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Nondegenerate π-Donor/π-Acceptor [2]Catenanes Containing Proton-Ionizable 1*H*-1,2,4-Triazole Subunits: Synthesis and Spontaneous Resolution

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Abstract: Chirality can hold the key to inducing directionality of motion in components of molecular devices. With this idea in mind, we describe here 1) the template-directed synthesis of two [2]catenanes wherein cyclobis(paraquat-*p*-phenylene) is interlocked with polyether macrocycles containing, in addition to one 3,5-bis(oxymethylene)-1*H*-1,2,4-triazole unit, either one 1,4-dioxybenzene or one 1,5-dioxynaphthalene ring system. We also report 2) the full characterization of both [2]catenanes by fast atom bombardment mass spectrometry (FABMS), X-ray crystallography, and dynamic ^{1}H NMR spectroscopy. We reveal 3) the fact that the [2]catenanes not only exist, both in the solution-state and in the solid-state, as strictly one of the two possible translational isomers, but that they also exhibit spontaneous resolution on crystallization leading to formation of homochiral crystals, as indicated by X-ray crystallography and circular dichroism (CD) experiments. Finally, we comment 4) on the chances of switching these catenanes chemically.

Keywords: catenanes · self-assembly · spontaneous resolution · supramolecular chemistry · template synthesis

Introduction

Catenanes and related molecular architectures[1] have been transformed from mere chemical and intellectual curiosities into key elements in the fabrication of nanoscale devices, including light- and redox-driven switches and most recently molecular logic gates.[2] A decisive contribution to these advances has been the development of templated syntheses that utilize noncovalent interactions as a major element of the self-assembly methodology,[3] as well as interdisciplinary research leading to singular approaches for the construction of molecular devices.[4] Furthermore, stereochemistry can induce directionality of motion,[5] and therefore chirality can be regarded as a control element for the construction of molecular switches and binary optical data-storage devices.[6] A vast number of configurational,[7] conformational,[8] or topologically[9] chiral interlocked systems has been described, and a major effort has been made to isolate them in an enantiomerically pure form.[10] Among them, only one example is known of the spontaneous resolution of a [2]catenane having elements of planar chirality,[11] although this was a degenerate (nonswitchable) case.

Incorporation of betainic subunits, for example, based on imidazoliummethylene 1,2,4-triazolate, into oligopolar and oligocationic macrocyclic scaffolds[12] has been one of our research interests and provided cyclophanes with a variety of properties such as anion binding.[13] In a project aiming at the preparation of betainic catenanes,[14] the design of interlocked structures calls on previous experience of our groups.

In this context, incorporation of proton-ionizable heteroaromatic systems, for example, *1H*-1,2,4-triazole units,[12,15] into mechanically interlocked structures is interesting for different reasons and permits examination of the characteristics of these entities, based on their distinctive properties:

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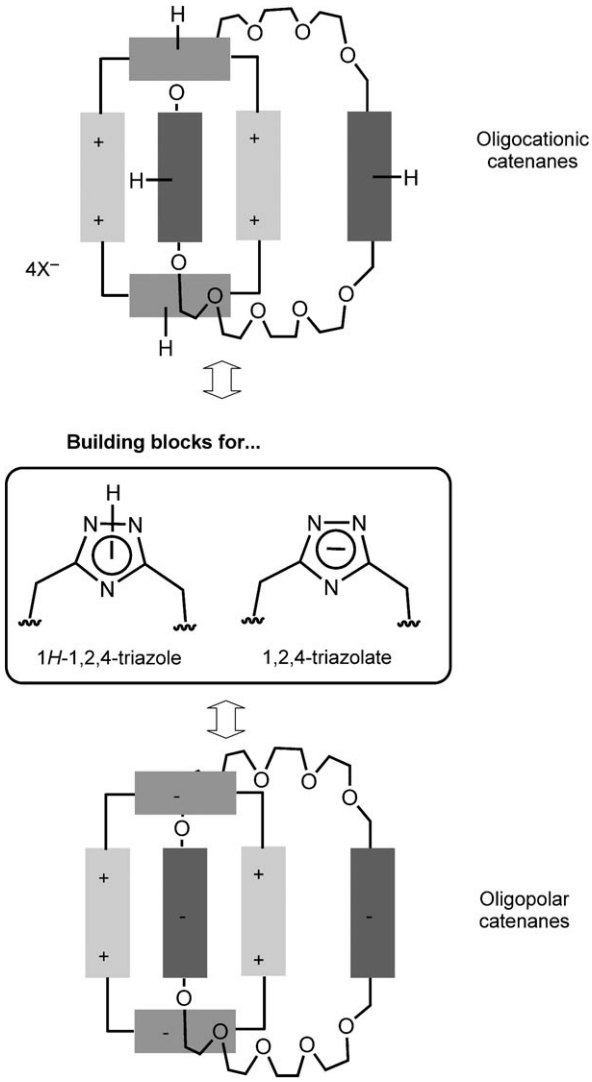
1) *1H*-1,2,4-triazole units are good hydrogen-bond donors, 2) they exhibit prototropic annular tautomerism, 3) they can be regarded as ligands for a variety of transition metal ions,[16] 4) the 3,5-bis(methylene)-1*H*-1,2,4-triazole fragment has a weak π-donor character[17] which could modulate the translational isomerism in dissymmetric catenanes, 5) its acid/base properties, that is, the *1H*-1,2,4-triazole/1,2,4-triazolate equilibrium can in principle be exploited as an element of a switch for the construction of molecular machines, and 6) the triazole unit is also advantageous for incorporation of these molecules onto surfaces, as it is easily functionalized.

In this work we have explored the use of *1H*-1,2,4-triazole/triazolate subunits as building blocks for the construction of π-donor/π-acceptor catenanes based on paraquat residues and π-electron-rich units,[18] aiming at the preparation and study of the properties of oligocationic and oligopolar catenanes and their potential use as molecular switches.

We describe here the synthesis of the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6, which incorporate the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) as the π-electron-deficient component and a macrocyclic polyether as the π-electron-rich component incorporating either one 1,4-dioxybenzene or 1,5-dioxynaphthalene ring and one 3,5-bis(oxymethylene)-*1H*-1,2,4-triazole unit. We report on the characterization of **13**·4 PF_6 and **14**·4 PF_6 by fast atom bombardment mass spectrometry (FABMS), X-ray crystallography, and dynamic ^{1}H NMR spectroscopy.

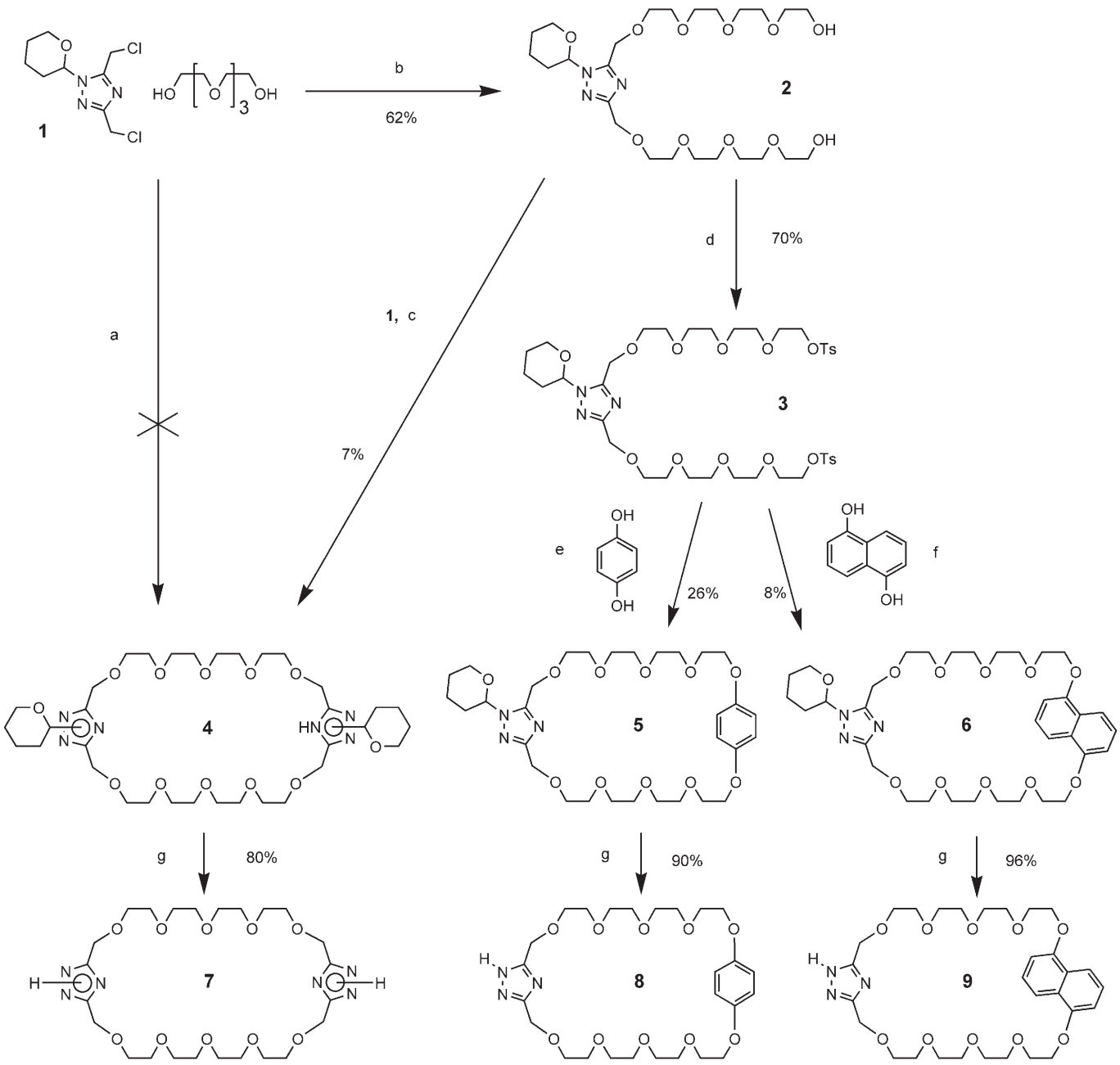
The most remarkable aspect of these new [2]catenanes is their existence both in solution and in the solid state as only one of the two possible translational isomers. Furthermore, both [2]catenanes exhibit spontaneous resolution on crystallization to form homochiral crystals (of the same type of chirality), as determined by X-ray crystallography and circular dichroism experiments. The potential use of the proton-ionizable *1H*-1,2,4-triazole moieties as elements of switches was also examined, but the tetracationic macrocycle is extremely unstable in the presence of 1,2,4-triazolate anions.



