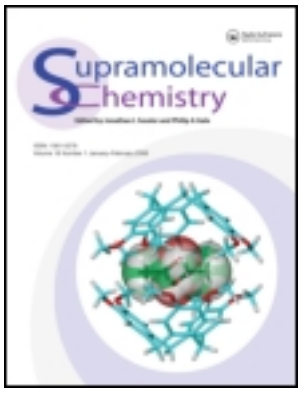

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An octaoxa[22]ferrocenophane **1** composed of 1,1′-ferrocenylene and C_6H_4-1,2-$\{(OCH_2CH_2)_3O\}_2$ groups was employed as macrocyclic component of a rotaxane-like complex with dialkylammonium. Ru-catalysed cross-metathesis reaction of $[\{C_6H_3$-3,5-$(OMe)_2\}CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2]$BARF (BARF = $B\{C_6H_3$-3,5-$(CF_3)_2\}_4$) with $CH_2{=}CHCOO(C_6H_4$-4-$C(C_6H_4$-4-tBu$)_3)$ in the presence of **1** yielded rotaxane-like complex $[(\mathbf{1})\{(C_6H_3$-3,5-$(OMe)_2)CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_4$-4-$C(C_6H_4$-4-$tBu)_3)\}]$BARF. It kept the interlocked structure in $CDCl_3$, benzene-d_6 and toluene-d_8. Dissolution of the rotaxane-like complex in polar solvents, such as CD_3CN and DMSO-d_6, caused the dethreading reaction to form the component molecules. A rotaxane having dibenzo[24]crown-8 as the macrocyclic component did not undergo the dethreading reaction in the solution.

Keywords: crown ether; rotaxane; ferrocene

Introduction

Rotaxanes and pseudorotaxanes composed of macrocyclic and liner molecules have increased attention because of their unique interlocked structures (*1–4*) as well as interesting properties making them suitable as intelligent materials (*5*). Their potential uses include, but are not limited to the following: molecular shuttle (*6*), molecular motor (*7*), molecular device (*8*), molecular tube (*9*), molecular bulb (*10*), molecular muscle (*11*, *12*), gels (*13–16*), drug delivery systems (*17*), supramolecular catalysts (*18*), micelles (*19*) and functional surface (*20*). The rotaxane-based molecular shuttle shows rapid and controlled sliding motion of the macrocyclic component along the axle component, which was studied by many research groups (*6*, *21*). Cavity size of the macrocyclic component is kept smaller than the terminal groups of the axles in most of the rotaxanes with functions as the potential materials in order to keep the interlocked structure. The interlocked system with the combination of the macrocycles and axle ends with comparable sizes is of recent interest. Hirose and Tobe designed the rotaxane of the macrocyclic crown ether, which changes the size of the cavity and degree of the attractive interaction between the macrocyclic and axle components by photochemical and thermal stimulus (*22*). It undergoes shuttling motion whose rate can be switched. Asakawa reported the threading-followed-by-shrinking method to synthesise [2]rotaxane via shrinking of the cavity of macrocyclic crown ether to smaller than the C_6H_4-4-tBu groups at the ends of the axle component (*23*). Similar interlocked systems, composed of the macrocyclic component with comparable size with the end groups of the axle component, are stabilised kinetically, but undergo slow dethreading reaction upon heating to yield the individual component molecules (*24–27*). They are classified into the category of pseudorotaxane, but are termed also as rotaxane-like complexes (*24*). The dethreading reaction of rotaxane-like complex is influenced by size and shape of the cavity of the macrocyclic component and of the structure of axle molecule (*27*, *28*). The rate of dethreading reaction of the rotaxane-like complex were affected by the isotope at a stopper of the axle (*29*), chirality of the component molecules (*29*) and strengths of the hydrogen bonds in the rotaxane-like complex (*30*). Recently, we prepared macrocyclic octaoxa[22]ferrocenophane, **1**, having a similar structure to DB24C8 (dibenzo[24]crown-8)

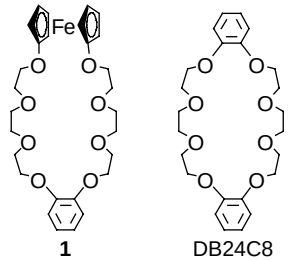

Chart 1. Structure of **1** and dibenzo[24]crown-8 (DB24C8).

