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# Spectral Diffusion in the Tunneling Spectra of Ligand-Stabilized Undecagold Clusters

Rachel K. Smith,[†,§] Sanjini U. Nanayakkara,[†] Gerd H. Woehrle,[¶,‡] Thomas P. Pearl,[£]
Meaghan M. Blake,[†] James E. Hutchison,[¶] and Paul S. Weiss*,[†]

*Departments of Chemistry and Physics, 104 Davey Laboratory, The Pennsylvania State University,*
*University Park, Pennsylvania 16802-6300, Department of Chemistry and Materials Science Institute,*
*1253 University of Oregon, Eugene, Oregon 97403-1253, and Department of Physics, North Carolina State*
*University, Raleigh, North Carolina 27695-7518*

Received February 13, 2006; E-mail: stm@psu.edu

Recent experimental and theoretical studies have shown that single electron transport through nanometer-scale particles is complex, and that the conductance may depend heavily on the particles' chemical and physical environment.[1] We have constructed precise assemblies of ligand-stabilized, undecagold clusters ($Au_{11}$) attached to 1,10-decanedithiolate (1,10-DDT) tethers inserted into *n*-octanethiolate (C8) host self-assembled monolayers (SAMs). We have measured their conductance properties with an ultrastable scanning tunneling microscope (STM)[2] operating at cryogenic temperatures (4.2 K) and at high gap impedances (>100 GΩ) to minimize environmental coupling factors. Even though this system is more chemically defined than those previously reported, with precise control of both cluster size and chemistry and the spatial distribution of tethers and clusters, we observe reversible diffusion in the conductance spectra across both *single* and multiple clusters. The spectra show considerable variability in the Coulomb blockade region (current suppression at low bias), as well as shifting in the energies of the conductance resonances, that is, spectral diffusion.

The charge transport dynamics of metal nanoparticles are of considerable interest for fundamental and application-based areas of nanoscience, from molecular-scale circuitry to sensing. Coulomb blockade has been reported previously on a variety of particle systems (i.e., sizes, materials, junctions), often measured in either dense particle arrays directly deposited onto surfaces with no decoupling electrical barriers or affixed to ill-defined or cross-linking SAMs with little potential for mobility.[3−5] Here, we present a system of experiments, creating well-defined interfaces where the exact structure of the particle is known (here, the $Au_{11}$ cluster), where we have investigated two ligand shells while retaining the same core size, and where we have created the highest quality of substrate support with pendant thiols inserted into an insulating host matrix. We propose that $Au_{11}$ possesses an electronic character that is more "molecular" in nature than larger nanoparticle analogues (supported by both electrochemical and electron relaxation dynamic studies[6]), and that its conductance spectra show discrete electronic states mixed with classical Coulomb blockade behavior. Similar findings have been reported for triphenylphosphine (TPP)-stabilized $Au_{55}$ particles deposited on weakly interacting graphite substrates; the results indicated that the charging states of the particle were convolved with confinement effects as well as "impurity" states arising from the ligand shell.[7]

$Au_{11}(PPh_3)_7Cl_3$ ($Au_{11}$−TPP) and $Au_{11}(S(CH_2)_7CH_3)_{10}$ ($Au_{11}$−C8) were synthesized in the solution phases,[8] and clusters were tethered to C8 SAMs grown on Au{111} with inserted 1,10-DDT at low fractional surface coverage (Figure 1 and Supporting Information). Figure 1 shows molecular resolution of the SAM lattice as well as the particle's location at a film defect site (Au step edge); missing C8s were observed near this defect, with desorption presumably occurring upon exposure to the deposition solutions.[9] We measured the conductance of isolated $Au_{11}$−TPP and $Au_{11}$−C8, acquiring the differential conductance (d*I*/d*V*, which follows the system's local density of states) simultaneously with the current−voltage [$I(V)$], using phase-sensitive detection. While these particles were immobilized atop the SAM, we hypothesize that these assemblies may be sufficiently dynamic to influence their transport properties significantly (*vide infra*).

