

Using Electrons Stored on Quantized Capacitors in Electron Transfer Reactions

Jeremy J. Pietron,[†] Jocelyn F. Hicks, and Royce W. Murray*

Contribution from the Kenan Laboratories of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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Abstract: Monolayer-protected clusters (MPCs) of gold with a majority composition of $[\text{CH}_3(\text{CH}_2)_6\text{S}]_{50}\text{Au}_{145}$ have been synthesized. Solutions of this material in a toluene–acetonitrile solvent, containing a supporting electrolyte, are shown to display quantized double layer capacitance charging in differential pulse voltammetry experiments. These solutions can also be electrolytically charged to controllable potentials, and the average number of electrons (or holes) stored on the metal-like MPC cores can be estimated from the pattern of single-electron quantized charging peaks. The charged solutions are stable for hours. The charged MPCs can also be isolated in dried form, and retain most of their charge upon redissolution. The electronic charge on the MPC cores can be employed to carry out redox reactions with electron acceptor and donor molecules, such as ethylferrocene and TCNQ. These reactions proceed in a predictable and quantifiable way. Charged MPCs also undergo electron transfer reactions when mixed with solutions of differently charged MPCs, and the potential of the resulting solutions is completely consistent with Nernstian predictions. In the use of double layer charges to carry out redox transformations, these experiments illustrate a more quantitative capability than has been previously described.

Monolayer-protected metal clusters (MPCs) consist of a nanometer-sized core of metal atoms coated with a ligand monolayer that passivates the metal cores against aggregation, even in dried, solvent-free forms.¹ In this study, the ligands are hexanethiolates (SC6), the core metal is Au, and the core is of sufficient size as to exhibit metal-like (as opposed to molecular) properties.² The samples of MPC used, while not exactly monodisperse in core size, have a dominant population of average formula ca. $\text{Au}_{145}(\text{SC}6)_{50}$, and average core diameters of 1.6 nm.³

Electrolyte solutions of MPCs whose monolayers contain mixtures of alkanethiolate ligands and redox ω -functionalized (such as ferrocene and anthraquinone⁴) alkanethiolate ligands display electrochemical currents for both (a) oxidation or reduction of the redox functional groups and (b) double layer charging of the MPC core. Only the latter currents are

observed^{2,5} for MPCs with solely alkanethiolate ligand monolayers, like those used here. Equilibration of MPC core potentials with that of the working electrode occurs when MPCs diffusively contact a working electrode, by electron storage on or removal from the MPC core. Concomitantly, an ionic space charge layer forms around the MPC, separated from the core by the monolayer, which serves as the dielectric medium of the double layer capacitor.

When the MPCs have uniform core sizes (and thus capacitances, C_{CLU}), the differential pulse voltammetry (DPV) of MPC solutions shows^{2,5} that the double layer charging can occur as a series of discrete (one electron), roughly evenly spaced, current peaks. The quantized charging behavior arises from the extremely small capacitances (sub-attoFarad, aF) of MPC nanoparticles. Storage of a single electron on an MPC core of capacitance $C_{\text{CLU}} = 0.5$ aF, for example, changes its potential by $e/C_{\text{CLU}} = \Delta V = 0.32$ V, where e is the electronic charge. The electrochemical phenomenon is roughly analogous to “coulomb staircase” charging of single nanoparticles,⁶ except that it occurs for ensembles of like-charged nanoparticles and the currents are diffusion controlled.^{2,5}

This paper describes the electrolysis of $\text{Au}_{145}(\text{SC}6)_{50}$ MPC solutions, so that the cores throughout the solution contain known quanta of double layer charge, and the use of these electronic charges in stoichiometrically quantified chemical reactions. In a recent paper,^{5b} we elaborated on an earlier theory by Weaver⁷ to show that the thermodynamics of quantized MPC

[†] Present address: Naval Research Laboratory, Washington, DC.

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capacitance charging is formally identical with that of conventional redox species. An ensuing prediction is that, in mixing equal numbers of moles of MPCs (having, for example, $C_{\text{CLU}} = 0.65$ aF and $\Delta V = 0.25$ V, and having been electrolytically charged to +1.0 V vs E_{PZC}) and an electron donor with $E^\circ \leq E_{\text{PZC}}$, the MPC can potentially deliver 4 equiv of oxidizing charge to the electron donor. (E_{PZC} is the MPC potential of zero charge.) The thermodynamics of MPC capacitive charging also predict that mixing of MPC solutions with different core charge states (z) results in electron transfers among the MPCs, producing a "mixed valent" $(z - 1)/z$ solution exhibiting an average potential determined by the stoichiometry of the mixture and the Nernst equation. These predictions are explored in experiments presented in this paper.

