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Dynamics and Extent of Ligand Exchange Depend on Electronic Charge of Metal Nanoparticles

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Abstract: Both the rate and extent of ligand place exchange reactions between the hexanethiolate monolayer of Au_{140} monolayer protected clusters (C6 MPCs) and dissolved 6-mercapto-1-hexanol thiol (HOC6SH) increase with increasing positive electronic charge on the Au cluster core. The rate constant of the ligand place exchange, taken at the early stage of the exchange, is increased by ca. 2-fold for reaction of +3 charged Au_{140} cores as compared to neutral ones. The initially exchanged ligands are thought to reside mainly on edge and vertex sites of the Au_{140} core, where the lability of the slightly more ionic Au−S bonds there becomes further enhanced by removing electrons from the core. The reactions slow markedly after 35−50% of the original ligands have been replaced, continuing at a much slower pace for some time to reach an apparent reaction equilibrium. On +2 charged Au_{140} cores, 85% of the C6 ligands have been exchanged with $HOC_6H_{12}SH$ after 20 h. The slower phase of the reaction includes exchange of thiolate ligands on terrace lattice sites most of which—owing to the small sizes of the nanoparticle's Au(111) faces—are no more than one Au atom row removed from the nanoparticle edge sites. This slower exchange, the extent of which is also enhanced by positively charging the core, occurs either by intramolecular place exchange with edge sites that subsequently place-exchange with solution thiol or by direct place-exchange with solution thiol. Acid−base studies show that thiolate is more reactive in place exchange reactions than the corresponding thiol.

The report by Schiffrin et al.[1] of an improved synthesis of gold nanoparticles (1−5 nm diameter) generated a wide range of opportunities to study the chemical and electronic nature of chemical materials whose dimensions lie near the transition between molecular and bulk metallic behaviors. These nanoparticles are coated with a dense monolayer of thiolate ligands that stabilize them against aggregation even when solvent is removed, enabling their isolation, purification, derivatization, and analytical characterization. We call[2] these nanoparticles "monolayer protected clusters", or MPCs.

The small core dimension and low monolayer dielectric properties of reasonably monodisperse alkanethiolate coated MPCs lead to single electron transfer (SET) characteristics in the charging of their electrical double layers in electrolyte solutions. This has been established[3] for both freely diffusing and electrode-attached MPCs. The size-dependent double layer property is termed "quantized double layer charging" (QDL). Research on core-charged MPCs can be summarized as follows: (a) The number of stored electronic charges[3] following single electron transfers can be estimated from the pattern of peaks for quantized double layer charging in MPC voltammetry (much as stored charge could be estimated for a polyvalent redox molecule). (b) Negatively and positively charged MPC cores can be used as electron donor and acceptor reagents in redox reactions.[4] (c) Mixing solutions of MPCs having different core charges results in electron transfers between the MPCs to reach an equilibrium solution potential describable by the stoichiometry of the mixtures and the Nernst relation.[4] (d) Electronic charging of cores of dodecanethiolate MPCs (C12 MPCs) causes a small shift in the surface plasmon (SP) band position in UV−vis spectra[5] that is comparable to previously observed SP band shifts for larger Au colloids.[6] (e) The related area of semiconductor nanoparticles (e.g., quantum dots) has also seen studies of their electrochemical charging,[7a,b] which provokes substantial changes of IR absorption properties and quenching of narrow band-edge photoluminescence.[7c,d]

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Other *chemical* consequences of nanoparticle charging, on the other hand, are relatively unknown. The reactions studied here are ligand place-exchanges on MPCs with electronically charged cores. Ligand place exchanges comprise an important synthetic route[2,8] to functionalized MPCs. A previous study[9] on (uncharged) Au_{314} MPC place exchange dynamics concluded that the room-temperature exchange reaction (i) has a 1:1 stoichiometry, liberating one thiol from the original MPC monolayer for every new thiolate incorporated into it, (ii) is an associative as opposed to dissociative reaction, (iii) does not involve disulfides or oxidized sulfur species, and (iv) probably occurs at a higher rate on vertexes and edges of the core surface as opposed to core terrace sites. Studies of ligand place exchange reactions on macroscopically flat self-assembled monolayers (2D SAMs) show[10−12] a large diversity of exchange reactivity of surface sites, some being readily reactive (presumably terrace edges, steps, and other defect sites) and others (Au(111) terraces) displaying extremely slow exchange. A similar greater reactivity of adsorbates and ligands on defect sites such as terrace edges is well-known in surface science.[13] The mechanism studies of exchange reaction in 2D SAMs diverge, however, in the conclusions drawn, producing evidence supporting both rate determining dissociative[14−16] and associative pathways.[10,17]

