

Poly-hetero- ω -functionalized Alkanethiolate-Stabilized Gold Cluster Compounds

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Received May 28, 1997[Ⓢ]

Abstract: This paper describes two synthetic approaches, simultaneous and stepwise exchange, to poly-hetero- ω -functionalized monolayer-protected cluster compounds (MPC's), as well their spectroscopic and electrochemical characterization. Poly-hetero- ω -functionalization of MPC's provides a framework within which to study intra- and intermolecular cluster chemistry and to design multistep, mutually supporting catalytic and electron donor/acceptor reactions on cluster surfaces. Factors affecting the extent of exchange (measured by NMR) include the steric bulk of the ω -functional group as well as the chain lengths of the protecting and incoming ligands. Poly-hetero- ω -functionalized clusters can incorporate mixed redox functions as illustrated by microelectrode voltammetry of a poly-ferrocene/anthraquinone mixed cluster. The cluster voltammetric waves lie at potentials consistent with those observed in dilute solutions of the unbound electroactive thiols, within the uncertainty of the Ag quasi-reference electrode potential. Diffusion coefficients and hydrodynamic radii suggest that the outer parts of the cluster chains may be free-draining. This research demonstrates that 3D-SAMs with mixed ω -functionalized alkanethiolate ligands (both redox and nonredox active) can be synthesized and characterized and provides the groundwork for synthesis of "nanofactory" cluster compounds designed to exhibit mutually supporting, multistep chemical and redox catalytic reactions, and for an enhanced capacity to study functional group reactivities at organized monolayer interfaces.

This paper describes a versatile synthetic pathway to, and the spectroscopic and electrochemical characterization of, poly-hetero- ω -functionalized monolayer-protected cluster (MPC's) compounds. The rapidly emerging literature¹ of alkanethiolate/Au-based MPC's includes examples of poly-homofunctionalized clusters² but none that are poly-heterofunctionalized. Poly-homo- and heterofunctionalization is ordinarily associated with proteins and protein complexes, as well as with synthetic polymeric and dendrimeric materials.³ However, polyfunctionalization based on a metal core is new and opens an unexplored avenue to study intra- and intermolecular cluster chemistry and to design multistep, mutually supporting catalytic and electron donor/acceptor reactions using clusters. Intramolecular cluster reactions could, for example, be investigated by means of clusters functionalized with mixtures of electron transfer mediator and substrate ligands. Multistep, electron transfer mediated reductions by clusters of substrates in solutions in which the substrate reactions require both electron and proton transfers could be accelerated using clusters bearing mixtures of proton donor and electrogenerated electron donor sites. The rates of such reactions could be further enhanced when the substrate is cationic by inclusion of negatively charged groupings on the

clusters. The present paper synthetically opens the way to exploration of such mixed cluster reactivity.

Alkanethiolate/Au MPC's, unlike many other clusters,⁴ have properties that are attractive for use as chemical reagents, including air stability, solubility in nonaqueous solvents, and isolability. Our synthetic strategy for preparation of poly-hetero- ω -functionalized clusters rests on alkanethiolate place-exchange reactions.^{2b}

Experimental Section

Chemicals. Dichloromethane (Fisher), toluene (Mallinckrodt), absolute ethanol (AAPER), and acetone (Mallinckrodt) were used as received. ω -Ferrocenyloctanethiol (FcC8SH),⁵ methyl-16-mercaptohexadecanoate (MeOC(O)C15SH),⁶ ω -bromododecanethiol (BrC12SH),⁶ and ω -hydroxydodecanethiol (HOC12SH)⁶ were prepared according to a literature procedure. ω -Phenylbutanethiol (Ph(CH₂)₄SH) was synthesized from Ph(CH₂)₄Br using a standard procedure.⁶ 1-(1,3-Dithiapropryl)anthracene-9,10-dione (AQSC3SH) was prepared on the basis of a modification of a literature method.⁷ Hx₄NClO₄ (Alfa) was dried under vacuum at 70 °C. Acetonitrile was distilled over calcium hydride. Water was purified with a Barnstead NANOpure system.

