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ELECTRON HOPPING CONDUCTIVITY AND VAPOR SENSING PROPERTIES OF FLEXIBLE NETWORK POLYMER FILMS OF METAL NANOPARTICLES

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ABSTRACT

Films of monolayer protected Au clusters (MPCs) with mixed alkanethiolate and ω-carboxylate alkanethiolate monolayers, linked together in a network polymer by carboxylate-Cu^{2+}-carboxylate bridges, exhibit electronic conductivities (σ_{EL}) that vary both with the numbers of methylene segments in the ligands and with the bathing medium (N_2, liquid or vapor). A chainlength dependent swelling/contraction of the film's internal structure is shown to account for changes in σ_{EL}. The linker chains appear to have sufficient flexibility to collapse and fold with varied degrees of film swelling or dryness. Conductivity is most influenced (exponentially dependent) by the chainlength of the non-linker (alkanethiolate) ligands – a result consistent with electron tunneling through the alkanethiolate chains and non-bonded contacts between those chains on individual, adjacent MPCs. The σ_{EL} results concur with the behavior of UV-Vis surface plasmon adsorption bands, which are enhanced for short non-linker ligands and when the films are dry. The film conductivities respond to exposure to organic vapors, decreasing in electronic conductivity and increasing in mass (quartz crystal microgravimetry, QCM). In the presence of organic vapor, the flexible network of linked nanoparticles allows for a swelling-induced alteration in either length or chemical nature of electron tunneling pathways, or both.

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INTRODUCTION

Substantial interest exists in the electronic properties of nanometer-scale materials—carbon nanotubes, fullerenes, conjugated molecular "wires", semiconductor nanoparticles, nanowires, clusters, and clusters of clusters—with respect both to their fundamental importance and to possible applications in molecular and nanoelectronics. Synthesis, assembly, alignment, and inter-connection of such materials, as well as methods of measuring their electronic properties, are crucial facets of this growing field. Likewise valuable are systematic ways to alter the *i*R electronic properties, including exploiting them for chemical sensing applications.

This paper reports on the electronic conductivity properties of network polymer films of Au$_{140}$ nanoparticles. The nanoparticles are coated with mixed monolayers of alkanethiolate (*non-linker ligands*) and ω-carboxyalkanethiolate (*linker ligands*) and are linked together by carboxylate-Cu^{2+}-carboxylate coordinative couplings. Scheme 1 shows the different combinations of methylene chainlengths used as linker and non-linker ligands, and the metal ion linking chemistry. We find that the nanoparticle film electronic conductivities are sensitive to both ligand chainlengths and the medium (liquid or vapor) bathing the films. The sensitivity is interpreted to reflect the inherent flexibility of the linker ligand structures and consequent solvent swelling of the network film. In air dried films, the linker ligand structures seem substantially folded and electron hopping between the Au$_{140}$ cores of the nanoparticles can be demonstrated to occur by non-bonded contacts of non-linker ligands. Solvation and swelling of the network polymer film upon contact by an organic liquid or vapor degrades these contacts and diminishes the film's electronic conductivity. The effect is reversible, which suggests a potentiality of these nanoparticle network polymers for chemical vapor sensing.

The gold nanoparticles employed are referred to as monolayer protected clusters (MPCs), a notation is continued here to emphasize the stabilizing aspect of the thiolate

ligand shells. Electronic communication between the metal-like MPC cores occurs by electron hopping (self exchange), with the intervening monolayer coatings serving as tunneling bridges. This electronic communication has been investigated[11] via the electronic conductivities of cast, non-networked films of arylthiolate and of alkanethiolate-coated MPCs. In the latter case, using MPCs having reasonably monodisperse Au core sizes with observable quantized double layer charging properties,[12] the cast films could be prepared[13] with well-defined mixtures of different core electronic "charge states". The ensuing electronic conductivity shows that a) the electron hopping is a bimolecular process b) with an extremely fast rate constant that c) varies exponentially with the core-core spacing as anticipated[14] for an electron tunneling reaction. The large rate constants and small activation barriers are consistent with Marcus relationships,[11a] and in summary arise from the low dielectric medium surrounding the Au core reaction centers and the large size of those centers.

