



# Fe-porphyrin attached to single-walled carbon nanotubes: Electronic and dynamical properties from *ab initio* calculations

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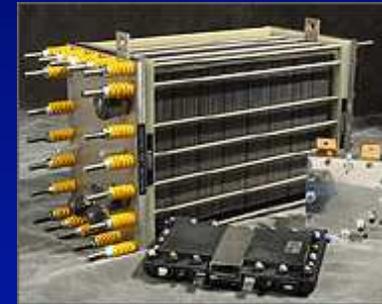
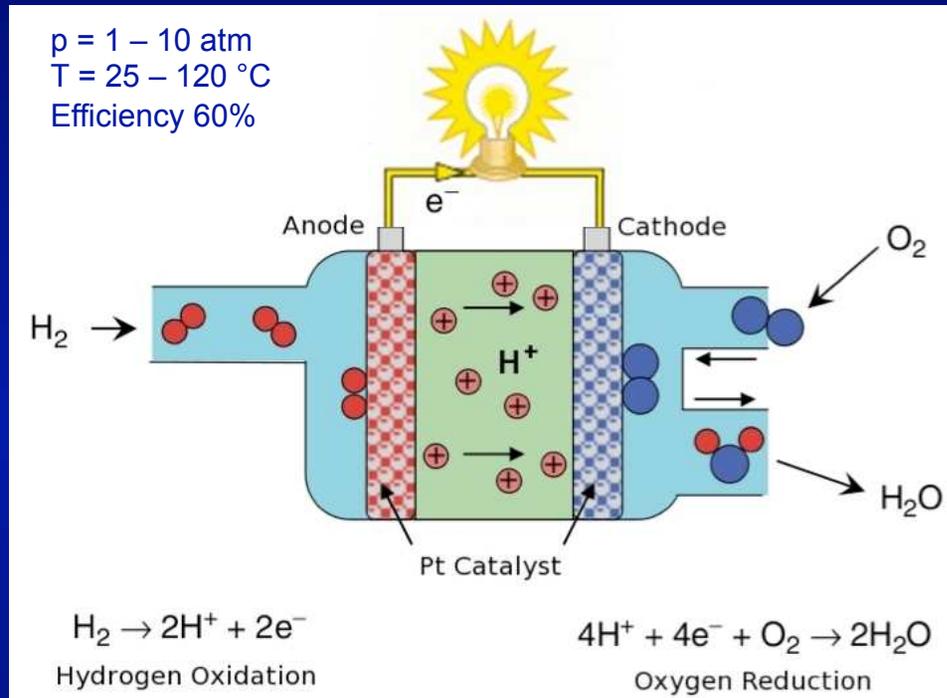
# Outline

- ✓ Motivation: New catalyts for PEM fuel cells
- ✓ Physisorption of Fe-Porphyrin on CNTs
- ✓ Chemisorption of Fe-Porphyrin on CNTs
- ✓ O<sub>2</sub> capture on CNT-supported Fe-Porphyrin



# Motivation

## Polymer electrolyte membrane (PEM) hydrogen fuel cell

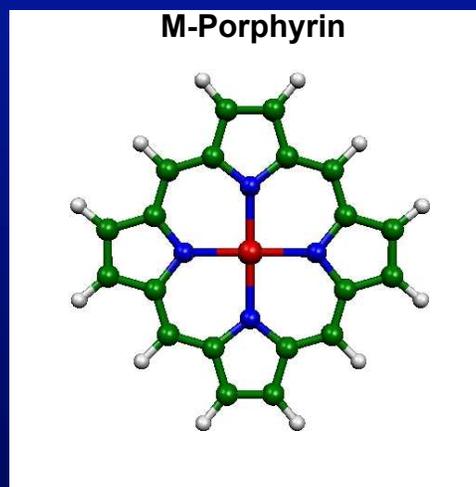
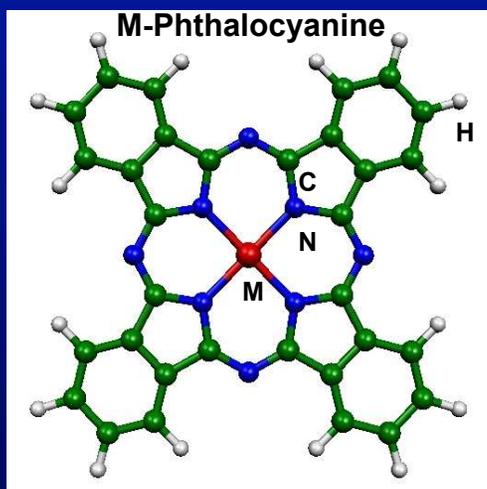


- ✓ The massive use of PEM fuel cells for transportation needs low-cost and abundant catalysts (alternative to Pt) for the oxygen reduction reaction (ORR) that work in the strong acid medium of the cathode.



# Nanoscale cathode catalyts for PEMFC

- ✓ Fe-N<sub>4</sub> and Co-N<sub>4</sub> macrocycles (porphyrin and phthalocyanine) can catalyze ORR in alkaline solutions, but are unstable in acidic enviroments, Jasinski, Nature 1964.
- ✓ Cabon-supported Fe-N<sub>4</sub> and Co-N<sub>4</sub> macrocycles obtained after heat treatment at 600-1000 °C in an inert atmosphere improve the stability and activity toward ORR in acidic enviroments, Jahnke, Top. Curr. Chem., 1976.
- ✓ Co-porphyrins anchored to multi-walled carbon nanotubes have shown superior catalytic performance for ORR in acidic medium at room temperature, Zhang, Chem Mater. 2009.
- ✓ The nature of the active sites and the origin of the improve catalytic activity of Fe-N<sub>4</sub>-C systems after heat treatment are still unknown.



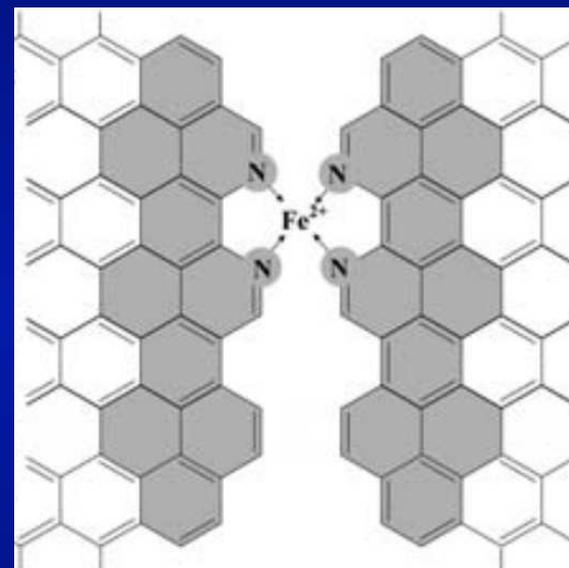


# Carbon-supported Fe-N<sub>4</sub> systems for ORR

## Iron-Based Catalysts with Improved Oxygen Reduction Activity in Polymer Electrolyte Fuel Cells

Michel Lefèvre,\* Eric Proietti,\* Frédéric Jaouen, Jean-Pol Dodelet†

Iron-based catalysts for the oxygen-reduction reaction in polymer electrolyte membrane fuel cells have been poorly competitive with platinum catalysts, in part because they have a comparatively low number of active sites per unit volume. We produced microporous carbon-supported iron-based catalysts with active sites believed to contain iron cations coordinated by pyridinic nitrogen functionalities in the interstices of graphitic sheets within the micropores. We found that the greatest increase in site density was obtained when a mixture of carbon support, phenanthroline, and ferrous acetate was ball-milled and then pyrolyzed twice, first in argon, then in ammonia. The current density of a cathode made with the best iron-based electrocatalyst reported here can equal that of a platinum-based cathode with a loading of 0.4 milligram of platinum per square centimeter at a cell voltage of  $\geq 0.9$  volt.



Science 324, 71 (2009)

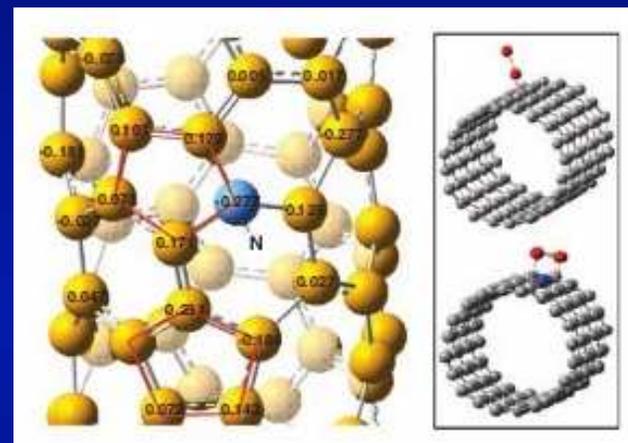


# N-doped Carbon Nanotubes for ORR

## Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction

Kuanping Gong,<sup>1</sup> Feng Du,<sup>1</sup> Zhenhai Xia,<sup>2</sup> Michael Durstock,<sup>3</sup> Liming Dai<sup>1,4\*</sup>

The large-scale practical application of fuel cells will be difficult to realize if the expensive platinum-based electrocatalysts for oxygen reduction reactions (ORRs) cannot be replaced by other efficient, low-cost, and stable electrodes. Here, we report that vertically aligned nitrogen-containing carbon nanotubes (VA-NCNTs) can act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction in alkaline fuel cells. In air-saturated 0.1 molar potassium hydroxide, we observed a steady-state output potential of  $-80$  millivolts and a current density of  $4.1$  milliamps per square centimeter at  $-0.22$  volts, compared with  $-85$  millivolts and  $1.1$  milliamps per square centimeter at  $-0.20$  volts for a platinum-carbon electrode. The incorporation of electron-accepting nitrogen atoms in the conjugated nanotube carbon plane appears to impart a relatively high positive charge density on adjacent carbon atoms. This effect, coupled with aligning the NCNTs, provides a four-electron pathway for the ORR on VA-NCNTs with a superb performance.

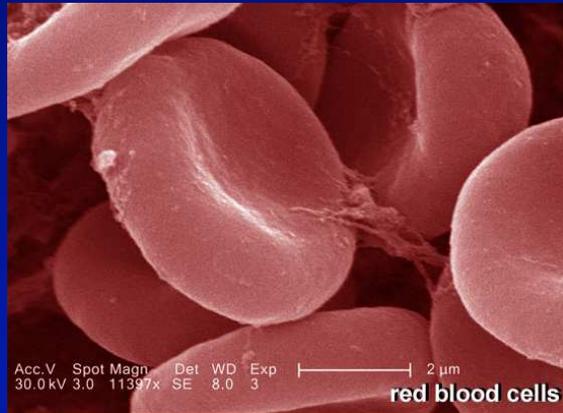


Science 323, 760 (2009)

