Supporting Information

Modelling the Interfacial Energy of Surfactant-free Amphiphilic Janus Nanoparticles from Phase Inversion in Pickering Emulsions

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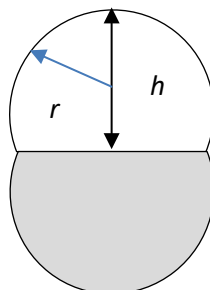## 1. Homologous series of Janus nanoparticles

Figure S1. Parameters of a Janus NP used for calculating the surface area of the lobes: r- radius and h- height of the lobe.

Table S1. Average diameters of PS- and P(3-TSPM)-lobes from *ca*. 20 nanoparticles.

JNP	Diameter of PS lobe (nm)	Diameter of P(3-TSPM) lobe (nm)	Height of PS lobe (nm)	Height of P(3-TSPM) lobe (nm)
0.5 ml 3-TSPM	140.0	89.2	103	62
1 ml 3-TSPM	140.0	108.4	109	62
2 ml 3-TSPM	140.0	167.7	88	108
3 ml 3-TSPM	140.0	192.0	82	106
4 ml 3-TSPM	140.0	229.8	90	167

Table S2. HLB numbers and aspect ratio of the homologous series of JNPs calculated from the ratio of the average values of the PS- and P(3-TSPM)-lobe surface areas. We have considered the PS lobe the non-polar lobe while the P(3-TSPM) was taken as the polar lobe.

JNP	[a]Area of PS lobe *1000 (nm^2)	[a]Area of P(3-TSPM) lobe *1000 (nm^2)	JNPs aspect ratio P(3-TSPM)/PS	[b]HLB number
0.5 ml 3-TSPM	44.6	15.5	0.35	5
1 ml 3-TSPM	41.5	18.5	0.45	6
2 ml 3-TSPM	40.4	54.1	1.34	11
3 ml 3-TSPM	38.7	60.4	1.56	12
4 ml 3-TSPM	32.6	119.4	3.66	16

[a] Calculated from $A = 2\pi Rh$, where h is the height of the lobe and R is its radius, Figure S1 and S2. [b] Calculated according to the previously reported procedure.[1]
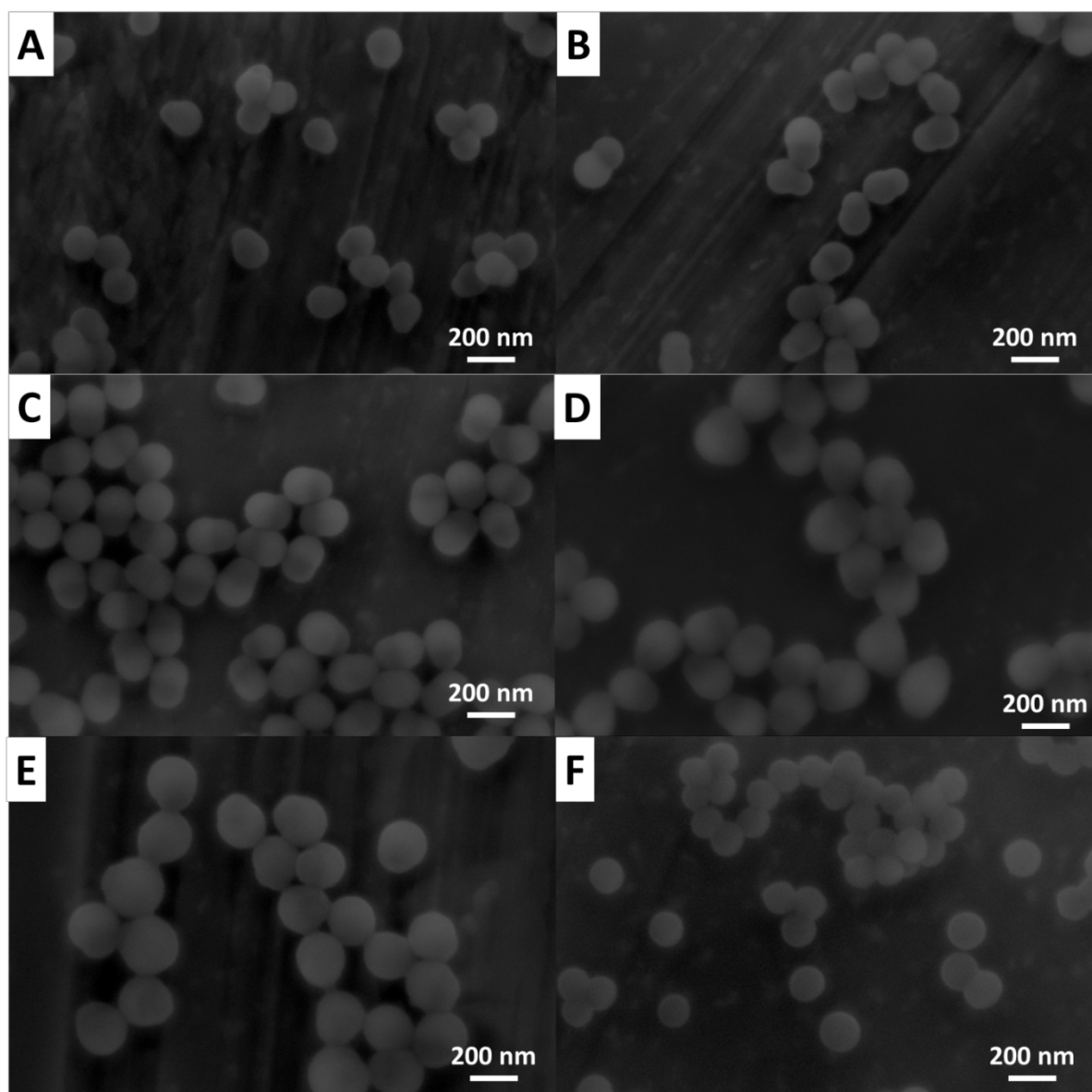

