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Article

Tetrahedral Geometry Induction of Stable Ag-Ti Nanoclusters by Flexible Trifurcate TiL3 Metalloligand

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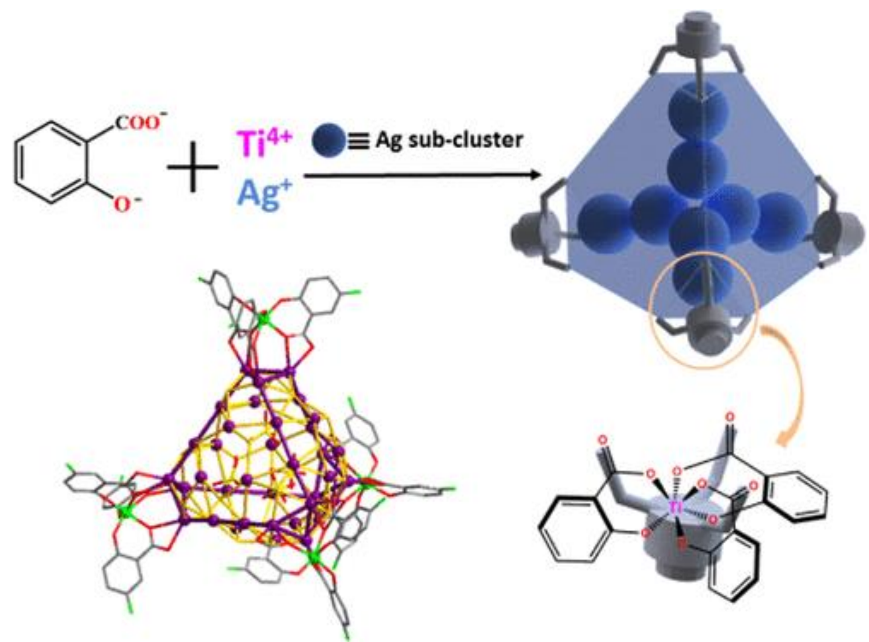

Publication Date: June 24, 2020

Paper presentation
Jayoti Roy
11-07-2020

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: *J. Am. Chem. Soc.* 2019, 141, 7107–7114

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Pd-Mediated Synthesis of Ag_{33} Chiral Nanocluster with Core–Shell Structure in T Point Group

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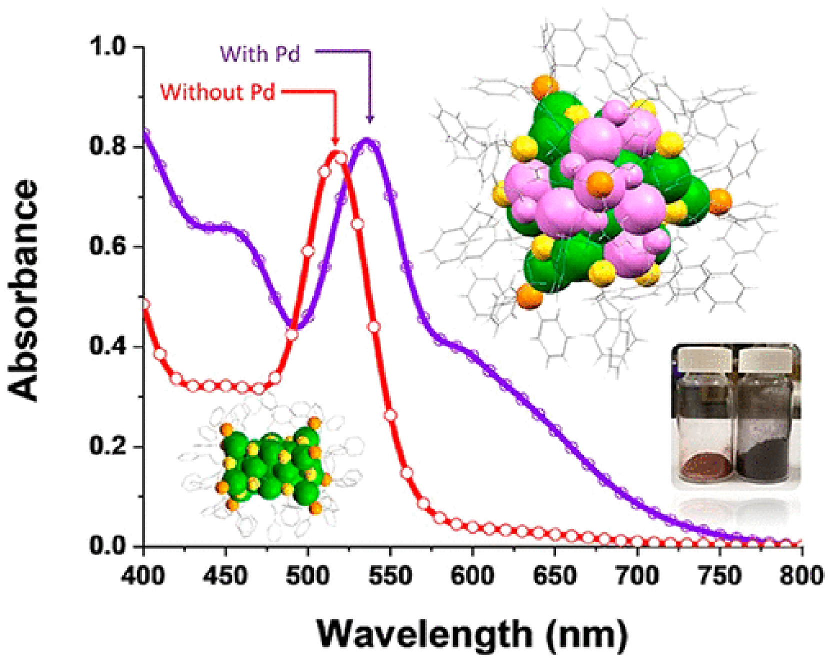
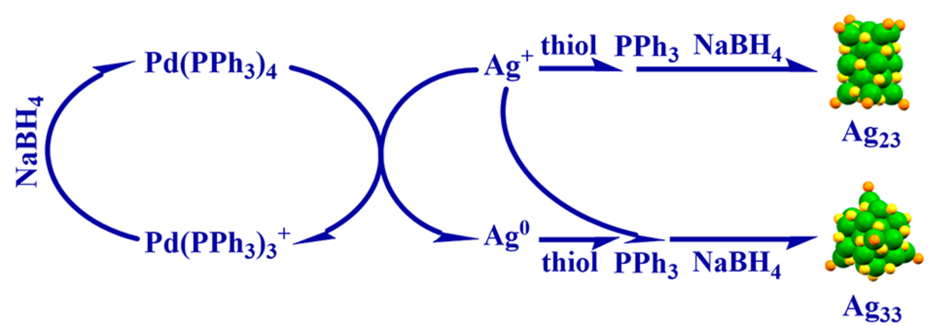


