

# Supramolecular Assemblies: Dendrimers, Linear Arrays, and Polypseudorotaxanes

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(ABSTRACT)

The chemistry of the non-covalent bond has developed rapidly over the last few decades. In particular, the successful construction of nanoscale assemblies by non-covalent forces has been described more frequently in the recent literature. This significant progress is largely due to transferring of concepts found in the biological systems (*e.g.*, the tobacco mosaic virus and the DNA double helix) to the area of synthetic chemistry. As an example, the architecture of the double helix, perhaps the most well-known biological self-assembling structure, remarkably demonstrates the ability of biological systems to construct large supramolecules by multiple aggregations of relatively simple building blocks by means of hydrogen bonding. Scientists have begun to employ such synthetic strategy adopted in Nature to construct nanoscale systems.

The use of pseudorotaxane assemblies formed between the suitably sized crown ethers and dipyridinium salts (paraquats) or dibenzylammonium ions is a viable synthetic strategy to construct non-covalent systems because of their selectivity and strong hydrogen bonding ability. We describe the syntheses and characterization of non-covalent assemblies of different sizes and shapes *via* the pseudorotaxane approach.

A series of dendritic pseudorotaxanes were efficiently prepared from self-assembling complimentary building blocks, namely a triply charged ammonium ion and the 1st, 2nd, and 3rd generations of benzyl ether dendrons bearing dibenzo-24-crown-8 moiety. The wholly complexed self-assembling dendrimers were evidenced by  $^1\text{H}$  NMR spectroscopy and mass spectrometry.

Linear supramolecular pseudorotaxane polymers were formed with reversible chain extension in solution by self-assembly of two complimentary homoditopic molecules with secondary ammonium ion and dibenzo-24-crown-8 moieties. The fraction of the cyclic dimer and the size of the linear suprastructures were determined in solution by  $^1\text{H}$  NMR spectroscopy as a function of concentration. Viscosity measurements corroborated the presence of aggregates of large hydrodynamic volume at high concentrations. The solid state samples of the supramolecular polymers, prepared by freeze-drying, were analyzed by DSC and optical microscopy and shown to be distinct from the starting materials and the cyclic dimer. Fibers and films were formed from high concentration solutions, corroborating the polymeric nature of the aggregates. Similarly, polymolecular arrays were formed in solution from a heteroditopic self-complimentary molecule, comprising bis-*m*-phenylene-32-crown-10 and a paraquat unit.

Side-chain polypseudorotaxanes were prepared from spontaneous association of polymethacrylates bearing dibenzo-24-crown-8 and secondary ammonium ions. The complexation behavior in solution was investigated using  $^1\text{H}$  NMR spectroscopy. The solid state samples of side-chain polypseudorotaxanes, prepared by freeze-drying, showed noticeable changes in thermal behavior and morphology from the individual components.

