

# This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.

Author(s): Bootharaju, Megalamane S.; Chang, Hogeun; Deng, Guocheng; Malola, Sami; Baek, Woonhyuk; Häkkinen, Hannu; Zheng, Nanfeng; Hyeon, Taeghwan

Title: Cd12Ag32(SePh)36 : Non-Noble Metal Doped Silver Nanoclusters

Year: 2019

Version: Accepted version (Final draft)

**Copyright:** © 2019 American Chemical Society.

Rights: In Copyright

Rights url: http://rightsstatements.org/page/InC/1.0/?language=en

# Please cite the original version:

Bootharaju, M. S., Chang, H., Deng, G., Malola, S., Baek, W., Häkkinen, H., Zheng, N., & Hyeon, T. (2019). Cd12Ag32(SePh)36 : Non-Noble Metal Doped Silver Nanoclusters. Journal of the American Chemical Society, 141(21), 8422-8425. https://doi.org/10.1021/jacs.9b03257



# Communication

# CdAg(SePh): Non-Noble Metal Doped Silver Nanoclusters

Megalamane S. Bootharaju, Hogeun Chang, Guocheng Deng, Sami Malola, Woonhyuk Baek, Hannu Häkkinen, Nanfeng Zheng, and Taeghwan Hyeon

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b03257 • Publication Date (Web): 14 May 2019

Downloaded from http://pubs.acs.org on May 15, 2019

# Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties. 1

2 3

8

9

10

11

12

13

14 15 16

17 18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44 45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

# Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub>: Non-Noble Metal Doped Silver Nanoclusters

Megalamane S. Bootharaju,<sup>†,‡,#</sup> Hogeun Chang,<sup>†,‡,#</sup> Guocheng Deng,<sup>§</sup> Sami Malola,<sup>⊥</sup> Woonhyuk Baek,<sup>†,‡</sup> Hannu Häkkinen,<sup>\*,⊥</sup> Nanfeng Zheng,<sup>\*,§</sup> and Taeghwan Hyeon<sup>\*,†,‡</sup>

<sup>†</sup>Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea

<sup>‡</sup>School of Chemical and Biological Engineering, and Institute of Chemical Processes, Seoul National University, Seoul 08826, Republic of Korea

<sup>§</sup>Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

<sup>1</sup>Departments of Physics and Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland

Supporting Information Placeholder

ABSTRACT: While there are numerous recent reports on doping of a ligand-protected noble metal nanocluster (e.g., Au and Ag) with another noble metal, non-noble metal (e.g., Cd) doping remains challenging. Here, we design a phosphine-assisted synthetic strategy and synthesize a Cd doped Ag nanocluster, Cd12Ag32(SePh)36 (SePh: selenophenolate), which exhibits characteristic UV-vis absorption features and rare near-infrared (NIR) photoluminescence at ~1020 nm. The X-ray single crystal structure reveals an asymmetric two-shell Ag<sub>4</sub>@Ag<sub>24</sub> metal kernel protected by four nonplanar Cd<sub>3</sub>Ag(SePh)<sub>9</sub> metal-ligand frameworks. Furthermore, the electronic structure analysis shows that the cluster is a 20-electron "superatom" and density functional theory predicts that its chiral optical response is comparable to the well-known Au<sub>38</sub>(SR)<sub>24</sub> cluster. Our synthetic approach will pave a new path for introducing other non-noble metals into noble metal nanoclusters for exploring their effect on optical and chemical properties.

