

**Universidad Politécnica
de Chiapas**

High Performance computing on the study of electronic properties of materials implemented in Renewable Energy

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Universidad Politécnica de Chiapas*

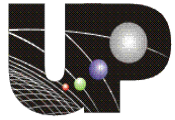
*Calle Eduardo J. Selvas S/N, Col. Magisterial, Tuxtla
Gutiérrez,
Chiapas, México. C.P. 29010*



Organization of
American States

Chiapas Seminar, May 2014

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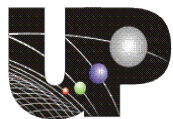


Universidad Politécnica de Chiapas.

Suchiapa

Centro de Investigación y
Desarrollo Tecnológico en
Energías Renovables, CIDTER





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Outline

- I. Introduction
- II. Computational methods
- III. Discussion of the title complexes
 - III.1 Electronic structure
 - III.2 Excited states
- IV. Summary



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What is high performance computing?

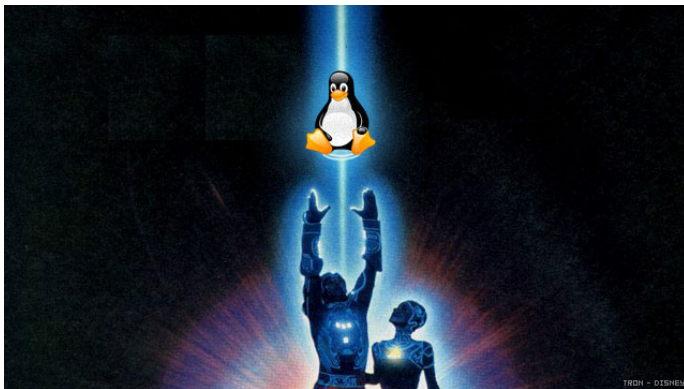
We're stronger if we stick together





NERSC's Edison

2.57 PetaFlops
≈130,000 processors



Linux OS

What is high performance computing?

Computer aided engineering (CAE): Automotive design and testing, transportation, structural, mechanical design

✓ Digital content creation (DCC) and distribution: Computer aided graphics in film and media

✓ Economics/financial: Wall Street risk analysis, portfolio management, automated trading

✓ Electronic design and automation (EDA): Electronic component design and verification

✓ Geosciences and geo-engineering: Oil and gas exploration and reservoir modeling

✓ Mechanical design and drafting: 2D and 3D design and verification, mechanical modeling

✓ Defense and energy: Nuclear stewardship, basic and applied research

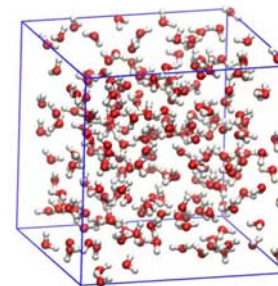
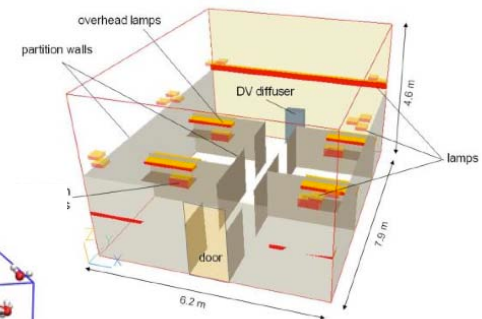
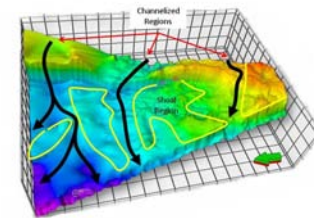
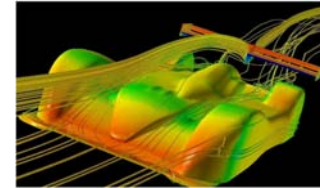
✓ Government labs: Basic and applied research

✓ University/academic: Basic and applied research

✓ Weather forecasting: Near term and climate/earth modeling

✓ Architectural engineering: Sustainable Building Design

✓ Chemical engineering: Process and molecular design

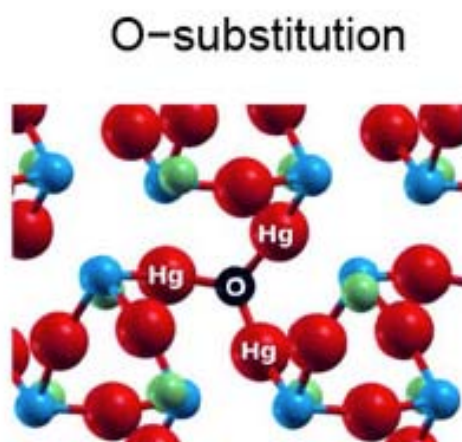
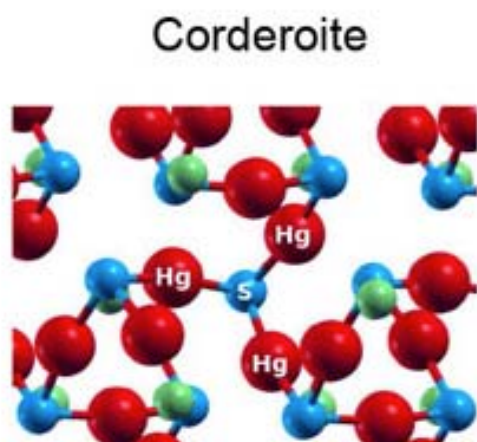


HPC and Art

Baroque art. Peter Paul Rubens



HPC and molecular simulations



Cinnabar

K Keune and J J Boon, *Anal. Chem.*, 2005, 77, 4742

I. Introduction

Renewable energy materials



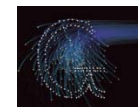
II. Computational methods

Density Functional Theory

Moller – Plesset at second order (MP2)

Calculations performed on:

Gaussian 09



Turbomole



Amsterdam Density Functional
(ADF)

FHI-aims

High Performance Computing at UPChiapas



27.65 TeraFlops



Collaboration with other institutions

Instituto de Investigaciones en Materiales, UNAM



Center of Scientific Computing (CSC-Finland)



CSC – IT Center for Science

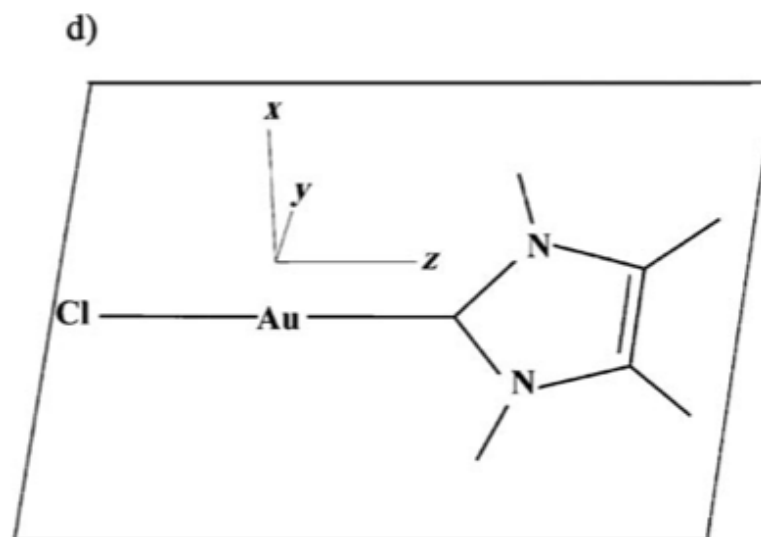
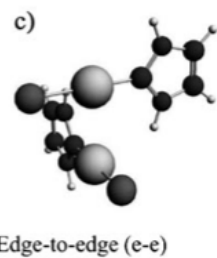
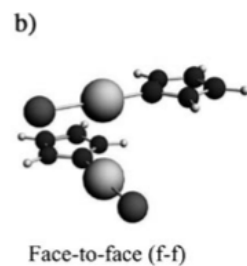
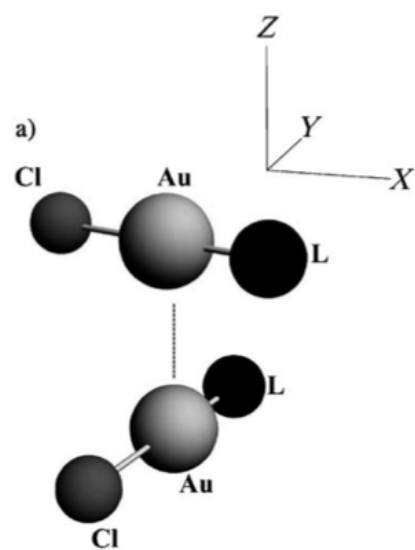
Fritz-Haber Institute, Max Planck Society



MAX-PLANCK-GESellschaft

Effect of the neutral ligand L on $[\{ClAuL\}_2]$ Systems

From Hamiltonians to Lab: Hydrogen storage materials



Intramolecular coordinates for Cl-Au-(NHC-H)

Muñiz, J., Wang C., Pyykko P. Chem. Eur. J. 2011, 17, 368 – 377



Dispersion(London-type) interactions

$$\Delta E_{\text{disp}}^{(2)} \approx -\frac{1}{4} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_{XX}^A \alpha_{XX}^B + \alpha_{YY}^A \alpha_{YY}^B + 4\alpha_{ZZ}^A \alpha_{ZZ}^B}{R^6}$$

$$\Delta E_{\text{disp}}^{(2)} \approx -\frac{3IP_1}{4R^6} \left[\alpha^2 - \frac{1}{3} \alpha (\alpha_{\parallel} - \alpha_{\perp}) \right]$$

Buckingham's expression

$$\Delta E_{\text{disp}}^{(2)} \approx -\frac{3IP_1}{4R^6} \alpha^2$$

Spherical Symmetry

$$\Delta E_{\text{ind},A \rightarrow B}^{(2)} = -\frac{1}{2} \frac{|d_X^A|^2 \alpha_{XX}^B + |d_Y^A|^2 \alpha_{YY}^B + 4|d_Z^A|^2 \alpha_{ZZ}^B}{R^6}$$

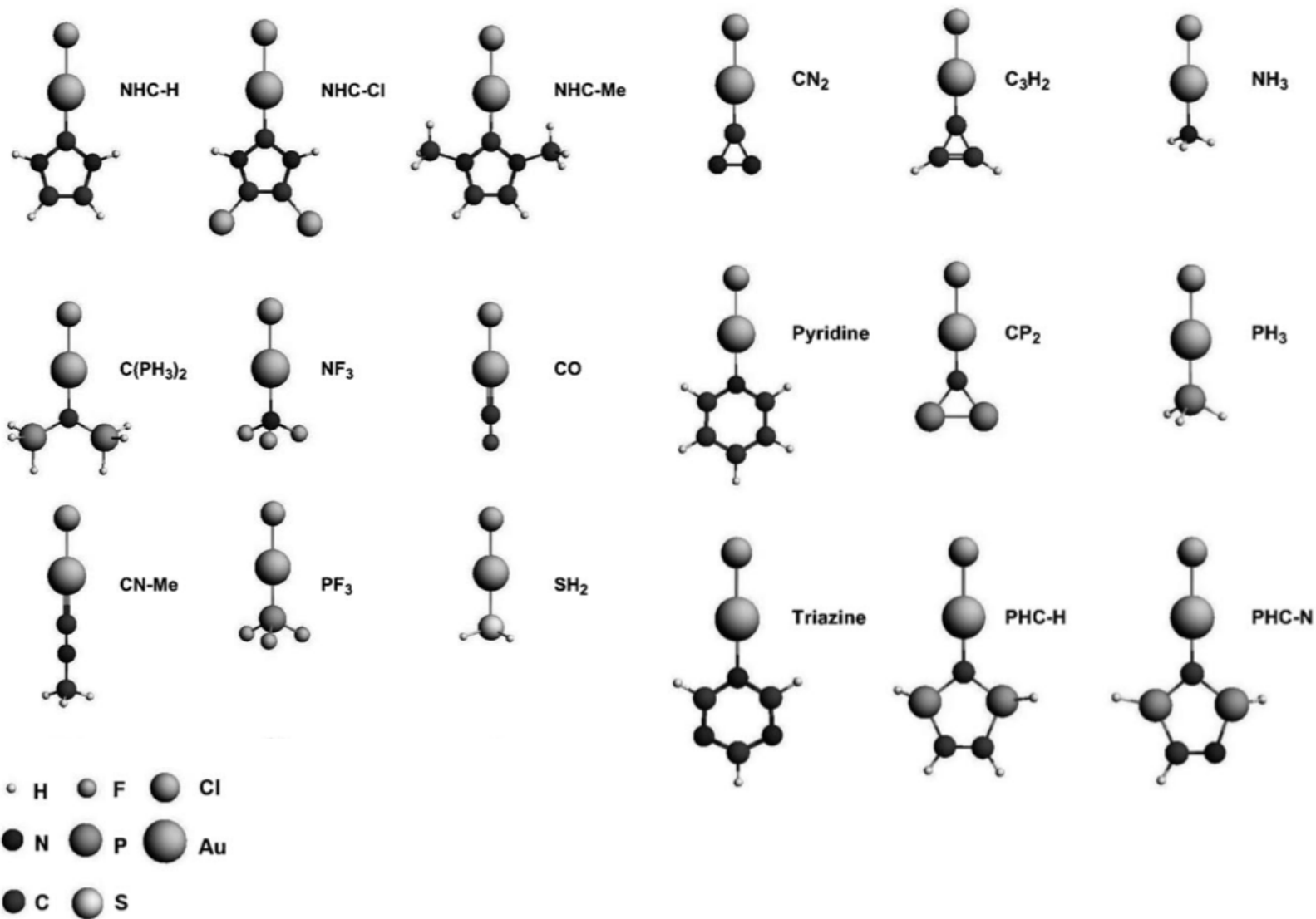
Induction Terms (C_{2v} symmetry)

