Surfaces and Interfaces: *Ab-initio* calculations for the study of material and design of devices

Pre-Thesis

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Materials science

We need novel materials for:

- Energy harvesting, conversion, storage, efficiency
- Environmental protection and reparation
- Health care and biomedical engineering
- Pharmaceuticals (crystallization, stability, polytypes)
- Monitoring safety of foods
- Information and communication technologies
- Fundamental science (graphene and 2D materials, topological insulators, entangled spins for quantum computing, high-T c)
- Experimental science (detectors, sensors, magnets)

Thesis Intent: Surface and Interface science

Surfaces and Interfaces between Organic and Inorganic Materials

- Inorganic/Inorganic Interface: Graphene on crystalline (0001) SiO_2
- Organic/Inorganic Interface: PDIF-CN_2 Organic crystal on crystalline (001) Silicon
- Organic/Organic Interface: PCBM Organic crystal on P3HT Polymer

Ab-initio calculation: what does it mean?

$$\left.\begin{array}{l}\text{Chemical Compound}\\ \\ \text{Crystalline Structure}\end{array}\right\} \xrightarrow[\text{Computational method}]{\textit{ab-initio}} \left\{\begin{array}{l}\textit{Chemical and}\\ \textit{Physical Properties}\end{array}\right.$$

Without the need for empirical *a priori* information
(even if such information can be useful)

Theoretical summary (I)

- Electrons and nuclei Hamiltonian

$$H_{tot} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_I \frac{\mathbf{P}_I^2}{2M_I} + \sum_i V_{nucl}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{z_I z_J e^2}{|\mathbf{R}_J - \mathbf{R}_J|}$$

$$V_{nucl}(\mathbf{r}) = -\sum_I \frac{z_I e^2}{|\mathbf{r} - \mathbf{R}_I|}$$

Density Functional Theory (DFT)

- Hohemberg-Kohn Theorem: bijective relation
  Electron charge density$\leftrightarrow$Potential
- Kohn-Sham equations
  - $\left[-\frac{\hbar^2\nabla^2}{2m} + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$
  - $V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$.

Theoretical summary (II)

Exchange-Correlation functionals

- Local-Density-Approximation (LDA)
  $E_{xc}^{LDA}[n] = \int \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$
- Generalized Gradient Approximation (GGA)
  $E_{xc}[n(\mathbf{r})] = \int \epsilon_{xc}(n(\mathbf{r}))F_{xc}\Big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\Big)n(\mathbf{r})d\mathbf{r}$

Hellmann-Feynman Theorem and the geometrical optimization problem

- $H(\lambda) \rightarrow H_e(\mathbf{r};\mathbf{R})$
- $H_e(\lambda)\psi_n(\mathbf{r};\mathbf{R}) = E_n(\lambda)\psi_n(\mathbf{r};\mathbf{R})$
- $\langle\psi_m(\mathbf{r};\lambda)| \frac{\partial H(\lambda)}{\partial\lambda_i} |\psi_m(\mathbf{r};\lambda)\rangle = \frac{\partial E_m}{\partial\lambda_i}$

Theoretical summary (III): long range interaction

GRIMME -Van der Waals interaction

$$E_{KS-vdW} = E_{KS} + s_6 \frac{1}{2} \sum_{i \neq j} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij})$$

$$f_{dmp}(R_{ij}) = \frac{1}{1 + exp(-d(\frac{R_{ij}}{R_r} - 1))} \qquad R_{ij} = |R_i - Rj|$$

Each pair contributes a R_{ij}^{-6}, f_{dmp} is a dumping function that works as a cutoff, R_r is the vdW radii for the two ions, s_6, C_6^{ij}, d come from experimental data

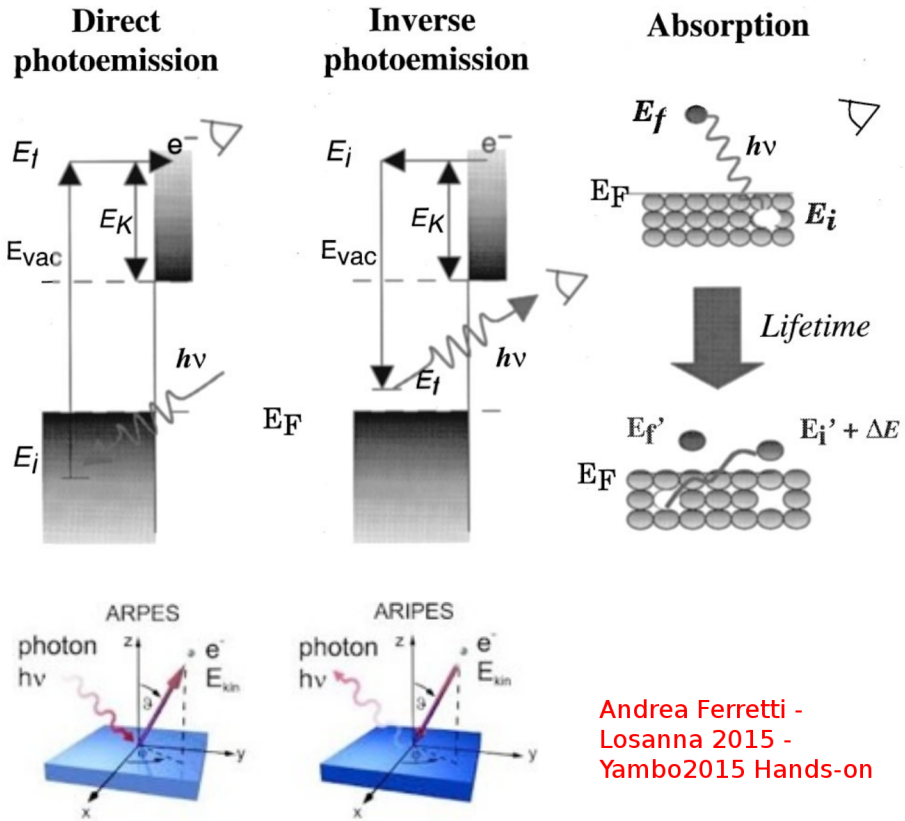
Hybrids

Combine orbital dependent HF exchange energy with explicit DF E_{xc}
Examples: B3LYP, HSEsol

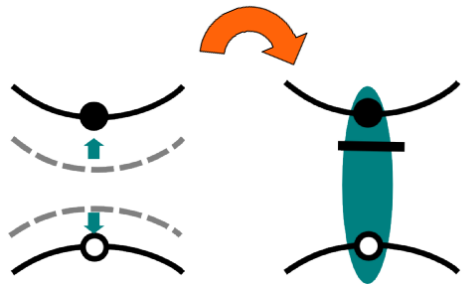
1. Heavier calculation
2. Better approximation of some properties (GAP)

Excited States and Excitons

DFT is a Ground State Theory → NOT excited states
We need more → Many body perturbation theory (MBPT)



