

# Precise Macroscopic Supramolecular Assembly by Combining Spontaneous Locomotion Driven by the Marangoni Effect and Molecular Recognition\*\*

Meng Xiao, Yiming Xian, and Feng Shi\*

**Abstract:** Macroscopic supramolecular assembly bridges fundamental research on molecular recognition and the potential applications as bulk supramolecular materials. However, challenges remain to realize stable precise assembly, which is significant for further functions. To handle this issue, the Marangoni effect is applied to achieve spontaneous locomotion of macroscopic building blocks to reach interactive distance, thus contributing to formation of ordered structures. By increasing the density of the building blocks, the driving force for assembly transforms from a hydrophobic–hydrophobic interaction to hydrophilic–hydrophilic interaction, which is favorable for introducing hydrophilic coatings with supramolecular interactive groups on matched surfaces, consequently realizing the fabrication of stable precise macroscopic supramolecular assemblies.

Macroscopic supramolecular assemblies are one of the advanced research topics in supramolecular science because they connect fundamental studies on molecular recognition and the potential application as bulk supramolecular materials. The concept of macroscopic supramolecular assemblies originated from Whitesides' idea<sup>[1,2]</sup> and was established by Harada's group through introducing host–guest recognition into hydrogel building blocks.<sup>[3,4]</sup> Afterwards, many groups demonstrated macroscopic assembly of hydrogel building blocks through supramolecular interactions.<sup>[5–18]</sup> To promote research on macroscopic supramolecular assemblies from the hydrogel systems to rigid building blocks, we have proposed a general principle of a flexible spacing coating to realize self-assembly of macroscopic polydimethylsiloxane (PDMS) or polymethyl methacrylate building blocks.<sup>[19]</sup> However, all of the aforementioned work involved an external energy source such as shaking or rotating to drive the building blocks larger than 10  $\mu\text{m}$  that could hardly diffuse or collide with each other by molecular thermal motion. Under shaking or rotating conditions, the contacting and interacting process between the building blocks occurred randomly, which made it difficult to realize precise assembly and form ordered structures.

There have been no reports of precise macroscopic supramolecular assembly being used to fabricate ordered structures that determine the functions of bulk supramolecular materials.

One possible strategy to address the aforementioned problem is to introduce a long-range force (for example, capillary force) for precise matching of building blocks<sup>[20–22]</sup> and then employ molecular recognition to stabilize the assembled structures. Regarding the precise ordering of building blocks with long-range forces, Whitesides et al. reported pioneering works by using capillary forces, hydrophobic interactions, surface tension, and so on whose force range is from millimeters to centimeters;<sup>[23–28]</sup> thus, the matching degree between two macroscopic building blocks could be adjusted in the interactive centimeter-scaled distance, which contributed to precise alignment and ordered structures. Based on the principle of minimizing the interfacial free energy, we combined spontaneous locomotion of millimeter-scale PDMS plates and their further assembly through capillary forces exerted on the hydrophobic surfaces to achieve ordered alignment.<sup>[29]</sup> However, the obtained ordered structures were highly dependent on the existence of an interface without post-solidification strategies. Therefore, combining spontaneous locomotion and molecular recognition to realize precise macroscopic supramolecular assembly and obtain stable ordered structures remains a challenge. Herein, we used the Marangoni effect to achieve spontaneous locomotion of macroscopic building blocks, which avoided the bubble-hindering effects of the hydrogen peroxide–platinum propulsion system. We adjusted building block density to change the precise matching manner from hydrophobic–hydrophobic to hydrophilic–hydrophilic, which was favorable for introducing molecular interactive groups on the matched surface. We achieved stable ordered supramolecular assemblies with precise matching by associating the hydrophilic surfaces with host or guest groups above a flexible spacing coating.

