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# CROWN ETHER-METAL “SANDWICHES” AS LINKING MECHANISMS IN ASSEMBLED NANOPARTICLE FILMS

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## Abstract

Crown ether ligands attached to monolayer protected clusters (MPCs) were assembled as films and the linking mechanism between the crown ether – metal ion – crown ether bridges between nanoparticles was examined. Thicker films exhibited a red shift in the absorbance maximum for the surface plasmon band which was attributed to the increasing aggregation and cross linking within the film. Quantized double layer charging peaks suggest that film growth is selective toward a specific core size or exchange rate, either of which affect the number of potential linking ligands in the periphery of the MPCs. Multi-layer growth of films was only achieved with metal ions capable of coordinating within the cavity of the 15-crown-5 ether. Our exchange reaction parameters are in stark contrast to other types of MPC film assemblies.

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Keywords: Nanoparticles, monolayer-protected cluster (MPC), crown-ether, metal ion coordination

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## Introduction

As the field of nanotechnology rapidly evolves, interest in the organized assembly of nano-scale structures into functional materials has intensified greatly.[1-5] Metallic nanoparticles continue to garner much attention in this area. To this end, the interconnection, alignment, and surface attachment of nanoparticles into organized architectures are important facets in their successful incorporation into nanoelectronics and/or the creation of macroscopic analytical devices that take advantage of the unique properties of nanoparticles.[6-8] In this vein, nanoparticles are becoming frequent targets for use as components in molecular machines as well as miniaturized and specialized sensors.[9-11]

First introduced by Brust and coworkers,[12] one of the more interesting nanoparticles being investigated in this field are metallic gold cores, several nanometers in diameter, passivated with a peripheral layer of alkanethiols. Due to their inherent stability, versatility, and ease of handling, these particular nanoparticles have attracted much attention and have been termed *Monolayer-Protected Clusters (MPCs)*.[13,14] Functionalized MPCs are created via simple place-exchange reactions,[15-17] where thiol ligands with terminal functional groups are incorporated into the peripheral skin of the MPCs. The success of MPC place-exchange reactions has promoted the exploration of thin films and organized assemblies of MPCs – materials of interest for fundamental electron transfer study through nanoparticles[18] and as innovative chemical sensors.[19-29]

Initial work with nanoparticle films focused on dropcast MPC films as a basis for chemiresistive sensing of chemical vapors. Wohltjen and Snow,[20] as well as Evans et al.,[19] showed the sensitivity of cast MPC films toward different concentrations of vapor by monitoring changes in the material's resistance (electronic conductivity). The well-supported mechanism proposed was that the film would swell in the presence of the organic vapor causing a subsequent increase in the core-to-core spacing within the film's

network. Taking advantage of the same phenomenon, Zellers and coworkers[21] employed MPC films as a novel gas chromatography (GC) detection material. Cast MPC films, however, are not well suited for organized assemblies; they are susceptible to degradation in liquids and lack sufficient selectivity to be sensors.[29]

More recently, the *organized self-assembly* of surface-anchored nanoparticle films with more complex architectures have been explored.[22,23,30,31] Zhong et al used both dithiol and hydrogen bonding interactions as means of interconnecting chemiresistive MPC films.[22] Likewise, Vossmeier and coworkers constructed nanoparticle-dendrimer composite films that are linked with amine chemistry, which perform well as a vapor sensing material.[23]

Carboxylic acid-modified MPCs can be tethered to substrates and used to build multi-layer MPC films networked with multiple carboxylic acid – metal ion (i.e.  $\text{Cu}^{2+}$ ) – carboxylic acid bridges.[30,31] Recent reports by Murray and coworkers[24,25] show an unprecedented understanding of the structure and electronic properties of these assembled films both as novel nanoparticle ensembles and potential chemical vapor sensors. Assembled films have excellent stability and exhibit several modes of vapor sensing including gravimetric (quartz crystal microbalance), optical (spectroscopic), and electronic (conductivity) signaling.[24,25] In spite of their superior stability, even in liquid environments limitations of these films include structural degradation at low pH and prohibitive electrochemical analysis when electroactive metal ion linkers are used (i.e.,  $\text{Cu}^{2+}$ ).