Figure S2. SEM images of the homologous series of JNPs with progressively enlarged P(3-TSPM) lobe (lighter gray/white) from the same PS seed NPs (dark gray). (A-E) JNPs with progressively larger lobes obtained for a volume of 3-TSPM monomer of (A) 0.5 mL, (B) 1 mL, (C) 2 mL, (D) 3 mL and (E) 4 mL added to 1 g of PS seed NPs. (F) PS seed NPs used in JNPs synthesis.

2. Fluorescence microscopy images of Pickering emulsions

The types of Pickering emulsion obtained as a function of oil:water ratio, JNP type and oil type are presented in Figures S1-S4 and Figure 2 in the main text. The six columns represent the emulsions conferred by each type of nanoparticle. The yellow line indicates the boundary between w/o and o/w emulsions; the vertical arrow indicates catastrophic phase inversion and the horizontal arrow represents "static" transitional phase inversion.
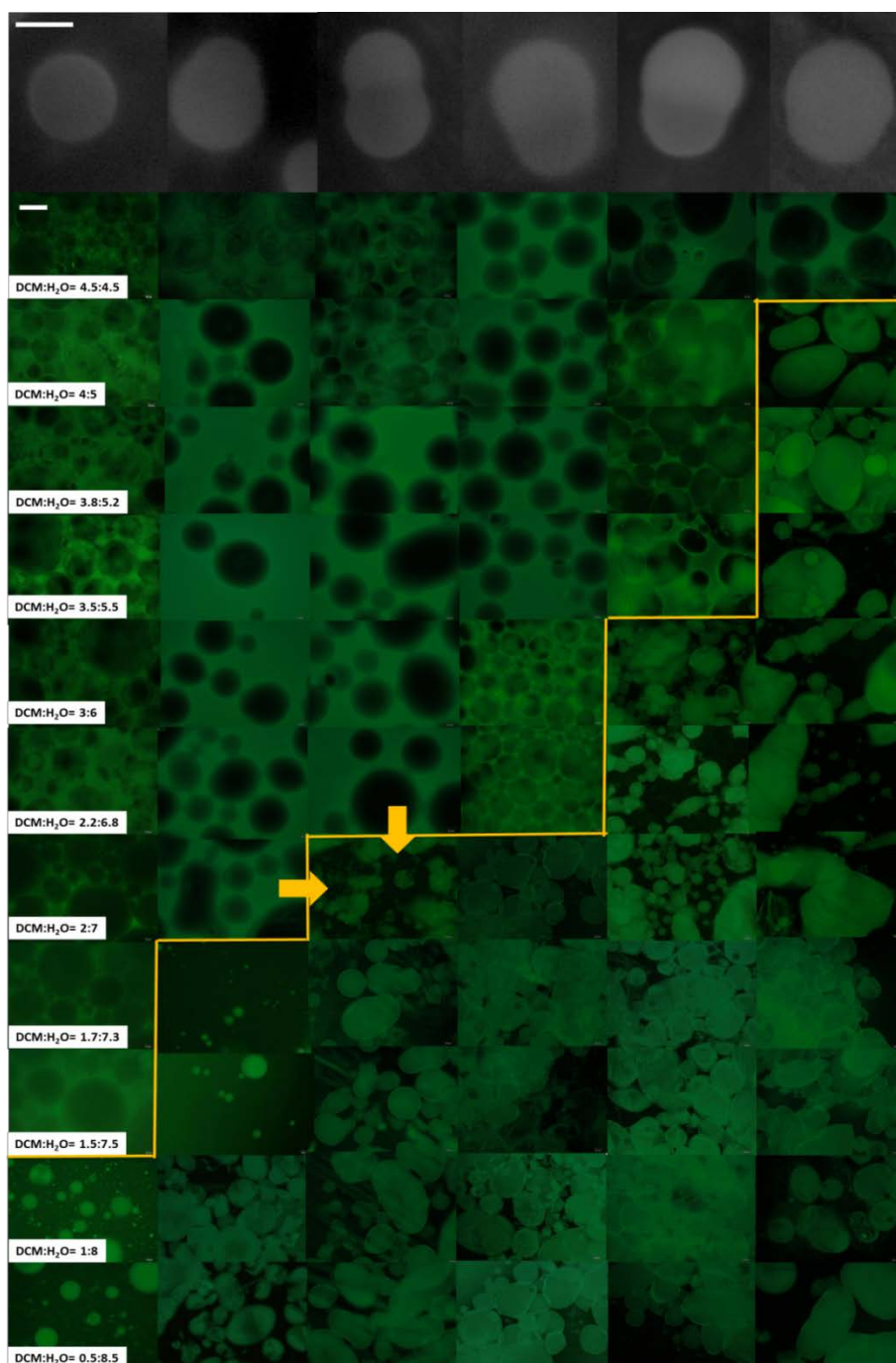

