Atomically precise nanoclusters with reversible isomeric transformation for rotary nanomotors

Zhaoxian Qin1,2,3,5, Jiangwei Zhang1,5, Chongqing Wan2, Shuang Liu1, Hadi Abroshan4, Rongchao Jin4, & Gao Li1,3

Thermal-stimuli responsive nanomaterials hold great promise in designing multifunctional intelligent devices for a wide range of applications. In this work, a reversible isomeric transformation in an atomically precise nanocluster is reported. We show that biicosahedral [Au13Ag12(PPh3)10Cl8]SbF6 nanoclusters composed of two icosahedral Au7Ag6 units by sharing one common Au vertex can produce two temperature-responsive conformational isomers with complete reversibility, which forms the basis of a rotary nanomotor driven by temperature. Differential scanning calorimetry analysis on the reversible isomeric transformation demonstrates that the Gibbs free energy is the driving force for the transformation. This work offers a strategy for rational design and development of atomically precise nanomaterials via ligand tailoring and alloy engineering for a reversible stimuli-response behavior required for intelligent devices. The two temperature-driven, mutually convertible isomers of the nanoclusters open up an avenue to employ ultra-small nanoclusters (1 nm) for the design of thermal sensors and intelligent catalysts.
stimuli-responsive materials are at the forefront of technological innovations to fabricate the next-generation devices with "intelligent", performance. To meet the self-activation and deactivation functionality requirements for smart materials, the stimuli-responsive behavior should be reversible. This can be satisfied by utilization of precise structural and phase transitions. In particular, reversible conformational isomerism, a fundamental concept in molecular sciences that is commonly observed in organic molecules, offers a unique platform to prepare rotary motors at the nanoscale with atomistic precision.

Despite recent advances in controllable synthesis and structure determination of atomically precise nanoclusters, the concept of reversible conformational isomerization for metal nanoclusters has not yet been explored. To date, irreversible structural isomerization of atomically precise nanoclusters has been reported in a few cases. One case pertains to Au_{42}(TBBT)_{26} (TBBT = 4-tert-butylbenzenedithiolate) in the form of fcc and non-fcc frameworks that were synthesized via two different procedures. However, the two isomeric structures of Au_{42} are dynamically stable biicosahedral Au_{38}(SC_{2}H_{4}Ph)_{24} was reported during the ESI-MS analysis. X-ray crystallographic analysis (vide infra) confirmed homogeneous [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{8}]^{+}, with no observation of [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{9}]^{+}. It is worth noting that loss of a Cl⁻ ligand often occurs during ESI-MS analysis. Therefore, the molecular formula of the synthesized nanoclusters is [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{8}]^{+}, and the product is highly pure.

Surprisingly, two species were identified in the Au_{13}Ag_{12} product by thin-layer chromatography (TLC) with CH_{2}Cl_{2}/CH_{3}OH (2:1, v/v) as the eluent. The two distinct bands (Fig. 2b) indicate two isomers of Au_{13}Ag_{12} since they share the same composition, hereafter denoted as E- and S-Au_{13}Ag_{12} (vide infra). The bands were cut out and extracted with CH_{2}Cl_{2}, and their optical spectra indeed show different profiles of the two isomers of Au_{13}Ag_{12} (see Supplementary Fig. 1). The ultraviolet-visible (UV-vis) spectrum of the mixed isomers exhibit peaks at 324, 361, 420, 500, and 656 nm. After TLC separation, the E-Au_{13}Ag_{12} nanocluster shows three peaks at 361, 418, and 497 nm, whereas the S-Au_{13}Ag_{12} isomer shows four peaks at 330, 423, 510, and 657 nm. The energy gaps of the E- and S-Au_{13}Ag_{12} isomers are 1.72 and 2.17 eV, respectively (see Supplementary Fig. 1, inset). Interestingly, the pure S- and E-Au_{13}Ag_{12} isomers show different 31P nuclear magnetic resonance (NMR) signals: 54.80 ppm for E-Au_{13}Ag_{12} and 57.36 ppm for S-Au_{13}Ag_{12} using Au(PPh_{3})Cl (31P NMR: 33.13 ppm) as the internal reference (Fig. 2c and see Supplementary Fig. 2). It demonstrates that the E-Au_{13}Ag_{12} and S-Au_{13}Ag_{12} nanoclusters have different structures (vide infra).

