Rotaxanes

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Cadiot–Chodkiewicz Active Template Synthesis of Rotaxanes and Switchable Molecular Shuttles with Weak Intercomponent Interactions**

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The noncovalent binding motifs used to template the synthesis of mechanically interlocked architectures are generally retained in the final products.[1] This feature has been widely exploited to make molecular shuttles,[2] rotaxanes with two or more discrete binding sites or "stations" on the thread between which the macrocycle incessantly shuttles through Brownian motion. However, the noncovalent interactions used to maximize the rotaxane yield and localize the position of the ring on the thread also provide the major contribution to the activation energy to shuttling.[3] To achieve faster moving rotaxane-based molecular machines, it will be necessary to make molecular shuttles with much weaker intercomponent interactions than are typically introduced with classical template methods.[4] Here we report on a new rotaxane-forming reaction that can produce rotaxanes with unsymmetrical threads (as required for switchable molecular shuttles) but does not leave strong intercomponent binding motifs in the rotaxane product. Instead the active template[5] Cadiot–Chodkiewicz[6] reaction is compatible with building blocks that can provide relatively modest macrocycle–thread binding motifs in the rotaxane, but which are still strong enough to afford good positional integrity of the ring. The methodology is exemplified through the synthesis of a "weak interaction" molecular shuttle in which a single hydrogen bond between the components determines the predominant position of the macrocycle in each of two well-defined states which can be switched between by reversible complexation with Li^+ or protonation.

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Active template syntheses differ from classical "passive-template" reactions in that a single species acts as both the template for the product architecture and the catalyst for the formation of the covalent bond(s) that captures it.[5] Although combining these two roles has several potential advantages,[5a] controlling the positions of the metal-ligated building blocks during the reaction to template the product puts additional demands (which can provide insight into the reaction pathway)[5d] on the mechanism of catalysis. Accordingly, successful combinations of ligands and metal-catalyzed reactions for active template syntheses are still rare and the development of new systems challenging.[5e]

The active metal template homodimerization of acetylenes to form rotaxanes[5b,c] introduces a relatively rigid linear connector which inhibits folding—potentially desirable for fully exploiting the spatial separation of the ring between different states[7]—but can only be used to make [2]rotaxanes with symmetrical axles. The coupling of two different building blocks is necessary to produce bistable molecular shuttles in which the macrocycle can be switched between two different positions on the thread. The Cu^I-mediated Cadiot–Chodkiewicz[6] heterocoupling of a terminal alkyne with an alkyne halide appeared a suitable candidate reaction for such studies (Table 1).

Promisingly, [2]rotaxane was produced (Table 1) using appropriately "stoppered" alkyne halide (**1a** or **1b**) and aryl alkyne (**2**) derivatives and a bidentate macrocycle (**3**) under typical conditions[6] used for the Cadiot–Chodkiewicz reaction in nonaqueous solvents. However, in these initial studies poor selectivity for the heterocoupled rotaxane (**4**) versus the homocoupled rotaxanes (**5** and **6**) was observed together with low overall conversion of the alkyne starting materials to bis-acetylene products. In an attempt to improve both the reaction yield and the selectivity for the heterocoupled rotaxane, we investigated changing the traditional Cadiot–Chodkiewicz procedure of mixing the alkyne and alkyne halide components with neutral amine bases, to preforming the copper acetylide by treatment of terminal alkyne **2** with *n*BuLi, followed by transmetalation with CuI (Table 2).[8]

Following this protocol, we were delighted to find that subsequent addition of bipyridine macrocycle **3** and bromoacetylene **1b** led to the desired [2]rotaxane **4** in high yield (84%) and with excellent selectivity (>98%) for the heterocoupled product (Table 2, entry 1).[9] Although the procedure did not prove compatible with reversing the reactive bromine/hydrogen functionalities of the alkyl and aryl acetylene building blocks (**7** with **8**, Table 2, entry 2),[10] when coupling

