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Controlled Assembly Synthesis of Atomically Precise Ultrastable Silver Nanoclusters with Polyoxometalates

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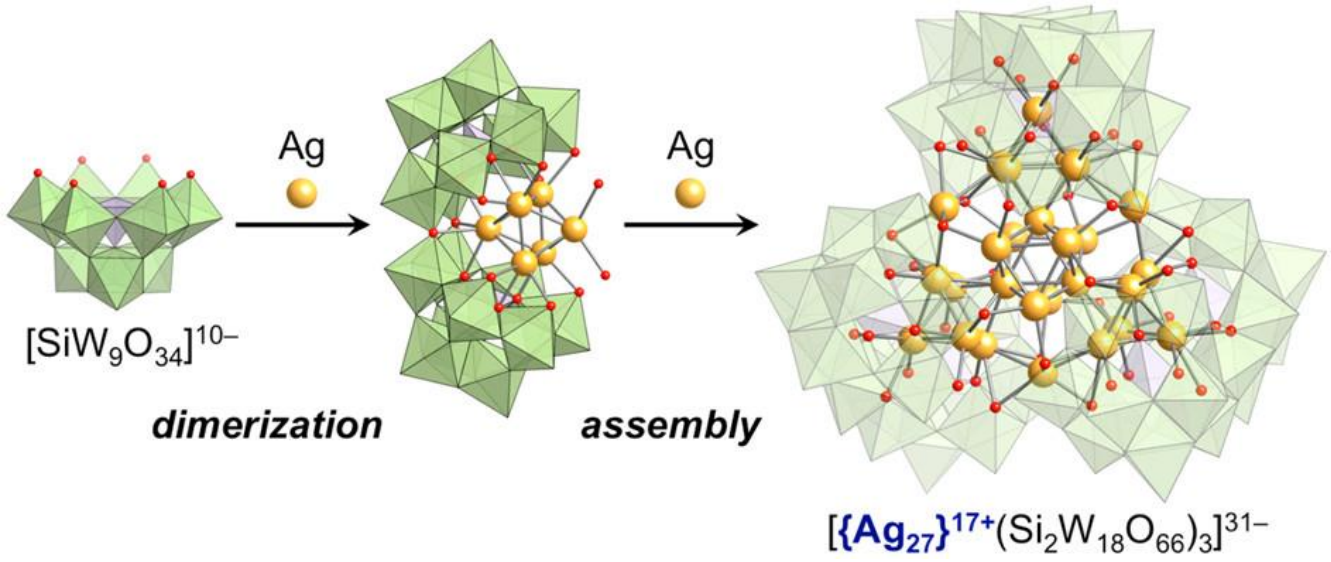

Anagha Jose
06-06-2020

Polyoxometalates

- Polyoxometalates (POMs) are combinations between oxygen and early transition metals (*e.g.*, M = V, Nb, Ta, Mo, W) at their highest oxidation states. They may also contain a variety of heteroatoms (*e.g.*, X = P, As, Si, Ge).

- They are bulky anionic metal-oxo clusters possessing unique structures and properties, such as acidity/basicity ,electronic states, and redox properties.

- POMs of the general formula $[M_mO_y]^{n-}$ containing only a transition metal and oxygen are called isopolyoxometalates.

- Compounds including a small number of additional elements $[X_xM_mO_y]^{n-}$ (X = heteroelement, x smaller than m) belong to the sub-class of heteropolyoxometalates.

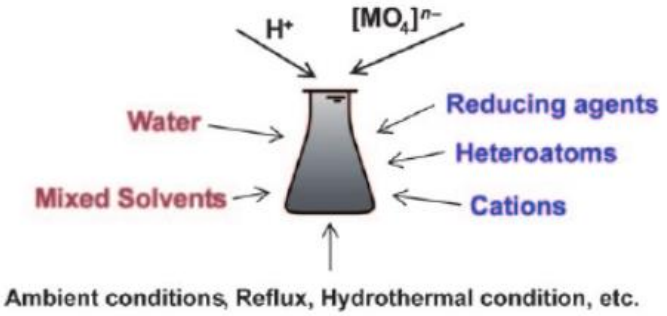

Figure 1. Parameters that are often adjusted in the synthesis/isolationof new POM clusters using the multi-parameter one-pot method

