JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: J. Am. Chem. Soc. 2018, 140, 1069–1076

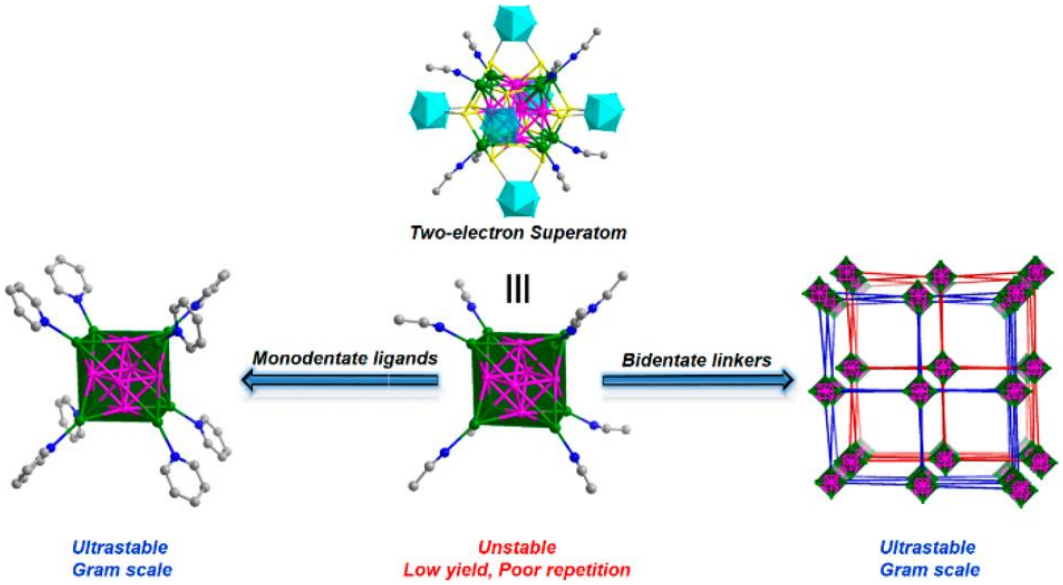
pubs.acs.org/JACS

Atomically Precise Site-Specific Tailoring and Directional Assembly of Superatomic Silver Nanoclusters

Zhao-Yang Wang,[†] Meng-Qi Wang,[†] Yan-Ling Li,[†] Peng Luo,[†] Tong-Tong Jia,[†] Ren-Wu Huang,[†] Shuang-Quan Zang,*[,†] and Thomas C. W. Mak[†,‡]

[†]College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China

[‡]Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories Hong Kong SAR, China



nature materials

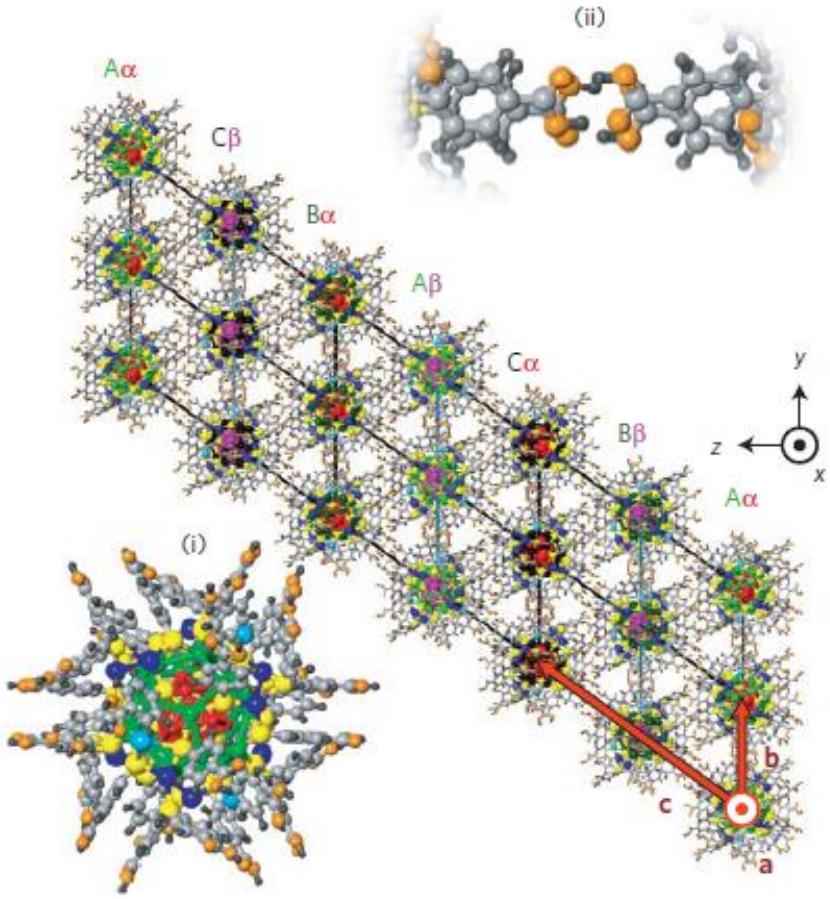
LETTERS

PUBLISHED ONLINE: 6 APRIL 2014 | DOI: 10.1038/NMAT3923

Hydrogen-bonded structure and mechanical chiral response of a silver nanoparticle superlattice