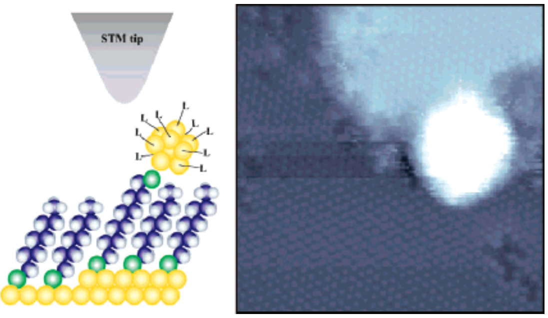

***Figure 1.*** (Left) Schematic of ligand (L)-stabilized $Au_{11}$ cluster immobilized via a 1,10-DDT tether inserted into a C8 SAM. (Right) A 157 Å × 157 Å STM image of a $Au_{11}$−TPP attached at a Au step edge. The location of the cluster, as well as the molecular lattice of the host SAM, can be easily resolved ($V_{sample} = +1.5$ V, $i_{tunnel} = 14$ pA, $T = 4.2$ K).

This hypothesis is supported by the observation of diffusion in the conductance resonances of the tunneling spectra of tethered $Au_{11}$ clusters; we observe significant spectral diffusion in a *single* cluster, as well as across multiple isolated $Au_{11}$. The observed results were independent of tunneling conditions; widely varying spectra were obtained for identical setpoint conditions (i.e., tunnel currents, bias voltages). A compilation of 22 representative tunneling spectra for the $Au_{11}$−TPP is presented in Figure 2. For clarity, two spectra (n and q) are shown, illustrating that the color scale of the compilation spectra corresponds to the intensities of the d*I*/d*V* resonances. While Figure 2 is specific to one cluster, spectral diffusion was observed for other $Au_{11}$−TPP and $Au_{11}$−C8, as well. *Reversible* spectral diffusion and hopping were observed by reversible interchange of small, intermediate, and large regions of zero conductance (see Supporting Information).

As shown in Figure 2, there appeared to be neither irreversible damage nor perturbation to the clusters. The widths of the region of zero conductance (before the first charging steps) spanned an order of magnitude, from 0.2 V (t) to greater than 2.5 V (a); a

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[†] The Pennsylvania State University.
[¶] University of Oregon.
[£] North Carolina State University.
[§] Current address: Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.
[‡] Current address: Abbott GmbH & Co. KG, Knollstrasse 50, 67008 Ludwigshafen, Germany.

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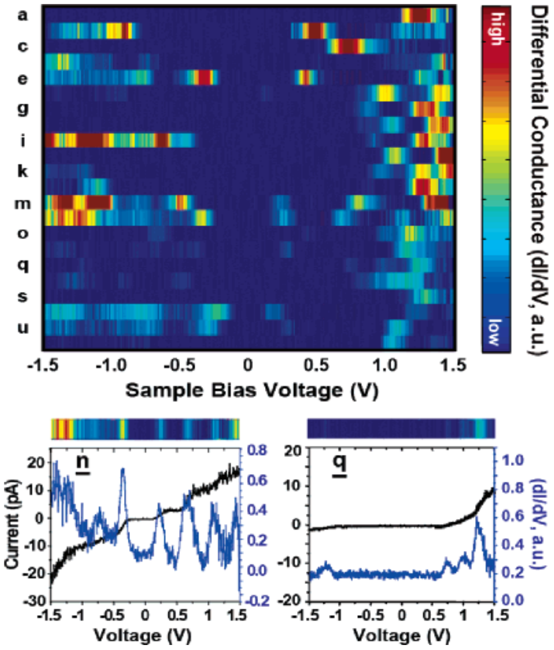

