

Optical Properties of Bi-Icosahedral Au₂₅ and Au₂₄ Clusters: Influence of Central Gold Atom

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Abstract

Temperature-dependent absorption and ultrafast luminescence measurements of [Au₂₄(PPh₃)₁₀(SC₂H₄Ph)₅Cl₂]²⁺ (bi-Au₂₄) were studied and compared with [Au₂₅(PPh₃)₁₀(C₆S)₅Cl₂]²⁺ (bi-Au₂₅). The investigations are carried out on these two clusters as they are structurally similar except for the absence of central Au atom for bi-Au₂₄. The objective of the work is to probe the influence of the central gold atom on the optical transitions and electron-phonon interactions in bi-icosahedral nanoclusters. The investigations are focused both on the electron-phonon as well as hydrogen bonding interactions of axial Cl atoms with hydrogen bonding solvents and their influence on the vibronic transitions. It was theoretically shown that the absorption at 670 nm arises due to coupling of two icosahedrons which Au₂₅ does have and Au₂₄ does not. While for Au₂₄, broad band at ~560 nm was observed which was due to the interactions of the two units (two Au₁₂ units), 415 nm shoulder and 383 nm band that is due to the electronic transitions related to the localized electronic structures of the individual 12 Au atoms in the icosahedron. All these peaks becoming sharper and blue shifted when it goes to lower temperatures and it increases the oscillator strength and also it showed a new peak around 480 nm in lower temperatures. The electron-phonon interactions were obtained from fitting the band gap data as a function of temperature. Solvent dependent absorption measurements and ultrafast luminescence measurements show the hydrogen bonding formation of clusters with alcoholic solvents.

Objectives

- To understand the influence of central gold atom on the optical properties of phosphine protected gold clusters
- To probe the influence of solvent H bonding on the temperature dependent optical properties of Au₂₅ rod
- To understand the core-shell electron-phonon interactions in bi-icosahedral Au₂₅ and Au₂₄ clusters

Introduction

Over last few years, atomically precise thiolate protected quantum sized gold clusters of different sizes and shapes were synthesized and reported. These clusters have received vast research attention because of their exciting linear and non-linear optical, electrochemical, magnetic and catalytic properties due to quantized states of the confined electrons [1-4]. This quantum confinement leads metallic behavior of gold to nonmetallic molecular behavior. Experimental and molecular simulation studies have been carried out to understand the fundamental theory behind the unique properties of the clusters and the cluster to nanoparticle transitions.

Starting from **Brust-Schiffrin** synthesis⁵, proper control of size and composition of thiol gold ratio yielded precise and stabilized gold clusters. However, with respect to other nanoclusters only few phosphine-protected gold nanoclusters were studied during past decade. **Tsukuda and co-workers**⁶ synthesized the first [Au₂₅(PPh₃)₁₀(SC₂H₅)₅Cl₂]²⁺ (bi-Au₂₅) and **Jin and co-workers**⁷ synthesize the same cluster with different thiol ligand and later they synthesize bi-Au₂₄⁸ [Au₂₄(PPh₃)₁₀(SC₂H₄Ph)₅Cl₂]²⁺ cluster. Bi-icosahedral clusters are exciting because the majority of gold atoms are from the core while shell-gold is minimum. Both bi-Au₂₄ and bi-Au₂₅ clusters are structurally similar except for the central gold atom in bi-Au₂₅ which is absent in bi-Au₂₄ cluster. (figure 1)

