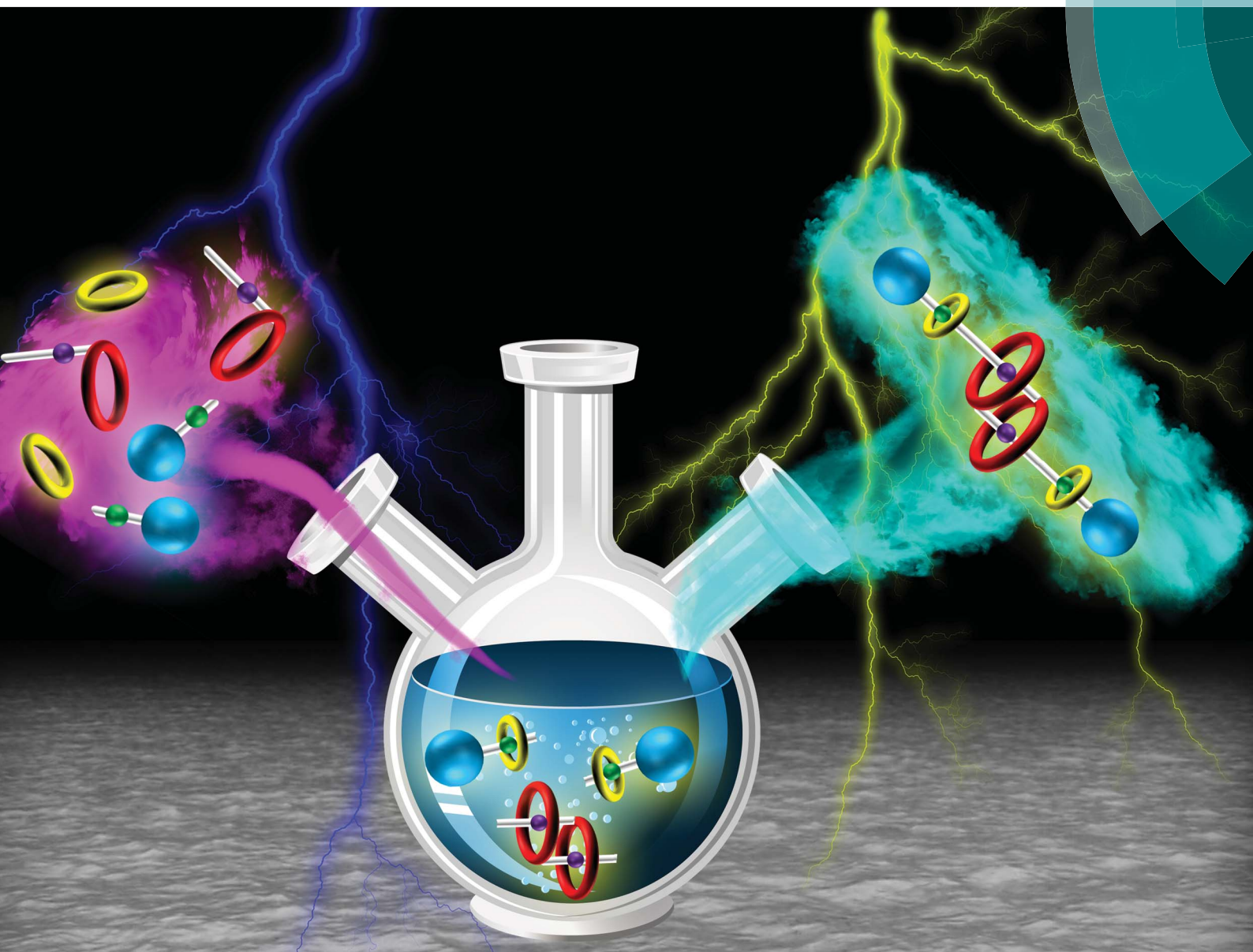


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One-pot synthesis of a [c2]daisy-chain-containing hetero[4]rotaxane via a self-sorting strategy

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One-pot synthesis of a [c2]daisy-chain-containing hetero[4]rotaxane *via* a self-sorting strategy†

