

## Carboranealkynyl-Protected Gold Nanoclusters: Size Conversion and UV/Vis–NIR Optical Properties

*Jie Wang, Zhao-Yang Wang,\* Shi-Jun Li, Shuang-Quan Zang,\* and Thomas C. W. Mak*

[\*] J. Wang, Dr. Z.-Y. Wang, Dr. S.-J. Li, Prof. S.-Q. Zang,

Prof. T. C. W. Mak

Green Catalysis Center, and College of Chemistry, Zhengzhou  
University

Zhengzhou 450001 (China)

E-mail: wangzy@zzu.edu.cn

zangsqzg@zzu.edu.cn

Prof. T. C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong  
Shatin, New Territories, Hong Kong SAR (China)

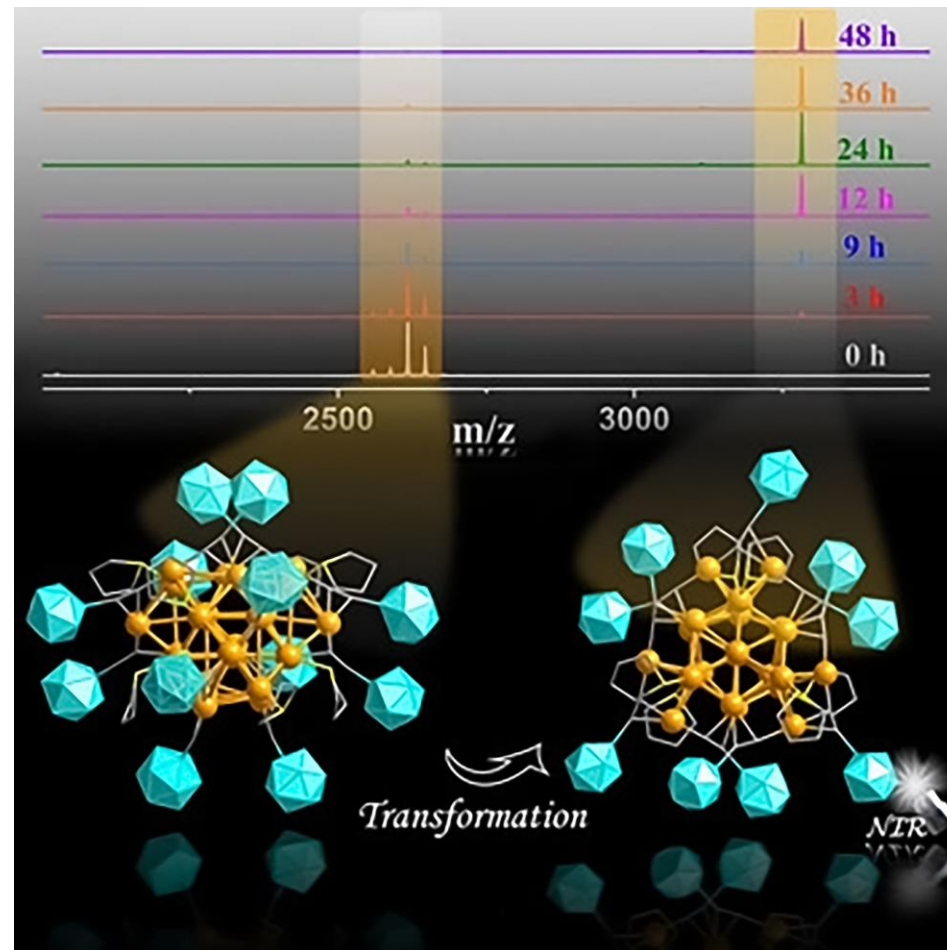
Presented by: Amoghavarsha R Kini

# Abstract

- They have reported the synthesis of a carboranealkynyl protected gold nanocluster

$[\text{Au}_{28}(\text{C}_4\text{B}_{10}\text{H}_{11})_{12}(\text{tht})_8]^{3+}$  using 9-HC $\equiv$ C-closo-1,2-C $_2\text{B}_{10}\text{H}_{11}$  as a two-in-one reducing and protecting agent.

(tht = tetrahydrothiophene)



## Chiroptical Activity Enhancement via Structural Control: The Chiral Synthesis and Reversible Interconversion of Two Intrinsically Chiral Gold Nanoclusters

Jia-Qi Wang,<sup>†</sup> Zong-Jie Guan,<sup>‡</sup> Wen-Di Liu,<sup>†</sup> Yang Yang,<sup>\*,§</sup> and Quan-Ming Wang<sup>\*,†,‡</sup>

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## Isomerization in Alkynyl-Protected Gold Nanoclusters

Zong-Jie Guan, Feng Hu, Jiao-Jiao Li, Zhao-Rui Wen, Yu-Mei Lin, and Quan-Ming Wang<sup>\*</sup>

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# Motivation

- To study the properties of carboranealkynyl protected nanoclusters compared to alkynyl and thiol protected clusters.
- To study the structural transformations of these carboranealkynyl protected clusters.

## Why this paper?

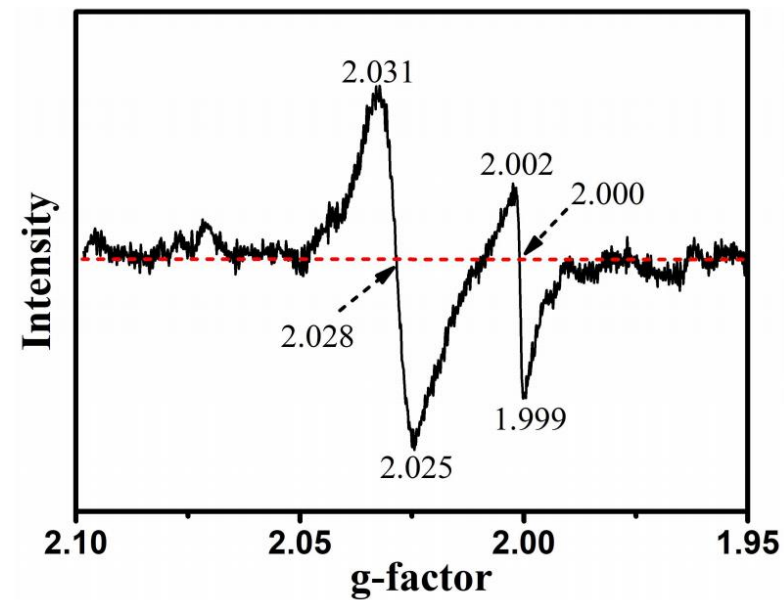
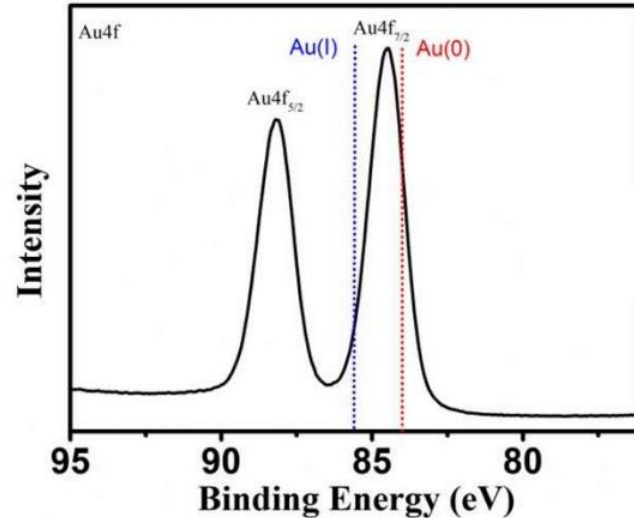
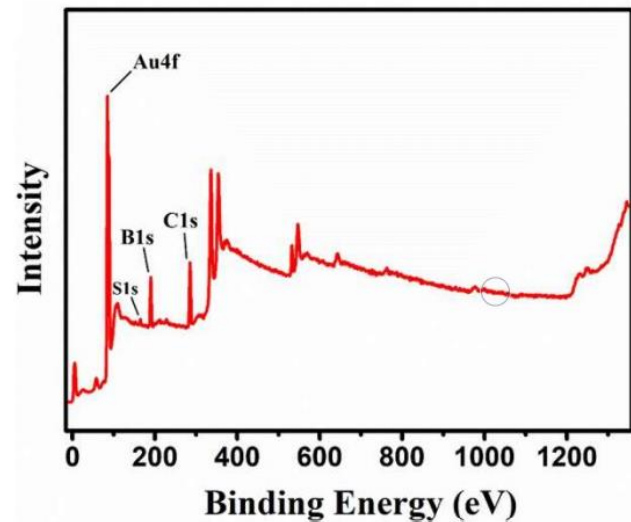
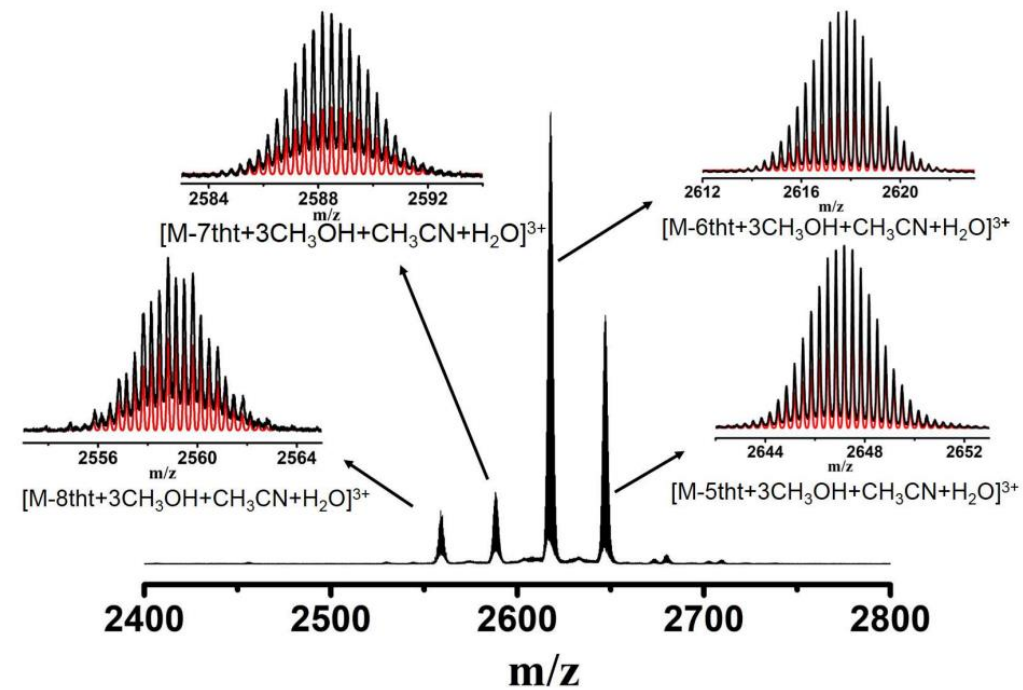
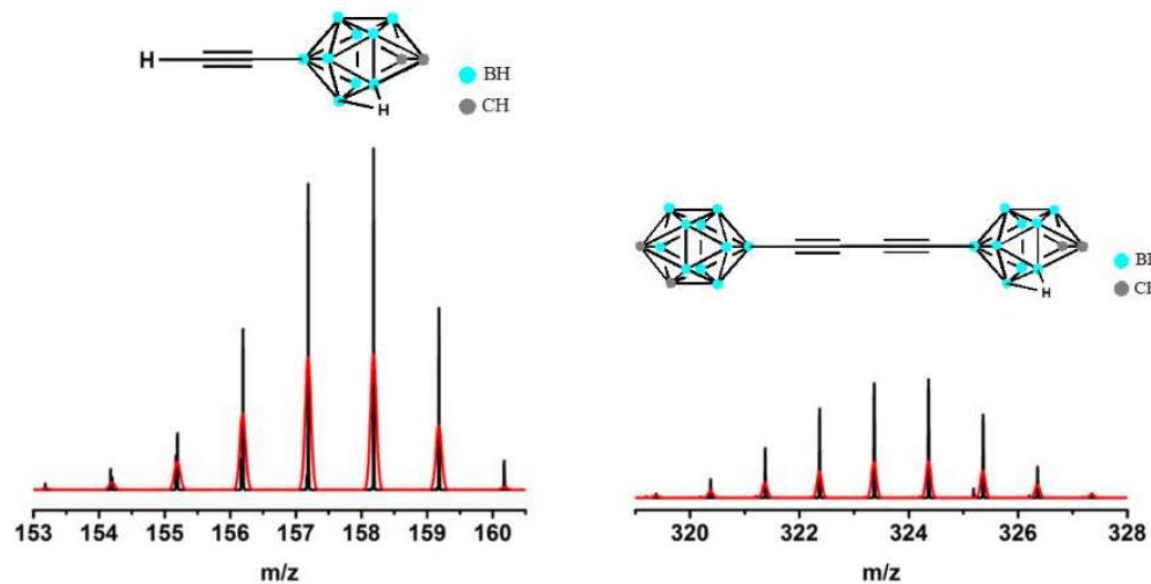
- Provides an opportunity to understand the use of carboranealkynyl as ligands to synthesize nanoclusters with interesting physical and chemical properties.
- Makes an attempt at understanding the mechanism of structural transformation of  $\text{Au}_{28}$  to  $\text{Au}_{23}$  in solution state.

