

Stimulus Responsive Organometallic Nanostructures for Release of Molecular Payloads

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Abstract - Redox stimulus responsive polyanionic and polycationic poly(ferrocenylsilanes) were used to prepare nanostructured molecular composites at conducting substrates using the layer-by-layer method. Molecular payloads were deposited at different depths of these supramolecular structures. Controlled sequential release of guest molecules was achieved by adjusting the electrochemical environment and film nanostructure. Release could be temporarily stopped by use of reducing potentials. Film morphology, release mechanism and release kinetics will be discussed.

Polyferrocenylsilanes (PFS) belong to organometallic polymers, which exhibit ferrocene units, bridged via Si linkages, in their main chain¹. They can be prepared by various controlled polymerization techniques, and also in fully water soluble forms². Positively or negatively charged side groups render PFS water soluble, and these groups also allow the use of layer-by-layer supramolecular assembly techniques to obtain molecular nanocomposite films. In this presentation we first briefly discuss the various fabrication approaches on planar³ and curved⁴ interfaces to obtain PFS molecular multilayer structures from water. These multilayers respond to redox stimuli and PFS can be re-dispersed in water by changing the oxidation state of Fe in the main chain. As addressing by redox electrochemical signals can be realized down to the length scales of 20 nm, these structures are "nanotechnology compatible". PFS multilayer structures can be loaded with various guest molecules, which can be released in a controlled fashion upon redox command (chemical or electrochemical oxidation)^{3,4}. We shall then focus on release kinetics and mechanism of fluorescent guest molecules, which we used as model molecular payloads. The temporal development of molecular payload release was monitored by optical fluorescence spectroscopy. The influence of the electrochemical stimulus potential on the release mechanism and kinetics will then receive attention. AFM results will be presented to demonstrate morphological changes of the films during release and as function of ionic strength. We will subsequently discuss a tentative mechanism based on the zone model for polyelectrolyte films, which accounts for differences in the release kinetics and morphology changes.

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