TEMPLATE-DIRECTED SYNTHESES OF ROTAXANES

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Rotaxanes are molecules comprised of a dumbbell-shaped component encircled by one or more macrocyclic components. The early syntheses of rotaxanes were mainly based upon statistical threading or upon directed methodologies involving chemical conversion. However, with the advent of supramolecular chemistry, a series of host–guest and template-directed approaches to rotaxanes have been developed and employed successfully. We have devised a template-directed approach to rotaxanes incorporating π-electron deficient bipyridinium-based components and π-electron rich hydroquinone-based polyether components. The noncovalent bonding interactions responsible for the self-assembly of these molecular compounds are (i) π–π stacking interactions between the complementary aromatic units, (ii) hydrogen bonding interactions between the acidic hydrogen atoms in the α-positions with

respect to the nitrogen atoms on the bipyridinium units and some of the polyether oxygen atoms, as well as, (iii) edge-to-face T-type interactions between some of the hydrogen atoms on the hydroquinone rings and the π-clouds of the aromatic spacers separating the bipyridinium units. By employing these methodologies, we have synthesised a range of [2]rotaxanes, [3]rotaxanes, and [4]rotaxanes. Furthermore, the dynamic processes involving the *shuttling* of the cyclic components along the dumbbell-shaped components associated with some of these rotaxanes have been investigated in some detail. The reversible control of the process via external stimuli – such as chemical and electrochemical – has been achieved in the case of a [2]rotaxane incorporating benzidine and biphenol recognition sites. These results suggest the possibility of generating, on the nanoscopic level, molecular devices in the shape of rotaxanes able to store and process informations, thus, affording molecular machines.

Key words: Molecular shuttle; Rotaxane; Self-assembly; Template-directed synthesis.

1. INTRODUCTION

1.1. *Self-Assembly*

Many transformations occurring in the living matter are based on the ability of biological systems to self-assemble[1] and self-replicate[2]. Large and complicated molecular architectures are constructed precisely and efficiently from small and relatively simple complementary subunits. The informations – in the shape of stereoelectronic characteristics imprinted in these modular components – holds the secret to the precise and easy formation of large biological molecules and supermolecules. As a result of noncovalent bonding interactions, the mutual recognition of the subunits creates an initial structure – the seed – which then evolves into the final thermodynamically-stable three-dimensional architecture. The synthetic chemist is now beginning to realise the potential of molecular recognition and the use of self-assembly processes to generate designed chemical systems[3] is becoming more and more an integral part of organic, as well as inorganic, synthesis. The ultimate goal is to design and make nanometer-scale molecules and supermolecules from appropriate and easily accessible subunits. Then, the controlled construction of nanoscale structures by self-assembly can, in principle, be used for the production of revolutionary new materials[4] having precise shapes and functions.

1.2. *Template-Directed Synthesis*

The assembly of a complex molecular structure can be facilitated by the presence in the reaction mixture of a *magic ingredient* – the so-called template – that sustains the template-directed synthesis[5]. As a result of noncovalent bonding interactions, the precursor species are self-assembled around the template, affording the seed. Once the optimal spatial arrangement of the subunits is achieved, covalent linkage of the components can

occur, affording (i) a molecular structure or (ii) a supramolecular superstructure. In the first case, as a result of covalent or mechanical bonds, the template is *trapped* within the final designed architecture and becomes an integral part of it. In the second case, dissociation of the supramolecular adduct affords the targeted molecular compound and the unchanged template: the latter can be recycled.

1.3. *Catenanes, Rotaxanes, and Pseudorotaxanes*

The syntheses of molecular compounds, such as catenanes and rotaxanes (Fig. 1), and supramolecular complexes, such as pseudorotaxanes, have aroused the interest of many investigators[6]. The synthetic challenge associated with the intriguing topology possessed by these molecular and supramolecular species, as well as the opportunity provided by mechanical entanglement to generate molecular device-like components having controllable properties, are the most attractive features associated with catenanes and rotaxanes. An [*n*]catenane is a molecule composed of *n* macrocyclic components mechanically-interlocked as links in a chain. Thus, catenanes are molecules having nonplanar molecular graphs, i.e., it is not possible to draw their structure on a plane avoiding crossing points. Rotaxanes are molecules comprised of a linear dumbbell-shaped component encircled by one or more macrocyclic components. The stoppers attached at both ends of the dumbbell-shaped component must be bulky enough to trap mechanically the macrocyclic components, thus avoiding the possibility of unthreading. Thus, an [*n*]rotaxane is a molecule formed by a dumbbell-shaped component and $n - 1$ macrocyclic components. A pseudorotaxane is a supramolecular species composed of a rod-like compound inserted through the middle of a macrocycle. As a result of the absence of stoppers at the ends of it, no mechanical bond links the macrocycle to the rod-like compound and so dissociation of the complex can occur. An [*n*]pseudorotaxane incorporates one linear and $n - 1$ macrocyclic components.

2. EARLY SYNTHESES OF ROTAXANES

2.1. *Statistical Syntheses*

The design of molecular compounds incorporating cyclic components threaded on to linear ones was discussed by Willstätter[7] as early as 1910. However, the first syntheses of [2]rotaxanes were not achieved until some fifty-seven years later by statistical and directed approaches by Harrison[8] and Schill[9], respectively. It was reasoned that, by mixing in solution, an acyclic with a macrocyclic molecule, a small portion of the linear species would be inserted through the cavity of the cyclic one as a result of statistical threading. Subsequent covalent attachment of two bulky groups at the end of the acyclic species would then provide a mechanical trap for the macrocycle, affording a rotaxane. Scheme 1 illustrates Harrison's statistical approach[8a] to the [2]rotaxane **3**.

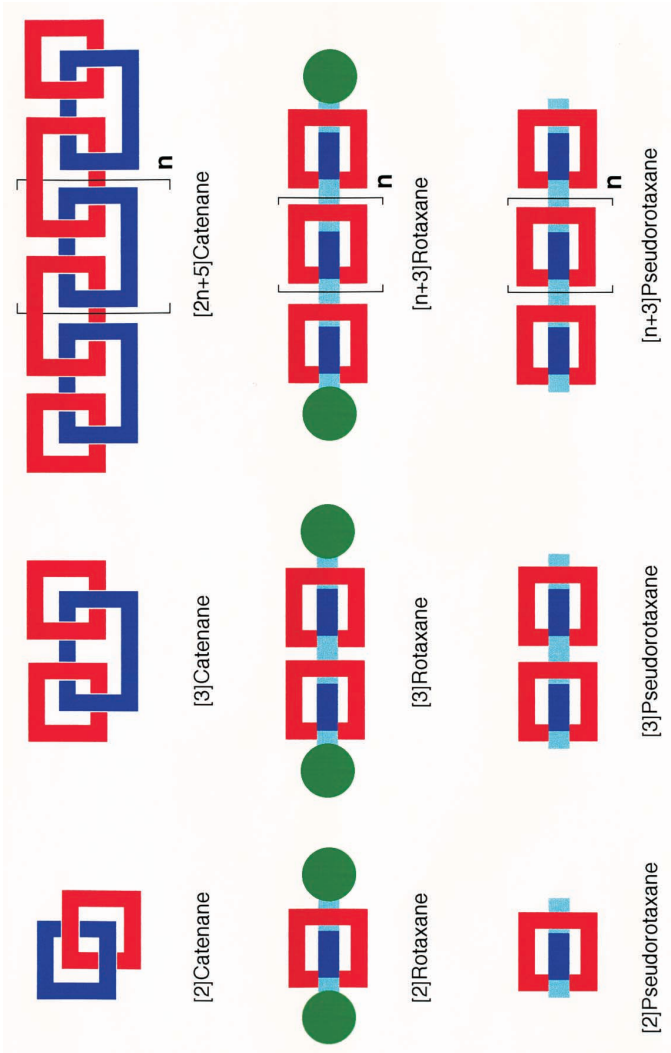


FIG. 1
Schematic representations of [*n*]catenanes, [*n*]rotaxanes, and [*n*]pseudorotaxanes

The polymer-supported cyclic component **1** was treated with a solution of 1,10-decanediol, followed by treatment with trityl chloride. Next, the resin was washed in order to remove the by-products and the overall procedure was repeated seventy times. The cleavage of the ester functionalities linking the rotaxane to the polymeric support released the [2]rotaxane **3** in a yield of 6%. Following Harrison's seminal experiments, the statistical approach was employed first by Zilkha[10] and then by Gibson[11] to synthesise both rotaxanes and polyrotaxanes.

2.2. *Directed Syntheses*

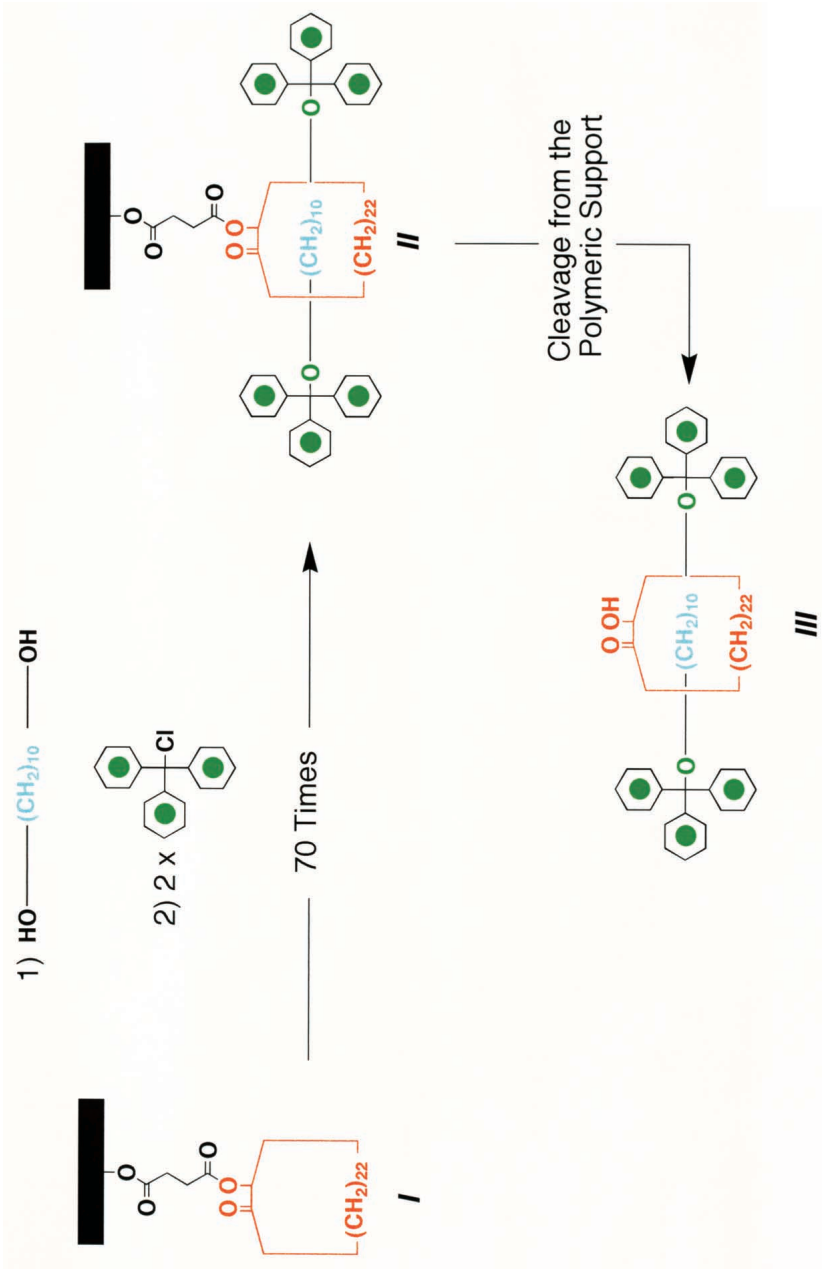
An alternative approach to the construction of rotaxanes was developed by Schill[9]. The methodology relies on the synthesis of prerotaxane species in which linear and cyclic subunits are linked covalently to each other. The attachment of two bulky stoppers at both ends of the linear subunit is followed by the cleavage of the covalent bonds holding together the dumbbell-shaped and macrocyclic components, affording the [2]rotaxane. An example is given in Scheme 2. The prerotaxane **4**, incorporating a benzene core common to both the macrocyclic and dumbbell-shaped components, was generated by a multistep synthesis[9]. The cleavage of the covalent linkages between the macrocycle and the dumbbell-shaped component was achieved in three additional steps to yield[9] the [2]rotaxane **5** after acetylation.