Xin Fu,‡ Qi Zhang,‡ Si-Jia Rao, Da-Hui Qu* and He Tian

The construction and efficient synthesis of hetero[n]rotaxanes with high structural complexity are always attractive challenges. Herein, we demonstrate a facile one-pot preparation of a hetero[4]rotaxane, by employing a self-sorting strategy, which contains an interpenetrated dibenzo-24-crown-8 (DB24C8) based [c2]daisy chain structure and is ended with a benzo-21-crown-7 (B21C7) based rotaxane at each side. The key to the design involved encoding the selective threading using a steric hindrance-related "language", where highly selective self-assemblies occurred in a three-component self-sorting process, which included the threading of a benzylalkylammonium into a B21C7 and interpenetrated dimerized formation of a DB24C8 based [c2]daisy chain simultaneously; the precise pre-assembled system resulted in the efficient synthesis of hetero[4]rotaxane with a high-level of structural complexity under the "CuAAC" reaction.

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Introduction

In the last twenty years, a variety of mechanically interlocked molecules (MIMs), especially rotaxanes and catenanes, have been delicately designed and constructed.¹ The unique structural features of MIMs are utilized by scientists to birth elegant functional molecules,² indicating the great potential of MIMs in functional materials. As a modification platform for functional groups, the structural complexity of MIMs significantly provides infinite possibilities in designing novel functional molecular machines.³ Hence, the construction and efficient synthesis of MIMs with high structural complexity have been greatly attractive but challenging.⁴ Recently, much attention has been focused on the topological,^{3a} interpenetrating,⁵ knotted⁶ structures of MIMs with high structural complexity. In this intriguing family, [c2] daisy chain molecules,⁵ a class of rotaxanes constructed from the dimerization of AB-type linear monomers with two self-complementary units, A (host) and B (guest), have shown their talent in mimicking the contraction and extension movements of natural biological machines.^{5f} Various elegant [c2] daisy chain molecules have been reported based on different host-guest systems including versatile macrocycles, such as crown ethers,^{5b,e,h} cucurbit[n]uril,⁵ⁱ cyclodextrins,^{5a,c,d} pillarenes,^{5g,m,p} and cyclophanes.^{5o}

A variety of hetero[n]rotaxanes, especially those comprising two or more different types of ring moiety, have been designed and constructed,⁷ some even in a one-step strategy.^{7b,d} This aroused our interest to integrate muscle-like daisy chain structures with hetero[n]rotaxanes to breed a hetero[n]rotaxane with a novel structural topology. However, it is difficult to synthesize this novel hetero[n]rotaxane based on traditional strategies for rotaxane synthesis,⁸ which are efficient in the preparation of typical [2]rotaxane but complicated when there is more than one type of ring moiety, due to them being "non-selective". The key challenge is the dramatically increased complexity of the interpenetration process in the formation of a [c2]daisy chain when additional recognition sites and rings are incorporated into the multi-component self-assembling system. Hence, a programming language for highly selective self-assembly is desperately needed to integrate hetero[n]rotaxane with the daisy chain structure.

