

Conductance of Single Cobalt Chalcogenide Cluster Junctions

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S Supporting Information

ABSTRACT: Understanding the electrical properties of semiconducting quantum dot devices have been limited due to the variability of their size/composition and the chemistry of ligand/electrode binding. Furthermore, to probe their electrical conduction properties and its dependence on ligand/electrode binding, measurements must be carried out at the single dot/cluster level. Herein we report scanning tunneling microscope based break junction measurements of cobalt chalcogenide clusters with Te, Se and S to probe the conductance properties. Our measured conductance trends show that the Co–Te based clusters have the highest conductance while the Co–S clusters the lowest. These trends are in very good agreement with cyclic voltammetry measurements of the first oxidation potentials and with density functional theory calculations of their HOMO–LUMO gaps.

Semiconductor quantum dots are useful in a multitude of materials and devices, but their application in single-dot devices has been limited primarily because of the coupled problems of the polydispersity in their size/composition and the multitude of sites for ligand/electrode binding. Despite these limitations, it has been shown that metal chalcogenides can be processed from solution into direct band gap absorbing layers.^{1,2} It is thus important to understand, at the single dot/cluster level, their electronic properties and dependence on ligand/electrode binding. Previous studies have elucidated the pathway for the formation of extended semiconducting solids through the synthesis of a series of metal chalcogenide clusters.³ Herein we report electrical transport measurements on junctions consisting of an atomically defined metal chalcogenide cluster bonded to two gold electrodes through Au–chalcogen bonds. The resulting conductance measurements were further investigated using cyclic voltammetry (CV) and density functional theory (DFT) calculations.

We chose atomically defined cobalt chalcogenide clusters for this initial study because these clusters have a wide solubility range and are relatively robust under ambient conditions. We synthesized the series of cobalt clusters $\text{Co}_6\text{Te}_8(\text{P}(\text{C}_2\text{H}_5)_3)_6$ (**1**), $\text{Co}_6\text{Se}_8(\text{P}(\text{C}_2\text{H}_5)_3)_6$ (**2**), and $\text{Co}_6\text{S}_8(\text{P}(\text{C}_2\text{H}_5)_3)_6$ (**3**) in 53–75% yield from one-pot reactions of $\text{Co}_2(\text{CO})_8$, the respective chalcogenides, and triethylphosphine in refluxing toluene using modified literature procedures.^{3b} The clusters were all isolated as pure crystalline solids. The UV–vis spectra illustrate the large absorption range of these clusters (see the Supporting

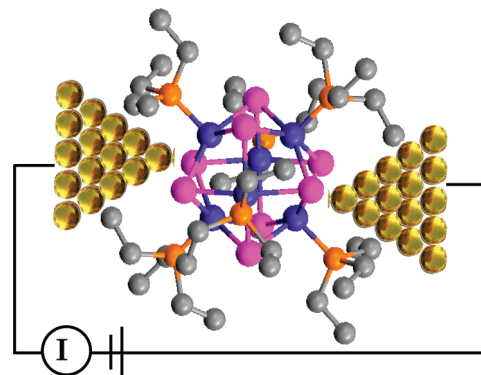


Figure 1. Illustration of the Au–1–Au junction to scale (trans binding).

Information). There is a progressive blue shift in the absorption in moving from Te to Se to S. This is expected because the decrease in the size of the chalcogenide and the delocalization of charge shift the absorbance to shorter wavelengths.

Electrical transport measurements were performed using the scanning tunneling microscopy (STM)-based break junction (STM-BJ) technique (see Figure 1 for a schematic).⁴ In this method, an Au point contact is first formed by bringing a Au tip in contact with a Au substrate. It is then pulled apart and broken in a solution of the analyte while the current is measured as a function of relative tip/sample displacement, yielding conductance (current/voltage)-versus-displacement traces. We illustrated the technique with the three molecules benzo[1,2-*b*:5-*b'*]ditellurophene (**4**), benzo[1,2-*b*:4,5-*b'*]diselenophene (**5**), and benzo[1,2-*b*:4,5-*b'*]dithiophene (**6**)⁵ to demonstrate binding of the chalcogen to Au.⁶ In the inset of Figure 2, we show sample conductance traces for **4**, **5**, and **6**; clear conductance plateaus can be seen near $10^{-2}G_0$, where $G_0 = 2e^2/h$ is the quantum of conductance. Conductance histograms constructed without any data selection (Figure 2) revealed a peak at a molecule-dependent value below G_0 . In addition, we also observed peaks at multiples of G_0 for **5** and **6**. Interestingly, however, these were absent for **4**, perhaps as a result of a strong interaction between Te and Au. A trend of conductance with chalcogenide was also observed: the tellurium-containing molecule **4** showed the highest conductance and the sulfur-containing molecule **6** the lowest. This trend in conductance behavior has

