# Towards the stereoselective synthesis of inherently chiral pseudorotaxanes†

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Herein is reported an investigation towards the stereoselective synthesis of inherently chiral pseudorotaxanes. Chiral ammonium threads were readily prepared in five steps from racemic or enantiopure (*M* or *P*) salts of di-*n*-propyl-1,13-dimethoxyquinacridinium cation. Their self-assembly with DB24C8 or disymmetrically oriented DB24C8F6 rings formed pseudorotaxanes as shown by $^{1}$H and $^{19}$F NMR spectroscopy as well as MS measurements. A determination of the association constants ($K_a$) was afforded. The crucial role played by the ammonium counter-ion in the threading process was further demonstrated as salts of TRISPHAT (tris(tetrachlorobenzenediolato)phosphate(V)) anion were quite more effective than their $PF_6^-$ analogues (× 7.3). A general lack of diastereoselectivity (de ≤ 8%) was unfortunately observed.

## Introduction

Molecular knots, catenanes, pretzelanes and (pseudo)rotaxanes are fascinating objects that can display chirality without having any classical stereogenic elements of centered, axial, planar or helical chirality in their backbone.[1] Whereas a trefoil knot is inherently chiral,[2] other topological molecules are not necessarily so. For instance achiral catenanes are obtained if one of the two interlocked rings is symmetrical.[3] If, on the contrary, a directionality is built in both rings, the catenane becomes intrinsically chiral.[4] A schematic representation of the enantiomers is shown on Fig. 1a. Such molecules were obtained in non racemic form by the Okamoto, Sauvage and Vögtle groups using an efficient preparative chiral stationary phase (CSP) HPLC methods.[5]

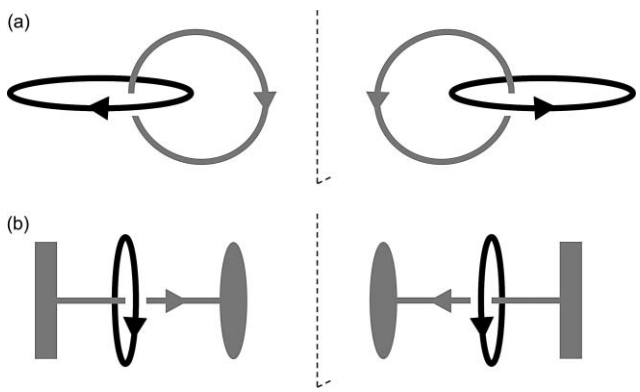


**Fig. 1** Enantiomers of inherently chiral [2]-catenanes (a) and (pseudo)rotaxanes (b). Schematic representation.

Rotaxanes and pseudorotaxanes are other members of this class of fascinating molecules.[1] They are assemblies composed minimally of a thread-like molecule surrounded by a macrocycle. These supermolecules have attracted significant attention, not only for their structural features, but also because of the variety of properties and functions that can be engineered within them.[6] As for the catenanes, (pseudo)rotaxanes are achiral if either thread or macrocycle (ring) are non-oriented. On the contrary, if a disymmetry is present in both structural elements, the resulting rotaxane become inherently chiral. A schematic representation of the enantiomers is shown in Fig. 1b. Relatively few studies have been devoted to the synthesis and resolution of such inherently chiral rotaxanes. The isolation of the topologically chiral molecules in non-racemic form was in some instances possible.[7] It involved the use of effective preparative CSP-HPLC procedures. These enantioseparations were real "tours de force" if one considers the high conformational flexibility of these mechanically bounded molecules.

There are two main possibilities to obtain such a chiral molecule in an enantioenriched or enantiopure form. One is the resolution of the racemic material. The other is a stereoselective synthesis. Whereas the first possibility was successful in the case of inherently chiral rotaxanes, there have been, to our knowledge and much of our surprise, very few reports of stereoselective synthesis of this class of compounds.[8,9] This relative lack of information thus led us to consider the stereoselective preparation of an intrinsically chiral rotaxane-like molecule.

However, rather than embarking on a project in which the source of stereocontrol would be an external chiral reagent, it was decided to validate the approach through the use of an intramolecular chiral auxiliary; the auxiliary chosen being a chiral stopper at one end on the thread (Fig. 2). In fact, the presence of a chiral stopper within the framework of an inherently chiral rotaxane generates two diastereomeric complexes. Selectivity will happen if discriminating interactions between the bulky stereogenic element and the oriented ring occur; the chiral stopper providing a possible source of spectroscopic differentiation of the stereoisomers and thus the opportunity of a direct measurement of the selectivity. A chemical system which would present (i) a sterically demanding chiral stopper at one end of the thread, (ii) an easily oriented macrocycle as a ring and (iii) established complementary sites for effective host–guest interactions was thus looked for.

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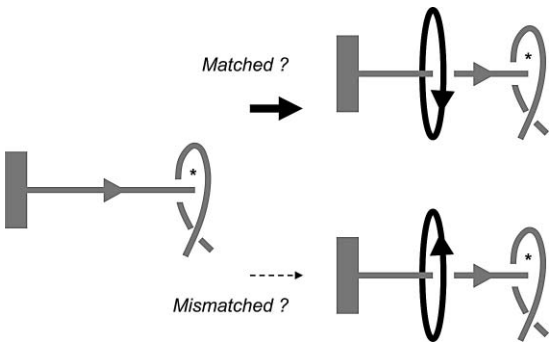
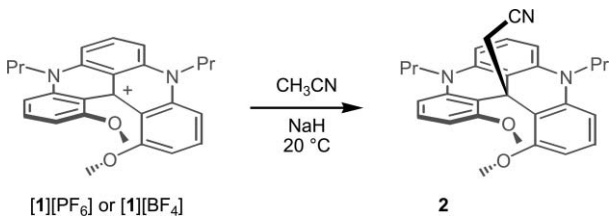



**Fig. 2** Chiral auxiliary approach to the stereoselective synthesis of inherently chiral (pseudo)rotaxanes; the auxiliary being represented by a helical stopper of *M* configuration.

