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N-Benzyltriazolium as Both Molecular Station and Barrier in [2]Rotaxane Molecular Machines

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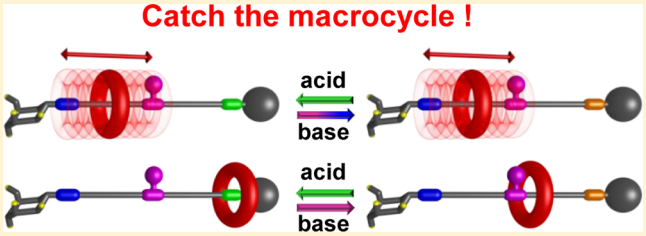
Supporting Information

ABSTRACT: A two-station [2]rotaxane, consisting of a dibenzo-24-crown-8 macrocycle (DB24C8) that surrounds a molecular axle containing an anilinium and a monosubstituted pyridinium amide molecular stations, has been synthesized via alkyne−azide "click chemistry". The subsequent *N*-benzylation of the triazole moiety, which is located in the middle of the threaded axle, was then envisaged. In addition to affording a third molecular station (i.e., a triazolium station) for the DB24C8, it was found that the benzyl moiety behaves as a kinetic molecular barrier that prevents the DB24C8 from shuttling along the molecular encircled axle from one extremity to the other. Depending on where the DB24C8 is initially located, the *N*-benzylation of the triazole allows trapping of the DB24C8 on either the "left" or the "right" side of the thread with respect to the triazolium station. The presence of the benzyl barrier thus affords two different three-station [2]rotaxane molecular machines, in which some of *co*-conformational states remain unbalanced and not at the equilibrium.



INTRODUCTION

Several interlocked molecular machines based on rotaxanes and incorporating a dibenzo-24-crown-8 (DB24C8) as a macrocycle have been reported. Most of them have been using a positively charged moiety as molecular station for this macrocycle. Among them, benzylic ammonium,[1] anilinium,[2] *N*,*N*′-dialkyl-4,4′-bipyridinium,[3] or 1,2-bis(pyridinium)ethane cation[4] have been used as good template to produce [2]rotaxanes. The interactions that take place between these template moieties and the DB24C8 are mainly based on ion−dipole interactions, hydrogen bonding, and $\pi-\pi$ stacking between the electron-rich catechol ring and electron-poor pyridinium rings. In 2008, we reported the synthesis of new molecular machines based on anilinium and triazolium stations, using a straightforward two-step sequence: (1) alkyne−azide "click chemistry" and (2) methylation of the triazole.[5] In our pH-sensitive system, the DB24C8 resides first around the best anilinium station, while it shuttles around the triazolium station upon deprotonation. We then proposed some [2]rotaxane molecular machines containing new mono- and disubstituted pyridinium amide molecular stations.[6] Among these two new molecular stations, the disubstituted pyridinium amide was found to be a very interesting station, when linked to a mannose via a *N*-mannosidic bond. Indeed, it was able to flip the chair conformation of the mannopyranose by switching on or off the reverse anomeric effect, depending on its interaction with the DB24C8. A little bit later, we then reported some three-station-based [2]rotaxanes molecular machines, which allowed us to determine the following increasing affinity order of the different stations for the DB24C8: (1) disubstituted pyridinium amide, (2) triazolium, (3) monosubstituted pyridinium amide, and (4) anilinium.[7] At acidic pH, we unambiguously reported for all of our molecular machines that the DB24C8 exclusively resides around the anilinium station. However, upon deprotonation of the anilinium, different bistable or oscillating *co*-conformational states were obtained depending on the stations involved. In some molecular machines, we observed that the deprotonation at one extremity of the threaded axle could cause a translational shuttling of the macrocycle, which was then able to induce a rotational movement of chemical bonds at the other extremity of the molecule, thus to entirely flip the chair conformation of a mannopyranose. In others, the translational shuttling of the DB24C8 induced a braking of the rotation of a σ bond.

Recently, Leigh et al. have developed the concept of the introduction of a kinetic molecular barrier in a [2]rotaxane molecular machine, in order to make the molecular machines be compartmentalized.[8] Herein, we propose the synthesis of three-station [2]rotaxane molecular machines including a monosubstituted pyridinium amide, a *N*-benzyltriazolium, and an anilinium as molecular stations. The aims are either to trap the DB24C8 around stations of weaker affinity than that of anilinium or to see how the DB24C8 can interact with stations only on one of the two sides of the molecular axle with respect to the triazolium station. For this purpose, the *N*-benzyltriazolium moiety was chosen so that it can be used as both a molecular station and a barrier for the macrocycle. The

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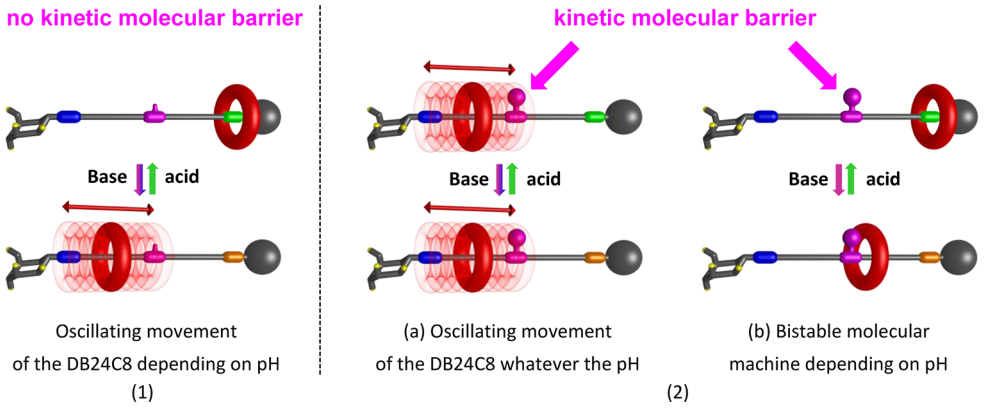

Figure 1. Cartoon representation of the different *co*-conformational states adopted by the three-station [2]rotaxane molecular machines in (1) the *N*-methyltriazolium series and (2) the *N*-benzyltriazolium series. The blue, pink, green, and orange colored shapes represent, respectively, the monosubstituted pyridinium amide station, the *N*-benzyl or *N*-methyl triazolium stations, the anilinium station, and the aniline moiety.

obtained molecular machines have then been studied by NMR and compared to the molecular machine obtained in the *N*-methyl triazolium series. This latter undergoes an oscillating movement of the DB24C8 between the monosubstituted pyridinium amide and the triazolium depending on pH (Figure 1, 1). In the first of the two new described molecular machines, the DB24C8 oscillates between the *N*-benzyltriazolium and the monosubstituted pyridinium amide stations in a manner similar to that in the *N*-methyltriazolium series, however, with the feature that this movement is not pH-dependent (Figure 1, 2a). The second system described consists of a pH-sensitive bistable molecular machine, where the localization of the DB24C8 is constrained to the "right side" of the axle between the anilinium and the triazolium stations, depending on pH (Figures 1 and 2b).

RESULTS AND DISCUSSION

Synthesis of the [2]Rotaxane 3 Containing Two Molecular Stations. The interlocked [2]rotaxane **3** was obtained, via the end-capping strategy, using the copper(I)-catalyzed Huisgen[9] alkyne−azide 1,3-dipolar cycloaddition, also called "the CuAAC click-chemistry"[10] (Scheme 1), between the azido pyridinium mannosides **1** (1 equiv) and the terminal anilinium alkyne **2** (1 equiv) in the presence of the DB24C8 (2 equiv) and a catalytic amount of 2,6-lutidine (0.1 equiv) and $Cu(CH_3CN)_4PF_6$ (1 equiv).[7] The [2]rotaxane **3** was isolated in a 75% yield after silica gel chromatographic column purification (Scheme 1).

No [3]rotaxane was detected, demonstrating the poor affinity of the monosubstituted pyridinium amide moiety for the DB24C8.

