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Heterophase Ligand Exchange and Metal Transfer between Monolayer Protected Clusters

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Abstract: This paper describes reactions in which ligands are exchanged and metals are transferred between monolayer-protected metal clusters (MPCs) that are in different phases (heterophase exchange) or are in the same phase. For example, contact of toluene solutions of alkanethiolate-coated gold MPCs with aqueous solutions of tiopronin-coated gold MPCs yields toluene-phase MPCs that have some tiopronin ligands and aqueous-phase MPCs that have some alkanethiolate ligands. In a second example, heterophase transfer reactions occur between toluene solutions of alkanethiolate-coated gold MPCs and aqueous solutions of tiopronin-coated silver MPCs, in which tiopronin ligands are transferred to the former and gold metal to the latter phase. These ligand and metal exchange reactions are inhibited when conducted under N_2. The results implicate participation of an oxidized form of Au (such as a Au(I) thiolate, Au(I)-SR) as both a ligand and metal carrier in the exchange reactions. Au(I)-SR is demonstrated to be an exchange catalyst.

Introduction

Our[1] laboratory, and others,[2] has devoted significant efforts over the past several years to understanding the chemistry of nanometer-sized metal particles protected from aggregation by self-assembled monolayers ("monolayer protected clusters", MPCs). It has been found that generally, MPC properties and reactivities respond to both metal core composition[3] and the nature of the monolayer ligand shell.[4] An important example is place (i.e., ligand) exchange reactions, which can be used to manipulate the chemical functionality of the monolayer shell. For example, in ligand exchange, a solution of alkanethiolate (−SR) MPCs is incubated with a different thiol (R′SH), whereupon the new thiolate (−SR′) becomes, to a reaction condition-dependent extent, exchanged with the original monolayer's thiolates. Our investigations[4] of this reaction have shown that it: (i) exhibits a 1:1 stoichiometry, liberating one thiol from the original Au MPC monolayer for every new thiolate incorporated into it; (ii) does not involve or require participation of disulfides or oxidized sulfur species; (iii) appears to occur at a higher rate on core surface vertexes and edges; (iv) is sensitive both kinetically and thermodynamically to cores that have been positively charged by electron removal; (v) appears to involve an associative mechanism at least at short reaction times; and (vi) is retarded under N_2 and accelerated by base. Another kind of MPC exchange reaction involves the metals of the core, producing bimetallic clusters[3] by reacting a salt of a noble metal with an MPC core of a less noble metal, such as for example, a Au^{I} or Pd^{II} thiolate salt reacting with silver core MPCs. Further, in procedures known as "etching"[5] and "annealing"[6] aimed at improving the MPC size mono-dispersity, metals are moved between MPC cores by, as yet, poorly defined mechanisms.

This report describes results from our continued inquiry[4] into how ligand and metal exchange reactions occur, namely, *how do core metal atoms and ligands of the monolayer shells of MPC nanoparticles become transferred from one kind of MPC to another*. What are the useful tactics for clarifying such questions? Mixing two MPCs having different monolayer constituents in a *single*-phase solvent, and observing how ligands or metals are exchanged or transferred between the two kinds of MPCs, is a conceptually simple approach. Sastry, et al.,[7] have done a related experiment, but where one of the nanoparticles was initially uncapped. The challenge encountered is analysis

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of the reaction products, which requires either their separation or existence of some selective optical or electrochemical probe of monolayer or core composition. Our program[8] on reversed phase liquid chromatography of MPC mixtures should ultimately aid analysis of homophase reactions. Another scheme deals with heterophase reactions, where the solubility-based confinement of the nanoparticle reactants to different phases circumvents the need for separation or phase-selective analysis. We describe here (a) exchange between thiolate ligands in a self-assembled monolayer on a flat surface (a 2D SAM) and those on an MPC in a solution contacting the SAM, (b) heterophase exchange between ligands on Au MPCs with different monolayer shells in contacting, immiscible solvents, and (c) exchange of ligands and transfer of metals (galvanically) between MPCs in contacting, immiscible solvents. We also investigate, in some cases, how these reactions are inhibited by the absence of air or promoted by added Au(I) thiolate salts. The collective results lead to an improved mechanistic model of the exchange reactions.

Experimental Section

Chemicals. Reagents from Aldrich are tetrabutylammonium perchlorate (Bu_4NClO_4, > 99%), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, > 99%), hexanethiol (HSC6, >99%), dodecanethiol (HSC12, >99%), 6-mercapto-1-hexanol thiol (HSC6OH, >99%), 12-mercapto-1-dodecanol thiol (HOC12SH, >97%), dichloromethane (CH_2Cl_2, 99.9%), acetonitrile (CH_3CN, 99.9%), toluene, methanol (99%), tetrahydrofuran (THF, 99%), copper(II) perchlorate hexa-hydrate ($Cu(ClO_4)_2 \cdot 6H_2O$), potassium *tert*-butoxide ($K^+t\text{-}BuO^-$, 1.0 M solution in tetrahydrofuran), silver nitrite ($AgNO_3$, 99.9%), *N*-(2-mercaptopropionyl)glycine (tiopronin, 99%) were used as received, as were acetic acid (99.7%) and I_2 (99.9%) from Fisher. $HS(CH_2)_8Fc$ (C8Fc)[9] and $Au^I[SCH_2(C_6H_4)C(CH_3)_3]$[10] were synthesized according to earlier reports, as were hexanethiolate-stabilized gold clusters (C6 MPCs).[11,12] For the latter, 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. It has been determined that this reaction produces 1.6 nm core diameter MPCs[13] with an *average* composition of $Au_{140}[S(CH_2)_5CH_3]_{53}$.[11] *N*-(2-mercaptopropionyl)glycine gold MPCs (tiopronin-coated Au clusters) were prepared according to an earlier report.[14] Briefly a 3:1 mole ratio of tiopronin and $AuCl_4^-$ was co-dissolved in 6:1 methanol/acetic acid. $NaBH_4$ dissolved in H_2O was added with rapid stirring. The black suspension was stirred for 30 min, and then the solvent was removed under vacuum at temperatures < 40 °C. The pH of the crude product was adjusted to 1 by dropwise addition of concentrated HCl. This product was purified by dialysis.