Crown ethers (CE) are well-known ionophores for metal ions and have often been targeted for connection to molecular scaffolds for the purpose of metal ion sensing materials.[32] Crown ethers are popular in this respect since they feature inherent sensor selectivity; a ring that is able to coordinate only very specifically sized ions. For

example, the 15-crown-5 moiety is known to reversibly coordinate to ions like  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ag}^+$ . [33]

Chen [34] reported the modification of large, colloidal nanoparticles with crown ether (15-crown-5) ligands to selectively bind or “sandwich” solution metal ions ( $\text{K}^+$  and  $\text{Na}^+$ ), stimulating both aggregation and a colorimetric indicator response. Again, coordination of a specific metal ion in a sandwich between neighboring nanoparticles causes the red solution to suddenly change to blue, an indication of the metal driven aggregation within the system. More recently, Chen also reported [35] the use of MPCs possessing both crown ethers and carboxylic acid functional groups. These bifunctionalized MPCs were successfully used to coordinate and detect  $\text{K}^+$  ions four orders of magnitude faster than MPCs with only CE functional groups. Chen used these systems to detect the presence of  $\text{K}^+$  and  $\text{Na}^+$  in human urine, a common use for metal ion sensors.

The crown ether interactions are capable of instigating significant core movement. An elegant illustration of this concept was presented by Mayes and coworkers [36] in a report where CE moieties were incorporated into nanoscopic rows of silver grains to create a holographic grating. Upon exposure to specific metal ions, the rows coordinate the metal and subsequently swell or contract depending on the interactions. As a result, reflectance spectra show a change upon exposure to certain metal ions.

In this paper, we utilize the coordinative selectivity of crown-ethers for specific metal ions to construct novel MPC film structures that selectively assemble and may be developed as metal ion sensing materials. Crown-ether monolayer-protected clusters (CE-MPCs) are tethered to a surface and formed into multilayer films through crown ether – metal ion – crown ether “sandwiches” that bridge adjacent MPCs. CE-MPC film characteristics and growth dynamics are examined. The CE-MPC assembled films utilize electrochemically inert metal ions to facilitate electrochemical analysis of the

nanoparticles comprising the films. Moreover, since the connectivity of these CE-MPC films revolves around chelation of a metal ion by two crown ether ionophores, they are generally more resilient toward acidic conditions when compared to the more traditional MPC films that feature more electrostatically sensitive carboxylic acid-metal ion-carboxylic acid linking bridges.[37] This work represents an initial study of potentially novel sensing materials that utilize the ionophoric capacity of crown-ethers. If successful in development as metal ion sensors, these nanomaterials are small enough to be considered for *in vivo* and remote sensing applications as well as portable measurement devices.

## Experimental and General Procedures

**Synthesis of Alkyl substituted 15-Crown-5 Thiol.** Thiol (**2**) was prepared in the route shown in **Scheme I**. Bromide (**1**) was prepared from 2-(hydroxymethyl)-15-crown-5 ether in a modified procedure of Lin *et al.*[34] The bromide (**1**) was converted into the thiol following the procedure of Kittredge and Fox.[38]

**Materials.** NaH (Aldrich, 60 % dispersion in mineral oil), 2-(hydroxymethyl)-15-crown-5 ether (Acros), 1,10-dibromodecane (Aldrich), tetrabutylammonium fluoride (Aldrich, 1.0 M in THF containing 5% water), hexamethyldisilathiane(Aldrich), and DMF (Acros) were used as received. THF was freshly distilled from a deep blue solution of sodium/benzophenone under Argon. All glassware was oven dried before use. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded at 300 MHz in CD<sub>2</sub>Cl<sub>2</sub> or at 250 MHz in CDCl<sub>3</sub> with Bruker instruments at the University of Richmond and Miami University, respectively. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Mass spectra were performed at the Mass Spectrometry and Proteomics Facility of Campus Chemical Instrument Center through the State of Ohio Mass Spectrometry Consortium.

