Rotaxanes of a macrocyclic ferrocenophane with dialkylammonium axle components†

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Received 15th April 2009, Accepted 9th September 2009
First published as an Advance Article on the web 6th October 2009
DOI: 10.1039/b907417a

Octaoxa[22]ferrocenophane, **1**, was synthesized and employed as the macrocyclic component of [2]rotaxanes. [2]Pseudorotaxanes composed of macrocyclic molecule **1** and dialkylammonium derivatives with a terminal vinyl group undergo end-capping *via* cross-metathesis of the terminal group with bulky acrylates. The [2]rotaxanes of **1** with axle components having bulky terminal groups, such as 3,5-dimethylphenyl, 9-anthryl, and ferrocenyl groups, maintain an interlocked structure in $CDCl_3$ solution, but they are gradually converted into a mixture of the individual components *via* dethreading of the end groups in polar solvents such as CD_3CN and dmso-d_6. The reaction rate varies depending on the end group and solvent. The cationic rotaxane with an anthryl end group of the axle component, $[(\mathbf{1})\{AnCH_2NH_2CH_2C_6H_4\text{-}4\text{-}OCH_2CH_2CH{=}CHCOOC_6H_4\text{-}4\text{-}C(C_6H_4\text{-}4\text{-}tBu)_3\}](BAr_F)$ (An = 9-anthryl, $BAr_F = B\{C_6H_3\text{-}3,5\text{-}(CF_3)_2\}_4$) shows weak emission upon excitation of the anthryl group (**12b**, $\lambda_{em} = 419$ nm, quantum yield, $\phi = 0.012$). The quantum yield is lower than that of the neutral rotaxane **13b** ($\phi = 0.030$) formed by *N*-acetylation of **12b** and a physical mixture of the corresponding free axle molecule, $AnCH_2N(Ac)CH_2C_6H_4\text{-}4\text{-}OCH_2CH_2CH{=}CHCOOC_6H_4\text{-}4\text{-}C(C_6H_4\text{-}4\text{-}tBu)_3$ (**8**), and **1** ($\phi = 0.34$). The efficiency of the quenching caused by the ferrocenylene group caused by energy transfer is affected significantly by the relative positions of the anthryl and ferrocenylene groups in the rotaxane. The rotaxane with axles having a secondary ammonium moiety has a redox potential $E_{1/2}$ = –0.03–0.02 V (*vs.* Ag^+/Ag), which is lower those of than compound **1** ($E_{1/2}$ = –0.10 V) and the neutral [2]rotaxanes with the *N*-acetylated axle components ($E_{1/2}$ = –0.11 and –0.22 V).

Introduction

Rotaxane, composed of interlocked cyclic and axle components, allows individual motion of the component molecules with restrictions on the direction and degree of the movement in the interlocked structure.[1] The design of the functional groups in either or both of the components enables changes in relative positions of the component molecules of the rotaxane upon chemical transformation. Typically, a chemical reaction of the functional group in the axle component induces a change in the interaction between the components and causes shifts of the macrocyclic component along the axle molecule.[2] This unique stimulus-response behaviour of the functionalized rotaxanes is applied to molecular shuttles,[3] molecular muscles,[4] molecular bulbs,[5] and the transportation of a droplet on a solid surface covered with rotaxanes.[6]

The ferrocenyl group is employed as a terminal blocking group of the axle component of many rotaxanes. [24]Crown-8-ethers,[7,8] cyclodextrins,[9,10] and viologens[11] were reported to form rotaxanes with the axle molecules containing ferrocenyl stoppers. The Fe(II)/Fe(III) redox of the ferrocenyl group in the axle component of the rotaxanes is affected by the structures and relative positions of the axle and cyclic components.[7,10,11] Recently, we prepared a pseudorotaxane having an axle component with a terminal ferrocenyl group[12,13] and found a structures[14] and chemical properties.[15] Rotaxanes with ferrocene-containing cyclic components are still rare. Willner,[16] Beer,[17] and Prato[18] reported rotaxanes with ferrocenyl pendant groups in the macrocyclic component. Ferrocenophanes,[19-21] which contain a ferrocenylene group as a part of the macrocycle, have not been employed as components of rotaxanes. In this paper, we report the preparation of octaoxa[22]ferrocenophane **1** (Chart 1), having a similar structure to DB24C8, and its rotaxanes with the axle molecule containing a dialkylammonium moiety. The rotaxanes exhibit unique chemical and photochemical properties.

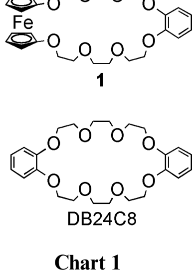

Chart 1

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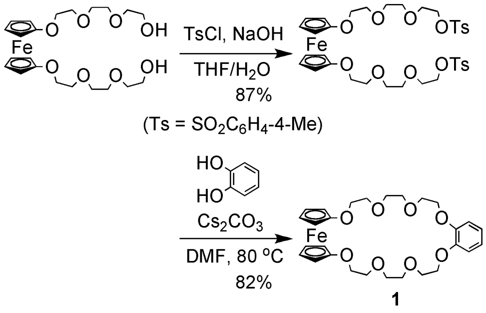
† Electronic supplementary information (ESI) available: Experimental section including characterization data for compounds. CCDC reference number 724381. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907417a

Results and discussion

Synthesis and dethreading reaction of rotaxanes

Scheme 1 summarizes the procedure for preparation of octaoxa[22]ferrocenenophane **1**. Tosylation of $Fe\{C_5H_4(OCH_2CH_2)_3OH\}_2$ and cyclizative condensation of the resultant $Fe\{C_5H_4(OCH_2CH_2)_3OTs\}_2$ (Ts = $SO_2C_6H_4$-4-Me) with *o*-catechol under dilute conditions ($[Fe\{C_5H_4(OCH_2CH_2)_3OTs\}_2]_0$ = [*o*-catechol]$_0$ = 5 mM) yield **1** in high isolated yield. Compound **1** was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and comparison of the data with oxa[*n*]ferrocenophanes ($n = 4, 7, 10, 13, 16$) and related ferrocenylene derivatives.[22] $^{13}C\{^1H\}$ NMR signals due to the CH carbons of the ferrocenylene group are observed at δ 56.1 and 62.1, and the quaternary carbon signal at δ 127.6 is broadened. Slow evaporation of an acetone/methanol solution of **1** and $KBPh_4$ caused separation of [K(**1**)]BPh_4 as single crystals, which were analyzed by X-ray crystallography. Fig. 1 shows the molecular structure of the cationic part of [K(**1**)]BPh_4 obtained by X-ray crystallography. The distance between K(1) and oxygen atoms of **1** (O(1)–O(8)) is in the range of 2.736(2)–2.927(2) Å. The two cyclopentadienyl ligands are in eclipsed positions. The dihedral angle between C(5)–O(1) and C(25)–O(8) bonds is 45°.



Scheme 1 Synthesis of **1**.

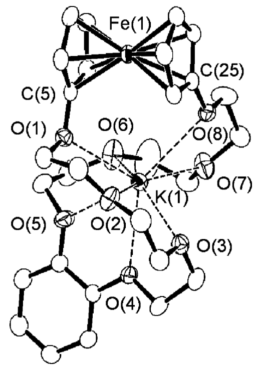


Fig. 1 Molecular structure of [K(**1**)]BPh_4. Hydrogen atoms and BPh_4^- have been omitted for clarity.

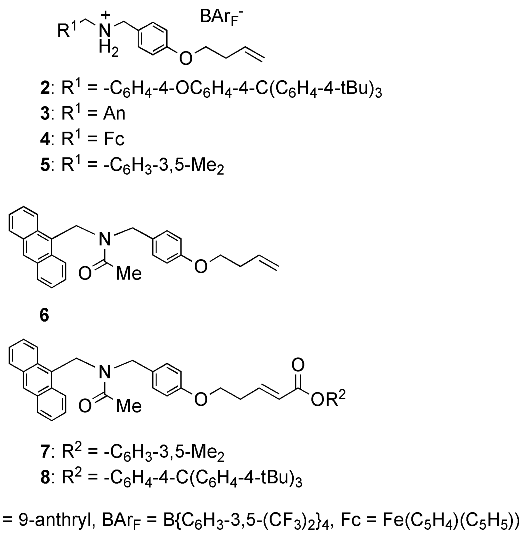
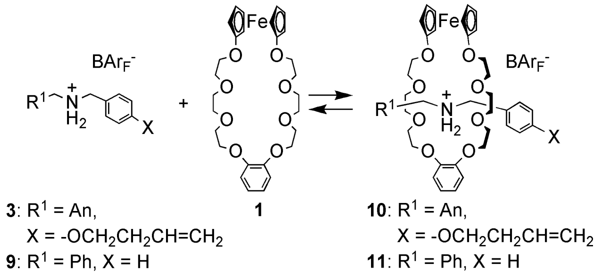


Chart 2

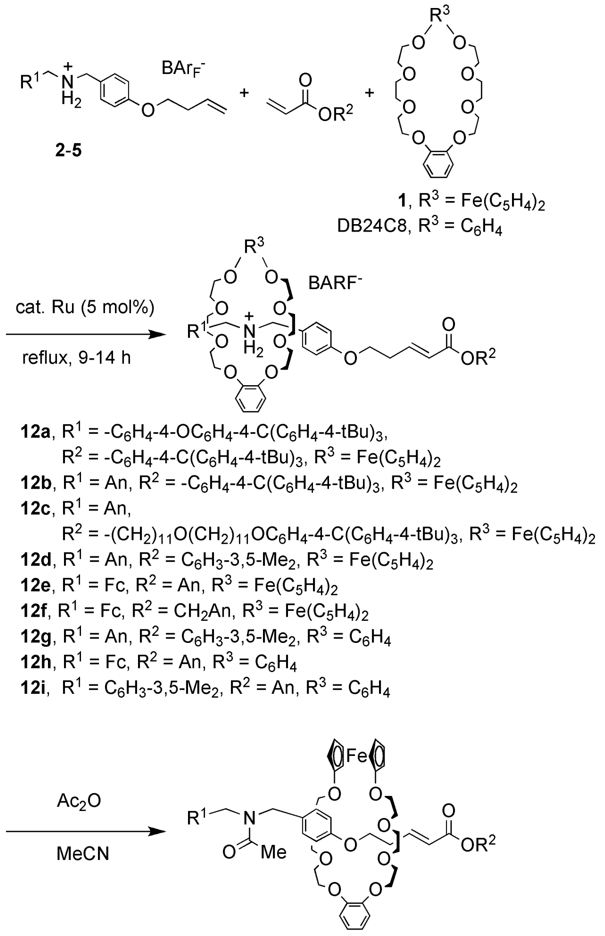
Chart 2 lists the compounds used as the axle components. Condensation of a primary amine with an aromatic aldehyde and further reduction of the imine produced with $NaBH_4$ (or $LiAlH_4$) form the dialkylamine with a bulky terminal group. Protonation of the amines produces the corresponding secondary dialkylammonium compounds $[R^1CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2](BAr_F)$ (R^1 = C_6H_4-4-OC_6H_4-4-$C(C_6H_4$-4-tBu$)_3$ (**2**), An (**3**), Fc (**4**)) (An = 9-anthryl, Fc = $Fe(C_5H_4)(C_5H_5)$, BAr_F = $B\{C_6H_3$-3,5-$(CF_3)_2\}_4$). $[(C_6H_3$-3,5-$Me_2)CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2](BAr_F)$ (**5**) was prepared from $NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ and $(C_6H_3$-3,5-$Me_2)COCl$.[7] Compounds **7** and **8** with amide groups were also prepared to compare their properties with those of the rotaxanes containing neutral molecules as the axle components (*vide infra*). *N*-acetylation of $[AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2](Cl)$, followed by cross-metathesis reaction[23] of the vinyl group of $AnCH_2N(Ac)CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ (**6**) with aryl acrylate catalyzed by $(H_2IMes)(PCy_3)Cl_2Ru{=}CHPh$ (H_2IMes = *N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) led to the amide derivatives.

