

Organic Molecular Shuttles based on Rotaxanes

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The word rotaxane is derived from the Latin word 'rota' meaning wheel and 'axis' meaning axle. **[n] Rotaxanes** are a class of molecules which consist of $(n-1)$ macrocycles encircling a large linear component (referred to as a thread or an axle) terminated by bulky stoppers which prevent the macrocycle from slipping out.

Another closely related class of compounds is **[n] Catenenes** in which (n) macrocycles interlock to form a chain. A **pseudorotaxane** is a rotaxane which has one or no bulky stoppers on the thread.

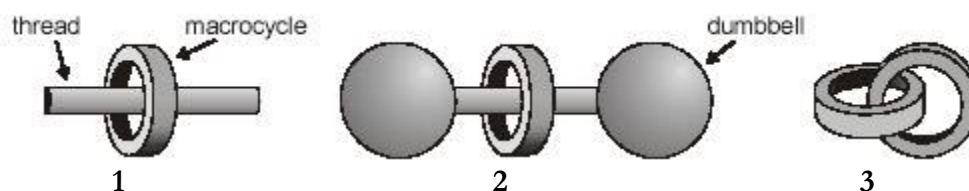


Figure 1: Schematic representation of **1.** A [2] pseudorotaxane, **2.** A [2] rotaxane and **3.** A [2] catanene

Rotaxanes can be made to behave as molecular shuttles because the macrocycle is free to glide over the thread/axle and this movement of the macrocycle can be controlled in certain cases with external input like light, pH gradient and electric current. This property of rotaxanes has prompted a lot of interest in this class of molecules as possible devices in the area of Computers and in mimicking Biological processes.

Even though rotaxanes and catanenes and their syntheses have been speculated upon for almost a century they were only actually synthesized in the 1960's. The early procedures of synthesis relied upon low yielding **statistical approaches** and the difficult yet very elegant **directed covalent syntheses**. The **statistical approach** relies on the existence of very small concentrations in the reaction mixture a species in which a macrocycle is threaded by an acyclic molecule. In the **directed syntheses** of rotaxanes multiple steps are required to prepare them from pre-rotaxanes composed of macrocyclic and acyclic components linked by covalent bonds which are then cleaved to result in the rotaxane.

With the advent of supramolecular chemistry, it is now much easier to synthesize rotaxanes and catanenes using self-assembly driven by stabilizing noncovalent interactions (hydrogen bonding, metal-ligand complexation, π - π stacking etc.) between the macrocycle and the thread/axle.

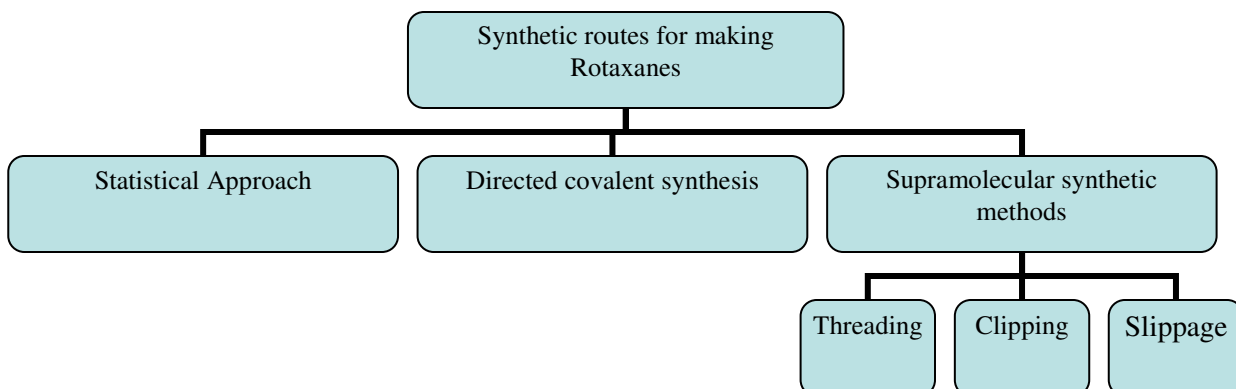


Figure 2: Synthetic methods of rotaxanes

Synthetic strategies for making rotaxanes using supramolecular chemistry

Three different routes can be followed for the preparation of rotaxanes. The first method is **threading** in which the macrocycle first encircles the thread which is then stoppered by bulky groups (dumbbells) to make the rotaxane. Another method is **clipping** which involves clipping together the macrocycle segments on the thread/axle which has already been stoppered. The third method, **slippage** involves the selection of the

