

**Supporting Information**

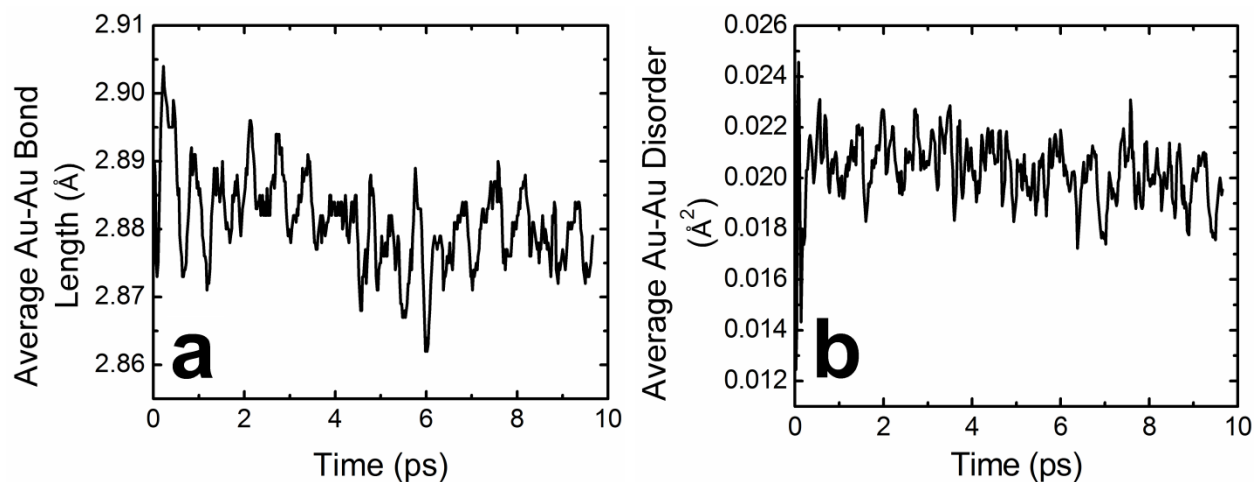
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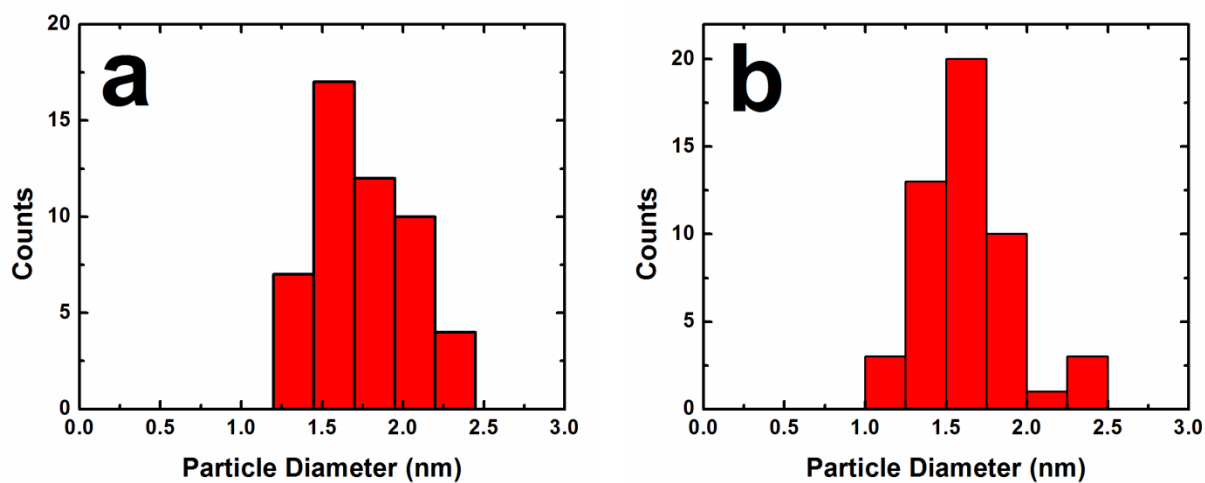
**A Theoretical and Experimental Examination of Systematic Ligand-Induced Disorder in Au Dendrimer-Encapsulated Nanoparticles**

