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Gold Nanoparticles

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Ligand Control over the Electronic Properties within the Metallic Core of Gold Nanoparticles

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Abstract: *The behavior of electrons within the metallic core of gold nanoparticles (AuNPs) can be controlled by the nature of the surface chemistry of the AuNPs. Specifically, the conduction electron spin resonance (CESR) spectra of AuNPs of diameter 1.8–1.9 nm are sensitive to ligand exchange of hexanethiol for 4-bromothiophenol on the surface of the nanoparticle. Chemisorption of the aromatic ligand leads to a shift in the metallic electron's g-factor toward the value expected for pure gold systems, suggesting an increase in metallic character for the electrons within the gold core. Analysis by UV/Vis absorption spectroscopy reveals a concomitant bathochromic shift of the surface plasmon resonance band of the AuNP, indicating that other electronic properties of AuNPs are also affected by the ligand exchange. In total, our results demonstrate that the chemical nature of the ligand controls the valence band structure of AuNPs.*

Nanomaterials are valued for their unique optical, electrical, thermal, and magnetic properties, which can be readily tuned for a wide range of applications. It has long been recognized that this tunability rests upon the sensitivity of the nanostructures to changes in size, geometry, crystalline phase, and composition.[1] However, recent work has employed surface chemistry to control the electronic properties of nanoparticles.[2] In particular, the electronic properties of semiconductor nanocrystals can be tuned with high precision by simple chemical modification of the ligand coordination sphere.[2a] In a concise study, Weiss and co-workers were able to demonstrate that increasing the electron-withdrawing strength of the *para* substituent on chemisorbed phenyldithiocarbamates led to an increase in the apparent excitonic hole radius (up to 0.4 nm) of CdSe quantum dots (QDs).[2a] They attributed this finding to the generation of ligand–QD hybrid bands formed by the interfacial mixing of the ligand's highest-occupied molecular orbital and the QD's valence band. Studies such as this have led to a growing awareness of how the nature of chemisorbed ligands control the electronic structure of nanomaterials; however, there is a paucity of experimental work extending these design principles to metallic nanosystems, and it remains unclear if ligands will exert strong control over the electronic properties of such systems. Herein, we address this discrepancy by demonstrating that minor changes to the ligand coordination sphere of gold nanoparticles (AuNPs) induce large changes in the electronic properties of the nanocrystals. This was determined by conduction electron spin resonance (CESR), an ESR technique sensitive to and selective for the behavior of valence band electrons near the Fermi level (E_F) of the metallic systems—the set of electronic states with a 50% chance of being occupied at any temperature.

Gold nanoparticles provide an excellent test bed for establishing the electronic ramifications of changes to the surface chemistry, as AuNPs are stable and have robust and flexible surface chemistry. Additionally, AuNPs are ubiquitous throughout science and engineering, with growing potential as photocatalysts, photosensitizers in plasmonic solar cells, chemical sensors, bio-imaging agents, and components of molecular electronics, to name a few.[3] All of these applications rely upon the electronic properties of the gold core, but also use the ligand sphere to tune the chemical behavior of the particles. Thus, it will be useful to understand the extent to which the electronic properties of the core are dependent upon the nature of the ligand sphere. Prior experimental work on AuNPs has only demonstrated that gross changes in the ligand head group that binds to gold (amine versus thiolate: effectively testing the difference between physisorbed and chemisorbed ligands) can alter the surface plasmon resonance (SPR), electron–phonon coupling, or magnetic properties.[2b,4] In contrast, the effects of more subtle changes to ligand structure (e.g. tail group variation or aliphatic versus aromatic thiolates) often employed in tuning the properties of the ligand sphere have not been demonstrated, despite theoretical studies which suggest that such subtle changes are strong enough to perturb the electronic band structure of AuNPs.[2c]

