

Luminescence

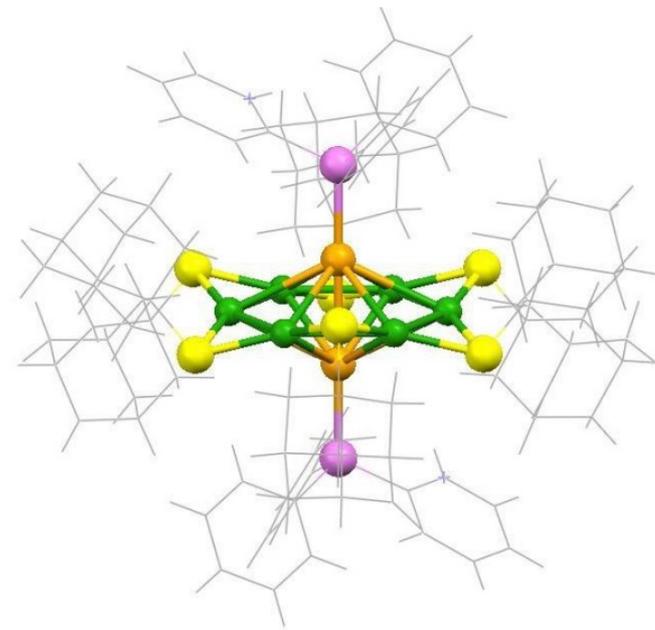
International Edition: DOI: 10.1002/anie.201600241

German Edition: DOI: 10.1002/ange.201600241

**Bimetallic Au₂Cu₆ Nanoclusters: Strong Luminescence Induced by the Aggregation of Copper(I) Complexes with Gold(0) Species***Xi Kang, Shuxin Wang, Yongbo Song, Shan Jin, Guodong Sun, Haizhu Yu,* and Manzhou Zhu**

Department of Chemistry and Center for Atomic
Engineering of
Advanced Materials, Anhui University
230601 (China)
E-mail : yuhaizhu@ahu.edu.cn
zmz@ahu.edu.cn

**Angew. Chem. Int. Ed. 2016, 55,
3611 -3614**



INTRODUCTION

- Atomically precise noble-metal nanoclusters have attracted extensive research interest. It is generally accepted that the structure of these NCs determines their physical and chemical properties (eg. electrochemical, catalytic and optical properties). Among these physical/chemical properties, **luminescence** represents one of the most fascinating features of these materials.
- To date, several fluorescent noble-metal NCs have been reported. Nonetheless, the **quantum yield of these NCs remained relatively low** compared to those of other fluorescent nanomaterials, such as quantum dots, carbon nanodots, and lanthanide nanoparticles.
- Various strategies have been developed to enhance the quantum yield of these NCs. In addition to the contribution from the M(0) core, the role of M(I)-SR shell

AGGREGATION INDUCED EMISSION (AIE)

Aggregation Induced Emission is a photoluminescence enhancement strategy for some of the organic molecules by aggregation.