$$\Delta E_{\text{ind},B \rightarrow A}^{(2)} = -\frac{1}{2} \frac{|d_X^B|^2 \alpha_{XX}^A + |d_Y^B|^2 \alpha_{YY}^A + 4|d_Z^B|^2 \alpha_{ZZ}^A}{R^6}$$

$$\Delta E_{QQ}^{(1)} = \frac{1}{R^5} \left\{ 6Q_{ZZ}^A Q_{ZZ}^B - \frac{16}{3} (Q_{XZ}^A Q_{XZ}^B + Q_{YZ}^A Q_{YZ}^B) \right. \\ \left. + \frac{1}{3} [(Q_{XX}^A - Q_{YY}^A)(Q_{XX}^B - Q_{YY}^B) + 4Q_{XY}^A Q_{XY}^B] \right\}$$

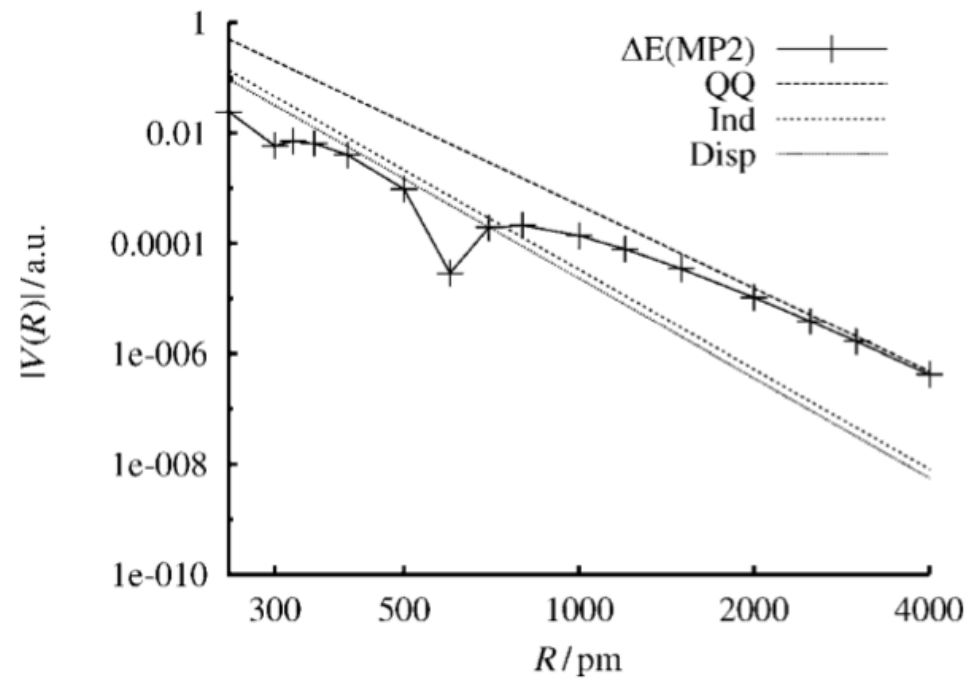
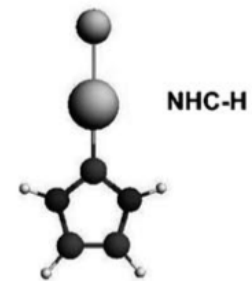
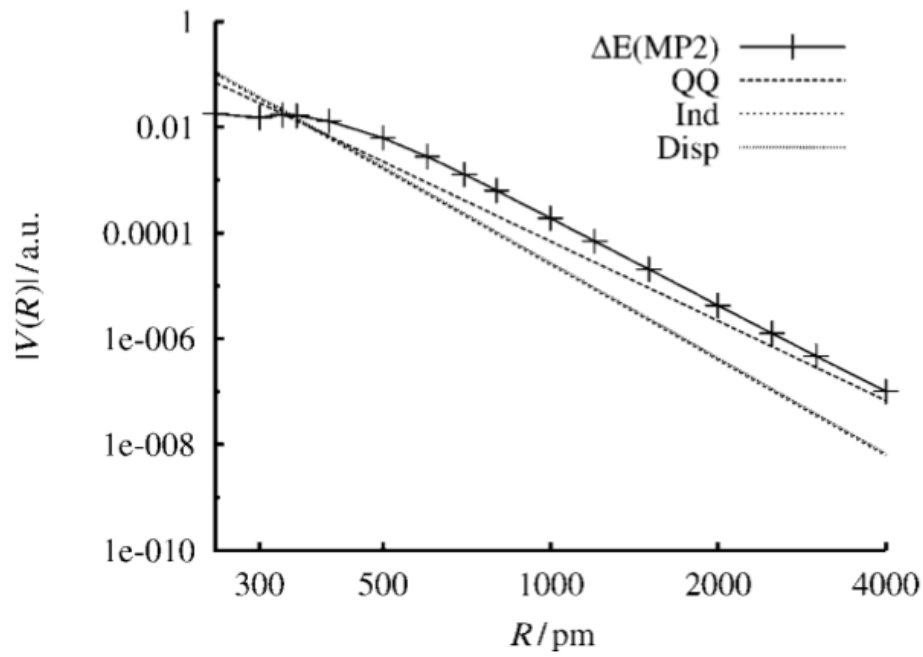
Quadrupole-Quadrupole electrostatic interactions

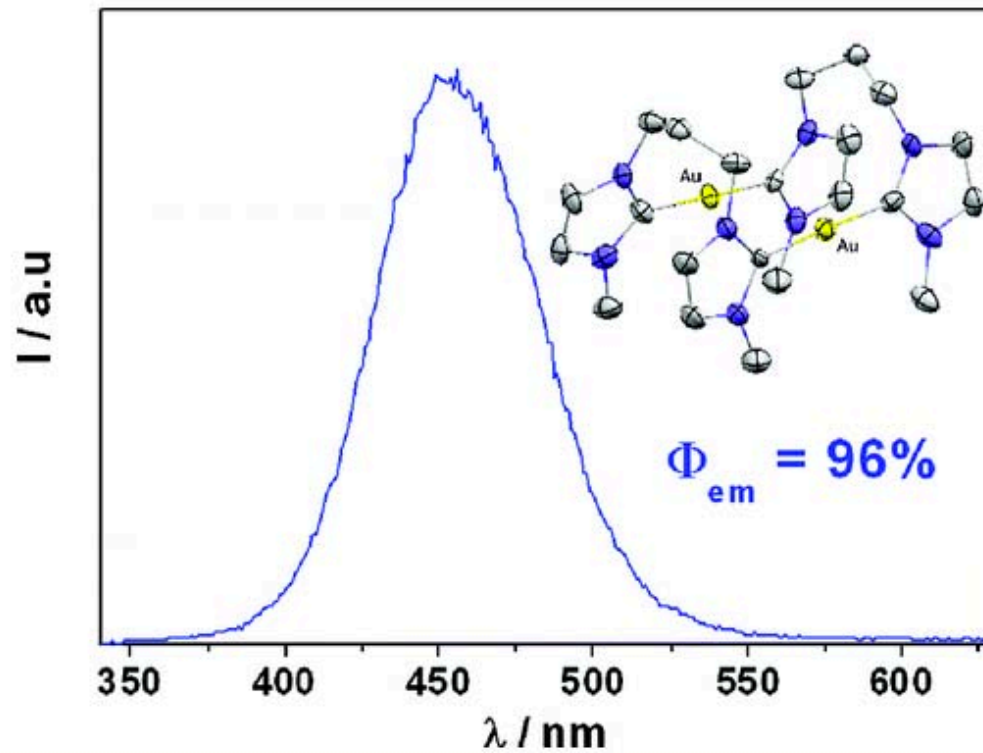




Muñiz, J., Wang C., Pyykko P. Chem. Eur. J. 2011, 17, 368 – 377

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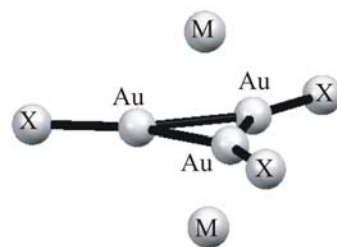
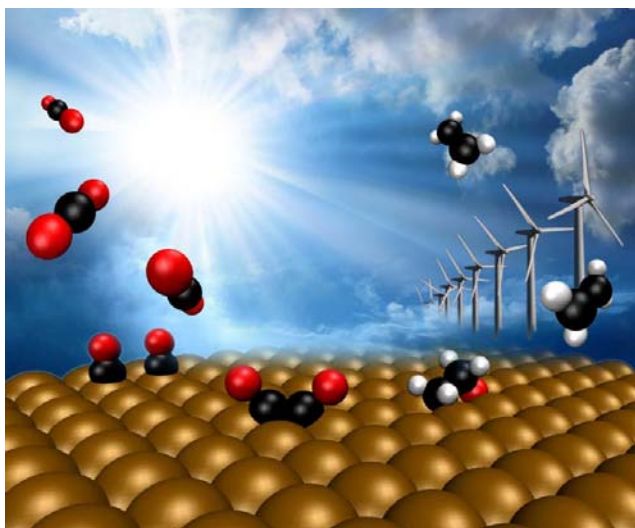


- Luminescent materials
- Electroluminescent devices

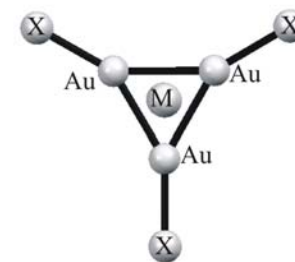
Blue-Emitting Dinuclear N-heterocyclic Dicarbene Gold(I) Complex Featuring a Nearly Unit Quantum Yield. *Inorg. Chem.* 2012, 51, 1778.