Common structures of iso- and heteropolyoxometalates

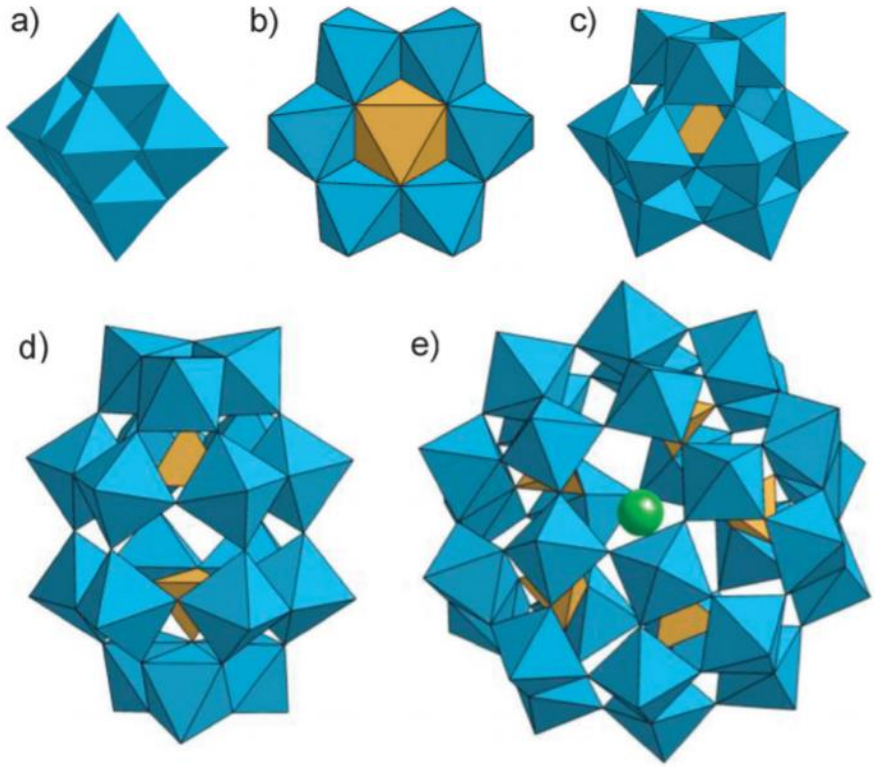

Figure. 2 Polyhedral representation of (a) Lindqvist,$[M_6O_{19}]^{n-}$(b) Anderson, $[XM_6O_{24}]^{n-}$ (c) Keggin, $[XM_{12}O_{40}]^{n-}$ (d) Wells–Dawson $[X_2M_{18}O_{62}]^{n-}$and (e) Preyssler, $[P_5W_{30}O_{110}]^{n-}$ polyoxoanions. The blue octahedrons conform the metal oxide core.

Poblet *et al.*,Chem. Soc. Rev .,2012,41,7537–7571

- Lacunary structures are obtained by the selective removal of one or more metal ions by addition of base.
- They present open coordination sites which can be occupied by other metal or non-metal atoms. This strategy is commonly used to modify the structure and properties of POMs.

Background Work

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A discrete octahedrally shaped $[Ag_6]^{4+}$ cluster encapsulated within silicotungstate ligands†

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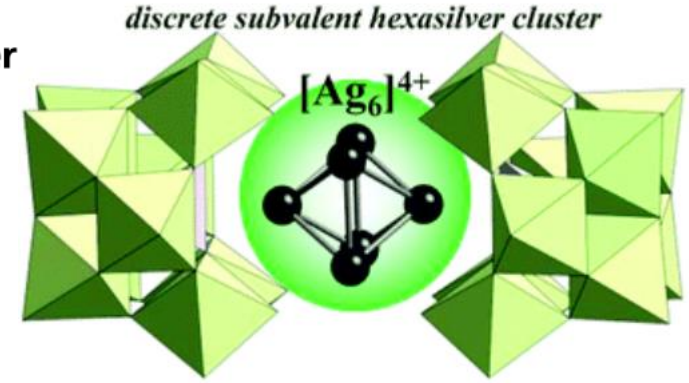
Yuji Kikukawa, Yoshiyuki Kuroda, Kosuke Suzuki, Mitsuhiro Hibino, Kazuya Yamaguchi and Noritaka Mizuno*



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ARTICLE

DOI: 10.1038/s41467-018-04499-9 OPEN

Trapping an octahedral Ag_6 kernel in a seven-fold symmetric Ag_{56} nanowheel

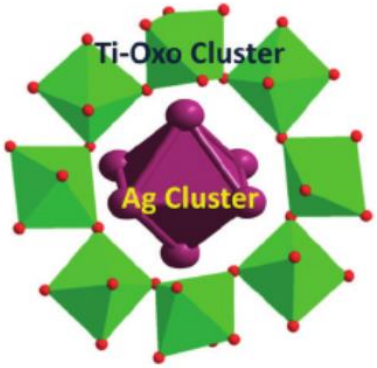
Zhi Wang[1], Hai-Feng Su[2], Mohamedally Kurmoo[3], Chen-Ho Tung[1], Di Sun[1] & Lan-Sun Zheng[2]

VIP **Cluster Compounds** *Very Important Paper*

International Edition: DOI: 10.1002/anie.201804569
German Edition: DOI: 10.1002/ange.201804569

Atomically Precise Multimetallic Semiconductive Nanoclusters with Optical Limiting Effects

Shuai Chen, Wei-Hui Fang, Lei Zhang, and Jian Zhang**



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Unusual fcc-structured Ag_{10} kernels trapped in Ag_{70} nanoclusters†

Yan-Min Su,‡[a] Zhi Wang,‡[a] Gui-Lin Zhuang,[b] Quan-Qin Zhao,[a] Xing-Po Wang,[a] Chen-Ho Tung[a] and Di Sun*[a]

Motivation

- POMs could act as structure-directing units for reactive polynuclear Ag clusters by both protecting the clusters from undesired aggregation and stabilizing the clusters.

- This synthetic approach could lead to unexplored, POM-based nanomaterials with unique geometric and/or electronic structures that cannot be realized using conventional, flexible organic ligands.

Why this paper?

- The first report on the charge transfer from structurally well defined Ag nanoclusters to inorganic oxometalates in the visible light region.

- The numbers of core Ag atoms were limited to 10 when using these inorganic ligands, and assembling the corresponding clusters into larger clusters has been difficult due to complete encapsulation of the clusters within POMs and oxometalates.