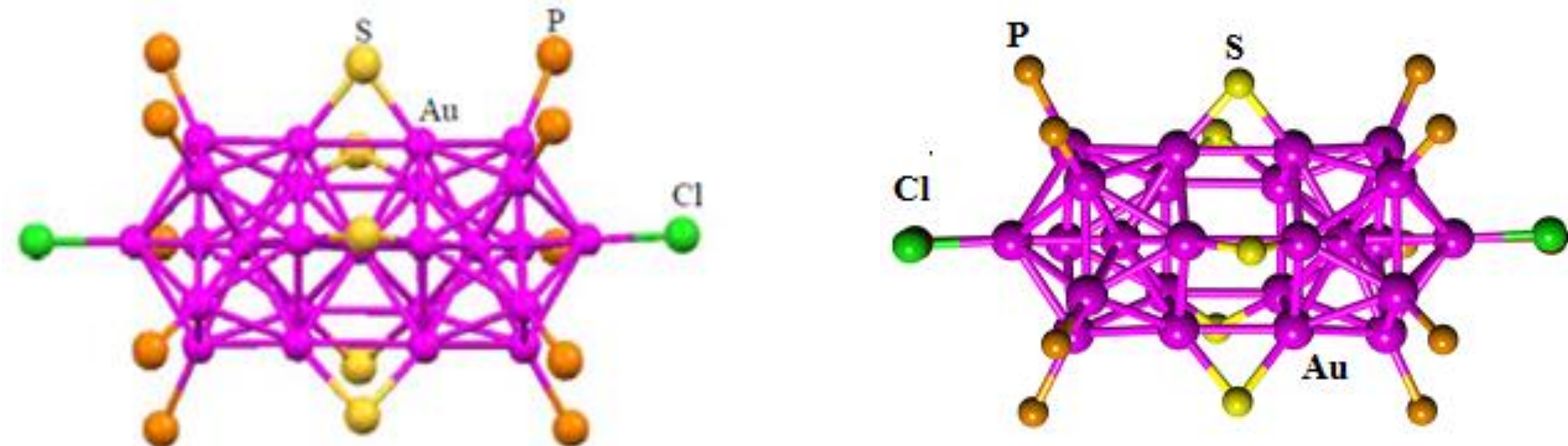
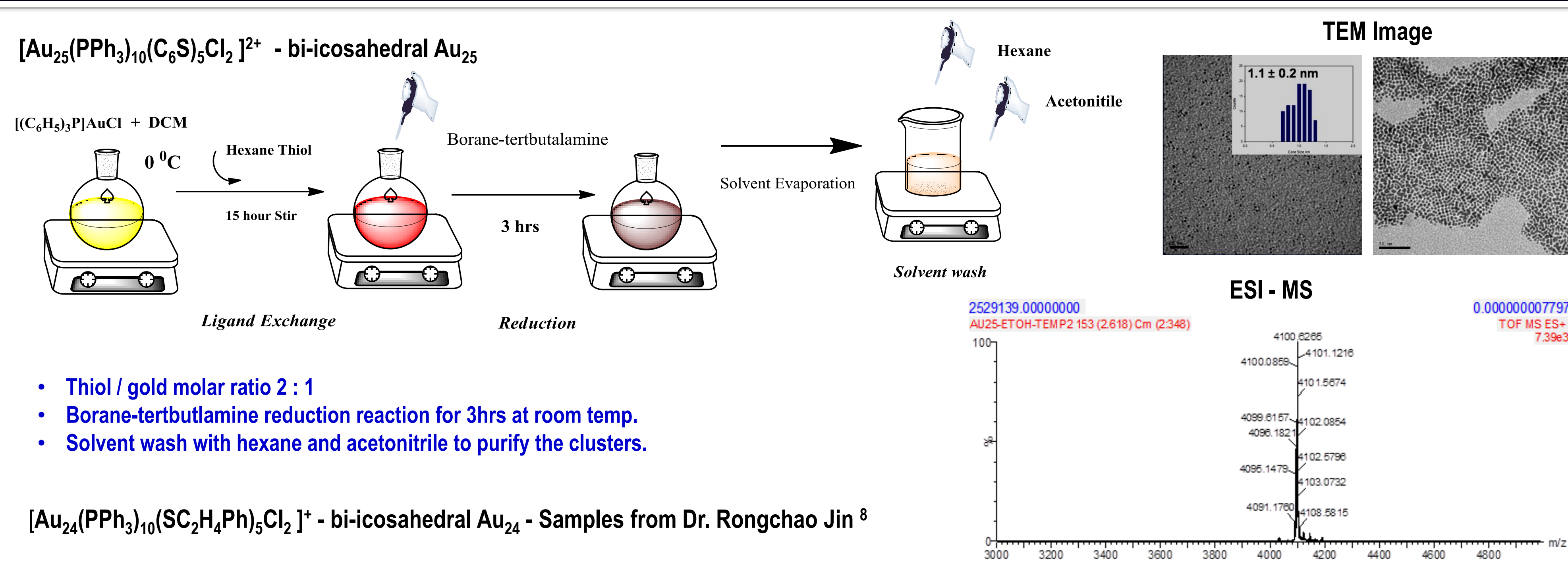