This work is not the first in a qualitative sense to use capacitatively stored electronic charge to drive chemical reactions (or the reverse). For example, in the venerable electrochemical "coulostatic" experiment,⁸ a macroscopic electrode is abruptly charged to a new potential, and its transient open circuit potential measured as the double layer charge is consumed by reaction with a redox constituent of the solution. Metal colloids (of generally much larger dimension than the MPCs used here) are well-known to be charged following their chemical generation under variously more or less reducing conditions.⁹ Electrolytic capacitors can be used as battery-like energy sources.¹⁰ The present work is distinct from these earlier cases in that (a) the capacitance charging is discrete and (b) as a result, one can for the first time explore its redox-like stoichiometry in well-defined, quantitative terms. The experiments can be likened to "doing redox chemistry with quantum capacitors".

Experimental Section

Chemicals. Tetrabutylammonium hexafluorophosphate, Bu_4NPF_6 (Fluka, >99% stored in a desiccator), ethylferrocene (Strem, 98%), 7,7,8,8-tetracyanoquinodimethane (TCNQ, Aldrich, 98%), and bis(pentamethylcyclopentadienyl)iron (decamethylferrocene, Aldrich, 97%) were used as received. Acetonitrile (Fisher, 99.9%) was distilled from CaH_2 and toluene (Mallinckrodt, 99.9%) dried over 4 Å molecular sieves.

Hexanethiolate-stabilized gold clusters (C6 MPCs) were prepared as in previous work.^{5a,11} Briefly, the reaction conditions were reduction of a 3:1 mole ratio of hexanethiol to AuCl_4^- at 0 °C by BH_4^- in large excess, allowing the reaction to proceed for 24 h. Clusters isolated from the reaction mixture were free (by NMR) from unbound thiol ligand. These reaction conditions produce clusters with an average, and most populous (by TEM and thermogravimetric analysis) core diameter of 1.6 nm. This diameter corresponds, on the basis of an assumed closed-shell shape,¹² to an MPC core of ca. 145 gold atoms and a monolayer of ca. 50 hexanethiolate ligands. A useful recent discovery¹⁴ has been that some, including the above, MPC syntheses yield material that, while not truly monodisperse, contains a sufficiently large proportion of certain cluster sizes as to display recognized quantized capacitance charging of this major population, *without fractionation*.

In one experiment (Figure 1), clusters were used that had been core-size fractionated³ so as to be more monodisperse in $\text{Au}_{145}(\text{SC}_6)_{50}$ (which

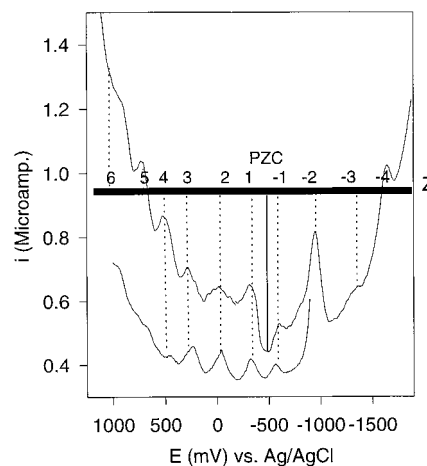


Figure 1. Differential pulse voltammetry (DPV) of C6 MPC solutions in 2:1 toluene– CH_3CN at a 20 mV/s DC potential scan rate and 200 ms, 50 ms, 50 mV, and 117 ms DPV pulse period, width, height, and sampling time, respectively. Both positive- and negative-going scans were measured; the negative-going scans shown are shifted by 17 mV to remove the average iR_{UNC} potential shifts. **Upper trace:** DPV of a 0.3 mM "as prepared" C6 MPC (most of which is $\text{Au}_{145}(\text{SC}_6)_{50}$) solution containing 0.1 M Bu_4NPF_6 electrolyte, at a 1.6 mm diameter Pt disk working electrode. **Lower trace:** DPV of a 0.12 mM solution of fractionated $\text{Au}_{145}(\text{SC}_6)_{50}$ MPC solution containing 0.05 M Hx_4NClO_4 electrolyte at a 1 mm diameter Au disk, multiplied by 4 and offset vertically for comparison to the upper trace. The numbered black bar indicates the change in MPC charge state occurring in the DPV peak, based on the indicated E_{PZC} .

by ionization–desorption mass spectrometry³ has a core mass of ca. 28 kD).

