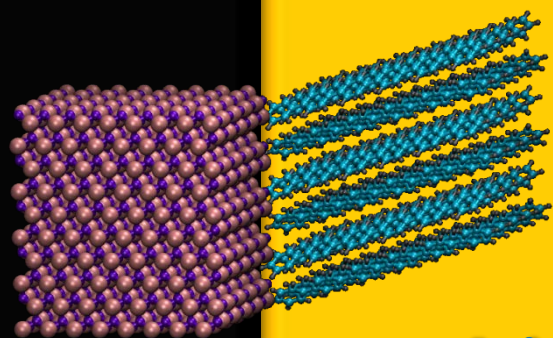


**Computational**

**concepts for**

**organic/ inorganic**

**solar cells**



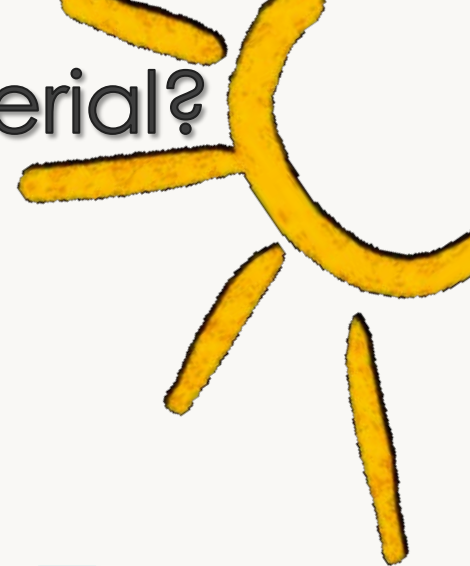
**combining DFT with**

**manybody perturbation theory**

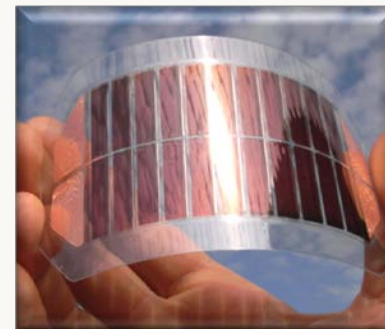
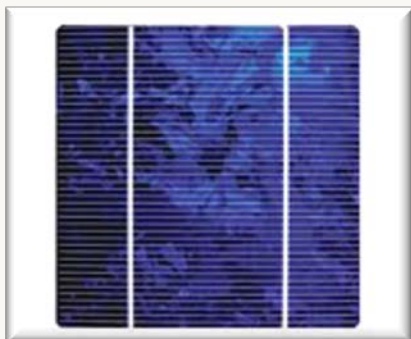


**Claudia Draxl**

# What is a good photovoltaic material?

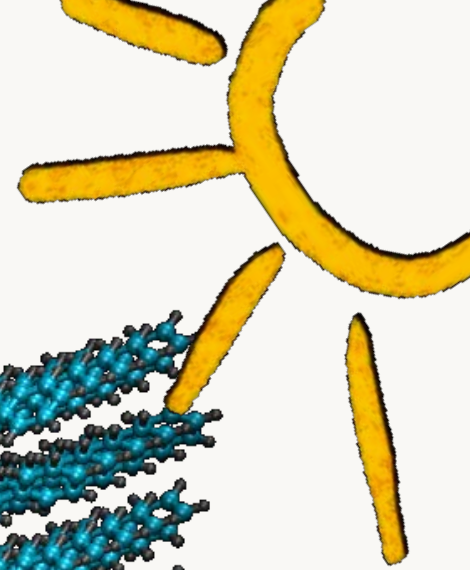
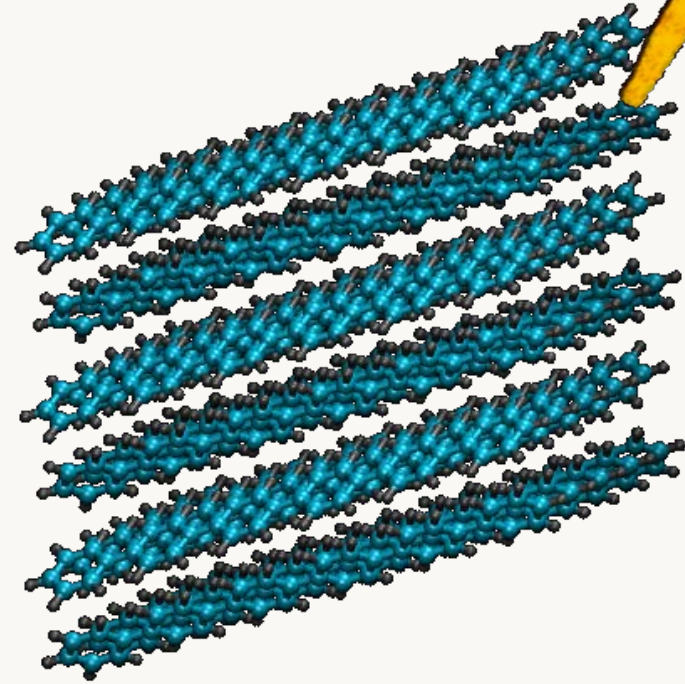
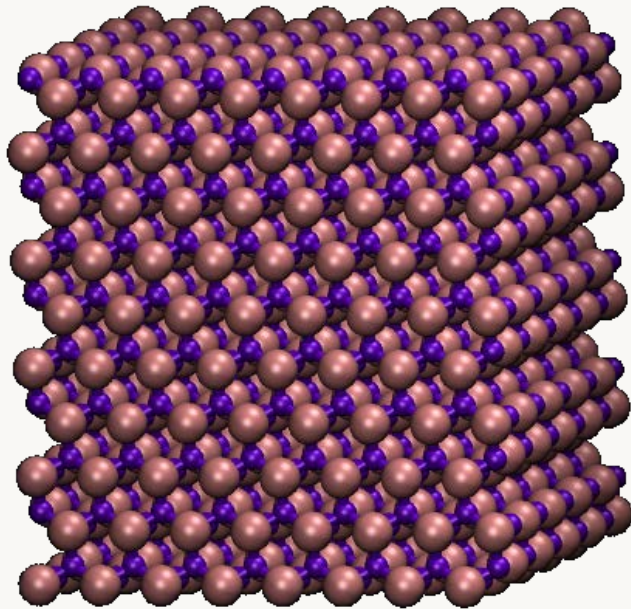


- + Nearly free charge carriers —
- High absorption cross section +
- + High carrier mobilities —



