

Selectivities among capillary bonds in mesoscale self-assembly

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This letter describes the capillarity-driven self-assembly of mm-sized plates of poly(dimethylsiloxane) at the perfluorodecalin/H₂O interface into complex arrays. The shape of the interacting menisci could be tailored by three strategies: (1) changing the shape of uniformly hydrophobic edges; (2) patterning the distribution of vertical hydrophobic strips on the edges and, in some cases, varying the density of the blocks; and (3) patterning the hydrophobic areas on a face to be chiral. © 1999 American Institute of Physics. [S0003-6951(99)02144-0]

The interaction between menisci at the faces of mm-scale objects floating at the perfluorodecalin (PFD)/H₂O interface results in forces between these particles that can be either attractive or repulsive, depending on the contours of these menisci.¹⁻⁸ These forces move the objects in directions that minimize the interfacial free energy of the system (a quantity determined primarily by the area of the PFD/H₂O interface, but containing gravitational terms).^{4,7,9,10} The menisci can be characterized by their height relative to the mean plane of the interface—positive menisci rising above this plane, and negative menisci sinking below it—and the sense of the interaction between menisci defined by the rule “like menisci attract; unlike menisci repel.”² Thus, for example, two positive menisci move toward one another, and a positive and negative meniscus move apart. We have suggested that the attractive interaction between two objects with “like menisci” can be considered as a type of bond—which we call a “capillary bond.”²

We have demonstrated that capillary bonds can be sufficiently strong to hold mm-scale objects together against substantial agitation of the supporting fluid phases.^{1,2,8,11-14} This letter demonstrates selectivity among different types of capillary bonds—that is, preferential interactions between specific shapes of positive menisci.^{1,2,8,12} Faces interact strongly when the contours of the menisci match; they interact weakly when the contours do not match. We hypothesized that it would be possible to use these selective capillary bonds to develop a methodology for the “synthesis” of aggregates of mm-scale particles, akin to the methodology that uses selectivity in noncovalent bonds between molecules for the self-assembly of ordered arrays of molecules.^{3,15-25} This letter describes several designs of hydrophobic faces that show high selectivity in their interaction with other faces in experiments involving the self-assembly of mm-scale plates floating at the PFD/H₂O interface. These demonstrations establish that it is possible to design capillary bonds that are selective, and to use this selective bonding to build complex aggregates using self-assembly.

We tested three strategies to control the shape of the menisci (Fig. 1). One changed the shape of uniformly hydrophobic faces; the second patterned the distribution of vertical

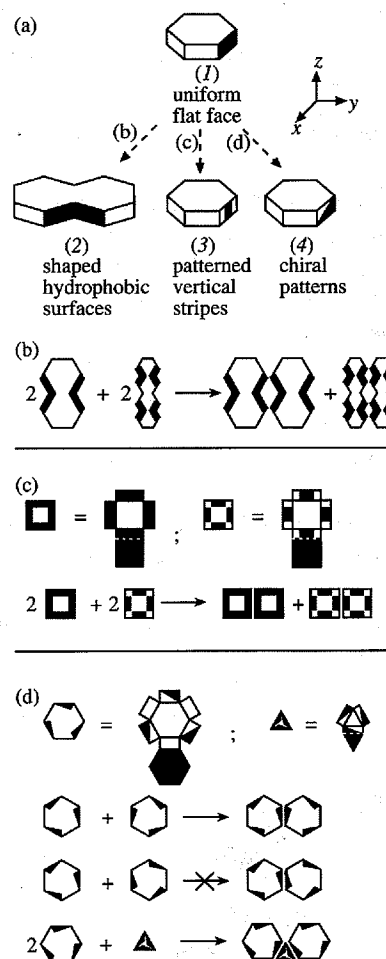


FIG. 1. Schematic illustration of interactions between objects tailored to show selectivity in bonding through capillary forces. All the objects floated at the PFD/H₂O interface. (a) The patterning of the hydrophobic area of the three different types of capillary bonds that were used in this study: shaped hydrophobic surfaces, patterned vertical hydrophobic stripes, and chiral hydrophobic patterns. (b) Each object had the same hydrophobic area on its face, but these hydrophobic areas differed in their shapes and distributions. The dark lines indicate hydrophobic faces; the thin lines indicate hydrophilic faces. (c) Changes in the fraction and distribution of hydrophobic area on the faces of different objects changed the contours of the menisci, the strength of the capillary bond, and the stability of the assembly toward disruption by shear. We show an unfolded pattern for squares with full and half hydrophobic faces. (d) Chiral hydrophobic patterns on different objects dictate selective assembly; only menisci on faces of opposite chirality have contours that match. We show an unfolded pattern for the hexagon and triangle with triangular hydrophobic patches on the faces.

