

Branched $[n]$ rotaxanes ($n = 2-4$) from multiple dibenzo-24-crown-8 ether wheels and 1,2-bis(4,4'-dipyridinium)ethane axles

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To investigate the possibility of incorporating the 1,2-bis(pyridinium)ethane \subset 24C8 [2]pseudorotaxane motif into dendrimer like macromolecules, a series of branched $[n]$ rotaxanes were prepared employing multiple dibenzo-24-membered crown ether wheels with various aromatic core structures and the 1,2-bis(4,4'-dipyridinium)ethane axle. Yields of branched [2]-, [3]- and [4]rotaxanes were dependent on the size of the core and the relative proximity of the crown ethers arranged around the core unit.

Introduction

Polyrotaxanes¹ and polycatenanes² are supramolecular polymers which contain macromolecular architectures built, in some fashion, around mechanical linkages. The interest in these chemical systems can be attributed in part to their aesthetic structures but also to the fundamental role that interlocked components might play in entanglements, rheology, elasticity and mechanical properties of polymers.¹⁻³ In particular, dendrimers and hyper-branched macromolecules based on interlocked components have attracted recent attention as both models for supramolecular polymers and interesting macromolecules in their own right.⁴ A number of templating motifs and synthetic strategies have been studied but the efficient incorporation of multiple mechanically linked subunits into a single macromolecule remains a challenge for the synthetic chemist.^{4a-d,5}

A single generation dendrimer (G1) contains three distinct components, the core, the terminal groups and the branches that connect the two. Further generations can be prepared if the terminal groups of the G1 molecule can be further branched and terminated to give G2 and this process repeated to give G3, G4, *etc.*⁶ There are therefore, a variety of ways that mechanical linkages can be introduced into dendrimers. These have been termed Types I, II and III by Lee and Kim, where the interlocked component occupies the core, the terminal group or the branches respectively.⁷ We are particularly interested in Type III dendrimers in which all the branching points of the macromolecule are mechanical linkages. These can be constructed by either (A) threading multiple ring components on to branches attached to a single core or (B) threading multiple axles on to rings appended to a central core.⁷

The [2]pseudorotaxane motif which combines 1,2-bis(pyridinium)ethane axles and 24C8 wheels (Fig. 1) has previously been used to construct various [2]- and [3]rotaxanes, [3]catenanes and molecular shuttles.⁸ Using metal-based linking nodes this motif has also been incorporated into 1D, 2D and 3D-polyrotaxanes.⁹ As a possible route to Type III-B dendrimeric polyrotaxanes, we describe herein, the application



Fig. 1 A [2]pseudorotaxane is easily formed between the dicationic "axle" 1,2-bis(4,4'-dipyridinium)ethane, **1**²⁺ (blue) and the macrocyclic "wheel" DB24C8 (red).

of this motif to the construction of larger branched $[n]$ rotaxanes built around new multiple site dibenzo[24]crown ethers; Fig. 2.

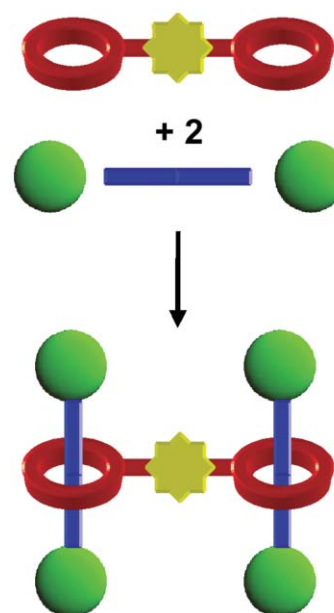
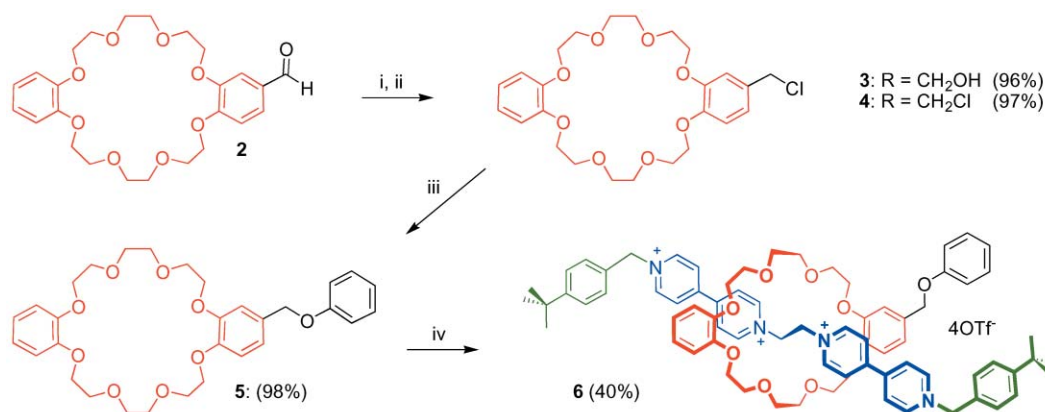


Fig. 2 A cartoon depiction of the pathway to a Type III-B dendrimeric polyrotaxane incorporating ring components at the branching points (axle = blue, wheel = red, core unit = yellow, stoppers = green).

Results and discussion

Our approach was to take various polyphenolic cores and attach DB24C8 appendages. The resulting multi-site crown ethers would then allow us to study the effects of the various geometries and spatial arrangements around the core upon threading the 1,2-bis(4,4'-dipyridinium)ethane dicationic axle, **1**²⁺. We naturally anticipated that spacing the crown ethers away from each other would lead to a higher proportion of the fully occupied core thereby introducing fewer defects into this divergent synthesis.

The simple phenyl ether **5** was prepared as a model for the multi-site DB24C8 derivatives used in this study; having a single macrocycle appended to the core benzene unit. As outlined in Scheme 1, the known aldehyde **2**¹⁰ was reduced to the alcohol **3** and chlorinated to yield **4** which upon reaction with phenol under typical Williamson ether synthesis conditions gave **5** in near quantitative yield; 98%. The ¹H NMR spectrum of **5** showed a characteristic resonance at 4.65 ppm for the



Scheme 1 Reagents and conditions: i, NaBH₄, EtOH–CH₂Cl₂ (1 : 1); ii, SOCl₂, CH₂Cl₂; iii, C₆H₅OH, K₂CO₃, CH₃CN; iv, 2 eq. 1.2OTf, 4 eq. *t*-Bu(C₆H₄)CH₂Br, MeNO₂–NaOTf(aq).

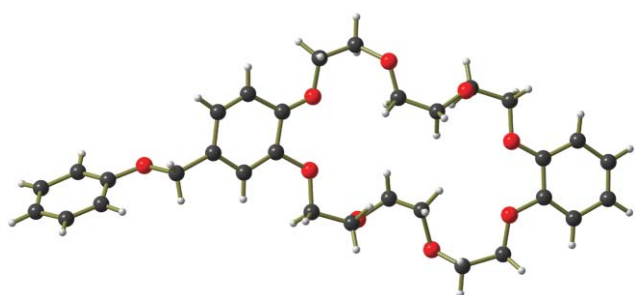


Fig. 3 A ball-and-stick representation of the X-ray crystal structure of **5**.

new benzyloxy methylene group as well as the expected peaks for methylene and aromatic protons from the DB24C8 and phenolic groups. A high-resolution electrospray ionisation mass spectrum (HR-ESI-MS) showed one significant, singly charged peak (577.2414) with a mass 23 m/z units higher than expected for **5** which was identified as [M + Na]⁺.

X-Ray quality crystals of **5** were grown by vapour diffusion of hexanes into a saturated chloroform solution of the compound. The solid-state structure¹¹ (Fig. 3) is interesting for two reasons; (i) it shows that the conformation of the DB24C8 macrocycle is essentially the same as that found for the parent DB24C8 and (ii) it demonstrates that the appended aromatic ring is rotated away from the opening of the crown cavity. Both these observations indicate that each individual macrocycle of the new multi-site crown ethers should be available for threading axle **1**²⁺ and formation of a [2]pseudorotaxane.

