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## Eight-electron copper-hydride nanoclusters: synthesis, structure, alloying chemistry and photoluminescence†

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The first copper-hydride nanocluster featuring eight free valence electrons has been successfully isolated and characterized spectroscopically. The structure of the nanocluster, represented by the chemical formula  $[\text{Cu}_{47}(\text{PhSe})_{15}(\text{PPh}_3)_5(\text{CF}_3\text{COO})_{12}\text{H}_{12}]$  (referred to as  $\text{Cu}_{47}\text{H}_{12}$ , where  $\text{PPh}_3$  denotes triphenylphosphine), has been precisely determined through single crystal X-ray diffraction analysis. Several distinguishing features differentiate the  $\text{Cu}_{47}\text{H}_{12}$  clusters from previously reported examples. In terms of composition, these clusters represent a rare instance of high-nuclearity Cu nanoclusters containing hydride and stabilized by selenolate ligands. From an electronic standpoint, the stabilization of the nanocluster is achieved through its eight free valence electrons, marking it as the first copper-hydride cluster with this configuration. The alloying chemistry of the nanocluster also introduces unexpected findings in the field. The incorporation of silver atoms leads to the formation of  $[(\text{CuAg})_{47}(\text{PhSe})_{18}(\text{PPh}_3)_6(\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$  clusters, which exhibit significant structural differences from the parent cluster. Both the homo and alloy clusters display dual-emission properties at 298 K, with the clusters additionally showcasing triple or even quadruple emission at 77 K. This work is anticipated to stimulate research interest in hydride-containing metal nanoclusters, focusing not only on compositional tailoring and structural engineering, but also on electronic structure details and potential applications.

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## 1 Introduction

Ligand-protected coinage metal nanoclusters (NCs) with precise molecular compositions and exact structural characteristics have garnered significant attention in fundamental research.<sup>1–6</sup> These nanomaterials are widely applicable in various fields, including catalysis, sensing, biology, and electronics, and they serve as model systems for gaining atomistic insights into the structure-and-property relationships of nanoscale/microscale materials.<sup>7–19</sup> Among metal NCs, those stabilized by hydrides are of particular interest due to their crucial roles in both the formation and stabilization of unique nanostructures, as well as in the functionalization of metal NCs to facilitate their applications.<sup>20–23</sup> In recent years, there has been a growing body of literature on metal-hydride NCs, encompassing metals ranging from copper, silver, gold to alloys.<sup>24–28</sup> These studies have explored a variety of ligands including phosphines, thiolates, alkynyls, and carbenes, highlighting promising applications in transformations, hydrogen evolution and catalysis.<sup>29–34</sup> For instance, through systematic investigation using neutron diffraction, Liu and colleagues have systematically demonstrated the coordination modes of hydride inside the metal framework in a family of hydride-containing copper and silver

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metal NCs.<sup>35–37</sup> Additionally, research groups led by Tsukuda, Cradden, and Wang have revealed that gold-hydride NCs serve as key intermediates for further transformation into metallic NCs or efficient catalysts in the reduction of unsaturated compounds such as ketones, alkynes, and CO<sub>2</sub>.<sup>38–42</sup>

Despite the significant progress, several fundamental issues regarding hydride-rich metal nanoclusters (NCs) remain: (1) in terms of synthesis, while efficient strategies are available for copper-hydride NCs, and recently a few silver variants, achieving high-nuclearity hydride-doped Cu NCs has proven more challenging.<sup>43–45</sup> (2) Metal-hydride NCs are typically considered metastable, making the attainment of hydride-rich metal NCs with a high number of free valence electrons quite challenging.<sup>46–48</sup> To the best of our knowledge, the existence of eight electron copper-hydride NCs has not been experimentally validated thus far.<sup>49,50</sup> (3) Although alloying strategies have been frequently employed to tailor the composition, electronic structure and properties of hydride-free NCs, wherein the structural integrity of parent clusters often remains intact, the alloying chemistry of copper-hydride nanoclusters is poorly understood.<sup>51–53</sup> In this scenario, there is a strong desire to expand the existing collection of copper-hydride nanoclusters in order to gain a comprehensive understanding of their various synthetic methods, bonding and electronic structures, and even the relationships between structure and property.

In this study, we present the synthesis, structural determination, electronic structure analysis, and alloying chemistry of a novel cluster known as [Cu<sub>47</sub>(PhSe)<sub>15</sub>(PPh<sub>3</sub>)<sub>5</sub>(CF<sub>3</sub>COO)<sub>12</sub>H<sub>12</sub>] (referred to as Cu<sub>47</sub>H<sub>12</sub> hereafter). This nanocluster is the first eight-electron copper nanocluster to incorporate hydrides. Its one-pot and high-yield synthesis involving the reduction of copper salts in the presence of selenolate ligands allows for comprehensive characterization of its composition, purity, structure, and electronic properties. Notably, the alloying of external silver ions into the cluster results in the formation of a new group of clusters, [(CuAg)<sub>47</sub>(PhSe)<sub>18</sub>(PPh<sub>3</sub>)<sub>6</sub>(CF<sub>3</sub>COO)<sub>12</sub>H<sub>6</sub>]<sup>3+</sup> [(CuAg)<sub>47</sub>H<sub>6</sub>], which exhibits a completely novel molecular structure. Both clusters are distinguished by their dual, triple, or even quadruple-emission photoluminescent properties.