Ligand stabilized few-atom (tens to hundreds) nanoclusters (NCs) of metals such as Au, Ag and Cu have gained much attention in recent years for their intriguing properties, including photoluminescence (PL), optical activity, catalysis, and size- and structure-conversion.<sup>1-4</sup> The NCs (typical size <3 nm) bridge the gap between the metal-ligand complexes and nanoparticles (NPs, size >3 nm). Unlike the classical NPs with large size and composition distributions, the NCs are truly single-sized with precise molecular formulae. Thus, NCs are the potential candidates to gain fundamental insights into the evolution of optical and catalytic properties of materials from discrete atomic to molecular levels.<sup>5-8</sup>

Since the first report on the X-ray crystal structure of ligated Au<sub>102</sub> cluster,<sup>9</sup> several Au, Ag and their heteroatom doped NCs have been synthesized and atomic structures determined.<sup>1-3, 10</sup> The size, structure and composition are shown to influence the cluster properties significantly. The former two are generally directed by the choice of ligands.<sup>1-3, 11</sup> The common ligands used to attain different clusters are thiols, selenols, alkynyls, halides, hydrides, phosphines or their combinations,<sup>1, 2, 12-17</sup> in which selenols are rarely used for stabilizing Ag clusters.<sup>18, 19</sup>

Another path to modulate the cluster properties is by modifying the metal composition through substitutional doping with heteroatoms.<sup>20, 21</sup> The doped NCs exhibit enhanced properties compared to undoped ones owing to synergistic effects.<sup>4, 22, 23</sup> The dopants incorporated into Au and Ag NCs are mostly the noble metals such as Pd and Pt due to their close atomic diameters.<sup>1, 20</sup> In contrast, doping a noble metal NC with a non-noble metal such as Cd is challenging largely due to mismatch in their atomic sizes and standard reduction potentials. Recently, several Cd doped Au NCs were synthesized by post-synthetic modification processes,<sup>24-27</sup> while those of Ag remain unexplored.

Here, we report a novel synthetic method for the non-noble metal doped Ag NCs by a phosphine assisted process. Specifically, by using triphenylphosphine (PPh<sub>3</sub>) as an assisting ligand and Cd as dopant, we successfully synthesized a selenophenolate stabilized Ag NC, Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub>. The details of its synthesis (Figure S1) and purification procedures are provided in the Supporting Information. The single crystals of NCs were grown (Figure S2) by the vapor diffusion of n-pentane into a DCM solution of the cluster.

The single crystal X-ray diffraction (SCXRD) analysis reveals that the final product is a 44 metal atom cluster stabilized by 36 SePh ligands with a molecular formula,  $Cd_{12}Ag_{32}(SePh)_{36}$  (Figure 1). Clearly, the Cd atoms are located on the cluster surface. The cluster crystallizes in a triclinic system of *P-1* space group (Table S1) and its unit cell comprises two NCs (Figure S3). No counterions were identified in the structure, indicating that the cluster is neutral.



**Figure 1.** The total structure of  $Cd_{12}Ag_{32}(SePh)_{36}$  cluster. H atoms of SePh ligands are omitted for clarity.

The detailed structural analysis (Figure 2) shows that the NC consists of a Ag<sub>28</sub> core stabilized by four Cd<sub>3</sub>Ag(SePh)<sub>9</sub> motifs. Further anatomy of the Ag<sub>28</sub> core unveils a Ag<sub>4</sub> tetrahedron (Figure 2A) at the center. The average Ag-Ag bond distance of 2.84 Å is close to that of the bulk Ag, indicating the strong Ag-Ag interactions in the NC. Six Ag atoms arrange nearly coplanarly to form a

Ag<sub>6</sub> facet with four triangles (Figure 2B). Such four Ag<sub>6</sub> facets cap the four faces of Ag<sub>4</sub> tetrahedron to form a structure shown in Figure 2C. The interfacet interactions through Ag-Ag bonding produce a Ag<sub>24</sub> layer and it completely encapsulates the Ag<sub>4</sub> tetrahedron, forming a two-shell Ag<sub>4</sub>@ Ag<sub>24</sub> core (Figure 2D). Notably, the central Ag<sub>3</sub> triangles of Ag<sub>6</sub> facets (placed exactly on top of the triangular faces of inner Ag<sub>4</sub> core) are significantly elongated from the Ag<sub>4</sub> core compared to other Ag-Ag bonds (Table S2).

