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Article

Structural Oscillation Revealed in Gold Nanoparticles

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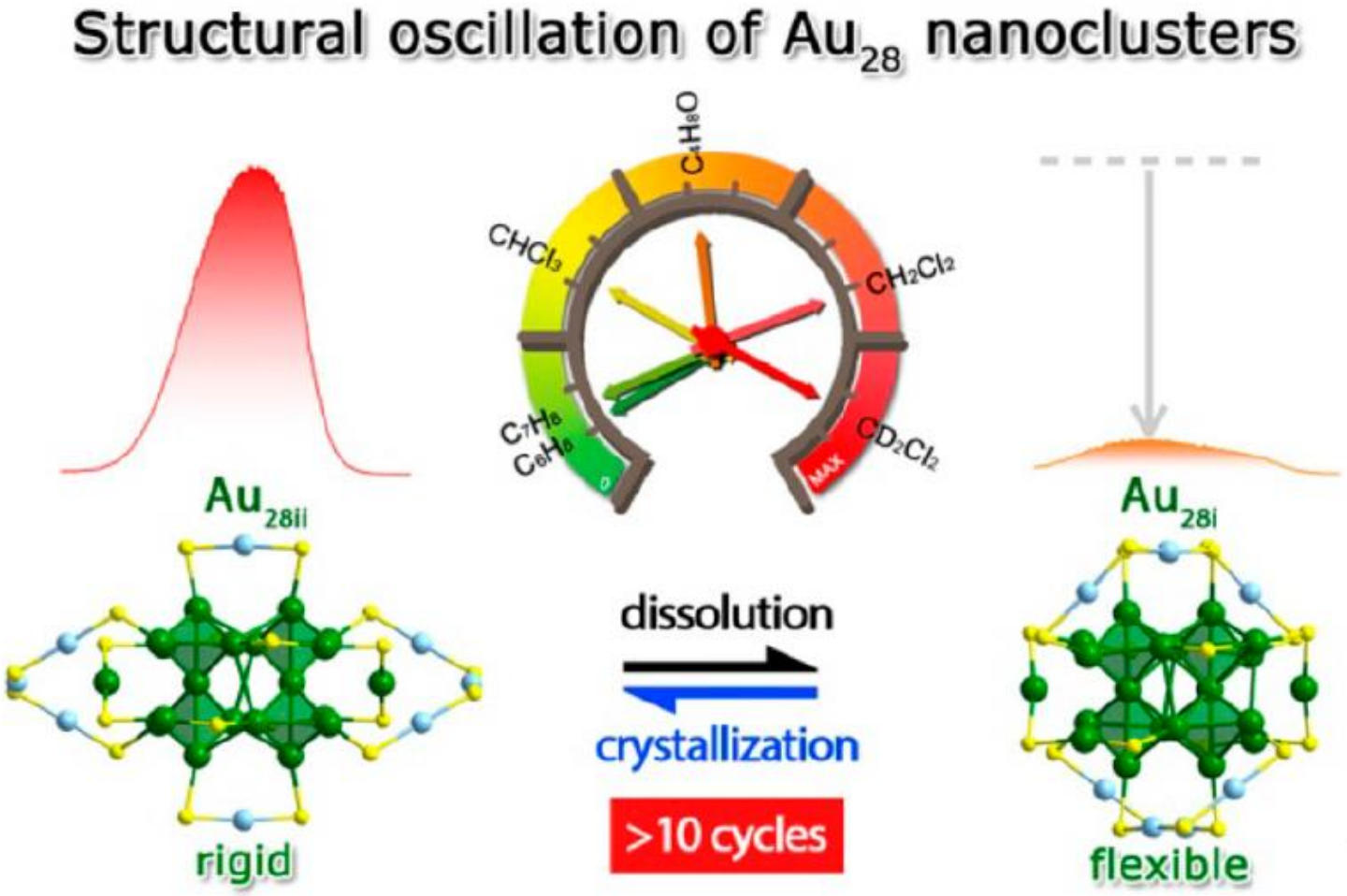
- Amoghavarsha R Kini

Abstract


Structural oscillation of Au_{28} nanoclusters
C_4H_8O
$CHCl_3$
CH_2Cl_2
C_7H_8
C_6H_6
CD_2Cl_2
MAX
0
Au_{28ii}
rigid
dissolution
crystallization
>10 cycles
Au_{28i}
flexible

Background

Metal Nanoparticles

Angewandte Communications

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Anti-Galvanic Reduction of Thiolate-Protected Gold and Silver Nanoparticles**

*Zhikun Wu**

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Structural isomerism in gold nanoparticles revealed by X-ray crystallography

Shubo Tian[1], Yi-Zhi Li[2], Man-Bo Li[1], Jinyun Yuan[3], Jinlong Yang[3], Zhikun Wu[1] & Rongchao Jin[4]

Angewandte Communications

VIP Gold Nanoclusters Very Important Paper

International Edition: DOI: 10.1002/anie.201813426
German Edition: DOI: 10.1002/ange.201813426

Fcc versus Non-fcc Structural Isomerism of Gold Nanoparticles with Kernel Atom Packing Dependent Photoluminescence

*Shengli Zhuang[+], Lingwen Liao[+], Jinyun Yuan, Nan Xia, Yan Zhao, Chengming Wang, Zibao Gan, Nan Yan, Lizhong He, Jin Li, Haiteng Deng, Zhaoyong Guan, Jinlong Yang, and Zhikun Wu**

Motivation

- To understand structural isomerism in gold nanoclusters.
- To explore potential areas of application where this property can be used.
- To find whether these isomeric structures can be reversibly transformed into each other.

Why this paper!

- First to report reversible structural oscillation between 2 isomeric structures of gold nanoclusters.
- An effort in understanding the mechanism of transformation.

