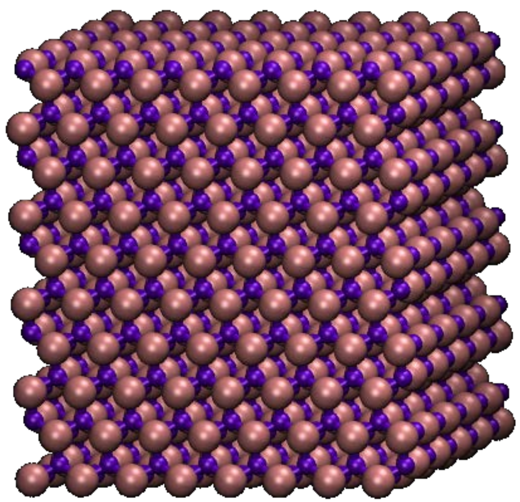
Claudia Draxl
Humboldt-Unversität zu Berlin

Organic molecular materials for light-emitting applications: a first-principles view

Inorganic vs organic semiconductors

G. Grem, G. Leditzky, B. Ullrich, G. Leising, Realization of a blue-light-emitting device using poly(p-phenylene), Adv. Mat. 4, 36 (1992).



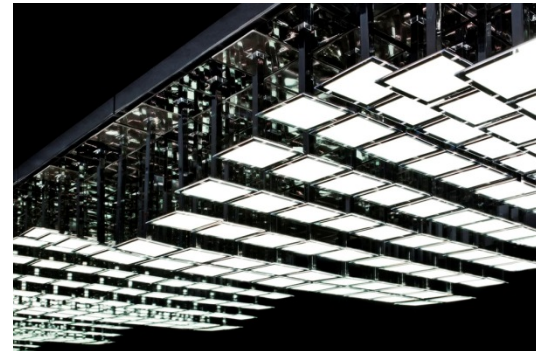
S. Nakamura, T. Mukai, and M. Senoh, Candela-Class High-Brightness InGaN/AlGaN Double-Heterostructure Blue-Light-Emitting-Diodes, Appl. Phys. Lett. 64, 1687 (1994).

Blue-light emitters

Applications

OLED TV

OLED lighting



Philips Lumiblade

Flexible OLED displays

Samsung Galaxy Round

Sony's rollable OLED display

ttp://www.techhive.com/article/197182/Sony_Rollable_Display.html

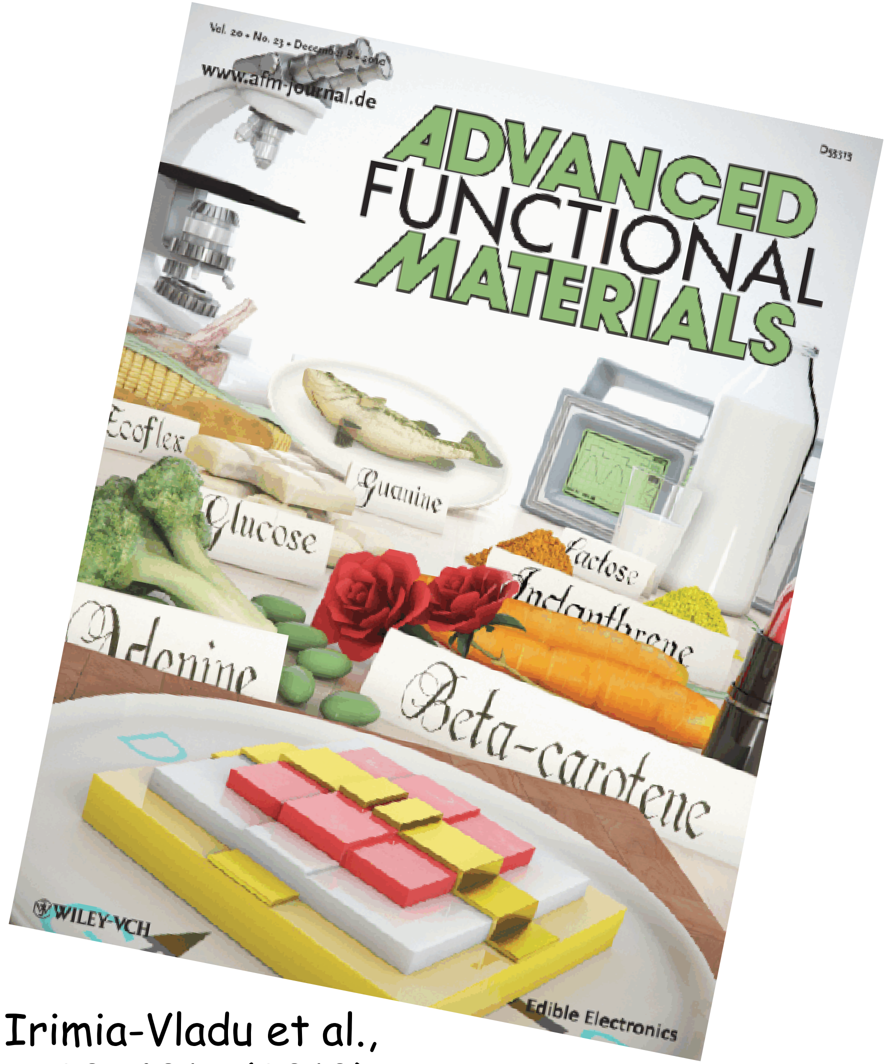
http://www.youtube.com/watch?v=nbTO5VM6s-4

... now

Applications

Edible electronics

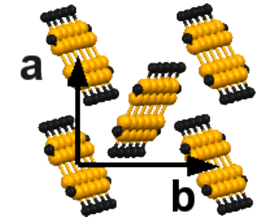
Biocompatible
Biodegradable
Sustainable



M. Irimia-Vladu et al.,
Adv. Mat. 20, 4017 (2010).

... and in the future

Good old friends …



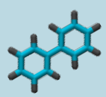
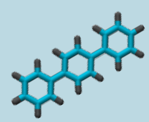
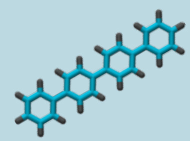
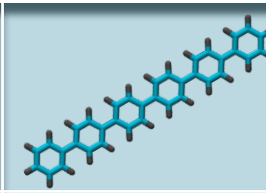
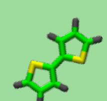
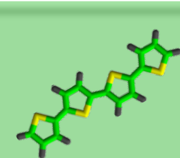
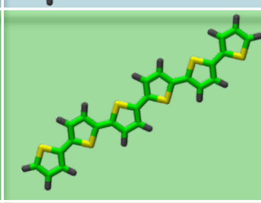
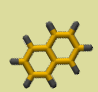
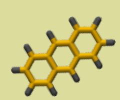
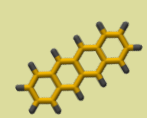
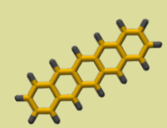
Organic π-conjugated molecules

