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Electrical fatigue in organic light-emitting diodes

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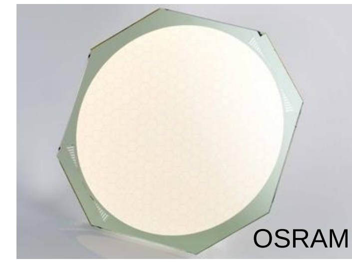
Philips



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Electrical fatigue in organic light-emitting diodes

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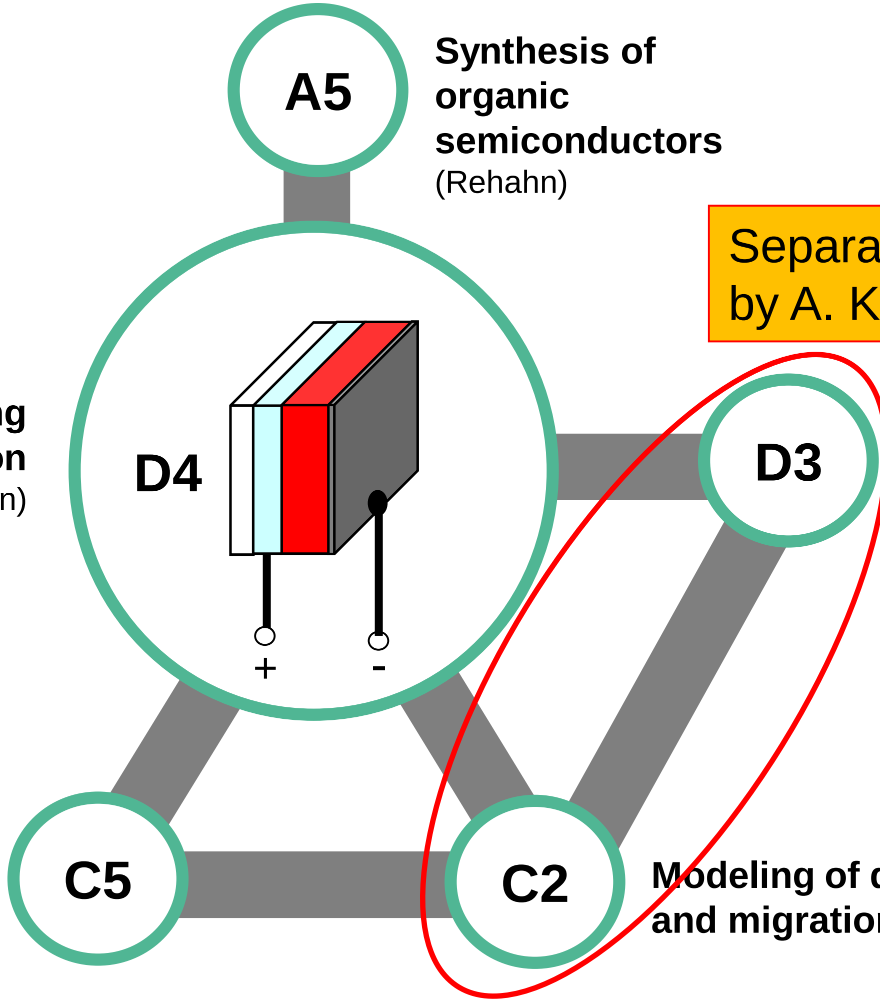
Organic Semiconductor Group
Heinz von Seggern

Synthesis of organic semiconductors (Rehahn)

Separate presentation by A. Klein, 12:00 today

Device preparation, fatiguing and characterization (Gassmann / von Seggern)



Preparation and characterization of oxide electrodes (Klein)

Modeling of charge carrier injection & transport in organic semiconductors (Genenko / von Seggern)

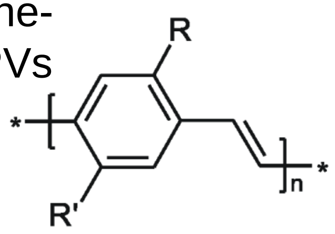
Modeling of defect formation and migration in oxides (Albe)

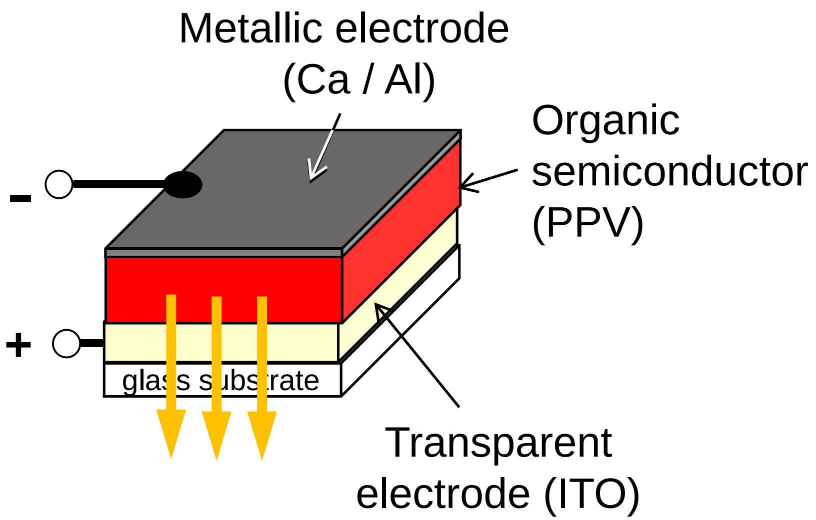
Outline

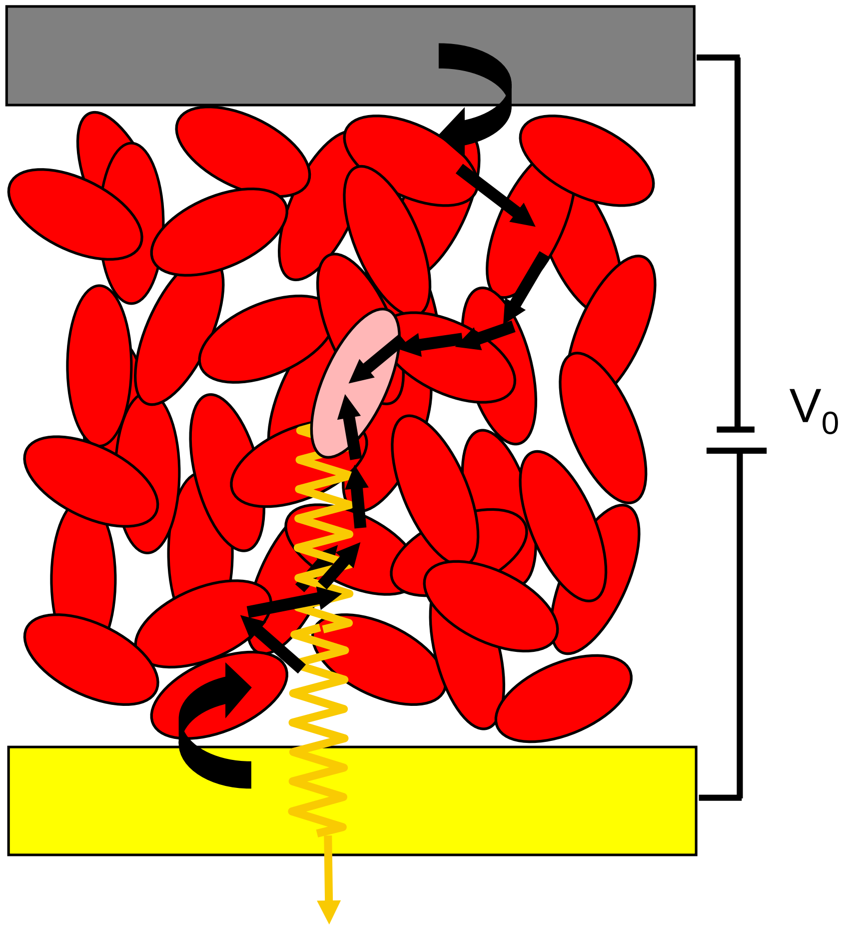
- OLED device structure and operational principle
- Phenomenon of electrical fatigue
- Factors that influence electrical fatigue:
  - Defects from chemical synthesis
  - Structural properties: Side chain symmetry
  - Impact of self absorption on lifetime
  - Impact of triplet excitons on lifetime
  - Phenomenon of “Sudden Death”
- Charge transport modeling
- Summary

PLEDs and their operation

Alkoxy-substituted poly(*p*-phenylene-vinylene) or PPVs







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PLEDs and their operation

Physical processes

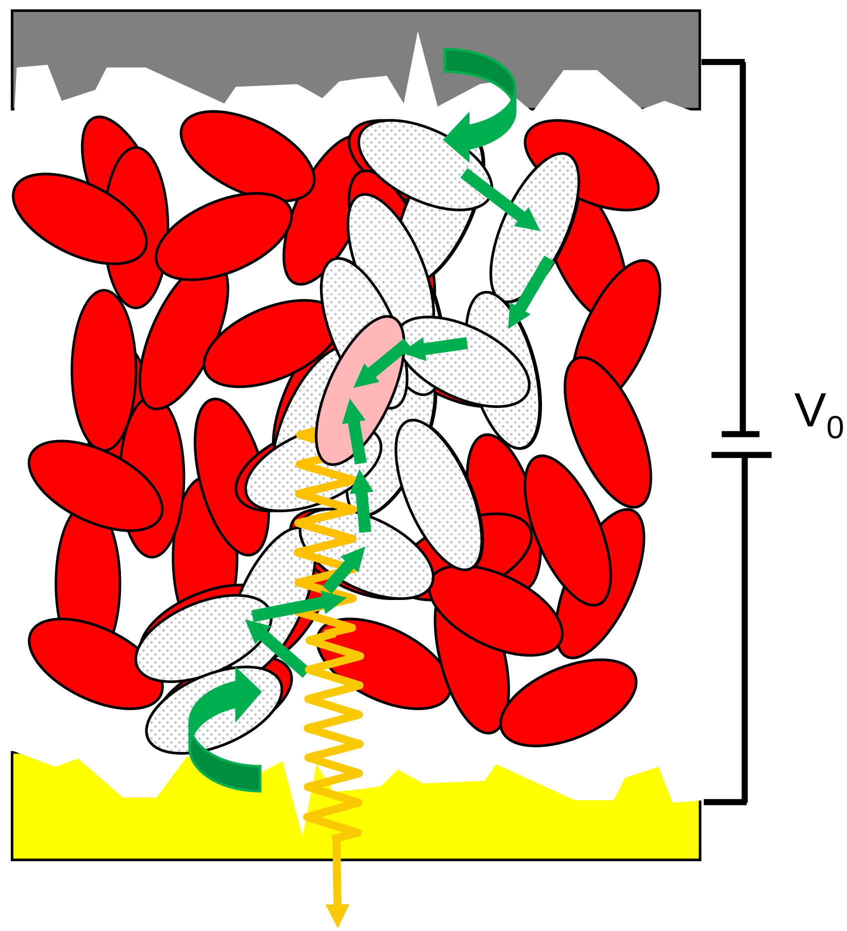
- Charge carrier injection
- Charge carrier transport
- Exciton formation and diffusion
- Recombination

