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Article

Carborane-Cluster-Wrapped Copper Cluster with Cyclodextrin-like Cavities for Chiral Recognition

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Cite This: J. Am. Chem. Soc. 2024, 146, 16729−16736
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June 5, 2024

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July 6, 2024

Why this paper?

- Chiral atomically precise metal clusters, known for their remarkable chiroptical properties, hold great potential for applications in chirality recognition.
- In this work, they have synthesized chiral Cu cluster which is designed with specific cavities and can be used for chiral recognition of amino acids.

Background work

› Sci Adv. 2016 Aug 12;2(8):e1600323. doi: 10.1126/sciadv.1600323. eCollection 2016 Aug.

Thiacalix[4]arene: New protection for metal nanoclusters

Zong-Jie Guan [1], Jiu-Lian Zeng [1], Zi-Ang Nan [1], Xian-Kai Wan [1], Yu-Mei Lin [1], Quan-Ming Wang [2]

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Communication
Cite This: J. Am. Chem. Soc. 2018, 140, 13590−13593
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Isomerism in Supramolecular Adducts of Atomically Precise Nanoparticles

Abhijit Nag, Papri Chakraborty, Ganesan Paramasivam, Mohammad Bodiuzzaman, Ganapati Natarajan, and Thalappil Pradeep*

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Communication

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

Miao-Miao Zhang, Kai-Kai Gao, Xi-Yan Dong, Yubing Si, Teng Jia, Zhen Han,* Shuang-Quan Zang,* and Thomas C. W. Mak

Cite This: J. Am. Chem. Soc. 2023, 145, 22310−22316
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Introduction

- This study reports the synthesis of a chiral $Cu_{16}(C_2B_{10}H_{10}S_2)_8$ (denoted as $Cu_{16}@CB_8$, where $C_2B_{10}H_{12}S_2H_2$ is 9,12-$(HS)_2$-1,2-closo-carborane) cluster.

- $Cu_{16}@CB_8$ cluster have cavities reminiscent of cyclodextrins, which are surrounded by carborane ligands.

- These cavities demonstrated the specific recognition of amino acids, as indicated by circular dichroism and circularly polarized luminescence studies.

- A quantitative enantioselective sensing is achieved by this cluster.

Results and Discussion

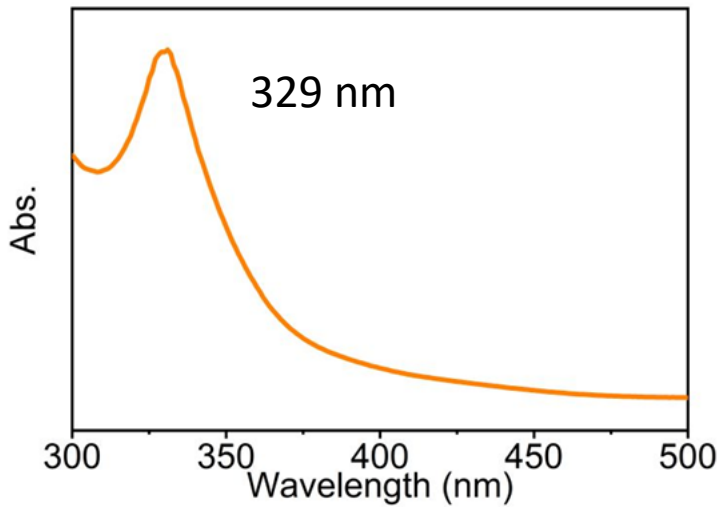
Fig 1

$Cu(CH_3CN)_4PF_6$ + $O_{9,12}$ CBT (9,12-dimercapto-1,2-closo-carborane) + CH_2Cl_2-DMAc(2:1)

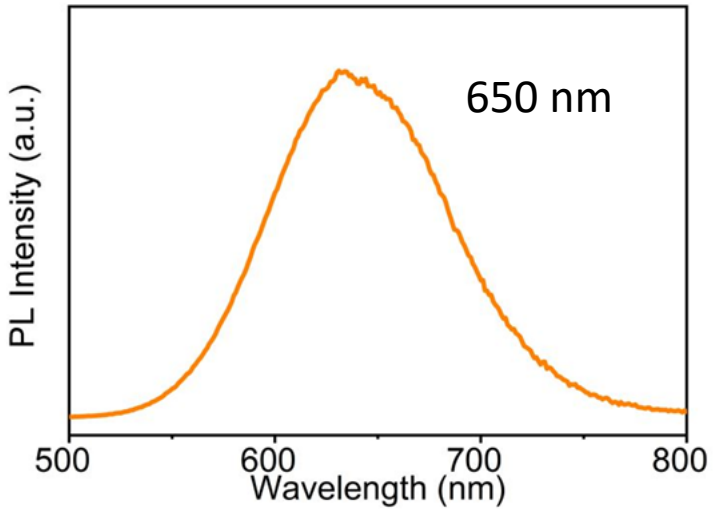
(150 mg) (42 mg)