3. SUPRAMOLECULAR APPROACHES TO ROTAXANES

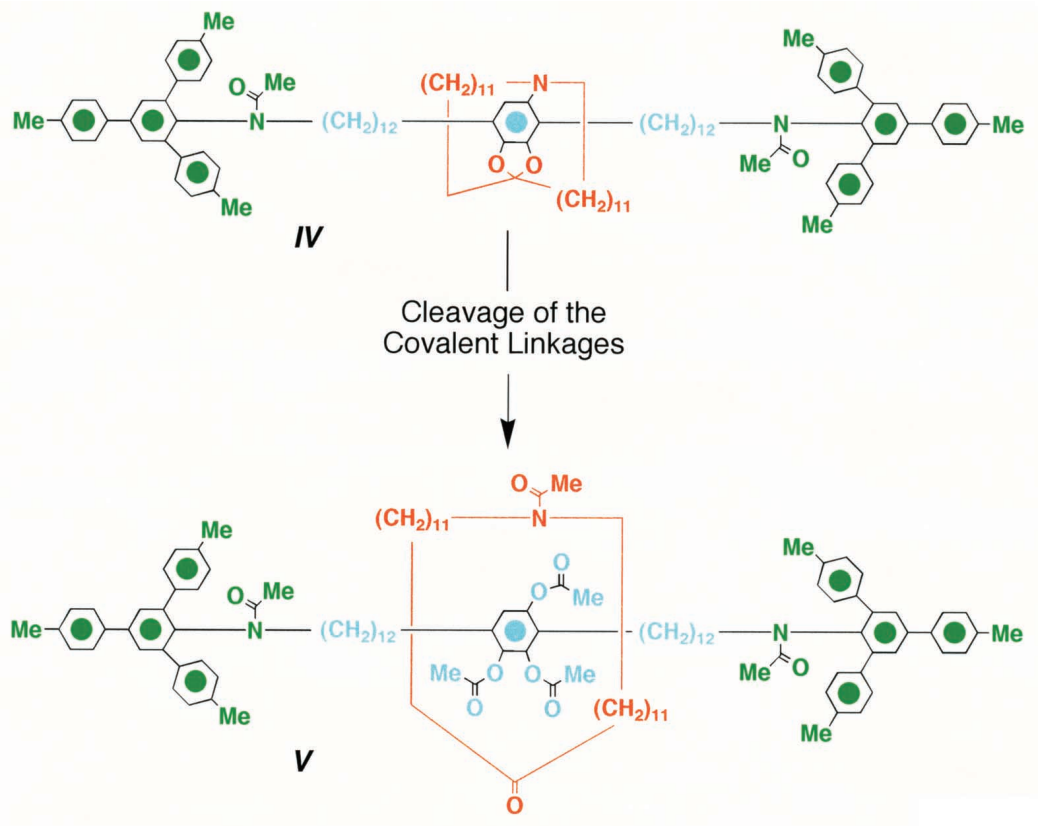
3.1. *From Host–Guest Complexes to Rotaxanes*

The early syntheses of rotaxanes were mainly based upon the low yielding statistical approaches or upon the elegant, but time-consuming and laborious, directed syntheses. With the advent of supramolecular chemistry[3], numerous high efficient and relatively simple synthetic methodologies for the construction of rotaxanes have been developed. A wide diversity of macrocyclic host molecules, such as cyclodextrins[12], crown ethers[13] and cyclophanes[14] have been investigated during the last twenty years. The ability of such macrocyclic hosts to bind a wide range of guests has been demonstrated and analysed thoroughly. Many of the resulting complexes possess a so-called *wheel and axle* geometry, i.e., the macrocyclic host – the *wheel* – encircles the linear guest – the *axle* – affording a pseudorotaxane-like superstructure. By simply attaching covalently, at both ends of the axle, stoppers bulky enough to trap mechanically the wheel, a rotaxane can be generated.

In 1981, Ogino reported[15] the synthesis of the [2]rotaxanes **6a**–**6c** incorporating either one α-cyclodextrin (α-CD) or one β-cyclodextrin (β-CD) unit, as the macrocycle, and linear alkyl chains of various length stoppered at both ends by bulky cobalt complexes. The ability of cyclodextrins to form inclusion complexes having pseudo-


1) HO—(CH2)10—OH
2) 2 x
Cl
70 Times
I
II
III
Cleavage from the
Polymeric Support
(CH2)22
(CH2)10
O OH

SCHEME 1


Me
O Me
N
Me
Me
(CH2)12
(CH2)11
N
O O
(CH2)11
(CH2)12
N
Me O
Me
Me
Me
IV
Cleavage of the
Covalent Linkages
O Me
(CH2)11
N
O
O Me
Me O O Me
O O
(CH2)11
O
V

SCHEME 2

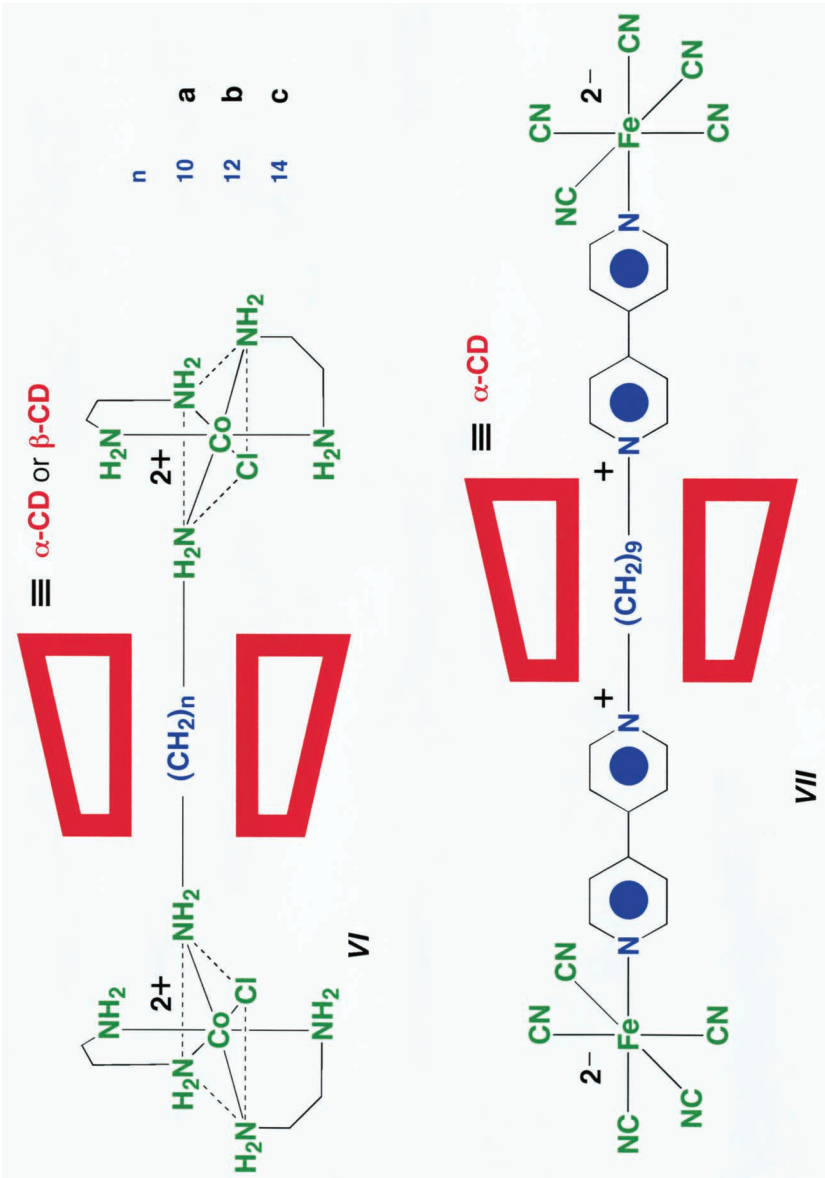
rotaxane-like geometries has been exploited by many other investigators in order to synthesise rotaxanes[16] and polyrotaxanes[17]. Examples of [2]rotaxanes synthesised from cyclodextrin–guest complexes are the compounds **7** (Macartney[16j]), **8a**, **8b** (Kaifer[16f,g]), and **9a**, **9b** (Wenz[16i]).

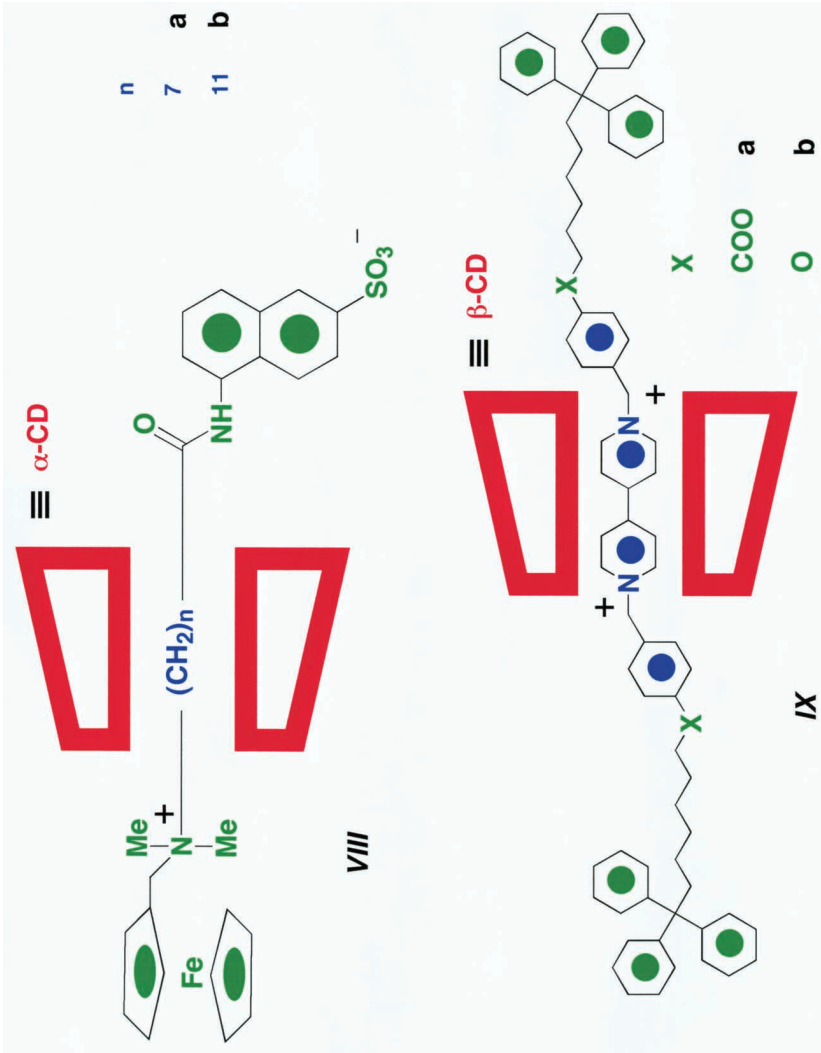
Crown ethers have been employed[11a–11c,18] as the macrocyclic components for the generation of rotaxanes. The ability of dibenzo-24-crown-8 **10** to bind linear secondary ammonium salts, such as **11**, has been exploited by Busch[18h] to self-assemble (Scheme 3) the [2]rotaxane **13**, after covalent attachment of a stopper at the *free* end of the linear component inserted through the cavity of the crown ether within the host–guest complex **12**. [2]Pseudorotaxanes and [3]pseudorotaxanes, incorporating one and two secondary ammonium recognition sites, respectively, within the linear component encircled by one and two dibenzo-24-crown-8 units, respectively, have been self-assembled recently by us[18i,j]. Similarly, by employing the larger macrocyclic polyether, bis-*para*-phenylene-34-crown-10, which is able to accommodate within its cavity two secondary ammonium recognition sites, a double-stranded [3]pseudorotaxane and a double-stranded double-encircled [4]pseudorotaxane comprised of one macrocycle and two linear components, and two macrocycles and two linear components, respectively, have been self-assembled[18j].

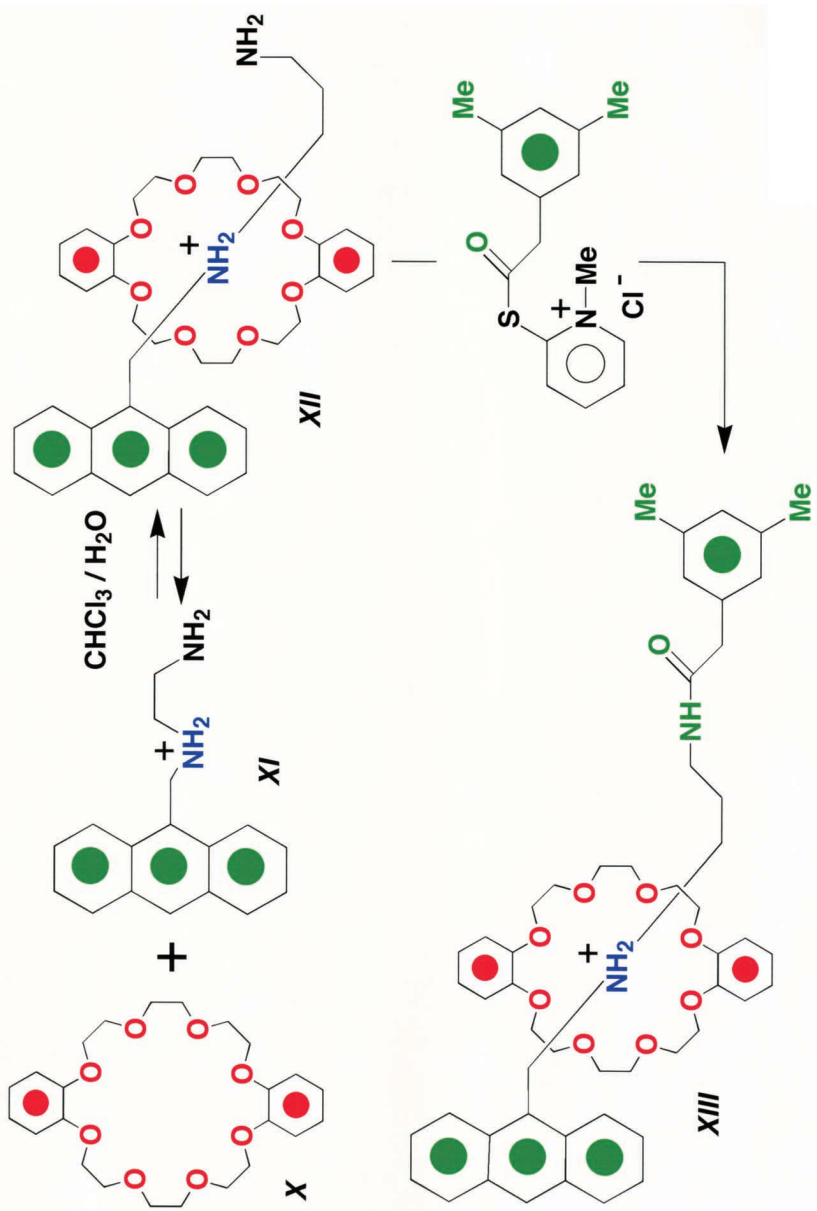
A similar approach has been used by Bickelhaupt[18a–18d] to synthesise organometallic rotaxanes, such as **14**, in which a diphenylmagnesium dumbbell-shaped component is encircled by a crown ether. An example of a [2]rotaxane incorporating a cyclophane, as the macrocyclic component, is the compound **15** synthesised by Butcher[19], whilst calixarenes have been used by Gutsche[20] as the macrocyclic component to generate so-called self-anchored rotaxanes.