anisotropic, functionalizeable, herringbone structure

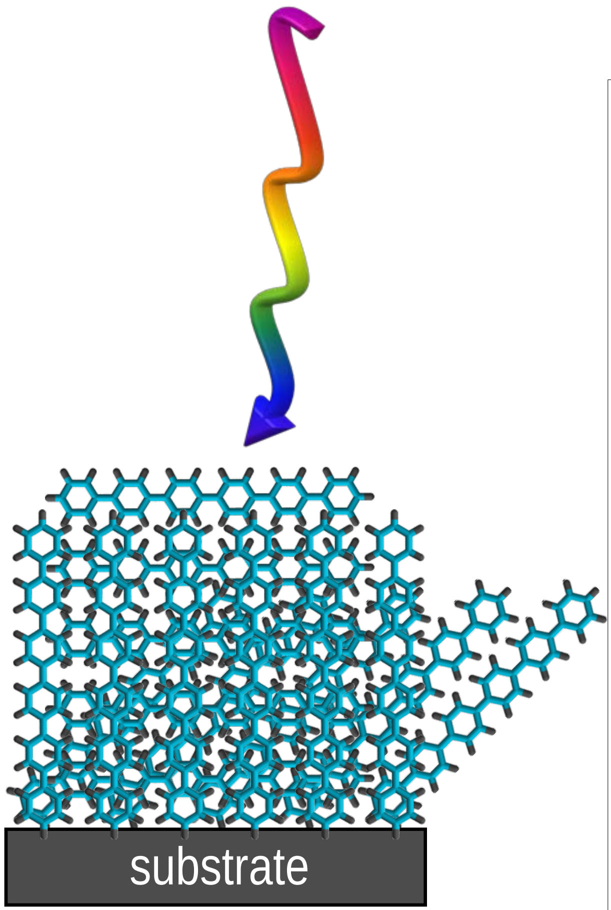
Strong light-matter interaction

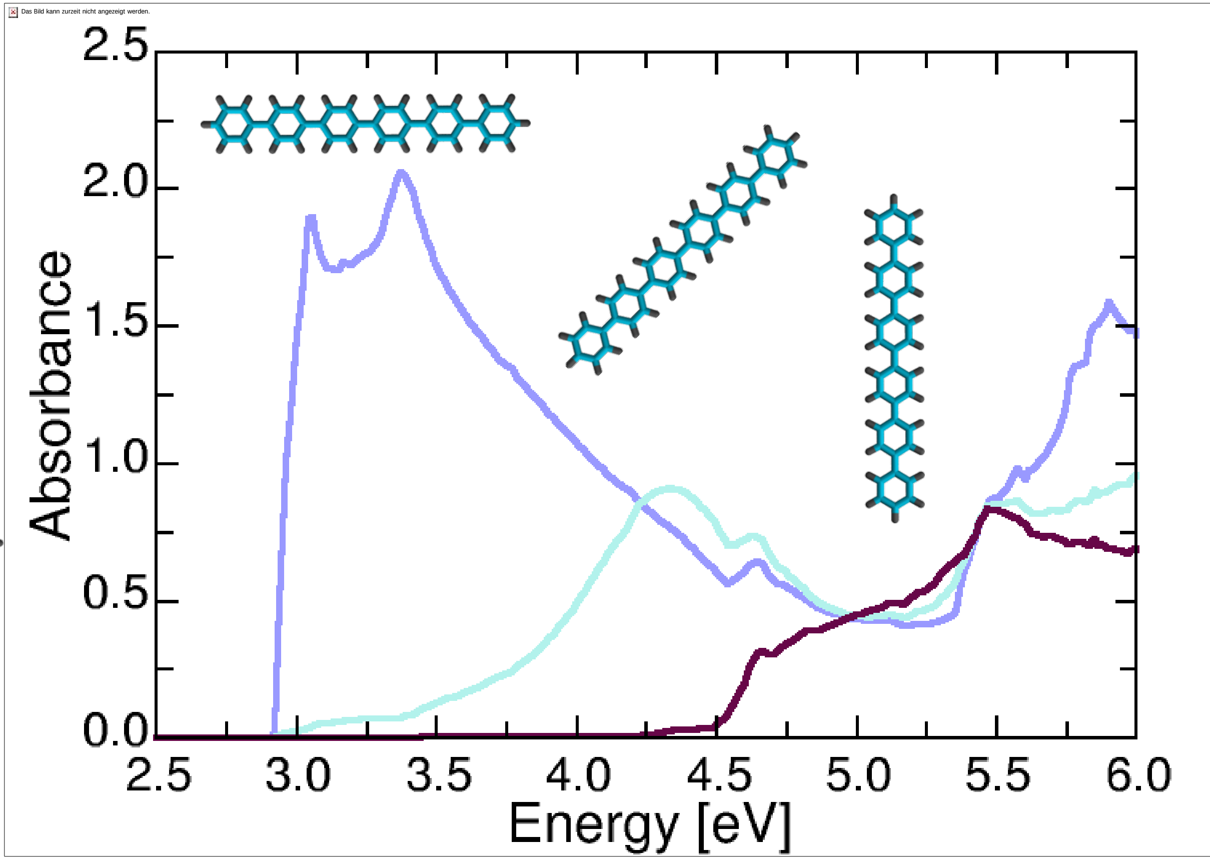
Band gaps in the visible range

scaling like 1/n

# rings, n	2	3	4	5	6
Oligophenyls					
Oligothiophenes					
Oligoacenes					

Anisotropy





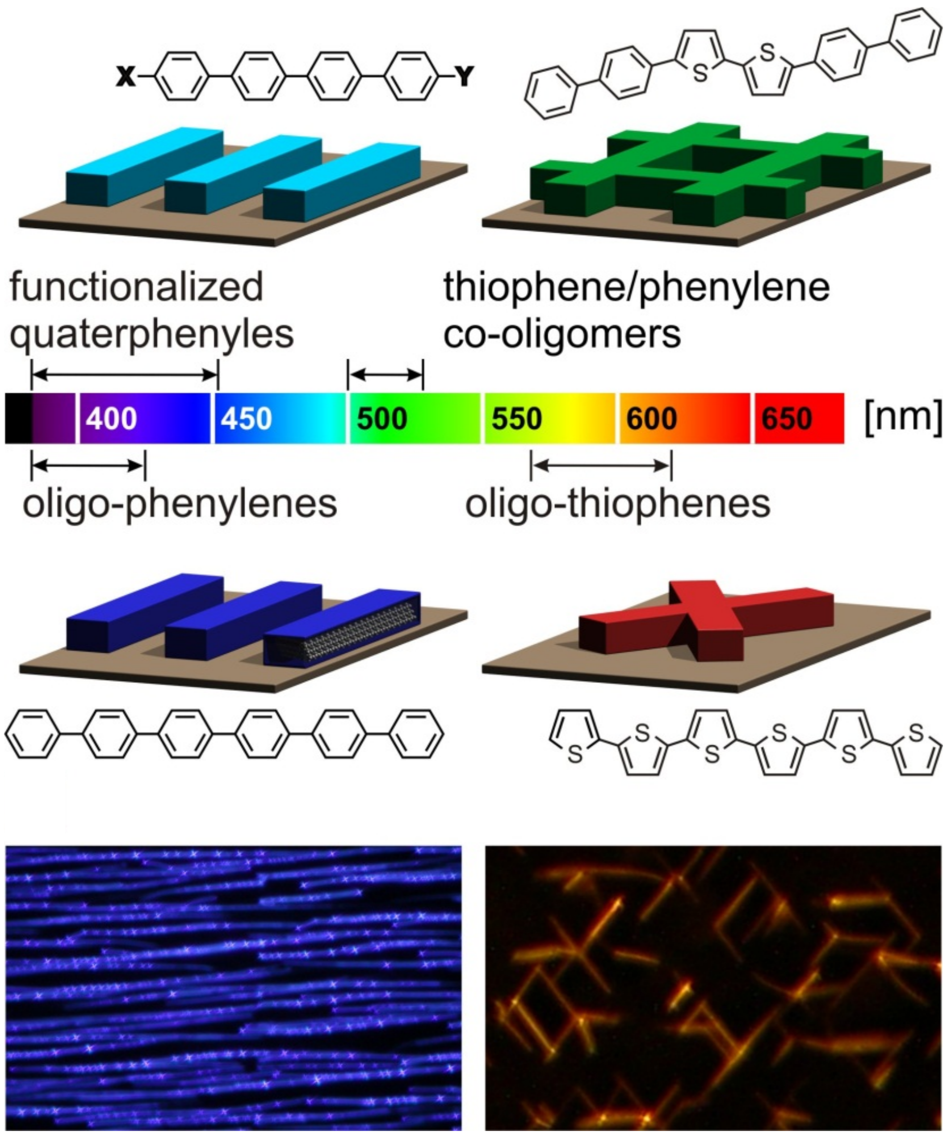
CAD, J. A. Majewski, P. Vogl, and G. Leising, PRB 51, 9668 (1995).
P. Puschnig and CAD, Adv. Eng. Mat. 8, 1151 (2006).
E. Zojer et al., PRB 61, 16538 (2000).

Optical excitations

Role of substrate …

Structure

Light emission



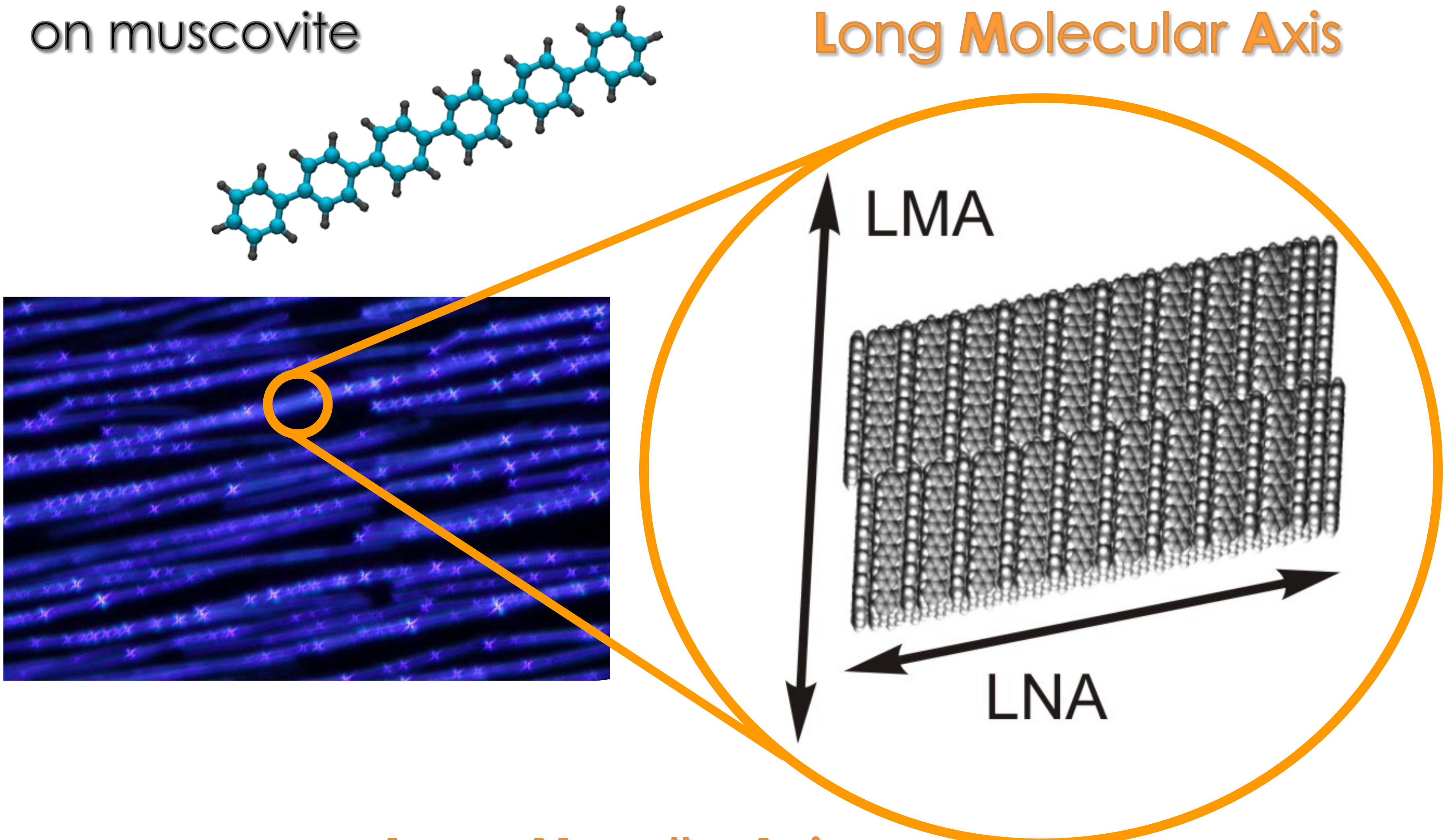
- Nano-needles on muscovite mica
- Parallel alignment only for phenylenes
- Anisotropy for thiophenes and co-oligomers
- Macroscopic polarized light emission only for parallel alignment