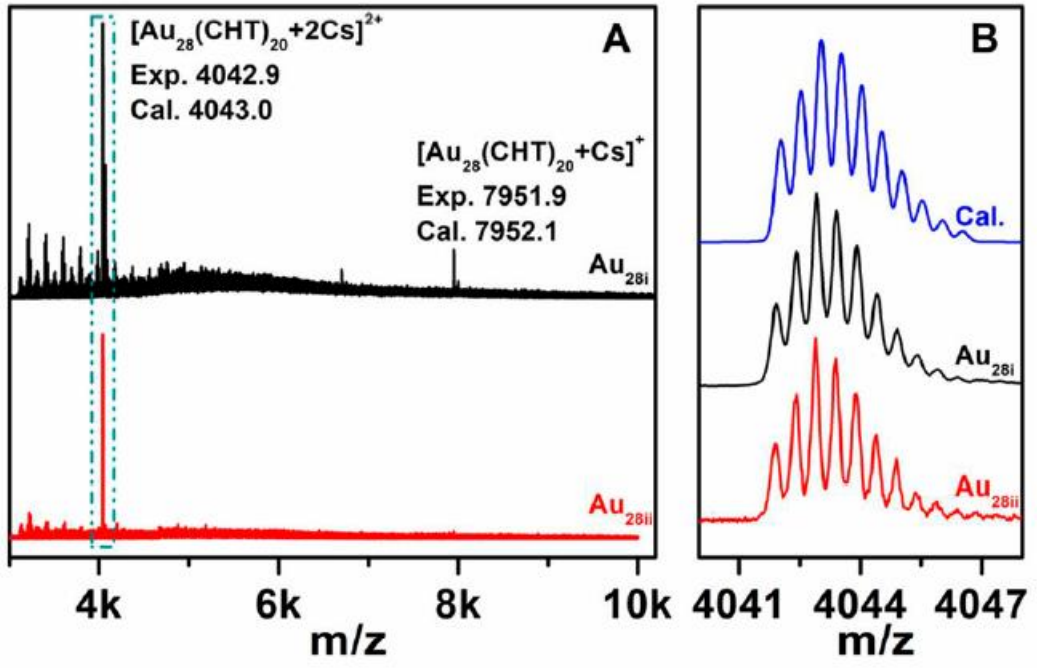
Introduction

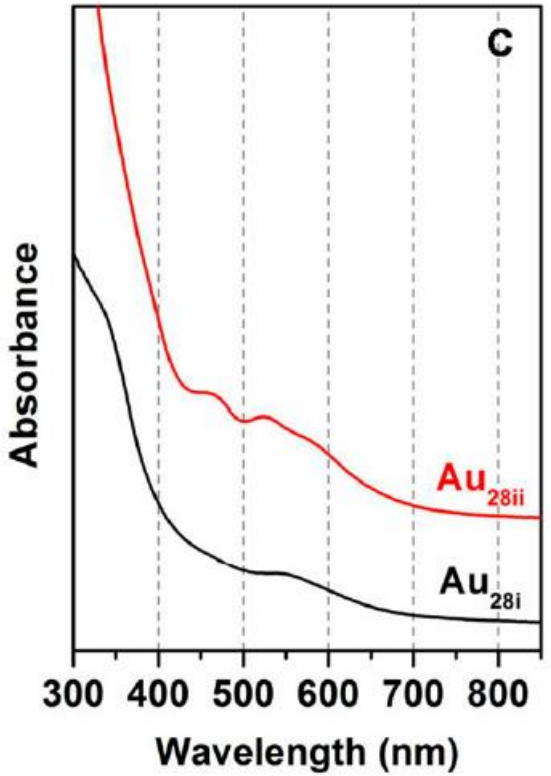
- Structural oscillation is the reversible transformation of a molecule between its isomers. However structural oscillations of nanoparticles is still unclear.
- This is due to challenges in obtaining intrinsic structures of these nanoparticles in atomic level. But the nanoclusters are ideal models to tackle this issue whose structures can be precisely determined.
- These structural oscillations can then be used to study the structure-property correlations and in exploring potential fields of application of these materials.

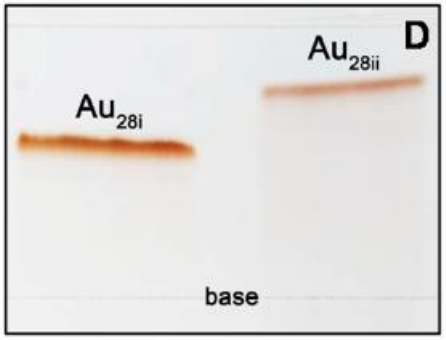
Preparation of Au_{28} nanocluster

- The $Au_{23}(CHT)_{20}$ (CHT – cyclohexanethiol) nanocluster is synthesized first by previously reported methods. ~10mg of Au_{23} nanocluster is then dissolved in 2 mL DCM.
- Freshly prepared DCM solution (0.5 mL) containing 1.7 equivalents of Au-CHT complex was then added to the Au_{23} nanocluster solution under vigorous stirring for 24 hours at room temperature and the reaction terminated by adding excess methanol.
- The reaction mixture was then concentrated by evaporating the solvent under reduced pressure and characterized by mass spectrometry. The formula of this nanocluster was found to be $Au_{28}(CHT)_{20}$.
- However, UV-vis-NIR spectra and PTLC show the presence of two different structures, indicating the two structures to be isomers.

Characterization of the isomers







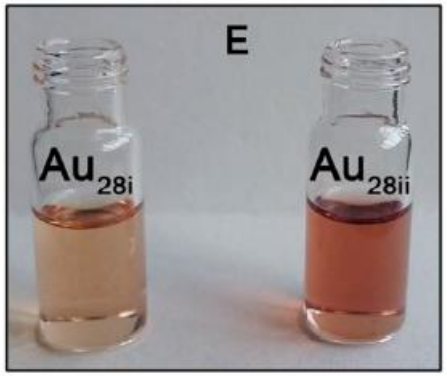
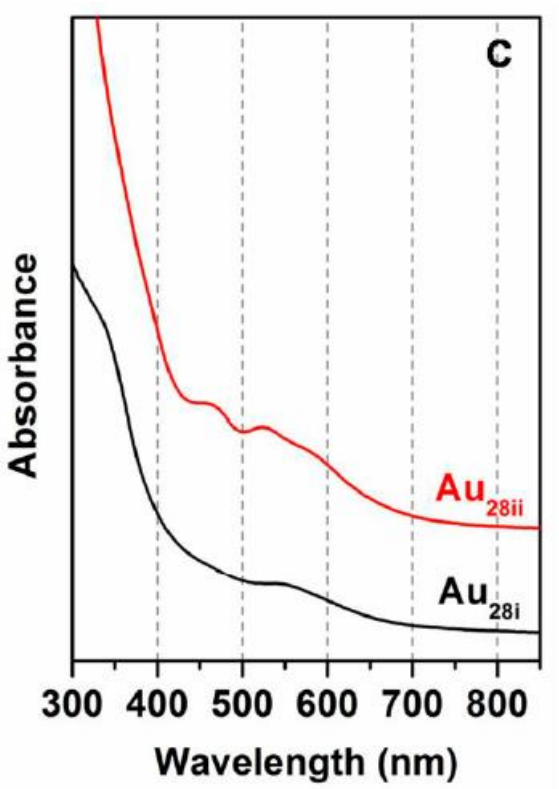
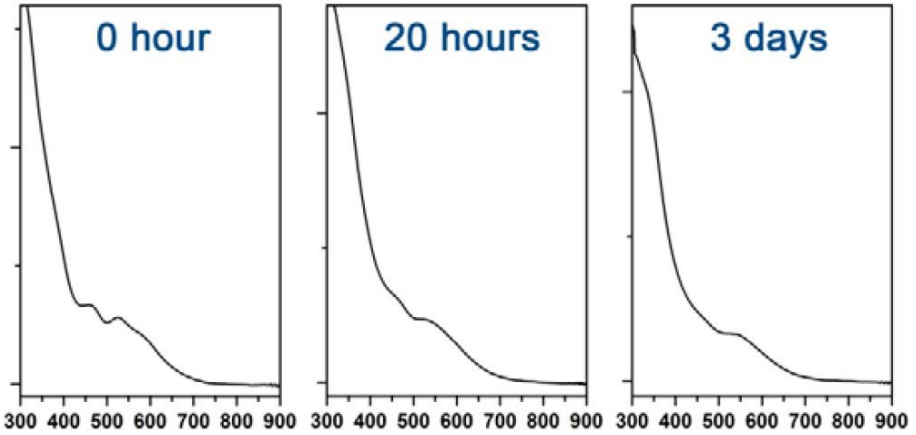