3.2. *Metal Template-Directed Syntheses of Rotaxanes*

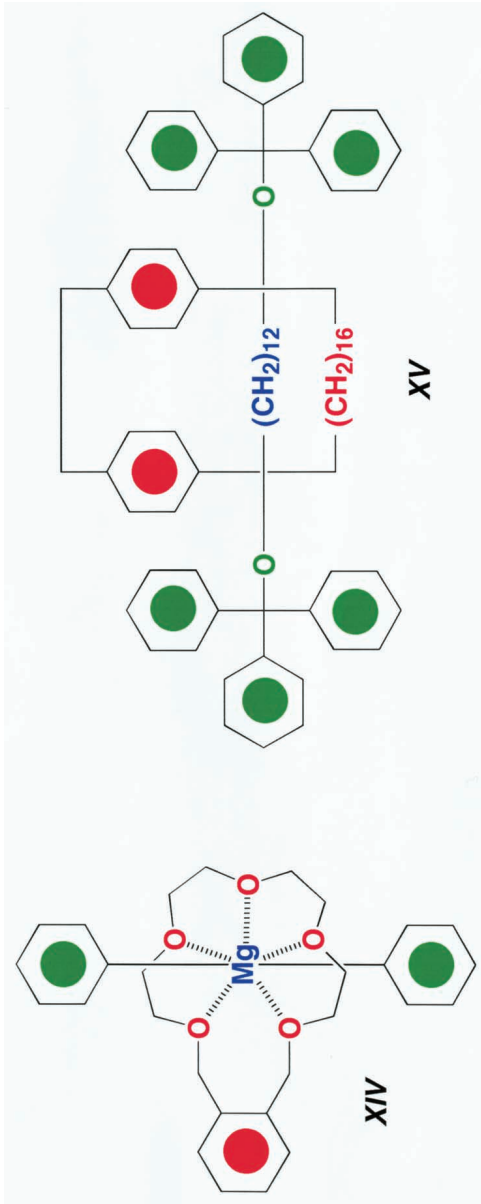
A metal-templated approach to rotaxanes has been developed by Sauvage[21]. By employing a phenanthroline-based macrocyclic ligand and a phenanthroline-based acyclic ligand bearing, at one end, a bulky gold(III)-porphyrin (Scheme 4), the threading of the cyclic on to the linear ligand can be promoted by a tetrahedral metal centre, such as copper(I), generating[21d] the supramolecular complex **16**. Reaction of the assembled complex **16** with di-*tert*-butyl-3,5-benzaldehyde and bis(3-ethyl-4-methylpyrryl-2)-methane gave[21d] the desired prerotaxane **17**. The removal of the metal template was achieved by treatment of **17** with an excess of KCN to afford[21d] the [2]rotaxane **18**. Similarly, [3]rotaxanes have been generated[21] by exploiting the template-effect associated with the use of the gathering tetrahedral metal centre. A metal template-directed approach to rotaxanes has been also employed by Lehn[22] and Gibson[23].

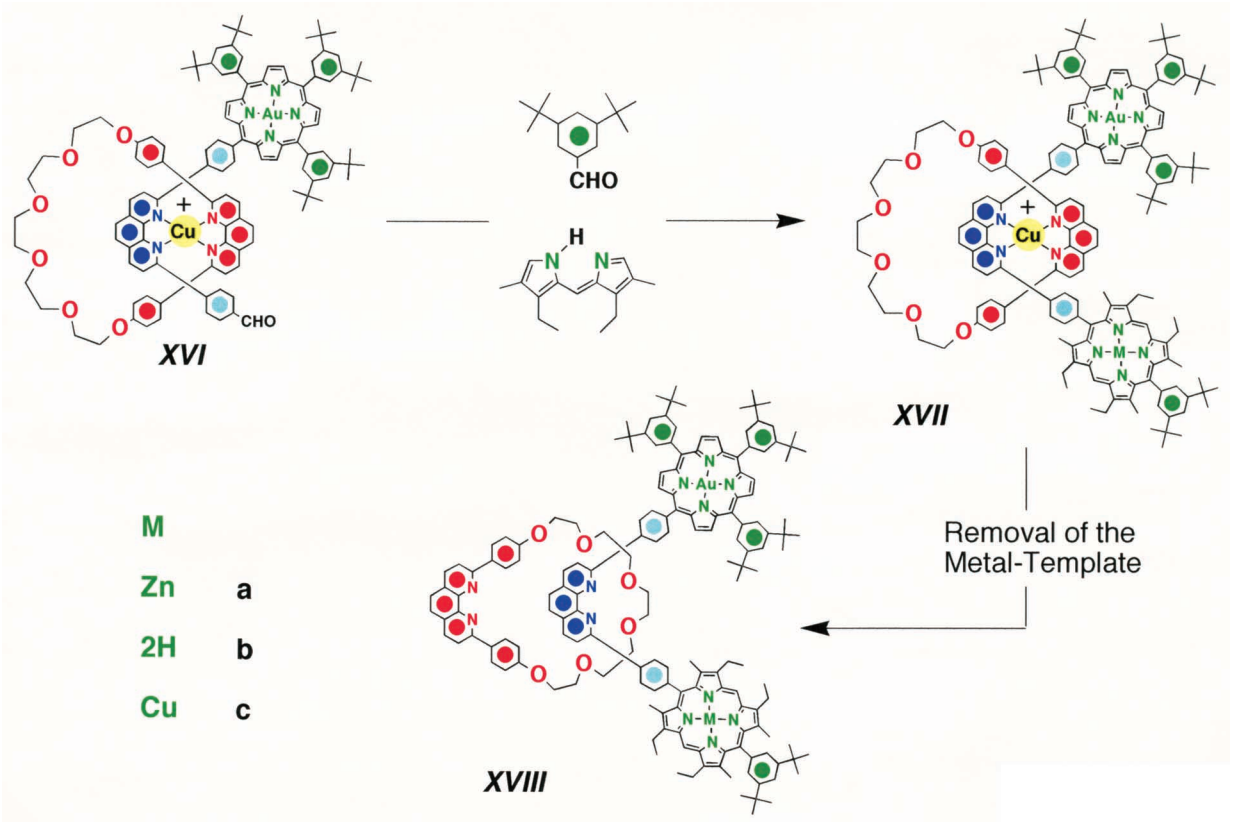

≡ α-CD or β-CD
n
a
b
c
10
12
14
(CH2)n
(CH2)9
VI
VII
≡ α-CD


α-CD
n
7
11
a
b
O
NH
SO3
(CH2)n
Me
N
Me
Fe
VIII
β-CD
X
COO
O
a
b
N
N
IX


NH2
+
NH2
XII
Me
Me
O
S
+
N
Me
Cl -
CHCl3 / H2O
NH2
+
NH2
XI
+
X
Me
Me
O
NH
+
NH2
XIII

SCHEME 3


O
(CH2)12
(CH2)16
O
XV
O
O
Mg
O
O
O
XIV


CHO
H
XVI
XVII
XVIII
Removal of the
Metal-Template
M
Zn a
2H b
Cu c

SCHEME 4

4. DONOR/ACCEPTOR TEMPLATE-DIRECTED SYNTHESES OF [*n*]ROTAXANES

4.1. *From Pseudorotaxanes to Rotaxanes*

The π-electron rich hydroquinone-based macrocyclic polyether bis-*para*-phenylene-34-crown-10 (BPP34C10) binds[24] (Fig. 2) the well-known herbicide paraquat[25] with pseudorotaxane-like geometry, both in solution and in the solid state. The noncovalent bonding interactions responsible for the complexation are (i) π–π stacking[26] between the π-electron rich hydroquinone rings and the π-electron deficient bipyridinium unit, as well as (ii) hydrogen bonding[27] between some of the polyether oxygen atoms and the acidic hydrogen atoms (Me and α-bipy) on the bipyridinium units. By reversing the role of the recognition sites, a bipyridinium-based macrocycle able to bind[28] (Fig. 2) hydroquinone-based acyclic polyethers with pseudorotaxane-like geometries, can be generated. In addition to π–π stacking and hydrogen bonding interactions, edge-to-face T-type interactions[29] between the hydrogen atoms attached to the hydroquinone ring and the π-clouds of the aromatic spacer separating the two bipyridinium units, are observed in the complex **20**. The wheel and axle geometries of the pseudorotaxanes **19** and **20** suggest the possibility of generating rotaxanes by simply attaching bulky stoppers at both ends of the axle inserted through the cavity of the macrocyclic component.

Three different synthetic approaches (Fig. 3) – namely, clipping, threading, and slipping – have been developed by us[30] to self-assemble in solution rotaxanes, incorporating π-electron rich and π-electron deficient components. In the case of clipping, the macrocyclisation of the cyclic component is performed in the presence of the preformed dumbbell-shaped component. In the case of threading, the complexation of a thread-like guest by the preformed macrocycle is followed by the covalent attachment of the stoppers to the ends of the thread.

In the case of slipping, size-complementary macrocyclic and dumbbell-shaped components are preformed separately and then cajoled into associating one with the other under the influence of an appropriate amount of thermal energy. As a result of the noncovalent interactions between the recognition sites incorporated within macrocyclic and dumbbell-shaped components, the energy barrier for the opposite process (slipping-off) is raised (Fig. 4), providing a *thermodynamic trap* for the macrocycle.

4.2. *Clipping and Threading Approaches to Rotaxanes Incorporating π-Electron Rich Dumbbell-Shaped Components*

On first [2]rotaxane, incorporating a π-electron rich dumbbell-shapped component, was self-assembled by both the clipping and the threading approaches. Reaction of the dication **21** with the dibromide **22** in the presence of the hydroquinone-based dumbbell-shaped component **23** – the template – affords[28b] (Scheme 5) the [2]rotaxane **24** in a yield of 14% as a result of a clipping procedure. The complexation of the hydro-