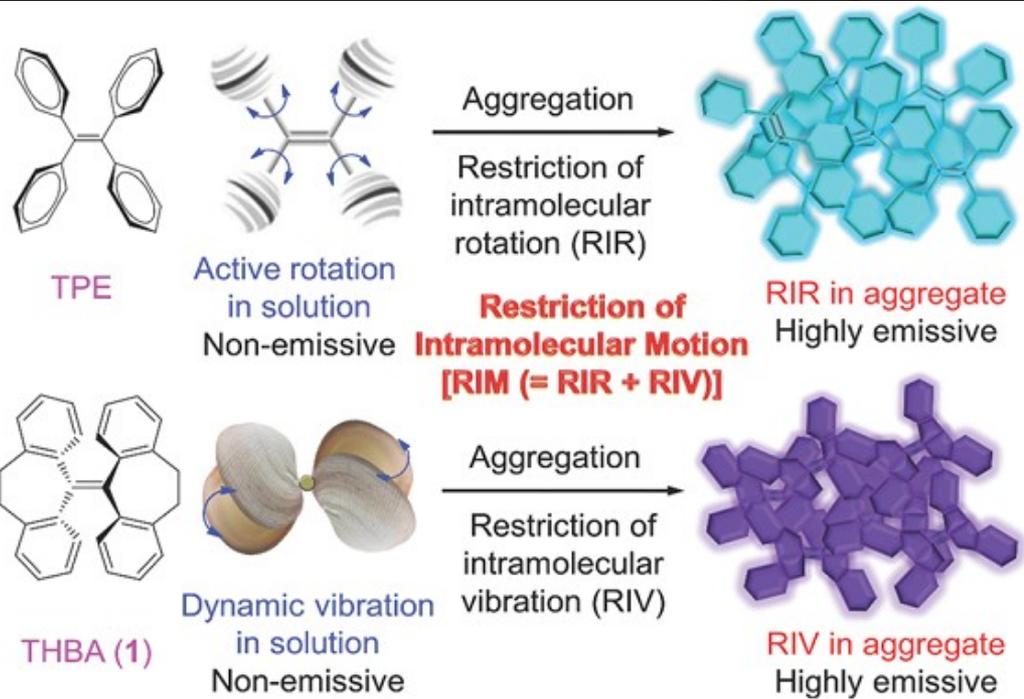
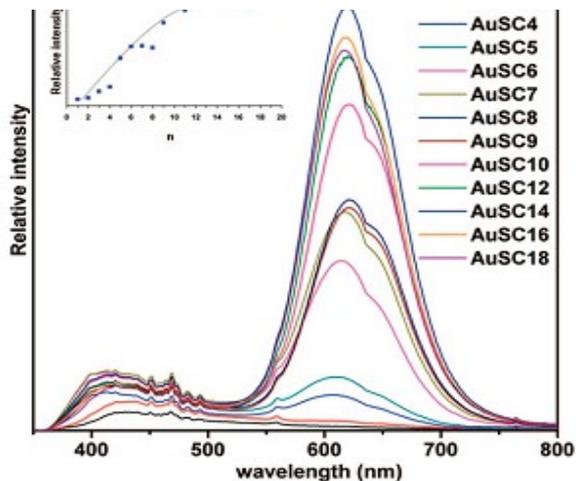


Figure . Schematic illustration of the AIE phenomenon of a propeller-shaped luminogen of tetraphenylethene (TPE) through RIR and a shell-like luminogen of 10,10',11,11'-tetrahydro-5,5'-bibiphenyl-2,2'-diylidene [a,d][7]annulenyliene (THBA) through RIV.

Recent studies suggest that the restriction of intramolecular motion (RIM) is responsible for the AIE phenomenon of these molecular rotor systems. In general, the AIE active molecules consist of a number of rotors, which can rotate or vibrate freely in dilute solution. However, rotations and vibrations of these rotors in the aggregated state are largely restricted, leading to the strong AIE effect.

AIE EFFECTS IN METAL THIOLATE COMPLEXES

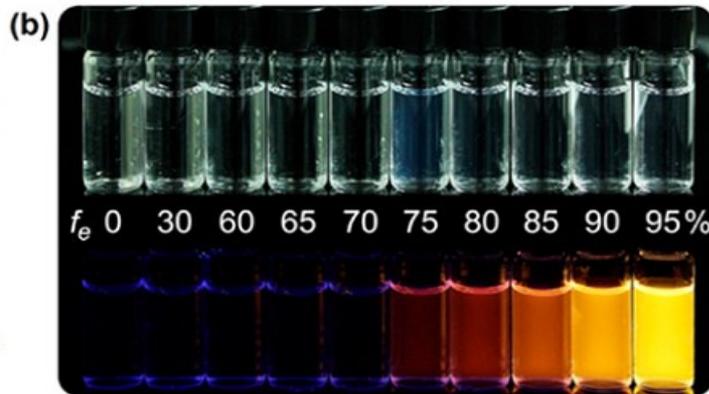
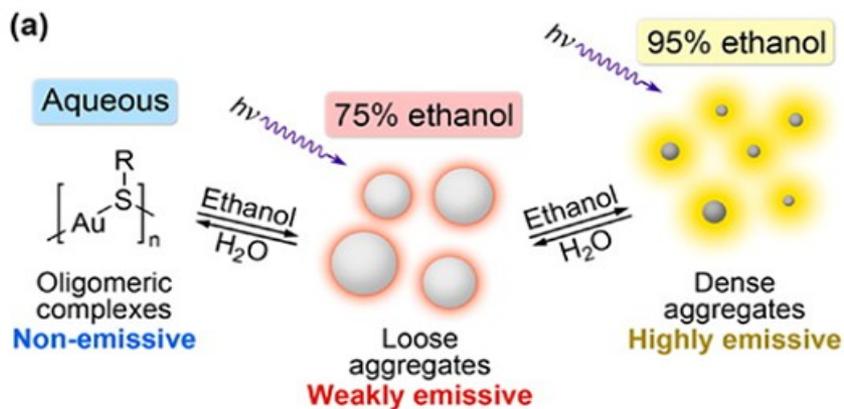
Gold(I)-Alkanethiolate Complexes Having Highly Ordered Supramolecular Structures



Chem. Mater. 2007, 19, 6297
–6303

Solvent-induced AIE properties of the oligomeric Au(I)

– (a)



J. Am. Chem. Soc. 2012, 134,

16662 – 16670

occured by certain divalent cation like Ca^{2+} which could electrostatically bind negatively charged Au (I) - SG complexes.