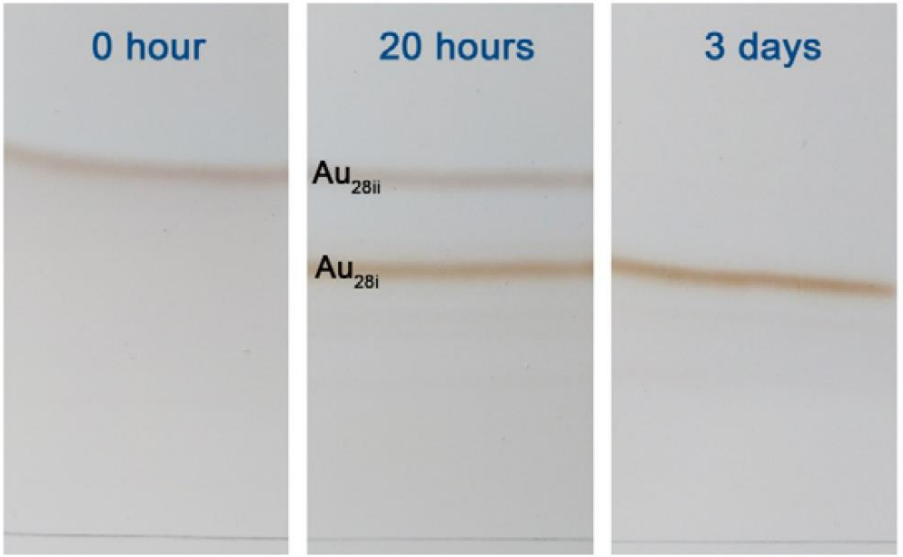
Figure 1. (A) The mass spectra of Au_{28i} and Au_{28ii} (positive ionization mode). (B) The experimental and calculated isotope patterns of $[Au_{28}(CHT)_{20}Cs_2]^{2+}$. (C) The optical spectra of Au_{28i} and Au_{28ii}. (D) The PTLC monitoring of Au_{28i} and Au_{28ii}. (E) Photograph of Au_{28i} and Au_{28ii} solutions under room lighting.