Nano-needles

Sexiphenyl

on muscovite

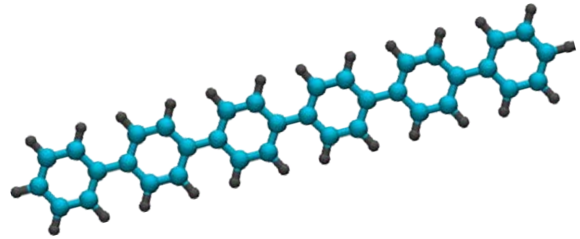
Long Molecular Axis



Long Needle Axis

Nano-needles

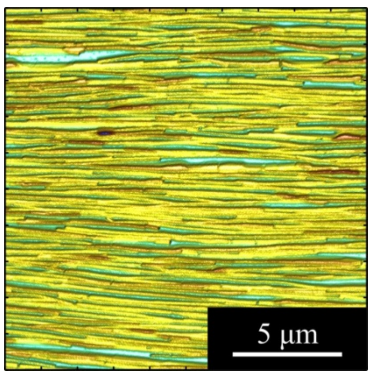
Sexiphenyl

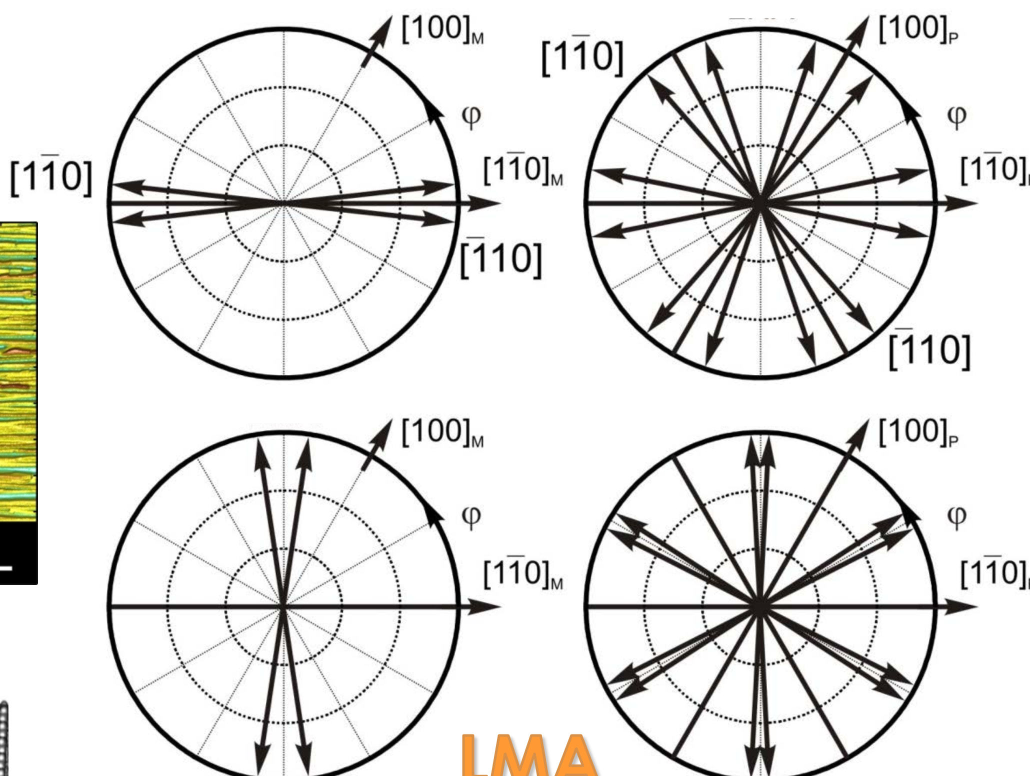


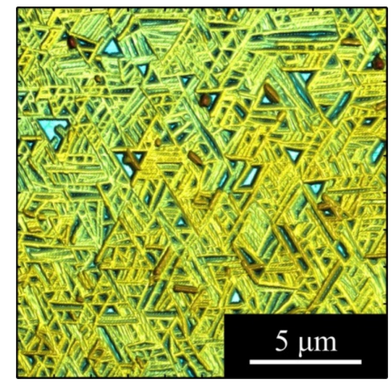
Muscovite

LNA

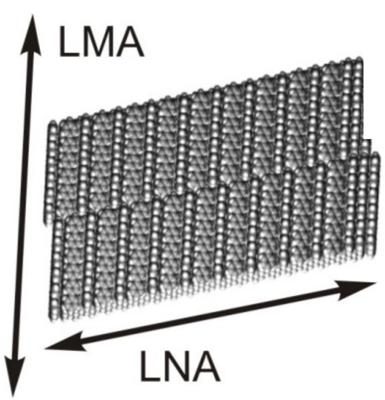
Phlogopite





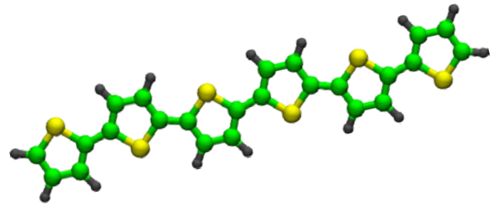


LMA



XRD & AFM

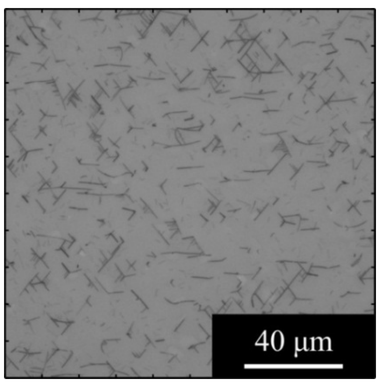
Sexithiophene

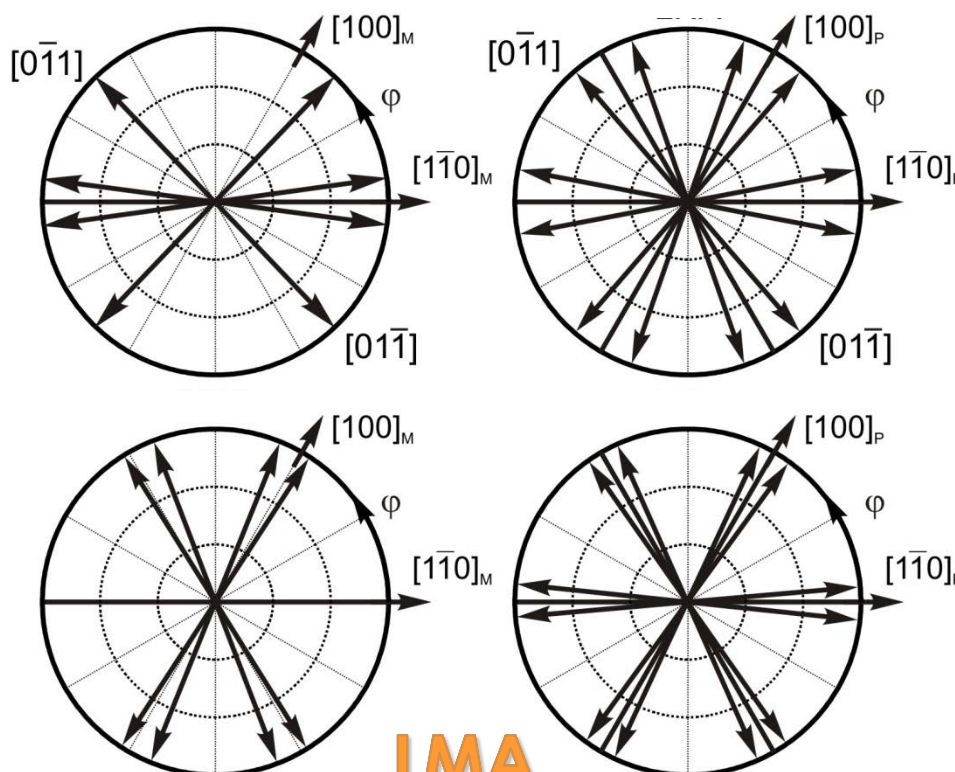


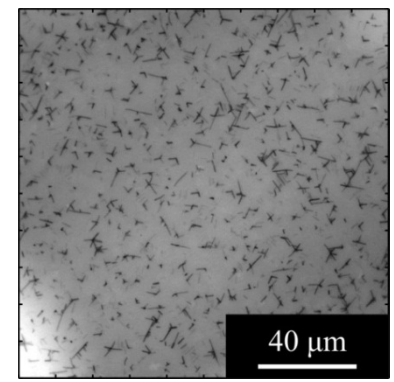
Muscovite

LNA

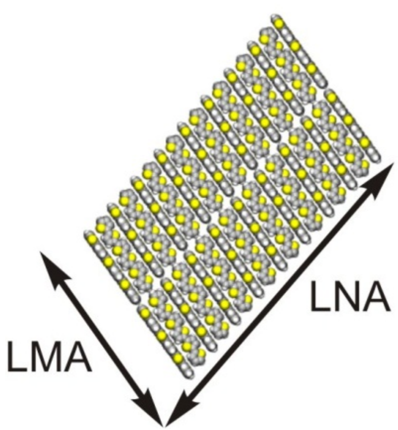
Phlogopite







LMA

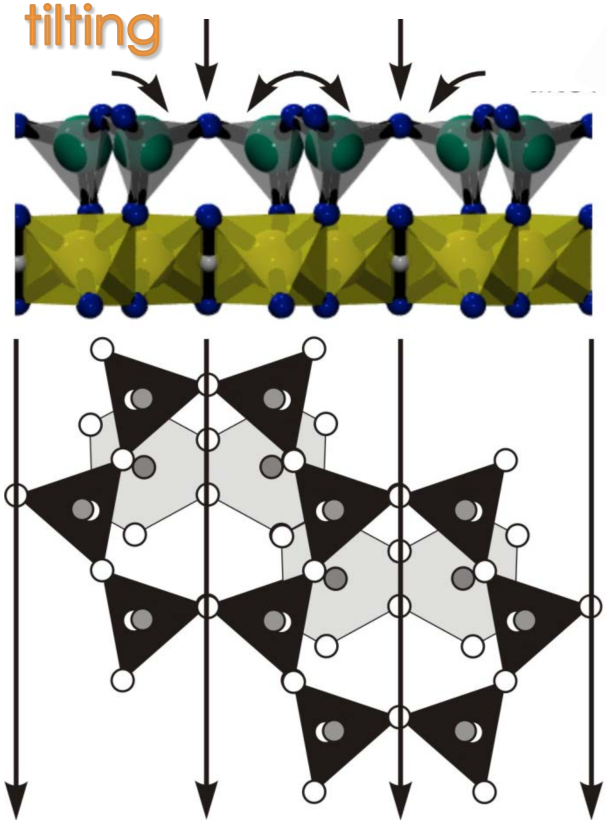


XRD & optical microscopy

Substrates

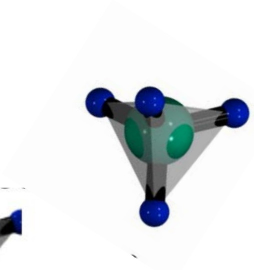
Muscovite

tilting



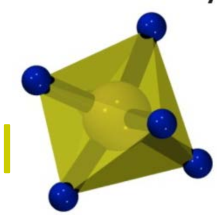
grooves
mirror plane

K



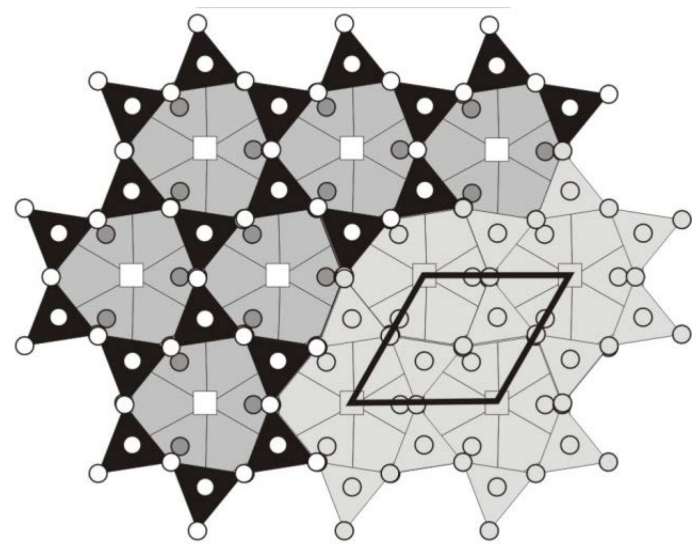
Al , Si

O



Al Mg

Phlogopite



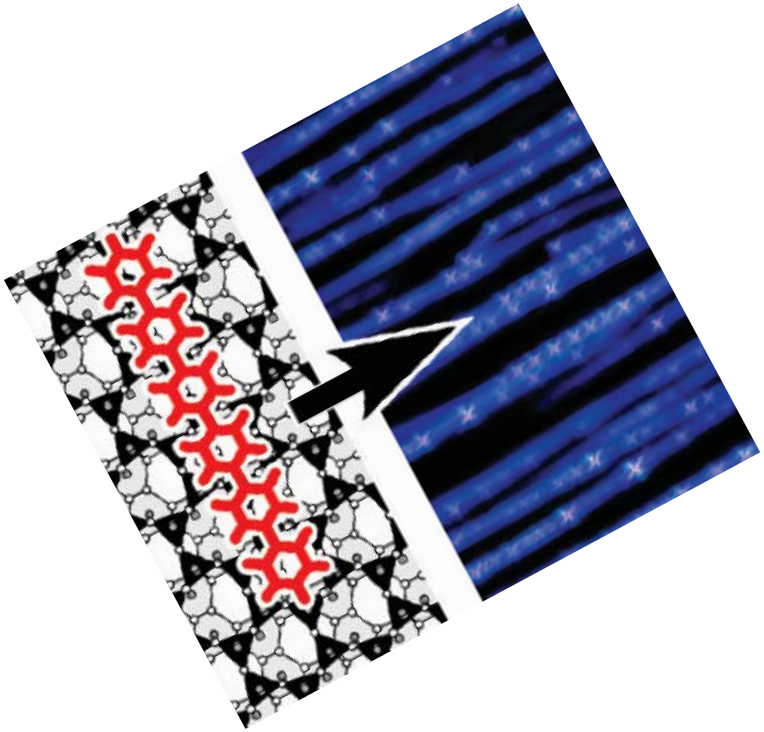
higher symmetry
3-fold axis

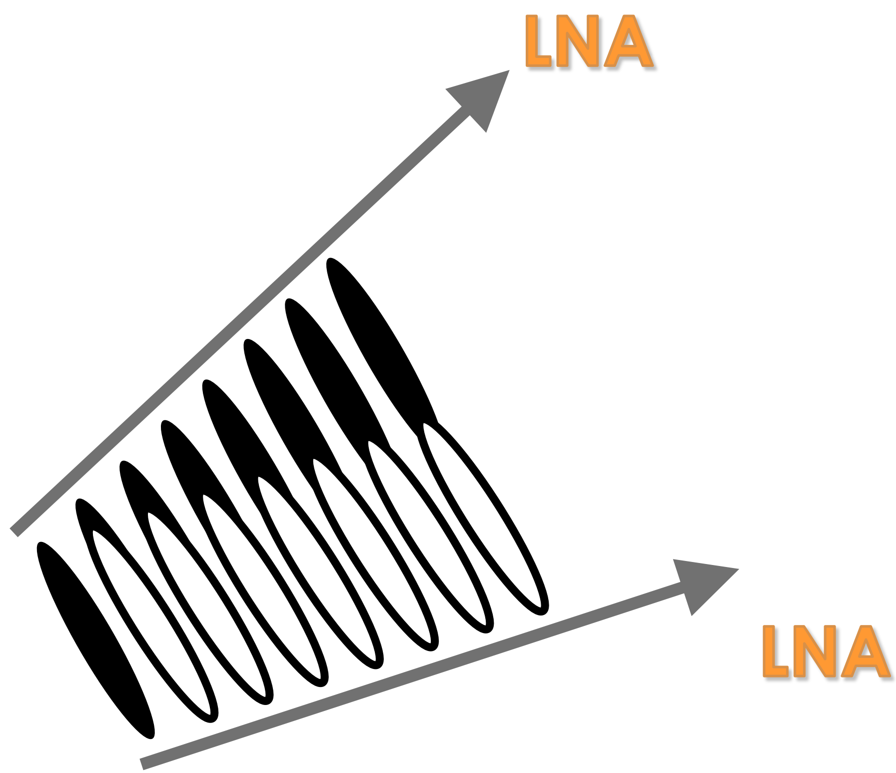
Micas

