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Communication

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Anisotropic Assembly of Ag_{52} and Ag_{76} Nanoclusters

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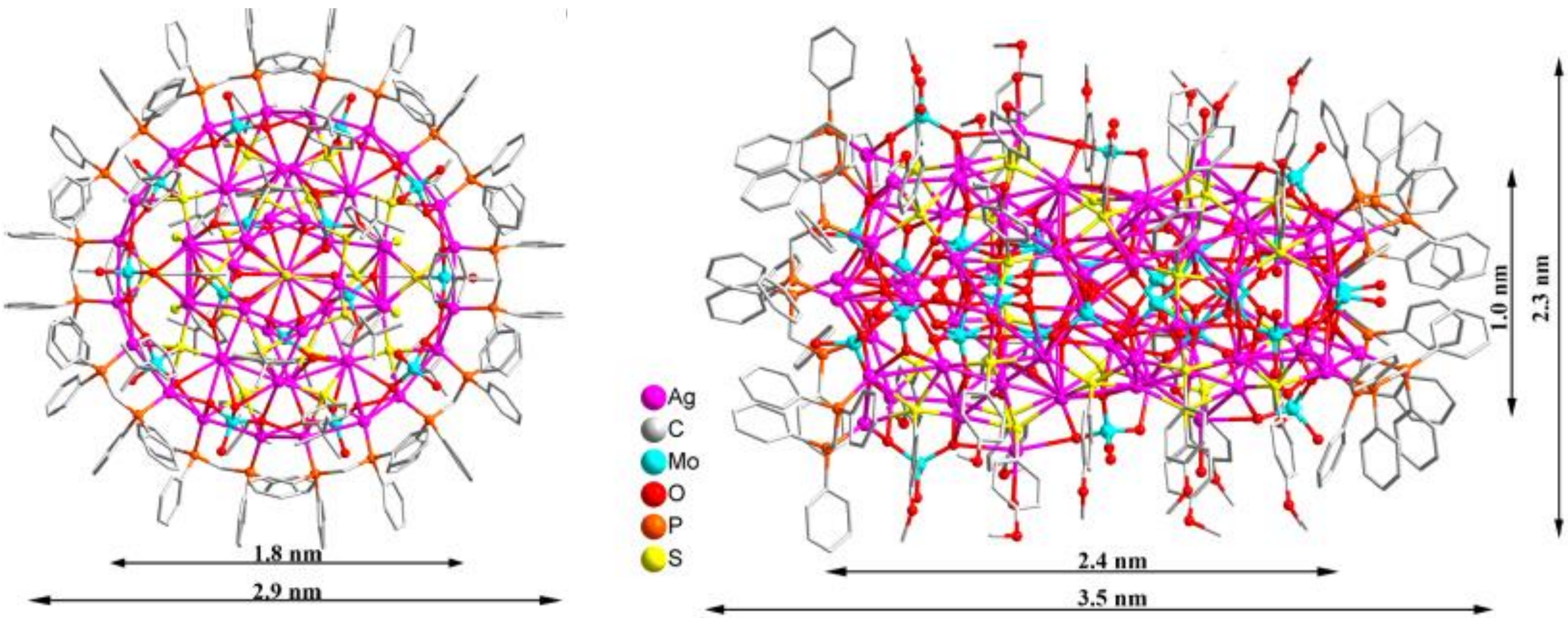

