# Resolving authentic time dependence of time-of-flight photocurrent in organic semiconductors

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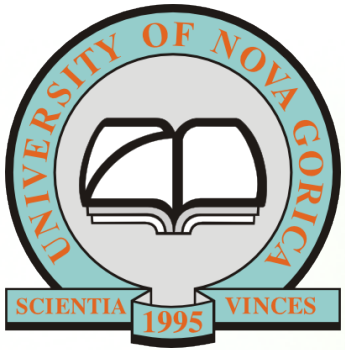
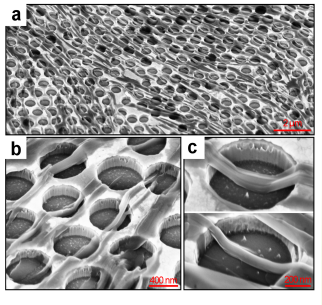


# Motivation

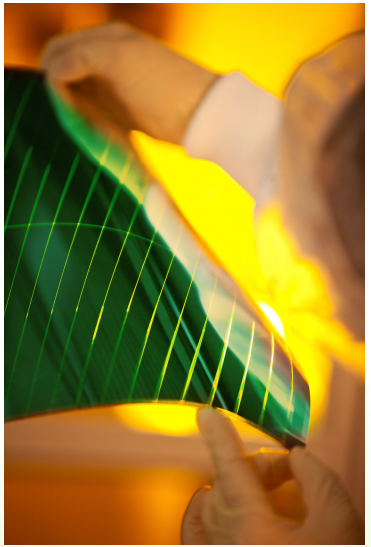
- Semiconductivity of “amorphous” materials
- Molecules with intrinsic **functional properties**
- Van-der-Waals interactions
- Novel **optoelectronic** devices




Fast vertical nanomesh photodetector

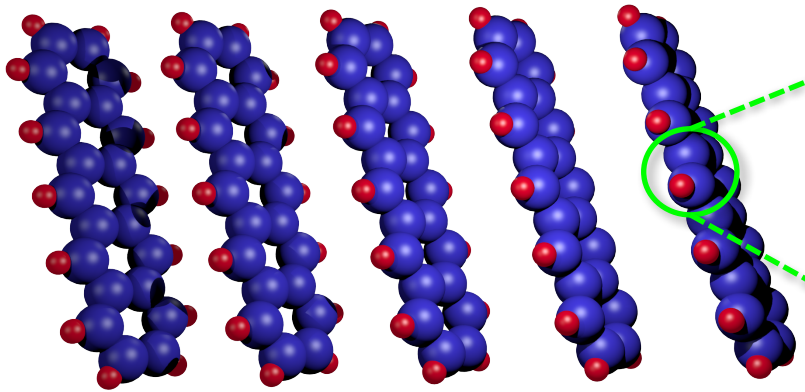
Skin electronics – Photo courtesy John Rogers (University of Illinois)

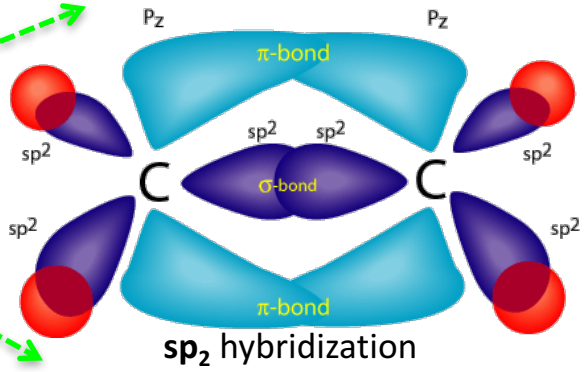
LG's and Samsung's OLED TVs – diagonal 197cm (77") and 140 cm(55").



