

TEMPERATURE-DEPENDENT CHIROPTICAL RESPONSES OF CHIRAL MONOLAYER-PROTECTED GOLD NANOCCLUSERS

Toshiyuki Fukui, Hiroshi Yao, Keisaku Kimura

*Graduate School of Material Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Akogun, Hyogo, 678-1297, Japan
skmasterhelm@yahoo.co.jp*

Recently, we have reported the synthesis and chiroptical properties of optically active gold nanoclusters protected by a pair of enantiomers of penicillamine [1]. On the basis of kinetic and structural considerations, we have attributed the observed optical activity to a dissymmetric field induced by the chiral penicillamine shell. A recent theoretical study supports the dissymmetric field model [2]; symmetric metal cores can be optically active when perturbed by a dissymmetric field originating from the surface adsorbates. On the other hand, the origin of optical activity of glutathione-protected gold nanoclusters has been discussed in the context of an inherently chiral core model [3,4]. Thus the arguments on the origin of optical activity are still fragmentary due to few examples of well-defined optically active nanoclusters. In the present study, to further determine the factors that govern the optical activity of such gold nanoclusters, we have investigated circular dichroism (CD) of the chiral penicillamine-protected gold nanoclusters in aqueous solution as a function of temperature. On the basis of the temperature-dependent chiroptical behaviors, the origins of their optical activity are discussed.

Each of two kinds of penicillamines (D- or L-form) was used as a monolayer protecting agent. Briefly, a freshly prepared aqueous NaBH₄ solution was added into mixture of HAuCl₄ and penicillamine (D-pen or L-pen) in methanol under vigorous stirring, followed by the addition of ethanol into the stored solution yielding a dark-brown crude precipitate. After completely washing the precipitate, the sample powder was obtained by a freeze-drying procedure. The gold nanocluster sample prepared by using D-pen or L-pen is termed as Au-D-pen or Au-L-pen, respectively. To separate or purify the gold nanoclusters that differ in size, charge or conformation, we applied polyacrylamide gel electrophoresis (PAGE) using a slab gel unit that employs a gel of 2-mm thickness. On the basis of electrophoretic mobility of the gold nanocluster compounds, the separated compounds are referred to as **1**, **2**, ... (consecutive numbers), with the order of mobility **1** > **2** > When distinguishing these compounds in regard to the stereochemistry of the surface ligands, a suffix L or D is added at the end the compound number; for example, **1**_D, **2**_D, ... for the Au-D-pen nanocluster sample.

A CD signal of the gold nanocluster compound should be correlated with its overall structure involving the core geometry and surface ligand conformations or fluctuations, so that perturbation by the temperature change may vary the CD response. CD spectra of the fractioned compounds **1**_D and **1**_L measured at 20 and 40 °C are shown in Figure 1a. The core diameter of compound **1** has been determined to be 0.6 nm by using small-angle X-ray scattering analysis [1]. The compounds **1**_D/**1**_L showed considerably complicated CD behaviors having a clear mirror-image relationship between the D- and L-form species. In addition, the spectra exhibited a temperature dependence. Figure 1b shows the difference between the spectra measured at 40 and 20 °C. In the figure, the CD differences observed in the wavelength region shorter than 270 nm are essentially attributed to those by chiral penicillamine itself. Note that we have confirmed the spectral reversibility in the CD response.

We can know the striking feature showing obvious spectral changes in the metal-based transition region of the CD signal (500-700 nm). For example, the difference spectrum exhibits CD signals with a positive (negative) band at around 600 nm and a negative (positive) band around 265 nm. More importantly, the difference spectra exhibited an

unequivocal mirror-image relationship between the compounds 1_D and 1_L , suggesting occurrence of similar stereochemical changes between the cluster enantiomers. We have confirmed that the ordinary absorption spectra of these compounds measured at 40 °C were almost identical with those at 20 °C, respectively. Therefore, the CD differences for compounds $1_D/1_L$ perturbed by the temperature change are exclusively correlated with the surface stereostructure of the gold nanoclusters. Further considerations based on the temperature-dependent chiroptical behaviors of the nanoclusters give us indication for the origins of their optical activity, and thus, we will give explanations in terms of a dissymmetric field model at the meeting

References:

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Figures:

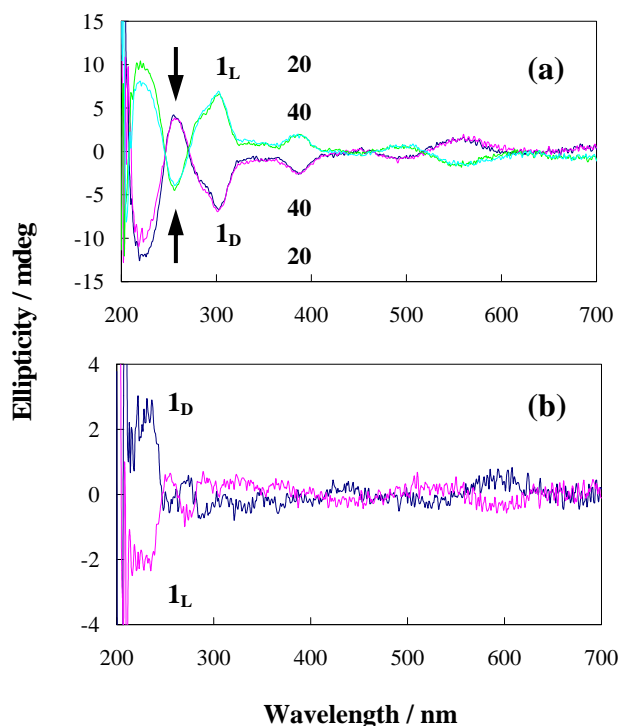


Figure 1. (a) Temperature-dependent CD spectra of $1_D/1_L$ in aqueous solution. (b) CD signal differences between the spectra at 40 °C and 20 °C.