Theoretical characterization of the interactions between organic ligands and metallic clusters

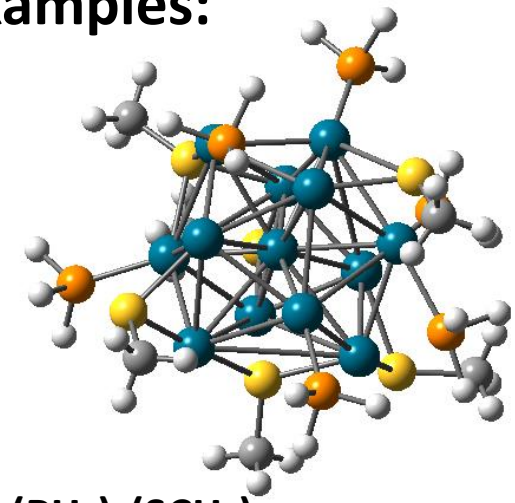
Barbara Fresch, Francoise Remacle
Laboratoire de Chimie Physique Théorique,
Université de Liège, Belgique
e-mail: bfresch@ulg.ac.be

Université de Liège

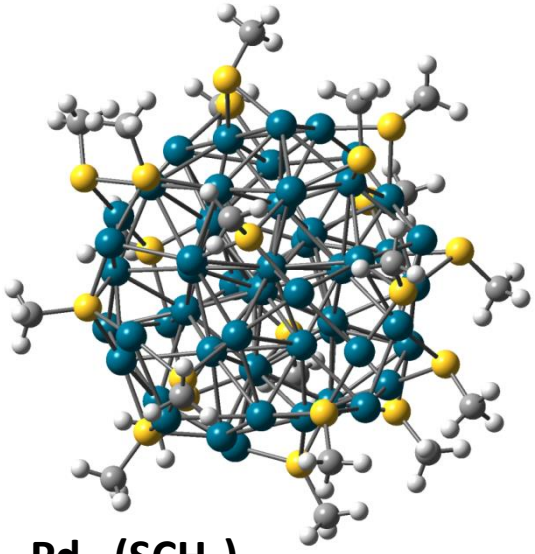
Motivations:

- ✓ 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…).

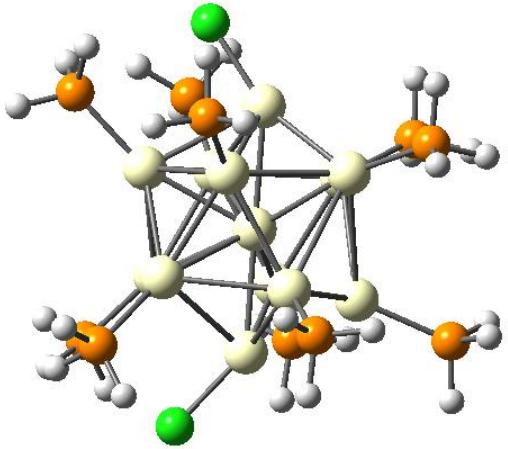
Examples:



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



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

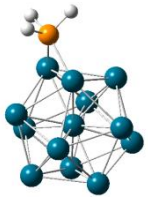


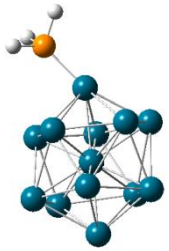
$[Au_{13}(PH_3)_{10}Cl_2]^{3+}$

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

- ✓ **studying the characteristic of the ligand-metal interaction in terms of binding mode, adsorption energy, charge transfer**

