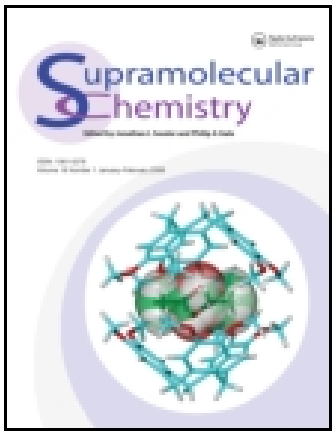

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

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Published online: 15 Nov 2010.

To cite this article: Hajime Iwamoto, Yukimi Yawata, Yoshimasa Fukazawa & Takeharu Haino (2010) Highly efficient synthesis of [3]rotaxane assisted by preorganisation of pseudorotaxane using bis(crown ether)s, Supramolecular Chemistry, 22:11-12, 815-826, DOI: 10.1080/10610278.2010.514611

To link to this article: http://dx.doi.org/10.1080/10610278.2010.514611

Supramolecular Chemistry
Vol. 22, Nos. 11–12, November–December 2010, 815–826

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Highly efficient synthesis of [3]rotaxane assisted by preorganisation of pseudorotaxane using bis(crown ether)s†

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(*Received 31 May 2010; final version received 22 July 2010*)

The tether-assisted synthesis of [3]rotaxane by olefin metathesis has been studied in detail. Bis(crown ether)s, in which two crown ethers are connected by a linker, were threaded onto ammonium salts bearing a terminal olefin to form pseudorotaxanes. The pseudorotaxanes were converted into tethered rotaxanes in the presence of Grubbs catalyst, followed by removal of the linkers to produce [3]rotaxanes in excellent yields. Preorganisation of the two reactive ends has led to a great improvement in the yield of [3]rotaxanes. The ring strain of the tethered rotaxanes and the flexibility of the pseudorotaxanes were responsible for the formation of the tethered rotaxanes.

Keywords: [3]rotaxane; preorganisation; bis(crown ether); olefin metathesis

Introduction

Rotaxanes, consisting of dumbbell-shaped molecules that are threaded through one or more macrocycles, are an attractive research field within supramolecular chemistry (*1*). Their unique molecular architectures have attracted great interest and imply potential applications in new materials and nanoscale molecular devices. Therefore, the synthesis of these molecules has been intensively studied. Initially, the synthesis of the interlocked rotaxane structures was accomplished using a statistical threading approach, in which the statistical probability of threading a linear molecule through the annulus of a macrocycle to form an interpenetrated rotaxane was very low (*2*). To overcome the low yields obtained by this technique, a variety of methodologies were developed. The application of templation strategies has led to a great improvement in the yields of the rotaxane synthesis. Templation based on supramolecular concept was achieved using hydrogen bonding, donor–acceptor interactions and metal complexation, leading to effective assembly of the cyclic components and the linear backbone (*3*). A variety of reactions, including copper(I)-catalysed alkyne–azide 1,3-dipolar cycloaddition, oxidative coupling of alkynes and imine formation, have been explored for successful formation of covalent bonds to prevent the dethreading of macrocycles from the linear backbone (*4*). Other possible strategies, such as clipping, capping, slipping and entering, were developed for the high-yield assembly of rotaxane (*5*). These recent developments in the synthesis of rotaxanes have allowed the fabrication of molecular machines, molecular muscles, nanoelectromechanical systems and nanovehicles (*6*).

The concept of preorganisation proposed by Cram (*7*) has played an important role in supramolecular chemistry and host–guest chemistry. Based on this concept, a variety of macrocyclic receptors, including crown ethers, cryptands, cyclophanes, calixarenes and spherands, were designed and synthesised to investigate their complexation properties (*8*). Preorganised host molecules decrease the loss of conformational entropy upon binding with matching guest species. Because of this minimisation of entropy loss, preorganised hosts show strong binding abilities. This concept is also applicable to organic synthesis. Metastable prereactive intermediates or complexes were formed in chemical reactions (*9*). Such preorganisation steps control reactivity and selectivity of chemical transformations.

Olefin metathesis has become a tool for synthetic organic and polymer chemists (*10*). Due to functional group tolerant catalysts for new C—C bond formation, olefin metathesis promoted by Grubbs catalyst was also applied to synthesise topological molecules, rotaxanes (*11*) and catenanes (*12*). We previously reported that the olefin metathesis reaction provided a powerful tool to prepare [3]catenane (*13*). In the course of this study, the metathesis reaction has been applied to the synthesis of rotaxane (*14*). Inspired by the concept of preorganisation,

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†Dedicated to the memory of Prof. Dmitry M. Rudkevich.

ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610278.2010.514611
http://www.informaworld.com

we describe here a full account of tether-assisted synthetic methodology of [3]rotaxane via olefin metathesis.

