Supporting Information for

Capillarity-induced directed self-assembly of patchy hexagram particles at the air-water interface

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KEYWORDS: patch hexagram particle, self-assembly, capillarity, interface deformation, anisotropy

Preparation of Patchy Hexagram Particles

Patchy hexagram particles were prepared by sequential photopolymerization of two different prepolymer solutions in a poly(dimethylsiloxane) (PDMS) micromold (Fig. S1). First, to fabricate the patchy region, a small aliquot of prepolymer solution-1 dissolved in ethanol was loaded onto a hexagram-patterned PDMS micromold prepared using soft lithography.[1] After removal of the excess solution by pipetting, the volatile ethanol solvent started to evaporate rapidly under ambient conditions. The evaporation of ethanol reduced the volume of the solution in the mold. The remaining prepolymer solution was divided by capillary action at the edge of each arm of the hexagram micromold (Fig. S1 and S3).[2-5] After the ethanol in prepolymer solution-1 was completely evaporated from the micromold, the remaining prepolymer was partially photopolymerized by UV irradiation for 30 sec in a nitrogen chamber (Fig. S1B). As shown in Fig. S2, the optical and fluorescence images clearly indicate that the patches formed readily within 10 sec using the hexagram micromold, as visualized with premixed rhodamine-B. The patchy formations in the hexagram micromold required approximately 10 sec (Fig. S3). As seen in Fig. S2 and S3, the fluorescent intensity represents the optical density; therefore, higher intensities corresponded to higher precursor concentrations. At the initial state (0.57 sec), as shown in Fig. S3, we observed that the fluorescence intensities were uniform and low before the evaporation of ethanol from prepolymer solution-1. Once the evaporation was completed, the intensity increased at the vertex region of the micromold, while the center became darker after 8.18 sec, as shown in Fig. S3. Subsequently, prepolymer solution-2 was added into the remaining micromold space via the same procedure, followed by complete photopolymerization of two prepolymer solutions by intense UV irradiation (Fig. S1C). To visualize the patch and body regions, two different fluorescence dyes rhodamine-B (orange) and fluorescein isothiocyanate (green) were added to the prepolymer-1 and -2 solutions, respectively. As

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shown in Fig. S2, the patchy regions (orange) gradually increased as the monomer concentration increased from 10% to 40%. The size of the patches in the hexagram particles monotonically increased with the TMPTA concentration in prepolymer solution-1. This micromolding method for fabricating patchy particles is highly advantageous because the patch sizes can be tuned readily by simply changing the concentration of prepolymer solution-1 (TMPTA solution).

Interface Deformation of Homogeneous Hexagram Particles

The random assembly behaviors of homogeneous particles have been attributed from an undulated contact line at the particle surface of each homogeneous particle, which can be described as capillary interaction between capillary multipoles in the presence of surface roughness (Fig. S6 and S7). The contact-line undulations produce distortions in the surrounding liquid interface, whose overlap engenders capillary interaction between the particles.[6-9]

