ESI

Pickering Emulsions Stabilized by Coloured Organic Pigment Particles

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Table S1. Elemental composition of the seven pure pigments.

Element	Composition/wt.%						
	PR	PO	PY	PG	PB	PI	PV
C	55.68	43.55	50.88	39.85	61.29	63.06	72.74
O	26.51	25.40	11.92	0.91	0.63	21.26	13.77
N	17.71	31.04	6.63	13.30	24.30	15.47	13.28
S	0.04	0.00	0.02	0.08	0.00	0.00	0.14
Cl	0.06	0.00	30.53	42.10	3.20	0.21	0.07
Al	0.00	0.01	0.02	0.25	0.00	0.00	0.00
Cu	0.00	0.00	0.00	3.51	10.58	0.00	0.00

Table S2. Values of the maximum wavelength and absorbance for each pigment (0.1 mg/ml) measured at room temperature in water and *n*-heptane for the unfiltered dispersion and its supernatant.

	***n*-Heptane**				**Water**			
Pigment	Dispersion		Supernatant		Dispersion		Supernatant	
	λ_{max}/nm	Abs.	λ_{max}/nm	Abs.	λ_{max}/nm	Abs.	λ_{max} /nm	Abs.
PR	600	0.133	351	0.106	607	0.292	364	0.094
PO	347	0.084	351	0.068	547	0.406	476	0.249
PY	490	0.022	352	0.148	479	0.108	465	0.062
PG	675	0.131	370	0.048	670	0.096	370	0.071
PB	647	0.424	410	0.047	384	0.177	370	0.096
PI	646	0.084	435	0.048	660	0.106	430	0.075
PV	610	0.107	610	0.039	610	0.098	590	0.060

Table S3. Values of apparent extinction coefficient for the seven pigments in water and *n*-heptane.

	***n*-Heptane**	**Water**
Pigment	ε/(mg/ml)$^{-1}$ cm^{-1}	ε/(mg/ml)$^{-1}$ cm^{-1}
PR	2.5	2.1
PO	0.3	28
PY	3.4	1.3
PG	6.7	2.4
PB	8.3	2.6
PI	1.2	0.8
PV	1.0	1.0

Figure S1. SEM images for the seven pigments at low magnification for (a) PR, (b) PO, (c) PY, (d) PG, (e) PB, (f) PI, (g) PV.

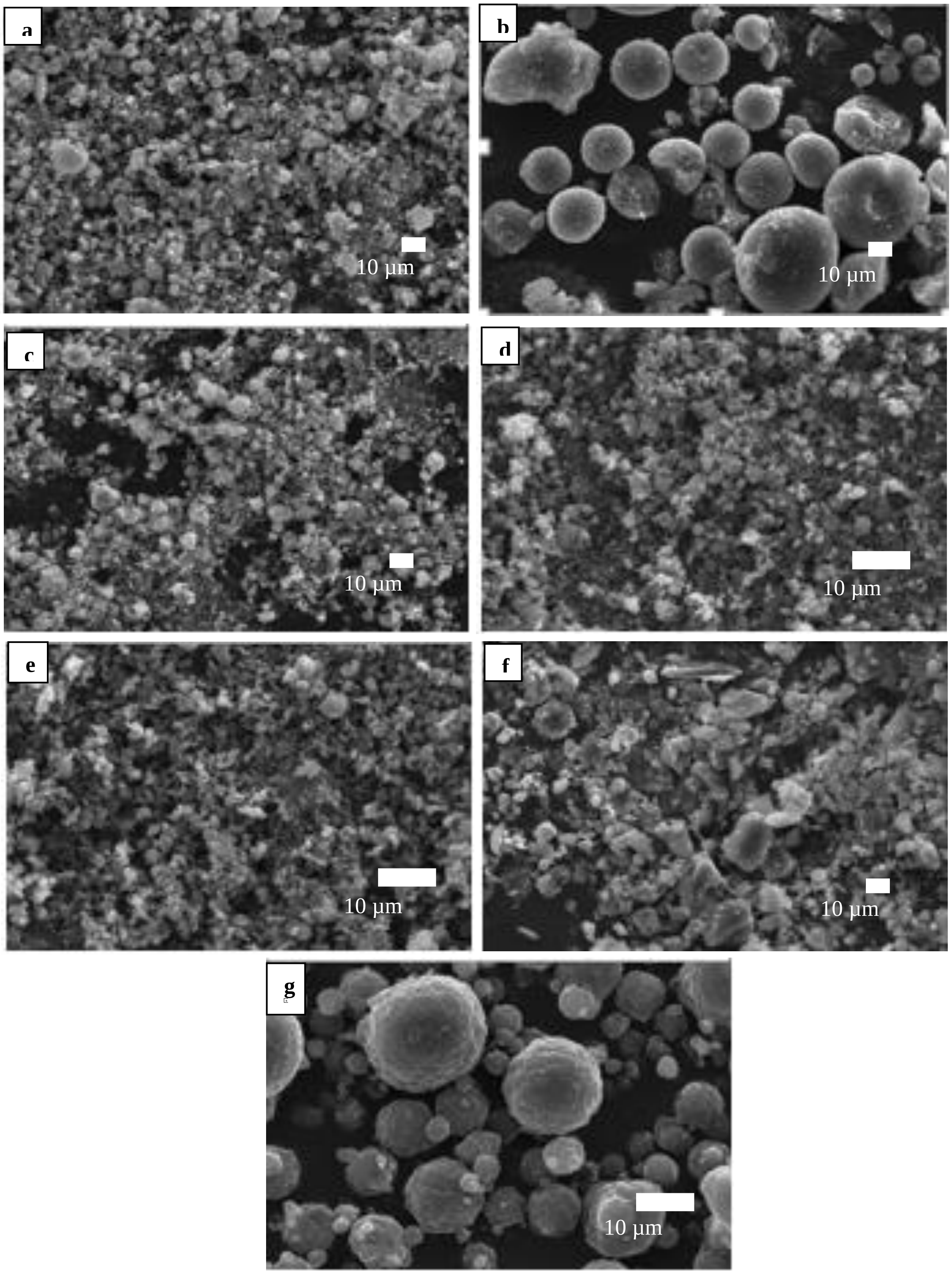


Figure S2. EDX spectra for the seven pigments for (a) PR, (b) PO, (c) PY, (d) PG, (e) PB, (f) PI, (g) PV.