N-(2-mercaptopropionyl)glycine silver MPCs (tiopronin-coated Ag clusters) have been recently decribed.[15] Briefly, a 3:1 mole ratio of tiopronin and $AgNO_3$ was co-dissolved in water and $NaBH_4$ dissolved in H_2O added with rapid stirring at 0 °C. The black suspension was stirred for 30 min, and then the product was quenched by methanol. The precipitates were cleaned and then dissolved again in water. This material was also purified by dialysis.

Spectra. Proton 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 5s relaxation delay time suffices for accurate peak integration. UV−vis spectra (200−800 nm, 1 nm resolution) were collected with an ATI UNICAM UV4 spectrometer. Fluorescence spectra were taken at a standard right angle configuration on an ISA Instrument Jobin Yvon-spex Fluorolog model FL3-21 spectrometer. Fourier Transform Infrared (FTIR) absorbance of cluster solutions (~0.1 mM in toluene) were acquired using a Bio-Rad 6000 spectrometer. Transmission Electron Microscopy (TEM) samples were prepared by placing a droplet of a ca. 1 mg/mL MPC solution (toluene for organic-soluble and water for water-soluble) on Formvar-coated (200−300 A) copper grids (200 mesh), with overnight drying. Phase-contrast images of the clusters were obtained with a side-entry Phillips CM12 electron microscope operating at 120 keV. Three typical regions of each sample were obtained at 560K magnification. Histograms of Au core diameter distributions were obtained from more than three photographic enlargements with Scion Image Beta Release 2. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Physical Electronics Industries model 5500 surface analysis system with an Al Kα X-ray source, a hemispherical analyzer, a toroidal monochromator, and a multichannel detector (pass energy, 187.9 eV; resolution, ~0.3 eV), referencing peak positions to the C1s peak at 284.9 eV. In the XPS data analysis, the peak area ratios of spin−orbit couplets were constrained to their appropriate values (e.g., 3:2 for Ag 3d, and 4:3 for Au 4f). The binding energy spacing between each doublet was similarly fixed, to 6.0 eV for Ag 3d and 3.67 eV for Au 4f.

Elemental Analysis. The elemental analysis was performed by Galbraith laboratory (Knoxville, TN).

Electrochemistry. Cyclic voltammetry was done using a Bioanalytical System (BAS) Model 100B potentiostat on gold-film working electrodes (4×7 mm^2) in cells where the reference electrode was Ag/Ag^+(acetonitrile), and the counter electrode is Pt. Bulk electrolyses of C6 MPC solutions (*i.e.*, to electronically charge the MPC cores to MPC^{3+} states) were performed (without degassing) at a large Pt mesh working electrode in a fritted three-component cell.[4c,16] The working electrode compartment contained the working and reference (Ag wire/1 mM $AgNO_3$ in 0.1M Bu_4NPF_6/CH_3CN) electrodes and a CH_2Cl_2 solution of 0.1 mM C6 MPCs, 50 mM Bu_4NClO_4; the middle compartment contained only electrolyte solution (50 mM Bu_4NClO_4 in CH_2Cl_2) and the third compartment a Pt mesh auxiliary electrode and only supporting electrolyte solution.

Ligand Exchange of 2D Self-Assembled Monolayers. Au film electrodes were prepared on clean glass slides by serially evaporating a 100 Å bonding layer of chromium and 2000 Å of Au. Such surfaces are known to consist of large Au(111)

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terraces.[17] Self-assembled monolayers of HSC12OH were prepared by soaking the Au films in a 0.2 mM solution of this thiol for 2 days,[18] using voltammetry to inspect the quality of the film. Ligand exchange reactions were carried out by soaking the self-assembled Au−SC12OH monolayer in a 0.1 mM THF solution of MPCs bearing a mixed monolayer of hexanethiolate and −SC8Fc for 2 days. The Au-coated glass slide was rinsed repeatedly with ethanol and THF and soaked in pure THF for 1 day to ensure removal of any MPCs, then washed with ethanol and THF several more times and finally dried in air.

The mixed monolayer MPCs were prepared by stirring a 3:1 (ligand) mole ratio THF solution mixture of hexanethiolate-coated MPCs and $HS(CH_2)_8Fc$ for 2 days, removing the solvent under vacuum, and rinsing the product with acetonitrile. The mixed monolayer was analyzed by ^1H NMR, following decomposition of the MPCs with I_2 as described previously.[1a] It was determined that the mixed monolayer MPCs contained, on average, 8 ferrocene-bearing ligands.

Heterophase Exchange Reactions. For reactions between MPCs with different monolayers, 5 mL each of 0.1 mM hexanethiolate-coated Au MPCs (Au C6 MPC, in toluene) and 0.01 mM tiopronin-coated Au MPCs in water (50 μM in the case of tiopronin-coated Ag MPCs) were rapidly stirred, exposed to air or under N_2. Heterophase exchange reactions at other reactant mole ratios (100:1, 50:1, 1:50, Au C6 MPC/Ag-tiopronin MPC) were carried out for comparison to the above 20:1 case. pH values of tiopronin-coated Au (or Ag) MPC aqueous solutions were ambient. All reactions were stopped by allowing them to separate into two phases, each of which was thoroughly cleaned by dialysis (the water phase), or by evaporating the toluene and rinsing with acetonitrile (for organic-soluble products).

Results and Discussion

Ligand Exchange between MPCs and 2D SAMs. Self-assembled monolayers on flat Au surfaces and "3-D" SAMs on gold MPCs should to some degree exhibit analogous surface chemistry.[12,19,20] The following experiment was designed to detect transfer of a redox-labeled thiolate ligand from the monolayer of a dissolved MPC to a SAM on a flat gold surface.

