Three-Dimensional Self-Assembly of Complex, Millimeter-Scale Structures through Capillary Bonding

Scott R. J. Oliver, Thomas D. Clark, Ned Bowden, and George M. Whitesides*

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

In this communication we describe the organization of millimeter-sized subunits into complex, three-dimensional (3-D) arrays using mesoscale self-assembly (MESA)—self-assembly of components with lateral dimensions comparable to the distance over which the attractive forces operate.[1,2] Previous reports have demonstrated the self-assembly of small objects into ordered arrays displaying simple translational symmetry in two or three dimensions; examples include mesoscale assemblies[1−3] and crystalline aggregates of spherical[4] or non-spherical[5] colloids. For possible application in the fabrication of functional constructs such as densely interconnected 3-D electronic[2b] or optical devices, we wished to extend the range of structures accessible through MESA. Here, we apply concepts derived from the study of molecules[6]—including shape and surface complementarity,[1] helicity, and enantioselective recognition[1,3]—to the self-assembly of mesoscale structures that display symmetries more complex than those resulting from simple extended 2- and 3-D crystalline arrays.

In the present study, as in our previous investigations of MESA, the force responsible for aggregation is capillarity, that is, the minimization of interfacial free energy.[1,2] Capillary interactions may be considered roughly analogous to chemical bonds; this analogy, though convenient, has limitations—we note that obvious differences exist between these two classes of bonds.[6] Here, capillary bonding occurs between films of a liquid metal—a low-melting (47 °C) bismuth alloy[7]—patterned on the surface of mm-sized polyhedral subunits (pieces).[2] When heated above its melting point, the alloy forms capillary bonds that are strong enough to support open lattice structures and, when cooled below its melting point, locks the structures in place.[2,8,9] In addition, the resulting metal−metal contacts can serve as a starting point for the design of systems that form electrical connections through self-assembly.[2b]

(1) (a) Wu, H.; Bowden, N.; Whitesides, G. M. *Appl. Phys. Lett.* **1999**, *75*, 3222−3224. (b) Bowden, N. B.; Weck, M.; Choi, I. S.; Whitesides, G. M. *Acc. Chem. Res.* **2001**, *34*, 231−238.

(2) (a) Breen, T. L.; Tien, J.; Oliver, S. R. J.; Hadzic, T.; Whitesides, G. M. *Science* **1999**, *284*, 948−951. (b) Gracias, D. H.; Tien, J.; Breen, T. L.; Hsu, C.; Whitesides, G. M. *Science* **2000**, *289*, 1170−1172.

(3) Rothemund, P. W. K. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 984−989.

(4) Recent reviews: (a) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693−713. (b) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545−610.

(5) Selected examples: (a) Wang, Z. L.; Harfenist, S. A.; Vezmar, I.; Whetten, R. L.; Bentley, J.; Evans, N. D.; Alexander, K. B. *Adv. Mater.* **1998**, *10*, 808−812. (b) Mann, S.; Davis, S. A.; Hall, S. R.; Li, M.; Rhodes, K. H.; Shenton, W.; Vaucher, S.; Zhang, B. *J. Chem. Soc. Dalton Trans.* **2000**, 3753−3763.

(6) For a discussion of the analogies between MESA and molecular self-assembly, see ref 1b.

(7) The composition of the alloy (Small Parts, Inc.) is as follows (wt %): 44.7% Bi; 22.6% Pb; 8.3% Sn; 5.3% Cd; 19.1% In. (a) Smith, W. C. *Min. Metall.* **1945**, *26*, 561−562. (b) Maribo, D.; Sondergaard, N. A. *IEEE Trans. Compon. Hybrids Manuf. Technol.* **1987**, *10*, 452−455.

(8) This strategy is reminiscent of self-alignment of electonic components during flip chip bonding: Lau, J. H. *Flip Chip Technologies*; McGraw Hill: New York, 1996.

(9) For studies of rotational self-assembly using the surface tension of molten solids, see: Syms, R. R. A.; Gormley, C.; Blackstone, S. *Sens. Actuators, A* **2001**, *88*, 273−283 and references therein.
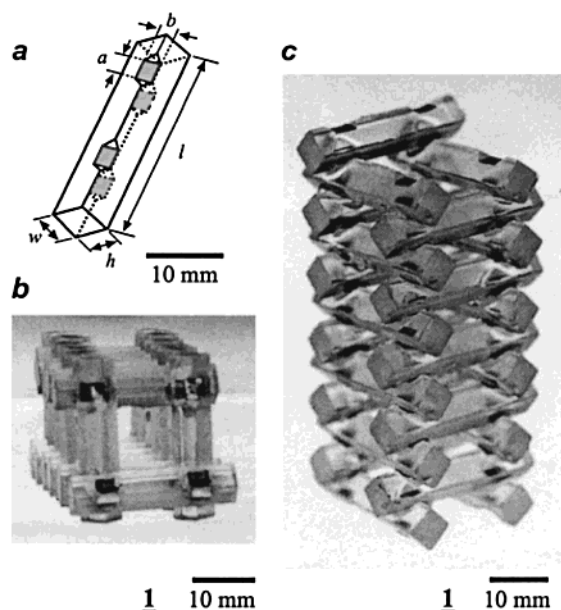

