A synthetic approach to a molecular crank mechanism: toward intramolecular motion transformation between rotation and translation†

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Received 14th December 2009, Accepted 29th January 2010
First published as an Advance Article on the web 15th March 2010
DOI: 10.1039/b926154k

A molecular crank mechanism that enables transformation between rotational and translational motions was designed and synthesized. This molecule consists of a molecular ball bearing as the rotational part in which two disk-shaped rotors can rotate relative to each other through ligand exchange and flipping motion, and a [2]rotaxane as a translational part in which an axle molecule can move back-and-forth through the cavity of a crown ether-based macrocycle. ^{1}H NMR analysis revealed that these two motions influence each other.

Introduction

Molecular machines that can realize mechanical motions on the nanoscale have attracted increasing attention.[1] Since rotation and translation are two fundamental elements of movement, much effort has been made for developing molecular rotary motors,[2] linear motors,[3] and related machinery such as rotors[4,5] and gears.[6] Current interest in this field turns to creating elaborate molecular machine systems in which multiple individual molecular machines are closely connected to work cooperatively like macroscopic machines. In this regard, we and other groups have recently developed molecules in which several movable parts are structurally interlocked and their motions are strongly correlated. In these systems, however, the correlation pattern in motion is limited to a combination of multiple rotations[6,7] or to that of translation and a partial angular motion,[8] and to our best knowledge no molecular machines that enable a transformation between rotational and translational motions have been reported. To take a macroscopic cylinder engine as an example of a crank mechanism, a piston and a crankshaft are connected with both sides of a connecting rod in the cylinder, and the reciprocating motion of the piston turns into a rotational motion of the crankshaft. Here we present a novel molecular crank mechanism that can mediate rotation and translation (Fig. 1). In view of structural features of macroscopic cylinder engines, molecular rotational and translational parts should be intramolecularly linked so as to closely correlate their two motions. To achieve this, we utilized a metal-mediated molecular ball bearing we previously reported[5] and an ammonium-crown ether-based [2]rotaxane[9,10] as rotational and translational parts, respectively. This paper describes molecular design and synthesis of a molecular crank mechanism and analysis of intramolecular correlation between rotational and translational movements.

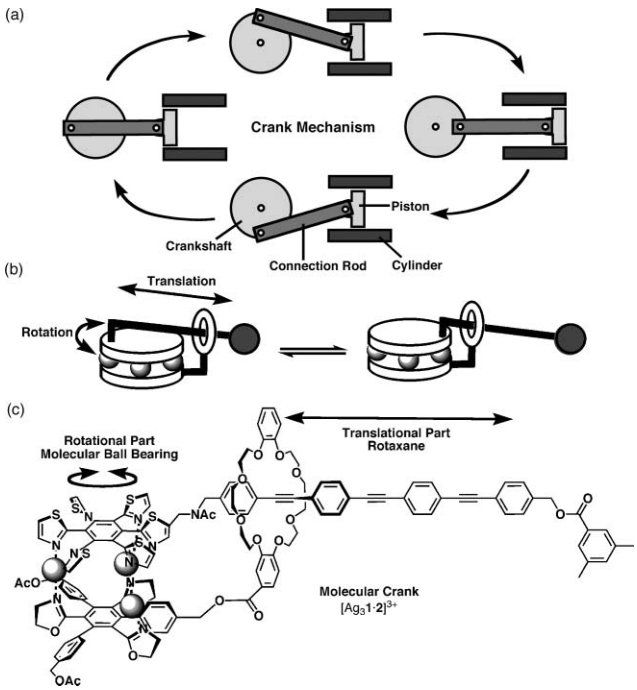

Fig. 1 (a) Schematic illustration of a crank mechanism found in a common cylinder engine. (b) Schematic illustration of a molecular crank mechanism. (c) Chemical structure of a synthetic molecular crank mechanism developed in this study.

Result and discussion

Molecular design

A crank mechanism is a common transformation between rotation and translation in cylinder engines, which have three mechanical parts, piston, crankshaft and connecting rod (Fig. 1a). The piston reciprocates in the cylinder, and the motion brings about the rotation of the crankshaft through the connecting rod. In our molecular design, two mechanical parts for rotational and translational motions were precisely designed so that these parts are efficiently correlated with one another. The molecular crank mechanism developed in this study is schematically drawn in Fig. 1b. Here two rotors forming a rotational part are connected

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† Electronic supplementary information (ESI) available: Experimental details for the syntheses of **3**, **13**, **15** and **17**. See DOI: 10.1039/b926154k

and stacked along a coaxis, one of which is attached to a ring part and the other to a rigid axle that can intramolecularly penetrate through the ring to form a rotaxane structure. A terminal stopper is attached to one end of the axle and thereby the axle can reciprocate without dethreading from the ring.

More specifically, as a rotational part of a molecular crank mechanism, a molecular ball bearing[5] was used in light of the following major features. Firstly, this sandwich-shaped helical molecule is quantitatively constructed from two different disk-shaped ligands as rotors and three Ag(I) ions. Secondly, since these two rotors have different ligand structures, that is, tris-monodentate and hexa-monodentate (**L3** and **L6**, respectively, in Fig. 2a), the ring and the axle parts can be individually connected with each rotor through aromatic rings attached to the central benzene ring. Thirdly, the relative rotation of the two rotors in the molecular ball bearing and the motional correlation in the whole crank mechanism can be estimated by NMR analyses of two fundamental motions, ligand exchange and flip motion, with the helix inversion of the ball bearing part (Fig. 2b).

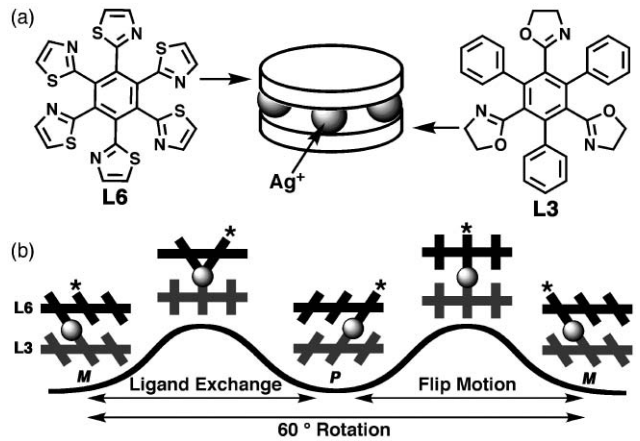


Fig. 2 A molecular ball bearing: (a) chemical structure of components, (b) schematic illustration of the rotational mechanism.

As for the translational part, [2]rotaxanes, in which an axle penetrates through a ring, are topologically attractive and useful as structural motifs for molecular machines. So far, several synthetic strategies have been developed for such mechanically-interlocked structures.[11] A frequently-used synthetic strategy includes formation of a pseudorotaxane with the aid of noncovalent interactions between an axle molecule and a macrocycle, followed by capping of the axle ends. Finally, decreasing the interactions between the two parts allows the translation of the macrocycle along the axle moiety. In this study, we applied this template-directed synthetic strategy for construction of a translational part of a molecular crank mechanism. Among a series of rotaxanes which are constructed utilizing molecular interactions such as electrostatic interaction,[9,10,12] metal-coordination,[11a,13] hydrogen bonding[14] and hydrophobic interactions,[15] an ammonium-crown ether-based rotaxane was selected as a translational part.[9,10] The axle part has a secondary ammonium group so as to interact with dibenzo[24]crown-8 (**DB24C8**) to form a rotaxane structure.[16] Notably, in this mechanism, **DB24C8** can stay at the positively-charged ammonium site in the rotaxane, whereas *N*-acetylation of the ammonium site facilitates the back-and-forth movement of the axle within the cavity of **DB24C8**.[17] Based on molecular modeling, an appropriate length of a phenylene–ethynylene trimer was used as a rigid axle.