## 2 Results and discussion

### 2.1 Synthesis and atomic structure

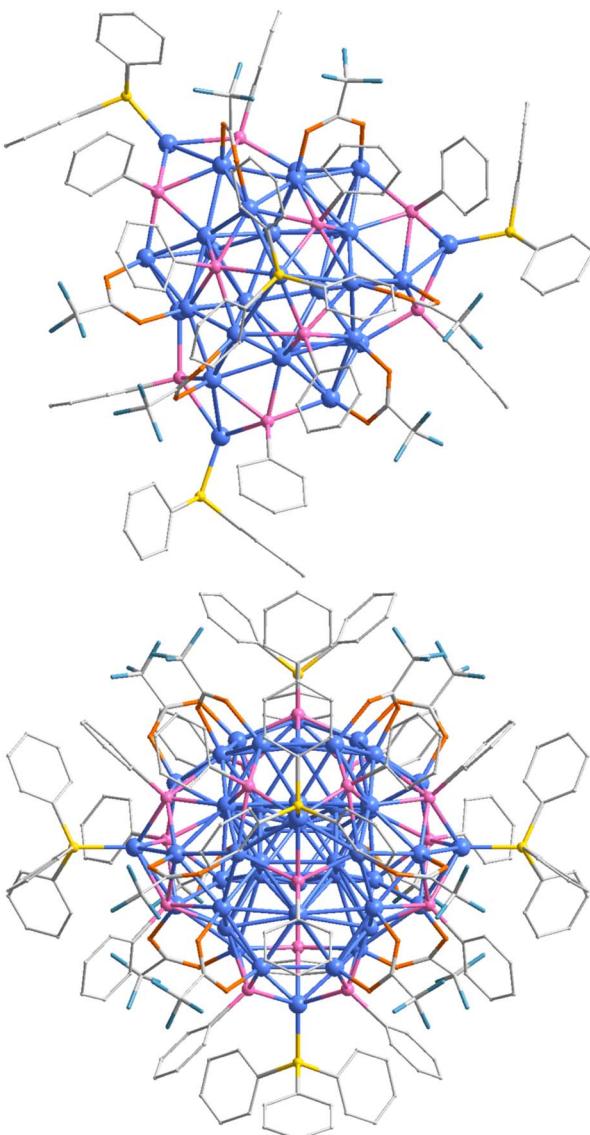
The absence of copper-hydride NCs with eight electrons in the literature underscores the challenges associated with effectively stabilizing Cu(0)-containing copper-hydride NCs. On one hand, the much lower half-cell reduction potential of copper (0.52 V) compared to silver (0.80 V) and gold (1.69 V) makes the Cu(0)-containing clusters highly sensitive to air, making their synthesis difficult.<sup>47,49</sup> On the other hand, the reactive nature of hydride atoms within these structures complicates the isolation of copper-hydride NCs.<sup>26,54</sup> To address these challenges, our strategy is to use bis(triphenylphosphine)copper tetrahydloborate ((PPh<sub>3</sub>)<sub>2</sub>CuBH<sub>4</sub>) as the reducing agent in the synthesis.<sup>54,55</sup> This reductant not only provides the necessary hydride atoms for reduction and stabilization but also acts as

a carrier for surface ligands.<sup>56,57</sup> The Cu<sub>47</sub>H<sub>12</sub> clusters were prepared by reducing a mixture of Cu(CF<sub>3</sub>COO)<sub>2</sub> and PhSeH ligands using (PPh<sub>3</sub>)<sub>2</sub>CuBH<sub>4</sub> as the reductant (further details can be found in the ESI†). It is important to note that the one-pot synthetic prototype was conducted out in the air using a mixed solvent of dichloromethane and methanol, resulting in a clear brown solution (Fig. S1†). High-quality single crystals were obtained by diffusing ether into the supernatant after centrifuging the raw product (Fig. S2†).

X-ray single-crystal diffraction was initially employed to determine the molecular structure of the Cu<sub>47</sub>H<sub>12</sub> NC (Fig. S3†). The cluster crystallized in the *P6<sub>3</sub>/m* space group of the hexagonal crystal system (Table S1†), with each unit cell containing two independent Cu<sub>47</sub>H<sub>12</sub> moieties and several dichloromethane solvent molecules (Fig. S4†). The absence of counterions in the lattice indicates that the cluster is electrically neutral. Detailed analysis reveals that the cluster consists of 47 copper atoms, 15 PhSe<sup>–</sup>, 5 PPh<sub>3</sub>, and 12 CF<sub>3</sub>COO<sup>–</sup> ligands, resulting in the overall formula of [Cu<sub>47</sub>(PhSe)<sub>15</sub>(PPh<sub>3</sub>)<sub>5</sub>(CF<sub>3</sub>COO)<sub>12</sub>H<sub>12</sub>] (Fig. 1). It should be noted that the number of hydride atoms in the cluster was determined by mass spectrometry (*vide infra*). The total size of the cluster was measured to be approximately 2.3 nm (Fig. S5†). The overall *C*<sub>3</sub> symmetry of the cluster is accompanied by a plane perpendicular to the symmetry axis that imparts mirror symmetry to the cluster (Fig. S6†), resulting in only one-sixth of the clusters being present in the asymmetric unit.