Dissolution of **1** and **3** in $CDCl_3$ forms an equilibrated mixture of **1**, **3**, and their [2]pseudorotaxane **10**, as shown in Scheme 2. Fast atom bombardment mass spectrometry (FABMS) reveals a peak at $m/z = 924$, which corresponds to the cationic [2]pseudorotaxane. The ^1H NMR spectrum of the $CDCl_3$ solution formed by mixing **1** and **3** at a concentration of 5 mM for each compound contains the signals of the alkylammonium group of **10** at δ 5.08–5.24 (NCH_2), 5.64 (NCH_2), and 7.09 (NH_2). The signals of **3** (δ 4.33 (NCH_2), 5.27 (NCH_2), 6.89 (NH_2)) were almost negligible. [2]Pseudorotaxane **11** was formed from **1** and $[NH_2(CH_2Ph)_2](BAr_F)$ (**9**) in $CDCl_3$ and showed a FABMS peak at the predicted position ($m/z = 754$).



Scheme 2 Pseudorotaxane formation.

Scheme 3 shows a summary of the preparation of the [2]rotaxanes of **1** and DB24C8 with the dialkylammonium

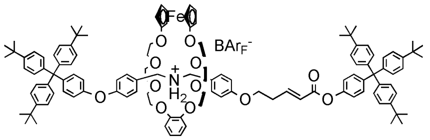
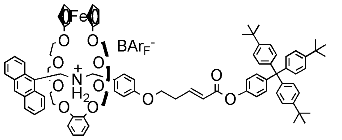
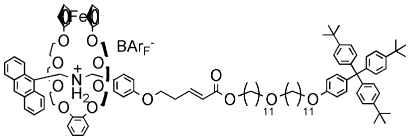
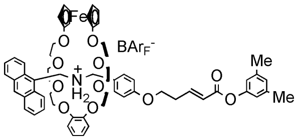
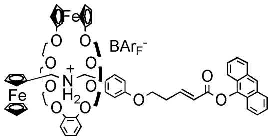
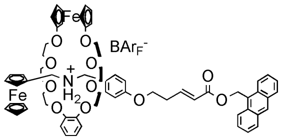
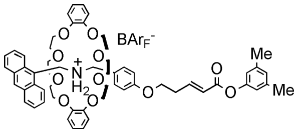
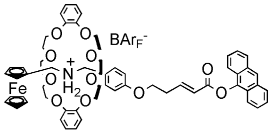
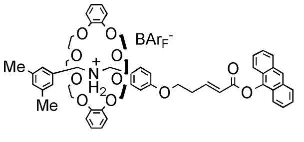


12a, $R^1 = \text{-}C_6H_4\text{-4-}OC_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$,
$R^2 = \text{-}C_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$, $R^3 = Fe(C_5H_4)_2$
12b, R^1 = An, $R^2 = \text{-}C_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$, $R^3 = Fe(C_5H_4)_2$
12c, R^1 = An,
$R^2 = \text{-}(CH_2)_{11}O(CH_2)_{11}OC_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$, $R^3 = Fe(C_5H_4)_2$
12d, R^1 = An, $R^2 = C_6H_3\text{-3,5-}Me_2$, $R^3 = Fe(C_5H_4)_2$
12e, R^1 = Fc, R^2 = An, $R^3 = Fe(C_5H_4)_2$
12f, R^1 = Fc, $R^2 = CH_2An$, $R^3 = Fe(C_5H_4)_2$
12g, R^1 = An, $R^2 = C_6H_3\text{-3,5-}Me_2$, $R^3 = C_6H_4$
12h, R^1 = Fc, R^2 = An, $R^3 = C_6H_4$
12i, $R^1 = C_6H_3\text{-3,5-}Me_2$, R^2 = An, $R^3 = C_6H_4$

13a, $R^1 = \text{-}C_6H_4\text{-4-}OC_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$,
$R^2 = \text{-}C_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$
13b, R^1 = An, $R^2 = \text{-}C_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$
13c, R^1 = An, $R^2 = \text{-}(CH_2)_{11}O(CH_2)_{11}OC_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$

Scheme 3 Synthesis of [2]rotaxanes. See Table 1 for structures of **12a–12i**.

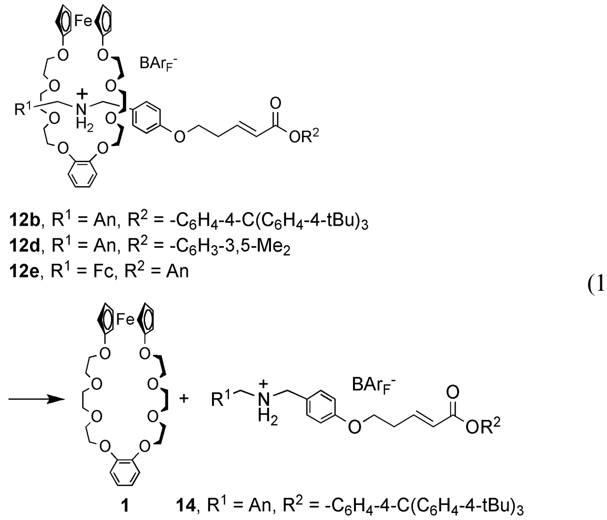
Table 1 Structure and yield of rotaxanes **12a–12i**

	Compound	Isolated yield
12a		88%
12b		65%
12c		42%
12d		64%
12e		50%
12f		44%
12g		53%
12h		52%
12i		88%

group and conversion of the cationic [2]rotaxanes into the neutral ones *via* acetylation of the axle component. The Ru-carbene-complex-catalyzed cross-metathesis reaction of **2** with $CH_2{=}CHCOOC_6H_4\text{-4-}C(C_6H_4\text{-4-}t\text{Bu})_3$ in the presence of **1** (**1** = 0.11 mmol, **2** = 0.10 mmol, $CH_2{=}CHCOOC_6H_4\text{-4-}C(C_6H_4\text{-4-}t\text{Bu})_3$ = 0.20 mmol) forms [2]rotaxane $[(\mathbf{1})(R^1CH_2NH_2CH_2C_6H_4\text{-4-}OCH_2CH_2CH{=}CHCOOR^2)](BAr_F)$ ($R^1 = C_6H_4\text{-4-}OC_6H_4\text{-4-}C(C_6H_4\text{-4-tBu})_3$, $R^2 = C_6H_4\text{-4-}C(C_6H_4\text{-4-}t\text{Bu})_3$) (**12a**) in 88% isolated yield. The FABMS peak (m/z = 1858) agrees with the molecular weight of the rotaxane. The ^{1}H NMR signals of the vinylene hydrogen atoms of the axle component show a large coupling constant (J(HH) = 16 Hz), indicating the selective formation of the selective formation of the *trans* linkage by cross-metathesis. The ^{1}H NMR signals of the NCH_2 hydrogen atoms were observed at a lower magnetic field (δ 4.51–4.58) than those of **2** (δ 4.04, 4.06), which is ascribed to the C–H$\cdots$O hydrogen bonds between the axle and the macrocyclic component.[24] Cyclopentadienyl ligands of the cyclic component show four independent $^{13}C\{^1H\}$ NMR signals for the CH carbons with equal intensity (δ 56.1, 56.4, 62.8, 62.8). This result provides additional evidence for formation of a rotaxane that contains **1** as the cyclic component. Similar reactions involving pseudorotaxane formation and end-capping of the terminal vinyl group *via* cross-metathesis produce [2]rotaxanes **12b–12i** in 42–88% isolated yields, as summarized in Table 1.

Acetylation of the ammonium groups of **12a**, **12b**, and **12c** with Ac_2O in MeCN forms neutral rotaxanes **13a** (38%), **13b** (81%), and **13c** (84%), respectively (Scheme 3).[25] The IR peaks of **13a** at 1653 cm^{-1} and of **13b** at 1651 cm^{-1} are assigned to vibration of the amide groups. The ^{1}H NMR spectrum of **13b** shows the signals of the vinylene hydrogen atoms (δ 6.43, 7.63) at lower magnetic field positions than those of **12b** (δ 6.18, 7.24–7.28), which is ascribed to shuttling of the macrocyclic component of **13a–13c** along the axle component. A similar reaction using rotaxane **12d** does not give **13d** but yields a mixture of **1** and **7** in 84 and 86% yields, respectively .

Rotaxanes **12a–12i** and **13a–13c** maintain the interlocked structures in $CDCl_3$ at room temperature, but dissolution of **12b**, **12d**, and **12e** in polar solvents (dmso-d$_6$, CD_3CN) or heating the solution in these solvents causes dethreading, as shown in eqn (1). Dissolving **12b** in CD_3CN or dmso-d$_6$ at 25 °C converts the rotaxane gradually into a mixture of the cyclic compound **1** and the dialkylammonium compound [$AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOOC_6H_4$-4-$C(C_6H_4$-4-$tBu)_3$]($BAr_F$) (**14**). The dethreading of **12d** in dmso-d$_6$ takes place rapidly at 20 °C, and the ^{1}H NMR and FABMS spectra after the reaction indicate quantitative formation of **1** and **15**. This behaviour is contrasted with that of **12g**, composed of the same axle component and DB24C8, which does not undergo dethreading, probably due to the smaller cavity size and the less flexible structure of DB24C8 compared with **1**. Fig. 2 shows profile and first-order plots of the dethreading reaction of **12d**. The reaction in dmso-d$_6$ is completed within 12 min at 20 °C ($k_{obs} = 4.9(5) \times 10^{-3}$ s^{-1}), while heating the CD_3CN solution of **12d** causes dethreading at lower rates ($k_{obs} = 1.0(1) \times 10^{-5}$ s^{-1} at 45 °C, $3.5(3) \times 10^{-5}$ s^{-1} at 60 °C, $8.9(4) \times 10^{-5}$ s^{-1} at 70 °C and $1.9(3) \times 10^{-4}$ s^{-1} at 75 °C). Kinetic parameters of the reaction in CD_3CN were determined as $\Delta G^{\ddagger}(318\ \text{K}) = 1.1(1) \times 10^2$ kJ mol^{-1}, $\Delta H^{\ddagger} = 79(5)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -91(14)$ J mol^{-1} K^{-1} from the temperature dependence of k_{obs}.



