The Abdus Salam
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Understanding the microstructure of polymer-metaoxide hybrid interfaces

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OLYPHEMO PROJECT

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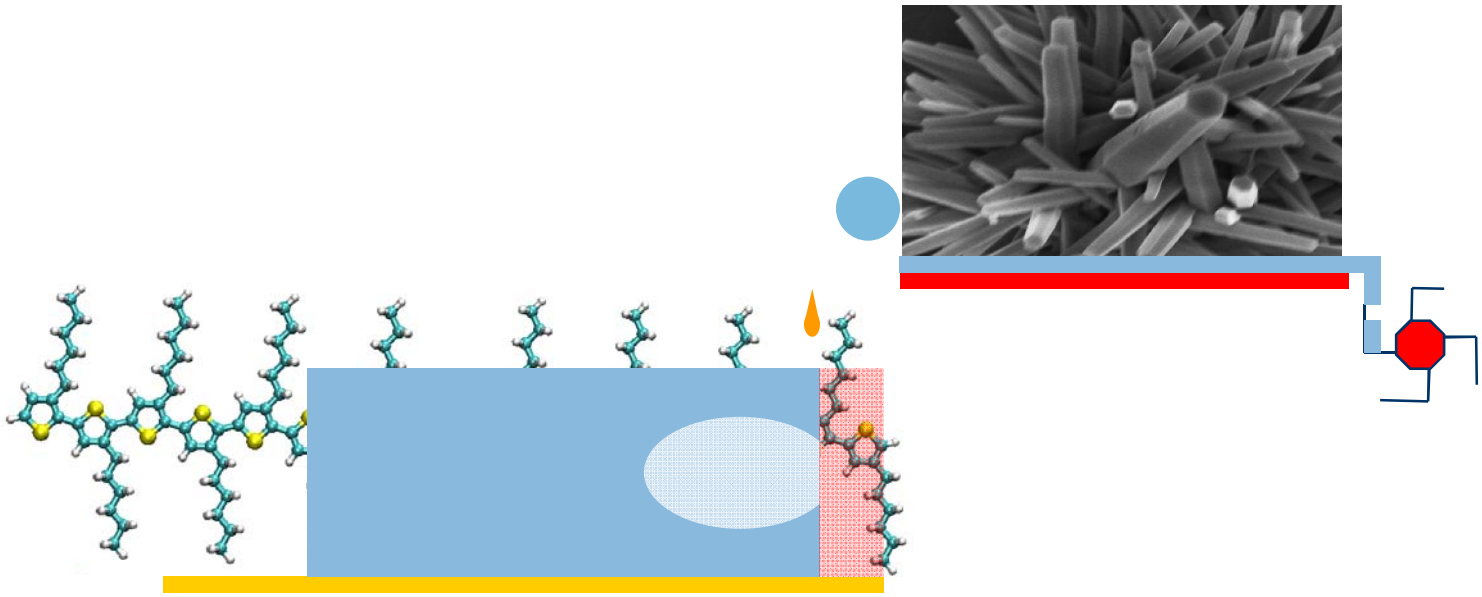
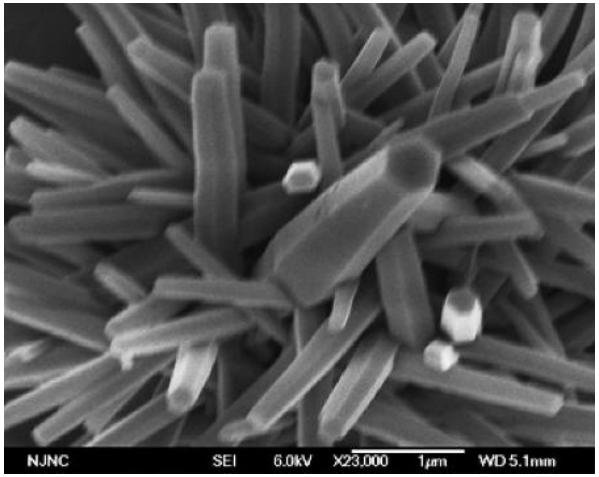
Polymer-based hybrid solar cells

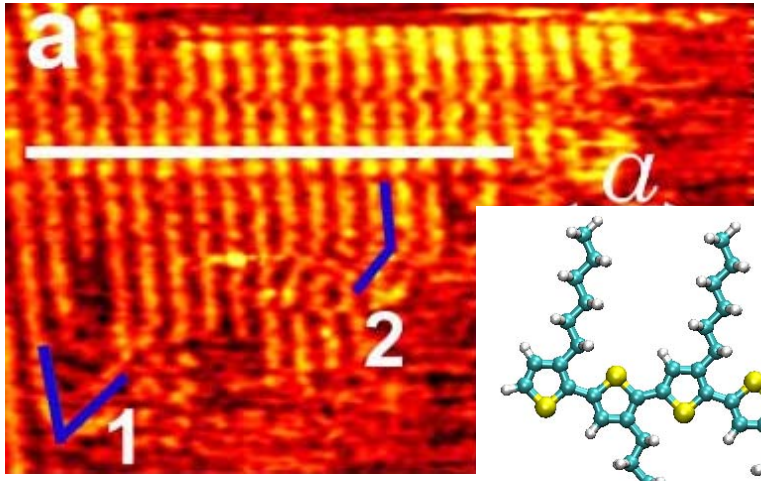
- Hybrid solid state donor/acceptor binary system
  - Polymer absorbs and transport holes (e.g. P3HT)
  - Metaloxides as electron acceptors (ZnO)
  - Combine advantages of both organic and inorganic

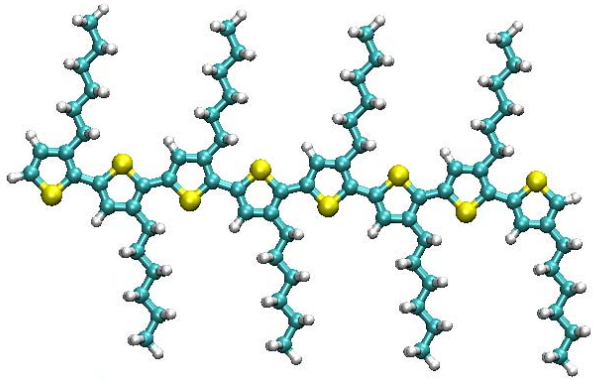
P3HT / ZnO,TiO_2



P3HT/ZnO

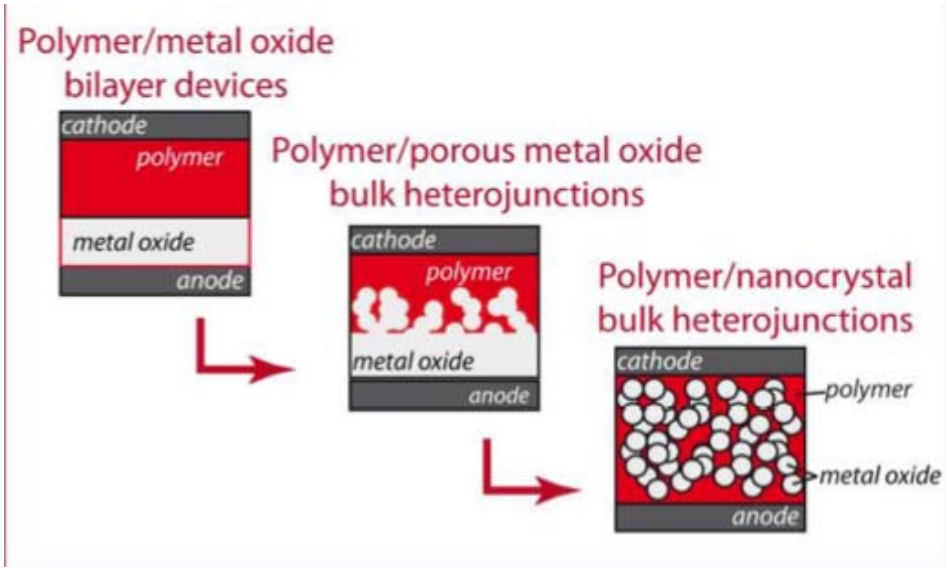


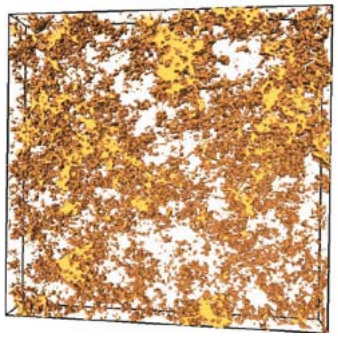




Microstructures of hybrids

- Bulk heterojunction concept
- Infiltration of organic component within nanostructured (nanopatterned or sintered nano- meso-porous structure)





S. D. Oosterhout, *The effect of three-dimensional morphology on the efficiency of hybrid polymer solar cells*, Nature Materials 8, 818 (2009)

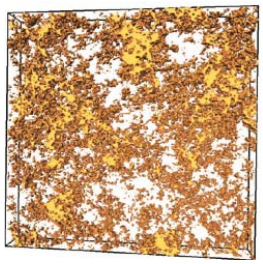
J. Boucle and J. Ackermann, Polymer International, in press

PCE

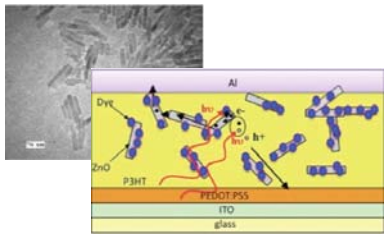
4.

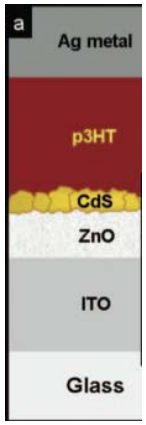
- P3HT/PCBM
  PCE 5%

- DSSC (EL/DYE/ZnO)
  PCE 5.6%
  T. Yoshida et al.Adv. Funct. Mater. 19 (2009)



- P3HT/ZnO
  PCE 2%
  S. D Oseterhout et al. Nature Mat. 8, 818 (2009)





- P3HT/ZnO
  PCE <0.04%
  Planar Junction
  Hsu et al. MRS Bull 35 422 (2010)

- P3HT/MOL/ZnO
  PCE 0.05%
  Planar SAM
  Hsu et al. MRS Bull 35 422 (2010)

- P3HT/MOL/ns-ZnO
  PCE 0.09-0.11%
  A. J. Said et al. JPC C114 11274 (2010)
  E.D Spoerke APL 95, 213506 (009)

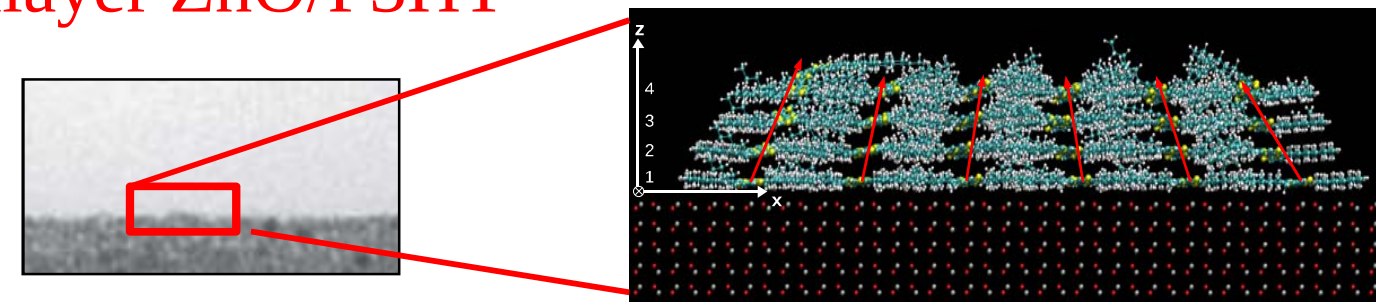
complexity →

ZnO/P3HT

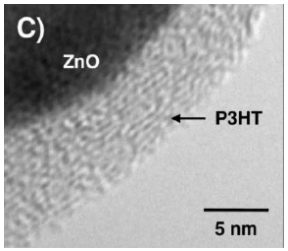
- Efficiencies polymer/metaloxide are below 2% still low compared to all organic systems (planar bilayer P3HT/ZnO has efficiency < 0.01% ten times below titania based systems)
- Some fundamental issues must be clarified for the hybrid interface

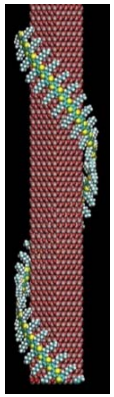
OUTLINE

- Planar bilayer ZnO/P3HT



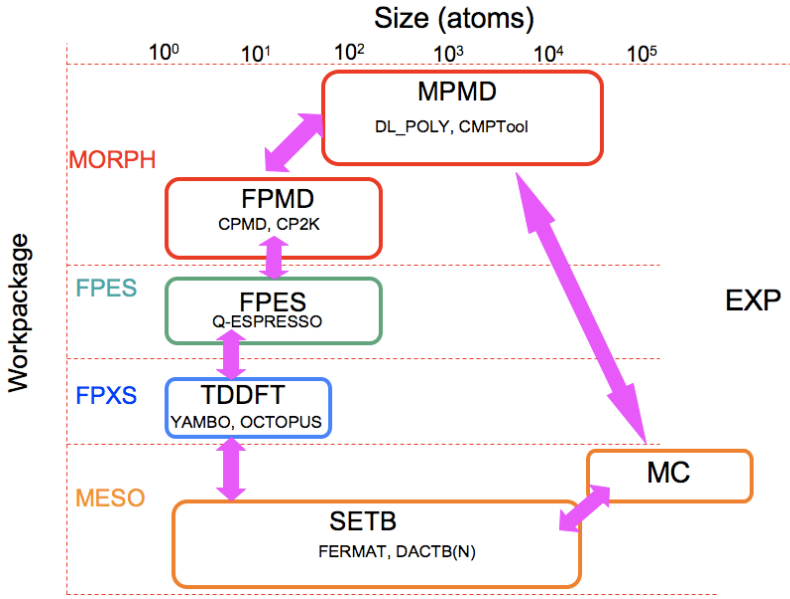
- Curved P3HT/ns-ZnO





Multiphysics to treat complexity

- Need of multi physics: atomic scale quantum chemistry for molecules, solid state methods for inorganic nanostructures, larger scale methods to include disorder, complex junctions architectures