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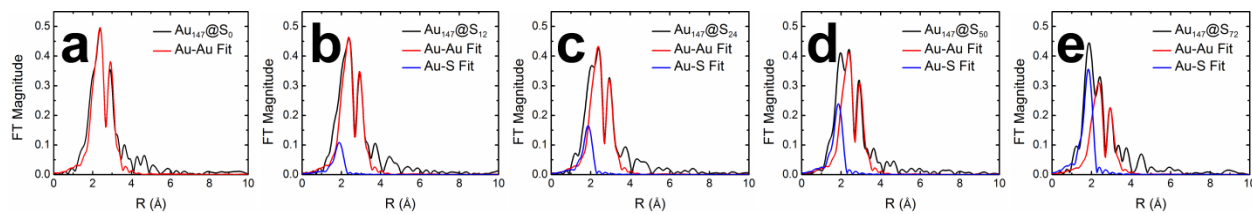
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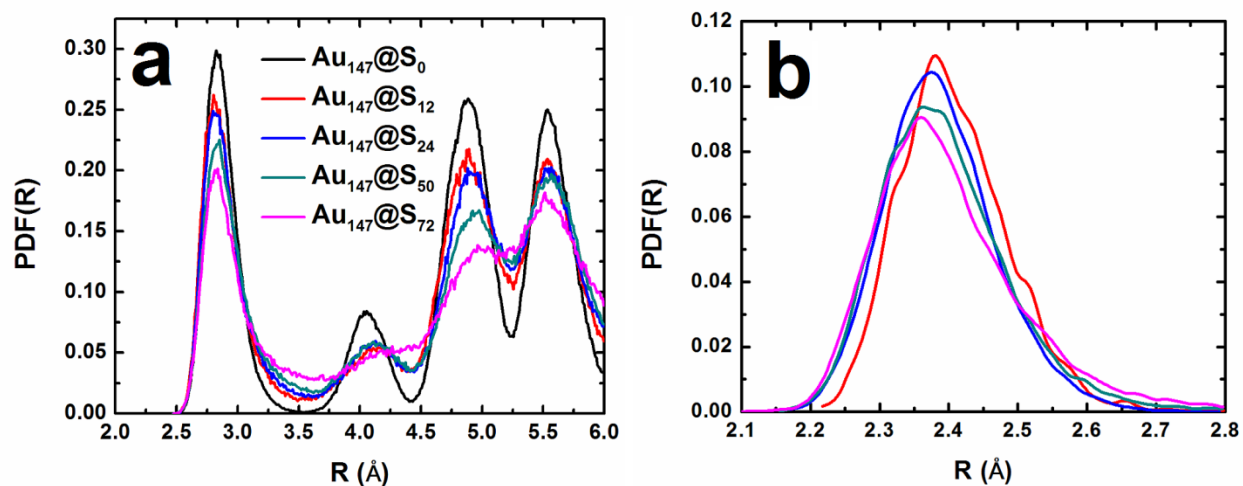
**Figure S1.** Instantaneous average Au-Au bond length (a) and bond disorder (b) for the Au<sub>147</sub>@S<sub>72</sub> DFT-MD trajectory demonstrating that 4 ps is sufficient for thermalization.



**Figure S2.** Particle-size histograms for (a) Au<sub>147</sub>@S<sub>0</sub> and (b) Au<sub>147</sub>@S<sub>72</sub> DENS.



