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Electronic Supplementary Information

Surface Coordination Chemistry of Germanium Nanocrystals Synthesized by Microwave-Assisted Reduction in Oleylamine

Sara R. Smock,[a] Katayoon Tabatabaei,[b] Travis J. Williams,[a,c] Susan M. Kauzlarich,[b] and Richard L. Brutchey*[a]*

[a] Department of Chemistry, University of Southern California, Los Angeles, California 90089 (USA)
[b] Department of Chemistry, University of California, Davis, Davis, California 95616 (USA)
[c] Loker Hydrocarbon Institute, University of Southern California, Los Angeles, California 90089 (USA)

Email: smkauzlarich@ucdavis.edu, brutchey@usc.edu

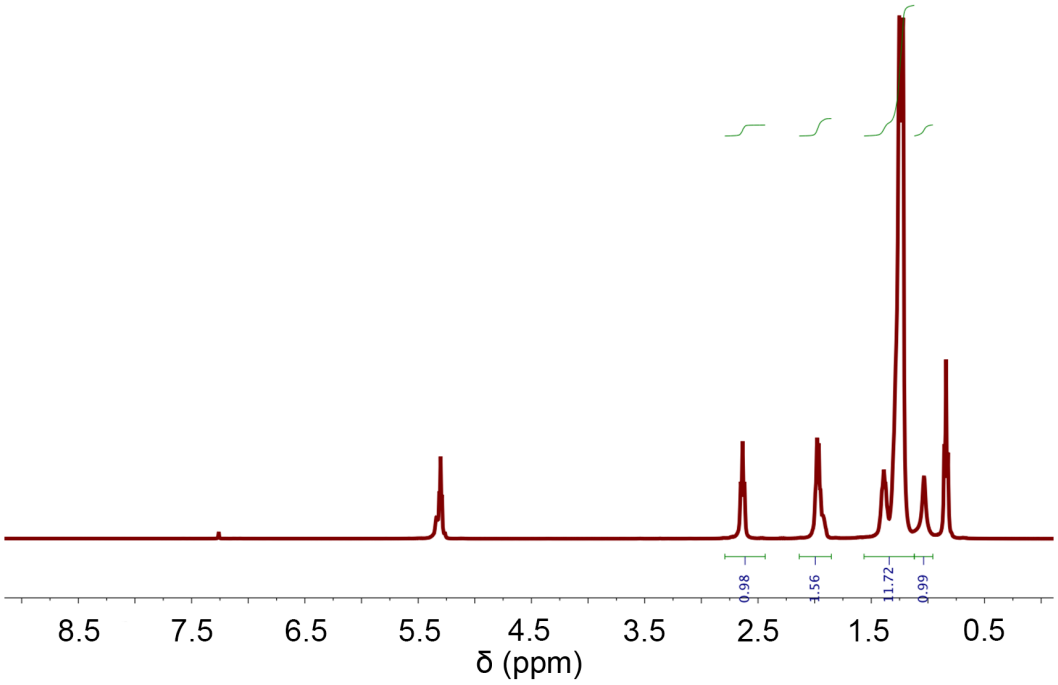

Fig. S1 ^{1}H NMR spectrum in $CDCl_3$ of 50% technical grade oleylamine after vacuum drying at 150 °C. The spectrum was integrated to give a $[CH_2]$:$[NH_2]$ ratio of 14.5, which is very close to the theoretical ratio of 15. This suggests the technical grade oleylamine is fairly pure, as no other functional groups are observed in the NMR spectrum.[1]