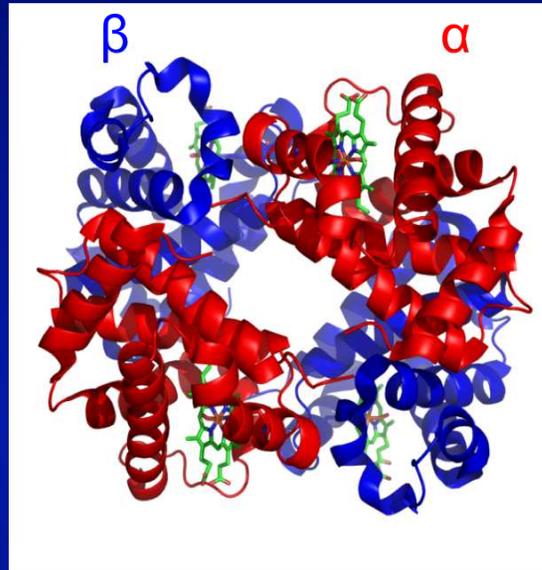


# Iron porphyrins: Capture oxygen in hemoglobin

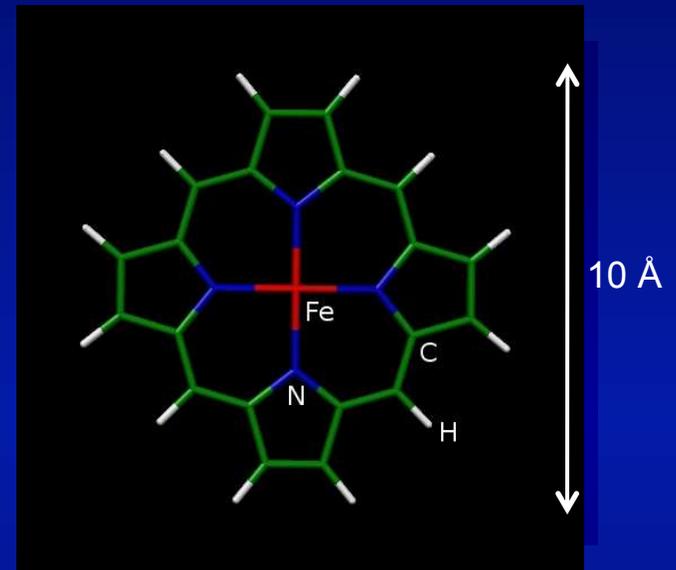
Blood cells



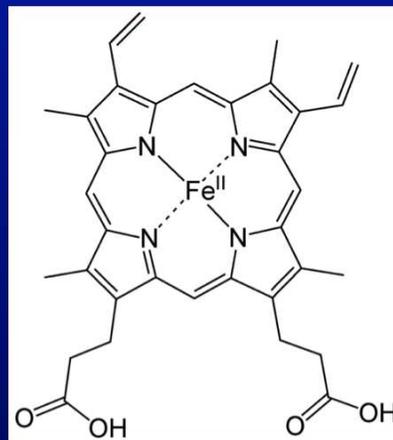
Hemoglobin:  
blood cell protein



Fe-Porphyrin (FeP)



Heme-b complex:  
active site for the  
O<sub>2</sub> capture





# Theoretical approach

We investigate the stability and electronic properties of iron porphyrin (FeP) physisorbed and chemisorbed on carbon nanotubes at room temperature.

- ✓ Spin-polarized DFT-LDA calculations (SIESTA code)
- ✓ Ab initio van der Waals DF calculations (sparse interaction)
- ✓ Basis set of numerical atomic orbitals (double  $\zeta$  + polarization functions)
- ✓ Norm-conserving pseudopotentials (Trouillier-Martins)
- ✓ The equilibrium geometry is obtained by constant-temperature molecular dynamic simulations (Nose thermostat approach), during 1 ps plus an annealing of 0.5 ps.
- ✓ The system is in thermal contact with a heat bath, which can exchange energy to fix the system temperature which can be described within the canonical (NVT) ensemble
- ✓ (8,8) metallic and (14,0) semiconducting single-walled carbon nanotubes.

Two different mechanisms for the FeP attachment on the CNT sidewalls are investigated:

- ✓ by physisorption through  $\pi$ - $\pi$  stacking interaction (vdW-DF)
- ✓ by chemisorption through  $sp^2$  and  $sp^3$  bonding (DFT-LDA)



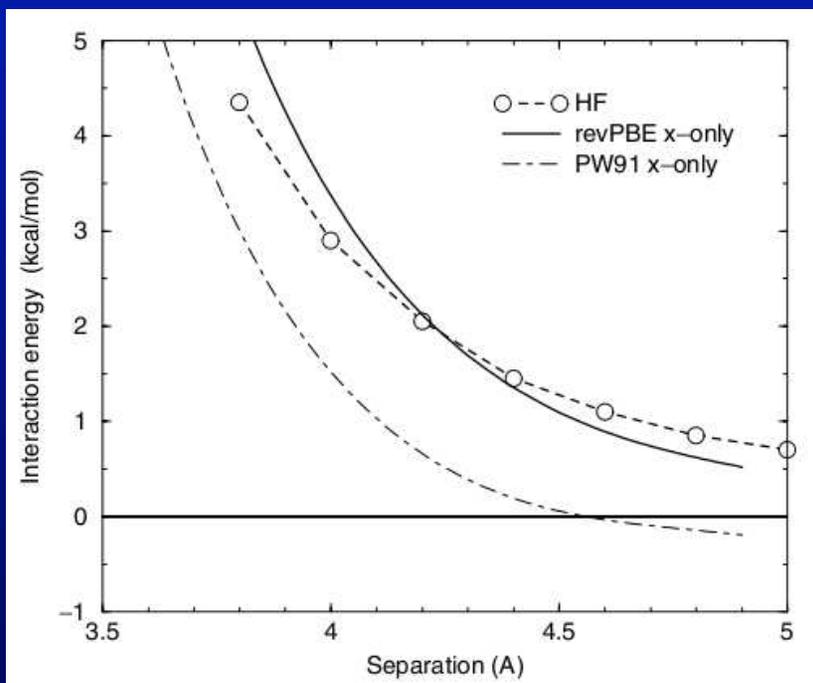
# van der Waals Density Functional

Dion et al. Phys. Rev. Lett. 92, 246401 (2004)

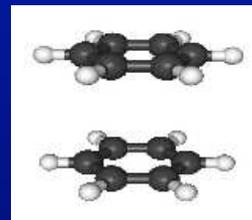
$$E_{xc} = E_x^{GGA} + E_c^{new}$$

← Properly constructed correlation functional including vdW

↑ Semilocal GGA exchange functional rev-PBE (Zhang-Yang) fitted to exact exchange calculations



benzene dimer





# van der Waals Density Functional

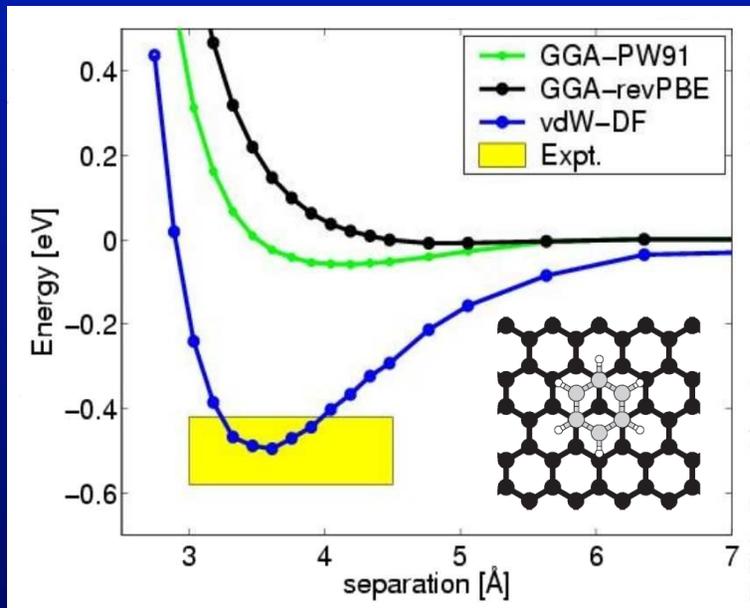
Total correlation energy:

$$E_c = E_c^0 + E_c^{nl}$$

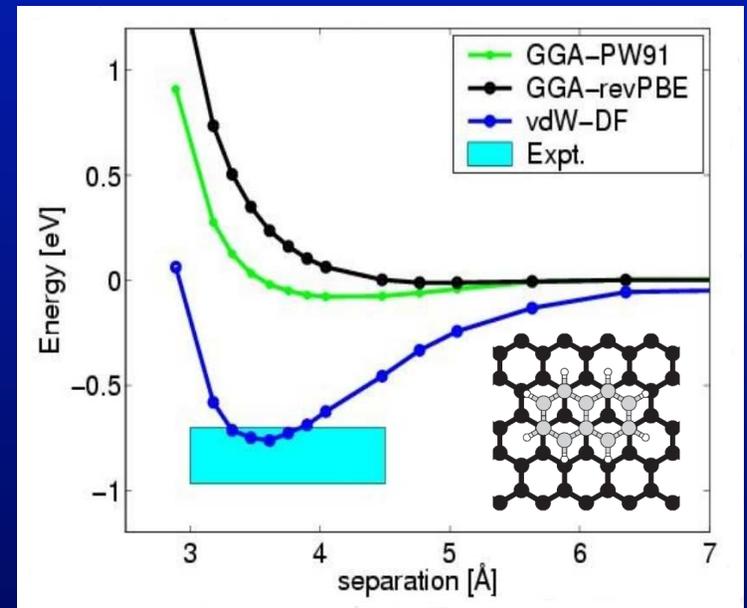
Shorter range: evaluated in the local density approximation (LDA) which implicitly uses the exact dielectric function.

Longer range: Contains principal vdW term evaluated with model dielectric function.

Benzene desorption from graphite

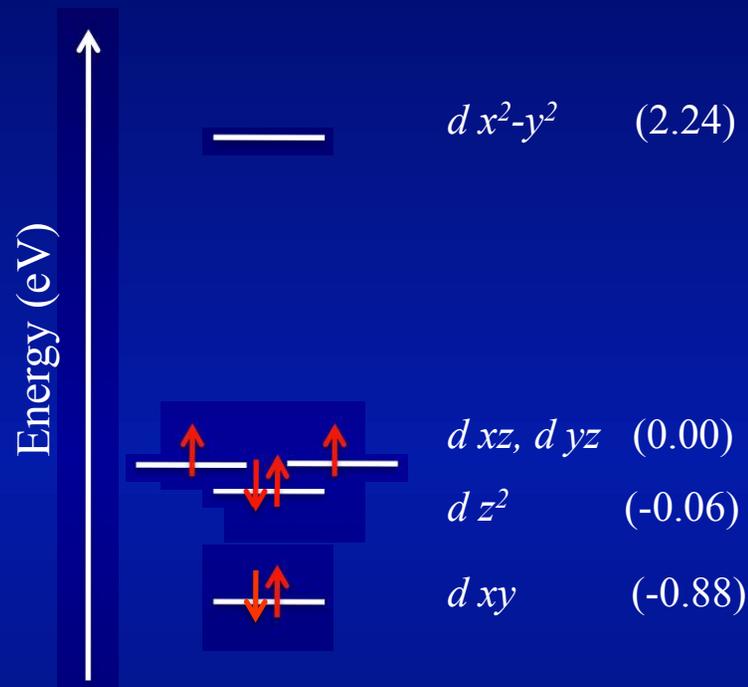
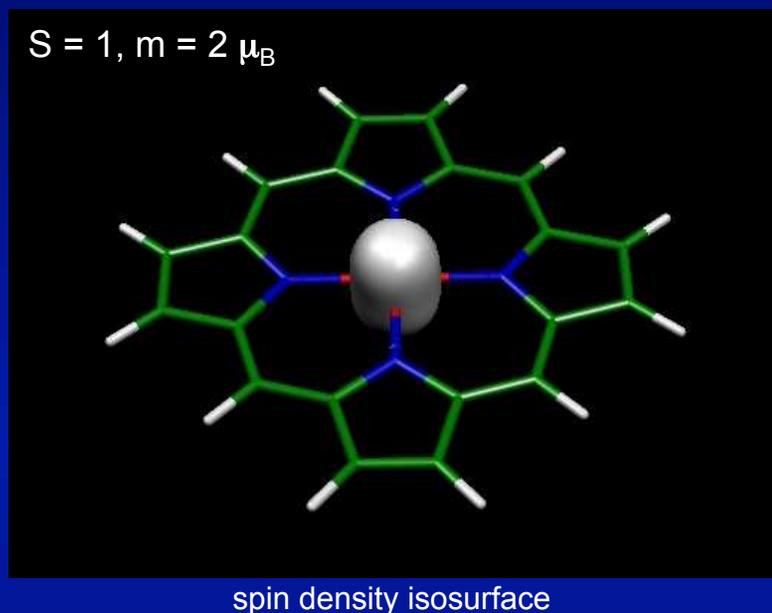


