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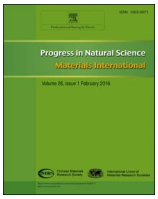

Chiral ligand-protected gold nanoclusters: Considering the optical activity from a viewpoint of ligand dissymmetric field[☆]

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ABSTRACT

Chirality is a geometric property of a physical, chemical, or biological object, which is not superimposable on its mirror image. Its significant presence has led to a strong demand in the development of chiral drugs, sensors, catalysts, and photofunctional materials. In recent years, chirality of nanoscale organic/inorganic hybrids has received tremendous attention owing to potential applications in chiral nanotechnology. In particular, with the recent progress in the syntheses and characterizations of atomically precise gold nanoclusters protected by *achiral* thiolates, atomic level origins of their chirality have been unveiled. On the other hand, chirality or optical activity in metal nanoclusters can also be introduced via the surface *chiral* ligands, which should be universal for the nanosystems. This tutorial review presents some optically-active metal (gold) nanoclusters protected by chiral thiolates or phosphines, and their chiroptical (or circular dichroism; CD) properties are discussed mostly from a viewpoint of the ligand dissymmetric field scheme. The examples are the gold nanoclusters protected by (*R*)-/(*S*)-2-phenylpropane-1-thiol, (*R*)-/(*S*)-mercaptosuccinic acid, phenylboronate-D/L-fructose complexes, phosphine sulfonate-ephedrinium ion pairs, or glutathione. Some methodologies for versatile asymmetric transformation and chiroptical controls of the nanocluster compounds are also described. In the dissymmetric field model as the origin of optical activity, the chiroptical responses of the gold nanoclusters are strongly associated with coupled oscillator and/or CD stealing mechanisms based on the concept of induced CD (ICD) derived from a perturbation theory, so on this basis, some characteristic features of the observed CD responses of chiral ligand-protected gold nanoclusters are presented in detail. We believe that various kinds of origins of chirality found in ligand-protected gold nanoclusters may provide models for understanding those of many related nanomaterials.

1. Introduction

Monolayer- or ligand-protected metal nanoclusters are composed of a metal core and protective organic ligands with a distinct core–ligand interface. In particular, a study of ligand-protected gold nanoclusters with a diameter smaller than ~2 nm has received great attention owing to their important applications in life science, catalysis, and nanotechnology [1] as well as their fundamental electronic/optical properties that evolve from the bulk metallic state to molecular-like energy levels [2]. The unique features of nanoclusters also make them promising in the use of them as functional units or building blocks for the construction of novel advanced materials. Recently, great progress has been achieved in determining the structures of atomically precise (or magic-numbered), thiolate-protected gold nanoclusters by X-ray crystallography. The X-ray structures of nanoclusters reveals that the surface thiolate ligands (-SR) do not simply passivate the gold core, instead, they form unique oligomeric units such as $\mathrm{Au(SR)_2}$ (–RS–Au–RS–) and $\mathrm{Au_2(SR)_3}$ (–RS–Au–S(R)–Au–SR–) (called staples or semirings), which bind to the surface (i.e. core-surface) gold atoms for protection; in other words, the staple units are anchored to the core by sulfur in atop positions [3]. Methodological refinements have also generated several particularly stable magic-numbered nanocluster compounds such as $\mathrm{Au_{25}(SR)_{18}}$ and $\mathrm{Au_{38}(SR)_{24}}$ whose total structures have been unequivocally determined [4–9]. To interpret the magic stability of such thiolate-protected $\mathrm{Au}_n\mathrm{(SR)}_m$ nanoclusters, a “superatom concept” has been proposed, in which the $\mathrm{Au}_n\mathrm{(SR)}_m$ nanoclusters with total numbers of valence electrons (N^*) of 2, 8, 18, 34, 58, 92, … are stable because of electronic structure closing [10]; for example, the N^* values are 8, 18, and 58 for $\mathrm{Au_{25}(SR)_{18}}^-$, $\mathrm{Au_{44}(SR)_{28}}^{2-}$ and $\mathrm{Au_{102}(SR)_{44}}$ [11], respectively.