We chose thiolate-protected AuNPs to study the effect of ligands on the electronic properties of gold nanoparticles as they can be prepared with reasonable monodispersity and postsynthetic modification of alkylthiolate-protected particles is straightforward and proceeds with excellent control over the size of the metal core. For this study, hexanethiolate-protected AuNPs (referred to as C6) were prepared by the two-phase Brust synthesis (see the Supporting Information).[5] We then used 50% of the total product from this initial synthesis for a ligand exchange (Figure 1a) with 4-bromothiophenol, performed in THF for three hours, to give mixed-monolayer hexanethiolate/4-bromothiophenolate-protected AuNPs (referred to as C6/Br). In Figure 1a we have assumed that the ligands in both the C6 and C6/Br particles are attached using the staple motif because this binding mode has been shown to dominate attachment of thiolates to gold nanoparticles[2c] (and to be preserved during ligand exchange reactions with 4-bromothiophenol).[6]

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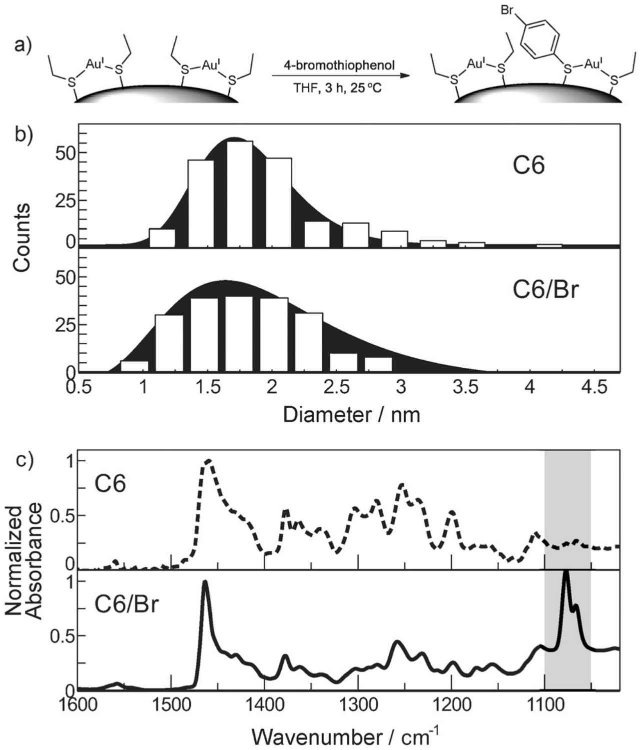

Figure 1. a) Synthesis of C6/Br AuNPs from C6 AuNPs and b) their respective histograms for diameter distributions (determined by TEM) fit to lognormal plots. Also shown are c) normalized IR spectra for C6 and C6/Br. The shaded region is the most diagnostic for ligand exchange. In (a), four methylene groups have been omitted for clarity.

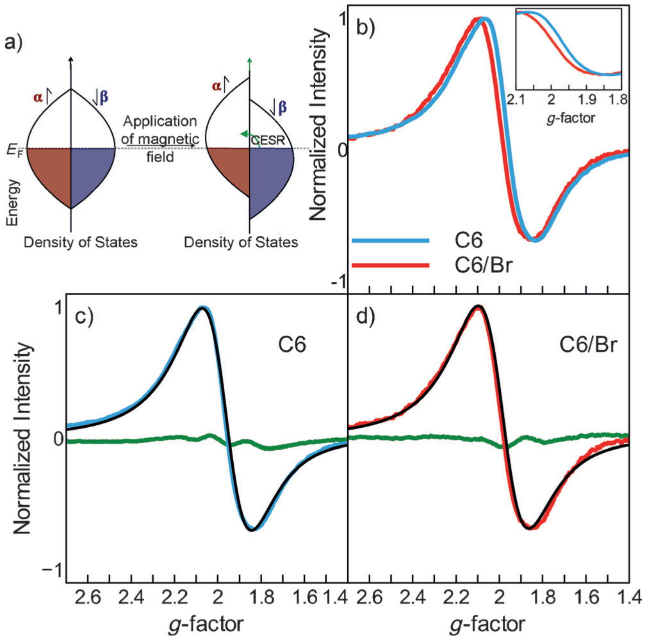

Figure 2. a) Schematic of Pauli paramagnetism and the associated CESR spin flip, b) X-band CESR spectra of C6 (blue) and C6/Br (red; inset shows the spectral shift) measured at 25 K, and fits of experimental CESR spectra for c) C6 and d) C6/Br to Equation S1 in the Supporting Information. In (c) and (d), the red and blue lines show the experimental data, the black line is the fit, and the green line is the residual of these fits.