Synthesis. The gold cluster compounds were synthesized using a modified literature method.^{1b,8} Toluene solutions containing a 2:1 mole ratio of alkanethiol to AuCl₄⁻ were reduced at 0 °C with BH₄⁻. Characterizations described elsewhere⁸ show that the average Au core size is 225 atoms and the average number of alkanethiolate ligands/core is ca. 90. Place-exchange reactions were accomplished via a slight modification of our previously reported^{2b} procedure. The incoming ω -functionalized alkanethiol and the alkanethiolate-protected gold cluster were codissolved in methylene chloride; the approximate concentration of cluster was 2 mg/mL. The reaction was stirred for

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Table 1. Results of Place-Exchange Reactions between ω -Functionalized Alkanethiols and Alkanethiolate MPC Gold Clusters

expt no.	MPC chain length	HS(CH ₂) ₄ Ph		HS(CH ₂) ₈ Fc		HS(CH ₂) ₁₂ Br		HS(CH ₂) ₁₂ OH		HS(CH ₂) ₁₆ CO ₂ Me		HS(CH ₂) ₃ SAQ		total product ratio ^c	$\nu(\text{C}=\text{O})$ (cm ⁻¹)
		feed ^a	prod. ^b	feed ^a	prod. ^b	feed ^a	prod. ^b	feed ^a	prod. ^b	feed ^a	prod. ^b	feed ^a	prod. ^b		
1	C8			1:3	1:8									10/80	
2	C8											1:4	1:7.4	11/79	
3	C12	1:4	1:7											11/79	
4	C12			1:4.4	1:14									6/84	
5	C12					1:3.6	1:8	1:13	1:17					10/80	
6	C12									1:3.5	1:7.5			11/79	1743.4
7	C8			1:3	1:11							1:3	1:8	16/74	
8	C8	1:4	1:14	1:8	1:14	1:4	1:7	1:14	1:17	1:3.8	1:7.6			29/61	1743.8
9	C12	1:3.7	1:11	1:8	1:23	1:4	1:5	1:14	1:12	1:4	1:8.3			32/58	1743.0
10	C16	1:4.2	1:16	1:7.6	1:44	1:3.8	1:11	1:14	1:17	1:3.6	1:9			12/78	1744.4

^a Mole ratio of ω -functionalized ligand to MPC-bound alkanethiolate ligand in place-exchange solution. ^b Average mole ratio of introduced ω -functionalized to nonderivatized alkanethiolate ligand remaining on product cluster. HS(CH₂)₁₂OH was present as an impurity with HS(CH₂)₁₂Br, so these were always exchanged as a mixture. ^c Ratio of total ω -functionalized ligands introduced to remaining *n*-alkanethiolate, based on original 90 alkanethiolates/cluster.

48 h at room temperature and the solvent removed under vacuum. The resulting precipitate was collected by filtration and washed serially with 100 mL of absolute EtOH and acetone, and for the AQ-functionalized clusters, 100 mL of acetonitrile.

Spectroscopic Characterization. ¹H NMR spectra (C₆D₆ or CD₂-Cl₂) were obtained with a Bruker AMX 200 Hz spectrometer. Infrared spectra (dropcast cluster thin films on a KBr plate) were collected on a Bio-Rad 6000 spectrometer over 256 scans which were ratioed against a spectrum of a clean KBr plate.

Electrochemical Measurements. Cyclic voltammetry was performed using a locally built potentiostat interfaced with an IBM-compatible PC, along with in-house software, via a 16 bit DAS-HRES A/D, D/A board. Platinum 26 and 10 μm diameter working electrodes were polished with a 0.5 μm alumina (Buehler) slurry followed by rinsing with NANOpure water and ethanol before each experiment. A Pt coil counter electrode and Ag wire quasi-reference electrode resided in the same cell compartment with the working electrode. A hermetically sealed cell was used to minimize oxygen within the cell and solvent evaporation. In addition, the solutions were degassed and then bathed with solvent-saturated N₂. A 2:1 (v/v) toluene:acetonitrile mixed solvent system was adopted on the basis of its ability to solubilize both cluster and 0.05 M Hx₄NClO₄ electrolyte.