Figure 1 - Crystal structures of bi-icosahedral Au₂₅ and Au₂₄ respectively

Our group studied the fundamental optical and electronic behavior of the quantum sized gold clusters to support the theoretical calculations. Earlier we studied bi-Au₂₅ and spherical Au₂₅ clusters and found that the core-shell electron phonon and exciton phonon transitions are not as prominent as that of spherical Au₂₅ clusters. ⁹ **Akola and co-workers**¹⁰ performed molecular simulation for stability studies of these two clusters and found that there is an effect of central gold atom for the stability of the cluster. However, there is no systematic study delineating the differences in optical properties of bi-icosahedral Au₂₅ and Au₂₄ clusters and also will be interesting to probe if the clusters behave as molecules and show hydrogen bonding with solvents.

In this work, we carried out temperature dependent absorbance measurements and ultrafast luminescence measurements on these clusters in order to study structural, electronic, and optical properties. To understand the effect of hydrogen bonding, measurements were carried out in alcoholic solvents such as ethanol, 1-butanol and 2,2,2-trifluoroethanol and compared with toluene.

Synthesis and characterization of bi-icosahedral Au₂₅ and Au₂₄ clusters



Results and discussion – Temperature-dependent optical absorption properties

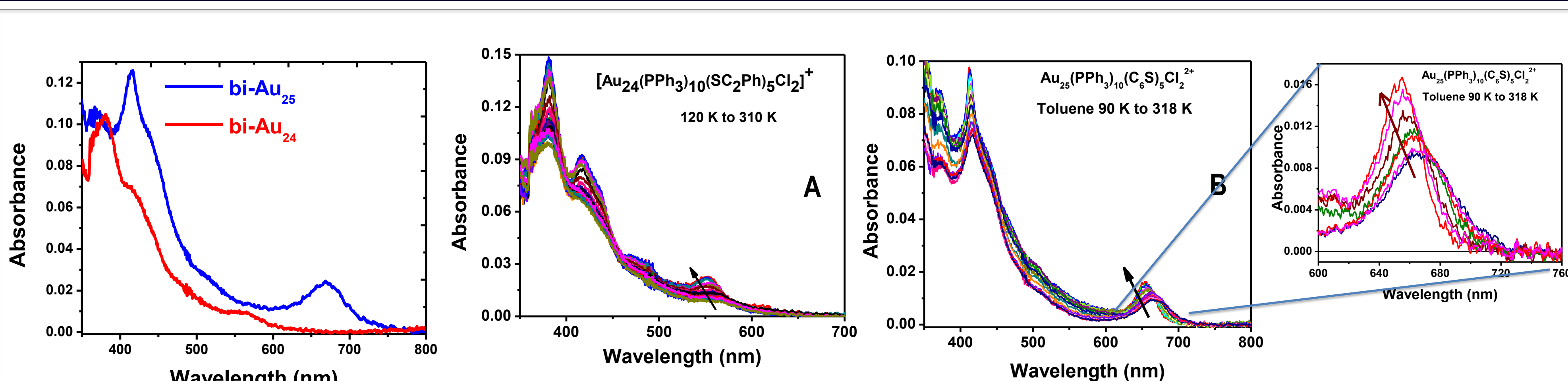


Figure 2: Optical absorption spectra of bi-Au₂₄ and bi-Au₂₅ clusters. Note the absence of 670 nm peak that arises out of coupling of two icosahedrons.