Figure S3. Formation-composition maps with corresponding fluorescence microcopy images (scale bar = 200 µm) for the Pickering emulsions obtained from DCM and water with the homologous series of JNPs.

The top row depicts PS seed nanoparticles and five JNPs with increasing P(3-TSPM) lobe sizes (scale bar = 100 nm), while the subsequent rows represent a different volume ratio of DCM to water (given).
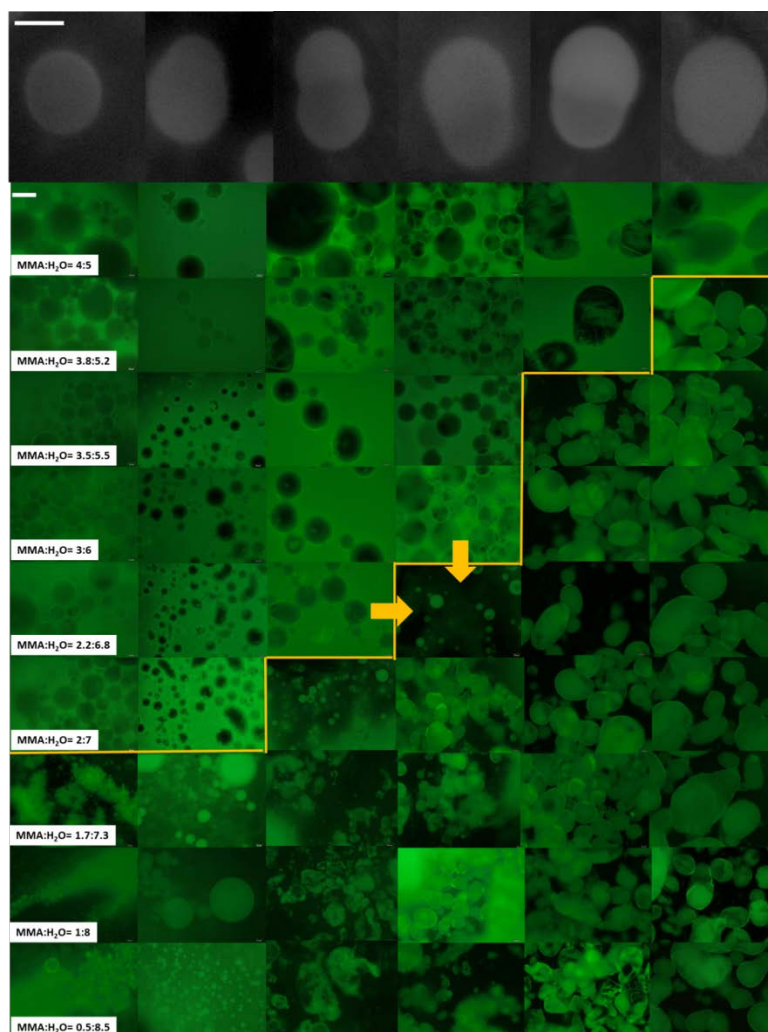