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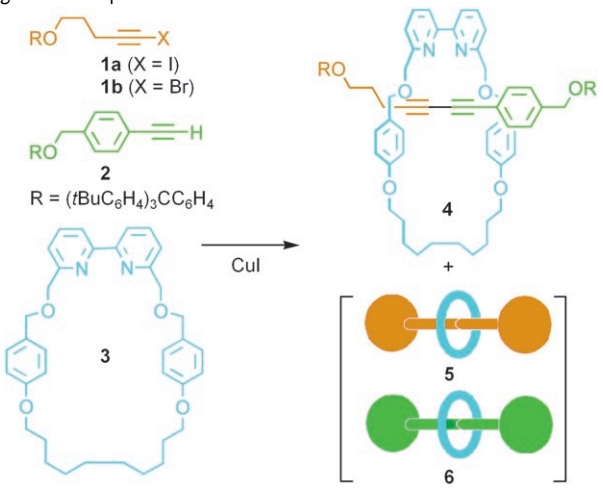
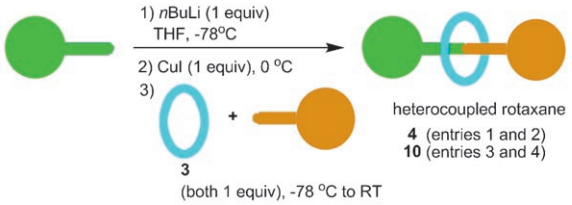
Table 1: Preliminary solvent screen for the bis-acetylene rotaxane forming active template Cadiot–Chodkiewicz reaction.[6]



Entry	Alkyne halide	Solvent	Rotaxane yield 1+2+3→4+5+6	Selectivity 4:5:6
1	**1a**	$(iPr)_2NH$	40%	10:9:1
2	**1a**	NEt_3	20%	2:15:1
3	**1a**	pyrrolidine	<2%	no rotaxane
4	**1a**	benzene[b]	35%	1.7:1:1
5	**1b**	$(iPr)_2NH$	<5%	2:5:1

[a] A solution of **1**, **2**, **3**, and CuI (all 1 equiv) was allowed to stir at 298 K under an atmosphere of N_2 for 18 h. [b] Plus 2 equiv of $(iPr)_2NH$.

Table 2: Substrate scope of the Cadiot–Chodkiewicz active metal template synthesis of heterocoupled [2]rotaxanes.

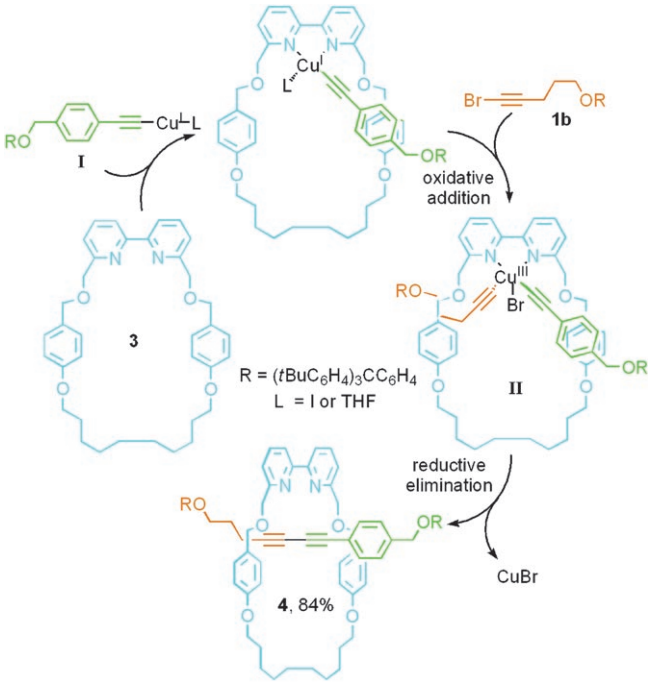


Entry	Terminal acetylene[a]	Bromo-acetylene	Rotaxane yield [%]	Selectivity
1	2	1b	84	>98%[b]
2	7	8	32	1.7:8:1 (**4**:**5**:**6**)
3	7	9	85	>98%[b]
4	11	1b	74	>98%[b]