Crystal structures. Furthermore, we found that keeping a fresh solution of the E-Au_{13}Ag_{12} nanocluster containing both isomers at 25°C for 4 weeks led to a solution containing only the S-Au_{13}Ag_{12} isomer. In contrast, under -10°C the same isomeric mixture completely transforms to the E-Au_{13}Ag_{12} isomer after 6 weeks. Crystallizations of the S-Au_{13}Ag_{12} and E-Au_{13}Ag_{12} isomers were performed via a vapor diffusion method, followed by X-ray diffraction analysis. The total structures of S-Au_{13}Ag_{12} and E-Au_{13}Ag_{12} are displayed in Supplementary Figs. 3 and 4. For the core frameworks, each isomer is composed of two icosahedral Au_{7}Ag_{6} units fused together by sharing a common vertex of Au (Fig. 3a). The two Au_{7} pentagons at the ends of the rod are ligated via bonding with 6 Cl⁻ ligands bridge the two icosahedra via bonding with 6 Cl⁻ ligands.

Results

**Synthesis and characterization of Au_{13}Ag_{12} isomers.** The Au_{13}Ag_{12} nanocluster was synthesized by reduction of a mixed solution of Ph_{3}PAuCl and AgSbF_{6} using NaBH_{4} in an ice bath (see Supplementary Methods). The nanoclusters were analyzed by electrospray ionization mass spectrometry (ESI-MS) in a positive mode. A weak mass peak at m/z = 6762.10 and an intense one at m/z = 3362.56 were observed in the mass spectrum (Fig. 2a), with the spacing of their isotope patterns being 1 and 0.5 (Fig. 2a, inset), hence, +1 and +2 charges, respectively. The two mass peaks correspond to [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{8}]^{+} (theoretical m/z: 6761.46 Da, deviation: 0.62 Da) and [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{9}]^{2+} (theoretical m/z: 3363.00 Da, deviation: -0.44 Da), respectively, with the latter (2+ ion) being formed via loss of a Cl⁻ from the intact 1+ cluster during the ESI-MS analysis.

**Fig. 1 Two isomers of the [Au_{13}Ag_{12}(PPh_{3})_{10}Cl_{8}]^{+} (SbF_{6})^{-} nanocluster with thermally responsive transformation (h = hour). E- eclipsed configuration, S- staggered configuration. Color code: Au = yellow; Ag = blue; Cl: green (C, H, P, and some Cl are omitted for clarity).**
Reversible transformation between the $E$- and $S$- isomer. The $E$-$\text{Au}_{13}\text{Ag}_{12}$ and $S$-$\text{Au}_{13}\text{Ag}_{12}$ isomers can be 100% selectively obtained at $-10$ and $25^\circ \text{C}$, respectively. To test the reversibility of the isomeric transformation, we monitored the process by UV-vis absorption spectroscopy using the crystal sample of $E$-$\text{Au}_{13}\text{Ag}_{12}$ nanoclusters as the starting material. We first studied the $E$-$\text{Au}_{13}\text{Ag}_{12}$ isomer in a dichloromethane solution at $25^\circ \text{C}$. The characteristic peak at 361 nm gradually decreased over time, indicating a transformation to the $S$-$\text{Au}_{13}\text{Ag}_{12}$ isomer. The process was monitored by UV-vis spectroscopy.
time and simultaneously peaks at 330, 423, and 657 nm gradually increased. The peak at 418 nm also red-shifted to 510 nm during a period of 28 days, Fig. 5a. The $^{31}$P NMR test of the sample gave a doublet-splitting peak centered at 57.36 ppm (see Supplementary Figs. 8 and 9). Of note, no byproduct was formed during the reversible transformation, evidenced by the ESI-MS tests (see Supplementary Figs. 10 and 11). These results imply that both isomers are stable, and the isomeric transformation process is reminiscent of typical phase transitions.