Andrea Ferretti - Losanna 2015 - Yambo2015 Hands-on



From quasiparticle corrections to e-h interaction: **Excitons**

Codes Used

Quantum ESPRESSO (QE)

- Basis set: Plane Waves (PW)

CRYSTAL14

- Linear Combination of Atomic Orbitals (LCAO) approximation $\rightarrow$ Basis Set: Gaussians

WAN-T (WANnier- Transport)

- Basis Set: Localised Wannier functions
- Landauer's approach: T(E)= $Tr(\Gamma_L G^r \Gamma_R G^a)$
- $I(V) = \frac{2e}{h} \int T(E)[f(E-\mu_L) - f(E-\mu_R)]dE$

YAMBO

- Basis Set: PW
- Many Body Perturbation Theory (MBPT)
- Optical Properties, Excitons, Bethe-Salpeter

Graphene on SiO_2

Production and processing

Mass production: scalable processes

- Micromechanical cleavage
- Liquid phase exfoliation
- Thermal exfoliation
- Chemical Vapour Deposition (CVD)
- Synthesis on SiC

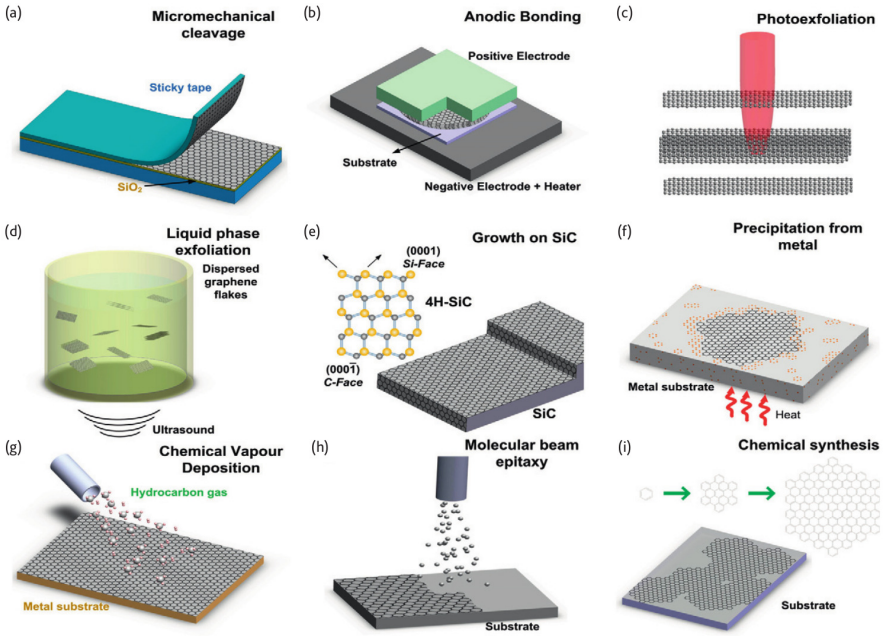


Figure : F. Bonaccorso et. al.,Materials Today **15**, 564 (2012) "Production and processing of graphene and 2d crystals"

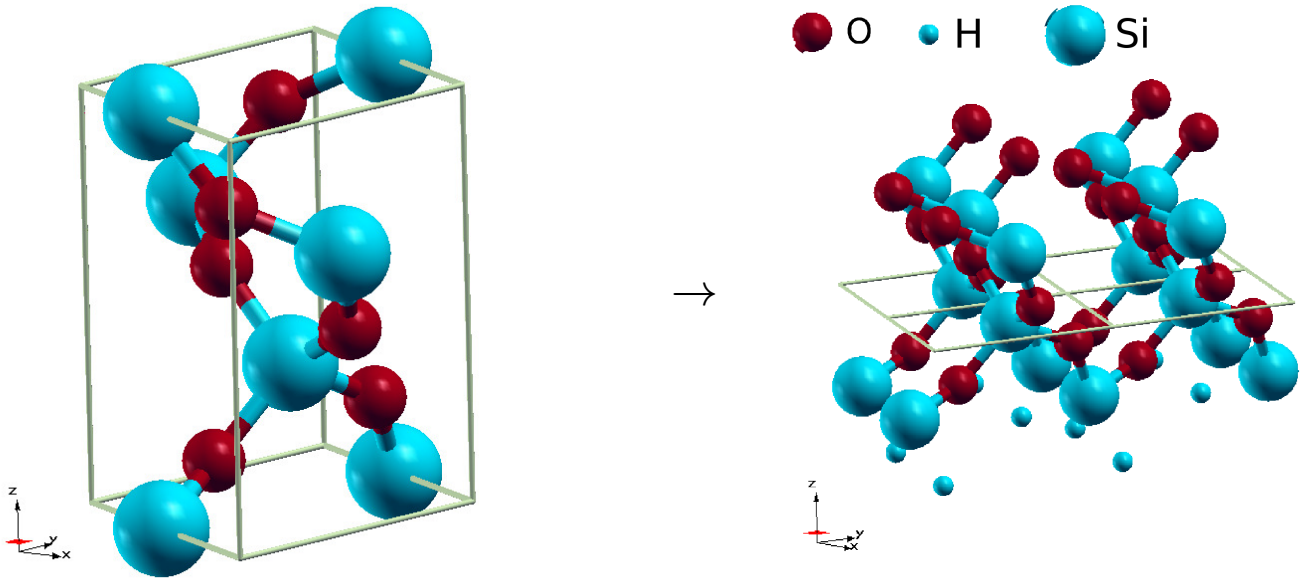
Graphene/SiO_2

Why Graphene/SiO_2 interface?

- Different attempts to synthesize Graphene call for accurate theoretical investigation.
- It is essential to understand and control at the nanoscale its interaction with the supporting substrates.
- SiO_2 is one of the most important and common substrate for application in electronic.

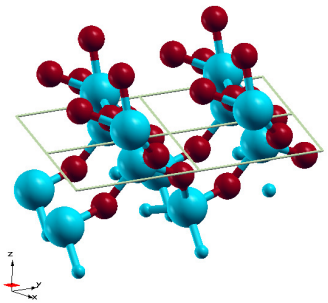
SiO_2: 3D→2D

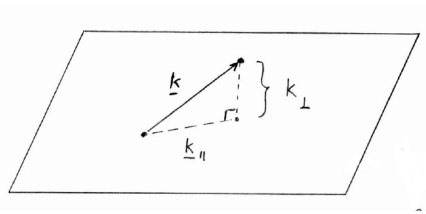
α-quartz SiO_2 Bulk Crystal: a=4.913 Å, c=5.405 Å
Slabcut (0001) O-terminated Surface



