

All-Carboxylate-Protected Superatomic Silver Nanocluster with an Unprecedented Rhombohedral Ag₈ Core

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- The synthesis and structure of the superatomic silver [Ag₈(pfga)₆]⁶⁻ nanocluster was reported
- The [Ag₈(pfga)₆]⁶⁻ cluster has a rhombohedral Ag₈⁶⁺ core, each of its faces protected by one dianionic perfluoroglutarate (pfga) ligand
- DFT confirms the stability of the two-electron cluster due to the shell closing of the superatomic orbital in the (1S)² configuration and explains the optical absorption of the cluster in the visible region as the transition from 1S to 1P orbital
- The [Ag₈(pfga)₆]⁶⁻ cluster emits bright green-yellow light in THF solution and bright orange light in the solid state -strong luminophore in both solution and the solid state at room temperature

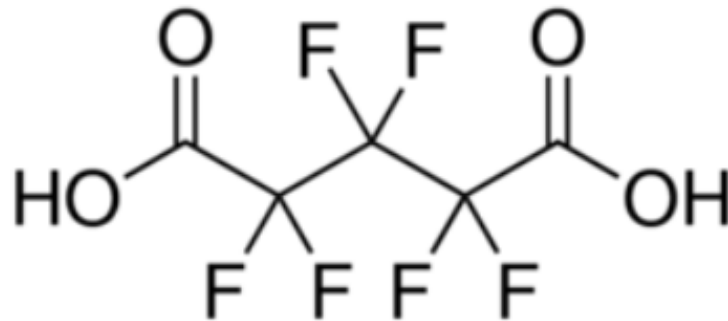
Presented by : SUBRATA DUARY

Date : 29-05-2021

Importance of the work

- Hard-base-ligand-protected CMNCs ; **contrary to HSAB theory**
- The synthesis and structure determination of the first all- carboxylate -protected superatomic silver nanocluster

- opens the door of using carboxylate groups to synthesize atomically precise Ag clusters



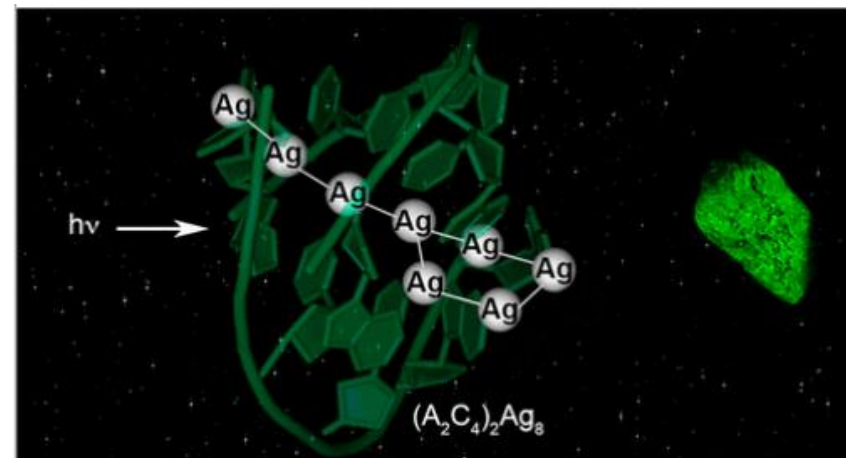
- ❑ Flexible and multidentate protecting agent
- ❑ Each pfga provides four oxygen donors for binding with multiple metal atoms

Atomic Structure of a Fluorescent Ag₈ Cluster Templated by a Multistranded DNA Scaffold

Dustin J. E. Huard,[†] Aida Demissie,[†] Dahye Kim,[‡] David Lewis,[‡] Robert M. Dickson,[†] Jeffrey T. Petty,^{*,‡} and Raquel L. Lieberman^{*,†}

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Atomically Precise Multimetallic Semiconductive Nanoclusters with Optical Limiting Effects