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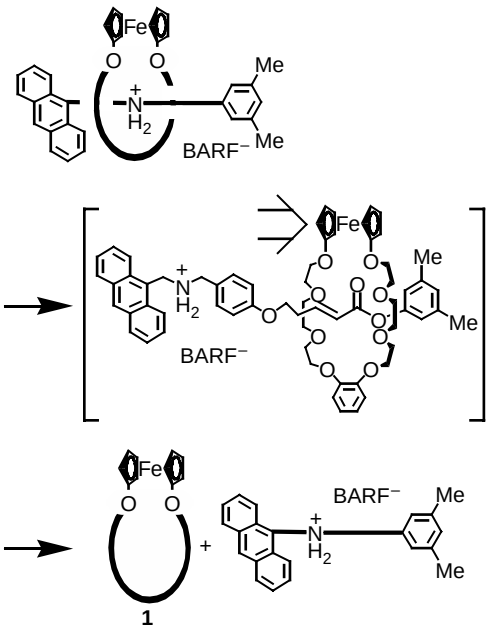
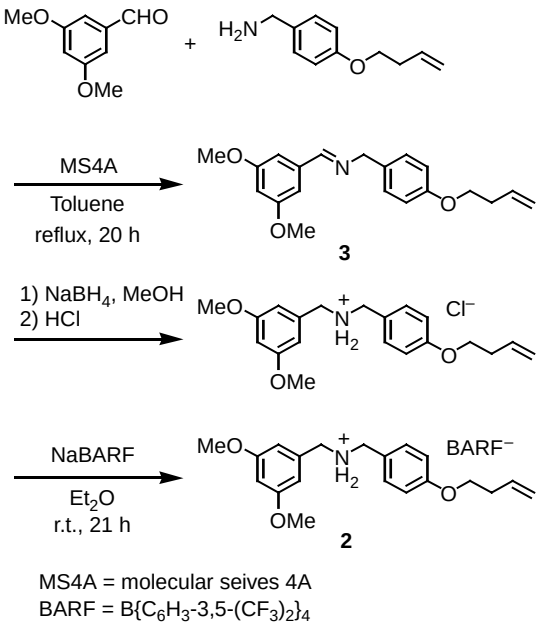


Scheme 1. Dethreading reaction of a rotaxane-like complex of **1** and [$AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_3$-3,5-$Me_2)$]BARF.



Scheme 2. Synthesis of ammonium salt **2**.

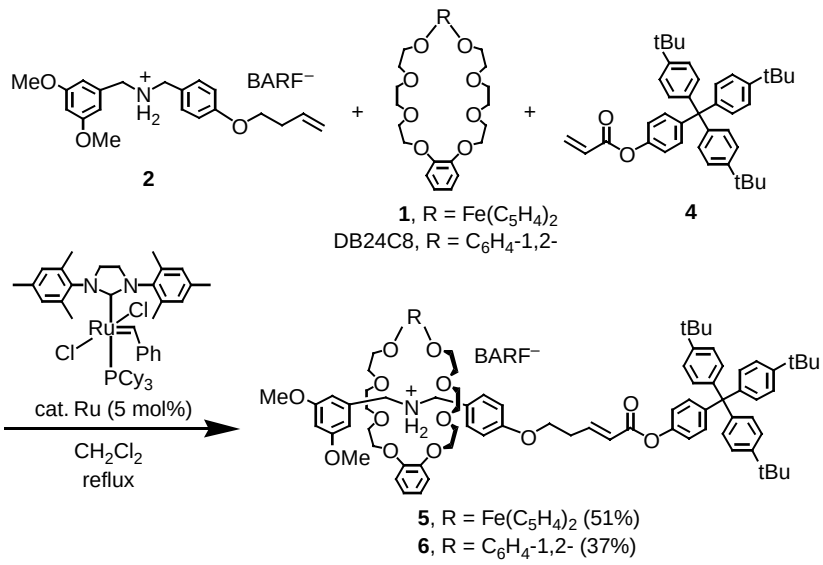
(Chart 1) (*27*). A rotaxane-like complex of **1** with dialkylammonium [(**1**){$AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_3$-3,5-$Me_2)$}]BARF (An = 9-anthryl, BARF = B{C_6H_3-3,5-$(CF_3)_2$}$_4$) undergoes dethreading reaction to yield the component molecules in polar solvents such as CD_3CN and DMSO-d_6 (Scheme 1). The terminal C_6H_3-3,5-Me_2 group of the axle component passes through the cavity of **1** during the reaction. In this paper, we report the synthesis of a rotaxane-like complex of **1** with the dialkylammonium axle molecule having C_6H_3-3,5-$(OMe)_2$ group at the end and its dethreading reaction in solution.

Results and discussion

Scheme 2 summarises the preparation of [{C_6H_3-3,5-$(OMe)_2$}$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$]BARF (**2**, BARF = B{C_6H_3-3,5-$(CF_3)_2$}$_4$) used as a precursor of the axle component of the rotaxane-like complex in this study. Condensation of {C_6H_3-3,5-$(OMe)_2$}CHO and $H_2NCH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ in toluene formed {C_6H_3-3,5-$(OMe)_2$}$CH{=}NCH_2C_6H_4$-4-$OCH_2CH{=}CH_2$ (**3**) having an imine group. Subsequent reduction of the C=N bond by $NaBH_4$, protonation by HCl and exchange of counterion with NaBARF yielded ammonium salt **2**.