    We have also investigated the electronic communication between MPC cores in nanparticle polymer films in which their monolayers have been networked together.[16] An electrochemical investigation[16c] of Au_{140} nanoparticles having mixed monolayers of hexanethiolate and 11-mercaptoundecanoic acid linked by metal ion-carboxylate coordinative coupling, produced 10^6 s^{-1} nanoparticle-nanoparticle electron transfer rate constants. This rate of electron transfer seemed too large to be rationalized by electron tunneling through the very long $-SC10CO_2CuCO_2C10S-$ linker ligand bridges. These nanoparticle films were contacted by CH_2Cl_2/electrolyte solutions. The present results show that thermal motions of the linker bridges and of the nanoparticles within the solvent swollen linked network must have allowed electron tunneling to follow shorter reaction pathways, such as through the non-bonded $-SC6/C6S-$ contacts.

    Films of materials whose electronic conductivities vary with chemical environment—notably vapors—are classically called "chemiresistors".[17] Carbon particles[18] embedded in polymers are an important example. There have been several[19]

chemiresistor studies of MPC films.   MPCs, however, do not have a high thermal tolerance,[11a,15] meaning the use of elevated temperatures during film preparation is inadvisable.[15a]   MPC films with networked films are tolerant to immersion in liquids (that would otherwise solubilize their monomeric constituents) as well as to vapors.   There have been no prior studies of the mechanistic aspects of MPC film responses to organic vapors.

EXPERIMENTAL

Chemicals. All chemicals were reagent grade and used as received.

Synthesis and Preparation of Mixed Monolayer MPCs. Alkanethiolate monolayer-protected clusters (MPCs) were synthesized using a modified Brust reaction.[17]   Briefly, butanethiol (C4), hexanethiol (C6), octanethiol (C8), decanethiol (C10), or dodecanethiol (C12) were combined in toluene in a 3:1 mole ratio with $AuCl_4^-$ followed by a 10-fold excess of reductant ($NaBH_4$ in water) at 0 °C.   The MPC product was recovered from the stirred reaction mixture after 24 hrs by precipitation, filtering, and thorough washing with acetonitrile on a glass fritted Buchner funnel. We label this 28kDa product[18] as Cn MPC, where n is the number of carbons in the alkanethiolate chain.

Linker ligands (6-mercaptohexadecanoic acid ($HS(CH_2)_5CO_2H$, MHA), 11-mercaptoundecanoic acid ($HS(CH_2)_{10}CO_2H$, MUA), and 16-mercaptohexadecanoic acid ($HS(CH_2)_{15}CO_2H$, MHDA) were place-exchanged[11] for some of the *non-linker* Cn ligands in the initial MPC monolayer.   Stirring tetrahydrofuran (THF) solutions of MPC and linker ligand (in selected molar ratios) for *ca.* four days gave mixed monolayer MPCs that were collected and washed as above. The mole ratio of linker to non-linker thiolates was determined by NMR of solutions of the disulfides that were quantitatively liberated from the mixed monolayer MPCs upon decomposition with iodine.[12]

Based on transmission electron microscopy (TEM) and thermogravimetry as described previously,[18] the Cn MPCs have *average* core diameters of 1.6±0.8 nm and $Au_{140}(Cn)_{53}$ composition.   The MPCs with mixed monolayers containing MUA have (by

NMR) the *average* composition $Au_{140}(Cn)_{53}(MUA)_{20}$. The compositions are averages in that a dispersion of Au core sizes exists (as determined by TEM). Additionally, some dispersity in the Cn/MUA ligand ratio is statistically expected within the overall MPC population.

Formation and Electronic Conductivities of Network MPC Films. Solid-state electronic conductivity measurements were made on nanoparticle network polymer films attached to interdigitated array electrodes (IDAs, Microsensor Systems, Inc). The IDAs consist of 50 interdigitated Au fingers (4800 μm long, 15 μm wide, 0.1 μm high) deposited on glass and separated by 15 μm gaps (d_o). The Au fingers are treated as parallel plate electrodes of total area[11a] $A_{TOTAL} = A_{FINGER}(N-1) = 4.8 \times 10^{-6}$ cm^2, where N=50 and A_{Finger} is finger length*height. The IDA geometric cell constant [d_o/A_{TOTAL}] is 6.3 cm^{-1}. The areas of the top faces of the IDA fingers are ignored since very little current is probably passed between these faces and the area comprising the ends of each finger is considered negligible. Wire leads were attached to the IDA contact pads with Ag epoxy (cured 48 hr, 100 ºC), which was insulated with an over-layer of torr-seal epoxy (cured 10 hr, 100 ºC). The IDA was cleaned in boiling toluene (10-15 min), rinsed with acetone and ethanol and dried under N_2.