Introduction

- Novel, controlled assembly strategy for constructing Ag nanoclusters with POM inorganic ligands, enabling the synthesis of a $\{Ag_{27}\}^{17+}$ nanocluster.
- The synthetic strategy involves the assembly of reactive Ag nanoclusters supported by C-shaped open-Dawson type POMs $[Si_2W_{18}O_{66}]^{16-}$ ($\{Si_2W_{18}\}$)in organic solvents.
- The resulting trefoil-propeller-shaped $\{Ag_{27}\}^{17+}$ nanocluster (**Ag27**) contains 10 valence electrons delocalized over the cluster and is ultrastable in solutions.
- The cluster shows unique $\{Ag_{27}\}$-to POM charge transfer bands in the visible light region.

Schematic of the assembly

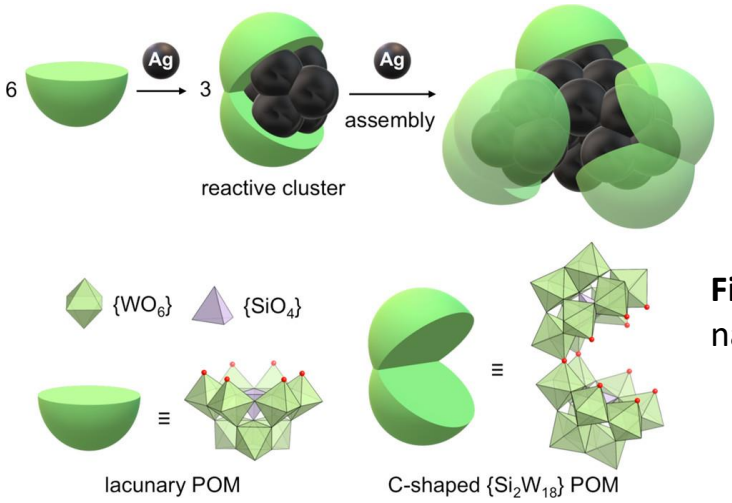


Figure1. Schematic of the assembly synthesis of Ag nanoclusters using POM-based building units.

Synthesis of $TBA_7H_2[Ag_2(SiW_9O_{31})_2(CH_3COO)_3]\cdot H_2O\cdot CCl_4$ (**Ag2**)

Silver acetate in acetone	+	$TBA_4[SiW_9O_{28}(OCH_3)_6]$	5h, RT / CCl_4 →	**Ag2**(colourless)
1	:	1		

Results

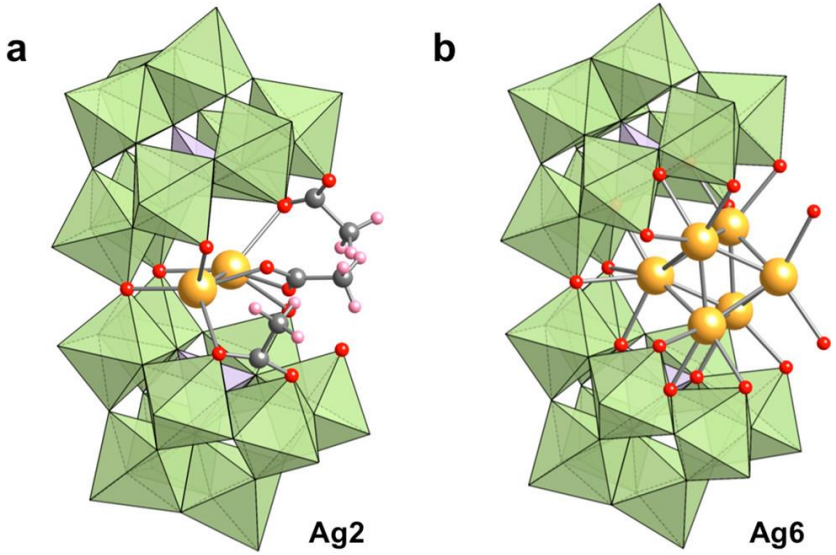


Figure 2. Crystal structures of the reactive precursors in the Ag nanocluster synthesis . (a) **Ag2** and (b) **Ag6**. Spheres: Ag, orange; O, red; C, gray; H, pink.

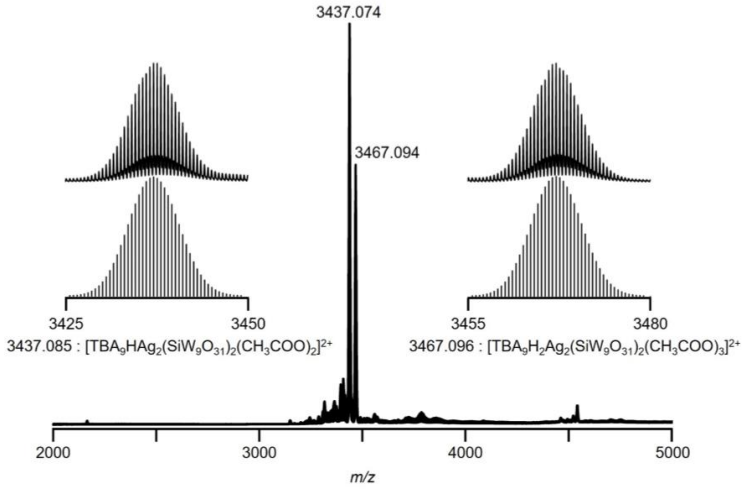


Figure S1. ESI-mass spectrum of Ag2 in acetone. Insets: spectra in the range of m/z 3425–3450 and 3455–3480, and simulated patterns for $[TBA_9HAg_2(SiW_9O_{33})_2(CH_3COO)_2]^{2+}$ (m/z 3437.085) and $[TBA_9H_2Ag_2(SiW_9O_{33})_2(CH_3COO)_3]^{2+}$ (m/z 3467.096).

