Self-assembly of Novel Hetero[3]rotaxane, [2]Rotaxanes and [2]Catenane†

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One linear template 13 and one cyclophane template 15, both incorporating two electron rich 1,4-dialkoxybenzene units and one diamide unit, have been synthesized. By utilizing donor-acceptor interaction and/or intermolecular hydrogen bonding assembling principles, one novel hetero[3]rotaxane 22·4Cl, possessing one neutral and one tetracationic ring components, has been synthesized from 13, through neutral [2]rotaxane 21 as intermediate. With 15 as template, tetracationic [2]catenane 23 ·4PF_6 was assembled by using donor-acceptor interaction, but no neutral [2]rotaxane could be obtained under the typical conditions of hydrogen bonding assembling principle. The interlocked supramolecular compounds have been characterized and their spectral properties are investigated.

Keywords self-assembly, rotaxane, catenane

Introduction

In recent years, interlocked supramolecular architectures, rotaxanes and catenanes, have received increasing attention as optimal platforms for studying intermolecular interactions due to their potential applications in material science.[1-7] Several efficient principles have been developed and a large number of rotaxanes and catenanes have been assembled. However, the assembly of all the reported interlocked systems is always based on one specific non-covalent force. In order to develop efficient approaches to new types of assembling systems and also to explore the interaction of different non-covalent forces within assembling systems, we had initiated one project to assemble interlocked systems by using two different non-covalent interactions. Previously, we had utilized a series of linear templates with symmetric arrangement of donor-acceptor interaction and hydrogen bonding recognition sites to assemble the first class of hetero[3]rotaxanes.[8] In this paper, we report the assembly and characterization of three new rotaxanes and one new catenane, from linear and cyclophane templates, both of which possess asymmetric arrangement of the donor-acceptor recognition sites.

Results and discussion

Two new template compounds **13** and **15** have been designed for inducing the formation of interlocked systems. Two 1,4-dialkoxybenzene units and one diamide unit are incorporated into both compounds. These units have been proved to be efficient for assembling interlocked supramolecules by intermolecular donor-acceptor interaction and hydrogen bonding interaction, respectively.[8] Both compounds are prepared starting from compound **11**, the synthesis of which is shown in Scheme 1. Thus, coupling reaction of **1** with **2** in the presence of potassium carbonate in refluxing acetonitrile afforded ester **3** in good yield. Compound **3** was hydrolyzed with sodium hydroxide quantitatively to generate acid **4**, which was treated with ethyl aminoacetate in the presence of *iso*-butyl chloroformate to afford **5** quantitatively. Compound **5** was then hydrolyzed to give acid **6** quantitatively. Treatment of bromide **7** with **1** in the presence of potassium carbonate in refluxing acetonitrile afforded ether **8** in high yield. The later was hydrolyzed with hydrazine to produce amine **9** quantitatively. Compound **9** was then coupled with **6** with *iso*-butyl chloroforamte as coupling reagent, to give **10**. Compound **10** is insoluble in common organic solvents and therefore hydrogenised without characterization, to afford diphenol **11** in good yield.

The synthetic routes of linear compound **13** and cyclophane **15** are presented in Scheme 2. Treatment of compound **11** with excessive bromide **12**[9] with potassium carbonate as the base in refluxing acetonitrile led to the formation of **13** in 77% yield, whereas the reaction of **11** with ditosylate **14**[10] under the similar conditions afforded com-

