

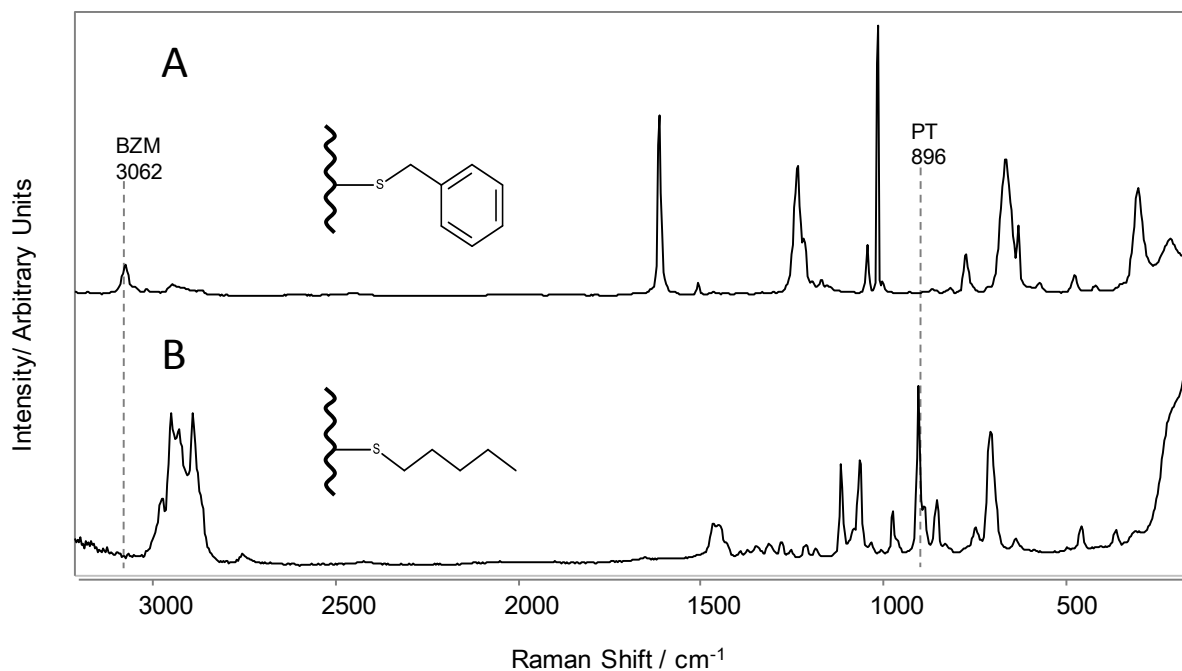
## **Controlling Assembly of Mixed Thiol Monolayers on Silver Nanoparticles to Tune Their Surface Properties**

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### **Supporting Information**

#### **S.1 – Spectra of BZM / PT on silver colloids**

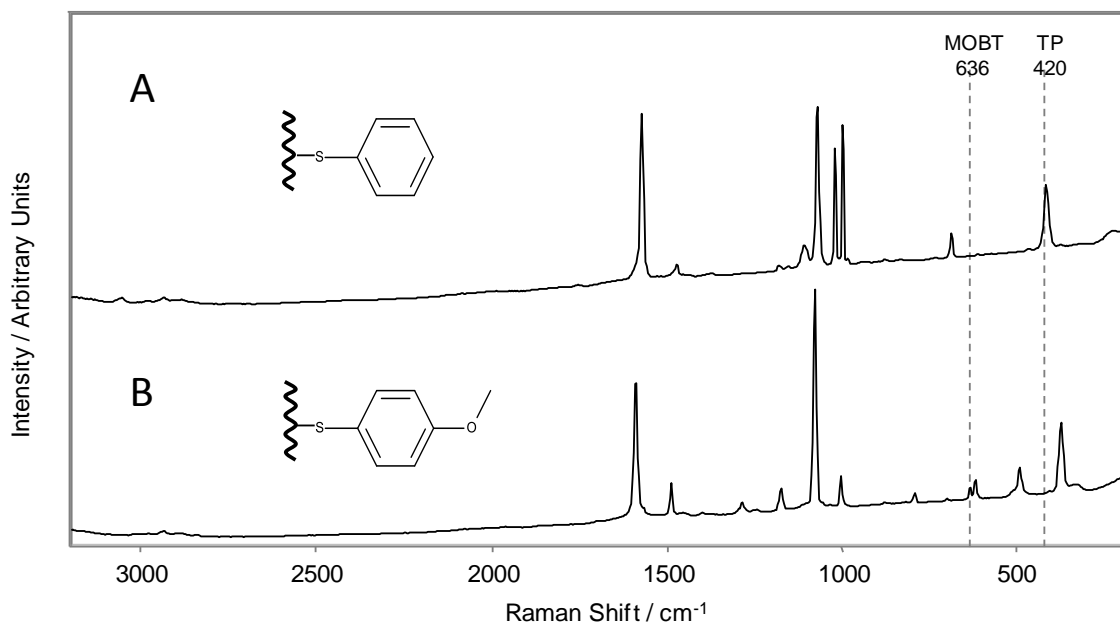
To determine which band to measure, 20  $\mu\text{L}$  aliquots of benzyl mercaptan (BZM) or 1-pentanethiol (PT) solutions ( $1 \times 10^{-4}$  M) were added to 200  $\mu\text{L}$  of silver colloids, then aggregated with 1 M NaCl. The SERS spectra of BZM and PT on hydroxylamine-reduced silver colloids (HRSC) are shown in Figure S1. The  $3062\text{ cm}^{-1}$  band was chosen for measuring BZM because it was unique to BZM and gave the most reliable isotherm when only BZM was used.  $896\text{ cm}^{-1}$  band was chosen for measuring PT for the same reason. The spectra were identical on HRSC and citrate-reduced silver colloid (CRSC), and the marker bands are the same.



