

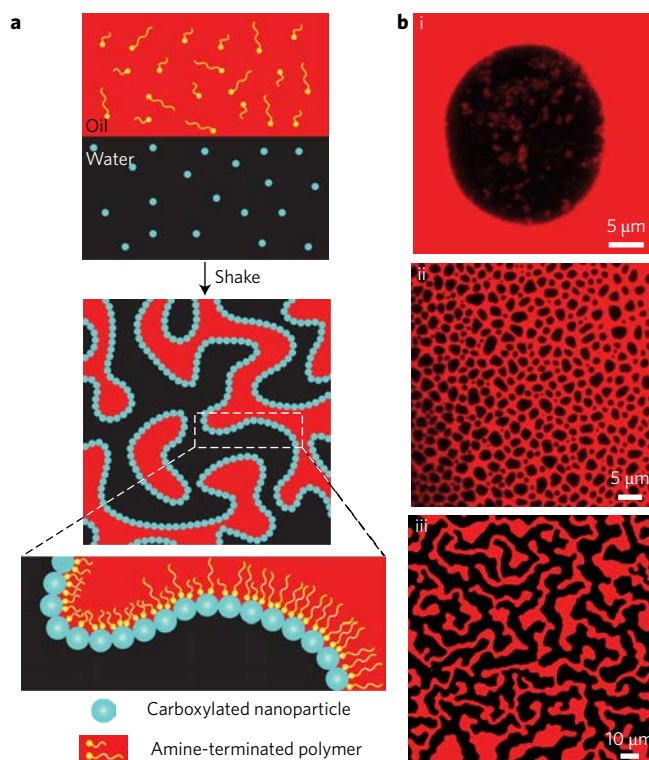
# Bicontinuous structured liquids with sub-micrometre domains using nanoparticle surfactants

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**Bicontinuous jammed emulsions (or bijels) are tortuous, interconnected structures of two immiscible liquids, kinetically trapped by colloidal particles that are irreversibly bound to the oil-water interface<sup>1,2</sup>. A wealth of applications has been proposed for bijels in catalysis, energy storage and molecular encapsulation<sup>3-5</sup>, but large domain sizes (on the order of 5  $\mu\text{m}$  or larger) and difficulty in fabrication pose major barriers to their use<sup>6-8</sup>. Here, we show that bijels with sub-micrometre domains can be formed via homogenization, rather than spinodal decomposition. We achieve this by using nanoparticle surfactants: polymers and nanoparticles of complementary functionality (for example, ion-pairing) that bind to one another at the oil-water interface<sup>9,10</sup>. This allows the stabilization of the bijel far from the demixing point of the liquids, with interfacial tensions on the order of 20  $\text{mN m}^{-1}$ . Furthermore, our strategy is extremely versatile, as solvent, nanoparticle and ligand can all be varied.**

In response to a change in temperature<sup>11</sup> or chemical composition<sup>7,12</sup>, certain liquids de-mix by spinodal decomposition, forming two continuous, interconnected domains with a single characteristic length scale. If colloidal particles that wet both liquids are included in this system, they can adsorb onto the oil-water interface during the demixing process. The energy cost of removing these particles from the interface is typically extremely large and can exceed thermal energy by several orders of magnitude depending on the size of the particles, the oil-water, oil-particle and water-particle surface tensions, and the line tension of the three-phase contact line<sup>13,14</sup>. As the system coarsens, the areal density of the particles increases and, provided the particles are adsorbed irreversibly to the oil-water interface, the particle assembly eventually jams, arresting further coarsening of the system and locking in its structure<sup>3,15</sup>. Remarkably, if the surface chemistry of the particles is tuned such that they wet both liquids equally, the particles impose no curvature on the system and an interconnected network of liquid domains known as a 'bijel' (bicontinuous jammed emulsions) is formed<sup>1,2,16</sup>. This requires that a number of rather rigid criteria be fulfilled, meaning that bijels are extremely difficult to produce<sup>4,5,17</sup>. Furthermore, the lower bound of the resultant domain size is typically rather large ( $\sim 5 \mu\text{m}$ ), limiting their potential for energy storage and catalysis applications.