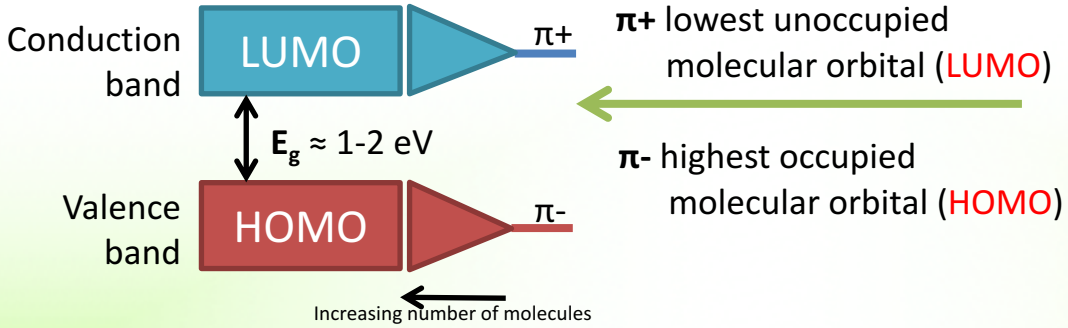
Flexible organic solar cells (Solarfolie by Heliatek)

# Organic Semiconductors



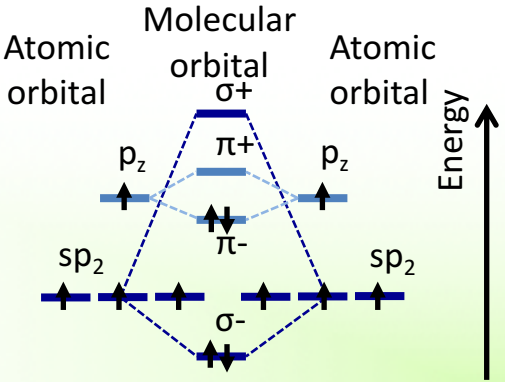



**sp$_2$** hybridization

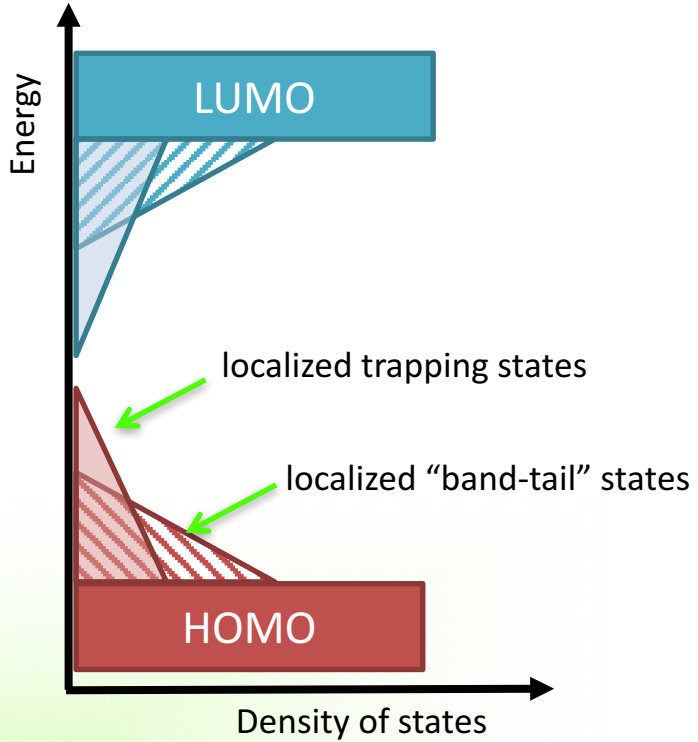



**π+** lowest unoccupied molecular orbital (LUMO)

**π-** highest occupied molecular orbital (HOMO)



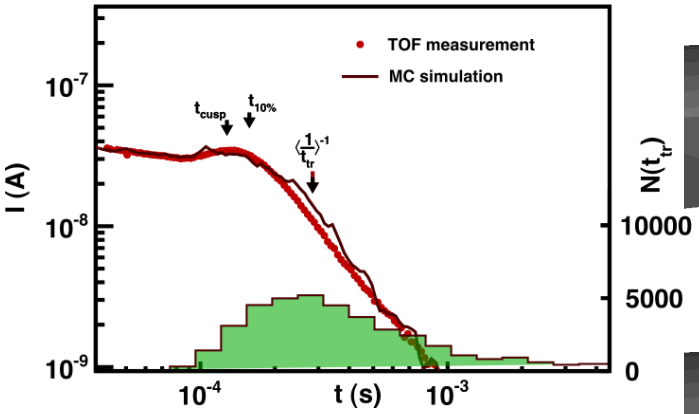
# Disorder

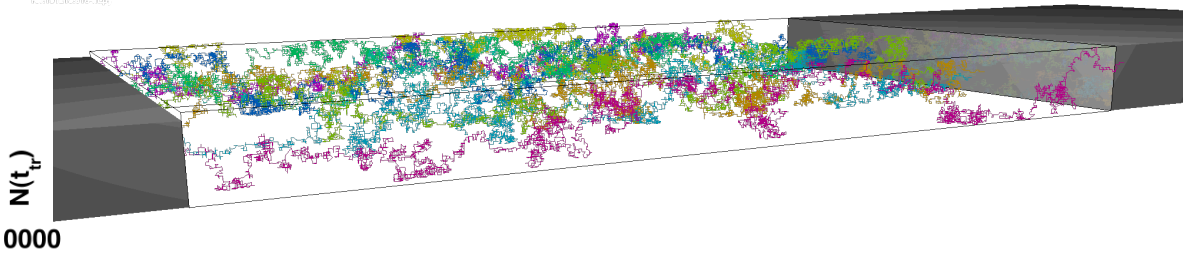



- Charge mobility: **$10^{-6}$ – $10^{2}$ $cm^2/Vs$**
