

博士論文（要約）

**Functions of [3]Rotaxane with Sliding
of Per-methylated Cyclodextrins**

（完全メチル化シクロデキストリンの
スライディングによる[3]ロタキサンの機能）

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General Introduction (Chapter 1)

A rotaxane is a mechanically interlocked molecular system composed of macrocycles, axles, and stoppers that is regarded as an important motif in supramolecular chemistry. Rotaxanes that have multiple stations—locations on the axle where interaction with the macrocycles occurs—can demonstrate shuttling motions as a structural characteristic. The positions of macrocycles can be switched between stations by movements along the axle (Figure 1). Many molecular shuttles driven by stimuli such as ions, redox, and light have been demonstrated. Partial molecular structures and electronic states at the stations, and consequently the thermodynamic stability between the macrocycle and the stations, have been designed to change in response to these stimuli, enabling sophisticated control of macrocyclic positions on the axle. Such molecular shuttles have been utilized as physical-property switching systems and have been applied as key components in molecular machines, memories and sensors.

Against rotaxanes driven with the abovementioned response, rotaxanes driven by thermal and mechanical stimuli have not progressed much because of difficult control. However, these stimuli are considered simple, convenient, and clean, because they do not involve the use of additional chemical reagents or the creation of byproducts. Moreover, systems based on switching via thermal and mechanical stimuli should generate rapid and highly reversible responses due to independent of chemical reactions. Shuttling of macrocycle results from the sliding motion which in turn is driven by thermal or mechanical stimuli. Considering this factor, thermally or mechanically driven sliding of the macrocycle could be utilized to alter slide-dependent rotaxane properties, instead of thermally and mechanically driven molecular shuttles. In this study, synthesis of rotaxane with various length axle for systematic investigation, and optical property change via thermally or mechanically driven sliding were conducted.

For optical property change via sliding, thermally or mechanically sliding in rotaxanes is combined with chromophore insulation to control exciplex emission. Here, it is designed a rotaxane bearing a luminescent station in which the luminophore is insulated under no stimuli. Rather than utilizing intramolecular interaction between the macrocycle and the station in the rotaxane, the emission color can be changed by exposing the luminescent station to external molecules, i.e., by exciplex formation; at high temperature or under stress, macrocyclic sliding occurs, which induces intermolecular interactions between the excited luminophore and external molecules (Figure 2). After luminescent emission, the luminophore at steady state needs to be shielded once more from the external molecules. This strategy is reasonable for creating optical properties switching via thermally or mechanically driven sliding.

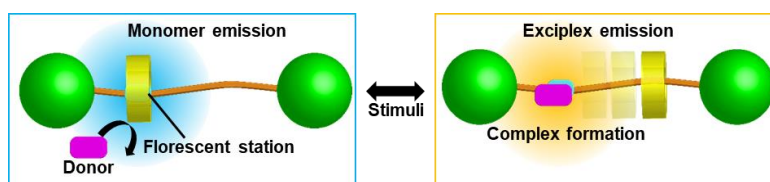


Figure 2. Conceptual illustration of optical property switching via sliding motion

As the ideal moiety for the abovementioned switchable insulated luminophore, we focused on the [3]rotaxane **S[3]R**, reported by Inouye *et al.*, which is composed of two permethylated α -cyclodextrins (PM α CDs), with an alkynyl pyrene as the station (Figure 3). Pyrene derivatives generally exhibit monomer emission upon photoexcitation, while this luminescence becomes an exciplex emission in the presence of donor molecules such as *N,N*-dimethylaniline (DMA), because of the formation of complexes between pyrene and DMA in the excited state. However, rotaxane structures can isolate such luminophores from external environments. In fact, the pyrene moiety in the **S[3]R** ($n = 0$) structure with a short axle distance was demonstrated to be completely protected from external molecules by the two PM α CDs; in this notation, n denotes chain and rotaxane axle lengths. In this thesis, using a pyrene station as the core, rotaxanes **M[3]R** ($n = 2$) and **L[3]R** ($n = 5$) were synthesized, possessing a long ethylene glycol chain inserted into the shaft, which enables slides over longer distances.

Synthesis of [2] and [3]Rotaxanes with Various Length Axle and Permethylated α -Cyclodextrin Derivatives (Chapter 2)

The synthesis of PM α CD-based rotaxanes of various axle lengths is discussed, as a systematic investigation of rotaxane sliding (Figure 3). The rotaxanes were synthesized according to the method of Inouye *et al.* Additionally, a rotaxane derivative was generated by replacing one of the methoxy groups on the PM α CD with a methoxy methyl ether group. Then, deprotection of the methoxy methyl ether was performed, affording a rotaxane bearing a hydroxy group, which could be further modified on the α -cyclodextrin.