Shuai Chen, Dr. Wei-Hui Fang, Prof. Dr. Lei Zhang✉, Prof. Dr. Jian Zhang✉

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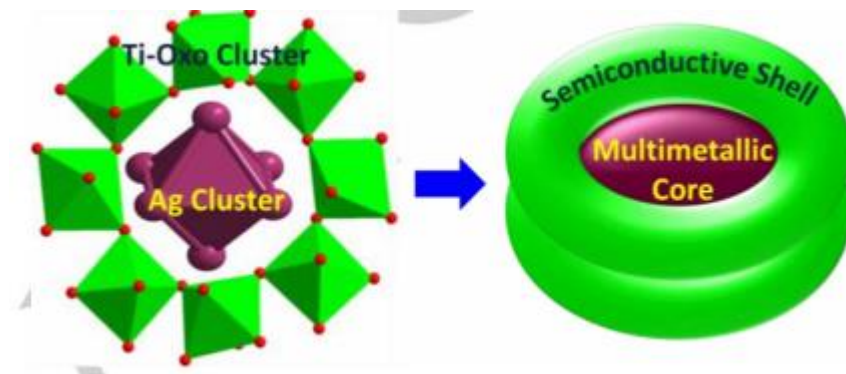
A discrete octahedrally shaped [Ag₆]⁴⁺ cluster encapsulated within silicotungstate ligands[†]

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

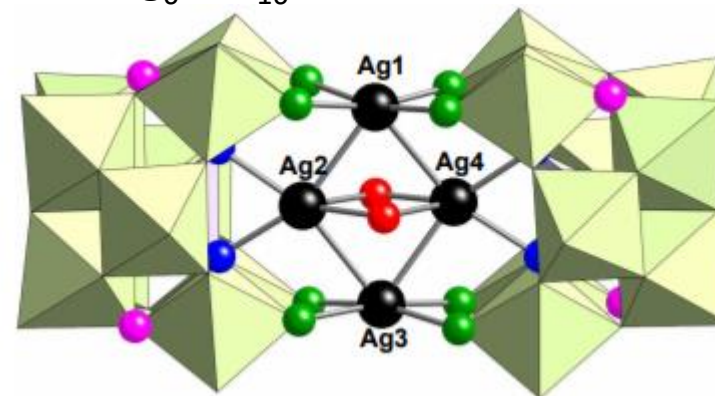
Cite this: *Chem. Commun.*, 2013, 49, 376

Received 18th October 2012,
Accepted 15th November 2012

DOI: 10.1039/c2cc37591e



Ag₆@Ti₁₆ - oxo nanocluster



TBA₈[Ag₆(γ-H₂W₁₀O₃₆)₂]·5H₂O

Synthesis of the cluster $[(\text{CH}_3)_2\text{NH}_2]_6[\text{Ag}_8(\text{pfga})_6]$

Perfluoroglutaric acid (0.144 g, 0.6 mmol) was dissolved in a solution of AgNO_3 (0.102 g, 0.6 mmol) in DMF (3mL)



