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Research Article

# Spontaneous Resolution of Chiral Multi-Thiolate-Protected Ag<sub>30</sub> Nanoclusters

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**ABSTRACT:** Despite significant progress achieved in the preparation of chiral nanoparticles, the enantioseparation of racemates still presents a big challenge in nanomaterial research. Herein, we report the synthesis and structural characterization of racemic anisotropic nanocluster  $Ag_{30}(C_2B_{10}H_9S_3)_8Dppm_6$  ( $Ag_{30}$ -*rac*), which is protected by mixed carboranetrithiolate and phosphine ligands. Spontaneous self-resolution of the racemates was realized through conglomerate crystallization in dimethylacetamide (DMAc). The homochiral nanoclusters in the racemic conglomerates adopt enantiomeric helical self-assemblies (R/L- $Ag_{30}$ ). Diverse noncovalent interactions as the driving force in directing superstructure packing were elucidated in detail. Furthermore, the nanoclusters show red luminescence in both solid and solution states, and the racemic conglomerates display a mirror-image CPL response. This work provides atom-precise helical nanoparticle superstructures that facilitate an in-depth understanding of the helical-assembly mechanism.



# ■ INTRODUCTION

Helical nanoparticle (NP) superstructures constitute a rapidly expanding subclass of chiral nanomaterials in which NPs are arranged in three dimensions about a screw axis.<sup>1</sup> Their intrinsic asymmetry gives rise to a variety of interesting properties, including plasmonic chiroptical activity in the visible spectrum,<sup>2,3</sup> and they hold immense promise as chiroptical sensors and as components of optical metamaterials.<sup>4</sup> The general method to achieve the helical NP assembly employs biological or bioinspired templates, such as peptide, protein, and DNA, as supports.<sup>5,6</sup> Due to missing structure information on the NPs, precise organization of the resulting NP assemblies is lacking, which significantly hinders an indepth understanding of the assembly dynamics and the weak interactions therein. Hence, atomically precise NPs for the assembly of helical NP superstructures are urgently sought to address such issues."

Atomically precise noble metal nanoclusters with diameters from subnanometer to a few nanometers constitute an emerging class of materials linking atoms and nanoparticles that have gained much interest due to their aesthetically pleasing structures and intriguing photophysical properties which arise from the quantum confinement effects.<sup>8–14</sup> Moreover, these metal nanoclusters may also serve as building blocks in a superstructure assembly through covalent bonding,<sup>15–18</sup> or noncovalent weak interactions such as C–  $H\cdots \pi$ ,  $\pi \cdots \pi$ , and van der Waals (vdW) forces,<sup>19–21</sup> and the assembled arrays usually exhibit distinct photophysical properties.<sup>20–24</sup> The atom-precise structure information on metal nanoclusters in combination with their function as building blocks makes them perfect candidates in the helical NP assembly. Hence, a structurally well-defined nanocluster-based helical assembly could extend the chirality study from the molecular to the supramolecular level.

Since the first observation of optical activity in the goldthiolate nanocluster reported in 1998,<sup>25</sup> chiral thiolateprotected metal nanoclusters have become an intensively studied field due to their prospective applications in catalysis, pharmaceutics, sensors, and optoelectronics.<sup>26–29</sup> To date, a series of chiral metal nanoclusters with atom-precise novel structures have been obtained, and the origin of their chirality has been partly elucidated.<sup>30–34</sup> However, the enantioselective synthesis of optically pure nanoclusters is still a challenge, as many chiral nanoclusters are obtained as racemates. Furthermore, enantioseparation of such chiral nanoclusters by HPLC, chiral ion-pairing, or other methodologies is generally tedious and plagued by low efficiency.<sup>35-38</sup> The spontaneous resolution of enantiomers upon crystallization is an intriguing and important phenomenon in a number of research areas, wherein noncovalent interactions usually play a key role in the process.<sup>39</sup> It is noteworthy that such supramolecular assembly-based separation has the advantages of high efficiency, simple operation, low cost, and easy scaleup, which is vital for subsequent studies.