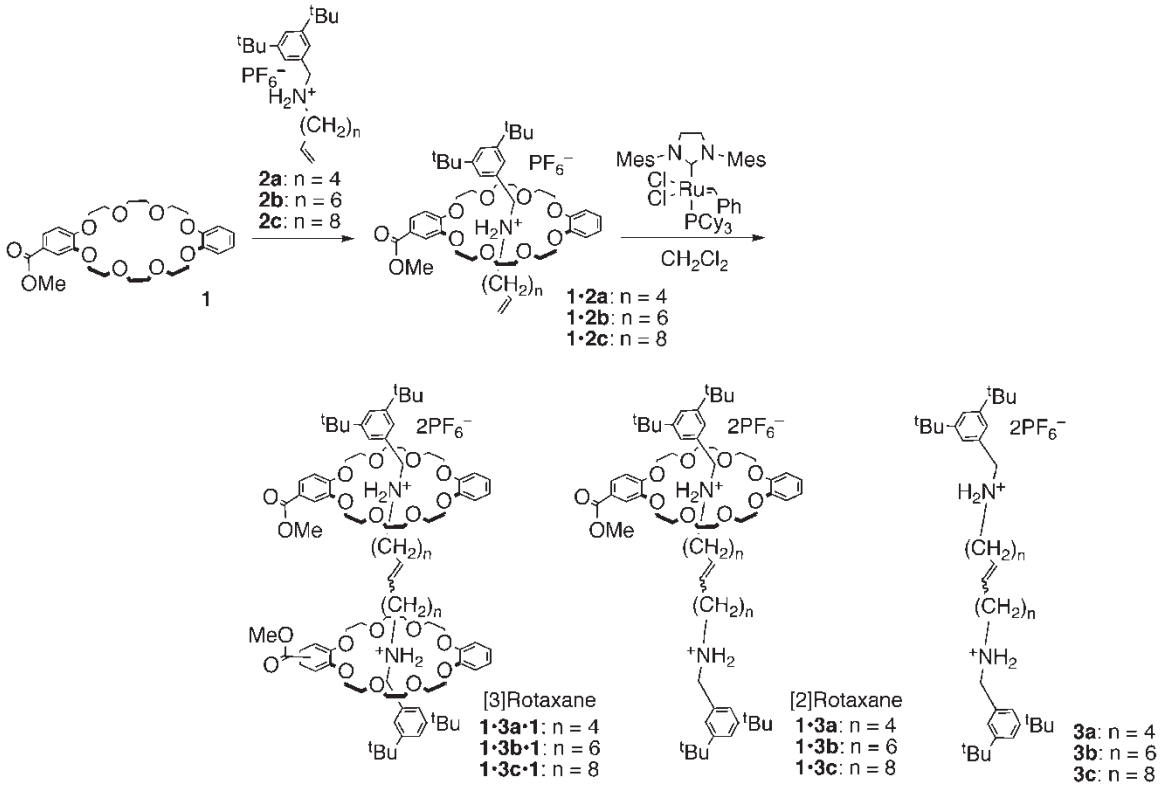
Results and discussion

One of the most straightforward [3]rotaxane synthetic methods is the coupling of two [2]pseudorotaxanes, which consist of a half dumbbell-shaped component threaded through a macrocyclic wheel. Half dumbbell-shaped ammonium salt **2** bearing a terminal C = C double bond threads through the cavity of crown ether **1** to give pseudorotaxane **1·2**, which can be directly subjected to the metathesis reaction to produce **1·3·1** (Scheme 1). This reaction process is sterically and entropically unfavourable. The encounter between the two macrocycles might create a serious steric interaction; one or both of the macrocycles can slip away from the half dumbbell-shaped molecule to form [2]rotaxane **1·3** and/or the simple dumbbell-shaped molecule **3**, reducing the yield of [3]rotaxane. When two half dumbbell-shaped components thread into bis-macrocycle **4**, in which the two macrocycles are covalently connected with each other with a suitable linkage, the subsequent coupling reaction should proceed easily because the two terminal olefins are already preorganised to react with each other to give the tethered rotaxane **3·4** (Scheme 2). The removal of the linkage can give rise to [3]rotaxane **1·3·1**.

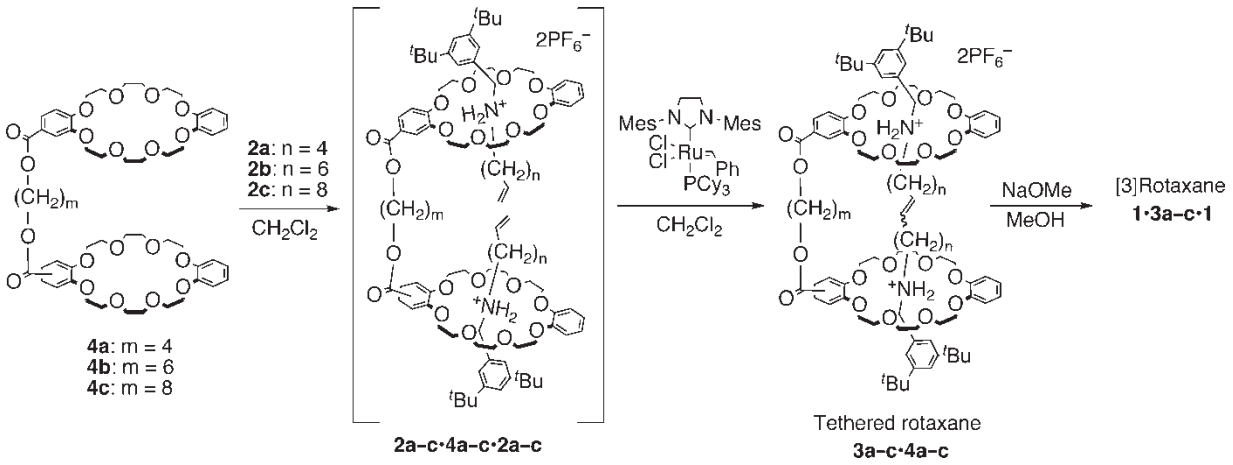
The synthesis of ammonium salts **2a–c** is illustrated in Scheme 3. Condensation of amines **5a–c** (*15*) with 3,5-di-*tert*-butyl-benzoic acid gives the corresponding amide, which was reduced with $LiAlH_4$ to give secondary amines **6a–c**. Treatment with hydrochloric acid, followed by anion exchange from chloride to hexafluorophosphate, gave **2a–c**.

The synthesis of bis(crown ether)s **4a–c** is shown in Scheme 4. Esterification of crown ether derivative **7** (*16*) with 1,4-butanediol, 1,6-hexanediol and 1,8-octanediol gave bis(crown ether)s **4a–c**.

To study the binding behaviour of crown **1** and ammonium salt **2b**, a standard titration experiment was carried out using ^{1}H NMR spectroscopy at room temperature in dichloromethane-d_2 (Figure 1). Simple mixing of the compounds yielded well-resolved signals resulting from the free and bound states, the equilibrium of which was in slow exchange on the NMR timescale. Methylene protons H_d and H_e adjacent to the ammonium moiety shifted downfield, whereas upfield shifts placed allylic proton H_c and methyl proton H_f within the shielding region of the two aromatic rings connected to the crown ring. The protons of crown **1** showed characteristic changes upon the addition of **2b**. The oxymethylene protons appeared in the region of 3.7–4.2 ppm in the absence of the ammonium salt. Upon the addition of **2b**, they became well resolved in the region of 3.3–4.3 ppm.



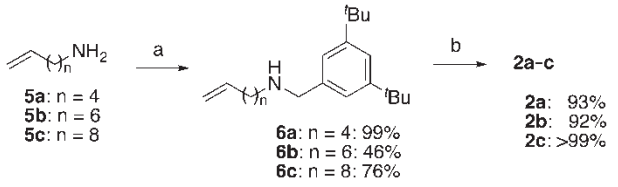
Scheme 1. Synthesis of [3]rotaxane by olefin metathesis using crown ether.



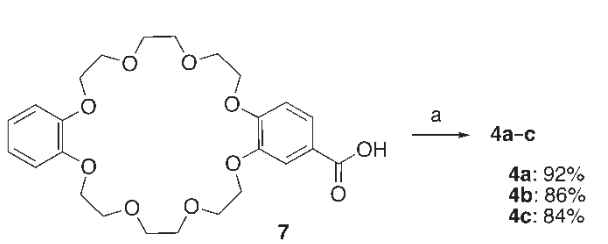
Scheme 2. Synthesis of [3]rotaxane by olefin metathesis using bis(crown ether)s.

Threading of **2b** into **1** reduces the molecular symmetry of crown ether **1**; each methylene proton of **1** becomes chemically non-equivalent; thus, this spectral change upon the addition of **1** is evidence of the formation of a guest–host complex between **1** and **2b**. Protons H_d, H_e and H_f were integrated in the free and bound states, and the binding constant (K_a) of the guest–host complex was determined as 5800 ± 1200 L mol^{-1} based on their ratio.

The synthesis of [3]rotaxane **1·3a–c·1** was performed without the assistance of tether linkages according to Scheme 1. A mixture of 50 mmol L^{-1} of crown ether **1** and 50 mmol L^{-1} of ammonium salts **2a–c** in CH_2Cl_2 was treated with 10 mol% of second-generation Grubbs catalyst (*17*). The isolated yields of [3]rotaxane **1·3a–c·1** and [2]rotaxane **1·3a–c** are listed in Table 1. In the reaction condition, 94% of ammonium salt **2** is estimated



Scheme 3. Reagents and conditions: (a) 3,5-di-*tert*-butylbenzoic acid, EDCI·HCl (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride), DMAP, CH_2Cl_2; $LiAlH_4$, THF, reflux and (b) HCl, MeOH; NH_4PF_6, acetone.



Scheme 4. Reagents and conditions: (a) diol, EDCI·HCl, DMAP, CH_2Cl_2. Diol is **4a** for 1,4-butanediol, **4b** for 1,6-hexanediol and **4c** for 1,8-octanediol.

to form the guest–host complex based on K_a determined above. According to their statistical distributions, theoretical yields of [3]rotaxanes and [2]rotaxanes are 88 and 11%, respectively (*18*).[1] The metathesis reactions of **2** in the presence of **1** produced [3]rotaxanes and [2]rotaxanes, the ratios of which were remarkably less than the theoretical value of 8.0. During the metathesis reaction, the two crown ethers come together and probably create a serious steric interaction that decreases the yield of [3]rotaxane and increases that of the [2]rotaxane; in fact, the shorter the ammonium salts **2**, the lower the ratio of chemical yields of [3]rotaxane to [2]rotaxane.