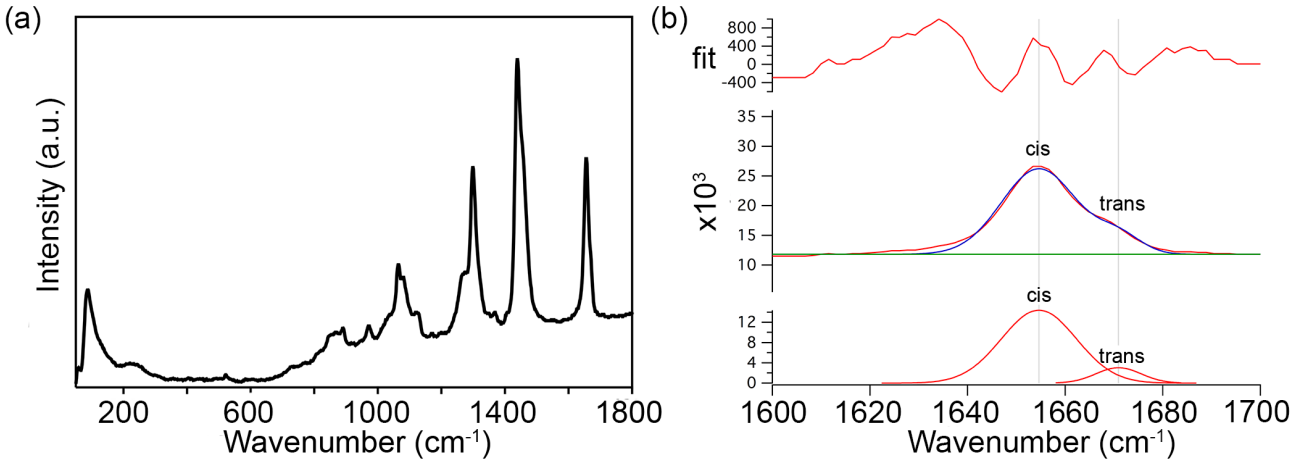

Fig. S2 (a) Raman spectrum of 50% technical grade oleylamine after vacuum drying at 150 °C. (b) The spectral region of the C=C stretch of oleylamine has two overlapping Raman bands associated with *cis* and *trans* isomers. The peaks were fit using Igor Pro by WaveMetrics software to give a *cis*:*trans* intensity ratio of 5:1.

Stokes-Einstein Equation and DOSY Analysis.

The Stokes-Einstein equation was used to analyze the Diffusion Ordered NMR Spectroscopy (DOSY) data:

$$D = \frac{k_B T}{f}$$

where D is the diffusion coefficient, k_B is the Boltzmann coefficient, T is temperature in Kelvin, and f is the friction coefficient ($f = 6\pi\eta r_s$, where η is the viscosity of the solvent and r_s is solvodynamic radius for a spherically shaped particle).[2] The theoretical diffusion coefficients and solvodynamic diameters were calculated using 298.15 K for the temperature and 0.56 mPa·s for the viscosity of toluene. To calculate the diffusion coefficients, we fit the Stejskal–Tanner equation to the signal intensity decay, and then confirmed the values with a 2D DOSY map (**Fig. S3 a-c**). In the Stejskal–Tanner equation, the intensity is proportional to $e^{-(\gamma g \delta \xi)^2 D(\Delta - \delta/3)}$, where γ is the gyromagnetic ratio of a proton (4258 $s^{-1}G^{-1}$), g is the gradient strength, δ is gradient duration, ξ is the gradient shape, D is the diffusion coefficient, and Δ is the echo delay. Using the MestreNova software, an interval graph of each distinct proton peak was created and fit to a monoexponential (Be^{-xF}) of intensity versus the gradient strength to calculate the diffusion coefficient (F) as shown below in **Fig. S3 d,e**.