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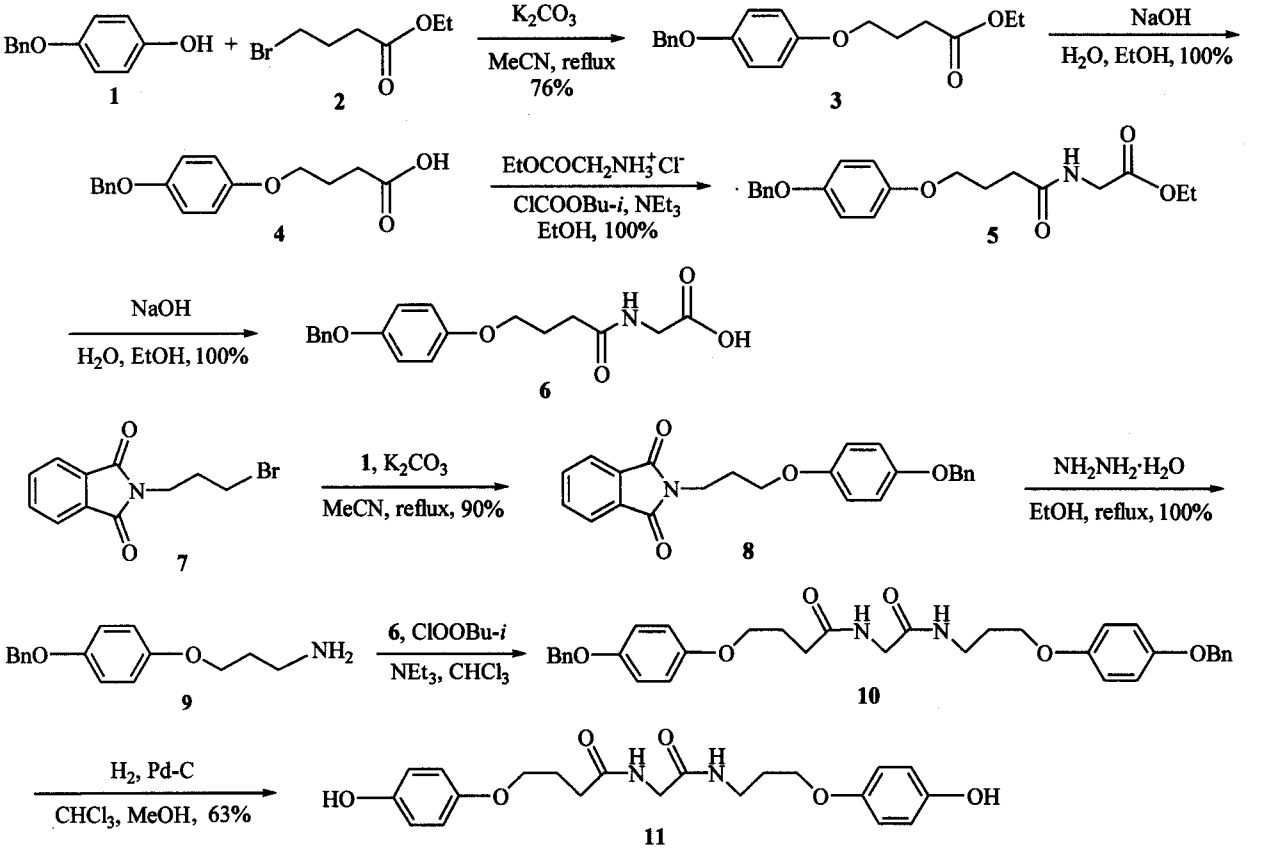
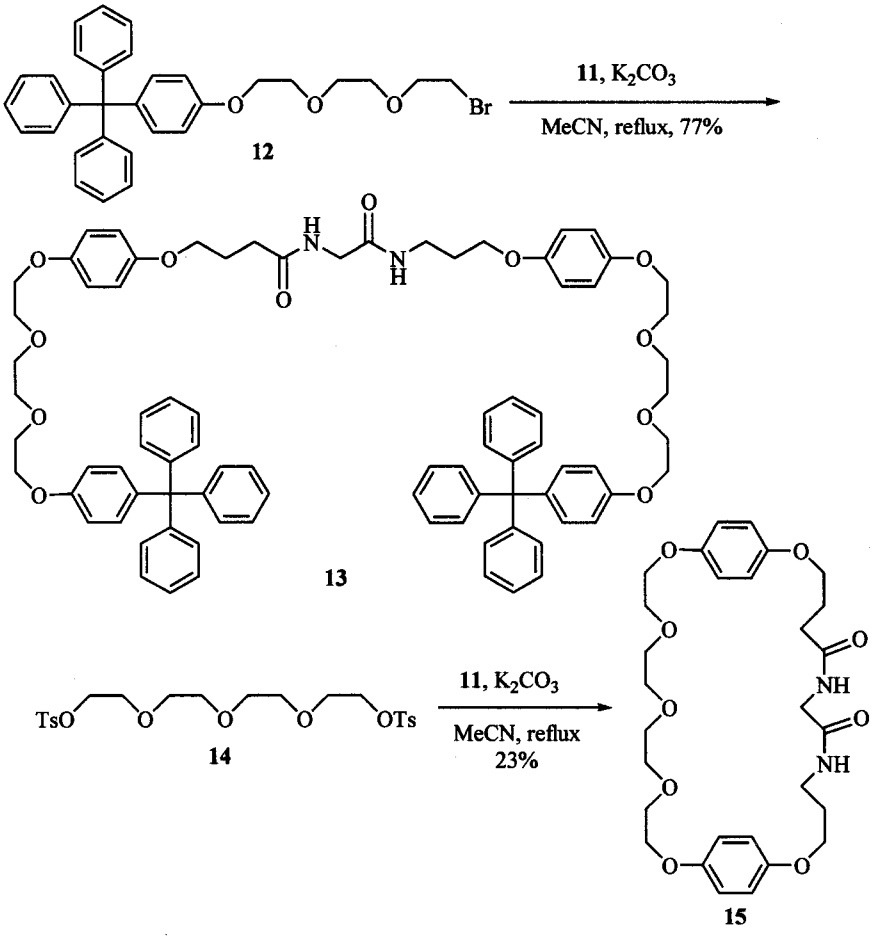
†Dedicated to Professor ZHOU Wei-Shan on the occasion of his 80th birthday.