This paper describes the changes in rates and extent of ligand place exchange reactions on Au MPCs that result from electronic charging of the MPC cores. There have been no previous reports on place-exchange reactions of core-charged MPCs. (Surprisingly, reports of exchange reaction dynamics of 2D SAMs as a function of the potential of the gold surface are also lacking.) We present results on place exchange reactions between hexanethiolate Au_{140} MPCs (C6 MPCs) with well-defined core charges and an alkanethiol with similar structure but differentiable by NMR: 6-mercapto-1-hexanol thiol (HOC6SH). The rate and extent of incorporation of the HOC6S- thiolate ligand into the MPC monolayer is measured by quenching the reaction, with subsequent NMR analysis of the MPC's mixed monolayer formed after different reaction times. We observe that electronic charging of the Au core influences both the rate of ligand exchange at short reaction times and the eventual extent of exchange, i.e., the number of ligands that have been exchanged after the second, much slower phase of the reaction. Both initial rate and ultimate extent of exchange increase when the core is positively charged. The positive charges are placed on the cores by a preceding electrolysis step.

Literature information on the nature of the Au−S bond is pertinent to our interpretation of the effect of charge on place exchange. In reference to 2D SAMs, the Au−S linkage is generally described as polar or partially ionic.[18] Porter et al. showed that the thiolate ligand could be desorbed from a Au surface when a sufficiently negative potential is applied ("reductive desorption").[18b] Majda et al.[19] reported partial Au−S charge transfer as a function of the potential applied to a Au(111) surface. Density functional calculations for a "naked" Au_{147} nanoparticle reveal smaller Au 4f binding energies for edge and corner (vertex) sites,[20] i.e., Au−S bonds formed there should be more ionic than those on terrace sites, and accordingly more labile to exchange reactions.

Experimental Section

Chemicals. Tetrabutylammonium perchlorate (Bu_4NClO_4, Aldrich, >99%), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich, >99%), hexane thiol (HSC6, Aldrich, >99%), 6-mercapto-1-hexanol thiol (HOC6SH, Aldrich, >97%), dichloromethane (CH_2Cl_2, Aldrich, 99.9%), acetonitrile (CH_3CN, Aldrich, 99.9%), toluene (Aldrich, 99%), methanol (Aldrich, 99%), tetrahydrofuran (THF, Aldrich, 99%), potassium *tert*-butoxide (K^+OtBu^-, Aldrich, 1.0 M solution in tetrahydrofuran), acetic acid (Fisher, 99.7%), and I_2 (Fischer, 99.9%) were used as received.

Hexanethiolate-stabilized gold clusters (C6 MPCs) were prepared as in previous work.[21] Briefly, a 3:1 mole ratio of hexanethiol (HSC6OH) and $AuCl^{4-}$ in toluene at 0 °C was reduced by excess BH_4^- over a 24 h period. We have determined that this reaction produces 1.6 nm core diameter MPCs[22] with an *average* composition of $Au_{140}[S(CH_2)_5CH_3]_{53}$.[21]

Spectroscopy. ^1H NMR spectra of $CDCl_3$ and CD_2Cl_2 Au MPC solutions and disulfide solutions following their I_2-induced decomposition (see below) were collected on a Bruker AC200 spectrometer. A 5 s relaxation delay time suffices for accurate peak integration.

Thermal Analysis. Thermogravimetric analysis (TGA) was performed with a Seiko RTG 220 robotic TGA.

Electrochemistry. Measurements of differential pulse voltammetry (DPV) and of solution rest potentials at 1.6 mm Pt disk working electrode and bulk electrolyses of C6 MPC solutions (i.e., to charge the MPC cores) at a large Pt mesh were performed in a fritted three-component cell, with a Bioanalytical System (BAS) Model 100B potentiostat. The working electrode compartment of the electrochemical cell contained the working and reference electrodes in a C6 MPC solution (0.1 mM C6 MPCs, 50 mM Bu_4NClO_4, in CH_2Cl_2), the middle compartment only electrolyte solution (50 mM Bu_4NClO_4 in CH_2Cl_2), and the third compartment a Pt mesh auxiliary electrode and supporting electrolyte solution. The reference was a Ag/Ag^+ (Ag wire/$AgNO_3$ (1 mM)/Bu_4NPF_6 (0.1 M)/CH_3CN) electrode. Charging of MPC cores was always toward positively charged MPCs. Air was not excluded.