The IDAs were chemically treated with the goal of attaching an initial MPC layer to both the Au fingers and SiO_2 gaps, to promote uniform MPC film growth. A layer of 3-mercaptopropyltrimethoxy silane (MPTMS)[20] was attached to the glass gap surface by exposing the IDA to 100 μL of MPTMS in 10 mL isopropanol (plus 2-3 drops deionized water) and heating to near boiling for 30 min. The IDA was rinsed with ethanol, dried under a N_2 stream, and heated at 100º C for 5-10 min. The IDA was again ethanol rinsed and its Au fingers derivatized by exposure to 2 mM mercaptoundecanoic acid (MUA) in ethanol (15 min), forming a COOH-terminated self-assembled monolayer (SAM).[21] Scheme 2 shows a cartoon of the thusly-treated IDA finger and gap surfaces.

The films were assembled using previously described copper(II)-carboxylate coordination, for example as follows for $Au_{140}(Cn)_{33}(MUA)_{20}$ MPCs where n = 4, 6, 8, 10, or 12 (see Scheme 1): The treated IDA was serially exposed to 0.1 M $Cu(ClO_4)_2 \bullet 6H_2O$ in ethanol (10 min), rinsed with ethanol, exposed to 1-2 mg/ml MPC in ethanol (30 min), rinsed with ethanol, and then dried under N_2. This protocol, a "dip cycle," deposits several monolayers of MPC. Additional dip cycles serve to build up the network film thickness. A similar procedure was employed to form Cn films possessing linker ligands of mercaptohexanoic acid (MHA) and mercaptohexadecanoic acid (MHDA).

The quantity of MPCs deposited on the IDAs was monitored spectrophotometrically at 520 nm (ATI Unicam spectrometer) using glass slides that had been subjected to an identical series of dip cycles, continuing them until the slide's absorbance A = 0.8 ± 0.2. Using a constant MPC surface coverage ensures that variations in conductivity due to different populations of electron hopping centers between the IDA fingers are minimized. Based on $\varepsilon_{Au140} \approx 4 \times 10^5$ $M^{-1}cm^{-1}$ A = 0.8 corresponds to an MPC surface coverage of 2.1×10^{-9} $mole/cm^2$ or *ca*. 140 monolayers of MPC at 1.5×10^{-11} $mole/cm^2$ for a cubic lattice-packed MPC monolayer. The physical thicknesses of the MPC films is less readily monitored; we estimate film thicknesses ranging from 0.2 to 2 μm depending on the non-linker chainlength and various assumptions about swelling and chain interdigitation.[11,23] These estimated thicknesses all exceed the 0.1 μm IDA finger height.

MPC film conductivity, $\sigma_{EL} = d_G \Delta i / A_{TOTAL} \Delta E$, was obtained from the slope $\Delta i / \Delta E$ (in the linear response range, ± 200 mV) of current-potential responses to ± 1.0V potential sweeps (100 mV/s, PAR Model 273 potentiostat). Changes in film conductivity (200 mV potential bias, Model CHI 660A Electrochemical Workstation, CH-Instruments) upon exposure to ethanol vapor were measured by alternately exposing the IDA to dry N_2 and to N_2/ethanol vapor mixtures (using flow rate controllers) ranging from 0 to 100% room

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temperature partial pressures.

Quartz Crystal Microbalance. The vapor phase partition of ethanol into MPC network films was assessed by weighing the films using quartz crystal microbalance (QCM) methods. MUA self-assembled monolayers were deposited on the 1.13 cm^2 gold films on polished 5 MHz AT cut crystals (Maxtek, Inc.) and MPC films were deposited on them using the IDA procedure. The crystals were mounted in the same flow cell as used for the conductivity measurements and alternately exposed to dry N$_2$ and ethanol vapors as above. QCM frequency changes were measured using a home-built instrument and a HP 53131A Universal Counter interfaced to a PC with Labview 4.0 software. The Sauerbrey equation with integral sensitivity, $C_F = 56.6$ Hz cm^2 μg^{-1}, was used to relate frequency changes to mass changes.

RESULTS & DISCUSSION

The nanoparticle films in this study were prepared from 1.6 nm (avg.) dia. Au MPCs containing mixed monolayers (Scheme 1) of alkanethiolates [S(CH$_2$)$_n$CH$_3$] and carboxylic acid terminated alkanethiolates [S(CH$_2$)$_n$COOH]. We have previously described both the assembly of the network films, using coordinative carboxylate/Cu^{2+}/carboxylate bridges, and the two anchoring chemistries (see Scheme 2) grafting the films onto the Au finger and silica gap parts of the IDAs. Repeated "dipping cycles" were employed to deposit network nanoparticle films so that they contained--according to their optical absorbances (see Experimental)--roughly equal surface coverages of MPCs. Eliminating film thickness effects permits a focus on how the monolayer architecture of the MPCs and their network linking chemistry influence the dynamics of MPC core-to-core electron hopping. The electronic conductivity of the nanoparticle films occurs by electron hopping between MPC cores, which as discussed above occurs by tunneling reactions through the intervening monolayer structures.