- Electric field and temperature dependent charge mobility (**Poole-Frenkel** type)
- Weak VdW interaction -> high level of structural imperfections
- Imperfections -> localized states
- Band theory + Multiple trap-and-release
- **Hopping theory** / Percolation simplification

# Kinetic Monte Carlo simulations

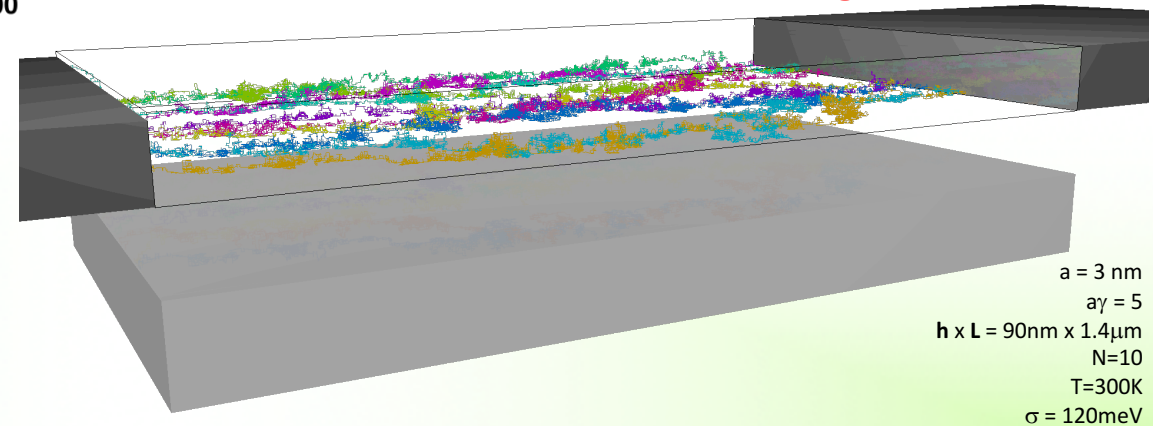
**TOF** -> charge in the whole layer




a = 3 nm
h x L = 90 nm x 130 µm
N = 10240
T = 300K
sigma = 150 meV
$t_0 = 10^{-19}$ s
$N_{ph} = 9.4 \times 10^7$