Model potentials

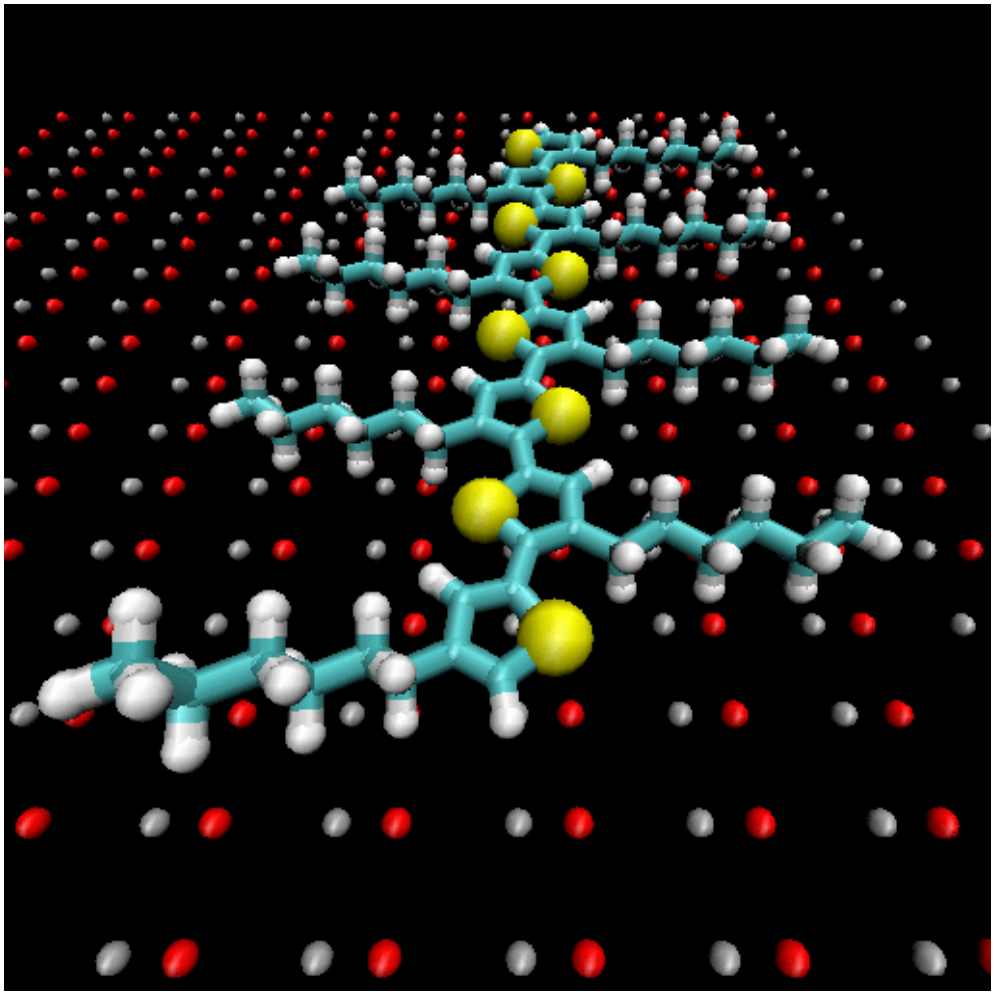
$$E_{Zn-O} = \frac{q_i q_j}{r_{ij}} + A \cdot \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}$$

$$E_{P3HT} = \sum_{\text{bonds}} K_r(r - r_{eq})^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{V_n}{2}[1 + \cos(n\phi - \gamma)] + \sum_{i<j}\left[\frac{q_i q_j}{\varepsilon r_{ij}}\right] + \sum_{i<j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

$$E_{P3HT/ZnO} = \frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Single P3HT chain on ZnO

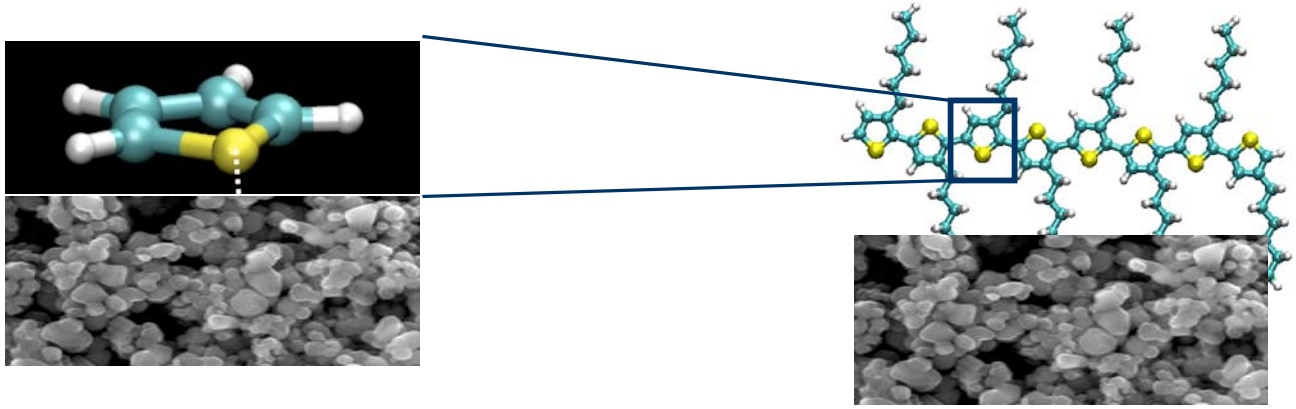
- P3HT/ZnO interaction and interface is generated by model potential molecular dynamics
- Forces from model potential including dispersive plus electrostatic interactions
- Atomic charges calculated by first-principles methods



physics of adhesion

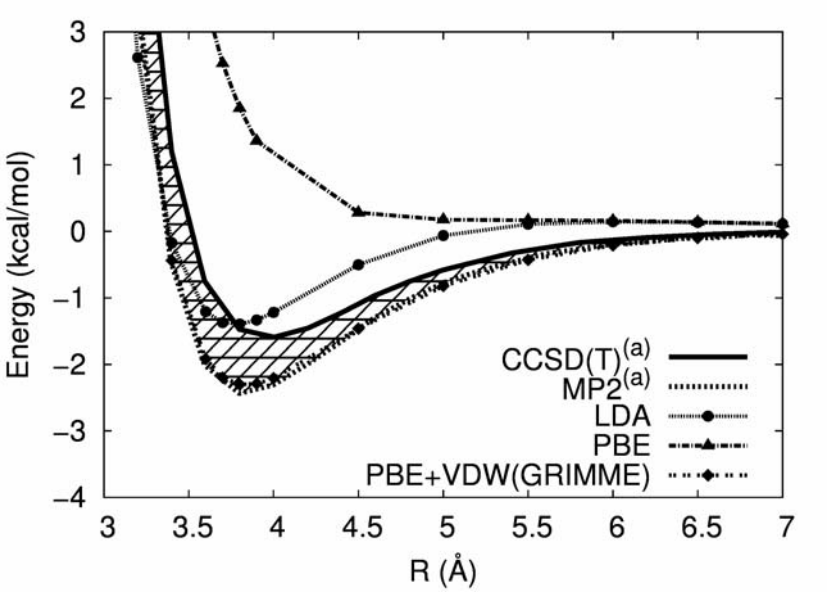
- Thiophene on CNT 0.38 eV C. Denis et al. J.Mol. Struct. THEOCHEM 957 114 (2010)
- Thiophene on TiO_2 0.52 eV C. Melis et al. JPC C (2010)
- Thiophene on ZnO 0.65 eV I. Saba et al. JPC C (2010) **EXP 0.64 eV**

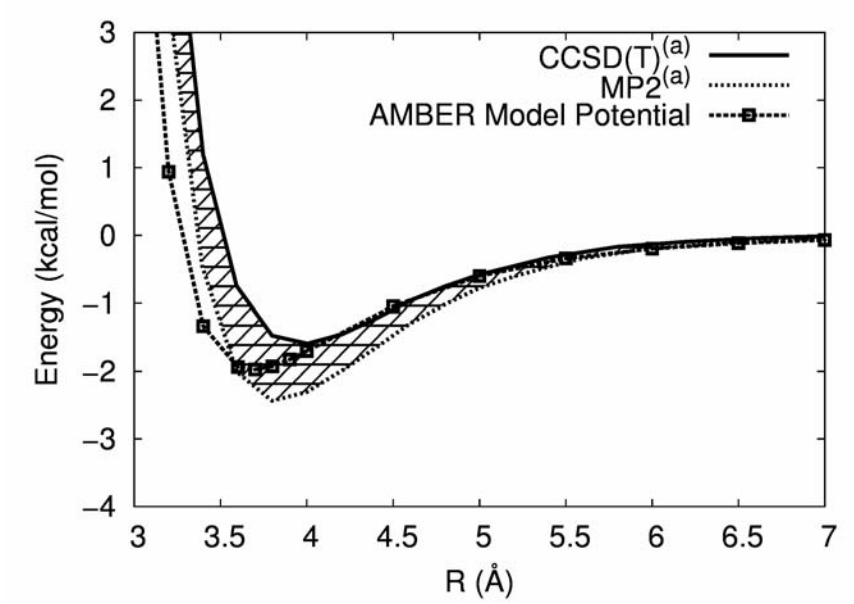
- Thiophene-Thiophene 0.1 eV C. Melis et al. JPC B (2010), Tsuzuki et al. JACS 124 12200

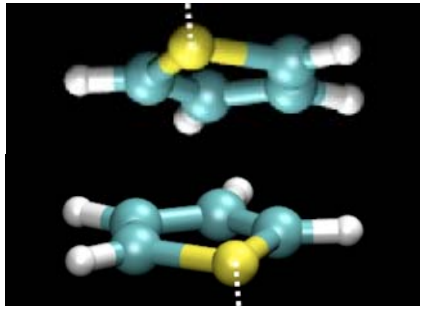


The role of dispersion forces

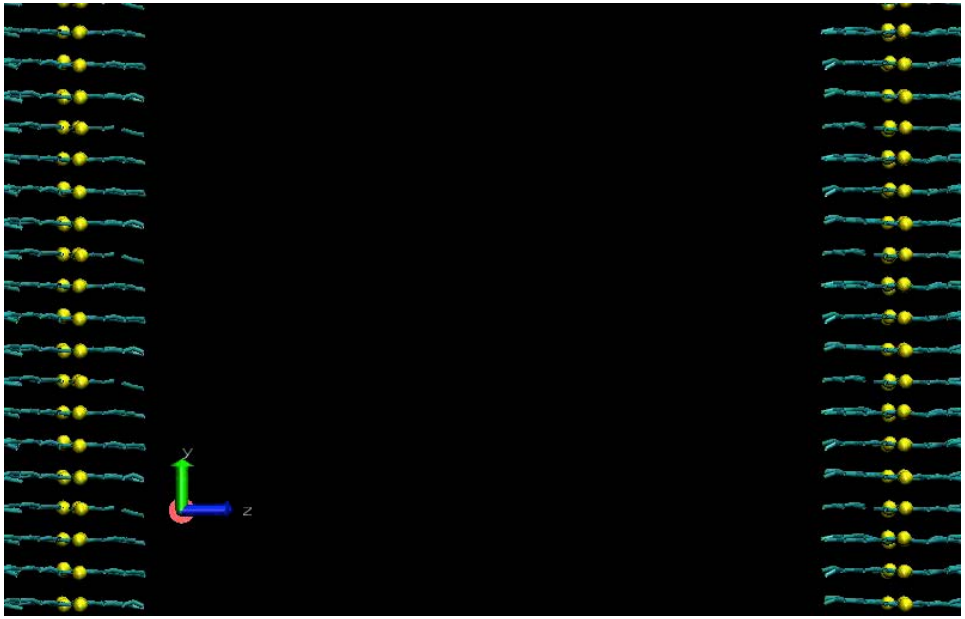
- Thiophene-Thiophene 0.1 eV C. Melis et al. JPC B (2010)