If a network polymer film of C6/MUA MPC nanoparticles (see Scheme 1) on an IDA is exposed to an ion-free bathing environment, such as air or a pure non-ionic

solvent, smooth current-potential responses (Figure 1) result from applying a potential bias between the IDA fingers. These responses reflect electronic conductivity supported by electron hopping (Scheme 2). The absence of hysterisis in the I-V response shows that there is no significant mass transport of ions internal to the nanoparticle films and no electrolytic double layer charging at the film/IDA electrode interfaces, at least on these experimental timescales.

It is obvious from Figure 1 that the network nanoparticle polymer film's electronic conductivity (σ_{EL} is the slope of the current-potential curve near its origin, see figure legend for values) varies strongly with the nature of the bathing medium. The conductivity--which is proportional to the rate of electron hopping--is large when the film is exposed to ambient laboratory air, but drops by over 10-fold when the film is immersed in various organic solvents. The responses shown were stable to repeated potential sweeping, and the nanoparticle film could be repeatedly immersed in pure solvent and air dried without noticeable degradation of the σ_{EL} response in either solvent or air. The inference of the variations in conductivity with bathing medium is that either the length or chemical nature (or both) of electron tunneling pathways can vary with partition from the bathing medium into the nanoparticle film.

That changes in nanoparticle separation distances accompany changes in bathing medium is qualitatively supported by electronic spectra of a C4/MUA nanoparticle film deposited on glass (Figure 2). It is well-known that the ca. 520 nm surface plasmon absorption band of Au particles is enhanced and red-shifted when the particles become aggregated or otherwise pushed closer together. We have, for example, noticed that the normally barely detectable plasmon band of dissolved Au_{140} nanoparticles becomes readily observable when the MPCs are assembled (and thus concentrated) into a network polymer film. Figure 2 shows that the plasmon band of the C4/MUA MPC film is more prominent in air relative to that in CH_2Cl_2 solvent. The film conductivities of Figure 1 fall in a similar order, being largest in air and smallest in CH_2Cl_2 solvent. It is plausible

from this comparison that variations in nanoparticle spacing are provoked by partitioning of organic solvent into the film, swelling it. Swelling is especially expected in CH_2Cl_2 vapor since the nanoparticles are quite soluble in liquid CH_2Cl_2.   Conversely, drying the film causes collapse to a more concentrated MPC structure.

While conductivity change with solvent swelling might be interpreted as simply reflecting changes in electron tunneling distances, the factors that control the rate of electron hopping are likely to be much more complex.   For example, the network of ligands linking the film together is probably more dis-ordered than ordered, so that electron tunneling occurs over a distribution of pathways and core-core distances. For conductivity measurements to be taken, however, the aggregate population of electron tunneling pathways must lie above a percolation threshold. Additionally the thermal motions of nanoparticle sites about equilibrium positions in solvent-swollen polymers may vary substantially with local, solvent-influenced microscopic viscosity. It follows then that nanoparticle film swelling will not necessarily alter conductivity on simply distance-related grounds.

Changes in Electron Hopping Rates in Dry Films with Ligand Chainlength

(σ_{EL}). The relation of monolayer structure to air-dry nanoparticle network polymer film conductivity was explored by varying the lengths of the methylene chain segments of both linker and non-linker ligands. Figure 3 shows conductivity results for air-dried nanoparticle films of MPCs having various non-linker chainlengths (C4/MUA, C6/MUA, C8/MUA, C10/MUA, and C12/MUA, see Scheme 1). Figure 3 is an important result, showing that large changes in conductivity, and thus electron hopping rates, can occur in films in which the linker ligand structure is *constant*. Clearly, and as was speculated in our previous report, the linker ligand is not the primary electron tunneling pathway in the network polymer. Instead, we see that the efficacy of electron hopping (tunneling) varies by nearly 10^3-fold with the chainlength of the *non*-linker ligand, and is largest for the shortest non-linker ligand. The conductivity measurements are summarized in Table

