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Supplementary Material

Approach to achieve controlled particle size synthesis of non- polar functionalised siloxane particles using a one-pot synthesis

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ATR-FTIR analysis of particles

ATR-FTIR spectroscopy of dried particles was used to confirm the presence of the functional R-groups provided by the silane precursor. The Peak assignments are shown in Table S1 and labelled in Figure S1.

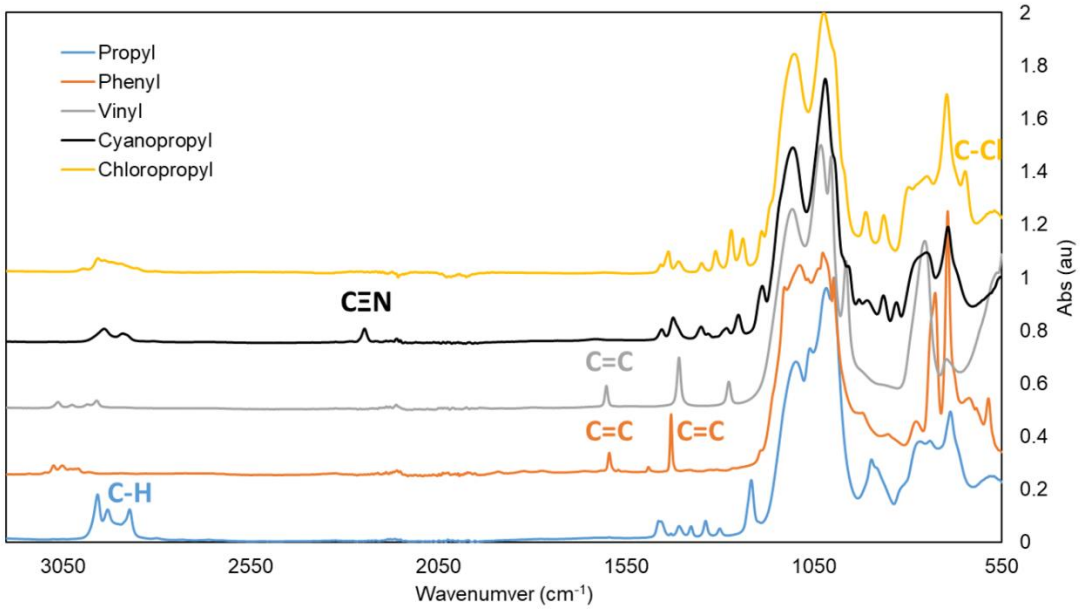

Figure S1: ATR-FTIR spectra of dried silica particle powders

Table S1: Peak assignments of ATR-FTIR of silica particle powders

SiNP	Peak position (cm^{-1})	Vibration
VTES	~1600	C=C double bond
PropylTMS	~3000	C-H alkyl
PhenylTES	~1600 and ~1400	C=C aromatic
CyanoPropylTes	~2100	C≡N
CloroptopylTES	~650	C-Cl

TGA analysis of particles

TGA can also be used to confirm particle functionality. Different functionalities show different TGA profiles with different temperatures of degradation events and mass loss proportions as shown in Figure S2.

Each species of particles can be considered as polysilsesquioxanes with repeating units of $SiO_{1.5}R$. During pyrolysis under N_2, a complex glass of unknown chemical composition forms. The introduction of air at high allows the removal of remaining carbonaceous material resulting in the transformation to SiO_2 with a molecular mass of 60.08 g mol^{-1}. This allows the average theoretical residual mass for each particle species to be determined and compared to the experimental residual mass as shown in Table S2. Very close agreement between theoretical and experimental values confirms that these organosilane groups are present within the mature particle.