# Introduction

- Alkynyls are newly recruited protecting ligands in coinage-metal nanoclusters in the past decade. In contrast to the extensively used thiolate and phosphine ligands, an important feature of an alkynyl ligand is that its  $C\equiv C$  bond may anchor on the metal surface via both  $\sigma$  and  $\pi$  bonds.
- They have mentioned some of the previous works ( by Tsukuda, Wang, Guan and Zheng groups) on alkynyl protected metal nanoclusters and their structural transformations which led to this study.
- A brief summary of their work reported in this paper and its application in photocatalysis and biomedical field.

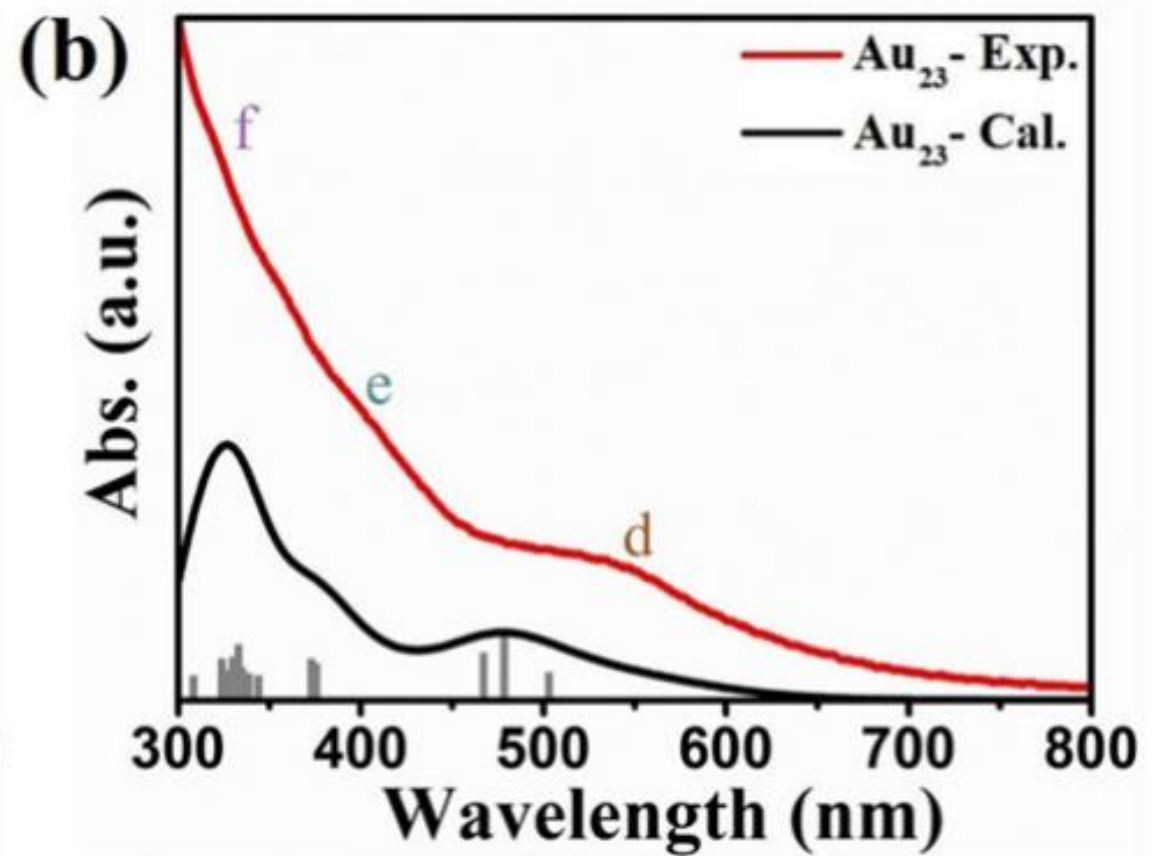
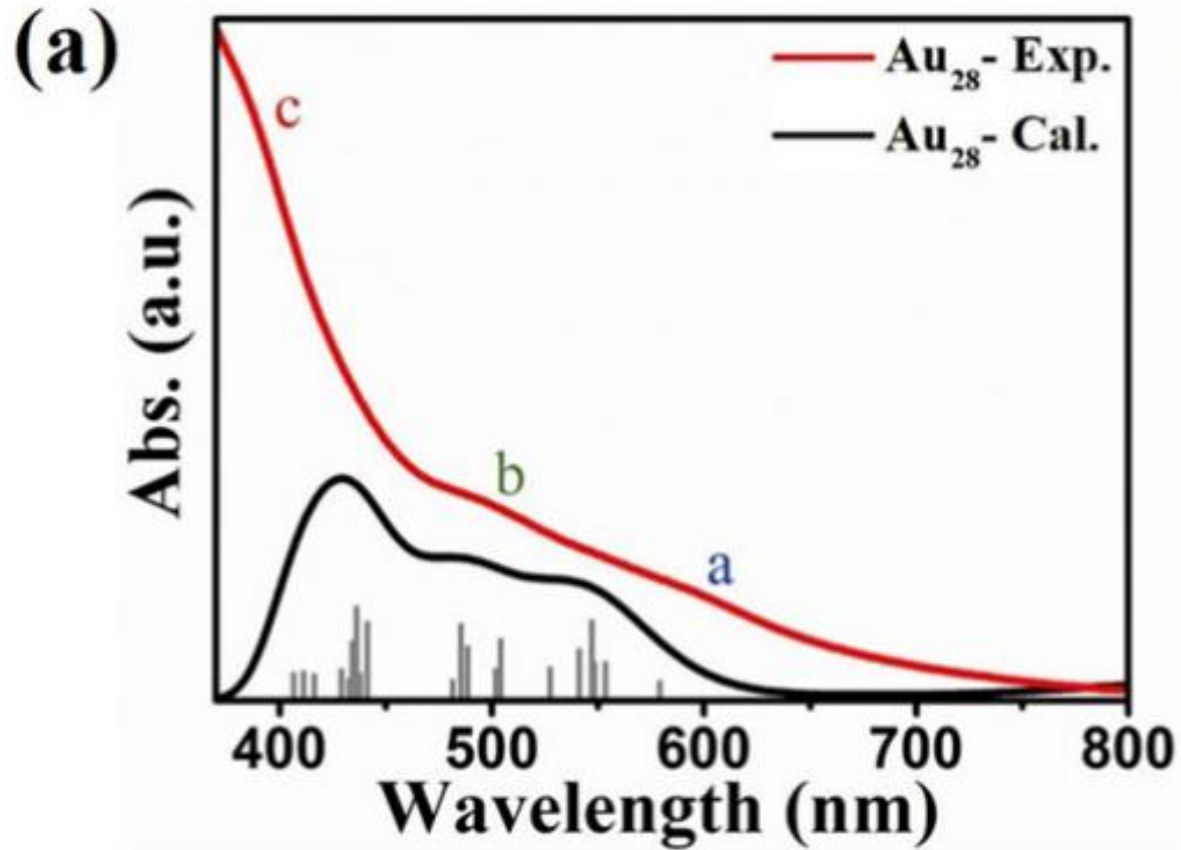