The reaction mixture was not deaerated; we have established¹¹ that none of the MPC ligands are in an oxidized (sulfonate,¹³ etc.) state. Exposure to air does minimize any residual reductive charging of the MPC cores caused by the excess borohydride.

Electrochemical Measurements. Differential pulse voltammetry (DPV) and bulk electrolyses of C6 MPCs (typically 0.3 mM, in mixed toluene–acetonitrile (2:1 (v/v)) solutions containing 0.1 M Bu_4NPF_6) were carried out in a fritted three-compartment cell, using a Bioanalytical Systems Model 100B Electrochemical Workstation. DPV was done at a 1.6 mm diameter Pt disk and bulk electrolysis at large Pt mesh working electrodes. The auxiliary electrode was a Pt mesh. The reference electrode was Ag/Ag^+ (Ag wire/ AgNO_3 (1 mM)/ Bu_4NPF_6 (0.1 M)/ CH_3CN).

In electrolyses of MPC solutions, the objective was exhaustive charging of the entire solution of cores. The working electrode compartment contained MPC solution as did the middle compartment. The third compartment contained both reference and auxiliary electrodes. A minor amount of mixing undoubtedly occurs between the electrolyzed working and quiescent middle electrode compartment, through the frit separator. Oxidatively charged MPC solutions were handled in air; those generated at reducing potentials were handled under N_2 .

Redox Reactions of MPC Solutions. Solutions of ethylferrocene and TCNQ (magnetically stirred) were oxidized and reduced, respectively, by sequential, syringed microliter additions of solutions of variously charged MPCs. The reactions were monitored by the equilibrium solution redox potential, measured at a Pt indicator electrode (vs Ag/Ag^+ reference electrode) and a Corning 445 high input impedance ($>10^{12}$ Ω) pH meter in potentiometer mode. Redox potentials of mixtures of charged MPC solutions were similarly monitored. All of the above results are stated vs a Ag/AgCl quasi-reference, for consistency with previous reports.^{2,5} (The Ag/AgCl reference is -220 mV vs Ag/Ag^+ and $+50$ mV vs SCE reference electrodes.)

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Results and Discussion

Controlled Charging of Clusters and Cluster z State. To use charged MPCs as controlled sources of oxidizing and reducing equivalents, it is necessary that (a) charged clusters are reasonably stable (as prepared by chemical reactions or, as done here, by electrolysis to a given potential) and (b) the number of stored electrons/MPC be estimable. Ideally, the latter is based on the quantization of capacitance charging that can be observed in monodisperse cluster samples.^{2,5} The C6 MPCs used here are prepared by a procedure that yields a sufficiently dominant population of Au₁₄₅ cores as to display quantized charging features. More monodisperse MPCs can be prepared by fractionation,³ at some cost of labor, to obtain quantities convenient for chemical reaction studies.

The upper portion of Figure 1 shows differential pulse voltammetry (DPV) illustrating quantized double layer capacitance charging of as-prepared (not fractionated) C6 MPCs in a toluene/acetonitrile solution. The DPV trace exhibits a series of current peaks, well-resolved above background, at -1.6 , -1.35 , -0.98 , -0.59 , -0.28 , 0.00 , $+0.30$, $+0.52$, $+0.70$, and $+1.0$ V vs Ag/AgCl. The lower portion of Figure 1 shows analogous DPV of a solution of fractionated C6 MPCs (see Experimental Section), taken over a more limited range of potential. The fractionated sample displays a series of well-resolved current peaks at similar potentials (-0.54 , -0.30 , -0.00 , $+0.25$, $+0.47$, and $+0.65$ V) for quantized successive, single-electron capacitance charging of clusters diffusing to the working electrode. In both voltammograms, the spacing ΔV between successive peaks for single-electron charging is e/C_{CLU} ^{5a} where e is the electronic charge and C_{CLU} is capacitance per cluster. Considering the various experimental uncertainties (translating reference electrode potential scales, iR_{UNC} effects), the unfractionated and fractionated C6 MPC solutions display remarkably similar quantized capacitance charging patterns.