Bokwon Yoon[1], W. D. Luedtke[1], Robert N. Barnett[1], Jianping Gao[1], Anil Desireddy[2], Brian E. Conn[2], Terry Bigioni[2] and Uzi Landman[1]*

NATURE MATERIALS | VOL 13 | AUGUST 2014 |



JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

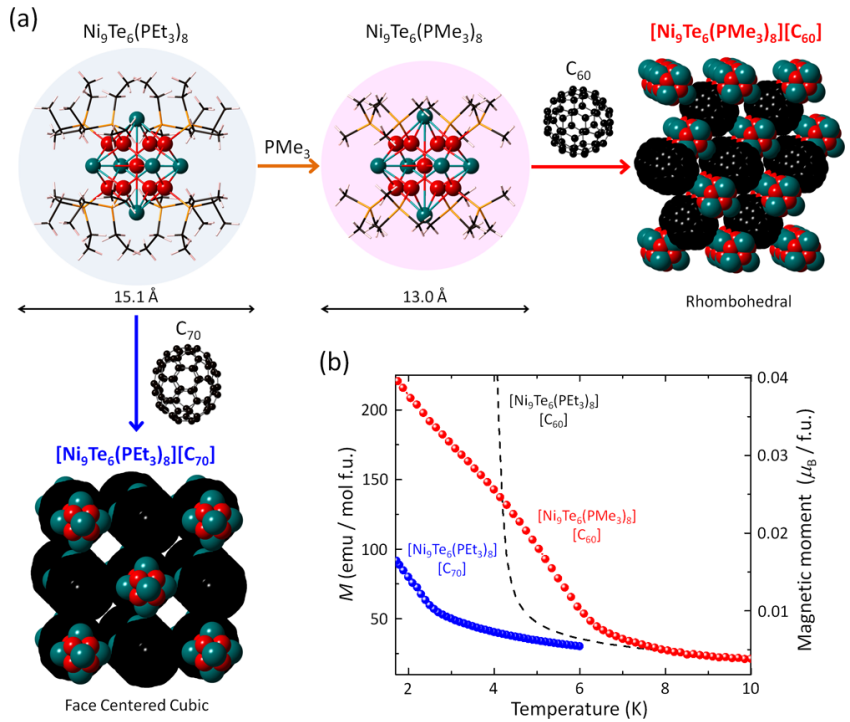
Article

pubs.acs.org/JACS

Ferromagnetic Ordering in Superatomic Solids

Chul-Ho Lee,[†,‡,§] Lian Liu,[‡] Christopher Bejger,[†] Ari Turkiewicz,[†] Tatsuo Goko,[‡] Carlos J. Arguello,[‡] Benjamin A. Frandsen,[‡] Sky C. Cheung,[‡] Teresa Medina,[∥] Timothy J. S. Munsie,[∥] Robert D'Ortenzio,[∥] Graeme M. Luke,[∥] Tiglet Besara,[⊥] Roger A. Lalancette,[▽] Theo Siegrist,[⊥,#] Peter W. Stephens,[○] Andrew C. Crowther,[◆] Louis E. Brus,[¶] Yutaka Matsuo,[¶] Eiichi Nakamura,[¶] Yasutomo J. Uemura,[‡] Philip Kim,[+] Colin Nuckolls,[†] Michael L. Steigerwald,[†] and Xavier Roy*[,†]

dx.doi.org/10.1021/ja5098622 | J. Am. Chem. Soc. 2014, 136, 16926−16931



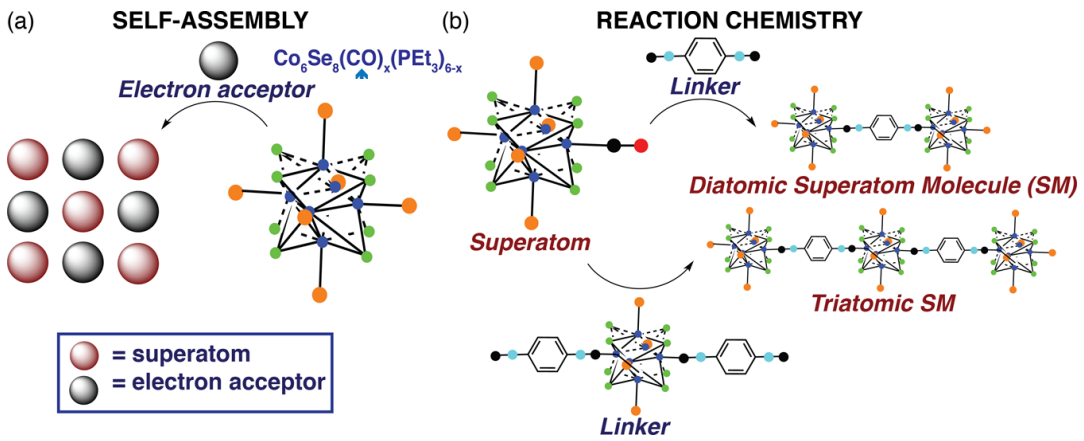
NANO LETTERS
Letter
pubs.acs.org/NanoLett

Building Diatomic and Triatomic Superatom Molecules

Anouck M. Champsaur, Alexandra Velian, Daniel W. Paley, Bonnie Choi, Xavier Roy,* Michael L. Steigerwald,* and Colin Nuckolls*