[a] R = $(tBuC_6H_4)_3CC_6H_4$. [b] No homocoupled rotaxanes observed.

two different alkyl alkynes (**7** with **9** or **11** with **1b** to give **10**) either could be used successfully as the bromoacetylene partner whilst maintaining high yields and apparent exclusive selectivity for the heterocoupled rotaxane (Table 2, entries 3 and 4).

The Cadiot–Chodkiewicz reaction is thought to proceed via a different mechanism to the (also Cu-catalyzed) Glaser homocoupling of alkynes,[11] and the proposed pathway for the active-metal template rotaxane assembly of **4** is shown in Scheme 1. The preformed copper(I)–acetylide **I** is sequestered by bipyridine macrocycle **3**.[12] Oxidative addition across the C–Br bond of the bromoacetylene occurs from the opposite face of the macrocycle to produce Cu^{III} intermediate **II** and subsequent reductive elimination furnishes the heterocoupled [2]rotaxane.



Scheme 1. Proposed mechanism for the Cadiot–Chodkiewicz active metal template formation of [2]rotaxane **4**.[11]

To demonstrate the utility of this new active template reaction, we synthesized a stimuli-switchable molecular shuttle **12** which has modest strength intercomponent interactions of a type that would be difficult or impossible to access by traditional template methods. The single contact H-bond that molecular modeling (see the Supporting Information) indicates (Figure 2) exists between the aniline unit of the thread and bipyridine group of the macrocycle in **12** is too weak to template rotaxane formation through "stoppering" or "clipping" strategies[1] and no passive metal templates which utilize a 1+2 donor ligand set have been reported to date. However, the modified Cadiot–Chodkiewicz active metal template method readily produced molecular shuttle **12** in good yield (61%) from functionalized building blocks **13** and **14** with no homocoupled rotaxane products being detected (Scheme 2).

^{1}H NMR Spectroscopy clearly shows the macrocycle to be predominantly held over the axle aniline unit in neutral molecular shuttle **12** at 300 K in CD_2Cl_2. The ^{1}H NMR spectrum of the rotaxane (Figure 1b) displays significant upfield shifts (H_d 0.2 ppm, H_e 0.4 ppm, H_g 0.6 ppm) of signals associated with the aniline station relative to those in the free thread (Figure 1a). Calculations on the macrocycle-station

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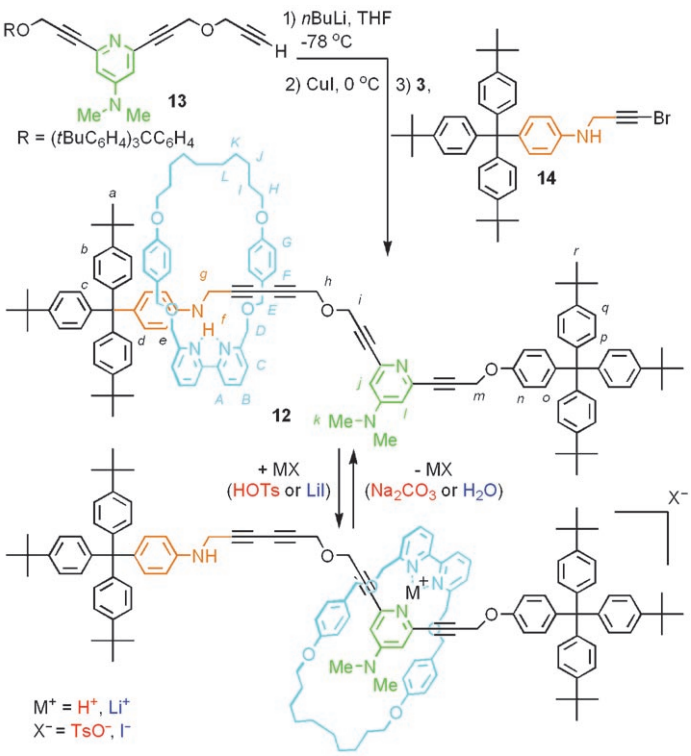