Orientation and symmetry

For each molecular orientation: 2 needle orientations

due to non-orthogoal surface unit cell

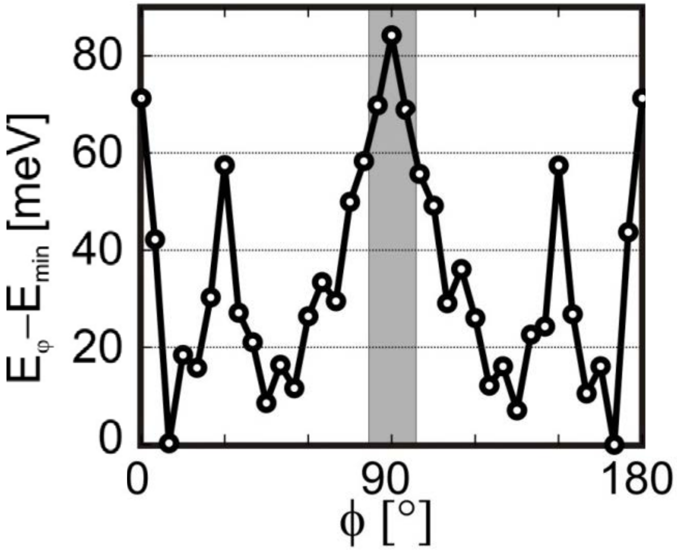


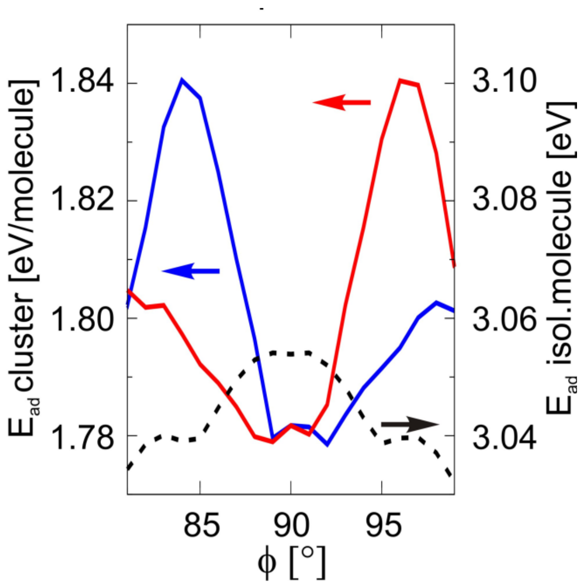


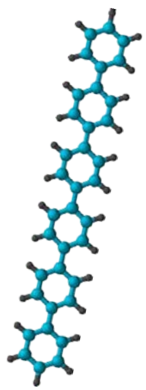
C. Simbrunner, et al. JACS 133, 3056 (2011).

Needle formation

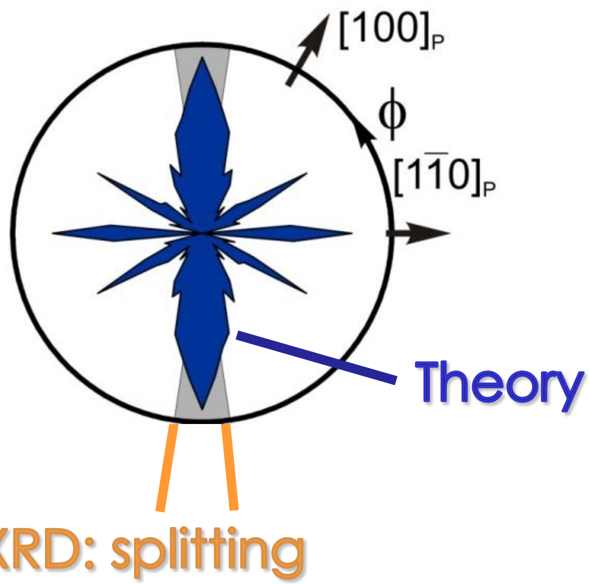
Re-adjustment of molecular orientation

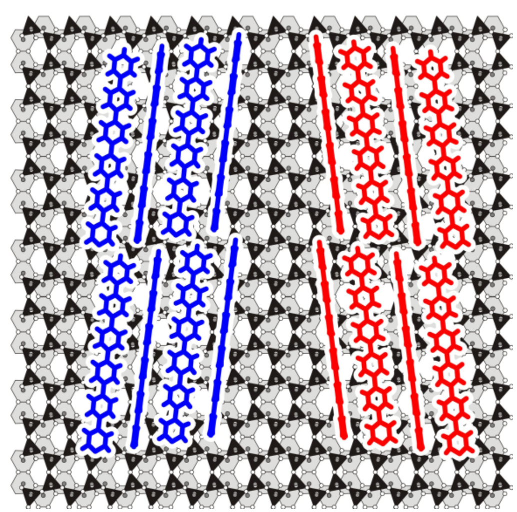






LMA

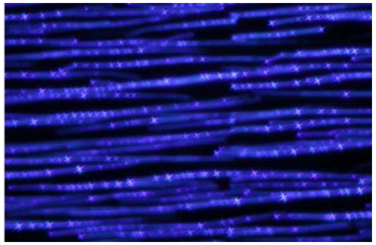




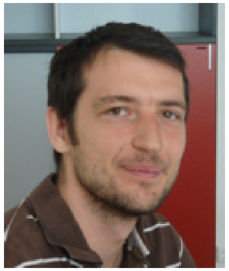
Needle formation

Growth model

- Molecular orientation pre-determines needle growth
- Needle orientation depends on symmetry of surface as well as molecule
- Re-adjustment due to molecular packing
- 6P & 4P are *lucky* cases with $\Phi = 0, 90°$



Lorenz Romaner



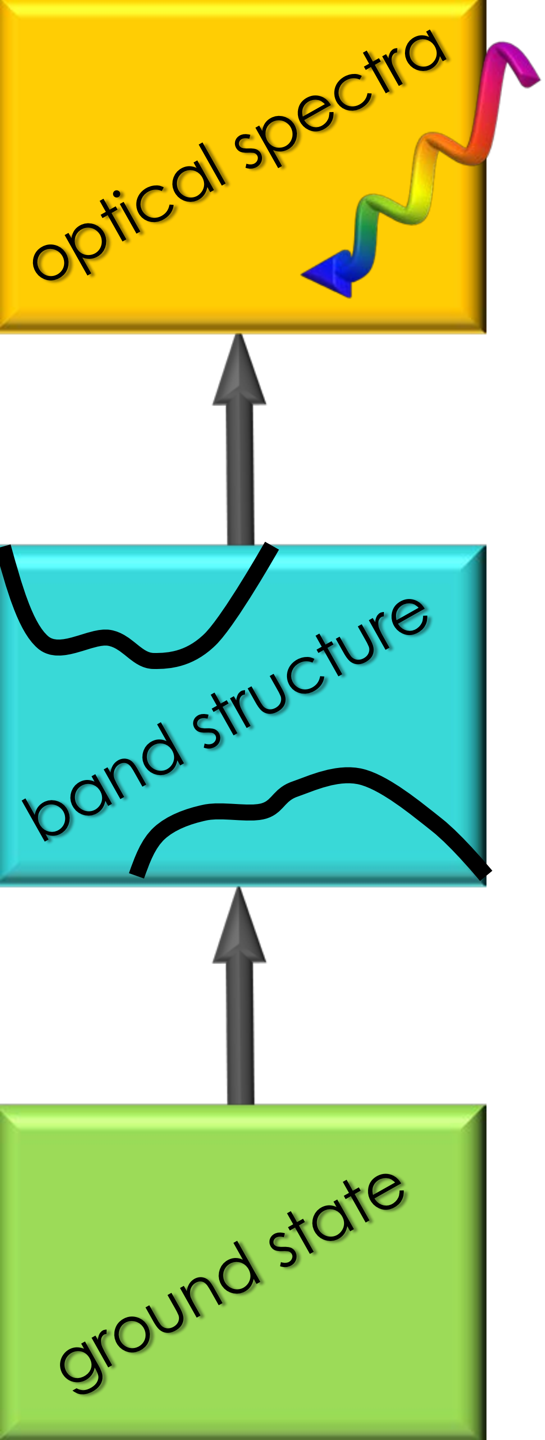
Dmitrii Nabok

C. Simbrunner, D. Nabok, G. Hernandez-Sosa, M. Oehzelt, T. Djuric, R. Resel, L. Romaner, P. Puschnig, CAD, I. Salzmann, G. Schwabegger, I. Watzinger, and H. Sitter, JACS 133, 3056 (2011).