The crown ether **5** was used to prepare the corresponding [2]rotaxane **6.4OTf**. This compound contains all the major subunits of the target branched [*n*]rotaxanes and was used as a guide for characterisation of these more complex macromolecules. The preparative conditions used were similar to those employed for other [2]rotaxanes prepared using this motif.⁸ Initially, **5** and 1.2OTf were dissolved in nitromethane to give a yellow solution indicative of π – π interactions and charge transfer between the electron rich rings of the crown ether

and the electron poor pyridinium rings. This is consistent with [2]pseudorotaxane formation. This solution was then stirred at room temperature overnight and 4 equivalents of 4-*tert*-butylbenzyl bromide added along with a layer of saturated aqueous sodium triflate. This two-phase reaction mixture was stirred for three days during which time the solution turned orange, indicative of a change in the charge transfer band due to conversion of the axle to a dipyridinium to a tetrapyridinium cation, and thus [2]rotaxane formation. The [2]rotaxane **6.4OTf** was isolated by silica column chromatography using a 6 : 1 : 3 ratio of methanol–nitromethane–2 M NH₄Cl(aq) as eluent. The isolated material was then anion exchanged with NaOTf to regenerate the salt **6.4OTf**, as an orange–red solid in 40% overall yield. HR-ESI-MS verified the production of **6.4OTf** as peaks corresponding to the loss of one, two, three and four triflate anions from the molecular ion were detected at 1635.5120 [6.3OTf]⁺, 743.2850 [6.2OTf]²⁺, 445.8500 [6.OTf]³⁺ and 297.1564 [6]⁴⁺, respectively. The interlocked nature of **6**⁴⁺ was confirmed by ¹H NMR spectroscopy. Hydrogen bonding between the α -pyridinium and ethylene protons of the axle and the polyether oxygens of the macrocycle was apparent from the downfield shift of these signals ($\Delta\delta$ = 0.31–0.34 ppm). In addition, π -stacking interactions were evident from the upfield shifts of the aromatic protons ($\Delta\delta$ = 0.14–0.52 ppm). Finally, a diagnostic chemical shift change occurs for the benzylic protons of the crown; **5** shows a singlet at 4.96 ppm but in the [2]rotaxane **6.4OTf** this signal shifts upfield to 4.55 ppm ($\Delta\delta$ = 0.41 ppm). As there is a clear difference between free and complexed crown for this signal and since it occurs in a relatively uncluttered part of the spectrum, this shift can be used to calculate (*vide infra*) the amount of each species in a mixture of [*n*]rotaxanes.

The first step towards preparing analogous branched [*n*]rotaxanes was to prepare the multi-site derivatives of DB24C8 shown in Fig. 4. As described for **5**, a Williamson ether synthesis from the chloromethyl derivative **4** was used to append DB24C8 units to a central benzene core through –OCH₂– linkages. 1,2-, 1,3- and 1,4-core substituted bis(crowns) **7–9** were prepared from catechol, resorcinol and hydroquinone, respectively. The ¹H NMR spectra of **7–9** exhibited OCH₂ (3.8–4.2 ppm)

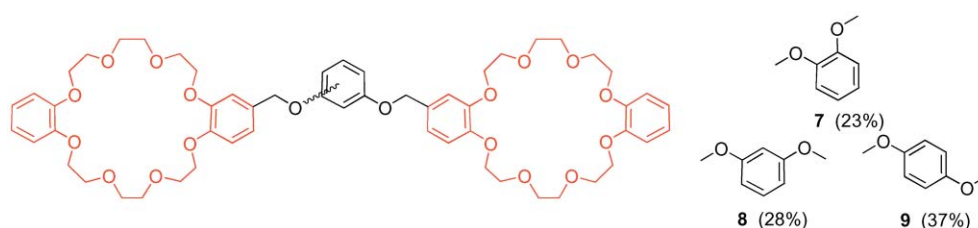


Fig. 4 Three bis(crown) ethers based on a single benzene core.

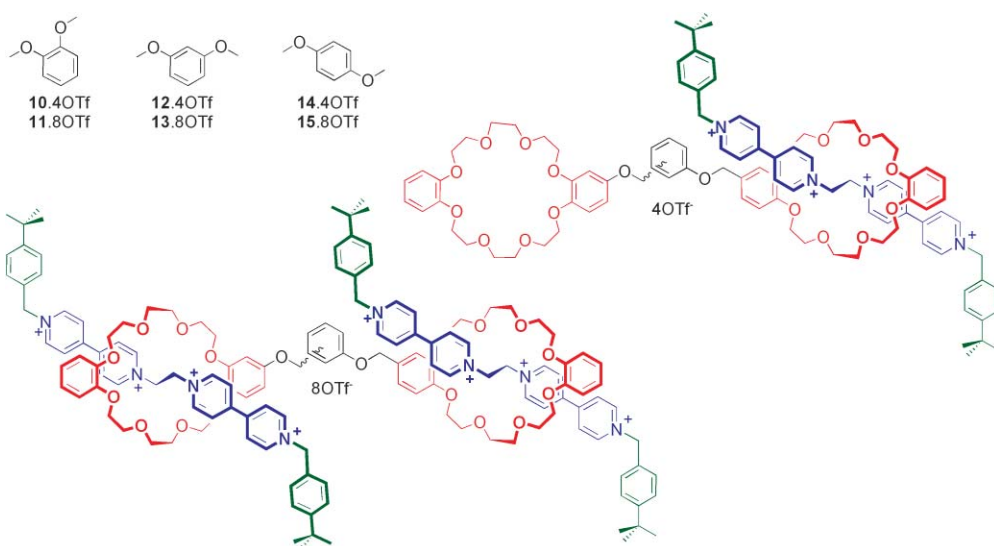


Fig. 5 The [2]rotaxanes **10**⁺, **12**⁺ and **14**⁺ and [3]rotaxanes **11**⁺, **13**⁺ and **15**⁺ formed from the bis(crown) ethers **7**, **8** and **9** respectively.

and aromatic resonances (6.8–7.0 ppm) attributable to an unsymmetrical DB24C8 along with a single benzylic resonance at ~5.0 ppm. Further aromatic resonances were consistent with the substitution patterns expected for the different cores. New crown ethers **7–9** were also identified by HR-ESI-MS as the $[M + Na]^+$ and $[M + 2Na]^{2+}$ ions (see Experimental section).

To investigate the ability of these crowns to form branched [2]- and [3]rotaxanes, **7–9** were combined with two equivalents of 1,2-bis(4,4'-bipyridinium)ethane triflate, **1.2OTf**, per crown ether moiety and an excess of 4-*tert*-butylbenzyl bromide added to effect stoppering. All six of the rotaxanes **10.4OTf–15.8OTf** (Fig. 5) were isolated by column chromatography and successfully characterized by ¹H NMR spectroscopy and HR-ESI-MS. The [3]rotaxanes exhibited simpler ¹H NMR spectra due to the inherent symmetry of having *both* crown ether sites involved in rotaxane formation. Characteristic shifts were similar to those observed for the model [2]rotaxane **6.4OTf** and this verified their interlocked nature. The [2]rotaxane ¹H NMR spectra were much more complicated as both complexed and uncomplexed crown peaks were present along with those from the complexed pyridinium axles. HR-ESI-MS showed ions due to the loss of 1–4 triflate anions and are summarized in Table 1.

Table 2 summarizes the yields for these reactions. Although the total isolated yield of [n]rotaxanes was variable, due to variations in work-up, there was a clear trend in the ratio of [2]rotaxane to [3]rotaxane produced. When the two crown ether rings were positioned adjacent to each other in the 1- and 2-positions of the central benzene core, the [2]rotaxane was heavily favoured. However, as the two macrocycles were positioned farther apart at the 1,3- and 1,4 positions, the yield of [3]rotaxane increased relative to the [2]rotaxane. Statistically, the [2]rotaxane should be favoured as it must form first but the trend indicates that the proximity of a neighbouring site inhibits the threading of a second axle through the second crown ether. This inhibition is more pronounced when the sites are closer together and this is mirrored in the relative yields of [2]rotaxane *vs.* [3]rotaxane.