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The Figure 3 conductivity results are consistent with the behavior of the surface plasmon absorbance shown in Figure 4.   The collective resonance effect of increasing MPC core proximity is greatest for the shortest non-linker ligand chainlengths. The collective band at 550 nm is also more pronounced when the film is in air rather than in a solvent (Figure 2), as discussed above.   In contrast, the spectra of all these MPCs dissolved in solution are substantially featureless, as reported before.[16]

Experiments where the non-linker methylene chainlength was held constant at C4 and that of the linker ligand was varied over C5, C10, and C15 are shown in Figure 5. These films are coded in the results as C4/MHA, C4/MUA, and C4/MHDA, respectively. The conductivities of these films decrease in the order given (Table 1), with the C4/MHA film being much more conductive than the others. The difference in conductivity between the C4/MUA and C4/MHDA is much less than that which might be expected were tunneling to occur *solely* through the linker chains.

We attempted to construct a similar series of nanoparticle films in which the linker ligand chainlength was long and that of the non-linker ligand was varied. Films with short non-linker ligands (C4/MHDA and C6/MHDA) exhibited large σ_{EL}, consistent with the preceding. However, reliable deposition of films with non-linker ligands containing $\geq$ 8 methylene units proved to be difficult, and results with such films were compromised owing to variations in nanoparticle film thicknesses.

Demonstration of Electron Tunneling in Dry Films. The principle signature of an electron transfer that occurs by a tunneling mechanism is an exponential dependency of its rate on the distance of tunneling (or the number of methylene units in a chain that serves as tunneling bridge). Figure 3 showed (see above) that the chainlength of the non-linker ligands on the MPCs has a major effect on the network polymer film's electronic conductivity. Figure 6 displays the conductivities from Figure 3 as an exponential plot, which is obviously respectably linear. This result is conclusive, showing that electron

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transfers in dry films occur by tunneling through non-bonded contacts between the *non-linker* chains. The obvious inference is that the longer, structurally flexible, linker ligand is a less effective tunneling bridge, and is folded or coiled to allow the non-bonded non-linker contacts.

The slope of the Figure 6 tunneling plot is the product of the electronic coupling factor (β) and the tunneling dimension (measured as either distance or number of methylene units). The actual tunneling dimension is unfortunately uncertain, since alkanethiolate ligands on MPCs are known both experimentally[a] and from theory[a] to interdigitate with the ligands of adjacent MPCs, to nearly their full length. There is consequent uncertainty in assessing β from the slope of Figure 6, since tunneling distance depends on the packing arrangement of the non-bonded ligands in the films. Interdigitation also appears to occur for the dry, network nanoparticle films. If Figure 5 were interpreted on the basis of electron transfer between methyl-methyl non-bonded tunneling contacts (i.e., 2n units in the overall bridge), one obtains a $\beta = 0.4$ C^{-1}, which is an unrealistically small value. If full non-linker chain interdigitation were assumed, a value of 0.8 C^{-1} is obtained that is close to previous results from research on well-ordered self-assembled monolayers.[1,27,28] Thus, not only does tunneling in dry Cn/MUA network films occur predominantly through the non-linker ligands, the structural folding of the linker chains allows the non-linkers to engage in the van der Waals interactions that promote chain interdigitation to some undetermined extent.   This latter result is somewhat surprising, as it implies that the network of bonding connections between linker ligands on adjacent MPCs is not only flexible but quite sparse. That is, only a fraction of the approximately 20 carboxylate sites on each MPC may actually be engaged in bonding together the polymeric network.[29]

The linker chains are however not completely lacking control over the electron hopping dynamics, as seen in Figure 4.   Long linker chainlengths yield similar

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conductivities, but a short linker (e.g., C4/MHA, Scheme 1) provides substantially higher conductivity.   Whether this corresponds to a more extensive interdigitation of the non-linker C4 chains, or to a more orderly packing with a higher density of MPC-MPC contacts, is unclear.

Response to Vapor Exposure.   It is obvious from the preceding results that the networked nanoparticle films have possibilities for analytical measurements of organic vapor concentrations, i.e., vapor sensing. Others[11] have also seen this possibility and reported results for different kinds of nanoparticle films. An initial report by Wohltjen and Snow[12a] examined the vapor response sensitivity, in terms of changing film resistance, of octanethiol modified gold nanoparticle films dropcast onto IDA electrodes (and unfortunately treated at temperatures conducive to MPC monolayer decomposition) and exposed to a variety of different solvent vapors. Evans and coworkers[13] investigated the vapor sensing capabilities of films comprised of nanoparticles stabilized with small, aromatic organothiol derivatives with a variety of substituted endgroups. While the focus of their study was to look at the role of functional groups in particle-particle interactions, they also explored each type of film's sensing potential by bathing them in different types of vapor. Core size effects were the focus of a QCM/$\sigma_{El.}$ based vapor sensing study by Zhong and coworkers[14] utilizing nanoparticles linked with dithiols or hydrogen bonding between carboxylic acid terminated alkanethiols.

