Isomerism in $Au_{28}(SR)_{20}$ Nanocluster and Stable Structures

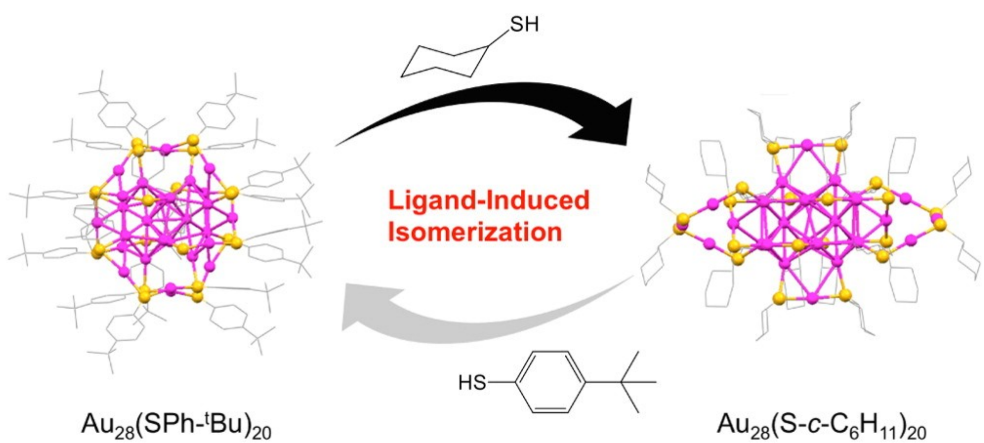
Yuxiang Chen,† Chong Liu,‡ Qing Tang,§ Chenjie Zeng,† Tatsuya Higaki,† Anindita Das,† De-en Jiang,*,§Nathaniel L. Rosi,‡ and Rongchao Jin*,†

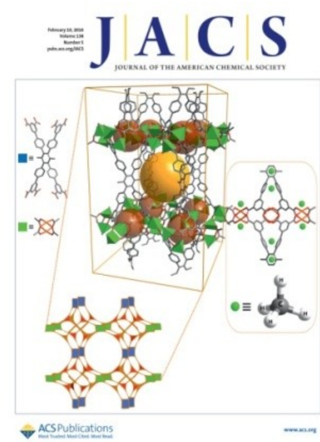
†Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

‡Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213, United States

§Department of Chemistry, University of California, Riverside, California 92521, United States

DOI: 10.1021/jacs.5b12094 J. Am. Chem. Soc. 2016, 138,1482−1485.

