Institut de Science des Matériaux de Mulhouse (IS2M)

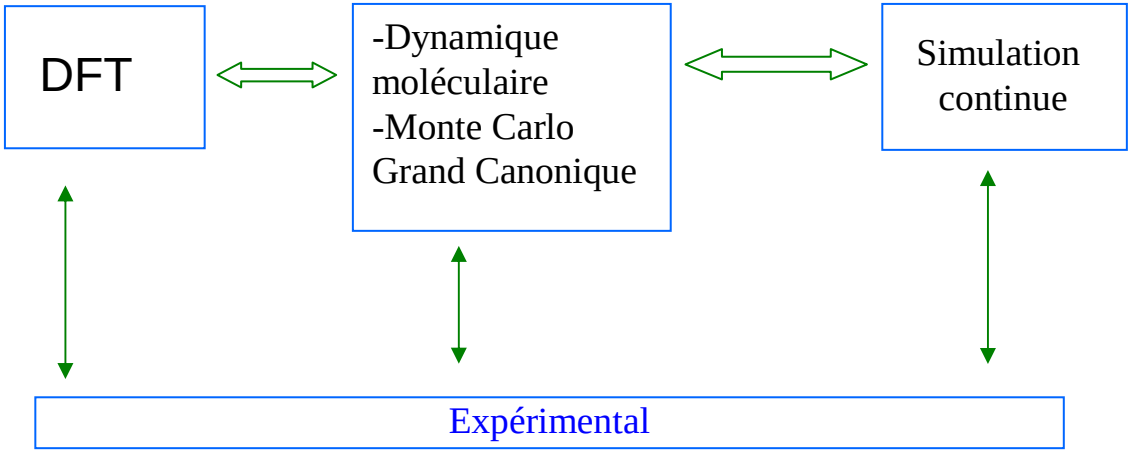
CNRS UMR 7361 – Université de Haute Alsace

Axe transverse « Simulation »

Khaoula Boukari (PhD), Irena Deroche (MC), Patrick Dutournié (PR), Louise Stauffer (PR-Em), Philippe Sonnet (PR)

Calculs multi-échelles de la molécule au matériau
(via les surfaces) pour accéder aux propriétés

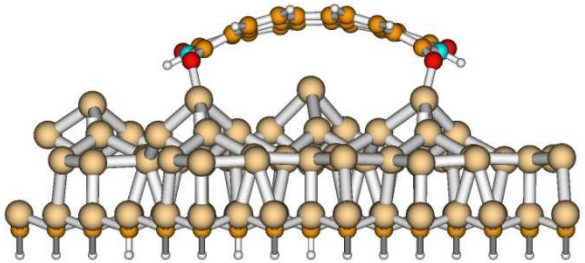
Molécules → Molécules en interaction avec une surface ou matériaux poreux……→ procédé industriel



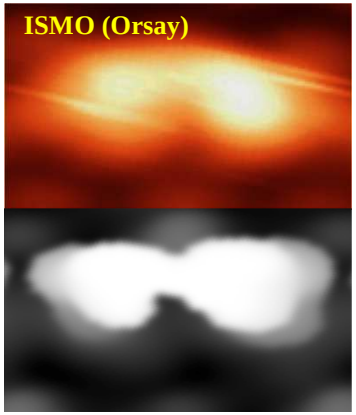
Quelques exemples….

-Découplage électronique partiel d'une molécule chimisorbée sur une surface de SiC(0001)3x3

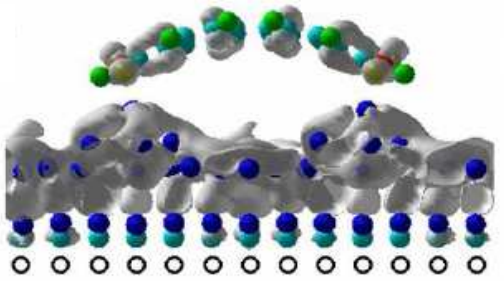
Propriété structurale



Comparaison image STM expérimentale et image STM calculée

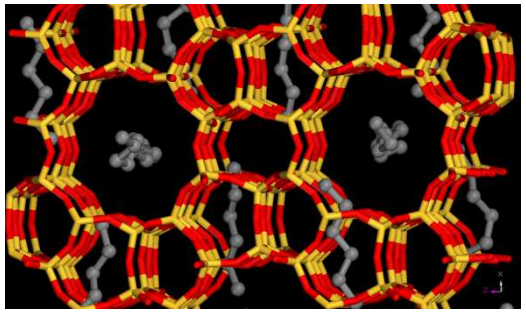


Propriété électronique



Références: *Physical Chemistry Chemical Physics* **14** (5),1700-1705 (2012), *Physical Review B* **85** (3) ,035423 (2012)

-Adsorption dans les matériaux poreux (zéolithes et matériaux carbonés)

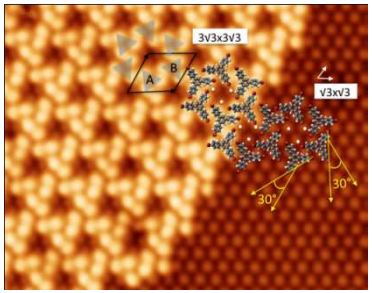


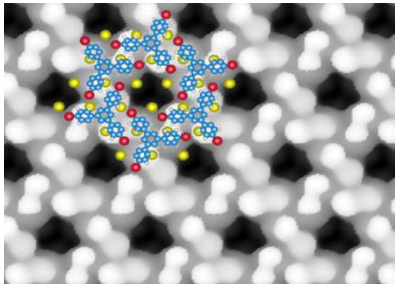
molécules d'hexane dans la silicalite

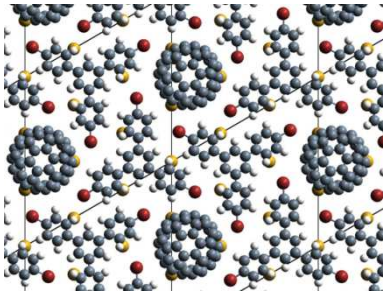
(zéolithe MFI de composition chimique purement silicatée)

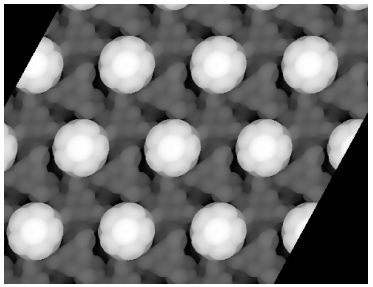
Référence: *Microp. Mesop. Mater* (2013) accepté

-Tapis moléculaires sur surface de semiconducteur passivé









2D Supramolecular network on silicon surface :Calculated STM images

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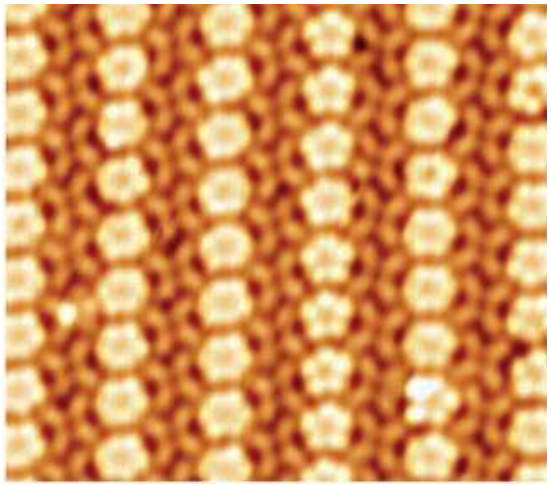
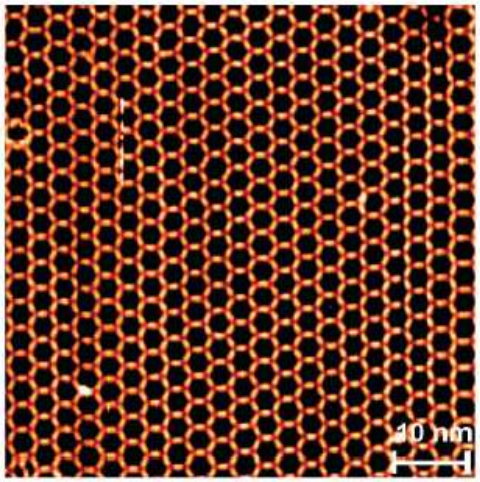
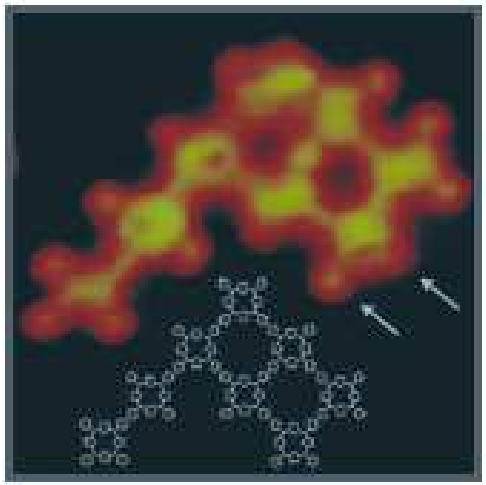
2012-2015

