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# COVALENTLY NETWORKED MONOLAYER PROTECTED NANOPARTICLE FILMS

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## Abstract

Covalently networked films of nanoparticles can be assembled on various substrates from functionalized monolayer protected clusters (MPCs) via ester coupling reactions.  Exposure of a specifically modified substrate to alternating solutions of 11-mercaptoundecanoic acid exchanged and 11-mercaptoundecanol exchanged MPCs, in the presence of ester coupling reagents, 1-3-dicyclohexyl-carbodiimide and 4-dimethylaminopyridine, results in the formation of a multilayer film with ester bridges between individual nanoparticles.  These films can be grown in a controlled manner to various thicknesses and exhibit certain properties that are consistent with films having other types of interparticle connectivity, including chemical vapor response behavior and quantized double layer charging.  Ester coupling of MPCs into assembled films is a straight forward and highly versatile approach that results in robust films that can endure harsher chemical environments than other types of films.  The stability of these covalent films is assessed and compared to other more traditional MPC film assemblies.

*Keywords: monolayer protected clusters, ester coupling, vapor sensing, nanoparticle films, covalent network*

**Introduction**

Research continues to expose the many characteristics and potential applications of nanoparticles. Specific nanoparticles called monolayer protected clusters (MPCs) have, in recent years, seen a great deal of attention due to their unique size-dependent properties and highly functional design – a metallic core surrounded with a peripheral layer of protective alkanethiols.[1,2] These colloidal gold nanoparticles are known to exhibit exceptional stability, resistance to aggregation, and superior handling properties, including being easily dissolved and recollected from solvent.[1] Additionally, MPCs can be functionalized via simple place exchange reactions that can incorporate various ω-substituted alkanethiols into the self-assembled monolayer surrounding their core (see Scheme I).[3] This type of manipulation has facilitated the exploration of nanoparticle films and the methods of connecting MPCs into controlled assemblies with specific architecture.

Films of MPCs have been formed based on non-specific interparticle interactions as well as more elaborate networking schemes. Non-specific, dropcast films have been investigated by Murray and coworkers[4] for electron transfer (ET) studies and have also been exploited by Wohltjen[5] and Evans[6] as chemical sensors. More elaborately connected nanoparticle films, including hydrogen bonded[7] and dithiol-linked systems,[7-9] have also been studied as chemically sensitive interfaces. Films linked with dithiol ligands represent some of the most stable nanoparticle films, exhibiting multiple linkages from each individual nanoparticle. Most work with

dithiol-linked MPC films is aimed at the immobilization of a single adlayer of MPCs

to a substrate[10-11] or the creation of a thick film via a one step exchange-cross linking-

precipitation reaction.[7-8] While extremely stable, these films lack a significant degree

of control over film thickness during growth,[12] as evidenced by the ~ 100 nm thick

film formed by Murray et al. after a single exposure to the dithiol/MPC deposition

solution.[13] A significant amount of research has also been dedicated to MPCs

networked into films via carboxylate–metal ion–carboxylate electrostatic bridges.[14-16]

Researchers in Murray's group and others have had much success with such films,

controlling their growth,[17-18] and exploring their potential as both ET model systems[19-21]

and chemical vapor sensors.[18,22]

In terms of their use as chemical sensors, current methods of MPC film

assembly exhibit certain disadvantages: poor adhesion to substrates (dropcast films),[5,6]

instability in certain chemical environments (electrostatically bridged,[14-16] hydrogen

bonded[7] and dropcast films[5,6]), difficult control over growth (dithiol linkages[7-12] and

dropcast films[5,6]), and/or extensive time requirements for growth (some electrostatic

bridged films).[14-16] Dropcast films immediately degrade with exposure to MPC-

friendly solvents, eventually losing adhesion to the substrate. Nanoparticle films

networked with carboxylate-metal ion-carboxylate linkages are also problematic,

despite their common usage.[14-21] Most notably, they are sensitive to high ionic strength

or low pH environments and can also require days to construct. Upon exposure to

solvents, metal ion linkers can be leeched out of this type of film[18] eventually altering

film connectivity and compromising film integrity.  Another complication with metal

ion–linked films is the solubility of the carboxylic acid exchanged MPCs in solution.

Their solubility in ethanol, a property intimately related to the number of carboxylic

acid moieties on the periphery of the MPCs, has been shown to be a vital part of

successful film growth.[18] Of interest would be a more versatile, relatively facile

method of nanoparticle film growth that is both highly controllable in terms of

thickness and results in a more robust film than those previously described.

   This paper describes a new method of covalently networking films of MPCs

through ester-coupling reactions.  Ester coupling has been used in the past to attach

ligands onto the periphery of MPCs but not as the primary interparticle linking

mechanism.[23] These covalently-linked films exhibit similar properties to the traditional

films described above, including ease of formation and controlled growth, but are also

shown to be much more robust when exposed to a range of chemical environments.


**Experimental**

   All solvents and reagents were used as received from the manufacturer.  As

reported by Goss *et al*.,[24] glass slides were cut (2.5 cm x 1.0cm) and submerged in

piranha solution (2:1 ratio of $H_2SO_4$ to 30% $H_2O_2$) for 15 minutes (piranha is

dangerous, handle with care).  Slides were then rinsed with copious amounts of

purified water. Clean glass slides were immersed in a heated mixture of

hydroxymethyltriethoxy silane (HMTES, Gelest), isopropanol, and purified water for

45 minutes. Slides were rinsed with propanol, dried with argon and cured in a 100ºC oven for 1 hour.

