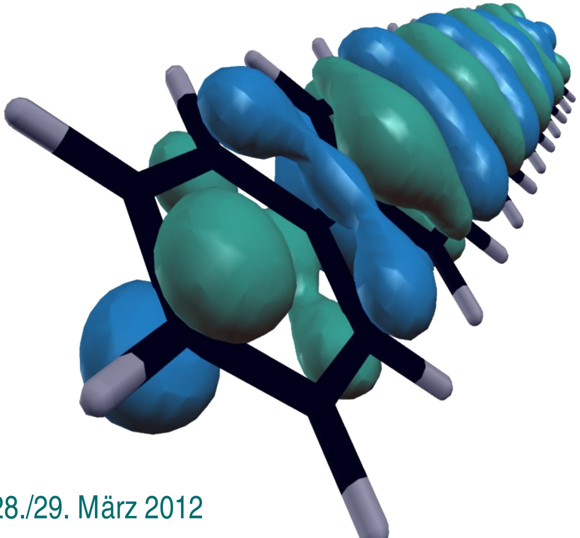
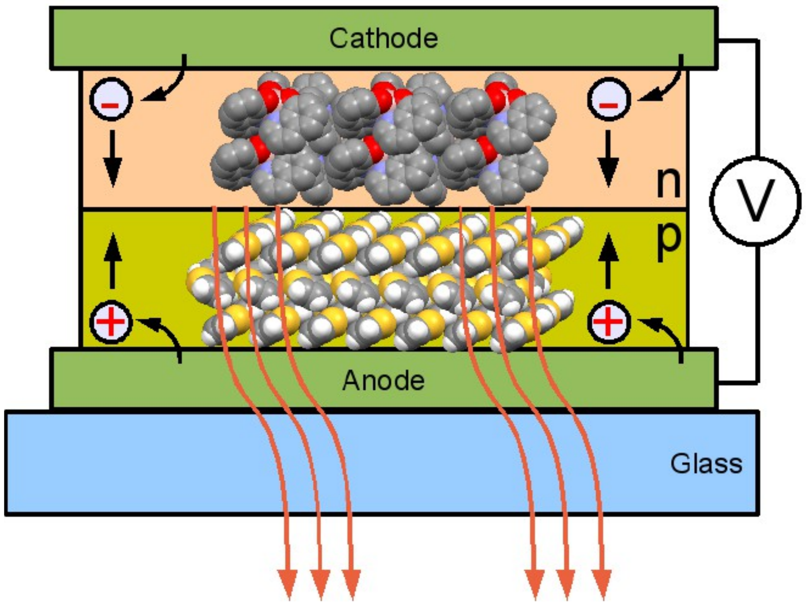
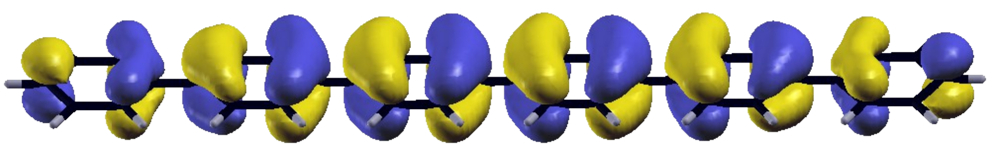
Modellierung molekularer Prozesse beim Wachstum organischer Schichten



Motivation

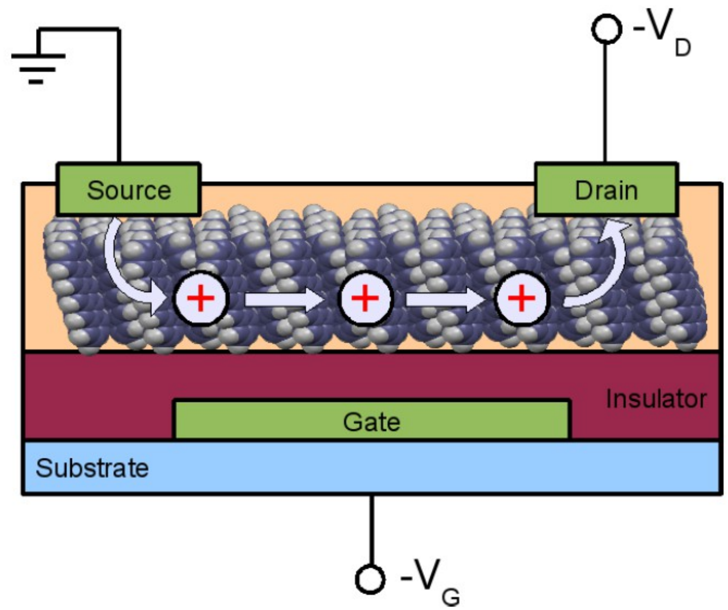
OLED

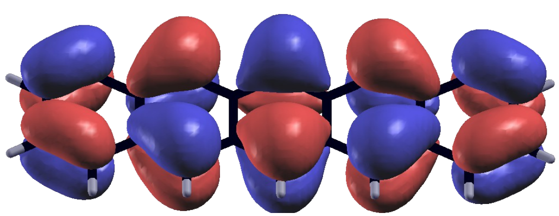




para-Sexiphenyl (6P) ($C_{36}H_{26}$)

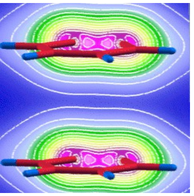
OFET



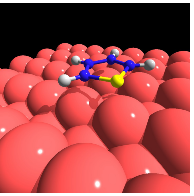


Pentacene (5A) ($C_{22}H_{14}$)

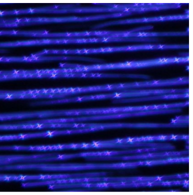
Outline



Methods and Materials

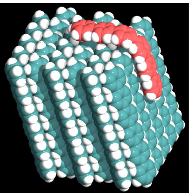


Cohesive, Surface, and Adsorption Energies



Growth of Chain-like Molecules on Mica

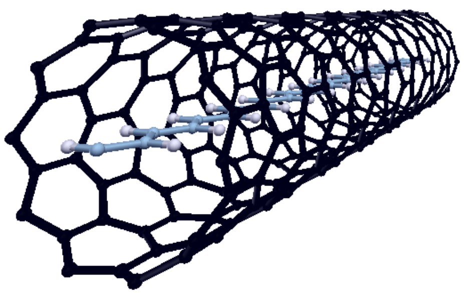
- Needle Growth and Orientations
- Critical Cluster Size



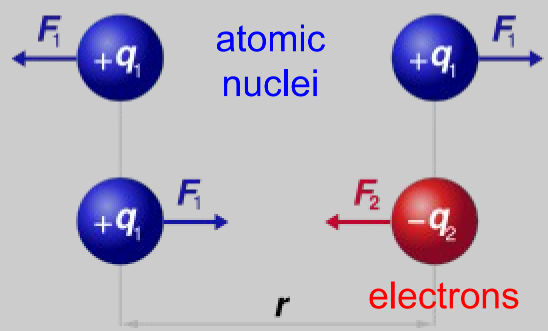
- Terraced Mounds and Step-Edge-Barrier

Ab-Initio Methods

Any Material



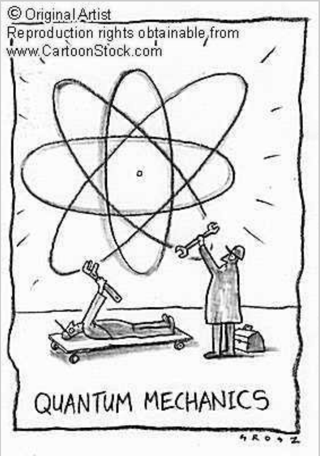
Coulomb Force



$$F_1 = F_2 = k_c \frac{q_1 \times q_2}{r^2}$$

+

Quantum Mechanics



Band structure

Elastic properties

vibrations

Magnetic properties

Optical properties

Density Functional Theory in a Nutshell

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

$$-\frac{Z}{r}$$

$$\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r'$$

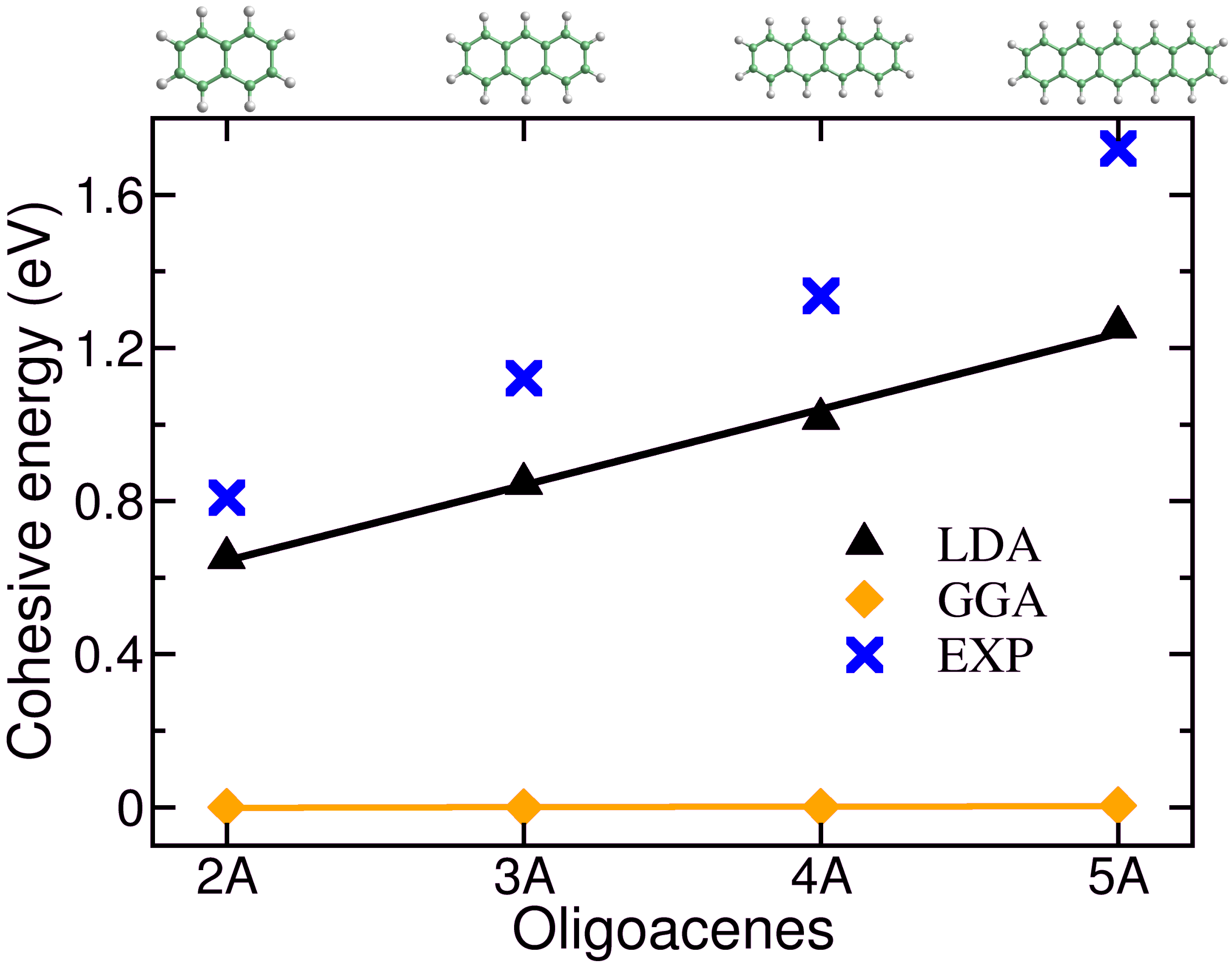
$$\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Approximations:
e.g.: LDA, GGA, ...

