Tailoring the Properties of Metallic Clusters by Ligand Coatings

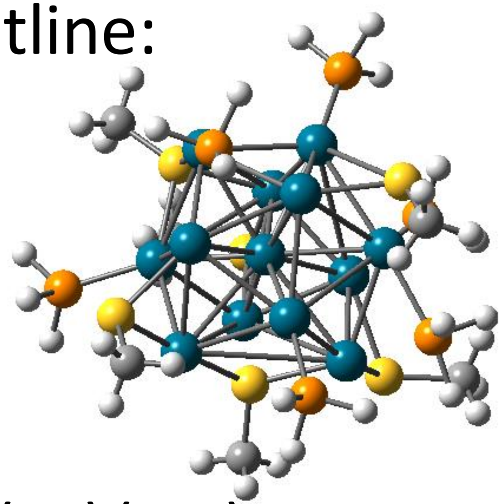
Barbara Fresch, Francoise Remacle
Laboratoire de Chimie Physique Théorique,
Université de Liège, Belgique
e-mail: bfresch@ulg.ac.be

Université de Liège

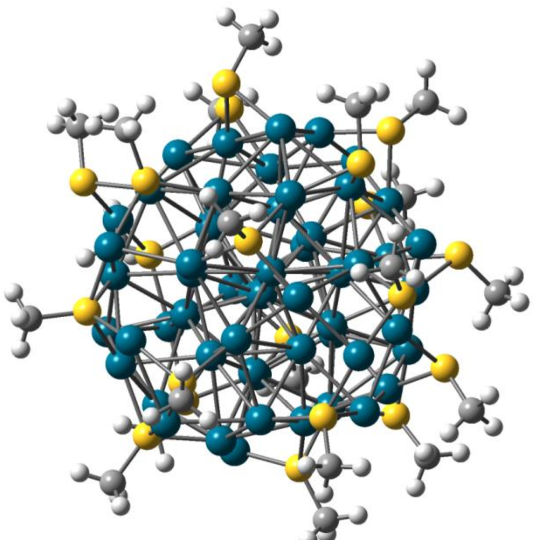
Motivations:

- ✓ Understanding the impact of protecting organic ligand shells on the structure-property relation of metallic clusters and nanoparticles.
- ✓ Exploiting ligands-metal core interactions to tune the properties of metal clusters according to specific applications (catalysis, nano-electronics, bio-labelling…).

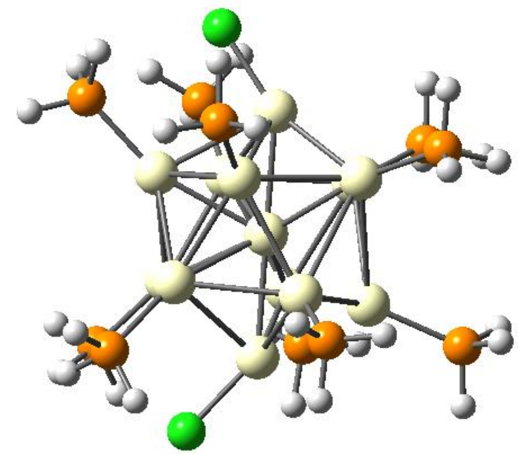
Outline:



$Pd_{13}(PH_3)_6(SCH_3)_6$

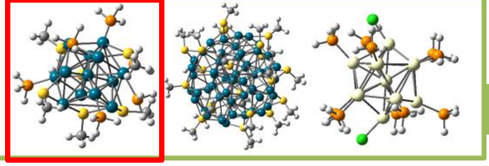


$Pd_{55}(SCH_3)_{20}$



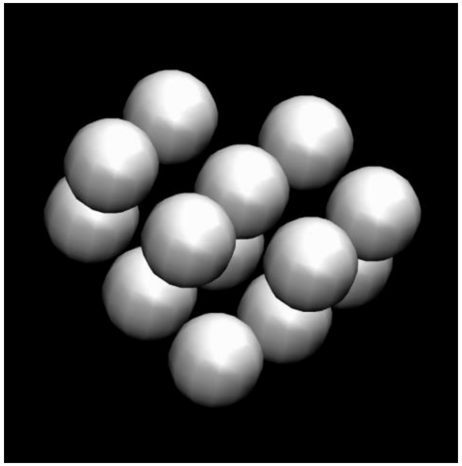
$[Au_{13}(PH_3)_{10}Cl_2]^{3+}$

Insights from quantum chemistry calculations at the level of density functional theory (B3LYP/cam-B3LYP/LanL2DZ/6-31+G(d))