Gold substrates were hand polished with successively smaller alumina pastes down to 0.05 μm particles, rinsed with purified water, and electrochemically cleaned in $H_2SO_4$, until well-defined voltammetry was achieved. The substrates were rinsed with purified water and ethanol, and dipped in a 5mM ethanolic solution of 11-mercaptoundecanoic acid (MUA, Aldrich) or 11-mercaptoundecanol (MUD, Aldrich) for 24 hours.

Hexanethiolate-coated MPCs were created using a modified Brust synthesis[25] where tetraoctylammonium bromide is used to phase-exchange aqueous gold salt $HAuCl_4$ into toluene. Subsequently, a Au(I) polymer is formed through the addition of hexanethiol (C6) in a 3:1 thiol to gold mole ratio. Addition of $NaBH_4$ to the solution at 0ºC induces the formation of the MPCs with an average composition of $Au_{140}C6_{53}$ and an approximate core diameter of 1.6 nm[26] that were collected on a glass frit and subsequently rinsed with copious amounts of acetonitrile (MeCN).

Previously described place-exchange reactions[3] were carried out with the addition of either MUA or MUD to a solution of hexanethiolate MPCs in THF for ~ 72 hours. Samples were rotary evaporated and precipitated using MeCN, and subsequently recollected via filtration. Extensive cleaning of the material was performed to remove residual disulfides and thiols. The samples were washed thoroughly with massive amounts of MeCN (~ 400 mLs MeCN / 10 mgs of MPC).

After collection from the filter funnel, samples were repeatedly sonicated and decanted for five cycles with fresh MeCN before being dried under vacuum. The resulting MUA-modified and MUD-modified MPCs were then characterized with NMR, IR, and UV-VIS spectroscopy (see Supporting Material). The approximate peripheral composition of ligands surrounding the cores was determined from NMR analysis of the thiols and disulfides that are liberated upon oxidative decomposition of the nanoparticles with iodine.[26]

As shown in Scheme I, covalently networked MPC films were grown on modified gold substrates via ester coupling reactions derived from work by Steglich and Neises.[27] Briefly, a gold substrate modified with a MUA self-assembled monolayer (SAM) was immersed in a chilled solution of dichloromethane ($CH_2Cl_2$; 1 mg/mL) containing MUD-modified MPCs. Over five minutes, 3-4 mg of the ester coupling reagent 1,3-dicyclohexyl-carbodiimide (DCC) was added to the solution. The mixture was allowed to stir for one hour before the slide was removed, rinsed thoroughly with $CH_2Cl_2$ and dried under a stream of $N_2$. In most cases, the reaction was carried out in the presence of 2-3 mg of a catalyst, 4-dimethylaminopyridine (DMAP), to further promote ester formation between the carboxylic acid terminal groups of the MUA-SAM and the peripheral hydroxyl groups of the MUD-modified MPC (step 1, Scheme I).[28]

To achieve multilayer film growth, the substrate, with attached MUD-modified MPCs (exposed hydroxyl groups), was immersed in a solution of MUA-

modified MPCs and ester coupling reagents (DCC and DMAP) in the same manner as described above to promote inter-nanoparticle ester bond formation, effectively growing the film to a greater thickness (step 2, Scheme I). This process was repeated with alternating exposure of the substrate to MUD-modified and MUA-modified MPC solutions to create a multi-layer film covalently networked with ester coupled linkages (see Scheme II).

Films grown on glass slides for spectroscopic measurements were grown in a similar manner with the exception of the glass first being modified with hydroxymethyltriethoxy silane (HMTES), requiring the first MPC exposure to be with MUA-modified MPCs.

Interdigitated array (IDA) electrodes consisting of both glass and gold surfaces were modified sequentially, first as a glass (silanized) and then as a gold substrate (SAM modified with MUD or MUA).[22] Films with thicknesses estimated to be greater than the height of the IDA fingers were used for conductivity and chemical sensing measurements. As in previous reports,[4,22] DC conductivity measurements were performed using linear sweep voltammetry between ± 200 mV at a scan rate of 100 mV/sec to generate current-potential responses which could be translated into electronic conductivities.[29]

Film growth was monitored spectroscopically using a dual beam UV-VIS spectrophotometer (JASCO, V-560). Spectra were collected on films that, after an ester coupling dip cycle, were rinsed with copious amounts of $CH_2Cl_2$ via a squirt

bottle and immersed in pure solvent for several minutes before being dried in a stream

of nitrogen. A silanized glass slide was employed as a reference for gathering the

spectra. Evidence for the formation of interparticle ester coupling was supported with

both NMR (Bruker) and IR (Nicolet) results (see Supporting Information).

Differential pulse voltammetry was performed on a CH Instruments potentiostat using

a gold working electrode, platinum counter electrode and silver quasi-reference

electrode in argon-purged 0.1M tetrabutylammonium perchlorate solution in $CH_2Cl_2$.

**Results and Discussion**

      Ester coupling reactions are very versatile and are well known for forming an

ester bridge between amines or alcohols and ligands with carboxylic acid

functionality.[28,30] Ester coupling reactions have already been applied as a synthetic

strategy to attach molecules to MPCs,[23,31] including a variety of redox moieties.[32-33]

Here, we use ester coupling to tether nanoparticles to a substrate and subsequently

grow a covalently networked film of MPCs. Following established procedures[23,26, 30-33]

and applying them to our heterogeneous system, we are able to grow multi-layers of

MPCs by forming ester bonds acting as interparticle bridges (See Scheme I and II).