Self-consistency

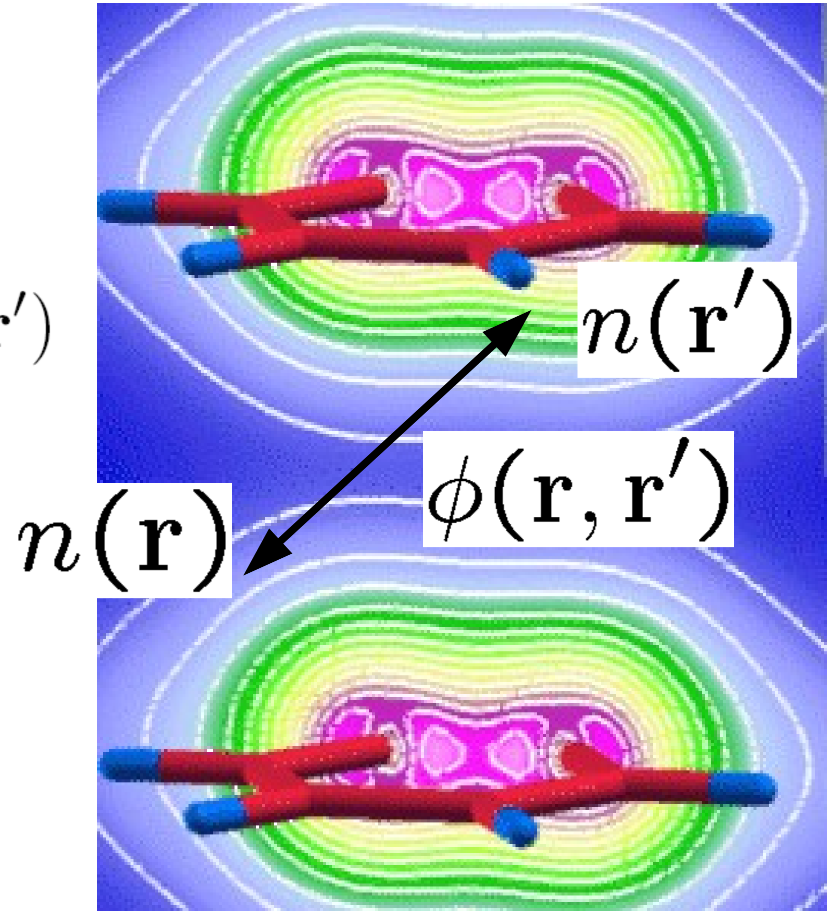
$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

Cohesive Energy of Molecular Crystals



Nonlocal Correlation Energy
leading to van-der-Waals interaction

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int d^3r d^3r' n(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}')$$

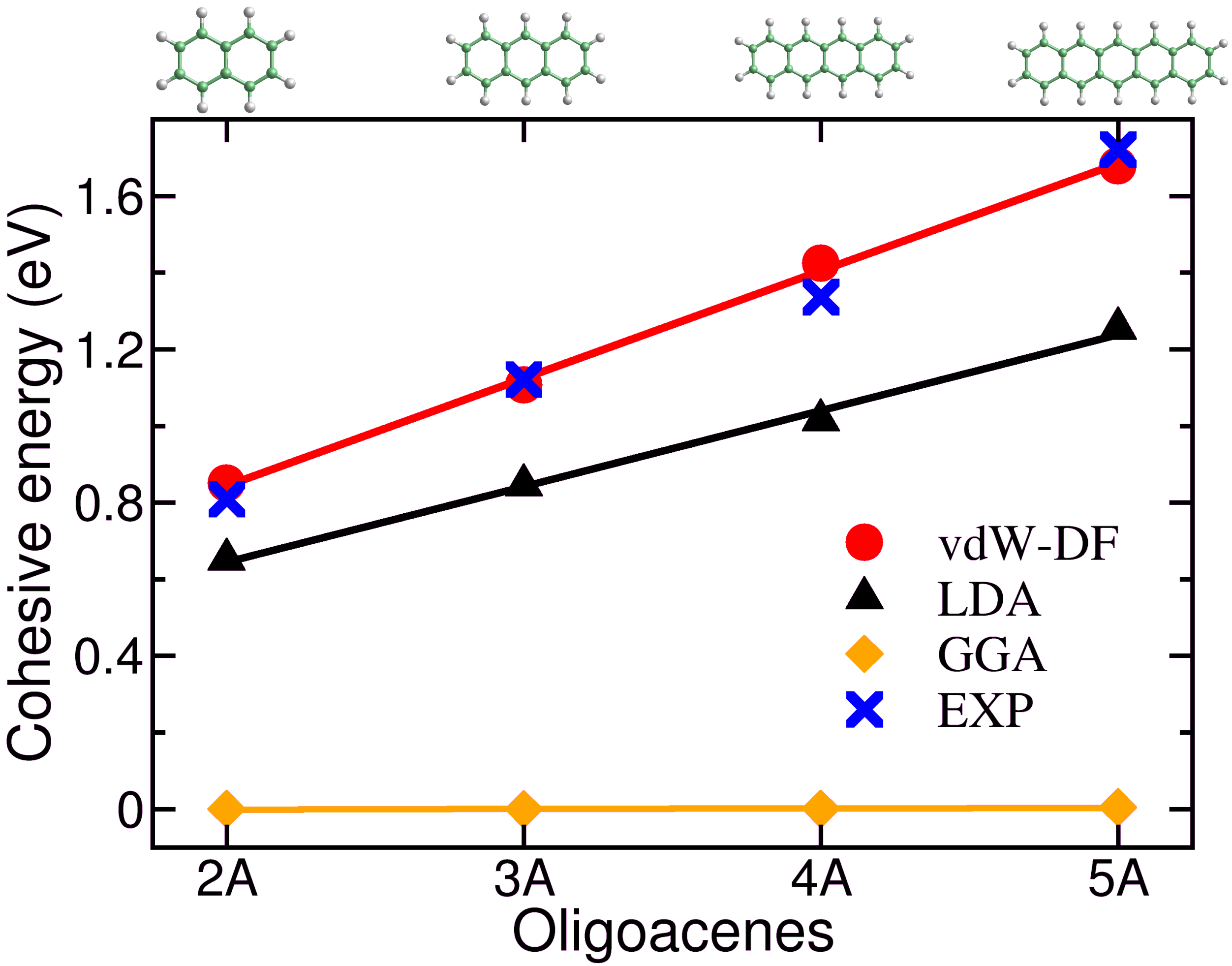


Exchange-Correlation Energy

$$E_{xc}^{\mathrm{vdWDF}} = E_x^{\mathrm{GGA}} + E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}}$$

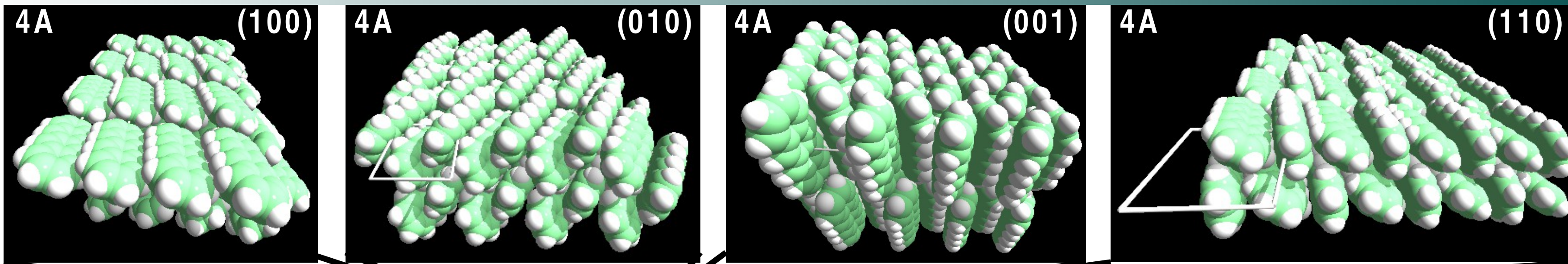
Dion et al, *Phys. Rev. Lett.* ***92***, *246401 (2004).*

Cohesive Energy of Molecular Crystals



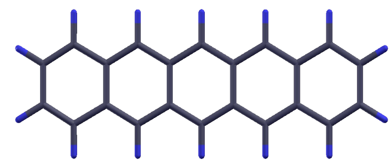
Nabok, Puschnig, Ambrosch-Draxl, *Phys. Rev. B* ***77****, 245316 (2008).*

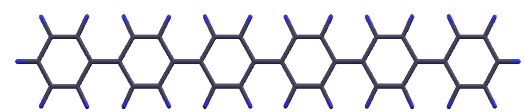
Surface Energies of Molecular Crystals

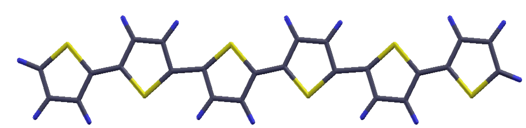


γ [mJ/m^2]

	(100)	(010)	(001)	(110)
2A	102	107	90	120
3A	100 (88[a])	115 (118[a])	81 (76[a])	108 (90[a])
	[66[b]]	[91[b]]	[53[b]]	
4A	109	124	84	106
5A	107	130	82	113
	[77[b]]	[103[b]] {140[c]}	[50[b]] {76[c]}	[75[b]] {150[c]}
2P	122	129	97	118
3P	124	136	99	123
4P	124	140	96	124
6P	142	142	107	135
2T	147	123	110	121
4T	134	133	102	125
6T	176	128	115	146

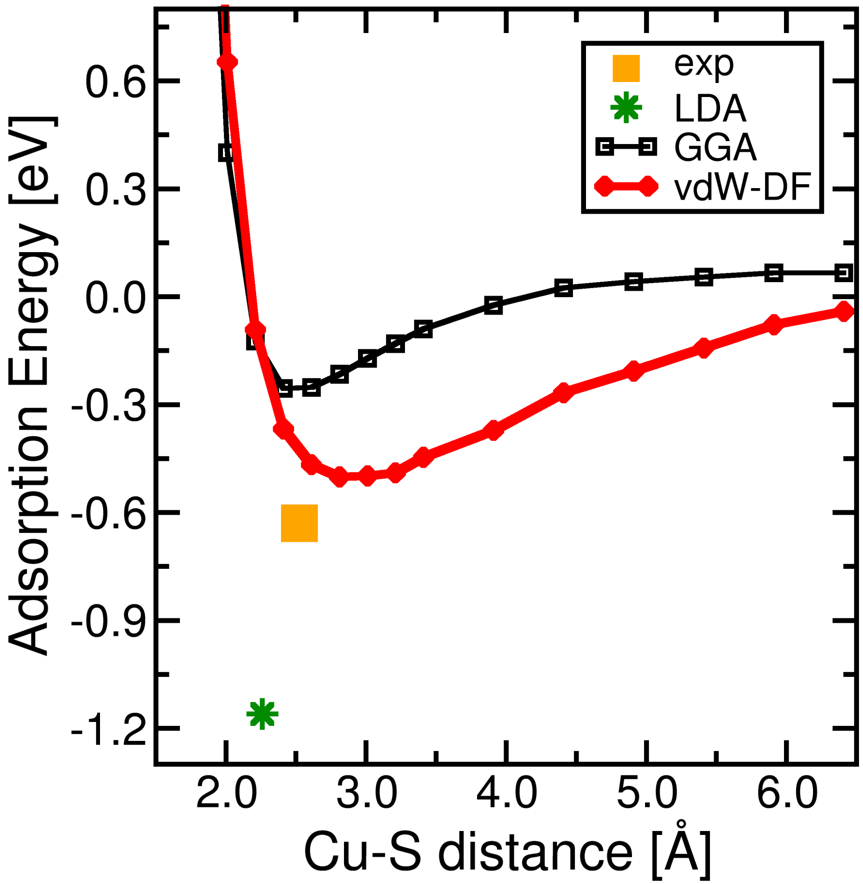


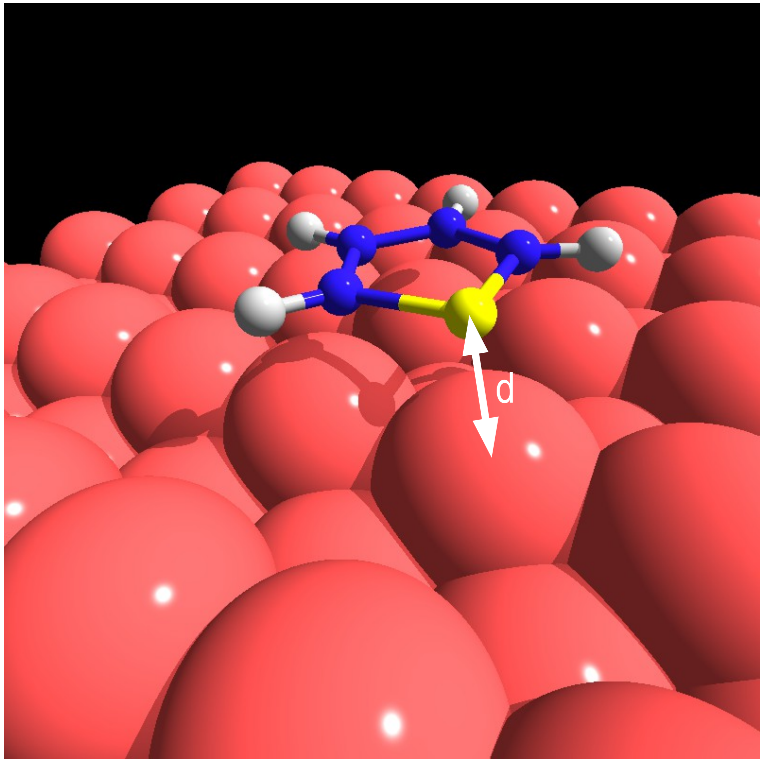




Nabok et al. *Phys. Rev. B* ***77****, 245316 (2008); Ambrosch-Draxl et al., New J. Phys.* ***11****, 125010 (2009).*

Thiophene / Cu(110)

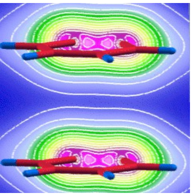




Thiophene@Cu(110): Sony et al., *Phys. Rev. Lett.* ***99****, 176401 (2007).*

PTCDA@Cu,Ag,Au(111): Romaner et al., New. J. Phys. ***11****, 053010 (2009).*

Outline



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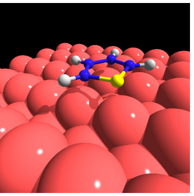

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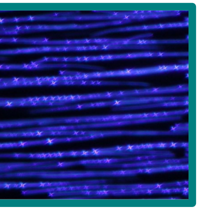
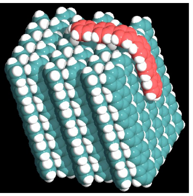