References

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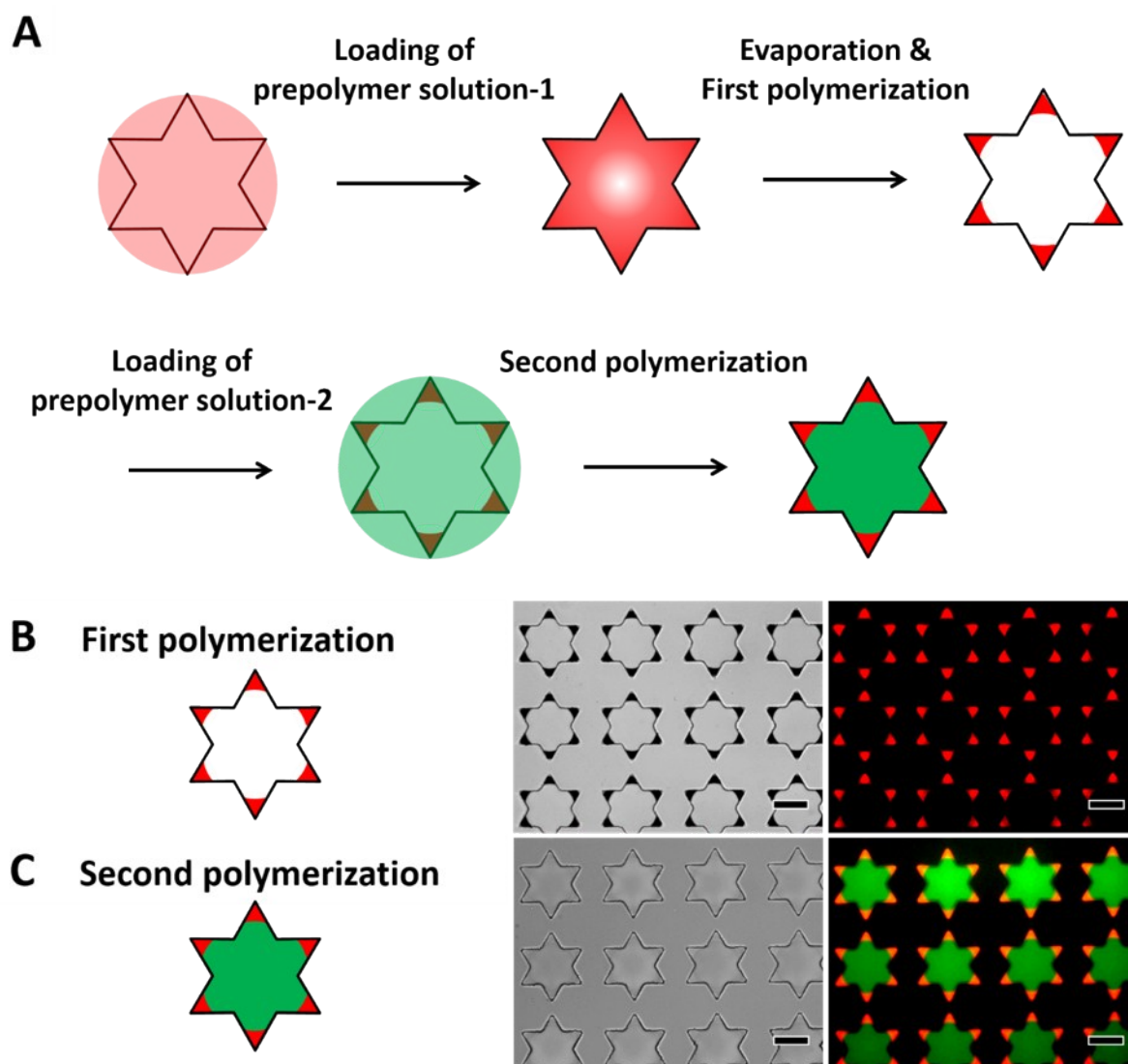
Fig. S1 Preparation of patchy hexagram particles using a simple micromolding method. (A) Schematic procedure of sequential photopolymerization of two different prepolymer solutions. (B) and (C) Optical and fluorescence images of the PDMS micromold after the two photopolymerization steps, which are