      Figure 1 tracks the growth of an ester coupled film on a glass slide using UV-

Vis spectroscopy. Overall, the spectra are typical of nanoparticle film comprised of

MPCs regardless of the linking mechanism within the film. In this case, as with

electrostatically-linked,[14-16,17-22] dithiol-linked,[8,9] and dropcast[5,6] MPC films, the observed

absorbance increases after each exposure to the MPC solutions, known as a dip cycle. As in previous studies,[17,18,22] the surface concentration of MPCs, a common measure of relative thickness, have been predicted from the absorbance at 300 nm.[34]  Individual absorbance increases with each dip cycle, when translated into film thickness, clearly indicating multi-layer growth rather than a layer-by-layer assembly.  Such growth, typical of other MPC assembled films,[17,18,22] is not surprising considering the MPCs have multiple functional groups per cluster that are capable of forming an ester linkage with additional MPCs during a single dip cycle.  Ester linkages under these conditions have been confirmed using ^{1}H NMR and IR. Both techniques show spectroscopic evidence supporting the formation of an ester after the reaction has been carried out, while the same ester based signals are absent prior to the coupling reaction (see Supporting Information).  The apparent multi-layer growth is at least partially enhanced in the spectra by additional non-specific interactions (i.e., hydrogen bonding) making contributions to the overall adsorption (discussed below).[7]

Figure 2 tracks film growth, or absorbance at 300 nm, and estimated film thickness over time with each exposure to the MPC solutions (alternating between MUA-MPC and MUD-MPC with each dip cycle).[35] The growth is sluggish at first and then abruptly increases after the fifth dip cycle.  This growth pattern is both repeatable and consistent with previous studies of MPC films utilizing different linking mechanisms.[17-22]  It is thought that initial, anchoring layers of MPC are required before substantial and consistent growth is possible.  The effect of adding the DMAP

catalyst is also shown (Figure 2) and clearly indicates a catalytic effect on promoting

ester coupling between nanoparticles.  Without catalyst, the reaction slows down

considerably and absorbance measurements show only a modest increase over time.[27]

When the procedure is run without either DCC or DMAP as a control some residual

growth due to non-specific interactions is observed.  In spite of strong evidence of

ester bond formation as the main film growth mechanism (see Supporting Materials),

two other types of linkages, intermolecular hydrogen bonding[7] and acid condensation

to anhydride[38] are also possible in these networks, albeit to a much lower degree.

Hydrogen bonding between MUA-MPCs and MUD-MPCs is cited for the small

observed growth without DCC or DMAP (see Figure 2).  Films grown under these

conditions disintegrated when immersed in a polar solvent, presumably due to the

disruption of the hydrogen bonding.  Likewise, films grown with excessive rinsing

with a polar solvent after each exposure to MPCs displayed a noticeably slower

growth rate (results not shown). On the other hand, films assembled with DCC and

DMAP exhibited spectral evidence of ester formation and were much more resilient

when exposed to the same environment.

  It is important to establish that these covalently networked films possess the

same characteristics and functional behavior as other, more traditionally-linked MPC

films.  One such property, quantized double layer (QDL) charging, is readily

observed with other assembled MPC films because of the nanoparticle's atto-farad

capacitance.[20-21]  Differential pulse voltammetry (DPV) applied to MPC films reveals

single electron transfers (SETs) in the form of sequential current peaks emanating

from MPCs in the film.  The peak spacing ($\Delta$V) of the charging peaks is indicative of

MPC core size, with smaller core sizes exhibiting larger peak spacing.  Likewise, the

potential (E) resulting in certain charged states of the MPCs adheres to the following

relationship:

$$E_p = E_{pzc} + Ze/C_{CLU} \qquad \text{Eqn. 1}$$

where $E_p$ is the peak potential of the core's charge transformation, $E_{pzc}$ is the potential

at zero charge, Z is the charged state of the MPC, e is the electronic charge, and $C_{CLU}$ is

cluster capacitance.  Thus, a plot of potential (E) versus cluster charge state (Z),

known as a "Z plot," yields a linear response where the slope can be used to

determine cluster capacitance.[39]

    Figure 3 shows the QDL charging behavior of the ester coupled films and the

slope from corresponding "z-plot" (inset) which is used to determine the average

capacitance of the MPCs comprising the film, as previously described.[20-21]  Individual

peaks are marked with the specific redox reaction taking place at the indicated

applied potential. Based on the peak spacing of the QDL charging for these covalent

attached films, the average capacitance of MPCs in the film is 0.59 ($\pm$0.02) aF,

corresponding to an average core diameter between 1.5 and 1.7 nm according to

literature reports.[39-40]  Electrochemical results are in agreement with other specifically

linked films, indicating that the ester coupled films are electronically connected and

composed of the same narrow distribution of stable MPC cores.  A dispersity of core

sizes within the film would have resulted in an averaged QDL charging signal with poorly resolved peaks, inconsistent peak spacing, and the appearance of peak shoulders/double apexes.[40]

By studying the electron transfer (ET) properties of MPC films using electronic conductivity ($\sigma_{EL}$) measurements, information about film structure and connectivity can be ascertained.[4,22] ET through these materials is believed to occur via an electron tunneling mechanism, indicated by a signature exponential decay in the conductivity over tunneling distance.[4] In the case of MPC films, this distance can be represented by the number of methylene units occupying the space between nanoparticle cores. The relationship between conductivity and distance has been defined by the following equation:[4]

$$\sigma_{EL}(n,T) = \sigma_o \exp[-n\beta_n]\exp[-E_a/RT] \qquad \text{Eqn. 2}$$

where n is the total number of carbons separating the cores, $\sigma_o$ is an infinite temperature electronic conductivity, $\beta_n$ is electronic coupling (decay factor), $E_a$ is the activation energy, R is the gas constant, and T is temperature. The decay factor is derived from the slope of an exponential plot of conductivity versus total carbons. The value of $\beta_n$ for ferrocene at a self-assembled monolayer (SAM) was determined to be 1.25 per carbon unit ($C^{-1}$), establishing a benchmark for electron tunneling through an adlayer of ordered, trans-staggered, alkane chains.[41]