**2-(10-Bromodecyloxymethyl)-15-crown-5 Ether (1).** NaH (0.42 g, 9.3 mmol) was mixed with 2-(hydroxymethyl)-15-crown-5 ether (1.0 g, 4 mmol) in DMF (15 mL) at room temperature for 30 min. 1,10-Dibromodecane (6 g, 20.7 mmol) was added and the reaction mixture was stirred overnight. The reaction was quenched with methanol (25 mL) and the solvent removed *in vacuo*. The product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed sequentially once each (100 mL) with water, 3 M NaOH, and again with water. The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent removed *in vacuo*. The oily residue was purified by column chromatography (SiO<sub>2</sub>, 1:1 hexane:ethyl acetate). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 1.21-1.43 (m, 8H), 1.45-1.61 (m, 8H), 3.30-3.45 (m, 6H), 3.49-3.85 (m, 19H). HRMS (*m/z*) calcd for C<sub>21</sub>H<sub>41</sub>BrO<sub>6</sub>: 468.2087. Found: 468.2091. Elemental analysis calcd for C<sub>21</sub>H<sub>41</sub>BrO<sub>6</sub>: C, 53.73; H, 8.80; Br, 17.02; O, 20.45. Found: C, 53.75; H, 8.79; Br, 17.04; O, 20.50.

**2-(10-Mercaptodecyloxymethyl)-15-crown-5 Ether (2).** An argon purged 25 mL flask containing bromide **1** (1.85 g, 3.95 mmol) in freshly distilled THF (8 mL) was cooled to -5 °C and tetrabutylammonium fluoride (4.3 mL, 4.3 mmol) and hexamethyldisilathiane (1.0 mL, 4.7 mmol) are added rapidly. The solution immediately turned green. The mixture was stirred at -5 °C for 30 min and an additional 2 h at room temperature. Methylene chloride (20 mL) was added and the reaction mixture washed once each (25 mL) with 1 M HCl, sat. NH<sub>4</sub>Cl, and brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent removed *in vacuo*. The dark orange-yellow oil was stored under argon until used to modify the gold nanoparticles. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 1.27-1.45 (m, 8H), 1.47-1.65 (m, 8H), 2.48 (q, 2H), 3.32-3.51 (m, 4H), 3.53-3.91 (m, 19H). HRMS (*m/z*) calcd for C<sub>21</sub>H<sub>42</sub>O<sub>6</sub>S: 422.2702. Found: 422.2688.

**Monolayer-Protected Clusters (MPC) Synthesis.** MPCs were synthesized by variations of a previously determined protocol.[12] The MPC gold was prepared using different thiol:gold ratios, so as to achieve larger or smaller core size and thus larger and

smaller clusters.[39] Addition of a smaller amount of thiol increased the core size. For this study, three core sizes, Au<sub>140</sub>, Au<sub>220</sub>, and Au<sub>309</sub> were prepared by varying the amount of thiol added according to the reaction stoichiometry, 3x, 2x, and 1x, respectively.[17][40] For a general MPC preparation, H<sub>2</sub>AuCl<sub>4</sub> · 3H<sub>2</sub>O (previously prepared[41,42]) in 25 mL of nanopure H<sub>2</sub>O was added to tetraoctyl ammonium bromide (TOABr) (Fluka) phase transfer reagent in toluene and allowed to stir. The orange organic layer, containing the cluster in toluene was separated from the water layer, which was subsequently discarded.

