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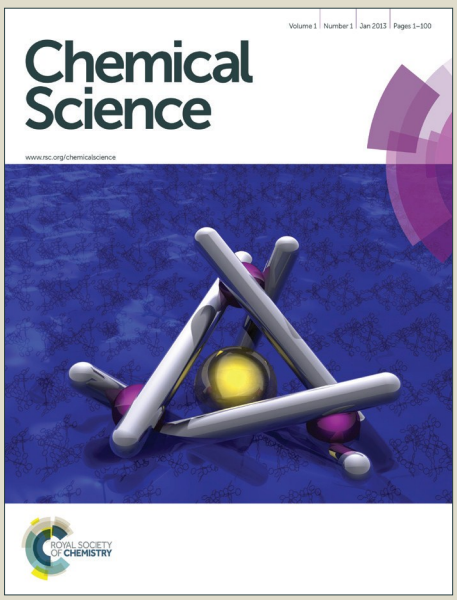

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Guest-dependent directional complexation based on triptycene derived oxacalixarene: formation of oriented rotaxanes

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The manipulation of supramolecular devices to carry out sophisticated and programmed tasks is bound up with the spatial allocation of their components, especially the threading direction of the guest which controls the host-guest orientation in the devices. However, insights are needed to probe more possibilities of steering the threading direction. We have developed a new system consisting of a three-dimensional nonsymmetric oxacalixarene (**H**) with fixed comformation and (bi)pyridinium salts (**G1**-**G3**), in which we found that based on the intrinsic discrepancies between the two semi-cavities of **H**, the electron densities of the axles greatly affect the threading direction, unequivocally demonstrated by NMR spectra and single crystal structures. With elaborate design, unidirectional threading is achieved, resulting in an oriented rotaxane. Therefore, we provide a new approach in which the threading direction and final orientation might be finely controlled by adjustment on structures of the guests.

Introduction

During the last two decades, great progress has been made in the synthesis of mechanically interlocked molecules (MIMs) such as rotaxanes and catenanes,[1] with interest rising from not only their aesthetic appeal[2] but alsotheir perceived potential to act as sophisticated molecular machines, switches and sensors.[3] The general approach to constructing (pseudo)-rotaxanes needs a macrocycle and a linear guest, as the wheel and the axle, respectively; if neither of them is in D_{nh} point group, two isomers will be obtained via the threading process, resulting in different orientation of components in the final MIMs.[4-7] Owing to difference in the spatial arrangement, a pair of orientational isomers may generate quite different properties.[8] However, the separation of isomers poses a big problem,[4,6,9b] so unidirectional threading which leads to an oriented rotaxane is highly appealing. Using cyclodextrin as the wheel, unidirectional threading was realized due to either kinetic[10] or thermodynamic[11] stability, which resulted in various oriented rotaxanes. Calixarenes with three-dimensional nonsymmetric structures provided another candidate to form oriented rotaxanes, based on its formation of *endo*-cavity complexes with organic cations.[9,12,13] Using triphenylureido-calix[6]arene as the host and dialkylviologen salt as the guest, Arduini and coworkers succeeded in synthesizing oriented pseudorotaxane through a kinetically controlled process.[9a] On that basis, they prepared a pair of isomeric oriented rotaxanes respectively for the first time, by reversing the sequence in which two different stopper groups were introduced onto the axle.[4] In contrast with the kinetically controlled unidirectional threading strategy, Neri and coworkers developed an "*endo*-alkyl" rule which controlled the threading directionality of alkylbenzylammonium axles with calix[6]arenes.[5] Applying the rule, they constructed stereo-isomeric (pseudo)[3]rotaxanes[13a,b] and an oriented handcuff rotaxane.[13c] Although some important results have been obtained, formation of oriented rotaxanes based on controllable threading directionality is still emerging as a challenge to be overcome.