**Figure S1** SERS spectra of 20  $\mu\text{L}$   $10^{-4}$  M (A) BZM and (B) PT adsorbed on HRSC and aggregated with 20  $\mu\text{L}$  1 M NaCl. Marker bands for BZM (3062  $\text{cm}^{-1}$ ) and PT (896  $\text{cm}^{-1}$ ) are highlighted. Spectra were acquired using an Avalon R2 Raman spectrometer. Total accumulation time was 30 s. The structure of each molecule is shown, and spectra are scaled and vertically offset for clarity.

## S.2 Spectra of MoBT / TP on Ag Nanoprisms

20  $\mu\text{L}$  aliquots of  $1 \times 10^{-4}$  M methoxybenzenethiol (MOBT) or thiophenol (TP) were added to 200  $\mu\text{L}$  of silver nanoprisms, and then aggregated with 0.1 M  $\text{MgSO}_4$ . The 636  $\text{cm}^{-1}$  band was used to track the concentration of MOBT and 420  $\text{cm}^{-1}$  band was chosen for measuring TP. The SERS spectra of  $1 \times 10^{-4}$  M of MOBT and TP on silver nanoprisms are shown in Figure S2.

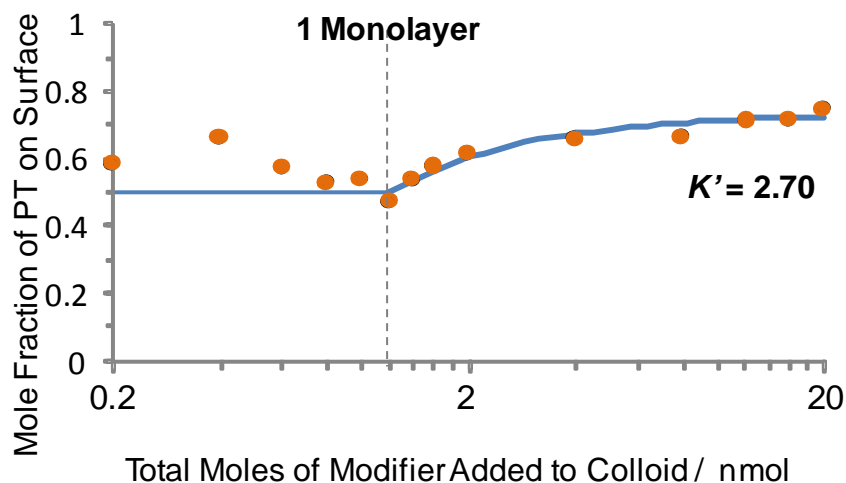


**Figure S2** SERS spectra of 20  $\mu\text{L}$   $1 \times 10^{-4}$  M (A) TP and (B) MOBT adsorbed on Ag nanoprisms and aggregated with 20  $\mu\text{L}$  0.1 M  $\text{MgSO}_4$ . Marker bands for MOBT ( $636 \text{ cm}^{-1}$ ) and TP ( $420 \text{ cm}^{-1}$ ) are highlighted. Spectra were acquired using an Avalon R2 Raman spectrometer. Total accumulation time was 30 s. The structure of each molecule is shown, and spectra are scaled and vertically offset for clarity.

