

Towards Mechanochromic Materials Based on Non-Covalent Interactions

The development of mechanoresponsive materials, which are often inspired by biological mechano-transduction pathways, elicit changes in materials properties by translating mechanical stimuli into chemical signals. Non-covalent interactions present great potential as mechanoresponsive motives by offering dynamic behavior, tunable interaction strength, and reversibility. In this thesis, two different approaches are presented that take advantage of supramolecular interactions to prepare materials, which upon mechanical activation exhibit a macroscopic response in the form of change of color.

The first approach relies on the use of novel excimer-forming, telechelic, end-functionalized macromolecule dyes, whose aggregation-dependent emission properties render a variety of polymers mechanochromic. Blending small amounts of these aggregachromic macromolecules into a wide range of polymer matrices, such as poly(ϵ -caprolactone), poly(isoprene), or poly(styrene-*b*-butadiene-*b*-styrene), appeared to improve stress transfer within the materials and enable mechanochromic responses to reliably furnish materials that display a fluorescence color change upon mechanical deformation that mirrors the stress-strain behavior of the respective matrices.

The formation of simple aggregachromic dyes with these macromolecules was also employed as an alternative pathway towards mechanoresponsive materials. To this end, microcapsules were used as a carrier for a solution of the molecularly dissolved dye. Composites of these capsules were prepared with polymer matrices such as poly(dimethylsiloxane) and mechanical stimulation in the form of tensile deformation, compression, incision, or impact led to rupture of the embedded capsules. Driven by solvent evaporation, the released dyes form excimer-type aggregates, leading to a readily detectable fluorescence color change in the damaged regions. The emission of the intact capsules serves as a built-in reference, so that quantitative assessment of the structural integrity becomes straightforward. This conceptual approach appears readily applicable to a wide range of matrices, dyes, and capsules.

To explore an alternative dye system, the so-called “binding-site signaling-site” approach was exploited to create molecules for chemical sensor applications. A thiosemicarbazide binding motif was covalently linked to a naphthalimide-based chromophore and the resulting sensor molecule was found to be deprotonated in the presence of different types of amines with a concomitant, drastic color change from yellow to purple. The proton transfer that occurred upon complex formation was found to be a reversible, highly sensitive, and broadly exploitable process. A paper-based amine sensor was prepared to demonstrate the system’s practicality and was successfully used for the detection of amine vapors in the solid state. This reversible proton transfer was also exploited in the context of mechanochemical transduction. Namely, grinding experiments with complexes of the chromophore in the solid state demonstrated that the proton transfer can be reversed by a mechanical stimulus. Complex dissociation is manifested by a color change from purple to yellow and the mechanically induced proton transfer fully characterized in the solid state. In addition, blends of originally yellow, bifunctional chromophores and acrylic polymers carrying amines furnish a purple-colored material whose color is characteristic of the thiosemicarbazide-amine complex. Transmittance measurements of deformed samples allowed for a demonstration of the dynamic dissociation of the thiosemicarbazide-amine complex and mechanically induced color change over time.

Taken together, the investigations presented in this thesis demonstrate the potential of non-covalent interactions for the preparation of a novel class of mechanochromic materials. Both frameworks can be exploited for different applications, are useful in a broad range of host matrices, and open new opportunities for the use of similar dyes or chemical motifs.

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