Rotaxane Synthesis

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Macrocycle Size Matters: "Small" Functionalized Rotaxanes in Excellent Yield Using the CuAAC Active Template Approach**

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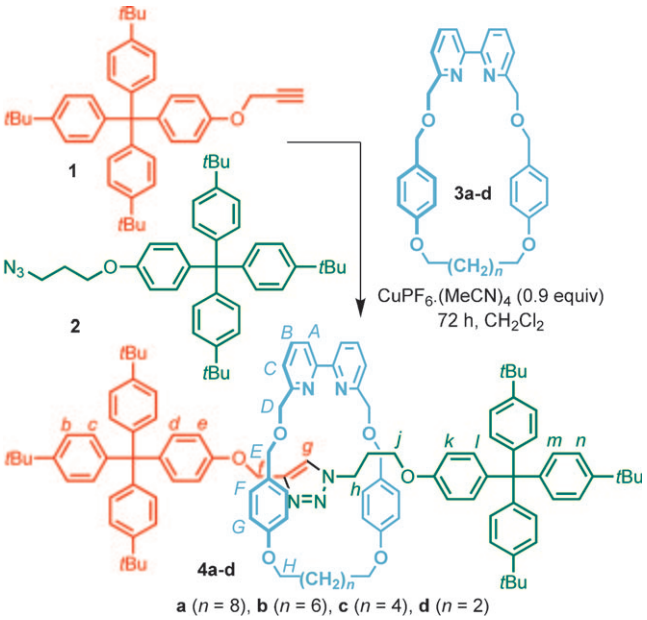
The conceptually novel active template (AT) approach to mechanically interlocked molecules recently introduced by Leigh and co-workers relies on a catalytically active metal center, bound within the cavity of macrocycle, which mediates the formation of a new covalent bond through the ring.[1] Much as the development of passive template methods over the last three decades has allowed the realization of increasingly complex interlocked molecular architectures[2] as well as prototypical molecular machines[3] such as switches,[4] motors,[5] and ratchets,[6] the AT approach has the potential to significantly increase the diversity of synthetically accessible interlocked structures. The AT approach is particularly synthetically powerful as, in principle, any metal-mediated bond formation can be adapted for use in the key bond forming step. Indeed in the six years since the first AT reaction was reported,[1a] based on the Sharpless–Huisgen–Meldal–Fokin copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction,[7] the concept has been extended to nine other metal-mediated bond forming reactions, and applied to the synthesis of molecular shuttles,[1d,e,g,l] catenanes,[1h,i] and molecules with multiple mechanical bonds.[1d,k]

However, although a number of different combinations of metal and ligand motif have been investigated and shown to effectively mediate rotaxane synthesis, all AT reactions disclosed have employed macrocycles with relatively large cavities, mandating the use of half-threads bearing extremely bulky stoppering units (typically substituted trityl moieties).[1] This prohibits the use of simple derivatives of commercially available materials and places limitations on the structure and properties of the rotaxane products, undermining the synthetic utility of the approach. Further, in some applications, including those where the macrocycle mechanically protects the thread from the local environment (prodrugs,[8] insulated molecular wires,[9] and mechanically protected dyes[10]) and situations in which information transfer between the thread and macrocycle is desirable (sensing[11] and mechanically interlocked chiral catalysts[12]), a "tight" fit between macrocycle and thread is required.

Thus, we set out to ascertain the effect of macrocycle size in the active template synthesis of rotaxanes using the CuAAC-AT reaction as a model. The results obtained indicate that, although size matters, bigger macrocycles are not always better. Indeed, we demonstrate that this approach allows ready access to "small" functionalized rotaxanes based on commercially available materials in consistently excellent yields.

The size of the macrocyclic cavity was varied by modifying the length of the alkyl linker between the phenolic oxygens in bipyridine macrocycles **3**, and their efficacy in the CuAAC-AT reaction was assessed (Scheme 1, Table 1). In the case of



Scheme 1. Variation of macrocycle size in the bipyridine-mediated CuAAC-AT reaction.

Table 1: The effect of macrocycle size in the bipyridine-mediated CuAAC-AT reaction[a]

Entry	Macrocycle	*T* [°C]	Consumption of **1** [%][b]	Yield of isolated **4** [%]
1	**3a**	25	>95	85
2	**3a**	80	>95	48
3	**3b**	25	<10	<5[b]
4	**3b**	80	>95	34
5	**3c**	80	>95	76
6	**3d**	80	>95	100

[a] Reactions were carried out as outlined in Scheme 1 employing 1 equiv each of **1**, **2**, and **3** (0.01 M in CH_2Cl_2) in a sealed CEM microwave vial. See Supporting Information for further details. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture.