The Marangoni effect originates from mass or heat transfer by a surface-tension gradient formed along an interface,<sup>[30–32]</sup> which is widely used to propel small objects from micrometer to macroscopic scales. To demonstrate this application in our system, we designed pan-like PDMS building blocks with a tiny pore in the center of the bottom surface of the PDMS building blocks, which could slowly release ethanol onto the water surface and generate random motions through the surface-tension gradient of water–ethanol, and hydrophilic copper foil tape attached to the side surfaces of the PDMS cuboid, which induced anisotropic surface wettability of the PDMS side surfaces for guided

[\*] M. Xiao, Y. M. Xian, Prof. Dr. F. Shi  
State Key Laboratory of Chemical Resource Engineering &  
Beijing Laboratory of Biomedical Materials  
Beijing University of Chemical Technology, Beijing 100029 (China)  
E-mail: shi@mail.buct.edu.cn

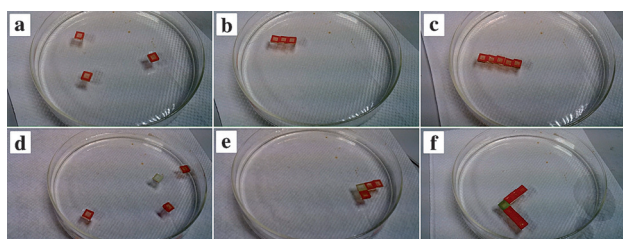
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macroscopic assembly (for details, see the Supporting Information, Section S1). When we placed two PDMS building blocks onto the air–water interface, they underwent self-propulsion quickly and randomly. Upon reaching the interactive distance of hydrophobic–hydrophobic interactions, the two PDMS building blocks moved towards the negative meniscus formed by the hydrophobic sides and assembled as an ordered dimer. Compared with the reported oxygen-bubble propulsion system,<sup>[29]</sup> the current assembled structure displayed a seamless connection between the two hydrophobic surfaces and eliminated the problem of bubble attachment onto hydrophobic surfaces, which hindered tight association of the building blocks (Supporting Information, Figure S2). Therefore, the driving force of Marangoni effect should be promising for the firm assembly of building blocks and provide the possibility of stabilizing the obtained structures through supramolecular interactions.

To confirm whether the anisotropy of the induced wettability favored the assembly of ordered structures with more than two building blocks, we designed two types of anisotropic PDMS building blocks, as shown in the Supporting Information, Figure S1: one with two opposite hydrophilic surfaces and the other with adjacent hydrophilic copper foil. Upon contacting water, the building blocks with opposite hydrophilic sides were propelled to the interactive distance through the Marangoni effect and assembled to an end-to-end line structure connected by hydrophobic surfaces based on the hydrophobic–hydrophobic interactions. After adding similar PDMS building blocks, the line structure was extended to an ordered end-to-end geometry (Figure 1 a–c).

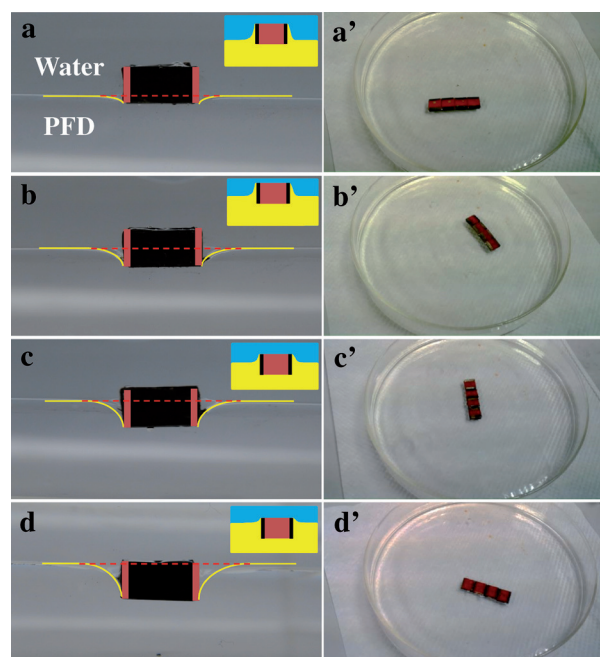


**Figure 1.** a)–c) The red PDMS with opposite hydrophilic surfaces and loaded with ethanol gradually assembled into a line structure on the air–water interface. d)–f) One green PDMS with adjacently hydrophilic sides assembled into an L shape with other opposite hydrophilic red PDMS.