Synthesis of the *N*-Methyl and *N*-Benzyltriazolium Stations and Actuation of the Molecular Machines. The *N*-methylation of the triazole moiety of **3** was realized using the iodomethane as reactant and solvent. After a counteranion exchange using ammonium hexafluorophosphate, the triazolium compound **4** was obtained in a high yield. At acidic pH, the DB24C8 resides around the best anilinium station, whereas in the [2]rotaxane **5**, an oscillation of the macrocycle between the pyridinium amide and the triazolium stations was observed at basic pH.[7]

In order to trap the macrocycle either on the "left" or on the "right" side of the encircled molecular axle, with respect to the triazole moiety, two different sequential steps were achieved. The first case that we envisaged was to trap the macrocycle

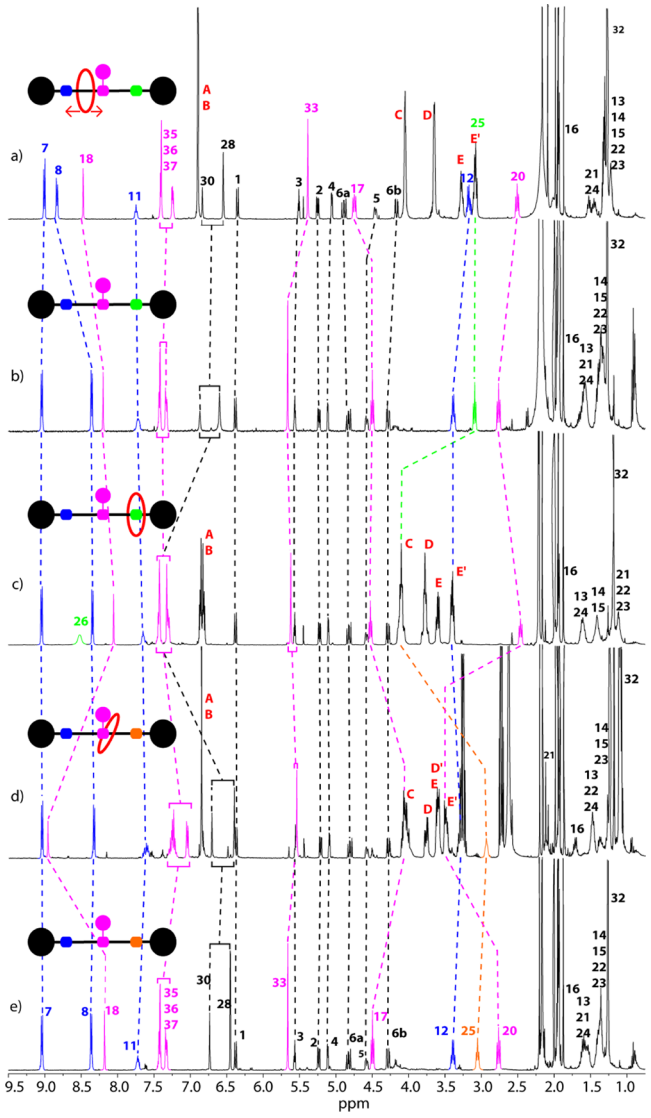

Figure 2. ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) the protonated [2]rotaxane **8**, (b) the protonated uncomplexed thread **8u** or **9u**, (c) the protonated [2]rotaxane **9**, (d) the deprotonated [2]rotaxane **10**, and (e) the deprotonated uncomplexed thread **10u**. The numbering and colorings correspond to the hydrogen assignments indicated in Scheme 1.

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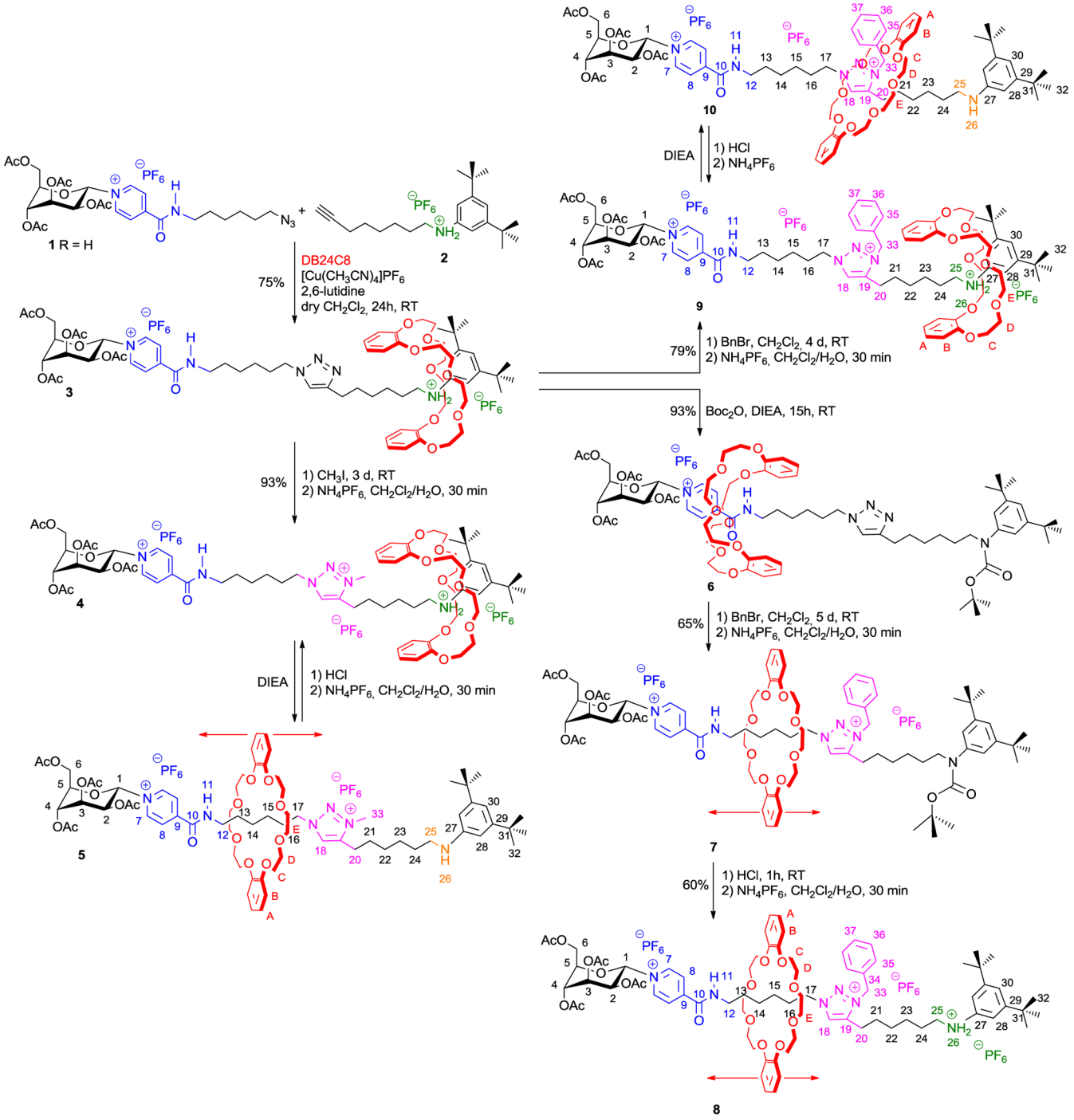
Scheme 1. Synthetic Routes to Oscillating or Bistable Molecular Machines Containing an Anilinium, a Mono-substituted Pyridinium Amide, and a Triazolium as Molecular Stations



between the monosubstituted pyridinium amide and the triazolium stations, whatever the pH, using a bulky benzyl side group as a steric molecular barrier. Thereby, in order to yield rotaxane **8**, in which the DB24C8 is located on the left side of the molecular axle with respect to the triazolium molecular barrier, the carbamoylated compound **6** was first synthesized, before being benzylated. The carbamoylation of the anilinium initially triggered the shuttling of the macrocycle around the pyridinium amide station, whereas subsequent benzylation of the triazole provided a new site of interaction for the DB24C8. This caused an oscillating movement of the macrocycle between the pyridinium amide station and the *N*-benzyltriazolium, suggesting, as already observed for rotaxane **5**, similar affinities of these two stations for the DB24C8. Subsequent decarbamoylation and acidification afforded the anilinium [2]rotaxane **8**. Even though the anilinium is a better binding site for the DB24C8, absolutely no change in the oscillating movement was noticed, demonstrating the efficient role of molecular barrier of the benzyl group, which trapped the macrocycle on only one compartment of the axle.