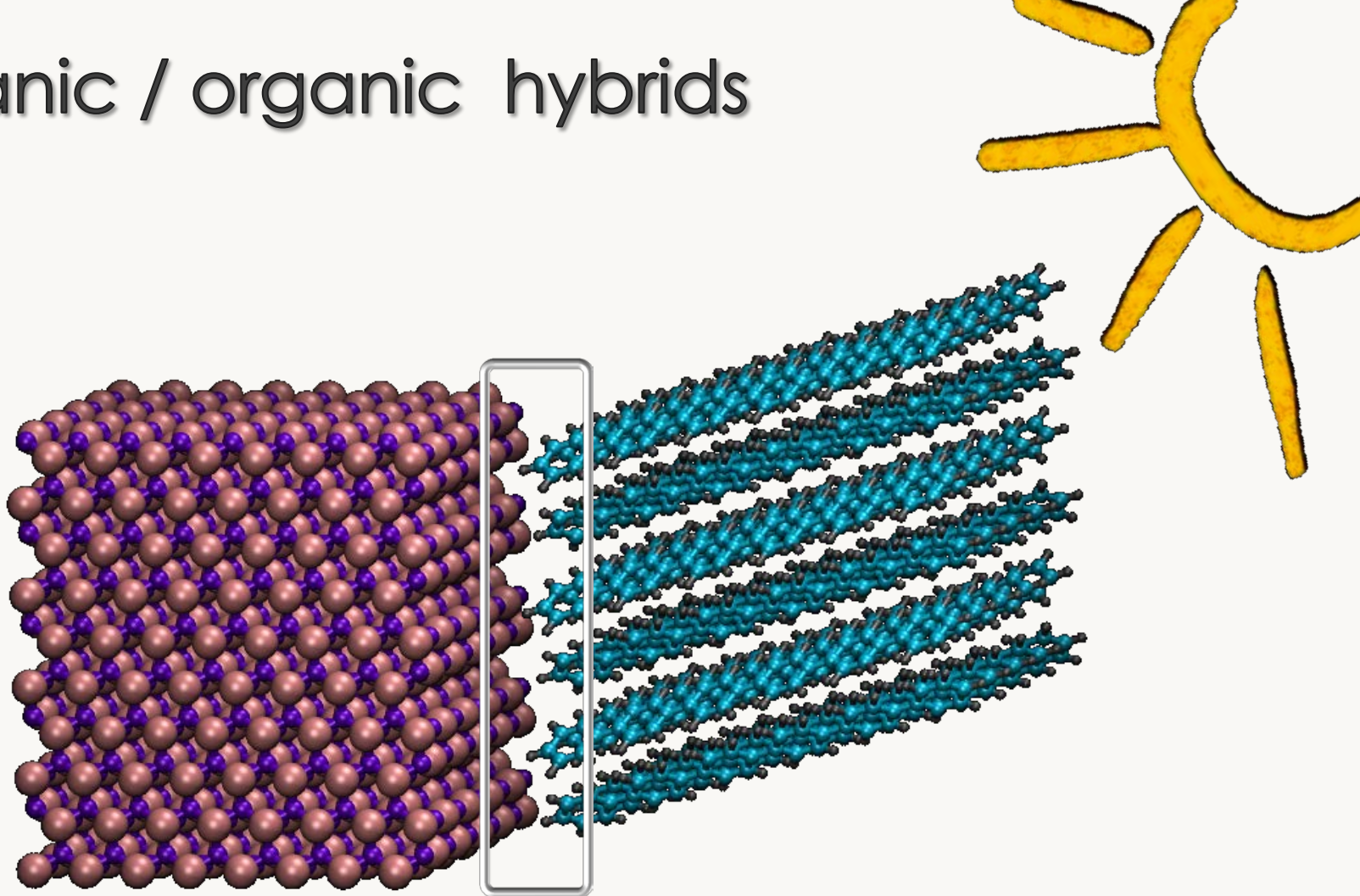
*Photovoltaics*

# Inorganic / organic hybrids



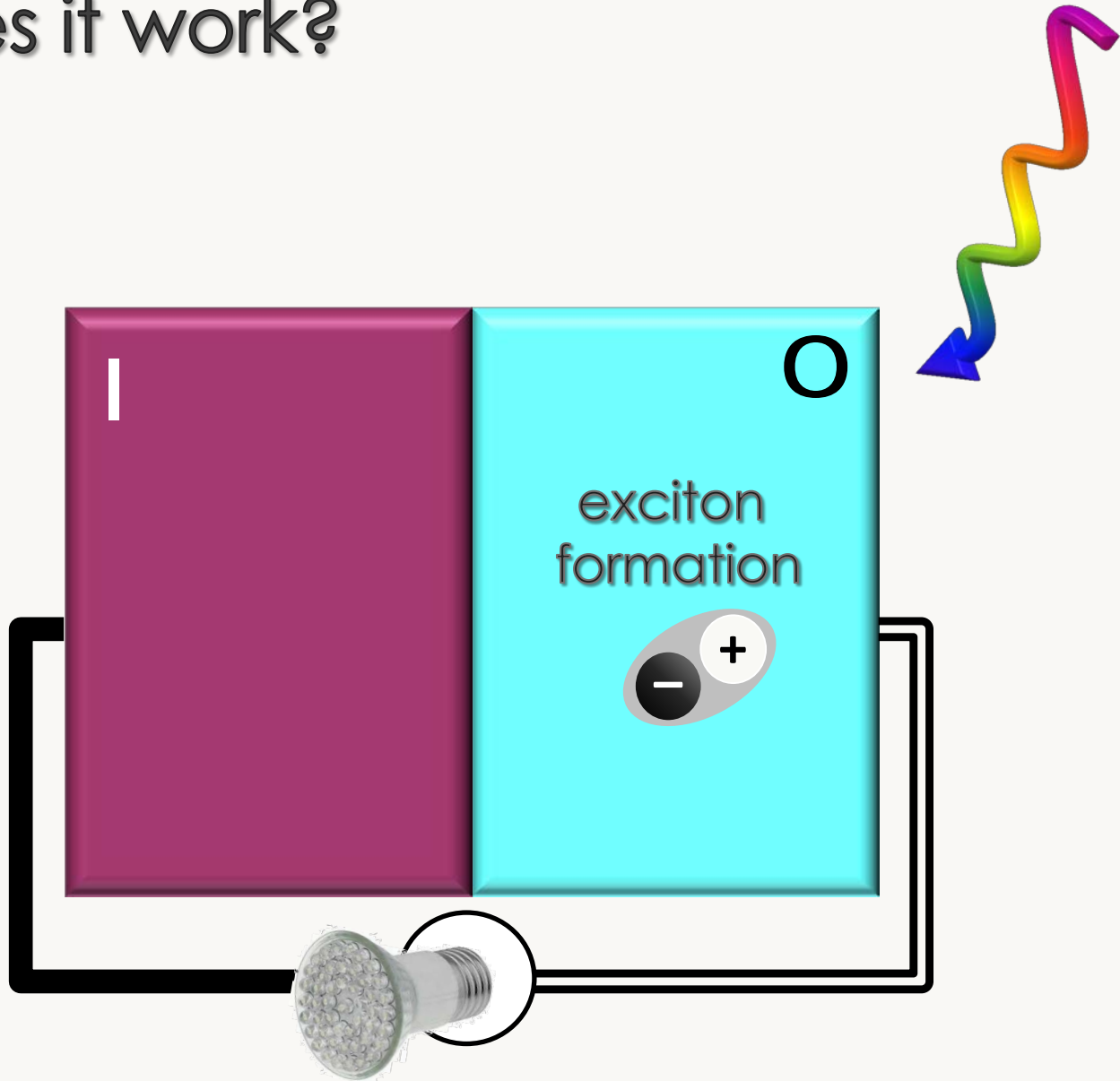
*Photovoltaics*

# Inorganic / organic hybrids



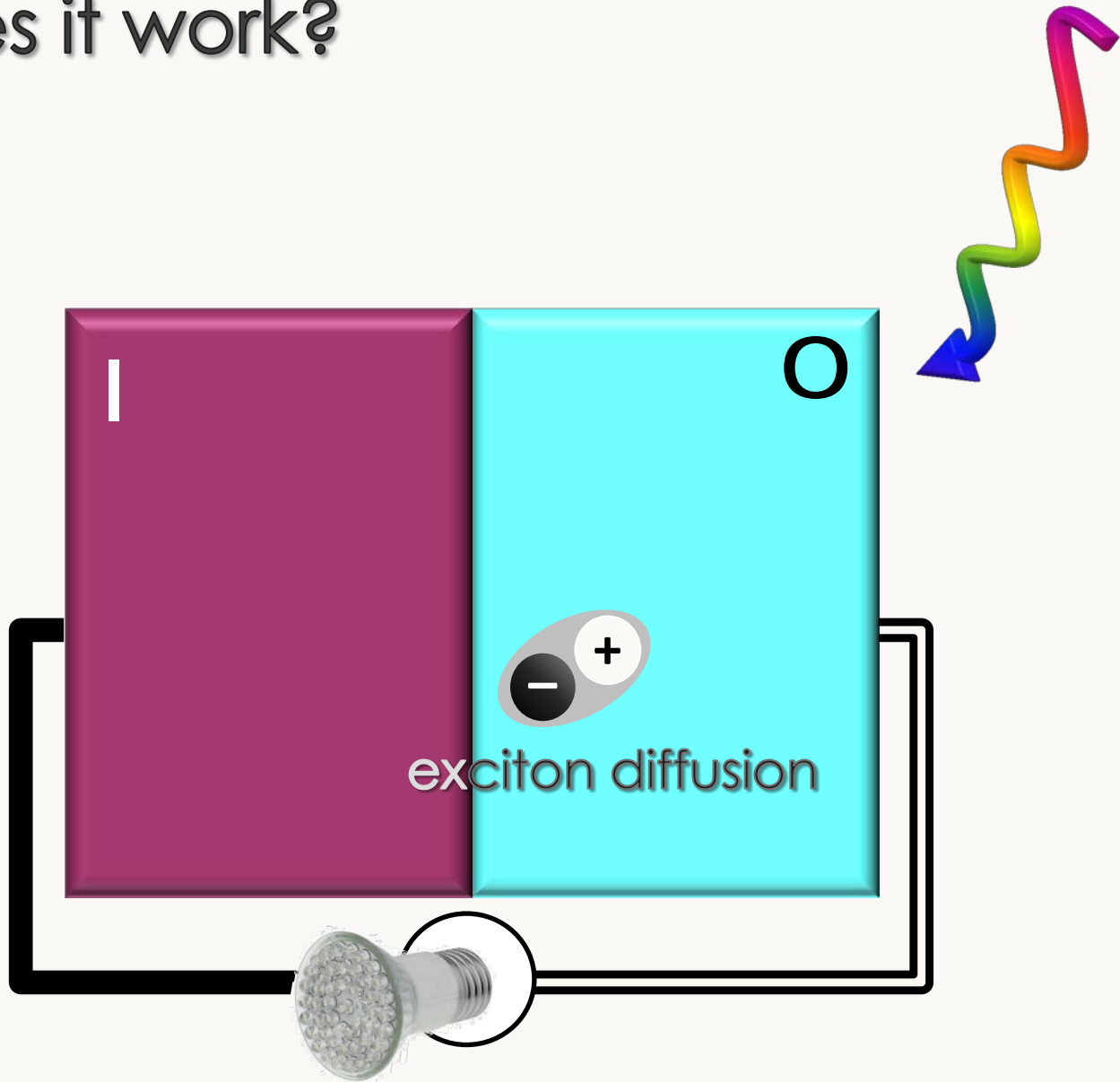
*Photovoltaics*

# How does it work?



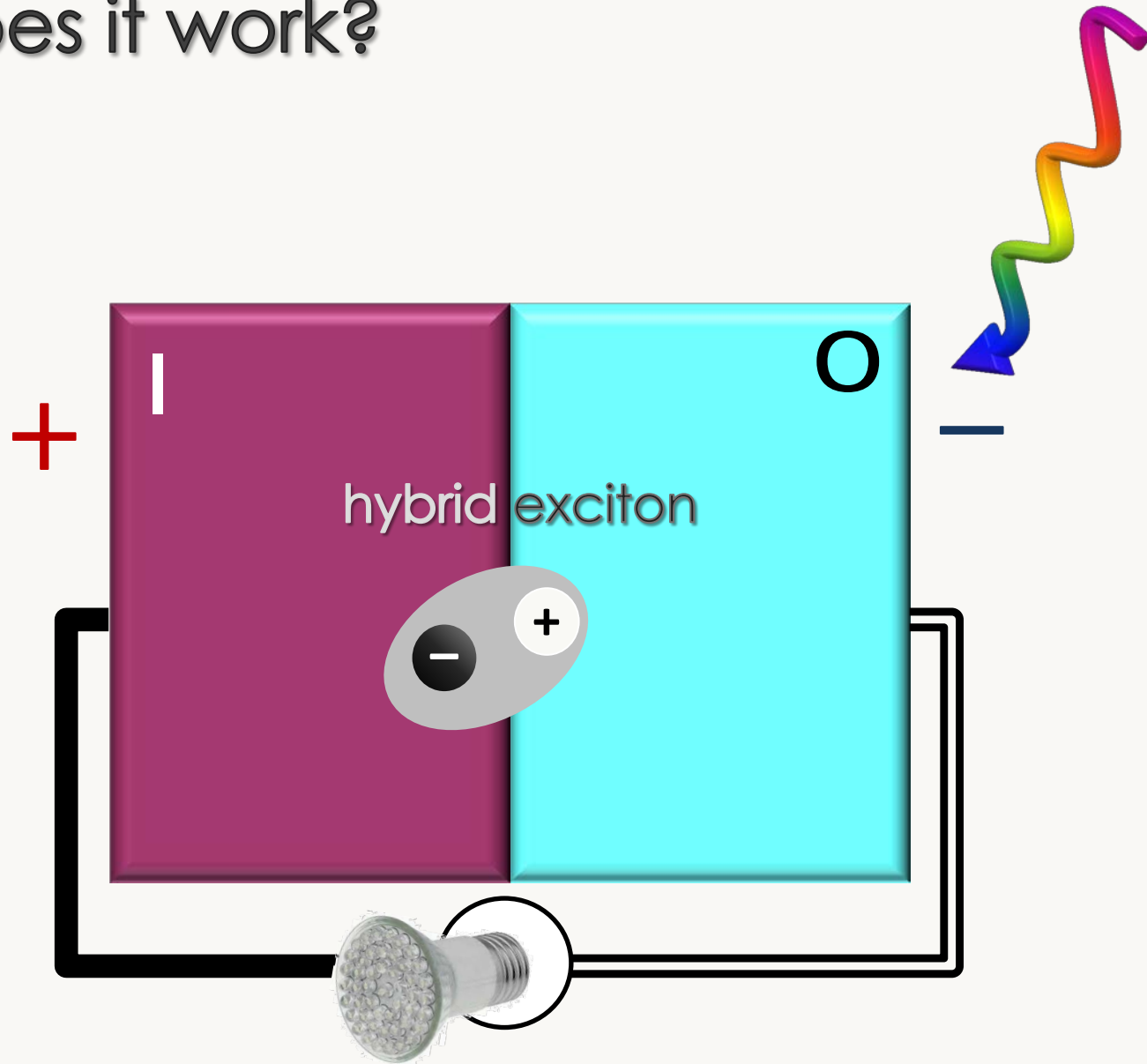
*Photovoltaics*

# How does it work?



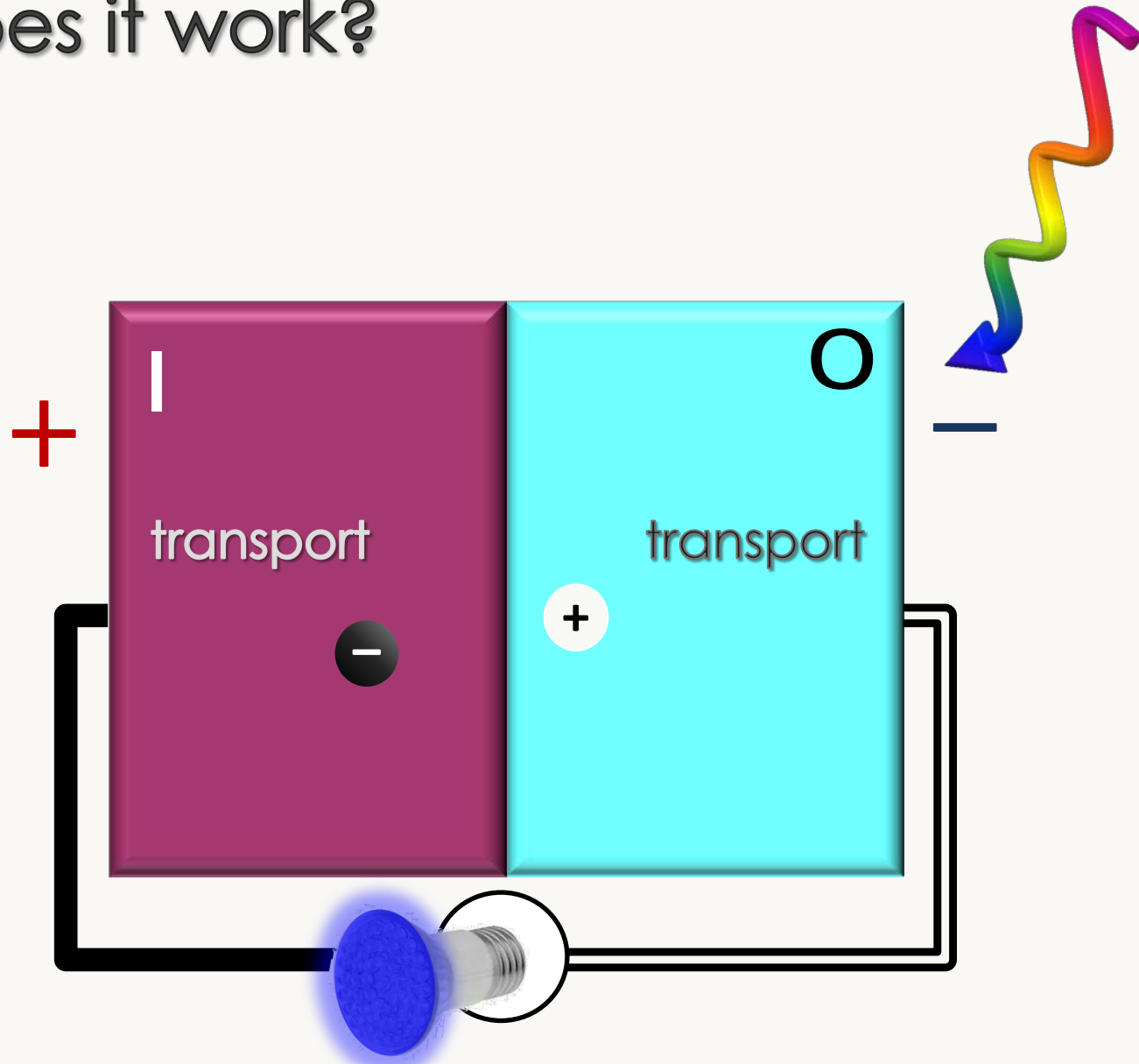
*Photovoltaics*

# How does it work?



*Photovoltaics*

# How does it work?



*Photovoltaics*

*How to describe hybrid materials?*

hybrid structures

level alignment  
polaronic effects

MBPT  
 $\Sigma$

electronic  
structure

structure

(an)harmonic  
vibrations

optical  
properties

MBPT  
BSE@GW

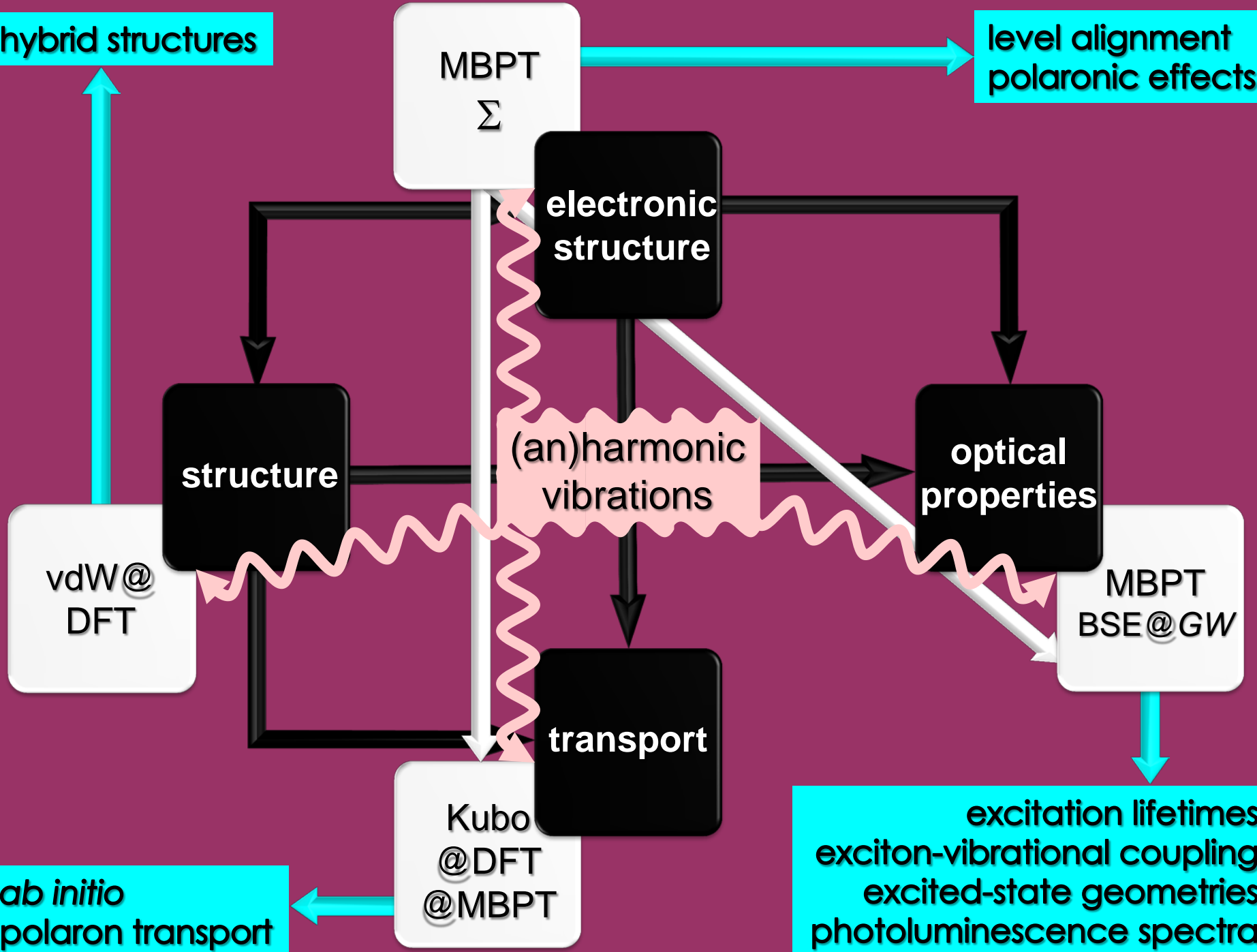
vdW@  
DFT