IN THIS PAPER

- The concept of aggregation-induced emission (AIE) has been exploited to render non-luminescent Cu^ISR complexes strongly luminescent. The Cu^ISR complex undergoes controlled aggregation with Au⁰.
- Six thiolated Cu atoms are aggregated by two Au atoms (**Au₂Cu₆ nanocluster**). X-ray crystallography has validated the structure of this highly fluorescent nanocluster. The quantum yield of this nanocluster is **11.7%**.
- The aggregation is affected by the **restriction of intramolecular rotation**. The high rigidity of the outer ligands enhances the fluorescence of the Au₂Cu₆ nanocluster.

Unlike previous AIE methods, this strategy does not require insoluble

The active metal complexes (e.g., Ag or Cu, which are frequently used as fluorescent complexes) could act as the surface ligand, and are controllably aggregated by an inert metal core (such as Au⁰). This core-shell structure might hopefully activate the RIR process and boost the AIE of the active metal complexes.

Au⁰ INDUCED AGGREGATION OF Cu^ISR

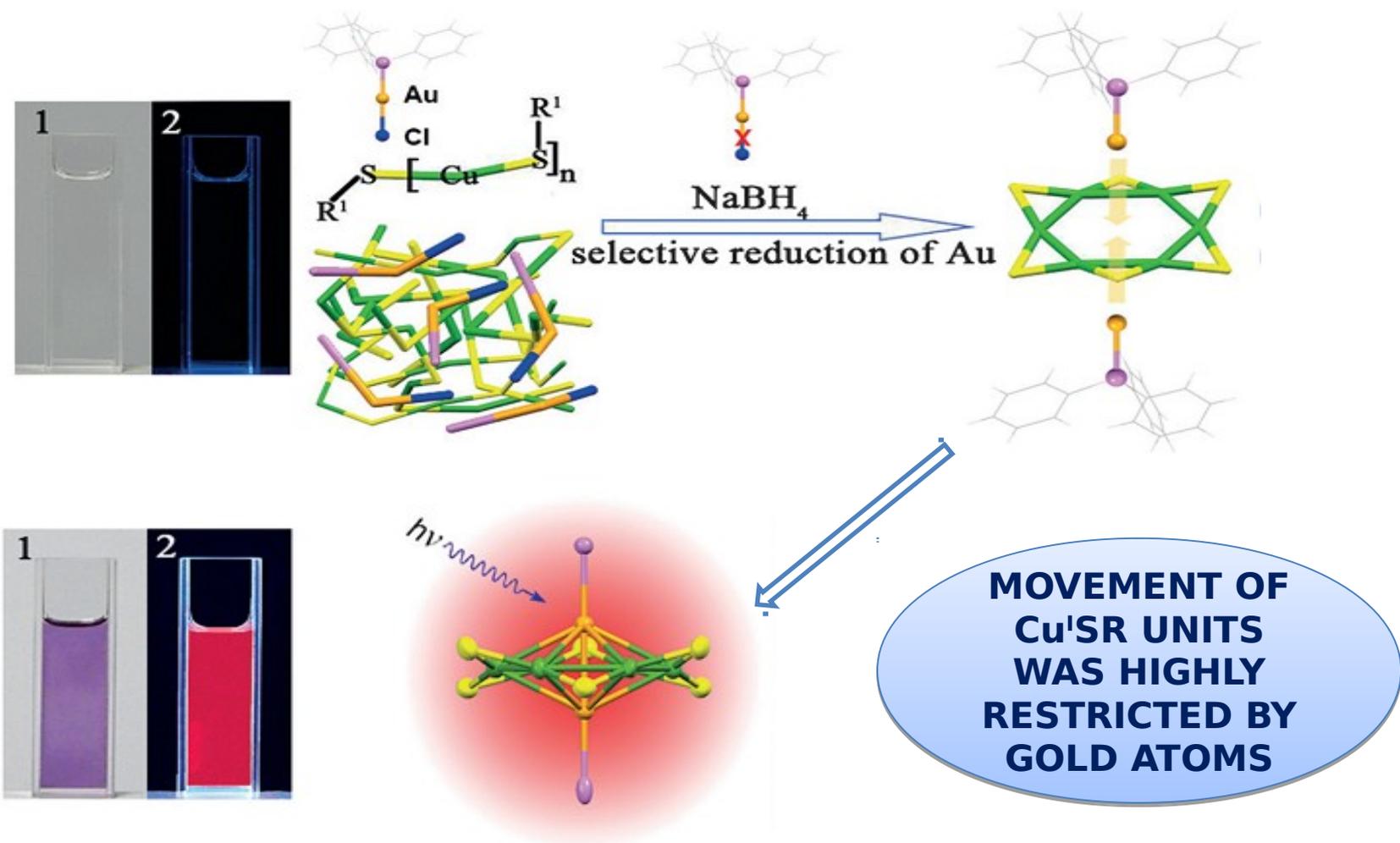


Figure. Illustration of the Au⁰-induced aggregation of Cu^ISR¹. Au⁰ was generated by the selective reduction of AuPR₂Cl with NaBH₄. Digital photographs of the corresponding complexes or NCs under visible (1) and UV light (2). Au gold, Cl blue, Cu green, P violet, S yellow.

CRYSTAL STRUCTURE OF $\text{Au}_2\text{Cu}_6(\text{PPh}_2\text{Py})_2(\text{SC}_{10}\text{H}_{15})_6$