Since it appeared that utilising a single aromatic ring as the central core might be sterically limiting, we also chose to look at two cores with multiple aromatic rings derived from 4,4'-biphenol and 1,3,5-tris(4-hydroxyphenyl)benzene. Crown ether **16** was prepared from 4,4'-biphenol and two equivalents of **4** in a fashion similar to that used to make **7–9**. Reaction of **16** with four equivalents of **1.2OTf** and excess 4-*tert*-butylbenzyl bromide gave the [2]rotaxane **17.4OTf** and the [3]rotaxane **18.8OTf**; see Fig. 6. Both the [2]rotaxane **17.4OTf** and the [3]rotaxane **18.8OTf** were isolated by column chromatography and successfully characterized by ¹H NMR spectroscopy and

Table 1 Mass spectrometry data^a for branched [n]rotaxanes **10–15**

[n]Rotaxane	Complex ion	Observed mass (<i>m/z</i>)
10.4OTf	[10.3OTf] ⁺	2111.7068
	[10.2OTf] ²⁺	981.3887
	[10.OTf] ³⁺	604.6057
	[10] ⁴⁺	416.2236
11.8OTf	[11.6OTf] ²⁺	1596.4931
	[11.5OTf] ³⁺	1014.6910
	[11.4OTf] ⁴⁺	723.7757
	[11.3OTf] ⁵⁺	549.2340
12.4OTf	[12.3OTf] ⁺	2111.7097
	[12.2OTf] ²⁺	981.3876
	[12.OTf] ³⁺	604.6085
	[12] ⁴⁺	416.2225
13.8OTf	[13.6OTf] ²⁺	1596.4929
	[13.5OTf] ³⁺	1014.6904
	[13.4OTf] ⁴⁺	723.7753
	[13.3OTf] ⁵⁺	549.2345
14.4OTf	[14.3OTf] ⁺	2111.7312
	[14.2OTf] ²⁺	981.3898
	[14.OTf] ³⁺	604.6115
	[14] ⁴⁺	416.2171
15.8OTf	[15.6OTf] ²⁺	1596.4932
	[15.5OTf] ³⁺	1014.7112
	[15.4OTf] ⁴⁺	723.7756
	[15.3OTf] ⁵⁺	549.2338
	[15.2OTf] ⁶⁺	432.8712

^a Data were recorded on a Micromass LCT electrospray ionisation mass spectrometer using MeCN–H₂O mixtures. HR spectra were recorded in lockmass mode.

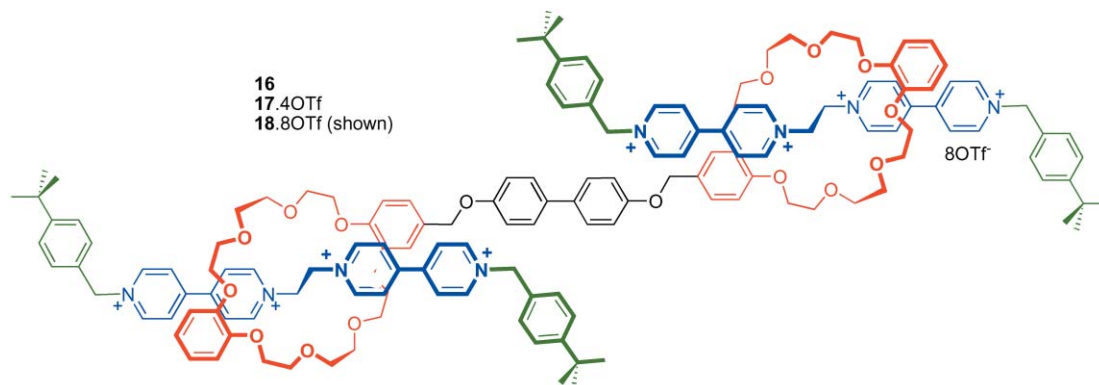
ESI-MS. As observed for **10.4OTf–15.8OTf**, the [3]rotaxane, **18.8OTf**, exhibited a less complicated ¹H NMR spectrum due to symmetry with characteristic shifts similar to those observed for the model [2]rotaxane **6.4OTf** thus verifying the interlocked structure. The ¹H NMR spectrum of [2]rotaxane **17.4OTf** exhibited resonances attributable to both complexed and uncomplexed crown in a 1 : 1 ratio as well as those from the pyridinium axle. HR-ESI-MS showed ions due to the loss of 1–4 triflate anions and are summarized in Table 3.

Crown ether **19** was prepared from 1,3,5-tris(4-hydroxyphenyl)benzene and three equivalents of **4**. Reaction of **19** with

Table 2 Yields of branched $[n]$ rotaxanes for crown ethers 7–9

Crown ether	Chemical yield of $[n]$ rotaxanes ^a (%)	[2]Rotaxane ^b (%)	[3]Rotaxane ^c (%)
7	92	82	18
8	83	70	30
9	68	62	38

^a Total chemical yield of all $[n]$ rotaxanes. ^b The percentage of the total $[n]$ rotaxane material that is [2]rotaxane. ^c The percentage of the total $[n]$ rotaxane material that is [3]rotaxane.

**Fig. 6** The bis(crown) ether **16** with a biphenyl spacer allows formation of the [2]rotaxane **17**⁺ and the [3]rotaxane **18**⁺ which is shown above.**Table 3** Mass spectrometry data^a for $[n]$ rotaxanes **17**, **18** and **20–22**

$[n]$ Rotaxane	Complex ion	Observed mass (m/z)
17.4OTf	[17.3OTf] ²⁺	2187.7471
	[17.2OTf] ²⁺	1019.3996
18.8OTf	[18.6OTf] ²⁺	1634.5197
	[18.5OTf] ³⁺	1040.0862
	[18.4OTf] ⁴⁺	742.7834
	[18.3OTf] ⁵⁺	564.4354
	[18.2OTf] ⁶⁺	445.5335
20.4OTf	[20.2OTf] ²⁺	1333.5374
	[20.OTf] ³⁺	839.3750
	[20] ⁴⁺	592.2961
21.8OTf	[21.6OTf] ²⁺	1948.6509
	[21.5OTf] ³⁺	1249.4468
	[21.4OTf] ⁴⁺	899.8655
	[21.3OTf] ⁵⁺	690.0938
	[21.2OTf] ⁶⁺	550.2519
22.12OTf	[22.5OTf] ⁷⁺	626.1077
	[22.4OTf] ⁸⁺	529.2

^a Data were recorded on a Micromass LCT electrospray ionisation mass spectrometer using MeCN–H₂O mixtures. HR spectra were recorded in lockmass mode.

six equivalents of **1.2OTf** and excess 4-*tert*-butylbenzylbromide gave the [2]rotaxane **20.4OTf**, the [3]rotaxane **21.8OTf** and the branched [4]rotaxane **22.12OTf**; see Fig. 7. In order to elute the highly charged [4]rotaxane, **22.12OTf**, a more polar solvent system (2 M NH₄Cl(aq)–DMF (1 : 1)) was applied after the elution of **20.4OTf** and **21.8OTf**. Like fractions (as determined by TLC), were combined and anion exchanged with NaOTf to regenerate the salt **22.12OTf** as a glassy dark orange–red solid. The ¹H NMR spectrum of the [2]rotaxane **20.4OTf** exhibited resonances attributable to both complexed and uncomplexed crown in a 1 : 2 ratio while for the [3]rotaxane **21.8OTf** this ratio was 2 : 1 as two of the three crown units are involved in rotaxane formation. Although the branched [4]rotaxane, **22.12OTf** is the largest molecule prepared in this study the ¹H NMR spectrum was again less complicated due to symmetry with characteristic shifts for complexed crown only along with resonances for the

Table 4 Yields of branched $[n]$ rotaxanes for crown ethers **16** and **19**

Crown ether	[2]Rotaxane ^a (%)	[3]Rotaxane ^b (%)	[4]Rotaxane ^c (%)
16	69	31	—
19	32	33	35

^a The percentage of the total isolated $[n]$ rotaxane material that is [2]rotaxane. ^b [3]Rotaxane. ^c [4]Rotaxane.

three pyridinium axes. The HR-ESI-MS results for compound **22.12OTf** allowed unambiguous determination of exact mass for the ion [**22.5OTf**]⁷⁺. Other ions observed at lower resolution limit were still sufficient to provide further evidence in terms of position and profile for the existence of the [4]rotaxane; see Table 3.