transport

Kubo  
@DFT  
@MBPT

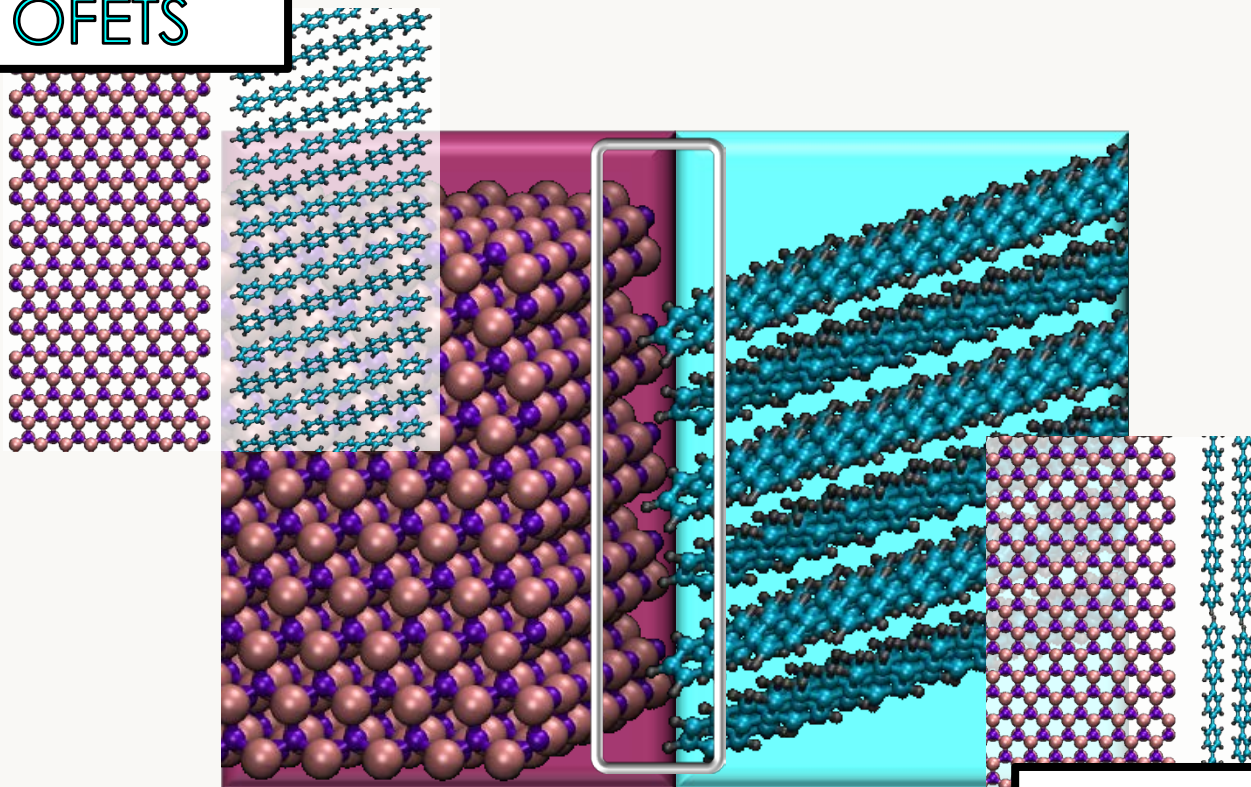
excitation lifetimes  
exciton-vibrational coupling  
excited-state geometries  
photoluminescence spectra

ab initio  
polaron transport



*How good is our understanding?*

Typical for  
OFETS

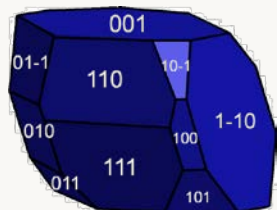


Typical for  
opto-electronics

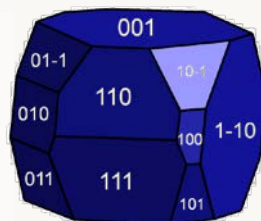
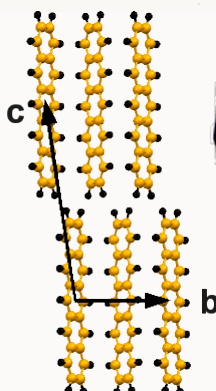
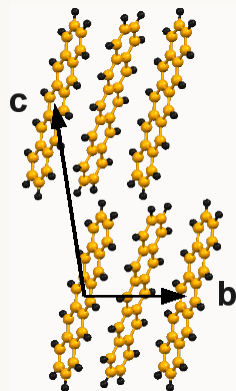
*Structure*

# Polymorphism

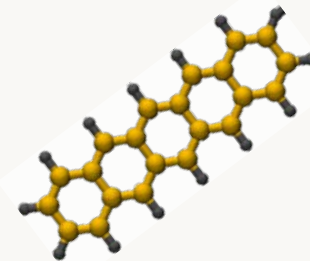
## Pentacene



thin-film phase



bulk phase

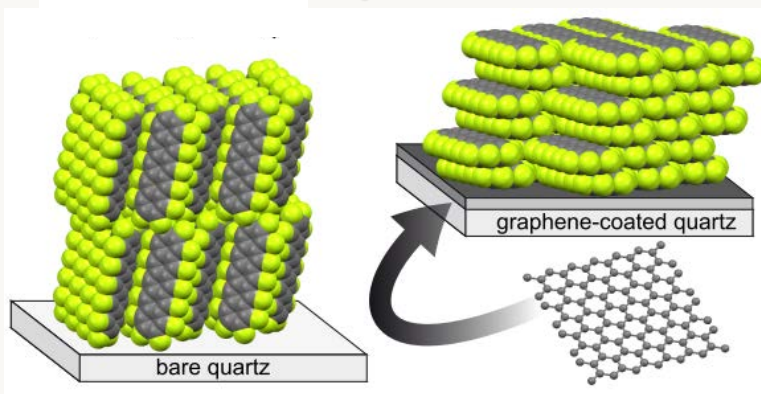


D. Nabok, et al.,  
PRB 76, 235322 (2007).

CAD, et al.,  
New J. Phys. 11, 125010 (2009).

Structure solution