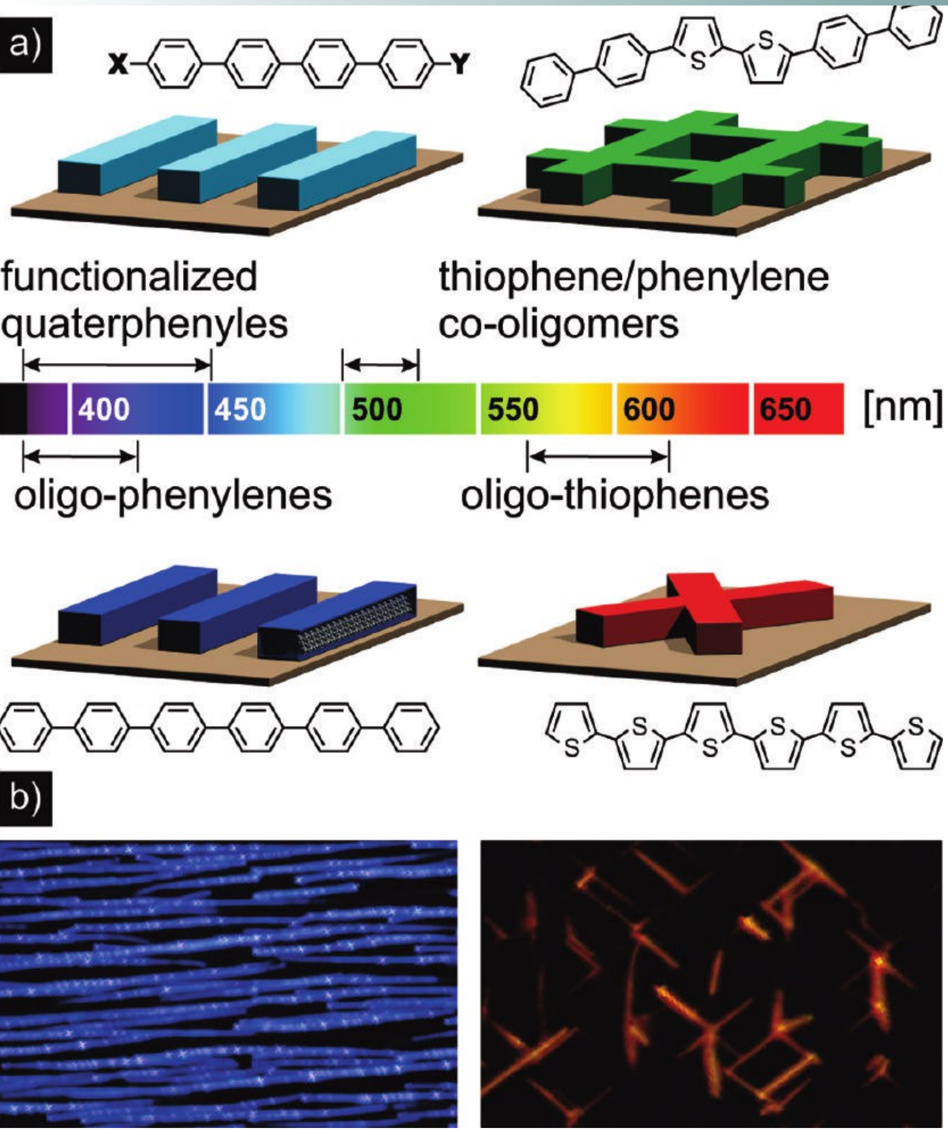
Growth of Chain-like Molecules on Mica

- Needle Growth and Orientations
- Critical Cluster Size



- Terraced Mounds and Step-Edge-Barrier

Nano-Needles on Mica

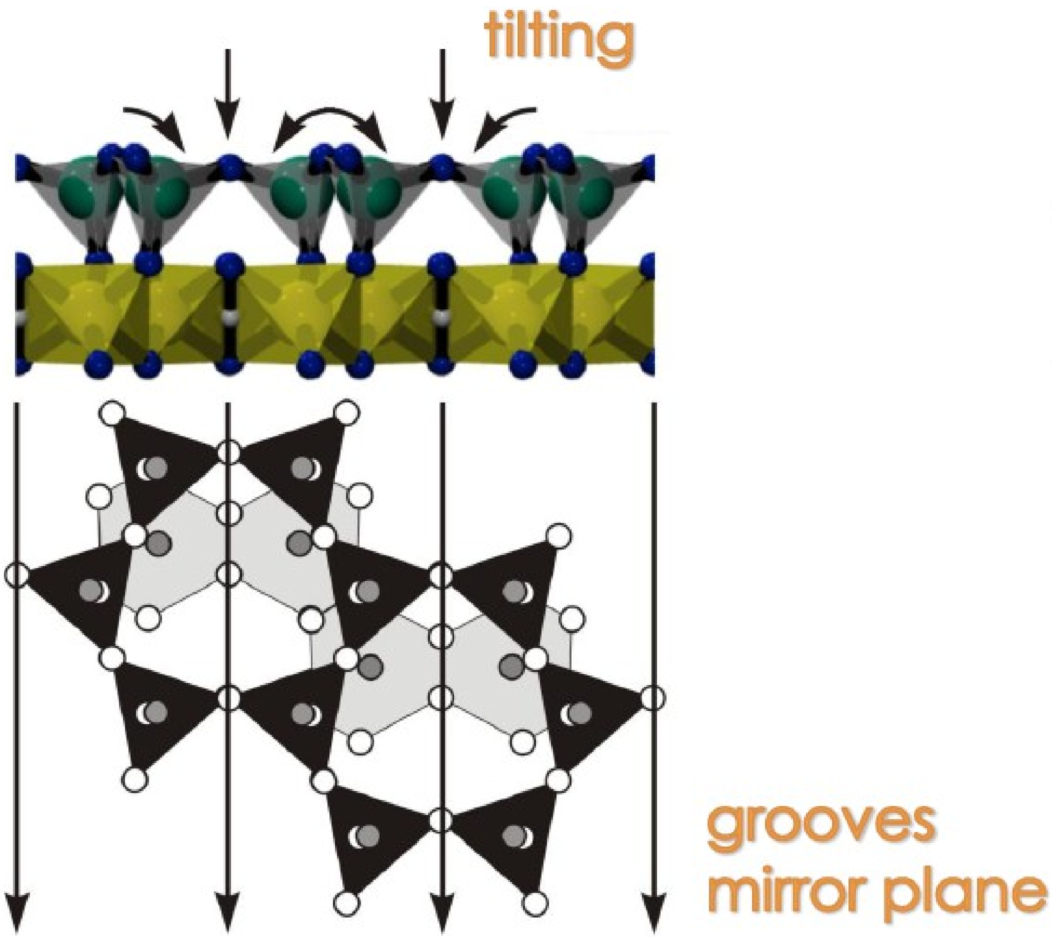


- Parallel alignment only for phenylenes
- Anisotropy for thiophenes and co-oligomers
- Macroscopic polarized light emission only for parallel alignment

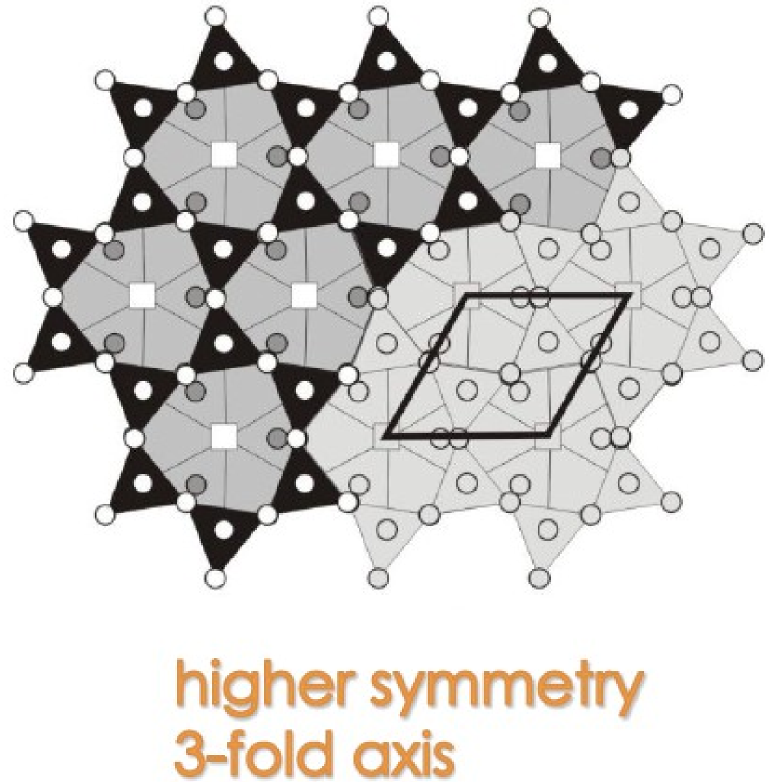
Simbrunner et al., *JACS* **133**, 3056 (2011).

