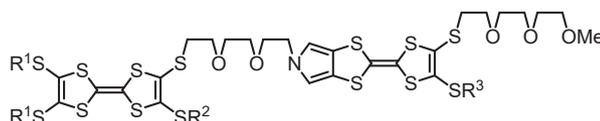


Abstract

The work presented in this PhD thesis is concerned with controlled unidirectional movement in [2]pseudorotaxanes, [2]rotaxanes and [2]catenanes. Within this field, special attention has been given to the electron rich tetrathiafulvalene (TTF). Especially the pyrrole-annelated TTF, monopyrroloTTF (MPTTF) has been given attention, as it easily forms a supramolecular complex with the electron deficient macrocycle cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺).

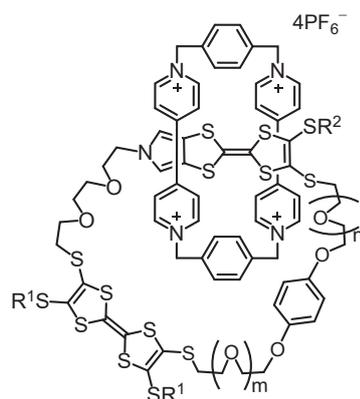
Chapter two describes the synthesis and investigations of [2]pseudorotaxanes incorporating TTF and MPTTF moieties in the pseudodumbbell (see illustration below). These [2]pseudorotaxanes are designed in an attempt to create unidirectional linear movement of CBPQT⁴⁺ upon mixing with and oxidation of the stations on the pseudodumbbells. Initially, CBPQT⁴⁺ should enter the pseudodumbbell via the TTF moiety, then move to the MPTTF moiety and finally fall off via the MPTTF dithiole-end upon oxidation of the TTF and MPTTF moieties. The [2]pseudorotaxanes have different substituents on the TTF and MPTTF moieties, which helps control and investigate the movement of CBPQT⁴⁺. When the pseudodumbbells are mixed with CBPQT⁴⁺ it is possible to follow the movement of CBPQT⁴⁺ on and off the pseudodumbbells, and from these data attempt at calculating rate constants for the movement by a numerical analysis. This yielded six different rate constants to describe the movement of CBPQT⁴⁺, however, the rate constants did not match the data obtained by other experiments. Oxidation of some of the [2]pseudorotaxanes at low temperatures yielded rate constants for the movement of CBPQT⁴⁺ off the oxidized pseudodumbbells passing either the TTF²⁺ or MPTTF²⁺ moieties. These rate constants are related to the Gibbs Free Energy of Activation and are used to calculate the barrier size of the oxidized MPTTF²⁺ and TTF²⁺ moieties, and it is found that the MPTTF²⁺ moiety is a smaller barrier for CBPQT⁴⁺ to cross as compared to the TTF²⁺ moiety.



Chapter three describes how the numerical analysis was tested on a [2]rotaxane, which is similar to the [2]pseudorotaxanes in chapter two. Oxidation of this [2]rotaxane yielded data for the movement of CBPQT⁴⁺ over an oxidized MPTTF²⁺. These data were then used to calculate the rate constants by a numerical analysis, which showed that the movement of CBPQT⁴⁺ over the MPTTF²⁺ moiety in a [2]rotaxane is easier (i.e., has a smaller barrier) than in the [2]pseudorotaxanes.

Chapter four describes how the data obtained for the barrier sizes of the MPTTF²⁺ and TTF²⁺ moieties are used to design multiple [2]catenanes with TTF, MPTTF and hydroquinone (HQ) moieties (see illustration below). Here, rotational unidirectional movement of CBPQT⁴⁺ is supposed to take place when the TTF and MPTTF moieties are oxidized and reduced. Initially, most of the CBPQT⁴⁺ is expected to be located at the MPTTF moiety of the [2]catenanes. Upon oxidation of the MPTTF and TTF moieties, CBPQT⁴⁺ moves to the HQ moiety, and upon reduction of the TTF²⁺ and MPTTF²⁺ moieties, CBPQT⁴⁺ moves back to the MPTTF moiety, preferably via the TTF moiety. By oxidation of the MPTTF and TTF moieties, followed by reduction and precipitation, it was made possible to

isolate the rotational HQ isomers of the [2]catenanes, where CBPQT⁴⁺ is encircling the HQ moiety. Dissolving this rotational isomer and following the equilibration of the solution yielded data that were used to calculate rate constants for the movement of CBPQT⁴⁺ by a numerical analysis. The rate constants were then related to Gibbs Free Energies of Activation for the movement of CBPQT⁴⁺, and these were in turn used to quantify the movement of CBPQT⁴⁺. The calculations showed, that the linkers, which are combining the TTF, MPTTF and HQ moieties, have an impact on the kinetics of the movement of CBPQT⁴⁺, and that in some of the [2]catenanes 32-71% unidirectional movement of CBPQT⁴⁺ is achieved upon one oxidation and reduction cycle, whereas only switching between some of the moieties (e.g. the HQ moiety and the MPTTF moiety) are taking place in the other [2]catenanes.



Chapter five is concerned with investigations of the azobenzene (AB) photoswitch, in order to determine whether it can act as a stopper or a barrier for CBPQT⁴⁺. To investigate the photoswitch, it is integrated into a pseudodumbbell, where the AB moiety is coupled to a MPTTF moiety, with a stopper unit in one end and the AB moiety in the other end. In this way, mixing the pseudodumbbell with CBPQT⁴⁺ will make CBPQT⁴⁺ cross the AB moiety to encircle the MPTTF moiety. Studies on these systems showed that substitution of an AB moiety with an MPTTF moiety lowered the quantum yields and the half-life of the *Z* to *E* isomerization. Furthermore, it was found that CBPQT⁴⁺ can easily cross both the *E* and the *Z* isomers of the AB moiety.

Chapter six is concerned with the development of new macrocycles to use in [2](pseudo)rotaxanes and [2]catenanes. The new macrocycles are composed of two MPTTF moieties, which allows for oxidation of the macrocycle. Different investigations were carried out on these macrocycles to elucidate the properties of the macrocycles and it was found that the macrocycles interact with the electron deficient paraquat and tetracyanoquinodimethane (TCNQ).