The structural anatomy of the Cu<sub>47</sub> cluster is depicted in Fig. 2. Its core lies a triaugmented triangular prism comprised of 9 copper atoms (Fig. 2a). The Cu<sub>9</sub> polyhedron is referred to as the Johnson solid *J*<sub>51</sub>, which is formed by placing a regular tetrahedron on each square face of an equilateral triangular prism, resulting in a convex deltahedron consisting of 14 equilateral triangles. While the framework is frequently observed in rare-earth metal complexes, the identification of a similar structure in coinage metal NCs is uncommon.<sup>58,59</sup> The bond lengths in the Cu<sub>9</sub> unit range from 1.620 to 3.240 Å, with an average value of 2.641 Å (see Table S2† for detailed bond lengths). The average Cu–Cu bond lengths within the Cu<sub>9</sub> kernel are notably shorter than those in previously reported copper NCs, indicating a robust interaction within the kernel.<sup>60</sup> Remarkably, the top shape of the Cu<sub>9</sub> core mirrors the Cu<sub>6</sub> motif found in the previously reported [Cu<sub>31</sub>(4-MeO-PhC≡C)<sub>21</sub>(dppe)<sub>3</sub>]<sup>2+</sup>[ClO<sub>4</sub>]<sub>2</sub> (Cu<sub>31</sub>, dppe = 1,2-bis(diphenylphosphino)ethane) (Fig. S7†).<sup>49</sup> Surrounding the Cu<sub>9</sub> core are *C*<sub>3</sub> symmetric Cu<sub>4</sub>Se<sub>3</sub> tiles at the top and bottom, flanked by two sets of three Cu<sub>7</sub> and Cu<sub>3</sub>Se<sub>3</sub> units along the *C*<sub>3</sub> axis, forming the Cu<sub>38</sub>Se<sub>15</sub> framework (Fig. 2b). The mirror symmetry of the overall structure is reflected in the mirror-symmetric Cu<sub>7</sub> units at the waist and Cu<sub>3</sub>Se<sub>3</sub> units at the head of the cluster. It is worth noting that although the subtle difference between Cu<sub>4</sub>Se<sub>3</sub> and Cu<sub>3</sub>Se<sub>3</sub> units is one copper atom, the Cu–Se bond lengths in the Cu<sub>3</sub>Se<sub>3</sub> units are shorter than those in the Cu<sub>4</sub>Se<sub>3</sub> units. The Cu–Se bond lengths range from 2.556 Å to 2.518 Å between the central Cu and Se atoms, and from 2.525 Å to 2.495 Å in the periphery. This discrepancy may be attributed to the unique geometry of the Cu<sub>9</sub> core that restricts the growth space of the outer atoms,





**Fig. 1** The structure of the  $\text{Cu}_{47}\text{H}_{12}$  nanocluster in top and side views. Color legend: Cu blue, Se pink, P yellow, O orange, F cyan, and C grey. All H atoms are omitted for clarity.

while the  $\text{Cu}_{38}\text{Se}_{15}$  framework envelopes the  $\text{Cu}_9$  core akin to a spider web. In the  $\text{Cu}_{38}\text{Se}_{15}$  framework, the average Cu–Cu bond length is 2.675 Å, which is longer than that of the  $\text{Cu}_9$  core, suggesting a loose arrangement of Cu atoms in the  $\text{Cu}_{38}\text{Se}_{15}$  framework. From the viewpoint of Se, there are two coordination modes of Se atoms in the clusters: a  $\mu_5$  coordination mode at the top and bottom of the overall structure, and a  $\mu_4$  coordination at the waist. The Cu–Se bond lengths range from 2.381 Å to 2.675 Å, comparable to those in  $[\text{Cu}_{23}(\text{PhSe})_{16}(\text{Ph}_3\text{P})_8(\text{H})_6]\text{BF}_4$ .<sup>61</sup> As shown in Fig. 2c, all phosphine ligands are positioned on symmetry elements (either plane of symmetry or axis of symmetry), collectively forming a double triangular cone shape. The  $\text{CF}_3\text{COO}^-$  ligands adopt the well-known Cu–O–C–O–Cu motifs on the surface of the cluster, arranged in a  $C_3$  symmetry to form a propeller.

## 2.2 Characterization and electronic structure

As previously mentioned,  $\text{Cu}_{47}\text{H}_{12}$  is proposed to be a neutral cluster, as no counterions were detected in the lattice. To determine the number of hydride atoms and confirm the exact composition of the molecule, mass spectrometry analysis data was obtained in the negative mode. To our satisfaction, a series of distinct peaks in the range of 3500–3900  $m/z$  are observed in the spectrum (Fig. 3a). Upon thorough examination of all potential candidates, the peak that most closely aligns with the target molecule is identified as  $[\text{Cu}_{47}(\text{PPh}_3)_2(-\text{CF}_3\text{COO})_{11}(\text{PhSe})_{18}\text{H}_{12}]^{2-}$ . This assignment is substantiated by the excellent correlation observed between the simulated and experimental isotopic patterns (Fig. 3a, inset). Additionally, other peaks can be recognized as fragments originating from the parent clusters (refer to Fig. S8 and S9† for more details). To further validate the presence of hydride atoms in the structure, we synthesized a deuterated analog, designated as  $[\text{Cu}_{47}(-\text{PPh}_3)_5(\text{CF}_3\text{COO})_{12}(\text{PhSe})_{15}\text{D}_{12}]$  (referred to as  $\text{Cu}_{47}\text{D}_{12}$ ) by using  $(\text{PPh}_3)_2\text{CuBD}_4$  in place of  $(\text{PPh}_3)_2\text{CuBH}_4$  during the cluster synthesis process. The mass spectrum of  $\text{Cu}_{47}\text{D}_{12}$  reveals discernible peaks, the most prominent of which corresponds to  $[\text{Cu}_{47}(\text{PPh}_3)_2(\text{CF}_3\text{COO})_{13}(\text{PhSe})_{14}\text{Cl}_2(\text{C}_4\text{H}_{10}\text{O})(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{D}_{12}]^{2-}$  (Fig. 3b and S10†). The above analysis unequivocally confirms the presence of 12 hydride (deuteride) atoms within the structure.