**Thin-film transistors** -> charge at interface

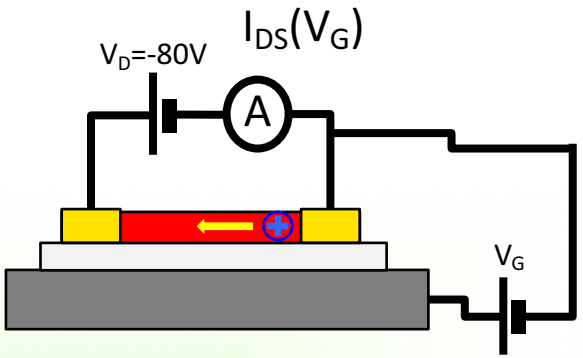


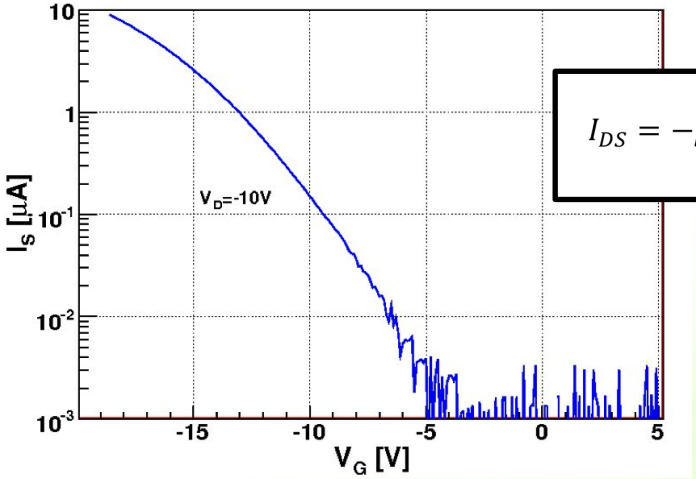
a = 3 nm
aγ = 5
**h** x **L** = 90nm x 1.4µm
N=10
T=300K
σ = 120meV

