Note about DLS –

Dynamic light scattering is based on the intensity of light scattered where the scattering intensity is biased towards larger particles. In the Rayleigh scattering regime the intensity is proportional to diameter to the sixth power. Therefore even a very small amount of a larger aggregate species would have a large bias on the signal. The intensity distributions for both the particles in the current study and the commercially produced nanourchins were compared as shown in Table S1. Both types of particles showed a peak at a larger size for the intensity distribution, which disappeared upon converting the size to a volume distribution. The conversion to the volume distribution was done through the algorithm built into the software from Brookhaven instruments (Dynamic light scattering software 9kdlsw32 ver. 3.34) which also accounts for contributions from Mie absorption and scattering. The conversion between distributions is given by

$$G_V^{'}(d) = G_I(d)/\left(d^3 P(\theta)\right)$$

where G'_v is the size distribution by volume, G_I is the size distribution by intensity, d is the scatterer diameter and $P(\theta)$ is the angular part of the Mie theory scattering coefficient. The real and imaginary refractive indices of pure Au at the laser wavelength of 660 nm where n = 0.11 and k = 3.6, repectively. It should be noted that the size was not very sensitive to the value used for the refractive indices.[1] All the sizes reported in the current study are the volume average size or the volume distribution determined as described above.

Supplemental Figures

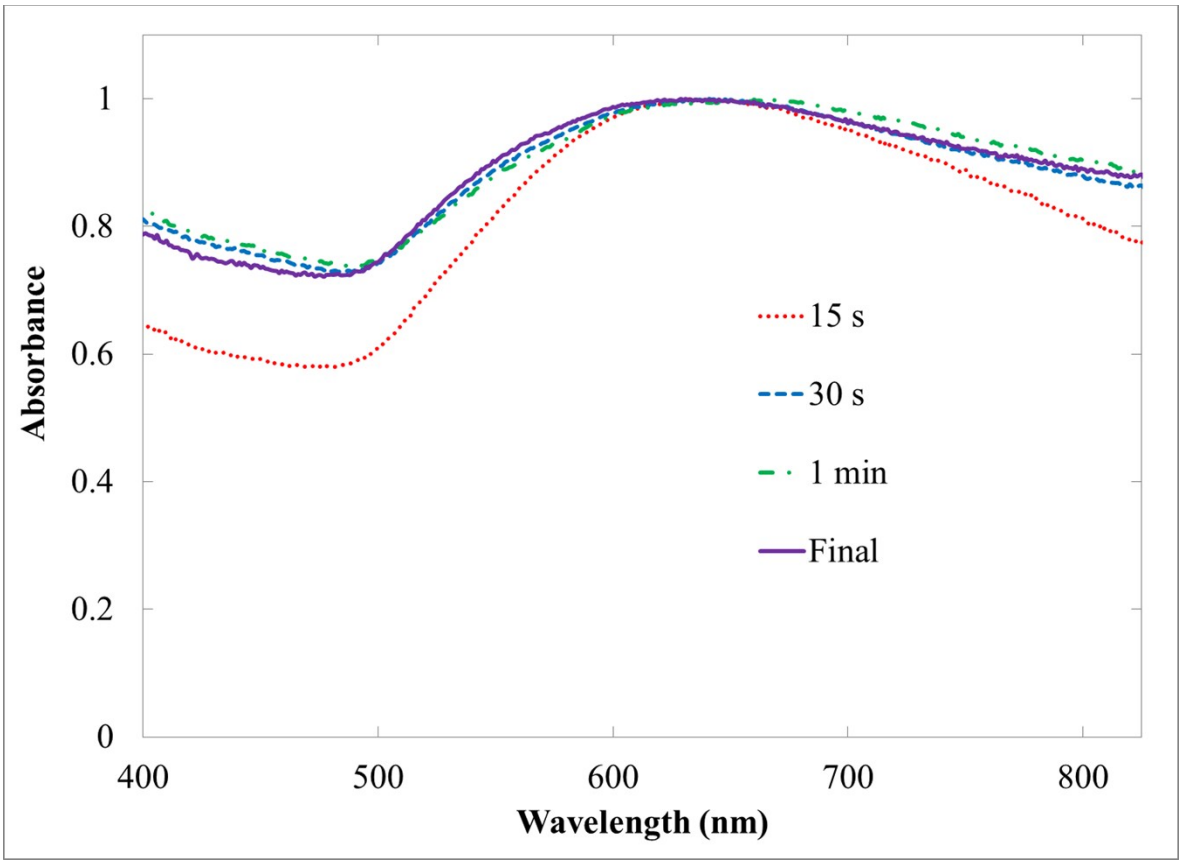


Figure S1. Evolution of Au nanocluster UV-vis extinction with time at 0.018 mM Au^{3+} precursor and pH 8.7, with the reaction quenched by mercaptoacetic acid at each time point.

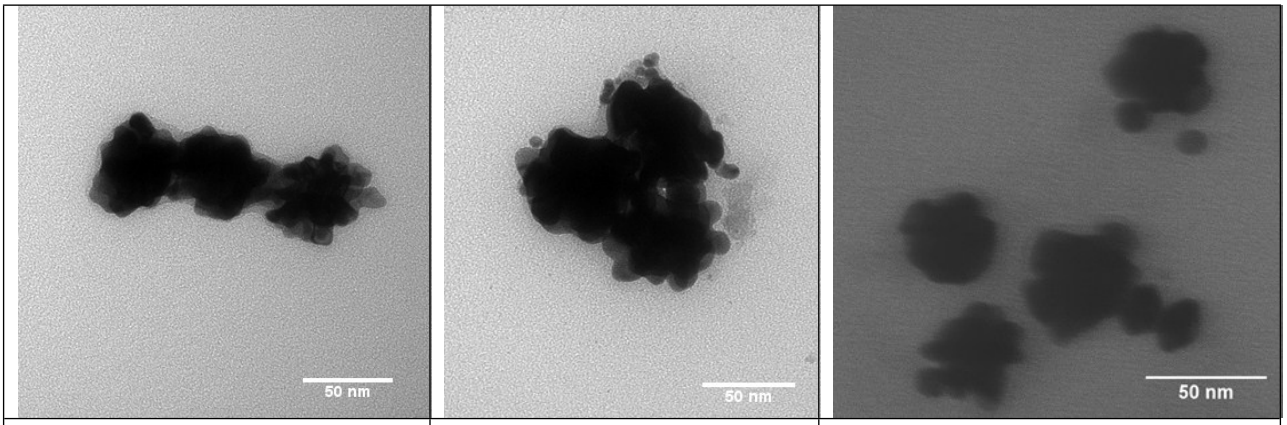


Figure S2. Time evolution of cluster morphology by TEM at 0.018 mM Au^{3+} precursor and pH 8.7, with the reaction quenched by mercapto acetic acid at: a, 15 s. b, 30 s. c, not quenched.