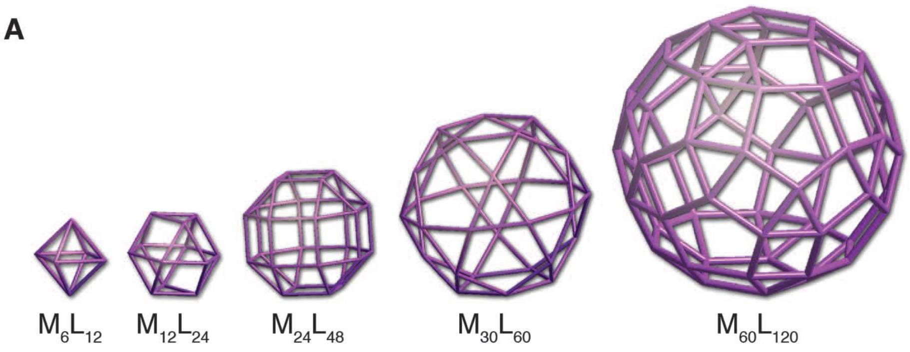


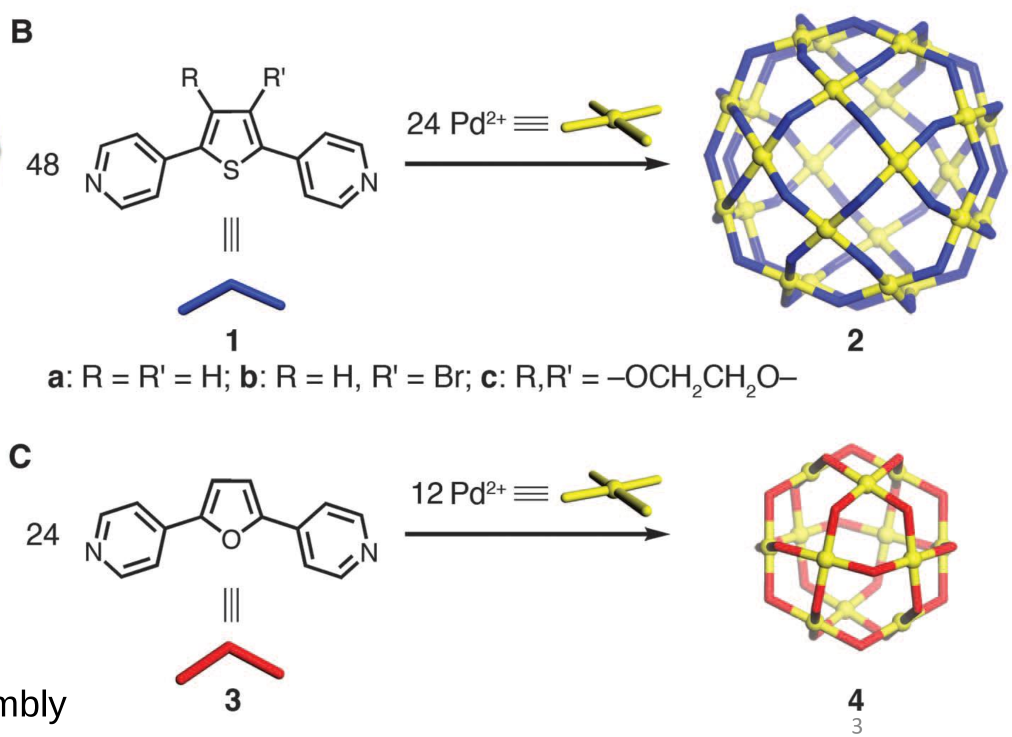
Pd Cycle in the Synthesis of the Ag_{33} Nanocluster

Self-Assembled $M_{24}L_{48}$ Polyhedra and Their Sharp Structural Switch upon Subtle Ligand Variation

Qing-Fu Sun,[1] Junji Iwasa,[1] Daichi Ogawa,[1] Yoshitaka Ishido,[1] Sota Sato,[1] Tomoji Ozeki,[2] Yoshihisa Sei,[3] Kentaro Yamaguchi,[3] Makoto Fujita[1*]

Qing-Fu Sun *et al.*,*Science* **328**, 1144 (2010)





(A) The family ofM_nL_{2n} polyhedra where metals (M) and bridging ligands (L) are mapped onto the vertices and edges, respectively, of the polyhedra.
(B) Self-assembly of $M_{24}L_{48}$ spheres 2. (C) Self-assembly of $M_{12}L_{24}$ sphere 4.

Motivation

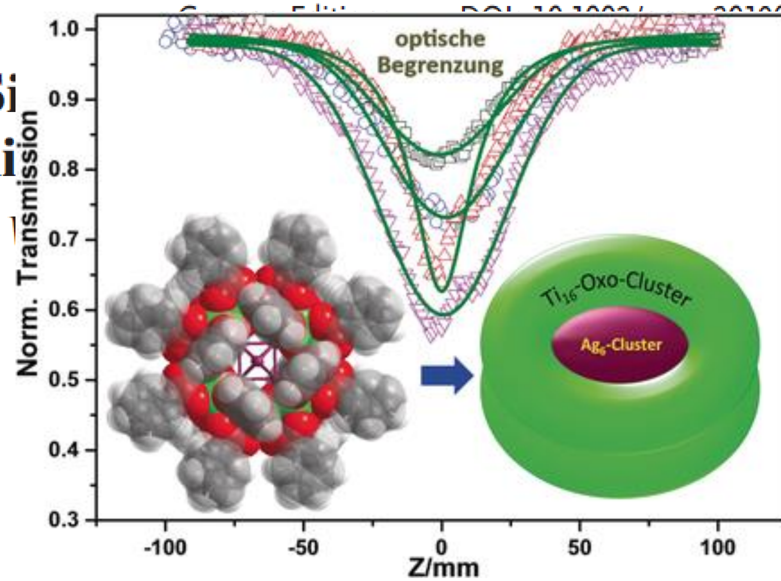
GDCh **Communications** Angewandte International Edition Chemie

Single-Atom Catalysts

International Edition: DOI: 10.1002/anie.201904680

$Ag_{10}Ti_{28}$-Oxo Cluster Containing Si
Structure and Synergistic Electroni

Shuai Chen[+], Zhe-Ning Chen[+], Wei-Hui Fang,



Angew. Chem. Int. Ed. 2019, 58, 10932 –10935

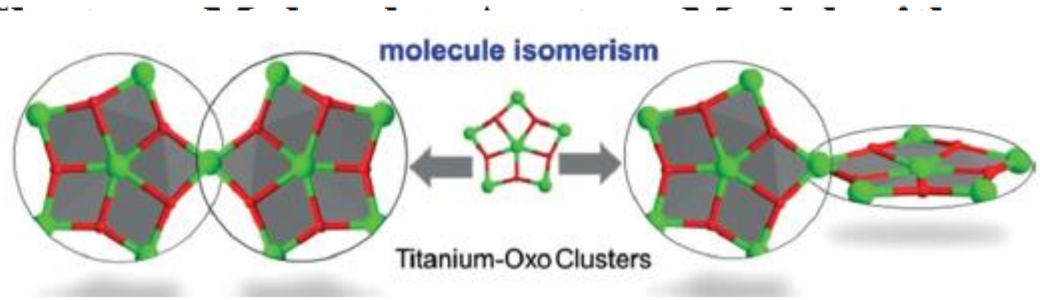
GDCh **Communications** Angewandte International Edition Chemie

Cluster Compounds

International Edition: DOI: 10.1002/anie.201809961
German Edition: DOI: 10.1002/ange.201809961

Isomerism in Titanium-Oxo
Atomic Structure and Impro

Xi Fan, Junhui Wang, Kaifeng Wu, L*



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

Why this paper?