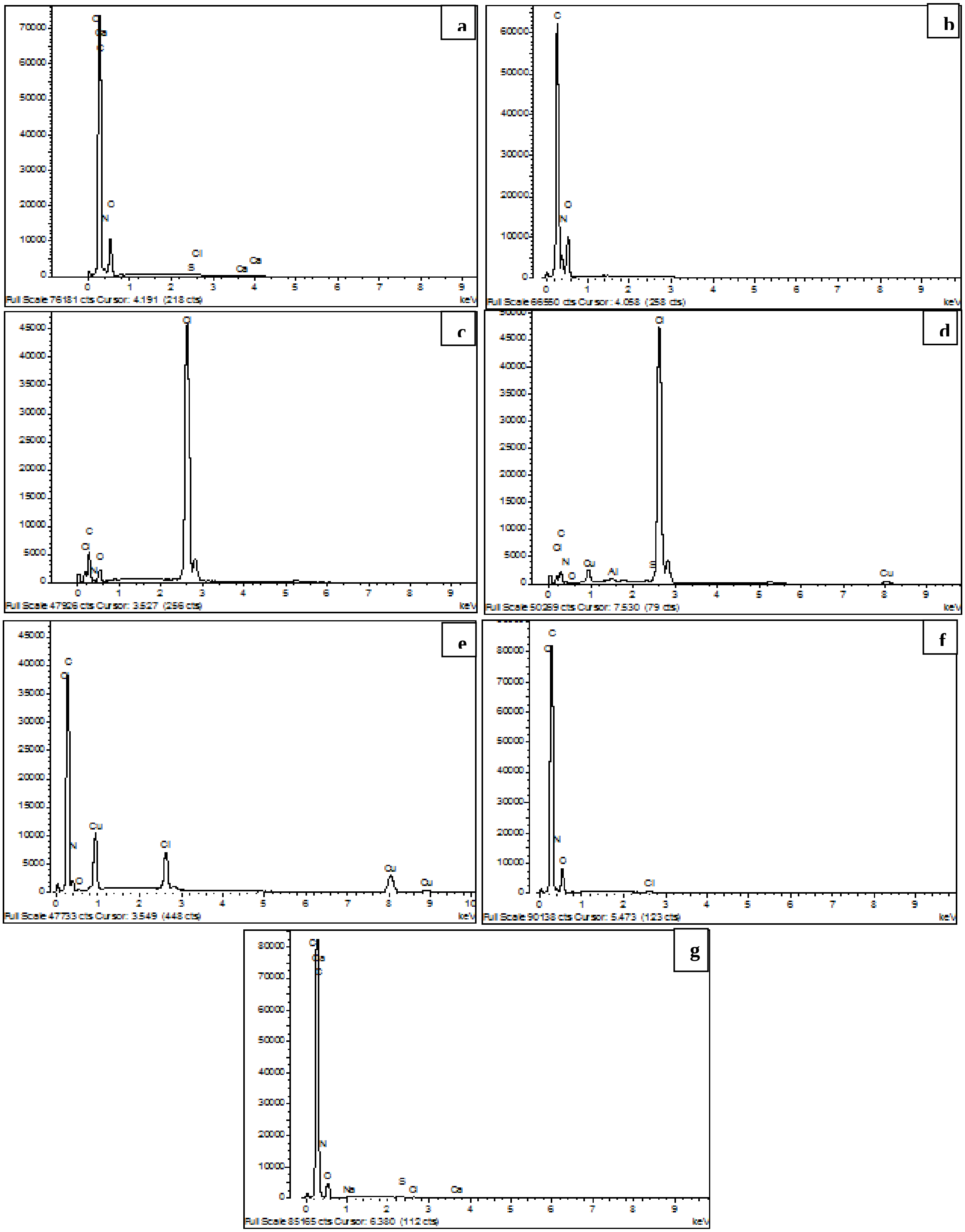
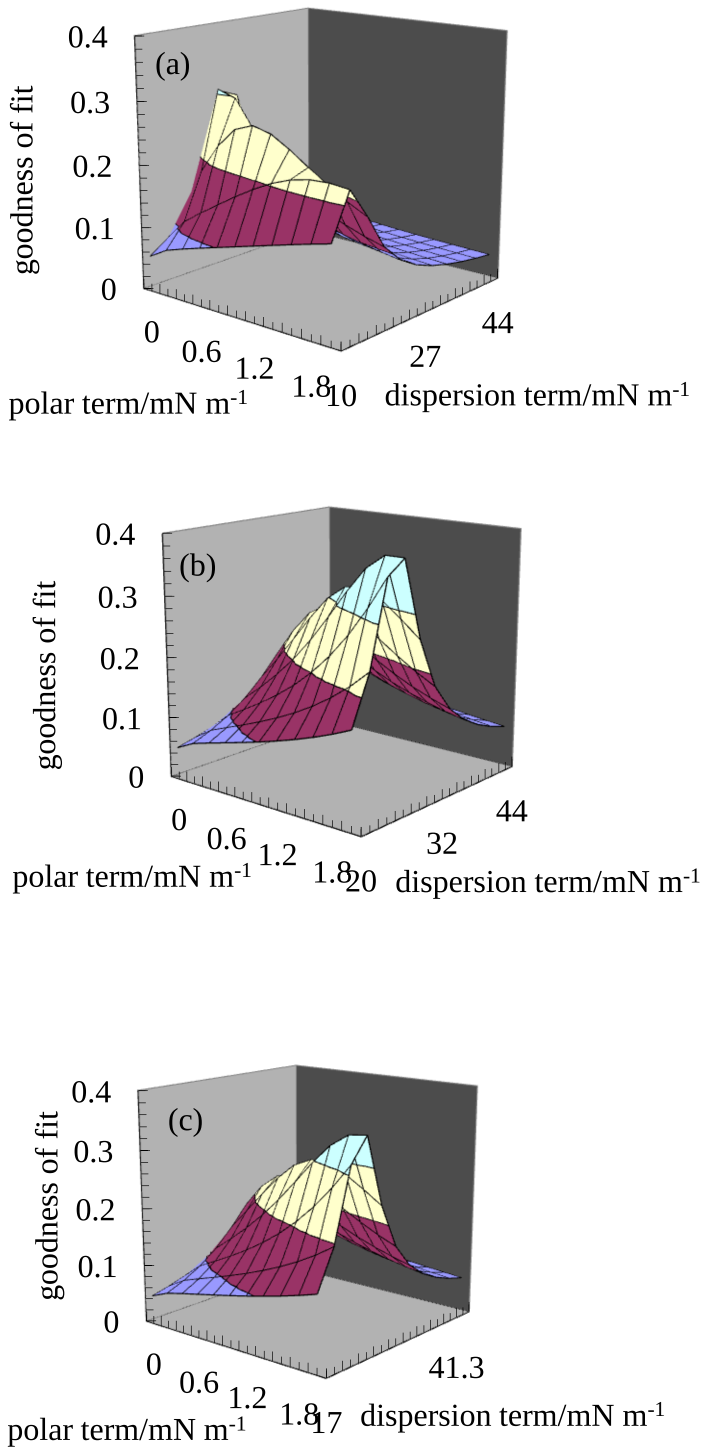


Figure S3. 3-D surface energy diagrams for pigment particles determined at various values of γ_{sa}^{d} and γ_{sa}^{p} for (a) PY, (b) PG, (c) PB, (d) PI.



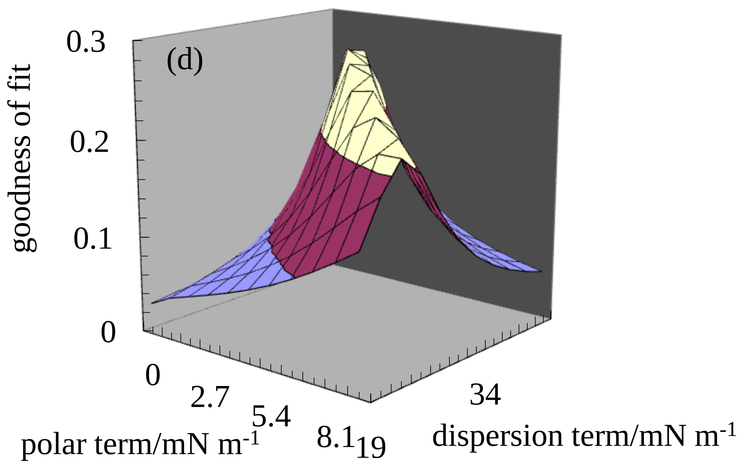
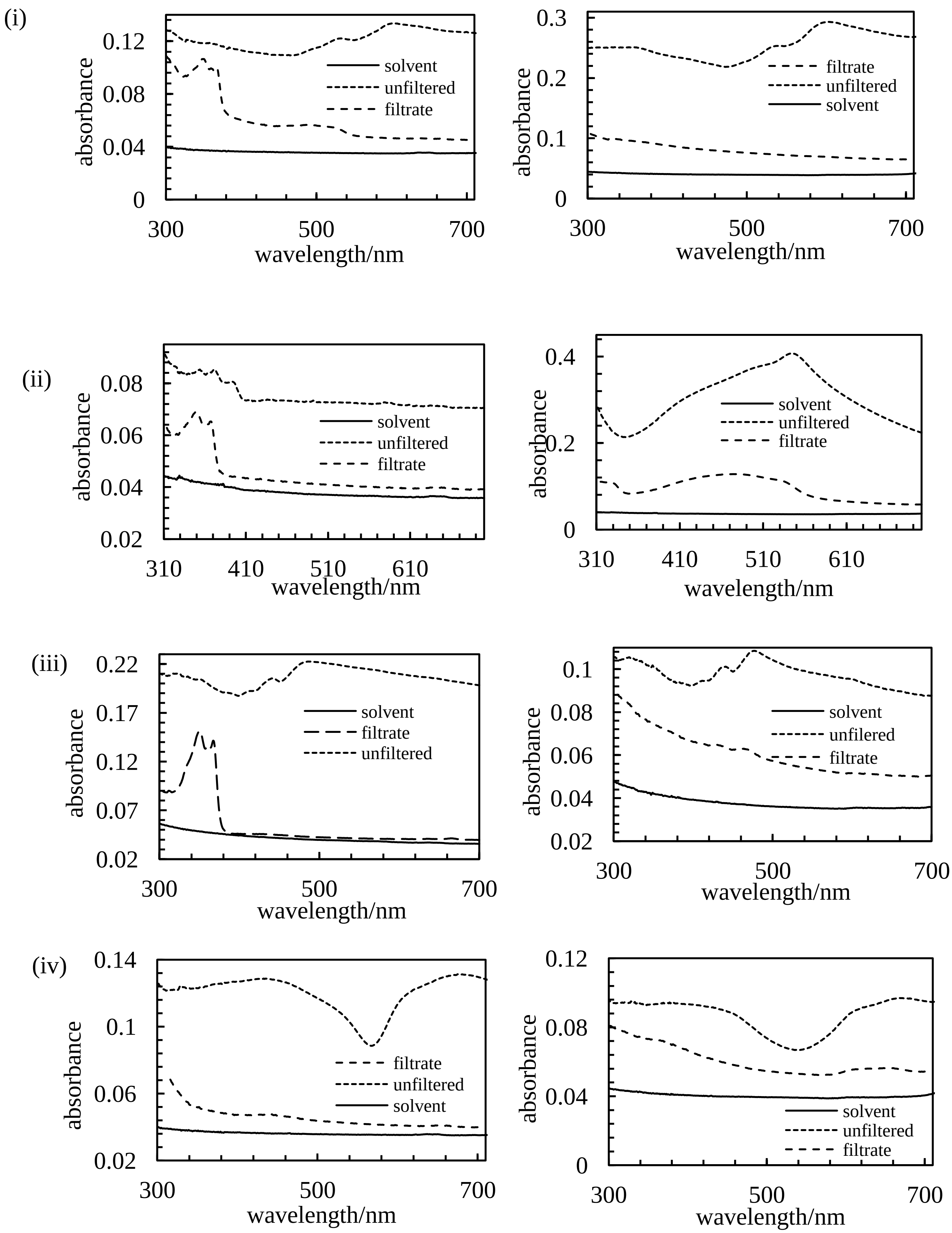
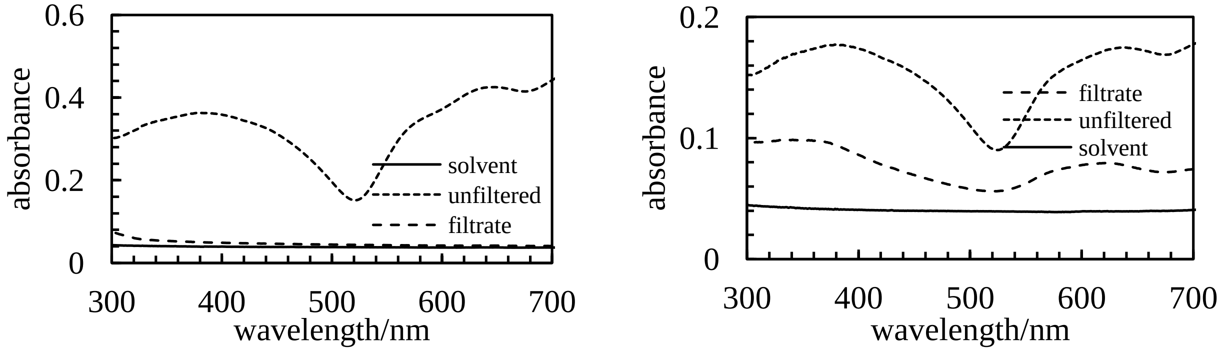

