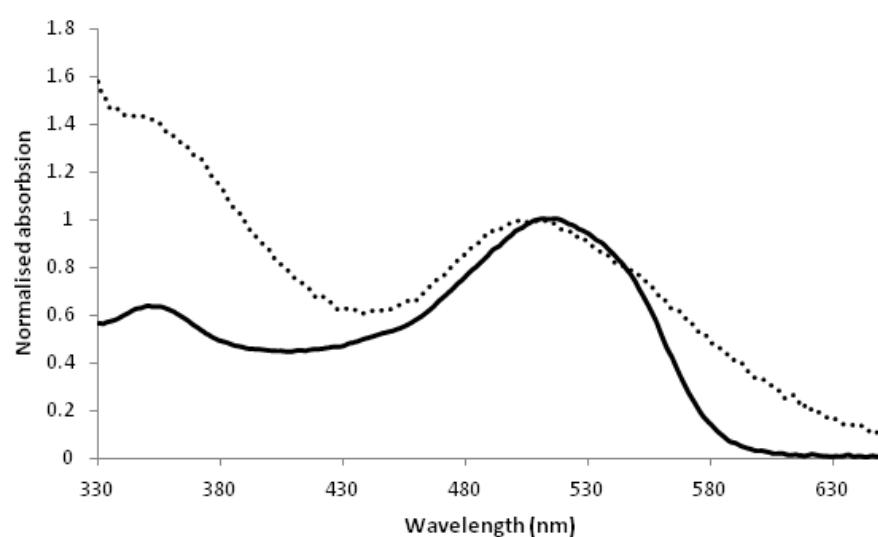


## **Reactions of hydrophobic organic nanoparticle mixtures in water: Nanoparticle-on-nanoparticle oxidative dye bleaching**

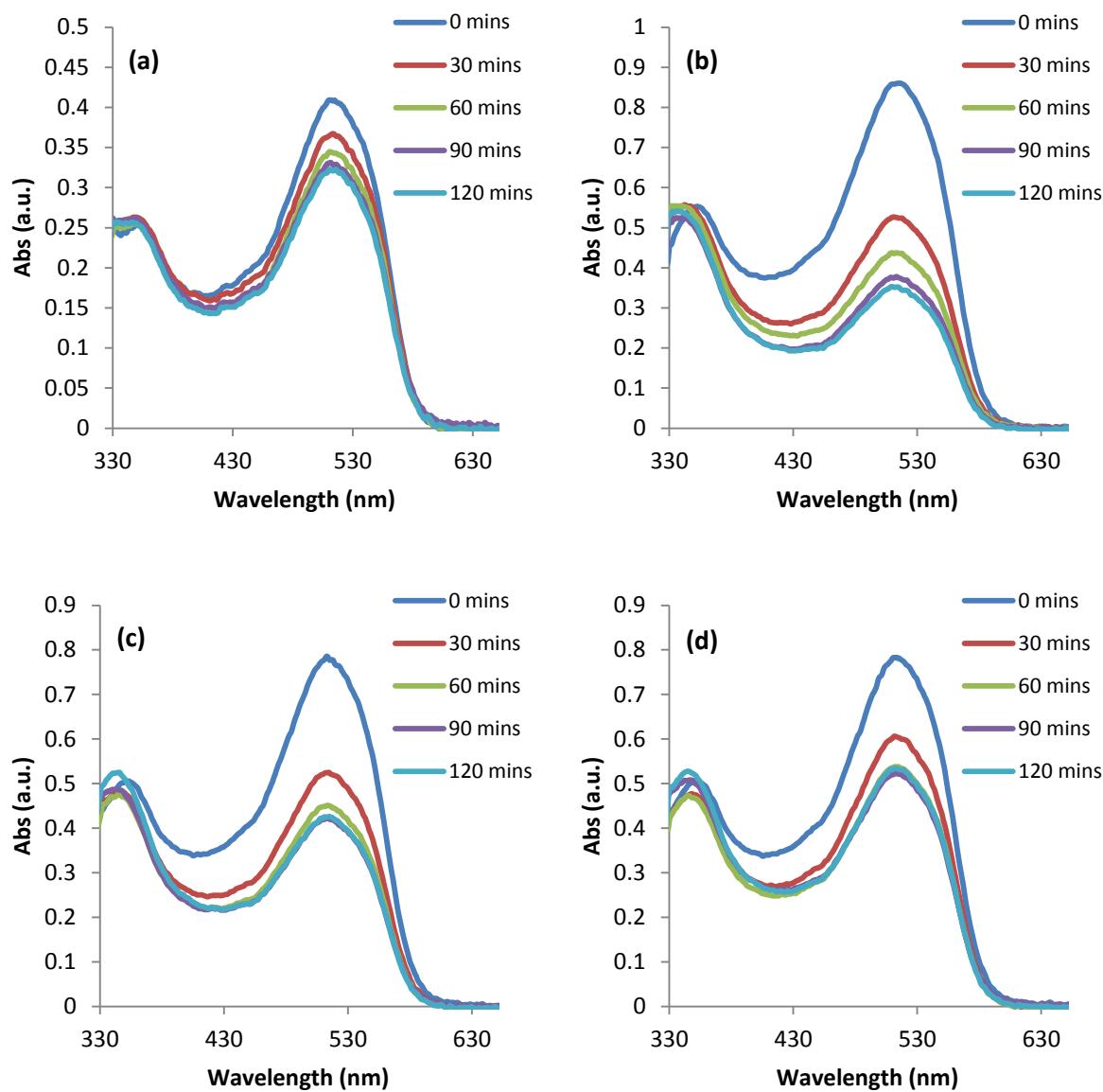
By *Marco Giardiello, Tom O. McDonald, Jet-Sing Lee, Aled D. Roberts, Andrew Owen\** and