The results in Figure 1 provide a means to estimate the average charge state (z) of the clusters in a solution exhibiting a given potential E . This can be done by using the number of DPV peaks interposed between E and E_{PZC} ; alternatively, the charge state can be estimated from the average value of C_{CLU} or ΔV and the potential difference $|E - E_{\text{PZC}}|$. The relation between charging potential and charge state is^{5b}

$$E_{\text{Z,Z-1}} = E_{\text{PZC}} + \frac{(z - 1/2)e}{C_{\text{CLU}}} \quad (1)$$

A plot of this relation for the DPV peaks of the unfractionated MPC solution is shown in Figure 2. This plot appears to exhibit different slopes in the positive and negative potential regions; this has been seen before^{5b} for a fractionated C6 MPC sample. Differences in double layer capacity between positive and negative potential regions are well-known¹⁵ for flat electrode/solution interfaces. Values of 0.64 and 0.47 aF/MPC result from the positive and negative branches of Figure 2, corresponding to $\Delta V = 0.25$ and 0.34 V, respectively. A plot of eq 1 for the fractionated MPC solution in Figure 1 is linear (and lies mainly in the positive potential region), and gives 0.67 aF/MPC for the monodisperse Au₁₄₅(SC6)₅₀ cluster cores. The earlier^{5b} C6 MPC DPV data gave $C_{\text{CLU}} = 0.65$ and 0.52 aF/MPC for the positive and negative potential branches, respectively. We see that the results for the fractionated and unfractionated materials are in good agreement.

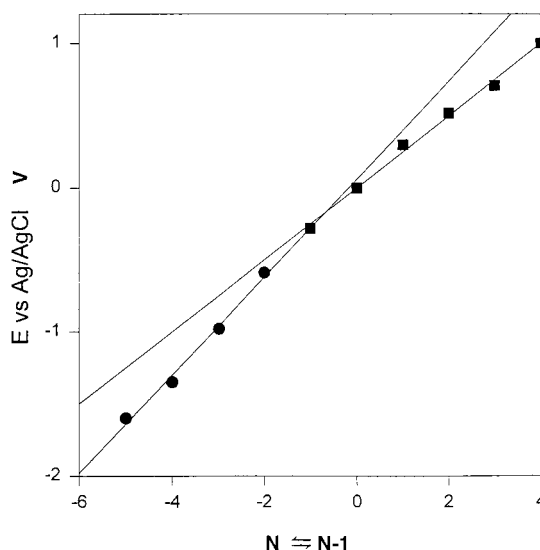


Figure 2. Plot of DPV peaks in Figure 1 for unfractionated C6 MPC according to eq 1.

The change in slope in Figure 2 is roughly centered on -0.2 V vs Ag/AgCl. An ac impedance study¹⁶ of an immobilized monolayer of monodisperse C6 clusters exhibited a capacitance minimum at the same potential. We assign this potential as E_{PZC} for MPCs in solutions of composition as used here. Actual cluster charge states can be estimated¹⁷ in reference to this E_{PZC} , according to eq 1. For example, solutions of unfractionated C6 MPCs exhibiting redox potentials of $+0.70$ and -0.98 V vs AgCl/Ag contain ca. 1:1 “mixed-valent” $z = +3/+4$ and $-2/-3$ charge states of the major Au₁₄₅(SC6)₅₀ cluster population.