(d)
goodness of fit
0.3
0.2
0.1
0
0
2.7
5.4
8.1
19
34
polar term/mN m-1
dispersion term/mN m-1

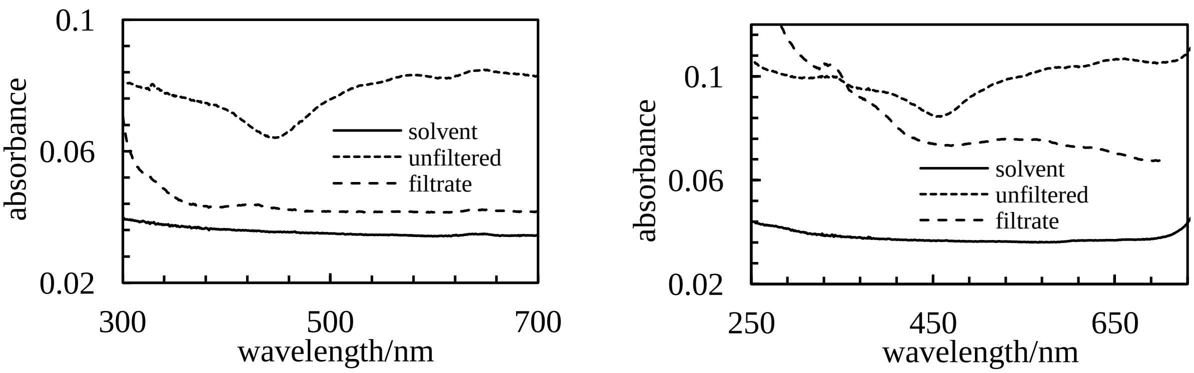
Figure S4. Graphs of absorbance against wavelength determined with 0.1 mg/ml of each pigment dispersion and its supernatant in *n*-heptane (left column) and water (right column) for (i) PR, (ii) PO, (iii) PY, (iv) PG, (v) PB, (vi) PI and (vii) PV.



(v)


0.6
0.4
0.2
0
absorbance
300
400
500
600
700
wavelength/nm
solvent
unfiltered
filtrate
0.2
0.1
0
absorbance
300
400
500
600
700
wavelength/nm
filtrate
unfiltered
solvent

(vi)


0.1
0.06
0.02
absorbance
300
500
700
wavelength/nm
solvent
unfiltered
filtrate
0.1
0.06
0.02
absorbance
250
450
650
wavelength/nm
solvent
unfiltered
filtrate

(vii)

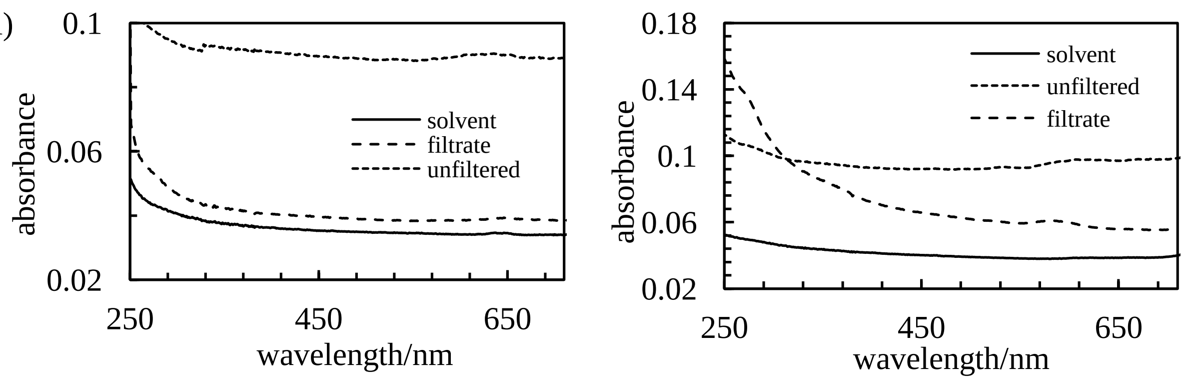
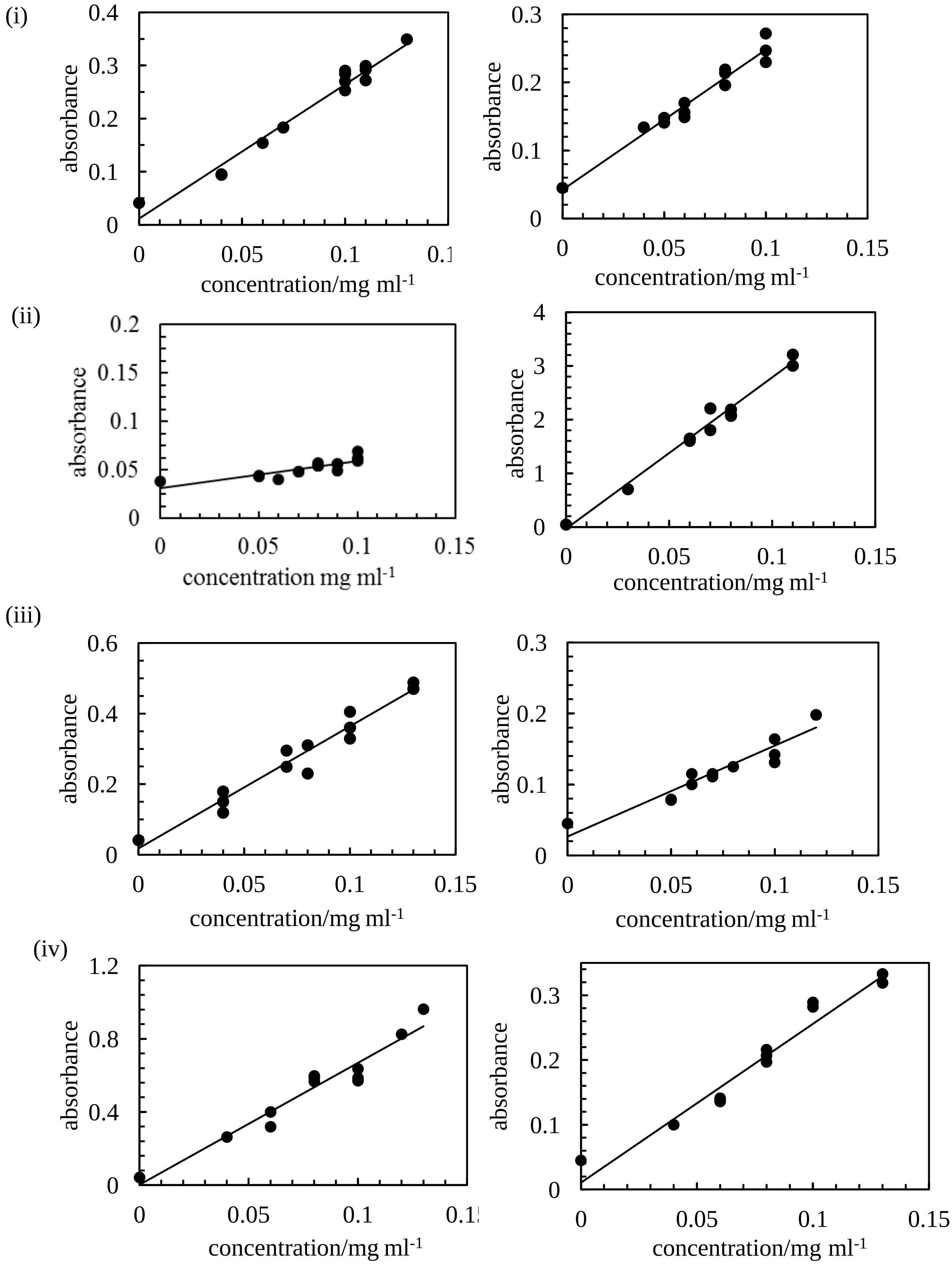
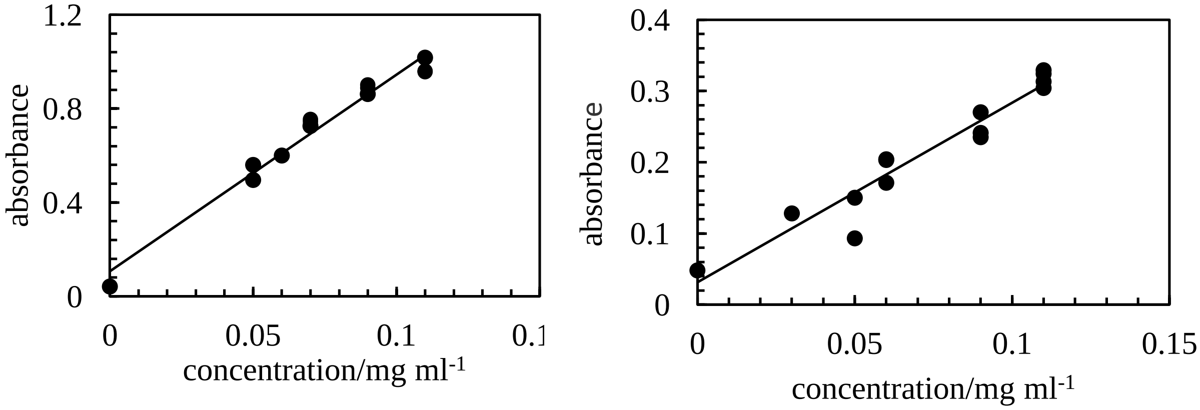