Scheme 3 shows the synthesis of the rotaxane-like complexes by Ru–carbene complex, $(H_2IMes)(PCy_3)Cl_2$-Ru=CHPh (H_2IMes = *N*,*N*-*bis*(mesityl)-4,5-dihydroimidazol-2-ylidene), catalysed cross-metathesis reaction of **2** with $CH_2{=}CHCOO\{C_6H_4$-4-$C(C_6H_4$-4-*t*$Bu)_3\}$ (**4**) in the presence of **1** (**1** = 0.043 mmol, **2** = 0.043 mmol, **4** = 0.086 mmol). Heating of the mixture in CH_2Cl_2 for 17 h under reflux condition afforded [(**1**){(C_6H_3-3,5-$(OMe)_2$)$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_4$-4-$C(C_6H_4$-4-*t*$Bu)_3$)}]BARF (**5**) in 51% isolated yield (*27*, *31*, *32*). A similar cross-metathesis reaction using dibenzo[24]crown-8 (DB24C8) instead of **1** gave rotaxane **6** in 37% yield.

Fast atom bombardment mass spectrum (FAB-MS) of **5** shows a peak at *m*/*z* = 1415 which agrees with molecular weight of the cationic rotaxane, [(**1**){(C_6H_3-3,5-$(OMe)_2$)$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_4$-4-$C(C_6H_4$-4-*t*$Bu)_3$)}]$^+$. The ^{1}H and $^{13}C\{^1H\}$ NMR signals of **5** were assigned using DEPT135 as well as ^1H–^1H and $^{13}C\{^1H\}$–^1H COSY spectroscopies. ^{1}H NMR spectrum of **5** in $CDCl_3$ contains signals at δ 2.73, 4.51–4.54, 7.66 assigned to OCH_2CH_2, NCH_2 and NH_2 hydrogens of the axle component (Figure 1(b)). The positions of these signals were at lower magnetic field positions than those of the signals of the corresponding hydrogens in **2** (δ 2.55 (OCH_2CH_2), 3.94–4.14 (NCH_2)) (Figure 1(a)). The shift of the ^{1}H NMR signals was ascribed to the N—H···O and C—H···O hydrogen bonds between oxygen atoms of **1** and hydrogens of the axle component of **5** (*33*, *34*). The trans-configuration of C=C bond in the axle component of **5** was confirmed by large ^1H–^1H coupling constant (J = 16 Hz) of vinylene hydrogens observed at δ 6.14. $^{13}C\{^1H\}$ NMR signals of CH carbons of cyclopentadienyl ligands in **5** (δ 56.3, 62.6) were observed at almost the same position to those of free **1** (δ 56.1, 62.1). ^{1}H NMR spectrum of **6** in $CDCl_3$ contains signals at δ 2.74 (OCH_2CH_2), 4.43–4.57 (NCH_2), 7.47 (NH_2) at similar



Scheme 3. Synthesis of **5** and **6**.

positions to the corresponding ^{1}H NMR signals of **5**. The above FAB-MS and NMR results show that **5** and **6** maintain the interlocked structures in $CDCl_3$ at 25°C.

Dissolving **5** in polar solvent such as CD_3CN and DMSO-d_6 and rising the temperature of the solution brings about dethreading reaction forming a mixture of free **1** and the axle molecule [{C_6H_3-3,5-$(OMe)_2$}$CH_2NH_2CH_2C_6H_4$-4-OCH_2CH_2CH=$CHCOO${C_6H_4-4-$C(C_6H_4$-4-tBu$)_3$}] BARF (**7**) as shown in Scheme 4. The dethreading of **5** in CD_3CN ($[\mathbf{5}]_0 = 5.0$ mM) was monitored by the ^{1}H NMR spectroscopy, and the conversion of **5** into a mixture of **1** and **7** obeys the first-order kinetics with $k_{obs} = 2.5 \times 10^{-6}\,s^{-1}$ at 40°C. The dethreading reaction of **5** in DMSO-d_6 ($k_{obs} = 8.2 \times 10^{-5}\,s^{-1}$ at 40°C) was faster than that in CD_3CN. Table 1 summarises the rate constants at 40–70°C. The temperature dependence of k_{obs} (Eyring plots) gave the thermodynamic parameters of the reactions as $\Delta G^{\ddagger} = 110$ kJ mol^{-1}, $\Delta H^{\ddagger} = 72$ kJ mol^{-1}, $\Delta S^{\ddagger} = -120$ J mol^{-1} K^{-1} in CD_3CN and $\Delta G^{\ddagger} = 102$ kJ mol^{-1}, $\Delta H^{\ddagger} = 32$ kJ mol^{-1}, $\Delta S^{\ddagger} = -220$ J mol^{-1} K^{-1} in DMSO-d_6. The dethreading reaction of **5** was not observed in $CDCl_3$ (50°C for 3 days), CD_2Cl_2 (room temperature for 12 days), C_6D_6 (50°C for 3 days) and toluene-d_8 (50°C for 3 days).

