Electronic Supplementary Material (ESI) for Chemical Communications

Micro-encapsulation using an oil-in-water-in-air "Dry Water Emulsion"

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Supporting Information

Experimental Details

Materials.

n-Dodecane (≥ 99.9 %), DiI (97 %) and Nile Blue A (dye content ~80 %) supplied by Sigma-Aldrich. DiO supplied by Invitrogen. Gellan gum (100%) supplied by Apollo Scientific. Hydrophobic silica (HDK grade H18) was kindly supplied by Wacker Chemie.

Experiments with purified dodecane (filtered through basic alumina[1]) showed no differences compared to those with fresh dodecane.

Branched copolymer surfactant synthesis. BCS synthesis was carried out as described previously, specifically sample 1 in Woodward *et al.*.[2] The branched polymer composition was $PEGMA_5/DEA_{95}$-$EGDMA_{15}$-DDT_{15}, M_n = 7400 g/mol, PDI = 2.80 (PEGMA = poly(ethylene glycol) methacrylate, M_n= 1.1 kg mol^{-1}); DEA = 2-diethylaminoethylmethacrylate ; EGDMA = ethylene glycol dimethacrylate; DDT = 1-dodecanethiol).

Preparation of emulsions. Dyed oil phases were prepared by heating *n*-dodecane and lipophilic dye to 338 K with stirring for 2 hr, before stirring overnight and filtering to remove undissolved dye (DiO, 0.4 mM, 8.0 mL; DiI, 0.08 mM, 20 mL). Aqueous phase was prepared

by dissolving BCS (3.0 wv%) in distilled water by dropwise addition of HCl (1.0 M) to pH ~2. The pH was adjusted to 8 by dropwise addition of NaOH (1.0 M). A 1.0 mL volume of aqueous phase was then combined with an equal quantity of dyed oil phase, before sonicating using a Covaris S2x Instrument (20 x 125 mm sample tube; 200 s, 277 K; duty cycle 20%, intensity 10, 500 cycles/burst; centre frequency 500 kHz, power ~70 W). In a typical DWE synthesis (DWE01), 3x 2.0 mL 50 vv% o/w emulsions thus prepared would be combined before diluting as described below. Where two dyed oil phases were required in a single emulsion (DWE02), 4x 2.0 mL emulsions were combined, two containing DiO and two DiI.

A stock solution of Nile Blue A was prepared by heating in distilled water to 333 K with stirring for 1.0 hr (0.7 mM, 10 mL), before filtering to remove undissolved dye. 1.0 mL of this stock solution was then diluted with 50.0 mL distilled water (< 0.013 mM), before adding NaOH (1 M) to pH 8. This was then added to the 50 vv% emulsion prepared above, up to a total volume equalling a 6 vv% emulsion, suitable for blending. It was necessary to remain below pH 9 however, to avoid quenching Nile Blue A fluorescence.[28]

Measurement of oil microdrop size distributions. Emulsions were characterized by laser diffraction using a Mastersizer 2000 (Malvern Instruments), equipped with a Hydro 2000 SM dispersion unit. 2-3 drops of o/w emulsion were dispersed in 100 mL distilled water at 1200 rpm. The mean volume-weighted oil microdrop diameter was calculated from at least 15 measurements.

Preparation of dry water emulsions. Hydrophobic silica (5.56 g, 10 wt% relative to emulsion) was added to 6 vv% emulsion prepared above (50.0 mL). These were blended at 16,450 rpm for 60 s (Breville, glass jug blender, BL18, 1.5 L; speed setting 1; total air volume with lid fitted estimated to be 1.7 L), to give a flowable powder.

Preparation of dry water and dry gel (DG). Stock Nile Blue A solution (5.0 mL) was added to distilled water (250 mL). Dyed DW was prepared by blending 95.0 g of this solution

with H18 silica (5.0 g, 5 wt%) at 19,000 rpm for 90 s. Dry gel was prepared by heating 99.0 g of the dilute dye solution to 323 K, before slowly adding gellan gum powder (1.0 g) with strong stirring. Following complete dissolution, the hot gel solution was combined with H18 silica (5.26 g, 5 wt%) in a pre-warmed blender jug to prevent the gel setting prior to blending, and was blended at 19,000 rpm for 90 s.

Preparation of dry gelled emulsion (DGE). 50 vv% DE01 emulsion (3x 2 mL) was prepared as above. This was warmed to 323 K for 40 min before diluting to 6 vv% by adding to dyed gellan gum solution (pH 8, 44 g, prepared as above) with strong stirring. Once fully dispersed, the gel-emulsion mixture was blended as for dry gel above.

