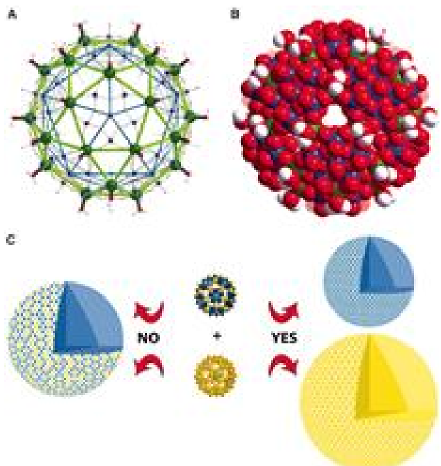
Inorganic molecules achieve self-recognition

April 25 2011, By Tricia Long



Liu's group studied the structures of the two macroion clusters (A and B) and discovered that in mixed dilute aqueous solutions, the clusters (middle of C) self-assemble into distinct blackberry structures (C, right) and do not form mixed species (C, left).

(PhysOrg.com) -- Tianbo Liu, associate professor of chemistry, and his research group have discovered a high-level molecular self-recognition in dilute aqueous solutions, something that was previously considered achievable only by biological molecules.

The group's results were published in the March 25 issue of *Science*, the nation's premier science journal. Liu was lead author on the article, which was titled "Self-Recognition Among Different Polyprotic Macroions During Assembly Processes in Dilute Solution."

"Publication of this work in *Science* is important recognition of the research being conducted in Tianbo's lab," said Robert Flowers, department chair and professor of chemistry. "His ability to succeed at such a high level shows that first-rate science is being done at Lehigh."

Liu's group has spent several years exploring the fascinating solutions of large, soluble ions called macroions. The behavior of these ions is completely different from the behavior of small ions, such as sodium chloride.

Despite being water-soluble and carrying the same type of charge, macroions tend to attract each other with surprising strength, says Liu, and to form very stable, uniform, single-layered hollow spheres known as "blackberry structures." The structures are common when ions become large, and they mimic some biological processes such as the virus capsid shell formation.

Forming two distinct blackberry structures

Exciting discoveries have been generated from blackberry solutions. Liu's group found that, when mixed into the same solution, two different types of 2.5-nm spherical macroions ({Mo72Fe30} and {Mo72Cr30}) with almost identical size, shape and molecular structures tend to form two types of individual blackberries instead of mixed ones.

The macroions—Bucky ball-shaped inorganic compounds—were synthesized by a research team led by Achim Müller, professor of chemistry at the University of Bielefeld, Germany. Müller was a coauthor on the Science article.

This result, says Liu, suggests that even in dilute solutions these two macroions can self-recognize during assembly.

PHYS ORG

This level of "intelligence," he adds, is usually believed to be achievable only by complex biological molecules. Self-recognition by large inorganic ions could lead to more opportunities for understanding the nature of biological interactions.

Liu's group believes the self-recognition results from the very slow formation of the dimers in the first step of the assembly. The slow speed ensures the formation of dimers with the lowest free energy, such as A-A and B-B dimers.

The differences in charge density between the two types of macroions play an important role in the recognition, says Liu, as does their surface water mobility difference.

More information: Self-Recognition Among Different Polyprotic Macroions During Assembly Processes in Dilute Solution, *Science* 25 March 2011: Vol. 331 no. 6024 pp. 1590-1592 DOI: 10.1126/science.1201121

ABSTRACT
We report a self-recognition phenomenon based on an assembly process in a homogeneous dilute aqueous solution of two nano-scaled, spherical polyprotic metal oxide–based macroions (neutral species in crystals), also called Keplerates of the type [(linker)30(pentagon)12]≡[{M(H2O)}30{(Mo)Mo5}12] where M is FeIII or CrIII. Upon deprotonation of the neutral species, the resulting macroions assemble into hollow "blackberry"-type structures through very slow homogeneous dimer-oligomerization processes. Although the geometrical surface structures of the two macroions are practically identical, mixtures of these form homogeneous superstructures, rather than mixed species. The phase separation is based on the difference in macroionic charge densities present during the slow homogeneous dimer or oligomer formation. The surface water ligands' residence times of

CrIII and FeIII differ markedly and lead to very different interfacial water mobilities between the Keplerates.

Provided by Lehigh University