Ultrasonication & Me_4NOH (0.1 mol/L) in 1 mL MeOH was added

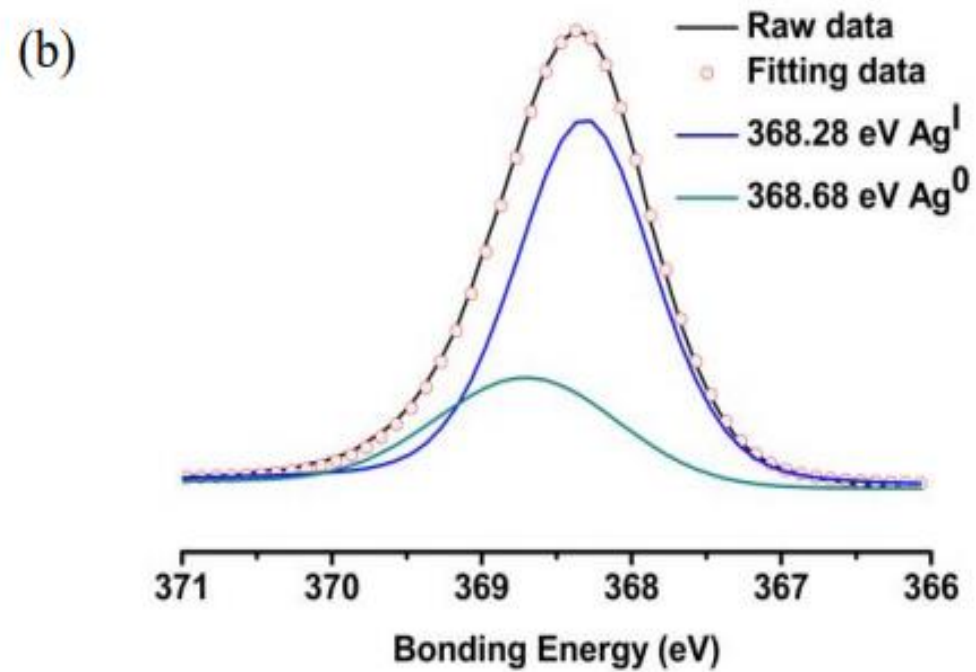
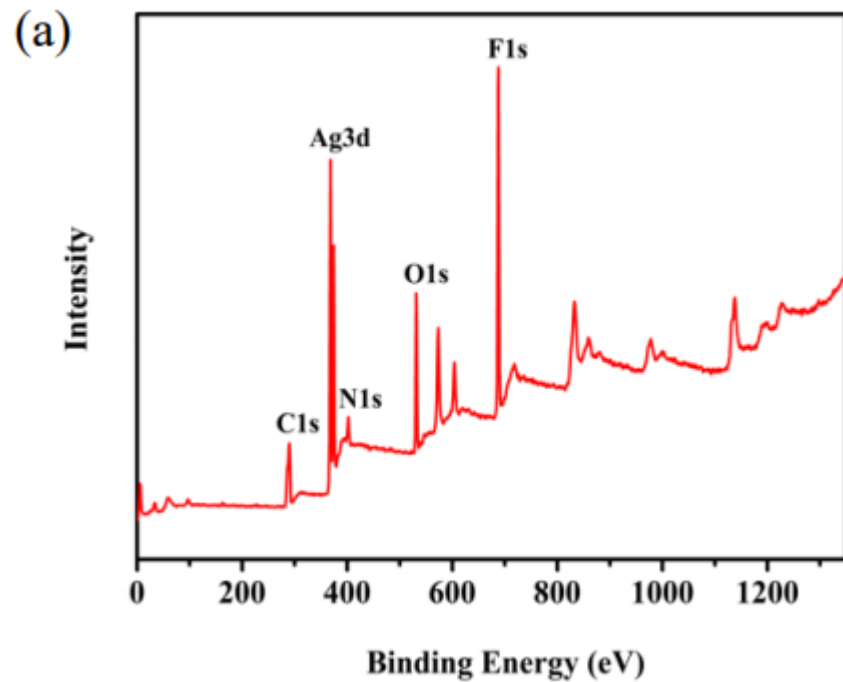
Colourless to pale yellow colour solution appeared



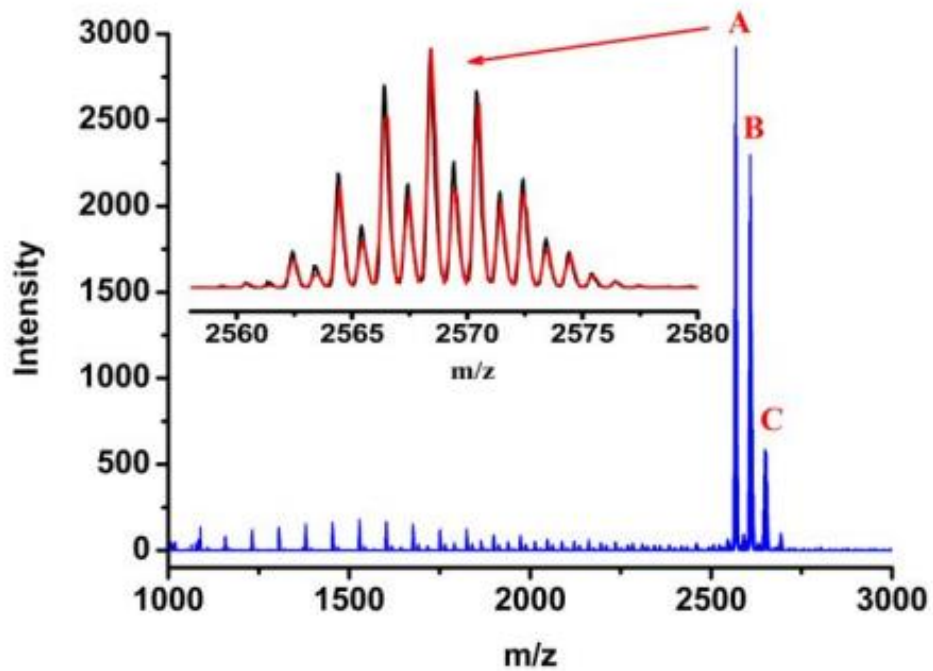
Sealed and kept at 70°C for 20 h.

