

# Self-Assembly: Synthesis and Complexation of Crown Ethers and Cryptands with R<sub>2</sub>-NH<sub>2</sub> Ions

William Stephen Bryant

The focus of the following research was to use the self-assembly process to create rotaxanes between several large bisphenylene crown ethers (> 22 atoms) with secondary ammonium salts. Also of great interest was to understand the complexation behavior of the crown ethers with the salts, with emphasis on determining the stoichiometries and association constants of the complexations in solution using NMR spectroscopy. The stoichiometry of the complexes was determined by the mole ratio method and the association constants were calculated graphically. Bis-(*m*-phenylene)-26-crown-8 did not form a complex in solution with several secondary ammonium salts even though the cavity size is large enough to allow the formation of pseudorotaxanes. However, the larger crown ether, bis-(*m*-phenylene)-32-crown-10 (BMP32C10), did form a complex. The complex stoichiometry varied between 1:1 (crown:salt) in solution and 1:2 in the solid state as evidenced by NMR and X-ray crystallography, respectively. The solid state complexes were pseudorotaxanes. Also, an interesting "exo" complex was formed in the solid state between BMP32C10 and a secondary diammonium salt. The major binding force for the complexes in the X-ray structures was hydrogen bonding. Weaker secondary stabilization was achieved via aryl-aryl aromatic interactions. The difference between the stoichiometries in the two phases and the observance of an "exo" complex demonstrates that one must be careful in describing the complexes in each phase. Also investigated was the complexation formed between dibenzo-24-crown-8 (DB24C8) and secondary diammonium salts. The association constants for the complexes were found to be relatively higher. Due to the weaker association constants and the different stoichiometries of complexation the meta-substituted bisphenylene crown ethers were not recommended for the formation of larger complexes, i.e. polyrotaxanes. However, it is suggested that the DB24C8 moiety be used in components of supramolecular assemblies. The functionalization of poly(propylene imine) dendrimers with two different crown ethers as peripheral moieties was attempted. The 1st, 3rd, and 5th generation poly(propylene imine) dendrimers were functionalized with 1,3-phenylene-16-crown-5 moieties by reacting the surface primary amines with the corresponding succinimide ester of the crown ether. The larger DB24C8 succinimide ester was not as reactive and full functionalization was not achieved.