*Steve P. Rannard\**

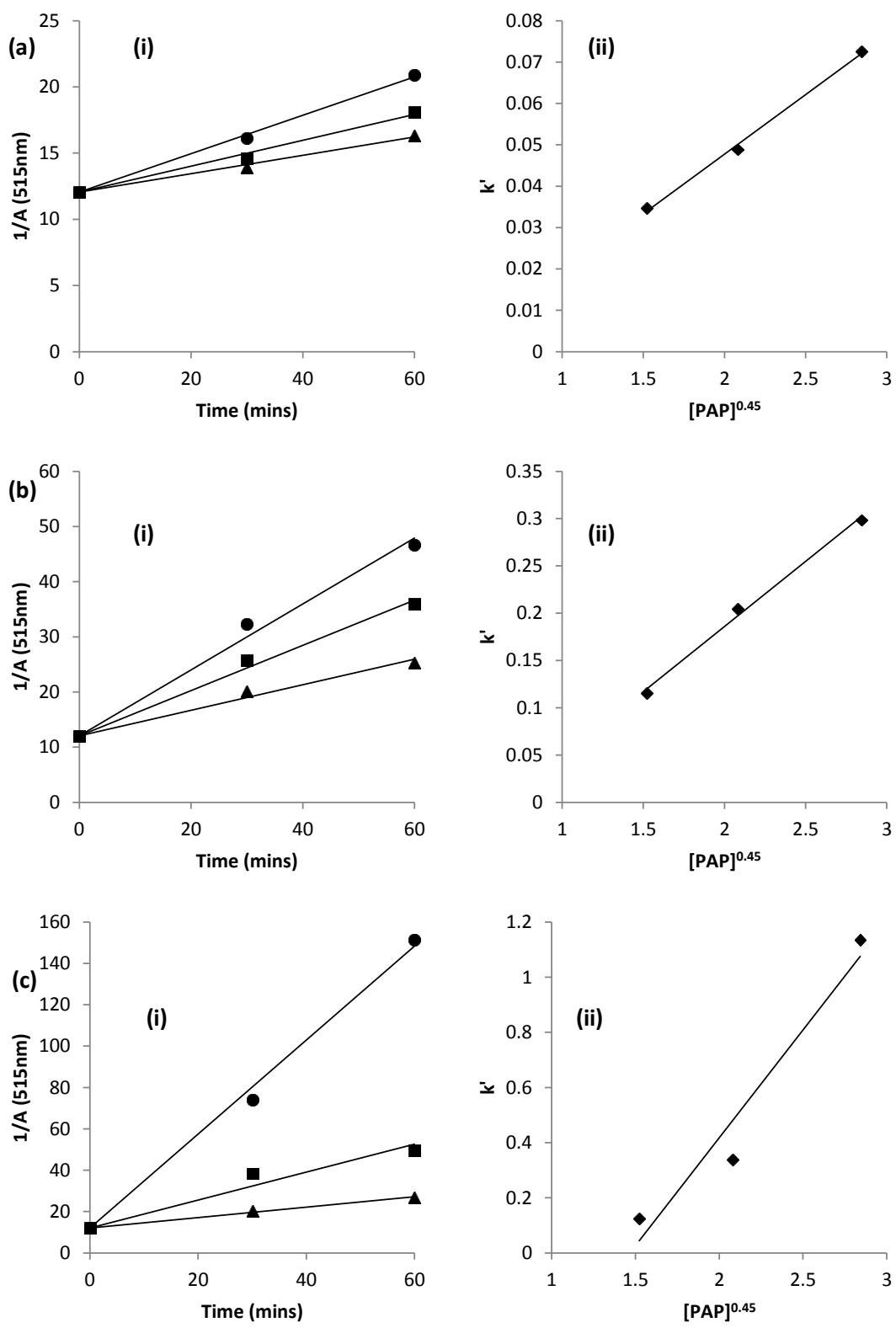
### Supporting Information



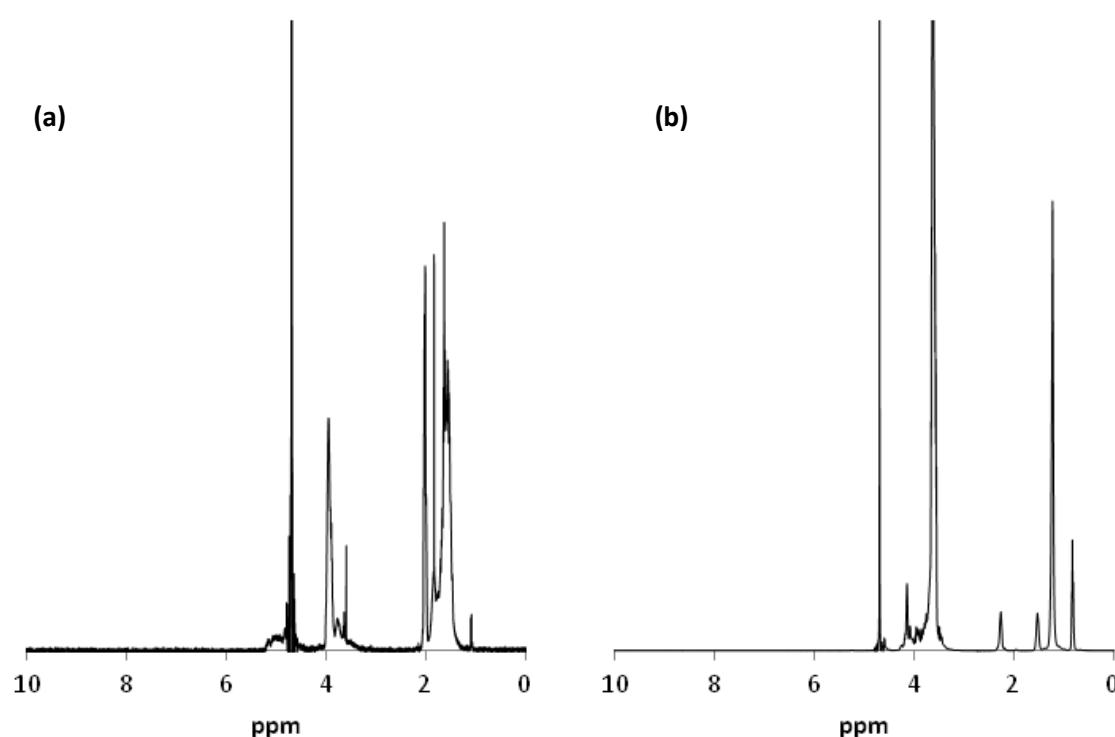
**Figure S1.** UV-visible spectra of **OR** in acetone (solid line,  $\lambda_{\max} = 515$  nm) and **OR** aqueous nanosuspension (dotted line,  $\lambda_{\max} = 501$  nm).