Heteracalixarenes[14] are a kind of calixarenes obtained by replacing conventional methylene bridges with heteroatoms. Introducing the bridging heteroatoms makes it possible to finely tune the size, conformation and binding properties of the macrocycle, since heteroatoms can not only adopt different electronic configurations but also form various degrees of conjugation with the neighboring aromatic rings.[15] Due to their difficulty to form "through-the-annulus" complexes with linear guests, utilizing heteracalixarenes as the host to realize directional threading and construction of oriented rotaxanes has still been a rather unexplored field. Previously, we reported that a triptycene-derived oxacalixarene **H**[16a] (Fig. 1a), with an upper semi-cavity encir-

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† Electronic Supplementary Information (ESI) available: Further details ofsynthesis, characterization, ^{1}H and 2D NMR experiments and computational modeling. CCDC 1009829, 1009830, and 1419743. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

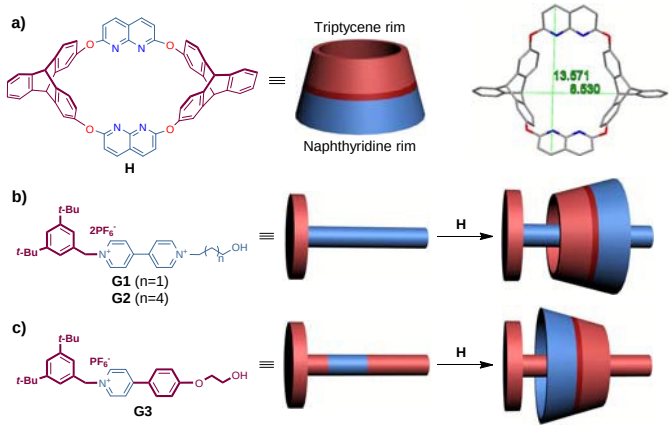


Fig. 1 a) Structure and representation of **H** and its crystal structure[16a] denoting sizes of the portals on both sides. b) Structures and representation of guests **G1**-**G2** and their directional threading into **H**. c) Structure and representation of guest **G3** and its directional threading into **H**.

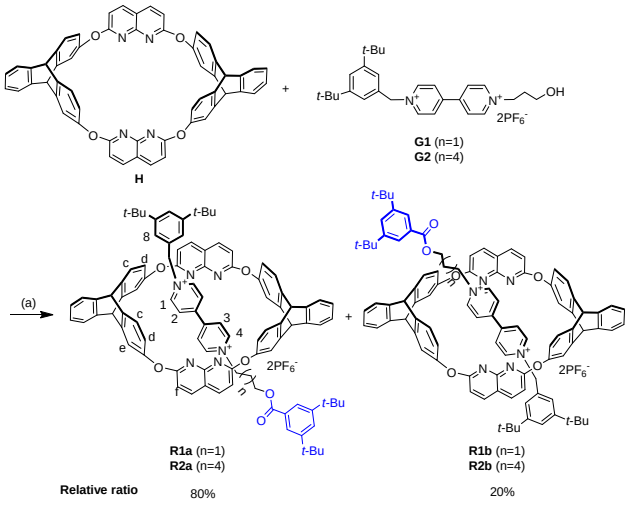
cled by two naphthyridine moieties and a lower semi-cavity by two triptycene moieties, could incorporate various 4,4'-bipyridinium salts to form pseudo-rotaxanes.[16b] This property had been applied by us to the synthesis of rotaxanes based on **H** and symmetric 4,4'-bipyridinium salts. Theoretically, if we mix **H** with a nonsymmetric axle, a pair of isomeric pseudorotaxanes might be obtained. The crystal structure of **H**[16a] disclosed that the portal of the lower semi-cavity was more crowded than that of the upper one (Fig. 1a, 8.53 Å versus 13.57 Å). Moreover, triptycene was known to be more electron-rich than the naphthyridine moiety (the N atoms excluded). Hence, we hypothesized the discrepancies in size and electron density between the two semi-cavities of **H** might exert different induction upon the threading of guests. Herein, we report a system employing **H** as the wheel in which we can control the dominant threading direction by partially changing the structures of axles and thus tuning their interaction with **H** in the threading process.