Confocal microscopy. DWE, DW, DG & DGE were imaged using a Carl Zeiss LSM 710 microscope at 283 K, with a 100x objective lens. Images were prepared using Carl Zeiss Zen 2009 Light Edition and LSM Image Browser (v.4.2.0.121) software. A blank, undyed emulsion was imaged under the same conditions as experimental samples, showing no fluorescence, an indication that all observed fluorsecence was as a result of the dyes, and not due to background or autofluorescence.

Surface tension measurements. A Kibron Delta-8 tensiometer was used, calibrated with distilled water at ambient temperature & pressure. 50 μL samples used for each measurement; each data point was averaged over at least eight measurements.

Optical Microscopy. Optical micrographs prepared using an Olympus CX41RF Microscope, fitted with a Linkam FDCS 196 variable temperature stage, and an Olympus C-5060 digital camera.

Fluorescence spectroscopy. Fluorescence spectra were obtained on a PerkinElmer luminescence spectrometer LS55, recorded between 500 and 700 nm by excitation at 514 nm. The slit widths for excitation and emission were 10 nm and 5 nm respectively, and the scan rate was 100 $nmmin^{-1}$.

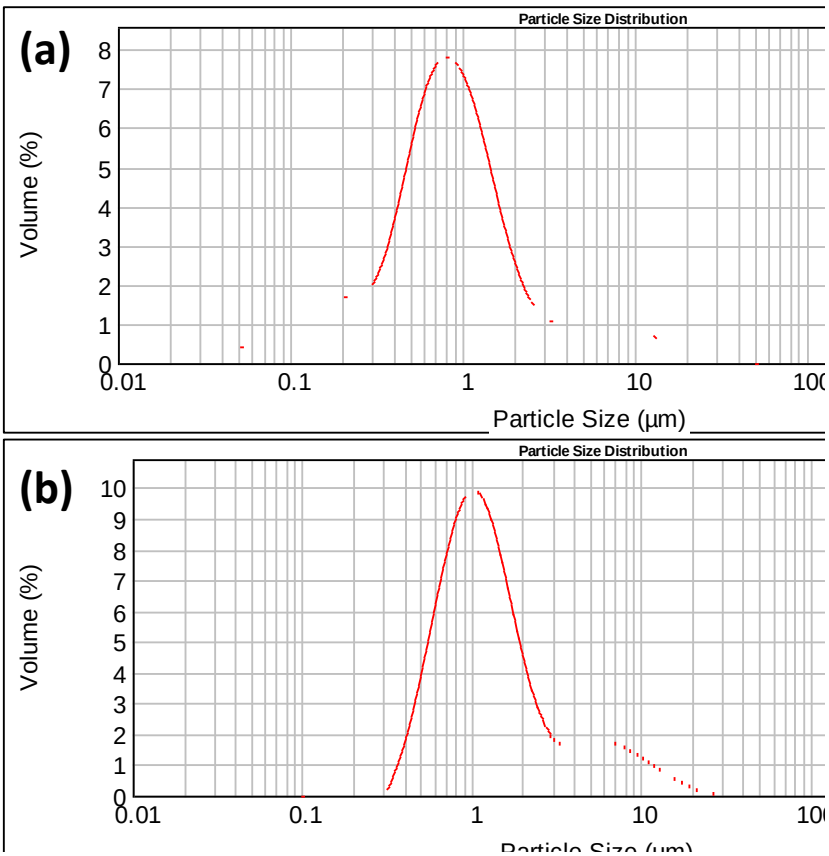

Figure S1. Oil microdroplet size distribution measurements for the following emulsions: (a) 50 vv% *n*-dodecane, in basic BCS aqueous solution; (b) 6 vv% *n*-dodecane, in basic BCS aqueous solution, following dilution of (a) with pH 8 NaOH solution.

