Review

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Supramolecular Assemblies Constructed by Cucurbituril-Catalyzed Click Reaction

Dönüs Tuncel,*[a] Özlem Ünal,[a] and Müge Artar[a]

Abstract: Cucurbituril homologues are multi-functional macrocycles that can find applications in many areas and have numerous interesting features setting them apart from the other macrocycles. Among them, the ability of one of the cucurbituril homologues, cucurbit[6]uril (CB6), to catalyze 1,3-dipolar cycloaddition in a regiospecific fashion is truly exceptional. Using this feature, small molecules can be clicked together to form complex structures in a very efficient way. Accordingly, in this article we review recent research involving the use of CB6-catalyzed 1,3-dipolar cycloaddition or the click reaction of CB6 in the construction of supramolecular assemblies including rotaxanes, pseudorotaxanes, polyrotaxanes, polypseudorotaxanes, molecular switches, machines, and nanovalves.

Keywords: 1,3-dipolar cycloaddition · click chemistry · cucurbiturils · rotaxanes · supramolecular chemistry

1. Introduction

Efficient synthesis of novel materials with defined functions and properties, as well as the construction of nanometer-scale devices and machines, are highly desirable for many applications in nanotechnology, energy, and health care. To this end, supramolecular assemblies that can be constructed through non-covalent interactions, molecular recognition, and host–guest chemistry are very appealing owing to their tunable functions and properties.[1]

Rotaxanes and pseudorotaxanes are supramolecular assemblies in which a wheel-like component (also known as a ring or macrocycle) is threaded onto an axle-like component through non-covalent interactions.[2–4] To prevent de-threading of the ring from the axle, bulky stoppers are attached at the ends of the axle. The molecule is called pseudorotaxane, if the ends of the axle are not blocked by bulky groups. If the macrocyles are threaded onto a polymer chain or the rotaxanes and pseudorotaxanes are incorporated into a polymer, the resulting entities are called poly(pseudo)rotaxanes. Although there are many different types of poly(pseudo)rotaxanes, they can be mainly classified as main-chain and side-chain poly(pseudo)rotaxanes depending on the location of the macrocyles. By encapsulation of a polymer with a suitable macrocycle, solubility, chemical and thermal stability, and the luminescent efficiency of the polymers can be altered.[2,5] Furthermore, stimuli-responsive polyrotaxanes can be used as smart materials and in drug-delivery systems.[6] Rotaxanes can behave as molecular switches in which the ring of the molecule can shuttle under external stimulus (chemical, electrochemical, or photochemical) from one location to others. In doing this, they convert chemical, electrochemical, or photochemical energy into mechanical energy by changing their shape or by switching processes or movements.[3–4] Moreover, when appropriately designed, bistable [3]rotaxanes in particular have great potential to act as stimuli-responsive artificial molecular muscles.[7–9]

Cucurbit[6]uril (CB6) and its homologues (CB5, CB7, CB8, and CB10) are examples of macrocycles that have been used in the preparation of (pseudo)rotaxanes, and poly(pseudo)rotaxanes.[10–15] Cucurbituril was initially discovered by Behrend et al.[16] about a century ago and 80 years later rediscovered by Mock et al., who has carried out extensive molecular recognition studies by revealing the remarkable features of CB6.[17] However, it took a while to capture the attention of chemists. In the 1990s Kim et al. started to report very elegant work on the cucurbit[6]uril and contributed substantially to the field of CB6.[18] Around the same time other groups, such as Buschman[19] and Steinke,[20] were working towards the synthesis of CB6-containing polymers. However, the real surge of interest in these fascinating macrocycles started to take off after the discovery of CB homologues in early 2000 by Kim and Day.[21,22] Especially, CB7 managed to excite the supramolecular chemistry community because

[a] D. Tuncel, Ö. Ünal, M. Artar
Department of Chemistry and
Institute of Materials Science and Nanotechnology
Bilkent University
06800 Ankara, Turkey
phone: +90 312266 0235
fax: +90 312266 4068
e-mail: dtuncel@fen.bilkent.edu.tr

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of its water-solubility, which is a very important feature for the biological applications.[23]