Results and discussion

Directional complexation between macrocycle H and bipyridinium salts G1 and G2 with alkyl chains of different length

We initially designed a linear nonsymmetric bipyridinium salt **G1** (Fig. 1b), stoppering one of its ends with a bulky terminal group in order to easily clarify its threading direction into the macrocycle. By comparison of the ^{1}H NMR spectra of **H**, **G1**, and the 1:1 mixture of them in a $CDCl_3/CD_3CN$ solution at room temperature, complexation between the two components was observed (Fig. S31, ESI†). The ^{1}H NMR spectra of the complex always exhibited only one set of signals whether the host or the guest was in excess (Fig. S34, ESI†), indicating a fast equilibrium on the NMR timescale. To acquire information on the relative orientation of the two components, we stoppered the pseudorotaxane(s) to synthesize the corresponding rotaxane(s) (Scheme 1).

As we had demonstrated in the previous work that macrocycle **H** adopted a fixed 1,3-alternate conformation and would not undergo comformational inversion mainly due to the bulky triptycene moieties,[17] the orientation of the obtained rotaxane(s) could represent the original threading



Scheme 1 Synthesis of isomeric [2]rotaxanes **R1a**-**b** and **R2a**-**b**. Conditions: (a) 3,5-di-*tert*-butylbenzoic anhydride, $(n\text{-Bu})_3P$, $CHCl_3/CH_3CN$ (2:1, *v/v*), r.t.

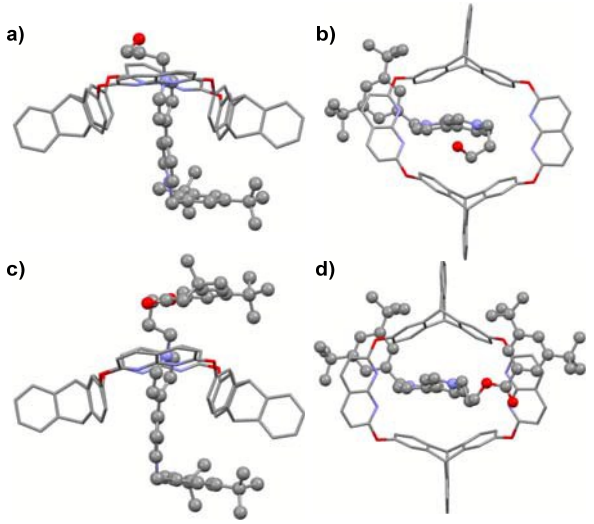


Fig. 2 (a) Side and (b) top view of crystal structure of **H@G1**. (c) Side and (d) top view of crystal structure of [2]rotaxane **R1a**. Hydrogen atoms and PF_6^- counterions are omitted for clarity.

direction of the axle into the wheel on statistic account.[9b] The stoppered products were isolated as a mixture of two orientational isomers, revealed both by ^{1}H NMR spectrum and ESI-HRMS. The integrals on the ^{1}H NMR spectrum (See Fig. S27) showed that the relative ratio of the two sets of signals (also the amount of the two isomers, **R1a**‡ and **R1b**) was approximately 4:1. The ratio calculated from the NMR spectrum revealed that the threading was highly directionally selective, but we could not ascertain the relative orientation of the wheel and axle in the two isomers.

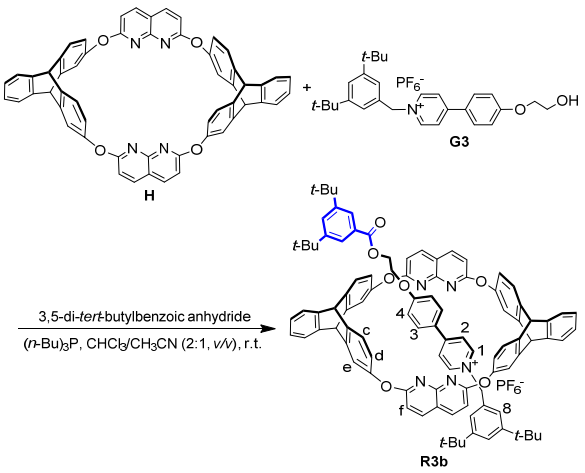
Fortunately, the single crystals of both the pseudorotaxane cultivated from the $CHCl_3/CH_3CN$ solution of the complex (Fig. 2a, b) and rotaxane **R1a** cultivated from its $CHCl_3$ solution (Fig. 2c, d) were obtained. Both crystal structures showed that the axle had threaded into the wheel from the triptycene rim (the lower rim, Fig. 1b).§ Weak correlations in 2D ROESY spectrum of **R1a** (Fig. S22, ESI†) between H_2 and H_c; H_2 and H_d; H_8 and H_c

were also detected, which indicated the same orientation of the host and the guest in **R1a** with its crystal structure.