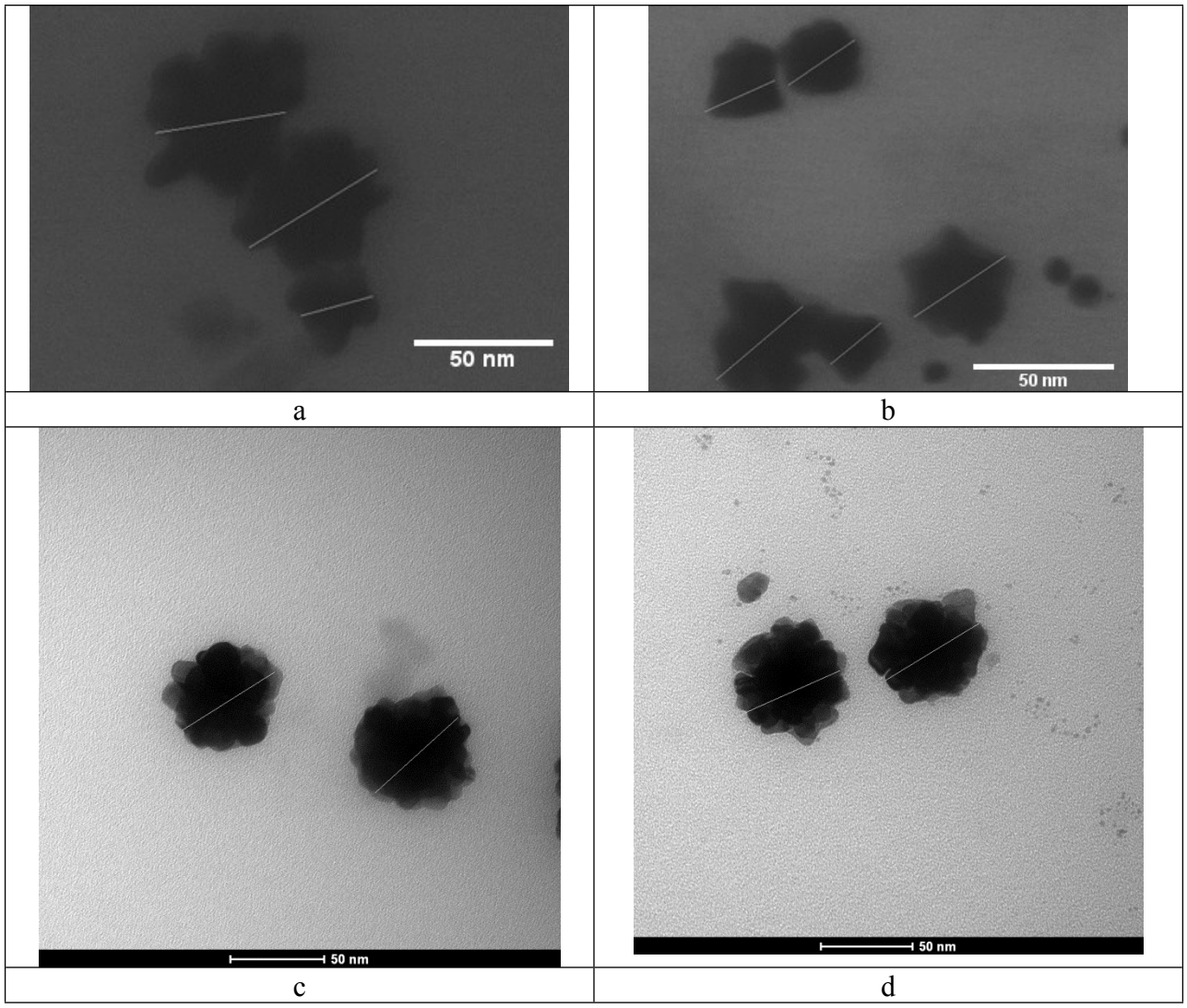


Figure S3. Additional STEM (a and b) TEM images (c and d) of particles synthesized at pH 8.7 at an Au^{3+} precursor concentration of 0.018 mM

