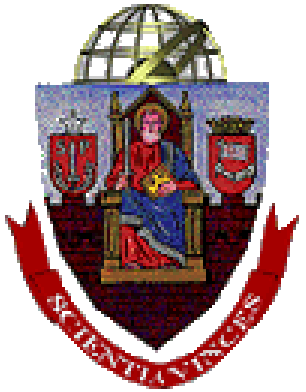
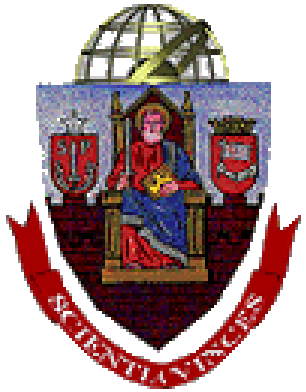
Challenges in understanding defects in organic materials:

a theorist view, focus on conjugated polymers

Marília J. Caldas
University of São Paulo



Scientia Vinces



Ronaldo Giro
Melissa F. Siqueira-Pinto

Járlesson G. Amazonas
José Maximiano F. Pinheiro Jr
Marcelo Alves-Santos
Regina Lélis-Sousa
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Arrigo Calzolari, Alice Ruini
Layla Martin-Samos,
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University of Modena & Reggio Emilia

NATIONAL CENTER OF CNR-INFM
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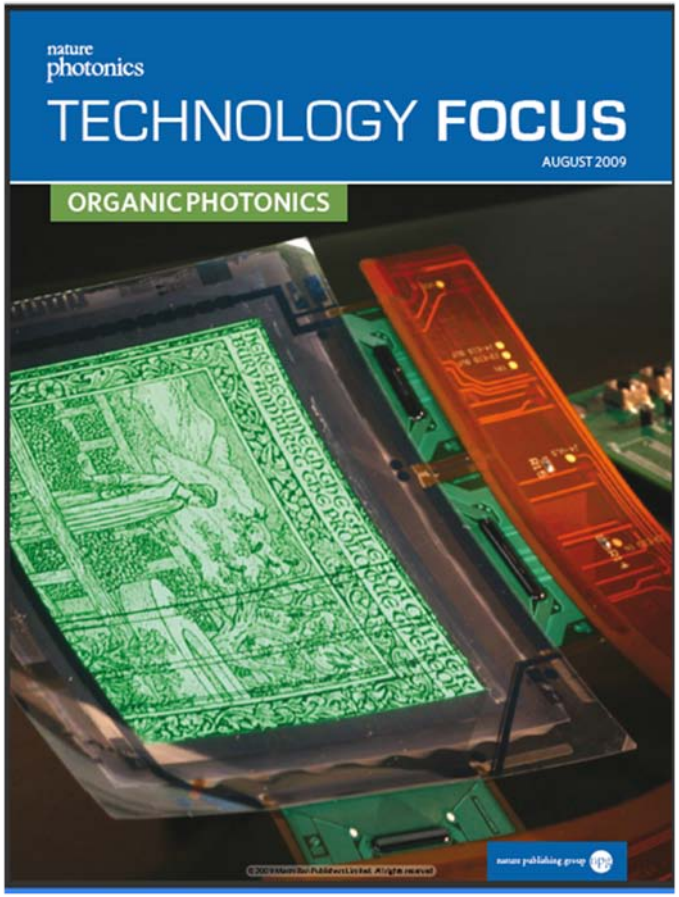
NANOSTRUCTURES AND BIOSYSTEMS AT SURFACES

UNIVERSITÀ DEGLI STUDI
DI MODENA E REGGIO EMILIA

Interest in Organic Conjugated Polymers

Optolelectronic devices such as light-emitting devices (OLED)
or organic solar cells (OPV):



one entire issue this August

lightweight (carbon-based),
cheap (wet chemistry, self-assembling) ,
flexible (plastic)

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Optolelectronic devices such as light-emitting devices (OLED)
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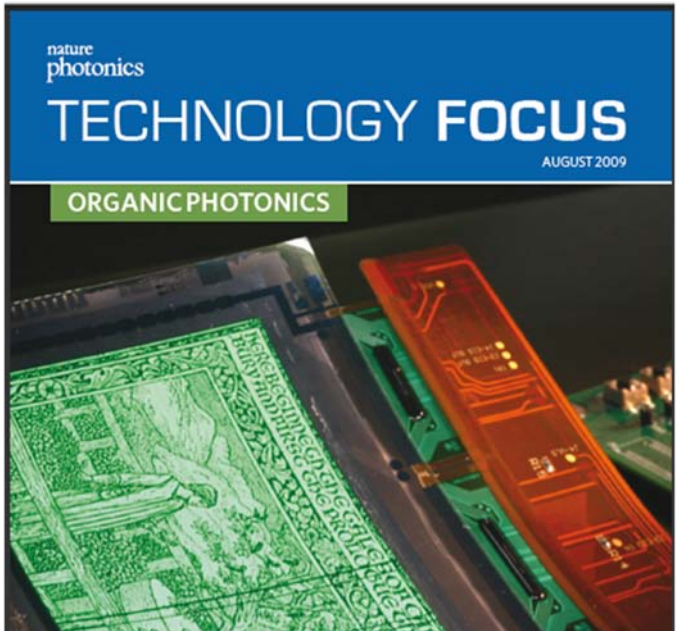


lightweight (carbon-based),
cheap (wet chemistry, self-assembling) ,
flexible (plastic)

Need to understand both
optical properties: light-matter interaction
carrier transport properties: mobilities, phonons, etc..

(sigh) no free lunch: cheap & flexible… bound to be dirty and difficult to characterize, difficult to model, difficult to understand, so on & so forth

Outline

Brief introduction of pertinent polymer properties

Theory focus on:

ground state only, DFT-based only
general morphology & electronic properties

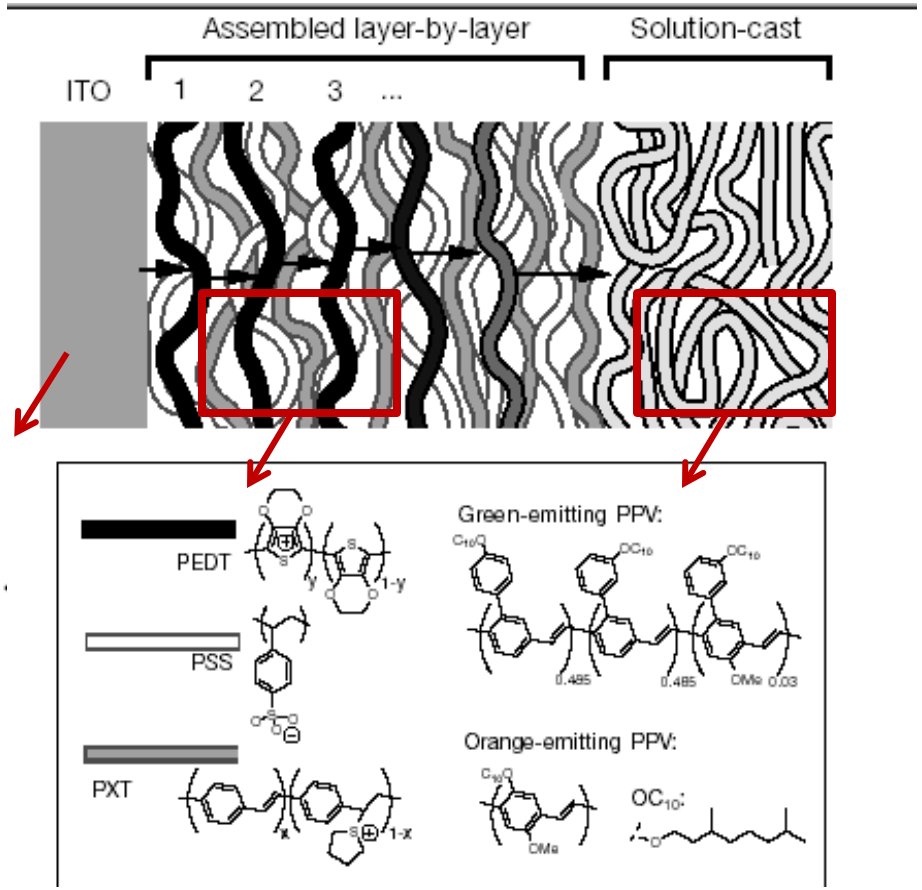
morphology of crystalline polymers
studies of disordered oligomer films
our work on defects in **PPV** crystals
poly-para-phenylene vinylene

Conclusions & Perspectives

Organic Devices OLEDs, OFETs, OPVs:

Very nice and revealing figure from Richard Friend's group:

whole soup of different disordered materials
(figure still lacks the metal electrodes)



Molecular-scale interface engineering for polymer light-emitting diodes

Peter K. H. Ho*†, Ji-Seon Kim*, Jeremy H. Burroughes†, Heinrich Becker‡, Sam F. Y. Li§, Thomas M. Brown*, Franco Cacialli* & Richard H. Friend*†

* Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Ho et al, ***Nature* 404**, 481 (2000)

Organic Devices OLEDs, OFETs, OPVs: what do we need to know

- Transport (electrons & holes)

  along the chain (intra) or inter-chain?

- Optical properties

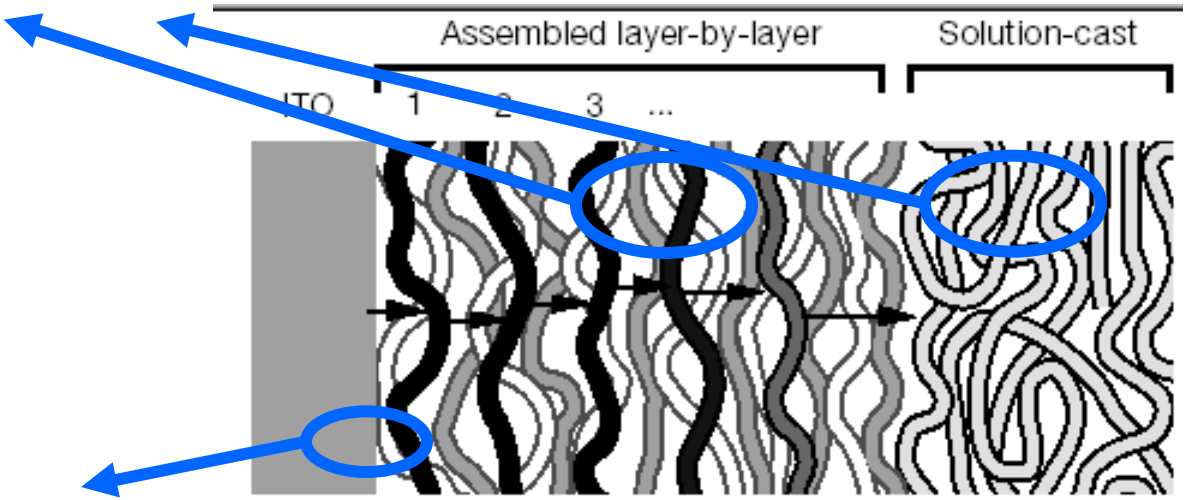
  excitons? excimers? SxT?

  - Interface:

    abrupt or rough ?

    injection possible ?

- Morphology virtually unkown
- Effects of morphology?



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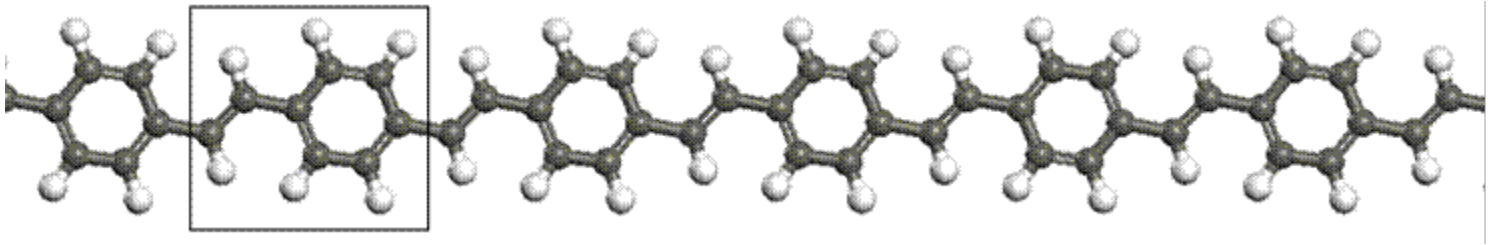
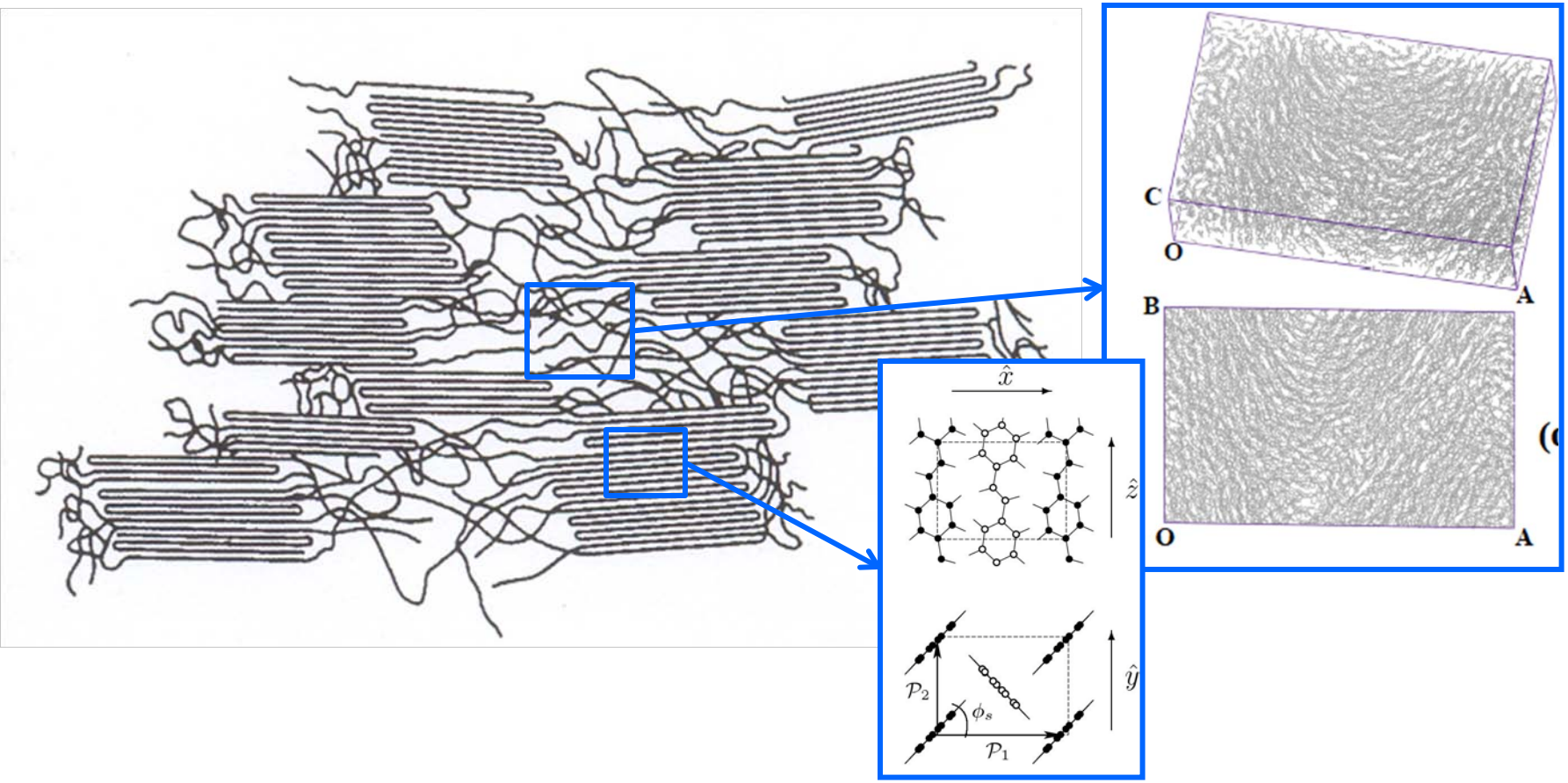
Organic Conjugated Polymers: what we do know