Several rotaxanes have been reported with chiral stoppers at one or both end(s) of the thread; the moieties being sugars, metal complexes, terpenes, and even molecular knots.[10] These moieties, introduced to avoid the slippage of the ring, were not used as chiral auxiliaries. Although there is no reason why they could not be used for the targeted project, some recent results in our group led us to consider another type of chiral bulky group.

Previously, Laursen *et al.* reported the synthesis of simple-to-make 1,13-dimethoxyquinacridinium derivatives of type **1** which contains four ortho-condensed aromatic rings.[11] Owing to the steric repulsion between the two methoxy substituents, these compounds adopt a twisted helical conformation with *P* or *M* configuration. As such, compounds of type **1** can be regarded as [4]heterohelicenium moieties. They are furthermore readily isolated in enantiopure form.[12,13] Despite their remarkable chemical stability, these carbocations can react with strongly nucleophilic carbanions. In the case of salt [**1**][$PF_6$], a reactivity with acetonitrile in presence of NaH has been documented (Scheme 1) and the product of $CH_2CN$ addition isolated (**2**).[12]




**Scheme 1** Reaction of salts [**1**][$PF_6$] or [**1**][$BF_4$] with $CH_3CN$/NaH to yield adduct **2**. The compounds are arbitrarily shown as the P enantiomer.

The helical part of compound **2** seemed ideal to play the role of a sterically demanding chiral stopper on a thread and the nitrile moiety, the perfect functional group to generate an ammonium ion; ammonium groups being well known for their host–guest chemistry with crown-ethers.[14] In fact, it has been shown previously that large enough crown ether rings can thread through suitably chosen dialkylammonium ions ($R_2NH_2^+$) giving pseudorotaxane/rotaxane species in solution by virtue of strong [$N^+$–H···O] and [C–H···O] hydrogen-bonding interactions.[15] This approach, which has been particularly studied with $R_2NH_2^+$ salts and dibenzo-24-crown-8 (**3**, DB24C8) derivatives appeared well adapted for the above mentioned project.

Herein we report the simple transformation of racemic or enantiopure nitrile **2** into thread-like ammonium salts of type [**4**·H][X] (Fig. 3) that bears a phenyl group at one end, the chiral helical stopper at the other, and a secondary ammonium in the core. A two step process for the desymmetrization of DB24C8 **3** into an aryl substituted macrocycle DB24C8F6 **5** is presented as well as the ability of this oriented ring to form supramolecular complexes in presence of [**4**·H][$PF_6$] threads; these results being compared to those of DB24C8 **3**.

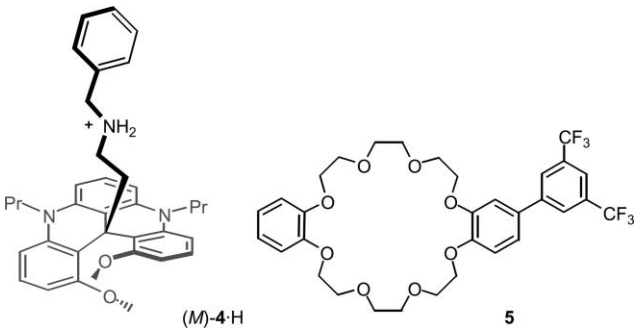


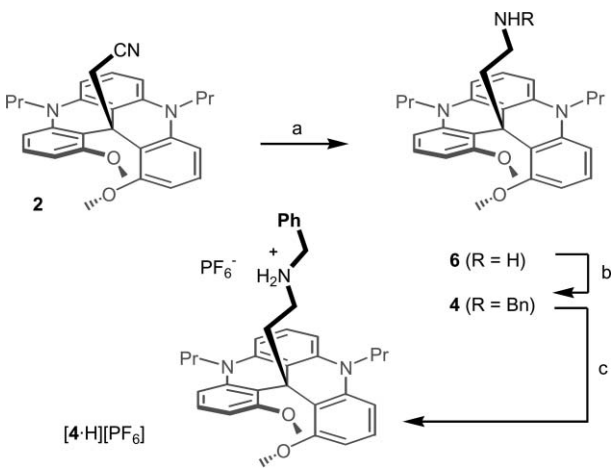

**Fig. 3** Chiral ammonium thread **4**·H and oriented ring **5**.

## Results and discussion

### Synthesis of ammonium thread 4·H (racemic, *P* and *M*)

As just mentioned, one sub-goal of this project was the making of an ammonium thread-like molecule derived from the nitrile-functionalized heterohelicene **2**. The making of the desired compound [**4**·H][$PF_6$] was effected following three classical synthetic steps: (i) nitrile reduction to a primary amine, (ii) reductive amination in the presence of benzaldehyde and (iii) salt formation in presence of $HPF_6$. The synthesis was short and practical as these steps, along with addition of $CH_2CN$ to the carbenium ions **1**, were conducted successively without any purification in between.

The synthesis (Schemes 1 and 2) thus started with the treatment of salts [*rac*-**1**][$BF_4$], [(*M*)-**1**][$PF_6$], and [(*P*)-**1**][$PF_6$] with NaH in acetonitrile as a solvent affording compounds *rac*-**2**, (*M*)-**2** and (*P*)-**2** respectively. The reduction of the nitrile group was then




**Scheme 2** Synthesis of salts [**4**·H][$PF_6$] (*rac*, *M* or *P*): (a) $LiAlH_4$, $Et_2O$, 20 °C; (b) PhCHO, $MgSO_4$; $NaBH_4$, MeOH; (c) $HPF_6$ (2 equiv.), acetone. Compounds are arbitrarily shown as the *P* enantiomer.

performed using a standard procedure ($LiAlH_4$, $Et_2O$, 20 °C). A rather large excess of reducing agent (10 equiv.) was necessary to bring the reactions to completion. The sluggish reactivity of LAH in this case may be attributed to the moderate accessibility of the nitrile group attached to the bulky [4]heterohelicene skeleton. After work-up, the resulting primary amines **6** (*rac*, *M* or *P*) were engaged to the next step without purification. Upon treatment with $PhCHO/MgSO_4$ and $NaBH_4/MeOH$,[16] the secondary amines **4** (*rac*, *M* or *P*) were afforded.

