

Supporting information for “Particle stabilization of oil – fluorocarbon interfaces and effects on multiphase oil-in-water complex emulsion morphology and reconfigurability”

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Supplemental Video S1. Double emulsions of particle-free PFO/hexane/water (smaller droplets) were mixed with PFO/hexane/water droplets that were fabricated with Particle #9 dispersed in PFO (larger droplets) in 0.1 wt% SDS. Upon addition of 1 wt% Capstone fluorosurfactant, droplets without particles reconfigure into Janus droplets, while droplets with particles remain in the double emulsion morphology. Video speed 5x. Scale, 100 μm .

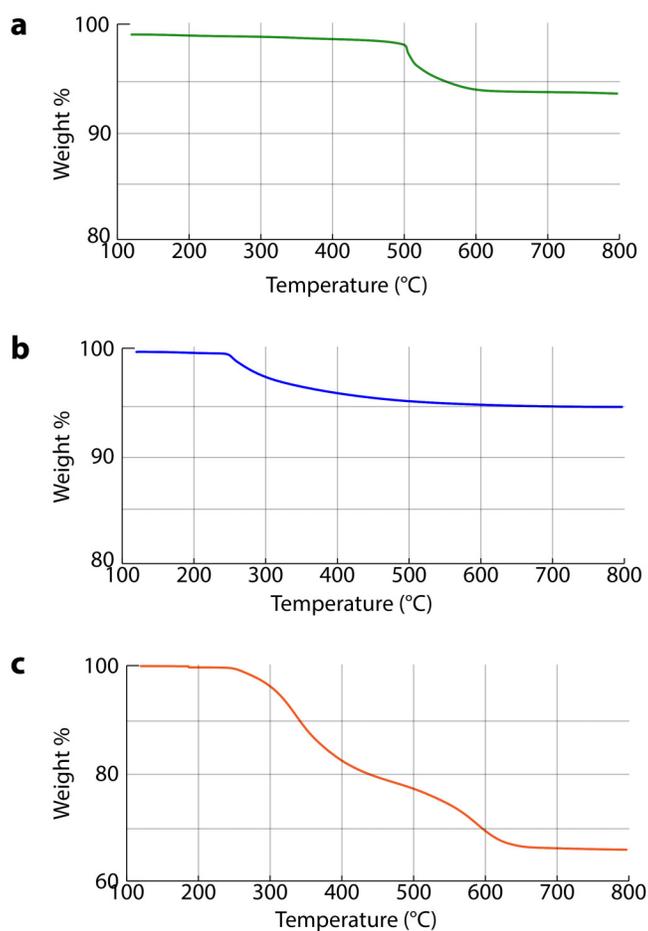


Figure S1. Thermogravimetric analysis (TGA) data of three representative particles. a-c, Three exemplary TGA traces show the mass loss of particle #5 (fluorinated particle), #3 (hexadecyl-modified particle), and #10 (bifunctional particle), respectively.

