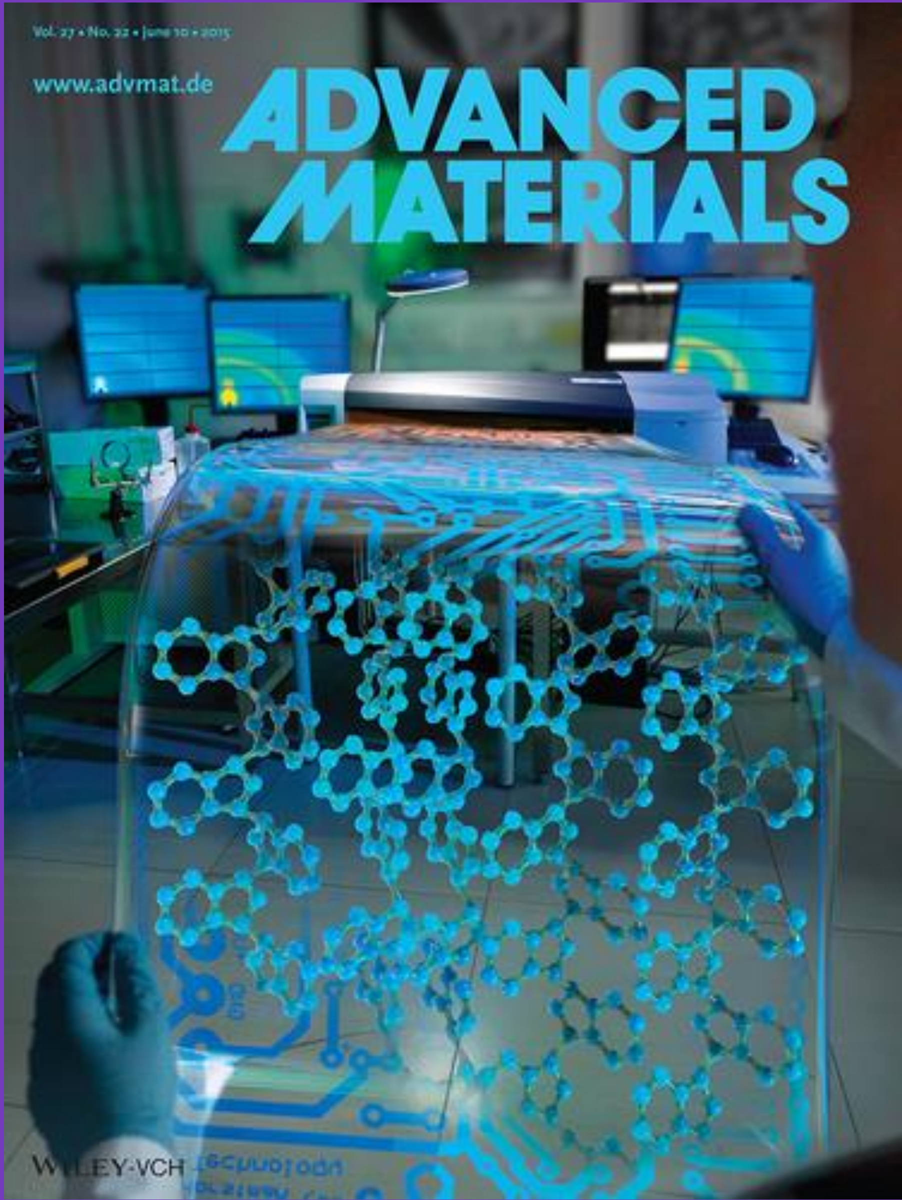
ELEC-E9210 Organic Electronics: Materials, Devices & Applications

Electronic Properties of Organic Materials

Aalto University
School of Electrical
Engineering

https://organicelectronics.aalto.fi



From Last Class

Previously….

- Organic materials are composed primarily (90%) of ***carbon***, ***hydrogen*** and ***oxygen*** held together by ***van der Waals forces***
- ***Small molecules*** or ***polymers***, and can transport either h^+ or e^-, often both

  polymer: repeated chain of single monomer in more complex structures
- ***Different morphologies*** and ***functional properties*** can be found (even for the same organic materials), depending on molecular packing, fabrication process and conditions.

