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*Vol. 80 Commemorative Accounts*

# Clicked Interlocked Molecules

**Ivan Aprahamian,[1] Ognjen Š. Miljanić,[1] William R. Dichtel,[1,2] Kyosuke Isoda,[3]**
**Takuma Yasuda,[3] Takashi Kato,[3] and J. Fraser Stoddart*[1]**

[1]California NanoSystems Institute and Department of Chemistry and Biochemistry, University of California,
Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095, U.S.A.

[2]Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, California 91125, U.S.A.

[3]Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

Received April 26, 2007; E-mail: stoddart@chem.ucla.edu

The $Cu^I$-catalyzed Huisgen 1,3-dipolar cycloaddition, popularized as "click chemistry," is one of the latest acquisitions to the synthetic arsenal for the making of mechanically interlocked molecular compounds. The high efficiency and functional group tolerance of "click chemistry" allows this reaction to be employed at the stoppering step in the "threading-followed-by-stoppering" sequence that produces rotaxanes, and in the macrocyclization step that affords catenanes. The use of this kind of "click chemistry" alleviates some of the drawbacks associated with previous approaches to the template-directed synthesis of mechanically interlocked molecular compounds—approaches such as "clipping;"—and opens up the way to more exotic mechanically interlocked molecules. Employing this new approach, [2]-, [3]-, and [4]rotaxanes and [2]catenanes have all been prepared in a convergent and efficient manner. Their template-directed synthesis relies, in the beginning, on the formation of [*n*]pseudorotaxanes, which can either (i) be stoppered, affording [*n*]rotaxanes, or (ii) induced to undergo an intramolecular cyclization, affording [2]catenanes. This new synthetic approach has also been employed in the template-directed synthesis of a self-complexing system as well as a two-station, degenerate [2]rotaxane (molecular shuttle) which was used to measure the energy barrier ($15\,\mathrm{kcal\,mol^{-1}}$) to shuttling by a cyclobis(paraquat-*p*-phenylene) ring between two identical 1,5-dioxynaphthalene (DNP) stations across a 1,2,3-triazole unit. It has also been found that the $Cu^I$-salt, employed in the click reaction between an azide and an alkyne, can act as both a catalyst and a template in the formation of [2]rotaxanes. The "click" approach has also been used in the formation of a bistable [2]rotaxane containing a DNP station and a tetrathiafulvalene one. Electrochemical experiments performed on this compound indicate that the presence of the triazole unit does not influence the kinetics or thermodynamics of the redox-controlled switching process. Finally, the synthesis of a liquid-crystalline bistable [2]rotaxane, which shows smectic A phase behavior over a wide range of temperatures, is described.

## 1. Introduction

The means by which mechanically interlocked molecules, such as catenanes, rotaxanes, and knots,[1] have been made, has undergone a major transformation during the past two decades. The use of $Cu^I$-based template-directed synthesis[2] by Sauvage et al.[3] in the early 1980's has paved the way for the efficient preparation of a large number of mechanically interlocked molecular compounds. Over the course of the past 25 years, synthetic protocols have evolved to encompass a myriad of recognition motifs[1]—such as donor–acceptor, hydrogen bonding, and hydrophobic interactions—as the key interactions presiding over the efficient formation of mechanically interlocked molecules. In the beginning, the research was driven by the synthetic challenge, as well as by the topological interest in and the exotic nature of the molecules themselves. In parallel with the development of template-directed synthetic strategies, interest in these molecules has also flourished with time, spearheaded largely by the introduction of functional attributes into these molecules. One of the key breakthroughs in the field was the introduction of bistable [2]rotaxanes and [2]catenanes,[4] a development which has led[5,6] to the use of such molecules in the fabrication of Molecular Electronic Devices (MEDs) and as actuating materials in NanoElectro-Mechanical Systems (NEMS) among other applications. The bistability present in two-station mechanically interlocked molecules stems from the mechanical bonds[4] and noncovalent forces that hold their components together in a rather precise way. These combined properties can give rise to relative movements, such as discrete circumrotation[7] and shuttling[8]

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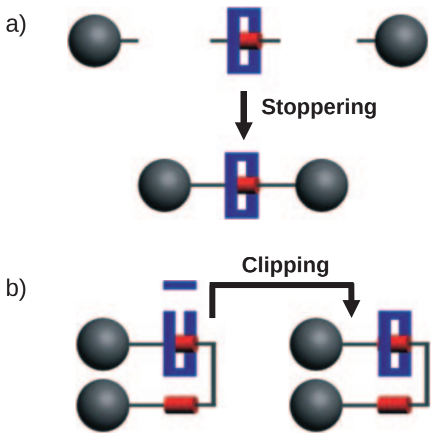


Scheme 1. Template-directed syntheses of donor–acceptor rotaxanes using, a) the clipping of a macrocycle around a dumbbell, and b) stoppering of a pseudorotaxane to form a [2]rotaxane.

motions which can, in principle, be controlled by external stimuli, enabling the development of such molecules as switches[5] and machines.[6]

The main synthetic protocols, employed in the synthesis of single station and bistable mechanically interlocked compounds are (Scheme 1) the "threading-followed-by-stoppering" and "clipping" approaches.[8a,b] The former approach is occasionally limited by the stoppering step which has to be tolerant of the other functional groups present in the noncovalently bound precursors, i.e., pseudorotaxanes. Until recently,[4–6] a template-directed "clipping" approach has dominated the synthesis of donor–acceptor catenanes and rotaxanes containing the $\pi$-accepting ring cyclobis(paraquat-*p*-phenylene)[9] (**CBPQT**$^{4+}$) (Chart 1) ring which is formed, using appropriate acyclic precursors, around rings and dumbbells, respectively, containing $\pi$-donating units. Since the **CBPQT**$^{4+}$ ring is sensitive to reducing agents, bases, and nucleophiles, the "clipping" reaction is almost always the final step in the synthesis of catenanes and rotaxanes. These constraints limit both the the structural complexity and practical preparative scale of the mechanically interlocked compounds that can be designed and produced.

Recently, new approaches have been pursued by us and other groups,[10–14] which proceed under conditions compatible with the functional groups and host–guest binding present in these mechanically interlocked molecules. One of these approaches involves the use of Cu$^{I}$-catalyzed Huisgen[15] 1,3-dipolar cycloaddition[16] in the formation of catenanes and rotaxanes. The "click chemistry" approach, popularized by Sharpless et al.,[16a] is highly efficient, functional group tolerant, and proceeds under mild reaction conditions, making it appropriate for the template-directed synthesis of mechanically interlocked molecules. When coupled with "threading-followed-by-stoppering" "click chemistry" can be used to overcome the limitations of the "clipping" approach. The synthetic strategy relies, in general, upon the formation of [*n*]pseudorotaxanes, wherein the appropriate macrocycle is threaded by linear molecules containing complementary recognition units and terminated by azide and/or alkyne functions which can subsequently undergo click reaction: it is a good example of supramolecular assistance to covalent synthesis.[17] Here, we describe the use of "click chemistry" by us and other researchers in the efficient synthesis of [*n*]rotaxanes and [2]catenanes.

## 2. Clicked [*n*]Rotaxanes

Retrosynthetic analysis of the architectures illustrated in Fig. 1 has led[10] recently to the development of a "toolkit" of alkyne- or azide-functionalized rods, stoppers, and **CBPQT**$^{4+}$ derivatives which provide modular access to a wide variety of mechanically interlocked molecular compounds.

The "toolkit" has been used in the synthesis of a series of 1,5-dioxynaphthalene (DNP)-based [*n*]rotaxanes by applying the "click chemistry" mediated "threading-followed-by-stoppering" method.[10] More often than not, the reaction usually starts (Scheme 1) with the formation of a stable pseudorotaxane precursor comprised of the appropriate $\pi$-electron donor–acceptor pair, followed by the stoppering reaction. Application of this general synthetic strategy involves (Scheme 2) the mixing of **CBPQT**$\cdot$4PF$_6$ in DMF at $-10\,^\circ$C with an azide-terminated DNP derivative. Under these conditions, the equilibrium lies predominantly in favor of formation of the [2]pseudorotaxane. A propargyl-terminated stopper can then be added to the reaction mixture, along with CuSO$_4\cdot$5H$_2$O and ascorbic acid as an in situ reductant. Following these mild reaction conditions and appropriate workup, the [2]rotaxane **1**$\cdot$4PF$_6$ can be isolated[10] in 82% yield.

