SYNTHESIS AND CHIROPTICAL STUDY OF OPTICALLY ACTIVE THIOLATE-CAPPED SILVER NANOCLUSTERS

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Recently, we have reported the synthesis and chiroptical properties of optically active gold nanoclusters protected by a pair of penicillamine enantiomers [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. We report here the synthesis and chiroptical properties of optically active D-/L-penicillamine-capped silver nanoclusters with the core size ranged in 1-3 nm.

Each of three kinds of penicillamines (D/L- or racemate-form) was used as a monolayer protecting agent. Briefly, a freshly prepared aqueous $NaBH_4$ solution was added into mixture of $AgNO_3$ and penicillamine (D/L-pen or rac-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 power was obtained by a vacuum-drying procedure. The silver nanocluster sample prepared by using D-pen, L-pen or rac-pen is termed as Ag-D-pen, Ag-L-pen or Ag-rac-pen, respectively. To separate or purify the silver nanoclusters that differ in size and charge, 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 silver 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, D or rac is added at the end the compound number; for example, $\mathbf{1}_D$, $\mathbf{2}_D$, … for the Ag-D-pen nanocluster sample. Size distributions of silver nanoclusters were determined by a small angle X-ray scattering (SAXS) technique in solution: The SAXS profiles of silver nanoclusters dispersed in solution were first measured, followed by analyzing the profiles based on the assumption that the size distribution of spherical cluster is approximated by the Γ–distribution function.

To obtain information on chiroptical properties of the prepared silver nanoclusters, we measured circular dichroism (CD) spectrum of each numbered compound. CD spectra of the fractioned compounds $\mathbf{1}_D$, $\mathbf{1}_L$ and $\mathbf{1}_{rac}$ are shown in Figure 1. The mean core size of the cluster compound 1 was determined to be 1.05 nm. For homochiral penicillamine-capped silver nanoclusters, ligand chirality had a dramatic effect on the CD spectra of the clusters. Note that optically active penicillamine contributes to the CD signal only in the UV region in the wavelength shorter than ~270 nm. The pair of CD spectra in Figure 1 showed measurable Cotton effects and a mirror-image relationship in metal-based electronic transition resion, suggesting that enantiomeric ligands can produce the corresponding enantiomeric silver nanoclusters.

To sharply elucidate the chiroptical responses of the optically active silver nanoclusters, we calculated the anisotropy factor (or *g*-factor) for the separated compounds $\mathbf{1}_D$ and $\mathbf{1}_L$. The result is shown in Figure 2. The obtained maximum anisotropy factor is 1.5 x 10^{-3}. The chiroptical response of the silver nanoclusters is surprisingly several-fold larger than that of the gold nanoclusters having the same ligand in comparable size [1]. In addition, we found that the anisotropy factor was increased with a decreased in the core size of the nanoclusters. In the present silver nanoclusters, the vicinal effect from asymmetric carbons in the ligands should be the universal origin for their optical activity, but its enhancement might be attributed to the additional contributions from a chiral silver core or chiral adsorption pattern. The field of optically active nanoclusters is a very broad one ranging from cluster science to surface science, so that we believe that our findings will give a new development of this fascinating subject in nanoscience.

References:

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Figures:

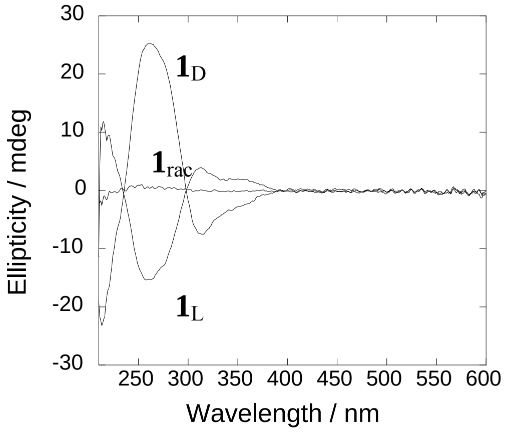

Figure 1 CD spectra of compounds **1**.

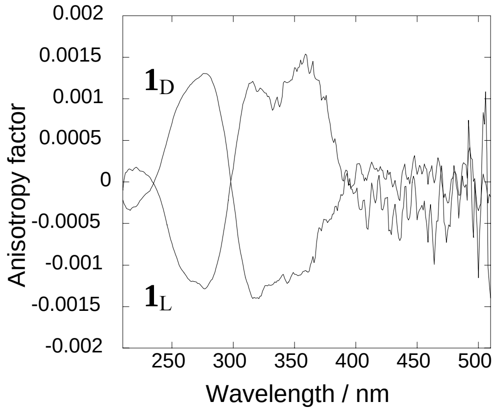

Figure 2 Anisotropy factor of **1**$_D$/**1**$_L$.