Results and Discussion

The synthetic strategy is founded on place-exchange reactions^{2b} in solution mixtures of ω -functionalized alkanethiols with alkanethiolate/Au MPC's. (Disulfide molecules do not undergo such place-exchange reactions onto MPC's.) Our procedure avoids⁹ alterations in the Au core size that may accompany *de novo* cluster synthesis from a mixture of thiols but exposes the fact that steric crowding can accompany^{2b} the introduction of numerous functional groups onto the roughly spherical surface that is occupied by the alkanethiolate termini.

Experiments in this work are based on minimizing intramolecular effects in place-exchange reactions by using low reaction feed ratios (1:3 ω -functionalized alkanethiol:MPC alkanethiolate, or less) and differing chain lengths for each ω -functionalized thiol (see Table 1) so as to place each functional group at a different level in the monolayer. In experiments 1–6, the propensity of individual ligands to place-exchange separately onto octanethiolate (C8) and dodecanethiolate (C12) MPC's was examined. As seen before,^{2b} the poly-homofunctionalized cluster products were ca. 2-fold more dilute in ω -functionalized ligands than was the exchange solution, i.e., introducing six ferrocene or 11 bromine groups (experiments 4 and 5) among the ca. total 90 chain termini produces a modest (but detectable) level of intramolecular ligand interaction.

Two routes to poly-*hetero- ω* -functionalized clusters were studied: (a) *simultaneous* exchange of a mixture of thiols onto

an MPC and (b) *stepwise*, progressive exchange of different thiols, isolating and characterizing the cluster product after each step. In the first method, using feed ratios of individual thiols similar to those in experiments 1–6, up to five different ligands were simultaneously exchanged onto three MPC's which had monolayers consisting of different^{10a} alkanethiolate chain lengths (Table 1, C8, C12, C16, experiments 7–10). The ligand ratios on the product clusters were analyzed by integration of the signature resonances of the different end groups in ¹H NMR spectra like that in Figure 1. The inset in Figure 1 is a schematic of the corresponding poly-*hetero- ω* -functionalized cluster.

Interestingly, the end-group NMR resonances in Figure 1 are broader when they are connected to the gold core via shorter alkanethiolate chains. This is qualitatively consistent with the view that chain packing near the core is more "solid-like",^{1a} an effect arising because the gold core has a radius comparable to the alkanethiolate chain lengths. The small Au core radius of curvature thus causes the attached hydrocarbon chains to fan out, on average, away from the gold core, and the average ligand packing density is necessarily higher near the gold core; for a fully extended C12 chain, for example, the density is approximately 9 times lower at the CH₃ terminus. The phenyl group, which is attached to the gold core via a C4 hydrocarbon chain thereby experiences a much higher average surrounding chain packing density as compared to the methyl ester (C15 hydrocarbon chain) end group. The resultant lowered mobility of the phenyl group causes its NMR resonance to be broader than that of the methyl ester end group, even in the case of both functional groups being bound to the same cluster (Figure 1).

The simultaneous exchange results (experiments 7–10) reveal an enhanced level of ligand interaction (relative to the overall extent in experiments 1–6) and an effect of chain length. In simultaneous place-exchange reactions of AQSC3SH and FcC8SH (experiment 7), the AQSC3S- ligand becomes incorporated into the mixed cluster to about the same extent as in the nonmixed cluster in experiment 2, but the FcC8S- ligand tends to be preferentially excluded relative to results in experiment 1, presumably owing to its greater steric bulk. Space demands are also evident in experiments 8–10 (compare experiment 9 with experiments 3–6), where five ligands with different alkanethiolate chain lengths (and thus different steric environments) were simultaneously exchanged onto MPC's. The trends in ω -functionalized ligand incorporation onto C8 vs onto C16 MPC's, and the fact that nearly 2/3 of the alkanethiolates

(9) Confirmed by small-angle X-ray scattering experiments: Hostetler, M. J.; Londono, J. D.; Murray, R. W. Unpublished results, 1996.