According to the equation reported by Häkkinen, the number of free valence electrons of  $\text{Cu}_{47}\text{H}_{12}$  is calculated to be 8.<sup>62</sup> It suggests that  $\text{Cu}_{47}\text{H}_{12}$  comprises Cu(0) atoms in its structure. The valence state of copper in the cluster compounds was further investigated utilizing X-ray photoelectron spectroscopy (XPS). In the Cu LMM Auger spectrum (Fig. S11†), the shoulder band observed at 918.5 eV, which is associated with Cu(0) species supports the partial zero oxidation state of copper atoms in  $\text{Cu}_{47}\text{H}_{12}$ , while the principal peak at 916.2 eV corresponds to the Cu(i) component. The binding energies for Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> are recorded at 932.6 and 952.4 eV, respectively, further suggesting that the Cu atoms in the cluster exist in a state that is intermediate between reduction and oxidation (Fig. S12†). Energy dispersive X-ray spectroscopy corroborated the presence of Se, P, O, F, and C elements in the sample (Fig. S13†). The X-ray powder diffraction (PXRD) pattern of this copper nanocluster aligns with the simulated pattern, indicating that the  $\text{Cu}_{47}\text{H}_{12}$  cluster exhibits good phase purity (Fig. S14†). The proton-decoupled <sup>31</sup>P NMR spectrum of  $\text{Cu}_{47}\text{H}_{12}$  in d<sub>6</sub>-DMSO is presented in Fig. S15.† The broad singlet peak indicates that the PPh<sub>3</sub> ligands are in a dynamic equilibrium in the solution, at least within the timescale of NMR measurement. From the aforementioned analysis, we conclude that: (1) this cluster represents a rare example of copper-hydride NCs, protected by selenate ligands. The presence of 12 hydrides in the structure endows the cluster with eight free valence electrons, marking it as the first copper hydride NC known to possess up to eight free valence electrons. (2) The involvement of three organic ligands, namely phosphine, selenite, and carboxylate, participated in the passivation of  $\text{Cu}_{47}\text{H}_{12}$  clusters, indicating the potential for customizing the surface and even



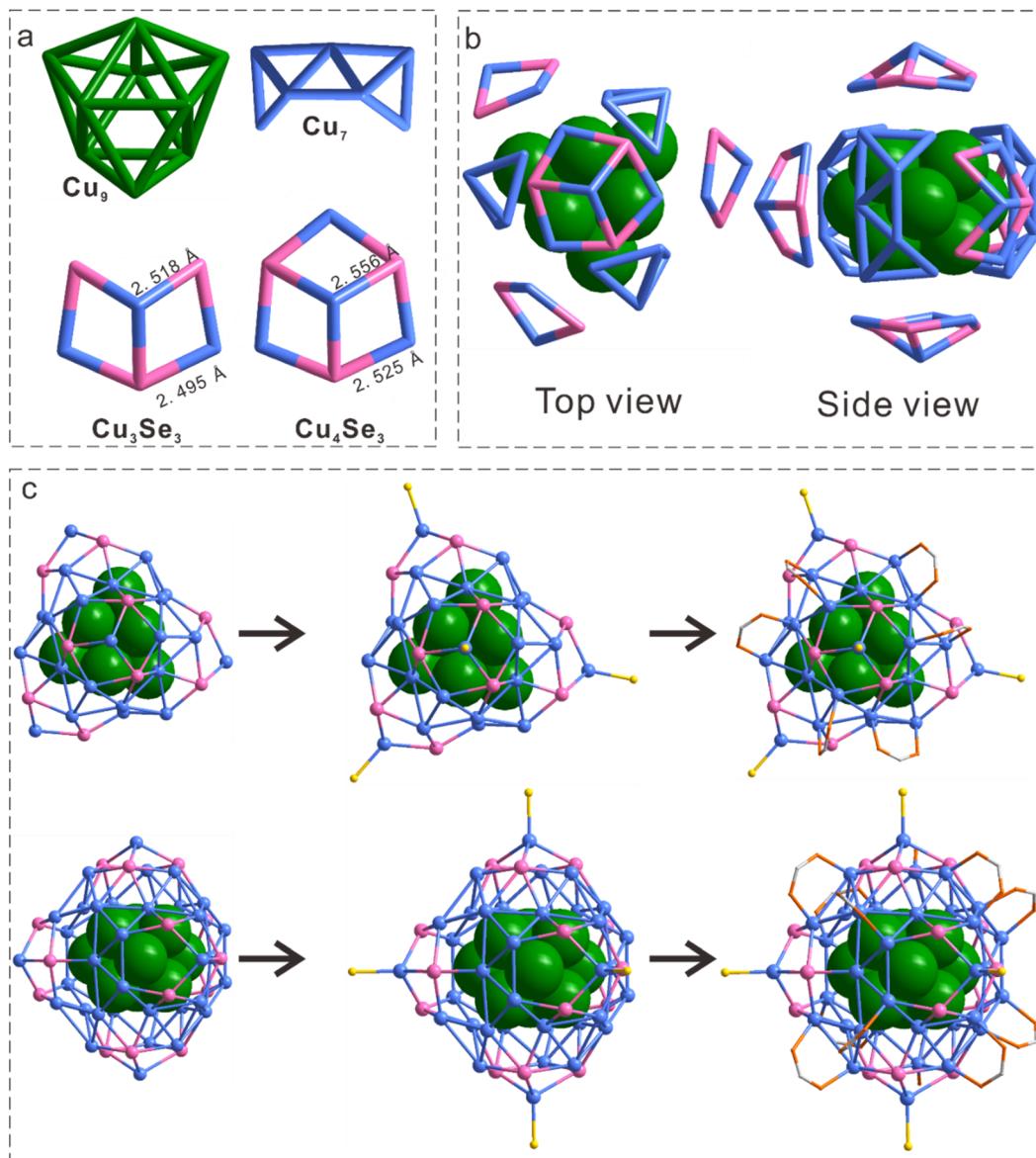


Fig. 2 Structural anatomy of the  $\text{Cu}_{47}\text{H}_{12}$  cluster. (a) The  $\text{Cu}_9$  kernel,  $\text{Cu}_7$ ,  $\text{Cu}_3\text{Se}_3$  and  $\text{Cu}_4\text{Se}_3$  motifs. (b) The top and side view of the assembled structure of the  $\text{Cu}_9@(\text{Cu}_{38}\text{Se}_{15})$  unit. (c) The top and side view of the  $\text{Cu}_9@(\text{Cu}_{38}\text{Se}_{15})@(\text{P}_5@(\text{RCOO})_{12})$  arrangement. Color legend: Cu blue and green, Se pink, P yellow, O orange and C grey. All other atoms are omitted for clarity.

geometric structure of hydride-containing metal NCs through ligand engineering (the related work will be discussed in a subsequent paper).

