Chemical Science

EDGE ARTICLE

Check for updates

Cite this: Chem. Sci., 2019, 10, 9684

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 5th June 2019 Accepted 4th September 2019

DOI: 10.1039/c9sc02736j rsc.li/chemical-science

Introduction

Metal nanoclusters represent an important stage in the evolution from discrete atoms to regular nanoparticles as many transitions in terms of structure and properties are expected to occur over the nanocluster regime.¹ Recent advances in solution-phase synthesis of atomically precise metal nanoclusters and their total structure determination by X-ray crystallography have opened up exciting opportunities for exploring the precise structure–property correlations.^{1–5} Significant progress has been achieved in controlling the size and structure of gold,^{6–12} silver,^{13–21} copper,^{22–24} and alloy nanoclusters.^{25–30} Such new materials hold potential in a wide range of applications,

Controlling magnetism of Au₁₃₃(TBBT)₅₂ nanoclusters at single electron level and implication for nonmetal to metal transition[†]

Chenjie Zeng, [10] ‡§ Andrew Weitz,‡ Gayathri Withers, Tatsuya Higaki, [10] Shuo Zhao, Yuxiang Chen, Roberto R. Gil, Michael Hendrich [10] * and Rongchao Jin [10] *

The transition from the discrete, excitonic state to the continuous, metallic state in thiolate-protected gold nanoclusters is of fundamental interest and has attracted significant efforts in recent research. Compared with optical and electronic transition behavior, the transition in magnetism from the atomic gold paramagnetism (Au 6s¹) to the band behavior is less studied. In this work, the magnetic properties of 1.7 nm $[Au_{133}(TBBT)_{52}]^0$ nanoclusters (where TBBT = 4-*tert*-butylbenzenethiolate) with 81 nominal "valence electrons" are investigated by electron paramagnetic resonance (EPR) spectroscopy. Quantitative EPR analysis shows that each cluster possesses one unpaired electron (spin), indicating that the electrons fill into discrete orbitals instead of a continuous band, for that one electron in the band would give a much smaller magnetic moment. Therefore, [Au133(TBBT)52]⁰ possesses a nonmetallic electronic structure. Furthermore, we demonstrate that the unpaired spin can be removed by oxidizing $[Au_{133}(TBBT)_{52}]^0$ to $[Au_{133}(TBBT)_{52}]^+$ and the nanocluster transforms from paramagnetism to diamagnetism accordingly. The UV-vis absorption spectra remain the same in the process of singleelectron loss or addition. Nuclear magnetic resonance (NMR) is applied to probe the charge and magnetic states of Au₁₃₃(TBBT)₅₂, and the chemical shifts of 52 surface TBBT ligands are found to be affected by the spin in the gold core. The NMR spectrum of Au₁₃₃(TBBT)₅₂ shows a 13-fold splitting with 4-fold degeneracy of 52 TBBT ligands, which are correlated to the guasi- D_2 symmetry of the ligand shell. Overall, this work provides important insights into the electronic structure of Au133(TBBT)52 by combining EPR, optical and NMR studies, which will pave the way for further understanding of the transition behavior in metal nanoclusters.

such as catalysis, chemical and biological detection, drug delivery, to name a few. $^{\rm 31-36}$

With respect to the optical transition, recent work has mapped out that the transition from excitonic to plasmonic state occurs between Au246(SR)80 to Au279(SR)84 for quasispherical gold nanoclusters.37-39 In contrast, the magnetic transition of Au_n(SR)_m nanoclusters remains largely elusive.^{40,41} It is known that discrete gold atoms are paramagnetic due to an unpaired electron in the 6s orbital $(6s^{1})$, while bulk gold is diamagnetic because the diamagnetic contribution from paired core-electrons outweigh the weak Pauli paramagnetism from itinerant electrons in the conduction band.42-44 Therefore, it is important to investigate the transition from atomic paramagnetism to bulk diamagnetism via atomically precise Au_n(- $SR)_m$ nanoclusters. However, this remains a challenge because of major difficulties in controlling nanoclusters at the singleelectron level.45-48 For example, oxidation treatment of the 8electron Au₂₃(SR)₁₆⁻ unfortunately led to size conversion,^{49,50} rather than the desired sole change of charge state as in $Au_{25}(SR)_{18}^{-.46-48}$

This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence. Open Access Article. Published on 04 September 2019. Downloaded on 4/16/2025 11:17:18 AM.



View Article Online

View Journal | View Issue

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Ave, Pittsburgh, PA, USA. E-mail: hendrich@andrew.cmu.edu; rongchao@andrew.cmu.edu

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c9sc02736j

[‡] These authors contribute equally.

 $[\]$ Current address: Department of Chemistry, University of Pennsylvania, 231 South $34^{\rm th}$ Street, Philadelphia, PA, 19104.