[Au₃X₃M₂], with
 X=H,F,Cl,Br, I and
 M=Li,Na,K,Rb,Cs

Heterogeneous Catalysis



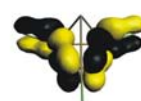
[Au₃X₃M₂]



Top view



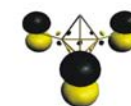
HOMO -13



HOMO -12

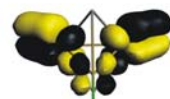


HOMO -7

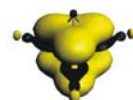


HOMO -3

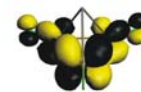
Au₃Cl₃Li₂



HOMO -12



HOMO -11



HOMO -8



HOMO -6

Au₃F₃Li₂



HOMO -9



HOMO -8

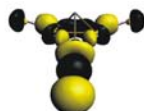


HOMO -5



HOMO -3

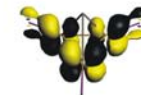
Au₃H₃Li₂



HOMO -12



HOMO -10



HOMO -7

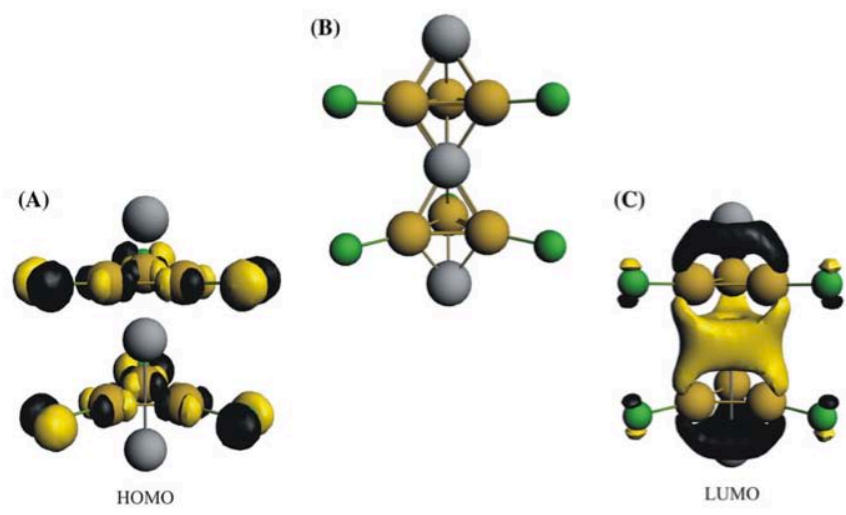
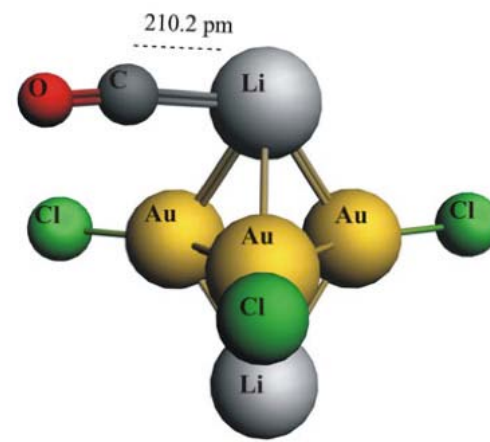
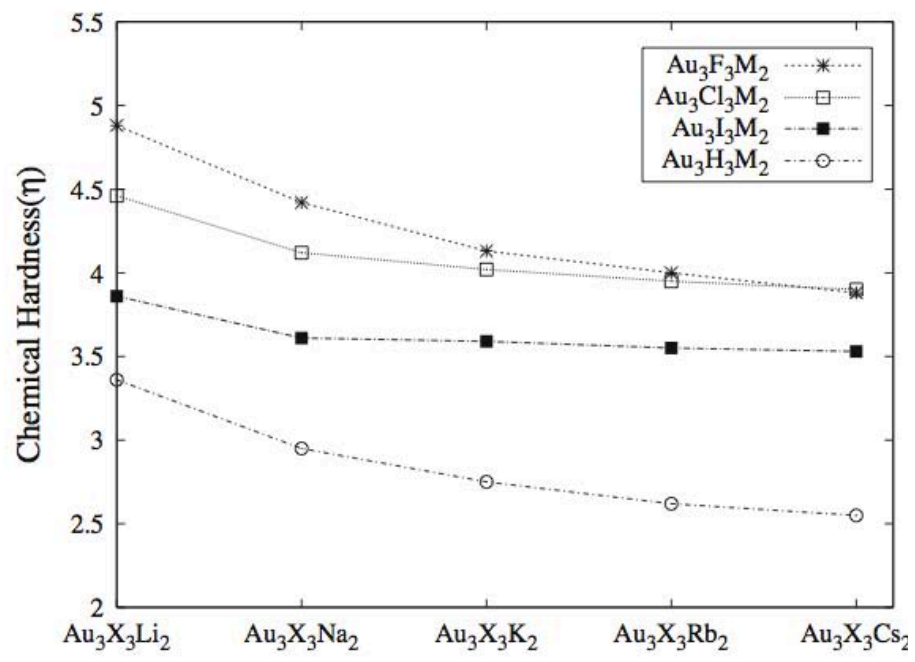


HOMO -4

Au₃I₃Li₂

J. Muñiz, E. Sansores, R.
 Castillo. Theo. Chem. Acc.
 2013, 132:1373

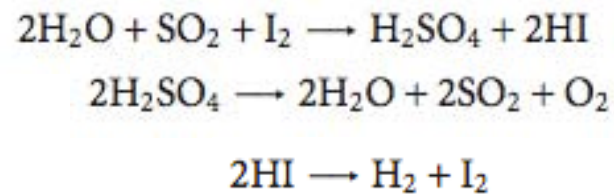
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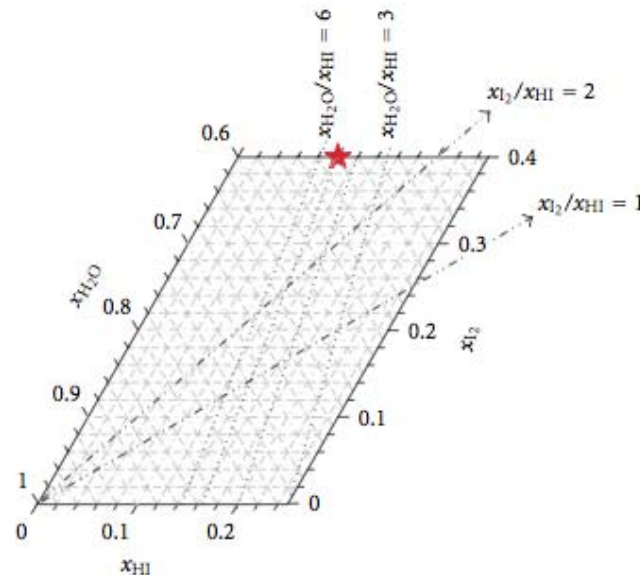
First Observation of Defined Structural Motifs in the Sulfur-Iodine Thermochemical Cycle and Their Role in Hydrogen Production

Raman and Inelastic Neutron scattering

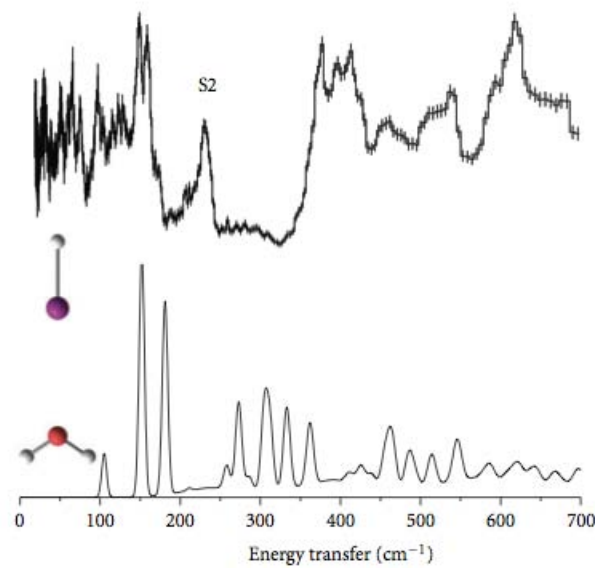
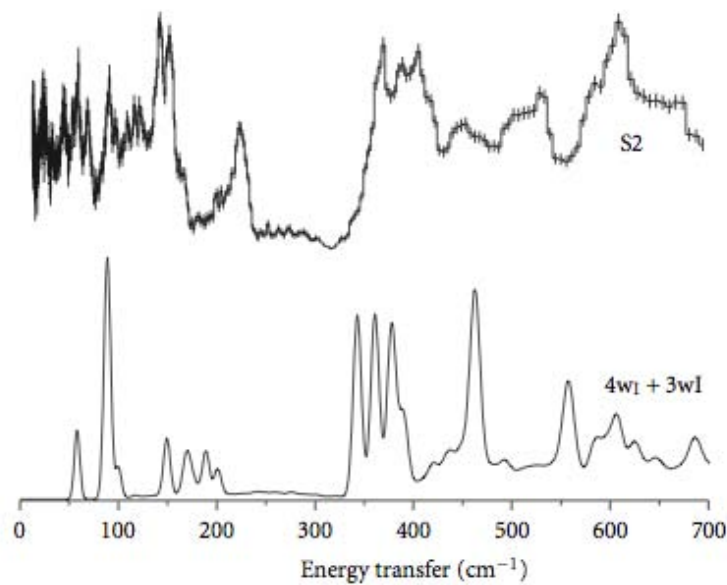
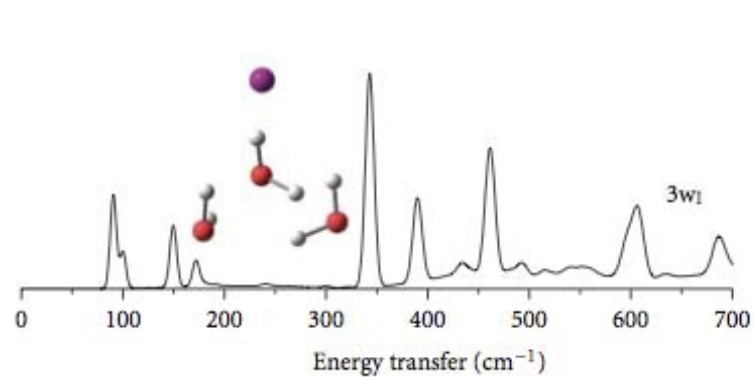
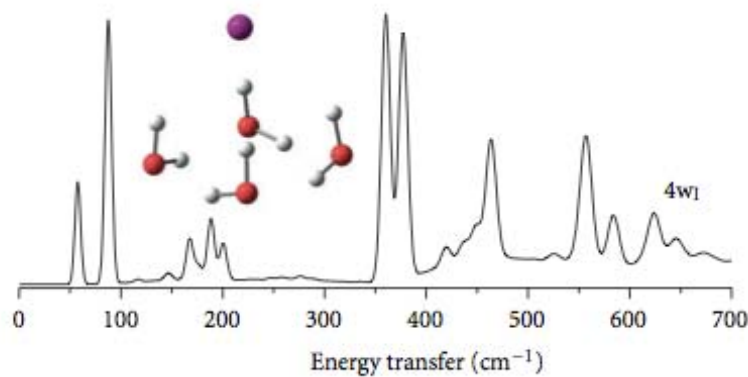
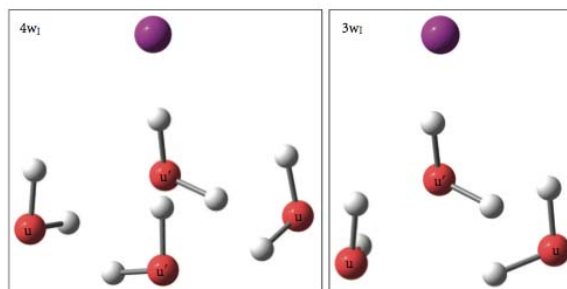
MP2 methodology to model the HI species in the TC.
Thermochemical cycle:

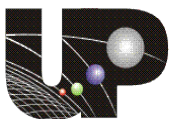


V. Ramos Sánchez, R. Devonshire,
J. Muñiz, E. Valenzuela, Int. J.
Spect. Volume 2011, Article ID
691217



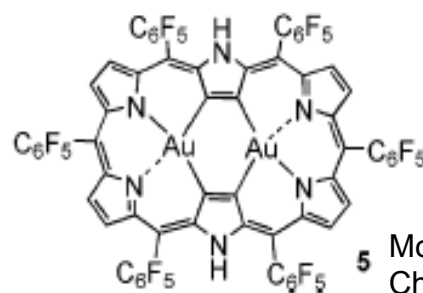
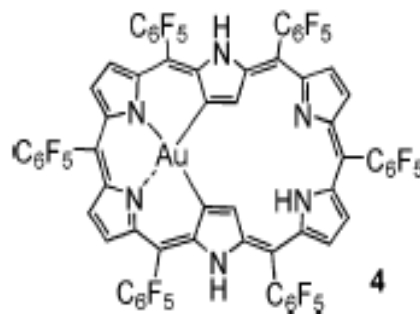
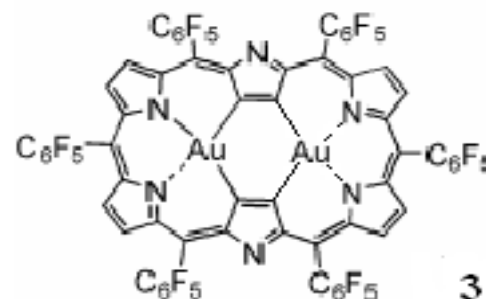
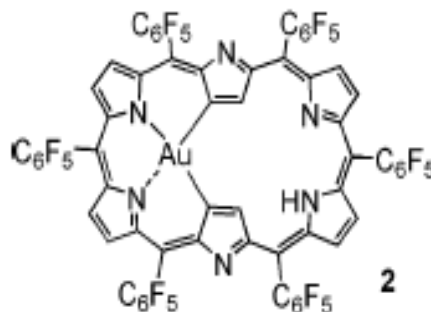
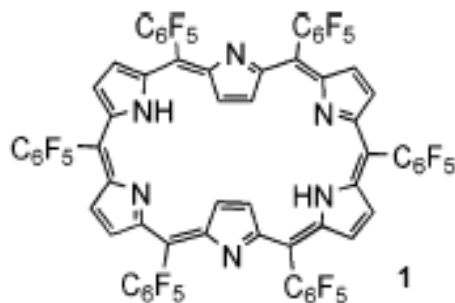
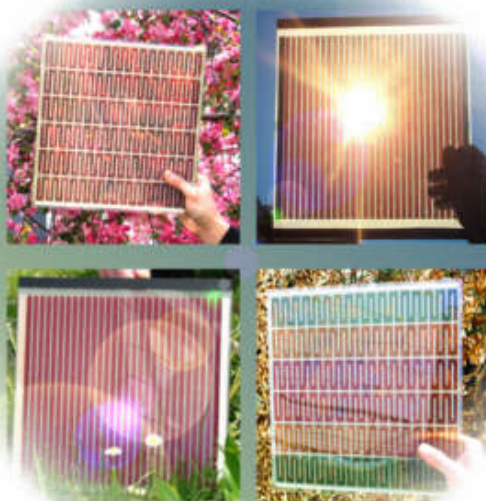
Theoretical spectrum vs experimental INS spectrum





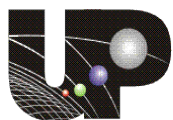
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Aromaticity in the building of nanohybrid materials

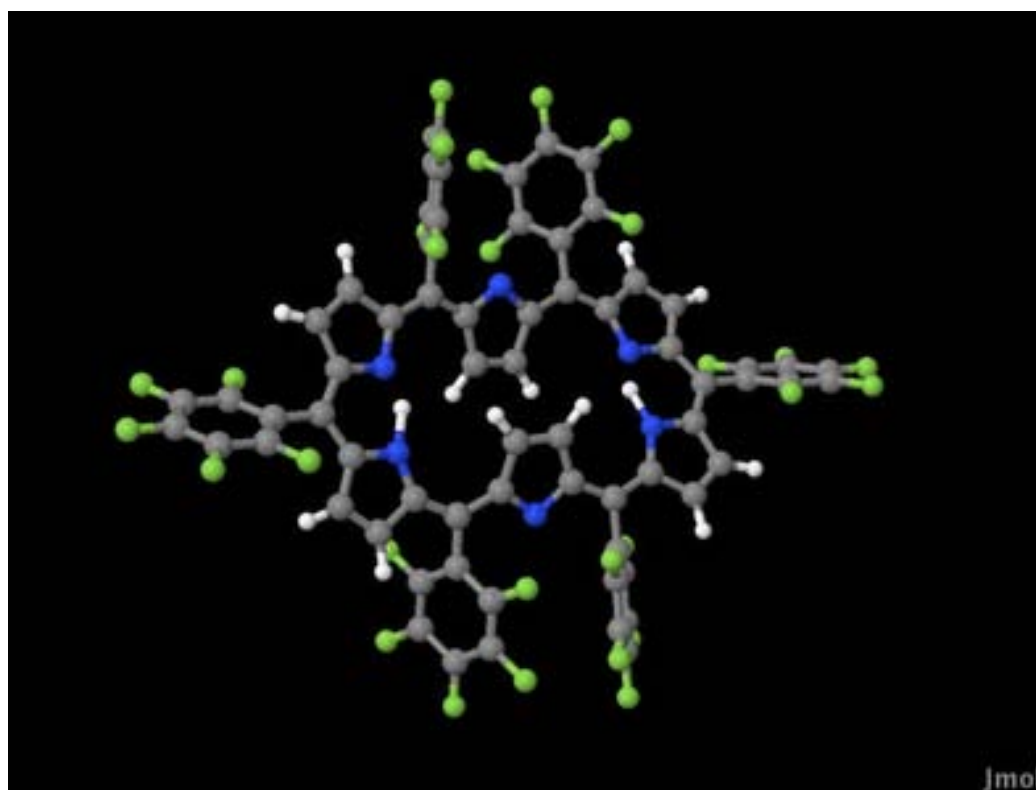


Meso-hexakis
(pentafluorophenyl)-
substituted[26] hexaphyrin
(1.1.1.1.1.1)

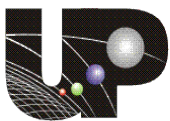
Mori S., Osuka A.; J. Am.
Chem. Soc. 127 (2005) 8030.



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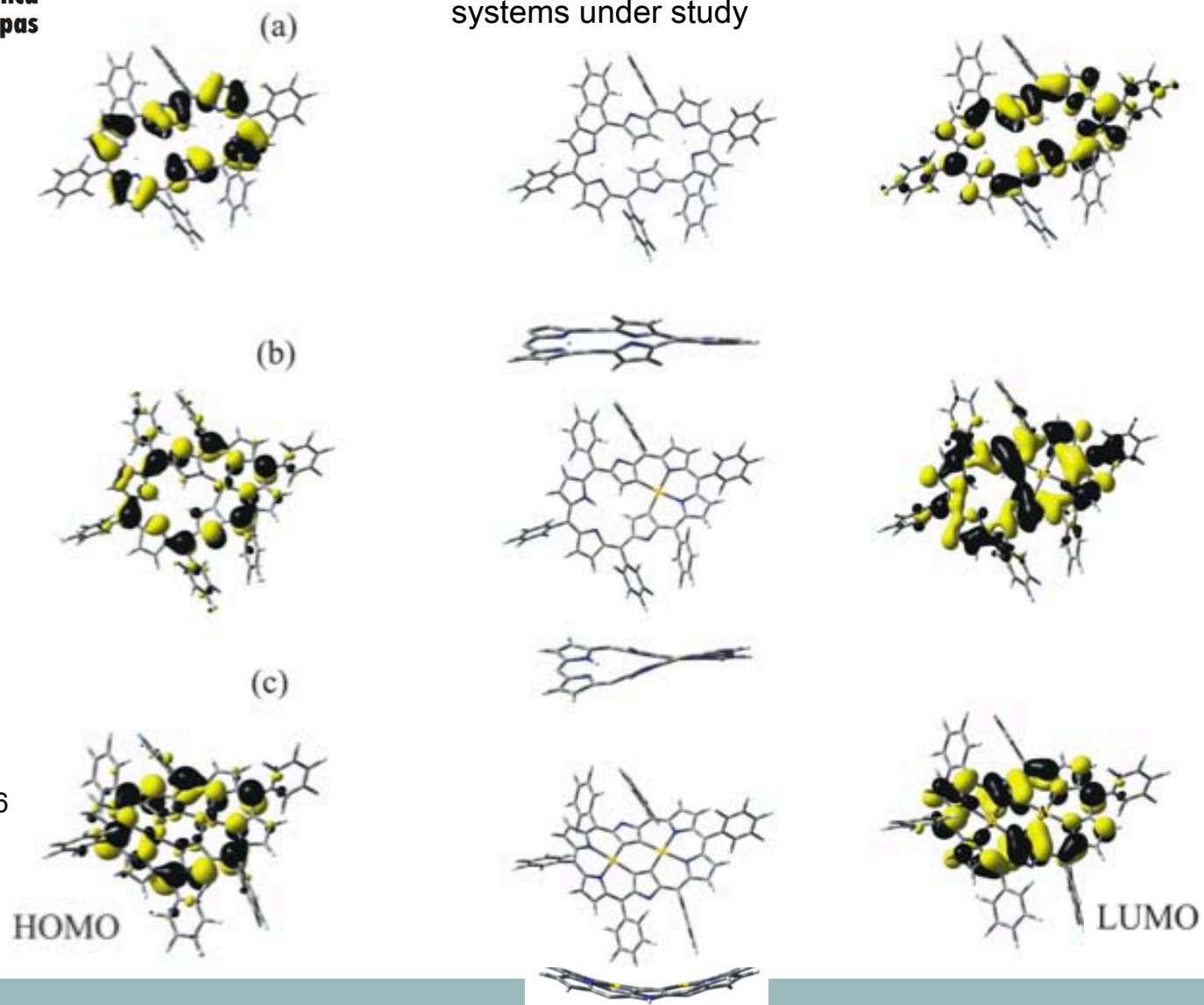


meso-hexakis(pentafluorophenyl)-substituted[26]
hexaphyrin(1.1.1.1.1.1)

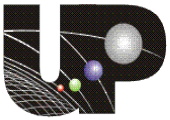


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Spatial representation and Frontier Molecular Orbitals of the
systems under study



Int. J. Quant.Chem,
(2013)113,1034-1046

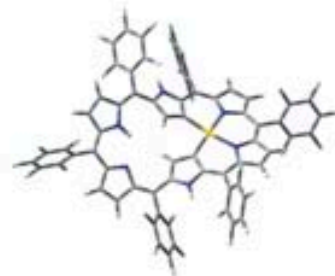


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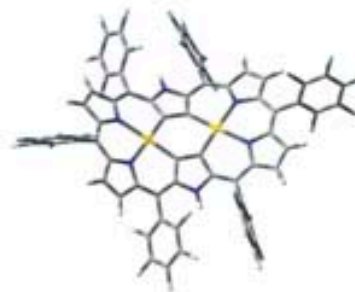
Spatial representation and Frontier Molecular Orbitals of the
systems under study



(e)



HOMO



LUMO

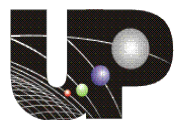
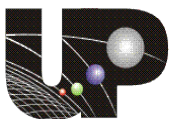


