

Synthesis of a Linked Donor-Acceptor Pair as a Mechanophore

Alyssa Jennifer Ghielmetti

Master thesis in Chemistry and Physics of Soft Materials

Mechanochromic polymers have gained considerable interest during the last decade since they have promising applications as sensors that allow for a visualization of mechanical stresses, as security plastics, and tamper-proof packaging materials to name a few. A common strategy towards mechanochromic polymers is the introduction of so-called mechanophores, *i.e.*, predefined weak linkages in the polymer chains that rupture in response to mechanical stimulation. Recently, the molecular-shuttle function of a rotaxane was used as a displacement mechanophore that exclusively and reversibly responds to mechanical stimulation. Inspired by this work, a looped molecular structure with adjacent donor and acceptor moieties was envisioned as a novel type of mechanophore. Such a looped structure was intended to be covalently integrated into a polymer and application of mechanical force was expected to disassemble the dye and quencher motifs, furnishing an increased fluorescence emission. Moreover, with a covalent linkage between the dye and quencher, relaxation into the loop conformation should be enabled after stress termination. Towards this end, the present thesis investigated the synthesis of a molecular loop with a donor-acceptor pair composed of a fluorescent 4,7-bis(phenylethynyl)-2,1,3-benzothiadiazole (donor) and 1,4,5,8-naphthalenetetracarboxylic diimide (acceptor) quencher moiety. The individual dyes were successfully prepared and an alkyl chain was employed as covalent linkage between the donor-acceptor pair. The dye and quencher moieties were expected to be held together through attractive π -interactions, giving rise to a looped conformation and causing the benzothiadiazole fluorescence to be quenched. To investigate whether such donor-acceptor pairs can be exploited as mechanophores, the prepared donor-linker-acceptor compound was characterized spectroscopically. While the fluorescence was found to be neither completely quenched in solution nor in the solid state, the fluorescence emission was significantly reduced when compared to the emission of a molecular mixture of the donor and acceptor dyes. The results of this work, hence, show that a looped structure comprised of a donor and acceptor pair is a promising mechanophore candidate. However, a complete quenching of the fluorescence of the mechanophore in the relaxed state is desirable in order to achieve a clearly detectable signal upon mechanical stimulation. Accordingly, the molecular structure of such loop mechanophores needs to be further developed and adapted.

Prof. Dr. Christoph Weder, Dr. Stephen Schrettl