# Paper Presentation

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Harshita Nagar

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Communication

# Chiral Hydride $Cu_{18}$ Clusters Transform to Superatomic $Cu_{15}Ag_4$ Clusters: Circularly Polarized Luminescence Lighting

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# Why this paper?

- The modulation of metal cluster enantiomers and their reconstruction remain challenging. Here, for the first time, they report an enantiomeric pair of hydride copper cluster made using chiral ligand.

- The introduction of foreign metal atoms to induce structural conversion of a parent metal cluster has emerged as a promising strategy for modulating the cluster's size and electronic structure.

- This approach can trigger the formation of bimetallic clusters with desired composition, novel structure, and tailored functionality.

# Background work

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Communication
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## Reconstructing the Surface of Gold Nanoclusters by Cadmium Doping

Qi Li,[†] Kelly J. Lambright,[‡] Michael G. Taylor,[‖] Kristin Kirschbaum,[‡] Tian-Yi Luo,[§] Jianbo Zhao,[†] Giannis Mpourmpakis,[‖] Soumitra Mokashi-Punekar,[§] Nathaniel L. Rosi,[§] and Rongchao Jin*,[†]

GDCh Communications Angewandte Chemie International Edition
Metal Nanoclusters
International Edition: DOI: 10.1002/anie.201600267
German Edition: DOI: 10.1002/ange.201600267

## Gold Doping of Silver Nanoclusters: A 26-Fold Enhancement in the Luminescence Quantum Yield

*Giada Soldan[+], Maha A. Aljuhani[+], Megalamane S. Bootharaju, Lina G. AbdulHalim, Manas R. Parida, Abdul-Hamid Emwas, Omar F. Mohammed,* and Osman M. Bakr**

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Communication
Cite This: J. Am. Chem. Soc. 2018, 140, 12314−12317
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## Hydride-Mediated Controlled Growth of a Bimetallic $(Pd@Au_8)^{2+}$ Superatom to a Hydride-Doped $(HPd@Au_{10})^{3+}$ Superatom

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Article

## $[Pt_2Cu_{34}(PET)_{22}Cl_4]^{2-}$: An Atomically Precise, 10-Electron PtCu Bimetal Nanocluster with a Direct Pt−Pt Bond

Sanghwa Lee,[⊥] Megalamane S. Bootharaju,[⊥] Guocheng Deng,[⊥] Sami Malola, Hannu Häkkinen,* Nanfeng Zheng,* and Taeghwan Hyeon*

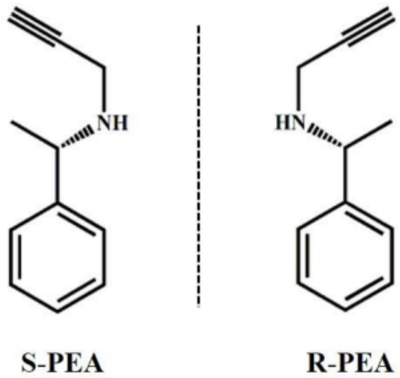
# Introduction

- Herein, for the first time, they have synthesized a pair of chiral copper hydride clusters $[Cu_{18}H(R/S\text{-}PEA)_{12}](BF_4)_5$ **(R/S-$Cu_{18}$H)**.

- When treated with $Ag^+$ ions, the R/S-$Cu_{18}$H precursor generates a novel enantiomeric pair of clusters $[Cu_{15}Ag_4(R/S\text{-}PEA)_{12}](BF_4)_5$ **(R/S-$Cu_{15}Ag_4$)** that lacks a hydride component and exhibits a $Cu_{15}Ag_4$ metal core.

- Moreover, R/S-$Cu_{18}$H exhibits circular dichroism (CD) responses, yet is non-emissive but by manipulation of R/S-$Cu_{18}$H with $Ag^+$ ions, R/S-$Cu_{15}Ag_4$ shows orange emission and CPL activities.