Conductivity through MPC assemblies can be measured by constructing a film across the fingers of an interdigitated array (IDA) electrode and measuring the current

that flows when a voltage is applied.[4,22]  Using this technique, Murray and coworkers were able to determine decay factors ($\beta_n$) of 1.2 $C^{-1}$ and 0.7 $C^{-1}$ for dropcast MPC films composed of $Au_{309}(C_n)_{92}$ and $Au_{140}(C_n)_{53}$, respectively.[4]  These values are consistent with the films being almost fully intercalated and, when the radial nature of the MPC structure is taken into account, agree nicely with the $\beta_n$ for SAMs.[41]  In a similar study,[22] MPC films linked with carboxylate-metal ion-carboxyate electrostatic bridges and having sequentially varied chain lengths of linker (acid terminated thiolates) and non-linker (hexanethiolates) ligands were formed on IDAs.  If ET occurred through the electrostatic bridge, conductivity would be sensitive to changes in the length of those linker ligands.  The results of the study, however, showed that the film was much more responsive to changes in the length of the *non-linker* ligand, exhibiting exponential distance dependence and a $\beta_n$ ~0.8 $C^{-1}$ as the chainlength of that ligand was systematically altered.  These results support that the MPCs remain almost completely intercalated in a compact and collapsed film structure.

It was hypothesized that the ester coupled linkage may make the films rigid with a more open architecture.  If MPCs in the ester coupled films were networked into a stiffer format dictated by the length of the acid and alcohol ligands involved in ester coupling, the conductivity of such films would be highly dependent on the chain lengths of those ligands.  Three different films were grown on IDA electrodes, each designed to have a significantly different number of methylene units involved in the ester linkage: (1) mercaptohexanol (MHOL) with mercatoundecanoic acid (MUA),

(2) mercaptoundecanol (MUD) with MUA, and (3) MUA with mercaptohexadecanoic acid (MHDA).  Each combination yields 16, 21, and 26 methylene units involved in the ester bridge, respectively.  With a difference of 5 methylene units in the linking bridge for each film, a substantial drop in conductivity was expected.  The overall magnitude of the measured conductivity values, summarized in Figure 4, is consistent with prior reports on metal linked films where the MPC ligands are almost completely interdigitated.  The observed differences in the electronic conductivity of the three systems (Figure 4), however, are minimal with only a small degree of exponential dependence through the ester coupled bridge observed.  The calculated $\beta_n$ of ~0.11 C[-1] is very low and strongly suggests that the predominant electron transfer pathway does not transverse the ester coupling bridge – a result that is consistent with these films, like the electrostatic films in previous studies,[4,22] being collapsed and not held in a significantly more rigid fashion due to the ester bonded links.[42]

   An important feature of our covalently-linked MPC films is that they maintain the functionality demonstrated with earlier MPC films, especially for use as chemiresistive sensors.  Previous MPC films used in this capacity exhibited a substantial drop in electronic conductivity ($\sigma_{EL}$) when exposed to a variety of chemical vapors and solvents, a phenomenon attributed to the sorption of the vapor/liquid and subsequent swelling of the film that results in an increase in electron tunneling distance which, in turn, causes a decrease in conductivity.[18,22]  These covalently networked films behave likewise, showing similar results to chemical vapors ranging

in degrees of polarity (Figure 5).   These results are achieved with covalently

networked films that, unlike the metal linked films, are essentially void of the same

levels of metal ions and are therefore not susceptible to problematic ion migration

that stunts growth and eventually degrades film structure (see below) as metal leeches

from the metal-linked system.[18]

Ester coupled films are expected to be much more stable in certain chemical

environments then their non-covalently networked counterparts.  Stability

experiments were performed on the covalent films and compared directly to both

dropcast and electrostatically bridged MPC films (Table 1).  UV-Vis spectroscopy

was performed on MPC films with three different linking mechanisms: nonspecific

drop cast films, electrostatic metal-carboxylic acid-linked films, and covalently

networked ester coupled films.  Each type of film was constructed on a glass slide and

initial, starting spectra were recorded.  Individual films were then exposed to a

specific chemical environment, including immersion in solvent or exposure to a

specific pH, for 15 minutes with agitation.  After drying the films, spectra were again

collected and compared directly to measurements before exposure.  Any degradation

in the film, meaning a loss of MPC material from the film due to the chemical

environment, would be indicated by a decrease in absorbance.  Several representative

spectra are provided in Figure 6 and the collective results of the stability experiments

are summarized in Table 1.  The response of each film to the specific environments

was the same regardless of whether it was the film's first exposure or if it had experienced other chemical conditions prior to that exposure.

Certain environments in the stability experiments showed substantial effects on the films, with > 90% degradation shown in bold in Table 1.  As expected, drop cast films were somewhat stable toward more polar solvents and the entire pH range but experienced almost total destruction when exposed to more non-polar solvents in which the nanoparticles were soluble (Fig. 6A).  On the other hand, metal-linked films were extremely stable toward all solvents tested (Fig. 6B) but showed extreme degradation in acidic environments capable of protonating the carboxylic acids linkers (Fig. 6C).   By comparison, the ester coupled films were more stable under all the experimental conditions and did not suffer significant degradation in any case – emphasizing their higher stability in both non-polar solvents (Fig. 6D, bottom two spectra) and acidic environments (Fig. 6D, top two spectra), conditions that were clearly weaknesses of the other, more traditional, films.[43] Thus, the new ester coupled films described are more resilient under all the chemical conditions tested.