The product distribution of $[n]$ rotaxanes for these multi-crown ethers with larger cores is interesting (Table 4). It appears that on going from a single benzene unit with a 1,4-positioning, **9**, to a biphenyl unit with the same positioning, **16**, there is no increase in the yield of the fully complexed [3]rotaxane; 38 vs. 31%, respectively. Presumably the negative factors preventing the threading of the second ring are already reduced to a minimum with the hydroquinone unit and that further separation with a biphenol group has no effect. For the tris-crown ether, **19**, the yields of [2]rotaxane, [3]rotaxane and [4]rotaxane are 32, 33 and 35%, reflecting a uniform decrease in the efficiency of each subsequent threading.

Summary and conclusions

The first generations of Type III-B dendrimeric polyrotaxanes can be prepared using the pseudorotaxane motif which combines 1,2-bis(pyridinium)ethane axes and 24C8 wheels. Multi-crown ethers are easily prepared from commercially available phenolic cores and the chloromethyl derivative of DB24C8. The product distribution of branched $[n]$ rotaxanes observed gives a crude measure of the efficiency of the threading process required to produce the fully saturated polyrotaxanes (*i.e.* all the crowns converted to rotaxanes). The size of the core can be a single benzene ring but this is only practical for the formation of two branches as the two crowns need to be positioned away from each other in the 1,4-orientation to minimize inhibitory interactions.

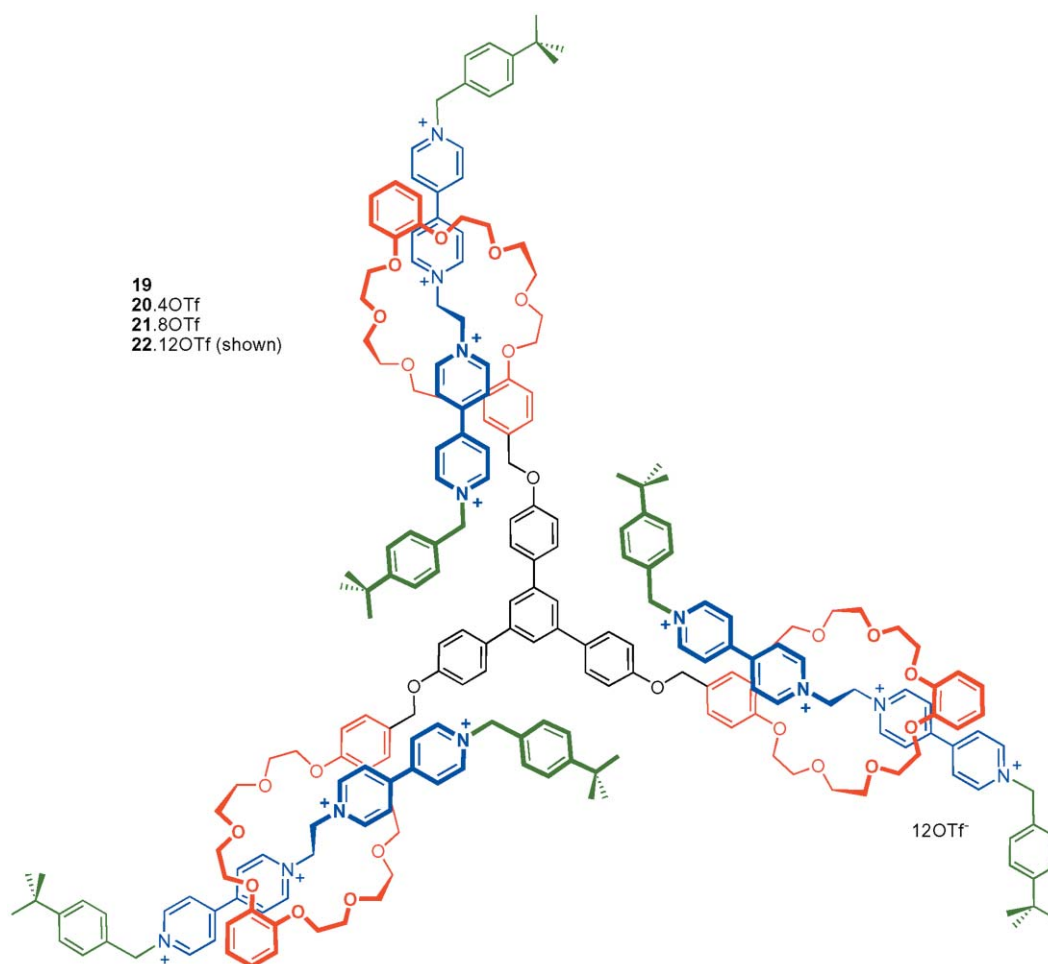


Fig. 7 The tris(crown) ether **19** allows the synthesis of the [2]rotaxane **20**⁴⁺, the [3]rotaxane **21**⁸⁺ and the [4]rotaxane **22**¹²⁺ which is shown above.

Attaching phenolic units to a central benzene ring allowed the formation of a larger [4]rotaxane with three branches. The efficiency of the threading steps decreased sequentially but was sufficient to allow a moderate yield of the [4]rotaxane under the limited conditions of this study.

The decrease in efficiency of the threading process upon addition of each new rotaxane can be attributed to three factors; (1) steric interactions between an already complexed crown ether site (pseudorotaxane or rotaxane) and the new incoming thread, (2) electrostatic repulsions between an existing rotaxane thread and the new incoming thread and (3) partial occupation of the unoccupied crown ether recognition elements by a neighboring rotaxane unit.

We are currently focused on optimising the yield of the fully occupied [*n*]rotaxanes while developing a strategy to further functionalise the peripheral stoppering units to allow for the addition of the new branches and the next generation of dendrimer.

Experimental

Ammonium chloride, *tert*-butylbenzyl bromide, sodium borohydride, pyridine, thionyl chloride, potassium carbonate, 4,4'-biphenol, catechol, hydroquinone, phenol, resorcinol, sodium triflate and 1,3,5-tris(4-hydroxyphenyl)benzene were purchased from Aldrich and used as received. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used as received. Solvents were dried using an Innovative Technologies Solvent Purification System. Thin Layer Chromatography (TLC) was performed using Merck Silica gel 60 F₂₅₄ plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230–400 mesh). ¹H NMR

experiments were performed on a Bruker Avance 500 instrument using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Conventional 2-D NMR experiments (¹H–¹H COSY and NOESY) were used to assign all peaks. High-resolution mass spectrometry experiments were performed on a Micromass LCT electrospray time of flight (TOF) mass spectrometer in lockmass mode. Solutions of 50–100 ng μL⁻¹ were prepared in MeCN–H₂O (1 : 1) (unless otherwise indicated) and injected for analysis at a rate of 5 μL min⁻¹ using a syringe pump. The diagram for the X-ray crystal structure was generated with the program *DIAMOND*.¹¹

Preparation of crown ether, **3**

To a solution of **2** (2.55 g, 5.35 mmol) in ethanol (50 mL) and methylene chloride (50 mL) cooled to 0 °C was slowly added sodium borohydride (0.607 g, 16.0 mmol) and the resulting solution allowed to come to room temperature and then stir overnight. The reaction mixture was acidified with 1 M HCl (3 × 30 mL) and then extracted with methylene chloride (100 mL). The organic layer was washed with 1 M NaHCO₃ (3 × 50 mL), water (2 × 50 mL), dried over anhydrous MgSO₄ and evaporated to yield the desired off-white solid **3**. Yield 2.48 g (97%). ¹H NMR (500 MHz, CDCl₃): δ 6.82–6.91 (m, 7H), 4.13–4.17 (m, 8H), 3.89–3.91 (m, 8H), 3.81–3.83 (m, 8H), 4.58 (s, 2H). Mp 95–96 °C. HR-ESI-MS: *m/z* [**3** + Na]⁺: calc.: 501.2101, found: 501.2100.