In addition, we envisaged the trapping of the macrocycle on the other side of the triazolium moiety, that is to say, between

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the anilinium and the triazolium stations. This was achieved in a more straightforward route than before since the macrocycle initially resides around the best anilinium molecular station. Thus, *N*-benzylation of the triazole moiety, followed by counteranion exchange, was first carried out on the protonated anilinium rotaxane **3** and afforded the [2]rotaxane **9** in a 79% yield. In this protonated compound, the DB24C8 resides around the best anilinium station. However, the deprotonation of the anilinium station, using the Hünig's base[11] diisopropylethylamine, triggers the shuttling of the DB24C8 around the *N*-benzyltriazolium station (rotaxane **10**). In comparison with the oscillating [2]rotaxane **7**, here no localization of the DB24C8 around the pyridinium amide station was noticed, demonstrating once again the efficient role of molecular barrier of the bulky benzyl side group. Furthermore, due to the steric hindrance of the benzyl group, differences in the localization of the DB24C8 around the triazolium station could be revealed by ^{1}H NMR spectroscopy between the [2]rotaxanes **8** and **10**.

Molecular Machinery on Rotaxane in the Benzyl Series. *Oscillating Molecular Machine* ***8****.* The comparison of ^{1}H NMR spectra between the protonated [2]rotaxane **8** and the uncomplexed thread **8u** reveals the interlocked molecular architecture and the localization of the DB24C8 along the threaded axle in **8** (Figure 2a,b). Indeed, the ^{1}H NMR signals for the hydrogens H_A−H_E belonging to the crown ether are noticed in rotaxane **8**, and among them, signals for hydrogens H_E are split, indicating that they are facing the two nonsymmetrical extremities of the encircled molecular axle. Interestingly, the hydrogens H_{17-18}, H_8, and to a lesser extent H_{11}, all belonging, to the triazolium and to the pyridinium amide stations, are more or less shifted downfield in the [2]rotaxane **8** (respectively, $\Delta\delta$ = +0.24, +0.28, +0.47, and +0.03 ppm) due to their hydrogen bonding interactions with the oxygen atoms of the DB24C8. Moreover, in **8**, the hydrogens H_{33} and H_{20}, which are, respectively, either part of the steric molecular benzyl barrier or just on the other side of it with respect to the DB24C8, experience the shielding effect of the aromatic ring of the DB24C8 (respectively, $\Delta\delta$ = −0.25 and −0.27 ppm). In a similar manner, the hydrogens of the aliphatic chain H_{12-15} and to a lesser extent H_{16} are all shielded ($\Delta\delta$ from −0.29 to −0.07 ppm) as a result of of their localization in the shielding cavity of the aromatic rings of the DB24C8 upon the oscillation of the DB24C8. No other significant variation of chemical shift is observed for the other hydrogens of the molecular axle and more especially for the hydrogens H_{25} belonging to the anilinium station. This last observation demonstrates the absence of any interaction between the anilinium station and the DB24C8. This also proves the efficient role of the benzyl group, which prevents the DB24C8 from shuttling until the best anilinium station. Instead, due to the steric constraint imposed by the molecular barrier, the macrocycle is obliged to interact with both the triazolium and the pyridinium amide stations, which have each very similar binding affinities for the DB24C8, but much poorer than that of anilinium. As already observed with the *N*-methyltriazolium **5**, a fast oscillation at the NMR time scale between these two stations occurred. This was revealed by the presence of only one set of NMR signals. Obviously, the deprotonation of the anilinium in **8** caused no change in the oscillating movement of the macrocycle because of the presence of the benzyl molecular barrier.

pH-Sensitive Bistable Molecular Machine ***9/10****.* The comparison between the ^{1}H NMR spectra of the protonated uncomplexed thread **9u** and the [2]rotaxane **9** reveals the presence and the localization of the DB24C8 (Figure 2b,c). As usual, the ^{1}H NMR signals for the hydrogen atoms of the crown ether H_{A-E} are split since they are facing the two nonsymmetrical ends of the encircled thread. More interestingly, only the chemical shift relative to the anilinium station, i.e., hydrogen atoms H_{25}, is tremendously shifted downfield in rotaxane **9** ($\Delta\delta$ = +1.02 ppm), due to their interactions by hydrogen bonding with the oxygen atoms of the DB24C8. At the same time, one can notice in **9** an upfield shift of the hydrogens H_{18} and H_{20-23} ($\Delta\delta$ from −0.14 to −0.44 ppm), suggesting a shielding effect due to their localization in the cavity of the aromatic ring of the DB24C8. No other variation in chemical shift was noticed, which is compatible with an evident localization of the DB24C8 around the best anilinium station. After deprotonation of the anilinium station, the macrocycle shuttles toward the sole triazolium station, even though we already reported that monosubstituted pyridinium amide was a molecular station of very similar but slightly better affinity for the DB24C8 than the triazolium one. This result is perfectly consistent with the fact that the benzyl moiety bonded to the triazolium station acts also as a steric molecular barrier that does not allow the macrocycle to pass over. This observation was demonstrated by the comparison between the ^{1}H NMR spectra of the protonated rotaxane **9** and the deprotonated rotaxane **10** (Figure 2c,d). Unsurprisingly, in **10**, an upfield shift is observed for the hydrogen atoms H_{25}, H_{28}, and H_{30} (respectively, $\Delta\delta$ = −1.06, −1.03, and −0.61 ppm), as a result of the deprotonation of the anilinium and the subsequent shuttling of the DB24C8. Concomitantly, the hydrogen atoms H_{18} and H_{20} belonging to the triazolium station experience a downfield shift (respectively, $\Delta\delta$ = +0.90 and +1.03 ppm). By the way, it is the first time we observed so marked a variation of chemical shift for triazolium hydrogens H_{20} in a [2]rotaxane. We assume that the restricted conformation adopted by the macrocycle around the triazolium is responsible for this strong interaction by hydrogen bonding between H_{20} and the oxygen atoms of the DB24C8. This is consistent with the presence of the bulky benzyl molecular barrier that traps the macrocycle on only one side of the triazolium station, more precisely around hydrogen atoms H_{20}. By comparison, it is interesting to notice that hydrogen atoms H_{20} are not involved in any hydrogen bonding interaction in rotaxane **8**, when the DB24C8 oscillates between the monosubstituted pyridinium amide and the triazolium station. On the contrary, in **8**, it is the hydrogen atoms H_{17} that interact by hydrogen bonding with the oxygen atoms of the DB24C8. To continue the discussion with rotaxane **10**, the hydrogen atoms H_{17} and to a lesser extent H_{33} and H_{35-37} are all more or less shielded due to their localization in the shielding cavity of the aromatic rings of the crown ether. No other variation in chemical shift was noticed for the other hydrogen atoms, especially for those of the monosubstituted pyridinium amide station, indicating unambiguously that the DB24C8 is not allowed to pass over the benzyl molecular barrier. The direct comparison of the deprotonated rotaxane **10** with the uncomplexed deprotonated thread **10u** confirmed the localization of the DB24C8 in **10** (Figure 2d,e), hence the molecular machinery between **9** and **10** upon variation of pH. In brief, as observed between the ^{1}H NMR spectra of rotaxanes **9** and **10**, the hydrogen atoms H_{18} and H_{20} of the thread **10u** are shifted downfield in the rotaxane **10** because of hydrogen bonding interactions, whereas H_{17} and to a lesser extent H_{33}, H_{35}, and

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H_{37} experience an upfield shift due to their localization in the shielding cavity of the aromatic rings of the DB24C8.