Despite the challenges in single-electron level control of metal nanoclusters,⁵¹ impressive progress has recently been achieved.52-57 Maran and coworkers have done a series of work on the magnetism of nanoclusters.⁴¹ Using Au₂₅(SR)₁₈ as an example, controlling its charge states has led to the observation of paramagnetism (e.g. neutral Au₂₅) and diamagnetism (e.g. ± 1 states of Au₂₅) probed by electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) measurements. In a simplified picture, neutral $[Au_{25}(SR)_{18}]^0$ has an electron count of 7e (*i.e.* 25 - 18 = 7); note that each monovalent thiolate covalently localizes one 6s1 electron from gold. The seven delocalized Au 6s¹ electrons are distributed in the superatomic orbitals (1s²1p⁵) of the Au₂₅.⁴⁰ The odd number of valence electron count leads to one unpaired electron (i.e. spin), which indeed explains the origin of the observed paramagnetism in $[Au_{25}(SR)_{18}]^0$. When the spin is removed by oxidation to $[Au_{25}(SR)_{18}]^+$ (6e) or is paired again with an electron *via* chemical reduction (*i.e.* $[Au_{25}(SR)_{18}]^{-}$, 8e), the nanocluster becomes diamagnetic.^{40,47,48,52} For Pd or Pt doped $[Au_{24}M(SR)_{18}]^0$ (M = Pd or Pt), Wu and coworkers reported the absence of paramagnetism despite the same charge state as [Au₂₅(SR)₁₈]^{0,55} Knappenberger et al. probed the spin-conversion dynamics in [Au₂₅(SC₈H₉)₁₈]⁰ and revealed multiple spin-polarized transient signals.⁴⁵ Solid-state magnetic properties of Au₂₅ have also been probed by various groups.58,59 Maran et al. has recently provided an excellent summary on the Au₂₅ magnetic properties.⁴¹ While much work has been done on the Au₂₅ system, there has been no extension yet to larger sizes of $Au_n(SR)_m$; the large-size regime (with hundreds of gold atoms) is desirable as transitions are expected to occur.

In this work we report our effort in controlling magnetism of a 1.7 nm Au₁₃₃(TBBT)₅₂ nanocluster (where TBBT represents 4*tert*-butylbenzenethiolate) at the single-electron level. Unlike the vast majority of nanoclusters ranging from small sizes (*e.g.* 4e Au₂₀(SR)₁₆,⁶⁰ 8e Au₂₈(SR)₂₀,^{61,62} 14e Au₃₈(SR)₂₄ (ref. 63)) to large ones (*e.g.* 80e Au₁₃₀(SR)₅₀,⁶⁴ 84e Au₁₄₄(SR)₆₀,⁸ 166e Au₂₄₆(SR)₈₀ (ref. 6)), where all the clusters have even counts on valence electrons, Au₁₃₃(TBBT)₅₂ is unique in that it possesses an odd count (81e).⁶⁵ Significantly, in this work we find that Au₁₃₃(TBBT)₅₂ exhibits interesting paramagnetism, with one spin per particle. This result is surprising given its large size and seemly metallic state.⁶⁶ We have further investigated the spin effects on the optical properties and ligand's chemical shifts, as well as comparisons with the classical Au₂₅ system.

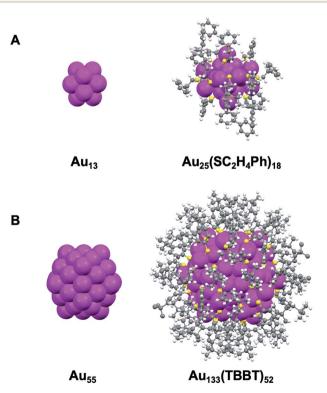
Results and discussions

The Au₁₃₃(TBBT)₅₂ nanocluster was synthesized by the LEIST method^{50,65} (where, LEIST = ligand-exchange induced size/ structure transformation reaction). Briefly, Au₁₄₄(SC₂H₄Ph)₆₀ nanoclusters were first made and then reacted with excess TBBT thiols at 80 °C under ambient conditions. After 4 days, Au₁₄₄(-SC₂H₄Ph)₆₀ were completely transformed into Au₁₃₃(TBBT)₅₂ (see ESI† for details). To ensure the highest purity and quality, Au₁₃₃(TBBT)₅₂ was crystallized prior to EPR, NMR and optical measurements. The total structure of Au₁₃₃(TBBT)₅₂ was reported by Zeng *et al.*;⁶⁵ of note, the partial structure without the surface ligand patterns was reported by Dass *et al.*⁶⁶ Both Au₁₃₃ and Au₂₅ possess a common icosahedral core,⁶⁵⁻⁶⁷ with Au₂₅ being built from a one-shelled icosahedron containing 13 atoms (Au₁₃@[Au₂(SR)₃]₆, Scheme 1A),⁶⁷ whereas Au₁₃₃ from a two-shell icosahedron containing 55 atoms (*i.e.* Au₁₃@-Au₄₂@Au₅₂@[Au(SR)₂]₂₆,^{65,66} Scheme 1B).

Spin properties of Au₁₃₃(TBBT)₅₂

To measure the EPR spectra, $[Au_{133}(TBBT)_{52}]^0$ crystals⁶⁵ were dissolved in a mixed solvent of toluene/CH₂Cl₂ (volumetric ratio of 1/1, which forms a clear glass at cryogenic temperatures). Fig. 1 shows S-band (3.480 GHz) and X-band (9.645 GHz) EPR spectra of $[Au_{133}(TBBT)_{52}]^0$. The spectra are displayed on different magnetic field scales that equate the *g*-value scales for both microwave frequencies. Both S- and X-band spectra display a signal with $g_{\parallel} = 2.47$ and $g_{\perp} = 1.69$. The signal at g = 2.03 (Sband only) is from a minor extraneous copper impurity. The temperature dependence of the signal intensity from 2 to 25 K was observed to obey the Curie law (intensity *vs.* 1/*T*), which indicate the behavior of molecular magnetism as opposed to the electron-conduction-band Pauli paramagnetism (*i.e.*, temperature independent).

EPR quantification reveals a S = 1/2 spin concentration that agrees with the molar concentration of the prepared $[Au_{133}(-TBBT)_{52}]^0$ solution. Thus, each $[Au_{133}(TBBT)_{52}]^0$ nanocluster hosts a total of one unpaired spin, which results from the odd 81 electrons. The observation of an unpaired spin in $[Au_{133}(-TBBT)_{52}]^0$ indicates that the 6s¹ electrons from Au atoms are



Scheme 1 Comparison between the X-ray structures of (A) $Au_{25}(-SC_2H_4Ph)_{18}$ and (B) $Au_{133}(TBBT)_{52}$ (TBBT = S-Ph-p-^tBu). Redrawn from ref. 65 and 67.

