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Effects of Axle-Core, Macrocycle, and Side-Station Structures on the Threading and Hydrolysis Processes of Imine-Bridged Rotaxanes

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Abstract: Imine-bridged rotaxanes are a new type of rotaxane in which the axle and macrocyclic ring are connected by imine bonds. We have previously reported that in imine-bridged rotaxane **5**, the shuttling motion of the macrocycle could be controlled by changing the temperature. In this study, we investigated how the axle and macrocycle structures affect the construction of the imine-bridged rotaxane as well as the dynamic equilibrium between imine-bridged rotaxane **5** and [2]rotaxane **7** by using various combinations of axles (**1A**,**B**), macrocycles (**2a–e**), and side-stations (XYL and TEG). In the threading process, the flexibility of the macrocycle and the substituent groups at the *para* position of the aniline moieties affect the preparation of the threaded imines. The size of the imine-bridging station and the macrocyclic tether affects the hydrolysis of the imine bonds under acidic conditions.

Keywords: hydrolysis · imines · molecular devices · rotaxanes · supramolecular chemistry

Introduction

Over the past two decades interlocked molecules have been developed for use in molecular devices and materials.[1] In particular, numerous rotaxanes and catenanes, which change their shape and properties in response to external stimuli such as a change in pH,[2,3] a change in the redox status,[4–7] and irradiation with UV/Vis light,[8–10] have been designed and prepared. For the effective generation of these molecules, noncovalent interactions, such as hydrogen bonding,[2,5,9,11] donor–acceptor interactions,[4,8] anion recognition,[12] metal coordination,[7,13] hydrophobic interactions,[3,6,10,14] as well as covalent bond formation,[15,16] have been used as the synthetic template. However, the range of combinations is limited by the structure of the interacting site because these noncovalent interactions are too particular to allow structural variation, especially with regard to the distance and geometry between the interaction sites.

We previously reported a novel rotaxane synthesis in which linking of the axle and the ring moieties was achieved through imine bonds.[16–18] These bridged rotaxanes could be readily obtained by threading an axle molecule with diformyl groups into a macrocyclic diamine, thus enabling imine bonds to be formed between the axle and macrocycle molecules, and then attaching end-cap groups. A unique temperature-dependent shuttling motion was observed when these imine-bridged rotaxanes were converted into unbridged [2]rotaxanes by cleavage/reformation of the imine bonds under acidic conditions.

This successful example relies on the matching of the geometries of the axle and the ring. In addition to exploring how to exploit the generality of the imine-directed threading methodology, it is also important that we study the size and flexibility of the axle and ring. We should also determine the effect of the substituent on the macrocycle, which can stabilize/destabilize the imine bridge through electronic effects. We report herein the preparation of a series of imine-bridged rotaxanes from the newly prepared hexahydropyrene axle **1B** and macrocycles **2c–e**, along with their behavior under acidic hydrolytic conditions. The core structures of the newly prepared assemblies were designed so that they are bulkier than those based on the hydrindacene axle **1A**.[16a,b] Some of the new macrocycles were designed to have an electron-donating/withdrawing substituent (**2c**: 4-methoxyphenyl; **2d**: 4-methoxycarbonylphenyl) at the *para* position of the aniline moiety. The size of the inner cavity of the macrocycle can be modified by altering the length and flexibility of the tether units that connect the two aniline moieties (**2a**: hexadiyne;[16a] **2b–d**: hexamethylene; **2e**: *m*-xylylene; Scheme 1).

By comparing the threading and hydrolyzing behaviors of these molecules with those of a previous example based on

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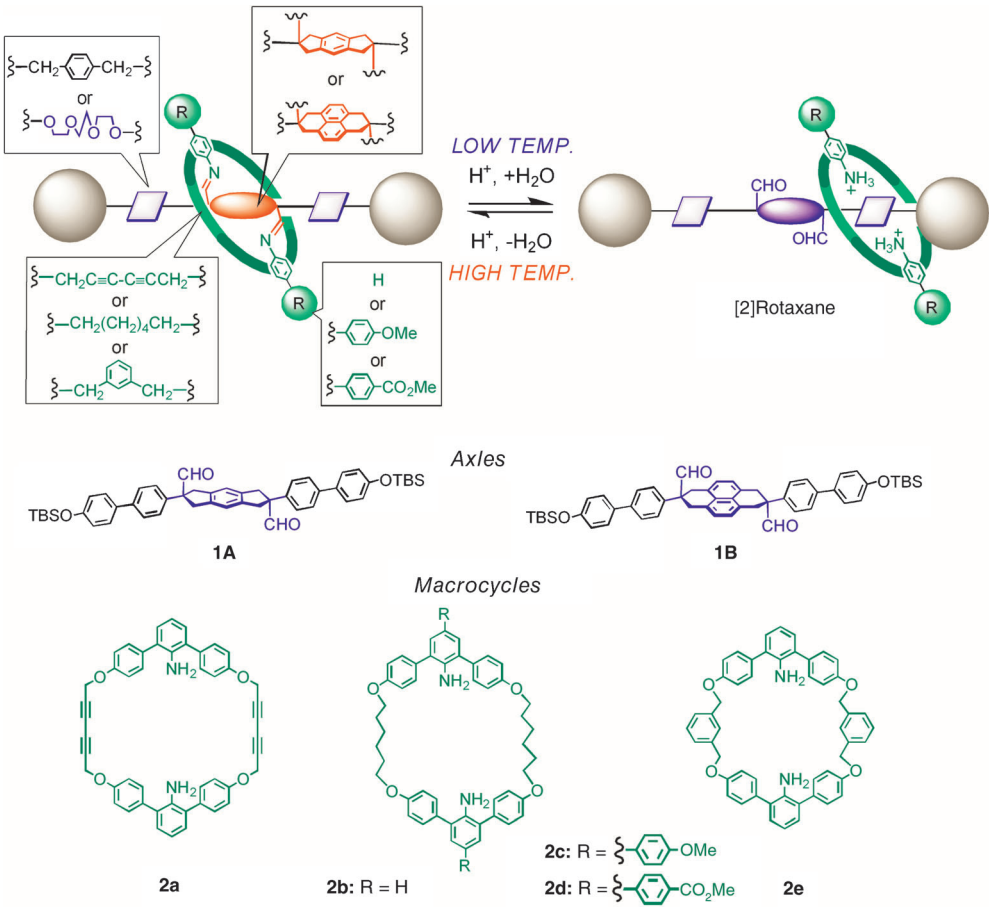


Scheme 1. Structures of the axles **1A**,**B** and macrocycles **2a–e**.

