Large Optical Activity of Gold Nanocluster Enantiomers Induced by A Pair of Optically Active Penicillamines

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FT-IR Absorption Spectroscopy

FT-IR absorption spectra of pure D-, L- and rac-penicillamine (Figure S1-a) along with those of the corresponding as-prepared penicillamine-capped gold nanoclusters (Figure S1-b). Note that the spectra were off-set by adding a constant for clarity.

![Figure S1. FT-IR spectra of (a) pure penicillamines and (b) as-prepared penicillamine-capped gold nanoclusters. For clarity, the spectra were off-set by adding a constant.](image)

Three kinds of pure penicillamine molecules showed quite similar IR spectra (Figure S1-a), and were revealed to be present in the zwitterion form. The broad features between 2200 and 3200 cm\(^{-1}\) were due to the N-H stretch of NH\(_3^+\). Two sharp bands observed at 1505-1515 and 1630-1650 cm\(^{-1}\) were attributed to the symmetric and the asymmetric N-H...
bending modes of NH$_3^+$, respectively. The two peaks at ~1400 and 1590-1605 cm$^{-1}$ exhibited the presence of the COO$^-$ stretch.$^1$

Figure S1-b shows the IR spectra of the penicillamine-capped gold nanocluster samples. Although we can find broad spectral features as compared to the parent modifiers, Figures S1-a and S1-b are similar to each other. No peak could be seen at around 2570 cm$^{-1}$ that corresponds to the S-H stretching vibration mode, indicating that penicillamine molecules anchor on the gold nanocluster surface through the S-Au bonding. All capping agents contained both the carboxylate (COO$^-$) and the primary amino (NH$_2$) group. This was confirmed by the existence of characteristic peaks for the stretch modes of COO$^-$ (~1390 and ~1590 cm$^{-1}$), and those for the N-H stretch (~3420 cm$^{-1}$) and the N-H bending (~1630 cm$^{-1}$) modes of NH$_2$.

Preparation and Characterization of DMSA-Capped Gold Nanoclusters

The DMSA-capped gold nanoclusters were prepared based on the reduction of HAuCl$_4$ by sodium borohydride in methanol using meso-2,3-dimercaptosuccinic acid (DMSA) as the surface capping agent.$^2$ Note that the mean core size could be controlled by changing the molar ratio of DMSA and HAuCl$_4$ (S/Au).

At S/Au = 3.0, small gold nanoclusters with core diameter of 0.6 nm, whose size is determined by the small-angle X-ray scattering (SAXS) analysis, were obtained. The absorption spectrum showed distinct peaks at ~390 and 285 nm, significantly different from that of the gold nanoparticle larger than ~2 nm in diameter. The absorption spectrum was

![SAXS profiles and estimated cluster size distribution](image)

**Figure S2.** (a) SAXS profiles of the DMSA-capped gold nanoclusters in aqueous solution. The simulated profile is shown by a solid curve. (b) Estimated cluster size distribution.
almost identical with that obtained by Tsukuda and co-workers for similar DMSA-capped gold nanoclusters composed of 11–13 gold atoms (~0.8 nm in diameter).\(^2\) Figures S2-a shows the SAXS profile along with the simulated curve obtained based on the assumption of \(\Gamma\)-distribution of the DMSA-capped gold nanoclusters in aqueous solution. Figure S2-b shows the estimated cluster size distribution. Figure S3-a shows absorption spectrum of the DMSA-capped gold nanoclusters in aqueous solution. Figure S3-b shows CD spectrum of the DMSA-capped gold nanoclusters, indicating no optical activity.

**References**
