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Photoluminescence Modulation of an Atomically Precise Silver(I) Thiolate Cluster via Site-specific Surface Engineering

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A series of pyridyl ligands functionallized silver-thiolate nanoclusters with identical cuboctahedron Ag_{12} core were prepared through site-specific surface engineering and fully characterized. The wide-range photoluminescence modulation of them were systematically studied.

Introduction

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Noble metal nanoclusters (NCs) with precise atomic number have attracted wide attention because of their structural diversity and potential use in various applications.¹⁻² Among them, silver(I) nanoclusters constitute one of the most important subclasses and have been studied extensively on account of their intriguing aesthetic structures and properties.³⁻⁴ photophysical However, Silver(I) chalcogenide/chalcogenolate clusters (SCCs) are reported to be emissive silent or emit only in a narrow typical color range.^{1e-1f} Such disadvantages limited the development of silver cluster-based nanomaterials in practical applications. To the best of our knowledge, the emission of metal NCs not only derives from the structure of the metal core, but also relates to the capping ligands on the NC surface. In recent years, ligand engineering represents one of the most versatile strategies to improve the fluorescence of metal NCs by either an electronic (i.e., electron-donating or -withdrawing ability) or steric effect of the peripheral ligands.⁵ However, enhancing the emission intensity and tuning the emission color of atomprecise silver(I) clusters by employing various fluorescent protecting ligands has seldom been observed so far.⁶⁻⁷

Moreover, the variation of protecting ligands, including change in the synthetic process and post-ligand exchange, usually tends to form different nuclearities. The core shape-

remain rare.⁶⁻⁷ This hindered the direct understanding of the influence of the protecting shell modification on an identical metal core. In this context, rational design of a structure defined silver(I) cluster by introducing fluorescent ligands to realize fluorescent adjustment remains highly desirable. Recently, our group has made great progress in core

controlled site-specific surface functionalized metal NCs still

structure retained site-specific surface modification of the silver-thiolate clusters, by which stability improvement, widerange luminescence modulation and molecular chirality introduction have been successfully achieved.⁶⁻⁸ As an extensive work, herein we report the site-specific surface modification of a reported SCC Ag₁₂ nanocluster⁸ with a series of fluorescent monopyridine ligands (Chart S1, ESI+), namely, $Ag_{12}(SCH_2C_6H_5)_6(CF_3COO)_6(L_1)_6$ (NC-1, L_1 = pyridine), $Ag_{12}(SCH_2C_6H_5)_6(CF_3COO)_6(L_2)_6$ (NC-2, L_2 = 4-phenylpyridine), $Ag_{12}(SCH_2C_6H_5)_6(CF_3COO)_6(L_3)_6$ (NC-3, $L_3 = 4-(1-naphthalenyl)$ pyridine), $Ag_{12}(SCH_2C_6H_5)_6(CF_3COO)_6(L_4)_6$ (NC-4, $L_4 = 4-(9-1)^{-1}$ anthracenyl)-pyridine), Ag₁₂(SCH₂C₆H₅)₆(CF₃COO)₆(L₅)₆ (NC-5, L₅ = 4-[4-(1, 2, 2-triphenylethenyl)phenyl]-pyridine) (Fig. 1a and S1). Benefitted from the intrinsic fluorescence of the pyridine derivatives and the resulted different intermolecular interactions in each stacking pattern, these clusters exhibit wide-range luminescence.

Results and discussion

Synthesis and characterization

NC-n were synthesized by a typical method. The polymeric precursor AgSCH₂Ph and CF₃COOAg were dissolved in methanol/toluene followed by the addition of the corresponding pyridine ligands. Evaporation of the resulting clear solutions afforded good quality crystals of the desired clusters.

The phase purity of **NC-n (n = 1** to **5)** was further verified by powder X-ray diffraction (PXRD) patterns (Fig. S2-S6, ESI⁺). To note, **NC-4** can retain their morphology and crystallinity for half a year under ambient conditions (Fig. S5, ESI⁺). The intact nature of **NC-4** in chloroform solution was also confirmed by

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Fig. 1 Syntheses and molecular structures of **NC-n (n=1, 2, 3, 4, 5)**. (a) Schematic representation of the one-pot synthesis strategy used to obtain the Ag₁₂ nanoclusters co-stabilized by different monopyridine ligands. (b) The identical skeleton of $Ag_{12}S_6^{-6-}$ core in these clusters. (c) Perspective view of C_{3v} cuboctahedron in $Ag_{12}S_6^{-6-}$ core skeleton with Ag₃-Ag₆-Ag₃ three-layer arrangement (Colour labels: green, Ag; yellow, S; gray, C; red, O; blue, N; turquoise, F. All hydrogen atoms are omitted for clarity).

TEM measurement. As shown in Fig. S7, the cluster diameter of about 2.5 nm measured from the TEM image, which is consistent with the single-crystal X-ray analysis result, indicating that the clusters exist as monodisperse particles.

