SAND2015-1292D

Possible New Approaches to the Synthesis of Small Luminescent Gold Clusters

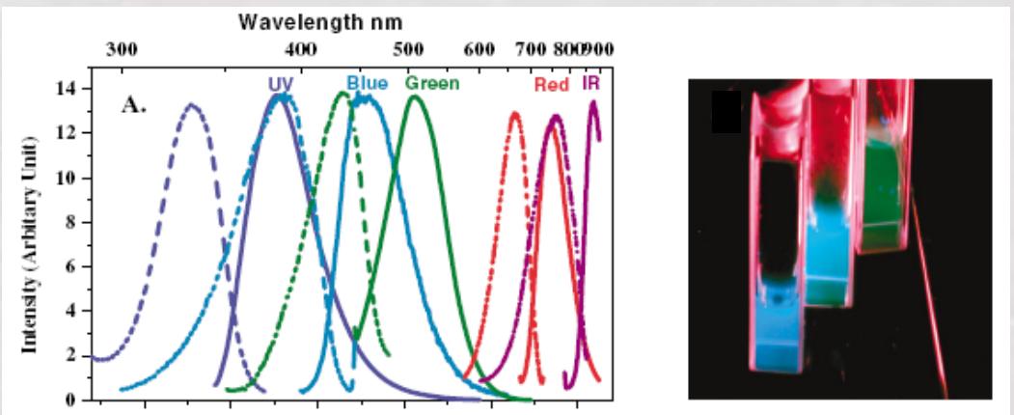
Indika Arachchige[1], Michael Brumbach[2], Sergei A. Ivanov[1*]

[1] MPA-CINT, Los Alamos National Lab, Los Alamos, NM 87545; [2]Sandia National Labs, Albuquerque, NM 87185; * ivanov@lanl.gov

Introduction

Biological molecular imaging and sensing requires fluorophores that are not only stable and bright, but also small enough to allow the unencumbered observation of the movement of proteins. In the past decade, there has been a tremendous interest in the synthesis of highly fluorescent species obtained by a noble metal reduction in the presence of biological ligands/templates. The luminescent species are assumed to be small and neutral noble metal clusters, although no definitive proof of their existence has yet been offered and no small, stable and *neutral* ligated clusters of Ag^0 or Au^0 have yet been characterized. However, bare Ag_n and Au_n clusters (n=2-4) were shown to emit in gas phase or Ar matrix.

$$HAuCl_4 \xrightarrow[\text{equilibration in water}]{\text{Dendrimer-NH}_2} \xrightarrow[\text{NaBH}_4^{*}\text{ or ascorbate}^{**}]{\text{Reduction}}$$



- clear or pale-yellow solutions
- 2-5 ns radiative decay
- 30-70% emission efficiency

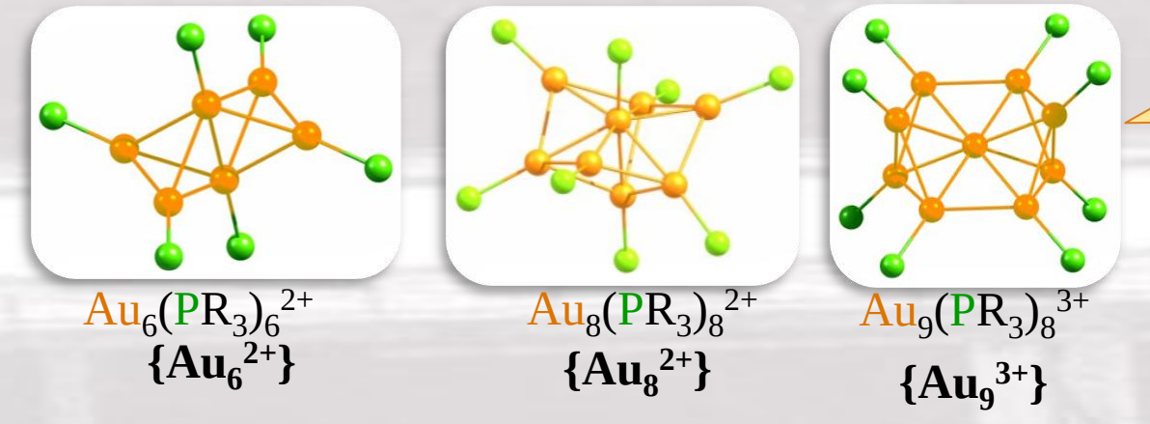
* J . Zheng, *et al. Phys. Rev. Lett.* **93(7)**,077402 (2004).
** Y. Bao, *et al. J. Phys. Chem. C* **111(33)**, 12194 (2007).

The goal of our work was to determine the nature of the luminescent species, find an alternative approach for their synthesis using simpler ligands (to understand the effect of molecular size and structure on photophysical properties), and elucidate the reaction pathway leading to their formation.

Main approach

Reaction of preformed cationic Au clusters with amines

Pre-formed cationic gold/phosphine clusters are the closest well-characterized and stable entities to the bare neutral gold clusters obtained in gas phase. Simple primary amines also could serve as an alternative to more complex dendrimers or peptides, currently used as ligands.