Cucurbiturils have a hydrophobic cavity and two identical hydrophilic carbonyl portals.[10] As a result of these structural features, CB binds well to protonated mono- and diaminoalkanes, through ion–dipole interactions/hydrogen bonding and the hydrophobic effect (Figure 1). Mock's extensive molecular recognition studies revealed that CB shows length-dependent selectivity for monoamino-

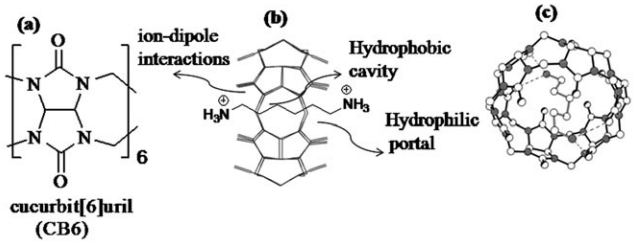

Figure 1. (a) Chemical structure of CB6 (left),(b) representation of the different binding regions of CB[6] and the geometry of the complex between CB6 and the hexanediammonium ion, (c) X-ray crystal structure of the inclusion complex of CB6 with 1,6-diaminohexane dihydrochloride salt (right).[13]

noalkanes and diaminoalkanes.[17] Figure 2 shows a plot of the log K_a value versus chain length. While diaminopentane and diaminohexane have very high affinity toward CB6 (with values of $K_a > 10^6\,\text{M}^{-1}$), the compounds with shorter or longer spacer groups between the ammonium groups (e.g., propanediamine or heptandiamine) bind significantly more weakly to CB6.[17f]

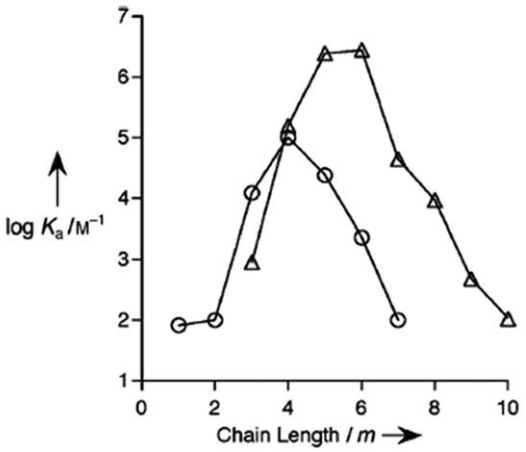

Figure 2. Relationship between the binding constant (log K_a) versus chain length m for $H(CH_2)_mNH_3^+$ (O) and $^+H_3N(CH_2)_mNH_3^+$ (Δ).[17f]

Figure 1c shows the X-ray crystal structure of the CB6–1,6-diaminohexane dihydrochoride salt.[13] As can be seen, the hexyl spacer is slightly folded in order to fit inside the cavity and benefit efficiently from the ion–dipole interactions. It was also found that CB6 has size- and shape-dependent properties.[17] For example, the largest molecule which CB6 can encapsulate is the para substituted benzene ring, but ortho or *meta*-substituted benzene rings have difficulty being encapsulated by CB6.

Dönüs Tuncel graduated from the University of North London and received her Ph.D. degree from Imperial College, London, in the area of supramolecular chemistry of cucurbiturils under the supervision of Dr. Joachim Steinke. She worked for about 3 years as a postdoctoral research assistant in the Chemistry Department of Oxford University under the direction of Professor Harry L. Anderson. Since 2003, she has been working in the Department of Chemistry at Bilkent University, Ankara, Turkey, as an Assistant Professor. Dr. Tuncel's research is highly interdisciplinary and combines synthetic organic, supramolecular, and polymer chemistry to prepare functional materials such as supramolecular polymers, cucurbituril containing rotaxanes and polyrotaxanes, water soluble conjugated polymers, and functional and mechanically-stable multi-functional conjugated polymer nanoparticles with potential applications in polymeric opto-electronic devices (LEDs, solid state lighting, and photovoltaic devices), molecular switches, and biomedicine.