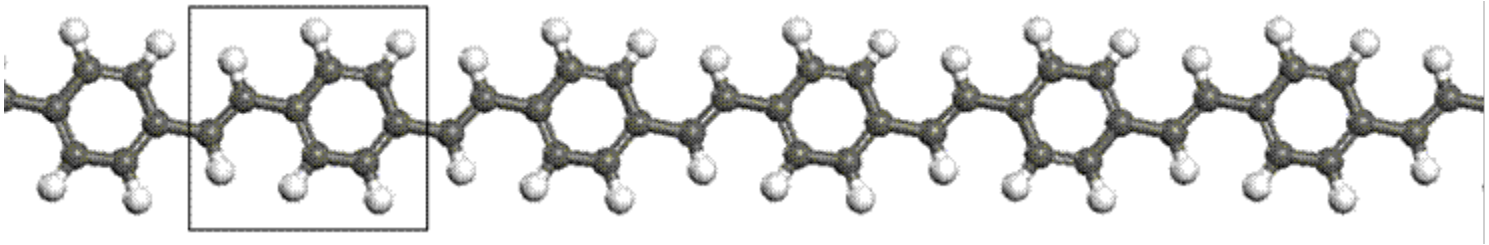


PPV

disorder in general, but different ways: semi-crystalline grains in amorphous medium



Organic Conjugated Polymers: what we do know



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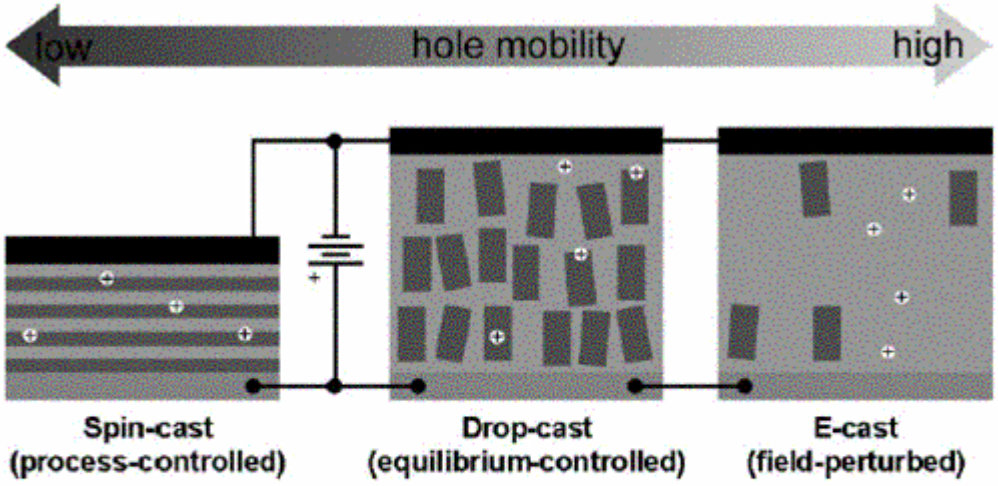


Figure 10. Charge-transport paths in ITO/MEH-PPV/Al devices. Ordered domains (dark grey) of high electron density are schematically shown as distributed within the lighter matrix of low electron density. Spatial distribution of ordered and disordered domains determines routes of holes (white crosses) traveling through the film.

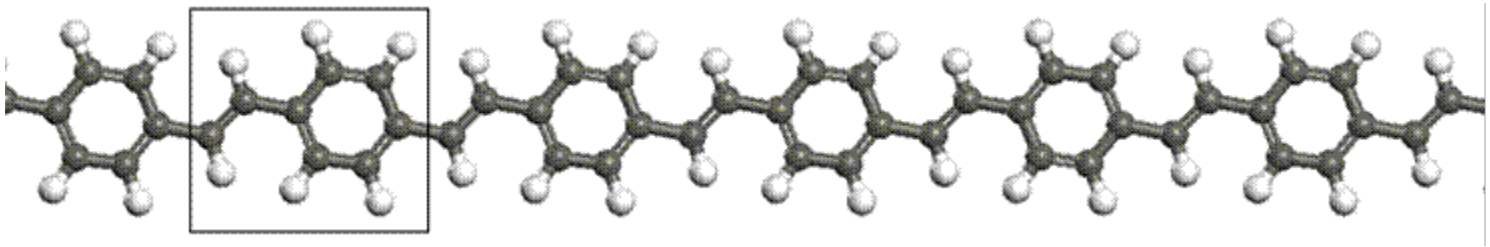
Huang et al, ***Adv. Funct. Mater.*** **17**, 2902 (2007)

ITO/MEH-PPV/Al

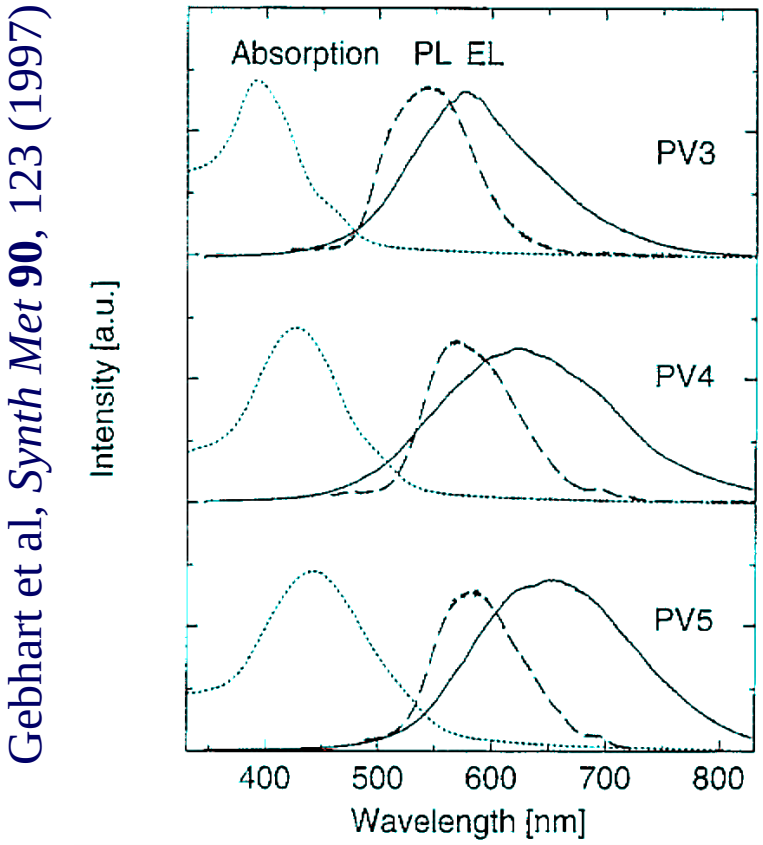
effect of disorder on transport is
not obvious

hint from optical properties:

Organic Conjugated Polymers: what we do know



disorder in general, but different ways: semi-crystalline grains in amorphous medium



Gebhart et al, *Synth Met* **90**, 123 (1997)

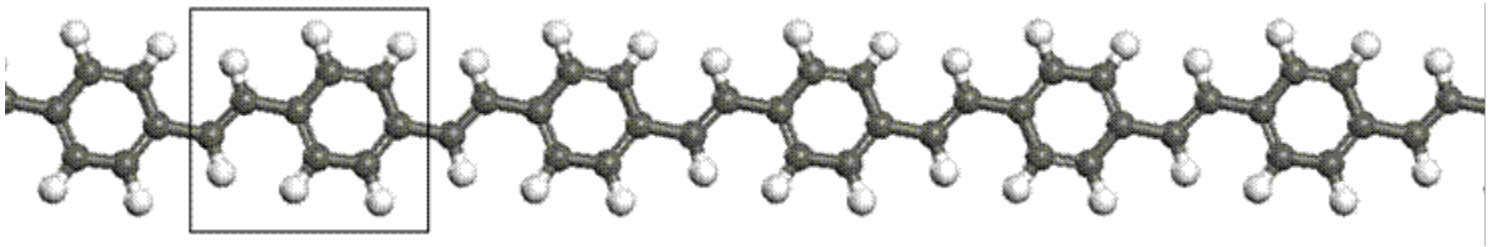
effect of disorder on transport is
not obvious

hint from optical properties:

first guess looking at oligomers:

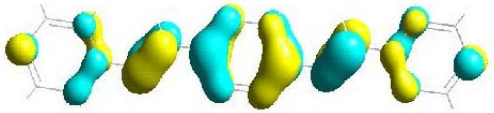
apart from broadening,
distinct shift with length

Organic Conjugated Polymers: what we do know

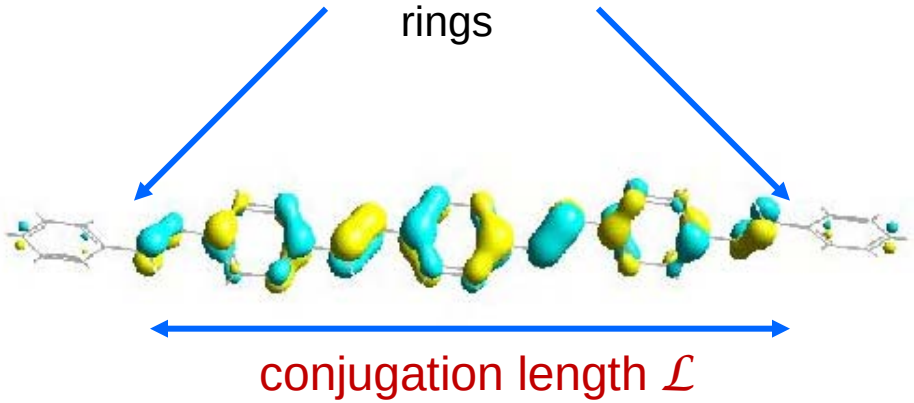


disorder in general, but different ways: semi-crystalline grains in amorphous medium

redshift with oligomer length caused by increase in delocalization of π-electrons …



...that can be blocked in a polymer by torsion between rings



effect of disorder on transport is
not obvious

Mostly wishful-thinking models:

- migration faster on longer $\mathcal{L}$
- grain-interfaces the problem
- DEFECTS: “kinks” , impurities (anything that goes wrong usually attributed to impurities)

Organic Conjugated Polymers: what we do know

Unhomogeneous plus impurities (wet chemistry...) → carrier transport difficult problem

Hopping across grains and in-grain transport : which is dominated by impurities?

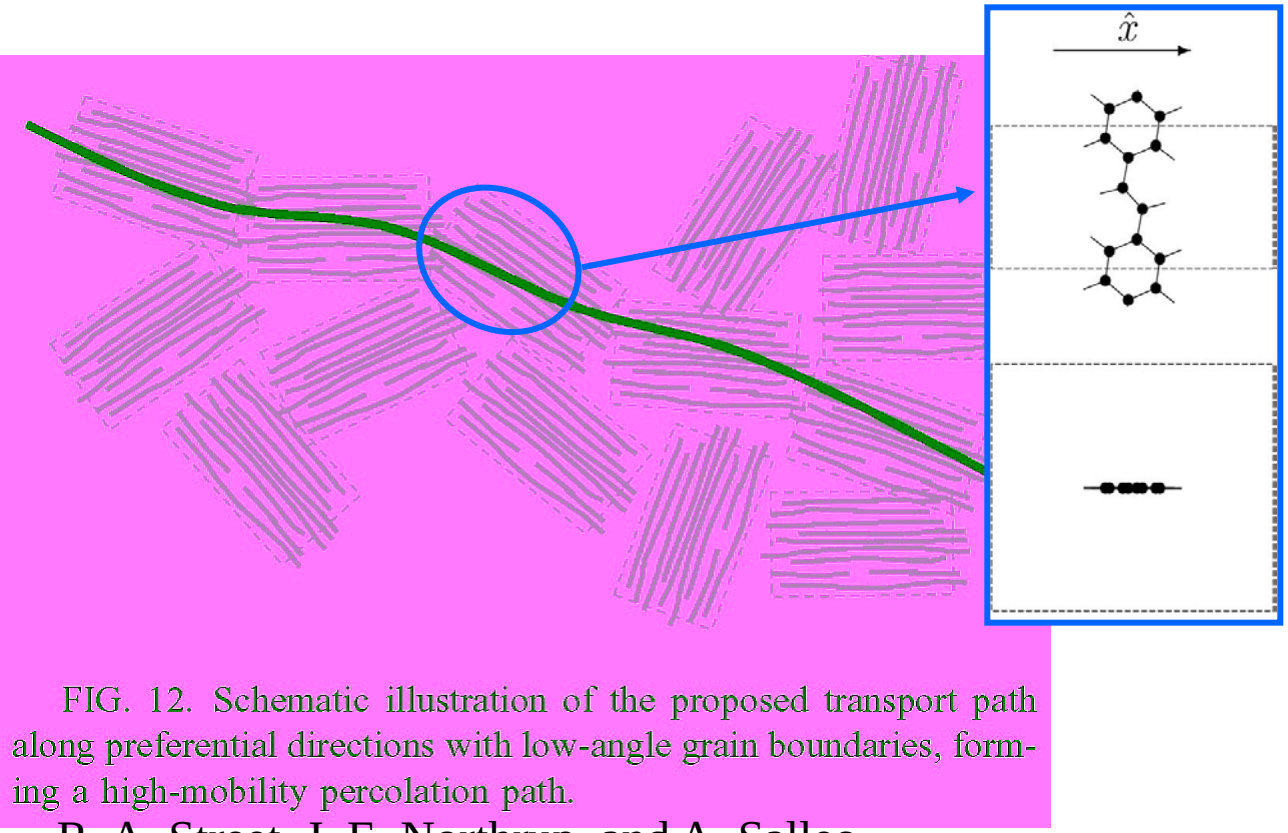


FIG. 12. Schematic illustration of the proposed transport path along preferential directions with low-angle grain boundaries, forming a high-mobility percolation path.