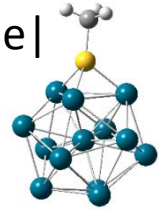
+0.2|e|

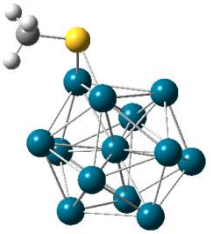




ε=-0.66eV ε=-0.62eV

-0.02|e|

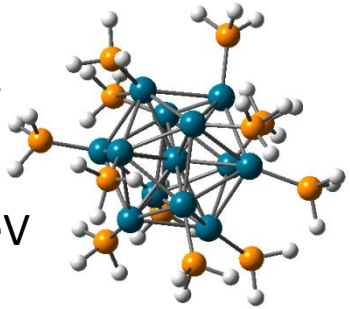




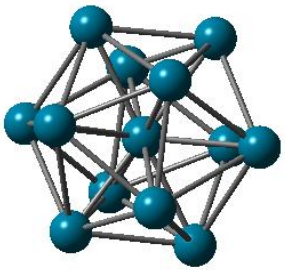
ε=-1.74eV ε=-1.89eV

- ✓ **From a single ligand to a ligand shell**

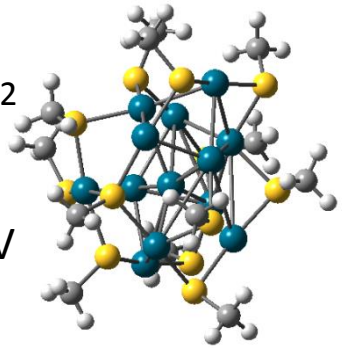
$Pd_{13}(PH_3)_{12}$



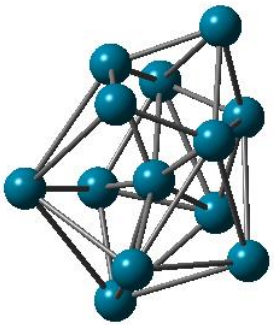
ε=-0.51eV



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



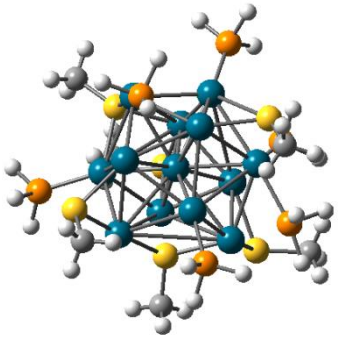
ε=-1.61eV



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

✓ **What if we mix different ligands: cooperative effects?**

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



P:+1.58|e| (0.26)
S: -0.64 |e| (-0.11)

Engineering the composition of the ligand shell to tailor the properties of the system

Integrating theoretical results and experimental expertise-1

✓ Structures: we can determine true minima of the PES but a search of the absolute minimum is prohibitive

→ Structural informations ideally in different environment (crystal/solution)

✓ Stoichiometry: how many ligands/ surface reconstruction

To what extent it is actually possible to control the composition of the ligand shell?

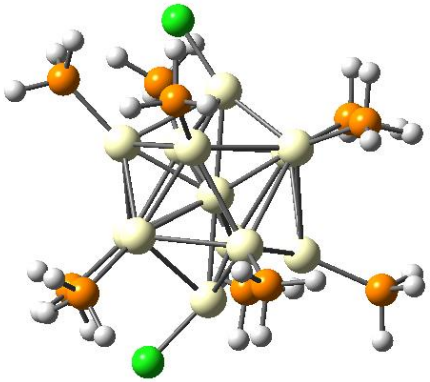
✓ Size selective and specific synthetic routes

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

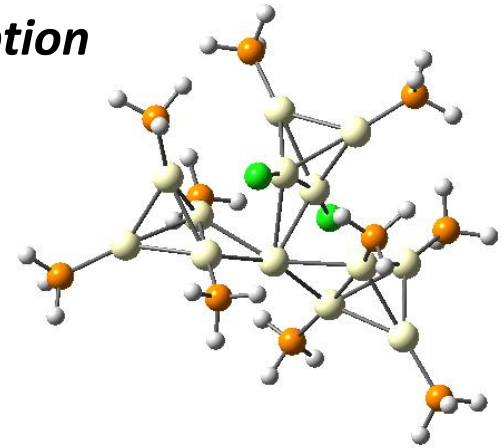
Y. Shichibu et al., Nanoscale **4**, 4125 (2012)

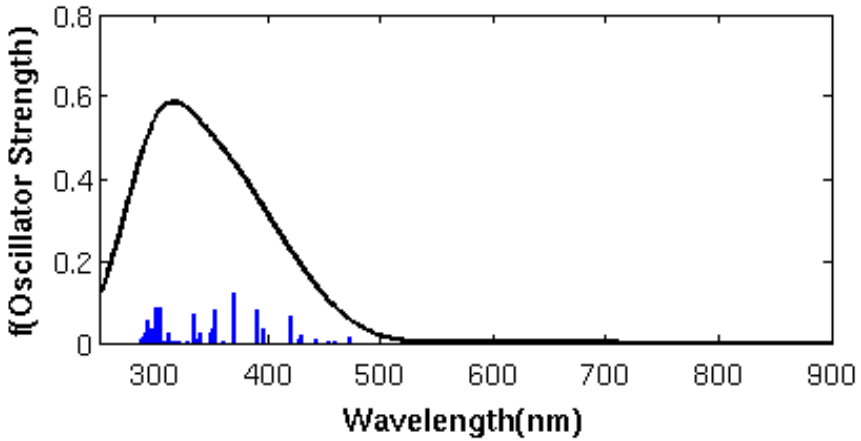
Integrating theoretical results and experimental expertise-2
Which properties?