A SAM monolayer of −SC12OH on a flat gold surface exhibits voltammetry as seen in Figure 1a. This surface was exposed for 2 days to a THF solution of MPCs having mixed monolayers of hexanethiolate and ferrocenyl-octanethiolate (−SC8Fc) ligands (C6/C8Fc MPCs), and was then thoroughly washed to remove any MPCs, and reexamined by cyclic voltammetry (Figure 1b). Now, the electrode surface displays the electrochemical signature of the ferrocene with a wave at ca. 500 mV. Clearly, some ferrocenated thiolate ligands were exchanged into the −SC12OH SAM from the MPCs in solution. The surface coverage of transferred ferrocenes was calculated as 2.6×10^{-13} mol/cm^2, which is ca. 0.1% of a monolayer (taking 3×10^{-10} mol/cm^2 as a monolayer of −SC8Fc ligands[9]). Similar results were obtained upon exposing SAM monolayers

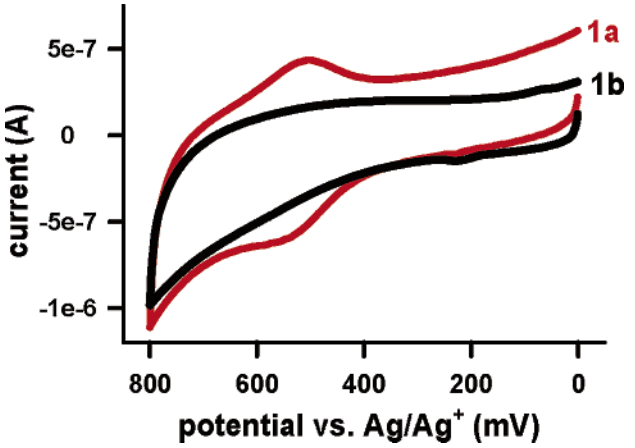

Figure 1. Cyclic voltammograms of gold 2D SAM (monolayer of −SC12OH) after (Figure 1a) and before (Figure 1b) exposure to solutions of C6/C8Fc MPCs for 2 days. Electrode area 0.28 cm^2, 50 mV/s potential scan rate.

of −SC12 and −C6 alkanethiolates to solutions of mixed monolayer C6/C8Fc MPCs, although even fewer SC8Fc ligands were exchanged in those cases. These results show that on a flat Au surface, ligand exchange does occur but to a very limited extent, as might be the case if exchange were confined to defect (terrace edge, etc.) sites on the flat Au surface. We note that, in contrast, the proportion of "defect" sites (nonterrace, i.e., edge, vertex) on the Au surface of the MPC nanocrystal is expected to be quite high, and exchange is thus more readily detected.

Heterophase Ligand Exchange between Au MPCs Dissolved in Immiscible Phases (toluene and water). Solubilities of MPCs are dominated by the character of the protecting monolayer shell. Hexanethiolate-coated Au MPCs (C6 Au MPC, avg. core diameter 1.6 nm) are hydrophobic, toluene-soluble and water-insoluble, whereas tiopronin-coated Au MPCs (tiopronin Au MPC, avg. core diameter 1.8 nm)[14,21] are hydrophilic, water-soluble, and toluene-insoluble. The core of tiopronin Au MPCs efficiently fluoresces at ca. 750 nm (excited at 450 nm).[14]

Small volumes of C6 Au MPCs in toluene and of tiopronin Au MPCs in water (see the Experimental Section) were rapidly stirred together for 15 h at room temperature. The C6 MPCs in toluene were in large excess (mole ratio 10:1 C6 Au MPC/tiopronin Au MPC). Figure 2a shows the fluorescence spectra of the aqueous phase before and after contact with the C6 Au MPC toluene solution; the emission wavelength is unchanged but its intensity has decreased. Relevant observations are that C6 Au MPCs (at least those with 1.6 nm core diameters) do not fluoresce within the wavelength range of Figure 2a, and that the fluorescence intensity of tiopronin Au MPCs at 750 nm decreases[22] when −SC6 thiolates are place exchanged into the tiopronin monolayer. The Figure 2a results are consistent with some hexanethiolate ligands having become transferred from the C6 Au MPCs in toluene to the tiopronin Au MPCs in the aqueous phase.

The reverse ligand transfer also occurs in the experiment of Figure 2a; tiopronin ligands are lost from the aqueous phase

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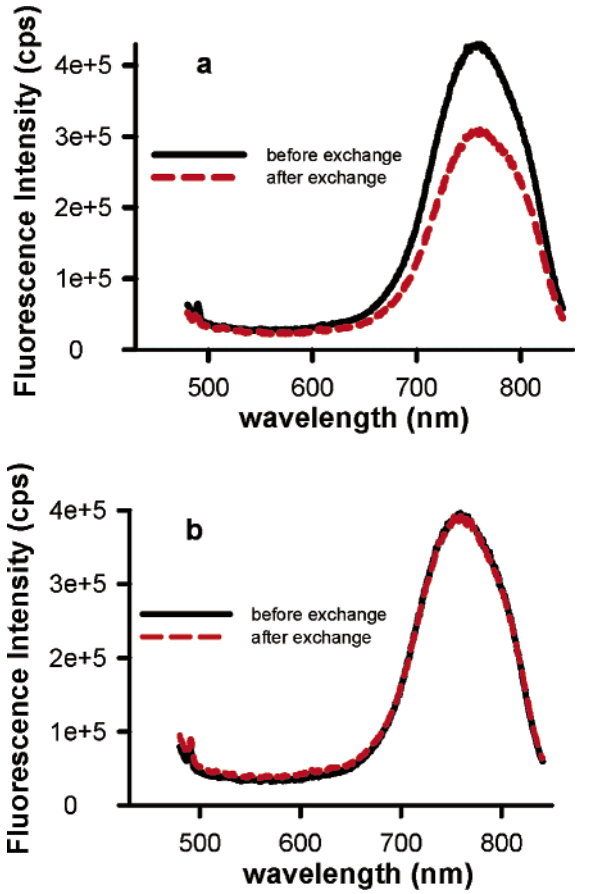

Figure 2. Fluorescence spectra (excited at 450 nm) of the aqueous phase before (—) and after (- — -) 15 h stirred contact between 5 mL each of 0.01 mM tiopronin-coated gold MPCs (aqueous) and 0.1 mM hexanethiolate-coated gold MPCs (toluene). Solutions were exposed to air (Panel a) or were under N_2 (Panel b).