(10) (a) While the same experiments on C4 MPC's clearly produced extensive exchange (up to two-thirds of the ligands could be exchanged off), the ¹H NMR linewidths were too broad to accurately assess product mole ratios. (b) The $\nu(\text{C}=\text{O})$ for the ester group for this material appeared at 1741.9 cm⁻¹.

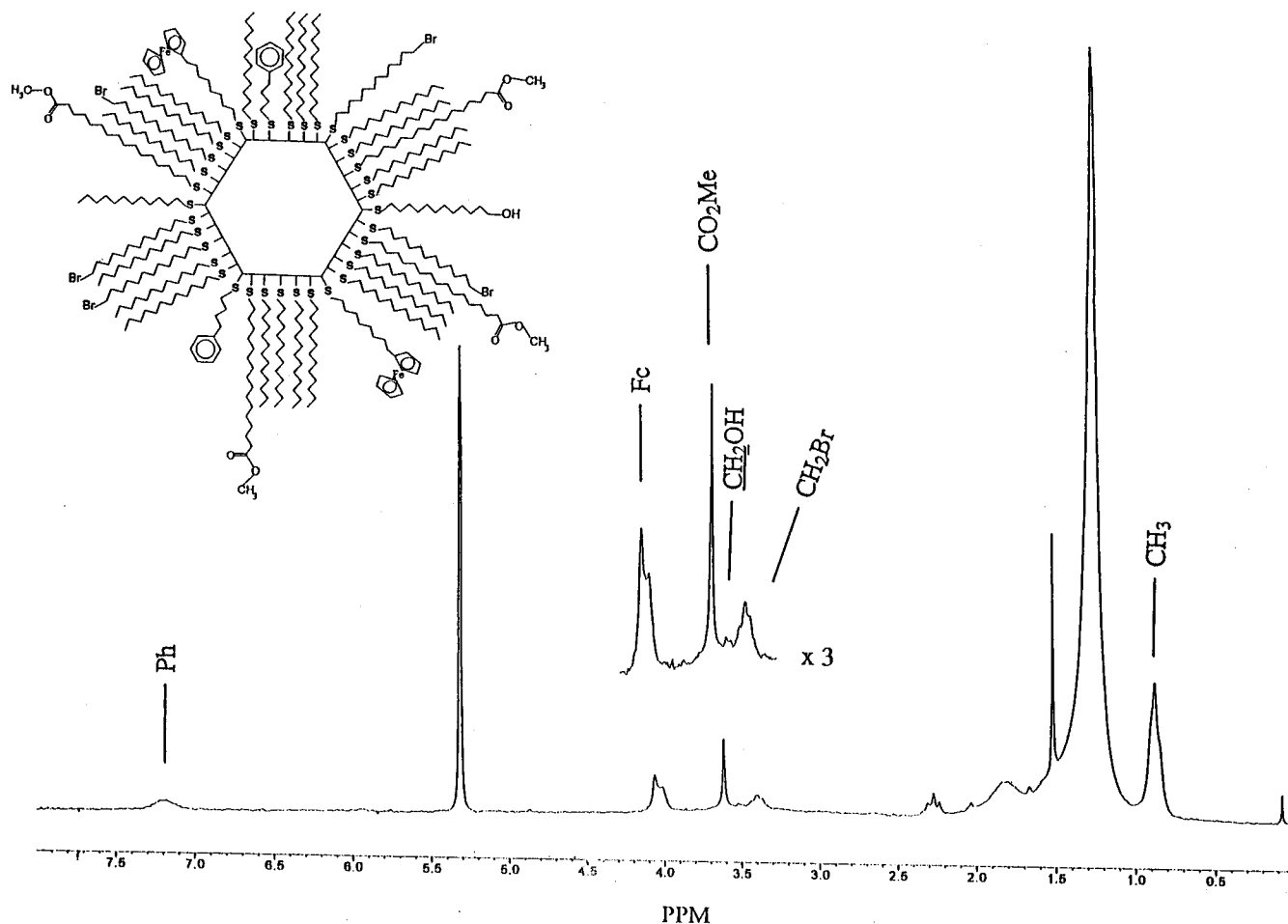


Figure 1. ^1H NMR spectrum of a C12/Au MPC after simultaneous exchange, illustrating the presence of bound PhC4S $^-$, FcC8S $^-$, BrC12S $^-$, HOC12S $^-$, and MeOC(O)C15S $^-$ ligands (in CD_2Cl_2). Inset: schematic representation of C12 MPC cluster prepared by simultaneous place-exchange reaction with PhC4SH, FcC8SH, BrC12SH/HOC12SH, and MeOC(O)C15SH thiols (Table 1, experiment 9).

on a C4 MPC could be replaced^{10a} but only 1/8 on a C16 MPC (experiment 10), also show that the extent of exchange depends upon the MPC's alkanethiolate chain length. For example, the FcC8S $^-$ and BrC12S $^-$ ligands tend to be preferentially excluded when the clusters onto which they are place-exchanged have longer surrounding alkanethiolate chain lengths. Kinetic studies of the simultaneous exchange of all five ligands onto a C12 MPC revealed that the *ratio* of bound functionalized alkanethiolate ligands to each other did not vary as the total number of bound ω -functionalized ligands increased, indicating that one type of functionalized alkanethiol does not exchange rapidly onto the cluster only to be displaced at later reaction times by another type of incoming ω -functionalized thiol (i.e., a quasi-equilibrium exists during place-exchange).

Stepwise synthesis of poly-heterofunctionalized clusters (data not in Table 1) was examined using ω -functionalized ligands with progressively longer linker chains (i.e., place-exchange reactions of a C8 MPC cluster with AQSC3SH and then with FcC8SH and of a C12 MPC cluster with, successively, PhC4SH, FcC8SH, BrC12SH/HOC12SH, and MeOC(O)C15SH), as well as reactions conducted in the opposite order. The stepwise synthetic approach additionally reveals the extent to which an exchange reaction can displace ω -functionalized vs nonfunctionalized