Introduction *: Molecule on metallic surface*

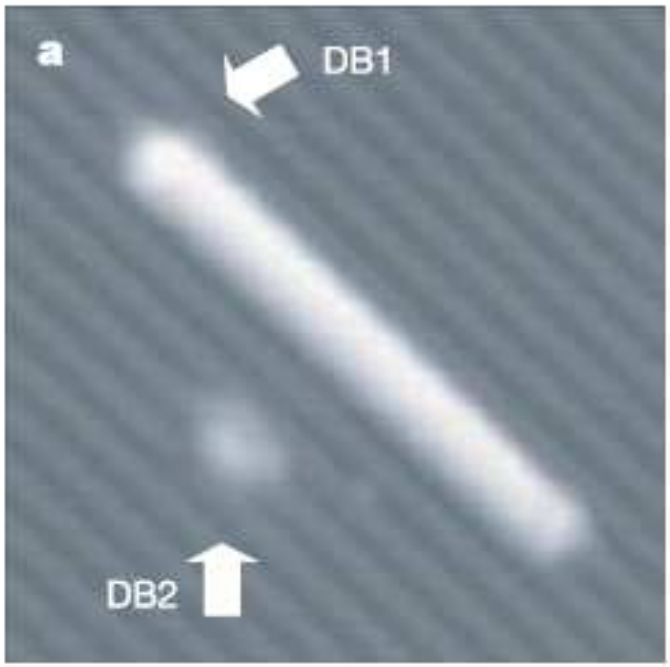
- Supramolecular assemblies: weak interactions between molecules
- The most papers concern molecules on metallic surfaces.

Compact	Porous	Covalent
		
Substitued corranulene and ZnPcCl8 adsorption on Ag(111)	Cobalt and NC-Ph3-CN co-adsorption on Ag (111)	Covalently assembled porphyrins on Au(111)
B. Calmettes et al., Angew. Chem. Int. Ed., ***2008****, 47, 6994*	*U. Schlickum et al., Nano Lett.* ***2007****, 7, 12*	*L. Grill et al., Nature Nano* ***2007****, 2, 687*

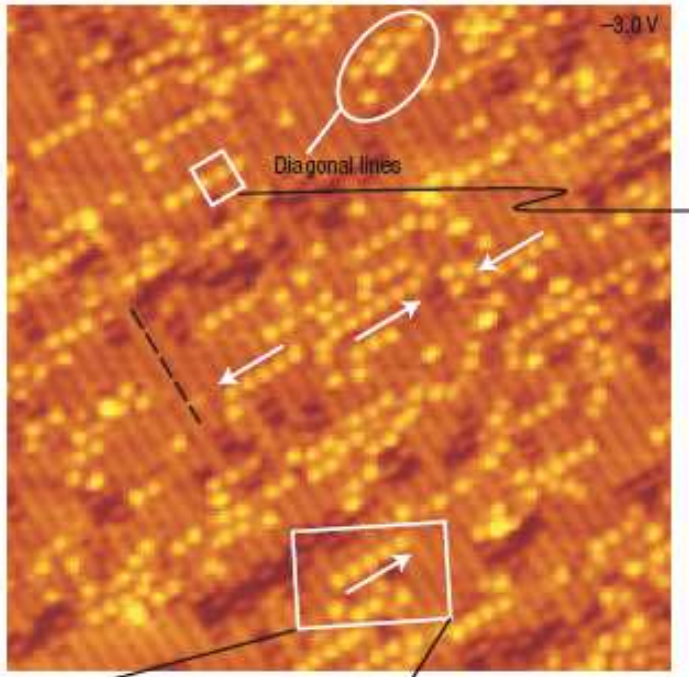
Introduction **:** *Molecule on silicon surface*

- To developp new organic/inorganic devices based on silicon substrate.
- Semi-conductors: self-assembly more difficult

Strong surface-molecules interactions



Styrene line on Si(100)
R. Wolkow et al., Nature **2005**, *435, 658*

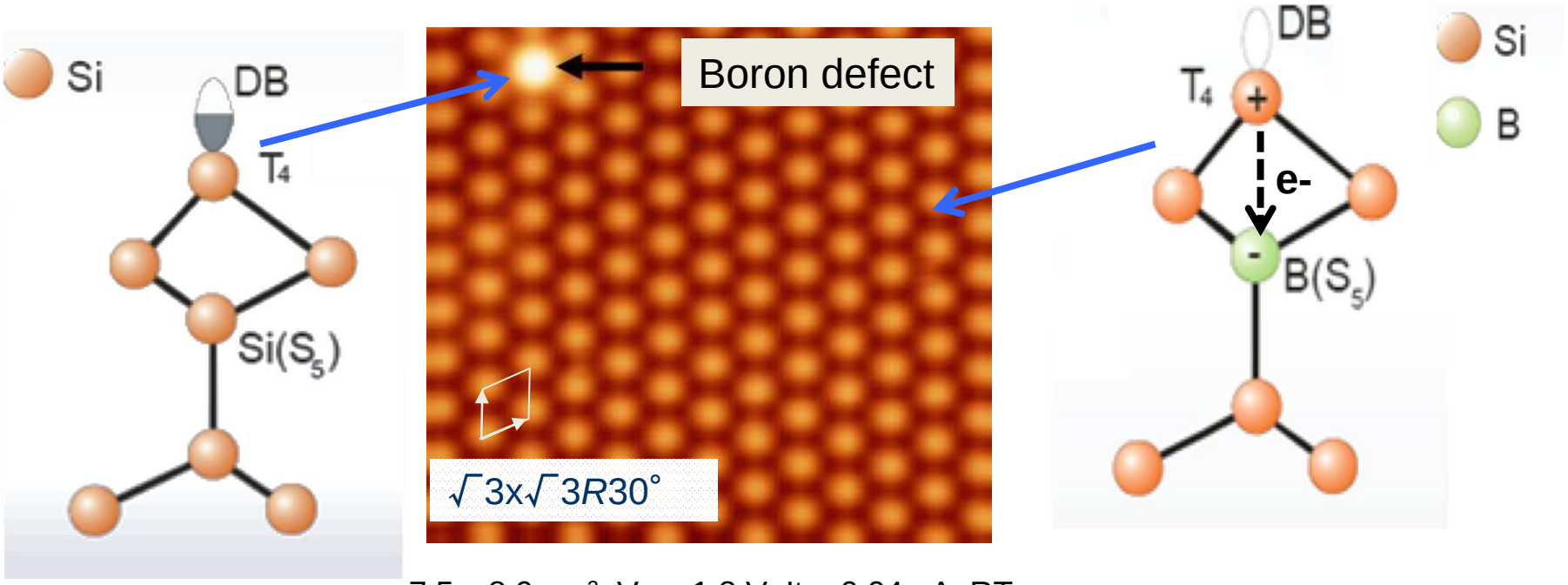


Dichloropentane on Si(100)
J. C. Polanyi et al., Nature Nano. **2008**, *3, 222*

Introduction *: The Si (111)-B substrate*

Undoped Si(111)

Boron doped Si(111)