- Absorption peaks become sharper and more pronounced features are observed with a decrease in temperature
- The energy maximum is shifted to higher energies with decrease in temperature

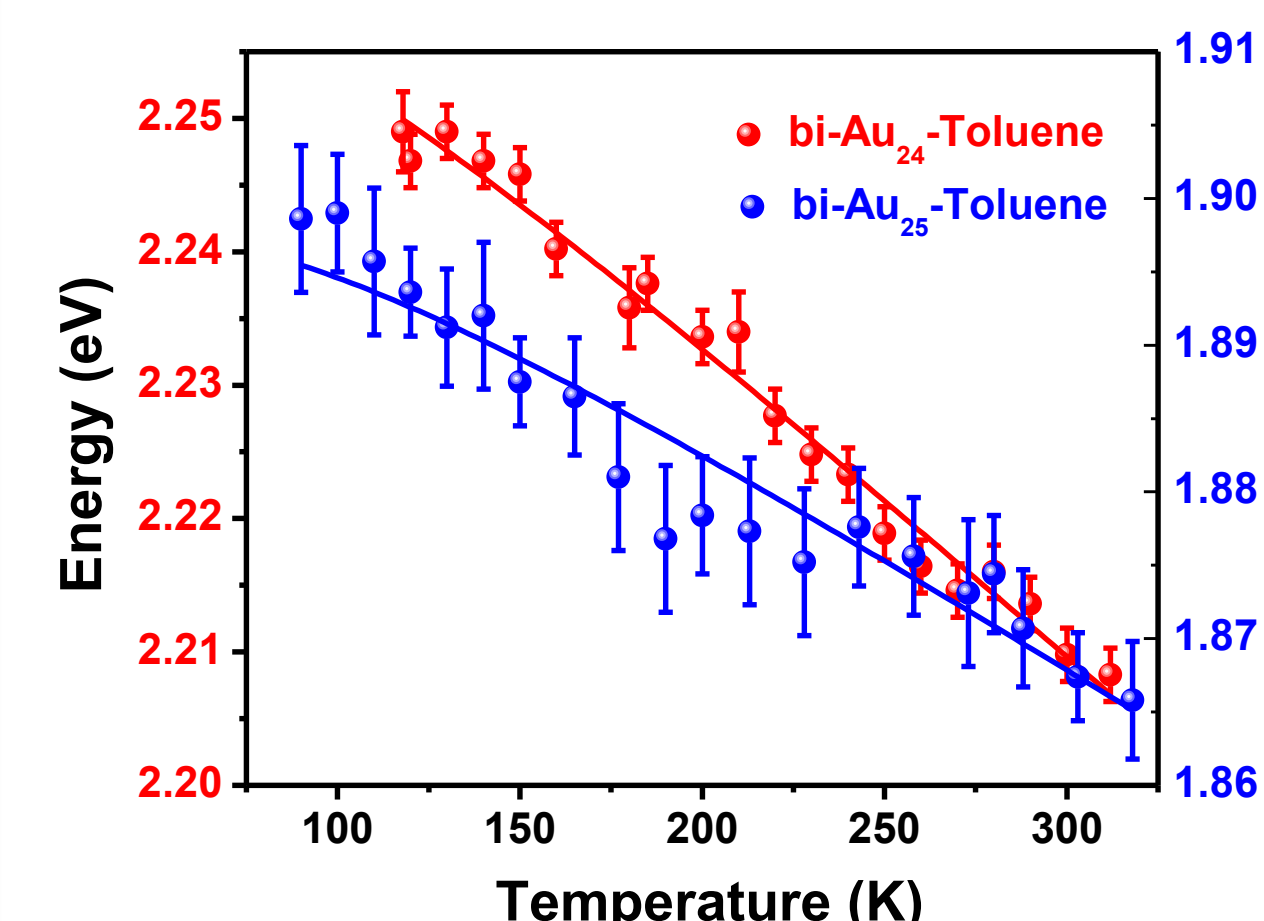


Figure 4: Temperature dependent absorption maximum vs. temperature for bi-Au₂₄ and bi-Au₂₅.