- Structure of multi-metallic poly-oxo titanium clusters.
- The use of structure-directing additives such as highly directional nature of metalloligands.
- Mass spectrometry based studies in PTCs.

Introduction

- The use of self-assembly of building blocks with directional features i.e. Metalloligand has resulted in assemblies that exhibit polyhedral geometry, including Archimedean and Platonic solids.

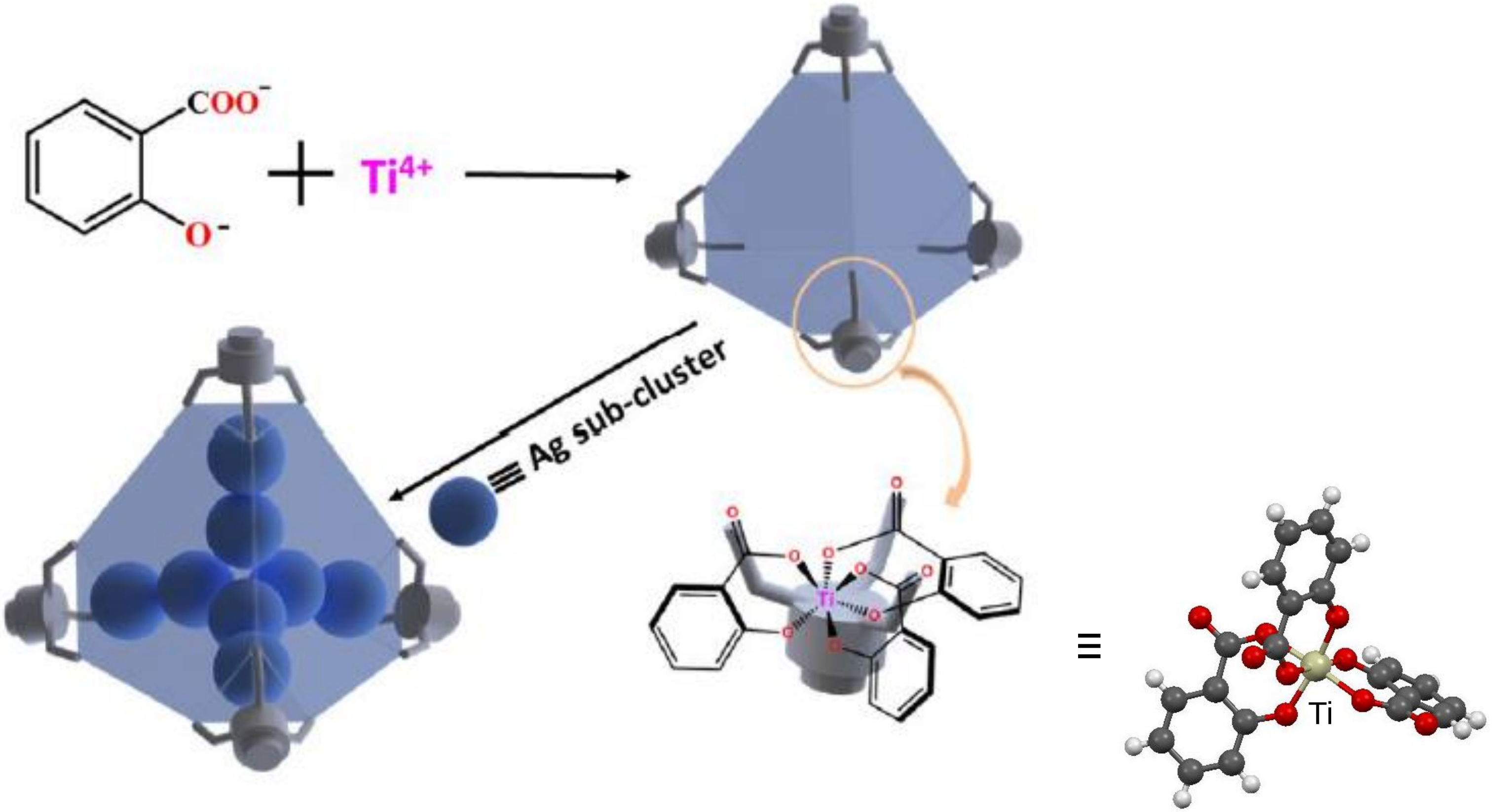
- The use of structure-directing additives such as the highly directional nature of metalloligands can play a significant role in the design of high-performance nanoclusters.

- Titanium-based metalloligands with trifurcate TiL_3 moieties (L= salicylate or 5-fluoro salicylate), could be envisaged to be well-suited for the controlled formation and stabilization of metallic nanoclusters owing to their conformational flexibility.

- In this work, a family of five novel heterometallic Ag-Ti clusters with tetrahedral geometry were assembled via the flexible trifurcate TiL_3 metalloligand : $Ti_4Ag_8(SA)_{12}$•MeOH (PTC-85), $Ti_4Ag_{12}(S^iPr)_6(SA)_{10}(HSA)_2$•$H_2O$ (PTC-86), $Ti_4Ag_{22}(S^iPr)_{12}(SA)_{12}SO_4$ (PTC-87), $Ti_4Ag_{42}(S)_4(S^iPr)_{18}(SA)_{12}(SO_4)_4$•8MeOH (PTC-88) and $Ti_4Ag_{36}(S^iPr)_{24}(SA\text{-}F)_{12}(SO_4)_2$ (PTC-89).

- These nanoclusters demonstrate ultra-stability in air for several months and in water over 3 days due to the encapsulation effects of the trifurcate TiL_3 metalloligands.

Synthesis of nanoclusters



Ag-precursors : AgOAc, $[Ag(^{i}PrS)]_n$
Ligands : Salicylic acid, 5-fluorosalicylic acid

Scheme 1. Illustration of tetrahedral geometry induction of Ag nanoclusters by the trifurcate TiL_3 metalloligands.