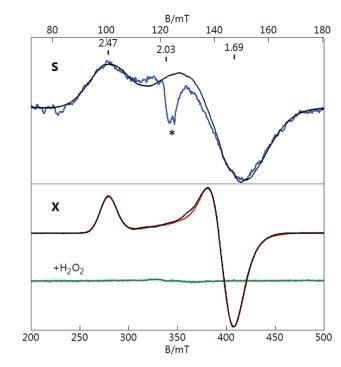


Fig. 1 S-band (3.480 GHz) and X-band (9.645 GHz) EPR spectra of $[Au_{133}(TBBT)_{52}]^0$ in 1 : 1 CH₂Cl₂ : toluene at T = 10 K (S-band), 6 K (Xband). Microwave power: 0.3 mW (S-band), 2 mW (X-band), see text for parameters of simulations (black lines). The green trace shows loss of signal after H_2O_2 addition. The g = 2.03 signal (indicated by *) is from the extraneous copper impurity.

filled onto discrete energy levels of the nanocluster, which infers that the continuous band structure has not formed in Au133(TBBT)52 despite its 1.7 nm size. Similar to the case of $[Au_{25}(SR)_{18}]^0$, the unpaired spin can be removed by oxidation to $[Au_{133}(TBBT)_{52}]^+$, which has an electron count of 80. As shown in Fig. 1 (green line), when reacting with H_2O_2 , the sample showed total loss of the paramagnetic signal, indicating that $[Au_{133}(TBBT)_{52}]^+$ is diamagnetic.

To gain a better understanding of the unpaired spin and the EPR spectrum of Au₁₃₃, we first consider the same effects from the previously characterized [Au₂₅(SR)₁₈]⁰ nanoclusters. Fig. 2 displays S- and X-band EPR spectra of $[Au_{25}(SR)_{18}]^0$ in 1:1 DCM : toluene solution at cryogenic temperatures. The X-band spectrum reproduces our previous work.40 Both spectra display a signal with a g-tensor of (2.61, 2.34, 1.81), which in contrast to $[Au_{133}(TBBT)_{52}]^0$ is not axial. If the larger two gvalues of Au₂₅ (2.61 and 2.34) are averaged and associated with an axial tensor to give $g_{\parallel}=$ 1.81 and $g_{\perp}=$ 2.48, then the values are roughly similar to Au133 but have swapped directions, indicating a change in symmetry for the orbital of the unpaired electron. If we follow the superatomic orbital sequence of 1S 1P 1D 2S 1F 2P 1G 2D 1H, we obtain 1H orbital (angular momentum quantum number l = 5, degeneracy 2l + 1 = 11, 13e filled) as the HOMO of $[Au_{133}(TBBT)_{52}]^0$ (cf. 1P⁵ as the HOMO of $[Au_{25}(SR)_{18}]^0$; apparently, if the last electron is indeed filled into the 1H orbital, then the 1H orbital (a set of 11) should be split, with the topmost orbital being non-degenerate. This is

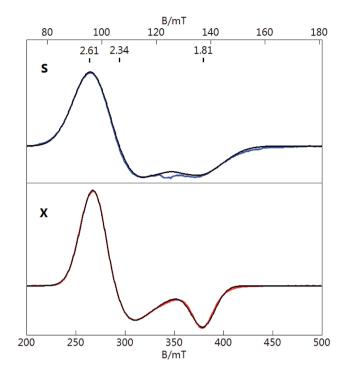


Fig. 2 S-band (3.489 GHz) and X-band (9.644 GHz) EPR spectra of $[Au_{25}(SR)_{18}]^{0}$ in 1 : 1 CH₂Cl₂ : toluene at T = 10 K (S), 6 K (X). Microwave power: 0.3 mW (S), 2 mW (X). See text for parameters of simulations (black lines).

reminiscent of the case of $[Au_{25}(SR)_{18}]^0$, in which the HOMO (1P set) is split into non-degenerate orbitals.52 Future theoretical simulations^{40,52} may reveal more insight into the cluster/ molecular orbitals of Au₁₃₃.

The S-band spectrum is broader that the X-band spectrum due to unresolved Au hyperfine structure of $[Au_{25}(SR)_{18}]^0$ (note: ¹⁹⁷Au nuclear spin I = 3/2, natural abundance 100%). The black traces overlaid on both spectra (Fig. 2) are simultaneous leastsquares fits to the data for S = 1/2 and 12 equivalent Au nuclei with an isotropic A-tensor of $A_{iso} = 48$ MHz. The value of Aiso agrees with that determined from ENDOR spectroscopy for the icosahedral core of inner Au nuclei.⁵³ One unpaired electron equally delocalized over 12 Au nuclei would equate to a value of $A_{\rm iso} \approx 600$ MHz for an unpaired electron localized at a single Au atom. This value can be compared to the value of Aiso for a free Au atom of 3050 MHz. The reduction of Aiso for the Au nanoclusters is consistent with the significant sp hybridization of the Au centers as described previously.40

The simulations displayed in Fig. 1 for $[Au_{133}(TBBT)_{52}]^0$ are least-squares fits for S = 1/2 and 12 equivalent Au (I = 3/2)nuclei with an isotropic A-tensor of $A_{iso} = 50$ MHz. These values are comparable to that of $[Au_{25}(SR)_{18}]^0$. We considered that the unpaired electron for $[Au_{133}(TBBT)_{52}]^0$ could be distributed over a significantly higher number of Au centers; for example, the inner 55 Au centers (Scheme 1) that are all bonded only to neighboring Au center. Simulations with 55 equivalent Au centers required $A_{\rm iso} = 26$ MHz. This value would give an $A_{\rm iso}$ for an unpaired electron localized at a single Au center of 1500 MHz. The higher values would require a significant change in

the hybridization of unpaired orbital, which is unlikely. Thus, although the number of Au centers is significantly greater for $[Au_{133}(TBBT)_{52}]^0$, the delocalization of the wavefunction of the unpaired electron is similar to that of $[Au_{25}(SR)_{18}]^0$. Therefore, the EPR analysis implies that the 1H orbital should be in the inner-most icosahedron.