CONCLUSIONS

In conclusion, we have described two new molecular machines incorporating a bulky side group located in the middle of the encircled molecular axle. This bulky group acts as a kinetic molecular barrier and allows these molecular machines to be statistically unbalanced and away from their equilibrium in some conditions. In the reported [2]rotaxane molecular machines, the *N*-benzyltriazolium proved to serve as both a molecular station for the DB24C8 and a molecular barrier of sufficient hindrance so that the DB24C8 cannot pass over it. The macrocycle was trapped on either one side or the other side of the barrier, depending on the synthetic route. Thus, two translational isomers **8** and **9**, which are not in equilibrium with respect to each other, were synthesized and differ by the restrained localization of the DB24C8 along the surrounded molecular axle. The first [2]rotaxane molecular machine **8** is not pH-dependent: it undergoes an oscillating shuttling of its macrocycle between the monosubstituted pyridinium amide and the *N*-benzyltriazolium stations, whatever the presence of the best anilinium station, putting this system away from its more energetically favored *co*-conformation. The [2]rotaxane **9** behaves as a pH-sensitive bistable molecular machine. At the protonated state, the DB24C8 resides around the best anilinium station. However, deprotonation of the anilinium triggers the shuttling of the macrocycle toward the *N*-benzyltriazolium station. Here again, in **10**, and similarly to the former protonated oscillating system **8**, the system remains statistically unbalanced and not at the equilibrium due to the kinetic molecular barrier that sterically prevents the DB24C8 from interacting with the monosubstituted pyridinium amide station of almost comparable affinity. In both molecular machines, the interactions between the DB24C8 and the *N*-benzyltriazolium station appear different. Restraining the localization of a macrocycle around poorer molecular station along a thread, out of its most energetically favored *co*-conformation, could be of interest for future applications of molecular machines.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of argon unless otherwise indicated. The reagents were used as received without further purification. Dichloromethane was distilled over P_2O_5 and was degassed by bubbling Ar for 20 min. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates. Compounds were visualized by dipping the plates in an ethanolic solution of 10% sulphuric acid, ninhydrine, or an aqueous solution of $KMnO_4$, followed by heating. ^{1}H NMR and ^{13}C NMR spectra were obtained respectively at 400.13 and 100.62 MHz. Chemical shifts of ^{1}H NMR and ^{13}C NMR are given in ppm by using CH_3CN as reference (1.94 ppm for ^{1}H spectrum, and 118.26 ppm for ^{13}C spectrum CD_3CN). ^{1}H assignments were deduced from 2D ^{1}H−^{1}H NMR COSY experiments. ^{13}C assignments were deduced from 2D ^{13}C−^{1}H NMR HMQC experiments. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), br (broad), d (doublet), t (triplet), q (quartet), m (multiplet). Low and high-resolution ESI mass spectra were recorded on a Q-ToF I mass spectrometer fitted with an electrospray ion source.

Starting Materials. The starting materials **1** and **2** were synthesized according to the procedure described by Coutrot et al.[7]

Synthesis and Characterizations of [2]Rotaxanes 3 and 6–10. *Synthesis of Rotaxane 3.* In a typical procedure, to a solution of **1** (461 mg, 0.63 mmol, 1 equiv), compound **2** (293 mg, 0.63 mmol, 1 equiv), and DB24C8 (571 mg, 1.27 mmol, 2 equiv) in dry CH_2Cl_2 (3 mL) were successively added $Cu(CH_3CN)_4PF_6$ (238 mg, 0.63 mmol, 1 equiv) and 2,6-lutidine (7 μL, 0.06 mmol, 0.1 equiv). The mixture was stirred at rt for 24 h, and then the solvent was removed under vacuo. The crude was directly purified by chromatography on a silica gel column (solvent gradient elution: CH_2Cl_2, then 25/75 acetone/CH_2Cl_2) to obtain the rotaxane **3** (783 mg, 75%) as a slightly yellow solid. Mp 78−85 °C. R_f 0.62 (40/60 acetone/CH_2Cl_2). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.04 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.60−8.42 (br s, 2H, H_{26}), 8.35 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 7.64 (br t, 1H, H_{11}), 7.41 (s, 1H, H_{18}), 7.39 (t, 1H, $^4J_{H30-H28}$ =1.6 Hz, H_{30}), 7.33 (d, 2H, $^4J_{H28-H30}$ = 1.6 Hz, H_{28}), 6.91−6.80 (m, 8H, H_A H_B), 6.37 (d, 1H, $^3J_{H1-H2}$ = 9.0 Hz, H_1), 5.56 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.4 Hz, H_3), 5.22 (dd, 1H, $^3J_{H2-H1}$ = 9.0 Hz, $^3J_{H2-H3}$ = 3.4 Hz, H_2), 5.10 (dd, 1H, $^3J_{H4-H3}$ = 3.4 Hz, $^3J_{H4-H5}$ = 2.1 Hz, H_4), 4.81 (dd, 1H, $^3J_{H6a-H6b}$ = 12.7 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.61−4.54 (m, 1H, H_5), 4.31−4.25 (m, 3H, H_{17} H_{6b}), 4.19−4.05 (m, 10H, H_C H_{25}), 3.84−3.72 (m, 8H, H_D), 3.65−3.58 (m, 4H, H_E), 3.44−3.36 (m, 6H, $H_{E'}$ H_{12}), 2.46 (t, 2H, $^3J_{H20-H21}$ = 7.6 Hz, H_{20}), 2.20 and 2.16 and 2.00 and 1.87 (4*s, 12H, CH_3CO), 1.86−1.80 (m, 2H, H_{16}), 1.67−1.56 (m, 4H, H_{13} H_{24}), 1.45−1.27 (m, 6H, H_{14} H_{15} H_{21}), 1.25−1.10 (m, 4H, H_{22} H_{23}), 1.18 (s, 18H, H_{32}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.5 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.4 (C_{10}), 153.6 (C_{29}), 153.0 (C_9), 148.4 (C_{19}), 148.3 (Cq D24C8), 144.1 (C_7), 136.1(C_{27}), 127.2 (C_8), 124.9 (C_{30}), 122.1 and 113.2 (C_A C_B), 122.0 (C_{18}), 117.8 (C_{28}), 89.1 (C_1), 78.6 (C_5), 71.6 (C_E), 71.0 (C_D), 69.6 (C_2), 69.1 (C_C), 68.3 (C_4), 67.4 (C_3), 60.9 (C_6), 51.6 (C_{25}), 50.4 (C_{17}), 40.9 (C_{12}), 35.6 (C_{31}), 31.4 (C_{32}), 30.8 (C_{16}), 29.9 and 29.4 and 29.4 and 28.2 and 26.7 and 26.6 and 26.4 (C_{13} C_{14} C_{15} C_{21} C_{22} C_{23} C_{24}), 25.9 (C_{20}), 21.0 and 20.9 and 20.8 and 20.4 ($\underline{C}H_3CO$). HRMS (ESI) [M − 2PF6]$^{2+}$ calculated for $[C_{72}H_{104}N_6O_{18}]^{2+}$: 670.3704, found 670.3683

Synthesis of Rotaxane 6. To a solution of rotaxane **3** (53 mg, 0.03 mmol, 1 equiv) in CH_2Cl_2 (2 mL) were introduced successively DIEA (11 μL, 0.06 mmol, 2 equiv) and Boc_2O (21 mg, 0.09 mmol, 3 equiv). The mixture was stirred at room temperature for 15 h. After solvent evaporation, the crude was purified by chromatography on a silica gel column (elution gradient: 5/95 acetone/CH_2Cl_2, then 10/90) to yield rotaxane **6** (48 mg, 93%) as a white foam. R_f 0.43 (acetone/CH_2Cl_2 20/80). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.31 (d, 2H, $^3J_{H8-H7}$ = 6.8 Hz, H_8), 9.00 (d, 2H, $^3J_{H7-H8}$ = 6.8 Hz, H_7), 7.96 (t, 1H, $^3J_{H11-H12}$ = 7.0 Hz, H_{11}), 7.53−7.42 (br s, 1H, H_7), 7.30 (t, 1H, $^4J_{H30-H28}$ = 1.7 Hz, H_{30}), 7.03 (d, 2H, $^4J_{H28-H30}$ = 1.7 Hz, H_{28}), 7.02−6.90 (m, 8H, H_A H_B), 6.34 (d, 1H, $^3J_{H1-H2}$ = 9.2 Hz, H_1), 5.48−5.43 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.5 Hz, H_3), 5.26 (dd, 1H, $^3J_{H2-H1}$ = 9.1 Hz, $^3J_{H2-H3}$ = 3.5 Hz, H_2), 4.99 (dd, 1H, $^3J_{H4-H3}$ = 3.5 Hz, $^3J_{H4-H5}$ = 1.8 Hz, H_4), 4.95 (dd, 1H, $^2J_{H6a-H6b}$ = 12.9 Hz, $^3J_{H6a-H5}$ = 9.7 Hz, H_{6a}), 4.37−4.32 (m, 1H, H_5), 4.19 (t, 2H, $^3J_{H17-H16}$ = 7.1 Hz, H_{17}), 4.16−4.02 (m, 9H, H_{6b} H_C), 3.73−3.53 (m, 10H, H_{25} H_D), 3.20−3.07 (m, 10H, H_{12} H_E), 2.70−2.57 (m, 6H, H_{20} $H_{E'}$), 2.13 and 2.00 and 1.97 and 1.84 (4*s, 12H, CH_3CO), 1.71−1.63 (m, 2H, H_{16}), 1.62−1.53 (m, 2H, H_{21}), 1.51−1.41 (m, 2H, H_{24}), 1.39 (s, 9H, H_{35}), 1.29 (s, 18H, H_{32}), 1.35−1.26 (m, 4H, H_{22} H_{23}), 1.16−0.99 (m, 6H, H_{13} H_{14} H_{15}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.7 and 170.2 and 170.0 and 169.8 ($\underline{C}OCH_3$), 163.0 (C_{10}), 155.4 (C_{33}), 152.4 (C_9), 152.0 (C_{29}), 148.6 ($C_{q\ DB24C8}$), 143.1 (C_{27}), 142.8 (C_7), 130.1 (C_8), 122.4 (C_{28}), 122.3 (C_{18}), 122.1 and 112.8 and 112.7 (C_A C_B), 120.6 (C_{30}), 88.6 (C_1), 80.1 (C_{34}), 78.9 (C_5), 70.3 (C_E C_D), 69.0 and 69.0 (C_2 C_C), 68.1 (C_4), 67.3 (C_3), 60.3 (C_6), 50.6 (C_{17} C_{25}), 40.6 (C_{12}), 35.4 (C_{31}), 31.5 (C_{32}), 30.6 and 30.1 and 29.4 and 29.3 and 28.9 and 27.0 and 26.5 and 26.5 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 28.5 (C_{35}), 26.0 (C_{20}), 21.0 and 20.8 and 20.8 and 20.7 ($\underline{C}H_3CO$). HRMS (ESI) [M − PF_6]$^+$ calculated for $[C_{77}H_{111}N_6O_{20}]^+$: 1439.7853, found 1439.7863