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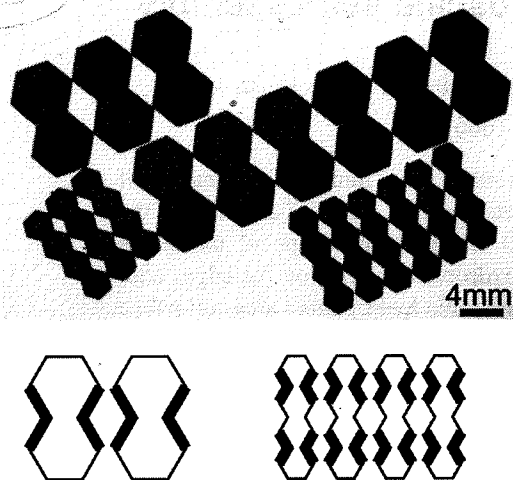


FIG. 2. Assembly of two sizes of objects of type 2 with different shapes and distribution of hydrophobic faces forms linear homoarrays. These linear arrays associate weakly by interactions between small negative menisci at the hydrophilic edges; during agitation, the arrays are separated.

hydrophobic strips on a face; the third made the hydrophobic patterns chiral. Each of these patterns generated menisci with characteristic shapes; faces with menisci with contours that matched most closely interacted most strongly.

The plates were fabricated as described previously.² [1,3] hexagons were glued together to form the extended structures having the patterns of hydrophobic faces shown in Fig. 2. The face of the small hexagonal plates in these structures is half of the length of the large ones. The hydrophobic patches on the faces were patterned by painting with a "SHARPIE" marker; or by covering the face with ScotchTM tape. The hexagons were oxidized in a plasma cleaner (Harriick PDC-23G) and the exposed poly(dimethylsiloxane) (PDMS) became hydrophilic. The paint and tape were removed. The PDMS that was covered with paint or tape remained hydrophobic; all other surfaces were rendered hydrophilic by the oxidation. The objects were placed with the

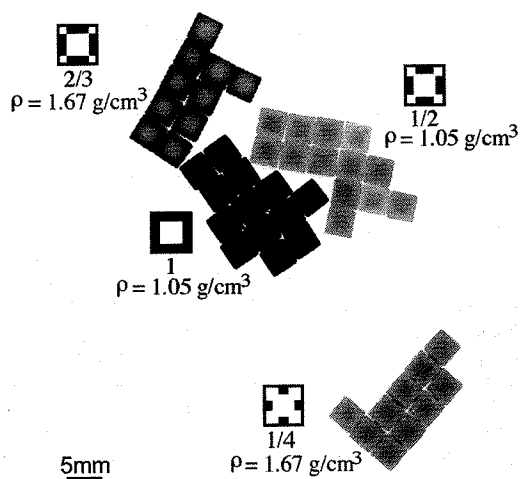


FIG. 3. Four separate close-packed arrays formed by assembly of four kinds of [1,2,3,4] square plates with different amounts of hydrophobic area on the faces and two different densities. The fractions beneath the squares indicate the amount of the area on each face that is hydrophobic. We increased the density of PDMS ($\rho = 1.05 \text{ g/cm}^3$) by mixing Al_2O_3 into it (a 1:1 mass ratio increases the density of the mixture to 1.67 g/cm^3). The densities of the fluid phases are: $\rho(\text{PFD}) = 1.91 \text{ g/cm}^3$; $\rho(\text{H}_2\text{O}) = 1.00 \text{ g/cm}^3$.