↓ KF (6 mg)

Solution changed from light yellow to dark yellow (Cu_{16}@CB_8)



UV–vis absorption spectrum



Emission spectrum

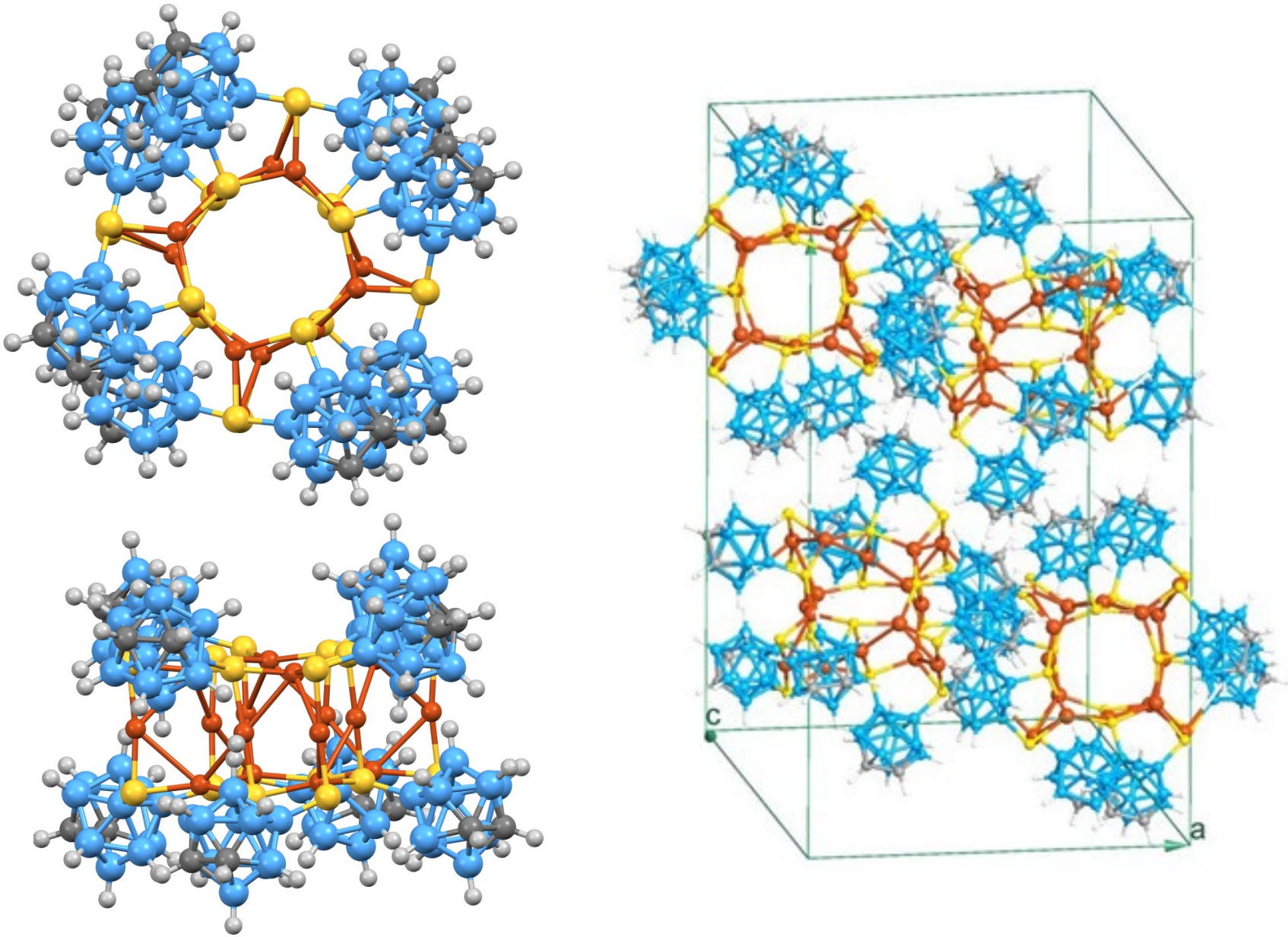


Fig 2. a) Drum-like crystal structure of $Cu_{16}@CB_8$ b) Unit cell contains left- and right-handed $Cu_{16}@CB_8$