The same general methodology was applied in the template-directed synthesis of [3]- and [4]rotaxanes. Previously, a doubly bistable [3]rotaxane had been synthesized[18] in only 9%

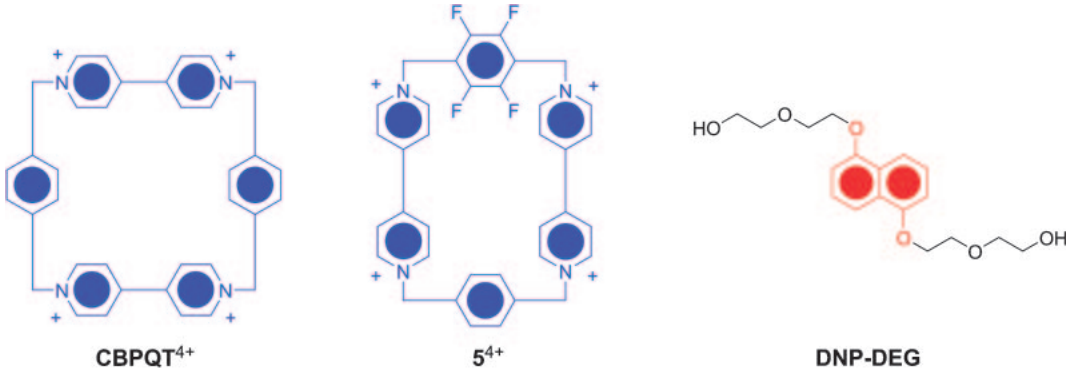


Chart 1.

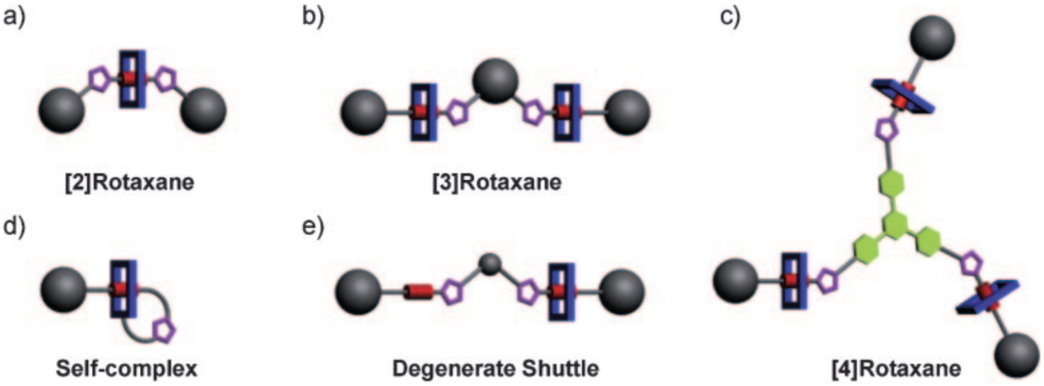
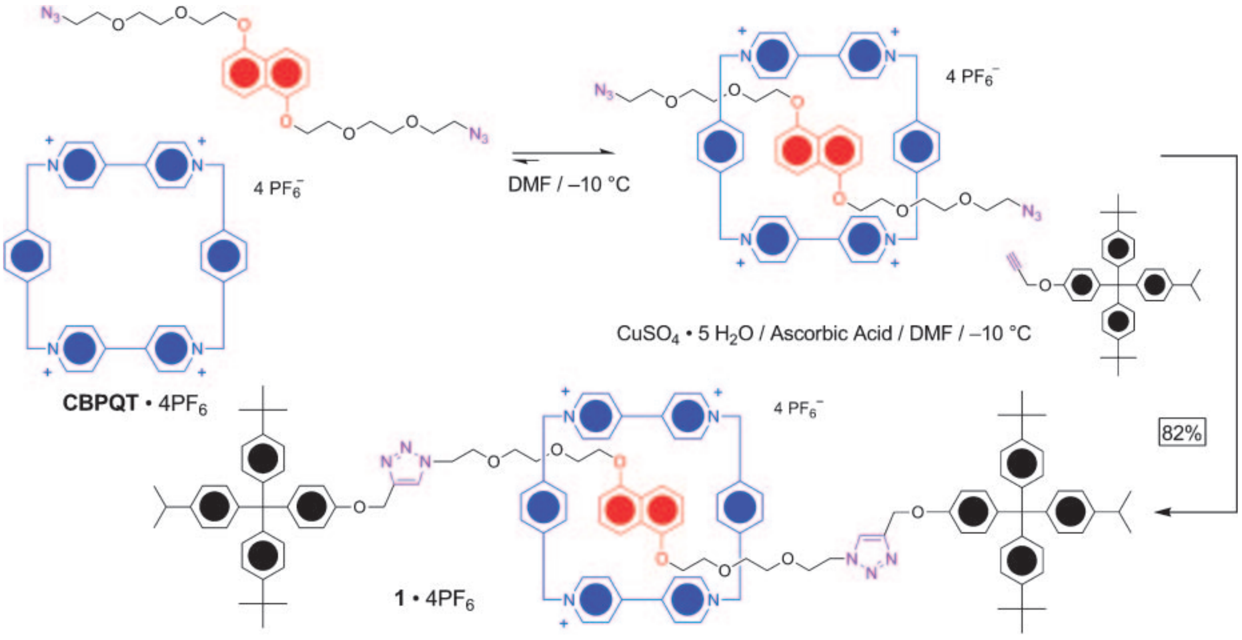


Fig. 1. A graphical representation of a collection of mechanically interlocked compounds synthesized via click chemistry, from simple azide- and alkyne-functionalized 1,5-dioxynaphthalene and **CBPQT**$^{4+}$ derivatives.

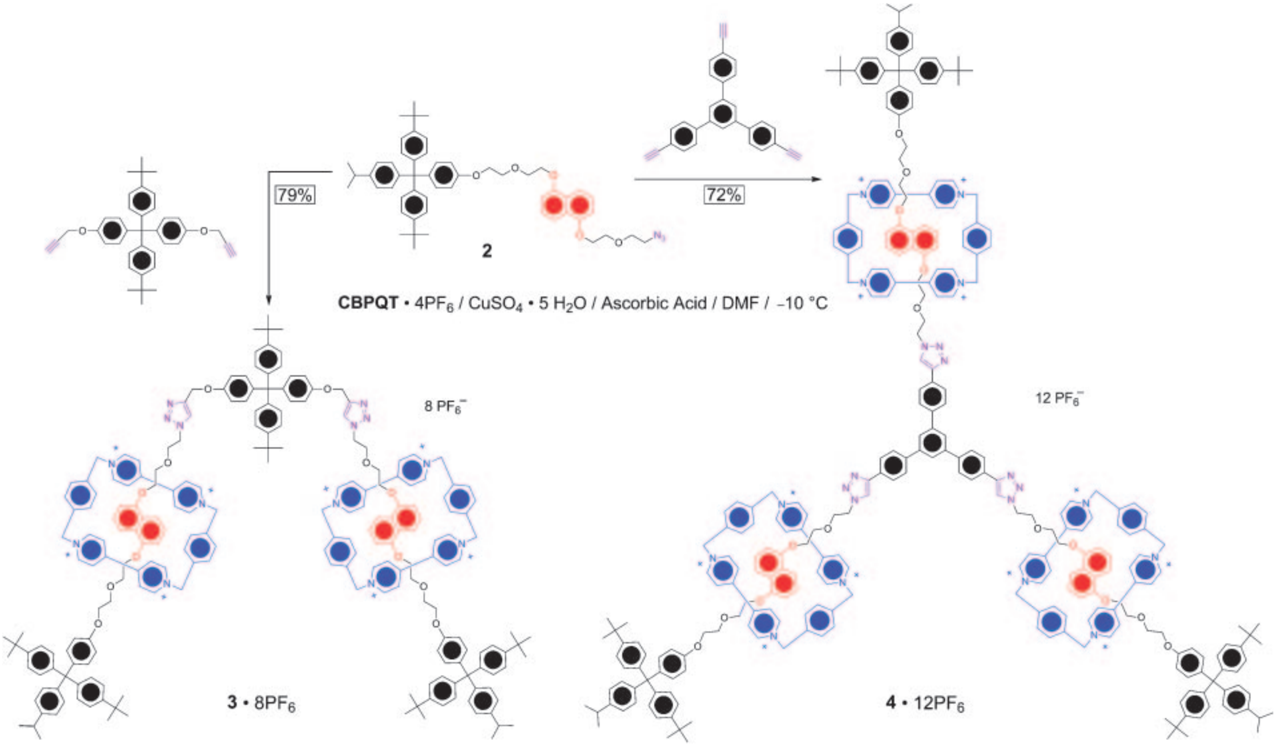
yield, following the “clipping” of the two **CBPQT**$^{4+}$ rings around a synthetically challenging palindromic dumbbell. Using the “click” methodology, in conjunction with a simple DNP derivative **2**, carrying an azide function at one end and a stopper at the other, a simple [3]rotaxane **3**•8PF$_6$ has been isolated[10] in 79% isolated yield (Scheme 3). The attractiveness of the “click” approach is best illustrated by the synthesis in 72% yield (Scheme 3) of the previously unknown [4]rotaxane **4**•12PF$_6$.