Solvent induced transformation



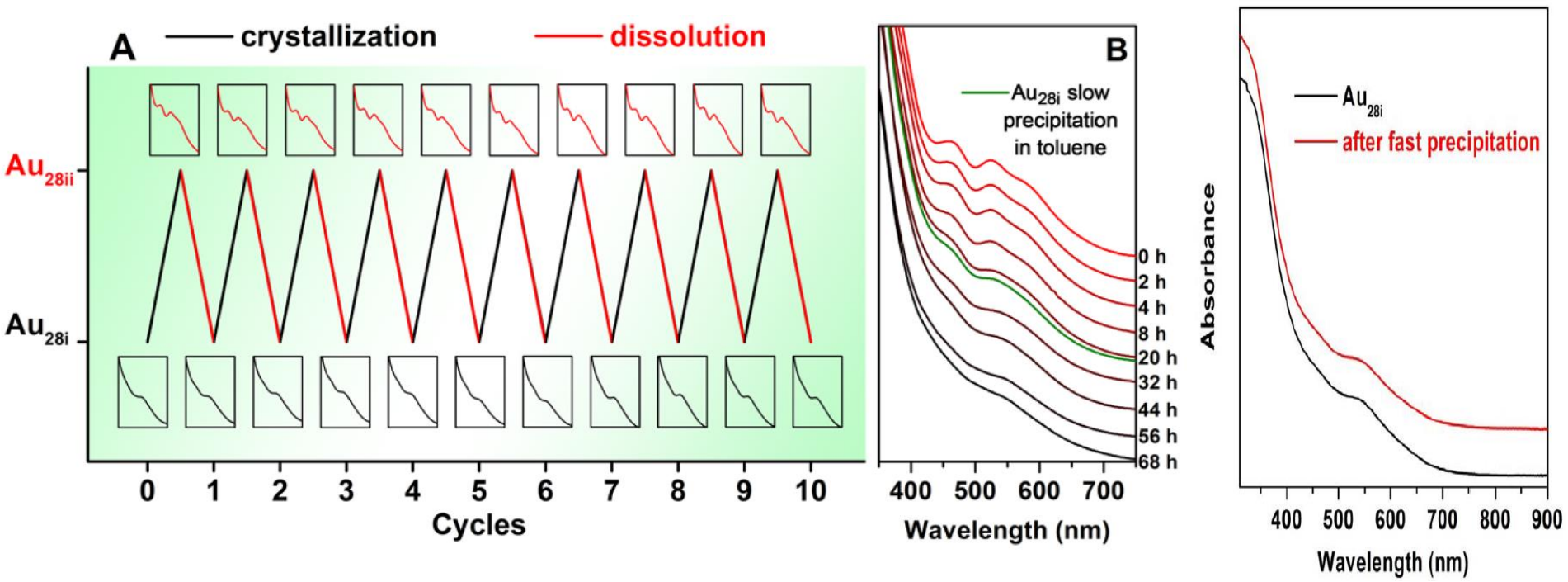
Solvent induced transformation





Reversible transformation

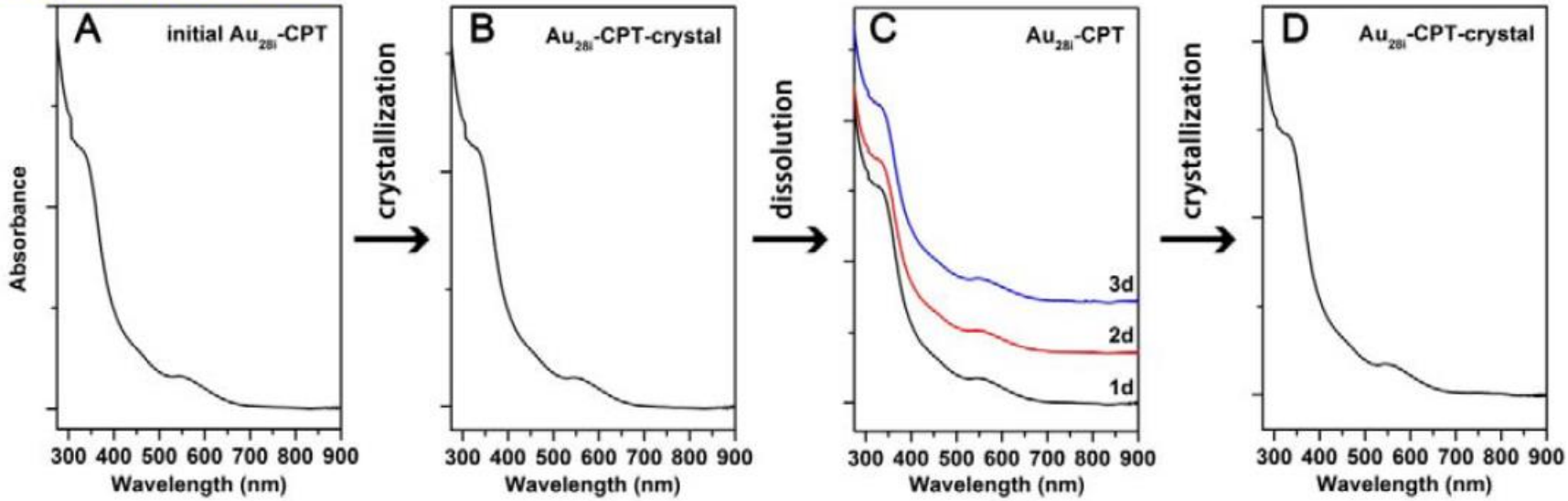
- The solvent induced transformation can be reversed by adding solvents like MeCN or MeOH in which the clusters are poorly soluble, giving crystals of Au_{28ii} again. This indicates that Au_{28i} and Au_{28ii} are structural oscillators whose transformation is triggered by crystallization-dissolution cycles (10 cycles are studied).



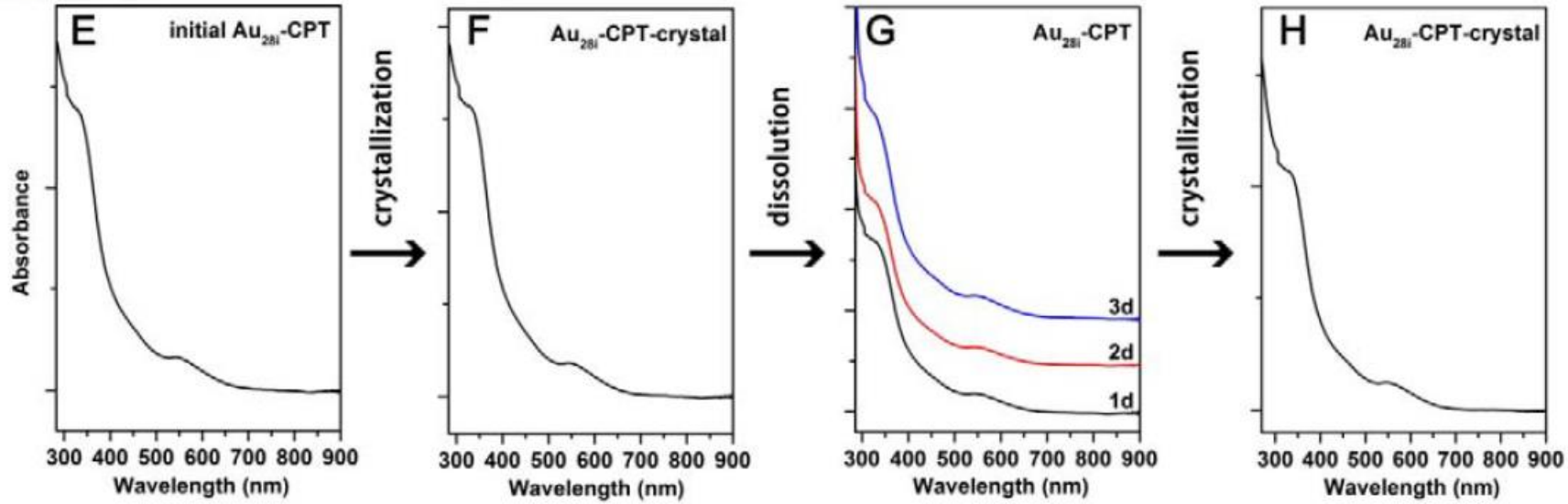
Ligand exchange in Au_{28} nanocluster

- The crystals of Au_{28i} cannot be obtained because upon crystallization it transforms to Au_{28ii}.
- A ligand exchange is carried out under mild conditions where CHT is replaced by CPT.
- SCXD of $Au_{28i}(CPT)_{20}$ shows that it has a structure similar to that of $Au_{28}(TBBT)_{20}$ (Au_{28t}).
- $Au_{28}(CPT)_{20}$ does not show structural oscillation which is proved by repeated dissolution and crystallization of the crystal of $Au_{28i}(CPT)_{20}$ in DCM and toluene.