Cool down to room temperature and slow evaporation of yellow filtrate afforded yellow rhombohedral crystal of the cluster

Characterization

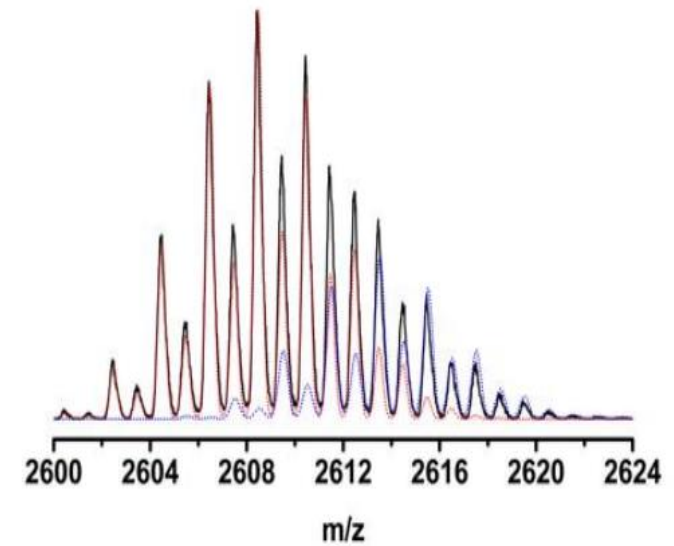


- (a) XPS spectra and (b) High resolution XPS spectrum of Ag 3d_{5/2} in [Ag₈(pfga)₆]⁶⁻



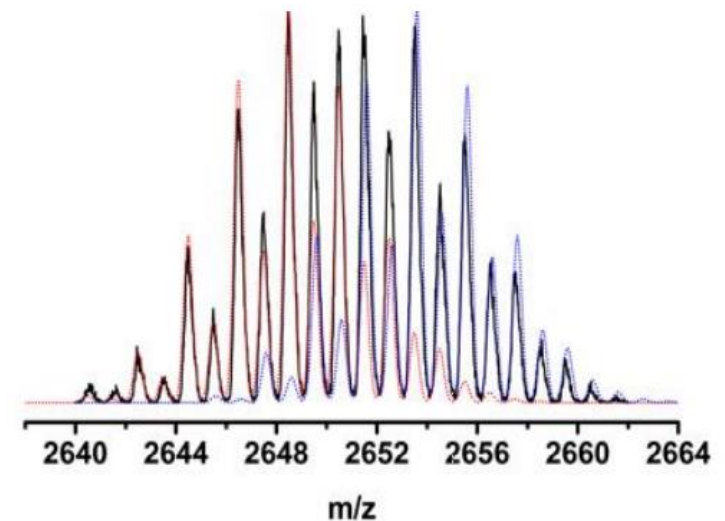
- Positive-ion mode ESI-MS of the crystal of $M=[(\text{CH}_3)_2\text{NH}_2]_6[\text{Ag}_8(\text{pfga})_6]$ dissolved in acetone/ CH_2Cl_2 (v:v=1:1). Inset: Zoom-in of the experimental (black) and simulated (red) isotopic patterns for species $A=[M + \text{H}^+]^+$ at 2568.46

