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Author(s)	Thazhathethil, Shakkeeb
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Title of Doctoral Dissertation

Cyclophane-based Supramolecular Mechanophores Using Charge-Transfer Complexes

(電荷移動錯体を利用したシクロファン型超分子メカノフォア)

The mechanochromic mechanophores are reliable molecular probes for the easy and discernible detection of polymer failures owing to the changes in the absorption or photoluminescence properties. Activation of mechanophores can be done by applying mechanical forces through grinding, stretching, compression, and sonication methods. Many mechanophores have been reported to require covalent bond scission for the activation. Because the activation of such mechanophores follows homolytic or heterolytic covalent bond scissions, it requires high activation energy and most of the mechanophores are irreversible in nature. In contrast, supramolecular mechanophores can be activated without covalent bond scission and are based on altering π - π interactions and charge-transfer (CT) interactions in the molecules which leads to changes in the photophysical properties. Such supramolecular mechanophores possess the advantages of instant reversibility and low activation energy. However, the number of supramolecular mechanophores is still limited.

I developed a cyclophane-based supramolecular mechanophore that contains a 1,6-bis(phenylethynyl)pyrene luminophore and a pyromellitic diimide quencher. A polyurethane elastomer containing the mechanophore displays orange emission in the absence of force, which is dominated by the CT-emission. Uniaxial tensile stretching causes ratiometric changes in emission color, due to the spatial separation between the luminophore and quencher. The response was rapid and reversible in nature.

The thesis contains three chapters including general introduction and conclusions. In the first chapter, I discuss a general introduction and background studies of mechanophores. In the second chapter, I discuss the synthesis of cyclophane-based supramolecular mechanophores, the mechanoresponsive luminescence behavior, and the detailed mechanism, demonstrating various experimental data including *in situ* emission spectroscopy upon deformation of the polymer films containing the mechanophores. When the mechanophore was dissolved in toluene, the blue monomer emission of the luminophore is effectively quenched and a faint reddish-orange emission that originates from a CT-complex was observed. The polyurethane elastomer containing cyclophane exhibited CT-complex emission dominated orange color. The deformation of polymer films causes decrease of the CT-emission and an increase of blue monomer emission. The ratiometric emission color change in response to mechanical force was instantly reversible. The ratio of the two emission intensities correlates with the applied stress. A linear reference compound was also synthesized containing the 1,6-bis(phenylethynyl)pyrene luminophore and pyromellitic diimide quencher. The linear reference compound exhibited partial quenching of luminophore emission in toluene. The deformation of polyurethane elastomer containing covalently integrated linear reference compound did not show change in emission color and always exhibited blue emission. The different mechanoresponsive behavior confirms that the cyclic structure plays a pivotal role to achieve the ratiometric emission color change. In the third chapter of the thesis, I discuss the general summary of the thesis and prospects of cyclophane-based supramolecular mechanophores.