# A Highly Sensitive Nanoscale pH-sensor using Au Nanoparticles Linked by a Multifunctional Raman-active Reporter Molecule (Supplemental)

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In the supplemental material we provide three additional figures. The first and second figures show the NMR and mass spectra of our final products, respectively. The third figure depicts TEM micrographs of nanoparticles after exposure to our hotspot inducing pH sensitive Raman reporter, 3,5-dimercaptobenzoic acid (3,5-DMBA).

To show that we successfully synthesized the final product we are providing both the $^{1}H$ and $^{13}C$ NMR of 3,5-DMBA in **Figure S1**. Analysis of the splitting is in the main text under the Results and Discussion section. To support the NMR and Raman analysis we also show the mass spectrum of our final product in **figure S2**. The mass spectra analysis is also in the main text under the section Results and Discussion. It is evident from the mass NMR and the mass spectra analysis that we successfully synthesized our final product. A thorough Raman analysis is also featured in the main text.

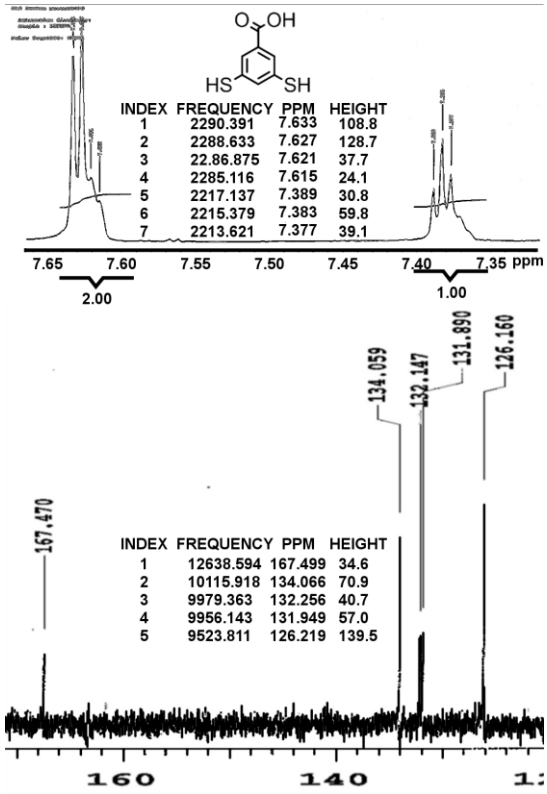


Figure S1: The NMR spectra of our final product. The top spectrum is the $^{1}H$ NMR and the bottom is the $^{13}C$ NMR.