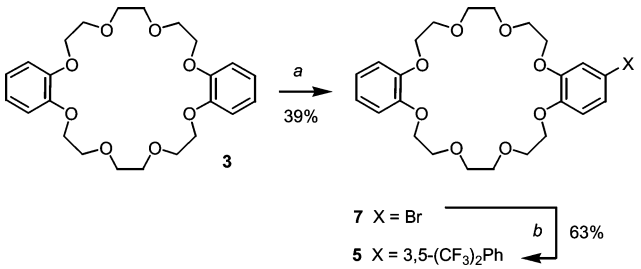
The formation of the ammonium hexafluorophosphate salts was performed by the direct treatment of amines **4** with $HPF_6$ (2 equiv.) in acetone; this protocol being preferred to the classical two steps procedure of HCl (excess) addition and ion pair metathesis with $[NH_4][PF_6]$. After purification by preparative chromatography ($SiO_2$, $CH_2Cl_2$–MeOH 98 : 2), salts [*rac*-**4**·H][$PF_6$], [(*M*)-**4**·H][$PF_6$] and [(*P*)-**4**·H][$PF_6$], were obtained in combined yields (five chemical steps) of 29%, 8%, and 13% starting from [*rac*-**1**][$BF_4$], [(*M*)-**1**][$PF_6$], and [(*P*)-**1**][$PF_6$] respectively.[17] $^1H$ and $^{31}P$ NMR spectroscopy, as well as ES-MS measurements, confirmed the expected structure of these salts. [(*M*)-**4**·H][$PF_6$] and [(*P*)-**4**·H][$PF_6$] presented rather large values for their optical rotation $[a]_D^{20} = -500$ and +560 respectively ($CH_2Cl_2$, $c = 0.05$ g per 100 ml). Circular dichroism spectra of [(*M*)-**4**·H][$PF_6$] and [(*P*)-**4**·H][$PF_6$] displayed symmetrical curves as expected. Only negative and positive Cotton effects were observed respectively and are related to valence transitions in the helical chromophore of the salts.

### Synthesis of the oriented macrocyle 5

With these chiral ammonium threads in hands, the synthesis of the oriented ring was tackled. Whereas DB24C8 is symmetrical, monofunctionalized derivatives of **3** with a substituent on one aromatic catechol are always disymmetrical. The case of disubstituted derivatives of **3** is a bit more complex. Many systems contain the substituents on the two different catechols and the resulting rings will be oriented or not depending of the regiochemistry of the disubstitution; *anti* and *syn* macrocycles being oriented and non-oriented respectively. The physical separation of these doubly substituted regioisomers being not always trivial,[18] we selected to study the synthesis of monofunctionalized derivatives exclusively.

A search of the literature indicated that most derivatives of DB24C8 are substituted either by nitrogen atoms (introduced as $NO_2$ groups) or carbon-based functional groups. In the latter case, the side chains are usually of carboxyl, carbonyl or alkyl nature. The relatively small size and rather high conformational freedom of these groups led us to consider the introduction of aryl substituent instead, although, to our knowledge, no such derivative of DB24C8 had been reported.

Another aspect taken into consideration in the design of the oriented ring was the introduction in the skeleton of NMR sensitive atoms to readily detect all species containing the macrocycle in solution. $CF_3$ groups were chosen for their appearance as single signals in $^{19}F$ NMR spectroscopy. Macrocycle DB24C8F6 **5** containing a 3,5-bis(trifluoromethyl)phenyl substituent was selected for the present study. Its formation was simply effected by (i) regioselective monobromation of a catechol unit (NaBr, CAN, $CH_3CN$),[19] followed by (ii) a Suzuki cross-coupling reaction with 3,5-bis(trifluoromethyl)phenylboronic acid ($ArB(OH)_2$, $Pd(PPh_3)_4$ 21 mol%, 80 °C, Scheme 3). Compounds DB24C8Br and DB24C8F6 were isolated in 39% and 63% yield respectively.




**Scheme 3** Synthesis of macrocycle **5**: (a) NaBr, CAN, $CH_3CN$; (b) $ArB(OH)_2$, $Pd(PPh_3)_4$ 21 mol%, $PhMe/H_2O$, 80 °C, 63%.

### Pseudorotaxane formation

Having in hand threads [*rac*-**4**·H][$PF_6$], [(*M*)-**4**·H][$PF_6$] and [(*P*)-**4**·H][$PF_6$] and rings DB24C8 **3** and DB24C8F6 **5**, the ability of these components to form supramolecular systems was tested in a succession of NMR experiments ($CDCl_3$, 500 MHz, 3.27 $10^{-3}$ mol $l^{-1}$).

The novel ammonium [**4**·H][$PF_6$] salts were first evaluated with the classical DB24C8 **3** to tabulate their reactivity. The $^1H$ NMR spectra of the equimolar mixtures were recorded. In all cases, the complexation process was slow on the $^1H$ NMR timescale as three different sets of resonances were observed; one for the free crown ether, one for the free salt, and one for the 1 : 1 complex. The consequences of the threading can be for instance noted on the benzylic protons on the thread for which a large downfield shift ($\Delta\delta$ −0.37 ppm) occurs upon complexation.[20] The pseudorotaxane formation was additionally established by electrospray mass spectrometry (ES-MS, positive mode); intense peaks being measured for the 1 : 1 complex with the loss of the counter-ion. Evidently, the presence of the voluminous chiral stopper does not prevent the self-assembly process with DB24C8 **3**.