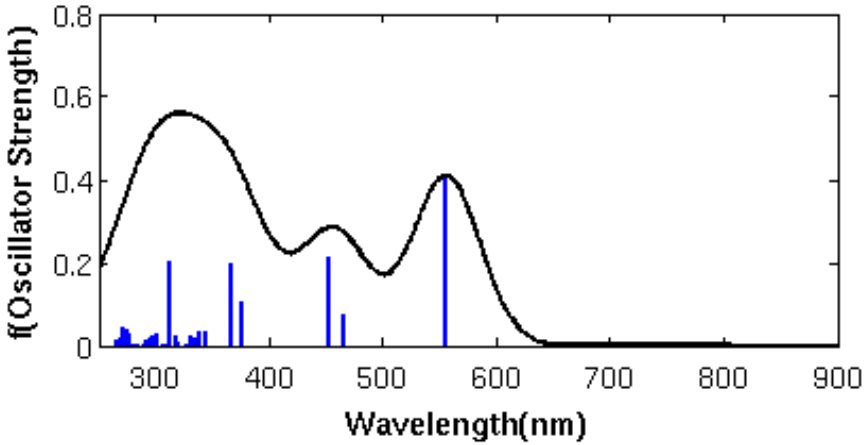
Structure dependent optical adsorption



ΔG=-0.34eV

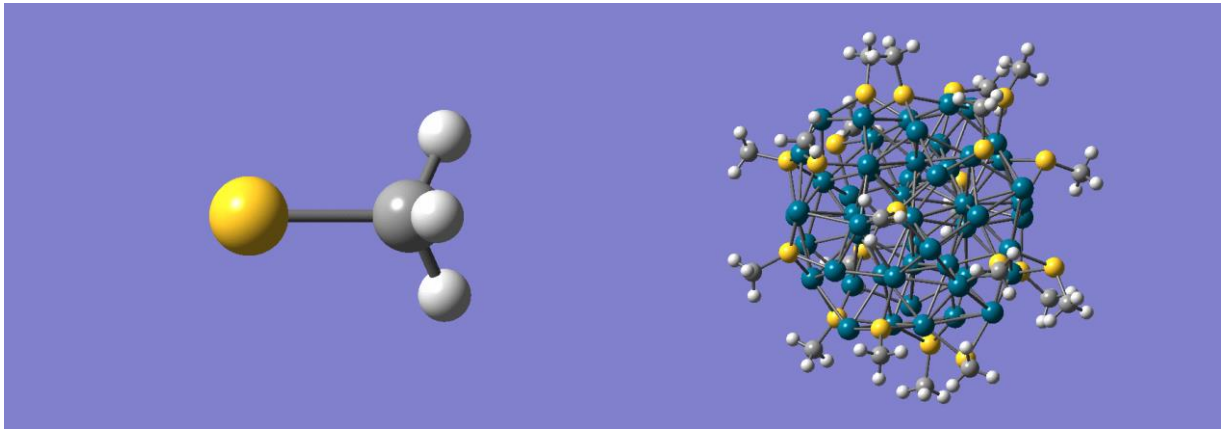






B. Fresch *et al.* *Eur. Phys. J. D* **2012,** *66* (12), 1-9.
F. Dufour *et al. J. Phys. Chem. C*, **2014**, 118 (8), pp 4362–4376.

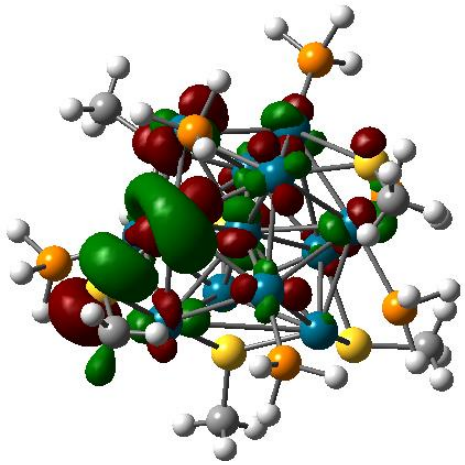
Vibrational Frequencies-IR spectra



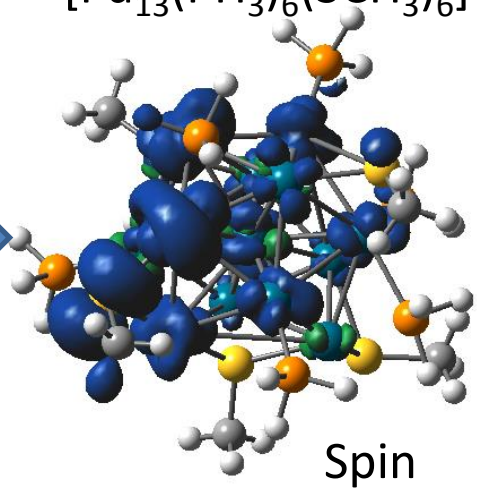
- ✓ S-C stretching frequencies: 712cm^{-1} versus 654cm^{-1} (weakening of the bond)

Ionisation potential, Electron Affinity, Charging Energy

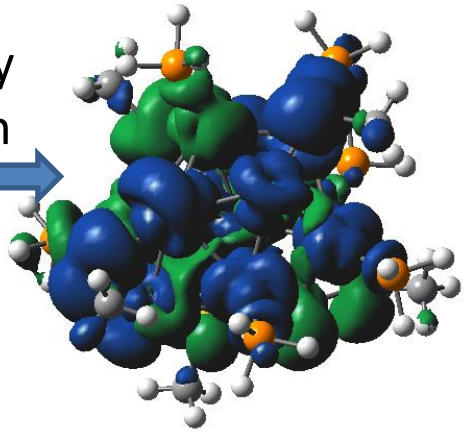
$Pd_{13}(PH_3)_6(SCH_3)_6$ → Vertical ionization → $[Pd_{13}(PH_3)_6(SCH_3)_6]^+$ → Geometry relaxation



