Supporting Information

Assembly of silver(I)-copper(I) bimetallic thiolate complexes assisting by phenacetylene stabilizers

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X-ray crystallography

Single crystal X-ray data of $\mathbf{Ag_{11-x}Cu_x}$ and $\mathbf{Ag_{21}Cu_4}$ were collected on a Bruker D8 Venture diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Data processing, absorption correction, integration and reduction were performed by multi-scan method and implemented in software Bruker APEX3 v2017.3-0. The structure was refined by full-matrix least-squares techniques against F2 using the SHELXL program.[1] Detailed crystal data and structure refinements for the compound are given in Tables S1and S2. CCDC 2381276 and 2381277 contain the supplementary crystallographic data for this paper. All the atoms were refined anisotropically with the exception of some solvent molecules and hydrogen atoms were placed in calculated positions refined using idealized geometries and assigned fixed isotropic displacement parameters. Intrinsic disorder in the two structures was handled with different strategies according to the electron density distribution. Structure refinement was operated with different restraints and constraints (DANG, EADP, DFIX, etc.) in the corresponding crystallographic CIF files.[2] For structure $\mathbf{Ag_{21}Cu_4}$, the H atoms of O2 and C110 were all omitted owing to the thermal vibration. Moreover, the X-ray intensity data of $\mathbf{Ag_{21}Cu_4}$ displayed no good quality because of the serious thermal vibration. The crystal structures are visualized

by DIAMOND 3.2. The detailed information of the crystal data, data collection and refinement results for all complexes are summarized in Tables S2 to Tables S3.

Table S1. Summary of Ag/Cu bimetallic clusters

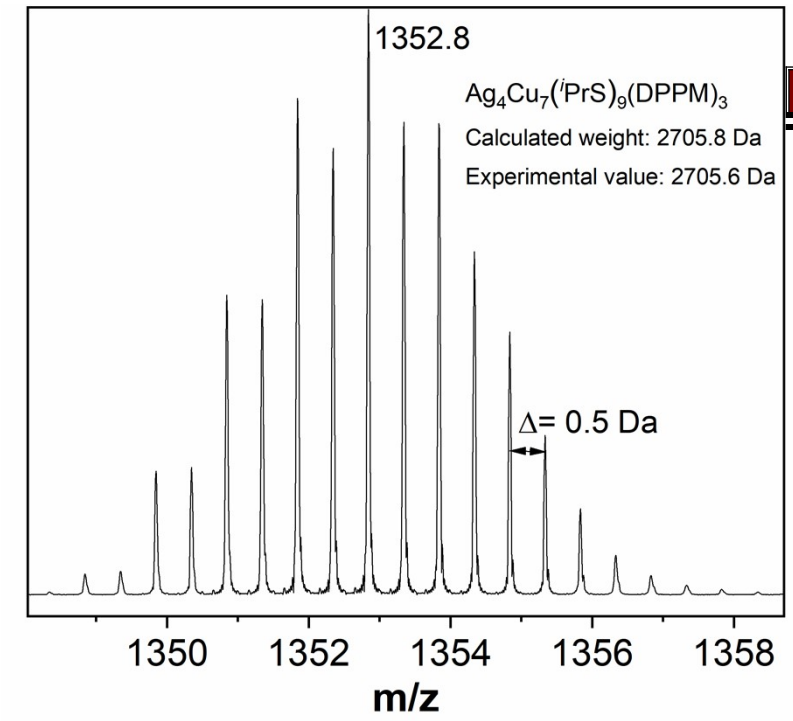
Cluster formula	Synthesis method	reference
$[Ag_{11-x}Cu_x(^{i}PrS)_9(DPPM)_3]^{2+}$	Self-assembly	**This work**
$[Ag_{21}Cu_4S_2(^{t}BuS)_{18}(CH_3CN)_4]^{3+}$		
$Ag_6Cu_8(C{\equiv}CAr)_{14}(DPPB)_2$		[3]
$[Cu_2Ag_{10}(C{\equiv}CR)_{12}(PPh)_2$		[4]
$[(SiW_9O_{34})@Ag_{34}Cu_6(^{t}BuC{\equiv}C)_{18}(^{t}BuPO_3)_9]$		[5]
$[Ag_{10}Cu_6(bdppthi)_2(C{\equiv}CPh)_{12}]$		[6]
$[Cl@Ag_8Cu_6(C{\equiv}C\mathit{Fc})_{12}]^{+}$		[7]
$Ag_6Cu(C{\equiv}CR)_3[(PPh_2)_3CH)_2](PPh_2O_2)$		[8]
$[Ag_6Cu_2(\mu\text{-}Ph_2PCH_2PPh_2)_3(C{\equiv}CR)_6(MeCN)]^{2+}$		[9]
$[Ag_{12}Cu_2(\mu\text{-}tpmp)_2(C{\equiv}CR)_{12}]^{2+}$		[10]
$[Ag_{16}Cu_9(\mu\text{-}dpepp)_3(C{\equiv}CR)_{20}]$		[11]
$[Ag_{62-x}Cu_xS_{12}(^{t}BuS)_{32}]^{4+}$	Template-method	[12]
$[Ag@Cu_{12}(S2CN^{n}Bu_2)_6(C{\equiv}CPh)_4][CuCl_2]$		[13]
$[Ag_8Cu_6(C{\equiv}C^{t}Bu)_{12}X]BF_4$		[14]
$Ag_{10}Cu_4(C{\equiv}CAr)_{14}(DPPB)_2$		[15]
$[Ag_8Cu_7(^{t}BuC{\equiv}C)_{12}]^{+}$	Co-reduction	[15]
$[Ag_9Cu_6(^{t}BuC{\equiv}C)_{12}]^{+}$		[16]
$Ag_{12}Cu_4(C{\equiv}CR)_{14}(PPh_3)_4$		[17]
$[Ag_{22}Cu_7(C{\equiv}CR)_{16}(PPh_3)_5Cl_6](PPh_4)$		[18]
$[Ag_{27}Cu_4Br_2(FUR)_{20}(TPP)_{10}]^{3+}$		[19]
$Ag_{20}Cu_{12}(C{\equiv}CAr)_{24}$		[20]
$[Ag_{37}Cu_2(PFBT)_{24}(TPP)_8]^{2-}$		[21]
$Ag_{77}Cu_{22}(CHT)_{48}$		[22]
$(^{n}Bu_4N)_4[Ag_{28}Cu_{12}(SR)_{24}]$		[23]
$[Ag_{40.13}Cu_{13.87}S_{19}(^{t}BuS)_{20}(^{t}BuSO_3)_{12}$		[24]