Reducing particle size to the nanoscale regime is a promising solution to many of these limitations. Owing to their smaller size and hence greater diffusion coefficient, nanoparticles are known to adsorb onto liquid-liquid interfaces more rapidly below a critical

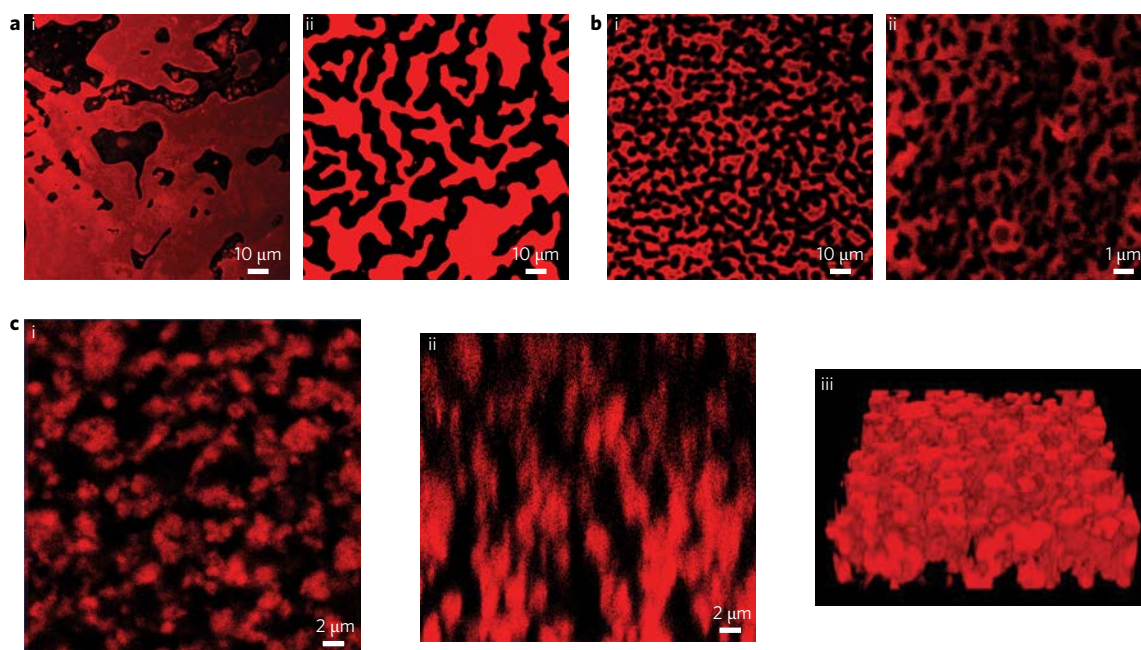


**Figure 1 | Formation of bijel structures.** **a**, Schematic showing the formation of bijels formed by the jamming of nanoparticle surfactants at the oil-water interface. **b**, Emulsions stabilized by a single molecular weight of PDMS-NH<sub>2</sub> in toluene (1.61 mmol l<sup>-1</sup>). (i)  $M_w = 1,000 \text{ g mol}^{-1}$ . (ii)  $M_w = 3,000 \text{ g mol}^{-1}$ ; water contains 1 mg ml<sup>-1</sup> nanoparticles. (iii) A liquid bicontinuous system stabilized by nanoparticle surfactants consisting of an equimolar mixture of 1,000 g mol<sup>-1</sup> and 3,000 g mol<sup>-1</sup> PDMS-NH<sub>2</sub> (1.61 mmol l<sup>-1</sup>) and nanoparticles (0.5 mg ml<sup>-1</sup>).

size of  $\sim 5 \mu\text{m}$  (refs 13,18). Furthermore, a nanoparticle dispersion will stabilize a greater surface area at a given volume fraction, as there will be greater particle cross-sectional area per unit volume<sup>13</sup>. However, ensuring uptake and irreversible binding of nanoparticles to the oil-water interface has proven to be difficult, as has producing the promised reduction in domain size<sup>19</sup>. Applying the binding of