This phenomenon was interpreted as follows: because the PDMS density was slightly larger than that of water, the top edge of the hydrophilic sides was immersed in water, which exhibited a small curvature deformation and low curvature force; in contrast, the hydrophobic sides caused a seriously deformed water surface and resulted in a large curvature force favorable for hydrophobic–hydrophobic assembly. When mixing the PDMS building blocks with oppositely (red) and adjacently (green) hydrophilic sides, an “L”-shaped assembly was obtained (Figure 1 d–f). The formation mechanism of this pattern was interpreted as follows: the green PDMS building block provided two adjacently hydrophobic sides as assembly sites for the red ones, to which the red

PDMS could be assembled driven by curvature forces. This phenomenon indicated that the assembled geometry could be controlled to be a line shape or an “L” shape with anisotropic building blocks fabricated by adjusting the location of hydrophilic surfaces (to opposite or adjacent sides).

Given that the modification of the polyelectrolyte multilayer with host–guest groups would change PDMS wettability from hydrophobicity to hydrophilicity, the hydrophobic surface-guided assembly was not suitable for introducing molecular recognition between the building blocks. Therefore, we considered whether we could use the principle of minimizing interfacial free energy to achieve hydrophilic–hydrophilic assembly. In an attempt to address this issue, we replaced the original air–water interface with a water–perfluorodecalin (PFD) interface, which has a density of  $1.9 \text{ g mL}^{-1}$ ; meanwhile, to enhance the effect of the principle of minimizing interfacial free energy, we amplified the wettability difference of PDMS from hydrophobic–hydrophilic to superhydrophobic–superhydrophilic (for details, see the Supporting Information, Sections S3 and S4). When we placed the as-prepared PDMS in the system (Supporting Information, Section S5), it floated on the water–PFD interface because of its density of  $1.1 \pm 0.1 \text{ g cm}^{-3}$ , which was larger than the density of water but smaller than that of the PFD. As shown in Figure 2 a, the two superhydrophilic sides exhibited a small water meniscus because the majority of the PDMS volume was immersed within the water phase; meanwhile, the meniscus deformation of the superhydrophobic surfaces was much larger than that of superhydrophilic surfaces (Figure 2 a, inset). Thus, the

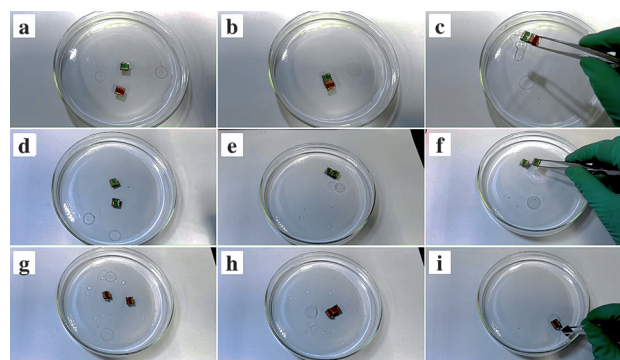


**Figure 2.** Photographs of PDMS with opposite superhydrophobic sides and superhydrophilic surfaces with different densities ( $\text{g cm}^{-3}$ ): a)  $1.1 \pm 0.1$ , b)  $1.3 \pm 0.1$ , c)  $1.6 \pm 0.1$ , and d)  $1.9 \pm 0.1$ . The yellow lines indicate the PFD–water interfaces, red indicates superhydrophilic surfaces and black indicates superhydrophobic surfaces. a')–d') Corresponding assembled structures, where the black sides indicate superhydrophilic surfaces.

hydrophobic-hydrophobic interaction was dominant for the assembly of PDMS building blocks, leading to a line structure guided by the superhydrophobic surfaces (Figure 2a'; details in the Supporting Information, Section S6). Although the replaced water-oil interface still relied on hydrophobic-hydrophobic interactions for assembly, we inferred that increasing the PDMS density could adjust the deformation degree of the superhydrophilic and superhydrophobic surfaces and further realize assembly through hydrophilic-hydrophilic interactions.

