Crystallization-induced emission enhancement: A novel fluorescent Au-Ag bimetallic nanocluster with precise atomic structure

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We report the first noble metal nanocluster with a formula of $\text{Au}_4\text{Ag}_{13}\text{(DPPM)}_3\text{(SR)}_9$ exhibiting crystallization-induced emission enhancement (CIEE), where DPPM denotes bis(diphenylphosphino)methane and HSR denotes 2,5-dimethylbenzenethiol. The precise atomic structure is determined by x-ray crystallography. The crystalline state of $\text{Au}_4\text{Ag}_{13}$ shows strong luminescence at 695 nm, in striking contrast to the weak emission of the amorphous state and hardly any emission in solution phase. The structural analysis and the density functional theory calculations imply that the compact $\text{C} - \text{H} \cdots \pi$ interactions significantly restrict the intramolecular rotations and vibrations and thus considerably enhance the radiative transitions in the crystalline state. Because the noncovalent interactions can be easily modulated via varying the chemical environments, the CIEE phenomenon might represent a general strategy to amplify the fluorescence from weakly (or even non-) emissive nanoclusters.

INTRODUCTION

Noncovalent interactions (such as hydrogen bonding, π–π stacking, and cation–π interactions) are ubiquitous in solid-state materials, biological structures, and organic molecules (1, 2). To date, the fascinating effect of the noncovalent interactions in dominating the physicochemical properties has attracted increasing research interests (3, 4). Specifically, with the recent progress of optical imaging and sensing, noncovalent interaction–induced luminescence has been extensively explored for higher structural flexibility, ease of adaptability, and good reversibility (5). In this context, fluorescent regulation (quenching or enhancement) has been successfully achieved for both macromolecules [such as nanosheets/biological structures (6, 7)] and small molecules [such as pure organic luminogens (8)]. This effect has never been reported for the atomically precise, ultrasmall noble metal nanoclusters (MNCs), which are the structural bridge between individual atoms and mesosized nanoparticles.

In the past decades, ultrasmall MNCs (9–13), typically with core sizes smaller than 2 nm, have attracted considerable interest for their fascinating molecular-like physicochemical properties [for example, magnetism (14, 15), chirality (16–18), and optoelectronics (19–21)]. Benefiting from low toxicity and good biocompatibility, luminescent MNCs have recently emerged as highly attractive materials, especially for biological imaging and sensing applications (22). Nonetheless, most of the reported luminescent MNCs are polydispersed materials or mixtures with variable compositions. The preparation of monodispersed fluorescent MNCs with precise atomic structure has long been challenging.

The precise atomic structure is fundamentally important in exploring structure-property relationships and the future design of more powerful materials. So far, several luminescent MNCs with precise structures determined by single-crystal x-ray crystallography have been reported (23–30). For example, Wang et al. (23) recently synthesized successfully a series of $\text{Ag}_n\text{Au}_{25-n}$ alloy nanoclusters (NCs) and found that doping the 13th Ag atom significantly enhances the fluorescence quantum yield (QY) by ~200 times. Similarly, another Au–Ag alloy NC (that is, $\text{Ag}_{23}\text{Au}$) was reported by Bootharaju and co-workers to show over 25 times luminescence enhancement compared to the $\text{Ag}_{25}$ NC (27). Meanwhile, our group found that $\text{Au}_4\text{Cu}_6$ NCs exhibit strong red emission, whereas neither Cu nor Au precursors are fluorescent. For these MNCs, the aggregation-induced emission mechanism has been proposed to account for the enhancement (31), in which the restriction of the rotation/vibration (32, 33) acts as the main driving force for photoluminescence. Thus, both the composition/structure of the metal core and the ligand shell are critical. However, the metal-metal and metal-ligand interactions all correspond to strong bonding interactions. By contrast, the weak interaction induced photoemission, which has been frequently observed in small molecules and macromolecules, has not been reported for MNCs.