Synthesis of Rotaxane 7. To a solution of rotaxane **6** (40 mg, 0.025 mmol, 1 equiv) in CH_2Cl_2 (4 mL) was introduced benzyl bromide (2 mL). After 5 days of stirring at room temperature, a solution of NH_4PF_6 (20 mg, 0.13 mmol, 5 equiv) in Milli-Q water (5 mL) was added. The biphasic mixture was vigorously stirred for 30 min. After separation, the aqueous phase was extracted with CH_2Cl_2 (2 × 10

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mL). The organic phases were combined, dried over $MgSO_4$, and concentrated. The crude was purified by chromatography on a silica gel column (elution gradient: 10/90 acetone/CH_2Cl_2, then 15/85) to give rotaxane **7** (30 mg, 65%) as a pale yellow solid. R_f 0.50 (acetone/CH_2Cl_2 20/80). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.01 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.83 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 8.46 (s, 1H, H_7), 7.77 (t, 1H, $^3J_{H11-H12}$ = 7.0 Hz, H_{11}), 7.41−7.37 and 7.25−7.21 (2*m, 5H, H_{35} H_{36} H_{37}), 7.31 (t, 1H, $^4J_{H30-H28}$ = 1.7 Hz, H_{30}), 7.02 (d, 2H, $^4J_{H28-H30}$ = 1.7 Hz, H_{28}), 6.92−6.85 (m, 8H, H_A H_B), 6.35 (d, 2H, $^3J_{H1-H2}$ = 9.1 Hz, H_1), 5.51 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.4 Hz, H_3), 5.37 (s, 2H, H_{33}), 5.24 (dd, 1H, $^3J_{H2-H1}$ = 9.1 Hz, $^3J_{H2-H3}$ = 3.4 Hz, H_2), 5.05 (dd, 1H, $^3J_{H4-H3}$ = 3.4 Hz, $^3J_{H4-H5}$ = 1.9 Hz, H_4), 4.89 (dd, 1H, $^2J_{H6a-H6b}$ = 12.8 Hz, $^3J_{H6a-H5}$ = 9.4 Hz, H_{6a}), 4.78−4.70 (t, 2H, $^3J_{H17-H16}$ = 7.9 Hz, H_{17}), 4.48−4.43 (ddd, 1H, $^3J_{H5-H6a}$ = 9.4 Hz, $^3J_{H5-H6b}$ = 3.6 Hz, $^3J_{H4-H4}$ = 3.4 Hz, H_5), 4.17 (dd, 1H, $^2J_{H6b-H6a}$ = 12.9 Hz, $^3J_{H6b-H5}$ = 3.6 Hz, H_{6b}), 4.11−3.98 (m, 8H, H_C), 3.72−3.60 (m, 8H, H_D), 3.56 (t, 2H, $^3J_{H25-H24}$ = 7.4 Hz, H_{25}), 3.32−3.23 (m, 4H, H_E), 3.21−3.13 (m, 2H, H_{12}), 3.12−3.05 (m, 4H, $H_{E'}$), 2.47 (t, 2H, $^3J_{H20-H21}$ = 7.7 Hz, H_{20}), 2.16 and 2.08 and 1.98 and 1.86 (4*s, 12H, $\underline{C}H_3CO$), 2.05−1.92 (m, 2H, H_{16}), 1.44−1.35 (m, 4H, H_{21} H_{24}), 1.38 (s, 9H, H_{40}), 1.34−1.17 (m, 10H, H_{13} H_{14} H_{15} H_{22} H_{23}), 1.30 (s, 18H, H_{32}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.6 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.7 (C_{10}), 155.4 (C_{38}), 152.6 (C_9), 152.1 (C_{29}), 148.6 ($C_{q\ DB24C8}$), 143.9 (C_{19}), 143.5 (C_7), 143.0 (C_{27}), 130.1 and 130.1 and 129.3 (C_{35} C_{36} C_{37}), 129.5 (C_{18}), 128.7 (C_8), 122.3 (C_{28}), 121.9 and 112.8 (C_A C_B), 120.7 (C_{30}), 88.8 (C_1), 80.2 (C_{39}), 78.8 (C_5), 71.0 (C_E), 70.5 (C_D), 69.3 (C_2), 69.0 (C_C), 68.2 (C_4), 67.4 (C_3), 60.6 (C_6), 54.6 and 54.5 (C_{17} C_{33}), 50.5 (C_{25}), 40.7 (C_{12}), 35.4 (C_{31}), 31.5 (C_{32}), 29.4 and 29.0 and 28.8 and 28.3 and 27.6 and 26.8 and 26.7 and 26.3 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 28.5 (C_{40}), 23.6 (C_{20}), 21.0 and 20.8 and 20.6 and 18.6 (CH_3CO). HRMS (ESI) $[M - 2PF_6]^{2+}$ calculated for $[C_{84}H_{118}N_6O_{20}]^{2+}$: 765.4200, found 765.4195