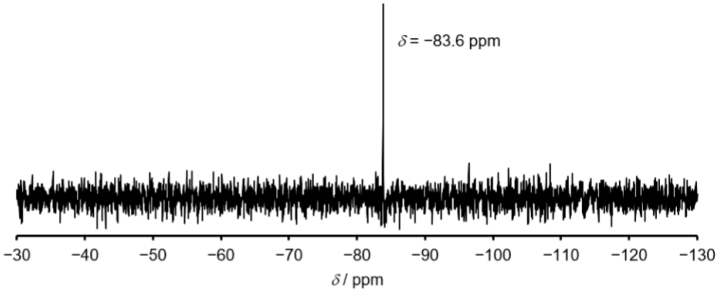


Figure S2. ^{29}Si NMR spectrum of Ag2 in an acetone-d6 solution solution containing 1 M ethylene carbonate.

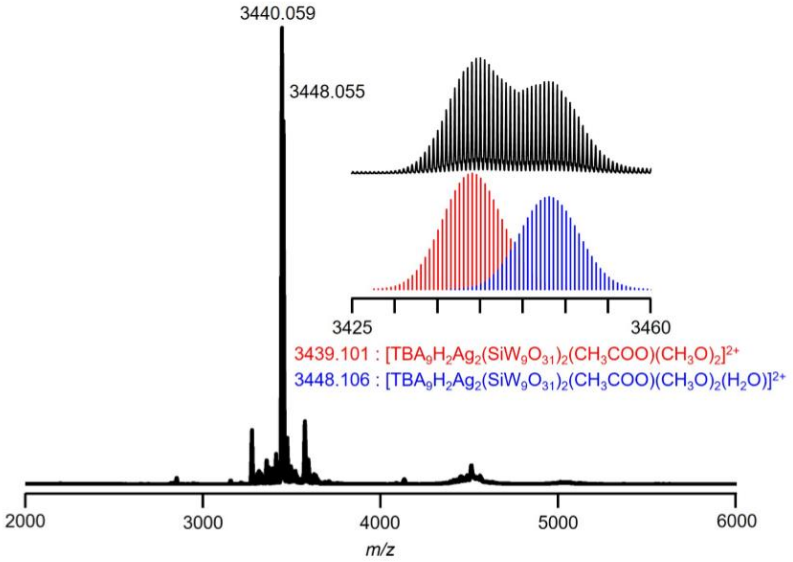
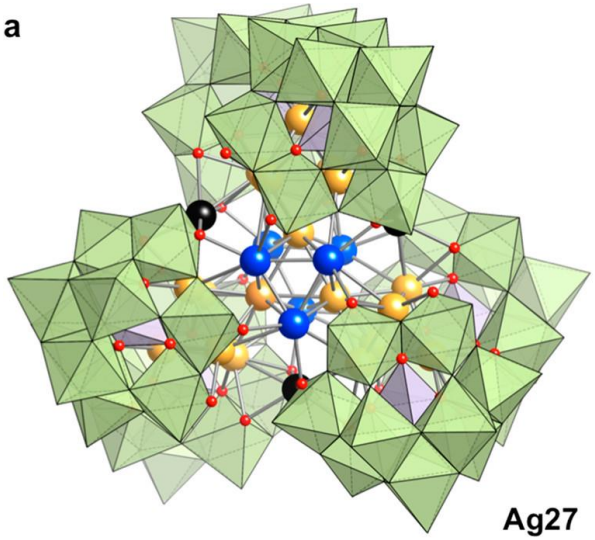


Figure S3. ESI-mass spectrum of the reaction solution of Ag2 and silver acetate (4 equiv with respect to Ag2) in acetone.

Synthesis $TBA_{16}(Me_2NH_2)_8H_5Ag_2[Ag_{27}(Si_2W_{18}O_{66})_3]\cdot 12C_3H_4O_3\cdot 34H_2O$ (**Ag27**)

Ag2 + Silver benzoate $\xrightarrow[(C_2H_5)_2O]{\text{DMF,48h,RT}}$ **Ag27** (Dark brown)



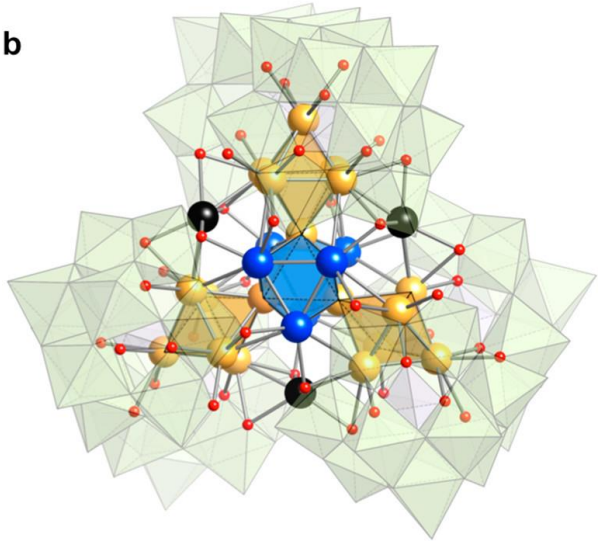


Figure 3. Crystal structures of Ag27. (a) Overall anion structure and (b) $\{Ag_{27}\}^{17+}$ cluster. Spheres: Ag, orange, blue, black; O, red.

