



## Review

## Roles of thiolate ligands in the synthesis, properties and catalytic application of gold nanoclusters



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## ABSTRACT

Ultrasmall (<2 nm) ligand-protected metal nanoclusters (NCs) have been an emerging class of functional materials with rich coordination chemistry, finding increasing acceptance in both basic and applied research owing to their atomic precision, well-defined molecular structure, and intriguing molecular-like properties. The presence of ligands on metal NCs is crucial not only for maintaining their atomic precision and well-defined structure, but also for their rich coordination chemistry with noble metals, influencing the synthesis, and physicochemical and catalytic properties of metal NCs. In this review, we discuss the important roles of ligands to metal NCs, taking water-soluble gold nanoclusters (Au NCs) as an example. The review covers the fundamental understandings (and advances) on the roles of ligands to water-soluble Au NCs in the synthesis (e.g., influencing the size and formation rate, and revealing the growth mechanisms), physicochemical properties (e.g., geometrical structure, chirality, stability, solubility, and electronic, photoluminescence and biological properties) and catalytic applications (e.g., accessibility, activity, selectivity, and coordination of catalytic mechanism of quasi-homogeneous catalysts and immobilization of heterogeneous catalysts). The review also highlights some challenging issues on how ligands and ligand engineering could expand the scope of metal NCs in the synthesis, physicochemical properties, and catalytic application.

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## 1. Introduction

Organic molecules functioning as protecting ligands are well demonstrated for their crucial roles in the synthesis and functionalization of metal nanoparticles (NPs). In the synthesis of metal NPs, organic ligands typically serve as protecting agents to prevent aggregation, as well as to control the size of metal NPs (often with a desired size). Recently, the functions of organic ligands on the NP surface have been further expanded to tune and improve the surface properties of metal NPs towards desired applications. Interestingly, organic ligands could play more important roles (and become a key factor in the coordination chemistry of noble metals) for the synthesis of a new class of ultrasmall metal NPs, which are atomically precise metal nanoclusters (NCs) with particle size below 2 nm. In general, the choice of protecting ligands for metal NPs (typically with size above 2 nm) is more flexible, and various organic ligands, such as polymers [1–4], dendrimers [3,5,6], and micelles [7,8] have been successfully used to protect metal NPs. However, in the system of atomically precise metal NCs, small organic ligands are more desirable, as a metal NC protected by a small ligand could facilitate the determination of the molecular formula of metal NCs by using high resolution analytical techniques, such as matrix-assisted laser desorption ionization (MALDI) [9–11] and electrospray ionization (ESI) [12–16] mass spectrometer. In addition, single-crystal X-ray crystallography can be used to determine the unique and well-defined structure of atomically precise ligand-protected metal NCs [17–22], making them more attractive.

The chemical formula of the ligand-protected metal NCs can be described as  $M_nL_m$ , where M and L refer to a certain type of metal and protecting ligand, and  $n$  and  $m$  are the number of metal atoms and protecting ligands, respectively. To date, various ligand-protected metal NCs (e.g., M = gold (Au) [23–27], silver (Ag) [28–35], and copper (Cu) [36,37]) have been successfully synthesized and characterized. Among these metal NCs, Au NCs have been intensively studied. Research on Au NCs has provided key fundamentals on noble metal chemistry and cluster chemistry. More interestingly, gold has good chemical stability and features with rich physical and chemical (physicochemical) properties at subnanometer size range, providing an ideal platform for both basic (e.g., self-assembly, electron transfer theories, and crystal growth) [23,38–41] and applied studies (e.g., sensing [42–45], electronics [46–48], bioimaging [49,50], therapy [51–56], and catalysis [57–60]). The past decade has witnessed a rapid growth in the research of Au NCs, especially for the ligand-protected Au NCs. There are several types of organic ligands that could be used to protect Au NCs, such as thiolates [57,61–65], phosphines [66–69], selenolates [21,70–75], tellurolates [76], carbenes [66], and alkynes [41,77–81]. Among these protecting ligands, thiolate ligands are the most attractive, as thiolate ligands could provide a good protection for Au NCs owing to the strong bonding between gold and sulfur (i.e., Au(I)-SR, like a covalent bond) [65,82]. With the use of thiolate ligands, the chemical formula of ligand-protected Au NCs can be further specified as  $Au_n(SR)_m$  (here, SR denotes a thiolate ligand) [39,83]. Recently, there is a number of successful attempts on the synthesis, characterization, and application of  $Au_n(SR)_m$  NCs. Some examples are  $Au_{25}(SR)_{18}$  [25,82,84–87],  $Au_{38}(SR)_{24}$  [88–91],  $Au_{102}(SR)_{44}$  [92–96], and  $Au_{144}(SR)_{60}$  [97,98]. Each of these  $Au_n(SR)_m$  NCs has an Au core of different number