Figure S4. Formation-composition maps with corresponding fluorescence microcopy images (scale bar = 200 µm) for the Pickering emulsions obtained from MMA and water with the homologous series of JNPs. The top row depicts PS seed nanoparticles and five JNPs with increasing P(3-TSPM) lobe sizes (scale bar = 100 nm), while the subsequent three rows represent a different volume ratio of MMA to water (given).
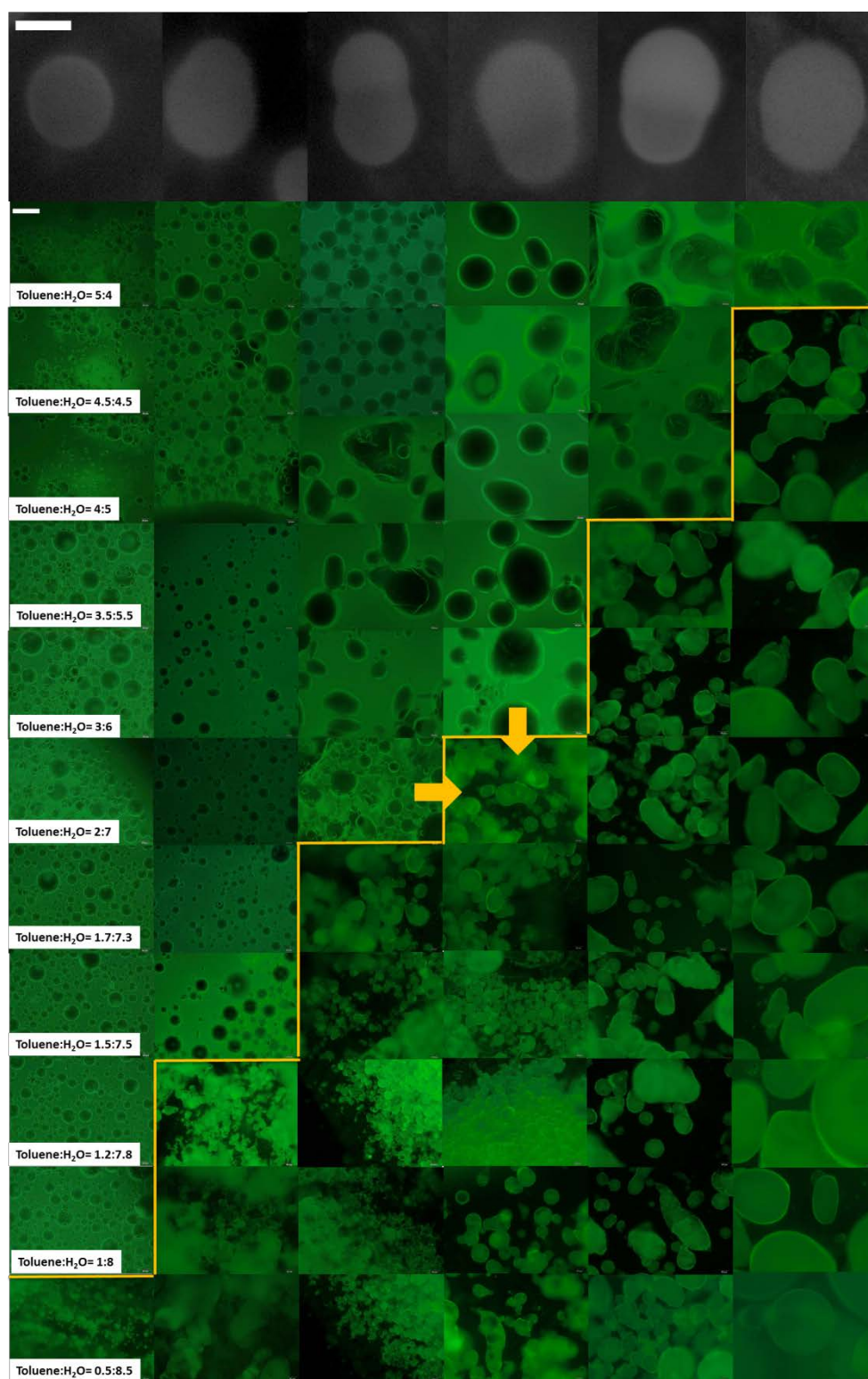
