Cluster Compounds | Very Important Paper

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Atomically Precise Multimetallic Semiconductive Nanoclusters with Optical Limiting Effects

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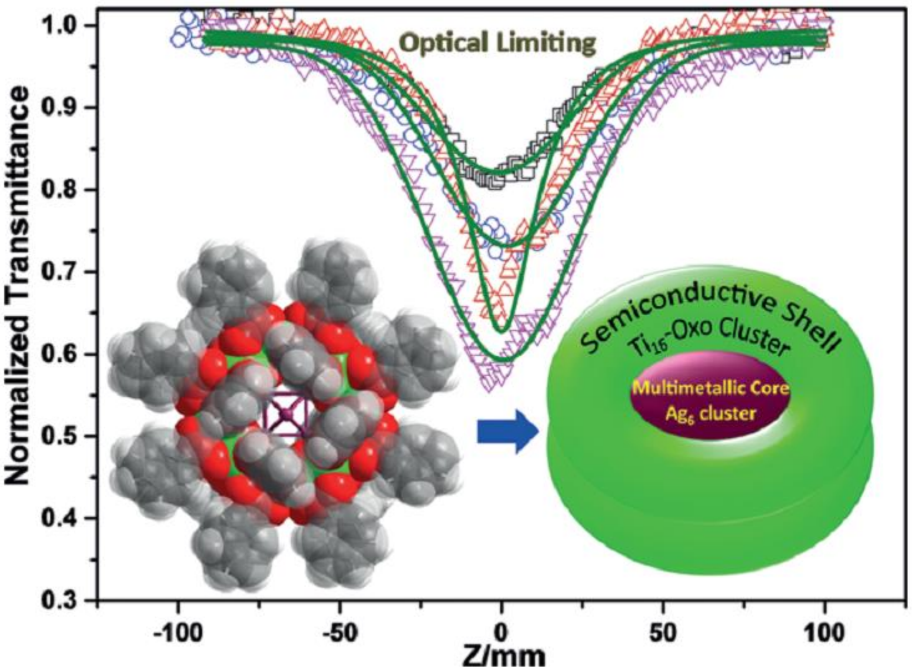


Papri Chakraborty
18.08.2018

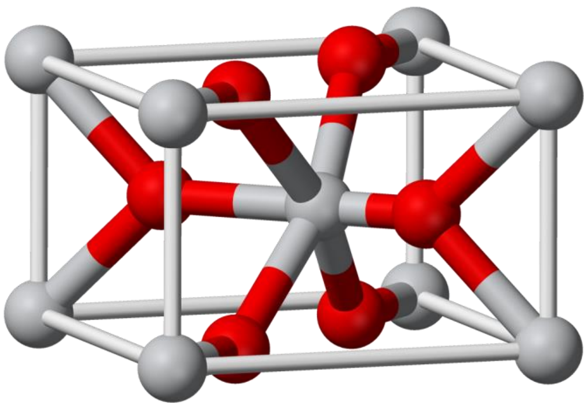
Semiconductors

A **semiconductor** material has an electrical conductivity value falling between that of a conductor – such as copper, gold etc. – and an insulator, such as glass.

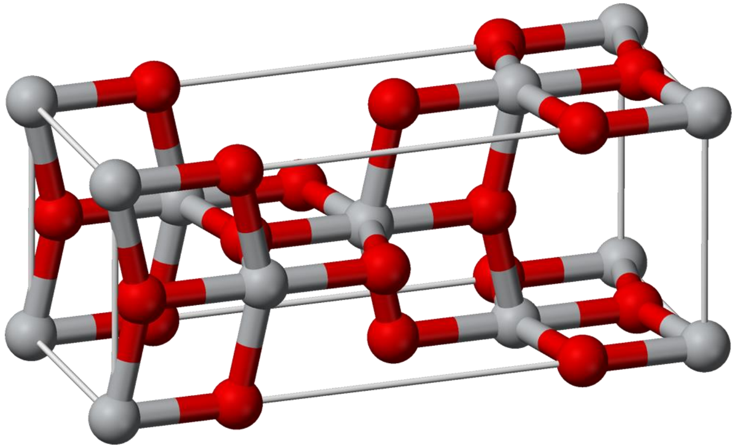
Properties

- Variable conductivity
- Heterojunctions
- Excited electrons
- Light emission
- Thermal energy conversion

Eg. Titanium dioxide is a semiconductor with a wide band gap.