R. A. Street, J. E. Northrup, and A. Salleo,
PRB **71**, 165202 (2005)

is transport completely dominated by 1D effects?

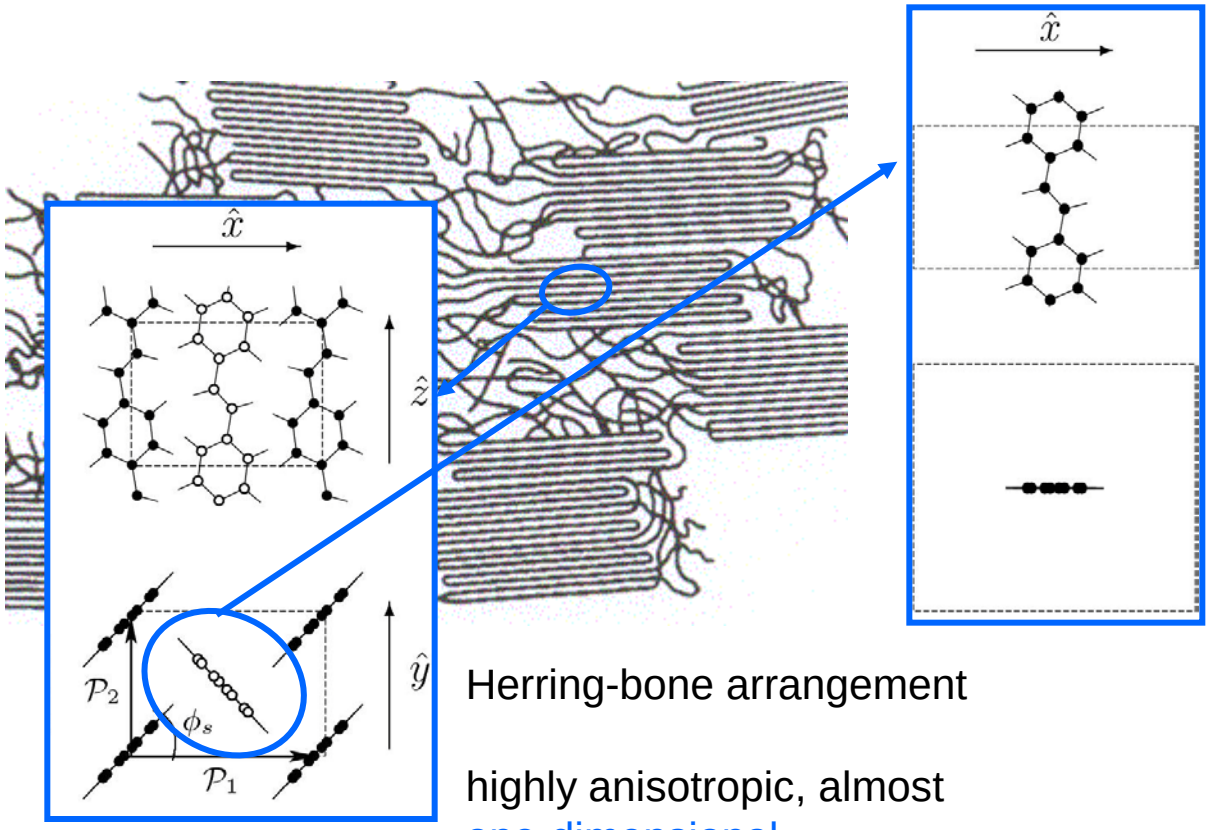
How to model transport?

Organic Conjugated Polymers: what we do know

Unhomogeneous plus impurities (wet chemistry...) → carrier transport difficult problem

Hopping across grains and in-grain transport : which is dominated by impurities?

focus here: unsubstituted PPV → grain crystallites



Herring-bone arrangement

highly anisotropic, almost one-dimensional

in-grain: can transport be completely dominated by 1D effects?

Organic Conjugated Polymers: what we do not know

can theory help for such a complicated problem?

Multi-scale

- Morphology, thousands of atoms
  - Classical Molecular Dynamics
- Electronic & Optical, up to few hundrends
  - Quantum, fixed geometries either from experiment or from CMD

Multi-formalism

- Classical MD (several different codes and "force fields" available, parametrization)
- Semi-empirical Tight-binding MD (also different codes, home made)
- Density Functional Theory & beyond DFT (*very* expensive G^0W^0 home made)
- Hartree-Fock & beyond HF (small, finite systems)

Multi-code

- DFT: Plane-waves + Diagonalization (ABINIT, espresso)
  - Local basis + Diagonalization (Siesta)
  - Mixed basis + Car-Parrinello (PAW)
- HF: Local basis (Gaussian)

Crystalline polymers: recent work

simplest that can be: *polyethylene* (non-conjugated, dense, reasonably well-characterized)

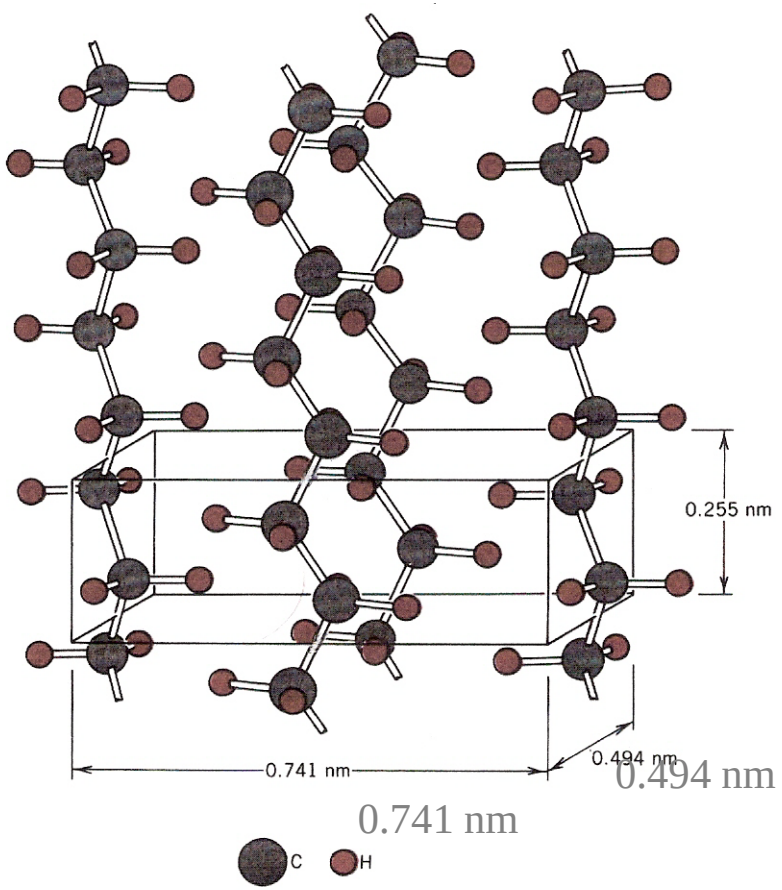


Figure 15.10 Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

Non-bonded interactions critical for morphology:

Quantum treatments must incorporate XC in a non-local fairly accurate functional form…

W.D.Calllister Jr, "Materials science and engineering – An introduction" John Willey & sons, NY 1994

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vdW-DF Dion et al, PRL 92, 246401 (2004)

DF: revPBE, 400 eV cutoff energy,
plane-waves basis set, Ultrasoft pseudopotentials,
4x4x10 Monkhorst-Pack
12 atoms, 20 valence electrons

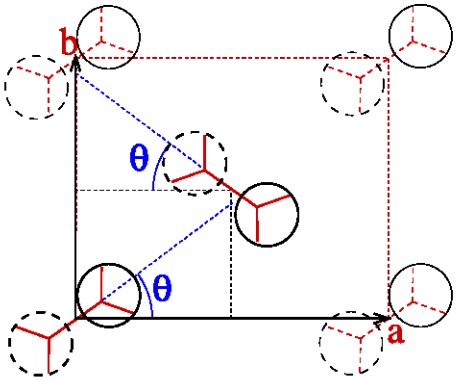

FIG. 1. (Color online) Schematics of the PE crystal structure in its base-centered orthorhombic unit cell. Lattice parameters a and b are indicated, while the parameter c, which is the polymer repetition length, is perpendicular to the plane shown. Solid (broken) circles represent CH_2 units in the plane (a distance $c/2$ out of the plane). The angular orientation of the polymers is determined by the setting angle θ, defined as the angle between the a axis ($a>b$) and the intrapolymer carbon plane.

Kleis et al PRB **76**, 100201R (2007)
Chalmers & Rutgers (D. Langreth)

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4x4x10 Monkhorst-Pack
12 atoms, 20 valence electrons

Very good agreement (~8%)
both LDA & GGA fail miserably

Kleis et al PRB **76**, 100201R (2007)
Chalmers & Rutgers (D. Langreth)

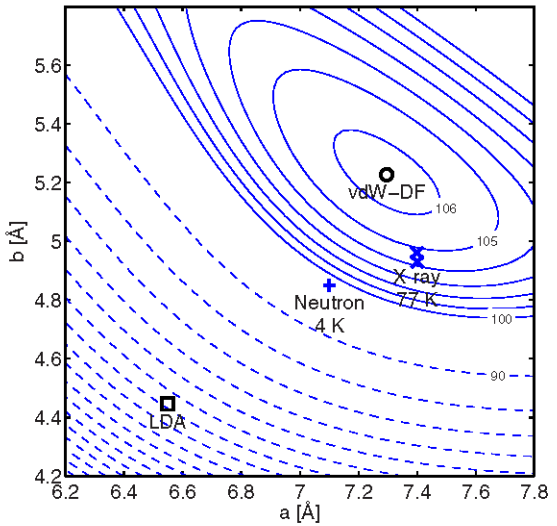

FIG. 3. (Color online) The cohesive-energy contour map calculated with vdW-DF, expressed as energy per CH_2 group as a function of the lattice parameters a and b. The plot (but not the calculation) is restricted to show the energetics at setting angle θ=44°, the optimal angle found with vdW-DF (Table I). The full (dashed) contour curves are separated by 1 (10) meV/CH_2, with values given in meV/CH_2. The equilibrium parameters (summarized in Table I) obtained from experiments and from a LDA-DFT study are shown for comparison.

Crystalline oligomers: recent work

Oligomer crystals: reasonably well-characterized

Acenes, phenylenes, thiophenes

vdW-DF Dion et al

DF: GGA, 550 eV cutoff energy,
plane-wave basis set,
ultrasoft pseudopotentials,
PWSCF
62 atoms, 170 valence electrons

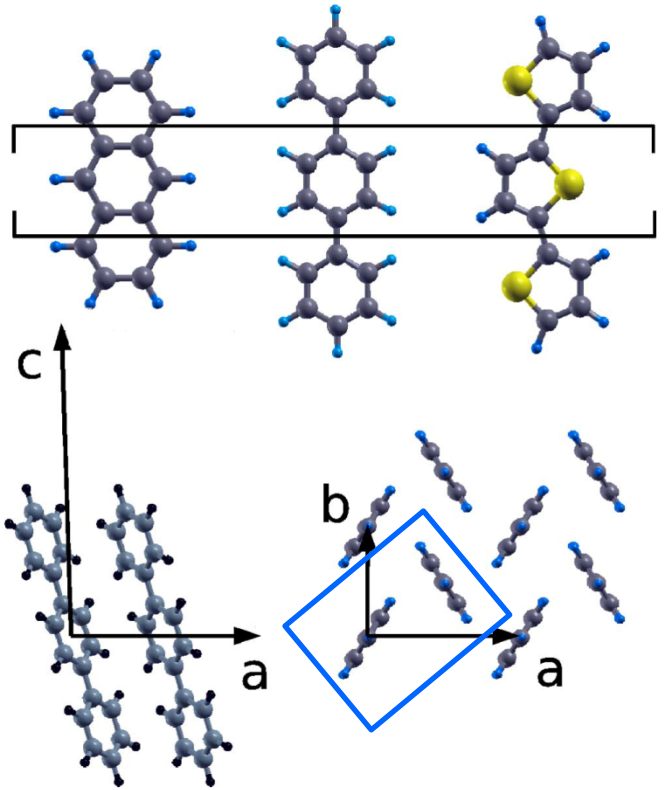

FIG. 1. (Color online) Molecular (top) and crystal structures (bottom) of the materials under investigation: The brackets indicate the building block of the oligoacene (left), oligophenylene (middle), and oligothiophene series (right). The lower panels show the orientation of the respective molecules within the common herringbone structure.

Nabok et al PRB **77**, 245316 (2008)
Leoben (C. Ambrosch-Draxl)

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vdW-DF Dion et al

DF: GGA, 550 eV cutoff energy,
plane-wave basis set,
ultrasoft pseudopotentials,
PWSCF
62 atoms, 170 valence electrons maximum

cohesive energies in very good agreement with experiment (where available)

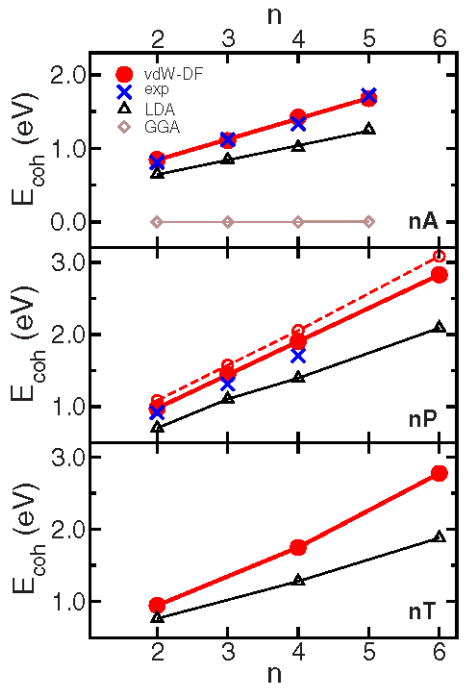


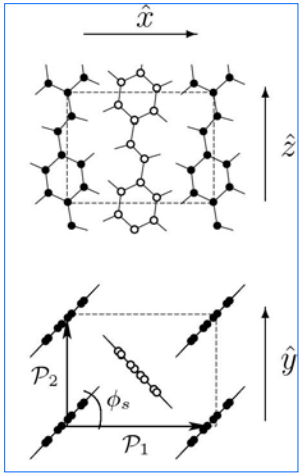
FIG. 2. (Color online) vdW-DF cohesive energies of the oligoacenes *n*A (top), the oligophenylenes *n*P (middle), and the oligothiophenes *n*T (bottom) in comparison with available experimental data (Ref. 19) The lines are guides to the eye. For the *n*P oligomers, the open circles represent the values obtained when the isolated molecules are considered to be planar. In addition, LDA and GGA values are given for comparison.