## Perfluoro-pentacene on graphene-coated quartz



New polymorph  
Small  $\pi$ -stacking distance  
Large dispersion  
Perspective to vertical transport

I. Salzmann, et al., ACS Nano 6, 10874 (2012).

# Interplay between ...

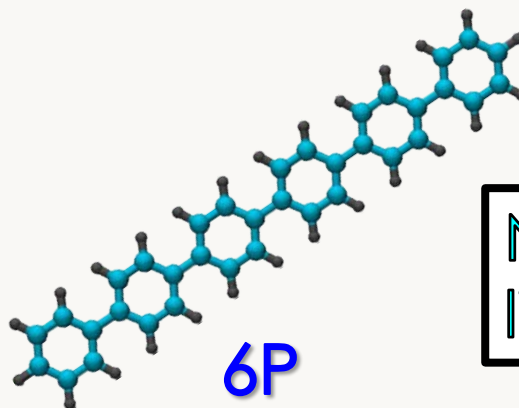
## intermolecular and molecule-substrate interaction

Ordered structure  
Metal/molecule junctions - electrodes

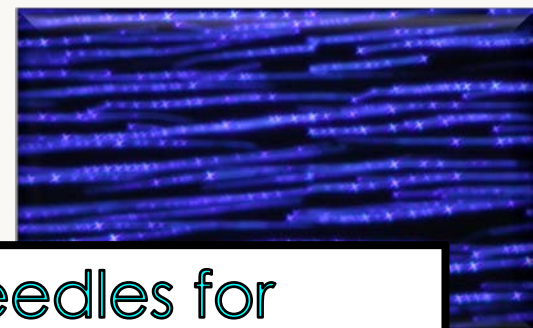


STM  
Cu(110)

M. Ramsey et al.  
Science 2009, PCCP (2011).

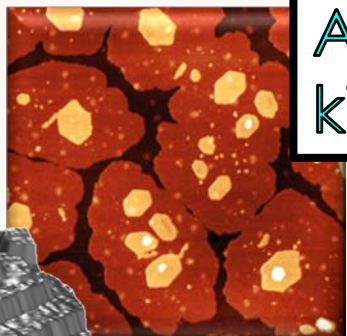


C. Simbrunner et al.  
JACS 133, 3056 (2011).



Nanoneedles for  
light-emitting devices

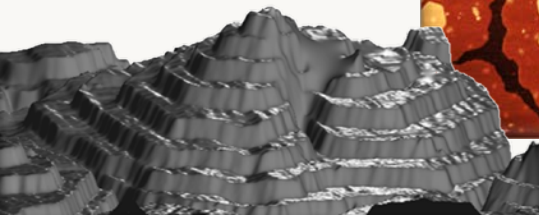
AFM  
disordered mica



Amorphous substrates:  
kinetic effects

Ch. Teichert et al.