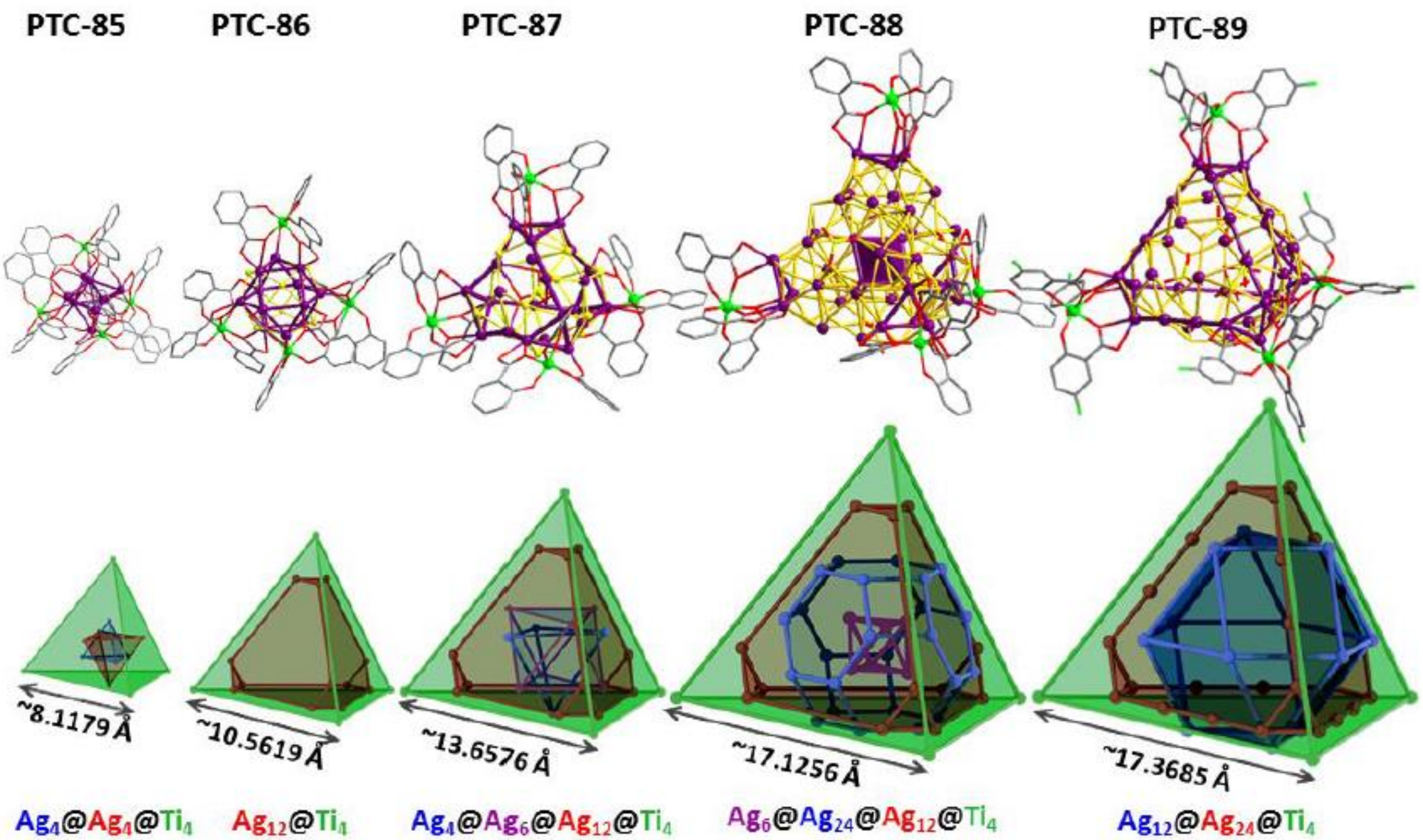


Figure 1. Molecular structures (top) and illustrations of the cluster assembly (bottom) of **PTC-85**, **PTC-86**, **PTC-87**, **PTC-88** and **PTC-89**. S^iPr^- and H atoms have been omitted for clarity. Green Ti; violet Ag; red O; yellow S; gray C.