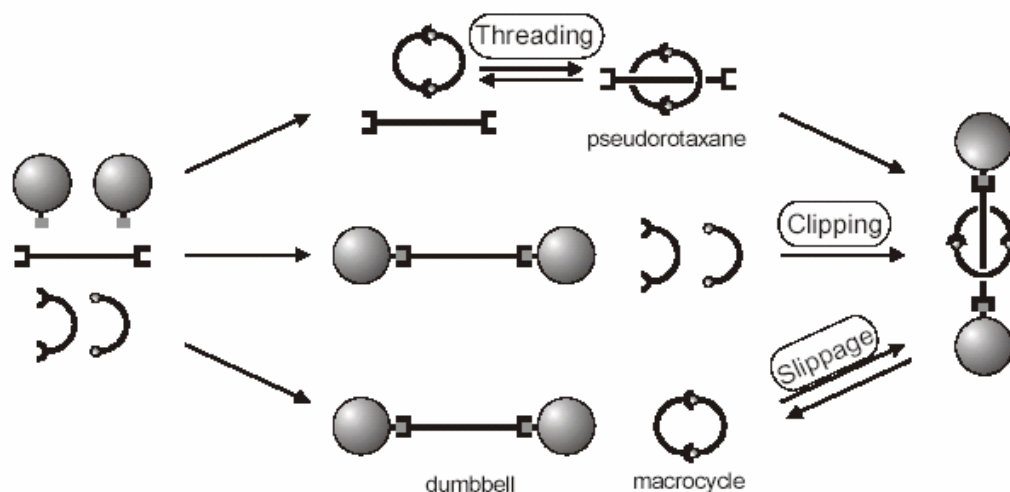


Figure 3: Different supramolecular strategies for making rotaxanes

macrocycle being similar in size with the dumbbell stopper and this enables the ring to slip over the stopper onto the thread at elevated temperatures.

A non-covalent interaction (hydrogen bonding, metal-ligand complexation etc.) between the two components usually is the driving force for these syntheses and the macrocycle usually resides near a location on the thread called a **station** with which is the site for interaction between the macrocycle and the thread. A rotaxane may have more than one station on its thread/axle and in this case the macrocycle can switch between these two positions if they are both the same. If the two stations are different, then the macrocycle is more likely to be on the station which has a greater interaction with it.