### S.3 Isotherm 1:1 BZM and PT adsorbed on HRSC

As a supplement of Figure 3, the adsorption isotherm of a 1:1 mixture of BZM and PT on HRSC is shown in Figure S3. 1:1 mixed feedstocks of varying concentrations, from  $1 \times 10^{-3}$  M to  $1 \times 10^{-5}$  M, were prepared and 20  $\mu\text{L}$  aliquots were added to 200  $\mu\text{L}$  of silver colloids, then aggregated with 1 M NaCl for spectral acquisition.

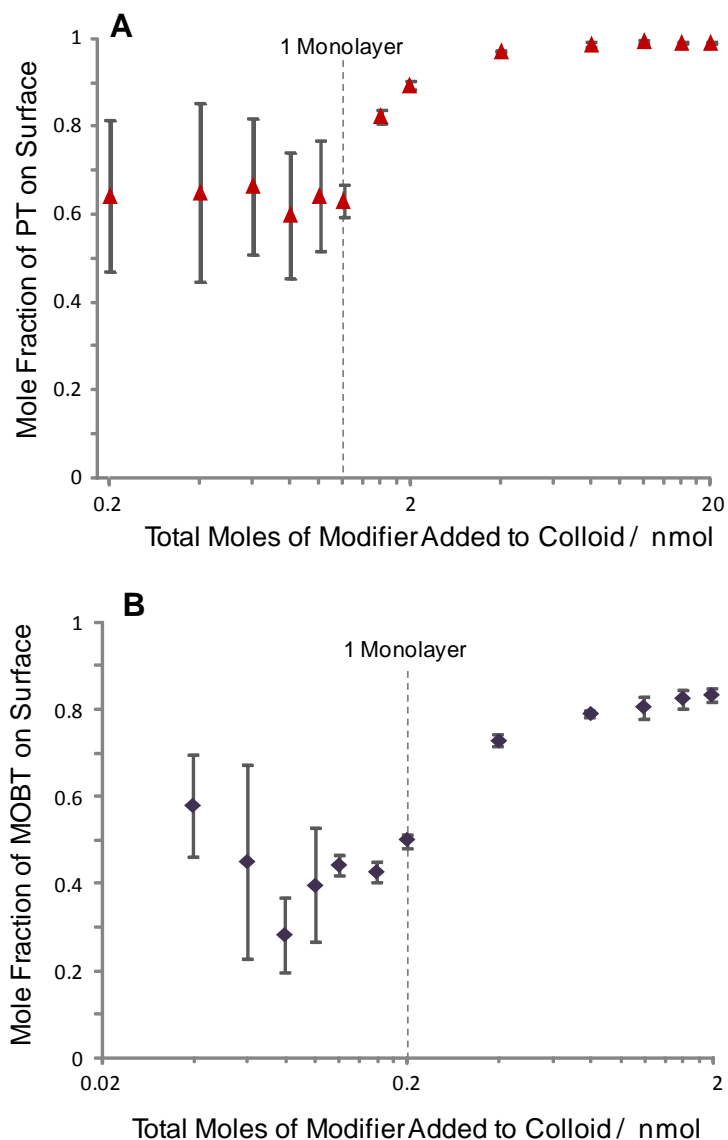
## Supporting Information



**Figure S3** Comparison of experimental and simulated data for the mole fraction of PT found on the surface of 200  $\mu\text{L}$  of silver colloid for a 1:1 binary feedstock of PT:BZM at varying total modifier concentrations.

It is clear from the Figure that the data follow the model above monolayer coverage, which is behaviour consistent with our other datasets. Comparison of this dataset to Figure 3A, where a different set of modifiers is used on the same colloid (HRSC), shows that  $K'$  can change dramatically between modifier sets even if the colloid is similar. In contrast, when the modifiers are kept the same and the type of nanoparticle changed, (*i.e.* comparing Figure S3 to Figure 3C) the  $K'$  values are similar.

### S.4 Replicate Measurements of Isotherms for 1:1 MPS and PT adsorbed on HRSC and 1:1 MOBT and TP on Nanoprisms



**Figure S4.** Plots showing replicate measurements of the fractions of: (A) PT adsorbed from a PT:MPS feedstock on HRSC, (B) MOBT from a MOBT:TP feedstock on Ag nanoprisms. Error bars are  $\pm 3\sigma$ .

