

Abstract

The electron rich tetrathiafulvalene (TTF) and monopyrrolo-TTF (MPTTF) units have been used widely in combination with the electron poor cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) in the construction of molecular machines based on rotaxanes and catenanes. In order to make a functional molecular machine that can generate work, unidirectional motion is essential. This thesis describes the synthesis and study of several molecular machines in the shape of [2](pseudo)rotaxanes and [2]catenanes in an attempt to design a system showing unidirectional motion.

Chapter 2 focuses on achieving unidirectional linear motion in a two-station [2]pseudorotaxane, both in the presence and absence of a stopper group. One station is a TTF derivative while the other is a MPTTF derivative. The studies suggested that CBPQT•4PF₆ will preferably slip onto the thread from the TTF side in the system without a stopper. This is also supported by the distribution between the translational TTF⊂CBPQT•4PF₆ and MPTTF⊂CBPQT•4PF₆ isomers at equilibrium in the two systems, which is 10:90 in the absence of the stopper and 14:86 in the presence of it. Hence, these systems displayed an impressive unidirectional linear motion with at least 86% of CBPQT•4PF₆ moving spontaneously from the TTF to the MPTTF station. It was further shown that CBPQT•4PF₆ is able to move towards the stopper group upon oxidation of the thread.

Chapter 3 describes the synthesis and investigation of three tristable [2]pseudorotaxanes and a tristable [2]rotaxane. These systems each contain a TTF, MPTTF, and HQ station connected in that order. For the [2]pseudorotaxanes, up to 23% of CBPQT•4PF₆ spontaneously moved from the TTF station to the HQ station. Upon oxidation of the TTF and MPTTF stations, the most efficient unidirectional motion of CBPQT•4PF₆ from the MPTTF to the HQ station was observed in the [2]rotaxane. The efficiency of this motion was determined to be 67%. Furthermore, it was revealed that entropy plays a crucial role in the efficiency of unidirectional motion. In addition, the studies suggested that upon oxidation of the dumbbell the motion of CBPQT•4PF₆ is primarily under kinetic rather than thermodynamic control.

Chapter 4 describes the synthesis and investigation of a tristable [2]catenane with a design inspired by the [2]rotaxane presented in Chapter 3, which contained a TTF, MPTTF, and HQ station. A monoethylene linker connected the TTF and HQ stations while triethylene glycol (TEG) chains made up the remaining linkers. Upon oxidation of the track CBPQT•4PF₆ residing on the MPTTF station initially moved onto the TEG chain connecting the TTF and MPTTF stations, before moving to the HQ station, as was also the case for the [2]rotaxane presented in Chapter 3. The direction in which CBPQT•4PF₆ moves from the TEG chain to the HQ station is unclear. Furthermore, elucidation of the route CBPQT•4PF₆ uses when it moves from the HQ back to the MPTTF station upon reduction of the oxidized track is yet to be achieved and studies are still ongoing on this subject. However, the studies so far do not disprove that unidirectional motion preferably takes place and is also supported by the many model systems studied not only in this thesis, but also in the past. Therefore, it is quite plausible that the targeted unidirectional motion has been achieved in the [2]catenane.

Chapter 5 presents two novel binding sites for $\text{CBPQT}\cdot 4\text{PF}_6$; naphtho[1,2-b:5,6-b']dithiophene (NDT) and benzo[1,2-b:4,5-b']dithiophene (BDT). Of the two, BDT showed a higher solubility and a stronger binding to $\text{CBPQT}\cdot 4\text{PF}_6$ and it became the building block of choice to incorporate into a two-station [2]pseudorotaxane together with a MPTTF station. No detectable amounts of $\text{CBPQT}\cdot 4\text{PF}_6$ were found to bind to the BDT station at equilibrium. TEG linkers on TTF and HQ derivatives are known to stabilize their binding to $\text{CBPQT}\cdot 4\text{PF}_6$ due to hydrogen bonding between the TEG chains and $\text{CBPQT}\cdot 4\text{PF}_6$. Therefore, the studies presented in this chapter indicate that a longer glycol linker may be necessary in the case of BDT for such interactions to take place in a [2]rotaxane. For this reason switching was not observed upon oxidation of the MPTTF station but is expected to be possible in the analogous [2]rotaxane. BDT shows great potential as a station for molecular machines, and these results will hopefully inspire new designs for candidate systems which could show further progress towards a molecular machine with unidirectional linear motion.