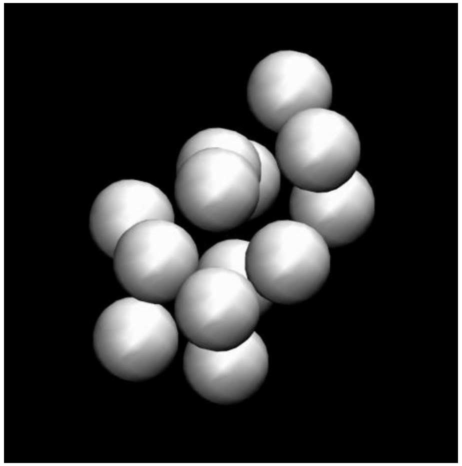


The elusive structure of Pd_{13} cluster:

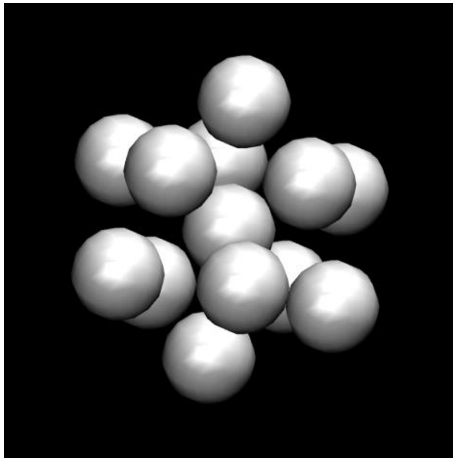
Structural and Magnetic Isomers



Cv-like
m=7
0eV

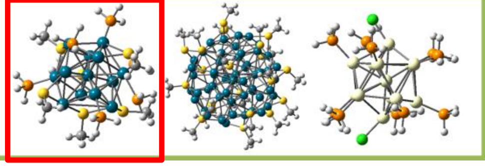


Cs
m=7
0.22 eV

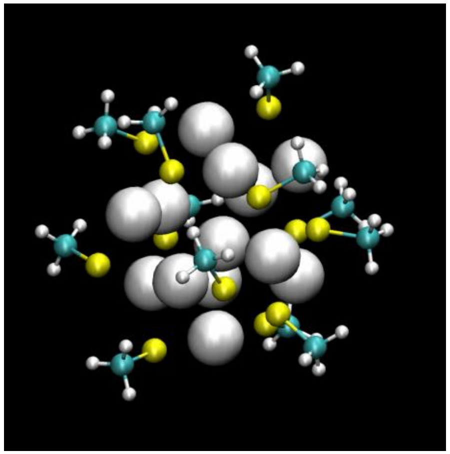


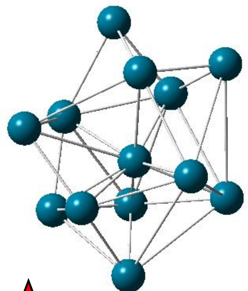
Ih-like
m=9
0.37 eV

- ✓ The relative energy of structural isomers is method dependent
- ✓ The magnetic ground states are of high spin multiplicities
  (M. Moseler et al., PRL, 86, 2545 (2001))



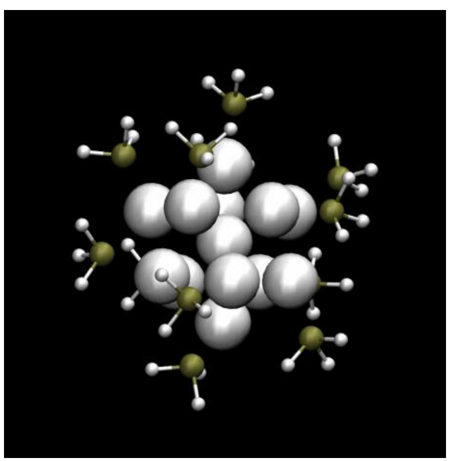
Effect of ligands: $Pd_{13}(SCH_3)_{12}$ and $Pd_{13}(PH_3)_{12}$

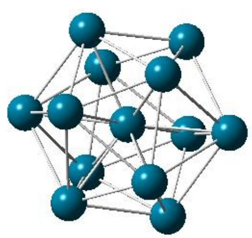




$4\mu_B$

- ✓ Stabilization of the Icosahedral core geometry
- ✓ Stabilization of different magnetic states: Thiol are less effective in quenching the magnetic moment



