Assembly-induced spin transfer and distance-dependent spin coupling in atomically precise AgCu nanoclusters

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Nanoparticle assembly paves the way for unanticipated properties and applications from the nanoscale to the macroscopic world. However, the study of such material systems is greatly inhibited due to the obscure compositions and structures of nanoparticles (especially the surface structures). The assembly of atomically precise nanoparticles is challenging, and such an assembly of nanoparticles with metal core sizes strictly larger than 1 nm has not been achieved yet. Here, we introduced an on-site synthesis-and-assembly strategy, and successfully obtained a straight-chain assembly structure consisting of Ag77Cu22(CHT)48 (CHT: cyclohexanethiolate) nanoparticles with two nanoparticles separated by one S atom, as revealed by mass spectrometry and single crystal X-ray crystallography. Although Ag77Cu22(CHT)48 bears one unpaired shell-closing electron, the magnetic moment is found to be mainly localized at the S linker with magnetic isotropy, and the sulfur radicals were experimentally verified and found to be unstable after disassembly, demonstrating assembly-induced spin transfer. Besides, spin nanoparticles are found to couple and lose their paramagnetism at sufficiently short inter-nanoparticle distance, namely, the spin coupling depends on the inter-nanoparticle distance. However, it is not found that the spin coupling leads to the nanoparticle growth.

Metal nanoparticles can be regarded as an assembly of metal atoms and surface-protecting ligands. The further assembly of nanoparticles enhances or even enriches the properties of sole metal nanoparticles and constitutes a novel type of promising material that is significant not only for fundamental research but also for practical applications. Due to numerous atoms and complex structures as well as instability, it is generally difficult to assemble metal nanoparticles in a controlled and atomically precise way. Even the controlled and atomically precise synthesis of metal nanoparticles has long been a target for the scientific community, and this target has only come into becoming a reality recently after many trials. Atomically precise nanoparticle assemblies provide excellent opportunities for structure (composition)-property correlation and rational tailoring of their performances, thus attracting extensive interest in recent years. Unfortunately, despite the successful assembly of small metal nanoclusters (NCs) with sizes less than 1 nm, the assembly of atomically precise metal nanoparticles with metal core sizes strictly larger than 1 nm has not yet been reported due to the increasing challenges. This study demonstrates a new approach for assembling atomically precise AgCu nanoclusters with metallic cores larger than 1 nm, which opens up new possibilities for the study of such material systems.
can be in-situ produced during the synthesis of thiolated metal
(vide infra) was used to determine the nanoparticle composition
(Fig. 7), excluding the existence of hydrides in the metallic core. SCXC
z = 7617.7 Da, corresponding to [Ag77Cu22(CHT)48]2+, a n d h e p e a k
of 3+ and 2+ components. The full range of the ESI-MS spectrum (acquired in
metry (ESI-MS) was employed to determine the exact formula of the
crystals both show a prominent peak at 655 nm and a shoulder peak at
mixed solvent of dichloromethane/hexane for crystallization (assem-
solution was obtained, which was rotary evaporated to give a dark
presence of triethylamine. After stirring for 6 h at 0 °C, a dark brown
applied to synthesize atomically precise bimetal nanoparticles42.
Surface. A kinetical control and thermodynamic selection strategy was
freshly prepared solution of NaBH4 and PPh4Br was added dropwise to
Brie
ments, among which two peaks are assigned to [Ag76Cu21(CHT)47 +S 
were observed at approximately 4900 and 7400 Da bearing 3+ and 2+
change of m/z in the mass spectrum of Ag77Cu22 (Supplementary
possible existence of surface S2
hes in the synthetic phase (Supplementary
were rarely employed as linkers, especially for the
– sk) and N3
first time, we successfully assembled
nanoparticles into straight chains by using S2
as a linker, resolved the atomic structure by using mass spectrometry and single crystal X-ray
crystallography (SCXC), and, more importantly, revealed interesting spin transfer and coupling phenomena, which will be discussed below.

Results
Synthesis and structure characterization
Silver salt was employed as the major metal precursor due to its
accessibility, and a second metal, copper salt, was added to strengthen
the stability and enrich the properties of the metal nanoparticles.
Cyclohexanethiol (CHTH) was employed as a protecting ligand due to
its relative flexibility, which is beneficial for S2 access to the metal
surface. A kinetical control and thermodynamic selection strategy was
applied to synthesize atomically precise bimetal nanoparticles42.
Briefly, the synthesis and assembly processes are shown below: a
freshly prepared solution of NaBH4 and PPh4Br was added dropwise to
a dichloromethane suspension containing AgCHT and CuCl in the
presence of triethylamine. After stirring for 6 h at 0 °C, a dark brown
solution was obtained, which was rotary evaporated to give a dark
solid. This solid was washed with methanol and then dissolved in
a mixed solvent of dichloromethane/hexane for crystallization (assem-
(b) see Methods for details).