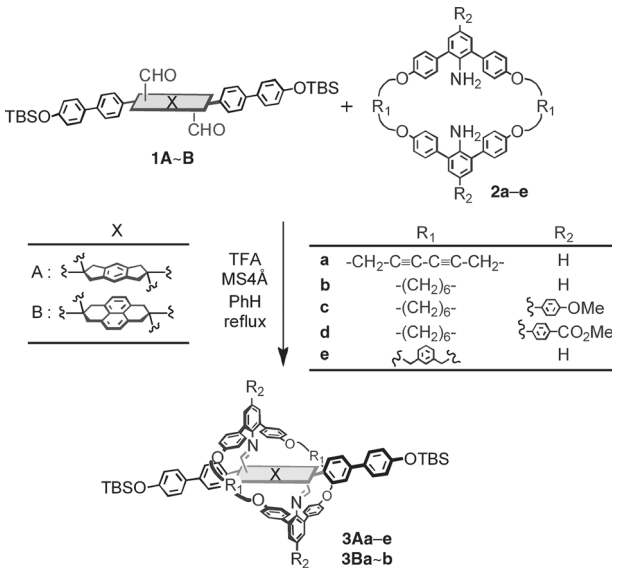
the hydrindacene unit, we report herein on the general applicability of our method for preparing rotaxanes and the scope and limitation for effective switching.

Results and Discussion

Effects of the axle and macrocycle structures on the threading process: The effects of the core structure of the axles were investigated with regard to their effects on the threading process. Threaded imines **3Aa–e** and **3Ba**,**b** were prepared by threading and the formation of an imine bond between the axle **1A** or **1B** and macrocycles **2a–e** under acidic dehydrating conditions, that is, in benzene at reflux with 4 Å MS by the addition of trifluoroacetic acid (TFA; Scheme 2).

X-ray analyses of imines **3Aa′** and **3Ab′** with a bromo-terminated hydrindacene unit unambiguously revealed that the hydrindacene axle passes through the macrocycle to create C_i-symmetric **3Aa′** or **3Ab′** (Figure 1).

As shown in Table 1, the yields of the threaded imines **3Aa**,**b** or **3Ba**,**b** prepared from axles **1A** and **1B** are dependent on the macrocycle structure rather than the axle structure, which shows that the efficiency of threading is similar for both rigid (**2a**)[16a] and flexible macrocycles (**2b**).[16a,b] The formation of an imine bond between the axle **1A** and the macrocycle **2e**, which has a smaller cavity than **2a** or **2b**, also proceeded under similar conditions. These results seem to demonstrate that an imine-directed threading



Scheme 2. Synthesis of threaded imines **3**.

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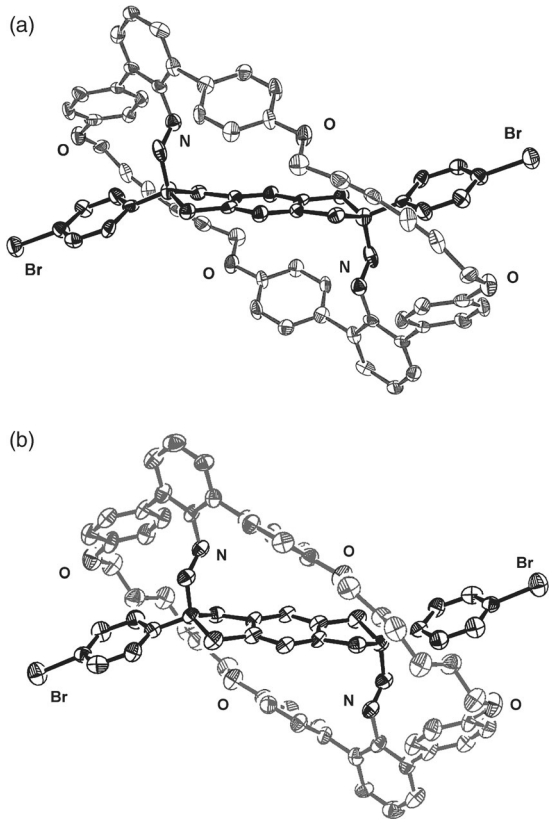


Figure 1. X-ray structures of bromo-terminated threaded imines **3Aa′**[16a] and **3Ab′**. Hydrogen atoms and solvents have been omitted for clarity.

Table 1. Isolated yields of threaded imines **3**.

Axle	Macrocycle		Isolated yields [%]
1A	**2a**	**3Aa**	95
	2b	**3Ab**	46
	2c	**3Ac**	64
	2d	**3Ad**	31
	2e	**3Ae**	50
1B	**2a**	**3Ba**	80
	2b	**3Bb**	52

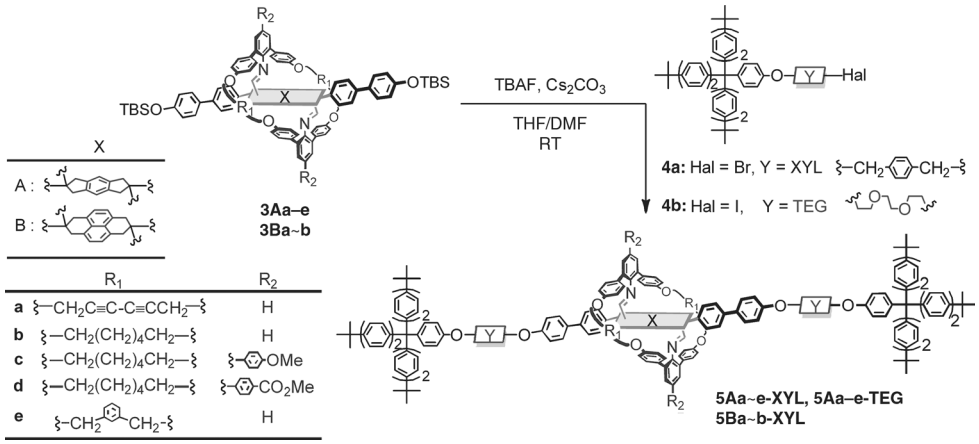
method for the synthesis of rotaxane-type structures is generally applicable to macrocycles with cavities of different sizes and axles with core structures that differ with regard to bulkiness.

Next, the electronic effects of the substituents at the *para* position of the aniline moieties were investigated.[19] Macrocycles **2c**,**d** have electron-donating (4-methoxyphenyl: **2c**) and -withdrawing (4-methoxycarbonylphenyl: **2d**) moieties at this position, respectively. The higher yield of the threaded form **3Ac** suggests that an electron-donating group at the *para* position of the aniline moieties favors imine-bond formation. Thus, electronic effects of the substituent at this position can be considered to promote efficient imine-directed threading by favoring the formation of imine bonds.

When threaded imines **3Aa–e** and **3Ba**,**b** were subjected to hydrolysis, the corresponding axles **1** and macrocycles **2** were both recovered quantitatively, which confirms the reversible formation/cleavage of the imine bonds in **3**. Before we studied the generation of [2]rotaxane **7**, the imines **3** were converted into the imine-bridged rotaxanes **5** by attaching end-cap units **4a**[16] (XYL) or **4b**[16b] (TEG). Imine-bridged rotaxane **5Aa**,**b-XYL** and **5Aa–e-TEG** with a hydrindacene core **A** and **5Ba**,**b-XYL** with a hexahydropyrene core **B** were prepared by attaching the end-cap units beyond the xylylenyl (XYL) or triethylene glycolyl (TEG) side-stations in the corresponding threaded imines **3Aa–e** and **3Ba**,**b** (Scheme 3).