Crystal structure analyses

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Single-crystal X-ray crystallographic analyses reveal that NC-1 and NC-2 crystallize in the monoclinic space group $P2_1/n$ and trigonal space group $R\overline{3}$, respectively (Table S1 in the ESI⁺). NC-**3**, NC-4 and NC-5 crystallize in triclinic space group $P\overline{1}$. All these NCs share similar molecular structures with an empty $Ag_{12}S_6^{6-}$ cuboctahedron co-stabilized by six CF₃COO⁻ anion and six pyridine ligands (Fig. 1a). Thus, only the crystal structure of NC-4 is described in detail here.

Similar to the previously reported Ag₁₂ cluster based materials,⁸ the core of NC-4 shaped in an empty cuboctahedron and consisted of twelve Ag atoms linked through Ag¹...Ag¹ argentophilic interaction with Ag...Ag contacts of 2.9437(5)-3.3315(7) Å. The cuboctahedron displays $C_{3\nu}$ symmetry and contains eight triangular faces: two triangles with Ag-Ag distances lying in the range of 2.9437(5)-2.9788(6) Å on the top and bottom layers, and six lateral triangles with the two short sides shared by a trapezoid capped by μ_4 -SCH₂Ph (Fig. 1b). Each thiolate ligand adopts μ_4 - η^1 , η^1 , η^1 , η^1 ligation mode to link four silver(I) ions and the Ag-S bond distances lie in the range of 2.4466(12)-2.5898(14) Å. Among the six auxiliary CF₃COO⁻ ligands in the outer layer, two are attached to three silver atoms in the syn- μ_3 -O, O', O' mode, with the Ag-O bond lengths of 2.324(4), 2.664(5) and 2.835(4) Å, respectively. While each of the remaining four CH_3COO^{-1} ligands chelates one silver ion with the Ag-O distances ranging from 2.381(4) to 2.826(5) Å. The twelve Ag atoms exhibit a disconnected C_{3v} Ag₃-Ag₆-Ag₃ three-layer arrangement (Fig.

1c), and six middle layer Ag(I) atoms each bears a terminal monodentate pyridine ligand to support the $Ag_{12}S_6$ cluster in the periphery. The nanoclusters are further extended into one-dimensional chains by the π - π stacking interactions between adjacent aromatic rings with a centroid-to-centroid distance of 3.820 Å (Fig. 2), which is corresponding to the excimer formation with two adjacent near parallel aromatic rings facing at a distance of 3–4 Å.⁹ While such intercluster weak interactions are not observed in other four structures.



Fig. 2 Intercluster π - π stacking interaction in **NC-4**. (Colour labels: green, Ag; yellow, S; blue, N; gray, C. CF₃COO⁻, PhCH₂- and H atoms are omitted for clarity).

Luminescence properties of NC-n (n = 1 to 5)

Solid-state luminescence properties of these five NCs were investigated at varied temperatures. NC-1, 2, 3 are almost emission silent at ambient temperature. With temperature decreasing from 298 to 83 K, the emission intensity of NC-1, 2, 3 increases accompanying with no obvious change of the emission peak position. At 83 K, they exhibit low energy emission band with the $\lambda_{
m em}^{
m max}$ value of 610, 618, 615 nm upon excitation at 383, 385 and 393 nm, respectively (Fig. 3a and S8-S10, ESI⁺). The nature of the red emission for NC-1, 2, 3 could be assigned to an excited state relating to charge transfer from S 3p to Ag 5s perturbed by Ag¹...Ag¹ interactions.^{10,11} As the temperature decreases, the enhanced rigidity, faster intersystem crossing process by the presence of the heavymetal ion,¹² and the restriction of the intramolecular vibration and rotation of ligands all effectively reduce the non-radiative energy loss, which leads to enhanced emission intensity.¹³

The electronic absorption spectrum of NC-5 exhibits broad peak in the UV region (Fig. S11, ESI⁺). The absorption band centered at ca. 368 nm can be ascribed to the intraligand n- π^* or $\pi - \pi^*$ transition of the aromatic rings moiety. As shown in Fig. 3a and S2, NC-5 exhibits bright blue emission in the solidstate at room-temperature with the λ_{em}^{max} = 490 nm under the excitation of 368 nm UV irradiation. The quantum yield (QY) was measured to be 24.93%. The nanoscale lifetime (Fig. S14 and Table S2, ESI⁺) accompanied with the highly related emission profile compared to that of the free ligands (Fig. S13, ESI⁺) indicates that the emission is ligand-centered and could be attributed to the cascade $n-\pi^*$ or $\pi-\pi^*$ interactions occurring between the aromatic rings of the coordinated ligands.¹⁴ The slight red-shift of the emission compared to that of the free ligand may be due to the coordination of L_5 to Ag atoms.^{15,16,17} Similar to our recent findings for the temperature-dependent fluorescent silver(I) thiolate clusters,^{6,7,18a} the emission at 490 nm for NC-5 is only 2-fold