**Conclusions**

We have reported an alternative linking method that can attach MPCs to substrates and to other MPCs through a covalent network of ester bonds. Heterogeneous ester coupling reactions using DCC and DMAP as a coupling reagent

and catalyst, respectively, were used to form linkages between MPCs with carboxylic acid ligands and MPCs with hydroxyl terminated ligands. The interparticle ester bridge formed by the reaction was verified spectroscopically and the film's collective properties were examined and compared to other MPC films. This covalently networked film of MPCs represents one of the more stable and versatile iterations of assembled nanoparticle films as these materials maintain their unique properties and functionality even after being networked through ester coupling reactions. In addition to their ability to withstand low pH conditions which broadens their potential applications, the overall versatility of these films is derived from several other factors as well. The films presented here can be grown with relative ease and offer a high degree of control over film thickness as well as superior stability in certain chemical environments compared to other assembled nanoparticle films. Electrostatic carboxylate-metal linked films have only been grown from ethanol solutions,[17-22] meaning that nanoparticles not soluble in that solvent, including both under-exchanged and over-exchanged MUA-MPCs, are useless for the purpose of film assembly. In light of this problem, significant care is required during exchange reactions to keep the MUA-MPCs soluble in ethanol. In contrast, the covalent linkage is less sensitive to the ethanol solubility of the exchanged MPCs. The presented method of assembly through ester coupling enables the use of more MPC-friendly chlorinated solvents (e.g., $CH_2Cl_2$) for film growth, a significant advantage and simplification over other techniques. The versatility of the ester coupled films

also stems from the facile nature of the ester coupling reaction itself which allows for

multi-functional MPCs to be linked together into films.  This option is useful for

novel applications where the properties of the MPC film are augmented with an

additional functionality (e.g., ionophore, fluorophore, biospecific ligands).[44-45]  For

example, MPCs bearing crown ether moieties have been recently explored by our

laboratory[46] and others[47] as materials with potential for metal ion sensing in solution.

Such an application clearly benefits from both the simplicity of the coupling reaction,

allowing MPCs with linking and sensing ligands to be easily incorporated into films,

and from the inherent pH resistance of the covalent film, a useful property for

operation in liquid environments where one might want to detect metal ions.  Similar

covalently linked films can be envisioned using amide coupling as well.[23]  It is our

hope that ester coupled MPC films will lend themselves to a variety of novel

nanoparticle film sensing applications, including continued vapor innovations,[5-7,18,22]

metal ion detection,[46-47] biosensor research.[48]

**Supplemental Materials**

NMR and IR spectroscopic evidence of ester linkages established with spectra taken before and after the coupling reaction. UV-Vis spectroscopy, transmission electron microscopy images and differential pulse voltammetry used to characterize core size and properties of the C6-MPC starting material.

**References**

1. Templeton, A.C.; Wuelfing, W.P.; and Murray, R.W. *Acc. Chem. Res.*, **2000**, *33*, 27; and references therein.

2. Feldheim, D.L.; and Foss, C.A Eds. *Metal Nanoparticles – Synthesis, Characterization, and Applications*, Marcel Dekker, Inc.: New York, 2000; and references therein.

3.  Hostetler, M.J.; Templeton, A.C.; and R.W. Murray, R.W.  *Langmuir*, **1999**, *15*, 3782.

4.  Wuelfing, W P.; Green, S.J.; Pietron, J.J.; Cliffel, D.E., Murray, R.W. *J. Am. Chem. Soc.* **2000**, *122*, 11465.

5.  Wohltjen, H.; and Snow, A.W.  *Anal. Chem.*  **1998**, *70*, 2856.

6.  Evans, S.D.; Johnson, S.R.; Cheng, Y.L.; Shen, T. *J. Mater. Chem.* **2000**, *10*, 183.

7.  Han, L.; Daniel, D.R.; Maye, M.M.; Zhong,C.-J.  *Anal. Chem.*,**2001**, *73*, 4441.

8.  Leibowitz, F.L.; Zheng, W.; Maye, M.M.; Zhong, C.-J. *Anal. Chem.* **1999**, *71*, 5076.

9.  Brust, M.; Blass, P.M.; Bard, A.J. *Langmuir* **1997**, *13*, 5602.

10. Chen, S.  *J. Phys. Chem. B* **2000**, *104*(4), 663-667.

11. Chen, S. and Murray, R.W. *J. Phys. Chem. B* **1999**, *103*, 9996-10000.

12. Branham, M. and Murray, R.W., unpublished results and correspondence.

13. Brennan, J.L.; Branham, M.R.; Hicks, J.F.; Osisek, A.J.; Donkers, R.L.; Georganopoulou, D.G.; and Murray, R.W. *Anal. Chem.* **2004**, *76*, 5611-5619.

14. Zamborini, F.P.; Hicks, J.F.; and Murray, R.W.  *J. Am. Chem. Soc.*, **2000**, *122*, 4514.

15. Templeton, A.C.; Zamborini, F.P.; Wuelfing,W.P.; and Murray, R.W. *Langmuir* **2000**, *16*, 6682.

16. Demsar, A.;  Kosmrlj, J.; Petricek, S. *J. Am. Chem. Soc.* **2002**, *124*(15), 3951.

17. Sheibley, D.; Tognarelli, D.J.; Szymanik, R.; Leopold, M.C. *J. Mater. Chem.* **2005**, *15*, 491.

18. Leopold, M.C.; Donkers, R.L.; Georganopoulou, D.; Fisher, M.; F.P. Zamborini, F.P.; and Murray, R.W. *Faraday Discuss.* **2004**, *125*, 63.