$Ag_{30}Cu_{14}(TPP)_4(SR)_{28}$	Co-reduction	[25]
$[Ag_{61}Cu_{30}(SAdm)_{38}S_3](BPh_4)$		[26]
$Ag_{13}Cu_{10}(SAdm)_{12}X_3$		[27]
$[Ag_{32}Cu_{12}(CH_3COO)_{12}(SAdm)_{12}(P(CH_3OPh)_3)_4]$		[28]
$[PPh_4]_4[Ag_{32}Cu_{18}(PFBT)_{36}]$		[29]
$Ag_{15}Cu_{12}(SR)_{18}(CH_3COO)_3\cdot(C_6H_{14}）$		[30]
$[Ag_{15}Cu_6(C{\equiv}CR)_{18}(DPPE)_2]^-$		[31]
$(Ph_4P)_2[Ag_{22}Cu_{12}(C{\equiv}CR)_{28}]$		[32]
$(Ph_4P)_3[Ag_{42}Cu_{12}Cl(C{\equiv}CR)_{36}]$		[32]

Table S2. Crystal data and structure refinement for $\mathbf{Ag_{11-x}Cu_x}$	
Empirical formula	$[Ag_{11-x}Cu_x(^{i}PrS)_9(DPPM)_3](PF_6)_2$
Formula weight	3088.60
Crystal system	Triclinic
Space group	*P*-1
a	18.2666(13) Å
b	21.1885(14) Å
c	21.1999(14) Å
α	60.445(2)°
β	64.889(2)°
γ	86.266(2)°
Volume	6353.8(8) $Å^3$
Z	2
ρ_{calc}	1.622 Mg/m^3
Absorption coefficient	2.027 mm^{-1}
F(000)	3096
Crystal color and habit	Orange
Theta range for data collection	2.767 to 23.256°
Index ranges	-20<=h<=20, -23<=k<=23, -23<=l<=23
Reflections collected	86630
Independent reflections	18212 [R(int) = 0.0634]
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1388
R indices (all data)	R1 = 0.0935, wR2 = 0.1647
Largest diff. peak and hole	2.024 and -0.890 $e.Å^{-3}$
CCDC number	2381276