12b, R^1 = An, R^2 = -C_6H_4-4-$C(C_6H_4$-4-tBu$)_3$
12d, R^1 = An, R^2 = -C_6H_3-3,5-Me_2
12e, R^1 = Fc, R^2 = An

(1)

1
14, R^1 = An, R^2 = -C_6H_4-4-$C(C_6H_4$-4-tBu$)_3$
15, R^1 = An, R^2 = -C_6H_3-3,5-Me_2
16, R^1 = Fc, R^2 = An

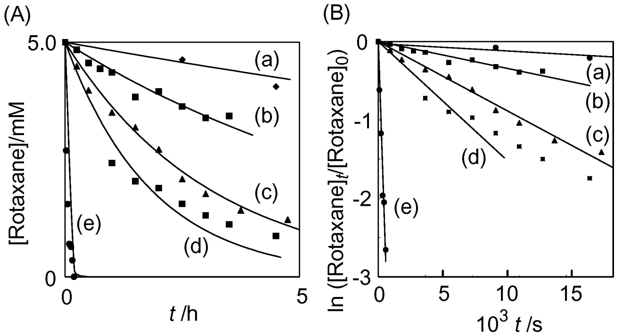


Fig. 2 (A) Profile and (B) first-order plots of the dethreading reaction of **12d** in (a) CD_3CN (45 °C), (b) CD_3CN (60 °C), (c) CD_3CN (70 °C), (d) CD_3CN (75 °C), and (e) dmso-d$_6$ (20 °C).

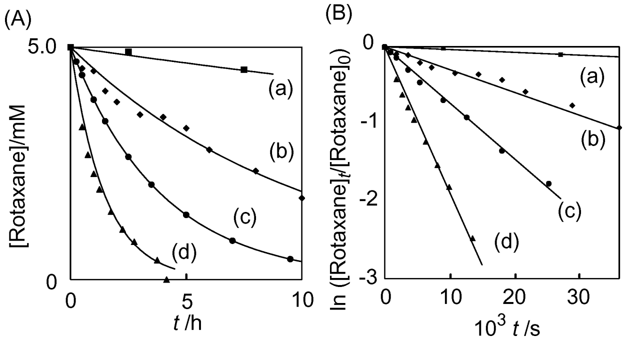


Fig. 3 (A) Profile and (B) first-order plots of the dethreading reaction of **12e** in (a) CD_3CN (25 °C), (b) dmso-d$_6$ (25 °C), (c) dmso-d$_6$ (35 °C) and (d) dmso-d$_6$ (45 °C).

The dethreading reaction of **12e** in dmso-d$_6$ ($k_{obs} = 2.7(2) \times 10^{-5}$ s^{-1} at 25 °C) is much slower than that of **12d** ($k_{obs} = 4.9(5) \times 10^{-3}$ s^{-1} at 20 °C), and complete consumption of the rotaxane requires 4 h even at 45 °C ($k_{obs} = 1.9(1) \times 10^{-4}$ s^{-1}), as shown in Fig. 3. Kinetic parameters of the reaction were determined as $\Delta G^{\ddagger}(318\ \text{K}) = 1.0(1) \times 10^2$ kJ mol^{-1}, $\Delta H^{\ddagger} = 72(1)$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -90(2)$ J mol^{-1}K^{-1} in dmso-d$_6$. The dethreading reaction in CD_3CN ($k_{obs} = 3.9(7) \times 10^{-6}$ s^{-1} at 45 °C) is slower than that in dmso-d$_6$. Observed $\Delta H^{\ddagger}$ values (**12d**: 79(5) kJ mol^{-1} in CD_3CN, **12e**: 72(1) kJ mol^{-1} in dmso-d$_6$) are smaller than those of the dethreading reaction of the rotaxane composed of DB24C8 and the axle molecule with tBu end groups ($\Delta H^{\ddagger}$ = 85–100 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −9 to −79 J mol^{-1}K^{-1}). The large negative activation enthalpy for the latter reaction was ascribed to the less favorable conformational change during the slippage of DB24C8 over the end groups.[26]

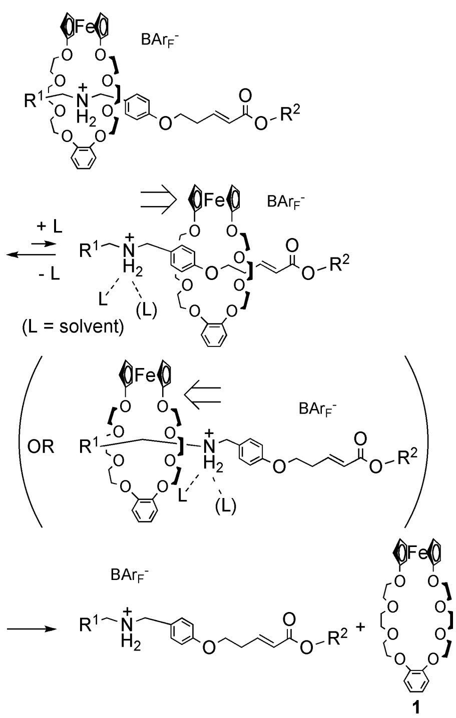
Table 2 shows a summary of the results of the kinetic study of the reactions. Dethreading reactions of **12a** and **13a** are not observed in CD_3CN or in dmso-d$_6$ during 4 d at 25 °C, probably because of the sterically bulky $C(C_6H_4$-4-tBu$)_3$ end groups of the axle components. Rotaxane **12b** undergoes dethreading in both solvents but more slowly than **12d** and **12e**. The dethreading of **13b**, having the same end group as **12b**, does not occur at all at 25 °C and requires heating for 20 h at 60 °C, although interaction between the two components of **13b** is weaker than the hydrogen bonding between the axle and cyclic components of **12b**.

A plausible mechanism of the dethreading reaction is shown in Scheme 4. Initial activation of hydrogen bonds between oxygen atoms in the cyclic component and NH_2^+ and CH_2 hydrogen atoms in the axle and sliding of the macrocycle to a neutral part of the axle component form an intermediate. It is enhanced by coordination of the polar solvent molecules to the NH_2^+ group. Subsequent slippage of the macrocyclic component over R^1 or R^2 end group leads to the dethreading. Dissolving the rotaxanes **12b**, **12d**, and **12e** in dmso-d$_6$ or in CD_3CN does not show the ^{1}H NMR signals assigned to the intermediate rotaxanes for dethreading, which indicates a pre-equilibration involving coordination of solvent to

Table 2 Kinetic rate constants, k_{obs}, of the dethreading reaction of rotaxanes[a]

Compound	Solvent	T/°C	k_{obs}/s^{-1}
12a	CD_3CN	25	[b]
	dmso-d_6[c]	25	[b]
12b	CD_3CN	25	$1.3(3) \times 10^{-7}$
	dmso-d_6	25	$4.3(2) \times 10^{-6}$
12d	CD_3CN	45	$1.0(1) \times 10^{-5}$
	dmso-d_6	20	$4.9(5) \times 10^{-3}$
12e	CD_3CN	45	$3.9(7) \times 10^{-6}$
	dmso-d_6	25	$2.7(2) \times 10^{-5}$
12g	dmso-d_6	25	[b]
12i	dmso-d_6	25	[b]
13a	CD_3CN[c]	25	[b]
	dmso-d_6[c]	25	[b]
13b	CD_3CN[c]	25	[b,d]
	dmso-d_6	25	[b,e]

[a] [Compound]$_0$ = 5.0 mM. [b] Dethreading is not observed (^{1}H NMR spectrum of rotaxane solution does not change for 4 d). [c] A part of the rotaxane remains undissolved. [d] Complete dethreading was observed after heating for 8 h at 60 °C. [e] Complete dethreading was observed after heating for 20 h at 60 °C.



Scheme 4 Plausible mechanism of dethreading reaction.

NH_2 and the shuttling of the crown ether, which is fast on the NMR timescale.

Stoddart *et al.* reported that the dethreading reaction of rotaxane composed of dibenzometaphenylene[25]crown-8-ether (DMP25C8) and [tBuC$_6$H$_4$-4-CH$_2$NH$_2$CH$_2$C$_6$H$_4$-4-CH$_2$PPh$_3$](PF$_6$)$_2$ was the passing of the crown ether over the end group ($\Delta G^‡$(298 K) = 109 kJ mol^{-1}, $\Delta H^‡$ = 66 kJ mol^{-1}, and $\Delta S^‡$ = −146 J mol^{-1}K^{-1} in CD_3CN). The large negative $\Delta S^‡$ value was ascribed to the limited conformations possible for the crown ether to pass over the end group and the solvation of polar solvent during the shuttling of the macrocyclic component.[26a] Similar thermodynamic parameters of the dethreading reaction of **12d** in CD_3CN ($\Delta G^‡$(318 K) = $1.1(1) \times 10^2$ kJ mol^{-1}, $\Delta H^‡$ = 79(5) kJ mol^{-1}, and $\Delta S^‡$ = −91(14) J mol^{-1}K^{-1}) suggests a similar transition state for dethreading in this study.