Figure S5. Formation-composition maps with corresponding fluorescence microcopy images (scale bar = 200 µm) for the Pickering emulsions obtained from toluene (Tol) and water with the homologous series of JNPs. The top row depicts PS seed nanoparticles and five JNPs with increasing P(3-TSPM) lobe sizes (scale bar = 100 nm), while the subsequent three rows represent a different volume ratio of toluene to water (given).
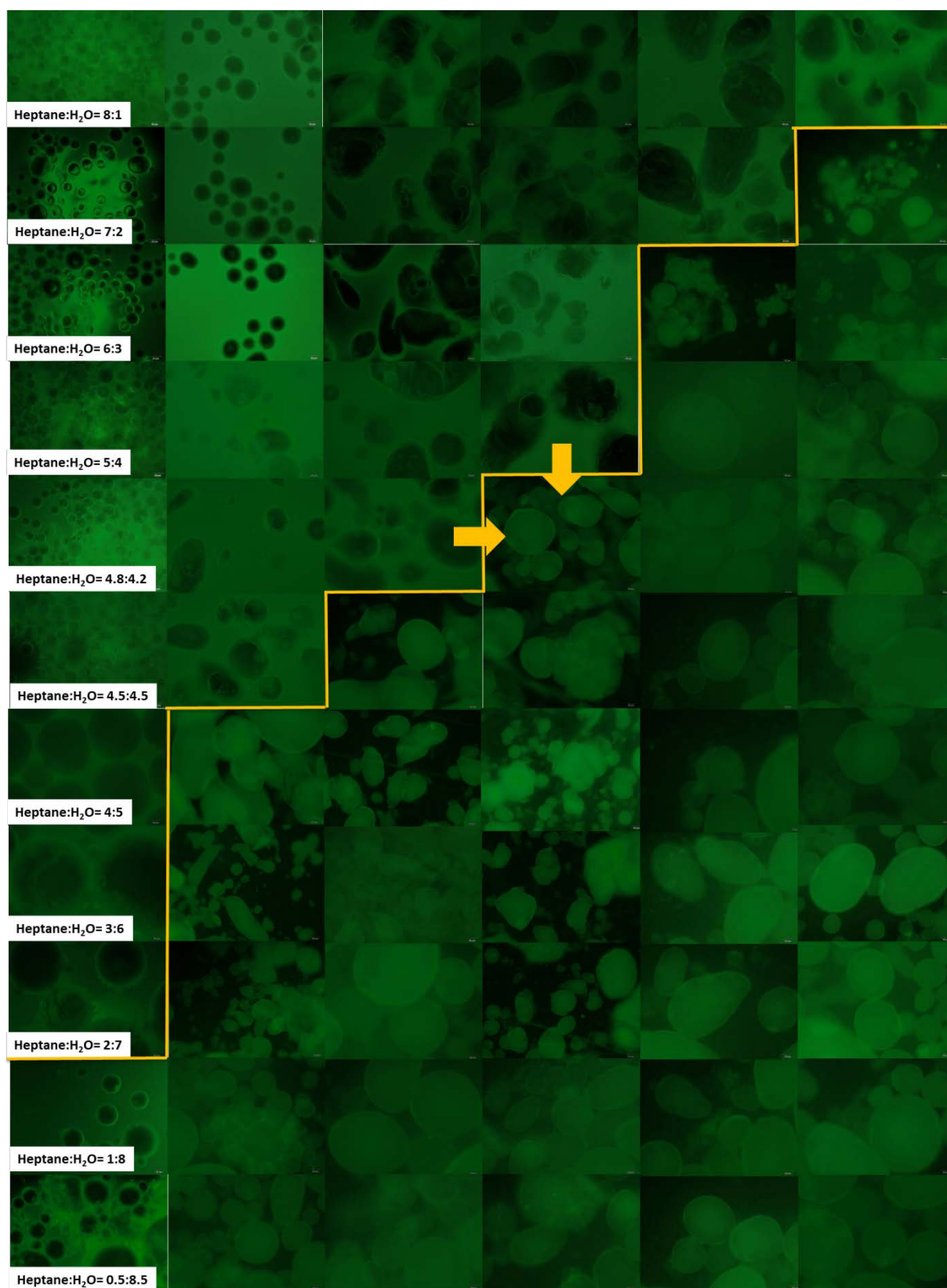
5