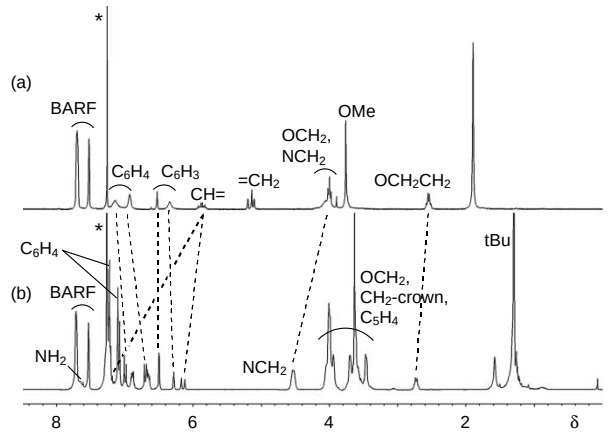
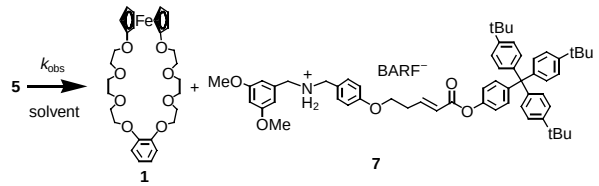


Figure 1. ^{1}H NMR spectra of (a) **2** and (b) **5** in $CDCl_3$ (300 MHz, 25°C).

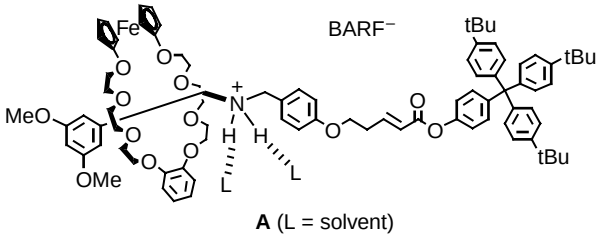
The dethreading of **6** was not observed not only in $CDCl_3$, CD_2Cl_2, C_6D_6 and toluene-d_8 but also in CD_3CN and DMSO-d_6 ($[\mathbf{6}]_0 = 5.0$ mM). It is because the cavity of DB24C8 is smaller than **1** and does not allow C_6H_3-3,5-$(OMe)_2$ group to pass through even in the polar solvents. These results indicate that **5** is categorised into rotaxane-like complex; it maintains the interlocked structure in the solvents with relatively lower polarity but undergoes the dethreading reaction in the polar solvents such as CD_3CN and DMSO-d_6. The activation entropies of the dethreading reactions of **5** are large negative values ($\Delta S^{\ddagger} = -120$ (CD_3CN) and -220 (DMSO-d_6) J mol^{-1} K^{-1}) which are larger than those of the recently reported rotaxane-like complex [(**1**){$AnCH_2NH_2CH_2C_6H_4$-4-OCH_2CH_2 CH=$CHCOO(C_6H_3$-3,5-$Me_2)$}]BARF in CD_3CN ($\Delta G^{\ddagger} = 110$ kJ mol^{-1}, $\Delta H^{\ddagger} = 79$ kJ mol^{-1}, $\Delta S^{\ddagger} = -91$ J mol^{-1} K^{-1}) (*27*). Stoddart et al. reported the dethreading reaction of rotaxane-like complex [(tBuC_6H_4-4-CH_2NH_2-$CH_2C_6H_4$-4-CH_2PPh_3)(BMP25C8)]$(PF_6)_2$ (BMP25C8 = dibenzometaphenylene[25]crown-8) and the large negative



Scheme 4. Dethreading reaction of **5**.

Table 1. Kinetic rate constants, k_{obs}, of the dethreading reaction of **5** ($[\mathbf{5}]_0 = 5.0\,mM$).

Solvent	Temp/°C	k_{obs}/s^{-1}
CD_3CN	40	2.5×10^{-6}
	50	1.1×10^{-5}
	60	1.8×10^{-5}
	70	3.5×10^{-5}
DMSO-d_6	40	8.2×10^{-5}
	50	1.1×10^{-4}
	60	1.8×10^{-4}
	70	2.6×10^{-4}



A (L = solvent)

Chart 2. Plausible intermediate of the dethreading reaction of **5**.

entropy change in CD_3CN ($\Delta G^{\ddagger}(298\,K) = 109\,kJ\,mol^{-1}$, $\Delta H^{\ddagger} = 66\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -146\,J\,mol^{-1}\,K^{-1}$) (*24*). They attributed the results to the solvation of the intermediate and the limited conformation for the dethreading. Chart 2 shows the intermediate **A** where the solvent molecules coordinate to the ammonium of the axle molecule.