The network MPC films investigated here are chemically linked to the electrode contacts and each other.   Their responses to exposure to vapors of ethanol or CH_2Cl_2 and nitrogen are rapid, stable, and reversible decreases in film conductivity, and increases in mass (by quartz crystal microgravimetry, QCM).   Figure 7 shows an illustrative set of results for ethanol vapors taken from a more extensive study. (The results of this study will be presented as a separate report[15].)   Figure 7A shows changes in the electronic conductivity of a C6/MUA MPC film on an IDA in response to exposure to pure N_2 and ethanol vapor of successively increased partial pressure.   The current changes are

measured using a constant potential bias (0.2 V). Figure 7B shows QCM results obtained in the same experiment and in the same flow cell housing the IDA, for a C6/MUA MPC film deposited on a gold covered quartz resonator. Assuming that the Sauerbrey relation is applicable for these experiments (see footnote Table 2), the decrease in QCM frequency corresponds to a proportionate increase in film mass, as ethanol partitions into the nanoparticle network polymer film.   In both sets of results, incremental increases of ethanol partial pressure provoke similarly incremental changes in conductivity and mass of the C6/MUA MPC film.   The data of Figure 7 were preceded by a preconditioning of the film by repeated, alternating exposure to ethanol vapor and N_2, which improves the film's response reversibility and response time.

Results for the response of network polymer films containing several different combinations of non-linker and linker chainlength to saturated ethanol vapor are summarized in Table 2.   The vapor-induced conductivity changes vary with film structure, and the response time (90% of final response) for current is generally faster than that for mass. The pervasive aspect of the results shown is that changes in conductivity are accompanied by changes in mass; i.e., film swelling leads to diminished rates of electron hopping.

REFERENCES

1. (a) Derycke, V.; Martel, R.; Appenzeller, J.; Avouris, Ph. *Nano Lett.* **2001**, *1*, 453-456. (b) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294*, 1317-1320. (c) Postma, H. W. C.; Teepen, T.; Yao, Z.; Grifoni, M.; Dekker, C. *Science* **2001**, *293*, 76-79.

2. (a) Joachim, C; Gimzewski, J. K. *Chem. Phys. Lett.* **1997**, *265*, 353-357. (b) Ami, S.; Joachim, C. *Nanotechnology* **2001**, *12*, 44-52.

15

3. Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791-804.

4. (a) Kim, S. H.; Markovich, G.; Rezvani, S.; Choi, S. H.; Wang, K. L.; Heath, J. R. *Appl. Phys. Lett.* **1999**, *74*, 317-319. (b) Jiang, P.; Liu, Z.-F.; Cai, S.-M. *Surf. Sci.* **2001**, *486*, L507-L512.

5. (a) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851-853. (b) Kovtyukhova, N. I.; Martin, B. R.; Mbindyo, J. K. N.; Smith, P. A.; Razavi, B.; Mayer, T. S.; Mallouk, T. E. *J. Phys. Chem. B* **2001**, *105*, 8762-8769.

6. (a) Simon, U. *Adv. Mater.* **1998**, *10*, 1487-1492. (b) Sato, T.; Ahmed, H.; Brown, D.; Johnson, B. F. G. *J. Appl. Phys.* **1997**, *82*, 696-701. (c) Schmid, G.; Liu, Y.-P.; Schumann, M.; Raschke, T.; Radehaus, C. *Nano Lett.* **2001**, *1*, 405-407. (d) Schmid, G.; Hornyak, G. L. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 204-212.

7. Feldheim, D. L.; Keating, C. D. *Chem. Soc. Rev.* **1998**, *27*, 1-12.

8. Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541-548.

9. (a) Zamborini, F.P.; Hicks, J.F.; Murray, R.W. *J. Am. Chem. Soc.* **2000**, *122*, 4514-4515. (b) Wuelfing, W.P.; Zamborini, F.P.; Templeton, A.C.; Wen, X.; Yoon, H.; Murray, R.W. *Chem. Mater.* **2001**, *13*, 87-95. (c) Hicks, J.F.; Zamborini, F.P.; Osisek, A.J.; Murray, R.W. *J. Am. Chem. Soc.* **2001**, *123*, 7048-7053. (d) Templeton, A.C.; Zamborini, F.P.; Wuelfing, W.P.; Murray, R.W.. *Langmuir.* **2000**, *16*, 6682-6688.