Sizing of the parent and ligand-exchanged particles was accomplished using TEM (see the Supporting Information for images) and fitting of the resulting distribution to a lognormal equation revealed that the parent particles exhibited a mean diameter (and associated standard deviation) of 1.8(0.2) nm, whereas the mean size (and standard deviation) of the surface-modified particles is 1.9(0.4) nm (Figure 1 b). Vibrational spectroscopic analysis verified the success of ligand exchange (see Figure 1 c for the IR spectra and Figure S2 in the Supporting Information for Raman spectra); the product showed bands characteristic of 4-bromothiophenol at 1557, 1176, 1077, and 1066 cm^{-1}.[7a] The vibrational bands at 1066 and 1077 cm^{-1} (shaded region, Figure 1 c) are most clearly seen in the IR spectrum, whereas the modes at 1557 and 1176 cm^{-1} are more clearly detected in the Raman spectrum (see the Supporting Information). Finally, a standard NMR approach[7b] was utilized to quantify the relative ratio of 4-bromothiophenolate to hexanethiolate ligands on the mixed monolayer particles as 1:6.4, or 16 % 4-bromothiophenolate (see the Supporting Information).

We next used CESR to probe the effect of the ligand environment on the electronic properties of the gold core. As mentioned above, CESR is selective for (and sensitive to) the properties of the metallic electrons near the E_F level.[8] The sensitivity and selectivity of CESR has its basis in the Pauli paramagnetism of metals. Briefly, metals may be approximated as a rigid lattice of cations suspended in a “sea” of delocalized electrons that diffuse with Brownian motion, act independent of one another, and are arranged in a near-continuous collection of electronic states held within two spin manifolds (α and β), as shown in Figure 2 a. For diamagnetic metals (such as gold), the spin states are degenerate; however, upon application of an external magnetic field, the degeneracy between spins is lifted (Zeeman splitting). Preservation of a constant Fermi level across the spin manifolds results in an asymmetry in the number of electron spins aligned parallel (α) and anti-parallel (β) to the applied field (Figure 2 a), thus giving rise to paramagnetism. Because the spin flip probed by CESR must proceed between identical electronic states in the α and β manifolds, CESR naturally probes only those electrons in states near the E_F. As a result of the dispersive nature of metallic systems, the detected CESR line shape is asymmetric and may be approximated as a linear combination of the first derivative of both absorptive and dispersive Lorentzian curves (a combination known as a Dysonian line shape). By fitting CESR spectra to this line shape, we obtain the spin lifetime (T_2) and electron g-factor from the full-width-at-half-maximum (FWHM) and resonance position of the spectra, respectively.

Figure 2 shows the continuous wave X-band ESR spectra collected at 25 K for solutions of the two AuNPs in THF. Also shown are fits of these spectra to the Dysonian line shape (black) and the residuals from these fits (green). Table 1 summarizes the parameters extracted from the fits. It is important to note that (as shown in the Supporting Information) a CESR simulation that explicitly accounts for the distribution of sizes shown in Figure 1 b provides a near

Table 1: Diameter, CESR data, and SPR of C6 and C6/Br AuNPs.

