Template Synthesis

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Sodium Ions Template the Formation of Rotaxanes from BPX26C6 and Nonconjugated Amide and Urea Functionalities**

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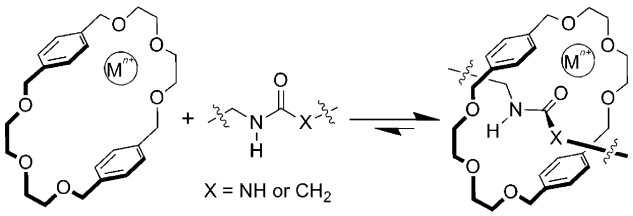
Pseudorotaxanes and rotaxanes are becoming increasingly important materials for gelation,[1] drug delivery,[2] and molecular electronics;[3] therefore, efforts continue toward developing new threading systems and new methods to synthesize these intertwined and interlocked molecules.[4] Although many elegant interlocked molecular compounds and threaded supramolecular complexes have been prepared in the past two decades,[5] the number of recognition motifs that can be exploited for the preparation of these systems remains limited. This shortcoming arises mainly from our limited ability to incorporate suitable recognition units in an appropriate arrangement in the molecular structures of the host and guest components so that weak noncovalent interactions can collaborate to stabilize the resulting pseudorotaxane complexes. In addition, the lack of structural flexibility of the recognition units that can form pseudorotaxane complexes hinders the application of their unique functions or structures into already used materials and/or biologically important (macro)molecules, many of which do not contain the necessary, suitably arranged recognition units in their native molecular structures. One possible solution to resolve this problem would be to develop a new molecular recognition system in which a simple and abundant functionality—one that is found commonly in many materials—is recognized by a host macrocycle with no need for structural preprogramming. Urea and amide units are ubiquitous in artificial and biological polymers (e.g. polyureas, nylons, peptides). We thus suspected that if it were possible to recognize macrocycles at single units of these functionalities, then the barrier hindering the use of such host/guest structures in practically useful materials would be decreased significantly. This would potentially allow many new and interesting properties to be introduced into molecules and materials that we encounter widely in our daily lives. Noting that diamide-based macrocycles have been applied previously in the recognition of threadlike species containing amides[6] and conjugated ureas,[7] herein we demonstrate that the macrocycle bis-*p*-xylyl[26]crown-6 (BPX26C6) is capable of forming pseudorotaxane-like structures with single, nonconjugated urea or amide moieties when assisted by templating Na^+ ions, thereby allowing the successful syntheses of the corresponding rotaxanes.[8] By using this metal-templating approach, we prepared rotaxanes featuring glycine residues and the repeating units of nylon-6,6 as key components in their threadlike units. This opens the possibility of employing this recognition system for the formation of (pseudo)rotaxane structures from biorelated (macro)molecules (e.g. peptides) and practically useful materials (e.g. nylon).

We exploited primarily ion–dipole interactions between the C=O group(s) of the guest species and spherical alkali-metal ions to achieve recognition of a single urea or amide functionality by a macrocycle without requiring the guest component to feature specific structural characteristics. Our previous study had shown that an interlocked BPX26C6 moiety in a rotaxane could collaborate with a 2,2′-bipyridine unit in the threadlike component to allow the mutual complexation of various metal ions.[9] We thus suspected that a suitable metal ion would template the threading of a urea or amide guest through the cavity of BPX26C6 by coordinating to the binding pocket formed from one diethylene glycol chain of the macrocycle and the C=O group of the guest (Scheme 1). In addition, N-H···O hydrogen bonds



Scheme 1. Structural representation of the concept of threading a nonconjugated urea or amide moiety through the cavity of BPX26C6 with the assistance of a templating metal ion.

formed between the NH proton of the urea or amide group and the other diethylene glycol chain of the macrocycle would presumably also assist in stabilizing the pseudorotaxane. We suspected that physiologically important and abundant alkali-metal ions, such as Na^+ and K^+ ions, might be appropriate templates because of their relatively strong interactions with the oxygen atoms of the oligo(ethylene glycol) chains of crown ethers.[10]