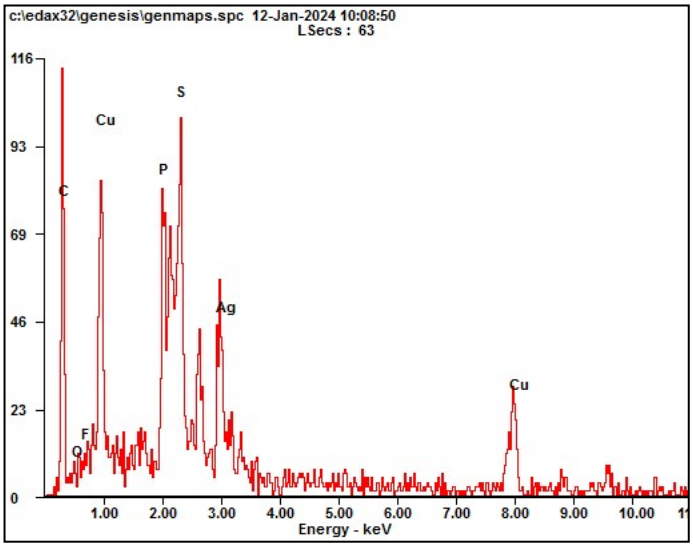
Table S3. Crystal data and structure refinement for **$Ag_{21}Cu_4$**

Empirical formula	$[Ag_{21}S_2Cu_4(^tBuS)_{18}(CH_3CN)_4](CH_3OH)_2(H_3O)(PF_6)_4$
Formula weight	5032.85
Crystal system	Triclinic
Space group	*P*-1
a	14.7623(9) Å
b	17.4036(12) Å
c	17.9645(11) Å
α	111.478(2)°
β	110.109(2)°
γ	98.581(2)°
Volume	3828.0(4) $Å^3$
Z	1
ρ_{calc}	2.183 Mg/m^3
Absorption coefficient	3.539 mm^{-1}
F(000)	2380
Crystal color and habit	Orange
Theta range for data collection	2.791 to 22.722°
Index ranges	-17<=h<=17, -20<=k<=20, -21<=l<=21
Reflections collected	31005
Independent reflections	13653 [R(int) = 0.0713]
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R1 = 0.0625, wR2 = 0.1554
R indices (all data)	R1 = 0.1101, wR2 = 0.1801
Largest diff. peak and hole	1.753 and -2.333 e $Å^{-3}$
CCDC number	2381277



Element	Wt%	At%

Fig. S1. the main peak of ESI-MS results of $\mathbf{Ag_{11-x}Cu_x}$ and peak separation.



CK	57.21	82.09
OK	02.37	02.55
FK	02.86	02.59
PK	06.44	03.58
SK	07.88	04.24
AgL	12.16	01.94
CuK	11.08	03.01
Matrix	Correction	ZAF

Fig. S2. EDS analysis of $\mathbf{Ag_{11-x}Cu_x}$.

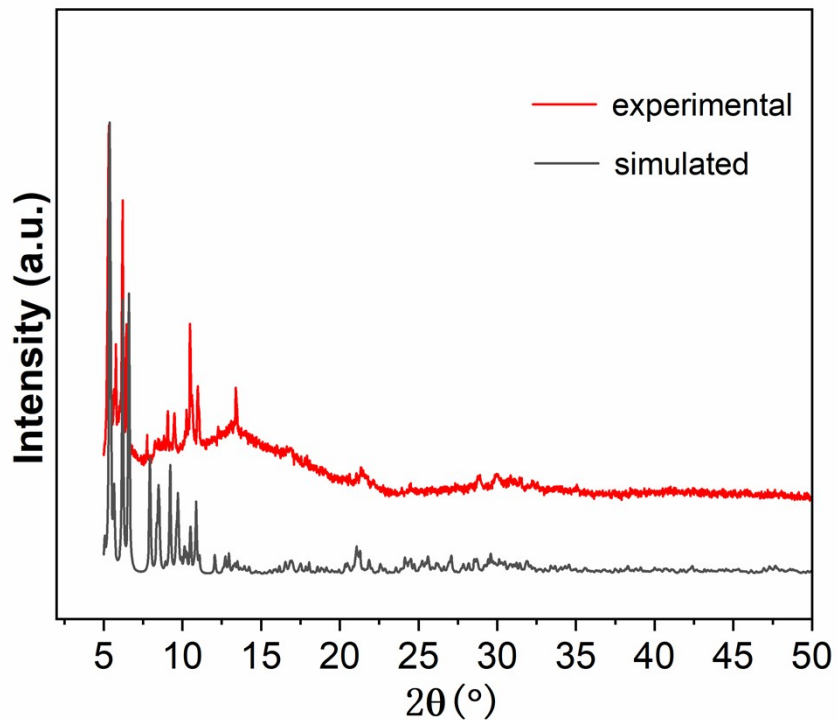


Fig. S3. Powder X-ray diffraction (PXRD) patterns of $\mathbf{Ag_{11-x}Cu_x}$.