Here we report the synthesis of chiral luminescent silver nanoclusters, formulated as  $Ag_{30}(C_2B_{10}H_9S_3)_8Dppm_6$  (Ag<sub>30</sub>-

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*rac*), as racemates by a facile one-pot method with the mixed achiral ligands 8,9,12-trimercapto-1,2-*closo*-carborane ( $C_2B_{10}H_{12}S_3$ ) and bis(diphenylphosphino)methane (Dppm) (Figure 1). Single-crystal structure analysis revealed that the



Figure 1. Schematic illustration of the synthesis and self-resolution of the racemic  $Ag_{30}$ -*rac.* Color labels: green, blue, red, and violet, Ag; yellow, S; pink, P; gray, C; cyan, B; light gray, H.

chirality of the nanocluster arises from the chiral arrangement of the ligands in the protective layer directed by hydrogenbonding interactions between the carboranyl units and the phenyl groups of phosphine ligands. Interestingly, the racemic nanoclusters dissolved in dimethylacetamide (DMAc) underwent conglomerate crystallization to give a mixture of racemic conglomerates. More strikingly, in each single crystal, the homochiral nanoclusters adopt a spontaneous helical assembly about a 3-fold screw axis. The racemic conglomerate crystals are designated R-Ag<sub>30</sub> and L-Ag<sub>30</sub> hereafter, where R and Lrepresent the right-handed and left-handed helix, respectively. The racemates  $(Ag_{30}$ -rac) and the racemic conglomerates (R/L-Ag<sub>30</sub>) both show bright red emission in the solid- and solution-state. Circularly polarized luminescence (CPL) of the enantiomeric conglomerates was recorded and showed a mirror-image response.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of the Ag<sub>30</sub>-rac and R/ L-Ag<sub>30</sub>. Ag<sub>30</sub>-rac nanoclusters were synthesized by a facile onepot process. In brief, Dppm was added to a yellow suspension containing carboranetrithiol and CF<sub>3</sub>COOAg in THF-CH<sub>3</sub>CN. To the resultant clear solution was added reducing agent hydrazine hydrate, and the reaction mixture was aged for 12 h in the dark. The afforded precipitate was isolated by centrifuge, and the yellow supernatant was evaporated slowly to produce yellow blocklike crystals of Ag<sub>30</sub>-rac (Figure S1). Powder X-ray diffraction (PXRD) patterns confirmed that the precipitate collected from centrifugation was also Ag30-rac but in the microcrystalline state (Figure S2). Thus, bulk synthesis is available for further studies. Notably, although hydrazine hydrate was commonly used in metal nanomaterial syntheses, it is not a popular reducing agent for the preparation of atom-precise small nanoclusters.<sup>40</sup> Hence, this work might motivate further metal nanocluster preparation with alternative reducing agents.

Prismlike single crystals of the racemic conglomerates R/L-Ag<sub>30</sub> were obtained by recrystallizing Ag<sub>30</sub>-rac in DMAc (Figure S1). The polar solvent molecules, likely acting collectively as a "conglomerator", are believed to be a key factor in the self-resolution. First, noncovalent interactions could be formed between the metal nanoclusters and the solvent molecules, which is prominent in the progress of spontaneous chiral resolution. Details of the weak interactions are elucidated in the structure analysis section. Also, the improved solubility of the nanoclusters in DMAc altered the kinetics of crystallization which might lead to a different packing mode.