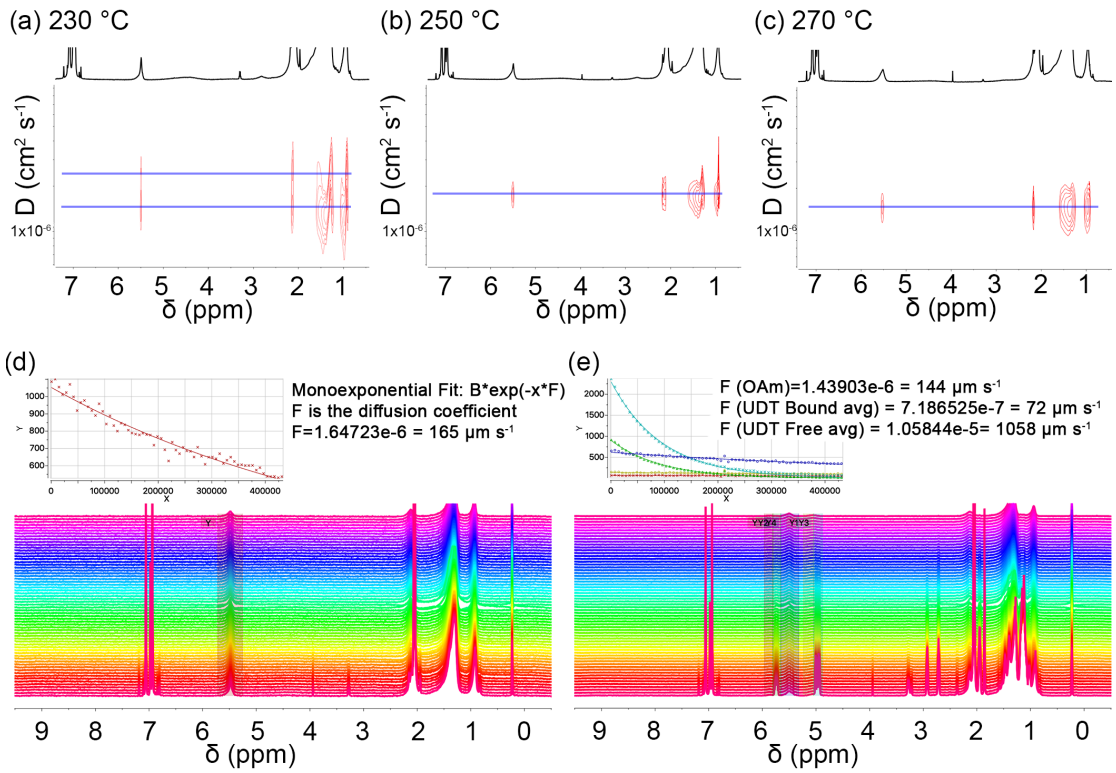

Fig. S3 (a-c) 2D DOSY NMR spectra of Ge nanocrystal suspensions synthesized at (a) 230 °C, (b) 250 °C, (c) 270 °C. (d) Room-temperature 600 MHz ^{1}H DOSY NMR spectrum of Ge nanocrystal suspension synthesized at 250 ˚C in toluene-d_8. Additionally, the signal intensity decay and monoexponential fit are presented. (e) Room-temperature 600 MHz ^{1}H DOSY NMR spectra of Ge nanocrystal suspension synthesized at 250 ˚C titrated with 30 mM undecenethiol (UDT) and 14 h heating at 90 ˚C in toluene-d_8. Additionally, the signal intensity decays and monoexponential fits are presented for both oleylamine (OAm) and UDT and the average (avg) of the downfield and upfield peaks of the vinylic protons of UDT are presented.

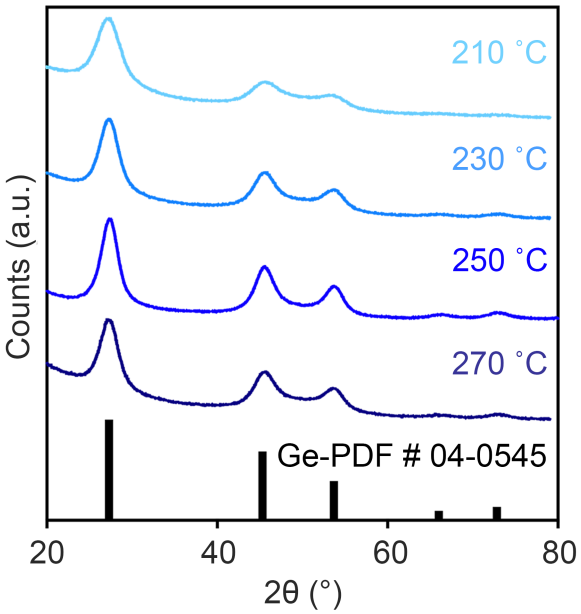

Fig. S4 Powder XRD patterns of Ge nanocrystals prepared at various temperatures (210 ˚C, 230 ˚C, 250 ˚C, and 270 ˚C) compared to the reference pattern (PDF #04-0545) showing the (111), (220, (311), (400), and (331) reflections of cubic Ge.