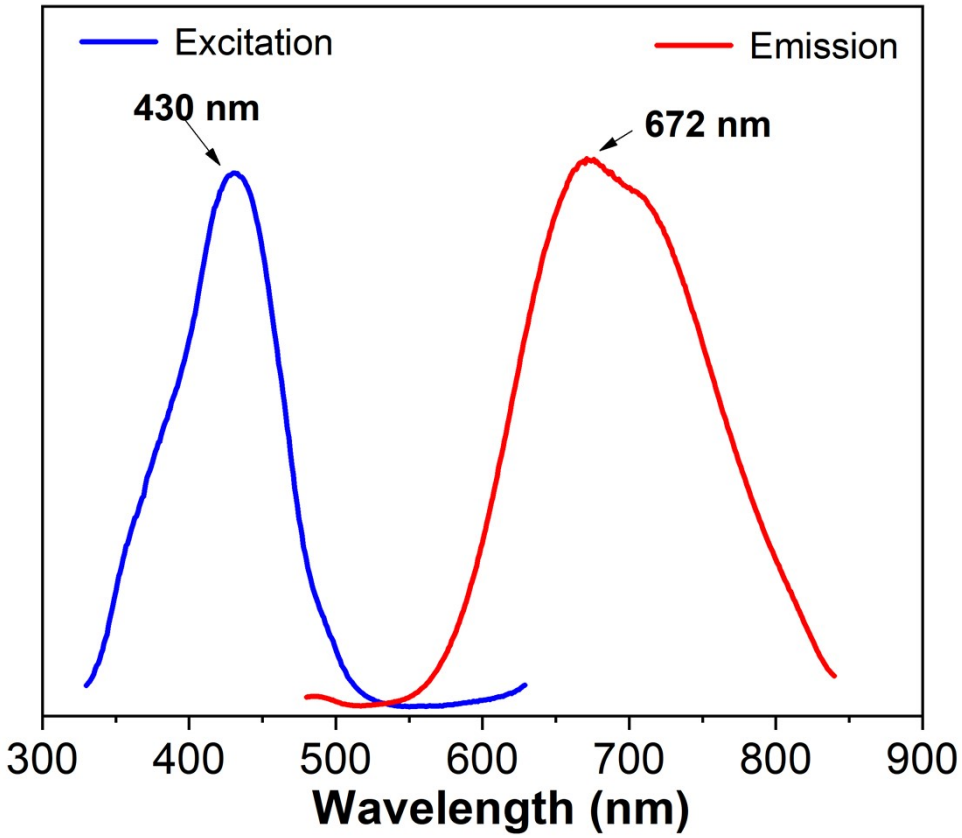


Fig. S4. Photoluminescence property of $\mathbf{Ag_{11-x}Cu_x}$ in CH_2Cl_2 solution.