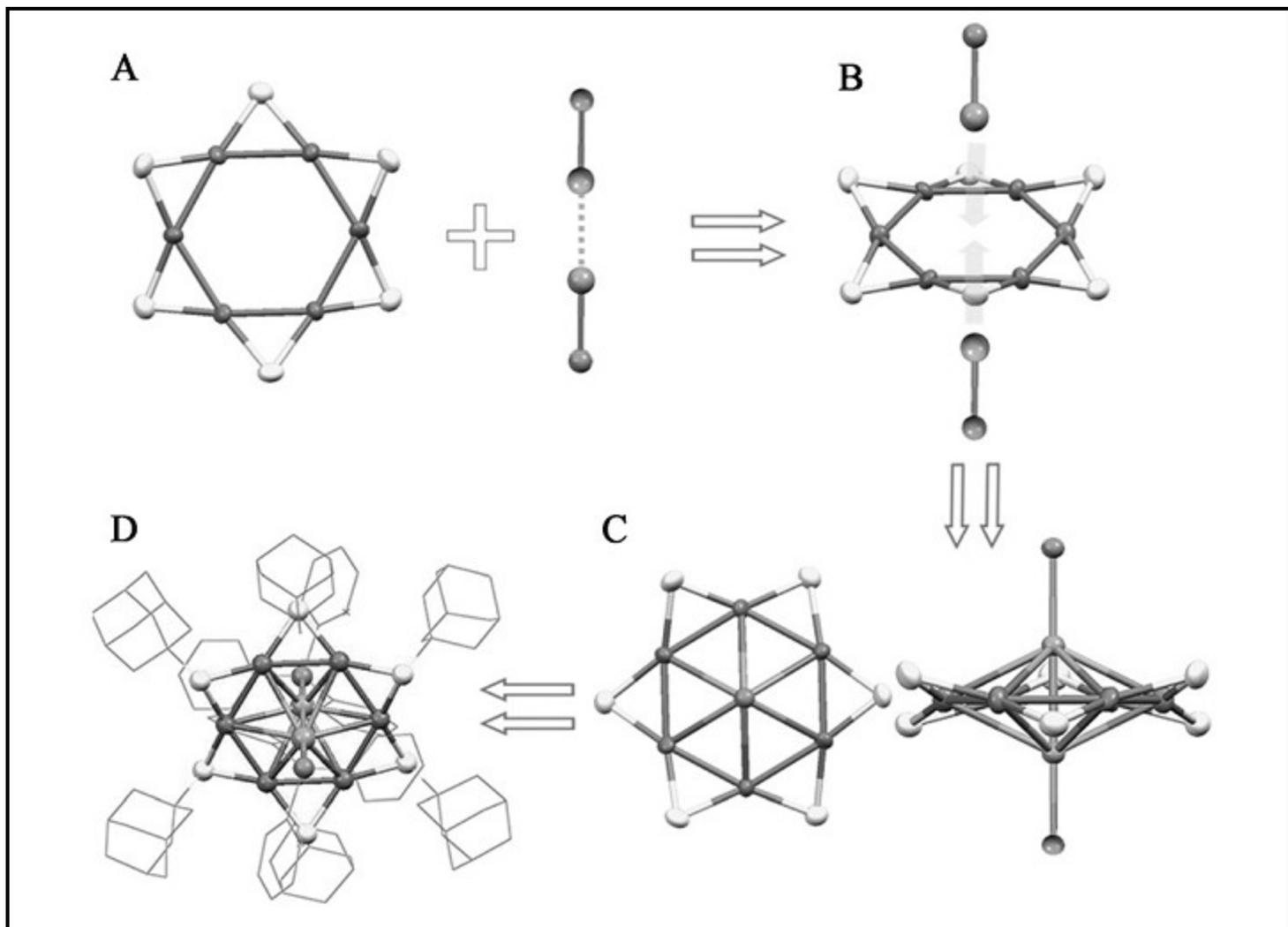


Figure . Crystal structure of Au_2Cu_6 nanocluster I. A) The outer-loop hexagonal Cu_6S_6 moiety as the benzenoid-like framework of I. B) The central Au_2P_2 line across Cu_6S_6 . C) Side view and top view of I. D) Overall structure of I. For clarity, the benzene and pyridine groups on the phosphine ligands and all H atoms are not shown, and the