Today´s Class

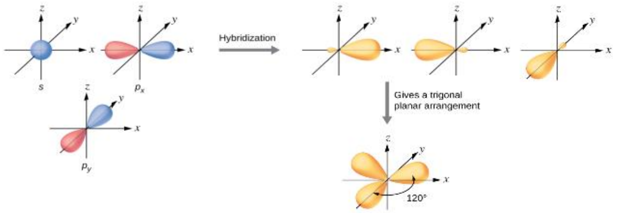
Electronic properties and ***different transport mechanisms*** in OSC:

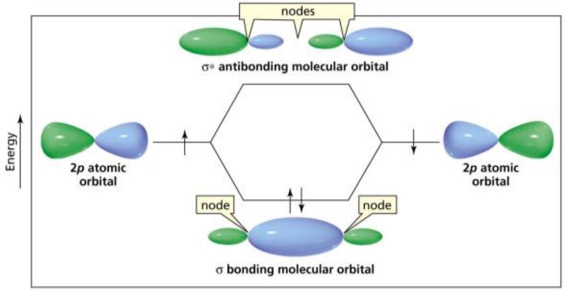
effect of disorder, *field-effect* transport, mobility, doping

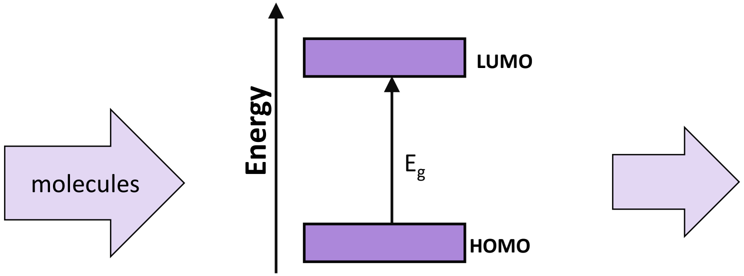
Electronic States in Organic Materials

Orbital hybridization leads to unpaired electrons in the molecule

single molecule picture







molecules proximity
leads to solid state bands

broad range of
optical & electronics properties

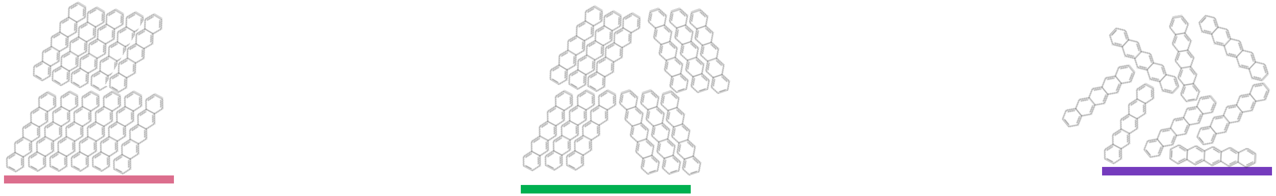
Charge Transport in Organic Semiconductors

increasing disorder

single crystal
(no disorder)

polycrystalline
(weakly disordered)

amorphous
(highly disordered)



Band Theory*

- Mobility Edge Model (ME)
- Multiple-Trap & Release* (MTR)
- Variable Range Hopping* (VRH)

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- Bässler´s Gaussian disorder model (BGD)
- Percolation (PER)

* more details to follow

From Band Theory to Disorder

For a ***disorder-free*, single crystalline semiconductor**, Einstein´s relation holds