Nabok et al PRB **77**, 245316 (2008)
Leoben (C. Ambrosch-Draxl)

Crystalline PPV: “ancient” work

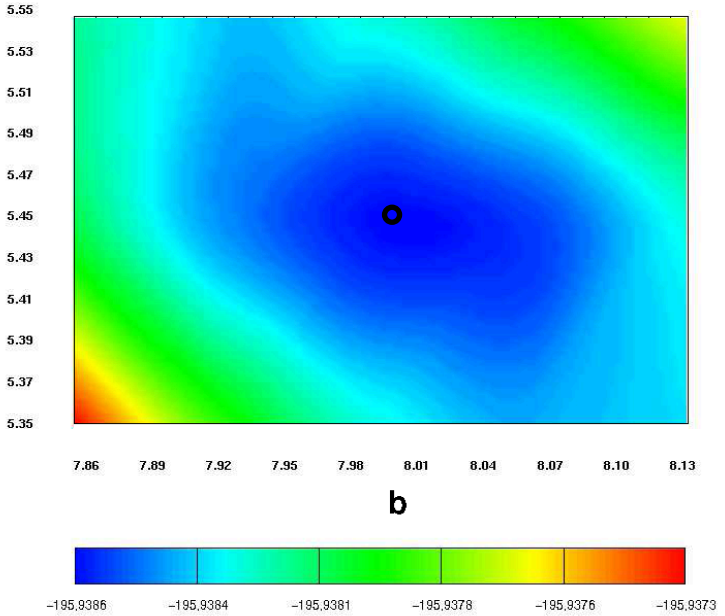
our focus today, conjugated, reasonably well-characterized

Pristine (non-derivatized) herring-bone packing



DF only: LDA, 600 eV cutoff energy,
plane-wave basis set,
norm-conserving pseudopotentials,
PWSCF
28 atoms, 76 valence electrons *unit cell*

c, setting angle, bxc angles fixed
(a,b) lattice constants, angstroms (5.45; 8.00)



experimental values (6.05; 8.07)
LDA much too small (GGA does not bind…)
need for vdW-DF but…

A. Ferretti, Laurea Thesis, 2001
UNIMORE

… disordered or defect-containing films???

Amorphous-PPV: recent work

disordered *polymer films* difficult to simulate: *oligomers*

Amorphous film:

744 atoms!

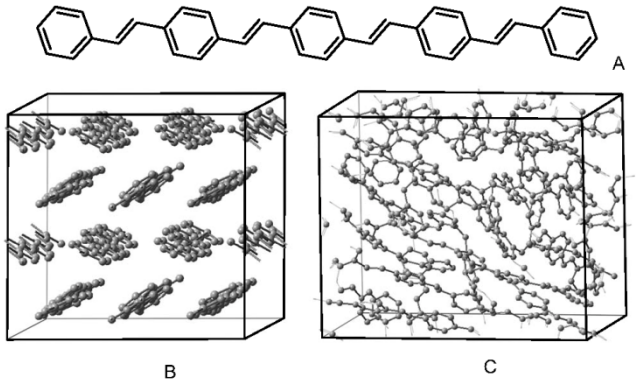


FIG. 1. (A) Molecular structure of the ordered oligomer. (B) Experimental crystal structure (Ref. 4). (C) Molecular structure of an oligomer cluster determined from the MD simulation. Hydrogen atoms are not shown for clarity.

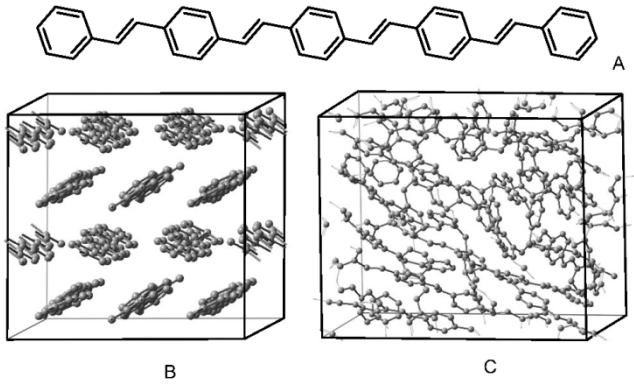
Yang et al PRB **76**, 241201R (2007)
Los Alamos NL

Amorphous-PPV: recent work

Start from Classical Force Fields!
disordered *polymer films* difficult to simulate: *oligomers*

Oligomer crystal: from experiment
Amorphous film:
MM3-2000 (reparametrized, fit B3LYP isolated oligomer)
condensation through pressure, anneal to get ensemble

Electronic: DFT-PW91, VASP/PAW
744 atoms, 2184 valence electrons



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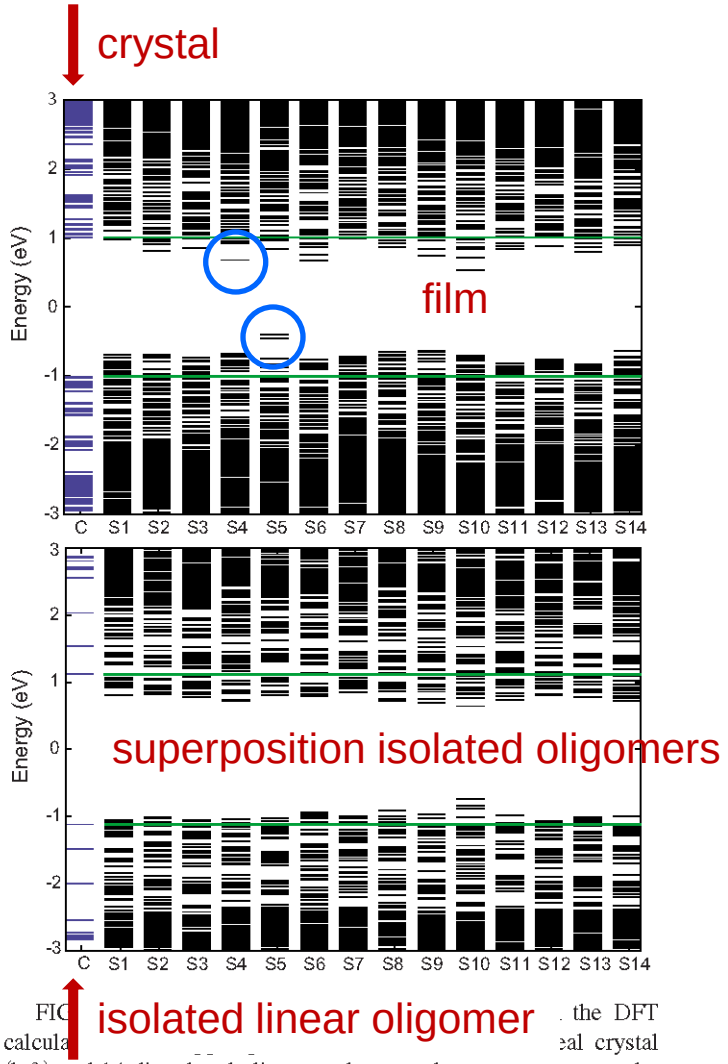


(left) and 14 disordered oligomer clusters whose geometry was determined from the MD calculations; the lower panel shows results for an isolated ordered oligomer (left) and an ensemble of 12 isolated oligomers with the same molecular geometries as in the corresponding column of the upper panel.

Yang et al PRB **76**, 241201R (2007)
Los Alamos NL

Amorphous-PPV: recent work

disordered *polymer films* difficult to simulate: *oligomers*

More linear chains (closer to ideal) would introduce the defects !

…in keeping with the conjugation length hypothesis

highlights relevance of interchain interaction

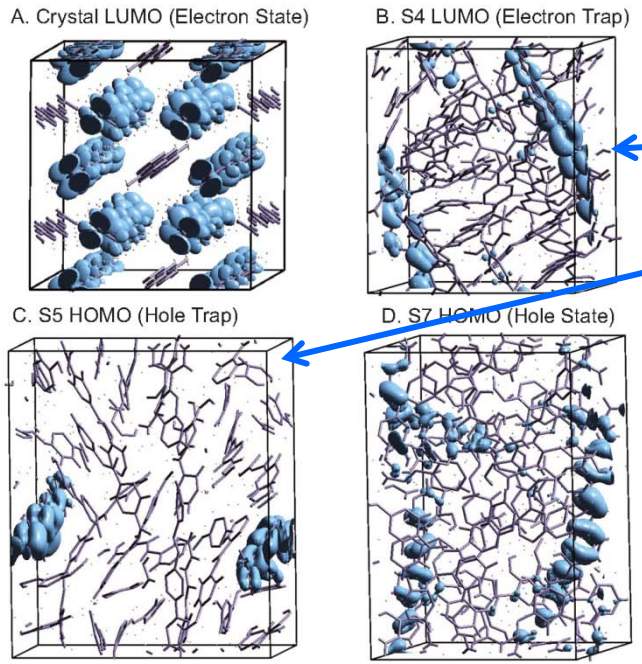
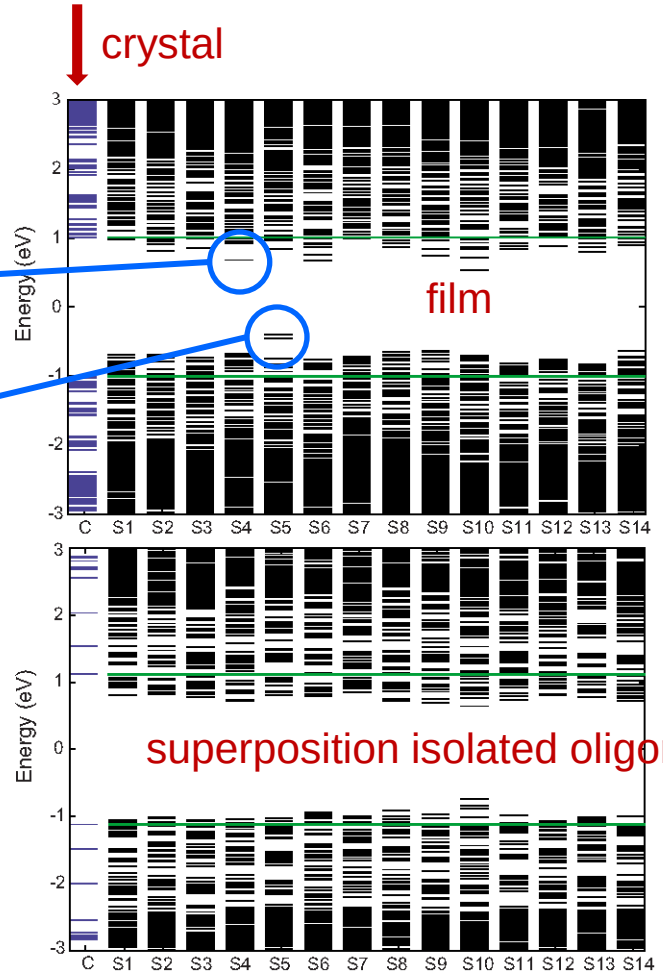


FIG. 4. (Color online) Calculated electron densities for selected states: (A) the crystal LUMO state, (B) the LUMO level for cluster *S*4, (C) the HOMO level for cluster *S*5, and (D) the HOMO level for cluster *S*7.



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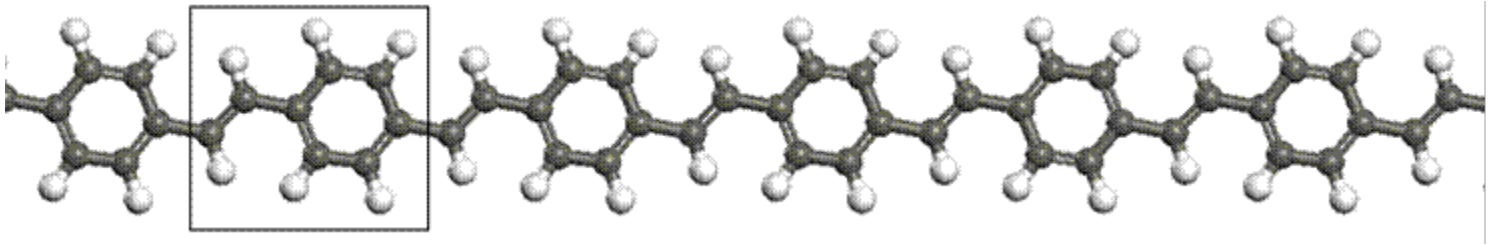
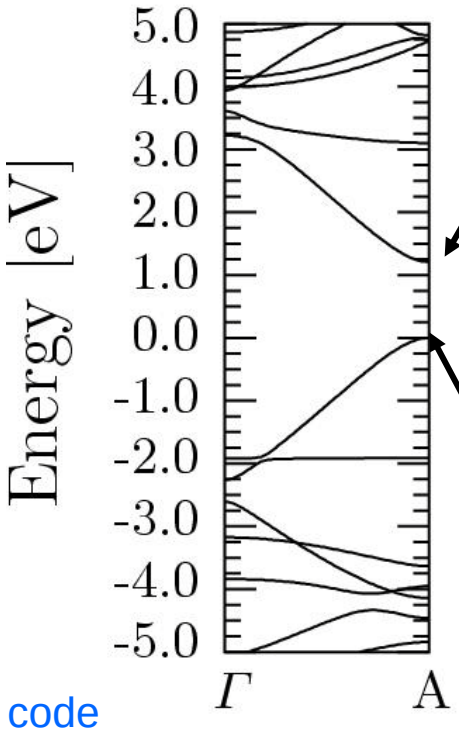
Yang et al PRB **76**, 241201R (2007)
Los Alamos NL