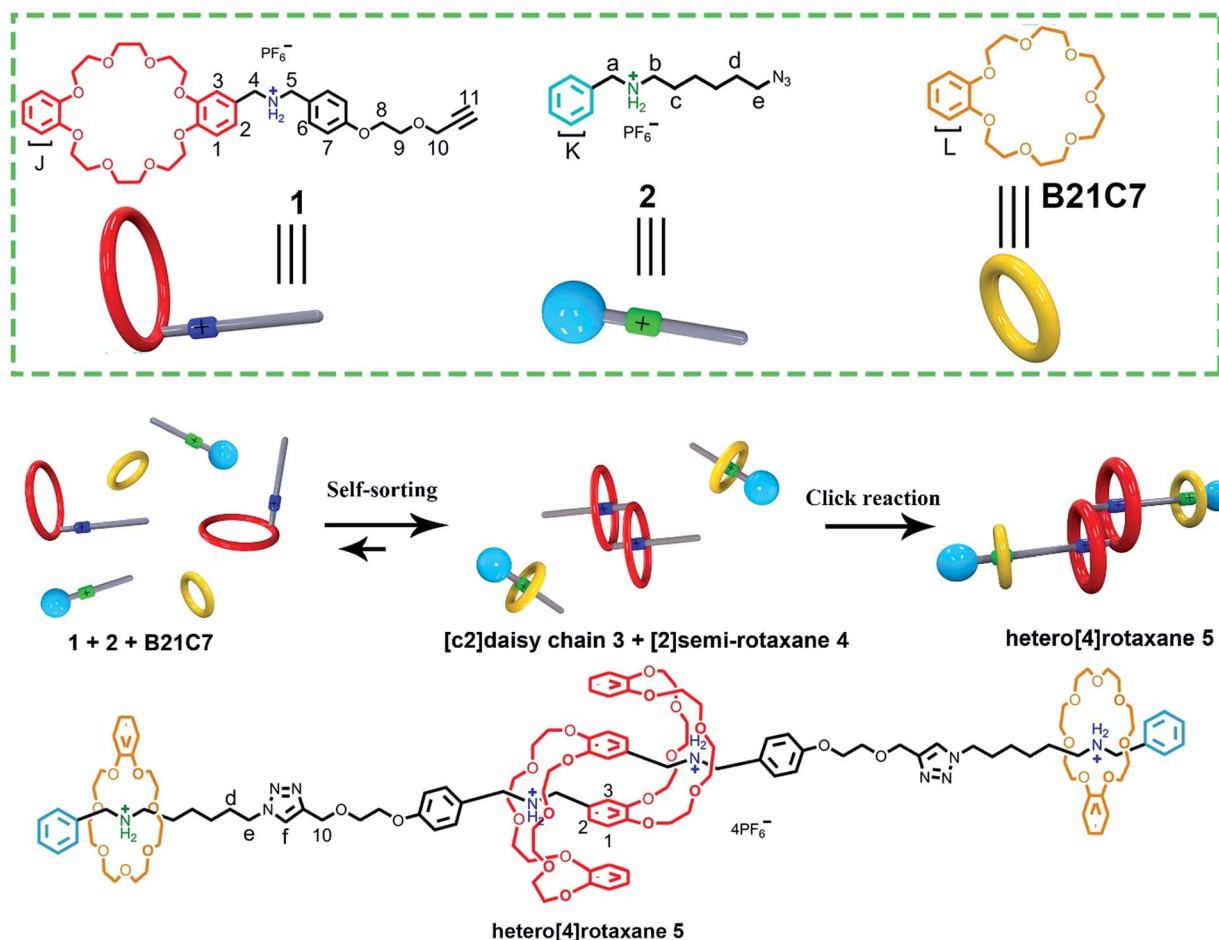
Self-sorting strategies have the unique capability of selective self-assembly in complex supramolecular systems.⁹ Schalley and co-workers¹⁰ have developed an efficient integrative self-sorting strategy for selective self-assembly to simultaneously incorporate two kinds of polyether macrocycles into a single axle molecule comprising two kinds of secondary ammoniums which, as a result, form a cascade-stoppered hetero[3]rotaxane. This self-sorting strategy has been proved to be very efficient in constructing many hetero[n]rotaxanes with increased structural complexity.¹¹ However, to the best of our knowledge, this self-sorting strategy has not been proved to be appropriate for a system simultaneously involving both threading and interpenetration, which are known for the formation of pseudorotaxanes and daisy chain structures, respectively.

Herein, a facile one-pot synthesis of hetero[4]rotaxane **5** is successfully realized *via* a three-component (**1**, **2** and B21C7 in

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Scheme 1 Schematic representation of the preparation of hetero[4]rotaxane **5** using a three-component modularized self-sorting system of **1**, **2** and **B21C7**. Only one main stereoisomer of hetero[4]rotaxane **5**, which is derived from the three possible [c2]daisy chain stereoisomers,^{5e} is shown here.

Scheme 1) self-sorting strategy. In principle, these initial components (**1**, **2** and **B21C7** in Scheme 1) could assemble into several self-assembly species, while only two kinds of precursors, [c2]daisy chain **3** and [2]semi-rotaxane **4**, were successfully formed through the highly selective self-assembly process as determined by ¹H NMR studies. In this pre-assembly process, both the self-interpenetration of compound **1** to form [c2]daisy chain **3** and the threading of **2** into the cavity of **B21C7** to form [2]semi-rotaxane **4** occurred simultaneously. Then the highly symmetrical hetero[4]rotaxane **5** containing [c2]daisy chain could be obtained by the following facile one-pot CuAAC click reaction.^{8d} We believe that the facile one-pot synthesis of hetero[4]rotaxane **5** would inspire the successful construction of MIMs with fascinating structures and potential functions.