To evaluate electrolytic charging of C6 MPC solutions and the stability of their stored charge, stirred (typically 0.3 mM) C6 MPC solutions were electrolyzed at Pt mesh working electrodes at various potentials for periods of 1–3 h. Subsequent potentiometric measurements on the resulting solutions, after transfer to a separate cell, showed that their potentials, while typically less oxidizing or reducing than the original electrolysis potential, were reasonably stable. For example, an MPC solution electrolyzed at 0.91 V vs Ag/AgCl, after transfer into a separate cell, displayed potentials of 0.69, 0.67, and 0.62 V vs Ag/AgCl when measured immediately, after 1 h, and after 1 day, respectively. The difference between the electrolysis potential and that resulting immediately afterward was typical, and at least in part reflects iR_{UNC} potential loss in the electrolysis cell (i.e., the potential actually operative at the working electrode was less positive than E_{APPLIED} ; the currents were $>100 \mu\text{A}$ and $R_{\text{CELL}} > 10^3 \Omega$). Additional factors could be bled through the frit to/from the MPC solution in the center cell compartment and/or discharge of high- z clusters by parasitic processes in the solution. These issues remain to be worked out. The more significant finding is the relative stability of the oxidant MPC solution, which is comparable to that of many metal complexes of similar oxidizing potential (such as ferrocenium and its carboxylate derivative) maintained in dilute solutions at room temperature. The slow drift (0.07 V seen over 1 day) in the cluster solution potential does show that some slow discharge mechanism does exist; the 0.07 V drift corresponds to a ca. 10-fold change in the ratio of one-electron-separated electron

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(17) While we believe that the above estimate of the MPC $E_{\text{PZC}} = -0.2$ V vs AgCl/Ag is correct, if in error, it would have to be offset by an entire charging step. Even such an error would have no consequence on estimating the oxidizing or reducing equivalents stored on MPCs, relative to some redox substrate, since both are referred to the same reference electrode.

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donor/acceptor MPC pairs. A cluster charged to +0.69 V corresponds to $z = +3.6$ electrons/cluster, based¹⁸ on the position of the PZC (ca. -0.20 V) in Figure 1 and the average C_{CLU} measured above.

In electrolyses conducted at reducing potentials, using the same procedures, charged MPC solutions have been obtained with reducing potentials as negative as -0.68 V vs Ag/AgCl, which based on the average C_{CLU} value corresponds to a $z = -2.0$ cluster charge state. Clusters charged to more negative potentials quickly relaxed to potentials of ca. -0.7 V upon exposure to air. It is likely that our inability to prepare solutions of MPCs at higher than $z = -2$ states is due to inadequate exclusion of dioxygen from the electrolysis solutions and solution transfer procedures. Access to more reducing clusters will require more stringent conditions than used in these early experiments.

The stability of charged clusters extends to their dried, solid-state forms. Electrolysis of a cluster solution at +1.7 V produced a transferred solution with a measured potential of +1.22 V vs Ag/AgCl (ca. $z = +6$ clusters). The toluene/acetonitrile solvent was pumped away under vacuum. Washing the cluster mass with an acetonitrile/water mixture yielded some gas bubbling suggesting discharge of some of the stored oxidizing power. After the material was dried again in vacuo and redissolved in fresh electrolyte (toluene/CH₃CN/Bu₄NPF₆), the MPC solution exhibited a redox potential of +0.94 V vs Ag/AgCl, i.e., the reconstituted MPC retained an oxidizing potency of nearly $z = +5$. In another experiment, the solvent was removed by rotary evaporation from a solution charged to +0.73 V vs Ag/AgCl (a $z = +4/+3$ charge state); upon redissolution, this material produced a nearly identical redox potential of +0.70 V. An NMR spectrum of the latter solution showed the characteristically broad¹¹ methyl and methylene peaks of intact cluster, sharp peaks for the Bu₄N⁺ electrolyte, and no other extraneous peaks.

These experiments show that electron deficient clusters are tolerant of solvent removal and redissolution. While no long-term solid-state charge storage results are available, the present results are highly encouraging and it is conceivable that charged MPCs can be prepared, dried, and stored as oxidizing and reducing reagents. In the preceding experiments, we did not isolate the supporting electrolyte from the electrolyzed cluster. Ideally, the dried materials would be monodisperse MPCs with well-defined counterion populations, free of excess electrolyte.

Incremental Oxidation and Reduction Reactions Using Solutions of Charged Clusters. The preceding experiments are encouraging in regard to using charged MPCs as redox reagents, but an equally interesting consideration is their use in quantitative redox procedures, relying on judging their electron storage stoichiometry from their DPV quantized charging behavior. This issue was probed by adding small increments of electrolytically charged cluster solutions to solutions of redox substrates, following the ensuing electron transfer reaction much as one would in a potentiometric titration.

