# Three-dimensional self-assembly of millimetre-scale components

Andreas Terfort, Ned Bowden
& George M. Whitesides

Department of Chemistry and Chemical Biology, Harvard University,
12 Oxford Street, Cambridge, Massachusetts 02138, USA

The spontaneous association of molecules, termed molecular self-assembly, is a successful strategy for the generation of large, structured molecular aggregates[1]. 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 microelectro-mechanical systems, sensors and microanalytical and micro-synthetic devices[2]. 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[3]. 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[4]. These play a role in other spontaneous self-assembly phenomena, such as the formation of bubble rafts[5,6], the patterned dewetting of surfaces[7,8], and the coalescence of liquid drops[9]. We apply self-assembled monolayer molecular films[10] 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
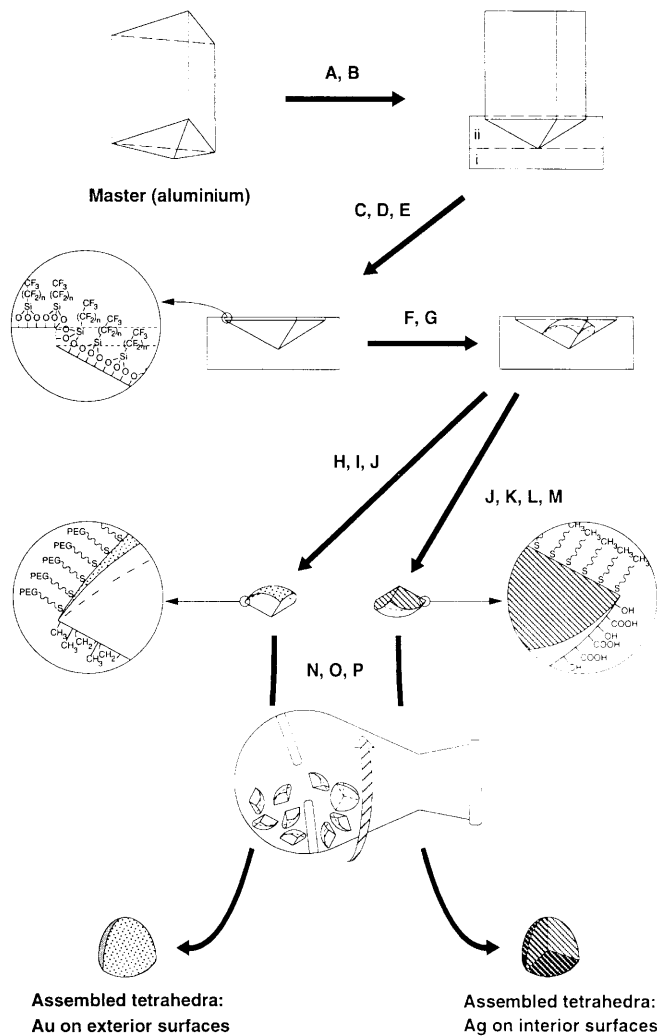
Figure 1 Schematic outline of the process used to fabricate and assemble components of the tetrahedra. The master (top left) was fabricated from aluminium by machining; the angles defining the edges at the tip were 109°. Process steps are as follows: (A) A pad of polydimethylsiloxane (PDMS, i) was cast and cured. (B) The master was cast into a second layer (ii) of PDMS. (C) After curing, the master was removed. (D) This PDMS mould was oxidized in an oxygen plasma to generate surface Si-OH groups. (E) Exposure to perfluoroalkyl tri-chlorosilane vapour resulted in the formation of a perfluoroalkylated surface (see inset). (F) A measured amount of the liquid polyurethane prepolymer was added by means of a syringe pump and (G) was cured in ultraviolet light. (H) Gold was evaporated on top of the parts while they remained in the mould. (I) A hydrophilic self-assembling monolayer was formed on the gold surface by immersion in a solution of a thiol terminating in a ... (PEG) groups (the PEG used was methoxy-terminated ... weight 350); this thiolate is hydrophilic and resists ... The parts were removed from the mould. (K) S ... the parts. (L) The parts were oxidized in ... plasma ... self-assembling monolayer was generated ... the parts in a solution of $CH_3(CH_2)_{15}SH$. (N) A number of parts (ca. 20–100) were placed in the assembly flask and the liquid adhesive and ethanol were added and distributed. (O) Water was added until the flask was completely filled, and the mixture was rotated mechanically for several hours; the tetrahedra assembled themselves. (P) If the glue was photocurable, the parts 'froze' into place on ultraviolet irradiation. They were then removed and examined.

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 in 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 surfaces hydrophobic, while making the exposed surfaces hydrophilic. In a second, differentiation was achieved by coating the regions with gold or silver by evaporation, and assembling mono-layers of hydrophobic or hydrophilic[10] thiols onto them. The components were placed in a flask, their surface was wetted with ethanol, a small amount (0.05–0.1 μl per mm^2 of hydrophobic surface) of a hydrophobic liquid—either an alkane or a photo-polymerizable adhesive, such as dodecyl methacrylate—was added, and the system was stirred gently to coat the surfaces. Water was added; the water displaced the hydrophobic liquid from the hydro-philic surfaces, while leaving a thin film of liquid coating the hydrophobic surfaces. The aqueous suspension of the components was tumbled in a rotating flask. This agitation brought the compo-

nents 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 lubricant–water interface. After the systems had approached equilibrium, ultraviolet irradiation (when the liquid was a photo-polymerizable adhesive) 'froze' the assembly into permanent form. These components were removed and examined.