Özlem Ünal is currently a final year undergraduate student in the Department of Chemistry at Bilkent University, Ankara. Her senior project thesis involves the synthesis of CB-based molecular switches triggered with fluorescence resonance energy transfer.

Müge Artar graduated from Bilkent University with a B.Sc. degree in Chemistry and is currently working on her Master's degree there. Her research focuses on cucurbituril leaded molecular recognition and cucurbituril-conjugated polymer interactions.

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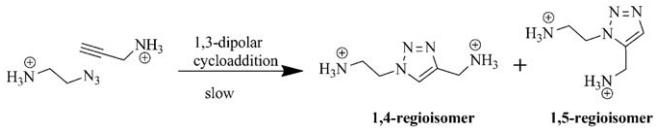
2. Discussions

2.1. 1,3-Dipolar Cycloaddition of Azide-Alkyne

The azide–alkyne Huisgen cycloaddition is a 1,3-dipolar or [3+2] cycloaddition between an azide and a terminal or internal alkyne to yield a 1,2,3-triazole as a mixture of 1,4- and 1,5-regioisomers.[34] For example the reaction in Scheme 1 has been shown to proceed slowly in formic acid at 40 °C ($k = 1.16 \times 10^{-6}\,M^{-1}s^{-1}$).



Scheme 1. The azide–alkyne Huisgen 1,3-dipolar cycloaddition reaction.

Mock et al. reported in the 1980s that a catalytic amount of CB6 accelerates the same reaction ca. 10^5 fold. The reaction is regiospecific and only the regioisomer 1,4-triazole forms.[17a,b] The mechanistic studies suggest that first a ternary complex forms between alkyne, azide, and CB6.[17a,b,35] The ammonium ions of azide and alkyne bind to carbonyl oxygens of CB6s through ion–dipole interaction and in the meantime the rest of the molecule enters the cavity of CB6 by freeing water molecules. The azide and alkyne groups are aligned inside the cavity in such a way as to facilitate the triazole formation. The presence of both alkyne and azide moities in the cavity apparently causes a strain and in order to release this strain triazole ring forms. Using bulky *tert*-butyl end groups [2]rotaxane was obtained, as depicted in Figure 3.

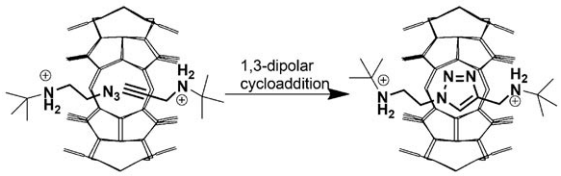


Figure 3. Synthesis of [2] rotaxane by CB6-catalyzed 1,3-dipolar cycloaddition.

In 2002, it was discovered that Cu^I could also catalyze the 1,3-dipolar cycloaddition between alkynes and azides in a regiospecific fashion, yielding selectively 1,4-isomer.[36] The reaction is fast and usually takes place at room temperature and in polar solvents including water, alcohol, DMF, and DMSO. This reaction is termed as "click chemistry" because it is a fast, high-yield reaction, does not produce side products and require time-consuming purification, and can be carried out in water.[37] This reaction has been used in many areas as well as in the synthesis of rotaxanes/pseudorotaxanes and catenane.[38]

CB6-catalyzed 1,3-dipolar cyloaddition can also be counted as one of the early example of a click reaction in which the substances are generated quickly and reliably by joining small units together. As in other click reactions, the CB6-catalyzed 1,3-dipolar cyloaddition reaction is fast, regiospecific, and very efficient, and forms no by-products. That it is free of copper residue is another advantage, because the presence of even trace amounts of copper is not desirable in many biological applications. This ability of CB6 was taken as an advantage and extended in the synthesis of various supramolecular assemblies that will be discussed in the following sections.

2.2. The Ability of CB Homologues to Catalyze 1,3-Dipolar Cycloaddition

We investigated whether other CB homologues besides from CB6 could catalyze 1,3-dipolar cycloaddition. The results show that CB7 and CB8 were not able to catalyze 1,3-dipolar cycloaddition, because they have different size and shape selectivities than CB6. This feature, among others, makes CB6 unique. Although CB6 is an excellent catalyst for 1,3-dipolar cycloaddition and the CB-catalyzed reaction gives high yield by rendering the regioselectivity, there are strict requirements for CB6 to act as a catalyst for 1,3-dipolar cycloaddition to form supramolecular assemblies.