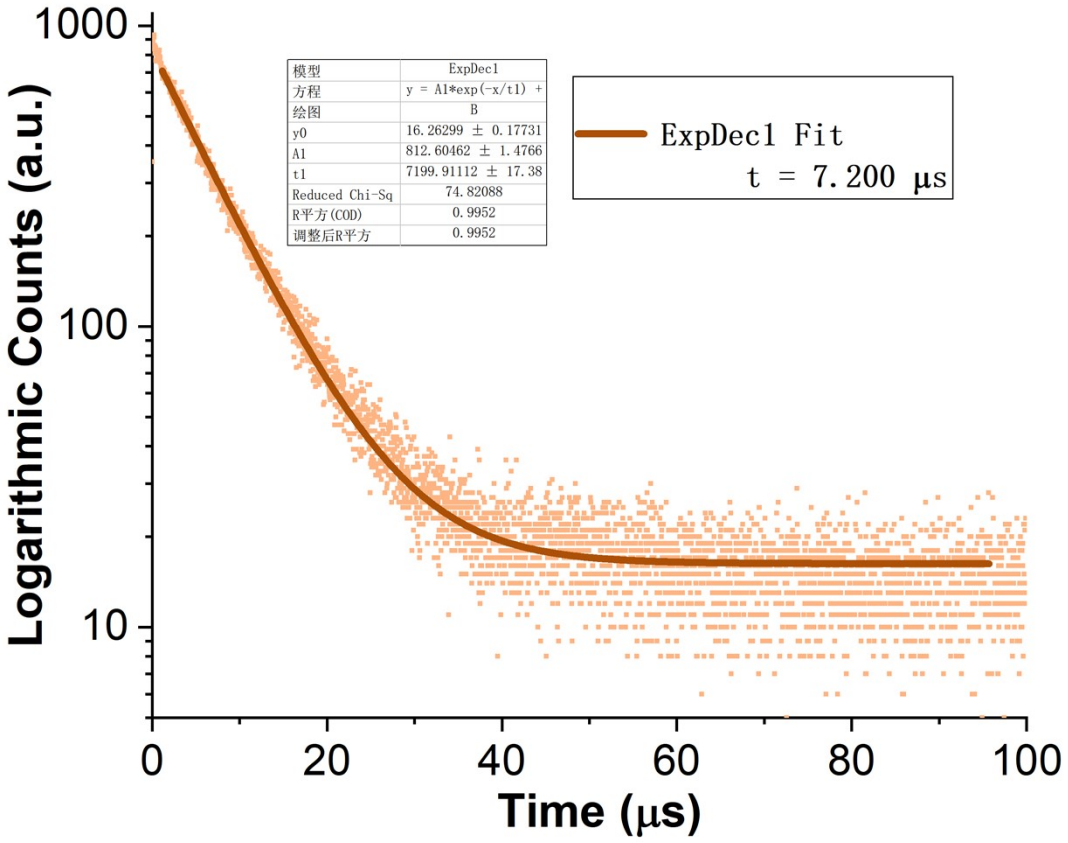


Fig. S5. Photoluminescence life analysis of $Ag_{11-x}Cu_x$ in solid state.

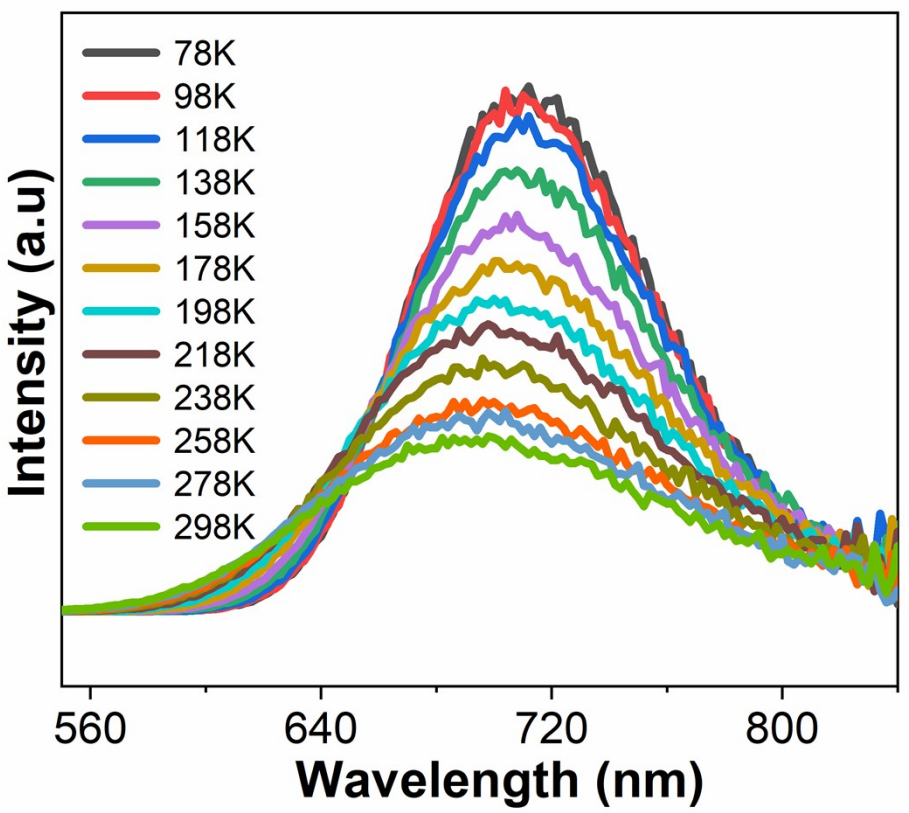
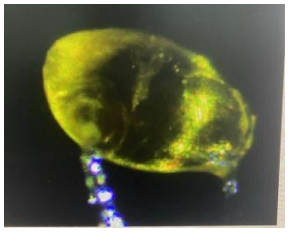
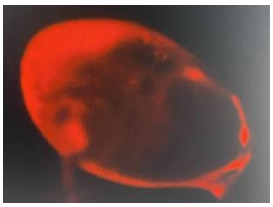


Fig. S6. Temperature-dependent emission spectra of the $\mathbf{Ag_{11-x}Cu_x}$ cluster in the solid state (λex = 467 nm).