Scheme 2. Active template synthesis and stimuli-induced [by protonation (MX = HOTs) or complexation with Li^+ (MX = LiI)] translocation of the macrocycle in molecular shuttle **12**.

fragments for **12** in CH_2Cl_2 at B3LYP/3-21G* level[13] (see the Supporting Information) show that the minimum structure intercomponent binding energy, ΔG_{bind}, of -3.9 kcal mol^{-1} is largely attributable to a single contact H-bond of 2.1 Å between the (N)H of the aniline and one nitrogen atom of the macrocycle bipyridine unit (Figure 2a). A review of the Cambridge Structural Database (CSD) reveals a range of 2.1–2.4 Å for similar aniline-to-pyridine contacts in the solid state.[14]

Addition of 1 equivalent of TsOH to a solution of rotaxane **12** in CD_2Cl_2 causes significant shifts in several of the axle signals in the ^{1}H NMR spectrum (Figure 1c).[15] Protons H_d, H_e, and H_g associated with the aniline unit return to the position they occupy in the non-interlocked thread in the presence of TsOH (Figure 1d), while those of the DMAP station shift to higher field (H_j and H_l each 0.5 ppm, H_k 0.2 ppm). This is consistent with protonation of the DMAP nitrogen and translocation of the macrocycle along the thread so that the pyridinium NH hydrogen bonds strongly with the bipyridine moiety of the macrocycle (Scheme 2, MX = HOTs). B3LYP/3-21G* level calculations (see the Supporting Information) indicate that the protonated-DMAP-bound co-conformation is now favored by ca. 0.9 kcal mol^{-1} (Figure 2b). A search of the CSD finds that the calculated H-bond contact distance of 1.8 Å is in the 1.4–1.9 Å range found for pyridinium-to-pyridine H-bonds in the solid state.[16] Treating a solution of rotaxane **12**·H^+ with solid Na_2CO_3 quantitatively regenerates the neutral molecular shuttle **12**, returning the macrocycle to its original position on the thread.

A similar change in co-conformation could be generated by shaking a solution of rotaxane **12** in CD_2Cl_2 with excess LiI (Scheme 2, MX = LiI). The ^{1}H NMR spectrum of the shuttle after treatment with LiI (Figure 1f) displays significant upfield shifts and broadening of the resonances of the DMAP station (H_j and H_k) compared with the corresponding protons in the non-interlocked thread in the presence of excess LiI (Figure 1e).[17] As was seen with protonation, the signals of the rotaxane aniline station H_d, H_e, and H_g return to the positions they occupy in the non-interlocked thread. These changes are consistent with the mechanically interlocked components of rotaxane **12** coordinating Li^+ through the bipyridine moiety of the macrocycle and the DMAP station of the axle. A simple aqueous wash removes the metal salt and regenerates rotaxane **12** in its original form.

The utility of the Cadiot–Chodkiewicz active template strategy has been exemplified through the construction and operation of a switchable molecular shuttle which features a single hydrogen bond between the