Rutile

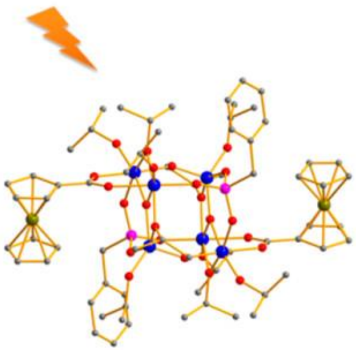


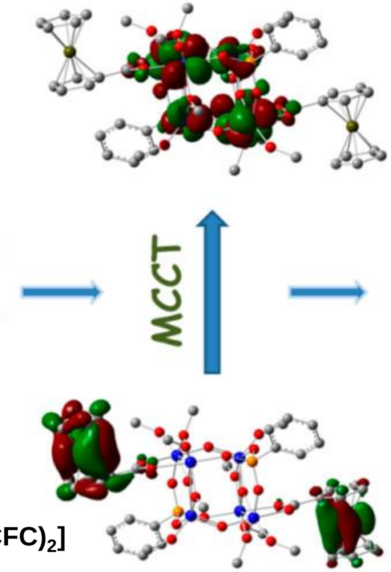
Anatase

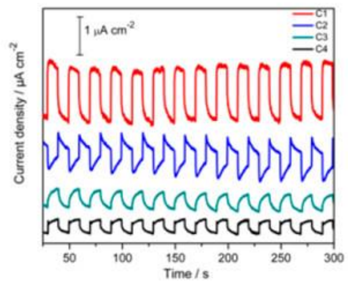
Color codes: gray: Ti, red: O.

Semiconductor Nanoclusters

Titanium-oxo clusters (TOCs) can be regarded as molecular analogues of TiO_2 semiconductors.

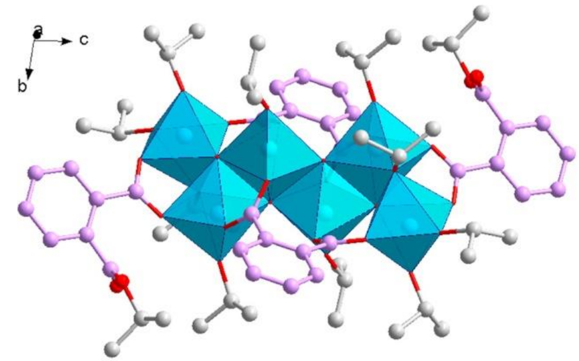




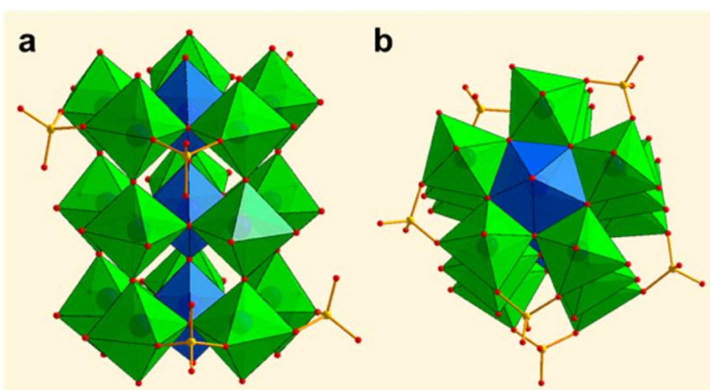


[T i_6(μ_3-O$)_2$(μ_2-O$)_2$(μ_2-O-iPr$)_4$(OiPr$)_6$($O_3PCH_2C_6H_5)_2$(O_2CFC$)_2$]