# Results and Discussion



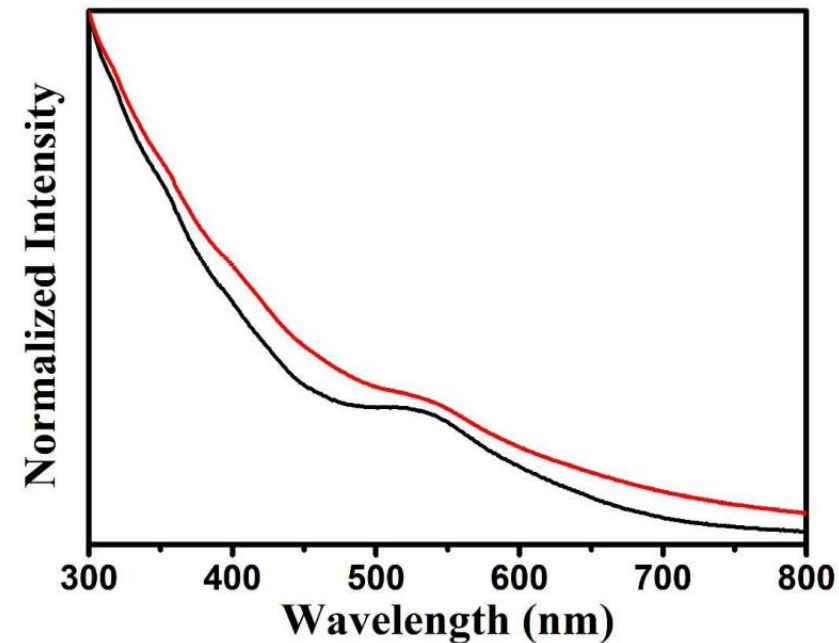
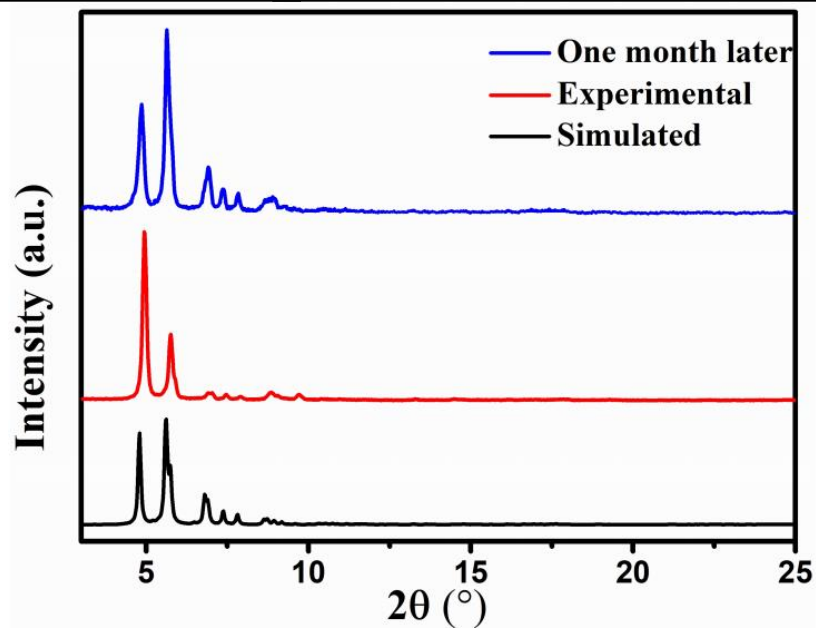


# Results and Discussion

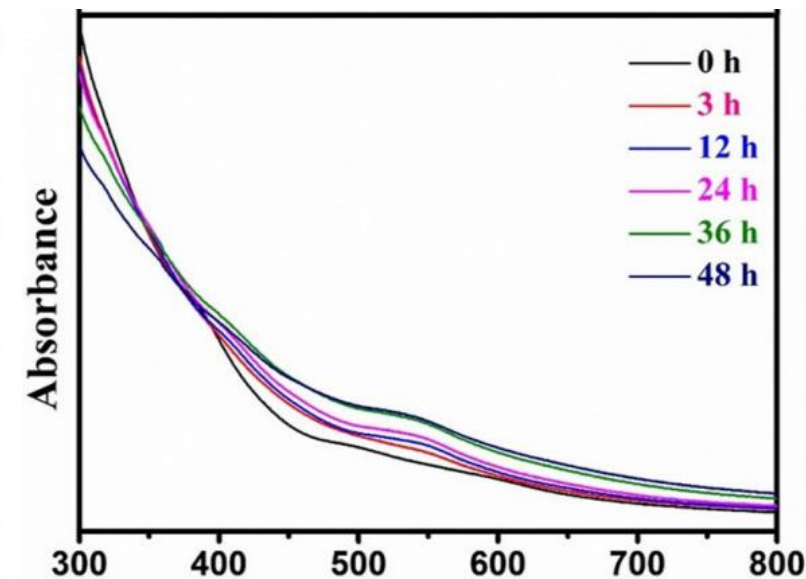
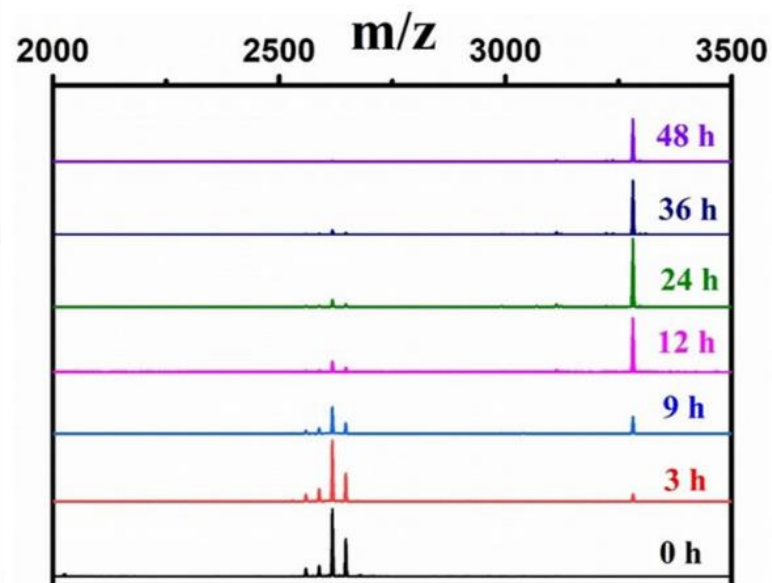
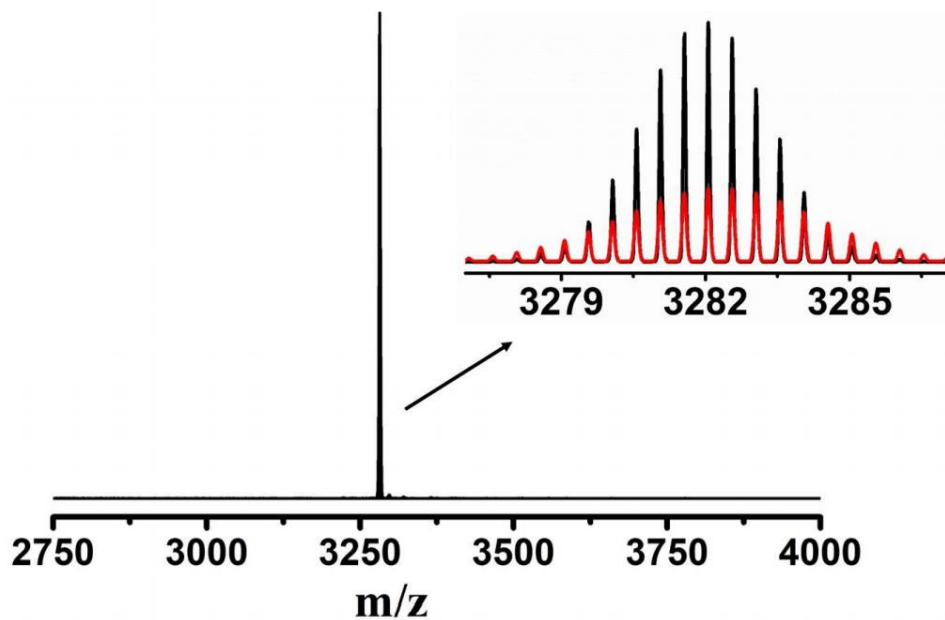