0.1
0.06
0.02
absorbance
250
450
650
wavelength/nm
solvent
filtrate
unfiltered
0.18
0.14
0.1
0.06
0.02
absorbance
250
450
650
wavelength/nm
solvent
unfiltered
filtrate

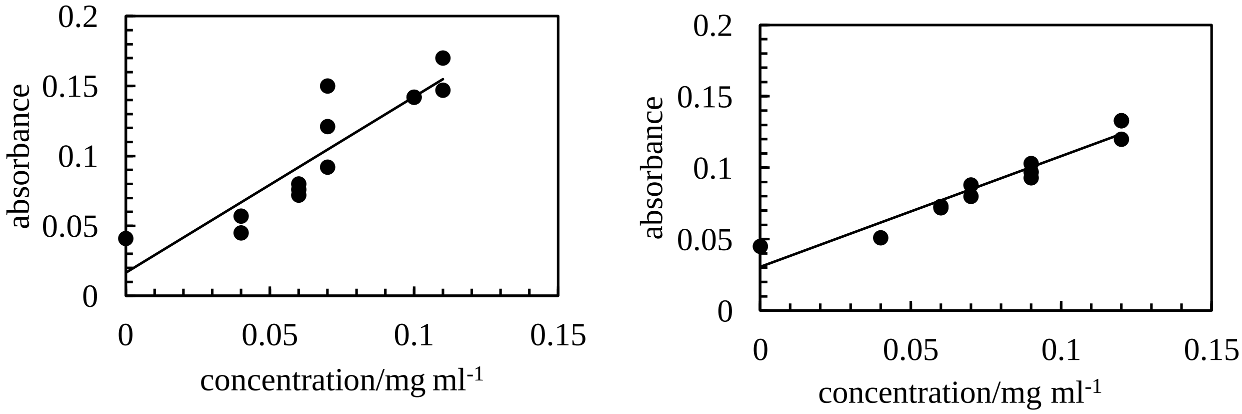
Figure S5. Graph of absorbance against concentration for dispersions of the seven pigments in *n*-heptane (left column) or water (right column) for (i) PR, (ii) PO, (iii) PY, (iv) PG, (v) PB, (vi) PI and (vii) PV.



(v)


absorbance
concentration/mg ml-1
absorbance
concentration/mg ml-1

(vi)


absorbance
concentration/mg ml-1
absorbance
concentration/mg ml-1

(vii)

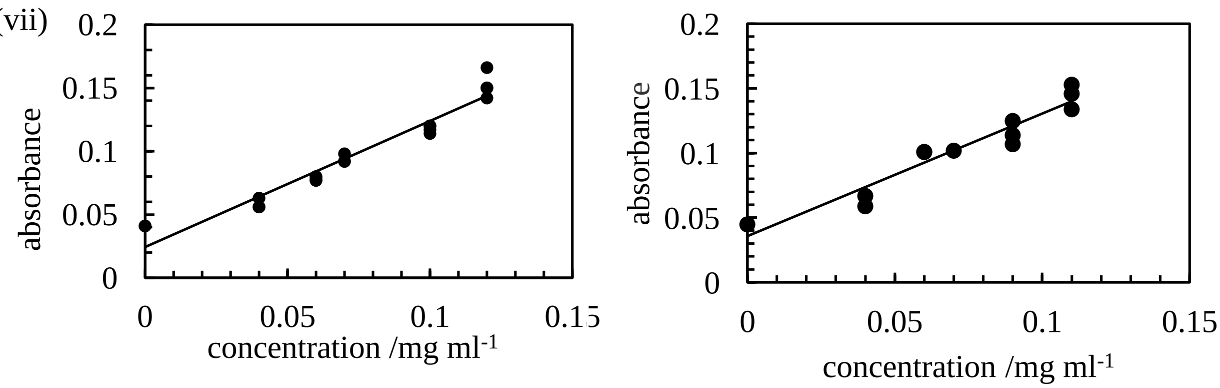
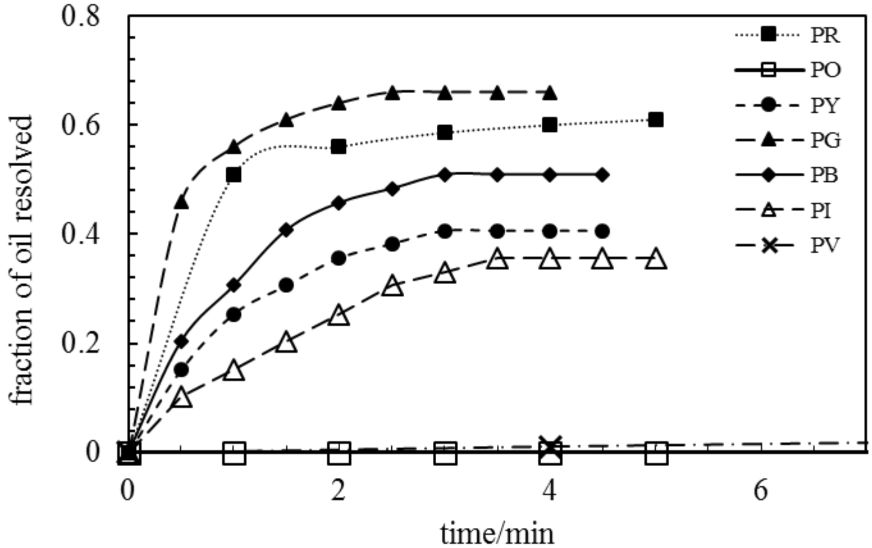

absorbance
concentration /mg ml-1
absorbance
concentration /mg ml-1

Figure S6. Fraction of (a) oil and (b) water resolved as a function of time for *n*-heptane-water emulsions stabilized by 1 wt.% of the different pigments at $\phi_w = 0.5$.

(a)



(b)