The observation of a single unpaired electron in the [Au₁₃₃(-TBBT)₅₂]⁰ infers that the Au₁₃₃ cluster has similar discrete electronic orbitals as in the Au₂₅ to hold the unpaired spin. In other words, Au₁₃₃ has a non-metallic nature; otherwise, an itinerant metallic-like conduction band would be formed and the cluster would show Pauli paramagnetism (much weaker than the observed molecular paramagnetism). The observation of molecular magnetism is important for understanding of the transition between molecular and metallic-state behaviors in Au nanoclusters/nanoparticles, and Au nanomagnetism in general. From the EPR study, the conclusion of Au133 being nonmetallic is consistent with the conclusion provided by the optical absorption of Au₁₃₃, which shows multiple peaks at 336, 421, 503 and 712 nm (Fig. 3), as well as the femtosecond transient signal which showed a laser-power independent decay rate of photoexcited electron,65 hence, nonmetallic or non-plasmonic nature of the Au133 cluster. Our results disagree with the previous conclusion that Au₁₃₃(SR)₅₂ was metallic.⁶⁶

Optical absorption properties of $[Au_{133}(TBBT)_{52}]^0$ and $[Au_{133}(TBBT)_{52}]^+$

We further measured the UV-vis absorption spectra of two charge states, which showed no distinguishable difference between $[Au_{133}(TBBT)_{52}]^0$ and $[Au_{133}(TBBT)_{52}]^+$ (Fig. 3). Therefore, it is difficult to differentiate the charge states of $Au_{133}(TBBT)_{52}$ by its absorption spectrum. This is different from the case of $Au_{25}(SR)_{18}$,⁴⁶ in which the change of the oxidation state from $[Au_{25}(SR)_{18}]^-$ to $[Au_{25}(SR)_{18}]^0$ resulted in a blue shift of the ~670 nm peak as well as an increase in the ~400 nm peak intensity. The similarity between the absorption spectra of $[Au_{133}(TBBT)_{52}]^0$ and $[Au_{133}(TBBT)_{52}]^+$ may be ascribed to the much less perturbation of one electron loss in Au_{133} (1 out 81e)

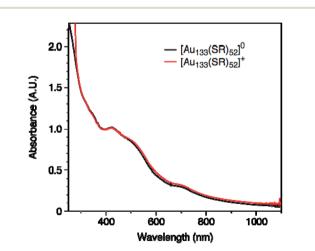


Fig. 3 UV-vis absorption spectra of $[Au_{133}(TBBT)_{52}]^0$ and $[Au_{133}(TBBT)_{52}]^+$.

than Au_{25} (1 out of 8e) as well as possibly less structural distortion in Au_{133} than Au_{25} when switching the charge state. 46,56,57

We also performed electrochemical oxidation of $[Au_{133}(-TBBT)_{52}]^0$ by applying positive voltages and monitored the optical spectra *in situ*,^{68,69} but no change in optical spectra was found, even after applying a 1 V bias for 90 min (Fig. S1†). This further indicates that the optical spectrum of Au_{133} is insensitive to the change of oxidation state. In comparison, the absorption spectra of $[Au_{25}(SR)_{18}]^-$ changed at 0.6 V (for 60 min) due to the formation of $[Au_{25}(SR)_{18}]^0$ (Fig. S2†).

Spin effects on the surface ligands probed by NMR

NMR analysis on ligand-protected nanoclusters can provide important information on the symmetry of surface ligand shell and the charge state of nanoclusters, as demonstrated previously.41,64,70-72 Unlike the free ligand in solution, the ligands on the surface of nanoclusters are confined to different chemical environments. Therefore, the same type of ligands can show different chemical shifts and split into different groups. When the charge state and the corresponding magnetic state of the nanocluster change, the NMR spectrum also changes accordingly. Here we employed NMR to first analyze the symmetry of ligand shell and then probe the redox properties of Au₁₃₃(-TBBT)₅₂. In the smaller Au₂₅(SCH₂CH₂Ph)₁₈ case, it was demonstrated that the NMR peaks shifted significantly when going from diamagnetic (q = -1) to paramagnetic (q = 0), especially for the α -carbon hydrogen atoms (-SC^{α}H₂C^{β}H₂Ph) since they are close to the gold core.47,48 Interestingly, we found that, despite Au_{133} (TBBT)₅₂ being two shells larger than Au_{25} , the NMR spectrum of Au133(TBBT)52 can still be affected by the magnetic state of the core. In addition, not only the closer aromatic ¹H but also the further *tert*-butyl ¹H can be influenced by the change in magnetism.

We first analyze the NMR spectra of free TBBT thiols and [Au₁₃₃(TBBT)₅₂]⁰ nanocluster. For the free TBBT thiol, HS- C_6H_4 -C(CH₃)₃, the nine identical hydrogens in the *tert*-butyl group give rise to an intense singlet peak at 1.30 ppm, and the four hydrogens in the aromatic part give rise to a pair of symmetrical doublets at 7.22/7.24 and 7.26/7.29 ppm (Fig. 4A and S3[†]). Such simple, symmetric and intense NMR signals of TBBT thiols greatly facilitate the further analysis of complex ligand patterns on the Au133 surface. When confined on the Au₁₃₃ surface, the 52 TBBT thiolates are split into 13 groups, with each group containing 4 ligands. This is mostly evidenced in the tert-butyl ¹H; the 1.30 ppm peak in free thiol is split into 13 peaks ranging from \sim 0.72 to \sim 1.39 ppm (Fig. 4B and S4[†]). A similar splitting pattern can also be identified in the aromatic region, but not as distinct as the singlet tert-butyl ¹H (i.e. 2H vs. 9H). As shown in the 2D correlation spectrum (¹H–¹H COSY) in the aromatic region (Fig. 4C), 10 pairs of aromatic doublets from the TBBT ligands can be clearly identified and the detailed peak positions are listed in Table S1.[†] It is difficult to identify the remaining 3 pairs, probably due to the overlap of signals or broadening of peaks when protons are very close to the gold core.