Table S2: Theoretical and experimental residual mass after pyrolysis in TGA of particle species

Particle Species	Repeating unit	MW (g mol^{-1})	Theoretical residual mass (%)	Experimental residual mass (%)
Propyl	$SiO_{1.5}C3H7$	95.17	63.1	61.8
Phenyl	$SiO_{1.5}$ C_6H_5	129.19	46.5	50.9
Vinyl	$SiO_{1.5}C_2H_3$	79.13	75.9	75.8
Chloropropyl	$SiO_{1.5}C_3H_6Cl$	129.62	46.4	52.4
Cyanopropyl	$SiO_{1.5}C_3H_6N$	108.17	55.5	50.4

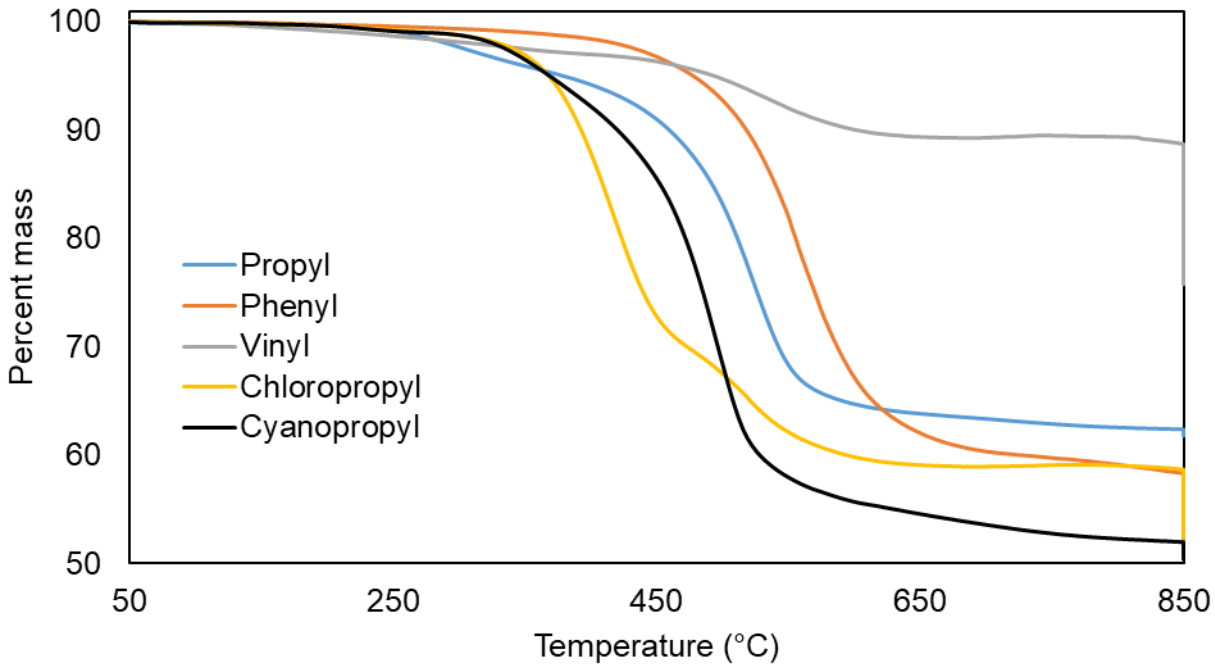

Figure S2: TGA plot of different particles

Construction of calibration curves for surface attachment density

Calibration curve for quantification for undecylenic aicd attachment to thiol particles

Two samples of SH-particles were taken, having diameters of 203 and 138 nm respectively (measured by DLS). Known quantities of undecylenic acid were added to the samples and used to prepare calibration curves of absorbance of the carbonyl signal against the mass concentration of undecylenic acid in the samples. Table S3 shows the masses of undecylenic acid and SH-particles used in creating the curves, converted to mass ratios. The ATR-FTIR spectra of the mixtures and resulting calibration curve are shown in Figures S3 and S4 respectively.