Meanwhile, chirality is one of the most fascinating events in the natural world. A chiral molecule is one that its two mirror-image forms are *non-superimposable*. Chirality plays an important role in many fields, including chemistry, biology, pharmacology, and medicine,

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because it is one of the key factors for specific molecular recognition. Therefore, the production or identification of enantiopure species is critical for the development of pharmaceuticals and agrochemicals. Moreover, chirality has also been envisaged to play an important role in nanoscience, and chiral nanomaterials are thus designed and fabricated in various ways [12]. During the last years, the area of chiral metal (gold or silver) nanoclusters has received a great deal of attention due to a wide range of potential applications offered by the materials in chiral sensing and catalysis, and by meta-materials in novel optical devices [12,13]. In such chiral metal nanoclusters, the use of chiral protecting molecules has opened an avenue for novel materials at the nanoscale [14,15]. Additionally, understanding the fundamental aspects of chirality in nanosystems has become indispensable for the advancement of nanoscience as well as nanotechnology. Among the chiral metal nanoclusters, thiolate-protected gold nanoclusters exhibit appreciable optical activity when chiral ligands are used. Schaaff and Whetten observed circular dichroism (CD) responses in glutathione-protected gold nanoclusters in 2000 [14], where glutathione is a chiral tripeptide composed of γ-L-glutamyl-L-cysteinyl-glycine. Further, observations of the energy location or strength of the CD response of such chiral thiolate-protected gold nanoclusters suggest that the electronic structure of the gold core should be highly sensitive to the chiral ligand environments [15]. These results not only offered evidence for the existence of novel nanomaterials with optical activity, but also indicated that chiral functionality can be present in matter at the nanoscale.

In this review, the author focuses on the research of optically-active or chiral ligand-protected metal (mostly gold) nanoclusters from a viewpoint of chiral chemistry of various organic compounds. Here, it should be noted that the reported works on chiral gold nanoclusters will be categorized into (roughly) two types; (i) chiral *metal cores* with achiral ligands, or (ii) achiral *metal cores* with chiral ligands [16]. In the above classification, the *metal core* refers to the inner core plus surface gold atoms incorporated into the gold-thiolate staple motifs. Indeed, there have been several reviews on chiral metal nanoparticles during the last several years, but the author thinks that they are mostly focused on the structural origins as listed in (i), which is based on the geometry distortion of the *metal cores* (including chiral arrangements of the surface Au). The examples include $Au_{20}(SR)_{16}$, $Au_{28}(SR)_{20}$, $Au_{38}(SR)_{24}$, $Au_{102}(SR)_{44}$, and $Au_{133}(SR)_{52}$ [17], where all different R substituents are typically achiral. Both left- and right-handed stereoisomers are found in each size of the chiral $Au_n(SR)_m$ nanoclusters, indicating that the achiral ligand exerts no preference during the synthesis, and thus producing the left- and right-handed isomers equally (that is, racemic mixture formation). In contrast, my objective will be in emphasizing the case of the origin (ii), that is, providing insights into the origin of optical activity induced by the chiral ligand (=*dissymmetric field model*) and methodology for versatile asymmetric transformation of optically-inactive gold nanoclusters using ligand modification by chiral reactions. Most of the works that will be presented here refers to thiolate-protected gold nanoclusters, but some results on phosphine-protected nanoclusters are also described. Note that this review is not intended to be a comprehensive one, so there might be possible oversights of some significant contributions. Understanding of nanoclusters' chirality from a viewpoint of the ligand dissymmetric field is expected to benefit future exploration of applications of chiral nanomaterials.

2. Rotational strength and circular dichroism

Molecules that are optically active have an asymmetry or chirality, which results in the possession of a handedness. Such molecules exhibit circular dichroism (CD), i.e. the difference between the absorption of left- and right-circularly polarized light (LCPL and RCPL, respectively), $\Delta\varepsilon$, since the two mirror-image objects have different interactions with the two CPL beams [18].