Inorg. Chem. 2017, 56, 12775-12782

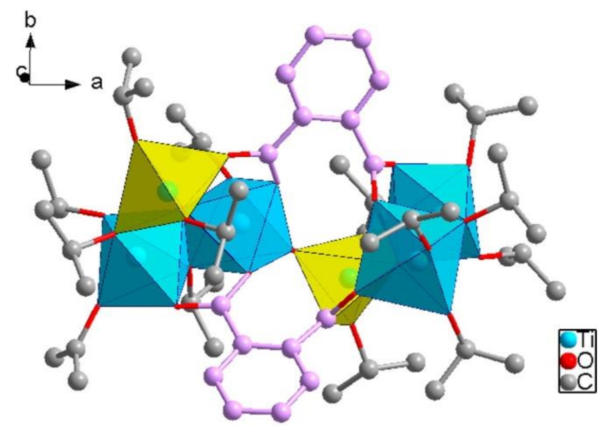


Ti_6O_4(o-BDC$)_2$(o-BDC-iPr$)_2$(OiPr$)_{10}$



(a) Side and (b) top views of $[Ti_{18}O_{27}(OH_2)_{30}(SO_4)_6]^{6+}$

J. Am. Chem. Soc. 2016, 138, 11097−11100

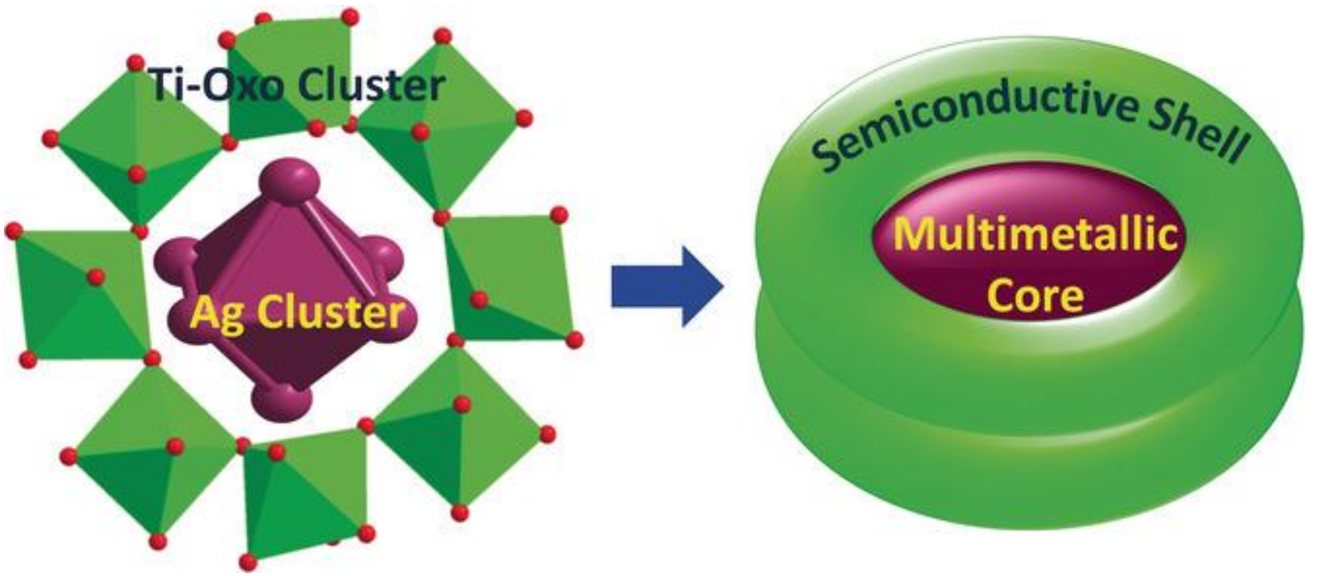


Ti_6O_3(o-BDC$)_2$(OiPr$)_{14}$

Inorg. Chem. 2012, 51, 8982−8988

In this page

- Multinuclear noble-metal clusters stabilized by Ti-oxo clusters.
- $Ag_6@Ti_{16}$-oxo nanoclusters with octahedral Ag_6 core further stabilized by direct Ag-O-Ti coordination interactions.
- Diverse geometric configurations of Ag_6 core inside the Ti_{16}-O shell.
- Influence of structural differences on their optical limiting effects.



Scheme 1. Illustration of the assembly of the multimetallic semiconductive core–shell nanostructure.

Relevance to the group

- Synthesis and crystallization of new noble metal nanoclusters is going on.
- Our group is mainly working on thiol or phosphine protected clusters. There is a need to look for different types of protecting groups.
- Synthesis of cluster-based hybrid materials is a new direction. Some work has been done with fullerenes/cyclodextrins.
- The protecting groups may be chosen by considering the property they can bring into the new composite.
- There is a need to look at the properties or applications of the clusters.

Synthesis

Solvothermal reaction $Ag(CH_3COO)_2$ + $Ti(OiPr)_4$ + benzoic acid

↓ Acetic acid/ ACN

Colorless crystals of **PTC-47**

$[Ag(CH_3CN)]_2[Ag_6Ti_{16}(\mu_3\text{-}O)_{18}(\mu_2\text{-}O)_4(\text{benzoate})_{26}(CH_3CN)_2]$

$Ag(CH_3COO)_2$ + $Ti(OiPr)_4$ + benzoic acid

↓ Formic acid/ ACN

Colorless crystals of **PTC-48**

$Ag_6Ti_{16}(\mu_3\text{-}O)_{16}(\mu_2\text{-}O)_4\text{-}(\text{benzoate})_{24}(CH_3COO)_4(CH_3CN)_2$