Fatigue

Impact on

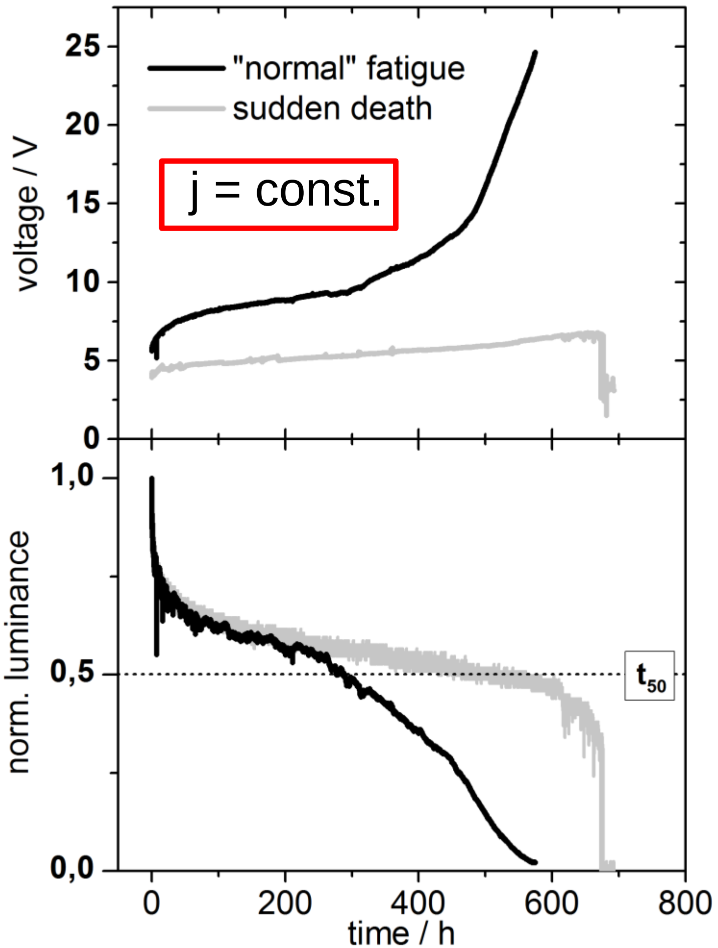
Degradation of

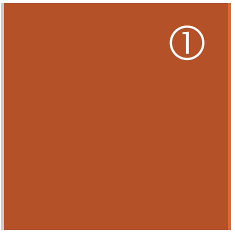
- Electrodes
- Organic semiconductor

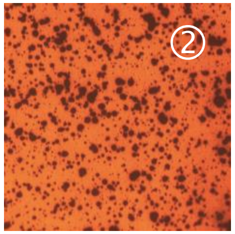


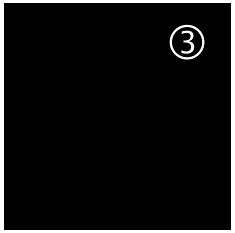
Phenomenology of electrical fatigue

D4

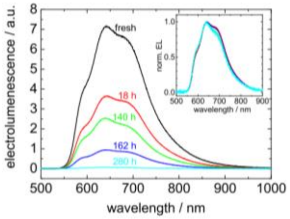








Fatigue modes



"Normal" fatigue

Homogeneous loss of light intensity

Dark spot formation

Inhomogeneous loss of light intensity and active volume

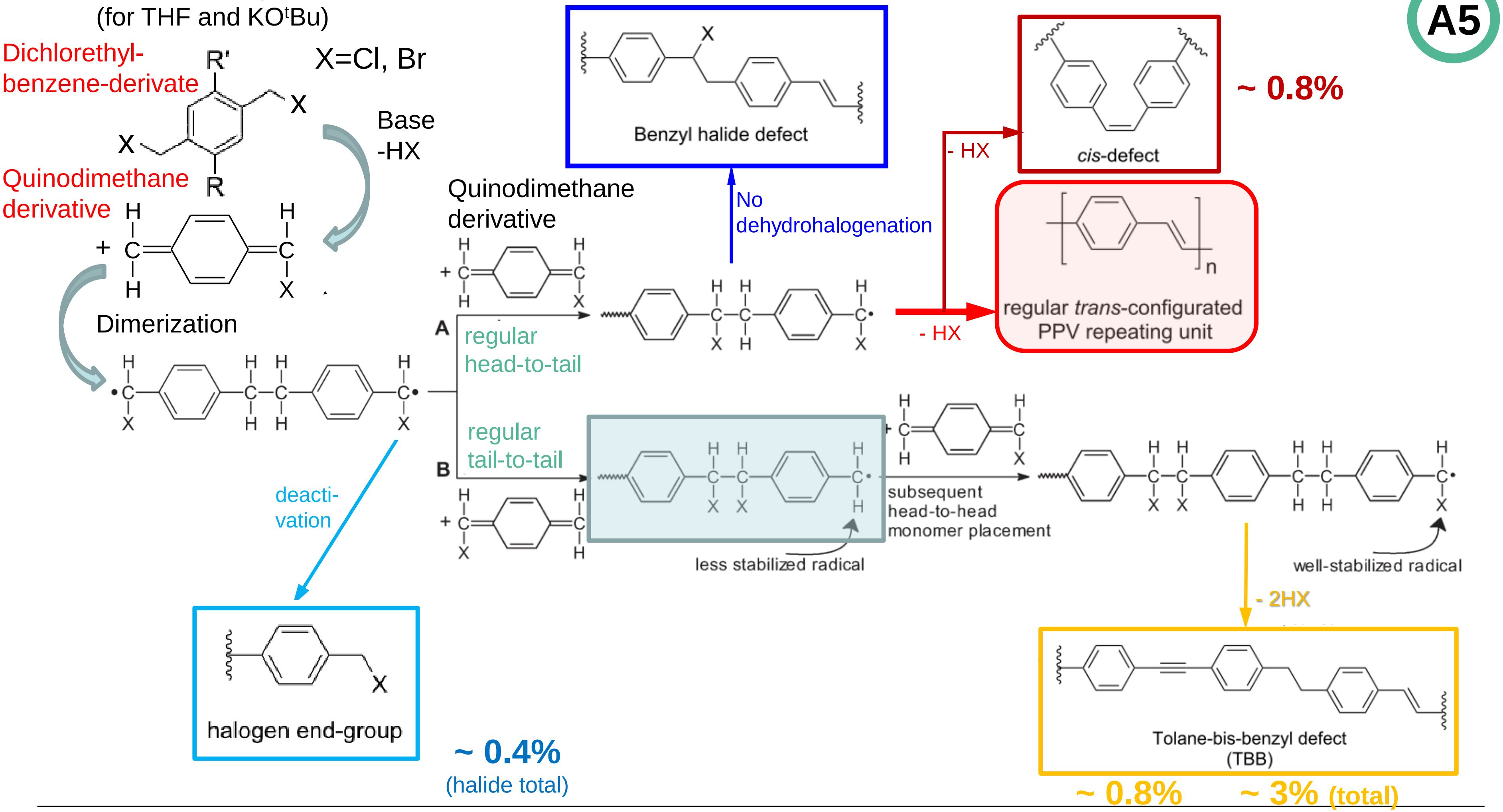
Sudden death

Unexpected catastrophic failure of device

Defects from chemical synthesis: Revisiting Gilch synthesis

A5

Radical chain growth mechanism (for THF and KO^tBu)



Schwalm et al., *Macromol. Rapid Commun.* **30**, 1295-1322 (2009).

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Defects from chemical synthesis: Revisiting Gilch synthesis

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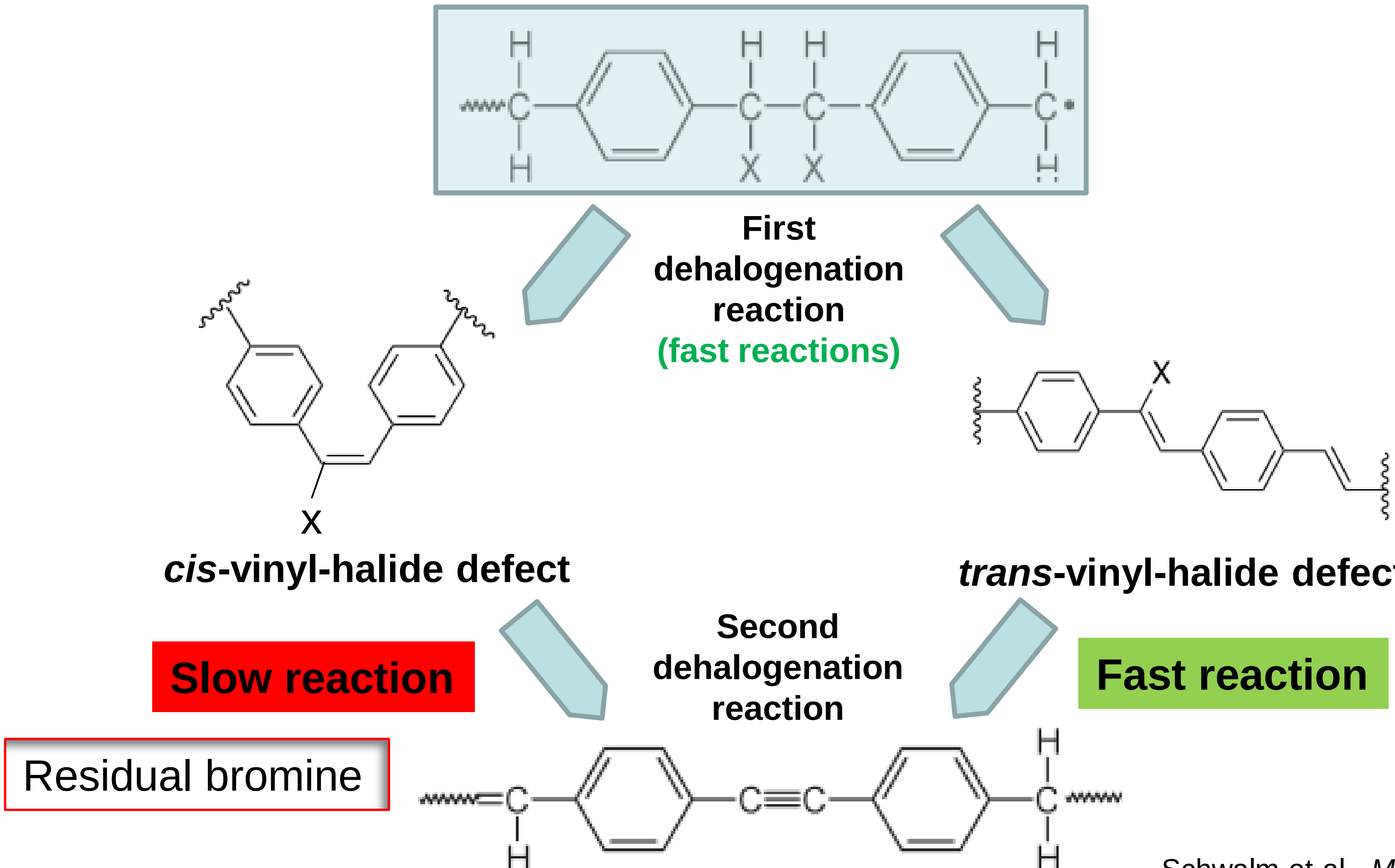

Schwalm et al., *Macromol. Rapid Commun.* **30**, 1295-1322 (2009).