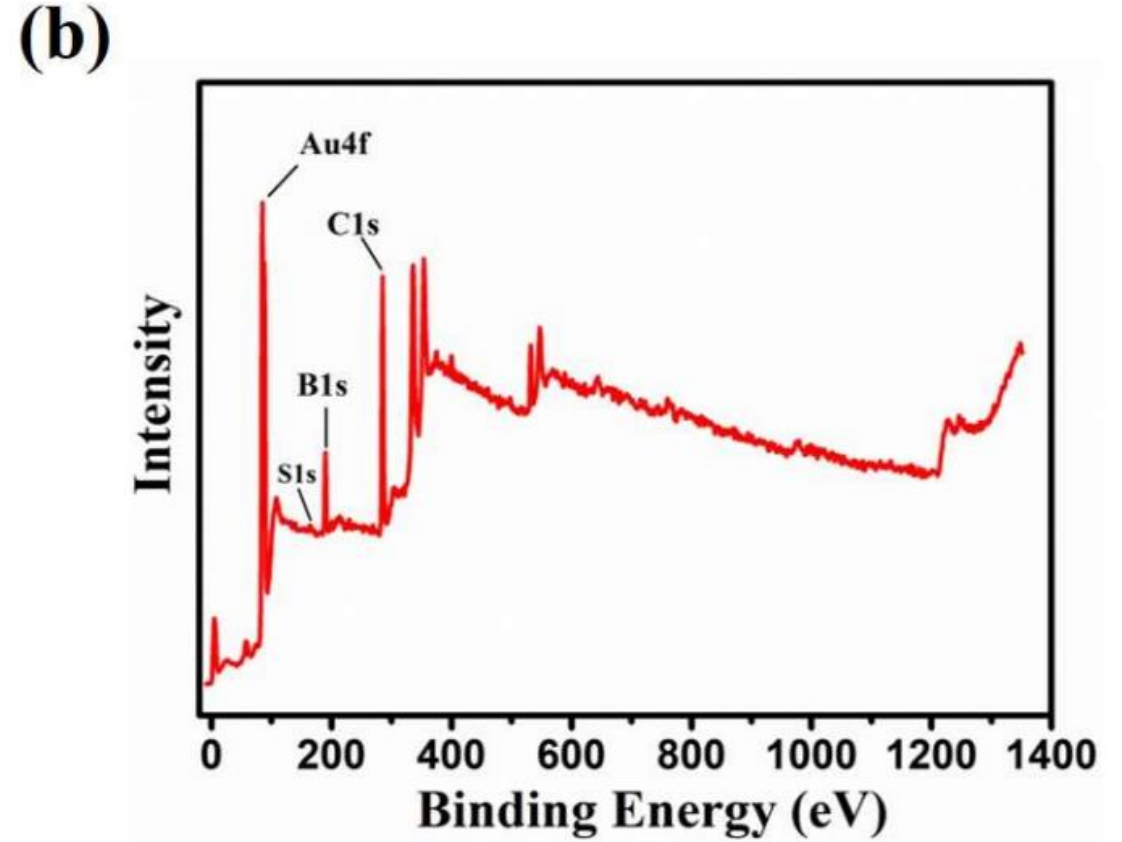
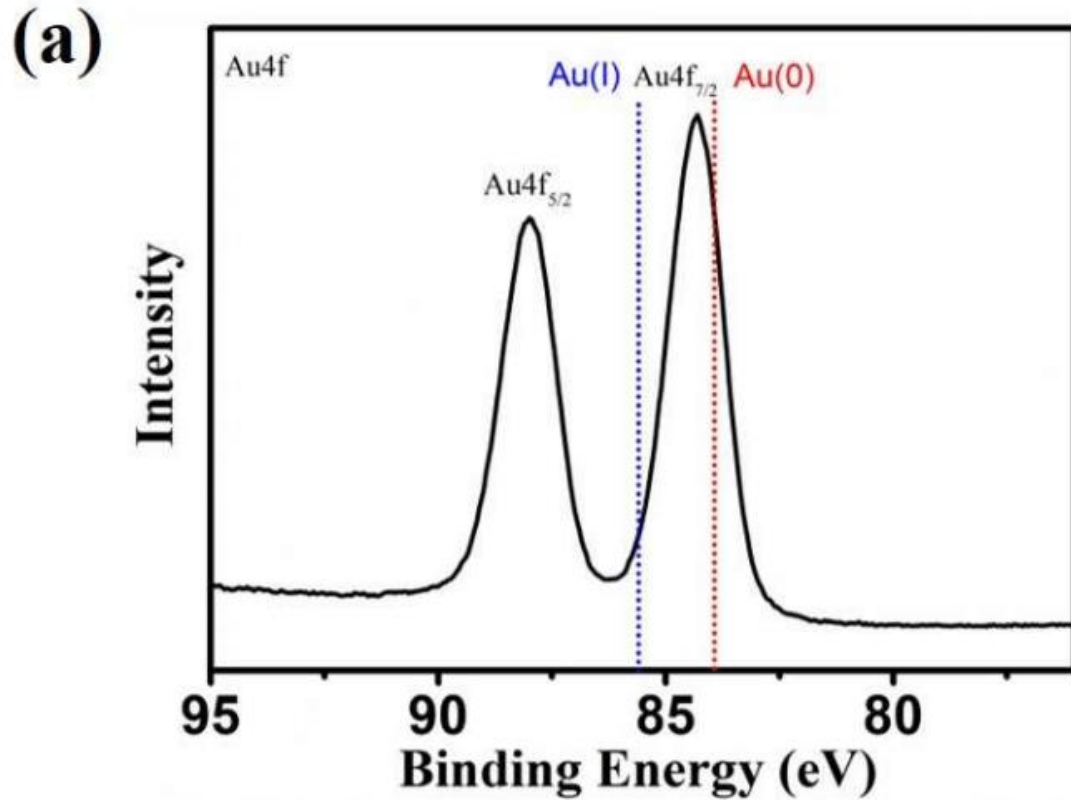
# Results and Discussion



Absorption spectrum of methanol solution of Au<sub>23</sub>(black) and Au<sub>28</sub>(red) after 48 hours

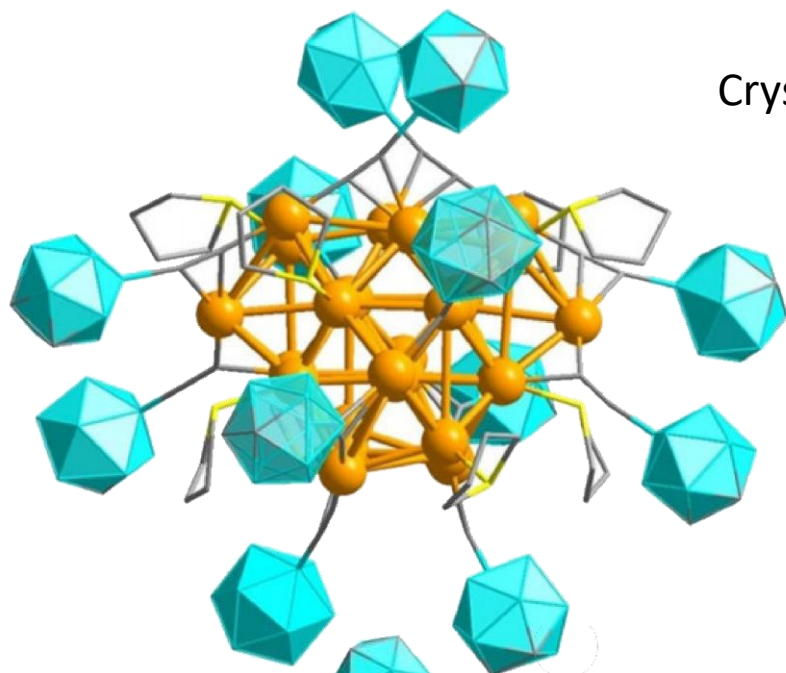


# Results and Discussion

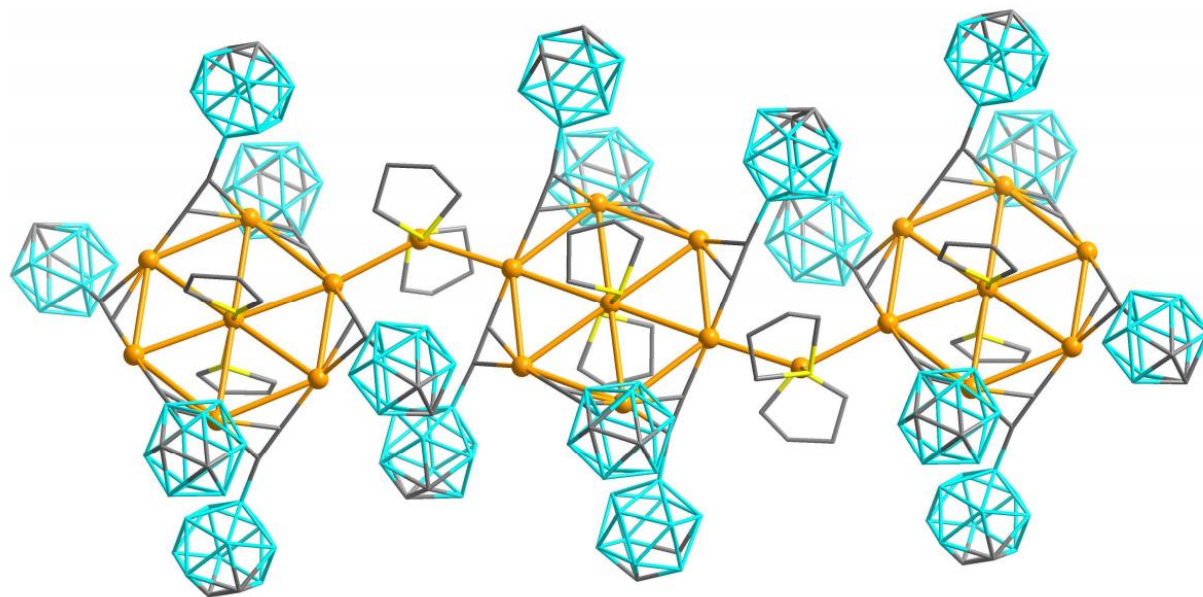


XPS spectrum of Au<sub>23</sub> nanocluster.