Synthesis of Rotaxane ***8***. To the neat rotaxane **7** (25 mg, 0.014 mmol, 1 equiv) was added a solution of HCl 2 M in Et_2O (4 mL). After stirring for 1 h at room temperature, the ethereal phase was removed, and then the crude was diluted in CH_2Cl_2 (5 mL). A solution of NH_4PF_6 (11 mg, 0.068 mmol, 5 equiv) in Milli-Q water (5 mL) was introduced, and the biphasic mixture was stirred vigorously for 30 min. After separation, the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The organic phases were combined, dried over $MgSO_4$, and concentrated. The crude was purified by chromatography on a silica gel column (elution gradient: CH_2Cl_2, 5/95 acetone/CH_2Cl_2, then 25/75) to yield rotaxane **8** as its deprotonated form. Thus a solution of HCl 2 M in Et_2O (4 mL) was added. After stirring for 1 h at room temperature, the ethereal phase was removed, and the crude was diluted in CH_2Cl_2 (5 mL). A solution of NH_4PF_6 (11 mg, 0.068 mmol, 5 equiv) in Milli-Q water (5 mL) was introduced, and the biphasic mixture was stirred vigorously for 30 min. After separation, the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The organic phases were combined, dried over $MgSO_4$, and concentrated to provide the protonated rotaxane **8** (15 mg, 60%) as a pale yellow solid. R_f 0.56 (acetone/CH_2Cl_2 30/70). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.01 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.83 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 8.47 (s, 1H, H_{18}), 7.75 (t, 1H, $^3J_{H11-H12}$ = 6.8 Hz, H_{11}), 7.43−7.38 and 7.27−7.22 (2*m, 5H, H_{35} H_{36} H_{37}), 6.92−6.86 (m, 8H, H_A H_B), 6.84 (t, 1H, $^4J_{H30-H28}$ = 1.5 Hz, H_{30}), 6.55 (d, 2H, $^4J_{H28-H30}$ = 1.5 Hz, H_{28}), 6.35 (d, 1H, $^3J_{H1-H2}$ = 9.1 Hz, H_1), 5.51 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.5 Hz, H_3), 5.39 (s, 2H, H_{33}), 5.25 (dd, 1H, $^3J_{H2-H1}$ = 9.1 Hz, $^3J_{H2-H3}$ = 3.5 Hz, H_2), 5.06 (dd, 1H, $^3J_{H4-H3}$ = 3.5 Hz, $^3J_{H4-H5}$ = 1.9 Hz, H_4), 4.89 (dd, 1H, $^2J_{H6a-H6b}$ = 12.8 Hz, $^3J_{H6a-H5}$ = 9.4 Hz, H_{6a}), 4.75 (t, 2H, $^3J_{H17-H16}$ = 7.9 Hz, H_{17}), 4.45 (ddd, 1H, $^3J_{H5-H6a}$ = 9.4 Hz, $^3J_{H5-H6b}$ = 3.6 Hz, $^3J_{H5-H4}$ = 1.9 Hz, H_5), 4.17 (dd, 1H, $^2J_{H6b-H6a}$ = 12.8 Hz, $^3J_{H6b-H5}$ = 3.6 Hz, H_{6b}), 4.10−3.99 (m, 8H, H_C), 3.71−3.57 (m, 8H, H_D), 3.32−3.22 (m, 4H, H_E), 3.21−3.12 (m, 2H, H_{12}), 3.11−3.04 (m, 6H, H_{25} $H_{E'}$), 2.51 (t, 2H, $^3J_{H20-H21}$ = 7.6 Hz, H_{20}), 2.16 and 2.09 and 1.98 and 1.86 (4*s, 12H, CH_3CO), 2.06−1.96 (m, 2H, H_{16}), 1.57−1.49 (m, 2H, H_{24}), 1.48−1.38 (m, 2H, H_{21}), 1.35−1.25 (m, 6H H_{13} H_{22} H_{23}), 1.27 (s, 18H, H_{32}), 1.24−1.19 (m, 4H, H_{14} H_{15}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 170.2 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.7 (C_{10}), 152.7 (C_9 C_{29}), 148.7 ($C_{q\ DB24C8}$), 144.0 (C_{19}), 143.5 (C_7), 133.2 (C_{34}), 130.2 and 130.2 and 129.4 (C_{35} C_{36} C_{37}), 129.7 (C_{18}), 128.8 (C_8), 122.0 and 112.9 (C_A C_B), 113.5 (C_{30}), 109.1 (C_{28}), 88.9 (C_1), 78.9(C_5), 71.1 (C_E), 70.6 (C_D), 69.3 (C_2), 69.1 (C_C), 68.3 (C_4), 67.5 (C_3), 60.7 (C_6), 54.6 (C_{17} C_{33}), 45.2 (C_{25}), 40.8 (C_{12}), 35.4 (C_{31}), 31.7 (C_{32}), 29.5 and 29.1 and 27.7 and 27.4 and 27.1 and 26.8 and 26.4 (C_{13} C_{14} C_{15} C_{21} C_{22} C_{23} C_{24}), 28.4 (C_{16}), 23.7 (C_{20}), 21.0 and 20.9 and 20.6 and 20.5 ($\underline{C}H_3CO$). HRMS (ESI) $[M - 3PF_6]^{3+}$ calculated for $[C_{79}H_{111}N_6O_{18}]^{3+}$: 477.2652, found 477.2624

Synthesis of Rotaxane ***9***. To a solution of rotaxane **3** (109 mg, 0.067 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was introduced benzyl bromide (3 mL). After 4 days of stirring at room temperature, a solution of NH_4PF_6 (54 mg, 0.33 mmol, 5 equiv) in Milli-Q water (5 mL) was added. The biphasic mixture was stirred vigorously for 30 min at room temperature. After separation, the aqueous layer was extracted with CH_2Cl_2 (2 × 15 mL). Organic layers were combined, dried over $MgSO_4$, and then concentrated. The crude was purified by chromatography on a silica gel column (elution gradient: 20/80 acetone/CH_2Cl_2, then 35/75) to yield rotaxane **9** (98 mg, 79%) as a white foam. R_f 0.40 (acetone/CH_2Cl_2 40/60). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.05 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.58−8.45 (br s, 2H, H_{26}), 8.35 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 8.06 (s, 1H, H_{18}), 7.65 (t, 1H, $^3J_{H11-H12}$ = 6.9 Hz, H_{11}), 7.47−7.39 and 7.34−7.28 (m, 6H, H_{30} H_{35} H_{36} H_{37}), 7.32 (d, 2H, $^4J_{H28-H30}$ = 1.6 Hz, H_{28}), 6.89−6.79 (m, 8H, H_A H_B), 6.38 (d, 1H, $^3J_{H1-H2}$ = 9.0 Hz, H_1), 5.62 (s, 2H, H_{33}), 5.57 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.4 Hz, H_3), 5.22 (dd, 1H, $^3J_{H2-H1}$ = 9.0 Hz, $^3J_{H2-H3}$ = 3.4 Hz, H_2), 5.11 (dd, 1H, $^3J_{H4-H2}$ = 3.4 Hz, $^3J_{H4-H5}$ = 2.0 Hz, H_4), 4.82 (dd, 1H, $^2J_{H6a-H6b}$ = 12.7 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.58 (ddd, 1H, $^3J_{H5-H6a}$ = 9.2 Hz, $^3J_{H5-H6b}$ = 3.7 Hz, $^3J_{H5-H4}$ = 2.0 Hz, H_5), 4.53 (t, 2H, $^3J_{H17-H16}$ = 7.2 Hz, H_{17}), 4.28 (dd, 1H, $^2J_{H6b-H6a}$ = 12.7 Hz, $^3J_{H6b-H5}$ = 3.7 Hz, H_{6b}), 4.16−4.05 (m, 10H, H_{25} H_C), 3.83−3.72 (m, 8H, H_D), 3.63−3.56 (m, 4H, H_E), 3.43−3.36 (m, 6H, H_{12} $H_{E'}$), 2.46 (t, 2H, $^3J_{H20-H21}$ = 7.5 Hz, H_{20}), 2.21 and 2.16 and 2.00 and 1.87 (4*s, 12H, CH_3CO), 2.00−1.96 (m, 2H, H_{16}), 1.67−1.53 (m, 4H, H_{13} H_{24}), 1.48−1.34 (m, 4H, H_{14} H_{15}), 1.28−1.04 (m, 6H, H_{21} H_{22} H_{23}), 1.19 (s, 18H, H_{32}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.6 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.5 (C_{10}), 153.7 (C_{29}), 153.0 (C_9), 148.4 ($C_{q\ DB24C8}$), 145.4 (C_{19}), 144.1 (C_7), 136.1 (C_{27}), 132.9 (C_{34}), 130.3 and 130.2 and 129.1 (C_{35} C_{36} C_{37}), 128.9 (C_{18}), 127.2 (C_8), 125.0 (C_{30}), 122.2 and 113.3 (C_A C_B), 117.7 (C_{28}), 89.1 (C_1), 78.7 (C_5), 71.6 (C_E), 71.0 (C_D), 69.6 (C_2), 69.1 (C_C), 68.3 (C_4), 67.4 (C_3), 60.9 (C_6), 55.1 (C_{33}), 54.7 (C_{17}), 51.5 (C_{25}), 40.9 (C_{12}), 35.6 (C_{31}), 31.4 (C_{32}), 29.6 and 29.4 and 29.1 and 28.0 and 27.5 and 26.7 and 26.3 and 26.2 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 23.7 (C_{20}), 21.0 and 20.8 and 20.8 and 20.4 ($\underline{C}H_3CO$). HRMS (ESI) $[M - 3PF_6]^{3+}$ calculated for $[C_{79}H_{111}N_6O_{18}]^{3+}$: 477.2650, found 477.2624