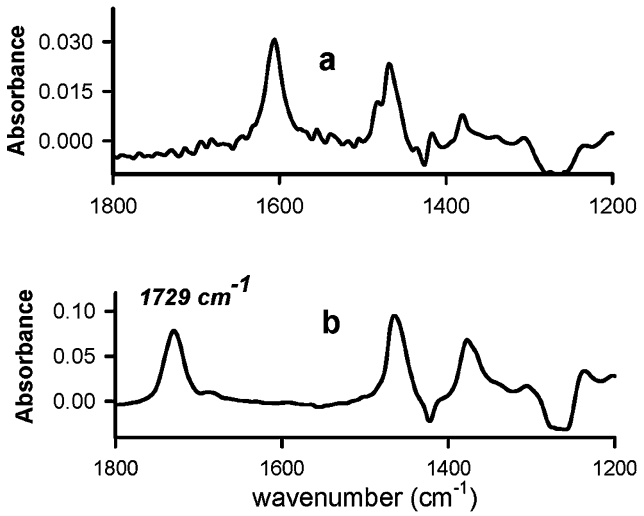

Figure 3. FTIR spectra of ca. 0.1 mM organic-soluble MPCs (in toluene) after 15 h contact under N_2 (Panel a) and in air (Panel b) between 0.01 mM tiopronin-coated Au MPCs (aqueous) and 0.1 mM hexanethiolate-coated Au MPCs (toluene). The band at ca. 1600 cm^{-1} in Panel a is an CH_3CN impurity from incompletely dried, CH_3CN-washed exchange product.

and are incorporated into C6 Au MPCs in the organic phase. This was ascertained by the appearance of a band at the carbonyl stretch energy in the FTIR (1729 cm^{-1}, Figure 3b) of MPCs isolated from the organic phase following the reaction. A further test for tiopronin ligands on the C6 Au MPCs in the toluene phase was the appearance, after a few minutes, of cluster aggregation and precipitation, following addition of a few drops of 5 mM $Cu(ClO_4)_2$ in ethanol. Metal ions (including Cu^{2+}) are known[23,24] to coordinately bind together clusters that contain carboxylate groups in their monolayers, causing aggregation, precipitation, and film-formation. The inferred carboxylic acid groups in the toluene phase could only have come from the aqueous tiopronin Au MPCs.

The extent of transfer of −SC6 and tiopronin ligands into the water and toluene phase MPC monolayers was not quantitatively assessed, but was probably modest. If the ligand exchange had replaced large fractions of the original ligands, then the resulting mixed monolayer C6/tiopronin Au MPCs would have become insoluble in both aqueous and toluene phases, and this was not observed.

An important observation was made upon repeating the experiment above under N_2. When the contact between toluene phase C6 Au MPCs and aqueous tiopronin Au MPCs was carried out *under* N_2 (Figure 2b, 3a), none of the above tests (Cu^{2+} induced aggregation, FTIR, fluorescence) signaled any ligand exchange between the two kinds of MPCs. The obvious inference, discussed below, is that dioxygen somehow plays a role in the ligand exchange process.

Heterophase Ligand Exchange and Metal Transfer between Au C6 MPCs in Toluene and Ag tiopronin MPCs in Water. Aqueous solutions of tiopronin-coated Ag MPCs[15] (1.6 nm avg. core diameter) exhibit absorbance spectra with a strong surface plasmon band at ca. 380 nm and a strong fluorescence at ca. 500 nm (excited at 380 nm). Tiopronin Au MPCs of 1.6 nm core size do not display a recognizable surface plasmon absorbance peak,[14] but do fluoresce, as was shown in Figure 2a. Given the results in Figure 2, ligand exchange is anticipated for contact of toluene C6 Au MPCs and aqueous tiopronin Ag MPCs. The difference in the metals of the two MPC cores raises the additional possibility of metal transfer between the different phases.

Small volumes of C6 Au MPCs in toluene and of tiopronin Ag MPCs in water (mole ratio 20:1 C6 Au /tiopronin Ag MPC) were rapidly stirred together for selected times at room temperature and the phases separated. Figure 4 shows the time dependencies of the aqueous phase fluorescence (Panel a) and of the aqueous phase absorbance (Panel b) spectra, which are initially those of the tiopronin Ag MPCs. The original fluorescence and surface plasmon absorbance bands of the aqueous silver nanoparticles are seen to decrease and essentially vanish after a few hours, whereas in Panel 4a, there concurrently grows in a fluorescence maximum that peaks above 700 nm. While the new fluorescence peak was not recorded in its entirety in Panel 4a, the leading edge strongly resembles the known[14] fluorescence of Au tiopronin MPCs. A similar diminution of the silver tiopronin surface plasmon absorbance observed in Figure 4b was seen[15] in the galvanic organic-phase reaction of alkanethiolate-coated Ag MPCs with a soluble Au(I) thiolate, where Ag atoms on the MPC surface were replaced with Au atoms. No plasmon band for the resultant tiopronin Au-coated MPC is seen because the nanoparticle is too small to give a

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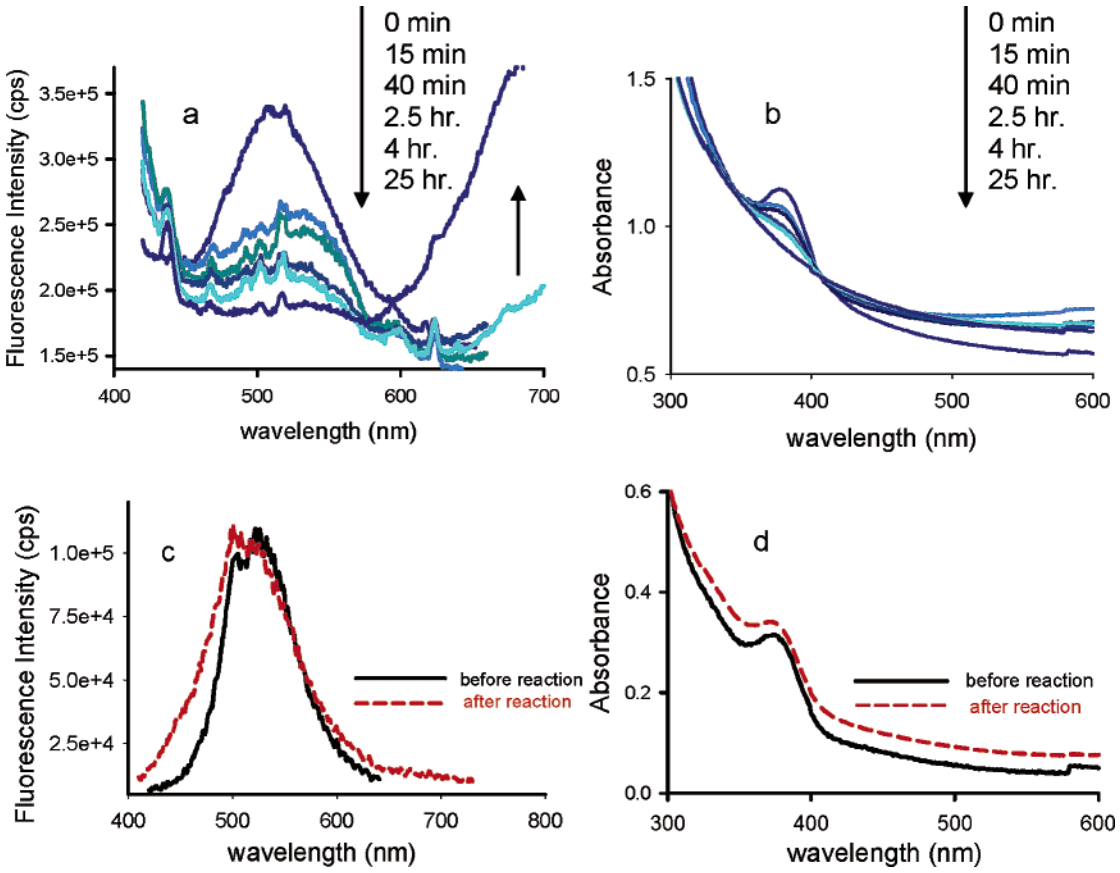

