Development of Rotaxane- and Cyclophane-based Supramolecular Mechanophores

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Mechanochromic mechanophores are reporter molecules that indicate mechanical events through changes in their photophysical properties.[1] Most mechanophores rely on the scission of covalent bonds. In contrast, our group has developed several supramolecular mechanophores that do not require breakage of covalent bonds.[2-6] As the first example, “rotaxane-based supramolecular mechanophore” was prepared.[2] The operating principle of the rotaxane mechanophores is depicted in Figure 1a. The interlocked assembly contains a fluorophore-carrying cycle, a dumbbell-shaped molecule with a matching quencher, and two stoppers. Reactive groups permit the integration into a polymer chain. In the idle state, the cycle is preferably located around the quencher (top) and the fluorescence is quenched. The force-induced displacement of the two elements (bottom) causes a fluorescence turn-on. Therefore, the polyurethane elastomer films in which the rotaxane mechanophores are covalently introduced exhibit instant and reversible on/off switching of the photoluminescence upon stretching in the cases the stoppers are sufficiently large. We also confirmed that the photoluminescence colors can be easily changed just by replacing the luminophore with other well-known planar fluorophores.[3] Furthermore, when the size of stoppers and ring are adequately designed, force-induced dethreading occurs, resulting in irreversible change in photoluminescence besides reversible changes upon cycle tests.[4]

We have also developed a cyclophane-based supramolecular mechanophore that exhibits ratiometric emission color change (Figure 1b).[5] The cyclophane mechanophore contains two fluorescent 1,6-bis(phenylethynyl)pyrene moieties that are capable of forming intramolecular excimers in the force-free state. When the cyclophane mechanophore is covalently embedded into polyurethane elastomer and the resultant films are stretched, the relative emission intensity of excimer emission gradually decreases compared to monomer emission. Very recently, a cyclophane mechanophore that utilizes charge transfer complex emission was also prepared in our group.[6]

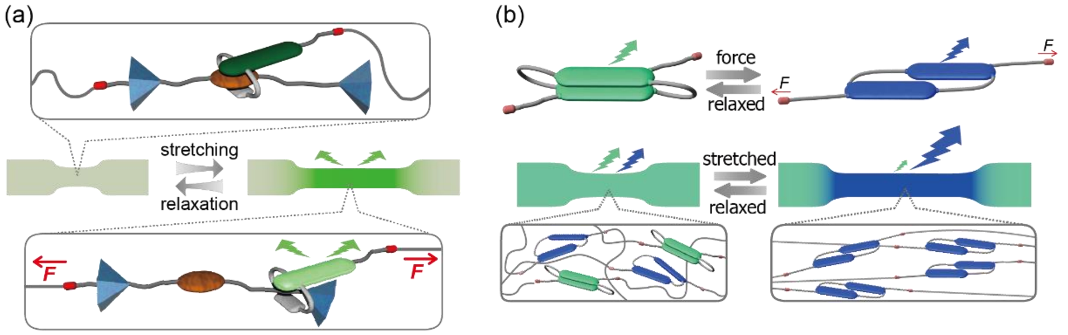

Figure 1. Schematic illustrations of the working mechanisms of (a) rotaxane-based and (b) cyclophane-based supramolecular mechanophores.

[1] Y. Chen, R. P. Sijbesma, *et al.*, *Chem. Soc. Rev.*, **2021**, *50*, 4100. [2] Y. Sagara *et al.*, *J. Am. Chem. Soc.*, **2018**, *140*, 1584. [3] Y. Sagara *et al.*, *ACS Cent. Sci.*, **2019**, *5*, 874. [4] T. Muramatsu *et al.*, *J. Am. Chem. Soc.*, **2021**, *143*, 9884. [5] Y. Sagara *et al.*, *J. Am. Chem. Soc.*, **2021**, *143*, 5519. [6] S. Thazhathethil *et al.*, *Angew. Chem. Int. Ed.*, **2022**, *61*, e202209225.