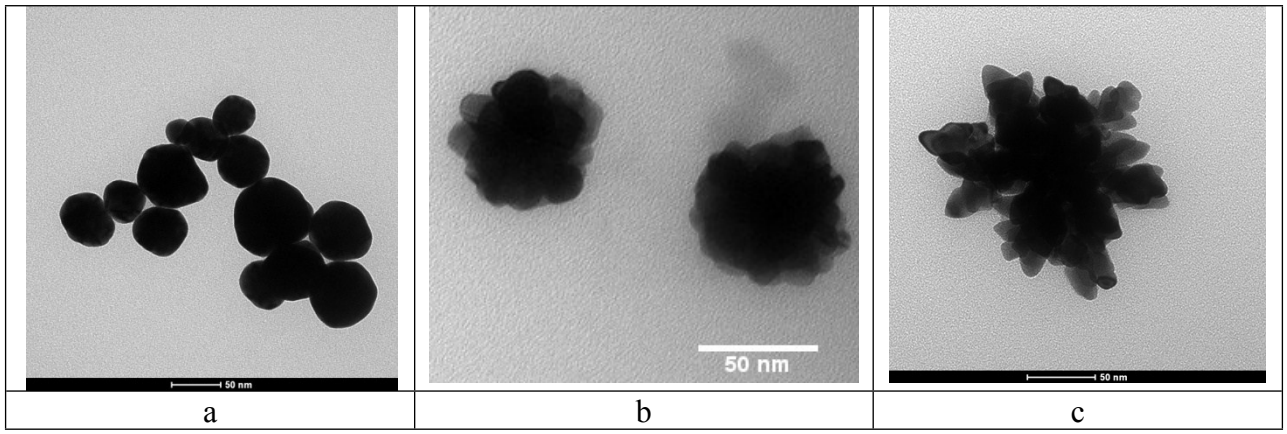


Figure S4. Low resolution TEM of nanoclusters synthesized with dextran as the stabilizing polymer with 0.018 mM Au^{3+} precursor at **a**, pH = 9.3. **b**, pH = 8.7. **c**, pH = 7.5. Scale bar is 50nm in all cases.