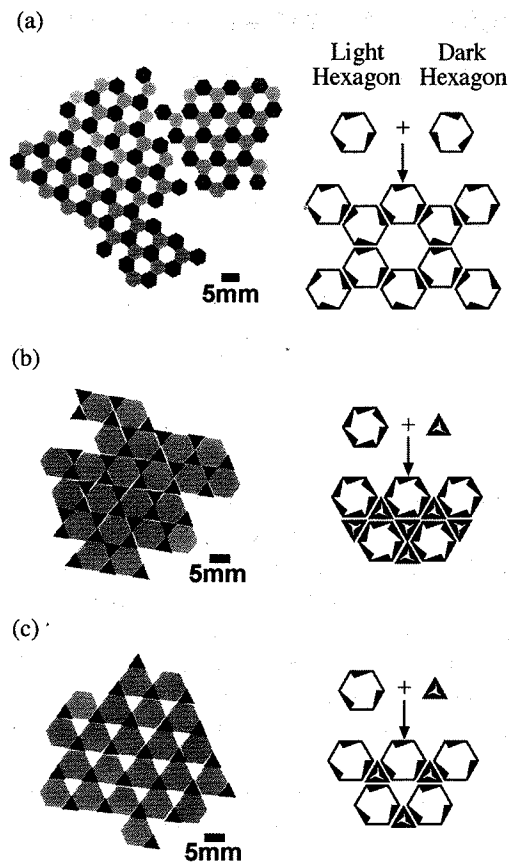


FIG. 4. Chiral self-assembly: all interacting faces have the same dimensions, and differ only in the chirality of the hydrophobic areas. The assemblies that form involve association of faces with opposite chiralities.

hexagonal hydrophobic face oriented down at the PFD/ H_2O interface in a glass dish (diameter 14.5 cm) using tweezers. The dish was agitated with an orbital shaker.² After the plates had assembled into stable arrays (1 h at a frequency of agitation $\omega = 1.5 \text{ s}^{-1}$), we stopped the agitation and photographed the arrays: Fig. 2 shows representative examples.

The plates formed linear arrays, and showed high selectivity in association with objects with hydrophobic faces with the same shapes. These assemblies are the result of steady-state rather than kinetic selectivities; assemblies formed between faces with different contours dissociated readily and reassembled into aggregates of the sort shown.

Patterning the faces with vertical hydrophobic stripes provided a second strategy for achieving selective assembly. Figure 3 demonstrates this strategy, and also illustrates the ability of the density of the objects to modify the shapes of the menisci, and thus their selectivity in self-assembly. Figure 3 shows aggregates of four sets of square plates: two were made from PDMS ($\rho = 1.05 \text{ g/cm}^3$), the other two were made from PDMS with Al_2O_3 cured into it ($\rho = 1.67 \text{ g/cm}^3$); Fig. 3 shows the pattern of vertical hydrophobic stripes. When a mixture of the four types of plates was agitated together at a common PFD/ H_2O interface, they segregated into four separate homoaggregates. The modification of the shapes of the menisci achieved by the differences in density was necessary to get the high selectivity shown: using PDMS squares with the same patterns of hydrophobic stripes on the surface, but with the same densities, led to substantial cross association between faces with similar pat-

terns (e.g., those with patterns represented by 2/3 and 1/2, and 1/2 and 1/4). All of the aggregates show, as expected, good order without slip along slip planes, except for that with entirely hydrophobic edges.

Figure 4 shows the self-assembly of objects with chiral hydrophobic patterns on their faces. The contours of the menisci match best when faces with opposite senses of chirality are opposed.²⁶

These results demonstrate that it is possible to design a number of different types of capillary bonds based on different patterns of hydrophobic and hydrophilic surfaces on the faces that generate the interacting menisci, and that these bonds form with pronounced selectivity. The strategy of matching the contours of menisci is a powerful tool in designing these types of self-assembling systems. We believe that it will be possible to form aggregates having even more complex structures.^{11,13,14,27} The mesoscale self-assembly (MESA) of objects is a relatively new area of strategy that has, we believe, the potential to generate structures useful in a variety of areas, including microelectronics, optics, and MEMS.

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¹N. Bowden, A. Terfort, J. Carbeck, and G. M. Whitesides, *Science* **276**, 233 (1997).