$Au_6(PR_3)_6^{2+}$ $\{Au_6^{2+}\}$ $Au_8(PR_3)_8^{2+}$ $\{Au_8^{2+}\}$ $Au_9(PR_3)_8^{3+}$ $\{Au_9^{3+}\}$

- "Pre-reduced" , with Au formal ox. state between 0 and 1
- Non-fluorescent
- Many are air-stable, easy to synthesize

$PR_3=PPh_3$ or $PCyPh_2$

Outcome

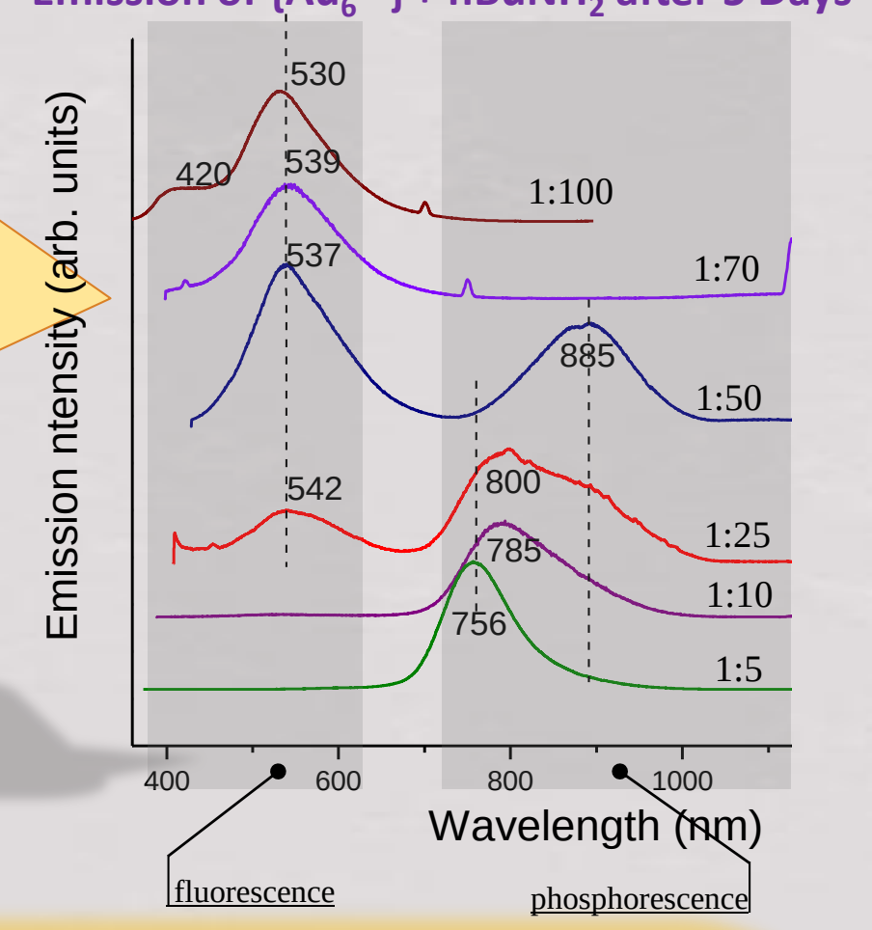
The treatment of preformed cationic gold-phosphine clusters with primary amines in solvents of medium/high polarity yielded isolable bright luminescent gold clusters (quantum efficiency up to 15-20%) with nanosecond emission from blue to orange color.

$$\{Au_n^{z+}\} + mRNH_2 \xrightarrow[\text{rm T}]{\text{solvent, 2-3 days}} \text{Au NPs} \xrightarrow[\text{rm T}]{\text{solvent, 1-2 days}} \boxed{\text{luminescent product}}$$

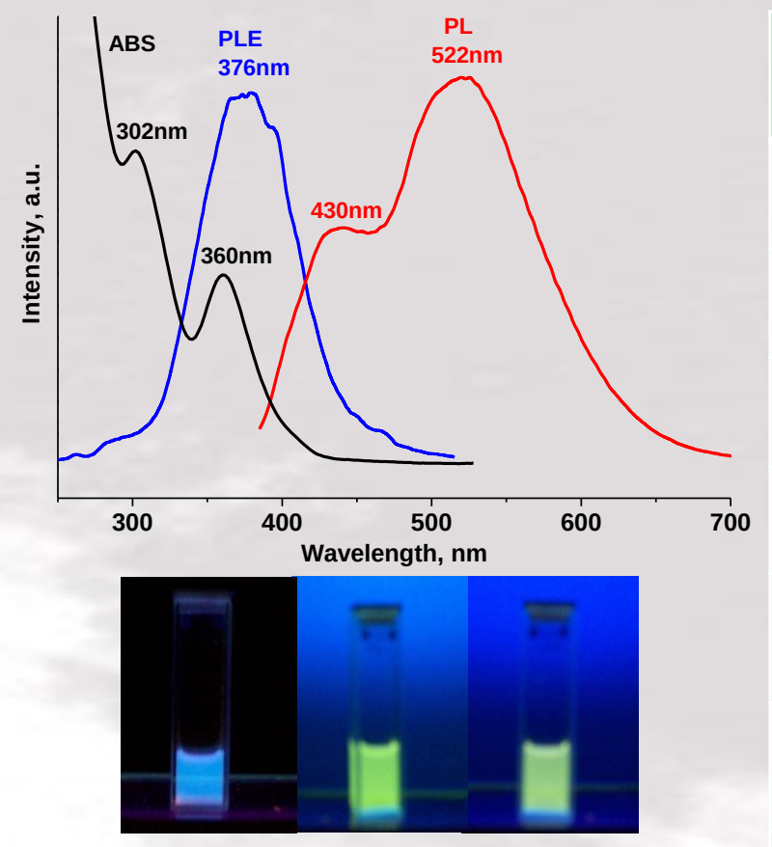
Cluster	Amine	Solvent	Ratios Au:L
$\{Au_6^{2+}\}$	$^nPrNH_2$	CH_2Cl_2	
	$^nBuNH_2$	Acetone	
$\{Au_8^{2+}\}$	$^nHexNH_2$		1:10 to 1:1000
	$^nOctylNH_2$	Methanol	
$\{Au_9^{3+}\}$	$(^nOctyl)_3N$	CH_3CN	
	G3-PAMAM-NH_2		

Photoluminescence monitoring (as well as UV-Vis absorption mesurements and TEM) confirms the formation of large Au clusters and Au nanoparticles as intermediates on the way to luminescent species.