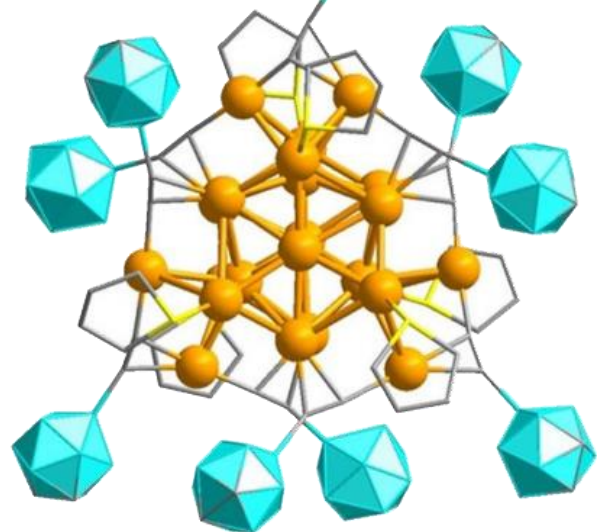
# Structures



Crystal structure of  $\text{Au}_{28}$  - Triclinic

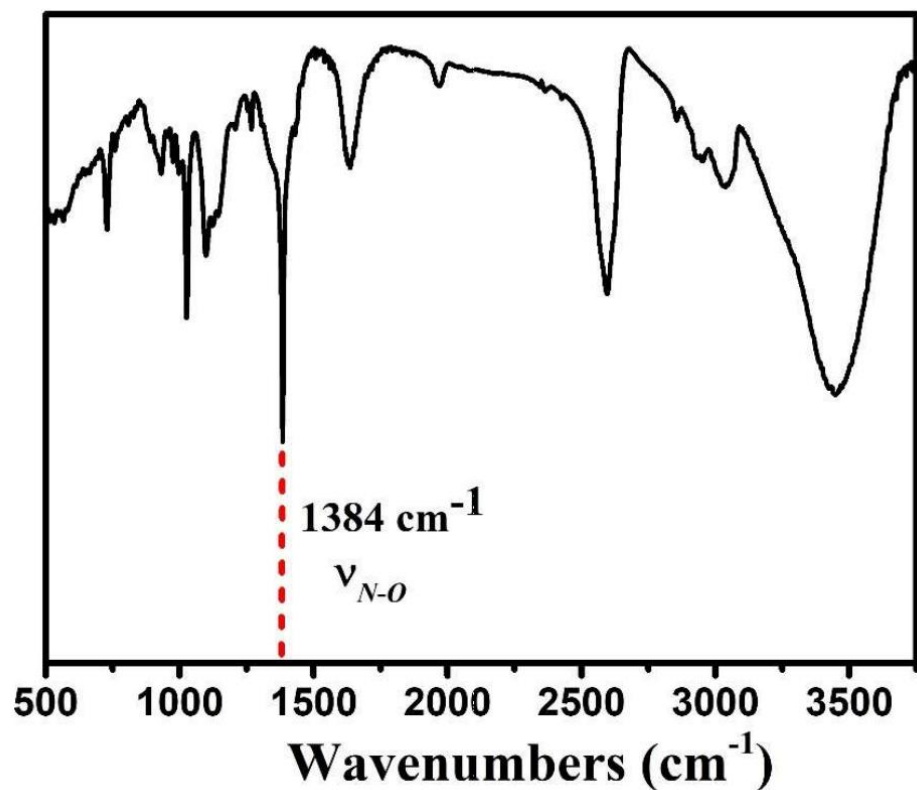


Crystal structure of by-product - Triclinic

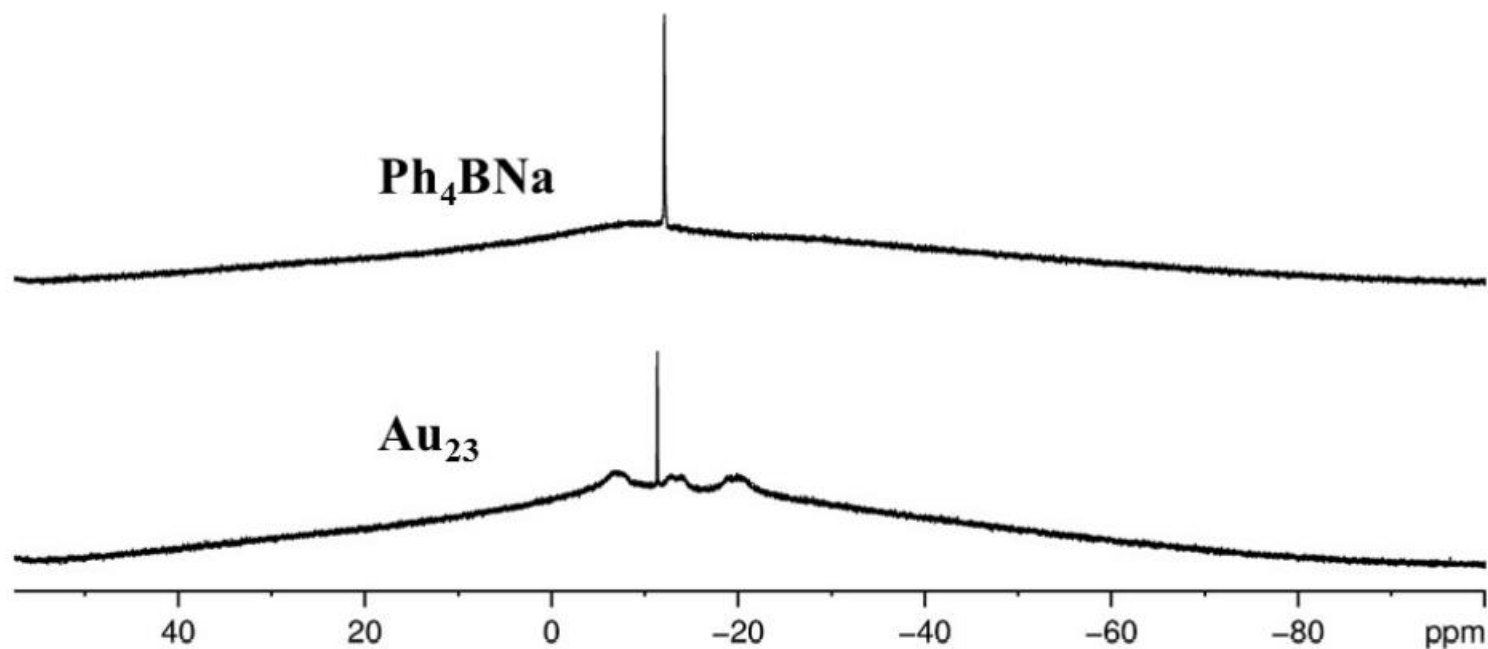


Crystal structure of  $\text{Au}_{23}$  - Monoclinic

# Results and Discussion

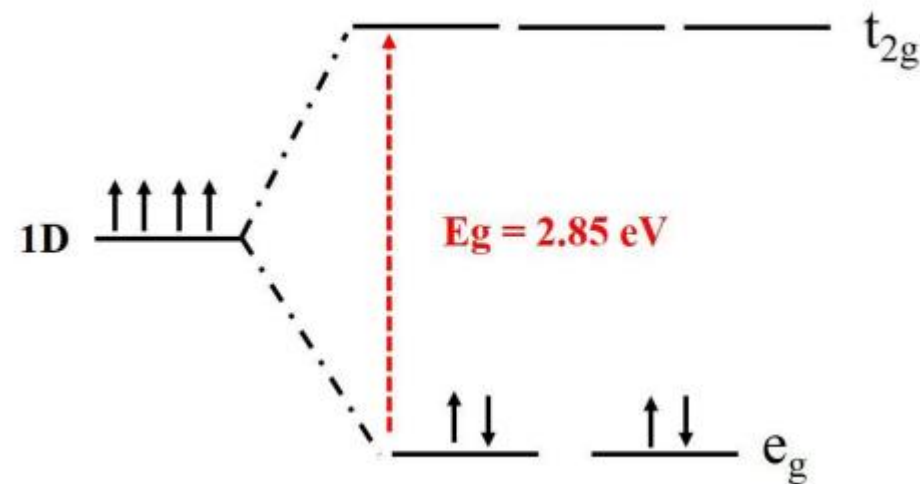
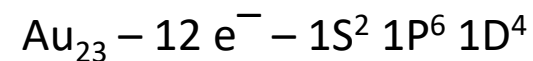
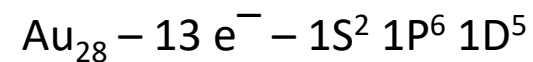
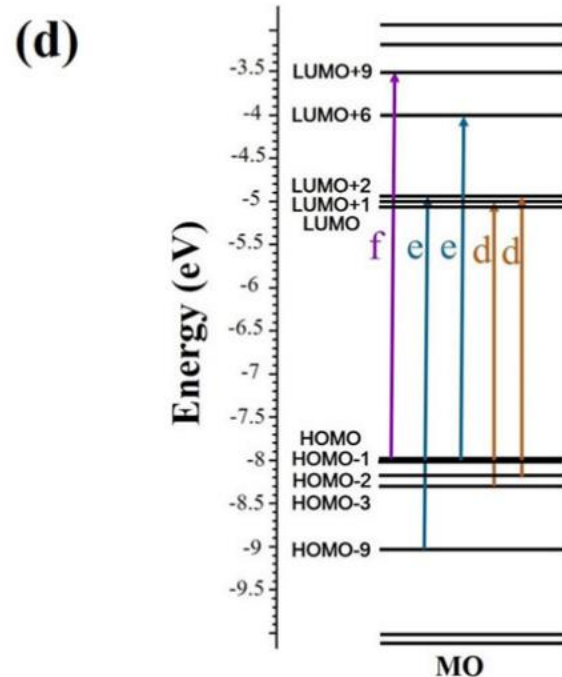
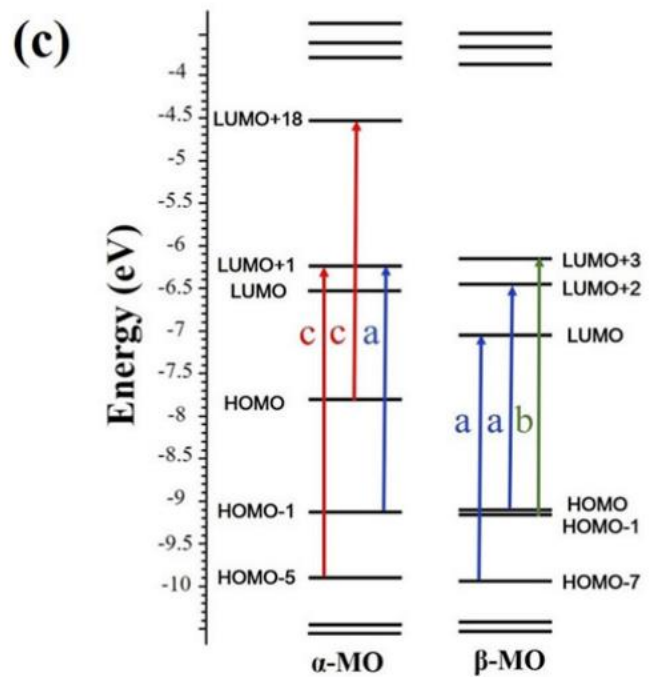
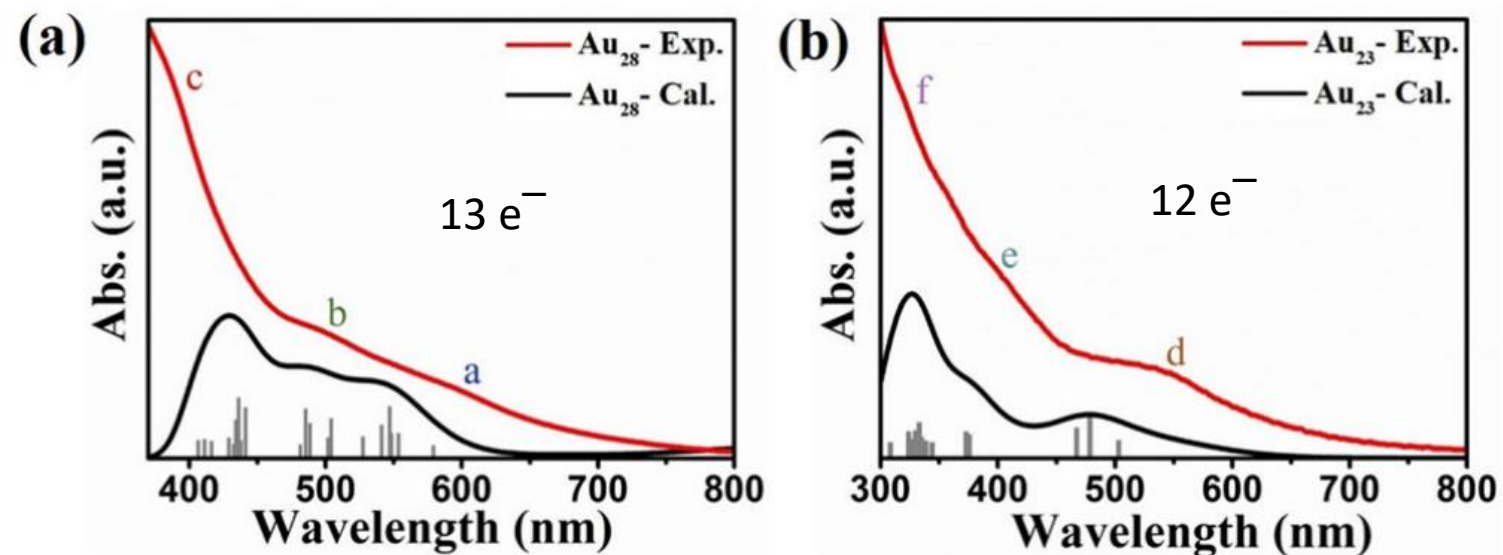