- Ligand- ((R/S)-1-phenylethyl)prop-2-yn-1-amine



# Results and Discussion

➢ Synthesis of $[Cu_{18}H(R/S\text{-}PEA)_{12}](BF_4)_5$ **(R/S-$Cu_{18}H$)**

$[Cu(MeCN)_4]BF_4$ + R/S-PEA + $NaBH_4$

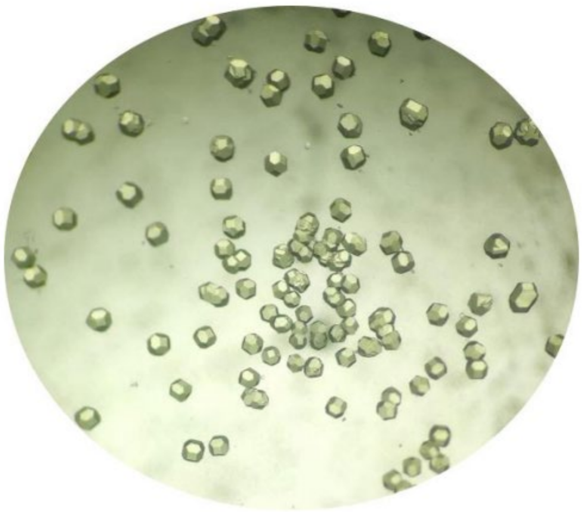
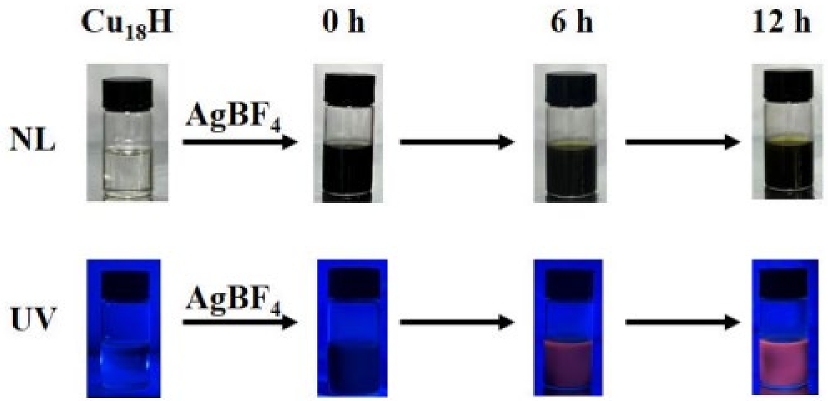


**Figure 1. (a)** Image of single crystals of S-$Cu_{18}H$ under natural light

➢ Synthesis of $[Cu_{15}Ag_4(R/S\text{-}PEA)_{12}](BF_4)_5$ **(R/S-$Cu_{15}Ag_4$)**



