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# Molecular Electron-Transfer Properties of $Au_{38}$ Clusters

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Formation of thiolate self-assembled monolayers is employed to limit the growth of gold nanoparticles to a restricted number of atoms, allowing the preparation of monolayer-protected clusters (MPCs).[1,2] The transition between bulk and molecule-like regimes, where electronic-band energetics lead to quantum confinement effects, is observed for MPCs smaller than a few nanometers. The cyclic voltammetry (CV) or differential pulse voltammetry (DPV) of MPCs displaying molecule-like properties (core diameters <1.5 nm)[1,3] is characterized by a size-dependent number of oxidation and reduction peaks. The $Au_{38}$ cluster, which has a core diameter of ~1.1 nm, is the most representative example of this class of MPCs.[4−7] $Au_{38}$ clusters are conveniently prepared in the presence of phenylethanethiol and have the average formula $Au_{38}(SR)_{24}$ (R = $(CH_2)_2Ph$).[8] The separation between the potentials of the +1/0 and 0/−1 peaks has been related to the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO−LUMO).[4a−d] The peaks significantly shift when the monolayer is modified with substituted thiophenols[4d] or peptides with an oriented molecular dipole moment.[7] Several aspects of the redox behavior of $Au_{38}$ clusters, however, are still unexplored. Which are the redox properties of $Au_{38}$ clusters as electron-transfer (ET) acceptors or donors at electrode surfaces? And as ET reagents with redox partners in solution? When charged, are these clusters sufficiently stable to be employed as redox reagents? What specific reorganization is involved in the electron uptake or release? Here we address these questions through analysis of the results obtained by using direct and indirect electrochemical methods.

The ET behavior of $Au_{38}(SR)_{24}$ was studied on both glassy carbon (GC) and Pt electrodes in *N*,*N*-dimethylformamide (DMF) and dichloromethane (DCM) containing 0.1 M $Bu_4NPF_6$.[9] The CVs of the first two oxidations (O1, +1/0; O2, +2/+1) and first reduction (R1, 0/−1) are illustrated in Figure 1. As one goes from DCM to DMF, the positive shift of the peaks is substantial and the separation between O1 and O2 decreases from 303 to 200 mV. This is in keeping with the expected effect exerted by switching to a more polar environment.[4b] At low scan rates ($v$) and for both peaks, the separation between the anodic and the cathodic peak potentials ($\Delta E_p$) exhibits the reversible value of ~60 mV.[10] $\Delta E_p$ increases only for sufficiently high $v$ values, and the effect is more pronounced for the second peak and in DCM. No significant difference between GC and Pt was observed. The diffusion coefficient ($D$) of $Au_{38}(SR)_{24}$ was calculated from peak current ($i_p$)[10] and convolution analysis[11] measurements of peak O1 (differences are <2%). The average values (GC and Pt) are $1.92 \times 10^{-6}$ (DMF) and $3.53 \times 10^{-6}$ $cm^2\ s^{-1}$ (DCM).[12] By using the Stokes−Einstein equation ($D = k_BT/6\pi\eta r$, where $k_B$ is the Boltzmann constant, $\eta$ is the solvent viscosity, and $r$ is the molecular radius), $r$ values of 14.2 (DMF) and 15.3 Å (DCM) ensue, in good agreement with the value of 13.7 Å estimated from the $Au_{38}$ core diameter and monolayer thickness.

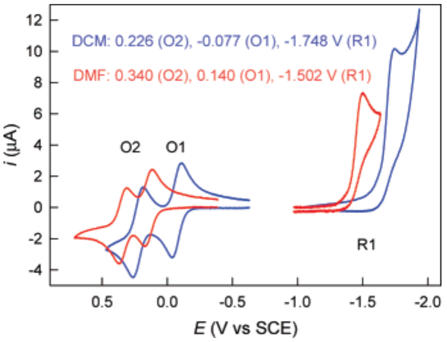

***Figure 1.*** Background-subtracted CVs of 1 mM $Au_{38}$ in DMF (red) or DCM (blue) containing 0.1 M $Bu_4NPF_6$. The potentials refer to $E°$s (O1 and O2) or $E_p$ (R1). The $E°$s are equal (<2 mV) to those obtained on Pt or from DPV. Conditions: $v = 0.2$ V $s^{-1}$, GC electrode, 25 °C.