Department of Chemistry, Columbia University, New York, New York 10027 United States

DOI: 10.1021/acs.nanolett.6b02471
Nano Lett. 2016, 16, 5273−5277



1,4-phenylene diisocyanide,

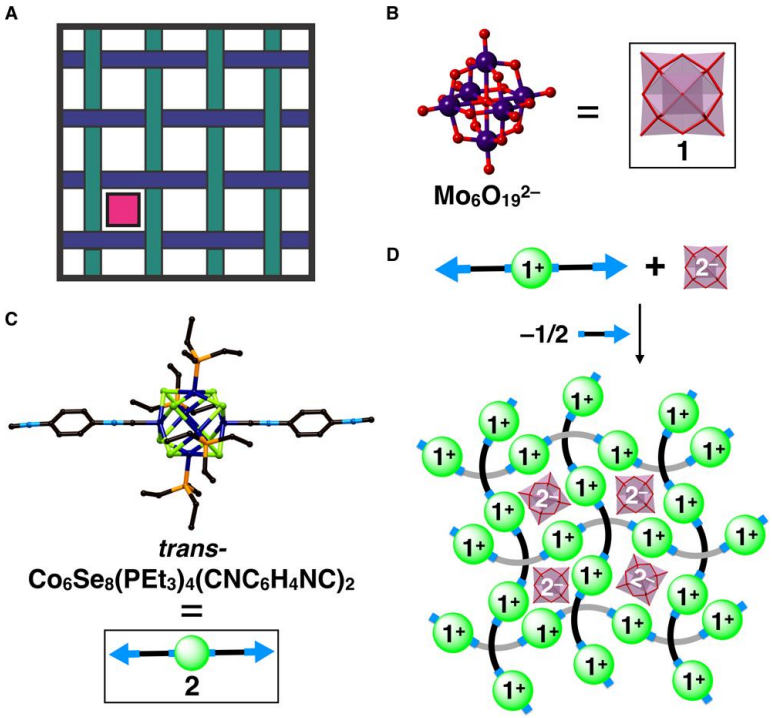
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Weaving Nanoscale Cloth through Electrostatic Templating

Anouck M. Champsaur,[†] Cécile Mézière,[‡] Magali Allain,[‡] Daniel W. Paley,[†,§] Michael L. Steigerwald,*[,†] Colin Nuckolls,*[,†] and Patrick Batail*[,†,‡]

[†]Department of Chemistry, Columbia University, New York, New York 10027, United States
[‡]Laboratoire MOLTECH, CNRS UMR 6200, Université d'Angers, 49045 Angers, France
[§]Columbia Nano Initiative, Columbia University, New York, New York 10027, United States

DOI: 10.1021/jacs.7b07279
J. Am. Chem. Soc. 2017, 139, 11718–11721



benzene bis-1,4-isonitrile

- New type ligand having reducing property
- N- Heterocyclic linker for assembly formation
- Cluster assembled materials have different properties and applications

Introduction

- Highly stable superatomic silver nanoclusters with atomically precise structure remains a great challenge, and to custom-tailor and assemble them as identical building blocks at the atomic level are even more difficult.

- Tailoring specific sites on a metal cluster surface can be expected to be capable of tuning their stability and functionality. However, variation of protecting motif invariably induces partial or complete dissection, resection, or even reconstruction of the metallic structure

- Controlled-assembly of superatomic clusters or atomically defined metal nanoclusters into extended solids are highly sought, because incorporating these unique building blocks into extended lattices would create more improved or coupled physical properties for application.

This paper

- Here, for the first time, a wide footprint and functional 1,2- dithiolate-o-carborane was employed to protect fcc-Ag_{14} clusters.

- The first-formed Ag^0-containing superatom compound, $[Ag_{14}(C_2B10H_{10}S_2)_6(CH_3CN)_8]\cdot 4CH_3CN$, was prepared via synchronous selfreduction by the 1-thiol-o-carborane ligand.

- Moreover, with such desired superatomic building blocks and length-variable bidentate N-heteroaromatic ligands [pyrazine, dipyridin-4-yl-diazene (dpd), 4,4′-bipyridine (bpy), 1,4-bis(4-pyridyl)benzene (dpbz)], we built unprecedented 1D-to-3D superatomic silver clusterassembled materials (SCAM-1,2,3,4) via site-specific and directional covalent-bond connection.

Synthesis of NC-1 by Self-Reduction of Ligand and Site-Specific Tailoring and Functionalizing Superatoms