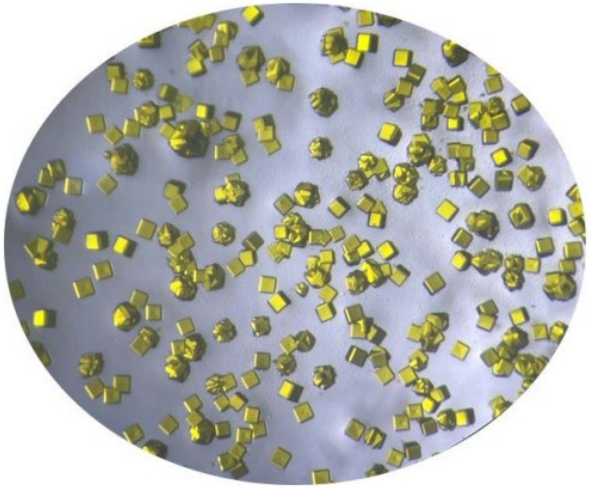



**Figure 1. (b)** Image of single crystals of S-$Cu_{15}Ag_4$ under natural light

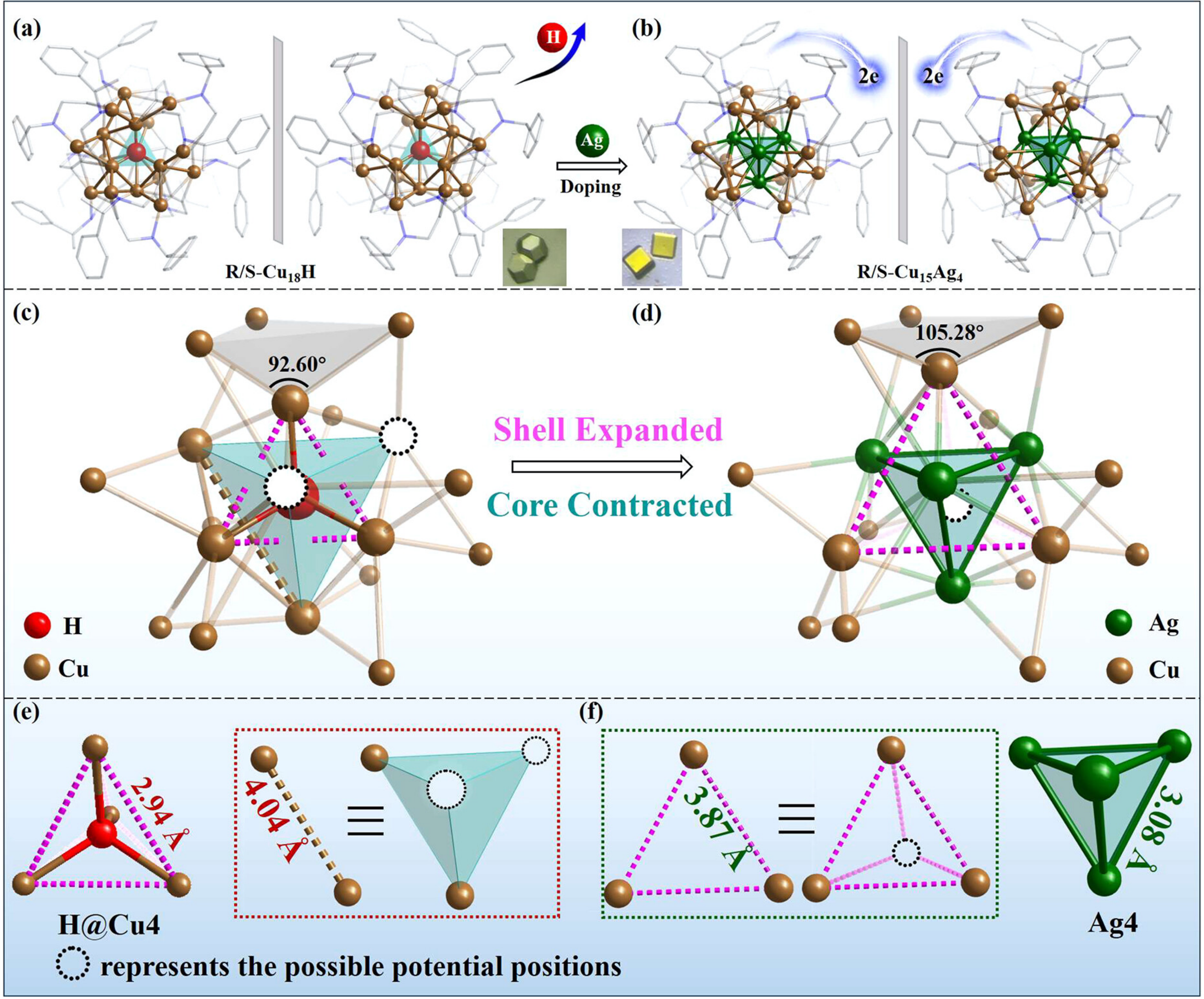



**Figure 2**. **(a)** Structures of R/S-$Cu_{18}H$ and **(b)** R/S-$Cu_{15}Ag_4$. Inset: images of S-$Cu_{18}H$ and S-$Cu_{15}Ag_4$ crystals under natural light. **(c, d)** Comparison of changes in S-$Cu_{18}H$ and S-$Cu_{15}Ag_4$. Bond lengths in **(e)** S-$Cu_{18}H$ and **(f)** S-$Cu_{15}Ag_4$. Inset: The disordered parts in S-$Cu_{18}H$ and S-$Cu_{15}Ag_4$ structures. In S-$Cu_{18}H$, two of the four positions are occupied by copper and show no difference. In S-$Cu_{15}Ag_4$, three of the four positions are occupied by copper and show no difference. Color codes: N, blue; C, gray. H atoms of ligands are omitted for clarity.