Effects of structure on the hydrolysis process: We investigated the effect of structure on the conversion of imine-bridged rotaxanes **5** into [2]rotaxanes **7** under acidic hydrolytic conditions (Scheme 4).

As previously reported, when TFA was added to a solution of **5Ab-XYL** in $CDCl_3$, a mixture of hydrolyzed [2]rotaxane $[\mathbf{7Ab\text{-}XYL}\cdot 2H]^{2+}$, mono-imine $[\mathbf{6Ab\text{-}XYL}\cdot H]^{+}$, and the starting diimine **5Ab-XYL** were obtained, the diimine being the major species in the equilibrated mixture. These three species were observed as independent components, and thus their rate of interconversion in this hydrolytic equilibrium is slower than the NMR timescale. The equilibrium



Scheme 3. Introduction of end-cap units **4a** and **4b** onto the threaded imines **3Aa–e** and **3Ba**,**b**.

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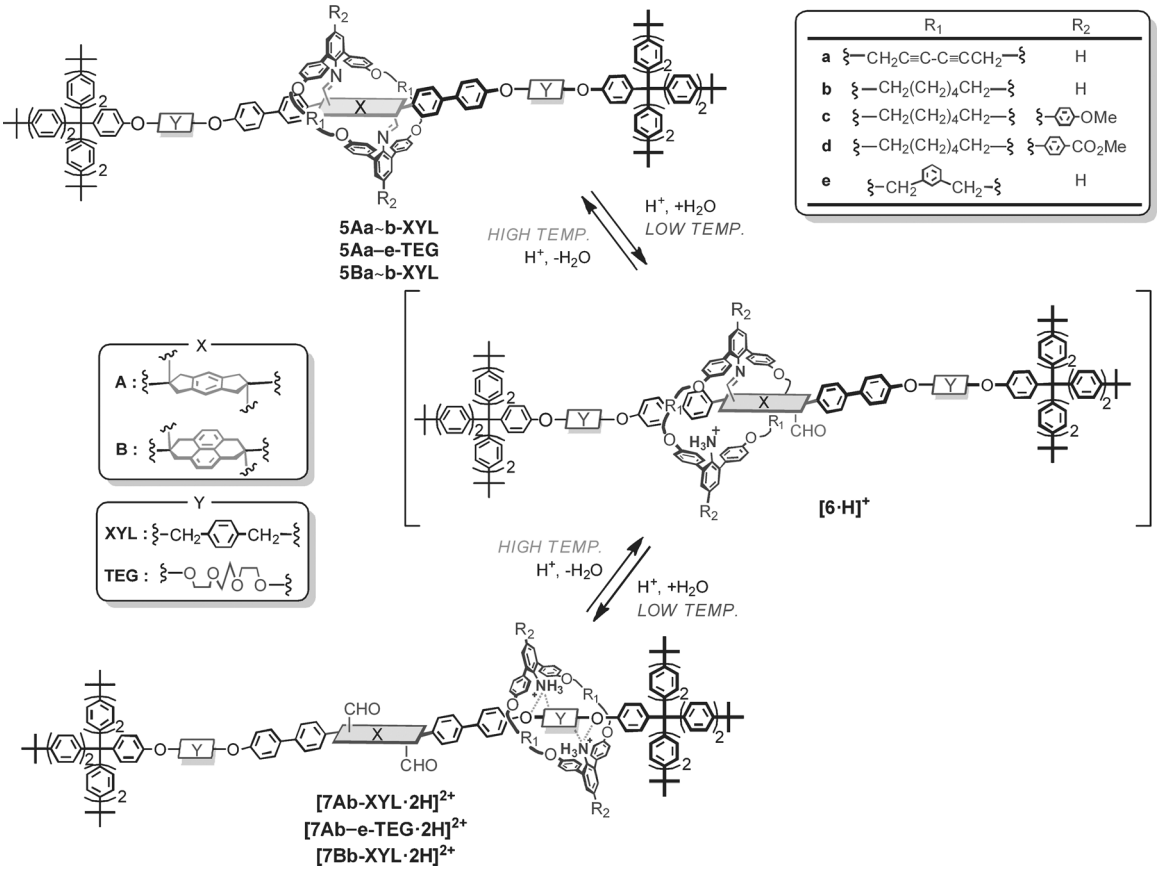

Scheme 4. Generation of [2]rotaxanes **7** by the hydrolysis of imine bonds in **5**.

ratio of **5Ab-XYL**/[**6Ab-XYL**·H]$^+$/[**7Ab-XYL**·2H]$^{2+}$ was 42:35:23 at 233 K and 81:18:1 at 313 K (Scheme 5a).[16a,b]

Effect of core structure—A versus B: We investigated the effect of the bulkiness of the axle core structures on the hydrolysis equilibrium by using imine-bridged rotaxanes **5Ab-XYL** and **5Bb-XYL**. When TFA was added to a solution of **5Bb-XYL** in wet C_6D_5Br, two sets of resonances for hydrolyzed [2]rotaxane [**7Bb-XYL**·2H]$^{2+}$ and monoimine [**6Bb-XYL**·H]$^+$ were observed as an equilibrium mixture with the starting diimine **5Bb-XYL** (Figure 2a–f).[20,21]

In comparison with the hydrolysis equilibrium of hydrindacene-type compound [**7Ab-XYL**·2H]$^{2+}$, the proportion of hexahydropyrene-type [2]rotaxane [**7Bb-XYL**·2H]$^{2+}$ with the bulkier core was higher than that of hydrindacene-type [**7Ab-XYL**·2H]$^{2+}$ (Scheme 5b). When this hydrolyzed sample was cooled, the proportion of **5Bb-XYL** decreased and below 268 K the equilibrium ratio of **5Bb-XYL**/[**6Bb-XYL**·H]$^+$/[**7Bb-XYL**·2H]$^{2+}$ was 0:30:70 (Figure 2g; cf. the equilibrium ratio of 50:42:8 for **5Ab-XYL**/[**6Ab-XYL**·H]$^+$/[**7Ab-XYL**·2H]$^{2+}$ at the same temperature).

To explain the differences between **7Ab** and **7Bb**, we determined the thermodynamic parameters ΔH and ΔS for the equilibration between **5Ab** and **7Ab**, and **5Bb** and **7Bb** by analyzing the van't Hoff plots (Figure 2h). The ΔS values for both compounds are almost the same ($\Delta S = -26.0 \pm 1.4$ for **Ab**, -28.6 ± 4.5 cal mol^{-1} K^{-1} for **Bb**). However, the value of ΔH for **Bb-XYL** is more negative than that for **Ab-XYL** ($\Delta H = -6.0 \pm 0.4$ for **Ab**, -9.0 ± 1.3 kcal mol^{-1} for **Bb**). This indicates that imine-bridged **5Bb-XYL** is thermodynamically destabilized compared with **5Ab-XYL** and that steric repulsion between the axle core and the macrocycle in the diimine could be the major factor: Repulsion in **5Bb-XYL** is greater than that in **5Ab-XYL**. Thus, [2]rotaxane [**7Bb-XYL**·2H]$^{2+}$ is the favored form, whereas in the case of the less bulky hydrindacene-type compound, the diimine form **5Ab-XYL** is the favored form. This result suggests that the bulkiness of the core structure in the axle is significant for efficient hydrolysis of imine-bridged rotaxanes with an XYL side-station.