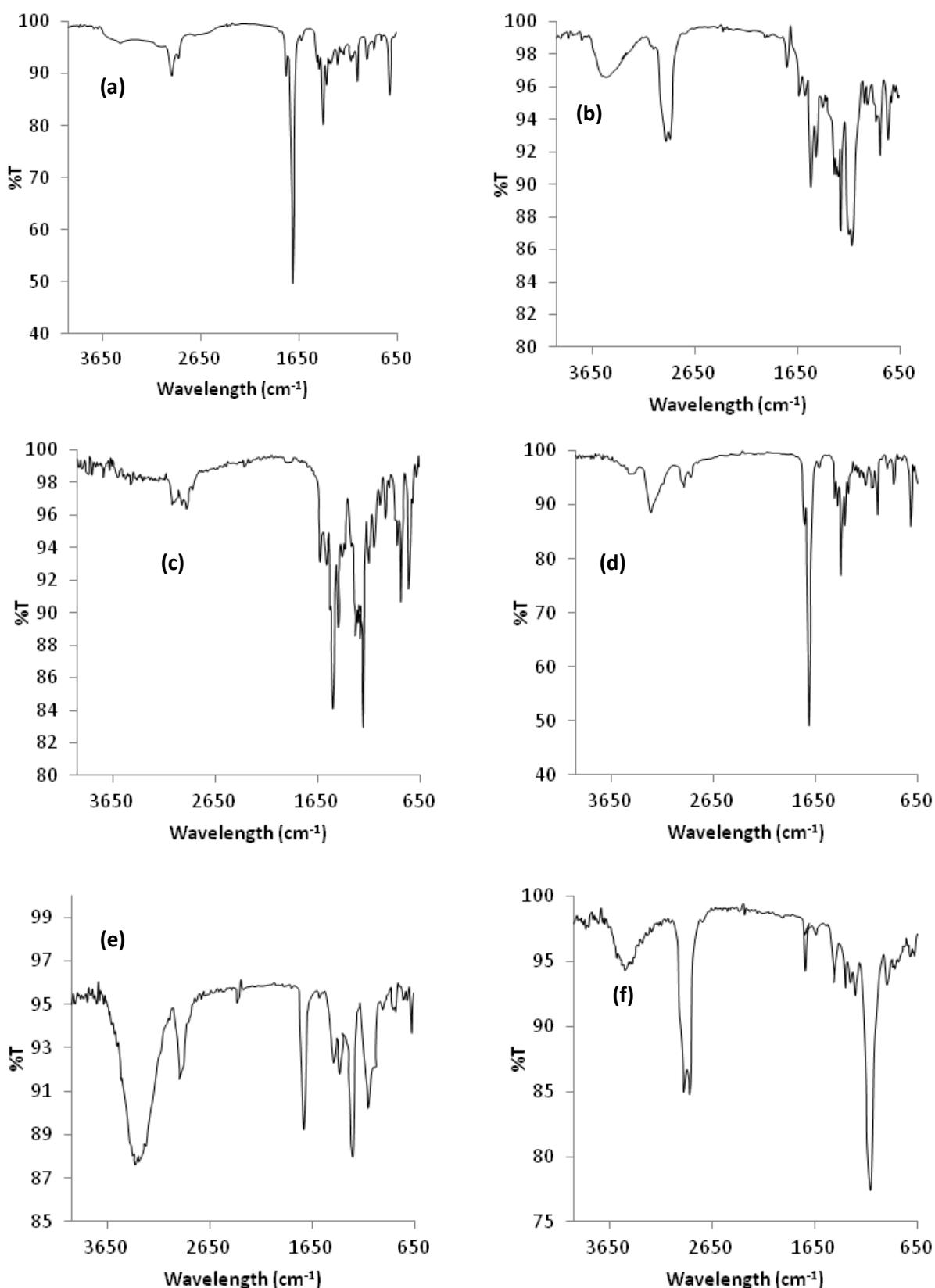
**Figure S2.** UV-visible spectra for homogenous oxidative bleaching of **OR** by **PAP** in acetone at 40°C over time at different PAP:OR molar ratios: (a) 35:0.5, (b) 35:1, (c) 17.5:1 and (d) 8.25:1. Initial rates were determined from the absorptions at 0 and 30 minutes.



