Boron-based rotaxanes by multicomponent self-assembly†

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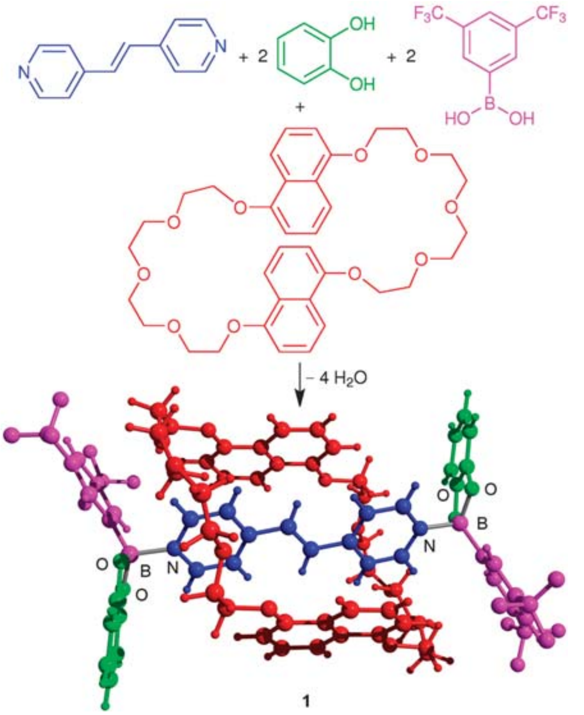
The multicomponent reaction of 1,2-di(4-pyridyl)ethylene, catechol, 3,5-bis(trifluoromethyl)phenylboronic acid and 1,5-dinaphtho-38-crown-10 or bis-*para*-phenylene-34-crown-10, respectively, resulted in the formation of rotaxanes, which were characterized by X-ray crystallography.

Over recent years, the perception of rotaxanes has changed substantially. Whereas initially they represented "exotic molecules"[1] and an "intriguing synthetic challenge",[2] they are now recognized as key components of molecular nanotechnology.[3,4] The basis for this development was the discovery of efficient synthetic routes to construct such mechanically interlocked species.[4] The most common strategies rely on preorganized building blocks, which are locked by covalent capture under kinetic control. An interesting alternative is the formation of rotaxanes under thermodynamic control using reversible covalent[5] or non-covalent bonds.[6] A key advantage of the latter approach is its efficiency, which allows complex structures to be generated, such as an [11]rotaxane[7] or rotaxane-based dendrimers, for example.[8] To further advance this field, new methods and building blocks for the synthesis of rotaxanes and polyrotaxanes under thermodynamic control are desirable. Below, we describe molecular assembles that—to best of our knowledge—represent the first examples of *boron*-based rotaxanes. They are obtained in good yield by the assembly of four chemically-distinct components.[9]

In a continuation of our studies concerning the utilization of boron compounds in supramolecular chemistry,[10] we recently observed that bis(dioxaboroles) can be polymerized by the addition of 4,4′-dipyridine or 1,2-di(4-pyridyl)ethylene (DPE).[11] Due to coordination to the Lewis acidic boronic esters, the dipyridyl linkers become electron deficient, and strong intrastrand charge-transfer transitions from the electron-rich dioxaborole moieties to the dipyridyl groups are observed.[11] This finding was the basis for our investigations concerning boron-based rotaxanes, which are detailed below.