O'Donnell and Chen relationship¹¹ – Absorption maximum dependence

$$E(T) = E(0) - \langle C \rangle \langle \hbar \nu \rangle \left[\coth \left(\frac{\hbar \nu}{2kT} \right) - 1 \right]$$

Table 1. Energy gap vs temperature and the strength of electron-phonon interactions from the analysis for bi-Au₂₄ and bi-Au₂₅ clusters.

Sample	E _g (0) (eV)	<ħν> (meV)	<C>
bi-Au ₂₅ in toluene	2.24 ± 0.01	20 ± 10	0.9 ± 0.1
bi-Au ₂₄ in toluene	2.25 ± 0.01	20 ± 10	1.4 ± 0.2

Solvent dependence of temperature-dependent absorption

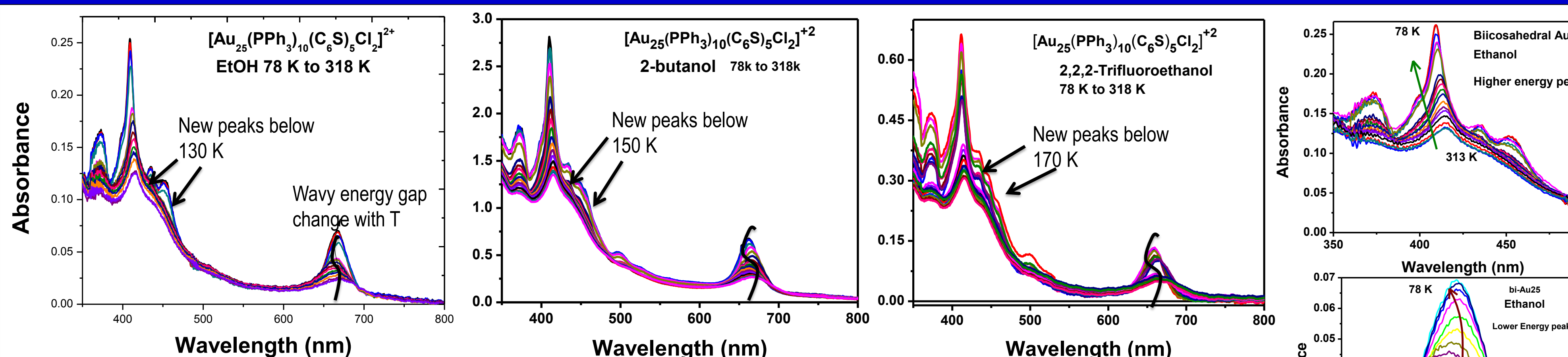


Figure 5: Temperature dependent absorption of bi-Au₂₅ in Ethanol, 2-butanol and 2,2,2-Trifluoroethanol.

- ❖ Bi-Au₂₄ rod breaks apart and form Au₂₅ in presence of above solvents
- ❖ Bi-Au₂₄ was not stable in any solvent other than toluene and hence no temperature-dependent absorption studies were possible

