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Monolayers in Three Dimensions: Synthesis and Electrochemistry of *ω*-Functionalized Alkanethiolate-Stabilized Gold Cluster Compounds

Michael J. Hostetler, Stephen J. Green,
Jennifer J. Stokes, and Royce W. Murray*

Kenan Laboratories of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27599-3290

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Following an important paper by Brust et al.,[1] we recently described[2] gold cluster compounds in which a *ca.* 1.2 nm radius Au core modeled as a 309 atom octahedron[3] is stabilized by monolayers of 95 alkanethiolate (C8, C12, or C16) ligands. These cluster molecules are exceptional in comparison to other large clusters,[4] being air stable, isolable, nonpolar solvent-soluble, black solids that exhibit significant electron hopping conductivity. Characterization tools (e.g., NMR spectroscopy, thermal analysis) not applicable to monolayers on planar surfaces[5] are readily applied to these three-dimensional variants of self-assembled monolayers.

Functionalization of these large cluster molecules is a prerequisite to their use as multifunctional reagents, catalysts, and chemical sensors, and to fabrication of 2- and 3-dimensional structures. This paper describes a versatile synthesis of *ω*-functionalized alkanethiolate−Au cluster compounds, based on place exchange reactions occurring when a *ω*-substituted alkanethiol is added to an alkanethiolate-cluster solution. This strategy offers the advantage of avoiding concurrent changes in the Au core dimension attendant to other functionalization strategies,[6] and has produced Au cluster compounds stabilized by mixed monolayers of unsubstituted and *ω*-substituted (cyano, bromo, vinyl, ferrocenyl) alkanethiolates. We also describe multi-electron electrochemical reactions of the latter, Fc-substituted cluster molecule.

Table 1 gives product compositions, determined by ^{1}H NMR spectroscopy,[7] resulting from place exchange reactions in toluene solutions of alkanethiolate−Au cluster (RS-Au) and *ω*-substituted alkanethiol (XRSH). Low feed ratios yield similarly low product ratios (see −Br 1:10 and −Fc 1:20), implying an *ω*-substituent-insensitive equilibrium. Constraints on the amount of *ω*-substituted alkanethiol exchanged into the clusters appear at high feed ratios presumably due to steric crowding in the monolayer's skin. Little previous information exists about *ω*-substituent steric effects in self-assembled monolayers on flat Au surfaces, other than voltammetric observations on crowded *ω*-ferrocenyl alkanethiolate monolayers.[8]

An extensive FTIR investigation[9] of the alkanethiolate−Au clusters (as solids, KBr pellet) has shown that their alkyl chain microenvironment mimics the crystallinity of bulk hydrocarbons[10] and of alkanethiolate monolayers on flat gold surfaces.[5] For example (Figure 1), methylene chains in the C8 cluster are predominantly *trans* based on sharp wagging and rocking progression bands and the position (2850 and 2920 cm^{-1}) of the methylene C−H stretching vibrations.[10] However, chain-end gauche defects can be detected from the wagging band at 1342 cm^{-1}. These spectral and thereby-deduced structural features are substantially preserved in exchanged clusters and in clusters with longer chains. Dis-order increases for shorter chains. Differential scanning calorimetry of longer chain cluster solids further documents a complex blend of different crystalline domains through a fine structure of melting and freezing transitions.[2,9] The pattern of melting transitions but not their enthalpy is altered by the presence of small amounts (20%) of ferrocenylalkanethiolate ligands. Qualitatively, the vibrational and thermal observations are consistent.

Cluster functionalization with redox-active *ω*-substituents leads to unusual multi-electron transfer reactions. Electrode reactions can be observed for *ω*-ferrocenyl groups on both adsorbed and dissolved cluster molecules. Figure 2 (− −) shows slow sweep cyclic voltammetry in a 1 *μ*M cluster solution at a stationary glassy carbon electrode; with increasing sweep rate such voltammetry exhibits increasingly symmetrical peaks, currents proportional to sweep rate, and small ΔE_{PEAK} values (15 mV). Analysis of charges under the peaks at higher sweep rates[11a] indicates reaction of a partial monolayer of adsorbed clusters.