Emission of $\{Au_6^{2+}\}$ + $nBuNH_2$ after 5 Days

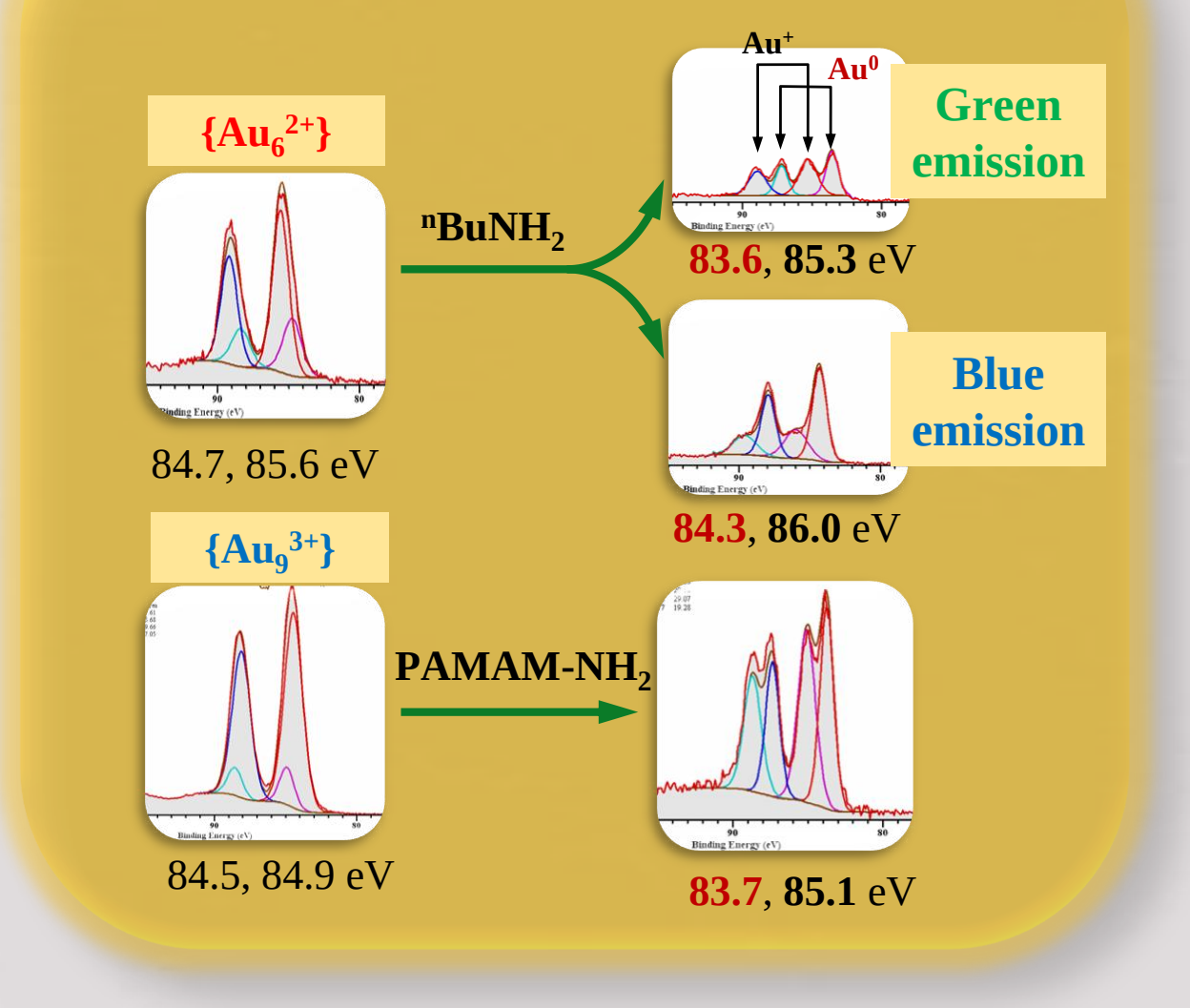


Electron spectroscopy



Sample	Excitation nm	Emission nm	Rad. lifetime ns
$Au_6(PCyPh_2)_6^{2+}$- PAMAM-NH_2	375	443	1.0 2.3
$Au_8(PPh_3)_8^{2+}$- PAMAM-NH_2	412	497	1.2 2.7
$Au_9(PPh_3)_8^{2+}$- PAMAM-NH_2	365	423	0.9 3.5
$Au_6(PCyPh_2)_6^{2+}$-$^nPrNH_2$	342, 393	485	3.9
$Au_6(PCyPh_2)_6^{2+}$-$^nBuNH_2$	355(sh) 385	420(sh) 525	1.0 3.9
$Au_6(PCyPh_2)_6^{2+}$-$^nHexNH_2$	368 655	554 694	3.0 7.1
$Au_6(PCyPh_2)_6^{2+}$-$^nOctylNH_2$	376	418, 435	4.7
$Au_6(PCyPh_2)_6^{2+}$-$(^nOctyl)_3N$	383	467	2.7