Grupo Nanomol

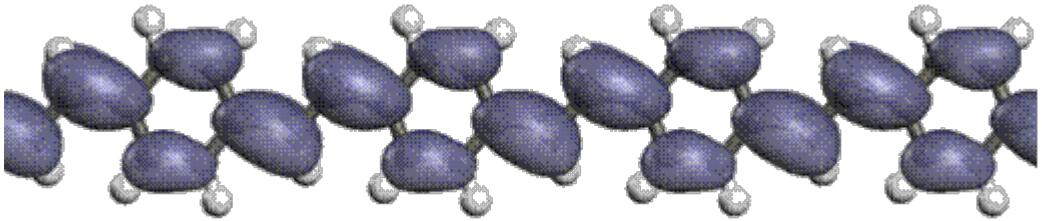
1D-PPV: brief recollection



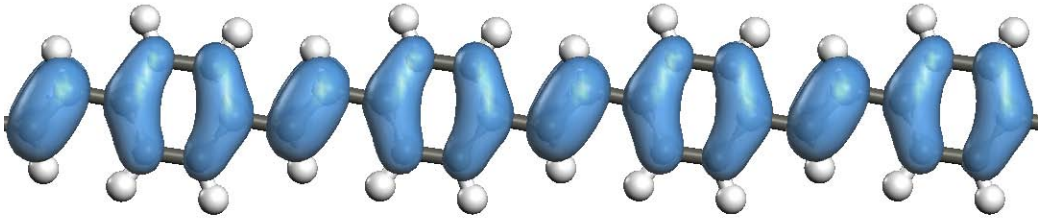
DFT-LDA , 600 eV cutoff energy, plane-wave basis set, norm-conserving pseudopotentials, PW-SCF* all calculations from now on



Conduction Band Minimum
Lowest Unoccupied or LUMO-band



π-conjugation dominating effect, transport & optical properties



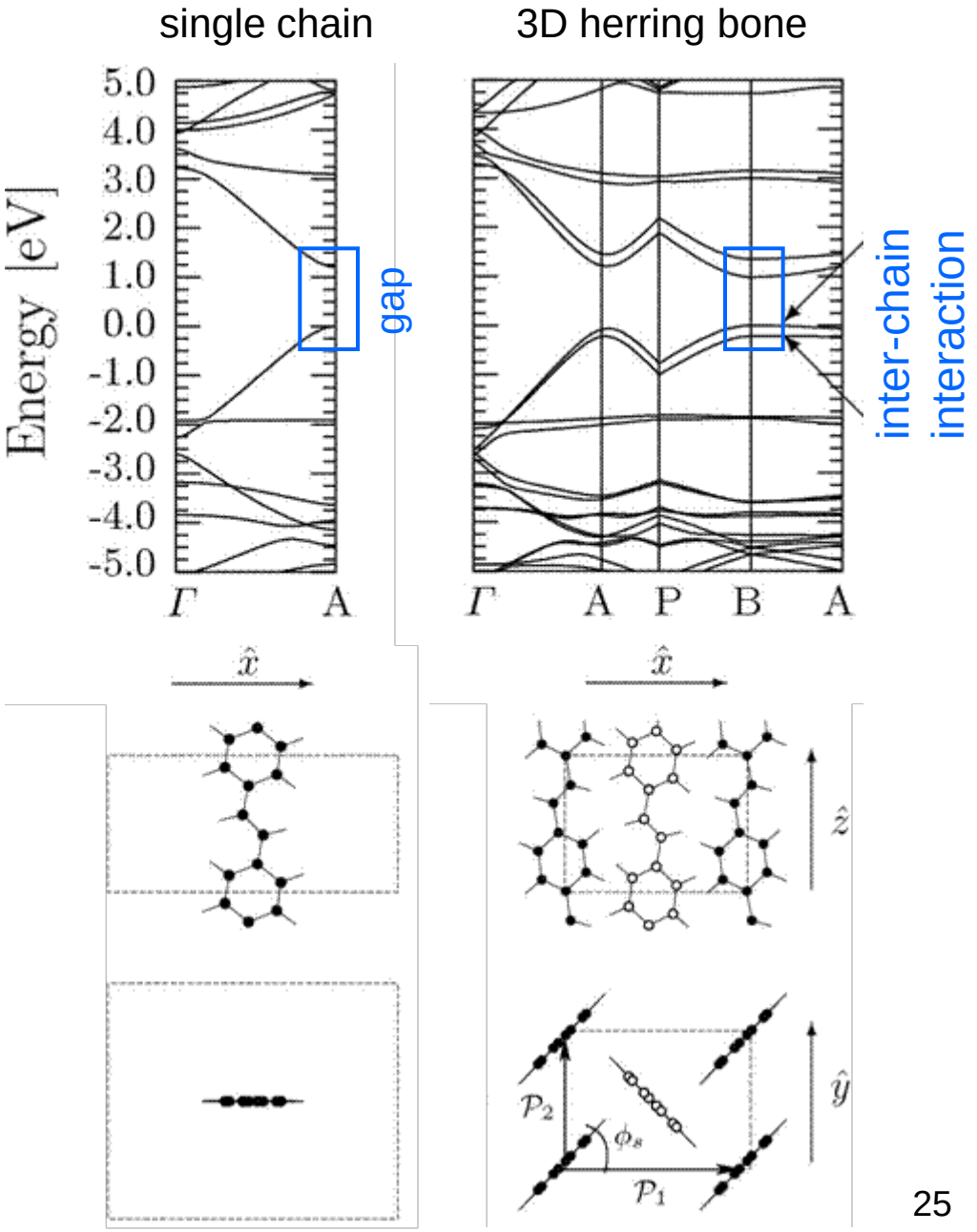
Valence Band Maximum
Highest Occupied or HOMO-band

*espresso code

S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, 2001 www.pwscf.org

Crystalline 3D-PPV: not so recent…

in the crystalline grains,
interchain interaction?



Ferretti el al PRL **90**, 086401 (2003);
PRB **69**, 205205 (2004)
UNIMORE&USP

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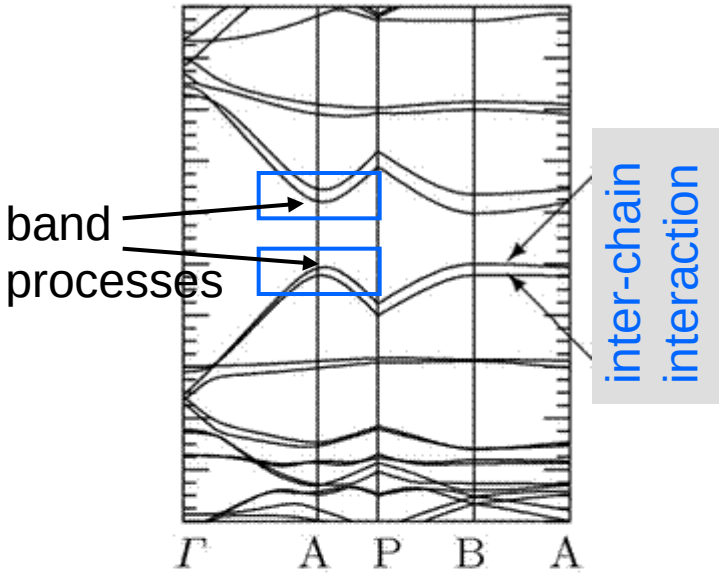
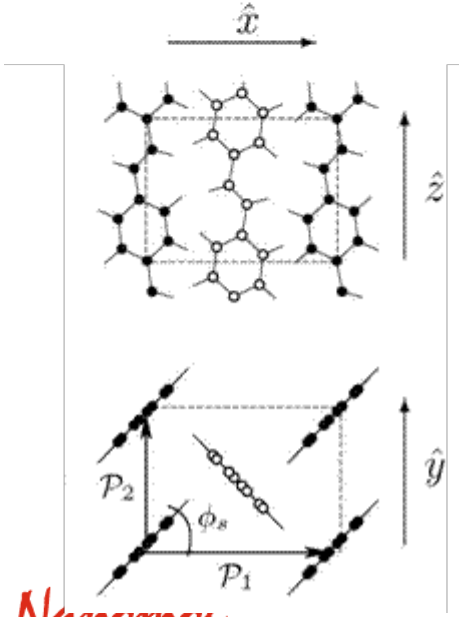
Crystalline 3D-PPV: not so recent…



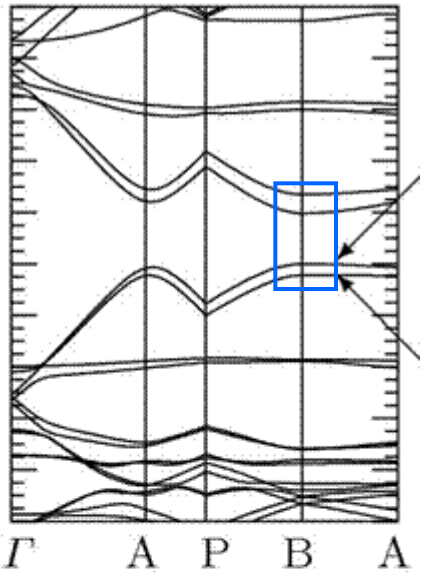


Effective masses for HB

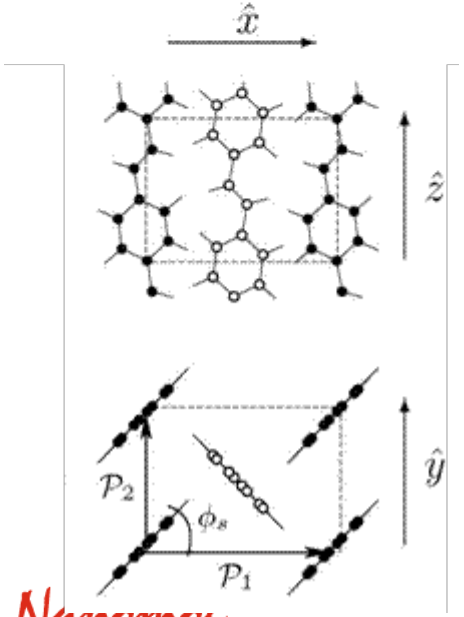
	HOMO	LUMO
$\hat{x}$	3.54	2.52
$\hat{y}$	5.24	1.31
$\hat{z}$	0.11	0.11

very large difference

Crystalline 3D-PPV: not so recent…



inter-chain interaction



Intra / Interchain transport :

$$H = \sum_i E_i a_i^+ a_i + \sum_{ij} E_{ij} a_i^+ a_j$$

Transfer integrals

activated hopping

$$\kappa_{ij} = \frac{1}{\hbar^2}\sqrt{\frac{\beta}{4\pi\lambda}}\exp[-\beta\frac{(\lambda+\Delta\varepsilon)}{4\lambda}]\cdot E_{ij}^2$$

	on-chain	inter-chain
TI (meV)	550	27.78

again, very large difference:

defect-containing crystals?
at least for transport, allows for a first approach through 1D single-chain (ballistic-transport), *but…*

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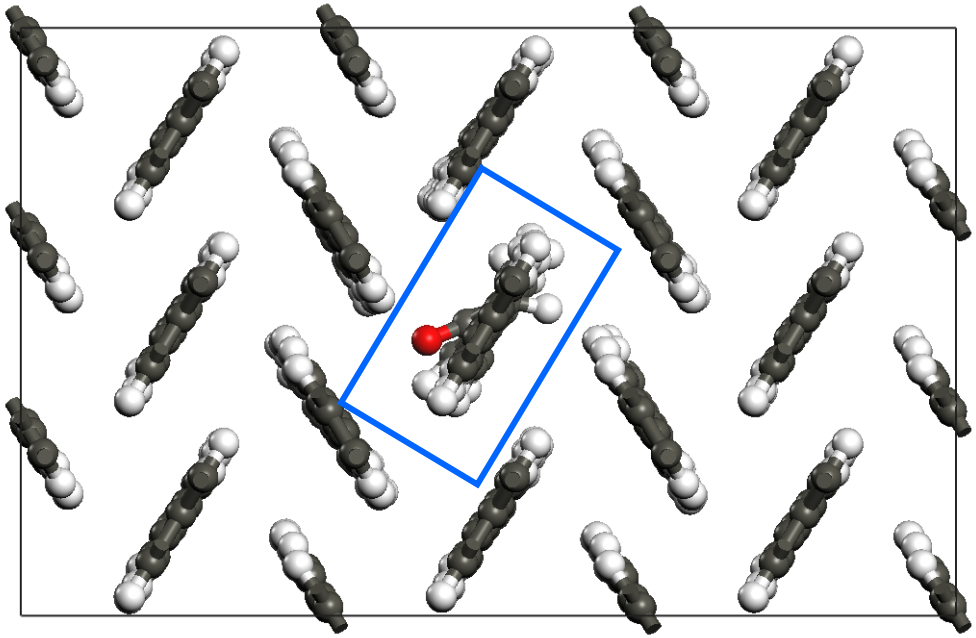
This work, computational approach:

…the chain is embedded in the crystal: how can we know the chain geometry?

we know that torsions and distortions will affect the conjugation length → transport!

