

Host-Guest Systems Based on Crown Ether, Cryptand, and Pseudocryptand Hosts with Paraquat, Diquat, Secondary Ammonium, and Monopyridinium Salt Guests

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(ABSTRACT)

Supramolecular host-guest chemistry is a topic of great current interest. However, the further development of host-guest chemistry is still limited by the number of available host-guest recognition motifs. This makes it necessary and valuable to find new host-guest recognition motifs and apply known host-guest recognition motifs in the preparation of novel supramolecular systems.

By comparing the crystal structures of the host and its taco complex, we proved that folding is a necessary step during the formation of taco complexes. Based on the known bis(*m*-phenylene)-32-crown-10/paraquat recognition motif, the first solid-state supramolecular poly(taco complex) was prepared.

We demonstrate not only that bis(*m*-phenylene)-32-crown-10-based cryptands are powerful hosts for paraquat derivatives compared with the simple crown ether, but also that cooperative complexation can be obtained with the cryptand structure. It was shown that the significant improvement in complexation was the result of the combination of the preorganization of the cryptand hosts and the introduction of additional and optimized binding sites. Furthermore, it was demonstrated that improved complexation of bis(secondary ammonium) and bisparaquat salts could also be achieved by the formation of the pseudocryptand structure. We also prepared two dimers of inclusion cryptand/paraquat complexes driven by dipole-dipole and face-to-face π -stacking interactions.

An interesting complex based on dibenzo-24-crown-10 and diquat was prepared. In its crystal structure the diquat guest lies in the concave cavity provided by two dibenzo-24-crown-8 hosts.

Monopyridinium-based [2]- and [3]-pseudorotaxanes were prepared based on the newly discovered bis(*m*-phenylene)-32-crown-10/monopyridinium salt and cryptand/monopyridinium salt recognition motifs.

Inspired by the formation of solid-state taco complexes between bis(*m*-phenylene)-32-crown-10 and paraquat derivatives, we designed and synthesized the first cylindrical bis(crown ether) host for paraquat derivatives and studied its complexation with paraquat.

We prepared three slow-exchange C_3 -symmetric inclusion complexes based on a newly discovered cryptand/trispyridinium recognition motif, in which 1,3,5-trispyridiniumbenzene salts act as guests.

Finally the application of several new and known recognition motifs in the preparation of a supramolecular poly[3]pseudorotaxane, and the first pseudorotaxane-type supramolecular star-shaped polymer, and the first supramolecular hyperbranched polymer was discussed.