Employment of trithiolate protective ligands in the metal nanocluster preparation is based on the following considerations. So far, the overwhelming majority of reported metalthiolate clusters are protected by monothiolate ligands. Multithiolate-protected metal clusters, by contrast, are expected to display enriched structural diversity, more enhanced stability, and emission performance due to their multiform binding and bridging modes, as well as relatively greater rigidity. In 2015, Bakr and co-workers first reported the crystal structure of a tetrahedrally symmetrical Ag<sub>29</sub>(BDT)<sub>12</sub>(TPP)<sub>4</sub> nanocluster protected by the wide-footprint bidentate 1,3-benzenedithiol (BDT) and triphenylphosphine (TPP).<sup>41</sup> Recently, our group reported the syntheses of a pair of isostructural face-centered cubic  $Ag_{14}$  and  $Cu_{14}$  clusters bearing the carboranedithiolate ligand.<sup>16,42</sup> These results might imply that multithiolate protective ligands could facilitate the formation of nonspherical metal nanoclusters.

No counterion was found in the crystal structure of Ag<sub>30</sub>-rac, suggesting that the Ag<sub>30</sub> nanocluster might be neutral. Energydispersive spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS) confirmed the existence of Ag, C, P, S, and B in Ag30-rac and further excluded the existence of possible counterions such as CF<sub>3</sub>COO<sup>-</sup> (Figures S3 and S4a). The positive-ion electrospray ionization mass (ESI-MS) spectrum of Ag<sub>30</sub>-rac in a mixed solvent of DMF, THF, and CH<sub>3</sub>CN showed sets of signals at m/z 3760.28 and 3821.23 Da with a +2 charge state, which were assigned to the species [M + 2K]<sup>2+</sup> (theoretical m/z 3760.25) and [M + 2K +  $3CH_3CN$ <sup>2+</sup> (theoretical m/z 3821.28), respectively, where  $M = Ag_{30}(C_2B_{10}H_9S_3)_8Dppm_6$  (Figure S5). The negative-ion ESI-MS spectrum also confirmed the inexistence of CF<sub>3</sub>COO<sup>-</sup> in  $Ag_{30}$ -rac (Figure S6). The XPS survey spectrum showed a Ag  $3d_{5/2}$  peak (BE of 368.42 eV) similar to those in other silver nanoparticles and fell between that of CF<sub>3</sub>COOAg (BE of 368.85 eV) and Ag(0) powder (BE of 367.76 eV) (Figure S4), suggesting the mixed-valent  $(Ag^{I/0})$  nature of the  $Ag_{30}$ cluster.<sup>15</sup> The phase purities of  $Ag_{30}$ -rac and R/L- $Ag_{30}$  were confirmed by PXRD measurements (Figure S2). Timedependent UV-vis absorption spectra and emission spectra verified the good stability of the cluster in solution (Figures S7 and S8).

Crystal Structure of Ag<sub>30</sub>-rac. Single-crystal X-ray diffraction (SCXRD) analysis revealed that Ag<sub>30</sub>-rac crystallizes in the trigonal space group  $P\overline{3}1c$  (no. 163). The unit cell contains two racemic nanoclusters,  $Ag_{30}$ - $\alpha$  and  $Ag_{30}$ - $\beta$ , and each cluster is composed of 30 silver atoms, 8 tridentate thiolate ligands, and 6 bidentate auxiliary Dppm ligands (Figure 2a, Figure S9). The discrete molecule exhibits  $D_3$ symmetry. The overall metal structure can be viewed as a regular triangle Ag<sub>3</sub> surrounded by a helically arranged irregular  $Ag_{27}$  crownlike motif. Interestingly, the chiral  $Ag_{30}$ framework is entirely built by triangles through vertex- or edgesharing with a 3-fold axis passing through the center of the regular triangle (Figure 2b). Ag<sub>30</sub>- $\alpha$  was chosen as a representative for the following detailed structural analysis. The Ag…Ag separations in Ag<sub>30</sub>- $\alpha$  fall in the range 2.911-3.409 Å, indicating the existence of argentophilic interactions.



Figure 2. Atomic structure of the cluster in  $Ag_{30}$ -*rac.* (a) Overall structure of the enantiomers. (b) Chiral triangle-based metal architectures in the enantiomers. (c) Illustration of the intracluster noncovalent interactions in the enantiomers. (d-f) Binding modes of carboranetrithiolate and phosphine in  $Ag_{30}$ - $\alpha$ .