indicated by the dotted square boxes. The scale bars indicate 100 μm.
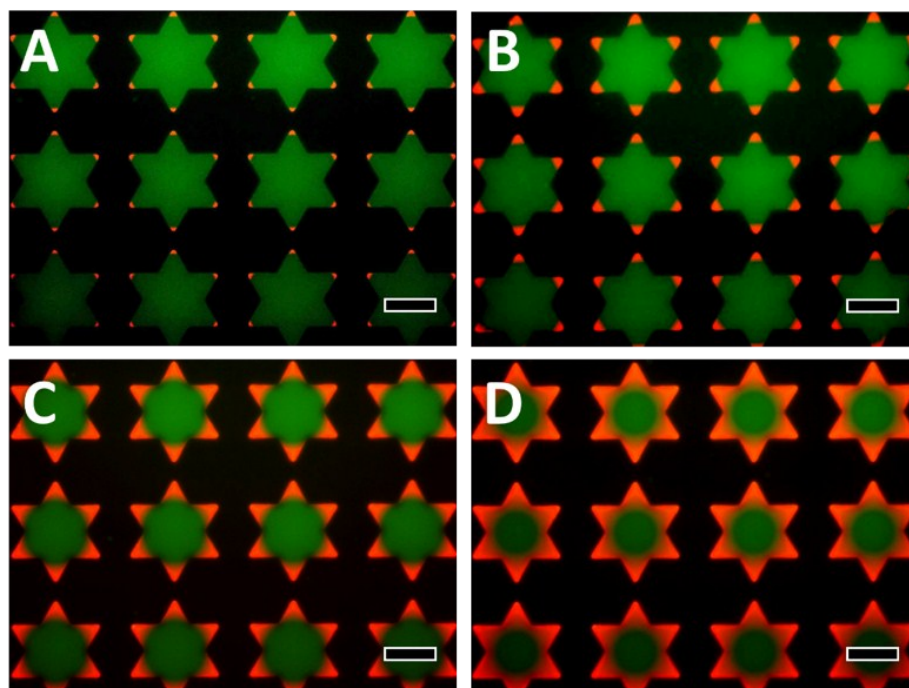
Fig. S2 Preparation of hexagram particles with different patch sizes. The vertex regions are occupied by hydrophobic TMPTA monomer (orange) with initial concentrations of (A) 10%, (B) 20%, (C) 30%, and (D) 40% in ethanol. The scale bars indicate 100 μm.
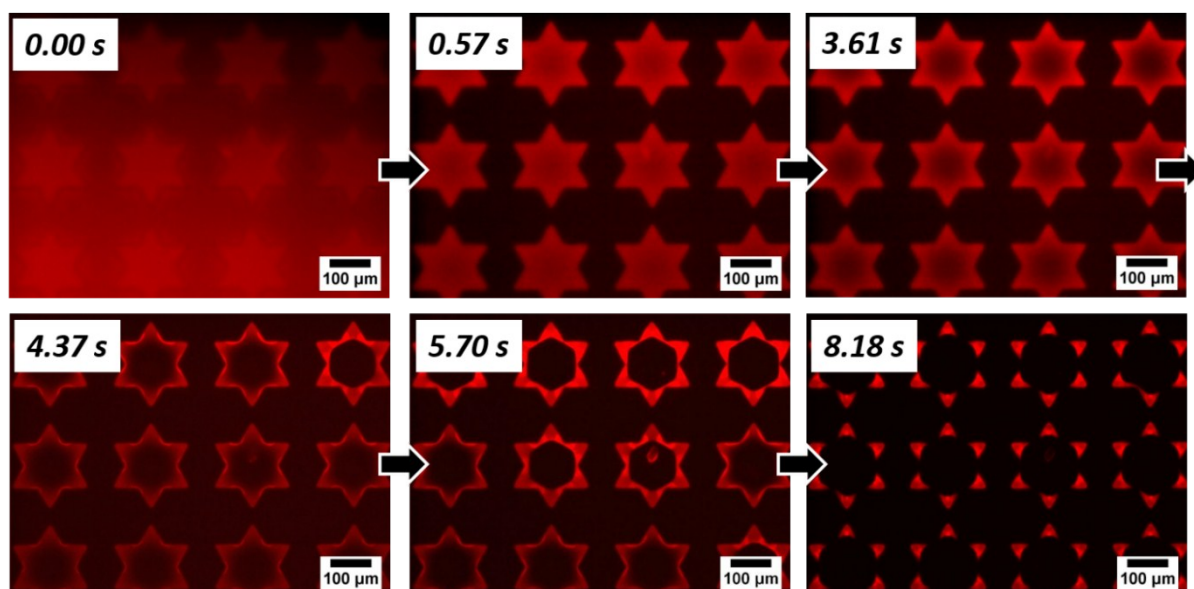