Photochemical and electrochemical properties

Fluorescence resonance energy transfer (FRET) was reported for the organic rotaxanes containing cumarines, naphthalenes, and anthracenes because of close contact of the fluorescent group in one component with the functional group with lower energy orbitals in the other within the rotaxane framework.[27–29] Combination of the energy transfer in the rotaxane with the molecular shuttling was applied to clear switching for the fluorescence.[28,29] Typically, a Ru(bpy)$_3$ unit in the axle component of a rotaxane changes its optical properties depending on the distance from the functional groups in the cyclic component. Ferrocene derivatives act as a fluorescent quencher of photoexcited organic species,[30] and they serve as the electron acceptor from viologen,[11] bis(phenanthroline)copper,[31] and the photoexcited state of C_{60} within the rotaxane framework.[8,18] We conducted TD-DFT calculations of the triplet energy level of [AnCH$_2$NH$_2$CH$_2$Ph]$^+$ and AnCH$_2$N(Ac)CH$_2$Ph, respective model compounds of **2** and **8**, to elucidate details of interaction between the functional groups in the rotaxanes in Table 1. The energies between the orbitals, 14 300 and 14 100 cm^{-1}, are consistent with the energy transfer reaction rather than the electron transfer (*vide infra*). Table 3 shows summary of the absorption and fluorescent properties of the rotaxanes and the component molecules. The rotaxanes **12b–12i**, **13b** and **13c**, and the axle compounds and their precursors **3** and **6–8** show the characteristic absorption due to the 9-anthryl terminal group at λ_{max} = 366–372 nm with molar absorption coefficient of ε = 6900–13 200 M^{-1}cm^{-1}. Excitation at respective λ_{max}(absorption), corresponding to π–π* transitions of the anthryl group, causes emission at wavelength lower than 400 nm. Compound **1** shows weak absorption due to ferrocene at λ_{max} = 437 nm and is not

Table 3 Photochemical data on compounds

	Absorption[a]		Emission[b]	
Compound	λ_{max}/nm	ε/M^{-1}cm^{-1}	λ_{max}/nm	ϕ[c]
1	437[d]	60[d]	—	—
3	371	7600	423	0.56
6	368	10 200	418	0.309
7	368	9400	418	0.337
8	368	10 700	418	0.344
12b	372	6900	419	0.012
12c	373	7100	414	0.0043
12d	372	7000	420	0.043
12e	366	8800	417	0.0010
12f	367	8900	414	0.024
12g	372	7100	424	0.73
12h	366	11 200	415	0.0008
12i	366	13 200	414	0.0046
13b	368	9800	418	0.030
13c	369	9600	418	0.097
1 + 3	372	7100	422	0.34
1 + 8	368	11 400	418	0.33
CH_2=CHCO$_2$An	366	7800	418	0.0047
CH_2=CHCO$_2$CH$_2$An	367	8400	416	0.24

[a] [Compound] = 1.0×10^{-2} mM, CHCl$_3$, 25 °C. [b] [Compound] = 2.0×10^{-3} mM, CHCl$_3$, 25 °C, λ_{ex} = λ_{max}(absorption). [c] Quantum yield. [d] [**1**] = 1.0 mM, CHCl$_3$, 25 °C.

responsible for the emission of the rotaxanes. Addition of **1** to a solution of **3** decreases emission intensity of **3** from $\phi = 0.56$ to $\phi = 0.34$. This change can be attributed to quenching of the fluorescence of the anthryl group by the ferrocenyl end group, which absorbs in a lower energy region than the emission.[30,32]

The ferrocenylene group of the rotaxanes **12b–12f** and **13b–13c** quenches the fluorescence of the 9-anthryl stopper of the axle molecule. Fig. 4(A) shows the UV-vis spectra of $CHCl_3$ solutions of **8**, **12b**, **13b**, and **13c** for comparison which show characteristic structural bands of the anthracene chromophoric unit with similar intensities. Emission spectra of the compounds upon excitation at the corresponding wavelength of maximum absorption (Fig. 4(B)) differ among these compounds. Intensity of emission of **8** ($\phi = 0.344$) is significantly higher than that of rotaxane **13b** ($\phi = 0.030$) and an equimolar mixture of **1** and **8** showed an emission spectrum with a quantum yield ($\phi = 0.33$) similar to that of **8** ($\phi = 0.344$). The quantum yield of fluorescence of the cationic rotaxane **12b** ($\phi = 0.012$) is lower than that of neutral rotaxane **13b** ($\phi = 0.030$). The degree of quenching is less significant in rotaxane **13c** ($\phi = 0.097$) having longer axle component. A similar decrease in emission from the anthryl unit was observed in rotaxanes **12d** ($\phi = 0.043$), **12e** ($\phi = 0.0010$), **12f** ($\phi = 0.024$), and **12h** ($\phi = 0.0008$), which are compared with those of CH_2CHCO_2An ($\phi = 0.0047$) and $CH_2CHCO_2CH_2An$ ($\phi = 0.24$). The decrease in emission from the anthracene unit is not observed for **12g** ($\lambda_{max} = 424$ nm, $\phi = 0.73$), which has DB24C8 as its macrocyclic component.

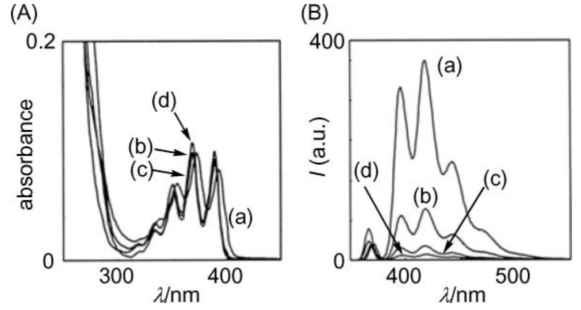


Fig. 4 (A) UV-vis spectra ([compound] = 1.0×10^{-2} mM) and (B) emission spectra ([compound] = 2.0×10^{-3} mM, $\lambda_{ex} = \lambda_{max}$(absorption)) of $CHCl_3$ solution of (a) **8**, (b) **13c**, (c) **13b**, and (d) **12b**.

The interlocked structure of **12b** fixes the distance between the ferrocenyl and anthryl groups within the range of effective quenching. Previous studies revealed the quenching pathway of the excited anthracene with the ferrocene group *via* dominant energy transfer mechanisms[30,33] rather than electron transfer reactions.[34] Herkstroester and Kikuchi suggest that ferrocene behaves as a non-luminescent energy acceptor, at least when the organic triplet energy level is higher than 15 000 ± 1000 cm^{-1}, while a triplet with a level lower than 13 000 cm^{-1} would be quenched by another pathway, such as electron transfer reaction. The quenching of fluorescence by the rotaxanes in this study may be attributed to the energy transfer reaction from the photoexcited anthryl group to the ferrocenylene unit in **1** rather than to an electron transfer reaction. The quenching of rotaxane **12b** is more efficient than that of **13b** and **13c** because of strong hydrogen bonds between the macrocyclic component and the ammonium moiety of **12b** and of the closer position of the anthryl and ferrocenylene groups in the former rotaxane than in the latter. The partial quenching of **3** by mixing with **1** is attributed to partial formation of [2]pseudorotaxane **10** in solution and an intrarotaxane energy transfer reaction. The association constant for the formation of pseudorotaxane **10** is estimated to be 6×10^5 M^{-1} at 25 °C by fluorescent spectroscopy on the basis of assumptions that pseudorotaxane **10** is non-luminescent owing to intrarotaxane quenching.[32]

Table 4 Electrochemical data on ferrocene compounds[a]

Compound	E_{pa}/V	E_{pc}/V	$E_{1/2}$ $(\Delta E)^b$/V
1	–0.07	–0.13	–0.10 (0.06)
1^c	0.02	–0.10	–0.04 (0.12)
4	0.32	0.25	0.29 (0.07)
12a^c	0.11	–0.10	0.05 (0.12)
12b	0.01	–0.07	–0.03 (0.08)
12c^c	–0.07	–0.17	–0.12 (0.10)
12d	0.02	–0.05	–0.02 (0.06)
12e^d	0.05, 0.37	–0.03, 0.29	0.01, 0.33 (0.08, 0.08)
12f^d	0.05, 0.37	–0.02, 0.30	0.02, 0.34 (0.07, 0.07)
12h	0.30	0.24	0.27 (0.06)
13a^c	0.02	–0.08	–0.03 (0.10)
13b	–0.06	–0.15	–0.11 (0.09)
13c	–0.16	–0.27	–0.22 (0.11)
Ferrocene	0.14	0.07	0.11 (0.07)

[a] Electrochemical results are obtained by cyclic voltammetry in MeCN containing nBu_4NPF_6 as the electrolyte. Potentials are referenced to Ag^+/Ag. Sweep rate: 0.10 V s^{-1}. [b] $\Delta E = E_{pa} - E_{pc}$. [c] In CH_2Cl_2. [d] Two-steps redox.

The redox potentials of the ferrocene-containing compounds are summarized in Table 4. Redox peaks of the ferrocenylene unit in the macrocyclic molecule of the cationic rotaxanes (**12b**, **12d–12f**) were observed at higher potentials ($E_{1/2}$ = –0.03 to +0.02 V, *vs.* Ag^+/Ag) than those of the neutral rotaxane ($E_{1/2}$ = –0.03 (**13a**), –0.11 (**13b**) V) and of **1** ($E_{1/2}$ = –0.10 V) in MeCN. Fe(II)/Fe(III) redox in the ferrocenylmethylammonium group of **4**, **12e**, **12f**, and **12h** was observed in the range of $E_{1/2}$ = +0.27 to +0.34 V. The redox peak positions of terminal ferrocenyl groups in **12e**, **12f**, and **12h** were similar to those reported for ferrocene containing [2]- and [3]rotaxanes.[15] Fig. 5 shows cyclic voltammograms of **1**, **4**, and **12e**. Two redox peaks of **12e** are observed, as shown in Fig. 5(C). Both oxidations ($E_{1/2}$ = 0.01, 0.33 V) were observed at higher potentials than in **1** and **4**. The redox potential of **12e** does not change significantly (E_{pc}: 0.046 ± 0.004, 0.366 ± 0.006 V, E_{pa}: 0.029 ± 0.004, 0.288 ± 0.003 V) in the range of scan rates from 0.01 to 1.0 V s^{-1}. These shifts in oxidation potential of the second ferrocene unit are attributed to the positive charge of the ferrocenium ion formed by the initial electrochemical oxidation, similarly to other supramolecular systems.[35,36]

Conclusions

In this paper, we present the synthesis and properties of rotaxanes containing macrocyclic compound **1** equipped with a ferrocenylene group. The compound of **1** with a slightly larger ring size and more flexible conformation than DB24C8 allows dethreading of the rotaxane having anthryl and ferrocenyl end groups in the polar solvents. The ferrocenylene group in the cyclic component of rotaxane works as a quencher of fluorescence from the excited anthryl group in the axle component. The efficiency

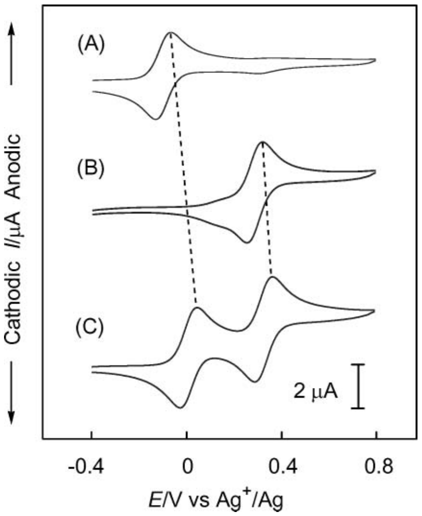


Fig. 5 Cyclic voltammograms of (A) **1**, (B) **4**, and (C) **12e** in MeCN (1.0 mM) containing 0.10 M nBu_4NPF_6.

of the quenching varies depending on the co-conformation of the component molecules of the rotaxane.