The coupling of “click chemistry” with the “threading-followed-by-stoppering” approach offers several additional advantages. For example, the procedure can be used in the preparation of [2]rotaxanes incorporating **CBPQT**$^{4+}$ derivatives that are weakly binding. The association constant ($K_a = 690 \pm 220\,\mathrm{M}^{-1}$) between **DNP-DEG** (Chart 1) and **5**•4PF$_6$, measured[10b] by isothermal titration microcalorimetry[19] (ITC) in MeCN at 298 K, is significantly lower than the value ($K_a = 36400 \pm 250\,\mathrm{M}^{-1}$) obtained[5h] for the parent system, [**DNP-DEG** ⊂ **CBPQT**]•4PF$_6$. This difference in binding ability has been used to test the scope of the “click” approach for the preparation of rotaxanes. The attempted synthesis[10b] of a [2]rotaxane by reacting **6**•2PF$_6$ and 1,4-bis(bromomethyl)benzene for two weeks in the presence of the DNP-containing dumbbell **7** resulted (Scheme 4a) in none of the desired [2]rotaxane being formed. Subjecting the diazide **8** and **5**•4PF$_6$ to the azide–alkyne cycloaddition conditions, however, has afforded (Scheme 4b) the [2]rotaxane **9**•4PF$_6$, in 11% yield. It was also demonstrated[10b] that the yield of **9**•4PF$_6$ can be increased to 37% by running the reaction in the presence of 3 equiv of **5**•4PF$_6$.

Vapor diffusion of *i*-Pr$_2$O into a solution of **5**•4PF$_6$ in MeCN yielded single crystals suitable for X-ray crystallography.[10b] The solid-state structure is shown in Fig. 2. The two adjacent pyridinium rings are twisted 33° out of the plane formed by the four N$^+$ atoms on account of the presence of the four fluorine atoms, whereas the pair of pyridinium rings adjacent to the *p*-phenylene bridges have only a 3° out-of-plane twist. The size of the binding cavity is reduced significantly compared to that in the parent **CBPQT**$^{4+}$ ring on account of the increased torsion between the bipyridinium rings,



Scheme 2. Template-directed syntheses of the [2]rotaxane **1**•4PF$_6$.

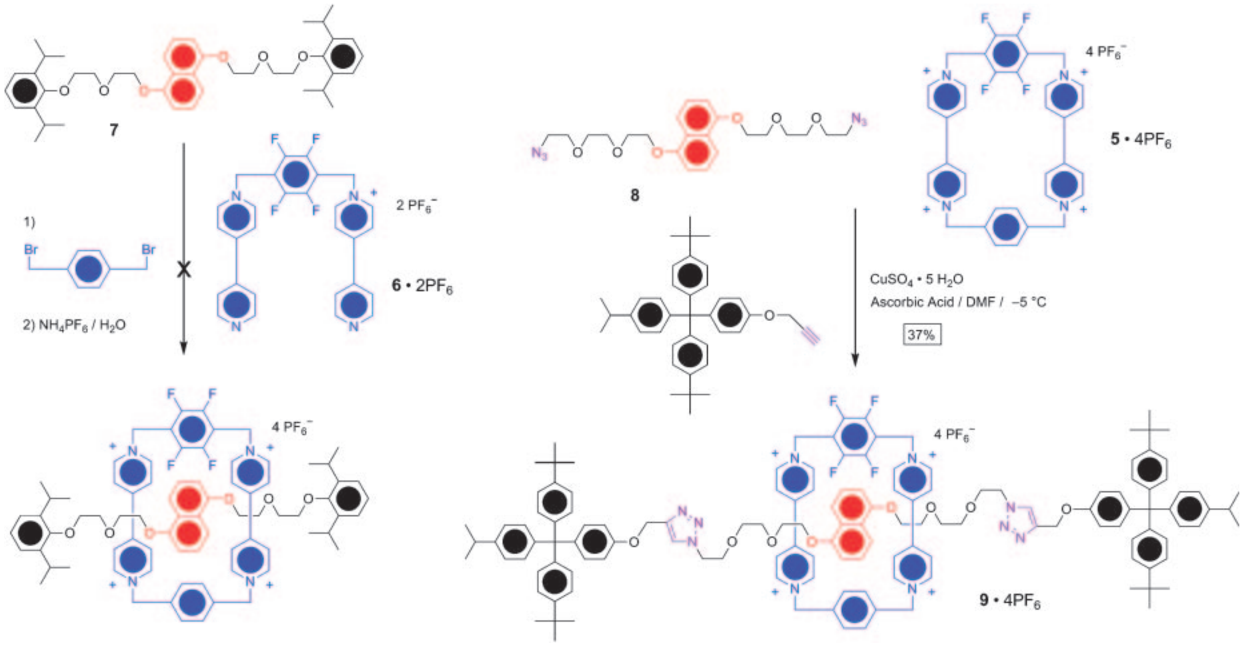


Scheme 3. Template-directed syntheses of the [3]rotaxane $\mathbf{3}\cdot 8\mathrm{PF}_6$, and [4]rotaxane $\mathbf{4}\cdot 12\mathrm{PF}_6$.

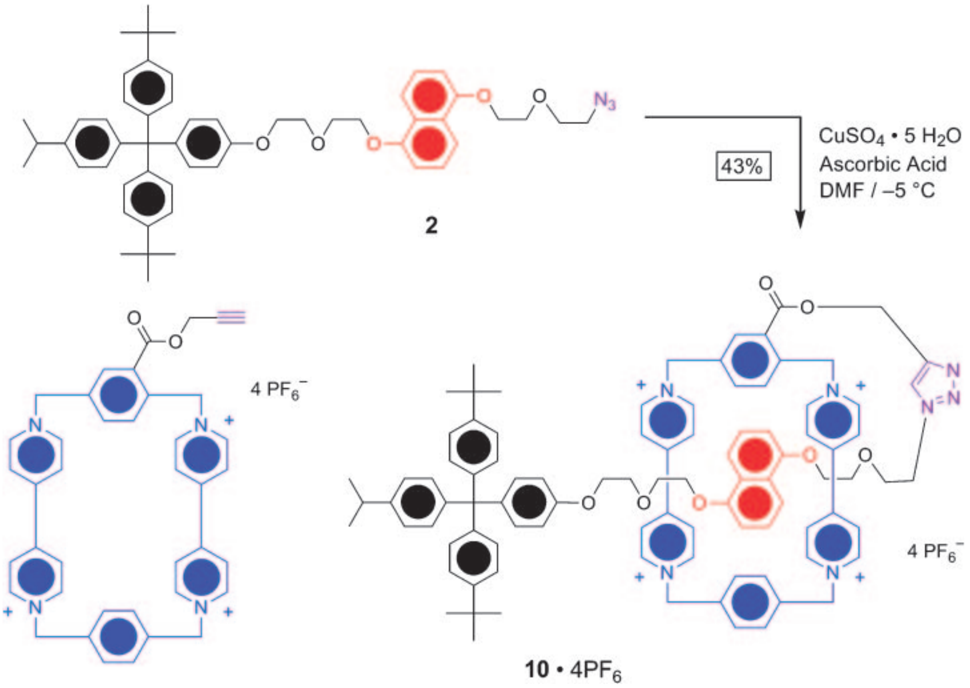
a factor which might explain, in part at least, the reduced ability of $\mathbf{5}\cdot 4\mathrm{PF}_6$ to form complexes with $\pi$-donating substrates.