The UV/Vis/NIR spectra for the as-prepared materials and the
crystals both show a prominent peak at 635 nm and a shoulder peak at
410 nm (Supplementary Fig. 2). Electrospinning ionization mass spectro-
metry (ESI-MS) was employed to determine the exact formula of the
components. The full range of the ESI-MS spectrum (acquired in
positive ion mode) is shown in Supplementary Fig. 3a. A series of peaks
were observed at approximately 4900 and 7400 Da bearing 3+ and 2+
charges, respectively. Detailed assignments are revealed in Supplementary
Fig. 3b, and the isotope patterns for the parent cluster and its
fragments match well with the calculated patterns (see Supplementary
Figs. 4 and 5). The peak of intact cluster ion was found at m/z = 7617.7 Da, corresponding to [Ag77Cu22(CHT)48]3−, and the peak of 3+
charged cluster ion with one missing CHT ligand was located at m/z = 5046.6 Da. The other peaks can be rationally assigned to the frag-
ments, among which two peaks are assigned to [Ag76Cu22(CHT)47]3−
and [Ag75Cu22(CHT)46]2− (Supplementary Fig. 6), indicating the possible existence of surface S2. The replacement of the reducing reagent NaBH4 with NaBD4 in the synthesis does not lead to the notable
change of m/z in the mass spectrum of Ag77Cu22 (Supplementary
Fig. 7), excluding the existence of hydrides in the metallic core. SCXC
(vide infra) was used to determine the nanoparticle composition
[Ag77Cu22(CHT)48]3−, which was also supported by additional EDX
measurements (Ag/Cu/S atomic ratio 1: 0.283: 0.637, in good agree-
ment with the expected ratio 1: 0.286: 0.623, see Supplementary Fig. 8).
Below, we will focus on the structure revealed by SCXC.

The crystal adopts a trigonal space group of P–3, and the 99 metal
atoms are distributed in four shells perceptually protected by 48 CHT
ligands (Supplementary Fig. 9 and Fig. 1a). Since the dissociation energy
of the Cu–Cu bond is higher than that of the Ag–Ag or Ag–Cu bond, Cu
atoms generally prefer to form a pure shell without enclosing Ag atoms
in AgCu alloy NCs. Herein, we found that 22 copper atoms and eight
silver atoms are distributed in the second outermost of the nanoparticle,
probably because the quantity of Cu atoms in Ag77Cu22 is not enough
to form a separate shell. The other three shells are fully occupied by silver atoms, and the nanoparticle has the structure of
Ag77Cu22[M94@Ag50S64(SR)46]3−, as illustrated in Fig. 1b–e (the carbon and hydrogen atoms are omitted for clarity). The central Ag atom
and the second shell form a conventional 13-atom icosahedron (Fig. 1b),
which is enclosed by a 30-atom icosidodecahedron. The icosidode-
cahedron shell can be described as 20 triangular faces and 12 pen-
tagonal faces joined together (see Fig. 1c), and every center of the
pentagonal face corresponds to each vertex of the 12-atom icosahed-
ron (Fig. 1c). The outermost shell consists of 56 Ag atoms and 48 S
atoms with three gradients viewed from the side (Supplementary
Fig. 10). Gradient 1 shows a dendritic growth mode to form a cone-
like shape that is composed of 19 Ag atoms and 18 S atoms (Ag30S18 for short). Gradient 3 is the inverted shape of gradient 1, which
appears as a mutual mirror from the top view. Six Ag32S2 units con-
stitute gradient 2, which means upward gradients 1 and 3. Ten sets of
equivalent Ag3S3 staple sites are found in the half shell, with the mea-
surement of the radial distances and marked by nine triangles and one
Ag on the apex (Fig. 1e). The other half (purple) has the same Ag
to atom sites and thus is not marked. 24 atoms in the (AgCu)30 shell are
coordinated to the Ag atoms in the Ag50S64 outer shell (every Ag or
Cu atom in the (AgCu)30 shell bonds 2 or 3 Ag atoms in the Ag50S64 outer shell) except for the six metal atoms closed to the six vertexes (Supplementary Fig. 11). This shell can also be described as a com-
bination of 36 distorted cyclic staples through edge- or vertex-sharing,
including one type of Ag3S3 (1 × 6) staple and five types of Ag3S4
(5 × 6) staples (see Supplementary Fig. 12). These cyclic staples, with
Ag and S atoms arranged alternately, are pieced together like dif-
ferent patches. Ag3S4 staples are located around the vertex of the
gradient 1 or 3 cone, and two types of Ag3S4 staples (b, c in Supple-
mentary Fig. 12) surround the Ag3S3 staples in a stepwise manner to
form the Ag50S18 cone. Gradient 2 consists of the other three Ag3S4
staples (d, e, f in Supplementary Fig. 12). Ag3S3 staples are planar
structures, while Ag3S4 staples are all distorted with zigzag or boat
shapes. Generally, the S atoms in the staples protrude from the sur-
face of thiolated nanoparticles, and, thus, can be viewed as a pro-
tected shell. However, the S atoms in the Ag50S18 shell almost lie in
the same planes as the Ag atoms. In other words, S atoms are inter-
laced with Ag atoms in this shell except for the six vertices S (red
atoms in Supplementary Fig. 10). This can also be proven by the fact
that 73% of the Ag–S–Ag angle on the Ag50S18 shell exceeds 90°, and
that such a ratio is the highest among the investigated thiolated
nanoparticles (nanoclusters) in the crystal phase (Supplementary
Fig. 13), probably due to the strong repulsion from the especially
close nanoparticles (vide infra).

