Chirality is a ubiquitous observation in an extremely wide spectrum from molecules to galaxies. It has attracted special interest among chemists as molecular chirality determines the optical, biomedical, and catalytic applications of many compounds. Since Pasteur’s first separation of enantiopure tartaric acid from their conglomerate crystals in the 1840s, chiral resolution has become a decisive task for the development of fine chemical and pharmaceutical industries. Now, Zhao-Yang Wang, Shuang-Quan Zang, and co-workers have made the enantioseparation of intrinsically chiral silver nanoparticles possible through a similar conglomerate crystallization method.1

In this work, intrinsically chiral silver nanoparticles consisting of a 30-silver-atom core (typically referred to as Ag30 nanoclusters), stabilized by 8 achiral carboranetrithiolate and 6 achiral phosphine ligands, were synthesized and crystallized as a racemic mixture in a dual-solvent system of tetrahydrofuran and acetonitrile. The X-ray crystallography analysis of single crystals of racemic nanoclusters (Ag30-rac) reveals an “outside-in” chirality transfer scheme of cluster chirality origin. Specifically, the interaction of B−H···π and C−H···π in the cluster between neighbored ligands organizes the surface phenyl ring (from the phosphine ligand) into a spiral pattern, which induces chiral arrangement of carboranetrithiolate and phosphine ligands at the metal−organic interface. In addition to the establishment of intrinsic cluster chirality, the rich surface functionality also provides a good means for the enantioseparation of racemic Ag30 nanoclusters by conglomerate crystallization. Recrystallization of racemic Ag30 nanoclusters in dimethylacetamide (DMAc) produces enantiomorphic crystals (R- or L-Ag30, Figure 1), where enantiopure nanoclusters are organized into a helical architecture reminiscent of double-stranded DNA (Figure 1a,b,d,e). The double-helical arrangement is maintained through diverse noncovalent interactions between clusters (e.g., B−H···π, π···π, C−H···O, and H···H interactions), among which the most notable one is the host−guest binding between DMAc molecules and enantiopure nanoclusters. With this facile chiral resolution method, Zhao-Yang Wang, Shuang-Quan Zang, and co-workers also demonstrated the circularly polarized luminescence (CPL)
activity of the enantiopure conglomerates, in which the mirror responses were recorded at \( \sim 650 \text{ nm} \) with a disymmetry factor of \( 7.0 \times 10^{-4} \) (Figure 1g,h).

With the accelerated development of nanochemistry in recent decades, chiral arrangements have been widely observed in various inorganic nanoparticles at the intra- and interparticle level.\(^7\) As the structure of conventional nanoparticles becomes ambiguous in atomic resolution, metal nanoclusters protected by organic ligands, which can be synthesized and characterized with atomic precision, have recently emerged as paradigm particles for revealing the origin of chirality at the nanoscale.

The discovery of optical activity in metal nanoclusters can be traced back to the seminal work by Whetten and co-workers in 1998, where chiral glutathione (H-SG) ligands were used to induce circular dichroism (CD) response in \( \text{Au}_{25}(\text{SG})_{18} \) nanoclusters.\(^3\) Since then, many other chiral ligands including thiols, dithiols, and diphosphines have been used to synthesize chiral metal nanoclusters. One of the most significant findings in cluster chirality research is the generation of intrinsic chirality in the absence of chiral ligands.\(^4,5\) In 2007, Kornberg and co-workers reported for the first time the crystal structure of thiolate-protected metal nanoclusters, where a pair of racemic \( \text{Au}_{102}(\text{p-MBA})_{44} \) (\( \text{p-MBA} \) denotes \( \text{p-mercaptobenzoic acid} \)) nanoclusters were identified in their single crystals.\(^4\) Although the \( \text{p-MBA} \) ligand is achiral, the asymmetric arrangement of the \( (\text{p-MBA})-\text{Au-(p-MBA)} \) protecting motifs on the \( \text{Au}_{79} \) core (Marks’ decahedron-based structure) establishes the intrinsic chirality of \( \text{Au}_{102}(\text{p-MBA})_{44} \). In addition to the asymmetric arrangement of metal–ligand protecting motifs, the intrinsic chirality of the clusters can also be attributed to the chiral atom packing in their metal core.

As the structure of conventional nanoparticles becomes ambiguous in atomic resolution, metal nanoclusters protected by organic ligands, which can be synthesized and characterized with atomic precision, have recently emerged as paradigm particles for revealing the origin of chirality at the nanoscale.
Since intrinsically chiral metal nanoclusters synthesized with achiral ligands are usually produced in the form of racemic mixtures, chiral resolution is generally required before chiroptical and many other applications. Bürgi and co-workers designed a chiral high-performance liquid chromatography (HPLC) method (Figure 2a) for the enantioseparation of chiral nanoclusters such as Au14(SR)24, Au40(SR)24, Au28(SR)20, and Au38Cu(SR)24 (SR denotes the thiolate ligand). In addition to chiral HPLC, the enantioseparation of chiral metal nanoclusters can also be achieved by ion-pairing reactions with chiral cations (Figure 2b). The chiral resolution by this method has been successfully applied to Au102(SR)44 and [Ag28Cu12(SR)24]4−. More recently, chiral molecules such as α-cyclodextrin have also been used as chiral resolution agents. Although previous chiral resolution methods inevitably depend on external “chiral stimuli” (e.g., chiral stationary phases, cations, and molecules), the conglomerate crystallization method developed in this work does not require external chiral stimuli (Figure 2c). This suggests that the “chiral–achiral” supramolecular interaction can be used as an alternative to the widely explored “chiral–chiral” supramolecular interaction, to selectively separate the cluster enantiomers. In addition, since the conglomerate crystallization method is essentially a recrystallization process, it can provide a sufficient amount of enantiopure nanoclusters for further chiroptical exploration. One fascinating example is the CPL responses investigated in this work. It is also important to note that the rich surface functionality of Ag30 nanoclusters can provide abundant sites to rigidify the cluster surface, which may further increase the CPL intensity through the aggregation-induced emission (AIE) mechanism.

We envision that the proteinlike hierarchical structure of metal nanoclusters lays the structural foundation for the biomimetic self-assembly behavior and may help produce more complex architectures in the near future. In summary, the conglomerate crystallization methodology developed in this study by Zhao-Yang Wang, Shuang-Quan Zang, and team provides a facile and efficient way for the enantioseparation of intrinsically chiral metal nanoclusters. This can not only unravel atomic-level clues for understanding the chirality origin and self-assembly behavior of metal nanoclusters but also pave the way for further applications of chiral metal nanoparticles.

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