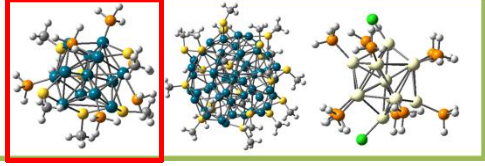


$2\mu_B$

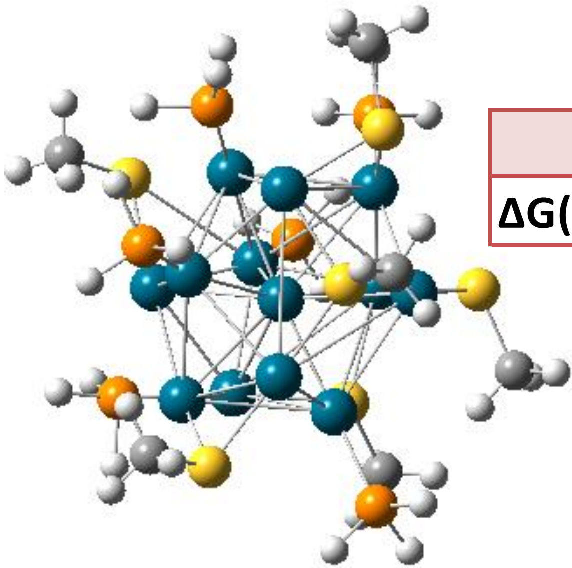
Natural charge of the metal core:
-2.32 $Pd_{13}(PH_3)_{12}$
+0.39 $Pd_{13}(SCH_3)_{12}$

Phosphines tend to fill the hole in the d orbitals quenching the magnetism

(B. Fresch et al. *Nanoscale* **2012,** *4* (14), 4138-4147)



Mixed ligand shell: $Pd_{13}(SCH_3)_6(PH_3)_6$

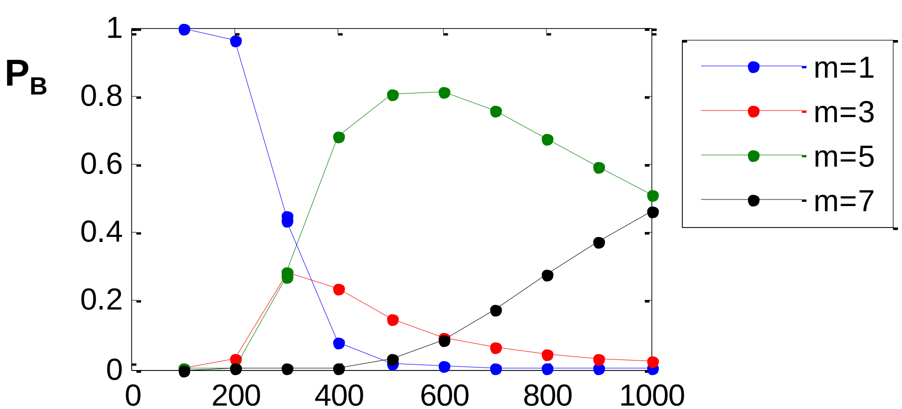


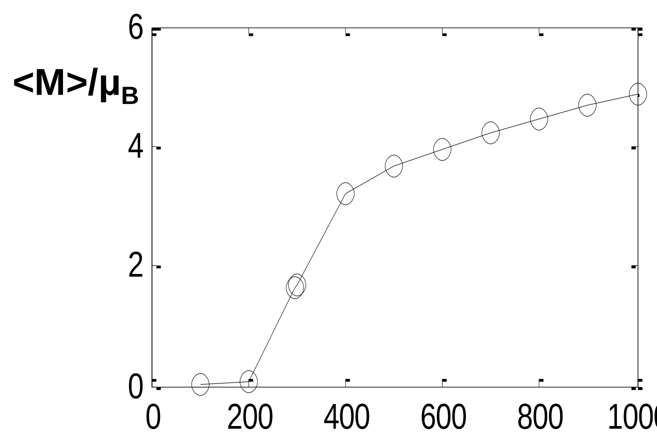
✓ Different magnetic isomers lie very close in energy

	m=1	m=3	m=5	m=7
ΔG(298K) eV	**0.00**	**0.01**	**0.01**	**0.21**

✓ This leads to an unusual dependence of the average magnetic moment on the temperature