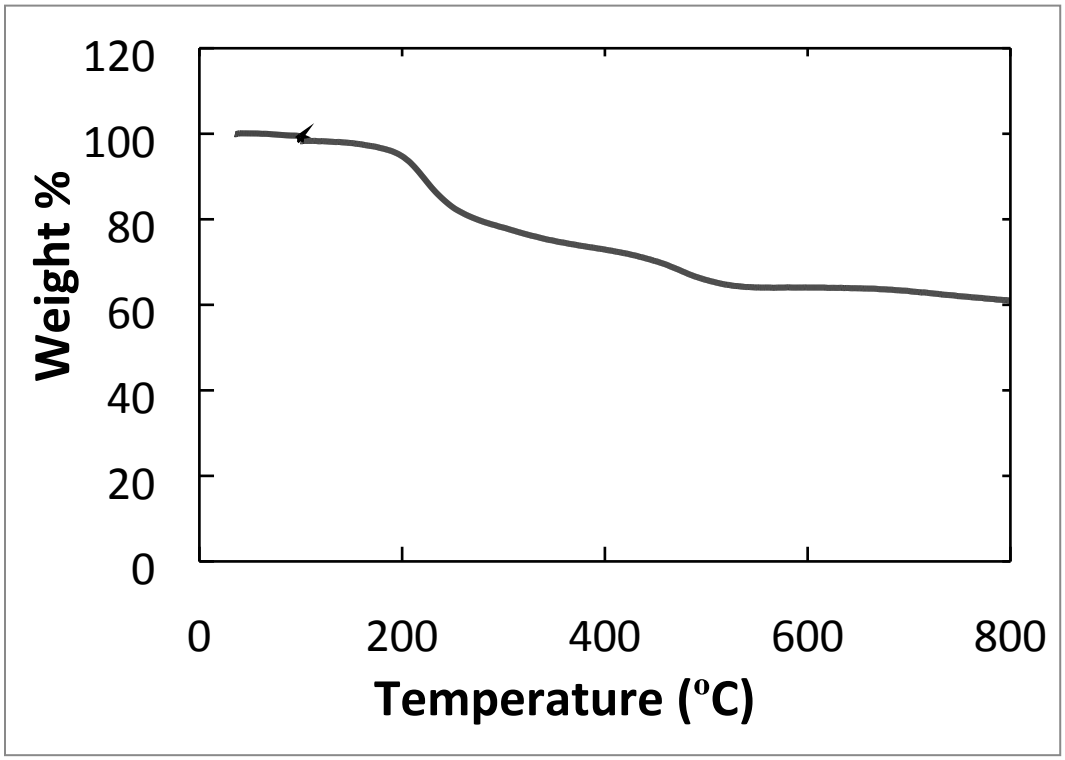
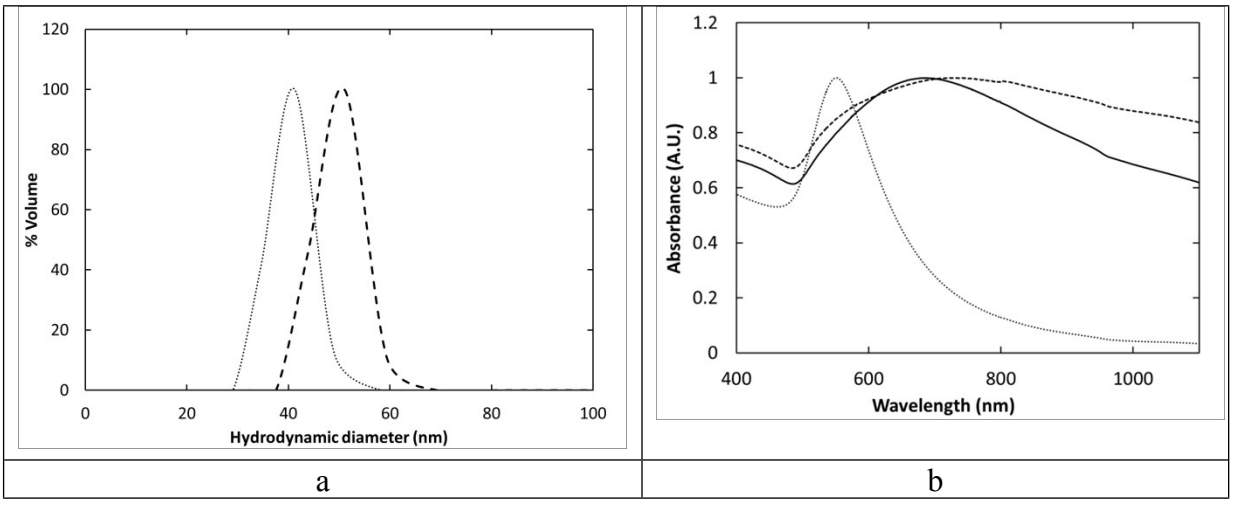
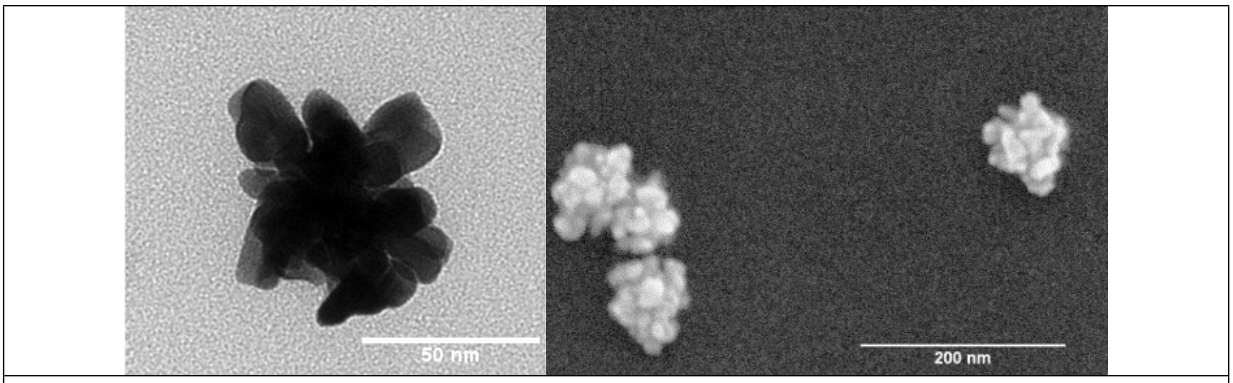


Figure S5. TGA of gold nanoclusters synthesized at 0.018 mM Au and a dextran coating at pH 8.7.