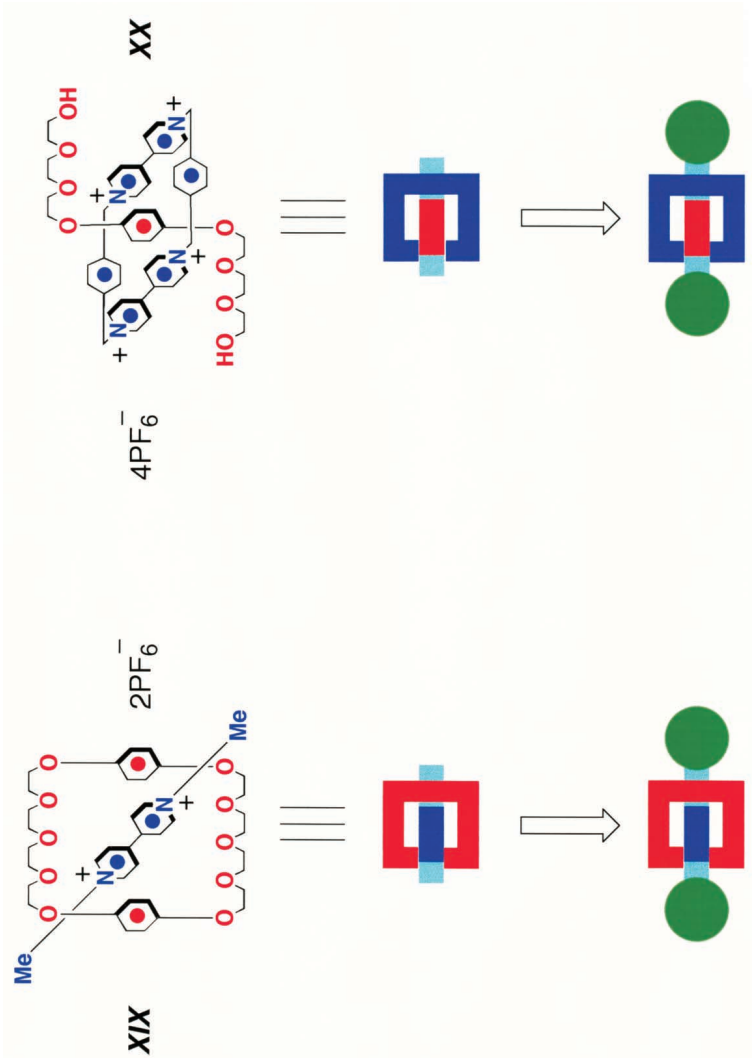


FIG. 2
From donor/acceptor pseudorotaxane-like complexes to rotaxanes

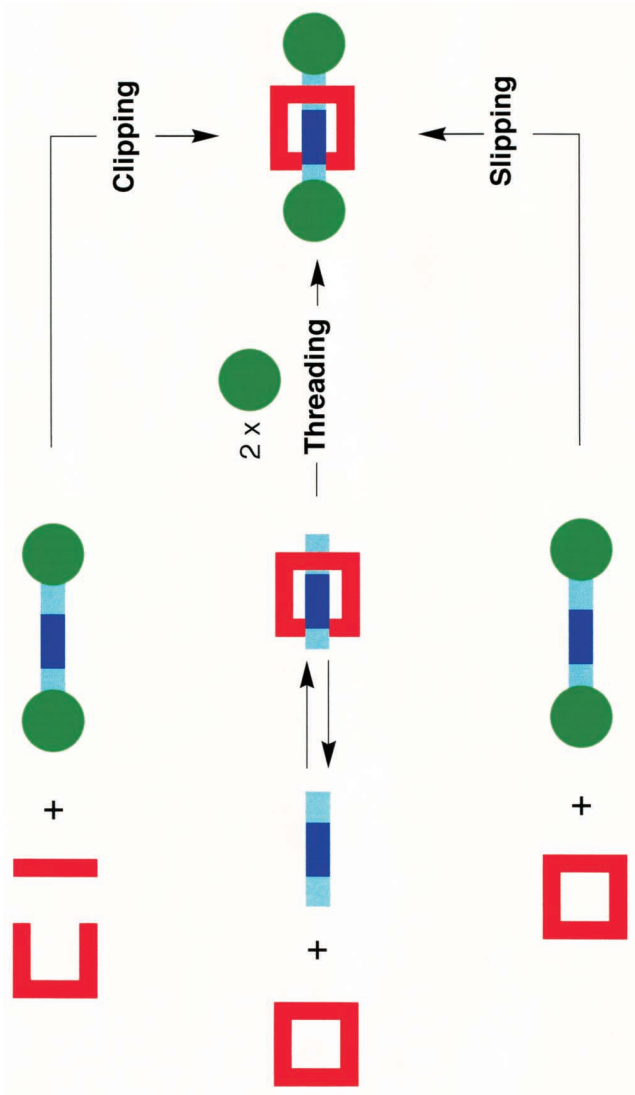


FIG. 3
Synthetic approaches to self-assembling rotaxanes

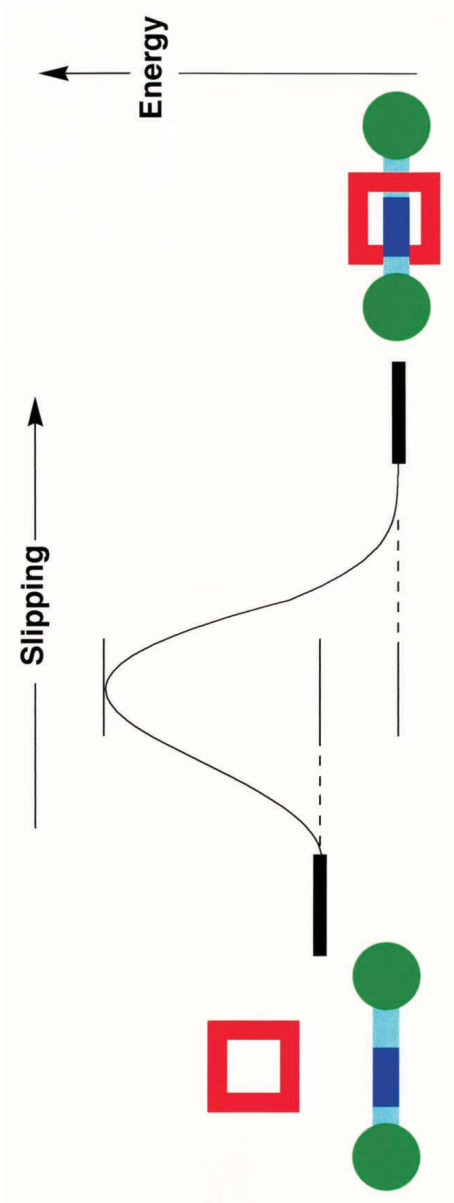


FIG. 4
A thermodynamic trap in action – the slipping approach

quinone-based acyclic polyether **26** by the bipyridinium-based cyclophane **25**, followed by covalent attachment of two triisopropylsilyl-based stoppers at both ends of the guest, affords[28b] (Scheme 5) the [2]rotaxane **24** in a yield of 22% as a result of a threading procedure.

The clipping methodology has been employed to synthesise[31] a series of [2]rotaxanes comprised of one π-electron deficient macrocycle and dumbbell-shaped components incorporating from two to six hydroquinone recognition sites, as shown in Scheme 6.

A bis[2]rotaxane has been also self-assembled by employing the clipping approach. Reaction of the tetrabromide **37** with the dication **21** in the presence of the preformed 1,5-dioxynaphthalene-based dumbbell-shaped component **38** gives[32] (Scheme 7) the bis[2]rotaxane **39** in a yield of 7%.

The [2]rotaxane **32** incorporates two hydroquinone recognition sites – the *stations* – within the dumbbell-shaped component but only one tetracationic macrocycle. Thus, the cyclophane moves back and forth from one station to the other, giving raise[31a] to the so-called *molecular shuttle* as illustrated in Fig. 5.

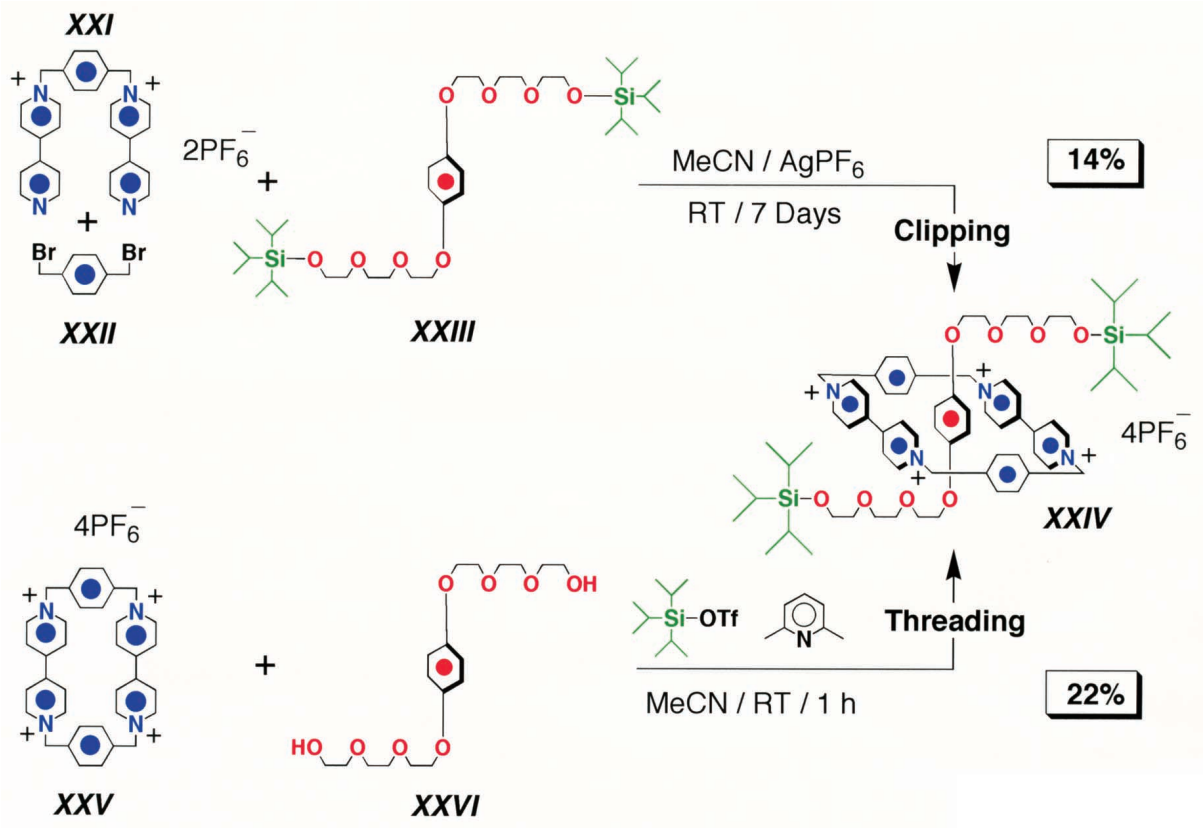
The molecular shuttles **40** (ref.[33]), **41** (ref.[34]), and **42** (ref.[35]) incorporating two different π-electron rich stations within the dumbbell-shaped component have been self-assembled by either a clipping or a threading approach.

4.3. *Threading Approach to Rotaxanes Incorporating π-Electron Deficient Dumbbell-Shaped Components*

By employing BPP34C10 as the macrocyclic component, bipyridine **44** as the thread, and the tris(*tert*-butylphenyl)methane-based chloride **43** as the stopper, the [2]rotaxane **45** can be self-assembled[30c] (Scheme 8) in a yield of 26% as a result of a threading procedure. Ultrahigh pressures have a pronounced effect on these self-assembly processes. Thus, when the reaction is performed at atmospheric pressure, no rotaxane can be detected.

By increasing the number of bipyridinium recognition sites incorporated within the thread-like component, the [2]rotaxane **46** and the [3]rotaxane **47** can be self-assembled[30c,36] (Scheme 9) under ultrahigh pressure conditions, using the threading approach. However, the proportions of the rotaxanes **46** and **47** depend upon the molar ratio of the macrocyclic compound (BPP34C10) to the thread derivative **21**. When only 1.5 molar equivalents of BPP34C10 were employed, the ratio of **46** to **48** was 6 : 1, whilst, on employing four molar equivalents of BPP34C10, the ratio changed to 1 : 6.

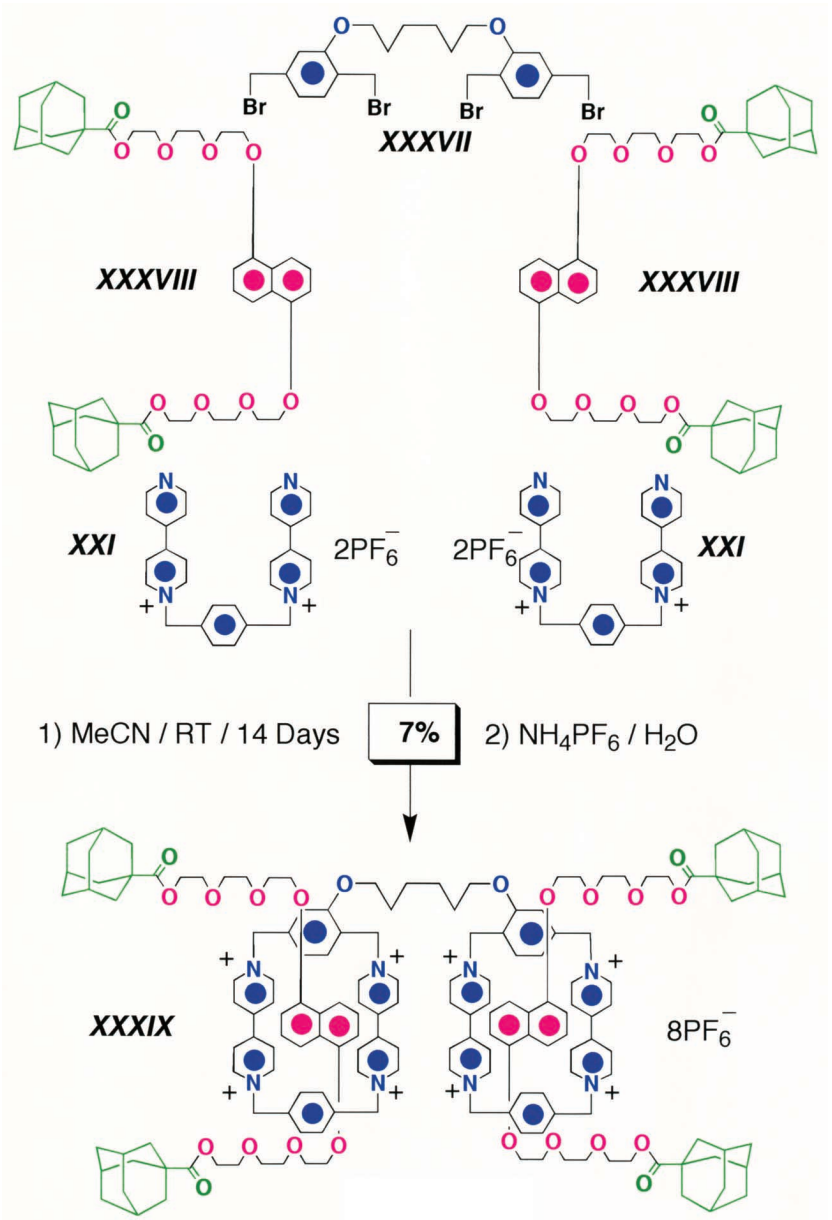
The threading methodology was employed[30c] (Scheme 10) to synthesise the [2]rotaxane **49**, the [3]rotaxane **50**, and the [4]rotaxane **51** incorporating three bipyridinium recognition sites, but in very low yields.