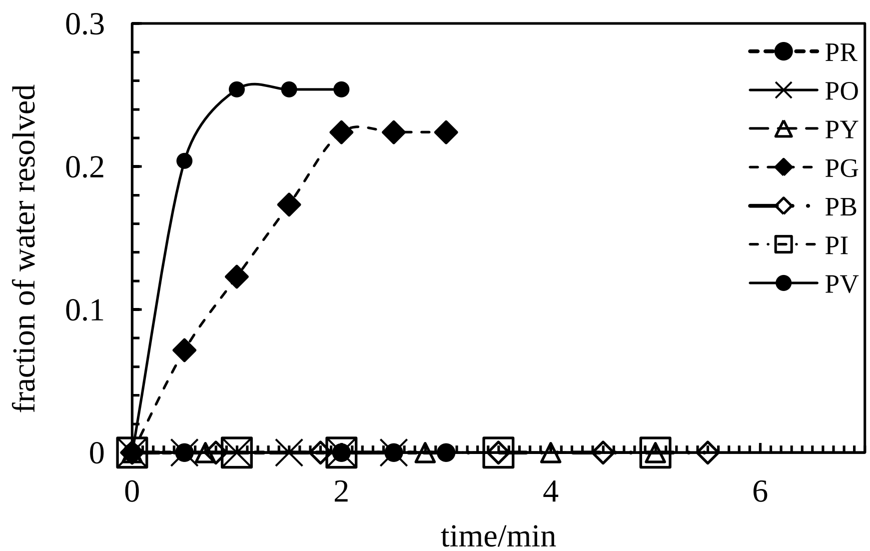
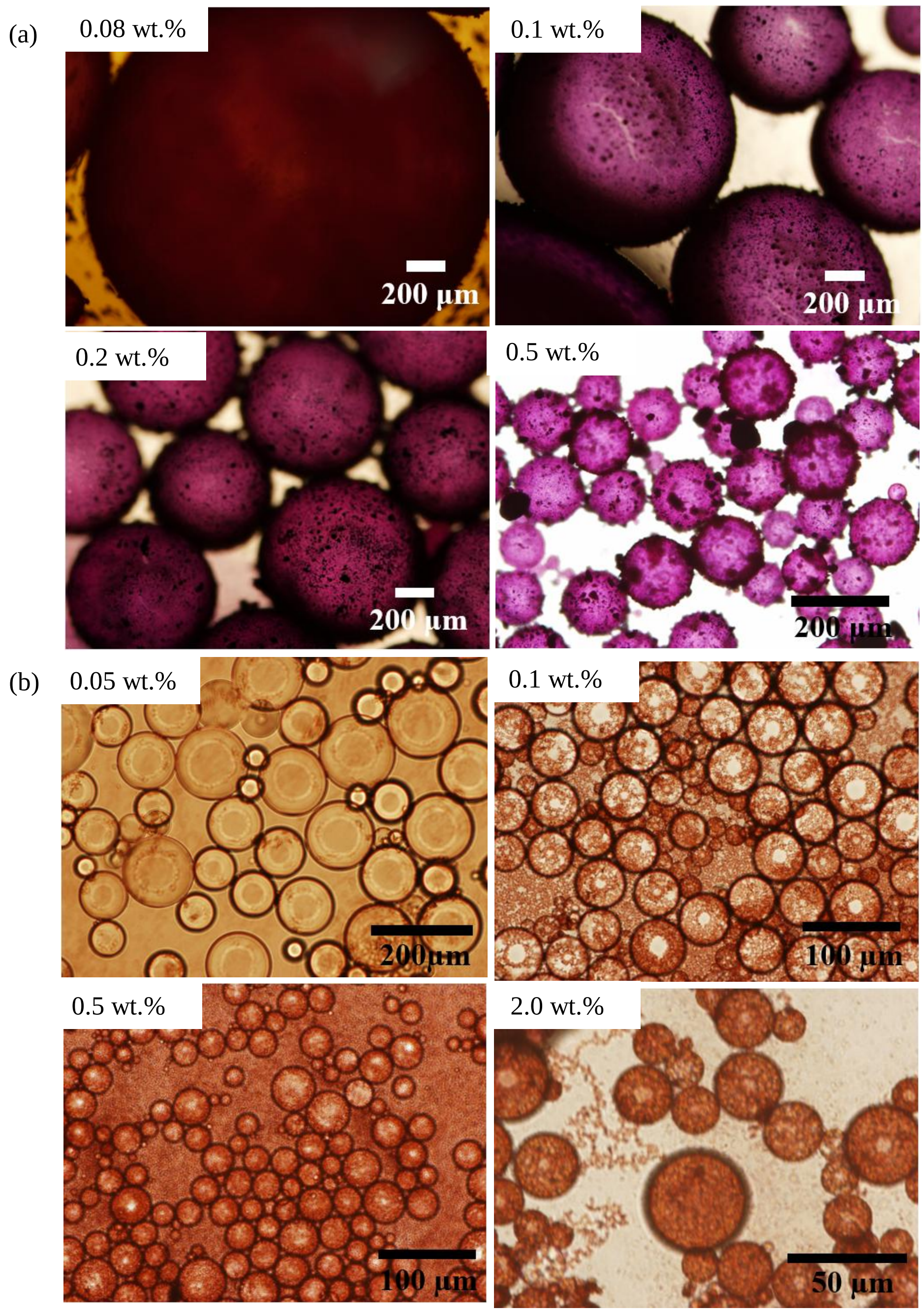
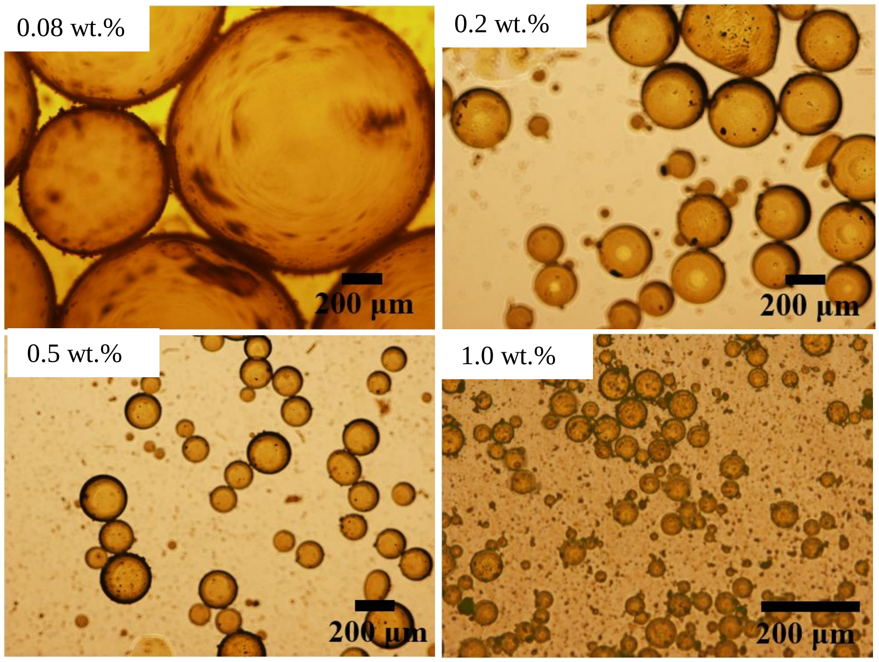


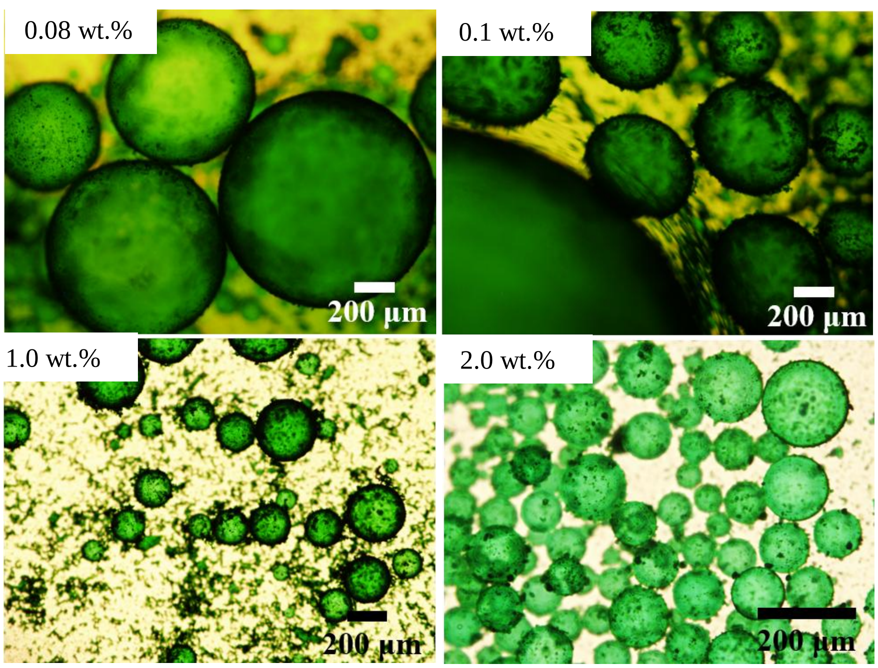
Figure S7. Optical micrographs of fresh emulsions ϕ_w = 0.5 stabilized by the seven pigments at different particle concentrations for (a) PR, (b) PO, (c) PY, (d) PG, (e) PB, (f) PI, (g) PV.



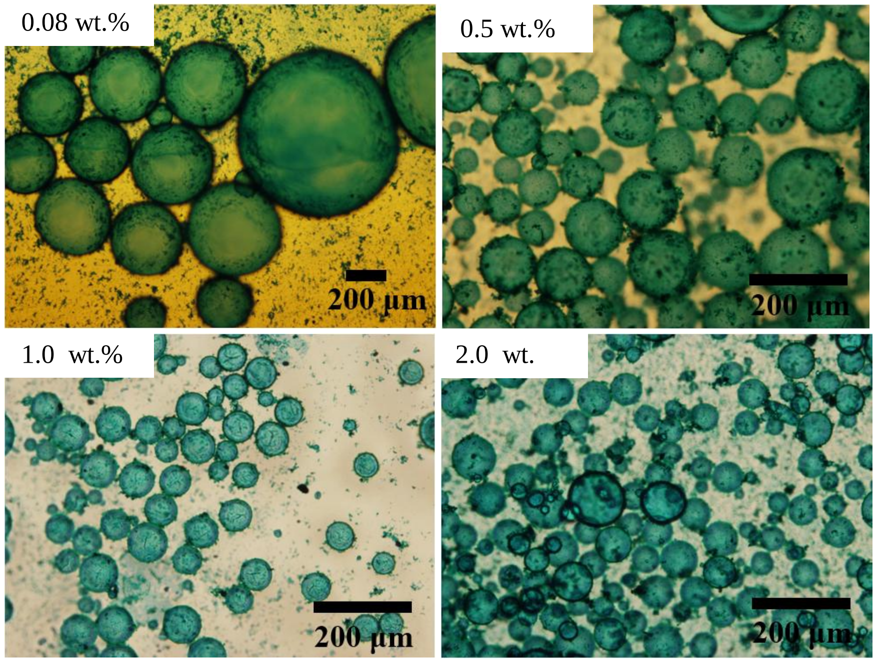
(c)


0.08 wt.%
200 μm
0.2 wt.%
200 μm
0.5 wt.%
200 μm
1.0 wt.%
200 μm

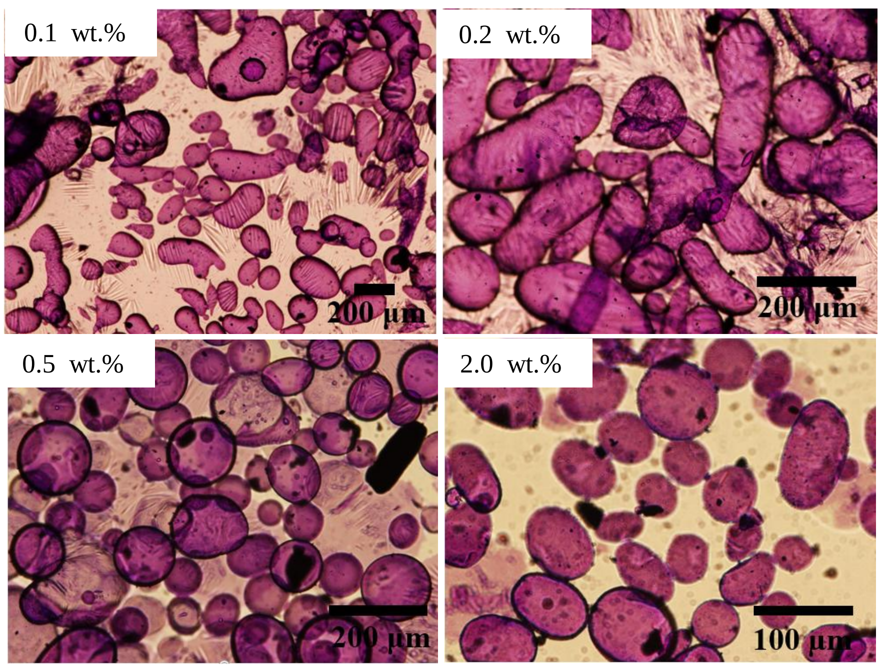
(d)


