Catalysis & Materials Science
Hokkaido University GCOE Program, 2007-2011

グローバル COE 物質科学イノベーション講演会

演 題：**Ligand-protected gold cluster superatoms**

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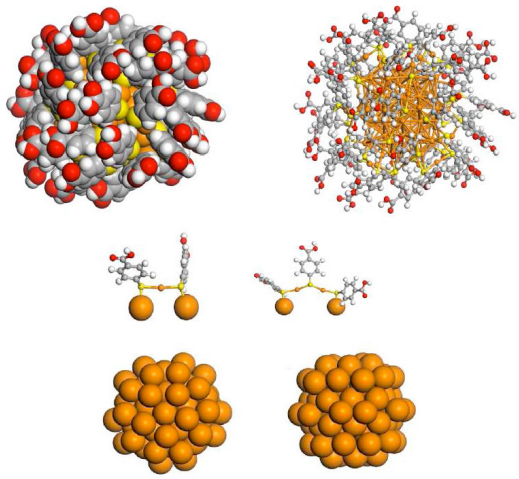
日 時：2008 年 11 月 5 日（水）15:00-16:15

場 所：理学部 7 号館・7-219/220 室

要 旨：Synthesis, characterization, and functionalization of self-assembled, ligand-stabilized gold nanoparticles are long-standing issues in the chemistry of nanomaterials. Factors driving the thermodynamic stability of well-documented, discrete sizes and compositions have been largely unknown. The recent breakthrough in total-structure-determination of an all-thiolate-protected Au_{102} cluster [1] triggered renewed interest in this field.

Herein, we provide a unified view of principles that underlie the stability of particles protected by thiolate (SR) or a combination of phosphine and halide (PR_3, X) ligands [2]. The picture has emerged from analysis of large-scale density functional theory calculations of structurally characterized compounds, namely $Au_{102}(SR)_{44}$, $Au_{25}(SR)_{18}^{(-)}$, $Au_{39}(PR_3)_{14}X_6^{(-)}$, $Au_{11}(PR_3)_7X_3$, and $Au_{13}(PR_3)_{10}X_2^{(+3)}$, where X is either a halogen or a thiolate. Attributable to a compact, symmetric core and complete sterical protection, each compound has a filled spherical electronic shell and a major energy gap to unoccupied states. Consequently, the exceptional stability is best described by a “noble-gas superatom” analogy. The success of our superatom model was highlighted during this work via simultaneous and independent theoretical prediction [3] and experimental confirmation [4] of the same ground-state structure for the $Au_{25}(SR)_{18}^{(-)}$ cluster.

Traditionally, the “phosphine chemistry” and the “thiolate chemistry” have been regarded as separate branches to prepare ligand-protected gold nanoparticles; no general, unifying theoretical concepts have been available to understand and classify the wealth of experimental information that points to well-defined, discrete compounds. Our work thus provides guiding principles for molecular-precision-synthesis and functionalization of these exciting building blocks of nanomaterials that are finding applications in diverse fields of biolabeling, photonics, sensing, molecular electronics and nanocatalysis. [5]



Top: two views of the Au_{102}(*p*-MBA)$_{44}$ cluster. Bottom: two views of the Au_{79} decahedral core. Middle: The protecting RSAuSR and SR(AuSR)$_2$ units, bound to core Au atoms (large balls). Adapted from ref. 2.

[1] P.D. Jadzinsky et al, *Science* **318**, 430 (2007). [2] M. Walter et al., *Proc. Natl. Acad. Sci USA* **105**, 9157 (2008). [3] J. Akola et al., *J Am. Chem. Soc.* **130**, 3756 (2008). [4] M.W. Heaven et al., *J. Am. Chem. Soc.* **130**, 3754 (2008). [5] O. Lopez-Acevedo et al., in preparation.

本講演は『化学研究総合講義Ⅱ』の一部として認定されております

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