Abstract in Catalan: *La quiralitat pot ser la clau per induir direccionalitat al moviment per al disseny de dispositius moleculars. Amb aquesta idea en ment, en aquest article descrivim 1) la síntesi dirigida per plantilla de dos [2]catenans que a la seva estructura entrellacen un ciclofà tetracatiònic (ciclobis(paraquat-p-fenilè) amb polièters macrocíclics que contenen, a mes d'una unitat de 3,5-bis(oximetilen)-1 H-1,2,4-triazole, un anell d' 1,4-dihidroxibenzè o 1,5-dihidroxinaftalè. També detallem 2) la total caracterització dels dos [2]catenans mitjançant espectrometria de masses per bombardeig d'àtoms ràpids (FABMS), cristal·lografia de raigs-X i espectroscòpia dinàmica de ^{1}H NMR. Es remarcable 3) que els [2]catenans existeixen, tant en dissolució com a l'estat sòlid, com un de dos possibles isòmers translacionals. A més, també experimenten resolució espontània per cristal·lització, conduint a la formació de cristalls homoquirals, tal com s'ha demostrat per cristal·lografia de raigs-X i experiments de dicroïsme circular (CD). Finalment, comentem 4) sobre el potencial d'actuar com interruptors controlats químicament d'aquests catenans.*

Results and Discussion

Synthesis: Preparation of macrocyclic polyether **7** was attempted by two procedures (Scheme 1), both of which involved the protected macrocycle **4** as key intermediate. Initially, synthesis of **4** was attempted by using CsCl as template in a one-pot reaction, following a procedure previously used for the synthesis of various dissymmetric crown ethers containing 1-methyl-3,5-bis(methylene)-1*H*-pyrazole.[19] However, reaction of the tetrahydropyranyl-protected bis(chloromethyl)triazole **1**[20] and tetraethylene glycol in equimolar proportion and using dimethoxyethane (DME) as the solvent under a variety of conditions did not lead to isolation of **4**. Instead, reaction of **1** with an excess of tetraethy-

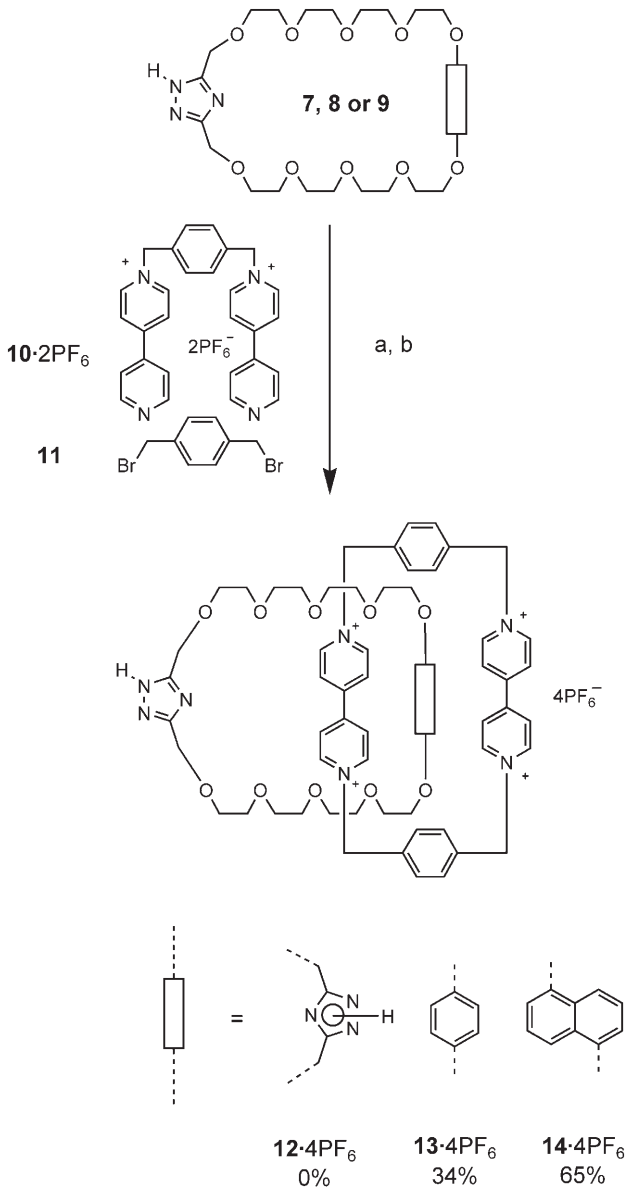


Scheme 1. Synthesis of the macrocyclic polyethers **7**, **8**, and **9**: a) one-pot, NaH, CsCl, DME, reflux; b) NaH, 60 °C; c) NaH, NaI, DMF, 80 °C; d) *p*TsCl, NaOH, H_2O/THF; e) Cs_2CO_3, CsOTs, DMF, 80 °C; f) Cs_2CO_3, CsOTs, DMF, 100 °C; g) 1.5 N HCl/MeOH, RT.

lene glycol and NaH afforded bis-alcohol **2** in 62% yield. Macrocyclization of **2** with **1** by using NaH and NaI in DMF yielded 7% of bis-protected macrocycle **4**, which was deprotected in acidic medium to give macrocyclic polyether **7** (Scheme 1).

Macrocyclic polyethers **8** and **9** were both obtained in three steps from intermediate **2** by tosylation, macrocyclization by reaction of the bis-tosylate **3** with 1,4-dihydroxybenzene and 1,5-dihydroxynaphthalene in basic medium (cesium carbonate in DMF) to give protected macrocycles **5** (26%) and **6** (8%) respectively, and deprotection in acidic medium (Scheme 1).

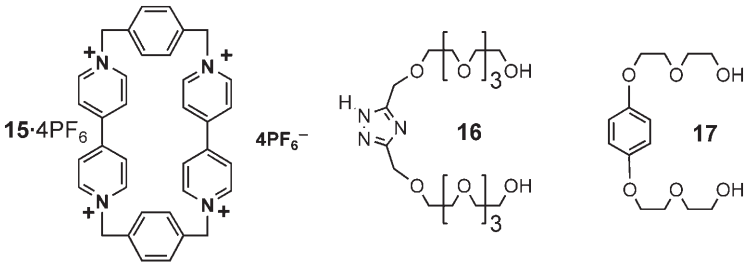
The [2]catenanes **13**·4PF_6 and **14**·4PF_6 were assembled by a template-directed methodology (Scheme 2). Reaction of **10**·2PF_6[21a] and **11** in the presence of the appropriate macrocyclic polyether **8** containing one 1,4-dioxybenzene unit and one 3,5-bis(oxymethylene)-*1H*-1,2,4-triazole unit as π-donor recognition motifs under high-pressure conditions (10 kbar) gave [2]catenane **13**·4PF_6 in 34% yield after counterion exchange (Scheme 2). In this case, the reaction performed at room pressure afforded [2]catenane **13**·4PF_6 with no significant difference in yield (33%). Following a similar procedure with macrocyclic polyether **9** containing one 1,5-dioxynaphthalene unit and one 3,5-bis(oxymethylene)-*1H*-1,2,4-



Scheme 2. Template-directed synthesis of the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6: a) DMF, RT, 10 kbar, 3 days; b) NH_4PF_6, H_2O.

triazole gave [2]catenane **14**·4 PF_6 in 65% yield. Once again, the 1,5-dioxynaphthalene unit shows its better ability as template for formation of the π-acceptor cyclophane within [2]catenanes of this type. Clearly, these yields indicate that the 3,5-bis(oxymethylene)-*1H*-1,2,4-triazole is a less efficient recognition unit for the formation of these [2]catenanes, reflecting the relatively weak π-donating ability[17] (see complexation studies below) in comparison to previously described [2]catenanes containing macrocyclic polyethers incorporating 1,4-dioxybenzene, 1,5-dioxynaphthalene, and *p*-xylyl aromatic units.[21] Additional evidence is provided by two facts: 1) no complexation is evident between open-chain polyether derivatives of 3,5-bis(methylene)-1*H*-1,2,4-triazole and cyclobis(paraquat-*p*-phenylene) (see below),[12] and 2) under the same conditions, no catenane is formed by reaction of **10**·2 PF_6 with **11** in the presence of the polyether **7** containing two 3,5-bis(methylene)-*1H*-1,2,4-triazole units (Scheme 2), and the only product formed was cyclobis(paraquat-*p*-phenylene) **15**·4 PF_6 in 17% yield. This smaller affinity is a consequence of the weaker π-donor character and the smaller π surface of the 1,2,4-triazole unit, along with the fact that no oxygen atoms are directly linked to it.[22,23]

Complexation studies: Complexation was studied by UV/Vis and ^{1}H NMR techniques in acetonitrile solution. First, the absence of any charge-transfer band for an equimolecular mixture of cyclobis(paraquat-*p*-phenylene) **15**·4 PF_6 and the extended open-chain polyether containing one 1,2,4-triazole unit **16** in CH_3CN indicates the lack of π–π interactions between the two components, and therefore the complex formed is extremely weak or it does not form at all. Also, an equimolar mixture of the same components in CD_3CN at 25°C did not indicate formation of a complex, with no changes in the ^{1}H NMR chemical shifts of the components. Under the same conditions, an equimolar mixture of **15**·4 PF_6, **16**, and extended polyether **17** containing one 1,4-dioxybenzene unit,[21a] led to exclusive formation of the 1:1 complex between **15**·4 PF_6 and **17** (see Scheme S1 and Table S1 in the Supporting Information). The high preference of the tetracationic cyclophane for the 1,4-dioxybenzene units compared with the 3,5-bis(methylene)triazole units may explain their different efficiencies as templates in the formation of the [2]catenanes and the isomer selectivity observed in the catenanes both in solution and the solid state (see below).



Mass spectrometry: All polyethers **2**–**9** and **16** containing the 1*H*-1,2,4-triazole unit were characterized by positive-ion ESIMS (see Table S2 in the Supporting Information).

The structures of [2]catenanes **13**·4 PF_6 and **14**·4 PF_6 were characterized by positive-ion FABMS, which revealed peaks characteristic of successive loss of one, two, three, and four PF_6^- counterions from the molecular ion. An additional peak corresponding to the dicationic fragment after the loss of two counterions is also observed. Peaks corresponding to the loss of one, two, and three PF_6^- counterions from the free cyclophane component of the [2]catenanes are observed, along with characteristic loss of the neutral crown ether component of the fragmented [2]catenane (Table 1). A doubly charged ion is also observed for both catenanes **13**·4 PF_6 and **14**·4 PF_6 corresponding to the loss of two PF_6^- counterions (Table 1). For **13**·4 PF_6 peaks were also observed

Table 1. Summary of data obtained from positive-ion FABMS of the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6.[a]

Compd	Ions, *m/z* (%)									
M	$[M-PF_6]^+$	$[M-2PF_6]^+$	$[M-3PF_6]^+$	$[M-4PF_6]^+$	$[M-PF_6-CE]^+$[b]	$[M-2PF_6-CE]^+$[b]	$[M-3PF_6-CE]^+$[b]	$[M-2PF_6]^{2+}$	$[CE+Li]^+$[b]	$[M+Na]^+$
13·4 PF_6	1511.1	1366.3	1221.3	1076.4	956.1	811.1	666.1	683.8	562.0	1679.1
1656.1	(9)	(22)	(8)	(3)	(5)	(28)	(17)	(24)	(100)	(1)
14·4 PF_6	[c]	[c]	1271.1	1126.4	955.8	811.0	665.9	708.3	[c]	[c]
1706.2			(77)	(13)	(18)	(90)	(100)	(36)		

[a] FABMS were obtained with a Fisons Instruments VG-Quattro spectrometer. The spectra were recorded with 10 eV voltage and *p*-nitrobenzyl alcohol matrix. [b] CE stands for the macrocyclic polyether. [c] No signal observed.

for association of the macrocyclic polyether component with Li $[CE+Li]^+$ and Na $[CE+Na]^+$, respectively (Table 1).

X-ray crystallography: Single crystals of **13**·4 PF_6 and **14**·4 PF_6 suitable for X-ray crystallography[24,25] were grown by vapor diffusion of iPr_2O into MeCN solutions.[26] Remarkably, both sets of single crystals belong to the same chiral space group and so contain only one pure enantiomer in the solid state, that is, spontaneous resolution occurs on crystallization.[27] Although this is not an uncommon phenomenon, it is, to our knowledge, the first time[28] that [2]catenanes of the π-donor/π-acceptor variety have undergone spontaneous resolution where 1) the basis for the chirality[29] is helical and planar and 2) inversion between enantiomers involves a co-conformational change[30] and either a conformational change or a prototropic annular tautomerism.[17] Figure 1 shows the inversion between two pairs of enantiomers, that is, (*pR*)-(*P*) and (*pS*)-(*M*), and (*pR*)-(*M*) and (*pS*)-(*P*), via diastereoisomers in a mutual fashion that requires sequential operation of two independent processes. The first involves rocking[21a] of the macrocyclic polyether ring with respect to the tetracationic cyclophane (process **I**), and the second involves either rotation of the triazole ring about its C3−C5 axis (process **II**) or a 1,2-shift of the proton on the triazole ring (process **II′**). These last two processes have stereochemically identical outcome. The structures represented in Figure 1 show changes associated with process **II** related to rotation of the triazole ring about its C3−C5 axis, although an equivalent figure could be drawn considering the prototropic tautomerism (process **II′**). Another stereochemically relevant transformation is process **III**, which involves exchange of the inside and alongside bipyridinium units as a consequence of a pirouetting movement by the triazole unit in the macrocyclic polyether. Application of this transformation to the molecules of the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6 leads to the same result as the transformation related to process **I** (exchange of diastereomers). The absolute stereochemical descriptors introduced in Figure 1 are defined and explained in Figure 2, and the structural parameters for the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6 are collected in Table 2 (see also Table S3 in the Supporting Information).

