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Two Switchable Star-Shaped [1](*n*)Rotaxanes with Different Multibranched Cores

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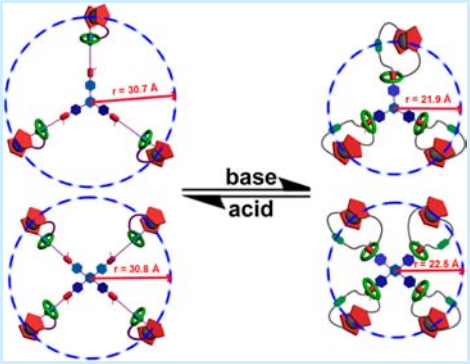
Supporting Information

ABSTRACT: Two novel star-shaped [1](*n*)rotaxanes with three and four identical [1]rotaxane arms but different multibranched cores were designed, synthesized, and well-characterized. In the two systems, external base−acid stimuli result in the uniform relative mechanical movement of the macrocyclic rings and threads of their [1]rotaxane arms. The energy-minimized structures of the two rotaxanes in different states were obtained using molecular dynamics simulations in acetone solution, suggesting the construction of more sophisticated molecular machines mimicking the extension and contraction motions.



Along with the rapid development of supramolecular chemistry, much attention has been paid to the design and construction of increasingly sophisticated mechanically interlocked molecules (MIMs)[1] possessing special structures and shapes. Until now, many of these MIMs and other supramolecular assemblies with special shapes, such as [2](2)rotaxane,[2] handcuff catenane,[3] molecular elevators,[4] molecular necklace,[5] molecular walkers,[6] and molecular muscles,[7] have been designed and constructed as potential components of molecular machinery.[8] Currently, there is a growing interest in [1]rotaxanes, as new types of MIMs, because of their intriguing topological structure[9] and their application as molecular muscle.[10] However, the construction of highly ordered and/or symmetrical assemblies containing multiple mechanically interlocked rotaxane building blocks still remains a challenge due to the increased complexity of their chemical structures.[11] This inspired us to construct multibranched mechanically interlocked molecular systems employing [1]-rotaxane building blocks as arms.

In this paper, two star-shaped [1](*n*)rotaxanes (here [1] indicates the number of molecular components and (*n*) stands for the number of interlocked structures involved[2b,c]), a novel tri- and tetrabranched [1]rotaxane, having identical [1]rotaxane arms but different cores, were designed, synthesized, and characterized. As shown in Figure 1, the [1]rotaxane arm bears a ferrocene (Fc)[12] unit that connects a dibenzo-24-crown-8 (DB24C8) macrocycle and a rodlike part through its cyclopentadienyl (Cp) rings. The rodlike part has two distinguishable recognition stations for DB24C8, namely a dibenzylammonium (DBA)[13] station and a *N*-methyltriazolium (MTA)[14] station. Because of their rigid structures and symmetrical shapes,[15] a 1,3,5-triphenylene and a 1,2,4,5-tetraphenylene core were used for the tribranched [1](3)rotaxane **Tri-Fc-1** and for the tetrabranched [1](4)rotaxane **Tetra-Fc-1**, respectively.

In these two [1](*n*)rotaxane systems, the uniform relative mechanical movements of their macrocyclic rings and threads can be driven by external base−acid stimuli, confirmed by ^{1}H NMR spectroscopy. Furthermore, the energy-minimized structures of the two [1](*n*)rotaxanes in different states have been investigated by molecular dynamics (MD) simulations[16] in acetone solution to gain further insight into the behavior of these highly complex and symmetrical [1]rotaxane systems. The calculated percentage changes for **Tri-Fc-1** and **Tetra-Fc-1** in their two states are about 28.7% and 26.9%, respectively, which are similar to the percentage change (∼27%) in human muscle. This indicates that these systems can mimic the extension and contraction motions of skeletal muscle while undergoing stimuli-induced structural changes.