By
Biswajit
26-05-18

Background

Controlling anisotropic nanoparticle growth through plasmon excitation

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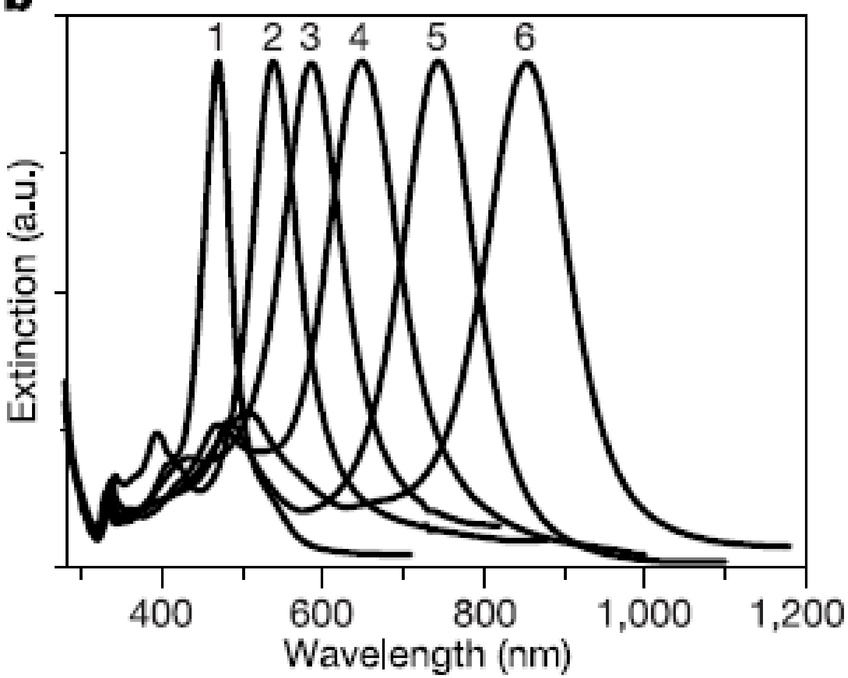

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Photochemical Synthesis of Gold Nanorods

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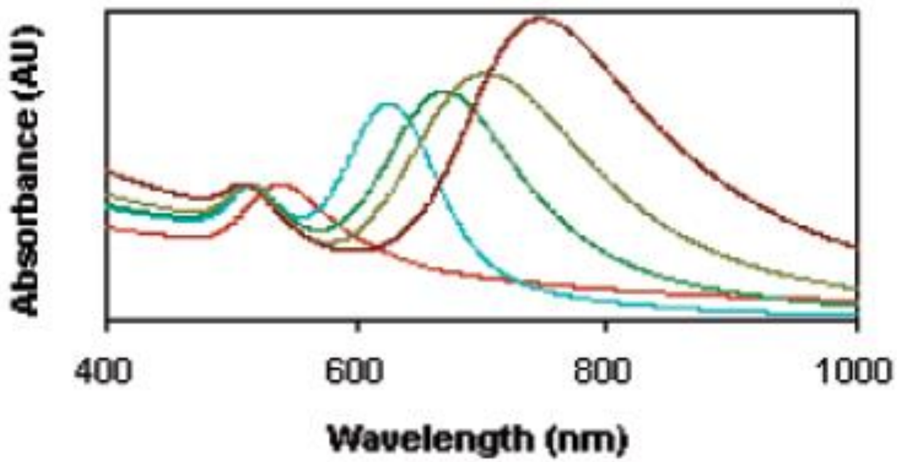
Received August 12, 2002



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CHEMISTRY OF MATERIALS
Perspective
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Anisotropic Noble Metal Nanocrystal Growth: The Role of Halides

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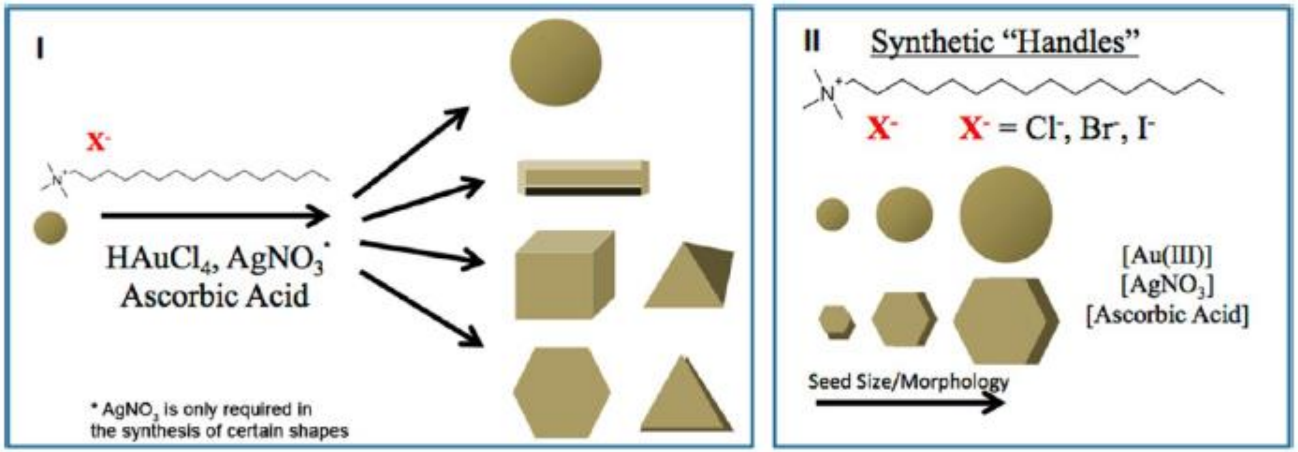

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Relevance to the group:

- We are trying to synthesis new gold and silver cluster and trying to crystalize them. We can try to synthesis this kind of anisotropic assemble of nanoparticles also.