The tether-assisted synthesis of [3]rotaxane **1·3a–c·1** was performed according to Scheme 2. A mixture of 25 mmol L^{-1} of bis(crown ether)s **4a–c** and 50 mmol L^{-1} of ammonium salts **2a–c** in CH_2Cl_2 was treated with 10 mol% of second-generation Grubbs catalyst (*17*) to create tethered rotaxanes **3a–c·4a–c**.[2] After removal of the linkage by methanolysis, the desired [3]rotaxane **1·3a–c·1** was obtained with [2]rotaxane **1·3a–c** as a by-product.[3] The metathesis reaction of ammonium salts **2a–c** in the presence of bis(crown ether)s **4a–c** dramatically improved the chemical yields of [3]rotaxane compared to their control reaction (entries 4, 8 and 12). The reactions of **2a–c** in the presence of the shortest **4a** (entries 1, 5 and 9) greatly improved the ratios of the chemical yields of [3]rotaxane to [2]rotaxane, more so than those of the control reactions (entries 4, 8 and 12). By contrast, the ratios in the reaction of **2a–c** in the presence of **4c** (entries 3, 7 and 11) are close to those of the control reactions. The metathesis reaction of **2b** in the presence of **4b** (entry 6), followed by methanolysis, resulted in the highest yield of [3]rotaxane **1·3b·1** and diminished the formation of [2]rotaxane **1·3b**. Tethering two crown moieties clearly enhanced the chemical yields of the [3]rotaxanes and suppressed the side reactions. The tethered bis-crown structures obviously play a key role in the preorganisation of reactive pseudorotaxanes **2·4·2**.

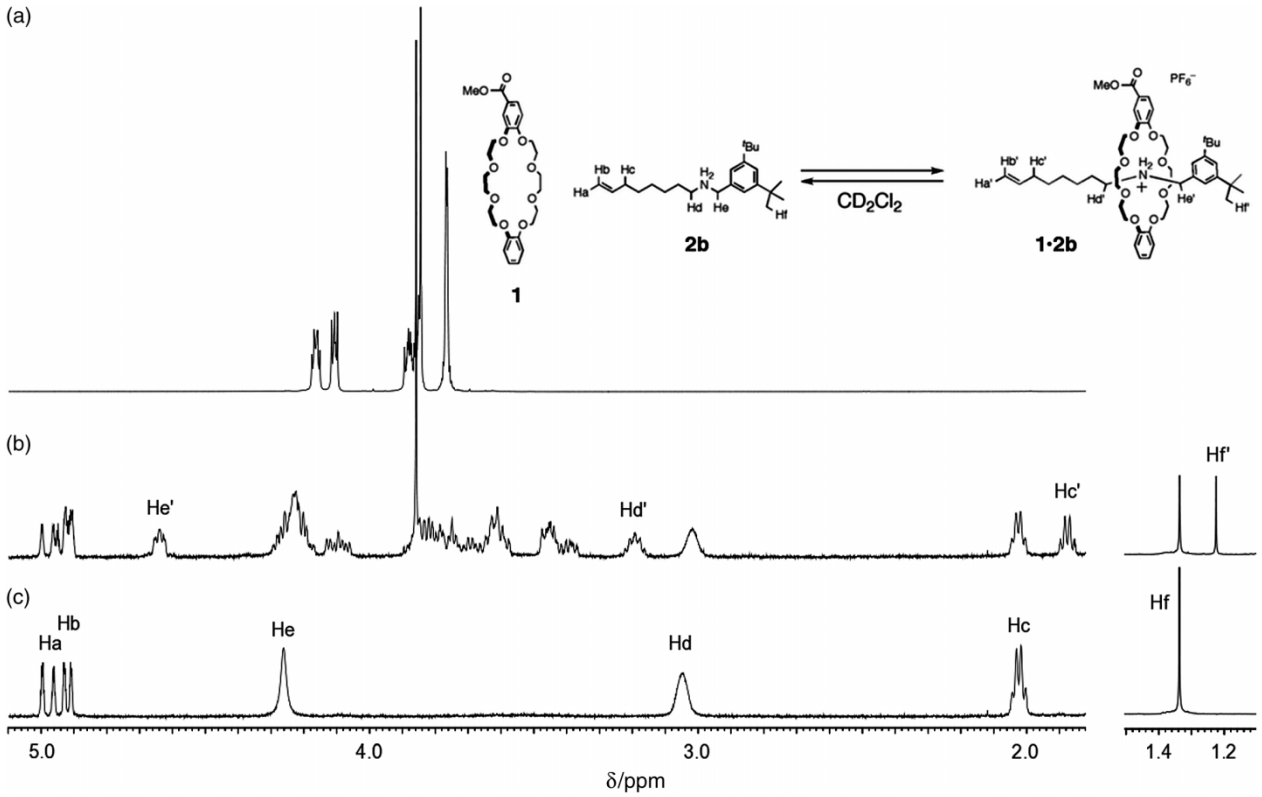


Figure 1. Partial ^{1}H NMR spectra in CD_2Cl_2 at 23°C of (a) **1**, (b) **1** (1.68×10^{-3} mol L^{-1}) + **2b** (3.93×10^{-3} mol L^{-1}), (c) **2b**.

Table 1. Yields of [3]rotaxane **1·3a–c·1** and [2]rotaxane **1·3a–c** and the ratio of chemical yields of [3]rotaxane to [2]rotaxane.

Entry	Ammonium salts	Crown ethers	Tethered rotaxanes	[3]Rotaxanes (%)		[2]Rotaxanes (%)		Ratio of chemical yields
1	**2a**	**4a**	**3a·4a**	**1·3a·1**	38	**1·3a**	18	2.1
2		**4b**	**3a·4b**		24		30	0.8
3		**4c**	**3a·4c**		32		29	1.1
4		**1**	–		21		22	1.0
5	**2b**	**4a**	**3b·4a**	**1·3b·1**	74	**1·3b**	9	8.2
6		**4b**	**3b·4b**		84		8	10.5
7		**4c**	**3b·4c**		61		16	3.8
8		**1**	–		40		23	1.7
9	**2c**	**4a**	**3c·4a**	**1·3c·1**	60	**1·3c**	7	8.6
10		**4b**	**3c·4b**		47		13	3.6
11		**4c**	**3c·4c**		53		10	5.3
12		**1**	–		44		16	2.8

The intramolecular cyclisation of the reactive pseudorotaxanes **2·4·2** must compete with side reactions involving [2]rotaxane formation, intermolecular polymerisation, etc. (Figure 2). The rate of cyclisation may be explained in terms of the activation energy and the probability of end-to-end encounters. The activation energy is thought to reflect the strain energy of the formation of small and medium rings, while the ring strain of large-membered cyclic system is commonly negligible (*18*). Although the formation process of the rotaxane is too complicated to be understood in detail, the entropic contribution upon the cyclisation may rationalise the results presented here. The tethered rotaxane forms via macrocyclisation; thus, the entropic contribution, meaning the probability of end-to-end encounters, should mainly drive the reaction pathway. The probability of an end-to-end encounter generally decreases with increasing distance between the two reactive ends. Increasing the length of the linkers connecting the two crown ethers reduces the probability of the encounter of the two terminal olefins for the formation of complex **2·4·2**. The probabilities are also influenced by the flexibility of the terminal olefin. The more flexible the pseudorotaxane **2·4·2** becomes, the greater is the entropic cost

