# Electron Transfer Through Organic Tunneling Barriers Between Monolayer Protected Clusters Assembled into Conductive Networks.

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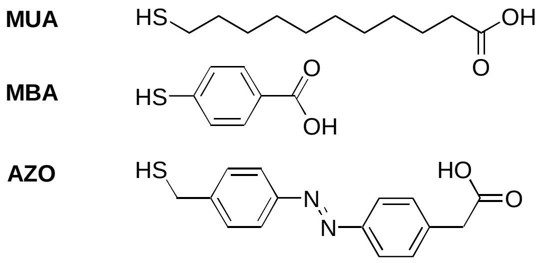
Nanometer sized conducting and semiconducting materials are receiving substantial research attention for their enormous theoretical interest and potential use in nanotechnology applications.[1] Recent synthetic advances[2] in the preparation of 1-5 nm gold and silver nanoclusters protected with a dense monolayer of thiolate ligands has provided access to an array of remarkably precise and stable nanoparticles that have potential use as nanoelectrodes or as components in nanoelectronic devices. We have termed these nanoparticles monolayer protected clusters (**MPC**s), a schematic representation is shown in the Figure. Investigations from our laboratory and others have shown that **MPC** properties are highly dependent on the core diameter and monolayer composition and for most optical and electrochemical considerations the properties of these particles undergoes a transition from bulk to molecular behaviour in this size range.[3,4] The presented research addresses distance dependent electron transfer (ET) between **MPC**s, a property that is highly sensitive to the monolayer composition, the inferred tunneling pathway.

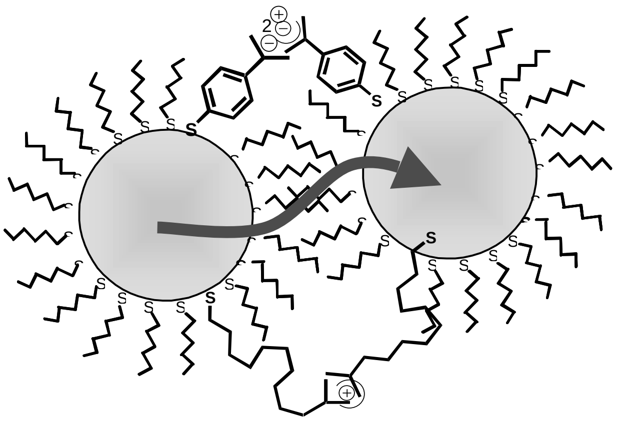
The **MPC**s used in this study had an average molecular composition of 140 gold core atoms (1.6 nm diameter) and 53 monolayer thiolate ligands. Mixed monolayers containing equal amounts of alkanethiolate and carboxylic acid terminated organothiolates were used. The carboxylic acid ligands formed linkages between **MPC**s as well as to anchor **MPC**s to gold and glass substrates using carboxylate-metal cation-carboxylate linkages, as demonstrated in the Figure. Three different types of linking carboxylate linking ligands were used: mercaptoundecanoic acid (**MUA**), 4-mercaptobenzoic acid (**MBA**) and an azobenzene substituted thiol (**AZO**). The metal cations used were $Ag^+$, $Zn^{2+}$, $Cu^{2+}$ and $La^{3+}$. **MPC** films were assembled on glass slides to probe film growth and provide an estimate of the film density. It was possible to then estimate the average core edge to edge separation (δ), or the tunneling distance, between **MPC**s in the film. Films were grown on interdigitated array electrodes to allow for investigation of the solid state conductivity of the dry films.

The conductivity and δ of assembled films using the **MUA** linking ligand were highly metal dependent. Conductivity depended on the length of the nonlinking alkanethiolate ligands, indicating these ligands provide the dominant ET pathway.[5,6] The most conductive **MUA** films were grown with the silver linking ion and provided a δ consistent with the minimum distance allowed by complete interdigitation of the alkanethiolate ligands between adjacent **MPC**s. An overall satisfactory agreement with accepted relationships between tunneling distance and conductivity for **MPC**s was maintained.

In contrast, films assembled using the more rigid and conductive **AZO** and **MBA** ligands exhibit no conductivity and density dependence on the metal linking cation. The **MBA** grown films had δ and conductivity consistent with the $Zn^{2+}$, $Cu^{2+}$ and $La^{3+}$ grown **MUA** films. Larger values of δ and lower conductivities were observed for the corresponding **AZO** films. The conductivity and δ values determined for these films are consistent with the ET pathway being through the nonlinking alkyl ligands as well although now at distances dictated more strongly by the rigid aromatic linking ligands. This pathway persists in spite of the linking ligands being significantly more conductive than their alkyl nonlinking counterparts.

These results, a discussion of the relationship between **MPC**-**MPC** ET kinetics to tunneling distance, and examples of these assembled films as vapour sensors will be presented.





(1) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
(2) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17-30.
(3) Chen, S.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Schaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098.
(4) Hicks, J. F.; Templeton, A. C.; Chen, S.; Sheram, K. M.; Jasti, R.; Murray, R. W.; Debord, J.; Schaff, T. G.; Whetten, R. L. *Anal. Chem.* **1999**, *71*, 3703.
(5) Zamborini, F. P.; Leopold, M. C.; Hicks, J. F.; Kulesza, P. J.; Malik, M. A.; Murray, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 8958-8964.
(6) Zamborini, F. P.; Smart, L. E.; Leopold, M. C.; Murray, R. W. *Manuscript Submitted.* **2002**.