Preparation of crown ether, **4**

To a solution of pyridine (5.29 g, 66.9 mmol) and thionyl chloride (7.54 g, 63.4 mmol) in methylene chloride (40 mL) was added a solution of **3** (6.54 g, 13.7 mmol) in methylene chloride

(10 mL) and the solution stirred at room temperature for 1 h. Chloroform (50 mL) was added and the reaction mixture poured over cold water (100 mL). The aqueous layer was extracted with methylene chloride (2 × 50 mL) and the combined organic layers washed with water (2 × 50 mL), 1 M NaHCO₃ (2 × 50 mL), a saturated sodium chloride solution (50 mL), dried (MgSO₄) and concentrated (5 mL). Hexanes were added to precipitate the desired white solid product, **4**. Yield 6.51 g (96%). ¹H NMR (500 MHz, CDCl₃): δ 6.80–6.90 (m, 7H), 4.14–4.17 (m, 8H), 3.90–3.92 (m, 8H), 3.81–3.82 (m, 8H), 4.52 (s, 2H). Mp 90–91 °C. HR-ESI-MS: *m/z* [**4** + Na]⁺: calc.: 519.1762, found: 519.1750.

Preparation of crown ether, **5**

To a solution of **4** (0.630 g, 1.27 mmol) and phenol (0.087 g, 0.92 mmol) in acetonitrile (30 mL) was added potassium carbonate (0.662 g, 4.79 mmol) and the mixture stirred under reflux for 5 days. The solvent was evaporated and the residue partitioned between chloroform and water. The organic layer was washed with water (2 × 50 mL), dried with anhydrous MgSO₄ and concentrated to give the desired off-white solid, **5**. Yield 2.48 g (97%). X-Ray quality crystals were grown by the slow diffusion of hexanes into a saturated chloroform solution of **5**. ¹H NMR (500 MHz, CDCl₃): δ 7.26–7.27 (m, 2H), 6.93–6.96 (m, 5H), 6.84–6.88 (m, 5H), 4.96 (s, 2H), 4.14–4.17 (m, 8H), 3.90–3.92 (m, 8H), 3.82 (s, 8H). Mp 105–106 °C. HR-ESI-MS: *m/z* [**5** + Na]⁺: calc.: 577.2414, found: 577.2427.

Preparation of [2]rotaxane, **6.4OTf**

Crown ether **5** (0.110 g, 0.198 mmol) and **1.2OTf** (0.050 g, 0.097 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.133 g, 0.586 mmol) and 3 mL of saturated NaOTf(aq) were added and the two-phase reaction stirred for 4 days. The organic layer was separated, dried over anhydrous MgSO₄ and evaporated to dryness. The orange residue was taken up in acetonitrile (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3)], (*R_f* = 0.47). Like fractions were combined, the solvent removed and anion exchanged with NaOTf(aq) to yield the product as an orange–red solid. Yield 0.0713 g (41%). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 4H, ³*J* = 6.7), 8.92 (d, 4H, ³*J* = 6.7 Hz), 8.24 (d, 4H, ³*J* = 6.7 Hz), 8.17 (d, 4H, ³*J* = 6.7 Hz), 7.54 (d, 4H, ³*J* = 8.3 Hz), 7.40 (d, 4H, ³*J* = 8.3 Hz), 7.36 (dd, 2H, ³*J* = 8.2 Hz, ³*J* = 7.5 Hz), 7.02 (t, 1H, ³*J* = 7.3 Hz), 6.93 (d, 2H, ³*J* = 8.2), 6.79 (d, 1H, ⁴*J* = 1.7 Hz), 6.66–6.64 (m, 3H), 6.50 (dd, 1H, ⁴*J* = 1.5 Hz, ³*J* = 8.2 Hz), 6.40–6.42 (m, 2H), 5.72 (s, 4H), 5.61 (s, 4H), 4.57 (s, 2H), 4.00–4.08 (m, 24H), 1.32 (s, 18H). Mp 130–131 °C. HR-ESI-MS: *m/z* [**6.3OTf**]⁺: calc.: 1635.5112, found: 1635.5120. [**6.2OTf**]²⁺: calc.: 743.2796, found: 743.2850. [**6.OTf**]³⁺: calc.: 445.8691, found: 445.8500. [**6**]⁴⁺: calc.: 297.1638, found: 297.1564.

Preparation of bis(crown ether), **7**

To a solution of catechol (0.0402 g, 0.365 mmol) and **4** (0.446 g, 0.897 mmol) in acetone (80 mL) was added potassium carbonate (0.879 g, 6.36 mmol). The mixture was refluxed for 7 days, cooled and then filtered. The filtrate was evaporated to dryness and the residue dissolved in chloroform (50 mL). The solution was washed with water (2 × 50 mL), dried with anhydrous MgSO₄ and evaporated to yield a yellow residue which was dissolved in chloroform (3 mL) and hexanes added to precipitate the desired white solid **7**. Yield 0.085 g (23%). ¹H NMR (500 MHz, CDCl₃): δ 6.81–6.97 (m, 18H), 4.07–4.15 (m, 16H), 3.85–3.91 (m, 16H), 3.80–3.82 (m, 16H), 5.03 (s, 4H). Mp 121–122 °C. HR-ESI-MS: *m/z* [**7** + Na]⁺: calc.: 1053.4460, found: 1053.4467. [**7** + 2Na]²⁺: calc.: 538.2179, found: 538.2084.

Preparation of bis(crown ether), **8**

To a solution of resorcinol (0.053 g, 0.48 mmol) and **4** (0.527 g, 1.06 mmol) in acetone (80 mL) was added potassium carbonate (0.957 g, 6.92 mmol). The mixture was refluxed for 7 days, cooled and then filtered. After the solvent was removed, the residue was dissolved in chloroform (50 mL), washed with water (2 × 50 mL) and dried with anhydrous MgSO₄. The solvent was evaporated to give a yellow residue which was dissolved in chloroform (3 mL). Hexanes were added to precipitate the desired white solid, **8**. Yield 0.138 g (28%). ¹H NMR (500 MHz, CDCl₃): δ 7.14 (t, 1H, ³*J* = 7.6 Hz), 6.83–6.93 (m, 14H), 6.54–6.58 (m, 3H), 4.90 (s, 4H), 4.12–4.15 (m, 16H), 3.88–3.90 (m, 16H), 3.80 (s, 16H). Mp 110–111 °C. HR-ESI-MS: *m/z* [**8** + Na]⁺: calc.: 1053.4460, found: 1053.4467. [**8** + 2Na]²⁺: calc.: 538.2179, found: 538.2207.

Preparation of bis(crown ether), **9**

To a solution of hydroquinone (0.033 g, 0.299 mmol) and **4** (0.366 g, 0.736 mmol) in acetone (80 mL) was added potassium carbonate (0.641 g, 4.64 mmol) and the mixture refluxed for 7 days. The reaction contents were filtered and the filtrate evaporated. The residue was dissolved in chloroform (50 mL), washed with water (2 × 50 mL), dried with anhydrous MgSO₄ and evaporated to yield a yellow residue. After dissolution in chloroform (3 mL), hexanes were added to precipitate the desired white solid, **9**. Yield 0.113 g (37%). ¹H NMR (500 MHz, CDCl₃): δ 6.84–6.94 (m, 18H), 4.90 (s, 4H), 4.14–4.16 (m, 16H), 3.89–3.91 (m, 16H), 3.82 (s, 16H). Mp 125–126 °C. HR-ESI-MS: *m/z* [**9** + Na]⁺: calc.: 1053.4460, found: 1053.4459.