19. Zamborini, F.P.; Smart, L.A.; Leopold, M.C.; and Murray, R.W. *Analytica Chimica Acta* **2003**, *496*, 3.

20. Hicks, J.F.;  Zamborini, F.P.; Murray, R.W.  *J. Phys. Chem. B* **2002**, *106*, 7751.

21. Hicks, J.F.; Zamborini, F.P.; Osisek, A.J.; and Murray, R.W. *J. Am. Chem. Soc.*, **2001**, *123*, 7048.

22. Zamborini, F.P.; Leopold, M.C.;  Hicks, J.F.;  Kulesza, P.J.;  Malik, M.A.; and Murray, R.W.; *J. Am. Chem. Soc.*, **2002**, *124*, 8958.

23. Templeton, A.C.; Hostetler, M.J.; Warmoth, E.K.; Chen, S.; Hartshorn, C.M.; Krishnamurthy, V.M.; Forbes, M.D.E.; Murray, R.W. *J. Am. Chem. Soc.* **1998**, *120*, 4845.

24. Goss, C.A.;. Charych, D.H.; and Majda, M.; *Anal. Chem.*, **1991**, *63*, 85.

25. Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D.J.; and Kiely, C.  *J. Am. Chem. Soc. Commun.* **1995**, 1655.

26. Hostetler, M.J.; Wingate, J.E.l Zhong C-J.; Harris, J.E.; Vachet, R.W.; Clark, M.R.; Londono, D.J.; Green, S.J.; Stokes, J.J.; Wignall, G.D.; Glish, G.L.; Porter, M.D.; Evans, N.D.; Murray, R.W. *Langmuir*, **1998**, *14*, 17-30.

27. Neises, B.; Steglich, W. *Organic Synthesis*, **1984**, *63*, 183.

28. Moore, J.S.; Stupp, S.I. *Macromolecules*, **1990**, *23*, 65-70.

29. IDA electrodes posses 50 interdigitated gold fingers (4800 μm in length, 15 μm in width, 0.05 μm in height) spaced apart by 15μm gaps ($d_g$). Conductivity is determined by treating the IDA gaps as parallel plate capacitors, multiplying the measured resistance ($\Delta I/\Delta V$) from an I-V curve by the IDA cell constant ($d_g/A_{total}$).  Note that $A_{total} = A_{finger}(N-1)$, where N is the number of fingers, $A_{finger} = $ (length)(width) of the finger, and current passing from the top faces of the IDA is ignored.  The cell constant for these IDAs was determined to be 6.3 cm$^{-1}$.[4]

30. March, J. *Advanced Organic Synthesis*; Wiley: New York, 1985.

31. Shon, Y.-S.; Choo, H. *Chimie* **2003**, *6*, 1009.

32. Miles, D.T.; Murray, R.W. *Anal. Chem.* **2001**, *73*, 921.

33. Kennedy, K.G.; Miles, D.T. *J. of Undergraduate Chemistry Research* **2004**, *4*, 145.

34. Using the relationship Abs = 1000·ε·Γ and an estimate of molar absorbtivity (ε) at 300 nm of approximately $4 \times 10^5$ $M^{-1}cm^{-1}$, surface coverages (Γ) are calculated in nmol per square cm.[17,18,22]

35. Film thickness estimations were performed as in previous reports[4,22,36] using specific assumptions about the film structure and density.  Surface concentrations[34] were converted to an approximate number of monolayers ($\Gamma_{MONO}$ ≈ $1.4 \times 10^{-11}$ $mol/cm^2$) based on a hexagonal close packed model for $Au_{140}$ MPCs in a layered film[37] and taking into account the significant interdigitation (core edge to edge spacing) that was observed for similar C6 MPC films utilizing MUA linking mechanisms (~60%).[19] A single MPC monolayer is estimated at 3.26 nm in thickness.  The calculation was adjusted to accommodate the fact that the film grows on both sides of the glass slide.

36. Wuelfing, W.P.; Zamborini, F.P.; Templeton, A.C.; Wen, X.; Yoon, H.; and Murray, R.W.  *Chem. Mater.* **2001**, *13*, 87-95.

37. Templeton, A.C.; Cliffel, D.E., and Murray, R.W. *J. Am. Chem. Soc.* **1999**, *121*, 7081-7089.

38. Ihre, H.; Padilla De Jesus, O.L.; Frechet, M.J. *J. Am. Chem. Soc.* **2001**, *123*, 5908.

39. Chen, S.; Murray, R.W., Feldberg, S.W. *J. Phys. Chem. B*, **1998,** *102*, 9898-9907.

40. Miles, D.T.; Leopold, M.C.; Murray, R.W. *J. Electroanal. Chem.* **2003**, *554-555*, 87-97.

41. (a) Smalley, J.F.; Feldberg, S.W.; Chidsey, C.E.D.; Linford, M.R.; Newton, M.D.; Liu, Y.-P. *J. Am. Chem. Soc.* **1995**, *117*, 1. (b) Curtiss, L.a.; Naleway, C.A.; Miller, J. *J. Phys. Chem.* **1993**, *97*, 4050.

