Supporting Information

Changes Without Exchanges: Modification of Native Custom Glycolic Ligands on Colloidal Cadmium Chalcogenide Quantum Dots

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Chemicals. Sodium hydroxide (NaOH, Fisher), oleic acid (HOA, 90%, Sigma Aldrich), hydrochloric acid (HCl, Fisher), potassium permanganate ($KMnO_4$, >99%, Sigma Aldrich), sodium sulfite (Na_2SO_3, 98%, Sigma Aldrich), cadmium oxide (CdO, 99.998%, Alfa Aesar), selenium powder (200 mesh, 99.999%, Sigma Aldrich), sulfur (99.998%, Alfa Aesar) diphenyl ether (DPE, 99%, Sigma Aldrich), dimethylformamide (DMF, 99.8%, Sigma Aldrich), trioctylphosphine (TOP, 97%, Sigma Aldrich), tributyl phosphine (TBP, 97%, Sigma Aldrich), 1-octadecene (ODE, 95%, Sigma Aldrich), tetrahydrofuran (THF, ≥ 99.9%, Sigma Aldrich), chloroform (≥ 99%, Sigma Aldrich), lead(IV) acetate (LTA, 95%, Sigma Aldrich), acetonitrile (AcN, 99%, Sigma Aldrich), hexanes (≥ 99%, Sigma Aldrich), ethyl alcohol (190 proof, Sigma Aldrich)