We endeavored to determine the positions of the hydrides utilizing a multifaceted approach that incorporated various characterization techniques, including mass spectroscopy, nuclear magnetic resonance (NMR), X-ray diffraction, and density functional theory (DFT) computations.<sup>63,64</sup> Fig. S16<sup>†</sup> shows that the only difference in the  $^1\text{H}$  NMR spectra of  $\text{Cu}_{47}\text{H}_{12}$  and  $\text{Cu}_{47}\text{D}_{12}$  reveals a singular distinction at 4.61 ppm, indicating the existence of only one chemical environment for the hydrides in the cluster. Similarly, a solitary peak at 4.43 ppm was observed in the  $^2\text{H}$  NMR of  $\text{Cu}_{47}\text{D}_{12}$  in  $\text{d}_6\text{-DMSO}$ , further substantiating the notion of a singular coordination mode for the deuterides (or hydrides) present in the cluster (Fig. S17<sup>†</sup>).

The proposed positions of the 12 hydrides, which share the same coordination environment, were inferred from the peaks observed in the difference electron density map derived from the crystallographic data (Fig. S18<sup>†</sup>). The accuracy of the proposed coordinates was corroborated through DFT calculations (*vide infra*). As shown in Fig. S18,<sup>†</sup> all 12 hydrides exhibit three-fold coordination, forming a triple bridge (or cap) over a triangular arrangement of Cu atoms. The Cu–H distances give an average value of 1.798 Å, which is consistent with the values documented for copper-hydride NCs in the existing literature.<sup>32,37</sup>

To gain deep insight into the electronic properties and rationalize the hydride positions of the title cluster, DFT calculations were then carried out. The electronic structure calculations of the  $\text{Cu}_{47}\text{H}_{12}$  cluster were performed using the



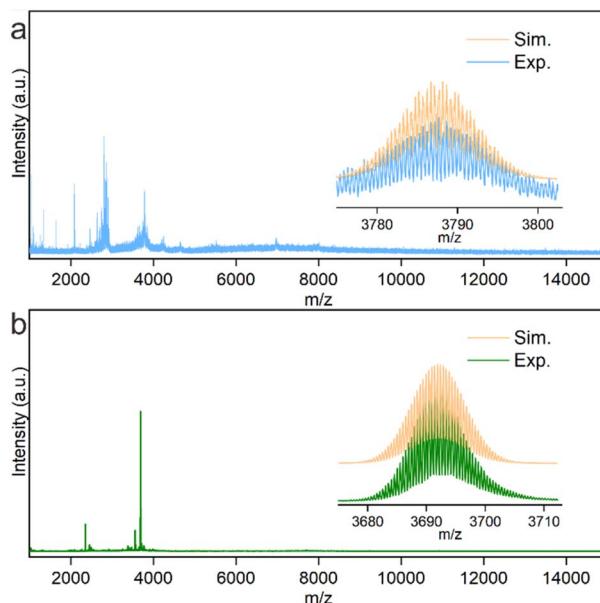


Fig. 3 The ESI-MS spectroscopy of  $\text{Cu}_{47}\text{H}_{12}$  (a) and  $\text{Cu}_{47}\text{D}_{12}$  (b) clusters in the negative mode. Inset is the comparison between the simulated (orange) and experimental (blue and green) isotopic pattern of  $[\text{Cu}_{47}(\text{PPh}_3)_2(\text{CF}_3\text{COO})_{11}(\text{PhSe})_{18}\text{H}_{12}]^{2-}$  and  $[\text{Cu}_{47}(\text{PPh}_3)_2(\text{CF}_3\text{COO})_{13}(\text{PhSe})_{14}\text{Cl}_2(\text{C}_4\text{H}_{10}\text{O})(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{D}_{12}]^{2-}$ .

Vienna Ab initio Simulation Package software. The accuracy of the proposed coordinates was corroborated through DFT calculations. The atomic coordinates of optimized structures of  $\text{Cu}_{47}\text{H}_{12}$  cluster are summarized in Table S3.† Shown in Fig. 4a is the frontier orbital charge densities of the  $\text{Cu}_{47}\text{H}_{12}$  cluster. The analysis reveals the charge density of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) orbitals is primarily located near Cu atoms. In the case of  $\text{Cu}_{47}\text{H}_{12}$  cluster, the energy gap between HOMO and LUMO is calculated to be 0.18 eV, suggesting its electronic stability. Fig. 4b displays the total density of states and projected density of states (PDOS) of each element of the  $\text{Cu}_{47}\text{H}_{12}$  cluster. Moreover, the HOMO and LUMO orbitals of the  $\text{Cu}_{47}\text{H}_{12}$  cluster are mainly provided by the Cu elements, which agrees well with the orbital charge densities in Fig. 4a.