Structure in-bulk
Classical molecular mechanics
Compass Force Field
3x3x7 (7 monomer units along chain)

Electronic structure single-chain



This work, computational approach:

Simple (important) defects coming from environment/preparation (water):

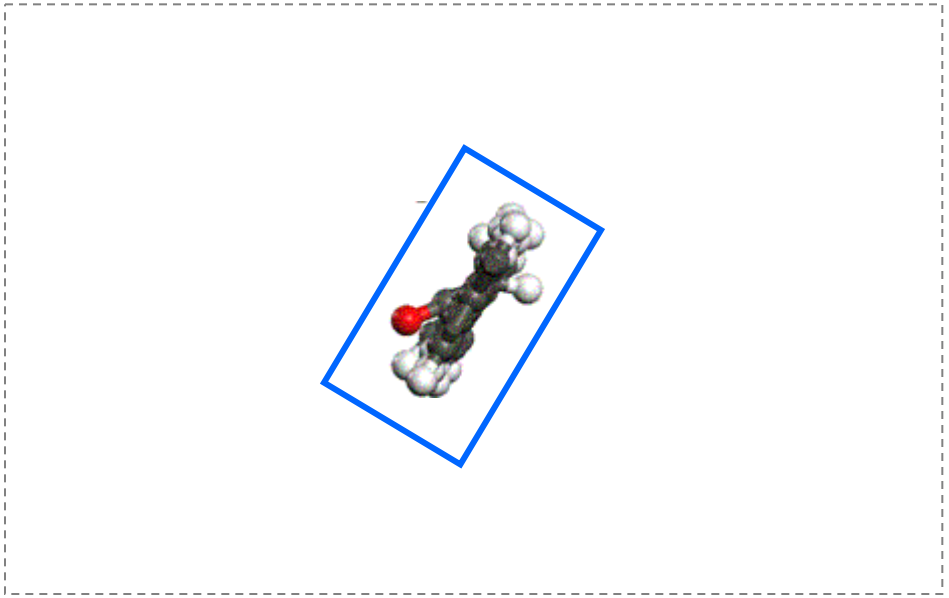
H-defects: vacancy H_{vac} and addition H_{plus}

O-defect: hydroxyl (OH)

Structure in-bulk
Classical molecular mechanics
Compass Force Field
3x3x7 (7 monomer units along chain)

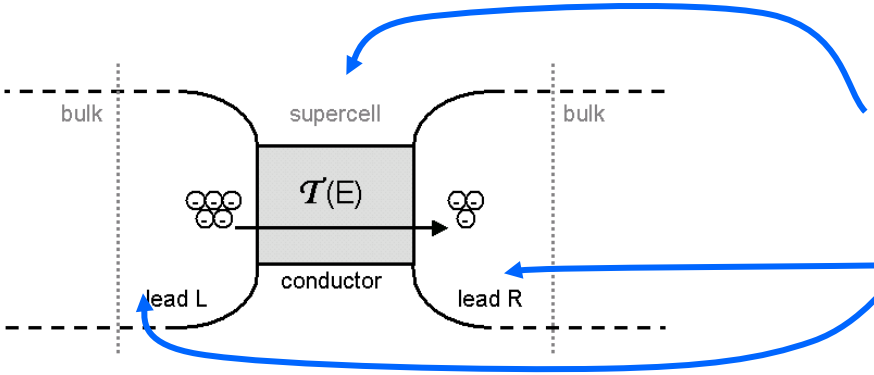
Electronic structure single-chain

fixed atomic positions
large supercell



Plane waves
ultrasoft potentials
XC PBE
espresso code
S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, 2001 www.pwscf.org

Coherent Electronic Transport (single chain)



defect region of polymer chain

perfect chain (semi-infinite)

- Quantum Conductance depends on the local properties of the conductor (transmission - scattering) and the distribution function of the reservoirs

$$G = \frac{2e^2}{h} T(E_f)$$

- Localized Basis Set → operators in block matrix form

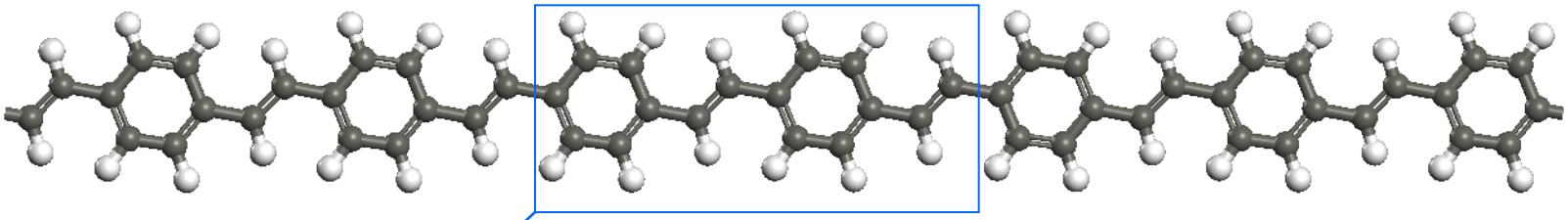
  Maximally Localized Wannier functions and WanT code*

- transmittance from Real-space Green's Function technique*

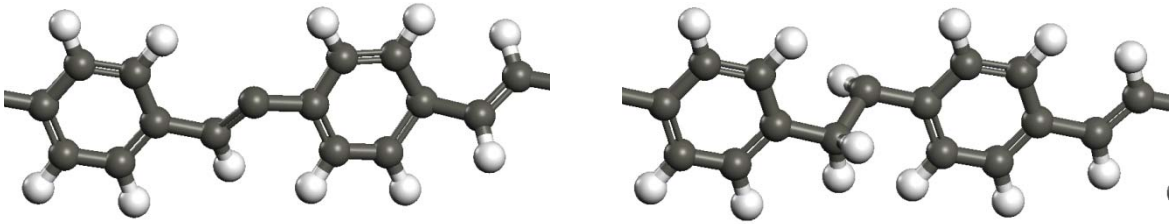
$$T(E) = \mathrm{Tr}\left\{ \Gamma_L G_C^r \Gamma_R G_C^a \right\}$$

*A. Calzolari, N. Marzari, I. Souza, and M.B. Nardelli, PRB 69, 035108 (2004).

Systems:

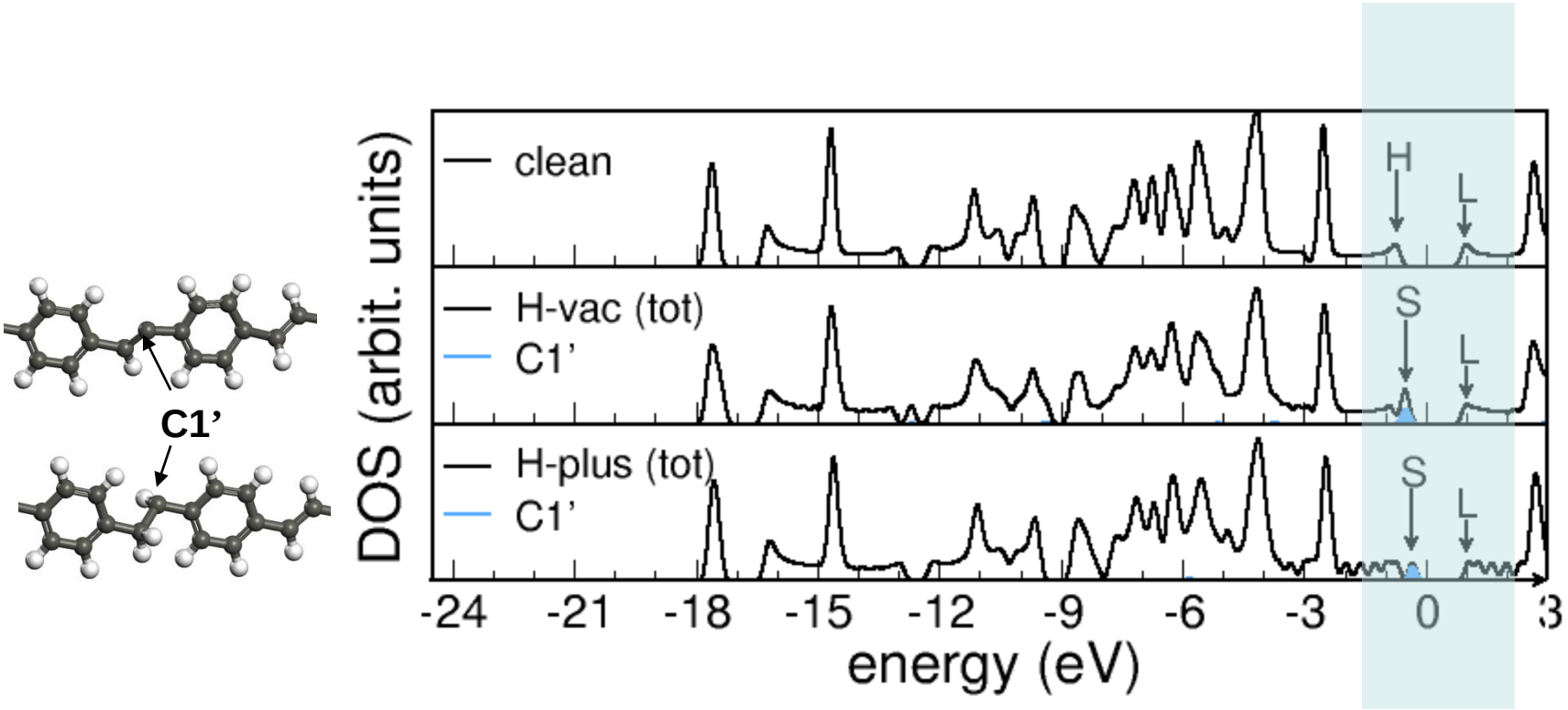


Hydrogen: H_{vac} H_{plus}



Hydrogen Defects: levels

Vacancy and addition introduce semi-occupied levels at the VBT

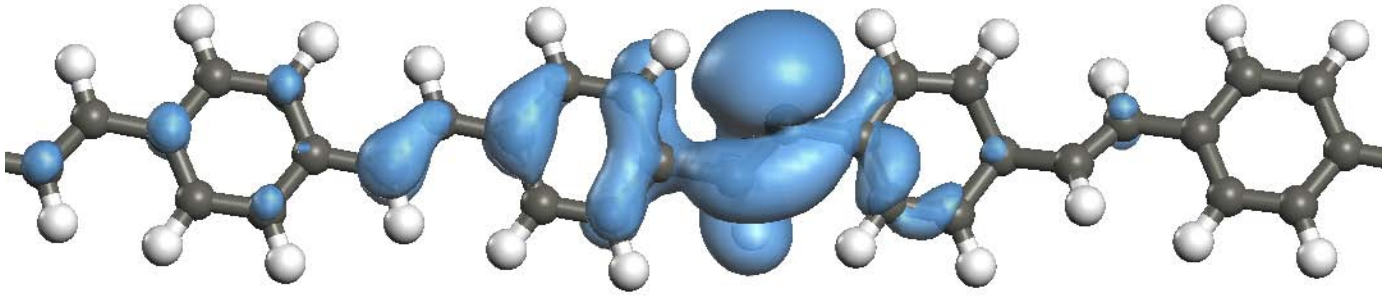


gap level concentrated on carbon atom

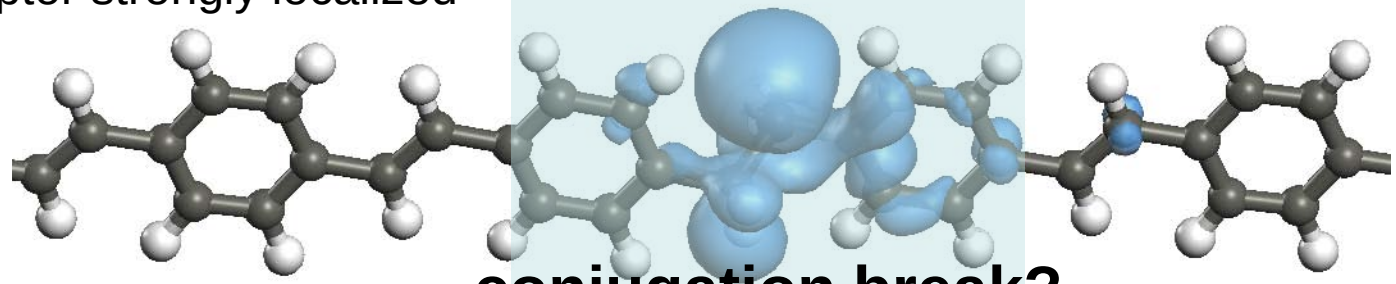
Zoppi et al, Phys. Rev. B 78, 165204 (2008)

Hydrogen Defects: gap states

H vacancy: acceptor delocalizes (over just more than two monomers)



H addition: acceptor strongly localized

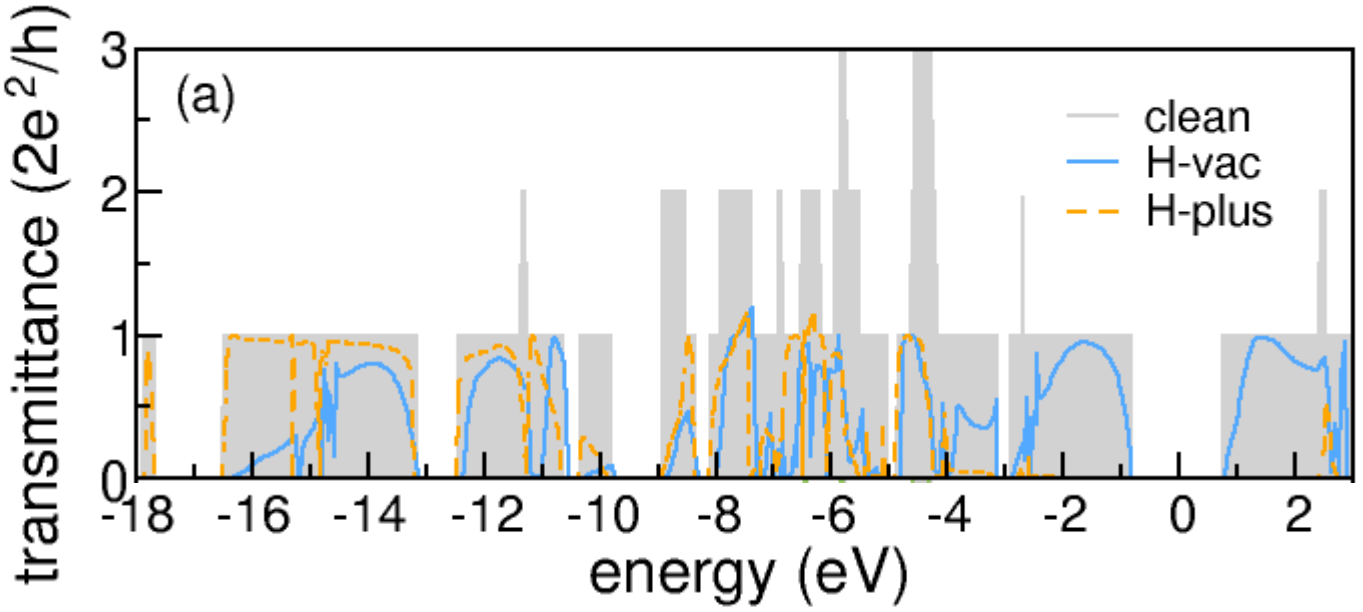


conjugation break?