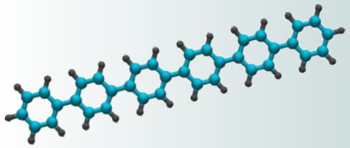
Mica Substrates

Muscovite



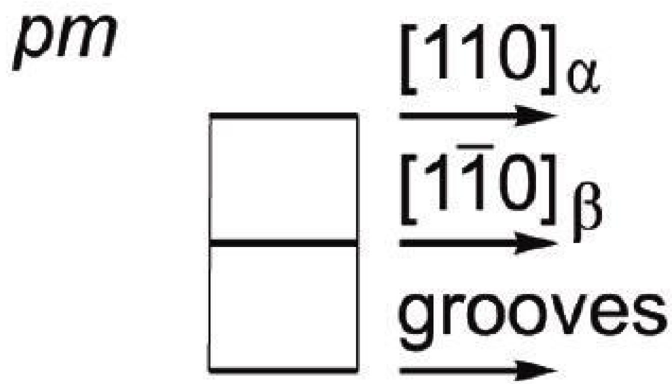
Phlogopite



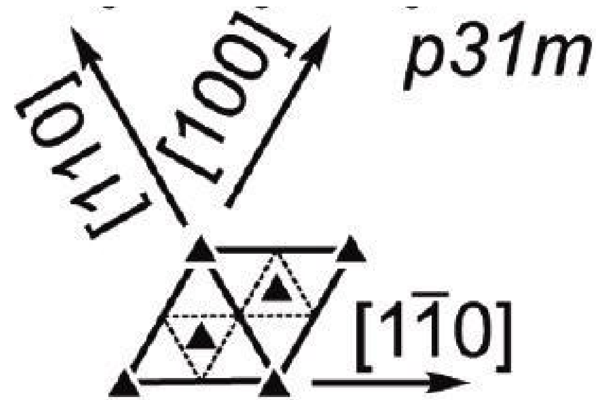


Sexiphenyl / Mica

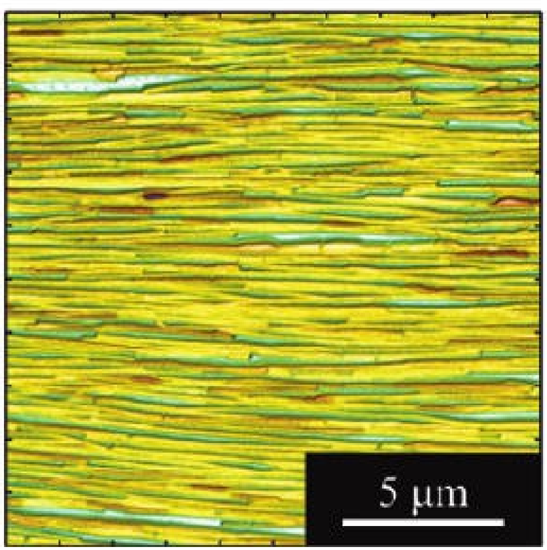
Muscovite

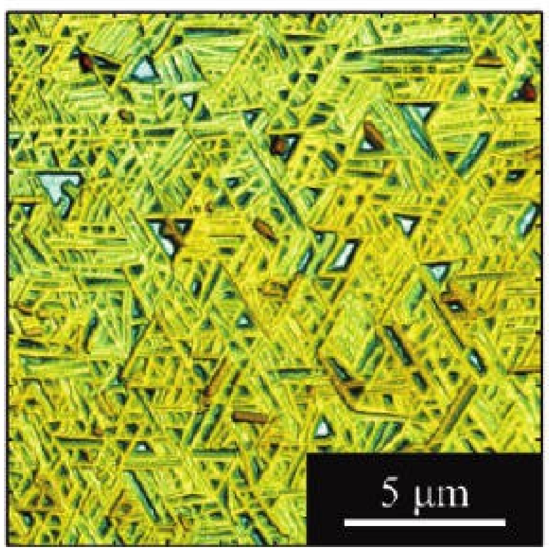


Phlogopite



AFM





Growth Models

(1) Electric fields of mica align molecules

F. Balzer et al., J. Vac. Sci. Technol. B, 26, 1619, (2008).
L. Kankate et al., Thin Solid Films 518, 130, (2009).

(2) Alignment by geometry/symmetry of mica and molecule

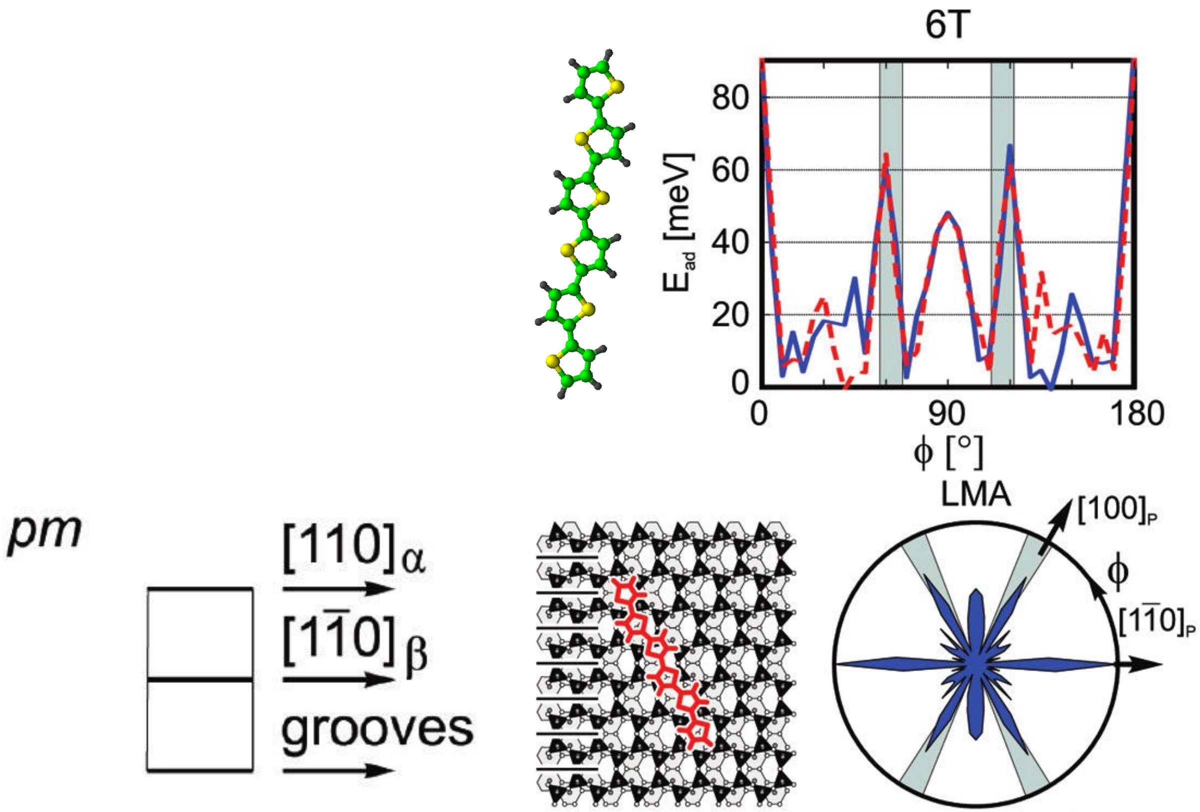
Simbrunner et al., *JACS* **133**, 3056 (2011).

Methodology

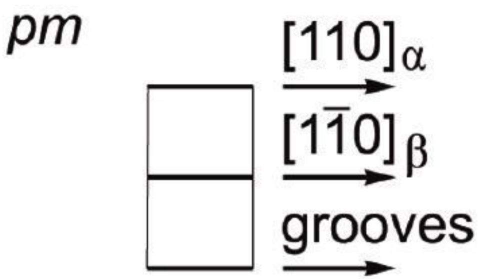
- Force-field simulations
- Adsorption energy as a function of adsorption position and orientation
- Substrates: muscovite → pyrophyllite
  phlogopite → talc

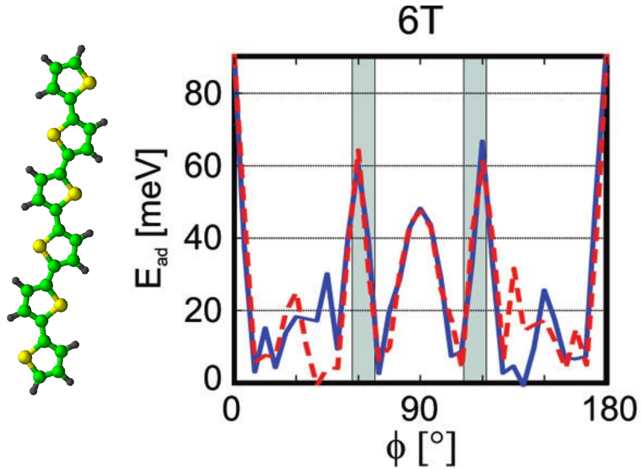
No charges, but the same surface corrugation