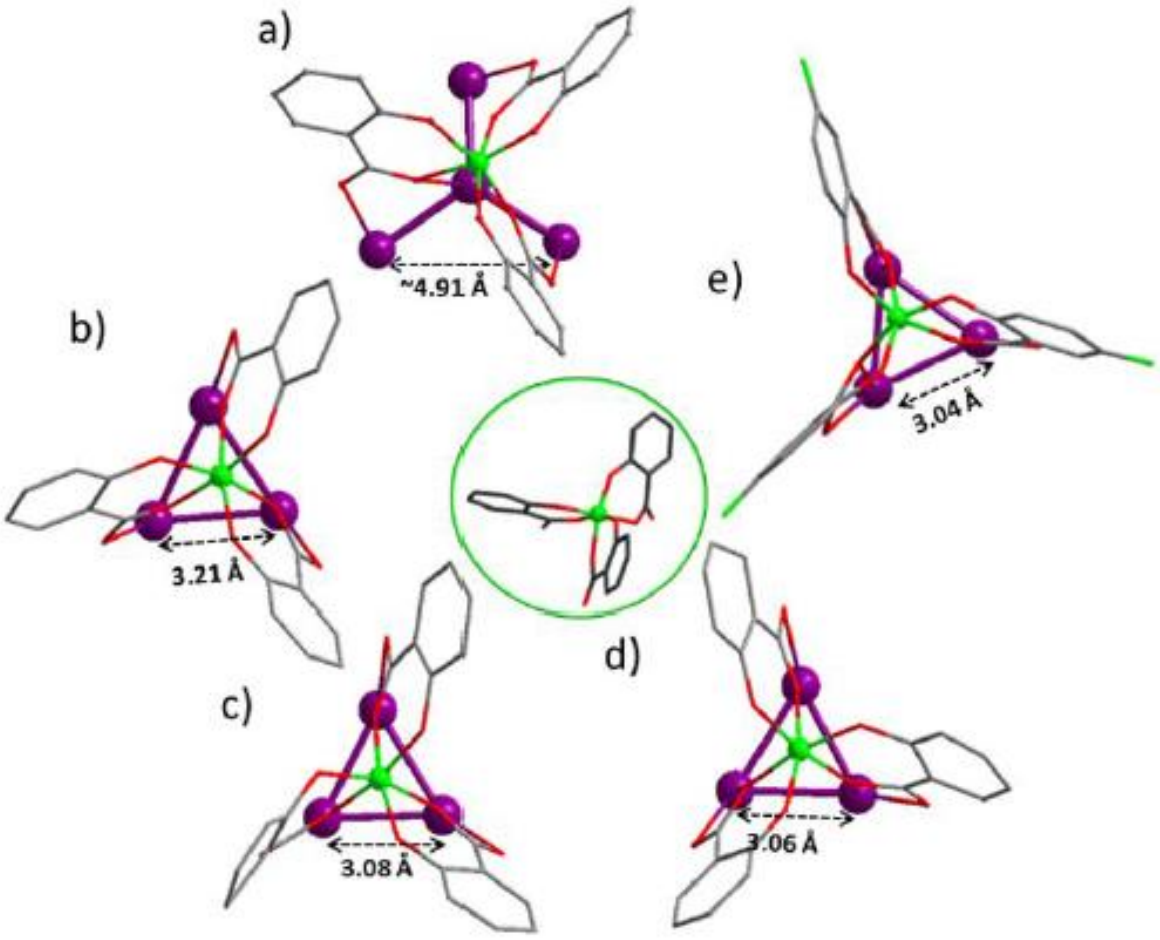


Figure 2. The structural parameters of TiL3 metalloligands and corresponding {Ag3} vertex units in **PTC-85** (a), **PTC-86** (b), **PTC-87** (c), **PTC-88** (d) and **PTC-89** (e), indicating the flexibility of the TiL_3 metalloligand.

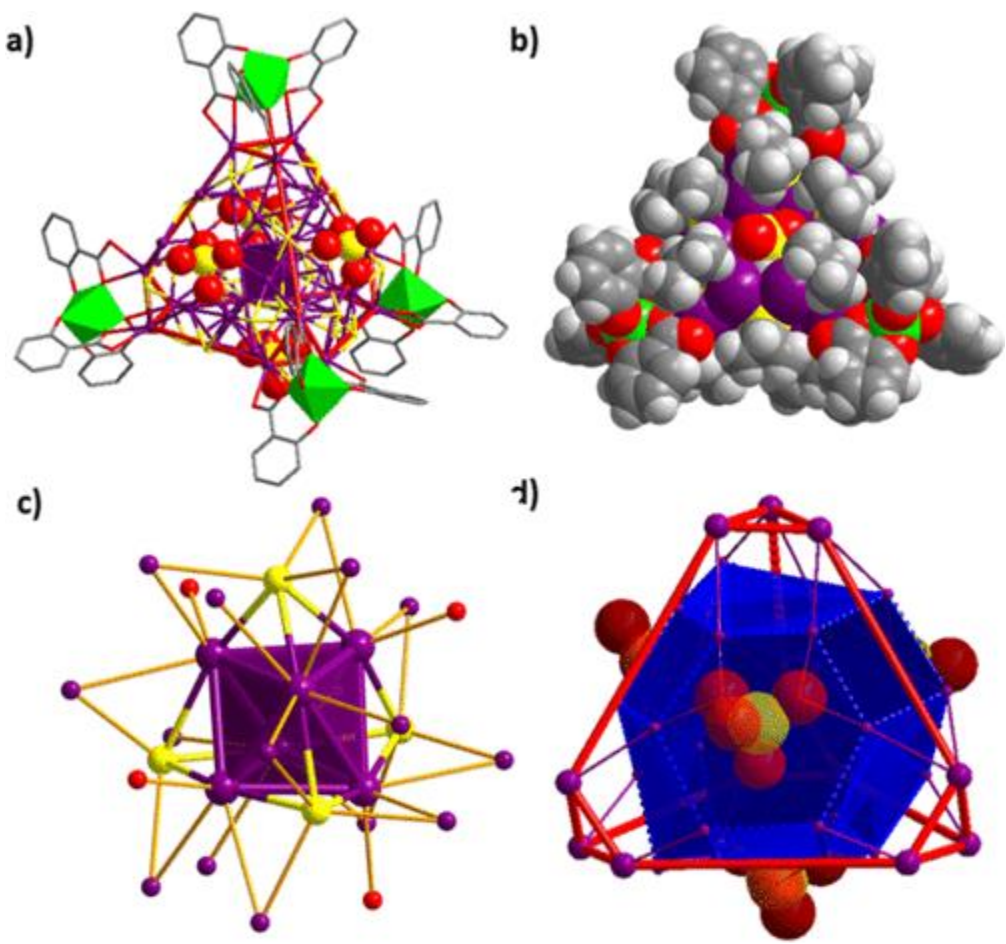


Figure 3. (a) Structure of **PTC-88** with the innermost $\{Ag_6\}$ platonic solid shown in polyhedron mode (the SiPr− groups are omitted); (b) Space-filling representation of **PTC-88**; (c) Coordination environment of the {Ag6} core in **PTC-88**; (d) Chemical bonds between the $\{Ag_{12}\}$ truncated tetrahedron and the distorted $\{Ag_{24}\}$ truncated octahedron in **PTC-88**, highlighting the four SO_4^{2-} ligands. S and O atoms are represented with the space-filling model. Green Ti; violet Ag; red O; yellow S; gray C.