XXI
XXII
2PF6−
XXIII
MeCN / AgPF6
RT / 7 Days
14%
Clipping
XXIV
4PF6−
4PF6−
XXV
XXVI
Si–OTf
Threading
MeCN / RT / 1 h
22%

SCHEME 5

	R	m	n	Yield	
XXVII		3	0	32%	XXXII
XXVIII		0	0	1%	XXXIII
XXIX		0	2	25%	XXXIV
XXX		0	3	29%	XXXV
XXXI		0	4	40%	XXXVI

SCHEME 6


XXXVII
XXXVIII
XXXVIII
XXI
2PF6−
2PF6−
XXI
1) MeCN / RT / 14 Days
7%
2) NH4PF6 / H2O
XXXIX
8PF6−

SCHEME 7

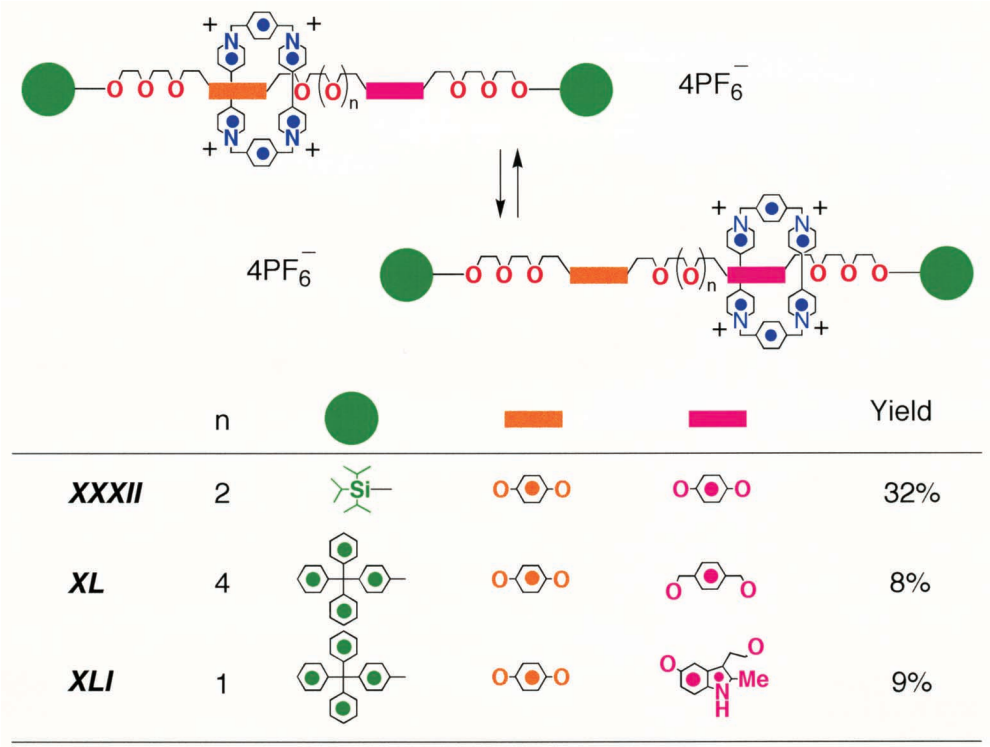
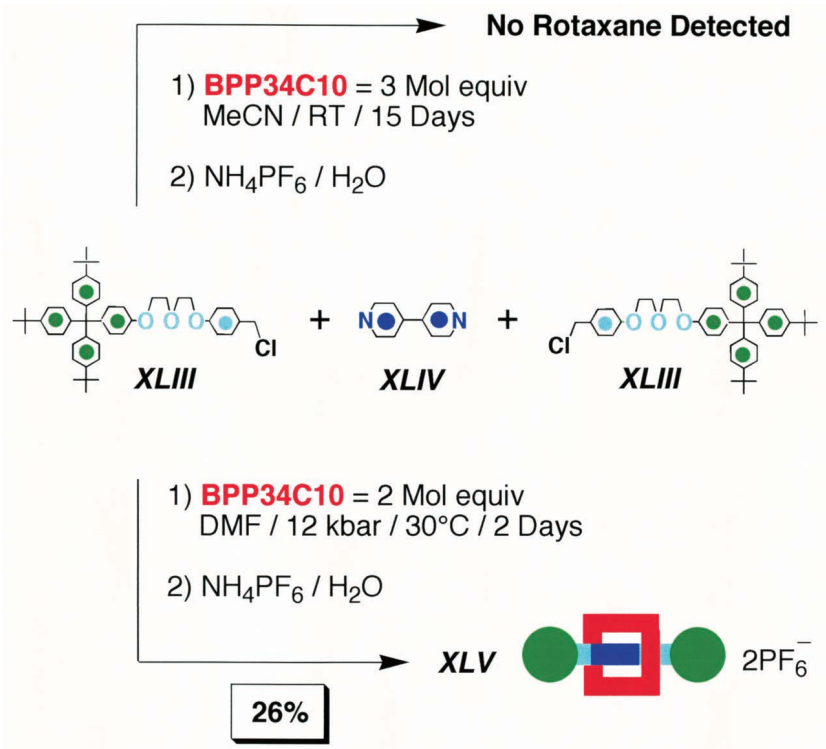
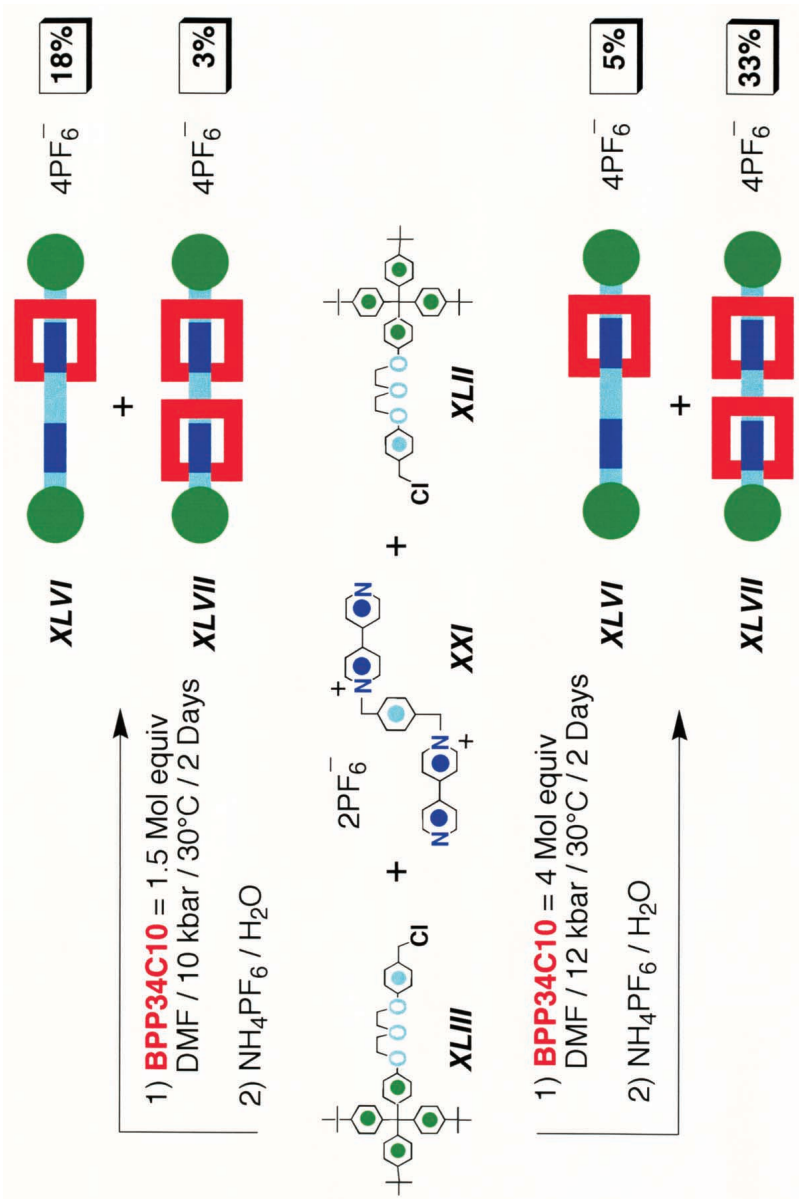


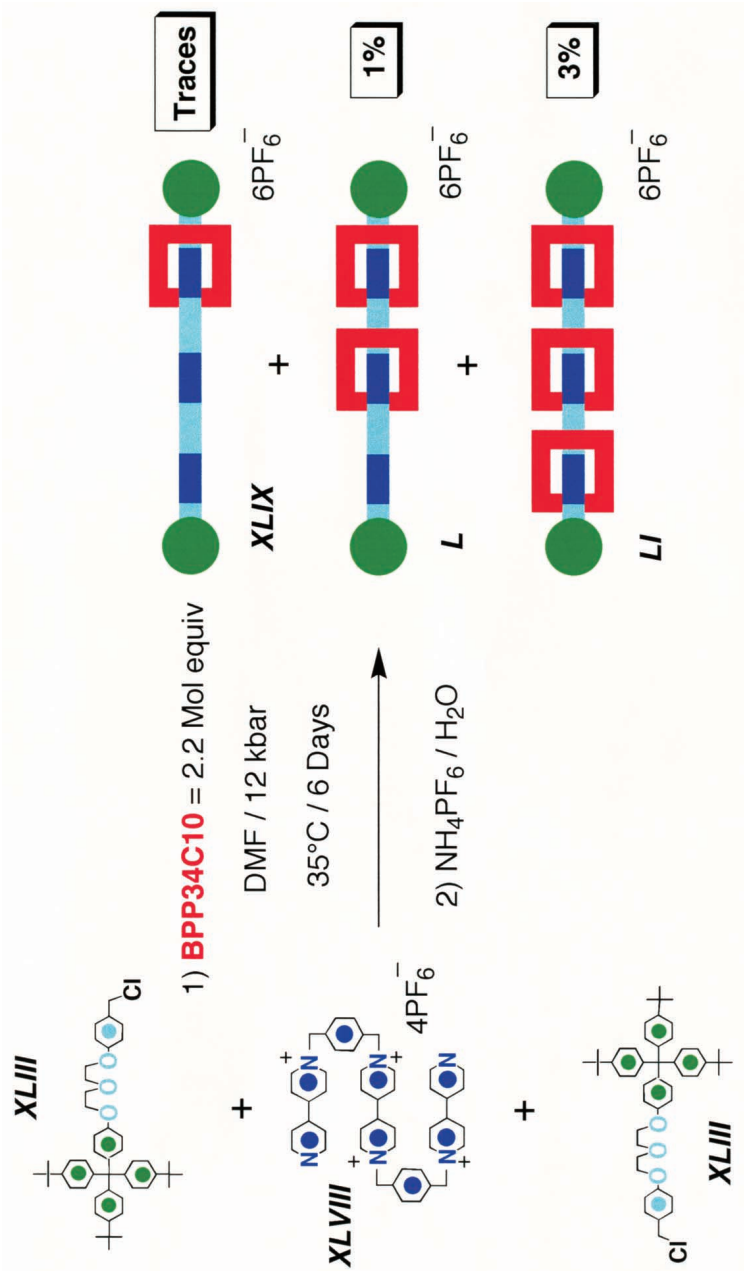
FIG. 5
The shuttling process associated with the [2]rotaxanes **32**, **40**, and **41**


No Rotaxane Detected
1) BPP34C10 = 3 Mol equiv
MeCN / RT / 15 Days
2) NH4PF6 / H2O
Cl
XLIII
+
N
N
XLIV
+
Cl
XLIII
1) BPP34C10 = 2 Mol equiv
DMF / 12 kbar / 30°C / 2 Days
2) NH4PF6 / H2O
XLV
2PF6−
26%

SCHEME 8


1) BPP34C10 = 1.5 Mol equiv
DMF / 10 kbar / 30°C / 2 Days
2) NH4PF6 / H2O
XLVI
4PF6−
18%
XLVII
4PF6−
3%
XLIII
Cl
2PF6−
XXI
Cl−
XLII
1) BPP34C10 = 4 Mol equiv
DMF / 12 kbar / 30°C / 2 Days
2) NH4PF6 / H2O
XLVI
4PF6−
5%
XLVII
4PF6−
33%

SCHEME 9


XLIII
Cl
+
XLVIII
4PF6−
+
1) BPP34C10 = 2.2 Mol equiv
DMF / 12 kbar
35°C / 6 Days
2) NH4PF6 / H2O
Traces
6PF6−
XLIX
+
1%
6PF6−
L
+
3%
6PF6−
LI
+
XLIII
Cl