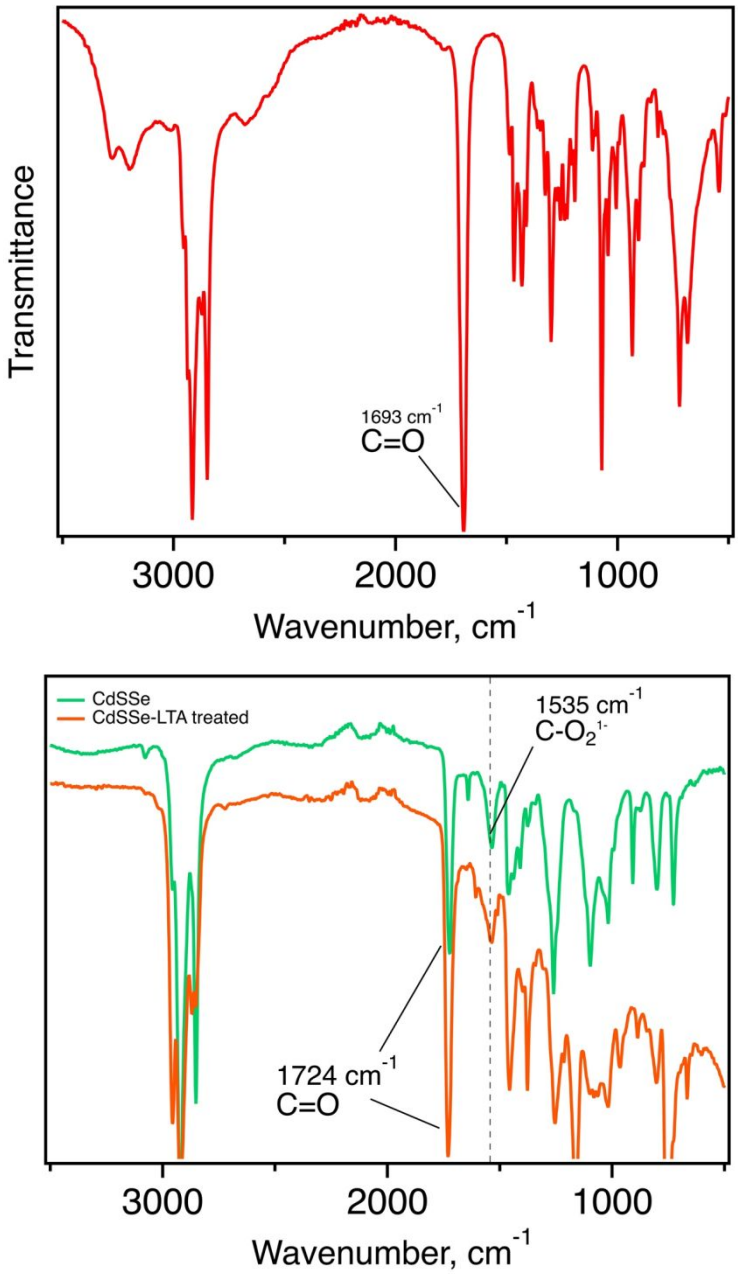

Figure S1. (top) FTIR spectrum of purified 9,10-dihydroxystearic acid (DHSA). Of note is the strong C=O carbonyl stretch in the 2700 cm^{-1} region, and the -OH thumb in the 2800-3300 cm^{-1} region. (bottom) FTIR spectrum of DHSA-coated QD samples pre- and post-treatment with lead tetraacetate (LTA). The emergence of a peak at 1535 cm^{-1} indicates the presence of carboxylate CO_2^- asymmetric stretching due to the deprotonated ligand headgroup binding. The carbonyl peak at 1724 cm^{-1} could be due to left over DMF in our sample, however we note the pronounced diminishing of the 1693 cm^{-1} DHSA C=O peak in our QD samples, which, once cleaned, should only contain deprotonated carboxylate ligand groups ($C\text{-}O_2^{-1}$). We also point

out here the disappearance of -OH stretching in the LTA-treated samples in the 3000-3300 cm^{-1} region due to the modification of the glycol group to the aldehyde.

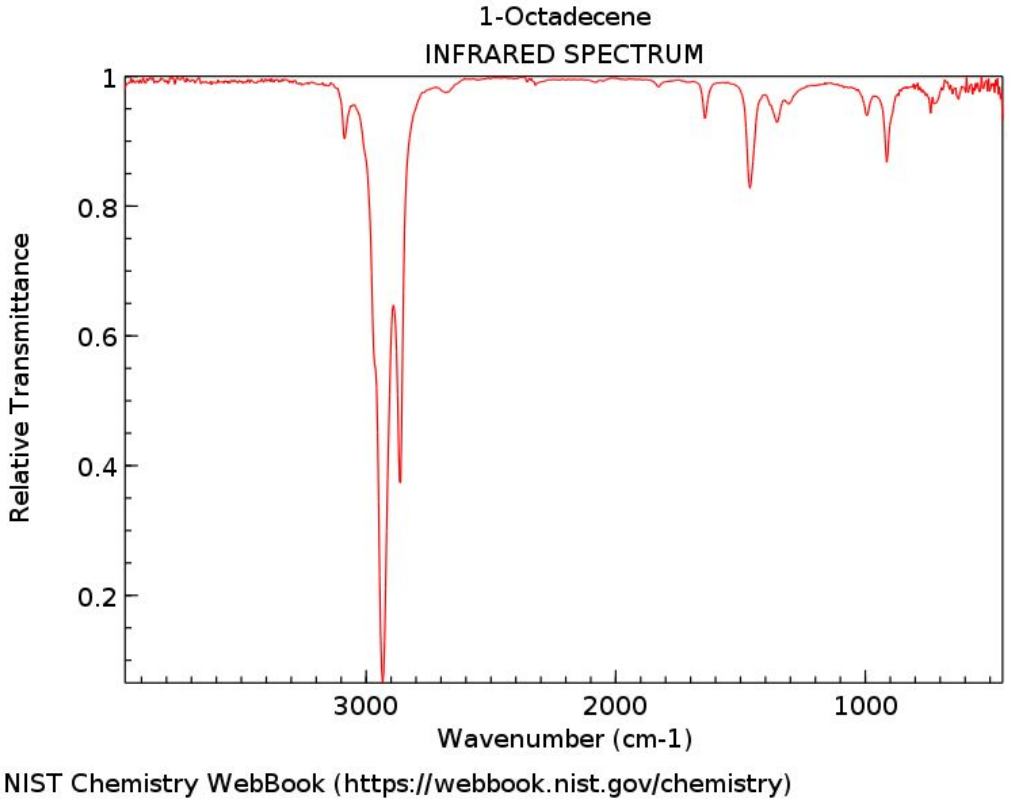

Figure S2. FTIR spectrum of 1-octadecene from the NIST Chemistry WebBook. Standard spectrum is shown to support our assertion that the peaks at 3077 cm^{-1} and, less prominently, 2686 cm^{-1} are indeed from native ODE present in our reaction samples, and not due to DHSA or derivatives thereof.