A measured amount of 1-hexanethiol (Aldrich) was added to the stirring organic layer. After the thiol was added, the solution was allowed to stir for ~30 minutes, until it had become a light yellow color. The solution was then placed on ice at 0°C for 20 minutes. At the same time, a solution containing the reducing agent NaBH<sub>4</sub> in nanopure water was allowed to chill in the ice bath. The reducing agent was added to the gold-thiol mixture at a set delivery rate and the solution then turned a black color. A second method used to isolate specific core sizes was the rate of delivering reducing agent to the reaction. As seen in the literature, slower delivery times, known as medium delivery (MD) (e.g., over 2 minutes), led to larger core sizes whereas a faster delivery (FD) speed (e.g., 2 seconds) favored smaller core sizes.[39]

The reducing agent was allowed to stir with the gold-thiol mixture overnight at 0°C. The black organic layer was separated from the water layer into a round-bottom flask and the toluene was removed by evaporation (Büchi Rotavapor R-200). The remaining solid in the bottom of the flask was precipitated using 95% methanol. The precipitate was collected by vacuum filtration using a 30 mL medium porosity glass frit and washed with 150 mL of acetonitrile. The product was verified using <sup>1</sup>H NMR (300 MHz). Overall, three different types of MPCs were prepared using this method: a 2 $\times$ , 0°C, FD C6-thiol MPC; a 2 $\times$ , 0°C, MD C6-thiol MPC; and a 1 $\times$ , 0°C, FD C6-thiol MPC.[39]

**Exchange of 15-crown- ether(CE) into the MPC core** was accomplished using essentially the same procedures as developed through previous work.[15-17] A small amount of the previously synthesized MPC was placed in 99.9% anhydrous methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) (Aldrich) in a round-bottom flask and started stirring. To this solution, a stoichiometric amount of the CE ligand was added and the solution was stirred briskly for ~72 hours. The  $\text{CH}_2\text{Cl}_2$  was removed by evaporation and 95% methanol was added to precipitate the charcoal, black product overnight. The CE-MPC product was collected by vacuum filtration using a 30 mL medium porosity glass frit and washed with 150 mL of acetonitrile. The number of CE ligands in the cluster was determined by analyzing  $^1\text{H}$  NMR (300 MHz) spectra of the disulfides liberated from the nanoparticles after being decomposed with iodine. [15-17] [43]

Numerous exchanges were performed where the target number of CE ligands varied according to different loadings of CE ligand. The number of CE ligands exchanged into the cluster was determined by both the size of the cluster, which was determined during the synthesis procedure, and by controlling the ratio of CEs to C6-thiol ligands attached to the gold core during the exchange reaction. An exchange factor of x1-x3 (CEx1, CEx2, or CEx3) was implemented throughout this work as another method of controlling the amount of CE ligands in the cluster. The stoichiometric amount of CE ligand used in the exchange was multiplied by one of these exchange factors depending upon the desired quantity to be exchanged.

**CE-MPC Film Assembly.** All CE-MPC films were formed based on modified procedures from prior research on MPC films.[30,31,37,44] In all cases, films were formed on pre-cut glass microscope slides which were prepared by cleaning in Piranha solution (2:1, sulfuric acid : hydrogen peroxide). **Warning: Use extreme caution when working with Piranha solution; it reacts violently with organic materials.** In preparation for any of the assembly procedures used the glass was first silanized with 3-mercaptopropyl trimethylsiloxane (3-MPTMS), except in one case noted below.

Subsequent treatment of the glass slides depended on the type of film to be assembled (see below) as well as the targeted experiment, this is described in the following sections.

For films assembled with CE-metal ion-CE sandwiching as their linking mechanism, two dipping solutions were prepared: a linker metal-ion salt solution (0.1 M sodium acetate or potassium acetate in ethanol) and a CE-MPC solution (10 mgs CE-MPC in 10 mL ethanol). A single dip cycle consisted of immersing the silanized glass in the salt solution for 15 minutes followed by a 1 hour dip in the CE-MPC solution. The slides were then thoroughly rinsed with ethanol to remove uncoordinated materials and dried under a stream of nitrogen. The type of CE-MPC used in the CE-MPC solution varied by the MPC cluster size and CE exchange factor. These dipping cycles were repeated numerous times until the film reached a desired thickness. After each dip cycle, the growth of the film was monitored by UV-Vis spectroscopy (Jasco), paying particular attention to the shape and position of the surface plasmon band (SPB).