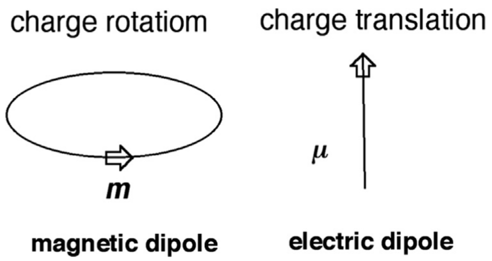

Fig. 1. Scheme for the magnetic or electric dipole.

We first define an electric and a magnetic transition dipoles (Fig. 1), which are essentially associated with optical and chiroptical properties. When the initial or final state is labeled as *i* or *j*, respectively, a linear charge translation brings about a non-vanishing electric transition dipole $\boldsymbol{\mu}_{ij}$ (or $\boldsymbol{\mu}$)≠0, whereas a “rotation” of electrons leads to a magnetic transition dipole $\boldsymbol{m}_{ij}$ (or $\boldsymbol{m}$)≠0. Both situations can lead to electronic absorption of radiation, and integration over the entire spectral band (*dv*) results in an oscillator strength *f* (dimensionless) [18,19],where ε is molar absorptivity. The absorption spectrum is typically obtained by plotting the above values in the wavenumber unit. Generally, the electric transition dipole term ($\boldsymbol{\mu}_{ij}$) is very much larger than the magnetic dipole, which can make a distinction between (electric-dipole) allowed ($\boldsymbol{\mu}_{ij}\neq0$) and forbidden ($\boldsymbol{\mu}_{ij}=0$) transitions. For example, ε of the electric-dipole allowed π–π* bands is at least $>\sim10^4$, but bands ascribed to the *d-d* transitions of some metal complexes, which are electric dipole forbidden, are at most $\sim10^2$. Note that a dipole strength, *D*, is also used and expressed as follows;Here, Ψ_0 and Ψ_a are the wavefunctions of the *ground* and *excited* states, respectively, which generally correspond to those of the initial (=*i*) and final state (=*j*). Additionally, *m*, *e*, *h* and *c* are the electron mass, charge of the electron, Plank constant, and the velocity of light, respectively. In the context of chiroptical spectroscopy, on the other hand, both transition dipole moments play a critical role. The simplest chiral electronic displacement that can yield CD response is along a helical path, which implies a simultaneous *translation* plus *rotation of charge*; that is a transition with $\boldsymbol{\mu}\neq0$ and $\boldsymbol{m}\neq0$ and for which the two vectors are not orthogonal (see Fig. 2).

The integral of a CD band is directly proportional to the rotational strength (*R*):where $\Delta\varepsilon$ is the molar dichroic (or differential) absorption. Moreover, rotational strengths are the product of wavefunction overlap integrals, and can be expressed as the *Rosenfeld equation*; that is, the imaginary part of the scalar product of the electric ($\boldsymbol{\mu}$) and magnetic ($\boldsymbol{m}$) dipole transition moments of an electronic transition:where Im refers to the imaginary component of the scalar product. If $<\Psi_0|\mu|\Psi_a>=0$ (in other words, if absorbance is zero), *R* is also zero. Thus absorbance is necessary for a CD signal. The superposition of $\boldsymbol{\mu}$ and $\boldsymbol{m}$ results in a helical displacement of charge, which interacts differently with left- and right-circularly polarized light. That is, the electric dipole operator ($<\Psi_0|\boldsymbol{\mu}|\Psi_a>$) results in a charge separation and the magnetic dipole operator ($<\Psi_0|\boldsymbol{m}|\Psi_a>$) a charge circulation, so the combination of the two yields both a charge separation and circulation along a screw axis (Fig. 2). When the molecule is symmetrical, there will be no preferred direction for the charge circulation, and *R* will be zero. This explains the strong CD signal is originated from helices, in

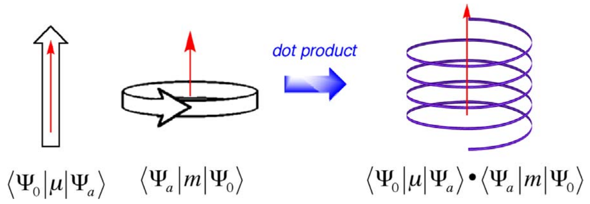

Fig. 2. Origin of chirality based on the combined electronic and magnetic transition moments.