Ag<sub>28</sub> core formation

1 2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60



**Figure 2.** Construction of the structure of  $Cd_{12}Ag_{32}(SePh)_{36}$ . (A)  $Ag_4$  inner core and (B)  $Ag_6$  facet. Capping of  $Ag_4$  core with  $Ag_6$  facets and interfacet interactions (purple arrows) result in C and D, respectively. Mounting of  $Cd_3Ag(SePh)_9$  motifs (E) on the  $Ag_{28}$  core (D) gives the total structure of the cluster (F). The phenyl rings of ligands are omitted for clarity.

In Cd<sub>3</sub>Ag(SePh)9 surface motif (Figure 2E), each Cd atom is tetrahedrally coordinated with four Se atoms of four SePh ligands. Totally, three Se atoms from three CdSe<sub>4</sub> tetrahedrons bind with one Ag to form a AgSe<sub>3</sub> cap-like structure, forming the Cd<sub>3</sub>Ag(SePh)9 motif. The capping of four Cd<sub>3</sub>Ag(SePh)9 motifs on four Ag<sub>6</sub> facets of Ag<sub>28</sub>, through Se atoms that are unbound to motif Ag atoms, produces the total structure of Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> cluster (Figure 2F). Notably, 12 and 24 Se atoms appear in  $\mu$ -3 and  $\mu$ -2 bridging modes, respectively. All the four Cd<sub>3</sub>Ag(SePh)9 motifs are mounted over four triangular faces of inner Ag<sub>4</sub> tetrahedron, and therefore, it imparts the tetrahedral shape to the final structure. A similar Ag<sub>28</sub> core of our cluster is observed in [Cu<sub>12</sub>Ag<sub>28</sub>(SR)<sub>24</sub>]<sup>4–</sup> cluster,<sup>28</sup> however with vividly different metal and ligand composition, electronic charge and the surface structure.

The presence of Cd, Ag and Se in the cluster was supported by energy dispersive X-ray spectroscopy (Figure S4). The matrix-assisted laser desorption ionization mass spectrometry shows only a single high-mass peak at ~9.6kDa, indicating that the cluster is single-sized. This peak with lower in mass by ~0.7kDa compared to 10.3kDa for Cd12Ag32(SePh)36 may be due to the fragmentation often observed in the Ag clusters<sup>11</sup> (Figure S5). The formula of the cluster is further validated by the elemental analysis (Figure S6). The thermogravimetric analysis shows a total weight loss of 54.5%, very close to a theoretical ligand weight of the cluster 54.0% (Figure S7). <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum of the cluster (Figure S8) shows proton signals spread between 6-8 ppm for SePh protection,<sup>12</sup> which is also in agreement with the infrared analysis (Figure S9A). The absence of H and P signals for PPh<sub>3</sub> ligands, which were used during the cluster synthesis, in <sup>1</sup>H and <sup>31</sup>P NMR spectra is consistent with the SCXRD results.

The "superatom" theory<sup>29</sup> calculates a free metal electron count of 20 for  $Cd_{12}Ag_{32}(SePh)_{36}$  cluster i.e., [(12x2)+(32x1)–(36x1)] by considering the *s*-valence of two for Cd and one for Ag as well as one-electron withdrawing character of the SePh ligand. This electron count predicts that the HOMO state and the molecular orbitals just below HOMO should have 1D-2S symmetries present in a spherical angular momentum analysis, and the LUMO state should have 1F character. This is indeed what we observe by performing symmetry analysis and inspecting visually the frontier orbitals (Figures S10, S11), although the HOMO has a mixed 2S-1F character probably due to the non-spherical symmetry of the metal core. Furthermore, atomic charge analysis (Table S3) shows that the Ag atoms in the Ag4Ag24 shells are close to neutral, whereas the Ag and Cd atoms in the ligand motifs are clearly positively charged by 0.20 e and 0.66 e, respectively. The SePh ligands are shown as electron-withdrawing with a clear negative total charge by -0.28 e per ligand.