To test this hypothesis we synthesized the threadlike urea **1**, in which the urea unit is conjugated to two aromatic rings. As less-polar solvents would promote hydrogen bonding

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between the urea unit of the guest and the macrocycle BPX26C6 as well as their ion–dipole interactions to the metal ion template, we chose sodium tetrakis(3,5-trifluoromethylphenyl)borate (NaTFPB)[11] as the templating salt because its ion pair associates relatively weakly in such solvents. Figure 1 presents the ^{1}H NMR spectrum of an equimolar mixture of BPX26C6 and the threadlike urea **1** (5 mM) in $CDCl_3$; when we added NaTFPB (5 mM) to this solution, the signals of the threadlike component underwent significant shifts. This observation suggested that the efficient threading of **1** through the cavity of BPX26C6 required the templating of Na^+ ions, and that the rates of complexation and decomplexation were both fast on the ^{1}H NMR spectroscopic timescale at 400 MHz and 298 K. The downfield shift of the signal of the NH protons and the upfield and downfield shifts of those of their adjacent (H_a) and distal (H_b) aromatic protons, respectively, upon gradually increasing the concentrations of BPX26C6 and NaTFPB to 20 mM, from an initial equimolar mixture of the host, guest, and template (each 5 mM), is consistent with the formation of a pseudorotaxane between the host and guest components under these conditions. The BPX26C6 macrocycle encircling the urea unit allowed the formation of N-H···O hydrogen bonds between the NH protons of the urea moiety and the diethylene glycol chain, thereby leading to a downfield shift of the signal of the NH protons; concomitant shielding and deshielding of the H_a and H_b protons, respectively, by the *p*-xylene motifs of the macrocycle led to upfield and downfield movements, respectively, of their signals in the ^{1}H NMR spectra.[12] Although this spectroscopic evidence supports the formation of threaded complexes, we sought to synthesize the corresponding rotaxanes to prove unambiguously that pseudorotaxanes formed from these recognition elements in solution.

Accordingly, we synthesized the threadlike urea-containing species **2**–**4**, in which the urea units are conjugated to two, one, and no aromatic rings, respectively (Scheme 2). Di-*tert*-butylphenyl isocyanate[6a,13] (**5**, 500 mM) was added to a solution of the threadlike species (**2**, **3**, or **4**), BPX26C6, and NaTFPB (100:250:250 mM) in CH_2Cl_2 and then the mixture was stirred at ambient temperature for 16 h to afford the corresponding [2]rotaxanes **6**–**8** in yields of 40, 25, and 8%, respectively, after column chromatography. The loss of the templating Na^+ ion during the aqueous extraction and chromatography process suggested that its complexation to the binding pocket in the [2]rotaxanes was not particularly strong throughout the synthetic process. The absence of any detectable signals for the [2]rotaxane **6** in the ^{1}H NMR spectra of the crude product obtained when the reaction of **2** was