Introduction

- Due to the close structure−property correlations, anisotropic nanoparticles have exhibited fascinating size- and shape-dependent properties.

- Down-sizing of them to nanoclusters caused the anisotropic assembly rather difficult owing to the inherently more complex assembly environments and the difficulty to achieve the atomically precise structures, especially for high-nuclearity metal cluster.

- Compared to spherical silver nanoclusters, anisotropic nanoclusters have regiospecific surface structures and metal skeleton shapes.

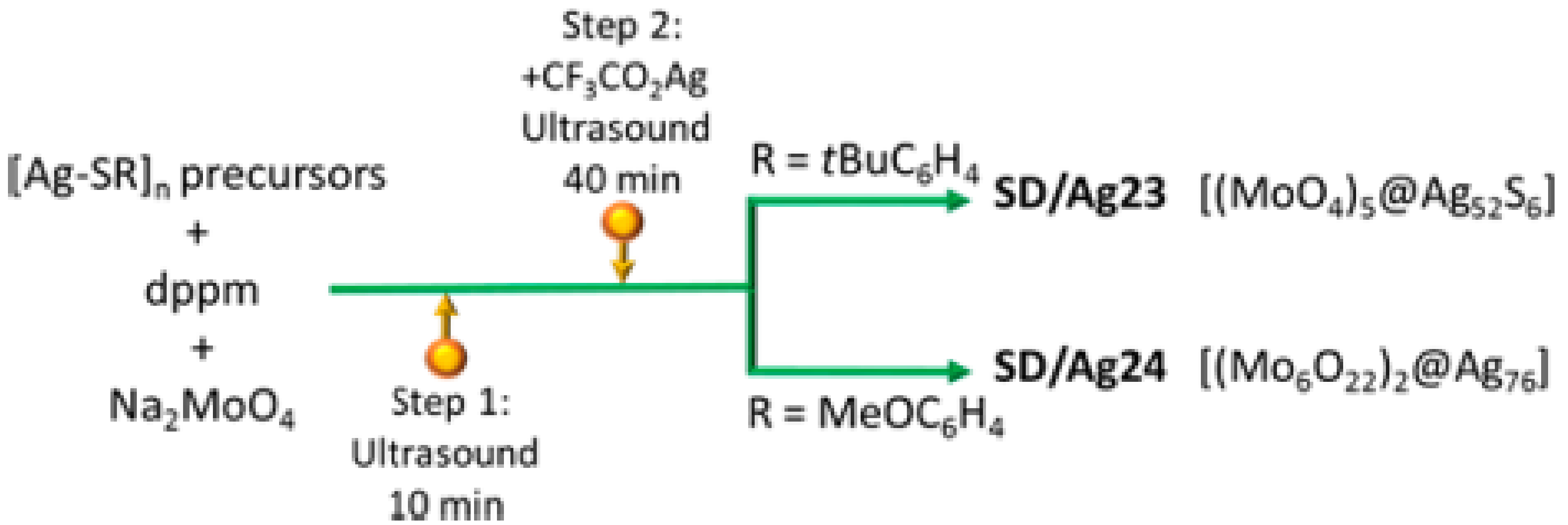
- Based on the inspirations from the anisotropic nanoparticles, understanding the coordination preferences of different ligands is probably the key for controlling the orientation and spatial arrangement of them to achieve anisotropic shapes.

In this paper

- Here they have synthesized and characterized anisotropic assemble of Ag_{52} and Ag_{76} nanoclusters.
- They have shown that ligand is the key for controlling the orientation and spatial arrangement of them to achieve anisotropic shapes.