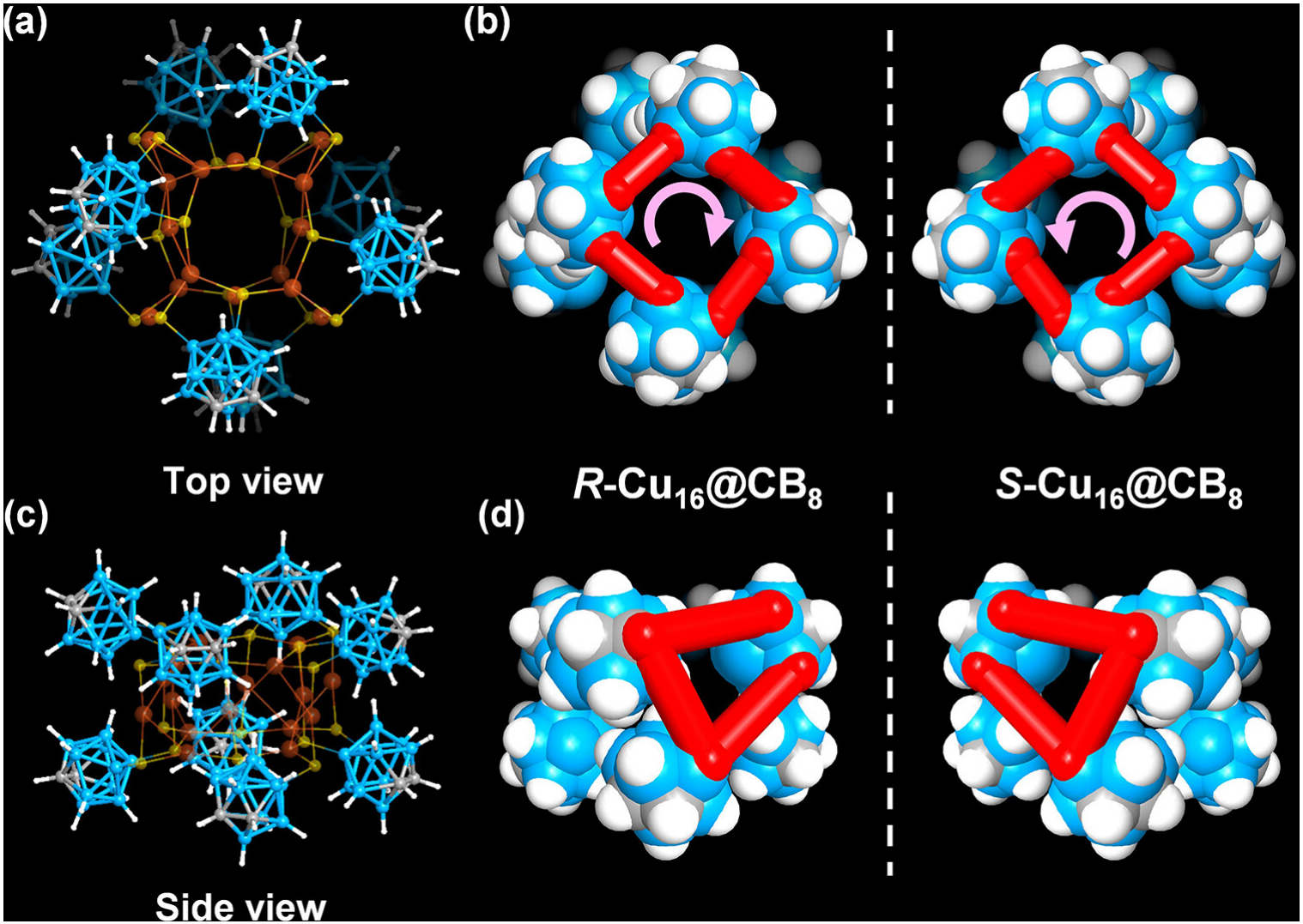
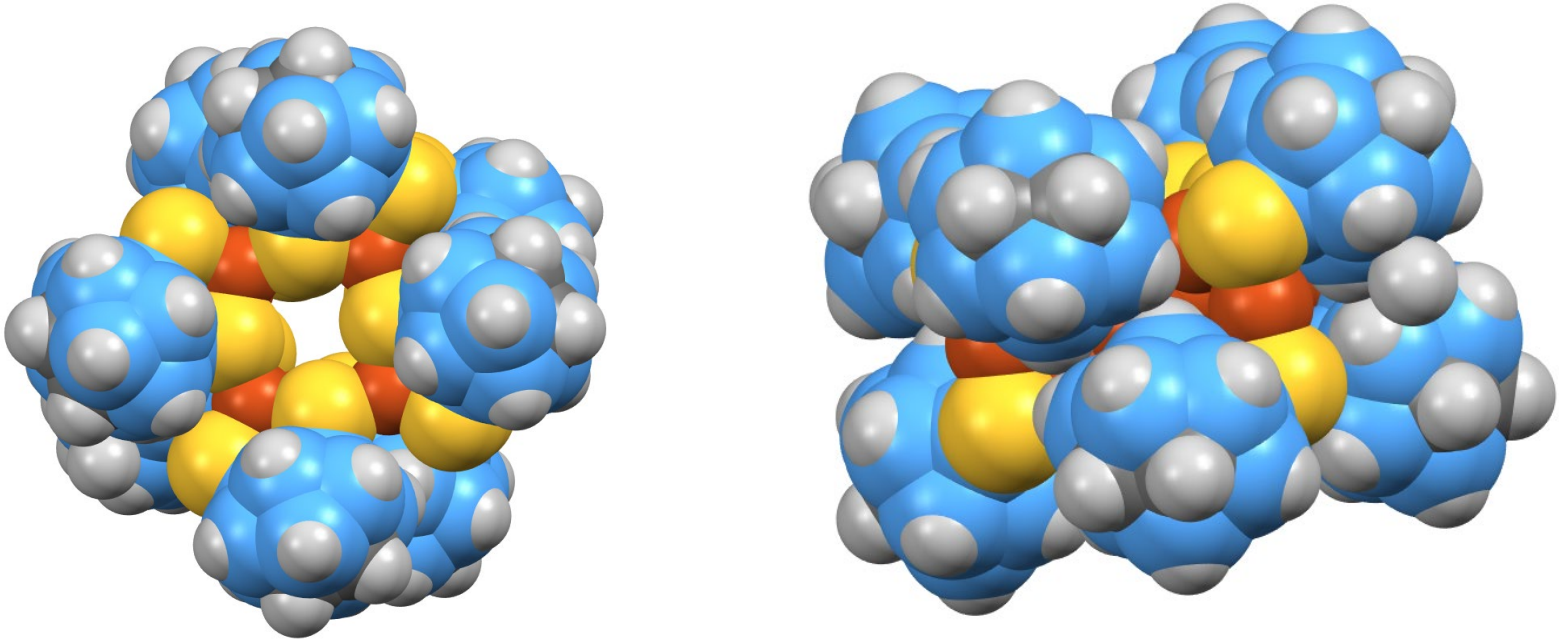