The solid-state (absolute) structure (Figure 3) of [2]catenane $\mathbf{13}^{4+}$ reveals, as expected, the presence of only one translational isomer. The macrocyclic polyether is threaded through the center of the tetracationic cyclophane, with the 1,4-dioxybenzene ring positioned inside the tetracationic cyclophane, sandwiched between the π-electron-deficient bipyridinium units, with the bis(oxymethyl)-1,2,4-triazole unit (the location of the hydrogen atoms on one of the nitrogen atoms is clearly defined) lying alongside. The separations between the π-electron-deficient bipyridinium units and the π-electron-rich hydroquinone ring are very similar to those observed[21a] in the [2]catenane wherein cyclobis(paraquat-*p*-phenylene) is interlocked by bis-*para*-phenylene[34]crown-10, as are the inclinations of the O-C_6H_4-O

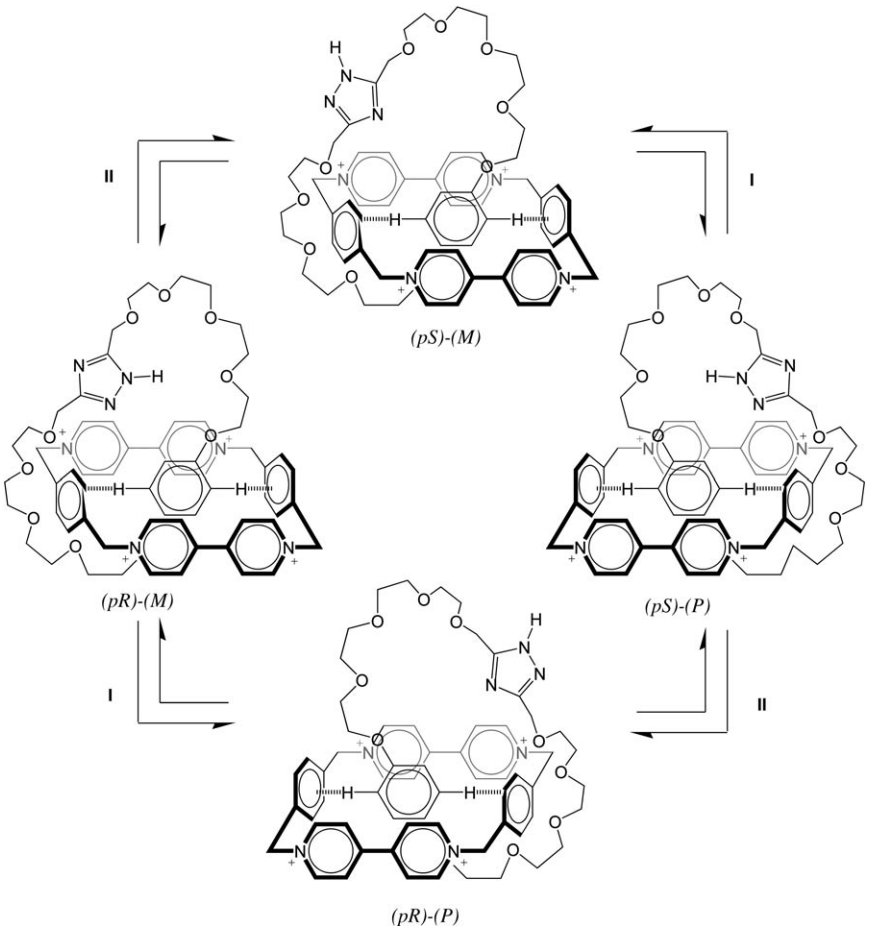


Figure 1. Processes **I** and **II** for interconverting diastereoisomers and inverting enantiomers of [2]catenane $\mathbf{13}^{4+}$. Process **I** corresponds to a change in helical chirality, while process **II** represents alteration of planar chirality. The descriptors of absolute stereochemistry are defined in Figure 2.

axes of the inside hydroquinone ring to the mean planes of the tetracationic cyclophanes (τ, Table 2). The interplanar separation (ca. 3.57 Å) between the alongside triazole ring system and the inside bipyridinium unit is greater than the stacking separations (<3.4 Å) previously observed[31] with pyridyl rings. The π–π stacking interactions are supplemented by intra-[2]catenane C–H···O and C–H···π interactions (a–e in Figure 3). There is no intra-[2]catenane N–H···X hydrogen bond involving the triazole ring; the ring hydrogen atom is directed toward the only ordered PF_6^- ion with formation of an N–H···F hydrogen bond (N···F 2.97, H···F 2.14 Å; N–H···F 153°). Surprisingly, no continuous polar stacks are formed and the shortest inter-[2]catenane contact of any significance is from one of the methylene hydrogen atoms of the tetracationic cyclophane in one molecule to one of the *p*-xylylene spacers in the next, though the H···π distance is long (3.10 Å).

The solid-state (absolute) structure (Figure 4) of $\mathbf{14}^{4+}$[26] is again chiral; it has the same source of conformational chirality as that of $\mathbf{13}\cdot 4PF_6$ and contains only a single conformational enantiomer.[32] The π-electron-rich 1,5-dioxynaphthalene ring system is positioned inside the tetracationic cyclophane, while the triazole ring lies only approximately alongside and is noticeably removed from the overlaying position observed in $\mathbf{13}^{4+}$. Consistent with the stronger π–π stacking interaction between the 1,5-dioxynaphthalene ring system (cf., the hydroquinone ring) and the bipyridinium units, the mean interplanar separations are reduced by more than 0.1 Å with respect to those in $\mathbf{13}^{4+}$. The sliding away of the triazole ring results in its lying above the plane of the tetracationic cyclophane with negligible overlap with either of the two pyridinium rings. Disorder of the triazole ring and one of its adjacent CH_2OCH_2 groups results in two slightly different orientations: the major conformation is depicted in Figure 4. Also, the position of the ring hydrogen atom could not be determined. Intra-[2]catenane stabilizing interactions include the usual complement of C–H···O and C–H···π hydrogen bonds, which supplement the π–π stacking interactions (a–d in Figure 4). Surprisingly, despite the presence of three ordered PF_6^- anions, there are no short F···[2]catenane contacts. Again, extended polar stacks are not formed, nor are there any noteworthy inter-[2]catenane short contacts, though one CH_2···*p*-xylylene separation is analogous to that described for $\mathbf{13}\cdot 4PF_6$ but with an even longer H···π distance of 3.19 Å.

In the case of [2]catenane $\mathbf{14}\cdot 4PF_6$ containing a 1,5-dioxynaphthalene ring system, the successive processes of interconversion between diastereoisomers that lead to inversion of enantiomers is different from that described for the [2]catenane containing a 1,4-dioxybenzene ring (Figure 1), and only two descriptors are used here, because helicity and planar chirality at the dioxynaphthalene subunit are interdependent. Process **IV** in $\mathbf{14}^{4+}$ corresponds to the 1,5-dioxynaphthalene ring system's leaving the cavity of the tetracationic cyclophane, rotating around the axis of its central carbon–carbon bond, and re-entering the cavity with a different relative orientation. This process is tantamount to its having undergone rocking (process **I** in $\mathbf{13}^{4+}$). The full sequence of events is illustrated in Figure 5.

Circular dichroism in the solid state: The phenomenon of spontaneous resolution operating in these [2]catenanes con-

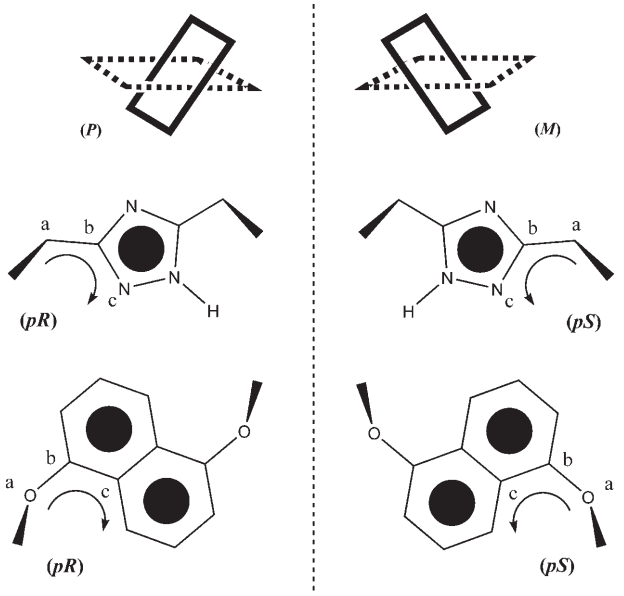
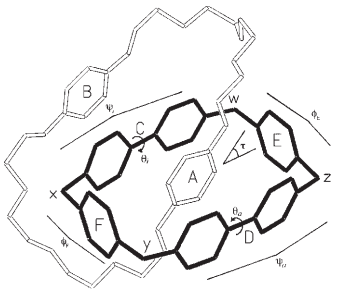


Figure 2. Definition of the absolute stereochemical descriptors. Helicities of plus and minus are indicated by *P* and *M*, respectively. We give the solid-line ring (containing oxygen atoms) higher priority than the dotted-line ring (containing nitrogen atoms) and, on that basis, display the solid-line ring in front of the dotted-lined ring when observing the helicity generated by the two rings. The planar chirality is denoted by *pR* and *pS* for clockwise and anticlockwise, respectively.

taining 3,5-bis(oxymethyl)-1*H*-1,2,4-triazole subunits needed confirmation. When chirality is of conformational origin, spontaneous resolution takes place under racemizing conditions, for which just a few examples are well studied.[27] In the case of [2]catenanes **13**·4 PF_6 and **14**·4 PF_6, from the multiple co-conformations existing in solution, four can be regarded as prevalent (see Figures 1 and 5): those arising from both prototropic tautomerism and conformational enantiomerism phenomena.[33] In addition to the X-ray study, we complemented the investigation of spontaneous resolution by using solid-state circular dichroism.[34]

Crystallization of [2]catenane **13**·4 PF_6 under the same conditions used to obtain single crystals suitable for X-ray crystallography, that is, by vapor diffusion of iPr_2O into a solution of **13**·4 PF_6 in MeCN, yielded small red crystals (300–500 μg) with no morphological indication that they constitute enantiomorphic crystals. From a mixture of such crystals, we separated manually 14 apparent monocrystals and used them to prepare KBr disks.[35] From these samples, three exhibited a Cotton effect at about 400 nm associated with a π–π transition between the bipyridinium units and the 1,4-dioxybenzene ring present in the [2]catenane.[36] The other 11 crystals were presumably twinned. The solid-state circular dichroism (CD) spectra of enantiomorphic crystals, which exhibit maxima at 397 nm ($\Delta\varepsilon = +0.11\ L\,mol^{-1}\,cm^{-1}$) and 403 nm ($\Delta\varepsilon = -0.18\ L\,mol^{-1}\,cm^{-1}$), are shown in Figure 6. Although no correlation of the optical properties has been made with the X-ray (absolute) structure of the [2]catenane, the solid-state CD experiments demonstrate the presence in a single crystal of a pure single enantiomer—presumably either (*pR*)-(*P*) or (*pS*)-(*M*)—in the solid state, that is, chiral induction and spontaneous resolution occur to give a conglomerate under freely racemizing conditions. Unfortunately, we have not been able to obtain any solid-state CD spectra for [2]catenane **14**·4 PF_6, due to the small size of the crystals it forms.

Table 2. Structural parameters for compounds **13**·4 PF_6 and **14**·4 PF_6.[a]



Parameter	**13**·4 PF_6	**14**·4 PF_6
θ_i [°][b]	20	19
θ_a [°][b]	16	10
ψ_i [°][c]	26	22
ψ_a [°][c]	26	22
φ_E [°][d]	12	16
φ_F [°][d]	11	14
τ [°][e]	42	38
A···B [Å]	7.06	6.86
C···D [Å]	7.07	6.81
E···F [Å]	10.22	10.39
A···C [Å]	3.53	3.40
A···D [Å]	3.57	3.41
C···B [Å]	3.57	3.89
A···E [Å]	5.01	5.20
A···F [Å]	5.22	5.19
w [°]	107.8(4)	108.5(5)
x [°]	109.0(5)	108.5(4)
y [°]	108.5(4)	107.3(5)
z [°]	109.2(5)	109.0(5)

[a] For the angles θ and ψ, the subscripts "i" and "a" refer to the inside and alongside ring systems, respectively. Distances to the ring systems A to F are calculated from centroid to centroid. [b] The twist angle θ is defined as the average of the moduli of the four normalized torsional angles about the central C–C bond within the bipyridinium unit. [c] The bowing angle ψ is the supplement of the angle subtended by the two N^+–CH_2 bonds emanating from the bipyridinium ring system. [d] The bowing angle φ is the supplement of the sum of the angles of the C–CH_2 bonds emanating from the spacer rings (E and F) and the associated ring plane. [e] The tilt angle τ is the angle between the O···O vector of the inside O,O′-substituted aromatic ring and the mean plane of the four corner methylene carbons atoms of the tetracationic cyclophane.