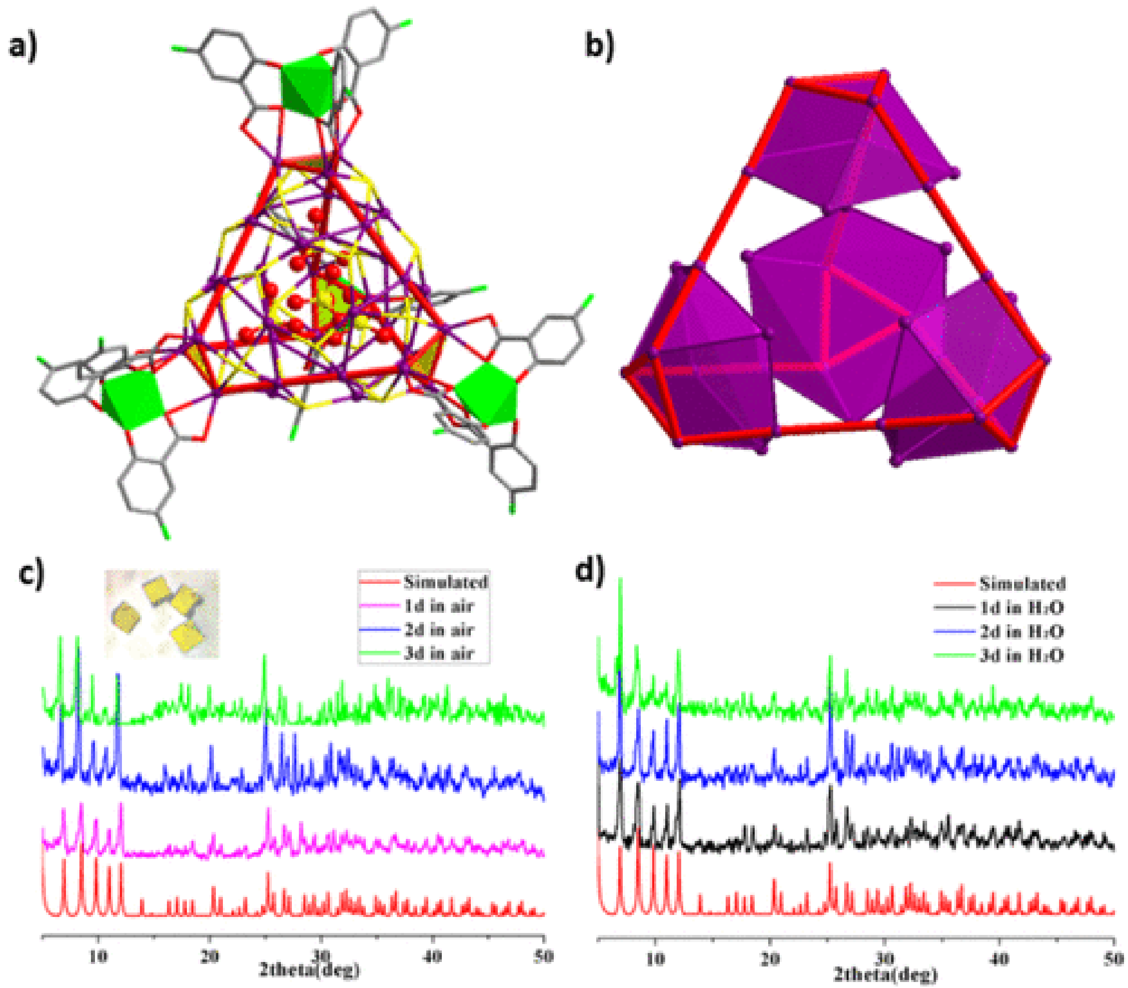


Figure 4. (a) **PTC-89** consists of an outermost tetrahedra formed from 4 Ti atoms, $\{Ag_{24}\}$ and $\{Ag_{12}\}$ Archimedean solids (the iPrS−groups are omitted); (b) The structure of $\{Ag_{36}\}$ polyhedron in **PTC-89**; Stability tests of **PTC-89** in (c) air and (d) water.

Results and discussion

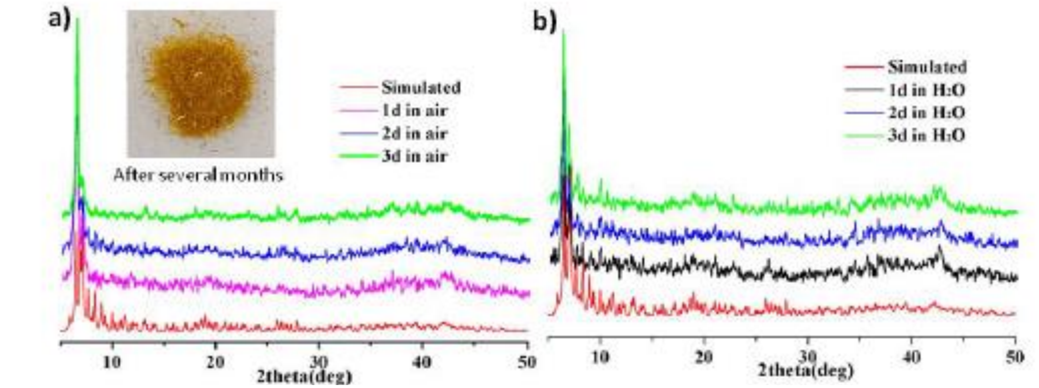


Figure S15. PXRD patterns for **PTC-85** in (a) air and (b) water. Inset: compound **PTC-85** in the air for several months.

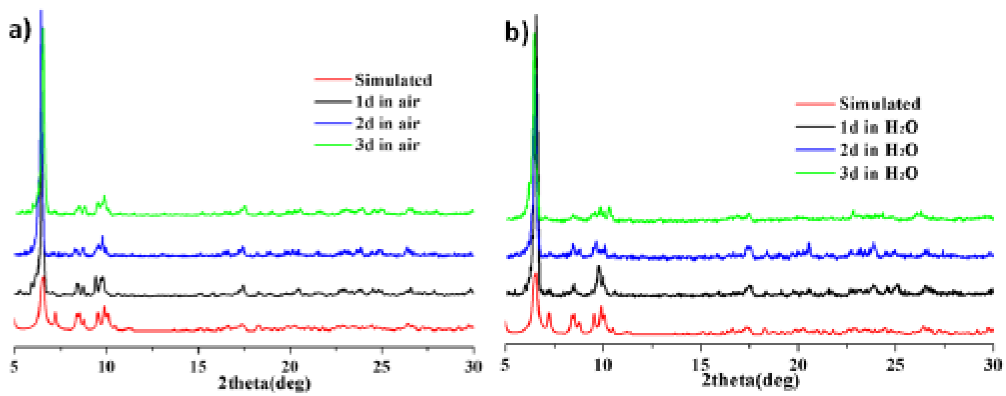


Figure S16. PXRD patterns for **PTC-86** in (a) air and (b) water.

