

Article

Chalcogens Induced Ag6Z4@Ag36 (Z= S or Se) Core-Shell Nanoclusters: Enlarged Tetrahedral Core and Homochiral Crystallization

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Publication Date (Web): 11 Oct 2019

Jayoti Roy 26-10-2019



Communication

pubs.acs.org/JACS

Yan et al., J. Am. Chem. Soc. 2016, 138, 12751-12754

Asymmetric Synthesis of Chiral Bimetallic [Ag₂₈Cu₁₂(SR)₂₄]^{4–} Nanoclusters via Ion Pairing

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(a) Overall structure of $(nBu_4N)_4[Ag_{28}Cu_{12}(SR)_{24}]$ (1·TBA). (b) Cluster 1 with the R groups omitted for clarity. (c,e) A pair of enantiomers of 1 having the chiral $Ag_{28}Cu_{12}$ metal frameworks with T symmetry. (d) Idealized fcc close-packing of the corresponding (hypothetical) achiral $Ag_{28}Cu_{12}$ metal framework with Td symmetry. (f) ACBAB stacking of Ag and Cu atoms: middle, idealized Td symmetry (ACBA of the Ag_{28} is fcc and BAB of the Ag–Cu interface is hcp); left and right, observed layer stacking in T symmetry of left- and right handed isomers of 1, respectively. Color codes: orange, Ag; blue, Cu; yellow, S; green, Cl; Pink, N; gray, C.

Nanoscale

CrossMark

Cite this: Nanoscale, 2015, 7, 8284

Received 23rd February 2015, Accepted 27th March 2015

DOI: 10.1039/c5nr01222h

(a)

COMMUNICATION

an unprecedented nanometre-sized Ag₃₇ cluster⁺

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Xiao-Yu et al., Nanoscale, 2015, 7, 8284-8288

A platonic solid templating Archimedean solid:

(b) (d) (c)



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Introduction

1. Control over core structure is much more challenging than that over shell structure in core-shell silver nanoclusters.

2. Herein, two isostuctural chalcogen-mediated $[Ag_6S_4@Ag_{36}]$ (SD/Ag42a) and $[Ag_6Se_4@Ag_{36}]$ (SD/Ag42b) nanocluster caging tetrahedral $[Ag_6S_4]$ and $[Ag_6Se_4]$ as cores is synthesized by introducing slow-release source.

3. Molecular enantiomers of $[Ag_6S_4@Ag_{36}]$ and $[Ag_6Se_4@Ag_{36}]$ segregate into different crystals.

4. Chalcogenide can enlarge the nuclearity of nanoclusters by altering the inner core structure.

Synthetic Route Summary for SD/Ag42a and SD/Ag42b.



Single crystal X-ray diffreaction (SCXRD)



Figure-1

The total structures of **Ag37** (a), **SD/Ag42a** (e) and **SD/Ag42b** (i). Color legend: Ag: purple; C: gray; S: yellow; Se: brown; F: green; O: red. The core-shell skeletal structures of **Ag37** (b), **SD/Ag42a** (f) and **SD/Ag42b** (g). The truncated tetrahedral silver skeletons of **Ag37** (c), **SD/Ag42a** (g) and **SD/Ag42b** (k). The tetrahedral AgS4 (d), Ag6S4 (h), and Ag6Se4 (l) core in **Ag37**, **SD/Ag42a** and **SD/Ag42b**.

Chirality origin and homochiral crystallization



Figure-2

A pair of enantiomers found in two different crystals of **SD/Ag42a** (a) and **SD/Ag42b** (b). Color legend: Ag: purple; S: yellow; Se: brown.

Figure-3

Schematic showing of the chirality originated from achiral T_d symmetric truncated tetrahedron to chiral *T*-symmetric truncated tetrahedron by rotating the apical trigons clockwise or anticlockwise.

The molecule packing of SD/Ag42a and SD/ Ag42b in the unit cell views along *a axis*





The aqua ligands present in the crystals



The aqua ligands (red) in the apical trigons of SD/Ag42a-AAAA (a), SD/Ag42a-CCCC (b), SD/Ag42b-AAAA (c) and SD/Ag42b-CCCC (d).

The emission decay curves of SD/Ag42a and SD/Ag42b



Mass Spectrometry of SD/Ag42a (top) and SD/Ag42b (down)

Figure-6



Conclusion

1. They had enlarged an earlier $AgS_4@Ag_{36}$ to two new $Ag_6Z_4@Ag_{36}$ (Z= S or Se) clusters using slow chalcogen-release reagents.

2. The nuclearity enlargement of overall clusters did not involve the Ag36 shell but is closely associated with inner core changing from tetrahedral AgS_4 to Ag_6Se_4 .

3. Homochiral crystallization was solely observed for $Ag_6Z_4@Ag_{36}$ clusters which can be rationalized by lower molecular symmetry induced by core-expansion, directing the crystals of one handedness over recemization during the crystallization.

4. The study presents the effectiveness of chalcogens in enlarging the nuclearity of nanoclusters by solely altering the inner core structure and afford a new strategy to synthesize chiral core-shell nanoclusters in a higher-order controlled fashion.

Cluster Compounds

Isomerism in Titanium-Oxo Clusters: Molecular Anatase Model with Atomic Structure and Improved Photocatalytic Activity

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Illustration of the highlighted anatase-type {Ti₈O₁₄} moiety in a) PTC-49V and b) anatase TiO₂



Figure 1. Crystal structures of a) **PTC-49**_v and b) **PTC-49**_H. c) Illustration of the pentagonal {Ti(Ti₅)} building units. The Ti–O core structures of d) **PTC-49**_v and e) **PTC-49**_H, highlighting the vertical and horizontal arrangements of two pairs of {Ti(Ti₅)} pentagons. Atom color codes: green Ti; red O; blue N; gray C. H atoms have been omitted for clarity.

Angew .Chem. Int.Ed. 2019, 58,1320-1323

Ion-mobility mass spectrometry



Thank You