Laboratory of Supramolecular Science

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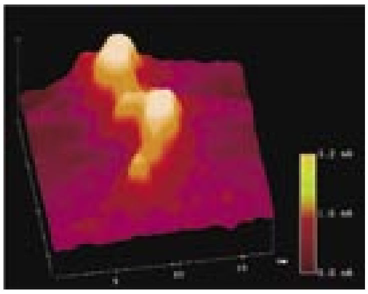
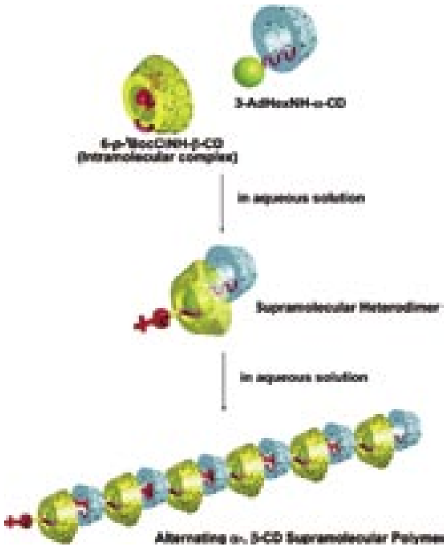
Cyclodextrin-based Supramolecular Polymers

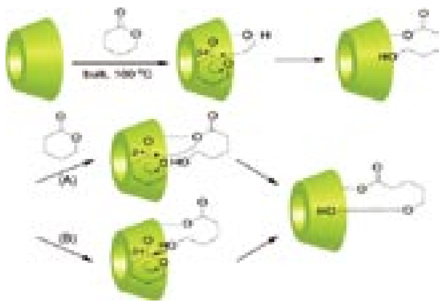


When a guest moiety is attached to a host molecule, the conjugate might form intramolecular complexes or intermolecular complexes to give supramolecular polymers. Although benzoyl β-CD does not form intramolecular complexes or intermolecular complexes, hydrocinnamoyl β-CD does form intramolecular complexes. The more rigid cinnamoyl β-CD forms intermolecular complexes, producing a supramolecular dimer. Cinnamoyl α-CD gives a supramolecular cyclic trimer (cyclic daisy chain). When the guest part is attached to a secondary hydroxyl group, the compound forms supramolecular oligomers. When a *t*-Boc group is attached to the cinnamoyl group, the α-CD derivative forms helical supramolecular polymers. When adamantane carboxylic acid is added to an aqueous solution of aminohydrocynnamoyl β-CD, the guest part is kicked out of the CD cavity. Then, when α-CD is added to this solution, the aminocinnamoyl part is included by α-CD. When the trinitrobenzene (TNB) sulfonic acid sodium salt is added to this solution, a unique [2]rotaxane is obtained, in which both a CD host and a TNB guest serve as stopper groups. In aqueous solution, the [2]rotaxane forms supramolecular alternating copolymers.



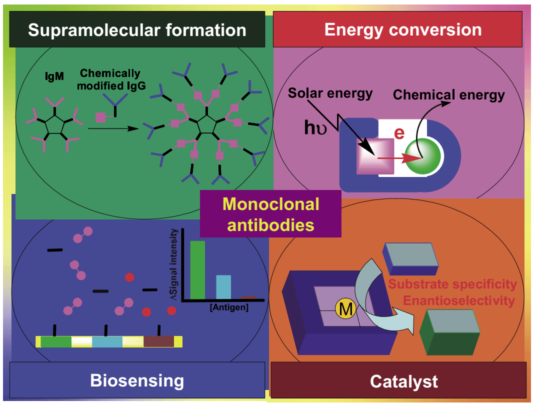
When α-CD having an adamantane group at the secondary hydroxyl group and β-CD with a cinnamoyl group at the primary hydroxyl group are mixed in a 1:1 ratio in an aqueous solution, they form alternating copolymers.

We have found that α-CD forms complexes not only with hydrophilic polymers but also with hydrophobic polymers to give poly-pseudorotaxanes. For example, α-CD gave inclusion complexes with polyesters like poly(ε-caprolactone). We also found that a polyester chain is easily hydrolyzed to its oligomers and monomers in CD cavities in aqueous solutions. Cyclic esters (lactones) were also found to be hydrolyzed in CD in aqueous solutions. Therefore, we thought that if CD and lactones are mixed without water, they might form polymers. Actually, we found that when CD and lactones were mixed without any solvents and heated at 100° C, ring-opening polymerization took place and polyesters were obtained. The products were found to be polyesters with a CD ring at the end of the polymer chain. The polymerization was found to take place by way of the inclusion of lactones in the CD cavity and activation and insertion between CD and a growing chain.



Functionalized Antibodies

Some functionalized materials can be constructed by using monoclonal antibodies. Energy conversion and catalytic systems have been realized by incorporating functional small molecules such as porphyrins or transition metal complexes into the antibody binding pocket. An antibody-rhodium complex catalyzes the hydrogenation of amino acid precursors to give L-amino acids in high (>98%) enantiomeric excess, with substrate specificity. We have utilized monoclonal antibodies as new building blocks to yield a novel supramolecular architecture and as signal amplification materials in a biosensing system.



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