In order to form polyrotaxanes and polypseudorotaxanes by CB-catalyzed click reaction, one should use difunctional A2, B2, or AB type monomers such as diazide, dialkyne, or a monomer containing both azide and alkyne groups.[13,20b] However, the spacer between the alkyne and azide groups should be chosen very carefully because CB6 is highly sensitive to the structure of the monomers selected, and a poorly designed monomer may deactivate the catalytic effect of CB6. Accordingly, the spacer shoud either be too bulky to fit inside the cavity of CB6, or not bulky but with a low affinity toward CB6. In the former approach, it would not be possible for CB6 to slide over the polymer chain; however, the use of latter approach enables CB6 to move around allowing us to design and synthesize stimuli-responsive assemblies.

The studies indicated that especially the nature of the spacer linking the two ammonium ions is quite important in order for CB6 to act as a catalyst and 1,3-dipolar cycloaddition to take place.[20b] If the spacer is a linear aliphatic group, then it should be shorter than butyl or longer than heptyl groups as Mock has demonstrated in his extensive binding studies. Tetramethylenediamine, pentamethylenediamine, and hexamethylenediamine have very high affinities toward CB6 because these spacer have the right length to fit into the cavity and benefit from the ion–dipole interaction efficiently.[17] Since trimethylenediamine is too short for the cavity of CB6, it has a low af-

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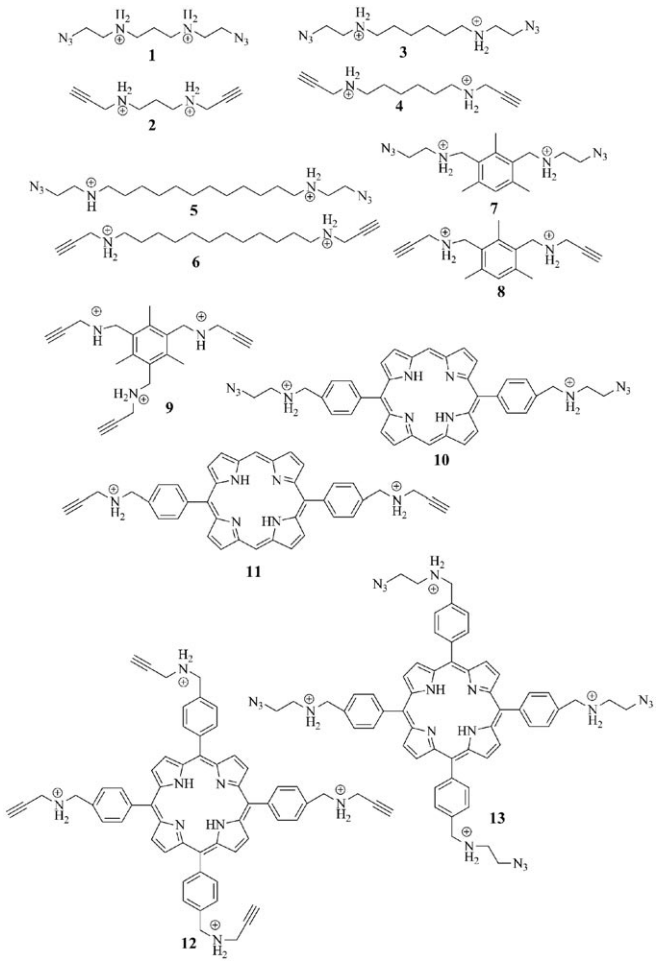

Figure 4. Structures of monomers used in the synthesis of various supramolecular assemblies. Chloride counterions have been omitted for clarity.

finity. Also very long dodecanediamine has low affinity toward CB6 because of unsatisfactory size matching with the CB6 cavity. The monomers depicted in Figure 4 have been designed and synthesized keeping in mind these criteria and have been used in the synthesis of (pseudo)rotaxanes and (pseudo)polyrotaxanes.