When potential sweep is slow and the disk electrode is rotated (Figure 2, −), currents from reactions of adsorbed clusters become relatively small and the voltammetric wave becomes dominated by hydrodynamic transport[11b] of dissolved ferrocenated cluster molecules. $E_{1/2}$ of the hydrodynamic voltammogram is identical to $E^{\circ\prime}$ of the adsorbed species. The clusters actually each contain (on average) 9 ferrocene sites, but analysis of the RDE wave shape is consistent with an "n" = 1 reaction.[12a] The latter shows that the ferrocene sites are not strongly electronically coupled and react successively at the electrode−solution interface more or less independently[12a,b] of one other (or that a few ferrocene sites on a cluster mediate electron transfers of others).

Diffusion coefficients and, via the Stokes−Einstein equation,[13] hydrodynamic radii can be measured for the cluster molecules from the hydrodynamically controlled[11b] limiting currents of the Figure 2 (−) voltammetry, affording an opportunity for comparison to previous NMR DOSY results[2] for clusters. Calculation of D depends on the fraction of the ferrocene sites on each cluster that react at the electrode (but not on models[2] for cluster shape). The DOSY and voltammetric results (Table 1) agree with one another, within experimental uncertainty, as long as *exhaustive electrolysis of all ferrocenes on the cluster molecules is assumed.* The most heavily functionalized sample (1:5.5) in Table 1 contains *ca.* 15 Fc/cluster; a *15-electron* reaction for any nonpolymeric molecule[12b]

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(12) (a) Figure 2 (−) gives slightly curved E vs $\log[(i_{\text{LIM}} - i)/i]$ plots with 30−60-mV slopes; the slope for $n = 1$ ideally is 59 mV. The slight curvature indicates a mild extent of dispersion in the ferrocene $E^{\circ\prime}$ values probably due to their proximity to one another.[8] (b) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

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Table 1. Characterization of ω-Functionalized Cluster Molecules[a]

ligand	alkanethiolate cluster	feed ratio[b] XRSH:RS-Au	product ratio[c] XRS:RS-Au	hydrodynamic radius, Å ECHEM[d]	hydrodynamic radius, Å DOSY[e]
$Br(CH_2)_{12}SH$	C12	1:0.1	1:1[f]		
		1:1	1:4.5		
		1:10	1:13		
$NC(CH_2)_{12}SH$	C12	1:3	1:4		
$H_2C{=}CH(CH_2)_6SH$	C8	1:0.1	1:0.43		
$Fc(CH_2)_8SH$	C8	1:2	1:5.5		
	C8	1:4	1:5.5	17.7	16.0
	C8	1:9	1:9.5	15.3	15.6
	C8	1:20	1:24	16.0	15.3

[a] Synthesis: Stir cluster compound and ligand in toluene solution at room temperature for 24 h, remove solvent under vacuum, wash precipitate copiously with ethanol and acetone, collect via filtration. [b] Mole ratio of ω-substituted alkanethiol to alkanethiolates on cluster in exchange solution. [c] From ^1H NMR spectroscopy. Concurrent changes in the Au core or total number of alkanethiolate ligands on the cluster do not appear to occur (ref 7). [d] Result from rotated electrode i_{LIM} currents and Levich[11a] and Stokes Einstein[13] equations. $D_{CLUSTER} = 2.4, 2.7, 2.6 \times 10^{-6}$ cm^2/s for 1:5.5, 1:9.5, 1:24 clusters. [e] Previous[2] DOSY result for C8 alkanethiolate cluster plus an estimated skin corresponding to the volume of the ferrocenes. [f] Insoluble, ligand ratio determined from IR spectroscopy.