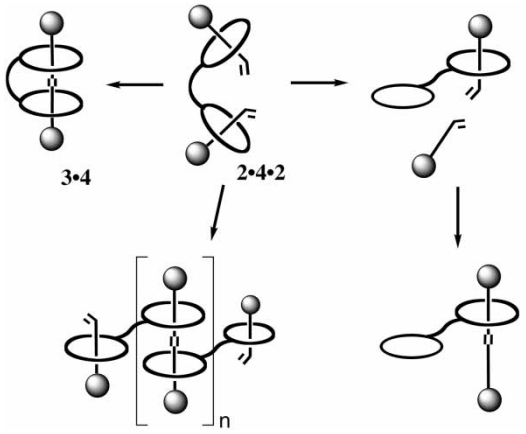


Figure 2. Schematic representation of the reaction pathway for the formation of [3]rotaxane and [2]rotaxane.

of complexation. In the series of the reaction of pseudorotaxane with **2b**, in which the [3]rotaxane was obtained in excellent yield, the most flexible pseudorotaxane **2b·4c·2b** must pay the largest entropic cost during the cyclisation; thus, the lowest yield of tethered rotaxane **3b·4c** [2] can be rationalised by the entropic contribution. However, **2b·4a·2b**, having a shorter linker, gave a lower yield of the [3]rotaxane than **2b·4b·2b** (entries 5 and 6). The macrocyclisation process may result in an increase in the steric energy of **3a·4b**, which may decrease the yield of the tethered rotaxane. This result suggests that the steric interaction between the two crown moieties cannot be negligible; in fact, [3]rotaxane **1·3a·1** was obtained with monocrown ether **1** in 21% yield (entry 4), which was lower than the yields of 40 and 44% when **2b** and **2c** were reacted with **1** (entries 8 and 12).

To estimate the steric interaction during the cyclisation of pseudorotaxanes **2·4·2**, molecular mechanics calculations of tethered rotaxanes **3·4** may be informative (*19*). Molecular mechanics calculations of tethered rotaxanes **3·4** were carried out using MacroModel V9.1. Initial geometries were generated using the Monte Carlo/low-mode search mixed method, and the structural optimisations were performed using the OPLS2005 force field with the GB/SA solvation parameters for chloroform (*19*). All of the combinations of **3a–c** and **4a–c** were calculated. A characteristic example of the calculated structures of tethered rotaxane **3b·4b** is shown in Figure 3. The ammonium salts form the hydrogen bonding interactions with the crown ethers, and the alkyl chains connecting the two crown rings adopt the extended zigzag conformation. The two aromatic rings of each crown moiety are tilted inward to reduce the unfavourable steric interactions with the two *tert*-butyl groups placed at the aromatic ring of the ammonium salt.

It is well known that the ring strain of cyclised products is closely associated with the ease of cyclisation for chain molecules (*20*); thus, the strain of the

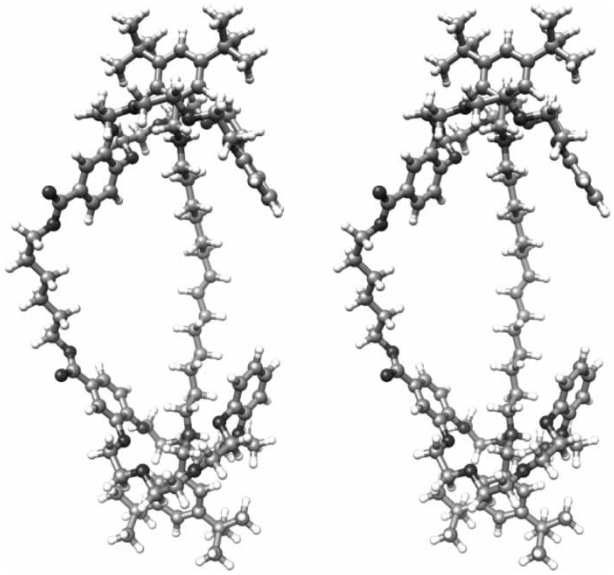


Figure 3. Stereoplot of the calculated structure of tethered rotaxane **3b·4b**.

Table 2. Calculated steric energy ΔSE[a] [kJ/mol] of tethered rotaxane **3·4** upon complexation.

	Diammonium salt		
Bis(crown ether)	**3a**	**3b**	**3c**
4a	−321.9	−328.9	−332.8
4b	−305.5	−314.5	−319.1
4c	−306.4	−310.1	−322.4

[a]The calculated values were obtained by following equation: $\Delta SE = SE_{\mathbf{3}\cdot\mathbf{4}} - (SE_{\mathbf{3}} + SE_{\mathbf{4}})$.

macrocyclic tethered rotaxanes **3·4** might govern the ease of cyclisation. The ring strain energies of **3·4** can be estimated by the steric energy differences (ΔSE) obtained from the steric energies of the tethered rotaxane **3·4**, axle **3** and bis(crown ether)s **4** (Table 2). The ΔSE gave large negative values, suggesting that all of the cyclisation processes are enthalpically favourable. Indeed, all of the cyclisation reactions of the complexes **2·4·2** produced the desired [3]rotaxane in good yields. **3a–c·4a** received the largest gain in ΔSE. Increasing the length of the tether alkyl chains of the bis(crown ether)s **4** reduced the stability of the tethered rotaxane **3·4**. These calculation results are fairly consistent with the fact that the reactions of **4a** with **2a–c** exhibited better results than the others in terms of yields of [3]rotaxanes **1·3·1**.

The cyclisation of **2·4·2** is an intramolecular process producing [3]rotaxane, whereas the intermolecular metathesis of **2·4** and **2** gives rise to [2]rotaxanes. The ratio of [3]rotaxane to [2]rotaxane may indicate the relative rate of the intra- and intermolecular processes in the cyclisation reaction of **2·4·2**; thus, the ratios (entries 1–3, 5–7 and 9–11) are greater than the values observed in the

metathesis reactions of **2·1** (entries 4, 8 and 12), perhaps suggesting that the intramolecular process is more preferable than the intermolecular processes. **3a–c·4a** provided ΔSEs of −332.8, −328.9 and −321.9 kJ/mol, while the highest ΔSEs of −305.5 and −306.4 kJ/mol resulted from **3a·4b–c**. On the basis of the large ratio of [3]rotaxane to [2]rotaxane, the cyclisation reactions of **2a–c·4a** should be favourable (entries 1–3). The ratios from the reactions of **2a·4b–c** (entries 2 and 3) are smallest and close to the control experiment (entry 4), suggesting that their cyclisation process should be unfavourable and must compete with other intermolecular processes. The ΔSEs of the formation of the tethered rotaxanes **3·4** seem to correlate with the ratios: the longer the tether of **4**, the higher the ΔSE, and the larger the decrease in the ratio. In other words, high ΔSEs should reduce the formation of the tethered rotaxanes and promote the dethreading process that increases the formation of [2]rotaxanes. Formation of the tethered rotaxane can be preferable with decreasing ΔSEs, resulting in the increase of the ratio of [3]rotaxane to [2]rotaxane. The results of the molecular mechanics calculations may explain the selective formation of [3]rotaxanes in terms of the steric factors upon macrocyclisation, even though the entropic contribution upon cyclisation cannot be quantified.

Conclusion

We have demonstrated the synthesis of [3]rotaxane using bis(crown ether)s under olefin metathesis conditions. The bis(crown ether)s are threaded by ammonium salts to form the pseudorotaxanes, in which the two terminal olefins are preorganised to accommodate the metathesis reaction. Bis(crown ether)s and ammonium salts thereby form pseudorotaxanes that show efficient reactivity to produce the tethered rotaxanes, subsequent tether cleavage of which affords [3]rotaxane in excellent yield. The formation of the tethered rotaxanes is influenced not only by the length of the tether connecting the two crown ethers but also by the flexibility of the axles. To achieve rational design of prereactive intermediates towards [3]rotaxane synthesis, enthalpic and entropic contributions must be carefully treated. This study does not perfectly rationalise the yield of [3]rotaxanes, but the molecular mechanics calculations of the tethered rotaxanes are informative for estimating their ease of cyclisation.