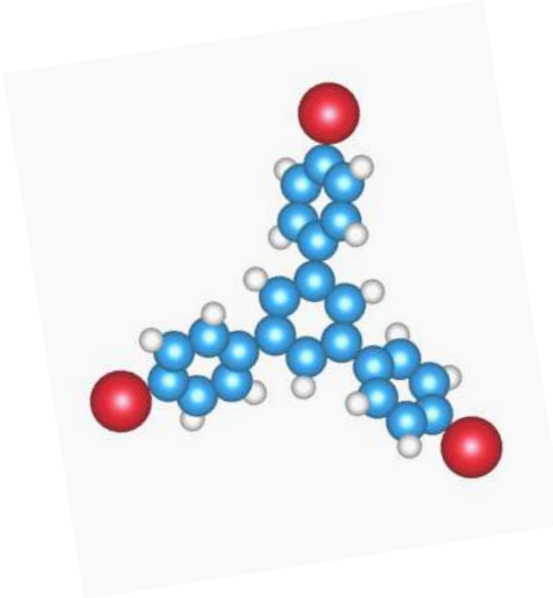
7.5 x 8.0 nm², Vs = 1.8 V, It = 0.04 nA, RT

Populated DB

Depopulated DB

Weak reactivity of Si-adatoms

TBB network: *1,3,5-tri(4'-bromophenyl)benzene*

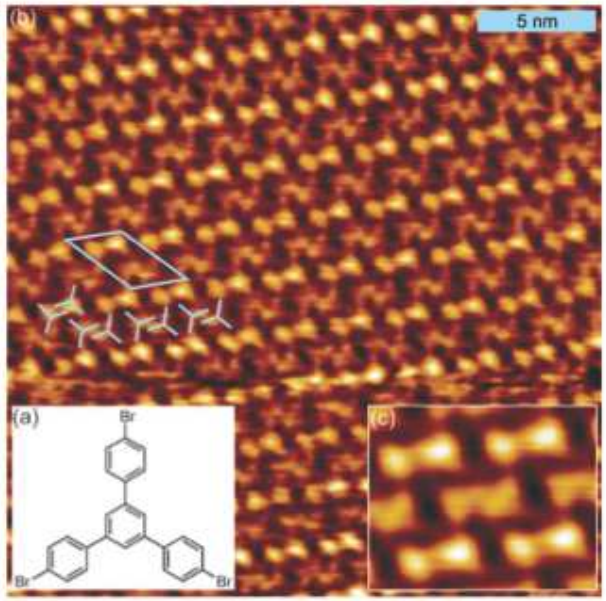


Br atoms

C atoms

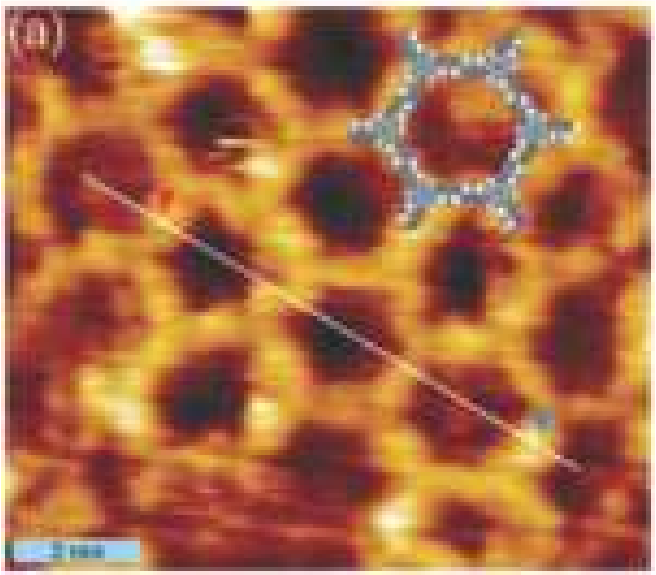
H atoms

Compact



●Supramolecular network on HOPG

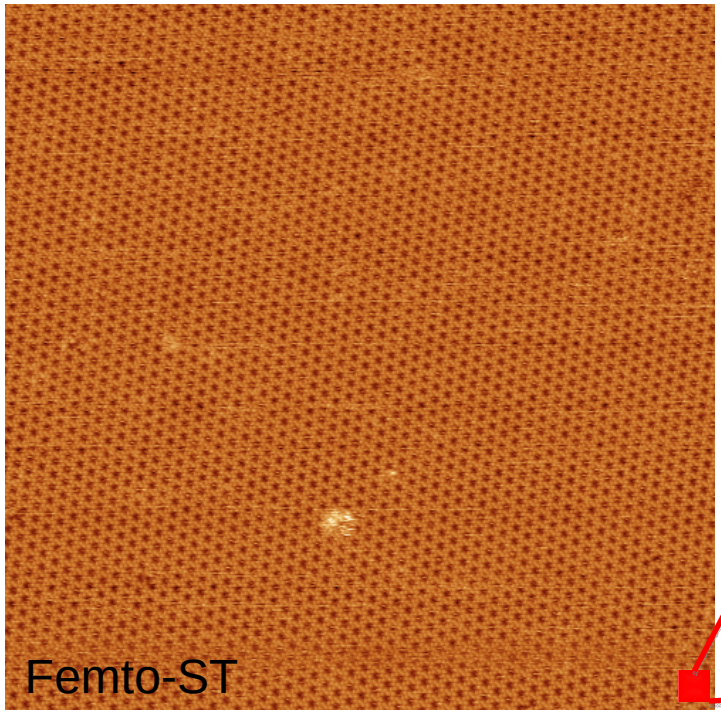
Porous



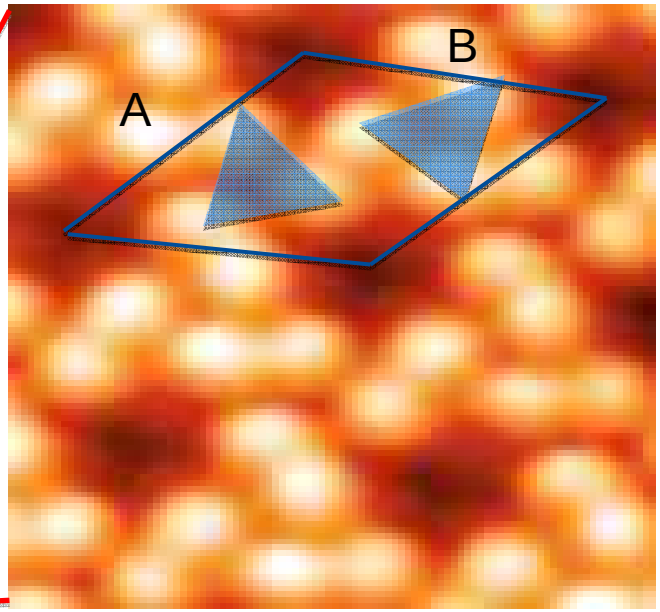
● Covalent assembly after annealing on Cu(111)

TBB on HOPG and Cu(111)*R. Gutzler et al. Chem. Commun.*, ***2009***, *4456*

TBB network: *STM image / Distance*



120x120 nm^2, Vs = 2.5 V, It = 0.034 nA, RT



4.2x4.2 nm^2, Vs = 2.5 V, It = 0.034 nA, RT

- Nanoporous network
- Large TBB islands (> 800x800 nm^2)
- Stable until 400 K

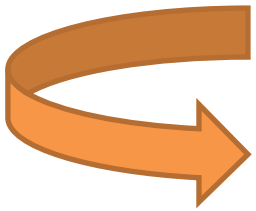
- Commensurable network
- Unit cell: six protrusions

Questions

- What is the importance of the Si-B substrate on the formation of 2D-network ?
- How can we validate the optimazed atomic structure?