Needle formation

From ground state to light absorption ...

Methodology



Bethe-Salpeter equation

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

Many-body perturbation theory

G_0W_0 approximation

$$\epsilon^{QP}_{n\mathbf{k}} = \epsilon^{KS}_{n\mathbf{k}} + \left\langle n\mathbf{k} \middle| \Sigma - V^{KS}_{xc} \middle| n\mathbf{k} \right\rangle$$

Density-functional theory

Kohn-Sham equation

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right]\psi^{KS}_i(\mathbf{r}) = \epsilon^{KS}_i \psi^{KS}_i(\mathbf{r})$$

Electron-hole interaction

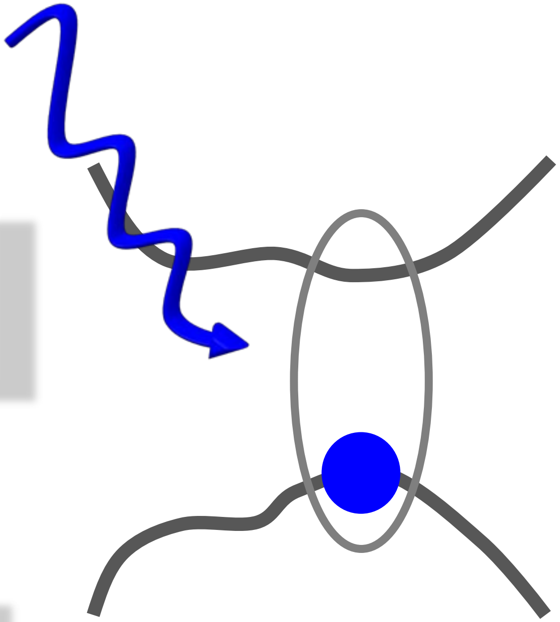
$$\left[H_e + H_h + H_{e-h}\right] \phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = E_\lambda \, \phi_\lambda(\mathbf{r}_e, \mathbf{r}_h)$$

Two-body wavefunction

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

Dielectric function

$$\mathrm{Im}\varepsilon \sim \Sigma_\lambda \Sigma_{cv} \left| \frac{\langle c \,|\nabla|\, v \rangle A_\lambda^{cv}}{E_c - E_v} \right|^2 \delta(E_\lambda - \omega)$$



Bethe-Salpeter equation

Electron-hole interaction

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

Diagonal term

$$H^{diag}_{vc\mathbf{k},v'c'\mathbf{k}'} = (E_{c\mathbf{k}} - E_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

Direct term - attractive

$$H^{dir}_{vc\mathbf{k},v'c'\mathbf{k}'} = -\int \frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\epsilon^{-1}(\mathbf{r},\mathbf{r}')\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

Exchange term - repulsive

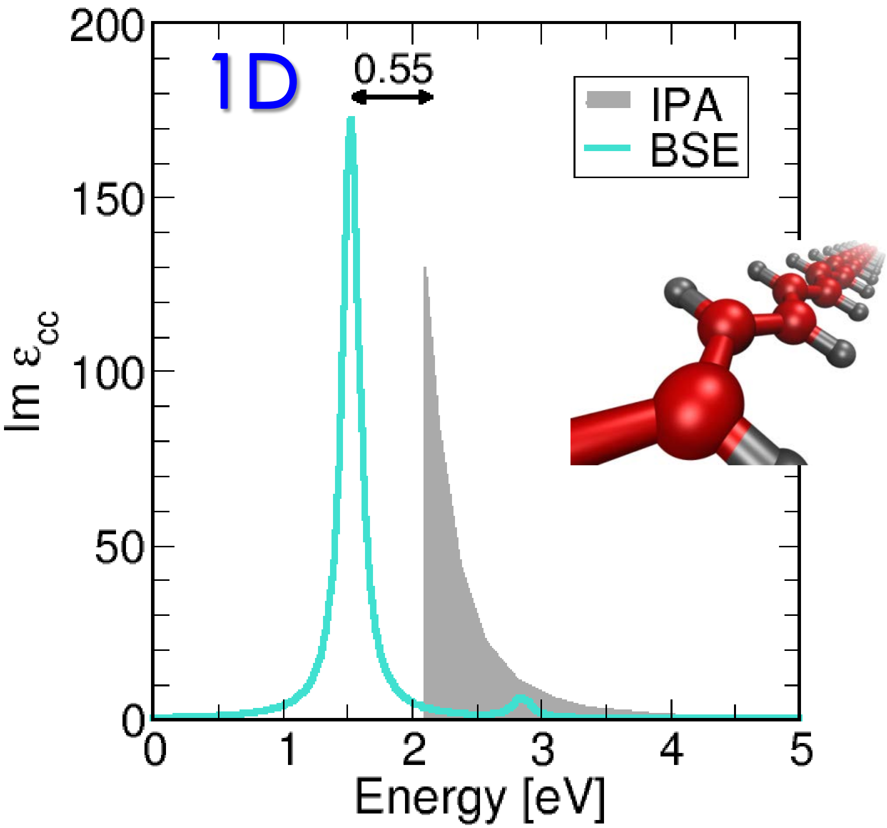
$$H^{x}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r})\psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'$$