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**Figure 2 | Impact of altering the particle concentration and molar ratio of functional polymer upon system morphology and its three-dimensional bicontinuous structure.** **a**, Liquid bicontinuous systems formed by nanoparticle surfactants with a nanoparticle concentration of (i) 0.1 and (ii) 0.5 mg ml<sup>-1</sup> at a fixed concentration of PDMS-NH<sub>2</sub> (1.61 mmol l<sup>-1</sup>). **b**, Bicontinuous morphologies formed by nanoparticle surfactants at constant particle concentration (1 mg ml<sup>-1</sup>) with varying concentration of PDMS-NH<sub>2</sub> from (i) 0.161 to (ii) 16.1 mmol l<sup>-1</sup>. **c**, Cross-sections of a confocal z stack of the bijels taken (i) parallel and (ii) normal to the focal plane and (iii) the reconstructed three-dimensional morphology of the system formed by nanoparticle surfactants with a nanoparticle concentration of 5 mg ml<sup>-1</sup> and PDMS-NH<sub>2</sub> of 16.1 mmol l<sup>-1</sup>.

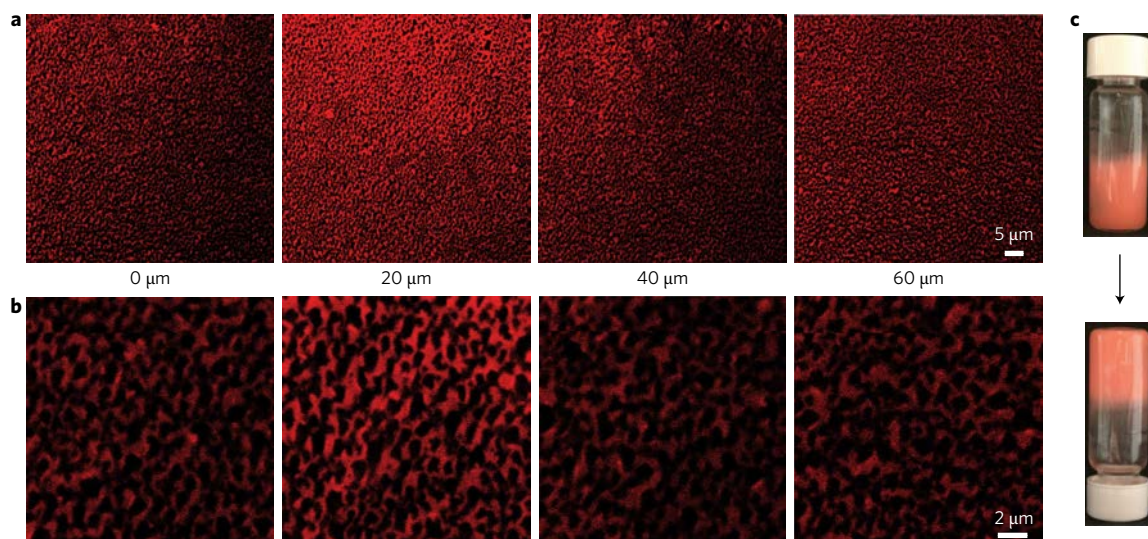
nanoparticles and functional polymers of complementary functionality at the oil–water interface to form elastic nanoparticle surfactant films<sup>9,10</sup> allows us to stabilize bijels using liquids far from their demixing point (that is, with an interfacial tension on the order of 10–30 mN m<sup>-1</sup>). These interfacial films consist of hydrophilic, carboxylic acid-functionalized polystyrene (PS-CO<sub>2</sub>H) nanoparticles dispersed in water and hydrophobic, amine-functionalized polydimethylsiloxane (PDMS-NH<sub>2</sub>) in oil (for example, toluene). A schematic of the system, showing the locations of the components and the resultant structures they stabilize against coalescence, is presented in Fig. 1a. There are many benefits to using such a system. Using colloidal particles alone requires extremely careful modification of the surface chemistry of the particle to achieve neutral wetting conditions. The requirement that the system undergo liquid–liquid phase separation limits the choices of fluids available and makes it challenging to generate large volumes of bicontinuous materials. Until now, nanoparticles (diameter <50 nm) have been of limited use in bijel stabilization owing to their comparatively low binding energies to the oil–water interface, especially at the low surface tensions present in bijels. The binding of the functional polymers to the particle surface increases this binding energy, trapping the nanoparticle surfactants at the interface despite their small size.