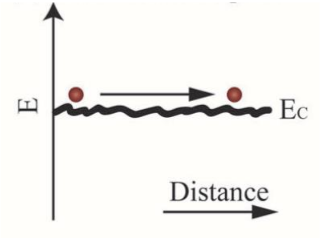
diffusion coefficient

Boltzmann´s constant

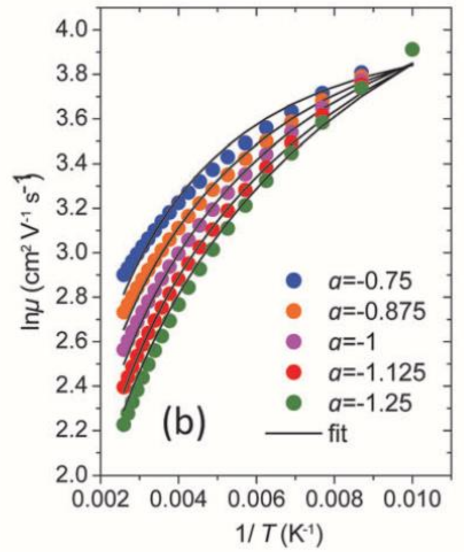
$$\frac{D}{\mu} = \frac{k_B T}{q}$$

mobility

electron charge



$\boldsymbol{\mu \propto T^{\alpha}}$ $\quad$ $with\ 0 < |\alpha| < 3$



Mater. Horiz. **4**, 608 (2017)

generalized Einstein relation
for a general charge-carrier energy distribution *n* and density of states (DOS) function

total carrier concentration

Fermi energy

$$\frac{D}{\mu} = \frac{1}{q}\frac{n(E_F,T)}{\frac{\partial n(E_F,T)}{\partial E_F}}$$

disorder

energy states becomes degenerate and behavior starts to deviate

Multiple-Trap & Release (MTR)

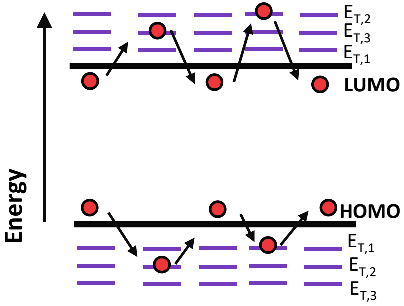
Trap states are *highly localized states,* where carriers are bound and cannot move easily from these sites. Traps can be either structural faults or added dopants (intentionally or not).

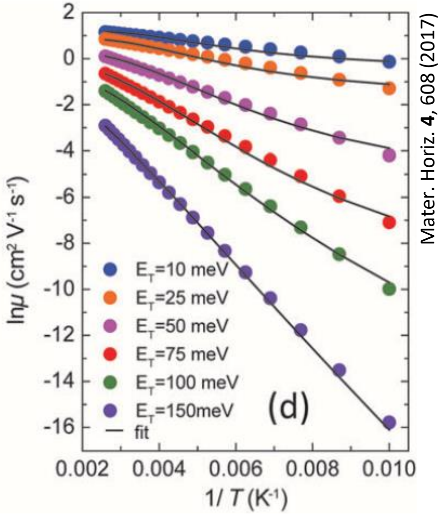
charge carriers are captured instantaneously and released through ***thermally-activated process***

shallow traps (2-3kT)

deep* traps (>3kT)

*very difficult to be removed without external action





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$$\mu = \mu_0 \alpha e^{-\frac{E_T}{k_B T}}$$

trap energy

trap-free mobility

trap density

@RT traps with 40meV with concentration as low as 10^{-7}, are already enough to reduce mobility by a factor of 2

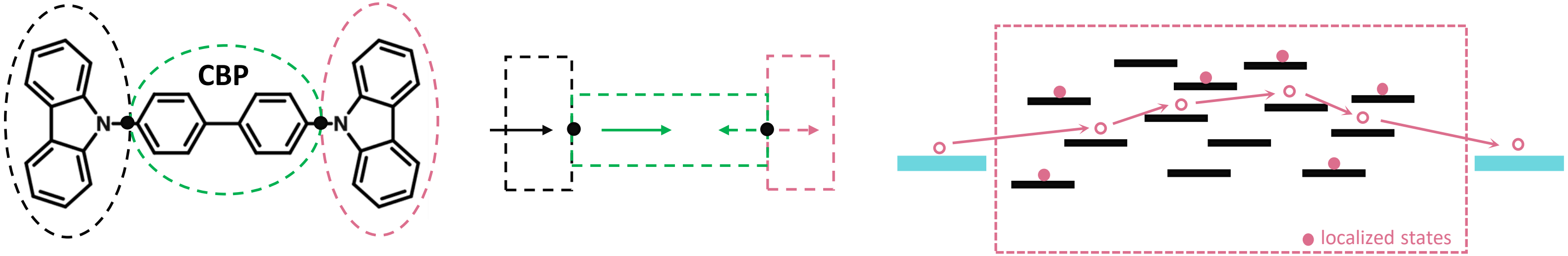
Disorder & Charge Hopping in Single Molecule