Table S3: Masses of undecylenic acid and SH-particles used to create the carbonyl calibration curve

Diameter (nm)	m(SH-SiNPs) (mg)	m(Undecylenic acid) (mg)	Mass ratio (%w/w)
138	~10	0	0
	13.5	0.07	0.5
	14.7	0.15	1.0
	20.6	0.42	2.0
	15.4	0.47	3.0
	20.1	0.82	3.9
	10.4	0.50	4.5
	10.2	0.82	7.4
	16.5	1.52	8.4
203	~10	0	0
	19.1	0.22	1.1
	17.1	0.39	2.2
	16.6	0.57	3.3
	25.3	1.14	4.3
	19.4	1.13	5.5
	17.0	1.23	6.7

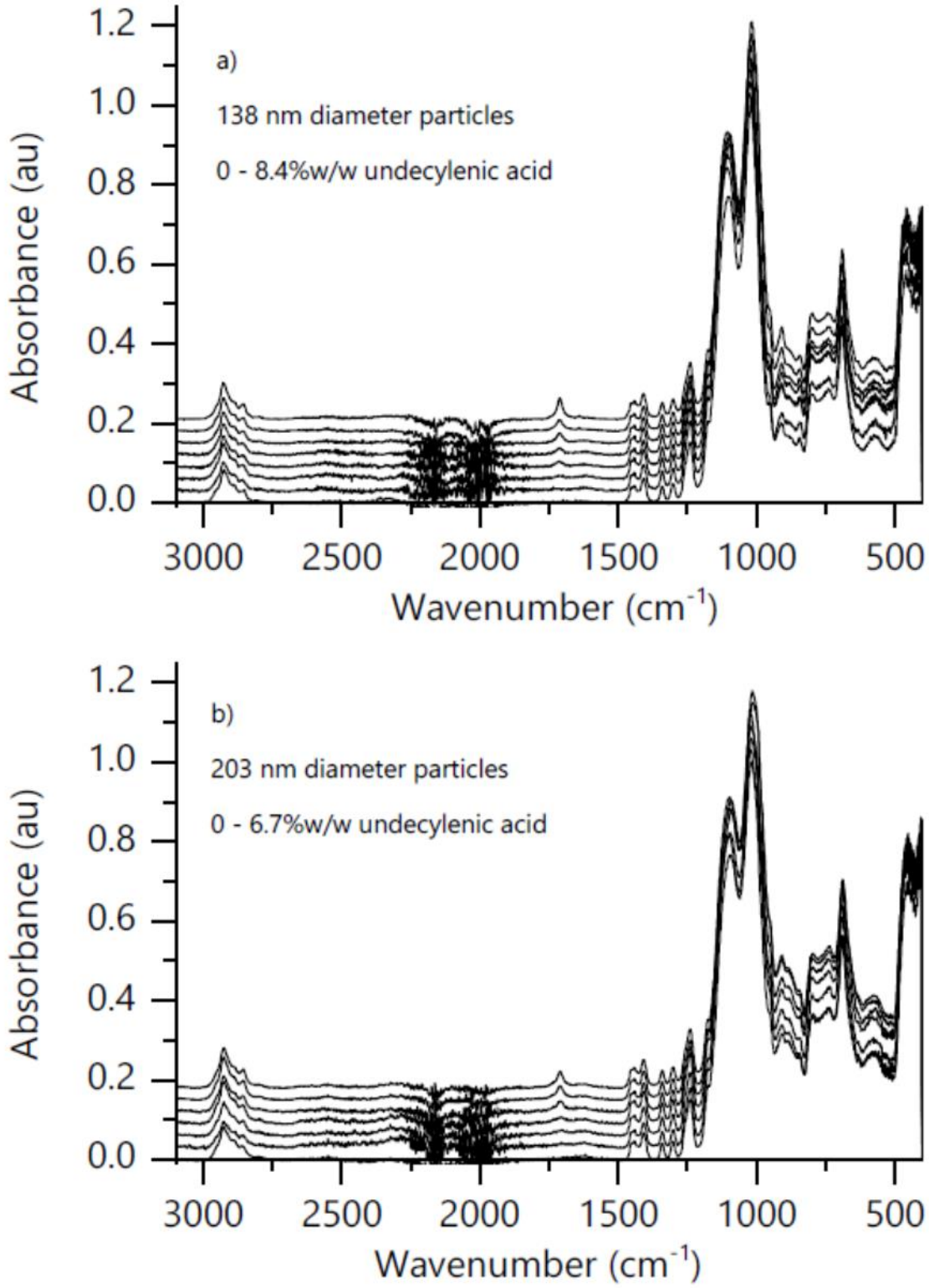

Figure S3: Offset ATR-FTIR spectra of SH-particles with undecylenic acid added in mass ratio indicated for a) 138 nm particles, b) 203 nm particles. Spectra normalised to Si-O-Si peak at 1070 cm^{-1}.