alkanethiolate ligands from a cluster. In stepwise exchanges using C8 MPC, 13% of initially incorporated AQSC3S $^-$ ligand was displaced by FcC8S $^-$ ligands, but in place-exchanges carried out in the reverse order, AQSC3S $^-$ ligands displaced 42% of the initially incorporated FcC8S $^-$ ligands. Similarly, in stepwise exchanges onto a C12 MPC cluster, longer chain length ω -functionalized ligands (BrC12S $^-$ /HOC12S $^-$ and MeOC(O)C15S $^-$) tended to displace those with

short linker chains (FcC8S $^-$ and PhC4S $^-$), but displacement of ligands with long linker chains by those with short linker chains was less likely to occur. All of these results indicate that short chain length, bulky, ω -functionalized alkanethiolates are the *least thermodynamically stable ligands*, consistent with a differential density of chain packing around the gold core. In other words, the free energy cost of disturbing chain packing is greater if the functional group is buried deep within the monolayer. The results from all of the exchange reactions are consistent with this concept; these observations and others on the mechanism of ligand exchange will be amplified in a forthcoming manuscript.¹¹

While steric properties of the ω -functionalized ligands are probably the main source of intracluster effects of one ligand on the extent of another's place-exchange, factors other than steric bulk may also intervene. Thus, we observe in FTIR experiments that $\nu(\text{C}=\text{O})$ depends upon the number and identity of coadsorbed ligands, as well as the chainlength of the diluent ligand (Table 1). For example, the lowest energy $\nu(\text{C}=\text{O})$ band (1741.9 cm^{-1}) was measured for the highly loaded (ca. two-thirds total exchange) C4 protected cluster,¹⁰ whereas the highest value (1744.4 cm^{-1}) was seen for the low loaded (ca. one-eighth total exchange) C16 protected cluster. The total measure of these effects indicates that both through-space electronic interactions and intracluster hydrogen bonding (via the C12OH ligand) play an important role in determining the ligand microenvironment surrounding each cluster.