Zoppi et al, Phys. Rev. B 78, 165204 (2008)

Hydrogen Defects: transmittance

shaded area = transmittance for clean, perfect PPV chain

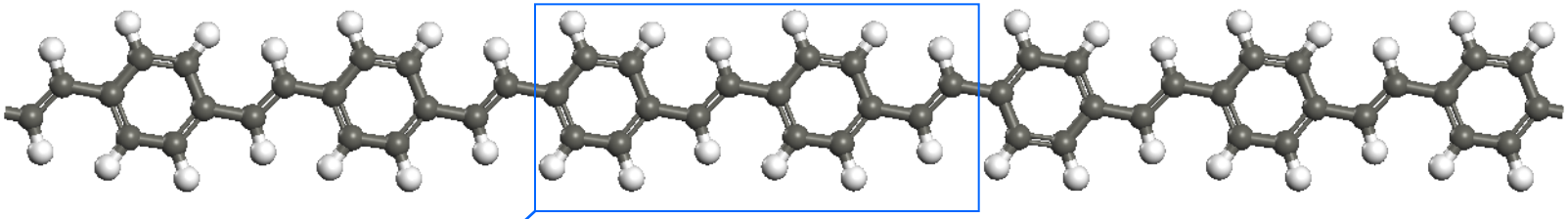


H vacancy is not detrimental to 1D transport, electrons or holes

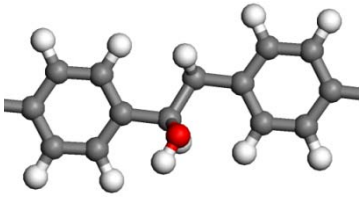
H addition completely blocks 1D transport, electrons or holes

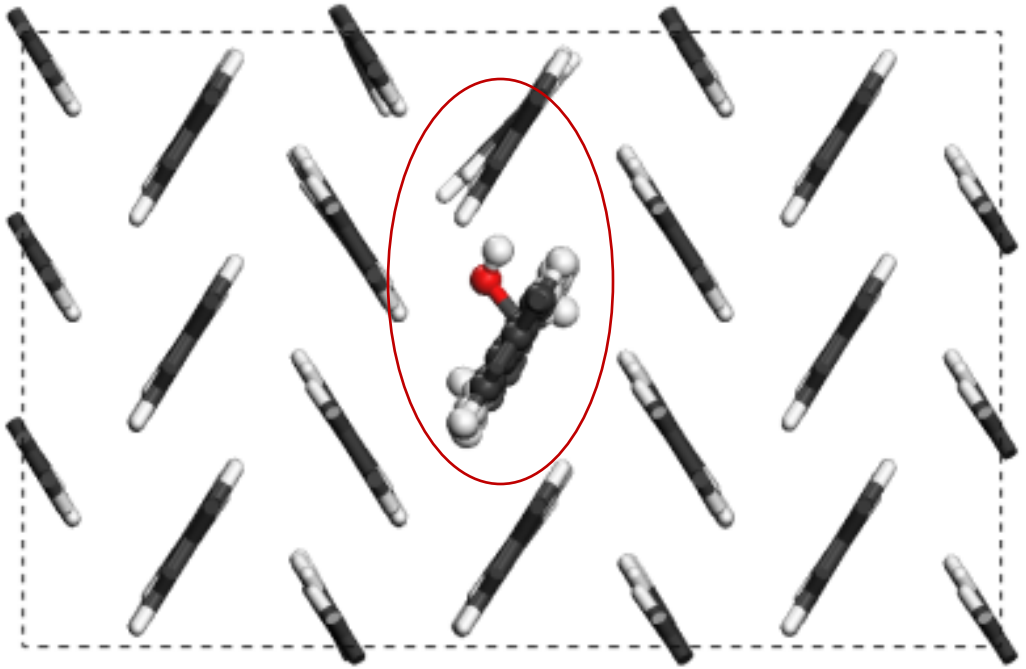
Over-coordination of vinylene segment always produces the same blocking of 1D transport

Systems:



Hydroxyl OH:



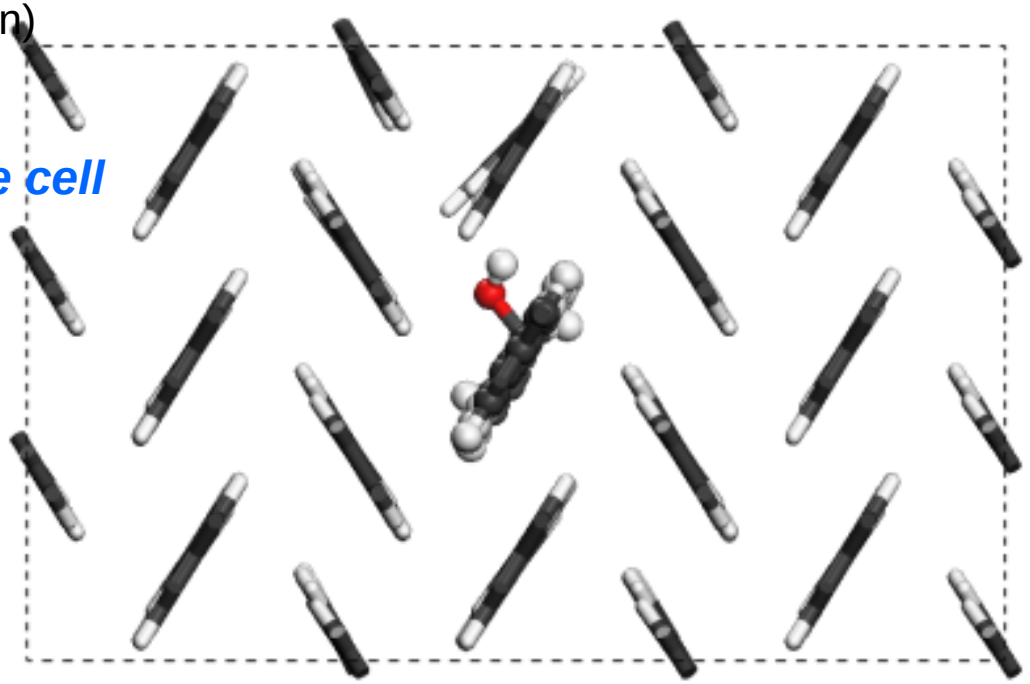


can we trust just a
single-chain calculation?

This work, computational approach:

For the hydroxyl defect, we must calculate also the negative (OH^-) charge state…
…later

Structure in-bulk neutral
Classical molecular mechanics
Compass Force Field
3x3x7 (7 monomer units along chain)



Electronic structure *complete cell*

fixed atomic positions
(~1760 atoms, ~4800 electrons)

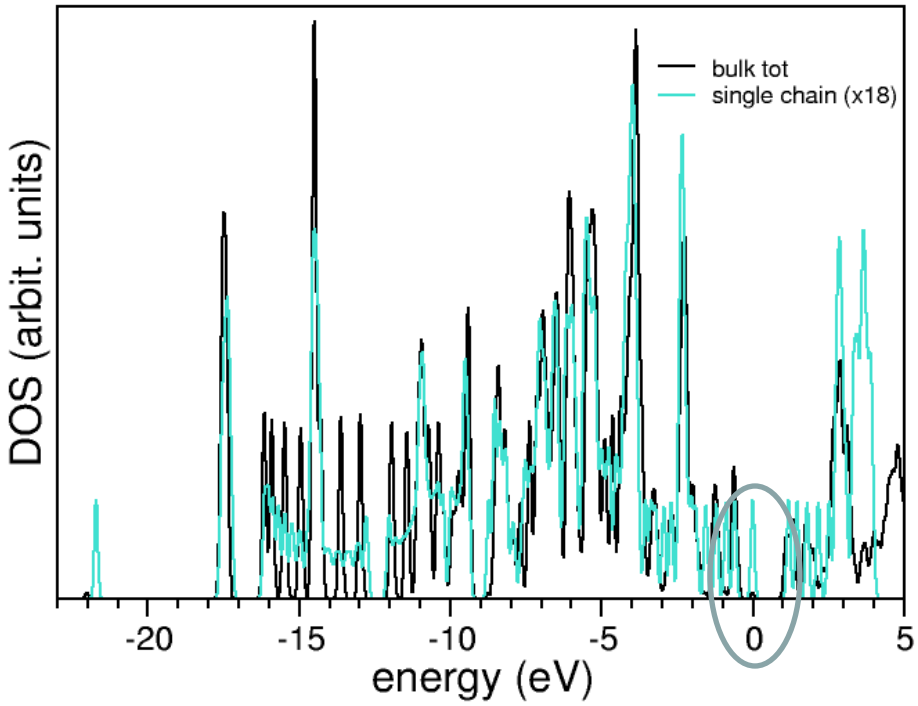
Plane waves **(4 x 10^6 !)**
ultrasoft potentials
PBE

espresso code
S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, 2001 www.pwscf.org

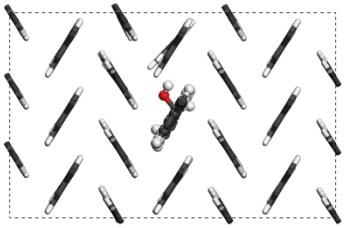
Hydroxyl Defect: levels

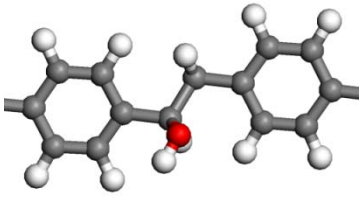
Effect similar to H_{plus}

(from here on, Fermi energy at highest occupied level)



Defect state in the gap, semi-occupied



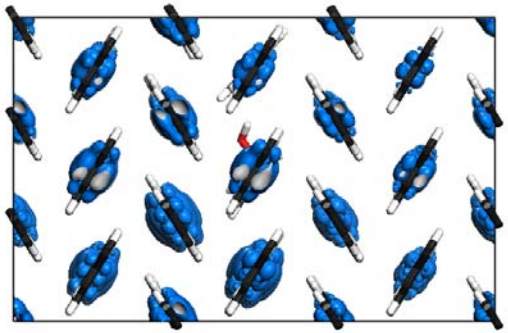


Complete bulk cell

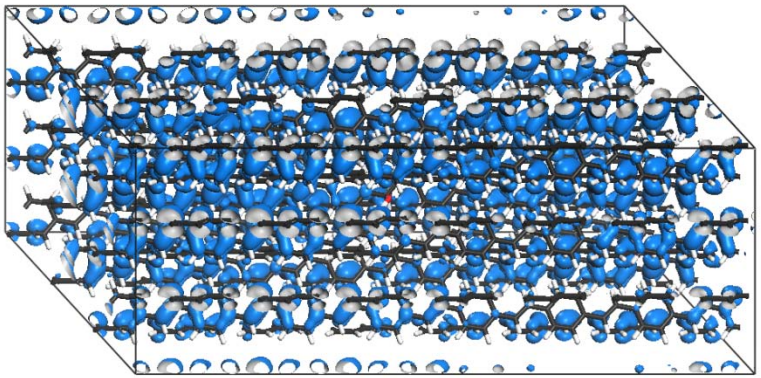
no striking difference with the isolated chain for the neutral state (use later)

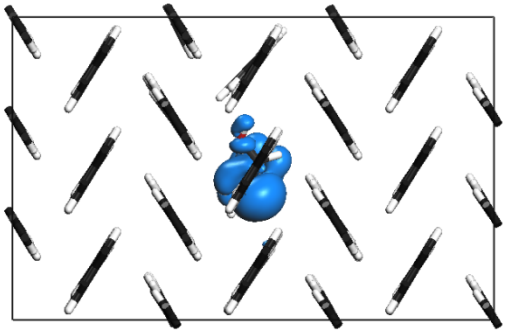
Calzolari, Ruini & Caldas, to be published