Scheme 1



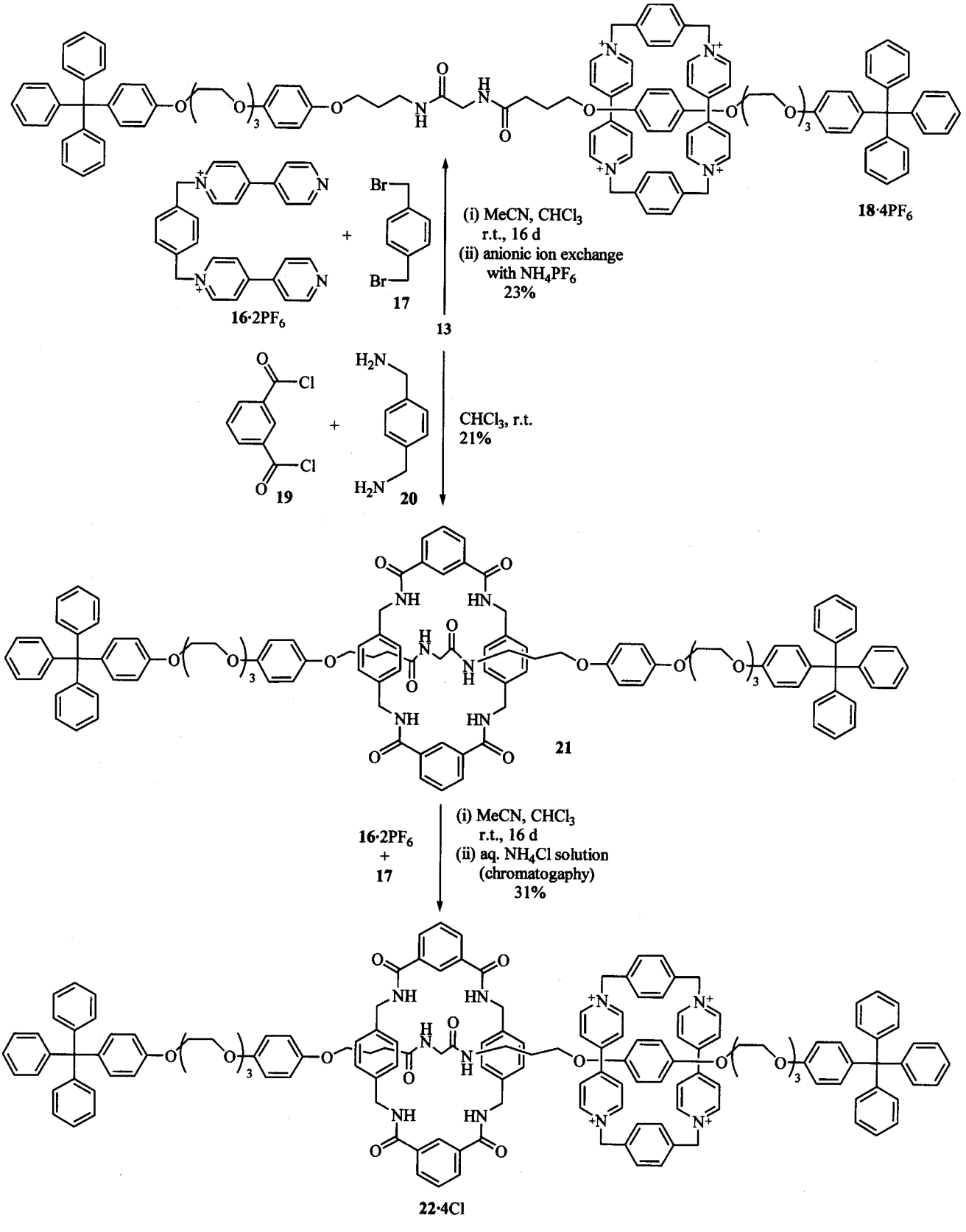
Scheme 2



pound **15** in 23% yield.

In the presence of compound **13**, the reaction of dicationic salt **16**·$2PF_6$[11] with dibromide **17** in acetonitrile-chloroform afforded tetracationic [2]rotaxane **18**·$4PF_6$ in 23% yield, after column chromatography and anionic exchange (Scheme 3). The reaction of **16**·$2PF_6$ with **17** to assemble rotaxanes is usually carried out in DMF or acetonitrile,[11] however, **13** is insoluble in DMF and exhibits very low solubility in acetonitrile. Therefore, chloroform was added in order to improve the solubility of **13**.