Synthesis of a molecular crank mechanism

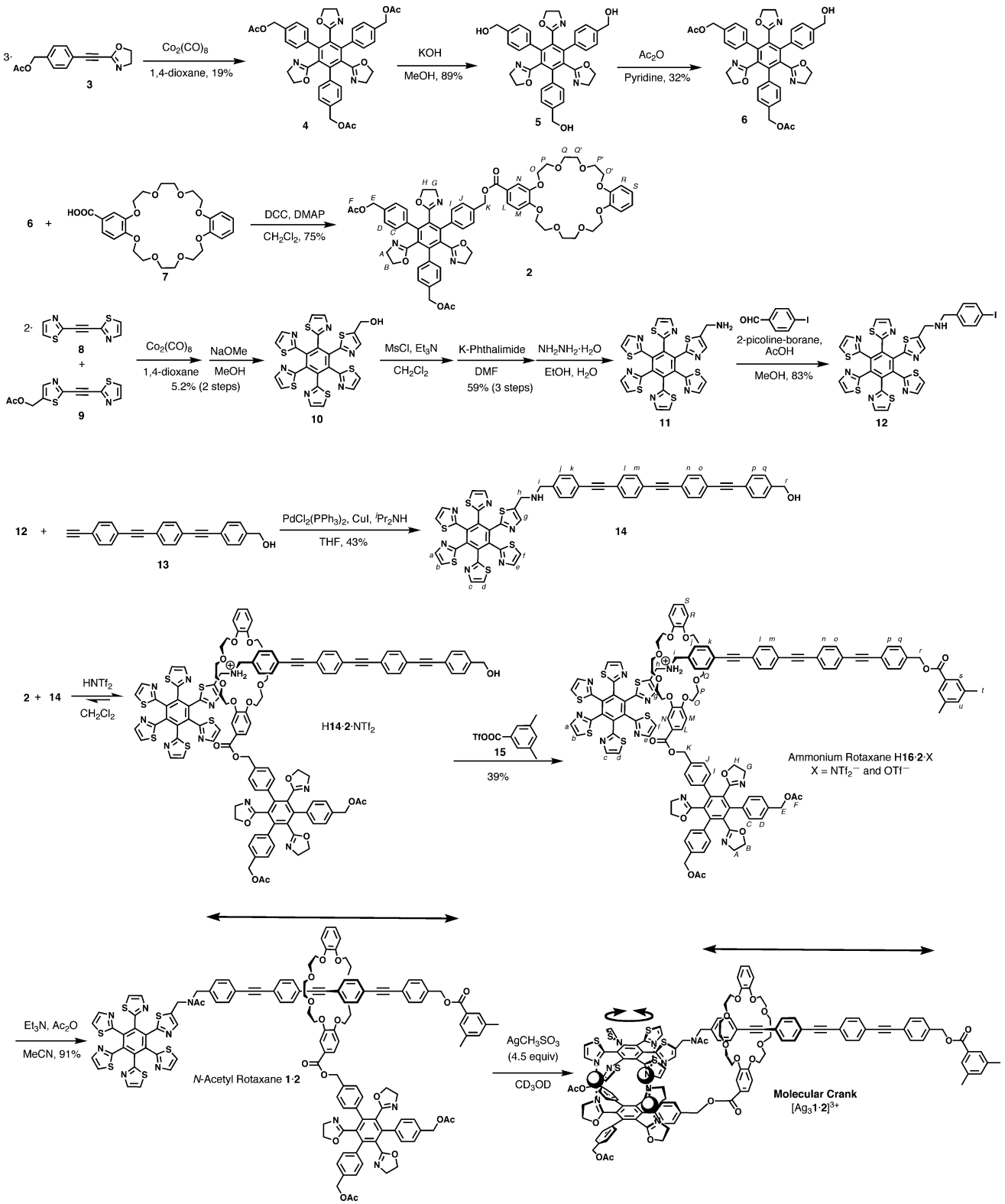
A molecular crank mechanism, $[Ag_3\mathbf{1}\cdot\mathbf{2}]^{3+}$, was synthesized according to Scheme 1. To construct a [2]rotaxane structure, a rotor-linked macrocycle **2** and a rotor-linked axle **14** were synthesized individually, and then an ammonium rotaxane H**16**·**2**·X (X: NTf_2^- or OTf^-) was constructed by capping of one of the axle ends of pseudorotaxane, H**14**·**2**·NTf_2, which was prepared by preorganizing these two components utilizing electrostatic interactions in the presence of $HNTf_2$. The subsequent *N*-acetylation of the ammonium site afforded a rotaxane **1**·**2**. A molecular crank was then constructed by Ag(I) complexation of **1**·**2** to form a molecular ball bearing part.

The rotor-linked macrocycle **2** was synthesized by coupling a tris-monodentate ligand **6** as a rotor and monofunctionalized **DB24C8**, **7**.[18] The rotor **6** was synthesized by Co-catalyzed trimerization of alkyne **3**, followed by deprotection of three acetyl groups and acetylation of two of the resulting three hydroxy groups. Esterification of the remaining hydroxy group of **6** with macrocycle **7** provided a rotor-linked macrocycle **2** in 75% yield.

Meanwhile, the rotor-linked axle **14** was synthesized by coupling rotor **12** and axle **13**. A hexa-monodentate ligand with a hydroxymethyl group, **10**,[5] was synthesized by Co-catalyzed trimerization of alkynes, **8** and **9**. First, a 1 : 1 complex of alkyne **9** and $Co_2(CO)_8$ was prepared, and then reacted with 2 equiv of alkyne **8** to afford a hexa-substituted benzene ring, followed by deprotection of an acetyl group to produce mono-hydroxymethylated rotor, **10**, in 5% yield. The hydroxy group of **10** was converted into an amino group to form mono-aminomethylated rotor, **11**, in 59% yield. Then, the aminated rotor **11** was reacted with 4-iodobenzaldehyde followed by reduction with 2-picoline-borane to form a secondary amine **12** in 83% yield. Finally, Sonogashira coupling reaction of rotor **12** and axle **13**[19] resulted in the formation of a rotor-linked axle **14** in 43% yield.

Prior to the synthesis of rotaxane, H**16**·**2**·X (X: NTf_2^- or OTf^-), we investigated the pseudorotaxane formation from **2** and **14** in the presence of acid by ^{1}H NMR measurement. Upon the addition of excess $HNTf_2$ to a 1 : 1 mixture of **2** and **14** in $CDCl_3$ ([**2**] = [**14**] = 5 mM), half of the macrocycle was associated with axle **14** to partially form a pseudorotaxane $[\mathrm{H}\mathbf{14}\cdot\mathbf{2}]^+$. This is probably due to a low fraction of protonation of the axle, **14**, as a result of decrease in the basicity of the amine group connecting with a conjugated phenylene-ethynylene axle. Unfortunately, because of the low solubility of the protonated axle, H**14**·NTf_2, both in $CHCl_3$ and CH_2Cl_2, the pseudorotaxane formation and the following end-capping reaction were performed at relatively low concentrations.

Several examples of end-capping reactions of ammonium-crown ether-based pseudorotaxanes have been reported.[9,10] Among them, most commonly utilized is esterification of terminal hydroxy group(s) of axle with esterification agents.[10] In this study, due to the instability of the pseudorotaxane arising from the low amine basicity of **14**, the esterification reaction was performed without additional bases to prevent dethreading of the macrocycle from the axle. Actually, a highly reactive mixed anhydride **15**, prepared



Scheme 1 Synthesis of a molecular crank mechanism.

from 3,5-dimethyl benzoic acid and trifluoromethanesulfonic acid, was used for esterification to obtain an end-capped rotaxane.[20] Esterification was performed using a dilute solution of macrocycle **2** (5 mM) in CD_2Cl_2 at −50 °C for 15 min, and finally an end-capped ammonium rotaxane H**16**·**2**·X (X: NTf_2^- or OTf^-) was obtained in 39% yield.

The mechanically-interlocked structure of rotaxane H**16**·**2**·X was confirmed by ^{1}H NMR (Fig. 3c) and ESI-TOF mass

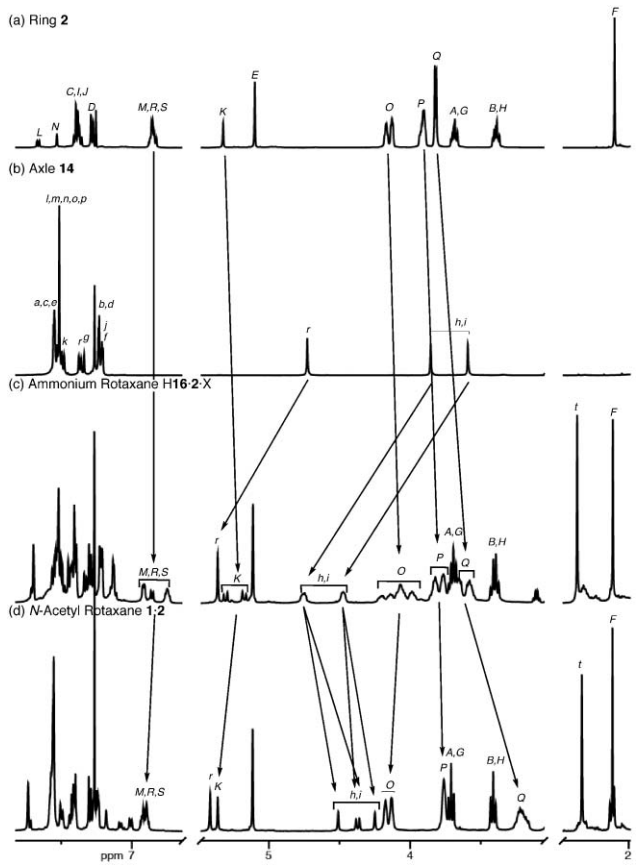
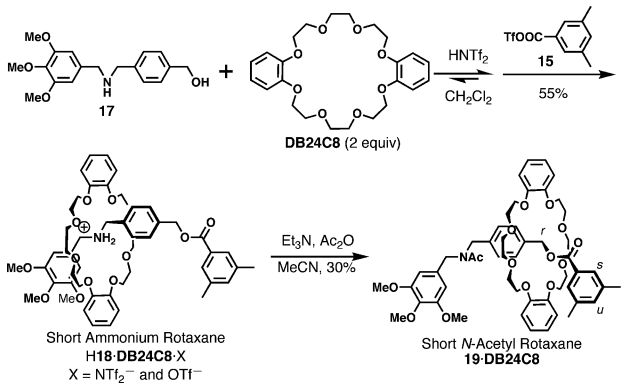


Fig. 3 ^{1}H NMR spectra of (a) free ring **2**, (b) free axle **14**, (c) ammonium rotaxane H**16**·**2**·X and (d) *N*-acetyl rotaxane **1**·**2** in $CDCl_3$ at 293 K.

measurements. The hydrogen-bonding interaction between the crown ether moiety and the ammonium group of the axle was proven by the significant shifts of the signals observed in the ^{1}H NMR spectrum. The signals of the benzylic protons (*h*, *i*) adjacent to the positively-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, suggesting the conformational locking of the macrocycle. Its 2D NOESY cross peaks also indicated the proximity of the ammonium group to the crown ether moiety. The generated rotaxane has a planar-chirality and is therefore in the racemic form.