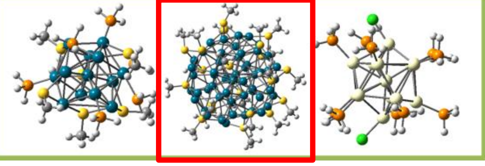
$$\langle \mathrm{M}(T) \rangle = \sum_{m=1}^{7} \frac{e^{-\frac{\Delta G_m(T)}{RT}}}{Q(T)} (m-1)\mu_B$$





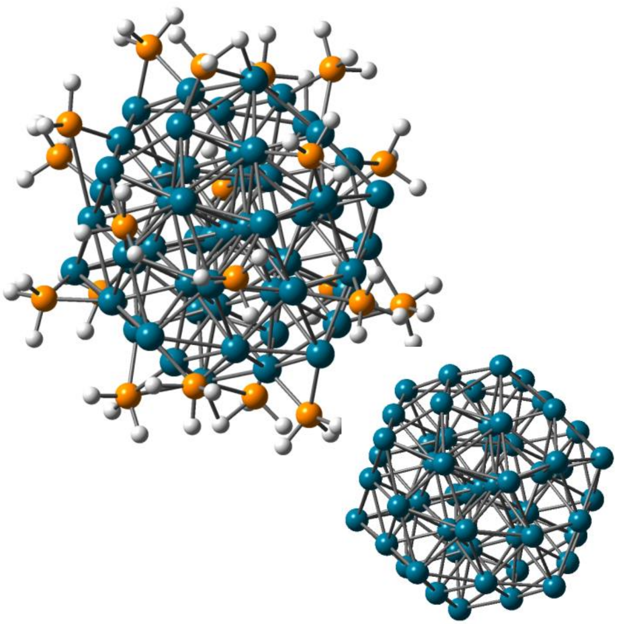
B. Fresch et al, Nanoscale 4(14), 4138 (2012)

T(K)

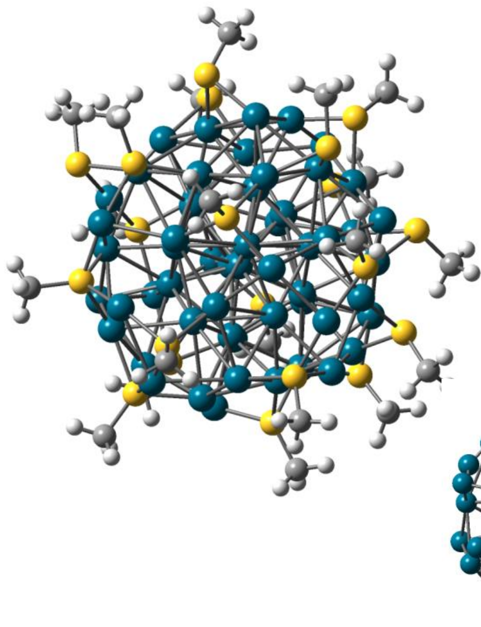


Toward nanometer-sized systems

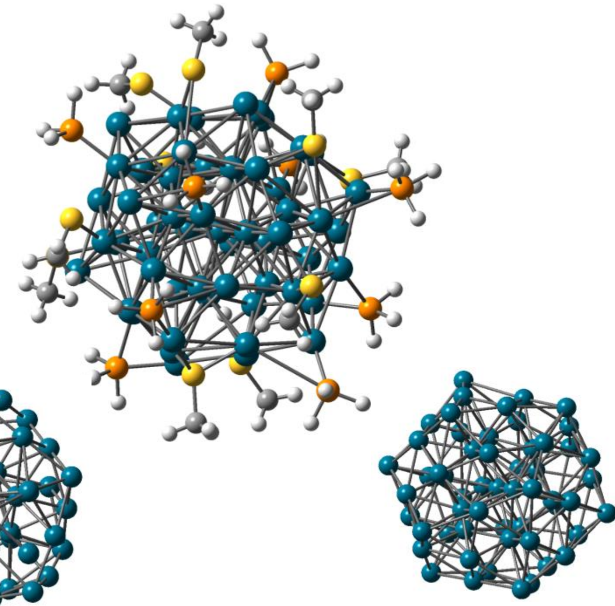
$Pd_{55}(PH_3)_{20}$



$Pd_{55}(SCH_3)_{20}$



$Pd_{55}(PH_3)_{10}(SCH_3)_{10}$



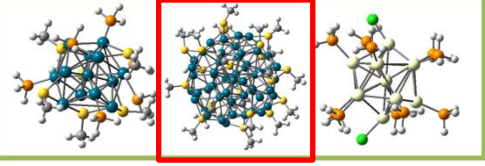
✓ Quenching of the catalytic activity in thiolate protected Pd nanoparticle:

drop in the population of the d-orbital of the metal core

formation of a passivating sulfide layer

Corthey et al., *J. Phys. Chem. C*, 2012, **116**, 9830

Azcarate et al. *J. Phys. Chem. Lett.*, 2013, 4, 3127



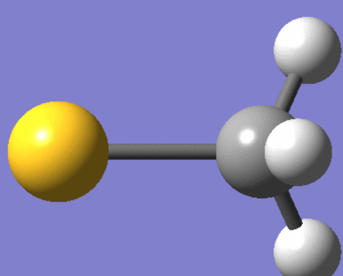
Natural Population Analysis

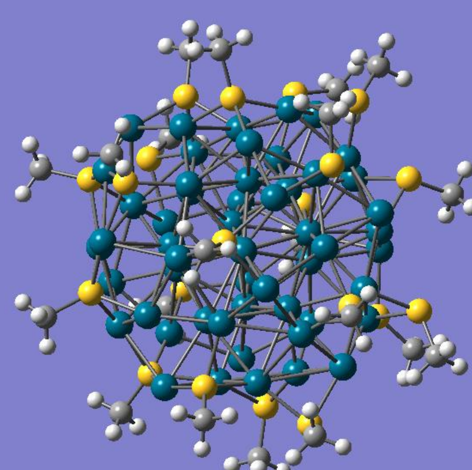
	Pd	SCH_3	PH_3
$Pd_{55}(PH_3)_{20}$	-4.46	-	+4.46 (0.223)
$Pd_{55}(SCH_3)_{20}$	+0.22	-0.22(-0.01)	-
$Pd_{55}(PH_3)_{10}(SCH_3)_{10}$	-2.34	-0.23(-0.023)	+2.57 (0.257)

- ✓ Confirm the withdrawing of electrons from the metal core in thiolate protected NPs and the decrease in d-population

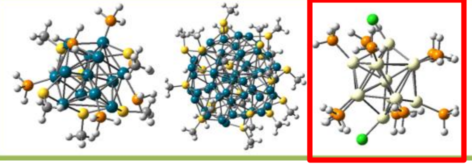
- ✓ Electronic density is transferred to S-C anti-bonding orbitals weakening the bond (stretching frequencies: 712cm^{-1} versus 654cm^{-1})

Frequency calculations



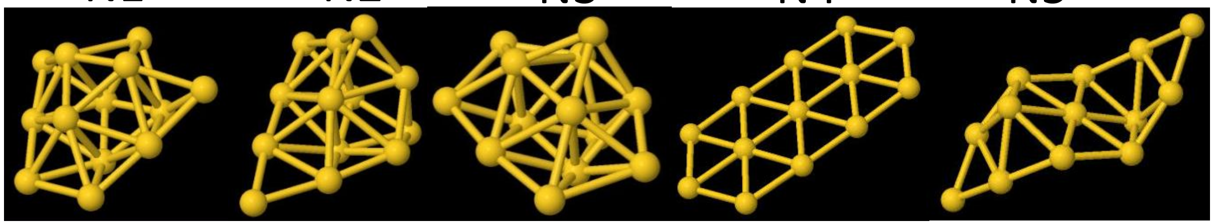


- ✓ Possibility of S-C rupture and formation of sulfide passivating layer



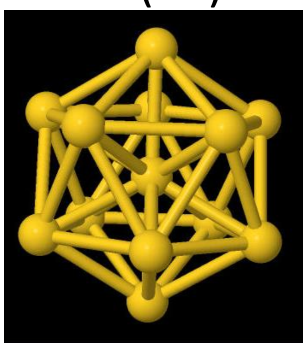
Gold Clusters

N1 N2 N3 N4 N5



Au_{13}

Ih (5+)