The dethreading reaction of **5** probably occurs at the C_6H_3-3,5-$(OMe)_2$ group of the axle because the other end groups are too bulky to allow the dethreading. The dethreading reaction of **5** is much slower than that of [(**1**){$AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO$ (C_6H_3-3,5-Me_2)}]BARF ($k_{obs} = 1.0 \times 10^{-5}\,s^{-1}$ (CD_3CN at 45°C), $4.9 \times 10^{-3}\,s^{-1}$ (DMSO-d_6 at 20°C)). Lower reactivity of **5** is ascribed to bulkier C_6H_3-3,5-$(OMe)_2$ end group than C_6H_3-3,5-Me_2.

The redox potentials of the ferrocene-containing compounds were determined by cyclic voltammetry (CV). Ferrocene-containing rotaxane, **5**, undergoes electrochemical oxidation and reduction at $E_{pa} = -0.09$ and $E_{pc} = -0.16\,V$ (in MeCN, vs. Fc^+/Fc, Fc = ferrocene) (Figure 2). The higher redox potentials of ferrocene-containing crown ether in **5** than

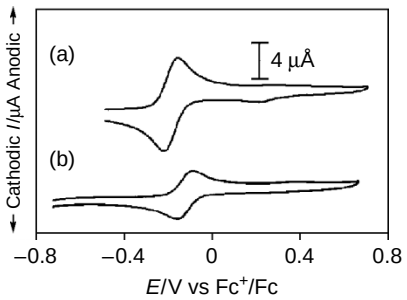


Figure 2. Cyclic voltammograms of (a) **1** and (b) **5** in MeCN (1.0 mM) containing 0.10 M nBu_4NPF_6.

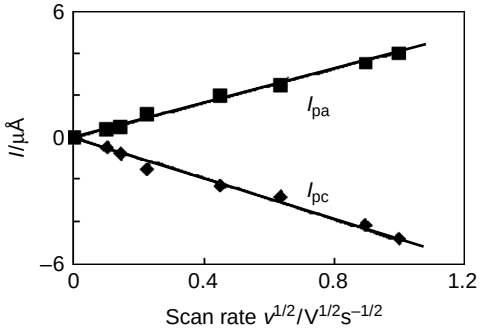


Figure 3. Scan-rate dependence of I_{pa} and I_{pc} of cyclic voltammograms of **5** in MeCN (1.0 mM) containing 0.10 M nBu_4NPF_6.

those of free **1** ($E_{pa} = -0.16$ and $E_{pc} = -0.23\,V$) are ascribed to the static repulsion of ammonium and $Fe(III)^+$ formed by oxidation (*27*). Figure 3 exhibits linear relationship of the peak currents I_{pa} and I_{pc} of **5**. These results indicate that the redox of **5** in solution shows high reversibility with the scan rate in the range below $1.0\,V\,s^{-1}$.

In summary, we present the synthesis and the dethreading reaction of a rotaxane-like complex composed of a macrocyclic [22]ferrocenophane **1** and dialkylammonium salt. The dethreading reaction of the rotaxane-like complex takes place in polar solvents, whereas a similar rotaxane having dibenzo[24]crown-8 (DB24C8) as the macrocyclic component does not undergo dethreading reaction due to smaller cavity of DB24C8.

Experimental section

General

Compounds **1** (*27*), **4** (*27*), $H_2NCH_2C_6H_4$-4-OCH_2CH_2-$CH{=}CH_2$ (*35*) and NaBARF (*36*) (BARF = B{C_6H_3-3,5-$(CF_3)_2$}$_4$) were prepared according to the literature method. The other chemicals were commercially available. NMR spectra (^1H, $^{13}C\{^1H\}$) were recorded on a Varian MERCURY300. The chemical shifts were referenced with respect to $CHCl_3$ (δ 7.26) for ^1H and $CDCl_3$ (δ 77.0) for ^{13}C as internal standards. FAB-MS was obtained from JEOL JMS-700 (matrix, 2-nitrophenyloctylether). Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. CV was measured in MeCN solution containing 0.1 M nBu_4NPF_6 with ALS Electrochemical Analyzer Model-600A. The measurement was carried out in a standard one-compartment cell equipped with Ag^+/Ag reference electrode, a platinum-wire counter-electrode and a platinum-disc working electrode (ID: 1.6 mm).