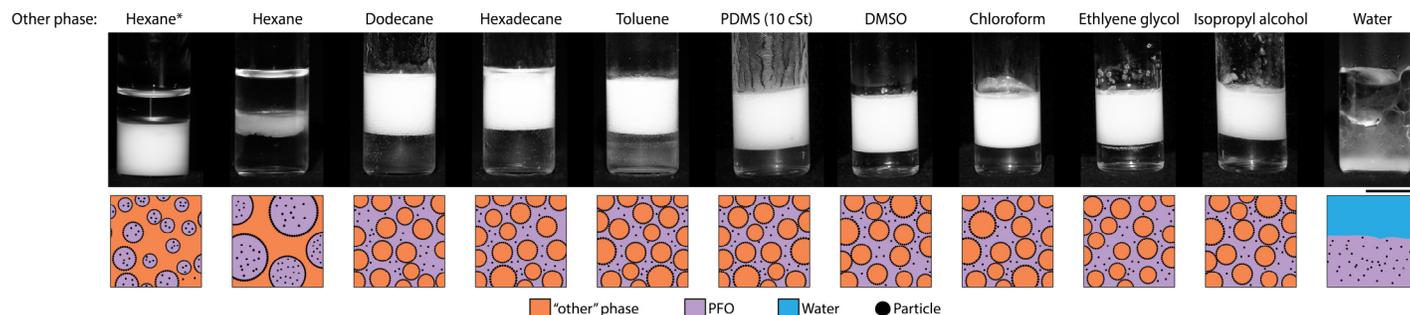


Figure S2. Stabilization of various oils or water with PFO containing biofunctional silica particles. Silica functionalized with both lipophilic and fluorophilic moieties (Particle #10, Table S1) stabilizes various hydrocarbon oils with PFO. Particle #9 behaves similarly to particle # 10. All particles were initially dispersed in PFO in 1 wt/vol% (except 3 wt/vol% for hexane*) and vortexed with the other phase in a 1:1 volume ratio. Schematic aligned beneath the vial photos pictorially represent the distribution of particles and oil phases. Vial photos were taken 15 minutes after emulsification. The water-PFO emulsion destabilizes almost immediately after emulsification. Hexane-PFO droplets at 1 wt% particles were not very stable compared to when 3 wt% particles was used. Chloroform-PFO droplets at 1 wt% particles destabilized over days as chloroform evaporated. Isopropyl alcohol-PFO emulsions destabilized slowly over two months. For the other oil combinations, droplets are stable for at least two months after initial emulsification. Scale, 1 cm.

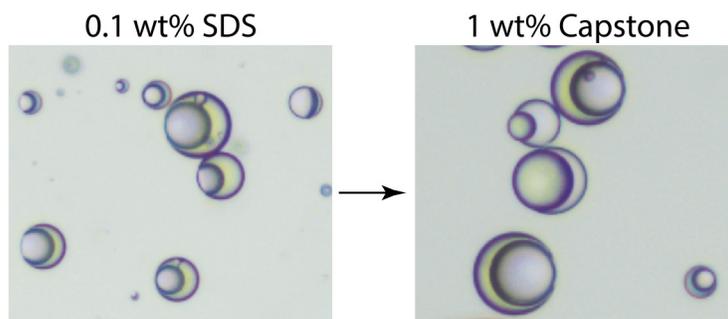


Figure S3. Hexadecane-PFO droplets with particles only reconfigure if they begin as Janus droplets. Hexadecane-PFO-water droplets in 0.1 wt% SDS prepared with 1 wt/vol% of Particle #9 as shown in Fig. 4 have a majority of PFO/hexadecane/water double emulsions, but also a small fraction of Janus droplets are found (left). Upon addition of 1% Capstone, the double emulsions do not change morphology, but Janus droplets do, resulting in a mixture of droplet shapes (right). These pictures are taken under light shaking of the droplets to tilt them on their side to better observe the fact that they are different morphologies. Scale, 50 μm .

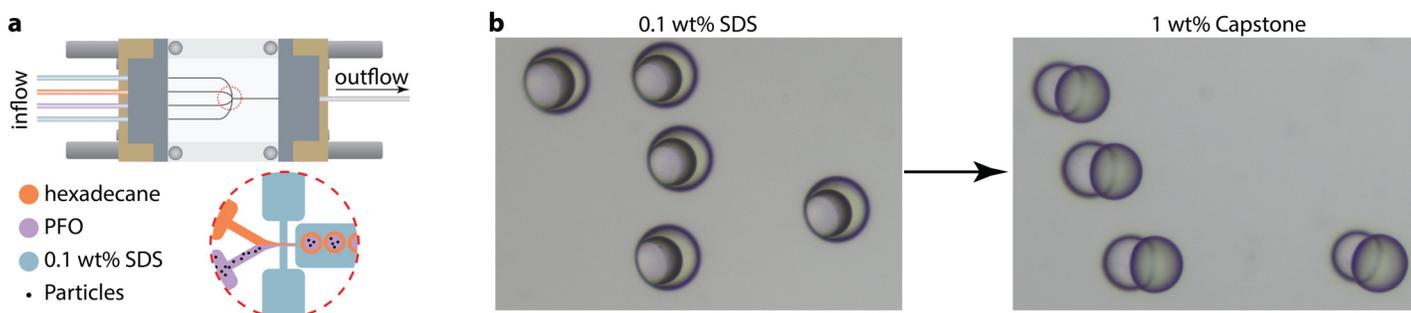


Figure S4. Microfluidic fabrication of hexadecane-PFO-water droplets and their reconfiguration. **a**, Schematic representation of microfluidic fabrication setup. 1 wt/vol% of Particle #9 was used. **b**, PFO-hexadecane droplets in 0.1 wt% SDS produced by microfluidic fabrication. Droplets start out as Janus (left) and convert a more “snowman-shaped” Janus upon addition of Capstone (right). These pictures are taken under light shaking of the droplets to tilt them on their side to better observe the fact that they are Janus. Scale, 100 μm .