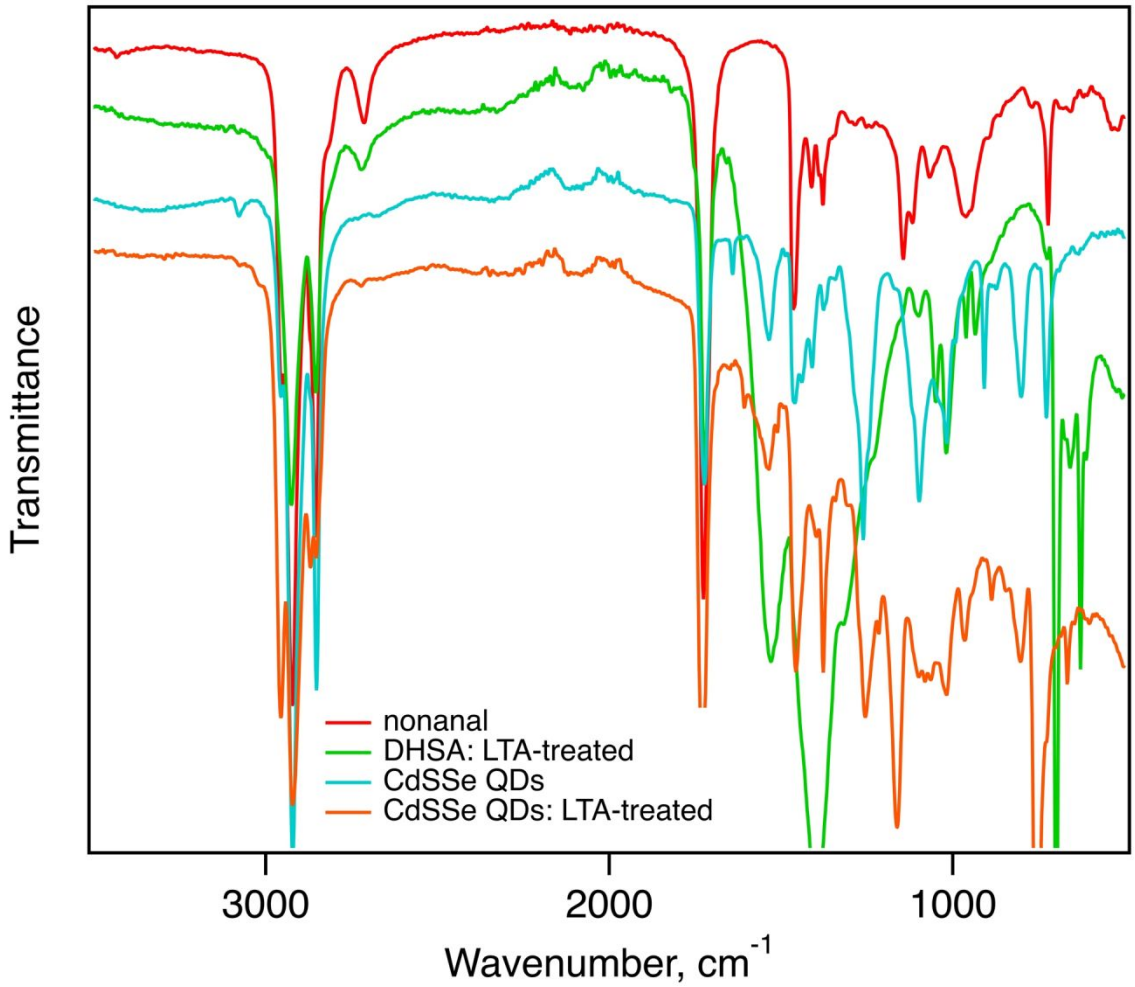

Figure S3. Full-width FTIR spectra of the samples compared in Figure 3. We note that, even in pure nonanal (red curve), aldehyde peak stretching (2725 cm^{-1}) is rather low intensity compared to C-H and C=O stretching. This fact is more apparent in the relative peak intensity for the aldehyde stretch in the LTA-treated QDs (orange curve), in which it is further lessened due to the presence of sample impurities from the reaction and cleanup phases.