SCHEME 10

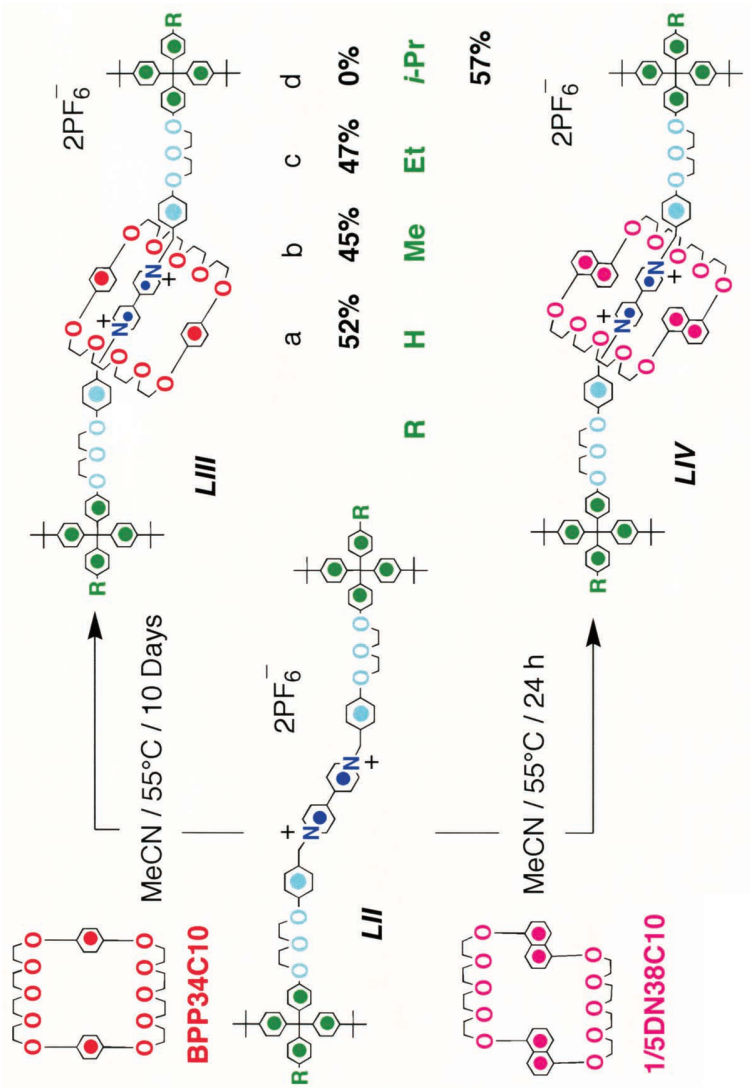
4.4. *Slipping Approach to Rotaxanes Incorporating π-Electron Deficient Dumbbell-Shaped Components*

The dumbbell-shaped compounds **52a**–**52d** incorporating one bipyridinium recognition site and tetraarylmethane-based stoppers, whose size can be varied systematically, have been synthesised[37]. By heating acetonitrile solutions of the dumbbell-shaped derivatives **52a**–**52c** and the macrocycle BPP34C10, the [2]rotaxanes **53a**–**53c** have been self-assembled[37] (Scheme 11) in yields of 52, 45 and 47%, respectively. However, when the dumbbell-shaped derivative **52d**, incorporating 4-isopropylphenylbis(4-*tert*-butylphenyl)-methyl stoppers, is reacted with BPP34C10 under otherwise identical conditions, no rotaxane is obtained[37]. Thus, the barrier to the slipping process for the hydroquinone-based macrocycle BPP34C10 is surpassed on going from the "ethyl substituted" to the "isopropyl substituted" stoppers. However, by employing the larger 1,5-dioxynaphthalene-based macrocyclic polyether, 1,5-dinaphtho-38-crown-10 (1/5DN38C10), the corresponding [2]rotaxane **54** bearing "isopropyl substituted" stoppers can be self-assembled[38] under otherwise identical conditions in a yield of 57%.

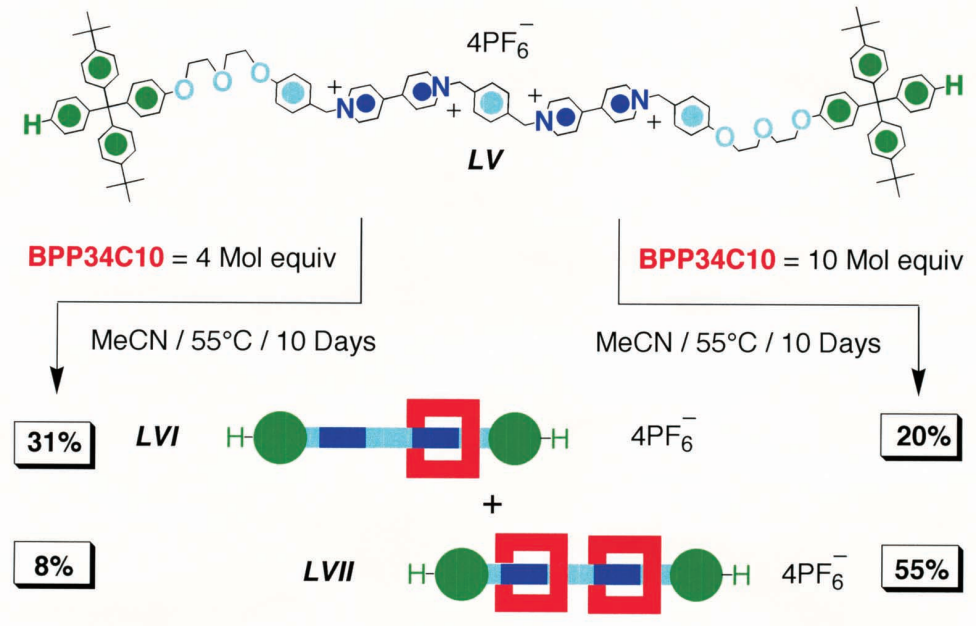
The slipping methodology was employed[30c,39] successfully to synthesise (Scheme 12) the [2]rotaxane **56** and the [3]rotaxane **57** incorporating two bipyridinium recognition sites within the dumbbell-shaped component. Interestingly, the proportions of the rotaxanes **56** and **57** can be controlled by changing the ratio of macrocycle BPP34C10 to the dumbbell-shaped derivative **55**. When four molar equivalents of BPP34C10 are employed, the yields of **56** and **57** are 31 and 8%, respectively, whilst, when 10 molar equivalents of BPP34C10 are employed, the yields of **56** and **57** become 20 and 55%, respectively.

Similarly, the [2]rotaxane **59**, the [3]rotaxane **60**, and the [4]rotaxane **61** (Scheme 13) incorporating three bipyridinium recognition sites were self-assembled[30c] via the slipping approach. Again, the proportions of the rotaxanes **59**, **60**, and **61** are related to the ratio of the BPP34C10 macrocycle to the dumbbell-shaped compound **58**. Thus, when two molar equivalents of BPP34C10 are employed, the yields of the rotaxanes **59**, **60**, and **61** are 19, 10, and 4%, respectively, whilst, on employing 20 molar equivalents of BPP34C10, the yields are 2, 12, and 19%, respectively.

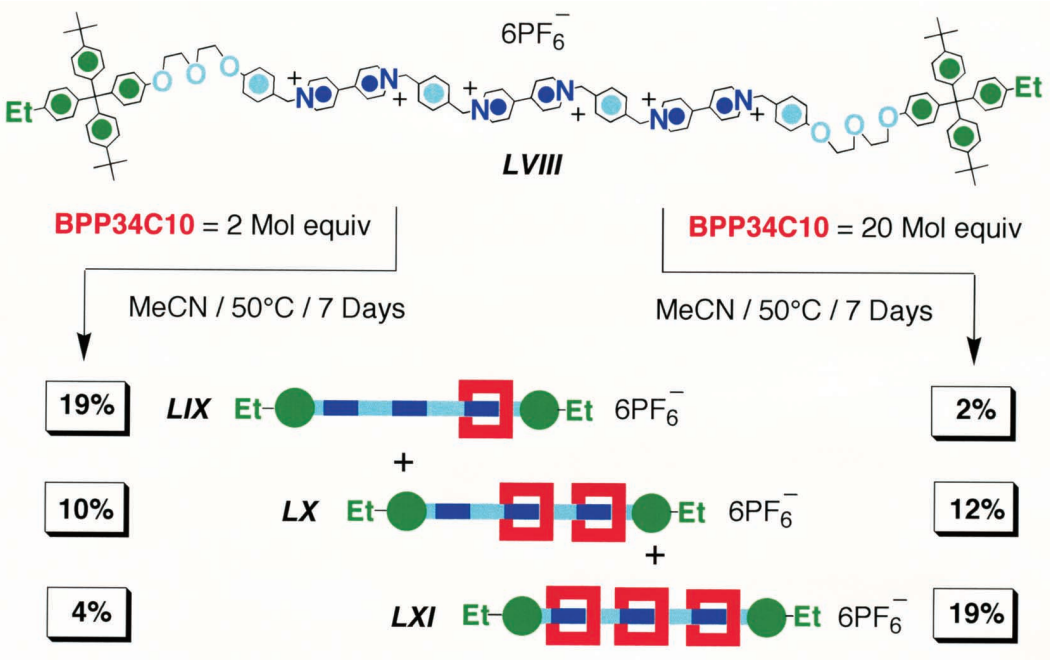
The versatility of the methodology has been demonstrated by the synthesis of branched rotaxanes. By simply changing the geometry of the bipyridinium-based backbone, the [2]rotaxane **63**, the [3]rotaxane **64**, and the [4]rotaxane **65** (Scheme 14) have been self-assembled[40]. The proportions of the resulting rotaxanes can be controlled by changing the ratio of the macrocycle BPP34C10 to the branched derivative **62**. However, in this case, the use of a large excess of macrocycle yielded the [3]rotaxane **64** as the major product and not the [4]rotaxane **65**, presumably, as a result of steric crowding around the central core.


BPP34C10
MeCN / 55°C / 10 Days
LII
LIII
LIV
2PF6−
a 52%
b 45%
c 47%
d 0%
R H Me Et i-Pr
57%
MeCN / 55°C / 24 h
1/5DN38C10

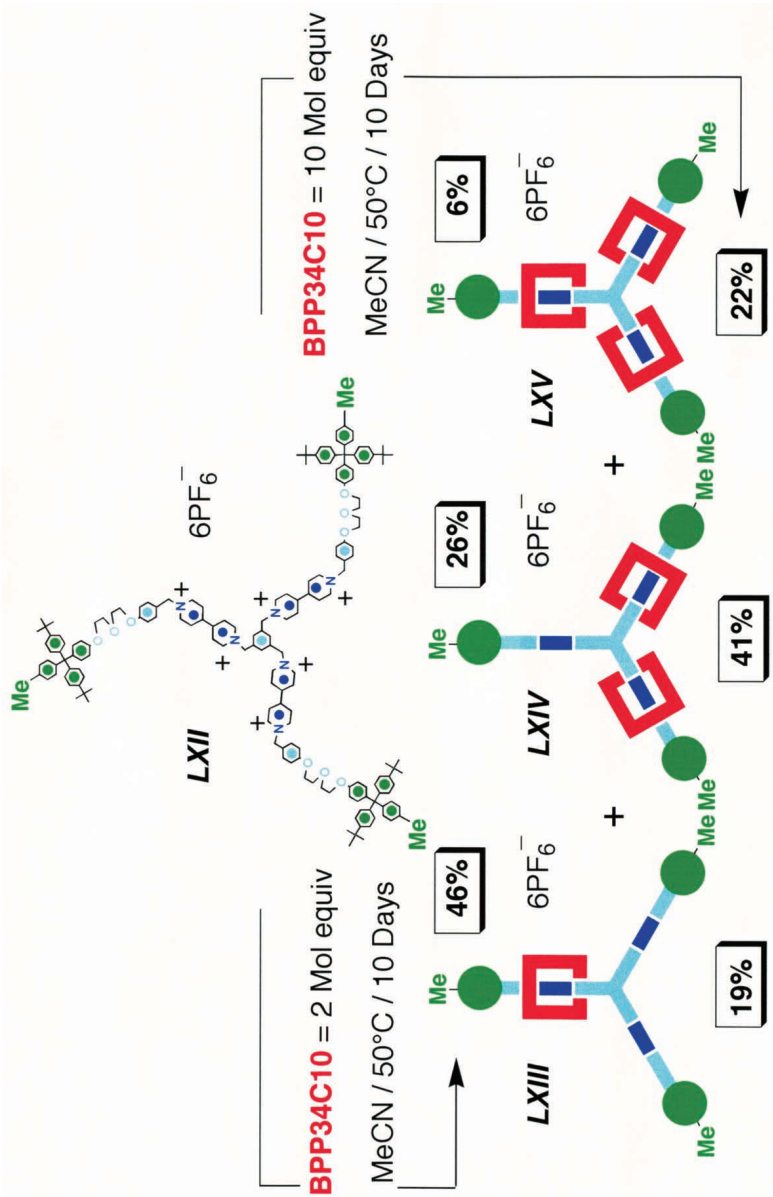
SCHEME 11


4PF6−
LV
BPP34C10 = 4 Mol equiv
MeCN / 55°C / 10 Days
BPP34C10 = 10 Mol equiv
MeCN / 55°C / 10 Days
31%
LVI
4PF6−
20%
+
8%
LVII
4PF6−
55%