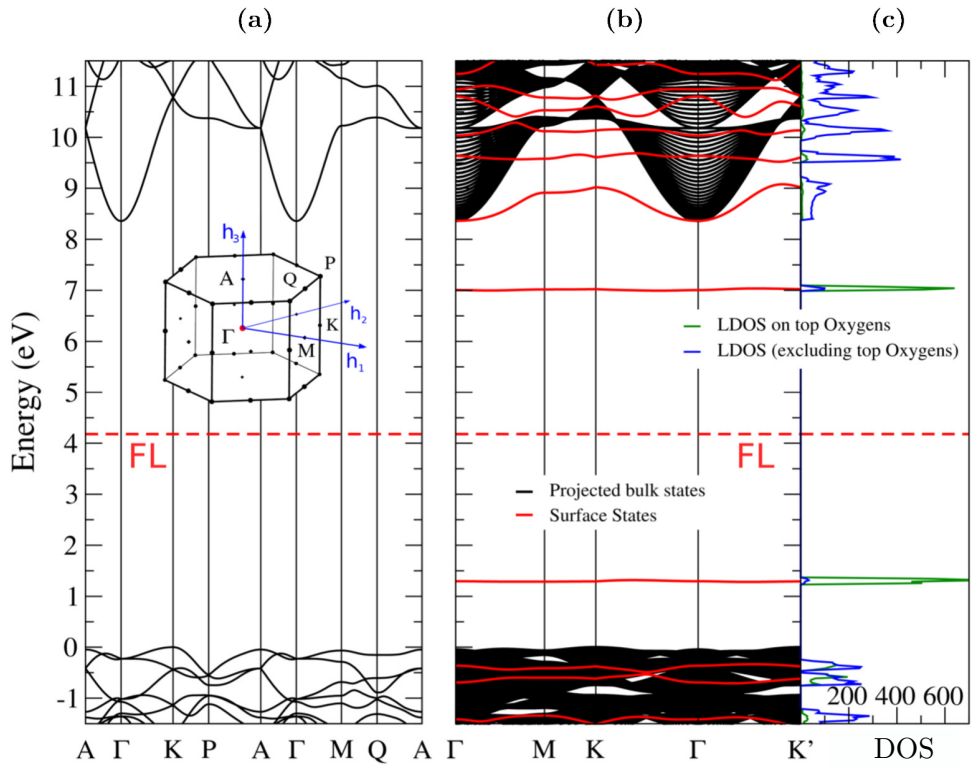
Geometrical relaxation with fixed cell parameters

The Total Energy minimization checks:
$\Delta E < 10^{-7}$ u.a., RMS of the gradient < 0.0003 a.u, RMS of the displacement < 0.0012 a.u.



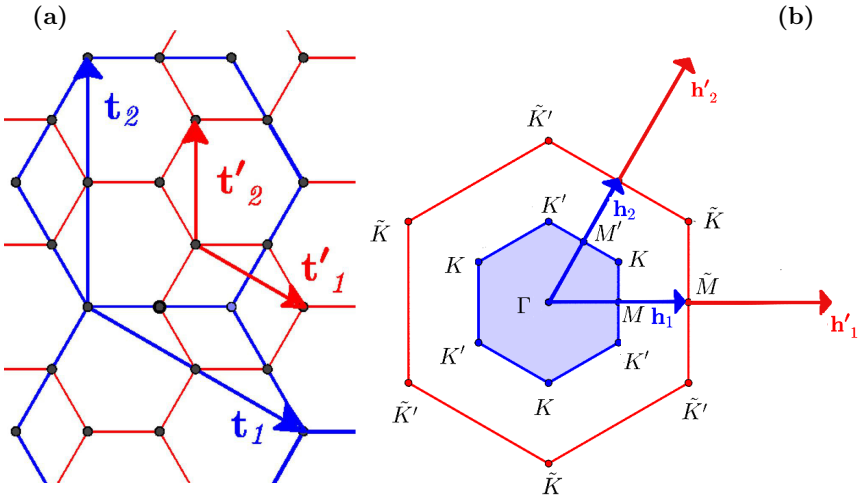


$\mathbf{k}_{||}$: component of **k** parallel to the surface; $k_{\perp}$: component of **k** orthogonal to the surface

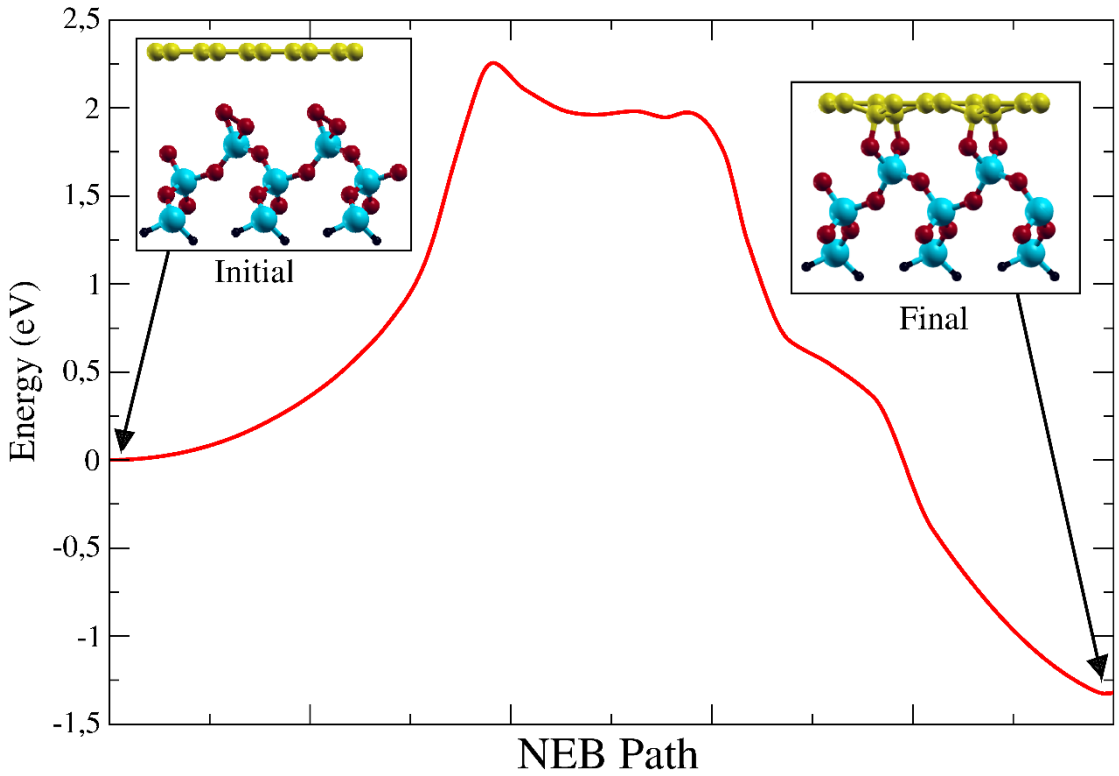


Graphene

a=4.913Å, a'=2.464Å ($\frac{2a'-a}{a} \simeq 0.3\% \rightarrow$ for the calculations a=4.92Å,a'=2.46Å