Hybridization

Disorder

(***Variable Range) Hopping (VRH)*** is one of the most common regimes for transport in organic materials (with high disorders):

charges are localized but can jump ("hop") to another localized state



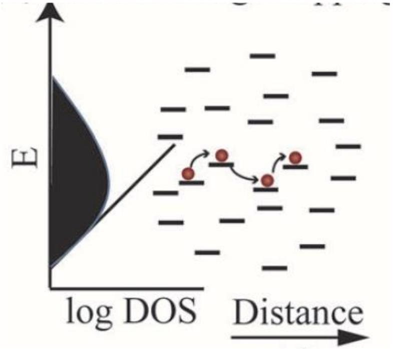
- ***reorganization energy*** (Marcus charge transfer model)
- ***electronic couplings*** between segments
- ***driving force*** (*i.e.* electric field)

$$P(R,W) = exp\left(-\underset{\uparrow\ \text{trap density}}{\overset{\text{spatial separation}\ \searrow}{\alpha}}R - \frac{\overset{\swarrow\ \text{energy separation}}{W}}{k_BT}\right)$$

hopping probability between two states with spatial separation *R* and energy separation *W*

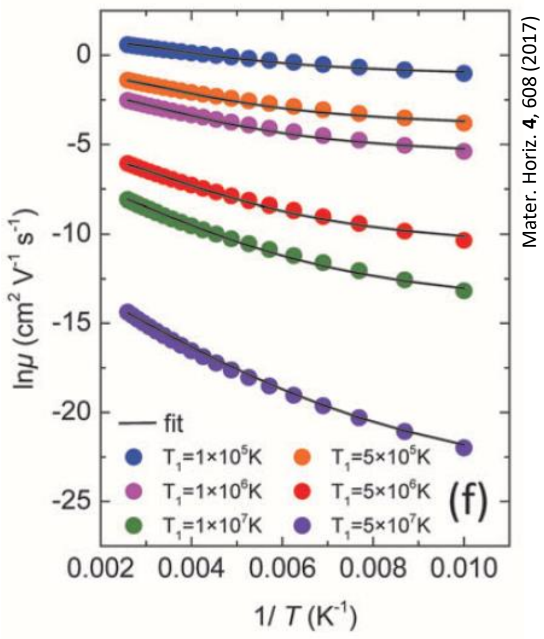
Hopping in Organic Materials Films

Molecules can pack in many different ways (depending on fabrication process, substrate interaction, etc.), leading to different hopping mechanisms



localized state size

$$\mu \propto e^{\left[-\frac{T_1}{T}\right]^{1/4}}$$



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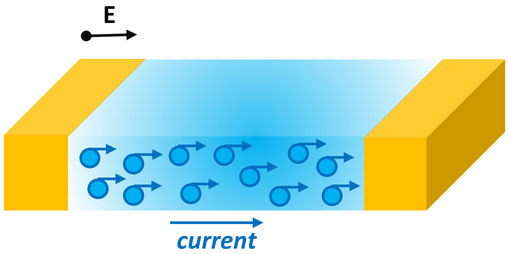
Charge Transport in Classical Terms: Mobility

Mobility describes how quickly a **charge** (hole or electron) **can move through a material**, under the effect of an **external electric field**