In order to determine which part of the axle might have exerted a crucial impact on the threading direction,[9d] we firstly altered the length of the alkyl chain by replacing the hydroxypropyl group with hydroxyhexyl group (**G2**, Fig. 1b), synthesized the corresponding isomeric rotaxanes **R2a** and **R2b** (the ratio was also found to be about 4:1, Fig. S28, ESI†) (Scheme 1), and compared the ^{1}H NMR spectrum of the major product **R2a** with that of **R1a**. After unambiguous assignment of all signals on the ^{1}H NMR spectrum of **R2a** on the basis of 2D NMR experiments (Fig. S23 and S24, ESI†), it was found that all the corresponding hydrogens of the two rotaxanes shared almost the same chemical shifts (Fig. S9 and S13, ESI†), indicating the identical orientation of the wheel and axle in **R1a** and **R2a**. Thus it was summarized that the length of the terminal alkyl chain had negligible influence on the threading direction at least when the chain was not quite long.

Unidirectional complexation between macrocycle H and pyridinium salt G3

In the dominant threading direction of **G1**, the process was electrostatically favorable but sterically unfavorable. Therefore, to disclose whether electrostatic effect might have played an important part in the directional selectivity, we replaced the terminal pyridyl ring in **G1** with a more electron-rich phenyl ring, substituted by an electron-donating alkoxy group (Fig. 1c). Pyridinium salt **G3** was encapsulated by **H** as expected (Fig. S33, ESI†), and similarly, the complex was in fast exchange on NMR timescale (Fig. S40, ESI†). As the relevant data of the pseudorotaxane(s) provided barely any information about the threading direction, the host-guest complex was stoppered to give the corresponding rotaxane(s) (Scheme 2). To our surprise, the product showed only one set of signals on the ^{1}H NMR spectrum (Fig. S19, ESI†), which meant only one (**R3b**) of the isomeric rotaxanes was actually formed and thus the threading had occurred unidirectionally. To clarify the threading direction of **G3**, we cultivated a single crystal that was suitable for X-ray crystal analysis by slow evaporation of diethyl ether into an acetone solution of **R3b** (Fig. 3). The crystal structure showed that **G3** had threaded into **H** from the naphthyridine rim (Fig. 1c), the direction of which was completely reversed compared with the dominant threading direction of **G1** and **G2**. This agrees well with the 2D ROESY experiment (Fig. S26, ESI†) in which correlations were observed between H_3 and H_c/H_d; H_2 and H_c/H_d; H_8 and H_f; H_8 and H_e.



Scheme 2 Synthesis of oriented [2]rotaxane **R3b**.

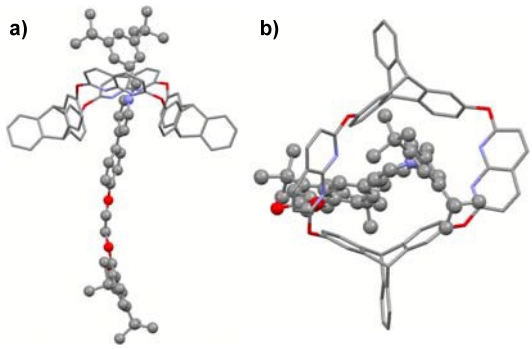


Fig. 3 Side (a) and top (b) view of crystal structure of **R3b**. Hydrogen atoms and PF_6^- counterions are omitted for clarity.