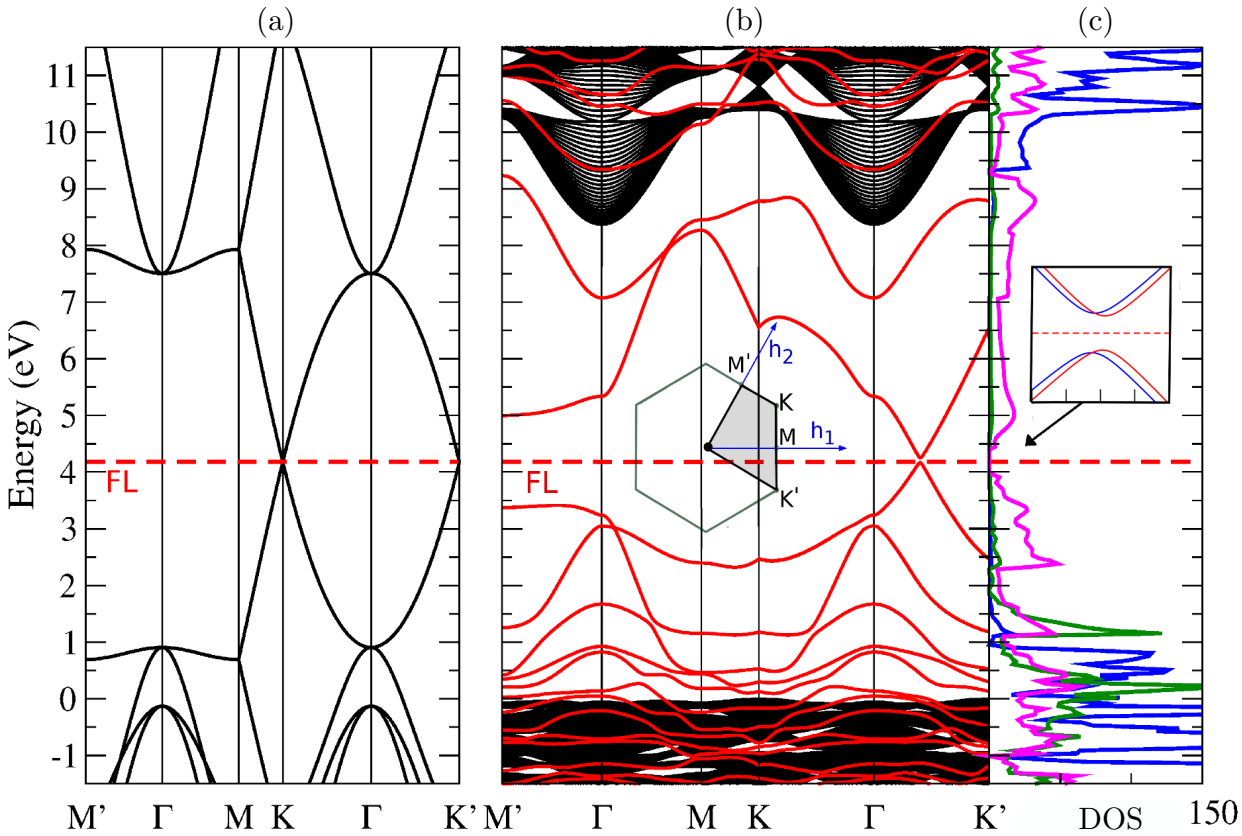
Graphene/SiO_2: Geometrical Relaxation (fixed cell parameter)



NOTE: About Covalent Bonds, depassivation of Hydrogen and UHV STM Y. Xu et al Nano Lett. 11,2735(2011), J.C. Koepke APL 107 071603(2015)

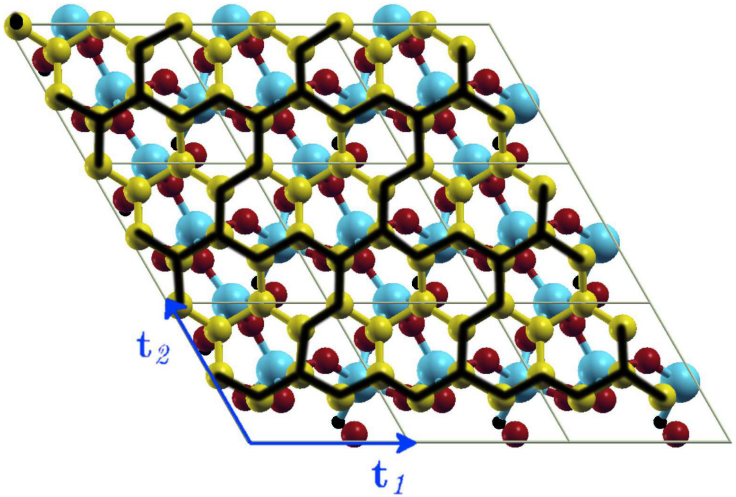
Graphene/SiO_2 bands structure

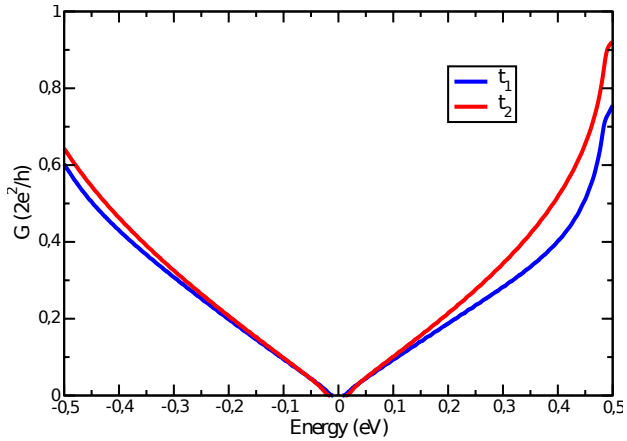
- Left: Graphene 2x2 cell
- Right: Graphene/SiO_2 relaxed with projected DOS Graphene/SiO_2

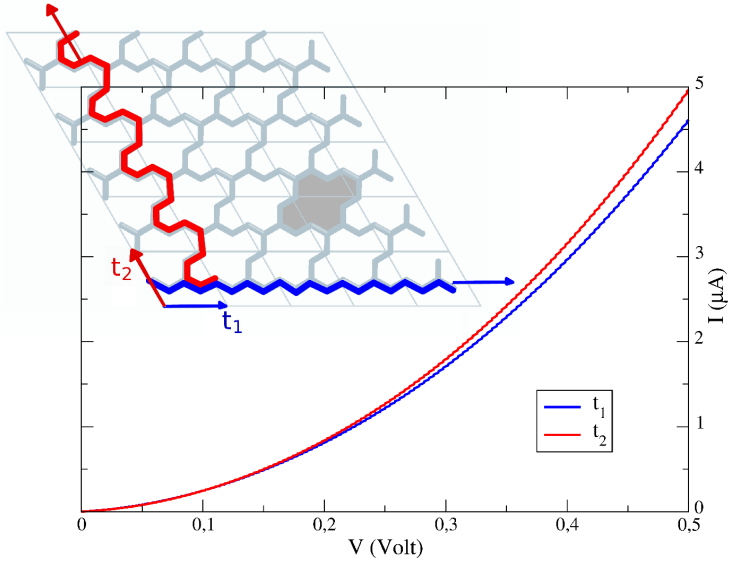


Asymmetry in Conductance and electrons current

Landauer's approach: $T(E) = Tr(\Gamma_L G^r \Gamma_R G^a)$
$I(V) = \frac{2e}{h} \int T(E)[f(E-\mu_L) - f(E-\mu_R)]dE$