Synthesis of anisotropic assemble of Ag_{52} and Ag_{76} NCs

Scheme 1. Synthetic Routes for SD/Ag23 and SD/Ag24



$(HNEt_3)_{10}[(MoO_4)_5@Ag_{52}S_6(tBuC_6H_4S)_{20}(dppm)_{10}(MoO_4)_{10}]$ Ξ (SD/Ag23)

$[(Mo_6O_{22})_2@Ag_{76}(MeOC_6H_4S)_{28}(dppm)_8(MoO_4)_{16}(H_2O)_8 \cdot 8CH_3OH \cdot 4CH_3CN]$ Ξ (SD/Ag24).

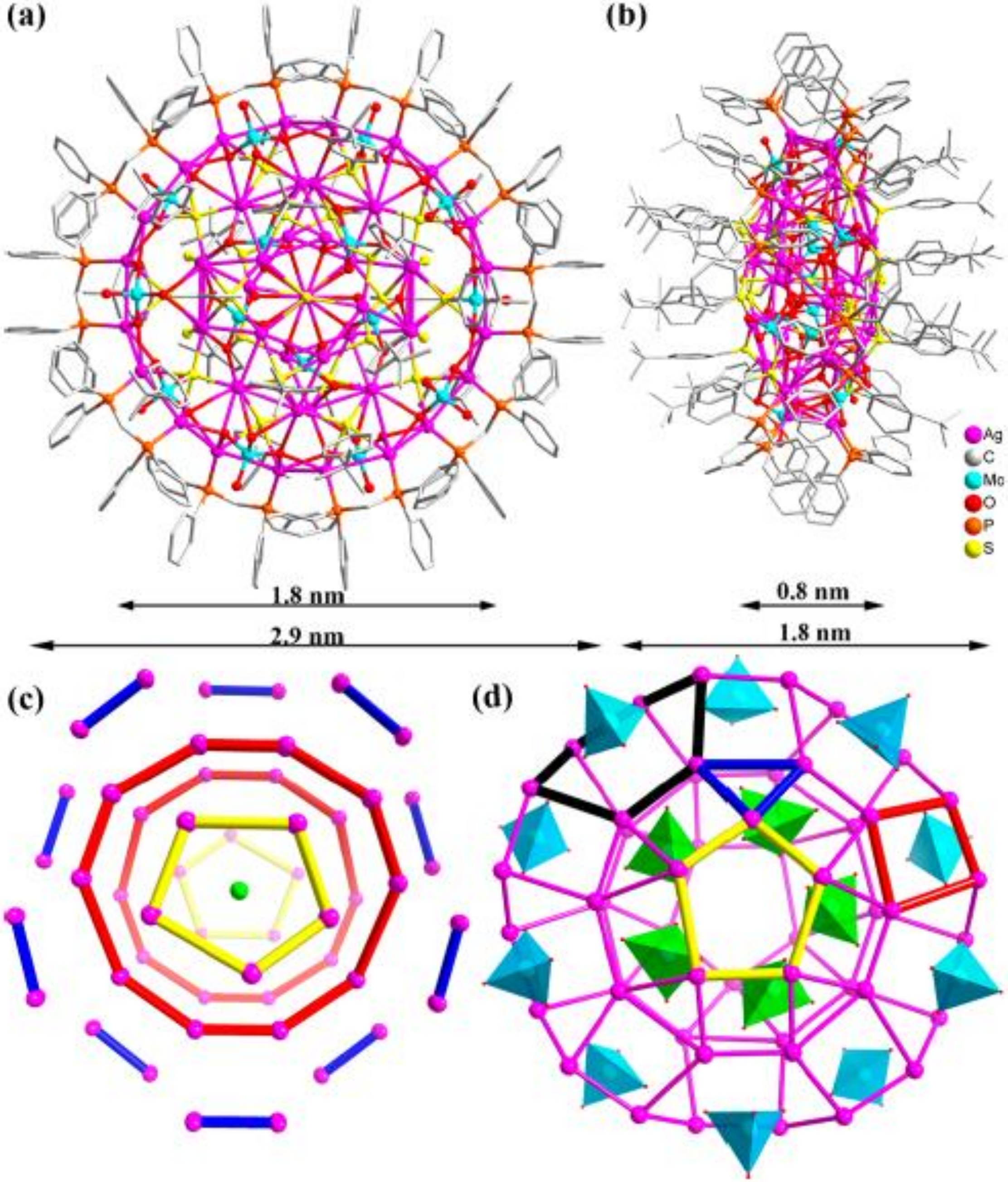


Figure 1. (a and b) X-ray crystal structure of Ag_{52} nanoclusters viewed along two orthogonal directions. (c) Layer-by-layer structure of 52-silver-skeleton. Different layers are highlighted individually by different colors. Two green balls along the polar radius direction are two interior Ag atoms. (d) Ag_{50} shell composed of diverse polygons. One boat-like hexagon, pentagon, tetragon and trigon were highlighted by bold black, yellow, red and blue bonds, respectively. Five interior and ten exterior MoO_4^{2-} anions are represented by green and cyan polyhedral.