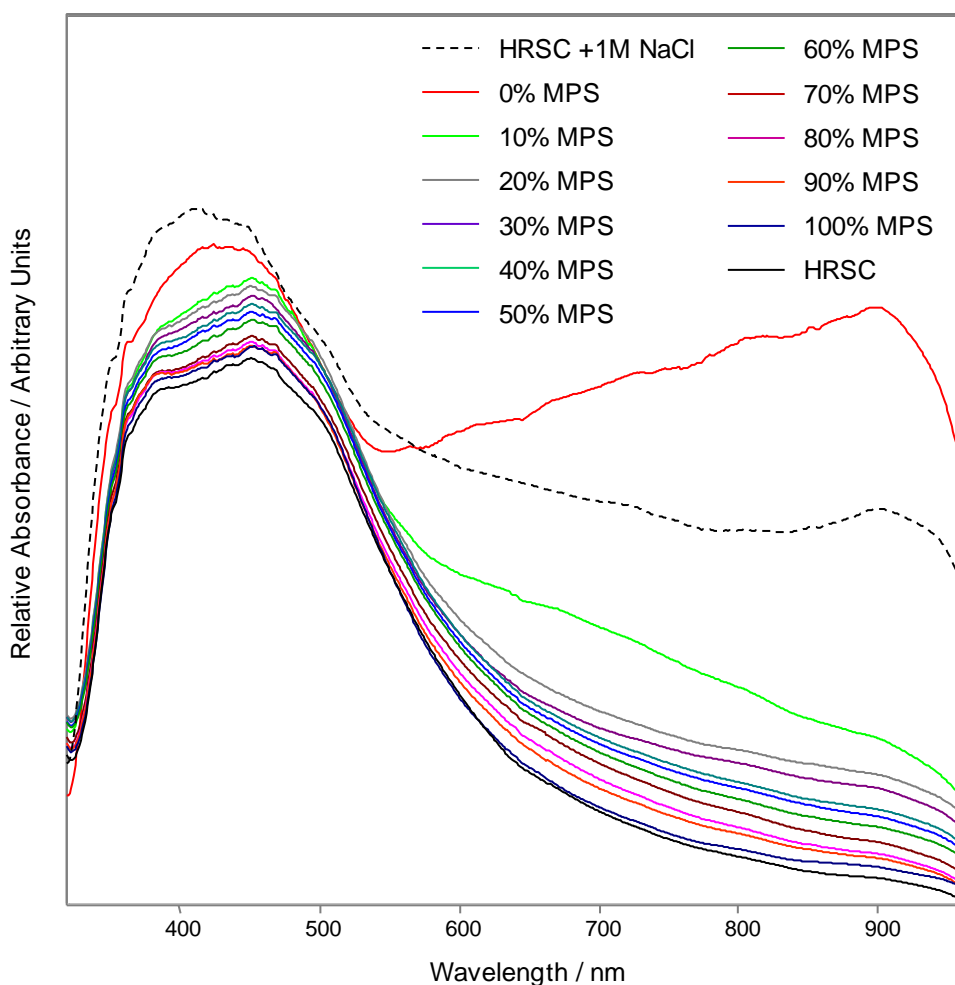
The data above show error bars calculated from 3 replicate measurements made during a single experimental run for each of the two sample types. These error bars ( $\pm 3\sigma$ ) reflect the variation due to fluctuations in the Raman signal and, as expected, show larger uncertainty at the sub-monolayer concentrations where signal levels are lower (this is also apparent in Figures 3A and S3). These data were recorded on completely independent experimental runs

## Supporting Information

from Figure 3, using different colloids and freshly determined intensity correction factors. Comparison of these plots with those in Figure 3 therefore shows the reproducibility between experimental runs. The main variation is in the ratio observed at sub-monolayer concentration, which is strongly dependent on the value selected for the intensity normalisation factor.

### **S.5 UV-Vis Spectra for MPS-PT Mixed Monolayers**

Figure S4 shows the UV-vis absorption spectra of HRSC modified with various mixed monolayers of MPS and PT. It was noted that as the amount of PT in the feedstock was increased, colloid stability eventually decreased, and feedstocks of 0 and 10% MPS aggregated the colloids in 1-2 seconds. However, colloids modified with feedstocks of 20% or more of MPS did not aggregate at all in the time studied.



**Figure S5** UV/vis absorption spectra of HRSC modified with various mixed SAMs of MPS and PT. Spectra have been normalized to the highest band and vertically offset slightly for clarity.

To obtain reasonable spectra, it was necessary to dilute HRSC by a factor of 2; otherwise the absorbance was too high (3.5 - 4) to measure accurately. The dilution would increase the inter-particle distance and therefore slow aggregation, so the mixtures were allowed to stand for a few minutes prior to measurement. Spectra were acquired using an Agilent 8453 spectrometer. The main observation from the Figure S4 is that 0 and 10% MPS show a large increase in absorption in the range of 600 - 900 nm, indicating aggregation. Although the main absorption band ( $\lambda_{\max} = 464$  nm) broadens slightly from 100% MPS down to 20% MPS there is only a small increase at 600 - 900 nm. This is consistent with simple visual observation of these mixtures, which also indicated that they did not aggregate in the time studied.