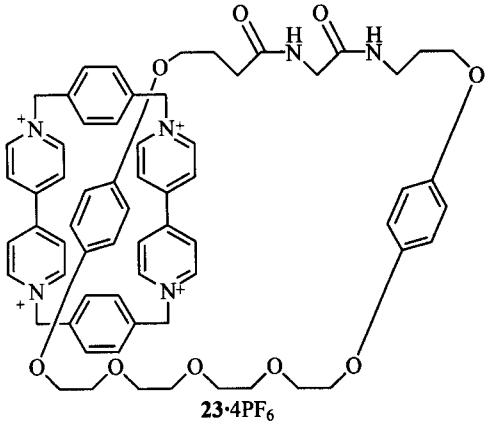
Scheme 3



With compound **13** as template, the reaction of diacyl chloride **19** and diamine **20** in chloroform led to the formation of neutral [2]rotaxane **21** in 21% yield (Scheme 3). Tetracationic [3]rotaxane **22**·4Cl was then assembled in 31% yield from the reaction of **16**·$2PF_6$ with **17** in acetonitrile-chloroform with [2]rotaxane **21** as the template, after column chromatography. Although in principle the presence of the neutral cyclophane in **21** would impose steric hindrance to the introduction of the tetracationic cyclophane, the yield of [3]rotaxane **22**·4Cl is still remarkably higher than that of **21**, probably due to the good solubility of **21**.[8] In principle, [3]rotaxane **22**·4Cl should be a mixture of two isomeric compounds. However, reverse phase HPLC spectrum revealed only one peak, presumably due to their extremely similar polarity. ^{1}H NMR spectrum could not provide useful information because of the low resolution. This linear template molecule, possessing two dialkoxybenzene units with different chemical environments, was actually initially designed for assembling separable hetero[3]rotaxane isomers. The present assembling result suggests that new linear template molecules need to be synthesized, in which the donor-acceptor interaction sites possess greater environmental difference.

The possibility of using cyclophane **15** to assemble [2]catenanes was then explored. In the presence of excessive **15**, the reaction of **16**·$2PF_6$ with **17** in acetonitrile-chloroform afforded dicationic [2]catenane **23**·$4PF_6$ in 24% yield, after column chromatography and anionic exchange with ammonium hexafluorophosphate (Scheme 4). However, no neutral [2]catenane could be obtained from the reaction of compounds **19** and **20** in the presence of **15**, probably because the conformation of **15** is too flexible or its cavity is not large enough.

Scheme 4



23·$4PF_6$

16·$2PF_6$ + **17**

(i) MeCN, $CHCl_3$ r.t., 16 d
(ii) aq. NH_4Cl solution (chromatogaphy)
(iii) anionic ion exchange with NH_4PF_6
24%

15 **19** + **20** → no catenane product
$CHCl_3$, r.t.

The structure of all the interlocked supramolecular compounds have been characterized by ^{1}H NMR, MS spectra and elemental analysis. Variable temperature ^{1}H NMR investigation revealed that [2]rotaxane **18**·$4PF_6$ exhibits typical molecular shuttling behavior. The corresponding activation energy was determined to be 53.6 kJ·mol^{-1} by using the coalescence method.[12] The value is comparable to that of a similar series of [2]rotaxanes,[8] showing that the presence of the amide moiety have no substantial effect to the shuttling movement of the tetracationic cyclophane between the two electron rich dialkoxybenzene sites. By using the same principle, the values of the activation energy associated with the circulating movement of the neutral cyclophane around the dipyridinium and the circulating movement of the tetracationic cyclophane around the dialkoxybenzene moiety of [2]catenane **23**·$4PF_6$ were also determined to be 44.8 and 48.5 kJ·mol^{-1}, respectively.

UV-vis spectra reveal a strong charge transfer absorption band for every ionic rotaxane and catenanes. The molar extinction coefficients were measured to be 350, 380, and 640 $(mol \cdot L^{-1})^{-1} \cdot cm^{-1}$ for [2]rotaxane **18**·$4PF_6$, [3]rotaxane **22**·4Cl and [2]catenane **23**·$4PF_6$, respectively. The obviously stronger electron-transfer interaction displayed by [2]catenane **23**·$4PF_6$ reflects the closer conformation of the templating cyclophane.

In conclusion, we had reported the assembly and characterization of four new rotaxanes and catenane from template molecules with asymmetric arrangement of the donor-acceptor interaction recognizing sites. Although the assembling efficiency of interlocked supramolecules is quite promising in the present work, the possible isomers of hetero[3]rotaxane **22**·4Cl could not be separated or analyzed. Therefore, new linear template molecules are needed to be designed to amplify the property difference of the corresponding hetero[3]rotaxanes.

Experimental

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Brucker 300 MHz spectrometer with TMS as internal standard. Mass spectra (EI, ESI) were obtained on a Varian SATURN 2000 or Brucker DALTONICS spectrometer. UV-Vis spectra were recorded with a Perkin-Elmer lambda 50 spectrophotometer. Elemental analysis was carried out with an ELEMENTAR VARIO elemental analyzer. All solvents were purified according to standard method before use.