Figure 4. Fluorescence (Panel a, excited at 380 nm) and UV−vis absorbance spectra (Panel b) of the aqueous phase following contact between 5 mL each aqueous 50 μM tiopronin Ag MPCs and toluene 0.1 mM hexanethiolate-coated Au MPCs, (dissolved in toluene) at different reaction times. Panel c and Panel d show changes of aqueous phase fluorescence and UV−vis absorbance spectra after reacting under N_2 for 15 h.

recognizable plasmon excitation. The results of Figure 4 clearly demonstrate the transfer of gold atoms from the C6 Au MPCs in the toluene phase onto the tiopronin-coated, initially all-silver MPCs in the water phase.

The above experiment, a reaction between toluene phase C6 Au MPCs and aqueous tiopronin Ag MPCs, was repeated, this time *under* N_2 and for 15 h. Figure 4c,d show that the fluorescence and UV−vis plasmon band spectra are unchanged following the reaction. This observation is consistent with the result of Figure 2a,b, namely that dioxygen must play some role in heterophase exchange reactions. In the present case (Figure 4), dioxygen must supply the oxidizing equivalents for the transfer reaction of Au atoms from MPCs in the organic phase to those in the aqueous phase. The aqueous phase MPCs lose their original Ag metal with production of oxidized Ag(I), in a 1:1 ratio; see the analysis below.

The charge state of the MPC core also affects the above heterophase exchange reaction, as shown by Figure 5. Figure 5a shows the time course of the decrease in the 380 nm aqueous tiopronin Ag surface plasmon band in Figure 4b, and Figure 5b shows the result of a similar experiment, except that the C6 Au MPCs in the toluene phase had been electrolytically charged to a MPC^{3+} charge state (see the Experimental section). The decay of the Ag surface plasmon band is substantially faster in the latter case, i.e., Au is being transferred from the toluene phase MPCs to the aqueous phase MPCs at an increased rate. The significance of this observation is discussed below. The decay of the plasmon band intensities in Figure 5 can be fit to a first-order two-parallel-reaction scheme. The intensities of

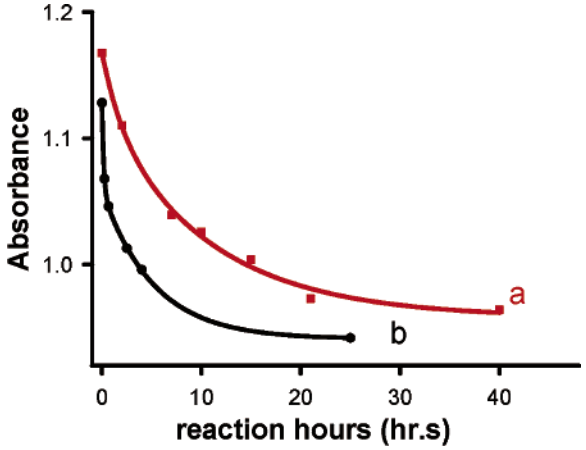

Figure 5. Curve a shows change of Ag MPC surface plasmon absorbance with time during reaction of 5 mL each of 0.1 mM C6 Au MPC (toluene) and 0.005 mM tiopronin Ag MPC (water). Curve b is the same except the C6 Au MPCs had been positively charged to *avg.* +3 state.

surface plasmon bands are known[25,26] to reflect the surface composition of metal nanoparticles. The quantitative relationship of data such as that in Figure 5 to the mole fraction of a surface atom (Ag) on a given nanoparticle is being explored in an ongoing project.[27]

A variety of other analyses were conducted on the toluene and water phase products of the reactions of Figure 4a,b above.

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(26) (a) Mulvaney, P. *Langmuir* **1996**, *12*, 788−800; (b) Wood, A.; Giersig, M.; Mulvaney, P. *J. Phys. Chem. B.* **2001**, *105*, 8810.
(27) Song, Y.; Patrick, S. unpublished results.

Table 1. XPS and Elemental Analysis Results of Reaction Products of Exchange Reaction between 5 mL 0.1 mM C6 Au MPC and 5 mL 0.005 mM Tiopronin Ag MPCs

XPS	organic phase (after exchange)	Au:Ag =10:1
	aqueous phase (after exchange)	Au:Ag = 1:1
elemental analysis	organic phase (after exchange)	Au:Ag = 60:1
	aqueous phase (after exchange)	Au:Ag = 1:1

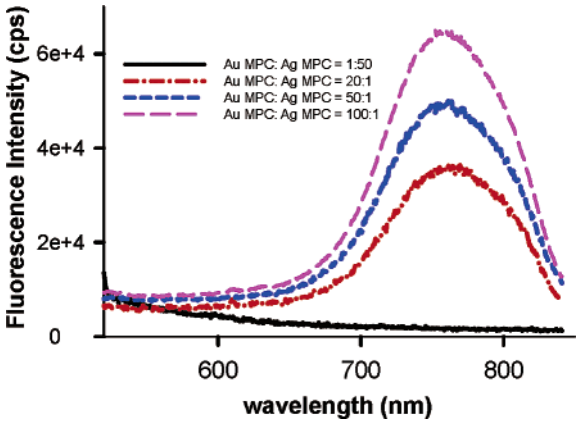

Figure 6. Fluorescence spectra of the aqueous phase products following exchange reactions between 5 mL of Au C6 MPCs and 5 mL of Ag tiopronin MPCs. The mole ratios between the two are 100:1, 50:1, 20:1, and 1:50, as noted in the figure.