Figure S6. Formation-composition maps with corresponding fluorescence microcopy images (scale bar = 200 μm) for the Pickering emulsions obtained from heptane (Hep) and water with the homologous series of JNPs. The top row depicts PS seed nanoparticles and five JNPs with increasing P(3-TSPM) lobe sizes (scale bar = 100 nm), while the subsequent three rows represent a different volume ratio of heptane to water (given). Note that the emulsions formed at Hep:water 0.5:8.5 and 1:8 ratios are o/w emulsions but this is

difficult to see in fluorescence imaging due to strong foaming and air bubble incorporation that also appear dark in the image, therefore the emulsion phase boundary was assumed at a 2:7 ratio.
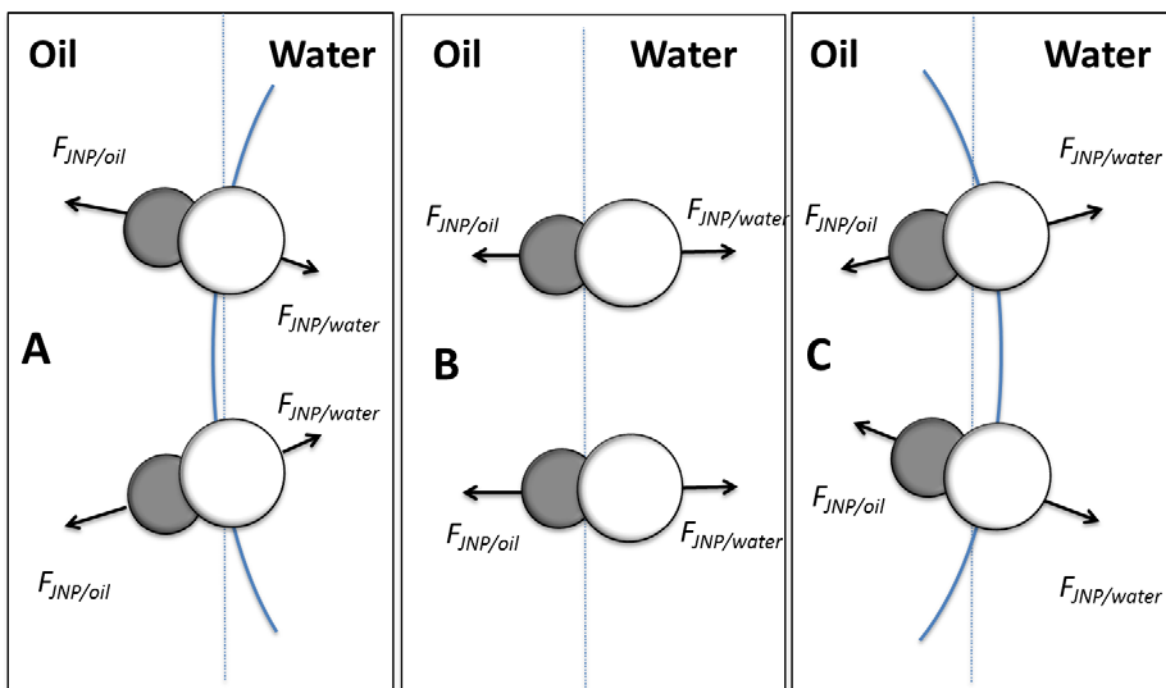

Figure S7. The balance between the adhesion force vectors $F_{JNP/water}$ and $F_{JNP/oil}$ determines the curvature of the interface. (A) If the adhesion of the JNP to the oil is much stronger than to water then the oil-water interface is concave on the water side and thus w/o emulsions are formed as observed above the curves in Figure 2 in the main text; (B) if the balance of adhesion forces remains equal then the oil-water interface remains flat and (C) if the adhesion of the JNP to water is much stronger than to oil the interface is concave on the oil side thus o/w emulsions will result as observed below the curves in Figure 2 in the main text.