# Experimental methods

- FET mobility, SCLC, THz spectroscopy, Hall effect, Photoconductivity

**Thin-film transistors** -> field-effect mobility - $\mu_{FET}$

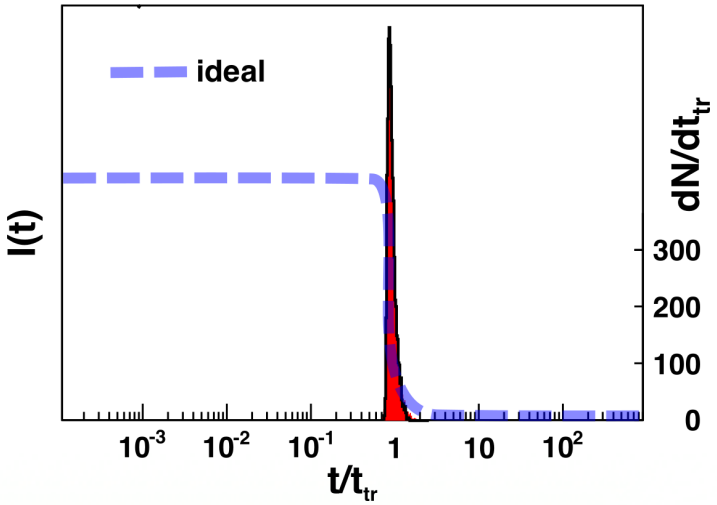


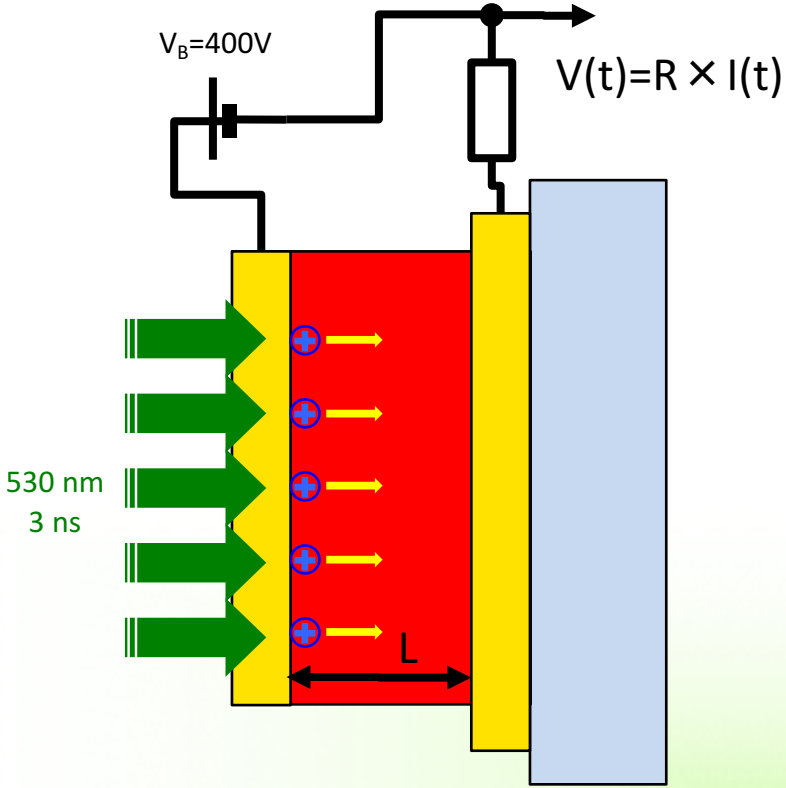

$$I_{DS} = -\mu_{FET}\frac{W \cdot C_i}{2L}(V_G - V_{th})^2$$

Pentacene TFT (L=5μm, W=10mm, BGBC)