### 2.3 Alloying chemistry and photoluminescence properties

The incorporation of heteroatoms through alloying has emerged as a highly effective approach for tailoring the compositions, structures, electronic structures, and properties of parent metal NCs.<sup>65,66</sup> Although the alloying chemistry of gold and silver NCs has been extensively studied, research concerning the alloying chemistry of copper NCs remains relatively scarce.<sup>67</sup> It is posited that the presence of hydride species in copper-hydride NCs facilitates a distinct alloying chemistry that distinguishes them from their gold and silver NCs. Consequently, the subsequent section investigates the influence of alloying heteroatoms, such as silver, on the parent  $\text{Cu}_{47}\text{H}_{12}$  NCs. From a synthetic perspective, the simultaneous reduction of  $\text{CF}_3\text{COOAg}$  and  $\text{Cu}(\text{CF}_3\text{COO})_2$  under identical reduction

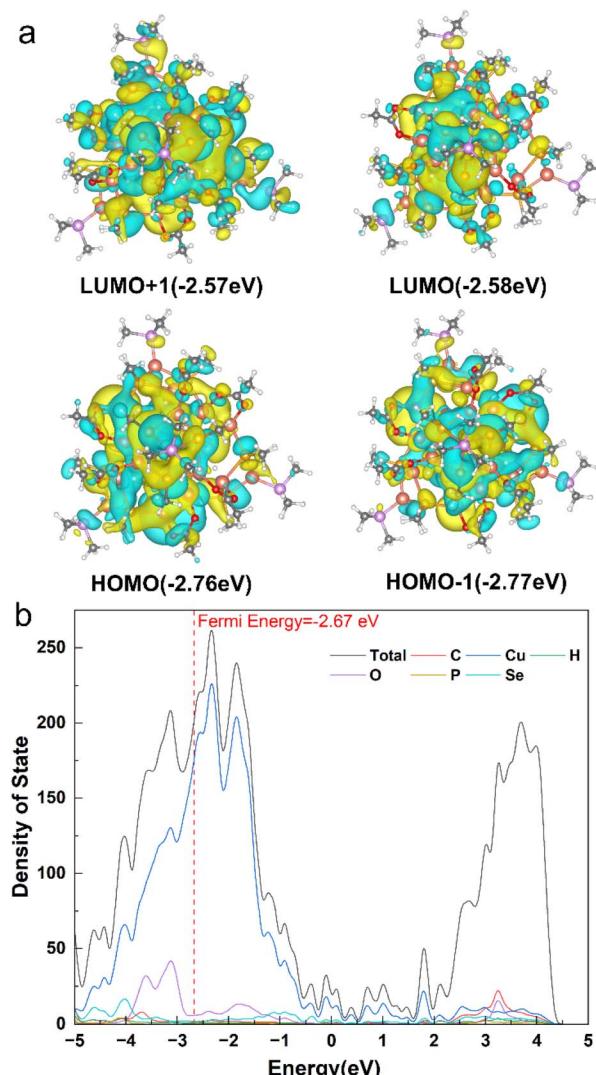


Fig. 4 (a) Frontier orbitals of  $\text{Cu}_{47}\text{H}_{12}$  cluster; (b) the total density of states and projected density of states of  $\text{Cu}_{47}\text{H}_{12}$  cluster. Color legend: Cu bronze, Se lime, P pink, O red, C gray, and H white.

conditions yields dark brown solutions, which exhibit UV-vis spectra that differ slightly from those of  $\text{Cu}_{47}\text{H}_{12}$  (Fig. S19†).

One might initially assume that akin to the general behaviour observed in gold and silver NCs, alloying would not significantly alter the structures of parent copper NCs. However, the alloying of silver atoms into the  $\text{Cu}_{47}\text{H}_{12}$  framework has a significant effect on its formula and structure, despite maintaining the same number of metal atoms and free valence electrons. Fig. 5a shows that the alloying of silver atoms during the synthesis results in completely different mass spectra. While the  $\text{Cu}_{47}\text{H}_{12}$  cluster is neutral in charge, the newly formed Ag–Cu NCs are positive. The ESI-MS analysis of the alloyed NCs, determined in positive mode, exhibits a series of clear peaks in the range of 2300–2800  $m/z$  (Fig. S20†). These peaks are attributed to the fragments originating from the parental  $[(\text{CuAg})_{47}(\text{PhSe})_{18}(\text{PPh}_3)_6(\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$  clusters, labelled as

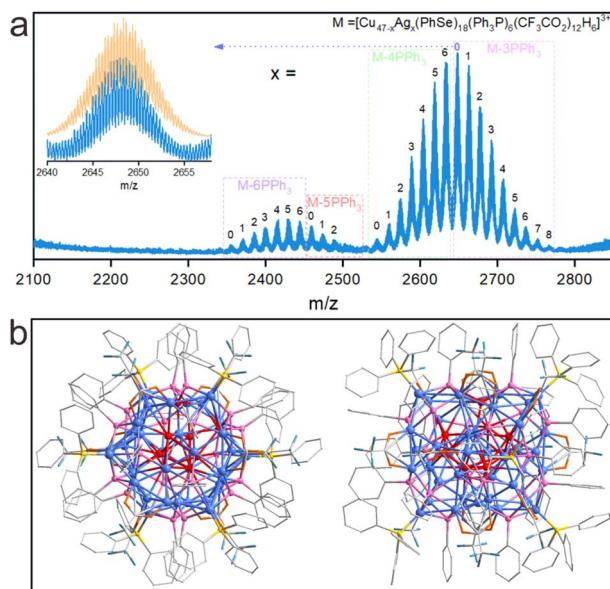


Fig. 5 (a) The ESI-MS spectroscopy of  $(\text{CuAg})_{47}\text{H}_6$  clusters in the positive mode. Inset is the comparison between the simulated (orange) and experimental (blue) isotopic pattern of  $[\text{Cu}_{47}(\text{PhSe})_{18}(-\text{PPh}_3)_3(\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$ . (b) Total structure of the  $(\text{CuAg})_{47}\text{H}_6$  nano-cluster in the top and side view. Color legend: Cu blue, Ag red, Se pink, P yellow, O orange, F cyan and C grey. All H atoms are omitted for clarity.