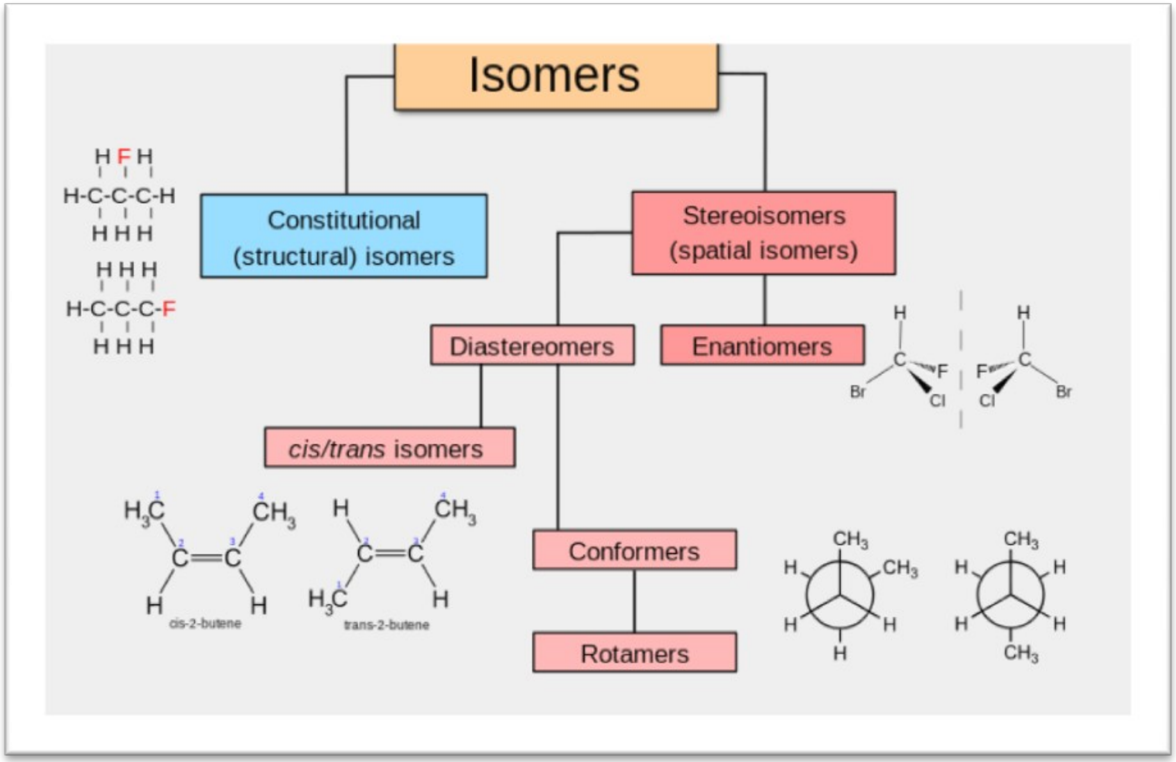




JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Sugi K S
13 - 02 - 16

Isomerism:



Isomers: are molecules with the same chemical formula as another molecule, but with a different chemical structure.

Isomerism: Is the occurrence of two or more compounds with same molecular formula but different physical and chemical properties.

Structural isomers: are those have same molecular formula but bonded together in different orders.

Stereo isomers: Molecules have same molecular formula and sequence of bonded atoms but differ in 3D orientations of their atoms in space.

Introduction:

- In case of atomically precise gold clusters commonly observed isomerism is stereoisomerism, ie, the optical isomerism of gold clusters.

- The structural isomerism in gold nanoclusters are rarely observed except in two cases ie, phospine protected Au_8 and thiolate protected Au_{38} clusters.

- For the latter, a low temperature synthetic method was employed to obtain a metastable $Au_{38}(SC_2H_4Ph)_{24}$ structure in contrast with the thermodynamically stable biicosahedral $Au_{38}(SC_2H_4Ph)_{24}$.

- The metastable Au_{38} isomer was found to irreversibly transform into the stable biicosahedral isomer under thermal conditions (e.g., 50 °C), indicating that the low temperature Au_{38} isomer is a kinetically trapped species, and there is only one thermodynamically stable structure thus far for the magic-sized cluster of 38 gold atoms.

- Different $Au_{24}L_{20}$ structures were reported, but different types of ligands are used(thiolate and selenolate).

In this paper:

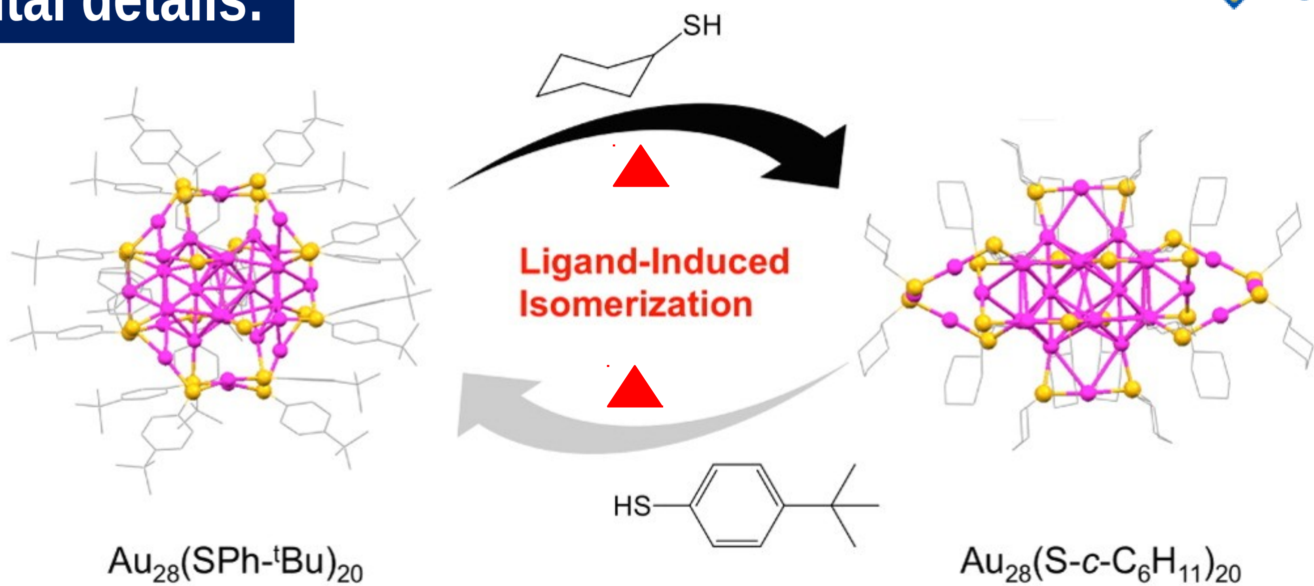
- Report structural isomerism in $Au_{28}(SR)_{20}$ nanocluster (R= c-C_6H_{11} vs Ph-tBu).

- A new $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ structure is determined, which differs from the previously reported $Au_{28}(SPh\text{-}tBu)_{20}$ counterpart.