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Defects from chemical synthesis: Dehydrohalogenation and OLED lifetime

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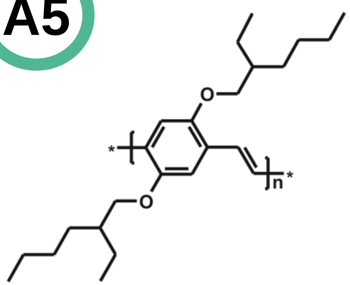
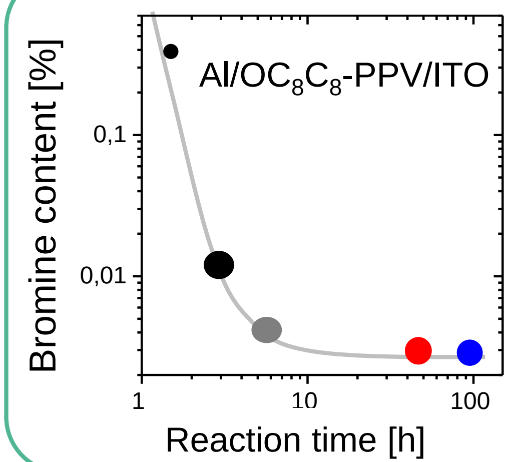


Control of halide defect concentration by reaction time



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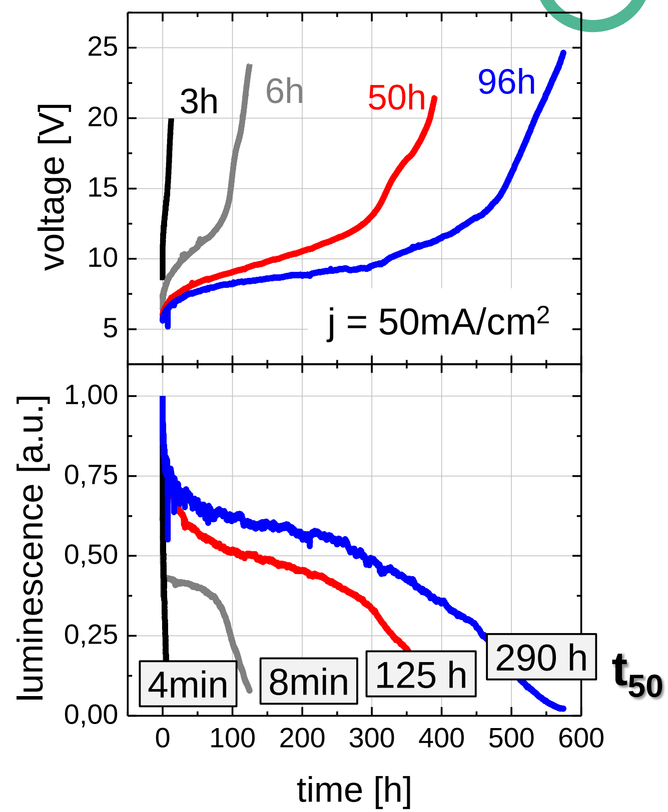
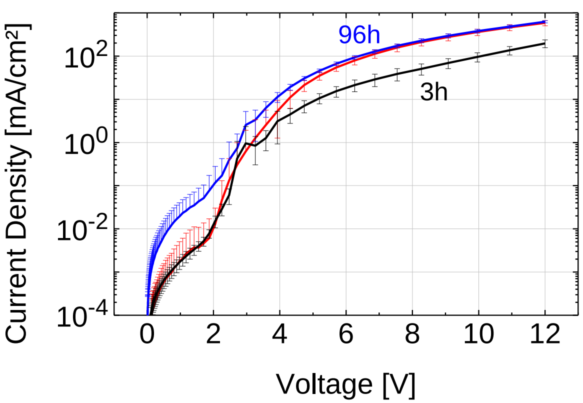
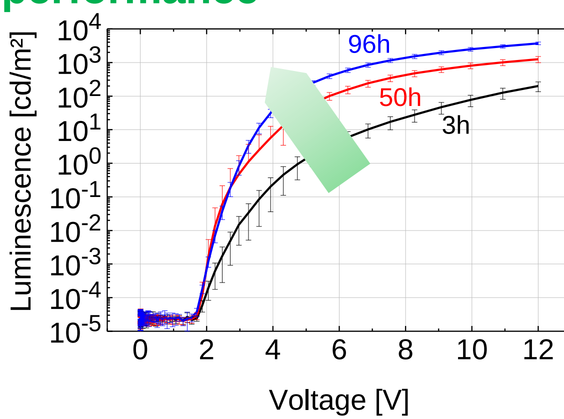
Enhanced lifetime



Improved device performance





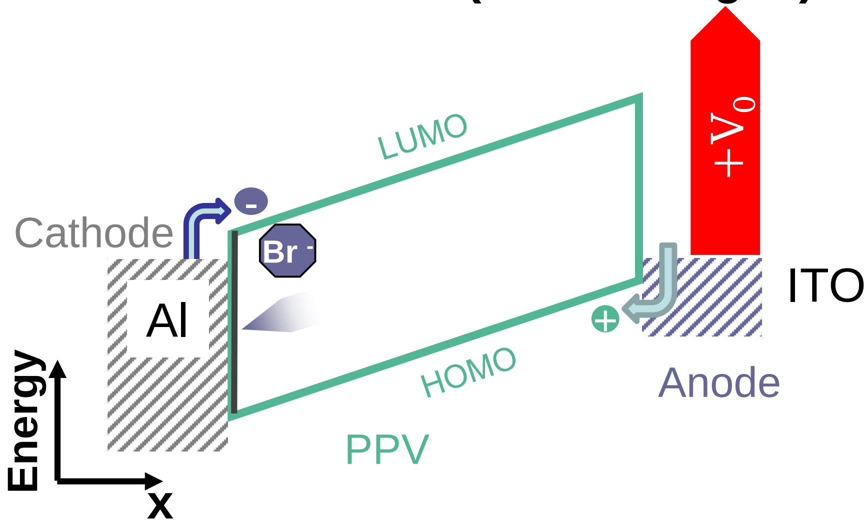
Improved device performance

Fleissner et al., *Chem. Mater.* **21**, 4288-98 (2009).

Defects from chemical synthesis: Model for bromide defect and lifetime

Under short circuit (before fatigue)

D4



Model:

- **Bromide released as anions from PPV-chain**
- **Transported in electric field to cathode**
- **Formation of blocking layer (e.g. CaBr)**

Defects from chemical synthesis: Model for bromide defect and lifetime

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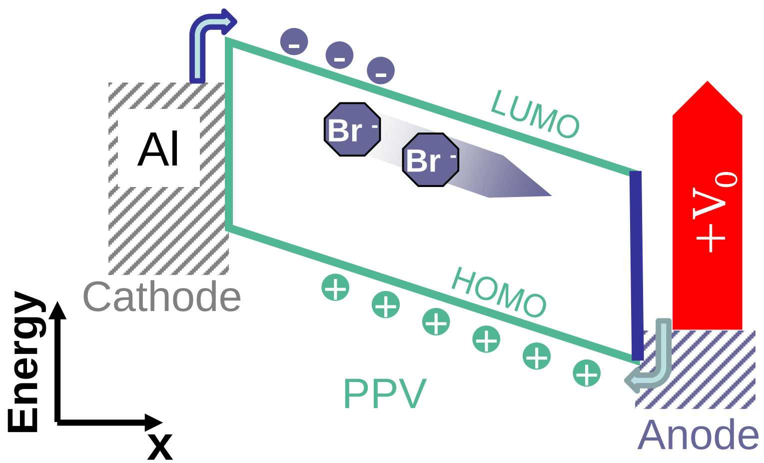
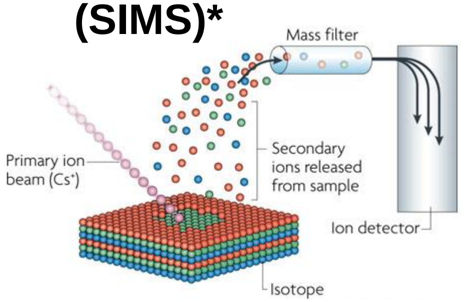
Under forward bias (during fatigue)



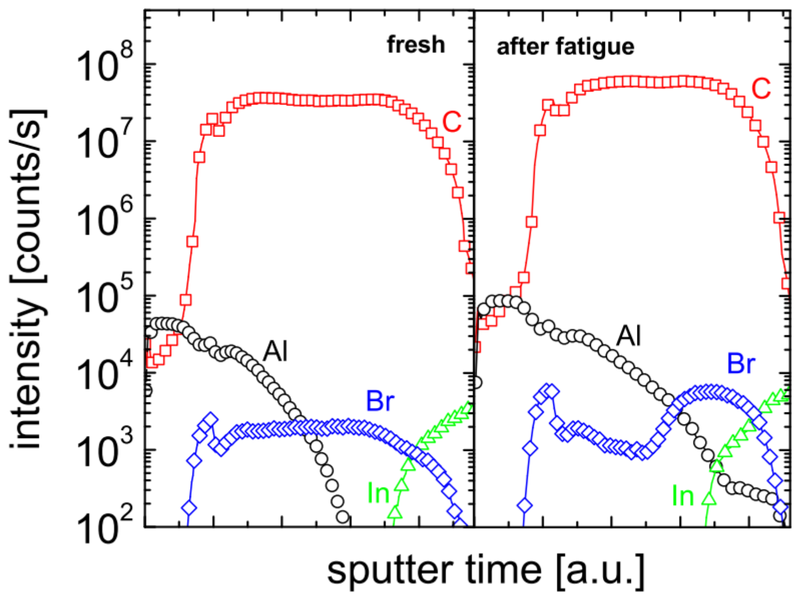
Secondary Ion Mass Spectroscopy (SIMS)*

D4



*picture adapted from Nat. Rev. Micr. 5, 689 (2007)

OLED profile from SIMS



Model:

- **Bromide released as anions from PPV-chain**
- **Transported in electric field to anode**
- **Formation of blocking layer (e.g. InBr)**

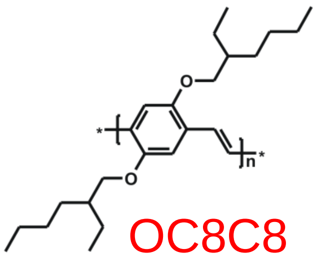
- Hole injection impeded due to formation of blocking layer at anode during fatigue

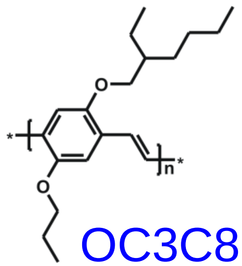
Structural properties: Influence of side chain symmetry on lifetime

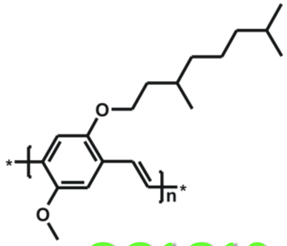
A5

Halide-defect poor systems

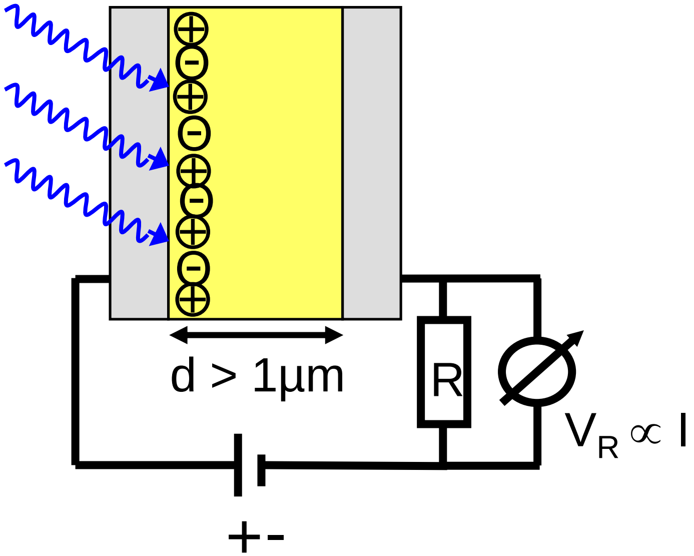
PPV derivatives

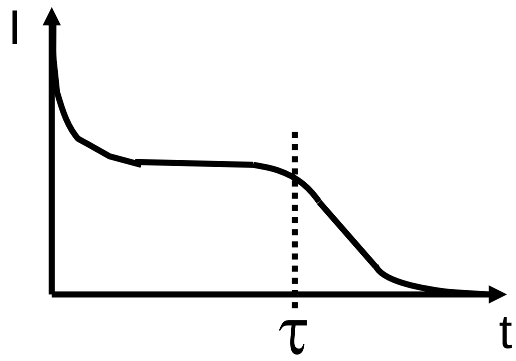






Time-of-flight technique (TOF)