Naphtalene desorption from graphite





# Fe-Porphyrin (FeP)



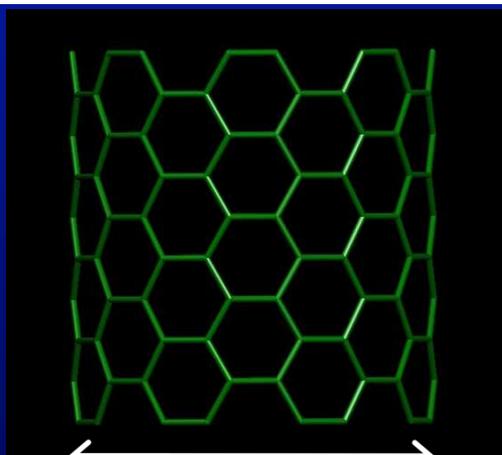
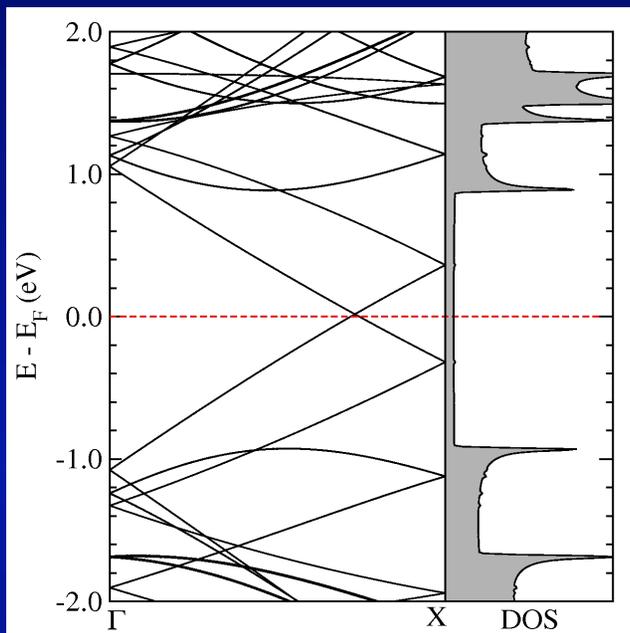
Six electrons can be associated with the Fe atom in the  $^3\text{FeP}$  state, suggesting that the Fe atom is in an oxidation state 2 ( $\text{Fe}^{\text{II}}$ )

$(2S+1)\text{FeP}$	$^1\text{FeP}$	$^3\text{FeP}$	$^5\text{FeP}$
$\Delta E$ (eV)	0.66	0.0	1.17
$d_{\text{Fe-N}}$ (Å)	1.94	1.95	2.01
$d_{\text{N-C}}$ (Å)	1.39	1.40	1.38



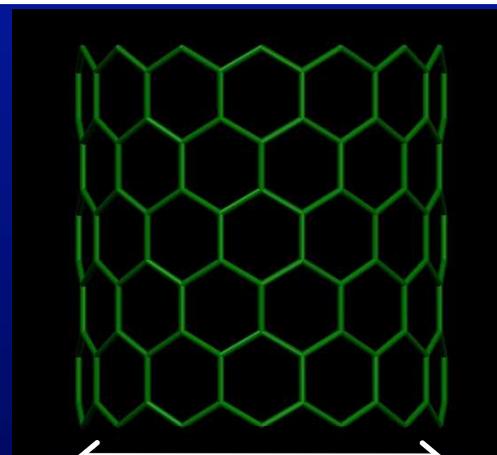
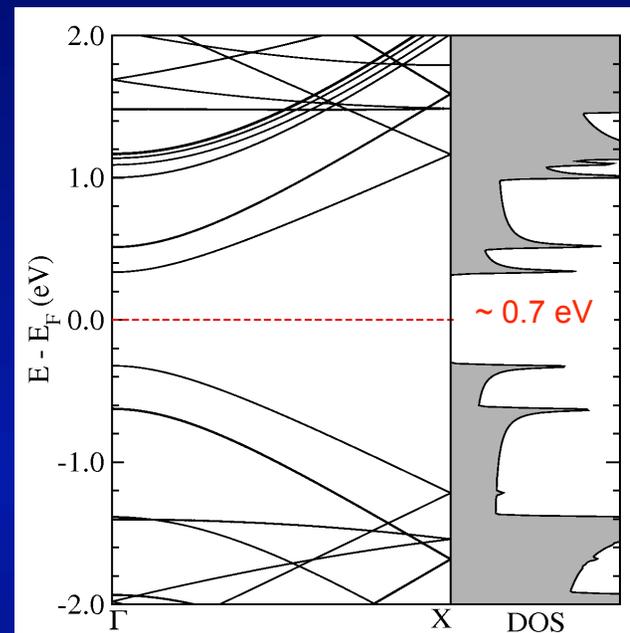
# The substrate: Single-walled carbon nanotubes

(8,8)



11.06 Å

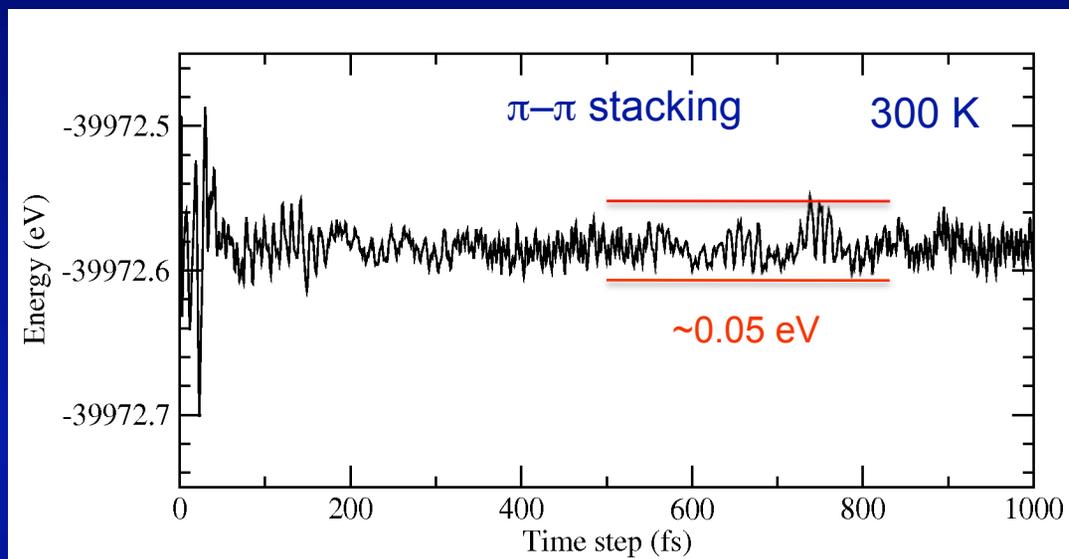
(14,0)



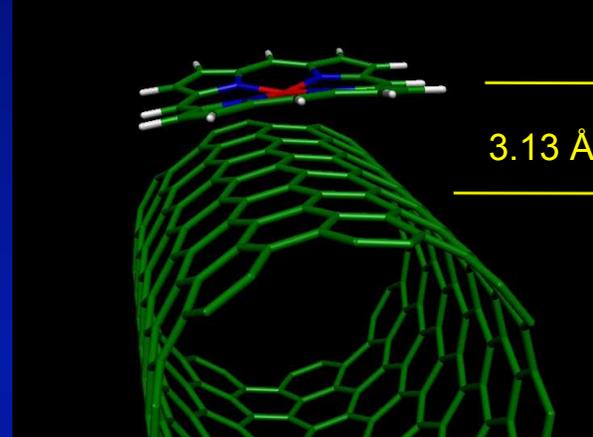
11.12 Å



# FeP Physisorption on the (8,8) CNT



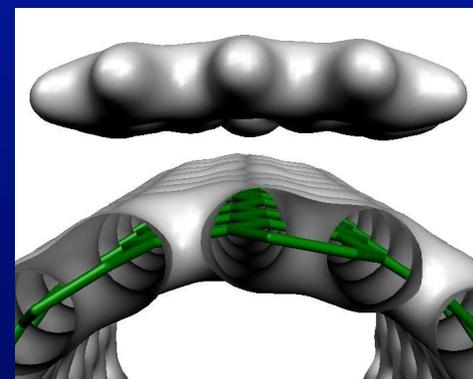
Equilibrium geometry after annealing.



$$E_b(\text{FeP}) = -1.09 \text{ eV}$$

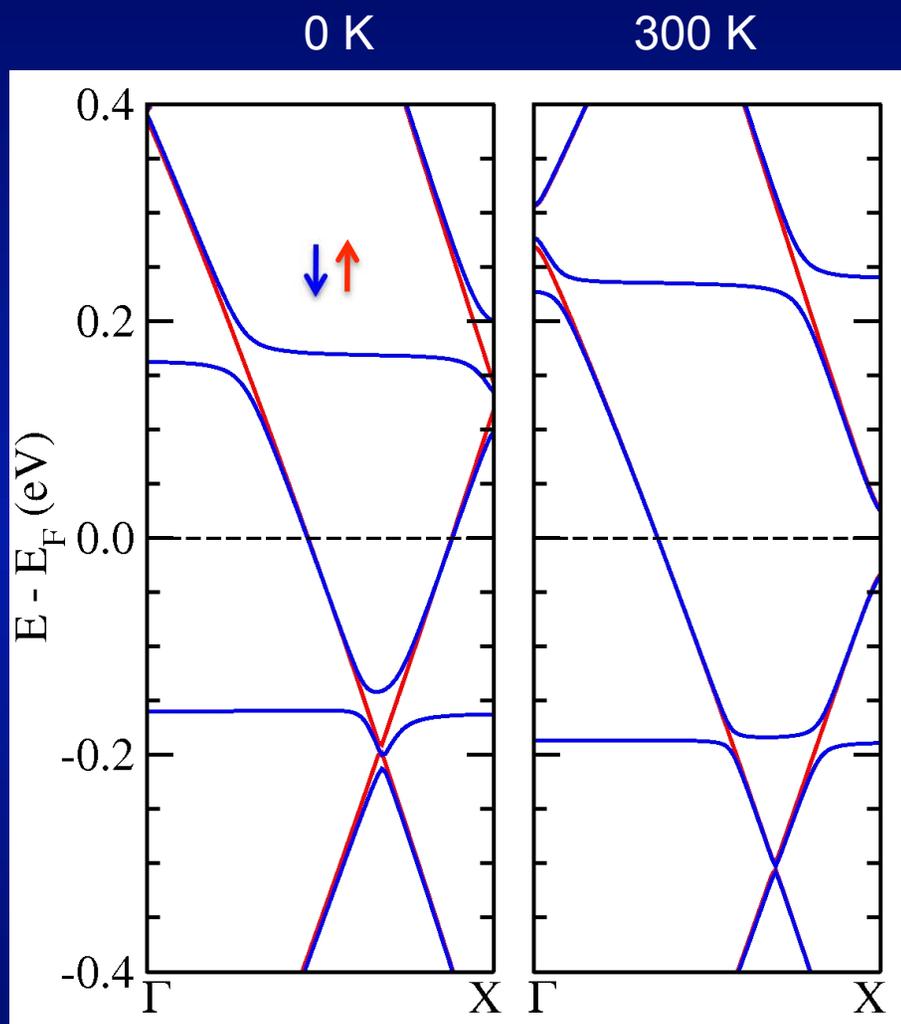
FeP moves through the nanotube surface without desorption bonded by dispersion forces. The Fe atom tends to move follows the nanotube C-C bonds.