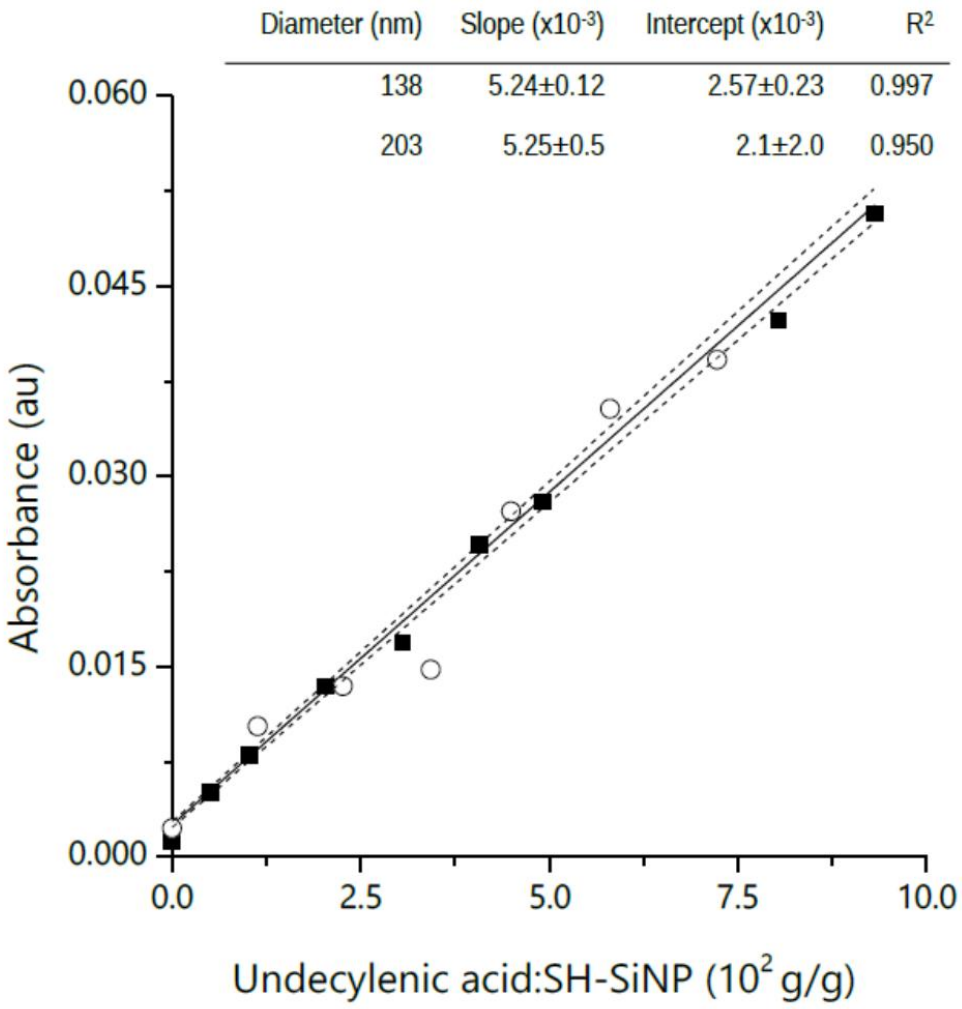

Figure S4: Calibration curve of carbonyl signal absorbance against relative mass of undecylenic acid in particle sample, with curve parameters inset. Solid symbols are 138-nm particles; open symbols are 203-nm particles. Solid line is curve based on 138-nm particles, dashed lines indicate upper and lower estimates of error based on calibration curve.