Preparation of Core-Charged MPCs. The rest potential of solutions of as-prepared C6 MPCs ($MPC^{as-prep}$) was typically about −0.45 V vs Ag/Ag^+, which given the ca. −0.2 V potential of zero charge[3c] and the double layer capacitance (C_{clu}) of the C6 MPCs (0.57 aF per MPC[23]) corresponded to a mixture of MPCs with 0 and −1 core charges.[3c] The potential increment for a one-electron change (e/C_{clu}, where e is the electronic charge) of these MPCs is about 280 mV. Thus,

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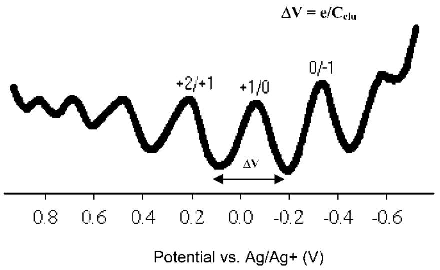

Figure 1. Differential pulse voltammetry of as-prepared C6 MPCs in CH_2Cl_2 (0.1 mM C6 MPCs, 50 mM Bu_4NClO_4, in CH_2Cl_2), measured at a 1.6 mm diameter Pt working electrode.

Table 1. Thermogravimetric Analysis of C6 MPCs Having Different Core-Charge States

charge state of MPCs	% organic	no. of organic ligands[a]	C_{clu}[b] (aF)
$MPC^{as-prep}$	18.1	53	0.57
MPC^0	18.1	52	0.58
MPC^{1+}	18.1	53	0.60
MPC^{3+}	18.2	53	0.56
MPC^{4+}	18.0	52	0.56

[a] The number of ligands L for MPC of charge state z, calculated from TGA percent organic weight using the folloing: $[L \times MW(L)]/[MW(C6MPC) + z \times MW(ClO_4)] = \%$ org. [b] $E_{z,z-1}$ is the "formal potential" of a $z/(z - 1)$ charge state "couple", C_{clu} is capacitance per MPC. A plot of $E_{z,z-1}$ versus z allows determination of the average value of C_{clu}, assuming that C_{clu} is independent of potential (which is usually, but not always[23,26] the case).

electrolysis of a solution of MPCs to a rest potential of 0.6 V vs Ag/Ag$^+$ would produce a solution of C6 MPCs with an average core charge of +3, or MPC^{3+}. In this way, a series of core charge-defined "0", "+1", "+2", and "+3" nanoparticles, or MPC^0, MPC^{1+}, MPC^{2+}, and MPC^{3+}, could be prepared.

After charging the MPC solution, the CH_2Cl_2 solvent was removed by rotary evaporation and the supporting electrolyte (Bu_4NClO_4) removed by washing three times with 20 mL portions of acetonitrile.[24] Removal of the electrolyte was confirmed by ^1H NMR.

Measurement of Apparent Exchange Equilibria. Solutions of approximately 20 mg (1.0×10^{-4} M) of C6 MPCs ($MPC^{as-prep}$, MPC^0, MPC^{1+}, or MPC^{2+}) in 10 mL of toluene were mixed with a 3-fold molar excess (in reference to the MPC monolayer content) of 6-mercapto-1-hexanol thiol (HOC6SH). The place exchange products were quenched by 100 mL of acetonitrile, cleaned on frits by rinsing with 100 mL of acetonitrile, and characterized by ^1H NMR after decomposing the MPC monolayers to mixed disulfides by adding I_2.[3a] The molar ratio of 6-mercapto-1-hexanol ligands ($-S-CH_2-$, ca. 3.6 ppm) to hexanethiolate ligand (methyl resonance, ca. 0.9 ppm) was determined from the relative NMR peak areas of the indicated resonances and the total ligand content of 53 ligands per MPC. After the mixture was stirred for 20 h at room temperature, the change in solution composition seemed to have ceased and an apparent equilibrium[25] was reached. (Because the reaction has slowed so much, it is uncertain whether it actually reaches a true equilibrium.)

Studies of Initial Reaction Rates. A mixture of approximately 100 mg of $MPC^{as-prep}$, MPC^0, MPC^{1+}, or MPC^{3+} C6 MPCs with a 2:3 mole ratio of the incoming ligand (HSC6OH) in 10 mL of toluene was stirred at room temperature. Periodically, 1 mL samples were taken, quenched by addition of 100 mL of acetonitrile (precipitating the MPC products), collected by suction filtration, rinsed with 100 mL of acetonitrile, and dried under vacuum. The product monolayer compositions were analyzed by ^1H NMR after I_2-induced decomposition to disulfides as above.