Experimental section

General procedures

The ^{1}H and ^{13}C NMR spectra at high field were recorded with JEOL-ECA 600, JEOL-Lambda 500 and Varian-Mercury 300 NMR spectrometers at 600, 500 and 300 MHz (^{1}H NMR), respectively, and with a JEOL-ECA 600 and Varian 700 MR NMR spectrometer at 150 and 175 MHz (^{13}C NMR), respectively. ^{1}H NMR chemical shifts (δ) are given in parts per million using the residual solvent as an internal standard. ^{13}C NMR chemical shifts (δ) are given in parts per million from internal chloroform-d ($\delta = 77.0$). The mass spectra were recorded with a JEOL JMS-SX 102A high-resolution double-focusing mass spectrometer at the Instrument Center for Chemical Analysis, Hiroshima University, and Thermo Scientific Exactive. Elemental analyses were performed on a PerkinElmer 2400 CHN elemental analyser.

All reactions were carried out under an argon atmosphere unless otherwise noted. THF was freshly distilled over sodium benzophenone. Dichloromethane was freshly distilled over CaH_2. Column chromatography was performed using Merck silica gel (70–230 mesh). All reagents were of commercial grade and were used without further purification.

3,5-Bis(1,1-dimethylethyl)-N-*5-hexen-1-yl-benzamide*

The addition of 5-hexen-1-amine (**5a**) (*15*) (100 mg, 1.01 mmol) to a solution of 3,5-di-*tert*-butylbenzoic acid (230 mg, 0.98 mmol), EDCI·HCl (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride) (300 mg, 1.56 mmol) and a catalytic amount of DMAP in dry CH_2Cl_2 (10 mL) was done at room temperature. After being refluxed for 5 h, the reaction was quenched with 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ and brine, and was dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane) to give 330 mg of amide (1.05 mmol, quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 3H), 6.07 (br, 1H), 5.82 (m, 1H), 5.03 (d, $J = 18.0$ Hz, 1H), 4.94 (d, $J = 12.8$ Hz, 1H), 3.46 (m, 2H), 2.12 (m, 2H), 1.66 (m, 2H), 1.51 (m, 2H), 1.13–1.40 (s, 18H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 151.2, 138.5, 134.5, 125.5, 120.9, 114.8, 39.9, 35.0, 33.4, 31.4, 29.2, 26.2; HRMS (ESI) *m/z* calcd for $C_{21}H_{34}NO$ 316.2635, found 316.2629 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*7-octen-1-yl-benzamide*

The addition of 7-octen-1-amine (**5b**) (*15*) (2.2 g, 17.3 mmol) to a solution of 3,5-di-*tert*-butylbenzoic acid (4.2 g, 17.9 mmol), EDCI·HCl (5.4 g, 28.2 mmol) and a catalytic amount of DMAP in dry CH_2Cl_2 (180 mL) was done at room temperature. After being refluxed for 5 h, the reaction was quenched with 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ and brine, and was dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (20% ethyl

acetate in hexane) to give 3.9 g of amide (11.4 mmol, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 3H), 6.07 (br, 1H), 5.82 (m, 1H), 5.03 (d, $J = 19.8$ Hz, 1H), 4.94 (d, $J = 11.3$ Hz, 1H), 3.46 (m, 2H), 2.12 (m, 2H), 1.66 (m, 2H), 1.42 (m, 6H), 1.34 (s, 18H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 151.2, 139.0, 134.6, 125.4, 120.9, 114.3, 40.1, 35.0, 33.7, 31.4, 31.3, 29.7, 28.8, 26.8; HRMS (ESI) *m/z* calcd for $C_{23}H_{38}NO$ 344.2948, found 344.2939 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*9-decen-1-yl-benzamide*

The addition of 9-decen-1-amine (**5c**) (*15*) (1.8 g, 11.6 mmol) to a solution of 3,5-di-*tert*-butylbenzoic acid (2.7 g, 11.5 mmol), EDCI·HCl (3.5 g, 18.3 mmol) and a catalytic amount of DMAP in dry CH_2Cl_2 (100 mL) was done at room temperature. After being refluxed for 5 h, the reaction was quenched with 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ and brine, and was dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (20% ethyl acetate in hexane) to give 3.5 g of amide (9.42 mmol, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (s, 3H), 6.07 (br, 1H), 5.81 (m, 1H), 4.99 (d, $J = 17.3$ Hz, 1H), 4.92 (d, $J = 10.2$ Hz, 1H), 3.42 (m, 2H), 2.03 (m, 2H), 1.60 (m, 2H), 1.27–1.41 (m, 28H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 151.2, 139.1, 134.6, 125.4, 120.9, 114.1, 40.1, 35.0, 33.8, 31.4, 29.8, 29.4, 29.3, 29.0, 28.9, 27.0; HRMS (ESI) *m/z* calcd for $C_{25}H_{42}NO$ 372.3261, found 372.3252 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*5-hexen-1-yl-benzenemethanamine (**6a**)*

$LiAlH_4$ (0.25 g, 6.59 mmol) was carefully added to a solution of 3,5-bis(1,1-dimethylethyl)-*N*-5-hexen-1-yl-benzamide (1.9 g, 6.02 mmol) in dry THF (60 mL) at 0°C. After being refluxed for 3 h, the reaction was quenched with saturated aqueous Na_2SO_4, and the resulting precipitate was filtrated off. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (5% methanol in $CHCl_3$) to give 1.8 g of amine **6a** (5.97 mmol, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (t, $J = 1.8$ Hz, 1H), 7.15 (d, $J = 1.8$ Hz, 2H), 5.80 (m, 1H), 4.99 (d, $J = 18.3$ Hz, 1H), 4.94 (d, $J = 12.0$ Hz, 1H), 3.78 (s, 2H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.69 (m, 2H), 1.48 (m, 2H), 1.41 (m, 2H), 1.33 (s, 18H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.7, 139.5, 138.8, 122.3, 120.9, 114.4, 54.7, 49.5, 34.8, 33.6, 31.5, 29.5, 26.7; HRMS (ESI) *m/z* calcd for $C_{21}H_{36}N$ 302.2842, found 302.2835 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*7-octen-1-yl-benzenemethanamine (**6b**)*

$LiAlH_4$ (0.5 g, 13.2 mmol) was carefully added to a solution of 3,5-bis(1,1-dimethylethyl)-*N*-7-octen-1-yl-benzamide (3.9 g, 11.4 mmol) in dry THF (100 mL), at 0°C. After being refluxed for 3 h, the reaction was quenched with saturated aqueous Na_2SO_4, and the resulting precipitate was filtrated off. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel ($CHCl_3$) to give 2.6 g of amine **6b** (7.9 mmol, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.19 (s, 2H), 5.75 (m, 1H), 4.99 (d, $J = 19.2$ Hz, 1H), 4.91 (d, $J = 11.1$ Hz, 1H), 3.84 (br, 2H), 2.66 (br, 2H), 1.99 (m, 2H), 1.54 (m, 2H), 1.10–1.312 (m, 24H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.7, 139.4, 139.1, 122.3, 120.9, 114.2, 54.7, 49.6, 34.8, 33.7, 31.5, 29.9, 29.0, 28.8, 27.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{40}N$ 330.3155, found 330.3145 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*9-decen-1-yl-benzenemethanamine (**6c**)*