Experimental

General

Dried solvents were purchased from Kanto Chemical Co., Inc. NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{1}H-^{1}H COSY, ^{13}C{^{1}H}-^{1}H COSY, DEPT, NOESY) were recorded on Varian MERCURY300 and JEOL EX-400 spectrometers. $Fe\{C_5H_4(OCH_2CH_2)_3OH\}_2$,[36] $H_2NCH_2C_6H_4OCH_2CH_2CH{=}CH_2$,[37] ($C_6H_4$-4-*t*Bu)$_3CC_6H_4$-4-OH,[38] 3,5-dimethylphenyl acrylate,[39] NaBAr$_F$ (BAr$_F$ = B{$C_6H_3(CF_3)_2$-3,5}$_4$),[40] [$NH_2(CH_2Ph)_2$](BAr$_F$),[41] and [FcCH_2-$NH_2C_6H_4OCH_2CH_2CH{=}CH_2$](Cl)[15] were prepared by the literature method. Other chemicals were commercially available. Cyclic voltammetry (CV) was measured in MeCN solution containing 0.10 mM ^{n}Bu$_4$NPF$_6$ 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-disk working electrode (ID: 1.6 mm). The absorption spectra were recorded using a JASCO V-530 UV-vis spectrometer as 1.0×10^{-5} M solution in MeCN. Photoluminescence spectra were recorded as 2.0×10^{-6} M solutions in MeCN. Quantum yields were estimated by comparison of standard solution of quinine sulfate (1.0 M, $\phi = 0.546$). Fast atom bombardment mass spectrum (FABMS) was obtained from JEOL JMS-700 (matrix, 2-nitrophenyloctylether). Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder.

$Fe\{C_5H_4(OCH_2CH_2)_3OTs\}_2$ (Ts = $SO_2C_6H_4$Me-4)

NaOH (0.10 g, 2.5 mmol) and TsCl (0.20 g, 1.0 mmol) was added to a solution (THF–H_2O = 1.0 cm^3 : 0.1 cm^3) of $Fe\{C_5H_4(OCH_2CH_2)_3OH\}_2$ (0.19 g, 0.39 mmol) at room temperature. The solution was stirred for 14 h at room temperature followed by addition of water and extraction of the product with CH_2Cl_2. The separated organic phase was dried over $MgSO_4$, filtered, and evaporated to give crude product as yellow oil. Purification by SiO_2 column chromatography (eluent: hexane–AcOEt 1 : 1) give $Fe\{C_5H_4(OCH_2CH_2)_3OTs\}_2$ as yellow oil (0.27 g, 0.34 mmol, 87%) (found: C 53.52, H 5.84, S 7.77. $C_{36}H_{46}O_{12}S_2Fe(H_2O)$ requires C 53.46, H 5.98, S 7.93%). δ_H(300 MHz; $CDCl_3$; r.t.) 2.43 (6 H, s, CH_3), 3.60 (8 H, m, CH_2), 3.68 (8 H, m, CH_2), 3.80-4.45 (8 H, C_5H_4), 3.93 (4 H, m, CH_2), 4.15 (4 H, m, CH_2), 7.33 (4 H, d, J = 8 Hz, C_6H_4) and 7.78 (4 H, d, J = 8 Hz, C_6H_4). δ_C(100 MHz; $CDCl_3$; r.t.) 21.5 (CH_3), 55.4 (C_5H_4), 63.1 (C_5H_4), 68.5 (CH_2), 69.1 (CH_2), 69.5 (CH_2), 69.7 (CH_2), 70.4 (CH_2), 70.5 (CH_2), 127.7 (C_6H_4), 129.6 (C_6H_4), 132.7 (C_6H_4) and 144.6 (C_6H_4). The signal of quaternary carbon of C_5H_4 ligand was not observed clearly probably due to overlapping with the signal at 127.7 ppm. R_f 0.20 (hexane–AcOEt 1 : 1).

Compound 1

A DMF solution (36 cm^3) containing $Fe\{C_5H_4(OCH_2CH_2)_3OTs\}_2$ (0.22 g, 0.28 mmol) and *ortho*-catechol (31 mg, 0.28 mmol) was added dropwise to the DMF suspension (18 cm^3) of Cs_2CO_3 (0.91 g, 2.8 mmol) at 80 °C for 1 h. The resulting solution was stirred for 3 d at 80 °C followed by evaporation. The obtained brown oil was dissolved in CH_2Cl_2 and the solution was washed with saturated NH_4Cl (aq). The separated organic phase was dried over $MgSO_4$, filtered and evaporated to form yellow oil. The crude product was purified by SiO_2 column chromatography (eluent: hexane/AcOEt 1:1) and HPLC (eluent: $CHCl_3$) to give **1** was brown oil (0.13 g, 0.23 mmol, 82%) (found: C 59.79, H 6.98. $C_{28}H_{36}FeO_8(H_2O)_{0.5}$ requires C 59.48, H 6.60%). δ_H(300 MHz; $CDCl_3$; r.t.) 3.70–7.85 (12 H, m, CH_2), 3.86 (4 H, br s, C_5H_4), 3.91 (4 H, m, CH_2), 4.01 (4 H, m, CH_2), 4.13 (4 H, br, C_5H_4), 4.17 (4 H, m, CH_2) and 6.91 (4 H, C_6H_4). δ_H(100 MHz; $CDCl_3$; r.t.) 56.1 (C_5H_4), 62.1 (C_5H_4), 69.3 (CH_2), 69.9 (CH_2), 69.9 (2 C, CH_2), 70.8 (CH_2), 71.0 (CH_2), 114.7 (C_6H_4), 121.5 (C_6H_4), 127.6 (C_5H_4) and 149.0 (C_6H_4); *m/z* (FAB) 556 (M$^+$. $C_{28}H_{36}FeO_8$ requires 556); R_f 0.25 (hexane–AcOEt = 1 : 1).

[(C_6H_4-4-*t*Bu)$_3$CC_6H_4-4-OC_6H_4-4-$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](BAr$_F$) (2)

To an Et_2O (7.0 cm^3) solution of [(C_6H_4-4-*t*Bu)$_3$CC_6H_4-4-OC_6H_4-4-$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](Cl) (0.24 g, 0.30 mmol) was added NaBAr$_F$ (0.27 g, 0.30 mmol), and the mixture was stirred for 11 h at room temperature. The precipitated salt was removed by filtration. Evaporation of filtrate gave **2** as a white solid, which was washed with hexane and dried under reduced pressure (0.44 g, 0.27 mmol, 90%) (found: C 63.37, H 4.81, N 0.87. $C_{87}H_{76}BF_{24}NO_2(H_2O)_{0.5}$ requires C 63.59, H 4.72, N 0.85%). δ_H(300 MHz; $CDCl_3$; r.t.) 1.31 (27 H, s, CH_3), 2.54 (2 H, dt, J = 7 and 7 Hz, CH_2CH=CH_2), 3.99 (2 H, t, J = 7 Hz, OCH_2), 4.04 (2 H, s, NCH_2), 4.06 (2 H, s, NCH_2), 5.12 (1 H, dd, J = 10 and 2 Hz, *cis*-CH=CH_2), 5.17 (1 H, dd, J = 17 and 2 Hz, *trans*-CH=CH_2), 5.87 (1 H, ddt, J = 17, 10 and 7 Hz, C*H*=CH_2), 6.90–6.93 (4 H, C_6H_4), 7.05–7.12 (4 H, C_6H_4), 7.10 (6 H, d, J = 8 Hz, ^{t}BuC$_6H_4$), 7.18 (2 H, d, J = 9 Hz, C_6H_4), 7.23–7.28 (2 H, C_6H_4), 7.26 (6 H, d, J = 8 Hz, ^{t}BuC$_6H_4$), 7.53 (4 H, s, *para*-C_6H_3) and 7.72 (8 H, br s, *ortho*-C_6H_3). δ_C(100 MHz; $CDCl_3$; r.t.) 31.4 (CH_3), 33.4 (CH_2CH=CH_2), 34.4 (*C*(CH_3)$_3$), 51.8 (NCH_2), 52.1 (NCH_2), 63.4 (*C*(^{t}BuC$_6H_4$)$_3$), 67.5 (OCH_2), 116.0, 117.4 (CH_2CH=*C*H_2), 117.5

(*para*-C_6H_3), 118.4, 119.1 119.2, 121.4, 124.1 (^{t}BuC_6H_4), 124.5 (q, CF_3, *J*(CF) 271), 128.4–129.3 (m, *C*CF_3), 130.6 (^{t}BuC_6H_4), 130.8, 132.9, 133.7, 134.7 (*ortho*-C_6H_3), 143.6, 144.1, 148.6, 152.8, 160.3, 161.1, 161.5 (q, CB, *J*(CB) = 50 Hz).