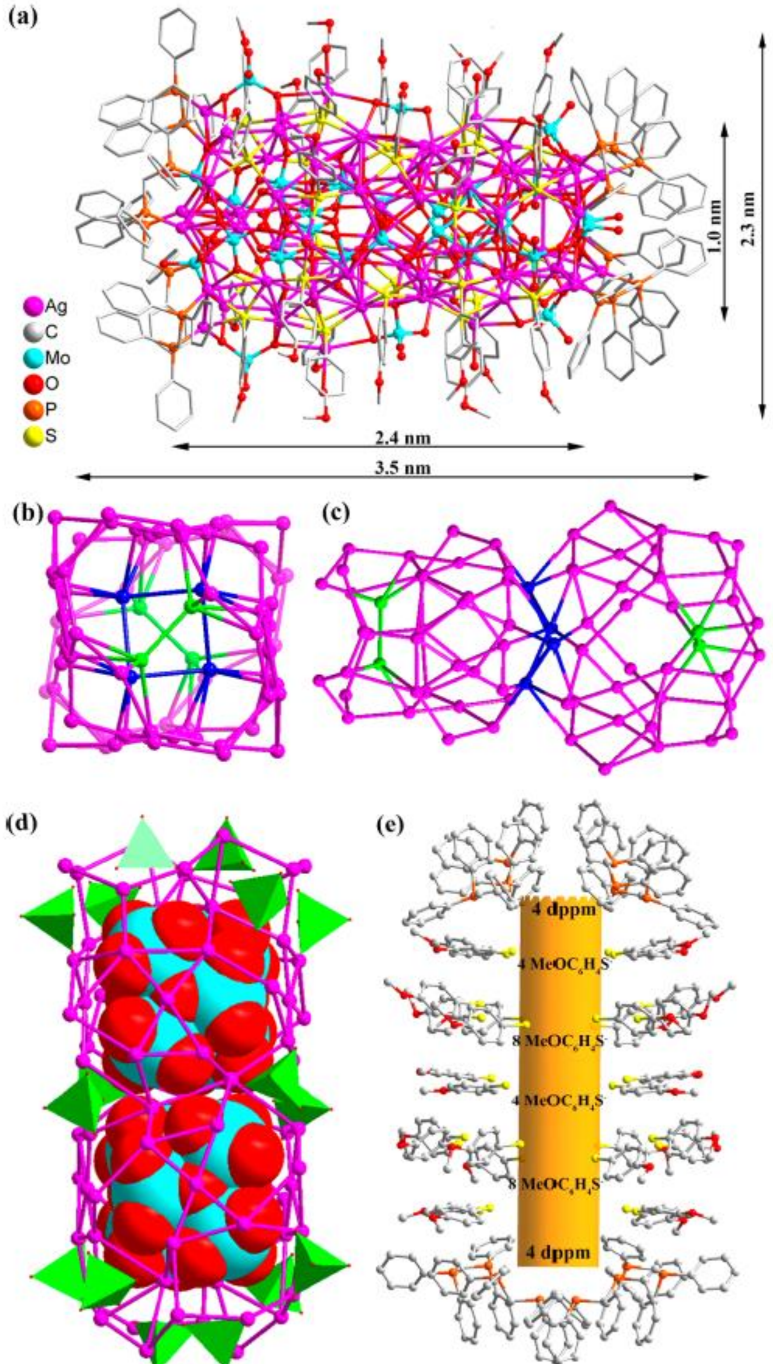
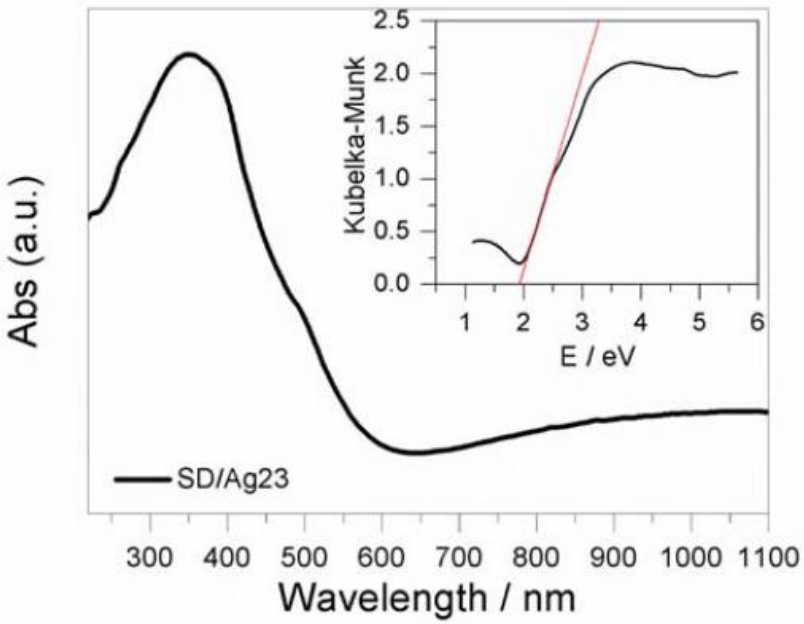