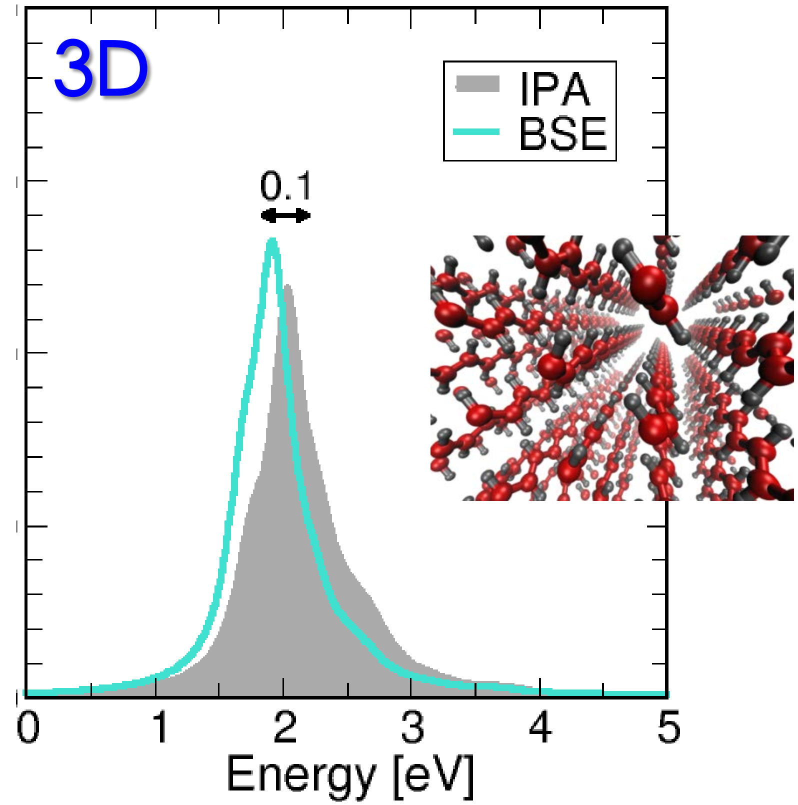
Bethe-Salpeter equation

Singlet exciton spectra

Impact of screening & extension of WF

Peter Puschnig

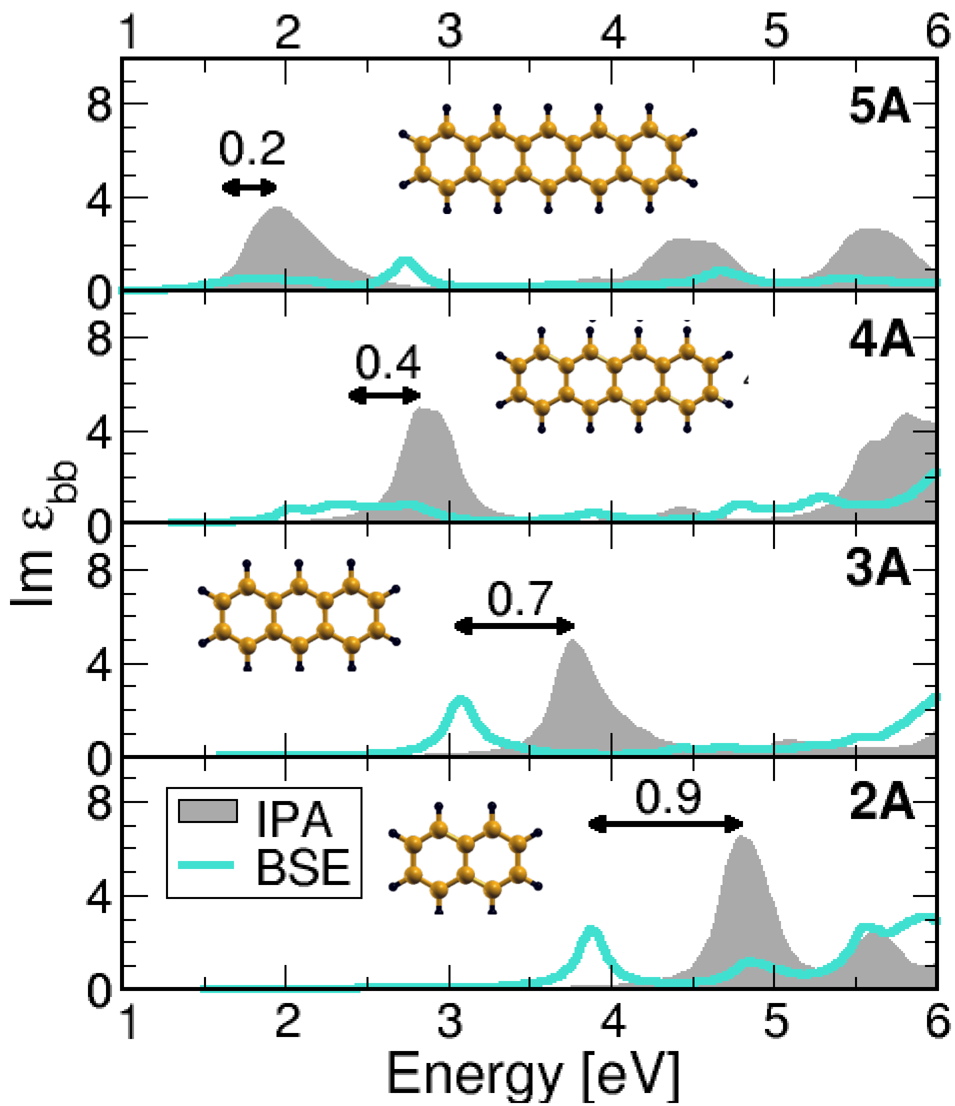


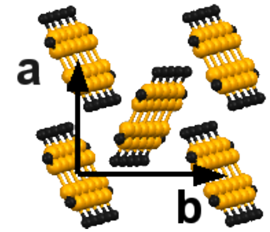


P. Puschnig and CAD, PRL 89, 056405 (2002).

Poly-acetylene

Organic molecular crystals





Kerstin Hummer

Smaller band gap

Enhanced screening

Wider extension of e-h wavefunction

Smaller exciton binding energy

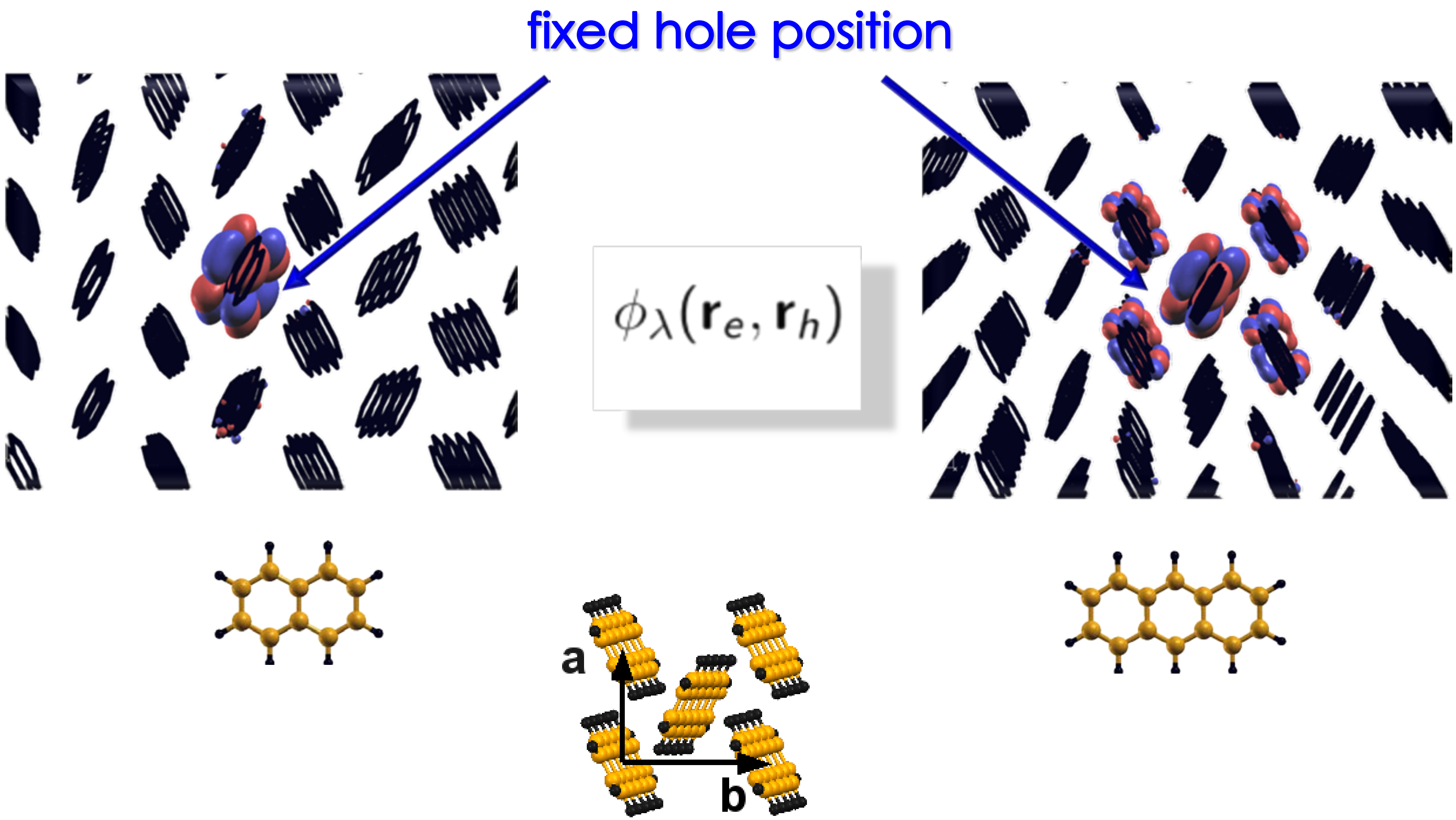
K. Hummer, P. Puschnig, and CAD, Phys. Rev. Lett. 92, 147402 (2004).

K. Hummer and CAD, Phys. Rev. B 71, 081202(R) (2005).

Oligoacenes

Example

Extension of exciton wavefunction

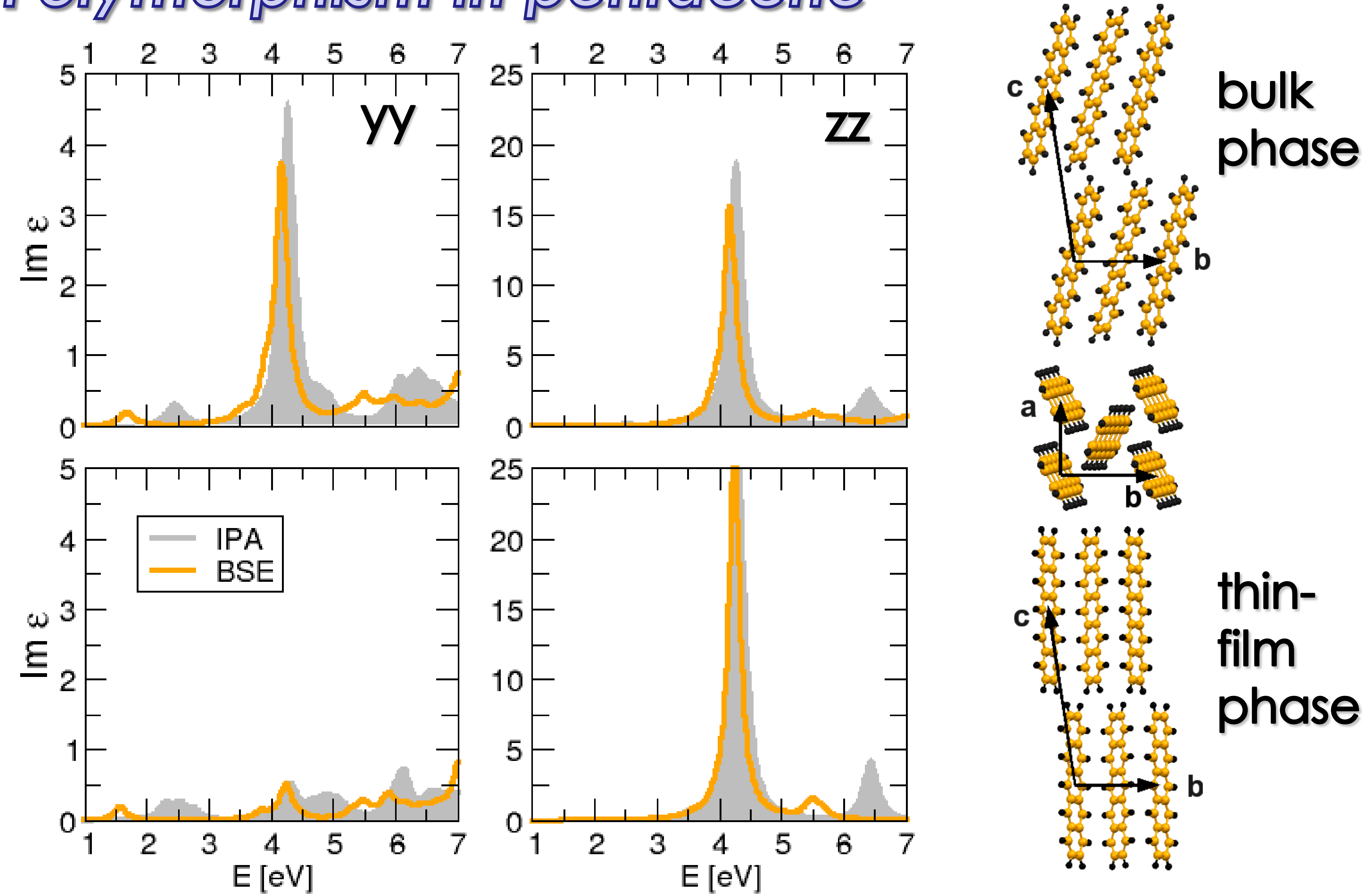


$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h)$$

K. Hummer and C. Ambrosch-Draxl,
Phys. Rev. B 71, 081202(R) (2005).

Oligoacenes

Polymorphism in pentacene

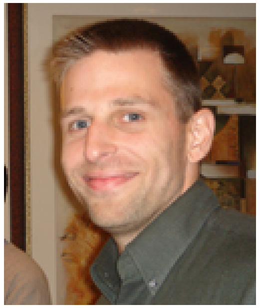


CAD, et al., New J. Phys. 11, 125010 (2009).