Synthesis of 4-(4-*benzyloxy-phenoxy*)-*butyric acid ethyl ester* (**3**)

A suspension of phenol **1** (10.0 g, 50.0 mmol), bromide **2** (7.20 mL, 50.0 mmol) and potassium carbonate (13.8 g, 0.10 mol) in acetonitrile (200 mL) was heated under refluxing for 8 h. The mixture was cooled to room temperature and the solid was filtered off. The solu-

tion was concentrated and the residue triturated with dichloromethane (200 mL). After washed with water (40 mL) and brine (40 mL), dried over sodium sulfate, the solvent was removed under reduced pressure and the residue was chromatographed (dichloromethane : methanol = 20:1, $V:V$) to afford compound **3** as a oily solid (12.0 g, 76%). ^{1}H NMR ($CDCl_3$) δ: 7.25—7.35 (m, 5H), 6.80—6.90 (m, 4H), 5.00 (s, 2H), 4.10—4.12 (m, 2H), 3.86—3.92 (m, 2H), 2.48—2.53 (m, 2H), 2.08—2.13 (m, 2H), 1.20 (t, J = 6.5 Hz, 3H); MS (EI) m/z (%): 314 (M^+, 45). Anal. calcd for $C_{19}H_{22}O_4$: C 72.59, H 7.05; found C 72.60, H 7.00.

Synthesis of 4-(4-*benzyloxy-phenoxy*)-*butyric acid* (**4**)

To a solution of compound **3** (10.0 g, 35.0 mmol) in ethanol (100 mL) and water (10 mL) was added sodium hydroxide (2.01 g, 52.5 mmol). The solution was stirred at room temperature overnight. Aqueous hydrochloride solution (2 mol·L^{-1}) was added to pH = 6 and the solvent was removed under reduced pressure. The solid was washed with water completely and dried to give acid **4** as a white solid (9.10 g, 100%). The sample for analysis was obtained by recrystallyzation from ethanol. m.p. 127—129 ℃; ^{1}H NMR (DMSO-d_6) δ: 7.38—7.42 (m, 5H), 7.00—7.10 (m, 4H), 5.00 (s, 2H), 3.89—3.92 (m, 2H), 2.35—2.37 (m, 2H), 1.90 (m, 2H); MS (EI) m/z (%): 286 (M^+, 56). Anal. calcd for $C_{17}H_{18}O_4$: C 71.31, H 6.34; found C 71.60, H 6.50.

Synthesis of [4-(4-*benzyloxy-phenoxy*)-*butylrylamino*]-*acetic acid ethyl ester* (**5**)

To a stirred solution of *iso*-butyl chloroformate (3.30 mL, 25.0 mmol) in chloroform (50 mL at −40 ℃) was added dropwise a solution of compound **4** (7.15 g, 25.0 mmol) and triethylamine (3.50 mL, 25.0 mmol) in chloroform (50 mL) in 45 min. The temperature was raised to −15 ℃ and stirred for 2 h at this temperature. Then, a solution of ethyl aminoacetate hydrochloride (4.19 g, 30.0 mmol) and triethylamine (45.0 mmol) in chloroform (50 mL) was added dropwise. The temperature was raised to room temperature and the mixture was stirred overnight. The solution was washed with 5% hydrochloride solution (40 mL), 5% sodium hydroxide (40 mL), water (40 mL) and brine (40 mL), and dried over magnesium sulfate. After the solvent was removed under reduced pressure, the residue was subjected to column chromatography (dichloromethane:ethyl acetate = 3:1, $V:V$). Compound **5** was obtained as a white solid (9.30 g, 100%). m.p. 89—91 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.38—7.42 (m, 5H), 6.80—6.90 (m, 4H), 5.00 (s, 2H), 4.24—4.26 (m, 2H), 3.95—4.10 (m, 4H), 2.44—2.47 (m, 2H), 2.10 (d, J = 5.4 Hz, 2H), 1.30—1.33 (m, 3H); MS (EI) m/z (%): 371 (M^+, 34). Anal. calcd for $C_{21}H_{25}NO_5$: C 67.91, H 6.78, N 3.77; found C 67.81, H 6.92, N 3.94.

Synthesis of [4-(4-*benzyloxy-phenoxy*)-*butylrylamino*]-*acetic acid* (**6**)

A solution of compound **5** (9.00 g, 24.0 mmol) and sodium hydroxide (1.44 g, 36.0 mmol) in ethanol (100 mL)-water (10 mL) was stirred at room temperature for 2 h. Dilute hydrochloride solution (1 mol·L^{-1}) was added to pH = 6. The solvent was then removed under reduced pressure and the solid was washed with water, dried, to give compound **6** as a white solid (8.30 g, 100%). The compound was further purified by recrystallyzation from ethanol for analysis. m.p. 156—157 ℃; ^{1}H NMR (DMSO-d_6) δ: 7.40—7.43 (m, 5H), 6.80—6.90 (m, 4H), 5.00 (s, 2H), 3.90—3.93 (m, 2H), 3.75 (d, J = 6.5 Hz, 2H), 2.35—2.38 (m, 2H), 1.90—1.94 (m, 2H); MS (EI) m/z (%): 343 (M^+, 54). Anal. calcd for $C_{19}H_{21}NO_4$: C 66.46, H 6.16, N 4.08; found C 66.56, H 5.94, N 4.38.