Next, the amino group of ammonium rotaxane H**16**·**2**·X was converted into an acetyl amide group according to Takata's method (Fig. 3d).[17] Acetic anhydride and excess triethylamine were added to a solution of H**16**·**2**·X in CD_3CN to obtain *N*-acetyl rotaxane **1**·**2** in 91% yield. In the resulting charge-free rotaxane, **1**·**2**, the interactions between the acetamide group and the crown ether moiety became negligibly small, and therefore the reciprocating motion of the rigid phenylene-ethynylene axle within the crown ether cavity became much easier. These changes in the positional relationship between the two parts were strongly supported by the disappearance of characteristic peak shifts for hydrogen-bonding interactions, leading to a loss of NOESY cross peaks observed with the ammonium rotaxane, and the coalescence of the signals for the crown ether moiety in the ^{1}H NMR spectra.[21]

A model *N*-acetyl rotaxane **19**·**DB24C8** with a shorter axle, was synthesized on the same protocol from short axle **17** and dibenzo[24]crown-8 (**DB24C8**) (Scheme 2).



Scheme 2 Synthesis of a rotaxane with a short axle, **19**·**DB24C8**.

The molecular crank mechanism, $[Ag_3\mathbf{1}\cdot\mathbf{2}]^{3+}$, was synthesized by adding a small portion of Ag(I) ions (up to 4.5 equiv) to *N*-acetyl rotaxane **1**·**2** in CD_3OD. Its ^{1}H NMR spectrum showed downfield shift of the signals around coordination sites of hexa-monodentate ligand (*a*, *c*) and tris-monodentate ligand (*A*, *B*, *F*, *G*, *H*), indicating immediate complexation of the rotational part (Fig. 5d). ESI-TOF mass spectrum also revealed the formation of a molecular crank mechanism, ($[Ag_3\mathbf{1}\cdot\mathbf{2}(OH)(H_2O)]^{2+}$: m/z = 1360.2) (Fig. 4). The rotational part was stable even at low concentrations probably due to the mechanically-interlocked structure.

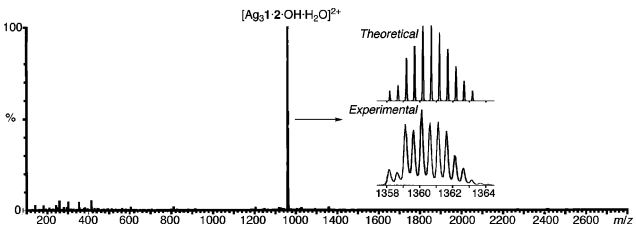


Fig. 4 ESI-TOF mass spectrum of a molecular crank mechanism, $[Ag_3\mathbf{1}\cdot\mathbf{2}]^{3+}$.

Rotation and translation in the molecular crank mechanism

The rotational mechanism of a Ag(I)-mediated molecular ball bearing used for the present molecular crank mechanism was previously reported in detail.[5] The molecular ball bearing consists of two different disk-shaped ligands (**L3** and **L6**) and three Ag(I) ions (Fig. 2a). The two disk-shaped ligands freely rotate relatively to each other through ligand exchange and flipping processes (Fig. 2b). The ligand exchange is a process in which the alternate coordinating thiazole rings of hexa-monodentate ligand are exchanged with the other three neighboring thiazole rings, which is a rate-determining step of the rotational motion. Since the rate of ligand exchange is comparable with the NMR timescale, changes in rotation behaviors can be estimated by variable-temperature (VT)-^{1}H NMR measurement. Similar to the reported molecular ball bearing, a single ball bearing, $[Ag_3\mathbf{6}\cdot\mathbf{10}]^{3+}$, which corresponds to a rotational part of molecular crank mechanism,

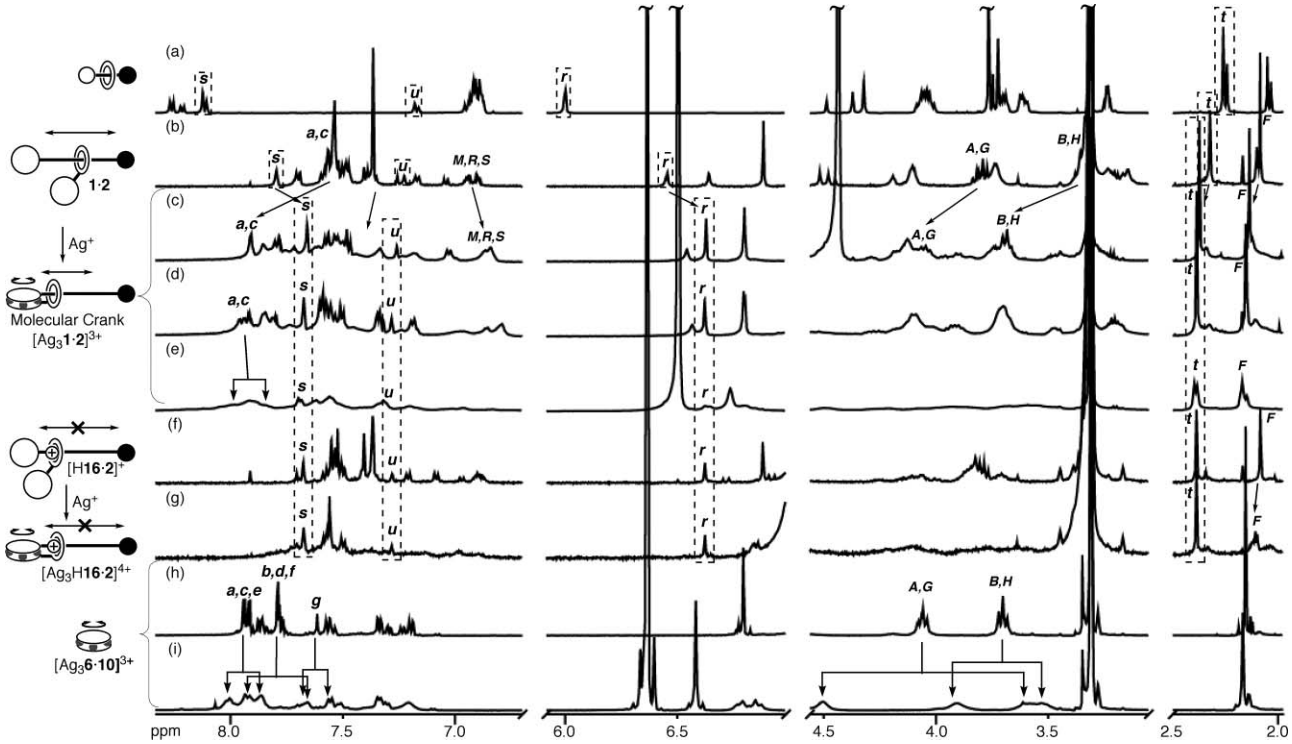
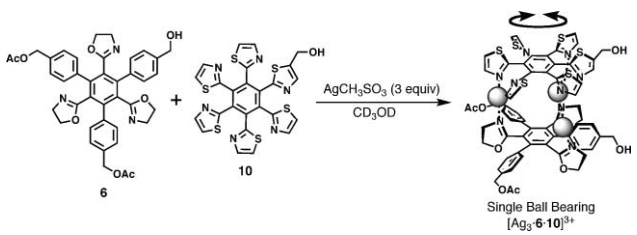


Fig. 5 ^{1}H NMR spectra of (a) short *N*-acetyl rotaxane **19·DB24C8**, (b) *N*-acetyl rotaxane **1·2**, (c) molecular crank mechanism $[Ag_3\mathbf{1·2}]^{3+}$ at 333 K, (d) 293 K, (e) 233 K in CD_3OD, [**1·2**] = 3.6 mM, (f) ammonium rotaxane $[\mathbf{H16·2}]^+$, (g) Ag(I) complex of ammonium rotaxane $[Ag_3\mathbf{H16·2}]^{4+}$ in CD_3OD, (h) single ball bearing $[Ag_3\mathbf{6·10}]^{3+}$ at 293 K and (i) 213 K in CD_3OD.

$[Ag_3\mathbf{1·2}]^{3+}$, exhibited a splitting of the signals of thiazole rings at lower temperatures due to the slower ligand exchange than the NMR timescale (Scheme 3 and Fig. 5h, i).



Scheme 3 Synthesis of a single molecular ball bearing as a simple model of rotational part.

The rotational behavior of trinuclear Ag(I) complex of *N*-acetyl rotaxane, $[Ag_3\mathbf{1·2}]^{3+}$, was assessed in the same way. The signals of thiazole rings (*a*, *c*) started to split around 233 K (Fig. 5c–e), indicating that ligand exchange on the Ag(I) ions takes place upon complexation as observed with $[Ag_3\mathbf{6·10}]^{3+}$, and that the rate of ligand exchange becomes slower than the NMR timescale below 233 K. However, the temperature at which the signals start to split is higher than that of $[Ag_3\mathbf{6·10}]^{3+}$ (213 K). This may arise from the restricted rotational motion through a whole range of motion of $[Ag_3\mathbf{1·2}]^{3+}$ with a mechanically-interlocked structure. At higher temperatures, the signals became sharper, suggesting that each part of $[Ag_3\mathbf{1·2}]^{3+}$ can move more smoothly.