2.3. Synthesis of Polyrotaxanes from Stopper Groups containing Monomers

In order to catalyze 1,3-dipolar cycloaddition, CB6 should have a higher affinity toward azidoethylammonium and propargylammonium end groups than to the spacer linking these groups, or the spacer should be large enough not to fit inside the cavity of CB6. Monomers **7**–**13** meet the latter requirement.

It was possible to prepare main chain and branched polyrotaxanes using monomers **7** to **9** in high yields with molecular weights up to 39000.[20] Figure 5 shows the structure of a main chain polyrotaxane (**PR1**) prepared from the monomers **7** and **8**. The formation of polyrotaxanes and the degree of polymerization were able to be followed by ^{1}H NMR spectroscopy. The most characteristic peak in the ^{1}H NMR spectrum is the peak for the triazole proton; if the triazole ring is encapsulated by CB6, it is observed at 6.5 ppm, which is about 1.5 ppm upfield-shifted compared to one that is not encapsulated. The degree of polymerization could also be estimated by comparing the ratio of the integral of the triazole proton versus the proton of the phenyl ring of the spacer. The polymerization reaction was usually carried out in 6 M HCl solution; however, reaction conditions such as time and temperature were varied in order to study the polymerization reaction in detail. Although it was difficult to determine the molecular weight of **PR1** using aqueous gel permeation chromatography (GPC), matrix assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS) produced satisfactory results. These polyrotaxanes are water-soluble and have well-defined structures in which each repeat unit contains one macrocycle.

In the synthesis of **PR2**[39] (see Figure 5 for its structure), monomers **10** and **11** were utilized. These monomers contain disubstituted porphyrin. Porphyrin has been

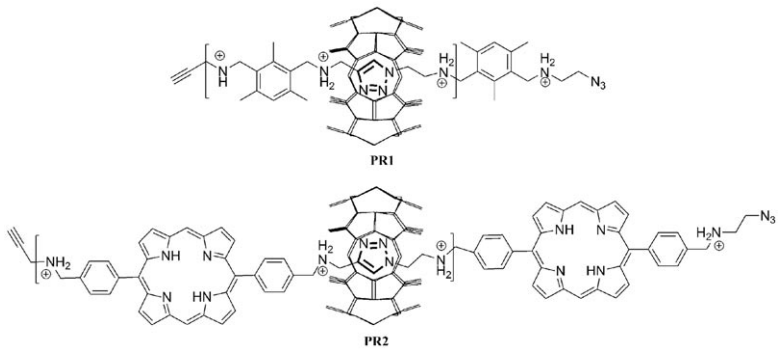

Figure 5. The structures of polyrotaxanes **PR1** and **PR2. PR1**, from monomers **7** and **8**, and **PR2**, from monomers **10** and **11**, were synthesized using CB6 as a macrocycle and catalyst. Chloride counterions have been omitted for clarity.

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selected as a spacer because it is an important molecule owing to its interesting spectroscopic properties and potential applications in the areas of artificial photosynthesis and molecular photonics. Furthermore, anionic and cationic water-soluble porphyrins have a particular importance in biology and photodynamic therapy. However, this polyrotaxane is not well-soluble in water and has a limited solubility in acidic water; this hampered the full characterization of **PR2**. In order to solve the solubility problem, counter ion chloride could be changed to other counter ions, or another possibility might be the metallation of porphyrins.[39]

2.4. Synthesis of Polypseudorotaxanes Using Aliphatic Spacers Containing Diazide and Dialkyne Monomers

Monomers **1** to **6** are investigated for their suitability in CB-catalyzed polymer synthesis. As we discussed earlier, the nature of the spacer is very important for the catalytic activity of CB6. We found that a monomer having a hexyl spacer deactivates the catalytic effect of CB6 because the binding constant of diaminohexane with CB6 is very high (ca. $10^6\,M^{-1}$). Even forcing conditions such as use of excess CB6 and elevated temperature do not work, because of the repulsion caused by CB6s.[20b]

On the other hand, monomers containing dodecyl[29] and propyl[40] groups have been polymerized very efficiently through CB6-catalyzed 1,3-dipolar cyloaddition even at room temperature (see Figure 6 for their structures). As mentioned in the previous sections, it is known from Mock's length-dependent binding studies on the mono- and diaminoalkanes that the binding constants for diaminopropane and diaminododecane are very low, meaning that CB6 can bind to the end groups of these monomers. These polypseudorotaxanes were characterized by spectroscopic techniques (^{1}H and ^{13}C NMR, FT-IR) and MALDI-TOF MS.

