

Exploiting loop structures as non-covalent mechanochromic motifs

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Analyzing the response of polymers to mechanical stresses is useful to understand the process of materials failure. Mechanophores are molecules that can be incorporated into polymers and bear a weak covalent bond that can break under mechanical force. In addition to such covalent mechanophores, non-covalent interactions have recently been exploited for the development of mechanochromic motifs that have a tunable interaction strength and high sensitivity at low stresses or strains. Despite their remarkable response to force, the use of such motifs is limited by their laborious synthesis. Within this thesis, approaches towards mechanophores were studied that exploit similar non-covalent dye interactions to gain a sensitive response, but are much easier to synthesize. In particular, a motif was envisioned that features covalently linked dye pairs that assemble into a looped structure based on intramolecular interactions. The mechanical deformation of polymers featuring such a loop motif was expected to cause a fluorescence color change or switch-on as the associated dye pair is (reversible) separated.

In a first approach, the formation of a potential loop-forming structure was explored by connecting a naphthalene diimide (quencher) and a π -extended benzothiadiazole (emitter). Such structures were accessed in few synthetic steps and incorporated into polymers. Photophysical investigations indicated that quenching is fostered in polar solvents, but the dye interactions were found to be too weak to furnish the formation of the closed loops with a quenched fluorescence in the polymer matrices.

To overcome the limitations of the initial loop system, two strongly associating, excimer-forming perylene diimide (PDI) dyes were used instead. The loop motif was subsequently implemented into a linear poly(methyl acrylate) (PMA). It was found that blend films between loop and pristine PMA (PMA/PMA-L) display orange excimer emission, while application of mechanical force led to a visibly discernible color change to the green emission of monomeric PDI. Investigations of the mechanochromic response confirmed that the loop structure acts as a strain sensor upon tensile deformation and allows to monitor deformation and relaxation processes reversibly.

To demonstrate the strain sensing capability of the loop structure in different polymer, the motif was equipped with two hydroxyl groups and incorporated in polyurethanes with different hard segments that provide the material with different degrees of stiffness. In comparison, the loop-containing polymers showed that the fluorescence response scales unanimously with the applied strain, but the intensity of the response increased with an increasing stiffness of the polymer samples.

In summary, this thesis shows that looped architectures are a useful tool for the development of non-covalent mechanochromic motifs.

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