

## Chapter II

### Thesis Statement

This thesis focuses on the discovery, understanding, and applications of a new recognition motif, the dibenzo-24-crown-8/paraquat recognition motif.

Host-guest chemistry is a topic of great current interest. It is being pursued by scientists from all over the world.<sup>1</sup> In this field two classic host-guest pairs are dibenzo-24-crown-8 (DB24C8) derivatives with secondary ammonium salts, and large crown ethers, such as bis(*m*-phenylene)-32-crown-10 derivatives and bis(*p*-phenylene)-34-crown-10 (BPP34C10) derivatives, with paraquat (N,N'-dialkyl-4,4'-bipyridinium) derivatives.<sup>2</sup> It is well known that for big crown ethers and single ammonium salts, not only are the interactions between them weak but also the stoichiometry is not 1:1.<sup>3</sup> For a long time, people ignored the DB24C8/paraquat recognition motif because they thought that the interactions between them are weak.<sup>4</sup> However, this is only partly true as we will see from this thesis.

First some complexes based on DB24C8 and paraquat derivatives will be discussed. We want to know what determines the interactions between DB24C8 and paraquat

derivatives. These complexes were characterized by proton NMR spectrometry, mass spectrometry, and X-ray analysis.

We have frequently been unable to reproduce the association constants reported for complexes involving ionic species. The association constant, a basic parameter, is a measure of the binding strength between the host and the guest. It is well known that the value of the association constant depends on temperature and polarity of solvent. Recently our group demonstrated that the concentration dependence of a slow-exchange systems, dibenzo-24-crown-8/dibenzyl ammonium salts, in low dielectric constant solvents can be attributed to ion pairing of the salts and the dissociated nature of the complex.<sup>5</sup> Since many host-guest complexes are fast exchange systems,<sup>2</sup> it is important to study ion pairing in such systems. In this thesis for the first time we report a study of concentration dependence of apparent experimental association constants of fast-exchange host-guest systems based on dicationic paraquat derivatives with two monovalent counterions ( $G^{++}2X^-$ ) as guest species and neutral crown ethers as hosts.

In order to compare the new recognition motif, the DB24C8-paraquat pair, with two widely used systems: BPP34C10-paraquat and DB24C8-ammonium,<sup>2</sup> selectivity experiments between two hosts, DB24C8 and BPP34C10, and two guests, dimethyl paraquat and dibenzyl ammonium salt, will be discussed. Obviously this part furthers our understanding of the new DB24C8/paraquat recognition motif.

Finally the application of the DB24C8-paraquat recognition motif in the preparation of the first star-shaped supramolecular polymer based on a tetraparaquat guest and a dibenzo-24-crown-8 functionalized polystyrene oligomer will be discussed.

## REFERENCES

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