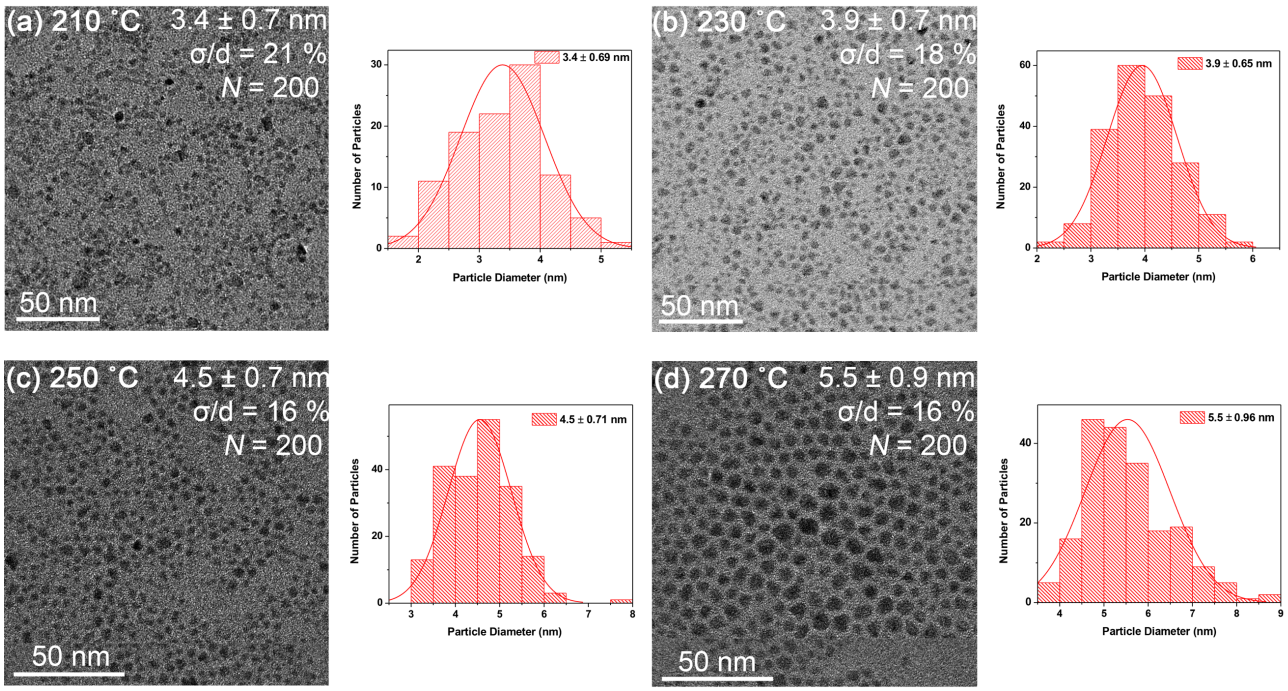

Fig. S5 TEM micrographs and size histograms of Ge nanocrystals prepared at (a) 210 ˚C, (b) 230 ˚C, (c) 250 ˚C, (d) 270 ˚C.

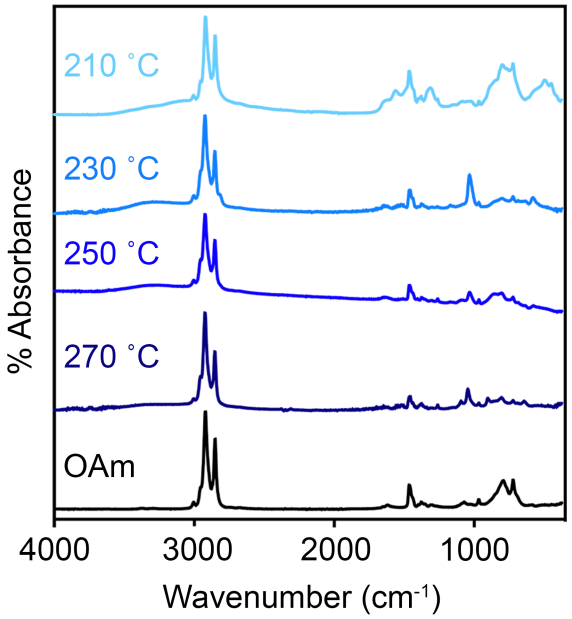

Fig. S6 Representative FT-IR spectra of pure oleylamine (OAm) and oleylamine-capped Ge nanocrystals prepared at various synthetic temperatures (210, 230, 250, and 270 ˚C) dispersed in hexanes and dispensed onto the attenuated total reflection (ATR)-crystal followed by drying.

