

Asymmetric Transformation of Monolayer-Protected Gold Nanoclusters via Chiral Phase-Transfer

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Size Determination by Solution Small-Angle X-ray Scattering (SAXS) Measurements

The core size of the gold nanoclusters was determined by the small angle X-ray scattering (SAXS) technique in solution. Briefly, the SAXS profile of gold nanoclusters dispersed in solution was first measured, followed by analyzing the profile based on the assumption that the size distribution is approximated by the Γ -distribution function. The Γ -distribution function, $P(D)$, is expressed as eq 1,

$$P(D) = \frac{1}{\Gamma(M)} \left(\frac{M}{D_0} \right)^M \exp \left(-\frac{D}{D_0} M \right) D^{M-1} \quad (1)$$

$$\Gamma(M) = \int_0^{\infty} x^{M-1} e^{-x} dx \quad (2)$$

where M is the shape (or distribution) parameter that relates to the dispersion of the estimated diameters. $\Gamma(M)$, expressed in eq 2, is the gamma function and D_0 denotes the mean diameter of the gold core. Hence, D_0 and M are determined based on the SAXS profile simulation.

Figure S1 (upper) shows the experimental scattering profiles of the compounds **1–3** (**1_s–3_s**) along with the simulated curves. The simulated curves well reproduced the scattering profiles using the Γ -distribution function as also shown in Figure S1 (lower). The obtained parameters are as follows: **1** for $D_0 = 0.57$ nm ($M = 6.25$), **2** for $D_0 = 1.18$ nm ($M = 68.3$), and **3** for $D_0 = 1.75$ nm ($M = 23.0$).

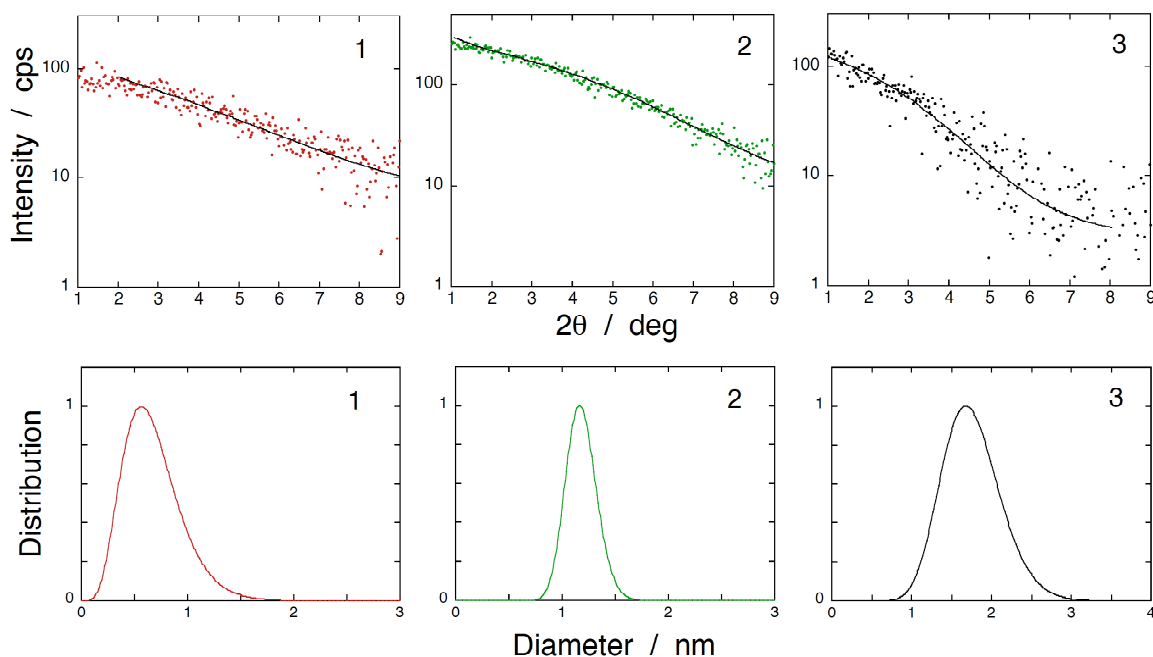


Figure S1. (Upper) SAXS intensity profiles of each numbered gold nanocluster compound. The experimental and the simulated profiles are shown by dots and curves, respectively. (Lower) Obtained nanocluster size distributions of each numbered compound.