We began by studying a system of two different molecular weights of PDMS-NH<sub>2</sub> containing a single amine group (molecular weight,  $M_w = 1,000$  and 3,000 g mol<sup>-1</sup>) in toluene and 16.5 nm PS-CO<sub>2</sub>H nanoparticles in water. When agitated by shaking, equal-volume mixtures of oil and water form emulsions with a characteristic diameter on the micrometre scale. Low-molecular-weight PDMS-NH<sub>2</sub> (1,000 g mol<sup>-1</sup>) tends to form either oil-in-water-in-oil double emulsions (Fig. 1b,i) or water-in-oil emulsions (Supplementary Fig. 5), while high-molecular-weight PDMS-NH<sub>2</sub> (3,000 g mol<sup>-1</sup>) tends to form water-in-oil emulsions (Fig. 1b,ii), suggesting that the relative size of the hydrophobic moiety of the functional polymer imposes a curvature upon the system. In both instances droplets are aspherical, demonstrating the interfacial elasticity of the system. We have also found that nanoparticle surfactant

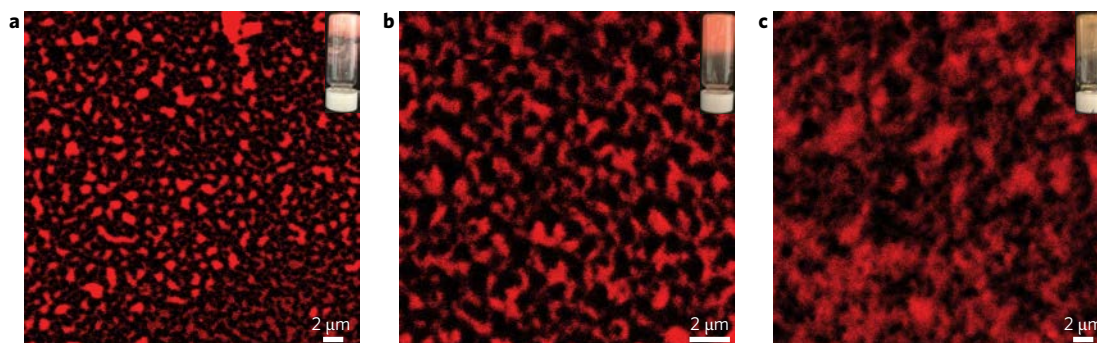
formation results in the spontaneous emulsification of toluene in a macroscopic water droplet (Supplementary Fig. 4). If a mixture of high- and low-molecular-weight functional polymers in toluene is used and the system is agitated in a vortex mixer, extended domains of oil and water form, creating a bijel. These regions have a characteristic channel diameter, of 10 μm or less, but extend far beyond the field of view accessible on a single micrograph, suggesting that the system is homogeneous, as shown in Fig. 1b,iii.

Insight into the formation mechanism and structure of these bijels is given by studying the parameters that govern their stability, structure and domain size. The particles alone are not interfacially active, and the functional polymers alone do not impart the system with the interfacial elasticity necessary to arrest coalescence. This synergistic stabilization mechanism means that reducing the concentration of either the functional polymers or the particles will increase the domain size of the system. At low particle concentrations of 0.1 mg ml<sup>-1</sup>, the system coalesces extensively (Fig. 2a,i). Increasing the particle concentration to 0.5 mg ml<sup>-1</sup> results in the stabilization of a bijel (Fig. 2a,ii). Varying the functional polymer concentration by two orders of magnitude, from 0.161 to 16.1 mmol l<sup>-1</sup>, has the effect of reducing the domain size by an order of magnitude from 10 to 1 μm (Fig. 2b,i and ii). We have also extensively probed the effect of using different mixtures of polymers of different molecular weights. We have successfully formed liquid-bicontinuous systems using a wide range of molecular weights of functional polymer ( $M_w = 1–10$  kg mol<sup>-1</sup>), a range of molar ratios of nanoparticles to polymer, and a broad scope of volumetric ratio between water and oil (Supplementary Figs 6–8). We find that the only necessary condition for the formation of these bijel structures is the use of a mixture of molecular weights of polymer, and a sufficiently high concentration of particles.