No chemical bond between FeP and the CNT are observed showing a rather strong van der Waals-like interaction





# FeP Physisorption on the (8,8) CNT

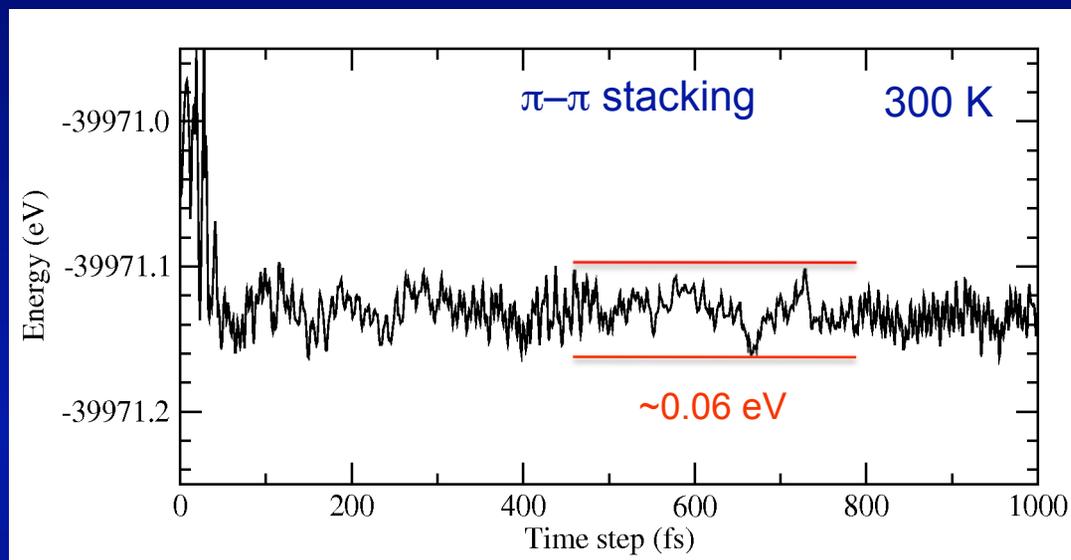


The band structure at 300K was obtained considering the FeP-CNT geometry after 1 ps of the MD simulation.

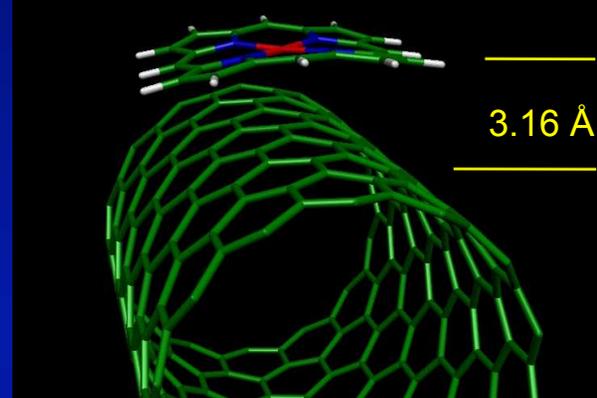
Spin-resolved band structure at 0K and 300 K. Room-temperature results are obtained with the static geometry after 1 ps of MD simulation.



# FeP Physisorption on the (14,0) CNT



Equilibrium geometry after annealing.



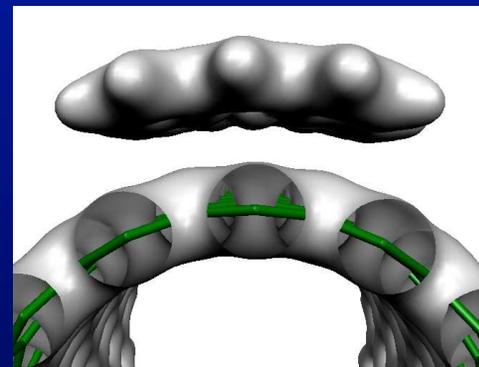
$$E_b(\text{FeP}) = -1.05 \text{ eV}$$

Experiments have explored the immobilization of metallomacrocycles on graphite and CNTs showing a strong mutually-interacting  $\pi$  systems with charge transfer features.

Tao, Phys. Rev. Lett. 76, 4066 (1995)

Rahman et al., J. Mater. Chem. 16, 62 (2006).

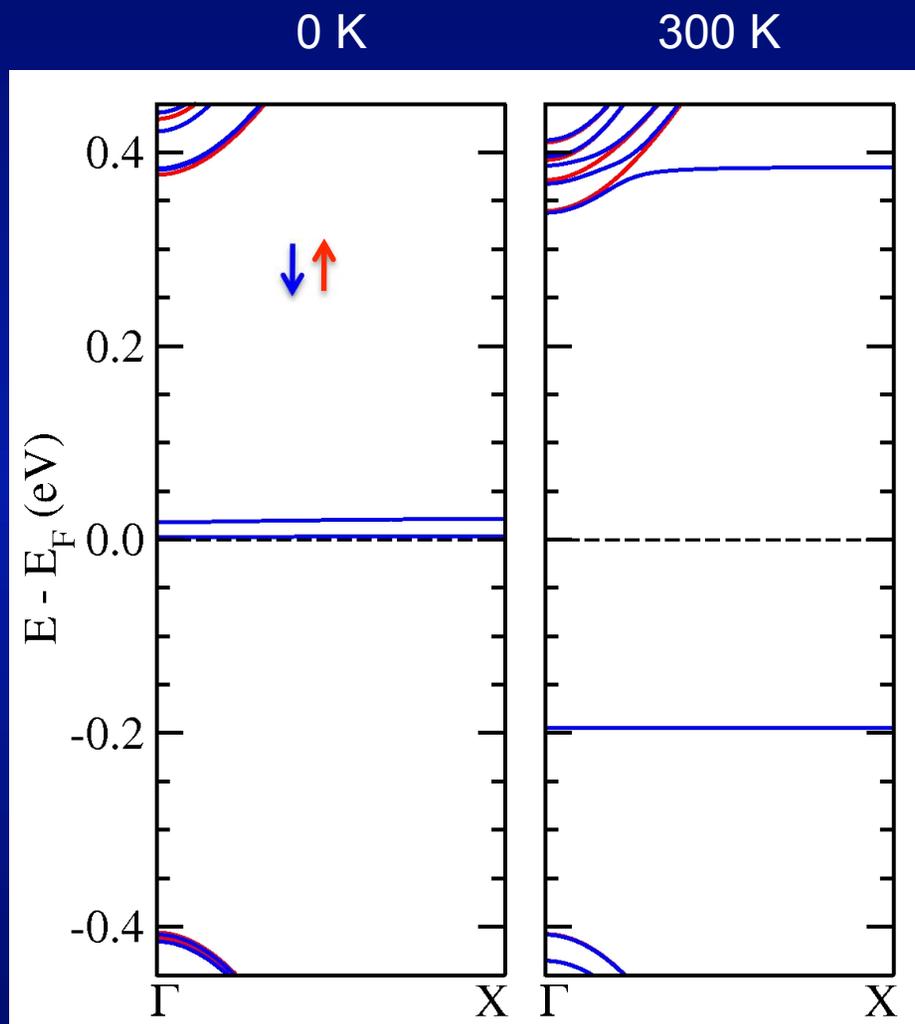
Our results confirm the unusually-strong  $\pi$ - $\pi$  stacking interaction which we attribute to the large FeP-CNT contact area.



Total charge density



# FeP Physisorption on the (14,0) CNT



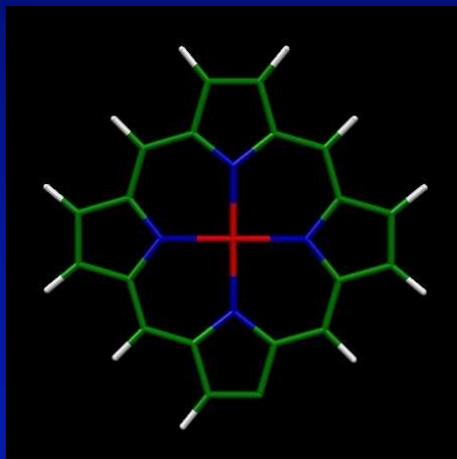
FeP physisorbed on the semiconducting CNT has the ability to reduce the gap up to 0.4 eV at 0 K, induced by the FeP molecular orbitals.

At room temperature, one of the empty orbitals captures an electron, while the other rises up to the bottom of the conduction band, increasing the gap up to 0.6 eV.



# FeP Chemisorption mechanisms

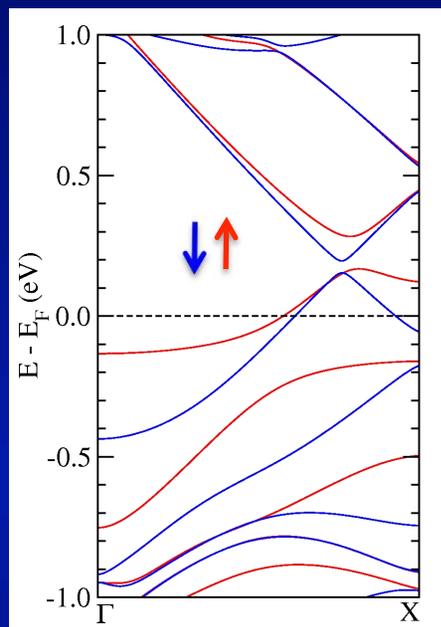
FeP\*



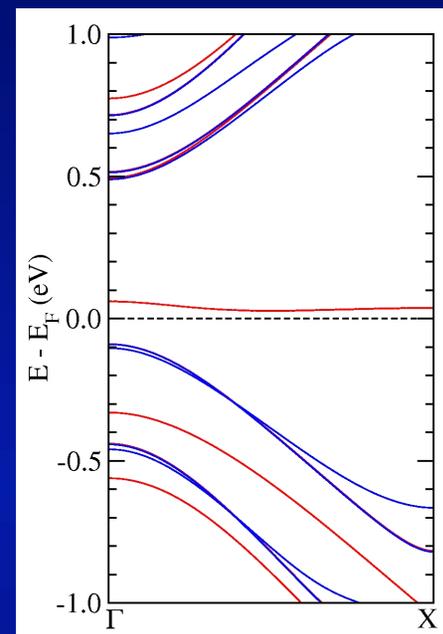
Removing an H atom from FeP it is possible to induce covalent bonds between FeP\* and both pristine and defective CNT (with a vacancy).