Preparation of [2]rotaxane, **10.4OTf** and [3]rotaxane, **11.8OTf**

Crown ether **7** (0.0153 g, 0.0148 mmol) and **1.2OTf** (0.0152 g, 0.0296 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.0229 g, 0.101 mmol) and 3 mL of a saturated NaOTf(aq) were added and the two-phase reaction stirred for 7 days. The organic layer was separated, dried with anhydrous MgSO₄ and evaporated to dryness. The orange residue was taken up in MeCN (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3)]. Like fractions were combined, the solvent removed and anion exchanged with NaOTf(aq) to yield the products as orange–red solids. Overall chemical yield 92%. **10.4OTf**: 0.0252 g (82% of total material) (*R_f* = 0.63). ¹H NMR (500 MHz, CD₃CN): δ 9.27 (d, 4H, ³*J* = 6.6 Hz), 8.90 (d, 4H, ³*J* = 6.5 Hz), 8.00 (d, 4H, ³*J* = 6.5 Hz), 8.15 (d, 4H, ³*J* = 6.6 Hz), 7.51 (d, 4H, ³*J* = 8.4 Hz), 7.40 (d, 4H, ³*J* = 8.4 Hz), 7.17–7.19 (m, 1H), 7.03–7.09 (m, 4H), 6.80–6.98 (m, 8H), 6.53–6.59 (m, 3H), 6.39 (d, 8H, ³*J* = 8.2 Hz), 6.33–6.35 (m, 1H), 5.75–5.77 (m, 4H), 5.52–5.54 (m, 4H), 4.86 (s, 2H), 4.57 (s, 2H), 3.46–4.22 (m, 48H), 1.32 (s, 18H). Mp 127–128 °C. HR-ESI-MS: *m/z* [**10.3OTf**]⁺: calc.: 2111.7158, found: 2111.7068. [**10.2OTf**]²⁺: calc.: 981.3819, found: 981.3887. [**10.OTf**]³⁺: calc.: 604.6039, found: 604.6057. [**10**]⁴⁺: calc.: 416.2149, found: 416.2236. **11.8OTf**: 0.0109 g (18% of total material) (*R_f* = 0.54). ¹H NMR (500 MHz, CD₃CN): δ 9.29 (d, 8H, ³*J* = 6.8 Hz), 8.94 (d, 8H, ³*J* = 6.8 Hz), 8.23 (d, 8H, ³*J* = 6.8 Hz), 8.15 (d, 8H, ³*J* = 6.8 Hz), 7.52 (d, 8H, ³*J* = 8.4 Hz), 7.42 (d, 8H, ³*J* = 8.4 Hz), 6.99–7.02 (m, 4H), 6.78 (d, 2H ⁴*J* = 1.5 Hz), 6.61–6.66 (m, 4H), 6.54 (d, 2H, ³*J* = 8.2 Hz), 6.44 (dd, 2H, ⁴*J* = 1.5, ³*J* = 8.2 Hz), 6.37–6.40 (m, 4H), 5.73 (s, 8H), 5.56 (s, 8H), 4.61 (s, 4H), 3.95–4.04 (m, 48H), 1.29 (s, 36H). Mp 175–176 °C. HR-ESI-MS: *m/z* [**11.6OTf**]²⁺: calc.: 1596.4877, found: 1596.4901. [**11.5OTf**]³⁺: calc.: 1014.6745, found: 1014.6815. [**11.4OTf**]⁴⁺: calc.: 723.7679, found: 723.7728. [**11.3OTf**]⁵⁺: calc.: 549.2239, found: 549.2340. [**11.2OTf**]⁶⁺: calc.: 432.8612, found: 432.8621.

Preparation of [2]rotaxane, 12.4OTf and [3]rotaxane, 13.8OTf

Crown ether **8** (0.0148 g, 0.0144 mmol) and **1.2OTf** (0.0185 g, 0.0359 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.0278 g, 0.122 mmol) and 3 mL of a saturated NaOTf(aq) were added and the two-phase reaction stirred for 7 days. The organic layer was separated, dried over anhydrous MgSO₄ and evaporated. The orange residue was taken up in MeCN (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3)]. Like fractions were combined and anion exchanged with NaOTf(aq) to yield the products as orange–red solids. Overall chemical yield 83%. **12.4OTf**: 0.0189 g (70% of total material) (*R*_f = 0.63). ¹H NMR (500 MHz, CD₃CN): δ 9.31 (d, 4H, ³*J* = 6.6 Hz), 8.86 (d, 4H, ³*J* = 6.5 Hz), 8.24 (d, 4H, ³*J* = 6.6 Hz), 8.15 (d, 4H, ³*J* = 6.5 Hz), 7.52 (d, 4H, ³*J* = 8.3 Hz), 7.36 (d, 4H, ³*J* = 8.3 Hz), 7.25 (t, 1H, ³*J* = 8.2 Hz), 7.03–7.05 (m, 2H), 6.89 (m, 1H), 6.80 (s, 1H), 6.63–6.69 (m, 5H), 6.57 (br s, 1H), 6.47–6.51 (m, 2H), 6.40–6.45 (m, 4H), 6.33 (dd, 1H, ⁴*J* = 1.5, ³*J* = 8.2 Hz), 5.68–5.72 (m, 4H), 5.60 (s, 4H), 5.05 (s, 2H), 4.51 (s, 2H), 3.97–4.14 (m, 32H), 3.65–3.80 (m, 16H), 1.31 (s, 18H). Mp 135–136 °C. HR-ESI-MS: *m/z* [12.3OTf]⁺: calc.: 2111.7158, found: 2111.7097. [12.2OTf]²⁺: 981.3819, found: 981.3876. [12.1OTf]³⁺: calc.: 604.6039, found: 604.6085. [12]⁴⁺: calc.: 416.2149, found: 416.2225. **13.8OTf**: 0.0131 g (30% of total material) (*R*_f = 0.40). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 8H, ³*J* = 6.8 Hz), 8.94 (d, 8H, ³*J* = 6.9 Hz), 8.28 (d, 8H, ³*J* = 6.8 Hz), 8.20 (d, 8H, ³*J* = 6.9 Hz), 8.94 (d, 8H, ³*J* = 6.9 Hz), 7.51 (d, 8H, ³*J* = 8.4 Hz), 7.41 (d, 8H, ³*J* = 8.4 Hz), 7.32 (t, 1H, ³*J* = 8.2 Hz), 6.81 (d, 2H, ⁴*J* = 1.6 Hz), 6.60–6.65 (m, 9H), 6.55 (dd, 2H, ⁴*J* = 1.6, ³*J* = 8.2 Hz), 6.39–6.42 (m, 4H), 5.61 (s, 8H), 4.63 (s, 4H), 4.00–4.06 (m, 48H), 1.31 (s, 36H). Mp 190–191 °C. HR-ESI-MS: *m/z* [13.6OTf]²⁺: calc.: 1596.4877, found: 1596.4929. [13.5OTf]³⁺: calc.: 1014.6745, found: 1014.6904. [13.4OTf]⁴⁺: calc.: 723.7679, found: 723.7753. [13.3OTf]⁵⁺: calc.: 549.2239, found: 549.2345. [13.2OTf]⁶⁺: calc.: 432.8612, found: 432.8674.