The eight carboranetrithiolate ligands can be classified into two groups: (1) Six of them decorate the waist of the crownlike motif adopting a  $\mu_6$ - $\eta^1$ , $\eta^1$ , $\eta^1$ , $\eta^1$ , $\eta^2$ , $\eta^2$  bridging mode with one  $\mu_2$ -thiolate and two  $\mu_3$ -thiolates in each ligand (Figure 2e), and the Ag-S bond lengths lie in the range 2.393-2.716 Å. (2) The remaining two occupied the concave portions on the top and bottom of the inner triangle with each thiolate bridging one silver atom from the inner triangle with a Ag-S bond length of 2.507 Å and two silver atoms from the outer crownlike motif with the Ag-S bond lengths of 2.466 and 2.580 Å (Figure 2d). The Dppm ligands anchor on the edge of the crownlike motif, and each ligand binds to two silver atoms from the same triangle (in red) with the Ag-P bonds of 2.408 and 2.381 Å (Figure 2f). To note, the phenyl groups from the phosphine ligands completely wrap the carboranyl moieties on the top and bottom of the inner Ag<sub>3</sub> triangle (Figure 2c).

To probe the origin of the chirality in the nanocluster, a detailed analysis of the surface ligands' arrangement was conducted. The unusual nonclassical B-H $\cdots\pi$  hydrogen bonding interaction, which was first described by the Yan group,<sup>43</sup> and the  $C_{(carb)}$ -H $\cdots$  $\pi$  interactions were found between the o-carborane cage and the phenyl groups wrapping it (Figure 2c). The H $\cdots\pi$  distance of the B–H $\cdots\pi$  and C<sub>(carb)</sub>– H… $\pi$  bond in Ag<sub>30</sub>- $\alpha$  is 2.348 Å, which is even shorter compared to the B-H… $\pi$  (2.40-2.76 Å) values reported by Yan et al.<sup>43</sup> Reinforced C–H… $\pi$  interactions also exist between the closest phenyl groups from the adjacent Dppm ligands with a bond distance of 3.239 Å. These weak interactions lead to the reverse spiral arrangement of the two sets of benzene rings (red and lavender, three benzenes for each set as shown in Figure 2c), which adopt an "outside-in" transfer of chirality to the silver-organic interface where the phosphine ligands and the six carboranetrithiolate ligands shows chiral arrangements via coordination (Figure 2a, Figure S10) to the  $Ag_{30}$  framework (Figure 2b).

In the crystal structure of  $Ag_{30}$ -*rac*, the racemic nanoclusters all align in the same direction and pack into a hexagonal closest

packed (hcp) superlattice. In the (001) plane of the crystal lattice, nanoclusters of the same chirality are organized into a hexagonal honeycomb close-packing mode with each nanocluster surrounded by six neighbors (Figure 3a). Between



**Figure 3.** Packing of enantiomers in the lattice of  $Ag_{30}$ -*rac.* (a, b) Packing structures viewed along the *c* and *a* axis. (c) Intercluster weak interactions in the same layer. (d) Intercluster weak interactions between neighboring layers. Color labels: green and violet, Ag; yellow, S; pink, P; gray, C; cyan, B; white, H. Red dashed lines indicate the week interaction.

adjacent nanoclusters, only weak H…H interactions are observed, wherein the distance between the H pairs from the closest phenyl groups is 2.71 Å; the H…H separation between the closest carborane and phenyl group is 3.05 Å, and the H… H distances between the closest carborane groups are 2.11 and 2.26 Å. The chiral layers of  $Ag_{30}$ - $\alpha$  and  $Ag_{30}$ - $\beta$  are alternatively stacked along the [001] direction in an AB packing pattern, forming a multilayer structure (Figure 3b). Thus, each nanocluster is further capped by six enantiomeric nanoclusters from the neighboring layers. Weak interenantiomer interactions, including the H…H interactions and the C-H… $\pi$  interactions, are also found. The distances between the close H pairs from the phenyl groups in the two enantiomers were found to be 2.61, 2.77, and 2.92 Å, respectively, while the C-H… $\pi$  distance is 2.92 Å.