Table S1. Reaction conditions for each sample characterized. H-silane is hexadecyltrimethoxysilane, and F-silane is 1H,1H,2H,2H-perfluorooctyltriethoxysilane. Normalized weight loss measured via TGA. Particle #12 is pristine H2ORH as received.

Particle #	Particle type (250 mg)	Solvent (mL)	Silane (μL)	Base (μL)	Time (min)	Wt loss (%)
1	S13	Acetone, 10	H-silane, 200	NH_4OH , 100	60	1.28
2	S13	Acetone, 10	H-silane, 600	NH_4OH , 100	60	2.26
3	S13	Acetone, 10	H-silane, 1,000	NH_4OH , 100	60	5.11
4	S13	Acetone, 10	F-silane, 25	NH_4OH , 100	60	1.43
5	S13	Acetone, 10	F-silane, 75	NH_4OH , 100	60	5.48
6	S13	Acetone, 10	F-silane, 100	NH_4OH , 100	60	13.78
7	S13	Acetone, 10	F-silane, 150	NH_4OH , 100	60	26.11
8	H2ORH	PFH, 6; Hexane, 4	F-silane, 400	Diethylamine, 200	60	15.08
9	H2ORH	PFH, 6; Hexane, 4	F-silane, 1,000	Diethylamine, 200	60	28.95
10	H2ORH	PFH, 6; Hexane, 4	F-silane, 1,200	Diethylamine, 200	60	34.09
11	H2ORH	PFH, 6; Hexane, 4	F-silane, 3,000	Diethylamine, 200	60	72.63
12	H2ORH	n/a	n/a	n/a	n/a	11.27

Method for estimating the ratio of lipophilic and fluorophilic groups on samples as reported in Fig. 3.

To create bifunctional Particles #8-11 in Table S1, we started with H2ORH particles (which already had lipophilic hexadecyl moieties as purchased) and functionalized those with fluorinated silane. We aimed to estimate the final molar ratio of lipophilic hexadecyl groups to the fluorophilic 1H,1H,2H,2H-perfluorooctyl groups on the particles. Using TGA, we measured mass loss from the pristine H2ORH and from each Particle #8-11 to yield information about degree of surface functionalization. To calculate the ratio of groups, we did as follows.

1. First, we calculated the % mass loss resultant from the fluorination on the H2ORH particle

$$\% \text{ weight loss from fluorination} = \% \text{ weight loss of bifunct. particle} - \% \text{ weight loss of H2ORH}$$

2. To compare the weight loss from fluorination to weight loss of hexadecyl groups, we converted to moles, where M_H is the moles of hexadecyl groups and M_F is moles of 1H,1H,2H,2H-perfluorooctyl groups on the bifunctional particle. However, the fluorinated triethoxysilane upon surface reaction may leave behind anywhere from zero to two unreacted ethoxy moieties that could be contributing to mass loss. To account for this in M_F , we use an average of the max and min values, as shown below.

$$M_H = \frac{\% \text{ weight loss of H2ORH}}{\text{Molar mass of hexadecyl group}}$$

$$M_F = 0.5 * \left(\frac{\% \text{ weight loss from fluorination}}{\text{Molar mass of 1H, 1H, 2H, 2H - perfluorooctyl with two ethoxy groups}} + \frac{\% \text{ weight loss from fluorination}}{\text{Molar mass of 1H, 1H, 2H, 2H - perfluorooctyl with zero ethoxy groups}} \right)$$

A sample calculation for Particle #9, where for ease of calculation, we assume as sample size of 100 g, and %mass loss of H2ORH (Particle # 12) is 11.27%:

$$M_H = \frac{11.27g}{225 \text{ g/mol}} = 0.000501 \text{ mol}$$

$$M_F = 0.5 * \left(\frac{28.95g - 11.27g}{347g/mol} + \frac{28.95g - 11.27g}{437g/mol} \right) = 0.000457 \text{ mol}$$

$$\frac{M_F}{M_H} = 0.91$$