Synthesis of Rotaxane ***10***. To a solution of rotaxane **9** in CD_3CN was introduced DIEA to provide the deprotonated rotaxane **10**. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.05 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.96 (s, 1H, H_{18}), 8.33 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 7.59 (t, 1H, $^3J_{H11-H12}$ = 6.9 Hz, H_{11}), 7.33−7.18 and 7.07−7.02 (2*m, 5H, H_{35} H_{36} H_{37}), 6.87−6.83 (m, 8H, H_A H_B), 6.71 (t, 1H, $^4J_{H30-H28}$ = 1.6 Hz, H_{30}), 6.40 (d, 2H, $^4J_{H28-H30}$ = 1.6 Hz, H_{28}), 6.38 (d, 1H, $^3J_{H1-H2}$ = 9.1 Hz, H_1), 5.56 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.5 Hz, H_3), 5.54 (s, 2H, H_{33}), 5.22 (dd, 1H, $^3J_{H2-H1}$ = 9.1 Hz, $^3J_{H2-H3}$ = 3.5 Hz, H_2), 5.10 (dd, 1H, $^3J_{H4-H3}$ = 3.5 Hz, $^3J_{H4-H5}$ = 2.0 Hz, H_4), 4.81 (dd, 1H, $^2J_{H6a-H6b}$ = 12.7 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.58 (ddd, 1H, $^3J_{H5-H6a}$ = 9.2 Hz, $^3J_{H5-H6b}$ = 3.7 Hz, $^3J_{H5-H4}$ = 2.0 Hz, H_5), 4.28 (dd, $^2J_{H6b-H6a}$ = 12.7 Hz, $^3J_{H6b-H5}$ = 3.7 Hz, H_{6b}), 4.11−3.95 (m, 10H, H_{17} H_C), 3.80−3.73 (m, 4H, H_D), 3.64−3.56 (m, 8H, H_E $H_{D'}$), 3.53−3.45 (m, 6H, $H_{E'}$ H_{20}), 3.34−3.24 (m, 2H, H_{12}), 2.94 (t, 2H, $^3J_{H25-H24}$ = 6.0 Hz, H_{25}), 2.15−2.05 (m, 2H, H_{21}), 2.21 and 2.16 and 2.00 and 1.87 (4*s, 12H, CH_3CO), 1.76−1.67 (m, 2H, H_{16}), 1.54−1.43 (m, 6H, H_{13} H_{22} H_{24}), 1.41−1.30 (m, 4H, H_{14} H_{23}), 1.24 (s, 18H, H_{32}), 1.11−1.08 (m, 2H, H_{15}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.6 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.4 (C_{10}), 152.9 (C_9), 152.2 (C_{29}), 149.1 (C_{27}), 148.7 ($C_{q\ DB24C8}$), 144.1 (C_7), 130.5 (C_{18}), 129.7 and

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129.5 and 128.9 (C_{35} C_{36} C_{37}), 127.2 (C_8), 121.9 and 113.3 (C_A C_B), 111.8 (C_{30}), 107.9 (C_{28}), 89.0 (C_1), 78.6 (C_5), 71.9 (C_E), 70.8 (C_D), 69.6 (C_2), 69.5 (C_C), 68.2 (C_4), 67.41 (C_3), 60.9 (C_6), 53.9 and 53.8 (C_{17} C_{33}), 44.3 (C_{44}), 40.8 (C_{12}), 35.2 (C_{31}), 31.6 (C_{32}), 29.8 and 29.7 and 29.6 and 29.3 and 29.2 and 27.9 and 26.5 and 26.2 and 26.1 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 23.7 (C_{20}), 20.9 and 20.8 and 20.7 and 20.4 ($\underline{C}H_3CO$). HRMS (ESI) $[M - PF_6]^+$ calculated for $[C_{79}H_{110}F_6N_6O_{18}P]^+$: 1575.7518, found 1575.7520

Synthesis and Characterizations of the Uncomplexed Threads 7u, 9u, and 10u. *Synthesis of Compound 7u.* To a solution of compound **6u**[7] (112 mg, 0.098 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was introduced benzyl bromide (3 mL). After stirring for 5 days at room temperature, a solution of NH_4PF_6 (80 mg, 0.49 mmol, 5 equiv) in Milli-Q water (5 mL) was added. The biphasic mixture was vigorously stirred for 30 min. After separation, the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The organic phases were combined, dried over $MgSO_4$, and concentrated. The crude was purified by chromatography on a silica gel column (elution gradient: 15/85 acetone/CH_2Cl_2, puis 35/65) to yield compound **7u** (81 mg, 60%) as a colorless oil. R_f 0.43 (acetone/CH_2Cl_2 30/70). ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.06 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.36 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 8.19 (s, 1H, H_{18}), 7.66 (t, 1H, $^3J_{H11-H12}$ = 6.9 Hz, H_{11}), 7.44−7.38 and 7.34−7.30 (2*m, 6H, H_{30} H_{35} H_{36} H_{37}), 7.02 (d, 2H, $^4J_{H28-H30}$ = 1.7 Hz, H_{28}), 6.39 (d, 1H, $^3J_{H1-H2}$ = 9.1 Hz, H_1), 5.65 (s, 2H, H_{33}), 5.57 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.4 Hz, H_3), 5.22 (dd, 1H, $^3J_{H2-H1}$ = 9.0 Hz, $^3J_{H2-H3}$ = 3.4 Hz, H_2), 5.10 (dd, 1H, $^3J_{H4-H3}$ = 3.4 Hz, $^3J_{H4-H5}$ = 2.0 Hz, H_4), 4.82 (dd, 1H, $^2J_{H6a-H6b}$ = 12.7 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.59 (ddd, 1H, $^3J_{H5-H6a}$ = 9.2 Hz, $^3J_{H5-H6b}$ = 3.7 Hz, $^3J_{H5-H4}$ = 2.0 Hz, H_5), 4.51 (t, 2H, $^3J_{H17-H16}$ = 7.2 Hz, H_{17}), 4.29 (dd, 1H, $^2J_{H6b-H6a}$ = 12.8 Hz, $^3J_{H6b-H5}$ = 3.7 Hz, H_{6b}), 3.57 (t, 2H, $^3J_{H25-H24}$ = 7.1 Hz, H_{25}), 3.40 (q, 2H, $^3J_{H12-H11}$ = $^3J_{H12-H13}$ = 6.9 Hz, H_{12}), 2.73 (t, 2H, $^3J_{H20-H21}$ = 7.7 Hz, H_{20}), 2.21 and 2.17 and 2.00 and 1.88 (4*s, 12H, $\underline{C}H_3CO$), 2.01−1.93 (m, 2H, H_{16}), 1.66−1.57 (m, 2H, H_{13}), 1.56−1.47 (m, 2H, H_{21}), 1.47−1.34 (m, 6H, H_{14} H_{15} H_{24}), 1.38 (s, 9H, H_{40}), 1.30 (s, 18H, H_{32}), 1.33−1.20 (m, 4H, H_{22} H_{23}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.5 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.5 (C_{10}), 155.4 (C_{38}), 152.9 (C_9), 152.1 (C_{29}), 145.5 (C_{19}), 144.1 (C_7), 143.0 (C_{27}), 132.9 (C_{34}), 130.1 and 130.1 and 129.1 (C_{18} C_{35} C_{36} C_{37}), 127.2 (C_8), 122.3 (C_{28}), 120.7 (C_{30}), 89.0 (C_1), 80.2 (C_{39}), 78.6 (C_5), 69.6 (C_2), 68.2 (C_4), 67.4 (C_3), 60.9 (C_6), 55.1 (C_{33}), 54.6 (C_{17}), 50.4 (C_{25}), 40.8 (C_{12}), 35.4 (C_{31}), 31.5 (C_{32}), 29.5 and 29.2 and 28.9 and 28.5 and 27.5 and 26.6 and 26.5 and 26.0 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 23.7 (C_{20}), 20.9 and 20.8 and 20.7 and 20.4 ($\underline{C}H_3CO$). MS (ESI) $[M - 2PF_6]^{2+}$ calculated for $[C_{60}H_{86}N_6O_{12}]^{2+}$: 541.32, found 541.31. HRMS (ESI) $[M - 2PF_6]^{2+}$ calculated for $[C_{60}H_{86}N_6O_{12}]^{2+}$: 541.3152, found 541.3192