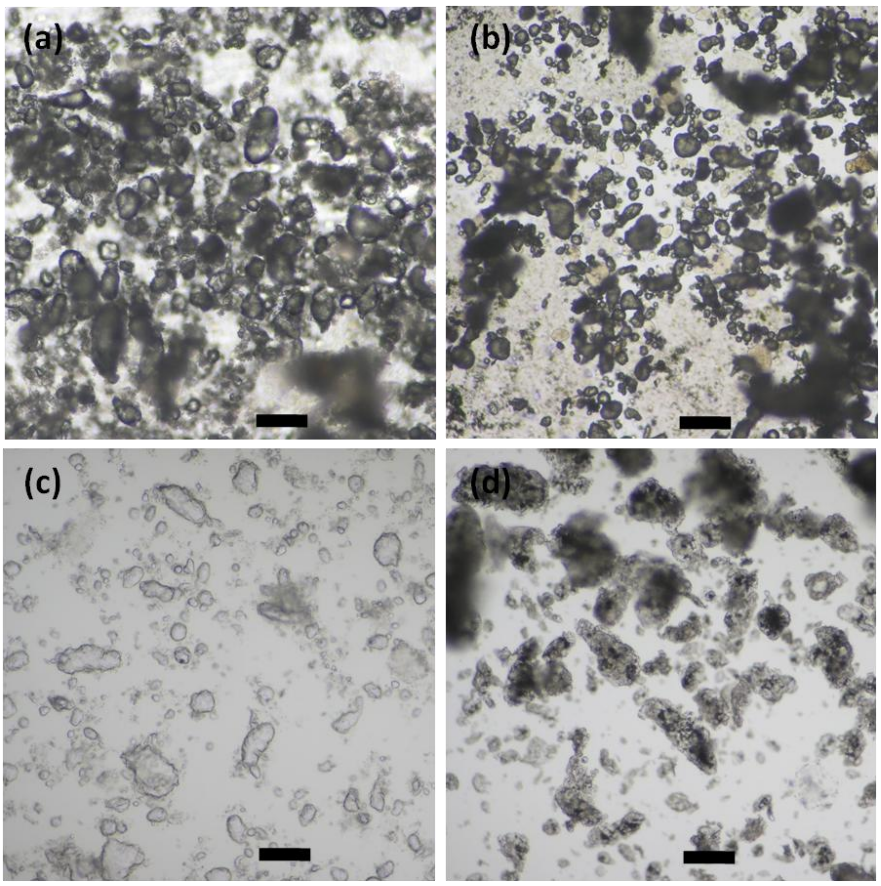

Figure S2. Optical micrographs at x100 magnification, 279 K. Scale bar = 100 μm. (a) DW (10 wt% silica), (b) undyed DE, 6vv % oil (10 wt% silica). (c) 298 K, as for (a) above, under *n*-dodecane. (d) 298 K, as for (b) above, under *n*-dodecane; note oil microdroplets visible in (d).

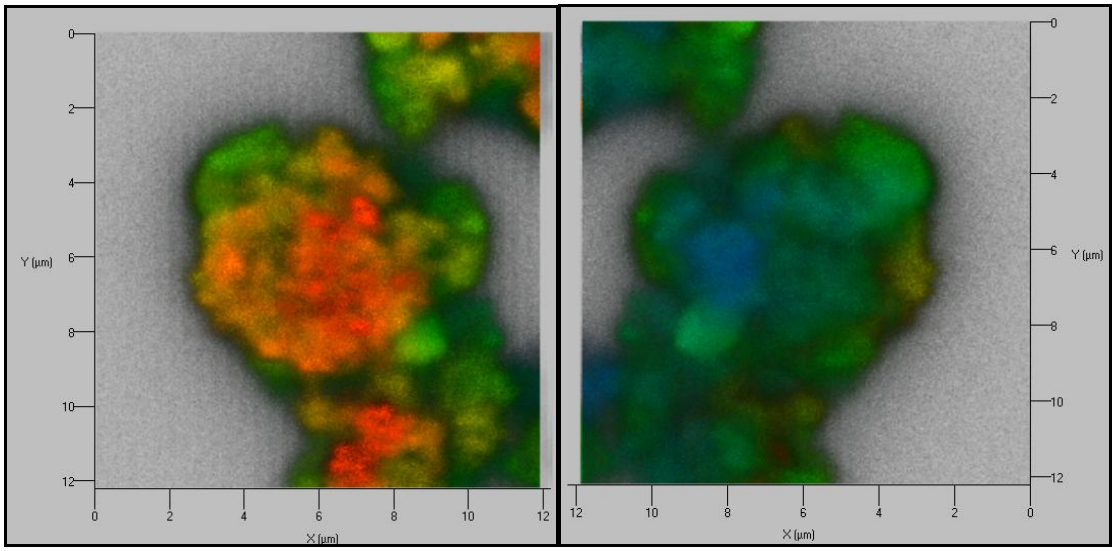

Figure S3. Depth-cued coloring applied to dry water droplet from Figure 2b, main text (closest points in black, fading to red, green and then blue (rear of image)).

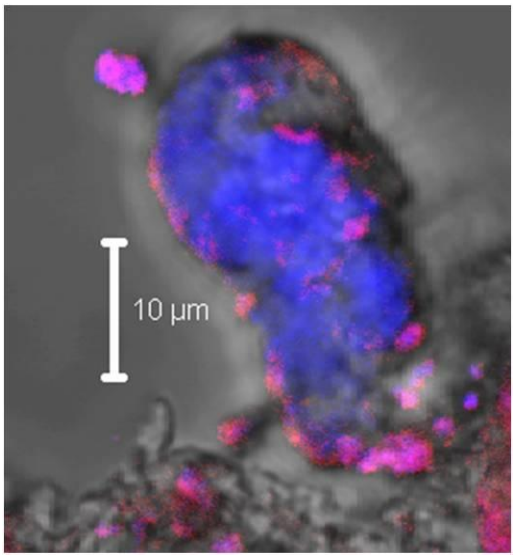

Figure S4. Confocal micrograph showing dry emulsion DE01, imaged using DiI (red, oil phase) and Nile Blue A (blue, aqueous).