$(\text{CuAg})_{47}\text{H}_6$ . The observed peak series corresponds to the loss of neutral  $\text{PPh}_3$  ligands in quantities of 3, 4, 5, and 6, respectively, from  $[(\text{CuAg})_{47}(\text{PhSe})_{18}(\text{PPh}_3)_6(\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$  molecules. The assignment is verified by the excellent concordance between the simulated and experimental isotopic patterns. Furthermore, adjacent peaks correspond to species undergoing Ag–Cu exchange, which is consistent with the observed partial occupancy of Ag and Cu in certain positions in the single crystal structure (*vide infra*). It is worth noting that the  $(\text{CuAg})_{47}\text{H}_6$

clusters also possess eight free valence electrons as well, prompting intriguing inquiries regarding their molecular structure.

High-quality single crystals of  $(\text{CuAg})_{47}\text{H}_6$  clusters were obtained by a methodology analogous to that employed for  $\text{Cu}_{47}\text{H}_{12}$ . In full agreement with the ESI-MS analysis, the tricationic cluster  $[\text{Cu}_{47}(\text{PhSe})_{18}(\text{PPh}_3)_6(\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$ , as elucidated through X-ray single crystal diffraction, comprises 47 copper atoms, 18  $\text{PhSe}^-$ , 6  $\text{Ph}_3\text{P}$  and 12  $\text{CF}_3\text{COO}^-$  ligands. As shown in Fig. 5b, the total structure of  $(\text{CuAg})_{47}\text{H}_6$  is a significant deviation from that of  $\text{Cu}_{47}\text{H}_{12}$ . Specifically, the addition of Ag atoms has caused the transformation of the originally regular polyhedral core into a twisted cube-like  $\text{Cu}_{15}\text{Ag}_8$  (Fig. 6a and e). In comparison to the  $\text{Cu}_9$  core, the  $\text{Cu}_{15}\text{Ag}_8$  structure presents an average Cu–Cu bond length of 2.762 Å and an average Ag–Cu bond length of 2.784 Å. Furthermore, the motifs surrounding the core have also changed from three to two similar  $\text{Cu}_3\text{Se}_3$  units (Fig. 6b and f). The number of phosphine ligands in  $(\text{CuAg})_{47}\text{H}_6$  has increased by one, leading to their different coordination positions from  $\text{Cu}_{47}\text{H}_{12}$  (Fig. 6c and g). Although the quantity of carboxylate ligands remains the same, their spatial arrangement is notably more compact (Fig. 6d and h). The pronounced structural alteration of  $(\text{CuAg})_{47}\text{H}_6$  relative to  $\text{Cu}_{47}\text{H}_{12}$  is likely attributable to the larger van der Waals atomic radii of Ag in comparison to Cu, which forces the deformation of the parent clusters upon substitution. Importantly, the alloying of silver also engenders obvious modifications in electronic structure and stability. As shown in Fig. S21,†  $\text{Cu}_{47}\text{H}_{12}$  and  $(\text{CuAg})_{47}\text{H}_6$  display distinct UV-vis absorption peaks. Meanwhile, the ambient decay rates of  $(\text{CuAg})_{47}\text{H}_6$  in solution were significantly slower than those of  $\text{Cu}_{47}\text{H}_{12}$ , which is consistent with previous reports (Fig. S22†).<sup>68</sup> The increased stability of  $(\text{CuAg})_{47}\text{H}_6$  compared to  $\text{Cu}_{47}\text{H}_{12}$  may be attributed to its larger HOMO–LUMO gap (0.22 eV for  $\text{Cu}_{47}\text{H}_{12}$  and 0.32 eV for  $(\text{CuAg})_{47}\text{H}_6$ , Fig. S23†).

Both  $\text{Cu}_{47}\text{H}_{12}$  and  $(\text{CuAg})_{47}\text{H}_6$  show luminescent properties. As shown in Fig. 7a, the  $\text{Cu}_{47}\text{H}_{12}$  cluster in *N,N*-

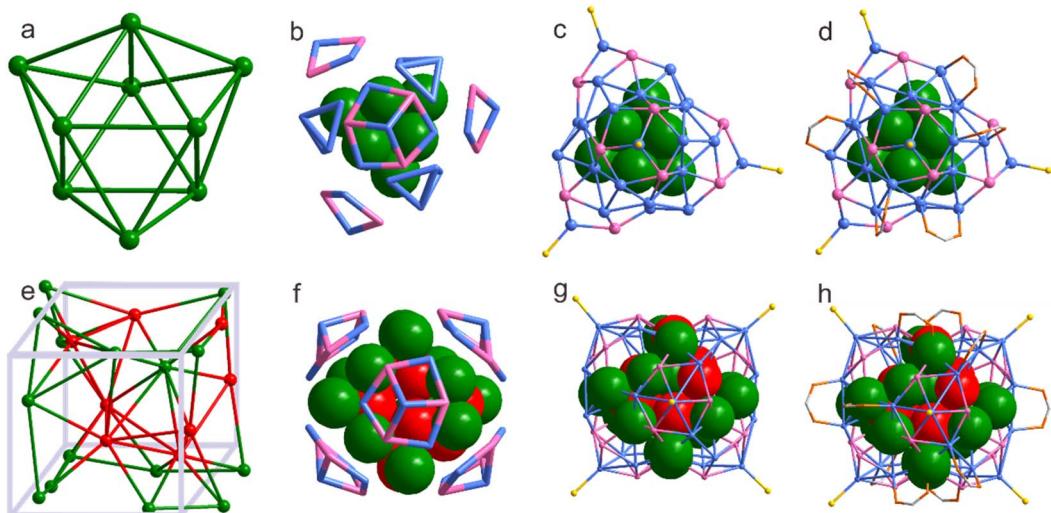


Fig. 6 Structural comparison of  $\text{Cu}_{47}\text{H}_{12}$  (a–d) and  $(\text{CuAg})_{47}\text{H}_6$  (e–h). Color legend: Cu blue and green, Ag red, Se pink, P yellow, O orange and C grey. All other atoms are omitted for clarity.