Peak R1 is irreversible. By increasing $v$ in the range of 0.1−10 V $s^{-1}$, $E_p$ shifts toward more negative potentials by 32 ± 5 mV/log $v$ (GC, DMF), indicating fast ET and following chemical reaction/s. The ratio $i_p/v^{1/2}$ increases as $v$ decreases, which implies that the number of electrons per molecule ($n$) also (calculated using for reference the $i_p/v^{1/2}$ of O1) increases significantly; in either solvent $n \approx 3.5$ at 0.1 V $s^{-1}$. As expected, the irreversibility of R1 is temperature dependent. When the CV experiments were carried out in DMF at −48 °C, reversibility and thus $n = 1$ was attained at ~3 V $s^{-1}$. These results indicate that initial ET triggers a cascade of chemical and electrochemical steps, causing $n$ to increase rapidly as $v$ decreases and/or $T$ increases. The reduction mechanism is ascribed to a sequence of stepwise dissociative ETs,[13] as $Au_{38}(SR)_{24}$ may be viewed as a molecule equipped with a series of identical leaving groups, $RS^-$. The initial steps of the reduction[14] can be described as follows,

$$Au_{38}(SR)_{24} + e \rightleftarrows Au_{38}(SR)_{24}^- \qquad (1)$$

$$Au_{38}(SR)_{24}^- \rightarrow Au_{38}(SR)_{23} + RS^- \qquad (2)$$

$$Au_{38}(SR)_{23} + e \rightleftarrows Au_{38}(SR)_{23}^- \qquad \text{etc.} \qquad (3)$$

in which the initial ETs and Au−S bond cleavage steps have essentially the same $E°$ and rate constants, respectively. At low $v$, as much as three ligands are thus stripped off. To provide support to this mechanism, we carried out a CV study of disulfide ($Ph(CH_2)_2S)_2$. As for other disulfides,[13b] its voltammetric reduction generates $Ph(CH_2)_2S^-$ ions in a stepwise dissociative ET; oxidation of the anion is detected at more positive potentials on the backward CV scan. The oxidation pattern of the disulfide was consistent with the corresponding behavior observed in the same $E$ range after reduction of $Au_{38}(SR)_{24}$ (not shown in Figure 1: for the pertinent CVs, see Supporting Information).

The standard heterogeneous rate constants ($k°$) at 25 °C were obtained with microelectrodes from the $v$ dependence of $\Delta E_p$[15] and digital simulation (Supporting Information). Table 1 shows that the $k°$ values of O1 are typical of common outer-sphere acceptors or

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**Table 1.** Standard Rate Constants (cm s$^{-1}$) and Energy Barriers (kcal mol$^{-1}$) for Oxidation and Reduction of $Au_{38}(SR)_{24}$ Clusters on GC at 25 °C

| solvent | log $k°_{O1}$ | log $k°_{R1}$ | $\Delta G_0^{\ddagger}{}_{O1}$ | $\Delta G_{0,i}^{\ddagger}{}_{O1}$ | $\Delta G_0^{\ddagger}{}_{R1}$ | $\Delta G_{0,i}^{\ddagger}{}_{R1}$ |
|---|---|---|---|---|---|---|
| DMF | −0.89[a,b,c] | −1.19[b,d] | 5.0 | 3.6 | 5.4 | 4.0 |
| DCM | −1.00[a,b,c] | −1.52[b,e] | 5.2 | 4.2 | 5.9 | 4.9 |

[a] $\Delta E_p$ method. [b] Digital simulation. [c] Uncertainty is 15%. [d] Uncertainty is 20%. [e] Uncertainty is 25%.

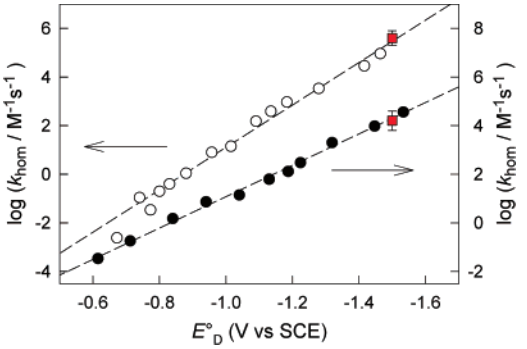

**Figure 2.** Homogeneous ET data to PhSSPh (○, left scale) and $PhCH_2Br$ (●, right scale) in DMF plotted against the donor $E°$. The $Au_{38}$ data (red blocks) are shown with their error bars. The lines are the best fit to the data in the activation region.

donors. $k°$ slightly decreases for O2 (DMF, log $k° = -1.10$) and in DCM. At −48 °C (DMF), log $k°_{O1}$ was calculated to be −2.21 (average of $\Delta E_p$, simulation, and convolution results). At −48 °C, we obtained −2.69 for log $k°_{R1}$ ($\Delta E_p$ and simulation). The O1−R1 log $k°$ difference is thus 0.5. At 25 °C, a slightly smaller difference (0.3 log units) was obtained by determining $k°_{R1}$ with digital simulation of peak R1 (Supporting Information). Noteworthy, $E°_{O1} - E°_{R1} = 1.64$ V in both DCM and DMF at 25 °C or in DMF at −48 °C. In terms of HOMO−LUMO band gap estimates,[4b] we obtain 1.44 (DMF) and 1.34 eV (DCM).