Preparation of [2]rotaxane, 14.4OTf and [3]rotaxane, 15.8OTf

Crown ether **9** (0.0151 g, 0.0146 mmol) and **1.2OTf** (0.0188 g, 0.0366 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.0278 g, 0.122 mmol) and 3 mL of a saturated NaOTf(aq) were added and the two-phase reaction stirred for 7 days. The organic layer was separated, dried over anhydrous MgSO₄ and evaporated. The orange residue was taken up in MeCN (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3)]. Like fractions were combined and anion exchanged with NaOTf(aq) to yield the products as orange–red solids. Overall chemical yield 68%. **14.4OTf**: 0.0139 g (62% of total material) (*R*_f = 0.61). ¹H NMR (500 MHz, CD₃CN): δ 9.30 (d, 4H, ³*J* = 6.8 Hz), 8.80 (d, 4H, ³*J* = 6.8 Hz), 8.15 (d, 4H, ³*J* = 6.8 Hz), 7.99 (d, 4H, ³*J* = 6.8 Hz), 7.56 (d, 4H, ³*J* = 8.4 Hz), 7.40 (d, 4H, ³*J* = 8.4 Hz), 6.82–6.97 (m, 10H), 6.60–6.72 (m, 5H), 6.48 (t, 1H, ³*J* = 8.3 Hz), 6.38–6.40 (m, 2H), 5.71 (s, 4H), 5.59 (s, 4H), 4.98 (s, 2H), 4.61 (s, 2H), 3.99–4.15 (m, 32H), 3.82–3.85 (m, 8H), 3.70–3.72 (m, 8H), 1.31 (s, 18H). Mp 135–136 °C. HR-ESI-MS: *m/z* [14.3OTf]⁺: calc.: 2111.7158, found: 2111.7312. [14.2OTf]²⁺: calc.: 981.3819, found: 981.3898. [14.OTf]³⁺: calc.: 604.6039, found: 604.6115. [14]⁴⁺: calc.: 416.2149, found: 416.2171. **15.8OTf**: 0.0138 g (38% of total material) (*R*_f = 0.30). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 8H, ³*J* = 6.8 Hz), 8.94 (d, 8H, ³*J* = 6.8 Hz), 8.26 (d, 8H, ³*J* = 6.8 Hz), 8.19 (d, 8H, ³*J* = 6.8 Hz), 7.55 (d, 8H, ³*J* = 8.4 Hz), 7.44 (d, 8H, ³*J* = 8.4 Hz), 6.94 (s, 4H), 6.78 (d, 2H, ⁴*J* = 1.7 Hz), 6.63–6.65 (m, 6H), 6.50 (dd, 2H, ⁴*J* = 1.7, ³*J* = 7.8 Hz), 6.39–6.41 (m, 4H), 5.72 (s, 8H), 5.61 (s, 8H), 4.54 (s, 4H), 4.00–4.06 (m, 48H), 1.29 (s, 36H). Mp 180–181 °C. HR-ESI-MS: *m/z* [15.6OTf]²⁺: calc.: 1596.4877, found: 1596.4932.

[15.5OTf]³⁺: calc.: 1014.6745, found: 1014.7112. [15.4OTf]⁴⁺: calc.: 723.7679, found: 723.7756. [15.3OTf]⁵⁺: calc.: 549.2239, found: 549.2338. [15.2OTf]⁶⁺: calc.: 432.8612, found: 432.8712.

Preparation of bis(crown ether), 16

To a solution of 4,4'-biphenol (0.044 g, 0.234 mmol) and **4** (0.213 g, 0.429 mmol) in acetonitrile (80 mL) was added potassium carbonate (0.353 g, 2.55 mmol). The mixture was refluxed for 4 days, cooled, filtered and then the solvent removed. The residue was dissolved in chloroform (50 mL), washed with water (2 × 50 mL), dried over anhydrous MgSO₄. The solvent was evaporated to yield a yellow residue. The crude material was dissolved in chloroform (3 mL) and hexanes added to precipitate the desired white solid, **16**. Yield 0.136 g (52%). ¹H NMR (500 MHz, CDCl₃): δ 7.45 (d, 4H, ³*J* = 8.7 Hz), 6.99 (d, 4H, ³*J* = 8.7 Hz), 6.94–6.97 (m, 4H), 6.86–6.89 (m, 10H), 4.99 (s, 4H), 4.14–4.18 (m, 16H), 3.90–3.91 (m, 16H), 3.82 (s, 16H). Mp 151–152 °C. HR-ESI-MS: *m/z* [16 + Na]⁺: calc.: 1129.4773, found: 1129.4790; [16 + 2Na]²⁺: calc.: 576.2335, found: 576.2343.

Preparation of [2]rotaxane, 17.4OTf and [3]rotaxane, 18.8OTf

Crown ether **16** (0.0308 g, 0.0278 mmol) and **1.2OTf** (0.0571 g, 0.111 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.0504 g, 0.222 mmol) and 3 mL of a saturated NaOTf(aq) were added and the two-phase reaction stirred for 7 days. The organic layer was separated, dried over anhydrous MgSO₄ and evaporated. The orange residue was taken up in MeCN (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3)]. Like fractions were combined, the solvent removed and anion exchanged with NaOTf(aq) to yield the products as orange–red solids. Overall chemical yield 37%. **17.4OTf**: 0.0167 g (69% of total material) (*R*_f = 0.59). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 4H, ³*J* = 6.8 Hz), 8.93 (d, 4H, ³*J* = 6.7 Hz), 8.26 (d, 4H, ³*J* = 6.8 Hz), 8.20 (d, 4H, ³*J* = 6.7 Hz), 7.58 (d, 2H, ³*J* = 8.8 Hz), 7.56 (d, 2H, ³*J* = 8.7 Hz), 7.52 (d, 4H, ³*J* = 8.4 Hz), 7.40 (d, 4H, ³*J* = 8.4 Hz), 7.07 (d, 2H, ³*J* = 8.7 Hz), 6.97–7.02 (m, 3H), 6.89–6.95 (m, 6H), 6.81 (d, 1H, ⁴*J* = 1.4 Hz), 6.64–6.68 (m, 3H), 6.53 (dd, 1H, ⁴*J* = 1.4, ³*J* = 8.2 Hz), 6.40–6.42 (m, 2H), 5.72 (d, 4H, *J* = 1.8 Hz), 5.62 (s, 4H), 5.04 (s, 2H), 4.60 (s, 2H), 4.00–4.13 (m, 32H), 3.78–3.81 (m, 8H), 3.68 (s, 8H), 1.30 (s, 18H). Mp 140–141 °C. HR-ESI-MS: *m/z* [17.3OTf]⁺: calc.: 2187.7471, found: 2187.7874. [17.2OTf]²⁺: calc.: 1019.3976, found: 1019.3996. **18.8OTf**: 0.00881 g (31% of total material) (*R*_f = 0.44). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 8H, ³*J* = 6.9 Hz), 8.94 (d, 8H, ³*J* = 6.8 Hz), 8.26 (d, 8H, ³*J* = 6.9 Hz), 8.20 (d, 8H, ³*J* = 6.8 Hz), 7.63 (d, 4H, ³*J* = 8.7 Hz), 7.52 (d, 8H, ³*J* = 8.4 Hz), 7.40 (d, 8H, ³*J* = 8.4 Hz), 7.02 (d, 4H, ³*J* = 8.7 Hz), 6.81 (d, 2H, ⁴*J* = 1.3 Hz), 6.64–6.67 (m, 6H), 6.52 (dd, 2H, ⁴*J* = 1.3, ³*J* = 8.1 Hz), 6.40–6.42 (m, 4H), 5.73 (s, 8H), 5.62 (s, 8H), 4.60 (s, 4H), 4.00–4.09 (m, 48H), 1.29 (s, 36H). Mp 175–176 °C. HR-ESI-MS: *m/z* [18.6OTf]²⁺: calc.: 1634.5034, found: 1634.5197. [18.5OTf]³⁺: calc.: 1040.0182, found: 1040.0862. [18.4OTf]⁴⁺: calc.: 742.7757, found: 742.7834. [18.3OTf]⁵⁺: calc.: 564.4301, found: 564.4354. [18.2OTf]⁶⁺: calc.: 445.5331, found: 445.5335.