RESULTS AND DISCUSSIONS

Absorption features of Au_2Cu_6 nanocluster are at **325, 420, 515 and 595 nm**.

Au_2Cu_6 nanocluster exhibits a strong emission centred at **665 nm** with a quantum yield of **11.7 %**.

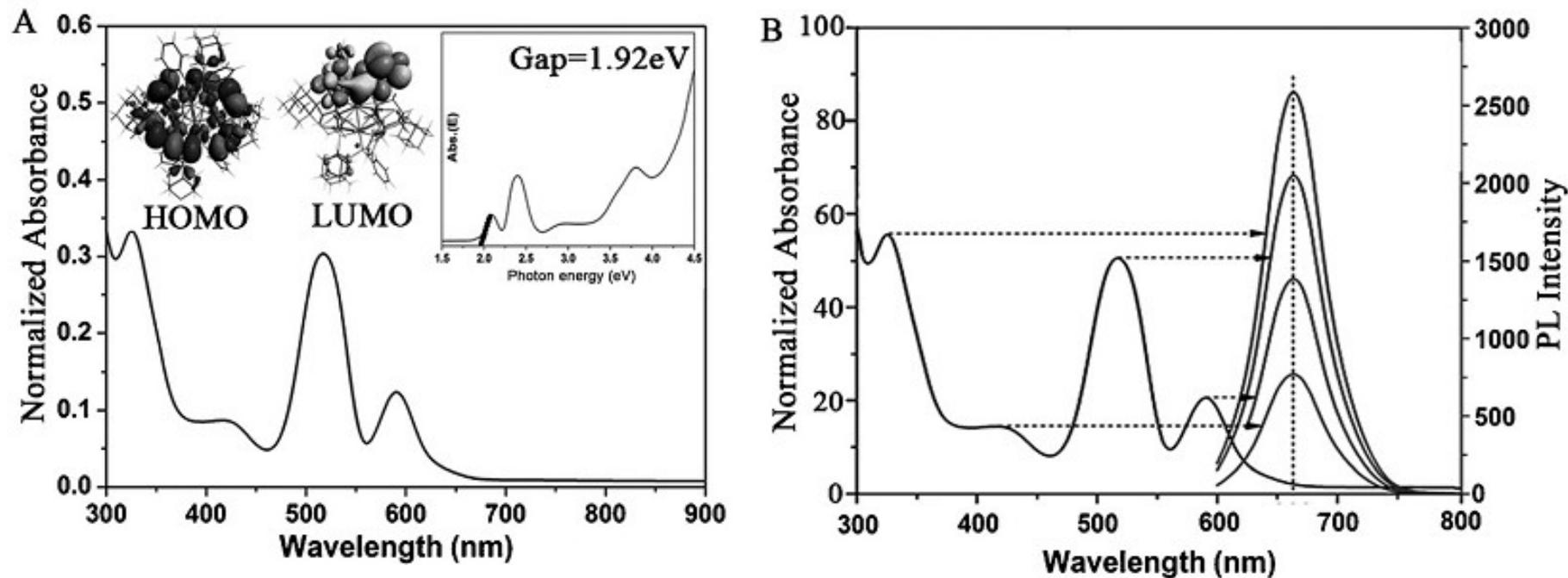
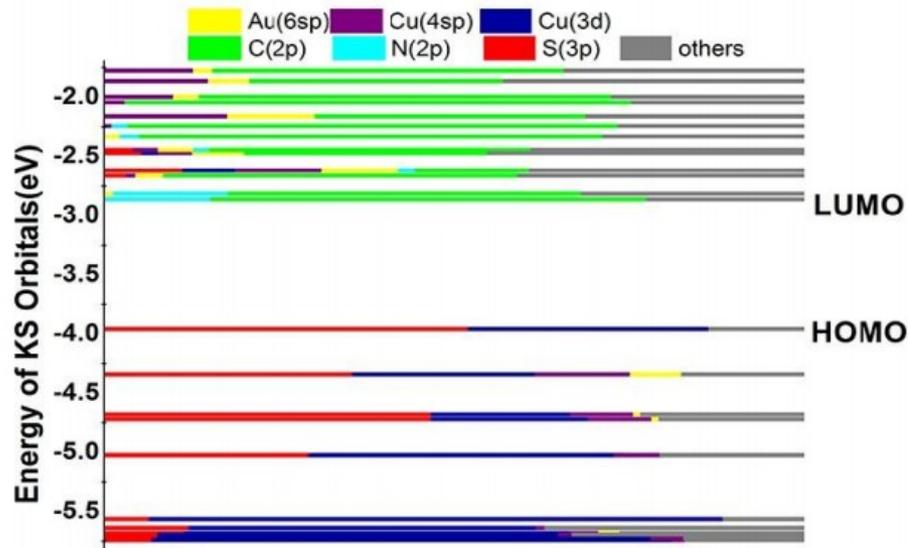