Surface morphology
The surface motifs consist of 48 thiolates, including six two-
coordinated and 42 three-coordinated thiolates, with an average
Ag–S bond length of 2.4125 Å. μ3–S can be further categorized into three
classes (μ1–S, μ2–S, and μ3–S) in terms of the Ag–S–Ag angle
(Fig. 10). The thiolate ligand in the μ1–S type binds to the shell deviating
from the Ag3 unit with small Ag–S–Ag angles, while the thiolate ligands
in the μ2–S and μ3–S types bind to the Ag3 unit at relatively large
angles. The difference between the μ1–S and μ3–S types is that the
three Ag–S–Ag angles in μ1–S are all approximately equal to 110°,
while one of the three angles in μ3–S turns to ca. 81°. It is worth noting
that with the angle decreasing in μ1–S, one Ag–S bond (indicated by a
black arrow) is elongated to 2.835 Å, which is obviously longer than the
common Ag–S bond (2.3–2.7 Å) (see the statistics in Supplementary Fig. 14) and rarely found in Ag nanoparticles (nanoclusters). Interestingly, a ripple-like arrangement was found for the Ag19S18 cone (gradient 1) in the outermost shell of Ag77Cu22, which has not been reported previously in silver nanoparticles (nanoclusters). Every three S atoms are assembled into a ring with one Ag atom at the center, leading to a ripple-like pattern with six rings (the six groups of S atoms are gradually marked from yellow to red, see Fig. 1g). Moreover, the S atoms, as well as the cyclohexyl tails with varying orientations (Fig. 1h), adopt a helical anticlockwise stripe pattern along the six rings. The same pattern is also observed on the opposite pole (gradient 3) but with a clockwise rotation.

Recently, hierarchically ordered patterns formed by the self-assembly of Au–SR on the surface of NCs have attracted extensive interest in manipulating property-related complex structures43. Here, the 48 ligands can be further divided into three sorts (Fig. 2a, b): six ligands (yellow in Fig. 2b) are equally distributed into two groups on the poles with ca. 60° rotation; 24 ligands in six groups (pink in Fig. 2a) are arranged on the surface perpendicular to the waist; and the remaining 18 ligands (orange in Fig. 2a) are aligned into six parallel groups to form an alternating pattern with the abovementioned 24 ligands (like a clock dial). A complete H–H interaction network is formed inside the Ag77Cu22 nanoparticle. For example, every ligand (yellow) around the poles shows H–H interactions with three adjacent ligands (Fig. 2c), and the 12 groups of ligands across the waist also show H–H interactions in two dimensions (see Fig. 2d–f, H–H spacing in Supplementary Table 1). Notably, the H–H spacing across the waist is very short (average value of 2.714 Å), which can influence the formation of interlocked ligands via the cyclohexane orientation. When the two neighboring groups (including seven ligands) are regarded as one unit, it is found that every cluster connects with the surrounding clusters through the six abovementioned units (Fig. 2g). As shown in Fig. 2h, i and Supplementary Table 1, the H–H interactions between clusters intersect between four contacting groups of ligands, indicating dense packing among clusters.

