

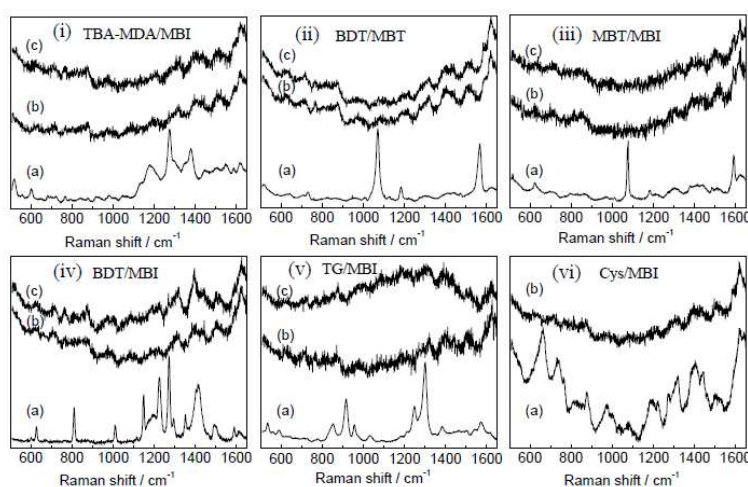
## Supporting Information

### Quantitative Comparison of Raman Activities, SERS Activities, and SERS Enhancement Factors of Organothiols: Implication to Chemical Enhancement

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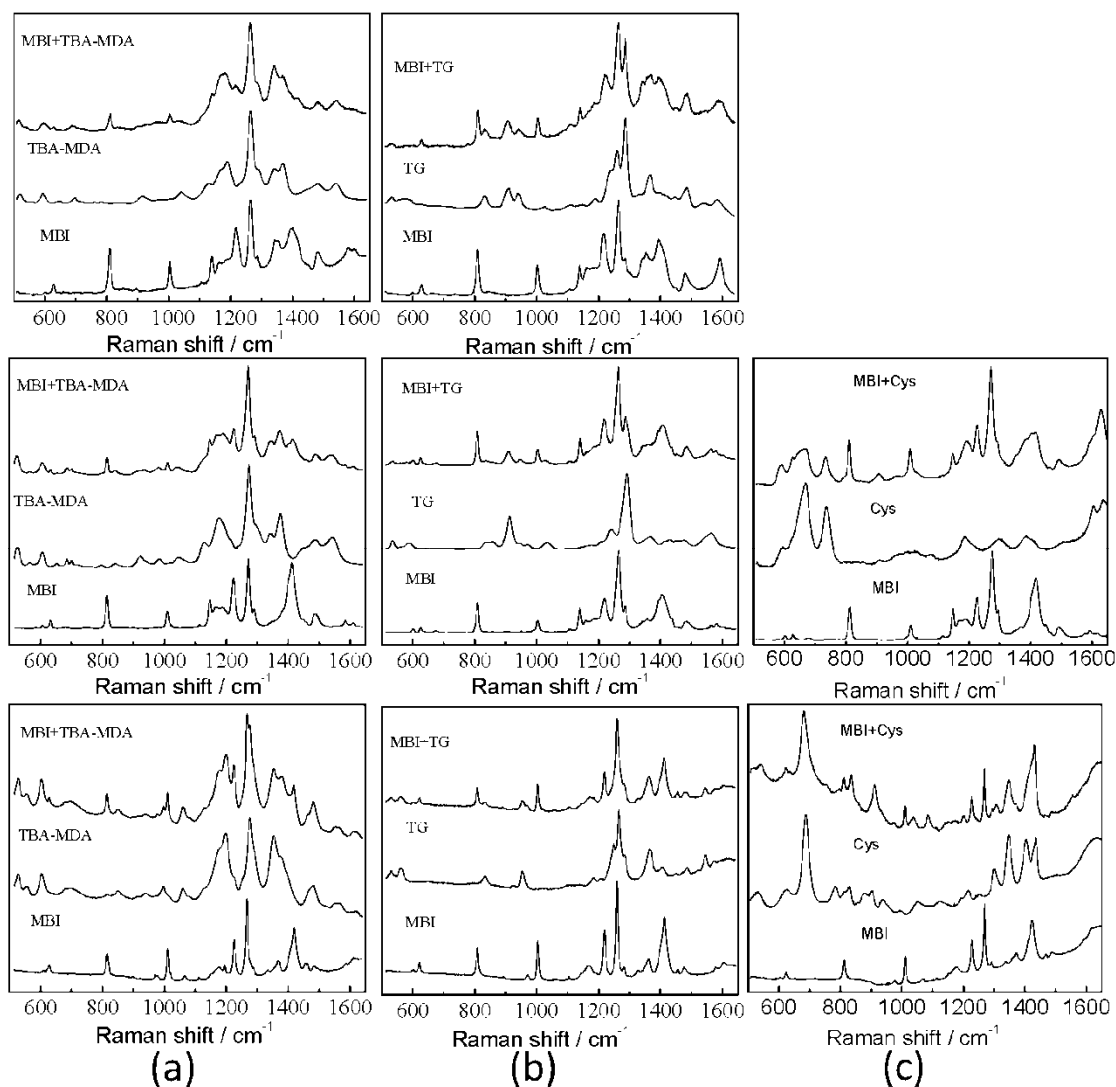
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#### 1: Estimation of the amount of organothiols adsorbed onto the AuNPs and AgNPs in the SERS activity comparison samples.



