Spectroscopic investigation of the semiconductor molecular packing in fully operational organic thin-film transistors

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Organic Semiconductors

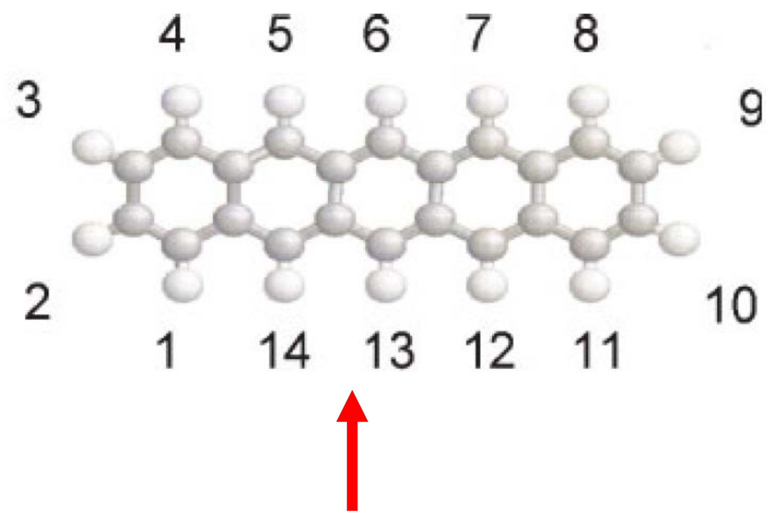
ADVANTAGES:

- Low cost/large areas
- Deposition on flexible substrates
- Tuning of the band-gap
- Transparent devices
- Sensors of atmospheric agents
- Compatible with byological systems

DISADVANTAGES:

- Low carrier mobility
- Low stability of the carrier parameters due to oxidation in atmosphere

Organic Semiconductors

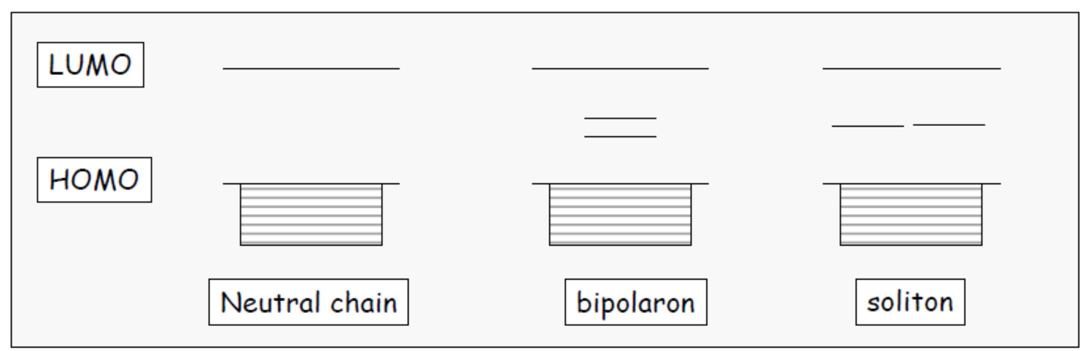


Pentacene: $C_{22}H_{14}$

Mobility comparable to amorphous Si:

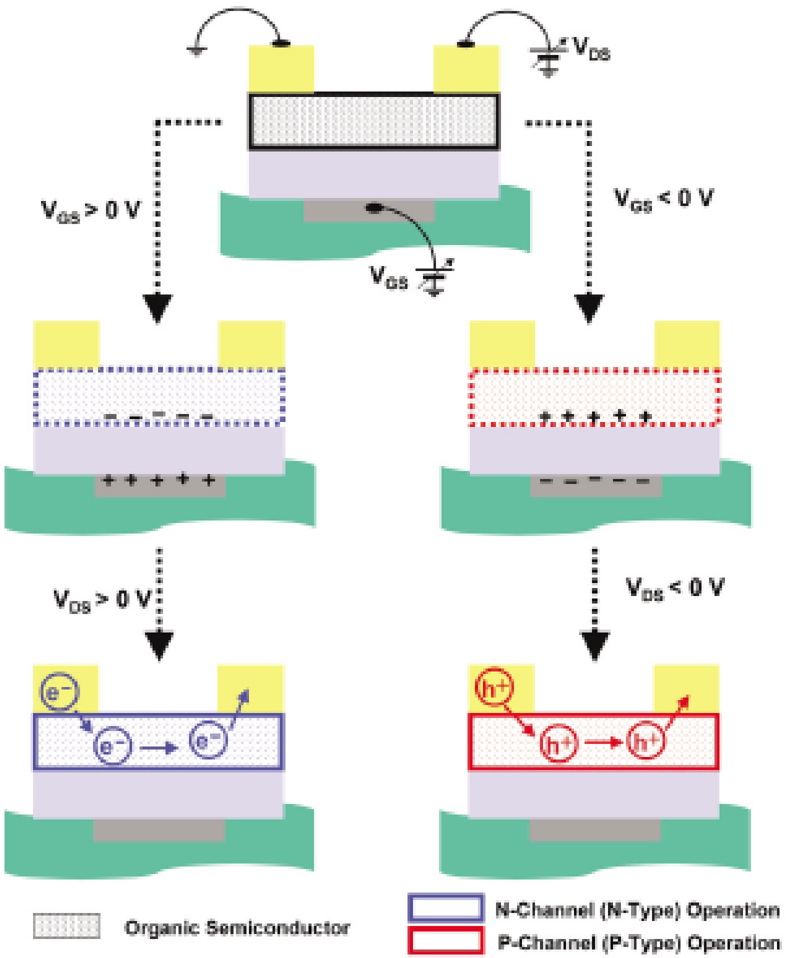
$\mu \sim 1\ cm^2/V \bullet s$

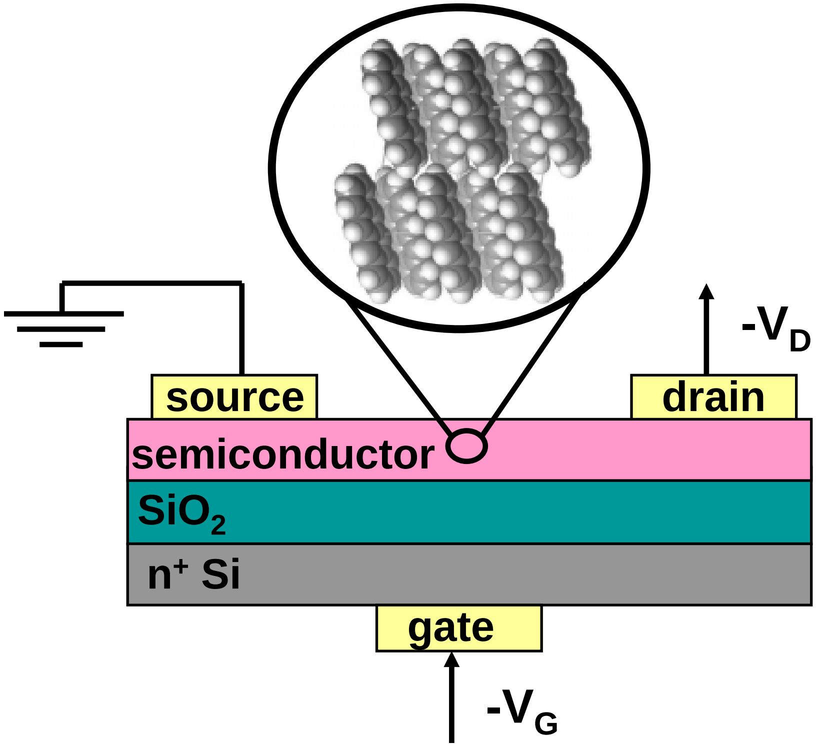
- Conjugate bonds $\pi - \pi$.
- Van der Waals interaction.
- Gap → HOMO-LUMO.
- Charge transport by hopping.