42. The slight decreasing trend in conductivity observed with an increase in the chainlengths of the ester coupled components is attributed to the simple addition of insulating material to the system. While some of the longer chain ligands will ester-couple, those not undergoing the reaction remain incorporated in the film, adding additional material to the periphery of the core and resulting in a probable decrease in electronic conductivity.

43. Stability results on the films were independent of film thickness. A thicker film and a substantially thinner film are used in Fig. 5D for illustrative purposes, but both results consistently observed regardless of thickness. It is noteworthy to point out that the absence of a strong surface plasmon band for the ester coupled films may imply that these films are less flexible or not as intercalated as other types of films, although such a difference is not observed to affect the film's behavior during vapor sorption.[22]

44. Aguila, A.; Murray, R.W. *Langmuir* **2000**, *16*(14), 5949-5954.

45. Niemeyer, M., *Angew. Chem. Int. Ed.* **2001**, *40*, 4128-4158; and references therein.

46. Pompano, R.R.; Russell, L.E.; Wortley, P.G.; Moatz, L.M.; Tognarelli, D.J.; Kittredge, K.W.; and Leopold, M.C., manuscript in preparation.

47. (a) Lin, S-Y; Liu, S-W.; Lin, C-M.; and Chen, C. *Anal. Chem.* **2002**, *74*, 330-335. (b) Lin, S-Y.; Chen, C.; Lin, M-C., and Hsu, H-F., *Anal. Chem.* **2005**, *77*(15), 4821-4828.

48. Kapourales, S.; Loftus, A.; Kidd, C.; Bredahl, C.; Leopold, M.C., manuscript in preparation.

**Captions**

**Figure 1.** UV-Vis spectroscopy tracking the growth of a covalently linked MPC film after exposure to alternating solutions of MUD-MPC (- - -) and MUA-MPC

( — ) in the presence of ester coupling reagents (DCC and DMAP).  Surface concentration of MPCs are estimated on the y axis as previously shown.[33]

**Figure 2.**  Representative UV-Vis spectroscopy monitoring film growth, absorbance at 300 nm, and estimated thickness[35] on glass slides during ester coupling reactions.  A dip cycle refers to sequential exposure of the slide to MUA-MPC and MUD-MPC solutions.  Reaction progress is tracked in the presence of ester coupling and catalytic reagents (●), the absence of both reagents (▲), and when the reaction is run without catalyst (♦).

**Figure 3.**  Differential pulse voltammtery showing cathodic quantized double layer (QDL) charging peaks of a covalently networked MUA/MUD MPC film immersed in a solution of $CH_2Cl_2$ with 0.1 M tetrabutyl ammonium perchlorate as a supporting electrolyte.  Each peak represents a change in the charge state of the MPC cores comprising the films as they undergo single electron oxidation or reduction.  Inset: The slope of the corresponding "Z-plot," based on the peak spacing ($\Delta V$) of the QDL signal, is used to determine the average capacitance of the nanoparticles in the films.

**Figure 4.**  Plot of electronic conductivity ($\log \sigma_{EL}$) versus the average MPC core separation in terms of the number of methylene units in the ester coupled bridge. The beta value for the ester coupled systems was calculated from the slope of the curve and determined to be only 0.11 C,[1] only a very slight exponential

dependence on distance.  Based on this result, ET within the film should occur through non-bonded interactions between nanoparticles, mean that the ester coupled films are intercalated and the film density is most likely not very different from other assembled MPC films.

**Figure 5** Linear sweep voltammetry (100 mV/sec) of a covalently networked MPC film in the presence of various chemical vapors (saturated).  As the film swells with solvent electron pathways are increased, thereby causing a decrease in conductivity ($\sigma_{EL}$) indicated by a lower slope on the potential-current responses shown.[29]

**Figure 6.**  UV-Vis spectra from stability experiments before (—) and after (----) exposure to chemical environments: (A) drop cast film exposed to $CH_2Cl_2$; (B) metal-linked film exposed to $CH_2Cl_2$; (C) metal-linked films exposed to acidic pH conditions and; (D) ester-coupled films exposed to $CH_2Cl_2$(x) or acidic pH conditions (●).

**Table 1.  Stability Results for Nanoparticle Films in Various Chemical Environments:  Percent Degradation Based on UV-Vis Spectroscopy** [a]

| Nanoparticle Film | Dropcast (non-specific) | Metal-Linked (electrostatic) | Ester Coupled (covalent) |
|---|---|---|---|

| Solvents: | | | |
|---|---|---|---|
| Toluene | **92** (1.0) | < 1 (0.3) | 4 (2.3) |
| Tetrahydrofuran | **92** (1.5) | < 1 (0.4) | 3 (1.8) |
| Dichloromethane | **94** (0.8) | < 1 (0.7) | 2 (0.1) |
| Acetone | 8 (1.9) | < 1 (0.7) | < 1 (0.1) |
| Ethanol | 2 (1.0) | 1 (0.8) | 2 (0.9) |
| **Acidity:** [b] | | | |
| pH range ~ 3-4 | 4 (0.5) | **97** (0.4) | 3 (3.1) |
| pH range ~ 7-8 | 2 (0.2) | 3 (3.0) | 4 (2.6) |
| pH range ~10-11 | 14 (4.4) | 2 (1.3) | 7 (1.4) |

[a] Based on absorbance at 350 nm; standard error shown in parentheses are the result of multiple films being tested in each case; variations in measurements due to positioning and repositioning of the film in the spectrometer were observed up to 3% meaning degradations of 3% or lower are essentially indicating no change in the film.