Furthermore, the self-complexing[20] mechanically interlocked compound $\mathbf{10}\cdot 4\mathrm{PF}_6$, was prepared in 43% yield (Scheme 5) by reacting[10b] an alkyne-functionalized **CBPQT**$^{4+}$ derivative with the azide **2**. Since self-complexing compounds have a rich stereochemistry and display[21] a variety of interesting dynamic processes, improved and efficient methods for their preparation will facilitate their further development and exploitation as molecular switches[5] and machines.[6]

The molecular shuttle $\mathbf{11}\cdot 4\mathrm{PF}_6$ was prepared[10b] in 16% yield (Scheme 6) by subjecting (i) 2 equiv of the azide **2**, (ii) 1 equiv of 1,4-diethynylbenzene, and (iii) 1 equiv of **CBPQT**$\cdot 4\mathrm{PF}_6$, to the Cu$^{\mathrm{I}}$-catalyzed cyclization conditions. The rate of shuttling of the tetracationic cyclophane over the 1,2,3-triazole units placed between the two equivalent DNP



Scheme 4. a) The unsuccessful synthesis of a tetrafluorinated-CBPQT$^{4+}$-containing [2]rotaxane using the clipping approach. b) The click approach affords the [2]rotaxane $\mathbf{9}\cdot 4\mathrm{PF}_6$, in 37% yield.



Scheme 5. Template-directed syntheses of the self-complexed rotaxane $\mathbf{10}\cdot4PF_6$.

recognition sites was measured by variable temperature $^1H$ NMR spectroscopy. Using the coalescence method, the energy barrier to shuttling was determined to be 15.5 kcal mol$^{-1}$. This value is similar to those (15.0 and 15.5 kcal mol$^{-1}$) obtained[8g] for other molecular shuttles in which the linking units between the two equivalent DNP rings contain triphenylene and tetraethylene glycol units, respectively. This observation demonstrates that the triazole rings do not affect appreciably the rate of the degenerate shuttling processes in molecular shuttles.

Recently, Sauvage et al.[11] have used a similar "threading-followed-by-stoppering" approach in the efficient synthesis (Scheme 7) of a labile $Cu^I$–rotaxane-like complex having a 2,2′-bipyridine ligand **12** extended outwards from its 5 and 5′ positions as the threaded chelate. The tetrahedral coordination geometry of $Cu^I$ enables the trapping of a pair of bidentate ligands—the thread **12** and a macrocycle **13**—in a mutually orthogonal orientation, creating a [2]pseudorotaxane which is capable of undergoing stoppering reactions to form the desired mechanically interlocked compound $\mathbf{14}\cdot PF_6$. "Click chemistry" was employed because the threaded chelate used in the synthesis was unhindered, a property which destabilizes the $Cu^I$-based pseudorotaxane required in the production of the [2]rotaxane. When sterically hindered chelates, such as 2,9-dianisyl-1,10-phenanthroline derivatives, are employed, very stable $Cu^I$-based [2]pseudorotaxanes, which do survive the stoppering reaction conditions, are obtained. The template-directed synthesis of [2]rotaxanes involving unhindered chelates, however, is much more desirable because the mechanically interlocked components will rotate much faster[22] than they do in their highly hindered counterparts, a property which is required in applications pertaining to molecular switches[5] and machines.[6] The synthesis (Scheme 7) of the $Cu^I$ complex precursor has been accomplished by preforming a [2]pseudorotaxane between a diazido-terminated 2,2′-bipyridine derivative **12** and the 30-membered ring compound **13** employing $Cu^I$-template-directed threading.[11] In the second step, an alkyne-terminated stopper was added to the reaction mixture, in addition to 0.75 equiv of the copper catalyst $[Cu(MeCN)_4PF_6]$ and 0.4 equiv of base ($Na_2CO_3$). The reaction mixture was then stirred for 21 h, followed by workup and purification by chromatography, to yield the targeted [2]rotaxane $\mathbf{14}\cdot PF_6$ in 62% yield. Cyclic voltammetry (CV) indicated that the [2]rotaxane behaves in a manner similar to that reported previously for related compounds,[22] confirming that the triazole ring does not alter appreciably the electrochemical properties of the [2]rotaxane.

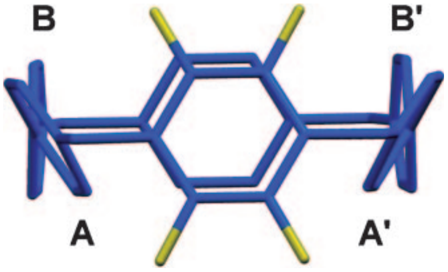
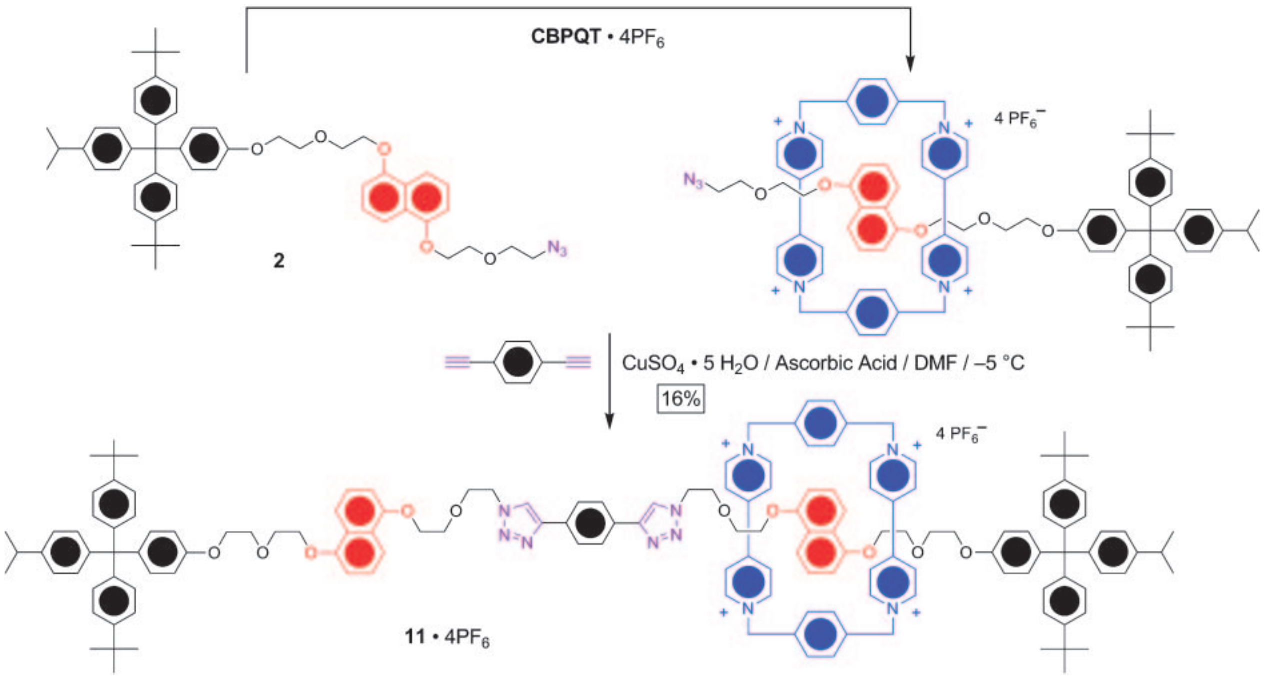


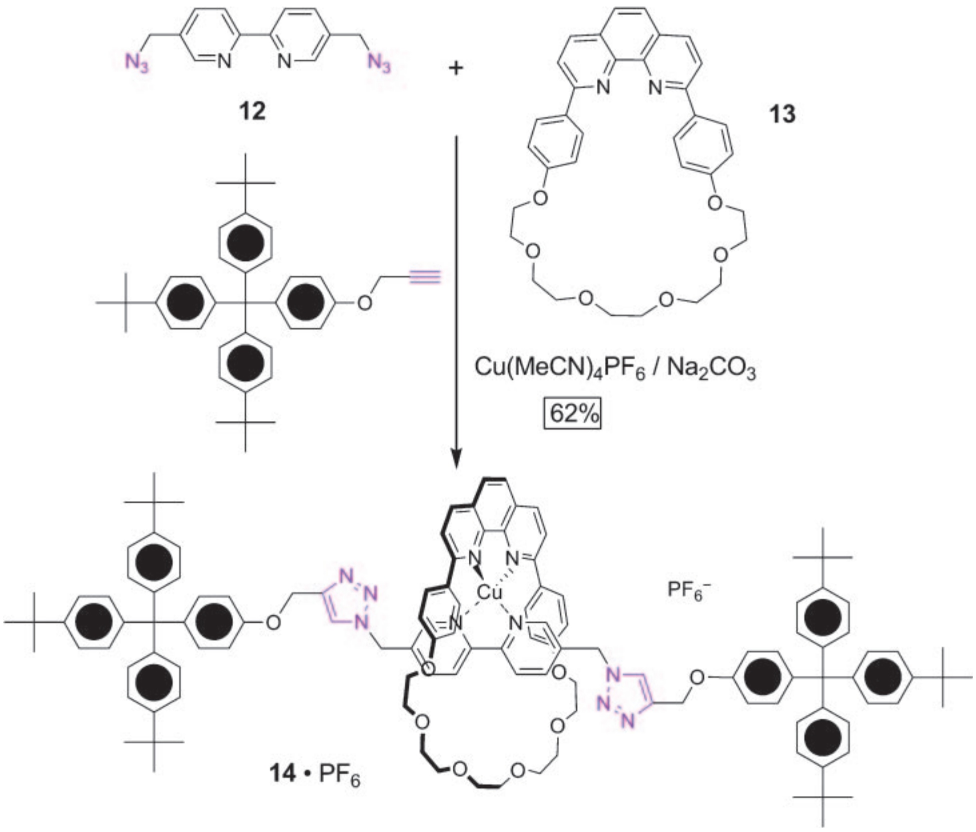
Fig. 2. A view along the axis of the $F_4$-xylene ring of $\mathbf{5}\cdot4PF_6$. The pyridinium rings nearest the perflourinated benzene (A and A′) ring in the uncomplexed cyclophane are twisted 33° out of the plane formed by the four nitrogen atoms.