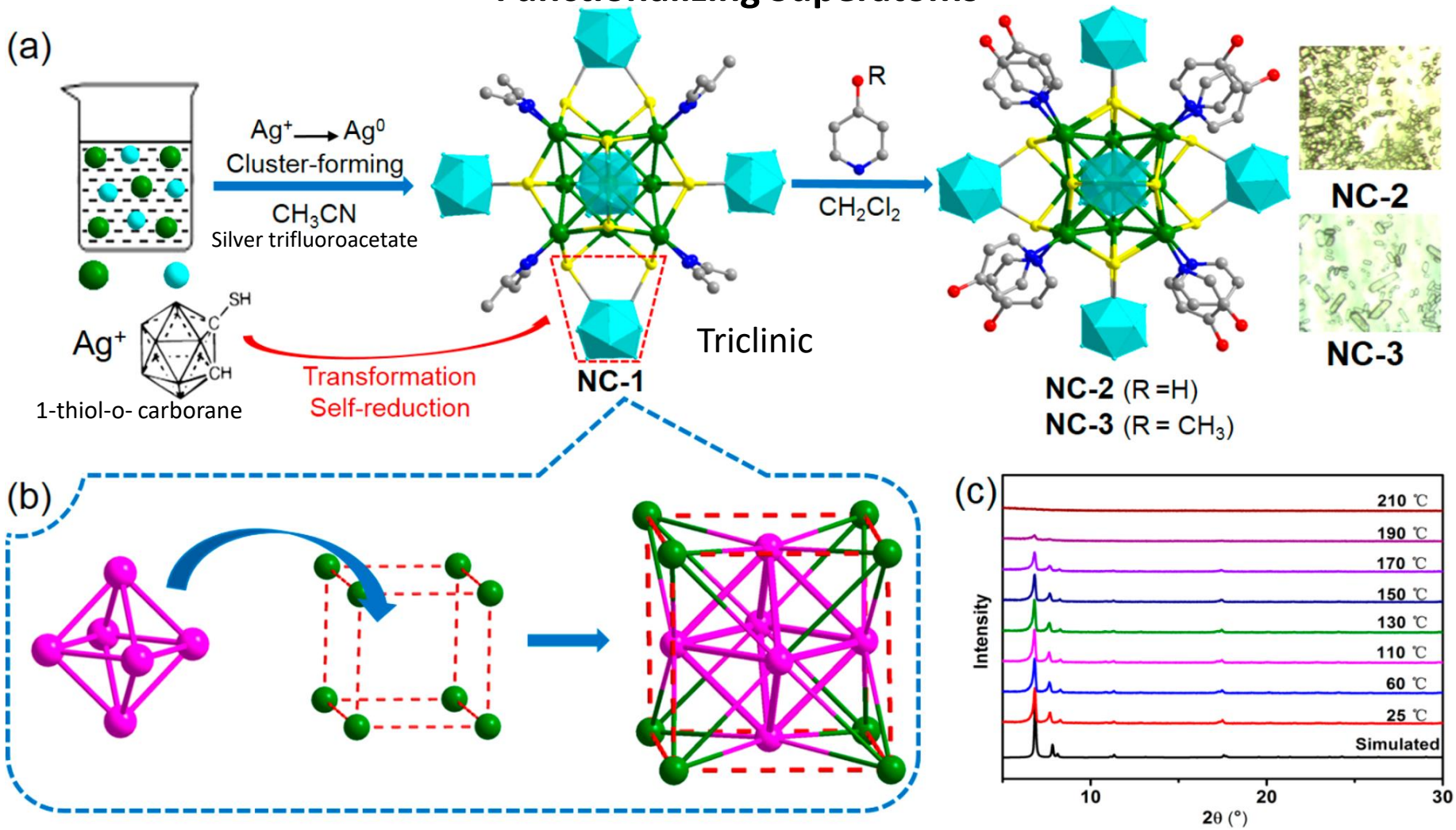
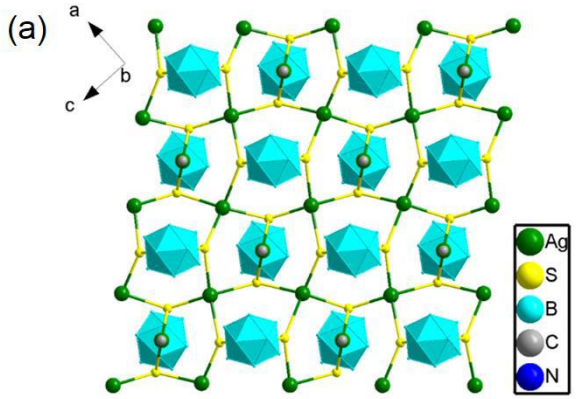


Figure 1. (a) Synthesis of desired Ag_{14} NCs; note that the (fcc) array (represented by green spheres) of Ag_{14} superatoms are stabilized by facecappin 1,2-dithiolate-o-carborane ($C_2B_{10}H_{10}S_2$) ligands. (b) Structural dissection of NC-1. (c) Variable-temperature PXRD patterns of NC-2. Color codes: green and pink = silver; yellow = sulfur; gray = carbon; blue = nitrogen; turquoise = carborane