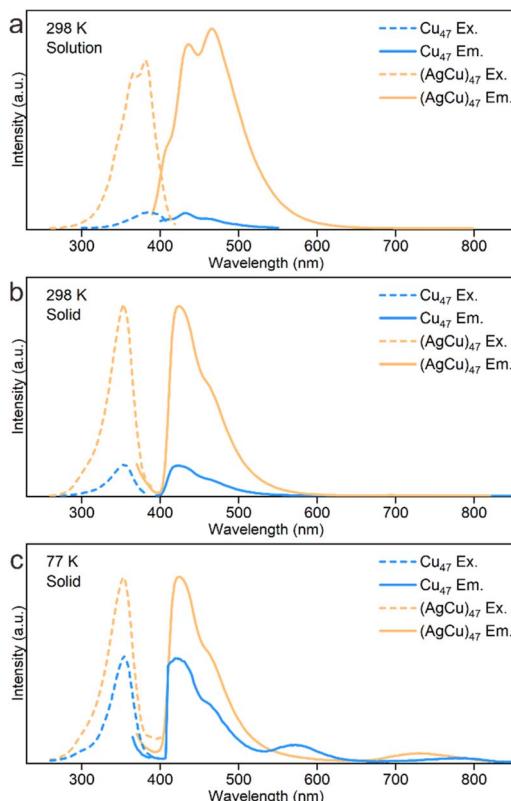


Fig. 7 Excitation and emission spectra of  $\text{Cu}_{47}\text{H}_{12}$  and  $(\text{CuAg})_{47}\text{H}_6$ . (a) DMF solution at 298 K. (b) Solid at 298 K. (c) Solid at 77 K.

dimethylformamide demonstrates dual emission characterized by two peaks at 420 and 463 nm upon excitation at 390 nm. The  $(\text{CuAg})_{47}\text{H}_6$  also displays a similar emission profile, however, its photoluminescence quantum yield (PLQY) is much lower (2.74% for  $\text{Cu}_{47}\text{H}_{12}$  and 0.31% for  $(\text{CuAg})_{47}\text{H}_6$ ). The clusters are expected to emit phosphorescence, as evidenced by their extended photoluminescence lifetimes (exemplified by a lifetime of 7.4840  $\mu\text{s}$  for  $\text{Cu}_{47}\text{H}_{12}$ ). In their crystalline state, these clusters are also luminescent, displaying blue-shifted emission peaks (Fig. 7b). It is interesting to note that the PLQY of the clusters in their crystalline form is significantly higher than that observed in the solution, for instance,  $\text{Cu}_{47}\text{H}_{12}$  exhibits a PLQY of 2.74% in solution (DMF), while the PLQY in the solid form is measured to be as high as 9.30%. More remarkably, the clusters exhibit triple or even quadruple emission characteristics in the solid state. Upon lowering the temperature from 298 K to 77 K, a new emission peak at 731 nm is observed in the spectrum of  $(\text{CuAg})_{47}\text{H}_6$ . The  $\text{Cu}_{47}\text{H}_{12}$  cluster surprisingly exhibits four peaks (420, 462, 577, and 791 nm) in its emission curves, including one in the near-infrared region. We note that although metal NCs with triple emission properties are infrequently reported in the literature, those exhibiting quadrupole-mode emissions have not been reported, to the best of our knowledge.<sup>69,70</sup> It is also worth noting that the intensities of the emission peak at 791 nm for  $\text{Cu}_{47}\text{H}_{12}$  increase significantly as the temperature decreases from 283 K to 83 K, suggesting that

the potential application of this cluster as a molecular luminescent thermometer operating in the NIR region.

### 3 Conclusions

In conclusion, we present the initial instance of copper nanoclusters doped with hydride, characterized by the presence of eight free valence electrons:  $[\text{Cu}_{47}(\text{PhSe})_{15}(\text{PPh}_3)_5(-\text{CF}_3\text{COO})_{12}\text{H}_{12}]$ . The successful isolation, comprehensive characterization, and determination of the structure of this specific cluster have been achieved, unequivocally demonstrating the potential for enhancing the geometric, surface, and electronic properties of metal-hydride nanoclusters in future research endeavors. The alloying chemistry associated with the cluster is relatively novel. The incorporation of silver heteroatoms results in alterations to both composition and structure, giving rise to another new family of eight-electron  $[(\text{CuAg})_{47}(\text{PhSe})_{18}(\text{PPh}_3)_6(-\text{CF}_3\text{COO})_{12}\text{H}_6]^{3+}$  clusters. Furthermore, these clusters exhibit double, triple, and even quadrupole emission properties, which endow them with promising applications in optoelectronics, ratiometric sensing, and biological contexts. This research not only presents the inaugural example of eight-electron copper-hydride nanoclusters, thereby significantly broadening the synthetic, compositional, and structural chemistry of hydride-containing metal nanoclusters but also emphasizes the unique nature of such materials in terms of alloying and photoluminescent properties.

### Data availability

The data supporting this article have been included as part of the ESI.<sup>†</sup>

### Author contributions

H. S. conceived and supervised the research project. J. S. synthesized and characterized the samples. W. J. and H. G. investigated the photoluminescence properties under the guide of J. W. S. W. supervised the DFT calculations and analysed the computational results together with J. L. who conducted the calculations. H. S., Z. X., X. T., Z. X. and S. L. were responsible for the data collection and analysis. X. G., D. J., N. Z., and H. S. revised the manuscript.

### Conflicts of interest

There are no conflicts to declare.

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