$$\mu = \frac{v}{E} = \frac{d^2}{\tau \cdot V}$$

Structural properties: Influence of side chain symmetry on lifetime

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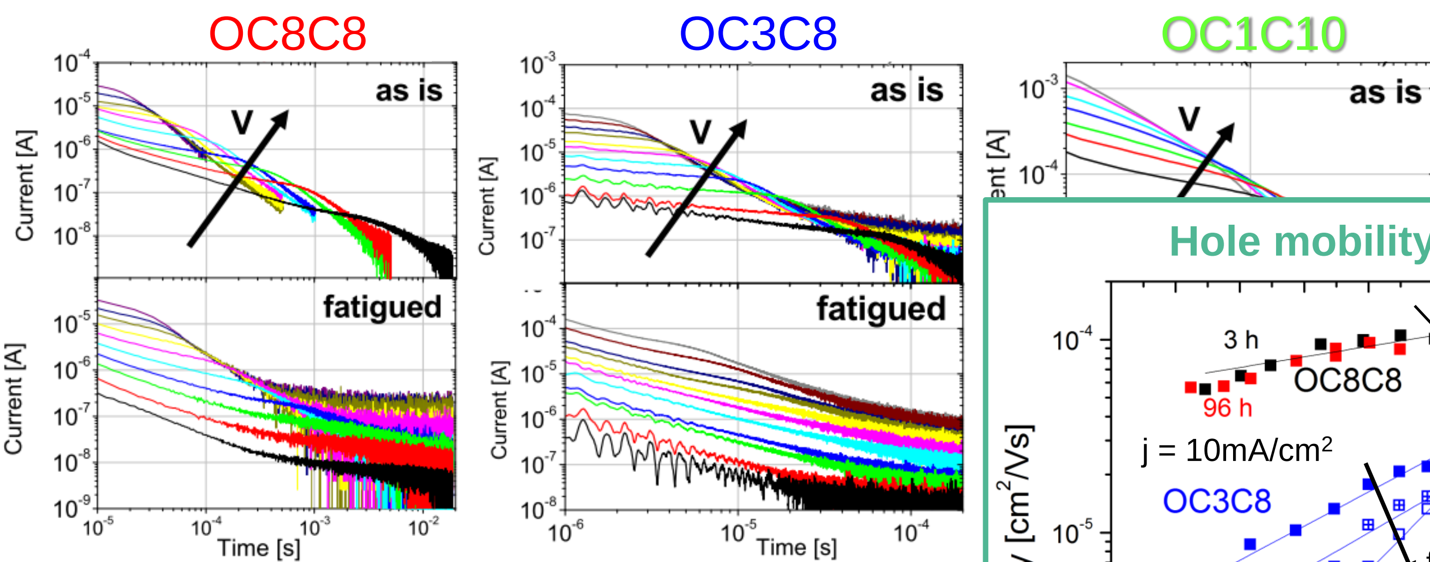
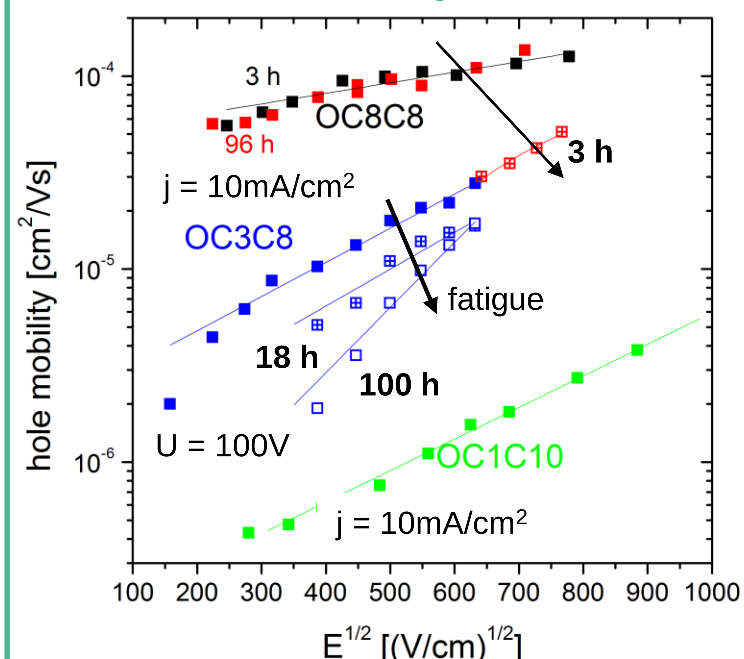


Hole mobility evolution



- Increasing disorder from side chain symmetry leads to decreasing hole mobility without fatigue
- Fatigue induces transition to dispersive transport and decreases hole mobility

Stegmaier et al., *Appl. Phys.* **110**, 034507 (2011).

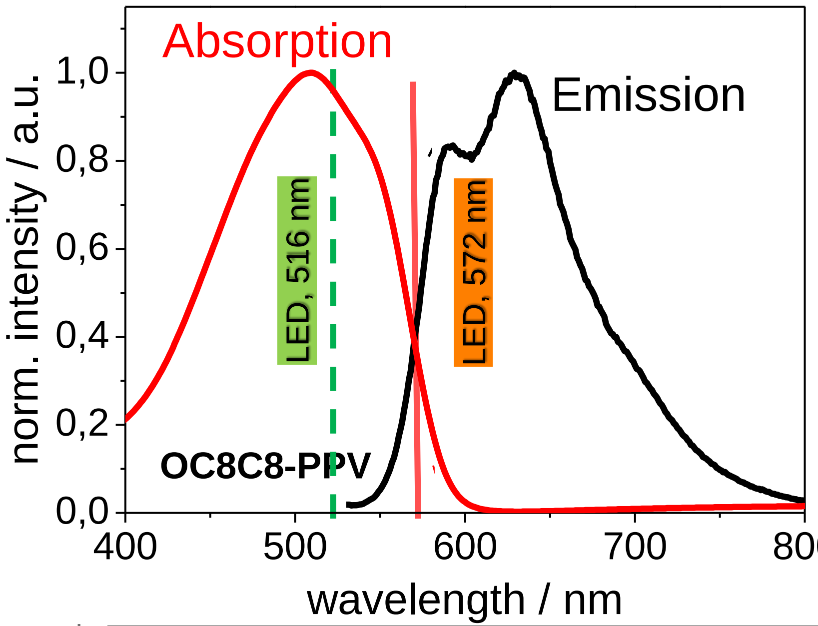
Impact of self-absorption on lifetime

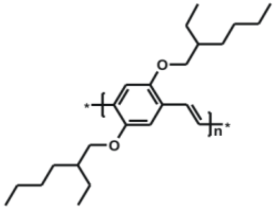
D4

Do holes alone fatigue a device?

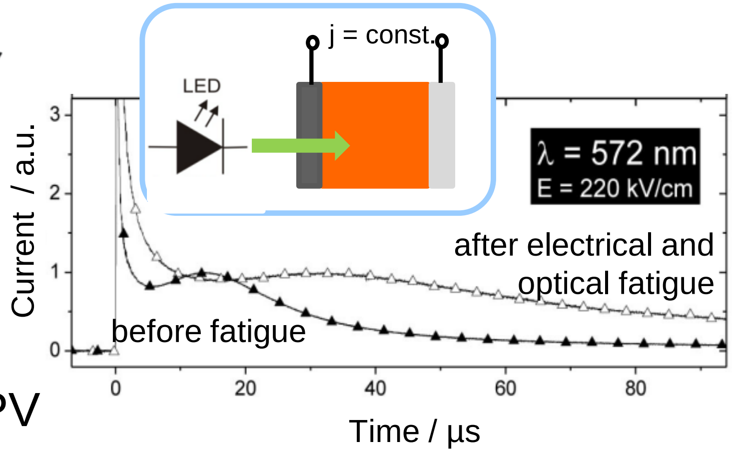
- **Experiment:**
  - **Hole-only devices under flatband condition and under additional light exposure show no fatigue (singlets)**
  - **Light illumination of electrically driven hole-only diodes leads to fatigue**

⇒ **Free electrons are essential for fatigue (formation of triplets)**





OC8C8-PPV



- Is the formation of triplets essential for fatigue?
- Self-absorption of emitted light can deliver additional free electrons for fatigue

Stegmaier et al., *Appl. Phys.* **110**, 034507 (2011).

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Impact of triplet excitons on OLED lifetime

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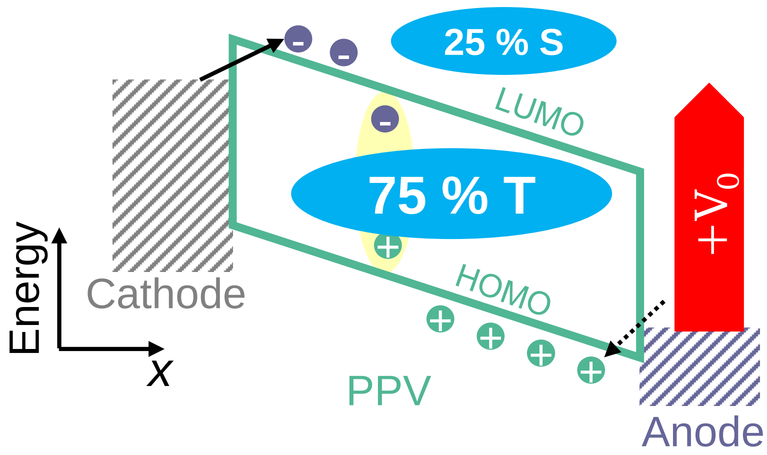
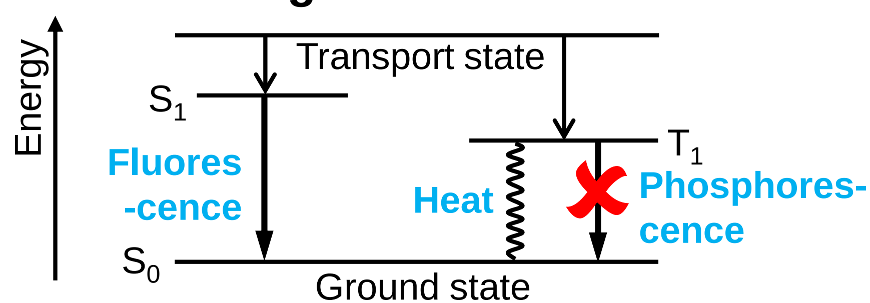
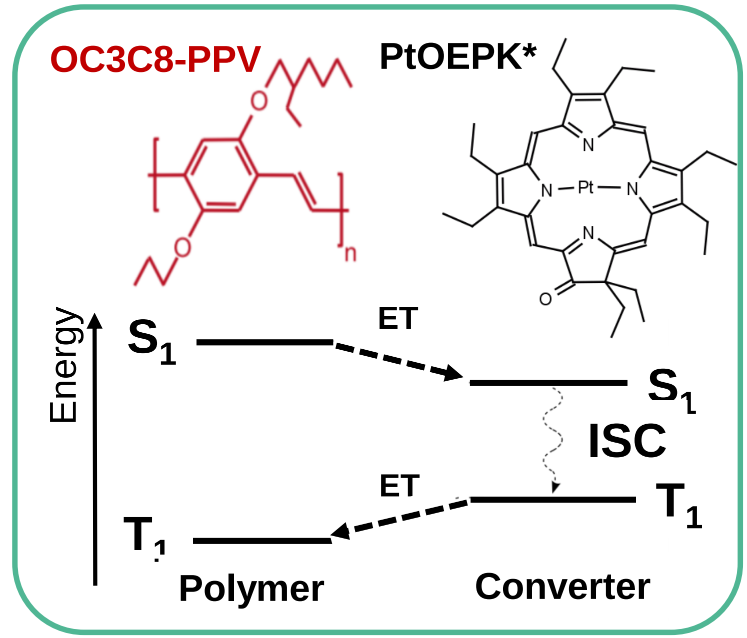
Under forward bias



Fate of an electron/hole pair in organic molecules



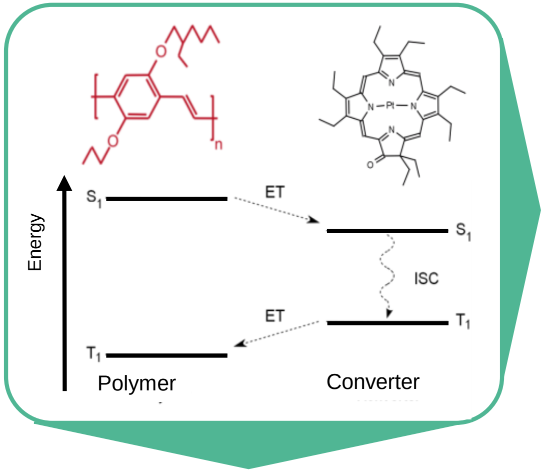
Singlet-Triplet conversion by use of triplet-sensitizer



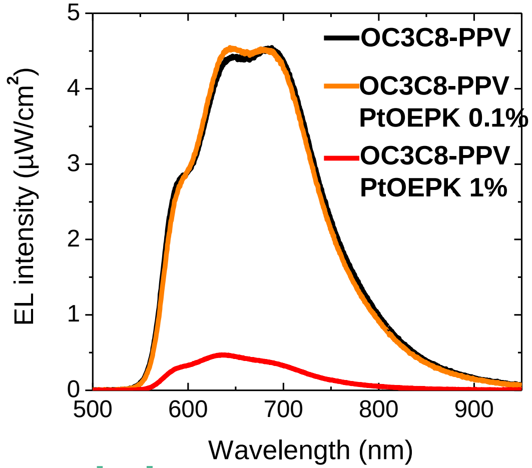
* Platinum (II) octaethylporphyrine ketone

Pekkola et al., *Phys. Status Solidi A*, 1-5 (2014), DOI 10.1002/pssa.201330411.