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macrocycle **3a** ($n=8$) which has previously been reported to participate efficiently in the CuAAC-AT reaction with half-threads **1** and **2**,[1d] completion is achieved after 72 h at room temperature resulting in 85% yield of [2]rotaxane **4a** (Table 1, entry 1). The first obvious effect of employing a macrocycle, **3b** ($n=6$), with a smaller cavity was to slow the reaction considerably: after 72 h at room temperature < 10% of the half-thread components had been converted to triazole products, although [2]rotaxane **4b** was formed despite the low conversion (entry 3). Raising the temperature to 80°C allowed the reaction to proceed to completion over 72 h to give [2]rotaxane **4b** in 34% yield (entry 4). Repeating the reaction with **3a** at 80°C revealed that some but not all of the reduced yield of [2]rotaxane with macrocycle **3b** can be attributed to the rise in reaction temperature (entry 2). Reducing the cavity size by a further two methylene units (macrocycle **3c**, $n=4$, entry 5) raised the yield of the interlocked product to 76%. When macrocycle **3d** ($n=2$) with only four methylene units between the phenolic ethers was employed the reaction proceeded in *quantitative yield* (entry 6). To our knowledge this is the highest-yielding AT reaction to date with all of the organic components used in the reaction being converted with 100% efficiency into interlocked product. Unfortunately, attempts to reduce the cavity size further in this series proved problematic as macrocycles with shorter alkyl linkers were synthetically inaccessible by Williamson ether synthesis.

Variation of macrocycle size also leads to large differences between the ^{1}H NMR spectra of rotaxanes **4a–d** (Figure 1). Most strikingly, the chemical shift of H_g appears > 1 ppm downfield in **4d** compared with **4a**, which appears to indicate significantly enhanced H-bonding of this polar C–H moiety[13] to the bipyridine nitrogens as the fit between macrocycle and thread becomes tighter. Secondly, the resonances corresponding to macrocycle protons H_D, H_E, and H_H split into pairs of diastereotopic signals as the macrocyclic cavity is reduced in size, indicating that the translational asymmetry of the thread is more clearly expressed in these more sterically congested, conformationally and co-conformationally restricted products.

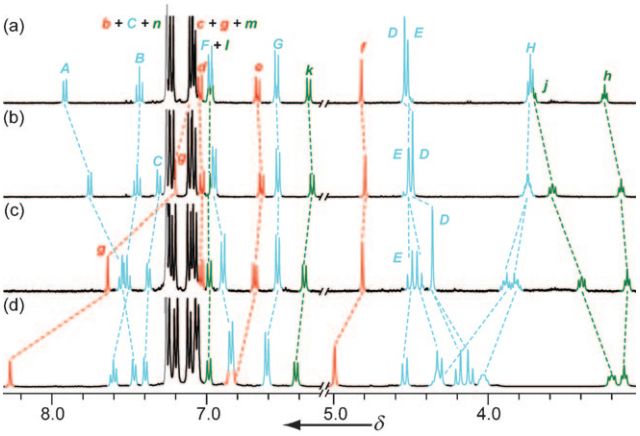

Figure 1. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 300 K) of a) rotaxane **4a**, b) rotaxane **4b**, c) rotaxane **4c**, and d) rotaxane **4d**. Labeling as shown in Scheme 1.

Macrocycle **3d** is, in principle, small enough to allow the synthesis of rotaxanes with significantly smaller stoppers than have previously been reported in the CuAAC-AT reaction with **3a** and we set out to explore this possibility using representative "small" functionalized half-threads. It should be noted that, despite the efficacy of macrocycle **3d** in the CuAAC-AT reaction with half-threads **1** and **2**, it is not immediately obvious that rotaxane formation should be successful with half-threads bearing smaller stoppers: both the size and shape of the half-thread components may significantly affect the outcome of the CuAAC-AT reaction. Indeed, the substituted trityl units may play a role by shielding one face of the macrocycle during covalent bond formation (Scheme 1).

Gratifyingly, [2]rotaxane formation was observed in all cases investigated when smaller functionalized half-threads were employed (Figure 2). In most cases (**5** and **7–9**), reactions employing one equivalent each of alkyne and azide half-threads resulted in ca. 40% yield of the corresponding [2]rotaxane. Increasing the number of equivalents of half-threads to five resulted in clean and quantitative conversion of macrocycle **3d** to [2]rotaxane (as judged by ^{1}H NMR analysis of the crude reaction mixture) and excellent