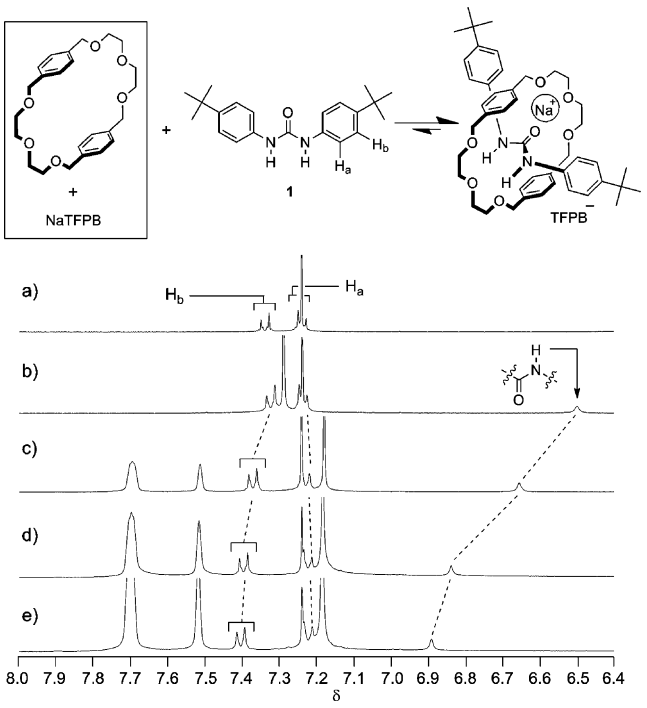
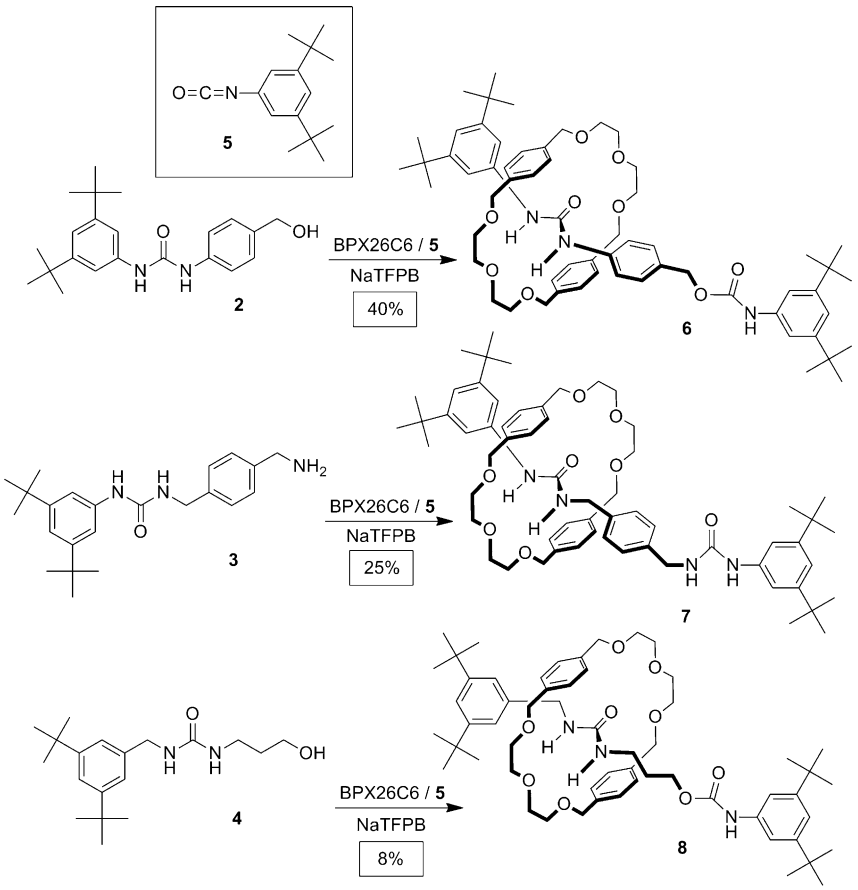