***Figure 2.*** (Top) A compilation of conductance spectra acquired over the center of the $Au_{11}$−TPP shown in Figure 1. Representative spectra (a−v, horizontal bands) are plotted with d$I$/d$V$ magnitude scaled in color (d$I$/d$V$ $\geq$ 1 au saturated). This emphasizes the appearance and disappearance of conductance resonances, their shifts in energies, as well as resonance widths. (Bottom) Two individual spectra (bands n and q in the top figure) current−voltage data ($I(V)$, black) are plotted with the simultaneously acquired d$I$/d$V$ data (blue). $V_{\text{sample}} = +1.5$ V; $i_{\text{tunnel}} = 18$ pA (n), 9 pA (q).

variety of plateau widths between charging steps also were found. On the basis of geometric models of the cluster and the junction thickness, we expect the capacitance of $Au_{11}$−TPP to be ~0.15 aF, a zero conductance width of ~1.3 V, and charging step widths of ~1 V. The monodisperse cluster size should, in principle, exhibit a uniform spectral response, but in the limit of isolated, chemically anchored particles, we observed different behavior. Additional observations included spatial dependence for the conductance spectra, but there was no obvious correlation between spectral diffusion and the acquisition location on the cluster. The observed fluctuation of the asymmetry of d$I$/d$V$ resonances around 0 V is consistent with variable background charge on the cluster.[10] The spectral hopping rate exceeded the time scale of STM measurements.

Several mechanisms may be responsible for the observed diffusion in the conductance spectra. Contributions to the diffusion may include the ligand shell (and whether a ligand may be within the tunneling junction), fluctuations in the attachment of the cluster to the SAM support, or fluctuations in the electrostatic environment of the particle. As spectral diffusion occurs for both $Au_{11}$−TPP and $Au_{11}$−C8 clusters (with ligands having energy states inside and out of the energy range of interest, respectively), the diffusion is not ligand-specific. We observe states in this range particular to the TPP ligand (i.e., 0.25 V), verified by the general disappearance of that resonance in the $Au_{11}$−C8 sample. Images do not show any change in the shapes or apparent heights of the clusters (ligand shell not resolved).

Significant electrostatic forces are present in the tip−sample junction. The high electric field of the STM tip exerts a force on the cluster, distorting the connection to its thiol tether and changing the transmission characteristics of the assembly. Even though the SAM has very low corrugation, it too is susceptible to compression by the probe tip even though low tunneling currents were used to avoid adverse tip−sample interactions (5−20 pA).[11] The SAM compresses elastically under forces of these magnitudes (~100 pN), and the particle can oscillate in concert with charge transfer events when connected to the substrate by "soft" linkers, such as alkanethiolates.[12] Assuming that the capacitive coupling to the cluster with the tip was constant, there may be shifts in the charging steps if the cluster−substrate distance changes with distortion in the SAM or tether underneath the $Au_{11}$ when the cluster is probed. Any geometrical changes of the particle near the surface due to mobility or tether compression would induce changes in the junction's behavior. The locations of the $Au_{11}$ are dictated by the dithiol tethers, which preferentially adsorb at defect sites in the SAM; thus, the clusters were not immobilized with an entirely crystalline SAM matrix underneath for electrical isolation. Notably, we saw no measurable change in the apparent height of the $Au_{11}$ relative to the SAM across the tunneling spectra. We are currently testing the mechanism of conductance change as a function of tether flexibility using an aromatic tether.

We report spectral diffusion in tethered $Au_{11}$ supported atop alkanethiolate SAMs and have demonstrated that the conductance of these particles is more complex and subtle than has been previously reported. Although precisely constructed and controlled, this spectral diffusion demonstrates the acute sensitivity of these nanoscale structures to their environment. While nanoscale structures created by self-assembly techniques have concomitant electronic and conformational dynamics that must be accounted for when integrated into molecule-based architectures, this behavior may allow for the development of sensors with unprecedented sensitivity. This diffusion provides opportunities for significant advances in physical chemistry, as the quantum effects dominating many aspects of charge transport through particles in junctions are beginning to be understood through both theory and experiment.[1,13]

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**Supporting Information Available:** Experimental procedures and supplementary spectroscopy material. This material is available free of charge via the Internet at http://pubs.acs.org.

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