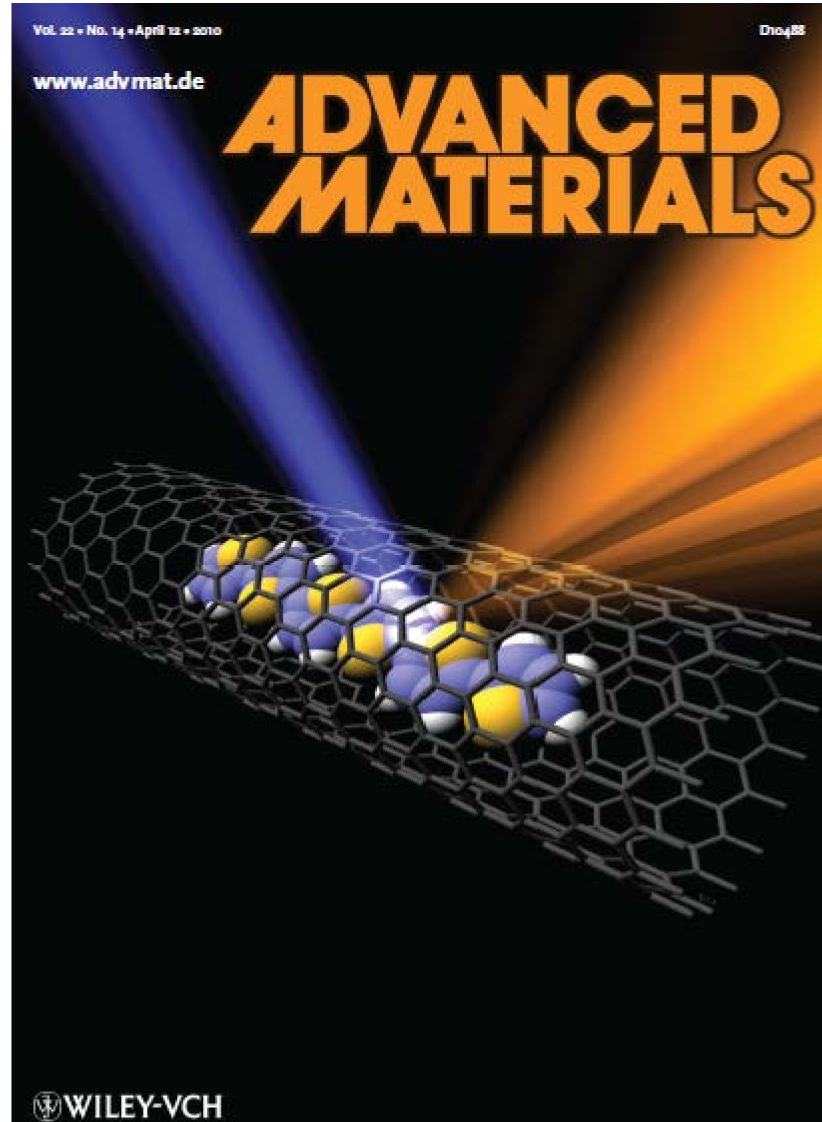
Oligoacenes

Light-emitting nano-objects

M. A. Loi, et al.
Adv. Mater. 22, 1635 (2010).

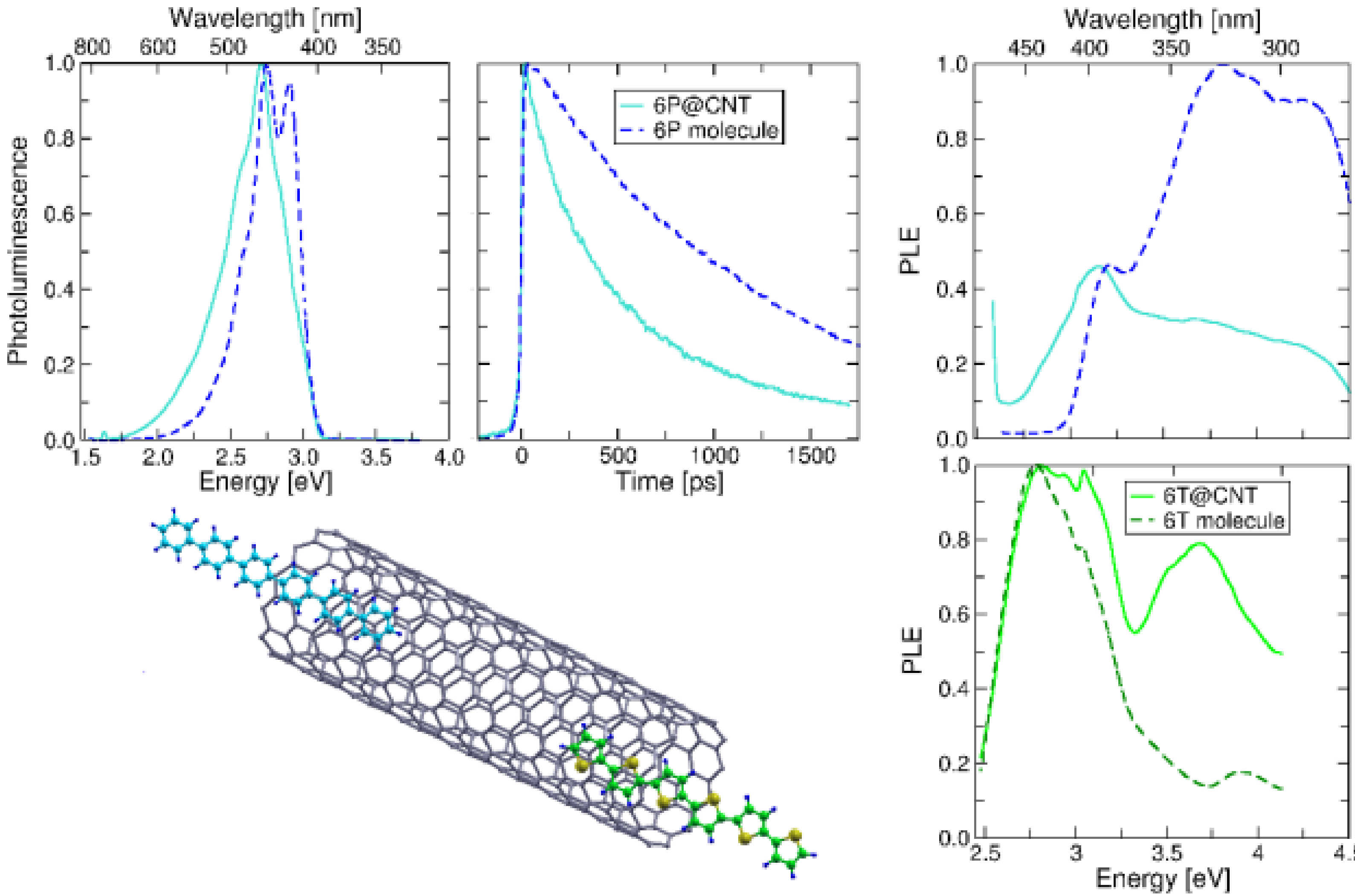


Matus Milko



Peapods

Experimental evidence



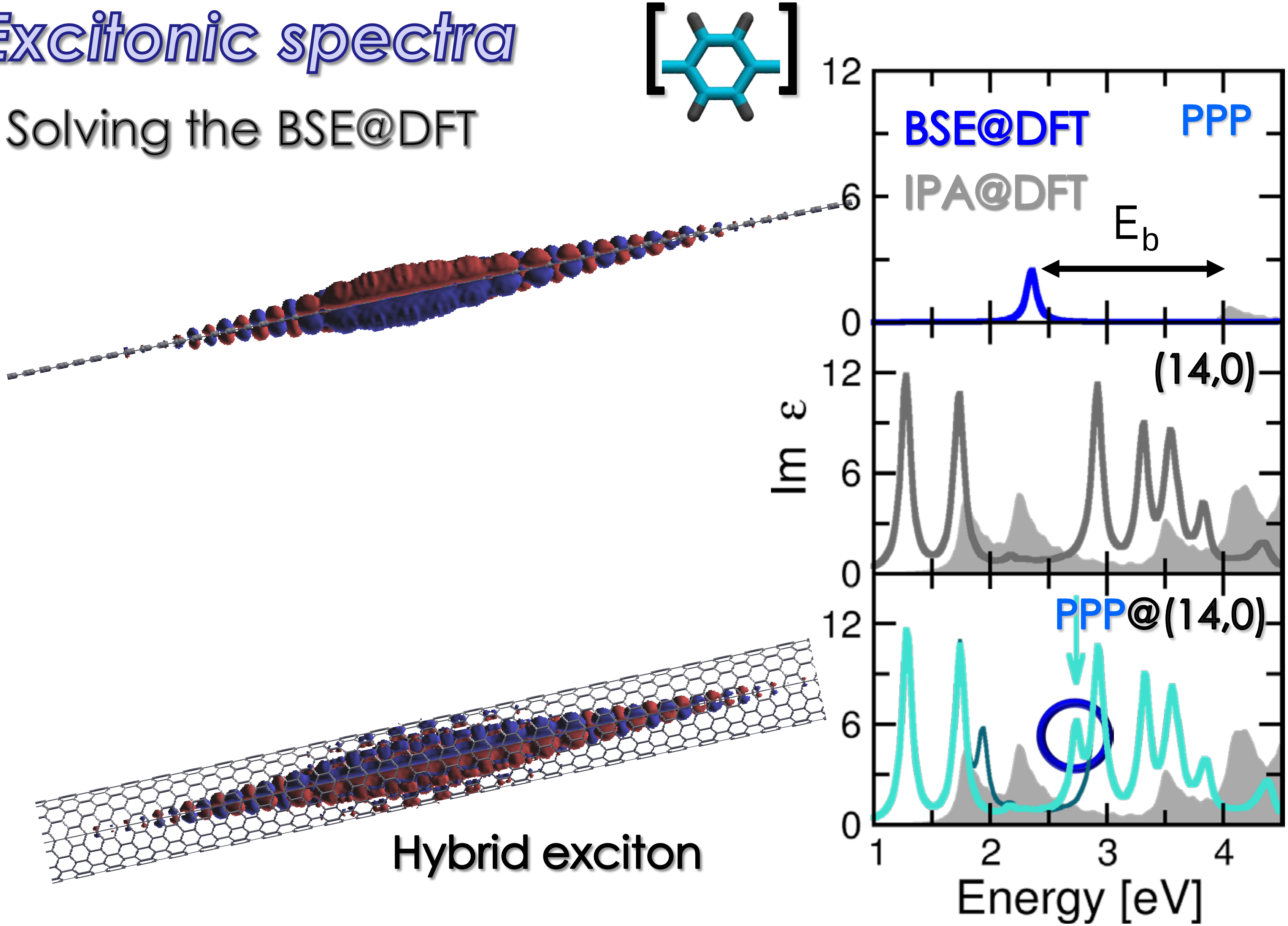
G. Jia, M. A. Loi, University of Groningen

Milko, et. al., J. Phys. Chem. Lett. 4, 2664 (2013).

Peapods

Excitonic spectra

Solving the BSE@DFT



But experimentally no blue shift observed!