The optical properties and electronic structure of  $Cd_{12}Ag_{32}(SePh)_{36}$  cluster were further studied both experimentally by UV-vis spectroscopy and theoretically by the linear response formulation of the time-dependent density functional theory (LR-TDDFT, see SI for details). The experimental absorption spectrum (Figure 3) displays clear peaks at 451, 534 and 640 nm along with shoulder peaks at 245, 288, 335, and 493 nm. The absorption onset (Figure S9B) at ~900 nm (1.37 eV) is very close to the calculated HOMO-LUMO gap of 1.35 eV, with a slight underestimation of the gap being a typical feature of the used DFT PBE xc-functional. The calculated absorption spectrum for both the experimental (Figure 3) and PBE-relaxed cluster structure show a good agreement with the experiment, with at least six peaks/shoulders identifiable in the computed spectrum (labels a–f).

The absorption features a-f were analyzed by creating the dipole transition contribution maps and by breaking down the contributions by different parts of the cluster to a given transition (Figure S12). The lower energy peaks (a–c) have all similar characters, namely they are superatom-to-superatom transitions concentrated in the Ag core (intraband Ag(sp) $\rightarrow$ Ag(sp) transitions). It is interesting to note that the energy difference between a and b peaks seems to be a direct measure to the energy splitting of the superatom 1F manifold by the overall tetrahedral symmetry of the cluster (Figure S10). The high-energy features, d–f have increasing contributions also from the metal-ligand interface (mainly from Se(p)) and weakening contributions from the superatom states. We note that the Ag d-band is not actively participating to optical transitions in the analyzed and measured energy range, nor are the Cd atoms (since they are in the formal Cd(II) state).



Figure 3. Experimental (black) and calculated (blue) absorption spectra of  $Cd_{12}Ag_{32}(SePh)_{36}$  cluster. For easier comparison, the calculated spectrum is blue-shifted uniformly by 0.3 eV. Red line: experimental PL (excitation: 490 nm).

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

Interestingly, the Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> cluster shows a broad NIR PL (quantum yield: ~0.28%) peak at ~1020 nm (Figure 3), which is different from the visible PL of Ag NCs.<sup>2</sup> The similar PL excitation and UV-vis spectra, and the same emission at 1020 nm for different excitations together (Figure S13) indicate that the PL is originated from the cluster. The PL of Cd doped Ag cluster at 1020 nm is clearly different from that of a Cu doped cluster at 900 nm,<sup>28</sup> suggesting the successful tuning of NIR PL by the non-noble metal doping (Figure S14). Theoretically estimated PL emissions (see SI for details) at 1134 nm and 1150 nm are in qualitative agreement with the experiment (1020 nm), strongly suggesting that the origin of the high-energy end of broad PL is the de-excitation over the HOMO-LUMO energy gap.<sup>30</sup> The low-energy end of PL is likely resulted from the relaxation through an intrinsic Cd<sub>3</sub>Ag(SePh)<sub>9</sub> surface state.

The SCXRD shows that the two clusters in the unit cell are enantiomers (Figure S15) due to asymmetric  $Ag_{28}$  core. Since the solution of Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> is racemic, we cannot experimentally measure the chiral optical response, however, it can be straightforwardly calculated for one of the enantiomers. Our calculations predict that the strength of the chiral response in the UV-vis region (Figure 4) is comparable to, e.g., the well-known thiolated chiral  $Au_{38}(SR)_{24}$  cluster.<sup>31, 32</sup>



Figure 4. Computed circular dichroism (CD) spectra of one of the enantiomers of  $Cd_{12}Ag_{32}(SePh)_{36}$  (red curve) and  $Au_{38}(SCH_2CH_2Ph)_{24}$  (black curve, offset vertically for better visualization) clusters. Inset: the DFT optimized structure of the  $Cd_{12}Ag_{32}(SePh)_{36}$  enantiomer.