Ethylferrocene (EtFc) was selected as a relatively easily oxidizable substrate; its formal potential is +0.38 V vs Ag/AgCl in toluene/acetonitrile. Clusters charged to potentials more positive than this should act as oxidants toward EtFc, generating the EtFc⁺⁰ couple, whose redox potential can be measured. Figure 3 shows three experiments in which small volumes of charged, 0.3 mM cluster solutions, containing nanomolar fractions of charged MPCs, are incrementally added to EtFc

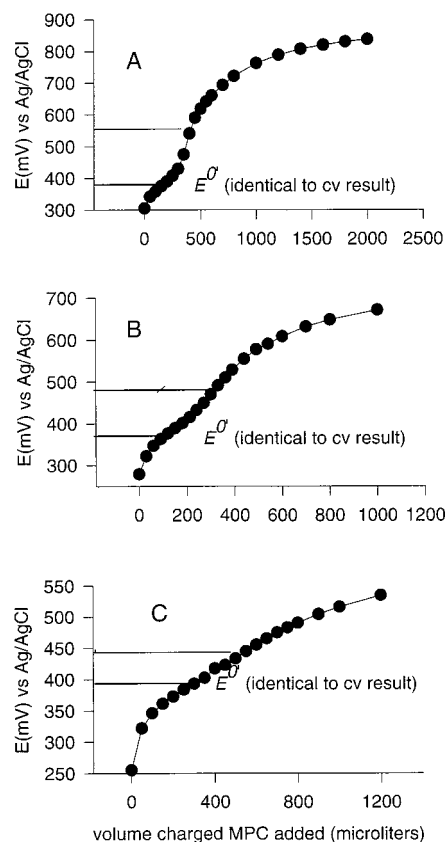


Figure 3. Incremental additions of charged 0.30 mM MPC solutions to solutions of ethylferrocene in 0.1 M Bu₄NPF₆/2:1 toluene-CH₃CN. Curve A: Additions of MPC solutions charged to +0.92 V to 5 mL of 76 μ M ethylferrocene. Curve B: Additions of MPC solutions charged to +0.72 V to 5 mL of 36 μ M ethylferrocene. Curve C: Additions of MPC solutions charged to +0.62 V to 5 mL of 36 μ M ethylferrocene.

solutions (as in a titration). The cluster solutions had been electrolytically charged to potentials of +0.92, +0.77, and +0.62 V vs Ag/AgCl (curves A-C, respectively). The curves in Figure 3 have the classically expected shape: a sharp rise in potential, a more gradual rise centered on the EtFc formal potential, a sharp rise at the equivalence point (determined as the maximum slope), followed by another gradual rise in potential as an excess of oxidizing agent (the charged cluster) is added. The rise in potential at the equivalence point becomes less distinct for the less oxidizing cluster solutions, consistent with classical expectations for redox reaction with progressively smaller free energy differences between electron donor and acceptor reactants. For the flatter part of each curve preceding the equivalence point, the slope minimum lies at a potential of ca. 0.38 V, which is the EtFc formal potential, as expected for delivery of 0.5 equiv of oxidizing charge to the solution by added clusters.

The EtFc solutions in Figure 3A-C contain 380, 180, and 180 nmol of EtFc, respectively. The volumes of charged MPC solution delivered to the EtFc solutions at the slope minimum are 200, 150, and 300 μ L in curves A-C, respectively. The ensuing equivalence points occur at MPC volumes twice as large, 400, 300, and 530 μ L, respectively, as ideally expected. From the initially present quantities of EtFc, one ideally expects that these latter volumes of charged MPC solutions contained 380, 180, and 180 equiv of oxidizing charge, respectively. These results compare favorably to the prediction of 300, 170, and 200 nequiv of oxidizing charge, respectively, in the three above volumes of charged MPC solutions. These predictions are based on referring the charging potentials of the MPC solutions (0.92, 0.77, and 0.62 V) to the initial rest potential of the EtFc solution

(18) Using the average C_{CLU} value to calculate the charge state assumes that concentrations vary linearly with E , which of course is not exactly true. This approximation is made just for simplicity of the presentation.