11-MUA attachment on vinyl particles calibration curve

Vinyl terminated particles with an average dimeter of 204 nm (as shown in the SEM image in Figure S5) and a specific surface area of 15.7 $\pm$ 1.7 m^2 g^{-1} (as determined by BET surface area analysis as shown in Figure S6) were used to construct a calibration curve for the attachment of 11-MUA to vinyl-terminated particles.

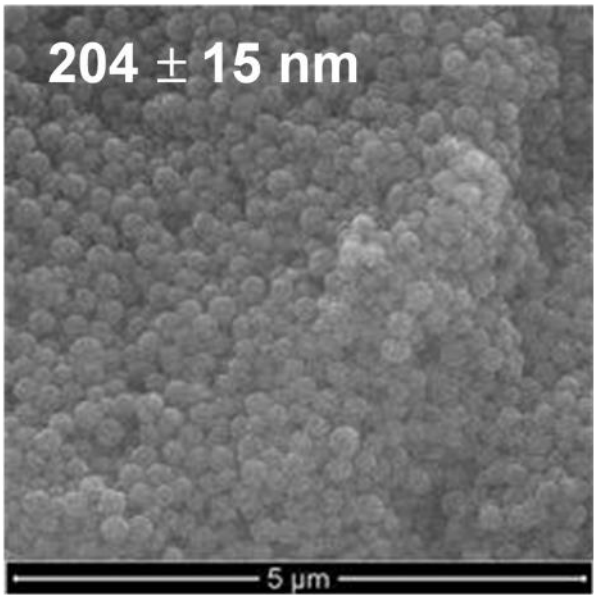

Figure S5: SEM images of vinyl-terminated particles with an average diameter of 204 ± 15 nm.

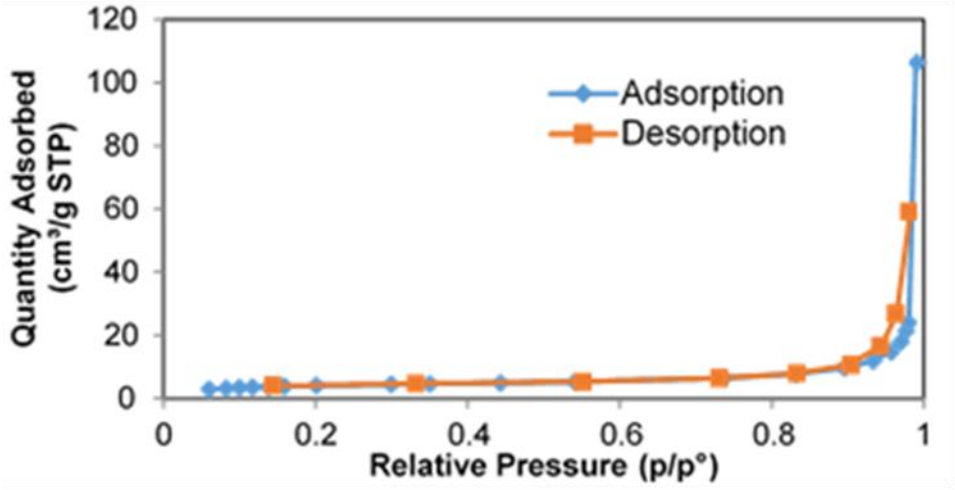

Figure S6: BET Isotherm of vinyl-terminated particles with average diameter of 204 nm giving a BET Surface area of 15.7 ± 1.7 m^2 g^{-1}.

Calibration curve for quantification for 11-mercaptoundecanoic acid attachment to vinyl particles

0.8, 1.6, 3.3, 4.9, 6.5, 8.2 and 9.8 µL of 0.229 M of 11-MUA in acetone was added to and homogenised with 15-mg amounts of dried vinyl terminated particles with an average diameter of 204 nm and a specific surface area of 15.7 ± 1.7 m^2 g^{-1}. The particles were then dried overnight under vacuum.