Differential scanning calorimeter (DSC) method was used to investigate the isomeric transformation process and the corresponding enthalpy. Starting from the S-Au$_{13}$Ag$_{12}$ isomer, a negative peak centered at 79.6 °C was observed during the DSC test, which points to endothermicity of the isomeric transformation of the S-Au$_{13}$Ag$_{12}$ to E-Au$_{13}$Ag$_{12}$ (Fig. 6a). Both UV-vis and $^{31}$P NMR analyses indicate that the S-Au$_{13}$Ag$_{12}$ isomer was partially converted to the E-Au$_{13}$Ag$_{12}$ isomer (see Supplementary Figs. 12 and 13). Furthermore, thermogravimetric analysis (TGA) revealed that the removal of Cl ligands from the nanoclusters occur at 175 °C (weight loss of ~3.7 wt%, consistent with the expected value of 4.0 wt%), Fig. 6b. Subsequently, the phosphine ligands began to desorb at ~210 °C, consistent with the desorption temperature reported for the phosphine-protected Au nanocluster. The TGA results indicate that the Au$_{13}$Ag$_{12}$ nanoclusters are intact below 100 °C (see Supplementary Figs. 14 and 15); thus the observed endothermic process in the DSC analysis is solely associated with the isomeric transformation, rather than with any ligand loss.

Owing to the higher symmetry of the E-Au$_{13}$Ag$_{12}$ ($D_{3d}$) than the S-Au$_{13}$Ag$_{12}$ ($D_{5d}$), the nanocluster is a potential prototype of thermal molecular motor where Gibbs free energy serves as the driving force. In a previous work, Teo et al. synthesized two isomers of Au$_{13}$Ag$_{12}$(PPh$_3$)$_{10}$Br$_8$ nanoclusters; however, no isomeric rotamerization was observed, which can be attributed to the stronger Ag–Br bonds than Ag–Cl. Our study shows that employing the –Cl ligand, instead of –Br, leads to higher flexibility on Ag–halide bonds, which is essential and critical to achieve a more flexible cluster framework for the thermally responsive, reversible transformation between the E-Au$_{13}$Ag$_{12}$ and S-Au$_{13}$Ag$_{12}$ isomers. Such a Cl-ligand-induced rotary nanomotor is simulated based on the experimental structures (see Supplementary Movie 1). For practical applications, the temperature will serve as the driving force.

In summary, two isomers of the biicosahedral [Au$_{13}$Ag$_{12}$(PPh$_3$)$_{10}$Cl$_8$]$^+$ (counterion: [SbF$_6$]$^-$) nanocluster (i.e., S-Au$_{13}$Ag$_{12}$ and E-Au$_{13}$Ag$_{12}$) are discovered, and these two isomers are reversibly transformable by controlling the temperature.
The metal configuration of the \(E\text{-}\text{Au}_{13}\text{Ag}_{12}\) isomer possesses a higher symmetry (\(D_{3h}\)) than that of the \(S\text{-}\text{Au}_{13}\text{Ag}_{12}\) isomer (\(D_{2h}\)) and is preferably formed at low temperature (\(-10 ^{\circ}C\)). As the temperature increases to \(25 ^{\circ}C\), the \(S\text{-}\text{Au}_{13}\text{Ag}_{12}\) isomer (lower symmetry) is exclusively formed. This study shows that the alloying and ligand engineering (i.e., Ag–halide bond) provide a rational strategy to make the framework of metal nanoclusters more flexible for achieving the conformational isomerism, which has the potential to be applied in designing intelligent molecular engines with Gibbs free energy as the driving force of the activity.