We note the absence of PPh<sub>3</sub> in Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> cluster (Figure 1), which could be synthesized only in the presence of PPh<sub>3</sub> and tetraoctylammonium bromide (Figure S16) in our experimental conditions. The absorption spectra (Figure S17) suggest that the formation of Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> proceeds through the intermediate clusters formed after NaBH<sub>4</sub> reduction of metal-ligand complexes. The <sup>31</sup>P and <sup>1</sup>H NMR spectra confirm the binding of PPh<sub>3</sub> in the metal-ligand complexes (Figures S18, S19). After NaBH<sub>4</sub> addition, the PPh<sub>3</sub> in the complex transfers the metals to form intermediates and subsequently released into solution, confirming PPh<sub>3</sub>-mediated synthesis of the Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> cluster. This cluster shows moderate and excellent ambient stability in the solution- and solid-state, respectively (Figure S20).

In summary, we designed a phosphine-assisted synthetic strategy to dope an atomically precise Ag nanocluster with a non-noble metal, Cd. By this method, we synthesized a single-sized neutral Cd<sub>12</sub>Ag<sub>32</sub>(SePh)<sub>36</sub> cluster and elucidated its total structure using Xray crystallography. The Cd dopant is found to prefer the cluster surface to its core. Our cluster exhibits NIR PL and a chiral core, resulting optical activity. The absorption spectrum and electronic structure of this cluster are well compared with those from the DFT. Our ligand-assisted synthesis of nanocluster may become a general method to introduce other active metals into noble metal clusters.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis, characterization and computational details of the  $Cd_{12}Ag_{32}(SePh)_{36}$  cluster (PDF).

 $Crystallographic \ data \ for \ the \ Cd_{12}Ag_{32}(SePh)_{36} \ cluster \ (CIF).$ 

## AUTHOR INFORMATION

#### **Corresponding Author**

thyeon@snu.ac.kr nfzheng@xmu.edu.cn hannu.j.hakkinen@jyu.fi

#### **Author Contributions**

#M.S.B and H.C contributed equally to this work.

#### Notes

The authors declare no competing financial interests.

### ACKNOWLEDGMENTS

T.H. acknowledges the financial support by the Research Center Program of the IBS (IBS-R006-D1) in Korea. H.H. acknowledges support from the Academy of Finland (grants 294217, 319208, and the Academy Professorship). The computations were made at the CSC supercomputing center in Espoo, Finland. N.F.Z. acknowledges the financial support from the National Key R&D Program of China (2017YFA0207302), the National Natural Science Foundation of China (21890752, 21731005, and 21420102001).

#### REFERENCES

- Jin, R.; Zeng, C.; Zhou, M.; Chen, Y. Atomically precise colloidal metal nanoclusters and nanoparticles: fundamentals and opportunities. *Chem. Rev.* 2016, 116, 10346.
- Chakraborty, I.; Pradeep, T. Atomically precise clusters of noble metals: emerging link between atoms and nanoparticles. *Chem. Rev.* 2017, *117*, 8208.
- Yan, J.; Teo, B. K.; Zheng, N. Surface chemistry of atomically precise coinage-metal nanoclusters: from structural control to surface reactivity and catalysis. *Acc. Chem. Res.* 2018, *51*, 3084.
- Liu, Y.; Chai, X.; Cai, X.; Chen, M.; Jin, R.; Ding, W.; Zhu, Y. Central doping of a foreign atom into the silver cluster for catalytic conversion of CO<sub>2</sub> toward C–C bond formation. *Angew. Chem. Int. Ed.* **2018**, *57*, 9775.
- Sakthivel, N. A.; Dass, A. Aromatic thiolate-protected series of gold nanomolecules and a contrary structural trend in size evolution. *Acc. Chem. Res.* 2018, 51, 1774.
- Tang, Q.; Hu, G.; Fung, V.; Jiang, D.-e., Insights into interfaces, stability, electronic properties, and catalytic activities of atomically precise metal nanoclusters from first principles. *Acc. Chem. Res.* 2018, *51*, 2793.
- Bhattarai, B.; Zaker, Y.; Atnagulov, A.; Yoon, B.; Landman, U.; Bigioni, T. P. Chemistry and Structure of Silver Molecular Nanoparticles. *Acc. Chem. Res.* 2018, *51*, 3104.
- Wang, Z.; Su, H. F.; Tung, C. H.; Sun, D.; Zheng, L. S. Deciphering synergetic core-shell transformation from [Mo<sub>6</sub>O<sub>22</sub>@Ag<sub>44</sub>] to [Mo<sub>8</sub>O<sub>28</sub>@Ag<sub>50</sub>]. *Nat. Commun.* **2018**, *9*, 4407.
- Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution. *Science* 2007, *318*, 430.