Effect of side-station: We previously investigated the effect of the side-station (XYL or TEG).[16a,b] In the case of **5Ab-XYL** with *p*-xylylene (XYL) side-stations, as mentioned above (Scheme 5b), pure **5Ab-XYL** in $CDCl_3$ solution was converted into a mixture of **5Ab-XYL**, [**6Ab-XYL**·H]$^+$, and [**7Ab-XYL**·2H]$^{2+}$ upon the addition of TFA. At equilibrium, the solution contained 23% of [2]rotaxane [**7Ab-XYL**·2H]$^{2+}$ at 233 K, and 1% at 313 K.[16a]

In the case of **5Ab-TEG** with triethylene glycol ether (TEG) side-stations, [2]rotaxane [**7Ab-TEG**·2H]$^{2+}$ was exclusively formed at 293 K in C_6D_5Br due to hydrogen bonding between the ring part and the TEG units.[16b] Both

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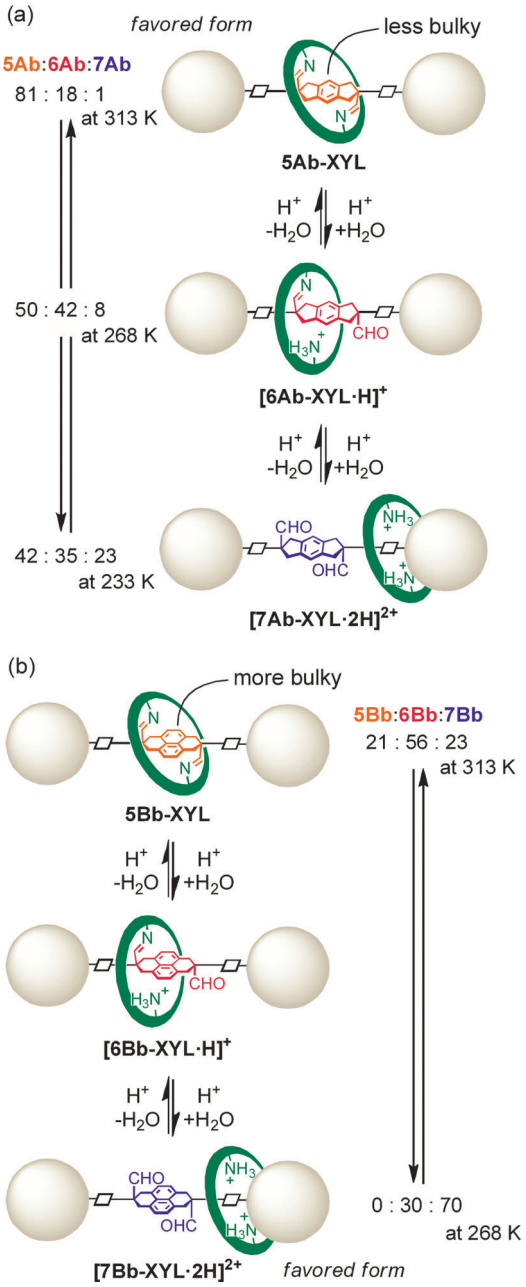

Scheme 5. Hydrolytic equilibrium of imine-bridged rotaxanes **5**, monoimines **6**, and [2]rotaxanes **7**. Equilibrium ratios were estimated by integration of the macrocyclic methylene protons in the ^{1}H NMR spectra for a) hydrindacene type **Ab** and b) hexahydropyrene type **Bb**.

imine-bond cleavage/hydrogen-bond formation and imine-bond formation/hydrogen-bond cleavage are thermodynamically matched processes.[19b] Thus, the TEG units form hydrogen bonds with the ammonium in the macrocycle (Scheme 6) and serve as hydrogen-bonding stations. Upon heating to 398 K under similar acidic conditions, imine-bridged **5Ab-TEG** was again formed by dehydration. The equilibrium ratio of [2]rotaxane [**7Ab-TEG**·2H]$^{2+}$ changed drastically from 100:0 to 0:100 over a temperature range of 293 to 398 K (Scheme 6a).[16b]

Effect of spacer within the macrocycles: We investigated the effects of different spacers in the macrocycles by comparing the hydrolytic behavior of **5Aa**,**b**,**e-TEG**/[**7Aa**,**b**,**e-TEG**·2H]$^{2+}$ (Scheme 6). Diimine **5Aa** has a rigid hexadiyne spacer whereas **5Ab** has a flexible hexamethylene spacer. Furthermore, **5Ae** with a *m*-xylylene spacer has a smaller cavity than either **5Aa**,**b**.

[2]Rotaxane **[7Ab-TEG·2H]$^{2+}$** with a hexamethylene spacer was successfully generated from **5Ab-TEG** under hydrolyzing conditions (shown above), and the macrocycle unit shuttled between two TEG side-stations under acidic hydrolyzing conditions.

In the case of **5Aa-TEG**, however, hydrolyzed [2]rotaxane [**7Aa-TEG**·2H]$^{2+}$ was not observed in the ^{1}H NMR spectrum, despite the assistance of the hydrogen-bonding station (Scheme 6b). When TFA was added to a solution of **5Aa-TEG**, the signals assigned to **5Aa-TEG** showed partial broadening. When this sample was cooled to 248 K, four doublets appeared around 5 ppm, which have been assigned to the propargylic methylene protons in the macrocycle, and no CHO signal was observed (see Figure S3 in the Supporting Information). This suggests that the vibrational motion of the macrocycle around the threading unit (hindered rotation)[16c] is slower than the NMR timescale at 248 K. Comparison of the results for **Aa-TEG** and **Ab-TEG** suggests that the flexibility of the macrocycle is an important factor in the efficient formation of a hydrogen bond with the TEG side-station and therefore the formation of the hydrolyzed [2]rotaxane **7**.

In the case of **5Ae-TEG**, imine bonds were hydrolyzed under similar hydrolytic conditions (Scheme 6c, Figure 3) and [2]rotaxane [**7Ae-TEG**·2H]$^{2+}$ was predominantly generated at 298 K. However, despite the presence of TEG side-stations in **5Ae-TEG**, monoimine [**6Ae-TEG**·H]$^+$ was observed in the hydrolyzed mixture at equilibrium. The less-favored **5Ae-TEG** relative to [**7Ae-TEG**·2H]$^{2+}$ may be attributed to the small size of the cavity of the macrocycle: The multipoint hydrogen bonds formed between the ammonium groups in the macrocycle and the TEG side-stations in the axle in [**7Ae-TEG**·2H]$^{2+}$ are not very strong because the distance between the two amine parts in the macrocycle **2e** is somewhat shorter than the ideal value. In fact, the value of ΔH for **Ae-TEG** determined from the van't Hoff plot is less negative than that in **Ab-TEG** ($\Delta H = -10.7 \pm 0.7$ for **Ae-TEG**, -15.7 ± 0.3 kcal mol^{-1} for **Ab-TEG**), as shown by the shallower regression line for the plot (Figure 3h). The value of ΔS for **Ae-TEG** is also less negative than that for **Ab-TEG** ($\Delta S = -30.7 \pm 2.1$ for **Ae-TEG**, -48.5 ± 0.8 cal mol^{-1} K^{-1} for **Ab-TEG**), which indicates that enthalpic stabilization and the loss of entropy due to hydrogen bonding[16b] with the TEG side-stations is small for the macrocycle **Ae** with the *m*-xylylene spacer.