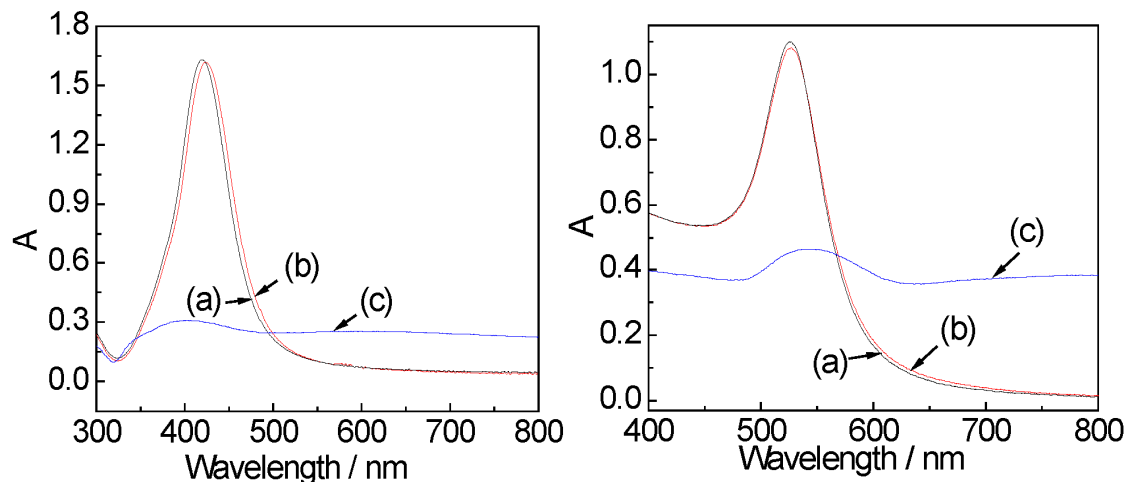
**Figure S1.** SERS confirmation of complete organothiol adsorption (>95%) onto NPs in the SERS activity comparison samples. SERS spectra (a) in (i)-(vi) were obtained with individual organothiol controls where the concentrations and the organothiols are (i) 1.5 nM TBA-MDA, (ii) 62.5 nM BDT, (iii) 62.5 nM MBT, (iv) 62.5 nM MBI, (v) 62.5 nM TG, and (vi) 1.25  $\mu$ M Cys. The concentrations of the organothiols in these controls are 20 times lower than their respective concentrations in the SERS activity comparison samples specified in Table II in the text. The spectra (b) and (c) in plot (i)-(vi) were acquired with the supernatants of the SERS activity comparison samples in which the SERS substrate was AgNPs and AuNPs, respectively. The spectra (b) and (c) in each plot showed that there was no detectable SERS signal from organothiols in the supernatant after centrifuge removal of the AuNPs or AgNPs together with their surface adsorbed organothiols. In contrast, high quality SERS spectra (Spectrum (a) in each plot) were obtained when the organothiols were 20 times more dilute than the concentrations used for the comparative SERS activity study. This indicates that at least 95% of the organothiols were adsorbed onto the AuNPs and AgNPs in the SERS activity comparison samples. For the SERS measurements, 50  $\mu$ L of the organothiol control or the supernatant solution was sequentially mixed with 10  $\mu$ L in-house synthesized colloidal AgNPs and 10  $\mu$ L 1% KCl. Spectral integration time is 100 s with a 632 nm laser. Laser power on the sample is  $\sim$  1.3 mW.

## 2: Normal and SERS spectra of organothiols and their mixtures.



**Figure S2.** (Bottom) Normal Raman and (Middle and Top) SERS spectra obtained with individual organothiols or their mixtures with MBI. The SERS spectra on top are obtained with AuNPs, and the ones in the middle with AgNPs. Concentrations of analytes A and B in the Raman and SERS sample mixtures of A/B were shown in Table II under the Experimental Method Section.

### 3: UV-Vis extinction spectra of AgNPs and AuNPs



**Figure S3.** UV-Vis spectra of AgNPs (left) and AuNPs (right), (a) NPs diluted with water, (b) NPs with MBI/MBT mixture which was taken after the sample was incubated overnight, (c) after addition of 10  $\mu$ l of 20% KCl to 1 mL of the sample used for spectrum (b). The concentration of NPs is  $\sim 0.1$  nM. The concentrations of MBI and MBT are both  $\sim 0.5$   $\mu$ M. It is important to note that MBI/MBT/NP mixtures used in the UV-Vis measurements were  $\sim 2.6$  times diluted from MBI/MBT/NP mixtures shown in Table II. The original solutions were too concentrated for direct UV-vis spectral acquisition.