Atomically Precise Gold Nanoclusters

Flavio Maran

Department of Chemistry, University of Padova, 1 Via Marzolo, 35131 Padova
Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, Connecticut 06269, U.S.A.

flavio.maran@unipd.it, flavio.maran@uconn.edu

Ligand-protected metal clusters are of continuously growing fundamental and applied interest. Several of these systems can be synthesized with atomic precision and this implies knowledge of their formula and often structure, which are impossible tasks for the popular gold nanoparticles. In molecular clusters, differences of only one gold atoms, charge state, or variations in the number or type of ligands may indeed affect their stability and properties very significantly. Here we focus on the preparation, characterization, and properties of typical molecular gold nanoclusters, especially $Au_{25}(SR)_{18}$ where SR = thiolate. The latter is, by far, the most studied thiolate-protected nanoclusters that can be prepared with atomic precision. As such, it has been the object of numerous studies focusing on its optical and NMR properties, magnetism, electrochemistry, theory, and several applications. $Au_{25}(SR)_{18}$ has indeed provided an effective benchmark for testing or developing new investigation methodologies and the resulting information is being borrowed to obtain insights into the properties and behavior of other clusters, such as the especially stable $Au_{38}(SR)_{24}$ and $Au_{144}(SR)_{60}$ nanoclusters.

Insights into the Dynamic Monolayer Protecting Gold Nanoclusters

In applications of molecular thiolate-protected gold clusters, whether in solution or solid state, assessing the dynamic behavior of the capping monolayer is crucial, as this determines, *e.g.*, the cluster's effective size and electron transfer (ET) properties. The main topics addressed will be: (i) The effect of the monolayer thickness and its dynamics on the ET between molecular nanoclusters in films and solution can be understood by a combination of electrochemistry and spectroscopy methods; (ii) In redox catalysis, the monolayer capping gold nanoclusters can be penetrated by molecular species: what kind of environment do they experience during the activation processes? (iii) Understanding the fine interactions between the cluster metal core and the thiolate monolayer is especially important because the latter interfaces the former to the surrounding medium: nuclear and electron magnetic methods can be used to understand orbital distribution outside the metal core; (iv) Ligand exchange in clusters and interactions between ligands of two clusters are instrumental to modify the cluster monolayer, cause polymerization in the solid state, and make two clusters fuse to form different clusters; (v) Nuclear magnetic resonance can be used to assess the thiolate-protected cluster structure in solution.