HOMO



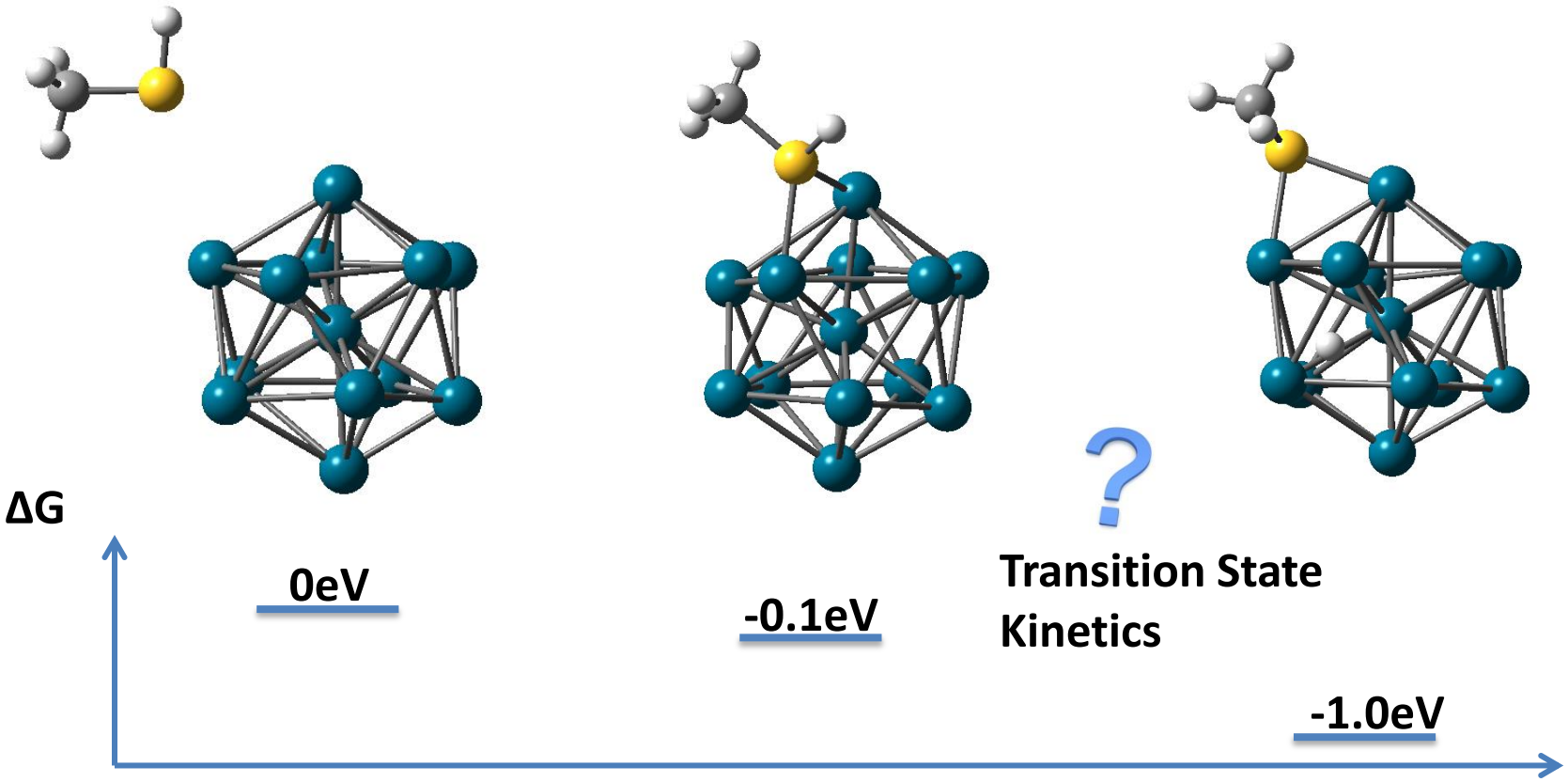
Spin Density



AIP=5.85eV

Directions of Research-1

Mechanism of Reactions



- ✓ Formation of molecular H_2?
- ✓ Sulfidation of the surface?