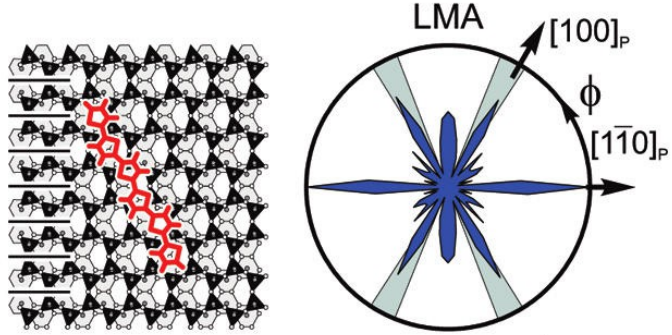
6T vs. 6P on Micas

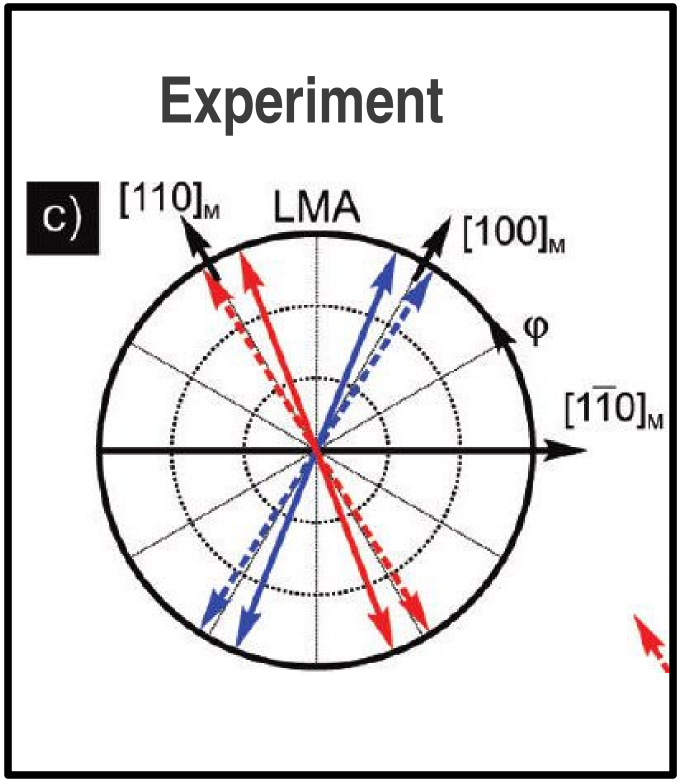


6T vs. 6P on Micas

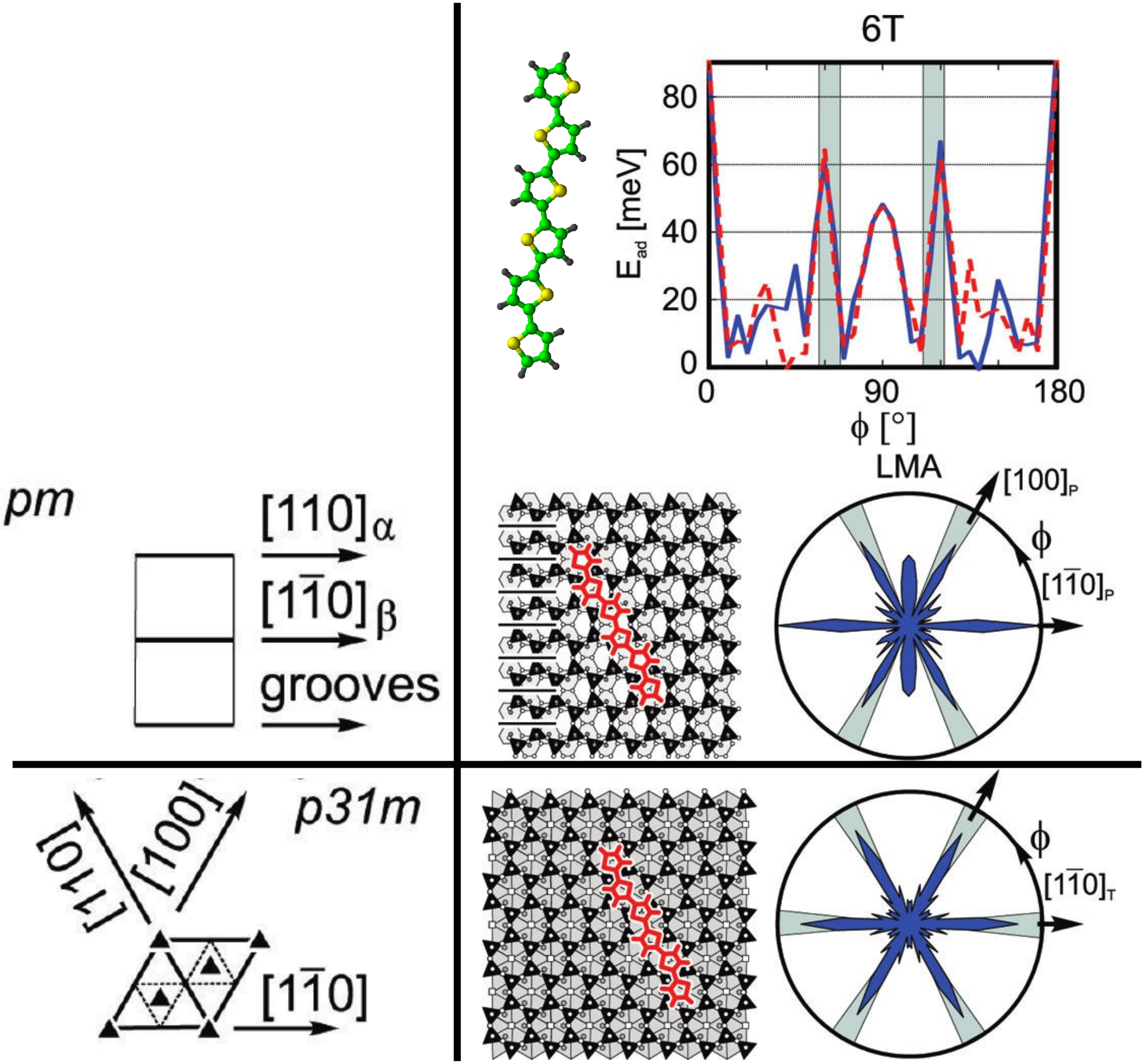




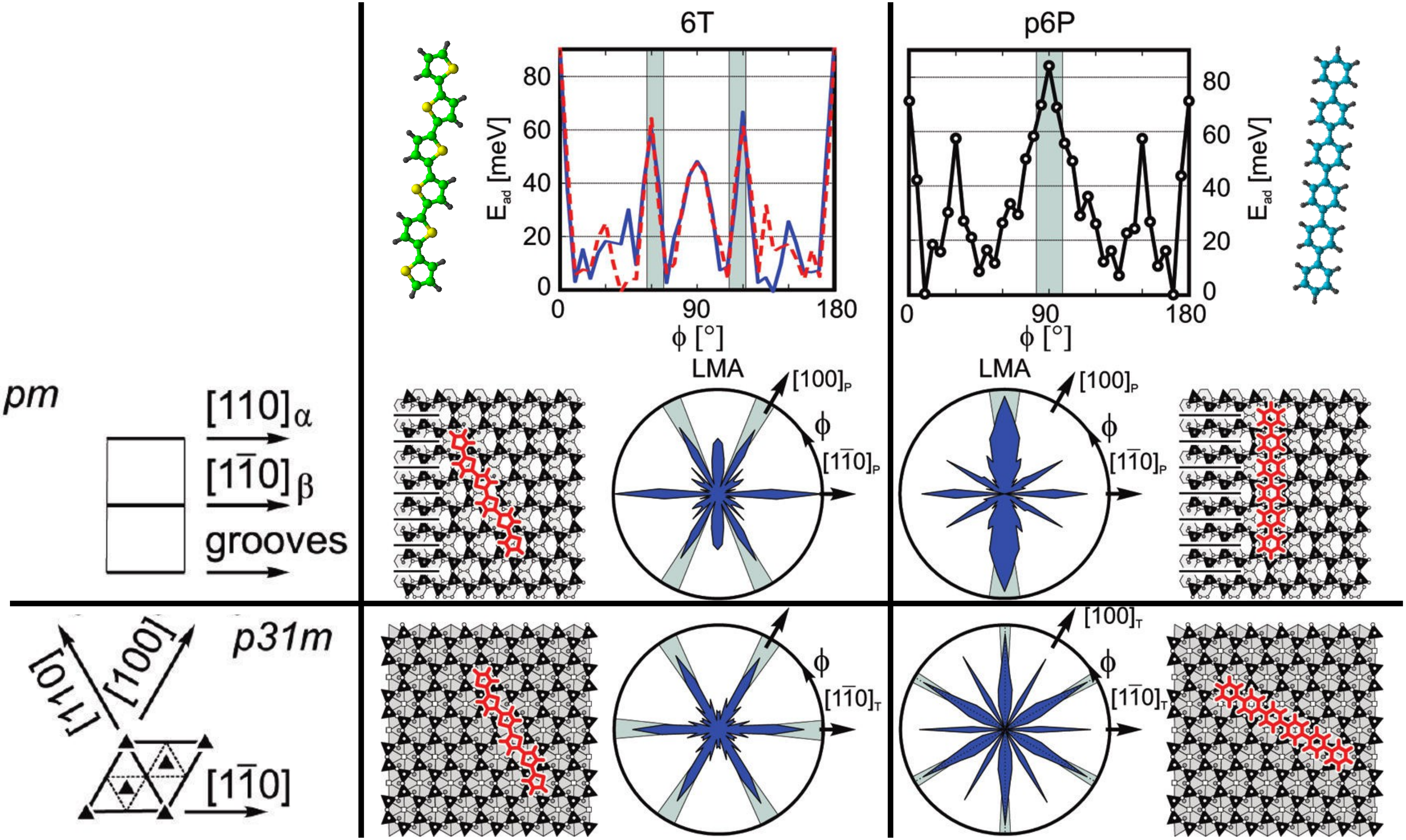




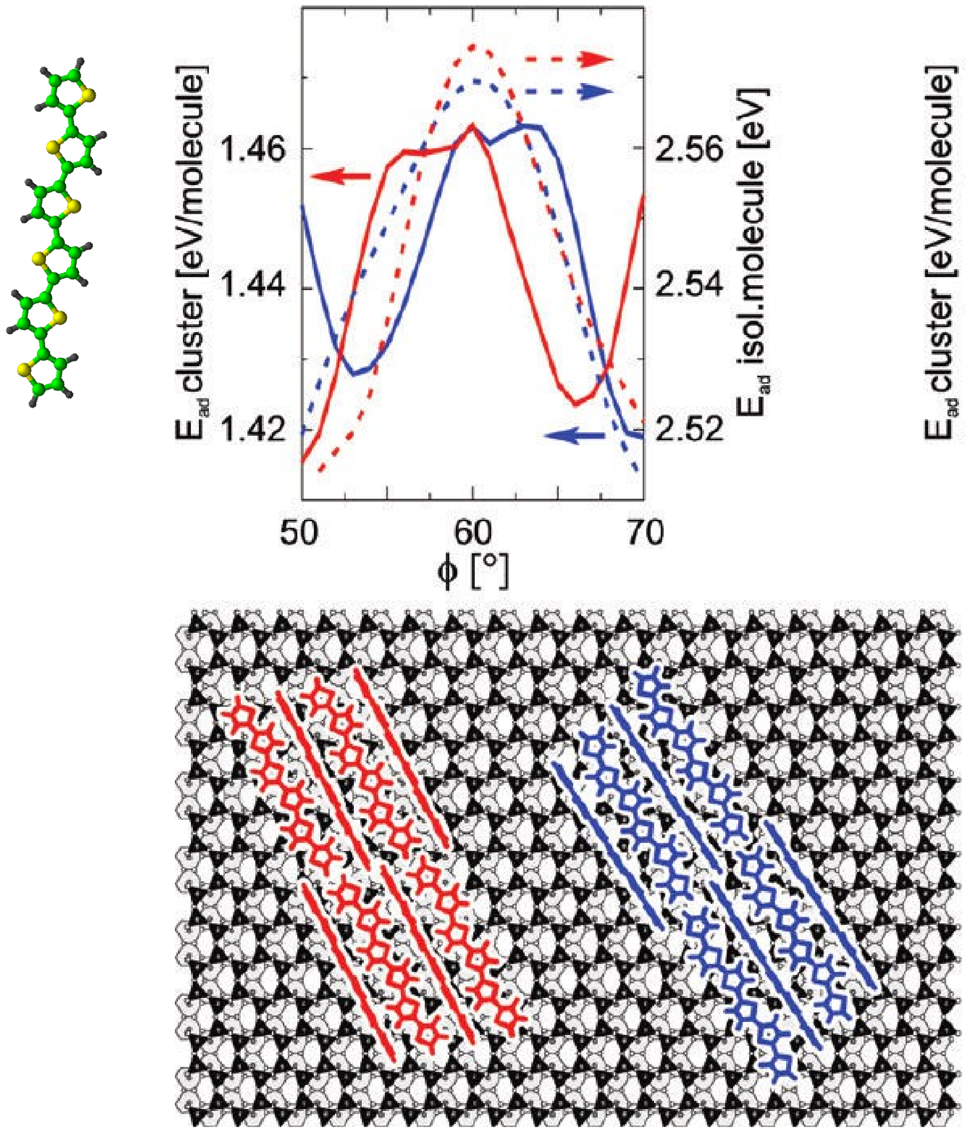
6T vs. 6P on Micas

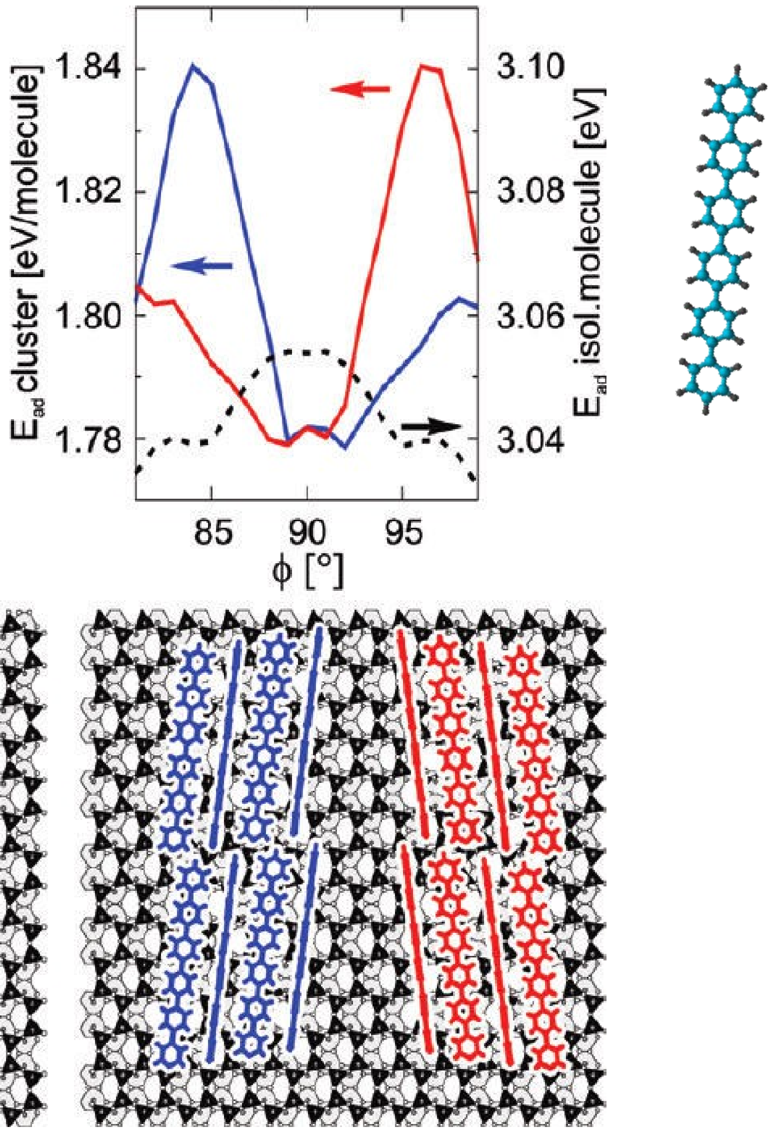


6T vs. 6P on Micas

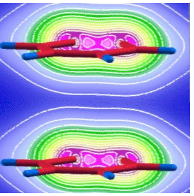


Re-Adjustment of Molecular Orientation

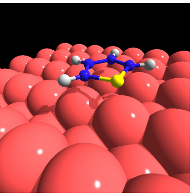




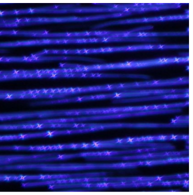
Outline



Methods and Materials



Cohesive, Surface, and Adsorption Energies



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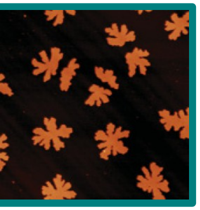
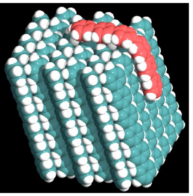


- Needle Growth and Orientations
- Critical Cluster Size

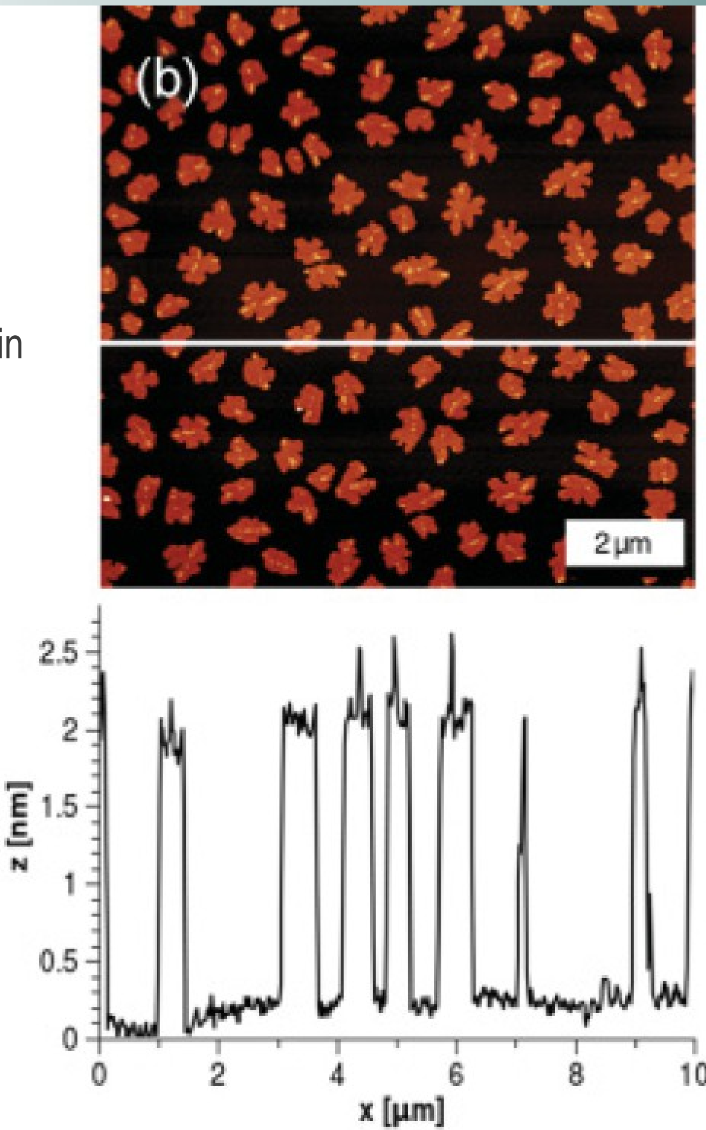


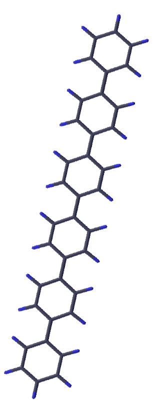
- Terraced Mounds and Step-Edge-Barrier

Island Growth on Amorphous Mica

AFM-image

10 x 10 µm^2
T = 300 K
θ = 0.32 ML
F = 0.02 ML/min





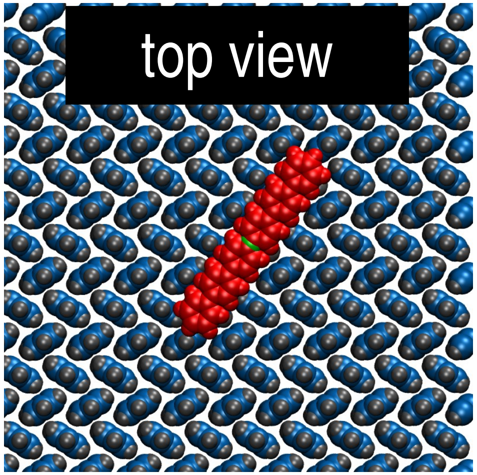
- Amorphous Mica (ion bombarded)
- Observation of islands consisting of standing p-6P
- What is the critical cluster size?
- Transistion from lying-to-standing p-6P?