SCHEME 12


6PF6−
Et
Et
LVIII
BPP34C10 = 2 Mol equiv
MeCN / 50°C / 7 Days
BPP34C10 = 20 Mol equiv
MeCN / 50°C / 7 Days
19%
LIX
Et
Et
6PF6−
2%
+
10%
LX
Et
Et
6PF6−
12%
+
4%
LXI
Et
Et
6PF6−
19%

SCHEME 13


BPP34C10 = 2 Mol equiv
MeCN / 50°C / 10 Days
LXII
6PF6
LXIII
46%
LXIV
26%
LXV
6%
BPP34C10 = 10 Mol equiv
MeCN / 50°C / 10 Days
19%
41%
22%
Me
Me Me

SCHEME 14

4.5. *The Controlled Self-Assembly of a [3]Rotaxane Incorporating Two Constitutionally Different π-Electron Rich Macrocyclic Components*

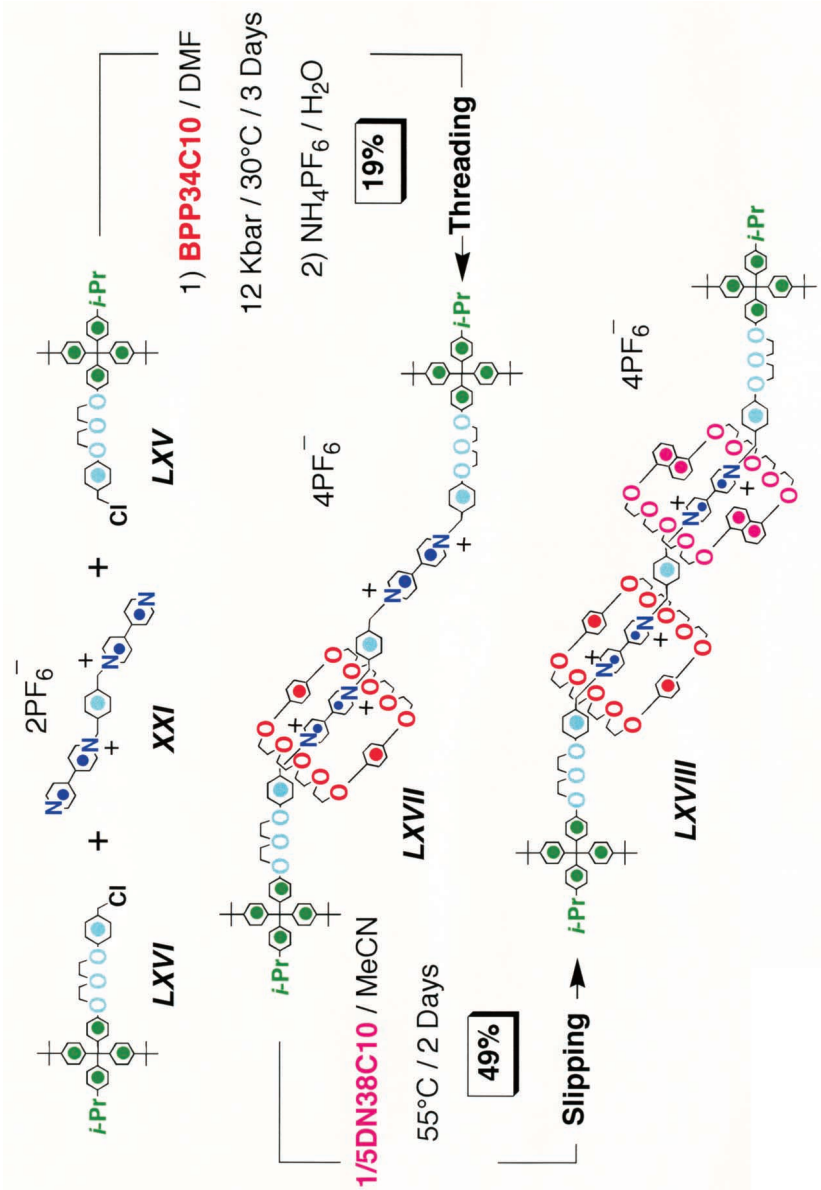
The controlled self-assembly of the linear [3]rotaxane **68** incorporating two constitutionally-different macrocycles has been achieved[39] (Scheme 15) by employing both the threading and the slipping approaches. The [2]rotaxane **67** has been self-assembled[39] under ultrahigh pressures in a yield of 19% by means of the threading approach. This [2]rotaxane **67** incorporates one *free* bipyridinium recognition site and 4-isopropylphenyl-bis(4-*tert*-butylphenyl)methyl stoppers compatible with the slipping of the 1/5DN38C10 macrocycle. Thus, heating an acetonitrile solution of the [2]rotaxane **66** and 1/5DN38C10 at 55 °C over two days results[39] in the self-assembly of the [3]rotaxane **68** incorporating two constitutionally-different macrocyclic components in a yield of 49%.

4.6. *Characterisation and Properties of Donor/Acceptor-Based Rotaxanes*

The rotaxanes incorporating π-electron deficient and π-electron rich complementary components, self-assembled according to the above synthetic methodologies, were fully characterised by means of the usual spectroscopic techniques, i.e. fast atom bombardment (FAB MS) and electrospray (ES MS) mass spectrometries, ^{1}H NMR and ^{13}C NMR spectroscopies. Figure 6 shows the FAB MS spectrum of the [3]rotaxane **57** incorporating a bipyridinium-based dumbbell-shaped component encircled by two BPP34C10 macrocycles. The peaks centered on *m/z* 3 030 and 2 885 correspond to the loss of two $[M - 2PF_6]^+$ and three $[M - 3\ PF_6]^+$ hexafluorophosphate counterions, respectively, whilst the peaks centered on *m/z* 2 639, 2 494, and 2 349 arise from the loss of one BPP34C10 macrocycle and one $[M - PF_6 - BPP34C10]^+$, two $[M - 2\ PF_6 - BPP34C10]^+$, and three $[M - 3\ PF_6 - BPP34C10]^+$ hexafluorophosphate counterions.

The ES MS spectrum of the [4]rotaxane **51** incorporating a bipyridinium-based dumbbell-shaped component encircled by three BPP34C10 macrocycles is illustrated in Fig. 7. Two peaks centered on *m/z* 2 115 and 1 362 corresponding to the loss of two $[M - 2\ PF_6]^{2+}$ and three $[M - 3\ PF_6]^{3+}$ hexafluorophosphate counterions are observed.

The [2]rotaxane **56** incorporating a bipyridinium-based dumbbell-shaped component encircled by a BPP34C10 macrocycle behaves like a molecular shuttle. Thus, the π-electron rich macrocycle moves (Fig. 8) back and forth from one bipyridinium recognition site to the other. This dynamic process is fast on the ^{1}H NMR timescale at 273 K and the ^{1}H NMR spectrum of the [2]rotaxane **56** in CD_3COCD_3 at this temperature shows (Fig. 9*a*) only two sets of sharp signals for the protons in the α-positions with respect to the nitrogen atoms on the bipyridinium units, as well as, only two sets of sharp signals for the β-pyridinium protons. On cooling a CD_3COCD_3 solution of **56**, the rate of the *shuttling process* decreases. As a result, broadening of the signals of both α-CH and β-CH protons is observed (Fig. 9*b* and 9*c*). At 213 K, the shuttling is slow on the ^{1}H NMR timescale: thus, the *occupied* and *unoccupied* bipyridinium recognition sites give rise to


LXVI
LXV
LXVII
LXVIII
LXVIII
1) BPP34C10 / DMF
12 Kbar / 30°C / 3 Days
2) NH4PF6 / H2O
19%
1/5DN38C10 / MeCN
55°C / 2 Days
49%
Slipping
Threading
i-Pr
Cl
2PF6
4PF6