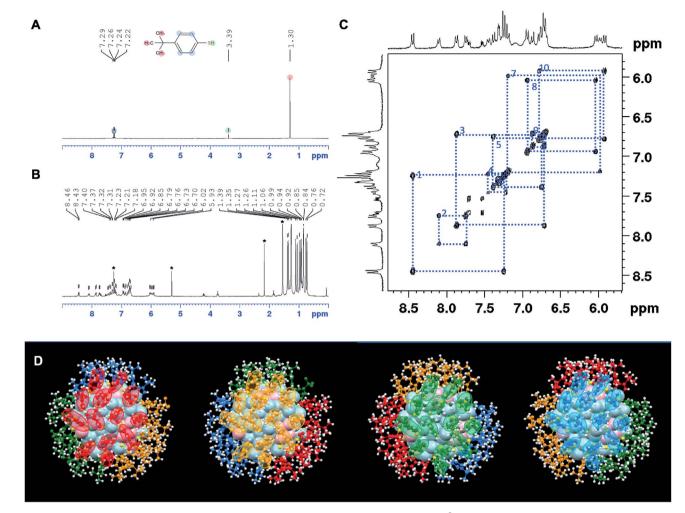


Fig. 4 Correlation between the NMR spectra and ligand shell symmetry of $[Au_{133}(TBBT)_{52}]^0$. (A) NMR of free TBBT thiol. (B) NMR of $[Au_{133}(TBBT)_{52}]^0$ nanoclusters, the stars indicate solvent peaks: chloroform (7.26), CH₂Cl₂ (5.30), acetone (2.17) and H₂O (1.56). (C) ¹H-¹H COSY of the aromatic region of $[Au_{133}(TBBT)_{52}]^0$ for the correlation of doublet pairs. (D) Symmetry of ligand shells. The four symmetrically identical surface ligand patches are highlighted in red, orange, green and blue colors, corresponding to the 4-fold degeneracy of 52 TBBT ligands. The 13 TBBT ligands in each patch correlate to the 13-fold splitting of NMR pattern. Au: pink and light blue; S: yellow; C: red, orange, green and blue; and H: white.

The 13-fold splitting and 4-fold degeneracy of the 52 TBBT ligands are the reflection of the symmetry of the ligand shell in Au₁₃₃(TBBT)₅₂. Since all the thiolates are assembled into monomeric staple motifs (*i.e.* 26 of -S-Au-S-) in Au₁₃₃(TBBT)₅₂, there is no symmetry breaking due to formation of different staple motifs. Therefore, the 4-fold degeneracy indicates that there are four identical ligand patches on Au₁₃₃ surface, and the 13-fold splitting infers that in each patch, there are 13 chemically different TBBT ligands. Indeed, this NMR splitting pattern can be correlated with the symmetry of surface ligand shell. As shown in Fig. 4D, the 52 TBBT ligands can be divided into four symmetrically identical patches as labeled in red, orange, green and blue colors. Each surface patch contains 13 TBBT ligands. Therefore, the ligand shell has a quasi- D_2 symmetry. Such splitting of NMR signal of ligands according to the symmetry of the nanoclusters have also been inferred in Au₁₃₀(SR)₅₀, which exhibits a 10-fold degeneracy and 5-fold splitting in its NMR spectrum, reflecting its quasi D₅ symmetry.⁶⁴ We note that it is

possible to qualitatively correlates some NMR peaks with ligands location based on the electron density around the ligands, but a quantitative correlation requires in-depth theoretical calculations given that 13 correlation needs to be made. Nonetheless, the detailed correlation of the complex NMR pattern with the symmetry of Au_{133} (TBBT)₅₂ proves the potential of using NMR to characterize the structural symmetry of atomically precise nanoclusters, similar to the case of the protein structure determination. It is worth noting that Maran *et al.* recently probed the Au_{144} (SR)₆₀ structure by NMR.⁷²

Redox properties of [Au₁₃₃(TBBT)₅₂]⁰ and [Au₁₃₃(TBBT)₅₂]⁺

As aforementioned, optical spectra of two charge states showed no discernable difference, but NMR can indeed be useful. We probed the aliphatic region (0–2 ppm) in the NMR spectra to further analyze the redox behavior of Au_{133} (TBBT)₅₂ since the *tert*-butyl ¹H gives stronger signals than the phenyl ¹H. Fig. 5

Edge Article

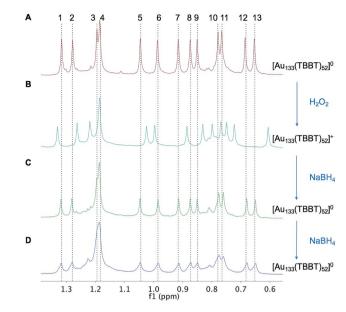


Fig. 5 Redox property of Au₁₃₃(TBBT)₅₂ probed by NMR. (A) NMR of tert-butyl-H in [Au₁₃₃(TBBT)₅₂]⁰. (B) Oxidation of $[Au_{133}(TBBT)_{52}]^0$ to $[Au_{133}(TBBT)_{52}]^+$ by H₂O₂. (C) Reduction of $[Au_{133}(TBBT)_{52}]^+$ to $[Au_{133}(TBBT)_{52}]^0$ by NaBH₄. (D) Further reaction of $[Au_{133}(TBBT)_{52}]^0$ with NaBH₄.