$LiAlH_4$ (0.37 g, 9.75 mmol) was carefully added to a solution of 3,5-bis(1,1-dimethylethyl)-*N*-9-decen-1-yl-benzamide (3.3 g, 8.88 mmol) in dry THF (90 mL) at 0°C. After being refluxed for 3 h, the reaction was quenched with saturated aqueous Na_2SO_4, and the resulting precipitate was filtrated off. The filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (5% methanol in CH_2Cl_2) to give 3.0 g of amine **6c** (8.39 mmol, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, $J = 1.8$ Hz, 1H), 7.15 (s, 2H), 5.81 (m, 1H), 4.98 (d, $J = 18.0$ Hz, 1H), 4.93 (d, $J = 10.8$ Hz, 1H), 3.77 (s, 2H), 2.65 (t, $J = 6.8$ Hz, 2H), 2.02 (m, 2H), 1.57 (m, 2H), 1.11–1.39 (m, 28H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 150.7, 139.2, 122.3, 121.0, 114.1, 54.6, 49.6, 34.8, 33.8, 31.5, 29.9, 29.5, 29.4, 29.1, 28.9, 27.4; HRMS (ESI) *m/z* calcd for $C_{25}H_{44}N$ 358.3168, found 358.3457 $[M + H]^+$.

3,5-Bis(1,1-dimethylethyl)-N-*7-octen-1-yl-benzenemethanammonium hexafluorophosphate (**2b**)*

Concentrated HCl was added dropwise to a solution of amine **6b** (1.9 g, 5.8 mmol) in methanol (25 mL) until the resulting solution was of pH 2. After being stirred for 2 h, evaporation of the solvents produced a white solid that was dissolved in acetone (25 mL). Excess NH_4PF_6 was added to the solution. The solvent was removed *in vacuo*, and the residue was dissolved by hot water and then cooled to room temperature. The precipitated white solid was collected by filtration to give ammonium salt **2b** (2.5 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, $J = 2.4$ Hz, 1H), 7.25 (s, 2H), 6.72 (br, 2H), 5.72 (m, 1H), 4.94 (d, $J = 17.1$ Hz, 1H), 4.90 (d, $J = 10.2$ Hz, 1H), 4.24 (s, 2H),

2.95 (m, 2H), 1.98 (m, 2H), 1.73 (m, 2H), 1.24–1.33 (m, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.5, 138.6, 128.2, 124.1, 114.5, 52.8, 46.9, 34.9, 33.4, 31.3, 28.4, 28.2, 25.9, 25.7; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{23}H_{40}N$ 330.3151, found 330.3161 $[M - PF_6]^+$; elemental analysis calcd (%) for $C_{23}H_{40}F_6NP \cdot$acetone: C 58.52, H 8.69, N 2.62. Found: C 58.69, H 9.08, N 2.89.

3,5-Bis(1,1-dimethylethyl)-N-*5-hexen-1-yl-benzenemethanammonium hexafluorophosphate (**2a**)*

Following the procedure for preparation of **2b**, 1.8 g of **2a** (4.02 mmol, 93%) was obtained from **6a** (1.3 g, 4.31 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, $J = 1.8$ Hz, 1H), 7.24 (d, $J = 1.8$ Hz, 2H), 6.49 (br, 2H), 5.70 (m, 1H), 4.95 (d, $J = 17.4$ Hz, 1H), 4.93 (d, $J = 9.8$ Hz, 1H), 4.23 (s, 2H), 2.99 (t, $J = 7.8$ Hz, 2H), 1.86 (m, 2H), 1.72 (m, 2H), 1.47 (m, 2H), 1.32 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.7, 137.2, 128.1, 124.3, 124.0, 115.6, 53.0, 46.9, 34.9, 32.7, 31.2, 25.1, 25.1; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{21}H_{36}N$ 302.2842, found 302.2873 $[M - PF_6]^+$; elemental analysis calcd (%) for $C_{21}H_{36}F_6NP \cdot$acetone: C 56.37, H 8.11, N 3.13. Found: C 56.73, H 8.31, N 2.97.

3,5-Bis(1,1-dimethylethyl)-N-*9-decen-1-yl-benzenemethanammonium hexafluorophosphate (**2c**)*

Following the procedure for preparation of **2b**, 3.8 g of **2c** (7.55 mmol, >99%) was obtained from **6c** (2.7 g, 7.55 mmol). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, $J = 1.5$ Hz, 1H), 7.24 (d, $J = 1.5$ Hz, 2H), 6.60 (br, 2H), 5.78 (m, 1H), 4.96 (d, $J = 17.8$ Hz, 1H), 4.91 (d, $J = 11.6$ Hz, 1H), 4.25 (s, 2H), 2.97 (m, 2H), 2.00 (t, $J = 7.2$ Hz, 2H), 1.70 (m, 2H), 1.24–1.35 (m, 28H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6, 139.0, 128.2, 124.2, 124.1, 114.2, 52.9, 47.1, 43.9, 34.9, 33.7, 31.3, 29.0, 28.8, 28.8, 26.0, 25.7; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{25}H_{44}N$ 358.3468, found 358.3502 $[M - PF_6]^+$; elemental analysis calcd (%) for $C_{25}H_{44}F_6NP \cdot$acetone: C 59.88, H 8.97, N 2.49. Found: C 59.42, H 9.41, N 2.71.

*Synthesis of bis(crown ether) **4a***

The addition of 1,4-butanediol (22 mg, 0.24 mmol) to a solution of 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenz[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosin-2-carboxylic acid (**7**) (250 mg, 0.51 mmol), EDCI·HCl (240 mg, 1.25 mmol) and a catalytic amount of DMAP in dry CH_2Cl_2 (2 mL) was done at room temperature. After stirring for 5 h, the reaction mixture was poured into ice-cooled 1 M HCl and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ and brine, and was dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (5% MeOH in $CHCl_3$) to give 240 mg of **4a** (0.23 mmol, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.9$ Hz, 2H), 7.52 (s, 2H), 6.88–6.83 (m, 10H), 4.36 (brs, 4H), 4.30–4.10 (m, 16H), 4.02–3.79 (m, 32H), 1.91 (brs, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2, 152.9, 148.8, 148.2, 123.8, 122.9, 121.4, 114.3, 114.0, 112.0, 71.4, 71.3, 71.2, 69.9, 69.7, 69.6, 69.5, 69.4, 69.3, 69.2, 25.6; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{54}H_{71}O_{20}$ 1039.4539, found 1039.4515 $[M + H]^+$; element analysis calcd (%) for $C_{54}H_{70}O_{20} \cdot H_2O$: C 61.35, H 6.86. Found: C 61.30, H 6.65.

*Synthesis of bis(crown ether) **4b***

Following the procedure for preparation of **4a**, **7** (250 mg, 0.41 mmol), EDCI·HCl (240 mg, 0.90 mmol), 1,6-hexanediol (22 mg, 0.19 mmol) and a catalytic amount of DMAP were reacted in dry CH_2Cl_2 (2 mL). Purification by column chromatography (SiO_2) with 19:1 $CHCl_3$/MeOH gave 170 mg of **4b** (0.16 mmol, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.52 (s, 2H), 6.99–6.82 (m, 10H), 4.29 (t, $J = 3.4$ Hz, 4H), 4.26–4.10 (m, 16H), 4.07–3.69 (m, 32H), 1.90–1.75 (m, 4H), 1.61–1.45 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 152.8, 148.9, 148.2, 123.8, 123.1, 121.4, 114.4, 114.0, 112.0, 71.5, 71.4, 71.3, 69.9, 69.8, 69.6, 69.5, 69.4, 69.3, 69.2, 28.7, 25.8; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{56}H_{75}O_{20}$ 1067.4852, found 1067.4861 $[M + H]^+$; elemental analysis calcd (%) for $C_{56}H_{74}O_{20} \cdot H_2O$: C 61.98, H 7.06. Found: C 61.83, H 7.03.