Study on the directionally selective mechanism

The results were exciting but not beyond expectation, and could be tentatively explained that in the threading process of **G1** (the bipyridinium salt), the electrostatic effect dominated the threading direction while the steric effect posed an opposite influence, and as a result, a pair of orientational isomeric rotaxanes in a ratio of 4:1 was yielded and in the major product the pre-stoppered end was in proximity to the lower rim of **H**; however, when axle **G3** (the pyridinium salt) threaded into the macrocycle, the electrostatic effect and the steric effect acted in a cooperative way, generating a single compound in which the pre-stoppered end was in proximity to the upper rim of **H**. Moreover, to manifest the high selectivity in the threading direction of **G3** into **H** in an in-situ way, a variable-temperature ^{1}H NMR experiment on the $CDCl_3$/CD_3CN solution of the pseudorotaxane based on **G3** and **H** (**G3**:**H** = 1.5:1) was conducted (Fig. S43-45, ESI†). From the spectra we observed that when the temperature was brought down to approximately 233K, the peaks of free guest started to appear, indicating that the threading and dethreading had become a slow exchange process on the NMR timescale. And meanwhile it was found that the pseudorotaxane still appeared as a single set of signals, which meant that at and below this temperature, it was clearly shown on the ^{1}H NMR spectra that the threading of **G3** into **H** occurred unidirectionally.§§

DFT theoretical modeling was done in order to establish whether, for each axle, the orientational outcome is dictated by kinetic reasons or by different thermodynamic stability of the two isomers.§§§ We calculated the relative Gibbs free energies of the two orientational isomers of pseudorotaxane **H@G1** (**PR1a** and **PR1b**), and found that the free energy of **PR1a** (corresponding to the orientation of **R1a**) was lower than that of its isomer **PR1b** by only 0.9 kcal/mol. However, for pse-

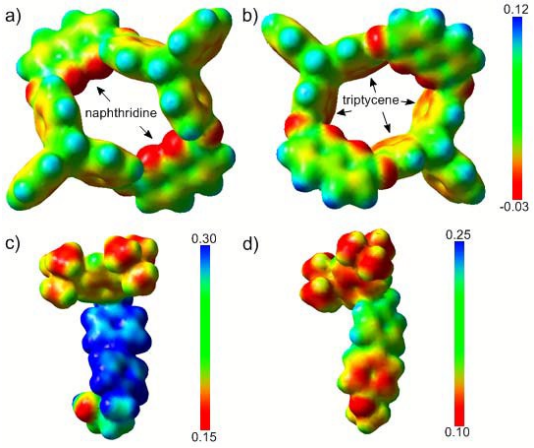


Fig. 4 ESPs mapped onto electron density isosurfaces (ρ = 0.01) for **H** viewed from lower rim (a) and upper rim (b), and for **G1** (c) and **G3** (d).

udorotaxanes based on **G3** and **H** (**PR3a** and **PR3b**), the calculations indicated that the relative Gibbs free energy of **PR3b** (corresponding to the orientation of rotaxane **R3b**) was lower than that of **PR3a** by sizable 3.6 kcal/mol. Thus, the DFT calculations verified the relative stabilities of the two pairs of isomers, respectively: both dominant isomers (**PR1a** and **PR3b**) were the relatively stable ones, though **PR1a** only had a small advantage over **PR1b** energetically.

The ESPs of **H** in the absence of guest molecules were also calculated, as depicted in Fig. 4a and b. Two features were notable; one was the electron-rich character of phenyl rings of the triptycene semi-cavity, and the other was the polar naphthyridine moieties characterized by the electron-rich N atoms and the rest part which was rather electron-poor. And the difference in electron densities of guests **G1** and **G3** was visualized by comparing their ESPs (Fig. 4c, d). **G3** had a clearly higher electron density than **G1** especially with respect to the unstoppered end (the phenyl ring). Therefore, the structures revealed the electrostatic repulsion of the electron-poor pyridinyl ring (the one farther from the pre-stopper) in **G1** and attraction of the electron-rich phenyl ring in **G3** exerted by the upper semi-cavity, and also the repulsion of the phenyl ring in **G3** by the lower semi-cavity in the threading processes of the two guests.