Barngrover, B. M.; J. Phys. Chem. A 2013, 117, 5377– 5384.
Askerka, M.; J. Phys. Chem. A 2012, 116, 7686– 7693

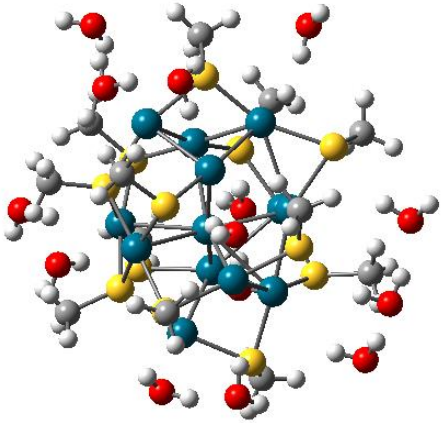
Directions of Research-2

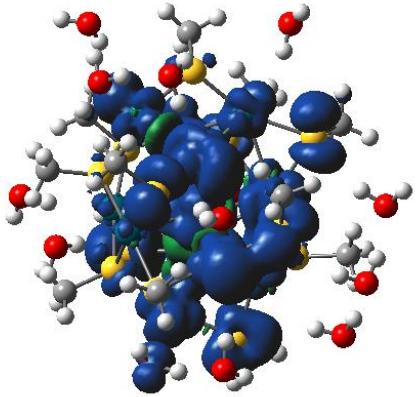
$Pd_{13}(SCH_3)_{12}(H_2O)_{14}$

Spin Density

Solvent

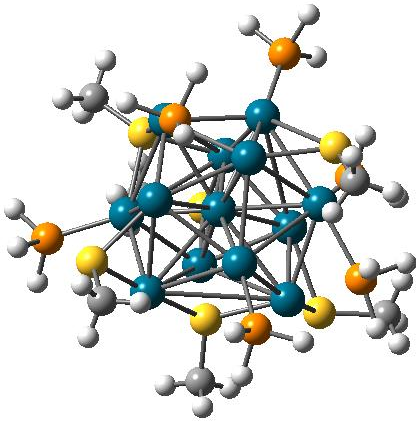
How it affects Properties?



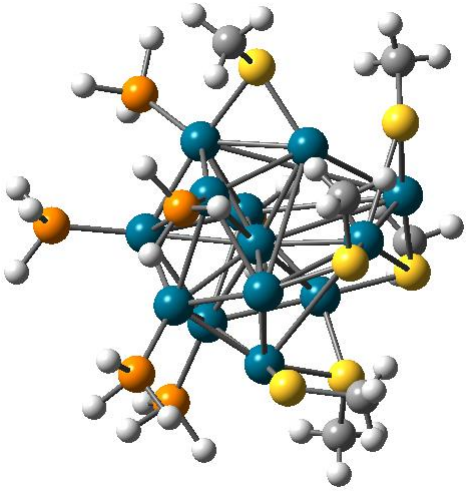


Spatial segregation of ligands

Is there a driving force allowing the synthesis of "Janus" clusters?



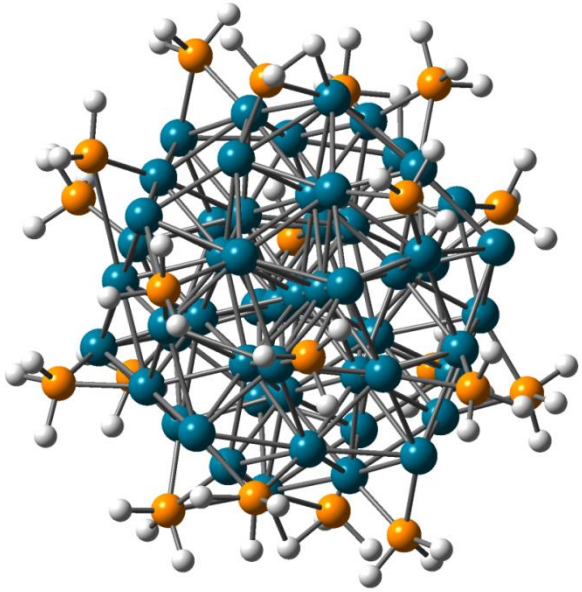
P:+1.58|e (0.26)
S: -0.64 |e (-0.11)
Pd: -0.94 |



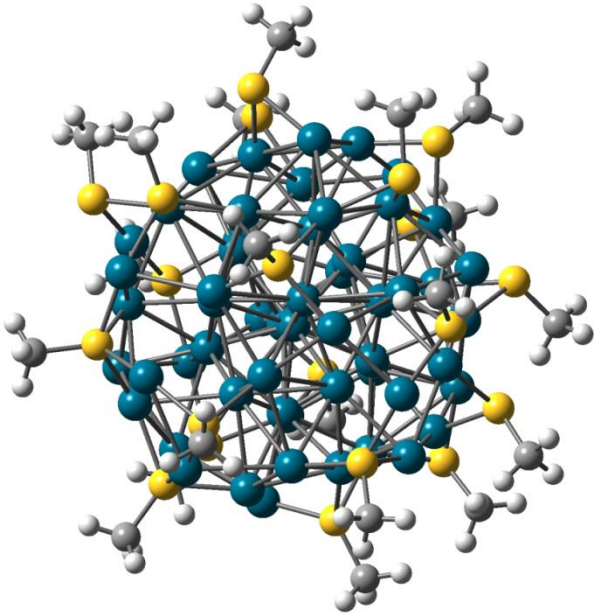
P:+1.31|e| (0.22)
S: -0.09|e| (-0.016)
Pd: -1.21 |e|

Truly nano-sized system?

