

Title: Chain length and solvent control over the electronic properties of alkanthiolate-protected gold nanoparticles at the molecule-to-metal transition

Authors: Anthony Cirri¹, Alexey Silakov¹, Lasse Jensen¹, Benjamin J. Lear^{1*}

Affiliations:¹Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, 16802, USA.

*Correspondence to: bul14@psu.edu

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1. TEM

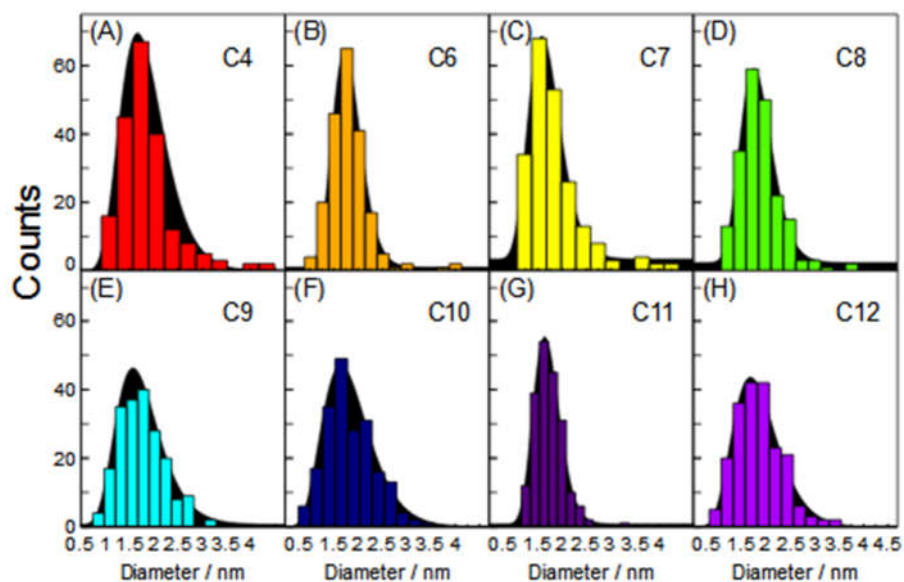


Figure S-1. Histograms and lognormal fits for size distributions of (A) butanethiolate, (B) hexanethiolate, (C) heptanethiolate, (D) octanethiolate, (E) nonanethiolate, (F) decanethiolate, (G) undecanethiolate, and (H) dodecanethiolate-protected gold nanoparticles, as measured by TEM

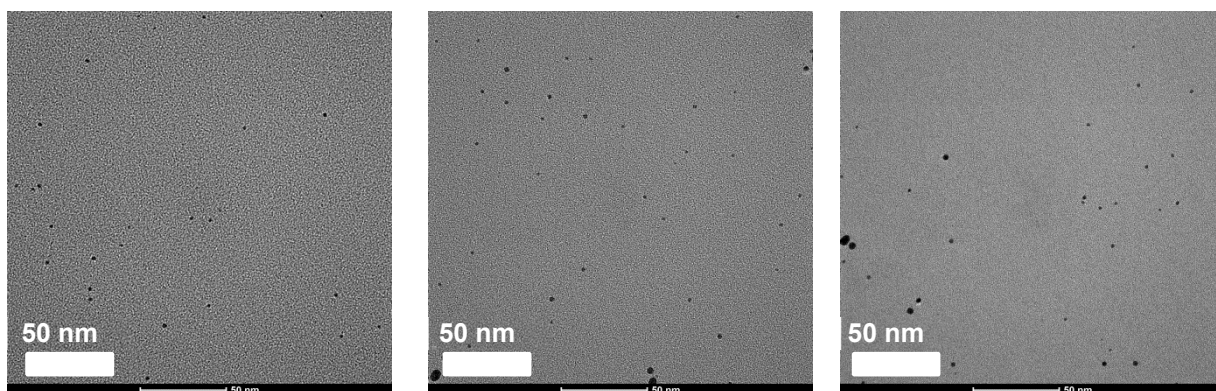


Figure S-2. Representative TEM images for butanethiolate-protected AuNPs (C4)