Here we note that the representation of adhesion forces tension perpendicular to the interface in Figure S7 is partly justified by the fact that the interfacial tension can be regarded both as a force mN/m (that can be treated purely mechanic) and as an energy mJ/m^2 (that can be treated purely thermodynamically). Because of this the Dupre's formalism between two interfaces can be written in two equivalent ways: $\gamma_{12} = \gamma_1 + \gamma_2 - 2F_a$ (units of force) where F_a is the adhesion force oriented perpendicular to the interface and secondly by the work of adhesion: $\gamma_{12} = \gamma_1 + \gamma_2 - W_{adh}$ (units of energy).
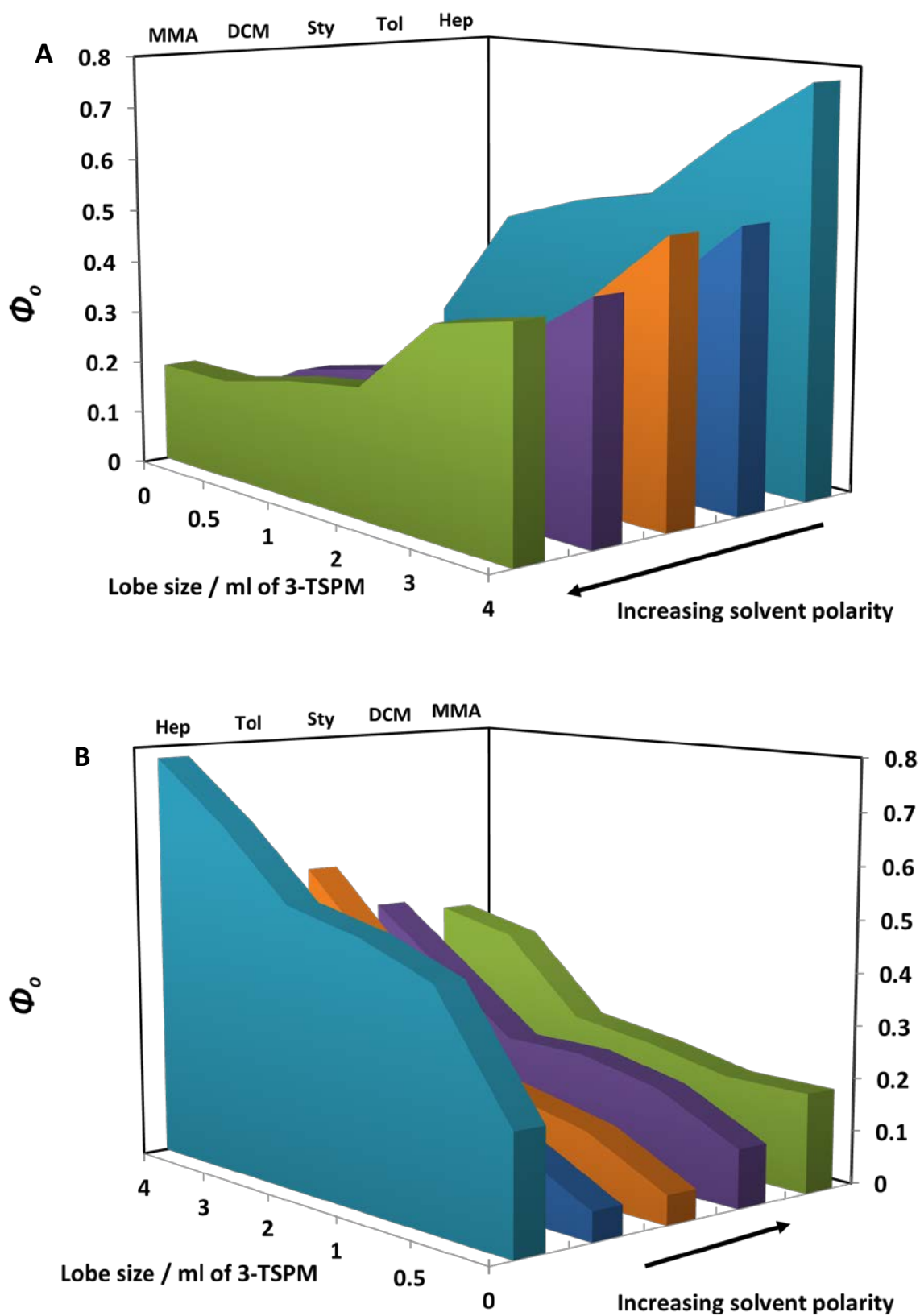
Figure S8. 3-D representation of the emulsion phase boundary curve relating the oil volume fraction, solvent polarity and JNP lobe size. The solvent order was ranked according to increasing polarity from Hep to MMA. The two different perspective of the same graphic depict the way the emulsion phase boundary depends on solvent polarity; two extreme situations can be observed (A) ϕ_o decreases with increasing solvent polarity

for the most polar particles ((4 mL 3-TSPM) JNPs) and (B) ϕ_o increases with increasing solvent polarity for the least polar particles (0.5 mL 3-TSPM) JNPs (exception for Hep).

3. Solvent properties

Table S3. Hansen parameters and solubility of the solvents used in water.