These results suggest that the flexible hexamethylene spacer in the macrocycle provides the best match for interconversion between imine-bridged rotaxane **5** and [2]rotaxane **7**.

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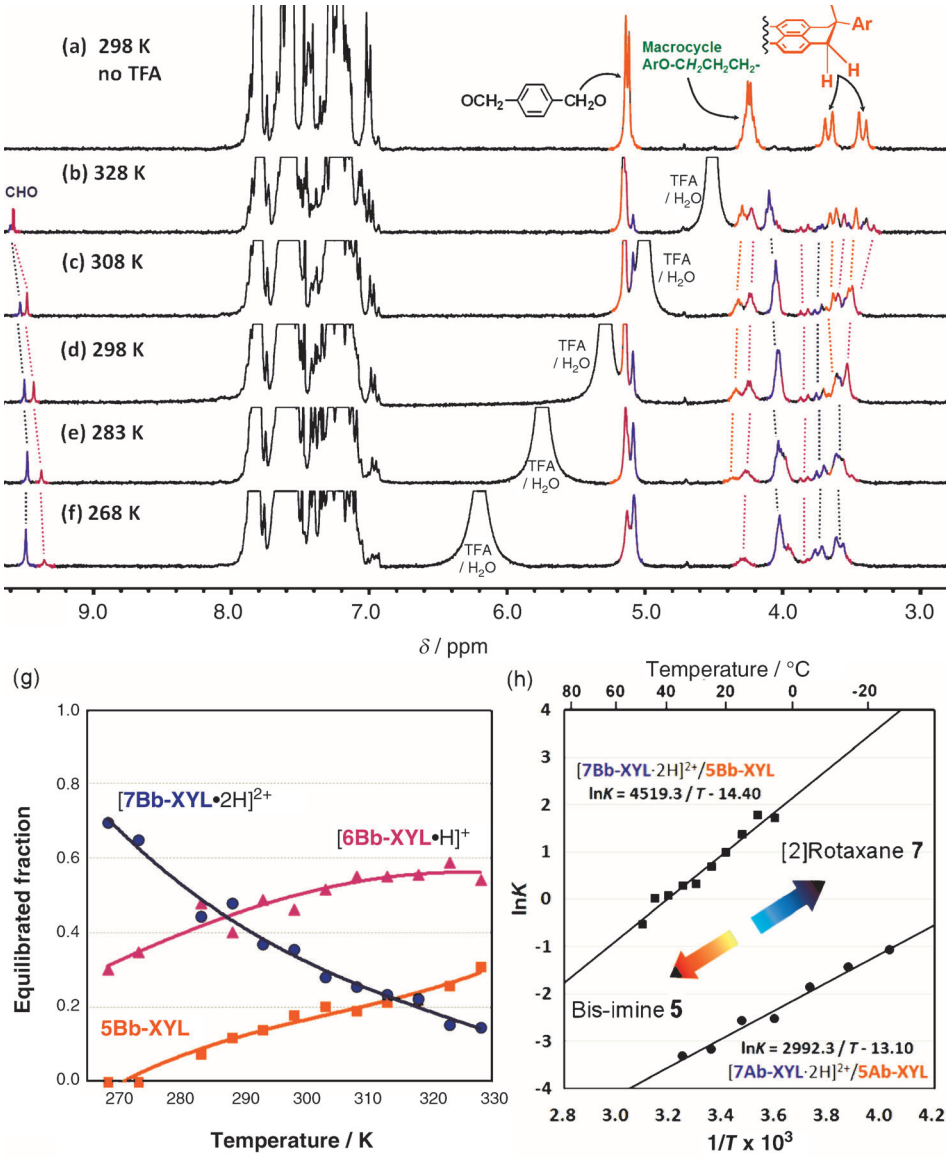

Figure 2. ^{1}H NMR spectra (300 MHz, wet C_6D_5Br) of a) imine-bridged rotaxane **5Bb-XYL** and b)–f) a hydrolyzed mixture containing **5Bb-XYL**, monoimine [**6Bb-XYL**·H]$^+$, and [2]rotaxane [**7Bb-XYL**·2H]$^{2+}$ recorded at b) 328, c) 308, d) 298, e) 283, and f) 268 K. g) Temperature-dependence of the ratio of **5Bb-XYL**, [**6Bb-XYL**·H]$^+$, and [**7Bb-XYL**·2H]$^{2+}$ at equilibrium in the hydrolyzed mixture in C_6D_5Br as estimated from the macrocyclic methylene protons in the ^{1}H NMR spectra.[21] h) van't Hoff plots for the hydrolysis of **5Ab-XYL** to **7Ab-XYL**·2H^{2+} and **5Bb-XYL** to **7Bb-XYL**·2H^{2+}.

Electronic effects of the substituent on the macrocycle: Imine-bond formation by the amine and hydrogen-bond formation by the ammonium are affected by the electronic effects of the substituents.[19] In the threading process in our rotaxane synthesis, imine-bond formation was favored by the use of aniline derivatives with an electron-donating group. Thus, we investigated the electronic effects of the substituents on the macrocycle on the hydrolysis of the imine bonds.

Under similar hydrolyzing conditions, imine-bridged rotaxanes **5Ab–d-TEG** were converted into [2]rotaxanes [**7Ab–d-TEG**·2H]$^{2+}$ and their ratios at equilibrium were found to be temperature-dependent (Figure 4). In each case, we observed that the equilibrium ratio changed drastically from 0:100 to 100:0 over the temperature range of 290 to 400 K. This temperature dependency is almost independent of the presence of the 4-mehoxyphenyl or 4-methoxycarbonylphenyl groups.