Leigh et al.[12] have recently announced an elegant rotaxane-forming protocol (Scheme 8) in which $Cu^I$ acts as both the catalyst and the template during the synthesis of the mechanically interlocked compound. The synthetic strategy relies on the fact that the kinetics of "click reactions" in organic solvents are enhanced[16a] in the presence of tertiary amines, especially pyri-

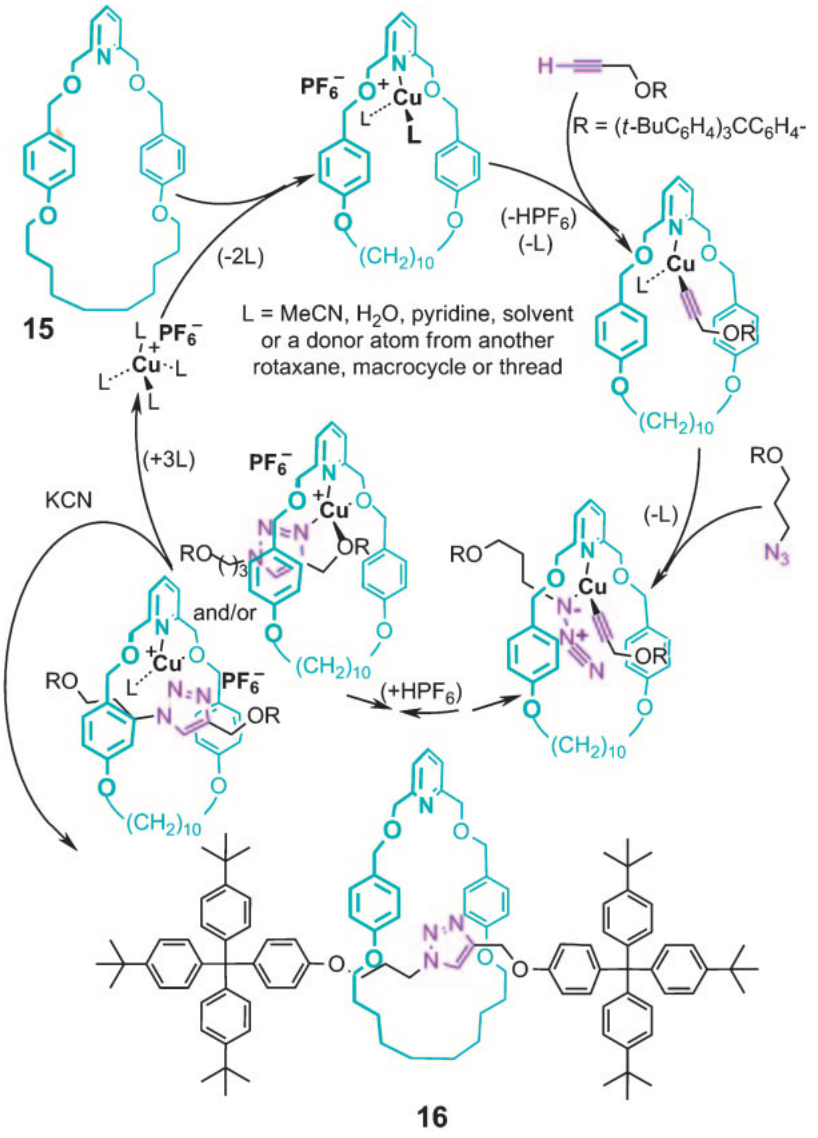


Scheme 6. Template-directed syntheses of the degenerate [2]rotaxane **11**•4PF$_6$.

dines. Therefore, a macrocycle bearing an endotopic ligating nitrogen can be used to direct the catalysis in its cavity. The 2,6-disubstituted pyridine macrocycle **15** was stirred overnight in the presence of alkyne- and azide-terminated stoppers, along with 1 equiv of Cu(MeCN)$_4$PF$_6$ as the copper source, in CH$_2$Cl$_2$ to obtain (Scheme 8), after demetalation with KCN, the desired [2]rotaxane **16** in 57% yield. When excess of the stoppering reagents were employed, the yield increased to 94%. When substoichiometric amounts of the copper salt (20 mol % relative to the macrocycle) were used and the reaction



Scheme 7. Template-directed syntheses of the Cu$^{I}$-rotaxane **14**•PF$_6$.



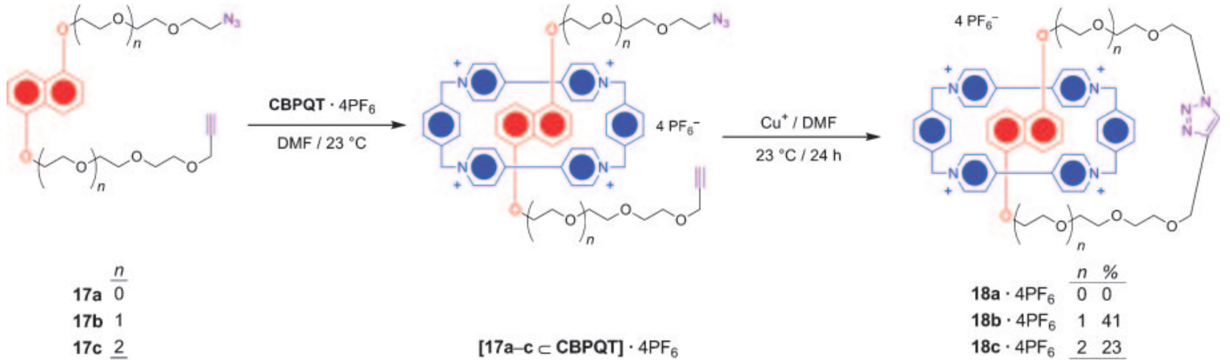
Scheme 8. The proposed catalytic cycle for the $Cu^I$-templated synthesis of the [2]rotaxane **16**.

run at room temperature, it stopped after the rotaxane, equivalent to the amount of copper, had formed (20% yield). The addition of pyridine as a competing ligand, however, enabled the catalyst to turn over, and a substoichiometric reaction was observed, affording yields in the range of 38–59%. Optimizing reaction conditions involving the elevation of temperature led to the isolation of the [2]rotaxane **16** in 82% yield after 36 h and using only 4 mol % of the copper salt with respect to the stoppers.

### 3. Clicked [2]Catenanes

The template-directed synthesis of [2]catenanes, wherein a kinetically controlled intramolecular "click reaction" takes place, requires[13] the formation (Scheme 9) of a [2]pseudorotaxane between, for example, an unsymmetrically substituted oligoether **17**, containing a $\pi$-electron-donating unit, and the $\pi$-accepting **CBPQT**$^{4+}$ ring. On mixing **17** with **CBPQT**$\cdot$4$PF_6$ in equimolar amounts, the solution turned deep purple, indicating the formation of the pseudorotaxane [**17** $\subset$ **CBPQT**]$\cdot$4$PF_6$. Treating the 1:1 complex formed between **17b** and **CBPQT**$^{4+}$ with $CuSO_4\cdot5H_2O$ and ascorbic acid, afforded[13] the [2]catenane **18b**$\cdot$4$PF_6$ in 41% yield. Employing the same methodology and using **17c** which has a longer oligoether thread, the [2]catenane **18c**$\cdot$4$PF_6$ was obtained in 23% yield. When the shorter threaded analogue **17a** was used, no reaction is observed, even after prolonged reaction times.