From the above calculations, we concluded that the two isomers of **H@G1** shared similar stability, but in forming **PR1b** from the less crowded upper rim, the barrier posed by electrostatic effect might be higher than that in forming **PR1a**, while the subordinate factor, the steric effect, acted oppositely; as a result, two isomers in a ratio of 4:1 were obtained. However, with regard to **H@G3**, on the one hand **PR3b** was more stable than its isomer by 3.6 kcal/mol, and on the other hand, threading from the upper rim was favorable in terms of both electrostatic effect and steric effect; and thus, unidirectional threading was attained.

As we hypothesized the directional selectivity in the **H@G1** system mainly resulted from the difference in the energy barriers in the threading processes of two directions, increasing the temperature ought to narrow the gap between them. To verify this consideration, rotaxanes based on **G1** and **H** were synthesized at raised temperatures (313 K and 333 K), and the ratios of the isomers were determined via ^{1}H NMR analysis (Fig. S29-30, ESI†). In agreement with our prediction, the directional selectivity in the threading process of **G1** decreased with the increase of temperature (Table 1). However, in the same experiments on **G3** and **H**, the orientational isomer of **R3b** had not even been traced. The results further demonstrated that at ambient temperature the threading of **G1** was kinetically controlled.

Table 1 Ratios of **R1a** and **R1b** obtained under different reaction temperature

Entry	Temperature (K)	Ratios of **R1a** and **R1b** [a]
1	298	4:1
2	313	1.7:1
3	333	1.2:1

[a]Determined by ^{1}H NMR.

Conclusions

In this work, we had successfully demonstrated that the threading direction of (bi)pyridinium salts (**G1-G3**) into a triptycene-derived oxacalixarene (**H**) could be effectively controlled by tuning the electron densities of the guests, and the single crystal structures of (pseudo)rotaxanes exclusively manifested the orientation of the host and the guests. As the directional selectivity could be varied by tuning the roles that steric effect and electrostatic effect played, this work potentially provided a new approach towards the construction of oriented and well-aligned hierarchical assemblies. This was the first report on the selective or unidirectional threading based on oxacalixarenes and high directional selectivity was attained with neither use of special counteranions[5,13] of the guest nor further functionalization on the calixarene.[4,9] Designing new guests and modifying the macrocycle by replacing the naphthyridine moieties with other electron-deficient moieties to obtain more precise control on directional selectivity from both sides, and the construction of high-order mechanically interlocked structures capable of performing unidirectional motion are currently under investigation in our laboratory.

Experimental

General remarks

The synthesis of precursors of the rotaxanes are described in the ESI.† All the other reagents and solvents were bought from commercial suppliers and used as received.

Synthesis of R1a and R1b.

A mixture of **H** (62 mg, 0.075 mmol) and **G1** (53 mg, 0.075 mmol) in chloroform (10 mL) and acetonitrile (5 mL) was stirred at ambient temperature for 12h. To the mixture was then added 3,5-di-*tert*-butylbenzoic anhydride (135 mg, 0.3 mmol) and (n-Bu)$_3$P (3 mg, 0.015 mmol). The reaction mixture was stirred under argon for 24 h at ambient temperature. The solvent was removed under vacuum, and the residue was

purified by column chromatography (CH_2Cl_2/acetone, 100:1 *v/v*) to give **R1a** and **R1b** as a mixture (73 mg) in total 56% yield. The macrocycle in unreacted pseudorotaxanes could be recycled nearly quantitatively. The mixture was further separated carefully by preparative thin-layer chromatography to give pure **R1a** and **R1b** both as yellow powder for characterization.