Table 1 Bond lengths and angles for the compounds under study

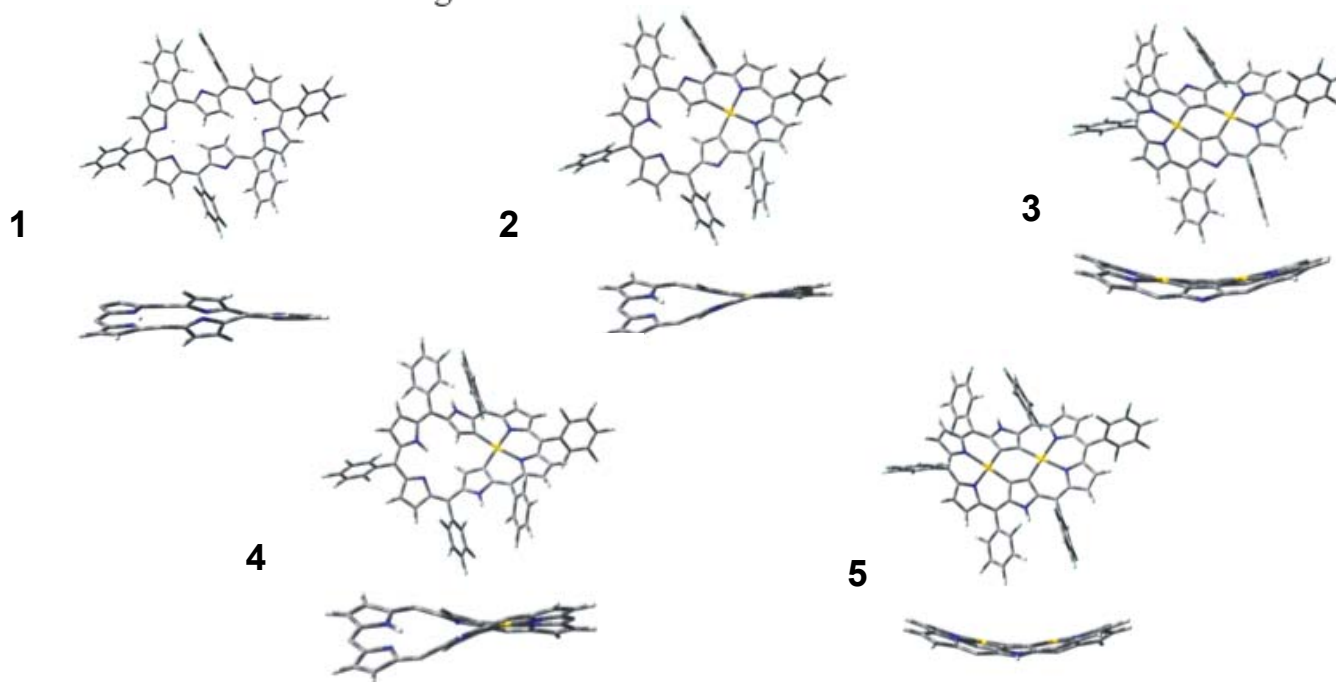
Bond	Experimental	Theory	Bond angle	Angle (deg.) Experiment	Angle (deg.) Theory
Bond lengths and angles for complex 1					
N1-C5	1.37	1.42	C7-N3-C8	105.23	104.06
N2-C9	1.38	1.42	C9-C15-N6	127.00	130.09
C5-C6	1.41	1.43	C11-N4-C12	107.74	104.19
C9-C10	1.38	1.43	C12-C13-C14	127.46	129.58
N3-C7	1.38	1.40	C13-C14-N5	126.65	130.28
Bond lengths and angles for complex 2					
Au1-C1	1.98	2.03	C1-Au1-C2	91.44	91.82
Au1-C2	2.01	2.03	N1-Au1-N2	88.88	88.67
Au1-N1	2.08	2.13	C5-N1-Au1	126.72	126.11
Au1-N2	2.08	2.13	C7-C2-Au1	124.16	122.82
N1-C5	1.37	1.38	N2-Au1-C1	90.73	90.37
Bond lengths and angles for complex 3					
Au1-Au2	4.22	4.21	C1-Au1-C2	88.57	89.74
Au2-C3	2.04	2.03	N1-Au1-N2	86.54	86.30
Au2-C4	2.02	2.03	C3-Au2-C4	88.98	89.74
Au2-N5	2.11	2.14	N6-Au2-N5	87.02	86.30
Au2-N6	2.10	2.14	C5-N1-Au1	126.28	125.58
Bond lengths and angles for complex 4					
Au1-C1	1.98	2.02	C1-Au1-C2	91.44	91.98
Au1-C2	2.01	2.02	N1-Au1-N2	88.88	89.07
Au1-N1	2.08	2.11	C5-N1-Au1	126.72	125.65
Au1-N2	2.08	2.11	C7-C2-Au1	124.16	122.62
N1-C5	1.37	1.40	N2-Au1-C1	90.73	90.40
Bond lengths and angles for complex 5					
Au1-Au2	4.22	4.26	C1-Au1-C2	88.57	89.48
Au2-C3	2.04	2.03	N1-Au1-N2	86.54	85.92
Au2-C4	2.02	2.03	C3-Au2-C4	88.98	89.48
Au2-N5	2.11	2.13	N6-Au2-N5	87.02	85.92
Au2-N6	2.10	2.12	C5-N1-Au1	126.28	125.32

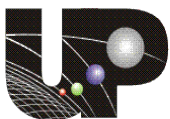


Aromatic and Aromatic character of the complexes under study

Compound [§]	1	2	3	4	5
NICS1(ppm)	-11.77				
NICS2(ppm)	-14.89	-12.33	-10.16	18.74	34.41
NICS3(ppm)	-11.97	-11.94		21.55	

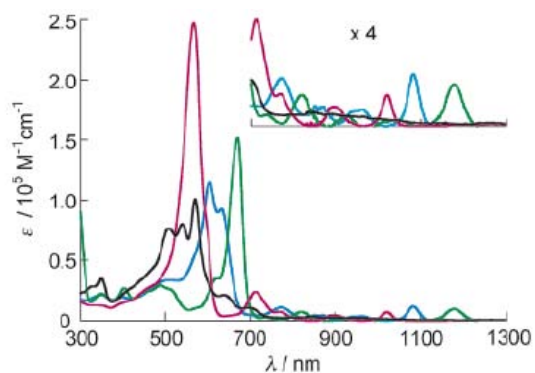
[§] NICS1 is at the left side of the geometrical center of the ring, NICS2 is at the geometrical center of the ring and NICS3 is at the right side of the center of the ring.





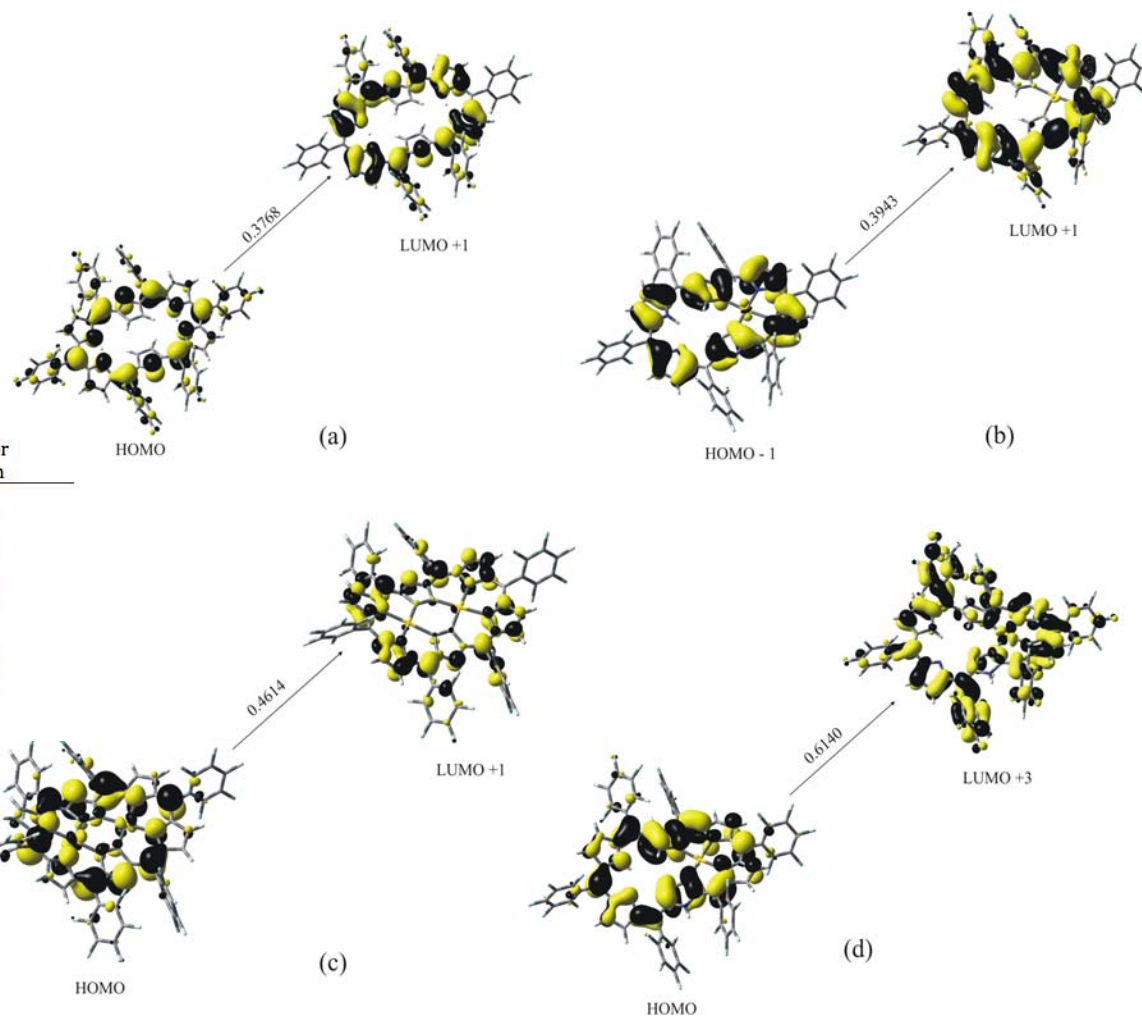
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Excited States calculations to understand the Absorption bands

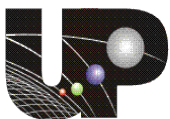


Model	Multiplicity	Energy (eV)	Wavelength (nm)	Oscillator strength
Aromatic compounds				
1. Hexaphyrin	Singlet	2.05	603.4 (550)*	0.8501
2. H. 1 Au atom	Singlet	1.98	625.8 (610)	0.2228
3. H. 2 Au atoms	Singlet	1.97	630.1 (680)	0.4493
4. H. 2 Ag atoms	Singlet	1.79	691.0	0.3031
5. H. 2 Cu atoms	Singlet	1.81	683.1	0.0918
Antiaromatic compounds				
1. H. 1 Au atom	Singlet	2.19	566.7	0.0102
2. H. 2 Au atoms	Singlet	1.96	630.8 (530)	0.0467