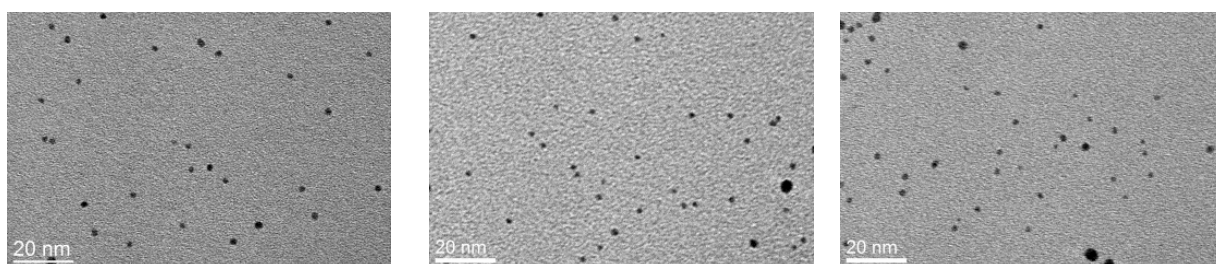


Figure S-3. Representative TEM images for hexanethiolate-protected AuNPs (C6)

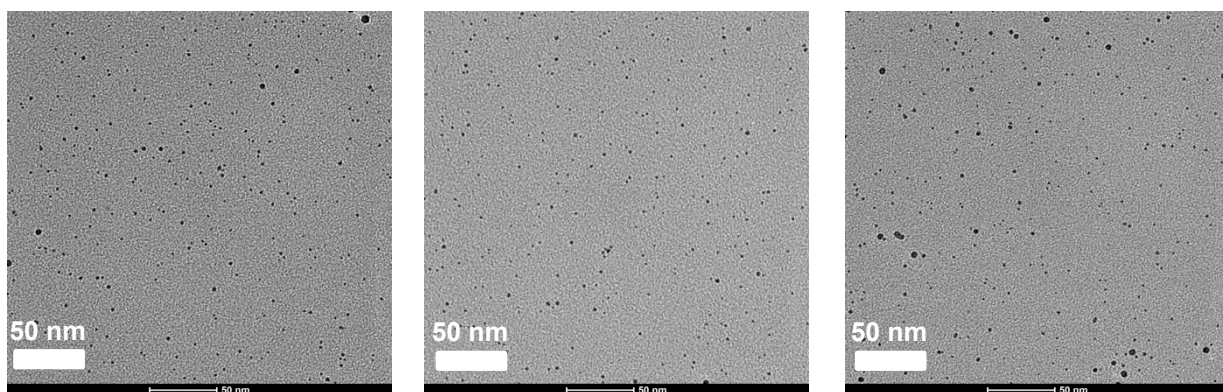


Figure S-4. Representative TEM images for heptanethiolate-protected AuNPs (C7)

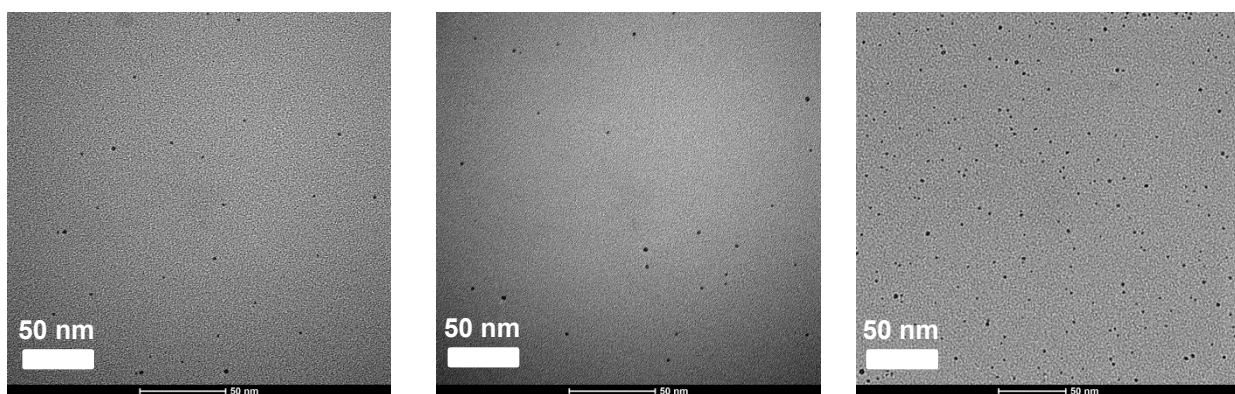


Figure S-5. Representative TEM images for octanethiolate-protected AuNPs (C8)