To obtain hydrophilic surface-guided assembly, we considered whether we could achieve favorable curvature deformation of the hydrophilic meniscus by increasing the PDMS density. Therefore, we incorporated different amounts of iron particles into the PDMS pre-polymer; the resulting PDMS density values were  $1.3 \pm 0.1$ ,  $1.6 \pm 0.1$ , and  $1.9 \pm 0.1 \text{ g cm}^{-3}$  (for details, see the Supporting Information, Section S7). When we placed a PDMS building block with a density of  $1.3 \pm 0.1 \text{ g cm}^{-3}$ , we observed that one third of the hydrophilic side was below the water-oil interface (Figure 2b) and the curvature deformation of the superhydrophilic side surfaces grew larger than that in Figure 2a. However, the curvature deformation of the superhydrophilic sides was still smaller than that of superhydrophobic surfaces (Figure 2b, inset). Under this condition, the hydrophobic-hydrophobic interaction was dominant; therefore, the PDMS building blocks still preferred to assemble through the superhydrophobic sides (Figure 2b'; details in the Supporting Information, Movie S1). When the PDMS density was increased to  $1.6 \pm 0.1 \text{ g cm}^{-3}$ , almost two-thirds of the hydrophilic sides reached below the water-oil interface (Figure 2c), thus inducing increased curvature deformation of the superhydrophilic sides. Meanwhile, the curvature deformation decreased in the case of the superhydrophobic surfaces, as shown in the inset. In this situation, the hydrophilic curvature dominated and could provide sufficient force for the assembly of line structures through the superhydrophilic surfaces, as shown in Figure 2c'. To strengthen the hydrophilic interactions, we further increased the PDMS density to  $1.9 \pm 0.1 \text{ g cm}^{-3}$ , which was comparable to that of PFD. As shown in Figure 2d, the PFD surface seriously deformed on the superhydrophilic surfaces, whereas the curvature deformation of the superhydrophobic side was small (Figure 2d, inset). Because of the remarkably advantageous curved forces of the superhydrophilic sides compared to those of superhydrophobic surfaces, the PDMS building blocks underwent hydrophilic-hydrophilic guided assembly to a regular line structure (Figure 2d'). To quantify the force difference provided by the hydrophobic and hydrophilic curvature, we evaluated the stability of the assembled dimer of building blocks by destroying the structure under shaking conditions, following the method of Whitesides et al.<sup>[26]</sup> The results are summarized in the Supporting Information, Figure S7, and they match well with the observed assembly behaviors in Figure 2. These results demonstrate that control over the curvature deformation degree through adjustment of the density of the building blocks can be used to tailor the manner of assembly of the macroscopic building blocks with hydrophobic or hydrophilic surfaces.

After we achieved macroscopic assembly of PDMS cuboids by combining the Marangoni effect and hydrophilic-hydrophilic interactions, we considered whether we could obtain stable assembled structures independent of the water-oil interface by introducing supramolecular interactions. For this purpose, we fabricated PDMS building blocks with two opposite hydrophilic sides modified with  $\beta$ -cyclodextrin (CD) or azobenzene (Azo) groups<sup>[19]</sup> and two opposite superhydrophobic sides. (for details, see the Supporting Information, Section S9). When we added two as-prepared PDMS building blocks to the water-oil system, they underwent random locomotion, propelled by the Marangoni effect. When they reached the interactive distance of hydrophilic-hydrophilic interactions, the cuboids assembled into a well-matched dimer (Figure 3a,b). After contact, when the

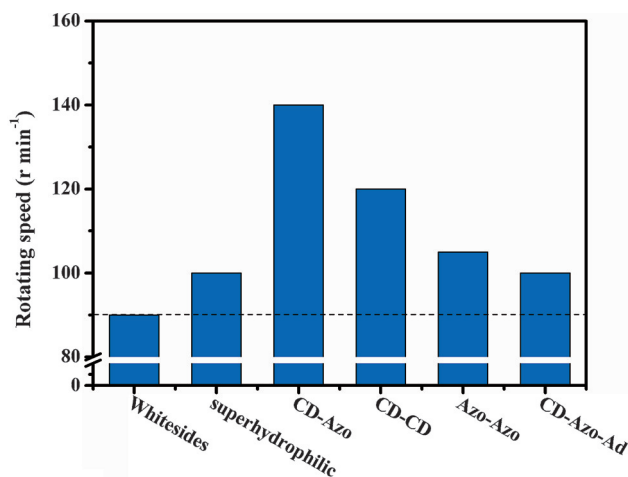


**Figure 3.** a)–c) Two PDMS modified with CD and Azo could assemble into a stable dimer. Two identical PDMS modified with d)–f) CD or g)–i) Azo assembled into a dimer but could not form a stable structure.