[$AnCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2$]($BAr_F$) (3)

$AnCH{=}NC_6H_4OCH_2CH_2CH{=}CH_2$ (0.50 g, 1.4 mmol) was dissolved in MeOH (10 cm^3) at room temperature. $NaBH_4$ (0.42 g, 11 mmol) was added to the solution in one portion and the mixture was stirred for 11 h at room temperature. After quenching the mixture with 4 M HCl (aq) (30 cm^3) and further stirring for 1 h caused the separation of [$AnCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2$](Cl) as a yellow solid from the solution. The solid product was collected by filtration, washed (Et_2O, water), and dried under reduced pressure (0.38 g, 0.94 mmol, 67%). To an Et_2O (15 cm^3) suspension of obtained [$AnCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2$](Cl) (0.26 g, 0.64 mmol) was added $NaBAr_F$ (0.57 g, 0.64 mmol), and the mixture was stirred for 14 h at room temperature. The precipitated salt was removed by filtration. Evaporation of the filtrate gave crude **3** as yellow oil, which is extracted with Et_2O and CH_2Cl_2, followed by evaporation to dryness. The product was extracted again with CH_2Cl_2 and the solution was filtered, evaporated. The crude product was washed with hexane to give **3** as pale-yellow solid (0.69 g, 0.56 mmol, 88%) (found: C 55.87, H 3.41, N 1.22. $C_{58}H_{38}BF_{24}NO(H_2O)$ requires C 55.74, H 3.23, N 1.12%). δ_H(300 MHz; $CDCl_3$; r.t.) 2.58 (2 H, dt, *J* = 7 and 7 Hz, OCH_2CH_2), 4.05 (2 H, t, *J* = 7 Hz, OCH_2), 4.33 (2 H, m, $NH_2CH_2C_6H_4$), 5.14 (1 H, d, *J* = 11 Hz, =CH_2), 5.18 (1 H, d, *J* = 17 Hz, =CH_2), 5.27 (2 H, m, NH_2CH_2An), 5.89 (1 H, ddt, *J* = 17, 11 and 7 Hz, C*H*=CH_2), 6.89 (2 H, br s, NH_2), 7.02 (2 H, d, *J* = 8 Hz, C_6H_4), 7.26 (2 H, d, *J* = 8 Hz, C_6H_4), 7.49 (4 H, s, *para*-C_6H_3), 7.46–7.61 (4 H, H2-An, H3-An), 7.68 (2 H, H1-An), 7.71 (8 H, br s, *ortho*-C_6H_3), 8.12 (2 H, dd, *J* = 9 and 2 Hz, H4-An) and 8.67 (1 H, s, H10-An). δ_C(100 MHz; $CDCl_3$; r.t.) 33.4 (OCH_2CH_2), 44.4 (NCH_2An), 53.5 (N$CH_2C_6H_4$), 67.7 (OCH_2), 116.4 (C_6H_4), 117.2, 117.4 (=CH_2), 117.5 (*para*-C_6H_3), 119.0, 119.5 (C1-An), 124.5 (quintet, *J*(FC) = 271 Hz, CF_3), 126.0 (C2-An or C3-An), 128.8 (quintet, *J*(FC) = 29 Hz, CF_3C), 129.5 (C2-An or C3-An), 130.0, 130.7 (C4-An), 130.9 (C_6H_4), 131.2, 132.5 (C10-An), 133.7 (*C*H=CH_2), 134.8 (*ortho*-C_6H_3), 161.5 (C_6H_4) and 161.5 (quintet, *J*(BC) = 50 Hz, BC). δ_F(282 MHz; $CDCl_3$; r.t.) –62.7 (CF_3).

[$FcCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2$]($BAr_F$) (4)

To an Et_2O (15 cm^3) suspension of [$FcCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2$](Cl) (0.26 g, 0.64 mmol) was added $NaBAr_F$ (0.57 g, 0.64 mmol), and the mixture was stirred for 11 h at room temperature. The precipitated salt was removed by filtration. Evaporation of the filtrate gave crude **4** as yellow oil, which is extracted with Et_2O and CH_2Cl_2, followed by evaporation to dryness to give **4** as pale-yellow oil (0.72 g, 0.58 mmol, 71%) (found: C 52.83, H 3.58, N 1.16. $C_{54}H_{38}BF_{24}NO(H_2O)_2$ requires C 53.18, H 3.47, N 1.15%). δ_H(400 MHz; $CDCl_3$; r.t.) 2.52 (2 H, dt, *J* = 7 and 6 Hz, OCH_2CH_2), 3.97 (2 H, t, *J* = 6 Hz, OCH_2), 4.02 (2 H, br s, C_5H_4), 4.03 (2 H, br s, C_5H_4), 4.15 (5 H, s, C_5H_5), 4.18 (2 H, m, NCH_2), 4.31 (2 H, m, NCH_2), 5.09 (2 H, d, *J* = 10 Hz, =CH_2), 5.11 (2 H, d, *J* = 17 Hz, =CH_2), 5.85 (1 H, ddt, *J* = 17, 10 and 7 Hz, C*H*=CH_2), 6.90 (2 H, d, *J* = 9 Hz, C_6H_4), 7.09 (2 H, d, *J* = 8 Hz, C_6H_4), 7.52 (4 H, s, *para*-C_6H_3) and 7.70 (8 H, br s, *ortho*-C_6H_3). δ_C(100 MHz; $CDCl_3$; r.t.) 33.4 (OCH_2CH_2), 54.0 (NCH_2), 56.2 (NCH_2), 67.5 (OCH_2), 69.4 (C_5H_5), 70.3 (C_5H_4), 71.0 (C_5H_4), 72.7 (*ipso*-C_5H_4), 115.9 (C_6H_4), 117.4 (=CH_2), 117.5 (*para*-C_6H_3), 119.4, 124.5 (quintet, *J*(FC) = 271 Hz, CF_3), 128.8 (quintet, *J*(FC) = 35 Hz, *C*CF_3), 131.2 (C_6H_4), 133.7 (*C*H=CH_2), 134.7 (*ortho*-C_6H_3), 160.8 (C_6H_4) and 161.8 (quintet, *J*(BC) = 50 Hz, BC).

[(C_6H_3-3,5-Me_2)-$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](BAr_F) (5)

To a methanol solution (10 cm^3) of (C_6H_3-3,5-Me_2)-$CH_2NHCH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ (1.6 g, 5.0 mmol) was added 4 M HCl (aq) (30 cm^3). The stirring the mixture for 1 h at room temperature causes separation of crude product from the solution. The solid product was collected by filtration and washed with Et_2O and dried under reduced pressure to give [(C_6H_3-3,5-Me_2)-$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](Cl) as a white solid (0.28 g, 0.84 mmol, 84%). δ_H(300 MHz; $CDCl_3$; r.t.) 2.29 (6 H, s, CH_3), 2.47 (2 H, dt, *J* = 7 and 7 Hz, C*H*$_2$CH=CH_2), 3.76 (4 H, m, NCH_2), 3.87 (2 H, t, OCH_2), 5.08–5.17 (2 H, CH=C*H*$_2$), 5.84 (1 H, ddt, *J* = 17, 11 and 7 Hz, C*H*=CH_2), 6.85 (2 H, d, *J* = 9 Hz, C_6H_4), 6.95 (1 H, s, *para*-C_6H_3), 7.09 (2 H, s, *ortho*-C_6H_3), 7.40 (2 H, d, *J* = 9 Hz, C_6H_4) and 10.06 (2 H, br s, NH_2). δ_C(100 MHz; $CDCl_3$; r.t.) 21.3 (CH_3), 33.5 ($CH_2CH{=}CH_2$), 48.1 (NCH_2), 48.4 (NCH_2), 67.1 (OCH_2), 114.8, 117.0 ($CH_2CH{=}CH_2$), 122.0, 127.9, 129.8, 130.8, 131.8, 134.1, 138.6 and 159.4. To an Et_2O (15 cm^3) solution of [(C_6H_3-3,5-Me_2)-$CH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](Cl) (0.20 g, 0.64 mmol) was added $NaBAr_F$ (0.57 g, 0.64 mmol), and the mixture was stirred for 12 h at room temperature. The precipitated salt was removed by filtration. Evaporation of filtrate gave **5** as a white solid which was washed with hexane and dried under reduced pressure (0.25 g, 0.22 mmol, 34%) (found: C 52.97, H 3.58, N 1.20. $C_{52}H_{38}BF_{24}NO(H_2O)$ requires C 53.03, H 3.42, N 1.19%). δ_H(300 MHz; $CDCl_3$; r.t.) 2.28 (6 H, s, CH_3), 2.55 (2 H, dt, *J* = 7 and 7 Hz, C*H*$_2$CH=CH_2), 3.99 (2 H, t, OCH_2), 4.02 (2 H, m, NCH_2), 4.06 (2 H, m, NCH_2), 5.10–5.20 (2 H, CH=C*H*$_2$), 5.87 (1 H, ddt, *J* = 17, 11 and 7 Hz, C*H*=CH_2), 6.81 (2 H, d, *J* = 9 Hz, C_6H_4), 7.11 (2 H, d, *J* = 9 Hz, C_6H_4), 7.13 (1 H, s, *para*-$C_6H_3(CF_3)_2$), 7.52 (4 H, s, *para*-$C_6H_3(CF_3)_2$) and 7.70 (8 H, m, *ortho*-C_6H_3). δ_C(100 MHz; $CDCl_3$; r.t.) 21.0 (CH_3), 33.4 ($CH_2CH{=}CH_2$), 52.3 (NCH_2), 52.4 (NCH_2), 67.5 (OCH_2), 116.0, 117.3 ($CH_2CH{=}CH_2$), 117.5 (*para*-C_6H_3), 120.4, 124.5 (q, *J*(FC) = 271 Hz, CF_3), 126.5, 127.8, 128.8 (q, *J*(FC) = 31 Hz, *C*CF_3), 130.7, 132.9, 1337, 134.7, 140.4, 161.1, 161.6 (q, *J*(BC) = 50 Hz, BC).

$AnCH_2N(Ac)CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$ (6)

To a solution of [$AnCH_2NH_2CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CH_2$](Cl) (1.5 g, 3.8 mmol) in MeCN (150 cm^3) were added Et_3N (2.5 cm^3, 19 mmol) and acetic anhydride (1.8 cm^3, 19 mmol), and the reaction mixture was stirred for 12 h at 60 °C. After the removal of the solvent by evaporation, the product was dissolved in CH_2Cl_2 and the organic layer was washed with water, dried over $MgSO_4$. Removal of solvent by evaporation gave **6** as yellow solid, which was washed with hexane and dried under reduced pressure (1.5 g, 3.5 mmol, 94%) (found: C 81.17, H 6.69, N 3.37.

$C_{28}H_{27}NO_2(H_2O)_{0.25}$ requires C 81.23, H 6.69, N 3.38%). ν(KBr disk; r.t.)/cm^{-1} 1640 (C=O). δ_H(300 MHz; $CDCl_3$; r.t.) 2.21 (3 H, s, CH_3), 2.57 (2 H, dt, *J* = 7 and 7 Hz, $CH_2CH{=}CH_2$), 4.03 (2 H, t, *J* = 7 Hz, OCH_2), 4.07 (2 H, m, NCH_2), 5.13 (1 H, dd, *J* = 17 and 2 Hz, $CH_2CH{=}CH_2$), 5.72 (2 H, m, NCH_2), 5.94 (1 H, ddt, *J* = 17, 11 and 7 Hz, $CH{=}CH_2$), 6.84 (4 H, C_6H_4), 7.37–7.48 (4 H, 2H-An, 3H-An), 7.99–8.10 (4 H, 1H-An, 4H-An) and 8.45 (1 H, s, H10-An). δ_C(75.5 MHz; $CDCl_3$; r.t.) 21.8 (CH_3), 33.6 ($CH_2CH{=}CH_2$), 39.0 (NCH_2), 48.5 (NCH_2), 67.2 (OCH_2), 114.8, 117.1, 124.3, 125.0, 126.3, 127.0, 127.5, 128.2, 128.3, 129.0, 131.2, 131.4, 134.4, 158.1 (C_6H_4) and 171.1 (C=O).