²N. Bowden, I. Choi, B. Grzybowski, and G. M. Whitesides, *J. Am. Chem. Soc.* **121**, 5373 (1999).

³P. A. Kralchevsky, V. N. Paunov, N. D. Denkov, I. B. Ivanov, and K. Nagayama, *J. Colloid Interface Sci.* **155**, 420 (1993).

⁴P. A. Kralchevsky and K. Nagayama, *Langmuir* **10**, 23 (1994).

⁵N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, *Langmuir* **8**, 3183 (1992).

⁶A. S. Dimitrov, M. Yamaki, and K. Nagayama, *Langmuir* **11**, 2682 (1995).

⁷M. A. Fortes, *Can. J. Chem.* **60**, 2889 (1982).

⁸I. S. Choi, N. Bowden, and G. M. Whitesides, *J. Am. Chem. Soc.* **121**, 1754 (1999).

⁹V. N. Paunov, P. A. Kralchevsky, N. D. Denkov, and K. Nagayama, *J. Colloid Interface Sci.* **157**, 100 (1993).

¹⁰D. Y. C. Chan, J. D. Henry, Jr., and L. R. White, *J. Colloid Interface Sci.* **79**, 410 (1981).

¹¹T. L. Breen, J. Tien, S. R. J. Oliver, T. Hadzic, and G. M. Whitesides, *Science* **284**, 948 (1999).

¹²W. T. S. Huck, J. Tien, and G. M. Whitesides, *J. Am. Chem. Soc.* **120**, 8267 (1998).

¹³A. Terfort, N. Bowden, and G. M. Whitesides, *Nature (London)* **386**, 162 (1997).

¹⁴J. Tien, T. L. Breen, and G. M. Whitesides, *J. Am. Chem. Soc.* **120**, 12670 (1998).

¹⁵H. Engelkamp, S. Middelbeek, and R. J. M. Nolte, *Science* **284**, 785 (1999).

¹⁶E. Winfree, F. Liu, L. A. Wenzler, and N. C. Seeman, *Nature (London)* **394**, 539 (1998).

¹⁷G. M. Whitesides, J. P. Mathias, and C. T. Seto, *Science* **254**, 1312 (1991).

¹⁸J. P. Mathias, C. T. Seto, J. A. Zerkowski, and G. M. Whitesides, in *Self-Assembly Through Networks of Hydrogen Bonds* (Royal Society of Chemistry, Cambridge, 1992), Vol. 111, p. 35.

¹⁹C. T. Seto, J. P. Mathias, and G. M. Whitesides, *J. Am. Chem. Soc.* **115**, 1321 (1993).

²⁰E. E. Simanek, X. Li, I. S. Choi, and G. M. Whitesides, in *Cyanuric Acid and Melamine: A Platform for the Construction of Soluble Aggregates and Crystalline Materials* (Elsevier Science, Oxford, 1996), p. 595.

²¹J. C. MacDonald and G. M. Whitesides, *Chem. Rev.* **94**, 2383 (1994).

²²M. M. Conn and J. Rebek, Jr., *Chem. Rev.* **97**, 1647 (1997).

²³*From Chloride Katapinates to Trinucleotide Complexes: Developments in Molecular Recognition of Anionic Species*, edited by C. Seel and J. D. Mendoza (Elsevier, Oxford, U.K., 1996), Vol. 2.

²⁴R. E. Melendez and A. D. Hamilton, *Top. Curr. Chem.* **198**, 57 (1998).

²⁵J.-M. Lehn, in *Supramolecular Chemistry: Concepts and Perspectives; A Personal Account* (VCH, Weinheim, 1995), p. 271.

²⁶The chiral plates floated parallel to the PFD/water interface because of the symmetry of the hydrophobic and hydrophilic areas. Asymmetry of the hydrophobic and hydrophilic areas (and hence, of the vertical forces due to surface tension) causes tilting of the objects (cf. Ref. 2).

²⁷Although the selectivities we have described are based predominantly on the relative strengths of capillary bonds—that is, on steady-state behavior—we have also seen hints of kinetic selectivities within classes of strong capillary bonds. Since kinetics is at least as important as thermodynamics in making possible the complexity of organic chemistry, kinetic selectivity provides a target for future work in structures built with capillary bonds.