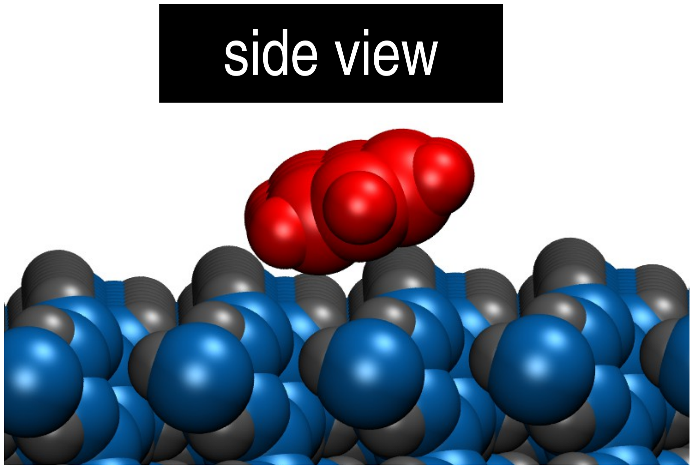
Potocar et al., *PRB* **83**, 075423 (2011).

p-6P / p-6P(001)

p-6P(001) as model substrate with weak Interactions

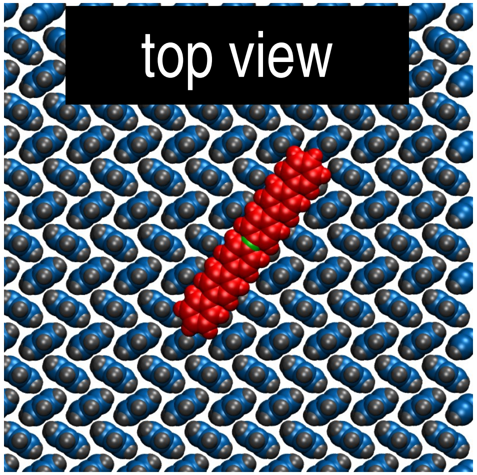
Adsorption geometry:

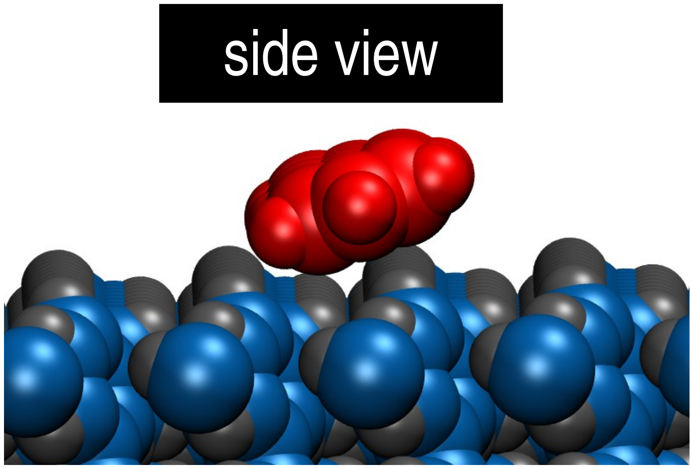




p-6P / p-6P(001)

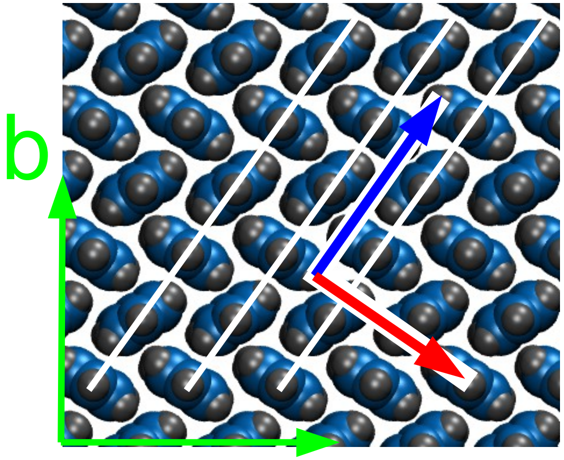
p-6P(001) as model substrate with weak Interactions

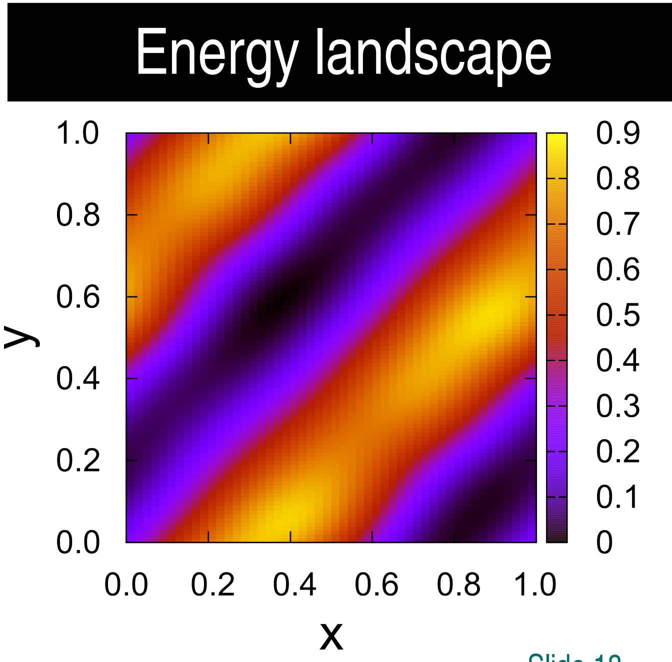




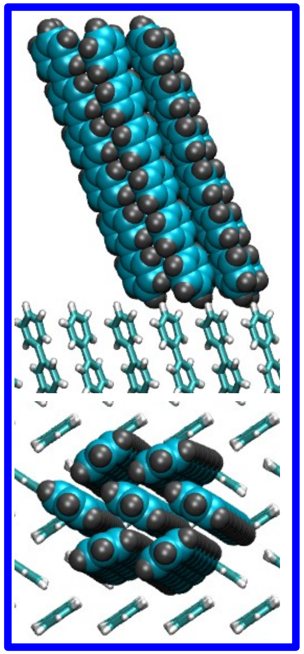
Adsorption geometry:

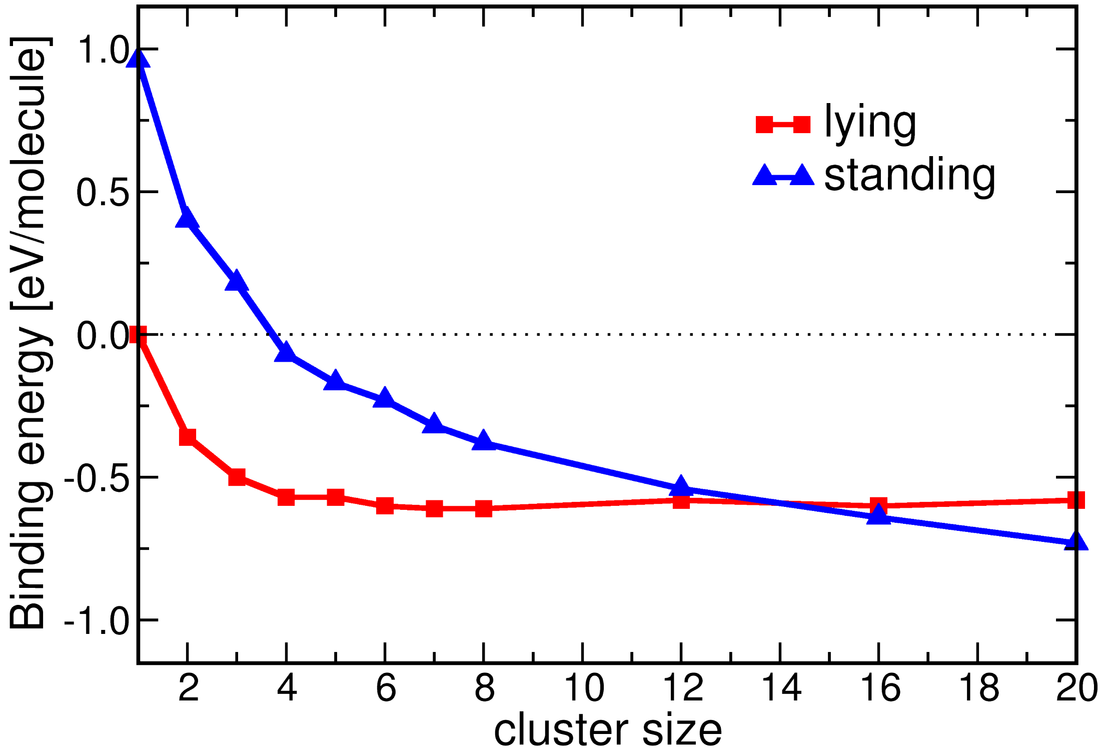
Diffusion path:

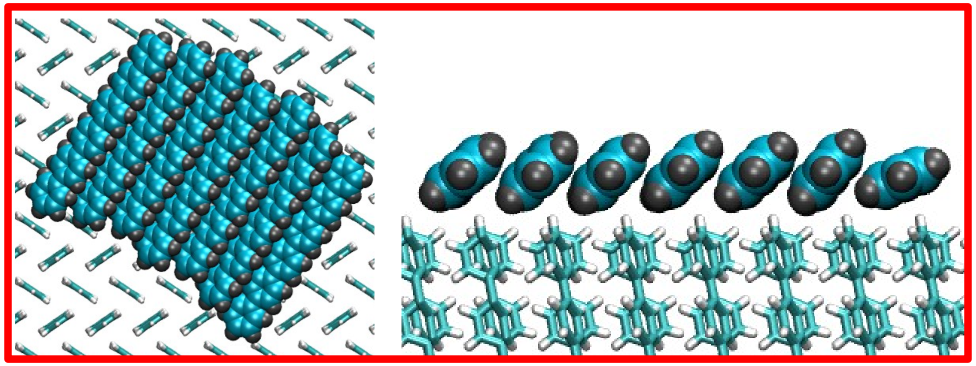




Lying bs. Standing p-6P

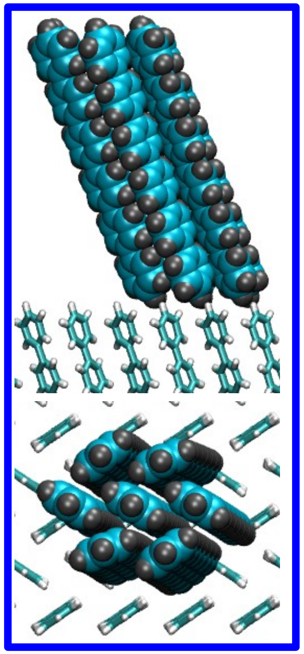


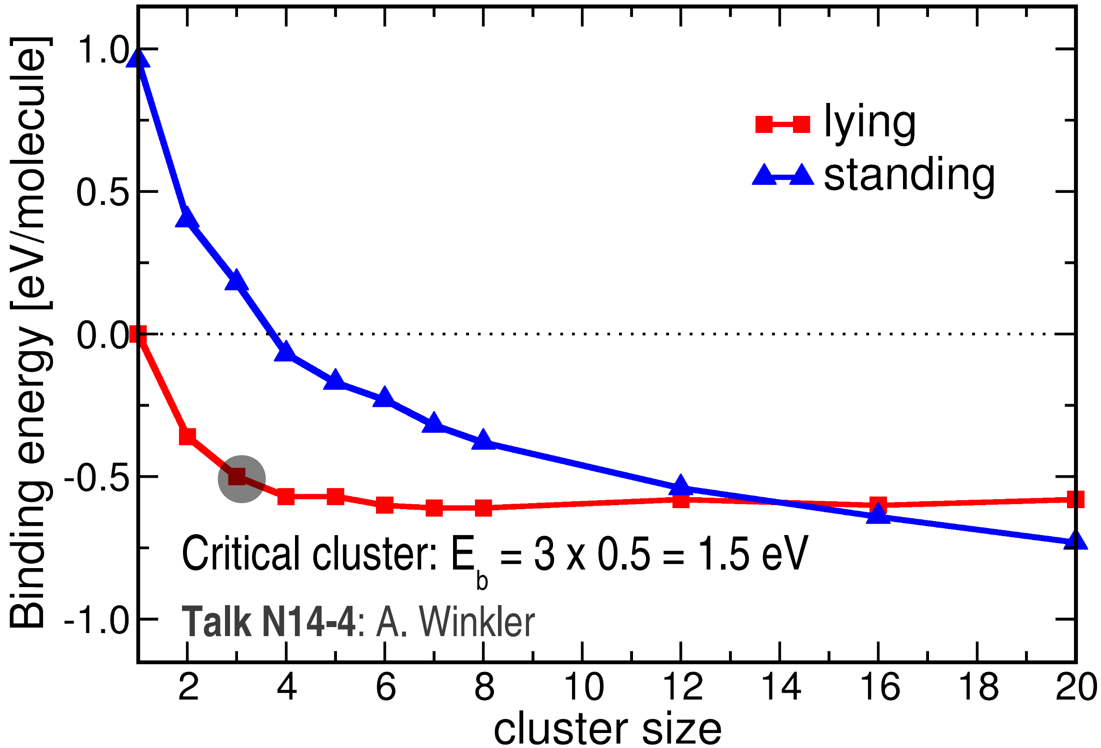


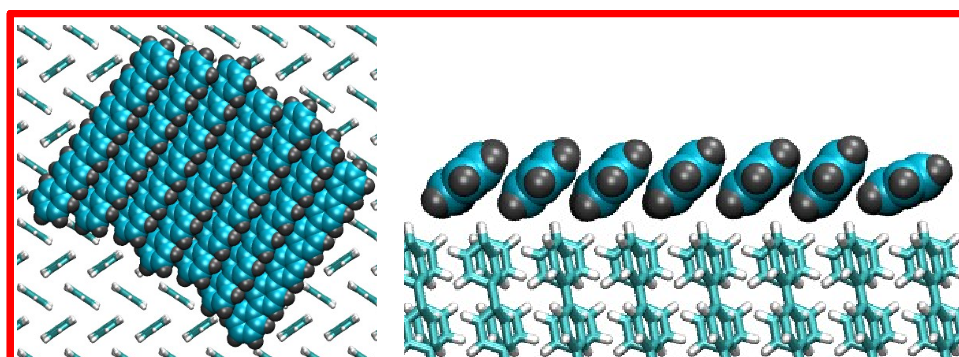


$E_{binding} = E^{n}_{cluster} / n - E_{lying\ molecule}$

Lying bs. Standing p-6P







$E_{binding} = E^{n}_{cluster} / n - E_{lying\ molecule}$

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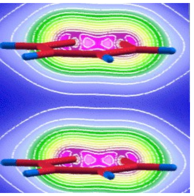
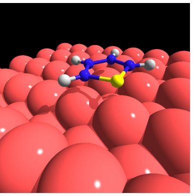
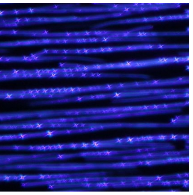