Preparation of {C_6H_3-3,5-$(OMe)_2$}$CH{=}NCH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ (3)

A toluene solution (50 ml) containing 3,5-dimethoxybenzaldehyde (0.50 g, 3.0 mmol) and $H_2NCH_2C_6H_4$-4-OCH_2

$CH_2CH{=}CH_2$ (0.53 g, 3.0 mmol) was stirred for 20 h under reflux condition in the presence of MS4A (4 Å molecular sieves). MS4A was removed by filtration, and the filtrate was evaporated to give $\{C_6H_3\text{-}3,5\text{-}(OMe)_2\}CH{=}NCH_2C_6H_4\text{-}4\text{-}OCH_2CH_2CH{=}CH_2$ (**3**) (1.0 g, 3.0 mmol, quant). ^{1}H NMR spectrum (300 MHz, $CDCl_3$, rt): ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 2.54 (dddt, 2H, CH_2CH=CH_2, $J = 7, 7, 1, 1$ Hz), 3.83 (s, 6H, OCH_3), 4.01 (t, 2H, OCH_2, $J = 7$ Hz), 4.78 (s, 2H, NCH_2), 5.10 (ddt, 1H, *cis*-CH=CH_2, $J = 10, 2, 2$ Hz), 5.18 (ddt, 1H, *trans*-CH=CH_2, $J = 17, 2, 2$ Hz), 5.90 (ddt, 1H, CH=CH_2, $J = 17, 10, 7$ Hz), 6.55 (brs, 1H, *p*-C_6H_3), 6.89 (d, 2H, C_6H_4), 6.99 (brs, 2H, *o*-C_6H_3), 7.23–7.26 (2H, C_6H_4), 8.23 (s, 1H, N=CH). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, rt): δ 33.4 (*C*H_2CH=CH_2), 55.1 (OCH_3), 64.1 (NCH_2), 66.9 (OCH_2), 103.2 (*p*-C_6H_3), 105.6 (*o*-C_6H_3), 114.3 (C_6H_4), 116.7 (CH=*C*H_2), 129.0 (C_6H_4), 130.9 (*ipso*-C_6H_4 or *ipso*-C_6H_3), 134.2 (*C*H=CH_2), 138.0 (*ipso*-C_6H_4 or *ipso*-C_6H_3), 157.8 (*ipso*-C_6H_4), 160.6 (*m*-C_6H_3), 161.3 (N=CH). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.30 Found: C, 74.09; H, 7.10; N, 4.28.

Preparation of [{C_6H_3-3,5-(OMe)$_2$}$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$]BARF (2)

Compound **3** (1.0 g, 3.0 mmol) was dissolved in MeOH (25 ml) at room temperature. $NaBH_4$ (0.9 g, 24 mmol) was added to the solution, and the mixture was stirred for 4 h at room temperature before the product was quenched with 4 M HCl(aq) (70 ml). The product was separated as a solid from the solution which was collected by filtration and purified by washing with water to give $[\{C_6H_3\text{-}3,5\text{-}(OMe)_2\}CH_2NH_2CH_2C_6H_4\text{-}4\text{-}OCH_2\text{-}CH_2CH{=}CH_2]Cl$ as a white solid (0.50 g, 1.3 mmol, 46%) which was used without further purification. $[\{C_6H_3\text{-}3,5\text{-}(OMe)_2\}CH_2NH_2CH_2C_6H_4\text{-}4\text{-}OCH_2CH_2\text{-}CH{=}CH_2]Cl$ (0.23 g, 0.64mmol) and NaBARF (0.57 g, 0.64 mmol) were dissolved in Et_2O (18 ml) and was stirred for 21 h at room temperature. The solid formed by the reaction was separated by filtration and the filtrate was evaporated to dryness to give a white solid. The crude product was washed with hexane to give **2** as a white solid (0.68 g, 0.57 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 2.55 (dt, 2H, CH_2CH=CH_2, $J = 7, 7$ Hz), 3.76 (s, 6H, OCH_3), 3.94–4.14 (brs, 4H, NCH_2), 4.00 (t, 2H, OCH_2, $J = 7$ Hz), 5.13 (dd, 1H, *cis*-CH=CH_2, $J = 10, 1$ Hz), 5.17 (dd, 1H, *trans*-CH=CH_2, $J = 17, 1$ Hz), 5.88 (ddt, 1H, CH=CH_2, $J = 17, 10, 7$ Hz), 6.34 (s, 2H, *o*-C_6H_3), 6.53 (s, 1H, *p*-C_6H_3), 6.93 (brs, 2H, C_6H_4), 7.15 (brs, 2H, C_6H_4), 7.52 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 7.70 (s, 8H, *o*-$C_6H_3(CF_3)_2$). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, rt): δ 33.3 (*C*H_2CH=CH_2), 52.0 (NCH_2), 52.2 (NCH_2), 55.4 (OCH_3), 67.5 (OCH_2), 101.2 (*p*-C_6H_3), 107.3 (*o*-C_6H_3), 116.0 (C_6H_4), 117.4 (CH=*C*H_2), 117.5 (*p*-$C_6H_3(CF_3)_2$), 119.5 (*ipso*-C_6H_4 or *ipso*-C_6H_3), 124.5 (quintet, CF_3, J(FC) = 271 Hz), 128.9 (quintet, *C*CF_3, J(FC) = 30 Hz), 130.1 (*ipso*-C_6H_4 or *ipso*-C_6H_3), 130.8 (C_6H_4), 133.8 (*C*H=CH_2), 134.8 (*o*-$C_6H_3(CF_3)_2$), 161.1 (*ipso*-C_6H_4), 161.6 (quintet, BC, J(BC) = 50 Hz), 162.1 (*m*-C_6H_3). Anal. Calcd for $C_{52}H_{38}BF_{24}NO_3(H_2O)_2$: C, 50.87; H, 3.45; N, 1.14 Found: C, 50.93; H, 3.57; N, 1.24.