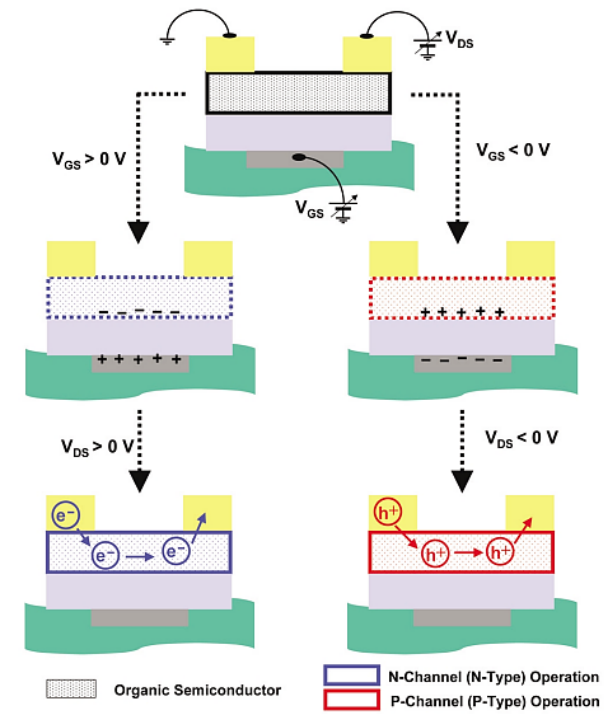




- Graphene/SiO_2 $\rightarrow$ corrugation: C-O covalent bonds
- Band gap opening, Band Profile modulation
- Modification of $\pi - \pi$ carbon conjugation: preferred directions for conduction

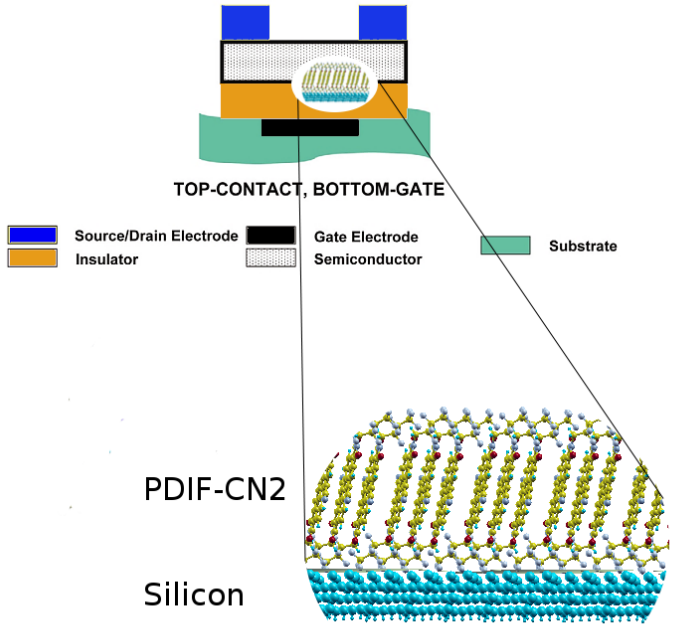
PDIF-CN_2/Silicon

Introduction

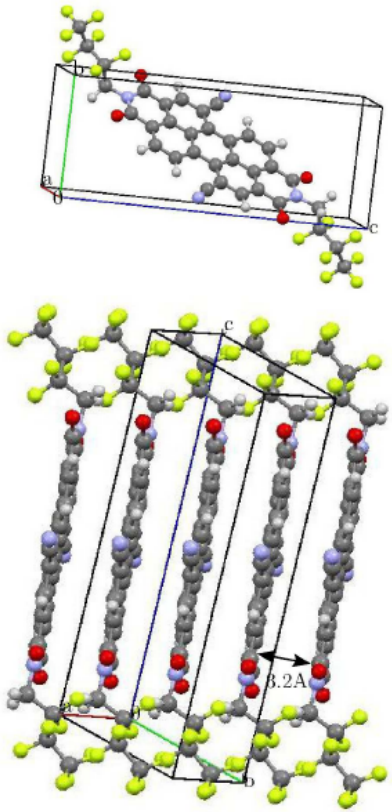


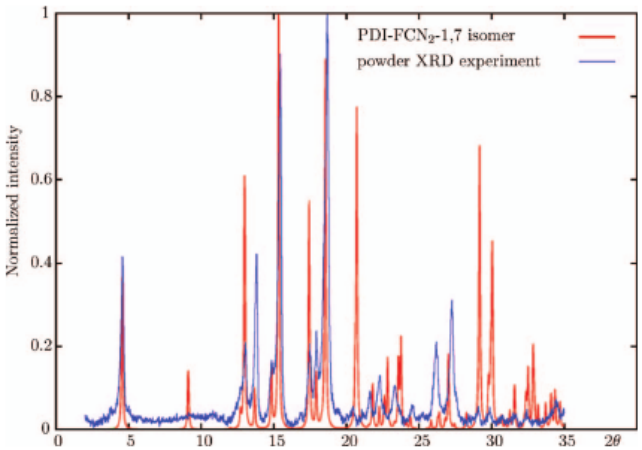
Materials Today, **10**:28, (2007).

- Organic Materials in electronic devices: OFET, OLED, OPV
- *n*-type OFET $\rightarrow$ PDIF-CN_2