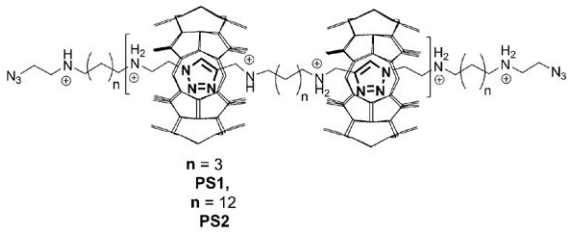

Figure 6. The structures of polyrotaxanes **PS1** and **PS2. PS1** from monomers **1** and **2**, and **PS2** from monomers **5** and **6** were synthesized using CB6 as a macrocycle and catalyst. Chloride counterions have been omitted for clarity.

After the synthesis of polypseudorotaxane ($n=12$) (**PS2**) we wished to dethread the CB6s using basic conditions in order to obtain CB6-free polytriazole but to our surprise, the CB6s moved onto the aliphatic spacer instead of slipping off the polymeric axle, revealing that the polypseudorotaxane having a dodecyl alkyl group behaves like a pH-driven polymeric switch.[29] Thus, when amine groups are protonated at an appropriate low pH, CB6s are located on the triazole rings due to ion–dipole interaction, whereas at high pH they move onto the hydrophobic aliphatic spacer rather than slipping off the polypseudorotaxane. This approach can be further improved by incorporating fluorophores as a stopper at the end of the polypseudorotaxane. Moreover, if one of these fluorophore is a donor and the other acts as an acceptor, the conformational changes of the polyrotaxane could be observed by Förster energy transfer (FRET) and this approach can also be used as a molecular ruler to determine the chain length of a polymer.

Since the preparation of polytriazole through base-induced de-threading was not successful, we wanted to polymerize monomers **7** and **8** using Cu^I-catalyzed click chemistry. However, we obtained an insoluble solid at the end of the reaction. The result suggests that when triazoles are not encapsulated by CB6s, there will be strong interactions between the polymer chains due to π–π interactions, hydrophobic effect, and hydrogen bonds. Another interesting finding was that, although monomers **1** and **2** could be polymerized efficiently by CB6-catalyzed click reaction, it was not possible to polymerize these monomers using Cu^I-catalyzed click reaction. The reason could be that Cu complexes form with propyl spacers containing monomers that prevent Cu^I formation which is needed to catalyze the 1,3-dipolar cycloaddition.[40]

2.5. Rotaxanes, Pseudorotaxanes, Molecular Switches and Machineries

Usually the (pseudo)rotaxane synthesis involves many steps and tedious purifications, resulting in poor yield. However, using most of the monomers depicted in Figure 4 various [3], [4], [5]rotaxanes and pseudorotaxanes have been synthesized very efficiently (i.e., straightforward reaction, simple purification, and almost quantitative yield). Furthermore, some of the rotaxanes having more than one recognition site have been shown to behave as stimuli-responsive molecular switches

[5]rotaxane[28] and [5]pseudorotaxane[28] from the monomers **11**, **12** and [3]rotaxane[40] and [3]pseudorotaxane[40] from the monomers **9**, **10** have been synthesized and characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, and UV), elemental analysis, and mass spectrometry. The pH-driven switching properties of [5]rotaxane have also been investigated through ^{1}H NMR spectroscopy. While [5](pseudo)rotaxane dissolves quite well in water at room temperature, the [3](pseudo)rotaxane dissolves to an appreciable extent in water only when it is heated. The solubility difference most probably stems from the structural differences of their porphyrin units; the former is tetraphenyl substituted whereas the latter is di-phenyl substi-

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tuted, leading to the conclusion that tetraphenyl substitution of porphyrin prevents π–π interactions between porphyrin units and as result aggregate formation.