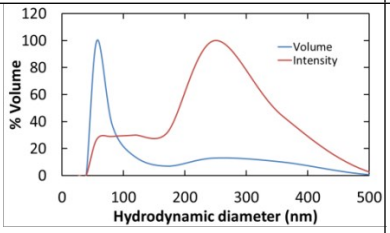
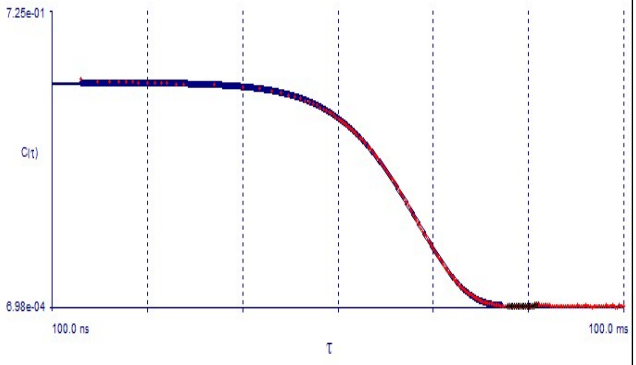
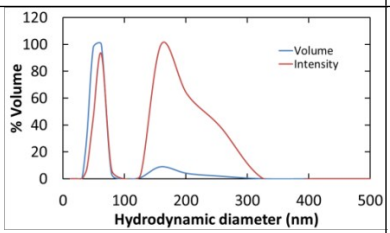
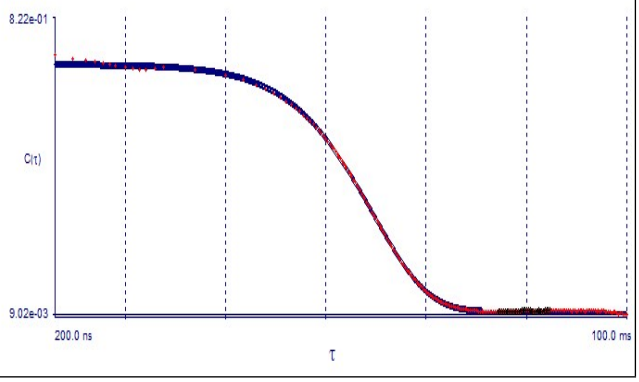
a b



c

Figure S6. Properties of nanocluster dispersions after 2 iterations of Au at pH = 9.3 (dotted line), pH = 8.7 (dashed line) and pH = 7.5 (solid line) characterized by a. Hydrodynamic diameter by DLS and b. UV- vis spectra. c. Example TEM and SEM images of particles synthesized at pH = 8.7.

Table S1. Dynamic light scattering ACFs and size distributions for commercial nanourchins contrasted with particles from the current study.

Fig. No. and pH	Size with autofit by volume (nm)	Volume and intensity distribution	ACF
100 nm nano urchins	101.7		
50 nm nano urchins	133.7		