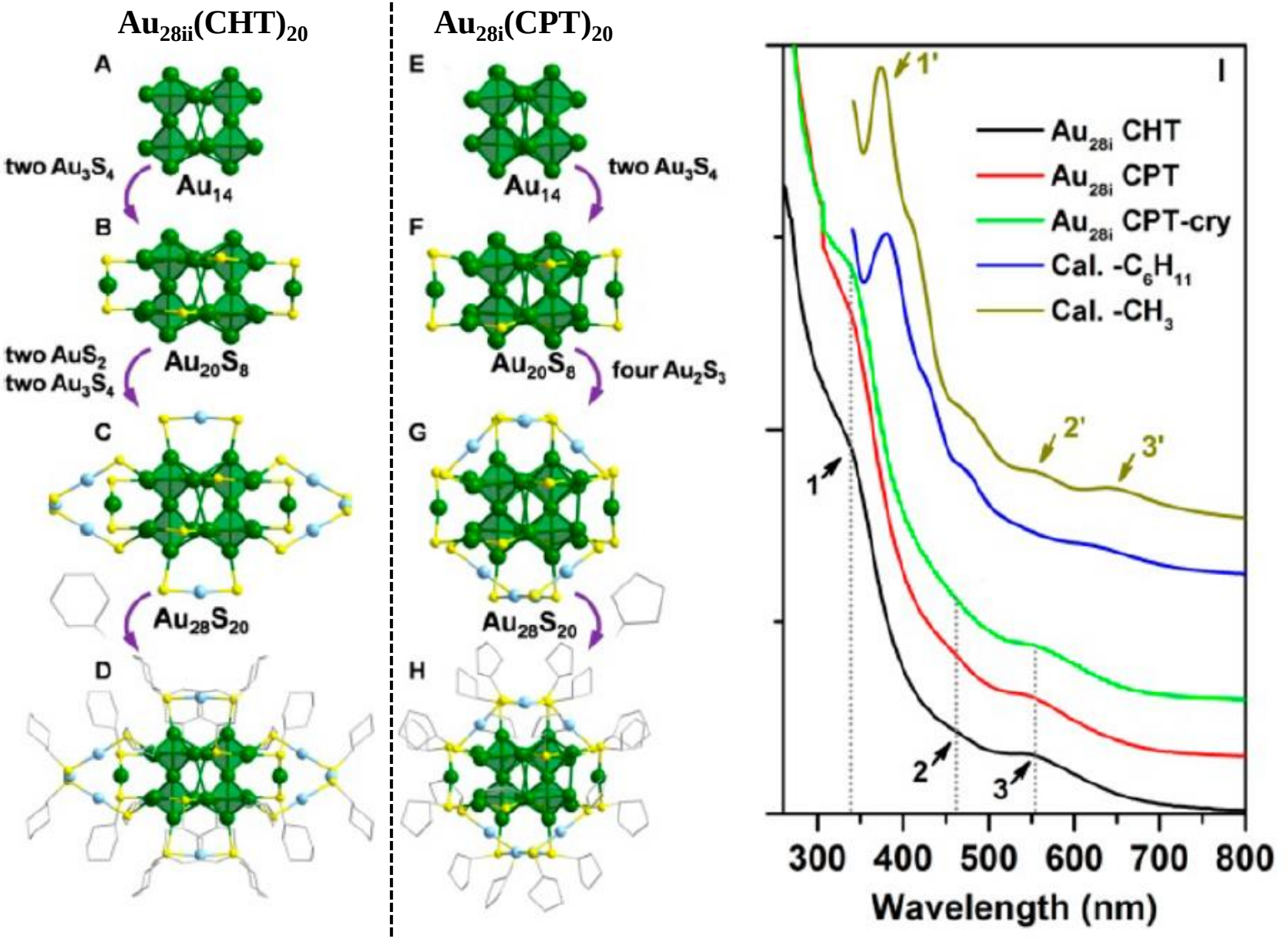
Dichloromethane:



Toluene:

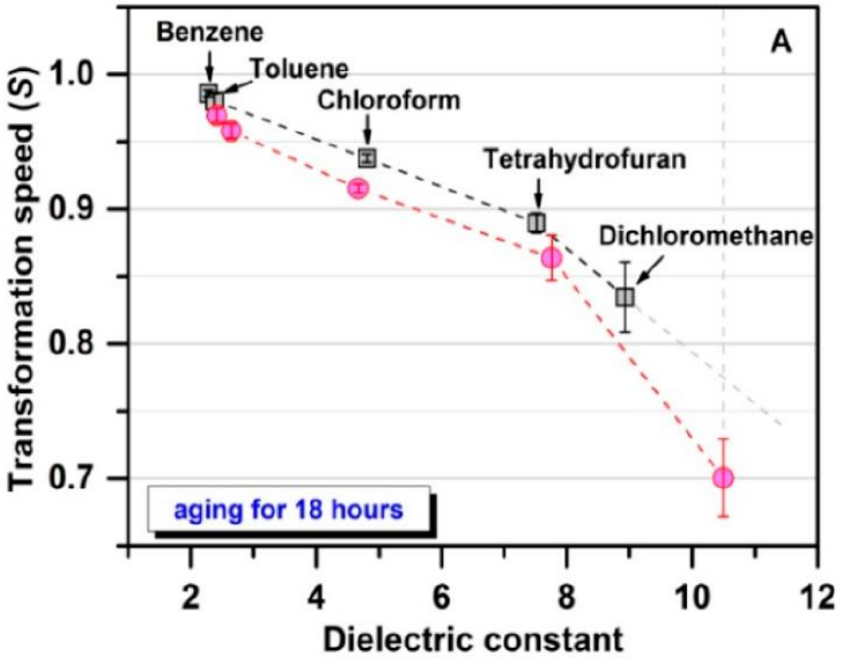


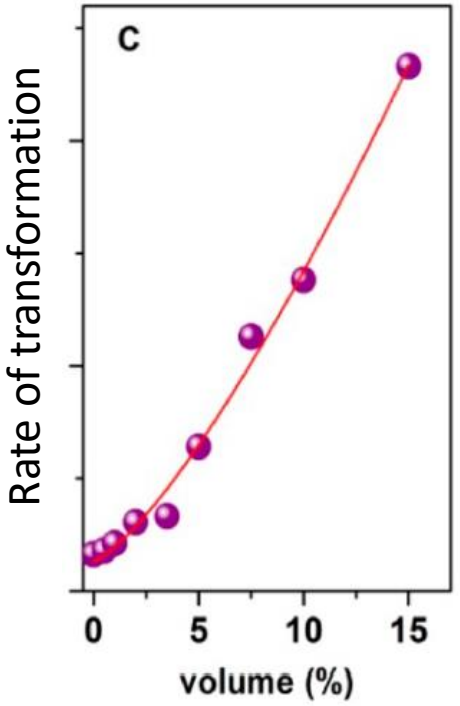
- Structures of Au_{28i} and Au_{28ii} and UV-vis spectra of $Au_{28i}(CPT)_{20}$.