Monomers **7**, **8**, and **9** have also been utilized in the synthesis of [n]rotaxanes and [n]pseudorotaxanes ($n=3$ and 4). These rotaxanes and pseudorotaxanes were characterized well using various techniques and have been observed to exhibit good solubility in water.[26]

A series of water-soluble [3]rotaxanes and [3]pseudorotaxanes with short (propyl, $n=1$) and long (dodecyl, $n=10$) aliphatic spacers have been prepared in high yields by a 1,3-dipolar cycloaddition reaction catalyzed by CB6, as shown in Figure 7. The pH-triggered dethreading and re-

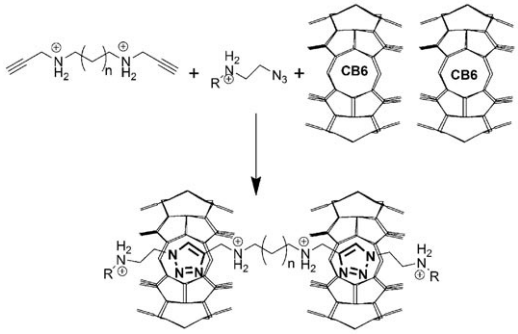

Figure 7. Synthesis of [3]pseudorotaxanes **P1** (R=H, $n=1$) and **P2** (R=H, $n=10$) and [3]rotaxanes **R1** (R=*t*Bu, $n=1$) and **R2** (R=*t*Bu, $n=10$) from monomers **2** ($n=1$) and **6** ($n=10$). Chloride counterions have been omitted for clarity.

threading of CB6 on these pseudorotaxanes was monitored by ^{1}H NMR spectroscopy.[30,31] It was found that treating pseudorotaxanes with base causes CB6s to dethread from the axle, and the de-threaded CB6s complex with sodium ions. This process is found to be repeatable. In the case of rotaxanes, blocking groups prevent CB6s from slipping off the axle; CB6s move over the axle, and the degree of movement depends on the nature of the spacer.

[3]rotaxane (**R2**), having a dodecyl spacer, behaves like a bistable molecular switch and has two recognition sites for CB6, that is, the diaminotriazole moieties and the dodecyl spacer. By changing the pH of the system, it is possible to observe more than one state in the shuttling process. At low pH values, both CB6 units are located on the diaminotriazole moieties owing to an ion–dipole interaction, whereas at high pH values both of the CB6 units are located on the hydrophobic dodecyl spacer. Surprisingly, the CB6 units shuttle back to their initial state very slowly after reprotonation of the axle. Even after eighteen days at room temperature, only about 50% of the CB6 units had relocated back onto the diaminotriazole moieties (Figure 8). The rate constants for the shuttling processes were measured as a function of temperature

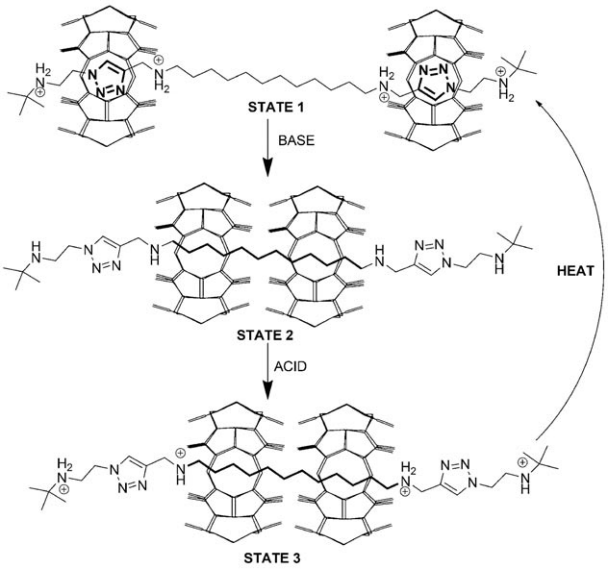

Figure 8. The pH and heat-induced shuttling processes of **R2**.

over the range of 313 to 333 K and the activation parameters (enthalpy, entropy, and free energy) were calculated by using the Eyring equation. The results indicate that this [3]rotaxane behaves as a kinetically controlled molecular switch. The switching properties of [3]rotaxane with a propyl spacer ($n=1$) have also been studied. However, even under extreme pH conditions this rotaxane has not shown any switching action, which confirms that the propyl spacer is too short to accommodate CB6 units.