Crystal Structure of R/L-Ag<sub>30</sub>. The racemic conglomerates L-Ag<sub>30</sub> and R-Ag<sub>30</sub> crystallize in enantiomorphic space groups  $P3_121$  and  $P3_221$  with absolute structure parameters of 0.017(8) and 0.012(4), respectively. The homochiral nanoclusters in the enantiomorphous crystals adopt enantiomeric helical assemblies. Because of mirror symmetry, the superstructure of R-Ag<sub>30</sub> is used as a representative in the following discussions. Viewing along the [001] direction, the superlattice contains a parallel array of helical tubes built with the nanoclusters in double helical arrangement, which is similar to the double-stranded DNA structure (Figure 4a,c). The pitch of the helical structure is 24.1 Å. Each helical tube is surrounded by six smaller reverse helices (Figure 4b, Figure S11). Diverse noncovalent weak interactions supporting the superstructure were observed. Between two neighboring nanoclusters in the same strand, the B-H $\cdots\pi$  H-bond with a distance of 3.45 Å, the  $\pi \cdots \pi$  interaction with a distance of 3.73 Å, and the H $\cdots$ H



**Figure 4.** Packing mode analysis of the R- $Ag_{30}$  and L- $Ag_{30}$ . (a) Perspective diagram of the superstructure viewed along the *c* axis. (b) Smaller helix surrounding the helical tubes. (c) Helical tubes built with double helical arranged nanoclusters. (d) Helically organized DMAc molecules in the crystal lattice. (e-g) Weak interactions among the nanoclusters and DMAc molecules. Color labels of the dashed lines: green,  $H(C)\cdots H(C)$ ; yellow,  $H(B)\cdots H(C)$ ; purple,  $B-H\cdots \pi$ ; blue,  $\pi \cdots \pi$ ; red,  $C-H\cdots O$ .

interactions with distances ranging from 2.14 to 2.90 Å were found (Figure 4e), while H…H interactions with separations in the range 2.55-2.62 Å were observed between adjacent nanoclusters from the neighboring strands (Figure 4f). Furthermore, a multitude of DMAc solvent molecules were located in between the nanoclusters in the reverse helices (Figure 4d), which bridged the nanoclusters together through reinforced C–H…O bonds and H…H interactions (Figure 4g). The C-H-O bond lengths are calculated as 2.53, 2.84, and 2.85 Å, and the H…H separations range from 2.22 to 2.88 Å. Of note, the DMAc molecules also adopt a helical arrangement consistent with the cluster-based helix (Figure 4d, Figure S11). In contrast to the dominant H…H vdW interactions in the crystal lattice of  $Ag_{30}$ -rac, the noncovalent interactions are more abundant in the helically organized superstructure, and these interactions, particularly the host-guest bonding, might be the driving force for helical packing instead of closest packing, which essentially lead to the spontaneous selfresolution. Significantly, the individual nanocluster in the helical assembly also shows slight distinctions in bond lengths compared to that in Ag<sub>30</sub>-rac; for example, the central regular triangle became an isosceles triangle, indicating that the symmetry of the nanocluster molecule is lowered from  $D_3$  to  $C_2$  in the helical assembly (Figure S12).