**Polymeric structure**

Another unusual feature of the crystal structure is the straight S-linked nanoparticle chains along the z-axis (Fig. 3) formed by connecting the pole Ag atoms with S ions. The linker “X” can be “S”, “SH”, “CI”, or “Br” on the basis of the starting materials used in this reaction, however, both X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 15) and energy dispersive spectrometer (EDX) (Supplementary Fig. 8) exclude the existence of Cl or Br. Ion chromatography (IC) and precipitation experiments (PEs) further exclude the...
existence of Cl or Br, and identify the “X” to be “S2–” (Supplementary Fig. 16). The strong alkaline reaction solution (NaBH4) does not prefer the forming of HS–, too. IR spectrum further excludes the existence of HS– since the feature signal of HS– at ~2550 cm^{-1} was not found in the IR spectrum (Supplementary Fig. 17). The bridging S2– ions are probably produced from the C–S bond cleavage of thiol or thiolate, as was studied by us44 and some other groups45–48. As shown in Fig. 3a, b, the Ag–S–Ag angle formed by the two pole silver atoms and the linker S is equal to exactly 180° and the radial direction of such chains coincides with the C3-axis of every single Ag77Cu22 NC, perpendicular to the x–y plane in the crystal packing. Therefore, the chains are perfectly straight lines without any rotation of the NCs. Note that to make room for the S linker, the three thiolates around the Ag pole stretch out compared with other ligands, forming a “hole” or an “open” Ag for the linkage (Fig. 3a). As shown in Fig. 3c, the two mirrored Ag19S18 cones on the shell marked with cyan and purple are also arranged alternately in the chains. The lengths of the Ag–S bonds for every sulfur atom linking two NCs are both equal to 2.5175 Å, which is even shorter than that of some typical Ag–S bonds (2.356–2.835 Å) in the shell. The metal core diameter of Ag77Cu22 is ca. 1.69 nm, and the interparticle distance along the chain is ca. 2.19 nm (Fig. 3a). However, the interparticle distances along the x- and y-axes are both ca. 2.5 nm (Fig. 3d), implying a stronger interaction between the neighboring nanoparticles along the chain direction, as also demonstrated by the inter-nanoparticle H···H interactions. As shown in Supplementary Fig. 18, the close inter-nanoparticle H···H spacings, such as 2.288, 2.561, and 2.642 Å, are observed along the chain direction, while the shortest inter-nanoparticle H···H spacing along the perpendicular direction (x- and y-axes) is 2.422 Å (Supplementary Table 1).

**Magnetism performance**

The nominal shell-closing electron count (\(n^*\)) for the Ag77Cu22 nanoparticle is 49 (\(n^* = \nu_{Ag} – M + z = 77 × 1 + 22 × 1 – 48 – 2 = 49\))\(^{49}\), reminding one of its paramagnetism\(^{50}\), which was confirmed by experiments. For comparison, the paramagnetism of neutral Au25 was also investigated. As shown in Fig. 4a, the EPR spectrum for a small amount of neutral Au25 single crystals shows multiple peaks (red curve). When the large crystals are broken into microcrystals by ultrasonication, the refined peaks disappear, and broadband (identical to the reported