Preparation of tris(crown ether), 19

To a solution of 1,3,5-tris(4-hydroxyphenyl)benzene (0.052 g, 0.147 mmol) and **4** (0.284 g, 0.571 mmol) in acetone (80 mL) was added potassium carbonate (0.694 g, 5.02 mmol) and the mixture was refluxed for 7 days. The reaction contents were filtered and the filtrate was evaporated. The residue was dissolved in chloroform (50 mL), washed with water (2 × 50 mL), dried with anhydrous MgSO₄ and evaporated to yield a yellow solid. This material was dissolved in chloroform (3 mL) and hexanes added to precipitate the desired white solid, **19**. Yield 0.102 g

(40%). ¹H NMR (500 MHz, CDCl₃): δ 7.64 (s, 3H), 7.60 (d, 6H, ³J = 8.7 Hz), 7.05 (d, 6H, ³J = 8.7 Hz), 6.96–6.98 (m, 6H), 6.87–6.88 (m, 15H), 5.02 (s, 6H), 4.13–4.19 (m, 24H), 3.90–3.92 (m, 24H), 3.82 (s, 24H). Mp 115–116 °C. HR-ESI-MS: *m/z* [19 + Na]⁺: calc.: 1757.7445, found: 1757.7448.

Preparation of [2]rotaxane, 20.4OTf, [3]rotaxane, 21.8OTf and [4]rotaxane, 22.12OTf

Crown ether **19** (0.053 g, 0.031 mmol) and 1.2OTf (0.110 g, 0.214 mmol) were dissolved in nitromethane (20 mL) and stirred overnight. 4-*tert*-Butylbenzyl bromide (0.100 g, 0.440 mmol) and 3 mL of a saturated NaOTf(aq) were added and the two-phase reaction stirred for 7 days. The organic layer was separated, dried over anhydrous MgSO₄ and evaporated. The orange residue was taken up in MeCN (1 mL) and filtered. The solvent was removed from the filtrate and the residue subjected to column chromatography [SiO₂: methanol–nitromethane–2 M NH₄Cl(aq) (6 : 1 : 3) up to DMF–2 M NH₄Cl(aq) (1 : 1)]. Like fractions were combined and anion exchanged with NaOTf(aq) to yield the products as orange–red solids. Overall chemical yield 85%. **20.4OTf**: 0.0243 g (32% of total material) (*R*_f = 0.63). ¹H NMR (500 MHz, CD₃CN): δ 9.33 (d, 4H, ³J = 6.4 Hz), 8.90 (d, 4H, ³J = 6.5 Hz), 8.23 (d, 4H, ³J = 6.4 Hz), 8.16 (d, 4H, ³J = 6.5 Hz), 7.73–7.81 (m, 9H), 7.50 (d, 4H, ³J = 8.3 Hz), 7.39 (d, 4H, ³J = 8.3 Hz), 6.91–7.12 (m, 20H), 6.83 (d, 1H, ⁴J = 1.5 Hz), 6.62–6.64 (m, 3H), 6.58 (dd, 1H, ⁴J = 1.5, ³J = 8.2 Hz), 6.40–6.42 (m, 2H), 5.71 (d, 4H, *J* = 4.1 Hz), 5.61 (s, 4H), 5.08 (s, 4H), 4.65 (s, 2H), 4.02–4.17 (m, 40H), 3.77–3.80 (m, 16H), 3.64–3.66 (m, 16H), 1.30 (s, 18H). Mp 137–138 °C. HR-ESI-MS: *m/z* [20.2OTf]²⁺: calc.: 1333.5312, found: 1333.5374 [20.OTf]²⁺: calc.: 839.3701, found: 839.3750, [20]⁴⁺: calc.: 592.2896, found: 592.2961. **21.8OTf**: 0.036 g (33% of total material) (*R*_f = 0.51). ¹H NMR (500 MHz, CD₃CN): δ 9.34 (d, 8H, ³J = 6.8 Hz), 8.93 (d, 8H, ³J = 6.7 Hz), 8.26 (d, 8H, ³J = 6.8 Hz), 8.20 (d, 8H, ³J = 6.7 Hz), 7.81–7.85 (m, 9H), 7.51 (d, 8H, ³J = 8.4 Hz), 7.40 (d, 8H, ³J = 8.4 Hz), 7.13–7.15 (m, 2H), 7.08 (d, 6H, ³J = 8.7 Hz), 7.04 (d, 1H, ³J = 8.3 Hz), 6.93–6.97 (m, 4H), 6.89 (d, 2H, ³J = 8.3 Hz), 6.83 (d, 2H, ⁴J = 1.2 Hz), 6.64–6.66 (m, 4H), 6.56 (dd, 2H, ⁴J = 8.3, ³J = 1.2 Hz), 6.41–6.42 (m, 4H), 5.72 (d, 8H, *J* = 4.0 Hz), 5.62 (s, 8H), 5.09 (s, 2H), 4.64 (s, 4H), 4.01–4.14 (m, 56H), 3.77–3.81 (m, 8H), 3.66 (d, 8H, ³J = 1.9 Hz), 1.27 (s, 36H). Mp 165–166 °C. HR-ESI-MS: *m/z* [21.6OTf]²⁺: calc.: 1948.6370, found: 1948.6509. [21.5OTf]³⁺: calc.: 1249.4406, found: 1249.4468. [21.4OTf]⁴⁺: calc.: 899.8425, found: 899.8655. [21.3OTf]⁵⁺: calc.: 690.0836, found: 690.0938. [21.2OTf]⁶⁺: calc.: 550.2443, found: 550.2519. **22.12OTf**: 0.0497 g (35% of total material) (*R*_f = 0.35). ¹H NMR (500 MHz, CD₃CN): δ 9.34 (d, 12H, ³J = 8.9 Hz), 8.95 (d, 12H, ³J = 8.9 Hz), 8.29 (d, 12H, ³J = 8.9 Hz), 8.22 (d, 12H, ³J = 8.9 Hz), 7.87 (s, 3H), 7.83 (d, 6H, ³J = 8.5 Hz), 7.73 (d, 12H, *J* = 2.9 Hz), 7.50 (d, 12H, ³J = 8.4 Hz), 7.40 (d, 12H, ³J = 8.4 Hz), 7.09 (d, 6H, ³J = 8.7 Hz), 6.83 (d, 3H, ⁴J = 1.5 Hz), 6.69 (d, 3H, ³J = 8.2 Hz), 6.64–6.66 (m, 6H), 6.55 (dd, 3H, ⁴J = 1.5, ³J = 8.2 Hz), 6.39–6.42 (m, 6H), 5.63 (s, 12H), 4.64 (s, 6H), 4.01–4.10 (m, 72H), 1.27 (s, 54H). Mp 190–191 °C. HR-ESI-MS: *m/z* [22.5OTf]⁷⁺: calc.: 626.1036, found 626.1077. LR-ESI-MS [22.4OTf]⁸⁺: calc.: 529.2, found 529.2.

X-Ray structure determination of crown ether, **5**

Colourless crystals of **5** were grown by slow diffusion of hexanes into a saturated chloroform solution. Crystals were mounted on a short glass fibre attached to a tapered copper pin and the crystal cooled to 173.0(1) K. A full hemisphere of data were collected with 30 s frames on a Brüker APEX diffractometer fitted with a CCD based detector. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. The data was relatively weak due to the poor quality of the crystals. Diffraction data and unit-cell parameters were consistent with the assigned space group. Lorentzian

polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data set. The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against |*F*²| data. All non-hydrogen atoms were refined anisotropically. The thermal parameter for atom C(26) was restrained using the ISOR command. There was evidence for a slight disorder for one of the OCH₂CH₂O linkages but this was not modelled. All hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library¹²

Crystal data. C₃₁H₃₈O₉, *M* = 554.61, triclinic, space group *P*1 (no. 1), *a* = 8.5216(13), *b* = 8.6643(13), *c* = 10.4987(16) Å, *a* = 92.857(3), *β* = 96.328(3), *γ* = 113.673(3)°, *V* = 701.82(18) Å³, *Z* = 1, *D*_c = 1.312 g cm⁻³, *μ*(Mo-Kα) = 0.096 mm⁻¹, colourless block; 2474 independent measured reflections, *F*² refinement, *R*₁ = 0.0961, *wR*₂ = 0.1034 [*I* > 2σ(*I*)], *R*₁ = 0.2339, *wR*₂ = 0.2423 (all data), goodness-of-fit = 1.42, 361 parameters, 9 restraints.

CCDC reference number 258420.

See <http://www.rsc.org/suppdata/ob/b4/b418772e/> for crystallographic data in .cif or other electronic format.

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