A quantification of the threading was performed as the proportion of all species could be determined by the integration of respective signals. The best region in the $^1H$ NMR spectra that allowed an accurate integration of the complexed and uncomplexed species was located between 3.4 and 3.0 ppm; the most appropriate signal being a methoxy group of the helical moiety (Fig. 4, spectra a and b). The equilibrium constants ($K_a$) were estimated using the classical relationship $K_a$ = [crown ether·salt]/([crown ether]·[salt]) and the values are reported in Table 1. Although the values are lower to that known for this kind of supermolecules, the magnitude remains in fair agreement with those of the literature.[21]

**Table 1** Stability constants ($K_a$) for the pseudorotaxane complexes formed between DB24C8 **3** or DB24C8F6 **5** and ammonium salts [*rac*-**4**·H][$PF_6$], [(*M*)-**4**·H][$PF_6$], [(*P*)-**4**·H][$PF_6$], [(*M*)-**4**·H][TRISPHAT]. Stability constants ($K_a$) were obtained as outlined in ref. 21 (percentage error ≤ 15%)

| Entry | Ammonium salt | DB24C8 **3** | DB24C8F6 **5** |
|---|---|---|---|
| 1 | [*rac*-**4**·H][$PF_6$] | 580 $M^{-1}$ | 260 $M^{-1}$ |
| 2 | [(*M*)-**4**·H][$PF_6$] | 450 $M^{-1}$ | 270 $M^{-1}$ |
| 3 | [(*P*)-**4**·H][$PF_6$] | 500 $M^{-1}$ | 320 $M^{-1}$ |
| 4 | [(*M*)-**4**·H][TRISPHAT] | — | 2070 $M^{-1}$ |

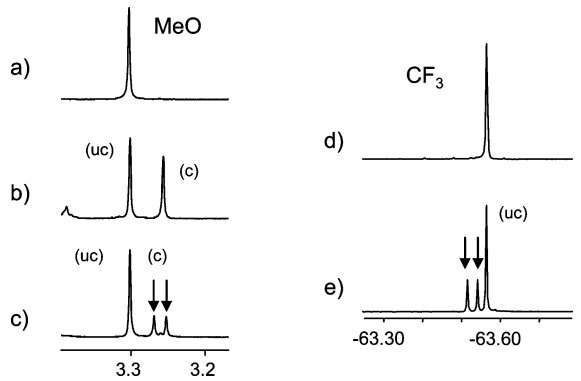



**Fig. 4** $^{1}$H NMR spectra (parts, 500 MHz) of (a) [(*M*)-**4**·H][$PF_6$], (b) [(*M*)-**4**·H][$PF_6$] + **3**, (c) [(*M*)-**4**·H][$PF_6$] + **5** and $^{19}$F NMR spectra (parts, 470 MHz) of (d) **5** and (e) **5** + [(*M*)-**4**·H][$PF_6$].

The same experiments were then conducted in presence of the disymmetrical DB24C8F6 **5** and the profile of NMR spectra changed. Whereas three sets of signals were observed previously, four were now recorded; one for the free crown ether, one for the free ammonium salt, and two for the 1 : 1 complex. This doubling of the signals of the pseudorotaxane was easily monitored in $^{1}$H NMR spectroscopy using again the singlet signal of one of the methoxy substituent of the chiral stopper (Fig. 4, spectrum c). In $^{19}$F NMR spectroscopy, the $CF_3$ groups appeared as three signals: one for the free oriented ring and two for the 1:1 complex. This doubling of the frequencies of the complex is obviously the direct consequence of the presence of two diastereomeric species in solution.

The quantification of the complexation with **5** was performed in a manner similar to that used previously with **3** by means of a single effective concentration of [crown ether·salt] for both diastereomeric species (Table 1).[22] A comparison of the results obtained for the complexation of **3** and **5** indicates clearly that the complexes formed with the classical DB24C8 are quite more stable than those made from **5** (× ~1.8). This reduced treading efficiency of **5** may be attributed to (i) a larger size (negative steric interaction with the bulky stopper) and, more likely, to (ii) the presence of the electron withdrawing $CF_3$ groups on the ring that render the oxygen atoms of the crown less prone to make effective [$N^+$–H · · · O] hydrogen-bonding interactions.[21]

### Diastereoselectivity

As said, two sets of signals were observed upon the threading of **5** onto ammonium [**4**·H][$PF_6$] salts corresponding to inherently chiral diastereomeric rotaxanes (Fig. 5). Unfortunately, whereas a difference in integration was hoped for the signals of these two species, a 1 : 1 ratio was measured showing clearly a lack of stereoselective induction from the stopper onto the orientation of the ring. A possible explanation for this lack of selectivity can be drawn from the X-ray crystallographic structure of salt [*rac*-**4**·H][$PF_6$] (Fig. 6).[23]

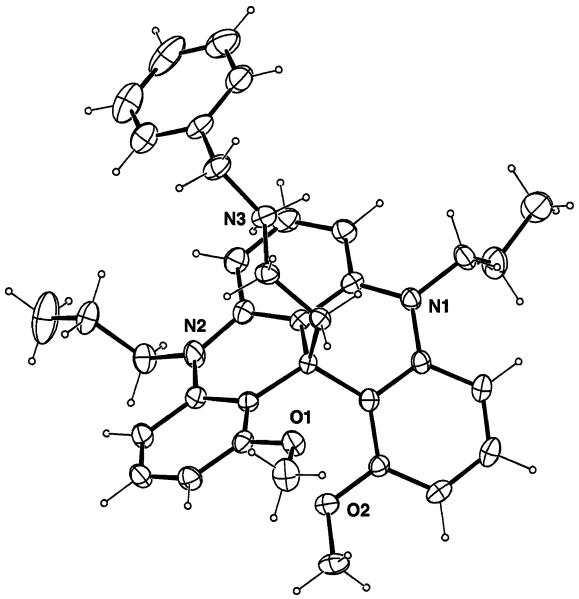



**Fig. 6** X-Ray crystal structure of [*rac*-**4**·H][$PF_6$]. Ellipsoids represent the 40% probability level. The $PF_6^-$ anion was removed for clarity.