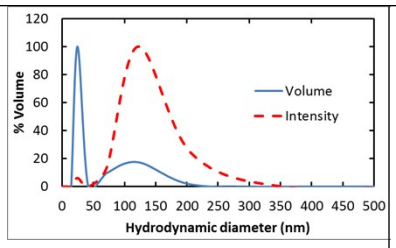
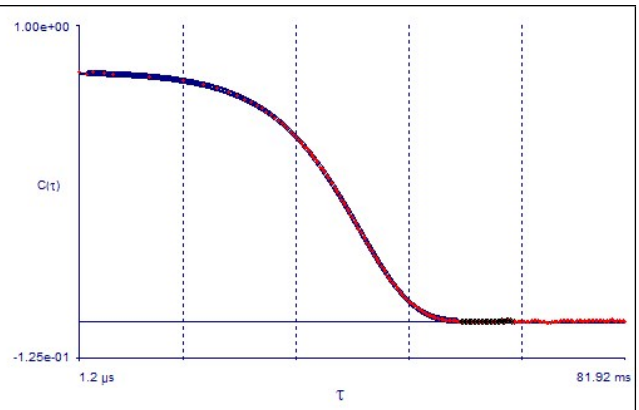
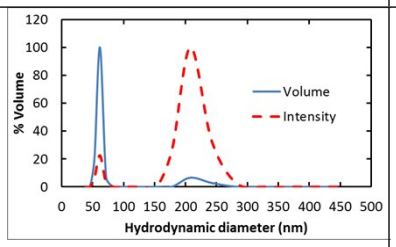
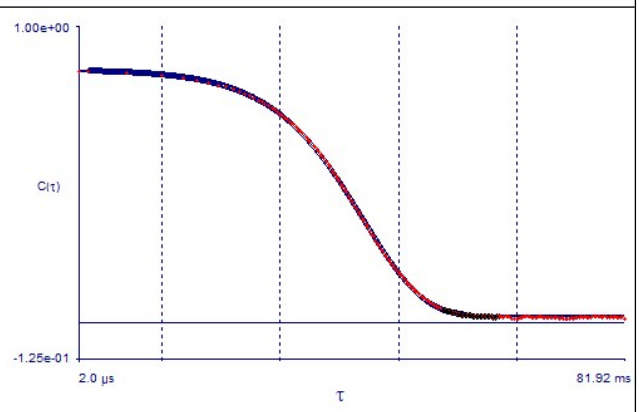
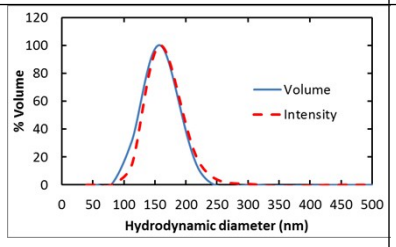
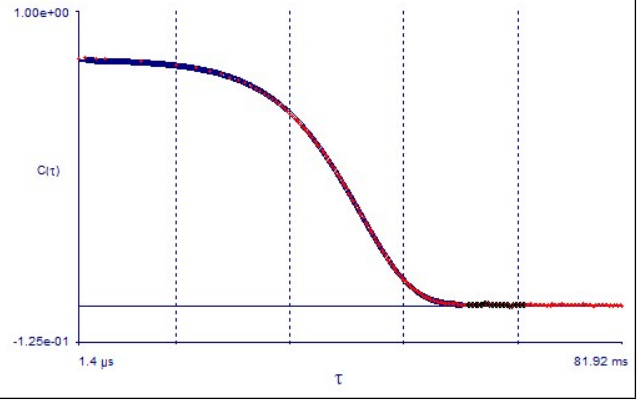
2a dotted line (pH 9.3)	25		
2a dashed line (pH 8.7)	64		
2a solid line (pH 7.5)	153		

Table S2: Summary of the NIR extinction properties and sizes of nanoclusters synthesized with dextran instead of CMD keeping all other parameters the same.

Polymer	**pH**	**Final Gold Concentration (mM)**	**Hydrodynamic Diameter (nm)**	**Extinction ratio (800nm/500nm)**	**Zeta Potential (mV)**
Dextran	8.7	0.018	39	1.24	-23.4 ± 1.8

(1) Raki, A. D.; Djuri?i, A. B.; Elazar, J. M.; Majewski, M. L. Appl. Opt. ***1998****, 37, 5271.*