Solvent \ Hansen parameter [a]	H_D	H_P	H_{H-H}	h [b]	Solubility in water (g/L)[c]	Surface tension (mN/m)[e]	Interfacial tension with water (mN/m)[e]
Methyl methacrylate	15.8	6.5	5.4	0.43	15.8	24.2[d]	14.7
Dichloromethane	18.2	6.3	6.1	0.41	17.6	27.2[c]	23.6
Styrene	18.6	1	4.1	0.22	0.32	32.0[d]	25.4
Toluene	18	1.4	2	0.16	0.54	27.7[c]	35.8
Heptane	15.3	0	0	0	0.0024	19.7[c]	50.8

[a] Hansen parameters are typically defined as the cohesion energy divided by the molar volume V_M, where the total cohesion energy E is the sum of the contributions of the dispersive interaction E_D, polar interaction E_P and hydrogen bond interaction E_{H-H}, values taken from ref. 2; [b] $h = \frac{H_P + H_{H-H}}{H_D + H_P + H_{H-H}}$; [c] At 20 °C taken from ref. 3; [d] Taken from ref. 4; [e] Measured at 21° C.

Table S4. Calculated interfacial energies based on equation 5 as a function of the lobe size of the JNP for different oils.

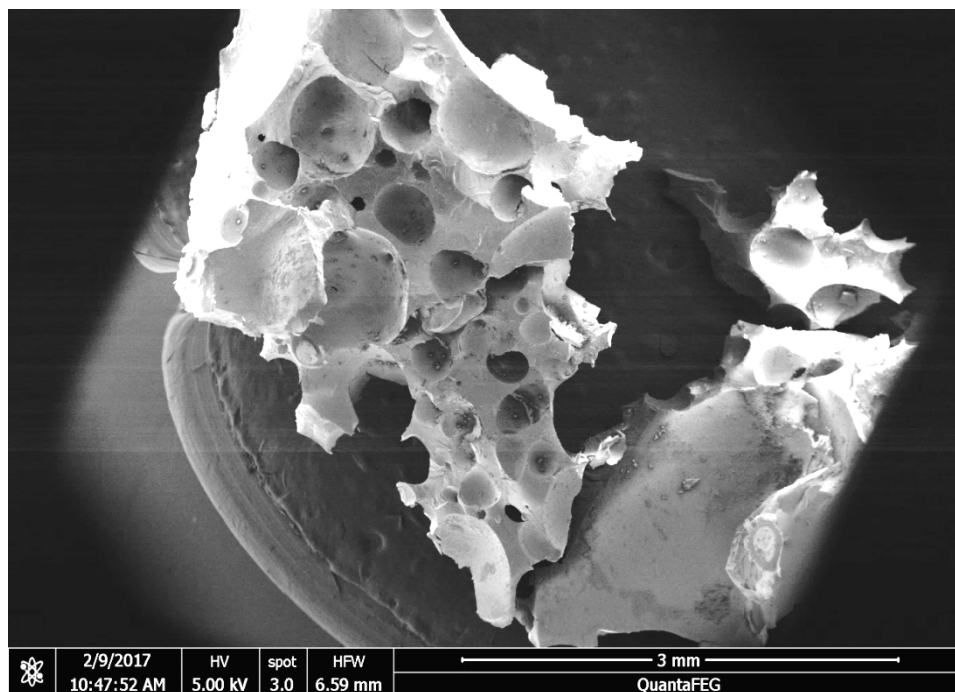| JNP lobe size	Interfacial energy (mN/m)					
	Water/NP	DCM/JNP	MMA/JNP	Sty/JNP	Tol/JNP	Hep/JNP
PS seed	16.8	11.6	18.2	9.2	0.0	1.8
0.5 ml 3-TSPM	15.1	9.9	15.4	7.6	0.0	11.2
1 ml 3-TSPM	13.7	8.2	13.2	6.0	0.0	13.7
2 ml 3-TSPM	12.8	6.8	11.8	5.2	0.0	15.3
3 ml 3-TSPM	6.5	0.8	4.7	2.3	0.0	21.3
4 ml 3-TSPM	3.1	0.9	1.4	4.6	5.3	29.6

4. Polymerization of w/o Pickering emulsion

Figure S9. SEM image showing the hollow structure material resulting from the polymerization of the w/o Pickering emulsion obtained at an MMA: water ratio = 5: 4 with (2 mL 3-TSPM) JNPs.

References

(1) Wu, D.; Chew, J. W.; Honciuc, A. Polarity Reversal in Homologous Series of Surfactant-Free Janus Nanoparticles: Toward the Next Generation of Amphiphiles. *Langmuir*, **2016**, *32*, 6376–6386.
(2) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*, 2nd ed.; CRC Press: Boca Raton, 2007.
(3) *CRC Handbook of Chemistry and Physics*, 90th ed.; Lide R. David, Ed.; CRC Press: Boca Raton, 2009.
(4) Diversified Enterprises. Surface Energy Data for PS: Polystyrene https://www.accudynetest.com/polymer_surface_data/polystyrene.pdf (accessed Nov 30, 2016).