W. O. and P. Fuentealba  
Surface Science 600, 4305 (2006)

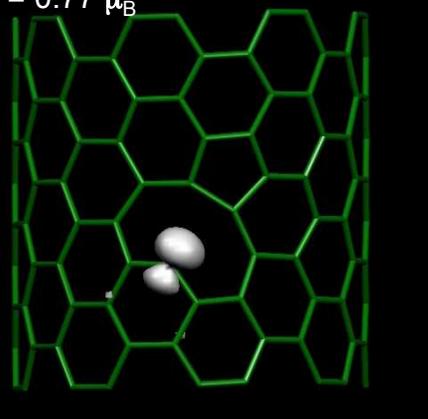
(8,8)-V



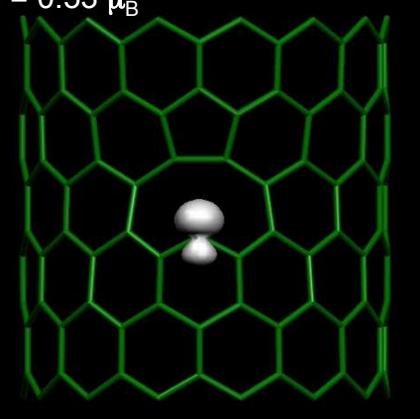
(14,0)-V



$m = 0.77 \mu_B$



$m = 0.53 \mu_B$

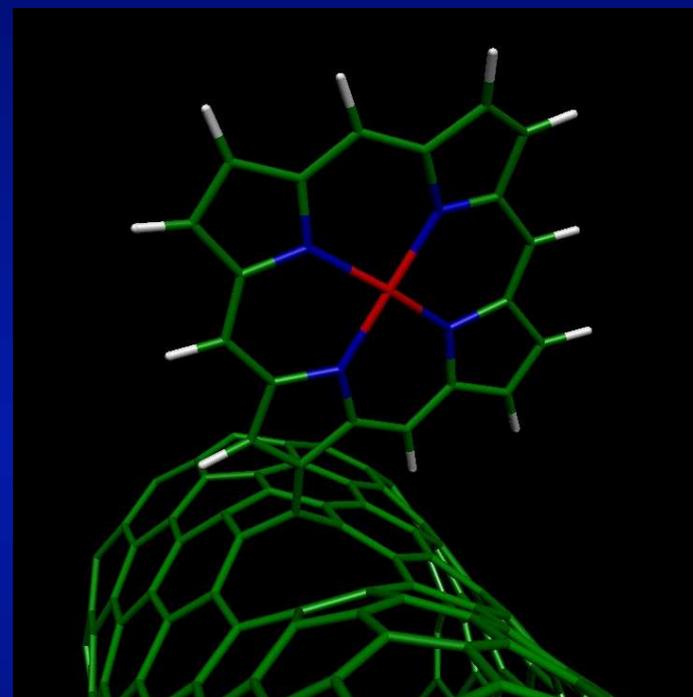
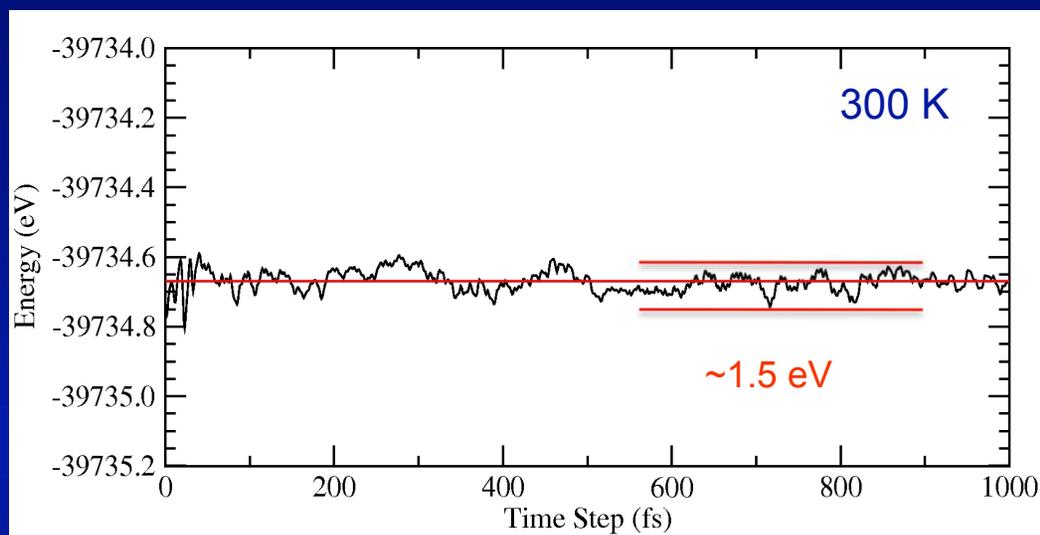


spin density isosurfaces

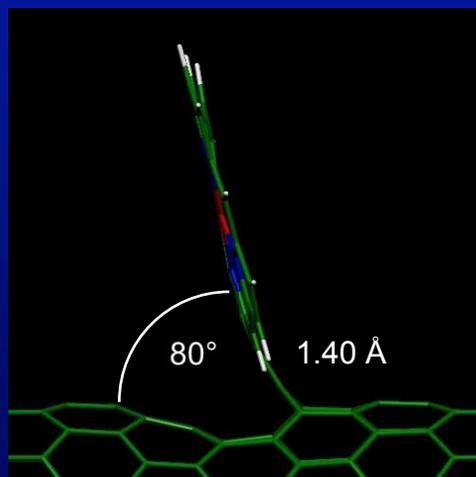


# FeP\* anchored on (14,0)+V (sp<sup>2</sup> bonding)

Equilibrium geometry after annealing



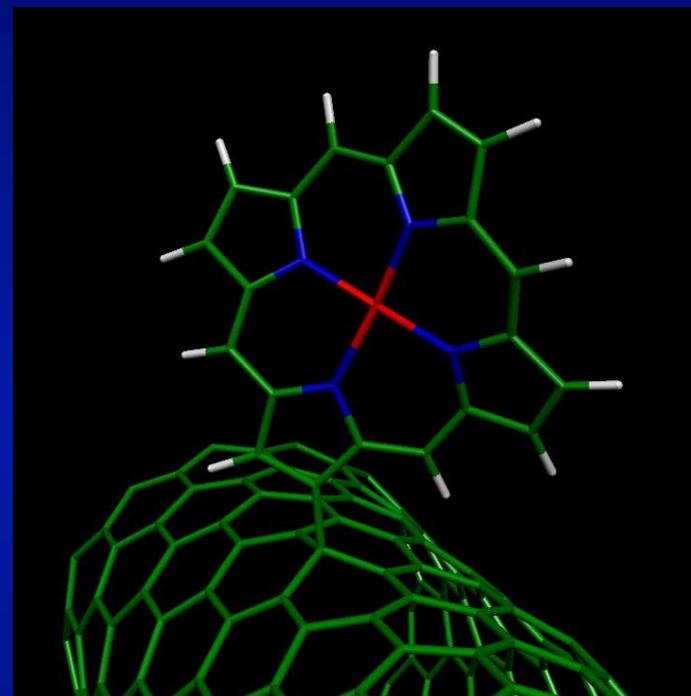
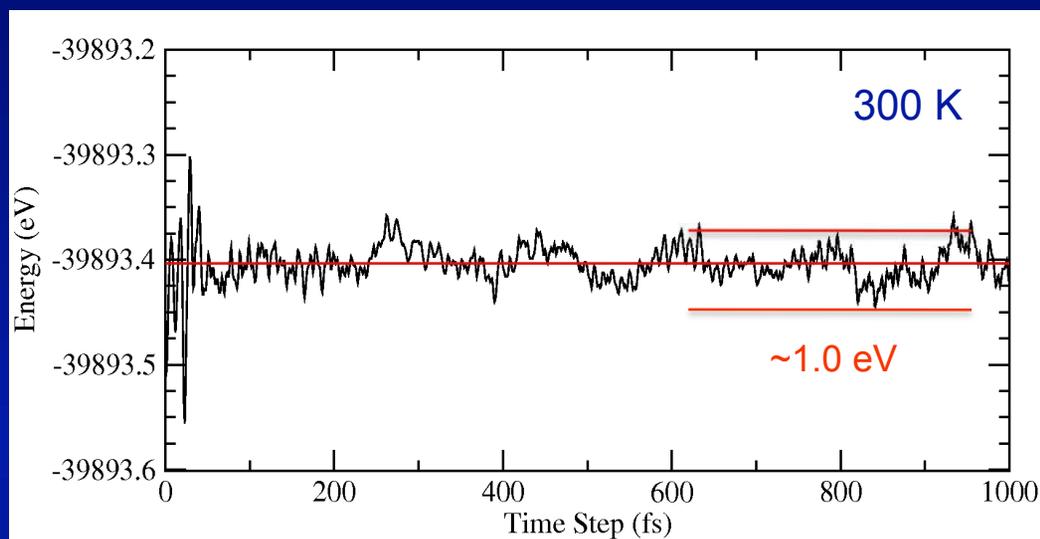
$$E_b(\text{FeP}) = -4.81 \text{ eV}$$



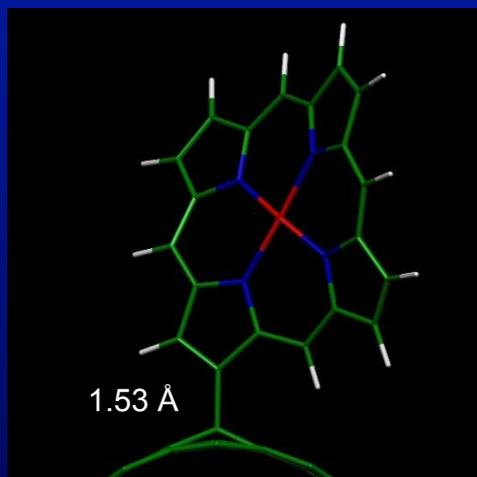


# FeP\* anchored on (14,0)+V (sp<sup>3</sup> bonding)

Equilibrium geometry after annealing



$E_b$  (FeP) = -1.80 eV





# (14,0)+V: FeP\* band structure

$sp^2$  bonding

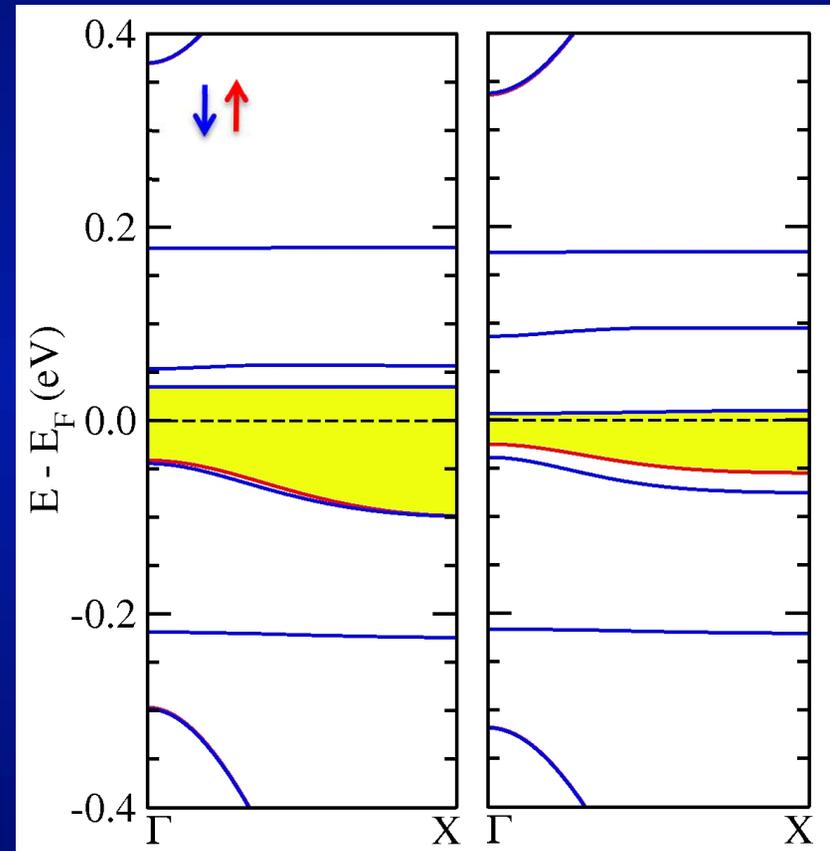
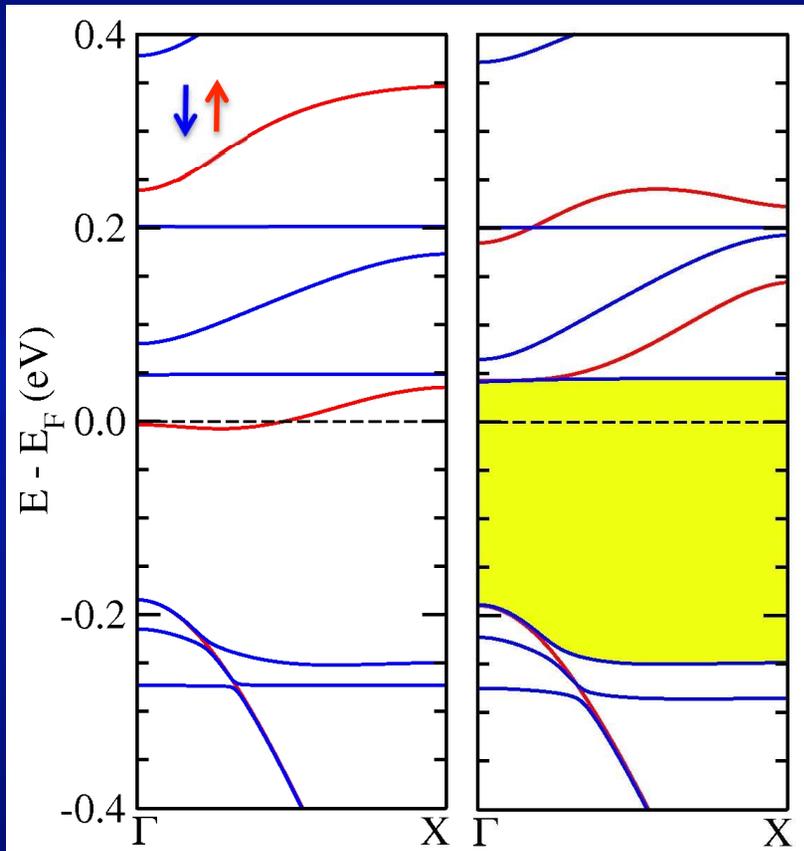
$sp^3$  bonding