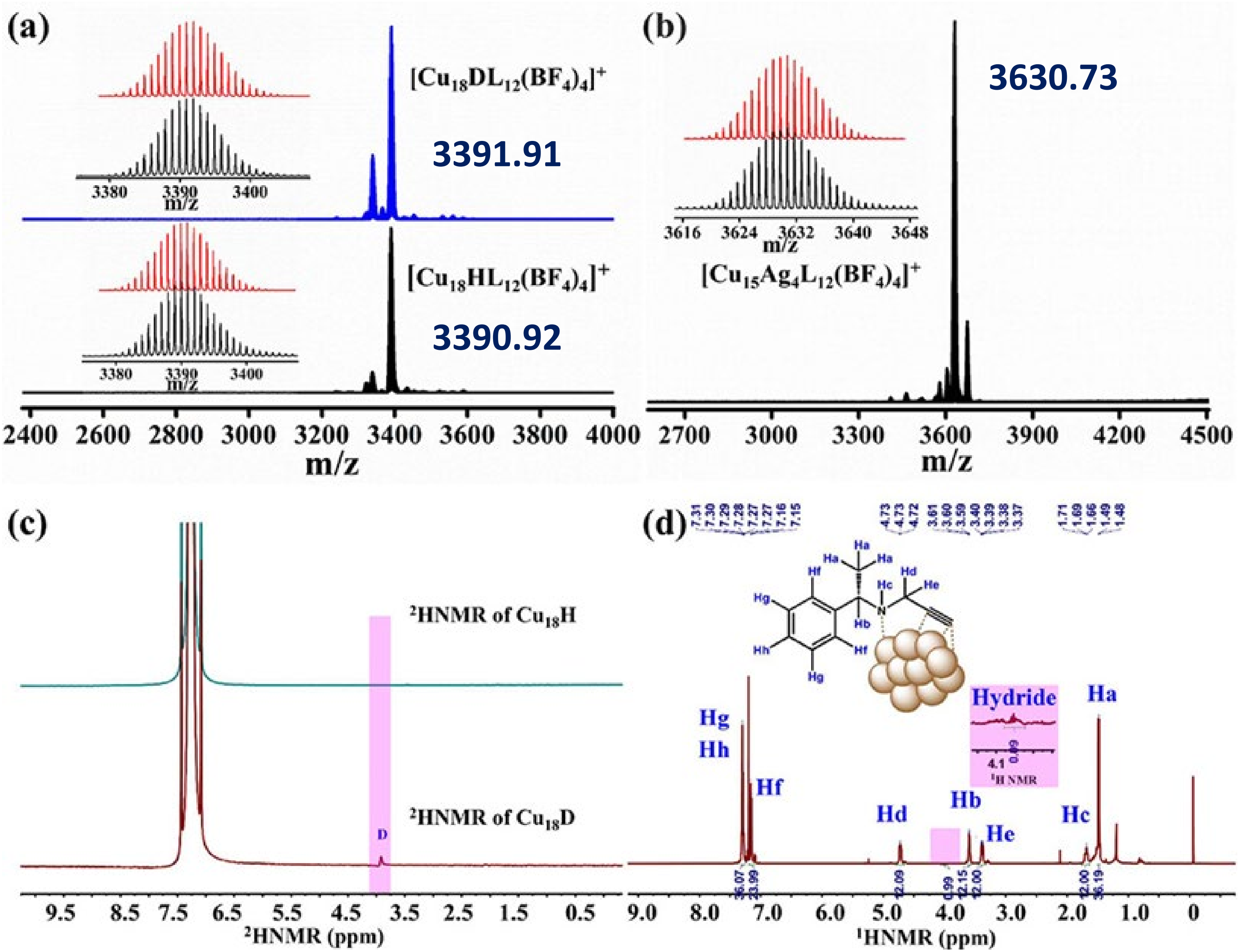



**Figure 3**. ESI-MS spectra of **(a)** S-$Cu_{18}H$, deuteride derivative, and **(b)** S-$Cu_{15}Ag_4$. Inset: The measured (black trace) and simulated (red trace) isotopic patterns of molecular ion peaks. **(c)** $^2$ H NMR spectra of S-$Cu_{18}H$ and the deuterated cluster in $CHCl_3$. **(d)** 1 H NMR spectrum of S-$Cu_{18}H$ in $CDCl_3$