of Au atoms, featuring with unique geometrical structure. The Au core is protected by thiolate ligands via different coordination chemistry, such as coordination of single and/or staple motifs of two or more thiolates. A staple motif is a polymer or oligomer of Au(I)-thiolate complexes with different length (e.g., monomer, dimer, trimer, and tetramer) [23]. The staple motifs would form a shell-like structure, which could provide a good protection to the Au core with a unique geometrical structure, further lending intriguing physicochemical properties to  $Au_n(SR)_m$  NCs as a whole.

The physicochemical properties of Au NCs are distinctly different from their larger counterparts – Au NPs, because Au NCs exhibit quantum confinement effects owing to their ultrasmall size (<2 nm and less than 150 Au atoms) [39,99,100]. Unlike plasmonic Au NPs (metal NPs often feature with surface plasmon resonance (SPR) property) which have continuous or semi-continuous energy levels [38,101], Au NCs have discrete electronic structures [39,98,102–105]. Therefore, ultrasmall Au NCs possess some intriguing molecular-like properties, such as HOMO–LUMO (highest occupied and lowest unoccupied molecular orbital) electronic transitions [12,57,106–110], quantized charging [111,112], enhanced photoluminescence [100,113], molecular magnetism [84,114–116], molecular chirality [65,117–121], and discrete redox behavior [39,122–124]. Moreover, Au NPs have collective and size-dependent properties, while the physicochemical properties of Au NCs are even more sensitive to cluster size, where a single atom difference would lead to totally different physicochemical properties (or it can be defined as atom-dependent properties) [39,125–127]. The physicochemical properties of Au NCs can be controlled by modifying the composition of NCs (e.g., removing, adding, or replacing at least one metal atom) [128–133]. Therefore, metal engineering of Au NCs has recently emerged as a powerful platform to facilitate fundamental understandings on the structure-property correlation, as well as to design metal NCs with novel (and desirable) properties [134–137].

Besides metal engineering, ligand engineering is another good strategy to tailor the physicochemical properties of ligand-protected Au NCs [138–145]. In particular, ligands on the NC surface are well exposed to the surroundings, which could affect the surface properties of Au NCs. Therefore, ligands on NC surface are the crucial components for the functionalization of Au NCs and for their further interactions with other molecules. Ligands of different properties (e.g., type, size, functional group, length, and solubility) would affect the synthesis, physicochemical properties, and applications of Au NCs. Fundamental understandings on the coordination chemistry of ligand engineering on Au NC surface require concerted efforts from communities of coordination chemistry, noble metal chemistry, cluster chemistry, and organic chemistry. For example, in terms of Au NC catalysis, there are several successful attempts on metal engineering of Au NC catalysts [146–153]. However, there are fewer reported studies on the roles of ligands (on the surface of Au NCs) to their catalytic properties (e.g., activity, selectivity, and stability), and in general, ligands on Au NC catalysts are considered as poisons to the Au active sites [125,154–157]. In addition, ligand-protected Au NCs are generally immobilized on a certain support material (e.g., metal oxides), followed by a removal of ligands from the NC surface to increase the exposure of the Au active sites [125,158–161]. Unfortunately, the immobilization of Au NCs and the removal of the organic ligands from Au NC surface might destroy their atomic precision and

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