Fig. S3 Capillarity-induced flows formed patches with hexagram shapes on the vertex regions. Time-sequential fluorescence images.
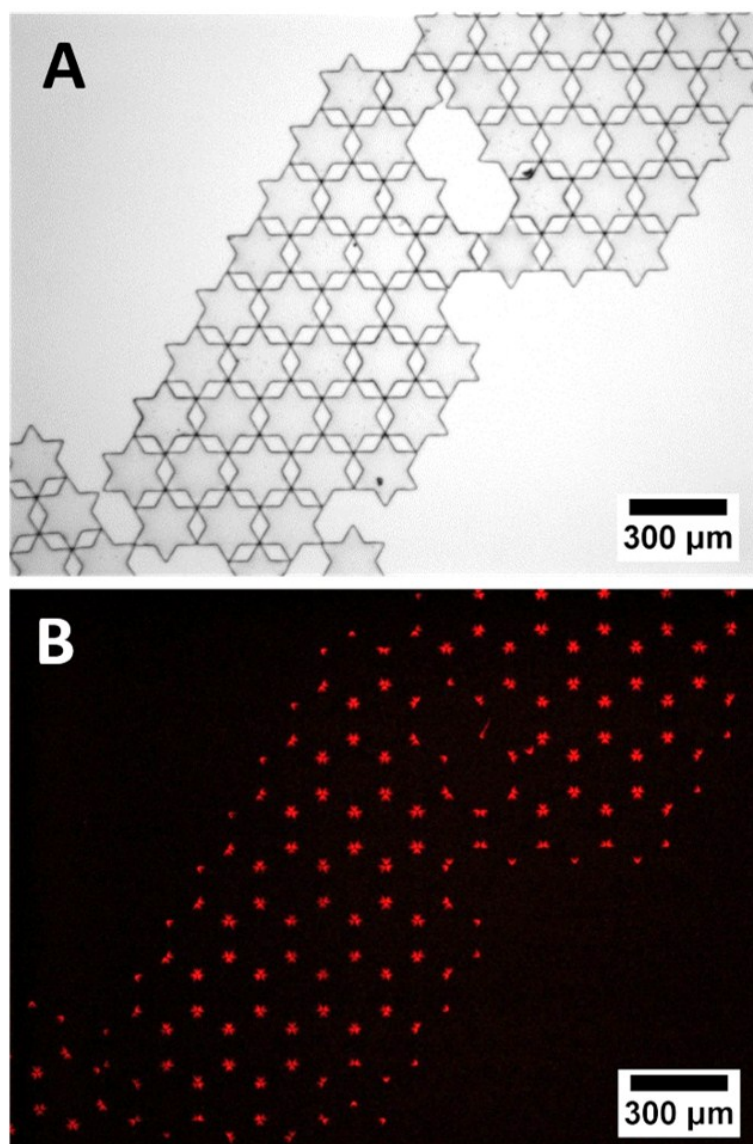
Fig. S4 Well-ordered assembly of PRs = 0.14 patchy hexagram particles at the air-water interface. (A) Optical and (B) fluorescence images.
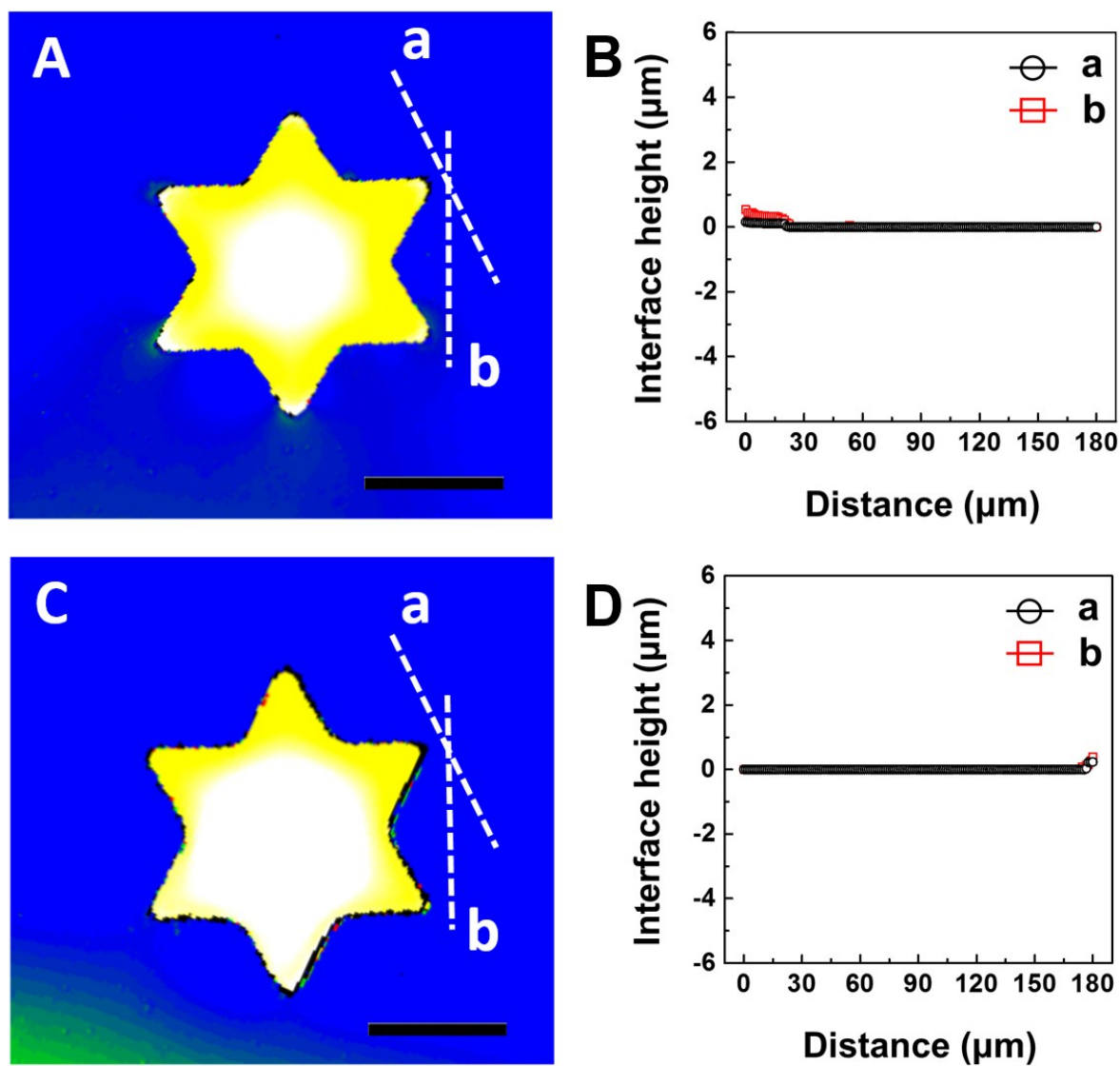
Fig. S5 Negligible interface deformation around homogeneous hexagram particles. Optical profilometry images of (A) hydrophilic PEG-DA and (C) hydrophobic TMPTA homogeneous hexagram particles at the air-water interface containing 2 wt % gellan in the aqueous phase. (B) and (D) The heights of the interface deformation were obtained from the dashed lines (a) and (b), respectively.