$v_d = \mu E$ charges move with an average drift velocity v_d

$\sigma = ne\mu$ conductivity of the material

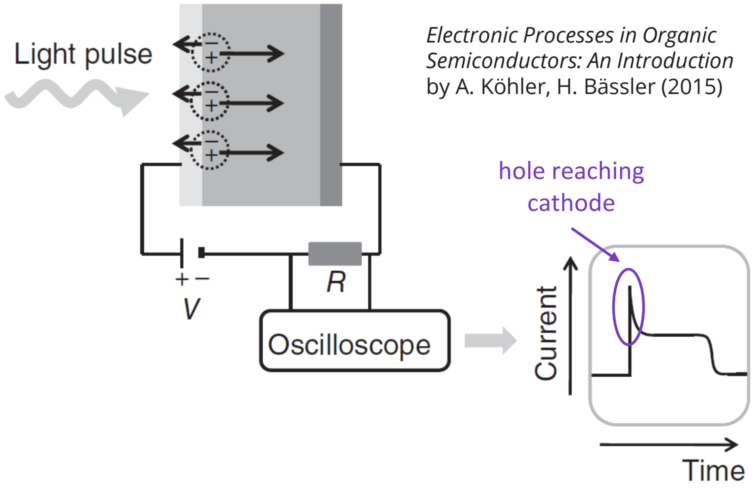
charge density

μ is function of temperature, energy, doping, traps density and energy, etc.

how to measure mobility?

- **Time-of-Flight (ToF)** method
- **Field-Effect Transistor (FET)** method
- Space-Charge-Limited Current (SCLC) method
- magnetic effect (*i.e.* Hall effect, magneto-resistance)
- σ/n method
- xerographic discharge method

Measure of Mobility: Time-of-Flight (ToF)



Electronic Processes in Organic Semiconductors: An Introduction by A. Köhler, H. Bässler (2015)

hole reaching cathode

light pulse creates *e-h* pairs close to the front electrode

while e^- leaves the device through the front electrode, h^+ moves through the OSC film to the other electrode

displacement current (measured though an oscilloscope)

sample thickness

$$\boldsymbol{transit\ time, t_{tr}} = {}^{d}/_{\mu E}$$

electric field

changing the polarity of the applied electrical field, electron mobility can also be measured

ToF measurement conditions:

- sample is free of charges (no excitation)
- RC time constant smaller that transit time
- spatial distribution smaller than *OSC thickness*
- *NO interacting charges*
- *NO deep trapping*
- *time-independent mobility*

Time-of-Flight (ToF) Study of Rubrene

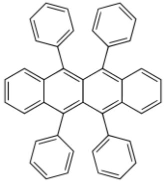
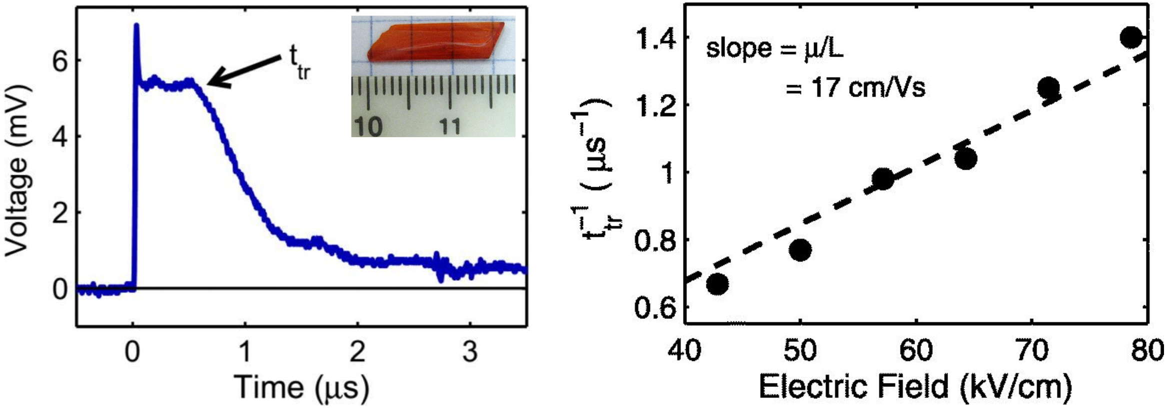


plate-like rubrene crystals, grown by physical vapor deposition

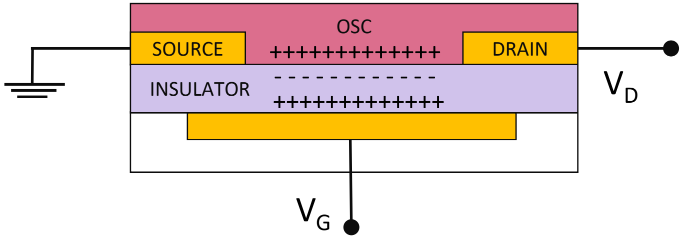
Appl. Phys. Lett. **106**, 113301 (2015)



(Left) Single ToF experiment/event and (center) transit time dependence from electric field.