Voltammetry of clusters bearing multiple ferrocenes has been previously described,² but not that of anthraquinone or of any

(11) Hostetler, M. J.; Murray, R. W. Manuscript in preparation.

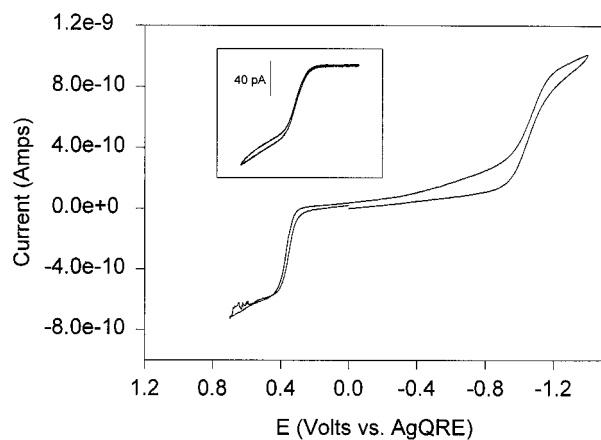


Figure 2. Cyclic voltammogram of a 30 μM solution (2:1 toluene/MeCN, v/v) of a mixed cluster prepared by stepwise exchange (product mole ratio of thiolate ligands is 1:1.3:6 FcC8S $^-$ /AQSC3S $^-$ /C8, average 12 Fc's and 16 AQ's/cluster), 0.05 M Hx $_4$ NCIO $_4$ electrolyte, 20 mV/s, 26 μm diameter Pt disk electrode. The small prewave at the base of the anthraquinone wave is probably due to trace oxygen. Inset: ferrocene oxidation wave in a similar solution of a pentafunctionalized C12 MPC like that in Figure 1 (inset) but stepwise-synthesized by place-exchanges done in order of shortest to longest chain linker, average 5 Fc's/cluster, 10 mV/s, 10 μm diameter Pt electrode.

redox mixture residing on the same cluster molecule. Microelectrode voltammetry of a stepwise-synthesized ferrocene/anthraquinone poly-heteroredox cluster solution (Figure 2) and of ferrocenes (Figure 2, inset) on a pentafunctionalized cluster like that in Figure 1, but prepared in a stepwise synthesis, exhibits waves for those redox groupings that lie at potentials indistinguishable from their reactions on homo-redox- ω -functionalized clusters and as solutions of their monomer thiols, at least within the ± 150 mV uncertainty of the quasi-reference electrode potential in the mixed toluene/acetonitrile solvent. While these redox cases display no strong electronic consequence of incorporation into a mixed MPC, minor effects cannot be ruled out. Importantly, the ratio of the anthraquinone reduction and ferrocene oxidation plateau currents (1:1.3 FcC8S $^-$:AQSC3S $^-$) agrees within 15% of their mole ratio deduced from the NMR of the cluster sample. Their individual currents can be used to evaluate the cluster diffusion coefficient¹² and (via Stokes–Einstein equation) the cluster hydrodynamic radius, r_H . The results, 2.7×10^{-6} cm 2 /s and 15.8 \AA from the ferrocene wave and 2.6×10^{-6} cm 2 /s and 16.4 \AA from the anthraquinone wave, are consistent with previous² data for exchanged clusters. Voltammetry for the ferrocene pentafunctionalized clusters (Figure 2, inset) shows that they diffuse at a similar rate ($D = 2.6 \times 10^{-6}$ cm 2 /s and $r_H = 16.4$ \AA) as well. It is significant that these hydrodynamic radii results are less than the sum of the Au core radius (9.8 \AA) and the length of a fully extended C8 chain (15 \AA), which along with NMR results⁸ leads to a picture that while dissolved clusters have densely packed chains near the Au surface (reflected in their small double-layer capacitances^{2a}), the chain termini are well solvated and may lie in a relatively free-draining environment. As expected, clusters more heavily exchanged or with a larger Au core exhibit larger hydrodynamic radii.¹³

As discussed elsewhere,^{2a} the sloping current baselines and plateaus in Figure 2 reflect currents for double-layer charging of the Au cores of the cluster molecules. Identical values of