* Experimental data



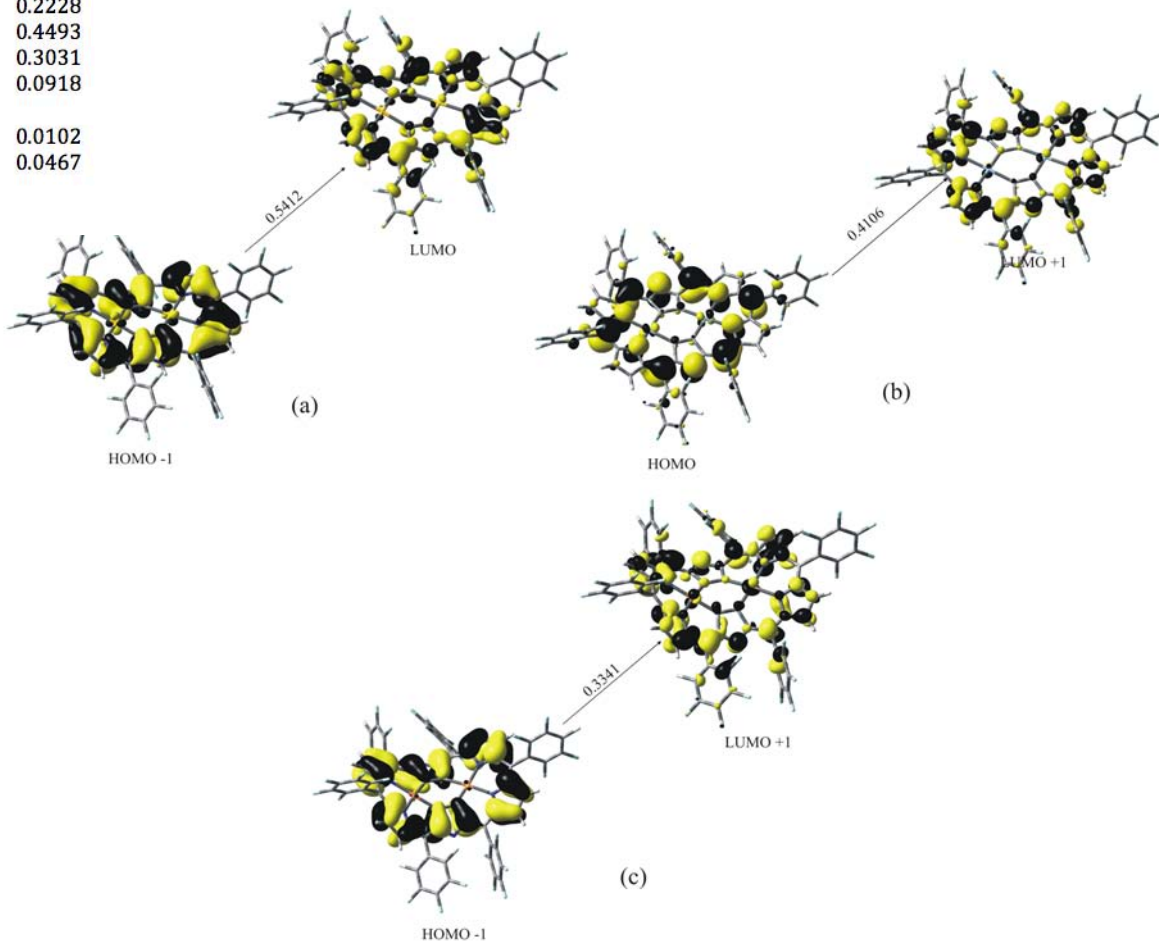
Int. J. Quant.Chem,
(2013)113,1034-1046

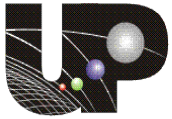


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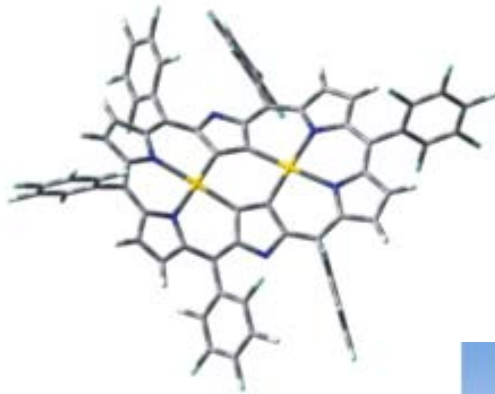
* Experimental data





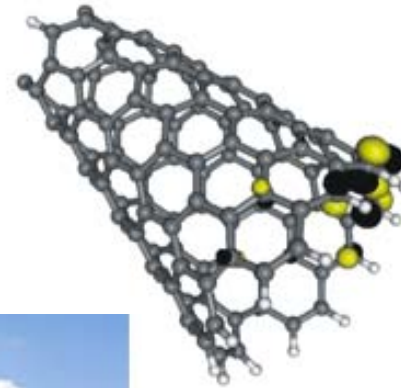
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Building of nanohybrid structured material
intended for Renewable energy applications: Solar cell material



Hexaphyrin

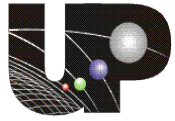
+



Carbon NanoHorn
(CNH)



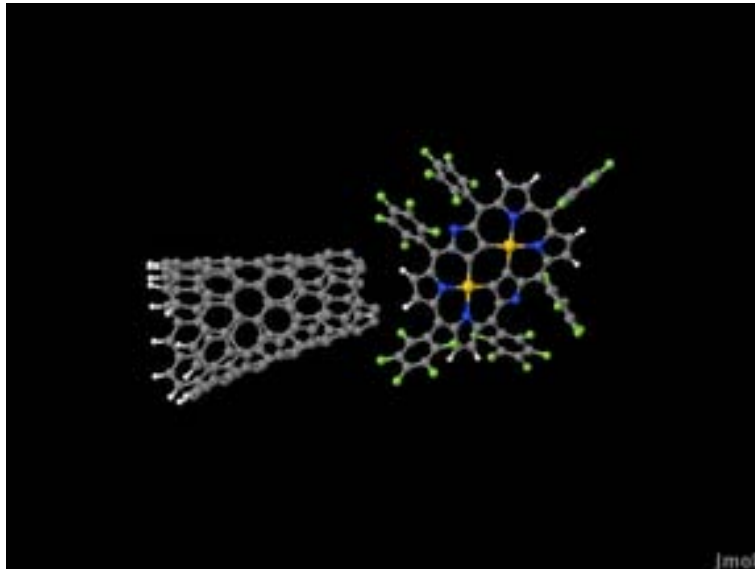
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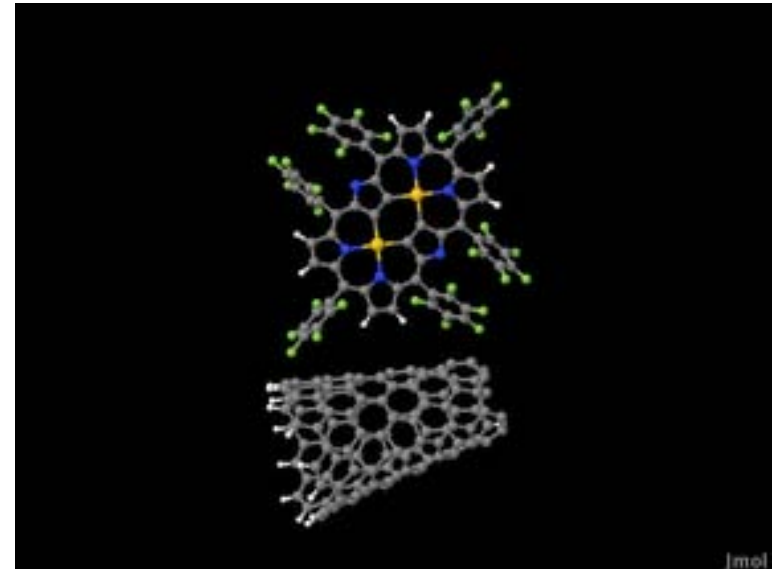
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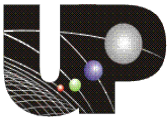
Modeling the interaction

CNH head to Hexaphyrin model

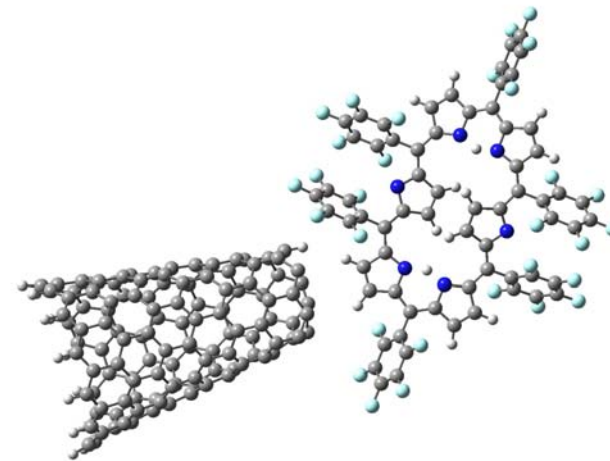
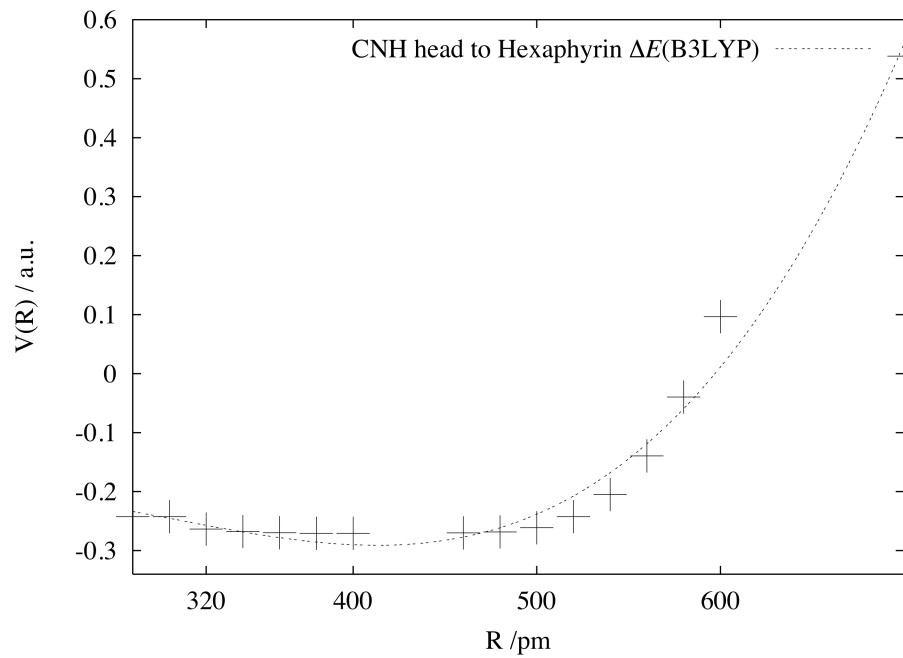


CNH lateral wall to Hexaphyrin

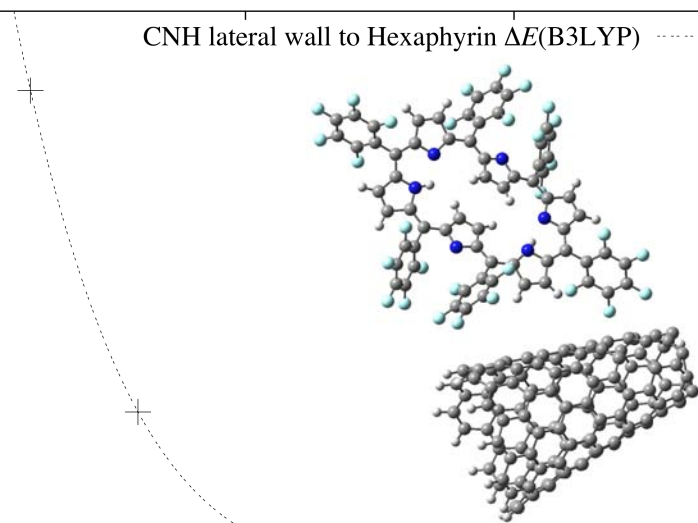
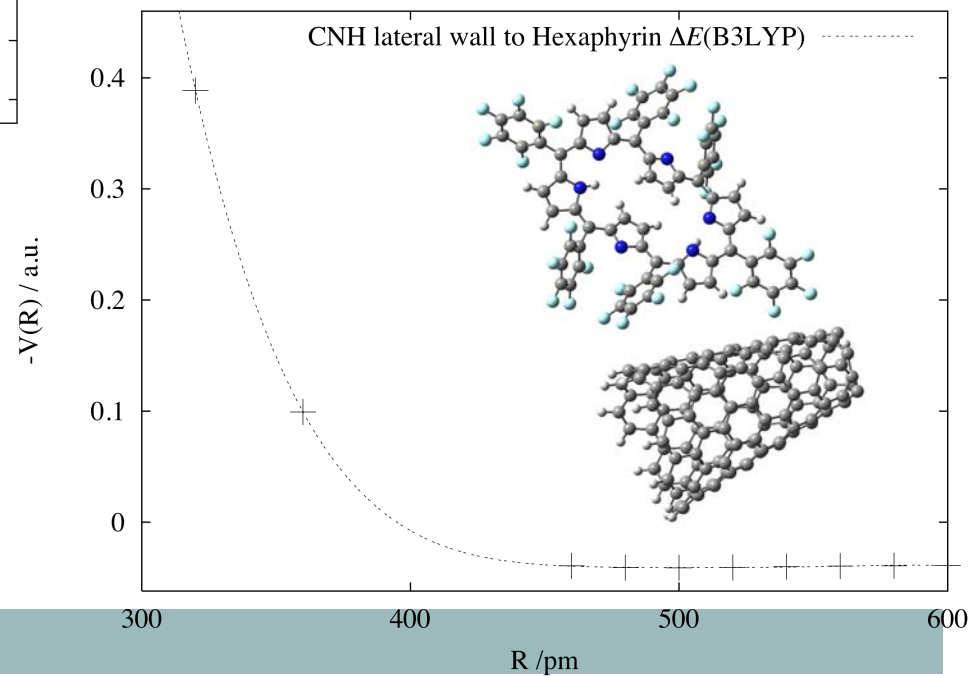