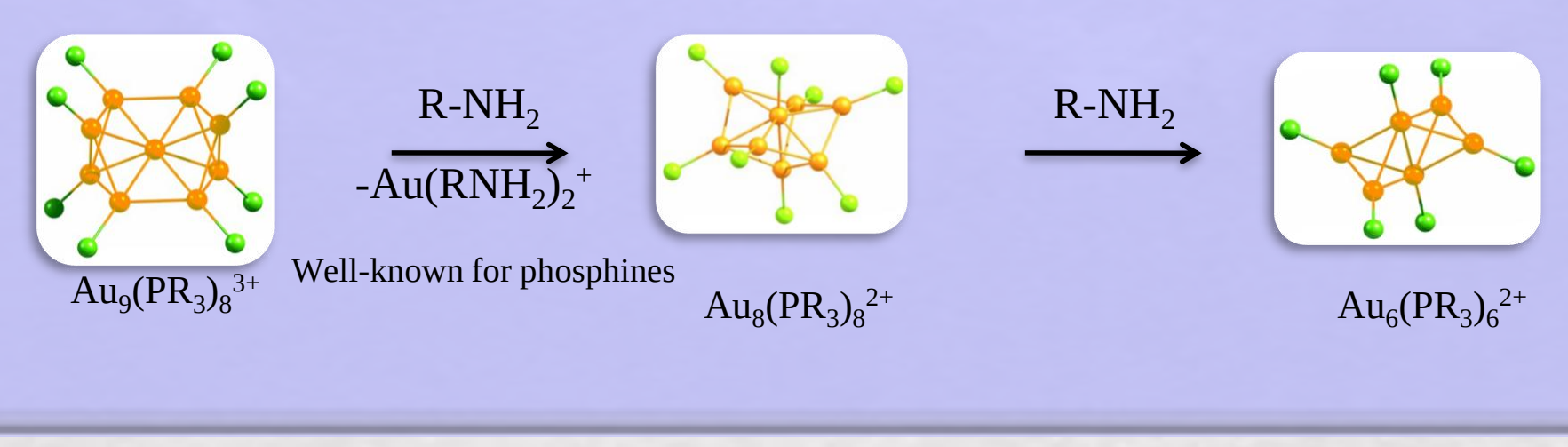
XPS of Au 4f electrons



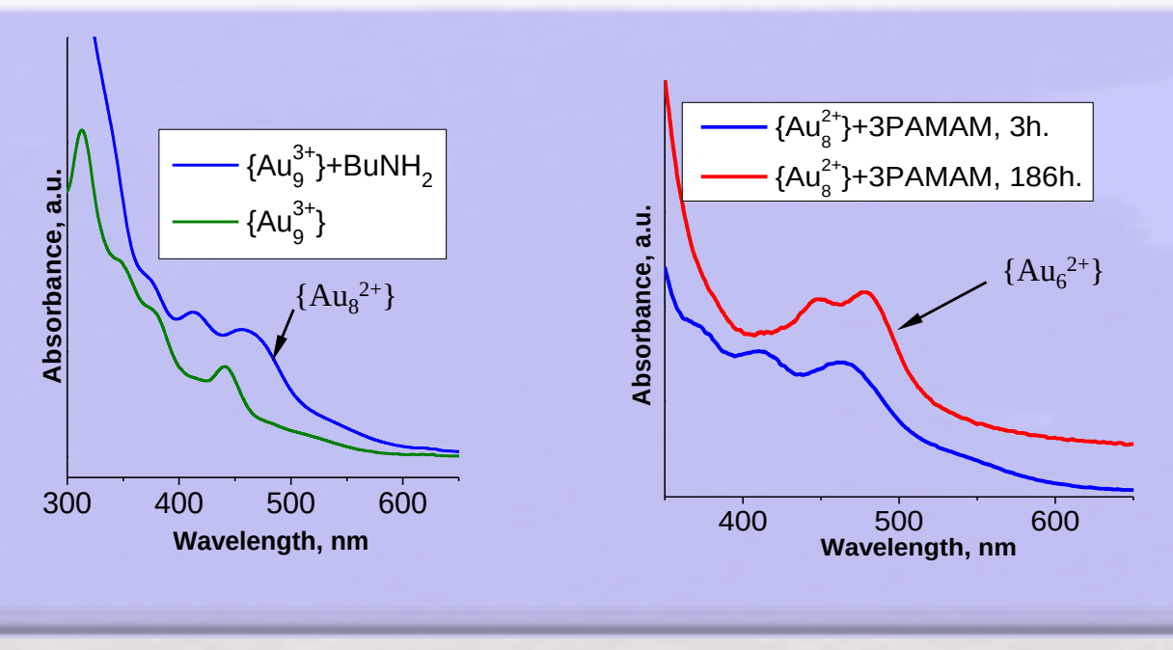
Neutral gold species with S-S emissive transitions