**Figure S3.** Kinetic data plots for homogenous **OR** and **PAP** oxidative bleaching reactions in acetone at (a) 25°C, (b) 40°C and (c) 50°C . For all temperatures: (i)  $1/[OR]^2 \times t$ , the gradient of which gives  $k'$  (the intercept was set at  $1/[OR_0]^2 = 12.05624$ . (ii)  $k' \times [PAP]^{0.45}$ , the gradient of which gives  $k$ .



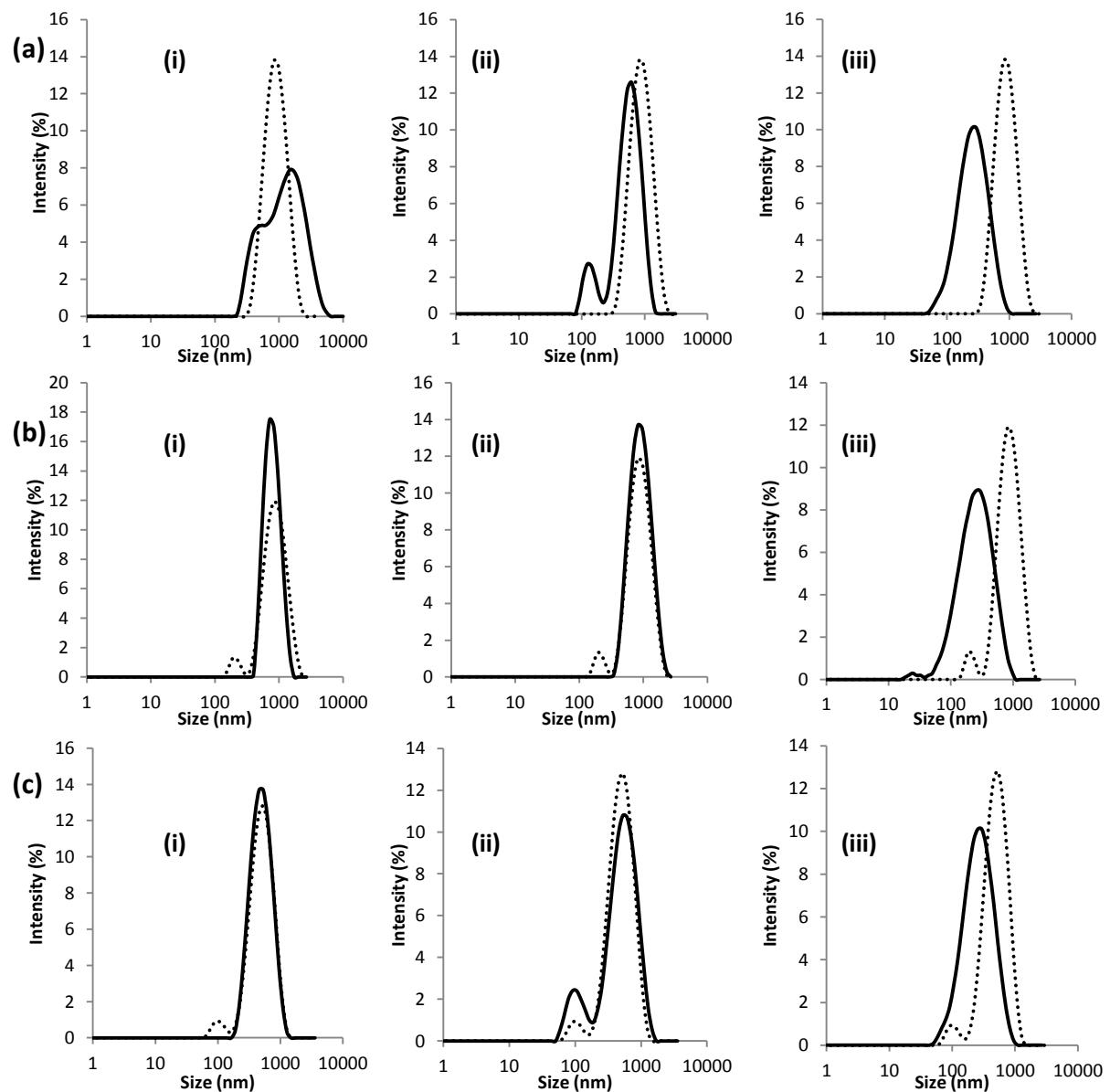
**Figure S4.** <sup>1</sup>H NMR spectra of (a) PVA and (b) Tween 20<sup>°</sup>. Spectra recorded at 400 MHz, 25°C, D<sub>2</sub>O.