- Structure and energetic studies
- STM images calculated
- Electronic study

To answer to these questions:



- DFT-D simulations
- STM images calculated (bSKAN + LDOS)

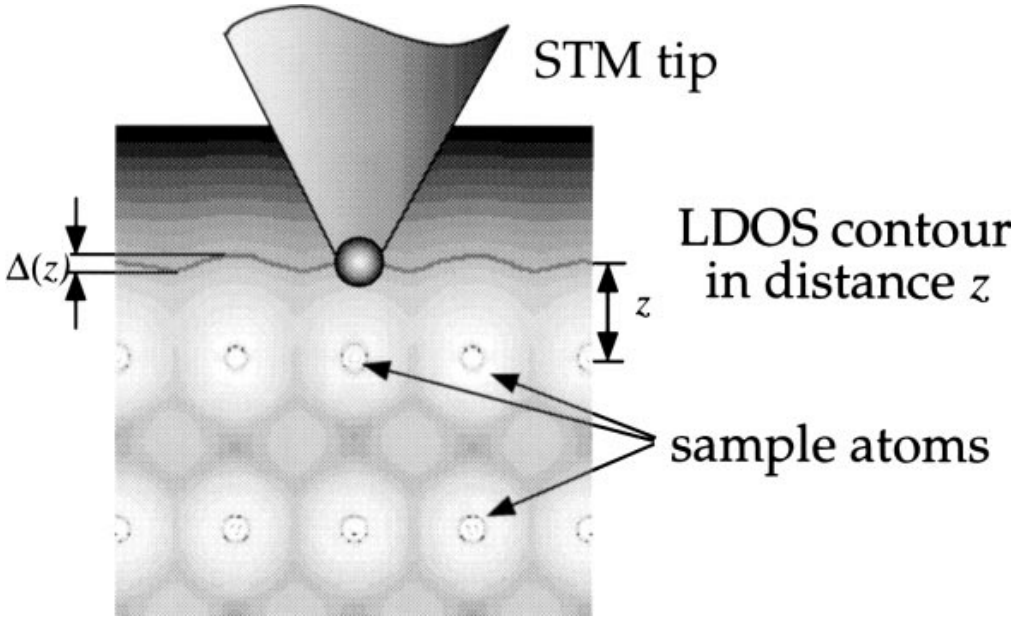
Methods

VASP

b-initio VASP ackage ienna imulation

●DFT-D : GGA + correction of Grimme *(Grimme, J. Comp. Chem. 27, 1787 (2006))*

Tersoff Hamann approximation

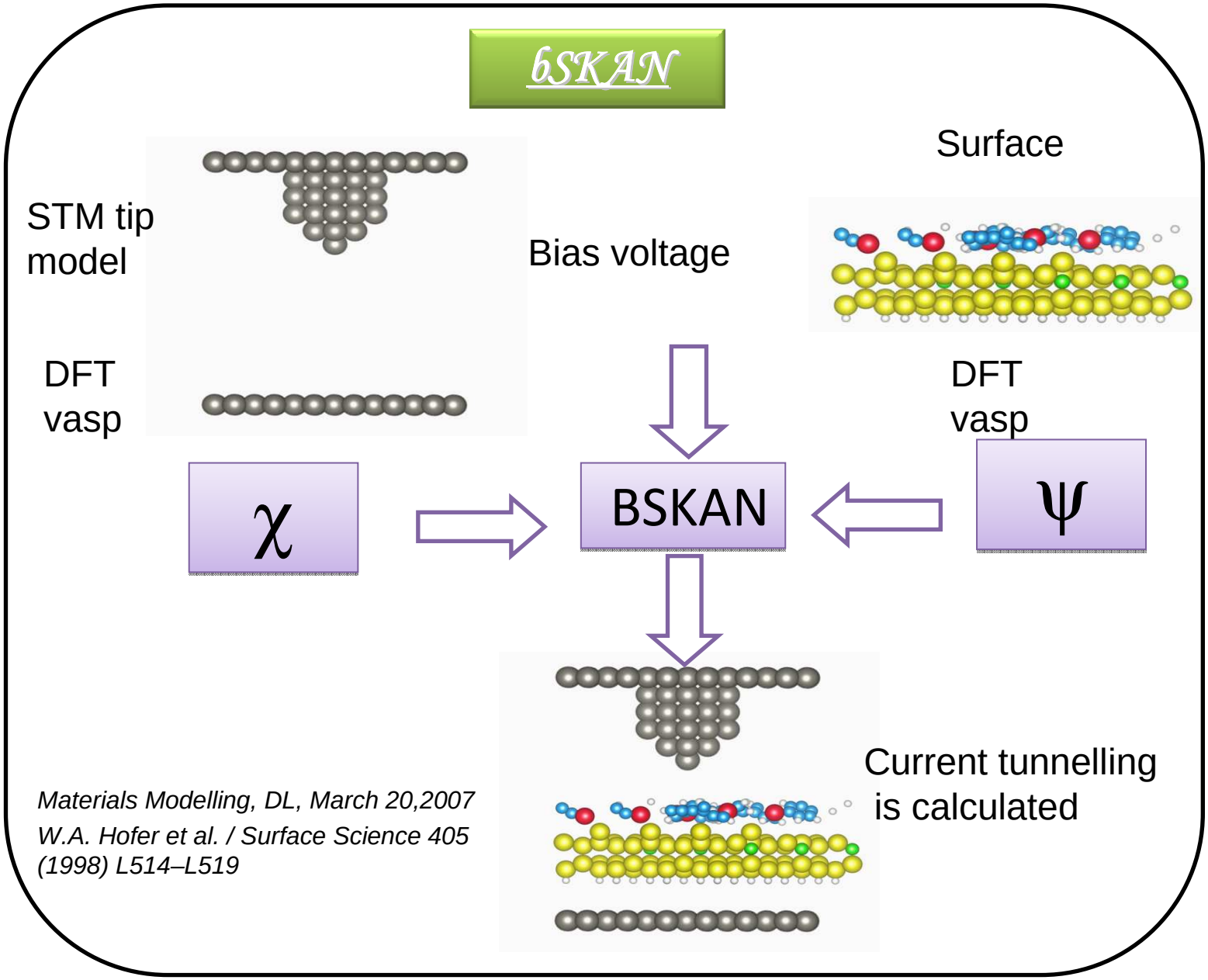


$$I_s \propto LDOS(\vec{r}_0, E_f)^*$$

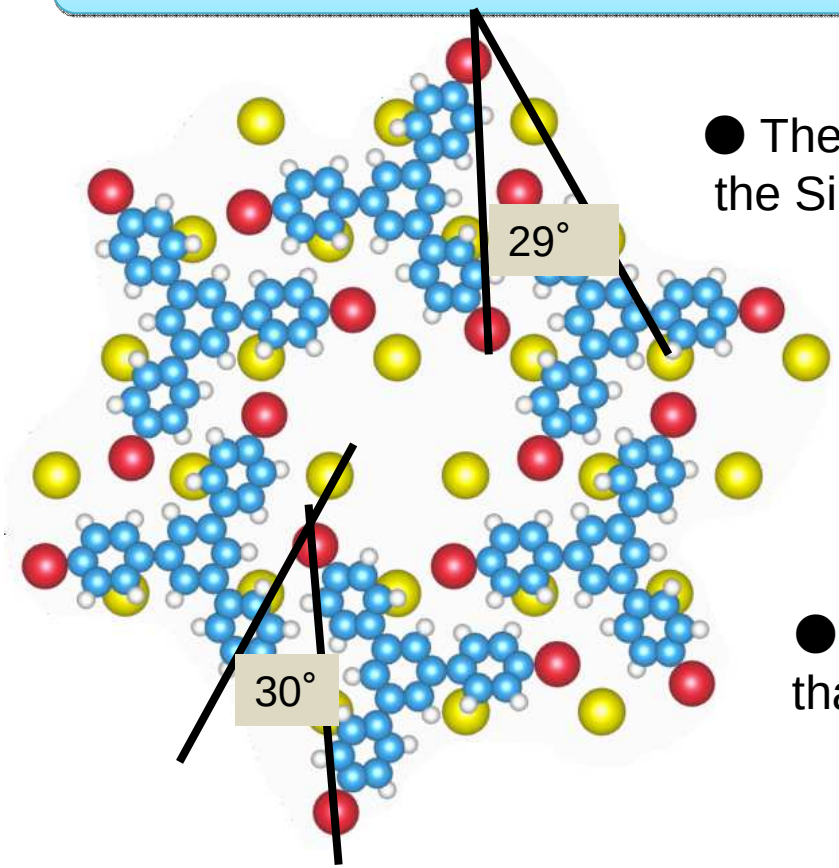
$$I_s \propto \int_{Ef-E}^{E_f} LDOS\,(\vec{r_0}, E)\,dE \qquad I_s \propto \int_{Ef}^{E_f+E} LDOS\,(\vec{r_0}, E)\,dE$$

* *J. Tersoff et al. / Phys. Rev. B 31 (1985) L805–L813*

Methods


bSKAN
STM tip model
Bias voltage
Surface
DFT vasp
DFT vasp
χ
BSKAN
ψ
Current tunnelling is calculated
Materials Modelling, DL, March 20,2007
W.A. Hofer et al. / Surface Science 405 (1998) L514–L519

Structural and energetic studies



● The angle between Br-Br axes of TBB molecule and the Si adatom rows is about 30° .