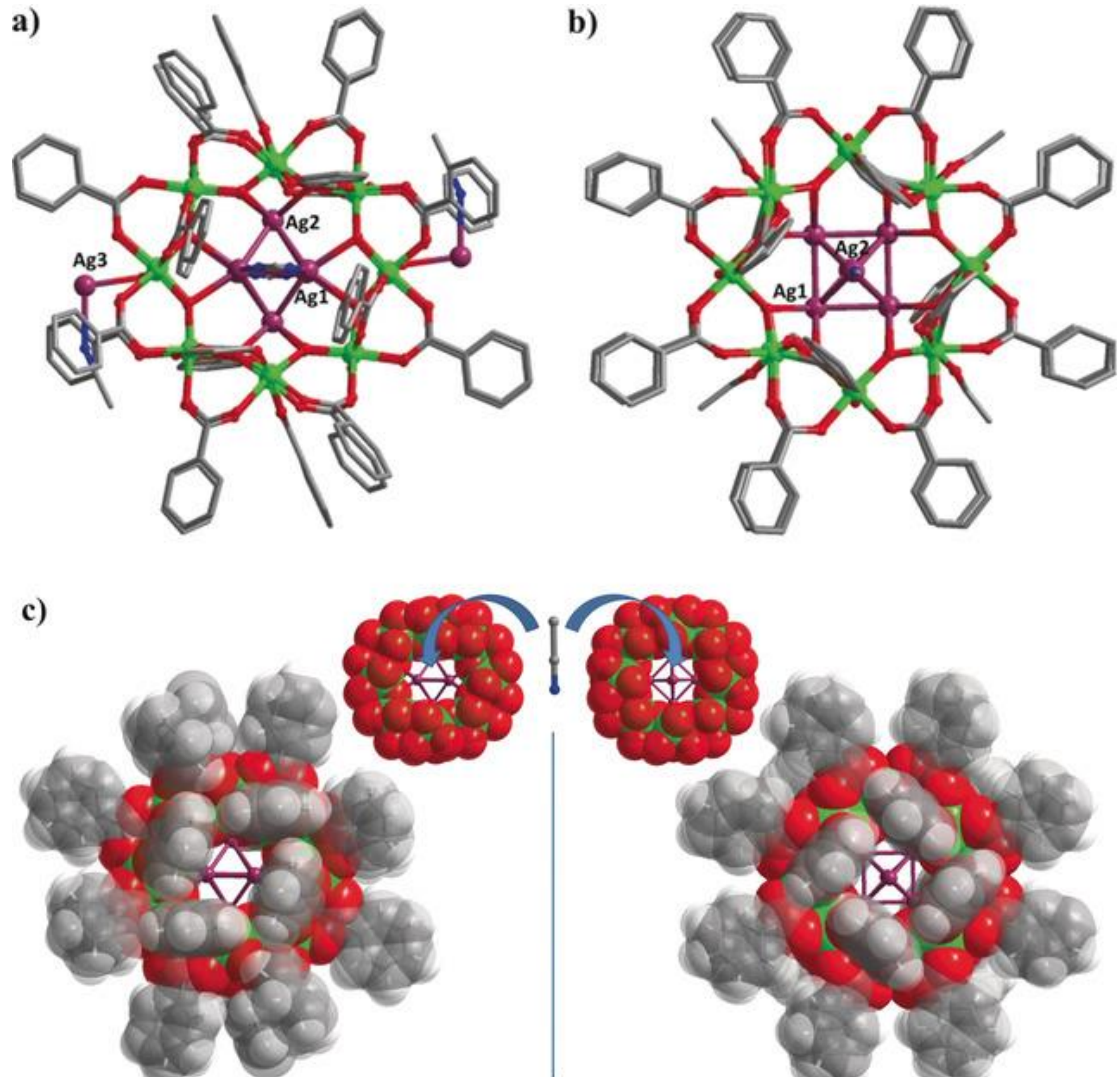


Figure 1. Crystal structures of a) PTC-47 and b) PTC-48. c) Illustration of the triple $Ag_6@Ti_{16}@(benzoate)_{26}$ core–shell structures of PTC-47 (left) and PTC-48 (right), highlighting the capture of acetonitrile molecule through the window of $Ag_6@Ti_{16}$-oxo cluster. C, H, O, and Ti atoms are presented with a space-filing model. Green Ti; violet Ag; red O; blue N; gray C.