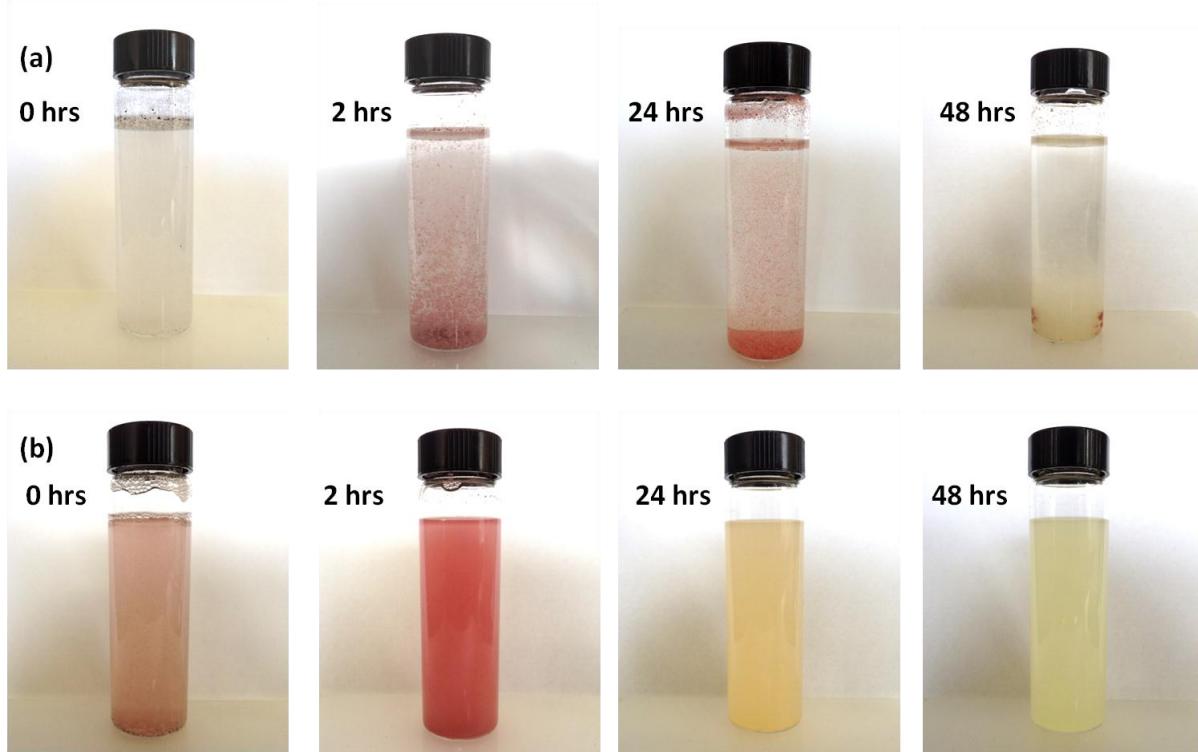
**Figure S5.** IR spectra of (a) 35:1 PAP: OR nanosuspension following 2 hours at 50°C in pure water, (b) OR nanosuspension following 2 hours at 50°C in pure water, (c) OR powder, (d) PAP powder, (e) PVA and (f) Tween 20°