Assembly and Structures of Superatomic Silver Cluster Networks



$[Ag_2(C_2B_{10}H_{10}S_2)(CH_3CN)_2]_n$

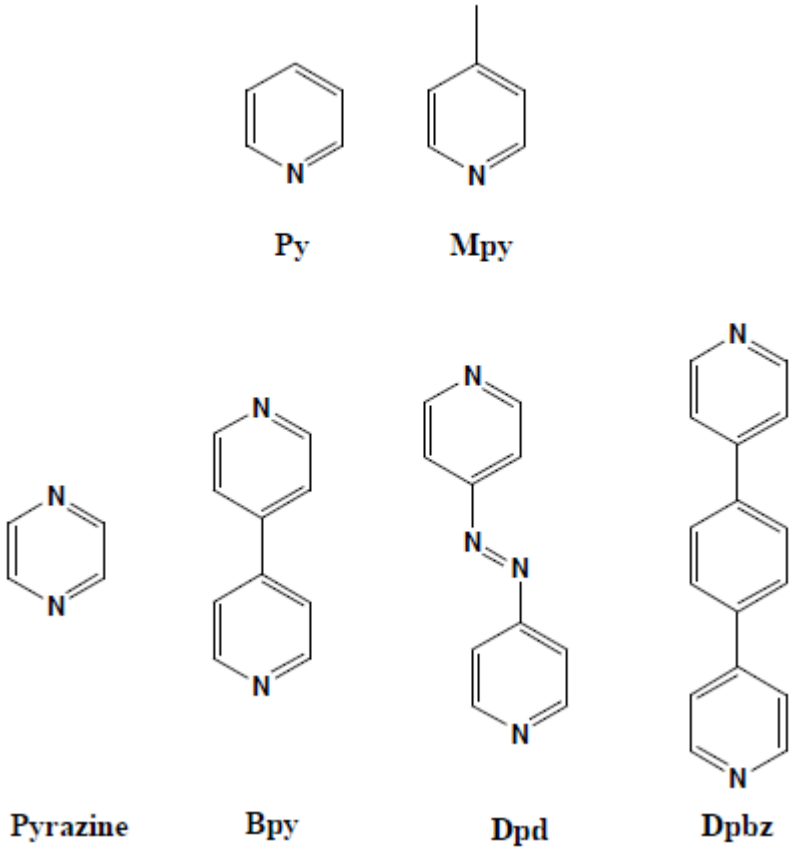
1,2-dithiol-o-carborane

+

Silver trifluoroacetate (ACN)

↓ Stirring

Microcrystals (recrystallized from DMF)



pyrazines

dipyridin-4-yl-diazene

4,4’-bipyridines.

1,4-bis(4-pyridyl)benzene

Superatomic cluster-assembled materials

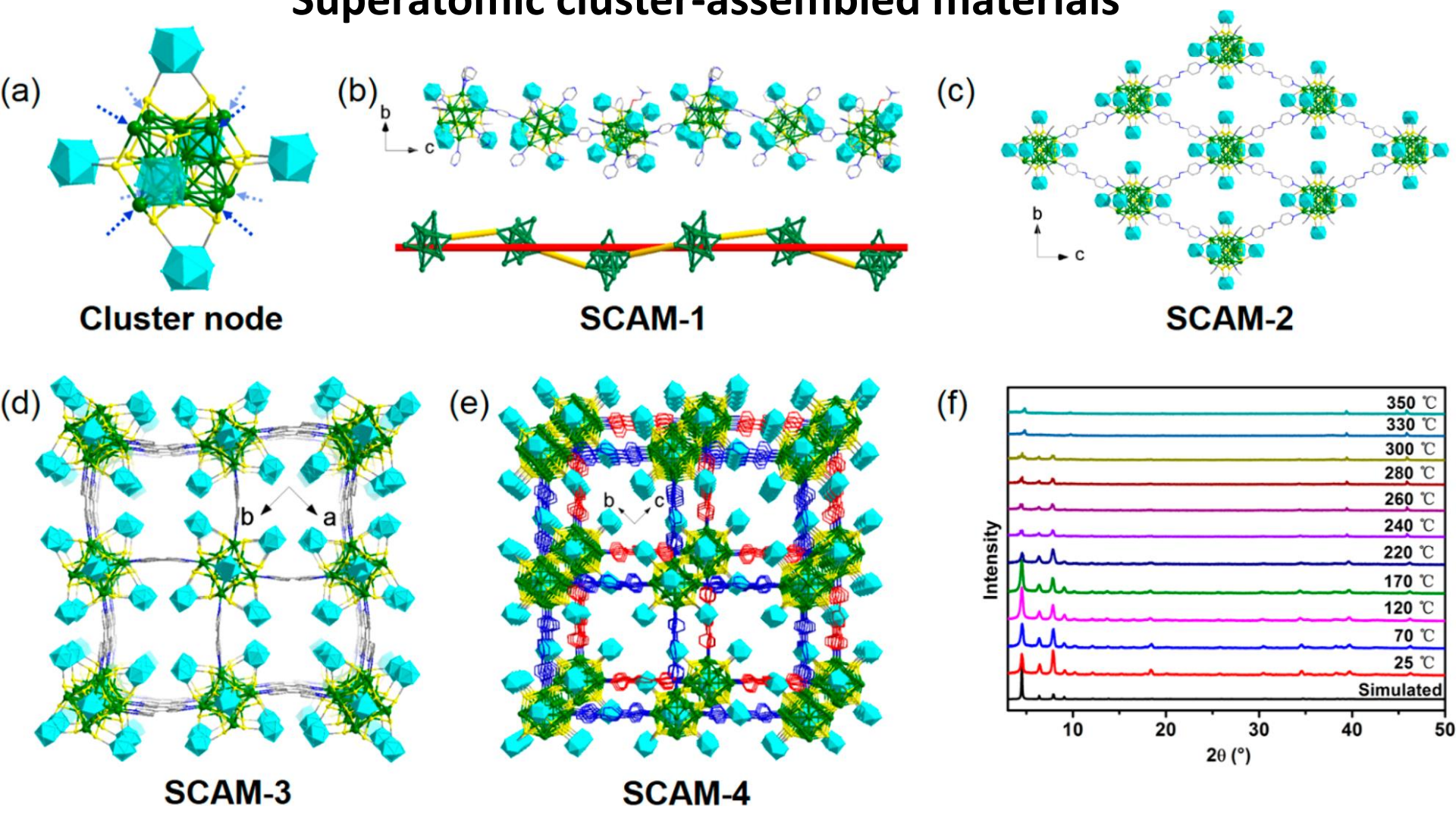
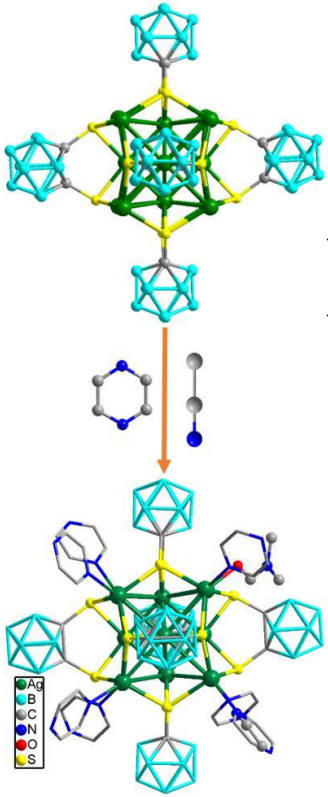
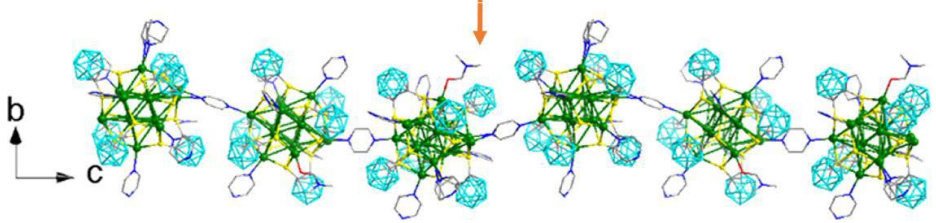