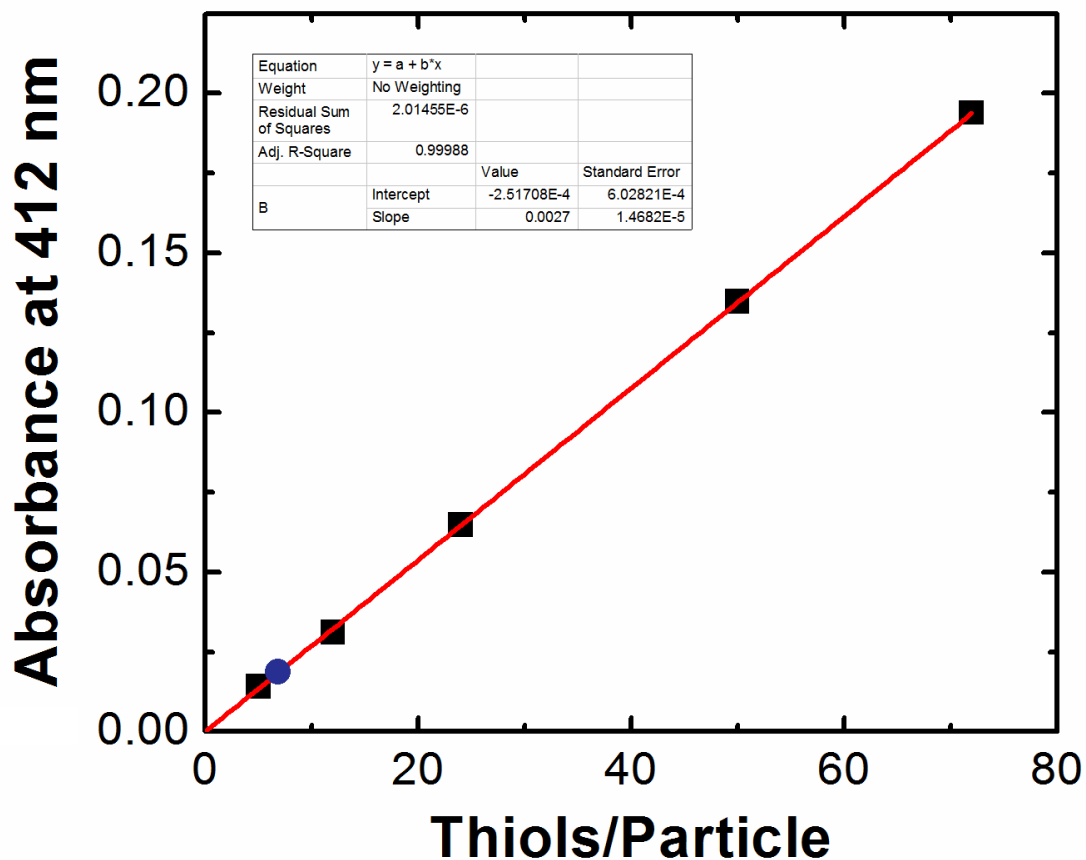
**Figure S3.** Individual contributions of Au-Au and Au-S paths to the fits of  $\text{Au}_{147}@\text{S}_n$  experimental data. (a)  $n = 0$ , (b)  $n = 12$ , (c)  $n = 24$ , (d)  $n = 50$ , (e)  $n = 72$ .