As for the translational part of $[Ag_3\mathbf{1·2}]^{3+}$, 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 macrocycle is located on the axle. The mobility of axle through the macrocycle in $[Ag_3\mathbf{1·2}]^{3+}$ was assessed by comparison with a model *N*-acetyl rotaxane **19·DB24C8** with a short axle, ammonium rotaxane $\mathbf{H16·2}^+$ and *N*-acetyl rotaxane **1·2**. In these three rotaxanes, the positional relationship between the macrocycle and the stopper is different from each other. In the short rotaxane **19·DB24C8**, the macrocycle locates close to the stopper all the time in view of the strong shielding and deshielding effects of the macrocycle observed in the ^{1}H NMR spectrum (Fig. 5a). In contrast, the ammonium rotaxane $\mathbf{H16·2}^+$, in which the macrocycle is possibly fixed around the ammonium moiety of the axle, showed a quite different spectrum from that of the short rotaxane (Fig. 5f). On the other hand, all the stopper's signals for *N*-acetyl rotaxane **1·2** were singlet, and the chemical shifts were between those of the short rotaxane **19·DB24C8** and the ammonium rotaxane $\mathbf{H16·2}^+$ (Fig. 5b). This indicates that the macrocycle of *N*-acetyl rotaxane runs over a wide range of the axle faster than the NMR timescale. In comparison of these results with the spectrum of molecular crank mechanism, $[Ag_3\mathbf{1·2}]^{3+}$, (Fig. 5d), it is most plausible that only parts of the axle rather distant from the stopper interact with the macrocycle, probably due to the motion limitation caused by an intramolecularly-attached ball bearing part.

Motional correlation between rotation and translation

To clarify the intramolecular interactions between circular and reciprocating motions, the Ag(I) complex of ammonium rotaxane,

$[Ag_3 \cdot H\mathbf{16}\cdot\mathbf{2}]^{4+}$, 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. 5g). On the other hand, the corresponding signals of Ag(I) complex of *N*-acetyl rotaxane, $[Ag_3\mathbf{1}\cdot\mathbf{2}]^{3+}$, showed no significant broadening even at low temperatures, indicating that both rotational and translational motions take place simultaneously although the reciprocating motion of the axle is restricted by the motion of the rotational part. Thus, the mobility of the macrocycle 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 in a molecule (Fig. 6). The detailed ^{1}H NMR study revealed that the rotational part restricts the range of reciprocation motion of the axle through the cavity of macrocycle in the rotaxane structure. Moreover, when the position of the macrocycle 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 long-range motional transmission and regulation at the molecular level. Further investigation on whether both motions can synchronize with a 360° rotation is currently underway.

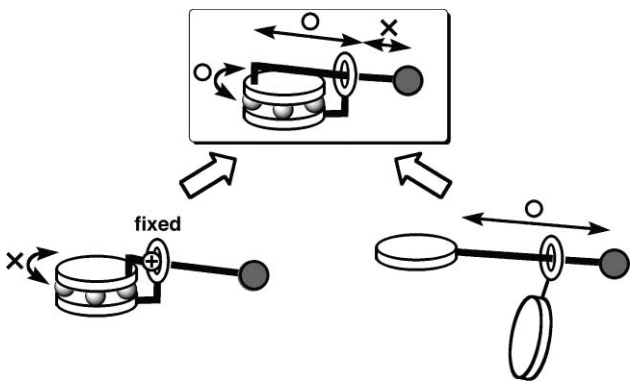


Fig. 6 Schematic illustration of a possible motion in molecular crank mechanism.

Experimental

General

All reactions were carried out in oven-dried glassware with commercial dehydrated solvents (Wako Pure Chemical Industries). Complexation with $AgCH_3SO_3$ was carried out in NMR tubes with commercial deutrated solvent (Isotec Inc.). 4-Iodobenzaldehyde and dibenzo[24]crown-8 were purchased from Tokyo Chemical Industry. $AgCH_3SO_3$ was purchased from Wako Pure Chemical Industries. 2-Picoline-borane,[22] a carboxylic acid derivative of dibenzo[24]crown-8 (**7**)[18] and monohydroxymethyl substituted hexa-monodentate ligand (**10**)[7] were prepared according to previously reported procedures. The syntheses of compounds **3**, **13**, **15** and **17** are described in the ESI.† Silica gel column chromatography was performed using silica gel 60 (70–230 mesh ASTM, Merck). ^{1}H, ^{13}C, ^{1}H-^{1}H COSY and NOESY spectra were measured on a Bruker DRX 500 (500 MHz for ^{1}H, 125.65 MHz for ^{13}C) spectrometer. The spectra are referenced to Me_4Si in $CDCl_3$ or the signal of the solvent (CD_3OD; 3.31 ppm). Chemical shifts (δ) are reported in ppm; multiplicities are indicated by s (singlet), d (doublet), t (triplet), dd (double doublet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hz. Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT spectrometer KB 201. Gel permeation chromatography (GPC) was performed on a recycling preparative HPLC (Japan Analytical Industry; LC-9204) with a UV-vis absorbance detector (S-3740) with a JAIGEL-2*H*-40 (40 × 600 mm) column.

Syntheses

4. $Co_2(CO)_8$ (1.18 g, 3.45 mmol, 15 mol%), **3** (5.56 g, 22.9 mmol, 1.0 equiv) and 1,4-dioxane (35 mL, 0.7 M) were placed in a pressure bottle. The solution was degassed and stirred at 110 °C for 1.5 h. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 100 : 1–10 : 1), alumina column chromatography (AcOEt–CH_3OH = 20 : 1) and GPC ($CHCl_3$) to obtain **4** (1.03 g, 1.41 mmol, 19%) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.12 (s, 9H, OAc), 3.41 (t, J = 9.5 Hz, 6H, NCH_2CH_2O), 3.71 (t, J = 9.5 Hz, 6H, NCH_2CH_2O), 5.12 (s, 6H, CH_2OAc), 7.30 (d, J = 8.3 Hz, 6H, C_6H_4), 7.41 (d, J = 8.3 Hz, 6H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 20.9 ($COCH_3$), 54.8 (NCH_2CH_2O), 65.8 (CH_2OAc), 67.2 (NCH_2CH_2O), 126.8 (CH of C_6H_4), 129.1 (CH of C_6H_4), 129.4 (hexa-substituted benzene), 135.2 (*ipso*-C_6H_4), 137.4 (*ipso*-C_6H_4), 142.4 (hexa-substituted benzene), 162.3 (C=N), 170.7 (C=O); HRMS (ESI-TOF) m/z exact mass $[M + Na]^+$ 752.2609, $C_{42}H_{39}NaN_3O_9$ requires 752.2584.

5. K_2CO_3 (0.226 g, 1.63 mmol, 1.1 equiv) was added to a solution of **4** (1.10 g, 1.51 mmol, 1.0 equiv) in CH_3OH (3.0 mL, 0.5 M). The reaction mixture was stirred at room temperature for 5 min. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 10 : 1) to obtain **5** (0.873 g, 1.45 mmol, 89%) as a colorless solid; ^{1}H NMR (500 MHz; $CDCl_3/CD_3OD$ = 1 : 1; 293 K) δ 3.71 (t, J = 9.3 Hz, 6H, NCH_2CH_2O), 3.81 (t, J = 9.3 Hz, 6H, NCH_2CH_2O), 4.65 (s, 6H, CH_2OH), 7.35 (s, 12H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ = 1 : 1; 293 K) δ 53.4 (NCH_2CH_2O), 63.3 (CH_2OH), 67.1 (NCH_2CH_2O), 125.4 (CH of C_6H_4), 128.5 (CH of C_6H_4), 128.6 (hexa-substituted benzene), 135.3 (*ipso*-C_6H_4), 140.7 (*ipso*-C_6H_4), 142.5 (hexa-substituted benzene), 163.2 (C=N); HRMS (ESI-TOF) m/z exact mass $[M + Na]^+$ 626.2275, $C_{36}H_{33}NaN_3O_6$ requires 626.2267.

6. Acetic anhydride (1.0 M solution in pyridine, 2.9 mL, 2.9 mmol, 2.0 equiv) was added dropwise to a solution of **5** (0.873 g, 1.45 mmol, 1.0 equiv) in pyridine (14 mL, 0.1 M) at 0 °C. The solution was stirred at 0 °C for 4 h. The reaction was quenched with CH_3OH (2.0 mL), and then the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH$ = 20 : 1–10 : 1) to give the desired **6** (0.316 g, 0.460 mmol, 32%) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.12 (s, 6H, OAc),

3.40 (t, $J = 9.3$ Hz, 4H, NCH_2CH_2O), 3.41 (t, $J = 9.3$ Hz, 2H, NCH_2CH_2O), 3.71 (t, $J = 9.3$ Hz, 4H, NCH_2CH_2O), 3.71 (t, $J = 9.3$ Hz, 2H, NCH_2CH_2O), 4.71 (s, 2H, CH_2OH), 5.12 (s, 4H, CH_2OAc), 7.30 (d, $J = 8.0$ Hz, 4H, C_6H_4), 7.31 (d, $J = 8.0$ Hz, 2H, C_6H_4), 7.40 (d, $J = 8.0$ Hz, 4H, C_6H_4), 7.40 (d, $J = 8.0$ Hz, 2H, C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 21.0 ($COCH_3$), 54.9 (NCH_2CH_2O), 54.9 (NCH_2CH_2O), 65.0 (CH_2OH), 65.9 (CH_2OAc), 67.3 (NCH_2CH_2O), 67.3 (NCH_2CH_2O), 125.8 (CH of C_6H_4), 126.8 (CH of C_6H_4), 129.1 (CH of C_6H_4), 129.2 (CH of C_6H_4), 129.2 (hexa-substituted benzene), 129.5 (hexa-substituted benzene), 135.2 (*ipso*-C_6H_4), 135.3 (*ipso*-C_6H_4), 137.5 (*ipso*-C_6H_4), 140.2 (*ipso*-C_6H_4), 142.5 (hexa-substituted benzene), 142.6 (hexa-substituted benzene), 162.4 (C=N), 162.5 (C=N), 170.8 (C=O); HRMS (ESI-TOF) *m/z* exact mass $[M + Na]^+$ 710.2503, $C_{40}H_{37}NaN_3O_8$ requires 710.2479.

