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Structure-Property Relationship of Stimuli-Responsive Metallosupramolecular Polymers

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Supramolecular materials are intrinsically dynamic and responsive, rendering them ideal building blocks for materials that respond in a useful and defined manner to external stimuli. Among the different available binding motifs, metal-ligand complexes are especially interesting, given that it is possible to attain a wide variety of responsive behaviors of the corresponding metallosupramolecular polymers (MSPs). These vastly different properties can be accessed via straightforward variation of the chemical structure of the ligand, the type of employed metal ion, or the counter ion.

Within the scope of this thesis, different responsive behaviors of MSPs were investigated. First, the ability to heal damage in MSPs was studied in detail, and the extent of diffusion across a damaged interface necessary to restore the original mechanical properties was correlated to the healing time by combining microscopic and macroscopic testing. Notably, this study constitutes the first example visualizing diffusion processes that result in healing on the length scale of only a few tens of nanometers. Secondly, the highly tunable nature of MSPs was exploited to study the influence of the metal ion, counter ion, and macromonomer molecular weight on the mechanical and viscoelastic properties of the corresponding materials. An in-depth analysis of MSPs with a judicious selection of metal salts showed that the thermal transitions and mechanical properties of these materials can be altered over a large range and allowed to correlate the relaxation processes in the MSPs to the activation of metal-ligand complexes. Thirdly, MSPs were exploited to act as sensors for chemical agents. In this regard, a blue-fluorescent ligand was synthesized, coupled to a polymeric backbone, and consecutively assembled with europium metal ions to yield red-light emitting MSPs. The materials were processed into thin films or coatings and a clearly visible luminescence color change was observed upon exposure of these MSPs to different stimuli such as heat, solvents (liquid or vapor), or other analytes that disrupt or alter the metal-ligand complexes. Finally, nanometer-sized single chain polymeric nanoparticles (SCPNs) were prepared featuring intermolecular metal-ligand crosslinks. These particles appear to provide a viable scaffold to answer the question of how much mechanical force is required to break individual metal-ligand complexes on the single-molecule level.

To summarize, the reversible and dynamic complex formation between metal ions and ligands was exploited using different approaches, which led to novel insights regarding the interplay between the materials properties and the ligand, metal-, as well as the counter-ion. Accordingly, the research presented within the framework of this thesis greatly contributes towards elucidating the structure-property relationships in MSPs both in solution as well as in the solid state.

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