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Fig.3 (a) The emission spectra of NC-n in the solid state (NC-1, 2, 3 were measured at 83 K; NC-4 and NC-5 were measured at 298 K). (b) Photoluminescence spectra of NC-4 at 298 K and 83 K (excited at 405 nm). (c) Emission lifetime of NC-4 at λ_{em} = 545 nm at 298 K. (d) Emission lifetime of NC-4 at λ_{em} = 511 nm at 83 K.

enhanced as temperature decreasing from 298 to 83 K and the relative low sensitivity to temperature further indicates that the irradiative excited state of the **NC-5** is quite different from the **NC-1**, **2**, **3**. (Fig. S12, ESI⁺). In view of the aggregation induced emission (AIE) feature of tetraphenylethylene moiety, we also studied the luminescence properties of **NC-5** in tetrahydrofuran with different concentrations. The emission of **NC-5** is significantly enhanced upon the increasing concentrations, displaying obvious AIE performance (Fig. S15 and S16, ESI⁺).

As shown in Fig. 3a, the solid-state emission spectrum of NC-4 at room temperature displays a broad emission band centered at 545 nm under 405 nm UV excitation. The decay measurement (Fig. 3c) at 298 K fitted to a mono-exponential function, giving lifetime value of τ = 22.75 ns. When cooling from 298 to 83 K, the intensity of the fluorescence increases and the maxima emission peaks blue shift from 545 to 511 nm (Fig. 3b), whereas the lifetime is prolonged to 153.95 ns at 83 K (Fig. 3d). Such blue-shifted phenomenon upon cooling for NC-4 may be caused by the restricted rotation of the peripheral aromatic rings at low temperature.^{18,19} By comparison, the emission spectrum of NC-4 in CH_2Cl_2 solution displays two major peaks at 400 nm and 418 nm arising from the ligand (Fig. S17 and S18, ESI⁺). The decay lifetime of two emission bands was calculated to be 5.51 ns and 5.56 ns, respectively (Fig. S19, ESI⁺). The emission at 545 nm disappeared probably because of the absence of the intercluster π - π stacking interaction due to the relatively lower solubility in solution. The largely redshifted featureless PL spectrum and longer lifetime suggested excimer formation in the NC-4 crystal.9,20

To further investigate the origin of the emission, the emission behavior of the free ligand was thoroughly studied. The emission spectra of L_4 in CH_2Cl_2 solution at different concentrations (Fig. S20, ESI⁺) indicate that the emission

profile retained between $10^{-6}-10^{-2}$ M, but totally changed when the concentration reached 0.4 M. The new bands at λ_{max} = 529 nm are attributed to the excimer species of anthracyl moieties. Such phenomenon is consistent with the characteristics of excimer emission.⁹

These findings combined with the molecular packing mode in the crystal structure suggest that the broad structureless emission band of the **NC-4** crystals is tentatively assigned to the excimer species formed through the intercluster π - π stacking interactions. Similar phenomenon has also been observed in some excimer-like luminescent compounds.^{21,22,23} It is noteworthy that excimer emissions are rare in solid state at room temperature for silver cluster with modified ligands. Such result provides a new possibility in achieving dual emission solid-state luminescence materials from excimer species and the central Ag-S cluster, and further research is in progress in our laboratory.

The origin of the emission of silver-thiolate clusters is complicated, which usually could be assigned to the clustercentered triplet excited state (³CC), the n- π^* and/or π - π^* transition excited state of the protecting ligands, ligand-tometal-metal charge transfer (LMMCT; S \rightarrow Ag) and in many cases a mixture of them. Our recent work revealed that the emission of pyridyl ligand modified silver-thiolate clusters also involves interligand trans-metallic charge transfer transition (ITCT, S/Ag \rightarrow py) when the energy levels match.^{8a} Dualemission or even multi-emission could be realized when the emission intensity originated from different excited states are comparable.^{6a} In fact, in most cases one excited state will be dominant although the contributions from other excited states could not be excluded. Eventually, the emission is highly dependent on the electronic structure and electronic effect of both the clusters and ligands. In this work, the emissions of NC-1, 2, 3 are dominated by metal cluster involved excited states, probably due to the weak emission of the L_{1-3} ligands. However, in NC-4 and NC-5, ligand-centered emissions are dominant probably benefited from the intense emission, intrinsic electronic structure and geometry of ligand L₄ and L₅.

Conclusions

In this work, site-specific surface modification of an identical silver-thiolate nanocluster with a series of fluorescent pyridyl ligands has been reported. The wide-range photoluminescence modulation from blue to red of these clusters benefiting from the emission nature of the pyridyl ligands and the facilitated instinct packing fashions was systematically studied. The atom-precise modification with controlled core-shape provide a platform to directly understand the ligand shell-property relationship of the NCs. This study also offers a perspective to design and prepare metal cluster-based materials with desired functionality.

Conflicts of interest

There are no conflicts to declare.

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Table of Content



Wide-range photoluminescence modulation of a ${\rm Ag}_{12}$ nanocluster was achieved by site-specific surface modification with a variety of fluorescent pyridyl ligands.