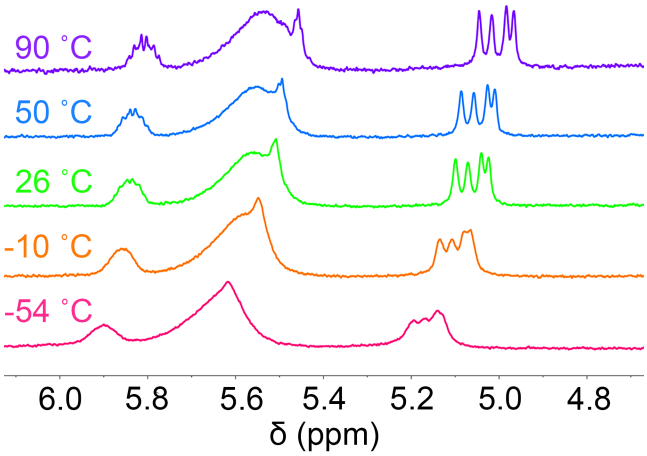

Fig. S7 Variable-temperature ^{1}H NMR spectra of 7 mg/mL Ge nanocrystal suspensions capped with oleylamine, titrated with 1:3 (mol/mol) undeceneamine to oleylamine in toluene-d_8.

Table S1 %Bound Oleylamine from **Fig. S4**.

Temperature	%Bound OAm
90 ˚C	89
50 ˚C	84
26 ˚C	85
-10 ˚C	79
-54 ˚C	76

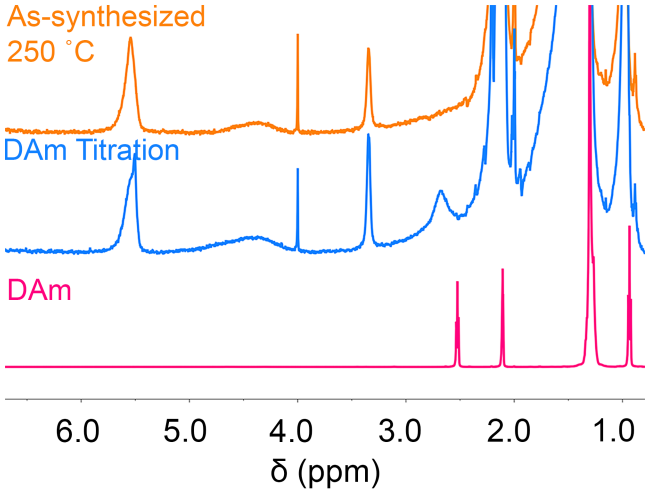

Fig. S8 ^{1}H NMR spectra of as-synthesized Ge nanocrystals prepared at 250 ˚C (orange), titrated with 1:2 (mol/mol) dodecylamine (DAm) to oleylamine (cyan), and free dodecylamine (pink) in toluene-d_8.

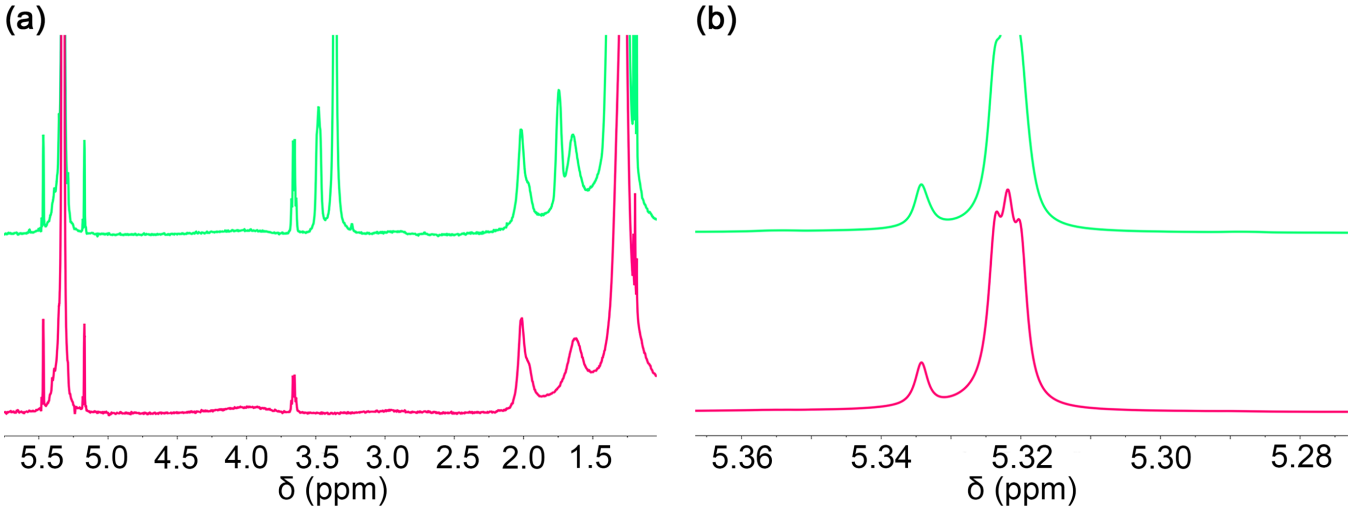

Fig. S9 (a) Full ^{1}H NMR spectra and (b) alkenyl region of as-synthesized Ge nanocrystals prepared at 250 ˚C (pink) and titrated with 6.3 mM CTAB in dichloromethane-d_2.