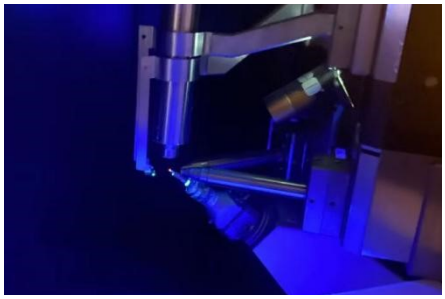


fluorescent lamp

365nm UV light/290 K

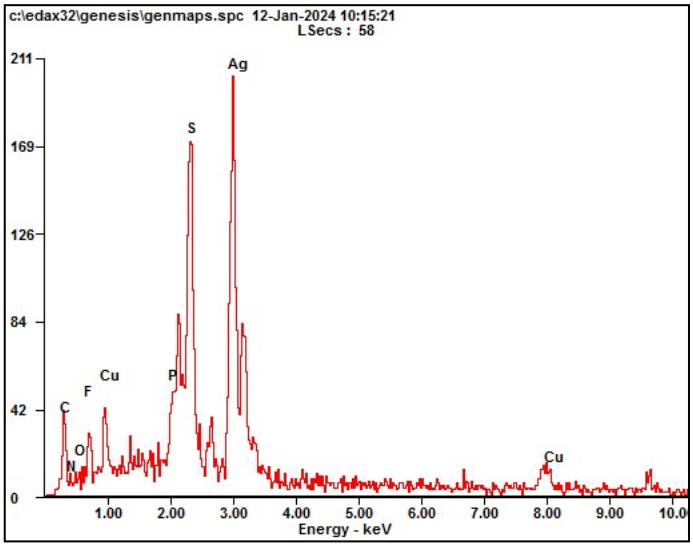


365nm UV light/173 K



Test Platform

Fig. S7.Photos of the single crystal under different excitation lights and temperature (The shadow on the surface of the single crystal is due to the use of glue to fix the single crystal on loop).



Element	Wt%	At%
CK	21.30	51.60
NK	01.70	03.53
OK	00.77	01.40
FK	08.44	12.93
PK	03.48	03.27
SK	13.98	12.68
AgL	44.97	12.13
CuK	05.35	02.45
Matrix	Correction	ZAF

Fig. S8.EDS analysis of $\mathbf{Ag_{21}Cu_4}$.

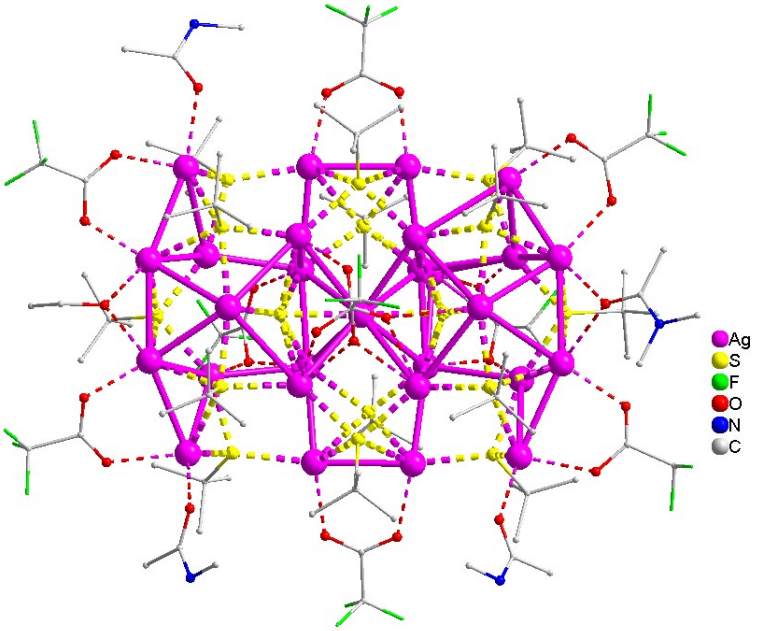


Fig. S9. Overview structure of $\mathbf{Ag_{27}}$.