Synthesis of 2-[3-(4-*benzyloxy-phenoxy*)-*propyl*]-*isoindole*-1,3-*dione* (**8**)

To a solution of phenol **1** (5.00 g, 25.0 mmol) and bromide **7** (6.70 g, 25.0 mmol) in acetonitrile (200 mL) was added potassium carbonate (7.00 g, 50.0 mmol). The suspension was heated under reflux for 6 h and cooled to room temperature. The solid was filtered off and the solvent was removed *in vacuo*. The residue was triturated with chloroform (300 mL), the solution was washed with hydrochloride solution (2 mol·L^{-1}, 50 mL), water (50 mL) and brine (50 mL), and dried over magnesium sulfate. After concentrated *in vacuo*, the residue was chromatographed (dichloromethane : methanol = 15 : 1, $V:V$) to afford compound **8** as a white solid (8.70 g, 90%). m.p. 144—146 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.88—7.91 (m, 2H), 7.72—7.75 (m, 2H), 7.44—7.47 (m, 5H), 6.86—6.90 (m, 2H), 6.78—6.82 (m, 2H), 5.00 (s, 2H), 4.94—4.98 (m, 4H), 2.20—2.25 (m, 2H); MS (EI) m/z (%): 387 (M^+, 34). Anal. calcd for $C_{24}H_{21}NO_4$: C 74.40, H 5.46, N 3.62; found C 74.41, H 5.50, N 3.67.

Synthesis of 3-(4-*benzyloxy-phenoxy*)-*propylamine* (**9**)

A solution of compound **8** (8.50 g, 22.0 mmol) and hydrazine monohydrate (2.50 g) in ethanol (200 mL) was refluxed for 10 h. The solvent was removed under reduced pressure and the residue was triturated with chloroform (300 mL). The organic phase was washed with water (40 mL) and brine (40 mL), and dried over sodium sulfate. After the solvent was removed, the residue was chromatographed (dichloromethane : methanol = 12 : 1, $V:V$) to afford compound **9** as a white solid (5.70 g, 100%). m.p. 80—82 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.40—7.46 (m, 2H), 6.80—6.90 (m, 4H), 5.00 (s, 2H), 4.00—4.05 (m, 2H), 2.90 (m, 2H), 1.90—1.94 (m, 2H); MS (EI) m/z (%): 257 (M^+, 54). Anal. calcd for

$C_{16}H_{19}NO_2$: C 74.68, H 7.44, N 5.44; found C 74.78, H 7.16, N 5.56.

Synthesis of 4-(4-*benzyloxy-phenoxy*)-*N*-{[3-(4-*benzyloxy-phenoxy*)-*propylcarbamoyl*]-*methyl*}-*butyramide* (**10**)

To a stirred solution of *iso*-butyl chloroformate (2.40 mL, 18.0 mmol) in chloroform (50 mL) at −35 ℃ was added a solution of acid **6** (6.30 g, 18.0 mmol) and triethylamine (2.5 mL, 18 mmol) in chloroform (50 mL). After stirred for another 2 h at −15 ℃, a solution of amine **9** (5.71 g, 22.0 mmol) and triethylamine (4.50 mL, 33.0 mmol) in chloroform (50 mL) was added and the mixture was stirred at room temperature overnight. The precipitate formed was filtered and washed with water, methanol and ether completely. After dryness, compound **10** (8.00 g) was obtained. Since this crude product is insoluble in most organic solvent, it was hydrogenised without further purification.

Synthesis of 4-(4-*hydroxy-phenoxy*)-*N*-{[3-(4-*hydroxy-phenoxy*)-*propylcarbamoyl*]-*methyl*}-*butyramide* (**11**)

To a suspension of compound **10** (8.00 g) in chloroform-methanol (150 mL, 1∶1, *V*∶*V*) was added Pd-C (10%, 200 mg). The mixture was stirred at room temperature under 1.0 (105 Pa of hydrogen for 4 h. The white solid dissolved completely. The catalyst was filtered off and the solvent was removed under reduced pressure. The resulting residue was then subjected to column chromatography (dichloromethane∶methanol = 20∶1, *V*∶*V*) to afford compound **11** as a pale yellow solid (4.60 g, 63%). m.p. 143—145 ℃; ^{1}H NMR (CD_3OD) δ: 8.90 (s, 2H), 8.10 (s, 1H), 7.90—7.94 (m, 1H), 6.70—6.76 (m, 8H), 3.90—3.95 (m, 4H), 3.60 (d, 2H), 3.10—3.14 (m, 2H), 2.30 (m, 2H), 1.70—1.90 (m, 4H); MS (EI) *m*/*z* (%): 402 (M^+, 24). Anal. calcd for $C_{21}H_{26}N_2O_6$: C 62.67, H 6.51, N 6.96; found C 62.60, H 6.68, N 6.80.