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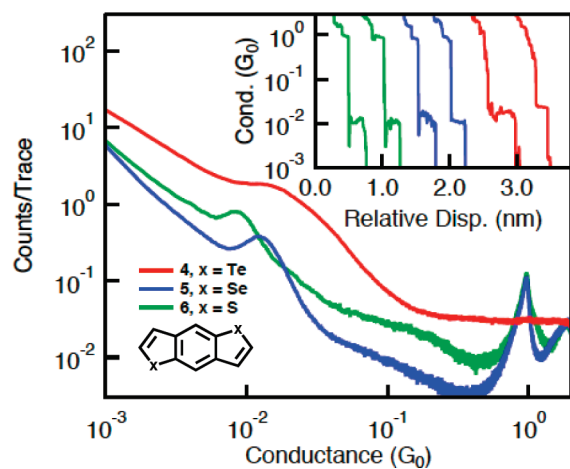


Figure 2. Linear-binned conductance histograms for 4 (red), 5 (blue), and 6 (green) constructed from over 10 000 conductance traces. Measurements were carried out at 25 mV bias; the bin size was $10^{-4}G_0$. Inset: Sample conductance traces showing plateaus at molecule-dependent values near $10^{-2}G_0$.

been observed both experimentally and theoretically for S- and Se-containing molecules.⁷

Figure 3 shows conductance histograms of 100 μM solutions of 1, 2, and 3 measured in anhydrous 1,2,4-trichlorobenzene. A conductance histogram constructed from over 5000 individual traces without any data selection revealed a broad increase in counts between $0.01G_0$ and $0.0001G_0$. Here we see that the peaks at G_0 and higher multiples are absent in the presence of both Te-containing cluster 1 and Se-containing cluster 2. To facilitate a comparison of the results for 1, 2, and 3, conductance histograms were constructed using logarithmic bins (Figure 3 bottom).⁸ The peaks seen in these log-binned histograms indicate that 1 has features at the highest conductance and 3 at the lowest, as was previously observed for 4–6. These broad peaks show that no clear conductance plateaus occurred with these clusters. It is likely that these signals were broad because the bonding between the clusters and the incipient Au electrodes was more complex than in the cases of 4–6 or other organic molecules terminated with exposed Lewis basic functional groups. Unlike these latter chalcogenide-containing organic molecules, the clusters contained eight chalcogenide atoms, and thus, the broad distribution of conductance could have resulted from bonding to different terminal chalcogens. From the illustration in Figure 1, it is possible to imagine that the cluster can easily accommodate both cis and trans connections to the Au contacts. The trends observed in the clusters as well as in the molecular example suggest that the features seen in the conductance traces resulted from electronic conduction through a metal–cluster–metal junction via the chalcogenide atom of the cluster.

Previously, chalcogenide interactions with gold electrodes via lone-pair binding have been demonstrated, and we believe that the conductance we observed is due to the same kind of interactions.⁶ To further investigate the lone-pair binding, we synthesized the clusters $\text{Co}_6\text{Te}_8(\text{P}(n\text{-Bu})_3)_6$ (7) and $\text{Co}_6\text{Se}_8(\text{P}(n\text{-Bu})_3)_6$ (8) containing bulkier phosphines.^{3b} The conductance data for 7 (Figure 3) and 8 showed sharp peaks at G_0 but not the broad increase at conductances below G_0 .⁹ The butyl phosphines are much bulkier than the ethyl phosphines, and our results indicate that increasing the steric bulk of the phosphine