- Unlike the case of $Au_{38}(SC_2H_4Ph)_{24}$ isomerization, the two Au_{28} nanoclusters are both thermodynamically stable and they can also be reversibly transformed into each other through ligand exchange reactions under thermal conditions (e.g., 80 °C).

- Although the carbon tails of the two thiolate ligands are different, these two Au_{28} isomers have the same number of gold atoms and of thiolate ligands; hence, they constitute quasi-isomers.

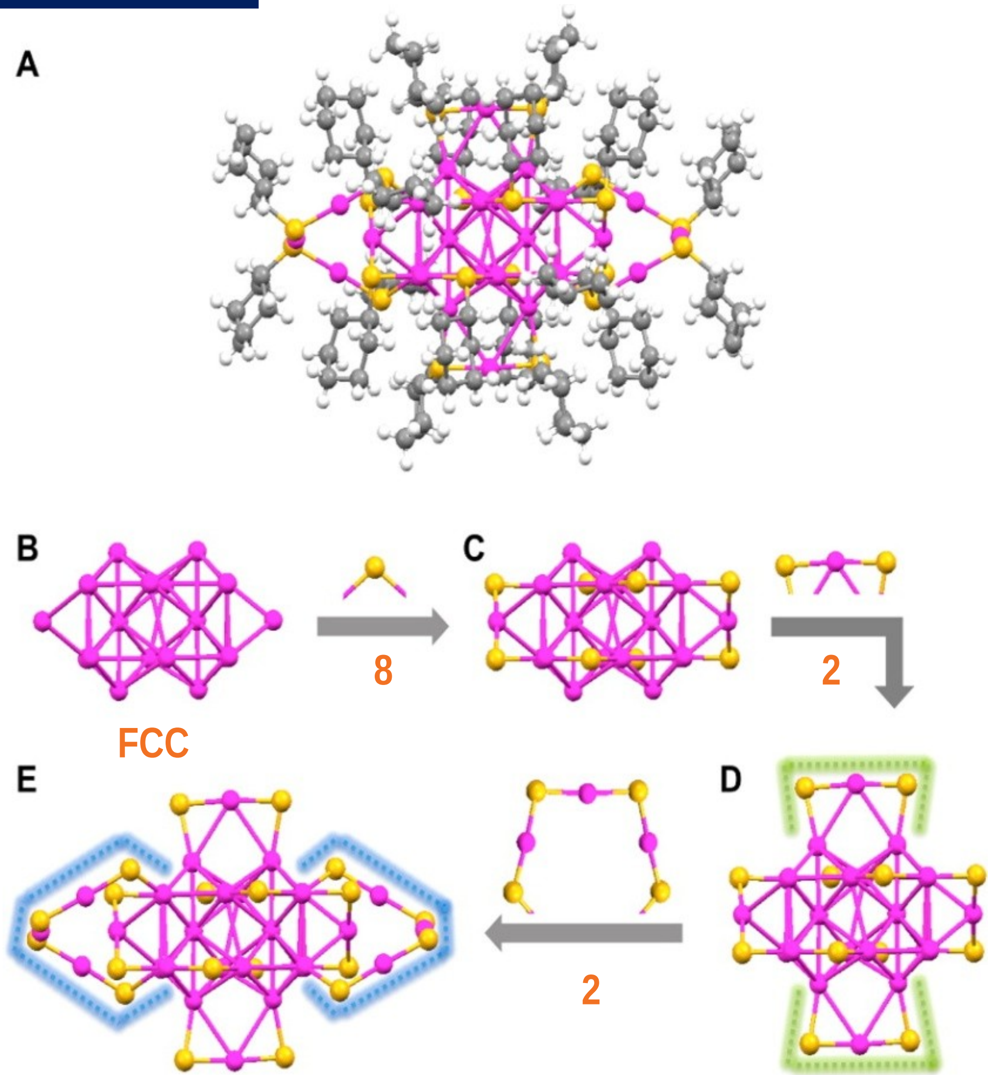
Experimental details:



Crystallization: Single crystal growth of $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ nanocluster was performed via vapor diffusion of pentane into a CH_2Cl_2 solution of nanoclusters. Dark orange crystals of $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ nanocluster were obtained after ~3 days.

A piece of brown needle-shaped crystal with dimensions 0.14 x 0.02 x 0.01 mm was mounted onto a MiTeGen Micromeshes with fluorolube. The data were collected under cold N_2 flow at 240 K. The $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ nanoclusters crystallize in to a monoclinic unit cell with centrosymmetric space group P2/c, and exhibits a prolate shape with quasi-D2 symmetry.