Preparation of [(1){(C_6H_3-3,5-(OMe)$_2$)$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOO(C_6H_4$-4-C($C_6H_4$-4-tBu)$_3$)}]BARF (5)

Compounds **2** (51 mg, 0.043 mmol) and **1** (24 mg, 0.043 mmol) were dissolved in CH_2Cl_2 (2.0 ml), followed by the addition of $CH_2{=}CHCOO\{C_6H_4\text{-}4\text{-}C(C_6H_4\text{-}4\text{-}t\text{Bu})_3\}$ (**4**) (48 mg, 0.086 mmol) and a Ru–carbene complex, (H_2IMes)(PCy_3)Cl_2Ru=CHPh, (1.8 mg, 2.2×10^{-3} mmol). The mixture was refluxed for 17 h and the solvent was removed by evaporation to give a brown oil. The crude product was purified by preparative HPLC ($CHCl_3$) to give **5** as a yellow oil (50 mg, 0.022 mmol, 51%). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.30 (s, 27H, $C(CH_3)_3$), 2.73 (dt, 2H, OCH_2CH_2, $J = 6$, 6 Hz), 3.45–3.47 (4H, OCH_2-Crown or C_5H_4), 3.63 (s, 6H, OCH_3), 3.54–3.70 (14H, OCH_2-Crown or C_5H_4), 3.93–4.05 (16H, OCH_2-Crown or C_5H_4, OCH_2-Axle), 4.51–4.54 (4H, NCH_2), 6.14 (d, 1H, $CH_2CH{=}CH$, $J = 16$ Hz), 6.28 (m, 1H, *p*-C_6H_3), 6.50 (m, 2H, *o*-C_6H_3), 6.65 (m, 2H, C_6H_4-Crown), 6.70 (d, 2H, C_6H_4-Axle, $J = 9$ Hz), 6.89 (m, 2H, C_6H_4-Crown), 6.99 (d, 2H, C_6H_4-Axle, $J = 9$ Hz), 7.09 (d, 6H, C_6H_4-*t*Bu, $J = 9$ Hz), 7.21–7.26 (11H, C_6H_4-Axle, C_6H_4-*t*Bu, $CH_2CH{=}CH$), 7.53 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 7.66 (brs, 2H, NH_2), 7.71 (m, 8H, *o*-$C_6H_3(CF_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 31.4 (C(*C*H_3)), 32.0 (OCH_2CH_2), 34.4 (*C*$(CH_3)_3$), 52.3 (NCH_2, 2C), 55.2 (OCH_3), 56.3 (C_5H_4, 2C), 62.6 (C_5H_4, 2C), 63.4 (*C*$(C_6H_4$-*t*Bu$)_3$), 65.7 (OCH_2-Axle), 68.2 (CH_2-Crown), 69.0 (CH_2-Crown), 69.9 (CH_2-Crown), 70.2 (CH_2-Crown), 70.6 (CH_2-Crown), 71.3 (CH_2-Crown), 99.6 (*p*-C_6H_3), 107.2 (*o*-C_6H_3), 112.0 (C_6H_4-Crown), 114.5 (C_6H_4-Axle), 117.4 (*p*-$C_6H_3(CF_3)_2$), 119.9 (C_6H_4-Axle), 121.8 (C_6H_4-Crown), 122.9 ($CH_2CH{=}CH$), 124.1 (C_6H_4-*t*Bu), 124.5 (quintet, CF_3, J(FC) = 271 Hz), 128.8 (quintet, *C*CF_3, J(FC) = 30 Hz), 130.6 (C_6H_4-*t*Bu), 130.8, 132.1 (C_6H_4-Axle), 133.0, 134.7 (*o*-$C_6H_3(CF_3)$), 143.6, 144.9, 146.4, 146.5 ($CH_2CH{=}CH$), 148.3, 148.4, 159.4, 161.0, 161.6 (quintet, BC, J(BC) = 50 Hz), 164.5 (C=O). Anal. Calcd for $C_{118}H_{116}BF_{24}FeNO_{13}(H_2O)_3$: C, 60.75; H, 5.27; N, 0.46 Found: C, 60.60; H, 5.64; N, 0.64. FAB-MS: Calcd for $C_{86}H_{104}NO_{13}$: 1415 Found: $m/z = 1415$ $[M - BARF]^+$.