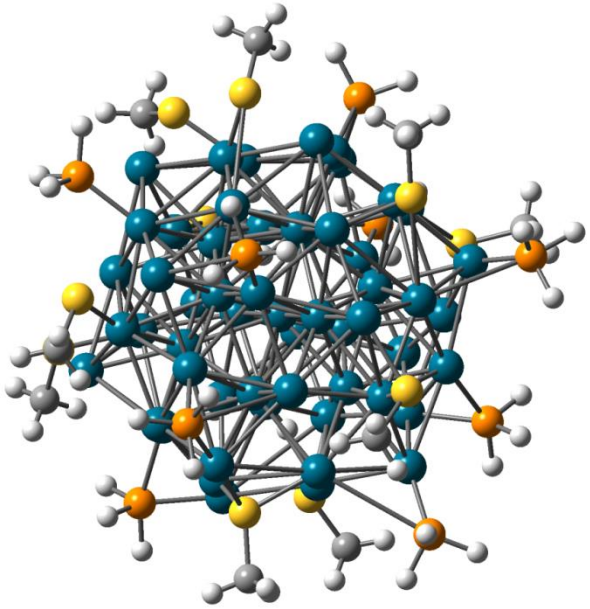
$Pd_{55}(PH_3)_{20}$



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

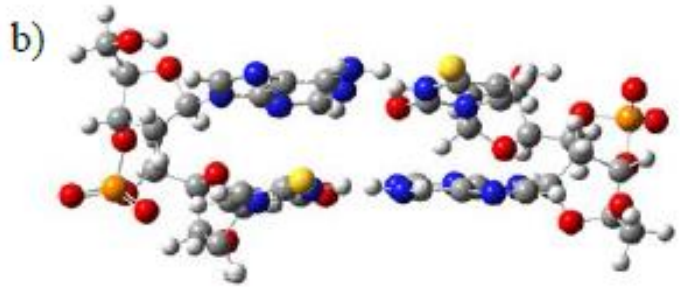


$Pd_{55}(PH_3)_{10}(SCH_3)_{10}$



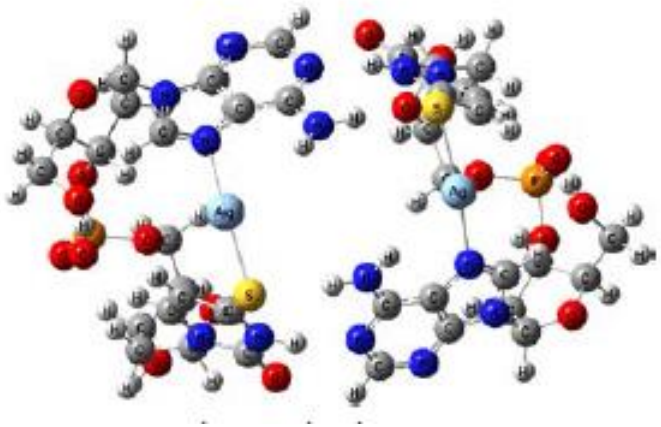
Metals (or Metallic clusters) in supra-molecular aggregates

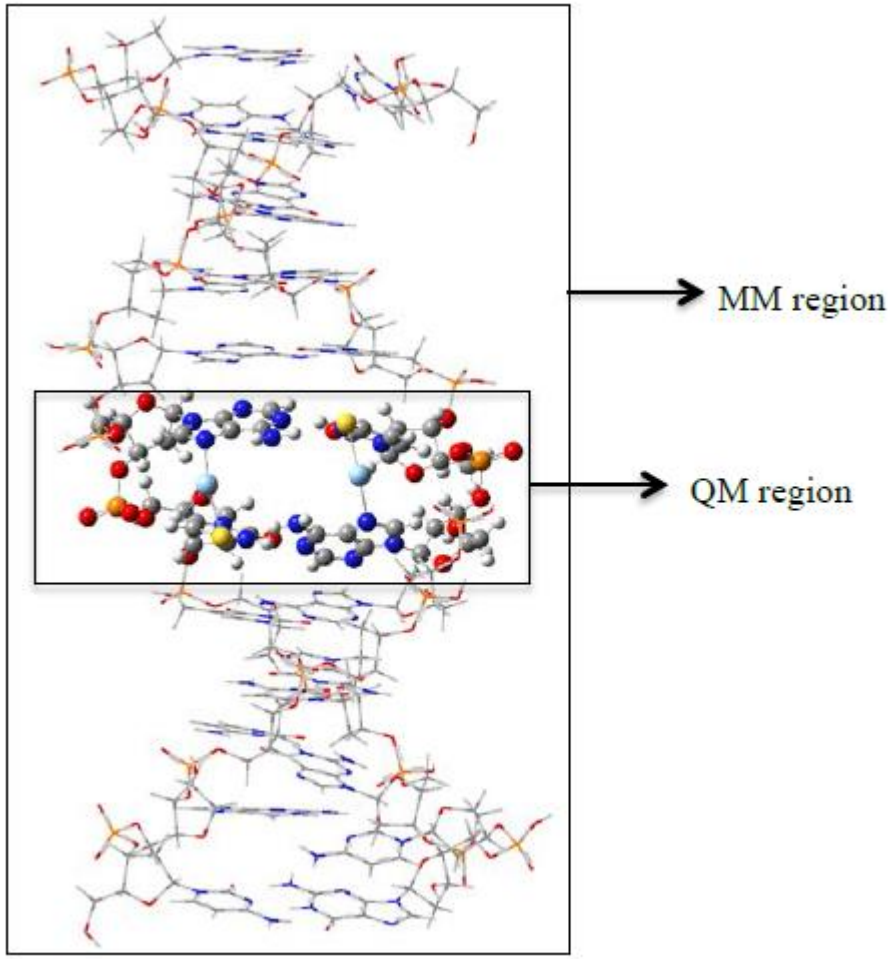
(Ph. Thesis, Dr. Renuka Ganesan)