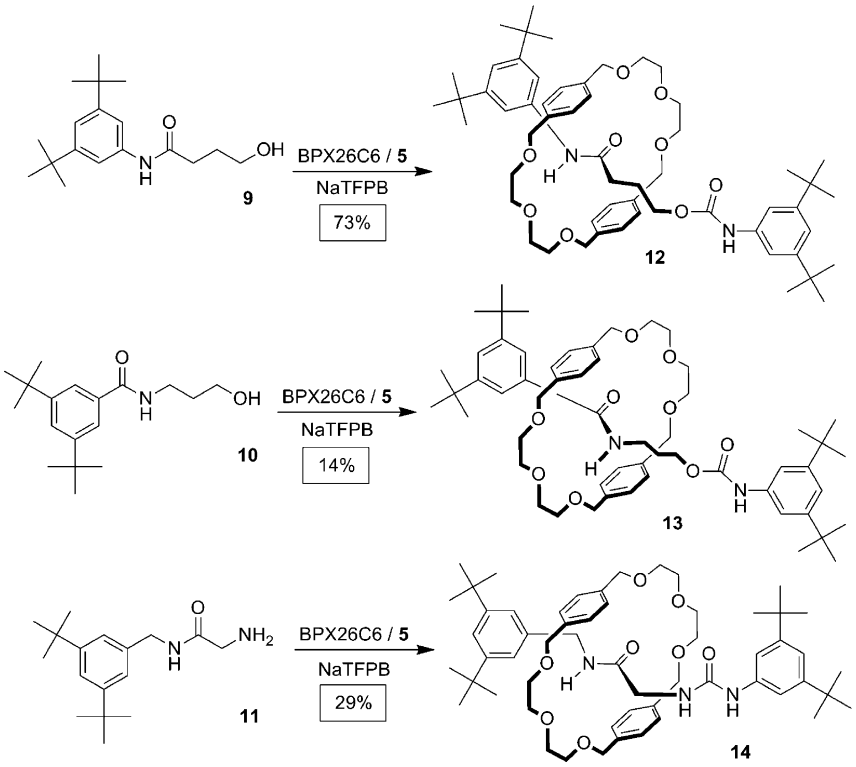
Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of a) the threadlike urea **1**, b) an equimolar mixture of **1** and BPX26C6 (5 mM), and c–e) mixtures of **1**, BPX26C6, and NaTFPB at concentrations of c) 5:5:5 mM, d) 5:10:10 mM, and e) 5:20:20 mM.



Scheme 2. Syntheses of the conjugated and nonconjugated urea-containing [2]rotaxanes **6**–**8**.

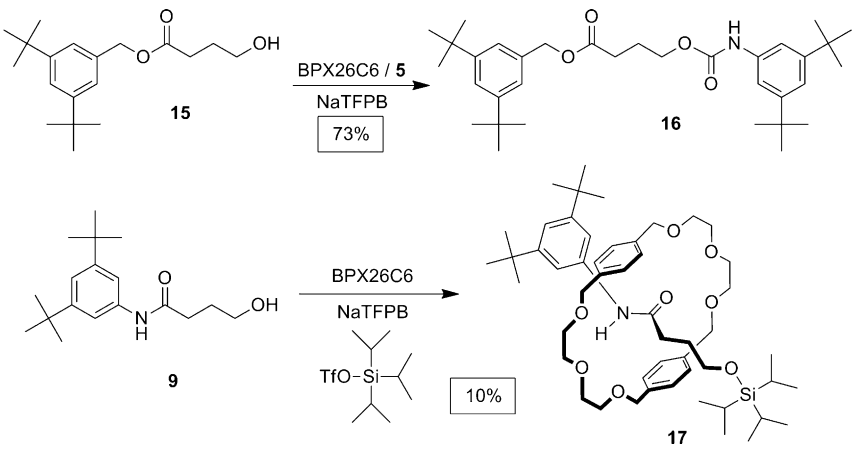
repeated in the absence of NaTFPB, but under otherwise identical conditions, suggested that the Na^+ ion template was crucial for efficient threading of the urea unit through the cavity of BPX26C6. The reaction yields suggested that conjugation of the urea moiety to the aromatic rings assisted in increasing the concentration of the [2]pseudorotaxane in solution, possibly because of the increased acidity of the NH group. Nevertheless, our successful synthesis of the [2]rotaxane **8** reveals that aromatic conjugation in the structure of the urea guest is not a necessity; it also suggests that we might be able to generate BPX26C6-containing pseudorotaxanes from many other urea-containing guests—as long as Na^+ ion templates are present.

Next, we turned our attention to whether Na^+ ions could also template the threading of simple amides through the cavity of BPX26C6 to form the corresponding pseudorotaxanes. Gratifyingly, when we added the isocyanate **5** (500 mM) to a solution of a threadlike amide (**9**, **10**, or **11**), BPX26C6, and NaTFPB (100:250:250 mM) in CH_2Cl_2, we isolated the corresponding [2]rotaxanes **12**–**14** in yields of 73, 14, and 29%, respectively (Scheme 3). Thus, threading of a single amide unit through the cavity of the macrocycle BPX26C6 in the presence of a templating Na^+ ion is feasible, even when the amide moiety is not linked directly to any aromatic rings.[14] Notably, the threadlike species **11** is a C-amidated glycine residue, thus opening up the intriguing possibility of applying this recognition system to the synthesis of peptide-based interlocked molecules.