Figure 2. (a) Molecular structure of Ag_{76} nanocluster. (b and c) Two orthogonal views of skeleton of Ag_{76} nanocluster with inner four and shared four silver atoms highlighted by green and blue, respectively. (d) Two $Mo_6O_{22}{}^{8-}$ templates caged in a Ag_{76} nanocluster. The green tetrahedra are 16 $MoO_4{}^{2-}$ anions on the surface. (e) Anisotropic distributions of dppm and $MeOC_6H_4S^-$ ligands around the Ag_{76} shell simplified to a yellow pillar.



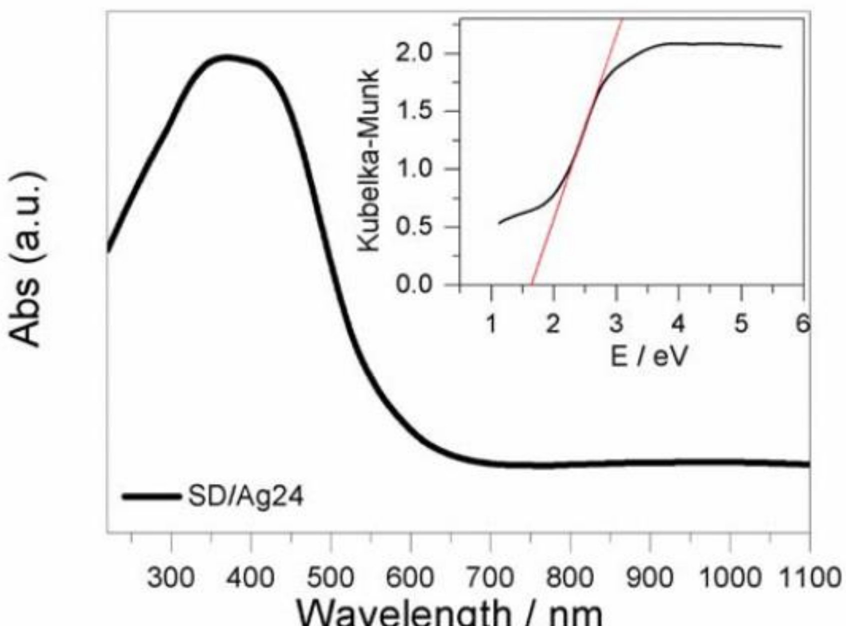


Figure S6: The solid-state UV-Vis spectra of **SD/Ag23** and **SD/Ag24** were measured with the diffuse reflectance mode (Figure S6). The absorptions of them are mainly in UV region and tailed to visible region. The maximum absorptions for **SD/Ag23** and **SD/Ag24** at 350 and 373 nm can be assigned to the $\pi \rightarrow \pi^*$ transition of dppm or/and RSH ligands. Based on the Kubelka-Munk plots, the HOMO–LUMO gaps of them were determined to 1.84 and 1.62 eV, respectively.