Stoddart and co-workers reported very elegant work on a pH-responsive supramolecular machinery prepared by CB-catalyzed pseudorotaxanes.[33] This supramolecular machinery is called nanovalves and is based on mesoporous silica nanoparticles. These 400 nm-sized particles have a pore diameter of about 2 nm. In the construction of nanovalves, first the surfaces of the silica nanoparticles were functionalized with molecules having alkyne groups, and then the particles were filled with dye molecules (rhodomine B). Subsequently, alkyne-decorated silica nanoparticles were treated with azidoethylammonium salt in the presence of CB6 to form pseudorotaxanes through CB6-catalyzed 1,3-dipolar cycloaddition. In this system, at acidic pH CB6s encapsulate the newly formed triazole units through ion–dipole interactions between ammonium ions of the axle and carbonyl groups of CB6. As a result, the pores of the silica particles are blocked because they are in close proximity with the CB6s. When the ammonium groups are deprotonated at pH 10, CB6s are dethreaded from the axle, and consequently, the dye molecules are released into the bulk. The release is followed by fluorescent emission intensity of rhodamine at 514 nm. More efficient release was observed when the CB6s werere held closer to the surface of the nanoparticle (Figure 9).

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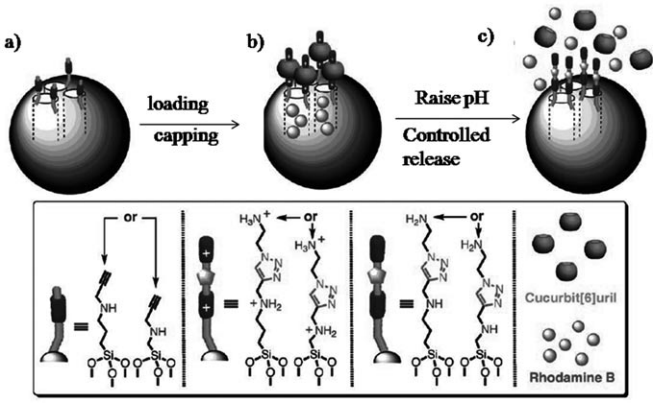

Figure 9. Graphical representations of operating supramolecular nanovalves constructed from [2]pseudorotaxanes. Alkyne-substituted mesoporous silica nanoparticles are loaded with rhodamine molecules and subsequently blocked with CB6-catalyzed 1,3-dipolar cycloaddition. Upon deprotonation of ammonium ions, ion-dipole interactions between ammonium ions and carbonyl oxygens are disturbed and as a result, CB6 s are dethreaded by triggering the release of dyes from the nanoparticle pores. (Reproduced with permission from ref. [33a]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA).

3. Summary

In this article, we reviewed the ability of CB6 to catalyze 1,3-dipolar cycloaddition. CB6-catalyzed click reactions are very versatile and can be used in the synthesis of simple entities as well as in the construction of complex supramolecular assemblies. Using this chemistry many supramolecular assemblies were reported; these assemblies exhibit many interesting properties and functions such as stimuli-responsive polymeric materials, switches, molecular machineries, etc. The reaction is not only straightforward but also very efficient and does not require complex purification steps; however, the monomers should be designed carefully in order for CB6 to show its catalytic activity. Because the presence of even trace amount of copper is undesirable in many biological applications, another advantages of CB6-catalyzed 1,3-dipolar cycloaddition is that it is free of copper residue. Therefore, this reaction seems to be very promising for the preparation of nanoscale biological materials as well as molecular switches and machines.

Acknowledgments

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