0.08 wt.%
200 μm
0.1 wt.%
200 μm
1.0 wt.%
200 μm
2.0 wt.%
200 μm

(e)


0.08 wt.%
200 µm
0.5 wt.%
200 µm
1.0 wt.%
200 µm
2.0 wt.
200 µm

(f)


0.1 wt.%
200 µm
0.2 wt.%
200 µm
0.5 wt.%
200 µm
2.0 wt.%
100 µm

(g)

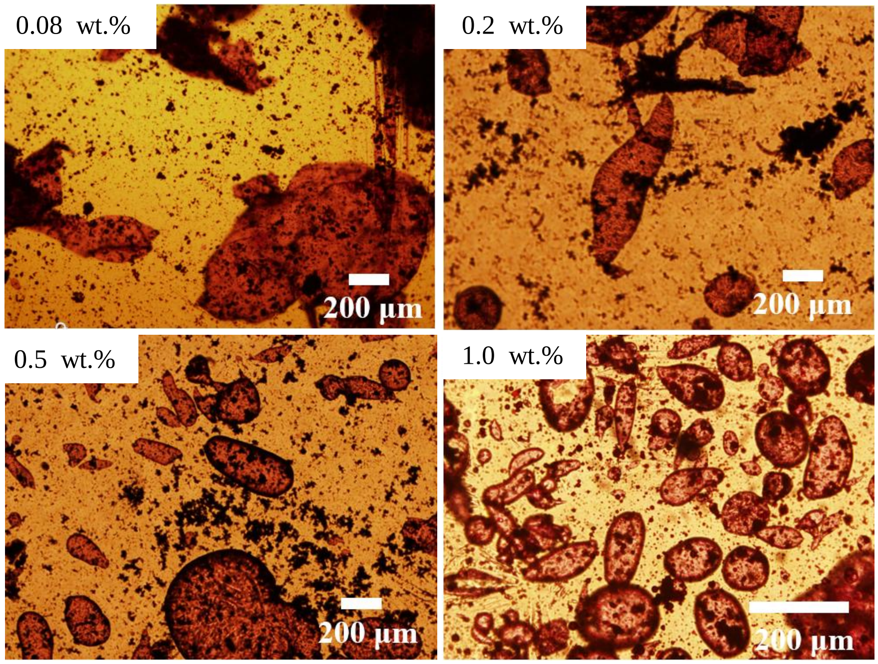


Figure S8. Variation of emulsion conductivity as a function of water volume fraction for 1 wt.% pigment-stabilized emulsions for (a) PR, (b) PY, (c) PB, (d) PI. Vertical dotted line signifies phase inversion.

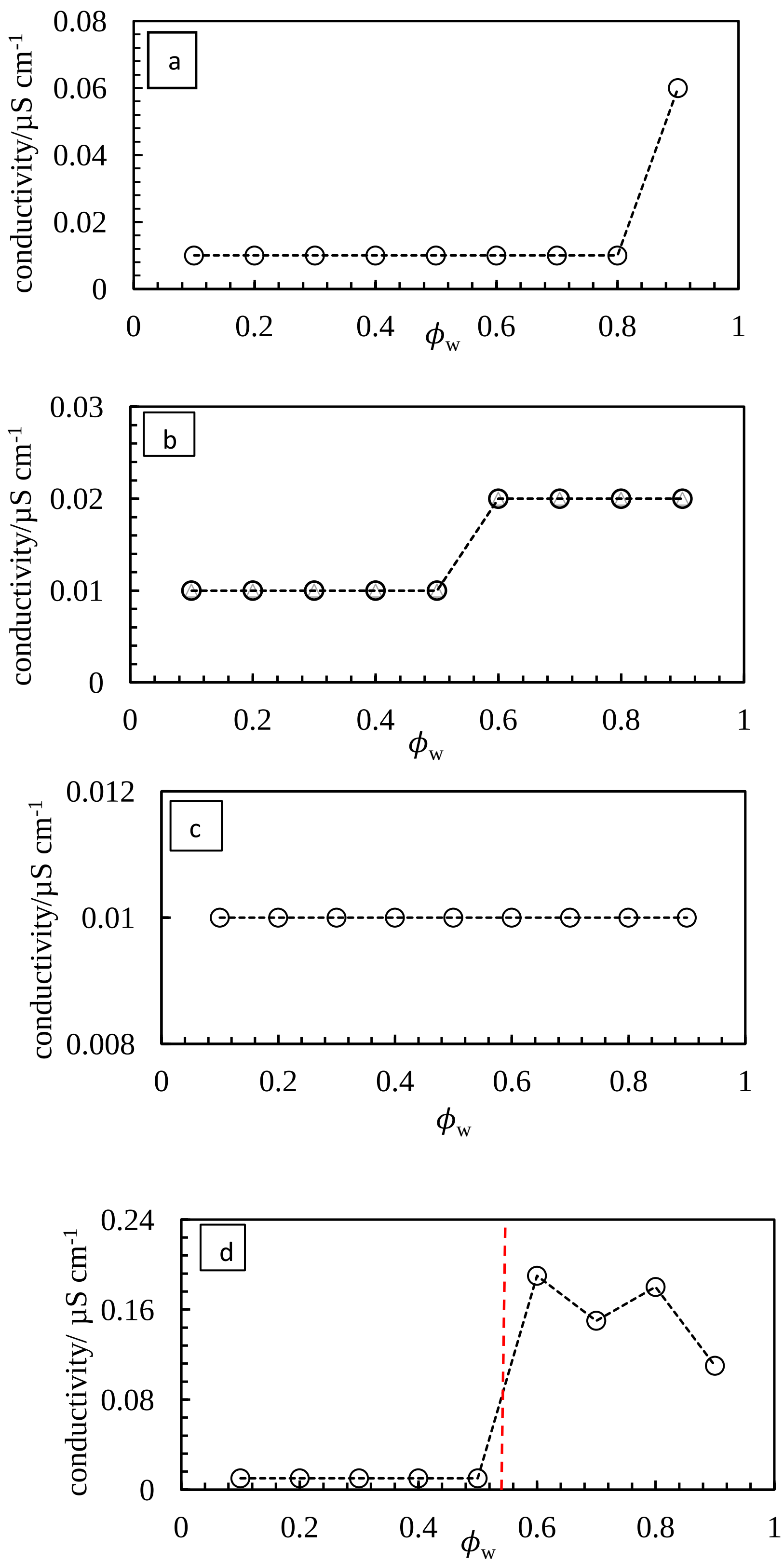
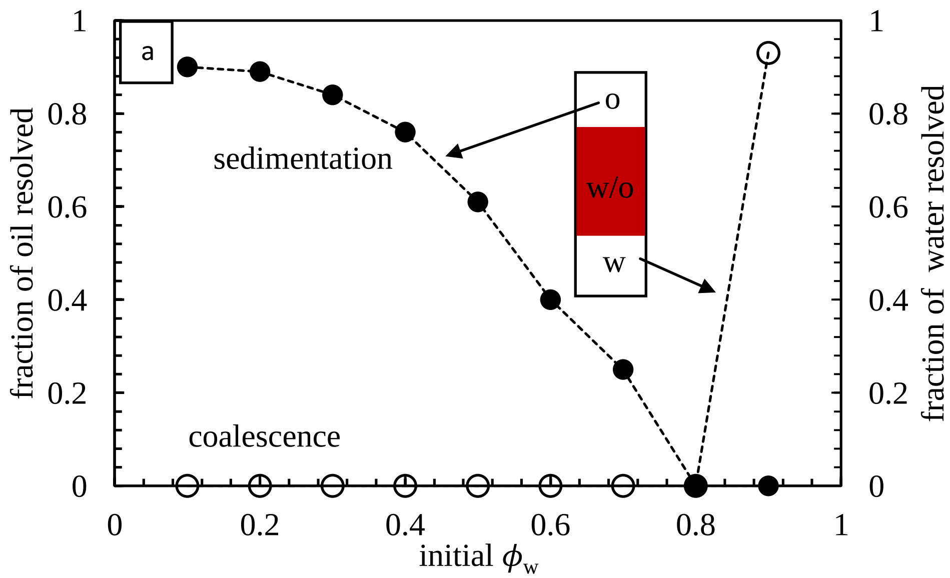
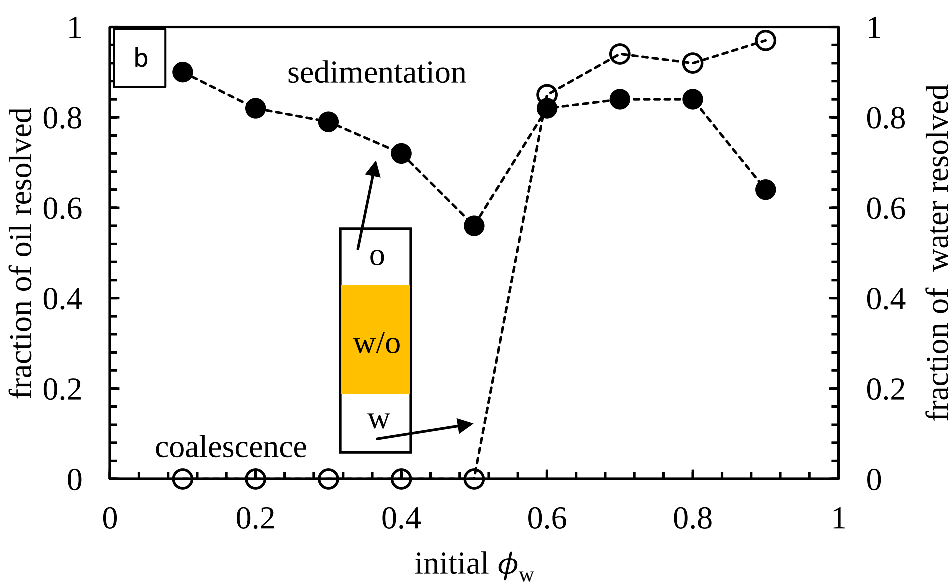
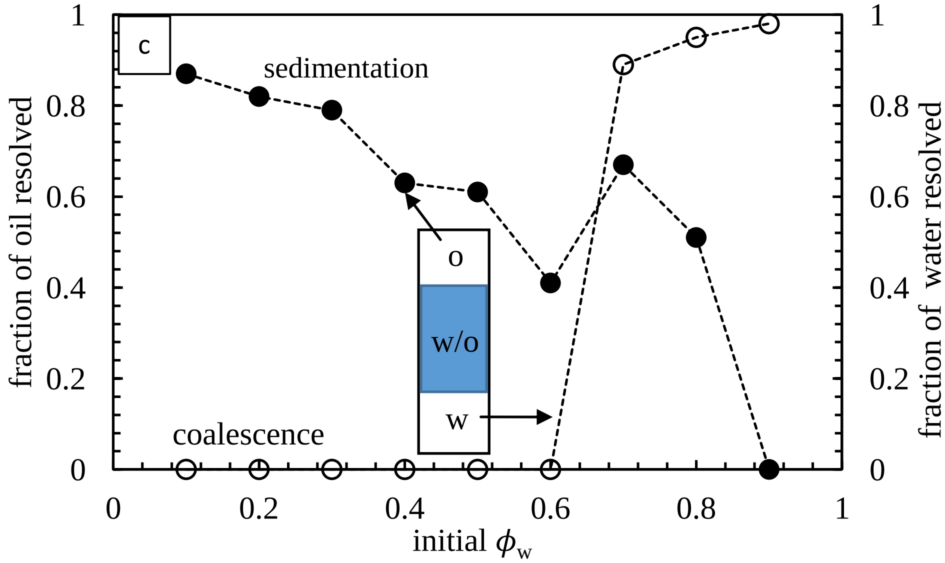