Organic Field Effect Transistor (OFET)

Accumulation mode

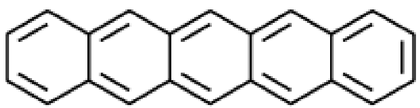


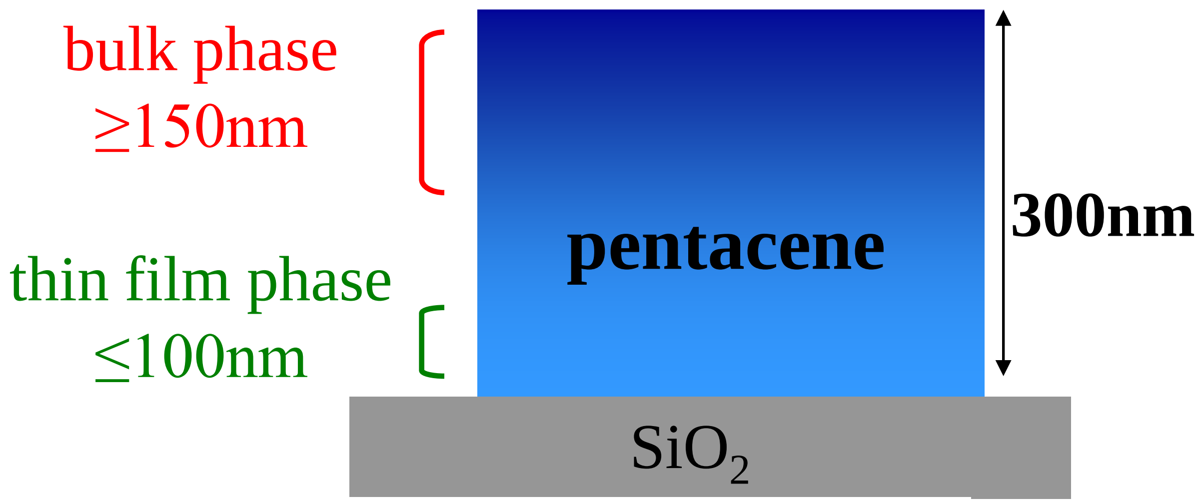


In OFET the conductivity is controlled by V_{GS} , only in the first layers of the SC (thin film phase) near the insulator interface.