2. **6** (316 mg, 0.460 mmol, 1.0 equiv), **7** (228 mg, 0.463 mmol, 1.0 equiv), 4-dimethylaminopyridine (6.3 mg, 0.052 mmol, 0.11 equiv) and *N*,*N*′-dicyclohexylcarbodiimide (99.4 mg, 0.482 mmol, 1.0 equiv) were suspended in CH_2Cl_2 (1.5 mL, 0.3 M). The resulting suspension was stirred at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH = 100:1$) and GPC ($CHCl_3$) to give desired **2** (401 mg, 0.345 mmol, 75%) as a pale yellow foam; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.12 (s, 6H, OAc), 3.44–3.39 (m, 6H, NCH_2CH_2O), 3.73–3.68 (m, 6H, NCH_2CH_2O), 3.84 (s, 4H, $PhOCH_2CH_2OCH_2$), 3.85 (s, 4H, $PhOCH_2CH_2OCH_2$), 3.95–3.92 (m, 8H, $PhOCH_2CH_2OCH_2$), 4.19–4.14 (m, 8H, $PhOCH_2CH_2OCH_2$), 5.12 (s, 4H, CH_2OAc), 5.34 (s, 2H, $CH_2OCOC_6H_3O_2$), 6.85–6.90 (m, 5H, C_6H_4 and C_6H_3 of crown ether), 7.30 (d, $J = 8.0$ Hz, 4H, C_6H_4 of tris-monodentate ligand), 7.38 (d, $J = 8.0$ Hz, 2H, C_6H_4 of tris-monodentate ligand), 7.41 (d, $J = 8.0$ Hz, 4H, C_6H_4 of tris-monodentate ligand), 7.42 (d, $J = 8.0$ Hz, 2H, C_6H_4 of tris-monodentate ligand), 7.55 (d, $J = 1.5$ Hz, 1H, C_6H_3 of crown ether), 7.68 (dd, $J = 1.5$, 8.5 Hz, 1H, C_6H_3 of crown ether); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 21.0 ($COCH_3$), 54.8 (NCH_2CH_2O), 54.8 (NCH_2CH_2O), 65.8 (CH_2OAc), 66.1 ($CH_2OCOC_6H_3O_2$), 67.2 (NCH_2CH_2O), 67.2 (NCH_2CH_2O), 69.2, 69.2, 69.3, 69.4, 69.5, 69.7, 69.9, 69.9, 71.2, 71.2, 71.3 and 71.4 (CH_2 of crown ether), 111.8 (CH of C_6H_3 of crown ether), 113.8 (CH of C_6H_4 of crown ether), 113.8 (CH of C_6H_4 of crown ether), 114.2 (CH of C_6H_3 of crown ether), 121.3 (CH of C_6H_4 of crown ether), 121.3 (CH of C_6H_4 of crown ether), 122.6 (*ipso*-C_6H_3 of crown ether), 123.9 (CH of C_6H_3 of crown ether), 126.7, 126.8, 129.1 and 129.1 (CH of C_6H_4 of tris-monodentate ligand), 129.4 (hexa-substituted benzene), 129.4 (hexa-substituted benzene), 135.2, 135.5, 137.5 and 137.5 (*ipso*-C_6H_4 of ligand), 142.4 (hexa-substituted benzene), 142.5 (hexa-substituted benzene), 148.2 (*ipso*-C_6H_3 of crown ether), 148.7 (*ipso*-C_6H_4 of crown ether), 148.7 (*ipso*-C_6H_4 of crown ether), 152.9 (*ipso*-C_6H_3 of crown ether), 162.3 (C=N), 162.3 (C=N), 166.0 ($C{=}OC_6H_3$), 170.8 ($C{=}OCH_3$); HRMS (ESI-TOF) *m/z* exact mass $[M + Na]^+$ 1184.4384, $C_{65}H_{67}NaN_3O_{17}$ requires 1184.4368.

Phthalimide derivative of 10. To a solution of **10** (171 mg, 0.284 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL, 0.07 M) were added triethylamine (0.20 mL, 1.4 mmol, 5.0 equiv) and methanesulfonyl chloride (0.11 mL, 1.4 mmol, 5.0 equiv) at 0 °C. The solution was stirred at room temperature for 4 h. The reaction was quenched with H_2O (3.0 mL), and extracted with CH_2Cl_2 (5 mL × 3). The organic extracts were combined, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude oil and potassium phthalimide (266 mg, 1.44 mmol, 5.1 equiv) were dissolved into DMF (4 mL, 0.07 M), and then the solution was stirred at 80 °C for 6 h. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH = 50:1$) to afford a phthalimide derivative (187 mg, 0.255 mmol, 90%) as a brown solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 4.86 (s, 2H, CH_2), 7.10 (d, $J = 3.1$ Hz, 2H, SCH), 7.21 (d, $J = 3.1$ Hz, 1H, SCH), 7.21 (d, $J = 3.1$ Hz, 2H, SCH), 7.43 (d, $J = 3.1$ Hz, 2H, NCH), 7.50 (s, 1H, $NCHCCH_2$), 7.53 (d, $J = 3.1$ Hz, 2H, NCH), 7.53 (d, $J = 3.1$ Hz, 1H, NCH), 7.75 (dd, $J = 3.1$, 5.1 Hz, 2H, phthalimide), 7.86 (dd, $J = 3.1$, 5.1 Hz, 2H, phthalimide); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 33.4 (CH_2), 122.2 (SCH), 122.2 (SCH), 122.2 (SCH), 123.6 (CH of phthalimide), 132.0 (C=O*C*), 134.4 (CH of phthalimide), 136.1 ($SCCH_2$), 137.2 (hexa-substituted benzene), 137.3 (hexa-substituted benzene), 137.3 (hexa-substituted benzene), 137.4 (hexa-substituted benzene), 142.1 ($NCHCCH_2$), 142.3 (NCH), 142.4 (NCH), 142.4 (NCH), 162.5 (SC=N), 162.6 (SC=N), 162.6 (SC=N), 163.7 (SC=N), 167.1 (C=O); HRMS (ESI-TOF) *m/z* exact mass $[M + Na]^+$ 757.9710, $C_{33}H_{17}NaN_7O_2S_6$ requires 757.9666.

11. To a suspension of the phthalimide derivative (242 mg, 0.329 mmol, 1.0 equiv) in C_2H_5OH/H_2O (6 mL/1 mL, 0.05 M) was added hydrazine monohydrate (35 μL, 0.72 mmol, 2.2 equiv). The reaction mixture was heated at reflux for 30 min. The solvent was removed under reduced pressure. H_2O (5 mL) was added to the residue and extracted with $CHCl_3$ (5 mL × 2). The organic extracts were combined, washed with saturated $NaHCO_3$ aq (5 mL). The product was then extracted with 1.0 *N* HCl (10 mL). The pH of the aqueous layer was adjusted to 9 with 1.0 M NaOH aq. The resulting suspension was extracted with $CHCl_3$ (10 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting pale yellow solid was dried *in vacuo* to give **11** (129 mg, 0.212 mmol, 65%); ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 3.91 (s, 2H, CH_2), 7.23 (d, $J = 3.0$ Hz, 1H, SCH), 7.23 (d, $J = 3.0$ Hz, 2H, SCH), 7.25 (d, $J = 3.0$ Hz, 2H, SCH), 7.33 (s, 1H, $NCHCCH_2$), 7.55 (d, $J = 3.0$ Hz, 1H, NCH), 7.55 (d, $J = 3.0$ Hz, 2H, NCH), 7.57 (d, $J = 3.0$ Hz, 2H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ 38.8 (CH_2), 122.2 (SCH), 122.2 (SCH), 122.2 (SCH), 137.2, 137.2, 137.3 and 137.4 (hexa-substituted benzene), 138.8 ($NCHCCH_2$), 142.3 (NCH), 142.3 (NCH), 142.4 (NCH), 145.0 ($SCCH_2$), 161.8 (SC=N), 162.7 (SC=N), 162.7 (SC=N), 162.7 (SC=N); HRMS (ESI-TOF) *m/z* exact mass $[M + H]^+$ 605.9834, $C_{25}H_{16}N_7S_6$ requires 605.9791.

12. To a solution of **11** (129 mg, 0.212 mmol, 1.0 equiv) in CH_3OH (2.0 mL, 0.1 M) were added 4-iodobenzaldehyde (49.1 mg, 0.212 mmol, 1.0 equiv), 2-picoline-borane (27.9 mg, 0.261 mmol, 1.2 equiv) and acetic acid (60 μL, 1.1 mmol, 5.0 equiv). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure. 1.0 *N* HCl (2 mL) was added to the residue and stirred at room temperature for 10 min. The pH of the resulting suspension was adjusted to 11 with 1.0 M NaOH aq., which was extracted with $CHCl_3$ (5 mL × 3). The organic extracts were combined, washed with sat. $NaHCO_3$ aq. (5 mL). The product was then extracted with 1.0 *N* HCl (10 mL).