X-ray photoelectron spectroscopy and elemental analysis showed (Table 1) that the water-soluble MPC product, originally all-silver, now contains equal populations of Au and Ag as expected (see above) because each transferred Au atom results in oxidation of one Ag. A minor amount of silver finds its way into the organic phase (Table 1), the amount is minor in comparison to Au. The XPS Ag 3d binding energy (372.5 eV) is suggestive of Ag(I) rather than Ag^0; there is no redox process available to reduce Ag(I) generated in the water phase back to a zero-valent state. The small amount of Ag(I) transferred to the organic phase could occur by its extraction as a counterion of tiopronin ligands or as an organic-soluble Ag(I)-SR salt. The transmission electron microscopy (TEM) results showed that the number average diameters of MPC cores in the organic and aqueous phases, originally 1.6 ± 0.8 nm (Au) and 1.4 ± 0.6 nm (Ag), are 1.4 ± 0.9 nm and 1.6 ± 0.7 nm, respectively, after a 24 h. reaction. These values, in which the organic phase nanoparticles shrink (losing Au atoms) whereas the aqueous ones grow (replacing Ag with larger Au atoms), are qualitatively consistent with the elemental analysis results; Au atoms are unilaterally transferred to the water soluble MPCs and not the reverse. The TEM dispersity is such however to make this not a firm conclusion.

Other experiments at 100:1, 50:1, and 1:50 mole ratio of Au C6 MPCs:Ag tiopronin MPCs were conducted for comparison to the 20:1 mole ratio used above, again following the day-long galvanic reaction by observing the Au-tiopronin MPC fluorescence (excited at 450 nm) in the water-soluble product (Figure 6). The intensity of the fluorescence—characteristic of Au atoms on the water soluble tiopronin-coated MPCs—increases at larger mole ratios of Au C6 MPCs to Ag tiopronin MPC, and is not detectable (absent or very small) at 1:50 mole ratio. The trend is clear that the extent of heterophase transfer of Au atoms from C6 Au MPCs onto the surfaces of aqueous

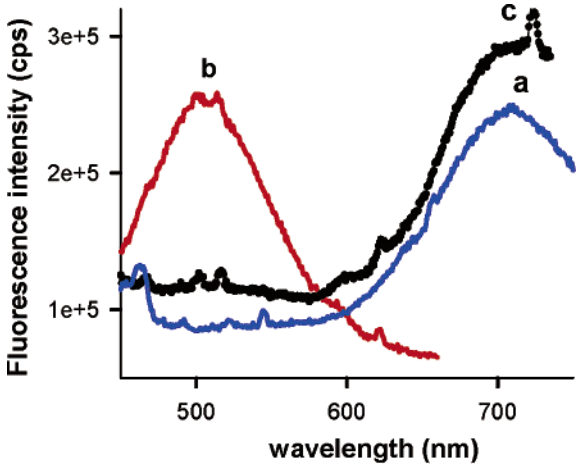

Figure 7. Fluorescence spectra of tiopronin Au MPCs (Curve a, excited at 450 nm), tiopronin Ag MPCs (Curve b, excited at 380 nm), both taken separately, and of the 15 h reaction product (Curve c, excited at 450 nm) of a mixture of 0.01 mM tiopronin Au MPCs and 0.005 mM tiopronin Ag MPCs (no tiopronin Ag MPC fluorescence is seen for excitation at 380 nm; data not shown). The reaction was in air and at room temperature.

originally all-Ag, tiopronin MPCs increases with the former population.

We have no clean evidence about the possible transfer of C6 ligands from MPCs in the toluene phase onto the water phase MPCs, but we can show that the reverse occurs; tiopronin ligands are transferred onto the toluene phase MPCs. Separating the two phases after a reaction of 24 h, both the Cu^{2+}-based MPC carboxylate aggregation test and FTIR spectra of the toluene phase showed the presence of carboxylic acid groups (and thus tiopronin ligands). Thus, ligand as well as metal transfers occur in the contact between toluene phase C6 Au MPCs and tiopronin Ag MPCs. We believe this the first demonstration of concurrent, heterophase ligand exchanges and metal transfers in reactions between nanoparticles.

Homophase Metal Transfer from Tiopronin Au MPCs to Tiopronin Ag MPCs in the Water Phase. Tiopronin Au MPCs (0.01 mM) and tiopronin Ag MPCs (0.005 mM) were co-dissolved in water in the experiment shown in Figure 7. The initial spectra (taken separately) of the Au (Curve a) and Ag (Curve b) MPCs had, after 15 h in their mixture, changed to the spectrum of Curve c. The initial fluorescence of the tiopronin Ag MPCs has become undetectable and only that characteristic of a tiopronin Au MPC appears. The obvious conclusion is that Au atoms have replaced the Ag atoms initially on the tiopronin Ag MPCs surface, just as was the case in the experiment in Figure 4a. This experiment was exposed to the air, and we anticipate that, again, dioxygen supplied the oxidizing equivalents and Ag(I) is produced.

Mechanism of Ligand and Metal Exchange Reactions. The preceding results are summarized in Table 2. Significant findings are (a) the strong influence of the presence of dioxygen on the heterophase transfer of ligands from one nanoparticle to another and on the heterophase transfer of Au atoms from Au MPCs to Ag MPCs, (b) the acceleration of heterophase Au atom transfer from C6 Au MPC^{3+} relative to uncharged C6 Au MPCs, and (c) the homophase transfer of Au from Au MPCs to Ag MPCs in the presence of air. The influence of oxidizing conditions (O_2, MPC^{3+}) is believed especially significant. In earlier[4c] organic phase studies of ligand exchange between as-prepared