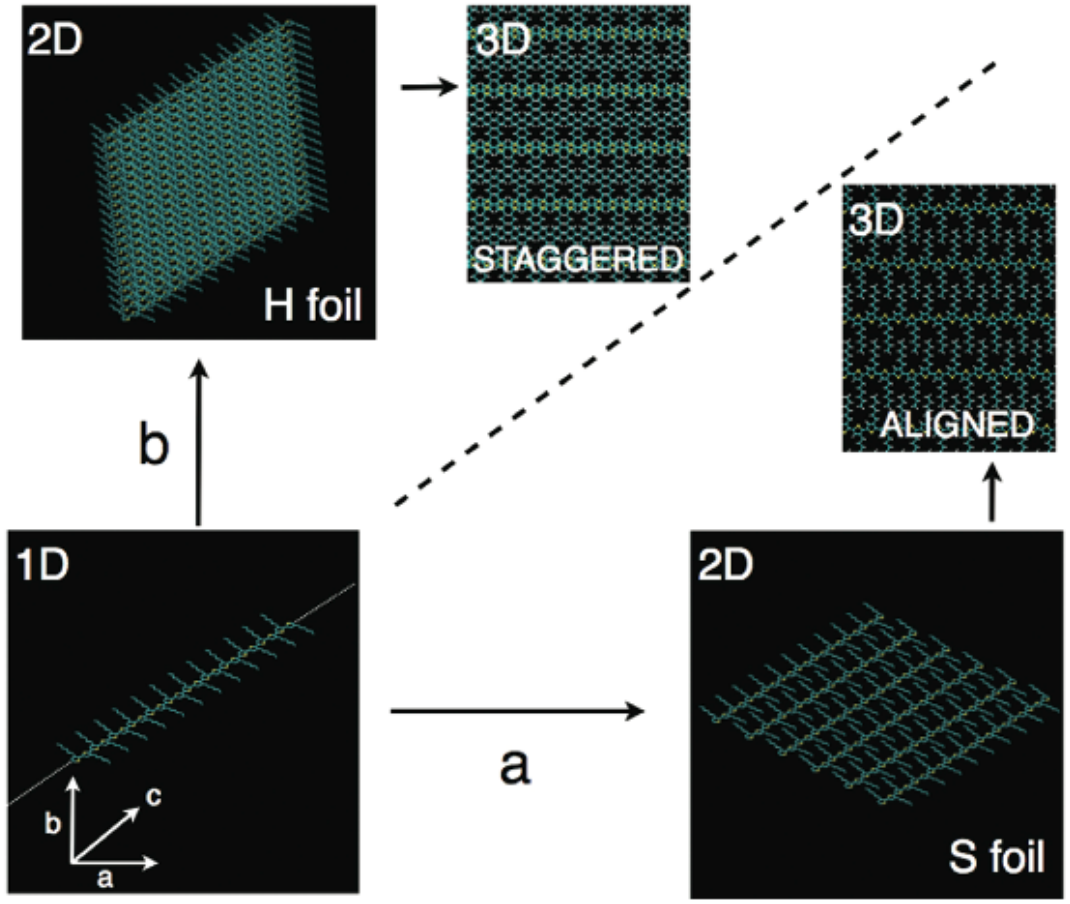
Polymer-polymer interactions



- Pi-pi drives hydrophobic foils with staggered alignement
- H-foils interacts and pack forming zigzag structure
- Kinetics rather than energy

Polymer crystal depend on assembling

J. Phys. Chem. C, Vol. 115, No. 2, 2011 579



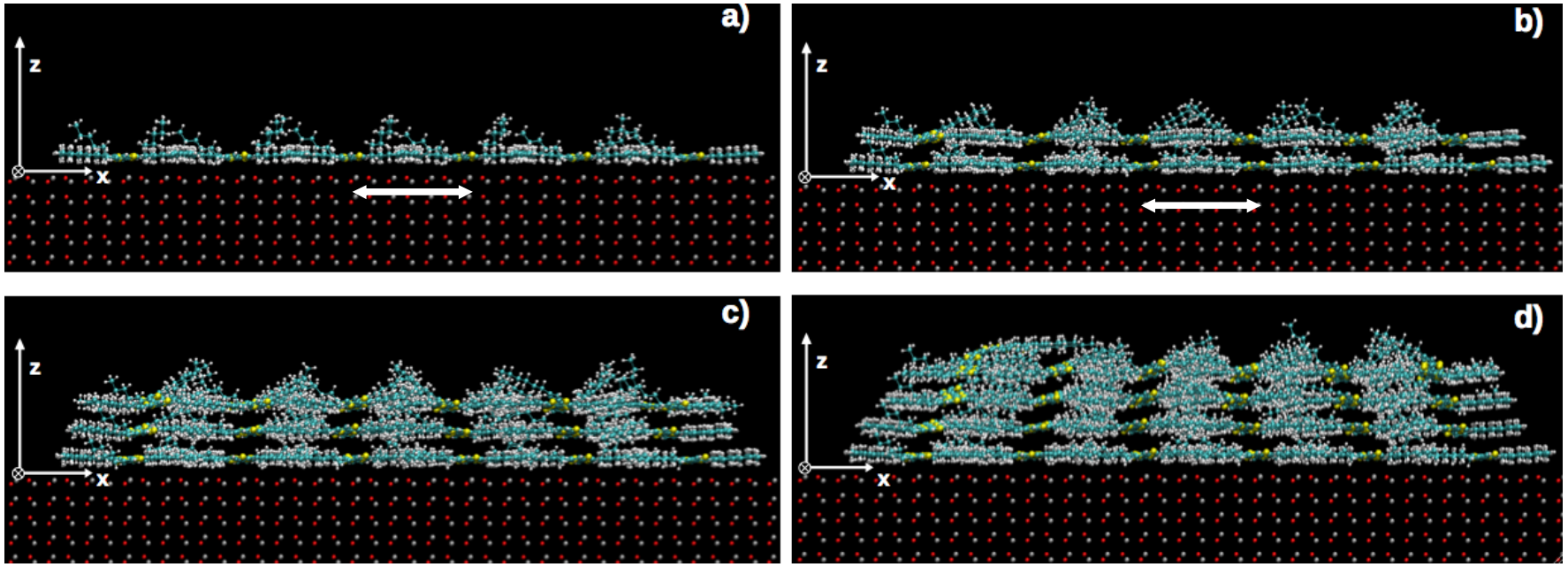
How to generate models of interface

- Polymer are sensitive to initial conditions (metastability is important)
- Two methods:
  - assembling (A)
  - merging (M)

Ideal conditions:
Ideal chemistry i.e. ideal vacuum (no chemical contamination, no solvent)
Ideal morphology i.e. low temperature, maximum possible order
No anchoring groups (just dispersive interactions)

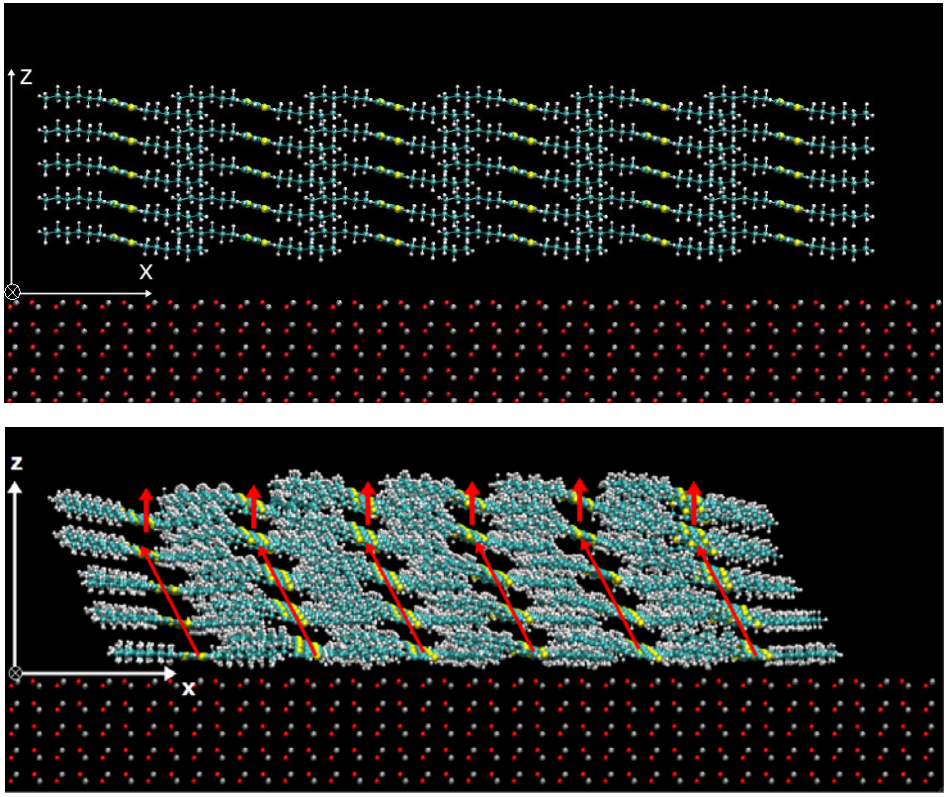
Assembling

- Successive stacking of polymer layers



M.I. Saba, C. Melis, L. Colombo, G. Malloci, and A. Mattoni "Polymer Crystallinity and Transport Properties at the Poly(3-hexylthiophene)/Zinc Oxide Interface" *J. Phys. Chem. C* **2011**

Merging



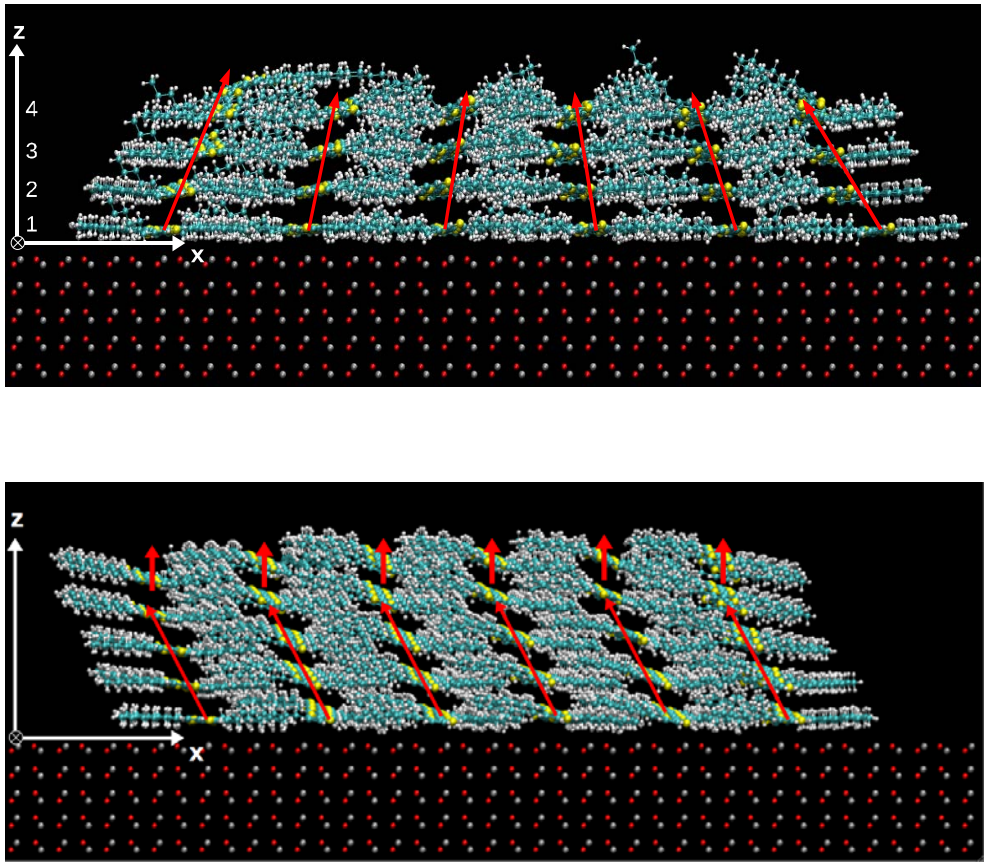
A perfect crystalline portion is cut out from a crystal and put on the surface

The system is relaxed

Distortions are observed

M.I. Saba, et al."Polymer Crystallinity and Transport Properties at the Poly(3-hexylthiophene)/Zinc Oxide Interface" *J. Phys. Chem. C* **2011**, ASAP

