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e Nanosistemi

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Evento organizzato da
Prof. **Federico Polo**

Molecular Gold Nanoclusters and the Hydrogen/Deuterium Puzzle

19 dicembre 2023, ore 10.45

Aula Delta 0A, Campus Scientifico Via Torino, Mestre

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Substituent effects have never been studied by changing a very large number of identical substituents. This kind of study obviously requires the use of very special molecules where this kind of substitution is indeed possible. In this context, ultrasmall ligand-protected gold nanoclusters, such as $\text{Au}_{25}(\text{SR})_{18}$ where SR is a thiolate, provide the opportunity to test the combined effect of changing 18 identical ligands. These systems are prepared with atomic precision, exhibit truly molecular properties, and their physicochemical, electrochemical, and electron transfer (ET) behaviors can be tuned by acting on both the metal and organic components.

We prepared the first fully deuterated gold nanocluster, $\text{Au}_{25}(\text{SC}_4\text{D}_9)_{18}$, and compared its electrochemical, ET, solid-state, and

photophysical behaviors in comparison with those observed for the corresponding nondeuterated $\text{Au}_{25}(\text{SC}_4\text{H}_9)_{18}$ cluster. We found that the deuterated molecule exhibits several unexpected differences. For example, the rates of heterogeneous ET and, particularly, intercluster ET in films are lower; the rate by which two deuterated clusters react in films to form Au_{38} is significantly lower than for $\text{Au}_{25}(\text{SC}_4\text{H}_9)_{18}$; single crystal X-ray crystallography evidences important differences also between the structures of $\text{Au}_{25}(\text{SC}_4\text{D}_9)_{18}$ and $\text{Au}_{25}(\text{SC}_4\text{H}_9)_{18}$. These and further results indicate that deuterated thiolates are far from being noninnocent ligands. The observed effects may be relevant, e.g., to affect the behavior of nanoclusters when used as building blocks for hierarchical structures.