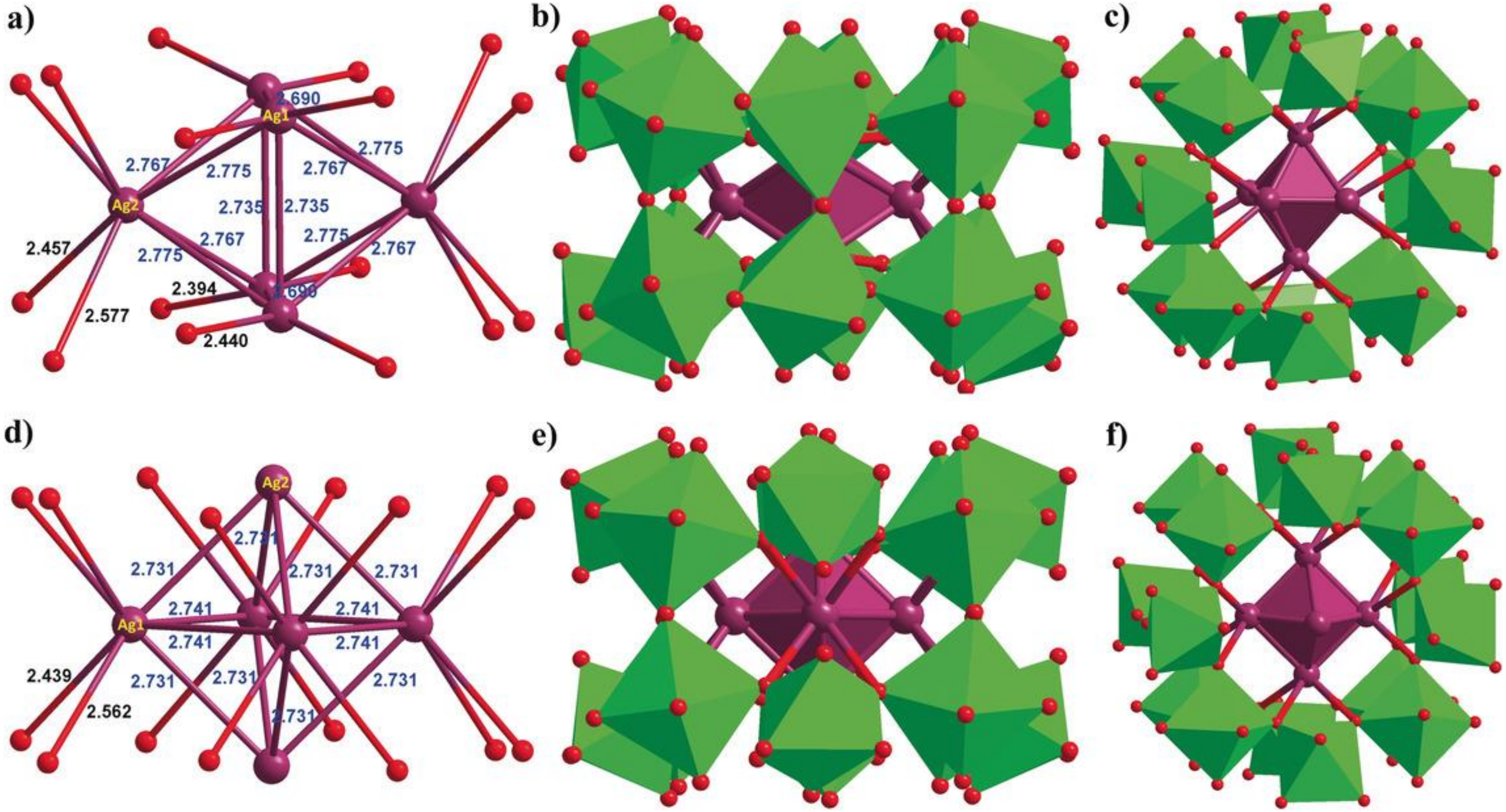


Figure 2. a) Structural details and coordination environments of the Ag_6 core in PTC-47, highlighting the Ag-Ag and Ag-O distances [Å]. b,c) Side and top-view of the encapsulation of the Ag_6 core by the Ti_{16}-oxo cluster in PTC-47. d) Structural details and coordination environments of the Ag_6 core in PTC-48. e,f) Side and top-view of the encapsulation of Ag_6 core by the Ti_{16}-oxo cluster in PTC-48. C, H, and N atoms have been omitted for clarity. Green polyhedra TiO_6; violet polyhedra Ag_6.

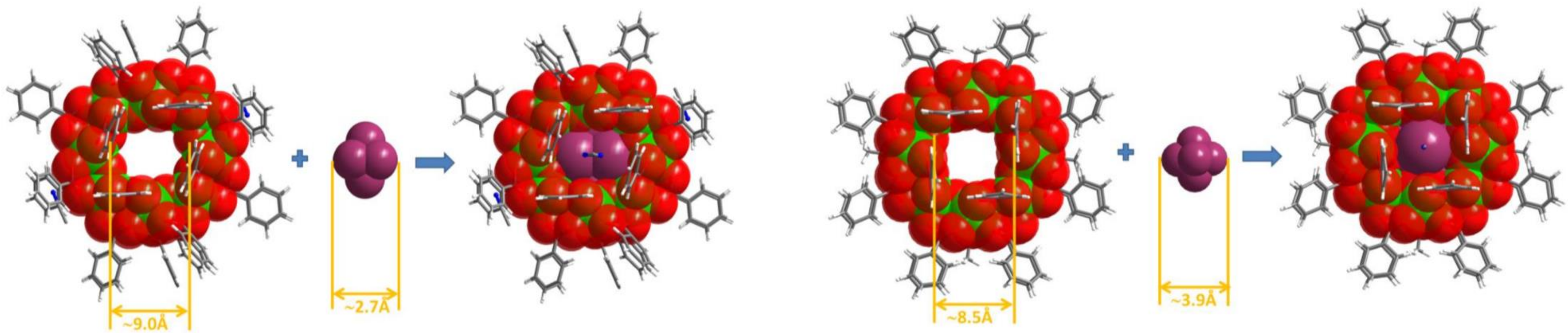


Illustration of the encapsulation of Ag_6 core by the Ti_{16}-oxo shell in **PTC-47 (left) and PTC-48 (right)**. The diameter of the Ti-O cavity is defined by the Ti-Ti distance.