In this structure, one can observe that the heterohelicene stopper has lost the $C_2$-symmetry of cation **1** and adopts a rigid skeleton containing two different domains. One domain is an essentially planar region constituted by a sequence of three 6-membered rings—with the middle heterocycle containing a $sp^2$-hybridized nitrogen atom (N2). The other domain is a methoxy-substituted phenyl group bent out of the major plane by the presence of the $sp^3$–hybridized central carbon and the intrinsic intramolecular repulsion between the oxygen atoms of the MeO substituents ($d_{O1–O2}$ 2.809(3) Å); the other nitrogen atom (N1, Fig. 6) exhibiting a deformed $sp^2$ hybridization. Consequently, stereocontrol by this moiety ought to come from this bent domain and not from the extended "flat" portion of the molecule.

Unfortunately, as seen on the crystallographic structure, the heteroalkyl chain ($CH_2CH_2N^+H_2CH_2Ph$) attached to the central carbon atom extends itself in a direction opposite to the chiral groove of the molecule. It is then understandable that the threading

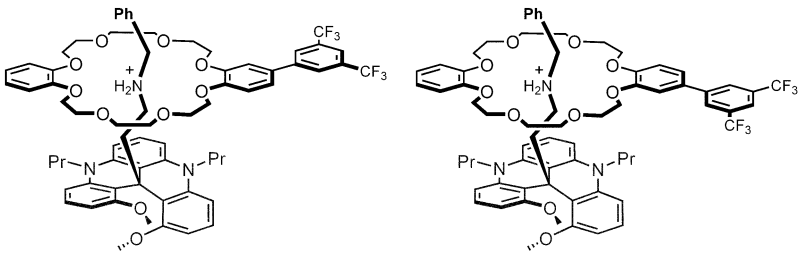



**Fig. 5** Inherently chiral diastereomeric rotaxanes.

of the oriented ring **5** is insensitive to the presence of the chiral stopper as the direct proximity to the "planar" domain of the helicene provides no handle for stereoselective discriminating interactions.

Further information can be drawn from the X-ray crystallographic structure. In the solid state, the flexible heteroalkyl chain is bent rather than linear. Its wrapping towards the helicene side of the molecule is however not sufficient to allow π–π interactions between the phenyl moiety and the aromatic groups of helicene counter-part. If this conformation is preferred in solution—something for which we have no evidence—it would be a further reason for the less efficient threading of **3** or **5** onto salts [**4**·H][$PF_6$].

Hydrogen bonding interactions between the fluorine atoms of the $PF_6^-$ counter ion and the hydrogen atoms of the ammonium group were also observed in the solid state. It is more than likely that these interactions also occur in chloroform; this low polarity solvent maximizing electrostatic interactions in solution.

### Ion pairing influence

In chloroform, salts tend also to form contact (intimate) ion pairs.[24] Recently, several studies have demonstrated the importance of ion pairing in processes between two molecular components where either one of them or both are charged. The nature of the negative counter ion was shown to strongly influence the behavior of the host–guest systems; anions with well dispersed negative charges leading in low polarity media to stronger complexes.[25] Previously, we and others have shown that the tris(tetrachlorocatecholato)phosphate(v) anion,[26] abbreviated TRISPHAT (Fig. 7), can exhibit such a behavior.[27] Its association with ammonium cation **4**·H was thus considered as a stronger association between the ammonium ion and ring **5** might possibly result in a better chiral discrimination.

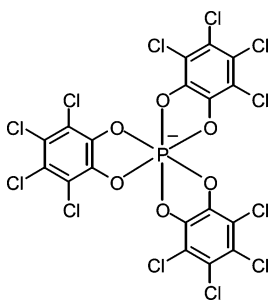


**Fig. 7** TRISPHAT anion.

Salt [(*M*)-**4**·H][$PF_6$] was dissolved in a 1:1 mixture of dichloromethane and acetone in presence of salt [$Et_2NH_2^+$][TRISPHAT] (1.2 equiv.). After elution over silica gel, pure [(*M*)-**4**·H][TRISPHAT] salt was isolated as the only eluting species ($CH_2Cl_2$ as mobile phase, 56% yield).[28] The chemical integrity of the salt was confirmed by various techniques including $^1$H-NMR and ES-MS. $^{31}$P-NMR spectroscopy indicated the disappearance of the septuplet signal of $PF_6^-$ anion and the presence of two singlet signals for the TRISPHAT anion ($\delta$ −81.9; −82.0 ppm). The doubling of the signal of the hexacoordinated phosphate anion is induced by the enantiopure cation **4**·H acting as an NMR chiral solvating agent.[29]

Threading of salt [(*M*)-**4**·H][TRISPHAT] was performed with both rings **3** and **5**. No value can be reported for the making of **3**⊃[(*M*)-**4**·H][TRISPHAT] as the methoxy signals of the free and complexed salts overlapped. With **5**, a value could be measured and a significant increase in $K_a$ (2070 $M^{-1}$) was noted for complex **5**⊃[(*M*)-**4**·H][TRISPHAT] over **5**⊃[(*M*)-**4**·H][$PF_6$] (× ~7.3, Table 1 and Fig. 8). The weaker ion pairing of the ammonium cation **4**·H to TRISPHAT obviously favors the threading of ring **5** while the better-coordinating $PF_6$ inhibits the pseudorotaxane formation by competing more strongly for the ammonium ion.[27] The MeO signal of one diastereomeric complex seems to be slightly predominant over the other, as shown by a deconvolution of the signals (54 : 46; de ~8%); the difference being however not sufficient to claim any decisive stereoselectivity.