As building blocks for the multicomponent synthesis of a rotaxane, we used DPE, catechol, 3,5-bis(trifluoromethyl)phenylboronic acid and 1,5-dinaphtho-38-crown-10[12] (Scheme 1). These compounds were dissolved in a 1 : 2 : 2 : 1 ratio in toluene, and then heated in a Dean–Stark trap. Under these conditions, the catechol was expected to condense with the boronic acid to give a boronic ester. The latter should coordinate to DPE *via* dative B–N bonds[13] to give an electron-deficient axle. Since the B–N bond formation is reversible, the crown ether can slip onto the axle to form a rotaxane. Spectroscopic and crystallographic analyses showed that this strategy was indeed successful. After cooling to room temperature, a yellow precipitate could be isolated (yield: 67%). NMR spectroscopic analyses of this product showed characteristic signals derived from all four building blocks in a 1 : 2 : 2 : 1 ratio (see ESI†). Clear evidence for the formation of rotaxane **1** was obtained by X-ray crystallography.‡ The structure of **1** is comprised of a dipyridyl axle, two boronic ester stoppers and the crown ether, which is wrapped around the axle (Scheme 1). The molecule has crystallographic C_2 symmetry about an axis passing through the center of the ethylenic double bond and the dioxonaphthalene rings. The lengths of the B–O (1.455(14) and 1.489(13) Å) and B–N (1.641(14) Å) bonds are within expected ranges.[13] The DPE linker is sandwiched between the two coplanar dioxonaphthalene groups of the crown ether, which are 7.71 Å apart from each other. The plane defined by the pyridyl groups of the axle is slightly twisted with respect to the plane defined by the dioxonaphthalene rings (twist angle: 29.9°). In addition to π-stacking interactions, there are C–H···O



Scheme 1 Synthesis of rotaxane **1**. The graphic representation of **1** is based on a crystallographic analysis.

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hydrogen bonds between the α-CH groups of the pyridyl rings and an O-atom of the crown ether.‡

To test whether rotaxanes are also formed with other crown ethers, we performed a multicomponent reaction with bis-*para*-phenylene-34-crown-10[14] instead of 1,5-dinaphtho-38-crown-10. As before, we were able to obtain a yellow precipitate (yield: 63%), which turned out to be rotaxane **2**, as evidenced by a crystallographic analysis (see ESI†). The overall structure of **2** is similar to that of **1**: the crown ether wraps around the dipyridyl axle, which is connected to two boronic esters *via* dative B–N bonds (Fig. 1).‡ The unit cell contains two halves of independent rotaxanes with C_2 symmetry, which display comparable bond lengths (B–O_{av} = 1.46 Å; B–N_{av} = 1.64 Å). Contrary to what was observed for rotaxane **1**, the planes defined by the phenylene rings of **2** are nearly coplanar with that defined by the DPE axle. Consequently, the aromatic rings of the crown ether in **2** are closer to each other (7.00 and 7.06 Å). The phenylene rings are aligned with the ethylenic double bond of the axle (Fig. 2, bottom). Several C–H···O contacts between the α-CH groups of the pyridyl rings and an O-atom of the crown ether are observed.‡

The multicomponent reaction of DPE, catechol and 3,5-bis(trifluoromethyl)phenylboronic acid with a third crown ether, dibenzo-30-crown-10, also resulted in the formation of a yellow precipitate. NMR spectroscopic analysis of this precipitate revealed the presence of signals derived from all four building blocks. Unfortunately, we were not able to obtain single crystals for a crystallographic analysis. In view of the known tendency of *ortho*-phenylene-based crown ethers, such as dibenzo-30-crown-10, to bind to cationic guest molecules in a clip-like fashion[15] (instead of wrapping around them as required for a rotaxane), we tried to obtain structural information for a closely related analogue. Suitable single crystals were obtained for an aggregate, **3**, containing 4,4′-dipyridine as the axle instead of DPE. Compound **3** was formed in 60% yield by the multicomponent reaction of 3,5-bis(trifluoromethyl)phenylboronic acid, 4,4′-dipyridine, catechol and dibenzo-30-crown-10 (see ESI†). Its crystal structure is depicted in Fig. 2. As observed for related guests, such as diquat,[15b] the crown ether acts as a "molecular clip"[16] rather than forming a rotaxane. The phenylene rings of the crown ether show π–π interactions with the pyridyl rings of the axle. In addition, there are a number of weak hydrogen bonds between the pyridyl H-atoms and the O-atoms of the crown ether. The lengths of the B–N (1.636(5) and 1.662(5) Å) and B–O bonds (B–O_{av} = 1.47 Å) are similar to those observed for **1** and **2**.‡