Dynamic NMR spectroscopy: Previous studies on π-donor/π-acceptor [2]catenanes[21] were of great value for the full assignment of the NMR spectra of the macrocyclic polyethers and [2]catenanes of this work. Unambiguous assignments for the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6 were possible by using HMBC, HMQC, COSY-2D and ROESY-2D techniques (Table 3; see also Table S4 in the Supporting Information for data on the polyether components).

The [2]catenanes **13**·4 PF_6 and **14**·4 PF_6 exhibit dynamic behavior in solution, observed by NMR spectroscopy, consequence of a number of dynamic processes operating in solu-

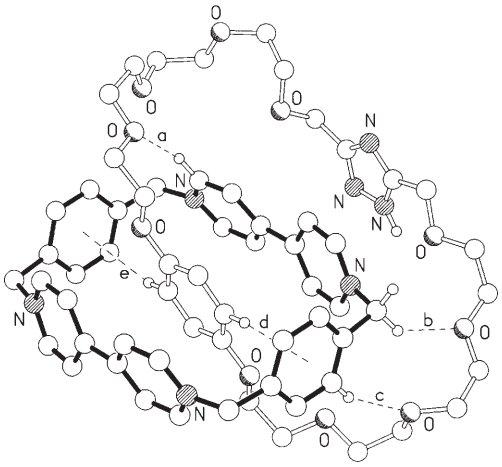


Figure 3. Ball-and-stick representation of the solid-state molecular structure of the (*pR*)-(*P*) isomer of $\mathbf{13}^{4+}$ showing the intra[2]catenane hydrogen-bonding interactions. Hydrogen-bond geometric parameters C···O, H···O [Å], C–H···O [°] are a) 3.37, 2.44, 144; b) 3.24, 2.44, 140; c) 3.41, 2.49, 159. The CH/π interactions have H···π [Å], C–H···π [°] of d) 2.70, 169; e) 2.99, 158.

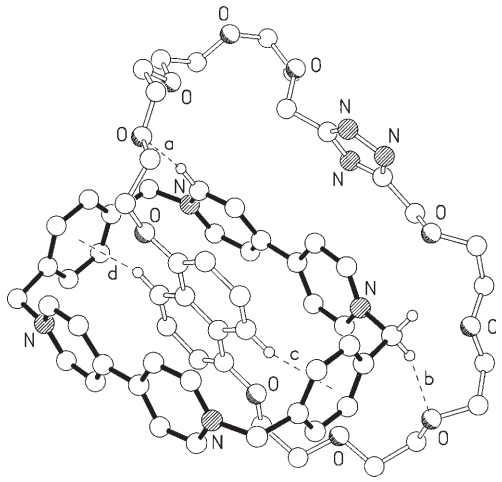


Figure 4. Ball-and-stick representation of the solid-state structure of the (*pR*/*pS*)-(*pS*) isomer of $\mathbf{14}^{4+}$ showing the intra-[2]catenane hydrogen bonding interactions. Hydrogen-bond geometric parameters C···O, H···O [Å], C–H···O [°] are a) 3.23, 2.34, 154; b) 3.42, 2.50, 162. The CH/π interactions have H···π [Å], C–H···π [°] of c) 2.54, 148; d) 2.50, 150.

tion, as described for similar compounds.[21a] The most distinctive feature of the ^{1}H NMR spectra of the [2]catenanes **13**·4 PF_6 and **14**·4 PF_6, recorded in both CD_3CN and CD_3COCD_3 solutions, is the presence of only one translational isomer in which the triazole units occupy the alongside positions with respect to the tetracationic cyclophanes, as illustrated in Scheme 2. This conclusion is based on the observation that, in the spectrum of **13**·4 PF_6 recorded in CD_3CN solution, the 1,4-dioxybenzene ring protons resonate as a singlet at $\delta = 3.56$ ppm, which indicates[21a] that the ring is residing inside the tetracationic cyclophane: the protons on the methylene groups attached to the triazole unit appear as a singlet at $\delta = 4.20$ ppm, a modest 0.40 ppm upfield from where they resonate in free macrocyclic polyether **8**.

The overwhelming presence of one translational isomer in the case of both [2]catenanes in solution renders it impossible to probe, by dynamic ^{1}H NMR spectroscopy, the rate of the circumrotation process that interchanges the hydroquinone ring in **13**·4 PF_6 and the 1,5-dioxynaphthalene ring system in **14**·4 PF_6, however fleetingly, with their cyclically appended 3,5-bis(methylene)-1*H*-1,2,4-triazole units.

Thus, it is clear that circumrotation of the macrocyclic polyether through the cavity of the tetracationic cyclophane does not occur, with no exchange of the 1,4-dioxybenzene and 3,5-bis(oxymethyl)-1*H*-1,2,4-triazole rings between the inside and alongside positions on the NMR timescale. This statement is based on two observations, 1) warming the CD_3CN solution to 343 K did not cause any shift or broadening of either the aromatic hydrogen atoms of the 1,4-dioxybenzene ring or the methylene hydrogen atoms linked to the triazole unit; 2) on cooling to 233 K the chemical shifts of these protons do not experience any significant variation (see Figure S1 in the Supporting Information). Consequently, control of the translational isomerism over a wide range of temperatures is operative, with total preference for one translational isomer, as observed in the solid state.

Nonetheless, by cooling a solution of [2]catenane **13**·4 PF_6 in CD_3COCD_3 (Figure 7), it was possible (Table 4) to identify three different kinetic processes: 1) rocking[37] of the 1,4-dioxybenzene ring inside the tetracationic cyclophane cavity (process **I** in Figure 1), 2) exchange of the inside and alongside bipyridinium units as a consequence of a pirouetting movement by the triazole unit in the macrocyclic polyether (process **III**), and 3) prototropic tautomerism of the 1*H*-1,2,4-triazole unit (equivalent to process **II′** in Figure 1).

In common with the behavior in CD_3CN solution, the room-temperature spectrum of **13**·4 PF_6 in CD_3COCD_3 (Figure 7a) shows only one signal for both the 1,4-dioxybenzene ($\delta = 3.90$ ppm) and 3,5-bis(oxymethylene)-1*H*-1,2,4-triazole ($\delta = 4.22$ ppm) units, that is, they are located inside and alongside the tetracationic cavity, respectively. These signals do not experience any shift on cooling the solution, that is, the circumrotation of the macrocyclic polyether does not take place on the NMR timescale at these temperatures.

On cooling the CD_3COCD_3 solution, the 1,4-dioxybenzene proton signals showed clear broadening, and (Figure 7c) their separation into two broad signals at 210 K indicates that rocking of the 1,4-dioxybenzene ring inside the tetracationic cyclophane cavity (Process I in Figure 1) is slowing down. At 193 K (Figure 7d) the process is already frozen on the NMR timescale, as indicated by the existence of two signals of equal intensity at $\delta = 2.12$ and 5.58 ppm that exhibit the maximum shift difference ($\Delta\delta = 3.46$ ppm) corresponding to the the protons oriented towards the *p*-xylyl spacer face and the outside of the cavity, respectively, as confirmed by COSY-2D and NOESY-2D experiments. The coalescence of this signal at 218 K allowed calculation of the energy barriers associated with the process as $\Delta G_c^{\ddagger} = 9.0$ kcal mol^{-1} (Process I, Table 4).

The protons of the tetracationic cyclophane also exhibit temperature dependence. The exchange of the aromatic pro-

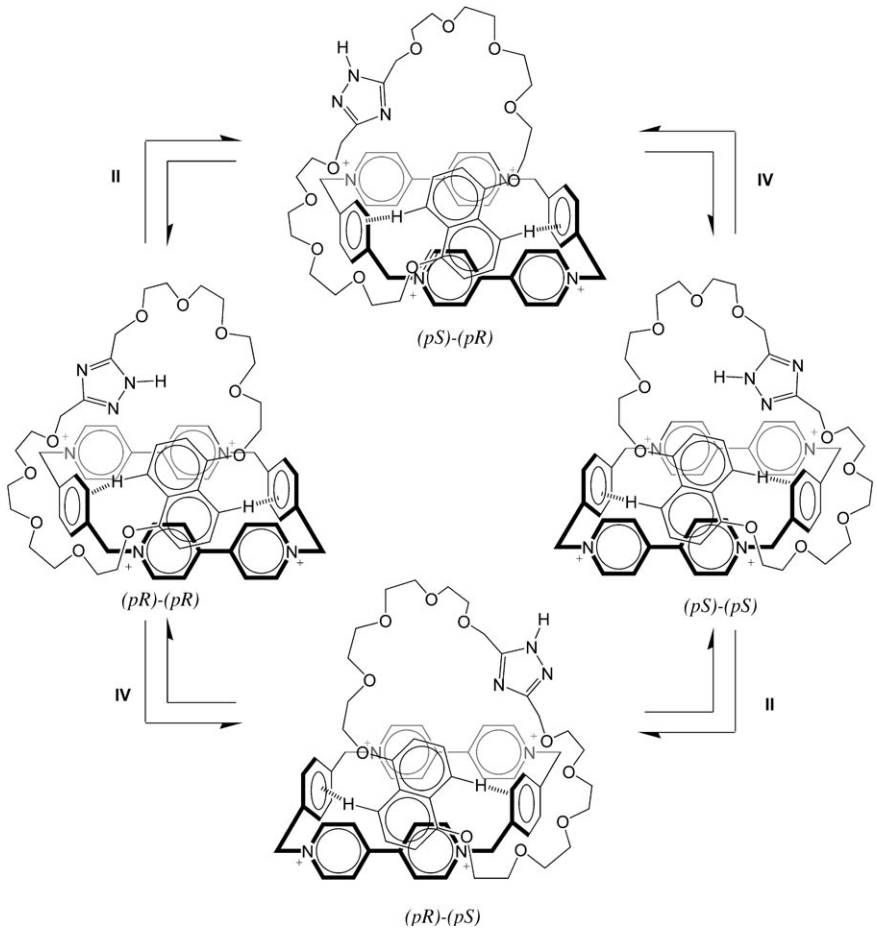


Figure 5. Processes **II** and **IV** for interconverting diastereoisomers and inverting enantiomers in [2]catenane $\mathbf{14}^{4+}$. Process **IV** corresponds to a change in the planar chirality of the 1,5-dioxynaphthalene ring system, and process **II** represents alteration of the planar chirality of the 3,5-bis(methylene)-1*H*-1,2,4-triazole unit. The descriptors of absolute stereochemistry are defined in Figure 2.

tons occupying the inside and alongside positions of the macrocyclic polyether is fast at room temperature in CD_3COCD_3, as indicated by the sharpness and good resolution of the corresponding signals (Figure 7a). As the solution is cooled, the α-CH, β-CH, and the xylyl protons experience broadening, that is, this process slows down. As seen in Figure 7d, at 193 K the process is frozen and all these protons appear at different chemical shifts, and in particular, the β-CH and α-CH protons each appear as two doublets (corresponding to the protons occupying the inside and the alongside positions of the macrocyclic polyether) centered at $\delta = 8.52$ and 9.52 ppm, respectively, as confirmed by a COSY-2D experiment. The coalescence of these protons at 210 K (Figure 7c) allowed the calculation of a energy barrier associated with the process of $\Delta G_c^{\ddagger} = 10.0\ \mathrm{kcal\,mol^{-1}}$ (process **III**, Table 4).

The resonances corresponding to the protons of the methylene group attached to the 1,2,4-triazole ring are also temperature-dependent. At room temperature in CD_3COCD_3 they appear as an already slightly broad signal at $\delta = 4.21$ ppm, which experiences broadening and, after coalescence at 270 K, appears as two equally intense singlets (Figure 7b). The maximum separation at 210 K for these singlets appearing at $\delta = 3.90$ and δ 4.07 ppm ($\Delta\delta = 0.17$ ppm) indicates that the process has frozen at this temperature. The dynamic process corresponds to the prototropic tautomerism, and its associated energy barrier was calculated as $\Delta G_c^{\ddagger} = 12.6\ \mathrm{kcal\,mol^{-1}}$ (process **II′**, Table 4).