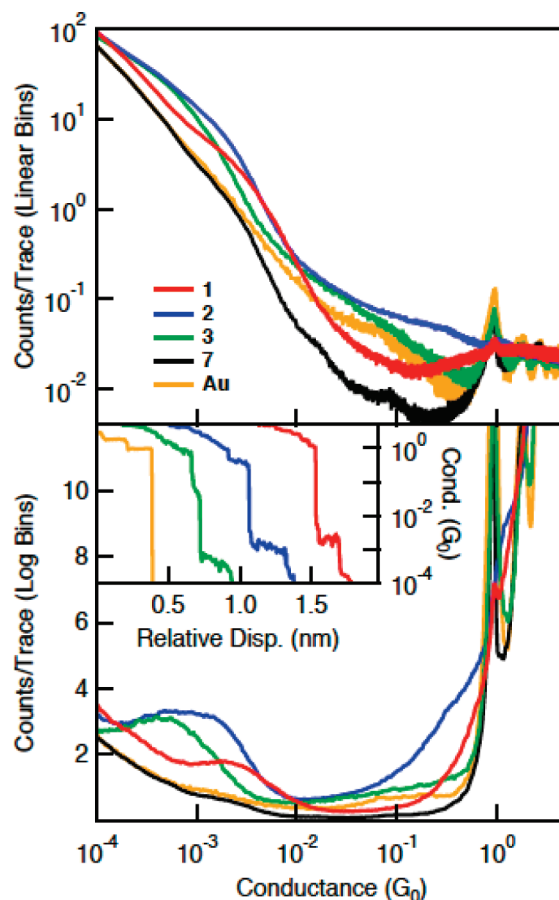


Figure 3. Conductance histograms of 1 (red), 2 (blue), 3 (green), 7 (black), and clean Au (gold) constructed from over 5000 individual traces measured at 25 mV bias using linear bins (top; bin size $10^{-4}G_0$) and log bins (bottom; 100 bins/decade).

can effectively eliminate the formation of a Au–cluster–Au junction via the chalcogenide in the cluster because it eliminates access to the lone pair on the chalcogen. Additionally, this indicates that the lack of a G_0 signal in the presence of 1 was due to a strong interaction between Au and Te, which was reduced in the presence of the bulky butyl groups. This was further confirmed by conductance measurements on SePet_3 , in which neither a G_0 signal nor broad conductance below G_0 was observed.⁹ The absence of the conductance peak indicates that a bare chalcogenide alone cannot form a Au–chalcogen–Au junction, since SePet_3 is a functional equivalent of atomically dispersed Se.

A simple evaluation of these conductance trends could be made according to soft/hard acid–base trends, in which the softest (Te) has the best overlap with Au and the hardest (S) has the worst. However, to understand further the trends observed in the conductance, we performed CV and absorption spectroscopy measurements as well as DFT calculations on 1–3. The oxidation potential determined by CV is related to the energy of the highest occupied molecular orbital (HOMO) of each cluster relative to the oxidation potential of Ag^+/AgCl .¹⁰ Cluster 1 showed the lowest oxidation potential and hence the highest-lying HOMO energy level (-4.4 eV), while 3 (-4.8 eV) had the lowest-energy HOMO of the three clusters.

Previous experimental work on the magnetic behavior of these clusters¹¹ has suggested that their electronic structure is quite

complex, so electronic structure calculations at this stage should be considered only as general guides. We assumed a singlet ground state for each cluster, and using the crystallographically determined structure of **1** as an initial geometry, we optimized the geometries of the PMe_3 -substituted analogues of **1**, **2**, and **3**. The optimized geometries of the inorganic cores of these molecules were in reasonable agreement with the available experimental data (see the Supporting Information). We report the calculated HOMO levels and band-gap (E_g) values.⁹ The trends agreed with the estimates based on electrochemistry and absorption spectroscopy. The calculations yielded three additional results: (1) in each cluster, the HOMO level is essentially triply degenerate; (2) these three HOMOs are concentrated on the chalcogen atoms; and (3) in each case, the lowest unoccupied molecular orbital (LUMO) is concentrated on the Co atoms. Since the HOMO levels are concentrated on the chalcogens and the electrode–cluster binding is most likely to be of the donor–acceptor type, we believe that the clusters are bound to the Au electrodes via the chalcogens. Since these clusters are more easily oxidized than more typical organic conductors (e.g., diamino-phenyl derivatives) and the latter are known to conduct via their HOMOs,¹² we conclude that the conduction in the clusters also occurs through their HOMOs. Since the near degeneracies of the cluster HOMOs give a spread in the effective HOMO energies, it is likely that the density of states at the occupied frontier contributes to the breadth of the conductance peaks.

In summary, we have shown that conductance measurements on molecular systems can be extended to measurements of the conductance of metal chalcogenide clusters. While the conductance histograms showed broad features, a clear trend could be determined by comparing clusters with different chalcogenide atoms. Additionally, increasing the alkyl bulk on the phosphine groups effectively eliminate the formation of Au–cluster–Au junctions. Thus, these measurements have opened up the opportunity to study materials that were once considered as tools for understanding the bulk properties of metal chalcogenide solids.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental procedures, electrochemistry and DFT details, and spectral and conductance data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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