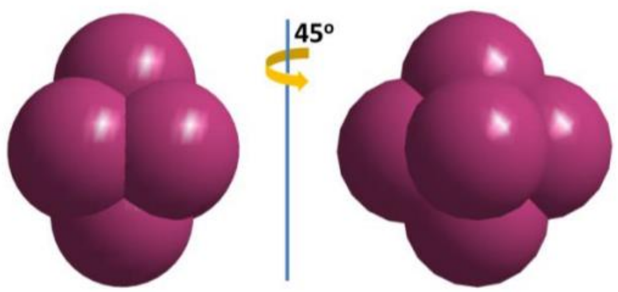
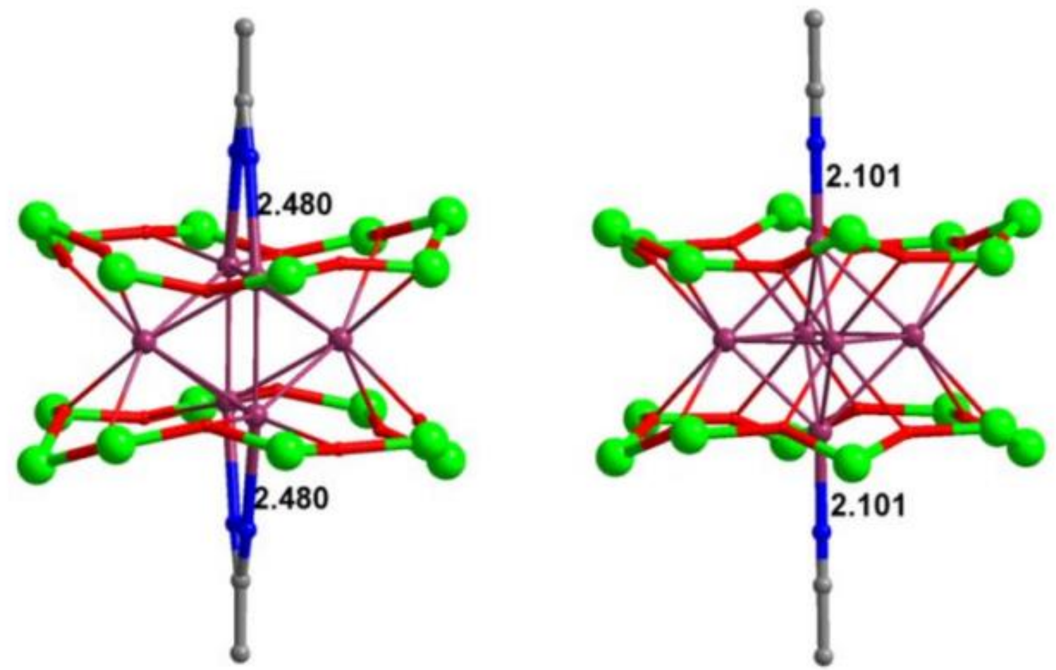


Illustration of geometric relationship between the configurations of Ag_6 core in **PTC-47** (left) and **PTC-48** (right).



The coordination bonding of CH_3CN with the Ag_6 core in **PTC-47** (left) and **PTC-48** (right). In **PTC-47**, the N atom of CH_3CN is disorderly coordinated to two adjacent Ag atoms.