From the $k°$ values and using an Eyring-type equation ($k° = Z \exp(-\Delta G_0^{\ddagger}/RT)$), the ET intrinsic barriers ($\Delta G_0^{\ddagger}$ = activation free energy at $\Delta G° = 0$) were calculated (Table 1). $Z$ was calculated to be 605 cm$^{-1}$ ($Z = (RT/2\pi M)^{1/2}$, where $M$ is the molar mass). From the temperature study (−48 to 25 °C), we obtained a very similar prefactor, 560 cm$^{-1}$, and $\Delta G_0^{\ddagger}$, 5.2 kcal mol$^{-1}$: this shows that, despite the thickness of the monolayer through which the electron tunneling occurs, the ET is adiabatic. The inner reorganization energies ($\Delta G_{0,i}^{\ddagger}$) were obtained by subtracting the solvent reorganization term ($\Delta G_{0,s}^{\ddagger}$) from $\Delta G_0^{\ddagger}$; the $\Delta G_{0,s}^{\ddagger}$ values were calculated from the Hush equation.[16] At difference with common delocalized redox molecules, for which $\Delta G_{0,s}^{\ddagger}$ is typically 80% of $\Delta G_0^{\ddagger}$, 72−83% of the otherwise comparable $\Delta G_0^{\ddagger}$ values of $Au_{38}(SR)_{24}$ (O1 and R1) are due to $\Delta G_{0,i}^{\ddagger}$ (Table 1). This behavior can be explained by considering that both the HOMO and the LUMO should involve the core periphery and thus the Au−S bonds.[17] Electron release by or injection into the MPC would thus imply some variations of the relevant bond lengths, which, though small, are amplified by the number of ligands. Our solution-phase results are in agreement with very recent electron hopping data in dry, mixed-valent films of the same clusters.[18]

The R1 step is accompanied by a slightly larger $\Delta G_{0,i}^{\ddagger}$ than the O1 (and O2) step, but the total barrier is still small. Thanks to the CV analysis results obtained for R1, $Au_{38}(SR)_{24}$ could be used as an ET mediator in homogeneous redox catalysis experiments.[19] We used the reactive acceptors diphenyl disulfide[20] and benzyl bromide[21] to ensure that on the homogeneous ET time scale the competitive Au−S bond cleavage in anion $Au_{38}(SR)_{24}^-$ (lifetime ~4 ms) was appreciably slow. The ET rate constants ($k_{hom}$) were obtained by digital simulation (Supporting Information). Figure 2 compares these $k_{hom}$ values with those obtained by others using conventional one-electron donors.[20,21] Figure 2 convincingly illustrates that also from the viewpoint of homogeneous ETs, $Au_{38}(SR)_{24}$ behaves as a simple molecule and, when charged, as an efficient one-electron donor. With both acceptors, the $k_{hom}$ value correlates well with the other ET data and this also indicates that the contribution of $Au_{38}(SR)_{24}$ to the homogeneous $\Delta G_0^{\ddagger}$ is undistinguishable from that of the other donors.

Main conclusions of this study are thus as follows. (i) The heterogeneous and homogeneous ET kinetic results point to the same fast ET behavior typical of delocalized molecules. (ii) For both reduction and oxidation the (small) $\Delta G_0^{\ddagger}$ is primarily due to inner reorganization. (iii) Reduction of $Au_{38}(SR)_{24}$ proceeds by (the first case of) a multistep dissociative ET. (iv) When charged and depending on the ET time scale the clusters behave as efficient redox mediators. (v) $Au_{38}(SR)_{24}$ is thus a normal redox molecule; one main difference, however, is the possibility of functionalizing the MPC periphery by ligand place exchange,[4d,7] which could expand the range of applications of these electroactive species.

**Supporting Information Available:** Chemicals, electrochemical setup and methodologies, and further ET data. This material is available free of charge via the Internet at http://pubs.acs.org.

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