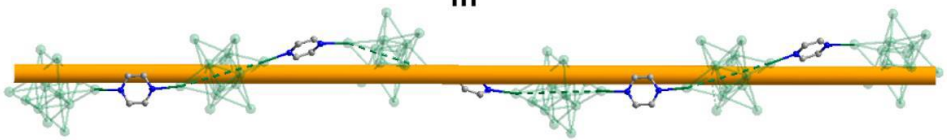
Figure 2. Structural represention of (a) 1,2-dithiolate-o-carborane-capped superatomic silver cluster, (b) 1D helix of SCAM-1, (c) 2D grid network of SCAM-2, (d) 3D porous framework of SCAM-3, and (e) 2-fold interpenetrated porous 3D frameworks of SCAM-4. (f) Variable-temperature PXRD of SCAM-4 from 25 °C to 350 °C.



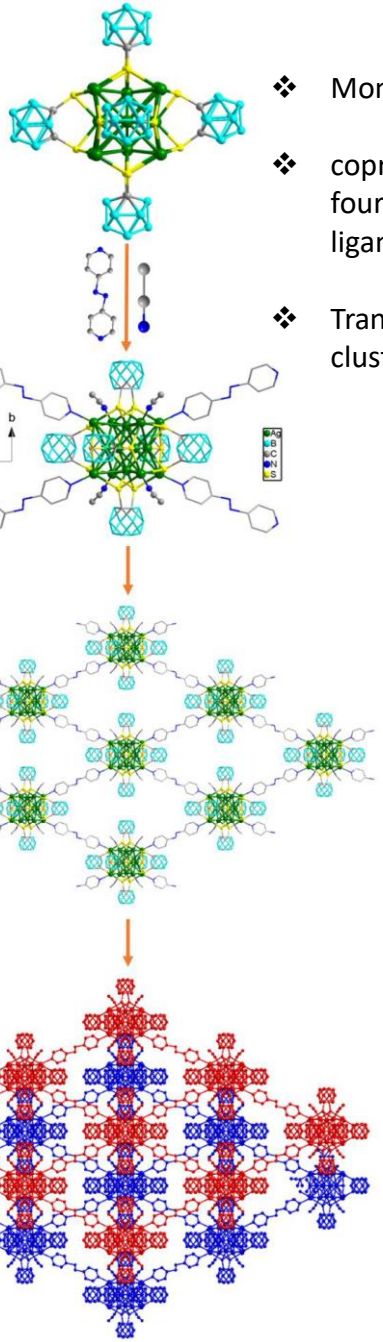
- Trigonal
- Connected only in diagonal direction



III

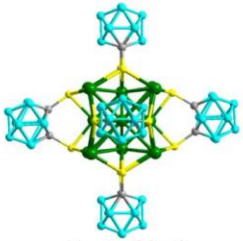


SCAM-1 pyrazines

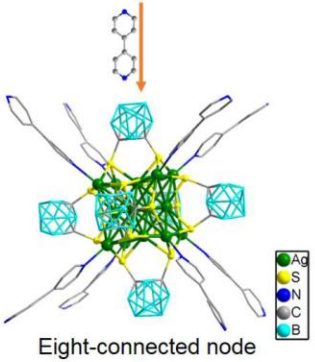


- Monoclinic
- coprotected by four CH_3CN and four dipyridin-4-yl diazene ligands
- Trans ligand further link the cluster and make a sheet