Reaction pathway

A. Conversion of large cationic clusters to $\{Au_6^{2+}\}$

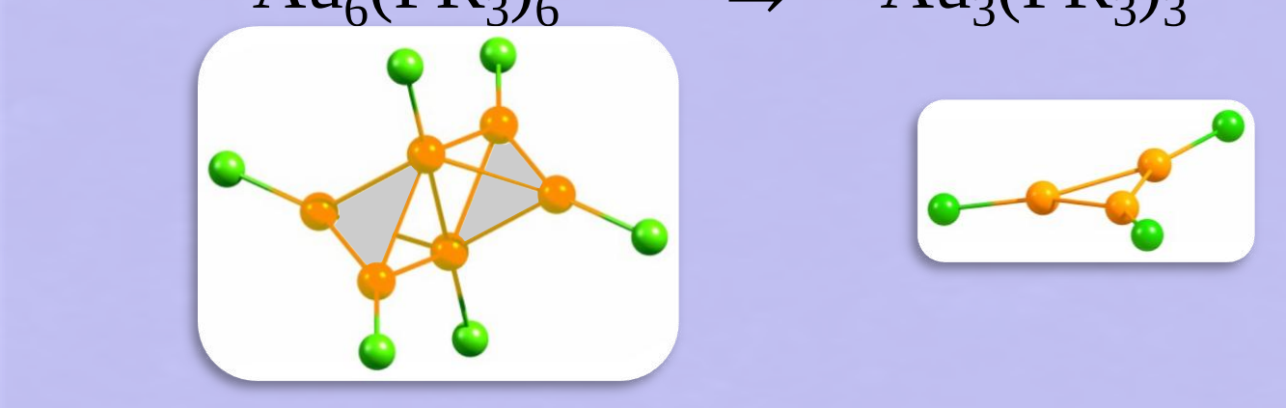

$$Au_9(PR_3)_8^{3+} \xrightarrow[-Au(RNH_2)_2^{+}]{R\text{-}NH_2} Au_8(PR_3)_8^{2+} \xrightarrow{R\text{-}NH_2} Au_6(PR_3)_6^{2+}$$

Well-known for phosphines



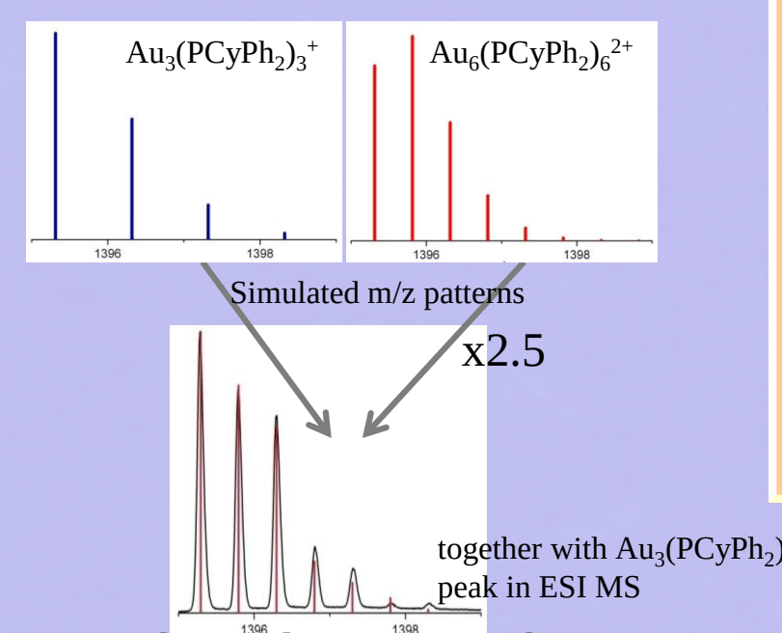
B. Cationic *cluster dissociation*

$$Au_6(PR_3)_6^{2+} \leftrightarrows Au_3(PR_3)_3^{+}$$



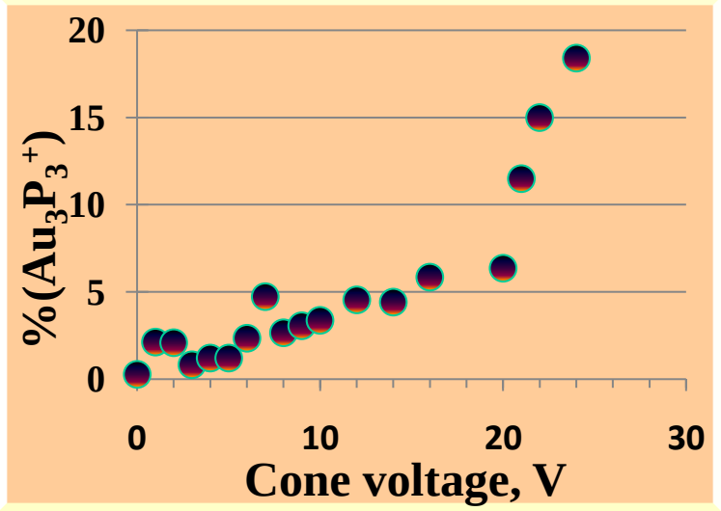
Co-existence of $\{Au_6^{2+}\}$ and $\{Au_3^+\}$ clusters

1. Theoretical estimate:
   |ΔG| of the dissociation < 1kcal/mol at SVWN5, PBE1PBE, BMK, or MP2 and TZVP level of theory, with CPCM solvation in CH_3CN
2. ESI mass-spectrometry data:



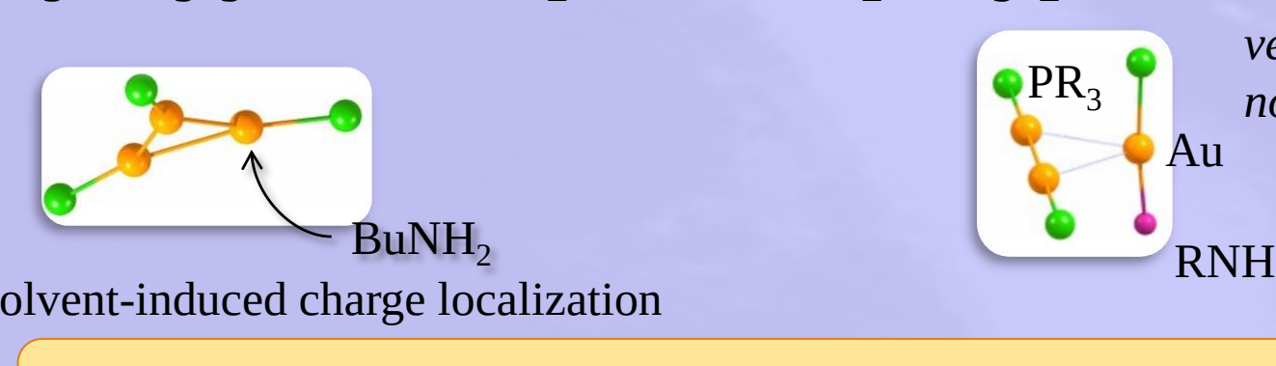
together with $Au_3(PCyPh_2)_2^+$ peak in ESI MS

Observed spectrum with fitted combination of $\{Au_3^+\}$ and $\{Au_6^{2+}\}$



C. Generation of *neutral* fragment

$$Au_3(PR_3)_3^{+} + BuNH_2 \longrightarrow Au_2(PR_3)_2 + [Au(PR_3)(BuNH_2)]^{+}$$



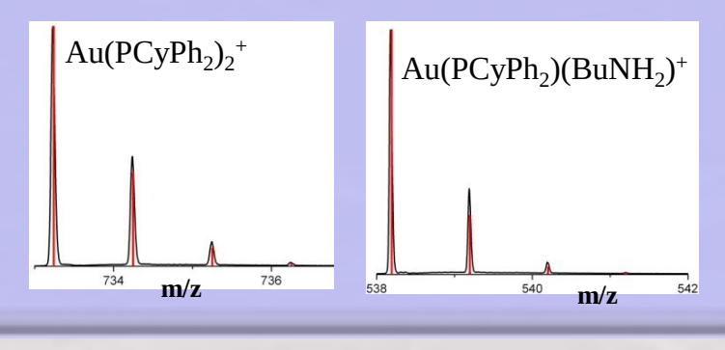
solvent-induced charge localization

very stable non-fluorescent

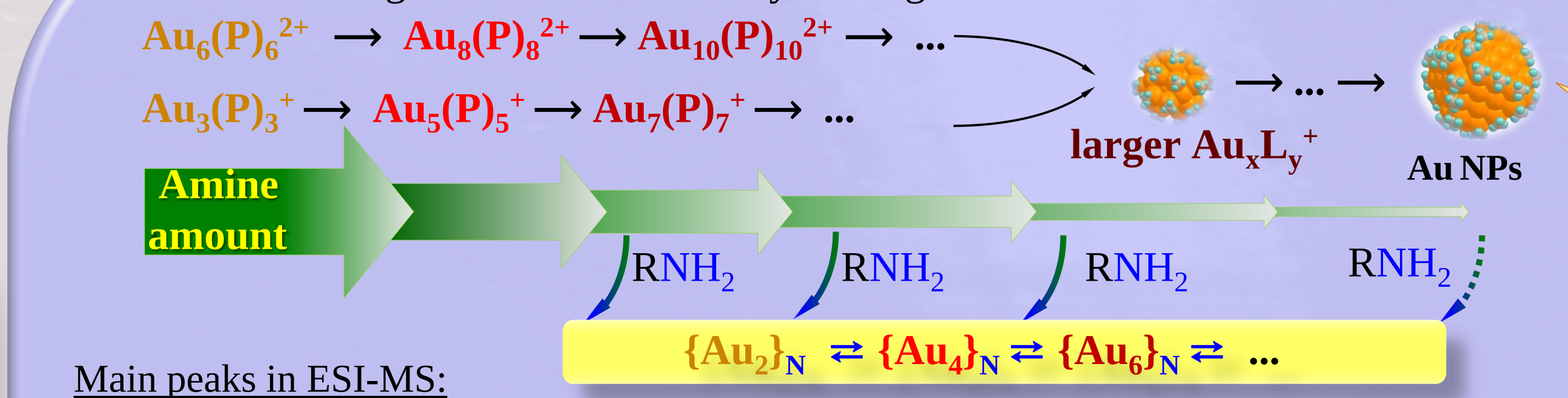
Generation of neutral $Au_2(PR_3)_2$ cluster is likely.

1. Theoretical estimate: ΔG_{rxn} = -8-10kcal/mol at SVWN5, PBE1PBE, BMK, or MP2 combined with TZVP level of theory, with CPCM solvation in CH_3CN.

