

Mesoscopic, Templated Self-Assembly at the Fluid–Fluid Interface

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This paper demonstrates templated self-assembly—based on capillary forces—of millimeter-scale poly(dimethylsiloxane) plates suspended at the water–perfluorodecalin interface. The system described abstracts the concept of “templating” from molecular templating and uses it to design millimeter-scale aggregates that self-assemble in ordered structures. This work points the way to new strategies for organizing complex, millimeter-scale structures.

This paper describes templated self-assembly¹—based on capillary forces—of millimeter-scale poly(dimethylsiloxane) (PDMS) plates suspended at the interface of water and perfluorodecalin (PFD).^{2–6} These self-assembled structures illustrate a new strategy for generating patterns using mesoscopic components, provide a system with which to test the characteristics (strength and directionality) of capillary bonds,⁴ and model some features of templated molecular self-assembly.^{7–28} Molecular templating is

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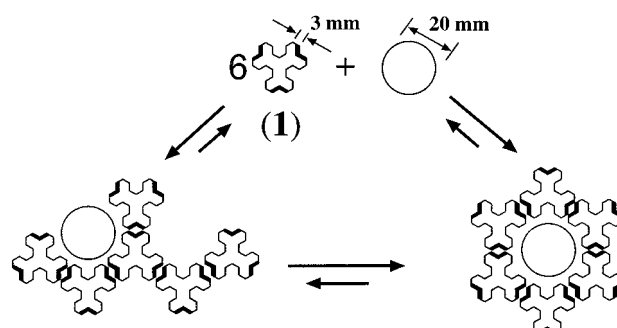


Figure 1. General self-assembly strategy. Hydrophobic edges are indicated with thick lines; hydrophilic edges are indicated with thin lines.

important in the construction of various complex supramolecular structures, ranging from bimolecular capsules such as hydrogen-bonding tennis balls¹⁹ to multi-molecular or lattice inclusion compounds such as hydrogen-bonded diamondoid networks¹² and gas hydrates.^{26–28}

Figure 1 shows the system that we examined. The objects labeled **1**—PDMS plates with hydrophobic (dark lines) and hydrophilic (light lines) edge faces—interact among themselves through three concave hydrophobic regions. PFD forms large, positive menisci on the hydrophobic faces, and these faces are strongly attracted to one another. Water forms small, negative menisci on the hydrophilic faces, and these faces are weakly attracted to one another; hydrophobic faces are repelled by hydrophilic faces.⁴ The interaction between the concave hydrophobic faces used in this study is sufficiently weak that aggregation is reversible under mild agitation.³ Because the object **1** has three regions capable of interaction through concave hydrophobic faces, it can form a range of different structures. These characteristics of the system make it attractive as a subject with which to study the effect of templating under reversible conditions.

The plates, fabricated as described previously,^{2,4} were placed at the PFD/water interface in a Petri dish 14.5 cm in diameter containing 200 mL of PFD and 200 mL of water and swirled on an orbital shaker at a frequency of $\omega = 0.6 \text{ s}^{-1}$. The agitation was stopped after 3–5 h. We performed each experiment at least 10 times.

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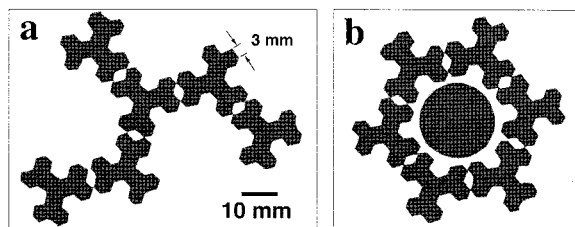


Figure 2. Templated self-assembly of six PDMS plates (**1**) (a) without a template and (b) with a circular template with hydrophilic edges.

First, we allowed six PDMS plates (**1**) (1.6 mm thick) to self-assemble in the absence of a template (Figure 2a). A variety of structures could, in principle, form, including a cyclic hexameric structure and a number of open, branched structures. In the absence of a template, **1** showed no tendency to form cyclic arrays under a range of conditions of agitation. We observed open, branched structures in $>90\%$ of the trials. Addition of a disk with hydrophilic sides as a template resulted in the formation of a cyclic hexamer (Figure 2b). The yield was high (9 out of 10 trials). We believe that the formation of the cyclic hexamer is directed by the capillary interactions between the hydrophilic face of the template and the hydrophilic faces of **1**.

In this system, where ρ^{PDMS} (1.05 g/mL) $\sim \rho^{\text{H}_2\text{O}}$ (1.00 g/mL) (PFD is more dense; $\rho^{\text{PFD}} = 1.95$ g/mL), menisci at hydrophilic faces are small and negative, and capillary interactions between these menisci are attractive, but substantially weaker than those between the large, positive menisci at hydrophobic faces. They are, however, strong enough to provide interactions that differentiate related structures energetically (for example, random and encapsulated).