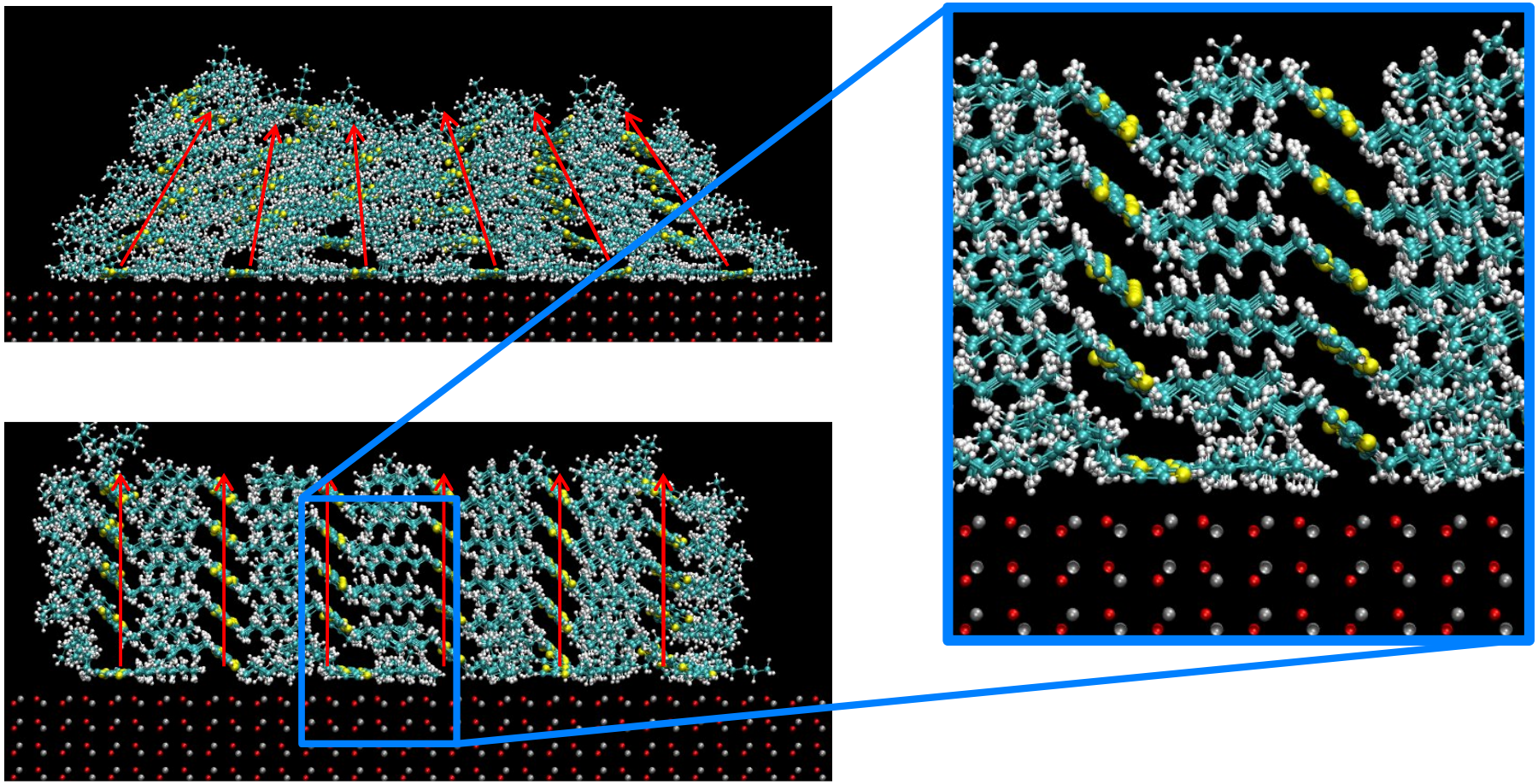
Two models of ordered interfaces



Final configuration of the system A (upper panel) and M (lower panel) on the ZnO surface. The red arrows correspond to the direction of the charge carriers

M.I. Saba, et al."Polymer Crystallinity and Transport Properties at the Poly(3-hexylthiophene)/Zinc Oxide Interface" *J. Phys. Chem. C* **2011**, ASAP

Finite temperature effects

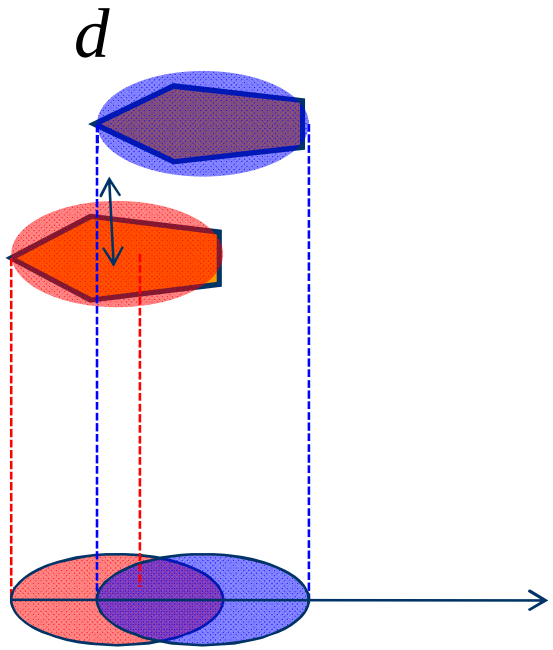


Transport efficiency: projected overlap area

$$J_{\alpha\beta} \sim e^{-\gamma\frac{d-d_0}{d_0}} \Theta_{\alpha\beta}$$

$$\mu \sim J_{\alpha\beta}^2$$

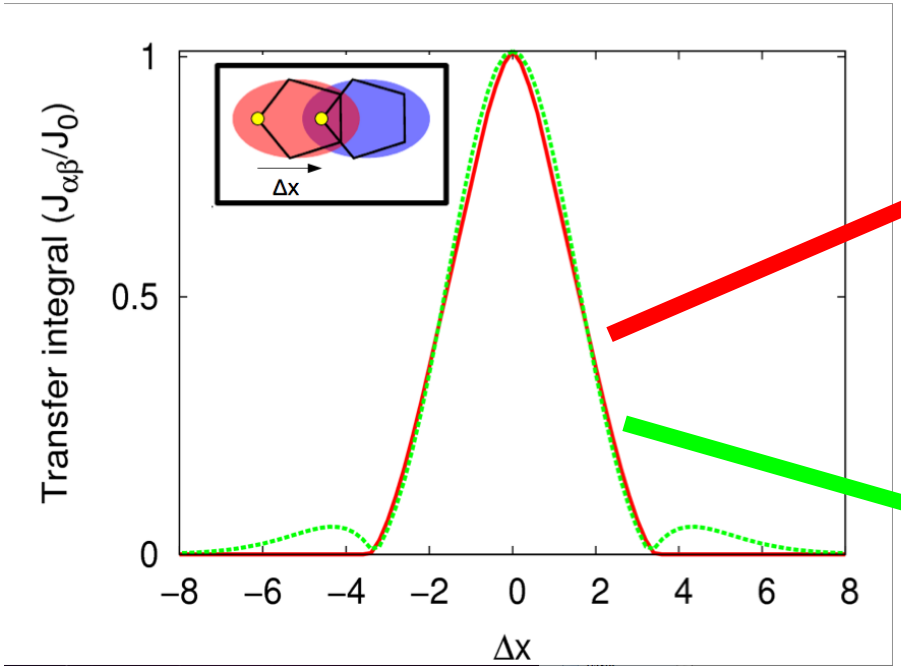
$$\frac{\mu}{\mu_0} = e^{-2\gamma\frac{d-d_0}{d_0}} \left(\frac{\Theta}{\Theta_0}\right)^2$$



$$\Theta = \Theta(\Delta x, \Delta y, \hat{\alpha}, \hat{\beta})$$

Projected overlap area ~ transfer integral

$$\Theta = \Theta(\Delta x, \Delta y, \hat{\alpha}, \hat{\beta})$$



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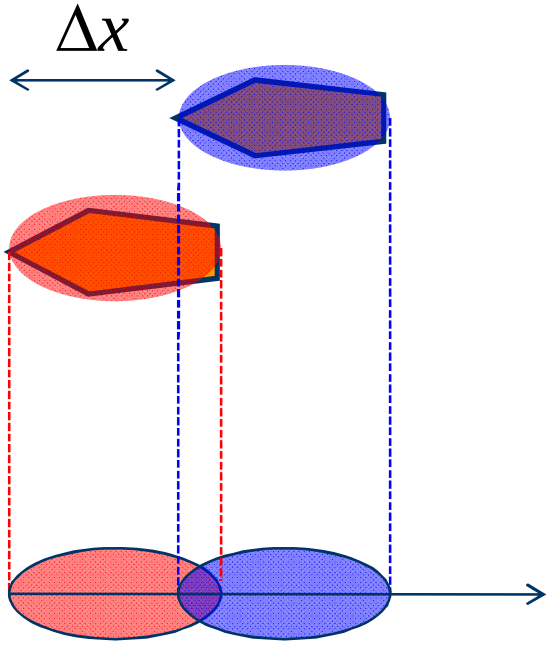
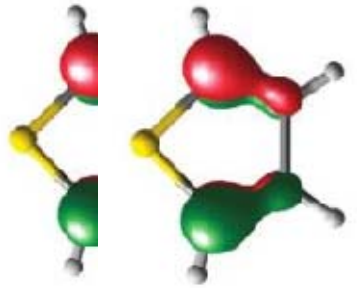
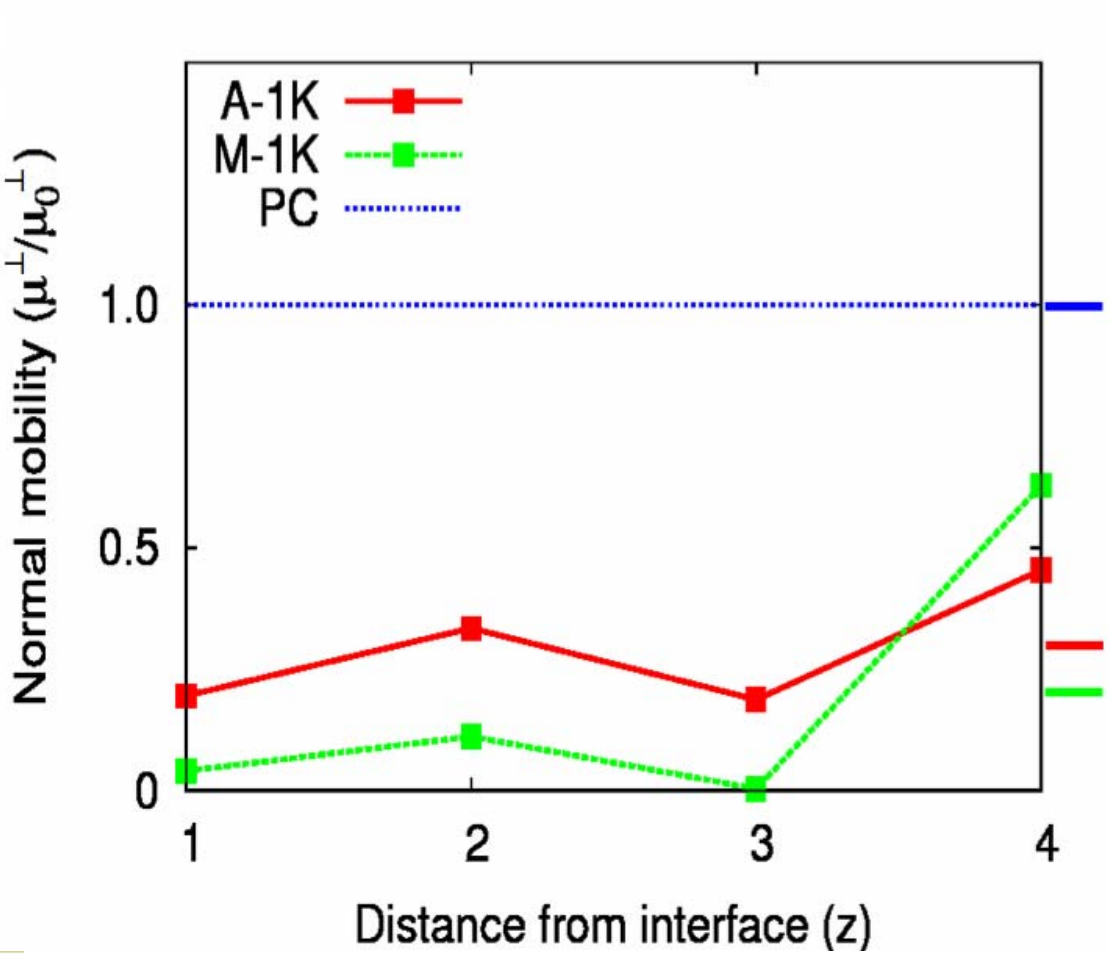
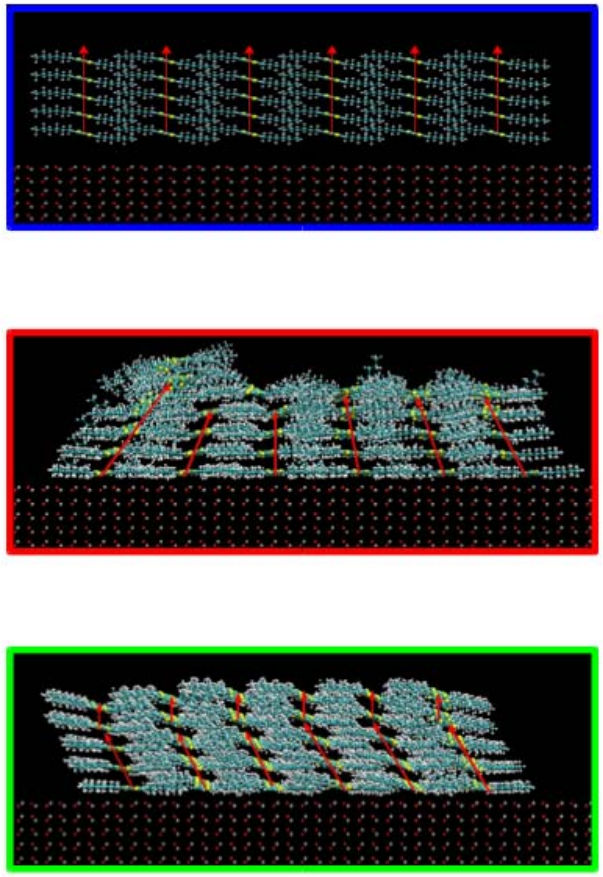