**Fig. 2 | Surface pattern of the ligands on Ag77Cu22 NCs.** The ligands are distributed perpendicular to the waist (a) or on the poles (b). c Interactions between the pole ligands and their surrounding ligands. d, e side views of a and b. f Interactions between the ligands perpendicular to the waist. g Seven close-packed Ag77Cu22 NCs with interactions in six directions. h Top view and i side view of the interparticle interactions point-by-point. Color codes: orange, pink, yellow, C; white, H; cyan, S, Ag, Cu.
The EPR measurement was conducted by automatically or manually rotating the single crystal sample (illustrated in Fig. 4d) to further probe the magnetic anisotropy. As shown in Fig. 4e, the intensity and position of the EPR signals for the Au25 single crystal change stepwise as the sample is rotated, further confirming the magnetic anisotropy of neutral Au25 crystals. In contrast, the Ag77Cu22 nanoparticle assembly shows a different EPR spectrum from that of a single Au25 crystal (Fig. 4e and Supplementary Fig. 19), indicating different origins for the magnetism. The blank experiments exclude the external introduction of magnetic impurities, see Supplementary Fig. 20. The simulated results (g = 2.0072, 1.9671, and 1.9659) are well consistent with the experimental observations (Supplementary Fig. 21). Particularly and interestingly, the EPR spectra remain the same after rotating the single crystal sample (Fig. 4f), indicating magnetic isotropy. Such magnetic isotropy is unusual and has rarely been reported in metal nanoparticles, which inspires our enthusiasm for further investigation. Due to the difficulty of experimentally mapping the magnetism resource, DFT calculations were performed to acquire the spin distribution using the crystal structure with simplified ligands to reduce the computational cost. The crystal structure is preserved (other than replacing R=cyclohexyl groups by R=H-atoms), and the collinearity of C3, the linker, and the z-axis is preserved when relaxed, see Supplementary Fig. 22. The spin density distribution is shown in Fig. 4g. Remarkably, the magnetic moment is found to be mainly localized at the S2– linker rather than the metal atoms (Ag or Cu). Only weak spin density is revealed on the surface or kernel atoms adjacent to S2–, and the magnetic moment of the linker S2– is almost 12 times larger than that of the Ag atom with the largest magnetic moment. The detailed spin distribution is given in Supplementary Table 2. In strong contrast, the magnetic moment of Au25 is found to be mainly localized at the kernel Au atom (see Supplementary Fig. 23 and Supplementary Table 3), similar to the results reported by ref. 50. It is generally believed that magnetic anisotropy has diverse origins, such as spin–orbit coupling (SOC), exchange interaction, etc. For Au25, the magnetic anisotropy can be attributed to the strong SO coupling of Au atoms since the noncollinear calculation reveals large magnetic anisotropy energy (MAE, ca. 200 μeV). The torque method was further applied for analysis, and it was revealed that the positive uu (27.78 meV) and dd (27.96 meV) channels contribute more (97 μeV) than the negative ud + du (−55.65 meV) channel, leading to a positive MAE, which provides further support for the SOC mechanism for the magnetic anisotropy. For the Ag77Cu22 assembly, given the consideration of the major spin on S2–, the SOC mechanism is not applicable since the SOC parameter for S (288 cm−1) with a relatively small atomic number is
Fig. 4 | Magnetic performance of Ag_{77}Cu_{22} and Au_{25}EPR spectra for
a Au_{25}^{0} and
b Ag_{77}Cu_{22} in different states (note: the solution samples were aged for 1 h before measurements, and the amorphous samples were prepared from the above-aged solutions by fast precipitation and drying). c EPR spectra measured for Au_{25}^{0} NCs with different CHT substitution numbers. d Schematic depiction of the rotational EPR experiment. 2D EPR density plots of e Au_{25}^{0} and f Ag_{77}Cu_{22}. g Spin distribution of polymeric Ag_{77}Cu_{22} (magenta: spin density). Spin-polarized PDOS of the h 3p orbitals of the S linkage and i 5s orbitals of Ag bonded with the S linkage. j Schematic representation of the electronic structures of the linkage.
EPR spectra, which might be interpreted by the delocalization 

Notably, the hyper 

can be captured by DMPO and lead to the emergence of the EPR signal 

The magnetic isotropy of the assembly can be ascribed to the major spin on sulfur confined in such a special structure. The note that the $g$-factor and specific magnetization (emu/g) are shown in Supplementary Figs. 21 and 24, respectively. The $g$-value (1.9790) was close to 2.0023 ($g$-value of a free electron) and the obtained effective moment $\mu_{\text{eff}} = 1.62 \mu_B$ is also consistent with $S = \frac{1}{2}$ per cluster molecule (1.73 $\mu_B$), supporting the notion that the magnetism of Ag$_{77}$Cu$_{22}$ assembly originates from the unpaired shell electron of the Ag$_{77}$Cu$_{22}$ nanoparticle. Notably, the hyperfine splitting (fine structure) was not observed in the EPR spectra, which might be interpreted by the delocalization of the unpaired spin or the weak spin–nuclei interaction due to the extremely low abundance of magnetic $^{34}$S nuclei. A natural question arises: why the magnetic moment mainly localizes on $S^2$–? It is proposed that electron transfer occurs from linker $S^2$– to the metal atom. Such electron transfer between sulfur and the nanoparticle core was revealed in our previous photoluminescence study.$^{15,16,20}$ The close linker (Ag–S distance) also provides support for such a phenomenon. A study of the projected density of states (PDOS) revealed that the linker $S$ shows a magnetic moment of $\sim 1 \mu_B$ with half-occupied spin-down states of $p_x/p_y$ orbitals, while the connected Ag exhibits a very small moment with partially occupied spin-up and spin-down states of $S$ orbitals (see Fig. 4h, i), providing further support for the above proposal. Consideration of the bonding of every $S^2$– linker with two nanoparticles, we suggest that the electron transfer for $S^2$– is divided between the two connected silver atoms (Fig. 4j), forming one unpaired spin, and the electron on Ag can further transfer to the neighboring atoms, resulting in a distribution of the magnetic moment for the nanoparticle (Fig. 4g and Supplementary Table 2). The $g$ = 1.9790 determined from the EPR spectrum (Supplementary Fig. 21) reminds one of the existence of sulfur radicals.$^{17}$ To further verify the electron transfer from sulfur to the connected silver (i.e., formation of the sulfur radical), DMPO was used to capture the radical. As shown in Supplementary Figs. 26 and 27, strong radical signals were observed for the case of Ag$_{77}$Cu$_{22}$ assembly, but no significant signals were detected for the case of Au$_{72}$, confirming the presence of sulfur radicals in the Ag$_{77}$Cu$_{22}$ assembly and the absence of sulfur radicals in Au$_{72}$, since the sulfur radicals can be captured by DMPO and lead to the emergence of the EPR signal of the trap adducts as well as the decrease of the paramagnetism signal. 