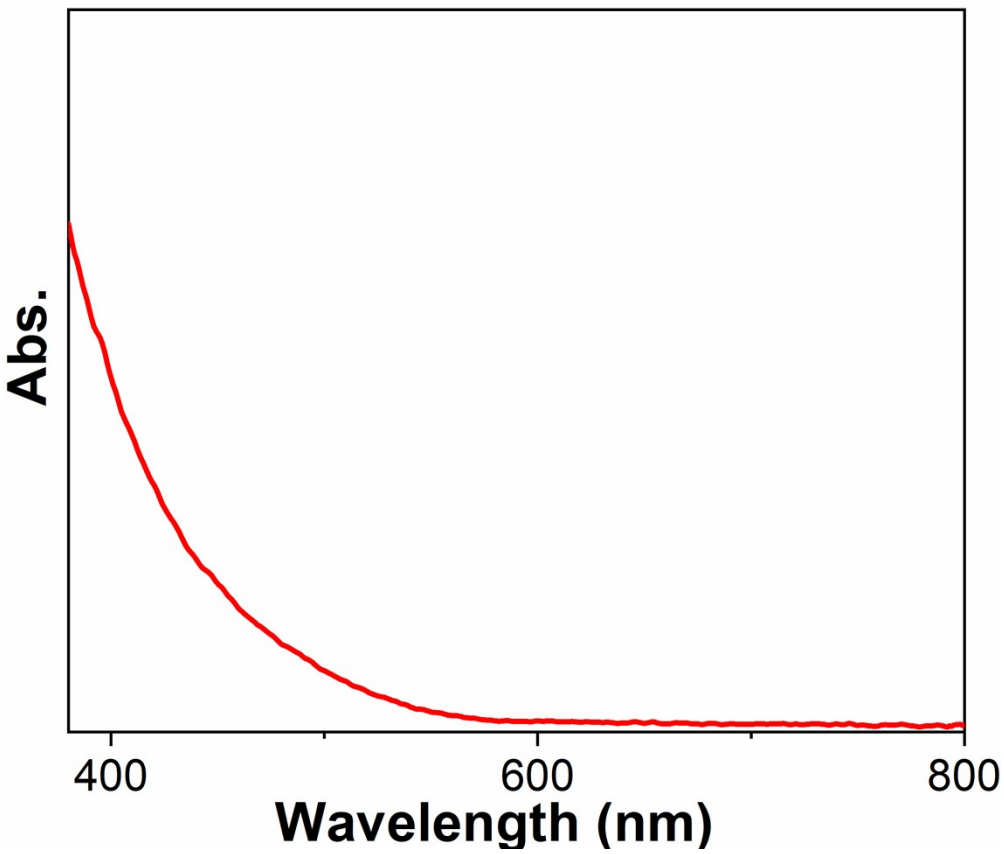


Fig. S10. UV-vis absorption spectrum of $\mathbf{Ag_{21}Cu_4}$ in CH_2Cl_2 solution.

Reference

[1] G. M. Sheldrick, *Acta Crystallogr., A Found. Adv*. **2015**, A71, 3–8.

[2] Guzei, I. A. *J. Appl. Crystallogr.* **2014**, 47, 806-809.

[3] J.-L. Jin, S.-F. Zhang, P. Zhao, Y.-L. Shen, J.-J. Fang, Z. Liu, M. Ehara, L.-W. Mi, Y.-P. Xie, X. Lu, *Chem.-Asian J.* **2023**, 18, e202300844.

[4] S. C. K. Hau, M. C. L. Yeung, V. W. W. Yam, T. C. W. Mak, *J. Am. Chem. Soc*. **2016**, 138, 13732.

[5] G.-X. Duan, Y.-P. Xie, J.-L. Jin, L.-P. Bao, X. Lu, T. C. W. Mak, Chem. *Eur. J.* **2018**, 24, 6762.

[6] Y. Wang, J.-J. Yan, S. Hu, Y. D. James, H.-X. Li, Z.-G. Ren, *Chem.-Asian J.* **2021**, 16, 2681.

[7] Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang, and Z.-N. Chen, *Organometallics* **2006**, 25,

4941.

[8] L.-J. Xu, X. Zhang, J.-Y. Wang and Z.-N. Chen, *J. Mater. Chem. C*, **2016**, 4, 1787.

[9] Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang, L.-X. Shi, Z.-W. Mao and Z.-N. Chen, *Inorg. Chem.* **2004** 43, 3484.