Figure S9. Variation of fraction of oil (filled points) and water (open points) resolved as a function of initial water volume fraction two months after preparation for emulsions stabilized by (a) PR, (b) PY, (c) PB, (d) PI.






c
sedimentation
coalescence
o
w/o
w
fraction of oil resolved
fraction of water resolved
initial ϕ_w

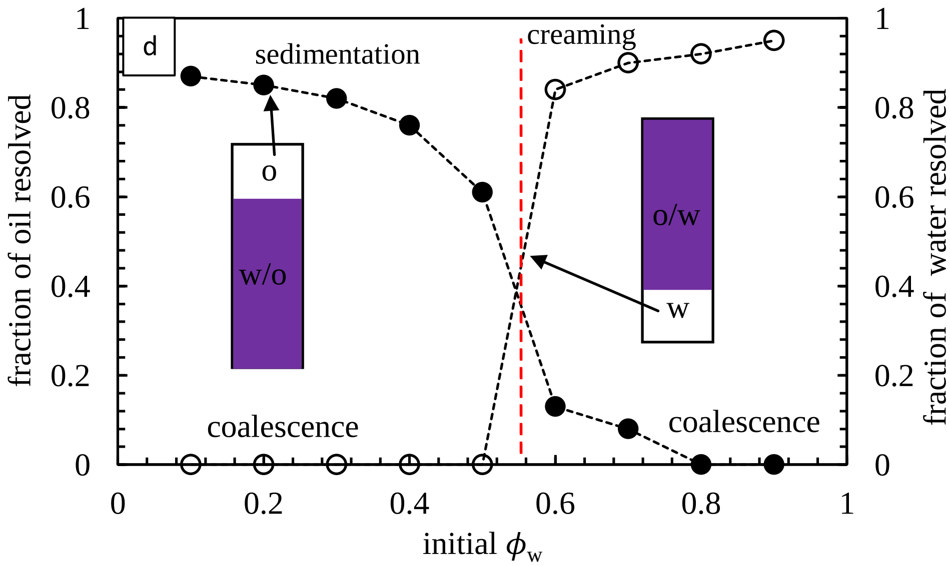
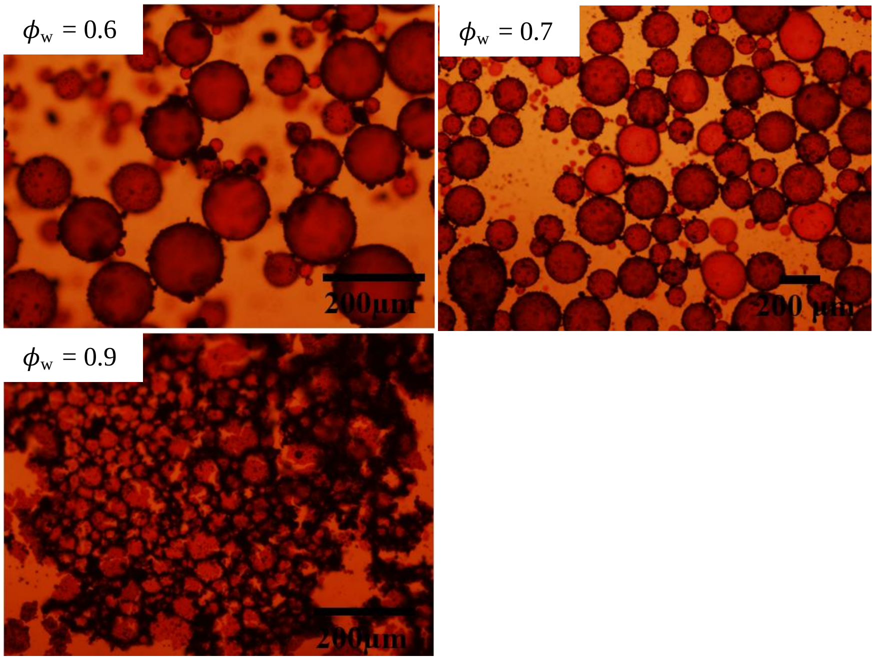
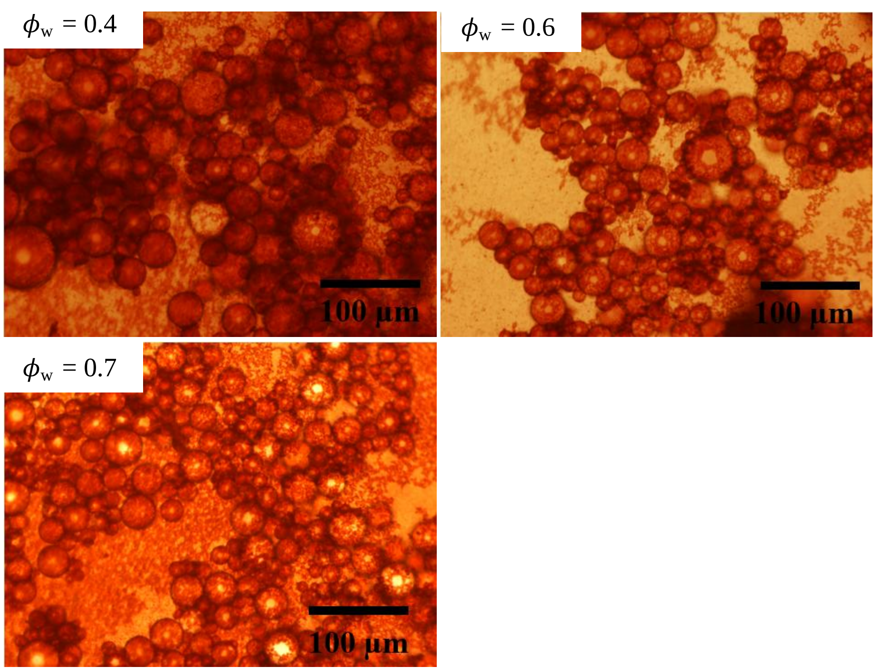

d
sedimentation
creaming
o
w/o
o/w
w
coalescence
coalescence
fraction of oil resolved
fraction of water resolved
initial ϕ_w

Figure S10. Optical micrographs of emulsions of Figure S8 after 20 min at different water volume fractions (given) for (a) PR, (b) PO, (c) PY, (d) PG, (e) PB, (f) PI, (g) PV.