Results and discussion

The rational design of block building is a prerequisite to realizing the precise construction of a multi-component system. As shown in Scheme 1, initial substrates include compound **1** (the synthesis information from compounds **7** and **8** can be found in the ESI†), which contains a **DB24C8** macrocycle modified with

a secondary dibenzylammonium branched chain; a secondary benzylalkylammonium **2**; and **B21C7**. The key part of the design involves the dibenzylammonium recognition site in compound **1**, where the phenyl group encodes the secondary ammonium as a selective site that only can be included by the larger macrocyclic **DB24C8**, but not by **B21C7**.^{7b,10,12} Therefore, even in one system, **B21C7** would not affect the formation of the [c2]daisy chain **3**. Meanwhile, this phenyl group also makes the secondary ammonium in compound **1** a preferred recognition site for **DB24C8**, over that in compound **2**.¹⁰ Considering the precise 1 : 1 proportion of **DB24C8** and the secondary ammonium in compound **1**, compound **2** would not affect the formation of [c2]daisy chain **3** from monomer molecule **1**, which has been proved by the ¹H NMR measurements (Fig. S1†). As a result, the self-assembly of the initial molecules was precisely encoded, where the self-sorting process included simultaneous threading and interpenetration, and then [2] semi-rotaxane **4** and [c2]daisy chain **3** were generated, respectively. Finally, in the presence of Cu(MeCN)₄PF₆, the subsequent CuAAC click reaction between [c2]daisy chain **3** and [2]semi-rotaxane **4** afforded the formation of hetero[4]rotaxane **5** in a one-pot strategy. In the obtained hetero[4]rotaxane **5**, two



B21C7 rings can be stopped by the outer phenyl groups, while the central [c2]daisy chain structures are cascade-stopped by the **B21C7** rings.

We performed ^1H NMR experiments to confirm the self-sorting behaviours in this three-component system, as shown in Fig. 1. The ^1H NMR spectra revealed that **1** existed as a monomer in polar solvents, such as $[\text{D}_6]\text{DMSO}$ (Fig. 1a), with normal and simple ^1H NMR signals. While in less polar solvents, such as $[\text{D}_3]\text{acetonitrile}$ (Fig. 1b), [c2]daisy chain **3** became the predominant species. The ^1H NMR signals of the NH_2^+ protons and crown ether moiety shifted and split, becoming much broader and more complicated. As shown in Fig. 1b, two sets of signals for the NH_2^+ protons were observed at $\delta = 7.0$ – 7.4 ppm, attributed to each ammonium facing the two non-symmetrical ends of the axle. According to the previous studies about the analogous [c2]daisy chains,^{13,14} there are three dimeric interlocked stereoisomers arising from the unsymmetrical substitution of the **DB24C8** ring, which were also observed in the ^1H NMR spectrum of [c2]daisy chain **3** (Fig. 1b). As shown in Fig. 1, the aromatic protons of **DB24C8** also become split, especially protons H_1 and H_3 . H_1 splits into two sets of double peaks (H_{1a} , 6.4 ppm and H_{1b} , 6.9 ppm), and H_3 splits into two sets of single peaks (H_{3a} , 6.8 ppm and H_{3b} , 6.2 ppm) with the ratio of 5 : 1, indicating the major supramolecular stereoisomer of the “meso” type, shown in Scheme 1, which is consistent with the previous report.^{5e} Meanwhile, the formation of [2]semi-rotaxane **4** from compound **2** and **B21C7** has been detected using the ^1H NMR spectra shown in Fig. 2. After mixing compound **2** and **B21C7** in a 1 : 1 molar ratio, the signals of the NH_2^+ protons shifted upfield with a $\Delta\delta$ of -0.97 ppm, and the signals of H_a , H_b and H_c shifted downfield with a $\Delta\delta$ of 0.26, 0.24 and 0.07 ppm, respectively, suggesting the formation of [2]semi-rotaxane **4**.¹² Then, the three compounds **1**, **2** and **B21C7** were mixed in $[\text{D}_3]\text{acetonitrile}$ in a molar ratio of 1 : 1 : 1. ^1H NMR spectra (Fig. 3) showed that the signals of H_{1a} , H_{3b} , H_4 and H_5 in [c2]daisy chain **3**, as well as those of H_a , H_b and H_c in [2]semi-rotaxane **4**, remain constant. These observations indicate that the two pseudorotaxanes still exist as the predominant species in this three-component self-sorting system.

