1-2-3. Metal Nanoclusters

Overview

Atomically Precise metal nanoclusters, typically consisting of several to hundreds of metal atoms, are located in the size regime between the metal complexes and bulk metal. These nanoclusters exhibit unique geometrical and electronic structures due to the quantum effect. For example, gold nanoclusters are reported to show highly diverse structures, such as an icosahedral core (e.g., $[Au_{25}(SCH_2CH_2Ph)_{18}]^-$ shown in Fig. 1), while bulk gold typically shows face-centered cubic (fcc) structure. In addition, gold nanoclusters possess an electronic structure with discrete energy levels, which is similar to molecules or complexes, while bulk gold shows a band-like electronic structure with continuous energy levels. Recently, metal nanoclusters have captured great attention due to the unique properties (e.g., photophysics, catalysis, magnetism, etc.), originating from these electronic and geometrical structures.

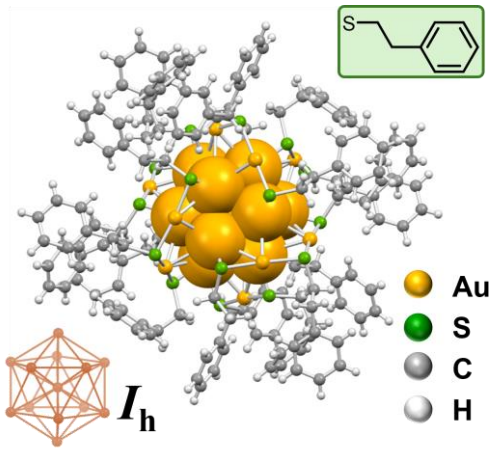

Figure 1. Crystal structure of $[Au_{25}(SCH_2CH_2Ph)_{18}]^-$. Countercation is omitted for structural clarity.

Current Status and Frontiers

Metal nanoclusters, especially ligand-protected metal nanoclusters synthesized in solution phase, have been intensively studied in terms of fundamental research. In addition to gold nanoclusters, silver, copper, and alloy nanoclusters are also studied intensively, particularly because they can be synthesized and stored in the air. These nanoclusters are protected by phosphine, which have been used as a ligand for a long time, as well as thiolate or alkynyl ligands (T. Tsukuda et al.). Multidentate phosphine (K. Konishi et al.) and *N*-heterocyclic carbene have been used as a ligand recently. Photochemical properties have been reported for these nanoclusters, so some of them are introduced in the following sections.

1. Photoluminescence of thiolate-protected gold nanoclusters

Atomically precise synthesis of thiolate-protected gold nanoclusters has been accomplished by using glutathione as protecting ligands (T. Tsukuda et al.). In the first

report, size separation of polydispersed gold nanoclusters is achieved by gel electrophoresis, resulting in the atomically precise preparation of $Au_m(SG)_n$ (m = 10-39, H-SG: glutathione). The photophysical properties of the series of nanoclusters are compared and it was revealed that the single-atom difference in the chemical formula leads to the dramatic difference in such properties. However, photoluminescence from these nanoclusters is weak with a low quantum yield ranging from 10^{-3} to 10^{-5}. Recent advances in the field have witnessed the improvement of the photoluminescence quantum yield by using different ligands (e.g., *N*-heterocyclic carbene) or doping silver or copper atoms.

2. Photogeneration of singlet oxygen

Thiolate-protected gold nanocluster, $[Au_{25}(SR)_{18}]^-$ (H-SR = 2-phenylethanethiol or captopril), can be used as a photosensitizer for singlet oxygen ($^1O_2$) generation under the irradiation of visible or infrared light (e.g., λ_{ex} = 532, 650, and 808 nm) (H. Kawasaki, R. Jin, et al.). Water-soluble gold nanoclusters protected by captoprils can be used as a photosensitizer for the photodynamic therapy with near-infrared light photoexcitation.

3. Photon upconversion (UP) by metal nanoclusters

Silver nanoclusters are reported to be used as a NIR-absorbing sensitizer for the triplet-triplet annihilation photon upconversion (M. Mitsui et al.). For example, upon photoexcitation of $PtAg_{24}(SR)_{18}$ (H-SR = 2,4-dimethylbenzenethiol) by near-infrared light (e.g., 785 nm), UC emission (λ_{ex} = 474 nm) from perylene is observed with UC quantum yield of 1.1%. The near-infrared emission of some silver nanoclusters can be enhanced by the addition of silver complexes (T. Nakashima et al.).

References

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Future Perspectives and Directions

Problems to be resolved within the next ten years: the excited state dynamics of metal nanoclusters with intriguing photophysical properties needs to be elucidated. Also, the application of metal nanoclusters needs to be pursued, especially for the photodynamic therapy by metal nanoclusters via photogeneration of singlet oxygen.

(Author: Tatsuya Higaki)