論文内容の要旨

Synthetic Studies on a Molecular Crank Mechanism Which Enables Motion Transformation between Rotation and Translation

(回転および並進運動の相互変換機能を持つ分子クランクに関する合成研究)

奥野絵里香

[Introduction]

Molecular machinery, which allows rotational or translational motion based on reversible state-to-state exchanges between a few structural isomers, has attracted increasing attention, and a number of excellent examples have been reported so far. However, it is still in an early phase and therefore it is necessary to address important factors in terms of controlling each motional device such as type (rotation or translation), rate, direction, position, and timing. In the next stage, cooperative motional transformation between multiple devices should be a significant cornerstone in the development of complex nano-mechanical systems.

This study has focused on establishing a molecular crank mechanism, which enables motion transformation between rotation and translation by means of metal-mediated self-assembly and molecular interlocking.

[Design and Synthesis of a Molecular Crank Mechanism]

A crank mechanism is often used to link rotational and translational parts to directly transform the two motions. To realize this motional correlation at the molecular levels, a metal-mediated molecular ball bearing and a rotaxane were combined as a rotational and a translational parts, respectively, as shown in Fig. 1.

As a rotational part, molecular ball bearing was used, in which three Ag(I) ions are put between a tris-monodentate disk-shaped ligand with three oxazoline rings and a

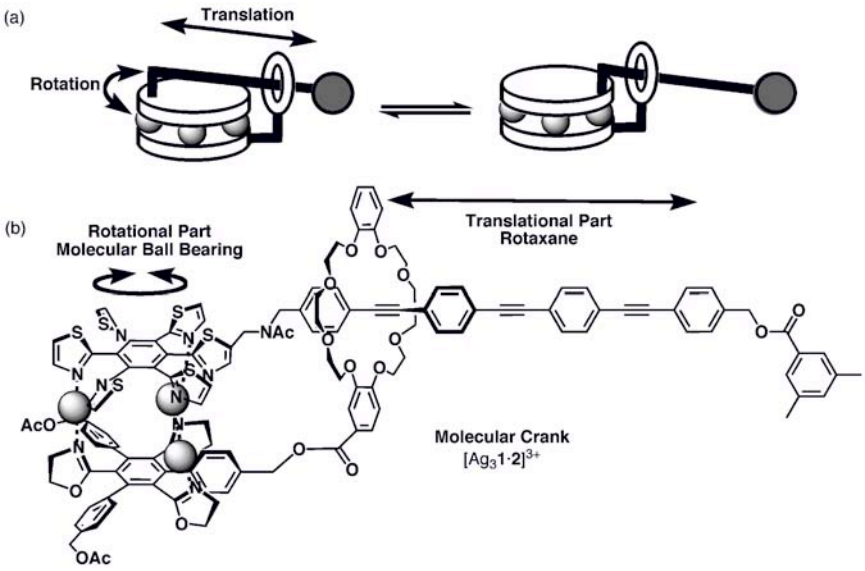

Fig. 1 (a) Schematic illustration of a molecular crank mechanism. (b) Chemical structure of a synthetic molecular crank developed in this study.

hexa-monodentate disk-shaped ligand with six thiazole rings. These two rotors can rotate relative to each other through ligand exchange and flipping processes with the helix inversion. Both ligands can be easily chemically-modified to tether some functional parts.

As for a translational part, a rotaxane, in which an axle part and a ring part are mechanically interlocked, was attached to the molecular ball bearing. That is, an axle molecule with a terminal bulky stopper is linked with one of the six thiazole rings of the hexa-monodentate ligand, while this axle part is intramolecularly threaded through a macrocyclic crown ether which is attached to one of the three phenyl rings of the tris-monodentate ligand. Here the rotaxane applied a type of secondary ammonium-templated crown ether so that a possible interaction between the crown ether and the ammonium cation on the axle part could control translational motions within the rotaxane.

The molecular crank mechanism was synthesized according to a scheme shown in Figs. 2 and 3 starting from ring **2** and axle **3**. Axle **3** was protonated and mixed with ring **2** in CH_2Cl_2, and then a trifluoromethanesulfonic acid anhydride derivative as the stopper was added to the mixture to obtain end-capped ammonium rotaxane, H**4**·**2**·X (X is a mixture of NTf_2^- and OTf^-) in 39% yield (Fig. 2c). The position of the crown ether in the ammonium rotaxane was fixed around the cationic ammonium moiety through electrostatic interactions. This was proven by the fact that the signals of the benzylic protons (*h*, *i*) adjacent to the positively-