Field-Effect (FE) Mobility & Transport*

(Organic) field-effect transistor can be fabricated using organic semiconductor as active material



$$I_D = \frac{W}{L} \mu C_i \left[(V_G - V_{th}) V_D - \frac{1}{2} V_D^2 \right]$$

channel length, L
channel width, W

dielectric capacitance

threshold voltage

source and drain electrodes enable a source-drain current I_D to be measured as function of the gate voltage V_G applied perpendicularly to a source-drain voltage V_D

applying V_G, induces a unipolar charge at the interface between the dielectric and organic

sweeping V_D (between source drain) induces a current increasing with V_D and V_G

FET mobility strongly depends on device (configuration)
- strictly speaking *NOT* (only) a *material properties*

*more details about *field-effect* transport and transistor regimes to follow

ToF & FET as Complementary Techniques

FET mobility

charges are injected into the device

(parameters related to device such as contact resistance, injection barriers will affect the measurement)

- **high carrier densities** are possible → charges spatial separation reduces leading to interacting charge carriers
- **gate dielectric polarization** can affect the motion of the carrier in the conduction channel
- **surface states** on the crystal may affect mobilities due to different surface packing than in the bulk and the possibility of oxidized or contaminated surface states

ToF mobility

charges are photo-generated in the device

- **NO injection/contact** effects
- **charge density can be tuned** through the incident light
- **e^-, h^+ mobilities** can be both measured on the same sample (switching electric field polarity)

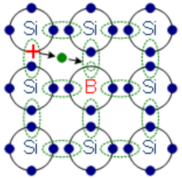
Tuning Mobility: Doping

Doping is an effective strategy to increase carrier concentration (and thus mobility)

“CLASSICAL” SENSE (inorganic)

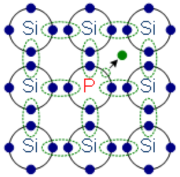
substitution of one atoms in the lattice

p-doping



free place (B atom) is filled with an electron → a new hole (“defect electron”) is generated and can move in the SC

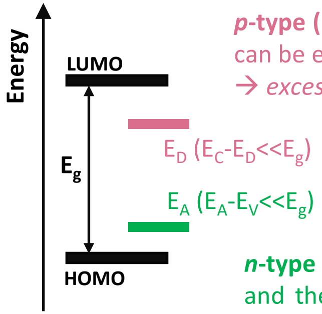
n-doping



P atom donates its excess valence electron, which behaves as a free charge in the SC

ORGANIC MATERIALS

introducing external atoms/molecules in the proximity of the OSC introduces new energy levels, with the effect depending on the structure of the inserted molecule

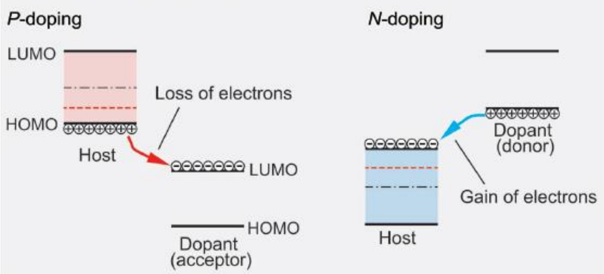


***p*-type (E_A-E_V<<E_g)**, with e^- close to E_A and they can be easily excited from HOMO to LUMO
→ *excess holes in the valence bands*

***n*-type (E_C-E_D<<E_g)**, with e^- in E_D close to E_C, and they can be removed from the dopant atom into the LUMO
→ *excess electrons in the conduction bands*

Doping Mechanism

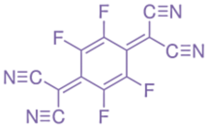
Charge Transfer Doping (*i.e.* chemical doping through red-ox)