shows that when paramagnetic $[Au_{133}(TBBT)_{52}]^0$ is oxidized by H_2O_2 to diamagnetic $[Au_{133}(TBBT)_{52}]^+$, the NMR spectrum changes, with shifts of peaks to both lower and higher fields. The differences in NMR spectra between $[Au_{133}(TBBT)_{52}]^0$ and $[Au_{133}(TBBT)_{52}]^+$ should result from the change of magnetic state and charge state of the gold core. The protons in *tert*-butyl group, about 1 nm away from the gold surface, can still sense the change of magnetic states of the gold core; while the slight shifts and similar splitting ranges indicates that magnetic field disturbance in Au_{133} is not as significant as in the smaller Au_{25} nanocluster. The shifts of the proton peaks may also imply that the superatomic orbital that hold the unpaired electron spin may have none-spherical shape which cause inhomogeneous distribution of magnetic field on the ligand shell, therefore leading to both up and down shifts.

The $[Au_{133}(TBBT)_{52}]^+$ can be reduced to $[Au_{133}(TBBT)_{52}]^0$ by NaBH₄, as evidenced in the recovery of the NMR spectrum to that of $[Au_{133}(TBBT)_{52}]^0$ (Fig. 5C). Increasing the reaction time as well as adding more NaBH₄ cannot further reduce $[Au_{133}(TBBT)_{52}]^0$ to $[Au_{133}(TBBT)_{52}]^-$, based on the identical peak positions in NMR spectra after adding more NaBH₄ (Fig. 5D). Instead, Au₁₃₃ gradually decomposed in the presence of large excess NaBH₄, as evidenced in the decreasing intensity and broadening of peaks in NMR. This may be due to the stripping of surface TBBT ligands by excess NaBH₄ and then the aggregation of nanoclusters.

Conclusion

In summary, paramagnetism is discovered in the 1.7 nm Au_{133} (TBBT)₅₂ nanocluster and reversible switch between

paramagnetism and diamagnetism is demonstrated. Through EPR measurements, we proved that $[Au_{133}(TBBT)_{52}]^0$ (an 81electron nanocluster) hosts one unpaired electron. The observation of one spin per cluster in Au133 implies that Au133 is nonmetallic, with its electrons being distributed in discrete orbitals instead of filling a continuous band. EPR simulations suggest that the unpaired spin is mainly delocalized in the inner 13atom icosahedral core, which is similar to the case of paramagnetic $[Au_{25}(SR)_{18}]^0$ (7e). NMR measurements show a 13-fold splitting and 4-fold degeneracy of the 52 TBBT ligands on the Au₁₃₃ surface, which is correlated to the D_2 symmetry of the ligand shell. When [Au₁₃₃(TBBT)₅₂]⁰ is oxidized to [Au₁₃₃(- $TBBT)_{52}^{+}$, the nanocluster changes to diamagnetism, as evidenced in the disappearance of EPR signal as well as the shift of NMR peaks. $[Au_{133}(TBBT)_{52}]^+$ can be reduced back to $[Au_{133}([\text{TBBT}]_{52}^{0}$ and the NMR peaks are restored, hence, a reversible process. Further reduction of Au₁₃₃(0) by NaBH₄ lead to degradation of nanoclusters instead of forming [Au₁₃₃(TBBT)₅₂]⁻. In future work, the spin effects on the ultrafast electron dynamics and catalytic reactivity deserve to be pursued.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge financial support from the National Science Foundation (DMR-1808675). Funding for the EPR spectrometer was from National Science Foundation grant CHE1126268.

References

- 1 R. Jin, C. Zeng, M. Zhou and Y. Chen, *Chem. Rev.*, 2016, **116**, 10346.
- 2 S. Takano, S. Hasegawa, M. Suyama and T. Tsukuda, Acc. Chem. Res., 2018, 51, 3074.
- 3 Y. Negishi, T. Nakazaki, S. Malola, S. Takano, Y. Niihori, W. Kurashige, S. Yamazoe, T. Tsukuda and H. Häkkinen, *J. Am. Chem. Soc.*, 2015, **137**, 1206.
- 4 Q. Yao, X. Yuan, T. Chen, D. T. Leong and J. Xie, *Adv. Mater.*, 2018, **30**, 1802751.
- 5 C. Zeng, Y. Chen, K. Iida, K. Nobusada, K. Kirschbaum, K. J. Lambright and R. Jin, *J. Am. Chem. Soc.*, 2016, **138**, 3950.
- 6 C. Zeng, Y. Chen, K. Kirschbaum, K. J. Lambright and R. Jin, *Science*, 2016, **354**, 1580.
- 7 Z. Lei, X. K. Wan, S. F. Yuan, Z. J. Guan and Q. M. Wang, Acc. Chem. Res., 2018, 51, 2465.
- 8 N. Yan, N. Xia, L. Liao, M. Zhu, F. Jin, R. Jin and Z. Wu, *Sci. Adv.*, 2018, 4, eaat7259.
- 9 K. Konishi, M. Iwasaki and Y. Shichibu, *Acc. Chem. Res.*, 2018, **51**, 3125.
- 10 N. A. Sakthivel and A. Dass, Acc. Chem. Res., 2018, 51, 1774.
- 11 S. Takano, H. Hirai, S. Muramatsu and T. Tsukuda, J. Am. Chem. Soc., 2018, 140, 8380.
- 12 Y. Z. Li, R. Ganguly, K. Y. Hong, Y. Li, M. E. Tessensohn, R. Webster and W. K. Leong, *Chem. Sci.*, 2018, **9**, 8723.