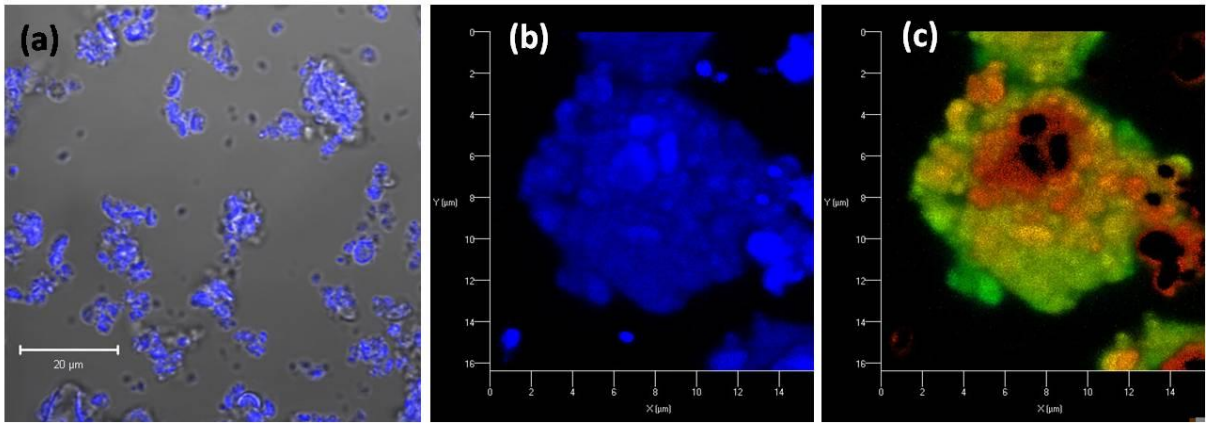

Figure S5. Dry gel, prepared using 1 wt% gellan gum solution, imaged using Nile Blue A. Shown as an overview (a), as a single droplet (b), and with depth-cued coloring (c; closest points in black, fading to red, green and then blue (rear of image)).

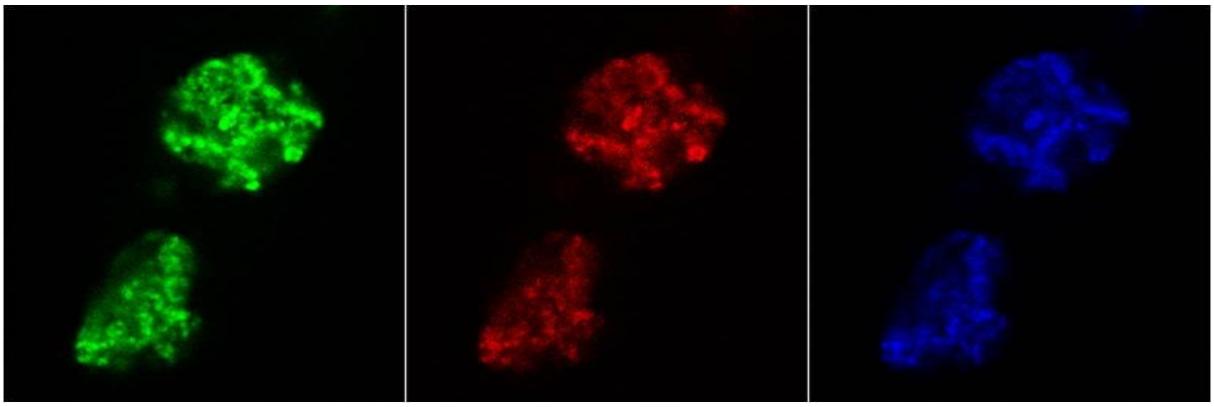

Figure S6. Confocal micrographs showing dry emulsion droplets prepared with 2 dyed oil phases and SDS surfactant, imaged using DiO, DiI (green & red, oil phases) and Nile Blue A (blue, aqueous). Phase transfer effect of SDS sees leaching of dyes into the individual phases, with regions of fluorescence overlaid to the extent that oil microdrops cannot be located accurately.

References

1. A. Goebel and K. Lunkenheimer, *Langmuir* **1997,** *13,* 369.

2. R. T. Woodward, R. A. Slater, S. Higgins, S. P. Rannard, A. I. Cooper, B. J. L. Royles, P. H. Findlay, J. V. M. Weaver, *Chem. Commun.* **2009**, 3554.