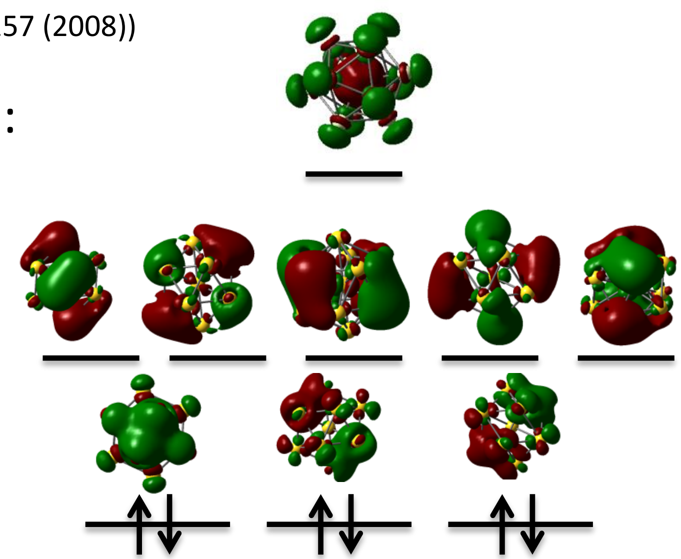
Au_{13}^{5+}

Super Atom model

(Walter et al., Proc. Natl. Acad. Sci. **105**, 9157 (2008))

Superatomic shell closure:

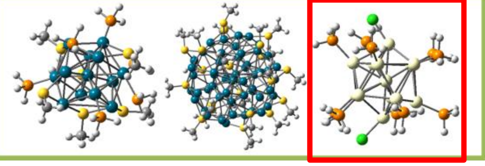
$[Au_N X_M L_S]^{z+}$ n=N-M-z



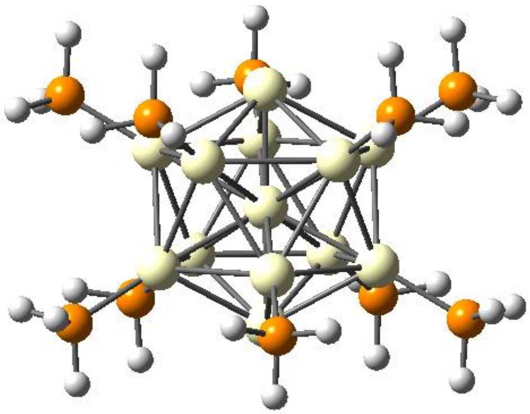
S-like SAO
-18.98eV

D-like SAO
-20.47eV

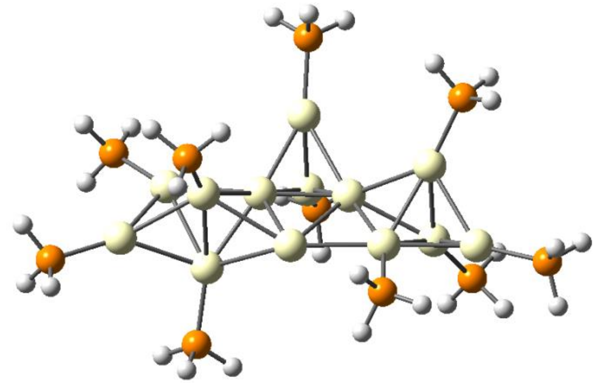
P-like SAO
-25.83eV



Phosphine capping: $Au_{13}(PH_3)_{10}^{5+}$

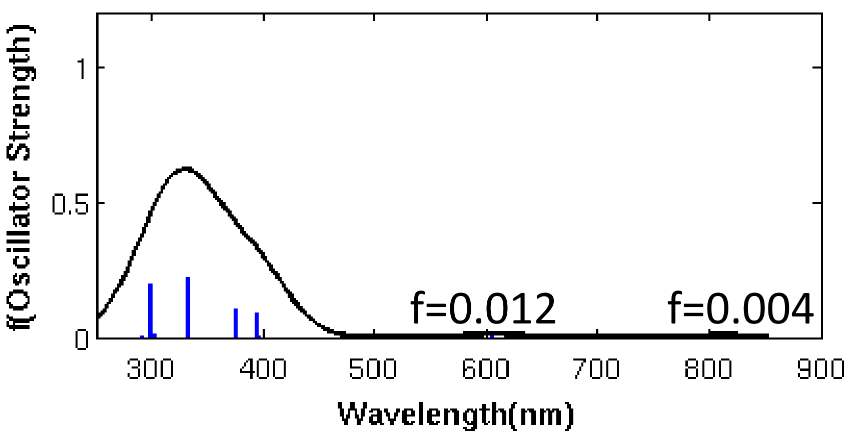


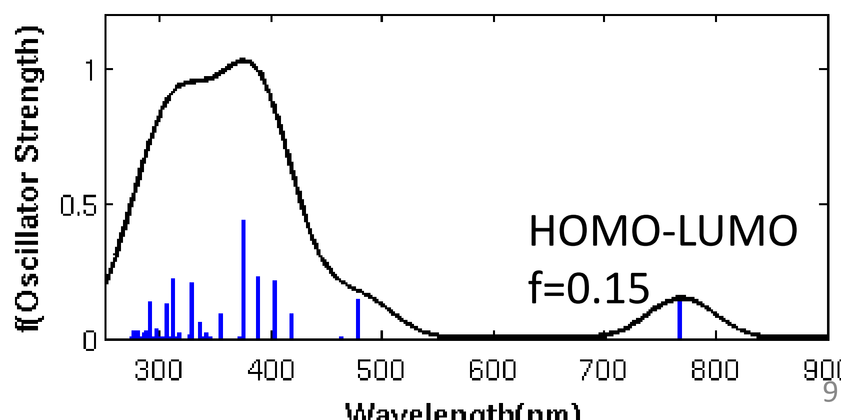
Free energy difference
ΔG=-1.78eV

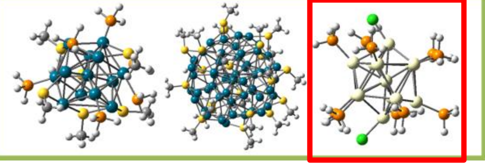


- ✓ Ligation with phosphines stabilizes flake core structures
  (B. Fresch et al, Eur. Phys. J. D **2012,** 66 (12), 1-9)
- ✓ Different optical properties

AbsorptionUV/VIS



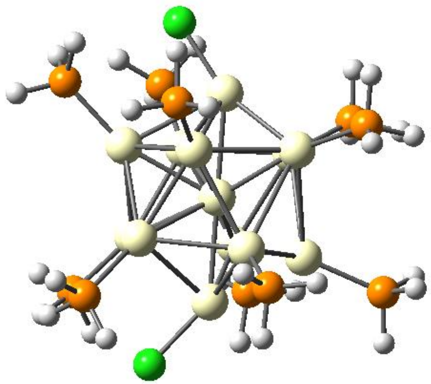




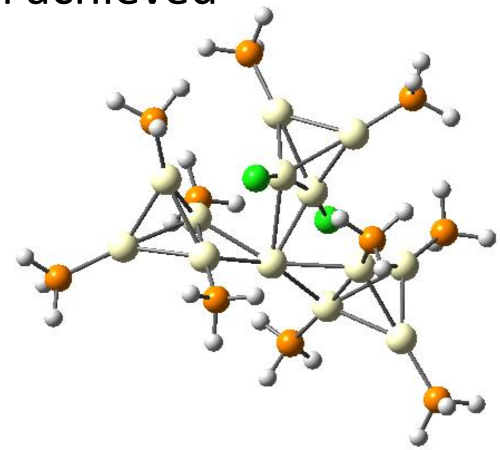
$Au_{13}Cl_2(PH_3)_{10}^{3+}$

Selective synthesis of this cluster has been achieved

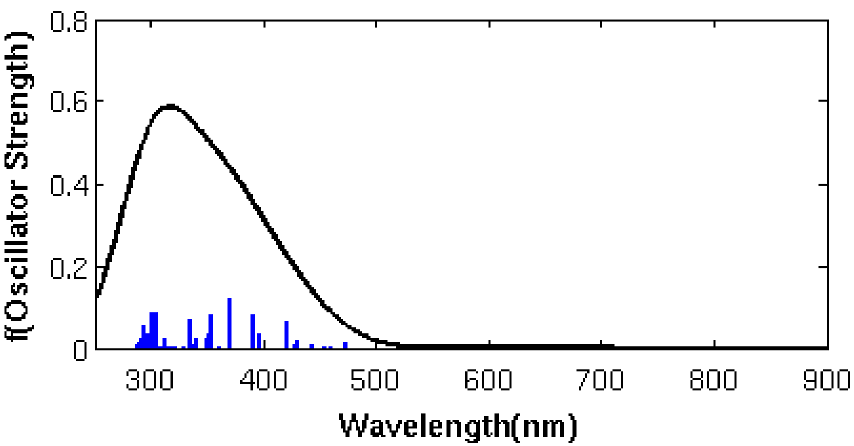
Y. Shichibu et al., Nanoscale **4**, 4125 (2012)