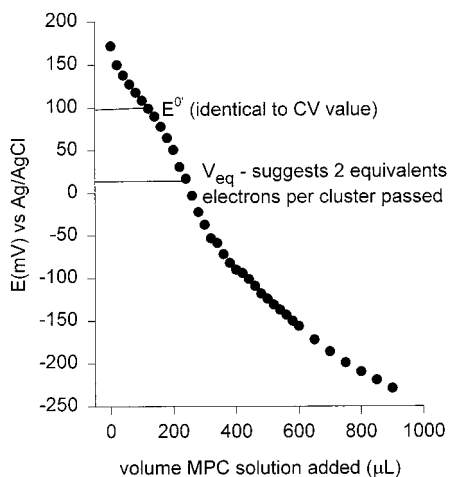


Figure 4. Incremental additions of a solution of 0.30 mM MPC with a rest potential of -0.44 V vs Ag/AgCl to 5 mL of 29 μ M TCNQ.

(0.29 V), using the 0.25 V/electron DPV peak spacing from Figure 2. Less good agreement is found if the oxidizing charge content of the MPC solutions is estimated by reference to the charging potentials to the Figure 3 equivalence point potentials; this gives 190, 90, and 110 mequiv, respectively. Titrations with cluster solutions charged to intermediate potentials (i.e., non-integral numbers of stored holes) were also performed and showed intermediate redox equivalencies, consistent with the results seen in Figure 3.

While the titrations in Figure 3 are classically behaved, one must remember that the oxidizing reagent is nanoscopic metallic nanoparticles, whose stoichiometric oxidizing capacity (i.e., oxidizing equivalents/mole) can be arbitrarily programmed by the potential at which it is prepared. As far as we are aware, this is the first demonstration of a stoichiometric measurement with a charged-metal-particle chemical reaction.

Incremental reductions with clusters charged at negative potentials were also briefly explored. Figure 4 shows the reduction of a TCNQ solution by using a cluster solution charged at a potential of -0.44 V vs Ag/AgCl. (This potential was typical for these cluster solutions, as made.) The DPV results (Figure 1) show quantized charging features at ca. -0.02 and -0.36 V, both of which are reducing relative to the $\text{TCNQ}^{0/-1}$ formal potential which lies at $+0.10$ V vs Ag/AgCl, and suggesting that each cluster should carry two reducing equivalents in this reaction. The potential midway to the equivalence point in Figure 4 is 0.10 V (which agrees with the $\text{TCNQ } E^\circ$), and the evaluated equivalence point showed that two reducing equivalents were delivered by the cluster solution. These results again agree with classical expectations and demonstrate that charged clusters can controllably deliver electrons, as well as holes.

Mixing Charged MPCs: Electron Transfers between MPCs. The preceding experiments imply that differently charged MPCs should undergo electron transfers with one another. Figure 5 shows the incremental addition of an MPC solution charged at $+0.12$ V to an MPC solution that had been charged to $+0.736$ V vs Ag/AgCl. Although one can view the various charge states of MPCs as redox couples, in a formal sense, Figure 5 shows no obvious “equivalence point” in the mixed solution, which may be due to the imperfect monodispersity of the unfractionated C6 MPC material. Nonetheless, one can analyze Figure 5 in terms of the Nernstian behavior that is predicted for mixed valent MPC solutions, as they are formed by electron transfers between oxidizing and reducing

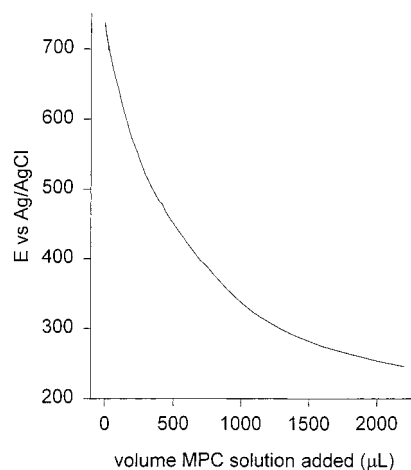


Figure 5. Incremental addition of a 0.3 mM MPC solution with a $+0.12$ V potential to a 0.3 mM MPC solution charged to $+0.736$ V.

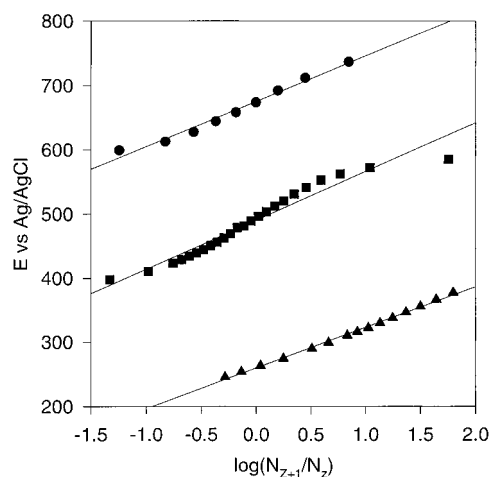


Figure 6. Plot of measured solution potentials vs the logarithm of computed population ratios of MPC in the $Z + 1$ and Z charge states.

