

Department of Physics & Astronomy

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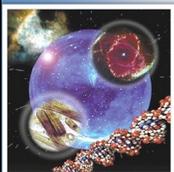
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Emergence of Protected Metallic Clusters as 21st-Century Molecular Materials

Protected metallic clusters (PMCs) have been known for a long time but only recently has their potential as molecular substances been recognized. Key aspects of their history are recalled, starting from early studies and culminating in the 1984 discovery of spherical electron-shell (superatomic) structure in unprotected metallic clusters. A critical insight, based on chemically modified electrodes, brought to light, in 1992, how PMCs could be developed systematically as high-purity, molecular materials. This led to the 1992-3 proposals Processing of Single Nanocrystals & "Perfecting Single Nanocrystals", along with initial measurements at UCLA. The GIT metallic-molecules research project was launched at Atlanta in 1994 and funded by the NSF in 1996, as Molecular Metal Nanocrystals and Their Crystalline Arrays. The GIT group (and others) selected thiolate-protected gold (& silver) clusters as the most viable route for demonstrating metallic molecules, and their seminal papers were published in 1995-6. A key finding therein was the "ubiquitous 30-kDa anomaly," later determined to be a 5th-generation metallic cluster compound of composition $\text{Au}_{144}\text{-6}(\text{SR})_{60}$. Subsequently, the field developed rapidly with improvements in preparation and separation methods; in size- and compositional-characterization, including structure-type determination; and in optical-spectroscopic (robust QSEs), electronic, and electrochemical (ensemble coulomb staircase) measurements. By 1998, the "longest nanometer" had been crossed, culminating with the complete electrophoretic separation of a 1st-generation "orange-gold" compound, later determined as $\text{Au}_{25}(\text{SR})_{18}(-1)$, and the initial systematic exploration of the molecular-crystalline phases had been completed. A critical issue affecting these solids concerned their residual disorder, blamed on the excessive conformational flexibility of the R-groups and the counterions. Attempts to employ only rigid benzenethiolates and TPP counterions met only limited success. The key breakthrough came in 2007, when a neutral 4th-generation (10244) compound, with $\text{R} = \text{p-carboxyphenyl}$, yielded to total structure determination, followed in rapid succession by three structure determinations of 1st & 2nd-generation compounds. Starting from the experimentally determined structure-coordinates, high-level electronic-structure calculations were used to rationalize, or to predict, the stability of these gigantic molecules. A simple SuperAtom Complex (SAC) Model was proposed to capture the regularities in the frontier (metallic) orbitals. Further applications of this SAC model are AuAg-thiolates, to phosphine-halide-protected Au, and to group-13 metallic clusters, notably the larger AlCp^* & Ga-halides. The analytical chemistry of PMCs has greatly advanced, and numerous reports describe applications of these compounds in the biomedical, optical, and catalytic sciences. The crystalline ordered solids, modified by variable doping, are of considerable interest as correlated electronic conductors and transitions to broken symmetry ground-states at comparatively high T_c .



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