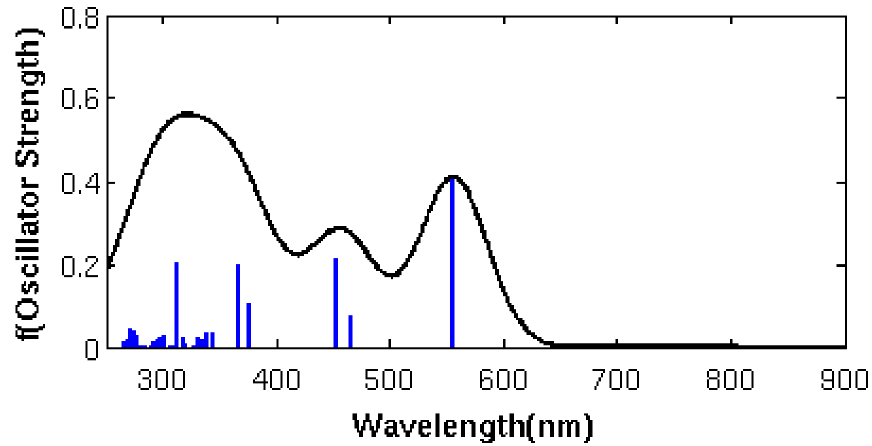


ΔG=-0.34eV



AbsorptionUV/VIS

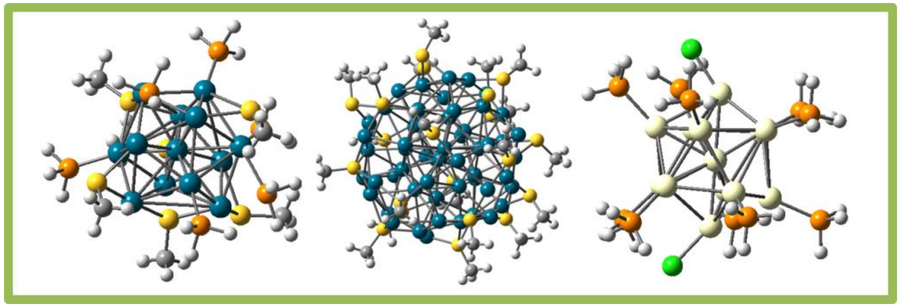




- ✓ First optical excitation at higher energy than $Au_{13}(PH_3)_{10}^{5+}$
- ✓ Weak in the compact isomer but strong in the flake isomers

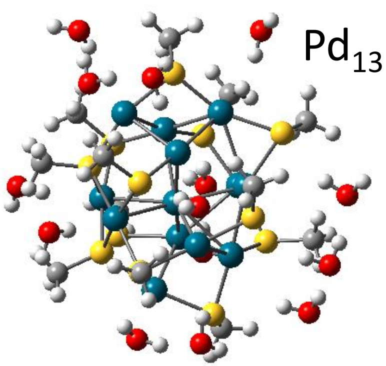
Conclusions and perpectives

- ✓ Capping systems can be used as advantage to control structures and properties of metallic clusters (magnetic moment, charging energetics and optical properties)

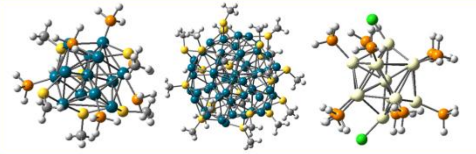


- ✓ Interesting cooperative effects within mixed ligand shell: any effect on spatial segregation («Janus» nanoparticles)?

- ✓ Role of solvent? Explicit solvation models



$Pd_{13}(SCH_3)_{12}(H_2O)_{14}$



Laboratoire de Chimie Physique Théorique:

Prof. Francoise Remacle

Fabien Dufour

Renuka Ganesan

Benoit Mignolet

Gustavo Lugo

Dr. Mike Klymenko

Dr. Tian Min Yan

Université de Liège

Partners in the **IAP project P6/42**

Prof. H.G. Boyen (IMO-University of Hasselt)

Prof. Chris Van Haesendonck (KU Leuven)

ARC-NANOFORCE project

Prof B. Champagne and the organization of QCB11