10) Conn, B. E.; Atnagulov, A.; Yoon, B.; Barnett, R. N.; Landman, U.; Bigioni, T. P. Confirmation of a de novo structure prediction for an atomically precise monolayer-coated silver nanoparticle. *Sci. Adv.* **2016**, 2, e1601609.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

57 58 59

60

- Bootharaju, M. S.; Burlakov, V. M.; Besong, T. M. D.; Joshi, C. P.; AbdulHalim, L. G.; Black, D. M.; Whetten, R. L.; Goriely, A.; Bakr, O. M. Reversible size control of silver nanoclusters via ligand-exchange. *Chem. Mater.* 2015, *27*, 4289.
- 12) Song, Y.; Zhong, J.; Yang, S.; Wang, S.; Cao, T.; Zhang, J.; Li, P.; Hu, D.; Pei, Y.; Zhu, M. Crystal structure of Au<sub>25</sub>(SePh)<sub>18</sub> nanoclusters and insights into their electronic, optical and catalytic properties. *Nanoscale* **2014**, *6*, 13977.
- 13) Lei, Z.; Wan, X. K.; Yuan, S. F.; Guan, Z. J.; Wang, Q. M. Alkynyl approach toward the protection of metal nanoclusters. *Acc. Chem. Res.* 2018, 51, 2465.
- 14) Zhang, S. S.; Alkan, F.; Su, H. F.; Aikens, C. M.; Tung, C. H.; Sun, D. [Ag48(C≡C'Bu)<sub>20</sub>(CrO<sub>4</sub>)<sub>7</sub>]: an atomically precise silver nanocluster coprotected by inorganic and organic ligands. *J. Am. Chem. Soc.* 2019, 141, 4460.
- 15) Qu, M.; Li, H.; Xie, L. H.; Yan, S. T.; Li, J. R.; Wang, J. H.; Wei, C. Y.; Wu, Y. W.; Zhang, X. M. Bidentate phosphine-assisted synthesis of an all-alkynyl-protected Ag<sub>74</sub> nanocluster. *J. Am. Chem. Soc.* 2017, 139, 12346.
- 16) Shichibu, Y.; Negishi, Y.; Watanabe, T.; Chaki, N. K.; Kawaguchi, H.; Tsukuda, T. Biicosahedral gold clusters [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> (n = 2–18): a stepping stone to cluster-assembled materials. *J. Phys. Chem. C* 2007, *111*, 7845.
- 17) Dhayal, R. S.; van Zyl, W. E.; Liu, C. W. Polyhydrido copper clusters: synthetic advances, structural diversity, and nanocluster-to-nanoparticle conversion. Acc. Chem. Res. 2016, 49, 86.
- 18) Chakraborty, I.; Kurashige, W.; Kanehira, K.; Gell, L.; Häkkinen, H.; Negishi, Y.; Pradeep, T. Ag<sub>44</sub>(SeR)<sub>30</sub>: a hollow cage silver cluster with selenolate protection. *J. Phys. Chem. Lett.* **2013**, *4*, 3351.
- 19) Fuhr, O.; Dehnen, S.; Fenske, D. Chalcogenide clusters of copper and silver from silylated chalcogenide sources. *Chem. Soc. Rev.* 2013, 42, 1871.
- 20) Ghosh, A.; Mohammed, O. F.; Bakr, O. M. Atomic-level doping of metal clusters. Acc. Chem. Res. 2018, 51, 3094.
- 21) Yang, J.; Muckel, F.; Baek, W.; Fainblat, R.; Chang, H.; Bacher, G.; Hyeon, T. Chemical synthesis, doping, and transformation of magicsized semiconductor alloy nanoclusters. J. Am. Chem. Soc. 2017, 139, 6761.