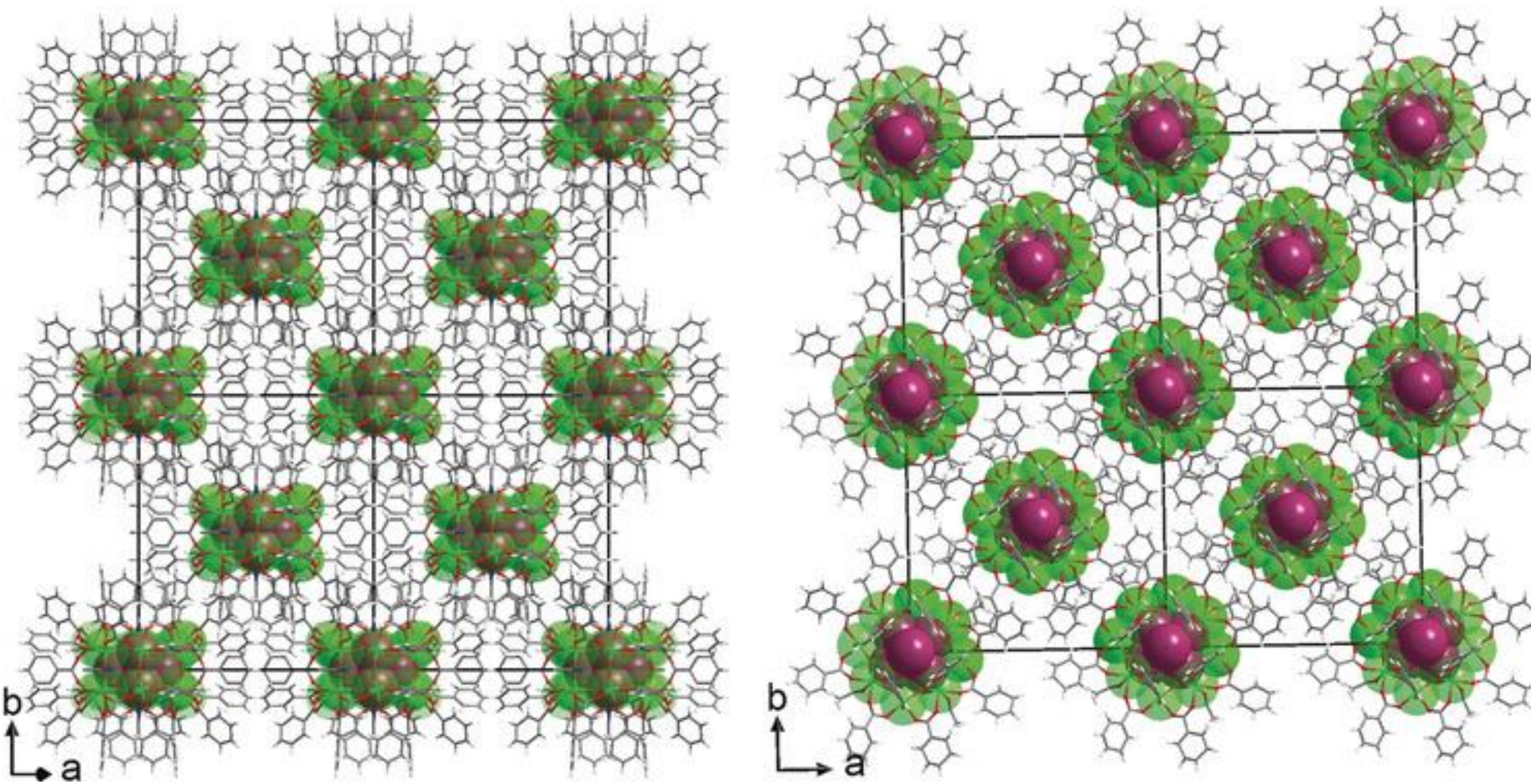
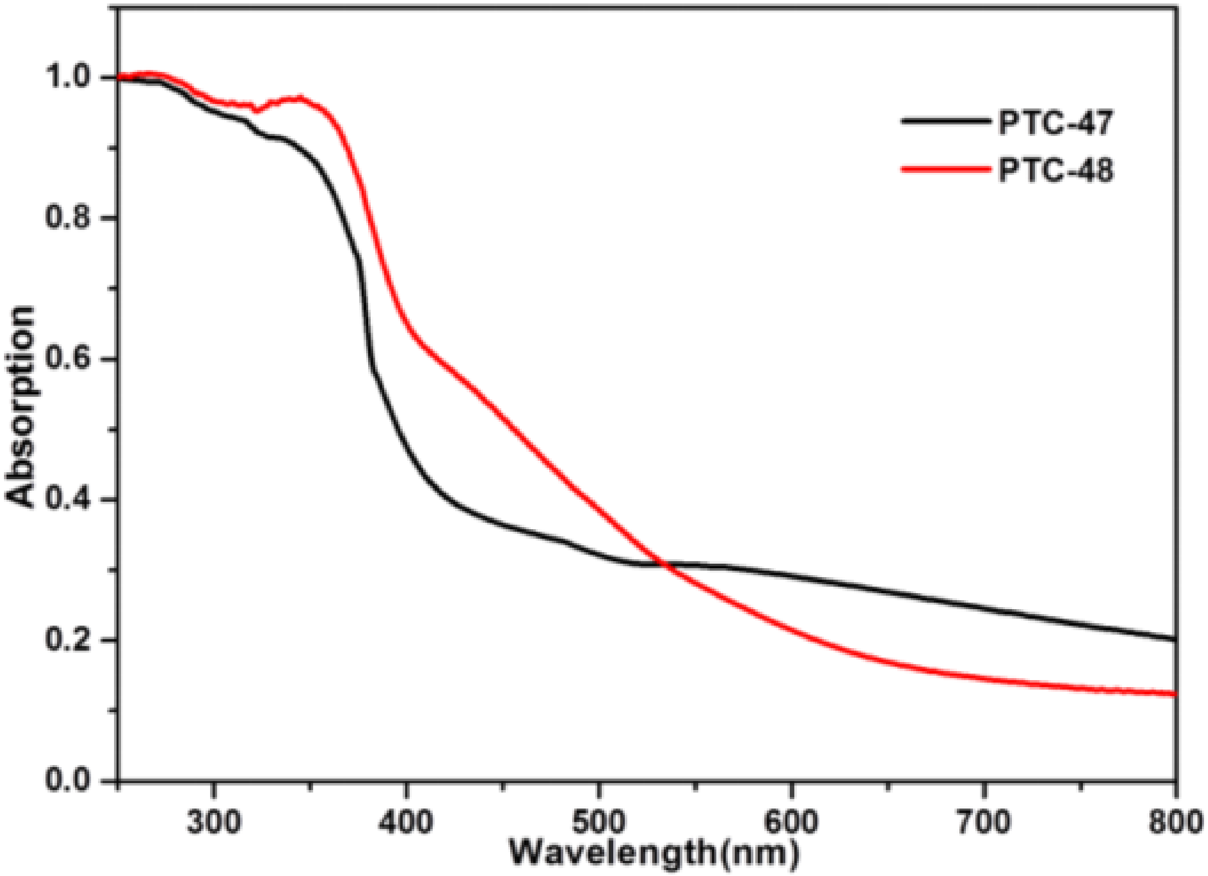


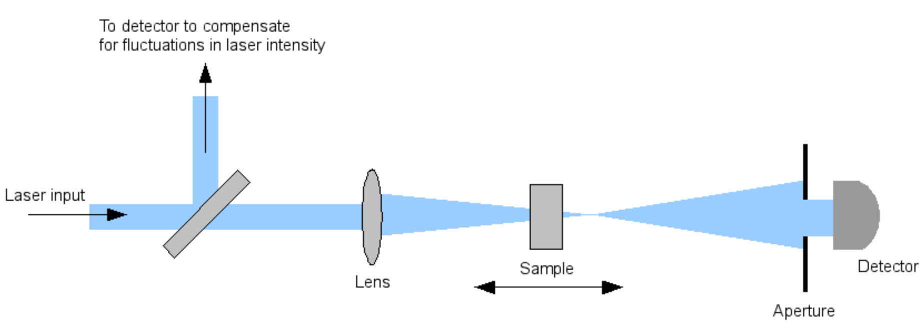
Figure 3. The packing view of PTC-47 (left) and PTC-48 (right) along c-axis.