Figure 1. (a) Schematic diagram of polyurethane notched square rods, where $l = 25$ mm, $w = h = 4.8$ mm, $a = 3.0$ mm, and $b = 2.5$ mm. Clear regions represent uncoated polymer, while shaded regions correspond to areas coated by copper tape and alloy. Notches in the rods forced the pieces to connect at right angles; the final product was open-square array **1**. (b) End view of **1**. (c) Oblique view of **1**.

We fabricated the polyurethane pieces using a replica molding procedure, patterned them with adhesive-backed copper tape, and selectively coated their exposed copper surfaces by dipping the pieces into molten alloy.[2,10] For the self-assembly experiments, we placed the pieces in an indented 500-mL round-bottomed flask, filled the flask with an approximately isodense KBr solution, and rotated it at 10−20 rpm while heating in a 60 °C water bath.[2,10] The alloy melted within a few minutes, and collisions between regions bearing molten alloy enabled the pieces to assemble. Upon completion, we stopped the agitation and allowed the solution to cool to room temperature, causing the alloy to solidify and furnishing aggregates sturdy enough to be removed and examined.

In the first system studied, we used shape complementarity between indented regions on square rods to direct the formation of an open-square array (Figure 1). The four indentations bearing alloy-coated copper tape forced adjacent rods to lie at right angles with respect to one another (Figure 1a). A well-ordered, defect-free "Lincoln log" aggregate **1**, defining an approximately orthorhombic open space, formed after ∼1 h of agitation (Figure 1b,c). Malformed aggregates—for example, three pieces defining an L-shape or a section with one or more missing piece—broke apart and reformed without defects under the agitation conditions used. We reproduced array **1** in each of four separate repetitions of the experiment and therefore believe it to be the most stable structure in this system. This stability is reasonable since **1** maximizes the number of capillary bonds and thus minimizes the interfacial free energy of the system. In addition, **1** is the most compact structure possible and should therefore be less susceptible than other aggregates to the mechanical shearing caused by rotary agitation.

Next, we designed a system to mimic the ubiquitous helical conformations of linear polymers (Figure 2).[11] Figure 2a depicts rectangular slabs designed to form helices. Self-assembly gener-

(10) See Supporting Information for details.

(11) Kirshenbaum, K.; Zuckermann, R. N.; Dill, K. A. *Curr. Opin. Struct. Biol.* **1999**, *9*, 530−535.
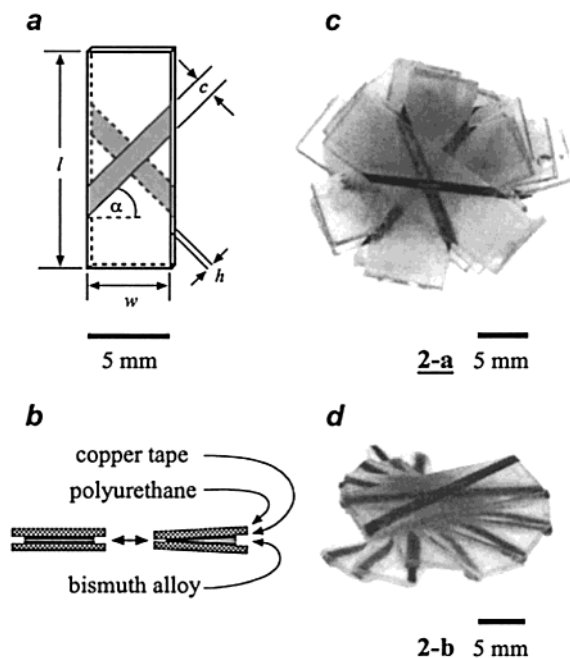
Figure 2. (a) Schematic diagram of rectangular slabs with a single strip of alloy-coated copper tape at angle α on both sides ($l = 15$ mm, $w = 5$ mm, $h = 1$ mm, $c = 1$ mm). Self-assembly generated helical arrays in which neighboring pieces meet at angle β. (b) Beading of alloy at one side of the contact area between adjacent components gave rise to bending along the vertical axis of the helices. (c) Helical structure **2-a**; $\alpha = 60°$, $\beta = 60°$. (d) Helical structure **2-b**; $\alpha = 75°$, $\beta = 30°$.