- 13 B. Bhattarai, Y. Zaker, A. Atnagulov, B. Yoon, U. Landman and T. P. Bigioni, *Acc. Chem. Res.*, 2018, **51**, 3104.
- 14 J. Yan, B. K. Teo and N. Zheng, Acc. Chem. Res., 2018, 51, 3084.
- 15 M. J. Alhilaly, M. S. Bootharaju, C. P. Joshi, T. M. Besong, A.-H. Emwas, R. Juarez-Mosqueda, S. Kaappa, S. Malola, K. Adil, A. Shkurenko, H. Häkkinen, M. Eddaoudi and O. M. Bakr, J. Am. Chem. Soc., 2016, 138, 14727.
- 16 S. M. Aly, L. G. AbdulHalim, T. M. D. Besong, G. Soldan, O. M. Bakr and O. F. Mohammed, *Nanoscale*, 2016, 8, 5412.
- S. Bestgen, O. Fuhr, B. Breitung, V. S. K. Chakravadhanula,
 G. Guthausen, F. Hennrich, W. Yu, M. M. Kappes,
 P. W. Roesky and D. Fenske, *Chem. Sci.*, 2017, 8, 2235.
- 18 I. Russier-Antoine, F. Bertorelle, R. Hamouda, D. Rayane, P. Dugourd, Ž. Sanader, V. Bonačić-Koutecký, P. F. Brevet and R. Antoine, *Nanoscale*, 2016, 8, 2892.
- 19 G. X. Duan, L. Tian, J. B. Wen, L. Y. Li, Y. P. Xie and X. Lu, *Nanoscale*, 2018, **10**, 18915.
- 20 L. Suber, P. Imperatori, L. Pilloni, D. Caschera, N. Angelini, A. Mezzi, S. Kaciulis, A. Iadecola, B. Joseph and G. Campi, *Nanoscale*, 2018, **10**, 7472.
- 21 Y. L. Li, Z. Y. Wang, X. H. Ma, P. Luo, C. X. Du and S. Q. Zang, *Nanoscale*, 2019, **11**, 5151.
- 22 T.-A. D. Nguyen, Z. R. Jones, B. R. Goldsmith, W. R. Buratto,
 G. Wu, S. L. Scott and T. W. Hayton, *J. Am. Chem. Soc.*, 2015, 137, 13319.
- 23 A. W. Cook and T. W. Hayton, Acc. Chem. Res., 2018, 51, 2456.
- 24 K. K. Chakrahari, R. P. B. Silalahi, J. H. Liao, S. Kahlal, Y. C. Liu, J. F. Lee, M. H. Chiang, J. Y. Saillard and C. W. Liu, *Chem. Sci.*, 2018, 9, 6785.
- 25 L. V. Nair, S. Hossain, S. Takagi, Y. Imai, G. Hu, S. Wakayama, B. Kumar, W. Kurashige, D. Jiang and Y. Negishi, *Nanoscale*, 2018, **10**, 18969.
- 26 S. Hossain, Y. Niihori, L. V. Nair, B. Kumar, W. Kurashige and Y. Negishi, *Acc. Chem. Res.*, 2018, **51**, 3114.
- 27 X. Kang, M. Zhou, S. Wang, S. Jin, G. Sun, M. Zhu and R. Jin, *Chem. Sci.*, 2017, **8**, 2581.
- 28 Z. Wang, R. Senanayake, C. M. Aikens, W.-M. Chen, C.-H. Tung and D. Sun, *Nanoscale*, 2016, 8, 18905.
- 29 Y. Song, Y. Lv, M. Zhou, T. Y. Luo, S. Zhao, N. L. Rosi, H. Yu, M. Zhu and R. Jin, *Nanoscale*, 2018, **10**, 12093.
- 30 K. R. Krishnadas, A. Baksi, A. Ghosh, G. Natarajan and T. Pradeep, *Nat. Commun.*, 2016, 7, 13447.
- 31 Z. Li, W. Li, H. Abroshan, Q. Ge, G. Li and R. Jin, *Nanoscale*, 2018, **10**, 6558.
- 32 S. Antonello, M. Hesari, F. Polo and F. Maran, *Nanoscale*, 2012, 4, 5333.
- 33 K. Kwak and D. Lee, Acc. Chem. Res., 2019, 52, 12.
- 34 Q. Li, Y. Pan, T. Chen, Y. Du, H. Ge, B. Zhang, J. Xie, H. Yu and M. Zhu, *Nanoscale*, 2018, **10**, 10166.
- 35 W. Kurashige, R. Kumazawa, D. Ishii, R. Hayashi, Y. Niihori, S. Hossain, L. V. Nair, T. Takayama, A. Iwase, S. Yamazoe, T. Tsukuda, A. Kudo and Y. Negishi, *J. Phys. Chem. C*, 2018, **122**, 13669.
- 36 M. Li, Y. H. Lao, R. L. Mintz, Z. Chen, D. Shao, H. Hu, H. X. Wang, Y. Tao and K. W. Leong, *Nanoscale*, 2019, 11, 2631.