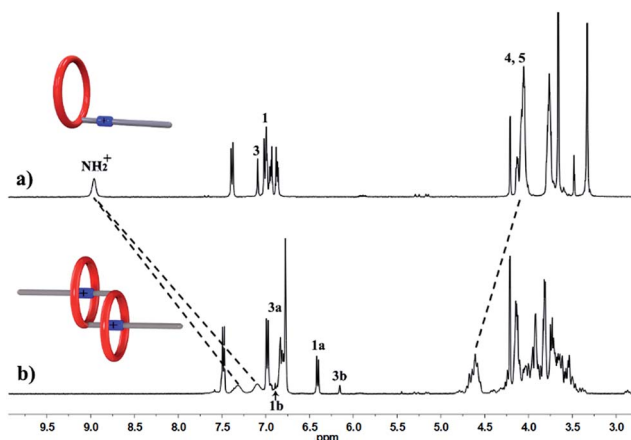


Fig. 1 Partial ^1H NMR spectra (400 MHz, 298 K) of compound **1** in (a) $[\text{D}_6]\text{DMSO}$, and (b) $[\text{D}_3]\text{acetonitrile}$.

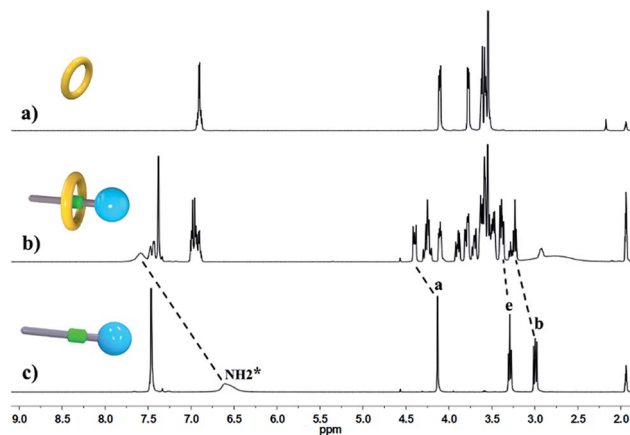


Fig. 2 Partial ^1H NMR spectra (400 MHz, 298 K, $[\text{D}_3]\text{acetonitrile}$) of (a) **B21C7**, (b) a 1 : 1 mixture of **2** and **B21C7**, and (c) compound **2**.

The synthetic route for hetero[4]rotaxane **5** is outlined in Scheme 1. At room temperature, the CuAAC reaction between [c2]daisy chain **3** and [2]semi-rotaxane **4** successfully afforded the formation of a white solid, hetero[4]rotaxane **5**, with a yield exceeding 50% in the presence of $\text{Cu}(\text{MeCN})_4\text{PF}_6$. As shown in Fig. 4a and b, the terminal alkynyl proton H_{11} of **3** disappeared after the CuAAC click reaction, indicating the successful formation of the triazole. The resonance for the triazole proton H_f appeared at $\delta = 7.72$ ppm and the adjacent protons H_{10} , H_b , H_d and H_e shifted downfield with a $\Delta\delta$ of 0.38, 0.22, 0.12 and 0.89 ppm, respectively. All of these changes demonstrated the importance of the CuAAC click reaction for the formation of hetero[4]rotaxane **5**, as illustrated in Scheme 1.¹⁵ The high resolution mass spectrum (HRMS) of hetero[4]rotaxane **5** showed major signals at m/z 628.0955, 885.7819 and 1401.1543, which correspond to the product after the loss of 4, 3 and 2PF_6^- ions, *i.e.* $[\text{M} - 4\text{PF}_6]^{4+}$, $[\text{M} - 3\text{PF}_6]^{3+}$ and $[\text{M} - 2\text{PF}_6]^{2+}$, respectively. The molecular ion peaks of $[\text{M} - 4\text{PF}_6]^{4+}$ and $[\text{M} - 3\text{PF}_6]^{3+}$, as well as the results of ^1H NMR, give enough evidence to show the formation of hetero[4]rotaxane **5**.¹⁵