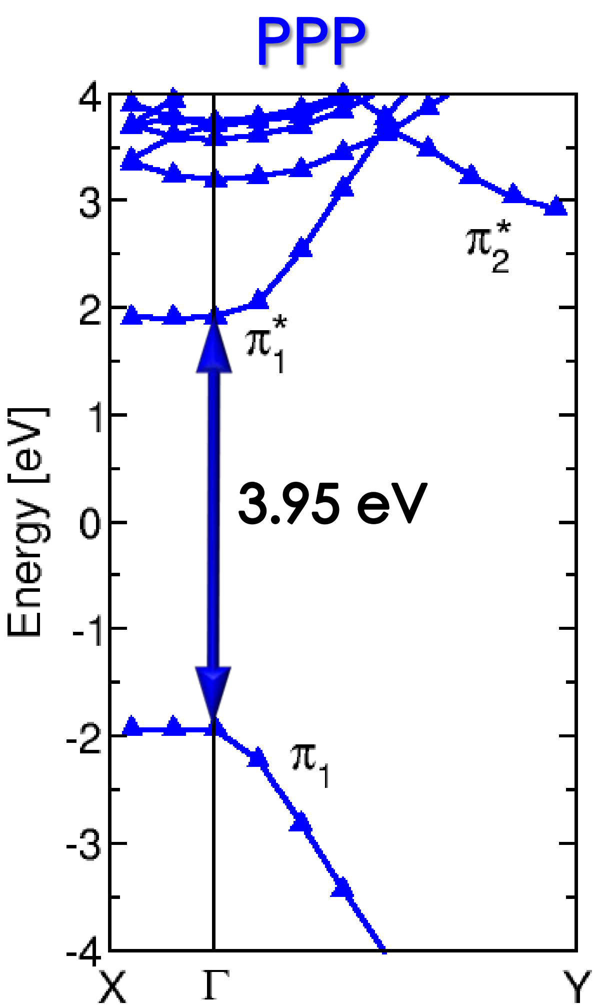
PPP on graphene

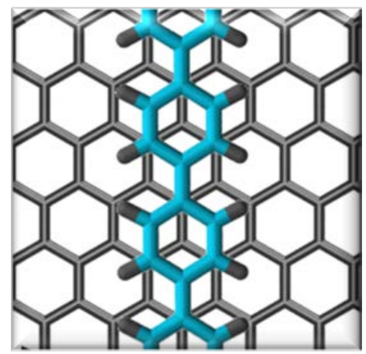
G_0W_0@LDA

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

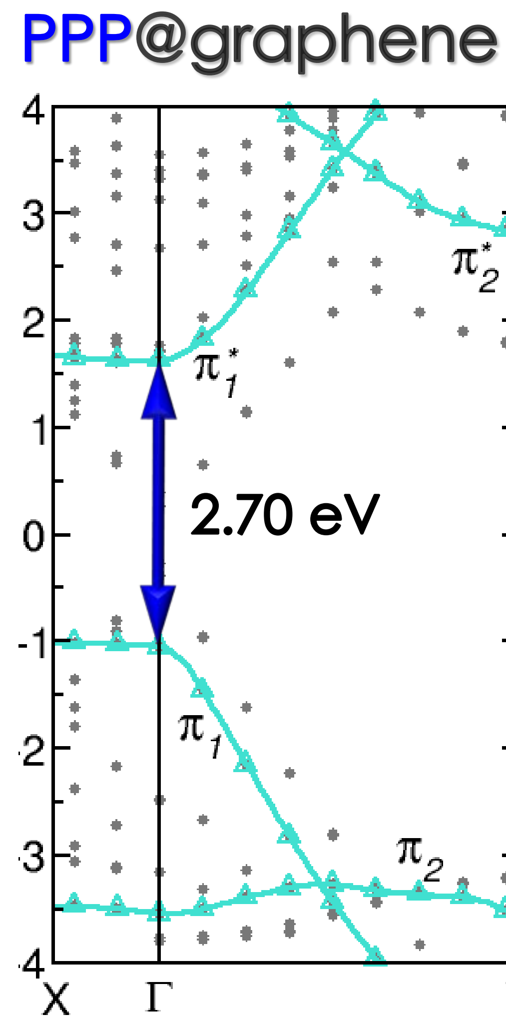
image-charge effect

Decrease of gap on adsorption

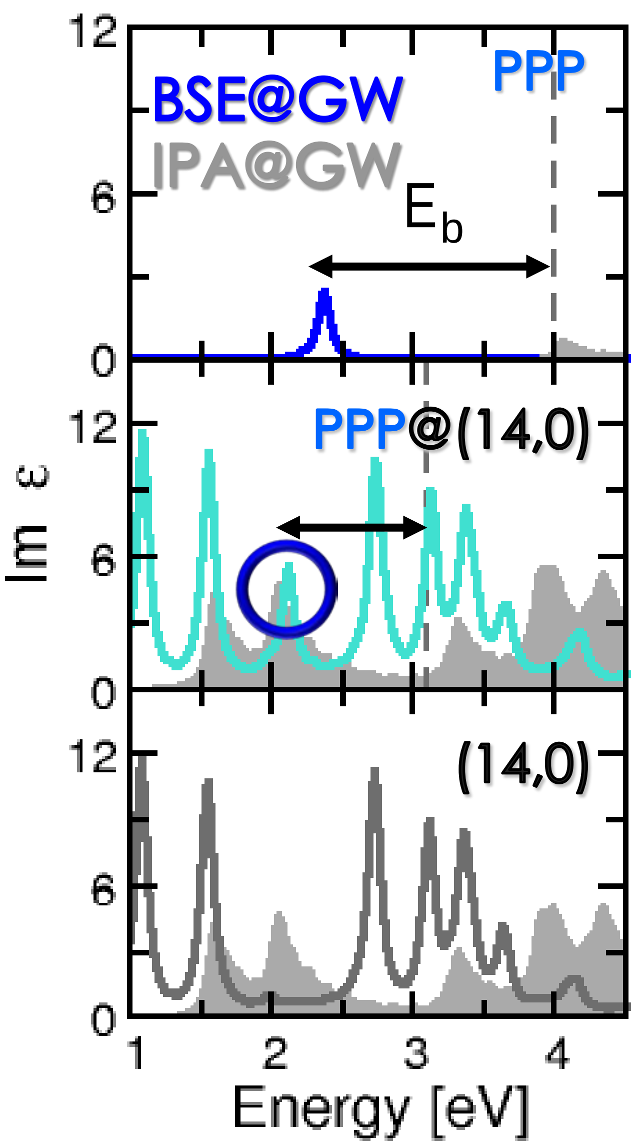


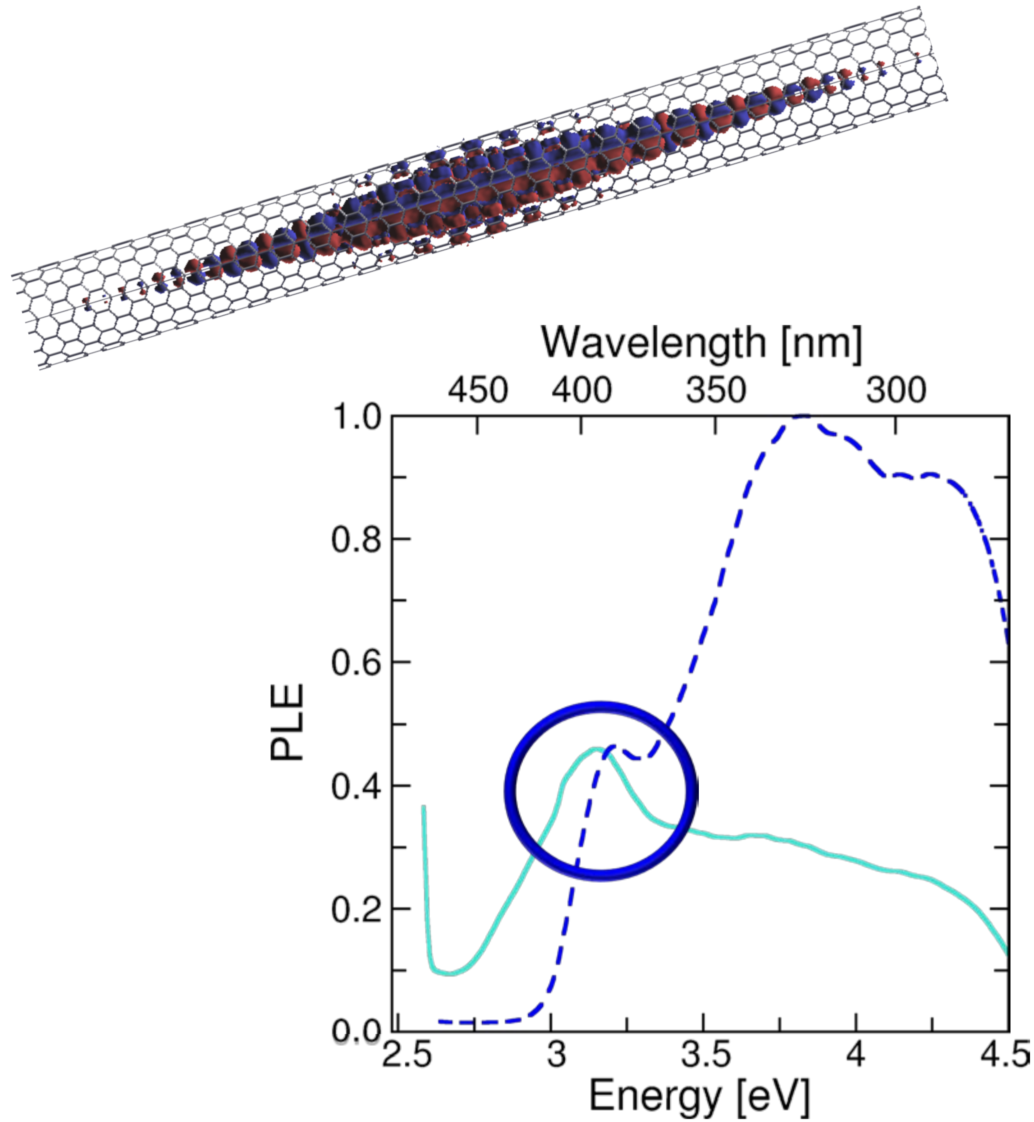


P. Puschnig, P. Amiri & CD
PRB 86, 085107 (2012).



Finally …



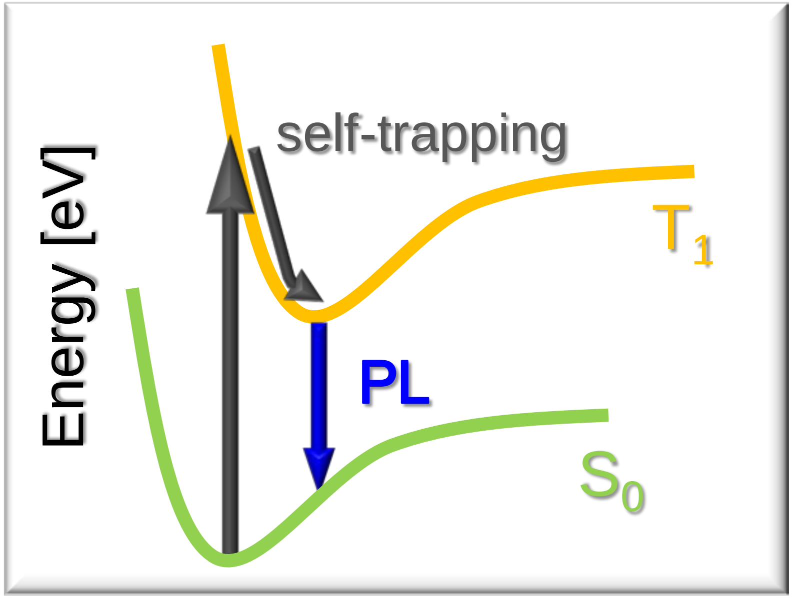


Peapods

Challenges for ab initio theory

Light-emission

- typically from the lowest (triplet) excitation



Dynamics

- Exciton formation, diffusion, lifetimes
- Interplay between electronic and vibrational degrees of freedom

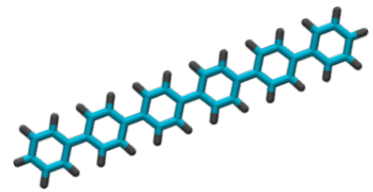
Outlook

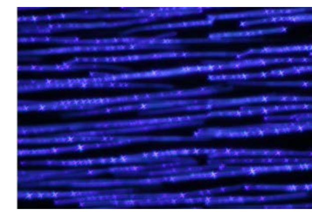
Organic π-conjugated molecules ...

exhibit exciting light-emitting properties

band gaps in visible range

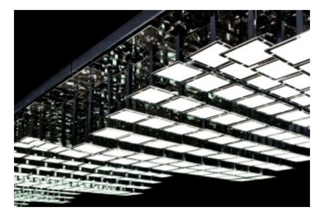
are highly anisotropic





grow in various manners

not trivial to control



can be tailored to specific needs

are used for flexible applications

... and are just fun !!

Summary

Thanks for your attention!