B

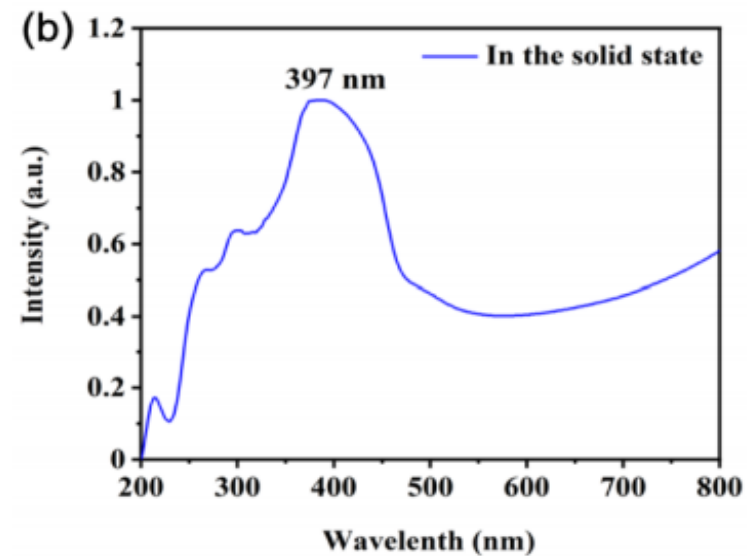
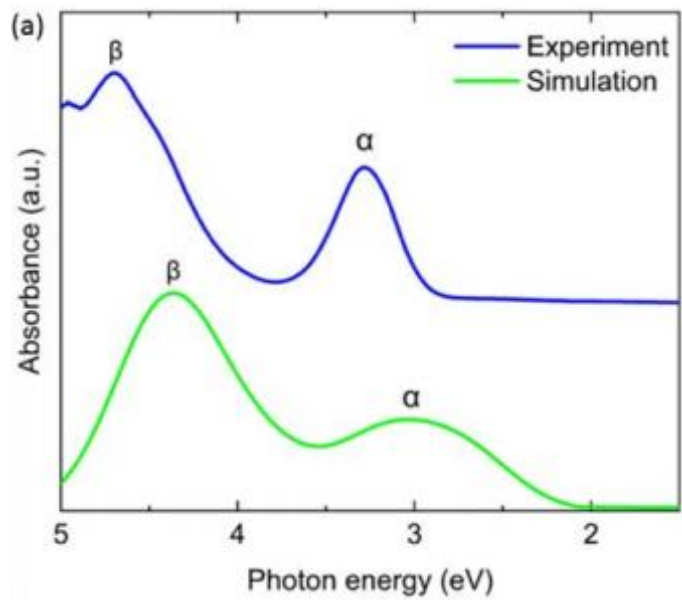


- $B = 2608.48 [\text{M} + \text{H}^+ + 2\text{HF}]^+$ (red) and $2613.52 [\text{M} + (\text{CH}_3)_2\text{NH}_2]^+$ (blue)

C

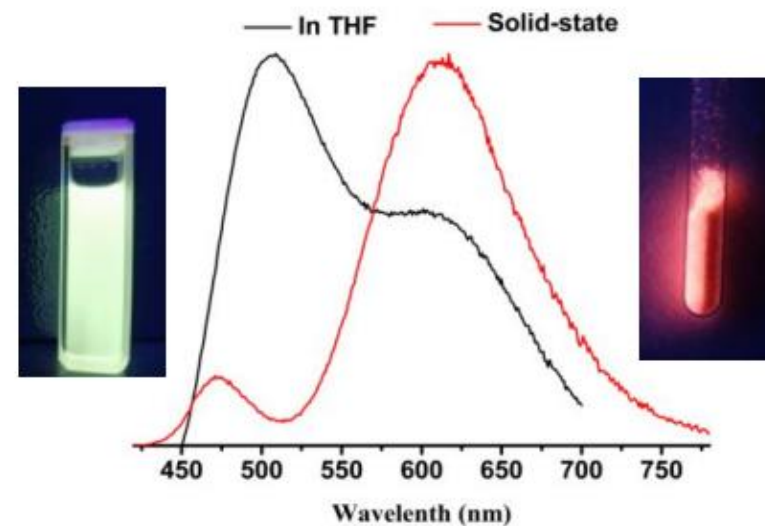
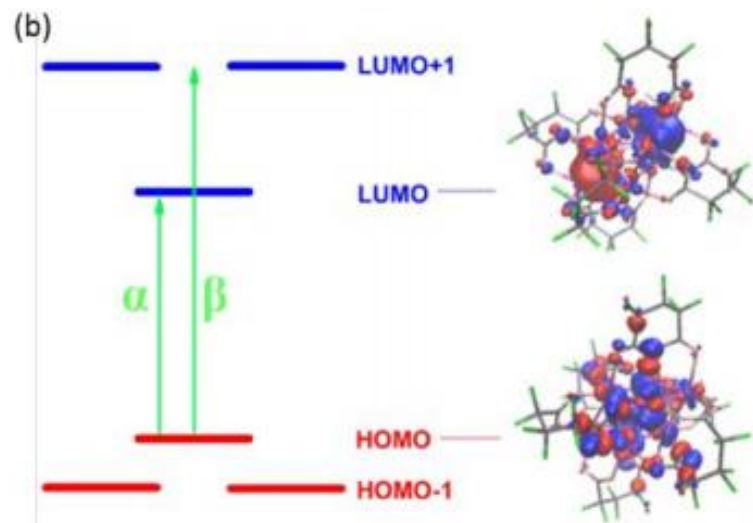