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

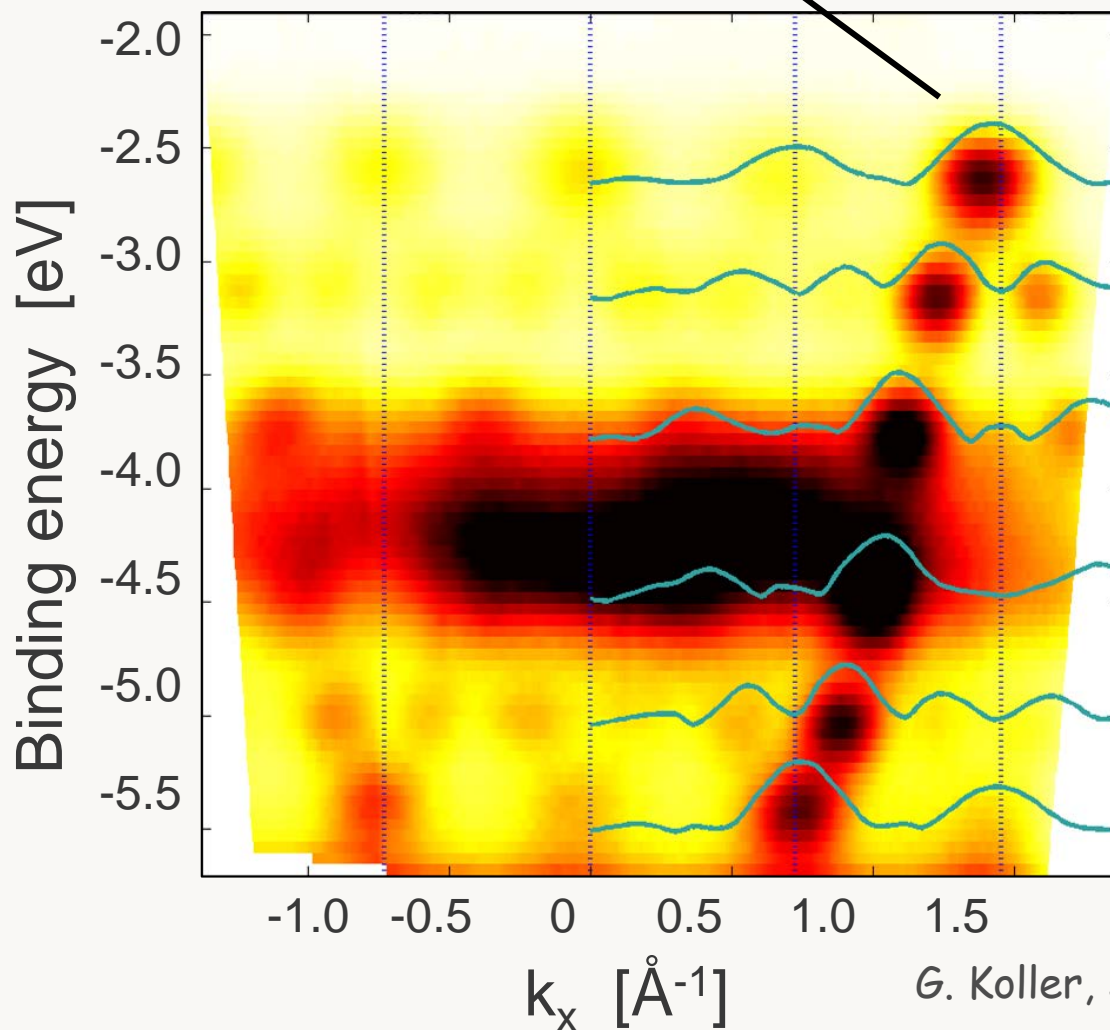


# Intramolecular bandstructure

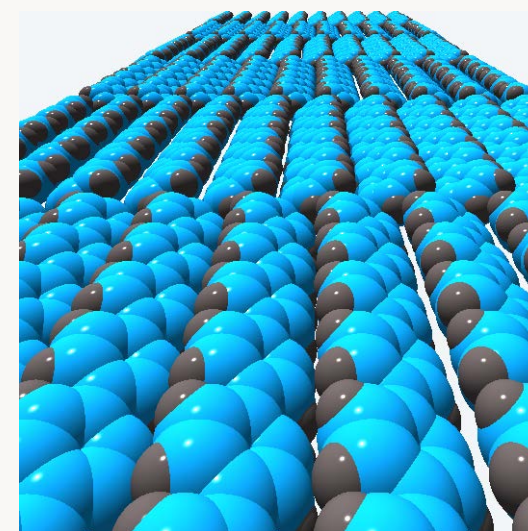
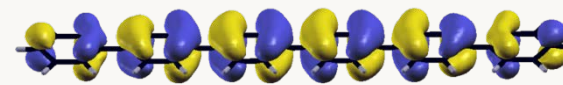
$h\nu=21\text{eV}$

One-step model

$$I_i(\theta, \phi) \sim |\mathbf{A}\cdot\mathbf{k}|^2 |\tilde{\psi}_i(\mathbf{k})|^2$$

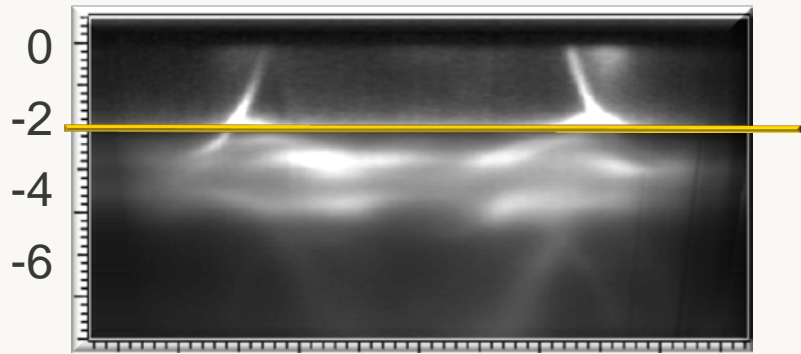


Fourier transform

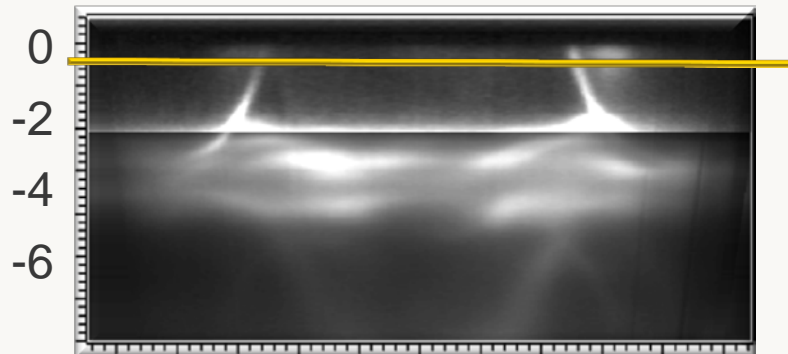


$6\text{P}@Cu(110)(2\times 1)\text{O}$   
thick film

G. Koller, S. Berkebile, M. Oehzelt, P. Puschnig, CAD, F. P. Netzer, and M. G. Ramsey, Science 317, 351 (2007).

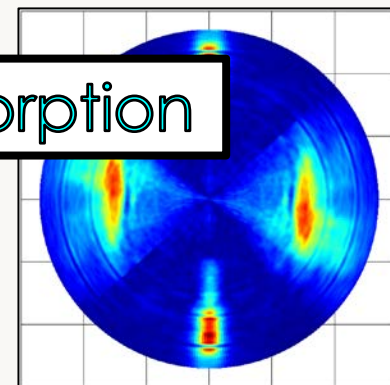
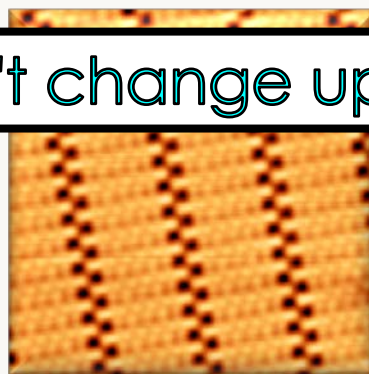
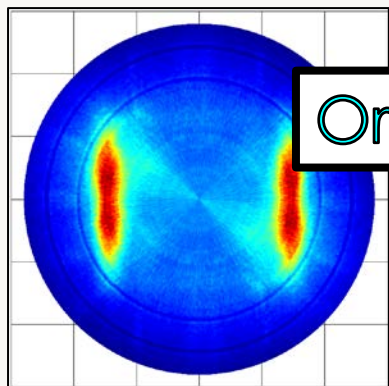


HOMO



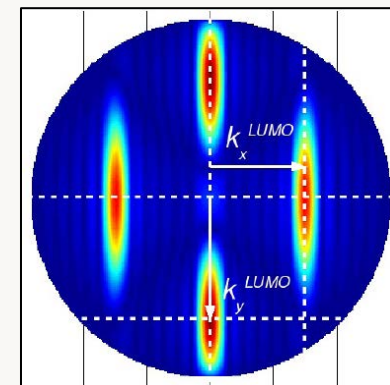
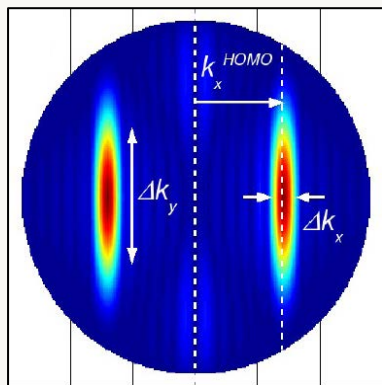
filled LUMO

Orbitals don't change upon adsorption



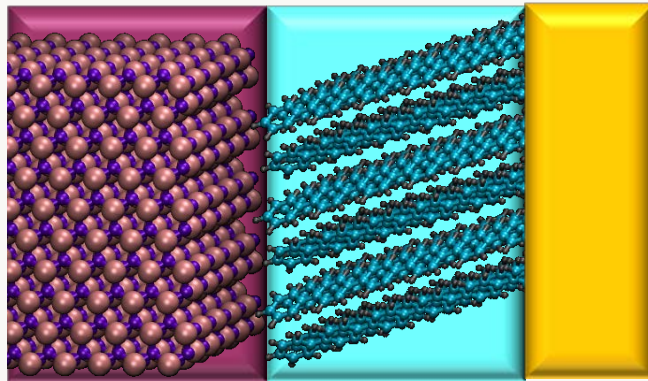
## 6P monolayer on Cu(110)

### Theory



S. Berkebile, et al., PCCP 13, 3604 (2011).  
 P. Puschnig, et.al., Science 326, 702 (2009).

# Challenges ...

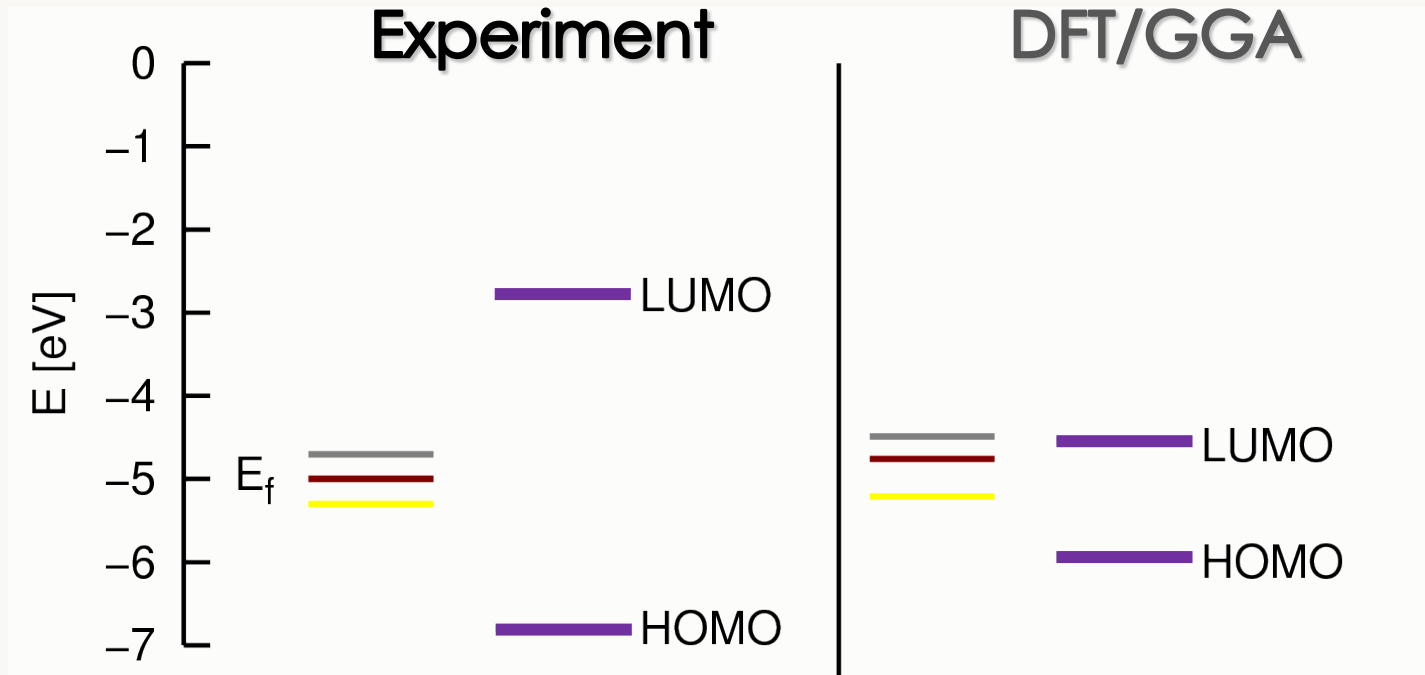
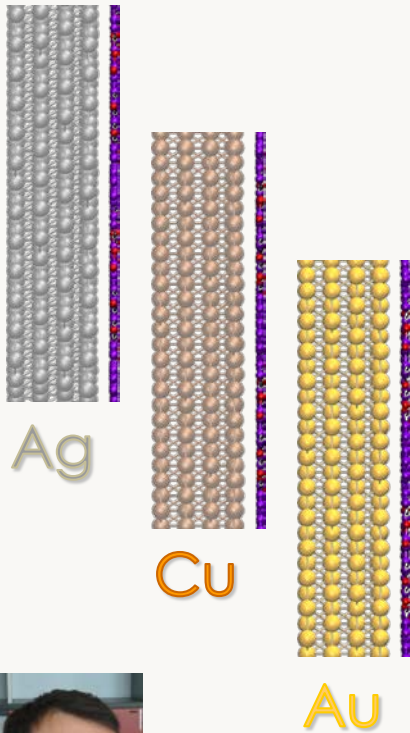
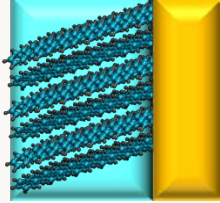