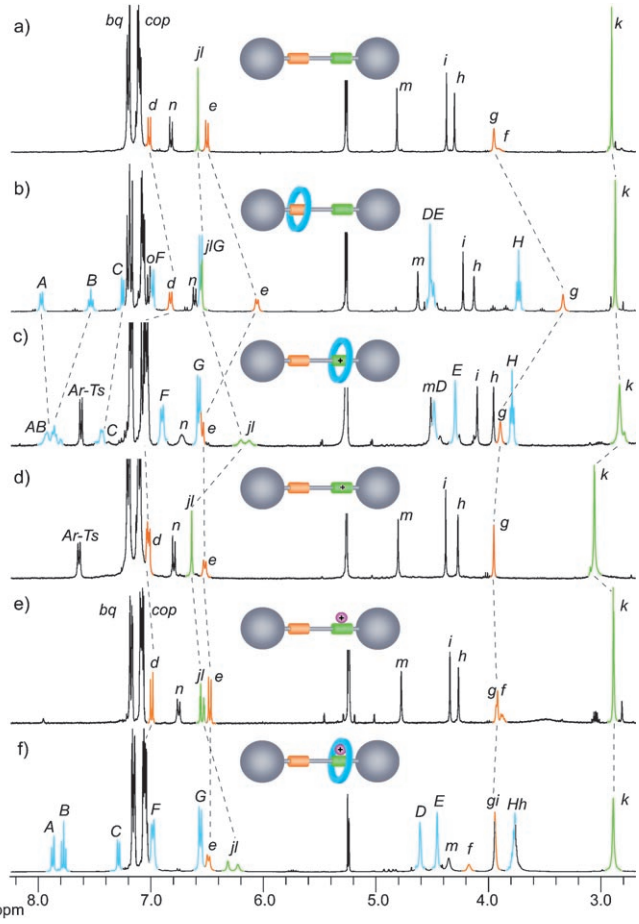

Figure 1. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 300 K) of a) non-interlocked thread, b) rotaxane **12**, c) rotaxane **12** + 1 equiv TsOH, d) non-interlocked thread + 1 equiv TsOH, e) non-interlocked thread in the presence of excess LiI, f) rotaxane **12** in the presence of excess LiI.

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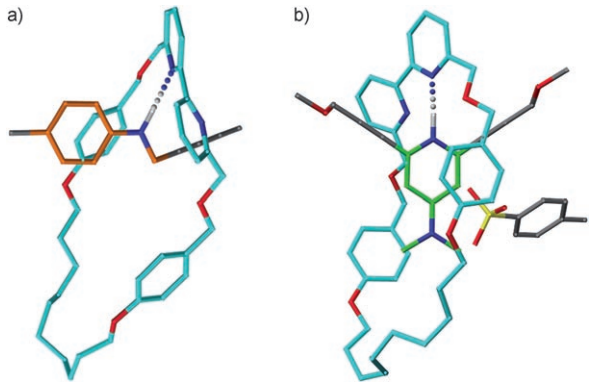

Figure 2. B3LYP/3-21G* level quantum chemical calculated minimum-energy macrocycle-station structures in CH_2Cl_2 at 298 K showing the single hydrogen-bond interactions between the macrocycle and a) aniline and b) protonated DMAP (dimethylaminopyridine; tosylate counterion) stations present in molecular shuttle **12** and **12**·H^+.[13] Hydrogen atoms not attached to N atoms are not shown for clarity. Intercomponent NH···N distances and angles: **12** 2.1 Å (153.6°); **12**·H^+ 1.8 Å (170.3°). Intercomponent binding energies (kcal mol^{-1}): electronic, ΔE_{bind}, **12** −8.0 (±0.05), **12**·H^+ −14.1 (±0.05); enthalpic, ΔH_{bind}, **12** −6.7 (±0.04), **12**·H^+ −11.4 (±1); free energy, ΔG_{bind}, **12** −3.9 (±0.1), **12**·H^+ −4.8 (±1). The errors in the calculations were estimated by increasing the solvent cavity radius by 0.5 Å.

mechanically interlocked components in each state, much less than half the intercomponent binding energy found in typical molecular shuttles yet still strong enough to ensure a high degree of positional integrity of the macrocycle in both forms. The methodology paves the way for faster moving, faster responding, mechanically interlocked molecular machines which can be designed to feature only the weakest non-covalent interactions necessary for their function.