Results and Discussion

Charging MPCs and Their Compositional Stability. Figure 1 illustrates the quantized double layer (QDL) charging seen in a typical differential pulse voltammetry (DPV) response for a 0.1 mM C6 MPC solution in 50 mM Bu_4NClO_4/CH_2Cl_2. The pattern of more or less evenly spaced current peaks corresponds[3a,b] to single electron changes in the charge state of the MPC cores as they diffuse to the electrode surface and equilibrate (by electron transfer) with the Fermi level of the electrode. The relationship[3c] between the potentials at which current peaks are observed and the change in core double layer charge state (Z) occurring there is

$$E_{z,z-1} = E_{pzc} + \frac{(Z - {}^1/_2)e}{C_{clu}} \qquad (1)$$

where the peak potential $E_{z,z-1}$ is the "formal potential" of a $z/(z - 1)$ charge state "couple", C_{clu} is the capacitance per MPC, E_{pzc} is the potential of zero charge and e is the electron charge (1.602×10^{-19} C). $z > 0$ and $z < 0$ correspond to positively and negatively charged cores, respectively. At the formal potential $E_{z,z-1}$, a 1:1 mixed valent solution of the charge state couple exists at the electrode/solution interface. A plot of $E_{z,z-1}$ versus z allows determination of the average value of C_{clu}, assuming that C_{clu} is independent of potential (which is usually, but not always[23,26] the case). The thusly determined QDL capacitance of the C6 MPCs used here is 0.57 aF. On the basis of this capacitance, C6 MPC solutions charged by bulk electrolysis to final rest potentials of −0.19, 0.085, 0.38, and 0.6 V correspond to solutions of C6 MPCs with cores charged as MPC^0, MPC^{1+}, MPC^{2+}, and MPC^{3+}. The solutions of core-charged MPCs give DPV responses similar to the one in Figure 1. Measuring their capacitances by the method stated above gives results that together with the capacitance of as-prepared MPCs are listed in Table 1 for comparison. They are within error all the same, i.e., the MPC capacitance and by inference the cluster and its dielectric shell are substantially unaltered by the core-charging process.

The rest potentials of MPC solutions are a reliable measure of their state of charge. These potentials are generally stable for several days for charged C6 MPCs, indicating the stability of the core charge for this length of time. Core-charged MPCs also can be stored[4] as solids and redissolved without seeming change. However, it has not yet been analytically confirmed that no changes occur in the composition of the monolayer as a result of the core charging process. This question is especially relevant in studying the place exchange reaction kinetics since the results are based on the analyzed number of ligands.

Results of TGA analyses of as-prepared and core-charged C6 MPCs are shown in Table 1 as is the number of ligands calculated to be present in the monolayer (see table footnote). Thermogravimetric analysis of MPCs is known[27] to yield an

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(25) Samples were taken from the exchange reactions of MPC^{2+} at 10, 15, 20, and 41 h. Results showed that after 10 h the number of ligands exchanged remained the same, so we assumed that 20 h was long enough for an apparent equilibrium to have been reached.

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Table 2. Apparent Equilibrium Extent of Place Exchange[a]

clusters	exchanged ligands (total ligands is 53)
$MPC^{as-prep\ b}$	19
MPC^{0}	23
MPC^{1+}	40
MPC^{2+}	45

[a] 3:1 mole ratio of the incoming thiol (HSC6OH) and the thiolate ligand (−SC6) on C6 MPCs, in toluene solvent. [b] The estimated average charge state of as-prepared MPCs is between 0 and −1.

organic weight fraction that is consistent with their elemental analysis, and has led to an average composition[21] for as-prepared C6 MPC ($MPC^{as-prep}$) of $Au_{140}[S(CH_2)_5CH_3]_{53}$. The ligand contents of core-charged MPCs shown in Table 1 are identical with this composition; i.e., the core charging process does not change the average MPC monolayer composition.

The mass of the counterion of positively charged MPCs is tiny compared to that of the MPC itself, and is neglected in the above comparison. The presence of counterion can be detected, however, as by ^{19}F NMR, as shown in the Supporting Information.

The Long-Time Extent of Place-Exchange as a Function of Core Charge. We next present results of place exchange reactions where the reaction was allowed to run its course to an apparent equilibrium. Four experiments were performed, in which the same amount of 6-mercapto-1-hexanol (HOC6SH) was added to each of four solutions containing equal concentrations of the Au clusters C6 $MPC^{as-prep}$, MPC^{0}, MPC^{1+}, and MPC^{2+}. The mole ratio of the added HOC6SH was 3:1 in relation to the moles of C6 thiolate on the MPCs. The solutions were stirred for 20 h, which was established[25] to yield an apparent equilibrium extent of exchange.

The results for the number of HOC6SH ligands exchanged onto the MPCs in the preceding experiments are shown in Table 2. It is obvious that much larger numbers of HOC6S- thiolates become incorporated into the cluster monolayer when the Au core is made more positive. The percentage of exchanged ligands varies from 36% to 85% of the total. For reference, the number of surface Au atoms on an Au_{140} core (the average size core in the MPC sample) is 96, of which over one-half lie[21] on the vertexes and edges of its presumed[28−31] truncated octahedral shape.