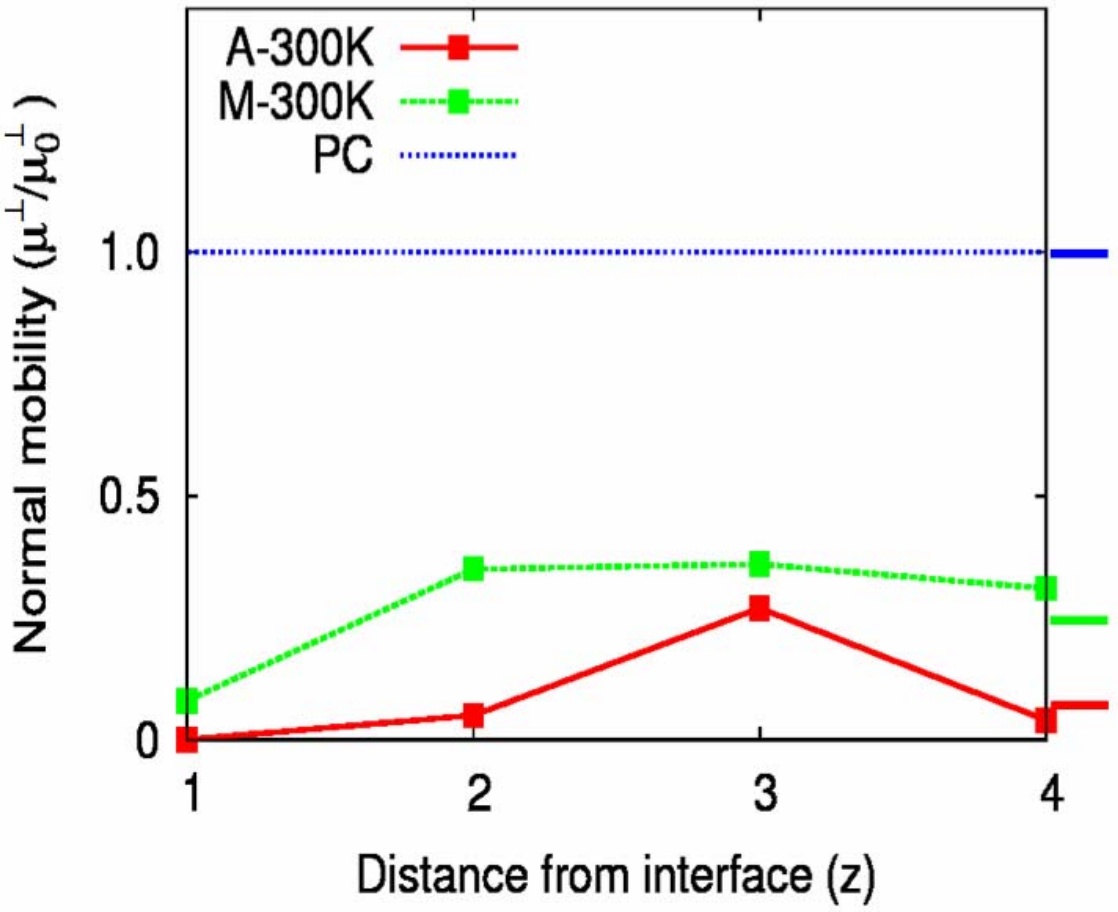


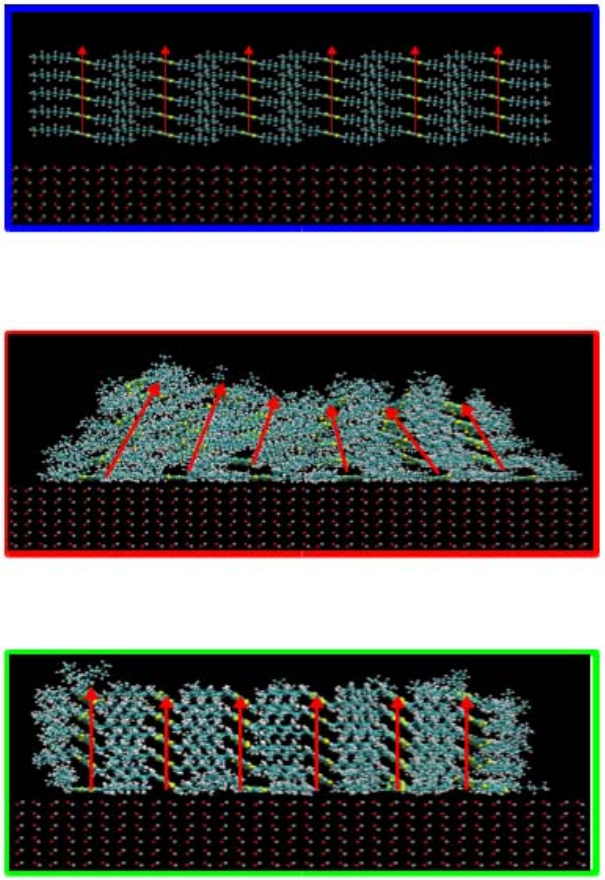
Mobility at the interface: T~ 0K



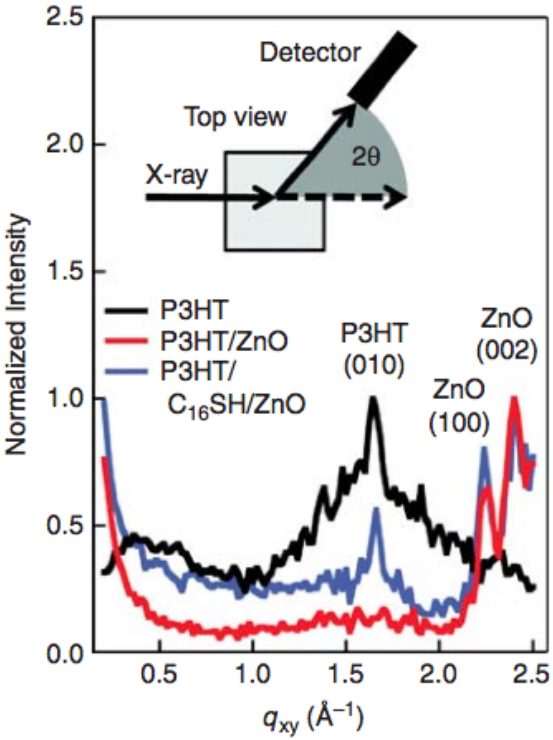


Mobility at the interface: T = 300K

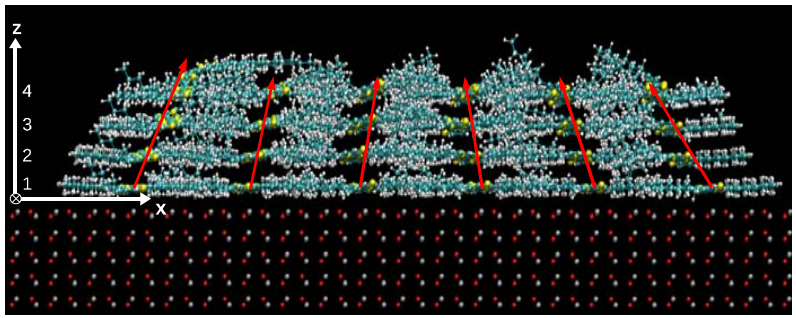


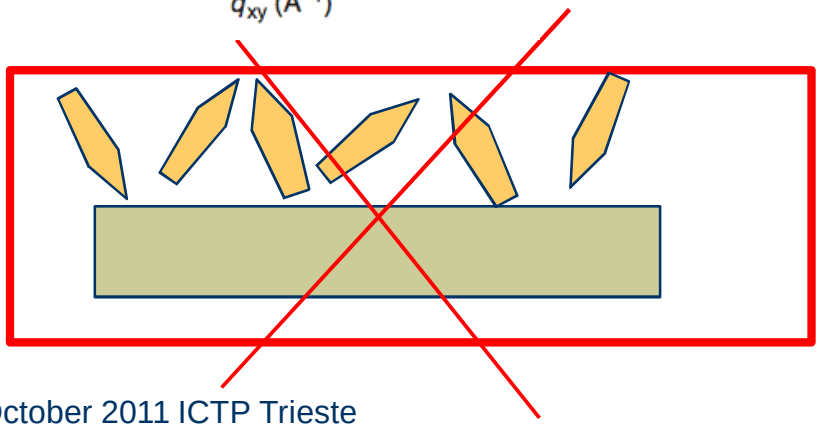


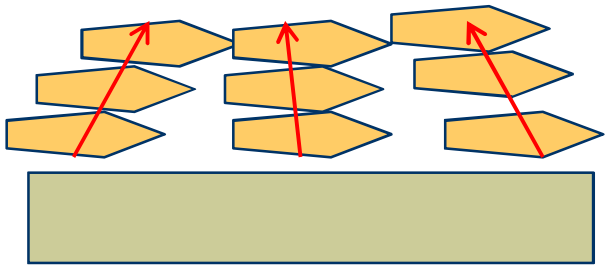
ZnO/P3HT planar interface: Th vs. Exp



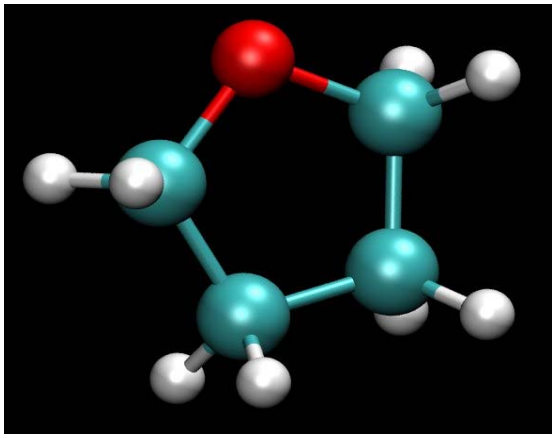
- *[th 1 ≠ exp1] π staking not parallel to the surface*
- *[th2 ~ exp1]Large substrate interaction*
- *[th3 = exp3]* Only the *interfacial P3HT layer is sensitive to the substrate*
- *[th4 ~ exp4]Amorphous DISORDER*