**Methods**

**Synthesis of \(\text{Au}_{19}\text{Br}_{16}\) nanoclusters.** \(\text{Au}(1)\text{PhCl}_{2}\) (25 mg, dissolved in 2 mL chloromethane/methanol with \(v:v = 1:1\)) was mixed with \(\text{AuCl}_{3}\) (17.2 mg, dissolved in 2 mL chloromethane/methanol with \(v:v = 1:1\)). The solution was stirred in dark and air atmosphere. Then the solution was cooled using an ice bath for 30 min, followed by dropwise addition of NaBH\(_4\) solution (2 mg, dissolved in 4 mL ice cold methanol). The mixture was kept in the dark and stirred for another 24 h. Next, the temperature was increased slowly to \(25 ^{\circ}C\). The mixture was then dried via vacuum evaporation and washed with hexane (2 x 1 mL) leaving a black solid. Finally, the black solid was dissolved in 2 mL dichloromethane/methanol (\(v:v = 1:1\)) and centrifuged at 10,000 rpm for 5 min. Red, plate-like crystals of \(E\text{-}\text{Au}_{11}\text{Ag}_{12}\) and 34.9% for \(S\text{-}\text{Au}_{11}\text{Ag}_{12}\) based on the consumption of \(\text{Ph}_{2}\text{P}\text{AuCl}\).

**Data availability**

The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1888164-1888165. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The datasets generated and/or analyzed during this study are available from the corresponding author upon reasonable request.

Received: 2 February 2020; Accepted: 19 October 2020; Published online: 26 November 2020