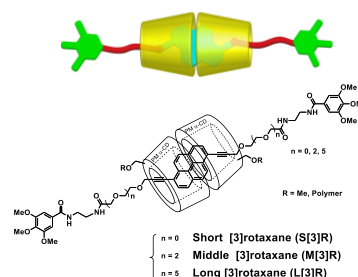


Figure 3. Structure of [3]rotaxanes

Macroscopic Change in Luminescent Color via Thermally Driven Sliding Motion in [3]Rotaxane (Chapter 3)

Through a systematic investigation of rotaxane structures, a rational design was formulated, with emphasis on the axle length and thermally driven switching, executed by

sliding (Figure 4). Essentially, at low temperatures, the luminophore is insulated by macrocycles and displays monomer emission; while at elevated temperatures, the luminophore is exposed due to a change in the macrocyclic location, and thus interacts with external molecules, giving rise to a thermally induced luminescent color change that is highly reversible and responsive. Our rational design ensured that the pyrene moiety in **M[3]R** are almost entirely shielded by PM α CD macrocycles at 298 K, and would hence display monomer emission, without any interaction with external molecules; the optical switching properties of **M[3]R** exhibit a highly dramatic response to thermal stimuli for use at room-temperature (~ 4.5 times). Furthermore, this optical property switching via thermally driven sliding was highly reversible and rapidly responsive.

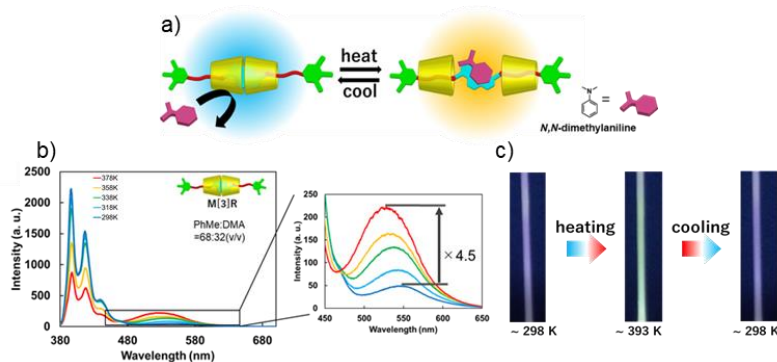


Figure 4. a) Conceptual illustration of optical property change of thermally driven sliding, b) temperature-dependent emission spectra, and c) thermochromic response of [3]rotaxanes
Optically Switching of Frozen Gel via Mechanical Sliding in [3]Rotaxane as Cross-linking Points (Chapter 4)

The [3]rotaxane cross-linked gels, (**S[3]R-Gel**, **M[3]R-Gel**, **L[3]R-Gel**) were prepared, entailing an optical property change induced by freezing the gel, which is one of the methods of applying stress. Investigation of the gels focused on a mechanochromic response and sliding (Figure 5). **L[3]R-Gel** exhibited stronger excimer emission, induced by freezing the polymer solution. On the other hand, **S[3]R-Gel** and **M[3]R-Gel** did not exhibit mechanochromic properties by freezing. This result is considered to be due to the fact that the long distance of sliding causes the transmission of stress to the entire material due to the sliding and the macrocycle is sufficiently separated from the pyrene so as not to cause steric hindrance. In addition, this mechanophore is the first time that a weak stress applied to a gel material is visually detected not by breaking a covalent bond but by a structural change of a supramolecule.

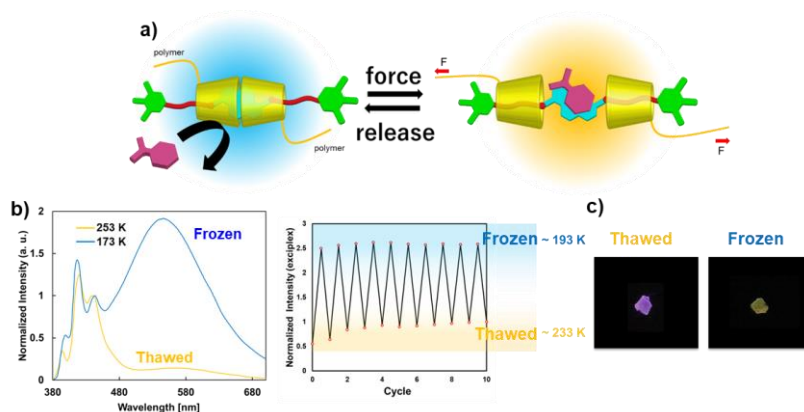


Figure 5. a) Conceptual illustration of optical property change of mechanically driven sliding, b) emission spectra of frozen gel and thawed gel, and c) optical property change by freezing gel

Conclusion (Chapter 5)

The switching system of optical properties using the thermal and mechanically activated sliding motion of [3]rotaxane with permethylated cyclodextrin were developed. In these studies, switching of physical properties was achieved for the first time by switching insulation and uninsulated station. This system would be expected to have high reversibility and rapid response by not passing through a chemical reaction. Furthermore, this method would be effective as a new molecular switch for achieving sensors that respond in real time to stimuli.