Schematic layout of the pentacene thin films

$C_{22}H_{14}$

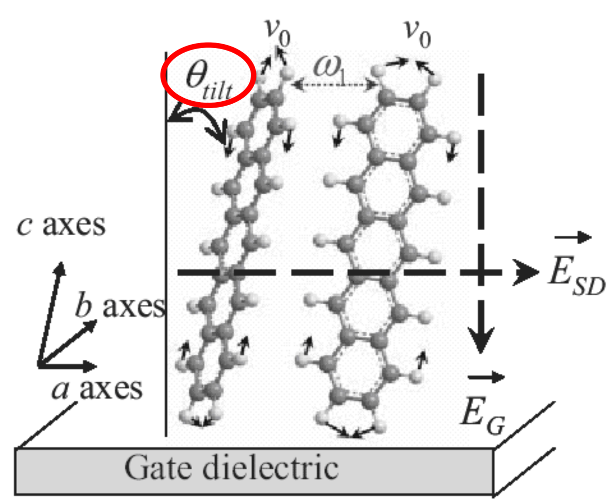




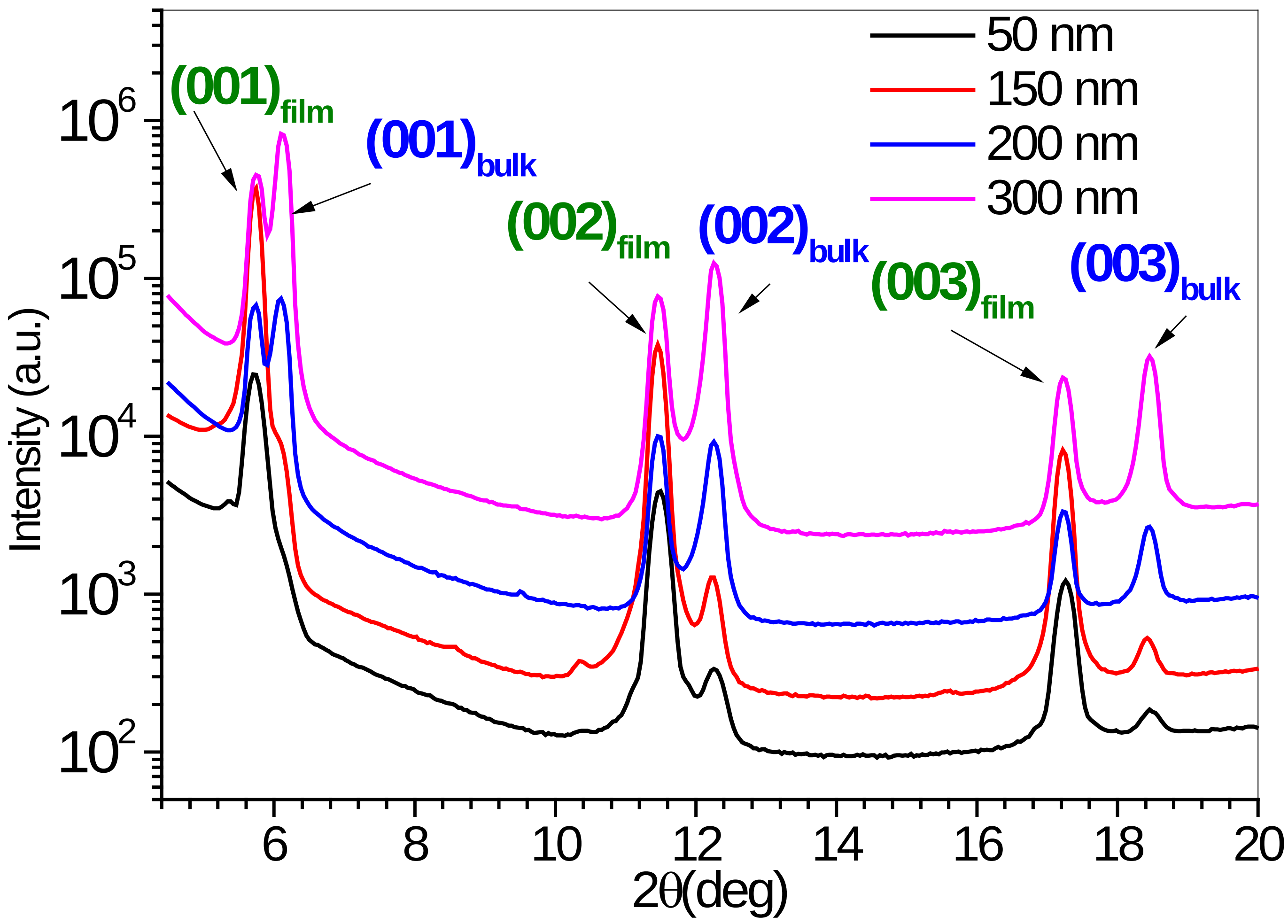
Herringbone structure

Thin film → θ_{tilt}= 17,1°

Bulk phase → θ_{tilt}= 25,7°



X-ray Diffraction



X-ray diffraction curves of pentacene thin films of different thickness → Bulk phase dominates over 150nm

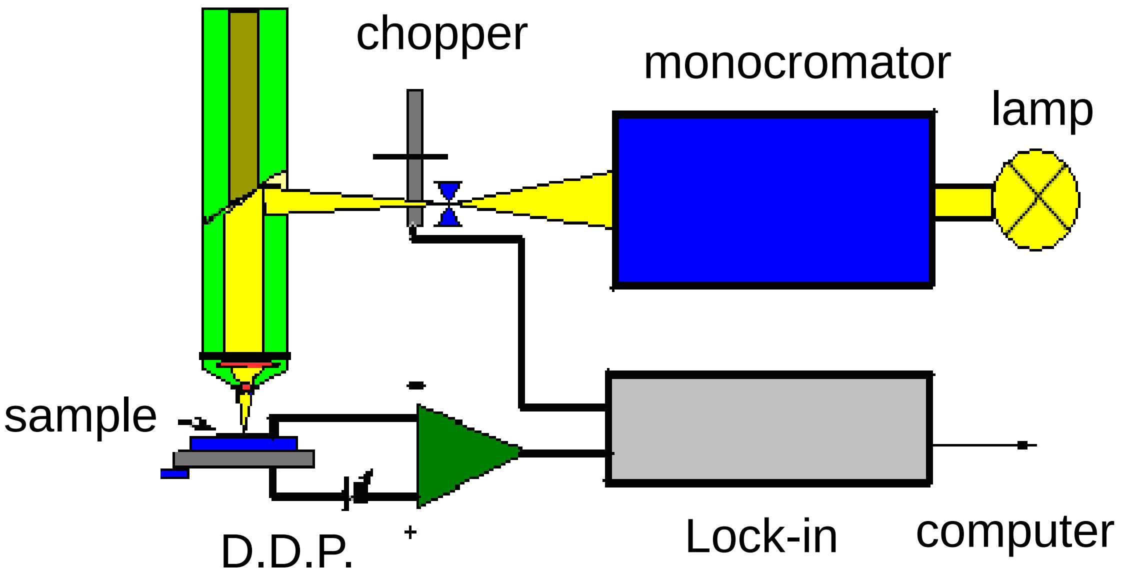
Photocurrent spectroscopy (PC)