	Diameter [nm][a]	T_2 [ns]	g-factor	SPR [eV]
C6	1.8 (0.2)	1.02 ± 0.01	1.978 ± 0.001	2.376 ± 0.001
C6/Br	1.9 (0.4)	1.02 ± 0.01	2.004 ± 0.001	2.342 ± 0.001

[a] The standard deviation for the diameters is given in parentheses.

identical spectrum to the one assuming a single average size, and so we use the single-average-size treatment when analyzing our data. A discussion of the fitting process, the expression for the Dysonian line shape, and the estimation of error associated with these measurements can be found in the Supporting Information.

Beginning with the extracted spin lifetimes, we find that the T_2 value for both the C6 and C6/Br AuNPs is 1.02 ± 0.01 ns. As the CESR spectra were acquired below the Debye temperature (170 K), spin relaxation occurs primarily via collisions with lattice defects and, for small particles, the dominant lattice defect is the surface of the particle.[8a] Thus, the identical values of spin lifetimes between the two systems are likely because of their near identical diameters.

In contrast to the similarities between spin lifetimes, the resonance position for the C6/Br AuNPs shows a clear shift to lower magnetic field relative to the C6 AuNPs, and the electronic *g*-factor was found to be 1.978 ± 0.001 and 2.004 ± 0.001 for C6 and C6/Br, respectively. While there is a known size dependence of the *g*-factor for small metallic systems,[9] the difference we observe is far outside the expected difference between particles of 1.9 nm and 1.8 nm sizes ($\Delta g = 0.001$). Thus the detected *g*-factors reveal a significant change in the properties of electrons within the metallic core of the AuNPs, caused by a partial change in the ligand set at the surface of the particles. The range in *g*-factors that can be accessed by pure gold systems is about 0.096 (bulk gold and atomic gold have *g*-factors of 2.1 and 2.0041, respectively).[9] The change in *g*-factor associated with partial exchange of aromatic for aliphatic ligands is 27% of this range, highlighting the large effect that the surface ligands exert over the properties of the electrons in the metal core.

Given this large change in the electronic behavior, it was important to verify if its origin lay in the exchange of aliphatic for aromatic ligands, rather than a simple restructuring of the surface during ligand exchange. To this end, we performed a control experiment, in which parent C6 particles underwent ligand exchange with additional C6 ligands (i.e. a homoexchange reaction). As can be seen in the Supporting Information, this exchange reaction produced particles that had a *g*-factor (1.979 ± 0.001) within error of the as-synthesized C6 particles (1.978 ± 0.001), indicating that it is the chemisorption of 4-bromothiophenolate that gives rise to the large change in *g*-factor.

The large change in *g*-factor is indicative of a change in the chemical environment experienced by the metal's valence electrons. In the absence of strong spin–spin interaction between unpaired electrons, spin–orbit coupling is the dominant contributor to any deviation of the *g*-factor from the free electron value ($g_e \approx 2.0023$). The spin–orbit coupling, in turn, depends upon the identity and relative energetic ordering of the orbitals involved in the paramagnetic system.[10] Thus, changes in the *g*-factor are a direct indication that the electronic structure (orbital identity, orbital energy) experienced by the electrons near the E_F level has changed, and our detected changes in the *g*-factor for C6 versus C6/Br systems is a direct indication that the ligands perturb the electronic structure experienced by the valence band electrons.

Another aspect of these measurements worthy of comment is that our measured *g*-factors are significantly different to that expected for pure metallic gold particles of 1.9 nm or 1.8 nm diameters ($g \approx 2.06$),[9] though of the two systems we examined, the *g*-factor for the AuNPs containing aromatic ligands is closer to that for pure gold.[9] From this, we find it likely that the interfacial mixing of the orbitals of the aromatic ligands contribute less to the electronic structure near E_F than do the orbitals associated with the alkyl ligands, leading to a higher contribution of gold-based orbital character at this energy. Prior computational work investigating the density of states of smaller gold systems has, in fact, revealed that replacement of aliphatic ligands with aromatic ligands results in an increase in the relative contribution of gold-based states to the total density of states near the E_F level, providing qualitative support to our hypothesis.[2c] However, further quantitative support will require detailed modeling of the complete nanoparticle systems, as a result of the fact that the precise value of the *g*-factor is extremely sensitive to the nature (i.e. angular momentum) and relative energy of the orbitals near the unpaired electron.