*Synthesis of bis(crown ether) **4c***

Following the procedure for preparation of **4a**, **7** (350 mg, 0.71 mmol), EDCI·HCl (335 mg, 1.75 mmol), 1,8-octanediol (51 mg, 0.35 mmol) and a catalytic amount of DMAP were reacted in dry CH_2Cl_2 (2 mL). Purification by column chromatography (SiO_2) with 19:1 $CHCl_3$/MeOH gave 320 mg of **4c** (0.29 mmol, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.52 (s, 2H), 6.94–6.80 (m, 10H), 4.27 (t, $J = 6.6$ Hz, 4H), 4.24–4.10 (m, 16H), 4.00–3.77 (m, 32H), 1.80–1.71 (m, 4H), 1.49–1.35 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 152.8, 148.9, 148.2, 123.8, 123.2, 121.4, 114.4, 114.0, 112.0, 71.4, 71.3, 71.2, 69.9, 69.8, 69.6, 69.5, 69.4, 69.3, 69.2, 29.2, 28.7, 25.9; HRMS (FAB, NBA matrix) *m/z* calcd for $C_{58}H_{79}O_{20}$ 1095.5165, found 1095.5165 $[M + H]^+$; elemental analysis calcd (%) for $C_{58}H_{78}O_{20} \cdot H_2O$: C 62.58, H 7.24. Found: C 62.22, H 7.24.

*General procedure for synthesis of [3]rotaxane **1·3·1***

A solution of ammonium salt **2** (0.1 mmol) and bis(crown ether) **4** (0.05 mmol) in dry CH_2Cl_2 (2 mL) was stirred for

30 min in a sealed tube. Second-generation Grubbs catalyst was added to the solution. After being stirred for 5 h at 50°C, the reaction mixture was passed through a silica gel pad (10% methanol in $CHCl_3$). The solvent was removed, and a brownish solid was obtained.

The solid was treated with KOMe in dry methanol at 50°C for 12 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4. After removing Na_2SO_4 by filtration, the solvent was concentrated *in vacuo*. The crude product was purified by GPC ($CHCl_3$) to give [3]rotaxane **1·3·1** and [2]rotaxane **1·3**.

*[3]Rotaxane **1·3b·1***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (brs, 2H), 7.52 (s, 2H), 7.32 (s, 2H), 7.28 (s, 4H), 7.18 (br, 4H), 6.95 (brs, 2H), 6.89 (brs, 8H), 5.19 (m, 2H), 4.62 (m, 4H), 4.01–4.32 (m, 16H), 3.36–3.97 (m, 38H), 3.20 (brs, 4H), 1.74 (m, 4H), 1.22–1.46 (m, 8H), 1.18 (s, 36H), 0.89–1.09 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 151.5, 151.2, 147.0, 131.4, 124.1, 123.8, 123.1, 121.7, 113.2, 112.5, 111.7, 70.5, 70.45, 70.4, 69.9, 69.7, 68.3, 68.2, 68.1, 52.6, 51.9, 48.9, 34.6, 32.1, 31.8, 31.2, 28.9, 28.5, 28.2, 26.2, 26.1, 25.7; HRMS (ESI) *m/z* calcd for $C_{96}H_{144}N_2O_{20}$ 822.5155, found 822.5132 $[M - 2PF_6]^{2+}/2$.

*[2]Rotaxane **1·3b***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, $J = 6.9$ Hz, 1H), 7.53 (s, 1H), 7.40 (m, 2H), 7.34 (br, 2H), 7.17 (br, 4H), 6.82–6.98 (br, 5H), 5.25 (m, 2H), 4.61 (m, 2H), 4.00–4.33 (m, 10H), 3.34–3.95 (m, 19H), 2.92–3.25 (br, 4H), 1.56–2.07 (m, 8H), 1.29 (brs, 18H), 1.19 (brs, 18H), 0.77–1.45 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 151.9, 151.6, 151.4, 147.2, 141.6, 131.5, 124.5, 124.4, 124.3, 123.3, 121.9, 113.4, 112.7, 111.9, 70.7, 70.6, 70.0, 69.9, 68.5, 68.4, 68.2, 52.8, 52.1, 49.1, 34.9, 34.8, 31.3, 29.7, 26.2; HRMS (ESI) *m/z* calcd for $C_{70}H_{110}N_2O_{10}$ 569.4075, found 569.4061 $[M - 2PF_6]^{2+}/2$.

*[3]Rotaxane **1·3a·1***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, $J = 8.2$ Hz, 2H), 7.49 (s, 2H), 7.28 (s, 2H), 7.23 (s, 4H), 7.18 (br, 4H), 6.92 (d, $J = 8.9$ Hz, 2H), 6.86 (s, 8H), 4.97 (m, 2H), 4.60 (m, 4H), 4.00–4.41 (m, 16H), 3.36–4.00 (m, 38H), 3.19 (brs, 4H), 1.69 (m, 4H), 1.38 (m, 4H), 1.16 (s, 36H), 1.07 (m, 4H); HRMS (ESI) *m/z* calcd for $C_{92}H_{136}N_2O_{20}$ 794.4838, found 794.4816 $[M - 2PF_6]^{2+}/2$.

*[2]Rotaxane **1·3a***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, $J = 8.2$ Hz, 1H), 7.54 (s, 1H), 7.43 (m, 2H), 7.34 (br, 4H), 7.18 (br, 4H), 6.72–7.05 (m, 5H), 5.32 (m, 2H), 4.61 (brs, 2H), 4.00–4.42 (m, 10H), 3.31–4.00 (m, 19H), 3.02–3.30 (br, 4H), 1.56–2.08 (m, 4H), 1.31 (m, 4H), 1.30 (brs, 18H), 1.19 (brs, 18H), 1.08 (m, 4H); HRMS (ESI) *m/z* calcd for $C_{66}H_{102}N_2O_{10}$ 541.3762, found 541.3773 $[M - 2PF_6]^{2+}/2$.

*[3]Rotaxane **1·3c·1***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.52 (s, 2H), 7.32 (s, 2H), 7.25 (s, 4H), 7.16 (br, 4H), 6.94 (d, $J = 8.9$ Hz, 2H), 6.89 (brs, 8H), 5.32 (m, 2H), 4.61 (m, 4H), 4.01–4.33 (m, 16H), 3.38–3.97 (m, 38H), 3.18 (brs, 4H), 1.85 (m, 4H), 1.36 (brs, 4H), 1.18 (s, 36H), 1.05–1.32 (m, 8H), 0.99 (brs, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 151.5, 151.3, 149.6, 147.2, 131.5, 124.2, 123.9, 123.6, 123.1, 121.8, 113.3, 112.6, 112.5, 111.8, 70.6, 70.5, 70.4, 70.0, 69.8, 68.4, 68.3, 68.2, 68.1, 52.7, 51.9, 49.0, 34.7, 32.3, 31.2, 29.4, 29.0, 28.8, 28.6, 26.3, 26.1; HRMS (ESI) *m/z* calcd for $C_{100}H_{152}N_2O_{20}$ 850.5464, found 850.5478 $[M - 2PF_6]^{2+}/2$.