## **Results and Discussion**

After synthesis and subsequent structural characterization the ionophoric behavior of the various CE ligands was verified using simple cyclic voltammetry diffusing experiments. Self-assembled monolayers (SAMs) of each of the synthesized thiolated crown ether ligands were formed on electrochemically cleaned evaporated gold substrates. After allowing the SAM to form for 18 hours (overnight), the electrochemistry of a freely diffusing probe molecule, ruthenium hexamine (RuHex), was examined in the presence and absence of sodium ions ( $\text{Na}^+$ ) for each of the CE-SAM modified substrates. The positively charged RuHex molecules exhibit characteristic diffusing behavior at the CE-SAMs in the absence of  $\text{Na}^+$ , indicating the molecule can easily access the electrode surface through defects in the monolayer. However, once  $\text{Na}^+$  ions are coordinated into the crown ether moieties the CE-SAM retains a layer of positive charge on its periphery and is more effective at blocking the approach of the RuHex to the electrode surface, subsequently eliminating or reducing the diffusion based

electrochemistry.[45] **Figure 1** illustrates a typical result from these experiments. The C8-CE SAM shows a diffusion shaped voltammetric peak without Na<sup>+</sup> present and a completely blocked electrode when NaCl is incorporated with the RuHex solution. Similar results were observed for all of the other CE ligands as well, each showing some measure of attenuated RuHex voltammetry when Na<sup>+</sup> is introduced.

Crown ether ligands (e.g., C10-CE) were effectively introduced into MPCs via place-exchange reactions as described for other thiolated ligands found in the literature.[15-17] The success of the exchange process, creating CE-modified MPCs (CE-MPCs), was verified with <sup>1</sup>H NMR and GC-mass spectrometry (Shimadzu) analysis after the samples had been treated with iodine to liberate the ligands as disulfides (**Figure 2**). Peaks at ~3.7 ppm are assigned to the protons of the methylene units adjacent to the ethers of the crown's ring. Using C10-CE-MPCs with Au<sub>20</sub> cores, assembled films were constructed with CE-metal ion-CE bridges acting as the linking mechanism between adjacent nanoparticles (see **Scheme II**). To construct these films, a layer of C10-CE-MPCs was first anchored to a silanized glass substrate. Glass slides initially modified with 3-mercaptopropyl-trimethoxy silane were exposed to a metal ion solution followed by the C10-CE-MPC solution in order to establish an initial layer of MPCs onto the substrate. This initial layer of CE-MPCs is believed to be anchored to the substrate through either a thiol-gold connection, a metal-CE interaction, or, most likely, a combination of the two.[46] Though effective at anchoring MPCs to glass, the exact mechanism of surface immobilization remains undetermined.[30,31] After an initial layer of CE-MPCs was deposited, the film was subjected to dip cycles involving sequential and repeated exposure to both a metal ion solution and a solution of C10-CE-MPCs. The growth of the film, as with other types of MPC assemblies, [24,25,30,31,37,44] was followed by UV-Vis spectroscopy by monitoring the absorbance of the film at 300 nm during the dip cycles. **Figure 3** shows the absorbance spectra of film growth using C10-CE-MPCs and sodium ions as the linking metal coordinated in a sandwich configuration. The spectra are typical of MPC films, exhibiting a decreasing absorbance toward higher

wavelengths and a surface plasmon band (SPB) at approximately 540 nm. With each dip cycle, the corresponding spectrum increases in intensity, indicating continuing film growth. As the film became thicker, a red shift in the absorbance maximum for the SPB was observed – the manifestation of increasing aggregation and cross linking within the film as it becomes thicker (**Figure 3, Inset**).[26-28] It should be noted that even though films were formed with CE-metal ion sandwich bridges, growth was significantly slower when compared to other assembled MPC films, including metal ion linked films[18,24,25,44]or covalent films (ester coupled[37] or dithiol linked films[22]). This suggests perhaps there are more severe alignment and spacing constraints for the necessary interactions to form the “sandwiched” bridge.