*Synthesis of Compound **8u** (Equivalent to **9u**).* Compound **7u** (25 mg, 0.018 mmol, 1 equiv) was dissolved in a solution of HCl 2 M in Et_2O (3 mL). After stirring for 1 h at room temperature, the ethereal phase was removed, and then a solution of NH_4PF_6 (15 mg, 0.09 mmol, 5 equiv) in Milli-Q water (5 mL) was introduced. After stirring for 30 min, the precipitate was filtered and then dissolved in CH_2Cl_2. The organic phase was dried over $MgSO_4$ and then concentrated to yield compound **8u** (15 mg, 60%) as a colorless oil. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.04 (d, 2H, $^3J_{H7-H8}$ = 6.7 Hz, H_7), 8.36 (d, 2H, $^3J_{H8-H7}$ = 6.7 Hz, H_8), 8.20 (s, 1H, H_{18}), 7.75−7.69 (m, 1H, H_{11}), 7.46−7.39 and 7.37−7.30 (2*m, 5H, H_{35} H_{36} H_{37}), 6.89−6.84 (br s, 1H, H_{30}), 6.62−6.57 (br s, 2H, H_{28}), 6.38 (d, 1H, $^3J_{H1-H2}$ = 9.1 Hz, H_1), 5.66 (s, 2H, H_{33}), 5.56 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.5 Hz, H_3), 5.23 (dd, 1H, $^3J_{H2-H1}$ = 9.0 Hz, $^3J_{H2-H3}$ = 3.5 Hz, H_2), 5.11 (dd, 1H, $^3J_{H4-H3}$ = 3.5 Hz, $^3J_{H4-H5}$ = 2.0 Hz, H_4), 4.83 (dd, 1H, $^2J_{H6a-H6b}$ = 12.7 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.58 (ddd, 1H, $^3J_{H5-H6a}$ = 9.2 Hz, $^3J_{H5-H6b}$ = 3.7 Hz, $^3J_{H5-H4}$ = 2.0 Hz, H_5), 4.50 (t, 2H, $^3J_{H17-H16}$ = 7.1 Hz, H_{17}), 4.28 (dd, 1H, $^2J_{H6b-H6a}$ = 12.7 Hz, $^3J_{H6b-H5}$ = 3.7 Hz, H_{6b}), 3.39 (dd, 2H, $^3J_{H12-H13}$ = 13.4 Hz, $^3J_{H12-H11}$ = 6.7 Hz, H_{12}), 3.09 (t, 2H, $^3J_{H25-H24}$ = 7.1 Hz, H_{25}), 2.76 (t, 2H, $^3J_{H20-H21}$ = 7.7 Hz, H_{20}), 2.21 and 2.16 and 2.00 and 1.87 (4*s, 12H, CH_3CO), 1.97−1.92 (m, 2H, H_{16}), 1.67−1.52 (m, 6H, H_{13} H_{21} H_{24}), 1.44−1.25 (m, 8H, H_{14} H_{15} H_{22} H_{23}), 1.27 (s, 18H, H_{32}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 171.6 and 170.3 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.5 (C_{10}), 153.0 (C_9), 152.7 (C_{29}), 150.0 (C_{27}), 145.6 (C_{19}), 144.2 (C_7), 133.0 (C_{34}), 130.3 and 130.2 and 129.6 and 129.2 (C_{18} C_{35} C_{36} C_{37}), 127.3 (C_8), 113.2 (C_{30}), 109.6 (C_{28}), 89.1 (C_1), 78.7 (C_5), 69.6 (C_2), 68.2 (C_4), 67.5 (C_3), 60.9 (C_6), 55.2 (C_{33}), 54.7 (C_{17}), 45.3 (C_{25}), 40.9 (C_{12}), 35.4 (C_{31}), 31.6 (C_{32}), 29.6 and 29.5 and 29.4 and 28.9 and 27.6 and 27.0 and 26.7 and 26.1 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 23.6 (C_{20}), 21.0 and 20.9 and 20.8 and 20.5 ($\underline{C}H_3CO$). MS (ESI) $[M - 3PF_6]^{3+}$ calculated for $[C_{55}H_{79}N_6O_{10}]^{3+}$: 327.86, found 328.08. HRMS (ESI) $[M - PF_6]^+$ calculated for $[C_{55}H_{79}N_6O_{10}F_{12}P_2]^+$: 1273.5141, found 1273.5115

*Synthesis of Compound **10u**.* To a solution of **8u** in CD_3CN was added DIEA to provide compound **10u**. ^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 9.04 (d, 2H, $^3J_{H7-H8}$ = 6.9 Hz, H_7), 8.36 (d, 2H, $^3J_{H8-H7}$ = 6.9 Hz, H_8), 8.18 (s, 1H, H_{18}), 7.72 (t, 1H, $^3J_{H11-H12}$ = 7.0 Hz, H_{11}), 7.45−7.40 and 7.35−7.31 (2*m, 5H, H_{35} H_{36} H_{37}), 6.73 (t, 1H, $^4J_{H30-H28}$ = 1.7 Hz, H_{30}), 6.45 (d, 2H, $^4J_{H28-H30}$ = 1.7 Hz, H_{28}), 6.38 (d, 1H, $^3J_{H1-H2}$ = 9.0 Hz, H_1), 5.66 (s, 2H, H_{33}), 5.56 (t, 1H, $^3J_{H3-H2}$ = $^3J_{H3-H4}$ = 3.4 Hz, H_3), 5.23 (dd, 1H, $^3J_{H2-H1}$ = 9.0 Hz, $^3J_{H2-H3}$ = 3.4 Hz, H_2), 5.11 (dd, 1H, $^3J_{H4-H3}$ = 3.4 Hz, $^3J_{H4-H5}$ = 2.0 Hz, H_4), 4.83 (dd, 1H, $^2J_{H6a-H6b}$ = 12.8 Hz, $^3J_{H6a-H5}$ = 9.2 Hz, H_{6a}), 4.58 (ddd, 1H, $^3J_{H5-H6a}$ = 9.2 Hz, $^3J_{H5-H6b}$ = 3.7 Hz, $^3J_{H5-H4}$ = 2.0 Hz, H_5), 4.50 (t, 2H, $^3J_{H17-H16}$ = 7.2 Hz, H_{17}), 4.28 (dd, 1H, $^2J_{H6b-H6a}$ = 12.8 Hz, $^3J_{H6b-H5}$ = 3.7 Hz, H_{6b}), 3.39 (dd, 2H, $^3J_{H12-H13}$ = 13.0 Hz, $^3J_{H12-H11}$ = 7.0 Hz, H_{12}), 3.05 (t, 2H, $^3J_{H25-H24}$ = 7.0 Hz, H_{25}), 2.76 (t, 2H, $^3J_{H20-H21}$ = 7.5 Hz, H_{20}), 2.21 and 2.17 and 2.00 and 1.88 (4*s, 12H, CH_3CO), 1.99−1.90 (m, 2H, H_{16}), 1.65−1.48 (m, 6H, H_{13} H_{21} H_{24}), 1.45−1.32 (m, 8H, H_{14} H_{15} H_{22} H_{23}), 1.26 (s, 18H, H_{32}). ^{13}C NMR (100 MHz, CD_3CN, 298 K) δ 170.3 and 170.1 and 170.0 and 169.9 ($\underline{C}OCH_3$), 162.5 (C_{10}), 153.0 (C_9), 152.4 (C_{29}), 149.6 (C_{27}), 145.6 (C_{19}), 144.2 (C_7), 133.0 (C_{34}), 130.3 and 130.2 and 129.2 (C_{18} C_{35} C_{36} C_{37}), 127.3 (C_8), 112.0 (C_{30}), 108.0 (C_{28}), 89.1 (C_1), 78.7 (C_5), 69.6 (C_2), 68.3 (C_4), 67.5 (C_3), 61.0 (C_6), 55.2 (C_{33}), 54.7 (C_{17}), 44.3 (C_{25}), 40.9 (C_{12}), 35.3 (C_{31}), 31.6 (C_{32}), 29.8 and 29.5 and 29.4 and 29.1 and 27.7 and 27.2 and 26.7 and 26.1 (C_{13} C_{14} C_{15} C_{16} C_{21} C_{22} C_{23} C_{24}), 23.8 (C_{20}), 21.0 and 20.9 and 20.8 and 20.5 ($\underline{C}H_3CO$). MS (ESI) $[M - 2PF_6]^{2+}$ calculated for $[C_{55}H_{78}N_6O_{10}]^{2+}$: 491.29, found 491.28. HRMS (ESI) $[M - PF_6]^+$ calculated for $[C_{55}H_{78}N_6O_{10}F_6P]^+$: 1127.5414, found 1127.5421

■ ASSOCIATED CONTENT

Supporting Information

All NMR spectra of rotaxanes and uncomplexed threads. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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