Methods and Materials

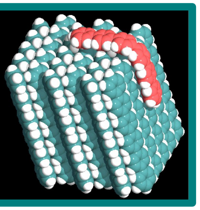


Cohesive, Surface, and Adsorption Energies



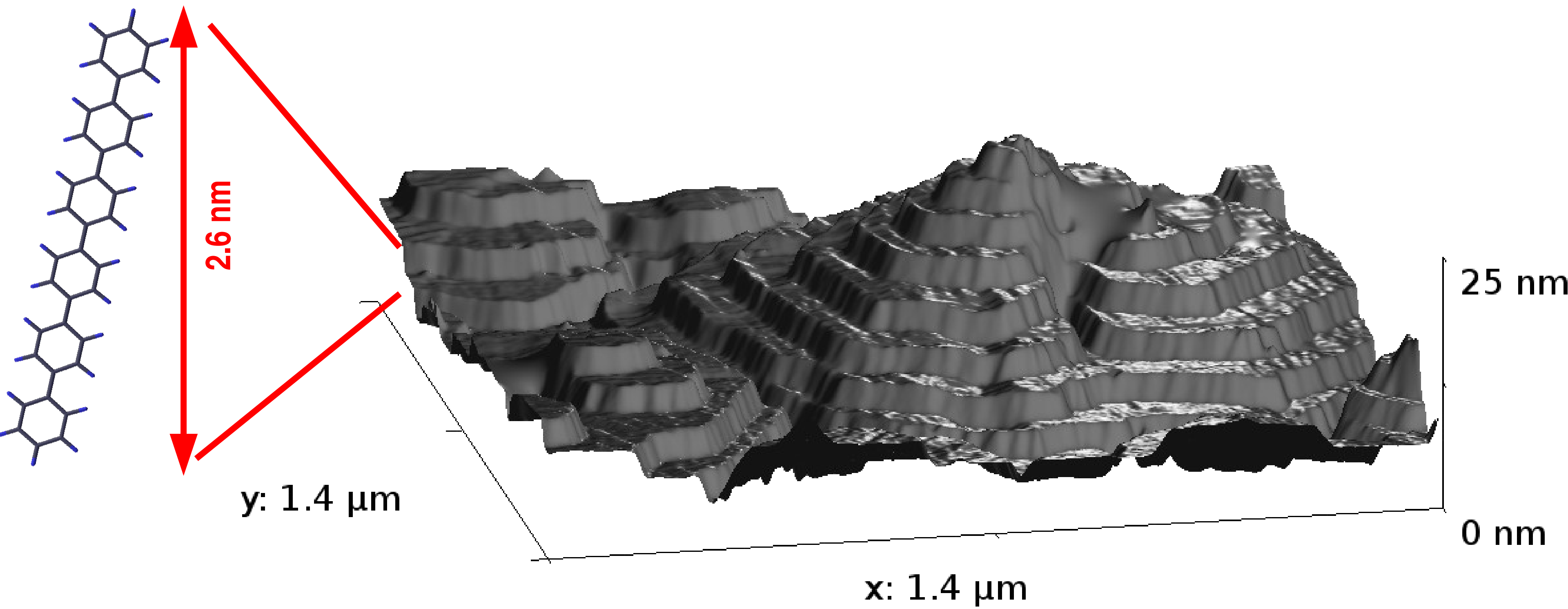
Growth of Chain-like Molecules on Mica

- Needle Growth and Orientations
- Critical Cluster Size



- Terraced Mounds and Step-Edge-Barrier

Terraced Mounds



AFM image: Sexiphenyl grown on a disordered mica surface

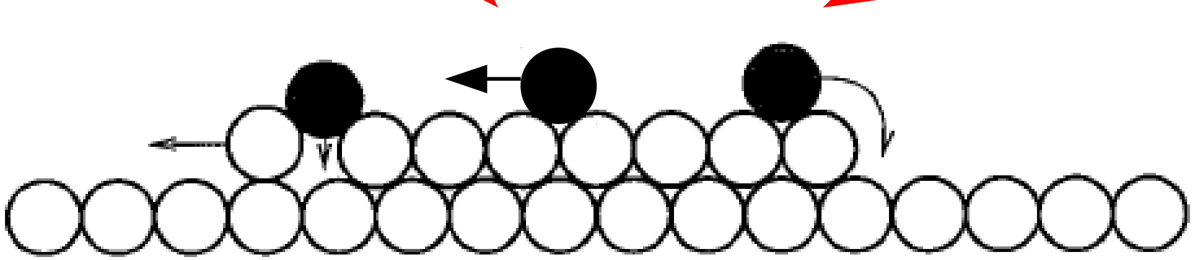
Ehrlich-Schwoebel Barrier (ESB)