Single crystals of **18b**$\cdot$4$PF_6$, suitable for X-ray crystallography, were grown[13b] by vapor diffusion of *i*-$Pr_2O$ into a MeCN solution of the catenane at 23 °C. The solid-state structure (Fig. 3) of the [2]catenane is reminiscent of DNP/CBPQT$^{4+}$-based systems in respect of its mechanically interlocked nature and the alignment of the donor–acceptor units. Also present is a non-repulsive interaction between the 1,2,3-triazole and one of the bipyridinium subunits in the tetracationic cyclophane. The distance between the centroid of the triazole ring and the average plane of the inner bipyridinium unit is 3.38 Å, i.e., very close to that of the DNP-bipyridinium separation. Additionally, the two planes are nearly parallel (7.3°) with the triazole ring being ever so slightly offset relative to one of the two pyridinium rings.



Scheme 9. Template-directed synthesis of the [2]catenanes **17b**•$4PF_6$ and **17c**•$4PF_6$ using click chemistry.

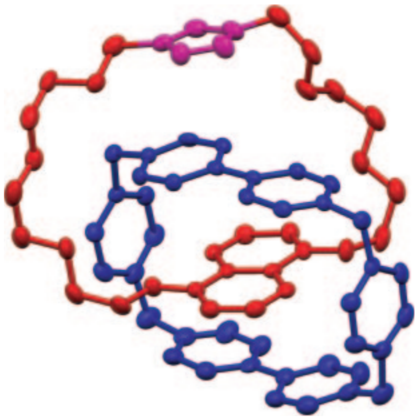


Fig. 3. The solid-state structure of $\mathbf{18b}^{4+}$. Acceptor ring shown in blue, donor thread in red, and triazole ring in purple.

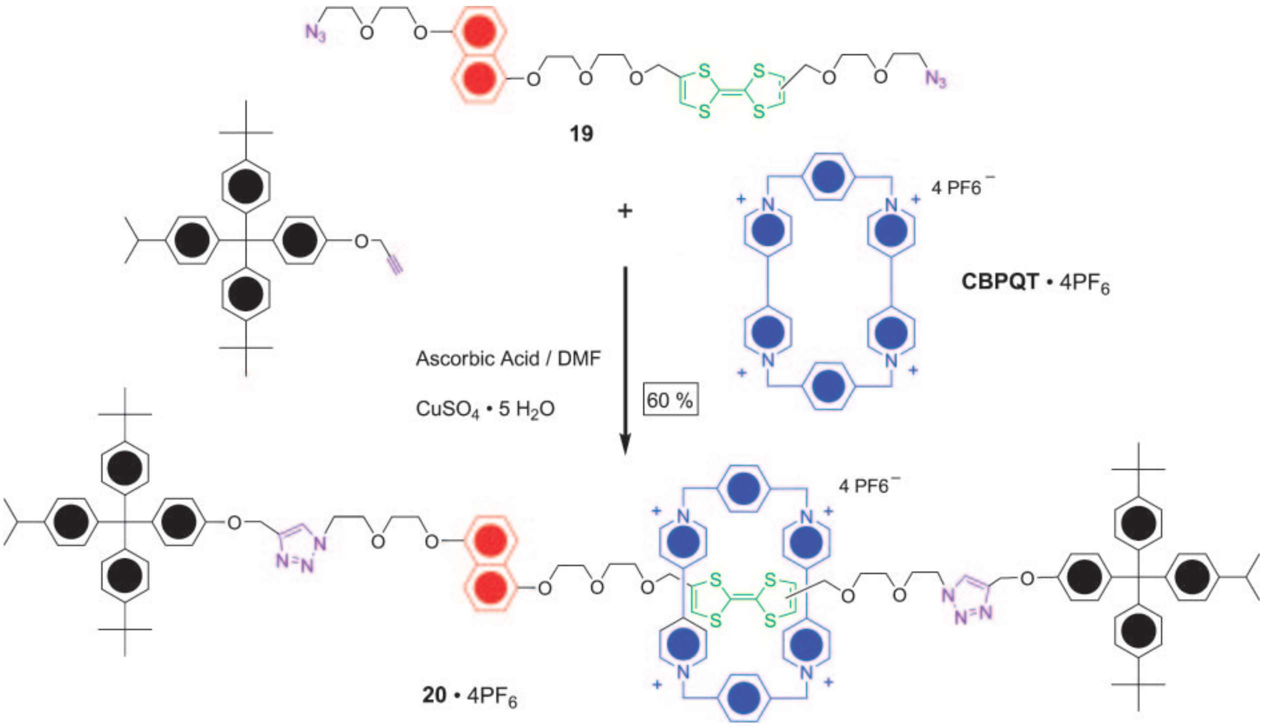
The triazole protons in **18b**,**c**•$4PF_6$ resonate in $CD_3CN$ at $\delta = 7.05$ and 7.31 ppm, respectively, as sharp singlets over a wide range of temperatures. These chemical shifts are notably different, i.e., $\delta = 8.02$ ppm in **1**•$4PF_6$, from those observed[10] in triazole-containing [2]rotaxanes (Scheme 2), suggesting that they are shielded by the closely located bipyridinium rings. Dynamic $^1H$ NMR spectroscopic investigations conducted on **18b**,**c**•$4PF_6$, revealed the dependence of their co-conformational features on the size and nature of [2]catenanes. The smaller catenane, **18b**•$4PF_6$, exhibits an energy barrier of 15.8 kcal mol$^{-1}$ for the circumrotation of the $\mathbf{CBPQT}^{4+}$ ring, whereas in **18c**•$4PF_6$ this energy barrier is lowered to 13.8 kcal mol$^{-1}$, an observation which is consistent with the presence of the larger, more relaxed constitution of the $\pi$-donating crown ether.

## 4. Clicked Bistable [2]Rotaxanes

The use of mechanically interlocked molecules in molecular switches[5] and machines[6] depends on the ability of such molecules to undergo stimuli-induced changes that can alter the properties of the molecules. The initial success[10] in the synthesis of rotaxanes using "click chemistry" led[14a] to the development (Scheme 10) of a diazido-terminated precursor **19**, containing two recognition sites—a tetrathiafulvalene (TTF) one as well as a DNP one—that can be used in the synthesis of a range of bistable [2]rotaxanes. When the diazide **19** was mixed with 1.1 equiv of **CBPQT**•$4PF_6$ in DMF, an intense green solution was obtained immediately, indicating the formation of the pseudorotaxane [**19** ⊂ **CBPQT**]•$4PF_6$. This [2]pseudorotaxane was then stirred for 2 days in the presence of (i) 2.0 equiv of a propargyl ether functionalized stopper, and (ii) a catalytic amount of $CuSO_4 \cdot 5H_2O$ and ascorbic acid as an in situ reductant. Chromatography of the crude product from the reaction mixture afforded[14a] the bistable [2]rotaxane **20**•$4PF_6$ as a green solid in 60% yield.

The $^1H$ NMR spectrum of **20**•$4PF_6$ in $CD_3COCD_3$ indicated the presence of predominantly (>95%) of a single translational isomer in solution—namely, the one in which the $\mathbf{CBPQT}^{4+}$ ring encircles the TTF unit. It may be concluded that the presence of the triazole rings in **20**•$4PF_6$ does not influence the isomeric distribution between the only two translational isomers that are populated to any extent. The NOESY spectrum shows no correlations between the chemical shifts of the triazole ring proton and the $\mathbf{CBPQT}^{4+}$ ring protons, indicating that the 1,2,3-triazole rings do not act as recognition units towards the $\mathbf{CBPQT}^{4+}$ ring.

The electrochemical behavior of **20**•$4PF_6$, as indicated by CV and differential pulse voltammetry (DPV) measurements, was found to be similar to those previously reported[5d,h] for TTF/DNP two-station [2]rotaxanes, suggesting that the presence of the two triazole rings does not affect either the thermodynamics or the kinetics of the switching process. The mechanical switching in $\mathbf{20}^{4+}$ has also been investigated (Fig. 4) by UV–vis spectroelectrochemistry (SEC), a technique which verified the full reversibility of the electrochemical reaction and thus switching process. The band (Fig. 4a), centered around 840 nm in the ground state ($E = 0$ V) and originating[7] from the CT interaction between TTF and $\mathbf{CBPQT}^{4+}$ started to bleach (Fig. 4b) as voltage is applied and the peaks ($\lambda_{\max} = 445$ and 595 nm) corresponding to the $TTF^{\bullet+}$ radical cation absorption increased until the applied potential reached +0.80 V. This observation indicates that the $\mathbf{CBPQT}^{4+}$ ring has moved away from the $TTF^{\bullet+}$ radical cation to the DNP unit. When the applied potential was increased above +0.80 V (Fig. 4c), the absorption band of the $TTF^{\bullet+}$ radical cation started to bleach and a new peak ($\lambda_{\max} = 380$ nm), assignable to the $TTF^{2+}$ dication emerged. At $E = +1.22$ V (Fig. 4c), a small absorption peak at around 530 nm, associated with the CT band between DNP and $\mathbf{CBPQT}^{4+}$, was detected. When the applied potential is switched off ($E = 0$ V), the spectrum (Fig. 4d) gradually changed back to its original form.