To further verify that the films were assembling via metal-CE sandwiches, films were grown with several ions known to complex with the 15-crown-5 cavity, including  $K^+$ ,  $Na^+$ , and  $Ag^+$ , and compared to another ion,  $Cu^{2+}$ , that is too small to coordinate with this particular CE moiety. If the films were indeed employing CE-metal ion-CE bridging, one would expect all the films to show substantial growth in all cases except for the  $Cu^{2+}$  film. The results of these sets of experiments, shown in **Figure 4**, indicate that the films utilize the metal ion coordinating into the 15-crown-5 cavity during their assembly process.  $Na^+$ ,  $K^+$ , and  $Ag^+$  films all yielded measurable, albeit slow, growth whereas the use of  $Cu^{2+}$  resulted in negligible growth. Growth of the  $K^+$  film is significantly less than for  $Ag^+$  or  $Na^+$ , most likely because of subtle differences in the requirements for the  $K^+$  ion, as opposed to the other metal ions studied, to coordinate to two CE cavities from separate nanoparticles. The  $Na^+$  ion is known to be a more natural fit for the 15-crown-5 cavity, whereas the larger  $K^+$ , a natural partner for the 18-crown-6 cavity, is coordinated to a lesser extent in the 15-crown-5, requiring some distortion of the crown ether ring as well [32]. These subtle binding differences have been identified and studied in work by Gokel[32] and Chen[34,35] and are suspected here to contribute to the ability of the different metals to form sandwich complexes with the crown ethers in

this study. Similar films were grown successfully with similar results using different chainlengths of CE ligands as well as with the smaller  $\text{Au}_{140}$  core size.

The SPB observed in the UV-Vis spectra of the MPC films can be used as a diagnostic tool to make qualitative observations about interparticle spacing within these CE-MPC films compared to MPC films utilizing other linking mechanisms. In general, SPBs are observed in two cases: when the core size of the nanoparticles is large enough to allow for this bulk surface property or when smaller clusters are forced into close proximity (i.e. assembled into a film) and act collectively as a bulk material. Two examples of this phenomenon are shown in **Figure 5**. **Figure 5A (inset)** shows the spectra of MPC solutions of unmodified  $\text{Au}_{140}$  and  $\text{Au}_{220}$  MPCs. As expected the  $\text{Au}_{220}$  core size shows a prominent SPB as the result of the larger particle diameters involved whereas the solution of  $\text{Au}_{140}$  particles reveals a featureless spectrum without a SPB. Spectra of modified CE-MPC solutions are identical to the unmodified spectra in **Figure 5A**, suggesting that, while dispersed in solution, the size of the SPB is very much a core size related property, independent of the specific MPC ligands. However, when the  $\text{Au}_{140}$  clusters are incorporated into a film the spectrum reveals a prominent SPB. **Figure 5B** shows the spectrum of a film comprised of MPCs with carboxylic acid ligands that have been networked together with metal ion linker ( $\text{Cu}^{2+}$ ) as seen in the literature.[24-25,30-31][24,25,30,31] The appearance of the SPB indicates that the core-to-core spacing of nanoparticles is significantly decreased compared to a solution.

**Figure 5C** shows the spectra for crown ether-metal bridged C10-CE MPC films assembled using both  $\text{Au}_{140}$  and  $\text{Au}_{220}$  core sizes. Again, a prominent SPB is displayed for the larger clusters, a result consistent with all measurements of  $\text{Au}_{220}$  films and attributed to the larger core size. However, unlike the metal-carboxylate linked films composed of  $\text{Au}_{140}$  core size clusters and displaying a SPB (**Figure 5B**), the CE-linked films made of the same sized clusters do not show a prominent SPB band. The absence of the band

suggests that the CE-bridged mechanism forces the Au<sub>140</sub> cores to be separated by a slightly greater distance compared to the metal-carboxylate linked films.