Interaction energy (eV)	GGA	DFT-D	LDA
Molecule-substrate	-1.07	-2.66	-2.52
Molecule-molecule	+0.16	-0.81	-0.74

●Molecule-molecule interaction is less important than molecule-substrate one.

● Molecule-molecule interaction is repulsive in a previous paper* while it is attractive in DFT-D approximation due to the dispersive term of Grimme.

The substrate plays a major role to stabilise the supramolecular network.

* Baris et *al* , Angew.Chem.Int.Ed.2011,50, 4094-4098.

Structural and energetic studies

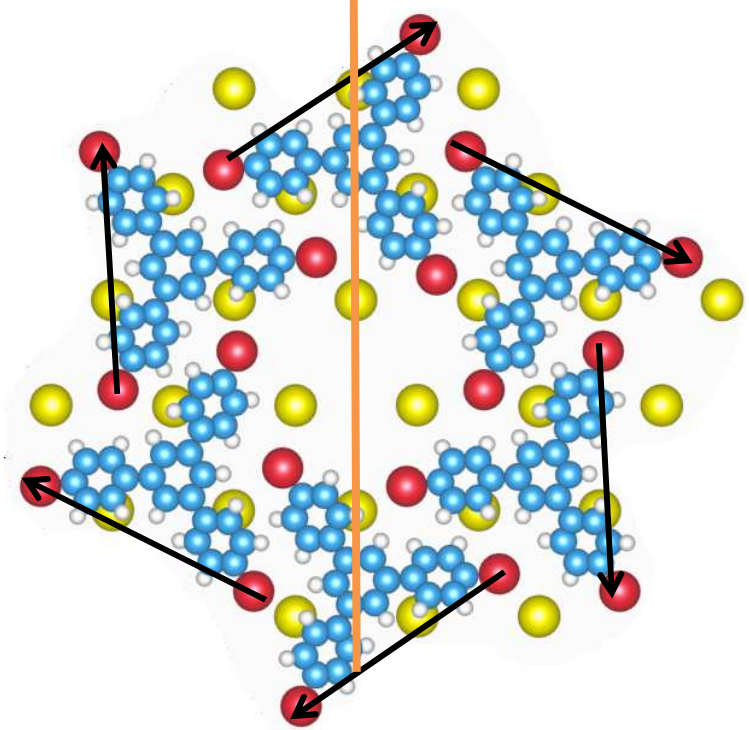
P enantiomer network

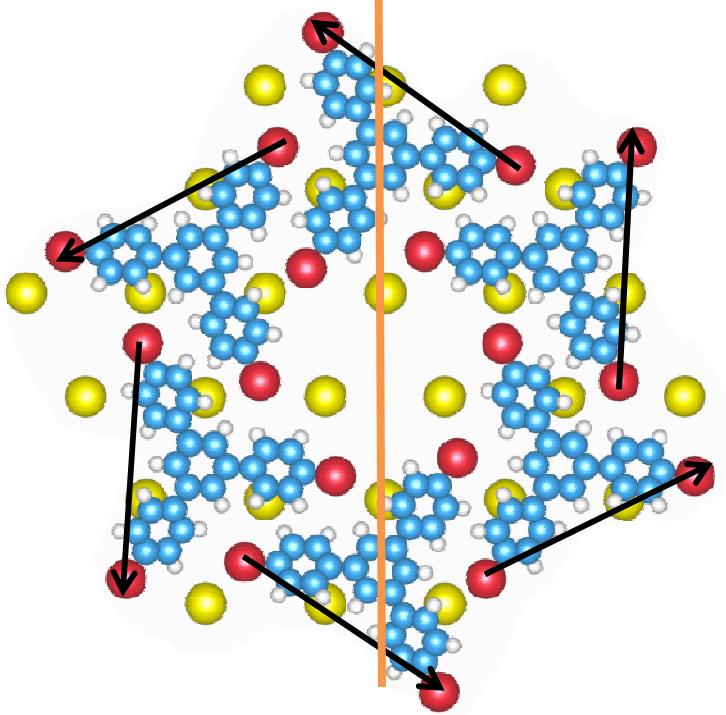
+30°

Chiral networks

-30°

M enantiomer network

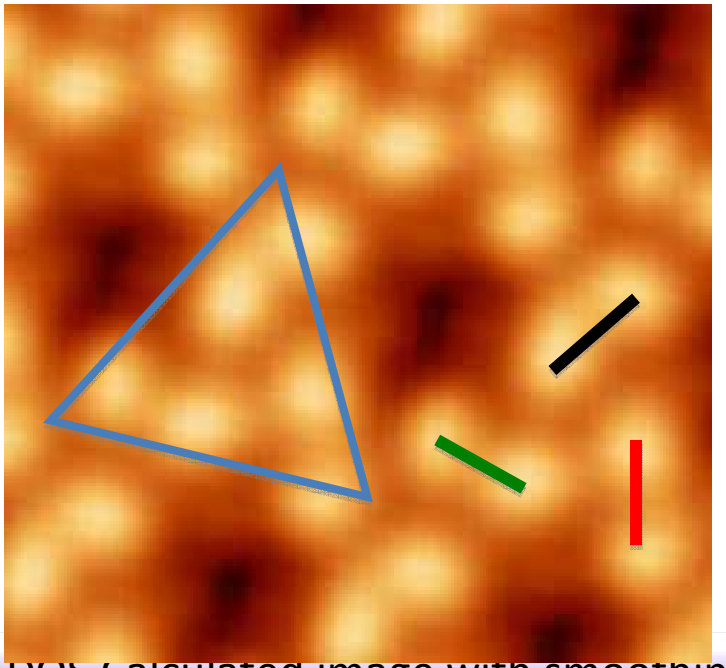




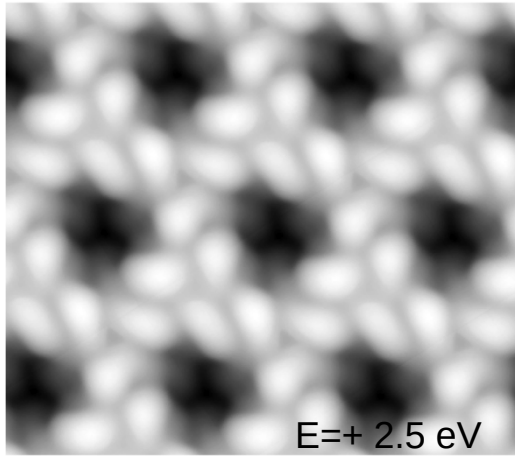
Interaction energy (eV)	P enantiomer network	M enantiomer network
Molecule-molecule	-0,81	-0,87
Molecule-substrate	-2,66	-2,61
Total energy	-3,47	-3,48