10. (a) Hostetler, M. J.; Murray, R. W. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 42. (b) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.

11. (a) Wuelfing, W. P.; Green, S. J.; Pietron, J. J.; Cliffel, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 11465-11472. (b) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.-C.; Poon, C.-D.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson, C. S.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537-12548.

12. (a) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098. (b) Chen, S.; Murray, R. W.; Feldberg, S. W. *J. Phys. Chem. B* **1998**, *102*, 9898. (c) Hicks, J. F.; Templeton, A. C.; Chen, S.; Sheran, K. M.; Jasti, R.; Murray, R. W. *Anal. Chem.* **1999**, *71*, 3703.

13. Janata, J. *Principles of Chemical Sensors*, Plenum Press: New York, 1989.

14. Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595-2626.

15. (a) Wohltjen, H.; Snow, A. W. *Anal. Chem.* **1998**, *70*, 2856-2859. (b) Evans, S. D.; Johnson, S. R.; Cheng, Y. L.; Shen, T. *J. Mater. Chem.* **2000**, *10*, 183-188. (c) Han, L.; Daniel, D. R.; Maye, M. M.; Zhong, C.-J. *Anal. Chem.* **2001**, *73*, 4441-4449.

16. Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; 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.

17. Brust, M.; Fink, J.; Schiffrin, D. J.; Kiely, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1655-1656.

18. (a) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428. (b) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R. L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. *J. Am. Chem. Soc.* **1997**, *119*, 9279-9280.

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

20. Goss, C. A.; Charych, D. H.; Majda, M. *Anal. Chem.* **1991**, *63*, 85-88.

21. (a) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self Assembly*; Academic Press, Inc.: San Diego, 1991. (b) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533-1554.

22. The MPC concentrations slightly varied for different chainlengths depending on the

solubility of the MPC in ethanol. Generally, 40 mg was dissolved in 10 mL of ethanol and filtered through glass wool and a syringe filter to remove insoluble clusters. Another 10 mL of ethanol was added and the solution was split into two vials each containing 10 mL. One vial was used for depositing the MPC film onto an IDA and the second vial was used for deposition onto a similarly treated glass slide, which was used to monitor film growth by UV-Vis spectroscopy.

23. Luedtke, W. D.; Landman, U. *J. Phys. Chem. B* **1998**, *102*, 6566-6572.

24. Buttry, D.A.; Ward, M.D. *Chem. Rev.* **1992**, *92*, 1355-1379.

25. (a) Sosnoff, C. S.; Sullivan, M.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 13643. (b) Terrill, R. H.; Hutchinson, J. E.; Murray, R. W. *J. Phys. Chem. B* **1997**, *101*, 1535. (c) Ritchie, J. E.; Murray, R. W. *J. Am. Chem. Soc.* **2000**, *122*, 2964. (d) Dickinson, E.; Masui, H.; Williams, M. E.; Murray, R. W. *J. Phys. Chem. B* **1999**, *103*, 11028. (e) Masui, H.; Long, J. W.; Malik, J.; Murray, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 1997.

26. Quinten, M.; Kreibig, U. *Surf. Sci.* **1986**, *172*, 557-577.

27. Smalley, J. F.; Feldberg, S. W.; Chidsey, C. E. D.; Linford, M. R.; Newton, M. D.; Liu, Y.-P. *J. Phys. Chem.* **1995**, *99*, 13141.

28. (a) Slowinski, K.; Fong, H. K. Y.; Majda, M. *J. Am. Chem. Soc.* **1999**, *121*, 7257-7261. (b) Holmlin, R. E.; Haag, R.; Chabinyc, M. L.; Ismagilov, R. F.; Cohen, A. E.; Terfort, A.; Rampi, M. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **2001**, *123*, 5075-5085. (c) Wold, D. J.; Frisbie, C. D. *J. Am. Chem. Soc.* **2001**, *123*, 5549-5556.

29. There is no information available at present on the dependency of conductivity on number of carboxylate sites.

30. Kulesza, P. J.; Malik, M. A.; Leopold, M. C.; Hicks, J. F.; Zamborini, F. P.; Murray, R. W. Manuscript in preparation.