Experimental Section

Procedure for the Cadiot–Chodkiewicz active template synthesis of rotaxane **4**: A solution of acetylene **2** (20 mg, 0.032 mmol) in THF (0.4 mL) was cooled to −78 °C. To this solution was added *n*BuLi (0.32 mL, 0.1 M in THF) at −78 °C. The resulting solution was allowed to warm to 0 °C over 15 min. CuI (6.2 mg, 0.032 mmol) was added at 0 °C and the resulting yellow solution allowed to warm to room temperature over 15 min. The reaction mixture was recooled to −78 °C and bipyridine macrocycle **3** (18 mg, 0.032 mmol) and bromoacetylene **1b** (22 mg, 0.032 mmol) were added as a solution in THF (0.6 mL). The resulting orange solution was allowed to stir at room temperature for 20 h before the reaction was quenched by addition of an aqueous solution of 17.5 % NH_3 saturated with ethylenediaminetetraacetic acid (EDTA). The layers were allowed to stir in air for 40 min during which time the aqueous layer turned blue. The aqueous layer was extracted with CH_2Cl_2 (×3) and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Chromatography (silica gel, 7:2.5:0.5 hexane:CH_2Cl_2:MeCN as eluent) yielded [2]rotaxane **4** as a colorless film (47 mg, 84 %).

Full details of the experimental procedures, compound characterization and molecular modelling are given in the Supporting Information.

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Keywords: Cadiot–Chodkiewicz reaction · heterocoupling · molecular shuttles · rotaxanes · template synthesis

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[9] Employing an iodoacetylene in place of the bromoacetylene led to poor selectivity (8:2:5 of **4**:**5**:**6**) and reduced (78 %) conversion.

[10] As well as producing only 32 % rotaxane (the majority arising from homodimerization of the bromoacetylene; Table 2, entry 2), **8** is prone to decomposition. To ensure high yields and selectivity of the heterocoupled rotaxane, it appears that aryl acetylenes should only be employed as the terminal acetylene coupling partner in such reactions.

[11] The mechanism of the Cadiot–Chodkiewicz coupling is generally held to proceed in an analogous fashion to the Castro–Stephens

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[12] The heterocoupling does not proceed in the absence of the bipyridine macrocycle ligand **3** under these conditions. A control reaction repeating this procedure in the absence of **3** resulted in no heterocoupled thread (by ^{1}H NMR analysis). The high yields of the active template rotaxane forming reaction without the need for excess reactants can be attributed to the absence of background reactivity.

[13] Geometry optimizations and frequency calculations for the macrocycle-station fragments of **12** and **12**·HOTs were carried out at B3LYP/3-21G* level with the Gaussian03 program (M. J. Frisch, et al. Gaussian 03, revision C.02; Gaussian, Inc., Wallingford CT, **2004**). The hybrid exchange-correlation B3LYP (A. D. J. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652) functional was adopted on the basis of its reported suitability in describing both hydrogen bonding interactions and aromatic stacking interactions (Y. Zhao, D. G. Truhlar, *J. Chem. Theory Comput.* **2005**, *1*, 415–432), particularly in the presence of N-based π-electron systems such as those considered here (G. Bouchoux, *Mass Spectrom. Rev.* **2007**, *26*, 775–835). Specifically, it has been shown to properly account for the geometry and proton and hydrogen bonding affinity of both aniline (N. Russo, M. Toscano, A. Grand, T. Mineva, *J. Phys. Chem. A* **2000**, *104*, 4017–4020; V. Q. Nguyen, F. Tureček, *J. Mass Spectrom.* **1997**, *32*, 55–63) and pyridinium based systems (H. Szatyłowicz, T. M. Krygowski, J. E. Zachara-Horeglad, *J. Chem. Inf. Model.* **2007**, *47*, 875–886). Solvent phase (CH_2Cl_2) calculations were performed with the self-consistent reaction field method (SCRF) (M. W. Wong, K. B. Wiberg, M. J. Frisch, *J. Am. Chem. Soc.* **1992**, *114*, 1645–1652, and references therein) implemented in the Gaussian program.

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