*Electronic structure*

# Organic / metal interface

## HOMO-LUMO position relative to Fermi level

### PTCDA@Me(111)



F.S. Tautz,  
Prog. Surf. Sci. 82, 479 (2007).

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

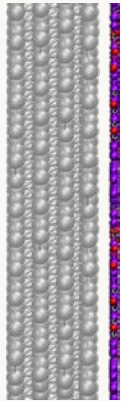
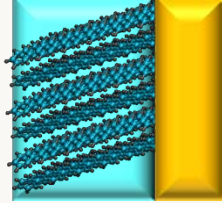
*Level alignment*



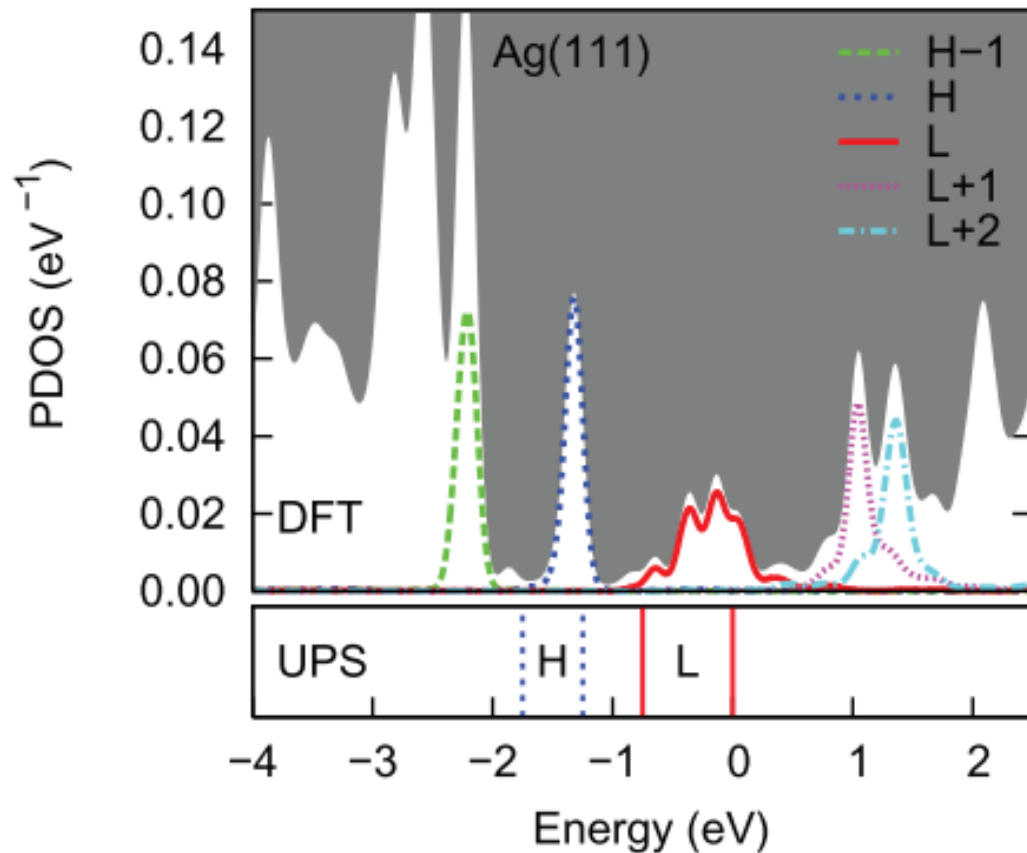
# Organic / metal interface

## HOMO-LUMO position relative to Fermi level

### PTCDA@Me(111)



Ag



DFT/GGA

— LUMO

— HOMO

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

*Level alignment*

# Organic / metal interface

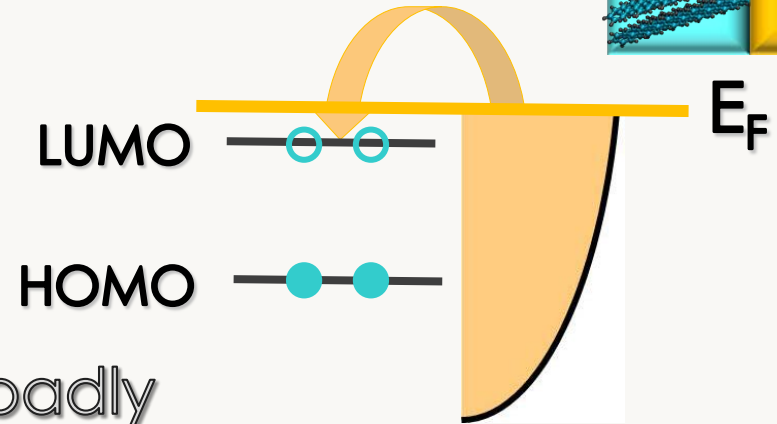
## HOMO-LUMO position relative to Fermi level

Popular xc functionals may fail badly  
Spurious charge transfer at large distances  
Starting-point problem for GW calculations

## Image-charge effects

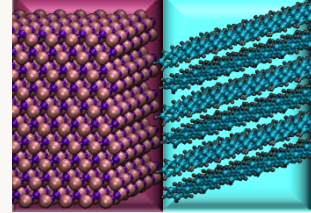
Not captured by semilocal DFT functionals

## Role of electron-vibrational coupling



*Level alignment*

# Inorganic / organic interface



## Individual self-interaction errors on both sides

How to tune amount of exact exchange in hybrid functionals?

## Role of zero-point vibrations

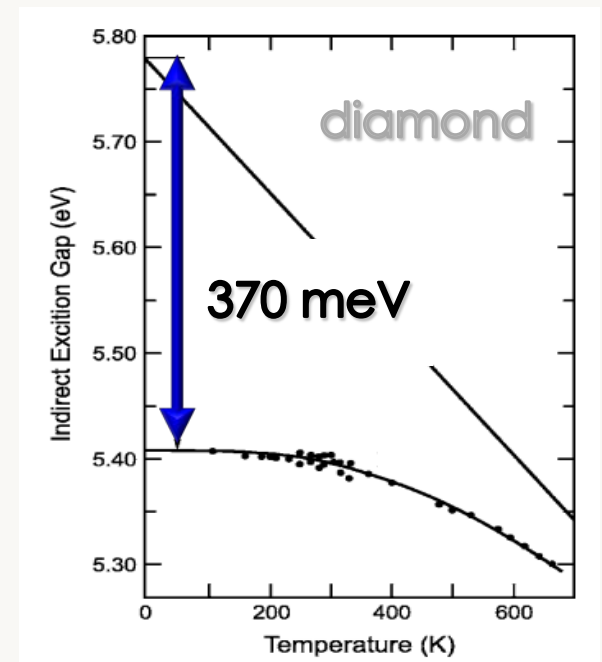
F. Giustino, et al., PRL 105, 265501 (2010)

**direct gap: 600 meV**

X. Gonze, A. Marini (2013)

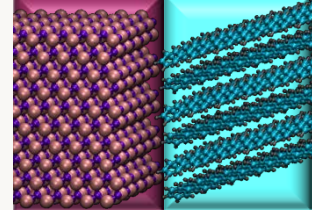
**direct gap: 400 meV**

M. Cardona and M.L.W. Thewalt  
Rev. Mod. Phys. 77 (2005).



*Level alignment*

# Inorganic / organic interface

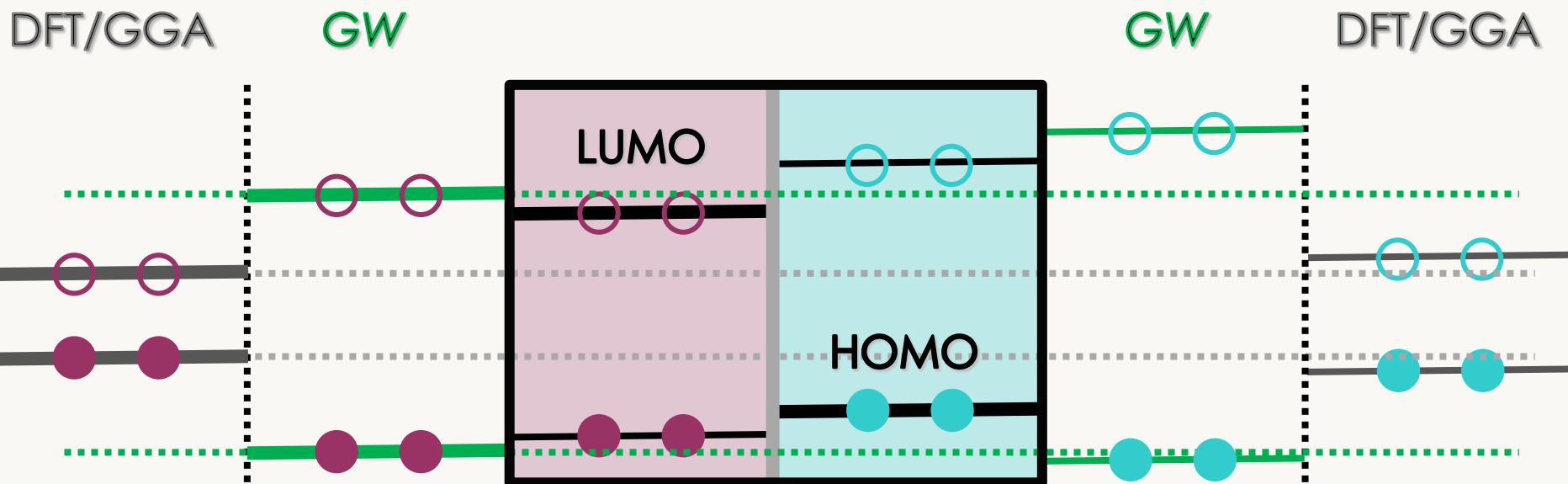


## Individual self-interaction errors on both sides

How to tune amount of exact exchange in hybrid functionals?