Although the monosulfur radical signal was once detected under some specific conditions, the precise structure involving monosulfur radicals was undocumented.$^{23,24}$ Herein, the active sulfur radical might be stabilized by the assembly structure, which was confirmed by subsequent experimental results. When the assembled crystals are dissolved in dichloromethane, the EPR intensity decreases with increasing time (see the time evolution of the integrated EPR intensity in Supplementary Fig. 28 and the green line in Fig. 4b), and the EPR signal remains weak in the amorphous state after the solvent is removed (see blue line in Fig. 4b). In contrast, the EPR intensity for neutral Au$_{72}$ crystals is not quite influenced by dissolution (green line in Fig. 4a). Taken together, these facts demonstrate that the sulfur radical is stabilized by the specific assembly structure, which has important implications for novel functional development based on the assembly of atomically precise nanoparticles. It is concluded that chain structure disassembly can lead to electron return and the recovery of $S^2$–, which was verified by ion chromatography: no other sulfur ion species except for $S^2$– is detected in the extract of the disassembly solution (Supplementary Fig. 16b). After the electron returns to sulfur, the Ag$_{77}$Cu$_{22}$ nanoparticle is expected to bear an unpaired shell-closing electron, and thus, exhibits paramagnetism in solution (Supplementary Fig. 29). However, unlike the neutral Au$_{72}$ nanocluster, Ag$_{77}$Cu$_{22}$ shows a decreasing EPR intensity with increasing time in the solution, as mentioned above. A plausible reason for this is the spin pairing of Ag$_{77}$Cu$_{22}$ nanoparticles due to the short and flexible ligands that enable the nanoparticles to approach each other. However, the Au$_{72}$ nanoclusters cannot couple in solution due to the interference of the relatively long and rigid ligands, which is verified by TEM images since nanoparticle pairs are found for Ag$_{77}$Cu$_{22}$ but not for 2-phenylethanolated Au$_{72}$, as shown in Supplementary Figs. 30, 31a. Previous work also provides support: polymeric Au$_{72}$ capped by n-butanethiolates was proven to be antiferromagnetic due to spin coupling along the polymer chain.$^{19}$ Au$_{72}$ clusters along the chain ($z$-direction) are connected directly via Au–Au interactions, and the interparticle distance is 1.3001 nm, which is significantly shorter than that in the $x$- and $y$-directions (1.6311 nm and 1.7982 nm, respectively). To further probe the influence of the ligand on nanoparticle coupling, we conducted an EPR test for neutral Au$_{72}$ protected by a sulfur ligand (napthahenethiolate, Nap) or a more flexible ligand (CHT) than 2-phenylethanolthiolate (PET). Note that the 2-phenylethanolthiolates on the Au$_{72}$ nanocluster are fully exchanged by napthalenethiolates but not by cyclohexanethiolates, as identified by SCXCs or mass spectra (Supplementary Figs. 32 and 33), and five samples with varying content of cyclohexanethiolates were prepared. All five samples share UV–Vis spectra that are similar to that of Au$_{72}$(PET)$_{12}$ (Supplementary Fig. 34), implying structural similarity with Au$_{72}$(PET)$_{18}$. The substitution numbers ($X$s) were estimated from ESI-MS as follows: Au$_{72}$–I, $x = 2$–4; Au$_{72}$–II, $x = 3$–6; Au$_{72}$–III, $x = 5$–9; Au$_{72}$–IV, $x = 11$–15; Au$_{72}$–V, $x = 13$–17 (Supplementary Fig. 33). The experimental results reveal that napthalenethiolated Au$_{72}$ shows similar EPR signals in both solution and crystals without the time-dependent intensity observed in solution (Supplementary Fig. 35), while cyclohexanethiolated Au$_{72}$ exhibits cyclohexanethiolate content and a time-dependent EPR intensity in solution (Fig. 4c and Supplementary Fig. 36). Furthermore, the decrease in the EPR intensity corresponds to the nanoparticle pairing degree observed in TEM images (that is, the larger the decrease in the EPR intensity, the denser nanoparticle pairing, see Supplementary Fig. 31). Similarly, Maran et al. previously revealed that the EPR intensity of ethanethiolated Au$_{72}$ is influenced more by its state (crystal or solution) than n-butanolated Au$_{72}$.$^{19}$ Taken together, these facts demonstrate that the inter-nanoparticle distance (M: metal atom) is critical for spin coupling (i.e., spin coupling only occurs when the inter-nanoparticle distance is short enough). It is worth noting that such spin coupling does not result in the growth of nanoparticles since no large nanoparticles (or dimers) were detected by ESI-MS, UV-Vis spectrometry, and TEM (see Supplementary Figs. 37 and 38).