Phase-Transfer Experiments on Fractions 3

Figure S2 summarizes the spectroscopic results on the phase-transfer for the fractioned compounds **3**. Figure S2-a or S2-b shows the absorption or CD spectra, respectively, of the original *rac*-Pen-protected gold nanocluster compound **3** in water ($\mathbf{3}_{\text{rac}}(\text{w})$) and its phase-transferred sample in chloroform ($\mathbf{3}_{\text{rac}}(\text{o})$). Figure S2-c or S2-d shows the absorption or CD spectra, respectively, of the original (*S*)-/(*R*)-Pen-protected gold nanocluster compounds **3** in the aqueous phase ($\mathbf{3}_{\text{S}}(\text{w})/\mathbf{3}_{\text{R}}(\text{w})$) and their phase-transferred samples in chloroform ($\mathbf{3}_{\text{S}}(\text{o})/\mathbf{3}_{\text{R}}(\text{o})$). In all cases, almost complete phase-transfer has been achieved. These compounds **3** ($\mathbf{3}_{\text{rac}}$, $\mathbf{3}_{\text{S}}$, and $\mathbf{3}_{\text{R}}$) exhibit featureless absorption spectra. It is important to note that the spectral shapes did not change upon the phase-transfer. In the transfer of $\mathbf{3}_{\text{rac}}(\text{w})$ across the water/chloroform interface, the induced chiroptical responses were almost indiscernible, so we can again conclude that the induced optical activity is size-dependent. In the case of enantiopure compounds $\mathbf{3}_{\text{S}}(\text{w})/\mathbf{3}_{\text{R}}(\text{w})$, on the other hand, discernable CD signals could be observed; however, their changes upon the phase-transfer were small, suggesting that the DME⁺ cation hardly influences the chiroptical responses of the gold nanocluster compound in this size region (1.75 nm in core diameter).