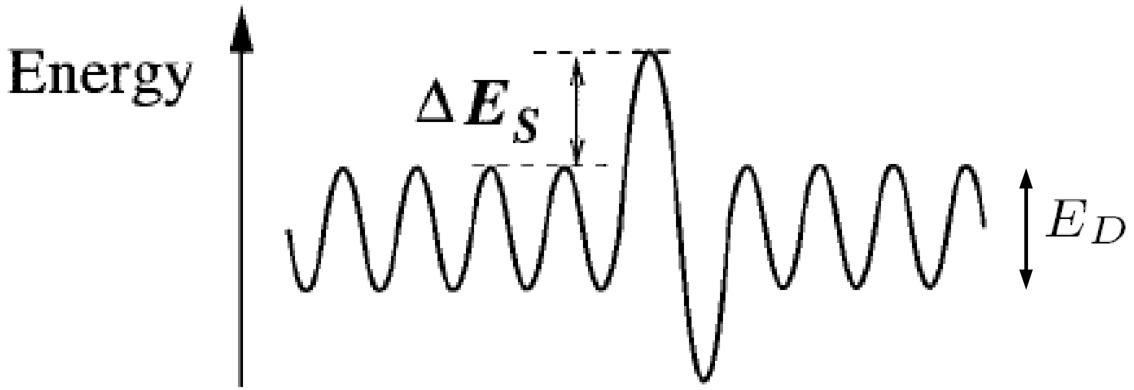
Diffusion on a terrace

$$\nu = \nu_0 e^{-E_D/k_B T}$$

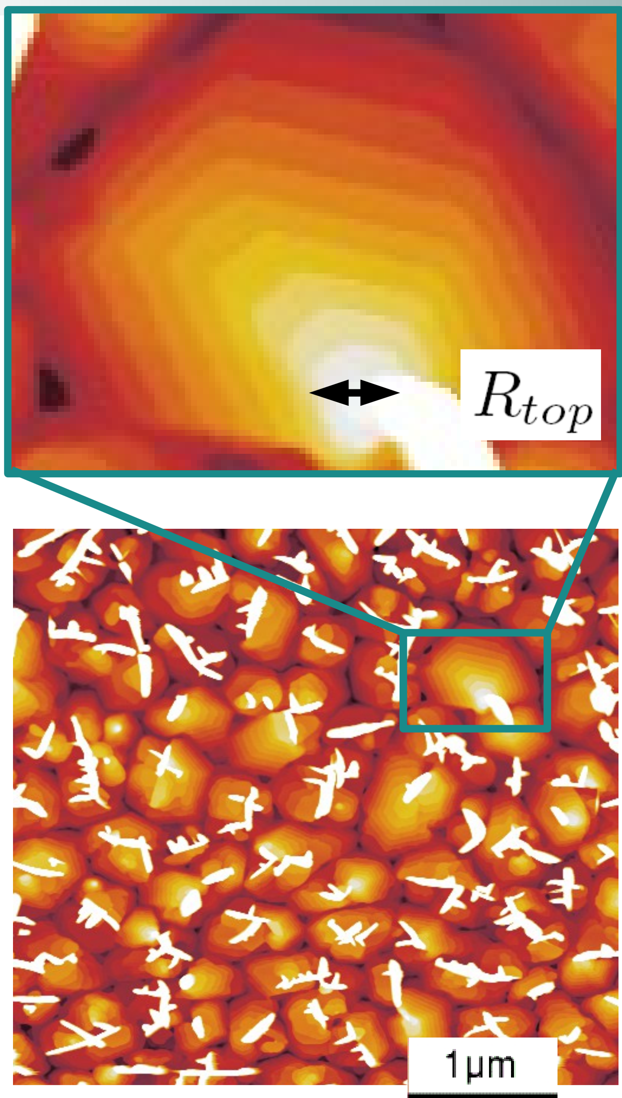
Interlayer jump rate

$$\nu' = \nu_0' e^{-E_S/k_B T}$$





Sexiphenyl on Mica



AFM image: Film thickness = 30 nm

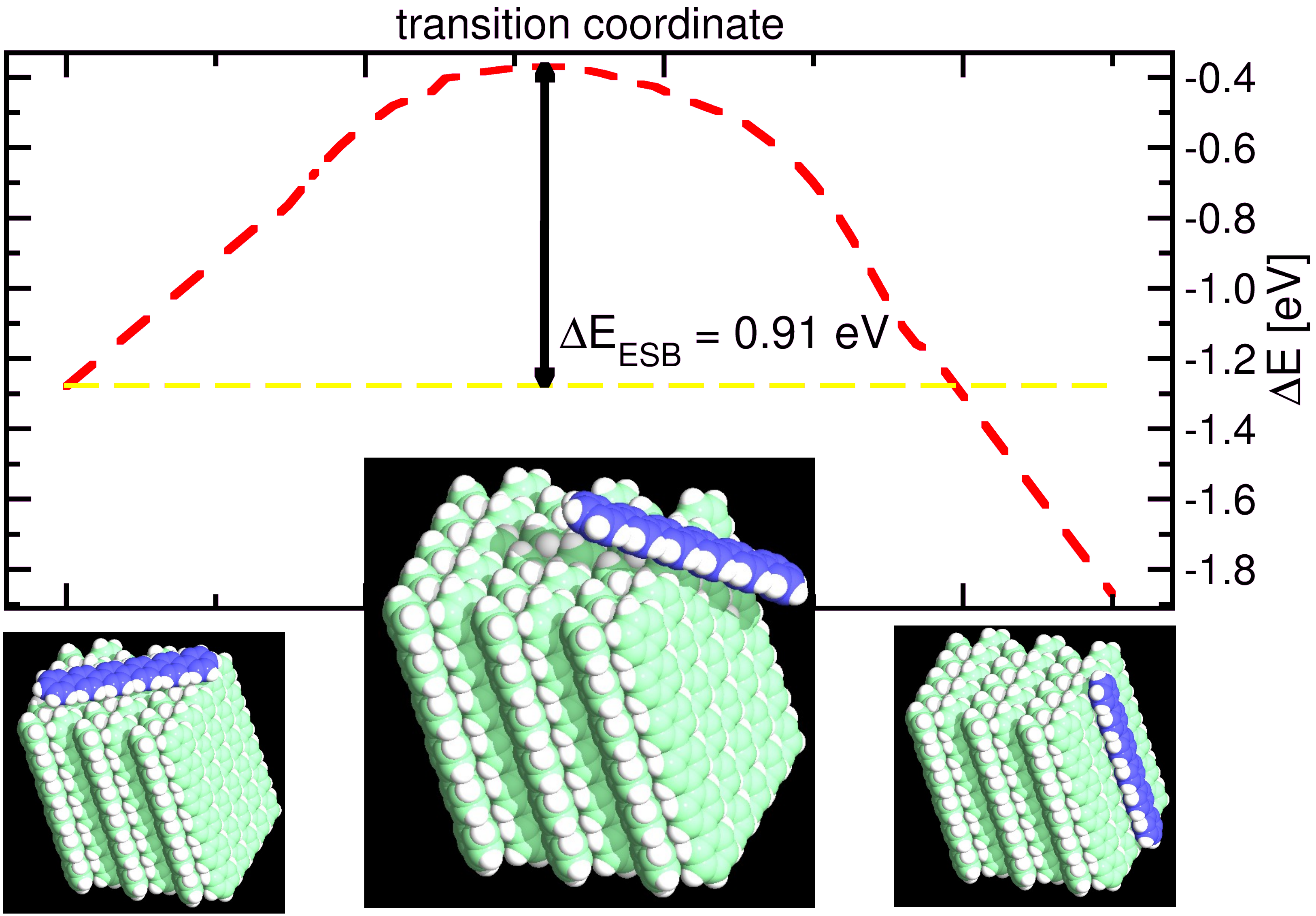
Ehrlich-Schwoebel Barrier = 0.67 eV

$$R_{top} \propto \left(\frac{\nu'}{F}\right)^{1/5} \approx 20 - 50nm$$

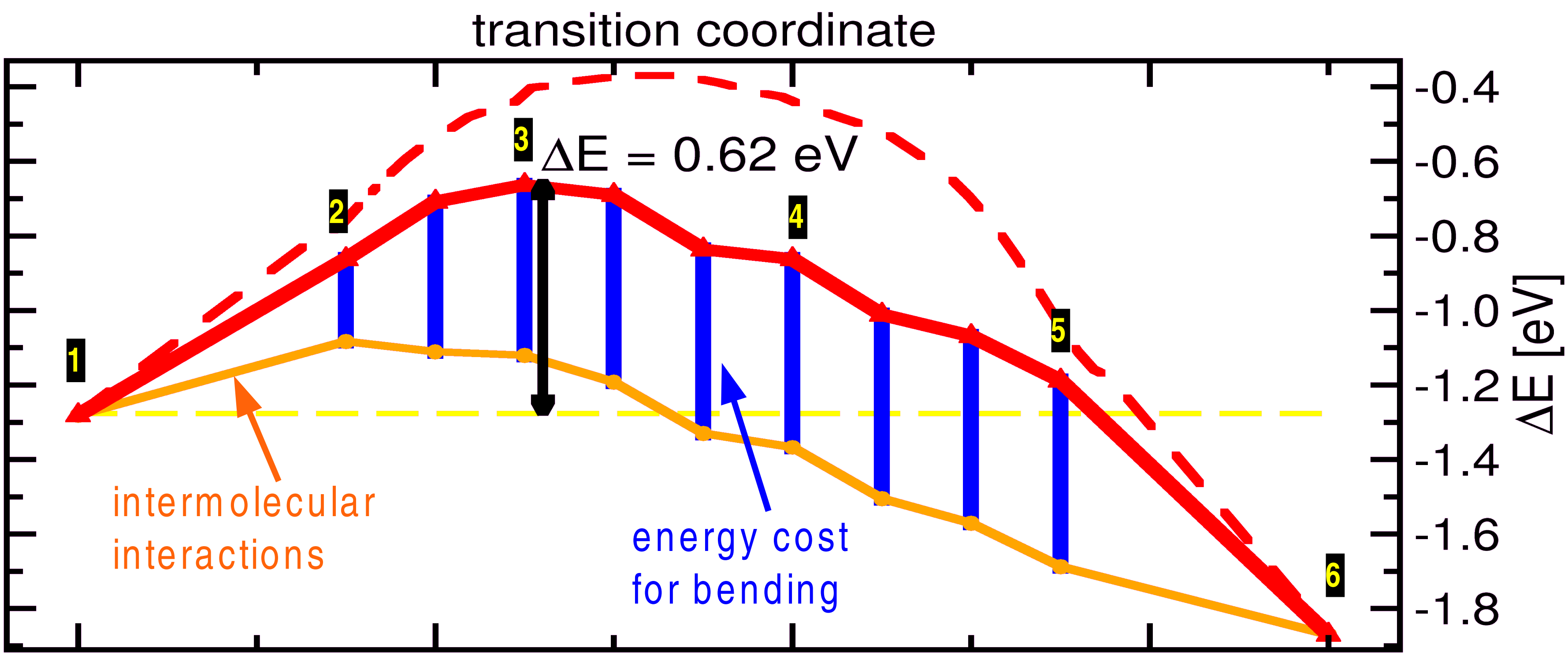
$$\omega = \frac{\tau}{(\Delta t)^2} = \frac{\text{residence time}}{(\text{deposition time})^2}$$

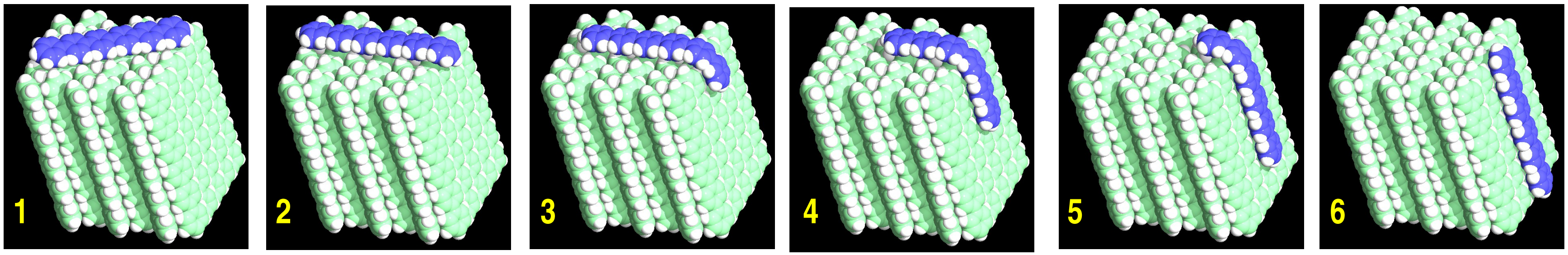
2nd layer nucleation rate

Step-Edge Barrier

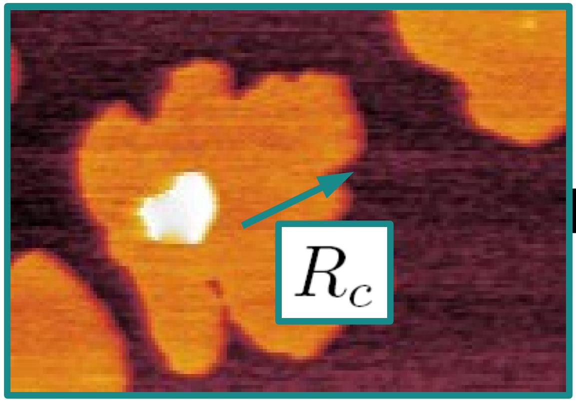


Step-Edge Barrier



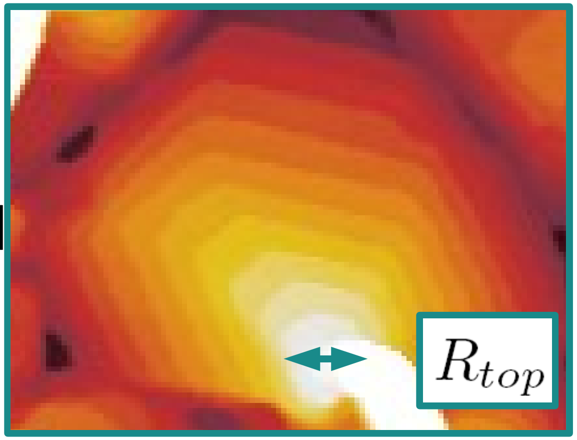


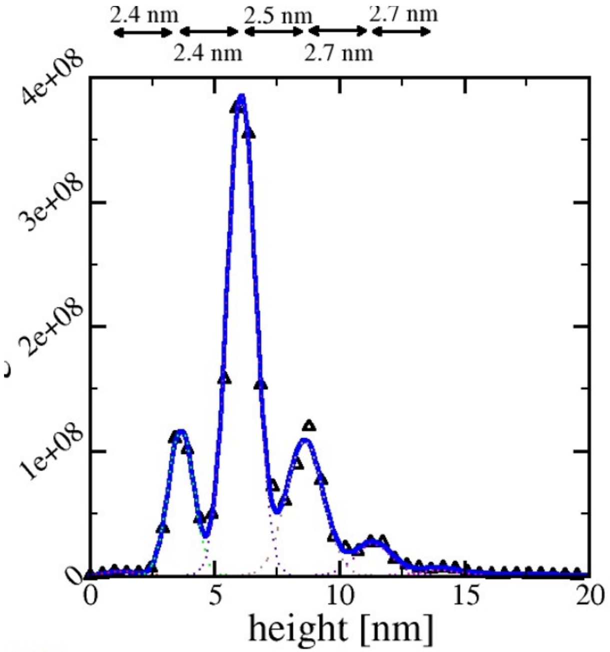
Layer-Dependent ESB

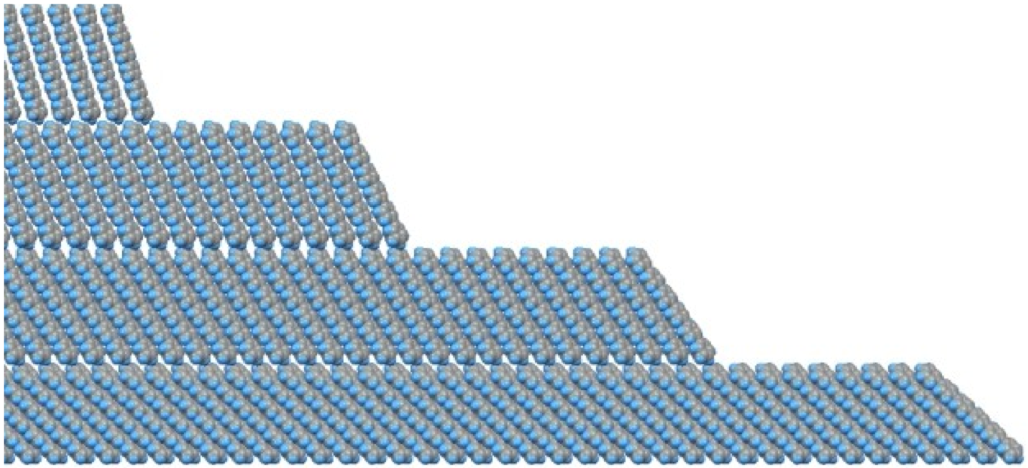


ESB

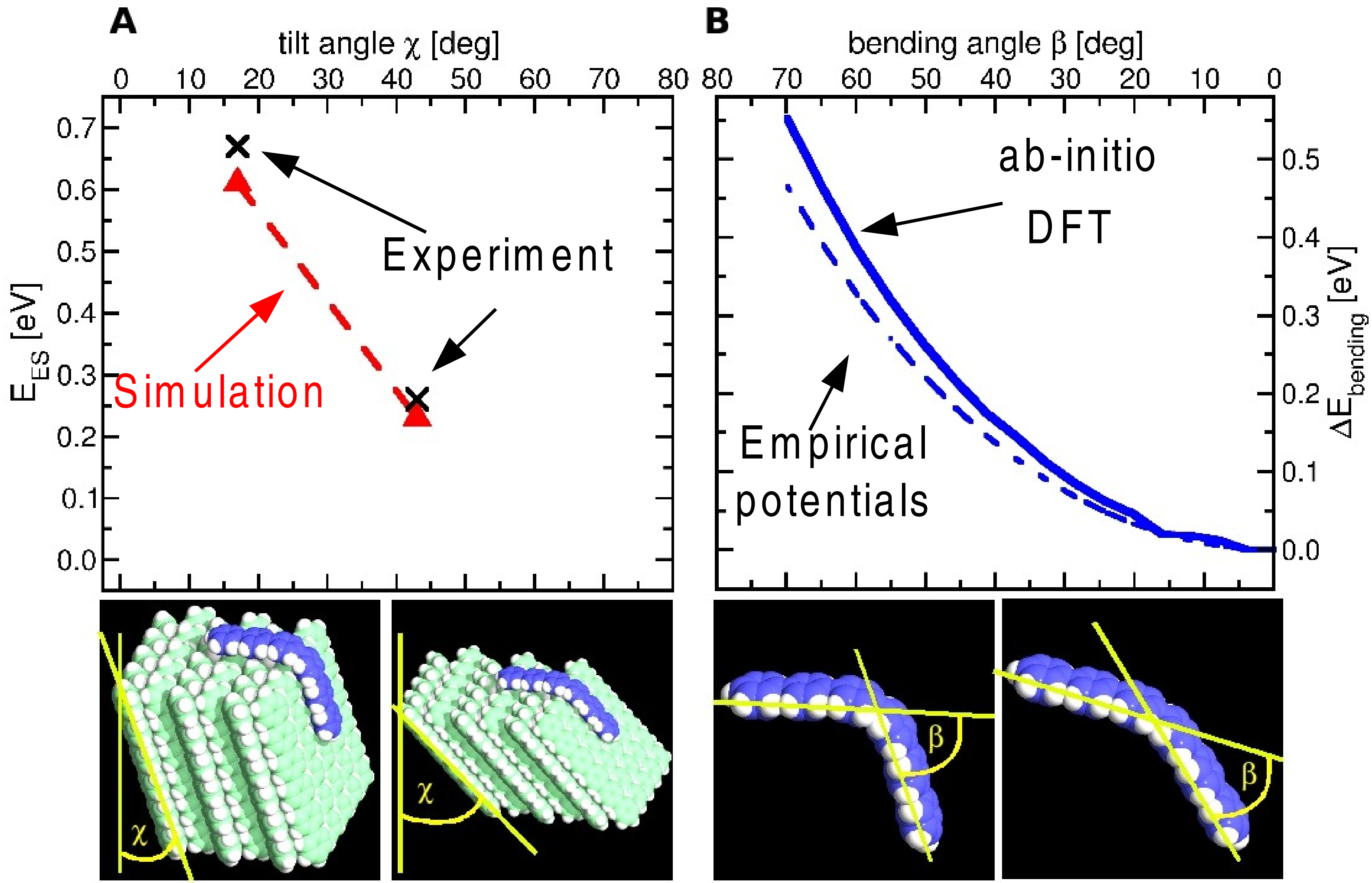
0.26 vs. 0.67





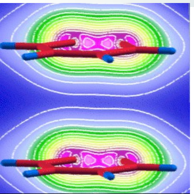


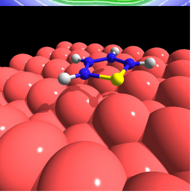
Layer-Dependent ESB



G. Hlawacek et al., *Science* ***321***, *108 (2008).*

Summary





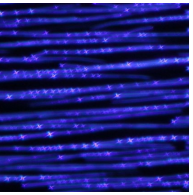
Van der Waals Interactions within DFT

Organic / organic works fine; organic / metal interactions still problematic

Nabok et al., *PRB* **77**, 245316 (2008).

Sony et al., *PRL.* **99**, 176401 (2007).

Romaner et al., *NJP* **11**, 053010 (2009).



Nano-Needle Orientation on Mica

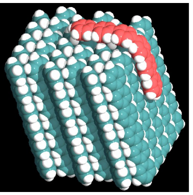
Alignment by geometry/symmetry of mica and molecule

Simbrunner et al., JACS ***133***, 3056 (2011).

Island Growth on Amorphous Mica

Critical cluster = 2-3, Transition lying → standing p-6P about 15 molecules

Potocar et al., PRB **83**, 075423 (2011).



Step-Edge Barriers

Some success in understanding certain kinetic barrieres,
but still a lot of work to do ...

G. Hlawacek et al., *Science* **321**, 108 (2008); see also: Goose et al., *PRB* **81**, 205310 (2010).

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