Preparation of [(DB24C8){(C_6H_3-3,5-($OMe)_2$)$CH_2NH_2CH_2C_6H_4$-4-OCH_2CH_2CH=$CHCOO(C_6H_4$-4-$C(C_6H_4$-4-$tBu)_3$)}]BARF (6)

Compounds **2** (60 mg, 0.05 mmol) and DB24C8 (22 mg, 0.05 mmol) were dissolved in CH_2Cl_2 (2.0 ml), followed by the addition of CH_2=CHCOO{C_6H_4-4-$C(C_6H_4$-4-tBu$)_3$} (**4**) (56 mg, 0.106 mmol) and a Ru–carbene complex, (H_2IMes)(PCy_3)Cl_2Ru=CHPh, (2.1 mg, 2.5×10^{-3} mmol). The mixture was refluxed for 15 h and the solvent was removed by evaporation to give a brown oil. The crude product was purified by preparative HPLC ($CHCl_3$) to give **6** as an off-white solid (41 mg, 0.019 mmol, 37%). ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 1.30 (s, 27H, C(CH_3)$_3$), 2.74 (brs, 2H, OCH$_2$C*H*$_2$), 3.41 (brs, 8H, CH_2-DB24C8), 3.61 (brs, 6H, OCH_3), 3.74 (brs, 8H, CH_2-DB24C8), 4.01 (brs, 2H, OCH_2-Axle), 4.09 (brs, 8H, CH_2-DB24C8), 4.43–4.57 (4H, NCH_2), 6.15 (d, 1H, CH_2CH=C*H*, J = 16 Hz), 6.29 (s, 1H, *p*-C_6H_3), 6.43 (s, 2H, *o*-C_6H_3), 6.69 (m, 2H, C_6H_4-Axle), 6.76 (m, 4H, C_6H_4-DB24C8), 6.90 (m, 4H, C_6H_4-DB24C8), 7.00 (d, 2H, C_6H_4-Axle, J = 9 Hz), 7.20–7.26 (2H, C_6H_4-Axle), 7.09 (d, 6H, C_6H_4-*t*Bu, J = 9 Hz), 7.21–7.26 (7H, C_6H_4-*t*Bu, CH_2C*H*=CH), 7.23 (d, 2H, C_6H_4-Axle, J = 9 Hz), 7.47 (brs, 2H, NH_2), 7.53 (s, 4H, *p*-$C_6H_3(CF_3)_2$), 7.71 (m, 8H, *o*-$C_6H_3(CF_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rt): δ 31.4 (C(*C*H$_3$)), 32.0 (OCH$_2$*C*H$_2$), 34.3 (*C*(CH_3)$_3$), 52.3 (NCH_2), 55.2 (OCH_3), 63.4 (*C*(C_6H_4-*t*Bu)$_3$), 65.8 (OCH_2-Axle), 68.1 (CH_2-DB24C8), 70.3 (CH_2-DB24C8), 70.6 (CH_2-DB24C8), 99.7 (*p*-C_6H_3), 106.9 (*o*-C_6H_3), 112.7 (C_6H_4-DB24C8), 114.4 (C_6H_4-Axle), 117.4 (*p*-$C_6H_3(CF_3)_2$), 119.9 (C_6H_4-Axle), 121.9 (C_6H_4-DB24C8), 122.9 (CH_2CH=*C*H), 123.6, 124.5 (quintet, CF_3, J(FC) = 271 Hz), 124.1 (C_6H_4-tBu), 128.8 (quintet, *C*CF_3, J(FC) = 31 Hz), 130.6 (C_6H_4-*t*Bu), 132.1 (C_6H_4-Axle), 133.7 (*o*-$C_6H_3(CF_3)_2$), 143.6, 144.9, 146.5 (CH_2-*C*H=CH), 147.3, 148.4, 159.2, 160.9, 161.6 (quintet, BC, J(BC) = 50 Hz), 164.5 (C=O). Anal. Calcd for $C_{114}H_{112}BF_{24}NO_{13}(H_2O)_2$: C, 62.04; H, 5.30; N, 0.63 Found: C, 62.16; H, 5.42; N, 0.74. FAB-MS: Calcd for $C_{82}H_{100}NO_{13}$: 1307 Found: m/z = 1307 [M − BARF]$^+$.

Dethreading reaction of rotaxanes

To an NMR tube was charged a CD_3CN (or DMSO-d_6) solution (0.6 ml) of rotaxane, **5**, **6** (3.0×10^{-3} mmol) and 2-chloro-2-methylpropane which is used as an internal standard. The NMR tube was heated in a thermostatic bath and stored when not being actively monitored. ^{1}H NMR spectra were checked occasionally and the reaction was monitored by comparison of peak area ratio between the rotaxane and the internal standard. After reaction, the solvent was removed by evaporation and the residue was checked by the FAB-MS measurement.

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