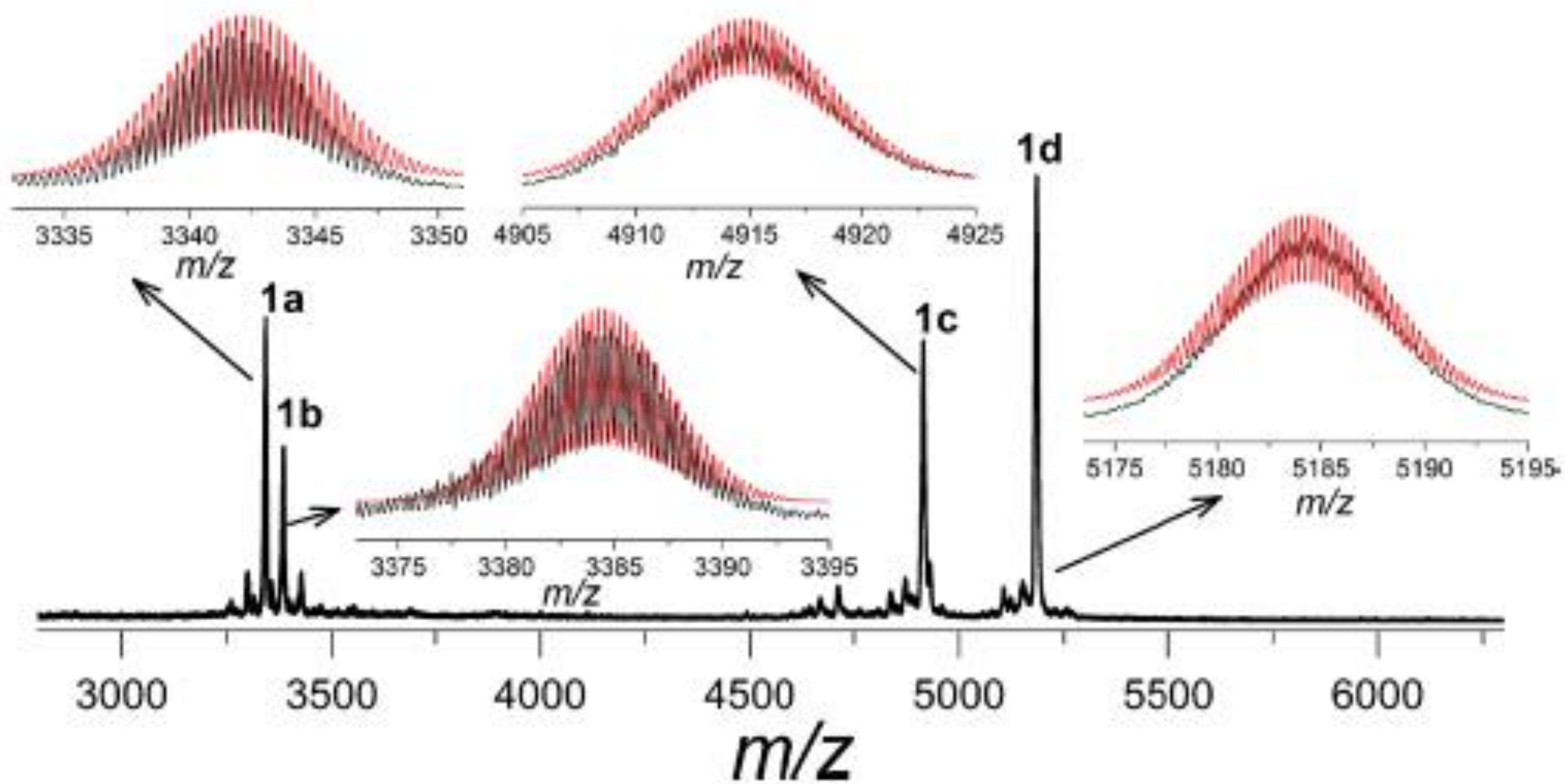


Figure 3. (a) Positive-ion ESI-MS of SD/Ag23 dissolved in dichloromethane. Insets show the experimental (black line) and the simulated (red line) isotopic distribution patterns of 1a−1d.