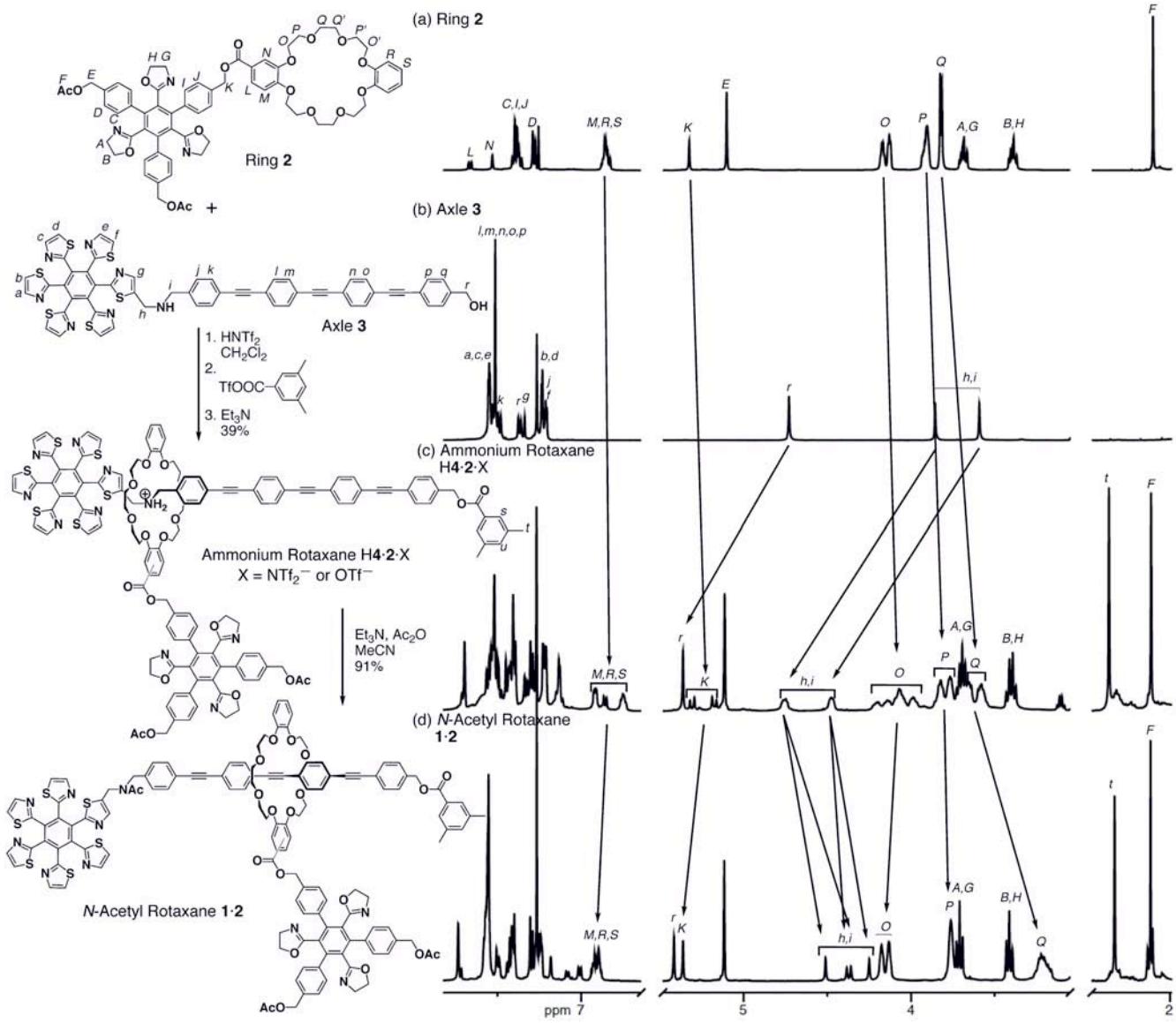

Fig. 2 Synthetic scheme of *N*-acetyl rotaxane (**1**·**2**) and ^{1}H NMR spectra of (a) free ring **2**, (b) free axle **3**, (c) ammonium rotaxane H**4**·**2**·X, and (d) *N*-acetyl rotaxane **1**·**2** in $CDCl_3$ at 293 K.

charged ammonium group was shifted downfield while the signals of the crown ether protons (*M*, *O*, *P*, *Q*, *R*, *S*) showed upfield shift with splitting in the ^{1}H NMR spectra. The generated rotaxane has a planar-chirality and is therefore in the racemic form.