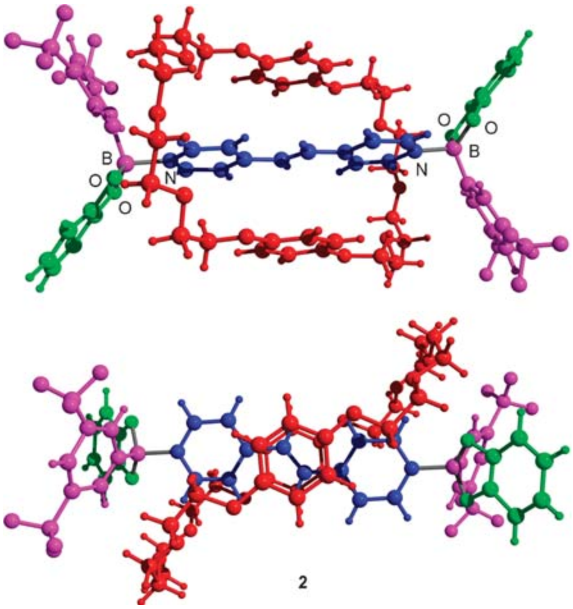


Fig. 1 Molecular structure of rotaxane **2** in the crystal. Bottom: view along the C_2 symmetry axis; top: view from the side. Only one of the two crystallographically-independent rotaxanes is shown. The co-crystallized toluene molecules are also not shown for clarity.

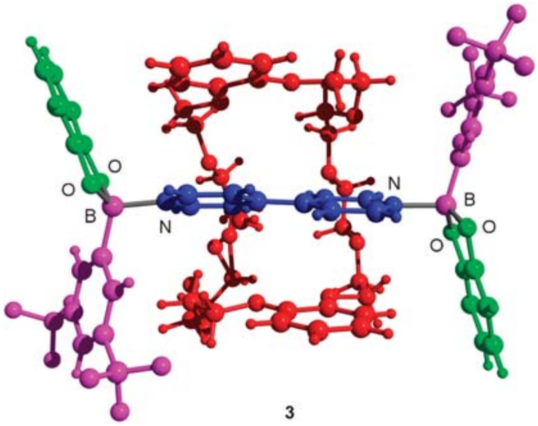
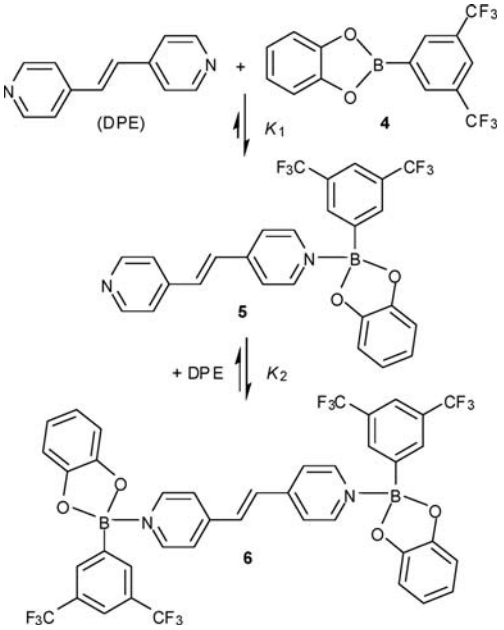


Fig. 2 Molecular structure of host–guest complex **3** in the crystal. The co-crystallized toluene molecule is not shown for clarity.

To obtain further information about the stability of the aggregates in solution, we performed NMR titration experiments with boronic ester **4** and DPE. Ester **4** was rapidly formed when 3,5-bis(trifluoromethyl)phenylboronic acid was heated with an equal amount of catechol (see ESI†). It thus represents a likely intermediate in the assembly of **1** and **2**.