The solid-state ultraviolet–visible absorption spectra of **PTC-47** and **PTC-48**.

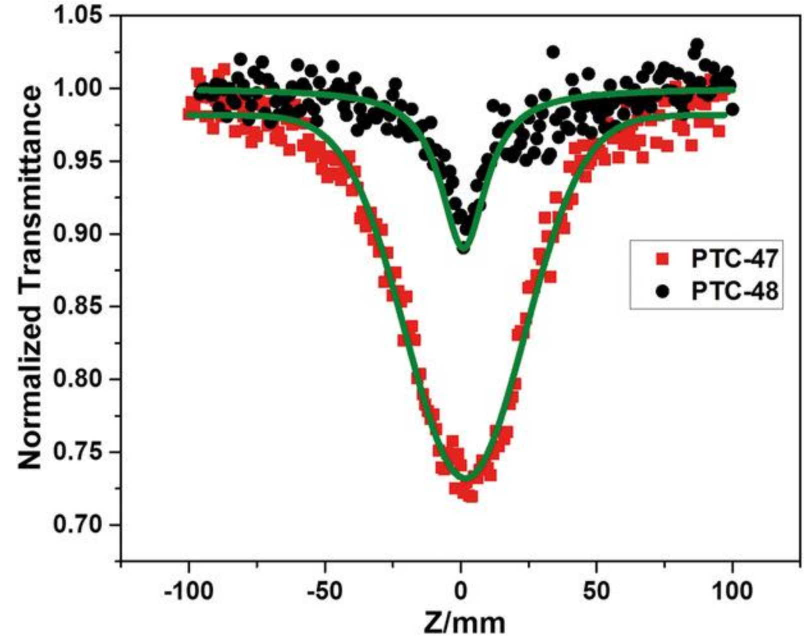
An **optical limiter** is a device designed to keep the power, irradiance, energy or fluence transmitted by an **optical** system below some specified maximum value regardless of the magnitude of the input.

Optical limiters that could be used to protect photosensitive objects (which could be human eyes as well as sensitive optical equipment) from intense light generated by lasers.



Z-scan technique

λ = 532 nm laser fluence



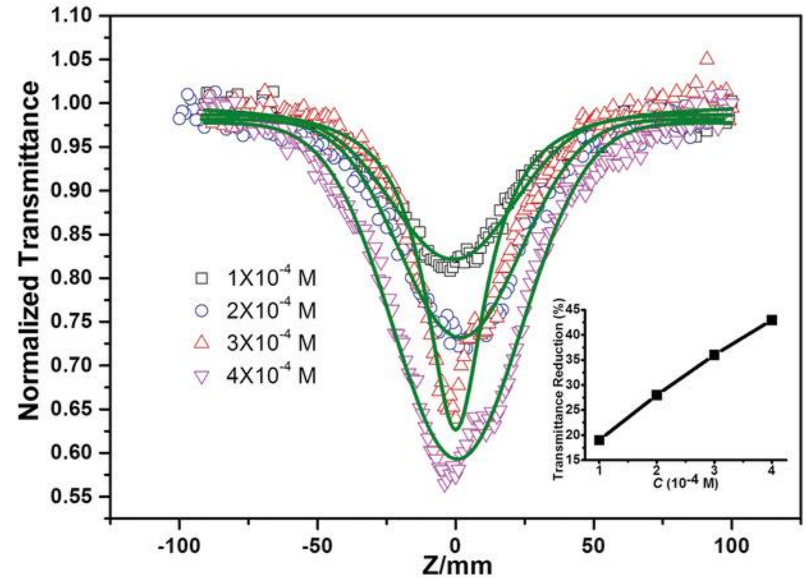


Figure 4. The open aperture Z-scan (points) and theoretical fit (solid lines) curves of PTC-47 and PTC-48 at 532 nm (upper), and different concentrations of PTC-47 (lower). Inset: transmittance reduction versus concentration plot.

Conclusion

- This is for the first time that a noble-metal cluster has been entirely surrounded by a metal-oxo cluster.

- An acidic/redox control assembly strategy has been developed to construct two $Ag_6@Ti_{16}$-oxo nanoclusters with direct Ag-O-Ti bonds and core–shell structures.

- Although having the same Ti_{16}-oxo shell, the relative configurations of the Ag_6 core inside the cavity differ by about 45° rotation. Attributed to its structure, PTC-47 displays better optical limiting activity towards 532 nm laser light than PTC-48.

- The transmittance reduction effect of PTC-47 exhibits nearly linear dependence on its concentration, making it a potential candidate for the fabrication of future optical limiting devices.

Thank you