Fig 3. a) Top view of $Cu_{16}@CB_8$ b) Top view of chiral arrangements of the carborane molecules ; the square chiral cavity surrounded by carborane is highlighted. c) Side view of $Cu_{16}@CB_8$ d) Chiral arrangements of the carborane molecules ; triangular chiral cavity surrounded by H atom is highlighted.



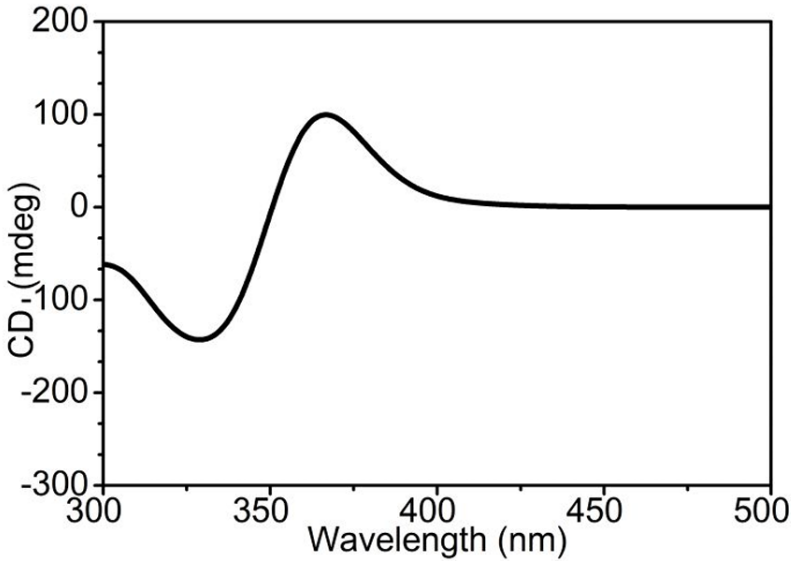


Fig 4. CD spectrum of R-Cu_{16}@CB_8

Photophysical Studies of Amino Acids@Cu_{16}

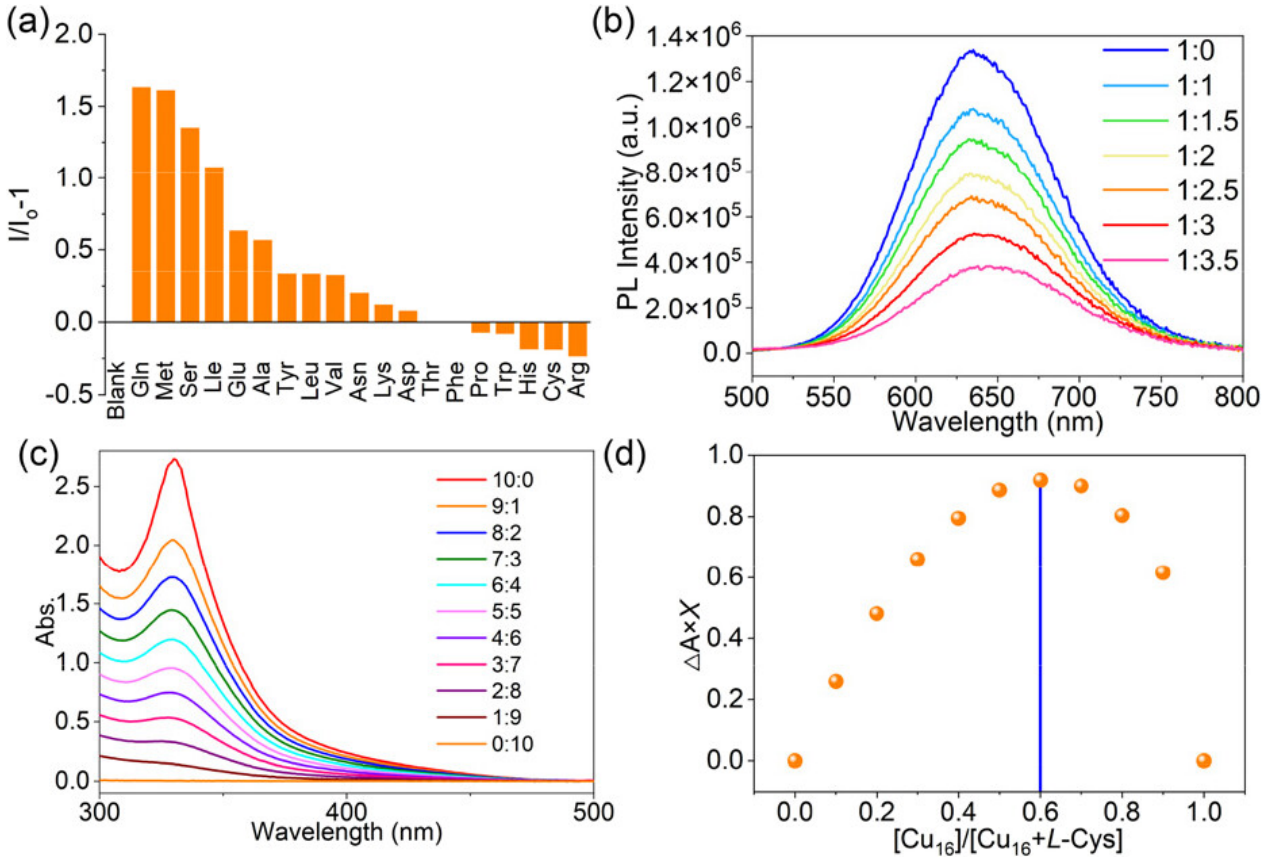