Three-dimensional laser scanning confocal microscopy demonstrates the interconnected nature of the structures. A fluorescence confocal z stack of the bijels was taken; Fig. 2c,i shows a single slice of this. An orthogonal slice of this z stack, in which



**Figure 3 | Probing the homogeneity of a small-domain bijel.** **a**, Confocal micrographs of a bijel made using high concentrations of particles ( $10 \text{ mg ml}^{-1}$ ) and PDMS-NH<sub>2</sub> ( $16.1 \text{ mmol l}^{-1}$ ) at increasing (left to right) depths within the sample. Red, toluene; black, water. **b**, Magnification of the images in **a**, generated by oversampling. **c**, Inversion of the vial containing the sample imaged in **a** and **b**.



**Figure 4 | Generalization of the bijel system.** **a–c**, Confocal fluorescence images of liquid bicontinuous systems formed by nanoparticle surfactants consisting of silica-CO<sub>2</sub>H nanoparticles ( $25 \text{ mg ml}^{-1}$ , aqueous dispersion) and PDMS-NH<sub>2</sub> ( $M_w = 1,000$  and  $3,000 \text{ g mol}^{-1}$ ,  $16.1 \text{ mmol l}^{-1}$ , in toluene) (**a**); PS-CO<sub>2</sub>H nanoparticles ( $10 \text{ mg ml}^{-1}$ , aqueous dispersion) and PS-NH<sub>2</sub> ( $M_w = 1,000$  and  $5,000 \text{ g mol}^{-1}$ ,  $16.1 \text{ mmol l}^{-1}$ , in toluene) (**b**); PS-CO<sub>2</sub>H nanoparticles ( $10 \text{ mg ml}^{-1}$ , aqueous dispersion) and PDMS-NH<sub>2</sub> ( $M_w = 1,000$  and  $3,000 \text{ g mol}^{-1}$ ,  $16.1 \text{ mmol l}^{-1}$ , in decane) (**c**). Insets: Vials containing the sample imaged in **a–c** show that the systems do not flow upon inversion.

we image  $100 \mu\text{m}$  into the system, is shown in Fig. 2c,ii. A three-dimensional reconstruction of the confocal  $z$  stacks is presented in Fig. 2c,iii. Several videos showing rotations of these three-dimensional reconstructions, of various sample thicknesses, are shown in the Supplementary Information; these clearly show the interconnected and bicontinuous nature of the structure.

Bijels are formed via arrested spinodal decomposition, yielding structures with approximately zero mean curvature<sup>20</sup>; this is achieved by using particles that wet both liquids equally and thus do not impose any curvature upon the system<sup>16,17</sup>. By contrast, our liquid-bicontinuous systems are produced using high shear rates and therefore during the initial stages of formation will consist of droplets. The bicontinuous structure of the system can be attributed to the coarsening processes that the system undergoes after being sheared—a combination of varying local curvature being imposed by the different molecular weights of functional polymer and a limited coalescence process in which the system coarsens until it reaches a critical interfacial density of particles that arrests further coalescence<sup>21</sup>. Increasing the molecular weight of the functional polymer reverses the sign of both principal radii of curvature of the nanoparticle surfactant stabilized emulsions (that is, it causes phase inversion from an oil-in-water to a water-in-oil emulsion) (Fig. 1a). The