ΔE=0,01 eV

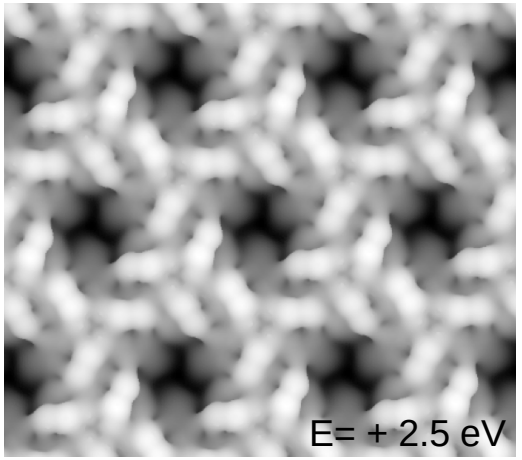
STM / LDOS/ bSKAN image

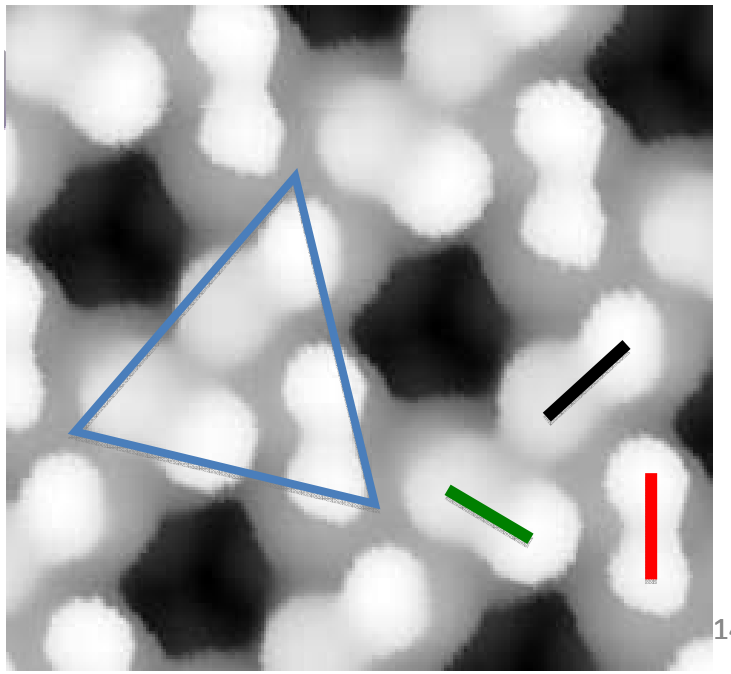


LDOS Calculated image with smoothing



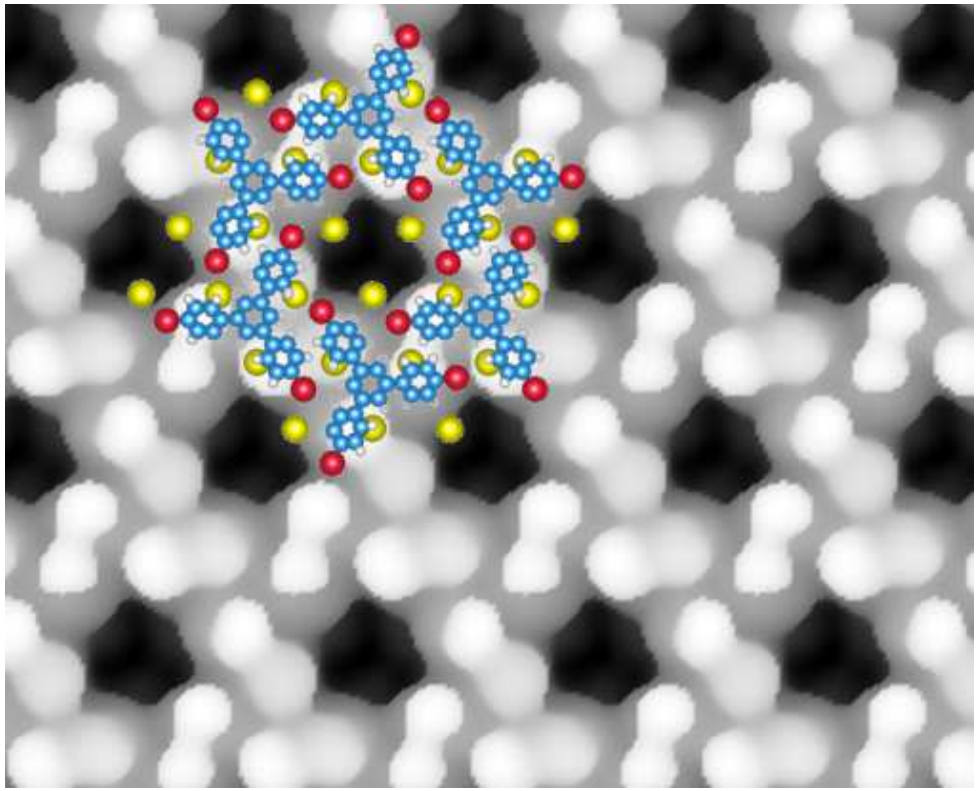
LDOS Calculated image without smoothing





STM / LDOS/ bSKAN image

- We observe triangles that consist of three disjoined pair protrusions.



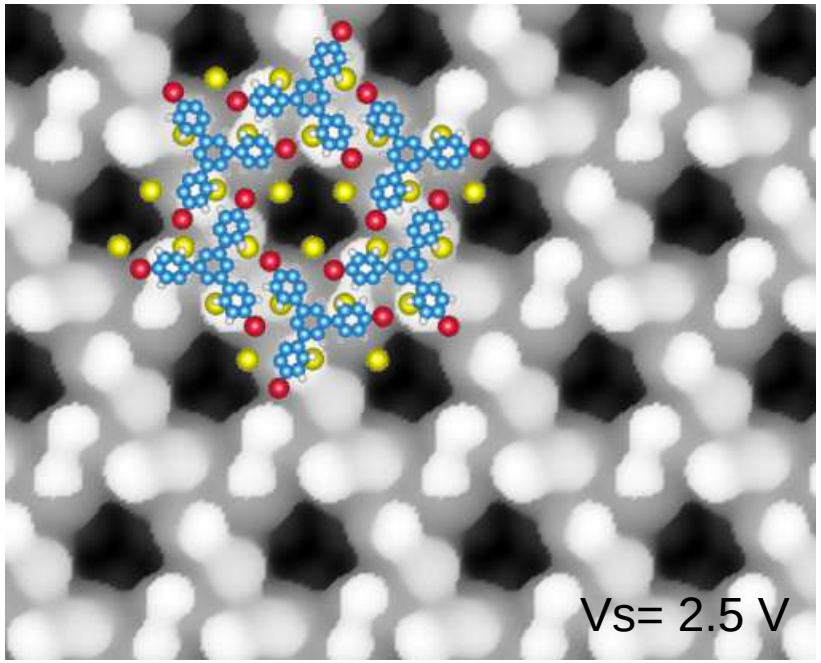
Vs= 2.5 V

- The protrusions correspond to the phenyl arms of TBB molecules.

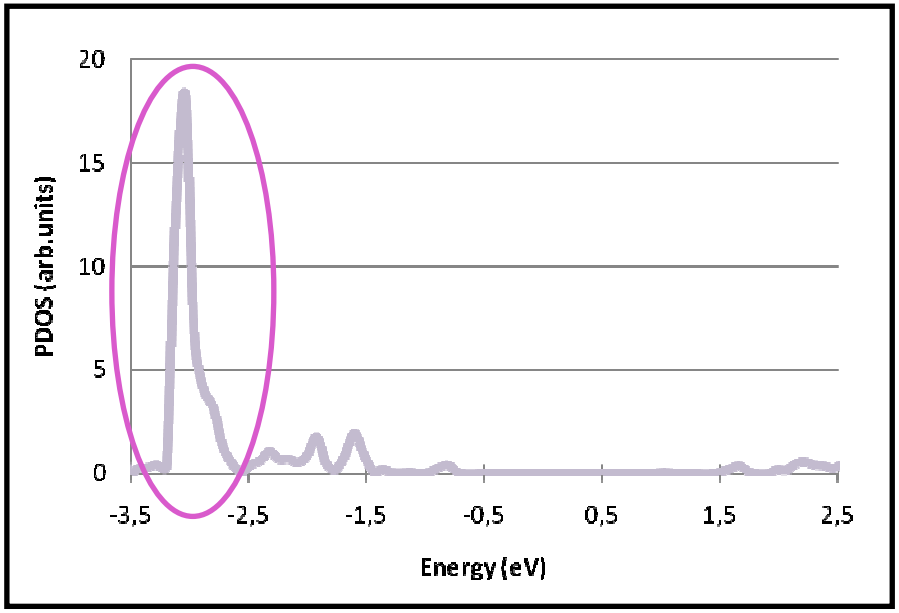
- The center of the TBB and the bromine atoms give a slight brightness.