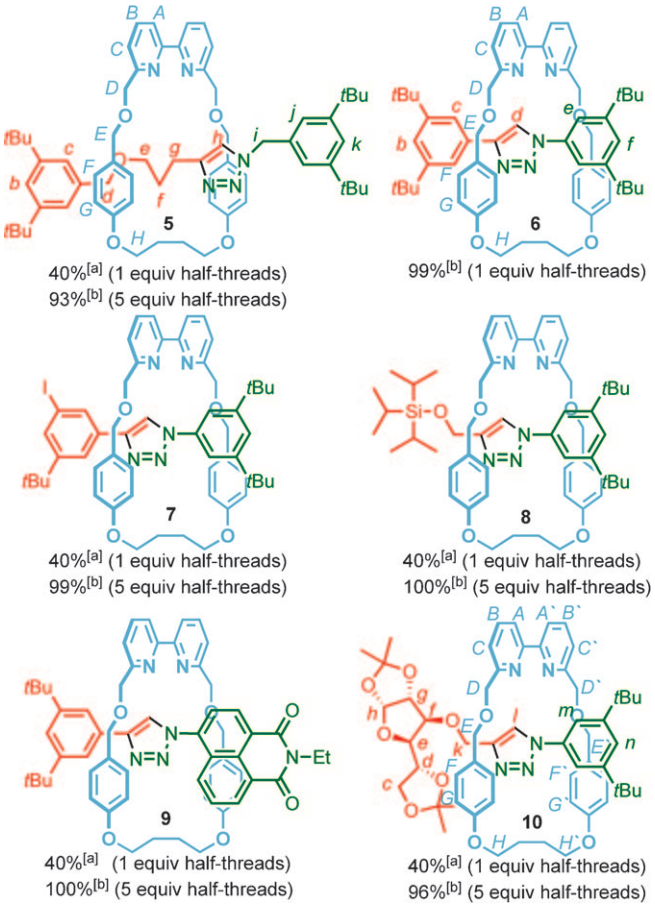

Figure 2. "Small" rotaxanes synthesized using the CuAAC-AT reaction. Reactions were carried out as outlined in Scheme 1 at 80°C. [a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Yield of isolated product after column chromatography.

isolated yields in all cases. Surprisingly, in the case of the reaction employing 1 equivalent each of 3,5-di-*tert*-butyl phenylazide and 3,5-di-*tert*-butyl phenylacetylene (the most sterically demanding of these substrates) a quantitative yield of [2]rotaxane **6** was observed by ^{1}H NMR spectroscopy and an excellent isolated yield (99%) obtained.

Slow evaporation of a saturated solution of [2]rotaxane **6** in Et_2O/hexane yielded crystals suitable for single-crystal X-ray analysis (Figure 3).[14] In addition to the anticipated CH···N hydrogen bonding interaction between the bipyridine nitrogens and H_d a number of weak CH···π interactions are observed between H_D and H_H and the triazole unit. The crystal structure clearly shows the extremely sterically congested environment around the triazole unit. Indeed, given the lack of space within the macrocyclic cavity it seems surprising that the CuAAC reaction occurs at all, let alone in the excellent yields obtained.

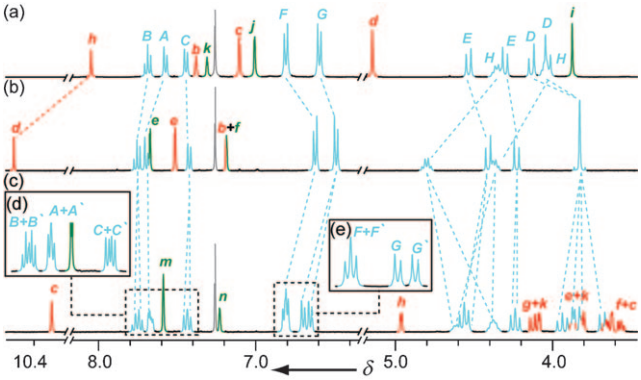

Figure 4. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 300 K) of rotaxanes a) **5**, b) **6**, c) **10**, and d) and e) expansions (600 MHz, $CDCl_3$) of the indicated regions of spectrum (c) demonstrating the rotational dissymmetry of the macrocycle. Labeling as shown in Figure 2.

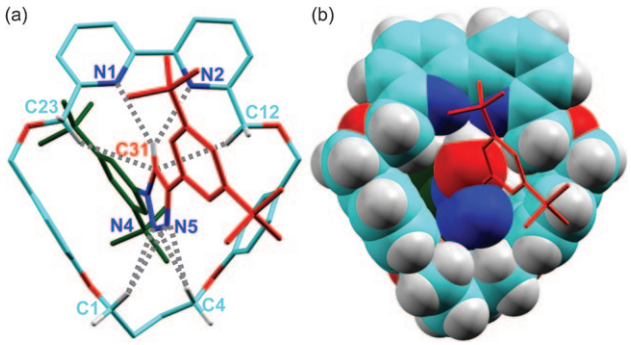

Figure 3. Single-crystal X-ray structure[14] of [2]rotaxane **6** viewed along the thread axis a) in capped sticks representation with selected close contacts indicated (majority of H atoms omitted for clarity) and b) in partial space-fill representation. Selected bond lengths (in Å): N1–H31 2.57, N2–H31 2.49, C31–H23 2.99, C31–H12 2.80, N4–H1 2.65, N4–H4 2.48, N5–H1 2.84, N5–H4 2.65.