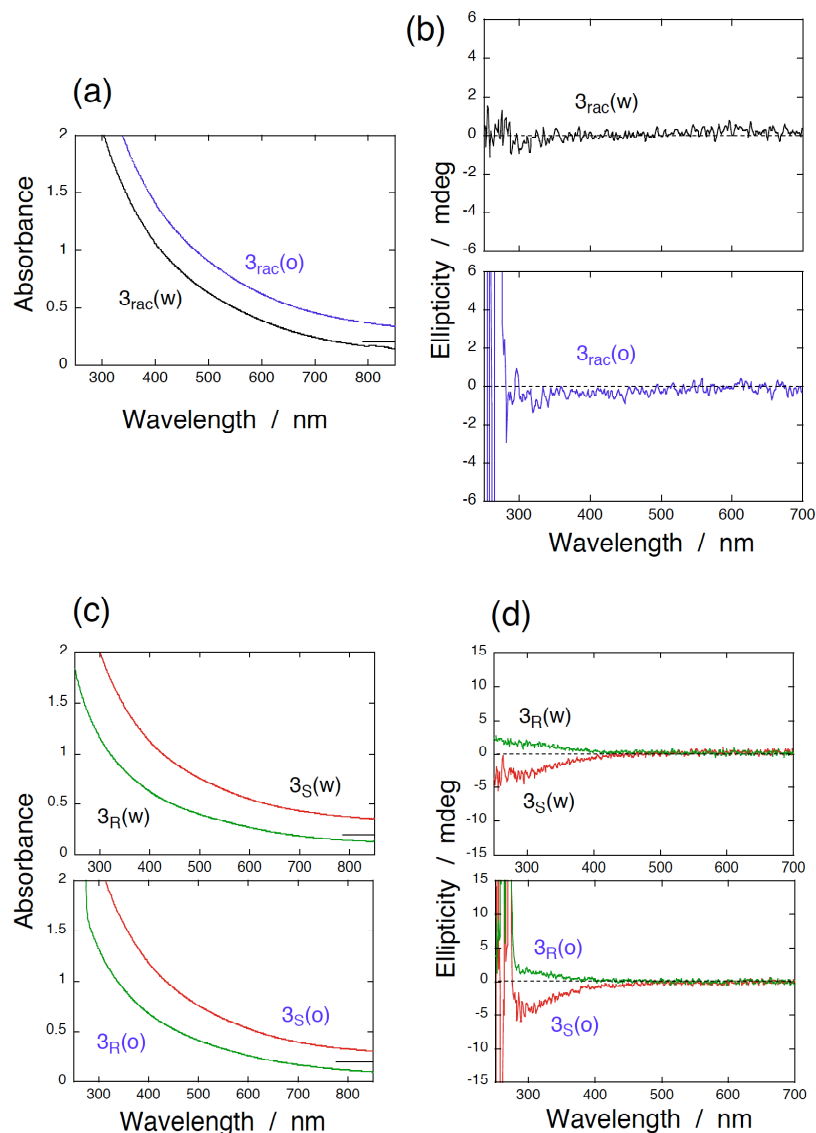


Figure S2. (a) or (b) shows the absorption or CD spectra, respectively, of the *rac*-Pen-protected gold nanocluster compound **3** in aqueous phase ($3_{\text{rac}}(\text{w})$) and its phase-transferred sample in chloroform ($3_{\text{rac}}(\text{o})$). The absorption spectrum in chloroform was off-set by adding a constant. (c) or (d) shows the absorption or CD spectra, respectively, of the original (*S*)-/(*R*)-Pen-protected gold nanocluster compounds **3** in aqueous phase ($3_{\text{S}}(\text{w})$ / $3_{\text{R}}(\text{w})$) and their phase-transferred samples in chloroform ($3_{\text{S}}(\text{o})$ / $3_{\text{R}}(\text{o})$). The absorption spectra for $3_{\text{S}}(\text{w})$ and $3_{\text{S}}(\text{o})$ were off-set by adding a constant.

Ordinary Absorption and CD Spectra of (1*R*,2*S*)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEBr) in Ethanol

Figure S3 shows the ordinary absorption (a) and CD spectra (b) of DMEBr in ethanol. This compound contributes to the CD signals only in the UV region ($\leq \sim 280$ nm). Note that we used ethanol instead of chloroform as a solvent, because chloroform has an absorption onset at around 260 nm.

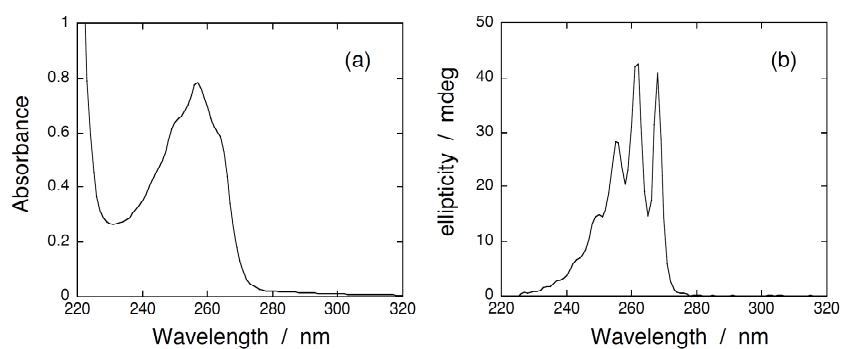


Figure S3. Absorption (a) and CD (b) spectra of DMEBr in ethanol.