Solvent effect on optical properties

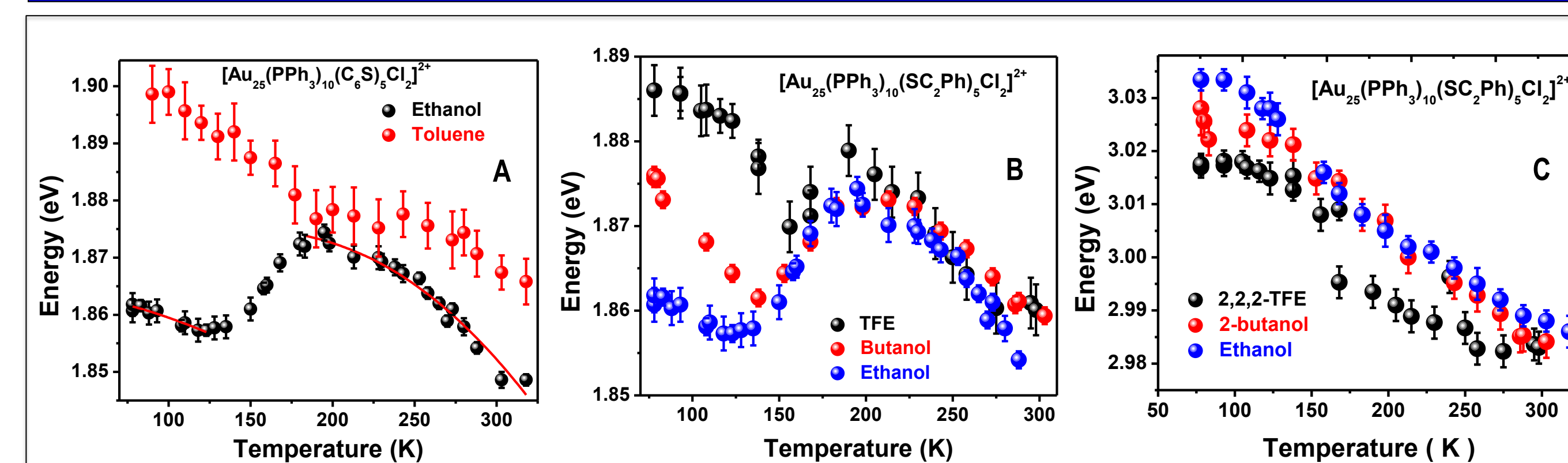


Figure 6 Absorption maximum as a function of temperature for bi-Au₂₅ of Ethanol, 2-butanol and 2,2,2-Trifluoroethanol. (A) comparison of low energy absorption in ethanol and toluene showing special influence of hydrogen bonding solvent, (B) low energy band as a function of temperature in hydrogen bonding solvents and (C) high energy absorption maximum as a function of temperature. Notice that the absence of wavy nature in high energy absorption maximum.