The ^{1}H NMR spectra of rotaxanes **5**–**10** reveal a number of interesting features (partial ^{1}H NMR spectra for rotaxanes **5**, **6**, and **10** are shown in Figure 4). Firstly, the triazole C–H, which is already significantly shifted downfield relative to the free thread in rotaxane **5** ($\Delta\delta = 0.8$ ppm), resonates even further downfield in rotaxanes **6**–**10**. In the case of rotaxane **6**, H_d appears at 10.5 ppm—a $\Delta\delta$ on interlocking of 2.5 ppm (Figure 2b). Secondly, the desymmetrization of the two faces of the macrocycle due to the mechanical bond is clearly visible in the ^{1}H NMR spectra of rotaxanes **5**–**10**, as had previously been observed for rotaxane **4d**. The chiral glucose-based stopper in rotaxane **10** leads to an even more complicated ^{1}H NMR spectrum as the macrocycle is now completely desymmetrized by the mechanical bond: while macrocycle **3d** displays 8 separate ^{1}H resonances, rotaxane **10** exhibits 23 which can be assigned to the macrocyclic component, indicating a high degree of chiral information transfer between thread and macrocycle. The same effect is evident in the ^{13}C NMR spectrum of rotaxane **10** with 25 resonances observed which can be assigned to the macrocyclic component compared with 13 in macrocycle **3b**.

The "small" rotaxanes synthesized (Figure 2) demonstrate a number of important advantages of the CuAAC-AT approach using smaller macrocycles: 1) operationally trivial and general access to functionalized rotaxanes with half-threads derived from commercially available materials such as simple dialkylbenzene units (**5** and **6**), benzene rings bearing single-atom-reactive functionalities (**7**), trialkyl silyl units (**8**), simple flurophores (**9**), and chiral pool materials (**10**) without the need to modify them to include bulky substituted trityl groups with the concomitant increase in molecular weight and limitations with respect to solubility that entails; 2) the ability to use simple aryl azides and alkynes to generate [2]rotaxanes in which the thread is fully conjugated (**6**, **7**, and **9**) with the potential to extend this methodology to the synthesis of oligomeric insulated molecular wires;[9] 3) ^{1}H NMR and X-ray crystallographic analysis of the rotaxane products indicate significantly increased interaction between macrocycle and thread. In the case of rotaxane **10** this results in efficient transfer of chiral information from the thread to the macrocycle, raising the possibility of using a chiral-pool-derived, enantiopure thread as a mechanical chiral auxiliary for achiral macrocyclic ligands in asymmetric catalysis.[12]

In conclusion, we have demonstrated that it is possible to vary the size of the macrocycle in the CuAAC-AT reaction and, by reducing the size of the macrocycle, gain access to functionalized products in excellent yield. Further, employing the smallest macrocycle investigated, perhaps surprisingly, leads to the most efficient active template reaction reported to date in which an equimolar mixture of macrocycle and half-thread components leads to a quantitative yield of [2]rotaxane product. Work is currently underway to apply these findings to the synthesis of functional materials and devices. We are also investigating the effect of macrocycle size on other AT reactions not only in order to increase their synthetic utility, but also to determine if the size dependency of the reaction yield can shed any light on the underlying mechanism of the process.

Experimental Section

Synthesis of [2]rotaxanes **4** and **5**–**10**: Macrocycle (0.025 mmol), $CuPF_6{\cdot}(MeCN)_4$ (8.4 mg, 0.0225 mmol), and the required equivalents of azide and acetylene half-threads were combined in CH_2Cl_2 (2.5 mL) in a sealed CEM microwave vial which was purged with N_2 and then heated at 80 °C for 72 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with a saturated solution of ethylenediaminetetraacetic acid (EDTA) in 17.5% aqueous NH_3 (50 mL). The aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL), the organic extracts dried (Na_2SO_4), and the solvent removed in vacuo. Chromatography (gradient elution: 1:1 CH_2Cl_2/petrol and 0→10% MeCN) gave the [2]rotaxane product.

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[14] The crystal data and details of the structural refinement for rotaxane **6** are provided in the Supporting Information. CCDC 808340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