The addition of increasing amounts of DPE to **4** resulted in gradual changes in the ^{1}H NMR spectra, indicating that pyridyl adduct formation was fast on the NMR time scale. Fitting of the titration isotherm (see ESI†) to a 2 : 1 binding model gave a first binding constant of K_1 = 1.3 (±0.9) 10^4 M^{-1} and a second binding constant of K_2 = 3.2 (±0.5) 10^2 M^{-1}. Rotaxane formation can be rationalized by assuming that the crown ether slips onto the mono adduct **5**, followed by reversible addition of the second boronic ester stopper to give the adduct **6** (Scheme 2).§ A similar analysis was performed for the interaction of boronic ester **4** with the 4,4′-dipyridyl axle, resulting in slightly lower binding constants of K_1 = 1.2 (±0.9) 10^4 M^{-1} and K_2 = 1.8 (±0.2) 10^2 M^{-1}.

In summary, we have described rotaxanes that are formed in a multicomponent assembly process from a dipyridyl linker, an arylboronic acid, catechol and crown ethers. A unique structural feature of these rotaxanes is that boronic esters are an integral part of the assembly. The boronic esters have a two-fold function: (a) they act as Lewis acids, which renders the coordinated dipyridyl ligands electron-deficient and thus increasing their affinity to electron-rich crown ethers; (b) they act as stoppers. A disadvantage for potential applications in molecular devices is the fact that the highly dynamic B–N bond cannot easily be fixed (*e.g.* by changing the temperature or solvent). However, the



Scheme 2 Step-wise assembly of adduct **6**.

dynamic nature of the B–N bond could be advantageous for the construction of boron-based polyrotaxanes[17] or covalent organic rotaxane frameworks, in analogy to the coordination polyrotaxanes and metal–organic rotaxane frameworks described by the groups of Kim and Loeb.[18] Current efforts in this direction are being pursued in our laboratory.

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Notes and references

‡Unfortunately, the quality of the structures of rotaxanes **1** and **2** are very low. The axles are well defined, but strong disorder is observed for the ethylene glycol part of the crown ethers and the CF_3 groups. This disorder, combined with the weakness of the observed diffraction and twinning problems for **1**, prevented us from obtaining better results. The distances of the C–H···O bonds are therefore not discussed in detail.
Data for **1**: $C_{76}H_{68}B_2F_{12}N_2O_{14}$, $M_r = 1482.94$, monoclinic, space group $P2_1/c$, $a = 11.7382(12)$, $b = 16.517(3)$, $c = 17.832(4)$ Å, $\beta = 98.670(13)°$, $V = 3417.7(10)$ Å^3, $Z = 2$, $T = 100(2)$ K, 40239 reflections collected, 5990 independent reflections, $R_{int} = 0.0786$, $R_1 [I > 2\sigma(I)] = 0.1633$, wR_2 (all data) = 0.5002. CCDC 683419.
Data for **2**: $C_{89}H_{88}B_2F_{12}N_2O_{14}$, $M_r = 1659.23$, triclinic, space group P-1, $a = 13.4013(9)$, $b = 14.5562(10)$, $c = 22.3107(17)$ Å, $\alpha = 96.487(6)$, $\beta = 107.062(6)$, $\gamma = 92.798(6)°$, $V = 4118.6(5)$ Å^3, $Z = 2$, $T = 140(2)$ K, 26573 reflections collected, 11389 independent reflections, $R_{int} = 0.1597$, $R_1 [I > 2\sigma(I)] = 0.1543$, wR_2 (all data) = 0.4318. CCDC 683420.
Data for **3**: $C_{73}H_{70}B_2F_{12}N_2O_{14}$, $M_r = 1448.93$, monoclinic, space group $P2_1/c$, $a = 14.0418(4)$, $b = 22.0219(6)$, $c = 22.2997(6)$ Å, $\beta = 96.386(3)°$, $V = 6852.9(3)$ Å^3, $Z = 4$, $T = 140(2)$ K, 45866 reflections collected, 12085 independent reflections, $R_{int} = 0.0413$, $R_1 [I > 2\sigma(I)] = 0.0696$, wR_2 (all data) = 0.2075. CCDC 683421.
For crystallographic data in CIF or other electronic format see DOI: 10.1039/b805437a
§ In view of the numerous species involved, we have not attempted to a derive binding constant for the interaction of **5** with crown ethers.

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