[10] X. Zhang, J.-Y. Wang, D. Qiao and Z.-N. Chen, *J. Mater. Chem. C*, **2017**, 5, 8782.

[11] Z.-H. Chen, L.-Y. Zhang and Z.-N. Chen, *Organometallics* **2012**, 31, 256.

[12] J. Zhou, S. Yang, Y. Tan, H. Cheng, J. Chai, M. Zhu, *Chem.-Asian J.* **2021**, 16, 2973.

[13] R. P. B. Silalahi, K. K. Chakrahari, J.-H. Liao, S. Kahlal, Y.-C. Liu, M.-H. Chiang, J.-Y. Saillard, C. W. Liu, *Chem.-Asian J.* **2018**, 13, 500.

[14] T. U. Connell, S. Sandanayake, G. N. Khairallah, J. M. White, R. A. J. O'Hair, P. S. Donnelly, S. J. Williams, *Dalton Trans.* **2013**, 42, 4903.

[15] Y.-L. Shen, D. Liu, X. Li, *J. Clust. Sci*. **2024**, 35, 1959.

[16] X. Ma, L. Xiong, L. Qin, Y. Tang, G. Ma, Y. Pei and Z. Tang, *Chem. Sci*. **2021** 12, 12819.

[17] G. Deng, K. Lee, H. Deng, M. S. Bootharaju, N. Zheng and T. Hyeon, *J. Phys. Chem. C* **2022**, 126, 20577.

[18] G. Deng, K. Lee, H. Deng, S. Malola, M. S. Bootharaju, H. Häkkinen, N. Zheng and T. Hyeon, *Angew. Chem. Int. Ed*. **2023**, 62, e202217483.

[19] L. Fang, W. Fan, G. Bian, R. Wang, Q. You, W. Gu, N. Xia, L. Liao, J. Li, H. Deng, N. Yan and Z. Wu, *Angew. Chem. Int. Ed*. **2023**, 62, e202305604.

[20] G. Ma, F. Sun, L. Qiao, Q. Shen, L. Wang, Q. Tang and Z. Tang, Nano Res. **2023**, 16, 10867.

[21] X.-H. Ma, Y. Si, L.-L. Luo, Z.-Y. Wang, S.-Q. Zang and T. C. W. Mak, *ACS Nano* **2022**, 16, 5507.

[22] N. Xia, J. Xing, D. Peng, S. Ji, J. Zha, N. Yan, Y. Su, X. Jiang, Z. Zeng, J. Zhao and Z. Wu, *Nat. Commun.* **2022**, 13, 5934.

[23] J. Yan, H. Su, H. Yang, C. Hu, S. Malola, S. Lin, B. K. Teo, H. Häkkinen and N. Zheng, *J. Am. Chem. Soc*. 2016, **138**, 12751.

[24] S. Yang, J. Chai, H. Chong, Y. Song, H. Yu and M. Zhu, *Chem. Commun*. **2018,** 54, 4314.

[25] J. Li, H. Li, H. Yu, J. Chai, Q. Li, Y. Song, Z. Zhang and M. Zhu, *Dalton Trans.* **2020**, 49, 7684.

[26] 11.X. Zou, Y. Li, S. Jin, X. Kang, X. Wei, S. Wang, X. Meng and M. Zhu, *J. Phys. Chem. Lett*. **2020**, 11, 2272 .

[27] 12.Y. Bao, X. Wu, H. Gao, M. Zhou, S. Chen, S. Jin, H. Yu and M. Zhu, *Dalton Trans.* **2020**, 49, 17164.

[28] J. Chai, S. Yang, T. Chen, Q. Li, S. Wang and M. Zhu, *Inorg. Chem*. **2021**, 60, 9050.

[29] X.-H. Ma, J.-T. Jia, P. Luo, Z.-Y. Wang, S.-Q. Zang and T. C. W. Mak, *Nano Res*. **2022**, 15, 5569.

[30] Z. Lin, T. Zhang, C. Fang, S. Jin, C. Xu, D. Hu and M. Zhu, *Dalton Trans*. **2023,** 52, 971.

[31] G. Deng, J. Kim, M. S. Bootharaju, F. Sun, K. Lee, Q. Tang, Y. J. Hwang and T. Hyeon, *J. Am. Chem. Soc.***2023***,* 145, 3401.

[32] F. Hu, Z.-J. Guan, S.-F. Yuan and Q.-M. Wang, *Chem. Asian J.* **2023**, 18, e202300605.