- 22) Hossain, S.; Ono, T.; Yoshioka, M.; Hu, G.; Hosoi, M.; Chen, Z.; Nair, L. V.; Niihori, Y.; Kurashige, W.; Jiang, D.-e.; Negishi, Y. Thiolate-protected trimetallic Au<sub>20</sub>Ag<sub>~4</sub>Pd and Au<sub>~20</sub>Ag<sub>~4</sub>Pt alloy clusters with controlled chemical composition and metal positions. *J. Phys. Chem. Lett.* **2018**, *9*, 2590.
- 23) Yuan, X.; Dou, X.; Zheng, K.; Xie, J. Recent advances in the synthesis and applications of ultrasmall bimetallic nanoclusters. *Part. Part. Syst. Charact.* 2015, 32, 613.
- 24) Wang, S.; Song, Y.; Jin, S.; Liu, X.; Zhang, J.; Pei, Y.; Meng, X.; Chen, M.; Li, P.; Zhu, M. Metal exchange method using Au<sub>25</sub> nanoclusters as templates for alloy nanoclusters with atomic precision. *J. Am. Chem. Soc.* 2015, *137*, 4018.
- 25) Zhu, M.; Wang, P.; Yan, N.; Chai, X.; He, L.; Zhao, Y.; Xia, N.; Yao, C.; Li, J.; Deng, H.; Zhu, Y.; Pei, Y.; Wu, Z. The fourth alloying mode by way of anti-galvanic reaction. *Angew. Chem. Int. Ed.* **2018**, *57*, 4500.
- 26) Yang, S.; Chen, S.; Xiong, L.; Liu, C.; Yu, H.; Wang, S.; Rosi, N. L.; Pei, Y.; Zhu, M. Total structure determination of Au<sub>16</sub>(S-Adm)<sub>12</sub> and Cd<sub>1</sub>Au<sub>14</sub>(S'Bu)<sub>12</sub> and implications for the structure of Au<sub>15</sub>(SR)<sub>13</sub>. J. Am. Chem. Soc. **2018**, 140, 10988.
- 27) Yao, C.; Lin, Y. J.; Yuan, J.; Liao, L.; Zhu, M.; Weng, L. h.; Yang, J.; Wu, Z. Mono-cadmium vs mono-mercury doping of Au<sub>25</sub> nanoclusters. *J. Am. Chem. Soc.* **2015**, *137*, 15350.
- 28) Yan, J.; Su, H.; Yang, H.; Hu, C.; Malola, S.; Lin, S.; Teo, B. K.; Häkkinen, H.; Zheng, N. Asymmetric synthesis of chiral bimetallic [Ag<sub>28</sub>Cu<sub>12</sub>(SR)<sub>24</sub>]<sup>4-</sup> nanoclusters via ion pairing. *J. Am. Chem. Soc.* 2016, *138*, 12751.
- 29) Walter, M.; Akola, J.; Lopez-Acevedo, O; Jadzinsky, P.D.; Calero, G.; Ackerson, C.J.; Whetten, R.L.; Grönbeck, H.; Häkkinen, H. A unified view of ligand-protected gold clusters as superatom complexes. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 9157-9162.
- 30) Aikens, C. M. Electronic and Geometric Structure, Optical Properties, and Excited State Behavior in Atomically Precise Thiolate-Stabilized Noble Metal Nanoclusters. Acc. Chem. Res. 2018, 51, 3065.
- 31) Lopez-Acevedo, O.; Tsunoyama, H.; Tsukuda, T.; Häkkinen, H.; Aikens, C.M. Chirality and electronic structure of the thiolate-protected Au<sub>38</sub> nanocluster. J. Am. Chem. Soc. 2010, 132, 8210-8218.
- 32) Dolamic, I.; Knoppe, S.; Dass, A.; Burgi, T. First enantioseparation and circular dichroism spectra of Au<sub>38</sub> clusters protected by achiral ligands. *Nature Comm.* 2012, *3*, 798.