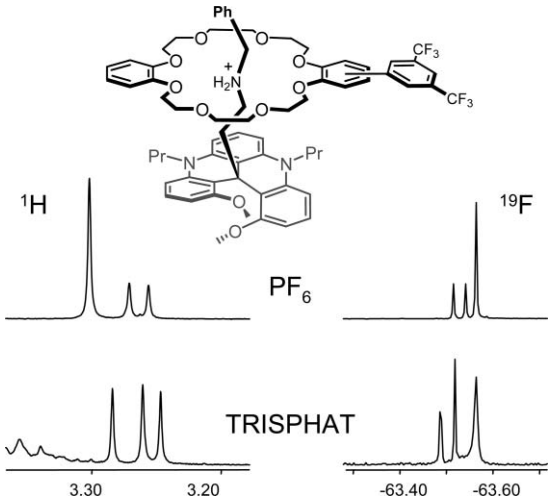



**Fig. 8** $^1$H and $^{19}$F NMR spectra (parts, 500 and 470 MHz) of [(*M*)-**4**·H] ammonium salts + **5**: $PF_6$ (top) and TRISPHAT (bottom) salts.

## Conclusion

A secondary ammonium thread containing as chiral stopper a heterohelicene moiety was synthesized in racemic and enantiopure form (*M* and *P*). Its interaction with aryl-substituted oriented macrocycle DB24C8F6-prepared in two steps from commercial DB24C8-led to the formation of two inherently chiral diastereomeric rotaxanes as shown by $^1$H and $^{19}$F NMR spectra. Although only a low diastereomeric excess resulted from the interaction between ring and thread (de ≤ 8%), an interesting ion pairing effect was noticed as TRISPHAT counter ion afforded a much better supramolecular association between the ammonium salt and the disymetrical crown ether than its $PF_6$ analog.

## Experimental

### General remarks

Solvents and chemicals were used without purification unless otherwise indicated. Salt [**1**][$BF_4$] was prepared according to the reported procedure.[12] NMR spectra were recorded on Bruker AMX-500 at room temperature. $^1$H-NMR: chemical shifts are given in ppm relative to $Me_4Si$ with the solvent resonance used as the internal standard. $^{13}$C-NMR (125 MHz): chemical shifts were

given in ppm relative to $Me_4Si$, with the solvent resonance used as the internal standard ($CD_3CN$ $\delta$ 117.8 ppm). Data were reported as follows: chemical shift ($\delta$) in ppm on the $\delta$ scale, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (Hz), and integration. IR spectra were recorded with a Perkin-Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (Mp) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and were uncorrected. Optical rotations were measured on a JASCO P-1030 polarimeter in a thermostated (20 °C) 10.0 cm long microcell with high pressure lamps of sodium and mercury and are reported as follows: $\alpha_{\lambda}^{T}$ ($c$ (g/100 ml), solvent). Circular dichroism spectra were recorded on a JASCO J-715 polarimeter in a 1.0 cm quartz cell; $\lambda$ are given in nm and molar circular dichroic absorptions ($\Delta\varepsilon$ in $cm^2$ $mmol^{-1}$). Electrospray mass spectra (ES-MS) were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy of the University of Geneva. Accurate mass measurements were performed on an quadrupole time of flight instrument (QStar XL, AB/MDS Sciex, Concord, Ontario, Canada) using electrospray positive mode ionization. The analytes were infused at typically 5–10 µl $min^{-1}$ using an Haward syringe pump. The instrument was optimized in such a way that up-front collision induced dissociation was minimized and the resolution was of about 10 000.