The pH of the aqueous layer was adjusted to 9 with 1.0 M NaOH aq. The resulting suspension was extracted with $CHCl_3$ (10 mL × 2). The organic extracts were combined, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH = 30:1$) to obtain **12** (144 mg, 0.175 mmol, 83%) as a pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 3.52 (s, 2H, CH_2), 3.83 (s, 2H, CH_2), 6.98 (d, $J = 8.3$ Hz, 2H, CH of C_6H_4), 7.20 (d, $J = 3.0$ Hz, 2H, SCH), 7.23 (d, $J = 3.0$ Hz, 2H, SCH), 7.23 (d, $J = 3.0$ Hz, 1H, SCH), 7.32 (s, 1H, NC*H*CCH$_2$), 7.54 (d, $J = 3.0$ Hz, 2H, NCH), 7.55 (d, $J = 3.0$ Hz, 2H, NCH), 7.55 (d, $J = 3.0$ Hz, 1H, NCH), 7.63 (d, $J = 8.3$ Hz, 2H, CH of C_6H_4); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 44.5 (CH_2), 51.3 (CH_2), 92.6 (*ipso*-C–I), 122.2 (SCH), 122.2 (SCH), 122.2 (SCH), 130.4 (CH of C_6H_4), 137.2 (hexa-substituted benzene), 137.3 (hexa-substituted benzene), 137.3 (hexa-substituted benzene), 137.6 (hexa-substituted benzene), 137.6 (CH of C_6H_4), 138.2 (S*C*CH$_2$), 139.2 (*ipso*-C_6H_4), 140.2 (N*C*HCCH$_2$), 142.4 (NCH), 142.4 (NCH), 142.4 (NCH), 162.5 (SC=N), 162.6 (SC=N), 162.6 (SC=N), 162.7 (SC=N).

14. **12** (144 mg, 0.175 mmol, 1.0 equiv), **13** (69.8 mg, 0.210 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (2.4 mg, 3.5 mmol, 2.0 mol%), CuI (0.5 mg, 2 mmol, 1 mol%), diisopropylamine (100 µL, 0.712 mmol, 4.1 equiv) and THF (3.0 mL, 0.06 M) were placed in a pressure bottle. The reaction mixture was degassed under N_2, stirred at room temperature for 5 days. The resulting suspension was filtered and the collected precipitate was washed with AcOEt. The combined organic layer was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography ($CHCl_3/CH_3OH = 100:1$–$20:1$) and GPC ($CHCl_3$) to afford **14** (77.8 mg, 75.8 µmol, 43%) as a yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 3.59 (s, 2H, C*H*$_2$NH), 3.85 (s, 2H, C*H*$_2$NH), 4.73 (s, 2H, C*H*$_2$OH), 7.21 (d, $J = 3.0$ Hz, 2H, SCH), 7.22 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$NH), 7.23 (d, $J = 3.0$ Hz, 2H, SCH), 7.23 (d, $J = 3.0$ Hz, 1H, SCH), 7.34 (s, 1H, NC*H*CCH$_2$), 7.36 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OH), 7.48 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$NH), 7.51 (s, 4H, C≡C–C_6H_4–C≡C), 7.51 (s, 4H, C≡C–C_6H_4–C≡C), 7.53 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OH), 7.55 (d, $J = 3.0$ Hz, 2H, NCH), 7.55 (d, $J = 3.0$ Hz, 2H, NCH), 7.55 (d, $J = 3.0$ Hz, 1H, NCH); ^{13}C NMR (125 MHz, $CDCl_3$; 293 K) δ 44.6 (*C*H$_2$NH), 51.7 (*C*H$_2$NH), 65.0 (*C*H$_2$OH), 89.2, 89.3, 91.1, 91.1, 91.4 and 91.4 (C≡C), 121.9 (*ipso*-C_6H_4), 122.2, 122.2 and 122.2 (SCH), 122.2, 122.9, 123.0, 123.4 and 123.4 (*ipso*-C_6H_4), 127.0 (CH of C_6H_4CH$_2$OH), 128.4 (CH of C_6H_4CH$_2$NH), 131.7, 131.7, 131.7 and 131.7 (*ipso*-*C*-C≡C), 131.8 (CH of C_6H_4CH$_2$NH), 131.9 (CH of C_6H_4CH$_2$OH), 137.3, 137.3, 137.4 and 137.6 (hexa-substituted benzene), 140.2 (N*C*HCCH$_2$), 141.5 (*ipso*-*C*-CH$_2$OH), 142.0 (S*C*CH$_2$), 142.4 (NCH), 142.4 (NCH), 142.4 (NCH), 162.5 (SC=N), 162.7 (SC=N), 162.7 (SC=N), 162.8 (SC=N).

Ammonium rotaxane H16·2·X (X = a mixture of Tf$^-$ and NTf$_2^-$). **14** (9.5 mg, 9.3 µmol, 1.0 equiv) and **2** (11.4 mg, 9.8 µmol, 1.0 equiv) were suspended in CH_2Cl_2 (2 mL, 5 mM), to which trifluoromethanesulfoneimide (5 mg, 0.02 mmol, 2 equiv) was added. Then, trifluoromethanesulfonic acid anhydride derivative (**15**) (10 µL, excess) was added dropwise to the suspension at –78 °C. The reaction mixture was stirred at –50 to –40 °C for 15 min. The reaction was quenched with triethylamine (0.4 mL, 2.9 mmol, excess) at –78 °C. The mixture was gradually warmed up to room temperature. Then the solvent was removed under reduced pressure. H_2O (5 mL) was added to the residue and extracted with CH_2Cl_2 (5 mL × 2). The organic extracts were combined, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by GPC ($CHCl_3$) to obtain H**16·2**·X (X = a mixture of OTf$^-$ and NTf$_2^-$) (9.4 mg, 3.6–3.8 µmol, 39–40%) as an orange solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.11 (s, 6H, OAc), 2.37 (s, 6H, $C_6H_3Me_2$), 3.37–3.43 (m, 6H, NCH$_2$C*H*$_2$O), 3.58–3.66 (m, 8H, PhOCH$_2$CH$_2$OC*H*$_2$), 3.67–3.73 (m, 6H, NC*H*$_2$CH$_2$O), 3.76–3.86 (m, 8H, PhOCH$_2$C*H*$_2$O), 3.96–4.21 (m, 8H, PhOC*H*$_2$CH$_2$O), 4.48 (br, 2H, NH$_2$C*H*$_2$), 4.76 (br, 2H, NH$_2$C*H*$_2$), 5.11 (s, 4H, C*H*$_2$OAc), 5.18 (d, $J = 13$ Hz, 1H, C*H*$_2$OCOC$_6$H$_3$O$_2$), 5.31 (d, $J = 13$ Hz, 1H, C*H*$_2$OCOC$_6$H$_3$O$_2$), 5.36 (s, 2H, C*H*$_2$OCOC$_6$H$_3$Me$_2$), 6.73–6.76 (m, 2H, C_6H_4 of crown ether), 6.86 (d, $J = 8.5$ Hz, 1H, C_6H_3 of crown ether), 6.90–6.93 (m, 2H, C_6H_4 of crown ether), 7.12 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$NH$_2$), 7.14 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$NH$_2$), 7.20–7.23 (m, 5H for SCH and 1H for C_6H_3Me$_2$), 7.30 (d, $J = 7.5$ Hz, 4H, C_6H_4CH$_2$OAc), 7.33 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OCOC$_6$H$_3$O$_2$), 7.40 (d, $J = 7.5$ Hz, 4H, C_6H_4CH$_2$OAc), 7.40–7.45 (m, 1H for C_6H_3 of crown ether, 2H for C_6H_4CH$_2$OCOC$_6$H$_3$O$_2$ and 2H for C_6H_4CH$_2$OCOC$_6$H$_3$Me$_2$), 7.48–7.52 (m, 8H, C≡C–C_6H_4–C≡C), 7.52–7.57 (m, 8H, 6H for NCH and 2H for C_6H_4CH$_2$OCOC$_6$H$_3$Me$_2$), 7.58 (br, 2H, NH$_2$), 7.70 (s, 2H, C_6H_3Me$_2$), 7.70 (d, $J = 8.5$ Hz, 1H, C_6H_3 of crown ether); HRMS (ESI-TOF) m/z exact mass [H**16·2** + Na]$^{2+}$ 1171.8113, $C_{131}H_{109}NaN_{10}O_{19}S_6$ requires 1171.8135.

