

Precisely Functionalized Molecular Nanoparticles Are Unique Elements for Macromolecular Science: From “Nanoatoms” to Giant Molecules

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We would like to present a unique approach to the design and synthesis of “giant molecules” based on “nano-atoms” for engineering structures across different length and energy scales and controlling their macroscopic properties. The concept of “nano-atoms” refers to shape-persistent molecular nanoparticles (MNPs) with precisely-defined chemical structures and surface functionalities that can serve as elemental parts of building blocks for the precision synthesis of “giant molecules” by methods such as a sequential “click” approach and other efficient organic transformations. Typical “nano-atoms” include those based on polyhedral oligomeric silsesquioxanes, fullerenes, polyoxometalates, and folded globular proteins. The resulting “giant molecules” are precisely-defined macromolecules. They can be represented but are not limited to giant surfactants, giant shape amphiphiles, and giant polyhedra. Giant shape amphiphiles are built up by covalently-bonded molecular segments with distinct shapes where the self-assembly is driven by the shape of the molecular segment as well as the chemical interaction. Giant polyhedra are either made of a large MNP or by deliberately placing “nano-atoms” at the vertices of a polyhedron. Giant surfactants are composed of “nano-atoms” tethered with flexible polymer tails of various compositions and architectures at specific sites that have drastic chemical differences such as amphiphilicity. Giant molecules capture the essential structural features of their small-molecule counterparts in many ways but possess much larger sizes; therefore, they are recognized in some cases as size-amplified versions of those counterparts and often, they bridge the gap between small-molecules and traditional macromolecules. Highly diverse, sometime completely unexpected, thermodynamically stable and metastable hierarchal structures can be observed in the bulk, thin-film, and solution of these giant molecules. Controlled structural variations by precision synthesis further reveal a remarkable sensitivity of their self-assembled structures to the primary chemical structures. In confined environments or through directed self-assembly unconventional nanostructures can also be obtained. All the results demonstrate that MNPs are unique elements for macromolecular science, providing a versatile platform for engineering nanostructures that are not only scientifically intriguing, but also technologically relevant.