

Investigations into the Role of Metal Ion Linkers in the Self-Exchange ET Between Monolayer Protected Cluster Molecules

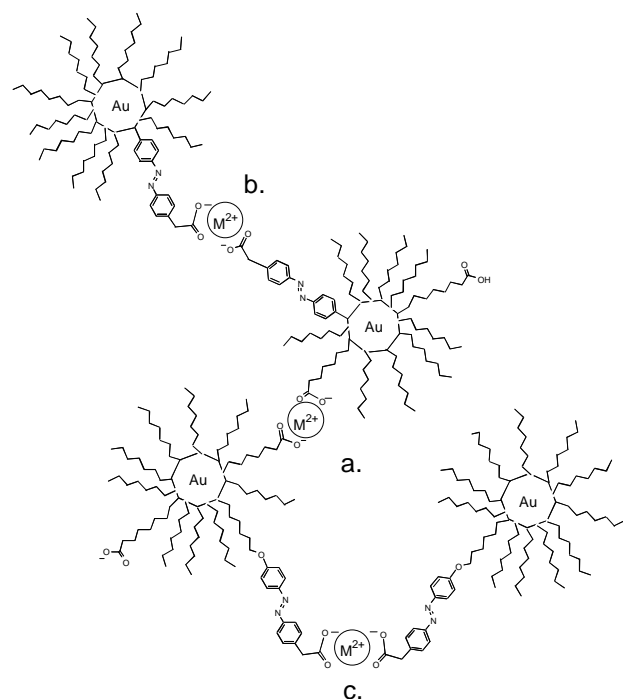
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Nanometer sized conductors and semiconductors have received considerable research attention over the past two decades. This size of material, between that of a small molecule and bulk material, often results in unusual electronic and physical properties that are useful in the field of nanoelectronics. Of particular relevance are monolayer protected clusters (MPC), molecules containing a cluster of gold atoms ranging from 1 to 5 nm in size surrounded by a protective organic layer bound to the core through a thiolate linkage.¹ The advantage of these clusters is their remarkable stability, ease of handling and the ability to introduce a wide variety of functional groups into the outer monolayer. For these reasons, the gold core can be considered to be a nanometer-sized electrode with a variable or tunable outer layer.

Recently, MPC's functionalized with mixed monolayers of alkyl thiolates and carboxylic acid terminated alkyl thiolates (with alkyl chain lengths ranging between 4 and 16 carbons) were linked to each other with carboxylate-metal ion-carboxylate bridges (a, Figure). The metal ion is usually Zn^{2+} , Cu^{2+} or Mn^{2+} .^{2,3} The MPC-MPC self exchange electron hopping rate constants were determined for these materials and was found to decrease, as predicted, as the length of the alkyl spacers in the monolayer increased. However, there is some difficulty in interpreting these results since little is known about the structure of these films and distance between adjacent MPC's. The extent of elongation of the alkyl chains is unknown and may lead to considerable uncertainty in determining the electron tunneling distance between MPC's. As well, to date it is uncertain whether or not the metal ion aids in mediating ET.

The investigation of two new linking ligands containing an azobenzene moiety will be presented. These ligands (b and c) were designed to provide a rigid and predictable distance between two MPC's as well as be much more conductive than the previously studied alkyl linkers. This provides a most favourable ET pathway between MPC's through the linking ligand.

The role of the metal ion as well as the structural impacts imposed by the new ligands will be presented along with a revised model for electron hopping self exchange between adjacent and rigidly held MPC molecules.



¹ Templeton, A. C., Wuelfing, W. P., Murray, R. W.; *Acc. Chem. Res.*; **2000**; 33(1); 27.

² Templeton, A. C. Zamborini, F. P., Wuelfing, W. P., Murray, R. W.; *Langmuir*; **2000**; 16(16); 6682.

³ Jocelyn F. Hicks, Francis P. Zamborini, Andrea J. Osisek, and Royce W. Murray; *Journal of the American Chemical Society*; **2001**; 123(29); 7048.