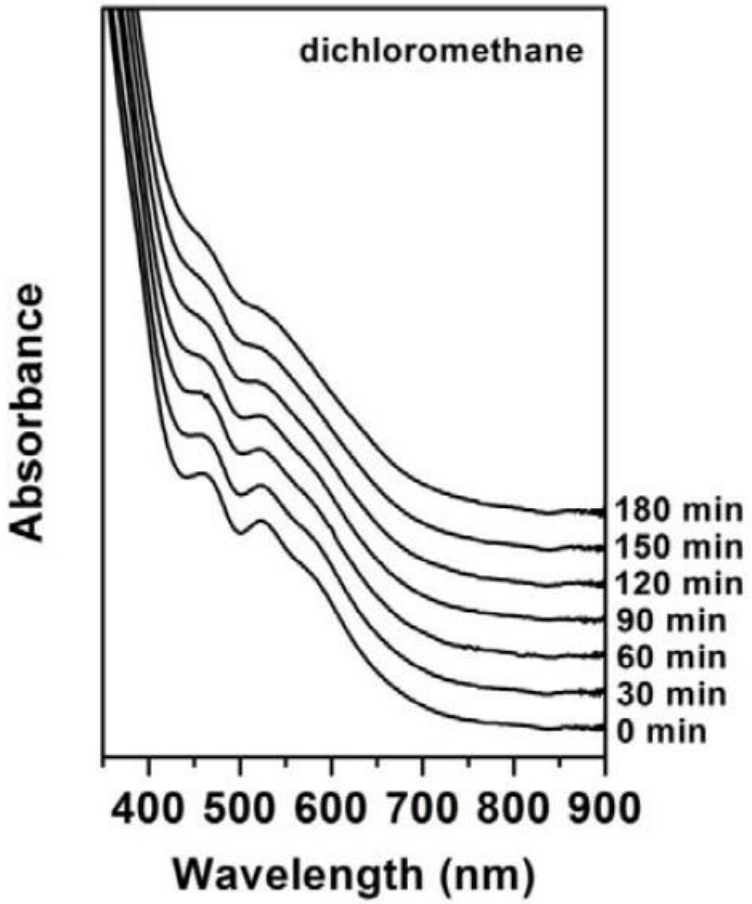
Effect of dielectric constant

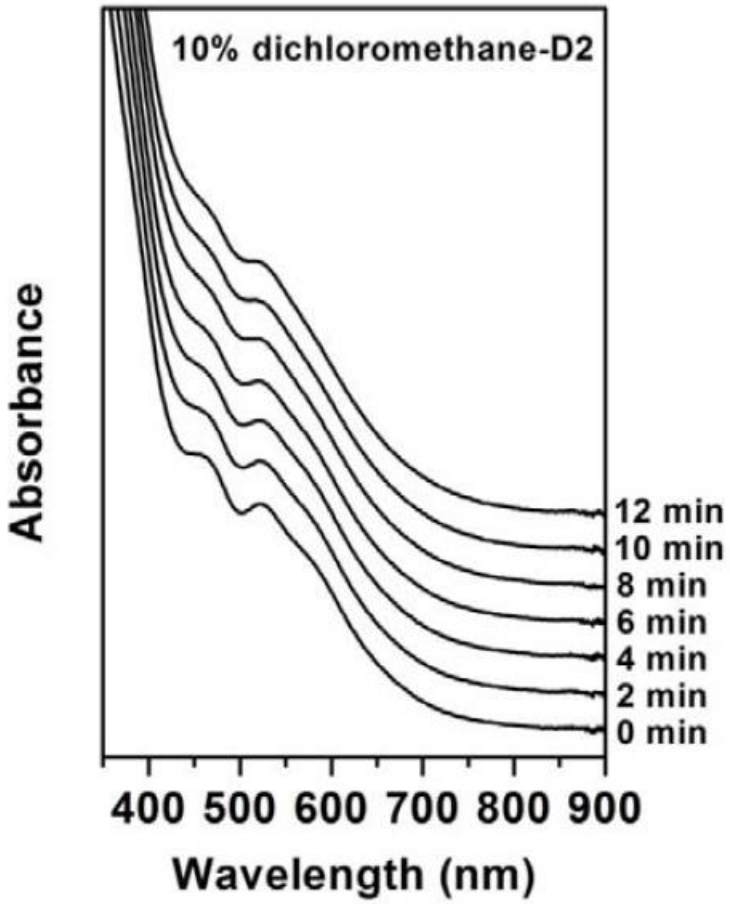
- The effect of solvent on the rate of transformation was studied using various solvents like benzene, toluene, chloroform, tetrahydrofuran, and dichloromethane, with the increasing dielectric constants (2.28, 2.38, 4.81, 7.52, and 8.93, respectively).
- The deuteration of the solvent also has great influence on rate of transformation as shown in the figure below.