Figure . A) Experimental absorption spectrum of nanocluster I. Inset: HOMO and LUMO of I. B) Photoluminescence properties of I. Excitation spectrum (left) and emission spectra (right) at different excitation wavelengths, as indicated by the arrows.

RESULTS AND DISCUSSIONS



According to the **Kohn-Sham (KS) molecular orbital (MO) energy levels**, \longrightarrow

HOMOs \longleftarrow S 3p and Cu 3d atomic orbitals. HOMOs extend to the hexagonal $(\text{CuSR}^1)_6$ unit of the overall structure \downarrow
 LUMOs \longleftarrow N 2p and C 2p orbitals.

Figure : The Kohn-Sham orbital energy level

diagram for the **Au₂Cu₆-I** nanocluster and the **Au atoms hardly contribute to the frontier orbitals of Au₂Cu₆**

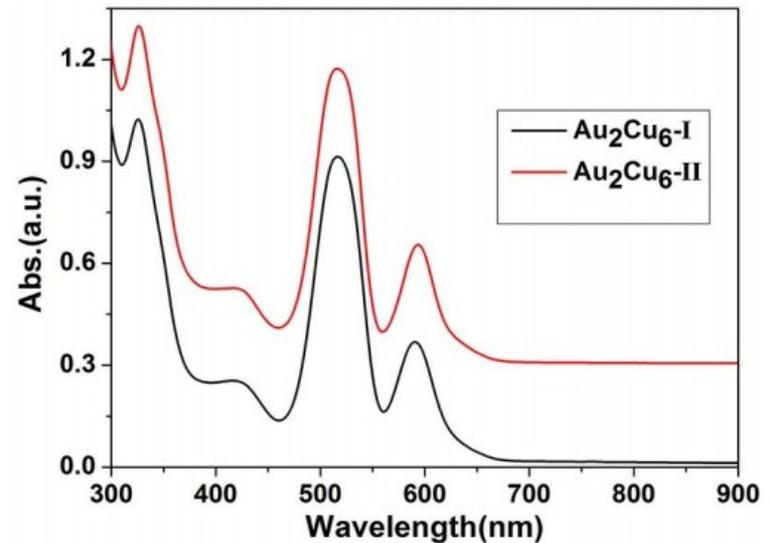
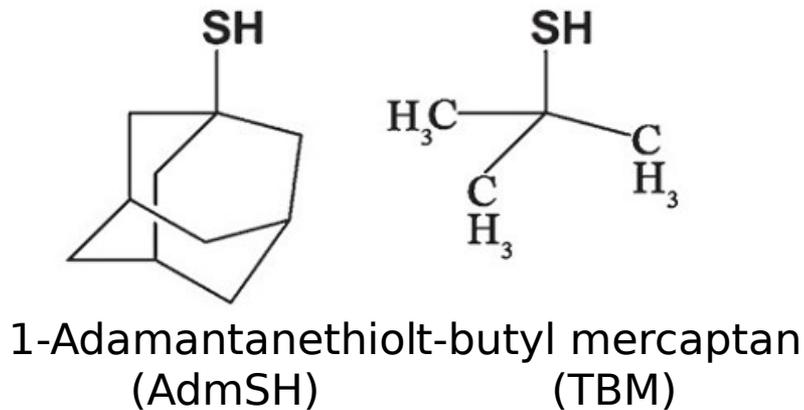
The HOMO-LUMO gap \sim **1.92 eV** , Emission peak \sim **1.87 eV**.