11 $\mu\text{F}/\text{cm}^2$ are obtained from each of the sloping ferrocene and anthraquinone plateau currents and of 3.2 $\mu\text{F}/\text{cm}^2$ from the sloping baseline currents between the two waves. These values are consistent with those reported previously^{2a} for clusters bearing only ferrocene ω -functionalities and are average capacitances since the cluster samples contain a distribution of Au core sizes.⁸ The double-layer capacitance of 4.9 $\mu\text{F}/\text{cm}^2$ for the oxidized ferrocene pentafunctionalized MPC is substantially smaller, possibly implying a more closed protective shell around the Au core due to chain flexibility of the HOC12S $^-$, BrC12S $^-$, and MeOC(O)C15S $^-$ ligands. Also, the current baseline preceding the ferrocene wave in Figure 2 (inset) is practically flat and gives an average capacitance of only ca. 0.3 $\mu\text{F}/\text{cm}^2$. The implications of these capacitance variations are not fully understood, but this result and the steric interactions revealed by experiments 8–10 and the changes in the C=O vibrational energies (Table 1) provide the first evidence probing intramolecular interactions within poly-hetero- ω -functionalized MPC's.

In the above, we have implicitly assumed that in solution place-exchange of MPC's with ω -functionalized thiols, all clusters undergo similar degrees of poly-heteroexchange, as opposed to formation of a solution mixture of clusters each of which had undergone only poly-homoexchange. Indeed, it would be remarkable if the latter occurred. It is probably true, however, that the degree of place-exchange of any one ligand is not exactly the same on all polyexchanged cluster molecules (mixed or nonmixed); some statistical distribution of the number of exchanged ligands per cluster will be present. For example, the NMR measurement in experiment 7 (Table 1) tells us only that an *average* of 7 ferrocene sites/cluster has been introduced onto the MPC; there will be some clusters bearing either 8 or 6 ferrocene sites, a smaller number bearing either 9 or 5, etc. In addition to this polydispersity in the extent of place-exchange, a modest distribution of Au core sizes exists,¹⁴ and the dispersity of place-exchange reactions could conceivably differ according to Au core size. While nonfunctionalized Au MPC's have been fractionated according to Au core size,^{1d} and electrochemical measurements carried out on such monodisperse samples,¹⁵ fractionation or other separations have not yet been carried out for the ω -functionalized clusters, so the extent of polydispersity in place-exchange reactions is an unexplored topic.

The above experiments are only a first step in elucidating the spatial and dynamical relationships between different ligand functionalities on MPC monolayer surfaces. Nevertheless, the results in this paper set the stage, in principle, for (a) the facile synthesis of “nanofactory” cluster molecules, in which combinations of appropriate functionalities mixed together on the same MPC cluster surface exhibit mutually supporting chemical and redox catalytic reactions, and (b) a study of reactivities of functional groups on these “three-dimensional” organic monolayer surfaces using techniques (IR, NMR, and DSC) that are less adaptable to two-dimensional self-assembled monolayer systems.

Acknowledgment. This research was supported by grants from NSF and ONR. We thank Dr. James E. Hutchison (University of Oregon) for the synthesis of the thiolated anthraquinone ligand.

JA971734N

(12) Calculated from $i_{\text{LIM}} = 4nr\text{FDC}\theta_{\text{SITES}}$, where θ_{SITES} is the average number of redox sites per cluster.

(13) For example, a 459 Au atom core C8 MPC, bearing by stepwise exchange seven Fc's and 28 AQ's per cluster, gave voltammetry like Figure 2 and D_{Fc} , D_{AQ} , R_{Fc} , and $R_{\text{AQ}} = 1.5 \times 10^{-6}$ cm 2 /s, 1.8×10^{-6} cm 2 /s, 28 \AA , and 24 \AA , respectively.

(14) The average core size of this polydisperse cluster preparation was determined using transmission electron microscopy, small-angle X-ray scattering, and ^1H NMR line width analysis as described in ref 8. The Au core diameter dispersity for this material was approximately $\pm 20\%$.

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