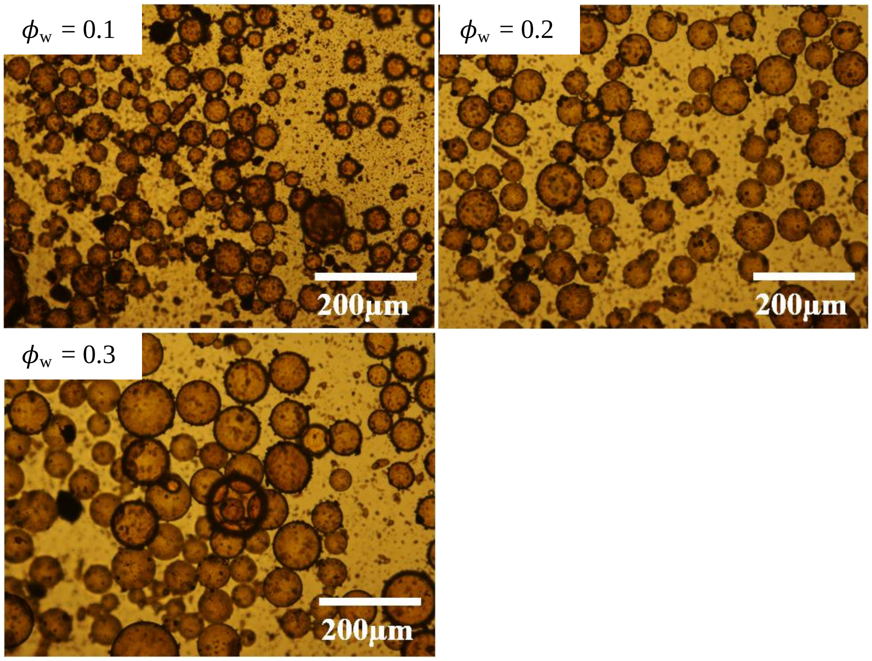
(a)



(b)

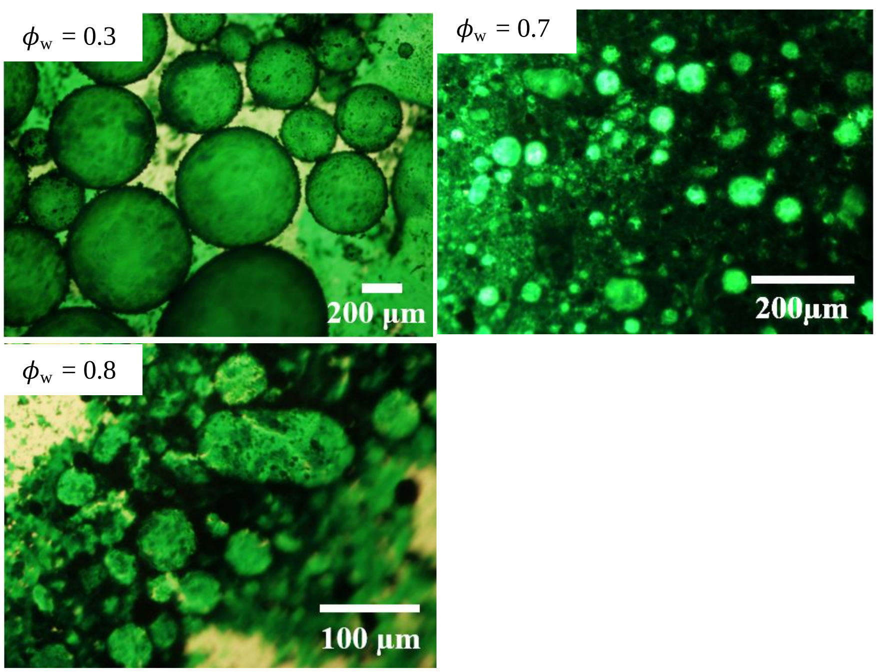


(c)



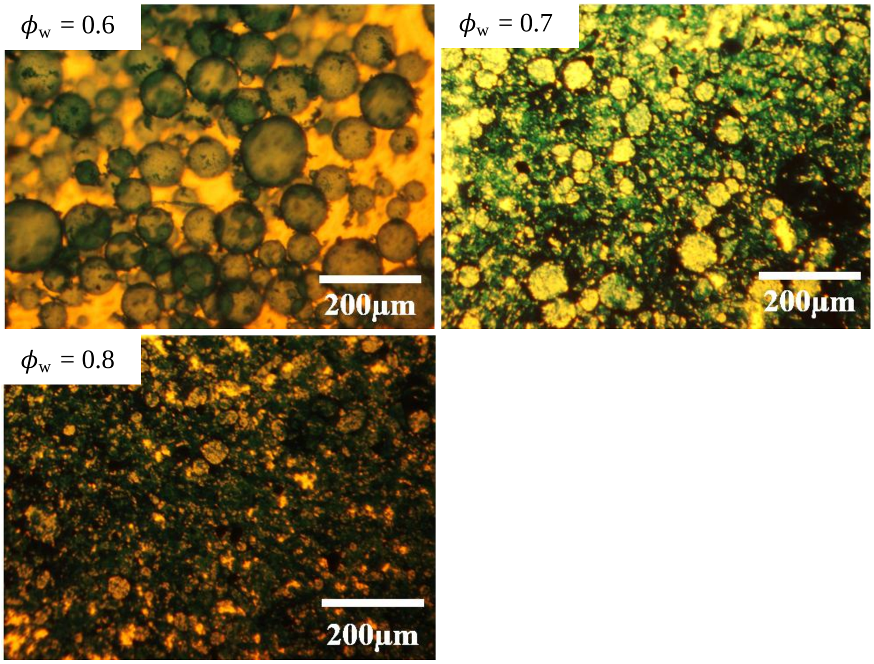
ϕ_w = 0.1
200μm
ϕ_w = 0.2
200μm
ϕ_w = 0.3
200μm

(d)

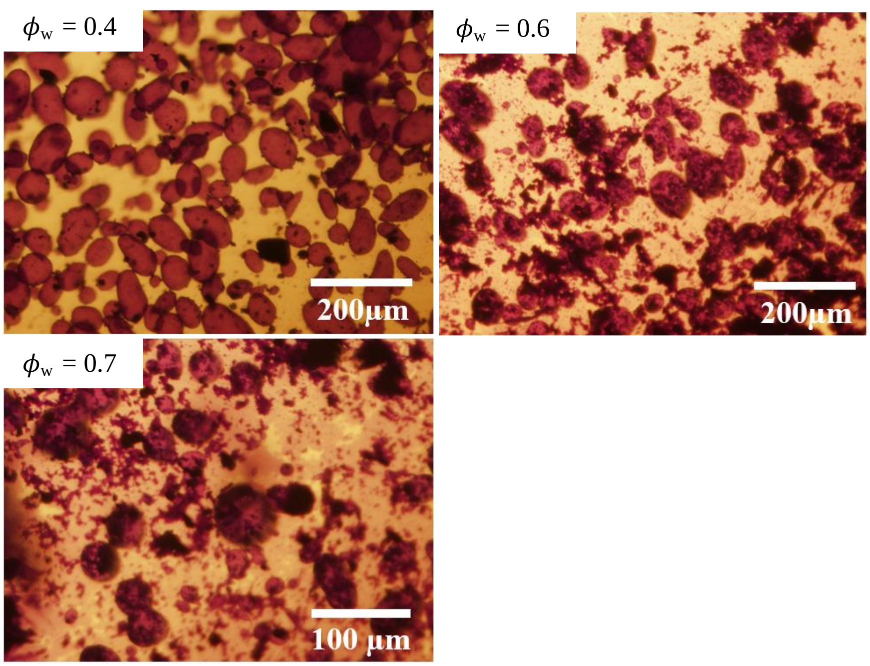


ϕ_w = 0.3
200 μm
ϕ_w = 0.7
200μm
ϕ_w = 0.8
100 μm

(e)


ϕ_w = 0.6
200μm
ϕ_w = 0.7
200μm
ϕ_w = 0.8
200μm

(f)


ϕ_w = 0.4
200μm
ϕ_w = 0.6
200μm
ϕ_w = 0.7
100 μm

(g)

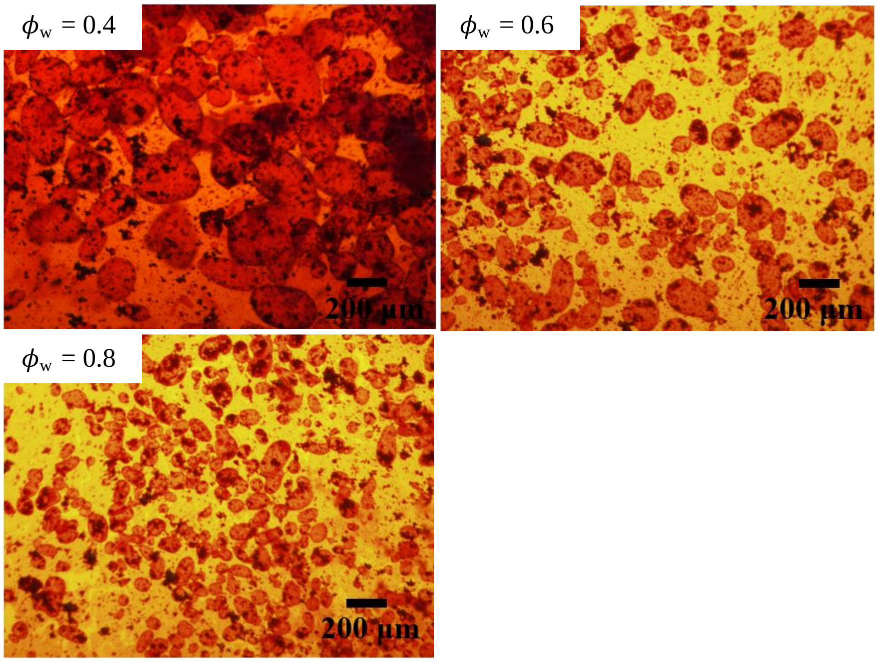


Figure S11. Variation of drop diameter with aqueous volume fraction for emulsions stabilised by 1 wt.% of pigment for (a) PR, (b) PY (c) PB, (d) PI.