FTIR spectrum of Au<sub>28</sub> crystal showing presence of NO<sub>3</sub><sup>-</sup> as the counter ion



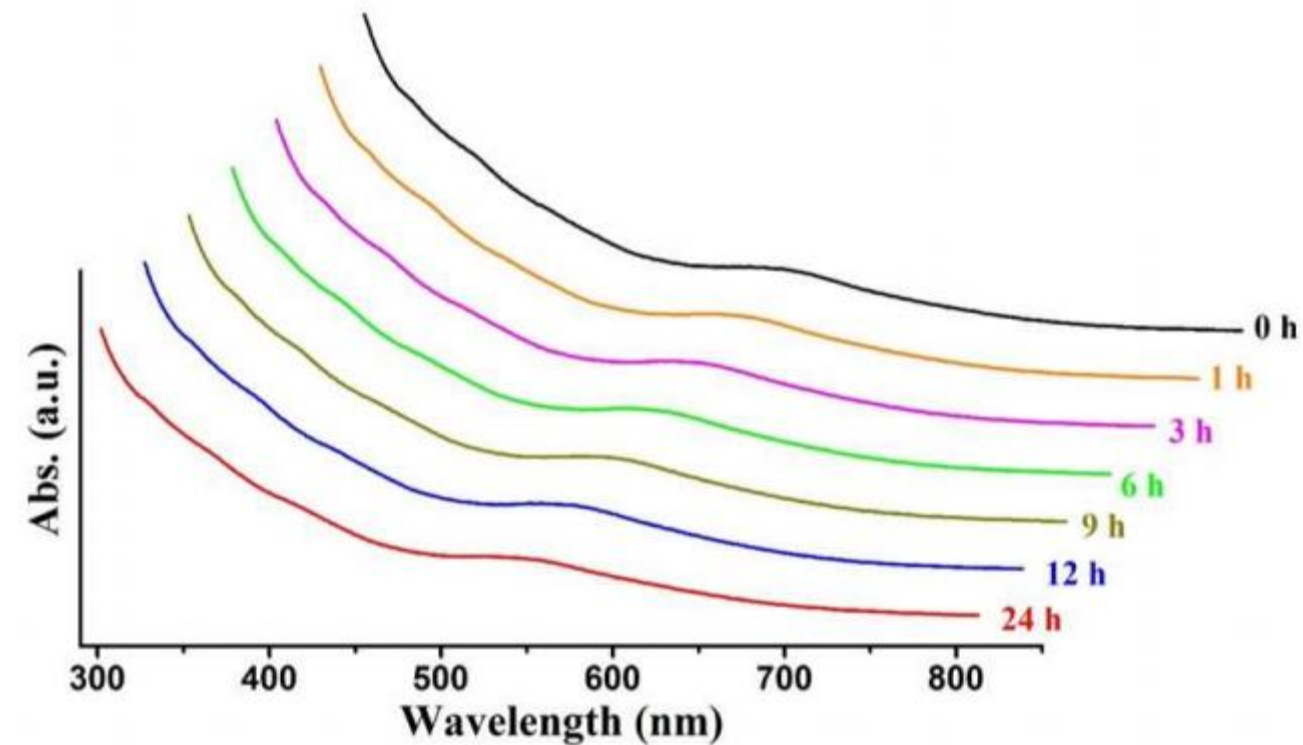
<sup>11</sup>B NMR of Ph<sub>4</sub>BNa and Au<sub>23</sub> crystal indicating the presence of Ph<sub>4</sub>B<sup>-</sup> as the counter ion