The syntheses of the target tribranched [1](3)rotaxane **Tri-Fc-1** and tetrabranched [1](4)rotaxane **Tetra-Fc-1** are shown in Figure 2. First, we designed and synthesized compounds **4** and **5** (Figure 2) the tri- and tetrabranched cores that are key intermediates toward the target rotaxanes (their detailed syntheses are shown in Scheme S1, Supporting Information). In the next step, we synthesized compound **3**[17] comprising two subunits, a DB24C8 macrocycle and a rodlike part with a DBA

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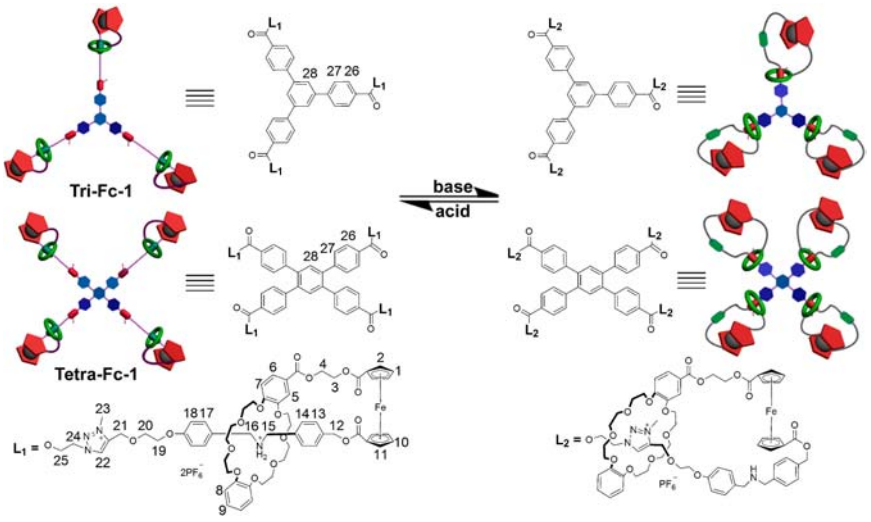

Figure 1. Switching processes and the schematic representations of the novel tri- and tetrabranched [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1**, respectively.

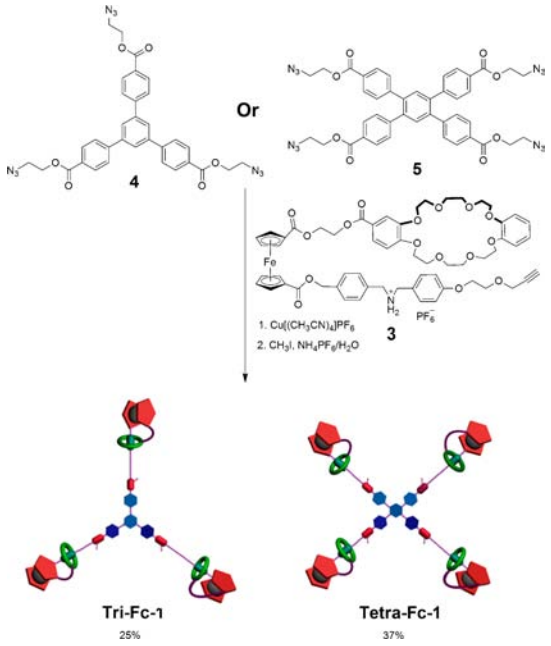

Figure 2. Syntheses of the target [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1**.

station and a terminal alkyne, both attached to the Cp rings of a cental ferrocene unit via ester bonds. Finally, as shown in Figure 2, the self-complexing [1]pseudorotaxane **3** in CH_2Cl_2 was coupled with the azides of the tri- and tetrabranched compounds **4** and **5** using $Cu(CH_3CN)_4PF_6$ as catalyst through a "threading-followed-by-stoppering" approach[18] to obtain intermediates **Tri-Fc-2** and **Tetra-Fc-2** (Figure S2, Supporting Information). Subsequently, **Tri-Fc-2** and **Tetra-Fc-2** were treated with CH_3I followed by anion exchange in acetone solution with saturated NH_4PF_6 to get the target rotaxanes **Tri-Fc-1** and **Tetra-Fc-1** in 25% and 37% yield, respectively (Figure 2).

Characterization of the target tribranched [1](3)rotaxane **Tri-Fc-1** and tetrabranched [1](4)rotaxane **Tetra-Fc-1** was performed by ^{1}H NMR and ^{13}C NMR spectroscopies and HR-ESI mass spectrometry. The HR-ESI mass spectrum of the tribranched [1](3)rotaxane **Tri-Fc-1** displays the strongest peak at *m*/*z* 1070.8320, corresponding to a species having lost four PF_6^- counterions, i.e., $[M - 4PF_6]^{4+}$, in agreement with the calculated value of 1070.8333 for $[C_{213}H_{234}N_{12}O_{54}Fe_3P_2F_{12}]$. Two other strong peaks at *m*/*z* 1476.0929 and 827.6719, corresponding to species having lost three and five PF_6^- counterions ($[M - 3PF_6]^{3+}$ and $[M - 5PF_6]^{5+}$), respectively, are also observed. Furthermore, the HR-ESI mass spectrum of tetrabranched [1](4)rotaxane **Tetra-Fc-1** also shows three intense peaks at *m*/*z* 1469.7020, 1146.7595, and 931.4730, corresponding to species having lost four, five, and six PF_6^- counterions, that is $[M - 4PF_6]^{4+}$, $[M - 5PF_6]^{5+}$, and $[M - 6PF_6]^{6+}$, respectively.