31. Grate, J.W. *Chem. Rev.* **2000**, *100*, 2627-2648.

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FIGURE CAPTIONS

Figure 1. I-V curves of a C6/MUA film in air (σ_{EL} 3.9 x 10^{-4} $\Omega^{-1}cm^{-1}$) and immersed in various liquids including: hexane (σ_{EL} 1.8 x 10^{-4} $\Omega^{-1}cm^{-1}$), acetone (σ_{EL} 1.3 x 10^{-4} $\Omega^{-1}cm^{-1}$), ethanol (σ_{EL} 1.1 x 10^{-4} $\Omega^{-1}cm^{-1}$), and dichloromethane (σ_{EL} 2.8 x 10^{-5} $\Omega^{-1}cm^{-1}$).

Figure 2. UV-Vis spectra of a C4/MUA MPC film on glass in various solvents. In air, the film shows a prominent SPR band at 550 nm. Immersing the film in organic solvents like acetone and CH_2Cl_2 red-shifts the band position and decreases the intensity of the band, due to film swelling. The SPR change is less apparent in a polar solvent like water since the film is fairly hydrophobic.

Figure 3. Current-potential responses (± 1.0V) of various Cn/MUA MPC films deposited onto IDA electrodes obtained in air at 100 mV/s. Higher slopes between ±200 mV are indicative of more conductive films. See Table 1 for the average results.

Figure 4. UV-Vis spectroscopy of Cn/MUA MPCs (dashed lines) in ethanol solution and (solid lines) assembled in films on glass slides using carboxylate-Cu^{2+}-carboxylate bridges. The spectra in solution are featureless, but the spectra of the films show an aggregation band near 550 nm for the shorter chainlengths presumably due to the close spacing of the gold cores. Spectra are offset for comparison (Abs. at 300 nm is 1.3 to 1.5 in all cases).

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Figure 5. Current-potential responses (± 1.0 V) of C4 MPC films attached by linkers of different chainlengths (MHA, MUA, MHDA) obtained in air at 100 mV/s. Higher slopes between ±200 mV are indicative of more conductive films.   See Table 1 for average results.

Figure 6. Plot of ln σ_{EL} for the C_n/MUA films vs. average Au MPC separation in terms of number of carbons (z). Depending on the packing arrangement within the film, z is shown as either **n (bold)** for full interdigitation or *2n (italics)* for no interdigitation, where n is the total number of carbons in the non-linker alkane chain. Beta values for the fully interdigitated film and the non-interdigitated film are 0.8/carbon and 0.4/carbon, respectively.

Figure 7. Upon application of a constant potential (-0.2 V) to an IDA electrode modified with an assembled C6/MUA MPC film, (A) current changes are monitored over time. Films were alternately exposed to pure nitrogen flow and successively increasing ethanol vapor. (B) Identical experiments were performed simultaneously on the same C6/MUA film formed on a QCM gold substrate. Ethanol vapor partial pressures were successively increased in a sequence of fractions, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 of the saturated ethanol vapor pressure (7.9 kPa). Baseline responses were recorded in the atmosphere of pure nitrogen purged through the flow system.

Table 1. Electronic Conductivities of Network Nanoparticle Films

Non-linker/linker ligand in MPC Monolayer	Electronic Conductivity, σ_{EL} ($\Omega^{-1}cm^{-1}$)
C4/MUA	2×10^{-4}
C6/MUA	7×10^{-5}
C8/MUA	9×10^{-6}
C10/MUA	2×10^{-6}
C12/MUA	5×10^{-7}
C4/MHA	5×10^{-3}
C4/MHDA	4×10^{-4}

[a] Average results for ≥ 1 films

[b] MHA ≡ mercaptohexanoic acid; MUA ≡ mercaptoundecanoic acid; MHDA ≡ mercaptohexadecanoic acid

Table 2. Response of Network Nanoparticle Films to Saturated (7.9 kPa) Ethanol Vapor

MPC Film	% Δi	−Δf (Hz)	Ethanol Absorbed (nmole)	Δi Response Time (sec)	QCM Response Time (sec)
C4/MUA	72	150	65	47	192
C6/MUA	75	156	68	8	-
C10/MUA	33	100	43	13	168
C4/MHA	51	na	na	9	na
C4/MHDA	83	na	na	7	na

Calculated from the Saurbrey equation, assuming absence of viscoeleastic effects. The change in volume upon partitioning of ethanol vapor is estimated to be ≤ 5%. Viscoelastic effects, expected to be negligible with these films at low vapor pressures, will be explored further in a subsequent report dedicated to vapor response.[30,31]
Obtained in a different flow cell.