**References**

1. Petermayer, C. & Dube, H. Indigoid photoswitches: visible light responsive molecular tools. *Acc. Chem. Res.* 51, 1153–1163 (2018).
2. Wei, P. et al. Multiple yet controllable photoswitching in a single AIEgen system. *J. Am. Chem. Soc.* 140, 1966–1975 (2018).
3. Zhang, B. et al. Thermally-induced reversible structural isomerization in colloidal semiconductor CdS magic-size clusters. *Nat. Commun.* 9, 2499–2508 (2018).
4. Fan, X., Wang, J., Wu, K., Zhang, L. & Zhang, J. Isomerism in titanium-oxo clusters: molecular anatase model with atomic structure and improved photocatalytic activity. *Angew. Chem. Int. Ed.* 58, 1320–1323 (2019).
5. Wang, H., Zhang, J. & Xie, Z. Reversible photothermal isomerization of carbene-cycled azaborole to borirane: synthesis and reactivity of carbene-stabilized carbaborane-fused borirane. *Angew. Chem. Int. Ed.* 129, 9326–9329 (2017).
6. Sun, J. et al. Stimuli-directed dynamic reconfiguration in self-organized helical superstructures enabled by chemical kinetics of chiral molecular motors. *Adv. Sci.* 5, 1700613–1700621 (2018).
7. Zhang, J. et al. The proton-controlled synthesis of unprecedented dinitro functionalized Anderson-type POMs. *Chem. Commun.* 52, 2378–2381 (2016).
8. Zhang, J. et al. Unprecedented \(\chi\) isomers of single-side trisfunctionalized Anderson polyoxometalates and their proton-controlled isomer transformation. *Chem. Commun.* 51, 9097–9100 (2015).
9. Konishi, K., Iwasaki, M. & Shichibu, Y. Phosphine-ligated gold clusters with \(\chi\)-exo doubly bridging ligands. *Inorg. Chem.* 51, 3125–3133 (2018).
10. Cook, A. W. & Hayton, T. W. Case studies in nanocluster synthesis and characterization: challenges and opportunities. *Acc. Chem. Res.* 51, 2456–2464 (2018).
11. Lei, Z., Wan, X.-K., Yuan, S.-F., Guan, Z.-J. & Wang, Q.-M. Alkynyl approach toward the protection of metal nanoclusters. *Acc. Chem. Res.* 51, 2465–2474 (2018).
12. Yao, Q., Chen, T., Yuan, X. & Xie, J. Toward total synthesis of thiolate-protected metal nanoclusters. *Acc. Chem. Res.* 51, 1338–1348 (2018).
13. Zheng, K. et al. Motif-mediated \(\text{Au}_{25}(\text{SPh})_{9}(\text{PPh}_{3})_{10}X_{2}\) nanorods with conjugated electron delocalization. *Nano Res.* 12, 501–507 (2019).
14. Zhang, J. et al. Diphosphine-induced chiral propeller arrangement of gold nanoclusters for singlet oxygen photogeneration. *Nano Res.* 11, 5787–5798 (2018).
15. Nieto-Ortega, B. & Bürgi, T. Vibrational properties of thiolate-protected gold nanoclusters. *Acc. Chem. Res.* 51, 2811–2819 (2018).
16. Chakraborty, P., Nag, A., Chakraborty, A. & Pradeep, T. Approaching materials with atomic precision using supramolecular cluster assemblers. *Acc. Chem. Res.* 52, 2–11 (2019).
17. Zhou, M. et al. Three-orders-of-magnitude variation of carrier lifetimes with crystal phase of gold nanoclusters. *Science* 364, 279–282 (2019).
18. Jin, R., Zeng, C., Zhou, M. & Chen, Y. Atomically precise colloidal metal nanoclusters and nanoparticles: fundamentals and opportunities. *Chem. Rev.* 116, 10346–10413 (2016).
19. Zhuang, S. et al. Fcc versus non-fcc structural isomerism of gold nanoparticles with kernel atom packing dependent photoluminescence. *Angew. Chem. Int. Ed.* 58, 4510–4514 (2019).
20. Teo, B. K. & Zhang, H. Molecular machines: molecular structure of [\(\text{p-Tol}(\text{P})\text{Au}_{13}\text{Ag}_{12}\text{Cl}(\text{PPh}_{3})]_{\text{2}}\) a cluster with a bicapped rotorlike metal core and an unusual arrangement of bridging ligands. *Angew. Chem. Int. Ed.* 31, 445–447 (1992).
21. Teo, B. K., Shi, X. B. & Zhang, H. Cluster structures of a novel cluster \([\text{Ph}_{2}\text{P}A_{13}\text{Ag}_{12}\text{Br}_{5}]_{\text{2}}\) containing an exact staggered-eclipsed-staggered metal configuration: evidence of icosahedral units as building blocks. *J. Am. Chem. Soc.* 113, 4329–4331 (1991).
22. Teo, B. K., Shi, X. B. & Zhang, H. Cluster rotamism of a 25-metal-atom cluster \([\text{Ph}_{2}\text{P}A_{13}\text{Ag}_{12}\text{Br}_{5}]_{\text{2}}\) + monocation: a molecular rotary unit. *J. Chem. Soc. Chem. Commun.* 1195–1196 (1992).
23. Teo, B. K. & Zhang, H. Cluster of clusters. Structure of a new 25-metal-atom cluster \([\text{p-Tol}(\text{P})\text{Au}_{13}\text{Ag}_{12}\text{Br}_{5}]_{\text{2}}\) containing a nearly staggered-eclipsed-staggered metal configuration and five doubly bridging ligands. *Inorg. Chem.* 30, 3115–3116 (1991).
24. Tian, S. et al. Structural isomerism in gold nanoparticles revealed by X-ray crystallography. *Nat. Commun.* 6, 8667–8672 (2015).
25. Chen, Y. et al. Isomerism in \(\text{Au}_{26}\text{(SR)}_{25}\) nanocluster and stable structures. *J. Am. Chem. Soc.* 138, 1482–1485 (2016).
26. Song, Y. et al. How a single electron affects the properties of the "non-superatom" \(\text{Au}_{25}\) nanoclusters. *Chem. Mater.* 28, 2609–2617 (2016).
27. Liao, L. et al. Quantitatively monitoring the size-focusing of Au nanoclusters and revealing what promotes the size transformation from \(\text{Au}_{44}(\text{TBBT})_{24}\) to \(\text{Au}_{64}(\text{TBBT})_{32}\). *Anal. Chem.* 88, 11297–11301 (2016).
28. Molar, Y. Clustomesogens: liquid crystalline hybrid nanomaterials containing functional metal nanoclusters. *Acc. Chem. Res.* 49, 1514–1523 (2016).
29. Liu, C., Abroshan, H., Yan, C., Li, G. & Haruta, M. One-Pot synthesis of \(\text{Au}_{77}(\text{PPh}_{3})_{9}\text{Br}_{5}\) for the highly chemoselective hydrogenation of nitrobenzaldehyde. *ACS Catal.* 6, 92–99 (2016).