0 K

300 K

0 K

300 K

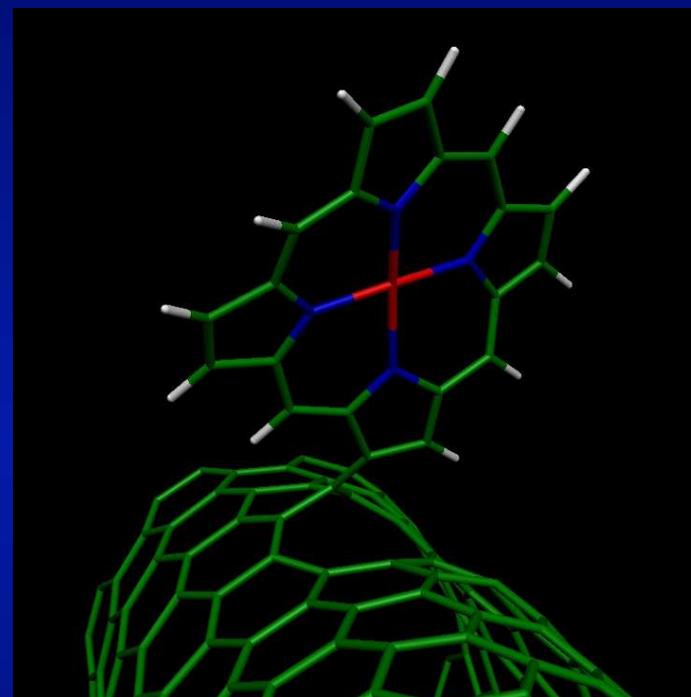
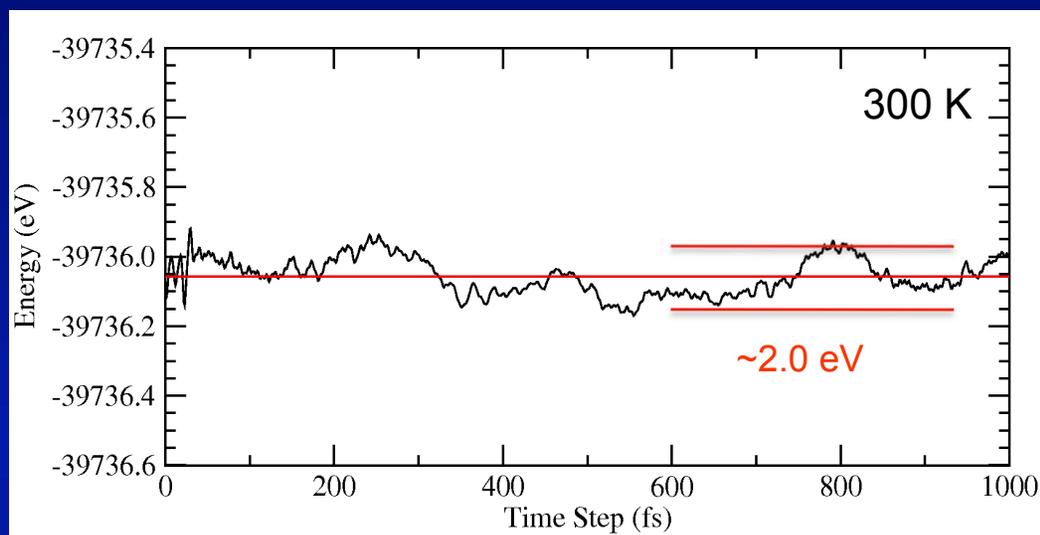


At room temperature the chemically attached FeP\* on both (14,0) and (14,0)-V have semiconducting character

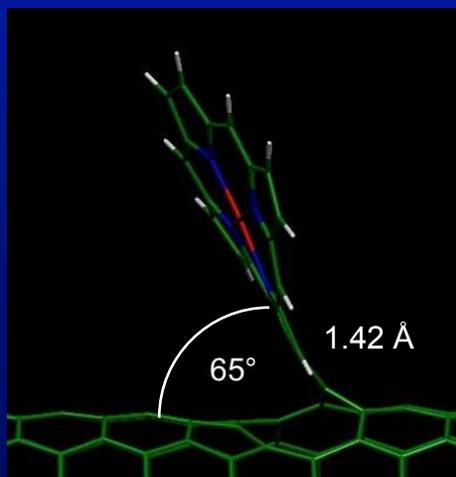


# FeP\* anchored on (8,8)+V (sp<sup>2</sup> bonding)

Equilibrium geometry after annealing



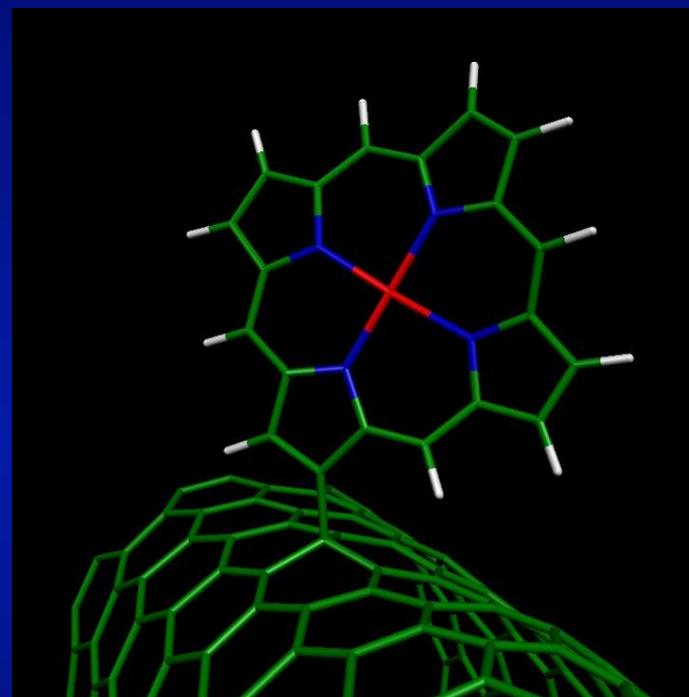
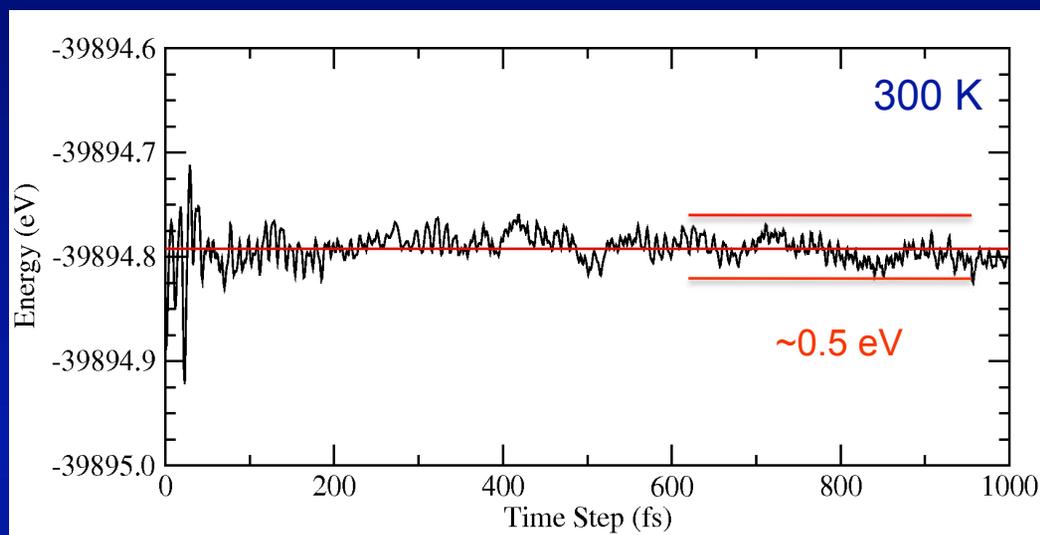
$$E_b(\text{FeP}) = -5.0 \text{ eV}$$