- 37 M. Zhou, C. Zeng, Y. Chen, S. Zhao, M. Y. Sfeir, M. Zhu and R. Jin, *Nat. Commun.*, 2016, 7, 13240.
- 38 M. Zhou, C. Zeng, Y. Song, J. W. Padelford, G. Wang, M. Y. Sfeir, T. Higaki and R. Jin, *Angew. Chem., Int. Ed.*, 2017, 56, 16257.
- 39 T. Higaki, M. Zhou, K. J. Lambright, K. Kirschbaum, M. Y. Sfeir and R. Jin, *J. Am. Chem. Soc.*, 2018, **140**, 5691.
- 40 M. Zhu, C. M. Aikens, M. P. Hendrich, R. Gupta, H. Qian,
 G. C. Schatz and R. Jin, *J. Am. Chem. Soc.*, 2009, 131, 2490.
- 41 M. Agrachev, M. Ruzzi, A. Venzo and F. Maran, *Acc. Chem. Res.*, 2019, **52**, 44.
- 42 Z. Wu, J. Chen and R. Jin, Adv. Funct. Mater., 2011, 21, 177.
- 43 G. L. Nealon, B. Donnio, R. Greget, J.-P. Kappler, E. Terazzi and J.-L. Gallani, *Nanoscale*, 2012, 4, 5244.
- 44 A. Cirri, A. Silakov and B. J. Lear, *Angew. Chem., Int. Ed.*, 2015, 54, 11750–11753.
- 45 L. J. Williams, P. J. Herbert, M. A. Tofanelli, C. J. Ackerson and K. L. Knappenberger Jr, *J. Chem. Phys.*, 2019, **150**, 101102.
- 46 M. Zhu, W. T. Eckenhoff, T. Pintauer and R. Jin, *J. Phys. Chem. C*, 2008, **112**, 14221.
- 47 A. Venzo, S. Antonello, J. A. Gascón, I. Guryanov,
 R. D. Leapman, N. V. Perera, A. Sousa, M. Zamuner,
 A. Zanella and F. Maran, *Anal. Chem.*, 2011, 83, 6355.
- 48 Z. Liu, M. Zhu, X. Meng, G. Xu and R. Jin, *J. Phys. Chem. Lett.*, 2011, 2, 2104.
- 49 T. Higaki, C. Liu, Y. Chen, S. Zhao, C. Zeng, R. Jin, S. Wang, N. L. Rosi and R. Jin, *J. Phys. Chem. Lett.*, 2017, **8**, 866.
- 50 C. Zeng, Y. Chen, A. Das and R. Jin, *J. Phys. Chem. Lett.*, 2015, 6, 2976.
- 51 Z. Wu, C. Gayathri, R. R. Gil and R. Jin, *J. Am. Chem. Soc.*, 2009, **131**, 6535.
- 52 S. Antonello, N. V. Perera, M. Ruzzi, J. A. Gascón and F. Maran, J. Am. Chem. Soc., 2013, 135, 15585.
- 53 T. Dainese, S. Antonello, J. A. Gascón, F. Pan, N. V. Perera, M. Ruzzi, A. Venzo, A. Zoleo, K. Rissanen and F. Maran, *ACS Nano*, 2014, 8, 3904.
- 54 M. Agrachev, S. Antonello, T. Dainese, J. A. Gascón, F. Pan,
 K. Rissanen, M. Ruzzi, A. Venzo, A. Zoleo and F. Maran, *Chem. Sci.*, 2016, 7, 6910.
- 55 S. Tian, L. Liao, J. Yuan, C. Yao, J. Chen, J. Yang and Z. Wu, *Chem. Commun.*, 2016, **52**, 9873.
- 56 S. Antonello, T. Dainese, F. Pan, K. Rissanen and F. Maran, *J. Am. Chem. Soc.*, 2017, **139**, 4168.
- 57 M. A. Tofanelli, K. Salorinne, T. W. Ni, S. Malola, B. Newell,
 B. Phillips, H. Häkkinen and C. J. Ackerson, *Chem. Sci.*, 2016,
 7, 1882.
- 58 K. S. Krishna, P. Tarakeshwar, V. Mujica and C. S. S. R. Kumar, *Small*, 2014, **10**, 907.
- 59 M. Agrachev, S. Antonello, T. Dainese, M. Ruzzi, A. Zoleo, E. Aprà, N. Govind, A. Fortunelli, L. Sementa and F. Maran, ACS Omega, 2017, 2, 2607.
- 60 C. Zeng, C. Liu, Y. Chen, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 11922.
- 61 C. Zeng, T. Li, A. Das, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10011.

- 62 Y. Chen, C. Liu, Q. Tang, C. Zeng, T. Higaki, A. Das,
 D. E. Jiang, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2016, 138, 1482.
- 63 H. Qian, W. T. Eckenhoff, Y. Zhu, T. Pintauer and R. Jin, J. Am. Chem. Soc., 2010, 132, 8280.
- 64 Y. Chen, C. Zeng, C. Liu, K. Kirschbaum, C. Gayathri, R. R. Gil, N. L. Rosi and R. Jin, *J. Am. Chem. Soc.*, 2015, 137, 10076.
- 65 C. Zeng, Y. Chen, K. Kirschbaum, K. Appavoo, M. Y. Sfeir and R. Jin, *Sci. Adv.*, 2015, **1**, e1500045.
- 66 A. Dass, S. Theivendran, P. R. Nimmala, C. Kumara, V. R. Jupally, A. Fortunelli, L. Sementa, G. Barcaro, X. Zuo and B. C. Noll, *J. Am. Chem. Soc.*, 2015, **137**, 4610.
- 67 M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz and R. Jin, *J. Am. Chem. Soc.*, 2008, **130**, 5883.

- 68 D. Wang, J. W. Padelford, T. Ahuja and G. Wang, *ACS Nano*, 2015, **9**, 8344.
- 69 J. W. Padelford, M. Zhou, Y. Chen, R. Jin and G. Wang, J. Phys. Chem. C, 2017, **121**, 21217.
- 70 H. Qian, M. Zhu, C. Gayathri, R. R. Gil and R. Jin, ACS Nano, 2011, 5, 8935–8942.
- 71 K. Salorinne, S. Malola, O. A. Wong, C. D. Rithner, X. Chen, C. J. Ackerson and H. Häkkinen, *Nat. Commun.*, 2016, 7, 10401.
- 72 T. Dainese, M. Agrachev, S. Antonello, D. Badocco, D. M. Black, A. Fortunelli, J. A. Gascón, M. Stener, A. Venzo, R. L. Whetten and F. Maran, *Chem. Sci.*, 2018, 9, 8796.