bicontinuous system in Figs 1b,iii, 2 and 3, in which mixtures of functional polymer of different  $M_w$  are used, clearly shows regions in which the domains have both the same and differing signs of principal radii of curvature, which we attribute to the presence of the different molecular weights of polymers used (illustrated in the schematic in Fig. 1a). We believe that the different molecular weights of polymer give rise to different effective contact angles for the particles in our system, with the larger-molecular-weight polymer giving rise to effectively hydrophobic particles. This effect is not entirely unlike that described in ref. 22, in which appropriately chosen mixtures of hydrophilic and hydrophobic particles also give rise to the formation of bicontinuous structures, albeit via spinodal decomposition. The spatial distribution of particles with contact angles above and below  $90^\circ$ , both within the bijels of ref. 22 and the shear-produced bijels shown here, is an open question and clearly one of great relevance given the results shown in our work.

Increasing the concentration of both functional polymers and particles in the system allows us to probe the smallest length scale that can be produced in our liquid bicontinuous systems. In emulsions and bijels, the domain size  $d$  (for example, droplet diameter and channel width) scales with emulsifier concentration  $c$  as  $d \sim c^{-1}$  (refs 2,3,23,24). Accordingly, using  $10 \text{ mg ml}^{-1}$  PS-CO<sub>2</sub>H nanoparticles

and 16.1 mmol l<sup>-1</sup> PDMS-NH<sub>2</sub> yields a bijel structure with remarkably small domains. Imaging the system by sampling above the diffraction limit adds no information, but clarifies the image significantly, showing that the channel width in the system is ~500 nm (Fig. 3b), roughly twice the diffraction limit of the objective used. This represents a reduction in domain size of over an order of magnitude relative to the current state of the art<sup>19</sup>. Significant further reductions in channel diameter could be achieved by using more energetic homogenization methods (for example, a rotor–stator or ultrasonic probe), and we are currently investigating this by hard and soft X-ray and neutron scattering methods. If the material is a gel, it cannot flow. When inverted for one week (Fig. 3c), this fully liquid system remains intact, demonstrating the presence of a yield stress, which is further indicative of the bicontinuous nature of the system.

In comparison with bijels produced via spinodal decomposition, which require the fulfilment of several stringent criteria for successful preparation, we can readily produce bijels structures using a range of chemistries. We show that, if a mixture of molecular weights of functional polymers is used to synthesize the system, the solvents, particles and functional polymers can all be changed. We have successfully synthesized bijel structures using silica-CO<sub>2</sub>H nanoparticles (Fig. 4a), PS-CO<sub>2</sub>H nanoparticles and PS-NH<sub>2</sub> functional polymer (Fig. 4b) and decane as the non-polar phase (Fig. 4c). In previous work we have shown that nanoparticles<sup>9,10</sup>, graphene sheets<sup>25</sup> and carbon nanotubes<sup>26</sup> can all be used to form nanoparticle surfactants that impart an interfacial rigidity upon liquid–liquid systems, suggesting potential for the facile generation of bijels with functionalized interfaces, tailored to a desired application.

In conclusion, nanoparticles have been successfully applied to generate bijel structures with sub-micrometre domains, bringing them into the realm of nanotechnology. This is an essential first step in formulating them for specific industrial applications, with homogenization (or stirring, in the case of highly viscous liquids)<sup>27</sup> providing a pathway to scale-up. We have shown that the benefits are manifold: bijel generation is greatly simplified, more versatile chemistries can be used, and domain size is reduced by over an order of magnitude. We foresee diverse applications for these systems as multiphase microreactors, microfluidic devices, membrane contactors and multiscale porous materials. Furthermore, the use of stimulus-responsive nanoparticle surfactants has the potential for the generation of reconfigurable liquid bicontinuous systems that can be reshaped by an external field on demand.

## Methods

Methods and any associated references are available in the [online version of the paper](#).

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## Author contributions

C.H., J.F., B.A.H. and T.P.R. designed the study, discussed the results and commented on the manuscript. C.H. performed all the experiments and analysed all the data. C.H. and B.A.H. synthesized and characterized the PDMS-NH<sub>2</sub>. C.H., W.W., K.H. and G.S.S. synthesized and characterized the PS-NH<sub>2</sub>. All authors contributed to manuscript completion and revision.