***N*-Acetyl rotaxane 1·2.** To a solution of ammonium rotaxane H**16·2**·X (X = a mixture of Tf$^-$ and NTf$_2^-$) (8.5 mg, 3.4 µmol, 1.0 equiv) in CD_3CN (0.50 mL, 7 mM) were added triethylamine (9.5 µL, 68 µmol, 20 equiv) and acetic anhydride (2.5 µL, 26 µmol, 7.8 equiv). The reaction mixture was allowed to stand at 40 °C for 8 h. The solvent was removed under reduced pressure. The crude product was purified by GPC ($CHCl_3$) to afford **1·2** (7.3 mg, 3.1 µmol, 91%) as an orange solid; ^{1}H NMR (500 MHz; $CDCl_3$; 293 K) δ 2.10 (s, 1.8H, NCO*Me*), 2.12 (s, 6H, CH$_2$OCO*Me*), 2.14 (s, 1.2H, NCO*Me*), 2.33 (s, 6H, $C_6H_3Me_2$), 3.16–3.24 (m, 8H, PhOCH$_2$CH$_2$OC*H*$_2$), 3.41 (t, $J = 9.3$ Hz, 6H, NCH$_2$C*H*$_2$O), 3.71 (t, $J = 9.3$ Hz, 6H, NC*H*$_2$CH$_2$O), 3.76 (br, 8H, PhOCH$_2$C*H*$_2$O), 4.13–4.18 (m, 8H, PhOC*H*$_2$CH$_2$O), 4.25 (s, 1.2H, NH$_2$C*H*$_2$), 4.36 (s, 0.8H, NH$_2$C*H*$_2$), 4.38 (s, 0.8H, NH$_2$C*H*$_2$), 4.51 (s, 1.2H, NH$_2$C*H*$_2$), 5.11 (s, 4H, C*H*$_2$OAc), 5.36 (s, C*H*$_2$OCOC$_6$H$_3$O$_2$), 5.42 (s, 2H, C*H*$_2$OCOC$_6$H$_3$Me$_2$), 6.88–6.94 (m, 1H for C_6H_3 of crown ether and 4H for C_6H_4 of crown ether), 7.01 (d, $J = 8.0$ Hz, 1.2H, C_6H_4CH$_2$NAc), 7.08 (d, $J = 8.0$ Hz, 0.8H, C_6H_4CH$_2$NAc), 7.18 (s, 1H, C_6H_3Me$_2$), 7.23–7.27 (m, 6H for SCH), 7.30 (d, $J = 8.0$ Hz, 4H, C_6H_4CH$_2$OAc), 7.40 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OCOC$_6$H$_3$O$_2$), 7.41 (d, $J = 8.0$ Hz, 4H, C_6H_4CH$_2$OAc), 7.44 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OCOC$_6$H$_3$O$_2$), 7.50 (d, $J = 8.0$ Hz, 0.8H, C_6H_4CH$_2$NAc), 7.50 (d, $J = 8.0$ Hz, 2H, C_6H_4CH$_2$OCOC$_6$H$_3$Me$_2$), 7.55 (s, 8H, C≡C–C_6H_4–C≡C), 7.55–7.58 (m, 1H for $C_6H_3O_2$ of crown ether, 5H for NCH, 1.2H for C_6H_4CH$_2$NAc and 2H for C_6H_4CH$_2$OCOC$_6$H$_3$Me$_2$), 7.72 (d, $J = 8.5$ Hz, 1H, C_6H_3 of crown ether), 7.74 (s, 2H, C_6H_3Me$_2$); HRMS (ESI-TOF) m/z exact mass [M + Na]$^+$ 2384.6343, $C_{133}H_{112}NaN_{10}O_{20}S_6$ requires 2384.6309.

Short ammonium rotaxane H18·DB24C8·X (X = a mixture of OTf$^-$ and NTf$_2^-$). To a solution of **17** (104 mg,

0.326 mmol, 1.0 equiv) and dibenzo[24]crown-8 (**DB24C8**) (293 mg, 0.652 mmol, 2.0 equiv) in CH_2Cl_2 (3.5 mL, 0.09 M) was added trifluoromethanesulfonimide (200 mg, 0.796 mmol, 2.4 equiv). The reaction mixture was cooled at −78 °C for 10 min. Then, trifluoromethanesulfonic acid anhydride derivative (**15**) (0.2 mL, excess) was added to the reaction mixture at −78 °C, which was stirred at −50 to −40 °C for 15 min. The reaction was quenched with triethylamine (1.0 mL, 7.2 mmol, 22 equiv) at −78 °C. The reaction mixture was gradually warmed up to room temperature. The solvent was then removed under reduced pressure. H_2O (5 mL) was added to the residue and extracted with CH_2Cl_2 (10 mL × 2). The organic extracts were combined, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by GPC ($CHCl_3$) to obtain H**18**·**DB24C8**·X (X = a mixture of OTf^- and NTf_2^-) (200 mg, 0.170–0.191 mmol, 52–59%) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.37 (s, 6H, $C_6H_3Me_2$), 3.53 (s, 8H, $C_6H_4OCH_2CH_2OCH_2$), 3.60 (s, 6H, OMe), 3.76 (s, 3H, OMe), 3.77–3.87 (m, 8H, $C_6H_4OCH_2CH_2O$), 4.07–4.14 (m, 8H, $C_6H_4OCH_2CH_2O$), 4.59–4.62 (m, 2H, NH_2CH_2), 4.65–4.67 (m, 2H, NH_2CH_2), 5.23 (s, 2H, $COOCH_2$), 6.56 (s, 2H, $C_6H_2(OMe)_3$), 6.75–6.78 (m, 4H, C_6H_4 of crown ether), 6.85–6.88 (m, 4H, C_6H_4 of crown ether), 7.21 (d, J = 8.0 Hz, 2H, C_6H_4 of axle), 7.22 (s, 1H, $C_6H_3Me_2$), 7.30 (d, J = 8.3 Hz, 2H, C_6H_4 of axle), 7.63 (br, 2H, NH_2), 7.68 (s, 2H, $C_6H_3Me_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 21.3 ($C_6H_3Me_2$), 52.4 (CH_2NH_2), 52.8 (CH_2NH_2), 56.1 (OMe), 61.0 (OMe), 65.7 (CH_2OCO), 68.0 ($C_6H_4OCH_2CH_2OCH_2$), 70.3 ($C_6H_4OCH_2CH_2OCH_2$), 70.6 ($C_6H_4OCH_2CH_2OCH_2$), 105.8 (CH of $C_6H_2(OMe)_3$), 112.6 (CH of C_6H_4 of crown ether), 121.8 (CH of C_6H_4 of crown ether), 127.4 (CH of $C_6H_3Me_2$), 127.5 (*ipso*-$C_6H_2(OMe)_3$), 128.1 (CH of C_6H_4), 129.5 (CH of C_6H_4), 129.8 (*ipso*-*C*Me of $C_6H_3Me_2$), 131.2 (*ipso*-C_6H_4 of axle), 135.0 (CH of $C_6H_3Me_2$), 137.8 (*ipso*-C_6H_4 of axle), 138.3 (*ipso*-*C*CO of $C_6H_3Me_2$), 147.3 (*ipso*-C_6H_4 of crown ether), 153.3 (*ipso*-$C_6H_2(OMe)_3$), 166.7 (C=O); HRMS (ESI-TOF) *m*/*z* exact mass [H**18**·**DB24C8**]$^+$ 898.4349, $C_{51}H_{64}NO_{13}$ requires 898.4377.

Short *N*-acetyl rotaxane 19·DB24C8. To a solution of ammonium rotaxane H**18**·**DB24C8**·X (X = a mixture of OTf^- and NTf_2^-) (41.9 mg, 35.5–40.0 μmol, 1.0 equiv) in CD_3CN (0.50 mL, 0.07 M) were added triethylamine (106 μL, 760 μmol, 20 equiv) and acetic anhydride (18 μL, 190 μmol, 5 equiv). The reaction mixture was allowed to stand at 40 °C for 6 h. The solvent was removed under reduced pressure. The crude product was purified by GPC ($CHCl_3$) to afford **19**·**DB24C8** (9.7 mg, 11.5 μmol, 30%) as a colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ 2.05 (s, 1H, NAc), 2.07 (s, 2H, NAc), 2.21 (s, 2H, $C_6H_3Me_2$), 2.23 (s, 4H, $C_6H_3Me_2$), 2.93–2.96 (m, 4H, $C_6H_4OCH_2CH_2OCH_2$), 3.26–3.32 (m, 4H, $C_6H_4OCH_2CH_2OCH_2$), 3.61–3.65 (m, 4H, $C_6H_4OCH_2CH_2O$), 3.72–3.77 (m, 4H, $C_6H_4OCH_2CH_2O$), 3.79 (s, 2H, OMe), 3.80 (s, 4H, OMe), 3.82 (s, 2H, OMe), 3.84 (s, 1H, OMe), 4.07–4.10 (m, 8H, $C_6H_4OCH_2CH_2O$), 4.22 (s, 0.7H, NCH_2), 4.24 (s, 1.3H, NCH_2), 4.34 (s, 1.3H, NCH_2), 4.52 (s, 0.7H, NCH_2), 5.98 (s, 0.7H, CH_2OCO), 6.01 (s, 1.3H, CH_2OCO), 6.26 (s, 0.7H, $C_6H_2(OMe)_3$), 6.41 (s, 1.3H, $C_6H_2(OMe)_3$), 6.81–6.85 (m, 4H, C_6H_4 of crown ether), 6.87–6.90 (m, 4H, C_6H_4 of crown ether), 6.90 (d, J = 8.0 Hz, 1.3H, C_6H_4 of axle), 6.95 (d, J = 8.0 Hz, 0.7H, C_6H_4 of axle), 7.09 (s, 0.3H, $C_6H_3Me_2$), 7.11 (s, 0.7H, $C_6H_3Me_2$), 8.09 (d, J = 8.0 Hz, 0.7H, C_6H_4 of axle), 8.11 (s, 0.7H, $C_6H_3Me_2$), 8.15 (s, 0.7H, $C_6H_3Me_2$), 8.17 (d, J = 8.0 Hz, 1.3H, C_6H_4 of axle); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K) δ 21.0 ($C_6H_3Me_2$), 21.7 ($NCOCH_3$), 21.9 ($NCOCH_3$), 47.9, 48.0, 50.6 and 50.9 (NCH_2), 56.3, 56.3, 61.0 and 61.0 (OMe), 66.9 and 67.0 (CH_2OCO), 68.0 ($C_6H_4OCH_2CH_2OCH_2$), 69.4 and 69.5 ($C_6H_4OCH_2CH_2OCH_2$), 69.7 and 69.7 ($C_6H_4OCH_2CH_2OCH_2$), 103.2 and 105.6 (CH of $C_6H_2(OMe)_3$), 111.6 and 120.6 (CH of C_6H_4 of crown ether), 125.6 and 126.9 (CH of C_6H_4 of axle), 128.4 and 128.4 (CH of $C_6H_3Me_2$), 129.1 and 129.5 (CH of C_6H_4 of axle), 130.9 (*ipso*-*C*Me of $C_6H_3Me_2$), 132.7 and 133.6 (*ipso*-$C_6H_2(OMe)_3$), 133.7 and 134.2 (*ipso*-C_6H_4 of axle), 134.3 (*ipso*-*C*CO of $C_6H_3Me_2$), 137.0, 137.3, 137.6 and 137.8 (*ipso*-C_6H_4 of axle and *ipso*-$C_6H_2(OMe)_3$), 137.9 (CH of $C_6H_3Me_2$), 148.5 and 148.6 (*ipso*-C_6H_4 of crown ether), 153.4 and 153.8 (*ipso*-$C_6H_2(OMe)_3$), 167.2 (C=OO), 171.0 and 171.2 (NC=O); HRMS (ESI-TOF) *m*/*z* exact mass [M + Na]$^+$ 962.4294, $C_{53}H_{65}NaNO_{14}$ requires 962.4303.