Hydroxyl Insertion: gap state

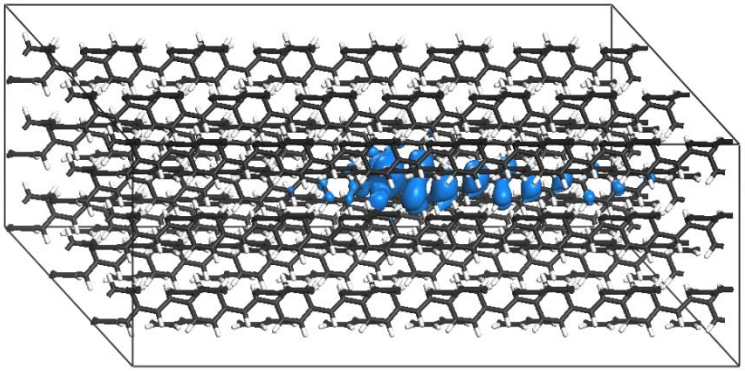


HOMO-1

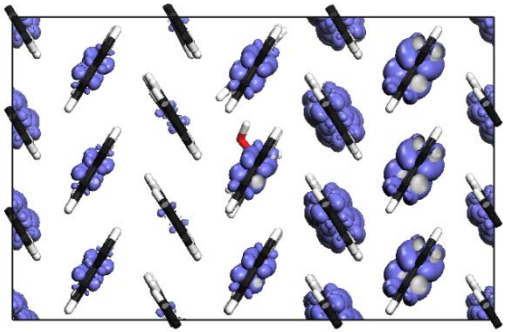




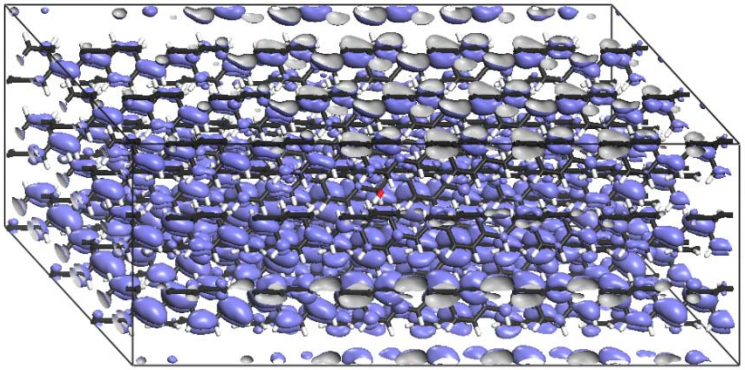
SOMO



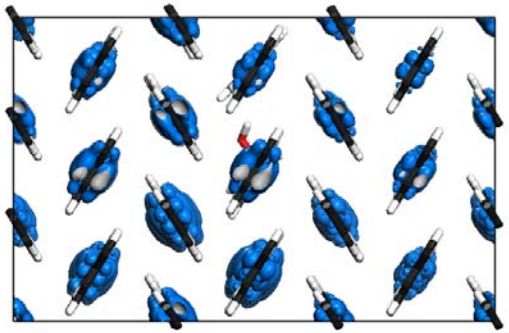
highly localized



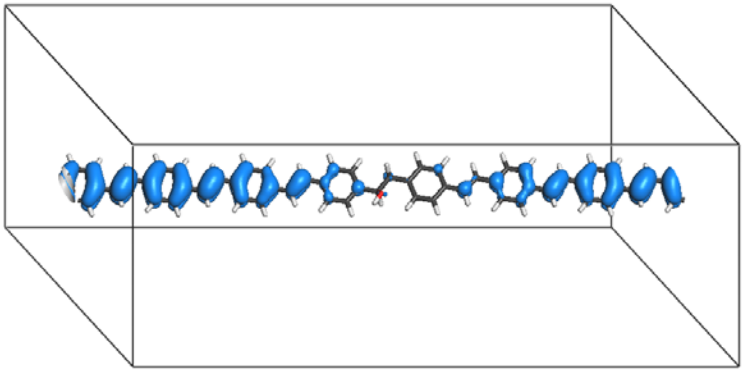
LUMO



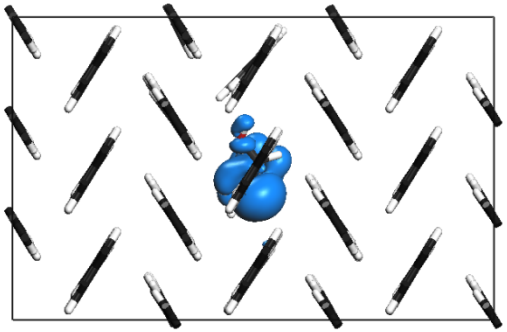
Hydroxyl Insertion: gap state



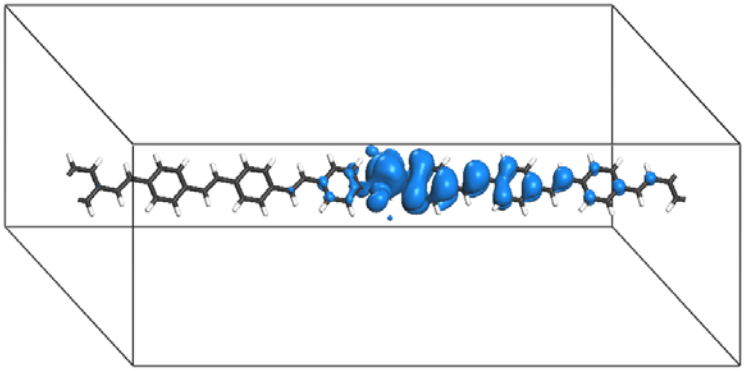
HOMO-1



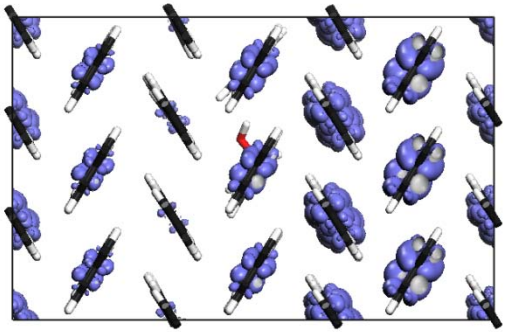
band-edge states repelled



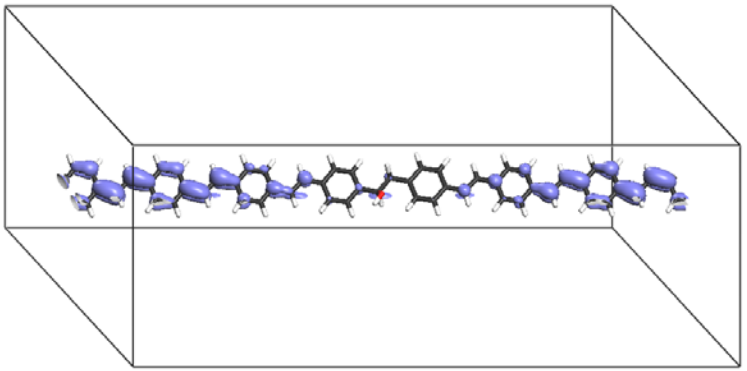
SOMO



highly localized



LUMO



OH^- most probable

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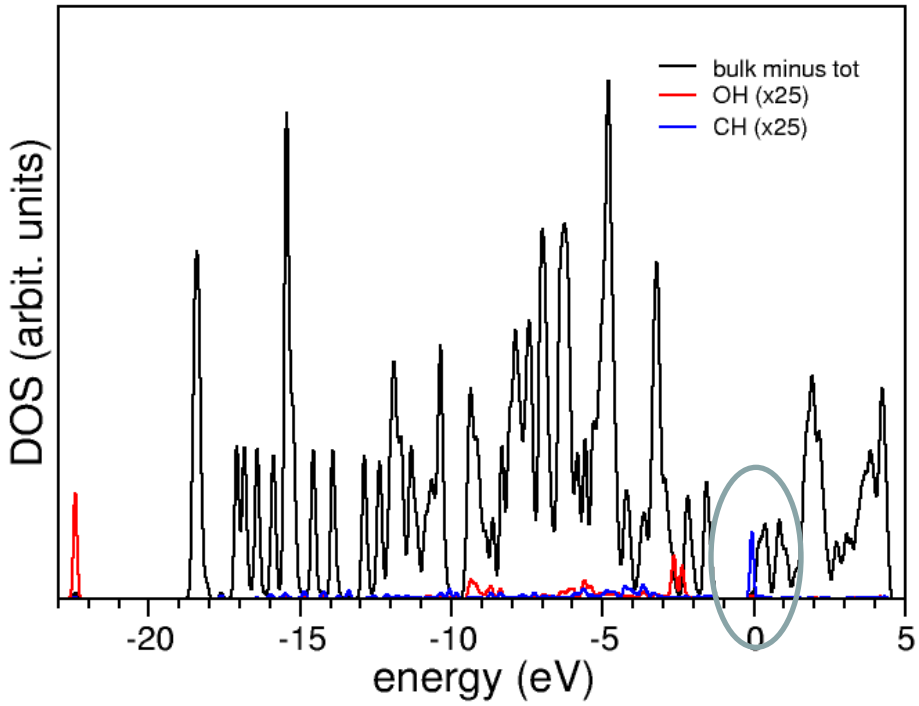
KITP 2009

Hydroxyl Insertion: gap state



neutral sate, semi-occupied level

negatively charged,
fully occupied bands

strong shift of defect state
towards conduction band

as we would expect from a highly localized gap state,
not really a shallow acceptor (but not a shallow donor either ?)

E_{CBM} - 0.2eV, full (0/-) DFT results

Calzolari, Ruini & Caldas, to be published

Small list of *unresolved questions*:

Simple “details” still missing:

•can we trust gap level positions?

Electrical gap only:
Many-body effects (including C-X compensation)
huge

DFT gap (crystalline cell) ~1.25eV

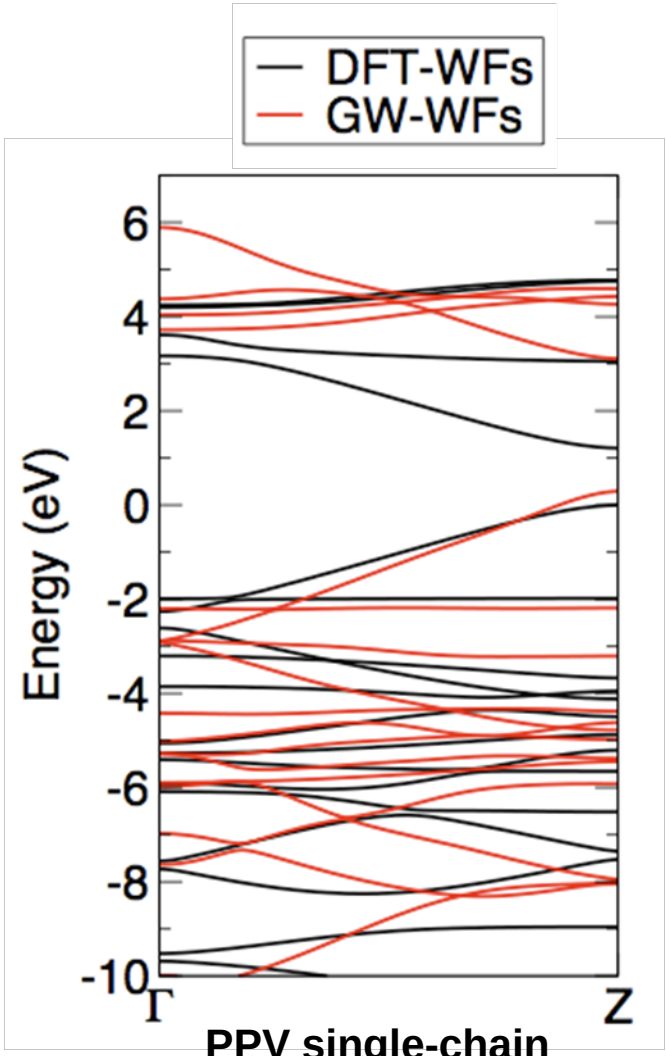
Charged calculations in the bulk cell

jellium (+ Markov-Payne, negligible=>1/5000 electrons)

128 SP5 processors, ~31.100 PW/proc =3.980.000 PWs
3000 Kohn-Sham states (>4 eV, ~5eV over Fermi)

E_g=1.37eV

…still miss sizeable proportion



PPV single-chain
L. Martin-Samos et al, work in progress

Small list of *unresolved questions*:

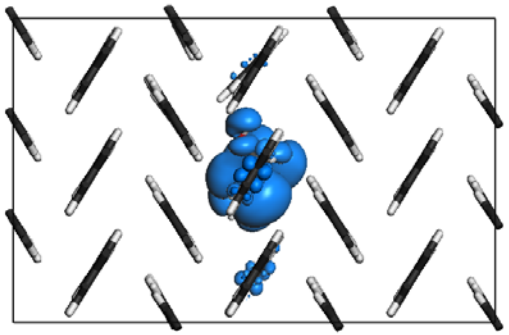
Simple “details” still missing:

•can we trust gap level positions?

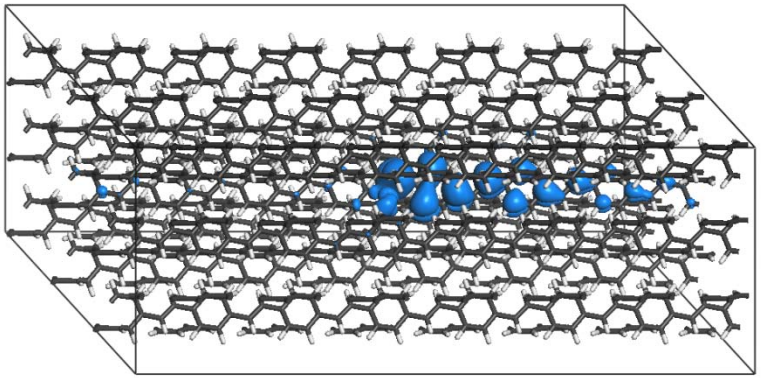
Electrical gap only:
Many-body effects (including C-X compensation)
huge

DFT gap (bulk cell) ~1.25eV

•Charged calculations in the bulk cell
still miss sizeable proportion
→ can we ever do GW in such a huge cell?



HOMO



slight delocalization

•Relaxation of charged defects?
bulk cell, DF relaxation of selected segment
(all those atoms and electrons!)

unreliable energies… (sigh)
→ can we include vdW-DF in such a huge calculation????

Conclusions & Perspectives:

".. in order to realize higher mobilities, it is necessary to improve crystalline quality and reduce disorder by using polymers that are less prone to structural defects or by employing growth techniques that allow better control over the defects incorporated into the polymer nanocrystals."

Chang et al PRB 76, 205204 (2007)

Carter, Science 321, 800 (2008)

Predicting the behavior of molecular, soft, amorphous, or heterogeneous materials poses notable challenges. Interactions in soft materials or molecular crystals are determined in large part by van der Waals forces, which are not described properly by standard XC functionals in DFT.

> Recent work applying specialized XC functionals (27), GW (28), and periodic local MP2 (5, 29) have the correct physics and show great promise for treating such dispersion forces. With such techniques, properties of materials composed of, e.g., polymers, colloids, and proteins, *will be accessible* with QM.

Caldas, KITP 2009

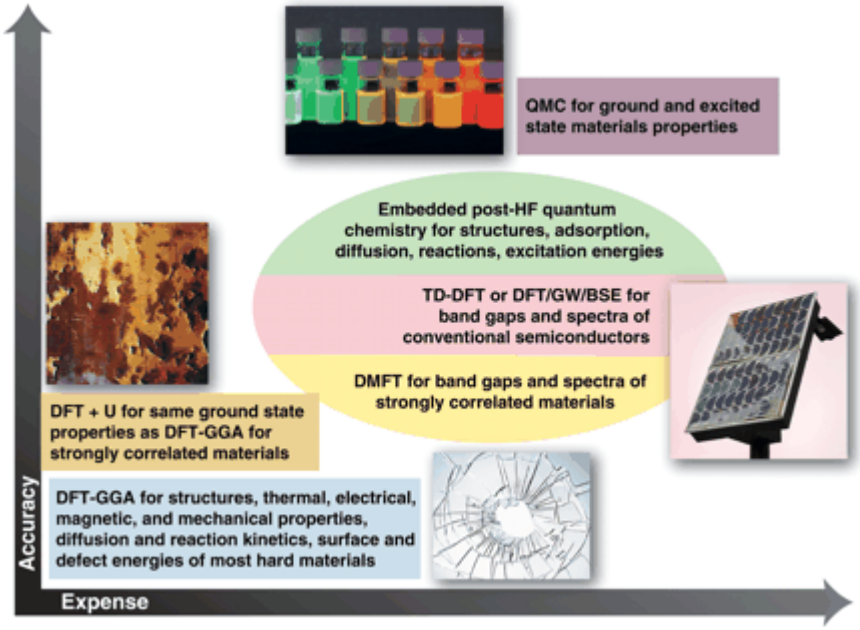
To understand transport properties, we must understand also hopping, and combine on-chain vs hopping (statistical, multiscale);

To do that, we must have good morphologies, and good electronic structure results;

→To reach multi-scale modeling, *we must be good at QM*.

Conclusions & Perspectives :

…and I did not even touch on optical properties, excitons, exciton migration, recombination, trapping at defects...



Carter, Science 321, 800 (2008)

note that she mentions explicitly hard materials, conventional semiconductors, strongly correlated materials

where are we for organic polymers?

we have in this room specialists on every single method quoted in the diagram:

might be another 20 US$ problem?

Thank you

Support

NATIONAL CENTER OF CNR-INFM

S3

NANOSTRUCTURES AND BIOSYSTEMS AT SURFACES

FAPESP

INCT/MCT INEO

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