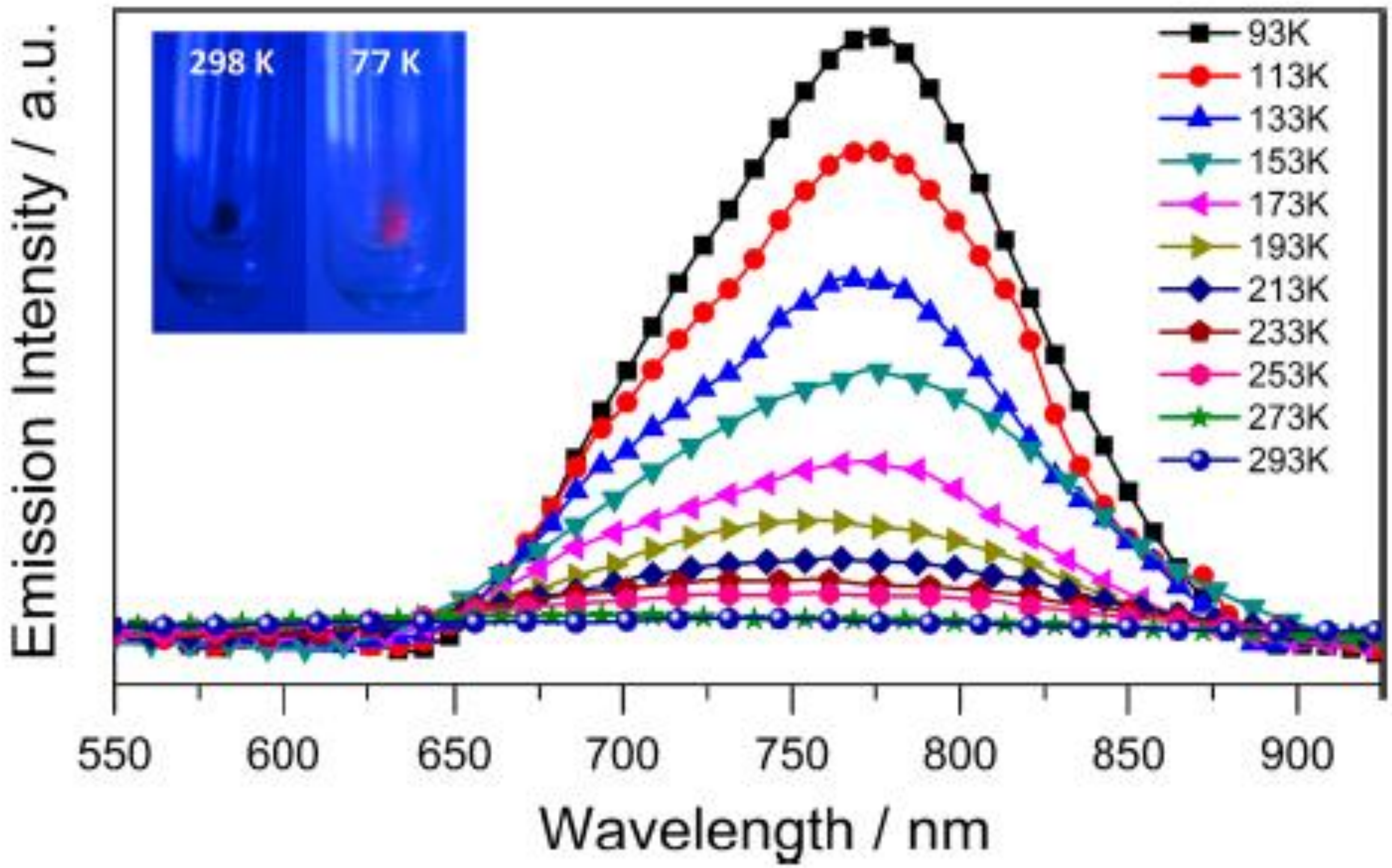


Figure 4. Emission spectra of SD/Ag23 recorded from 93 to 293 K. Insets show the photographs of sample SD/Ag23 under a hand-held UV lamp (365 nm) at 298 and 77K.

Conclusion

- In conclusion, they synthesized and characterized two unprecedented mixed ligands coprotected Ag_{52} and Ag_{76} nanoclusters that are interiorly templated by five MoO_4^{2-} and a pair of bicubane $Mo_6O_{22}^{8-}$ anions, respectively.

- Regiospecific distribution of diphosphine ligands on the surface and the arrangement of multiple molybdate templates within the nanoclusters synergetically tailor their shapes to anisotropic oblate spheroid and elongated rod, respectively.

- This work not only enriches the anisotropic silver clusters but also give important insights for the anisotropic growth of silver nanoclusters through surface modifications or/and template organizations.


Thank You!