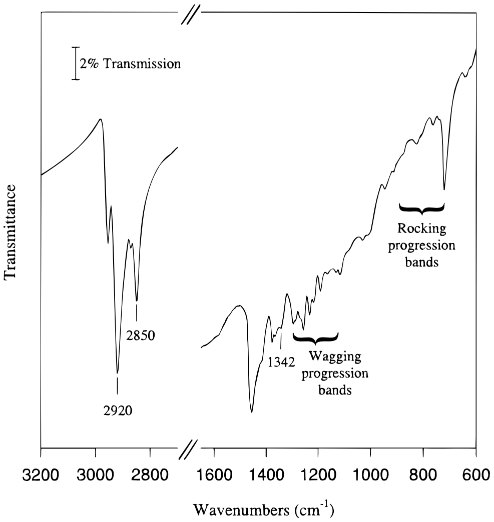

Figure 1. FTIR spectrum of the C8 gold cluster compound (KBr pellet).

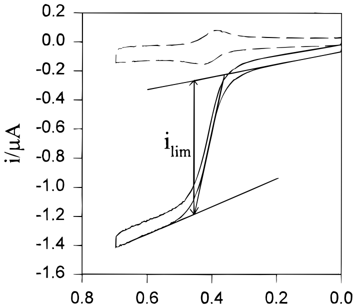

Figure 2. Cyclic voltammograms at 5 mV/s for the 1 μM 1:9.5 C8Fc/C8 cluster compound (avg 9 Fc/cluster) in 0.1 Bu_4NClO_4/CH_2Cl_2 at 0.15 cm^2 stationary (— —) and rotated (—, 1600 rpm) glassy carbon disk electrode.

is highly unusual. This result suggests that redox-modified cluster molecules have promise as multi-electron donor/acceptor reagents and catalysts.

It is well-known that colloidal metal particles exhibit double-layer structures and can be electronically charged via redox species in solution.[14] This phenomenon appears in Figure 2 (—) by the pronounced slopes of the currents preceding the ferrocene wave and on its limiting current plateau. These slopes (absent in the absence of cluster) reflect the passage of current to equilibrate the potential of the metal-like Au cores of the cluster molecules with that of the electrode. This double layer charging current is controlled by mass transport of the clusters, and the prediction[15] of pre- and post-wave slopes ($\Delta i/\Delta E$) proportional to [electrode rotation rate]$^{1/2}$ is in fact observed.[7,15] This analysis also leads by theoretical treatment[15] to the capacitances of the clusters, which when normalized to the Au core surface area are larger in the ferrocenium than ferrocene clusters and are in the same range as monolayers on flat Au surfaces.[8] The capacitance phenomenon (details described elsewhere[15]) shows that the clusters are actually molecule-sized "nanoelectrodes" and as such are among the smallest electrodes known.

Finally, the cluster molecules reacting in Figure 2 (— —) are only physisorbed, since simply rinsing with fresh CH_2Cl_2 removes all of the electroactive layer from Pt electrodes and 95% of it from Au electrodes. (The latter result shows, incidentally, that little ferrocene octanethiolate dissociatively desorbs from the adsorbed cluster molecule.) Clusters can however be firmly affixed[16] to Au surfaces using dithiol linkers. Soaking an octanethiol-coated gold electrode successively in toluene solutions of $HS(CH_2)_{12}SH$ and of 1:7.5 C8Fc/C8 cluster compound (10 min), followed by copious rinsing in CH_2Cl_2 and voltammetry in 0.1 M Bu_4NClO_4/CH_2Cl_2, gave a ferrocene surface wave corresponding to a 0.14 monolayer coverage of cluster. This coverage, 10-fold that obtained in control experiments omitting the dithiol, demonstrates chemical attachment of the Au cluster compounds to the electrode by dithiol linkers and supports the notion[6b] of using dithiols (and other difunctional linkers) to bind Au clusters together in two- and three-dimensional architectures.

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Supporting Information Available: Description and illustrative spectra for NMR analysis of exchanged clusters, evidence for no change in Au core after exchange, and discussion of double layer charging correction (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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