Dark conductivity:

$$\sigma_0 = e(n_0\mu_{n0} + p_0\mu_{p0})$$

Irradiated with a frequency ν:

if $h\nu \geq E_g$



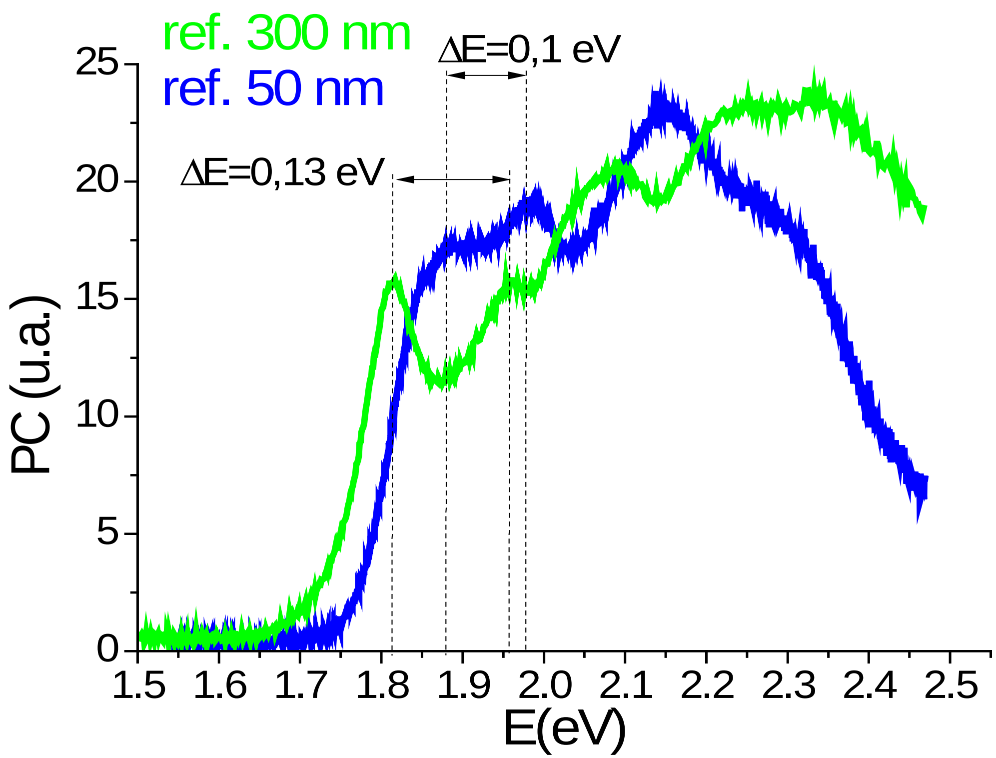
$$\sigma_{TOT} = \sigma_0 + \Delta\sigma$$

$$\sigma_0 + \Delta\sigma = q(n_0 + \Delta n)(\mu_0 + \Delta\mu)$$

$\Delta\sigma = q\mu_0 R\tau + qn\Delta\mu$ ⟶ photoconductivity

$\tau = 1/(\mathrm{v}sN)$ ⟶ charge carrier mean lifetime

Davydov splitting



Different thicknesses of Organic Semiconductors have different Density Of States (DOS).

Davydov splitting is the separation of the first two singlet levels (first exciton).

The DOS distribution can be measured by photocurrent or by optical absorption.