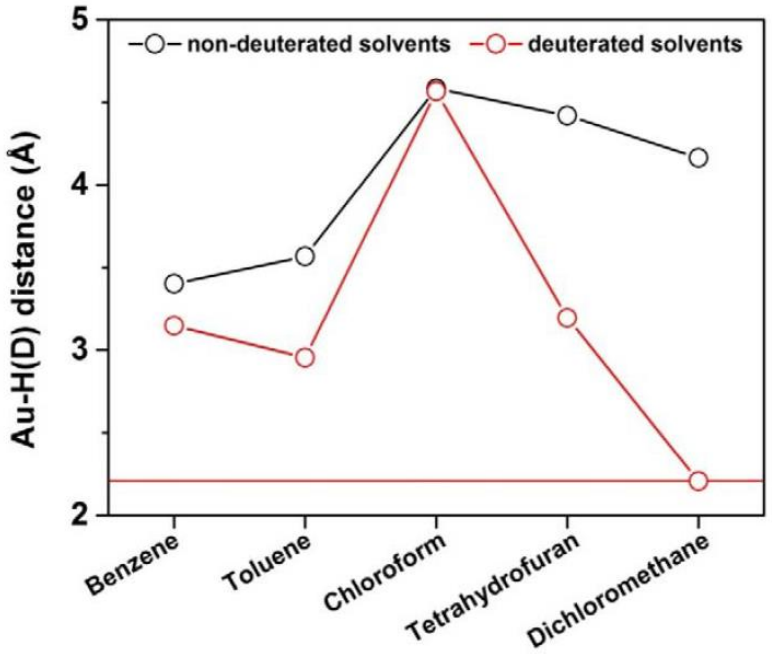
Effect of deuteration





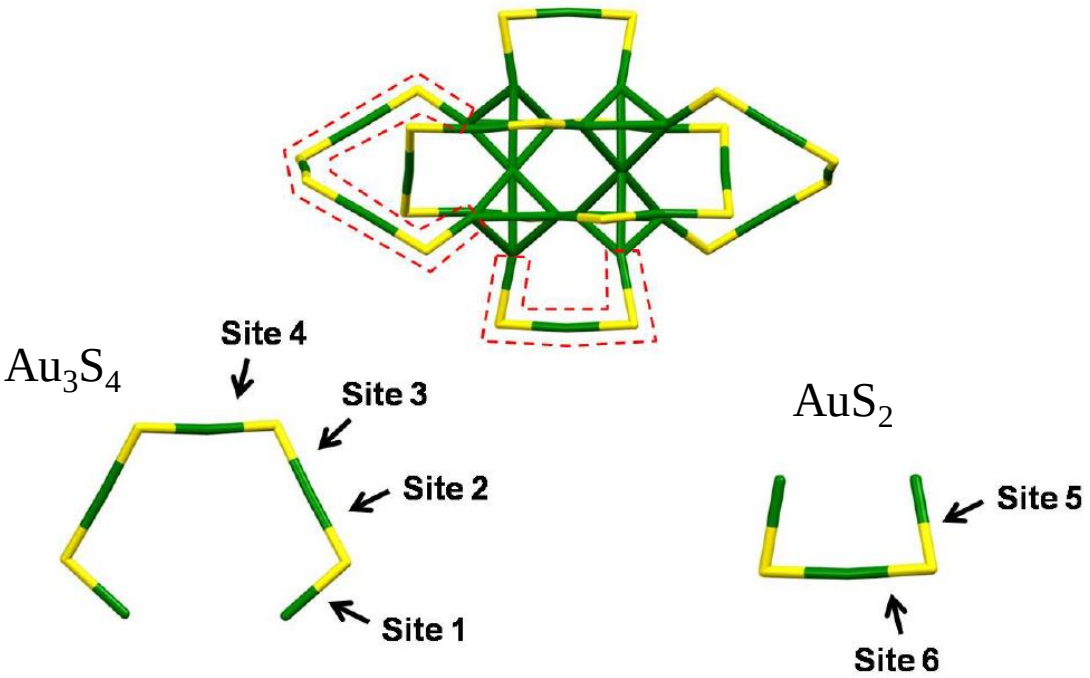
Adsorption of solvent

- It was found by DFT calculations that the solvent adsorption will decrease the energy of Au_{28ii} nanocluster and this decrease becomes more obvious with the increase in the solvent dielectric constant, indicating solvent participation in the structural transformation.
- The energy decrease is thought to be due to Au-H or Au-D interactions.



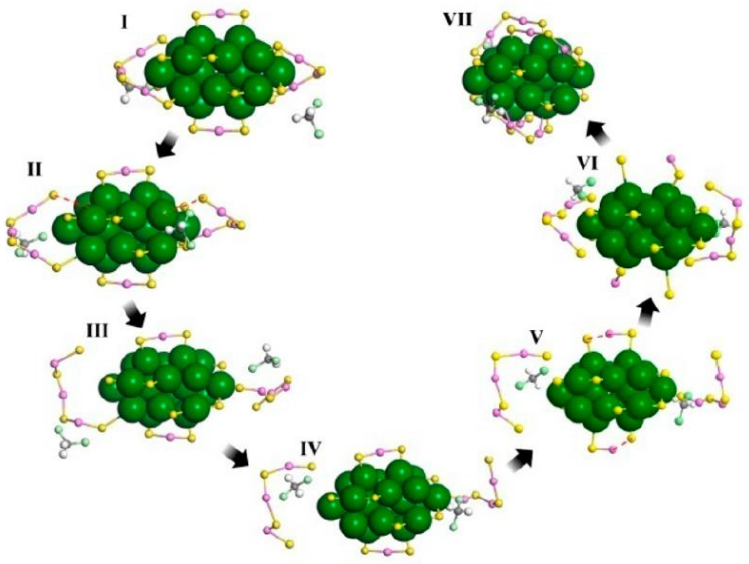
Solvent	Adsorbed energy (kJ/mol)	
	E_H	E_D
Benzene	-31.89	-41.76
Toluene	-41.89	-46.89
Chloroform	-39.12	-42.34
THF	-43.67	-54.98
DCM	-56.24	-89.45

Transformation pathway



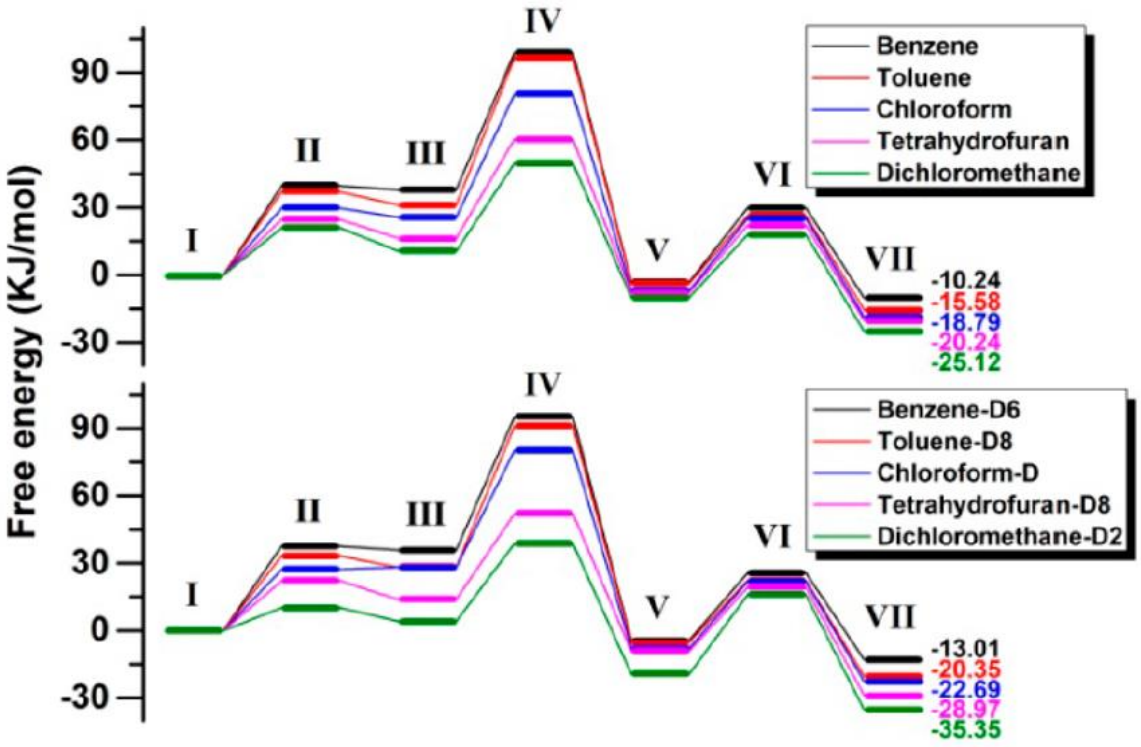
Solvent	Trimer staple			Monomer staple	
	Site 1	Site 2/3[a]	Site 4	Site 5	Site 6
Benzene	-32.19	-20.23	-25.78	-19.56	-30.73
Toluene	-40.39	-30.17	-36.89	-27.45	-38.51
Chloroform	-38.12	-29.98	-34.12	-28.98	-41.56
Tetrahydrofuran	-42.61	-31.78	-38.45	-32.56	-49.87
Dichloromethane	-54.94	-37.45	-46.28	-36.76	-49.12

Transformation pathway



- I – The initial Au_{28ii}.
- II–IV – The breakup and departure of Au_3S_4.
- V – The breakup of AuS_2.
- VI – The approach of Au_3S_4 towards the kernel
- VII – The final Au_{28i}.