MPCs with different formal potentials (the DPV peaks), which can be stated as^{5b}

$$E = E^\circ_{\text{MPC}} + 0.059 \log\left\{\frac{[N_Z]}{[N_{Z-1}]}\right\} \quad (2)$$

where

$$E^\circ_{\text{MPC}} = E_{\text{PZC}} + (z - 1/2)e/C_{\text{CLU}} \quad (3)$$

From Figure 1, the formal potentials of the three MPC “couples” generated by reactions between the two charged MPC solutions lie at $+0.30$, $+0.52$, and $+0.70$. Figure 6 recasts the data of Figure 5 according to plots of the measured solution potential against the right-hand term of eq 2, which is calculated from the stoichiometric proportions as a function of MPC volume added. It can be seen that the variation of potential is indeed Nernstian, as expected from the theory for the formal redox behavior of charged MPCs, adding to our view^{2,5} that MPC solutions can be modeled as having discrete formal oxidation states. The slopes of the segments of Figure 6 are 70, 76, and 63 mV, going from more positive to more negative potentials. That the slopes are larger than the ideal 59 mV may be due to overlapping of formal potentials of minor populations of MPCs with different core sizes. It has been shown before¹⁹ that formal potentials of redox moieties attached to MPC monolayers are

(19) Green, S. J.; Pietron, J. J.; Stokes, J. J.; Hostetler, M. J.; Vu, H.; Wuelfing, W. P.; Murray, R. W. *Langmuir* 1998, 14, 5612–5619.

somewhat disperse, giving similar deviations from Nernstian behavior in their voltammetry. The DPV peaks in Figure 1 have full-width-at-half-maxima somewhat larger than the ideal²⁰ 90 mV, consistent with the larger slopes in Figure 6.

As a side note, the ease of mixing MPCs with different charges is a preparative route to solutions having desired states of MPC charge. One simply charges one MPC solution to a potential more positive (or negative) than the desired potential and then titrates this solution with one of equal MPC concentration but at an as-obtained (rest) potential, until the desired potential is reached. From our initial work, it should be possible to program MPC solution potentials in this manner to within roughly 10 mV.

Solubility Effects. We have noticed that charging of MPC cores can produce substantial changes in their solubility. While the details of this are somewhat scanty at present, some data gathered are summarized in Table 1. The general effect of charging at positive potentials is to decrease solubility in nonpolar relative to polar solvents. In previous studies in which the monolayers of MPCs have been variously functionalized, sizable change in solubility have appeared. The present results show that the charge on the metal core itself plays a significant role as well. Polar substituents of monolayers cause solubility changes analogous to that of positive core charging.

Conclusions

The primary conclusion of this paper is that electronic charges associated with double layer charges of MPCs can be used in

(20) Reference 8a, p 195.

Table 1. Solubility Change of C6 MPCs upon Charging to a +6 State

| solvent | native C6 MPC, soluble? | MPC charged to ca. +0.70 V (MPC ⁶⁺), soluble? |
|-------------------|-------------------------|-----------------------------------------------------------|
| acetonitrile | no | yes |
| methanol | no | no |
| ethanol | sparingly | no |
| dimethylformamide | no | yes |
| acetone | yes | yes |
| water | no | no |
| toluene | yes | no |

a controllable and quantifiable way to drive electron transfer reactions. These electronic charges are isolable and storable in a dry state. They differ from molecular redox chemistry in having numerous, regularly spaced redox-like formal potentials and in their solutions being continuously adjustable through the succession of formal potentials to a desired charge state. Charges on Au MPC core charges that are stabilized by alkanethiolate monolayers are likely to undergo electron transfers whose rates are controlled solely by reaction free energies and outer sphere²¹ reorganizational energy barriers. These reactions are thus likely to be quite fast, and furthermore unselective in terms of chemical specificity toward reaction substrates. In this sense, charged MPCs are a "pure" source of electronic charges for electron transfer reactions.

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