# Results and Discussion

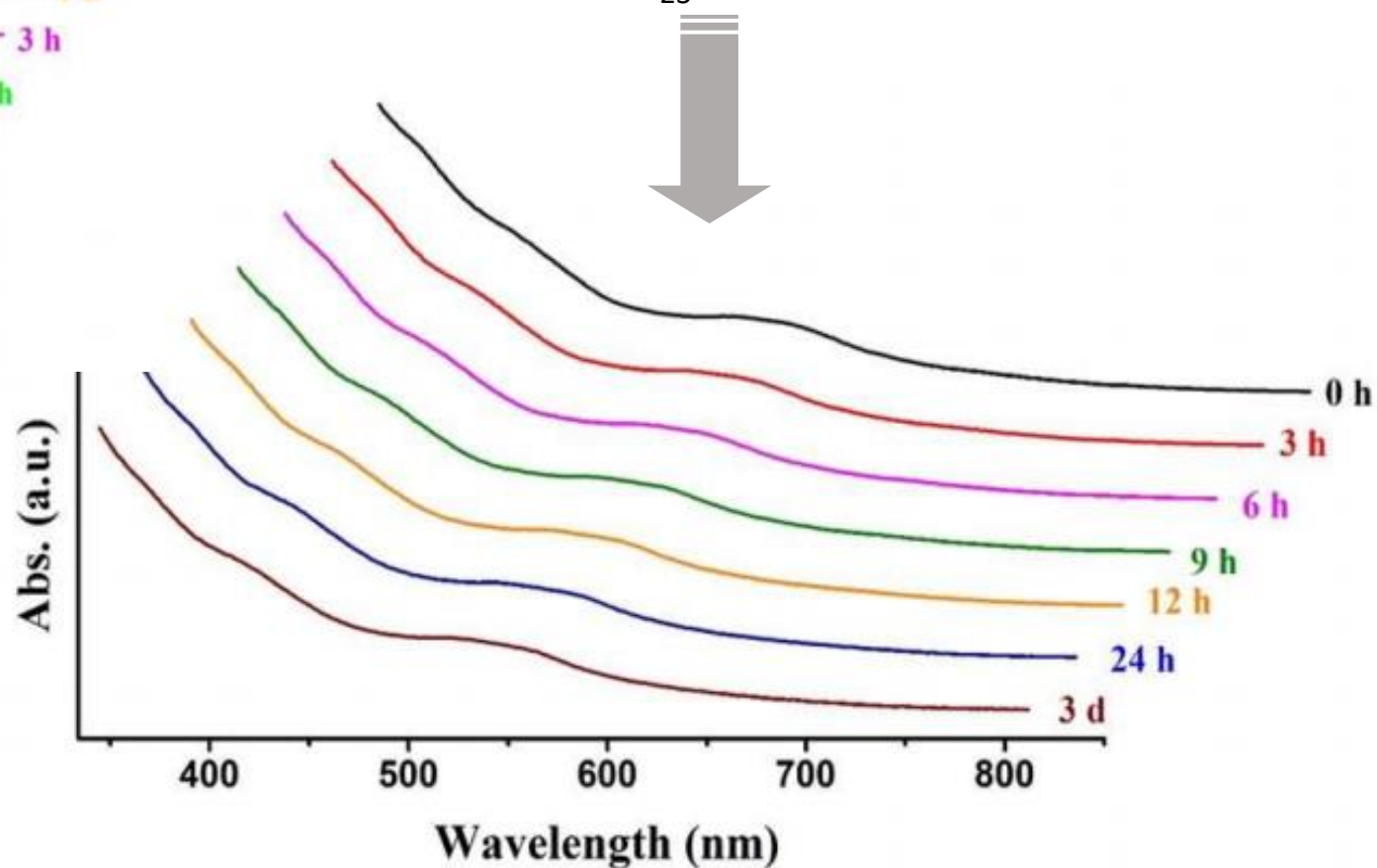




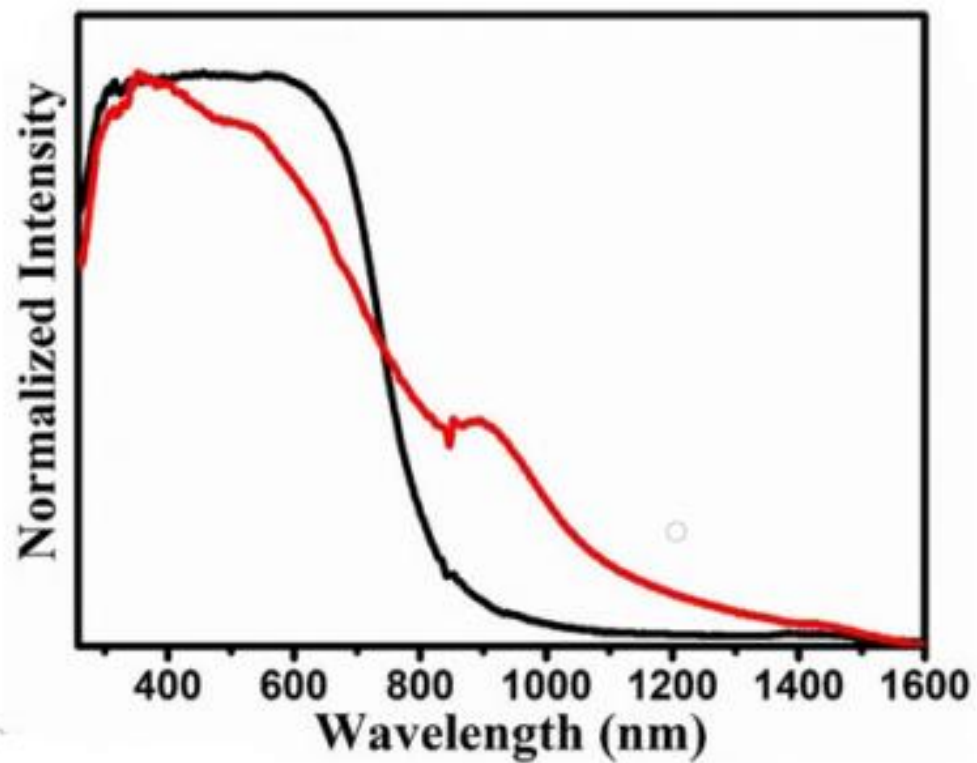
# Results and Discussion



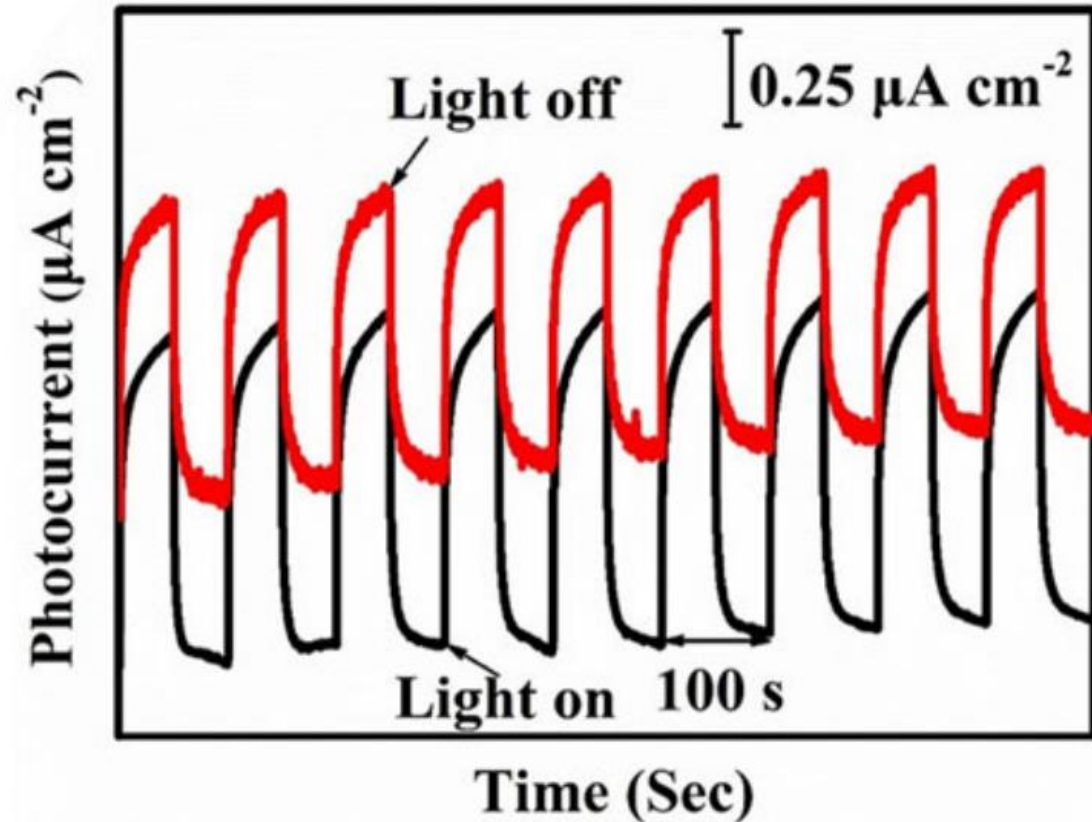
UV/Vis spectrum of  $\text{Au}_{23}$  in Acetone



# Results and Discussion



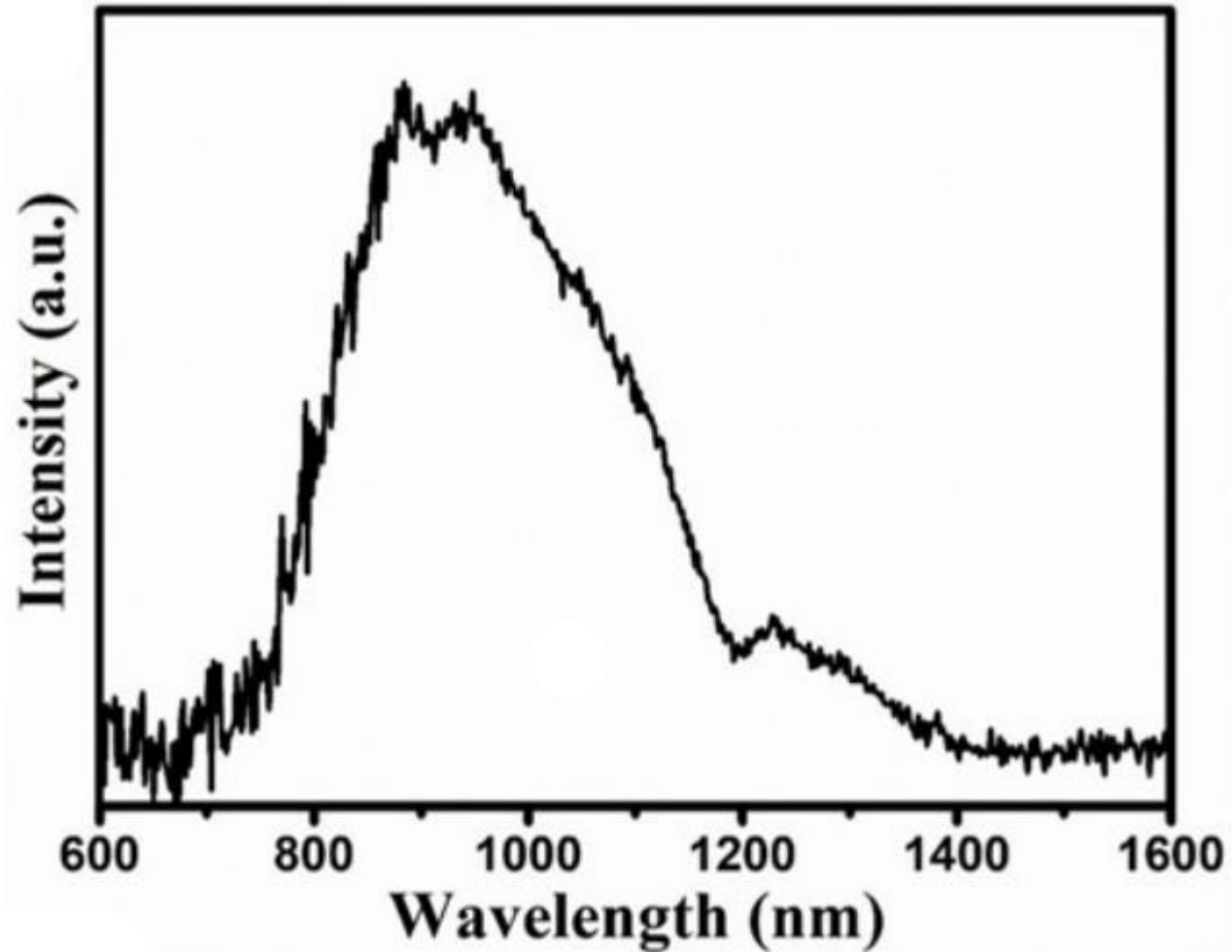
Normalized UV-visible diffuse reflectance spectra of Au<sub>28</sub> (black) and Au<sub>23</sub> (red) in the solid state at room temperature