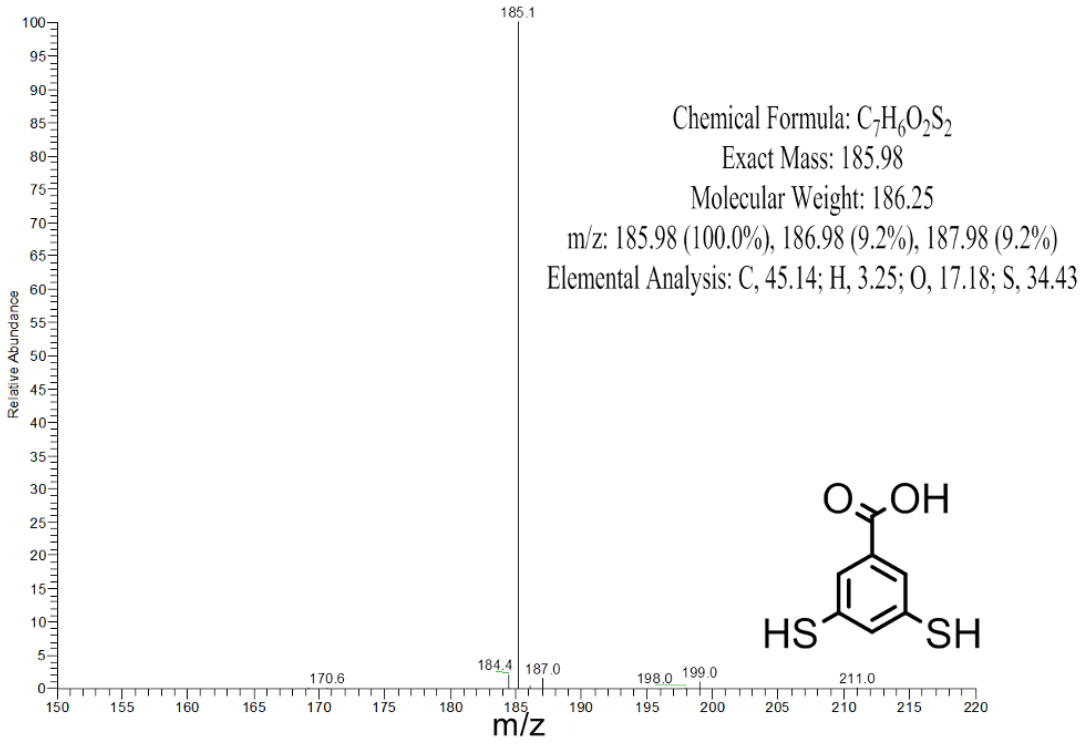


**Figure S2: The mass spectrum of the final product 3,5-Dmercaptobenzoic acid.**

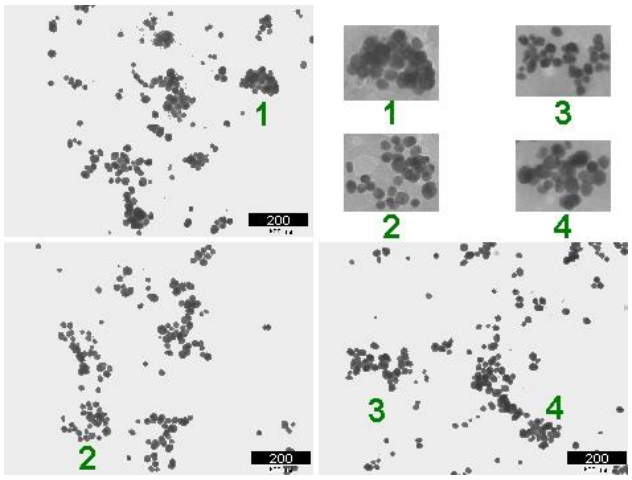


**Figure S3: Nanoparticles exposed to 3,5-dimercaptobenzoic acid. These are three separate TEM measurements of Au nanoparticles exposed to 3,5-DMBA. This image shows that most of the particles help to compose small multimers. The scale bar in the bottom right hand corners are 200 nm.**

To support our dynamic light scattering (DLS) spectra in Figure 2 of the main text, we present in **Figure S3** gold nanoparticles have been exposed to 3,5-DMBA. Although, TEM is not usually used to characterize the size distribution of agglomerates because of clustering artefacts that may emerge during the TEM grid preparation process[1-2], we present three TEM images with a larger field of view than the TEM in **Figure 2** of the main document. This image shows that the nanoparticle themselves retain their individual shapes and sizes after exposure to 3,5-DMBA. This image also shows that most of the particles are involved in multimer formation. The size distribution of nanoparticle clusters range from a couple of nanoparticles to many nanoparticles. This is consistent with the DLS measurements in **Figure 2** of the main text. However because of the reasons mentioned above the DLS measurement gives us a better understanding of the size distribution of our multimers than the TEM data. The DLS indicates that the size distributions shift upon the addition of 3,5-DMBA in solution. The size distributions before the addition of 3,5-DMBA range roughly between 10 nm and 400 nm, with the majority being found at roughly 35 nm. The size distributions after the addition of our reporter molecule shifts to between 50 nm and 700 nm with a mean diameter at approximately 160 nm. The TEM images above agree with the DLS, in that most of the nanoparticles participate in clustering, and that most of the clusters are multimers.

1. J. M. Zook, V. Rastogi, R. I. MacCuspie, A. M. Keene, J. Fagan, Measuring Agglomerate Size Distribution and Dependence of Localized Surface Plasmon Resonance Absorbance on Gold Nanopartide Agglomerate Size Using Analytical Ultracentrifugation. *Acs Nano* 2011, *5*. 8070-8079, DOI: 10.1021/nn202645b.
2. A. M. Keene, K. M. Tyner, Analytical characterization of gold nanoparticle primary particles, aggregates, agglomerates, and agglomerated aggregates. *Journal of Nanoparticle Research* 2011, *13*. 3465-3481, DOI: 10.1007/s11051-011-0268-4.