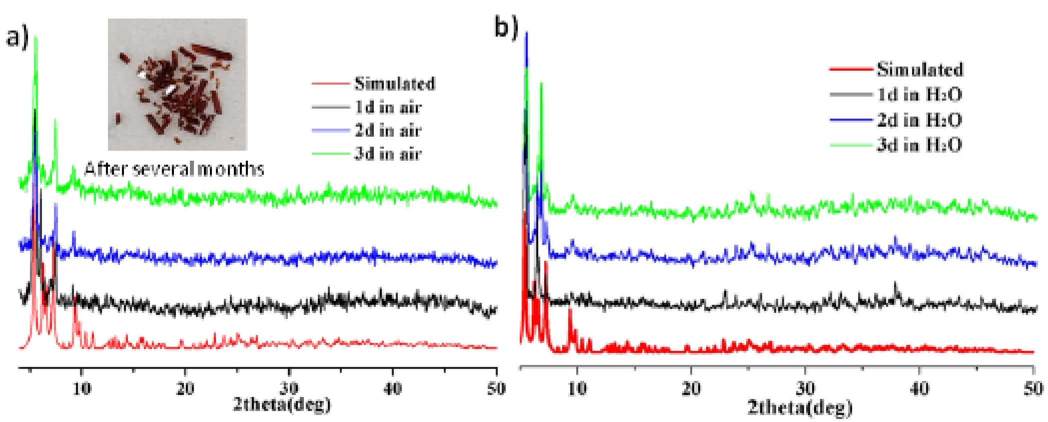


Figure S17. PXRD patterns for **PTC-87** in (a) air and (b) water. Inset: compound **PTC-87** in the air for several months.

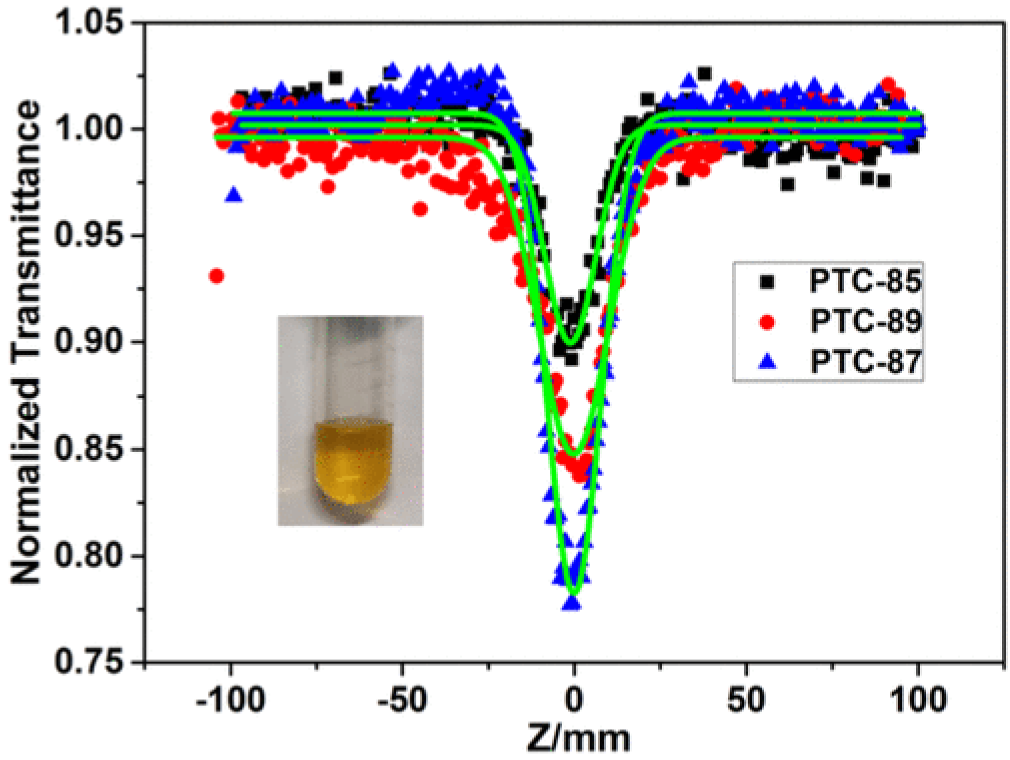
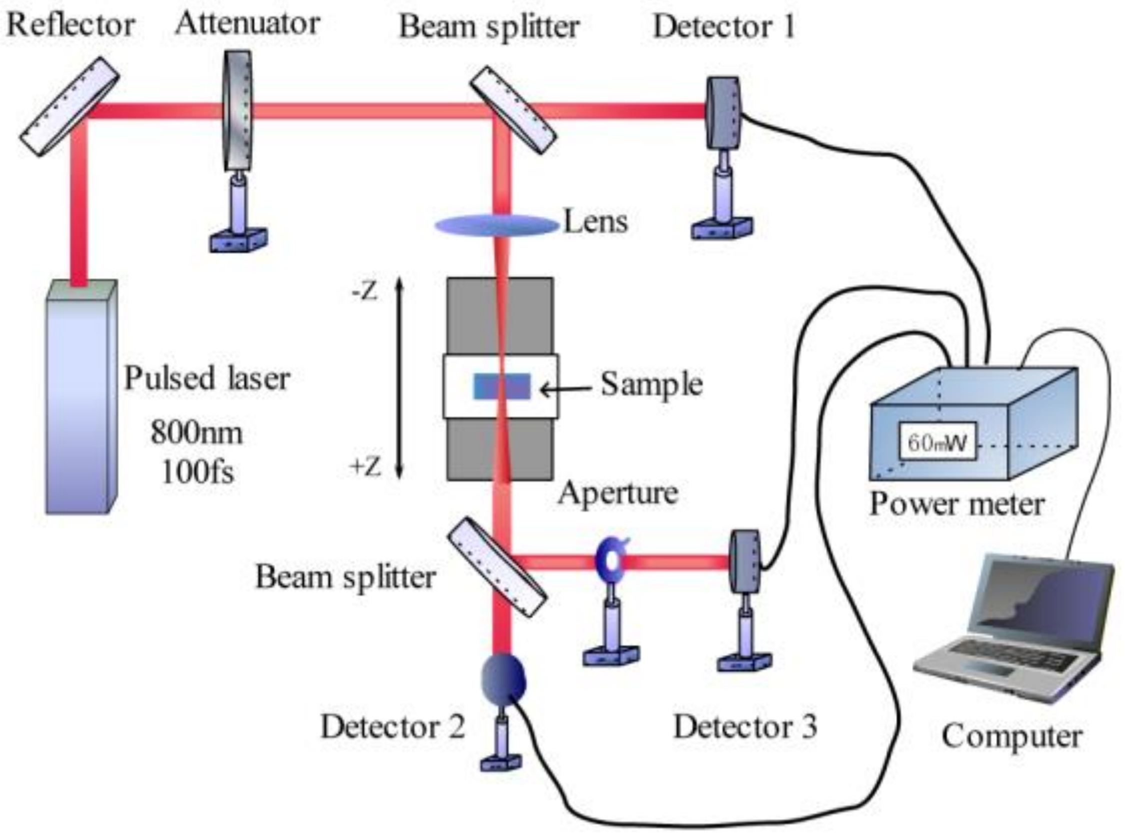