Scheme 3. Syntheses of the conjugated and nonconjugated amide-containing [2]rotaxanes **12**–**14**.

To eliminate the possibility that the [2]rotaxanes **12**–**14** were formed from pseudorotaxane-like complexes obtained after threading the isocyanate **5** into the cavity of BPX26C6 in the presence of a templating Na^+ ion,[15] we mixed the threadlike ester species **15** with BPX26C6, NaTFPB, and the isocyanate **5** under conditions similar to the synthesis of [2]rotaxane **14** (Scheme 4). Gratifyingly, we observed no detectable signals for the corresponding [2]rotaxane in the ^1H NMR spectrum of the crude product; the dumbbell-shaped species **16** was isolated in 73% yield. Our inability to synthesize the [2]rotaxane from the ester-containing threadlike species **15** under conditions similar to those we had used for the successful syntheses of the amide-containing [2]rotaxanes suggested that a pseudorotaxane formed from the isocyanate **5**, a Na^+ ion, and BPX26C6 was not the key intermediate for the assembly of the [2]rotaxanes **5**–**7** and **12**–**14**. Our results also confirmed the importance of ion–dipole and hydrogen-bonding interactions between the amide unit and the templating metal ion and the macrocycle BPX26C6, respectively, for the generation of the pseudorotaxane structures in solution. The successful synthesis of the [2]rotaxane **17** from the reaction of the threadlike species **9**, BPX26C6, NaTFPB, and triisopropylsilyl triflate in CH_2Cl_2 (Scheme 4)[16] is consistent with the formation of a [2]pseudorotaxane structure based on the recognition of **9** by BPX26C6 in the presence of a templating Na^+ ion in solution. The low yield (10%) of this reaction, relative to that for the



Scheme 4. Exploring the synthesis of rotaxanes from ester-containing thread and triisopropylsilyl triflate stopper.

synthesis of the [2]rotaxane **12**, can be rationalized by considering that the triflate anions released during the progress of this reaction destabilized the corresponding [2]pseudorotaxane by weakening the metal ion chelating and/or hydrogen-bonding interactions among the components.[17]

It is known that the cooperation of a few suitably arranged amino acid residues and their side chains can prevent the dethreading of interlocked macrocycles;[18] therefore, we suspected that the construction of rotaxanes from BPX26C6 and pure peptide chains would be possible if a proper sequence of amino acid residues was positioned at the terminus. To demonstrate that no additional functionality need be introduced into the structure of the peptide (unlike the urea moiety found in the [2]rotaxane **14**), thereby allowing this recognition system to be used to construct interlocked or interwoven structures featuring pure peptide chains, we applied a common peptide coupling reaction in the stoppering process.[19] Gratifyingly, when we added *N*,*N*′-dicyclohexylcarbodiimide (DCC) activated 3,5-di-*tert*-butylbenzoic acid **18** (105 mM) to a solution of the threadlike species **11**, $NaClO_4$, and BPX26C6 (100:250:250 mM) in CH_2Cl_2, we isolated the desired [2]rotaxane **19** in 31% yield after column chromatography (Scheme 5).[20]

We grew single crystals suitable for X-ray crystallography through liquid diffusion of hexane into a solution of the [2]rotaxane **19** in CH_2Cl_2. The solid-state structure of **19** reveals[21,22] the expected [2]rotaxane geometry (Figure 2), in which the amide groups of the threadlike component penetrate through the BPX26C6 component, with the NH units of the former hydrogen bonded to the oxygen atoms of the latter.