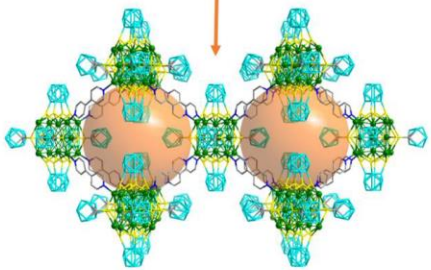
SCAM-2 dipyridin-4-yl-diazene



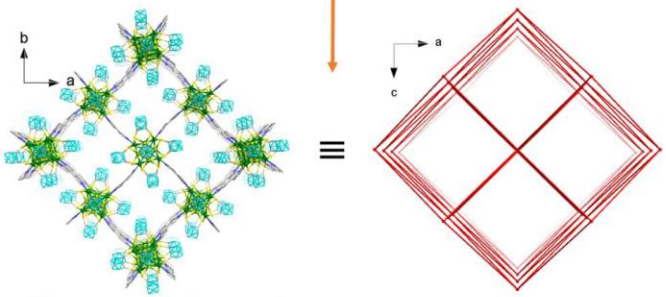
Cluster block



Eight-connected node



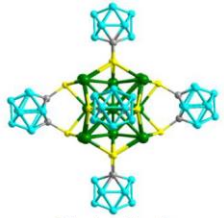
Octahedral SBUs



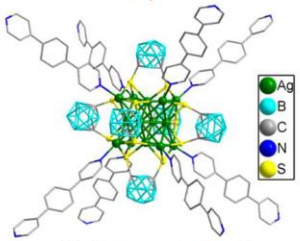
3D large porous framework bcu-type topology

- Tetragonal
- Assembled with all eight vertices of the fcc cluster coprotected with 4,4;-bipyridines
- The second building units (SBUs) can be seen as octahedral cages with six clusters on the vertices and six ligands on the edges

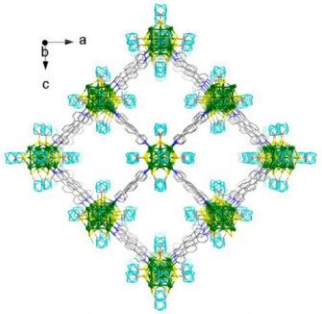
SCAM-3 4,4’-bipyridines.



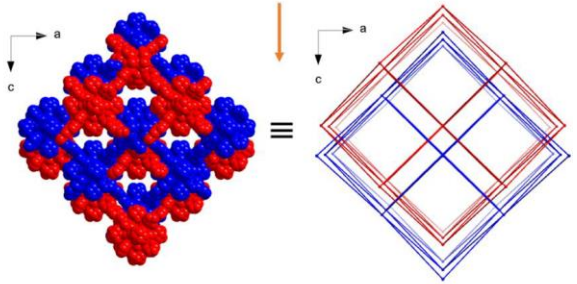
Cluster block



Eight-connected node



3D porous framework



Two-fold interpenetrated porous structure bcu-type topology

- Tetragonal.
- A pair of parallel interwoven 3D frame work.
- Carborane occupy the intersites.
- High porosity: pore size= 1.12 nm and surface area=69.3m2/g
- High stability up to 220˚C

SCAM-4 1,4-bis(4-pyridyl)benzene

Optical Absorption of NC-2,3 and SCAM-4,

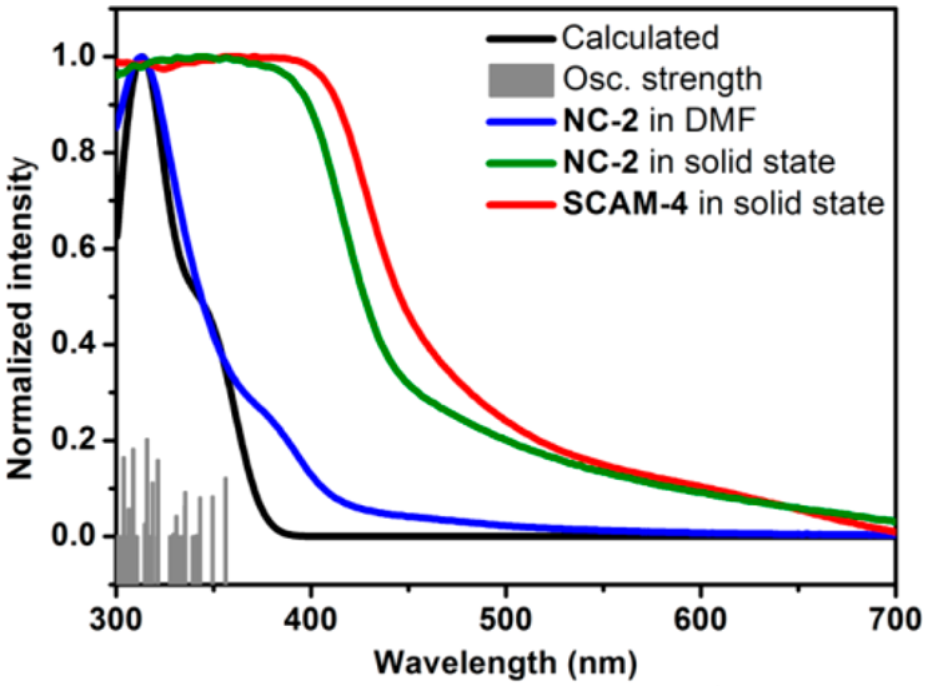


Figure 3. (a) Computed optical absorption spectrum of the cluster NC-2 (black) compared to the experimental data (blue). Gray bars show the individual transitions (delta-function-like peaks showing the relative oscillator strengths) (Table S1). The continuous computational spectrum is sums of Gaussian smoothed individual transitions (width of 15 nm). The intensity of the computational spectrum is scaled so that the dominant peaks are approximately of similar intensity.