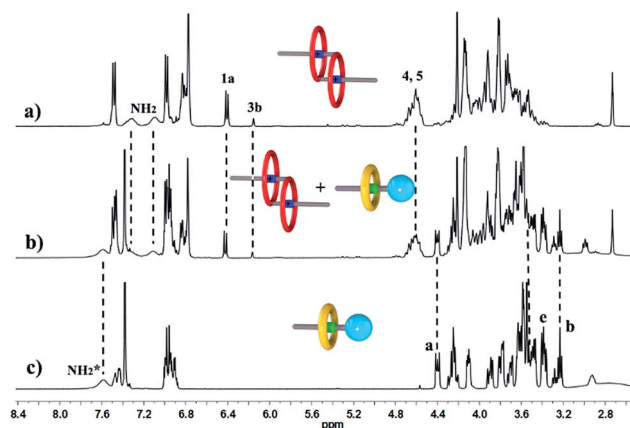


Fig. 3 Partial ^1H NMR spectra (400 MHz, 298 K, $[\text{D}_3]\text{acetonitrile}$) of (a) compound **1**, (b) a 1 : 1 : 1 mixture of **1**, **2** and **B21C7**, and (c) a 1 : 1 mixture of **2** and **B21C7**.

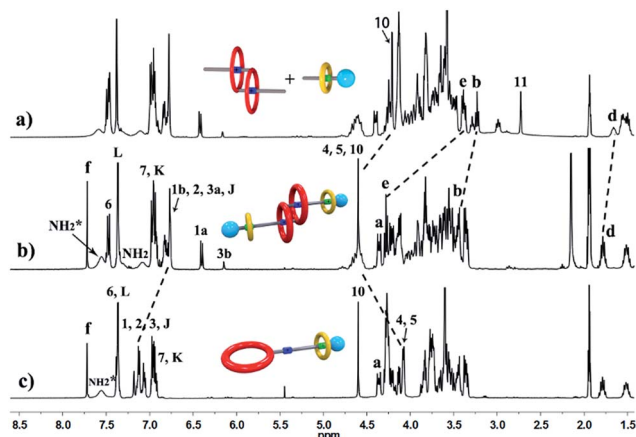
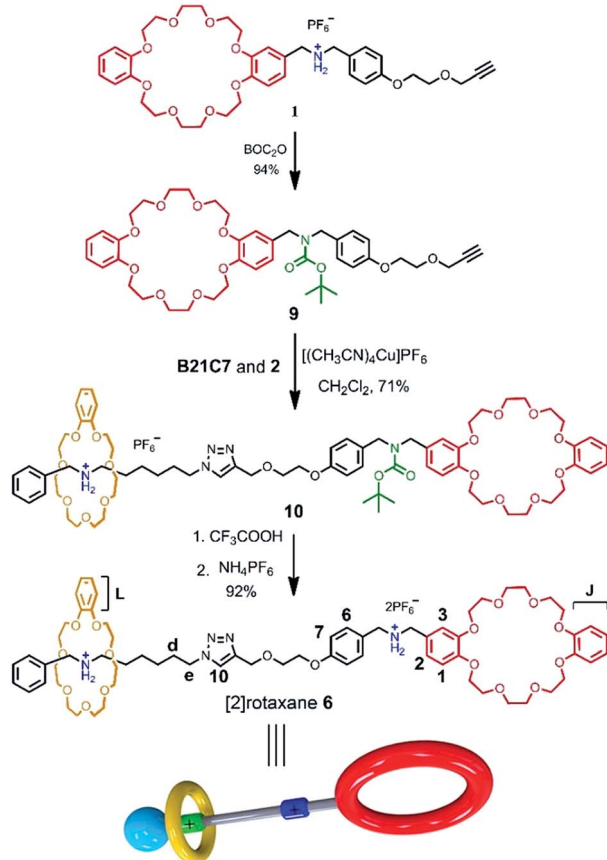


Fig. 4 Partial ^1H NMR spectra (400 MHz, 298 K, $[\text{D}_3]\text{acetonitrile}$) of (a) a 1 : 1 : 1 mixture of **1**, **2** and **B21C7**, (b) hetero[4]rotaxane **5**, and (c) [2]rotaxane **6**.