Scheme 10. Template-directed syntheses of the bistable [2]rotaxane **20**•4PF$_6$, using the precursor **19**.

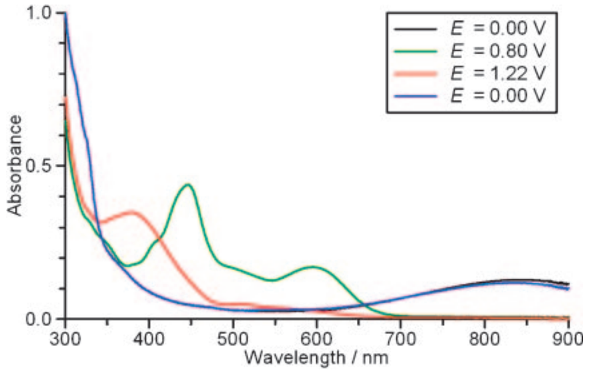


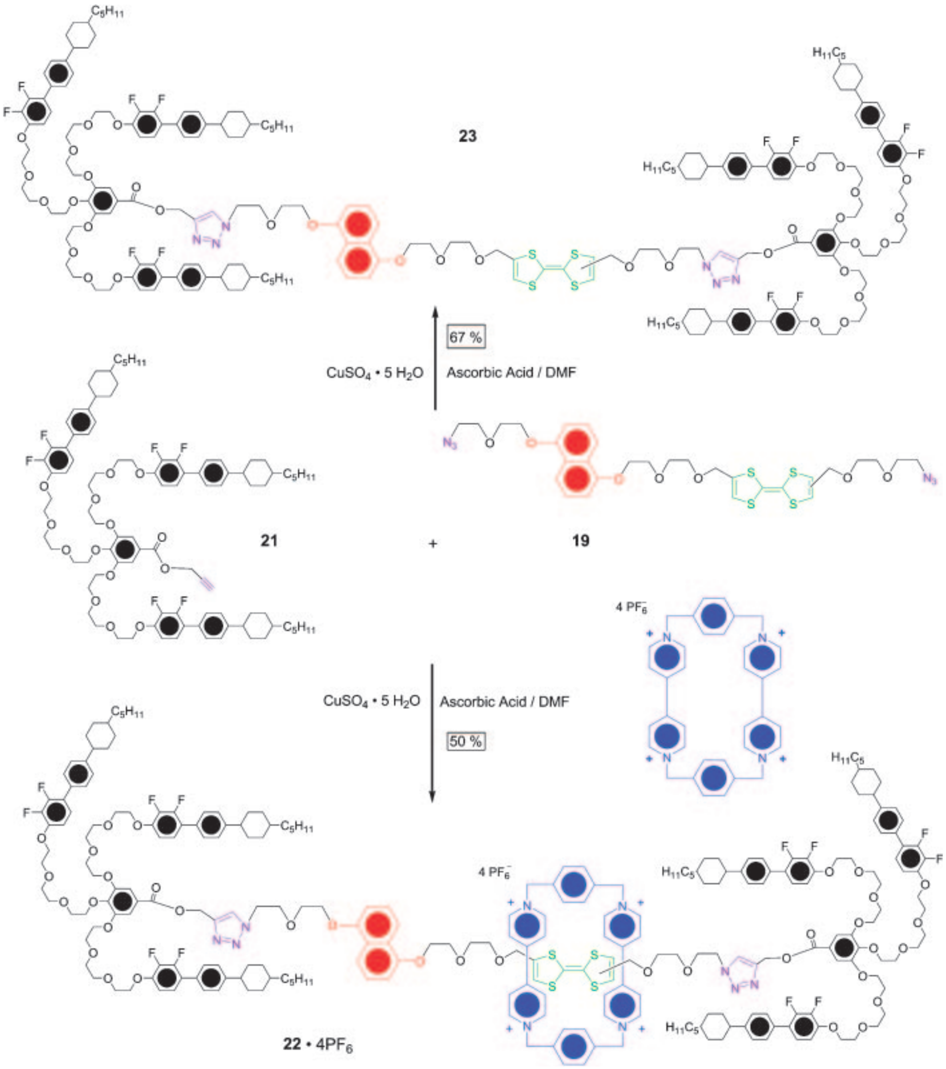
Fig. 4. The change in UV–vis spectra during the SEC measurements. The applied potential changes from $E = 0$ to $+1.22$ V and then back to $E = 0$ V.

## 5. Clicked Liquid-Crystalline Bistable [2]Rotaxanes

Liquid crystals are ordered, condensed, and fluidic states of molecules that can be used as dynamically functional materials for (i) information and mass transport, (ii) sensing, (iii) catalysis, and (iv) stimuli responsiveness as well as for (v) electro-optical displays.[23–25] The introduction of liquid-crystalline (LC)-ordered structures into bistable [2]rotaxanes might provide a promising approach to the realization of bulk materials, formed from dynamically functional redox-switchable molecular machines. In this regard, the forklike LC dendron **21**, comprising of rod-like cyclohexylbiphenyl mesogenic units[26] has been introduced recently as the stoppering component of an LC bistable [2]rotaxane (Scheme 11). The LC bistable [2]rotaxane **22**•4PF$_6$ was synthesized in 50% yield, by subjecting the diazido precursor **19**,[14b] and two equiv of the alkyne-terminated LC dendron **21**, to Cu$^I$-catalyzed "click reaction" conditions. The model LC dumbbell-shaped compound **23** was also obtained (Scheme 11) in 67% yield, using the same procedure, except for the fact that **CBPQT**•4PF$_6$ was excluded from the reaction mixture.

The bistable [2]rotaxane **22**•4PF$_6$ exhibited, over the temperature range from 10 to ca. 150 °C, an LC smectic A (S$_A$) phase which is a birefringent, viscous fluid state, as observed (Fig. 5) by polarized optical microscopy. When the temperature was raised above 150 °C, the sample decomposed gradually before reaching the isotropic state. The small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements revealed that the bistable [2]rotaxane formed an S$_A$ phase with a layered structure. In this ordered self-assembled state, the cyclohexylbiphenyl mesogenic units should force the [2]rotaxanes to align parallel (Scheme 12) to one another. The layer spacing of 8.3 nm observed for the S$_A$ phase corresponds to the extended molecular length of **22**•4PF$_6$. The model dumbbell compound **23** also exhibited an S$_A$ phase from 7 up to 146 °C on heating. In contrast to **22**•4PF$_6$, the dumbbell compound **23** clearly showed the isotropization transition at 146 °C ($\Delta H = 3.8$ kcal mol$^{-1}$) without thermal degradation, presumably because of the absence of the **CBPQT**$^{4+}$ ring. The layer-spacing found for **23** was 7.1 nm at 40 °C, a distance which is smaller than that (8.3 nm) observed for the bistable [2]rotaxane **22**•4PF$_6$. This observation suggests that the central part of **23** forms a coiled conformation on account of the absence of the **CBPQT**$^{4+}$ ring, which increases the flexibility and decreases the volume of the molecule, resulting in a decrease in the thickness of the smectic layer.

The CV and DPV analysis of the bistable [2]rotaxane gave results which are almost identical to those described for **20**•4PF$_6$ and previously[5d,h,14a] investigated bistable [2]rotaxanes,



Scheme 11. Template-directed syntheses of the LC bistable [2]rotaxane, **22**$\cdot$4PF$_6$, and the LC dumbbell component **23**.

thus establishing the ability of the LC [2]rotaxane to be switched electrochemically in solution. The SEC results (Fig. 6) were also in agreement with previous results, although some extra peaks were observed (Fig. 6c) around 420–480 and 840 nm when the applied voltage was raised[14b] to +0.90 V. These peaks were not observed (Fig. 4) for **20**$\cdot$4PF$_6$ and so they were attributed tentatively to CT interactions between the $\pi$-electron deficient **CBPQT**$^{4+}$ ring and the $\pi$-electron rich mesogenic stoppers. The redox switching of the bistable [2]rotaxane in the LC state and monitoring of the effects of the mechanical switching on the LC properties of the system are currently under investigation.