Next, the ammonium group of ammonium rotaxane H**4**·**2**$^+$ was neutralized by triethylamine, and then converted into an acetamide form with acetic anhydride (Fig. 2d). In the resulting *N*-acetyl rotaxane **1**·**2**, the interactions between the crown ether and the ammonium moieties become negligibly-small, and therefore the crown ether ring starts migrating along the rigid phenylene-ethynylene oligomer axle. As a result, ^{1}H NMR signals of the ring and the axle shifted individually, and the ring signals coalesced again.

Molecular crank [Ag_3**1**·**2**]$^{3+}$ was synthesized by titration of *N*-acetyl rotaxane **1**·**2** with Ag(I) ions (up to 4.5 equiv) in methanol-d_4. Its ^{1}H NMR spectra showed the downfield shift of the signals for coordination sites of hexa-monodentate ligand (*a*, *c*) and tris-monodentate ligand (*A*, *B*, *F*, *G*, *H*). This indicates the efficient complexation of the rotational part with Ag(I) ions (Fig. 3d). ESI-TOF mass spectrum also established the formation of molecular crank ([Ag_3**1**·**2**(OH)(H_2O)]$^{2+}$: *m*/*z* = 1360.7). The rotational part was stable even at low concentrations probably due to the interlocked structure.

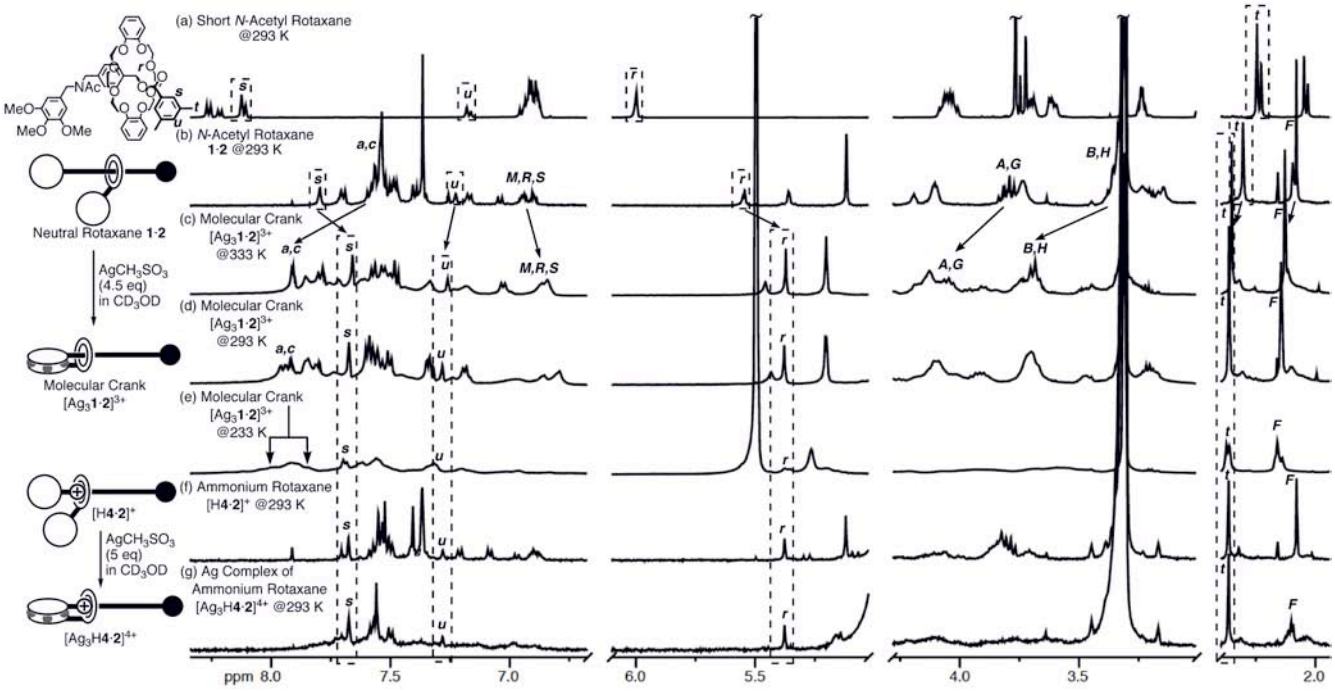

Fig 3. ^{1}H NMR spectra of (a) short *N*-acetyl rotaxane, (b) *N*-acetyl rotaxane, (c) molecular crank Ag_3**1**·**2**$^{3+}$ at 333 K, (d) 293 K, (e) 233 K, (f) ammonium rotaxane, and (g) Ag(I) complex of ammonium rotaxane in CD_3OD. [**1**·**2**] = 3.9 mM.