Herein, a novel Au–Ag bimetallic NC co-protected by thiolate and phosphine ligands has been successfully synthesized. The precise structure was elucidated by x-ray crystallography, and the formula is $\text{Au}_4\text{Ag}_{13}\text{(DPPM)}_3\text{(SR)}_9$, where DPPM denotes bis(diphenylphosphino)methane and HSR denotes 2,5-dimethylbenzenethiol. The four–Au–doped icosahedral $\text{M}_{13}$ (that is, $\text{Au}_4\text{Ag}_{9}$) kernel in this NC is protected by three $\text{Ag}_2\text{S}_2\text{P}$ and one $\text{Ag}_3\text{S}_2$ motifs. The $\text{Au}_4\text{Ag}_{13}$ NC exhibits a unique crystallization-induced emission enhancement (CIEE) effect (Fig. 1), that is, the crystalline state shows strong luminescence at 695 nm, whereas the amorphous state (obtained via drying the CH$_2$Cl$_2$ solution of the $\text{Au}_4\text{Ag}_{13}$ crystals) is weakly emissive, and the solution has essentially no emission. After careful analysis, we found that the CIEE effect is mainly caused by highly restricted vibrations and rotations in the crystalline state (34–37). In detail, both the triblade fan configuration of the framework and the C–H⋯π interactions contribute to the structural restrictions. This study sheds light on a general strategy to amplify the fluorescence of weakly emissive NCs by taking advantage of the readily available weak interactions in the assembled NCs.

RESULTS AND DISCUSSION

The $\text{Au}_4\text{Ag}_{13}\text{(DPPM)}_3\text{(SR)}_9$ NC was prepared by a one-pot method (see details in Materials and Methods). Briefly, a methanol solution of...
AgNO₃ was first mixed with HAuCl₄·3H₂O in CH₂Cl₂. After that, DPPM and HSR were added and then NaBH₄ was added, resulting in an immediate formation of the raw product. Finally, after washing with methanol three times, dissolving in CH₂Cl₂/ether, and recrystallization, red crystals were obtained in the crystallization (CCDC 1544143).

The structure of the Au₄Ag₁₃(DPPM)₃(SR)₉ NC was determined by x-ray crystallography. Each unit cell contains four pairs of enantiomers (see fig. S1 for the entire unit cell). Figure 2 shows the structure of one pair of enantiomers, and Fig. 3 shows the framework of the clockwise enantiomer.

As shown in Figs. 2 and 3, the structure consists of an icosahedral Au₄Ag₉ kernel, three Ag₄S₂P, and one Ag₃ staple motifs. The four Au atoms occupy the icosahedral center and three symmetric sites on the icosahedral shell. Meanwhile, each Au atom on the icosahedral shell binds with one P atom of the bidentate DPPM ligands, whereas the other P atom of DPPM ligates with another Ag atom on the staple motif. Aside from the phosphine ligation, two thiolate ligands are also connected to satisfy the electronic and steric environments of the staple Ag atoms. The three Ag₄S₂P motifs adopt the same configuration (Fig. 3). The Ag–S bond lengths range from 2.451 to 2.549 Å (2.500 Å in average), and the Ag–P bond lengths are all 2.410 Å. In addition to the structural motifs, the remaining four Ag atoms constitute a tetrahedral structure, with one Ag atom located on the C₃ symmetric axis of the remaining three Ag atoms on the icosahedral shell. This final Ag atom is symmetrically surrounded by the three S atoms of the thiolate ligands, constituting an Ag₃S₉ motif. Here, each Ag–S bond in Ag₃S₉ is 2.544 Å in length, and the S–Ag–S angle is 119.61° (Fig. 3). The entire single-crystal structure adopts a C₃ point group, and the three Ag₃S₉ motifs constitute a triblade fan configuration. According to the direction of the triblade fan configuration, the enantiomers are classified into one clockwise and one anticlockwise structure (Fig. 2).

We used x-ray photoelectron spectroscopy (XPS) to analyze the electronic states of the metal atoms in the Au₄Ag₁₃ NC. From Fig. 4, the Au 4f peak is higher than that of Au(0) (84.8 eV versus 84.0 eV), indicating the oxidation state of the Au atoms. The Ag 3d peak is higher than that of Ag(0) (368.5 eV versus 367.9 eV), indicating that the Ag atoms are negatively charged. Therefore, the XPS analysis implies the partial charge transfer from Au to Ag, and the reason for this anti-galvanic reduction might relate to the enhanced reducing ability within the very small MNCs (38). The similar Au→Ag electron transfer has also been observed in the recently reported Au₁₅Ag₃(SR)₁₄ (39). The product was further characterized by thermogravimetric analysis (TGA). A weight loss of 52.03% was observed (Fig. 5A), which is consistent with the theoretical loss of 52.16% for Au₄Ag₁₃(DPPM)₃(SR)₉.