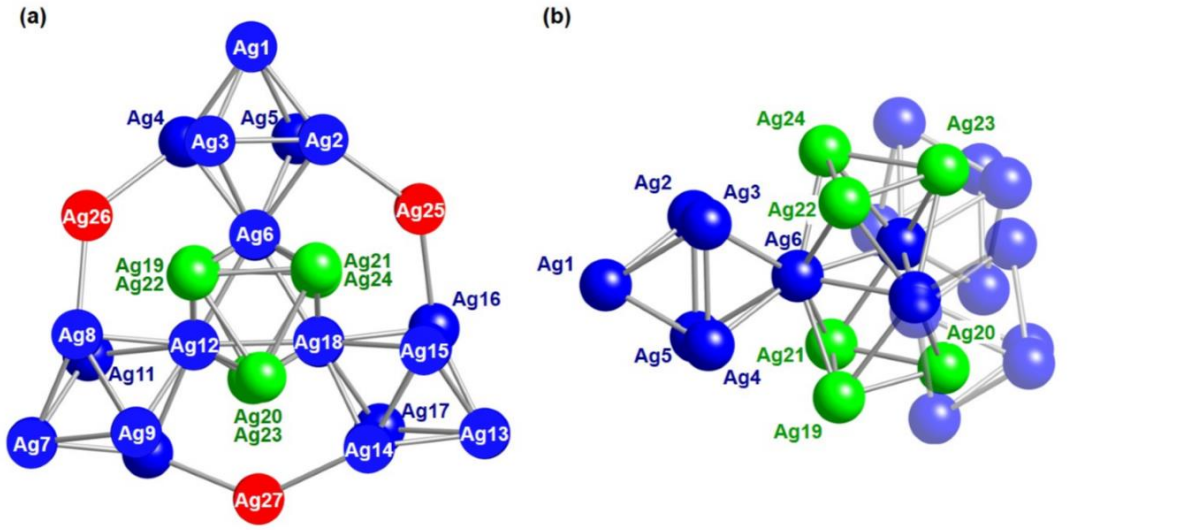


Figure S4. (a) Top view and (b) side view of the silver nanocluster $\{Ag_{27}\}^{17+}$ of **Ag27**.

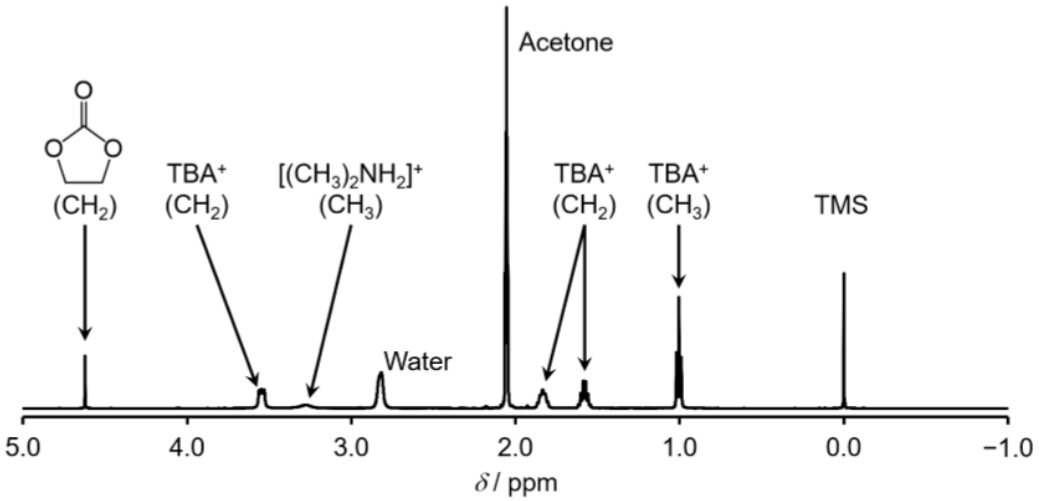


Figure S7. ^{1}H NMR spectrum of **Ag27** in acetone-d_6.