$AnCH_2N(Ac)CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOOC_6H_3$-3,5-$Me_2$ (7)

A mixture of **5** (0.41 g, 1.0 mmol) and 3,5-dimethylphenyl acrylate (0.35 g, 2.0 mmol) was dissolved in CH_2Cl_2 (5.0 cm^3), followed by addition of a Ru–carbene complex ((H_2IMes)(PCy_3)$Cl_2Ru{=}CHPh$, H_2IMes = *N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) (42 mg, 5.0×10^{-2} mmol). The mixture was refluxed for 11 h and the solvent was removed by evaporation to give crude **7**, which was purified by SiO_2 column chromatography (eluent: hexane–CH_2Cl_2 1 : 1) (0.26 g, 0.47 mmol, 47%) (found: C 79.60, H 6.47, N 2.49. $C_{37}H_{35}NO_4$ requires C 79.69, H 6.33, N 2.51%). ν(KBr disk; r.t.)/cm^{-1} 1646 and 1728 (C=O). δ_H(300 MHz; $CDCl_3$; r.t.) 2.22 (3 H, s, $COCH_3$), 2.32 (6 H, s, $C_6H_3(CH_3)_2$), 2.79 (2 H, ddt, *J* = 7, 6 and 2 Hz, $CH_2CH{=}CH$), 4.08 (2 H, m, $NCH_2C_6H_4$), 4.14 (2 H, t, *J* = 6 Hz, OCH_2), 5.73 (2 H, m, NCH_2An), 6.19 (1 H, dt, *J* = 16 and 2 Hz, $CH_2CH{=}CH$), 6.75 (2 H, m, *ortho*-C_6H_3), 6.85 (4 H, m, C_6H_4), 6.89 (1 H, m, *para*-C_6H_3), 7.26 (1 H, dt, *J* = 16 and 7 Hz, $CH_2CH{=}CH$), 7.39–7.48 (4 H, 2H-An, 3H-An), 8.00 (2 H, m, 4H-An), 8.11 (2 H, d, *J* = 8 Hz, 1H-An), 8.45 (1 H, s, H10-An). δ_C(100 MHz; $CDCl_3$; r.t.) 21.3 ($COCH_3$), 21.9 ($C_6H_3(CH_3)_2$), 32.2 ($CH_2CH{=}CH$), 39.2 (NCH_2An), 48.6 ($NCH_2C_6H_4$), 65.9 (OCH_2), 114.8 (C_6H_4), 119.1 (*ortho*-C_6H_4), 122.8 ($CH_2CH{=}CH$), 124.3 (1C-An), 124.9 (2C-An or 3C-An), 126.3 (2C-An or 3C-An), 127.0 (C_6H_4 or *para*-C_6H_3), 127.5 (C_6H_4 or *para*-C_6H_3), 127.8, 128.2 (10C-An), 128.8, 129.0 (3C-An), 131.2, 131.4, 139.2, 146.6 ($CH_2CH{=}CH$), 150.4, 157.7 (C_6H_4), 164.7 (NC=O) and 171.0 (C=O); R_f 0.16 (CH_2Cl_2).

$AnCH_2N(Ac)CH_2C_6H_4$-4-$OCH_2CH_2CH{=}CHCOOC_6H_4$-4-$C(C_6H_4$-4-*t*Bu$)_3$ (8)

6 (0.20 g, 0.50 mmol) and $CH_2{=}CHCOOC_6H_4$-4-$C(C_6H_4$-4-*t*Bu$)_3$ (0.56 g, 1.0 mmol) was dissolved in CH_2Cl_2 (2.5 cm^3), followed by addition of a Ru–carbene complex ((H_2IMes)(PCy_3)$Cl_2Ru{=}CHPh$, H_2IMes = *N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) (21 mg, 2.5×10^{-2} mmol). The mixture was refluxed for 54 h. The reaction mixture was partitioned by addition of water and CH_2Cl_2. The separated organic phase was washed with water, dried over $MgSO_4$, filtered, and evaporated to give **8** as a white solid which was purified by SiO_2 column chromatography (eluent: CH_2Cl_2) (0.27 g, 0.29 mmol, 57%) (found: C 84.16, H 7.56, N 1.56. $C_{66}H_{69}NO_4$ requires C 84.31, H 7.40, N 1.49%). ν(KBr disk; r.t.)/cm^{-1} 1651 and 1740 (C=O). δ_H(300 MHz; $CDCl_3$; r.t.) 1.30 (27 H, s, $C(CH_3)_3$), 2.22 (3 H, s, $COCH_3$), 2.79 (2 H, dt, *J* = 7 and 7 Hz, $CH_2CH{=}CH$), 4.09 (2 H, s, $NCH_2C_6H_4$), 4.14 (2 H, t, *J* = 6 Hz, OCH_2), 5.73 (2 H, s, NCH_2An), 6.18 (1 H, d, *J* = 16 Hz, $CH_2CH{=}CH$), 6.84 (4 H, m, $NCH_2C_6H_4$), 7.01 (2 H, d, *J* = 9 Hz, $C_6H_4({}^tBuC_6H_4)_3$), 7.10 (6 H, ${}^tBuC_6H_4$), 7.21–7.26 (9 H, ${}^tBuC_6H_4$, $C_6H_4({}^tBuC_6H_4)_3$, $CH_2CH{=}CH$), 7.38–7.48 (4 H, 2H-An, 3H-An), 8.00 (2 H, dd, *J* = 9 Hz and 2, 4H-An), 8.10 (2 H, d, *J* = 9 Hz, 1H-An) and 8.45 (1 H, s, 10H-An). δ_C(75.5 MHz; $CDCl_3$; r.t.) 22.0 ($COCH_3$), 31.4 ($C(CH_3)_3$), 32.3 ($CH_2CH{=}CH$), 34.4 ($C(CH_3)_3$), 39.2 (NCH_2An), 48.7 ($NCH_2C_6H_4$), 63.4 ($C({}^tBuC_6H_4)_3$), 65.9 (OCH_2), 114.8 ($NCH_2C_6H_4$), 119.9 ($C_6H_4({}^tBuC_6H_4)_3$), 122.8 ($CH_2CH{=}CH$), 124.1 (${}^tBuC_6H_4$), 124.3 (1C-An), 125.0 (2C-An or 3C-An), 126.3 (2C-An or 3C-An), 127.0 ($NCH_2C_6H_4$), 127.8, 128.2 (10C-An), 128.9, 129.0 (4C-An), 130.6 (${}^tBuC_6H_4$), 131.2, 131.4, 132.1 ($C_6H_4({}^tBuC_6H_4)_3$), 143.6, 144.7, 146.7 ($CH_2CH{=}CH$), 148.4, 157.7, 164.4 (NC=O) and 171.0 (C(=O)O); R_f 0.31 (CH_2Cl_2).

Pseudorotaxane $[(1)(AnCH_2NH_2C_6H_4OCH_2CH_2CH{=}CH_2)]$-$(BAr_F)$ (10)

^{1}H NMR spectrum was obtained from $CDCl_3$ solution (0.7 cm^3) containing **1** (3.5×10^{-3} mmol) and **3** (3.5×10^{-3} mmol). δ_H(300 MHz, $CDCl_3$, r.t.) 2.53 (2 H, dt, *J* = 7 and 7 Hz, $CH_2CH{=}CH_2$), 3.25–4.23 (34 H, OCH_2, C_5H_4), 5.08–5.24 (4 H, NCH_2, $CH_2CH{=}CH_2$), 5.64 (2 H, br s, NCH_2), 5.71 (2 H, m, C_6H_4-Crown), 5.87 (1 H, ddt, *J* = 17, 11 and 7 Hz, $CH_2CH{=}CH_2$), 6.53 (2 H, m, C_6H_4-Crown), 6.95 (2 H, *J* = 9 Hz, C_6H_4-Axle), 7.09 (2 H, br s, NH_2), 7.42–7.58 (6 H, H2-An, H3-An, C_6H_4-Axle), 7.52 (4 H, s, *para*-C_6H_3), 7.71 (8 H, br s, *ortho*-C_6H_3), 7.83 (2 H, d, *J* = 8 Hz, An), 8.11 (1 H, s, H10-An) and 8.41 (2 H, d, *J* = 9 Hz, An). *m*/*z* (FAB) 924 ($[M - BAr_F]^+$. $C_{54}H_{62}FeNO_9$ requires 924).

Spectrofluorimetric determination of association constant of the reaction of 1 and 3 to form 10

The association constant K_{obs} for formation of pseudorotaxane **10** was estimated by analyzing the fluorescence intensity of **10** as a function of the concentration. Pseudorotaxane **10** was assumed to be non-luminescent due to intrarotaxane quenching. Intermolecular quenching between **1** and **3** was not considered. The intensity read at the maximum of anthracene band was fitted to $[\mathbf{10}] = I_{obs}/I_0[\mathbf{10}]_0$. K_{obs} satisfies usual 1 : 1 binding expressed in eqn (2).

$$K_{obs} = [\mathbf{10}]/\{([\mathbf{1}]_0 - [\mathbf{10}])([\mathbf{3}]_0 - [\mathbf{10}])\} \tag{2}$$

Pseudorotaxane $[(1)\{NH_2(CH_2Ph)_2\}](BAr_F)$ (11)

The ^{1}H NMR spectrum was obtained from $CDCl_3$ solution (0.7 cm^3) containing **1** (7.0×10^{-3} mmol) and **9** (7.0×10^{-3} mmol). δ_H(300 MHz; $CDCl_3$; r.t.) 3.28 (4 H, br s, OCH_2), 3.47 (12 H, br s, OCH_2), 3.94–4.10 (12 H), 4.29 (4 H, br s, C_5H_4), 4.98 (4 H, br s, NCH_2), 6.63 (2 H, m, C_6H_4-Crown), 6.69 (2 H, m, C_6H_4-Crown), 7.24 (4 H, br s, C_6H_4-Axle), 7.53 (4 H, s, $C_6H_3(CF_3)_2$), 7.71 (2 H, br s, NH_2) and 7.72 (8 H, s, $C_6H_3(CF_3)_2$). *m*/*z* (FAB) 754 ($[M - BAr_F]^+$. $C_{42}H_{52}FeNO_8$ requires 754).