The ATR-FTIR spectra of the particles were recorded and normailsed to the Si-O peak of the vinyl terminated particles at ~1100 cm^{-1}, which also served as an internal reference, as shown in Figure S7. The peak height ratio of the C=O stretch of 11-MUA to the Si-O band was plotted as a function of simulated 11-MUA attachments per square nanometre of particle surface as shown in Figure S8. This linear calibration curve is similar to that obtained by Mangos *et al*., for quantifying 11-bromoundecene attachment density on the surface of thiol particles. This demonstrates the utility of this technique for other particle species.

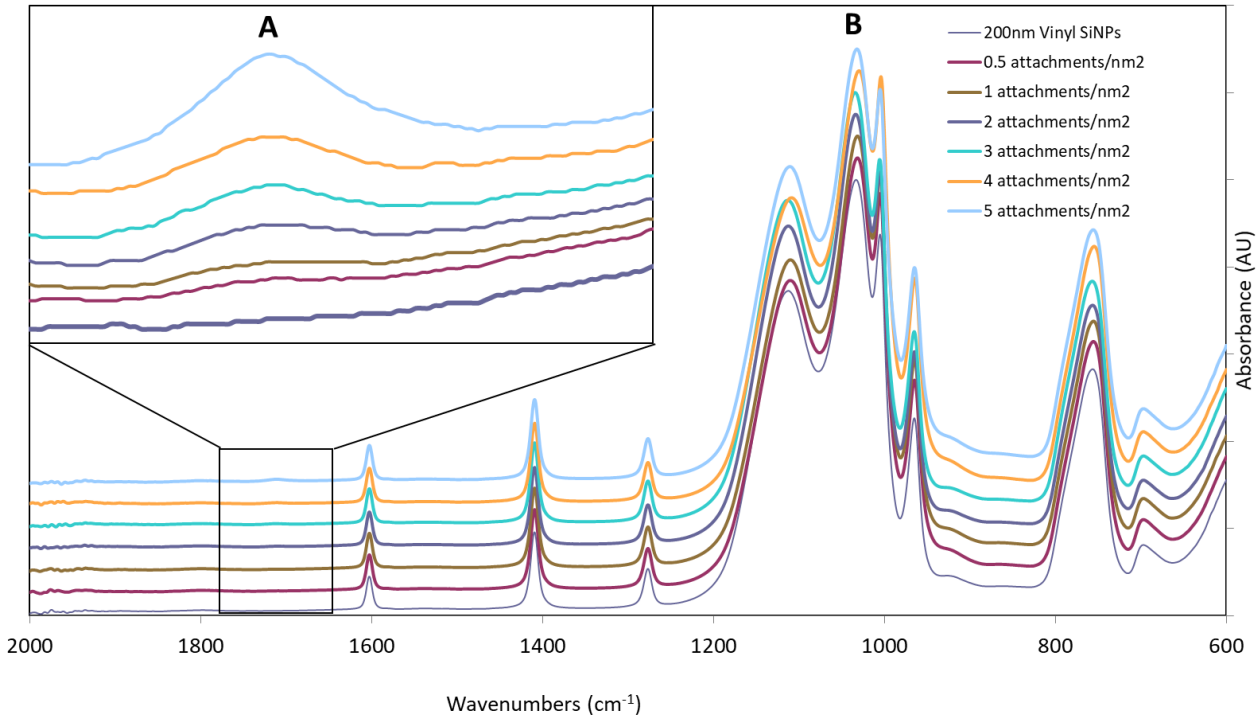

Figure S7: ATR-FTIR spectra of 11-MUA standards mixed with vinyl-terminated particles