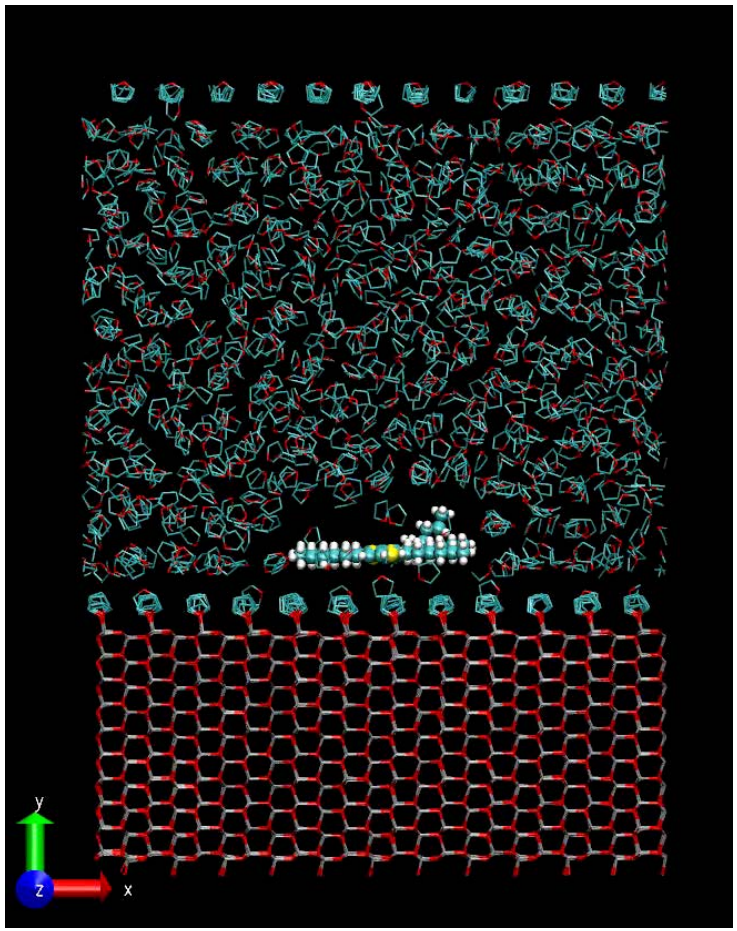


The role of solvent on the microstructure

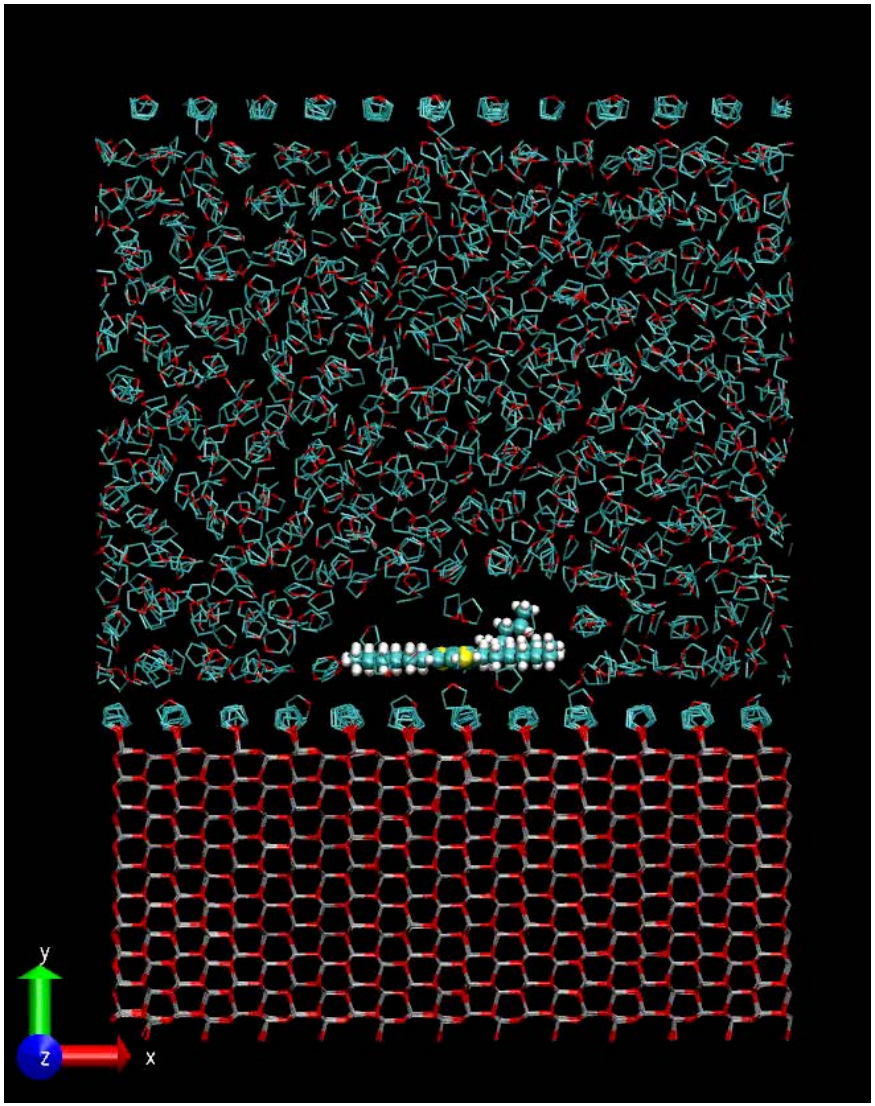


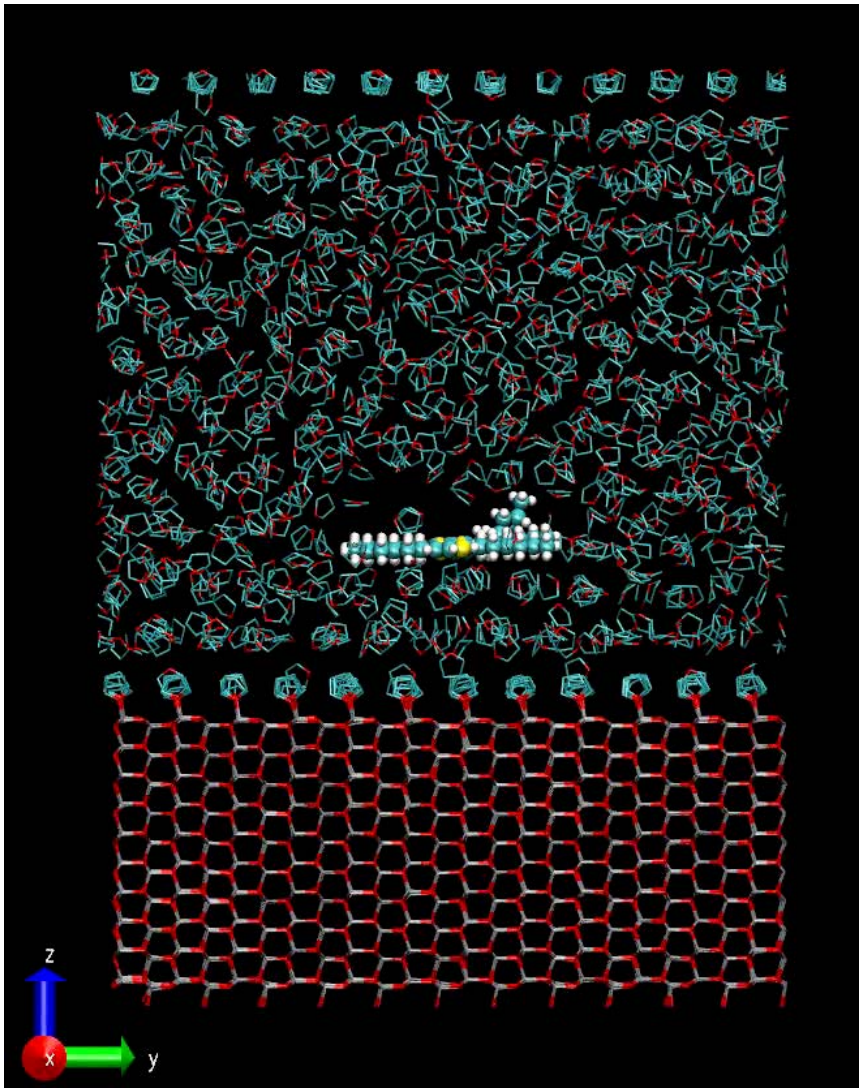
C_4H_8O

THF is a typical solvent for P3HT; the presence of the solvent can significantly affects the physics of the molecule adhesion and the final morphology