R1a: Mp: 229-232 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ9.03 (d, J = 6.3 Hz, 2H), 8.45 (d, J = 6.4 Hz, 2H), 8.33 (d, J = 6.3 Hz, 2H), 8.00 (d, J = 8.6 Hz, 4H), 7.97 (s,2H), 7.71 (s,1H), 7.57 (s, 2H), 7.51 (m, 3H), 7.20 (d, J = 6.7 Hz, 2H), 7.13 (d, J = 6.7 Hz, 2H), 7.04-7.05 (m, 4H), 6.92 (d, J = 8.6 Hz, 4H), 6.72-6.83 (m, 8H), 6.40 (d, J = 7.9 Hz, 4H), 5.79 (s, 2H), 5.24 (s, 4H), 4.25 (t, J =6.8 Hz, 2H), 3.94 (t, J =5.8 Hz, 2H), 1.93-2.02 (m, 2H), 1.36 (s, 18H), 1.29 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 164.1, 153.6, 153.3, 151.3, 151.2, 150.7, 149.1, 147.8, 146.7, 145.3, 145.1, 144.8, 144.3, 141.4, 140.3, 131.2, 128.5, 127.9, 127.4, 126.1, 125.3, 124.9, 124.4, 124.2, 123.7, 123.5, 117.2, 116.4, 116.0, 112.6, 60.4, 58.0, 57.0, 53.2, 51.4, 35.1, 34.9, 31.7, 31.3, 29.7. ESI-HRMS calcd for $C_{99}H_{90}N_6O_6$ $[M\text{-}2PF_6^-]^{2+}$ 729.8472; found 729.8485.

R1b: Mp: 223-225 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, J = 6.3 Hz, 2H), 8.20-8.22 (m, 6H), 8.06 (s,2H), 7.82 (d, J = 6.3 Hz, 2H), 7.76 (s, 1H), 7.67 (d, J = 6.3 Hz, 2H), 7.55 (s, 1H),7.21-7.30 (m, 4H), 7.14-7.16 (m, 4H), 7.12 (s, 2H), 7.02-7.05 (m, 8H), 6.88-6.91 (m, 4H), 6.67 (d, J = 7.9 Hz, 4H), 5.53 (s, 2H), 5.37 (s, 2H), 5.32 (s, 2H), 4.28 (t, J = 6.2 Hz, 2H), 4.03 (t, J = 6.3 Hz, 2H), 1.99-2.02 (m, 2H), 1.38 (s, 18H), 1.29 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.4, 164.0, 153.1, 151.7, 151.2, 148.7, 148.3, 147.2, 145.0, 144.8, 144.6, 144.3, 141.6, 141.2, 130.1, 129.7, 129.5, 129.0, 128.1, 125.4, 125.3, 125.0, 124.5, 124.1, 124.0, 123.7, 123.4, 117.8, 116.6, 115.9, 113.4, 60.6, 58.6, 54.8, 52.9, 52.2, 35.1, 35.0, 31.4, 31.3, 29.7. ESI-HRMS calcd for $C_{99}H_{90}N_6O_6$ $[M\text{-}2PF_6^-]^{2+}$ 729.8472; found 729.8454.

Synthesis of R2a and R2b.

A mixture of **H** (62 mg, 0.075 mmol) and **G2** (56 mg, 0.075 mmol) in chloroform (10 mL) and acetonitrile (5 mL) was stirred at ambient temperature for 12h. To the mixture was then added 3,5-di-*tert*-butylbenzoic anhydride (135 mg, 0.3 mmol) and (n-Bu)$_3$P (3 mg, 0.015 mmol). The reaction mixture was stirred under argon for 24 h at ambient temperature. The solvent was removed under vacuum, and the residue was purified by column chromatography (CH_2Cl_2/acetone, 100:1 *v/v*) to give **R2a** and **R2b** as a mixture (71 mg) in total 53% yield. The macrocycle in unreacted pseudorotaxanes could be recycled nearly quantitatively. Then, the mixture was carefully separated by preparative thin-layer chromatography to give a fraction of pure **R2a** as yellow powder, but it turned out to be difficult to obtain pure **R2b** for further characterization.