Figure 3. Chirally patterned square rods ($a = 2.0$ mm, $b = 8.5$ mm, $c = 2.0$ mm, $l = 25$ mm, $w = h = 4.8$ mm, $\alpha_1 = 45°$, and $\alpha_2 = 135°$) gave rise to an open assembly **3** containing channels. (a) Oblique view of **3**. (b) End view of **3**.

ated helical arrays **2-a** (Figure 2c) and **2-b** (Figure 2d), displaying the expected screw axis symmetry. The angles of intersection between adjacent slabs (helical twists) for structures **2-a** and **2-b** are approximately 60° and 30°, respectively. Although well-ordered, the helices were somewhat bent due to beading of the alloy at the points of contact between slabs (Figure 2b).

In the final system examined, we chose to mimic a process of fundamental importance to molecular recognition and self-assembly—discrimination between enantiomeric species.[12] The system consists of chirally striped square rods designed to assemble into open lattices (Figure 3). We divided the pieces into two enantiomeric groups by placing copper stripes on the sides of the pieces at an angle, using a different angle (90 ± 45°) for each group (Figure 3).[10] If all four sides of the pieces in each group were patterned with stripes, a close-packed array would form. We chose a more interesting illustration of the principle by patterning one group on all four sides and the other group on two opposite sides. Rods patterned on four sides therefore connect only to rods of the opposite chirality patterned on two sides. Upon self-assembly, the pieces arranged themselves in a strictly alternating manner to define an open array **3** (Figure 3a,b). This geometry was reproducible, but the aggregate size was limited to approximately 25 pieces, likely due to increased susceptibility of larger aggregates to shearing forces during agitation.

We believe that the success of the methods described here for generating well-ordered, topographically complex aggregates

renders MESA a promising strategy for fabricating three-dimensional structures. In addition, this work provides further support for the notion that concepts abstracted from the molecular sciences can find fruitful application in building structures at larger-size scales.[1b] Although the aggregates presented here are large enough to be fabricated using conventional methods such as manual or robotic assembly, miniaturization of the components could lead to structures that would be difficult to prepare using any other method and, ultimately, to assemblies displaying a range of interesting functions. In other work, we have already demonstrated the formation of regular arrays of 10-μm-sized polyhedral plates[13] and the formation of electrical connections in three dimensions between mm-sized subunits,[2b] using MESA. We are currently developing methods for fabricating more complex micrometer- and submicrometer-scale components that should give rise to small, complex, three-dimensional structures similar to those described in the present study.

Supporting Information Available: Details of the design, fabrication, and self-assembly of the pieces used here (PDF). This material is available free of charge at http://pubs.acs.org.

JA010845Q

(12) Selected references: (a) Mason, S. F. *Chirality* **1989**, *1*, 183−91. (b) Testa, B. *Acta Pharm. Nord.* **1990**, *2*, 137−44. (c) Kuroda, R. *Enantiomer* **2000**, *5*, 439−450.
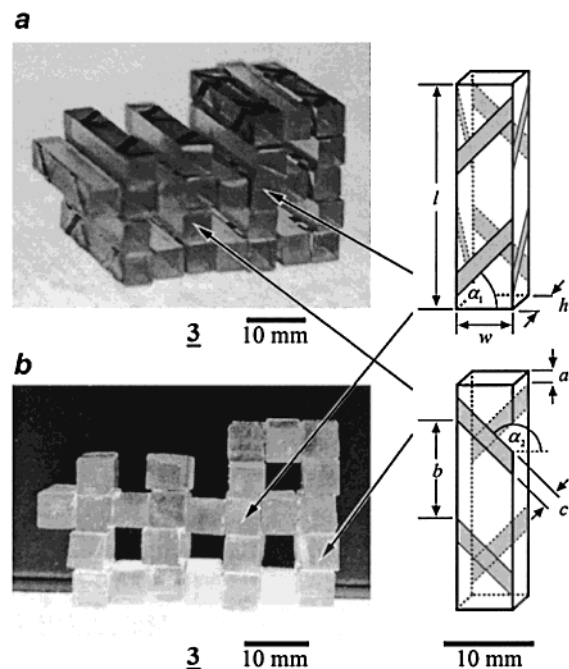
(13) Clark, T. D.; Tien, J.; Duffy, D. C.; Paul, K. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **2001**. In press.