

Some Assembly Required

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Self-assembly—the spontaneous organization of matter into ordered arrangements—is a governing principle by which materials form (1). The patterns arising from self-assembly are ubiquitous in nature, from the opalescent inner surface of the abalone shell to the internal compartments of a living cell. Much of materials science and soft condensed-matter physics in the past century involved the study of self-assembly of fundamental building blocks (typically atoms, molecules, macromolecules, and colloidal particles) into bulk thermodynamic phases. Today, the extent to which these building blocks can be engineered has undergone a quantum leap. We are on the verge of a materials revolution in which entirely new classes of “supermolecules” and particles will be designed and fabricated with desired features, including programmable instructions for assembly. These new building blocks will be the “atoms” and “molecules” of tomorrow’s materials, self-assembling into novel structures made possible solely by their unique design.

What happens when traditional atoms and molecules are replaced with these new building blocks? What types of ordered structures are possible, and what unique properties do they have?

Colloidal polyhedra (2), nanocrystals in the form of tetrapods (3) and triangles (4), and tiny cubes of molecular silica (5) are just a few examples of new building blocks being made today. In most cases, these building blocks may not naturally assemble into any desired structures. One emerging approach to confer upon nanoparticles and colloids predetermined “instructions” for assembly is to decorate the surface of the particles with “sticky patches,” made, for example, of synthetic organic or biological molecules. This strategy takes its inspiration in part from biology, where the precision of self-assembled structures such as viruses and organelles originates in the selectivity of the interactions between their constituents. According to computer simulations, synthetic “patchy par-

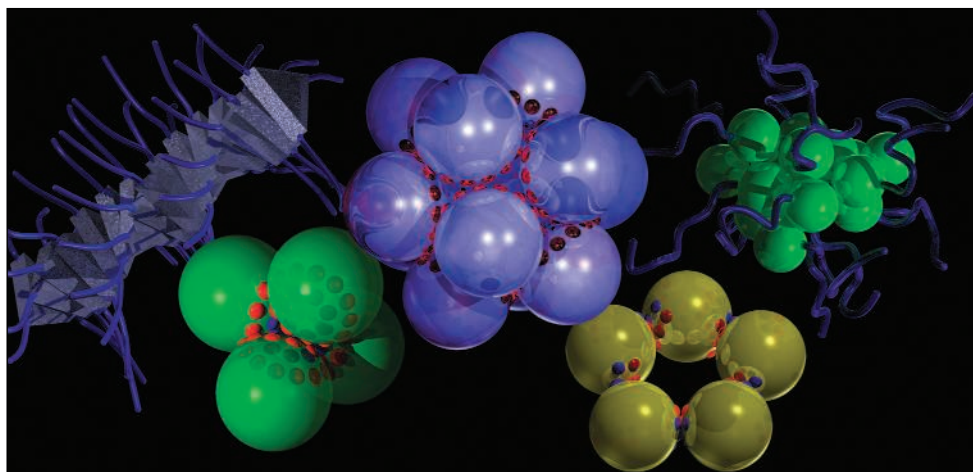
ticles” should self-assemble under the right conditions into structures atypical of traditional materials (6) (see the figure).

On macroscopic scales, millimeter-sized plastic wedges patterned with patches of solder and hydrophobic lubricant self-assemble under surface tension when dispersed in water to form tiny electronic devices whose structure resembles that of the tobacco mosaic virus (7). Making patchy particles with precise patterns of interactions on nanometer scales is much more challenging, but exciting developments are being reported. For example, Stellacci and co-workers (8) recently synthesized gold and silver particles 4 nm in diameter, using organic molecules to control the size of the nanoparticles. Although the use of organic stabilizing layers is commonplace in nanoparticle synthesis, these researchers used a mixture of ligands that, on flat surfaces, would tend to phase separate into bulk phases or random domains. Instead, the ligands self-organized on the nanoparticle surface into repeating patterns of stripes and dots with spacings as small as 0.5 nm, imparting a controllable, precise, and unprecedentedly small pattern of attractive and repulsive patches to the surfaces of the particles. Striped spheres and

spheres with polar patches were obtained, providing a striking demonstration of the role of curvature in pattern formation (9). This method suggests an exciting strategy for controlling the symmetry of nanoparticle assemblies through anisotropic interactions achieved by patterning. In another example, Mokari *et al.* recently patterned semiconductor tetrapods and nanorods with gold patches on the tips (10), potentially providing a new way to assemble components for nanocomputing devices.

Genetic engineering of biomolecules like DNA and proteins opens up further possibilities for conferring recognition (11) and chemical specificity to particles, creating building blocks that are potentially capable of assembling into hierarchically arranged structures. In a recent twist, a new patchy particle was synthesized by precisely positioning gold particles onto specific sites on the surface of the cowpea mosaic virus, creating a new type of building block with the potential for self-assembly (12).

Patchy particles are but one example of “shape amphiphiles”—building blocks of potentially complex shapes with competing interactions that expand the range of self-assembled structures beyond those exhibited by traditional amphiphiles such as surfactants and block copolymers. By attaching polymeric “tethers” to nanoparticles, another new class of shape amphiphile may be fabricated (13). These building blocks can



Predicted self-assembled structures for model building blocks. When selective interactions are introduced to particle surfaces through patterning of ligands or polymeric tethers, competing interactions can cause the particles to self-organize into complex structures (6, 13). (Left) Twisted wire of tethered triangular nanoparticles; (middle) tetrahedron, icosahedron, and ring self-assembled from spherical patchy particles; (right) micelle of tethered nanospheres. To fabricate rings from patchy particles, selective sticky patches are placed anisotropically on the equatorial plane at a relative angle of $< 180^\circ$. The diameter of the rings is controlled by the angle between the patches. Tetrahedra and icosahedra form from particles with selective, ringlike patches shifted off the equatorial plane.

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