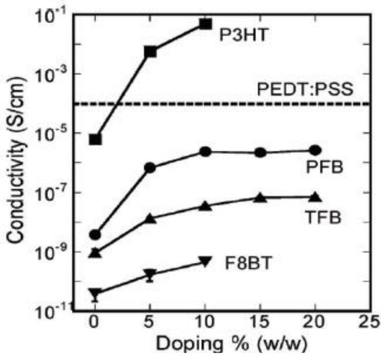
no doping: @RT, almost all the valence electrons are distributed in the HOMO with very few electrons thermally activated in the LUMO → additional electrons cannot be accepted by HOMO

doping: dopants can interact with adjacent OSC molecule by *charge transfer* and excess electrons are received by LUMO acceptor

F4TCNQ,
dopant molecule



2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane

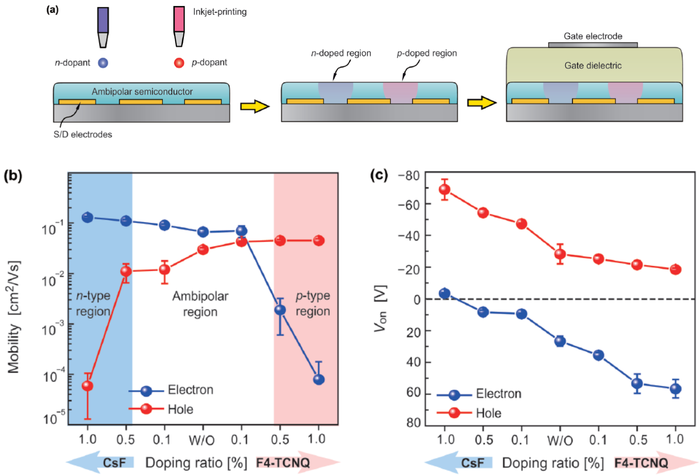


Adv. Mat. **30**, 1801830 (2018)

Conductivity as function of different doping level of F4-TCNQ for several organic molecules

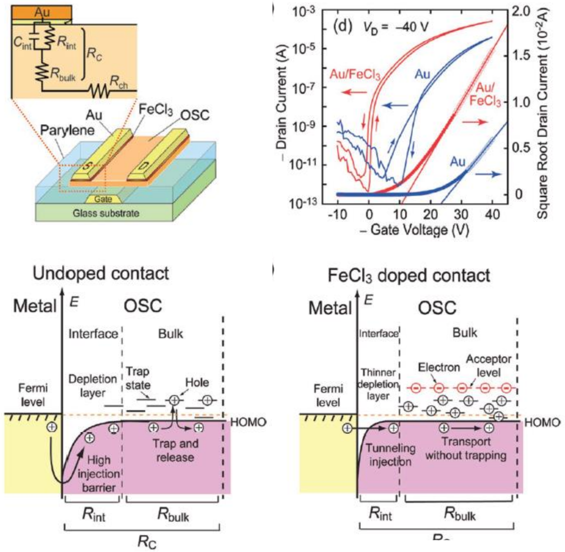
Doping Approaches

Channel* Doping**: transport is dominated by ***hopping transport and ***Coulomb traps*** (disorders)
→ doping lowers the hopping barrier and passivates traps



Inkjet printing of selective *p*- and *n*-doping of channel region in a device with corresponding mobility and threshold voltages dependence from doping ratio.

***Contact* Doping**: reduce contact resistance due to charge injection at the metal-semiconductor interface and contact transport through OSC bulk



Doping in a C8BTBT-based device with FeCl$_3$ at contacts, with corresponding electrical characterization and schematics of the effect of doping on the energetics of the device.

Adv. Mat. **30**, 1801830 (2018)

Summary

Electronic properties of organic semiconductors

- ***different transport mechanisms*** in OSC (depending on disorder)
- ***mobility*** and its ***measurement*** (ToF and *field-effect*)
- how to ***enhance mobility*** (doping)

Next

- ***Optical properties*** of organic materials (1 video)
- ***Characterization*** of ***organic materials*** (in class, recording will be available)