The three kinetic processes identified are thus associated with energy barriers[38] of 9.0, 10.0, and 12.6 kcal mol^{-1}, respectively. The $\Delta G^{\ddagger}$ value of 10.0 kcal mol^{-1} is considerably less than that (11.2 kcal mol^{-1}) observed for the pirouetting process in the prototypical [2]catenane incorporating two 1,4-dioxybenzene residues in the ring, and this reflects the much weaker π–π stacking interaction between a triazole ring and a bipyridinium unit. Finally, the $\Delta G^{\ddagger}$ value of 12.6 kcal mol^{-1} is smaller than those reported[39] for other 1*H*-1,2,4-triazole units, and possibly indicates that it does not enter into any strong hydrogen bonding interactions

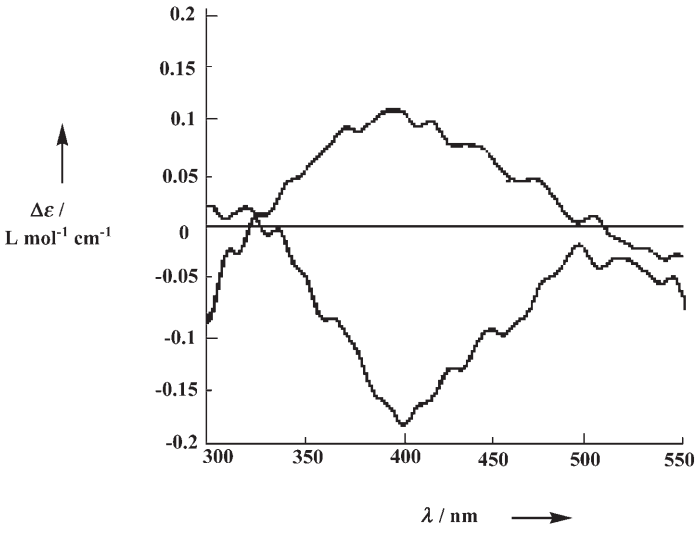


Figure 6. Solid-state CD spectra of "enantiomorphic crystals" of [2]catenane **13**·4 PF_6.

Table 3. Selected ^{1}H NMR (500 MHz) data for [2]catenanes **13**·4 PF_6, **14**·4 PF_6 and their free components **8, 9** and **15**·4 PF_6.[a]

	Tetracationic component							Macrocyclic polyether		
	αCH	βCH	C_6H_4	CH_2N^+	H4/8	H3/7	H2/6	OC_6H_4O	CH_2-T	OCH_2
15·4 PF_6[b]	8.88	8.18	7.54	5.76	–	–	–	–	–	–
8[b]	–	–	–	–	–	–	–	6.77	4.60	4.00/3.71/3.56–3.70
13·4 PF_6[b]	8.94	7.79	7.80	5.73	–	–	–	3.56	4.20	3.93–3.34
	(+0.06)	(−0.39)	(+0.26)	(−0.03)				(−3.21)	(−0.40)	
13·4 PF_6[c]	9.38	8.29	8.08	6.08	–	–	–	3.90	4.22	2.82–4.03
9[b]	–	–	–	–	–	–	–	–	4.50	4.28/3.96/3.80/3.70–3.69
14·4 PF_6[b]	8.87	8.03	7.32	5.80	2.48	6.01	6.27	−4.31	4.31–3.37	4.30/4.21/4.05/3.90/3.73/3.57/3.44/3.37
	(−0.01)	(−0.15)	(−0.22)	(−0.03)	(−5.32)	(−1.29)	(−0.55)	(−0.19)		
14·4 PF_6[c]	9.31	8.32	7.79	6.13	2.78	6.27	6.46	−4.36	3.41–4.50	4.50/4.33/4.12/3.97/3.81/3.65/3.50/3.41

[a] The values in parentheses are chemical shift differences ($\Delta\delta$) between the free component and the [2]catenane. [b] CD_3CN (300 MHz). [c] CD_3COCD_3 (500 MHz).

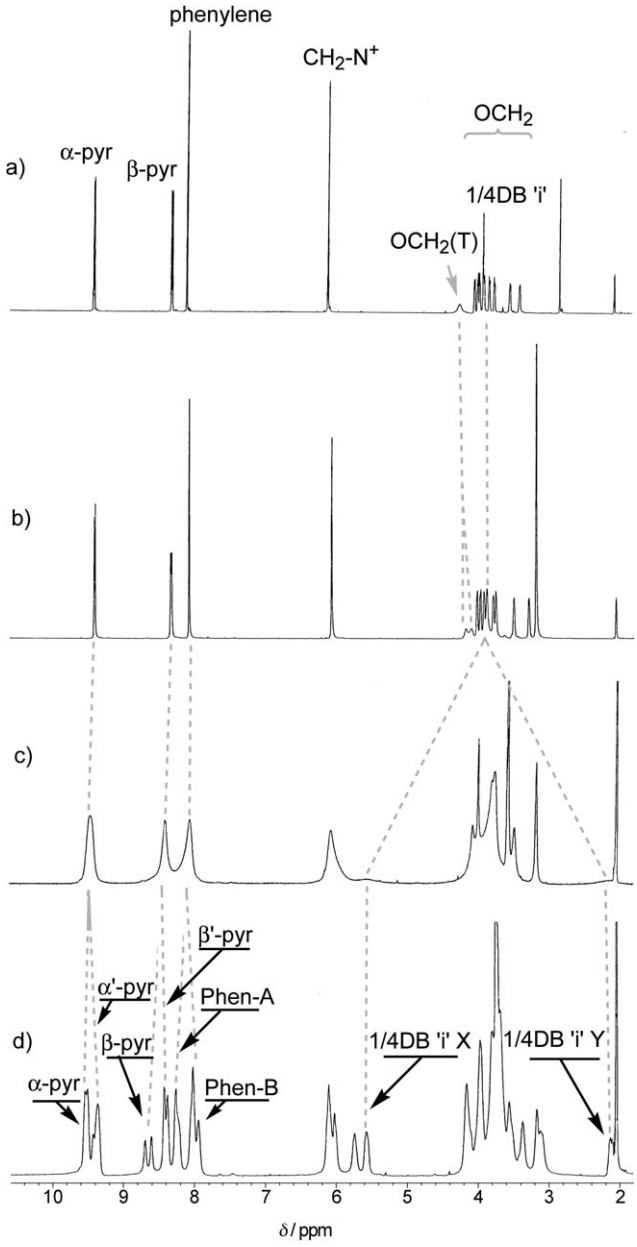


Figure 7. ^{1}H NMR spectrum of [2]catenane **13**·4 PF_6 in CD_3COCD_3 at a) 298 K; b) 253 K; c) 210 K; d) 193 K.

(N−H···X) in solution, as also observed in the solid-state structure reported above.

Similar dynamic behavior in solution was observed for catenane **14**·4 PF_6. The room-temperature δ values in CD_3CN of $\delta = 6.27$, 6.01, and 2.48 ppm for the H-2/6, H-3/7, and H-4/8 protons of the 1,5-dioxynaphthalene ring system in the spectrum of **14**·4 PF_6 are indicative[40] of the position it occupies inside the tetracationic cyclophane in this [2]catenane. The absence of significant shifts on warming or cooling the solution (Figure 8) indicates a lack of circumrotation.

The aromatic protons of the tetracationic cyclophane also have signals which exchange positions: slowly at room temperature as shown by the appearance of two broad signals for each of the α- and β-CH protons, which on warming the solution appeared as a average resonance signal as a consequence of faster exchange of these protons (Figure 8).

On the other hand, cooling a solution of the [2]catenane **14**·4 PF_6 in CD_3COCD_3 (Figure 9) to 198 K results in splitting of the α- and β-CH proton signals, that is, freezing of the dynamic processes (**II**, **II′**, **III**, and **IV**) takes place in this catenane. In particular, the CH_2N^+ methylene group is affected, the singlet of which at room temperature splits into two signals at 253 K. The $\Delta G^{\neq}$ value of 14.2 kcal mol^{-1} for the bipyridinium exchange process is in good agreement with energy barriers reported in the literature[40] for reorganization of 1,5-dioxynaphthalene ring systems, the local C_{2h} symmetry of which causes separation of α-CH bipyridinium protons in π–π stacked systems into two signals, with respect to the tetracationic cyclophane by leaving its cavity and thus allowing mutual reorientation (process **IV**) to occur (Table 4).

The prototropic tautomerism could also be evaluated by following the coalescence of the signals for the methylene hydrogen atoms linked to the 1,2,4-triazole unit, which evolves from a singlet at room temperature to two signals ($\delta = 4.00$ and 4.66 ppm) at 198 K (Figure 9). In comparison with **13**·4 PF_6 ,the $\Delta G^{\neq}$ value of 11.4 kcal mol^{-1} for the tautomerism process in [2]catenane **14**·4 PF_6 is even smaller.

Chemical switchability: Due to the presence of the proton-ionizable 1*H*-1,2,4-triazole group, switching of the translational isomers was attempted by using pH to reversibly in-

Table 4. Kinetic and thermodynamic parameters[a] obtained from the temperature-dependent ^{1}H NMR spectra of [2]catenanes **13**·4PF$_6$ and **14**·4PF$_6$ in solution.

Compound	Probe protons	$\Delta\nu$[b] [Hz]	k_c[c] [s^{-1}]	T_c[d] [K]	$\Delta G_c^{\ddagger}$[e] [kcal mol^{-1}]	Process[f]
13·4PF$_6$	OC_6H_4O	1725	3832	218	9.0	**I**
	α-CH bipy	73	161	210	10.0	**III**
	OCH_2Tr	149	331	270	12.6	**II′**
14·4PF$_6$	OCH_2Tr	333	738	253	11.4	**II′**
	CH_2N^+	50	111	290	14.2	**IV**

[a] Determined by variable-temperature ^{1}H NMR spectroscopy (500 MHz) in CD_3CN above room temperature and in CD_3COCD_3 below room temperature. [b] Limiting frequency separation. [c] Rate constant at the coalescence temperature. [d] Coalescence temperature. [e] Free-energy barrier at the coalescence temperature calculated from the Eyring equation. [f] Processes discussed in the text and for calculations of rate constants and free-energy barriers, see reference [38].

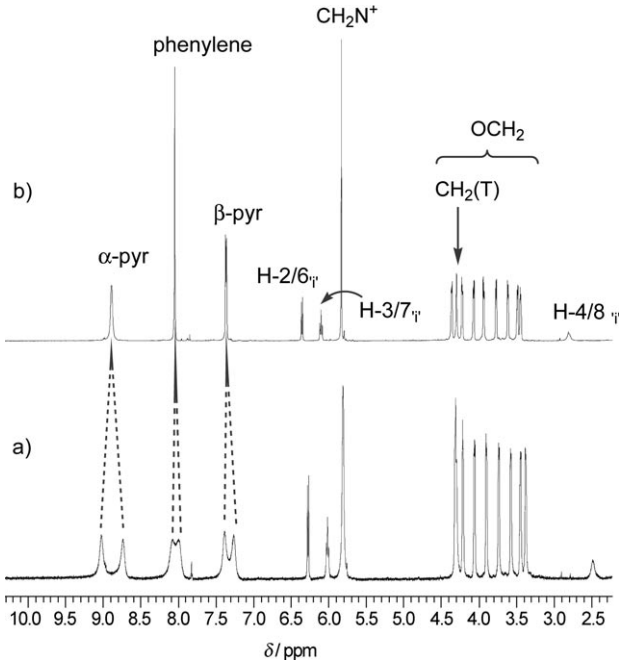


Figure 8. ^{1}H NMR spectrum of [2]catenane **14**·4PF$_6$ in CD_3CN at a) 298 K; b) 363 K.

terconvert the 1*H*-1,2,4-triazole/1,2,4-triazolate system.[41] Although a priori the instability of 4,4′-bipyridinium units to bases and/or nucleophiles is an issue, some examples are known that indicate its stability towards pyridine and triethylamine[41b] or Hünig's base.[41c,d] Furthermore, once the bipyridinium units are within the catenane structure, additional stability can be expected on account of the stabilizing π-donor/π-acceptor interactions.

When **13**·4PF$_6$ was treated with hindered bases such as *i*Pr$_2$NEt and DBU in CD_3CN solution (Scheme 3), ^{1}H NMR spectroscopy revealed the onset of switching as a consequence of deprotonation of the 1*H*-1,2,4-triazole ring to give the 1,2,4-triazolate anion.[42] However, rapid decomposition of the deprotonated compound was observed, presumably because of the labile nature of the bipyridinium units in the tetracationic cyclophane component of the [2]catenane. Specifically, the use of diisopropylethylamine partially deprotonated the 1,2,4-triazole ring in [2]catenane **13**·4PF$_6$ (Scheme 3), and decomposition products were immediately observed in the mixture; after 48 h no traces of starting materials could be detected. The use of stronger bases, such as DBU or an anion-exchange resin (AER) fully deprotonated the triazole unit, but only decomposition products were formed.