As noted in the Introduction, an earlier place exchange study[9] of as-prepared MPCs (neutral or slightly negative, with larger cores than in the present paper, $Au_{314}(SR)_{108}$, and with an assortment of initial MPC ligands), suggested that the rate of place exchange is more rapid for Au sites on vertexes and edges of the core surface ("defect" sites) as opposed to core terrace sites. This proposal is sterically reasonable and also consistent with the more ionic (and thereby labile) character of the Au−S bonds on the nanoparticle edges anticipated from lower Au 4f electron binding energies there.[20] Figure 2 examines the earlier results of ligands exchanged at long reaction times (apparent equilibrium) in terms of the relative quantities of in-coming and initial MPC ligands, [X]/[L]. While the reaction's apparent equilibrium positions depend on the ratio [X]/[L], the attained equilibrium positions appear to plateau after replacement of between 35 and 50% of the initial MPC ligands. Since approximately 40% of the surface Au atoms on Au_{314} MPC cores (assuming a truncated octahedral shape[21,28,29]) lie on edge or vertex sites, the roll-over corresponds roughly to the total of edge plus vertex sites.

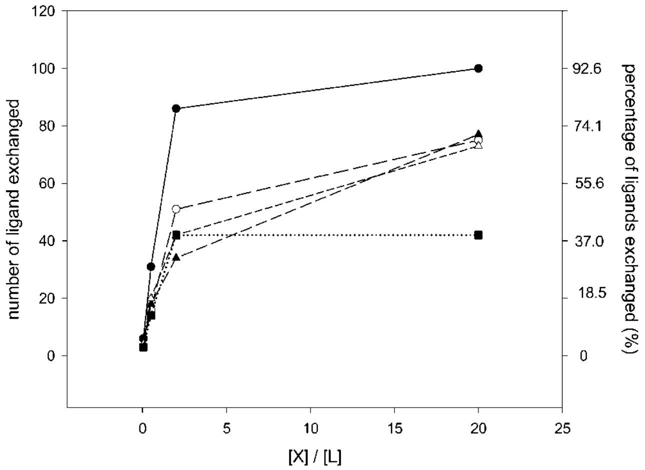

Figure 2. The number and percentage of exchanged ligands at apparent equilibrium versus the mole ratio of the incoming ligand (X = MeO_2-CC11SH) and the leaving ligand (L). L is C4S- (●), C8S- (○), C12S- (■), C16S- (△),and C16S- (▲). (In the last curve, the incoming ligand is MeO_2-CC15SH.) Data from ref 9.

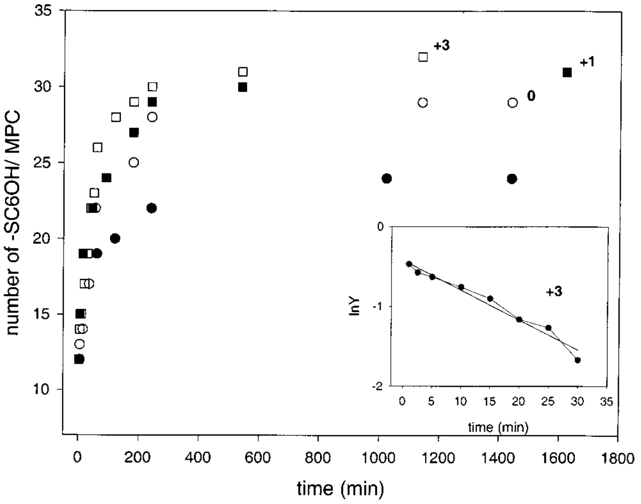

Figure 3. Plot of the number of -SC6OH ligands exchanged on C6 MPCs versus the reaction time for different charge states. The concentrations of the cluster solutions are all 4.8 × 10^{-4} M, and the concentrations of the incoming HSC6OH thiol ligands are 1.7 × 10^{-2} M. From the top to the bottom, they represent the following: MPC^{3+} (□), MPC^{1+} (■), MPC^{0} (○), and $MPC^{as-prep}$ (●). The inset is a plot of ln Y (Y = $[Au_{140}[S(CH_2)_5CH_3]_{53-x}[S(CH_2)_5OH]_x]_{TIME}/[Au_{140}[S(CH_2)_5CH_3]_{53}]_{INIT}$) versus time for place exchange of MPC^{3+} C6 MPCs.