Impact of triplet excitons on OLED lifetime

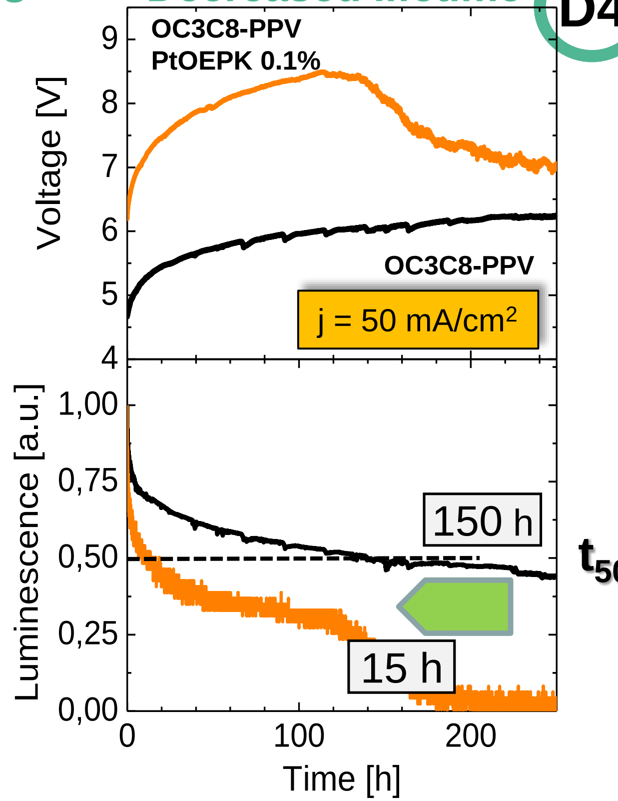


Conversion proven in OLEDs

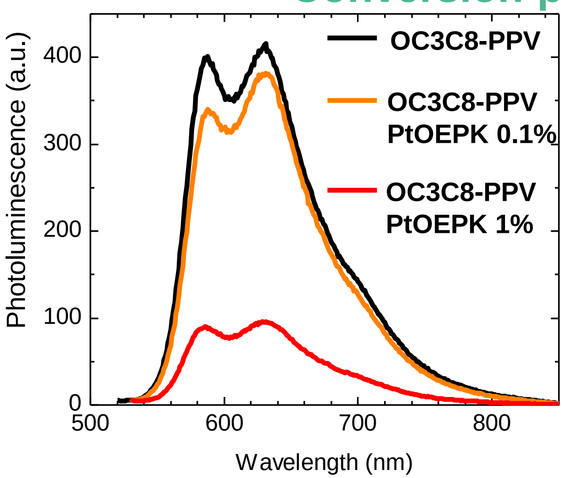


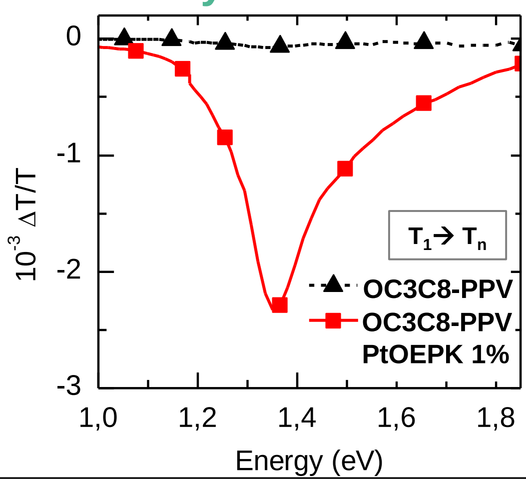
Decreased lifetime

D4



Conversion proven in layers



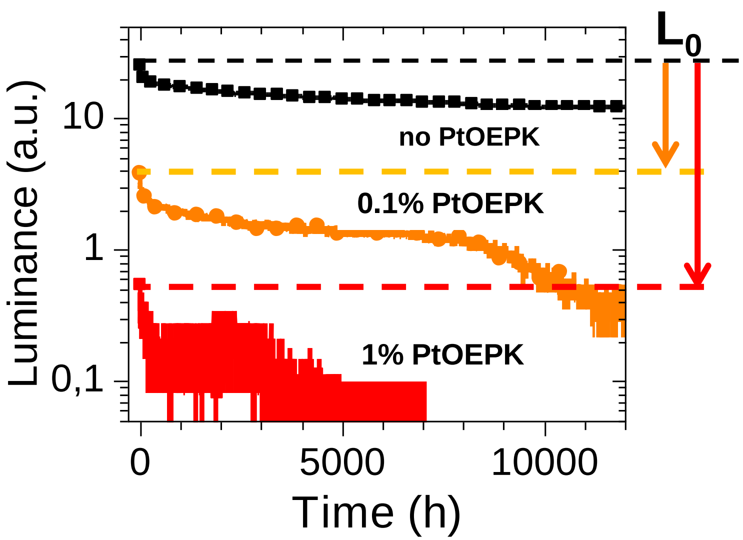


- Enrichment with triplet excitons weakens the device stability

Impact of triplet excitons on OLED lifetime

D4

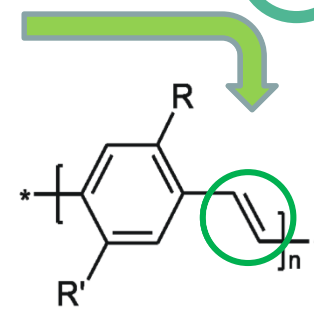
Triplet-triplet annihilation (TTA)



- Loss of initial intensity L_0
- Steepened initial decay
- Shortened plateau region
- Extra singlets generated by TTA unlikely

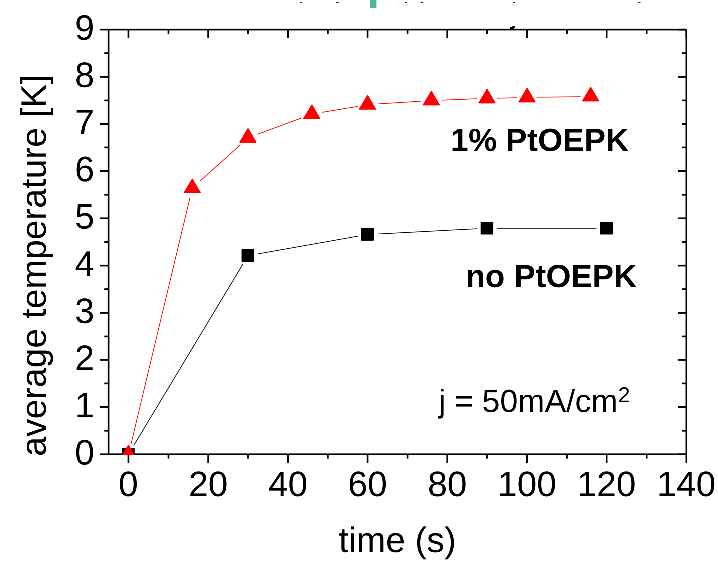
Reaction with triplet oxygen

$^{T}PPV + {}^{T}O_2 \rightarrow PPV + {}^{S}O_2$



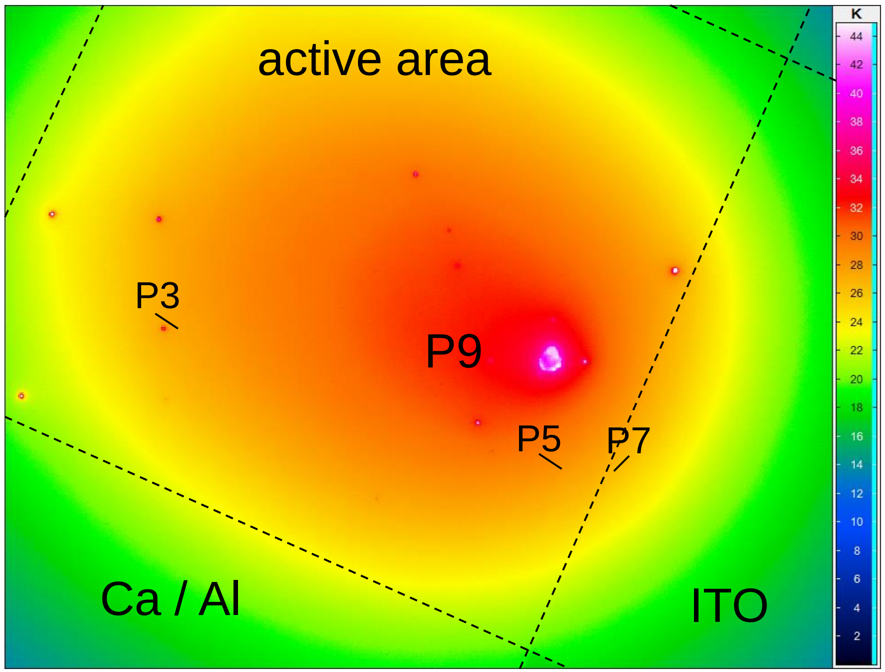
- Destruction of polymer chain due to reaction with $^{T}O_2$ possible