Electronic study

Calculated image with bSKAN



PDOS of bromine atom

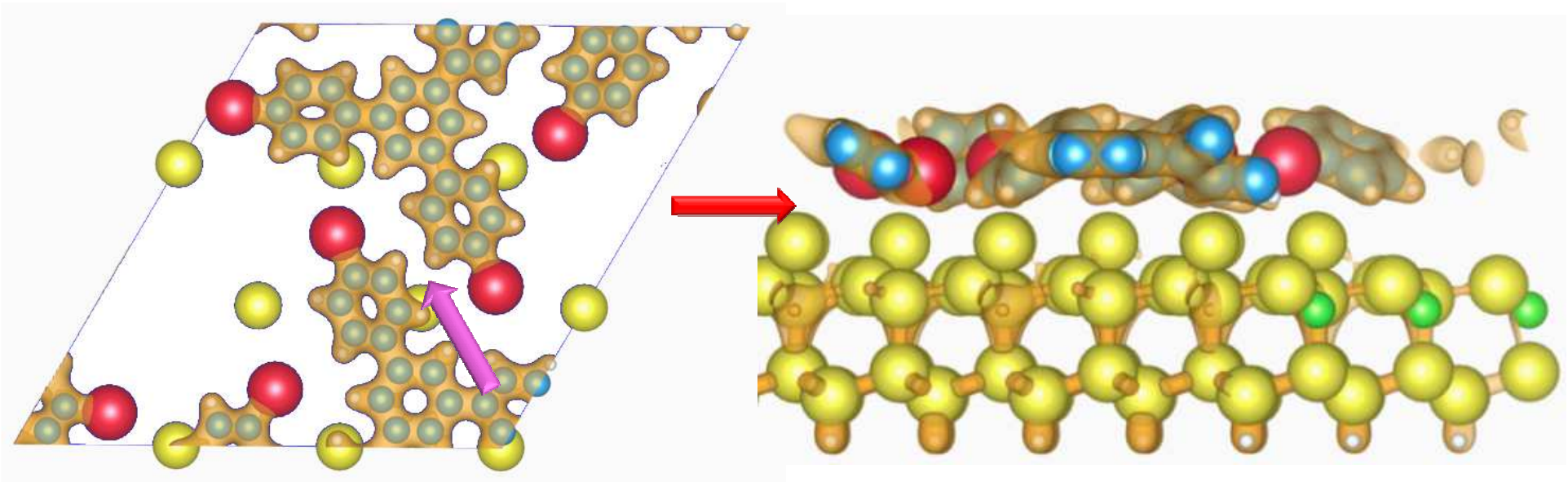


Bromine atoms are not visible in STM image.

Bromine elertronic states are located at -3.eV

Charge density

Unit cell



Top view

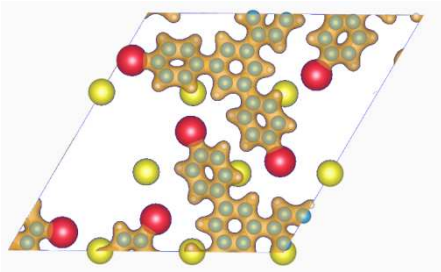
Side view

No shared charge density between molecule-molecule and molecule-substrate : no covalent interaction

Conclusion

- The surface plays a major role for the stabilization of the molecular network.

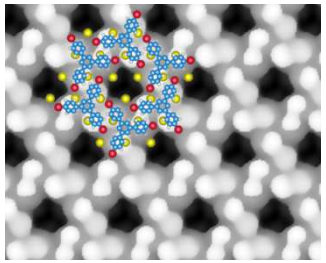
- No covalent molecular network ⇒ DFT-D



- Very good agreement between STM experimental images and simulation ones

=>Theoretical STM image permits to interpret STM experimental one: the observed protrusions are due to phenyl arms.

⇒ STM tip should be considered

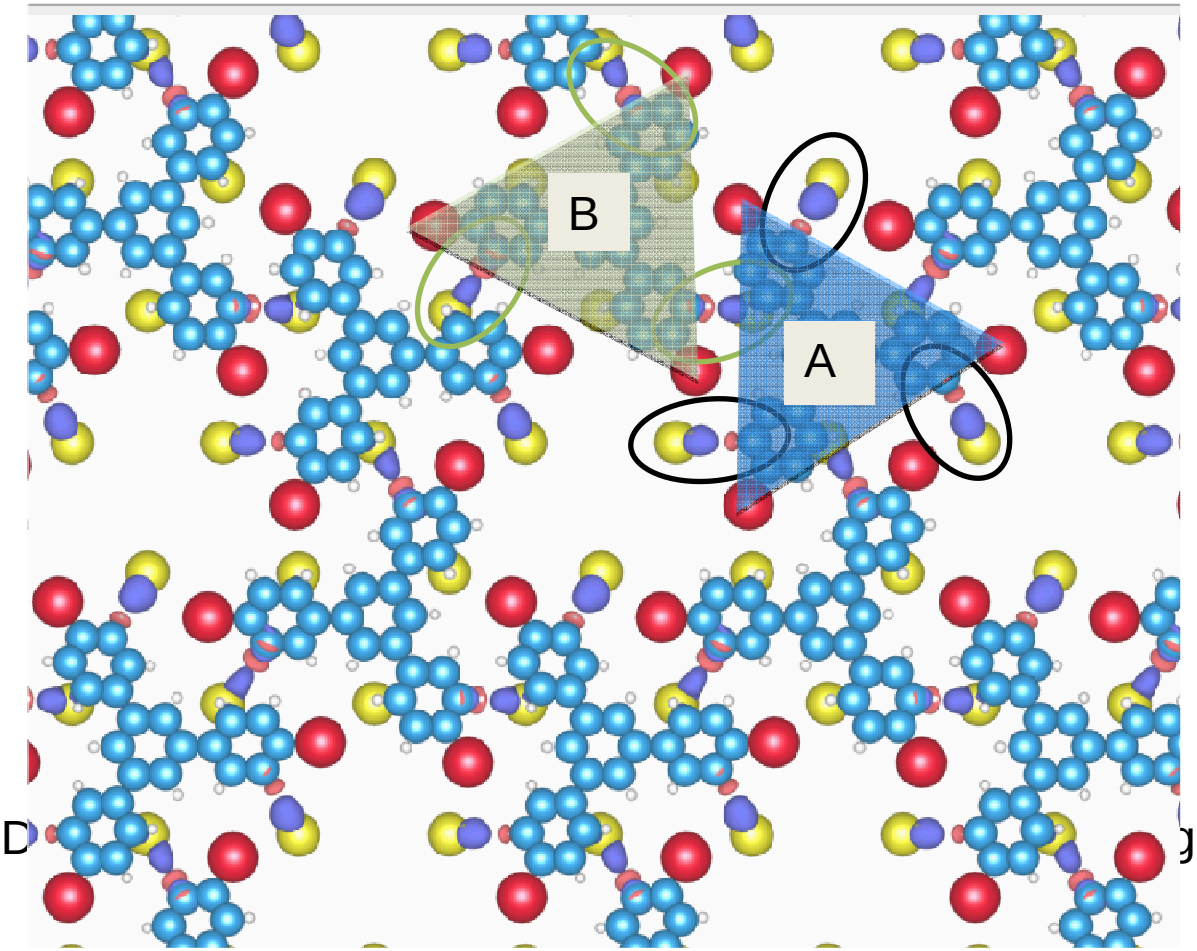


K. Boukari, E. Duverger, and P.Sonnet, J.Chem.Phys :138 (2013)

Thank You For Your Attention

Charge density difference Δρ

Δρ=ρ(molecules+substrate)-ρ(molecules)-ρ(substrate)