The above observations clearly demonstrate that the chemical nature of the surface ligand is capable of modulating the properties of electrons near the E_F level. For this reason, we thought it reasonable to assume that other properties associated with the metallic electrons should be responsive to a change in the ligand set. To test this hypothesis, we isolated the surface plasmon resonance (SPR) band from the UV/Vis spectra of our AuNPs (Figure 3; see the Supporting Information for methods). The SPR is the most exploited physical property of nanoscale gold and so understanding the sensitivity of the SPR to the ligand set carries implications across multiple fields. Though the mean size of the AuNPs we examined are quite small, we note that the same metallic electrons that give rise to the SPR are responsible for the CESR, and the presence of an SPR band and a CESR signal are expected to be co-indicative. Furthermore, we note that for all particles we examined, the distribution of sizes extended to at least 3 nm diameters—a size that clearly has a SPR. Thus, it is possible that our CESR and UV/Vis spectra are reporting on the subpopulation of larger particles. Future work will explore this possibility, but the present work clearly shows that the measured properties of the nanoparticles depend upon the ligand set.

Fitting of the isolated SPR bands (Figure 3, inset; see the Supporting Information for details) allowed extraction of the λ_{max} value for the resonance, which showed a slight red-shift of the SPR upon ligand exchange (2.376 ± 0.001 eV to 2.342 ± 0.001 eV). Although, in general for AuNPs, a red-shift in the SPR is correlated with an increase in the particle diameter or increase in the refractive index of the environment, for

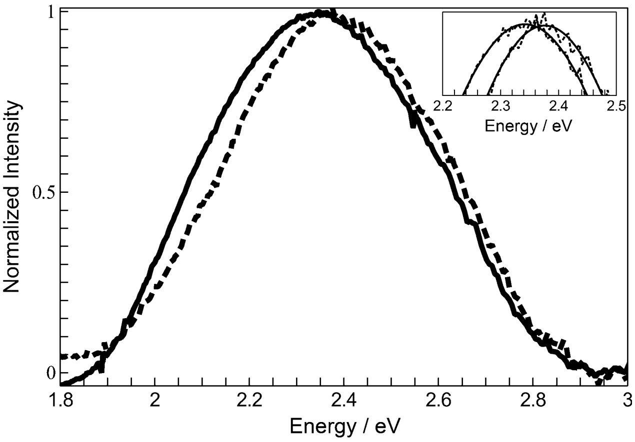

Figure 3. Isolated SPR bands for C6 (dashed line) and C6/Br (solid line). Inset: the experimental spectra (dashed line) and Gaussian curves (solid line) fit to these data.

alkanethiolate-protected AuNPs with diameters below 5.2 nm, the SPR has been shown to be insensitive to size and refractive index.[11,12] Therefore, we conclude that it is the changes in the surface chemistry that control the changes in the position of the SPR in our systems, and that the shift of the SPR detected indicates a fundamental change in the behavior of the metallic electrons. This conclusion supports our interpretation that the ligands control the electronic properties within the gold core.

In conclusion, nanoscale materials offer a wide array of tunability in their electronic properties, attainable through changes in size, geometry, crystalline phase, dopants, and surface chemistry—the latter of which is a relatively new area of study. This report marks one of the first experimental studies investigating the effects of the ligand tail group (alkyl versus aromatic) upon the electronic properties within the core of metallic nanoparticles. Further experimental and theoretical work will be needed to elucidate the exact relationship between ligand properties, CESR spectra, and UV/Vis spectra; however, this report clearly demonstrates that the electronic properties of the AuNP's metal core are quite sensitive to subtle changes in the surface chemistry of the AuNP.

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Keywords: electron spin resonance · gold · ligand exchange · nanoparticles · surface plasmon resonance

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