Another common difference between the core sizes (Au<sub>140</sub> & Au<sub>20</sub>) examined in this study is the ability of the smaller nanoparticles to display quantized double layer (QDL) charging. Because of their design, electron rich metallic cores surrounded by a layer of insulating alkanethiols, smaller core MPCs have extremely small capacitances (attofarads). Upon application of a voltage across such materials, quantized single electron transfers (SETs) can be observed. This phenomenon is most easily observed as a series of inflections or peaks during cyclic or differential pulse voltammetry experiments, respectively.[18] The spacing of the SET signals (peaks) obeys the equation below, where  $E_p$  is the peak potential,  $E_{pzc}$  is the potential of zero charge,  $Z$  is the charged state of the cluster,  $e$  is the charge of a single electron, and  $C_{CLU}$  is the cluster capacitance:

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

From the linear trend of peak potentials ( $E_p$ ) versus charged state ( $Z$ ), known as a “z-plot,” the average peak spacing or slope can be easily translated into an average diameter of cores comprising the sample.[47] For smaller nanoparticles like the Au<sub>140</sub> MPCs, QDL charging is expected for solutions[48] of MPCs and also translates to assembled films of the materials as well.[18,44] The larger Au<sub>20</sub> clusters, on the other hand, are known to exhibit only very weak QDL signals if at all. Thus, for films composed of CE-modified MPCs, QDL charging should only be observed with the smaller Au<sub>140</sub> core size.

Differential pulse voltammetry of the C10-CE-MPC, K<sup>+</sup> linked MPC films is shown in **Figure 6** with a corresponding z-plot (**Figure 6, inset**). Small QDL peaks are observed as indicated by black arrowheads pointing to the apex of the peaks and the charged states of the clusters are indicated on the graph as well. The peaks are very small due to the extremely slow growth which allows for only a very thin film to be assembled in a reasonable amount of time. Nevertheless, even with a very thin film, QDL charging is visible and analysis of the peaks, shown in the z-plot, indicates an average peak

spacing of 243 ( $\pm 11$ ) mV. This range of peak spacing corresponds to MPCs with capacitances in the range of 0.62 to 0.68 aF, or clusters with diameters between 1.7 and 1.9 nm. These results are most consistent for films made of the typical 28 kDa C6 MPCs with  $\text{Au}_{100}$  cores,[47,48] although the presence of the crown ether ligands and proximity of metal cations within the film may have some effect on the analysis.

The emergence of QDL charging peaks from these CE-linked films suggests that, like other types of assembled MPC films, film growth is selective toward a specific core size or exchange rate (number of linking ligands in the periphery of the MPCs).[19] With this in mind, the growth dynamics as they relate to the number of CE linking ligands of these films was examined. Films were grown using a single chainlength of CE ligand (C10-CE) and a single metal ion ( $\text{Na}^+$ ) with varying degrees of crown ether exchange. The exchange reaction has two parameters which control the amount of CE incorporated into the nanoparticles: the time the exchange reaction is allowed to take place and the stoichiometric ratio of CE thiol added to the reaction flask.

Typically, an exchange reaction is allowed to run for 72 hours.[15-17] In this study, C10-CE ligands were allowed to exchange over 3, 4, and 5 days. Each material was then used to grow a film and the growth was tracked by measuring the UV-Vis spectroscopy and noting the absorbance at 300 nm. **Figure 7** shows the results of this experiment with the growth rate being essentially identical regardless of the exchange time. Longer exchange times appear to only slightly decrease growth, perhaps indicative of the possible steric restrictions that inevitably accompany a greater number of CE ligands being attached to the MPC cores.

Varying the stoichiometric amount of CE-thiols to the exchange reaction also had very little substantial impact on growth. For the  $\text{Au}_{20}$  core sizes, as shown in **Figure 8**, growth between reactions with 3x and 1x exchange factors was not significantly different and the 2x exchange factor showed only a very slight and, most likely, insignificantly

higher growth rate. Likewise, for Au<sub>40</sub> core sizes, (**Figure 8, inset**) growth was very slow and only slightly improved with the 1x exchange factor. This result again suggests that greater quantities of CE moieties may hamper growth slightly. However, from the collective results of **Figure 7** and **8**, it appears as though the CE-ligands are successfully exchanged into the MPCs after 3 days, with further exchange, either in terms of reaction time or amount of reactant thiol, not rendering significant improvements in growth. This type of indifference to the exchange reaction parameters stands in stark contrast to the other types of MPC film assemblies which are very sensitive to these variables.[24,25,30,31,37,44]