Figure 2 shows small assemblies fabricated using this procedure. The most complicated of the structures formed was approximately a sphere: four pieces with hydrophobic faces defined by planes meeting at the tetrahedral angle (109°) were the components that assembled. A key component to these assemblies was to make 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 dock-ing of unsymmetrical components using shape-selective recog-nition; Fig. 2d is a demonstration of the principle. The assembly of complementary shapes is integral to the formation of most
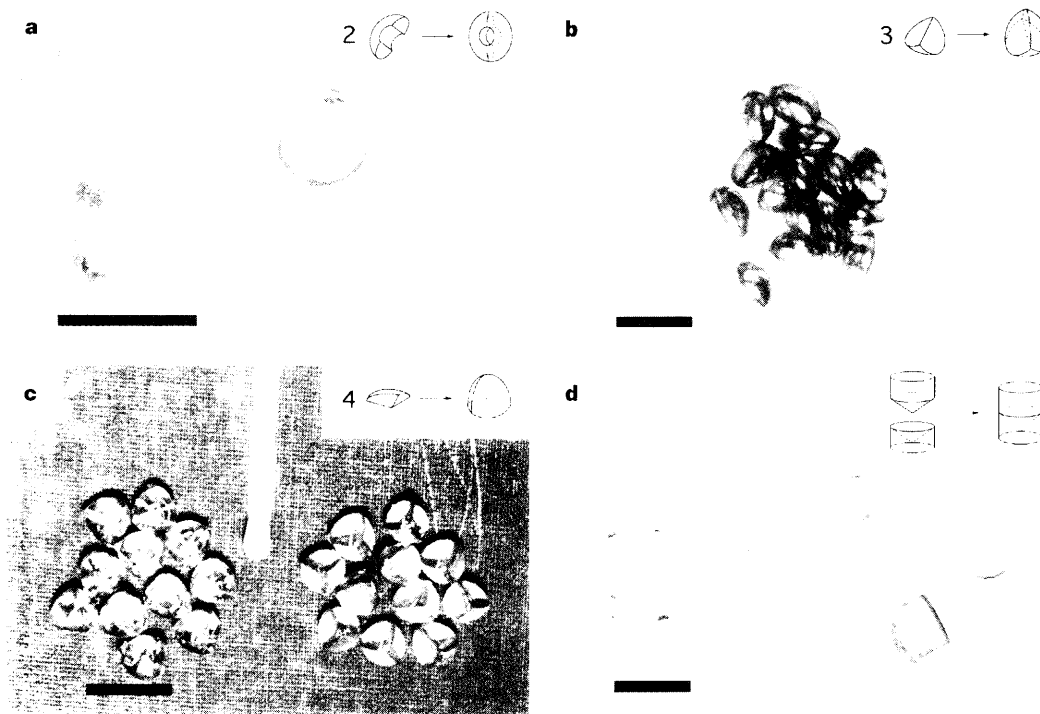
Figure 2 Several examples of self-assembled structures. Scale bars, 1 cm. **a**, Two arches (one of them at the left) form small 'doughnuts'. The differentiation was achieved in this case by oxidation of the outer sides, while the adhering surfaces were unmodified photocurable polymer NOA-63. **b**, Small 'doughnuts' from three identical parts. The adhering sides were unmodified polymer NOA-63 and the curved outer surface has a 20-nm thick layer of gold, and underneath a 3-nm layer of titanium. The adhering surfaces were covered with a self-assembling monolayer of a hydrophobic adhesive derived starting from triethylene glycol-terminated thiol. **c**, Tetrahedron-like structures formed by self-assembly of four identical parts. The surface treatment for the objects on the left was as in **b** (gold on the exterior faces, see also Fig. 1). On the right, the adhesive, interior sides of the tetrahedra were covered with a hydrophobic self-assembling monolayer $CH_3(CH_2)_{15}SH$, and on the outer sides were plasma-oxidized polymer. This resulting structure is held together not by adhesion of the interior surfaces. **d**, Two polygon prisms assembled in a head-to-tail manner. The adhering surfaces were unmodified polymer, and the outer sides were made hydrophilic 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.

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. □

1. Philp, D. & Stoddart, J. F. *Angew. Chem. Int. Edn Engl.* **35**, 1155–1196 (1996).
2. Harrison, D. J., Fluri, K., Chiem, N., Tang, T. & Fan, Z. in *Sensors and Actuators B Chemical* Vol. B33 (eds Middelhoek, S. & Cammann, K.) 105–109 (Elsevier, Amsterdam, 1996).
3. Moreau, W. M. *Semiconductor Lithography: Principles, Practices, and Materials* (Plenum, New York, 1988).
4. Kim, E. & Whitesides, G. M. *Chem. Mater.* **7**, 1257–1264 (1995).
5. Simpson, A. W. & Hodkinson, P. H. *Nature* **237**, 320–322 (1972).
6. Schober, S. T., Friederich, J. & Altmann, A. *J. Appl. Phys.* **71**, 2206–2210 (1992).
7. Gorman, C. B., Biebuyck, H. A. & Whitesides, G. M. *Chem. Mater.* **7**, 252–254 (1995).
8. Biebuyck, H. A. & Whitesides, G. M. *Langmuir* **10**, 2790–2793 (1994).
9. Blass, E. *Chem. Ing.-Tech.* **60**, 935–947 (1988).
10. Pale-Grosdemange, C., Simon, E. S., Prime, K. L. & Whitesides, G. M. *J. Am. Chem. Soc.* **113**, 12–20 (1991).