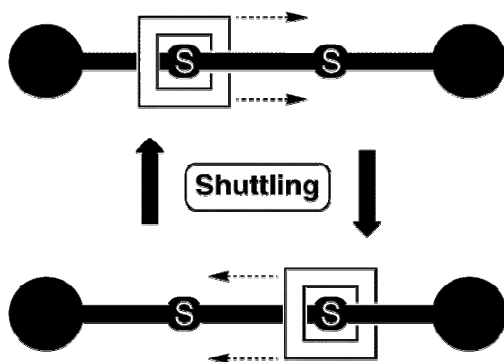


Figure 4: The shuttling process in a 2-rotaxane with two identical stations

A shuttling 2-rotaxane

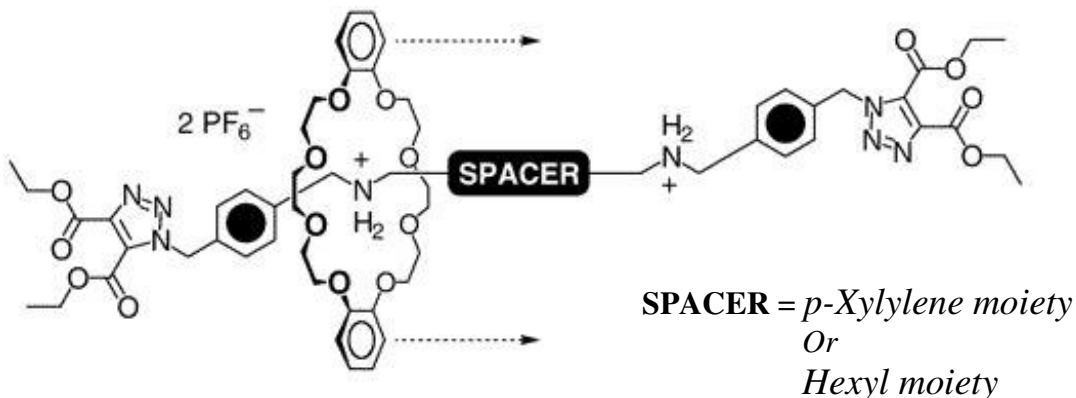


Figure 5: A 2-rotaxane with two identical dialkyl ammonium stations

This shuttling 2-rotaxane was synthesized by Stoddart et al.³ The route used by the authors is interesting because initially only a 3-rotaxane is formed with two crown ether rings on each dialkyl ammonium station (the dialkyl ammonium ion is stabilized by the electron rich crown ether macrocycle).

The authors therefore devised a route in which they first protected one of the dialkyl ammonium stations on the axle with a Boc (tert- butoxycarbonyl) protecting

group and then introduced the threading of the crown ether macrocycle, which enabled the formation of the 2- rotaxane shown above. This shuttling process was then studied under various conditions like altering the temperature and the introduction of a base.

A shuttling 3-rotaxane

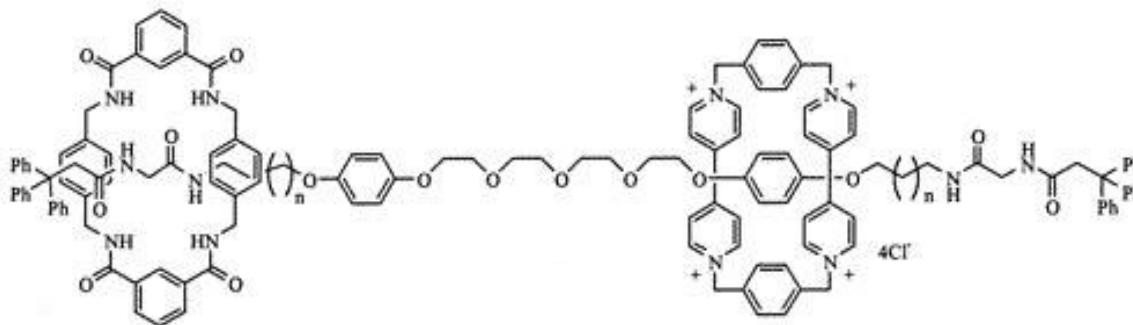


Figure 6: A heterocyclic 3-rotaxane in which one of the macrocycles acts as a shuttle

This 3-rotaxane reported by Li et al.⁴ is a very unusual shuttle which also happens to be the first example of a heterocyclic 3-rotaxane (the two macrocycles on the axle are different). This rotaxane is synthesized by the process of clipping in the case of both the neutral and the tetra-cationic cyclophanes macrocycles. The tetracationic macrocycle shuttles between the two hydroquinone stations.