An analogous roll-over is seen in the kinetic study (Figure 3, vide infra) of Au_{140} MPCs after about 20−25 ligands are exchanged, again near the sum of edge plus vertex sites for this core size. The numbers of ligands exchanged at much longer times, shown in Table 2, require, however, that at apparent equilibrium, exchange of ligands that were initially on terrace sites must have occurred in addition to exchange on edge and

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Table 3. Kinetic Studies of Place-Exchange Reactions of MPCs at Different Charge State[a,b]

cluster	[C6 MPC] , M	[HSC6OH], M	pseudo-first-order rate constant (s^{-1})	second-order rate constant ($M^{-1}\,s^{-1}$)
$MPC^{AS-PREP}$	4.8×10^{-4}	1.7×10^{-2}	1.2×10^{-4}	7.1×10^{-3}
MPC^{0}	4.8×10^{-4}	1.7×10^{-2}	1.4×10^{-4}	8.2×10^{-3}
MPC^{1+}	4.8×10^{-4}	1.7×10^{-2}	1.5×10^{-4}	8.8×10^{-3}
MPC^{3+}	4.8×10^{-4}	1.7×10^{-2}	2.4×10^{-4}	14×10^{-3}
MPC^{3+}	4.8×10^{-4}	1.7×10^{-2}	2.4×10^{-4}	14×10^{-3}
MPC^{3+}	4.8×10^{-4}	2.6×10^{-2}	2.8×10^{-4}	11×10^{-3}
MPC^{3+}	4.8×10^{-4}	7.6×10^{-2}	4.0×10^{-4}	5.3×10^{-3}

[a] 2:3 mole ratio of the incoming thiol (HSC6OH) and the thiolate ligand (−SC6) on C6 MPCs. [b] Reactions are performed in toluene.

vertex sites of the Au_{140} core. We demonstrated in the previous study[9] that there is some mobility of ligands on the MPC core surface. Intramolecular ligand migration of ligands newly exchanged onto edge/vertex sites to terrace sites on Au_{314} cores was evidenced[9] by results showing that ligands newly place-exchanged into an MPC monolayer are not completely removed in a second place exchange reaction by using a differently labeled in-coming ligand. This result was verified in the present work for the Au_{140} cores. An experiment was performed where 14 HOC6S- ligands were place exchanged onto C6 MPCs in a half-hour reaction. This product was isolated, and subjected to a reverse place exchange reaction with C6SH thiol. Only 8 of those ligands were lost from the MPC core surfaces even when the reverse exchange reaction in C6SH solution was prolonged for 4 days.

From the Au_{140} results, place exchanges of ligands in numbers exceeding the edge plus vertex sites appear to occur mostly in the later, slow phase of the ligand exchange reaction. Exchanges of ligands that were originally on the MPC Au(111) terrace sites could take place through an intrinsically slower place-exchange of ligands on terrace sites with in-coming thiol, or we believe (given the reverse place exchange results) more likely by an *intramolecular* place exchange of ligands between terrace and edge sites. It is important here to keep in mind the tiny dimension of the Au(111) terrace on a Au_{140} nanoparticle. In fact, in the structure calculated by Luedtke and Landman,[29] *all* of the terrace Au atoms are *adjacent* to Au atoms that lie on the nanoparticle edges. An intramolecular exchange of a ligand bound to an edge atom with one located in a 3-fold hollow one lattice unit away is all that is required to position a ligand originally on a terrace into a more readily exchangeable edge site.

The eventual extent of terrace site exchange is according to Table 2, enhanced by positively charging the core. Between 40 and 50% of the original C6 ligands on Au_{140} cores are displaced from as-prepared and neutral MPCs (as was found[9] for Au_{314} MPCs. However, for MPCs with positively charged cores (MPC^{1+} and MPC^{2+}), a larger proportion of exchanged ligands is observed, which requires replacement of a substantial fraction of the original ligands of Au(111) terrace sites. We will propose below that the acceleration of place exchange between original and in-coming ligands onto the edge and vertex sites arises from enhancing the lability of the partially ionic Au−S bonds there by positively charging the Au core. This charge-enhanced lability of edge site ligands should also facilitate their intramolecular place exchange with adjacent terrace site ligands.

Finally, we should comment that it is not clear why core charging should so seriously alter the apparent equilibrium position of the place exchange process, as it seems from Table 2. Although the reaction times were allowed to be very long, some sites may exchange only on an even longer time scale. For the faster exchanging positively charged cores, a larger proportion of these sites may react on the time scales employed.

Place Exchange Kinetics. In the kinetic study, a smaller (2:3) mole ratio of incoming ligand (HSC6OH) to C6 MPCs thiolate ligand was employed in order to slow the exchange reaction. The same amount of 6-mercapto-1-hexanol (HOC6SH) was added to each of four solutions containing equal concentrations of the Au clusters C6 $MPC^{as-prep}$, MPC^{0}, MPC^{1+}, and MPC^{3+}. Figure 3 shows NMR results of sampling the composition of MPC monolayers in the reaction mixture over time. The initially rapid place exchange reaction slows down after exchange of 20−25 ligands, which is about the proportion of edge plus vertex Au sites as noted above.

The reaction kinetics results in Figure 3 were analyzed at short times (<1 h) and are satisfactorily represented as a pseudo-first-order process with rate constant $k_{obs} = k_{p-e}$[HSC6OH], as illustrated in the inset of Figure 3. The results for k_{obs} are listed in Table 3 (top) and show that MPCs with +3 charges react about 2-fold faster than those of as-prepared clusters. This is a modest kinetic acceleration, but its existence is unequivocal from the systematic trend seen for MPCs with increasingly positive core charge.