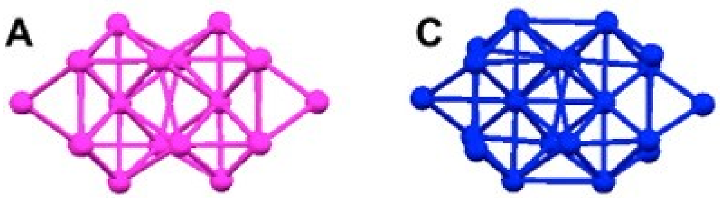
Results and discussion:



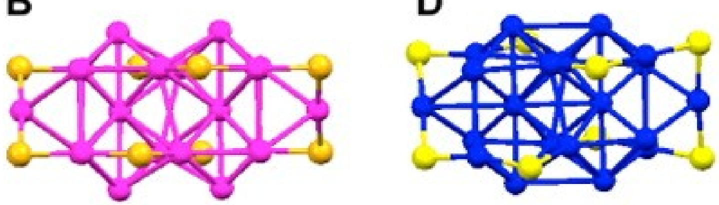
$Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ nanocluster and its structural dissection. (A) Total structure; (B) Au_{20} kernel; (C) Au_{20} kernel capped by eight simple bridging thiolates; (D) Monomeric staples highlighted in green lines; (E) Trimeric staples highlighted in blue lines. Color codes: magenta = gold; orange = sulfur; gray = carbon; white = hydrogen.

Results and discussion:

$Au_{28}(CH)_{20}$ $Au_{28}(TBBT)_{20}$

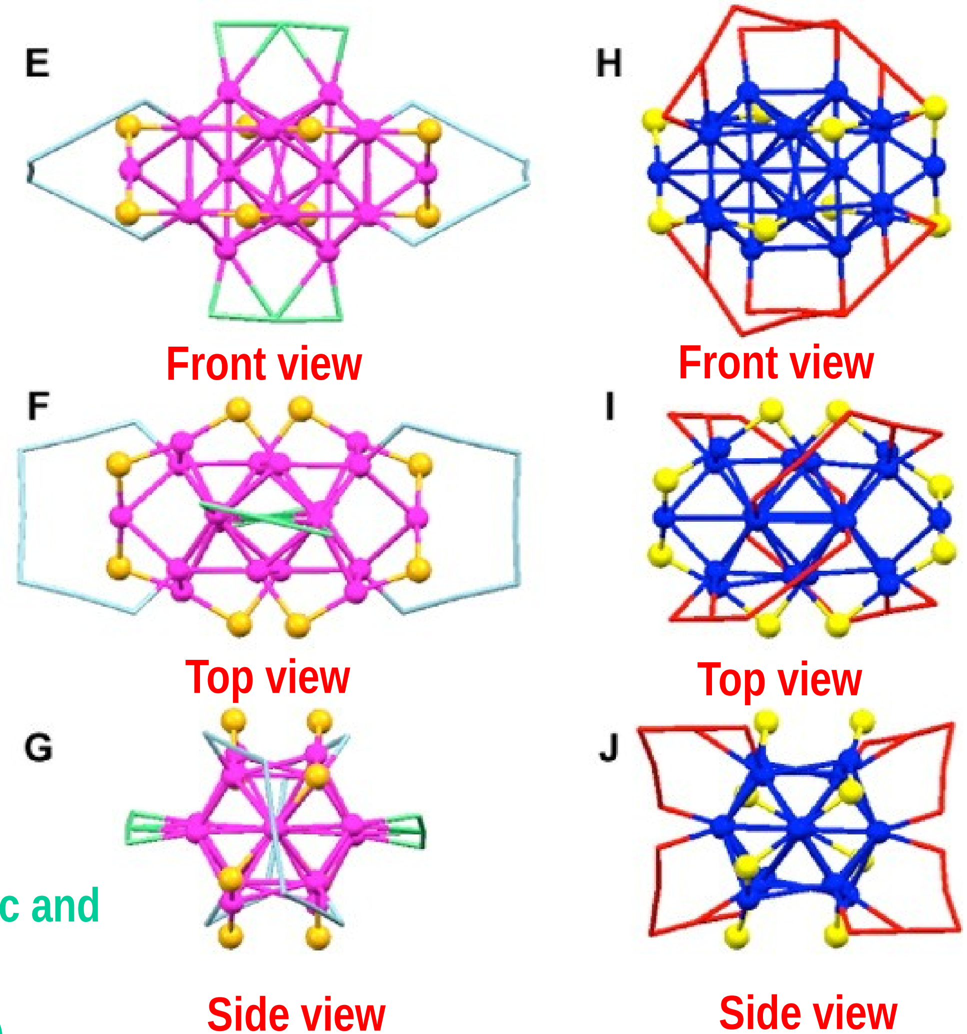


FCC based Au_{20} kernel



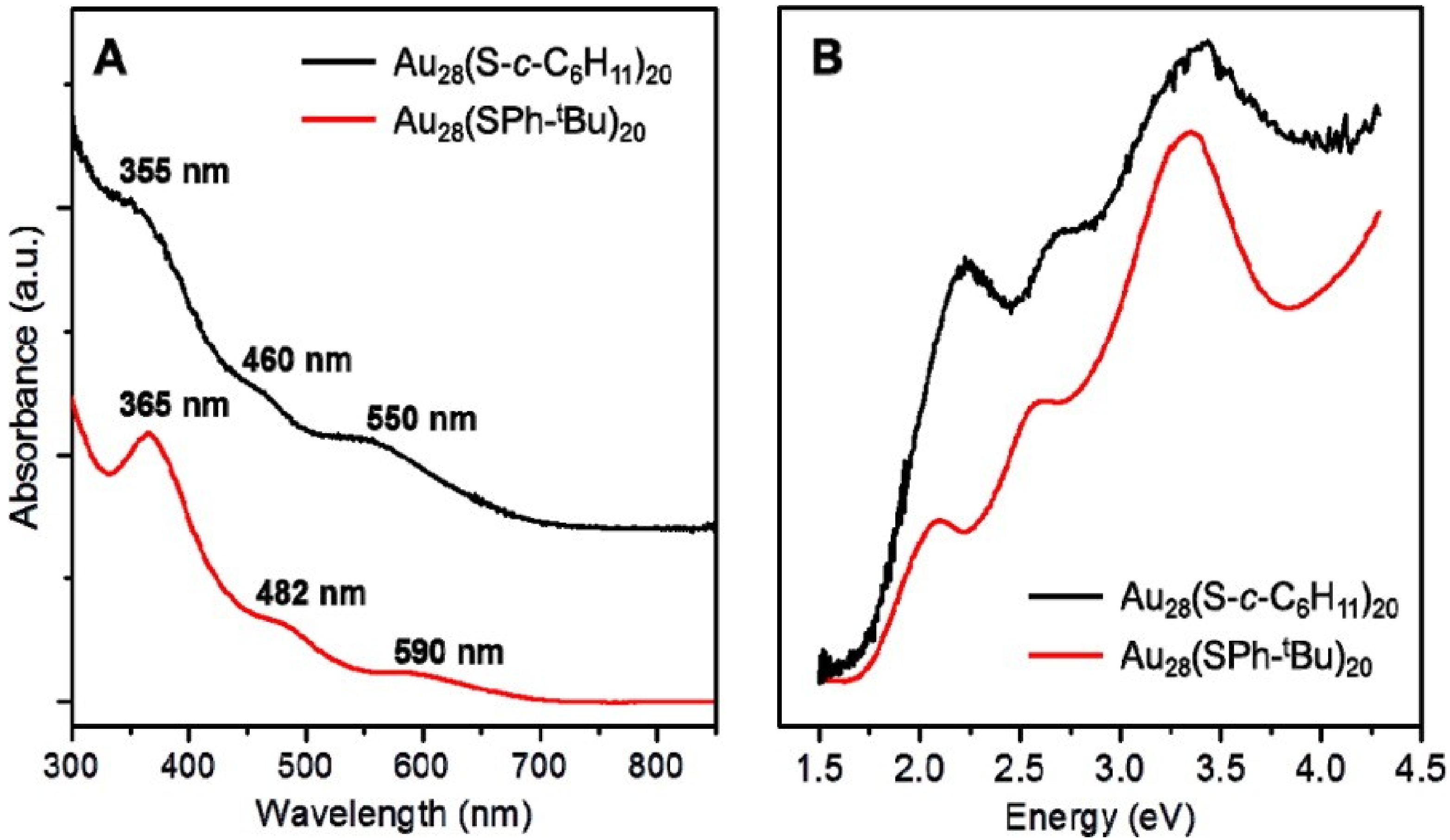
Au_{20} kernel + 8 bridging ligands

The $Au_8(SR)_{12}$ units are arranged as 2 trimeric and monomeric staples in case of $Au_{28}(CH)_{20}$ and 4 dimeric staples in case of $Au_{28}(TBBT)_{20}$.



Structural comparison of kernel structures (A-B vs C-D) and surface structures (E-G vs H-J) of $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ and $Au_{28}(SPh\text{-}tBu)_{20}$.