**Discussion**

In summary, we introduced an on-site synthesis-and-assembly strategy to solve the challenge of assembling atomically precise metal nanoparticles. A straight-chain structure composed of [Ag$_{77}$Cu$_{22}$($\text{CHT}_{48}$)]$^{2+}$ nanoparticles and linker $S^2$– was obtained, and it was precisely characterized by using ESI-MS and SCXCs. Interestingly, a rare Ag/Cu alloy shell was observed in the nanoparticles, and cyclic staples and a ripple-like thiolate distribution on the nanoparticles were, to the best of our knowledge, also reported for the first time. In particular, both calculations and experiments such as EPR and DMPO probing were used to reveal that the linker is sulfur radical with magnetic isotropy, which is formed by 2p electron transfer from $S^2$–.
to the connected silver atoms and stabilized by the chain structure. The disassembly of the straight-chain structure in solution leads to the return of the electron to $S^2$ and restoration of the paramagnetism of the $\text{Ag}_7\text{Cu}_{22}$ nanoparticles. However, the EPR intensity for $\text{Ag}_7\text{Cu}_{22}$ decreases with increasing time, which is ascribed to the spin coupling of $\text{Ag}_7\text{Cu}_{22}$ nanoparticles in solution. Further experiments reveal that the inter-nanoparticle distance is critical to the nanoparticle (nanocluster) spin coupling (i.e., coupling only occurs when the inter-M-M distance is short enough). Such an assembly-induced spin transfer and inter-nanoparticle distance-dependent spin coupling are not only interesting and surprising but also have important implications for the novel functional development of nanoparticles and the understanding of the shell-closing electron behavior of superatoms. It is expected that our work will extend a promising but still challenging field—the assembly of metal nanoparticles with atomic precision.

**Methods**

**Chemicals**

All chemicals were commercially available and used as received. Silver nitrate ($\text{AgNO}_3$, 99.99%), cuprous chloride ($\text{CuCl}$, 95%), cyclohexanethiol (CHT, 98%), tetraphenylphosphonium bromide (TPPB, 98%), naphthalenethiol ($\text{Nap}$, 99%), 2-phenylethanthiol (97%), and sodium borohydride ($\text{NaBH}_4$, 98.0%) were purchased from Aladdin. 5, 5-Dimethyl-1-pyrroline N-oxide (DMPO) was obtained from Dajindo. Triethyramine (99%), ethanol (AR), dichloromethane (AR), hexane (AR), Toluene (AR), and ethanol (AR) were purchased from Sinopharm chemical reagent co., ltd.

**Synthesis of AgCu nanoclusters**

AgCHT complexes were prepared by mixing 120 mg of AgNO$_3$ and 200 μl of CHT in MeOH. Then, 22 mg of the washed AgCHT complexes and 10 mg of CuCl were dissolved in 40 ml of $\text{CH}_2\text{Cl}_2$ in a 100 ml of single-neck round-bottom flask under vigorous stirring. Then, 20 μl of triethyramine was immediately added to the reaction solution. After that, 4 ml of an ethanol solution of NaBH$_4$ (38 mg) and TPPB (42 mg) was added dropwise to the mixture, which showed a color change from yellow to dark brown. The reaction was then kept under continuous stirring for 6 h under ice-cold conditions in the absence of light. The mixture was rotary evaporated to dryness to give a dark solid, which was added to the mixture, which showed a color change from yellow to dark brown. The reaction was then kept under continuous stirring for 6 h under ice-cold conditions in the absence of light. The mixture was rotary evaporated to dryness to give a dark solid, which was washed with methanol three times. Then, the tube was carefully capped and stored in a refrigerator at 4°C. Black crystals were obtained after approximately 1 month.