Two modified base pairs (tio-uracil)

Interaction with
Silver cations



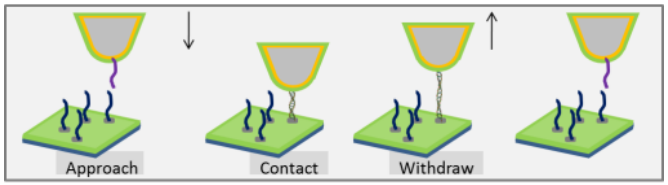


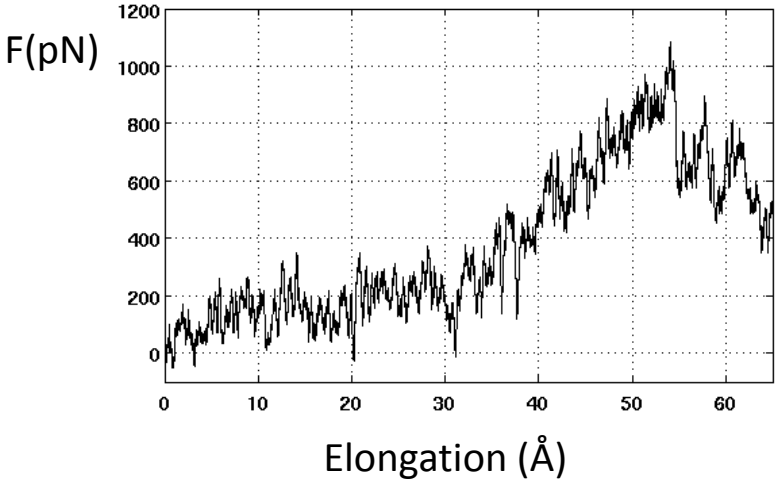
Hybrid QM/MM approach

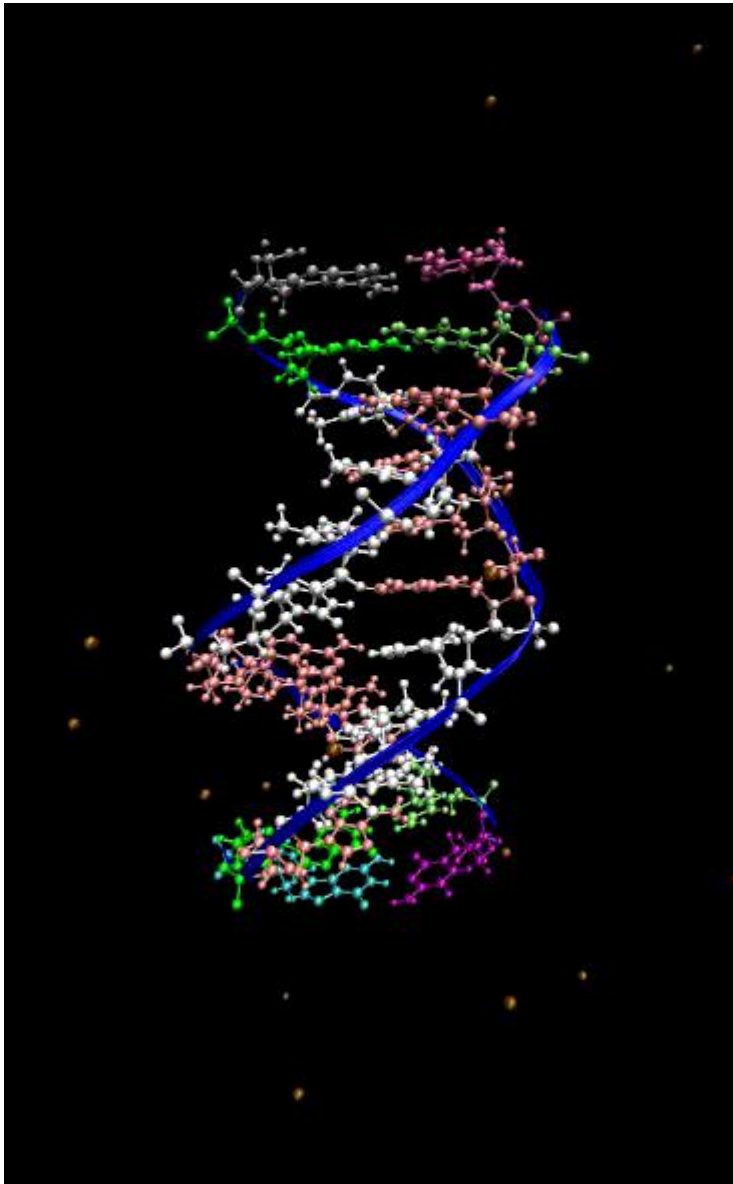
Exploring conformational space and Dynamics of molecular aggregates