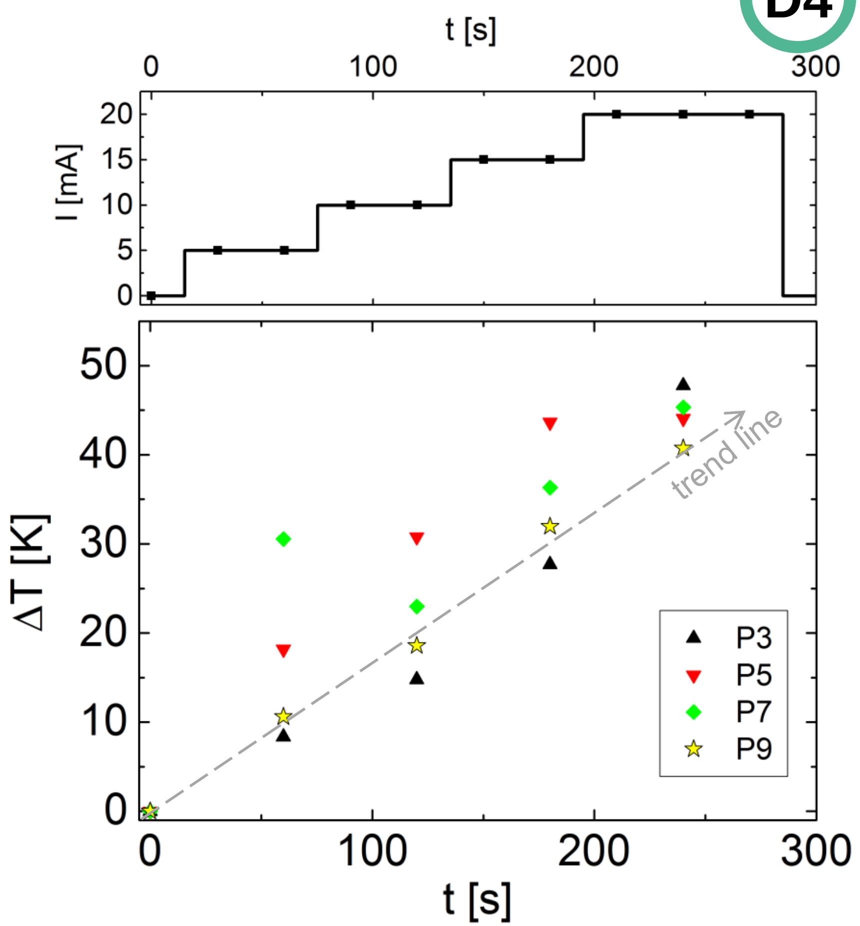
Increased heat dissipation



- Multiple processes are possible for sensitized devices to explain fatigue

Phenomenon of Sudden Death



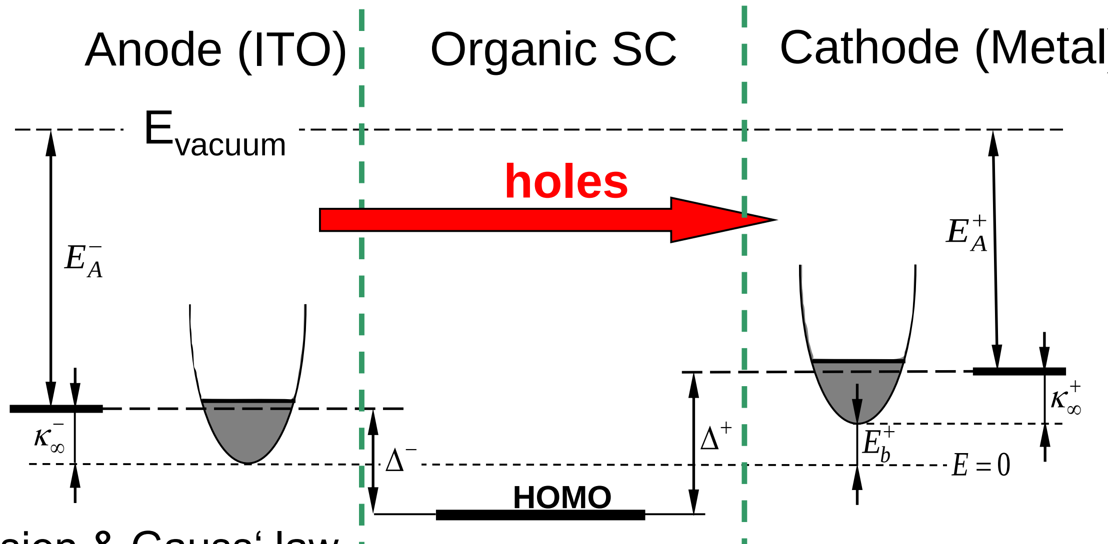


- Device temperature under operation for variable currents
- Diode exhibits hot spots that evolve during electrical fatigue
- Image taken shortly before sudden death.

Charge-carrier transport: Mean-field model

Mean-field (MF) model for unipolar diode

C5
D4



- Drift-diffusion & Gauss‘ law
- Boltzmann statistics of carriers and narrow DOS: $g(E) = P\delta(E - E_{\mathrm{HOMO}})$
- Continous electrical potential, displacement and electrochemical potential at the interface
- At the interfaces: $p_i(\pm L/2) = P\exp\left[-\frac{\Delta^\pm}{kT} \mp \frac{el_{TF}^\pm}{kT}\left(\frac{\varepsilon_i}{\varepsilon^\pm}F_i(\pm L/2) - \frac{j}{\sigma^\pm}\right)\right]$

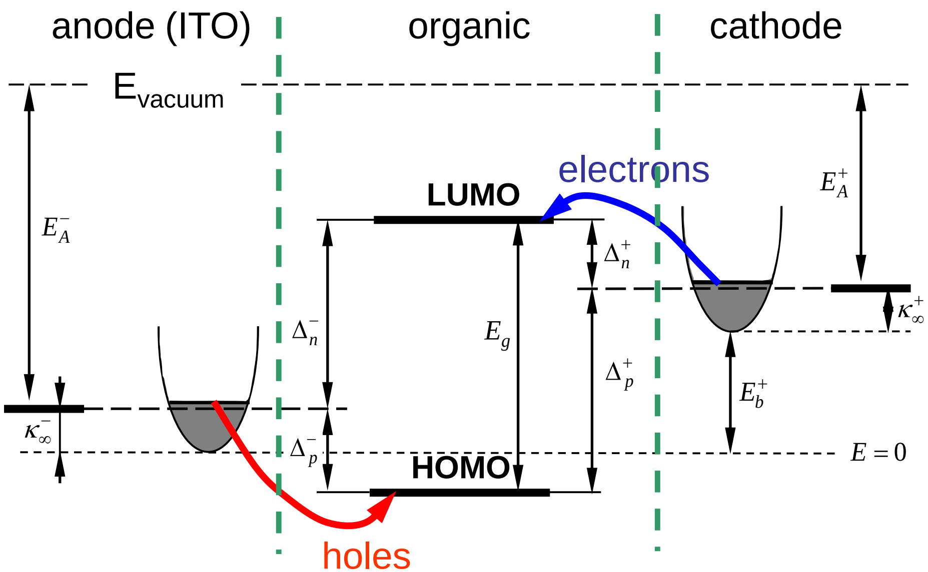
Neumann et al., JAP **100**, 084511 (2006); PRB **75**, 205322 (2007).

Charge-carrier transport: Mean-field model

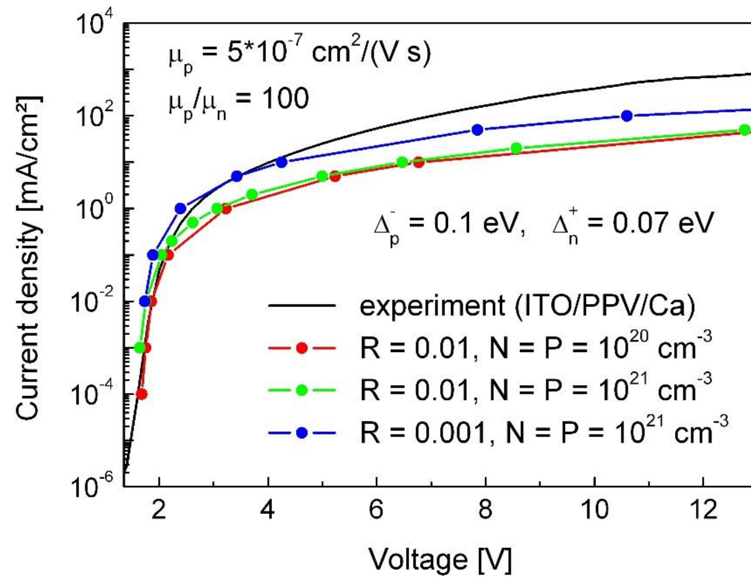
Bipolar injection and transport

C5

D4



ITO/OC_1C_{10}-PPV(100nm)/Ca diode



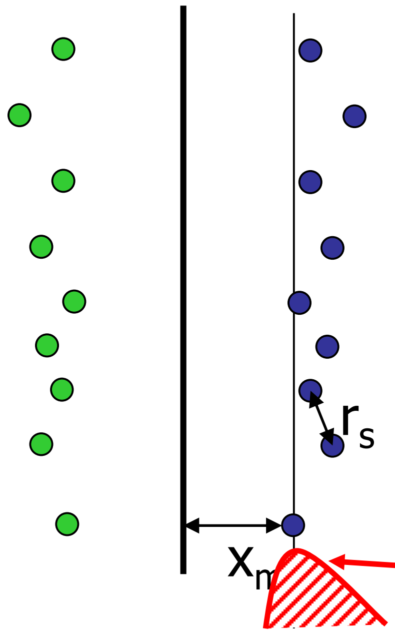
- Injection of holes and electrons
- Direct recombination between HOMO and LUMO (R-efficiency); no impurity levels
- Narrow DOS for both HOMO and LUMO

Yampolskii et al. JAP **104**, 073719 (2008).

Charge-carrier transport

C5

Many-particle vs. single-particle (SP) mechanism

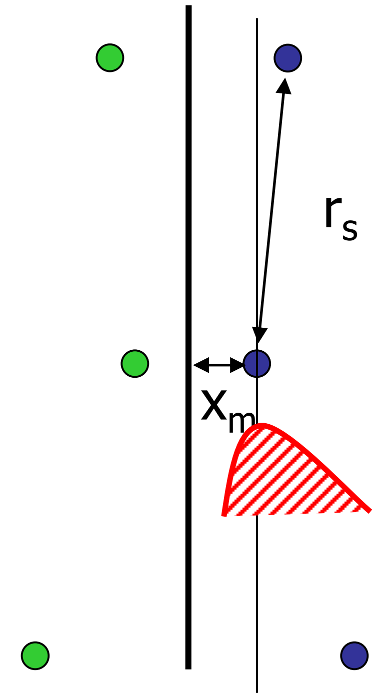


SP/MF criterion

Individual image force = mean-force from other particles

$$x_m \cong 0.2 r_s$$

SP Schottky barrier



When $x_m < 0.2 r_s$, mean-field boundary conditions are modified:

$$p_i(\pm L/2) = P\exp\left[-\frac{\Delta^{\pm}}{kT} \mp \frac{eF(\pm L/2) l_{TF}^{\pm}}{kT}\frac{\varepsilon_i}{\varepsilon^{\pm}} + \left(1 - \frac{x_m^{\pm}}{0.2 r_s^{\pm}}\right)\frac{e\delta\varphi_{sch}^{\pm}}{kT}\theta\left(\mp F(\pm L/2)\right)\right]$$

Genenko et al., PRB **81**, 125310 (2010).