**Table S1.** IR absorption values for stabilizers, reactants and samples taken experiments at 50°C.

PAP:OR 2hr 50°C		OR NP 2hr 50°C		OR Powder		PAP Powder		PVA		Tween 20*	
cm <sup>-1</sup>	%	cm <sup>-1</sup>	%	cm <sup>-1</sup>	%	cm <sup>-1</sup>	%	cm <sup>-1</sup>	%	cm <sup>-1</sup>	%
719	86	752	93	752	92	717	85	669	94	723	95
876	95	831	92	831	90	881	93	841	95	947	93
953	93	949	95	868	94	953	96	1093	90	1107	78
1049	88	985	95	985	96	1049	88	1248	88	1252	93
1113	92	1105	86	1097	94	1084	93	1375	92	1352	93
1188	94	1207	87	1151	93	1157	93	1431	92	1462	94
1254	92	1234	90	1207	22	1211	94	1734	89	1736	94
1313	80	1274	90	1232	88	1261	96	2939	92	2868	85
1363	97	1450	91	1277	89	1336	92	3336	87	2924	85
1396	80	1500	90	1448	89	1367	85	-	-	3485	94
1439	90	1620	95	1502	84	1396	77	-	-	3759	98
1464	91	1736	97	1554	93	1436	89	-	-	-	-
1709	49	2922	92	1620	93	1466	90	-	-	-	-
1772	90	3485	96	2920	96	1614	96	-	-	-	-
2935	90	-	-	3741	98	1711	50	-	-	-	-
-	-	-	-	3888	98	1757	86	-	-	-	-
-	-	-	-	-	-	2862	95	-	-	-	-
-	-	-	-	-	-	2933	93	-	-	-	-
-	-	-	-	-	-	3257	89	-	-	-	-
-	-	-	-	-	-	3442	95	-	-	-	-
-	-	-	-	-	-	3735	98	-	-	-	-



**Figure S6.** DLS particle distributions for (a) 35:1 reaction of **PAP+OR** nanosuspensions, (b) **PAP** nanosuspension alone and (c) **OR** nanosuspension alone at (i) 25°C, (ii) 40°C and (iii) 50°C. In each case, dotted line shows measurement taken at 0 time, solid line shows measurement taken at 2 hours.



**Figure S7.** Photographs of aqueous 35:1 **PAP:OR** molar ratio reaction vials at 50°C. (a) **OR** and **PAP** powder suspended in pure water, (b) **OR** and **PAP** powders in aqueous surfactant/polymer solution. Note; at 0 hrs for the powdered reaction in pure water both **OR** and **PAP** floated on the water surface, hence the vial appears clear.