Fig 5 . (a) Relative luminescence intensity of the $Cu_{16}@CB_8$ solution after the addition of different L-amino acids under 365 nm ($Cu_{16}@CB_8$: L-amino acids=1:1). (b) Luminescent titration spectra of $Cu_{16}@CB_8$ with L-Cys ,λ_{ex}=365nm. (c) UV–vis titration spectra of $Cu_{16}@CB_8$ with L-Cys. (d) Job's plot of the variation of the UV–vis measurements at 330 nm for $Cu_{16}@CB_8$ and L-Cys.

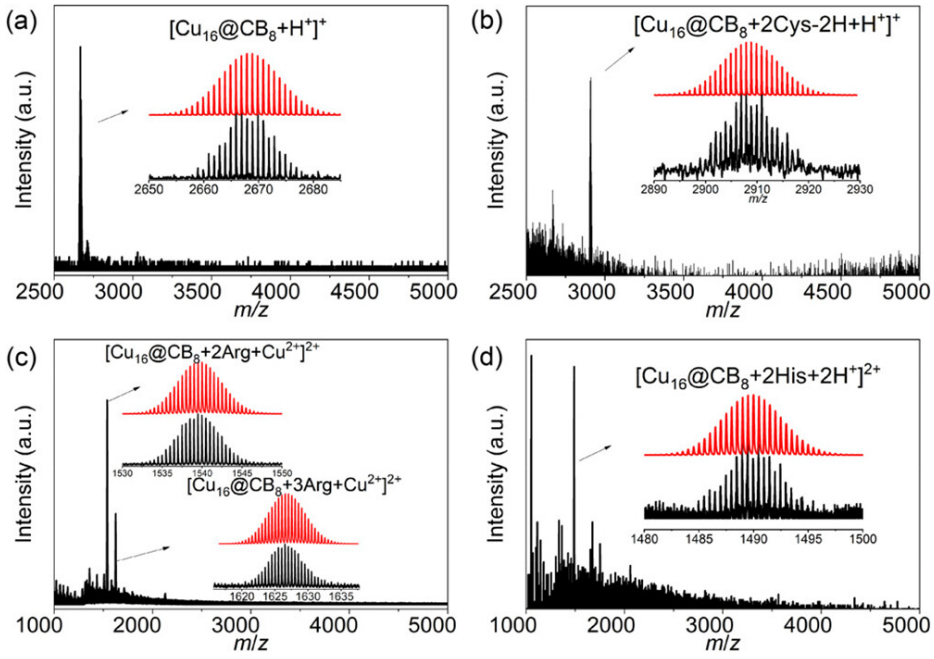


Fig 6. Positive-mode ESI-MS spectra of (a) $Cu_{16}@CB_8$ and (b) mixtures of $Cu_{16}@CB_8$ and L-Cys, (c) $Cu_{16}@CB_8$ and L-Arg, and (d) $Cu_{16}@CB_8$ and L-His.