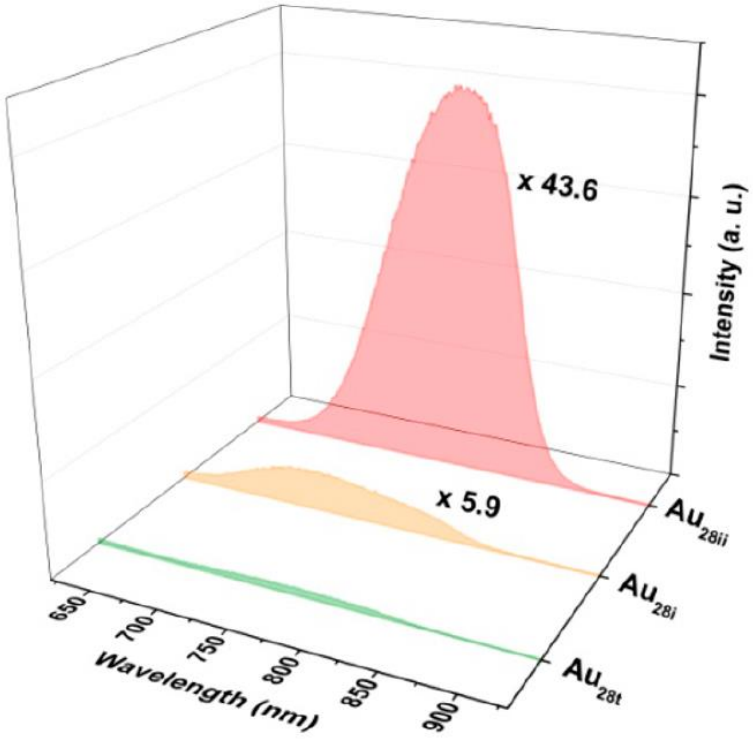
Solvent	ε
Benzene	2.28
Toluene	2.38
Chloroform	4.81
THF	7.52
DCM	8.93



Photoluminescence behaviour

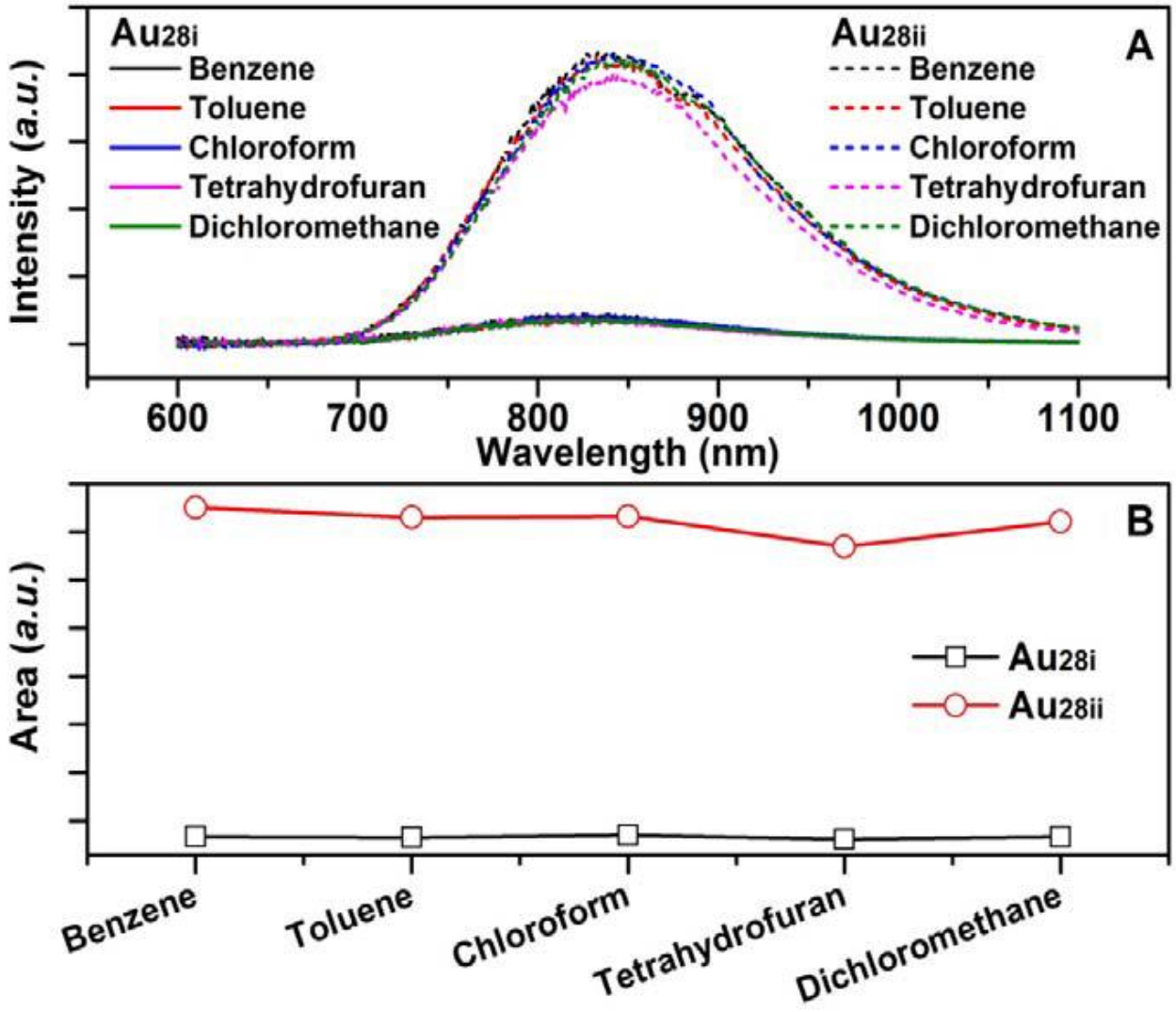
- Even though the Au_{28i} and Au_{28ii} have same Au_{14} kernels they show difference in both maximum emission wavelength and emission intensity. λ_{max} for Au_{28i} is 725 nm while it shifts to 790 nm for Au_{28ii}.
- The fluorescence intensity of Au_{28ii} is 7.4 times enhanced when compared to Au_{28i} indicating that the surface staples play an important role in dictating the photoluminescent behaviour of the nanoclusters.

- Au_{28i} has two lifetimes, ~0.3 µs (~13%) and ~1.9 µs (~87%) indicating two different radiative pathways.
- Au_{28ii} has only one fluorescence lifetime of ~1.9 µs indicating similar radiative pathway as in Au_{28i}.



Solvent effect

- It was found that the solvent had very little effect on photoluminescent behaviour of nanoclusters which is proved by the figure below.



Conclusion

- This is the first report on reversible structural oscillation in Au nanocluster systems.
- The two isomers have same Au_{14} kernel but different surface staple structures hence show different spectroscopic behaviours and different stabilities.
- The rigid Au_{28ii} nanocluster shows strong photoluminescence while the flexible Au_{28i} shows weak photoluminescence, which can be used in sensors.