PDIF-CN_2 crystal Structure



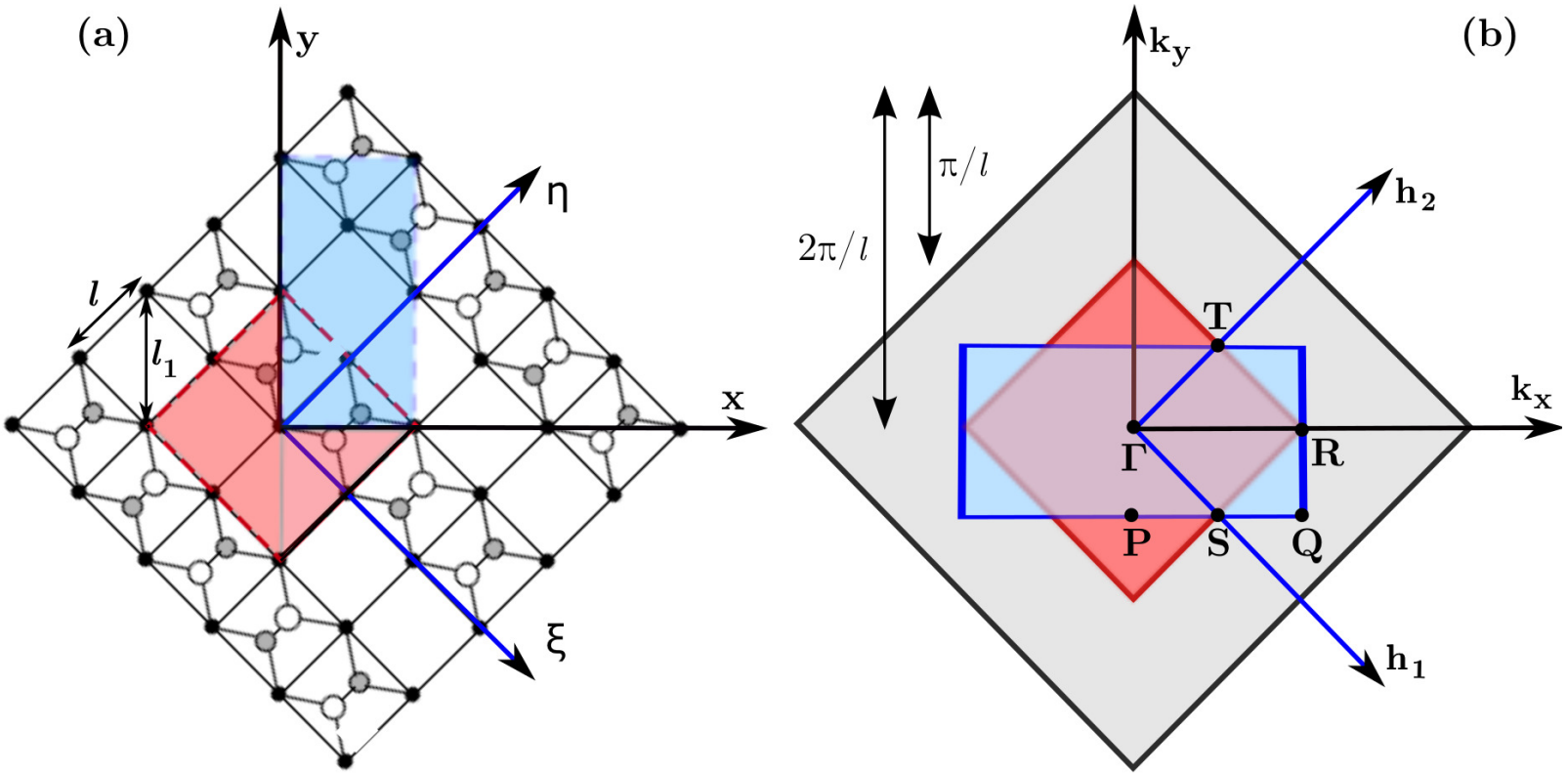


J. Chem. Phys., **139**:114507, (2013).

- XRD on crystal powder + *ab-initio* calculation $\rightarrow$ Geometrical structure
- $\pi - \pi$ stacking $d = 3.2\mathring{A}$
- triclinic cell: $a = 5.135\mathring{A}$, $b = 7.385\mathring{A}$, $c = 19.598\mathring{A}$, $\alpha = 92.35$ deg, $\beta = 82.22$ deg, $\gamma = 93.25$ deg.

Surface Silicon reconstructed and Simulation Cell (I)

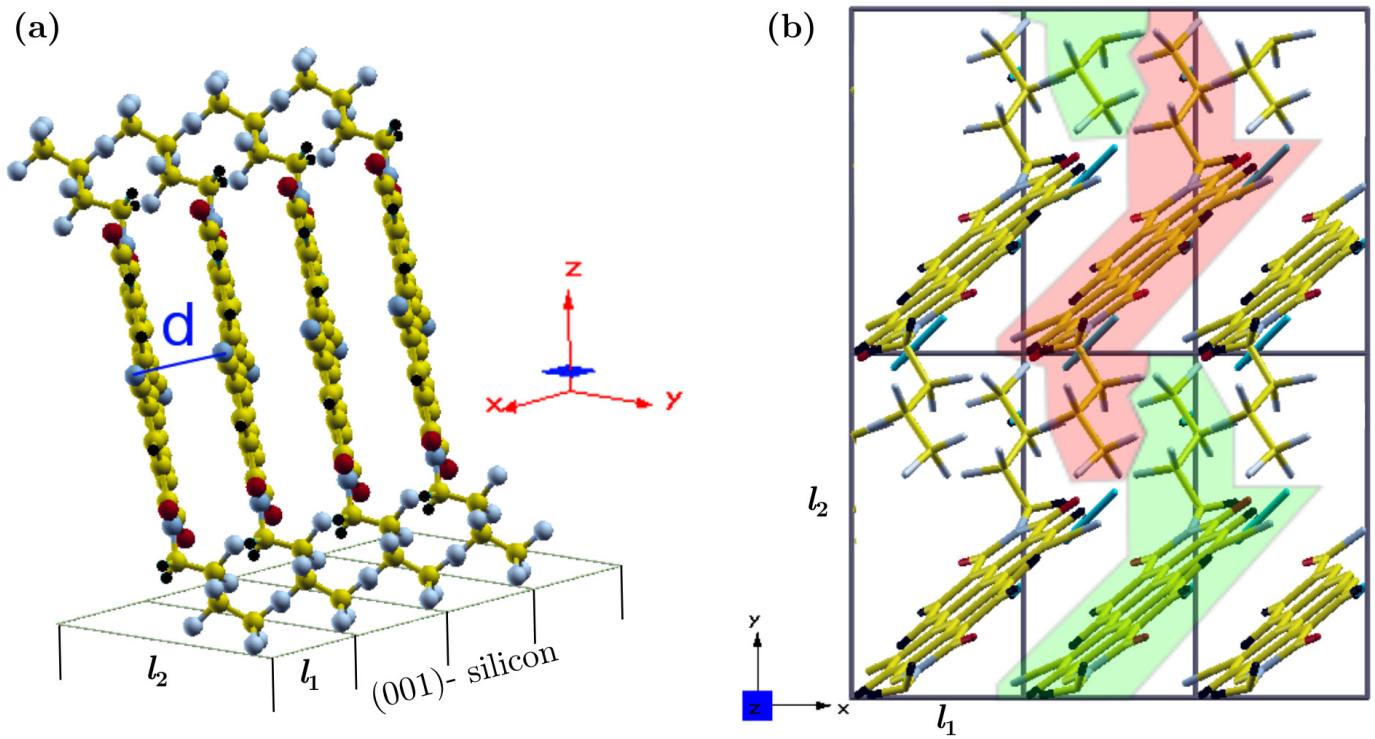
(001) Silicon surface unit-cell lattice parameter l=3.83Å