Table S2 %Bound Undecenoic acid in **Fig. 5**.

Temperature	%Bound undecenoic acid
Initial	Negligible
After 90 ˚C for 15 min	31 %
After 90 ˚C for 14 h	43 %

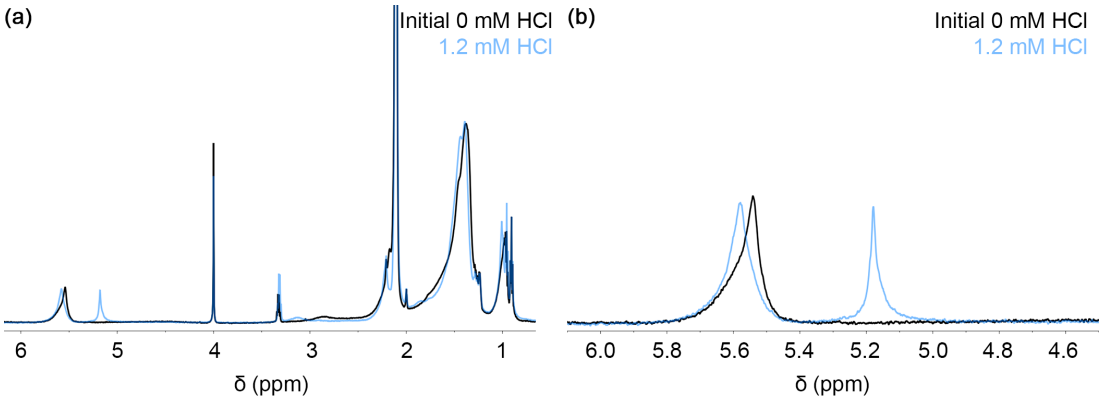

Fig. S10 (a) Full ^{1}H NMR spectrum and (b) alkenyl region of as-synthesized Ge nanocrystals prepared at 250 ˚C (black) and titrated with 1.2 mM aqueous HCl heated to 80 ˚C for 4 h (blue) in toluene-d_8. The HCl solution was prepared in D_2O and 5 μL of the HCl/D_2O solution was added.

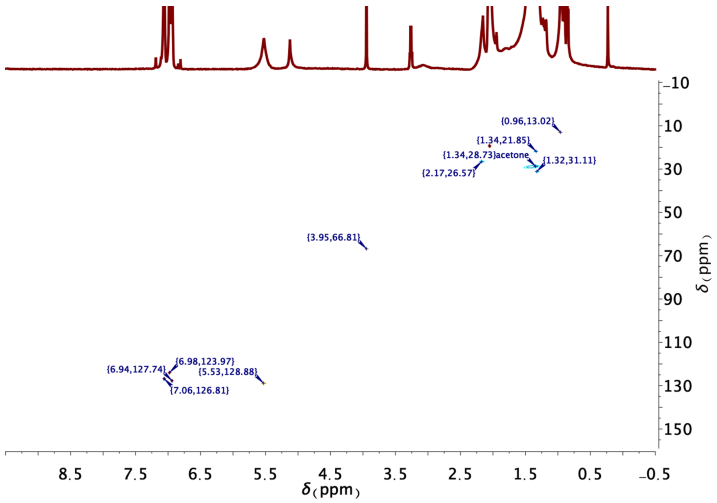

Fig. S11 2D ^{1}H-^{13}C HSQC spectrum of Ge nanocrystal suspension synthesized at 250 ˚C and titrated with 1.2 mM aqueous HCl in toluene-d_8. This spectrum does not show a cross peak for the N-H proton resonance ($\delta \approx 5.18$ ppm), demonstrating that these protons are not attached to an oleyl carbon.

References

1 M. He, L. Protesescu, R. Caputo, F. Krumeich and M. V. Kovalenko, *Chem. Mater.*, 2015, **27**, 635–647.

2 Z. Hens and J. C. Martins, *Chem. Mater.*, 2013, **25**, 1211–1221.