Table 2. Summary of Ligand and Metal Exchange Reactions

reactants			products	
MPC (solvent A)	MPC (solvent B)	conditions	solvent A	solvent B
C6 Au MPCs (toluene, 0.1 mM)	tiopronin Au MPCs (H_2O, 0.01 mM)	air	tiopronin ligand found	−SC6 ligand found
		N_2	no tiopronin ligand found	no −SC6 ligand found
		N_2 w/Au(I)-SR	tiopronin ligand found	-SC6 ligand found
C6 Au MPCs (toluene, 0.1 mM)	tiopronin Ag MPCs (H_2O, 0.005 mM)	air	trace Ag(I) found, tiopronin ligand found	Au found, tiop-Ag MPC SP band gone, tiop-Au MPC fluorescence appears
		N_2	no tiopronin ligand found	tiop-Ag MPC fluorescence remains, no tiop-Au MPCfluorescence
		N_2 w/Au(I)-SR	tiopronin ligand found	Au found, tiop-Au fluorescence appears
positively charged C6 Au MPCs (toluene, 0.1 mM)	tiopronin Ag MPCs (H_2O, 0.005 mM)	air	Ag found, tiopronin ligand found	tiop-Ag SP band gone, tiop-Au fluorescence appears, reaction accelerated compared to uncharged C6 MPCs
tiopronin Au MPCs (H_2O, 0.01 mM)	tiopronin Ag MPCs (H_2O, 0.005 mM)	air	tiop-Ag fluorescence gone tiop-Au fluorescence remains	

alkanethiolate-coated Au MPCs and labeled thiols, we showed that, relative to reaction under N_2, the presence of O_2 accelerates the exchange of −SC6OH ligands for the MPC's original −SC6 ligands.

The present results strongly suggest that the formation of soluble, oxidized gold species must be considered for a full understanding of ligand and metal exchange reactions of MPCs. Au(I) thiolate (Au(I)SR) has in fact been previously suggested to be involved in elevated temperature thiol-etching of Au nanoparticles[5] at elevated temperature, and in size-focusing annealing reactions.[6] To provide more definitive evidence of the involvement of soluble Au complexes, some of the above reactions were conducted under N_2 and with an added Au(I)SR complex. The complex used is $Au^I[SCH_2(C_6H_4)C(CH_3)_3]$, which Shon et al.[3] showed was galvanically reactive toward dodecanethiolate-coated Ag MPCs, replacing some Ag atoms with Au atoms to form bimetal MPCs. The result of one reaction is summarized in Table 2,top. A catalytic concentration (0.1 μM) of $Au^I[SCH_2(C_6H_4)C(CH_3)_3]$ was added to N_2-blanketed, day-long reactions of C6 Au MPCs in toluene (5 mL, 0.1 mM) with tiopronin Au MPCs (5 mL aqueous, 0.01 mM). Another reaction is also shown in Table 2, middle, where the Au(I)SR complex was added to a N_2-blanketed mixture of C6 Au MPCs with tiopronin Ag MPCs (5 mL, 0.005 mM). When these reactions had been conducted (vide supra and Table 2) under N_2, no exchange occurred. In the presence of the Au(I)SR catalyst, however (Table 2), the products were as though O_2 had been admitted to the reaction; tiopronin ligands were found (Cu^{2+} induced aggregation, FTIR, fluorescence) on the C6 Au MPCs in toluene, and fluorescence characteristic of tiopronin Au MPCs was seen from the water-soluble, formerly all-Ag tiopronin MPCs. In the first of the above experiments in which Au(I)SR is added, it clearly acts as a catalyst for ligand exchange. In the second, it additionally must act as a source of oxidizing equivalents.

To further support the hypothesis that a Au(I)SR complex can act as a catalyst in ligand exchange reactions, we repeated a previous ligand exchange[4c] of −SC6OH ligands for −SC6 ligands on Au MPCs (2:3 mole ratio of −SC6OH and −SC6). Under N_2 (Table 3), few (6) −SC6OH ligands were incorporated into the Au MPC monolayer, whereas under air, 23 were place exchanged. Adding 10^{-6} to 10^{-3} M concentrations of $Au^I[SCH_2(C_6H_4)C(CH_3)_3]$ caused substantial exchange to take place, even under N_2 (Table 3, italics). The quantities exchanged after 1 h were ascertained by quenching the reaction by acetonitrile addition (precipitating the MPCs), thoroughly washing the products, and decomposing the MPC monolayers to disulfides (with I_2) for analysis by ^{1}H NMR. The quantities of −SC6OH ligands introduced increased with the dilute Au(I)SR up to the same number (27) as observed in the presence of air or when the C6 Au MPC had been positively charged prior to the reaction. This number is thought[4c] to represent that of the more readily exchanged Au sites on core vertexes and edges.

Table 3. Extent of Ligand Place Exchange[a] between HSC6OH Thiol and −SC6 Ligands on C6 Au MPCs in THF Depends on the Presence of Air, Positive C6 Au MPC Core Charging, and Presence of Catalytic Amounts of Au(I)SR, Where SR = $-SCH_2(C_6H_4)C(CH_3)_3$

reaction medium	additives	no. ligands exchanged[b] MPC	no. ligands exchanged[b] MPC^{1+}	ref
THF, air		23	27	4c
THF, N_2		6	26	4c
THF, N_2[b]	Au(I)-SR, 10^{-6} M	8		this work
THF, N_2	Au(I)-SR, 10^{-5} M	17		this work
THF, N_2	Au(I)-SR, 10^{-4} M	27		this work
THF, N_2	Au(I)-SR, 10^{-3} M	27		this work

[a] The incoming thiol (HSC6OH) was in 0.15 mM concentration and in 2:3 mole ratio to the initial −SC6 thiolate ligands (hexanethiolate) on C6 Au MPCs, 1 h reaction time. [b] no resonances of the $-SCH_2(C_6H_4)C(CH_3)_3$ ligand of the Au(I)SR catalyst, even when it was used at 1 mM concentration, was detected in the exchange products. Its exchange into the C6 Au MPC monolayer is evidently inhibited, relative to −SC6OH, by the bulkiness of the $-SCH_2(C_6H_4)C(CH_3)_3$ ligand.