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Charge-carrier transport

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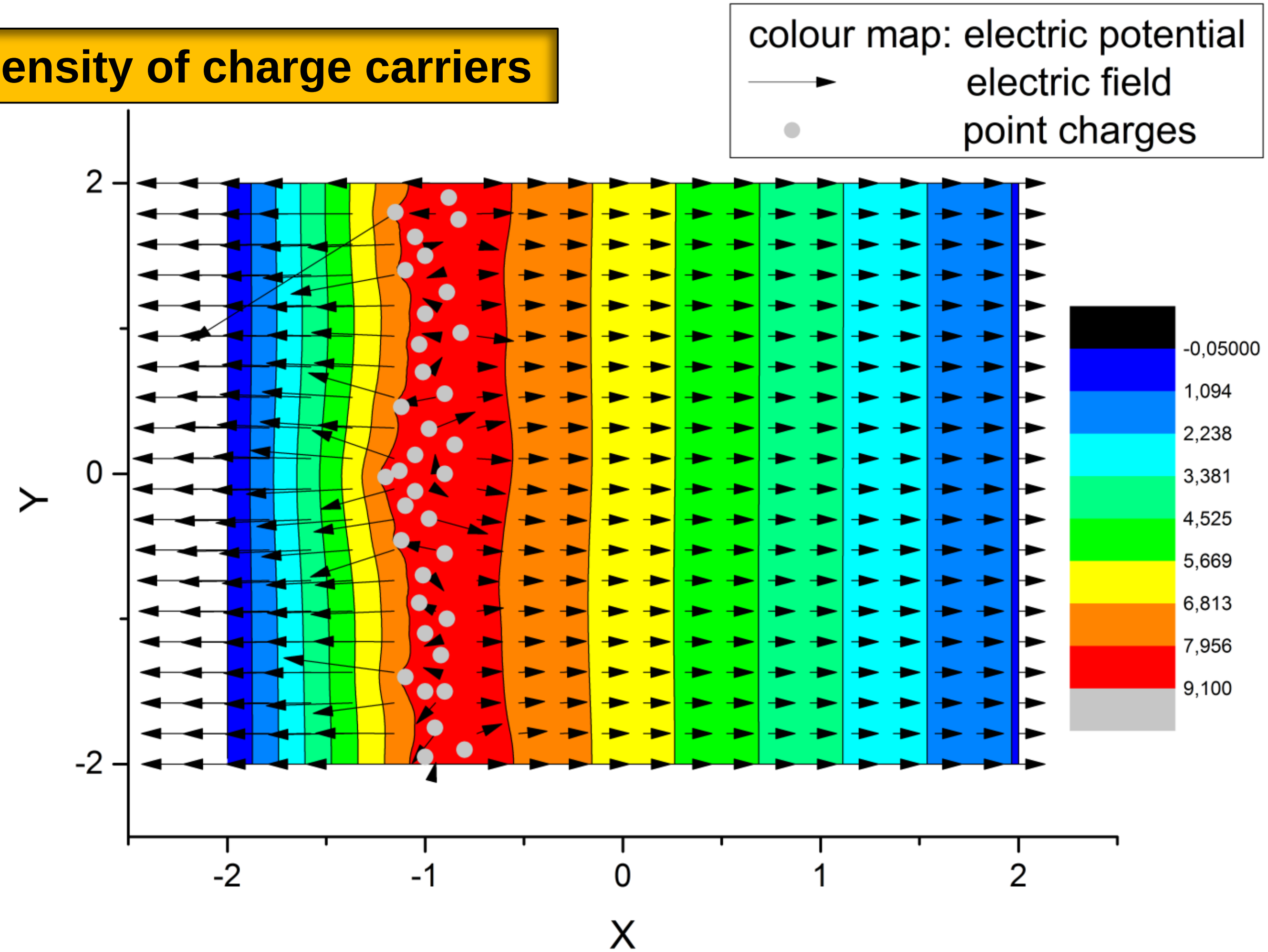
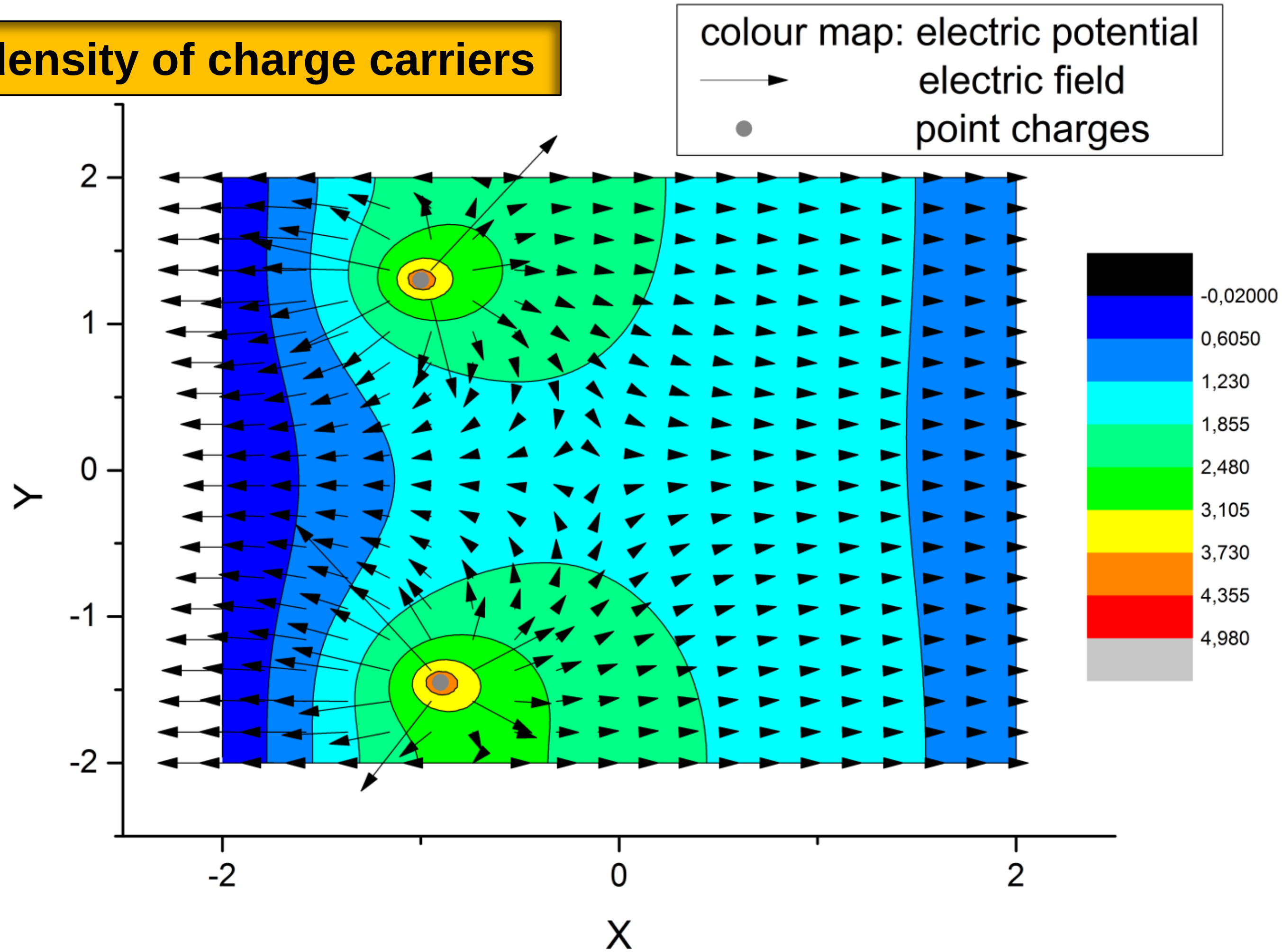
High density of charge carriers



Charge-carrier transport

C5

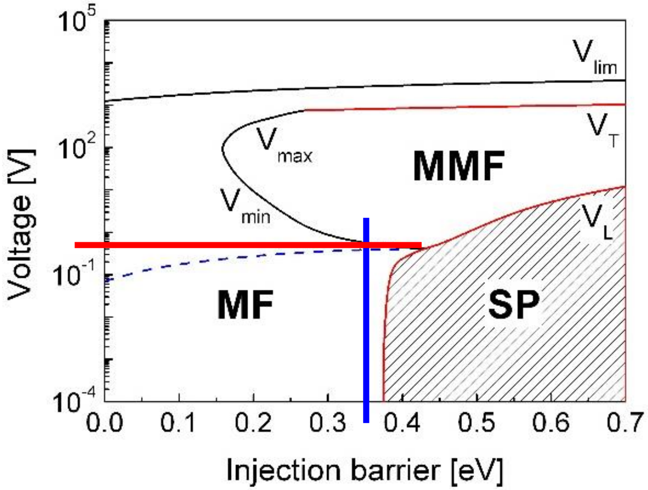
Low density of charge carriers

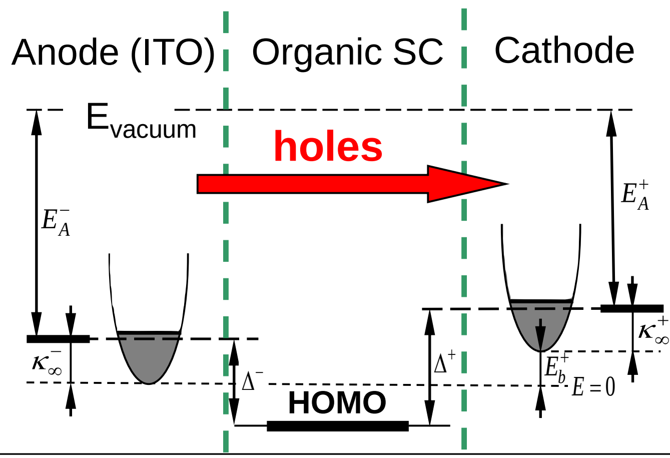


Charge-carrier transport

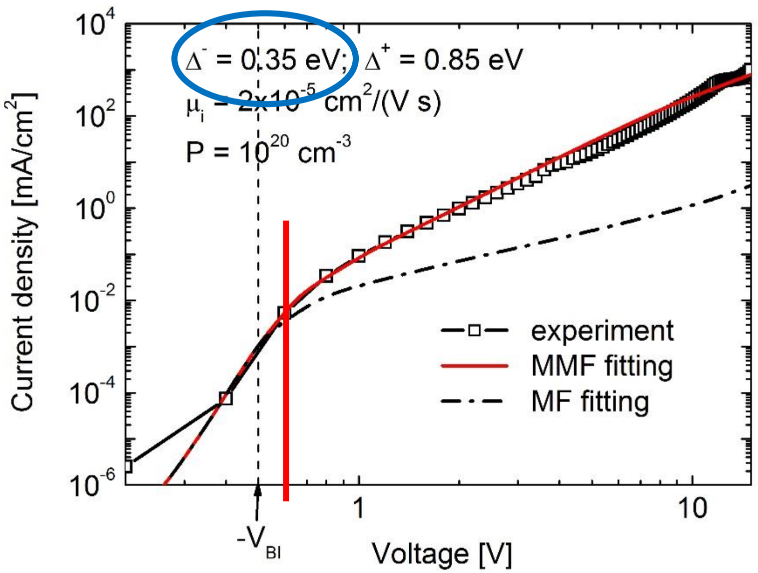
Unipolar diode: modified mean-field (MMF) model

C5
D4





ITO/OC_1C_{10}-PPV(100nm)/Au diode

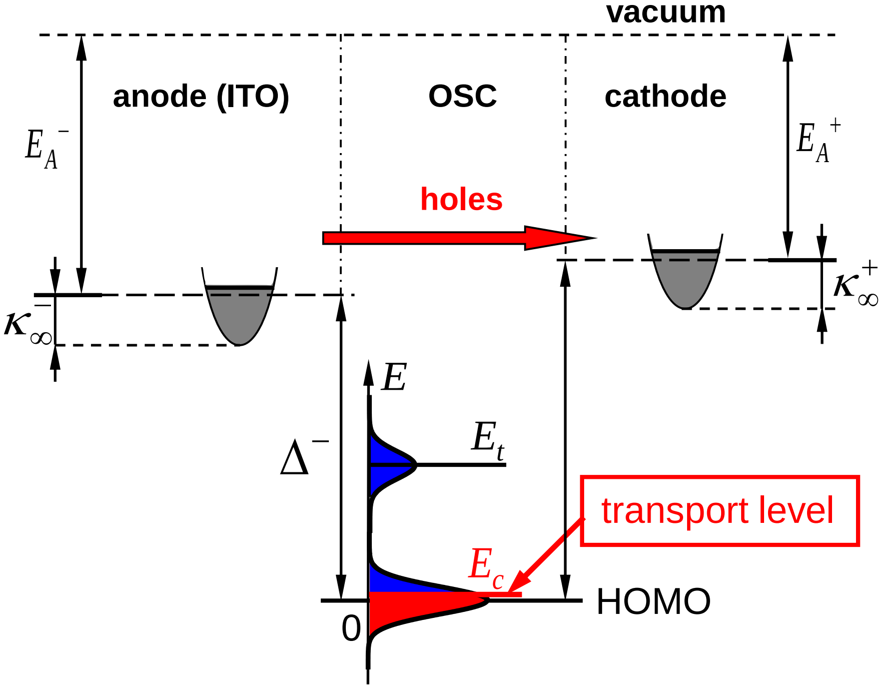


Genenko et al., PRB **81**, 125310 (2010).