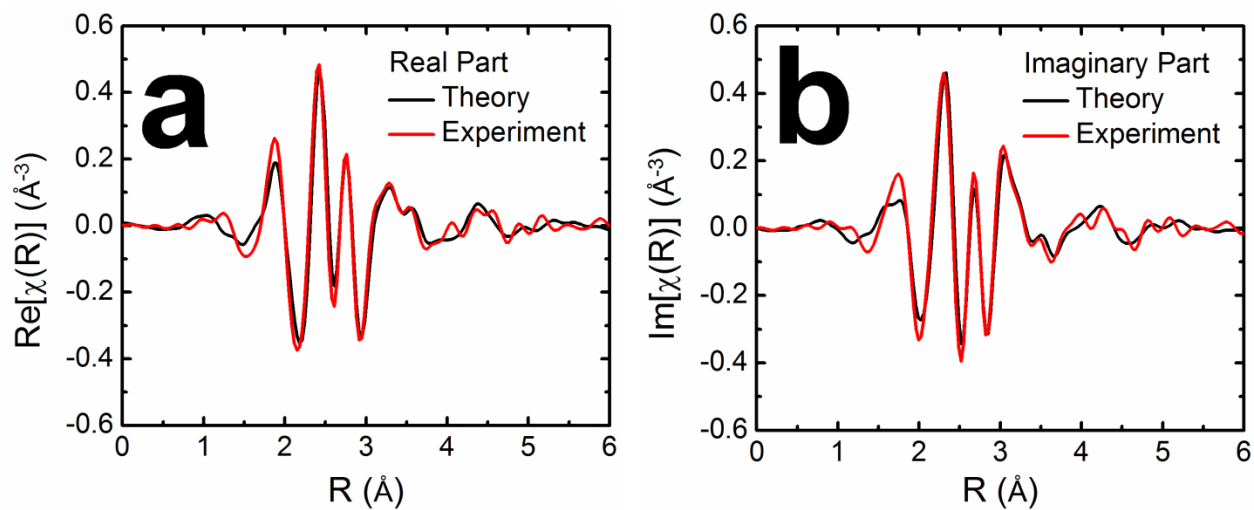
**Figure S4.** (a) Full Au-Au PDFs calculated from the equilibrated structures for  $\text{Au}_{147}@\text{S}_n$  ( $n = 0, 12, 24, 50$ , and  $72$ ). (b) Au-S PDFs of the equilibrated structures for  $\text{Au}_{147}@\text{S}_n$  ( $n = 12, 24, 50$ , and  $72$ ).

**Test for Unbound Thiols.** To test the assumption that all of the 2-mercaptoethanol (2-ME) added to Au DEN solutions were bound to their surfaces, the Ellman's test<sup>1</sup> for free thiols was carried out. The most likely case for observing unbound thiols would be for the Au<sub>147</sub>@S<sub>72</sub> DENs, because this material has the largest S: Au ratio. To prepare the Au<sub>147</sub>@S<sub>72</sub> DENs, 72 2-ME equivalents were added to a 2.0 μM solution of Au<sub>147</sub> DENs. The solution was stirred for 5 min, transferred to the top section of a 10,000 molecular weight cut-off (MWCO) centrifugal filtration device, and then centrifuged for 5 min at 4500 RPM. Free 2-ME will pass through the filter and the Au DENs, and any thiols bound to the encapsulated nanoparticle surface, will be retained. For reference, the G6-NH<sub>2</sub> PAMAM dendrimer has an ideal molecular weight of 58,048 g/mol. A calibration curve was constructed using free 2-ME solutions corresponding to concentrations of 5, 12, 24, 50, and 72 thiols/particle.

Samples and standards were prepared by combining 50.0 μL of 50 mM 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB), 2 mM sodium acetate, 100 μL of 1 M Tris buffer (pH 8), 350 μL of H<sub>2</sub>O, and 500 μL of the sample or standard solution. The absorbance of these solutions at 412 nm was used to quantify the amount of free thiol. The spectra were blanked with a solution prepared in the same way as the standards, but in the absence of 2-ME. The resulting calibration curve is shown in Figure S3. The concentration of free thiol found after 5 min of stirring was equivalent to 6.6 thiols/particle, which represents less than 10% of the total thiol added to solution. An additional test was carried out where the solution was allowed to stir for 1 h before centrifugal filtration. In this case, no detectable free thiol was present.



**Figure S5.** Calibration curve used to quantify the amount of free (unbound) thiols in solution. Standards are denoted by black points (squares). The DENs solution measured 5 min after addition of the thiol is denoted by the blue circle. The DENs solution measured 60 min after addition of the thiol had no measured absorbance at 412 nm.



**Figure S6.** Comparisons of the (a) real and (b) imaginary parts of the Fourier transform presented in Figure 6 in the main text.

### Reference

1. Sedlak, J.; Lindsay, R. H. Estimation of total, protein-bound, and nonprotein sulfhydryl groups in tissue with Ellman's reagent. *Anal. Biochem.* **1968**, *25*, 192-205.