*[2]Rotaxane **1·3c***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (br, 1H), 7.52 (br, 1H), 7.38 (br, 2H), 7.34 (br, 4H), 7.16 (br, 4H), 6.83–7.10 (br, 5H), 5.32 (m, 2H), 4.61 (m, 2H), 4.01–4.33 (m, 10H), 3.38–3.97 (m, 19H), 2.97–3.37 (br, 4H), 1.70–2.16 (m, 4H), 1.27 (brs, 18H), 1.19 (brs, 18H), 0.80–1.67 (br, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 151.7, 151.5, 147.1, 141.5, 131.4, 124.3, 123.9, 123.3, 123.2, 121.9, 113.3, 112.6, 111.8, 70.6, 70.5, 70.0, 69.9, 68.5, 68.4, 68.2, 52.7, 52.0, 49.0, 34.8, 34.7, 32.4, 31.3, 31.2, 29.6, 29.3, 28.9, 28.8, 26.3, 25.9; HRMS (ESI) *m/z* calcd for $C_{74}H_{118}N_2O_{10}$ 597.4388, found 597.4365 $[M - 2PF_6]^{2+}/2$.

*General procedure for synthesis of tethered rotaxane **3b·4***

A solution of ammonium salt **2b** (0.1 mmol) and bis(crown ether) **4** (0.05 mmol) in dry CH_2Cl_2 (2 mL) was stirred for 30 min in a sealed tube. Second-generation Grubbs catalyst was added to the solution. After being stirred for 5 h at 50°C, the reaction mixture was passed through a silica gel pad (10% methanol in $CHCl_3$). The solvent was removed, and the residue was purified by GPC ($CHCl_3$) to give tethered rotaxane **3b·4**.

*Tethered rotaxane **3b·4a***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.67 (m, 2H), 7.60–7.55 (m, 2H), 7.41 (br s, 2H), 7.38 (br s, 4H), 7.20–7.08 (br, 4H), 7.06–7.01 (m, 2H), 6.91 (br s, 8H), 5.12–4.98 (m, 2H), 4.61 (br s, 4H), 4.50–4.27 (m, 8H), 4.26–4.02 (m, 12H), 3.94–3.68 (m, 16H), 3.61 (br s, 8H), 3.43–3.23 (m, 8H), 3.12–2.98 (m, 4H), 1.91 (br s, 4H), 1.67–1.46 (m, 4H), 1.26 (br s, 40H), 0.90–0.71 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 151.5, 151.4, 147.5, 147.1, 131,7, 129.9, 124.55, 124.47, 124.2, 123.5, 123.3, 121.9,

113.3, 112.9, 112.1, 70.6, 70.5, 70.0, 69.8, 69.6, 68.7, 68.6, 68.3, 64.9, 64.8, 64.6, 52.7, 49.1, 34.8, 32.03, 31.99, 31.7, 31.35, 31.28, 31.23, 29.0, 28.9, 28.12, 28.08, 26.3, 26.2, 26.0, 25.6; HRMS (ESI) *m/z* calcd for $C_{98}H_{146}N_2O_{20}$ 835.5235, found 835.5203 $[M - 2PF_6]^{2+}/2$.

*Tethered rotaxane **3b·4b***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.67 (m, 2H), 7.60–7.53 (m, 2H), 7.41 (br s, 2H), 7.38 (br s, 4H), 7.20–7.11 (br, 4H), 7.05–6.99 (m, 2H), 6.91 (br s, 8H), 5.20–5.02 (m, 2H), 4.62 (br s, 4H), 4.50–4.05 (m, 20H), 3.96–3.70 (m, 16H), 3.62 (br s, 8H), 3.46–3.28 (m, 8H), 3.12–2.99 (m, 4H), 1.77 (br s, 4H), 1.70–1.46 (m, 8H), 1.26 (br s, 40H), 0.90–0.72 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 152.9, 151.6, 151.3, 148.9, 147.2, 131.6, 124.2, 124.0, 123.5, 123.2, 121.8, 121.5, 114.1, 113.2, 112.6, 71.3, 70.7, 70.1, 69.9, 69.6, 69.4, 69.2, 68.5, 68.2, 64.9, 64.7, 52.8, 49.2, 34.7, 31.9, 31.3, 28.7, 26.4, 26.2, 25.7; HRMS (ESI) *m/z* calcd for $C_{100}H_{150}N_2O_{20}$ 849.5364, found 849.5383 $[M - 2PF_6]^{2+}/2$.

*Tethered rotaxane **3b·4c***

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72–7.65 (m, 2H), 7.58–7.53 (m, 2H), 7.41 (br s, 2H), 7.38 (br s, 4H), 7.21–7.10 (br, 4H), 7.04–7.00 (m, 2H), 6.91 (br s, 8H), 5.20–4.98 (m, 2H), 4.62 (br s, 4H), 4.48–4.04 (m, 20H), 3.95–3.70 (m, 16H), 3.61 (br s, 8H), 3.40–3.28 (m, 8H), 3.10–2.98 (m, 4H), 1.74 (br s, 4H), 1.74–1.52 (m, 4H), 1.46–1.33 (m, 8H), 1.26 (br s, 36H), 0.98–0.74 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 151.4, 149.7, 147.4, 147.1, 135.9, 131.7, 129.9, 129.5, 124.4, 124.3, 124.2, 123.7, 123.3, 121.9, 113.3, 113.0, 112.9, 112.1, 70.59, 70.51, 70.46, 70.0, 69.8, 69.6, 68.7, 68.6, 68.3, 64.9, 64.9, 52.7, 49.1, 34.8, 32.2, 31.9, 31.4, 31.3, 29.1, 29.0, 28.93, 28.85, 28.7, 28.5, 28.2, 26.3, 26.2, 26.11, 26.07, 25.9, 25.8, 25.7; HRMS (ESI) *m/z* calcd for $C_{102}H_{154}N_2O_{20}$ 863.5548, found 863.5526 $[M - 2PF_6]^{2+}/2$.

Determination of the association constant

Determination of the association constant for crown ether **1** and axle precursor **2b** was carried out using a ^{1}H NMR titration technique in dichloromethane-d2. The complex of **1** with **2b** at 25°C was in slow exchange on the NMR timescale and displayed well-resolved signals for the free and bound forms. The relative intensities of the protons of free and bound **2b**, along with the known concentrations of **1** and **2b**, were used to determine an association constant (K_a) at 25°C, 5800 ± 1200.

Molecular modelling

Molecular mechanics calculations on the tethered rotaxanes were performed with the MacroModel V9.1 program package. Ten thousand initial geometries were generated by a low-mode and Monte Carlo mixed search option, and the given geometries were optimised by a conjugate gradient energy minimisation using the OPLS2005 force field with the GB/SA solvation parameters for $CHCl_3$.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research for Young Scientists (B) (No. 19750035) from the Japan Society for the Promotion of Science (JSPS). We are grateful to the Izumi Science and Technology Foundation, the Electric Technology Research Foundation of Chugoku, the Kinki-chiho Hatsumei Center, the JGC-S Scholarship Foundation and the Uchida Energy Science Promotion Foundation for financial support.

Notes

1. [3]Rotaxane **1·3b·1** is formed by the homo coupling reaction of complexed form **1·2b**; thus, on probability theory and statistics, the theoretical yield (88%) of [3]rotaxane **1·3b·1** can be estimated from the square of the statistical distributions (94%) of complexed form **1·2b**. [2]Rotaxane **1·3b** is formed by the coupling reaction between complexed form **1·2b** and uncomplexed form **2b**; thus, the theoretical yield (11%) of [2]rotaxane **1·3b** can be estimated from twice as much as the product of the statistical distributions (94%) of complexed form **1·2b** and those (6%) of uncomplexed form **2b**.
2. Isolated yields of tethered rotaxane **3b·4a-c** are 54%, 61%, and 47%, respectively. The yield of the tethered rotaxanes **3b·4a-c** might be reduced during the purification process.
3. The olefin geometries of the [3]- and [2]rotaxanes, newly formed through olefin metathesis reaction, were not determined.

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