On the basis of the preceding experimental observations, a general mechanism is proposed for ligand exchange and metal transfer reactions (Figure 8). Under oxidizing (O_2[4c] or positively

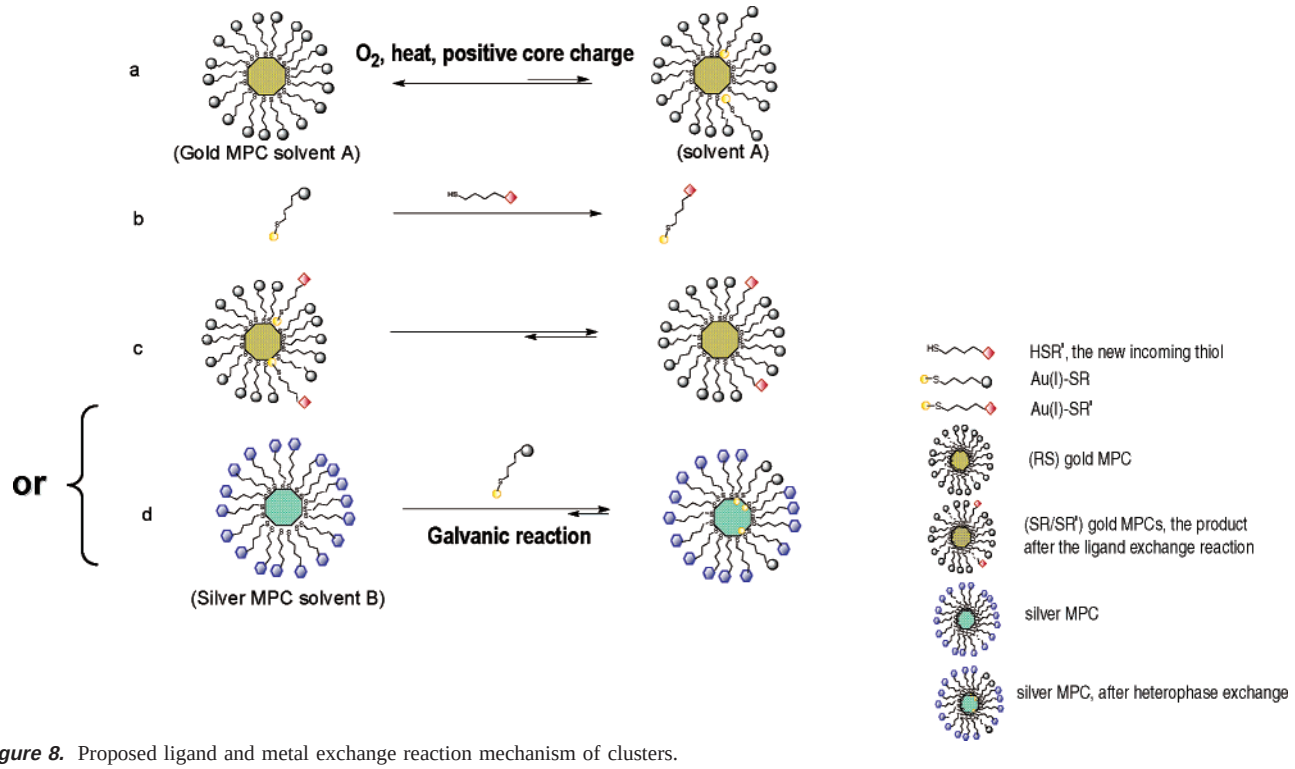

Figure 8. Proposed ligand and metal exchange reaction mechanism of clusters.

charged core[4c]) or thermally forcing[5] conditions, equilibria between the MPC and dissociated Au(I)thiolate complexes are established in which the Au(I)thiolate moiety becomes either loosely or fully dissociated (Reaction a). The number of Au(I) and thiolate ligands per complex is unknown, but Au(I) complexes are expected to be substitution-labile, so the ligands of dissociated Au(I)thiolate complexes should be exchangeable with an alternative thiolate.[4a,4c] That is, the Au(I)thiolate ligands can exchange (reaction b) with any thiols present in the solution (such as Au(I)SC6 with HSC6OH, Table 3). Consequently, upon reassociation of the Au(I)thiolate moiety with the MPC (Reaction c), new ligands (e.g., −SC6OH) become introduced into the Au MPC monolayer. This process is, in effect, a dissociative mechanism for ligand place exchange, which must function in parallel with the much slower associative one[4c] that is dominant when the reaction is conducted under N_2 and non-oxidizing conditions.

The above situation differs from an earlier homophase study[7] in which ligand exchange occurred between ligand-capped Au (or Ag) nanoparticles and naked Ag (or Au) nanoparticles, and was interpreted as *direct heterocolloidal particle interaction*. Our interpretation is based on the Au(I)SR mechanism.

When the reaction involves heterophase transfer of ligands between different Au MPCs (such as between C6 Au MPCs and tiopronin Au MPCs, Figure 2), Au(I)SR complexes dissociated from them can exchange ligands (Reaction b). We do not know whether Au(I)SR ligand exchange occurs at the phase boundary or is extractive, i.e., involving partition of Au(I)SR complexes from one phase to another; the former is more likely given the poor solubility of Au(I)SC6 in water. Again, reassociation (Reaction c) consummates the ligand transfer. In any event, Au(I)SR again acts as a catalyst for exchange.

When the reaction is heterophase between C6 Au MPC and tiopronin Ag MPCs (Figure 4), two kinds of exchange reactions happen—heterophase ligand exchange (i.e., tiopronin ligand transferred from water to toluene) and heterophase metal transfer (i.e., gold atoms transferred onto water-soluble tiopronin MPCs). The heterophase metal transfer happens when the Au(I)SR complexes dissociated from the MPC in the organic phase provide oxidizing equivalents for a redox reaction with the Ag MPC cores in the aqueous phase, replacing the Ag atoms with Au ones (Reaction d), and generating a Ag(I) product in equimolar amount. The reverse cannot (thermodynamically) occur, owing to the different redox potentials of Au and Ag. Most of the Ag remains in the aqueous phase, as Ag^{I}.

When the reaction is homophase between tiopronin Au MPC and tiopronin Ag MPCs, the Au(I)SR complexes dissociated from the former again will react galvanically with the Ag cores, displacing them as Ag(I) and covering the residual Ag core with Au atoms to produce tiopronin Au MPC-like fluorescence (Figure 6). The overall reaction is driven by oxidizing equivalents from dioxygen.

The Figure 8 scheme serves to explain all of the ligand and metal exchange reaction data obtained in our studies, including previously unexplained aspects of ligand exchange kinetic studies.[28] As presented, the scheme is qualitative, and is desirably buttressed by more quantitative kinetics. The ligand exchange process is in particular implicated to contain both associative and dissociative pathways (depending on oxidizing conditions needed for the latter case), and the kinetics of ligand exchange appear to vary widely among the surface sites on the MPC core.[4c]

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(28) This refers to un-explained intercepts in the kinetic plots in ref 4c.