The acceleration of place exchange caused by positively charging the nanoparticle cores is understandable by considering the nature of Au−S bonds in MPCs. In the Introduction, we summarized literature observations, salient ones of which are (a) Au−S bonds between chemisorbed alkanethiolates and a Au(111) surface are[19,20] polar (i.e., partially ionic) and are even (according to theory[20]) more-so for edge and vertex atoms on a Au nanoparticle surface, and the site occupancy[29,31] is larger near nanoparticle edges than on Au(111) terraces. It follows that positively charging the MPC core should further increase the polarity of the Au−S bond, making it more labile and reactive to ligand exchange.

Figure 4 and Table 3 (middle) show additional experiments in which the concentration of incoming thiol (HSC6OH) was varied and the concentration of a core-charged MPC (C6 MPC^{3+}) held constant. If the rate-determining step in ligand exchange were the dissociation of MPC-bound ligand, then the overall reaction rate should be independent of the in-coming ligand. As seen, however, the pseudo-first-order rate constant varies with the concentration of incoming ligand (HSC6OH), which is consistent with an associative mechanism for the exchange reaction. In an associative place exchange reaction, the incoming ligand penetrates the MPC monolayer and in some manner replaces (displaces) a bonded thiolate ligand. An associative reaction process was also concluded in a previous[9]

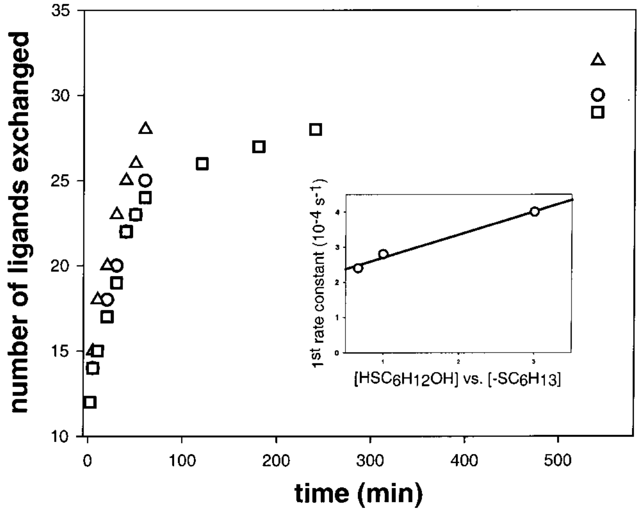

Figure 4. Plot of the number of -SC6OH exchanged onto 1 × 10^{-4} M MPC^{3+} C6 MPCs versus time, for 3:1 (△), 1:1 (○), and 2:3 (□) mole ratios of the incoming ligand (HSC6OH) to thiolate ligand (-SC6) on clusters. The pseudo-first-order rate constants are respectively 4.0 × 10^{-4}, 2.8 × 10^{-4}, and 2.4 × 10^{-4} s^{-1}. The inset is a plot of the pseudo-first-order rate constants of the above reactions versus the mole ratio.

Table 4. Media Effects on Place-Exchange Reactions[a] of HSC6OH Thiol with As-Prepared and +1 Charged C6 MPCs

		no. of ligands exchanged[b]	
reaction medium	additives	$MPC^{as-prep}$	MPC^{1+}
THF, N_2	K^+t-BuO^- [d]	37	42
THF, N_2	0.1 M Bu_4NClO_4 [f]		19
THF, N_2	acetic acid[e]		16
THF, air[c]		23	27
THF, N_2		6	26

[a] 2:3 mole ratio of incoming thiol (HSC6OH) to initial thiolate ligands (hexanethiolate) on C6 MPCs. [b] After reaction time of 1 h. [c] The data in air were taken from the results in Figure 3. [d] Potassium *tert*-butoxide in 1:1 mole ratio to the incoming thiol. [e] Acetic acid in 1:1 mole ratio to the incoming thiol. [f] Tetrabutylammonium perchlorate electrolyte.

Table 5. Solvent Effects on Place-Exchange Reactions of +2 Charged C6 MPCs[a]

solvents	no. of SC6OH ligands exchanged	no. of SC12Br ligands exchanged
toluene	37	32
dichloromethane	29	
THF	29	23
toluene/acetonitrile (1:1 v/v)	29	
methanol	28	0

[a] 2:3 mole ratio of the incoming thiol (HSC6OH or HSCl2Br) and the thiolate ligand (-SC6) on C6 MPCs.

place-exchange kinetics study of neutral-core $Au_{314}(SR)_{108}$ MPCs, where a ferrocenated octanethiolate ligand exchanged onto C8, C12, and C16 MPCs. The pseudo-first-order rate constants obtained in the present study are plotted in the inset of Figure 4 against the mole ratio of in-coming ligand [HSC6OH] and MPC [-SC6]. The relationship is linear, again consistent with an associative reaction, but exhibits a considerable intercept. This was also observed in the previous study,[9] but is not seen in an ongoing study[32] of arylthiolate ligand exchanges which are more ideally behaved. The origin of the intercept is not understood.