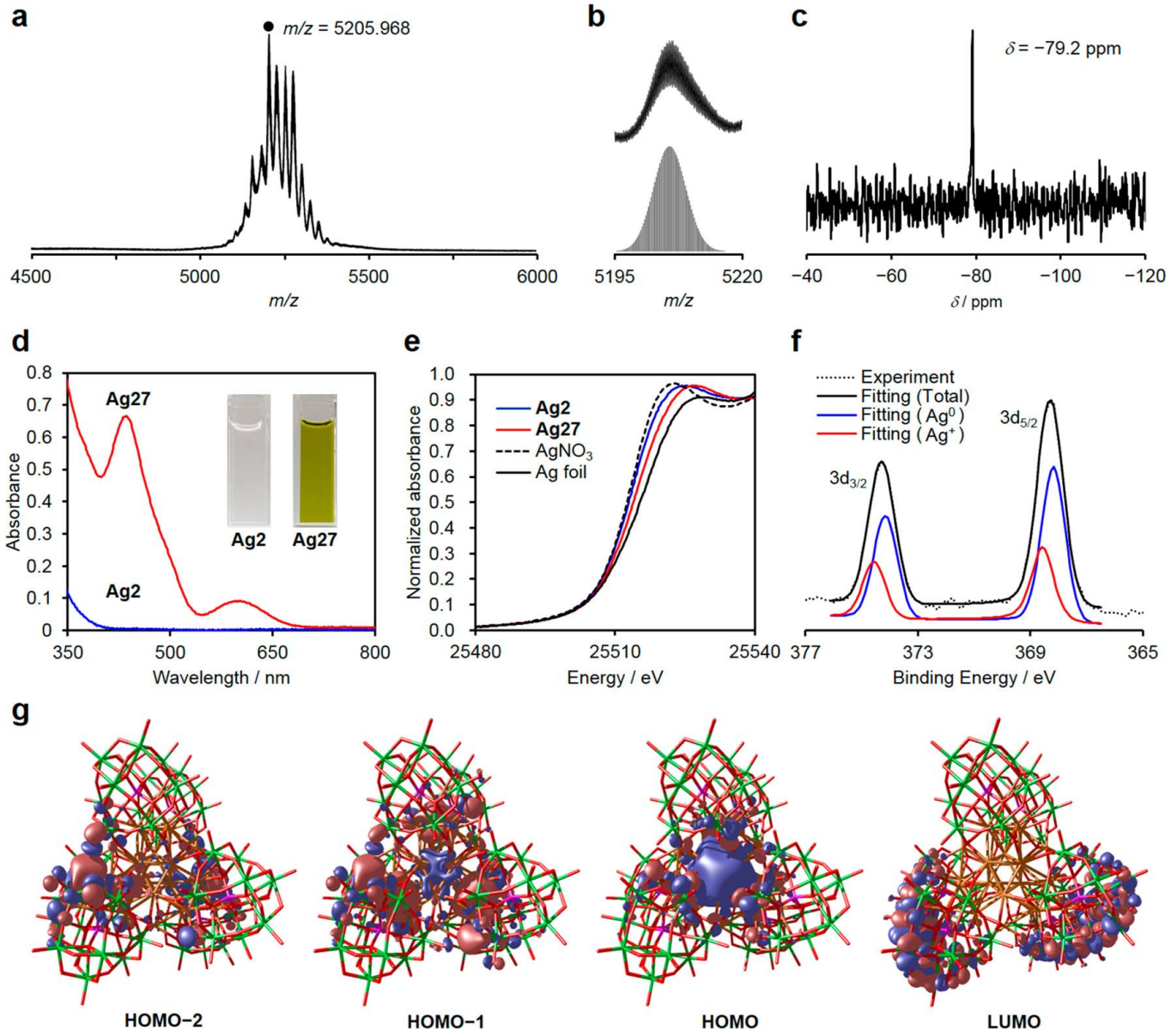


Figure 4. (a) Total and (b) enlarged view of the ESI mass spectrum of Ag27 in acetone (top, observed spectrum; bottom, simulated pattern for $[TBA_{16}(Me_2NH_2)_6H_{11}Ag_{29}(Si_2W_{18}O_{66})_3(C_3H_4O_3)_3]^{4+}$). (c) ^{29}Si NMR spectrum of Ag27 in acetone-d_6 containing ethylene carbonate (1 M). (d) UV−visabsorptionspectraofAg2(30μM)and Ag27(10μM)in acetone containing ethylene carbonate (1M).(e)AgK-edge XANES spectra of Ag2 and Ag27. (f) XPS spectrum of Ag27. Ag $3d_{3/2}$ and Ag $3d_{5/2}$ peaks were deconvoluted into Ag^0 and Ag^+ peaks. (g) Molecular orbitals of Ag27.

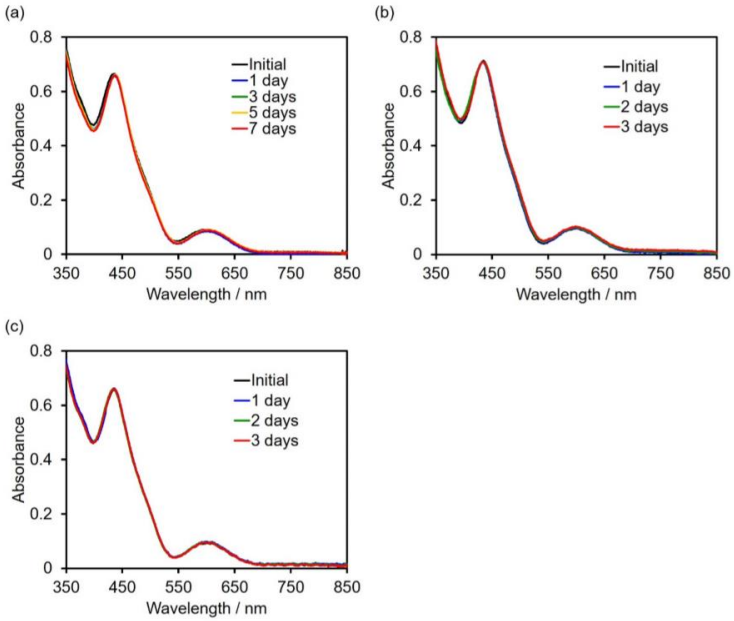


Figure S10. UV-Vis spectra of **Ag27** (10 μM) in (a) acetone containing ethylene carbonate (1 M), (b) acetone, and (c) acetonitrile.