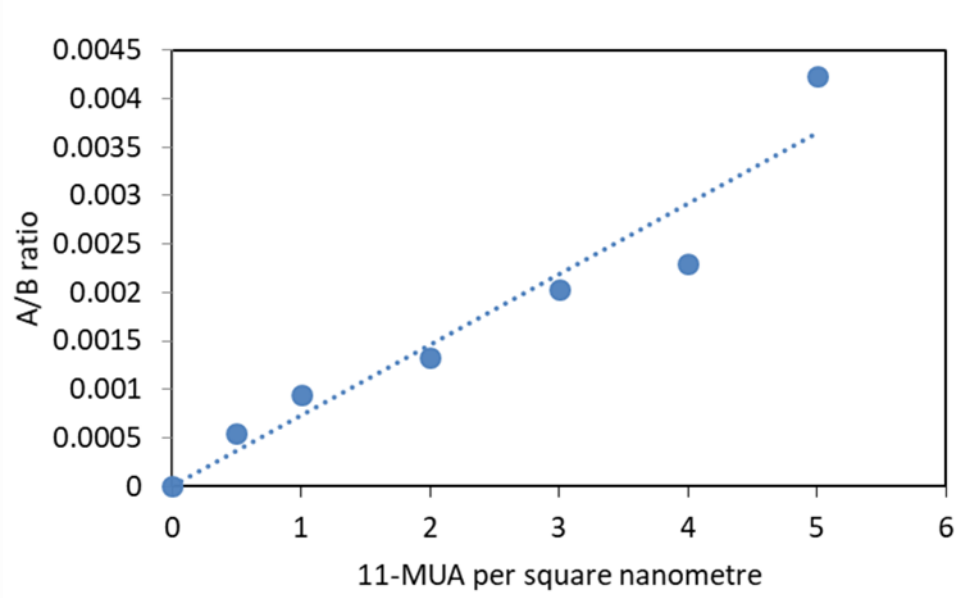

Figure S8: 11-MUA attachment calibration curve with vinyl particles

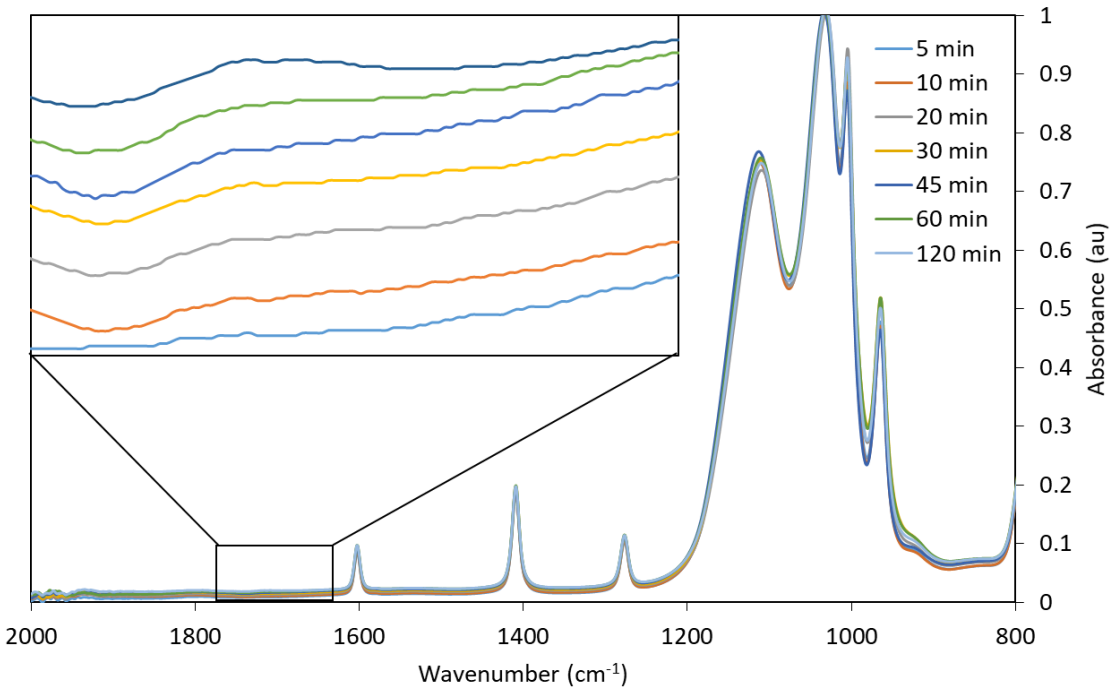

Figure S9: ATR-FTIR spectra of vinyl particles over duration of 11-MUA attachment reaction.