Figure 5. The open aperture Z-scan (points) and theoretical fit (solid lines) curves of **PTC-85**, **PTC-87** and **PTC-89** at 532 nm with a laser power of 120 μJ (inset: solution of **PTC-89** in DMF).

Schematic representation of Z-scan technique



Xin Zheng et al., Vol. 23, No. 12 | DOI:10.1364/OE.23.015616 | OPTICS EXPRESS 15616

Luminescence spectra

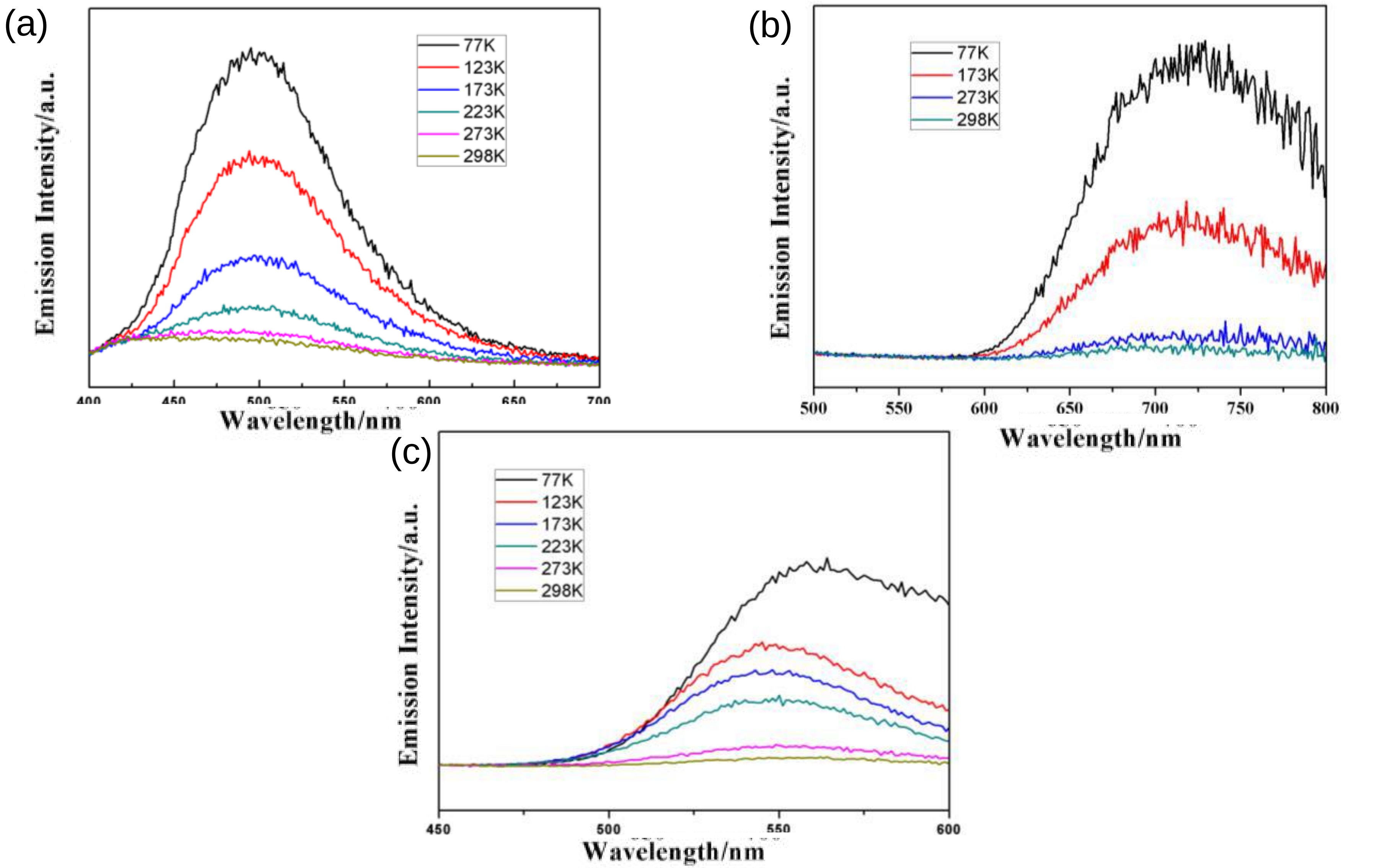


Figure S18-20. Luminescence spectra of (a) **PTC-85 (b) PTC-86 (C) PTC- 89** as a function of temperature from 77 to 298 K in the solid state for excitation at 340 nm 365 nm and 350 nm respectively.

Conclusion

- The flexible trifurcate TiL_3 metalloligand reported herein can serve as a structure-directing and functionalizing ligand to form a family of interesting tetrahedral nanoclusters with complicated combinations of Archimedian and Platonic solids.

- The structures were determined by single-crystal X-ray diffraction analysis to give core compositions of $Ag_4@Ag_4@Ti_4$, $Ag_{12}@Ti_4$, $Ag_4@Ag_6@Ag_{12}@Ti_4$, $Ag_6@Ag_{24}@Ag_{12}@Ti_4$ and $Ag_{12}@Ag_{24}@Ti_4$, which all presented tetrahedral geometry.

- The protective effect of the TiL_3 metalloligand makes the obtained silver nanoclusters highly stable in air and water.

- Optical limiting properties and photoluminescent behaviours of these complexes were studied,which displayed noteworthy performance.