Next, we investigated the uniform relative mechanical movements of the macrocyclic DB24C8 rings and threads in response to external base–acid stimuli using ^{1}H NMR spectroscopy. In the tribranched [1](3)rotaxane **Tri-Fc-1** system, the MTA recognition stations were migrated into the DB24C8 rings upon addition of 4.0 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to its CD_3COCD_3 solution because of the deprotonation of the DBA stations by the excess DBU. These structural changes were accompanied by some obvious ^{1}H NMR spectral changes (Figure 3). As shown in Figure 3b, the protons H_{15}, H_{16} on the DBA station were split and shifted upfield with $\Delta\delta$ of −0.28, −0.41 ppm, respectively. Similarly, the phenyl protons H_5, H_6, H_9 on the macrocycle DB24C8 were also changed (0.10, −0.13, and −0.08 ppm, respectively). Meanwhile, the protons H_{22} and H_{23} on the MTA station were shifted dramatically with $\Delta\delta$ of 0.22 and −0.56 ppm, respectively. It should be noted that the protons H_{12} near the ferrocene were merged into a single doublet from the orignal two doublets (−0.10 and −0.31 ppm, respectively). All this evidence indicated that the three MTA stations all migrated into the DB24C8 rings upon addition of excess DBU.

The generated dibenzylamine center could be reprotonated again by the addition of 8.0 equiv of CF_3COOH (TFA), which led to the regeneration of the original ^{1}H NMR spectrum (Figure 3c). Collectively, these data demonstrate that in the tribranched [1](3)rotaxane **Tri-Fc-1** system the uniform relative mechanical movement of the DB24C8 rings and threads can be reversibly switched in response to external

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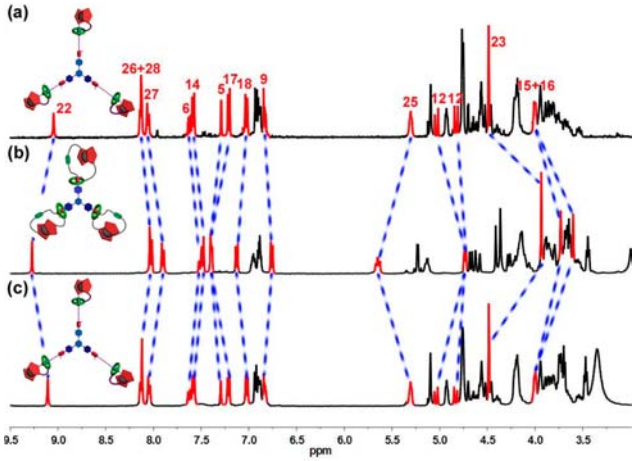

Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K, 2.0 × 10^{-3} M) of (a) [1](3)rotaxane **Tri-Fc-1**, (b) deprotonation upon addition of 4.0 equiv of DBU to sample a, and (c) reprotonation upon addition of 8.0 equiv of TFA to sample b.

base−acid stimuli. Similarly, in the tetrabranched [1](4)-rotaxane **Tetra-Fc-1** system, the uniform and reversible relative mechanical movement of its macrocyclic rings and threads in response to external base−acid stimuli has the same trend as that observed in the tribranched [1](3)rotaxane **Tri-Fc-1** system (Figure 4).