*Worst-case scenario*

## Role of zero-point vibrations



*Level alignment*

*A particular example*

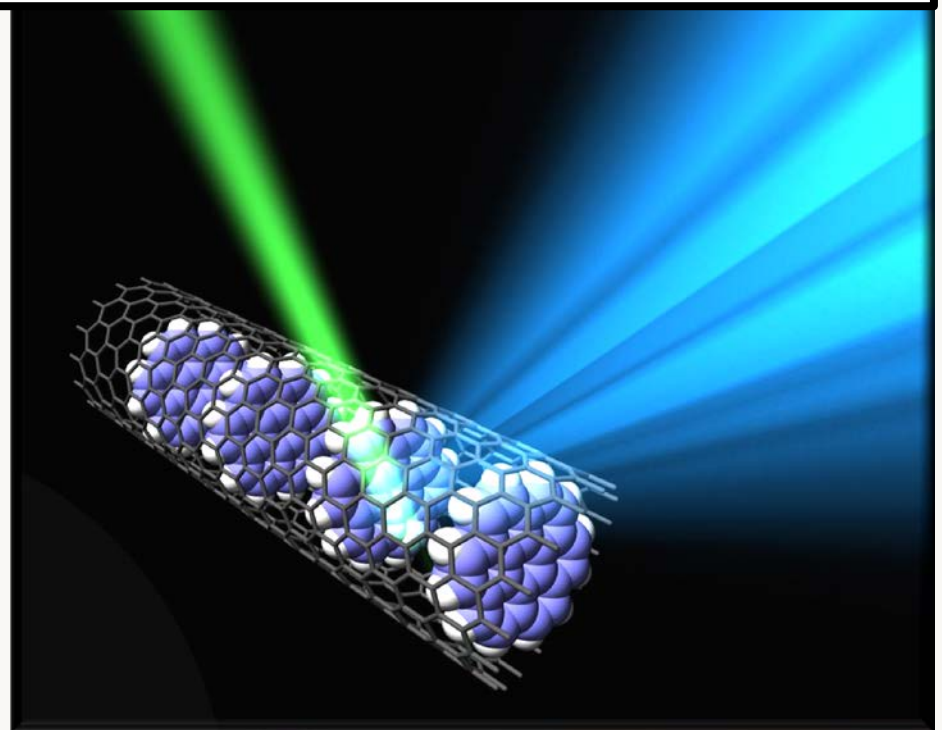
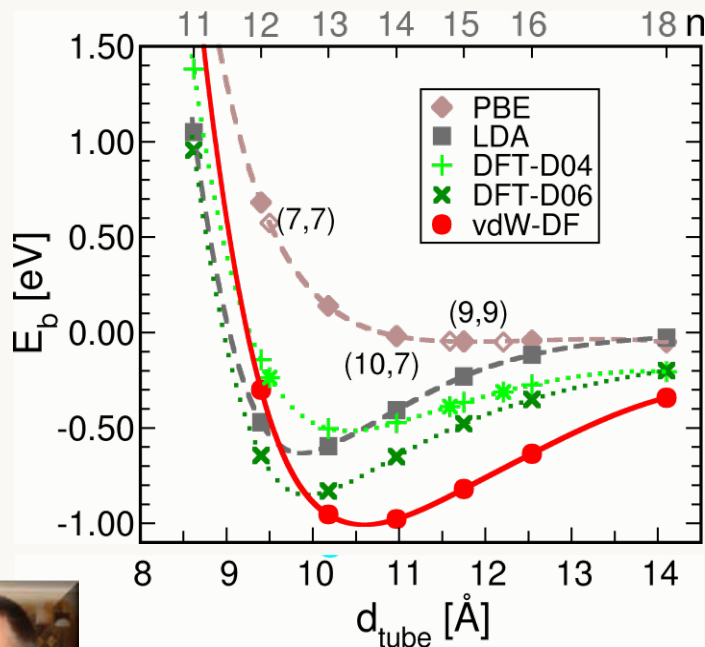
# Light-emitting nano-peapods

## Prediction of stability – experimental realization

ZPV have small effect on cohesive energies



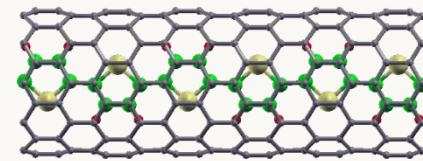
benzene@CNT



M. Milko and CAD,  
Phys. Rev. B 84, 085437 (2011).

M. A. Loi, et al., Adv. Mater. 22, 1635 (2010).  
J. Gao, et al., Small 7, 1721 (2011).

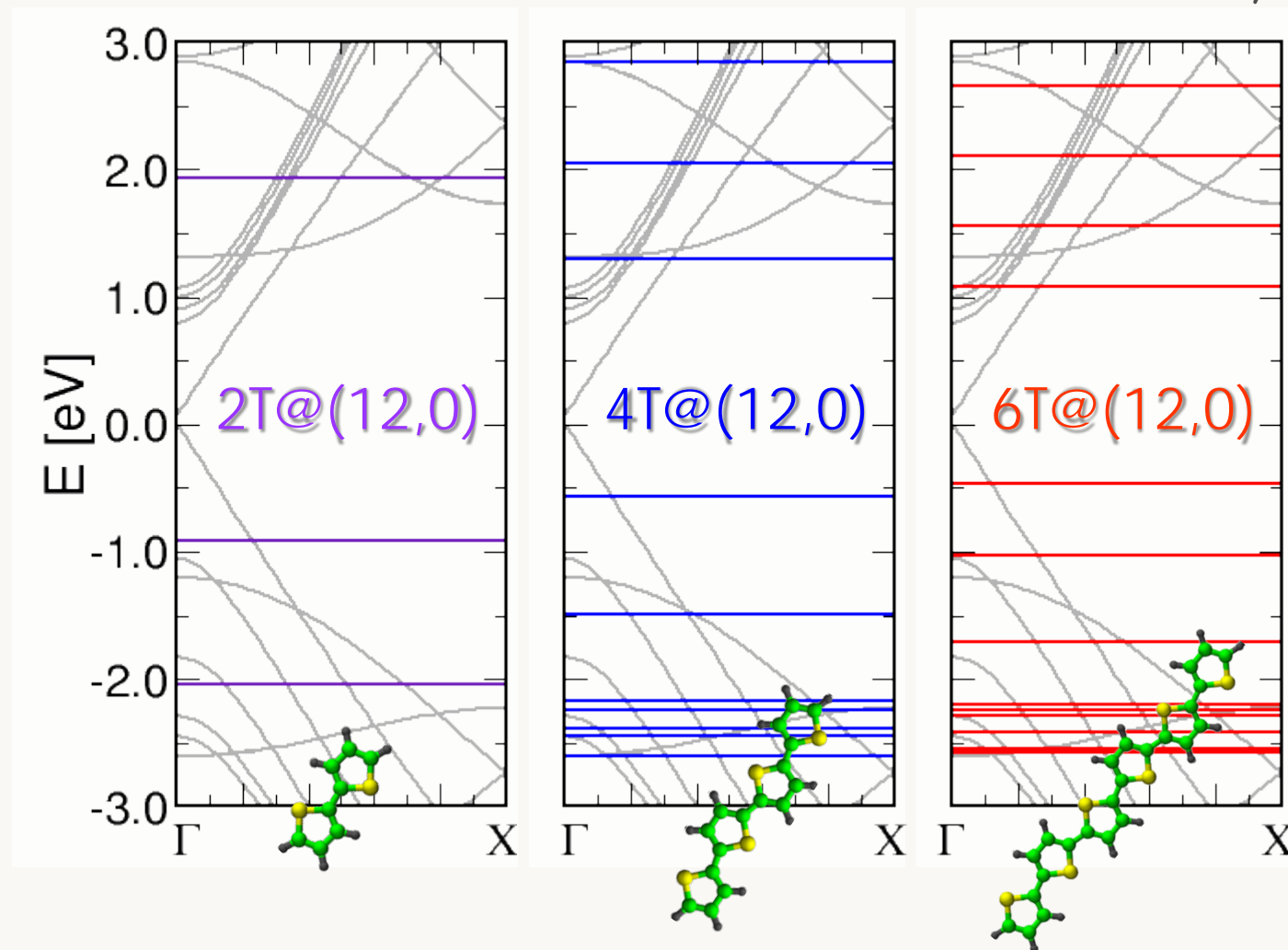
# Electronic structure



Level alignment governed by charge asymmetry

stemming from the tube curvature

J. Gao, et al.,  
Small 7, 1721 (2011).



Obviously, ...

due to the vdW binding, we can predict the electronic structure of the hybrid material simply by the properties of its constituents

... Or is there anything else?