To confirm that the instability of the bis(methylene)bipyridinium unit was caused by the triazolate ring, two experiments were carried out (Scheme 4). First, [2]catenane **13**·4PF$_6$ was mixed in CD_3CN with (4-dimethylaminopyridinio)methyl-1,2,4-triazolate (**18**)[43] (Scheme 4); ^{1}H NMR spectra only showed the formation of decomposition prod-

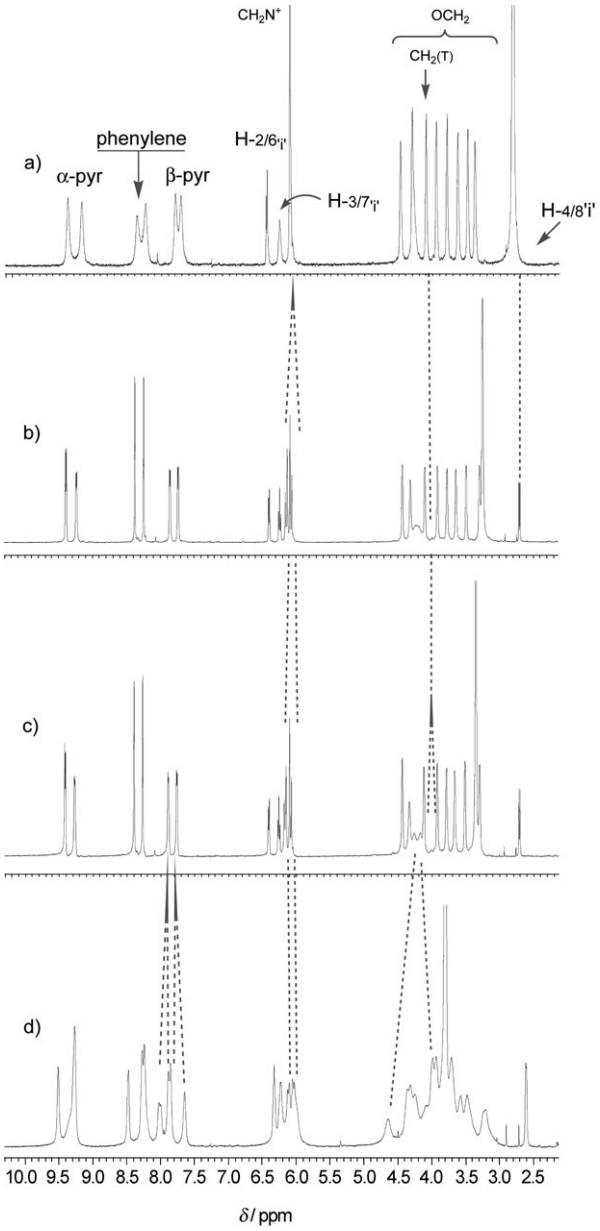
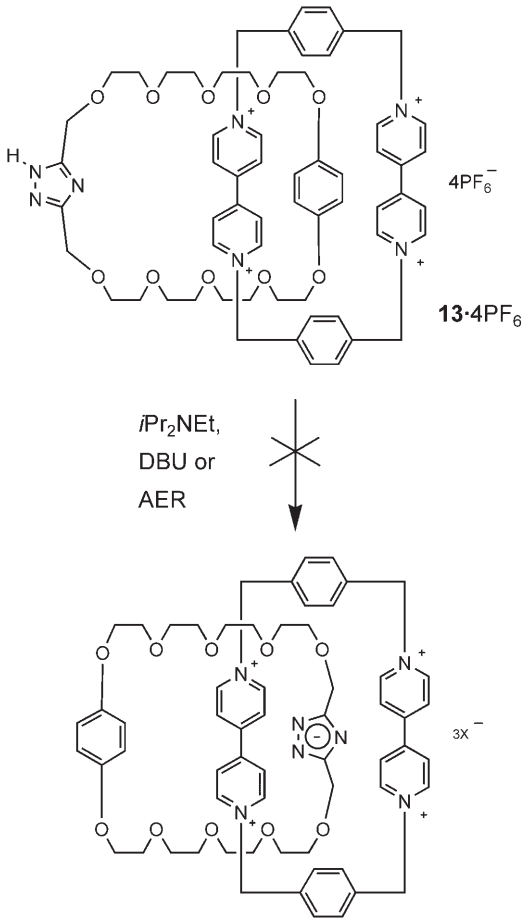


Figure 9. ^{1}H NMR spectrum of the [2]catenane **14**·4PF$_6$ in CD_3COCD_3 at a) 298 K; b) 253 K; c) 243 K; d) 198 K.

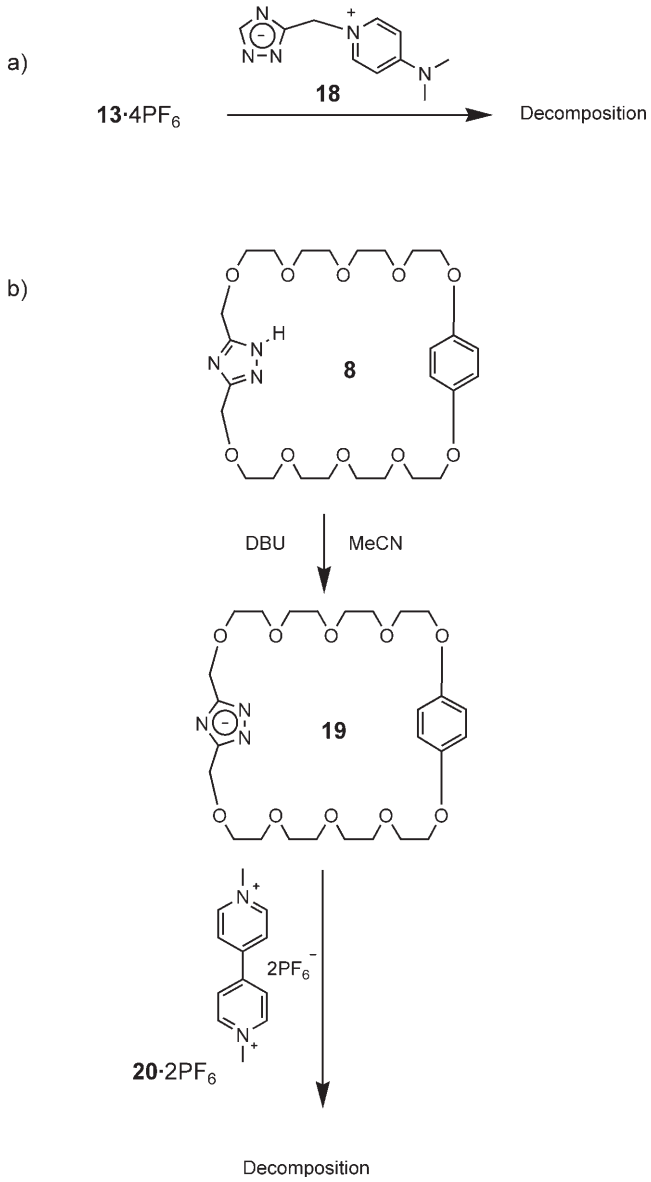


Scheme 3. Treatment of [2]catenane **13**·4 PF_6 with different bases.

ucts. Second, paraquat bis(hexafluorophosphate) (**20**·2 PF_6) was mixed with the triazolate-containing macrocyclic polyether **19** in CD_3CN solution (Scheme 4); the equimolecular mixture turned blue and then green and the signals corresponding to the bipyridinium aromatic protons experienced broadening until they almost disappeared, as shown by ^{1}H NMR spectroscopy, owing to the presence of paramagnetic bipyridinium-derived species in solution. These experiments manifest the extreme instability of the bipyridinium units of the tetracationic cyclophane within the catenane towards strong bases such as 1,2,4-triazolate ions.[44] Thus, the catenane architecture provides no additional stability to the bipyridinium units towards triazolate anions. These results presents us with a considerable challenge to be addressed before the prospect of pH-driven molecular machines and switches can be realized, although it does rule out its use in systems which contain different π-electron-deficient macrocycles.

Conclusion

The two [2]catenanes described here constitute rare examples of selective isomerization processes. First, they exist, both in solution and in the solid-state, as only one of two possible translational isomers. Second, on crystallization,



Scheme 4. Effect of triazolate ions on different 4,4′-bipyridinium derivatives.

they both undergo spontaneous resolution under conditions for which the enantiomers racemize rapidly in solution. In the light of the very large number of solid-state structures of [2]catenanes of this kind which do not resolve spontaneously on crystallization, these two examples each containing a 3,5-bis(methylene)-1*H*-1,2,4-triazole unit, appear to be exceptional at this time. The reasons may be associated with the disturbance in the crystal of the well-established continuous polar π-donor/π-acceptor stack, as well as the well-known tautomerism of the proton on the triazole ring, but in any case is a structure-based property: The incorporation of the triazole ring seems to favor symmetry breaking. These are the first cases of spontaneous resolution in nondegenerate catenanes.

The triazole ring will allow attachment of these catenanes to appropriately activated surfaces. To exploit the new struc-

ture-based properties and functional possibilities of these catenanes, further study is merited, and undoubtedly the potential for controllable chirality offers promising perspectives for the construction of molecular electronic and chiroptical devices.

Experimental Section

General methods: Melting point: CTP-MP 300 hot-plate apparatus with ASTM 2C thermometer. IR (KBr disks): Nicolet 205 FT spectrophotometer. ^{1}H NMR: Varian Gemini 200, Varian Gemini 350, and Varian VXR 500 spectrometers (200 MHz, and 350, and 500 MHz). ^{13}C NMR: Varian Gemini 200 and Varian Gemini 300 spectrometer (50.3 and 75.4 MHz). HMQC and HMBC: Varian VXR 500 spectrometer (500 MHz). COSY-2D and ROESY-2D: Bruker 500 spectrometer (500 MHz). NMR spectra were determined in [D]chloroform, [D_6]dimethylsulfoxide, [D_3]acetonitrile, [D_4]methanol, or [D_6]acetone, and chemical shifts are expressed in parts per million (δ) relative to the central peak of the solvent. ESMS and FABMS: VG-Quattro mass spectrometer. TLC was performed on Merck precoated 60 F_{254} silica gel plates in the solvent system methanol/2 M ammonium chloride/nitromethane (6/3/1) as developing solvent; and the spots were located with UV light and developed with a 10% aqueous solution of potassium iodide or 3% aqueous solution of hexachloroplatinic acid. Chromatography: SDS silica oxide 60 ACC (30–75 μm) and Merck aluminum oxide 90 standardized. UV/Vis: CARY-Varian spectrophotometer. When a rotary evaporator was used, the bath temperature was 25 °C. In general, the compounds were dried overnight at 25 °C in a vacuum oven. Microanalyses were performed on a Carbo Erba Fisons EA1108 analyzer in the Serveis Científico-Tècnics (UB). HR-MS: Autospec/VG analyzer, recorded in the Departament de Química Orgànica Biològica (C.S.I.C.) de Barcelona. Experiments at high pressure were performed in an Andreas Hofer press at 14 kbar; reactions were carried out in a thermally sealed Teflon tube located in the press cylinder with *n*-hexane as the external solvent. Solvents were distilled under nitrogen or argon over a variety of drying agents.[45] DMF and DME were distilled over calcium hydride and stored with molecular sieves (4 Å). CH_3CN was of HPLC grade (SDS) and dried with molecular sieves (4 Å). When an anionic exchange resin was used, the previously established protocol was employed.[12]

Materials: Commercial compounds: Ammonium hexafluorophosphate, 1,4-bis(bromomethyl)benzene (**11**), 1,8-diazabiciclo[5.4.0]undec-7-ene (DBU), 1,4-dihydroxybenzene, 1,5-dihydroxynaphthalene, diisopropylethylamine, and NaH 95% dry were purchased from Aldrich. Compounds prepared according to literature procedures: 3,5-bis(chloromethyl)-1*H*-1,2,4-triazole hydrochloride,[12] 3,5-bis(chloromethyl)-1-(tetrahydro-2-pyranyl)-1*H*-1,2,4-triazole (**1**),[20] **10**·2PF_6,[21a] cyclobis(paraquat-*p*-phenylene) (**15**·4PF_6)[21a] 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (**17**),[21a] (4-dimethylaminopyridinio)methyl-1,2,4-triazolate (**18**),[43] 1,1′-dimethyl-4,4′-bipyridinium bis(hexafluorophosphate) (Paraquat) (**20**·2PF_6).[21a]

CD spectroscopy: CD spectra were recorded on a JASCO 720 spectrophotometer. The samples were prepared as KBr disks by mixing about 50 mg of dried KBr (Aldrich, 98%, dried under vacuum-pump pressure at 100 °C for 5 h) and 0.3–0.6 mg of sample. The mixture was milled and compressed at 10 tonnes for 10 min. The thickness of the disks was measured to be between 15 and 25 μm. The initially transparent disks became opaque with time, and this affected the resolution of the CD spectra; therefore, all disks were prepared immediately before analysis. The correct position of the sample was confirmed by checking that the light beam was passing through the disk. For each sample the disk was rotated manually 3–5 times to avoid linear dichroic effects. Prior to the analysis of samples a spectrum of a pure KBr disk was registered and subtracted from the spectra recorded by using the mathematical treatment in the Standard Analysis JASCO CD program. The molar ellipticity values were calculated as $7.8\cdot10^5$ deg cm^2 g mol^{-1} and $-8.6\cdot10^5$ deg cm^2 g mol^{-1} for the positive and negative spectra, respectively.