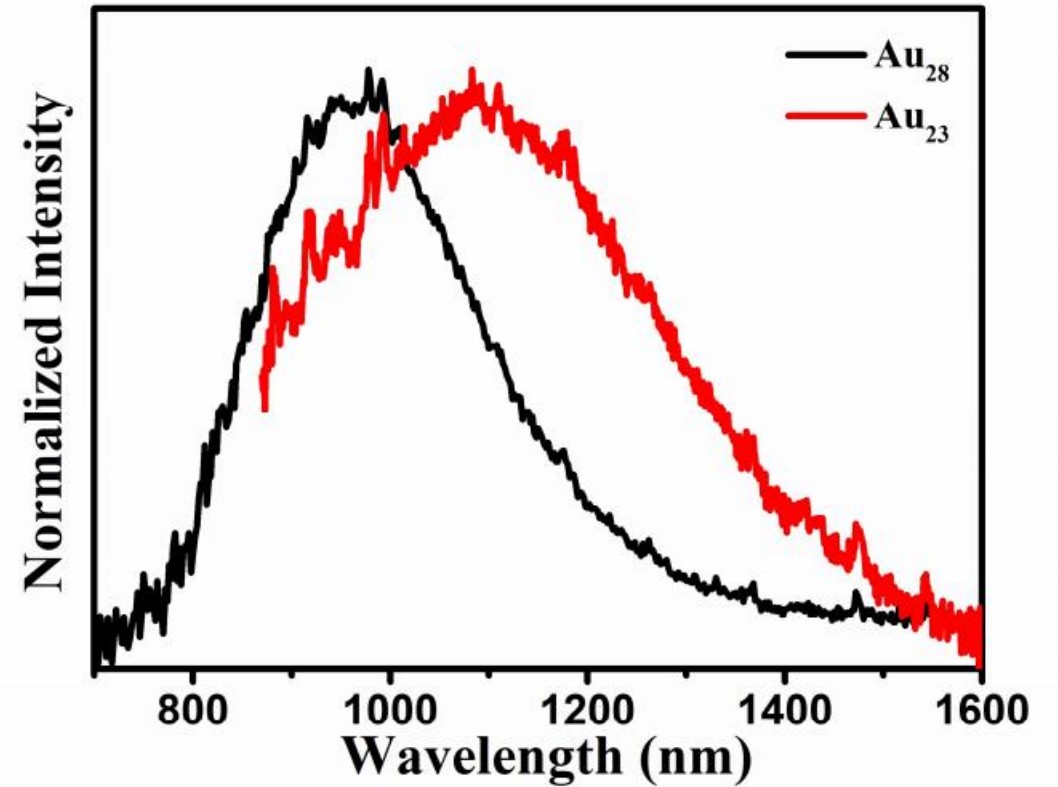
Visible light driven (420 nm) photocurrent responses of Au<sub>23</sub> (red) and Au<sub>28</sub> (black) derived electrodes with 0.6 V bias potentials under repetitive irradiation.



# Results and Discussion

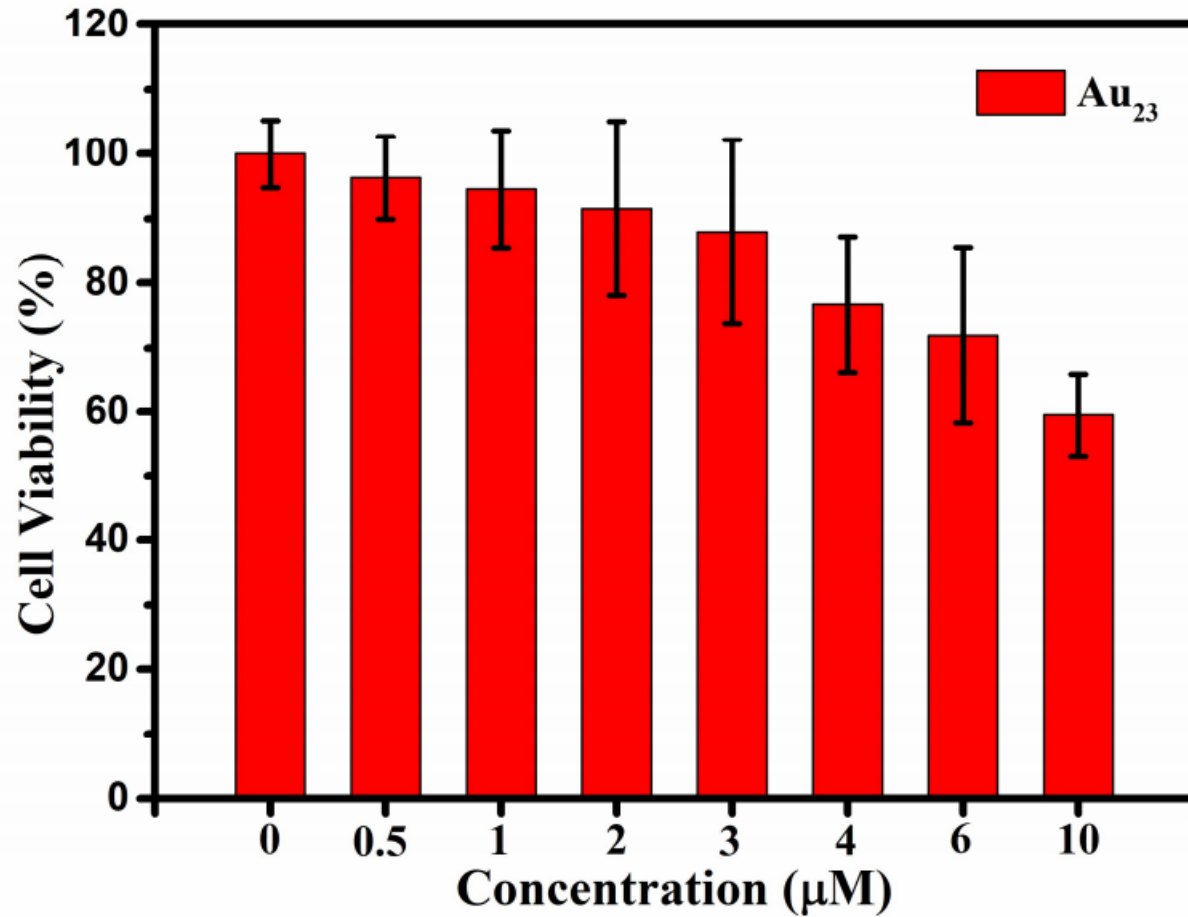


NIR emission spectrum of  $\text{Au}_{23}$  in methanol

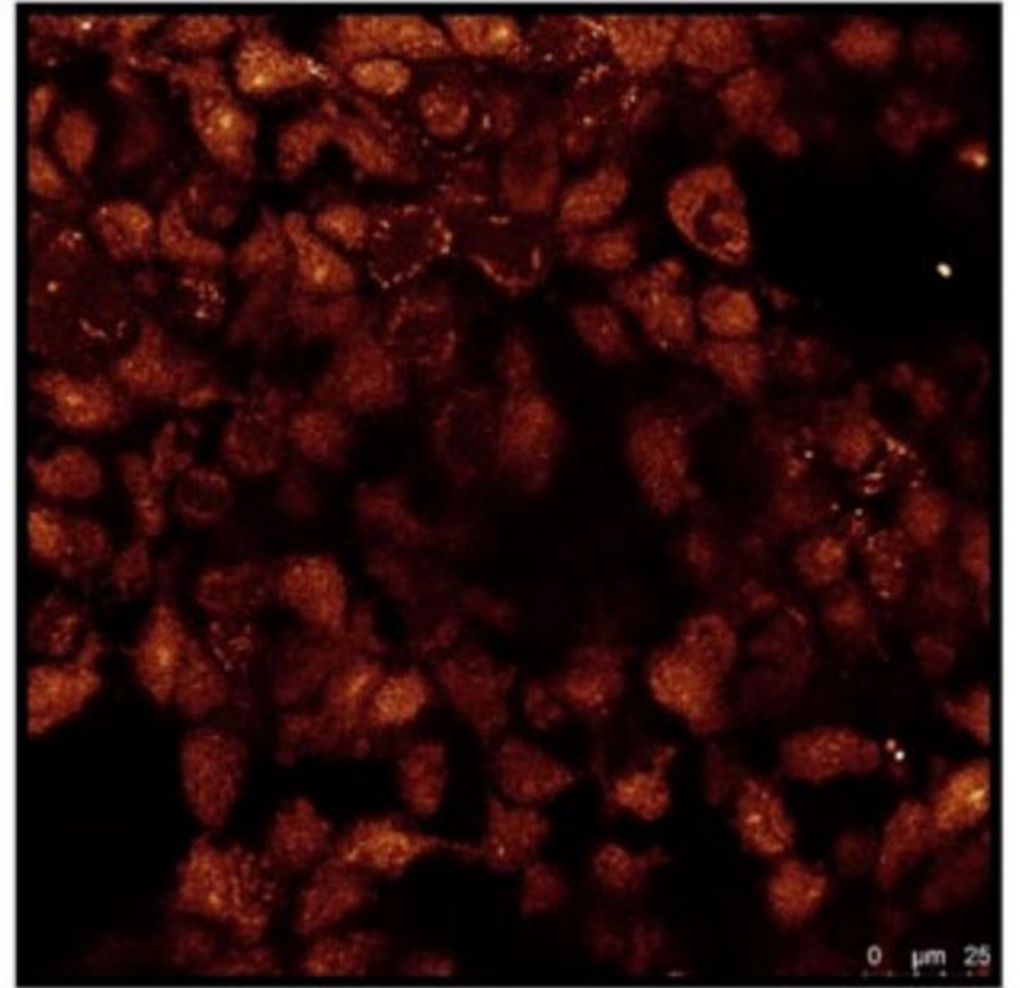


NIR emission spectra of the solid-state  $\text{Au}_{28}$  and  $\text{Au}_{23}$

# Results and Discussion



The cytotoxicities of  $\text{Au}_{23}$  to HeLa cells. The  $\text{IC}_{10}$  of  $\text{Au}_{23}$  was found to be 2  $\mu\text{M}$ .



Confocal fluorescence image of HeLa cells incubated with 2  $\mu\text{M}$  of  $\text{Au}_{23}$  for 6 h at 37 °C.

# Conclusion

- They have reported a facile self-reducing synthesis of  $\text{Au}_{28}$  nanoclusters using a carboranealkynyl ligand which serves as a two-in-one reducing and protecting agent.
- $\text{Au}_{28}$  nanocluster transforms into a smaller  $\text{Au}_{23}$  nanocluster when dissolved in methanol.
- These clusters exhibit absorption in the entire UV/Vis/NIR range and show NIR luminescence, which finds application in photocatalytic and biomedical fields.

## Relevance to the group

- Our group is working on Carboranethiol ligand protected nanoclusters. We can explore Carboranealkynyl ligand as well.
- Using this facile synthetic procedure we can aim at synthesizing alloy nanoclusters with these ligands.
- In this paper it was evident by EPR study that the  $\text{Au}_{28}$  cluster had an unpaired electron in it. This observation can be used to further study the magnetic property of these clusters or similar ones which we synthesize.

*Thank  
you!*