

In summary, novel red and blue phosphors have been developed through tuning the local crystal-line environments of the activated ions. This concept opens a way to develop new phosphors with high luminescent quality. (Reported by Yu-Jong Wu)

This report features the work of (1) Ru-shi Liu and his co-workers published in *Angew. Chem. Int. Ed.* **57**, 1797 (2018); (2) Lixin Ning, Zhiguo Xia and their co-workers published

in *J. Am. Chem. Soc.* **140**, 9730 (2018).

TPS 09A Temporally Coherent X-ray Diffraction TLS 01C2 SWLS – X-ray Powder Diffraction

- X-ray Powder Diffraction
- Luminescent Materials

References

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Inverse-Coordination Clusters from a Two-Electron Superatomic Copper Nanocluster

The inverse-coordination clusters show enhanced luminescence properties and increased ionic component of the host–guest interaction. No formal covalent bonding exists between the d^{10} metal centers, only some metallophilic interactions.

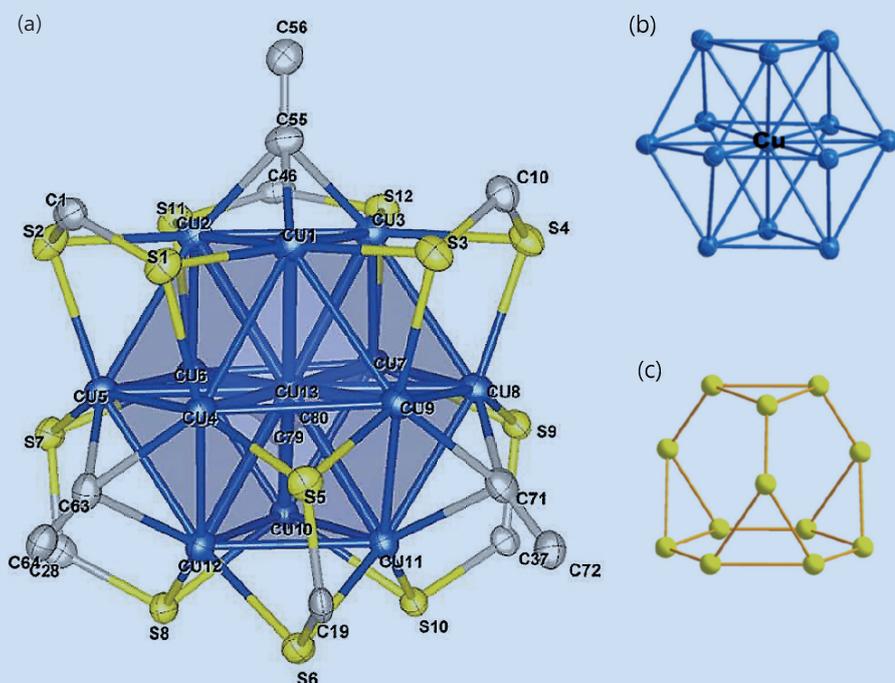


Fig. 1: (a) X-ray structure of $[\text{Cu}_{13}(\text{S}_2\text{CN}^n\text{Bu}_2)_6\text{X}_4]^+$ with N^nBu_2 and X moieties omitted for clarity; (b) centred cuboctahedral framework of 13 copper atoms; (c) 12 sulfur atoms that surround the copper core in a truncated tetrahedral geometry. [Reproduced from Ref. 2]

The concept of inverse coordination, as recently defined by Haiduc, applies to metal complexes in which the arrangement of acceptor and donor sites is opposite that occurring in Werner-type coordination complexes. Inverse-coordination complexes are formed around a non-metal species as the central atom (ion) surrounded by a number of metal atoms (ions) connected or not by internal bridging (intramolecular) linkers. Discarding the nature of metal–metal interactions (if any), inverse coordination complexes can thus be viewed simply as transition-metal clusters (with or without metal–metal bonding) encapsulating a main-group anion.

Centred cuboctahedral copper clusters have been synthesized and structurally characterized in a series. $[\text{Cu}_{13}\{\text{S}_2\text{CNR}_2\}_6\{\text{C}\equiv\text{CR}'\}_4](\text{PF}_6)_n$, ($\text{R} = n\text{-Bu}$, $\text{R}' = \text{CO}_2\text{Me}$) is the first structurally characterized copper