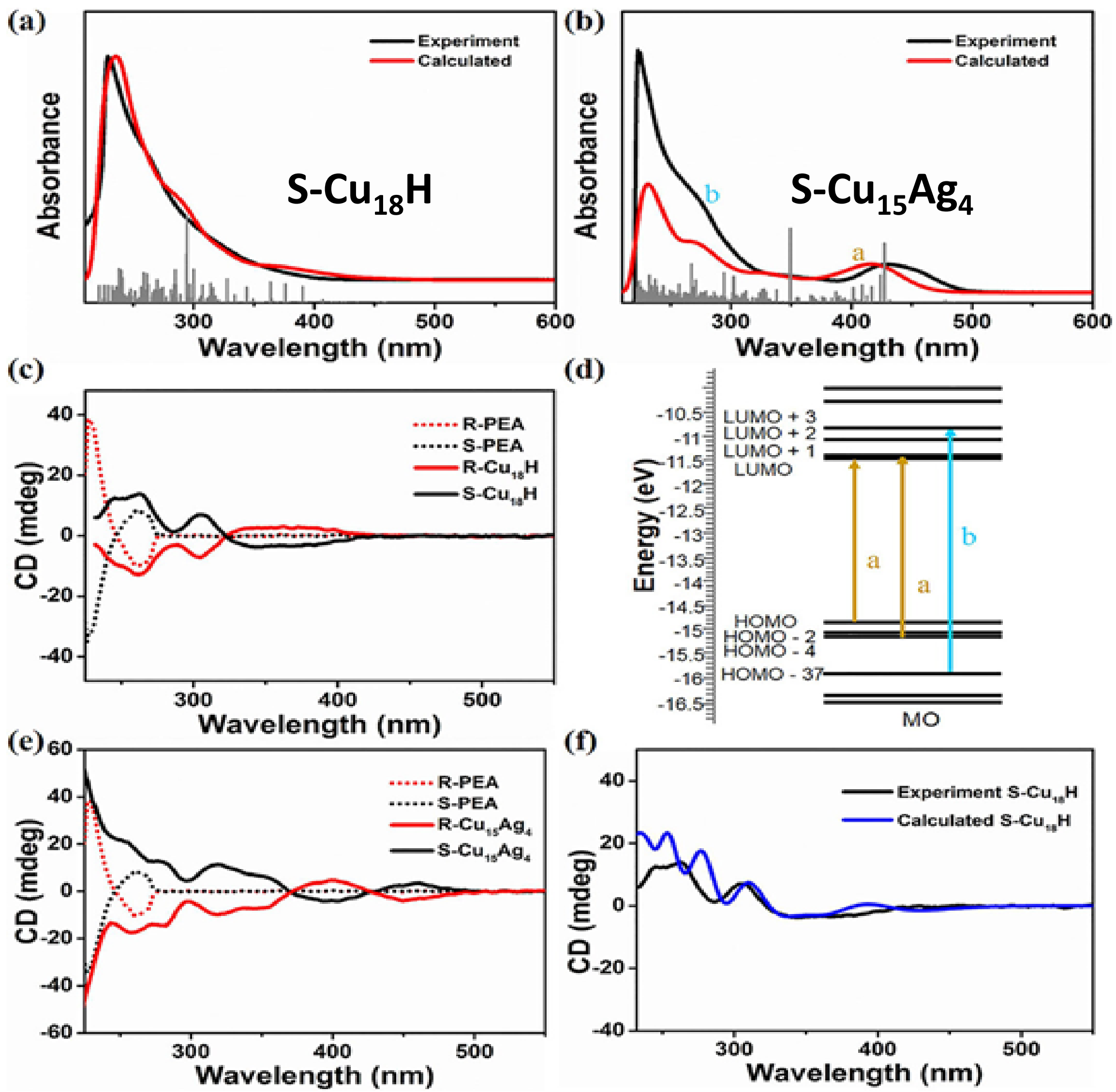



**Figure 4.** Experimental and calculated absorption spectra of **(a)** S-$Cu_{18}H$ and **(b)** S-$Cu_{15}Ag_4$ **(c,e)** CD spectra of R/S-$Cu_{18}H$, R/S-$Cu_{15}Ag_4$, and ligands in dichloromethane. **(d)** Energy alignment of the MOs of S-$Cu_{15}Ag_4$. **(f)** Experimental and calculated CD spectra of S-$Cu_{18}H$.