## Conclusions

The versatility of MPCs has allowed for their incorporation into networked films that offer potential as sensing materials. In this work, ionophoric crown ether moieties are attached to the MPCs and used as an integral part of a novel linking mechanism. CE modified MPCs can be linked together and grown on a substrate by utilizing CE-metal ion-CE sandwiches – an interaction shown to be effective enough to grow substantially thick films. Such a bridge is only possible with metal ions capable of coordinating in the specific crown ether cavity being used (e.g., 15-crown-5). The films networked in this manner are sufficiently electronically connected as evidenced by voltammetric measurements. This type of MPC film is unique compared to others in that it selectively assembles and will have less of a pH dependence than traditionally linked carboxylic acid-metal ion-carboxylic acid films. Currently our research is aimed at using these CE-MPC films in metal ion sensing applications as well as generating an aqueous film system of citrate stabilized MPCs that can monitor metal ion concentrations in solution.[34,35,49]

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## Captions

**Scheme I.** Preparation of 2-(10-mercaptodecyloxymethyl)-15-crown-5 ether.

**Scheme II.** Crown ether-metal ion-crown ether “sandwich” interparticle bridge.

**Figure 1.** Cyclic voltammetry of freely diffusing ruthenium hexamine (1 mM) at a gold electrode modified with a C8-CE self-assembled monolayer in a solution of 100 mM Et<sub>4</sub>NCl (–) and 80 mM Et<sub>4</sub>NCl with 20 mM NaCl (----) [scan rate = 100 mV/sec].

**Figure 2.** <sup>1</sup>H NMR (300 MHz) spectra prior to (top) and after (bottom) an exchange reaction with CE ligands that verify the successful incorporation of CE ligands into the periphery of the MPCs.

**Figure 3.** (A) UV-Vis spectra after each dip cycle during the growth of C10-CE MPC assembled film where the nanoparticles are networked via CE-metal ion-CE “sandwich” linking mechanisms. As the films grows thicker, the absorbance maximum of the surface plasmon band red shifts with increasing numbers of dip cycles, shown in (B), an indication of increasing aggregation and cross-linking.

**Figure 4.** Multi-layer growth, tracked with the absorbance at 300 nm as a function of the number of dip cycles, for CE-MPC “sandwich” films assembled with sodium, silver, potassium, and copper ion linkers.

**Figure 5.** UV-Vis spectroscopy of (A) solutions of unmodified Au<sub>220</sub> (----) and Au<sub>140</sub> (–) core sized MPCs; (B) Au<sub>140</sub> core sized MPC film with a traditional electrostatic linking mechanism of deprotonated carboxylic acid functionalized MPCs connected through metal ions and; (C) Au<sub>220</sub> (----) and Au<sub>140</sub> (–) core sized CE-MPC “sandwich” films.

**Figure 6.** Differential pulse voltammetry showing quantized double layer charging in the form of single electron transfer peaks of the very thin CE-MPC film assembled with Na<sup>+</sup> ions in a CE-Na<sup>+</sup>-CE sandwiched linking bridge. The regular spaced peaks (black arrowheads) are analyzed via the Z-plot [inset] where the slope can be related to core diameter (see text).

**Figure 7.** Multi-layer growth, tracked with the absorbance at 300 nm as a function of the number of dip cycles, for CE-MPC “sandwich” films grown from MPCs were functionalized during 3, 4, and 5 day place-exchange reactions.

**Figure 8.** Multi-layer growth, tracked with the absorbance at 300 nm as a function of the number of dip cycles, of CE-MPC “sandwich” films grown from (A) CE-MPCs with Au<sub>220</sub>

cores that were functionalized with place-exchange reactions of varying stoichiometric additions of CE ligands (1x,2x,3x). (B) Similar growth results for CE-MPCs with Au<sub>140</sub> core sizes. [Note: the labeled notations within the figure indicate core size and exchange factor designations as described in the text.]