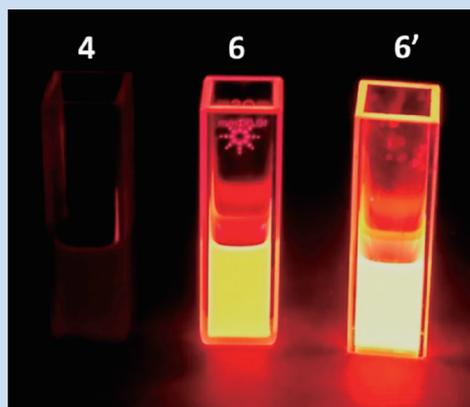


Fig. 2: Photograph of 4, 6, and 6' under UV-excitation at ambient temperature. [Reproduced from Ref. 2]

cluster having a Cu_{13} centred cubo-octahedral arrangement, **Fig. 1(a)**, a miniature of the bulk copper fcc structure. Inverse-coordination clusters with Cu_{12} , $[\text{Cu}_{12}(\mu_{12-\text{S}})\{\text{S}_2\text{CNR}_2\}_6\{\text{C}\equiv\text{CR}'\}_4]^+$, are the first examples of copper clusters containing main-group elements (Cl, Br, S). These clusters show enhanced luminescence properties and increased ionic component of the host-guest interaction, **Figs. 1(b) and 1(c)**. No formal covalent bonding exists between the d^{10} metal centers, only some metallophilic interactions.

In a first approximation, the bonding within these two-electron superatoms can be described as resulting from the interaction of an encapsulated and formally M^- anion with a cubo-octahedral cage composed of twelve Cu^+ ions. One fascinating query is whether it should be possible to substitute the encapsulated closed-shell M^- anion with a closed-shell main-group anion, and further, to replace this encapsulated main-group element with another one, the corresponding substitution reactions occurring without cluster disintegration.

The galvanic exchange of the central Cu with Ag or Au results in a similar anatomy of formed bimetallic $[\text{Au}/\text{Ag}@\text{Cu}_{12}(\text{S}_2\text{CN}^n\text{Bu}_2)_6(\text{C}\equiv\text{CPh})_4][\text{CuC}_{12}]$ species, which is unique in

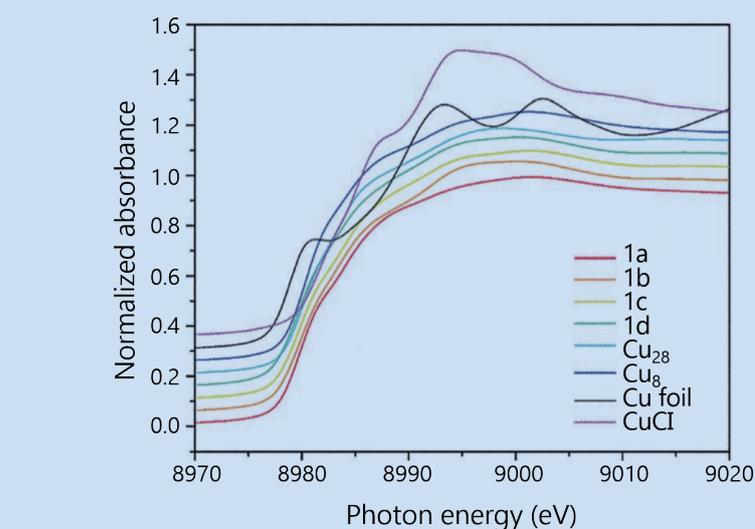


Fig. 3: Comparison of Cu K-edge XANES profiles for Cu foil, CuCl, copper(I) hydrides and NCs 1a–d (see ref. 1 for the abbreviation). [Reproduced from Ref. 1]

the sense that other contemporary M_{13} cores in group 11 superatomic chemistry are compact icosahedra. The central doping of Ag or Au significantly affects the physiochemical properties of the bimetallic Cu-rich clusters. Markedly enhanced both emission intensity and quantum yield was observed in gold–copper alloys $[\text{Au}@\text{Cu}_{12}(\text{S}_2\text{P}(\text{O}i\text{Pr})_2)_6(\text{C}\equiv\text{CPh})_4]^+$ (6, 6') on comparison with cluster $[\text{Cu}_{13}\{\text{S}_2\text{CN}^n\text{Bu}_2\}_6\text{R}_4]^+$ (4) (**Fig. 2**).

In summary, the authors have isolated and fully characterized $[\text{Cu}_{13}(\text{alkynyl})_4(\text{dtc})_6](\text{PF}_6)$ clusters, the first copper-centred cubo-octahedral copper NC, a miniature of the bulk copper fcc structure, with partial $\text{Cu}(0)$ character confirmed with XANES (**Fig. 3**). Novel chalcogen and halogen-centred cubo-octahedral copper clusters $[\text{Cu}_{12}(\text{m}_{12-\text{X}})(\text{alkynyl})_4(\text{dtc})_6]^{2+}$ ($\text{E} = \text{Cl}, \text{Br}, \text{S}$) have been synthesized. These clusters are the first examples of compounds in which a sulfide, chloride or bromide ion holds such a large coordination number (12). Before this report, the largest coordination number for sulfur and bromine was nine, and eight for chlorine. (Reported by Hwo-Shuenn Sheu)

This report features the work of Chen-Wei Liu and his collaborators published in Chem. Sci., 9, 6785 (2018).

TLS 17C1 W200 – EXAFS

- XANES, ESI-MS, ^1H , ^{13}C NMR, XRD
- Materials Science, Hyper-coordination Number Chemistry, Superatomic Copper Nanocluster, Luminescence

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