Abstract of Doctoral Dissertation

Degree requested Doctor of Life Science Applicant's name Thuluvanchery Salim Fazil

Title of Doctoral Dissertation

Development of Catenane-based Supramolecular Mechanophores

（カテナン型超分子メカノフォアの開発）

Mechanochromic mechanophores are reporter molecules that disclose mechanical events by exhibiting changes in their photophysical properties. Supramolecular mechanophores can be activated without covalent bond scission. Several supramolecular mechanophores, including rotaxane, cyclophane, and loop-forming structures, have recently been developed to exhibit various activation behaviors. Catenane, a promising molecular motif with mechanically interlocked architecture consisting of two or more interlocked macrocycles, can be explored to expand the library of supramolecular mechanophores.

The thesis consists of four chapters. The first chapter provides a general introduction, explores prior research on mechanophores, and shows the aim of this thesis.

The second chapter focuses on investigating the potential of catenanes as mechanochromic mechanophores. In this chapter, a model catenane was synthesized, and its molecular structure was thoroughly characterized. The catenane consists of a fluorescent ring containing 9,10-bis(phenylethynyl)anthracene and a quencher ring with two naphthalene diimide moieties. Upon formation of the interlocked structure, the initial strong fluorescence of the fluorophore was completely quenched. While the fluorescent ring exhibited a high fluorescence quantum yield ($\Phi = 0.91$), this was completely quenched upon catenane formation ($\Phi < 0.01$). This pronounced fluorescence quenching makes the [2]catenane a promising candidate for supramolecular mechanophores.

The third chapter focuses on the synthesis, mechanoresponsive luminescence behavior, and the detailed mechanism of catenane-based supramolecular mechanophore **Cat**. The **Cat** mechanophore consists of one quencher ring and one photoluminescence ring **Lum**. The latter ring features a 1,6-bis(phenylethynyl)pyrene luminophore, while the former has two 1,4,5,8-naphthalene tetracarboxylic diimide (NpI) quenchers. Both rings are equipped with a triethylene glycol chain terminated with a hydroxyl group, serving as flexible handles that enable the covalent incorporation of the mechanophore into polymer chains. Upon the application of mechanical force via polymer chains to the catenane mechanophore, spatial separation between the luminophore and the quenchers can be induced, resulting in strong photoluminescence. In chloroform solutions, the fluorescence of the luminophore in **Cat** is almost completely quenched by the NpI groups. After covalently incorporated into polyurethane elastomer (**Cat-PU**), thin films of **Cat-PU** were prepared. When the film is deformed, blue photoluminescence was observed. Furthermore, the incorporation of the blue-emitting catenane and orange-emitting rotaxane mechanophore into the same segmented polyurethane elastomer revealed distinct activation behavior between the rotaxane and catenane. The activation efficiency of the catenane mechanophore, which contains two NpI groups, is more than ten times lower than that of the rotaxane mechanophore, which contains only one NpI group when the polymer films are deformed to 600% strain.

In the fourth chapter of the thesis, I present a general summary of the work and discuss the prospects of catenane-based supramolecular mechanophores.