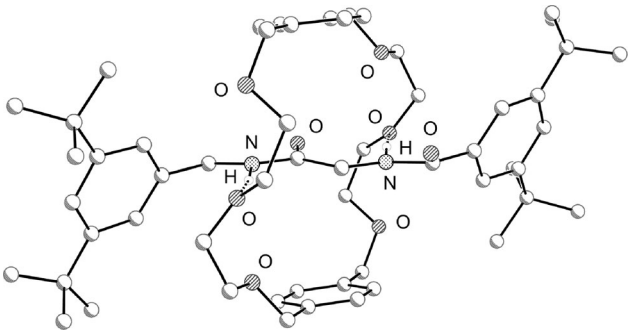
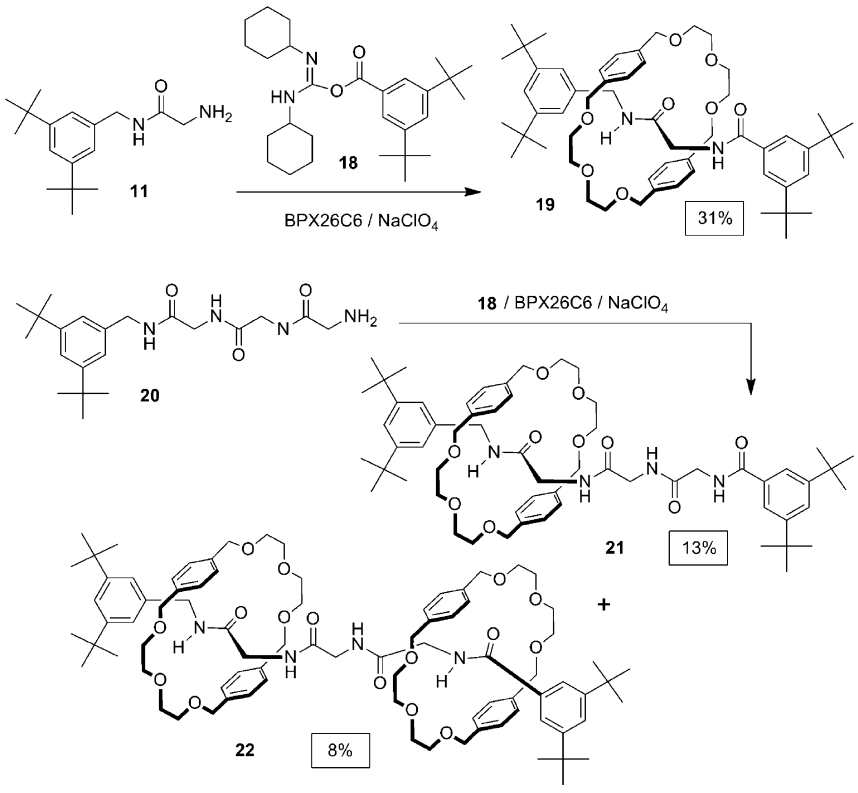


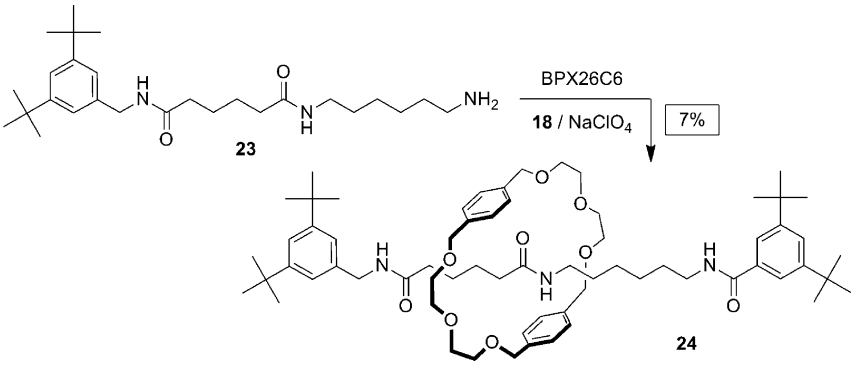
Figure 2. Ball-and-stick representation of the solid-state structure of the [2]rotaxane **19**.