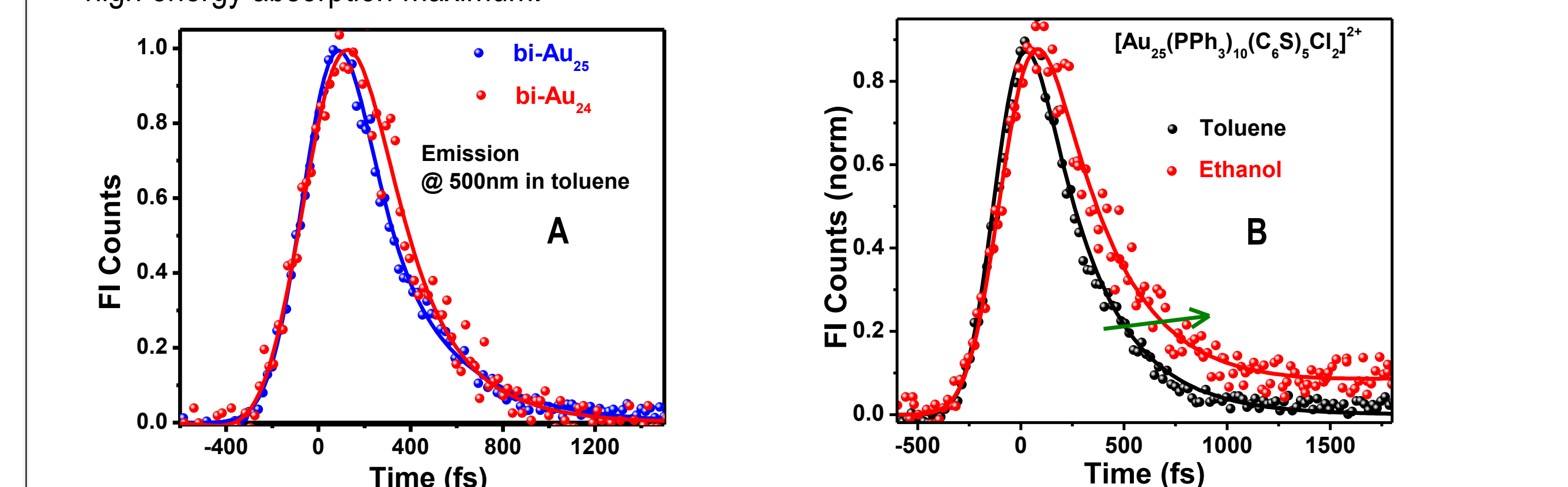
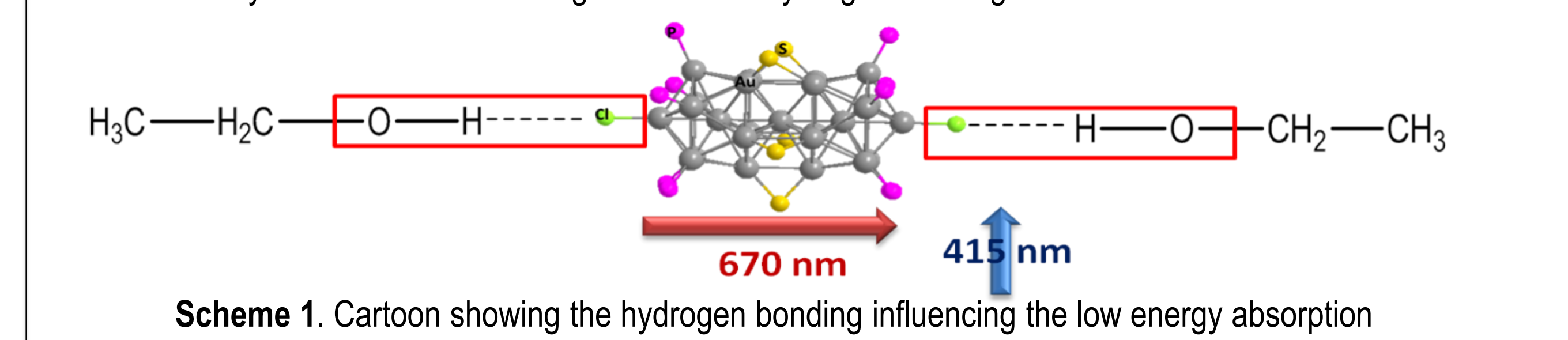


Figure 7: Luminescence decays of **A)** bi-Au₂₅ and Au₂₄ in Toluene. **B)** bi-Au₂₅ in two solvents. Note the increased decay time in ethanol showing the effect of hydrogen bonding on core-shell transitions.



Conclusions

- ❖ Absorption spectral features became sharper and the absorption maximum is shifted to higher energies for both the clusters with decrease in temperature.
- ❖ Interesting solvent dependent absorption is observed for bi-Au₂₅ in ethanol when compared to toluene.
- ❖ Combined measurements show that hydrogen bond of bi-Au₂₅ with ethanol is the reason behind this behavior.
- ❖ Au₂₄ and Au₂₅ both can form H bonds but Au₂₅ rod is more stable than the Au₂₄ structure when it comes to H bond solvents.
- ❖ The H bonding with coaxial Cl atoms cause the low energy absorption to swing around glass transition temperatures of the alcohols. Below the glass transition temperature, new optical features were observed.
- ❖ Ultrafast luminescence measurements indicate the relaxation is similar for both clusters but temperature dependence has a dramatic influence on the relaxation.

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