Charge-carrier transport

C5 D4

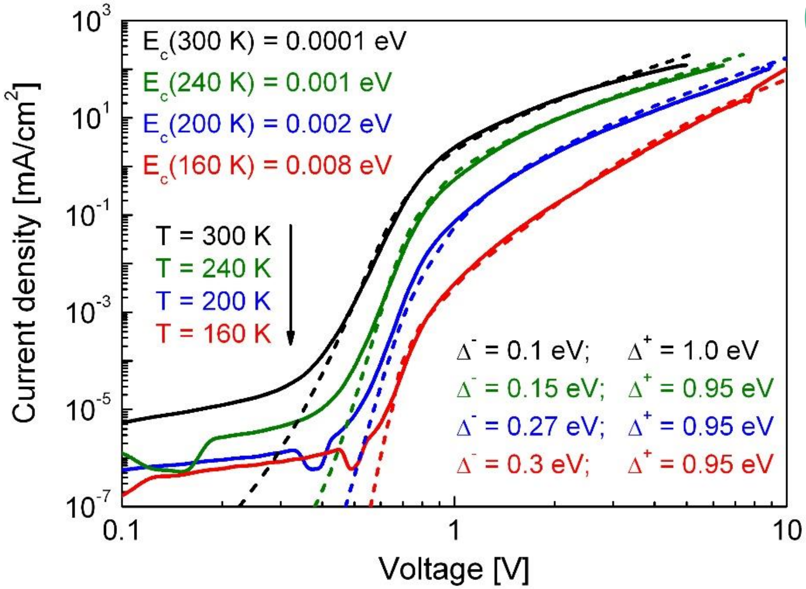
Unipolar diode:
MMF for a realistic shape of DOS



Both HOMO and trap levels exhibit a Gaussian DOS

ITO/P3HT(125nm)/Al diode

(from Nikitenko et al. JAP 94, 2480 (2003))



$\mu = 6.7*10^{-4}$ cm^2/(V s); $E_t = 0.5$ eV

$P_c = 10^{21}$ cm^{-3}; $P_t = 5*10^{15}$ cm^{-3}

$\sigma_c = 0.035$ eV; $\sigma_t = 0.02$ eV

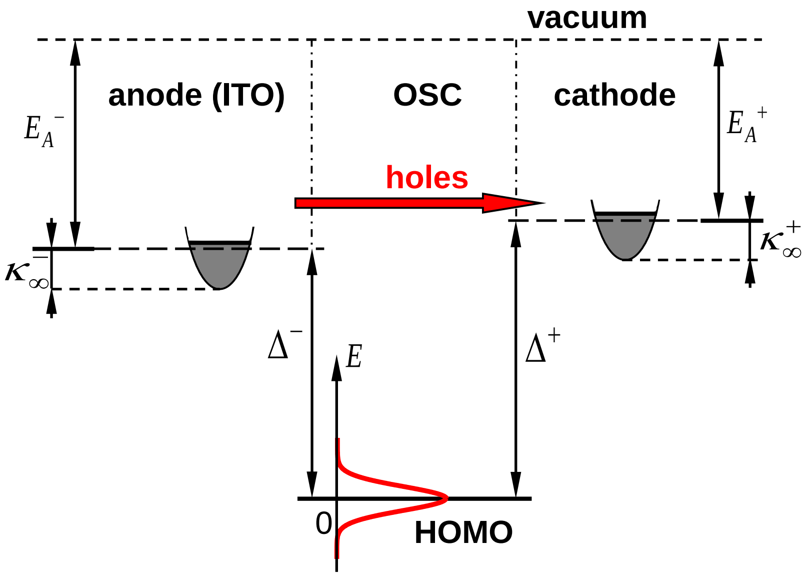
Yampolskii et al. JAP **109**, 073722 (2011).

Charge-carrier transport

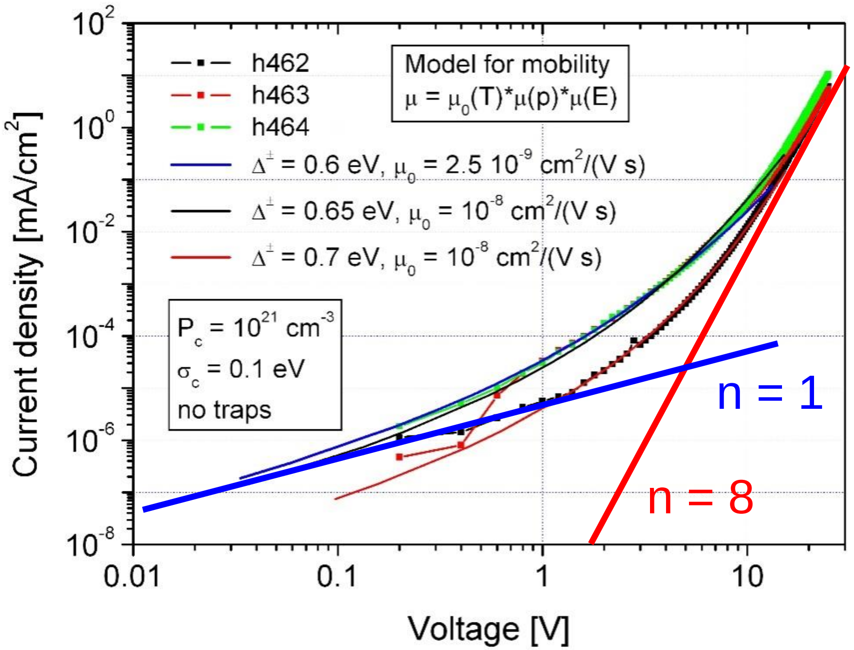
Unipolar diode: Gaussian DOS with E- and n-dependent mobility

C5

D4



ITO/OC_1C_{10}-PPV(130nm)/Au diode



Effective carrier mobility is field- and concentration-dependent

$$\mu_p(x) = \mu_0(T)\, g_1\big(p(x)\big)\, g_2\big(F(x)\big)$$

submitted to SFB review

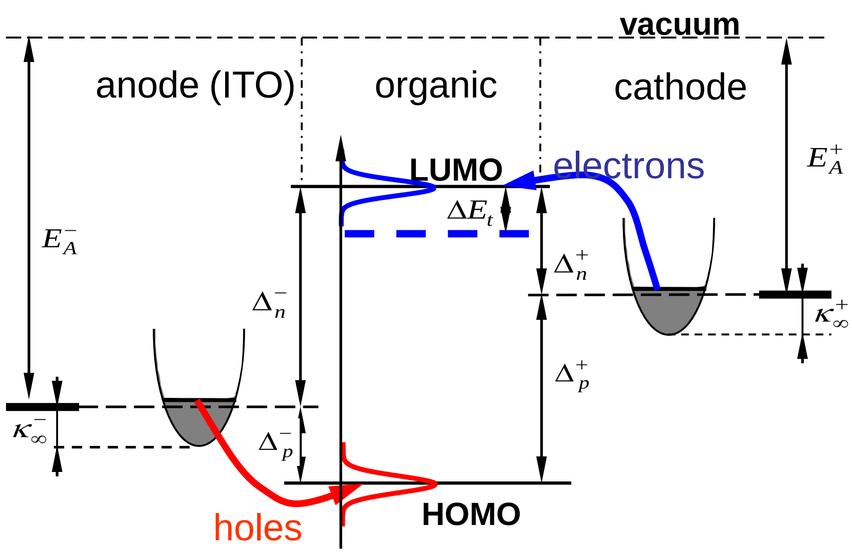
from Pasweer et al. PRL 94, 206601 (2005) [R. Coehoorn, Uni Eindhoven]

Charge-carrier transport

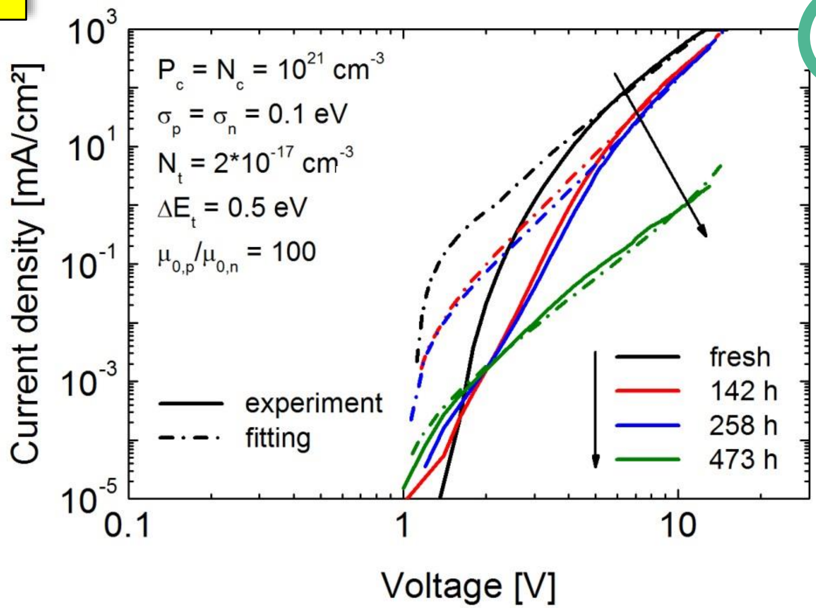
C5

D4

Fatigue in bipolar diode: Gaussian DOS, e⁻-traps and E- and n-dependent mobility



ITO/PEDOT:PSS/OC_3C_8-PPV(130nm)/Ca/Al



- Direct recombination between HOMO and LUMO
- Electron trap levels
- Gaussian DOS for HOMO and LUMO
- Field- and concentration-dependent mobilities

fatigue time	Δ_p [eV]	Δ_n [eV]	$\mu_{0,p}$ [cm^2 V^{-1} s^{-1}]
0 h (fresh)	0.55	0.55	$2.20 \cdot 10^{-6}$
142 h	0.60	0.60	$1.65 \cdot 10^{-6}$
258 h	0.60	0.60	$1.30 \cdot 10^{-6}$
473 h	0.60	0.80	$5.90 \cdot 10^{-8}$

submitted to SFB review

Summary

A5

Polymer synthesis:

✓ Avoid halide residuals in the organic semiconductors

D4

Device preparation and characterization:

✓ Symmetric side chain derivatives show higher hole mobility

✓ Fatigue induces decreasing hole mobility and transition to dispersive transport

✓ A large Stokes shifts avoids fatigue due to light absorption from the OLED emission

✓ Large triplet exciton density speeds up fatigue

C5

Modeling of charge carrier injection and transport:

✓ Self consisting modeling of uni- and bipolar transport in OLEDs

✓ Modified mean-field improves diode model for low carrier densities

✓ Attempt to derive fatigue parameters is still in its infancy

SFB 595 Deutsche Forschungsgemeinschaft DFG

Additional contriburions on OLEDs

TECHNISCHE UNIVERSITÄT DARMSTADT

Katja Stegmaier et al.

- **Invited Talk 11:00: Status, Technology and Challenges in OLED Development**

Oili Pekkola et al.

- **Poster P 27: The harmful influence of triplet excitons on the lifetime of polymer light-emitting diodes**

Nicole Villbrandt et al.

- **Talk 11:30: Poly(p-phenylene vinylene)s Highlights of 12 years of research within the SFB 595**
- **Poster P 15:: Poly(p-phenylene vinylene)s Highlights within the SFB 595**

Sergey V. Yampolskii et al.

- **Talk 11:45: Self-consistent description of charge carrier injection at a conductor/organic semiconductor interface: extension to the case of a degenerate semiconductor**
- **Poster P 23: Phenonenological modelling of field, charge and polarization distributions in ferroelectric and organic semiconductors**

Christian Melzer et al.

- **Poster P 04: The harmful influence of triplet excitons on the lifetime of polymer light-emitting diodes**

SFB 595
Deutsche Forschungsgemeinschaft
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Acknowledgement

TECHNISCHE UNIVERSITÄT DARMSTADT

To all involved people

A5: M. Rehahn, N. Vilbrandt, V. Rittscher, S. Nickel, R. Sander, J. Wiesecke, J. Langecker, M. Preuss, T. Schwalm, M. Schütz

D3: A. Klein, M. Hohmann, A. Wachau, Y. Gassenbauer

D4: H. von Seggern, A. Gassmann, O. Pekkola, C. Melzer, K. Stegmaier, H. Janning, A. Fleissner, R. Schmechel

C2: K. Albe, A. Fey, P. Ágoston, P. Erhart

C5: Y. A. Genenko, H. von Seggern, S. V. Yampolskii, F. Neumann†, V. Arkhipov†

2004-2014

- ✓ 31 people
- ✓ more than 100 conference contributions
- ✓ 81 publications, thereof 20 joint papers

To the DFG for 12 years of funding

SFB 595

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Acknowledgement

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To all involved people

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D3: A. Klein, M ... u, Y. Gasse ...

D4: H. von S ... Melzer, K. Stegmaie ... R. Schmechel

C2: K. Albe, A. Fey, P. Ágoston, P. Erhart

C5: Y. A. Genenko, H. von Seggern, S. V. Yampolskii, F. Neumann†, V. Arkhipov†

and you for your kind attention

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