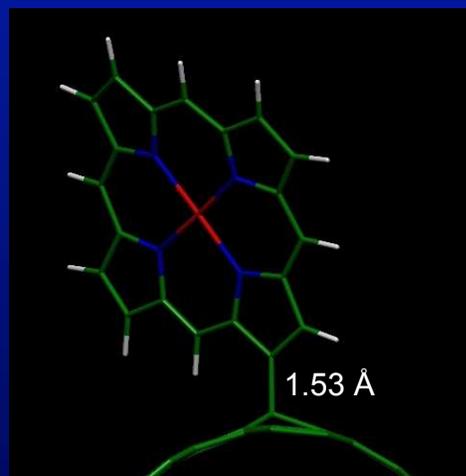


# FeP\* anchored on (8,8)+V (sp<sup>3</sup> bonding)

Equilibrium geometry after annealing



$$E_b(\text{FeP}) = -1.80 \text{ eV}$$



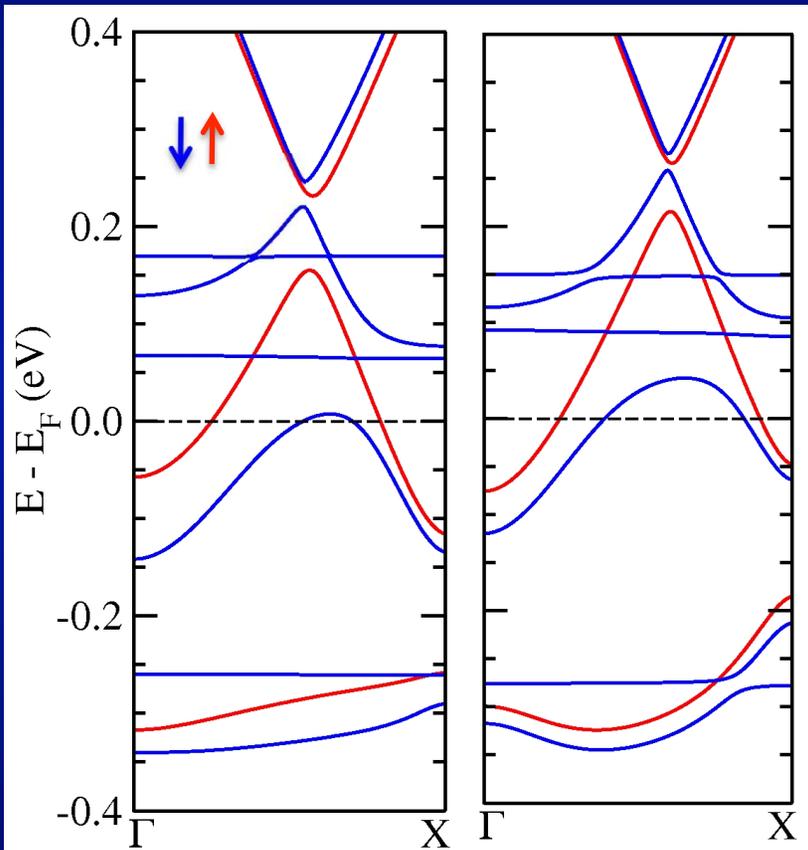


# (8,8)+V: FeP\* band structure

$sp^2$  bonding

0 K

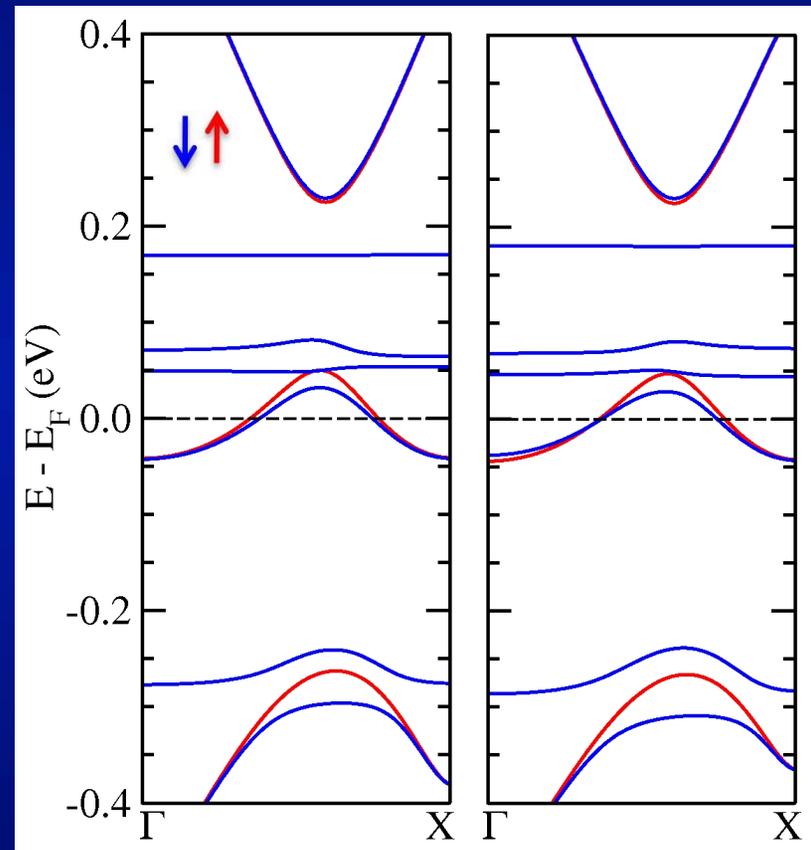
300 K



$sp^3$  bonding

0 K

300 K

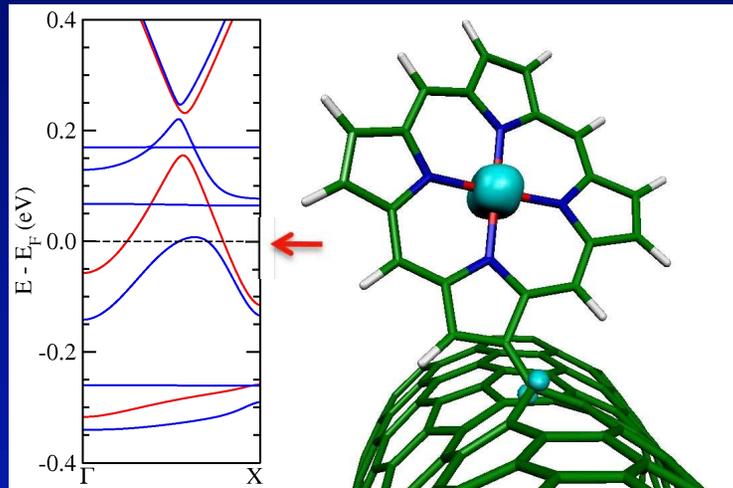


At room temperature the chemically attached FeP\* on (8,8) and (8,8)-V have metallic character. Minor differences between 0K and 300K electronic properties are observed.

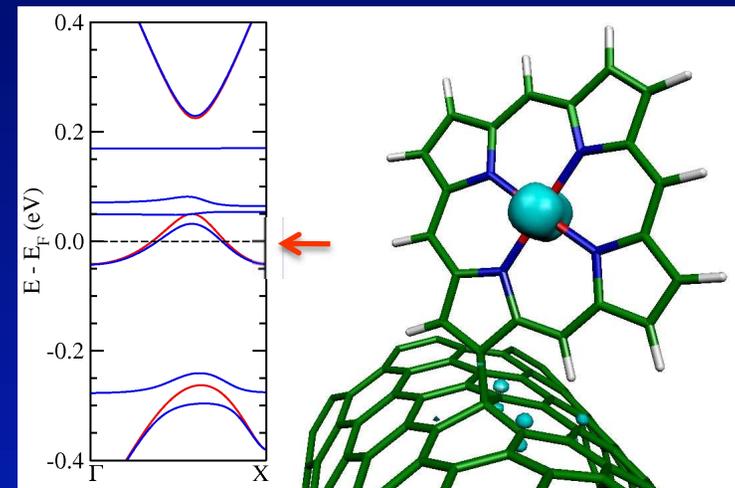


# LDOS at the Fermi level

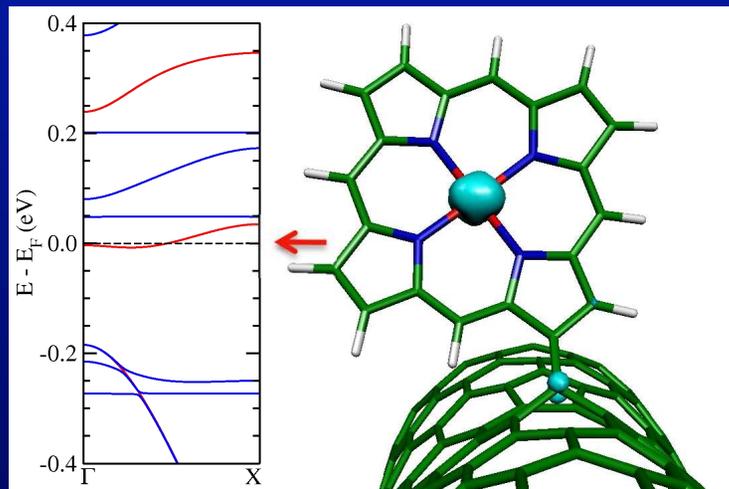
(8,8)-FeP ( $sp^2$  bonding)



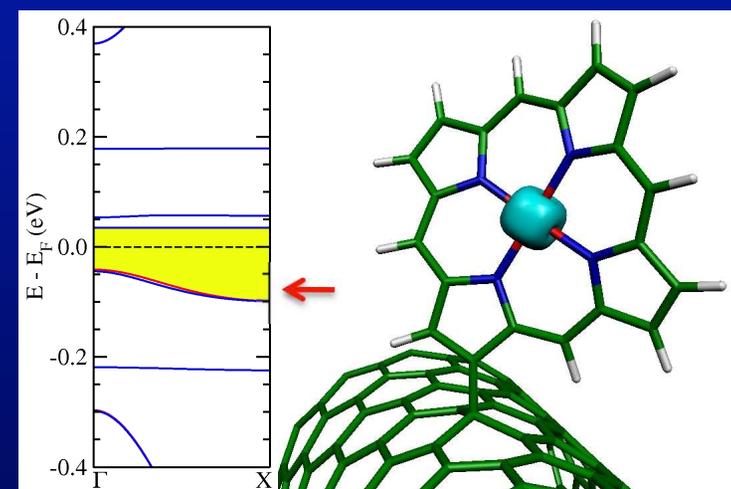
(8,8)-FeP ( $sp^3$  bonding)



(14,0)-FeP ( $sp^2$  bonding)



(14,0)-FeP ( $sp^3$  bonding)





# In summary

System	Bonding	$E_b$ [FeP] (eV)	$m$ ( $\mu_B$ )	E-property
FeP-(8,8)	$\pi-\pi$	-1.090	2.02	metallic
FeP*-(8,8)+V	$sp^2$	-4.997	2.20	metallic
FeP*-(8,8)	$sp^3$	-1.626	2.19	metallic
FeP-(14,0)	$\pi-\pi$	-1.051	2.05	semiconductor
FeP*-(14,0)+V	$sp^2$	-4.813	1.93	semiconductor
FeP*-(14,0)	$sp^3$	-1.796	2.16	semiconductor

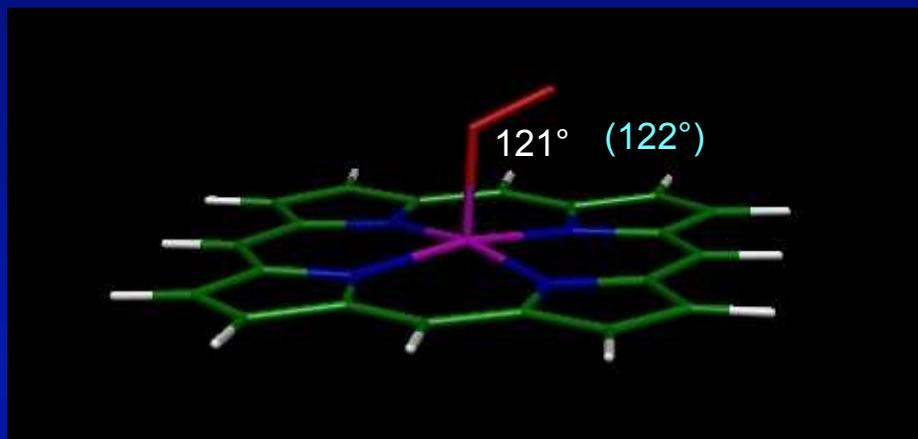
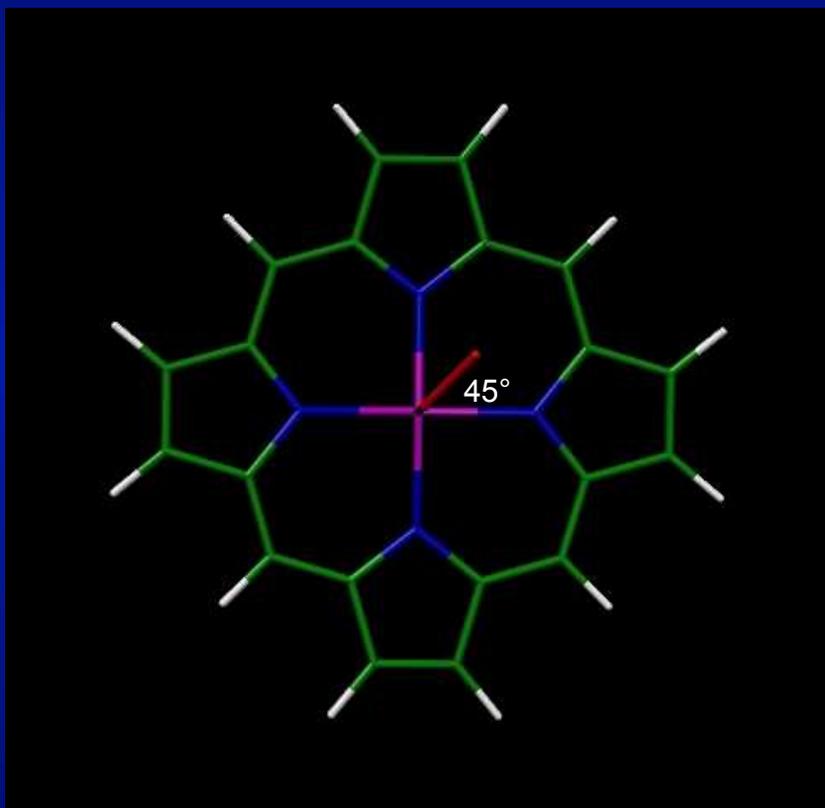
Supramolecular FeP-CNT systems need to be metallic to supply charge to the macrocycle in order to work as a catalyst. Thus, metallic nanotubes would be the correct substrate to attach the macrocycles.