two PDMS cuboids approached the molecular interactive distance, the host-guest molecular recognition occurred to stabilize the assembled dimer, which could be removed from the interface, as shown in Figure 3c (for details, see the Supporting Information, Section S10). To clarify the significance of the introduced supramolecular interactions on the stability of the assembled structure, we carried out control experiments using two PDMS cuboids modified with CD (Figure 3d–f) or Azo (Figure 3g–i). Under both conditions, the cuboids assembled by the hydrophilic-hydrophilic guided manner; however, without supramolecular recognition for the stabilization, the assembled structure could not be maintained out of the water-oil interface. This result demonstrated a new avenue to fabricate ordered structures through macroscopic supramolecular assembly based on the concept of introducing a long-range force for precise matching of building blocks and then employing molecular recognition to stabilize the assembled structures.

To quantify the binding strength between the cuboids with and without CD-Azo recognition, we used a rotating shaker to destroy the assembled structure and subsequently evaluated the binding strength using a critical disassembly condition. The structure assembled through hydrophobic-hydrophobic interactions at the water-PFD interface could be stable below the rotating speed of  $90 \text{ r min}^{-1}$ .<sup>[26]</sup> In our experiment, when we enhanced the anisotropic wettability

by using PDMS ( $1.6 \pm 0.1 \text{ g cm}^{-3}$ ) with opposite superhydrophilic and superhydrophobic sides, the assembled structure could resist external shaking disturbance up to  $100 \text{ r min}^{-1}$ . After supramolecular interactions of CD-Azo were introduced on the hydrophilic surfaces, the rotating speed could be increased to  $140 \text{ r min}^{-1}$ . In comparison, with identical surface groups of CD or Azo only, the dimers with CD-CD or Azo-Azo interactions exhibited a weaker resistance to shaking (critically  $120 \text{ r min}^{-1}$  and  $105 \text{ r min}^{-1}$ , respectively; Figure 4).



**Figure 4.** Correlation between the rotating speed of the shaker and the assembled PDMS dimers under different conditions: result reported by Whitesides et al. in Ref. [26]; hydrophilic–hydrophilic interactions; PDMS modified with CD–Azo or CD–CD or Azo–Azo interactions; with Ad solutions introduced into the assembled CD–Azo structures.

These results matched well with the phenomenon that, with CD–Azo recognition, the assembled dimer could be removed from the interface, whereas the control dimers could not. Furthermore, the dimers with CD–CD or Azo–Azo interactions were more stable than those with hydrophilic–hydrophilic interactions because of the weak interactions between the CD molecules or un-grafted PAA molecules.

To further clarify the supramolecular interactions between two PDMS cuboids with CD and Azo groups, we carried out a competitive adsorption experiment by adding a 1-adamantane carboxylic acid (Ad) aqueous solution ( $0.5 \text{ mM}$ ) to the assembled structures. Because the intrinsic binding constant between CD and Ad ( $10^5 \text{ L mol}^{-1}$ ) was much higher than that between CD and Azo ( $10^3 \text{ L mol}^{-1}$ ), the assembled CD–Azo dimer could be disassembled by competitive replacement of Ad in the cavity of CD. Therefore, the critical rotating speed decreased to  $100 \text{ r min}^{-1}$ , which was comparable to that under Azo–Azo interactions.

To summarize, we demonstrated a concept for precise macroscopic supramolecular assembly through introducing a long-range force for precise matching of building blocks and then employing molecular recognition to stabilize the assembled structures. We realized spontaneous locomotion of the PDMS building blocks through the Marangoni effect; we transformed the traditionally hydrophobic–hydrophobic guided assembly to hydrophilic–hydrophilic directed assem-

bly by adjusting the building block density; and we obtained stable ordered structures independent of the interface based on supramolecular interaction introduced onto the hydrophilic surfaces. We believe that the precise supramolecular assembly of macroscopic building blocks could provide a novel strategy to promote fundamental studies on molecular recognition for the fabrication of bulk supramolecular materials.

**Keywords:** host–guest recognition · macroscopic supramolecular assembly · Marangoni effect · ordered structures · polydimethylsiloxane

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