3,5-Bis(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)methyl-1-(tetrahydro-2-pyranyl)-1*H*-1,2,4-triazole (2): 3,5-Bis(chloromethyl)-1-tetrahydropyranyl-1*H*-1,2,4-triazole (**1**)[20] (2.0 g, 8 mmol) was added to a solution of NaH (0.81 g, 32 mmol) in tetraethylene glycol (41 mL) under N_2 and was stirred for 48 h at 60 °C. After this mixture had cooled to room temperature, H_2O (100 mL) was added, and the solution was extracted with Et_2O (3×50 mL) and CH_2Cl_2 (4×50 mL). The CH_2Cl_2 layers were combined, washed with H_2O (2×50 mL), and dried ($MgSO_4$), and the solvent removed. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH increasing polarity) to yield **2** as a colorless oil (2.8 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.59 (dd, J = 9.6, 2.6 Hz, 1H, H^2(THP)), 4.74 (dd, J = 13.2 Hz, 2H, CH_2-5), 4.58 (dd, J = 13.0 Hz, 2H, CH_2-3), 4.00 (m, 1H, H^6(THP)), 3.62 (m, 32H, CH_2O), 3.62 (m, 1H, H^6 (THP)), 2.70 (br s, 2H, OH), 2.29 (m, 1H, H^5(THP)), 2.04 (m, 1H, H^4(THP)), 1.91 (m, 1H, H^5(THP)), 1.67 (m, 1H, H^4(THP)), 1.67 (m, 1H, H^3(THP)), 1.56 ppm (m, 1H, H^3(THP)); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.7, 152.8, 84.0, 72.4, 70.45, 70.4, 70.3, 70.2, 70.1, 70.0, 69.8, 67.7, 66.0, 63.5, 61.5, 61.4, 29.6, 24.6, 22.2 ppm; ESI-MS (60 eV): *m/z* (%): 1132 (1) [2M^++H], 589 (8) [M+Na], 566 (100) [M^++H], 482 (6) [M^+−THP+H]; elemental analysis calcd (%) for $C_{25}H_{47}N_3O_{11}$: C 53.1, H 8.4, N 7.4; found: C 53.4, H 8.5, N 7.6.

1-(Tetrahydro-2-pyranyl)-3,5-bis(2-{2-[2-(2-*p*-toluensulfonylethoxy)ethoxy]ethoxy)methyl-1*H*-1,2,4-triazole (3): A solution of **2** (1.5 g, 2.65 mmol) in H_2O/THF (1/1, 4 mL) was added to a suspension of NaOH (0.30 g, 7.42 mmol) in H_2O (2 mL) cooled to 0–5 °C. After this a solution of tosyl chloride (1.06 g, 5.57 mmol) in THF (2 mL) was added over 0.5 h, keeping the temperature between 0 and 5 °C. After stirring for 3 h, the reaction mixture was poured into an ice/water mixture (10 mL) and extracted with toluene (20 mL). The organic layer was washed with a 0.5 M aqueous solution of NaOH (2×15 mL) and dried with $MgSO_4$. Removal of the solvent afforded **3** as a colorless oil (1.64 g, 71%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.64 (dd, J = 8.0 Hz, 4H, H^{2,6}(OTs)), 7.21 (dd, J = 8.0 Hz, 4H, H^{3,5}(OTs)), 5.48 (dd, J = 9.6, 2.6 Hz, 1H, H^2-(THP)), 4.62 (dd, J = 13.2 Hz, 2H, CH_2-5), 4.46 (dd, J = 13.1 Hz, 2H, CH_2-3), 4.00 (m, 4H, CH_2O-δ,δ'), 3.89 (m, 1H, H^6 (THP)), 3.49 (m, 32H, CH_2O), 2.29 (s, 6H, CH_3), 2.14 (m, 1H, H^5(THP)), 1.94 (m, 1H, H^4-(THP)), 1.80 (m, 1H, H^5(THP)), 1.57 (m, 1H, H^4(THP)), 1.57 (m, 1H, H^3(THP)), 1.45 ppm (m, 1H, H^3(THP)); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): δ = 158.9, 152.4, 144.3, 132.3, 129.3, 127.4, 83.7, 70.1, 70.0, 69.95, 69.9, 69.8, 69.6, 69.5, 68.9, 68.8, 68.1, 67.4, 65.7, 63.2, 29.3, 24.3, 21.8, 21.2 ppm; ESI-MS (60 eV): *m/z* (%): 898 (5) [M^++Na], 875 (34) [M^++H], 790 (50) [M^+−THP+H], 720 (100) [M^+−OTs+H]; elemental analysis calcd (%) for $C_{39}H_{59}N_3O_{15}S_2$: C 53.6, H 6.8, N 4.8; found: C 53.3, H 6.8, N 5.1.

17(37,38)-Bis(tetrahydro-2-pyranyl)-2,5,8,11,14,22,25,28,31,34-decaoxa-[15.15](3,5)triazolophane (4): A solution of **2** (1 g, 1.77 mmol) in anhydrous DMF (30 mL) was added under argon over 30 min to a degassed suspension of NaH (116 mg, 4.60 mmol) and NaI (584 mg, 3.90 mmol) in anhydrous DMF (80 mL). After 15 min a solution of **1** (443 mg, 1.77 mmol) in anhydrous DMF (40 mL) was added under argon over 15 min. The reaction mixture was then heated at 80 °C for 6 d. After cooling to room temperature, the suspension was filtered, and the solvent removed in vacuo. The residue was partitioned between CH_2Cl_2 (70 mL) and H_2O (150 mL). The aqueous phase was extracted again with CH_2Cl_2 (3×70 mL), and the organic extracts were concentrated in vacuo. Column chromatography (SiO_2, CH_2Cl_2/MeOH increasing polarity) afforded **4** as a pale yellow oil (0.96 g, 7%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.58 (dd, J = 9.4, 2.2 Hz, 2H, H^2(THP)), 4.72 (dd, J = 13.2 Hz, 4H, CH_2-5), 4.57 (dd, J = 13.1 Hz, 4H, CH_2-3), 4.02 (m, 4H, H^6-(THP)), 3.62 (m, 32H, CH_2O), 2.29 (m, 2H, H^5(THP)), 2.04 (m, 2H, H^4-(THP)), 1.91 (m, 2H, H^5(THP)), 1.67 (m, 2H, H^4(THP)), 1.67 (m, 2H, H^3(THP)), 1.56 ppm (m, 2H, H^3(THP)); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): δ = 159.6, 152.9, 84.2, 70.6, 70.5, 70.4, 70.3, 70.1, 69.9, 69.8, 67.8, 66.1, 63.7, 29.7, 24.7, 22.3 ppm; ESI-MS (60 eV): *m/z* (%):765 (12) [M^++Na], 743 (100) [M^++H], 288 (72) [M^{2+}−2THP+2H].

36-(Tetrahydro-2-pyranyl)-2,5,8,11,14,21,24,27,30,33-decaoxa[14]paracyclo[14](3,5)triazolophane (5): A solution of 1,4-dihydroxybenzene (0.28 g, 2.54 mmol) in anhydrous DMF (100 mL) was added under argon

over 15 min to a degassed suspension of $CsCO_3$ (7.5 g, 22.9 mmol) in anhydrous DMF (160 mL). After 15 min a solution of CsOTs (1.4 g, 4.58 mmol), tetrabutylammonium iodide (TBAI, 0.17 g, 0.46 mmol), and **3** (1.85 g, 2.12 mmol) in anhydrous DMF (310 mL) was added over 15 min. After this the reaction mixture was heated at 80 °C for six days. After cooling to room temperature, the suspension was filtered, washed with anhydrous DMF (50 mL), and the solvent was removed in vacuo. The brown residue was partitioned between CH_2Cl_2 (100 mL) and H_2O (200 mL). The aqueous phase was extracted again with CH_2Cl_2 (4× 70 mL) and washed with a saturated solution of NaCl (150 mL). The organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (SiO_2, CH_2Cl_2/MeOH increasing polarity) afforded **5** as a colorless oil (0.35 g, 26 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.75$ (s, 4H, C_6H_4), 5.52 (dd, $J = 9.4$, 2.4 Hz, 1H, H^2(THP)), 4.64 (dd, $J = 13.2$ Hz, 2H, CH_2-5), 4.50 (dd, $J = 12.3$ Hz, 2H, CH_2-3), 4.02 (m, 2H, H^6(THP)), 4.00 (m, 4H, $CH_2O(\alpha)$), 3.71 (m, 4H, $CH_2O(\beta)$), 3.63 (m, 24H, CH_2O), 2.29 (m, 1H, H^5(THP)), 2.04 (m, 1H, H^4(THP)), 1.91 (m, 1H, H^5(THP)), 1.67 (m, 1H, H^4(THP)), 1.67 (m, 1H, H^3(THP)), 1.56 ppm (m, 1H, H^3(THP)); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 159.6$, 152.8, 152.7, 115.4, 83.9, 70.6, 70.5, 70.4, 70.35, 70.3, 70.2, 70.0, 69.9, 69.7, 69.5, 67.9, 67.6, 66.0, 63.5, 29.5, 24.5, 22.1 ppm; ESI-MS (60 eV): *m/z* (%): 1279 (4) [$2M^+$+H], 662 (5) [M^++Na], 640 (100) [M^++H], 556 (4) [M^+−THP+H]; HRMS calcd for $C_{31}H_{49}N_3O_{11}$: 639.3393; found: 639.3367.

40-(Tetrahydro-2-pyranyl)-2,5,8,11,14,25,28,31,34,37-decaoxa[14]-(1,5)naphthalene[14](3,5)triazolophane (6): 1,5-Dihydroxynaphthalene (365 mg, 2.28 mmol) was added to a degassed suspension of Cs_2CO_3 (14.8 g, 45.6 mmol) and CsOTs (1.38 g, 4.56 mmol) in anhydrous DMF (400 mL) at 80 °C. After 45 min a solution of **3** (2 g, 2.28 mmol) in anhydrous DMF (230 mL) was added, and the reaction mixture was then heated at 100 °C for six days. After cooling to room temperature, the suspension was filtered and washed with DMF (50 mL), and the solvent was removed in vacuo. The brown residue was partitioned between CH_2Cl_2 (100 mL), H_2O (200 mL), and asaturated solution of NaCl (50 mL). The aqueous phase was extracted again with CH_2Cl_2 (2x100 mL), and the organic extracts were concentrated in vacuo. Column chromatography (SiO_2, CH_2Cl_2/MeOH increasing polarity) afforded **6** as a yellow oil (0.13 g, 8 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.82$ (dd, $J =$ 8.2, 3.2 Hz, 2H, $H^{2,6}$(Naph)), 7.31 (m, 2H, $H^{3,7}$(Naph), 6.81 (d, 2H, $H^{4,8}$-(Naph), 5.48 (dd, $J = 9.6$, 2.6 Hz, 1H, H^2(THP)), 4.58 (dd, $J = 13.2$ Hz, 2H, CH_2-5), 4.50 (dd, $J = 12.3$ Hz, 2H, CH_2-3), 4.27 (m, 4H, $CH_2O\alpha$), 3.95 (m, 4H, $CH_2O\beta$), 3.95 (m, 1H, H^6(THP)), 3.60 (m, 24H, CH_2O), 2.29 (m, 1H, H^5(THP)), 2.04 (m, 1H, H^4(THP)), 1.91 (m, 1H, H^5(THP)), 1.67 (m, 1H, H^4(THP)), 1.67 (m, 1H, H^3(THP)), 1.56 ppm (m, 1H, H^3-(THP)); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 159.4$, 154.2, 154.1, 152.7, 126.6, 124.9, 114.5, 114.3, 105.7, 84.0, 71.0, 70.9, 70.7, 70.6, 70.5, 70.4, 70.2, 70.0, 69.8, 69.7, 67.9, 67.7, 66.0, 63.5, 61.6, 29.6, 24.6, 22.2 ppm; ESI-MS (60 eV): *m/z* (%): 690 (100) [M^++H], 606 (14) [M^+ −THP+H]; HRMS calcd for $C_{35}H_{51}N_3O_{11}$: 689.3426; found: 689.3523.