Molecular crank mechanism, $Ag_3$1·2·$(CH_3SO_3)_3$. To a suspension of **1**·**2** (3.19 mg, 1.35 μmol, 1.0 equiv) in CD_3OD (350 μL, 3.9 mM) was added a solution of $AgCH_3SO_3$ (6.1 μmol, 4.5 equiv) in a mixture of CD_3OD and D_2O (CD_3OD/D_2O = 5 : 1, 25 μL, 0.24 M) at room temperature. The reaction mixture was sonicated for 5 min and then allowed to stand at room temperature for a few minutes; ^{1}H NMR (500 MHz, CD_3OD, 293 K) δ 2.10–2.15 (m, 3H, NAc), 2.14 (s, 3H, OAc), 2.14 (s, 3H, OAc), 2.36 (s, 6H, $C_6H_3Me_2$), 2.69 (s, 9H, CH_3SO_3), 3.17–3.23 (m, 5H, $PhOCH_2CH_2OCH_2$), 3.44–3.48 (m, 3H, $PhOCH_2CH_2OCH_2$), 3.67–3.72 (m, 6H, NCH_2CH_2O), 3.67–3.95 (m, 8H, $PhOCH_2CH_2O$), 4.00–4.30 (m, 8H, $PhOCH_2CH_2O$), 4.09–4.14 (m, 6H, NCH_2CH_2O), 4.49–4.52 (br, 4H, $NAcCH_2$), 5.20 (s, 2H, CH_2OAc), 5.21 (s, 2H, CH_2OAc), 5.38 (s, 2H, $C_6H_4CH_2OCOC_6H_3Me_2$), 5.44 (br, 2H, $C_6H_4CH_2OCOC_6H_3O_2$), 6.80–6.88 (m, 1H for C_6H_3 of crown ether and 4H for C_6H_4 of crown ether), 6.96–7.04 (br, 2H, C_6H_4 of axle), 7.17 (d, J = 7.5 Hz, 1H, C_6H_4 of tris-monodentate ligand), 7.19 (d, J = 7.5 Hz, 2H, C_6H_4 of tris-monodentate ligand), 7.28 (s, 1H, $C_6H_3Me_2$), 7.31–7.35 (m, 3H for C_6H_4 of tris-monodentate ligand and 2H for C_6H_4 of axle), 7.49–7.60 (m, 12H for C_6H_4 of axle, 1H for C_6H_3 of crown ether and 3H for C_6H_4 of tris-monodentate ligand), 7.67 (s, 2H, $C_6H_3Me_2$), 7.80–7.86 (m, 6H for SCH, 1H for C_6H_3 of crown ether and 3H for C_6H_4 of tris-monodentate ligand), 7.91–7.96 (m, 5H, NCH); MS (ESI-TOF) *m*/*z* exact mass [Ag_3**1**·**2**·(OH)(H_2O)]$^{2+}$ 1360.12, $C_{133}H_{113}N_{10}O_{22}S_6Ag_3$ requires 1360.18.

Constrained rotaxane Ag_3H16·2·X (X = a mixture of CH_3SO_3, OTf^- and NTf_2^-). To a suspension of H**16**·**2**·X (X = a mixture of OTf^- and NTf_2^-) (0.36 mg, 0.14 μmol, 1.0 equiv) in CD_3OD (350 μL, 0.39 mM) was added a solution of $AgCH_3SO_3$ (0.7 μmol, 5.0 equiv) in a mixture of CD_3OD and D_2O (CD_3OD/D_2O = 7 : 1, 11 μL, 64 mM) at room temperature. The reaction mixture was sonicated for 5 min and allowed to stand at room temperature for a few minutes; ^{1}H NMR (500 MHz, CD_3OD, 293 K) δ 2.09 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.11 (br, 3H, NAc), 2.36 (s, 6H, $C_6H_3Me_2$), 2.70 (s, CH_3SO_3), 3.3–4.3 (br, 36H, crown ether, oxazoline ring, CH_2NAc), 5.14–5.15 (m, 4H, CH_2OAc), 5.25–5.31 (br, 2H, $CH_2OCOC_6H_3O_2$), 5.38 (s, 2H, $CH_2OCOC_6H_3Me_2$), 6.8–7.9 (br, 34H for aromatic rings of crown ether, tris-monodentate ligand, axle, thiazole ring), 7.29 (s, 1H, $C_6H_3Me_2$), 7.49–7.59 (m, 12H for aromatic rings of tris-monodentate ligand and axle), 7.67 (s, 2H, $C_6H_3Me_2$); MS (ESI-TOF)

m/z exact mass $[Ag_3\mathbf{D16{\cdot}2}{\cdot}Cl]^{3+}$ 894.12, $C_{130}H_{109}N_{10}O_{19}ClS_6Ag_3$ requires 894.11, $[Ag_3\mathbf{D16{\cdot}2}{\cdot}(OTf){\cdot}(CH_3SO_3){\cdot}(H_2O)_2]^{2+}$ 1460.14, $C_{133}H_{119}N_{10}O_{27}F_3S_8Ag_3$ requires 1460.15, $[Ag_3\mathbf{D16{\cdot}2}{\cdot}(OTf)_2{\cdot}(H_2O)]^{2+}$ 1481.11, $C_{133}H_{114}N_{10}O_{26}F_6S_8Ag_3$ requires 1481.14.

Single ball bearing $Ag_3$6·10·$(CH_3SO_3)_3$. To a solution of **10** (1.59 mg, 2.62 μmol, 1.0 equiv) and **6** (1.80 mg, 2.62 μmol, 1.0 equiv) in CD_3OD (450 μL, 5.8 mM) was added a solution of $AgCH_3SO_3$ (7.8 μmol, 3.0 equiv) in a mixture of CD_3OD and D_2O ($CD_3OD/D_2O = 4:1$, 39 μL, 0.20 M) at room temperature. The reaction mixture was allowed to stand at room temperature for a few minutes; ^{1}H NMR (500 MHz, CD_3OD, 293 K) δ 2.14 (s, 6H, OAc), 2.69 (s, 9H, CH_3SO_3), 3.70 (t, $J = 9.5$ Hz, 4H, NCH_2CH_2O), 3.70 (t, $J = 9.5$ Hz, 2H, NCH_2CH_2O), 4.06 (t, $J = 9.5$ Hz, 4H, NCH_2CH_2O), 4.07 (t, $J = 9.5$ Hz, 2H, NCH_2CH_2O), 4.69 (s, 2H, $SCCH_2OH$), 4.72 (s, 2H, $C_6H_4CH_2OH$), 5.21 (s, 4H, $C_6H_4CH_2OAc$), 7.19 (d, $J = 8.0$ Hz, 2H, $C_6H_4CH_2OAc$), 7.24 (d, $J = 8.0$ Hz, 1H, $C_6H_4CH_2OH$), 7.29 (dd, $J = 1.5$, 8.0 Hz, 1H, $C_6H_4CH_2OH$), 7.34 (dd, $J = 1.5$, 8.0 Hz, 2H, $C_6H_4CH_2OAc$), 7.54 (d, $J = 8.0$ Hz, 1H, $C_6H_4CH_2OH$), 7.57 (d, $J = 8.0$ Hz, 2H, $C_6H_4CH_2OAc$), 7.61 (s, 1H, $NCHCCH_2$), 7.77 (d, $J = 3.3$ Hz, 1H, SCH), 7.78 (d, $J = 3.3$ Hz, 2H, SCH), 7.79 (d, $J = 3.3$ Hz, 2H, SCH), 7.85 (dd, $J = 1.5$, 8.0 Hz, 1H, $C_6H_4CH_2OH$), 7.87 (dd, $J = 1.5$, 8.0 Hz, 2H, $C_6H_4CH_2OAc$), 7.92 (d, $J = 3.3$ Hz, 2H, NCH), 7.93 (d, $J = 3.3$ Hz, 1H, NCH), 7.94 (d, $J = 3.3$ Hz, 2H, NCH).

Acknowledgements

This work was supported by Grants-in Aid from MEXT of Japan and the Global COE Program for Chemistry Innovation. E.O. thanks JSPS Research Fellowship for Young Scientists from the Japan Society for the Promotion of Science.

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