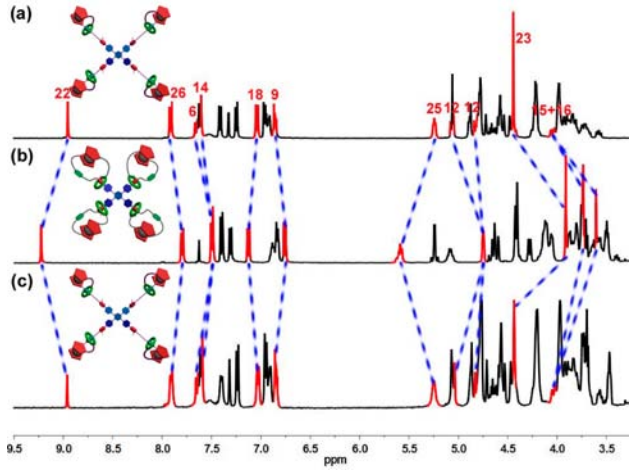

Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3COCD_3, 298 K, 2.0 × 10^{-3} M) of (a) [1](4)rotaxane **Tetra-Fc-1**, (b) deprotonation upon addition of 5.0 equiv of DBU to sample a, and (c) reprotonation upon addition of 10.0 equiv of TFA to sample b.

To further recognize the structural differences of the two [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1** in two states, their energy-minimized structures in different states have been investigated by MD simulations in acetone solution. It can be seen from Figure 5 that the two [1](*n*)rotaxanes in original states have their three and/or four crown ether macrocycles encircled at the protonated amine groups and feature extended conformations, considering the flexibility of the rotaxane arms; this illustrates the near-maximal separation between the central aromatic core and the peripheral ferrocene units. The average distances of the extended conformations in [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1** between the central phenyl ring and the Fe(II) atom are about 30.7 and 30.8 Å, respectively (Figure

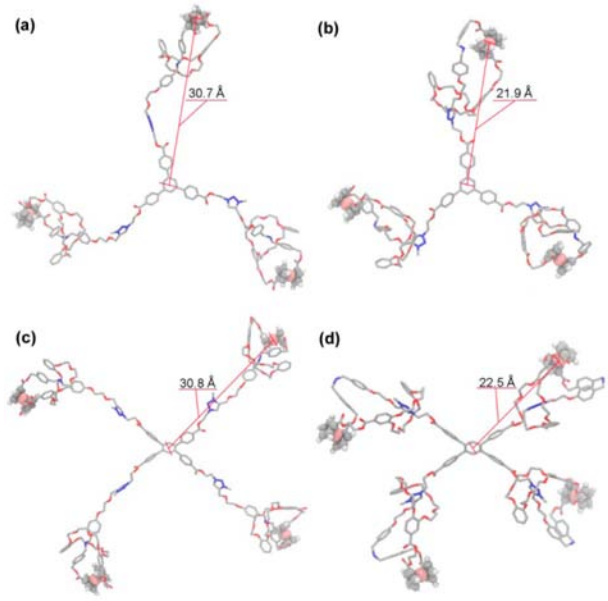

Figure 5. Snapshots for the structures of the [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1** at their two states, extracted from molecular dynamics trajectories. The optimized conformations at different states were obtained through molecular dynamics simulations employing the general Amber force field.

5a,c). However, upon addition of excess DBU, all of their three and/or four crown ether macrocycles encircle on the MTA stations, and the optimized structures exhibit contraction motions and partial folding of the rotaxane arms, leading to a shortened distance between the central phenyl ring and the Fe(II) atoms of 21.9 and 22.5 Å, respectively (Figure 5b,d). As such, a fair estimation of the percentage changes of dimension in each arm of [1](*n*)rotaxanes **Tri-Fc-1** and **Tetra-Fc-1** in two different states is obtained as 28.7% for the former and 26.9% for the latter, which are similar to the percentage change (∼27%) in human muscle. These results confirmed that the two [1](*n*)rotaxanes systems could mimic the extension and contraction motions in response to external base−acid stimuli.

In summary, we have designed and constructed two switchable star-shaped [1](*n*)rotaxanes by introducing a tribranched and a tetrabranched core that connects [1]rotaxane building blocks. The external base−acid stimuli resulted in the reversible relative mechanical movement between the macrocycle and the thread components in each arm of the two star-shaped systems, ultimately generating uniform extension and contraction of the whole molecular system. The energy minimized structures obtained from molecular dynamics simulations showed that the percentage change of the dimension in each arm is very similar to that in human muscle. These kinds of systems can pave the way for designing more complicated molecular and supramolecular assemblies with increased structural complexity and specific functions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental procedures and characterization data (^{1}H NMR, ^{13}C NMR, and HR-ESI) of all new compounds including tribranched [1](3)rotaxane **Tri-Fc-1**, tetrabranched [1](4)rotaxane **Tetra-Fc-1**, and key intermediates. This

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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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