The extremely low difference in energy (0.05 eV) implies that the fluorescence possibly corresponds to the LUMO-HOMO transition.

DFT calculations indicate that the LUMO-HOMO transition predominantly occurs between the ligands (aromatic) and the copper centers through weak conjugation of the π -orbitals of the aromatic groups and the Cu (d) orbitals. The emission is due to LMCT.

RESULTS AND DISCUSSIONS

AIE is mostly caused by the RIR. Therefore, we expected the fluorescence of the NCs to benefit from the increased rigidity of the capping ligands and the resulting activation of the RIR.



I → **Au₂(PPh₂Py)₂Cu₆(Adm)₆**

II → **Au₂(PPh₂Py)₂Cu₆(TBM)₆**

Figure. The UV/Vis absorption spectra of Au₂Cu₆ NCs protected by different ligands.

RESULTS AND DISCUSSIONS

STUDY OF THE THERMODYNAMIC STABILITY OF ANALOGOUS NANOC

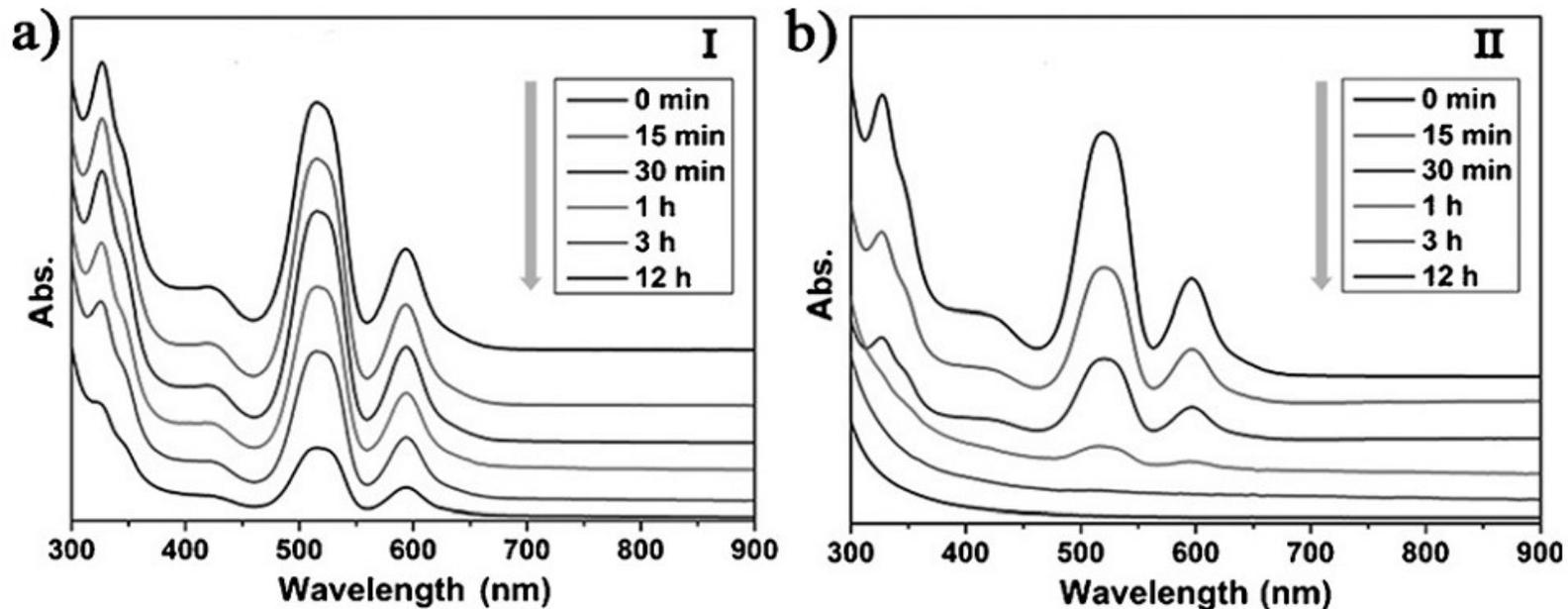


Figure. UV/Vis spectra confirming the thermal stability of a) I and b) II over time.