- $C = 2648.49 [\text{M} + \text{H}^+ + 4\text{HF}]^+$ (red) and $2653.60 [\text{M} + \text{H}^+ + 5\text{NH}_3]^+$ (blue)



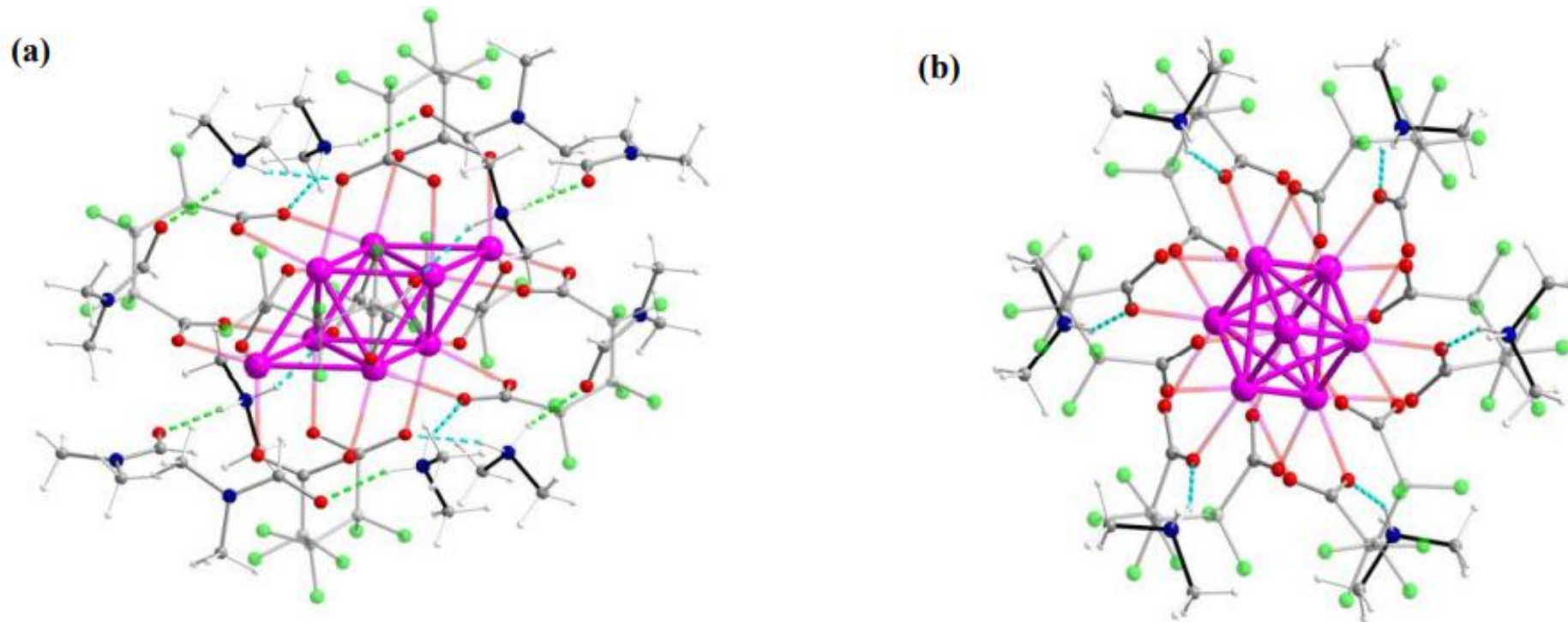
- The UV-vis absorption spectra of 1 in the solid state

- (a) Experimental UV-vis absorption spectrum (blue) of 1 in THF and simulated spectrum of $[\text{Ag}_8(\text{pfga})_6]^{6-}$ from time-dependent density-functional theory (green)