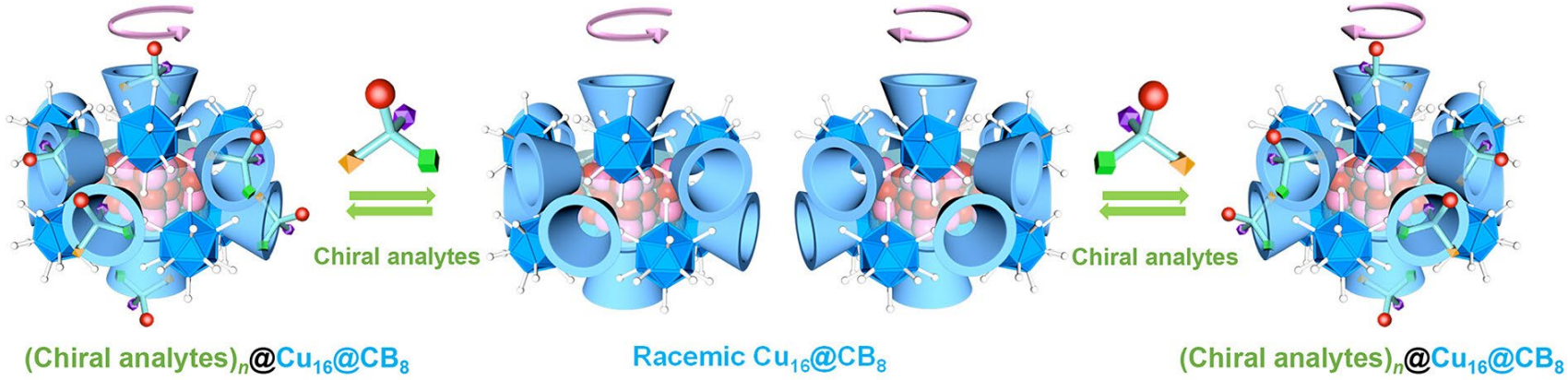


Fig 7. Schematic representation of the assembly of $Cu_{16}@CB_8$ and chiral analytes, the blue conical hourglass represents the cavities surrounded by carboranes.