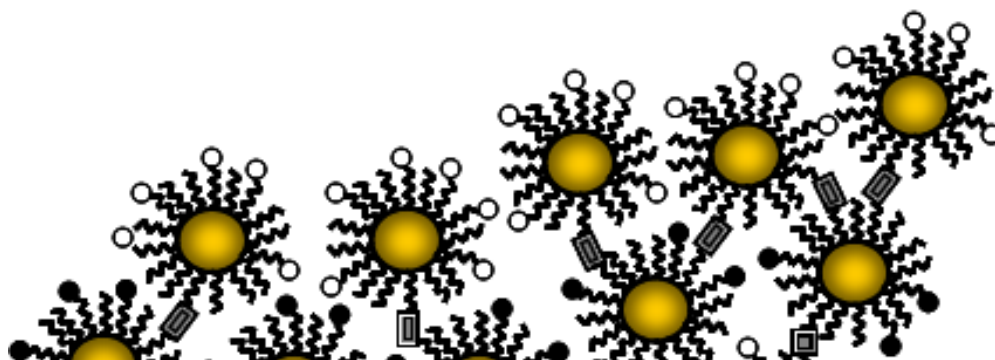[b] Acidity experiments conducted in pH adjusted ethanol solutions.
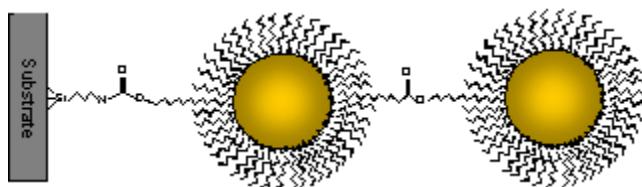
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**KEY**

○ Mercaptoundecanoic acid

● Mercaptoundecanol

▨ Ester-coupled linkage

Note: Steps **2** & **3** repeated for multi-layer films to desired thickness

MUA modified Au substrate
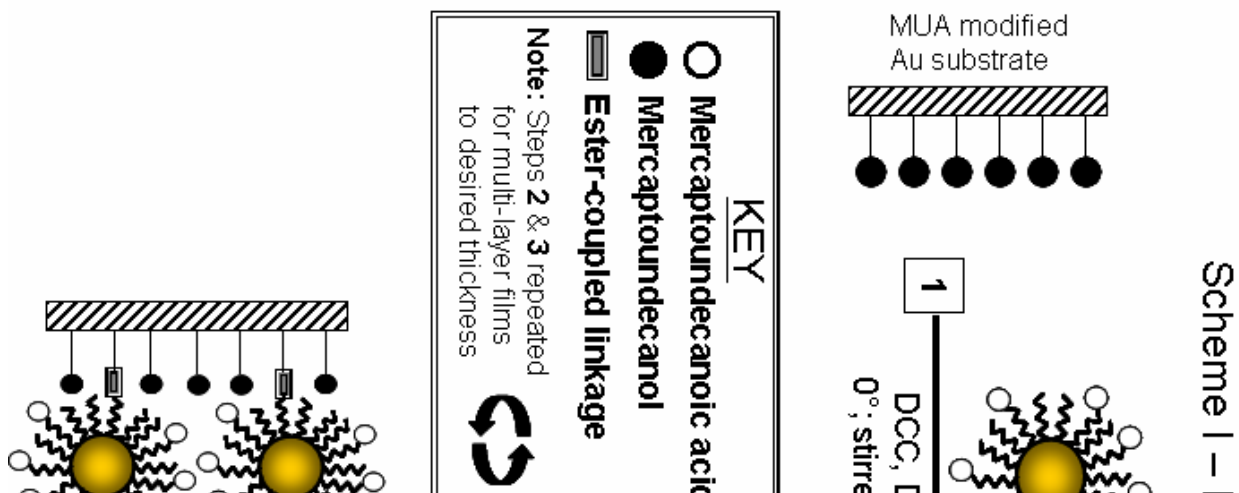
Scheme I –

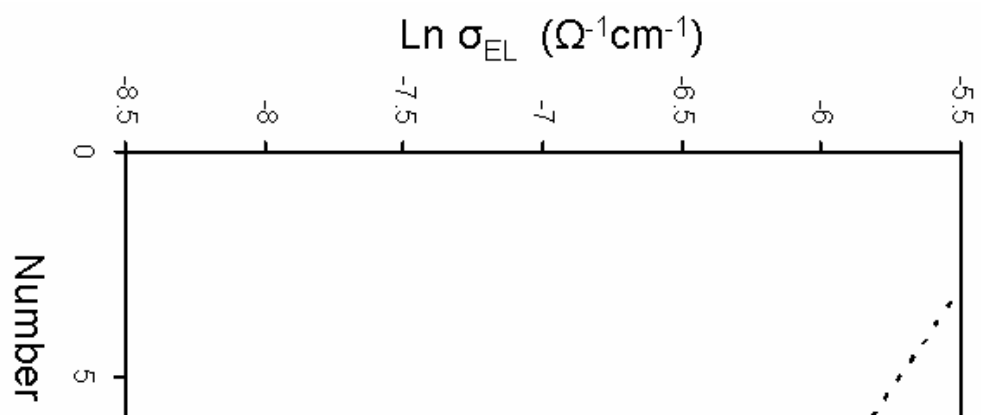**Scheme II.** Multilayer Ester-linked Film

Figure 1



Absorbance at 300 nm

Films grown wi...
Film grown wit...
Film grown wit...

Figure 2.

Figure 3.



$Ln\ \sigma_{EL}\ (\Omega^{-1}cm^{-1})$

Number

Figure 4.

Figure 5.



Dropcast films / CH₂

Metal-linked films / pl

Absorbance

Absorbance

Figure 6.