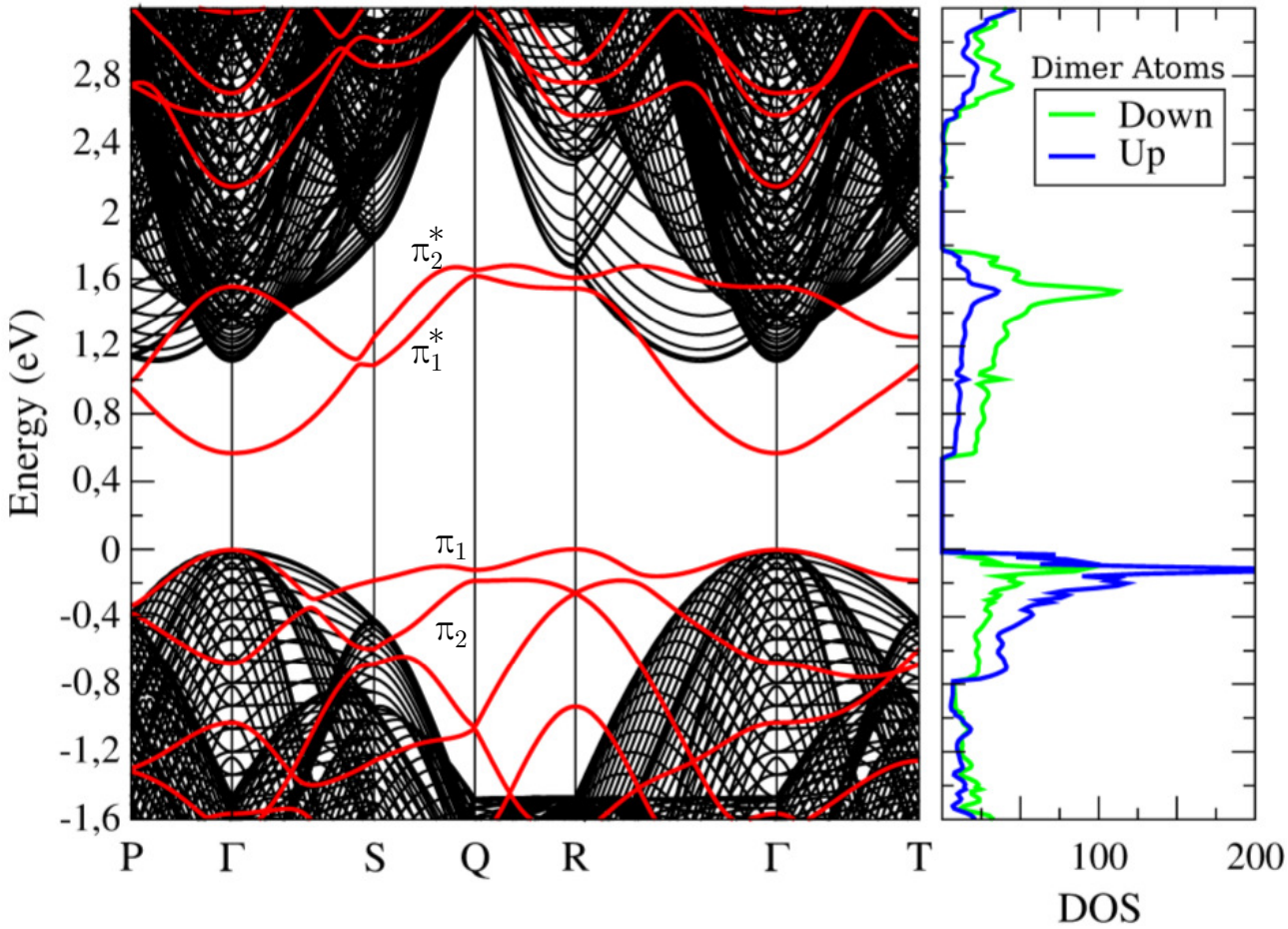
a) Direct lattice and Dimer structure; b)Corresponding Brillouin zones

Surface Silicon reconstructed and Simulation Cell (2)

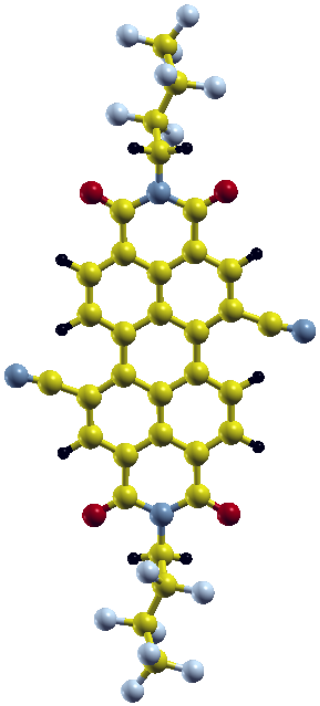
The distance between adjacent perylene planes $d = 3.4$Å