$[\{(C_6H_4$-4-*t*Bu$)_3CC_6H_4$-4-OC_6H_4-4-$CH_2NH_2CH_2C_6H_4$-4-OCH_2-$CH_2CH{=}CHCOOC_6H_4$-4-$C(C_6H_4$-4-*t*Bu$)_3\}(1)](BAr_F)$ (12a)

Compounds **2** (163 mg, 0.10 mmol) and **1** (61 mg, 0.11 mmol) were dissolved in CH_2Cl_2 (2.0 cm^3), followed by addition of

CH$_2$=CHCOOC$_6$H$_4$-4-C(C$_6$H$_4$-4-*t*Bu)$_3$ (111 mg, 0.20 mmol) and a Ru–carbene complex ((H$_2$IMes)(PCy$_3$)Cl$_2$Ru=CHPh) (4.2 mg, 5.0×10^{-3} mmol). The mixture was refluxed for 14 h and the solvent was removed by evaporation to give brown oil. The crude product was purified by preparative HPLC (CHCl$_3$) to give **12a** (160 mg, 0.088 mmol, 88%) (found: C 66.39, H 5.95, N 0.54. C$_{153}$H$_{154}$BF$_{24}$FeNO$_{12}$(H$_2$O) requires C 66.21, H 5.81, N 0.50%). δ_H(300 MHz; CDCl$_3$; r.t.) 1.31 (54 H, s, CH$_3$), 2.73 (2 H, dt, J = 6 and 6 Hz, C*H*$_2$CH=CH$_2$), 3.42–4.30 (34 H, OCH$_2$-Axle, CH$_2$-Crown, C$_5$H$_4$), 4.51–4.58 (4 H, m, NCH$_2$), 6.16 (1 H, d, J = 16 Hz, CH$_2$CH=C*H*), 6.68 (2 H, m, C$_6$H$_4$-Crown), 6.74 (2 H, d, J = 9 Hz, C$_6$H$_4$-Axle), 6.83 (2 H, d, J = 9 Hz, C$_6$H$_4$-Axle), 6.87–6.91 (4 H, C$_6$H$_4$-Crown, C$_6$H$_4$-Axle), 7.01 (2 H, d, J = 8 Hz, C$_6$H$_4$-Axle), 7.10 (6 H, d, J = 9 Hz, ^{t}BuC$_6$*H*$_4$), 7.11 (6 H, d, J = 8 Hz, ^{t}BuC$_6$*H*$_4$), 7.19–7.32 (21 H, ^{t}BuC$_6$*H*$_4$, C$_6$H$_4$-Axle, CH$_2$C*H*=CH), 7.55 (4 H, s, *para*-C$_6$H$_3$), 7.65 (2 H, br s, NH$_2$) and 7.74 (8 H, br s, *ortho*-C$_6$H$_3$). δ_C(100 MHz; CDCl$_3$; r.t.) 31.4 (CH$_3$), 31.4 (CH$_3$), 32.0 (*C*H$_2$CH=CH$_2$), 34.3 (*C*(CH$_3$)$_3$), 51.8 (NCH$_2$), 52.1 (NCH$_2$), 56.1 (C$_5$H$_4$), 56.4 (C$_5$H$_4$), 62.8 (2C, C$_5$H$_4$), 63.3 (*C*(^{t}BuC$_6$H$_4$)$_3$), 63.4 (*C*(^{t}BuC$_6$H$_4$)$_3$), 65.7 (OCH$_2$-Axle), 68.3 (CH$_2$-Crown), 68.9 (CH$_2$-Crown), 69.8 (CH$_2$-Crown), 70.2 (CH$_2$-Crown), 70.6 (CH$_2$-Crown), 71.2 (CH$_2$-Crown), 112.1 (C$_6$H$_4$-Crown), 114.5 (C$_6$H$_4$-Axle), 117.4 (*para*-C$_6$H$_3$), 117.8 (C$_6$H$_4$-Axle), 118.3 (C$_6$H$_4$-Axle), 119.9 (C$_6$H$_4$-Axle), 119.9 (C$_6$H$_4$-Axle), 122.0 (C$_6$H$_4$-Axle), 122.9 (CH$_2$CH=*C*H$_2$), 124.1 (^{t}Bu*C*$_6$H$_4$), 124.1 (^{t}Bu*C*$_6$H$_4$), 124.5 (q, J(CF) = 271 Hz, CF$_3$), 124.5 (q, J(CF) = 31 Hz, *C*CF$_3$), 125.2, 130.6 (^{t}Bu*C*$_6$H$_4$), 130.6 (^{t}Bu*C*$_6$H$_4$), 130.7 (C$_6$H$_4$-Axle), 130.7 (C$_6$H$_4$-Axle), 132.1 (C$_6$H$_4$-Axle), 132.7 (C$_6$H$_4$-Axle), 134.7 (*ortho*-C$_6$H$_3$), 143.2, 143.6, 143.6, 144.8, 146.4, 146.6 (CH$_2$*C*H=CH$_2$), 148.3, 148.4, 148.6, 153.6, 158.5, 159.4, 161.6 (q, J(CB) = 50 Hz, CB) and 164.5 (C=O). *m/z* (FAB) 1858 ([M − BAr$_F$]$^+$. C$_{121}$H$_{142}$FeNO$_{12}$ requires 1858). Rotaxanes **12b–12i** were synthesized similarly to **12a** from corresponding crown ether and olefins. See Electronic Supplementary Information (ESI) for more detail.†

[(1){(C$_6$H$_4$-4-*t*Bu)$_3$CC$_6$H$_4$-4-OC$_6$H$_4$-4-CH$_2$N(Ac)CH$_2$C$_6$H$_4$-4-OCH$_2$CH$_2$CH=CHCOOC$_6$H$_4$-4-C(C$_6$H$_4$-4-*t*Bu)$_3$}] (13a)

To a solution of **12a** (0.22 g, 0.080 mmol) in MeCN (3.0 cm^3) were added Et$_3$N (5.6×10^{-2} cm^3, 0.40 mmol) and acetic anhydride (3.8×10^{-2} cm^3, 0.40 mmol), and the reaction mixture was stirred for 14 h at room temperature. After the removal of the solvent by evaporation, the product was purified by SiO$_2$ column chromatography (eluent: hexane–AcOEt 1 : 1), preparative HPLC (eluent: CHCl$_3$), and SiO$_2$ column chromatography (eluent: hexane–AcOEt 2 : 1) to give **13a** as a yellow solid (82 mg, 3.0×10^{-2} mmol, 38%) (found: C 75.52, H 7.16, N 0.80. C$_{123}$H$_{143}$FeNO$_{13}$(CHCl$_3$)$_{0.5}$ requires C 75.72, H 7.38, N 0.71%). ν(KBr disk; r.t.)/cm^{-1} 1653, 1734 (C=O). δ_H(300 MHz; CDCl$_3$; r.t.) 1.32 (54 H, s, C(CH$_3$)$_3$), 2.21 (3 H, m, COCH$_3$), 3.14 (2 H, m, C*H*$_2$CH=CH), 3.50–4.60 (38 H, C$_5$H$_4$, CH$_2$-Crown, NCH$_2$), 6.41 (1 H, d, J = 16 Hz, CH$_2$CH=C*H*), 6.82–7.29 (20 H, OC$_6$H$_4$, C$_6$H$_4$-Crown), 7.11 (6 H, d, J = 8 Hz, ^{t}BuC$_6$H$_4$), 7.12 (6 H, d, J = 9 Hz, ^{t}BuC$_6$H$_4$), 7.26 (6 H, d, J = 9 Hz, ^{t}BuC$_6$*H*$_4$), 7.26 (6 H, d, J = 8 Hz, ^{t}BuC$_6$*H*$_4$) and 7.60 (1 H, dt, J = 16 and 6 Hz, CH$_2$C*H*=CH). *m/z* (FABMS) 1898 ([M − BAr$_F$]$^+$. C$_{123}$H$_{143}$FeNO$_{13}$ requires 1898). R_f 0.43 (hexane–AcOEt 1 : 1). Rotaxanes **13b** and **13c** were synthesized similarly to **13a** from corresponding rotaxanes, **12b** and **12c**. See Electronic Supplementary Information (ESI) for more detail.†

Reaction of Ac$_2$O with 12d

To a solution of **12d** (0.14 g, 0.073 mmol) in MeCN (3.0 cm^3) were added Et$_3$N (5.6×10^{-2} cm^3, 0.40 mmol) and acetic anhydride (3.8×10^{-2} cm^3, 0.40 mmol), and the reaction mixture was stirred for 14 h at room temperature. After the removal of the solvent by evaporation, the products were isolated by SiO$_2$ column chromatography (hexane–AcOEt 1 : 1) to give **1** (34 mg, 0.061 mmol, 84%, R_f 0.10, hexane–AcOEt 1 : 1) and **7** (35 mg, 0.063 mmol, 86%, R_f 0.18, hexane–AcOEt 1 : 1).

Dethreading reaction of rotaxanes

To an NMR tube was charged a CD$_3$CN (or dmso-d$_6$) solution (0.6 cm^3) of rotaxane, **12a**, **12b**, **12d**, **12e**, **12g**, **12i**, **13a**, **13b**, (3.0×10^{-3} mmol) and 2-chloro-2-methylpropane, which was used as internal standard. The NMR tube was heated in a thermostat bath and stored when not being actively monitored. ^{1}H NMR spectra were checked occasionally and reaction was monitored by comparison of peak area ratio between rotaxane and internal standard. After reaction, the solvent was removed by evaporation and the residue was checked by FABMS measurement.

Crystal structure determination

Crystals of [K(**1**)]BPh$_4$ suitable for X-ray diffraction study were obtained by recrystallization from an acetone/methanol solution of **1** and KBPh$_4$ (found: C 67.97, H 6.25. C$_{52}$H$_{56}$O$_8$FeKB requires C 68.28, H 6.17%). All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated MoKα radiation and a rotating anode generator. Data were analyzed by assuming disorder between C(21) and C(22).

Crystal data

C$_{52}$H$_{56}$O$_8$BFeK, M = 914.76, monoclinic, a = 13.846(2), b = 22.065(4), c = 14.893(3) Å, U = 4545(2) Å^3, T = 113 K, space group $P2_1/n$ (no. 14), Z = 4, 32 533 reflections were measured, 10 119 unique (R_{int} = 0.021), which were used in all calculations. The final Rw was 0.0624 ($I > 2\sigma(I)$).

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research for Young Scientists from the Ministry of Education, Culture, Sports, Science and Technology, Japan (19750044) and by a Global COE Program "Education and Research Center for Emergence of New Molecular Chemistry". We thank Tomohito Ide for the theoretical calculation of the triplet level of the model compounds.

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