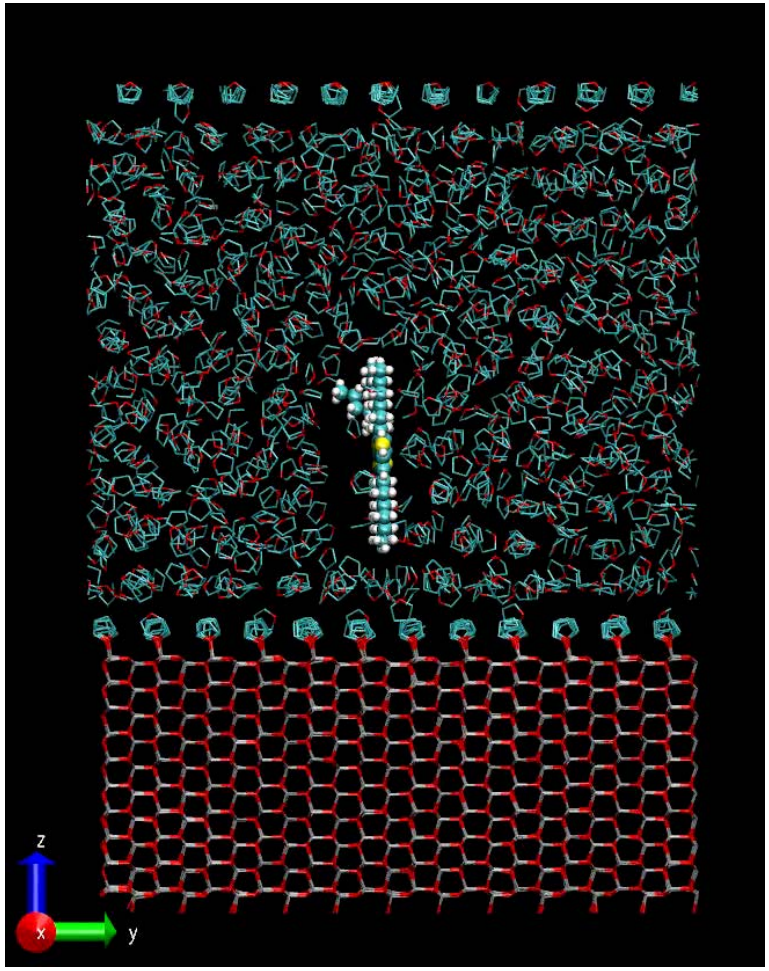


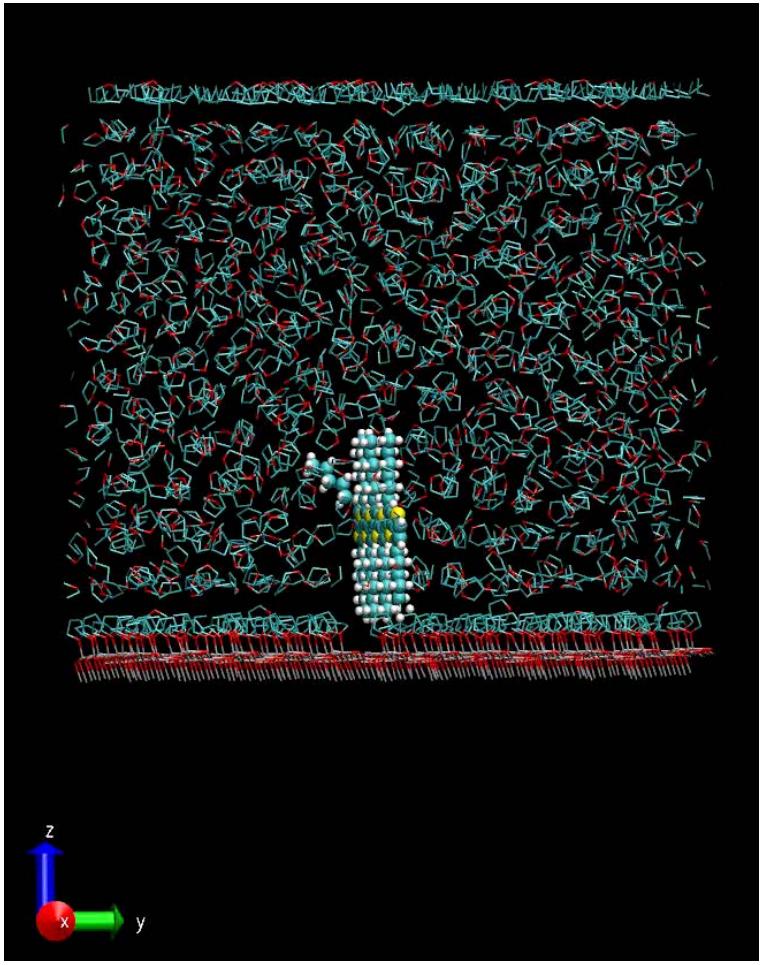
The role of the solvent

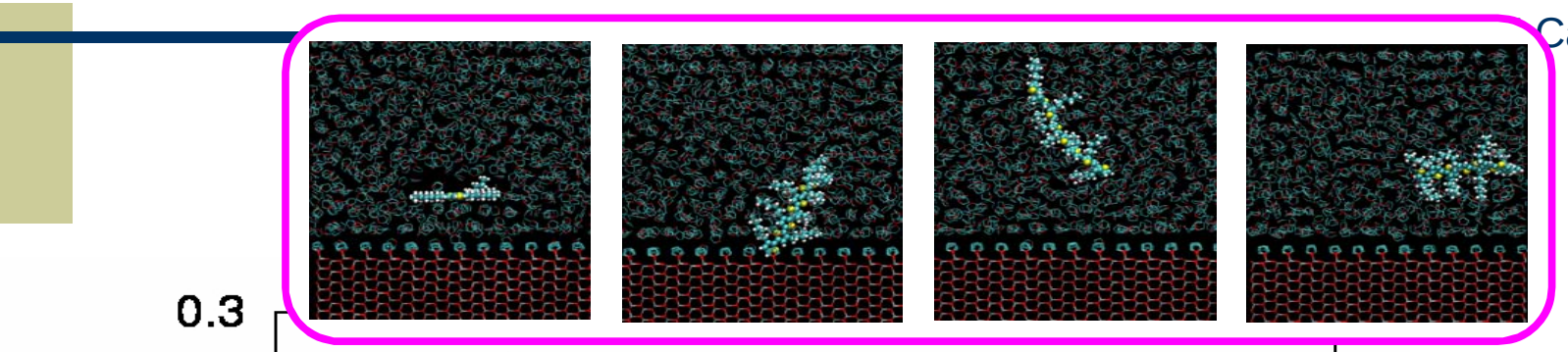


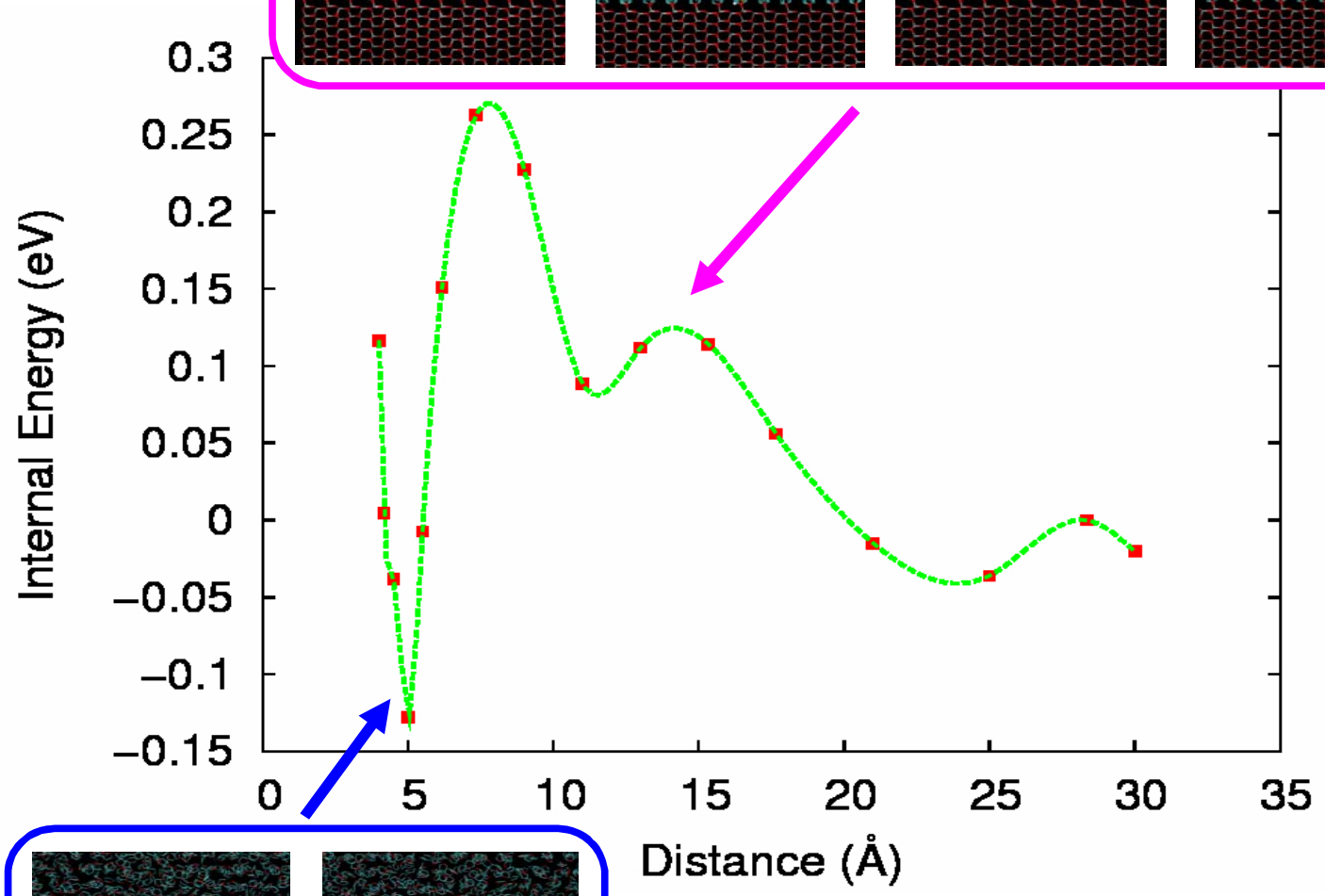


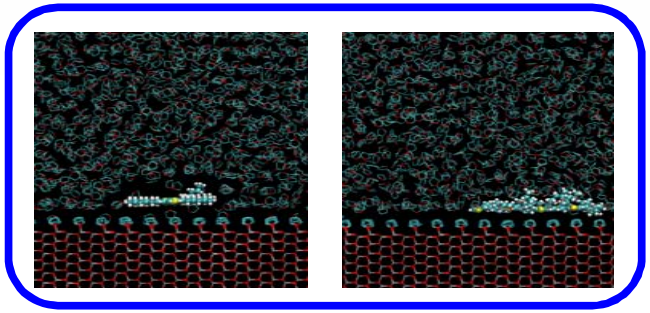
The role of the solvent







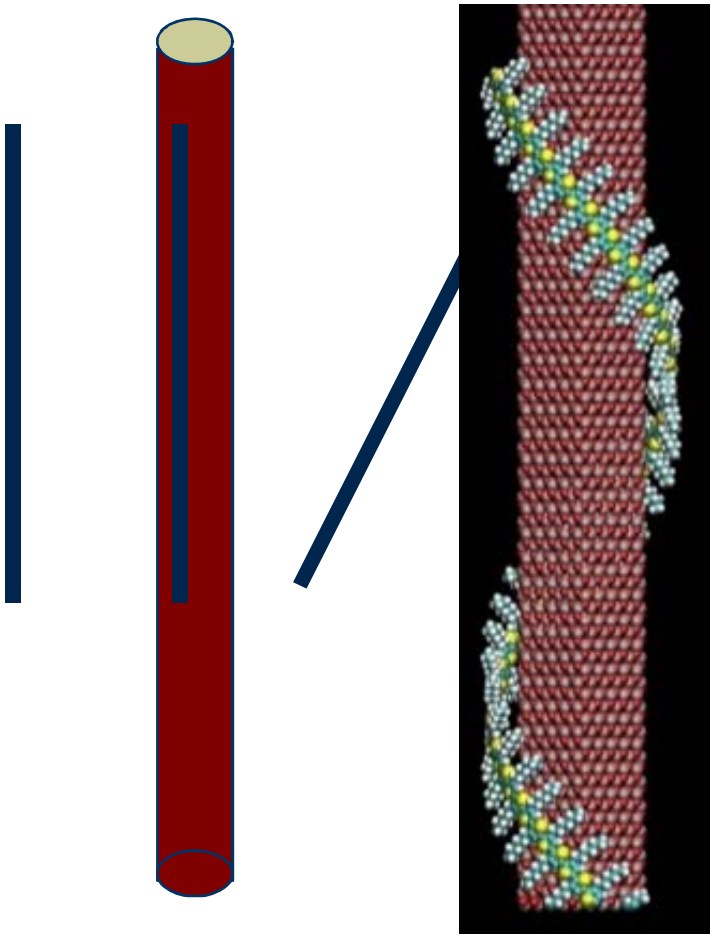

Internal Energy (eV)
0.3
0.25
0.2
0.15
0.1
0.05
0
−0.05
−0.1
−0.15
0
5
10
15
20
25
30
35
Distance (Å)



P3HT/nanoneedle ZnO interface

- *[4]*NANO-CURVATURE of the substrate: in dispersed nanoparticles the conformation of thiophenes deviate from planarity which in turn *reduces the conjugation length*

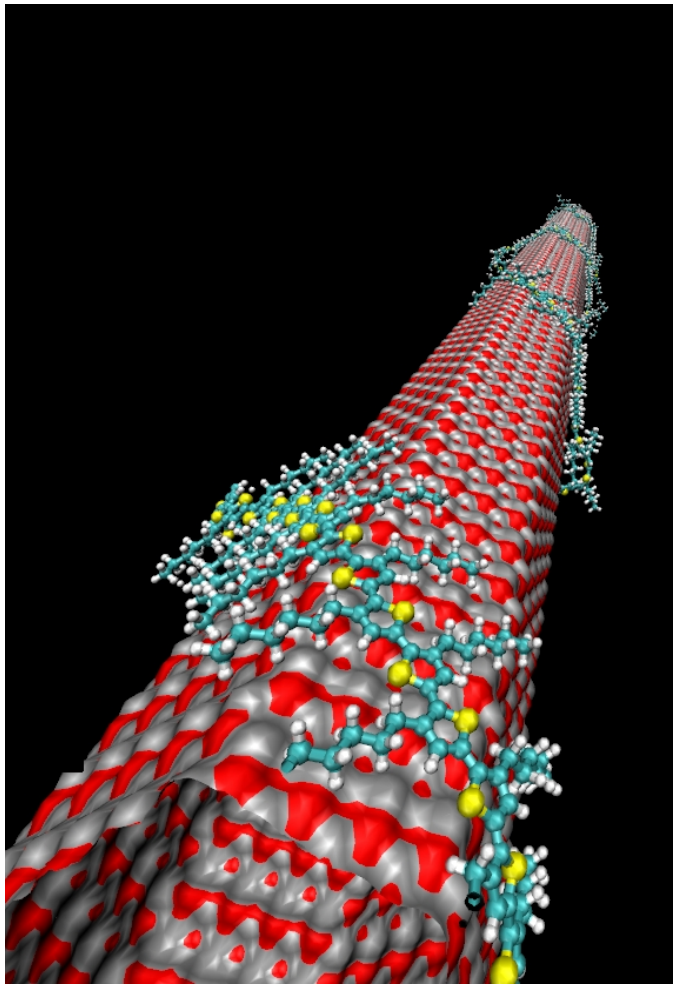
- There is an attractive interaction between P3HT-ZnO and when the polymer is not aligned we expect wrapping of the polymer



C. Caddeo, R. Dessì, C. Melis, L. Colombo, and A. Mattoni
"Poly(3-hexylthiophene) adhesion on zinc oxide nanoneedles"
submitted for publication

P3HT/nanoneedle ZnO interface

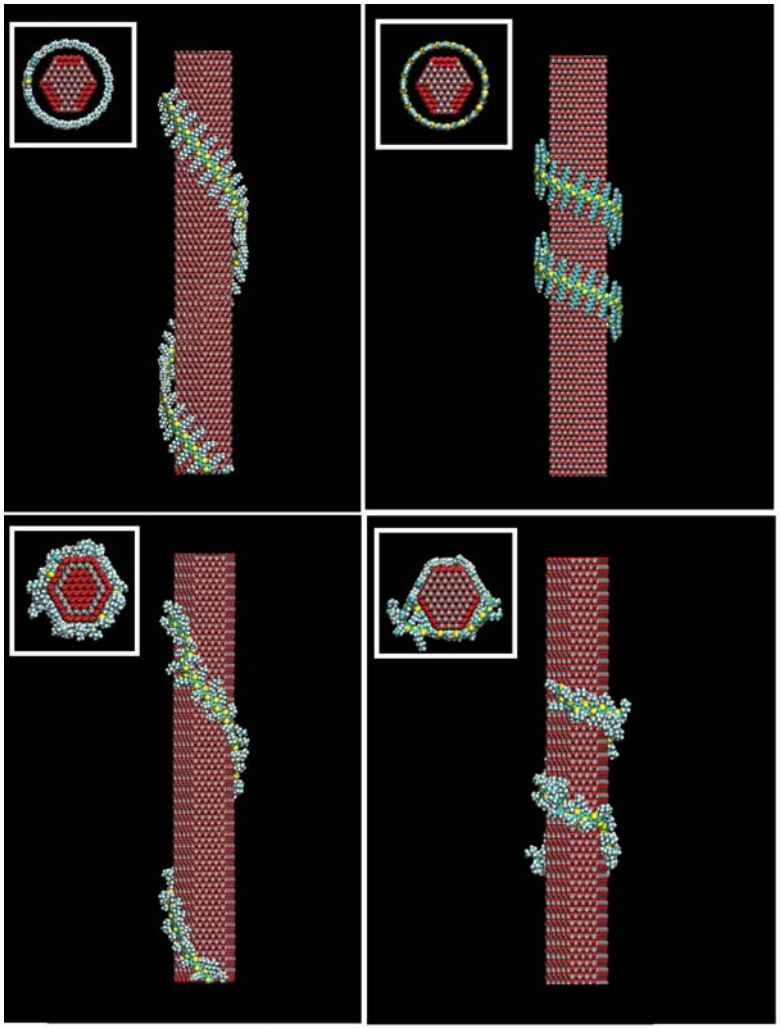
- An isolated polymer chain interacting by dispersive forces with a single ZnO nanoneedle (a small rod, 2.5 nm diameter)
- P3HT chains as large as 24 nm (64 monomers)
- 12000 atoms in the simulation cell (mostly in the needle)



C. Caddeo, R. Dessì, C. Melis, L. Colombo, and A. Mattoni "Poly(3-hexylthiophene) adhesion on zinc oxide nanoneedles" submitted for publication

P3HT/nanoneedle ZnO interface

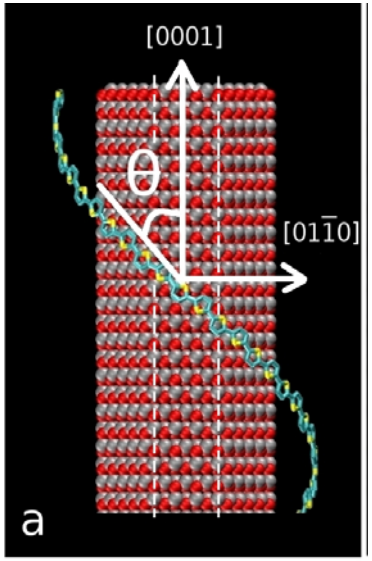
- *MD simulations to relax perfect helices and to generate relaxed configurations of the polymer around the nanoneedle*
- Straight polymer chains are expected to be favored but wrapped configurations are possible and turns out to be stable

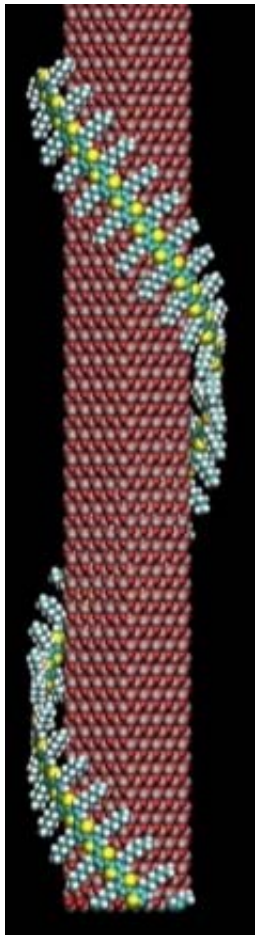


C. Caddeo, R. Dessì, C. Melis, L. Colombo, and A. Mattoni “Poly(3-hexylthiophene) adhesion on zinc oxide nanoneedles” submitted for publication

Wrapping defined by coiling angle

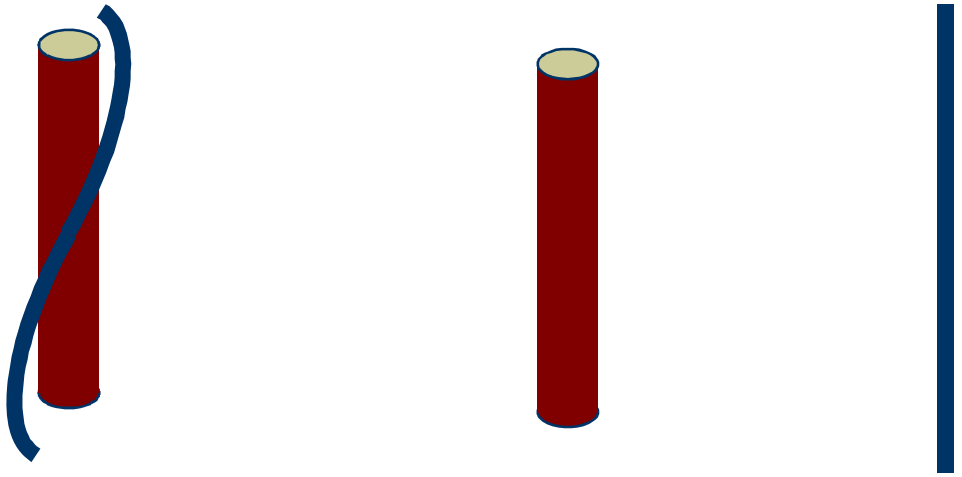
The adhesion energy depends on the coiling angle. Straight polymers along the nanoneedle axis are favored because of strain and edges effects





Polymer adhesion on nanoneedles

$$U_B^N(\theta) = U_{ZnO+P3HT}^N(\theta) - U_{ZnO}^N - U_{P3HT}^0$$



The binding energy of the hybrid system depends on the coiling angle.

