Chapter VII

Conclusions and Future Work

The research presented in this thesis focused on pseudorotaxanes and supramolecular polymers based on a new recognition motif, the dibenzo-24-crown-8/paraquat recognition motif.

By preparation and characterization of a series of pesudorotaxanes based on DB24C8 and paraquat derivatives, it was found these pseudorotaxane were stabilized by $N^+\cdots O$ interactions, C-H$\cdots$O hydrogen bonding, and face-to-face π-stacking interactions. Because methyl protons of paraquat are involved in hydrogen bonding to the host, the substitution of any methyl hydrogen atom on paraquat causes K_a to decrease.

The concentration dependence of apparent association constants, $K_{a,exp}$, of fast exchange host-guest systems was studied for the first time by using complexes based on viologens and crown ethers as examples. While the bis(hexafluorophosphate) salts of paraquat derivatives are predominantly ion paired in acetone (and other low dielectric constant solvents presumably) the complex based on dibenzo-24-crown-8 and paraquat is not ion paired in solution, resulting in concentration dependence of $K_{a,exp}$. However, four complexes of two different bis(*m*-phenylene)-32-crown-10 (BMP32C10) derivatives and

bis(p-phenylene)-34-crown-10 (BPP3C10) with viologens are ion paired in solution, as shown by the fact that $K_{a,exp}$ is not concentration dependent for these systems involving hosts with freer access to bound guests. X-ray crystal structures support these solution-based assessments in that there is clearly ion pairing of the cationic guest and its PF_6^- counterions in the solid states of the latter four examples whereas the former does not. The complexes based on the new dibenzo-24-crown-8/paraquat recognition motif are thus different from the complexes based on two old recognition motifs: the BPP34C10/BMP32C10-paraquat and DB24C8-ammonium motives.

In order to compare these recognition motifs further, the selectivity between two hosts, DB24C8 and BPP34C10, and two guests, dimethyl paraquat and dibenzyl ammnonium salt, was discussed. By individual and competitive complexation studies, it was demonstrated that DB24C8 is a better host than BPP34C10 for paraquat, and that paraquat is a better guest than dibenzyl ammonium salt for DB24C8.

At last the DB24C8-paraquat recognition motif was successfully applied in the preparation the first star-shaped supramolecular polymer based on a tetraparaquat guest and a DB24C8 functionalized polystyrene oligomer. A model system based on this guest and DB24C8 was also studied for comparison. It was found that the complexation in these two systems is cooperative.

Due to the ready availability of DB24C8 and paraquat derivatives, the new recognition motif should prove to be very valuable for self-assembly of other more sophisticated

supramolecular systems. Therefore future work will be preparation of supramolecular systems based on DB24C8 and paraquat derivatives. First, it is desirable to make some rotaxanes based on DB24C8 and paraquat derivatives. We can compare properties of them with those of numerous known rotaxanes based on DB24C8 and secondary ammonium salts. Second, polypseudorotaxanes and polyrotaxanes based on DB24C8 and polymer chains containing paraquat units can be synthesized. These new interlocked macromolecules should have some unique properties that are not observed before in similar reported ones based on big crown ethers. Third, this new recognition motif can be extended to prepare the complexes based on DB24C8 derivatives and bisparaquat derivatives.