### Salts [4·H][$PF_6$]

In a typical procedure, salt [**1**][$BF_4$] (0.150 g, 0.3 mmol) was dissolved in degassed acetonitrile (5 ml). To this dark green solution was added a large excess of NaH (120 mg). The reaction mixture was stirred at room temperature until a colorless solution was obtained (4 h). Then, the mixture was carefully poured into cold water (0 °C, 20 ml) and dichloromethane was added (30 ml). The organic layer was extracted, dried ($Na_2SO_4$), and concentrated *in vacuo* to give an oily liquid. After dissolution in a small amount of $Et_2O$ (~3 ml), selective precipitation was effected by addition of pentane to give a white solid (**2**) which was collected by filtration. In a 50 ml two-necked round bottom flask, under an atmosphere of dinitrogen, intermediate **2** dissolved in dry and degassed $Et_2O$ (20 ml). $LiAlH_4$ (110 mg, 2.9 mmol) was then added as a solid and the resulting mixture stirred overnight at room temperature. Excess lithium aluminium hydride was destroyed by carefully pouring the mixture into cold ethanol (0 °C, 20 ml). After a slow addition of water (50 ml), the aqueous solution was extracted with dichloromethane (3 × 40 ml) and the combined organic layers were concentrated *in vacuo* to give white solid (**6**). To a solution of **6** in dichloromethane (2.5 ml) were added successively benzylamine (30 µl, 0.3 mmol) and $MgSO_4$ (0.5 g). The reaction mixture was stirred overnight at room temperature, and the solid removed by filtration. The resulting solution was concentrated *in vacuo* and directly engaged to the next step. The obtained solid was dissolved in hot MeOH (10 ml). $NaBH_4$ (22.1 mg, 0.6 mmol) was added portion-wise and the resulting solution heated at reflux for 14 h. The reaction was allowed to cool to room temperature and concentrated *in vacuo*. The resulting product (**4**) was triturated in dichloromethane (20 ml). The organic layer was washed with water and then concentrated *in vacuo*. Salt formation was effected by dissolution of compound **4** in acetone, and addition of an aqueous solution of $HPF_6$ (4 ml, 0.15 mol $l^{-1}$). After stirring for 90 min, dichloromethane was added (20 ml), and the resulting fraction was washed with water (3 × 5 ml). The organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. Purification by chromatography ($SiO_2$, 25 × 1.5 cm, $CH_2Cl_2$–MeOH 99 : 1) then afforded a white solid. The overall yield for the five consecutives steps fluctuated from 8 to 29%: $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.39 (t, $J$ = 7.4 Hz, 1H), 7.33 (t, $J$ = 7.4 Hz, 2H), 7.20 (t, $J$ = 8.4 Hz, 1H), 7.10 (t, $J$ = 8.2 Hz, 1H), 7.04 (m, 3H), 6.78 (d, $J$ = 7.7 Hz, 2H), 6.59 (d, $J$ = 8.2 Hz, 1H), 6.48 (d, $J$ = 8.2 Hz, 2H), 6.45 (d, $J$ = 8.2 Hz, 1H), 6.39 (d, $J$ = 8.2 Hz, 1H), 4.05–3.85 (m, 2H), 3.78 (s, 2H), 3.71 (s, 3H), 3.65–3.50 (m, 2H), 3.28 (s, 3H), 2.78–2.69 (m, 3H), 2.53–2.49 (m, 1H), 1.97–1.89 (m, 2H), 1.71–1.66 (m, 2H), 1.07 (t, $J$ = 7.2 Hz, 3H), 1.02 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 160.4 (C), 157.4 (C), 142.7 (C), 142.0 (C), 140.0 (C), 138.0 (C), 130.0 (CH), 129.5 (CH), 129.3 (CH), 129.1 (CH), 127.4 (CH), 126.2 (CH), 107.7 (CH), 106.1 (CH), 105.9 (CH), 105.8 (CH), 105.6 (CH), 104.6 (CH), 102.2 (CH), 56.0 ($CH_3$), 55.0 ($CH_3$), 52.6 ($CH_2$), 48.7 ($CH_2$), 48.4 ($CH_2$), 47.3 ($CH_2$), 39.4 ($CH_2$), 19.9 ($CH_3$), 19.9 ($CH_3$). $^{31}$P NMR ($CDCl_3$, 202 MHz) $\delta$ 145.6 (m). IR 3224, 2963, 1585, 1475, 1457, 1382, 1231, 1169, 1132, 1059, 831, 733, 700. ES-MS (m/z) positive mode 549, 441, 415, 370. Mp 100 °C. UV–vis ($CH_2Cl_2$, 3.8 $10^{-5}$ M) $\lambda_{max}$ $\varepsilon$ 286 (15670), 312 (16270), 325 (14570).

### [(*M*)-4·H][$PF_6$]

$[\alpha]_D^{20} = -500$ ($c = 0.05$, $CH_2Cl_2$). CD ($CH_2Cl_2$, 3.8.$10^{-5}$ M, 20 °C) $\lambda$ ($\Delta\varepsilon$) 328 (−35.2), 280 (−16.8), 247 (−17.9). Mp 101 °C.

### [(*P*)-4·H][$PF_6$]

$[\alpha]_D^{20} = +560$ ($c = 0.05$, $CH_2Cl_2$). CD ($CH_2Cl_2$, 3.8.$10^{-5}$ M, 20 °C) $\lambda$ ($\Delta\varepsilon$) 328 (39.5), 281 (19.7), 247 (19.4). Mp 103 °C.

### 4-Bromo-dibenzo-24-crown-8, DB24C8Br (7)

Under an inert atmosphere of dinitrogen, dibenzo-24-crown-8 (0.800 g, 1.78 mmol) and anhydrous NaBr (0.182 g, 1.78 mmol) were suspended in dry acetonitrile (35 ml). To this mixture, a solution of ceric ammonium nitrate (1.173 g, 2.14 mmol) in dry acetonitrile (15 ml) was added dropwise over 15 min. The reaction was stirred at room temperature for 30 min, then quenched with $H_2O$ (50 ml) and extracted with $Et_2O$ (3 × 80 ml). The combined organic extracts were washed with $H_2O$ (2 × 50 ml), dried ($Na_2SO_4$) and the solvent was removed under reduced pressure. The monobromated product was separated from the starting materials and the dibromated adduct by repeated silica gel column chromatography ($CH_2Cl_2$–MeOH 49 : 1). The title compound **DB24C8Br** was afforded as a white solid (0.366 g, 39%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.99 (dd, $J$ = 8.4, 2.3 Hz, 1H), 6.96 (d, $J$ = 2.3 Hz, 1H), 6.91–9.83 (m, 4H), 6.71 (d, $J$ = 8.5 Hz, 1H), 4.14 (t, $J$ = 4.4 Hz, 8H), 4.12–4.08 (m, 8H), 3.93–3.87 (m, 8H), 3.84–3.78 (m, 8H).$^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 149.7, 148.9, 148.1, 123.9, 121.4, 117.1, 115.2, 114.0, 113.2, 71.3 (m), 69.9, 69.8, 69.7, 69,6, 69.5, 69.4. IR 2930.4, 2868.1, 1591.2, 1502.1, 1449.0, 1401.4, 1355.9, 1245.0, 1217.9, 1123.7, 1101.6, 1050.9, 1032.1, 958.6, 922.1, 831.0, 796.5, 739.3, 642.7. EI-MS (m/z) 526/528, 216/214, 201/199, 163, 137, 136 (100%), 121, 110, 109, 108. Mp 98 °C.