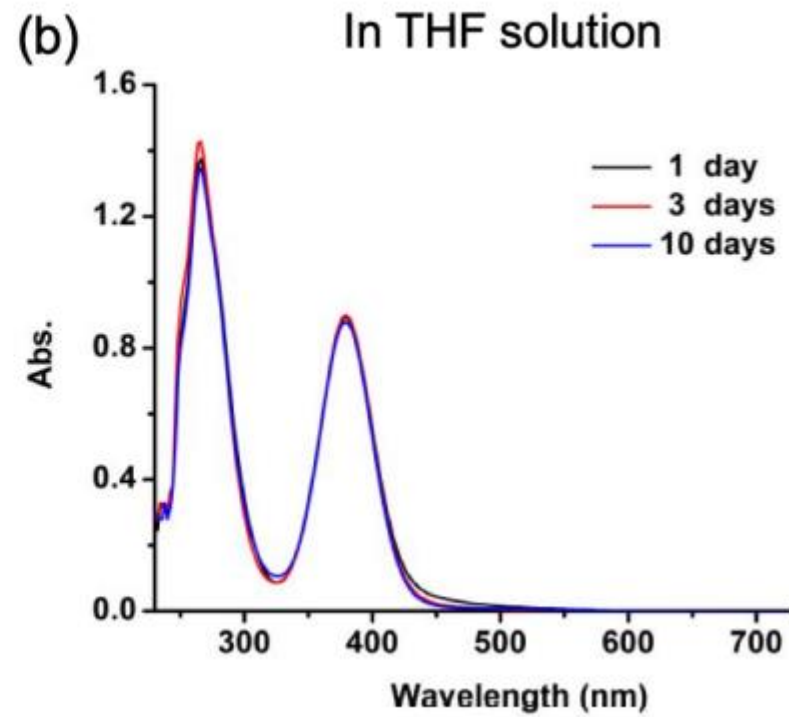
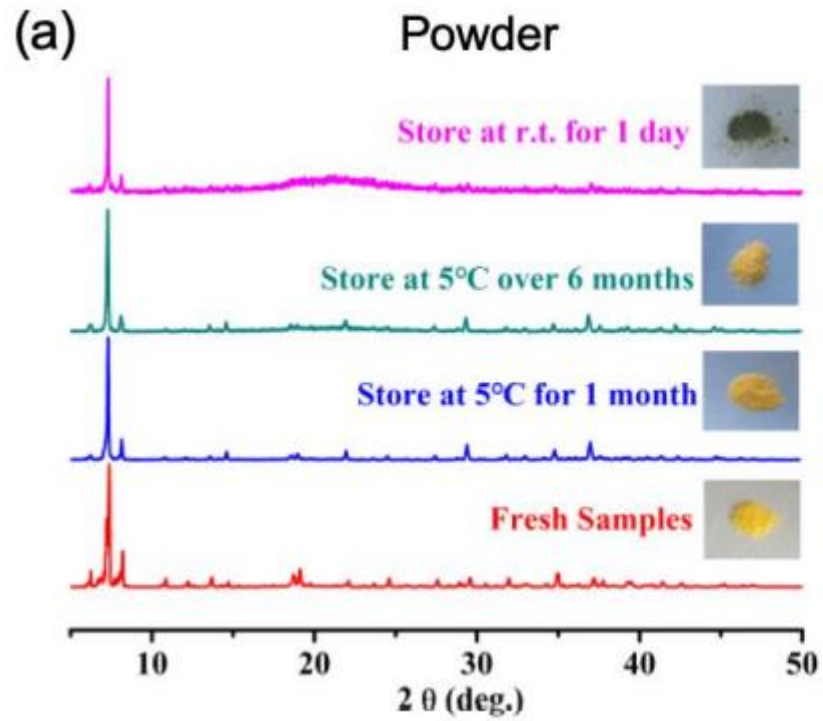


- Emission spectra of 1 in THF under 365 nm irradiation (black) and the solid state under 397 nm irradiation (red) at room temperature (RT). Inset: Photographs of the luminescence of 1 in THF (left) and the solid state (right)

- (b) Orbital diagram and frontier orbitals of $[\text{Ag}_8(\text{pfga})_6]^{6-}$.



- Hydrogen-bonding interactions (dashed lines; NDMA—H...Opfga) between the six dimethylammonium (DMA) cations and the $[\text{Ag}_8(\text{pfga})_6]^{6-}$ center in 1: (a) view along a face of the rhombohedral core; (b) view along the long axis of the rhombohedral core. Color legend: pink, Ag; red, O; blue, N; white, H; gray, C; green, F. The C–N bonds of DMA cations are highlighted in black



- Stability of 1: (a) the powder XRD pattern of the solid-state sample of the cluster stored at 5 °C and room temperature; (b) the UV-vis spectra of the THF solution of the cluster stored at 5 °C.