The optical properties of the Au₄Ag₁₃ NC were then investigated. From Fig. 5B, it can be seen that the Au₄Ag₁₃ NCs display three absorption peaks (260, 330, and 430 nm) and one weak shoulder peak at 540 nm. To explore the electronic characteristics, time-dependent density functional theory (TD-DFT) calculations (40, 41) were carried out. Meanwhile, Kohn-Sham (KS) molecular orbitals (MOs) were calculated to analyze the compositions of the frontier orbitals (Fig. 5C). The two methyl groups on the thiolate ligand were simplified with H atoms to reduce the computational cost, and the full details of the calculation methods are provided in the Supplementary Materials.
Despite the systematic red shift of the theoretical absorption peaks (42–45), the overall profile is consistent with the experimental one. The first band on ultraviolet-visible (UV-vis) (~750 nm) corresponds to the highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) transition. According to the KS orbital analysis (46–48), the HOMO is mainly constituted by the π-conjugations of the thiolate groups on the AgS₃ motif, whereas the main contribution of LUMO comes from the Ag(5sp) and Au(6sp) atomic orbitals in...
During the synthetic processes (Fig. S3), the crystalline state of Au\(_4\)Ag\(_{13}\) transition is mainly the ligand-to-metal charge transfer (LMCT). Meanwhile, the second band (\(<\sim 680\) nm) mainly corresponds to the transition of HOMO to LUMO+3 and LUMO+4. Because of the similar orbital compositions of LUMO+3+/4 to that of LUMO, the transition here is also mainly the \(\pi\rightarrow\sigma\) transition (LMCT). By contrast, the former two bands (\(<\sim 540\) and 600 nm) on the theoretical UV-vis mainly correspond to the transition from the lower two HOMOs (that is, HOMO−1/HOMO−2) to the upper LUMOs (LUMO+8 and LUMO+12 for the third band and LUMO+8 and LUMO+17 for the fourth band). To this end, the \(\sigma\rightarrow\sigma\) sp interband transition mainly accounts for these two bands.

The photoluminescence of the CH\(_2\)Cl\(_2\) solution of Au\(_4\)Ag\(_{13}\) is very weak (QY = 4.1 \times 10^{-5} in Fig. S2) and so is that of the MeOH solution (Fig. 5D). These observations are in sharp contrast to the UV-vis light–stimulated strong emissions of the as-prepared NCs observed during the synthetic processes (Fig. S3). The crystalline state of Au\(_4\)Ag\(_{13}\) shows strong red emission (Fig. S4) with a maximal emission wavelength of \(~695\) nm in the fluorescence spectrum (Fig. 5D). Meanwhile, the lifetime of the solution and crystalline state is 3.31 and 0.65 ns, respectively (Fig. S5, A and B). For comparison, the amorphous state of Au\(_4\)Ag\(_{13}\) generated by the evaporation of CH\(_2\)Cl\(_2\)-dissolved Au\(_4\)Ag\(_{13}\) crystal (or by grinding the solid-state crystal) exhibits relatively weak fluorescence, and the maximal wavelength red shifts by \(10\) nm when compared to that of the crystalline state. Both the weakened intramolecular \(\pi\)-\(\pi\) stacking interactions (35) and the smaller torsion angle (49, 50) of aromatic rings in the less regulated amorphous state (compared to the crystalline state) might account for the spectroscopic red shift. The fluorescence quantum efficiency (\(\Phi_F\)) of the amorphous and the crystalline state is 1.14 and 2.68\%, respectively.

The CIEE phenomenon in the Au\(_4\)Ag\(_{13}\) NC is remarkable, and such a phenomenon has not been reported for MNCs before. Because the N\(_2\)-bubbled solution shows the same optical phenomenon as the normal solution, the possibility of the interference of oxygen (in solution/amorphous state) could be eliminated. After carefully examining the structure of the Au\(_4\)Ag\(_{13}\) NCs, we noticed some unusual structural features. First, the overall framework is in a triblade fan configuration (Fig. 6A). According to recent studies on luminescent small molecules, such a structure is capable of restricting the vibrational/rotational movement during the electronic transitions and thus altering the optical properties (51). We anticipate that such a structural restriction is mainly responsible for the photoluminescence of the amorphous state. Nonetheless, this effect is unable to explain the significantly enhanced photoemission in the crystalline state compared to that of the amorphous state. To this end, we noticed that the spacing between each group of enantiomers is unnecessarily narrow, especially the distance between the -SPh on one enantiomer and the -PPh\(_2\) groups on its neighboring enantiomer (Fig. 1). In detail, the distances between the hydrogen atom (para to the S atom) of the thiolate ligand and the centroid of the nearby phenyl ring of the DPPM ligand range from 2.564 to 2.573 Å (2.568 Å on average; fig. S5). The distances remind us of the C–H···\(\pi\) interactions, and these weak interactions are widely spread in the entire crystal structure. As shown in Fig. 6B, each single crystal consists of six groups of C–H···\(\pi\) interactions with the nearby enantiomers. The C–H bonds exclusively come from the phenyl group of the thiolate ligands, and the \(\pi\) moieties all come from the phenyl groups of the phosphine ligands binding with the Au atoms in the M\(_{13}\) core surface. We anticipate that these covalent C–H···\(\pi\) interactions mainly account for the CIEE phenomenon.