These results show that the electron-donating/withdrawing effects of the 4-methoxyphenyl/4-methoxycarbonylphenyl groups only marginally influence the hydrogen bonding between the TEG side-station and macrocycle. In the case of **5Ac-TEG**, an electron-donating group (4-methoxyphenyl) would favor imine-bond formation (see Table 1; **3Ab** vs. **3Ac**), but the effects of the hydrogen bond would be exceeded by the electron-donating effect. Thus, the [2]rotaxane form [**7Ac-TEG**·2H]$^{2+}$ is favored, as is the case in [**7Ab-TEG**·2H]$^{2+}$. Overall, the combination of a hexam-

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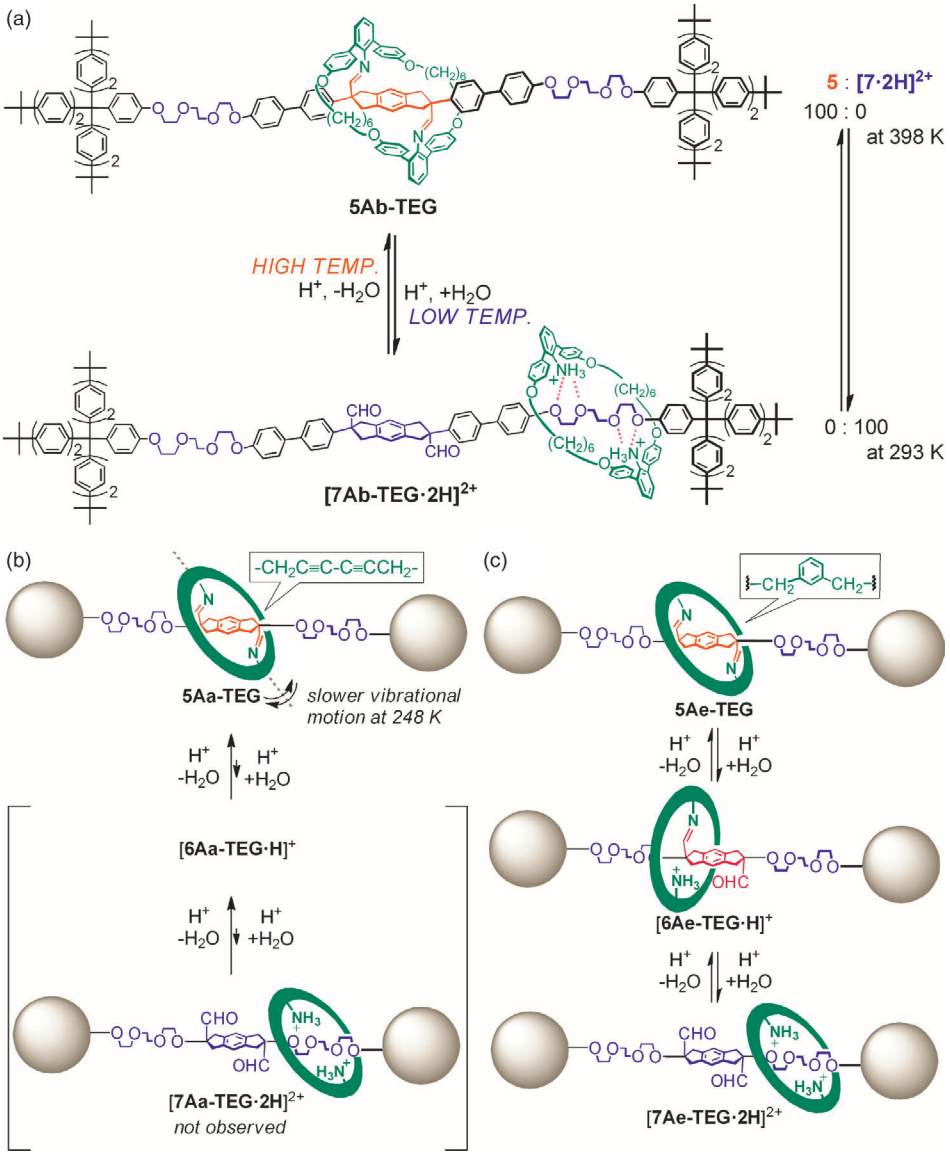

Scheme 6. Hydrolytic equilibrium of imine-bridged rotaxane **5**, monoimine **6**, and [2]rotaxane **7** with TEG side-stations and a) hexamethylene spacer **Ab**, b) hexadiyne spacer **Aa**, and c) *meta*-xylylene spacer **Ae**. The equilibrium ratios were estimated by integration of the macrocyclic methylene protons in the ^{1}H NMR spectra in C_6D_5Br.[16b]

ethylene spacer and a TEG station is suitable for realizing complete switching between a wide range of bridged rotaxanes **5** and [2]rotaxanes **7**.

Conclusions

We have shown that variation of the imine-bridging station, side-station, and/or macrocycle structures all affect the threading process of the axle in the macrocycle and the process of hydrolysis to generate nonbridged [2]rotaxanes **7**. The electronic effects of the substituent groups on the macrocycle have only marginal effects on the hydrolysis process, which is useful for constructing advanced systems: Any substituent group can be introduced at this position without disturbing the hydrolysis process. We are currently constructing more complex interlocked molecules, such as stretching daisy chains, that respond to the hydrolysis/condensation of imine bonds.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-300 (^{1}H/300 MHz, ^{13}C/75 MHz) or α400 (^{1}H/400 MHz, ^{13}C/100 MHz) spectrometer. IR spectra were taken on a JASCO model FT/IR-230 infrared spectrophotometer. Mass spectra were recorded on JEOL JMS-600 (EI), JEOL JMS-T100GCV (FD), JMS-SX102A (FD, FAB) spectrometers. Column chromatography was performed on silica gel I-6-40 (YMC, particle size 40-63 μm) and standardized aluminum oxide 90 (Merck, 63-200 μm), respectively. Thin-layer chromatography (TLC) was performed on

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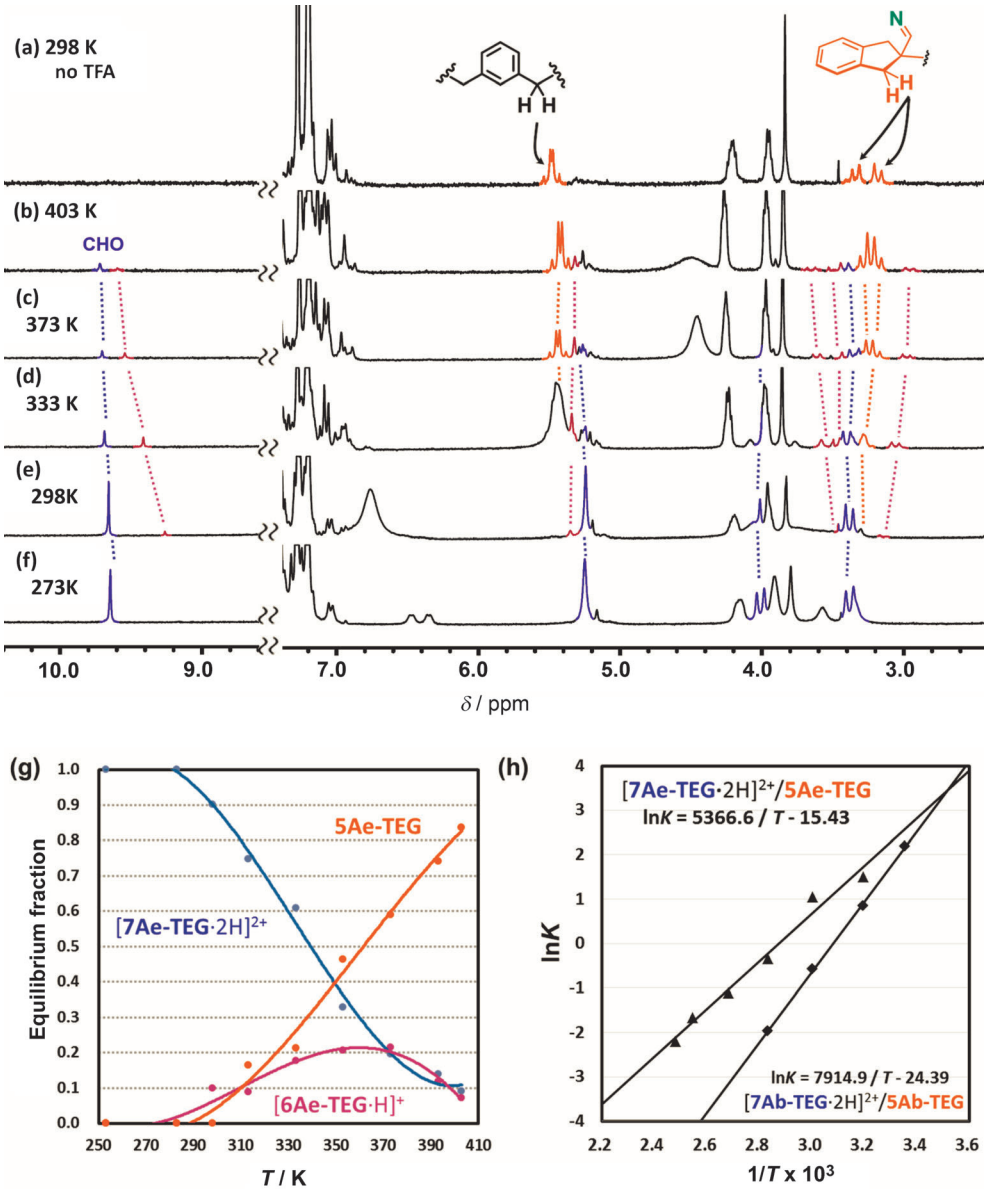