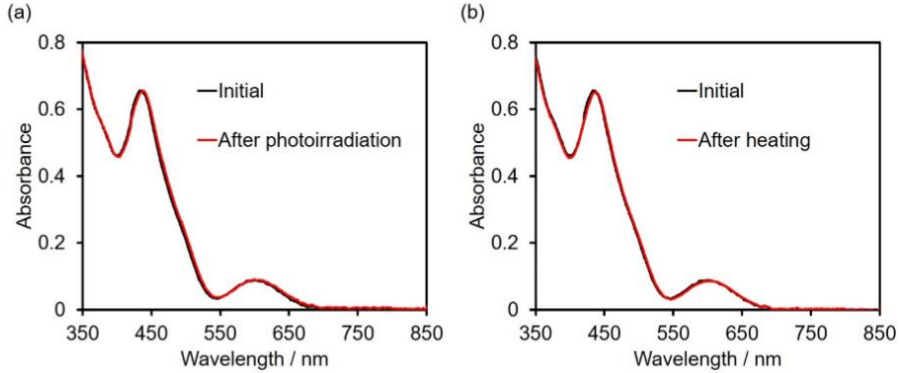
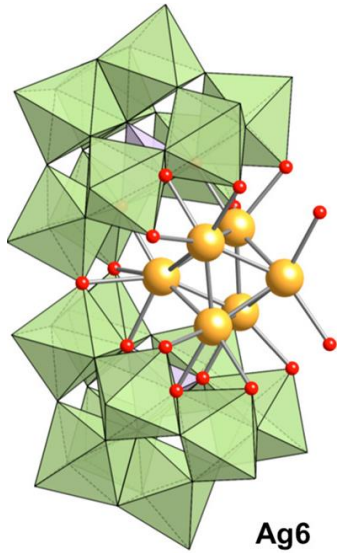


Figure S11. UV-Vis spectra of **Ag27** (10 μM) in acetonitrile before and after (a) photoirradiation (λ > 400 nm, 300 W Xe lamp) for 6 h and (b) heating at 60 °C for 6 h.



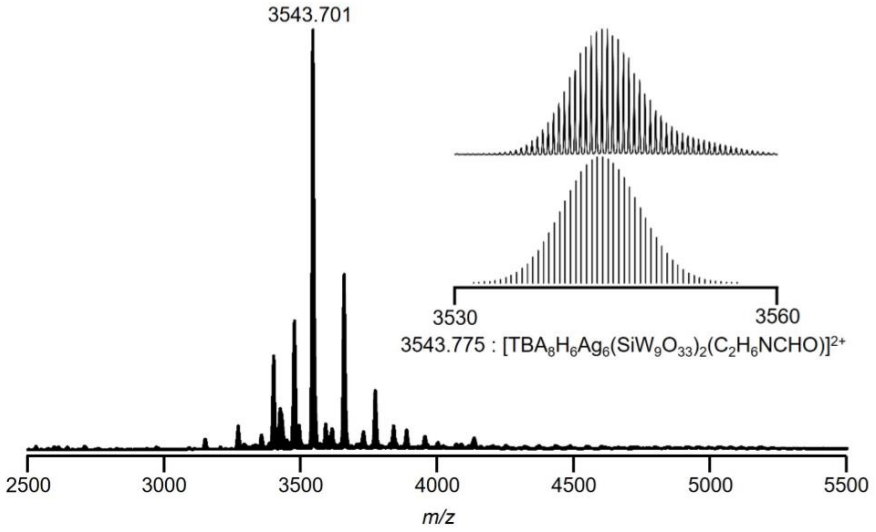


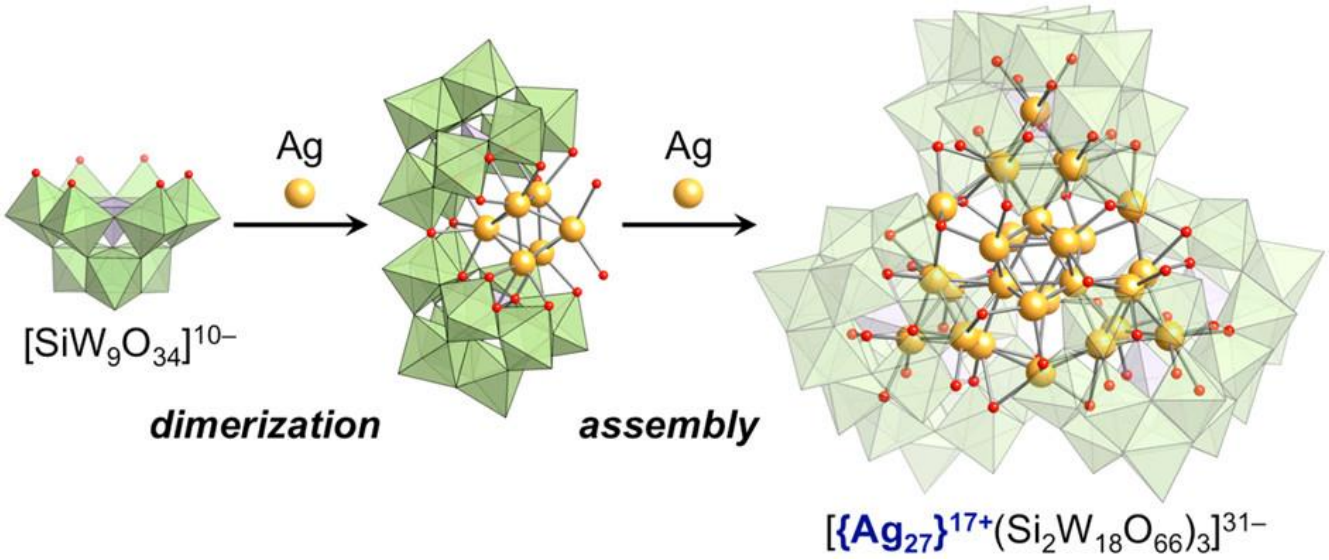
Figure S12. ESI-mass spectrum of the synthetic solution of **Ag27**. Insets: spectrum in the range of *m/z* 3530–3560, and simulated pattern for $[TBA_8H_6Ag_6(SiW_9O_{33})_2(DMF)]^{2+}$ (*m/z* 3543.775).