**Ligand exchange of Au$_{25}$(PET)$_{18}$**

Neutral Au$_{25}$ NCs were first prepared according to the previous literature. 10 mg Au$_{25}$ anions were dissolved in 8 ml $\text{CH}_2\text{Cl}_2$ and treated with 200 μl H$_2$O (30%) for 20 min at room temperature, then the organic solution was extracted and purified using preparative thin-layer chromatography to obtain Au$_{25}$ NCs. Six milligrams of neutral Au$_{25}$ was dissolved in 300 μl of toluene and then reacted with different amounts of CHT at room temperature for 30 min or 60 min. The products were precipitated and washed with methanol. Au$_{25}$(Nap)$_{18}$ was synthesized at 70° by mixing neutral Au$_{25}$ with excess Nap. The final product was purified using preparative thin-layer chromatography.

**Characterization**

Optical absorption spectra were acquired in the wavelength range of 190–900 nm using a Shimadzu UV-2600 spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Waters Q-TOF mass spectrometer equipped with a Z-spray source. Single crystal X-ray diffraction data were collected on a Bruker D8 Venture X-ray diffractometer (Bruker, Germany). The possible reasons for the high residual density are the inadequate absorption correction of silver which strongly absorbs X-rays or the uncertainty of the metal atoms (Ag or Cu), resulting in unresolved Q peaks. The low C-C bond precision originates from the constraints on the hexasyl ligands (S2 and S3) due to their varied configuration and weak diffraction intensity. X-band CW-EPR spectra were collected using a Bruker EMX plus 10/12 X-band EPR spectrometer equipped with an ER419HS (TE011) high-Q cavity. Cryogenic temperatures were achieved using an Oxford Instruments ESR910 liquid helium flow cryostat and an Oxford Instruments ITC503 temperature controller. A programmable one-axis goniometer was used for the sample rotation. Transmission electron microscopy (TEM) images were recorded using a Tecnai G2 TF20 instrument (FEI Co., USA). Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed on an Autoflex Speed TOF/TOF mass spectrometer (Bruker) in positive ionization mode. Magnetization measurements were carried out for the NCs (sealed into nonmagnetic capsules) as a function of temperature and field by using a SQUID magnetometer (Quantum Design MPMS3).

**Theoretical methods**

Ab initio calculations were performed based on spin-polarized density functional theory (DFT), as implemented in the Vienna Ab initio Simulation Package (VASP). The ion-electron interaction was described by the projector augmented wave (PAW) approach. The generalized gradient approximation (GGA) in the scheme of the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation interaction. The force and energy convergence criteria used for the electronic structure calculations were less than 0.02 eV/Å and 10−4 eV, respectively. Given the consideration of the strong correlation effect on the d orbitals of Ag and Cu, GGA + U calculations with effective U values of 1.5 eV (Au) and 1 eV (Ag and Cu) were performed by including a Hubbard U term. The spin moment and MAE were calculated by taking into consideration of spin-orbital coupling and magnetic noncollinearity. EPR simulations were carried out by assuming a distribution of randomly oriented S = 1/2 spin centers with a Lorentzian lineshape using the EasySpin toolbox working on the Matlab software platform.

**Reporting summary**

Further information on research design is available in the Nature Research Reporting Summary linked to this article.

**Data availability**

The X-ray crystallographic coordinates for structures reported in this work have been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition numbers 2207144 for the polymeric $\text{Ag}_7\text{Cu}_{22}$ nanoclusters, respectively. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif. Checkcif file for $\text{Ag}_7\text{Cu}_{22}$ CIF file is given as Supplementary Dataset. All data supporting the findings of this study are available within the article and its Supplementary Information files. Data were available from the first author and the corresponding author upon request.

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Author contributions
Z.W. conceived the project and analyzed the data. J. Zhao, and Z.Z. co-supervised the project and discussed the structure-magnetism correlation. N.X. designed the experiments and wrote the manuscript. J.X. carried out the DFT calculations. D.P. carried out the magnetism discussions on the calculation results.

Competing interests
The authors declare no competing interests.

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