## Additional information

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## Competing financial interests

The authors declare no competing financial interests.

## Methods

**Materials.** Crosslinked PS-CO<sub>2</sub>H nanoparticles (diameter, 16.5 nm) and silica-CO<sub>2</sub>H nanoparticles (diameter, 25 nm) were obtained as an aqueous dispersion from Microspheres-Nanospheres. The pH of the aqueous dispersions was adjusted to ~6 using 1.0 M NaOH or HCl. Monoamino-terminated polydimethylsiloxanes (PDMS-NH<sub>2</sub>,  $M_w = 1,000, 3,000, 5,000$  or  $10,000 \text{ g mol}^{-1}$ ) were synthesized using organocatalytic ring-opening polymerization with a procedure reported in our previous work<sup>28</sup>. Monoamino-terminated polystyrenes (PS-NH<sub>2</sub>,  $M_w = 1,000$  or  $5,000 \text{ g mol}^{-1}$ ) were synthesized via living anionic polymerization in a sealed glass apparatus under high-vacuum conditions ( $10^{-7}$  torr). Styrene, 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, 2-chlorobutane, benzene, hexane and diphenylethylene were purchased from Sigma Aldrich and purified under high-vacuum conditions<sup>29</sup>. Lithium, *n*-butyl lithium, tetrabutylammonium fluoride (1.0 M in THF) and Nile red were purchased from Sigma Aldrich and used as received. *Sec*-butyl lithium was prepared by reacting 2-chlorobutane with lithium metal under vacuum<sup>30</sup>. Chloroform and hexanes were purchased from Fisher Scientific and used as received. Deionized water was obtained from a Milli-Q water purification system.

**Characterization.** Proton nuclear magnetic resonance (<sup>1</sup>H NMR) was carried out on a Varian VNMRs 500 instrument. Samples were dissolved in deuterated chloroform (CDCl<sub>3</sub>). Number-average molecular weights ( $M_n$ ) and polydispersity (PDI) were measured by size exclusion chromatography in THF ( $1 \text{ ml min}^{-1}$ ) at 40 °C using a Waters Alliance 2695 separations module, three Polymer Labs PLgel 5  $\mu\text{m}$  mixed C columns in series, a Wyatt DAWN HELEOS II ambient 18-angle light-scattering detector, and a Wyatt Optilab T-rEX differential refractive index detector. Matrix-assisted laser desorption/ionization-time of flight spectroscopy (MALDI-TOF MS) measurements were obtained on a Bruker Reflex III instrument equipped with a nitrogen laser ( $\lambda = 337 \text{ nm}$ ) in reflection mode. The matrix was dithranol (>99%, Sigma Aldrich). The ratio of matrix to sample was 10:1 (in  $\text{mg ml}^{-1}$ ), with silver trifluoroacetate (>99%, Sigma Aldrich) used as the cation source. Confocal

microscopy morphologies were obtained using a Zeiss LSM 710 confocal laser scanning microscope with a Plan-Apochromat  $\times 63, 1.40$  oil-immersion objective. Three-dimensional reconstructions of the confocal *z* stacks were generated using the 3D Viewer plug-in for ImageJ<sup>31</sup>.

**Preparation of emulsions and bicontinuous liquids.** Nile red ( $0.1 \text{ mg ml}^{-1}$ ) was introduced to the toluene solution for fluorescent labelling. Emulsions or bicontinuous liquids were prepared by mixing the organic solvent phase (toluene containing PDMS-NH<sub>2</sub> in different concentrations and/or molecular weight, or containing PS-NH<sub>2</sub>; or decane containing PDMS-NH<sub>2</sub>) and the aqueous phase (deionized water containing PS-CO<sub>2</sub>H nanoparticles in different concentrations, or containing silica-CO<sub>2</sub>H nanoparticles) in different volumetric ratios and stirring vigorously by vortex at 3,200 r.p.m.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon reasonable request.

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