Conclusions

- They reported a controlled assembly strategy for fabricating atomically precise silver nanoclusters using polyoxometalates (POMs) as structure-directing as well as functionalizing units.

- The $\{Ag_{27}\}^{17+}$ nanocluster possessed 10 delocalized valence electrons and showed unprecedented ultrastability in solutions.

- The cluster showed unique $\{Ag_{27}\}$-to-POM charge transfer bands in the visible light region.



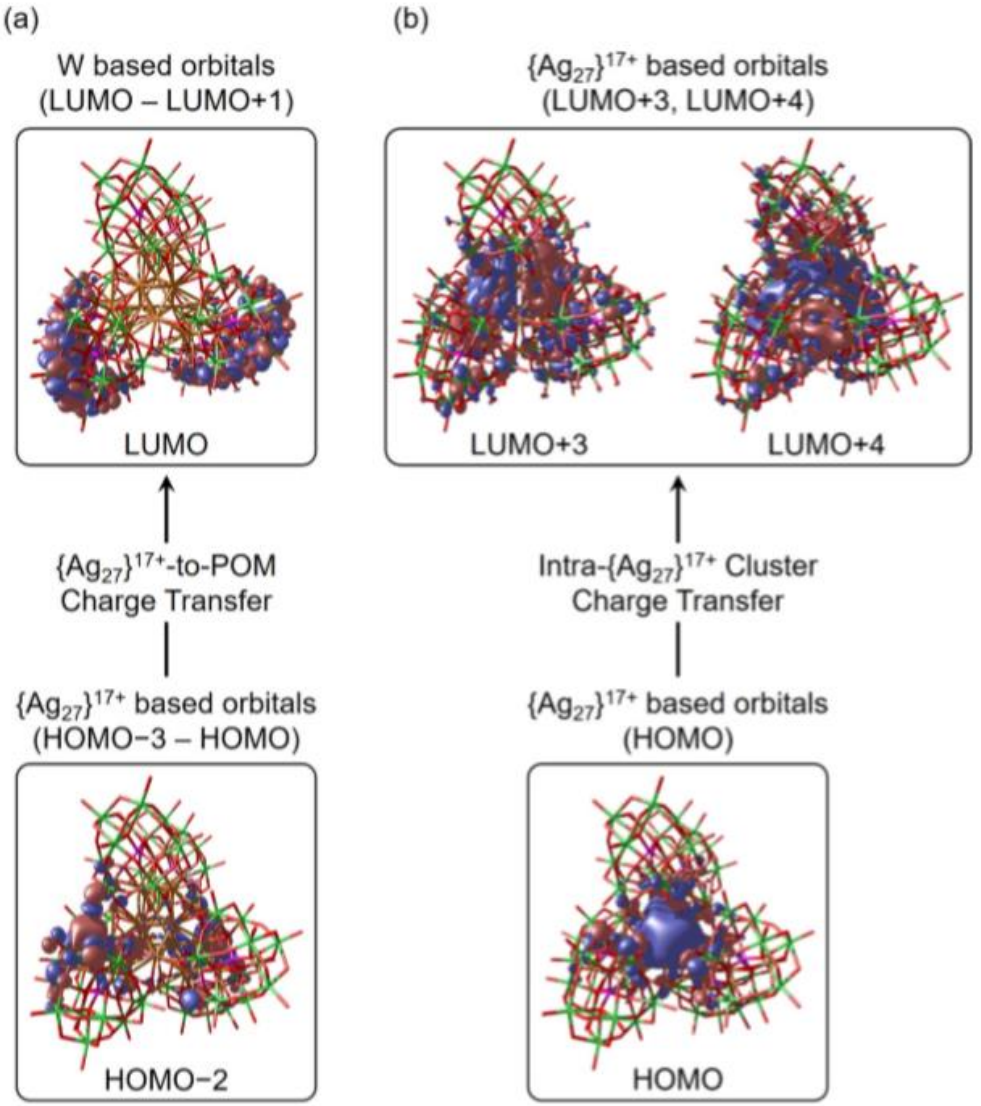


Figure S13. Two types of possible visible-light-induced charge transfer on **Ag27** based on the TD-DFT calculation. (a) $\{Ag_{27}\}^{17+}$ nanocluster core to POM ligands charge transfer and (b) Inter-$\{Ag_{27}\}^{17+}$ core charge transfer.