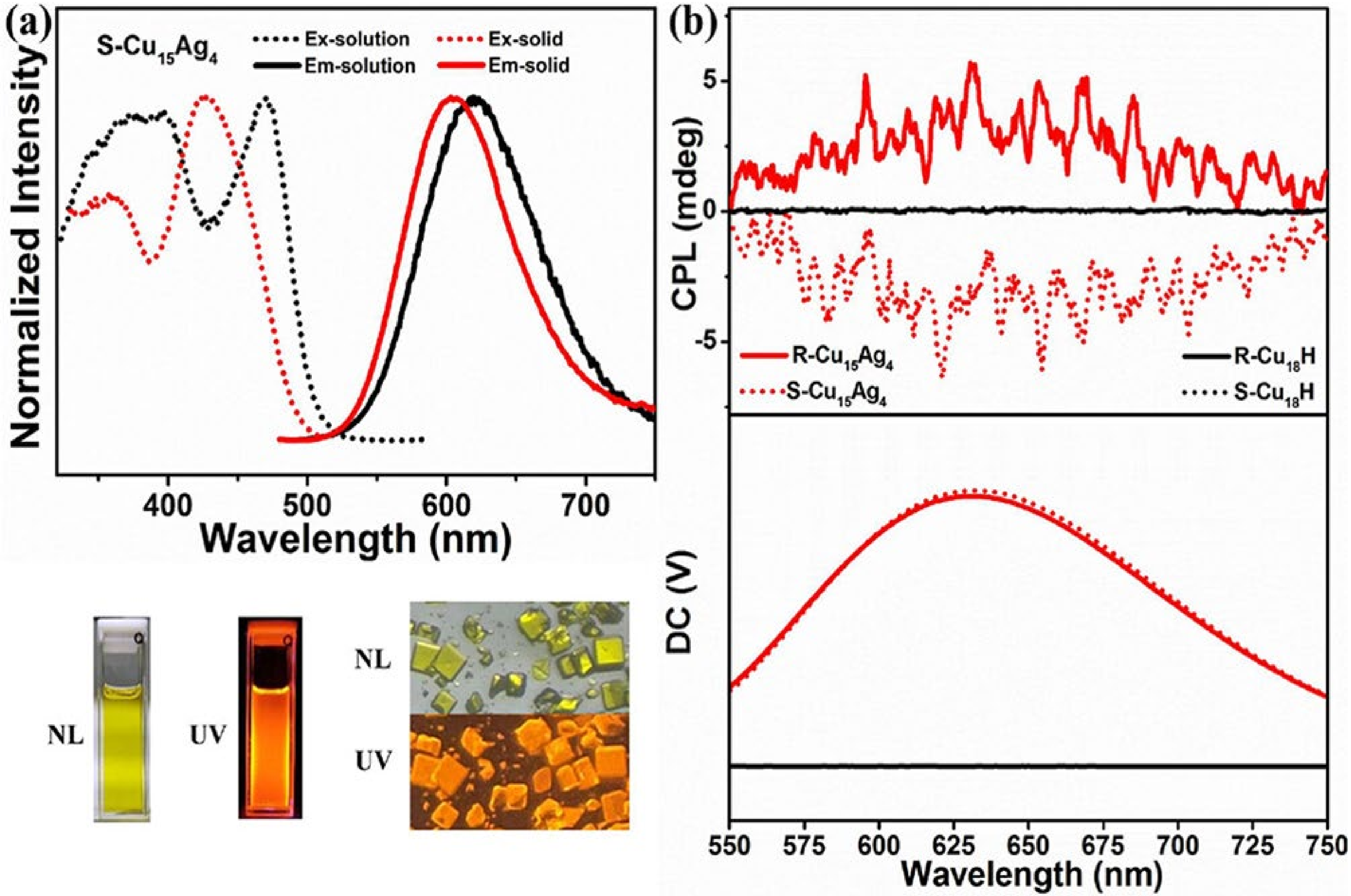



**Figure 5. (a)** Luminescence spectra of S-$Cu_{15}Ag_4$ in solid and solution states. Inset: Images of S-$Cu_{15}Ag_4$ crystals and solution under natural light (NL) and UV irradiation. **(b)** CPL spectra of R/S-$Cu_{15}Ag_4$ and R/S-$Cu_{18}H$ crystals.

# Conclusion

- They have reported, for the first time, the synthesis and characterization of a pair of enantiomeric Cu hydride cluster R/S-$Cu_{18}H$.

- Through manipulation of R/S-$Cu_{18}H$ by $Ag^{+}$ ions, hydride is released, leading to the formation of a novel superatom, R/S- $Cu_{15}Ag_{4}$.

- The solid state R/S-$Cu_{15}Ag_{4}$ exhibited a photoluminescence quantum yield of 7.02% and excellent circularly polarized luminescence.

- The site-specific metal replacement in the cluster molecule and the accompanying dramatic changes in optical properties elucidate the explicit correlation between structure and luminescence.