Synthesis of 4-[4-(2-{2-[2-(4-*Trityl-phenoxy*)-*ethoxy*]-*ethoxy*}-*ethoxy*)-*phenoxy*]-*N*-({3-[4-(2-{2-[2-(4-*trityl-phenoxy*)-*ethoxy*]-*ethoxy*}-*ethoxy*)-*phenoxy*]-*propylcarbamoyl*}-*methyl*)-*butyramide* (**13**)

A suspension of compound **11** (1.00 g, 2.50 mmol), bromide **12** (3.71 g, 7.00 mmol) and potassium carbonate (1.38 g, 10.0 mmol) in acetonitrile (150 mL) was refluxed for 6 h. The mixture was then cooled to room temperature and the solid was filtered off. The solvent was removed under reduced pressure and the residue was triturated with chloroform (100 mL). The solution was washed with water (30 mL) and brine (30 mL), and dried over sodium sulfate. After the solvent was distilled, the resulting residue was chromatographed (dichloromethane∶methanol = 20∶1, *V*∶*V*) to afford compound **13** as a white solid (2.50 g, 77%). m.p. 86—87 ℃. ^{1}H NMR ($CDCl_3$) δ: 7.30—7.35 (m, 30H), 7.05—7.09 (m, 4H), 6.80—6.85 (m, 12H), 6.40 (s, 1H), 6.30 (s, 1H), 4.05—4.10 (m, 8H), 3.45—3.50 (m, 6H), 3.35—3.38 (m, 8H), 3.20—3.24 (m, 8H), 2.95 (d, *J* = HZ, 2H), 2.40—2.45 (m, 2H), 1.90—2.10 (m, 4H); MS (ESI) *m*/*z*: 1303 ($M^+ + 1$). Anal. calcd for $C_{83}H_{86}N_2O_{12}\cdot H_2O$: C 76.47, H 6.65, N 2.15; found C 76.58, H 6.79, N 2.17.

Synthesis of 2,5,8,11,14,19,31-*heptaoxa*-23,26-*diaza*-*tricyclo*[30.2.2.215,18]*octatriaconta*-1(35),15,17,32(36),33,37-*hexaene*-24,27-*dione* (**15**)

To a solution of compound **11** (3.41 g, 8.51 mmol) and ditosylate **14** (4.31 g, 8.51 mmol) in acetonitrile (150 mL) was added potassium carbonate (2.30 g, 17.0 mmol). The suspension was refluxed for 24 h and then cooled to room temperature. After work-up, the crude product was subjected to column chromatography (ethyl acetate∶methanol = 40∶1, *V*∶*V*). Compound **15** was obtained as a white solid (1.10 g, 23%). m.p. 116—119 ℃; ^{1}H NMR ($CDCl_3$) δ: 6.80—6.84 (m, 5H), 6.60—6.64 (s, 1H), 6.20—6.23 (m, 1H), 4.05—4.07 (m, 2H), 3.90—3.94 (m, 8H), 3.80—3.84 (m, 4H), 3.70—3.74 (m, 8H), 3.40—3.45 (m, 2H), 2.35—2.37 (m, 2H), 2.05—2.08 (m, 2H), 1.90—1.94 (m, 2H); MS (EI) *m*/*z* (%): 560 (M^+, 45). Anal. calcd for $C_{29}H_{40}N_2O_9\cdot 0.5H_2O$: C 75.51, H 6.51, N 2.12; found C 75.80, H 6.79, N 2.17.

Synthesis of [2]*rotaxane* **18**·4PF_6

A solution of dicationic salt **16**·2PF_6[11] (77.0 mg, 0.11 mmol), bromide **17** (29.0 mg, 0.11 mmol) and compound **13** (0.65 g, 0.35 mmol) in acetonitrile (30 mL) and chloroform (5 mL) was stirred at room temperature for 16 d. The solvent was distilled and the residue was triturated with chloroform (20 mL) to remove the un-reacted **13**. The resulting solid was chromatographed (2 mol·mL^{-1} aqueous ammonium chloride solution∶methanol∶nitromethane = 2∶7∶1, *V*∶*V*∶*V*), the solution of the orange band was collected and concentrated. The solid was washed with methanol and the solvent was removed. The solid was dissolved in water, saturated aqueous ammonium hexafluorophosphate solution was added until no solid was produced. The solid was filtered and washed with water. After dryness in air, [2]rotaxane **18**·4PF_6 was obtained as an orange solid in 23% yield. m.p. 167—169 ℃; ^{1}H NMR (DMSO—d_6) δ: 9.30—9.32 (m, 8H), 8.30—8.35 (m, 10H), 7.90—7.94 (m, 10H), 7.30—7.34 (m, 18H), 6.80—6.84 (m, 16H), 5.80—5.85 (m, 8H), 4.00—4.04 (m, 16H), 3.30—3.34 (m, 24H), 2.30—2.35 (m, 2H), 2.00—2.04 (m, 4H); MS (ESI) *m*/*z*: 1057 $(M - PF_6)^{2+}$, 948 $(M - PF_6)^{3+}$. Anal. calcd for $C_{119}H_{118}F_{24}N_6O_9P_4\cdot 4H_2O$: C 57.70, H 5.09, N 3.39; found C 57.71, H 5.22, N 3.30.