Straight polymers along the nanoneedle axis are favored because of strain and edges effects

Polymer adhesion on nanoneedles

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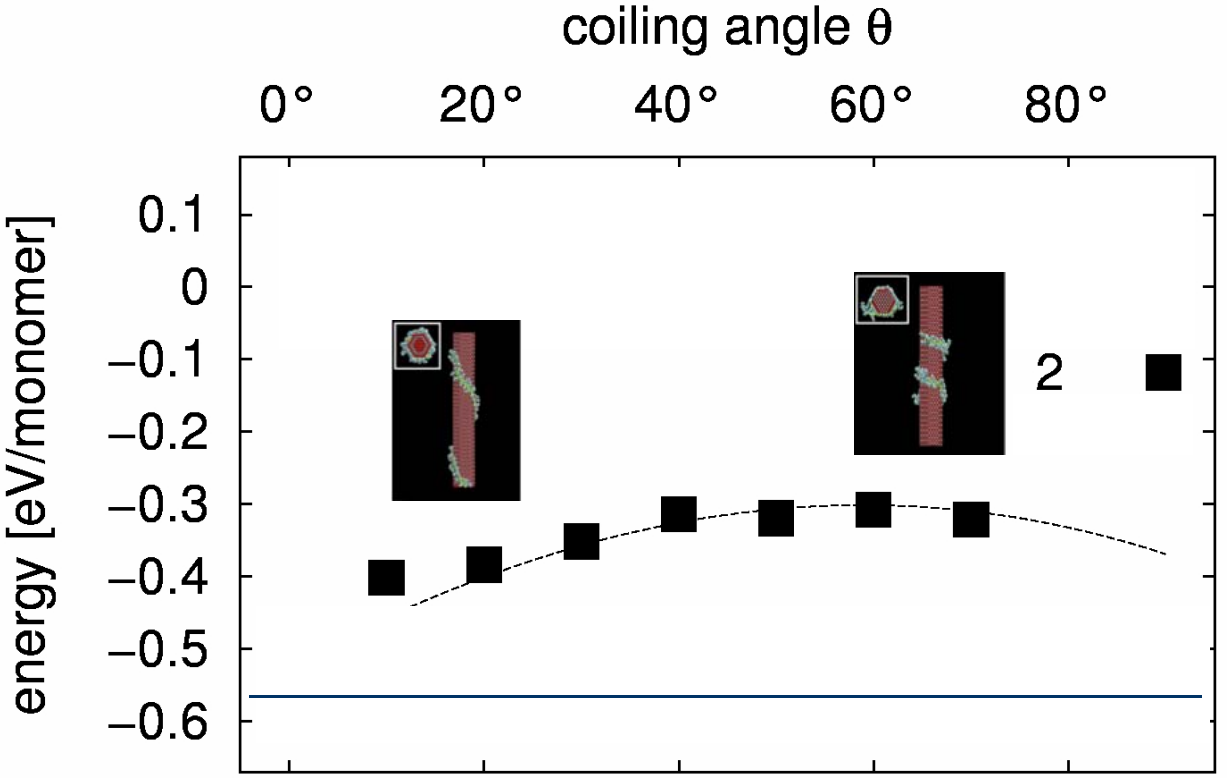
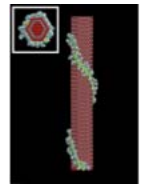


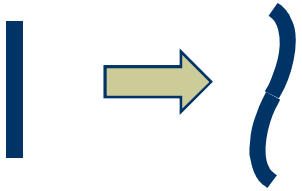
Polymer adhesion on needles



$$U^N{}_B(\theta) = U_C(\theta) + U^P{}_B(\theta) + P^N{}_e N_{edges}(\theta)$$

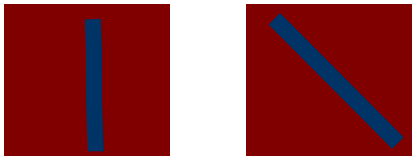
Configurational energy of an isolated polymer wrapped

$U_C(\theta)$



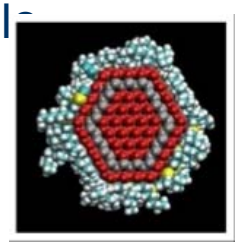
Molecular orientation with respect to the substrate

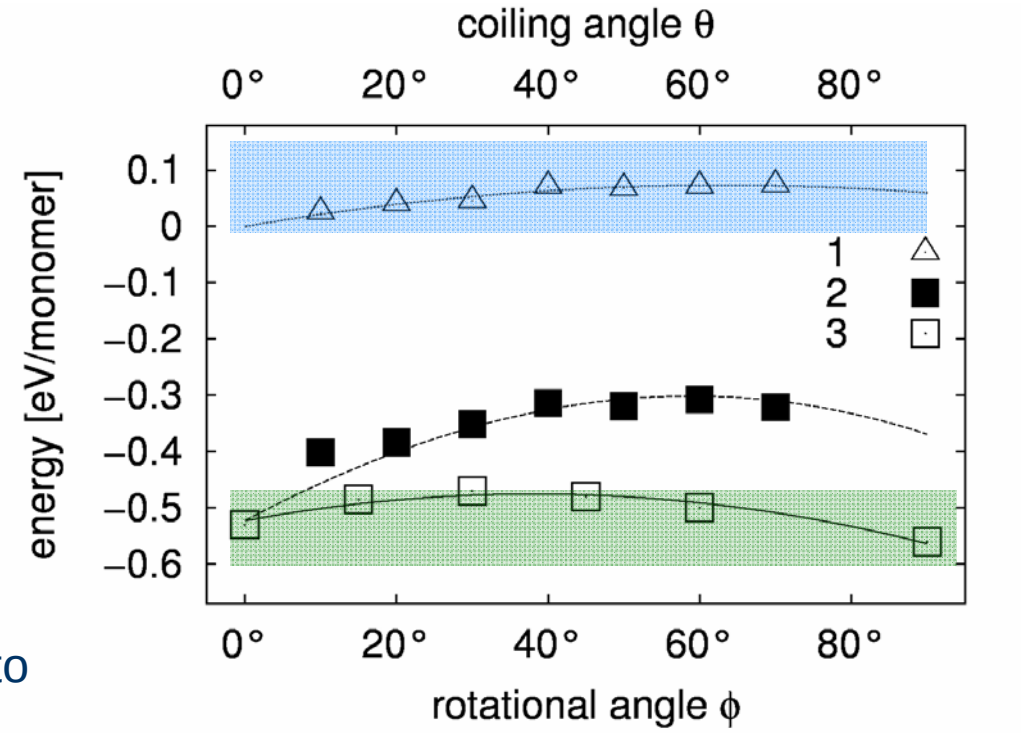
$U^P_B(\phi)$



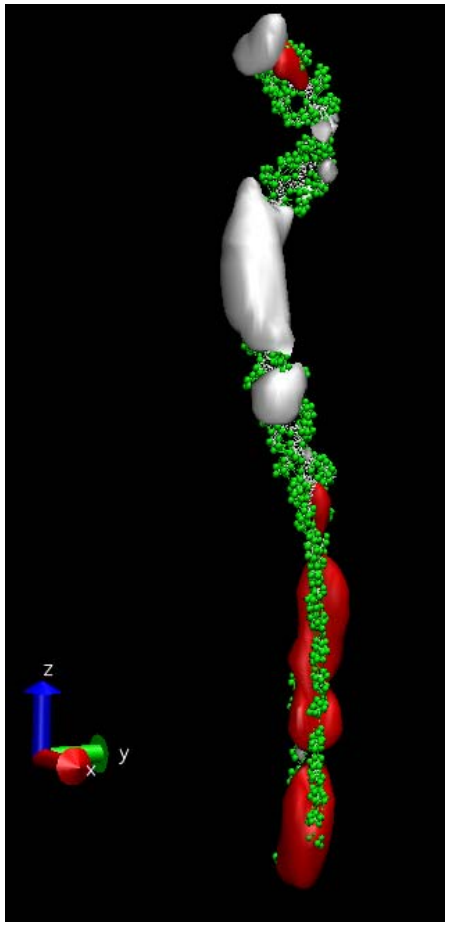
Reduction of polymer adhesion due to edges of the nanoneedl

$P^N_e N_{edges}$





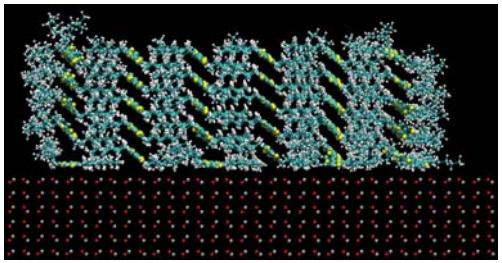
Charge localization in wrapped polymers



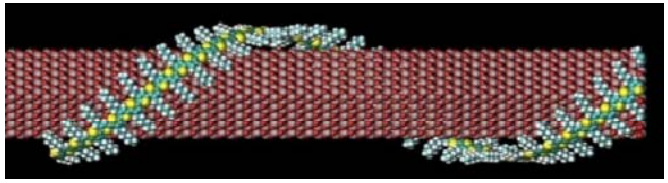
The wrapping and the local strain induces localization phenomena of the electronic states

Conclusions

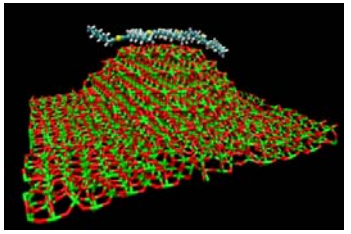
- There is an upper limit for the crystallinity at a planar interface (temperature, deposition and solvent have strong impact)

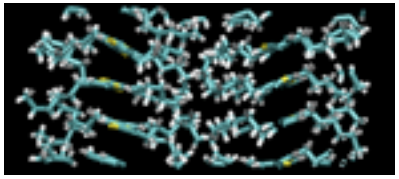


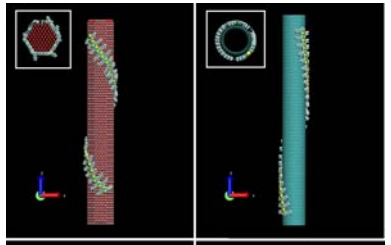
- There important effect related to the nanocurvature of the metaloxide (e.g. the adhesion and the electronic localization is strongly affected by wrapping phenomena)

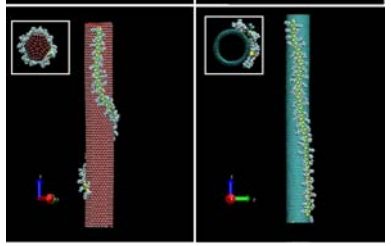


Ongoing research









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[] C. Caddeo, R. Dessì, C. Melis, L. Colombo, and A. Mattoni "Poly(3-hexylthiophene) adhesion on zinc oxide nanoneedles" *J. Phys. Chem C* **2011,** *115* 16833

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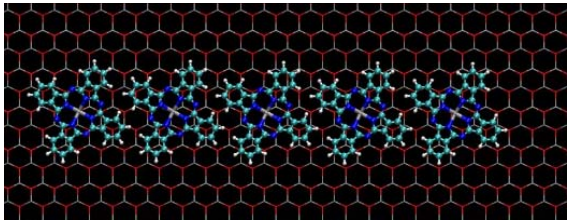

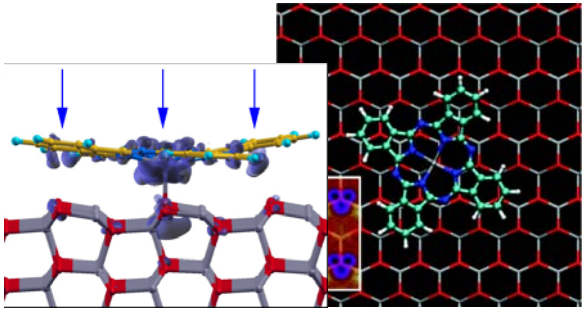

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http://sites.google.com/site/polyphemoproject

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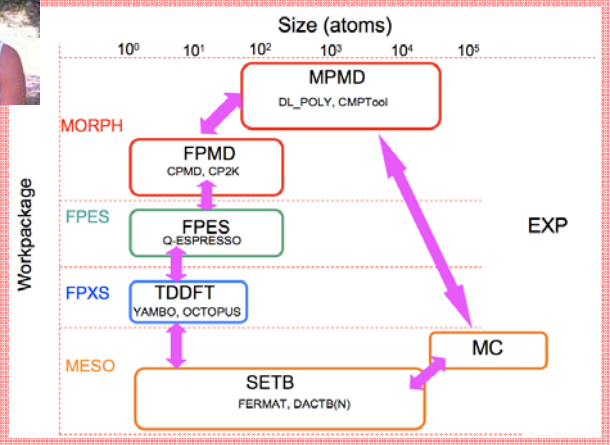

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