

## Protein-Ligand Binding Investigated by a Single Nanoparticle TERS Approach.

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### Supplementary Material

Figure S1: Raman spectra of different nanoparticles. Part (a) shows the data from Figure 1, which has a similar spectrum to the single nanoparticle in part (b). Part (c) images several nanoparticles and shows a significant difference from a single nanoparticle spectrum. Several features show more enhancements in the multiple nanoparticle spectrum, possibly due to the surface selection rule where position of the nanoparticles increase the enhancement of certain vibrational modes associated with the differing polarizations experienced by the molecules. In either case the observed modes can be assigned to biotin, streptavidin, or the biotin-streptavidin complex as detailed in Table S1. The insets show Raman maps of the biotin 680  $\text{cm}^{-1}$  band with the scale bars of 100 nm. The spectra shown were obtained from the circled pixel.

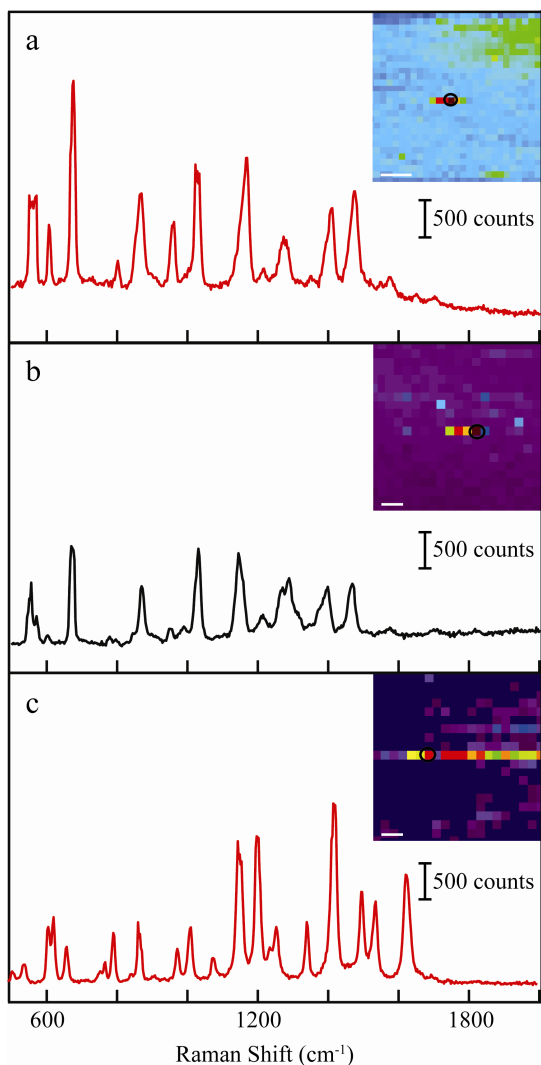


Table S1: Band assignments of the spectrum of Biotin-Streptavidin complex shown in Figures 1(a) and S1(a). The streptavidin literature values shown are for the complexed form, and the biotin values are estimated from the free biotin spectrum in reference 1.

<u>Experimental</u>	<u>Literature</u>	
Band (cm <sup>-1</sup> )	Band (cm <sup>-1</sup> )	Assignment
558-571	560; 567	Biotin; Streptavidin (Trp)
605	610	Biotin
680	686	Biotin
801	810	Biotin
870	880-895; 852	Biotin; Streptavidin (Tyr)
961	960	Streptavidin (Trp, Val)
1030	1010-1030; 1011 & 1027	Biotin; Streptavidin (Trp, Phe, Ala, Ser)
1120-1170	1155; 1126 & 1160	Biotin; Streptavidin (C-N, Trp, Val, Glu, Lys)
1216	1205	Biotin
1250-1280	1275; 1261 & 1278	Biotin; Streptavidin (Amide III Random & $\alpha$ -helix)
1340-1365	1340; 1339 & 1360	Biotin; Streptavidin (Trp)
1410	1415	Streptavidin
1475	1449	Streptavidin ( $\delta$ CH <sub>2</sub> , $\delta$ CH <sup>3</sup> )
1548	1548	Streptavidin (Trp)
1576	1576	Streptavidin (Trp)

## References

1. C. Fagnano, G. Fini and A. Torreggiani, *Biospectroscopy*, 1996, **2**, 225-232