For further understanding of the self-sorting process and confirming the chemical structure of hetero[4]rotaxane **5**, the dibenzylammonium site in compound **1** was protected with a BOC group to yield compound **9** (Scheme 2), leading to a recognition failure between macrocyclic **DB24C8** and the DBA site. As a result, there was only one type of secondary



Scheme 2 Synthetic route for [2]rotaxane **6**.

ammonium recognition site in the mixed systems of compound **9**, compound **2** and **B21C7**, meaning that a non-self-sorting process would occur among these building blocks. Then, a CuAAC click reaction of compound **9** and [2]semi-rotaxane **4** successfully afforded [2]rotaxane **10** in the presence of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ in a 1 : 1 volume ratio of dichloromethane/acetonitrile at room temperature. After being treated with trifluoroacetic acid, the reference compound [2]rotaxane **6** with an unoccupied **DB24C8** ring was obtained. The HRMS spectrum of [2]rotaxane **6** shows major signals at m/z 1400.6526, corresponding to the product after a loss of the PF_6^- ion, confirming the interlocked structure. Furthermore, we compared all of the resonances between hetero[4]rotaxane **5** and [2]rotaxane **6** by analysing their ^1H NMR spectra (Fig. 4b and c). As shown in the ^1H NMR spectra of **5** and **6** in $[\text{D}_3]\text{acetonitrile}$ (Fig. 4b and c), the protons H_1 , H_2 , H_3 and H_j of [2]rotaxane **6** shifted downfield with a $\Delta\delta$ of about 0.2 ppm, and the stereoisomer signals of H_{1a} and H_{3b} disappeared, which was attributed to the fact that the DBA site was not surrounded by the **DB24C8** macrocycle to give a simple chemical shift environment. It is notable that the DBA protons in [2]rotaxane **6** cannot be detected because there are no hydrogen bonding interactions between the crown ether and the DBA hydrogen atoms.¹⁶ Compared with the ^1H NMR spectrum of hetero[4]rotaxane **5**, H_4 and H_5 which are adjacent to the DBA site were observed to shift upfield with a $\Delta\delta$ of -0.53 ppm in the ^1H NMR spectrum of [2]rotaxane **6**, which confirmed that the DBA sites were not bound by the host macrocycle **DB24C8**. Therefore, the phenyl-stopped **B21C7** played an important role in inhibiting the dethreading of the daisy chain structure in the middle, this is also called a cascade-stopped strategy.^{10,7b} Importantly, this inhibiting behaviour also caused the stable structure of hetero[4]rotaxane **5** instead of a meta-stable pseudorotaxane.

Meanwhile, 2D NOESY spectra of hetero[4]rotaxane **5** and [2]rotaxane **6** validated their chemical structures. The NOESY spectrum of **6** in $[\text{D}_3]\text{acetonitrile}$ (Fig. S1†) shows two cross-peaks (peak F and G) between the phenyl protons H_L and ethylene protons of **B21C7**, thus clearly indicating that **B21C7** is located on the outer ammonium site which is far away from the **DB24C8** ring. In the meantime, no cross-peaks between **DB24C8** and the inner DBA site were found. Nevertheless, in the NOESY spectrum of **5** (Fig. S2†), we found not only cross-peaks (peaks P, Q, R and S) between the phenyl protons H_L and ethylene protons of **B21C7**, but also cross-peaks (peak N and O) between the phenyl protons H_7 and ethylene protons of **DB24C8**, and cross-peaks (peak T and U) between the phenyl protons H_6 and ethylene protons of **DB24C8**, thus clearly indicating the existence of a [c2]daisy chain structure in **5**.

Conclusion

In conclusion, a novel hetero[4]rotaxane containing a [c2]daisy chain can be facilely synthesized in one pot by employing a multi-component self-sorting strategy followed by the well-known CuAAC stopping reaction. The highly selective self-assembling process that occurred among the three kinds of building blocks provides the possibility for the formation of



only two kinds of rotaxane precursors, by employing a steric hindrance-related “language”. This work serves as one of few successful examples of the construction of hetero[n]rotaxane with a [c2]daisy chain cored structure directed by a self-sorting strategy. Significantly, the integration of hetero[n]rotaxane and a [c2]daisy chain structure enlarges the family of mechanically interlocked molecules and this synthetic methodology can be utilized in the preparation of mechanically interlocked compounds with increasingly complicated structures and functions.

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