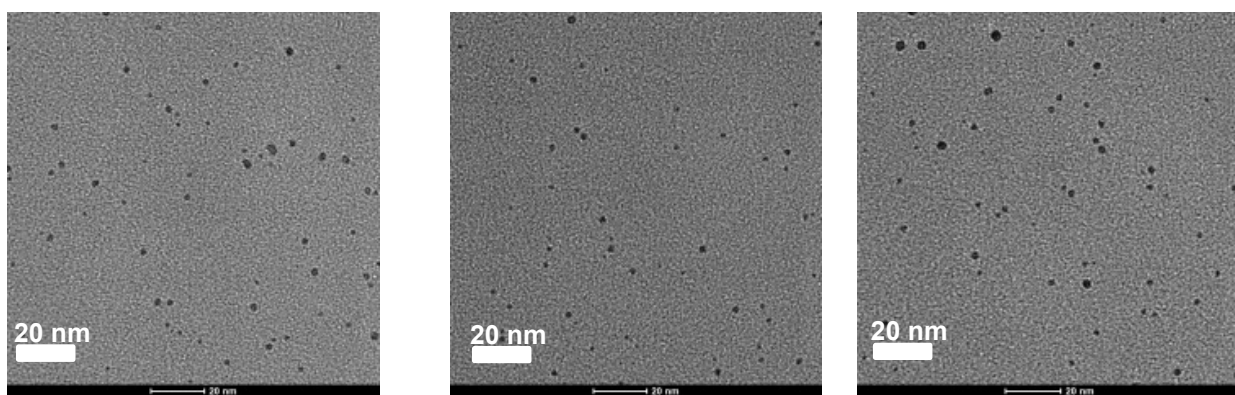


Figure S-6. Representative TEM images for nonanethiolate-protected AuNPs (C9)

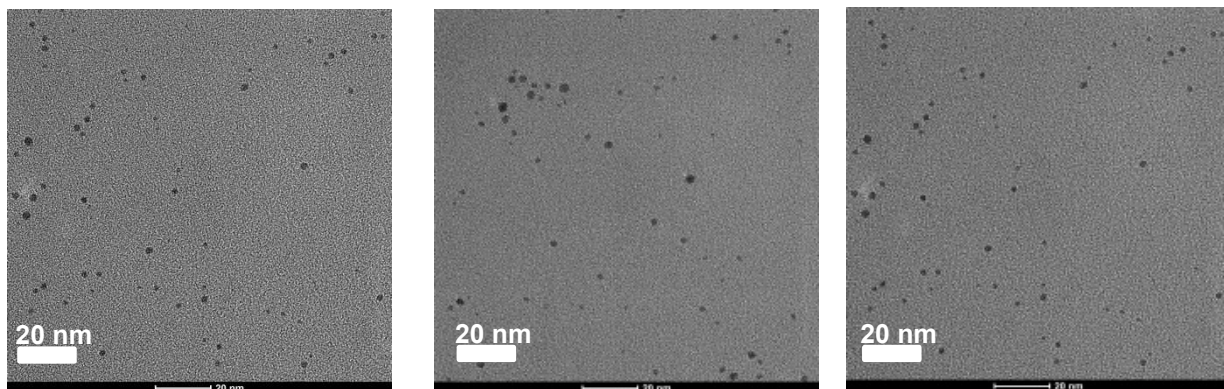


Figure S-7. Representative TEM images for decanethiolate-protected AuNPs (C10)

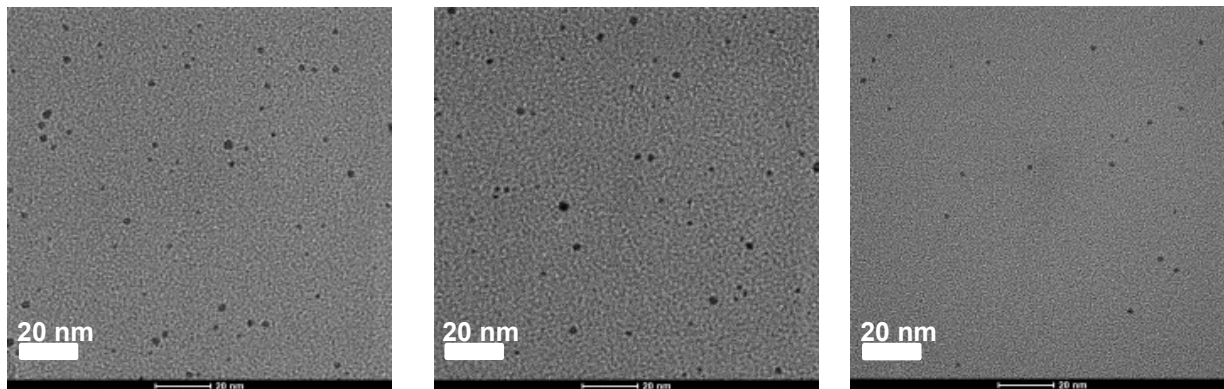


Figure S-8. Representative TEM images for undecanethiolate-protected AuNPs (C11)