How Davydov Splitting can detect the molecular packing

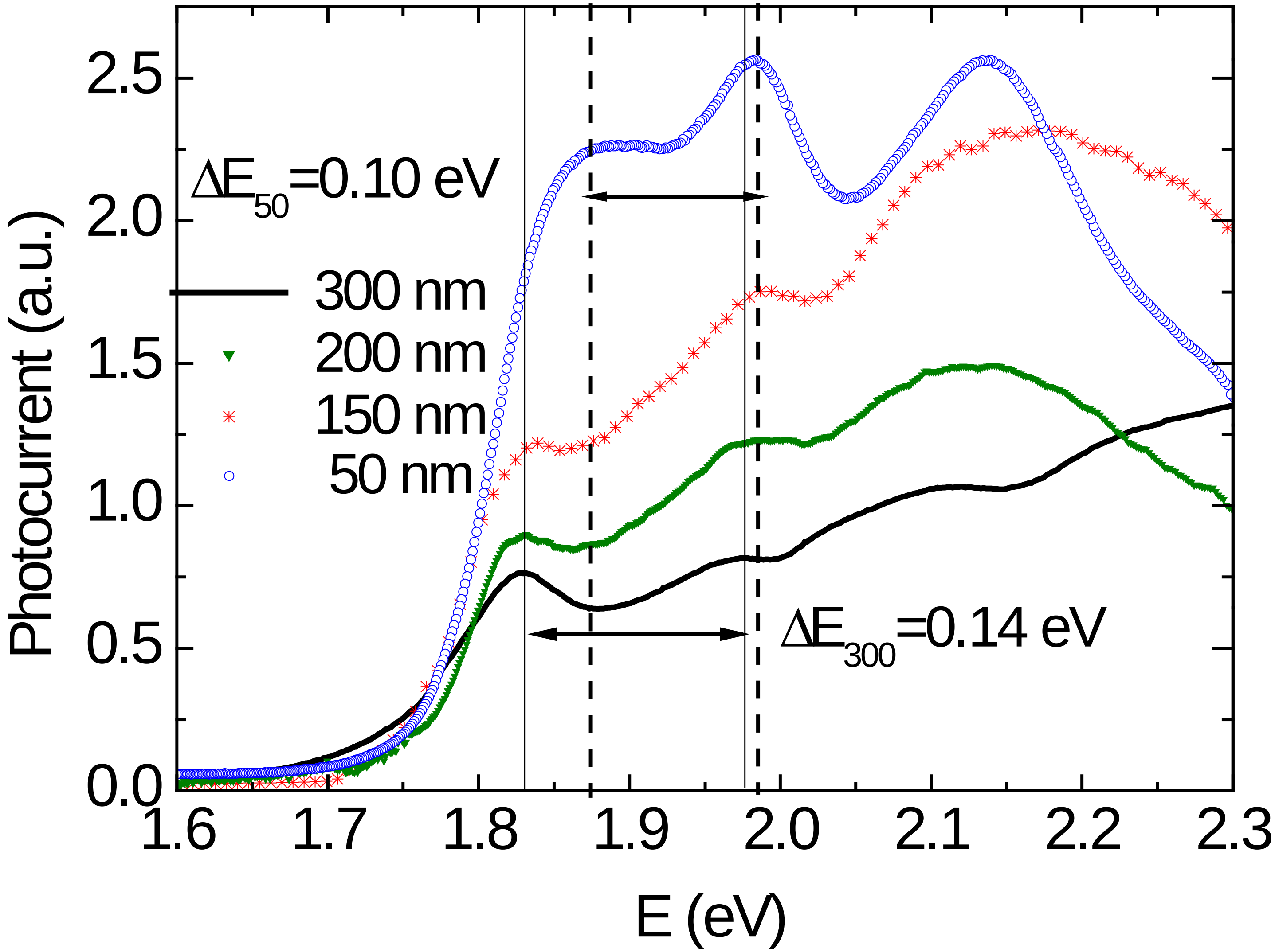
The bulk phase shows a molecular spacing smaller than the thin-film phase