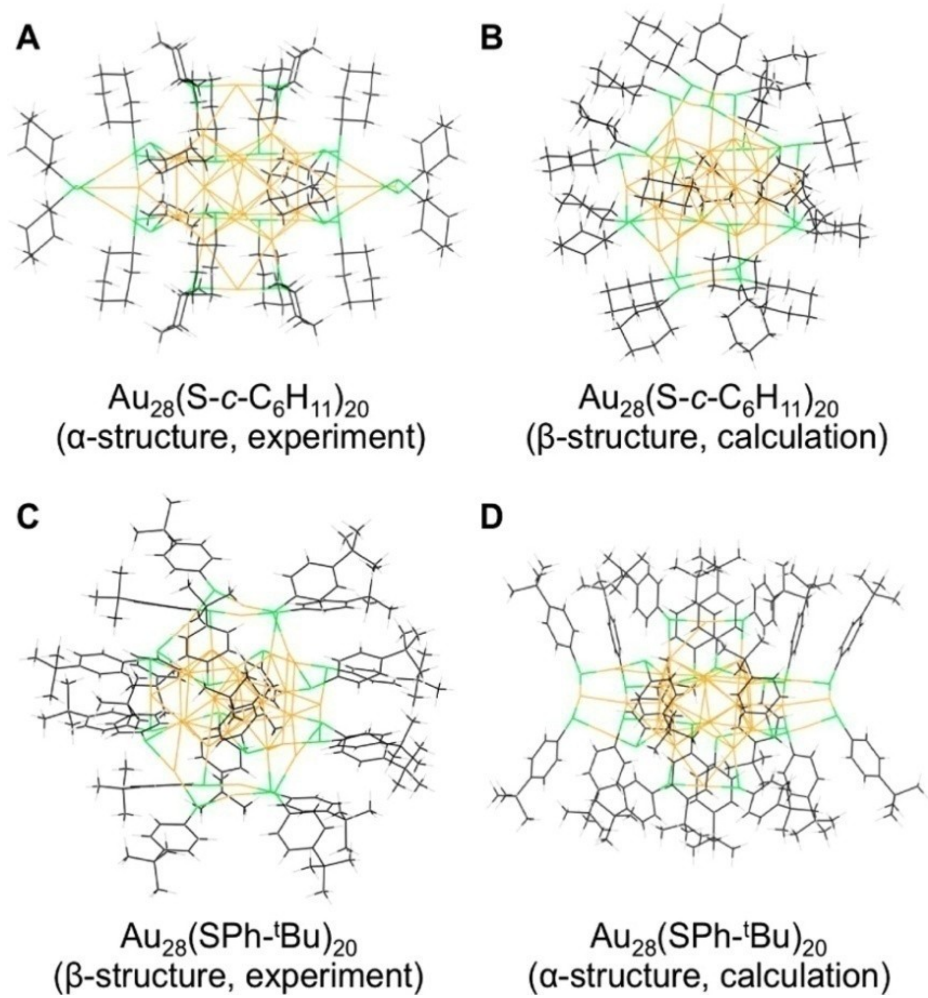
Results and discussion:



(A) Optical spectra of $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$ (black profile) and $Au_{28}(SPh\text{-}tBu)_{20}$ (red); (B) Photon-energy plot.

The surface – staple differences are reflected in optical spectra

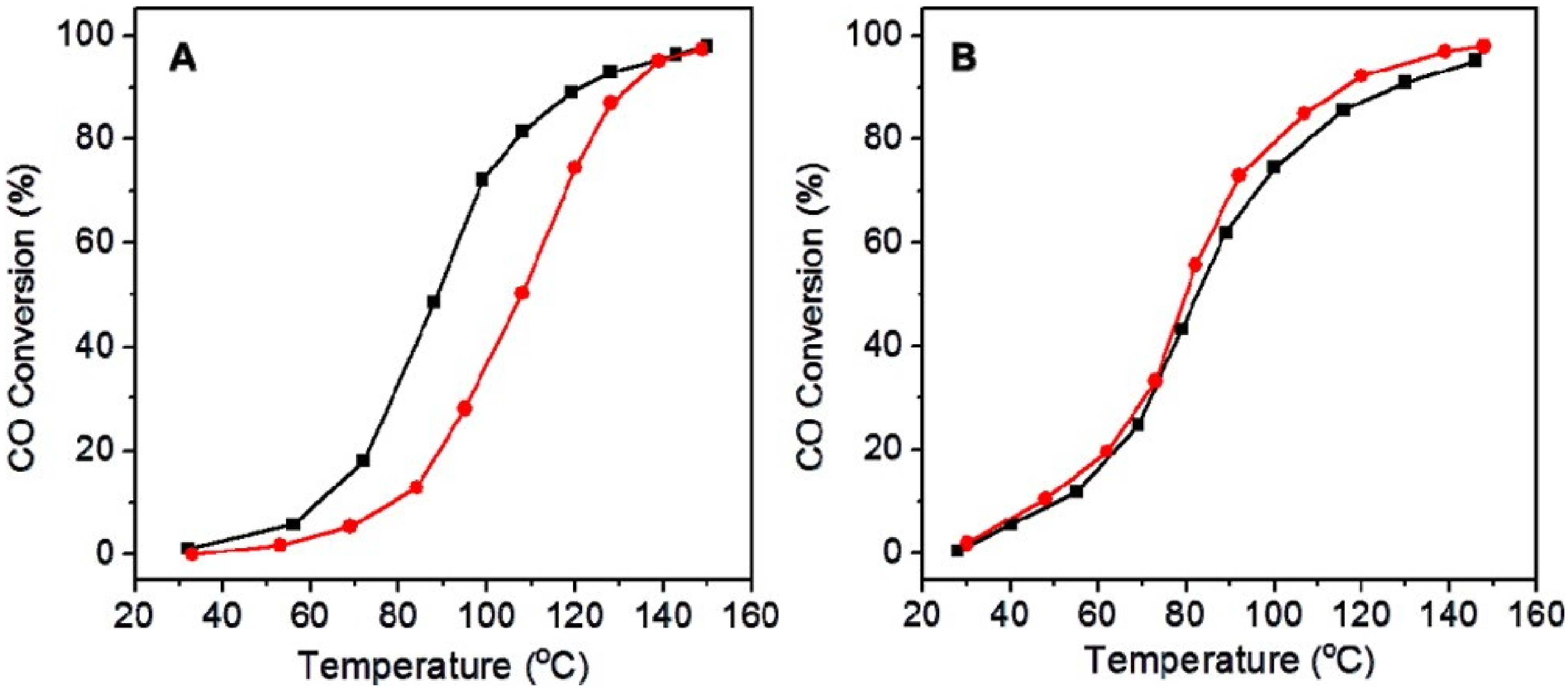
Results and discussion:



Optimized structures of the four possible $Au_{28}(SR)_{20}$ quasi-isomers.

In case of $Au_{28}(CH)_{20}$ α structure is preferred because of low DFT energy whereas in case of $Au_{28}(TBBT)_{20}$ β structure is preferred due to low Van der Waals interaction of packing ligand.

Results and discussion:



CO oxidation light-off curves of CeO_2 supported Au_{28}(S-*c*-$C_6H_{11})_{20}$ (black profile) and $Au_{28}(SPh\text{-}tBu)_{20}$ (red) catalysts. (A) Catalysts pre-treated with O_2 at 150 °C for 1 h; (B) pre-treated with O_2 at 300 °C for 1 h to remove ligands.

Conclusion:

ACS Publications
High quality. High impact.

✓ **Ligand-induced reversible isomerization between two thiolate-protected Au_{28} nanoclusters is demonstrated.**

✓ **The two stable $Au_{28}(SR)_{20}$ quasi-isomers (R = Ph-tBu vs c-C_6H_{11}) possess the same Au_{20} kernel but distinctly different surface structures.**

✓ **The origin of reversible isomerization lies in the thiolate ligand's carbon tail structure, which is found to dictate the specific isomer's stability, as revealed by DFT calculations of energies.**

✓ **The different surface structures of the two Au_{28} isomers render different catalytic properties.**

✓

Future directions:

Angewandte Communications

Gold Nanoclusters

International Edition: DOI: 10.1002/anie.201502667
German Edition: DOI: 10.1002/ange.201502667

Observation of Body-Centered Cubic Gold Nanocluster**

*Chao Liu, Tao Li, Gao Li, Katsuyuki Nobusada, Chenjie Zeng, Guangsheng Pang, Nathaniel L. Rosi, and Rongchao Jin**

Angew. Chem. Int. Ed. 2015, 54, 9826 –9829.

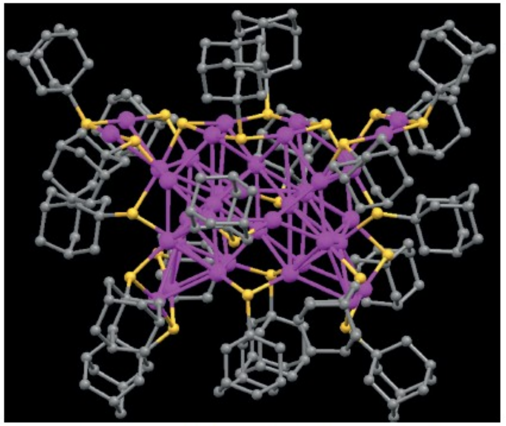
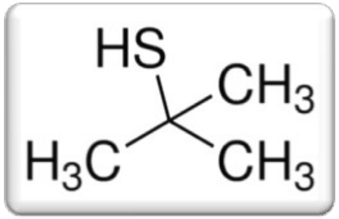
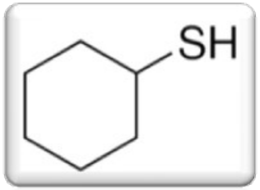


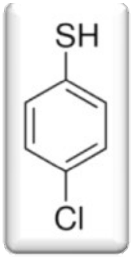
Figure 1. X-ray structure of $[Au_{38}S_2(S\text{-}Adm)_{20}]$ (magenta Au, yellow S, gray C, all H atoms are omitted for clarity).