   Combinations of $Au_2(PR_3)(RNH_2)$ and $[Au(PR_3)_2]^+$ or $Au_2(RNH_2)_2$ and $[Au(PR_3)(RNH_2)]^+$ are even more preferred over $Au_2(RNH_2)_2/Au(PR_3)_2^+$ or $Au_2(PR_3)_2/Au(RNH_2)_2^+$ (probably for entropic reasons).
2. Mass-spectrometry data:



D. 1 Cluster augmentation followed by etching


$$Au_6(P)_6^{2+} \longrightarrow Au_8(P)_8^{2+} \longrightarrow Au_{10}(P)_{10}^{2+} \longrightarrow \dots$$
$$Au_3(P)_3^{+} \longrightarrow Au_5(P)_5^{+} \longrightarrow Au_7(P)_7^{+} \longrightarrow \dots$$
$$\text{larger } Au_xL_y^{+} \longrightarrow \dots \longrightarrow \text{Au NPs}$$

$$\{Au_2\}_N \rightleftarrows \{Au_4\}_N \rightleftarrows \{Au_6\}_N \rightleftarrows \dots$$

Fluorescent clusters

Au NPs observed as intermediates prior to luminescent species, with size inversely proportional to the amount of RNH_2

Main peaks in ESI-MS:
$Au_3(P)_n^+$ (n=2,3) $Au_8(P)_n^{2+}$ (n=8,5)
$Au_5(P)_n^+$ (n=2-5) $Au_{10}(P)_n^{2+}$ (n=6,7)
$Au_7(P)_n^+$ (n=3,4)

D.2 Amine enrichment (*ligand exchange*)

$$Au_x(P)_y \rightleftarrows Au_x(P)_{y-1}(N) \rightleftarrows Au_x(P)_{y-2}(N)_2 \rightleftarrows \dots \rightleftarrows \{Au_x(N)_y\}$$

Amine (*or other weak ligand*) is essential to generate fluorescent gold cluster.

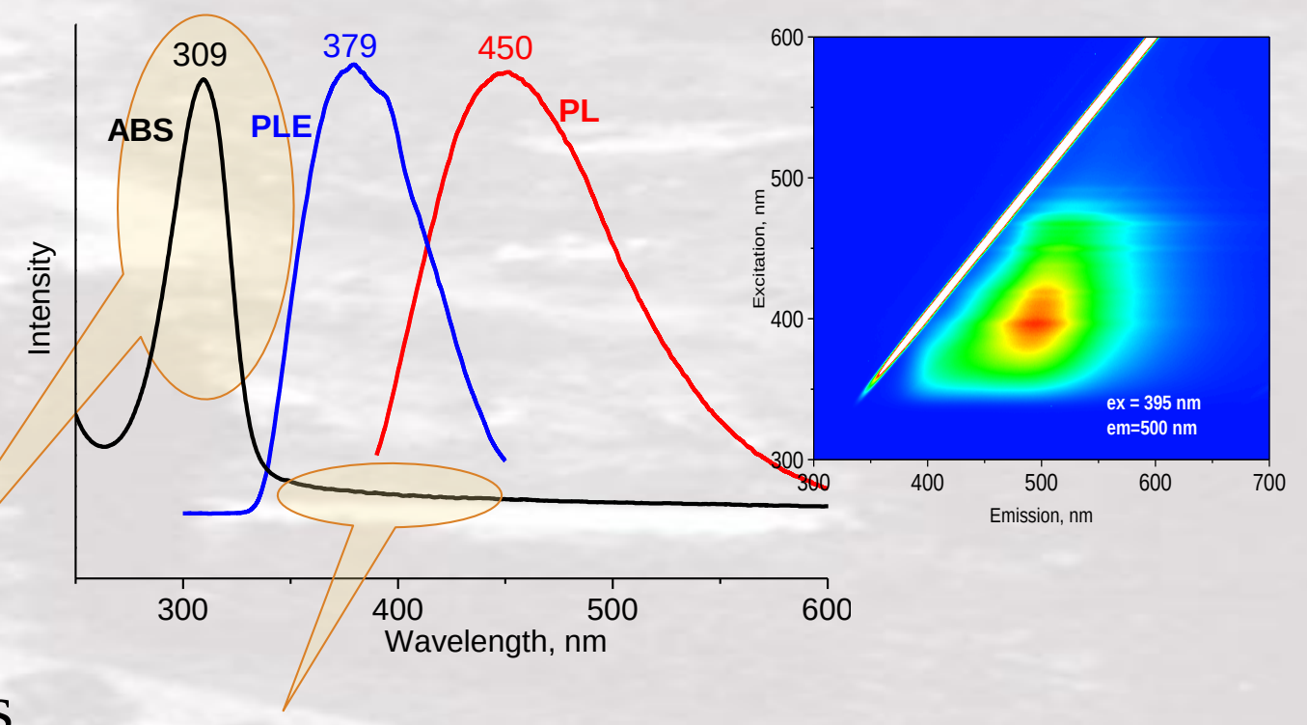
Alternative approach

High phosphine content complicates the reaction, requiring high concentrations of amine and longer reaction times. Alternative approach would be the phosphine-free (or other strong ligand, like X^-, RS^-) reaction conditions

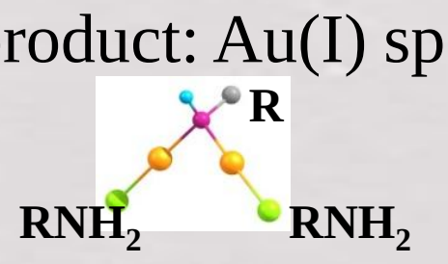
Reduction of $Au(CH_3COO)_3$ or $[Au(NO_3)_4]^-$ in the presence of simple amine

$$Au(III) + mRNH_2 \xrightarrow[40^oC]{\text{solvent, 1-2h}} \xrightarrow[40^oC]{NaBH_4} \text{Au NPs} \xrightarrow[40^oC]{\text{1-2days}}$$