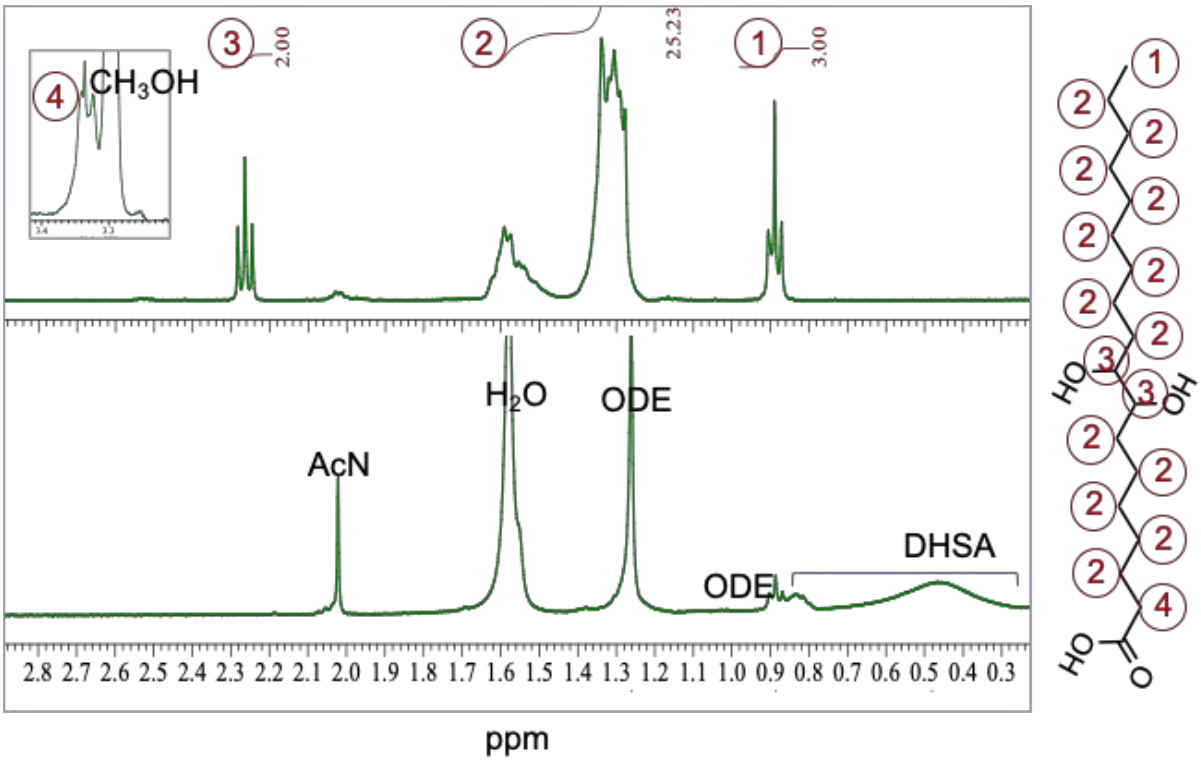

Figure S4. ^{1}H NMR spectra in CD_3OD of pure DHSA (top) and DHSA-coated CdSSe QDs in $CDCl_3$ (bottom). The pure DHSA spectrum shows clear signal for all pertinent hydrogens, with appropriate integral values and few impurities. NMR studies on DHSA-coated molecules were complicated by persistent peak broadening of the ligand species, as seen in the broad region in the bottom spectrum. We attribute this to complexation with the glycol in the ligand shell near the surface of the QD causing immense shielding and difficulty in obtaining high quality signal. This finding and our inability to avoid this sort of NMR data, regardless of solvent used, lead us to focus our characterization efforts on FTIR spectroscopy.