↓

the coupling of intermolecular-electron system becomes stronger

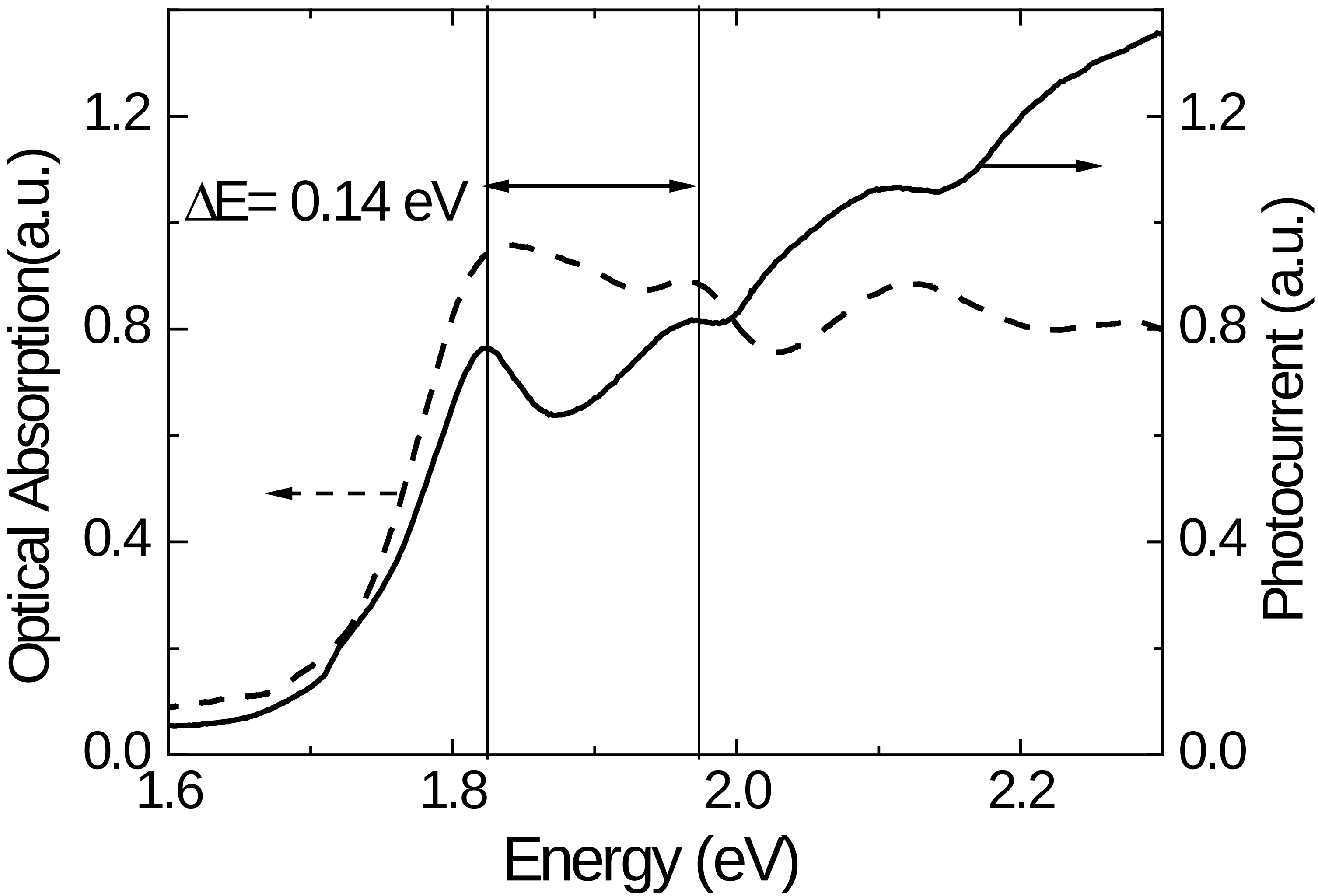
↓

the Davydov splitting is enhanced



Photocurrent spectra of OTFTs with different active pentacene layer thickness → PC can monitor the gradual modification of the molecular packing.

Optical absorption vs. Photocurrent



PC (solid line) and OA (dashed line) spectra of a pentacene thin film 300nm thick → Good agreement!

Conclusions

- We report on Photocurrent (PC) and optical absorption spectroscopy analyses of the electronic density of states (DOS) distribution around the band-edge of pentacene films of different thicknesses, from 50 to 300 nm.
- Both methods allow us to monitor the increase, with increasing film thickness, of the Davydov splitting of the first absorption band, correlated with modifications in the film molecular packing when passing from a dominant "thin film" to a dominant "bulk" phase.
- We show how PC spectroscopy has the remarkable ability to detect the modification of the DOS distribution in a non-invasive way, thus allowing the study of the active semiconducting organic film in fully operational organic thin-film transistors.