- ✓ Classical Force Field
- ✓ Application of external forces

(nano-manipulation experiments)

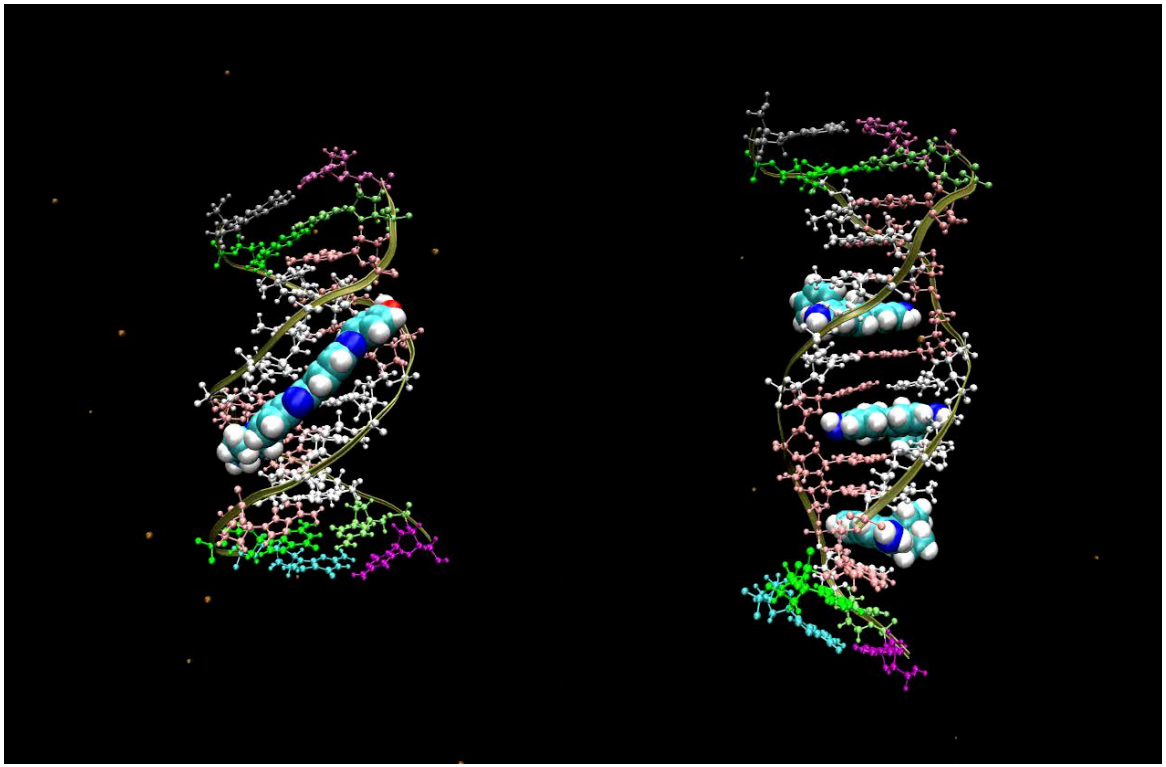






Exploring conformational space and Dynamics of molecular aggregates

- ✓ **Molecular recognition**



- ✓ **rather “big” systems, explicit solvation**
- ✓ **well developed for “all-organic” system (metals and surfaces can be modelled)**
- ✓ **transitions between different minima of the potential energy surface**

Laboratoire de Chimie Physique Théorique:
Prof. Francoise Remacle
Dr. Fabien Dufour
Dr. Renuka Ganesan
Benoit Mignolet
Gustavo Lugo
Dr. Mike Klymenko
Dr. Tian Min Yan

ARC-NANOFORCE project

MULTI
TOLOP

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