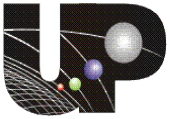
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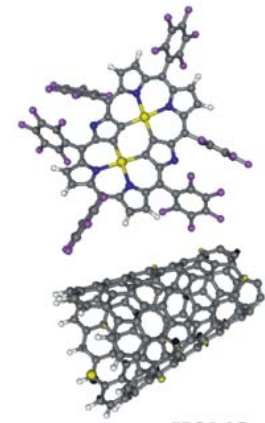
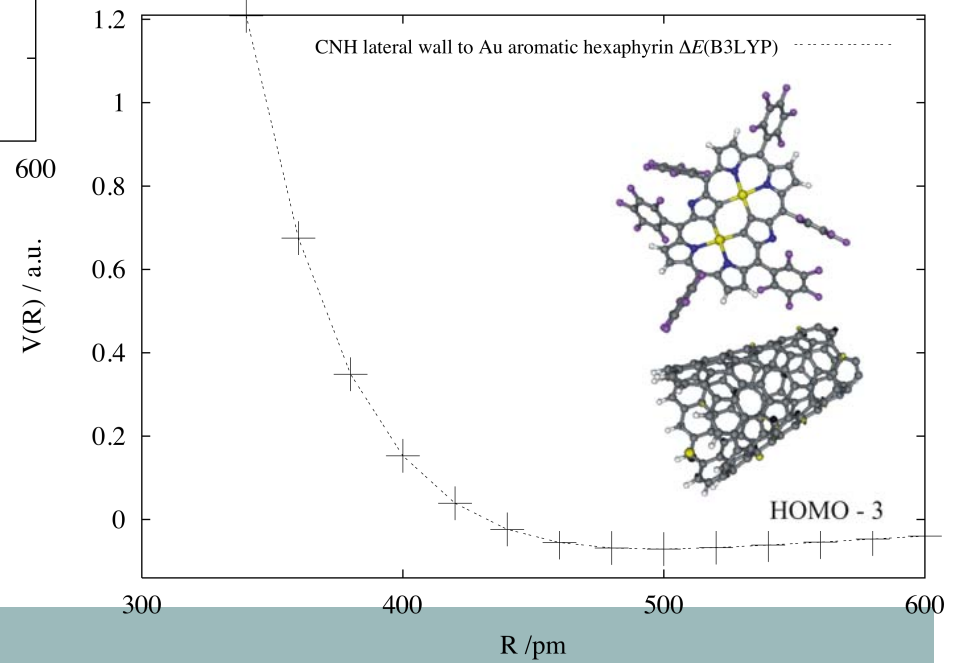
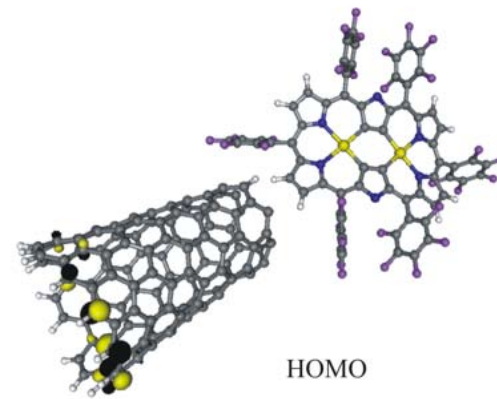
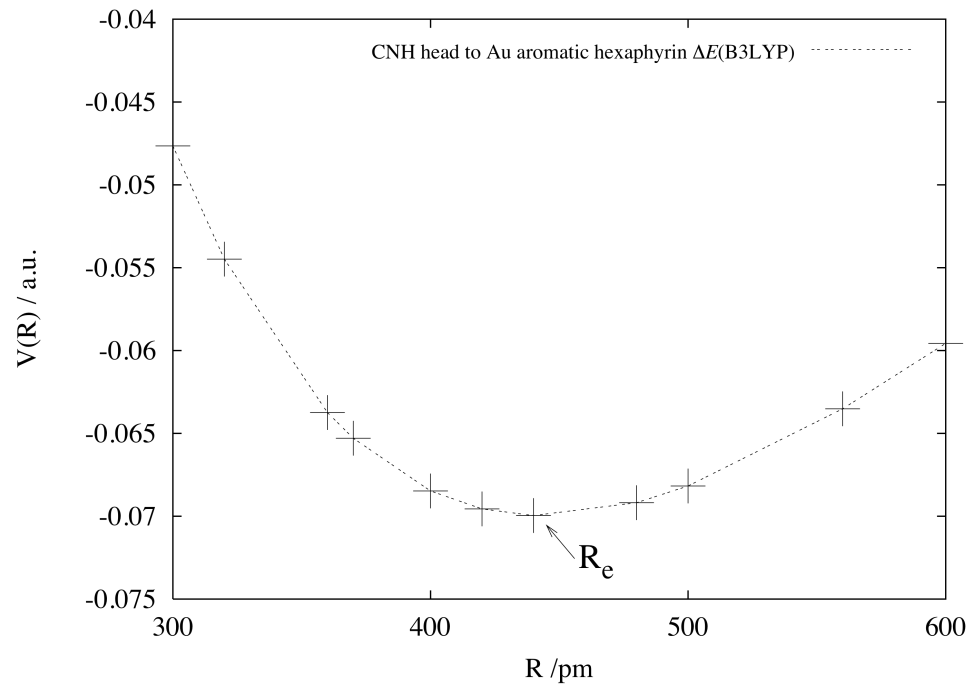
Int. J. Quant.Chem,
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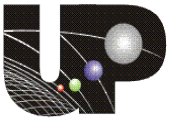


R / pm



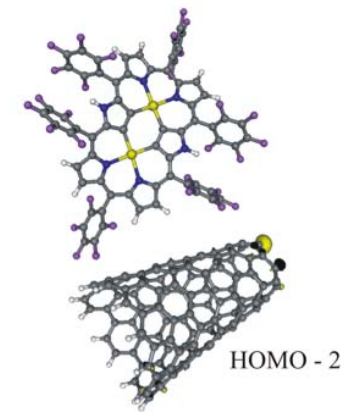
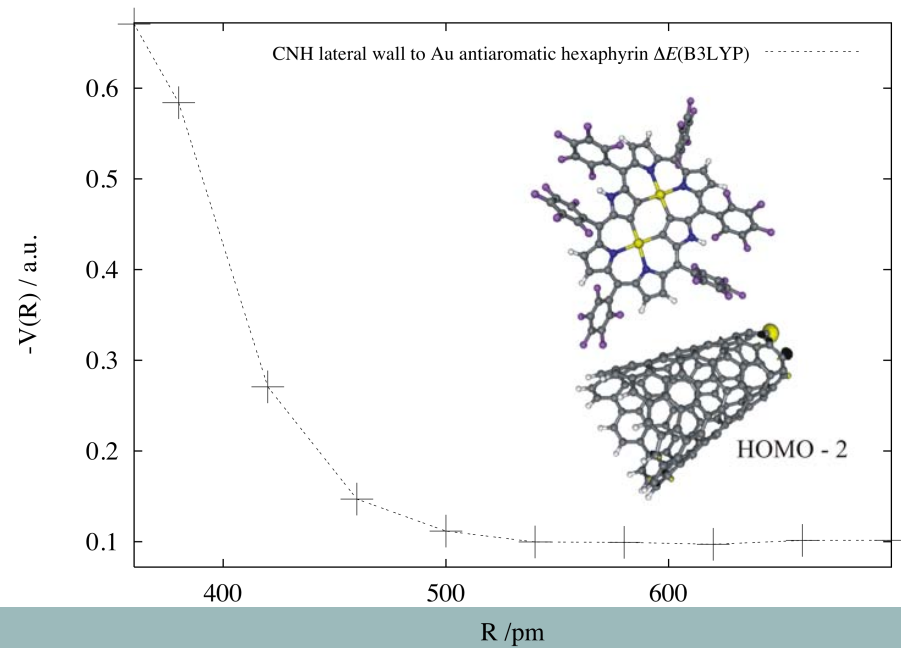
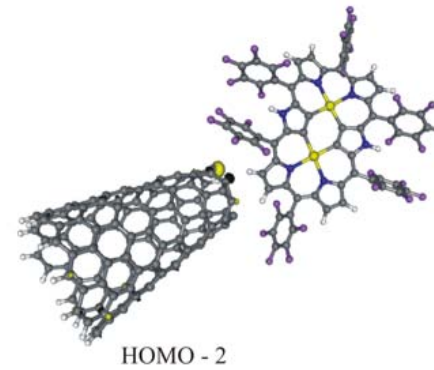
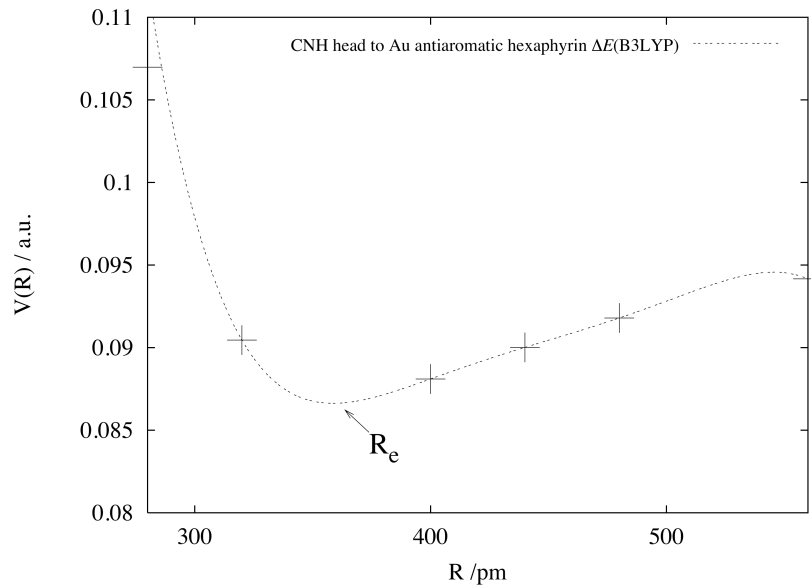
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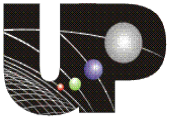