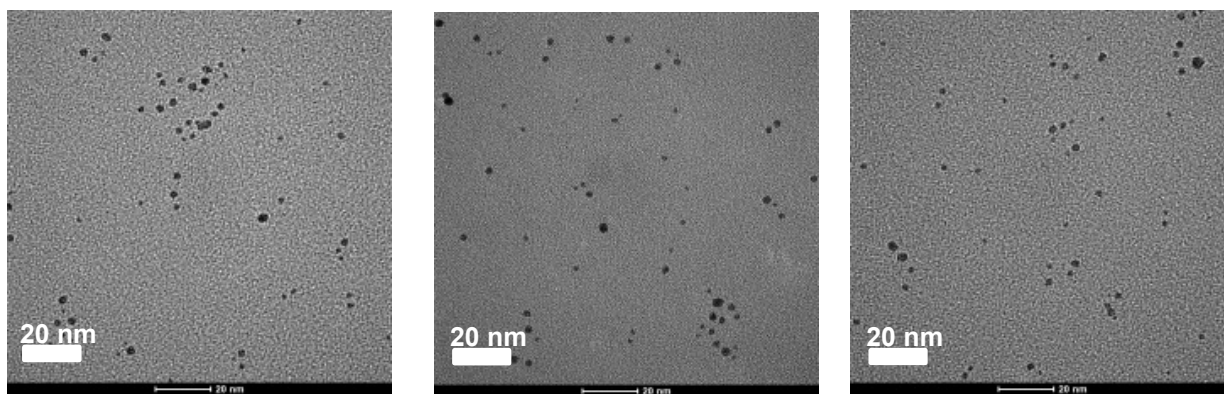


Figure S-9. Representative TEM images for dodecanethiolate-protected AuNPs (C12)

2. CCSR spectra, fits, and residuals

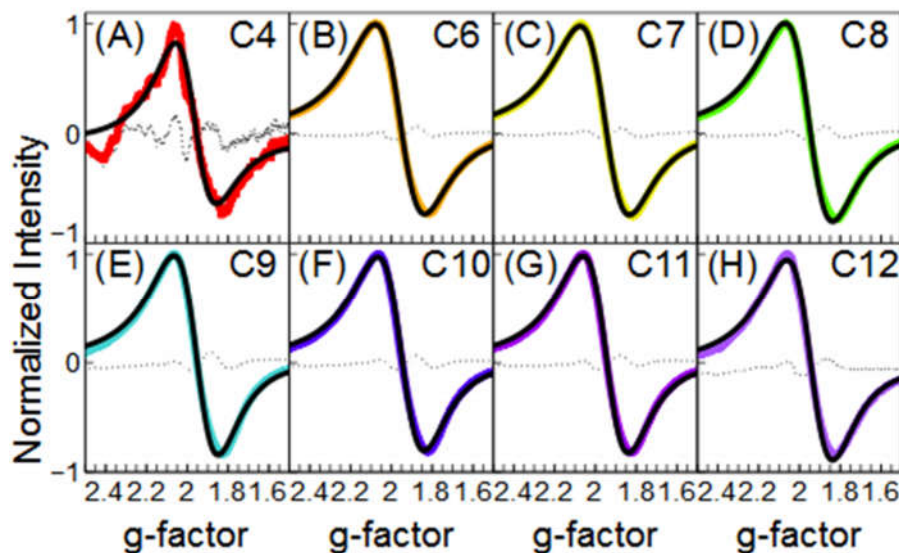


Figure S-10. CCSR spectra for (A) butanethiolate, (B) hexanethiolate, (C) heptanethiolate, (D) octanethiolate, (E) nonanethiolate, (F) decanethiolate, (G) undecanethiolate, and (H) dodecanethiolate-protected gold nanoparticles in **n-hexane**. The colored line is the background subtracted experimental spectrum, the black line is the fit to the experimental spectrum using Equation 1, and the dotted line is the residual from the fit to the experimental data