[Rotational and Translational Motions in the Molecular Crank Mechanism]

Intramolecular motional correlation was examined by variable temperature (VT)-^{1}H NMR spectroscopy. ^{1}H NMR spectrum of molecular crank [Ag_3**1**·**2**]$^{3+}$ at 233 K showed the split signals of thiazole ring (*a*, *c*) of hexa-monodentate ligand, whereas these signals were not split at 293 K (Figs. 3c, d). The rate of ligand exchange between the neighboring thiazole rings appears to be slower than the NMR timescale at relatively low temperatures in view of the individual observation of the signals for protons of coordinating and non-coordinating thiazole rings. In contrast, at 333 K, signals became sharper and highly symmetric, suggesting that each part of [Ag_3**1**·**2**]$^{3+}$ can move more smoothly (Fig. 3e).

Similarly in the case of the translational part of [Ag_3**1**·**2**]$^{3+}$, the sharpness of the signals for the axle and the crown ether parts highly depends on temperature, suggesting that the axle part can move back and forth through the cavity of crown ether-based macrocycle. Notably, the chemical shifts (*r*, *s*, *t*, *u*) for the bulky stopper at the axle end was proven to be susceptible to how far the crown ether part is located on the axle. In a model rotaxane

with a very short axle, the ring locates close to the stopper all the time, as observed in the strong shielding and upshielding effects of the ring (Fig. 3a). In contrast, the ammonium rotaxane H**4**·**2**$^{+}$ in which the ring is fixed around the ammonium cation showed quite different chemical shifts from the short rotaxane (Fig. 3f). In comparison of the differences in the chemical shifts, all the stopper's signals for *N*-acetyl rotaxane **1**·**2** show singlet signals whose chemical shifts are between those of the short *N*-acetyl rotaxane and the ammonium rotaxane (Fig. 3b). This indicates that the crown ether part of *N*-acetyl rotaxane **1**·**2** runs over a wide range of the axle faster than NMR timescale. However, the chemical shifts of the stopper in the molecular crank [Ag_3**1**·**2**]$^{3+}$ are close to those of ammonium rotaxane, indicating that the crown ether part is mostly kept far from the stopper (Fig. 3d). Therefore, the rotational part in motion restricts the operating range of the crown ether part along the axle.

To clarify the intramolecular interactions between the rotational and translational motions, the Ag(I) complex of ammonium rotaxane, [Ag_3·H**4**·**2**]$^{4+}$, as a constrained model was examined by VT-^{1}H NMR spectroscopy. As mentioned above, the macrocycle is located around the ammonium group of the axle so that the signals of movable parts were broadened from 213 to 333 K due to the relatively slow and restricted motions on the NMR timescale (Fig. 3g). On the other hand, the corresponding signals of Ag(I) complex of *N*-acetyl rotaxane, [Ag_3**1**·**2**]$^{3+}$, showed no significant broadening even at low temperatures (Fig. 3d), indicating that both rotational and translational motions take place simultaneously although the translational motion of the axle is restricted by the motion of the rotational part. Thus, the mobility of the crown ether part on the axle has close relationship with the rotation behavior.

[Conclusion]

In this study, a metal-mediated molecular crank mechanism has been synthesized which consists of a rotational and a translational parts within a molecule. The detailed ^{1}H NMR study revealed that the rotational part restricts the range of translational motion of the axle through the cavity of crown ether part in the rotaxane structure. Moreover, when the position of the crown ether is fixed on the axle through electrostatic interactions, the rate of rotation becomes extremely slow. Thus, the rotational and translational parts in the molecule crank mechanism dominantly interact with one another. Such a molecule would provide a clue to a transformation and transmission of regulation of motions at the molecular level.

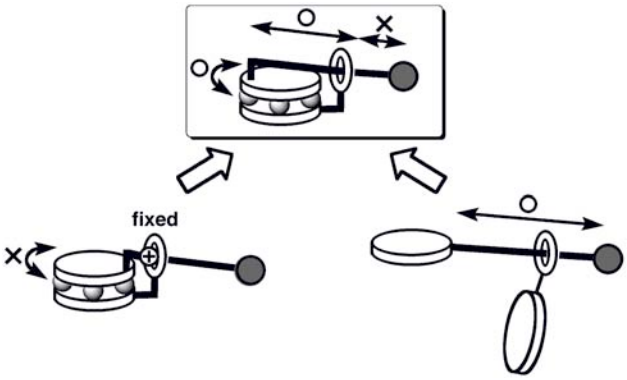

Fig 4. Schematic illustration of a possible motion in the molecular crank mechanism.