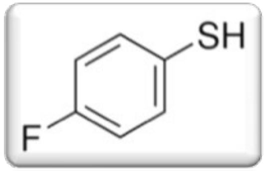
The bcc structure of $[Au_{38}S_2(S\text{-}Adm)_{20}]$ was observed, as no bcc structure has been previously observed in gold nanoclusters or larger gold nanoparticles. Its occurrence is attributed to the adamantanethiol ligand.

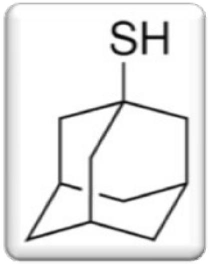
- **Ligand induced structure transformation methodology for new clusters??**












Thank you!

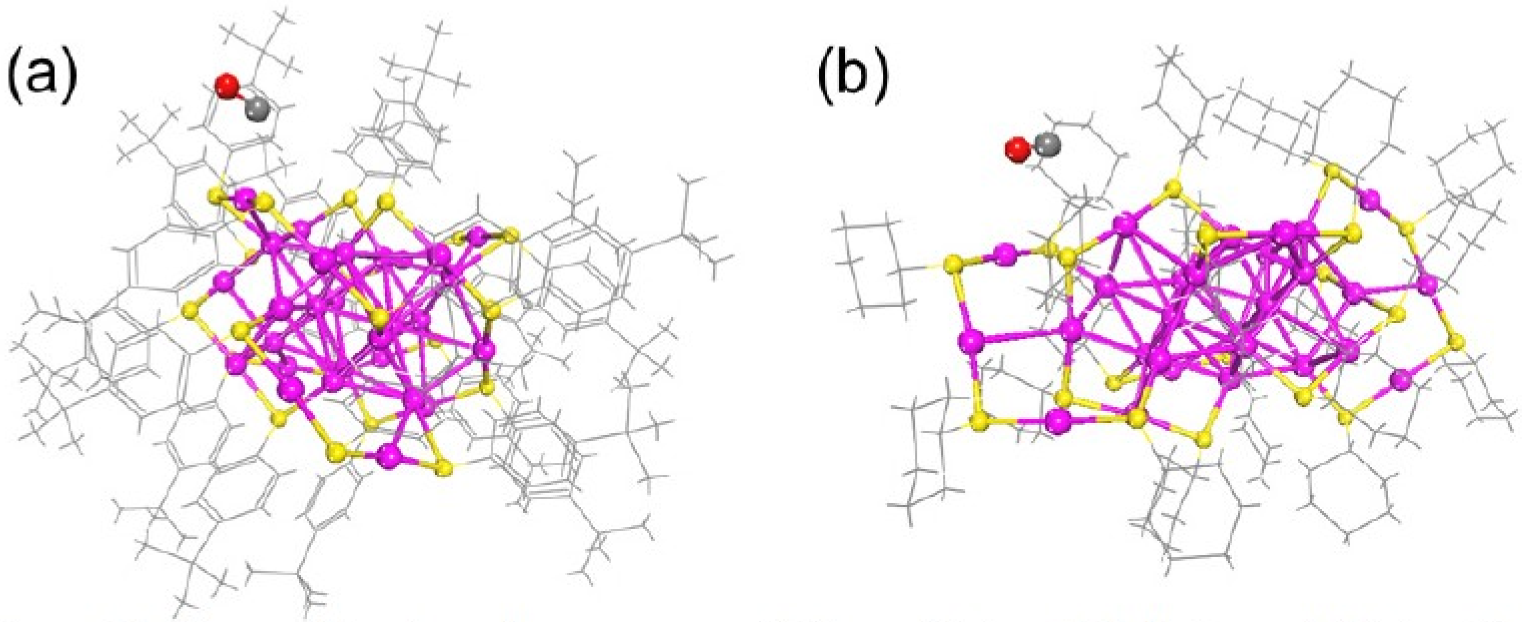


Figure S4. Most stable adsorption geometry of CO on (a) $Au_{28}(SPh\text{-}^{t}Bu)_{20}$ and (b) $Au_{28}(S\text{-}c\text{-}C_6H_{11})_{20}$. Au, pink; S, yellow; C, grey; O, red; R groups, lines.

Chirality in Thiolate-Protected Gold Clusters

Stefan Knoppe*,† and Thomas Bürgi*

dx.doi.org/10.1021/ar400295d | Acc. Chem. Res. 2014, 47, 1318−1326.

Racemization of a Chiral Nanoparticle Evidences the Flexibility of the Gold−Thiolate Interface

Stefan Knoppe, Igor Dolamic, and Thomas Bürgi*

dx.doi.org/10.1021/ja3053865 | J. Am. Chem. Soc. 2012, 134, 13114−13120.