Figure 3. ^{1}H NMR spectra (300 MHz, wet C_6D_5Br) of a) imine-bridged rotaxane **5Ae-TEG** and b)–f) a hydrolyzed mixture containing **5Ae-TEG**, monoimine [**6Ae-TEG**·H]$^+$, and [2]rotaxane [**7Ae-TEG**·2H]$^{2+}$ recorded at b) 403, c) 373, d) 333, e) 298, and f) 273 K. g) Temperature-dependence of the ratio of **5Ae-TEG**, [**6Ae-TEG**·H]$^+$, and [**7Ae-TEG**·2H]$^{2+}$ at equilibrium in the hydrolyzed mixture in C_6D_5Br, as estimated from the hydrindacene methylene protons in the ^{1}H NMR spectra.[21] h) van't Hoff plots for the hydrolysis of **5Ab-TEG** to **7Ab-TEG**·2H^{2+} and **5Ae-TEG** to **7Ae-TEG**·2H^{2+}.

silica gel 60 (Merck) of particle size 5-20 μm. Gel permeation chromatography (GPC) was carried out on LC-908 (Japan Analytical Industry) with JAIGEL 1H+2H, 2H+2.5H or 2.5H+3H columns eluted with $CDCl_3$. Elemental analyses were taken on a Yanako MT-6 CHN recorder at the Center for Instrumental Analysis of Hokkaido University. Reactions were carried out under an argon atmosphere.

2,6-Bis(4-bromophenyl)-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbaldehyde (**1A′**), 2,6-bis(4-bromophenyl)-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarbaldehyde (**1A**),[16a] macrocycles **2a**,[16a] **2b**,[16a] threaded imine **3Aa′**,[16a] α-[4-{tris(4′-*tert*-butylbiphenyl-4-yl)methyl}phenoxy]-α′-bromo-*p*-xylene (**4a**),[16a] and 1-{tris(4′-*tert*-butylbiphenyl-4-yl)methyl}-4-{2-[2-(2-iodoethoxy)ethoxy]ethoxy}-benzene (**4b**)[16b] were prepared by following the known procedures. All commercially available compounds were used without further purification unless otherwise indicated.

Preparation of threaded imine 3Bb: TFA (2 drops, ca. 20 μL, 0.26 mmol) was added to a mixture of **1B** (60 mg, 73 μmol) and **2b** (55 mg, 77 μmol) in benzene. The mixture was heated at reflux for 28 h with stirring under dehydrating conditions (Soxhlet apparatus with a thimble filter containing 4 Å MS), and additional TFA (2 drops, ca. 20 μL, 0.26 mmol) was added to the mixture every 15 h. After the reaction mixture had cooled to room temperature, it was filtered through aluminum oxide. The crude product obtained by concentrating the filtrate was purified by GPC separation (1H+2H) to give **3Bb** (57 mg, 52%) as a white solid. M.p. 193.0–195.0 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26–6.68 (m, 44H), 4.20–4.00 (m, 8H), 3.24 (d, J = 15.9 Hz, 4H), 3.08 (d, J = 15.9 Hz, 4H), 1.88–1.60 (m, 16H), 0.98 (s, 18H), 0.20 ppm (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.48, 157.36, 155.05, 141.71, 139.27, 133.76, 133.68, 132.66, 131.74, 130.95, 128.90, 128.87, 127.92, 127.04, 126.65, 123.99, 120.03, 114.36, 68.12, 47.56, 38.10, 29.15, 26.00, 25.68, 18.21, −4.40 ppm; IR

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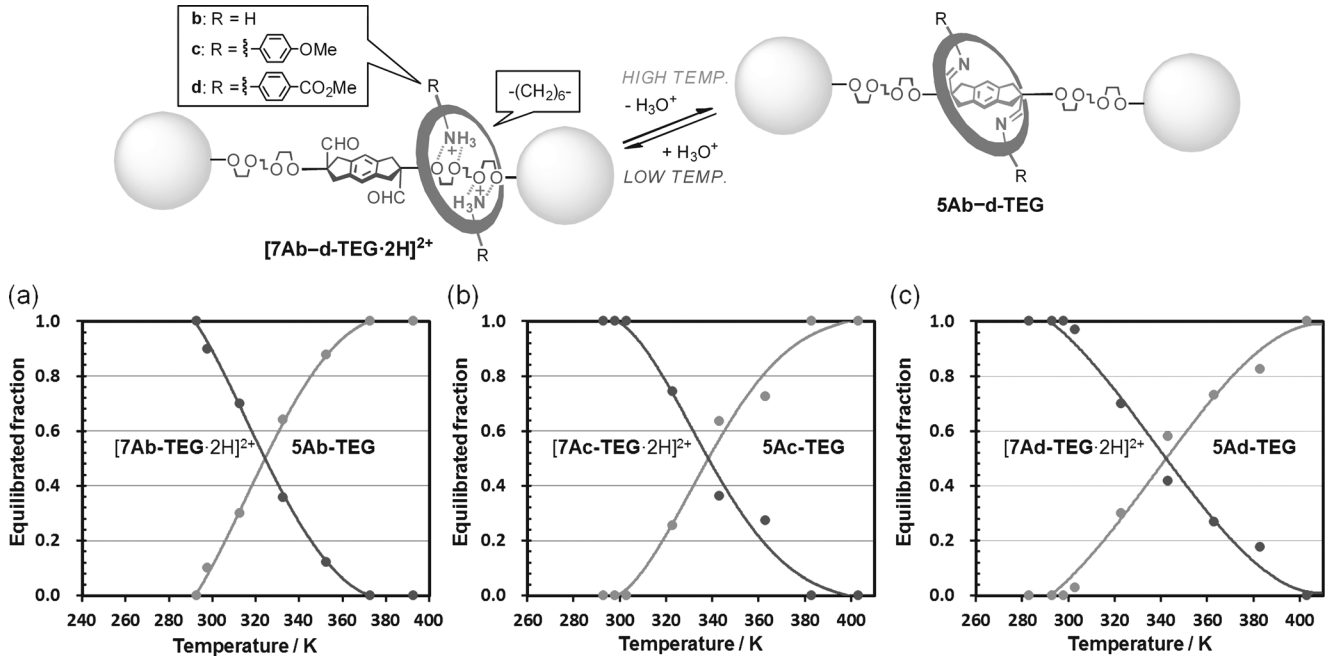