$Au(III) = Au(AcO)_3$ or $[Au(NO_3)_4]^-$



Second product: Au(I) species with close $Au^+...Au^+$ contacts

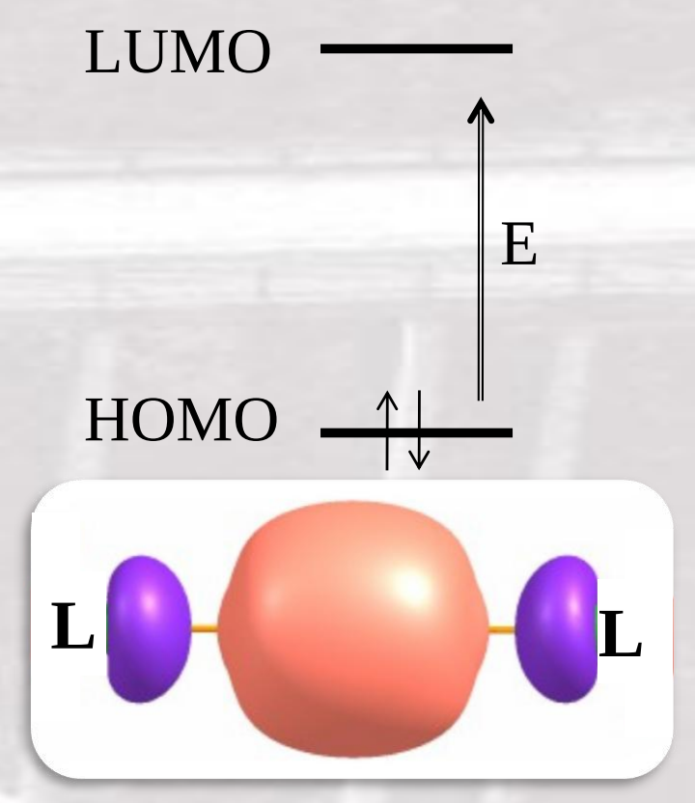


, $(\mu_3\text{-NR})(AuN(R)H_2)_3^+$ ...

Weak absorption of emissive species

Electronic origin of the luminescence and ligand effect

From the theoretical analysis of the absorption/luminescence of the neutral gold clusters with various ligands, it follows that **the *larger* the ligand contribution to the cluster LUMO, the *lower* the intensity of the first electronic transition**, and, as a consequence, the weaker the cluster emission.

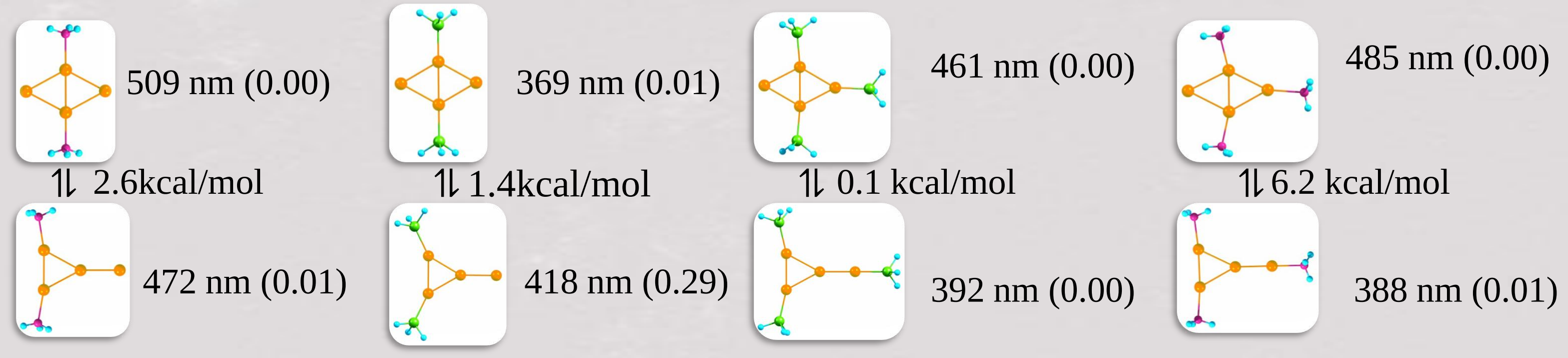


Ligand	E, eV (osc)
H_2O	4.87(0.31)
NH_3	5.07(0.22)
CH_3SH	4.81(0.13)
PH_3	4.40 (0.07)
Pyridine	4.67(0.04)

Increase in ligand contribution

Decrease in osc. strength

Even without a change in cluster nuclearity, the cluster's absorption and luminescence depend on the type of isomer, the type of ligand and the number of ligands (B3LYP/TZVPP(Au)/6-311G(df,p) (P/N,C,H).



Conclusion

- We have established the likely nature of the luminescent species formed in reactions of pre-formed cationic gold/phosphine clusters with primary amines
- We have proposed a plausible reaction pathway leading to the formation of these neutral gold-amine clusters
- By means of theoretical analysis, we have demonstrated that even such changes in the cluster surroundings as the type and the number of protecting ligands might have a significant effect on the energy of the emission. As such, the conventional attribution of the cluster emission energy to cluster size is not necessarily valid.
- Theoretical analysis also sheds light on the nature of neutral gold cluster emission, where the type of protecting ligand dramatically affects the emission efficiency. As it was demonstrated, the degree of ligand involvement in the accepting orbital of the first absorption transition directly controls the intensity of that transition.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.