Capillary multipoles
(due to irregular contact line)

A) Hydrophilic particles

B) Hydrophilic particles
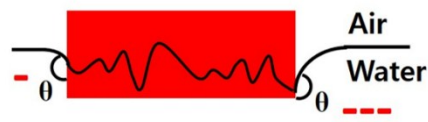
(**+** : Positive interface deformation magnitude)

(**−** : Negative interface deformation magnitude)

Fig. S6 Lateral capillary force is due to the overlap of interfacial deformations created by the separate particles. (A) Homogeneous hydrophilic particles, (B) Homogeneous hydrophobic particles. When the normal force (particle weight and buoyancy) is negligible, interfacial deformations could be engendered by an undulated contact line at the particle surface. In this case, forces between the particles can be described as interactions between 'capillary multipoles' in analogy with electrostatics.
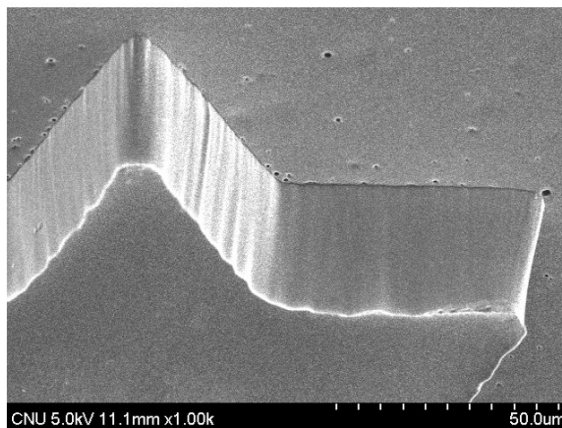
PEG-DA
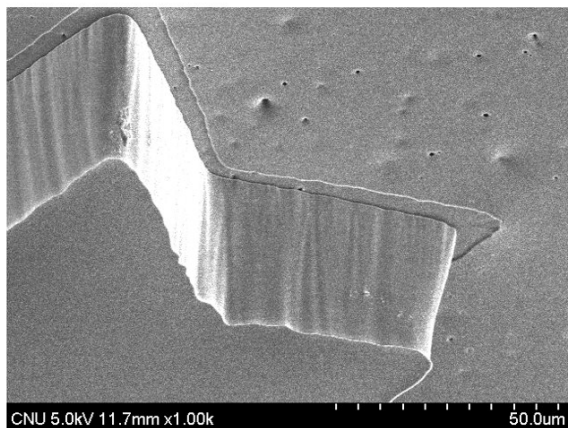
TMPTA

Fig. S7 Scanning electron microscopy images of homogeneous particles.