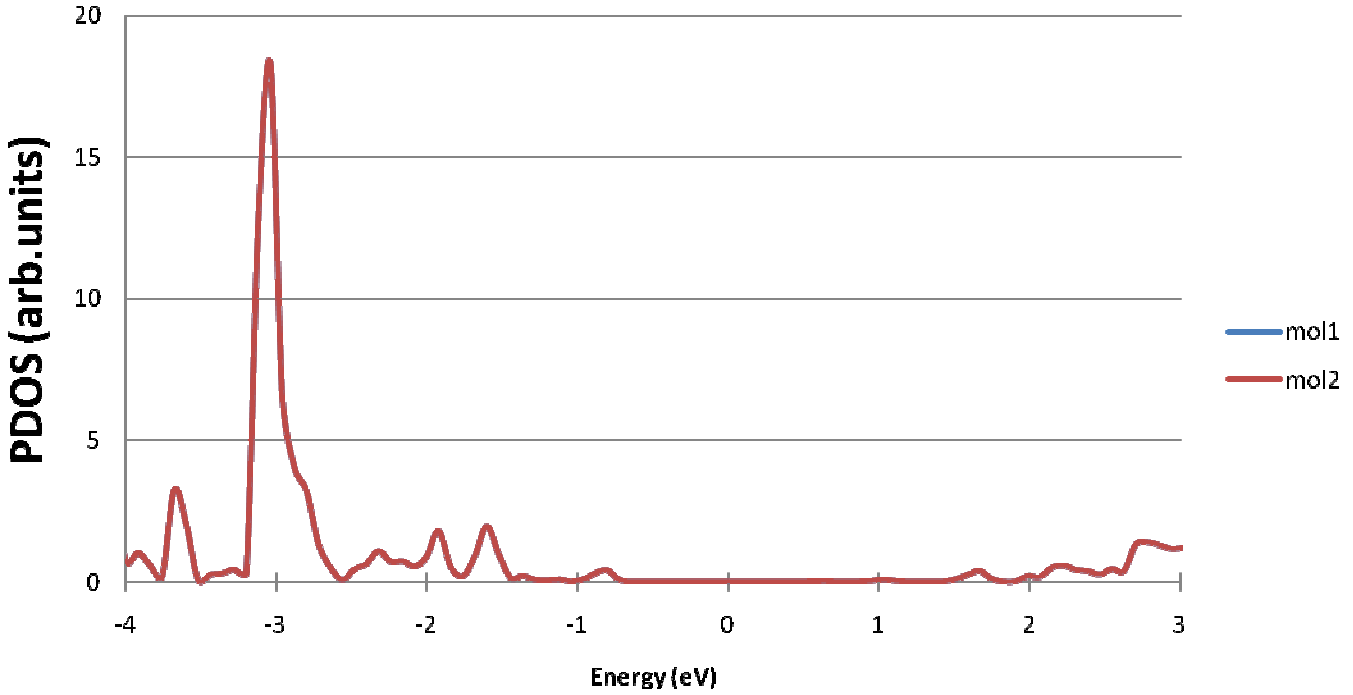


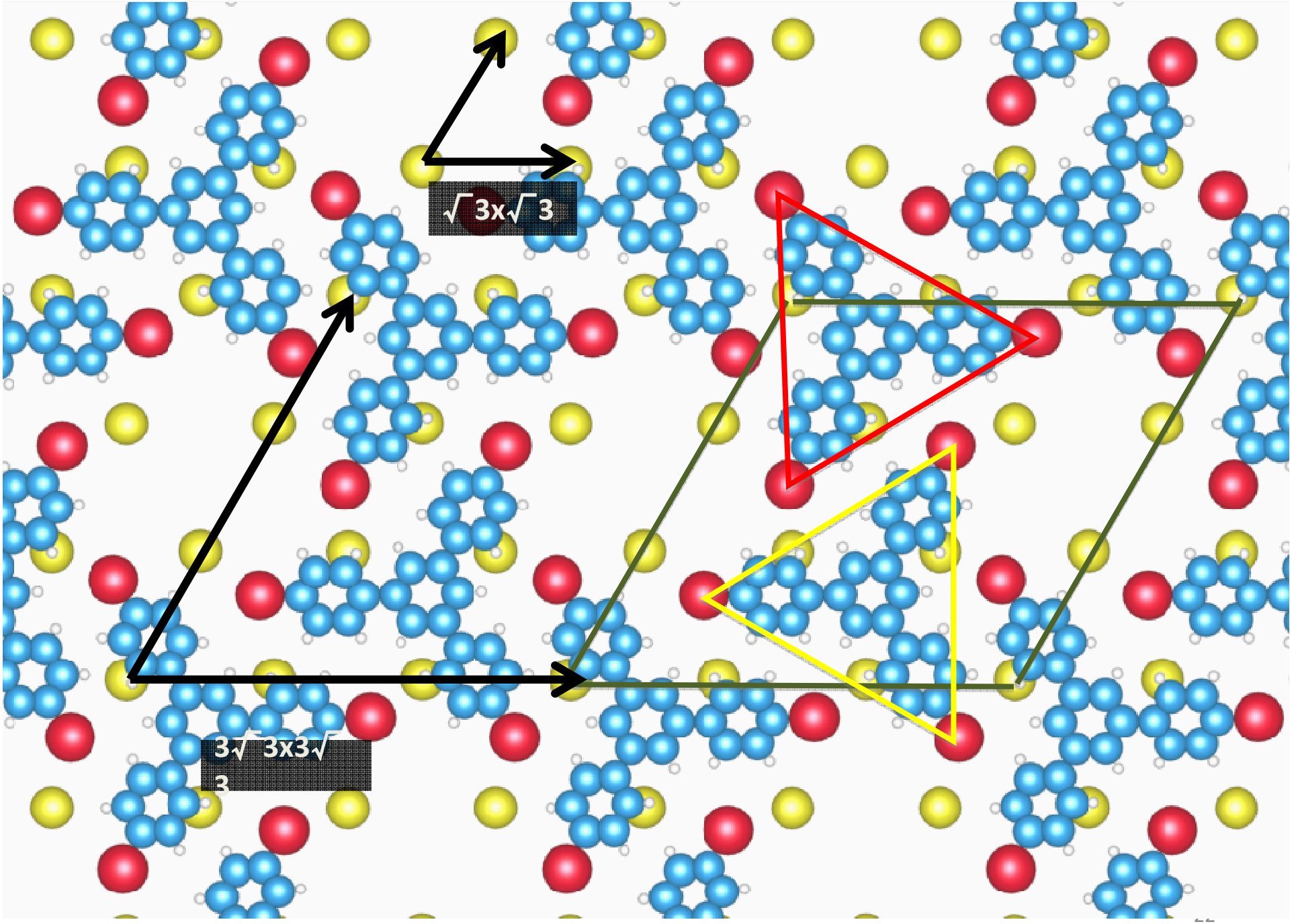
Blue : Δρ>0 => e ↗

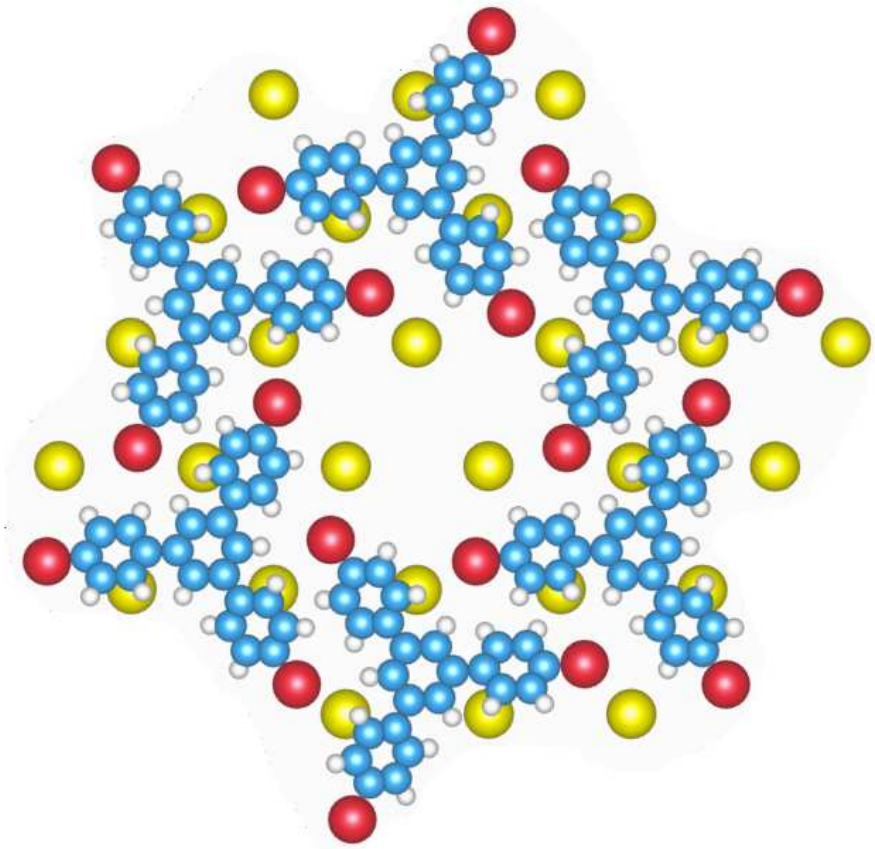
Red: Δρ<0 => e ↘

Electron rich phenyls interact with electron poor silicon adatoms

Electrostatic interaction


PDOS (arb.units)
20
15
10
5
0
-4
-3
-2
-1
0
1
2
3
Energy (eV)
mol1
mol2


√3x√3
3√3x3√3



Δz (Å)	DFT	DFT-D
Molecule A	3,86	2,72
Molecule B	3,96	2,81