Figure 4. Temperature dependence of the ratio of imine-bridged rotaxanes **5-TEG** and [2]rotaxanes [**7-TEG**·2H]$^{2+}$ at equilibrium, as estimated from the macrocyclic methylene protons in the ^{1}H NMR spectra in C_6D_5Br. a) Hydrogen (R = H), b) 4-methoxyphenyl (R = 4-MeOC_6H_4-), and c) 4-methoxycarbonylphenyl (R = 4-MeOCOC_6H_4-) groups were attached at the *para* position of the aniline moieties.[21]

(KBr): $\tilde{\nu}$ = 3031, 2929, 2857, 1655, 1607, 1510, 1496, 1471, 1459, 1401, 1252, 1172, 1034, 1002, 914, 825, 782, 758, 538 cm^{-1}; LRMS (FD): *m*/*z* (%): 1513 (35) [*M*+3]$^+$, 1512 (71) [*M*+2]$^+$, 1511 (100) [*M*+1]$^+$, 1510 (85) [*M*]$^+$; HRMS (FD): calcd. for $C_{102}H_{106}N_2O_6Si_2$: 1510.7589 [*M*]$^+$; found: 1510.7593.

Preparation of imine-bridged rotaxane 5Bb-XYL: Tetrabutylammonium fluoride (TBAF; 1.0 M solution in THF, 33 μL, 33 μmol) was added to a solution of **3Bb** (25 mg, 17 μmol) in dry DMF (1.5 mL) and dry THF (4.0 mL) at room temperature under an argon atmosphere. After stirring the mixture for 15 min, Cs_2CO_3 (27 mg, 83 μmol) and **4a** (38 mg, 41 μmol) were added. The mixture was stirred for 23 h at room temperature before being poured into water. The aqueous mixture was extracted with $CHCl_3$ and the extract was washed with water and brine, dried over $MgSO_4$, and then filtered. The crude product was separated by GPC (2H+2.5H) to give **5Bb-XYL** (18 mg, 38%) as a white solid. M.p. 244–246 °C (dec.); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.63–7.20 (m, 64H), 7.09–6.87 (m, 44H), 6.77 (d, *J* = 8.8 Hz, 8H), 4.73 (s, 4H), 4.69 (s, 4H), 3.88 (m, 8H), 3.45 (d, *J* = 16.1 Hz, 4H), 3.17 (d, *J* = 16.1 Hz, 4H), 1.80–1.52 (m, 8H), 1.40–1.26 (m, 8H), 1.23 ppm (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.08, 157.35, 156.82, 151.01, 150.14, 145.77, 139.76, 139.31, 139.13, 138.37, 137.69, 136.89, 136.74, 133.75, 133.47, 132.65, 132.26, 131.72, 131.44, 130.94, 128.85, 128.02, 127.82, 127.69, 127.09, 126.66, 126.58, 126.35, 125.92, 125.66, 124.00, 121.50, 121.30, 114.84, 114.35, 113.62, 69.76, 69.67, 68.12, 63.64, 47.54, 38.08, 34.51, 31.35, 29.14, 26.00 ppm; IR (KBr): $\tilde{\nu}$ = 3027, 2951, 2885, 1607, 1510, 1494, 1460, 1396, 1369, 1292, 1240, 1175, 1109, 1003, 816, 763, 565, 532 cm^{-1}; LRMS (FD): *m*/*z* (%): 2957.8 (28), 2954.5 (100) [*M*]$^+$, 732.4 (27); HRMS (FD): calcd. for $C_{216}H_{202}N_2O_8$: 2951.5461 [*M*]$^+$; found: 2951.5447; elemental analysis calcd (%) for $C_{216}H_{202}N_2O_8$·2CH_3CH_2OH: C 86.75, H 7.08, N 0.92; found: C 86.91, H 7.43, N 0.94.

Hydrolysis of imine-bridged rotaxanes 5: A solution of 10% TFA in $CDCl_3$ or C_6D_5Br (10 μL, 13.4 μmol) was added to a solution of imine-bridged rotaxane **5** (3 mg, 1 μmol) in wet $CDCl_3$ (0.6 mL, 48 ± 2 mM of water) or wet C_6D_5Br (0.6 mL, 27 ± 2 mM of water) in an NMR tube. The time-course of the hydrolysis and attainment of equilibrium were monitored by ^{1}H NMR spectroscopy. Equilibrium was achieved just after the addition of TFA. The mixture was subjected to VT-NMR analysis.

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[20] When a small amount of TFA (0.08 % *v*/*v*) was added to the solution of **5Ab-XYL** in wet $CDCl_3$, the dynamic equilibrium in Figure 2 was observed. However, when a large excess of TFA (>1 % *v*/*v*) was added, hydrolysis of the imine bonds was not observed. This observation resembles the results observed by Giuseppone and Lehn.[19b]

[21] We have checked that the equilibrium ratio of **5**/[**7**·2H]$^{2+}$ was maintained for several cycles of the heating/cooling process. Although evaporation of water upon heating during the VT-NMR process cannot be completely ruled out, such a change did not affect the results over repeated experiments.

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Supramolecular Chemistry

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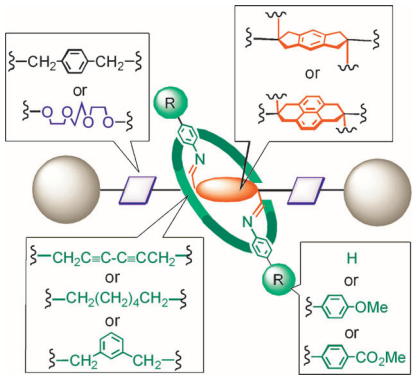
Effects of Axle-Core, Macrocycle, and Side-Station Structures on the Threading and Hydrolysis Processes of Imine-Bridged Rotaxanes



Threading macrocycles: Variation of the imine-bridging station, side-station, and/or macrocycle structures all affect the threading process of the axle in the macrocycle and the hydrolysis generating nonbridged [2]rotaxane (see scheme).

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