Our successful syntheses of the [2]rotaxanes **14** and **19** suggested that the recognition of BPX26C6 required only a single amide moiety in a peptide chain, thereby potentially allowing higher-order [*n*]rotaxanes to be prepared from relatively long peptides. Indeed, when we mixed the threadlike tripeptide **20**, which features three BPX26C6-recognizable amide moieties in its GlyGlyGly sequence, with BPX26C6, $NaClO_4$, and the stoppering agent **18** in CH_2Cl_2, we isolated the [2]rotaxane **21** and the [3]rotaxane **22** in 13 and 8% yields, respectively, after column chromatography (Scheme 5). This result demonstrates the potential application of this recognition system in the assembly of interlocked structures from biomolecules or other polymeric materials. Toward this goal, when we treated the threadlike species **23**, which contains a single repeating unit of nylon-6,6, with BPX26C6, $NaClO_4$, and the stoppering agent **18** in CH_2Cl_2, we isolated the corresponding [2]rotaxane **24** in 7% yield (Scheme 6). Thus, the Na^+ ion assisted threading of amides through the cavity of the macrocycle BPX26C6 can also be applied directly to form interwoven or interlocked structures from common peptides and polymers without altering their key molecular structures.

We have discovered a new molecular recognition system in which a single conjugated or nonconjugated urea or amide functionality is recognized by the macrocycle BPX26C6 through the templating effect of a Na^+ ion. We have also demonstrated that this recognition system can be used to synthesize rotaxanes from important and practically useful artificial or biological (macro)molecules featuring glycine residues or nylon-6,6 repeating units as threading components. We believe that the extremely high structural flexibility of the guests for this recognition system will facilitate the introduction of interlocked or interwoven structures



Scheme 5. Syntheses of C-amidated glycine-based rotaxanes.



Scheme 6. Synthesis of a [2]rotaxane containing a nylon-6,6 repeating unit.

into (bio)materials found commonly in our daily lives, possibly endowing them with new functions or properties; such studies are currently in progress.

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[20] When we replaced $NaClO_4$ by NaTFPB and performed the reaction under similar conditions, the yield of the isolated [2]rotaxane **19** was 29%, but the purification process became more tedious. Signals of the protons of the TFPB anion remained in the ^{1}H NMR spectrum of purified **19**, possibly because of relatively strong interactions between this [2]rotaxane and the Na^+ ion. Further anion exchange, aqueous extraction, and column chromatography were necessary to obtain the pure [2]rotaxane **19**.

[21] CCDC 917834 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.

[22] Crystal data for **19**: $C_{56}H_{78}O_8N_2$, $M_r = 907.2$, triclinic, space group $P\text{-}1$, $a = 10.1895(8)$, $b = 10.417(1)$, $c = 13.3620(11)$ Å, $V = 1333.4(2)$ Å^3, $\rho_{calcd} = 1.130\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 1.134\ mm^{-1}$, $T = 295\ (2)$ K, colorless plate, 4,846 independent measured reflections, F^2 refinement, $R_1 = 0.1284$, $wR_2 = 0.3959$.

Communications

Template Synthesis

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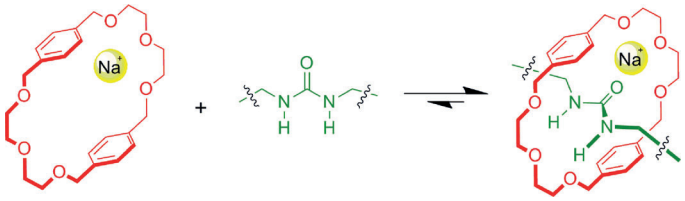
Sodium Ions Template the Formation of Rotaxanes from BPX26C6 and Nonconjugated Amide and Urea Functionalities



Picking up the thread: The macrocycle bis-*p*-xylyl[26]crown-6 is capable of forming pseudorotaxane-like structures with single, nonconjugated urea or amide moieties when assisted by templating Na^+ ions (see example). By using this approach, rotaxanes were synthesized with glycine residues or the repeating unit of nylon-6,6 as key components in the threadlike units.