We observed the same templating effect using both pentagonal and circular templates (Figure 3); we infer that the encapsulation is not a selective function of the symmetry of the encapsulated components. We varied the diameter, d , of the circle that circumscribed the pentagonal template from $1.2D$ to $0.45D$, where D is the diameter of the circular cavity formed by a cyclic hexamer of **1**. Figure 3c shows the cyclic hexameric structure with $d/D = 0.96$. Cyclic hexameric aggregates formed with pentagonal templates that had values of d/D ranging from 0.96 to 0.5. Templates with $d/D \geq 1.0$ did not allow cyclic structures to form, but the aggregates were still compact and organized around the template (Figure 3a,b). Templates with $d/D \leq 0.5$ formed five-membered cyclic aggregates of **1** and disorganized, noncyclic, branched structures (Figure 3i–h). These observations are compatible with the hypothesis that the template organizes the aggregates through capillary interactions that are weaker than the capillary interactions between hydrophobic faces that hold equivalents of **1** together. In the case of molecular templation (or encapsulation), Mecozzi and Rebek reported that the optimum d/D values range from 0.82 to 0.89 depending upon the nature of interactions involved,²⁹ and in the case of gas hydrates the lowest ratio of the radius of a guest molecule relative to the radius of the cavity is 0.77.²⁸

Figure 4 shows the self-assembly of 37 PDMS plates (**1**) and 11 circular templates.³⁰ We observed template-

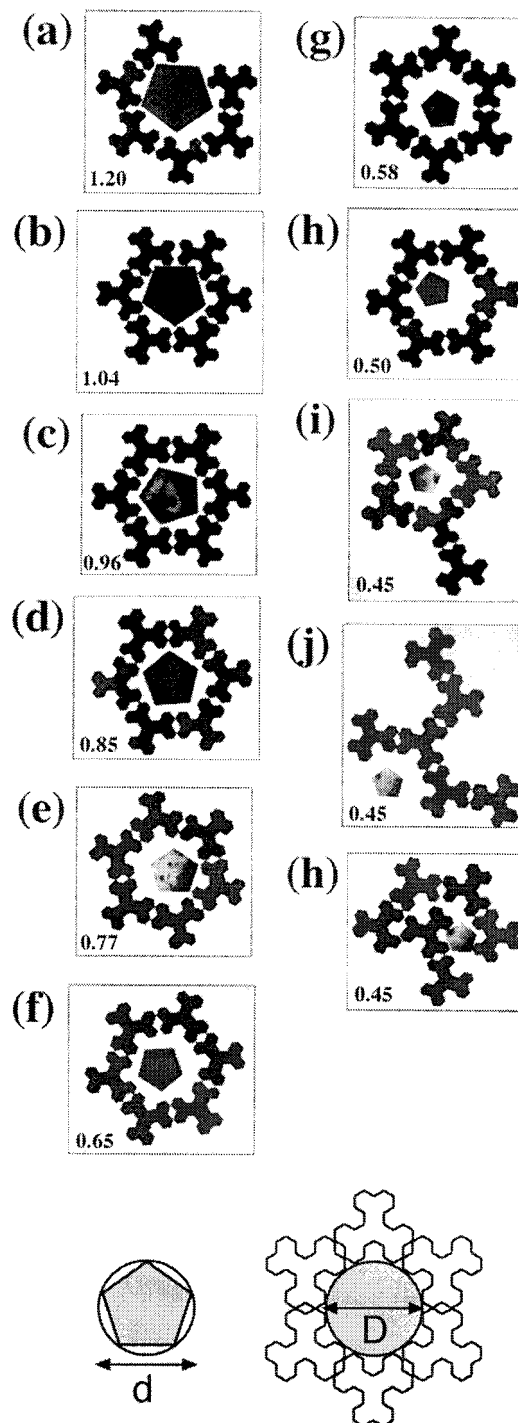


Figure 3. Effect of size of a pentagonal template on the structure of the aggregates formed. The value d is the diameter of the circle that circumscribed the pentagonal template, and the value D is the diameter of the circular cavity formed by a cyclic hexamer of **1**. The value of d/D is shown in each figure.

directed compact structures that were built up of cyclic hexamers of **1**. This assembly can be considered as a two-dimensional model of molecular crystallization (formation of inclusion compounds or gas hydrates).^{11,26–28}

To show templating, the dimensions of the objects examined had to be within a narrow range. We observed templating for **1** when its thickness was 1.6 mm and the edges were 3 mm wide. The same height, but with faces that were 1 or 4 mm wide, did not yield cyclic structures, with or without a template. The differences among these structures reflect, we presume, differences between the

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(30) The pieces were placed at the interface of PFD and water in a Petri dish 27.5 cm in diameter containing 700 mL of PFD and 1200 mL of water and swirled on an orbital shaker at a frequency of $\omega = 0.6$ – 0.8 s^{-1} . The agitation was stopped after 5–10 h. We performed the experiment five times.

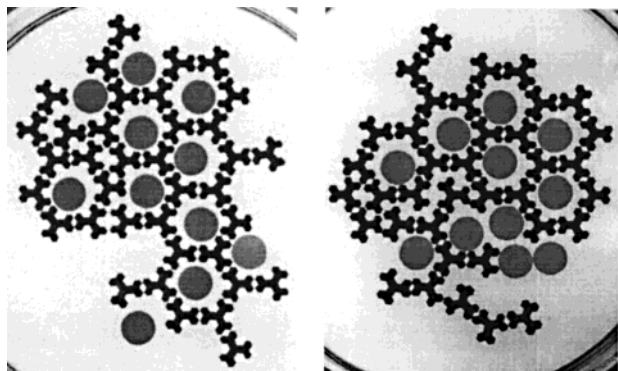


Figure 4. Self-assembly of 37 PDMS plates (**1**) and 11 circular disks. The two figures are representative of those obtained.

strengths of the various capillary interactions involved in forming templated structures. We do not presently have an analytical model that predicts when templated structures will and will not form.

When a millimeter-scale structure such as **1** can form a range of aggregates, a template can cause one of these to dominate. Templating in molecular systems occurs in the same way: the interactions between a guest molecule—that is, a template—and host molecules (through noncovalent bonds) directs the spatial orientation of host molecules to form templated aggregates. The system described here utilizes the same concept of templating to assemble millimeter-scale aggregates and points the way to new strategies for organizing complex millimeter-scale and micrometer-scale structures.

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