SCHEME 15

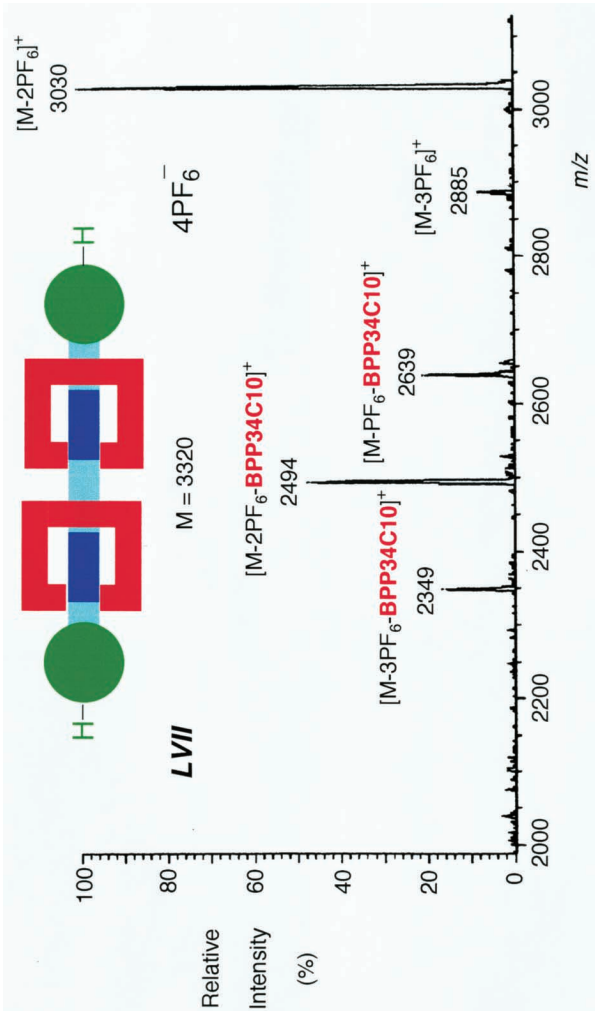


FIG. 6
FAB MS of the [3]rotaxane **57**

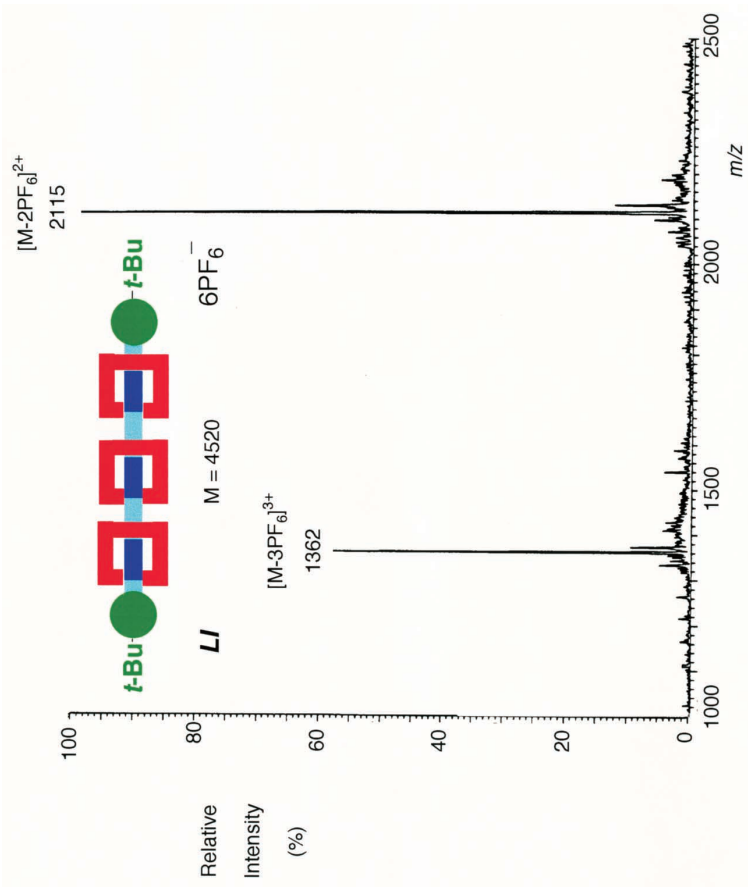


FIG. 7
ES MS of the [4]rotaxane **51**

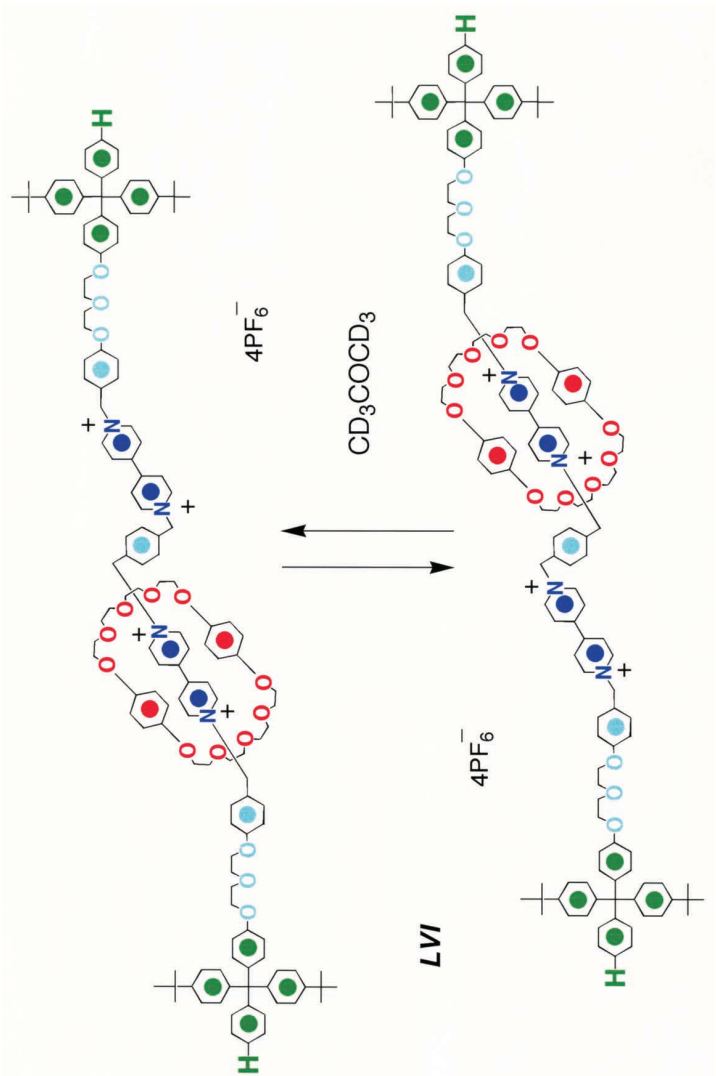


FIG. 8
The shuttling process associated with the [2]rotaxane **56**

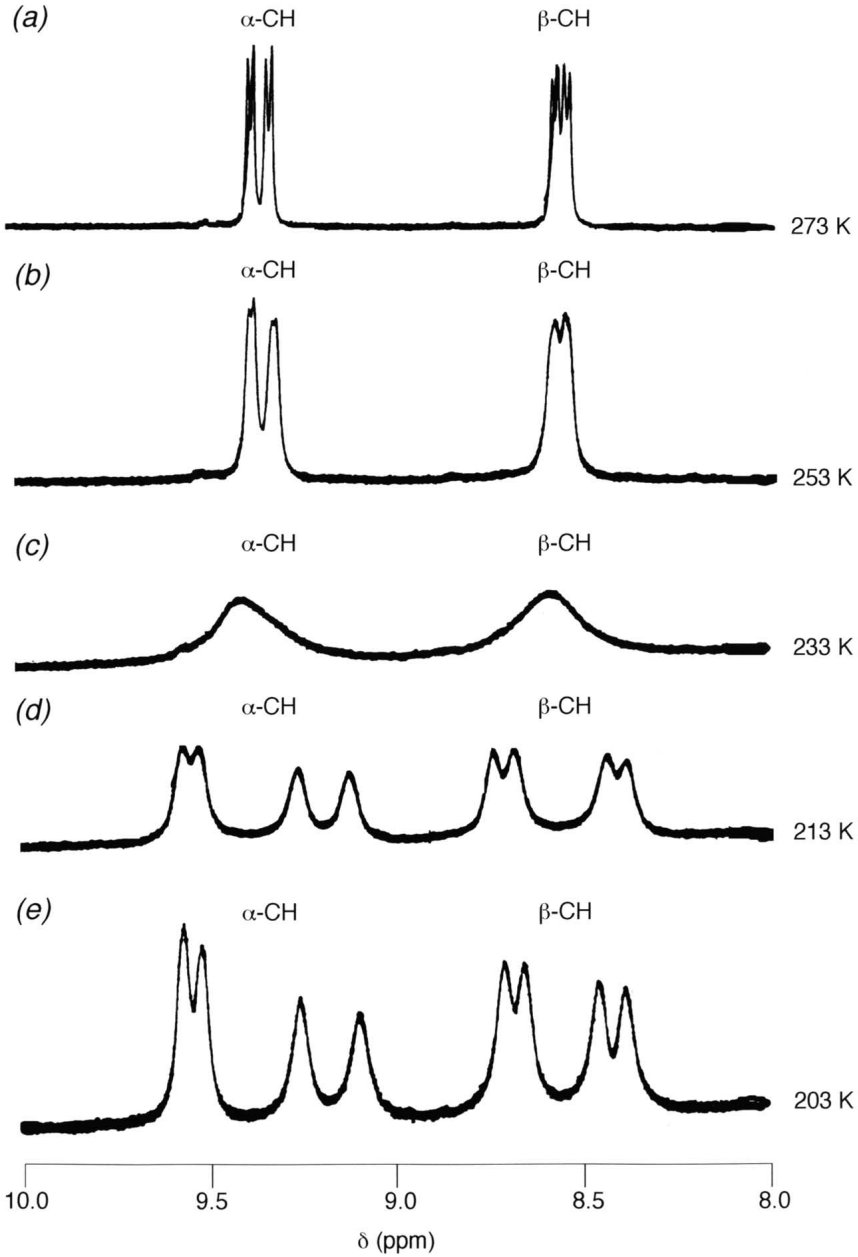


FIG. 9

Partial ^{1}H NMR spectra of a CD_3COCD_3 solution of the [2]rotaxane **56** recorded at (*a*) 273 K, (*b*) 253 K, (*c*) 233 K, (*d*) 213 K, and (*e*) 203 K

distinct sets of signals. The partial ^{1}H NMR spectra of a CD_3COCD_3 solution of **56** recorded at 213 K (Fig. 9*d*) and 203 K (Fig. 9*e*) show four sets of signals for the α-CH protons, as well as four sets of signals for the β-CH protons. By employing the coalescence method[41], the free energy of activation ($\Delta G^{\neq}$) for the degenerate exchange process associated with the [2]rotaxane **56** was calculated[39] to be ca 10 kcal mol^{-1}.

The idea of controlling the shuttling process suggested the synthesis of [2]rotaxanes incorporating (Fig. 5) two different stations within the dumbbell-shaped component. Interestingly, the dynamic process associated with the [2]rotaxane **42** incorporating one benzidine and one biphenol station can be reversibly controlled[35] (Fig. 10) both chemically and electrochemically. The bipyridinium-based cyclophane resides mainly on the benzidine station. However, upon either electrochemical oxidation or protonation of the benzidine unit, the tetracationic macrocycle is obliged to move away from the positively-charged station and go to the neutral one – the biphenol station. Upon electrochemical reduction or deprotonation of the benzidine unit, the macrocyclic component moves back from the biphenol station to the benzidine station. Thus, the [2]rotaxane **42** is a molecular shuttle reversibly controllable by means of external stimuli that can be chemical or electrochemical.

5. CONCLUSIONS

Molecular compounds composed of discrete components held together by means of mechanical constriction, such as rotaxanes, are an intriguing synthetic challenge. The early syntheses of rotaxanes were mainly based upon either statistical or directed approaches. However, the yields associated with the statistical syntheses were relatively low, whilst, the directed methodologies were tedious and time-consuming. With the advent of supramolecular chemistry, series of host–guest approaches to rotaxanes have been developed. A wide range of macrocyclic host molecules, such as cyclodextrins, crown ethers, cyclophanes, and, in one case, a calixarene have been employed as the cyclic components to generate numerous rotaxanes and polyrotaxanes. Metal-templated and donor/acceptor-templated approaches to rotaxanes have been developed in Strasbourg and Birmingham, respectively. By relying upon template-directed approaches a wide range of [2]rotaxanes, [3]rotaxanes, and [4]rotaxanes have been generated in relatively high yields. The high degree of control imposed by the use of templates upon these synthetic methodologies has raised the possibility of self-assembling efficiently and precisely rotaxanes incorporating a wide diversity of chemical modifications. A range of rotaxanes – namely, molecular shuttles – incorporating free recognition sites within the dumbbell-shaped component have been generated and the dynamic process – namely, the shuttling – associated with them has been investigated in some detail. In particular, the reversible control of the shuttling process has been achieved using external stimuli by incorporating, within the dumbbell-shaped component of the rotaxane, electrochemically- or chemically-addressable stations. The relative simplicity, together

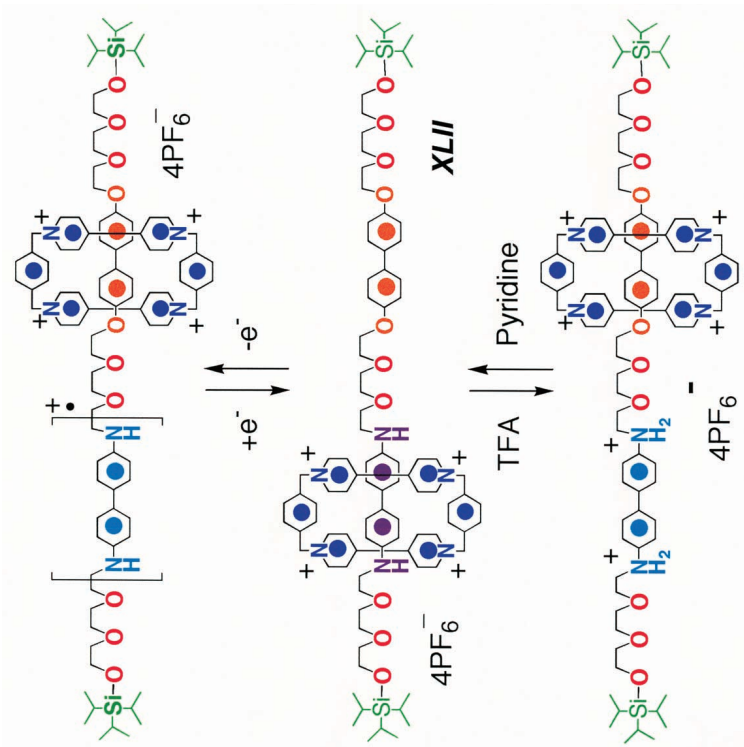


FIG. 10
A chemically- and electrochemically-controllable molecular shuttle

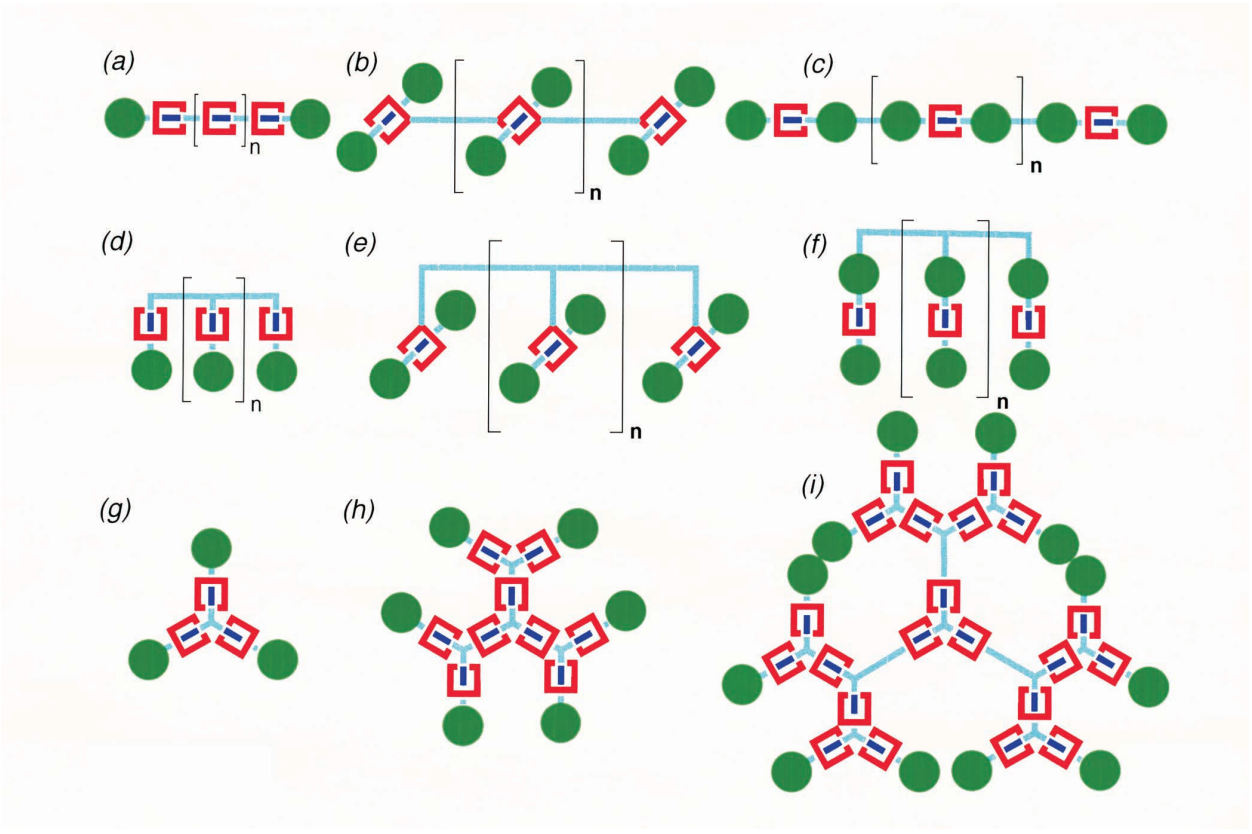


FIG. 11
Schematic representations of (*a*, *b*, and *c*) main-chain and (*d*, *e*, and *f*) side-chain polyrotaxanes, as well as (*g*, *h*, and *i*) dendritic rotaxanes

with the efficiency and high degree of control of the template-directed syntheses, are strong recommendations for their use as a synthetic approach to even more complex molecular and macromolecular structures, such as those depicted in Fig. 11. The ultimate achievement in this area of research will be the design and synthesis of molecular and supramolecular devices[3,4] on the nanoscopic scale having precise shapes and functions.

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