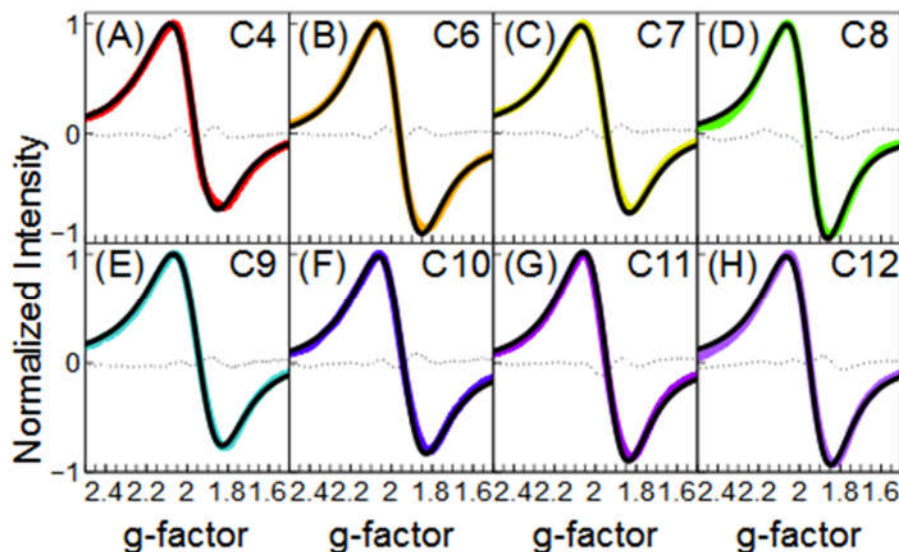


Figure S-11. CCSR spectra for (A) butanethiolate, (B) hexanethiolate, (C) heptanethiolate, (D) octanethiolate, (E) nonanethiolate, (F) decanethiolate, (G) undecanethiolate, and (H) dodecanethiolate-protected gold nanoparticles in **THF**. The colored line is the background subtracted experimental spectrum, the black line is the fit to the experimental spectrum using Equation 1, and the dotted line is the residual from the fit to the experimental data

3. Experimental section

Synthesis of AuNPs: The following chemicals were purchased from Sigma Aldrich: butanethiol (97%), hexanethiol (95%), heptanethiol (98%), octanethiol (98.5%), nonanethiol (95%), undecanethiol (98%), dodecanethiol (98+%), sodium borohydride (98%), THF (98+%), and n-hexane (97%). Tetraoctylammonium bromide (98+%) and chloroauric acid trihydrate (99.999%) were purchased from Alfa Aesar, and toluene was purchased from Aqua Solutions. All chemicals were used as received without further purification.

AuNPs protected with butanethiolate (C4), hexanethiolate (C6), heptanethiolate (C7), octanethiolate (C8), nonanethiolate (C9), decanethiolate (C10), undecanethiolate (C11), and dodecanethiolate (C12) were prepared via the Brust method. The details of the general procedure may be found elsewhere,¹ however, it is important to note that for each synthesis a $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ -to-alkanethiol ratio of 0.90 : 2.81 mmol was used in this study.

Characterization: CW-CESR measurements were performed using a Bruker ESP 300 X-band spectrometer with an ER 041MR microwave bridge and an ER 4116DM cavity operating in the perpendicular TE102 microwave mode ($\nu_{\text{MW}} = 9.623 \text{ GHz}$). Temperatures of 25 K were achieved using an ER 4112-HV Oxford Instruments variable temperature helium flow cryostat. The following parameters were used for collecting all spectra: microwave power, 200 mW; modulation amplitude, 2 G; time constant, 40.96 ms; conversion time, 81.92 ms; number of points, 4096. Saturated solutions of AuNP samples were prepared with n-hexane or THF, degassed by sparging with argon, and sealed with paraffin wax tape in clear fused quartz tubes with 4mm O.D./3mm I.D. Following CW-CESR analysis, the particles were sized using a JEOL2010 TEM (C6) or and FEI Talos (C4, C7 – C12) with a LaB_6 emission source and an accelerating voltage of 200 kV. Dilute samples of the AuNPs in THF were drop-cast onto carbon-coated copper mesh grids, purchased from Electron Microscopy Sciences.