R2a: Mp: 208-210 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.96 (brs, 2H), 8.39 (brs, 2H), 8.27 (brs, 2H), 8.00 (d, J = 7.8 Hz, 4H), 7.88 (s, 2H), 7.63 (s, 1H), 7.57-7.61 (m, 4H), 7.52 (s, 1H), 7.18 (d, J = 7.2 Hz, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.01 (brs, 4H), 6.90 (d, J = 7.8 Hz, 4H), 6.70-6.79 (m, 8H), 6.44 (d, J = 7.5 Hz, 4H), 5.77 (s, 2H), 5.25 (s, 2H), 5.22 (s, 2H), 4.09 (t, J = 7.8 Hz, 2H), 4.01 (brs, 2H), 1.48-1.50 (m, 2H), 1.35-1.38 (m, 2H), 1.31 (s, 18H), 1.27 (s, 18H), 1.07-1.10 (m, 2H), 0.84-0.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 164.0, 153.5, 153.2, 151.2, 150.5, 148.9, 147.5, 146.7, 145.2, 145.0, 144.7, 144.4, 141.5, 140.4, 131.5, 129.6, 127.5, 127.2, 126.1, 125.3, 124.9, 124.8, 124.2, 123.7, 123.56, 123.52, 117.2, 116.4, 116.2, 112.5, 64.3, 60.8, 53.1, 51.5, 35.1, 34.9, 31.38, 31.35, 31.1, 29.7, 28.2, 25.2, 25.0. ESI-HRMS calcd for $C_{102}H_{96}N_6O_6$ $[M\text{-}2PF_6^-]^{2+}$ 750.8707; found 750.8716.

Synthesis of R3b.

A mixture of **H** (62 mg, 0.075 mmol) and **G3** (43 mg, 0.075 mmol) in a solution of chloroform (10 mL) and acetonitrile (5 mL) was stirred at ambient temperature for 12h. Then, to the mixture was added 3,5-di-*tert*-butylbenzoic anhydride (135 mg, 0.3 mmol) and (n-Bu)$_3$P (3 mg, 0.015 mmol). The reaction mixture was stirred under argon for 24 h at ambient temperature. The solvent was removed under vacuum. The residue was purified by column chromatography (CH_2Cl_2/acetone, 100:1 *v/v*) to give **R3b** (63 mg, 52% yield) as white powder. The macrocycle in unreacted pseudorotaxanes could be recycled nearly quantitatively. Mp: 211-213°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.6 Hz, 4H), 8.03 (d, J = 8.5 Hz, 2H), 8.00 (s,2H), 7.79 (d, J = 6.2 Hz, 2H), 7.66 (s, 1H), 7.53 (d, J = 6.2 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.23 (s, 1H), 7.17-7.23 (m, 4H), 7.02 (d, J = 8.6 Hz, 4H), 6.98 (brs, 4H), 6.87-6.89 (m, 4H), 6.79-6.85 (m, 8H), 6.55 (s, 2H), 5.15 (s, 2H), 4.95 (s, 2H), 4.86 (brs, 4H), 4.61 (t, J = 4.2 Hz, 2H), 1.35 (s, 18H), 1.08 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 164.1, 162.1, 153.8, 153.0, 151.9, 151.2, 150.1, 146.2, 145.3, 144.6, 141.9, 141.0, 140.0, 130.5, 129.9, 129.3, 127.4, 126.9, 125.3, 125.0, 124.0, 123.7, 123.55, 123.50, 123.4, 117.1, 117.0, 115.7, 112.3, 66.6, 62.7, 53.5, 52.3, 35.0, 34.6, 31.4, 31.1, 29.3. ESI-HRMS calcd for $C_{99}H_{88}N_5O_7$ $[M\text{-}PF_6^-]^+$ 1458.6678; found 1458.6679.

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Notes and references

‡In this paper, isomers of pseudorotaxanes and rotaxanes are entitled in the way that *a* denotes that the corresponding guest threaded from the triptycene rim, while *b* denotes that the corresponding guest threaded from the naphthyridine rim.

§ The absence of the pseudorotaxane in which macrocycle and axle oriented in the other way (**PR1b**) in the crystal might be caused by the difference in the relative amount of the two isomeric pseudorotaxanes and the selective crystallization of the dominant one.

§§ As the signals of the pseudorotaxane changed gradually with temperature decreasing without saltation of each chemical shift, we could safely deduce that the threading direction did not change during the cooling process.

§§§ See Supporting Information for details.

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