**4-(3,5-Bis(trifluoromethyl-)benzene-)dibenzo-24-crown-8, DB24C8F$_6$ (5)**

The following solutions were prepared under inert conditions and purged by bubbling dinitrogen for 15 minutes: **DB24C8Br** (0.300 g, 0.569 mmol) in toluene (60 ml), 3,5-bis(trifluoromethyl-)benzeneboronic acid (0.367 g, 1.42 mmol) in methanol (18 ml), and aqueous $Na_2CO_3$ (30 ml, 2M). To the solution of **DB24C8Br**, catalytic $Pd(PPh_3)_4$ (45 mg, 39 μmol, 7 mol%) was added, and the other two solutions were added by canulation. The reaction mixture was stirred at 80 °C for 48 h under a dinitrogen flow and the composition was monitored by NMR (aliquots). Two further catalyst additions were necessary during the reaction (2 × 7 mol%) to bring the reaction to completion. After a quench with water (50 ml), the crude product was extracted with $Et_2O$ (3 × 80 ml) and the organic phase washed with water (50 ml), $Na_2CO_{3\,(aq)}$ (0.1M, 2 × 50 ml) and $H_2O$ (50 ml). The solution was then dried ($Na_2SO_4$) and the solvent removed under reduced pressure. Purification was performed by silica gel column chromatography ($CH_2Cl_2$–MeOH 49 : 1), followed by two selective precipitations in $CDCl_3$–pentane. The title compound **DB24C8F$_6$** was obtained as a white solid (0.236 g, 63%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.93 (s, 2H), 7.79 (s, 1H), 7.14 (dd, $J$ = 8.5, 2.0 Hz, 1H), 7.09 (d, $J$ = 2.0 Hz, 1H), 6.96 (d, $J$ = 8.4, 1H), 6.91–6.84 (m, 4H), 4.25 (t, $J$ = 4.1 Hz, 2H), 4.21 (t, $J$ = 4.3 Hz, 2H), 4.15 (m, 4H), 3.98–3.89 (m, 8H), 3.85 (s, 8H). $^{13}$C NMR (100.6 MHz, $CDCl_3$) $\delta$ 149.9, 149.4, 148.9, 143.0, 132.2, 131.9, 131.4, 126.8, 121.5, 120.5, 114.0, 113.2, 71.4, 71.4, 71.3, 70.0, 69.9, 69.9, 69.8, 69.5 69.4, 69.3. $^{19}$F NMR (470.6 MHz, $CDCl_3$) $\delta$ −63.57. IR 2876.3, 1592.2, 1504.7, 1450.0, 1401.9, 1380.9, 1356.0, 1329.2, 1273.7, 1252.1, 1218.0, 1123.4, 1103.6, 1052.1, 959.8, 921.8, 843.4, 831.0, 810.9, 796.6, 779.0, 741.7. EI-MS (m/z) 661, 660, 349, 348, 333, 321, 137, 136, 121, 109, 80, 73, 71, 45. Mp 120 °C.

**Salt [(*M*)-4·H][*rac*-TRISPHAT]**

Salts [(*M*)-4·H][$PF_6$] (7 mg, 0.01 mmol) and [$Et_2NH_2$][*rac*-TRISPHAT] (10.2 mg, 0.12 mmol) were dissolved in $CH_2Cl_2$–acetone (1 : 1, 1.5 ml). The reaction mixture was stirred for 30 min at room temperature and the solvent was removed under reduced pressure. Column chromatography ($SiO_2$, 13.5 × 1.2, $CH_2Cl_2$) afforded a single eluted fraction, which was concentrated under reduced pressure to give salt [(*M*)-**4**·H][*rac*-TRISPHAT] as a solid (7.5 mg, 56%): $R_f$ ($SiO_2$, $CH_2Cl_2$) 0.27. $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 7.31 (m, 2H), 7.16–7.10 (m, 4H), 6.91 (d, $J$ = 7.1 Hz, 2H), 6.71 (d, $J$ = 8.05 Hz, 1H), 6.59 (d, $J$ = 8.2 Hz, 1H), 6.55 (d, $J$ = 8.3 Hz, 1H), 6.49 (d, $J$ = 7.9 Hz, 2H), 6.45 (d, $J$ = 8.2 Hz, 2H), 4.10 (s, 2H), 3.90–3.50 (m, 8H), 3.26 (s, 3H) 2.94–2.72 (m, 3H), 2.51–2.45 (m, 1H), 1.80–1.65 (m, 4H), 1.01 (t, $J$ = 7.4 Hz, 3H), 0.94 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 160.5 (C), 157.3 (C),142.6 (C), 142.0 (C), 141.0 (C), 140.9 (C),140.9 (C), 140.8 (C), 140.1 (C), 138.1 (C), 130.2 (CH), 129.6 (CH), 129.1 (CH), 129.1 (CH), 127.6 (CH), 126.5 (CH), 123.4 (C), 123.3 (C), 116.1 (C), 114.2 (C), 114.1 (C), 114.0 (C), 110.4 (C), 109.8 (C), 107.5 (CH), 106.5 (CH), 105.9 (CH), 105.8 (CH), 104.8 (CH), 102.2 (CH), 56.2 ($CH_3$), 55.1 ($CH_3$), 52.0 ($CH_2$), 48.4 ($CH_2$), 48.3 ($CH_2$), 46.6 ($CH_2$), 39.3 ($CH_2$), 30.2 ($CH_2$), 29.6 ($CH_2$), 19.9 ($CH_2$), 19.8 ($CH_2$), 11.5 ($CH_3$), 10.9 ($CH_3$). $^{31}$P NMR ($CDCl_3$, 202 MHz) $\delta$ − 81.8 (s), −81.9 (s). IR 2962, 2925, 1586, 1445, 1389, 1259, 1235, 1009, 989, 817, 718, 670. Mp 117 °C. $[\alpha]_D$ = − 240 ($c$ = 0.05, $CH_2Cl_2$). UV–vis ($CH_2Cl_2$, 4.8 $10^{-5}$ M) $\lambda_{max}$ $\varepsilon$ 328 (15000), 300 (26000). CD ($CH_2Cl_2$, 4.8.$10^{-5}$ M, 20 °C) $\lambda$ ($\Delta\varepsilon$) 329 (−34.6), 282 (−23.1), 247 (−22.6). ES-MS (m/z) positive mode 548, 415, 414, 370, negative mode 768.8.

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