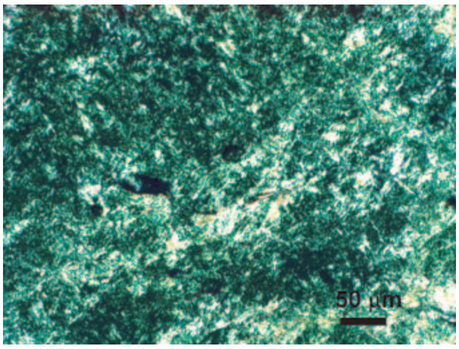
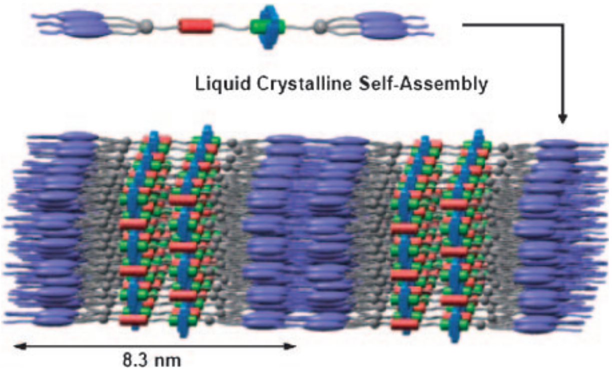


Fig. 5. Polarized optical photomicrograph of the LC bistable [2]rotaxane **23**$\cdot$4PF$_6$ at 25 °C.



Scheme 12. A graphic representation of the self-assembly of **22**$\cdot$4PF$_6$.

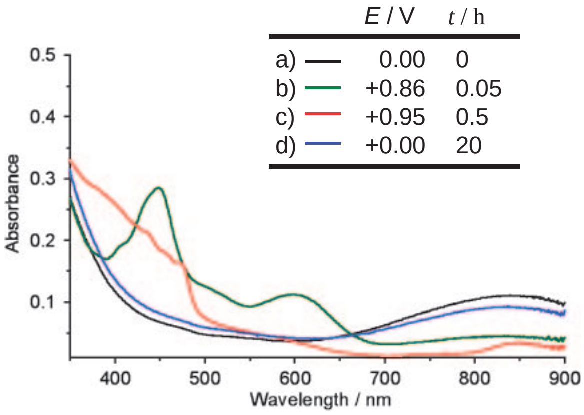


Fig. 6. The results of SEC measurements carried out on **22**•4PF$_6$. The UV–visible spectra were recorded at a) the starting state ($E = 0.00$ V), b) at +0.86 V, c) at +0.95 V for 30 min, and d) at 0.00 V for 20 h.

## 6. Conclusion

It is now clear that "click chemistry" carried out between azides and alkynes can be used in the efficient synthesis of mechanically interlocked compounds. The relatively simple precursors required for their synthesis and the inherent simplicity of the Cu$^{I}$-catalyzed Huisgen 1,3-dipolar cycloaddition will do much to propagate the use of this kind of "click chemistry" in the making of mechanically interlocked molecules and establish it as an indispensable method of synthesis. The methodology also opens up the pathway to new highly ordered mechanically interlocked compounds which would have not been accessible earlier by previous synthetic routes. The fact that the 1,2,3-triazole units, introduced as a consequence of the 1,3-dipolar cycloaddition between an azide and an alkyne, has little appreciable impact on (i) the shuttling rates, (ii) switching behavior, and (iii) the electrochemical properties of the mechanically interlocked compounds isolated will do much to popularize this particular approach to mechanically interlocked molecules that exhibit dual and multi-state switching[5] and/or behave like molecular machines.[6] This synthetic approach, wherein kinetically controlled "click chemistry" becomes important in the synthesis of catenanes and rotaxanes, as well as other mechanically interlocked compounds, is here to stay.

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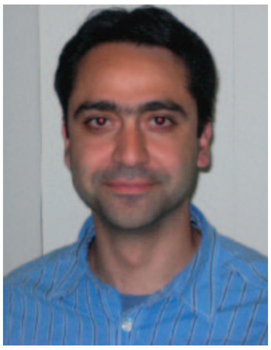

Ivan Aprahamian was born in Jerusalem (Israel) in 1978. He received all his degrees (B.Sc., M.Sc., and Ph.D.) from the Hebrew University of Jerusalem, Israel. His Ph.D. research was conducted under the supervision of Professors Mordecai Rabinovitz and Tuvia Sheradsky, and focused on NMR spectroscopic studies of alkali metal reduced polycyclic aromatic hydrocarbons. Presently, he is a postdoctoral researcher in Professor J. Fraser Stoddart's Supramolecular Chemistry Group at UCLA. His research focuses on the synthesis of exotic and highly ordered bistable [*n*]rotaxanes.

Ognjen Š. Miljanić was born in Belgrade (Serbia) in 1978, where he completed primary and secondary education. He obtained a Diploma degree in Chemistry from the University of Belgrade in 2000. Following a brief stay at the Institute of Animal Nutrition in Leipzig (Germany), he started graduate studies with Professor K. Peter C. Vollhardt at the University of California, Berkeley (U.S.A.) in early 2001. His Ph.D. thesis on synthetic and spectroscopic studies of dehydrobenzannulenes and [*N*]phenylenes, was completed in 2005. Since October 2005, Ognjen has been working as a postdoctoral researcher in the group of Professor J. Fraser Stoddart at UCLA (U.S.A.), exploring novel methods for the synthesis of interlocked molecules, such as catenanes and rotaxanes.

William Dichtel was born in Houston, Texas, in 1978 and grew up in Roanoke, Virginia. He received his B.S. in chemistry in 2000 from the Massachusetts Institute of Technology and his Ph.D. in 2005 from the University of California, Berkeley under the supervision of Professor Jean M. J. Fréchet. He is currently a research associate working jointly with Professor J. Fraser Stoddart at the UCLA, and Professor James R Heath at the California Institute of Technology. His research interests include molecular electronics, novel macromolecular architectures and functional materials.

Kyosuke Isoda was born in 1981 in Saitama, Japan. He obtained his M.S. degree from Tokyo University of Science in 2006. Since then, he has been working with Prof. Takashi Kato as a Ph.D. student at the University of Tokyo. His current research interest is stimuli-responsive liquid-crystalline materials.

Takuma Yasuda was born in 1977 in Aichi, Japan. He received Ph.D. degree in 2005 form Tokyo Institute of Technology under the supervision of Prof. Takakazu Yamamoto. Then, he joined the research group of Prof. Takashi Kato at the University of Tokyo as a postdoctoral fellow, and began the work on functional liquid-crystalline $\pi$-conjugated materials. He was selected as a Research Fellow of Japan Society for the Promotion of Science (JSPS) in 2006.

Takashi Kato received his Ph.D. from the University of Tokyo in 1988. After postdoctoral research at Cornell University with Prof. Jean M. J. Fréchet on supramolecular hydrogen-bonded liquid crystals, he joined the University of Tokyo. His research highlights the development of self-assembled functional materials including supramolecular liquid crystals, liquid-crystalline physical gels, ion-conductive liquid crystals and organic/inorganic composites. He received the Chemical Society of Japan Award for Young Chemists (1993), the Sakurada Memorial Award (1993), the IBM Japan Science Prize (2003), and the Japan Society for the Promotion Science (JSPS) Prize (2004). He has published 260 articles including original papers, reviews, and chapters of books.

J. Fraser Stoddart was born in Edinburgh, Scotland in 1942. He received all (B.Sc., Ph.D., and D.Sc.) of his degrees from the University of Edinburgh, U.K. In 1967, he went to Queen's University (Canada) as a National Research Council Postdoctoral Fellow, and then in 1970, to Sheffield University as an Imperial Chemical Industries (ICI) Research Fellow, before joining the academic staff as a lecturer in Chemistry. After spending a sabbatical (1978–1981) at the ICI Corporate Laboratory in Runcorn, he returned to Sheffield where he was promoted to a readership in 1982. In 1990, he took up the Chair of Organic Chemistry at Birmingham University and was Head of the School of Chemistry there (1993–1997) before moving to UCLA as the Sual Winstein Professor of Chemistry in 1997. Presently, he holds the Fred Kavli Chair in NanoSystems at UCLA. His current research interests are concerned with the transporting well-established concepts in biology from the life sciences into materials and medicinal chemistry.