DFT CALCULATIONS TO EVALUATE RELATIVE STABILITY OF I

DFT calculations were performed to evaluate the relative stabilities of I and II by calculating the reaction enthalpy of the ligand-exchange reaction:



This reaction was found to be endothermic by $16.10 \text{ kcal mol}^{-1}$, indicating that Au_2Cu_6

RESULTS AND DISCUSSIONS

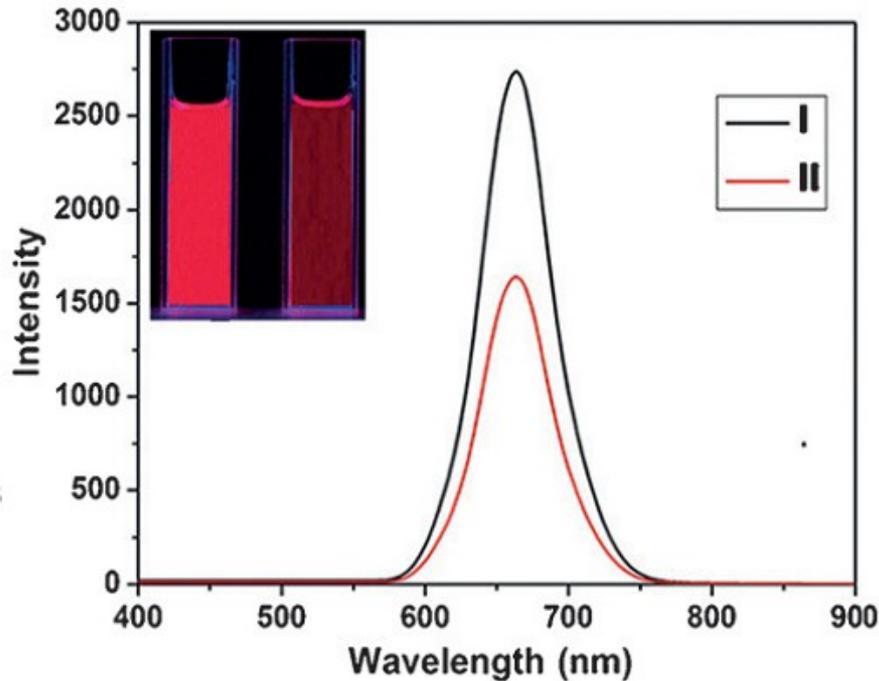


Figure : Emission spectra of solutions of nanoclusters I (left) and II (right) under UV light

The luminescence spectra of these two NCs had the same optical density (OD max: 0.05). The maxima in both emission spectra were located at about 665 nm.

The fluorescence of the more rigid Au_2Cu_6 nanocluster I is significantly stronger than that of II (with less rigidity).

QY of nanocluster I is 1
QY of nanocluster II is 8

It is thus concluded that the enhanced fluorescence of Au_2Cu_6 nanocluster I had indeed been achieved by activating the RIR of the outer ligands.

SUMMARY AND CONCLUSIONS

- ✓ A novel strategy to activate aggregation-induced emission, which is based on the aggregation of active metal complexes ($\text{Cu}^{\text{I}}\text{SR}$) with neutral gold atoms has been developed.
- ✓ The structures of the resulting products (Au_2Cu_6 NCs) were successfully determined by X-ray crystallography, which revealed that six CuSR^{I} complexes were aggregated by Au^0 atoms.
- ✓ This compound showed strong emission centered at 665 nm with a quantum yield of 11.7 %.
- ✓ It was found that the fluorescence is due to ligand-to-metal charge-transfer process.
- ✓ The rigidity of the ligands positively correlates with the quantum yield,

FUTURE DIRECTION

- ❖ This paper gives direction for synthesis of luminescent nanoclusters and the origin of luminescence in noble metal clusters.
- ❖ It might be possible to synthesize highly luminescent clusters that could function as quantum dots and organic dyes.
- ❖ Luminescent nanoclusters may find good applications in sensing and imaging.



Thank You