Acid Base Controlled shuttle

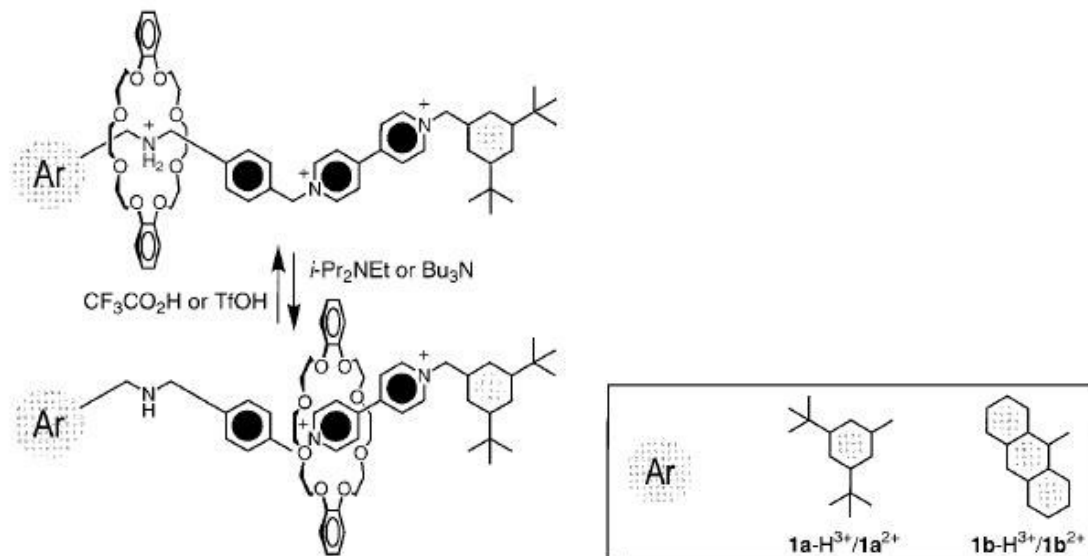


Figure 7: A 2-rotaxane shuttle in which the position of the macrocycle can be controlled by changing the pH

This 2-rotaxane synthesized by Stoddart et al.⁵ is an example of a rotaxane in which the movement of the crown ether macrocycle along the axle can be controlled by the

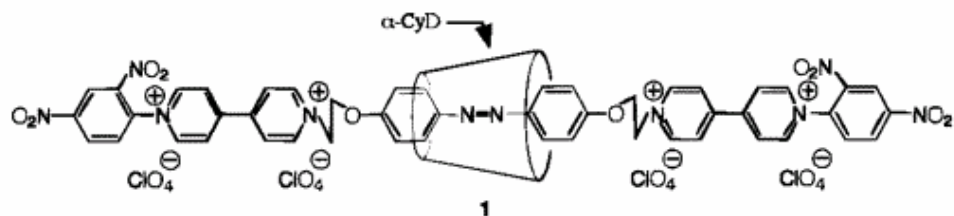


Figure 9: A 2-rotaxane in which the position of the macrocycle can be controlled by light

A cyclodextrin macrocycle is used by the authors Nakashima et al.⁷, to make this 2-rotaxane. The macrocycle is initially around the azobenzene station on the axle and irradiation of the rotaxane at 360 nm causes the photo-isomerism of azobenzene from trans to cis and this forces the cyclodextrin to move away to the methylene spacer. Irradiation of the rotaxane at 430 nm brings back the cyclodextrin to its original position.

Bibliography

1. *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buckecher, C. O., Eds.; Wiley-VCH: Weinheim, **1999**.
2. Reed, M.A.; Tour, J.M. *Scientific American* **2000**, 282, 6, 86
3. Cao, J; Fyfe, M.C.T; Stoddart, J.F. *J. Am. Chem. Soc* **2000**, 65, 1937-1946
4. Zhao, X; Jiang X.K; Shi, M; Yu, Y.H.Y.; Xia W.; Li Z.T. *J.Org.Chem.* **2001**, 66, 7035-7043
5. Ashton, P. R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gomez-Lopez, M.; Martinez-Diaz, M.-V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J.; *J. Am. Chem. Soc.*; **1998**; 120(46); 11932-11942.
6. Armaroli, N.; Balzani, V.; Collin, J.-P.; Gavina, P.; Sauvage, J.-P.; Ventura, B.; *J. Am. Chem. Soc.*; **1999**; 121(18); 4397-4408.
7. Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N.; *J. Am. Chem. Soc.*; **1997**; 119(32); 7605-7606.
8. Lane, A. S.; Leigh, D. A.; Murphy, A.; *J. Am. Chem. Soc.*; **1997**; 119(45); 11092-11093
9. *Molecular Switches*, Feringa, B.L, Ed.; Wiley-VCH: Weinheim, **2001**.
10. Anelli, P.L.; Spencer, N; Stoddart, J.F *J. Am. Chem. Soc.*; **1991**; 113(13); 5131-5133.
11. Bissell, R. A.; Cordova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, 369, 133-137.
12. Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, 285, 391-394.
13. Jager, R.; Vogtle, F. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 930.
14. Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, 99, 1643-1664.