Reaction Medium and Acid−Base Effects. This section presents an assortment of experiments seeking to identify other factors that influence place exchange reactions on Au nanoparticles. The experiments, as above, are based on place exchanges of $HOC_6H_{12}SH$ with C6 Au_{140} MPCs.

Table 4 shows results of experiments probing acid−base effects, in which C6 $MPC^{as-prep}$ and C6 MPC^{1+} were place-exchanged with HSC6OH thiol in dry THF for 1 h. The top entries reveal a pronounced acid−base effect; the extent of exchange within 1 h is substantially enhanced by the presence of base and depressed by the presence of acid. (So many SC6OH thiolate ligands exchanged in 1 h that the product MPCs started to precipitate, which lead us to set the comparative observation times at 1 h. The results accordingly do not represent even apparent equilibria.) Under N_2, while as-prepared C6 MPCs incorporated only 6 SC6OH ligands after 1 h, for the MPC^{1+} cluster this jumped to 26 ligands; the comparable numbers in the basic medium were not as different (37 and 42 respectively for as-prepared and core-charged MPC^{1+}). Fewer ligands (16) were exchanged for core-charged MPC^{1+} in acidic medium (where thiol proton dissociation should be repressed) than in base. These results make it clear that *thiolates* are much more reactive in MPC place exchange reactions than the corresponding thiols. Other results[33] show that thiolates are also more reactive in exchanges on 2D SAMs.

That thiolate is more reactive in ligand exchange than thiol, especially with a positively charged Au core, is qualitatively plausible. The underlying reason(s) have, however, a number of subtleties, and we will defer further interpretation toward further experimental results with arylthiolate reactions.[32]

Table 4 additionally shows that the presence of O_2 can accelerate the exchange reactions of (negatively charged) $MPC^{as-prep}$ cores (from 6 to 23 ligands exchanged as compared to under N_2), while O_2 has a negligible effect on exchanges of positively charged cores such as MPC^{1+} (exchange of 27 versus 26 ligands). This suggests complexity that will require further investigation. O_2 can act as an oxidant toward negatively charged MPC cores, especially in the presence of thiols, which can act as proton donors toward the basic superoxide product. Thiolate ligands would be the product of such a reaction, and would lead to a faster rate of place exchange. Positively charged MPCs, however, should be less reactive toward O_2.

Turning to solvent effects, previous studies[34,35] on 2D self-assembled monolayers have considered effects of solvent on both formation and self-exchange reactions of the monolayer. Substantial solvent effects have not been reported on surface coverage of single-component 2D SAMs, but the composition of mixed monolayers can be quite solvent dependent.[19]

There are some constraints imposed on studying solvent effects for MPC exchange reactions because not only the thiols, but also the Au MPCs must be soluble in the selected solvents. Suitable solvents for the HSC6OH/C6 MPC place exchange included toluene, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene/acetonitrile (1:1 v/v), and methanol. HSC6OH and MPC^{2+} C6 MPCs were reacted at a 2:3 mole ratio for 20

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(32) Donkers, R.; Song, Y. University of North Carolina, 2002, unpublished results.

(33) Song, Y. University of North Carolina, 2002, unpublished results.

(34) (a) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir−Blodgett to Self-Assembled Monolayer*; Academic Press: San Diego, CA, 1991. (b) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

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h, i.e., producing an apparent equilibrium product. A second series of exchanges used the longer chain, non-hydrogen bonding thiol, HSC12Br. The results are given in Table 5.

Table 5 shows that for the HSC6OH exchanging thiol, the apparent equilibrium extent of exchange is largest in the least polar solvent (toluene), and somewhat lower, and uniform, for solvents of intermediate polarity (CH_2Cl_2, THF, toluene/acetonitrile) and for a more polar, hydrogen bonding solvent (methanol). The reactivity of HSC12Br is somewhat less in toluene and THF solvents, but startlingly is negligible in methanol. This last observation shows that solvent effects on MPC place exchanges may often be mild, but occasionally dominant. Usually, longer chain alkanethiols place exchange quite readily into shorter chainlength alkanethiolate monolayers of MPCs.[9] We do not attempt to rationalize this dramatic result, lacking convincing arguments.

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Supporting Information Available: Experimental details and ^1H and ^{19}F NMR spectra of MPC^{2+} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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