CHIRAL CROSS-LINKING BETWEEN MONOLAYER-PROTECTED GOLD NANOCLUSTER SURFACES: LARGE CHIROPTICAL EFFECTS

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Recent important topic in nanoscience concerns gold nanocluster assemblies and their interesting optical/chiroptical studies [1]. One way to fabricate such assemblies is to use cross-linkers, and better control of strong binding between the gold nanoclusters should be achieved using $\alpha,\omega$-dithiols. Aggregation of gold nanoclusters via cross-linking with $\alpha,\omega$-dithiols is a well-known phenomenon, but that via “chiral linkage” and the related chirality transfer from (through) the surface chiral cross-linkers to nanomaterials is not well studied. In the present study, we report chiroptical properties of gold nanocluster assemblies fabricated via a one-step ligand exchange cross-linking using a bidentate chiral dithiol. This study would involve a high-throughput approach to the finding of new optically active nanomaterials.

The model system is consisting of racemic (optically inactive) penicillamine-protected gold nanoclusters without optical activity and L-dithiothreitol (L-DTT) as the chiral cross-linker (and exchangeable ligand) (see Fig. 1a). The gold cluster assemblies produced via cross-linking were separable by gel electrophoresis. Chiroptical effects were evaluated by circular dichroism (CD) spectra.

The products of the ligand exchange reaction included gold nanoclusters containing both penicillamine and L-DTT, which implied that the exchange was partial (~67%). Gel electrophoresis with a very low gel concentration (3%) could yield a purified assembly. The mean core diameter was ~0.8 nm, and the assembly size ranged in 20–50 nm. Very large chiroptical responses with the maximum anisotropy factors ($\Delta\varepsilon/\varepsilon = \text{intensity of the molar dichroic absorption } \Delta\varepsilon/\text{normalized to the extinction coefficient } \varepsilon$) of about $1.0 \times 10^{-3}$ were found for the assembly (Fig. 1b). We then propose a model that the origin of the observed large optical activity is surface intrinsic chirality or handedness caused by cyclic cross-linking between clusters with at least two L-DTT molecules (Fig. 1c). We believe that such chiral nano-engineering methodology will play a fundamental role in an entire new class of materials, for example, metamaterials, in the future.

Keywords: Gold nanoclusters; Chiral cross-linking; Optical activity; Surface intrinsic chirality

References