Spectral fitting procedure: A detailed account of our spectral fitting procedure can be found elsewhere,¹ however a brief overview will be given. All CESR spectra were fit to an approximate Dysonian lineshape, composed of a linear combination of first derivative Lorentzian dispersion and absorption lineshapes. The commercially available Mathematica 10.0.0 was used to perform the computations, where the Levenberg-Marquardt fitting algorithm with default accuracy and precision goals was employed. Due to irregularities in the baseline, a third order polynomial (neglecting the quadratic term) was incorporated into the approximate Dysonian equation. Initial guesses of 0.33 T and $1 \times 10^{-9} \text{ s}$ for the peak position and linewidth, respectively, were used. All other parameters were given starting guesses of 1.

Calculations: Ionization potentials of the free alkanethiols, in n-hexane and THF, were calculated on a local version of the Amsterdam Density Functional (ADF) program package at the BP86 functional level using a TZP basis set.^{2,3}

4. Ligand length calculation

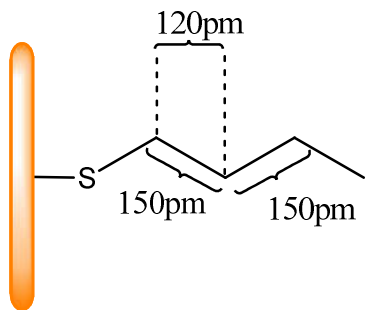


Figure S-12. Sample model used to calculate the linear ligand length

To calculate the linear length of each ligand, we assumed tetrahedral angles of 109.5° about each central carbon and a C-C single bond length of ~ 150 pm. This gave us a linear displacement between carbons of 120 pm, which was multiplied by an integer scalar equivalent to the number of C-C bonds. All calculations used the center of the methylene alpha to the sulfur as the origin. It is important to note that for the layer thickness calculations in C4-C12 series, we approximated the surfactant to exist in an all-trans conformation with a fully extended structure.

5. Determination of the ligand coverage of nanoparticles.

To determine if there was any dependence of the ligand concentration at the AuNP surface, we performed the following analysis. We took aliquots of both hexanethiol and dodecanethiol protected nanoparticles, and exposed them to I_2 . This treatment cleaves the thiols from the surface of the nanoparticles. We then collected the cleaved ligands, and performed NMR on them, quantifying the amount of ligands versus an internal standard. This is an established way in which to quantify the ligands of nanoparticles.⁴ Using the size of the nanoparticles and the number of ligands that we obtained, we found that the ligand coverage was within error for both nanoparticles. Specifically, we found that the ligand coverage ratio for hexanethiol:dodecanethiol was 1.00:0.95 with an error of 0.05 on each of these numbers. Thus, the coverages that we determined were within error identical for these two nanoparticle populations.

6. Iterative fitting procedure to electrostatic model

The extraction of α and ϕ begins with the linear fit of the hexane data shown in Figure 3, which provides a starting value for the ϕ term. We then fit the THF data to Equation 4 where ϕ is restricted as being equal to the value from the n-hexane fit, and obtain an initial value for the α term. This requires that we calculate the IP values of the ligands in THF in order to obtain $IP_{THF}^{ligand}(l)$. We have done so for both the n-hexane and THF data, and the results are presented in the insets of Figures 3 and 4, respectively. The functional forms of $IP_{THF}^{ligand}(l)$ obtained from fits of this data are given in the captions of these figures. As might be expected, given the much larger dielectric constant of THF, the dependence of the IP values on chain length are much less (~ 13.6 times) than in n-hexane.

Once we obtain the α term from the fit to the THF data, we then introduce this value into a new fit for the n-hexane data, where α is kept fixed and a new value for ϕ is obtained. This is then passed to a new fit for the THF data. In this iterative approach to fitting, the constant g' is the only parameter which is not restricted at any time during fitting. This procedure is followed until self-consistent values for both α and ϕ are obtained. In the case of our data sets, we obtain self-consistency in four iterations.

7. References

1. Cirri, A.; Silakov, A.; Lear, B.J. *Angew. Chem. Int. Ed.* **2015**, *54*, 11750 – 11753.
2. Guerra, C.F.; Snijders, J.G.; te Velde, G.; Baerends, E.J. *Theoretical Chemistry Accounts* **1998**, *41*, 721 – 729.
3. Te Velde, G.; Bickelhaupt, F.M.; Baerends, E.J.; Guerra, C.F.; van Gisbergen, S.J.A.; Snijders, J.G.; Ziegler, T. *J. Comp. Chem.* **2001**, *22*, 931 – 967.
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