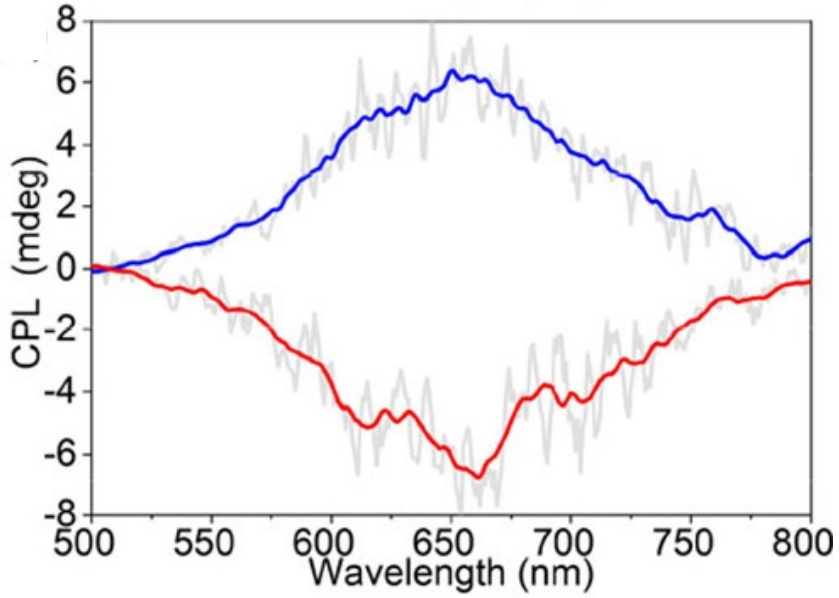


Fig 8. CPL spectra of a mixture of $Cu_{16}@CB_8$ and D- / L Cys

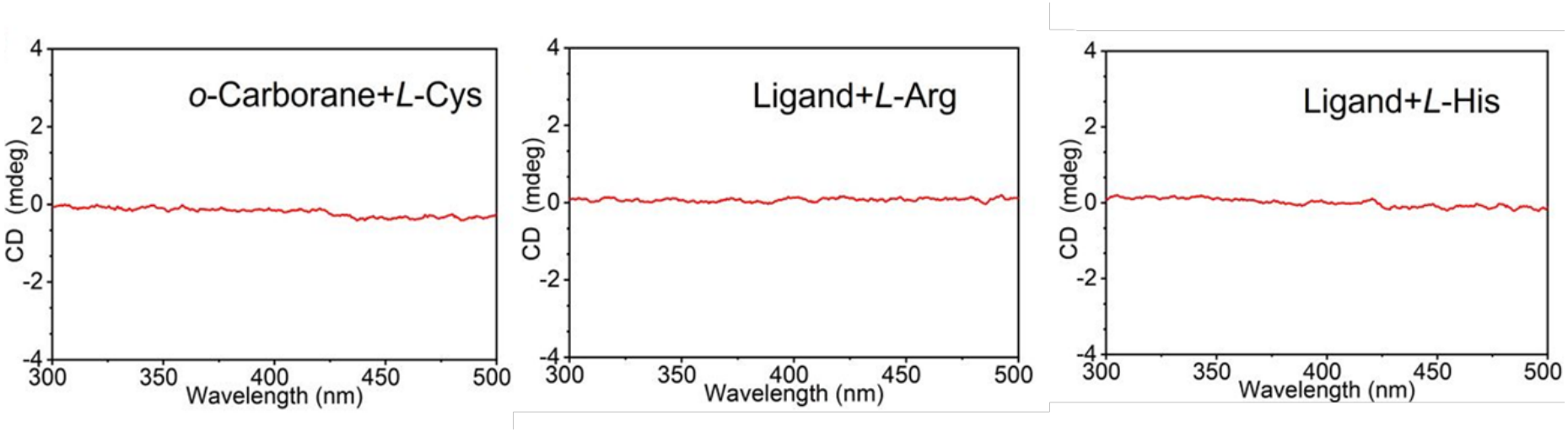


Fig 9. CD spectrum of the mixture of ligand and amino acids.

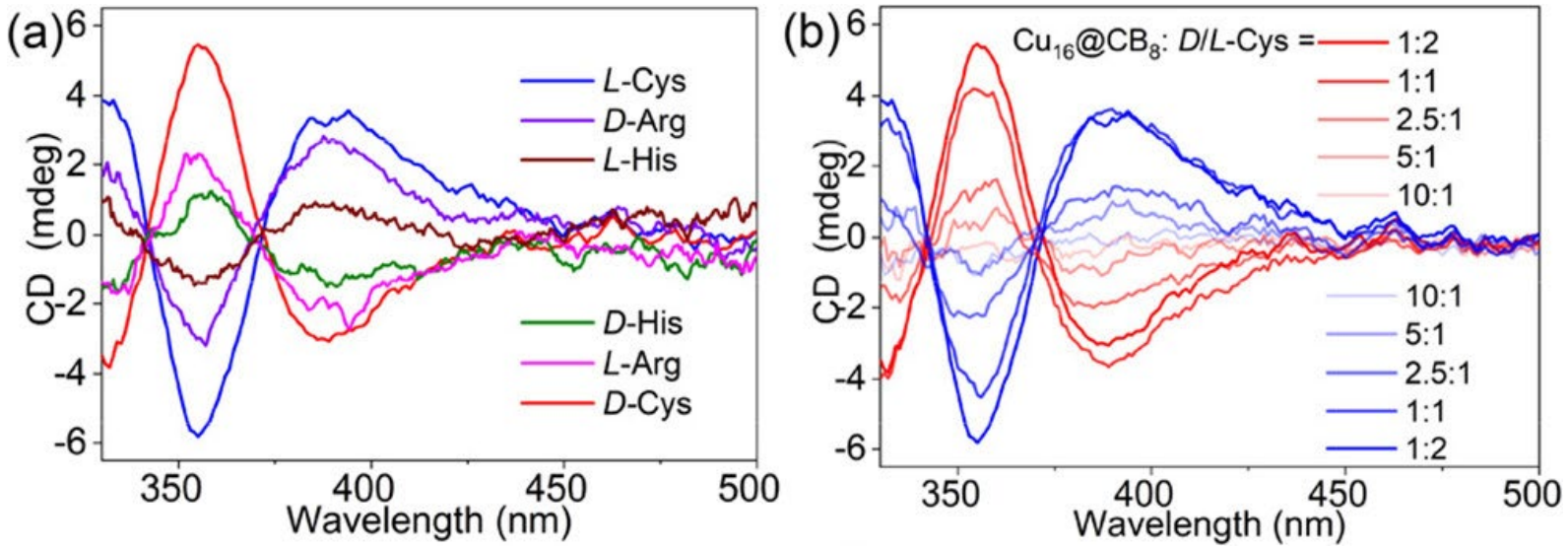


Fig 10. (a) CD spectra of the mixtures of $Cu_{16}@CB_8$ and D-/ L-Cys, D-/ L-Arg, and D-/ L-His. (b) CD spectra of the mixture of $Cu_{16}@CB_8$ and different amounts of L-/ D-Cys.