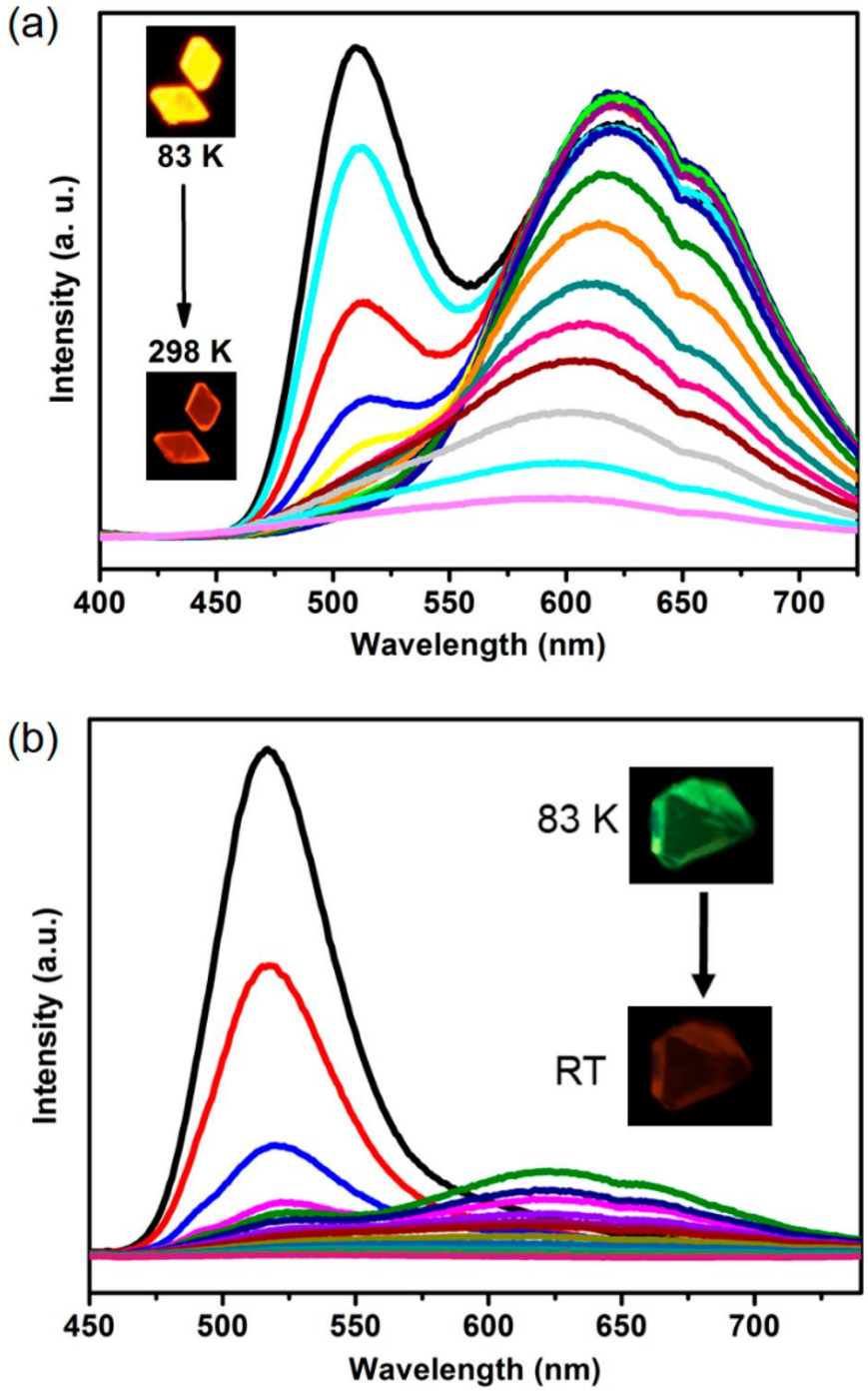


Figure 4. Variable-temperature emission spectra of (a) solid-state NC-2 (exited at 370 nm) and (b) the evacuated SCAM-4 (excited at 380 nm) from 83 K to 298 K in air. Inset: the corresponding photographs of NC-2 and SCAM-4 under 365 nm UV irradiation.

Conclusion

- 1,2-dithiolate-o-carborane was employed in the ligand shell to protect a 2e fcc-Ag_{14} superatom.

- The one-pot synthesis involved synchronous Ag^{+} to Ag^{0} by self-reduction of the thiol ligand and the formation of the unstable superatomic silver cluster NC-1.

- Site-specific surface modification of NC-1 with pyridyl-type ligands afforded highly thermostable superatomic clusters.

- various 1D-to-3D superatomic silver cluster-assembled materials were predesigned and obtained through progressively optimized ligand-bridging approach.