forces, that allow one to observe and manipulate nanostructures, have been playing an increasingly important role also in *nanotechnology* due to the widespread use of AFM-based platforms (e.g. in nanofabrication). These platforms enable controlled probing and placement of isolated nanoscale objects in a one-to-one fashion between the given nano-objects and the macroscale tool (AFM set-up). As a step towards achieving full control over objects with molecular scale dimensions, SMFS has been applied in this Thesis to previously unexplored supramolecular and polymer systems.

Expanding on previous work that addressed the unbinding force of ferrocenyl-derivatized guest molecules and β -CD SAMs, Chapter 3 describes the rupture forces of individual host-guest complexes between β -CD in SAMs and various apolar guest molecules in aqueous medium determined by force spectroscopy measurements. The analysis of the rupture force histograms revealed periodic distributions of forces, which were characteristic for each guest moiety. The observed force quanta of 39 ± 15 , 45 ± 15 , 89 ± 15 , and 102 ± 15 pN determined for anilyl, tolyldyl, tert-butylphenyl, and adamantly guests, respectively, were attributed to the unbinding forces of single host-guest complexes. The host-guest complex rupture forces were probed under thermodynamic quasi-equilibrium as indicated by the lack of loading rate dependences. The force quanta and the thermodynamic parameters of the inclusion complexes, determined by isothermal titration calorimetry and surface plasmon resonance measurements, followed the same trend. The experimental data agreed well with an equilibrium model based on the evaluation of the potential energy landscape of AFM tip-surface interactions. Finally, the unbinding forces measured for multivalent interactions using a bis-adamantly-derivatized guest were consistent with theoretical considerations.

A substrate-immobilized molecular platform for the controlled immobilization and growth of supramolecular architectures was developed based on the self-complementary molecular recognition of 2-ureido-4[1H]-pyrimidinone (UPy) moieties via quadruple hydrogen bonding, as presented in Chapter 4. Two novel asymmetric UPy disulfides, as well as trifluoromethyl and ferrocenyl-derivatized UPy guests were synthesized. The observed surface-enhanced apparent dimerization constant could be tuned by solvent composition and temperature, which allowed us to control the complex stability. This feature opens the possibility for the construction of more complex, directionally defined surface-immobilized supramolecular architectures, as well as for the study of pyrimidinone-based supramolecular polymers at surfaces and interfaces.

Unbinding behavior of individual supramolecular complexes of UPy derivatives formed via self-complementary quadruple hydrogen bonds studied by SMFS was described in Chapter 5. The rupture forces of individual quadruple H-bonding arrays were 180 ± 21 pN at a loading rate of 35 ± 0.7 nN/s in hexadecane and were found to be loading rate dependent in the range of 5 nN/s to 500 nN/s at 301 K. The rupture forces changed with temperature and were independent of loading rate in the range of 5 nN/s to 200 nN/s at 330 K. Thus the rupture forces of supramolecular H-bonded UPy complexes showed a crossover from quasi-equilibrium to non-equilibrium following changes in temperature. The crossover force was found to be 145 ± 20 pN. These results constitute the first report of force measurements in synthetic H-bonding systems that revealed transitions from non-equilibrium to quasi-equilibrium states controlled by

temperature. A similar crossover was also observed following changes of the solvent composition.

The AFM data discussed in Chapter 6 showed that reversible supramolecular polymers could be investigated at the single molecule level. In poly(ethylene glycol) – based UPy supramolecular polymer materials, the individual reversible linking sites along a supramolecular polymer chain, i.e. the complexes based on self-complementary recognition of UPy groups, acted as independent bonds in series. The rupture force of an individual self-complementary UPy complex in supramolecular polymers was measured to be 173 ± 23 pN at a loading rate of 35 ± 0.7 pN/s. Since material properties, including viscosity, composition, or chain length, are functions of various external parameters and stimuli, which can be investigated in situ, highly useful information for the design and construction of nanometer scale devices and stimuli-responsive systems has now become directly accessible from SMFS experiments.

Systematic investigations of the insertion behavior of ethylene sulfide end-functionalized poly(ferrocenylsilane) (PFS) derivatives into pre-formed SAMs were carried out, as described in Chapter 7. A robust and reproducible procedure allowed us to obtain individually isolated PFS macromolecules covalently attached to solid substrates. AFM, contact angle and electrochemical measurements were carried out to characterize the morphology, wettability and surface coverages of the mixed layers. PFS surface coverages depended on the chain lengths of the thiol molecule and the concentration of the PFS solution in toluene, but not on the insertion time and the chain length of the end-functionalized PFS molecules. Very low surface coverages were achieved by insertion from very dilute PFS solutions into long-chain SAMs. Differential pulse voltammetry provided a very useful tool to elucidate the isolation effects that existed in mixed layers of lower PFS surface coverage. In samples with very low PFS surface coverages most of the interchain interactions were avoided, which was a requirement for the investigation of single PFS chain elongation by SMFS. The immobilized isolated PFS macromolecules were subjected to in situ AFM for SMFS measurements for the first time in isopropanol. The elasticity of PFS single polymer chains was determined by fitting the experimental results with the modified freely-jointed chain (m-FJC) model, which showed, depending on the applied force, entropic and partly enthalpic elastic behavior of this polymer.

Chapter 8 demonstrates that external chemical or electrochemical stimuli could be used to induce reversible elasticity changes of individual PFS chains on surfaces by changing the redox state between neutral and oxidized. The changes were assessed at the single molecule level by SMFS. Using the m-FJC model to fit the force-extension data measured on single oxidized PFS chains, an increased Kuhn length of ~ 0.65 nm and segment elasticity of ~ 45 nN/nm were

Summary

obtained compared to neutral PFS with a Kuhn length of ~ 0.40 nm and a segment elasticity of ~ 30 nN/nm. The detected changes of the elasticity of individual stimuli-responsive PFS macromolecules were the basis for the demonstration of the principle of a electrochemically or chemically driven single (macro)molecular motor. For PFS homopolymer with a degree of polymerization of 80, a work of 3.4×10^{-19} J and an efficiency of 5% were estimated based on the experimental data.