PHYSICAL CHEMISTRY

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

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Structure and composition are important factors in determining the luminescent property



Introduction

- Noncovalent interactions are well-known in solid-state materials, biological structures, and organic molecules. Its fascinating effect in dominating the physicochemical properties has attracted increasing research interest. The noncovalent interaction-induced fluorescent regulation (quenching or enhancement) has been successfully achieved for both macromolecule and small molecules but has never been reported for the atomically precise, ultrasmall noble metal nanoclusters (MNCs).
- Benefiting from low toxicity and good biocompatibility, luminescent MNCs have recently emerged as highly attractive materials, especially for biological imaging and sensing applications. 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.
- For these MNCs, the aggregation-induced emission mechanism has been proposed to account for the enhancement, in which the restriction of the rotation/vibration 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.

In this paper...

- The first noble metal nanocluster with a formula of Au₄Ag₁₃(DPPM)₃(SR)₉ exhibiting crystallization induced emission enhancement (CIEE) is reported. The precise atomic structure is determined by x-ray crystallography.
- The crystalline state of Au₄Ag₁₃ 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 C–H···π interactions significantly restrict the intramolecular rotations and vibrations and thus considerably enhance the radiative transitions in the crystalline state.

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





fig. S1. The overall structure of the Au4Ag13 NC. Color legend: Color labels: yellow = Au, Light blue = Ag, Red = S, magenta = P. All H atoms are omitted.



Framework

Fig. 2 The structure of one pair of enantiomers. Color labels: Ag, light blue; Au, yellow; P, magenta; S, red; C, gray; all H atoms are omitted.

Fig. 3 The framework of the Au_4Ag_{13} NC. Color labels: Ag, light blue; Au, yellow; P, magenta; S, red; C, gray; all other carbon (except the bridging carbon atoms between two P atoms in DPPM) and hydrogen atoms are omitted.



Fig. 4 Au 4f XPS spectrum and Ag 3d XPS spectrum.

Fig. 5 Characterization of the Au₄Ag₁₃(DPPM)₃(SR)₉ NC.(A) TGA the Au_4Ag_{13} NCs. (**B**) UV-vis of spectrum of the Au₄Ag₁₃ NCs in CH₂Cl₂and theoretical spectrum with TD-DFT methods (inset). (C) KS MOs of the $Au_4Ag_{13}NC$. (**D**) Emission spectra of crystalline (red line), solution the (magenta line for CH₂Cl₂ and black line for MeOH solvent), and amorphous states (blue line) with excitation at 500 nm. a.u., arbitrary units.



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 DMI3000 B).



fig. S5. Fluorescence decay profile of the Au4Ag13(DPPM)3(SR)9 NCs. (A) Solution (B) Crystalline state (excitation: 460 nm, emission monitored at 695 nm).



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



Fig. 7 The solid-state ¹H NMR of (**A**) crystalline state and (**B**) amorphous state of Au_4Ag_{13} , and the reaction enthalpy of the C–H··· π interaction (A inset). (B) Amorphous state. (**C**) XRD diffractograms for the Au_4Ag_{13} crystalline (black) and amorphous states (red) and theoretical pattern (inset).

Conclusion

- > A novel bimetallic NC [that is, $Au_4Ag_{13}(DPPM)_3(SR)_9$] 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).

THANKS FOR LISTENING