**Photophysical and Optical Properties.** The DMAc solution of  $Ag_{30}$ -*rac* shows a molecular-like optical adsorption spectrum with a weak peak at 340 nm (Figure 5a). No obvious absorption was found in the visible light range; thereby, the  $Ag_{30}$  nanoclusters appear pale yellow in color, both in the crystalline form and in solution. At room temperature,  $Ag_{30}$ -*rac* emits bright red light upon UV irradiation in both solid and solution states. The luminescence spectrum of the crystalline sample displays a weakly structured broad emission band with two peaks at 619 and 649 nm upon the maximum excitation of 367 nm (Figure 5b, Figure S13), while in solution the emission performs a slight red-shift to 629 and 663 nm under the same



**Figure 5.** Photophysical properties. (a) UV–vis absorption spectrum of  $Ag_{30}$ -*rac* in DMAc. (b) Solid-state emission spectra of  $Ag_{30}$ -*rac* and the racemic conglomerates R/L- $Ag_{30}$ . (c) CPL spectra of R- $Ag_{30}$  and L- $Ag_{30}$  excited at 367 nm.

excitation wavelength (Figure S14), respectively. Nonirradiation energy loss caused by increased molecular vibration in the solution might account for such a red-shift. The microsecond decay time (4.42  $\mu$ s) indicates the spin-forbidden triplet phosphorescent characteristic, which is tentatively assigned to the ligand-to-metal charge transfer (LMCT) disturbed by Ag... Ag argentophilic interactions (Figure S15).<sup>16,42</sup> The solid-state R/L-Ag<sub>30</sub> mixture shows an identical emission spectrum to that of the racemate with a slightly enhanced intensity (Figures 5b), indicating that the emission is an intrinsic property of the nanocluster, and the assembly only influences the intensity of the emission probably through the enforced weak interactions which could impact the rigidity of the nanoclusters. The similar shape and color of the R-Ag<sub>30</sub> and L-Ag<sub>30</sub> crystals make manual separation of racemic conglomerates impossible, and hence, their circular dichroism (CD) spectra were not recorded. Nevertheless, circularly polarized luminescence (CPL) measurements with one single crystal were carried out. As shown in Figure 5c and Figure S16, the obvious symmetric CPL response of the enantiomeric conglomerates appears in the same wavelength region with a dissymmetry factor of  $|g_{lum}| =$  $7.0 \times 10^{-4}$ , which is comparable to those of the reported metal nanoclusters.44,45

In summary, we have carried out the synthesis of racemic Ag<sub>30</sub>-rac nanoclusters by a facile one-pot method with carboranetrithiolate and phosphine as coprotective ligands utilizing hydrazine as the reducing agent. Crystal structure analysis revealed that the chirality of the nanocluster arises from the spiral arrangement of the ligands directed by unusual B-H... $\pi$  and C-H... $\pi$  bonding interactions among the carborane cages and the benzene rings. The racemate underwent a spontaneous self-resolution upon recrystallization in DMAc and formed a mechanic mixture of racemic conglomerates. Astoundingly, the enantiomeric nanoclusters in the racemic conglomerates are organized helically to form separate atom-precise helical NP assemblies. Abundant weak interactions including B-H··· $\pi$ , C-H··· $\pi$ ,  $\pi$ ··· $\pi$ , and vdWs types were found in the helical superstructure, which are believed to be the driving force leading to nonclosest packing. Furthermore, the Ag<sub>30</sub> nanoclusters display red luminescence in both solid and solution states, and the mirror-image CPL spectra of the optically pure R- $Ag_{30}$  and L- $Ag_{30}$  were also recorded. The unique properties of these chiral nanoclusters might facilitate their potential application in optical displays and encrypted transmission. This work not only suggests a new perspective to prepare metal nanoclusters of novel anisotropic structures with multithiolate ligands but also provides a platform to investigate the self-assembly mechanisms and the role of weak interactions in the atomically precise helical NP assembly.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c01045.

Crystal data for Ag<sub>30</sub>-rac (CIF)

Crystal data for L-Ag<sub>30</sub> (CIF)

Crystal data for R-Ag<sub>30</sub> (CIF)

Additional experimental details and figures including photographs, PXRD patterns, EDS mapping, XPS survey scan, positive-ion ESI-MS spectra, negative-ion ESI-MS spectra, time-dependent UV-vis absorption spectra, time-dependent luminescent spectra, structures, excitation spectra, PL spectra, decay times, CPL spectra, and <sup>1</sup>H-NMR spectra (PDF)

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## **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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