Synthesis of [2]*rotaxane* **21**

To a stirred solution of compound **13** (2.40 g, 1.80 mmol) and triethylamine (4.20 mL, 29.5 mmol) in chloroform (50 mL) were added simultaneously the solution of dichloride **19** (3.00 g, 14.7 mmol) in chloroform (50 mL) and the solution of diamine **20** (2.00 g, 14.7 mmol) in chloroform (50 mL) at room temperature for 5 h. The mixture was stirred overnight and the precipitate was filtered off. The solvent was then removed under reduced pressure. The resulting residue was subjected to column chromatography (ethyl acetate:methanol = 25:1, *V*:*V*) to afford [2]rotaxane **21** as a white solid (0.70 g, 21%). m.p. 103—104 ℃; ^{1}H NMR ($CDCl_3$) δ: 7.45—7.49 (m, 4H), 7.30—7.35 (m, 8H), 7.20—7.24 (m, 30H), 7.10—7.15 (m, 12H), 6.90 (s, 1H), 6.60—6.80 (m, 12H), 5.80 (s, 1H), 4.50—4.54 (m, 10H), 4.05—4.08 (m, 10H), 3.90—3.95 (m, 2H), 3.80—3.86 (m, 8H), 3.65—3.68 (m, 2H), 3.25 (s, 1H), 2.90 (s, 1H), 2.10—2.14 (m, 2H), 1.80—1.85 (m, 4H); MS (Maldi-tof) *m*/*z*: 1835 ($M^+ + 1$). Anal. calcd for $C_{115}H_{114}N_6O_{16}$: C 75.29, H 6.20, N 4.60; found C 75.57, H 6.10, N 4.30.

Hetero[3]*rotaxane* **22**·4Cl.

This rotaxane was prepared from compound **13**, **16**·$2PF_6$ and **17** according to the procedure as described for [2]rotaxane **18**·$4PF_6$, but without anionic exchange. The orange band was combined and the solvent was removed under reduced pressure. The resulting solid was washed with water and then recrystallyzed from methanol to afford **22**·4Cl as an orange solid in 31% yield. m.p. 212—213 ℃; ^{1}H NMR (DMSO-d_6) δ: 8.60—8.90 (m, 12H), 8.00 (s, 12H), 7.20—7.24 (m, 54H), 6.75—6.79 (m, 8H), 5.90—5.95 (m, 8H), 4.30—4.36 (m, 2H), 4.05—4.10 (m, 8H), 3.70—3.75 (m, 18H), 3.30—3.34 (m, 20H), 2.90—2.94 (m, 8H), 2.70—2.74 (m, 2H), 2.30—2.35 (m, 2H), 2.10—2.16 (m, 4H); MS (ESI) *m*/*z*: 1214 $(M - Cl)^{2+}$, 798 $(M - Cl)^{3+}$. Anal. calcd for $C_{151}H_{146}Cl_4N_{10}O_{16}\cdot 4H_2O$: C 70.54, H 6.04, N 5.45; found C 70.08, H 6.32, N 5.24.

[2]*Catenane* **23**·$4PF_6$

This catenane was prepared from compounds **15**, **16**·$2PF_6$ and **17** according to the procedure as described for [2]rotaxane **18**·$4PF_6$ as an orange solid in 24% yield. m.p. 300 ℃; ^{1}H NMR (DMSO-d_6) δ: 9.30—9.35 (m, 4H), 8.20—8.25 (m, 4H), 7.90—7.96 (m, 4H), 7.30—7.36 (m, 8H), 6.80—6.86 (m, 8H), 5.80—5.86 (m, 4H), 4.00—4.05 (m, 32H), 2.30—2.35 (m, 2H), 2.00—2.06 (m, 4H); MS (ESI) *m*/*z*: 686 $(M - PF_6)^{2+}$. Anal. calcd for $C_{65}H_{72}F_{24}N_6O_9P_4\cdot 4H_2O$: C 45.01, H 4.62, N 4.85; found C 45.22, H 4.85, N 4.64.

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