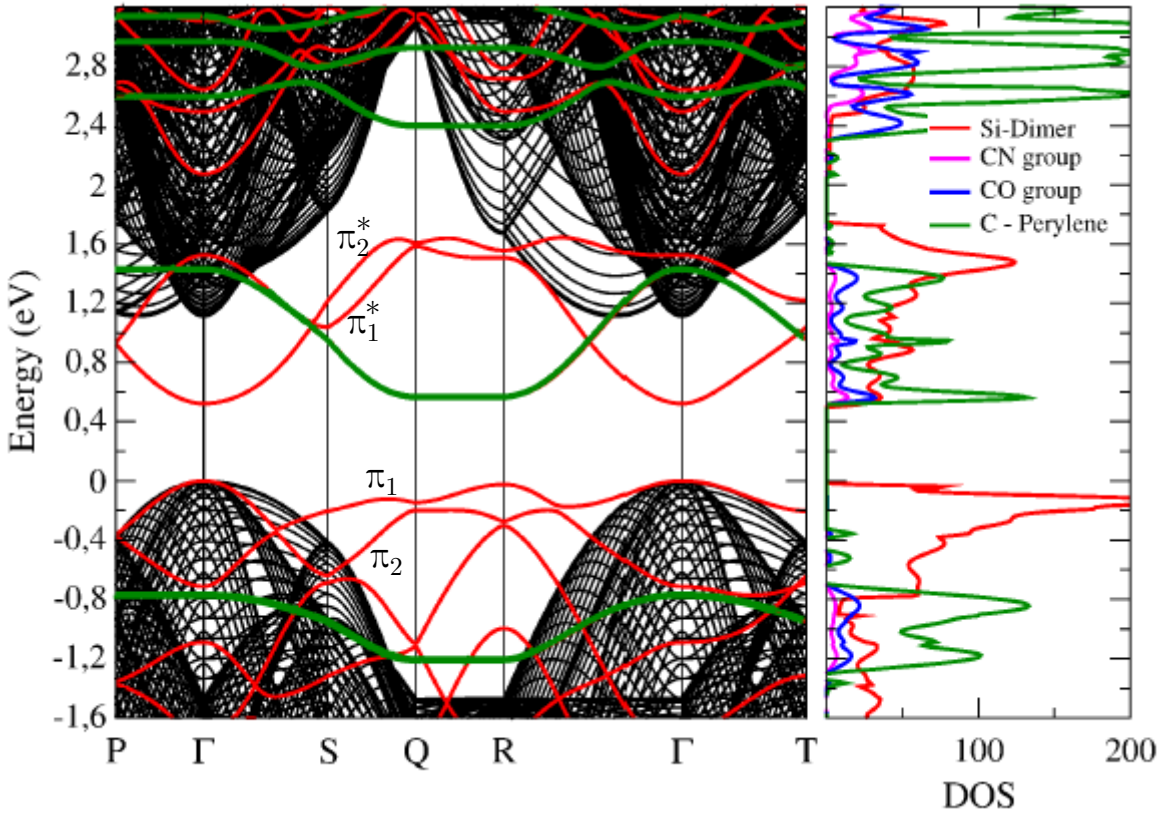


Side (a) and top (b) view of the side-on arrangement; PDIF-CN_2(66 atoms)+4 Silicon Layers (16 atoms)+ 1 Hydrogen Layer(4 atoms)

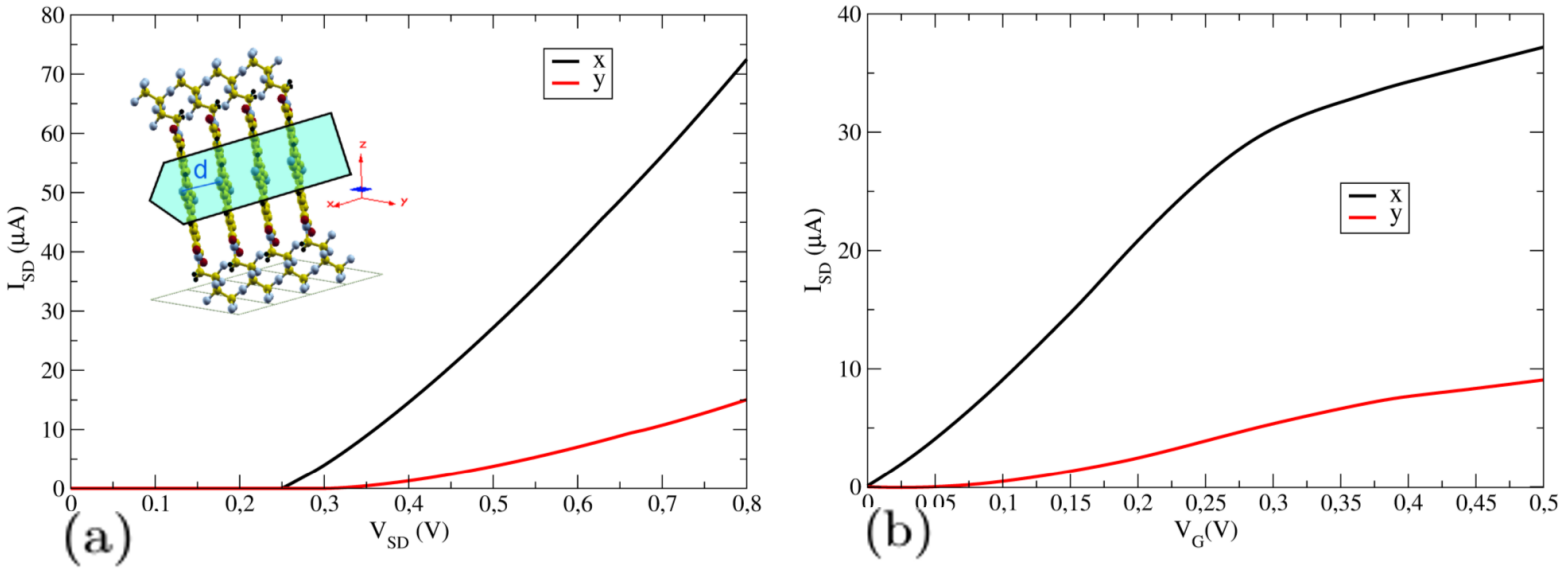


DFT electronic band structure and projected density of states of Relaxed *p*(2x2) reconstructed Si surface





DFT electronic band structure and projected density of states of PDIF-CN2 on the relaxed *p*(2x2) reconstructed Si surface.

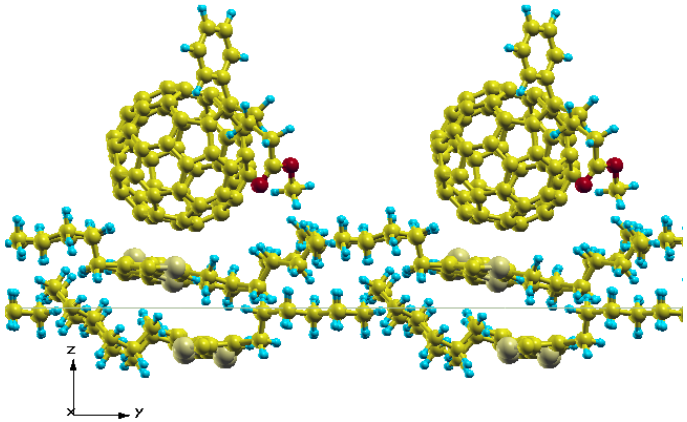


(a) Output plots for the I_{SD}-V_{SD} characteristics at zero gate voltage V_G=0V, and (b) transfer plots of I_{SD} at different biases, in linear regime (V_{SD} = 0.25V), for PDIF-CN_2 on Si. The black (red) line corresponds to current flowing along the *x* (*y*) directions. In the inset is reported schematically the network of π-conjugated perilene planes which are stacked along the *x* direction.

Work in progress

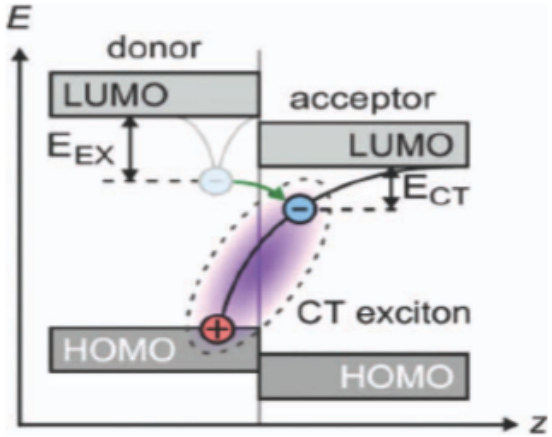
Organic Photovoltaic cell: PCBM on P3HT

Work Done:
Geometrical structure and Band Structure



Relaxed geometry of a PCBM molecule over 2x1 cell of P3HT: 288 atoms per cell, 794 electrons.

Work in progress:
Optical Properties and excitons



A schematic diagram depicting the dissociation of an exciton to form a charge transfer exciton across a donor-acceptor interface. E_{ex} is the single exciton binding energy and E_{CT} is the charge transfer exciton binding energy.