Phys. Rev. B 82, 115406 (2010).



# O<sub>2</sub> capture by an isolated FeP

Equilibrium geometry of an O<sub>2</sub> molecule attached to the Fe atom of FeP



$$E_b(\text{O}_2) = 1.21 \text{ eV} \quad (1.55 \text{ eV})$$

$$d_{\text{O-O}} = 1.26 \text{ \AA} \quad (1.27 \text{ \AA})$$

$$d_{\text{Fe-O}} = 1.70 \text{ \AA} \quad (1.68 \text{ \AA})$$

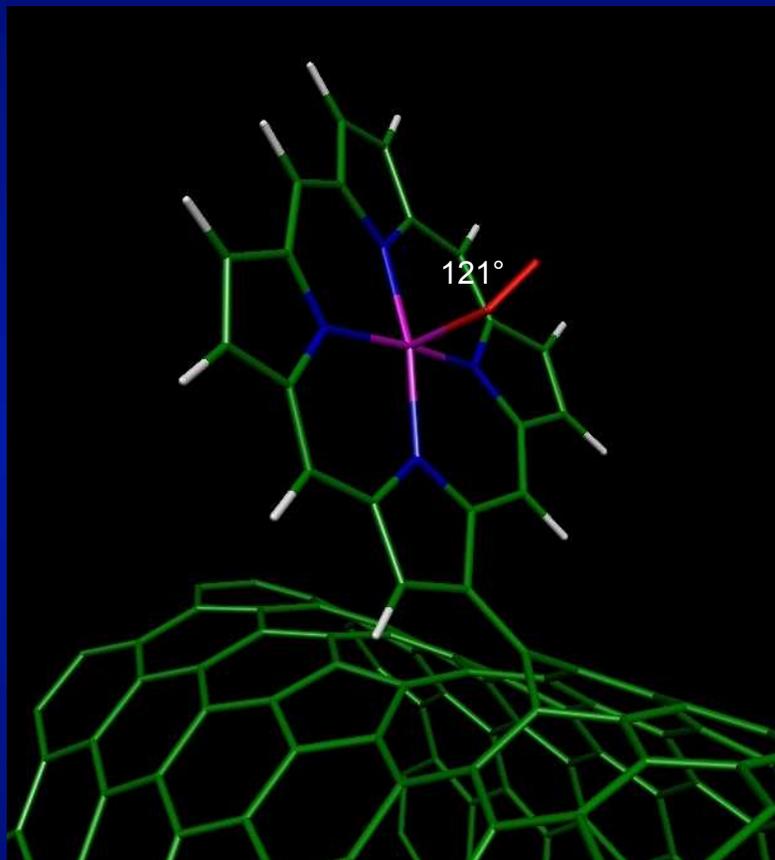
↑  
PW

Rovira *et al.* J. Phys. Chem. A101, 8914 (1997) → GGA

$$\left\{ \begin{array}{l} E_b(\text{O}_2) = 0.4 \text{ eV} \\ d_{\text{O-O}} = 1.28 \text{ \AA} \\ d_{\text{Fe-O}} = 1.74 \text{ \AA} \end{array} \right.$$



# O<sub>2</sub> capture by the FeP-CNT system

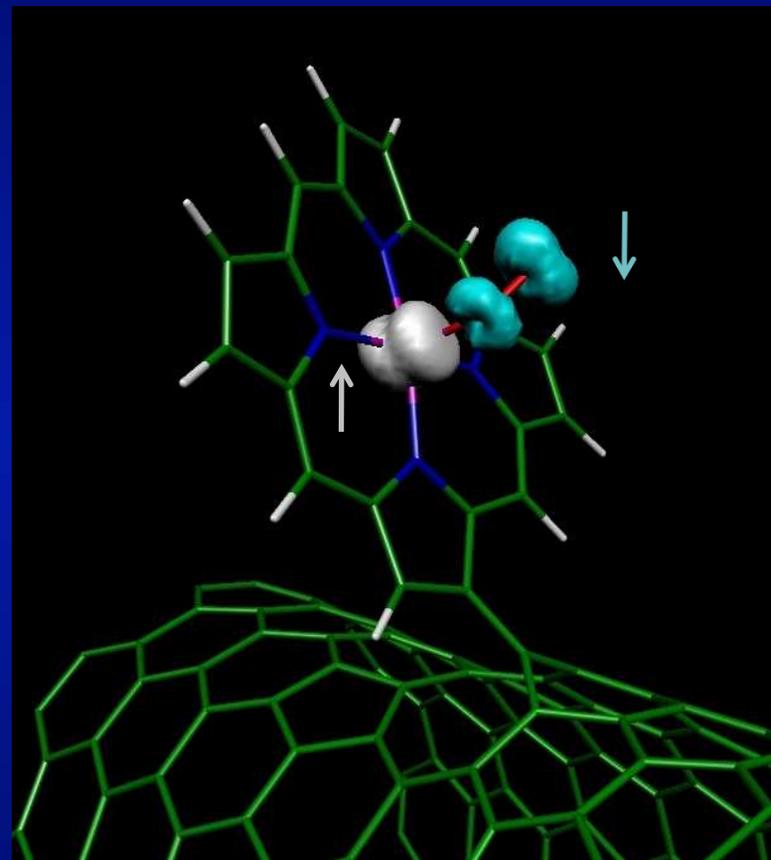


$$E_b(\text{O}_2) = 1.05 \text{ eV} \quad -13\% !$$

$$d_{\text{O-O}} = 1.26 \text{ \AA}$$

$$d_{\text{Fe-O}} = 1.70 \text{ \AA}$$

$$m = 0 \mu_B$$

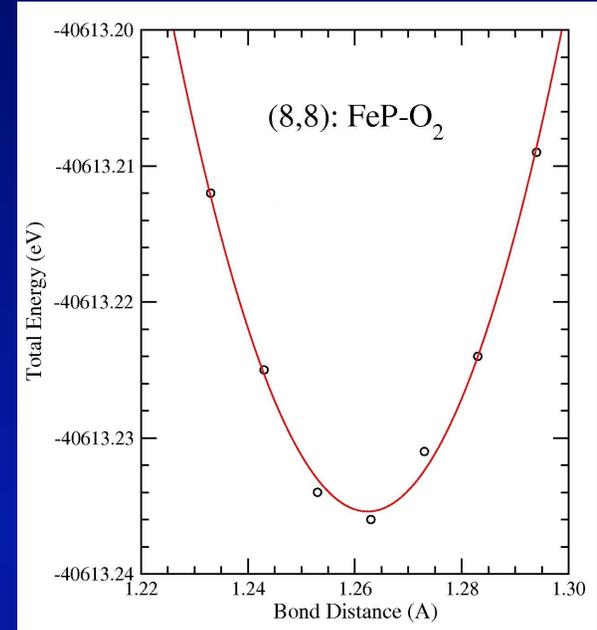
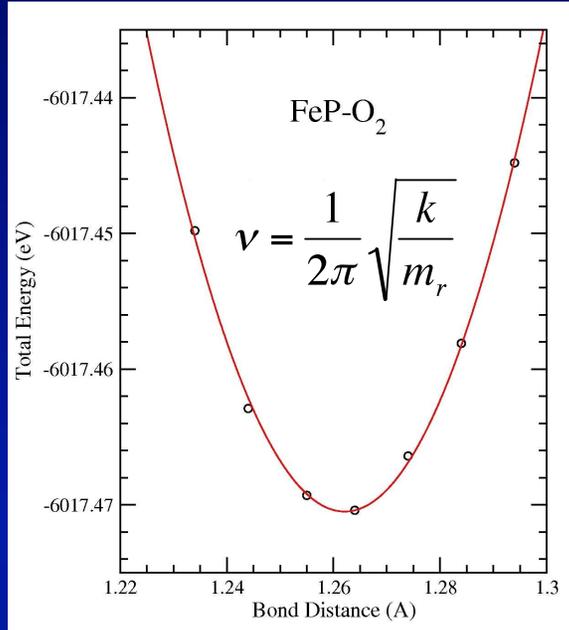
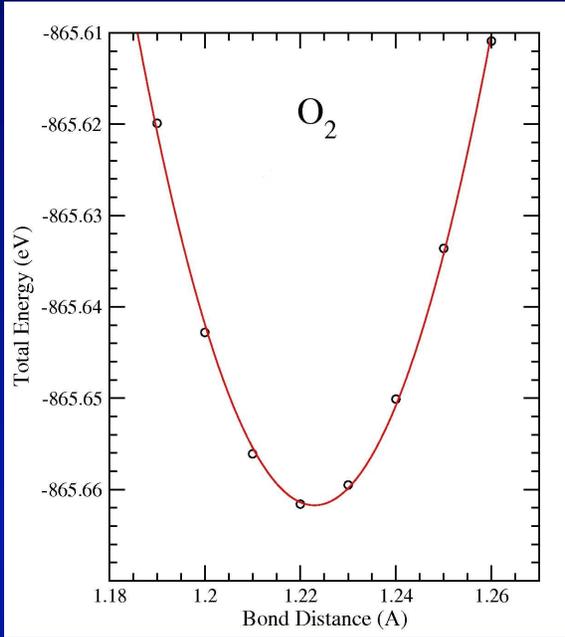


Antiferromagnetic coupling !

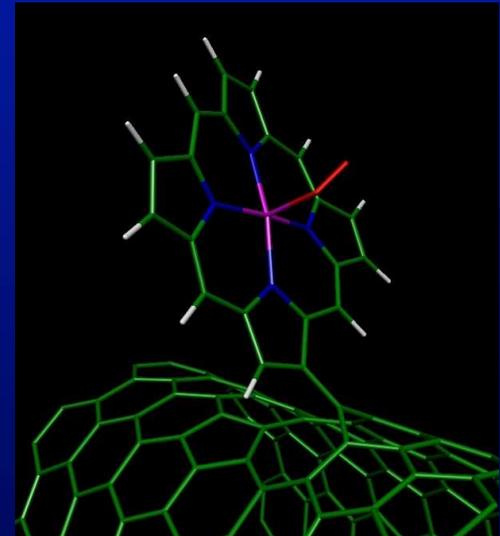
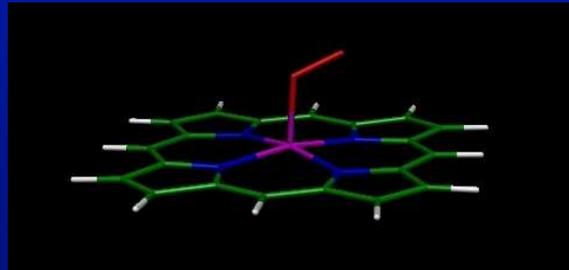
$$J = E_{\text{AFM}} - E_{\text{FM}} = 0.9 \text{ eV}$$



# O<sub>2</sub> Vibrational Properties



Experimental O<sub>2</sub>:  
 $\nu = 1580 \text{ cm}^{-1}$   
 $d = 1.206 \text{ \AA}$



	O <sub>2</sub>	FeP-O <sub>2</sub>	(8,8):FeP-O <sub>2</sub>
$\nu \text{ (cm}^{-1}\text{)}$	1599 (+1.2%)	1318 (-18%)	1351 (-16%)
$d \text{ (\AA)}$	1.223 (+1.4%)	1.262 (+3%)	1.262 (+3%)



# Conclusions

FeP attached on metallic carbon nanotubes would show catalytic activity due to the metallic character of the nanoensemble.

Chemical attachments forming  $sp^2$  and  $sp^3$  bonding would be those observed in carbon supported Fe-N<sub>4</sub> catalysts after heat treatments.

The spin multiplicity of the FeP molecule are preserved when it is attached to carbon nanotubes

The O<sub>2</sub> capture by CNT-supported FeP would be mediated by an antiferromagnetic coupling between O<sub>2</sub> and FeP.

The vibrational frequency of O<sub>2</sub> attached on CNT-supported FeP notably decreases with respect to the gas phase, indicating the bond weakness.