2,5,8,11,14,22,25,28,31,34-Decaoxa[15.15](3,5)triazolophane (7): **4** (40 mg, 0.054 mmol) was dissolved in MeOH/1.5 N HCl (2 mL). After stirring for 4 h at room temperature the solution was evaporated in vacuo. The oil obtained was dissolved in H_2O (5 mL) and neutralized with Na_2CO_3 until pH 7–8. The aqueous solution was extracted with CH_2Cl_2 (6×5 mL), dried ($MgSO_4$), and concentrated in vacuo. **4** was obtained as a colorless oil (25 mg, 80 %). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.71$ (s, 8H, CH_2), 3.69 ppm (m, 32H, CH_2O); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 156.6$, 69.4, 69.3, 69.2, 69.0, 64.6 ppm; ESI-MS (60 eV): *m/z* (%): 597 (86) [M^++Na], 575 (100) [M^++H]; HRMS calcd for $C_{24}H_{42}N_6O_{10}$: 574.6285; found: 574.6297.

2,5,8,11,14,21,24,27,30,33-Decaoxa[14]paracyclo[14](3,5)triazolophane (8): A solution of macrocycle **5** (0.16 g, 0.25 mmol) in MeOH/1.5 N HCl (8 mL) was stirred for 4 h at room temperature, and the solution was evaporated in vacuo. The oil obtained was dissolved in H_2O (20 mL) and neutralized with Na_2CO_3 until pH 7–8. The aqueous solution was extracted with CH_2Cl_2 (4×10 mL), dried ($MgSO_4$) and concentrated in vacuo. **8** was obtained as a colorless oil (0.125 g, 90 %); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 6.77$ (s, 4H, C_6H_4), 4.60 (s, 4H, CH_2), 4.03–3.70 ppm (m, 32H, OCH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 157.8$, 152.7, 115.5, 70.5, 70.4, 70.3, 70.2, 70.0, 69.6, 67.8, 65.7 ppm; ESI-MS (60 eV): *m/z* (%): 556 (100) [M^++H]; HRMS calcd for $C_{26}H_{41}N_3O_{10}$: 555.2799; found: 555.2791;

2,5,8,11,14,22,25,28,31,34-Decaoxa[15.15](3,5)triazolophane (9): Macrocycle **6** (0.095 g, 0.14 mmol) was deprotected by dissolution in MeOH/1.5 N HCl (5 mL). After stirring for 4 h at room temperature the solution was evaporated in vacuo. The oil obtained was dissolved in H_2O (20 mL) and neutralized with Na_2CO_3 until pH 7–8. The aqueous solution was extracted with CH_2Cl_2 (3×15 mL), dried ($MgSO_4$), and concentrated in vacuo. **9** was obtained as a yellow oil (80 mg, 96 %); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.80$ (d, $J = 7.8$ Hz, 2H, $H^{2,6}$), 7.30 (dd, $J = 7.9$ Hz, 2H, $H^{3,7}$), 6.82 (d, $J = 8.4$ Hz, 2H, $H^{4,8}$), 4.50 (s, 4H, CH_2), 4.28–3.70 ppm (m, 32H,OCH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 157.2$, 126.5, 125.0, 105.7, 70.8, 70.5, 69.6, 67.7, 65.4 ppm; ESI-MS (60 eV): *m/z* (%): 606 (100) [M^++H].

{[2]-[2,5,8,11,14,21,24,27,30,33-Decaoxa[14]paracyclo[14](3,5)triazolophane]-[2,11,22,31-tetrazonia[1.0.1.1.0.1]paracyclophane]catenane} tetrakis(hexafluorophosphate) (13·4 PF_6) and {[2]-[2,5,8,11,14,21,24,27,30,33,36-decaoxa[14](1,5)naphthalene[14](3,5) triazolophane][2,11,22,31-tetraazonia[1.0.1.1.0.1]paracyclophane]catenane} tetrakis(hexafluorophosphate) 14·2 PF_6: **10**·2 PF_6 (1 mmol), 1,4-bis(bromomethyl)benzene (**11**) (1.1 mmol), and **8** or **9** (2.5 mmol) were dissolved in dry DMF (2 mL) in a high-pressure vessel which was pressurized to 10 kbar for three days at room temperature. The colored suspension obtained was poured into Et_2O (30 mL) and the precipitate was filtered off, washed with Et_2O (2×5 mL), and dried. The residue was purified by column chromatography (SiO_2, MeOH/NH_4Cl 2 M/CH_3NO_2 5.5/3/1.5). The fractions containing the product were combined and concentrated, and the residue was dissolved in H_2O (5 mL) before a saturated aqueous NH_4PF_6 solution was added until no further precipitation occurred. The suspension was filtered off, and the solid recrystallized from MeCN/*i*Pr_2O to give **13**·4 PF_6 or **14**·4 PF_6 as a red or violet solid, respectively. **13**·4 PF_6 (34 %): m.p. 244–245 °C; ^{1}H NMR (500 MHz, CD_3CN, 25 °C): $\delta = 8.94$ (d, $J = 7.0$ Hz, 8H, α-CH), 7.79 (d, $J = 7.0$ Hz, 8H, β-CH), 7.80 (s, 8H, C_6H_4), 5.73 (s, 8H, CH_2N^+), 4.20 (s, 4H, CH_2), 3.56 (s, 4H, $H^{1,4}$(DB)), 3.93–3.34 ppm (m, 32H, OCH_2); FABMS (10 eV): *m/z* (%): 1679 (1) [M^+ +Na], 1511 (9) [M^+−PF_6], 1366 (22) [M^+−2 PF_6], 1221 (8) [M^+−3 PF_6], 1076 (3) [M−4 PF_6]$^+$, 956 (5) [M^+−PF_6−CE], 811 (28) [M^+−2 PF_6−CE], 683 (24) [M^{2+}+2 PF_6], 666 (17) [M^+−3 PF_6−CE], 562 (100) [CE$^+$+Li]; elemental analysis calcd (%) for $C_{62}H_{73}N_7O_{10}F_{24}P_4{\cdot}1H_2O$: C 44.5, H 4.5, N 5.8; found: C 44.7, H 4.9, N 6.2. **14**·4 PF_6 (65 %): m.p. 252–254 °C; ^{1}H NMR (500 MHz, CD_3CN, −40 °C): $\delta = 8.96$ and 8.75 (2×d, $J = 6.0$ Hz, 8H, α-CH), 8.06 and 7.91 (s, 8H, C_6H_4), 7.37 and 7.18 (2×d, $J = 5.0$ Hz, 8H, β -CH), 6.17 (d, $J = 8.0$ Hz, 2H), 5.95 (dd, $J = 8.0$ Hz, 2H), 5.75–5.83 (m, 8H, CH_2N^+), 4.22 (s, 4H, CH_2), 4.28–3.31 (m, 32H, OCH_2), 2.31 ppm (d, $J = 8.0$ Hz, 2H); FABMS (10 eV): *m/z* (%): 1271 (77) [M^+ −3 PF_6], 1126 (13) [M−4 PF_6]$^+$, 956 (18) [M^+−PF_6−CE], 810 (90) [M^+ −2 PF_6−CE], 708 (36) [M^{2+}+2 PF_6], 666 (100) [M^+−3PF_6−EC]; elemental analysis calcd (%) for $C_{66}H_{75}N_7O_{10}F_{24}P_4$: C 46.5, H 4.4, N 5.7; found: C 46.4, H 4.6, N 5.4.

In a similar procedure using macrocyclic polyether **7**, no formation of catenane **12**·4 PF_6 was observed, and only the tetracationic cyclophane **15**·4 PF_6[21a] was isolated (17 %).

3,5-Bis(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)methyl-1*H*-1,2,4-triazole (16): A solution of **2** (520 mg,0.92 mmol) in 1.5 N MeOH/HCl (20 mL) was stirred for 4 h at room temperature and then the solution was evaporated in vacuo. The oil obtained was dissolved in H_2O (20 mL) and neutralized with Na_2CO_3 until pH 7–8. The aqueous solution was extracted with CH_2Cl_2 (3×10 mL), dried ($MgSO_4$), and concentrated in vacuo. **16** was obtained as a colorless oil (77 %).^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 4.52$ (s, 4H, CH_2), 3.50 (m, 32H, CH_2O); ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 157.7$, 72.2, 72.0, 69.9, 69.8, 69.5, 69.4, 69.3, 65.5, 60.7, 60.6 ppm; ESIMS (60 eV): *m/z* (%): 504 (10) [M^++Na], 482 (100) [M^++H], 963 (1) [$2M^+$+H]; HRMS calcd for $C_{20}H_{39}N_3O_{10}$: 481.2641; found: 481.2635.

Sodium 2,5,8,11,14,21,24,27,30,33-decaoxa[14]paracyclo[14](3,5)triazolate (19): Macrocyclic polyether **8** (20 mg, 0.036 mmol) was added to a sus-

pension of sodium hydroxide (4 mg, 0.1 mmol) in dry acetonitrile (2 mL), and the mixture was vigorously stirred at room temperature for 4 h. The suspension was then filtered and the solution concentrated in vacuo. **19** was obtained as a colorless oil (83%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): $\delta = 6.82$ (s, 4H, C_6H_4), 4.51 (s, 4H, CH_2), 3.55–4.04 ppm (m, 32H, CH_2O).

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[25] Data were collected on a Siemens P4/PC diffractometer by using ω scans. The structures were solved by direct methods and refined based on F^2 using the SHELXTL program system a) SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, **1994**; b) SHELXTL PC version 5.1, Bruker AXS, Madison, WI, 1997. The absolute structures of **13**·4 PF_6 and **14**·3.2 PF_6·0.8 ClO_4 were determined by a combination of *R*-factor tests (for **13**·4 PF_6, $R1^+$ = 0.0502, $R1^-$ = 0.0521; for **14**·3.2 PF_6·0.8 ClO_4, $R1^+$ = 0.0591, $R1^-$ = 0.0605) and by use of Flack parameters (for **13**·4 PF_6, x^+ = 0.06(6); for **14**·3.2 PF_6·0.8 ClO_4, x^+ = +0.12(6)]. CCDC-190346 and CCDC-190347 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

[26] Analysis of the X-ray data for **14**·4 PF_6 revealed that the "fourth" PF_6^- ion is overlaid by a partial-occupancy ClO_4^- ion in a ratio of about 20:80. We believe that the presence of this trace of ClO_4^- anion is a consequence of repeated recrystallization in glassware that had previously been contaminated with perchlorate.

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[32] The extent of the spontaneous resolution process might depend not only on the catenane architecture but also on the conditions of the crystallization; poor quality crystals obtained from an evaporating acetone solution led to only poor refinement factors from X-ray diffraction data. The collected data showed two independent molecules in a centrosymmetric monoclinic space group, that is, no spontaneous resolution had taken place. In this case, the crystals had grown under different conditions implying faster nucleation. This constitutes the first example of polymorphism in this family of compounds.

[33] An equal number of co-conformations are possible for the series of translational isomers containing 1*H*-1,2,4-triazole units inside the cavity of the tetracationic cyclophane.

[34] CD spectra of dissolved single crystals in solution in a range of temperatures from 25 to −40 °C seem to indicate the preferential formation of one conformational enantiomer at low temperature, but the very low intensities of the Cotton effects indicate rapid isomerization upon dissolution.

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