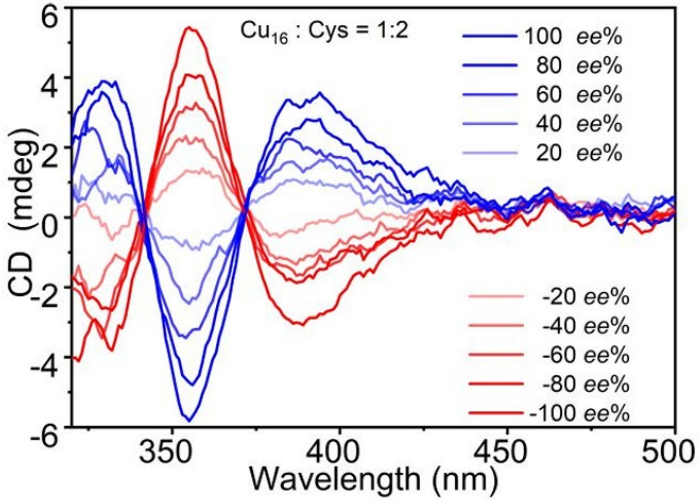


Fig 11. CD spectra of the $Cu_{16}@CB_8$ with the addition of D/ L-Cys with various ee% values.

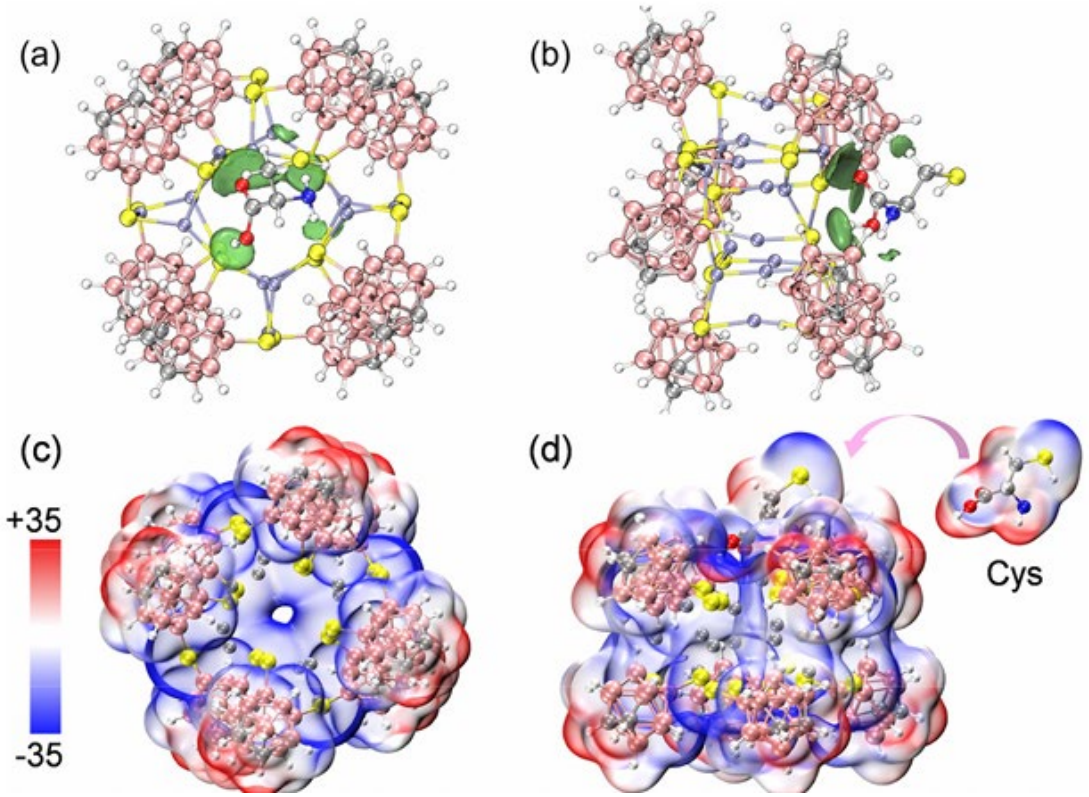


Fig 12. (a) Top view and (b) side view of the colored isosurfaces for the binding site of $Cu_{16}@CB_8$ and cysteine. (c)Top view of the ESP maps of $Cu_{16}@CB_8$. (d) Side view of the ESP map of $Cys@Cu_{16}@CB_8$, with Cys located in the square cavity.

Conclusion

- This work introduced a new type of structure based copper cluster protected with carborane ligands that has tiny cavities resembling cyclodextrins (a type of molecule known for its ability to capture other molecules). These cavities are designed to capture and recognize chiral molecules.

- In this work, they mixed racemic $Cu_{16}@CB_8$ with amino acids and they came together to form supramolecular assembly and chirality transfer occurred.

- $Cu_{16}@CB_8$ was developed for the quantitative determinations of the enantiomeric excess of chiral analytes.

Thank You