The solid-state \(^1\)H nuclear magnetic resonance (NMR) analysis (Fig. 7) was then carried out. Both the crystalline state (Fig. 7A) and the amorphous state (Fig. 7B) show two main groups of peaks: 0 to 3.8 parts per million (ppm) corresponding to the H atoms on the alkyl groups of the DPPM ligands (-CH\(_2\)) and thiolate ligands (-CH\(_3\)) and 3.8 to 9.8 ppm for the H atoms on the aryl groups of both DPPM and SR ligands (52). Nonetheless, the \(^1\)H NMR peaks of the crystalline state are significantly more discrete than those of the amorphous state, indicating that the molecular arrangement in the former case is more organized than that in the latter case.

Powder x-ray diffraction (PXRD) analysis was also performed on the crystalline and amorphous states. According to Fig. 7C, these two states show distinct characteristic peaks. The x-ray diffraction (XRD) curve of the crystalline state is very similar to that of the theoretical one (generated with Mercury 3.0 software; Fig. 7C, inset). Both the 2\(\theta\) = 5.5° (corresponding to the Miller indices of 102) and 6.3° (corresponding to the Miller indices of 210 and 003) can be clearly identified. Nevertheless, the relative intensity of the second peak was significantly stronger than the theoretical one, presumably because of the slight weathering effect of the crystal under air. By contrast, the prominent peak of 2\(\theta\) = 5.5° completely disappeared in the XRD

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**Fig. 6. (A)** Illustrative diagram for the triblade fan configuration. **(B)** The compact C–H···\(\pi\) interactions in the single crystal.
CONCLUSION

In summary, a novel bimetallic NC [that is, Au₄Ag₁₃(DPPM)₃(SR)₉] was synthesized. An interesting CIEE phenomenon was observed for this structure. In dilute solution and amorphous solid state, the NCs show weak luminescence, whereas in the crystalline state, a strong red emission is observed. According to the structural analysis, solid-state ¹H NMR, and the DFT calculations, both the triblade fan configuration of the framework and the multiple weak interactions (that is, C–H⋯π interactions) contribute to the restriction of the molecular vibrations and rotations, and the latter effect is the determinant for the CIEE (compared to the amorphous state).

MATERIALS AND METHODS

Synthesis of the Au₄Ag₁₃(DPPM)₃(SR)₉ NC

The Au₄Ag₁₃(DPPM)₃(SR)₉ was synthesized by one-pot method. AgNO₃ (34 mg, 0.2 mmol) was first dissolved in 5 ml of methanol. Then, 36 mg (0.2 mmol) of DPPM ligand was added to the mixture, and the solution turned from colorless to white. After about 30 min, 5 ml of NaBH₄ aqueous solution (6.0 mg/ml) was quickly added into the solution. The color of the solution immediately turned to black. The reaction was continued for 6 hours, and the raw products were then obtained. From the crude product, the pure crystals were then obtained by two steps: raw crystallization and recrystallization. First, the raw Au₄Ag₁₃(DPPM)₃(SR)₉ NCs were dissolved in CH₂Cl₂/ether, from which the red crystals were crystallized for about 12 hours. After that, the regular crystals could be obtained by recrystallization in systems such as CH₂Cl₂/ether, CH₂Cl₂/ethanol (1:3), and CH₂Cl₂/hexane (1:3) for 6 hours. For all tests (for example, XPS and UV-vis), the sample crystal was freshly prepared. Detailed descriptions about the materials and characterizations are given in Supplementary Materials and Methods.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/8/e1700956/DC1

Supplementary Materials and Methods

fig. S1. The overall structure of the Au₄Ag₁₃ NC.

fig. S2. The QY of Au₄Ag₁₃(DPPM)₃(SR)₉ in CH₂Cl₂ [with the reference Ru(bipy)₃Cl₂].

fig. S3. Digital photos of the single-crystal bottle under UV light excitation.

fig. S4. The bright-field image of Au₄Ag₁₃ crystals and its fluorescent images under green light excitation (Leica DM3000 B).

fig. S5. Fluorescence decay profile of the Au₄Ag₁₃(DPPM)₃(SR)₉ NCs.

fig. S6. Distances between the hydrogen atom of one thiolate ligand and the centroid of nearby phenyl group of the DPPM ligand.

table S1. Crystal data and structure refinement for the Au₄Ag₁₃(DPPM)₃(SR)₉ NC.

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