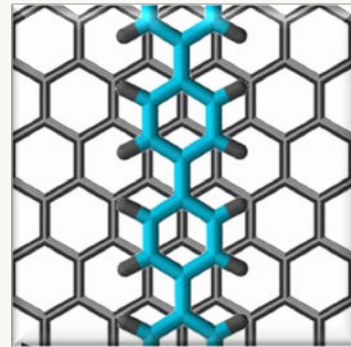
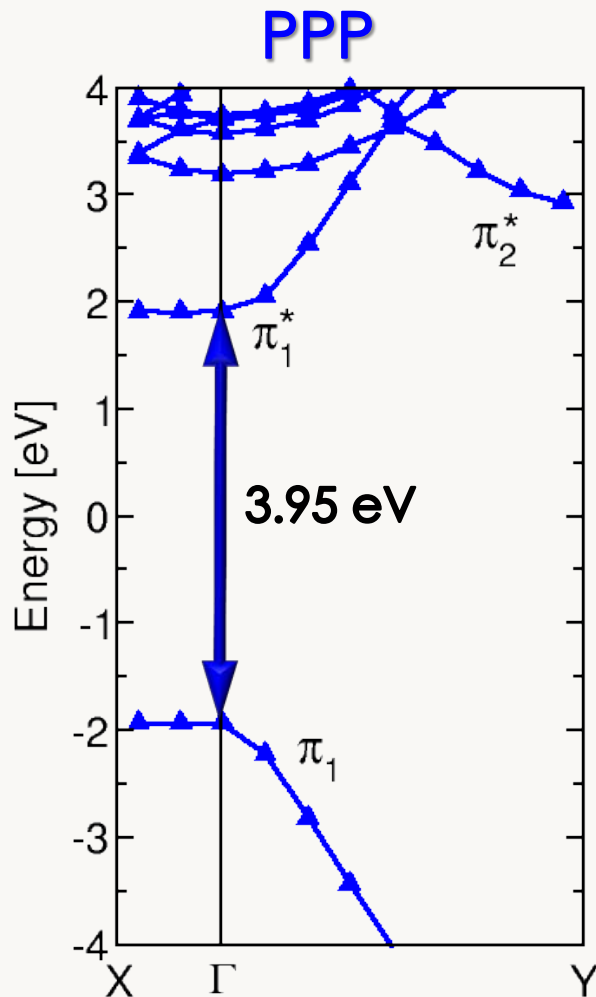
# PPP on graphene

$G_0W_0@LDA$

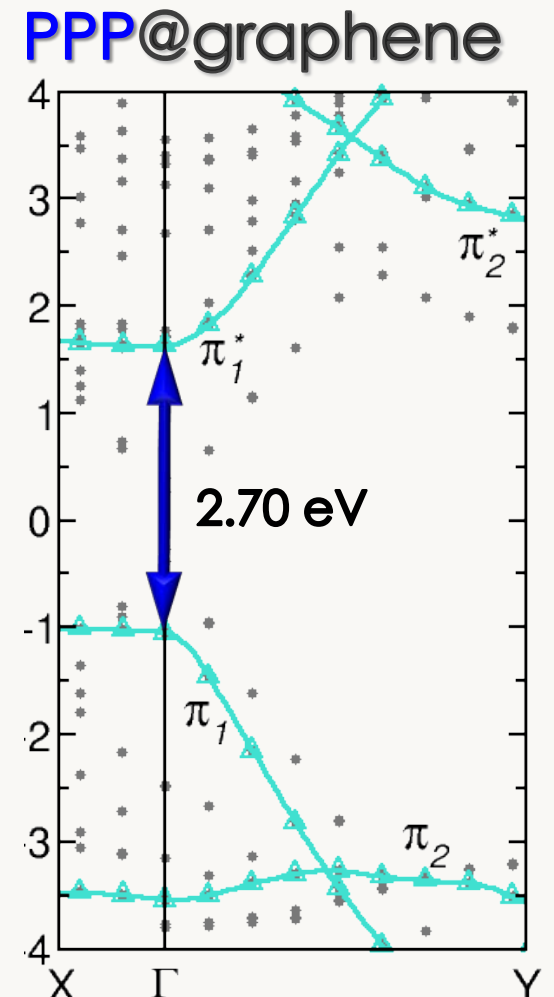
Decrease of gap on adsorption

see J. Neaton *et al.*,  
PRL 97, 216405 (2006).

image-charge effect



P. Puschnig, P. Amiri & CD  
PRB 86, 085107 (2012).



*Optical excitations*

# Bethe-Salpeter equation

Two-body equation

$$\left[ H_e + H_h + H_{e-h} \right] \phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = E_\lambda \phi_\lambda(\mathbf{r}_e, \mathbf{r}_h)$$

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e) \psi_v(\mathbf{r}_h)$$

$$\sum_{c'v'k'} H_{cvk, c'v'k'}^{e-h} A_\lambda^{c'v'k'} = E_\lambda A_\lambda^{cvk}$$

# atoms

# atoms

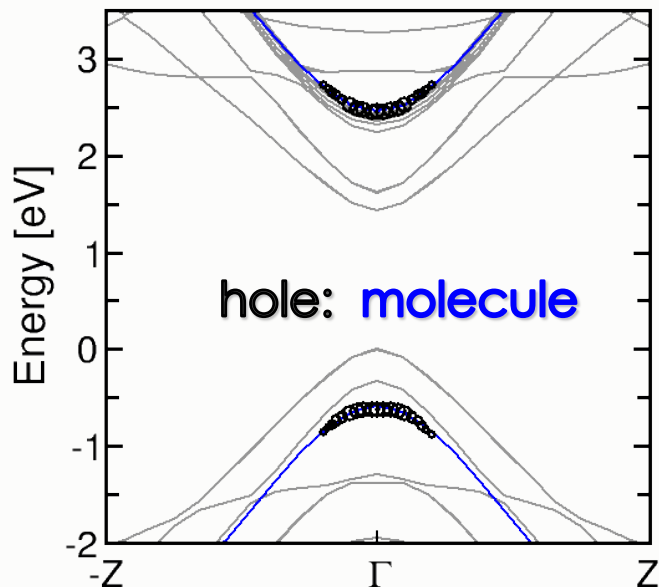
# k-points

# q-points (k-k')

degree of localization

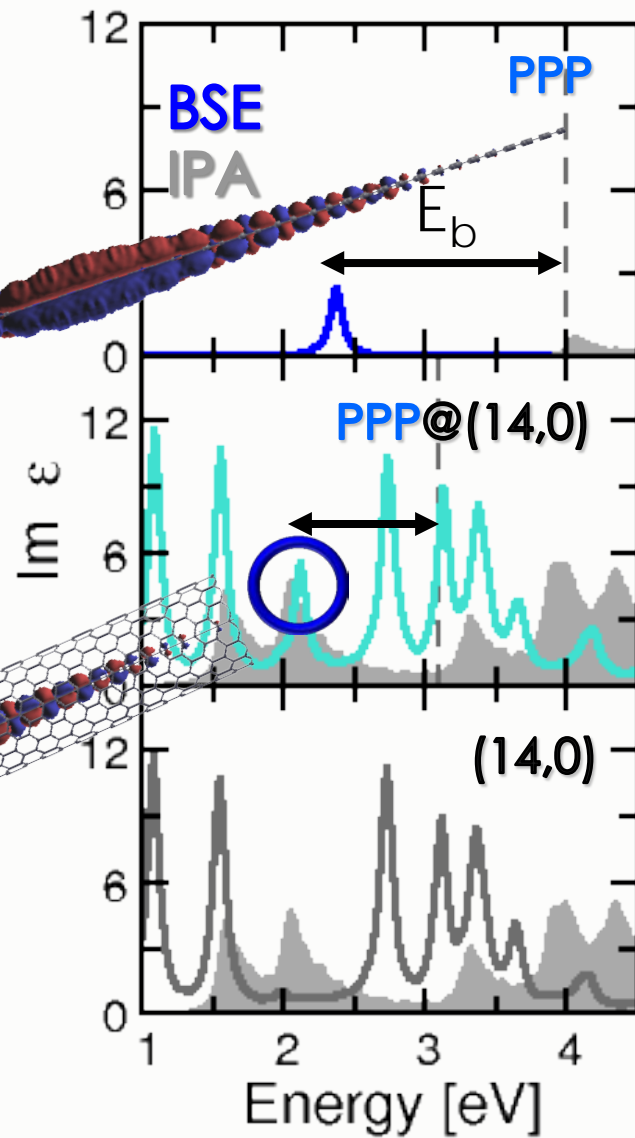
# BSE@GW

electron: CNT & molecule



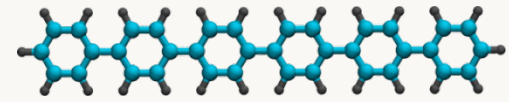
Hybrid exciton

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e) \psi_v(\mathbf{r}_h)$$

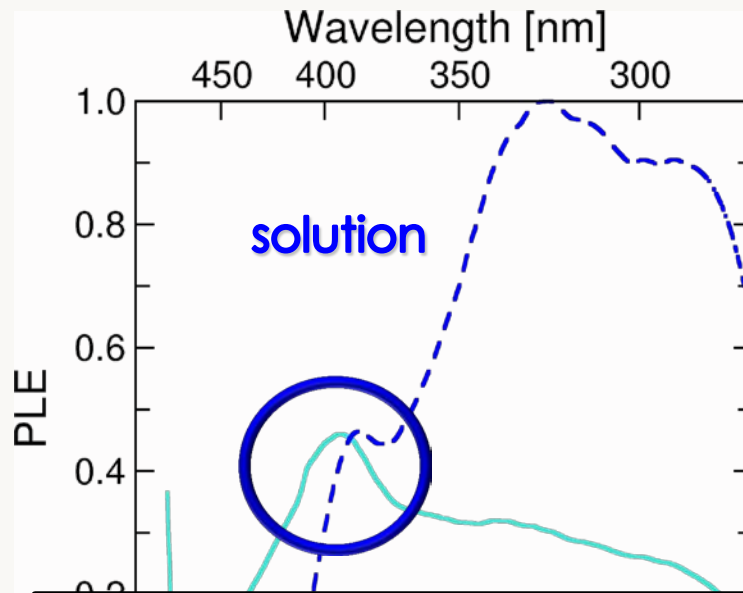


*Optical excitations*

# Optical spectroscopy



strong PL signal, but reduced lifetime



Many-body theory (BSE)

explanation:  
formation of hybrid exciton

Compensation of 2 effects to large extent:

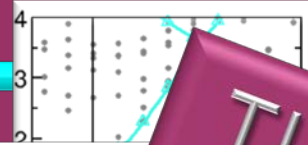
**Red**-shift due to smaller band gap

**Blue**-shift due to exciton delocalization

*Summarizing ...*

hybrid structures

MBPT



level alignment  
polaronic effects

THANKS !!

Many steps towards a quantitative understanding of hybrid materials ...

Single aspects are well understood

Predictive power requires new methodology

Systematic experimental investigations are as important

A lot of work in front of us – and we enjoy it!

ground state geometries  
polaron transport

@MBPT

excited state geometries  
photoluminescence spectra