Chirality control in silver cluster

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Magic number metal clusters with atomically precise structures have attracted great interest over the recent two decades because of their fascinating structural, electronic and optical properties. Furthermore, optical activity could be induced in the electronic transitions of metal clusters either by an asymmetric arrangement of constituents or by a dissymmetric field of a chiral ligand layer. Recently, we reported on the induction of optical activity in the luminescent silver clusters with employing enantiomeric ligands, demonstrating circular polarized luminescence (CPL) activity for the first time.[1] However, the origin of optical activity has remained unclear. The mass analysis revealed that the silver cluster possesses a composition of $[Ag_{29}(dithiolate)_{12}]^{3-}$. The X-ray crystal structure of a silver cluster with an analogous composition, $Ag_{29}(BDT)_{12}(TPP)_4$ (BDT: 1,3-benzenedithiol; TPP: triphenylphosphine), manifested the presence of intrinsic chirality in the atomic arrangement.[2] However, the cluster crystal included a mixture of enantiomeric clusters to form a racemic composition. In the present study, we succeeded in the separation of enantiomeric forms using a chiral column with a HPLC technique. The separated fraction afforded mirror image circular dichroism (CD) spectra, confirming the presence of intrinsic chirality and successful separation of enantiomers (Figure 1). The mechanism of chiral induction in the synthesis of $Ag_{29}(DHLA)_{12}$ (DHLA: a-dihydrolipoic acid) NCs with a chiral ligand system is further discussed with the aid of DFT calculations. The use of the enantiomeric DHLA ligand preferentially leads to a one-handed atomic arrangement which is more stable than the opposite one, inducing the enantiomeric excess in the population of intrinsically chiral Ag_{29} NCs with CD activity.

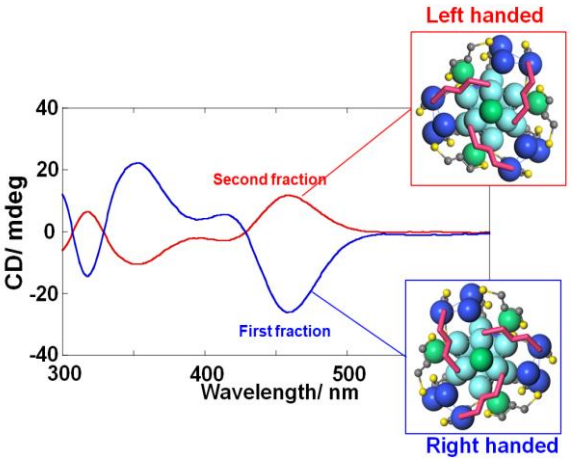

Figure 1. CD spectra and structure model of chiral Ag_{29} clusters.

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