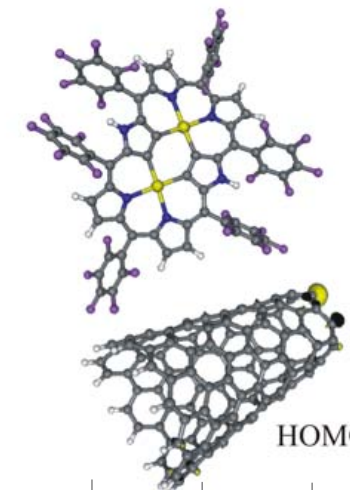
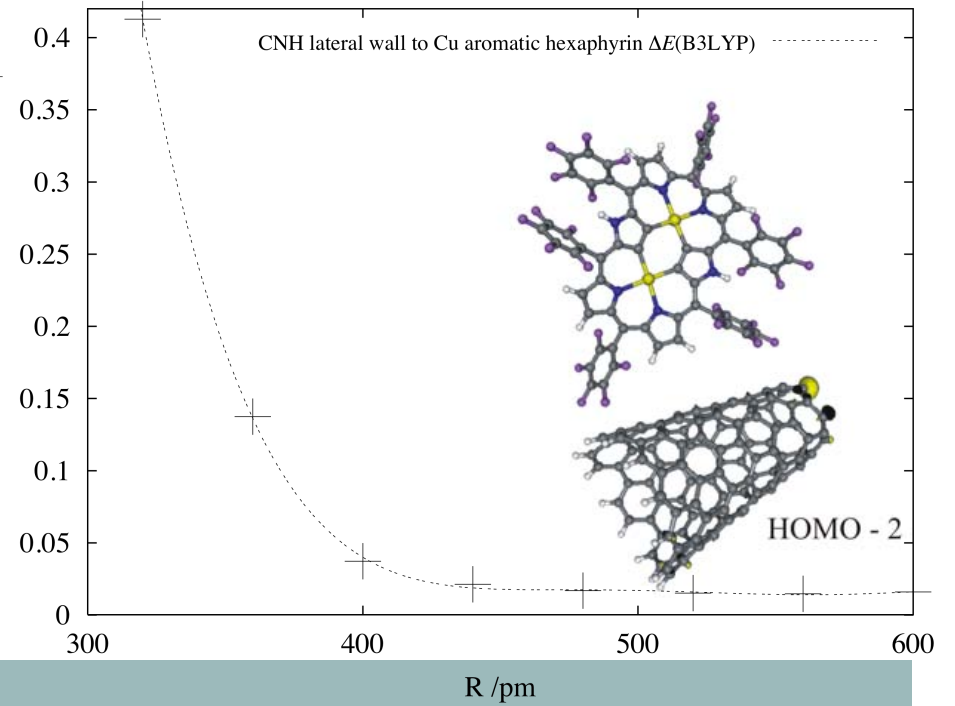
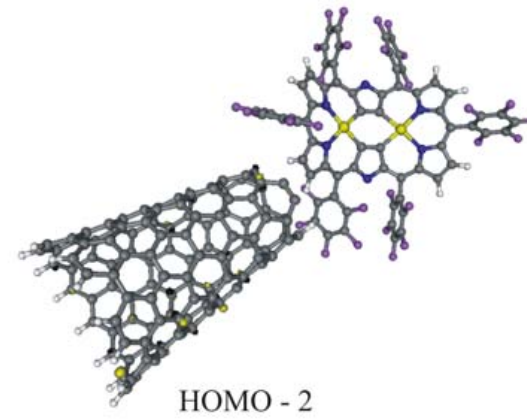
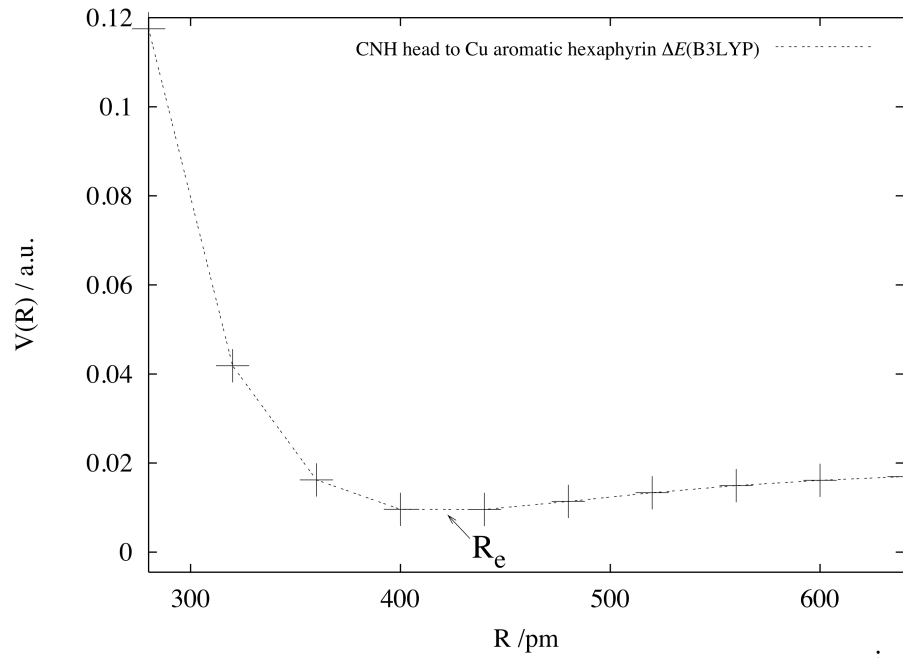
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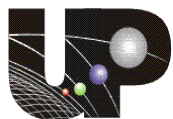
Antiaromatic porphyrin to CNH





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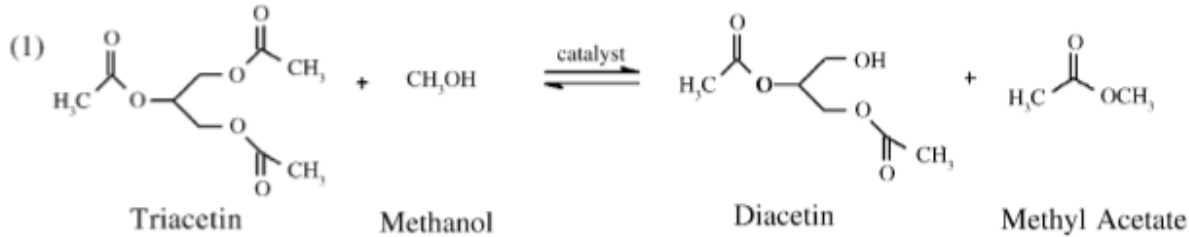
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1. The geometrical parameters and ground state properties are in agreement with those found experimentally
2. The aromatic and antiaromatic character of the complexes is basically ruled by the symmetry breaking at the cycle
3. Excited state calculations give us a picture on the nature of the experimental absorption bands, which in some cases are ruled the intrametallic interaction
4. The metallated hexaphyrins are good candidates to be used on nanohybrid materials applications.

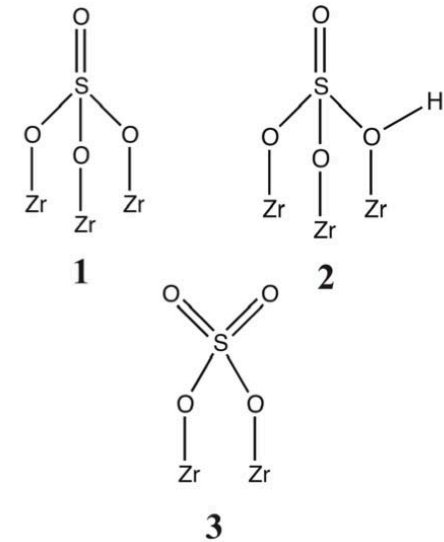


Modelling of transesterification reaction of triacetin con methanol for the Biodiesel production

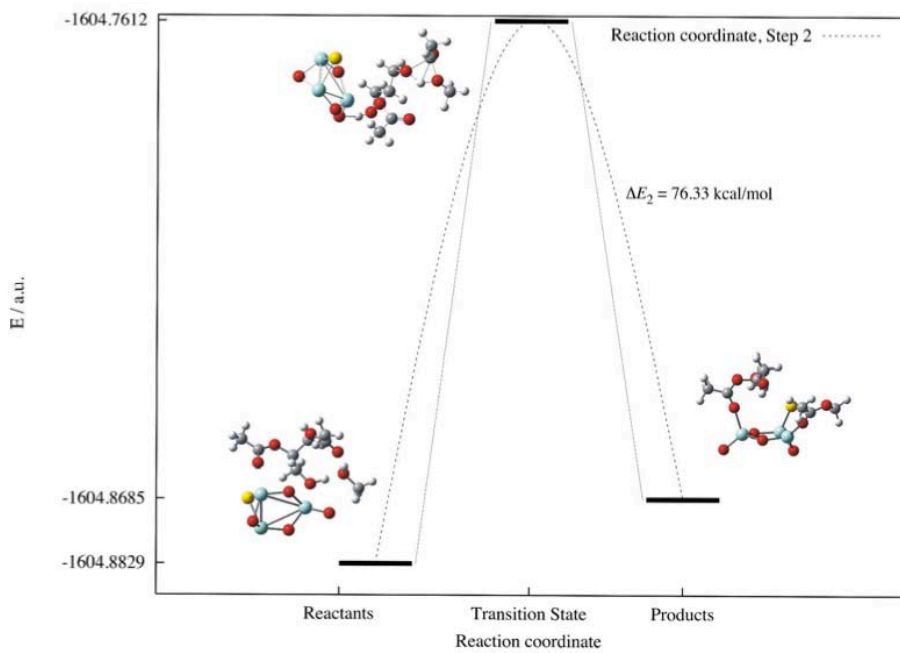
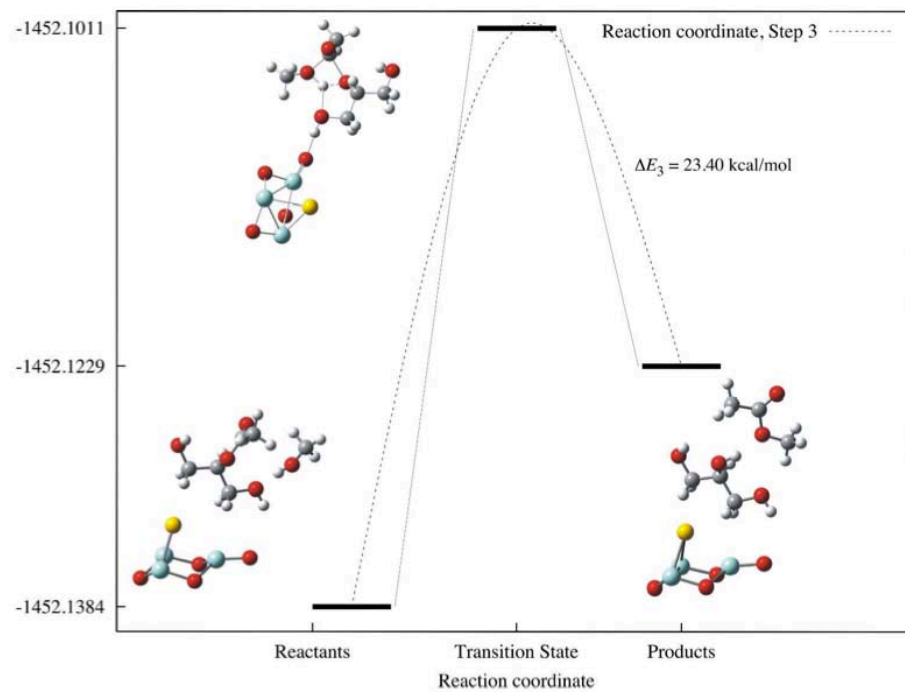
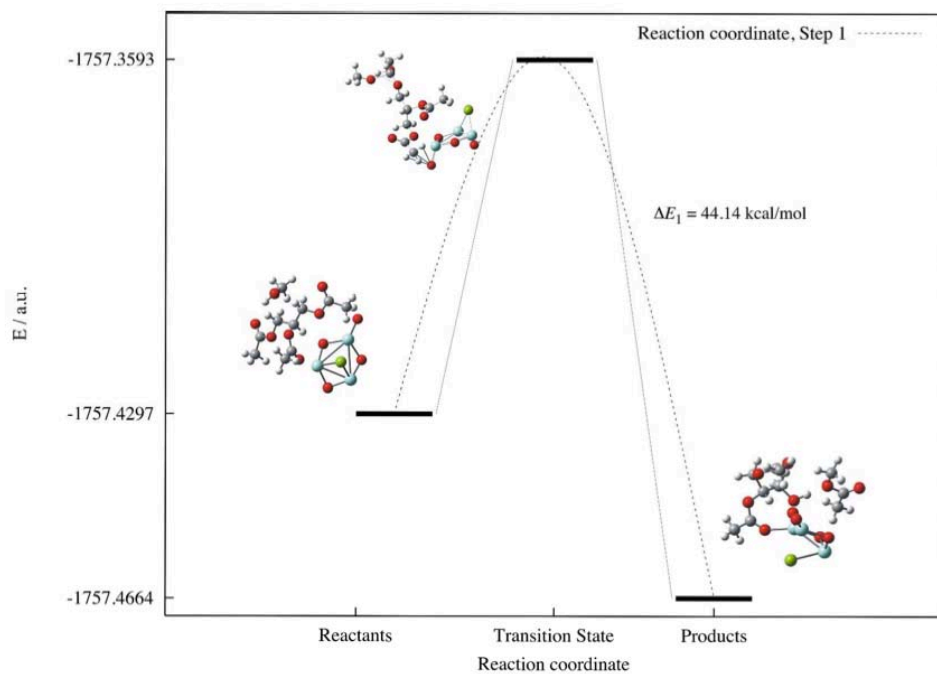
Stepwise reactions :



Overall reaction:



□



Muñiz J., et al, submitted

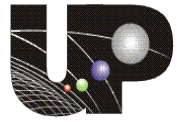
Acknowledgements

- Programa de Mejoramiento del Profesorado PROMEP-SEP under grant No. UPCHS-PTC-039, for financial support.

- Consejo Nacional de Ciencia y Tecnología, Ciencia-Básica under grant No. 156591, for financial support.



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THANK YOU FOR YOUR ATTENTION!!!!

