Three-dimensional self-assembly of millimetre-scale components

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The spontaneous association of molecules, termed molecular self-assembly, is a successful strategy for the generation of large, structured molecular aggregates. The most important source of inspiration for this strategy is the biological world, in which many processes involve interfacial interactions and shape selectivity that guide the formation of complex, multicomponent three-dimensional structures. The success of molecular self-assembly notwithstanding, many objectives in science and technology require the assembly of components that are much larger than molecules: examples include microelectronic and microelectromechanical systems, sensors and microanalytical and microsynthetic devices. Photolithography, the principal technique used to make such microstructures, has certain limitations: it cannot easily form non-planar or three-dimensional structures; it generates structures that are metastable; and it can be used only for a limited set of materials. Here we describe an approach for the self-assembly of millimetre-scale components that uses two concepts to direct the assembly process: shape recognition and the minimization of liquid–liquid interfacial free energies. These play a role in other spontaneous self-assembly phenomena, such as the formation of bubble rafts, the patterned dewetting of surfaces, and the coalescence of liquid drops. We apply self-assembled monolayer molecular films to the surfaces of shaped macroscopic objects to render them hydrophilic or hydrophobic, depending on the terminal groups of the bound molecules. In aqueous solution, hydrophobic surfaces bearing a thin film of a
hydrophobic, lubricating liquid adhere to similar surfaces with complementary shapes, while being able to adjust their relative alignment to ensure a good fit. In this way, the components assemble into well defined aggregates, which can be bound permanently when the hydrophobic liquid films consist of a polymerizable adhesive.

Figure 1 outlines our process. The individual components to be assembled were formed from a hydrophobic polymer (typically a polyurethane: NOA-63 or NOA-88; Norland, New Brunswick, NJ) by moulding. The surface of these components was patterned into hydrophilic and hydrophobic regions using two procedures. In one, some portions of the surface were covered (often by leaving the units in the moulds in which they were made), and the exposed surfaces were oxidized with an oxygen plasma. This process left the hidden hydrophobic surfaces. The aqueous suspension of the components into contact. The hydrophilic surfaces stuck neither to other hydrophilic surfaces nor to the hydrophobic surfaces with their thin coating of liquid, whereas the hydrophobic surfaces adhered to one another. Once the surfaces were in contact, the liquid acted as a lubricant, allowing the components to adjust their position relative to one another by lateral movement. This movement minimized the interfacial free energy of the system by minimizing the surface area of the systems. The contacting surfaces smooth; if they were rough, the lateral motion required to reach the configuration with the maximum contacting surface was hindered by direct, unlubricated contact and adhesion of the surfaces. To generate suitably smooth surfaces, the faces of the aluminium master were polished to a mirror finish; we did not measure the surface roughness.

The assemblies in Fig. 2a-c are symmetrical. It was also possible to generate unsymmetrical assemblies by taking advantage of docking of unsymmetrical components using shape-selective recognition; Fig. 2d is a demonstration of the principle. The assembly of complementary shapes is integral to the formation of most
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complex biological systems. Our demonstration indicates that the same strategy can be applied to non-biological assemblies.

This work establishes that shape-selective recognition of surfaces and minimization of interfacial free energies can be combined to provide a strategy for assembling small components into three-dimensional assemblies. Because association is reversible, the system is self-repairing: the experiments described here usually result in quantitative formation of correctly assembled objects. We believe that we will be able to assemble smaller structures using the same or a similar methodology, and that we will be able to build functional devices.

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Figure 2 Several examples of self-assembled structures. Scale bars, 1 cm. a. Two arches were assembled at the left to form small 'doughnuts'. The differentiation was achieved for this case by etching of the outer sides of the two adhering surfaces were made hydrophobic with a hydrophobic self-assembling monolayer (Fig. 1a). Semi-roughened with the outer sides were plasma-oxidized polymer. The latter was used to the exchanger surface processing). b. Two parts were assembled at the left to form another doughnut. The adhering surfaces were made hydrophobic by treatment with an oxygen plasma (see Fig. 1 for details of surface processing). Complex biological systems. Our demonstration indicates that the same strategy can be applied to non-biological assemblies.