# Parallel time-of-flight photoconductivity



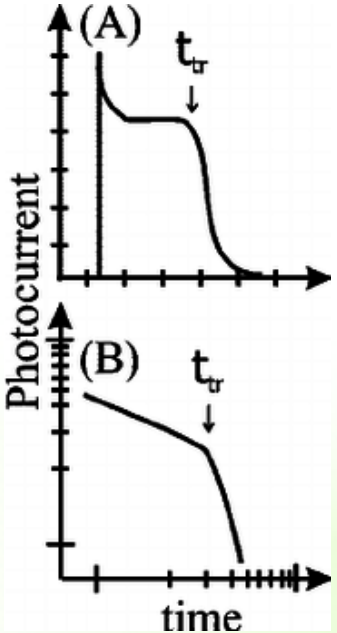

$$\mu_{TOF} = {}^{v}/_{E} \qquad E = {}^{V_B}/_{L} \qquad v = {}^{L}/_{t_{tr}}$$



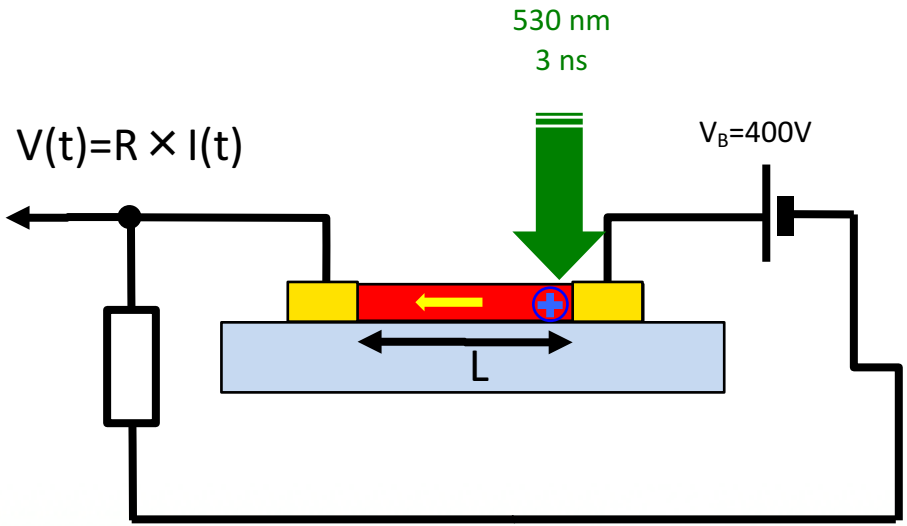
# Scher-Montroll formalism

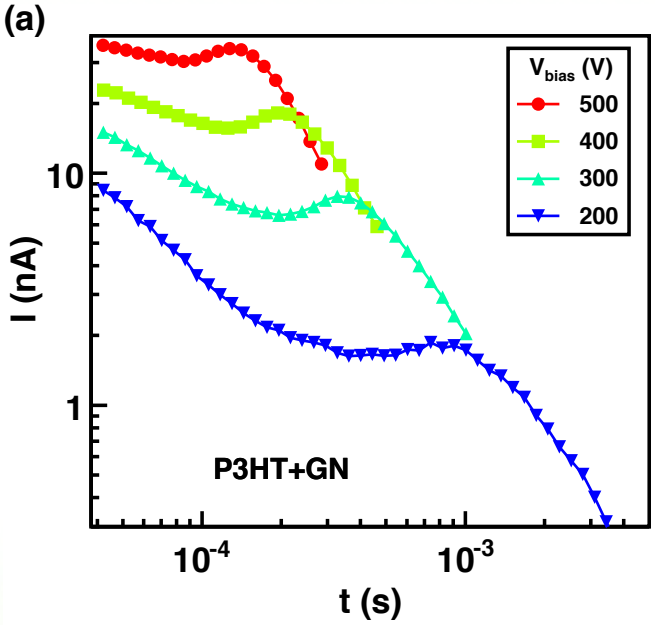
- Gaussian distribution of carriers velocity
- Uniform electric field
- Finite lifetime

$$I_M(t) = I_0 t^{\alpha-1}\left[1+\left({}^{t}/_{t_{tr}}\right)^{a}\right]^{-\frac{k}{a}}$$



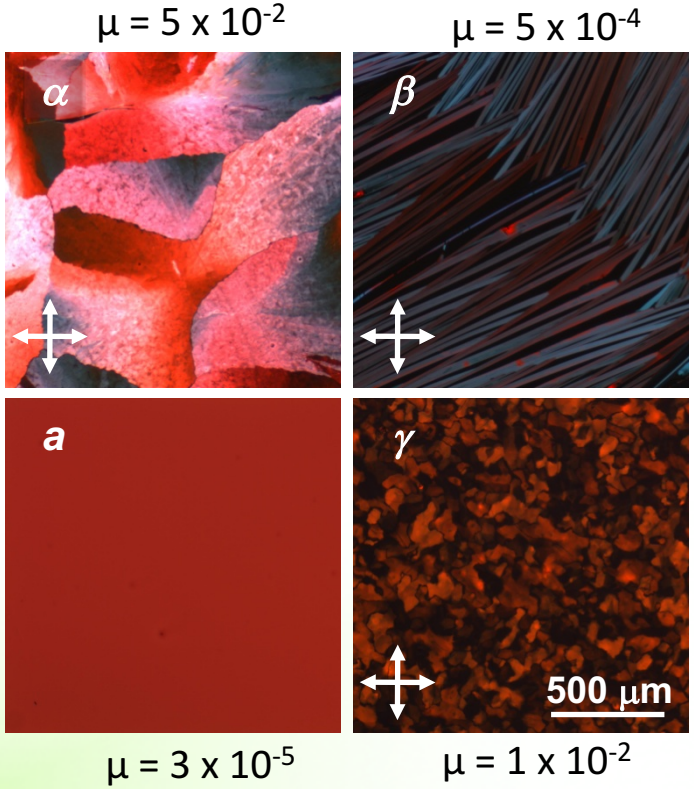
# Coplanar time-of-flight photoconductivity

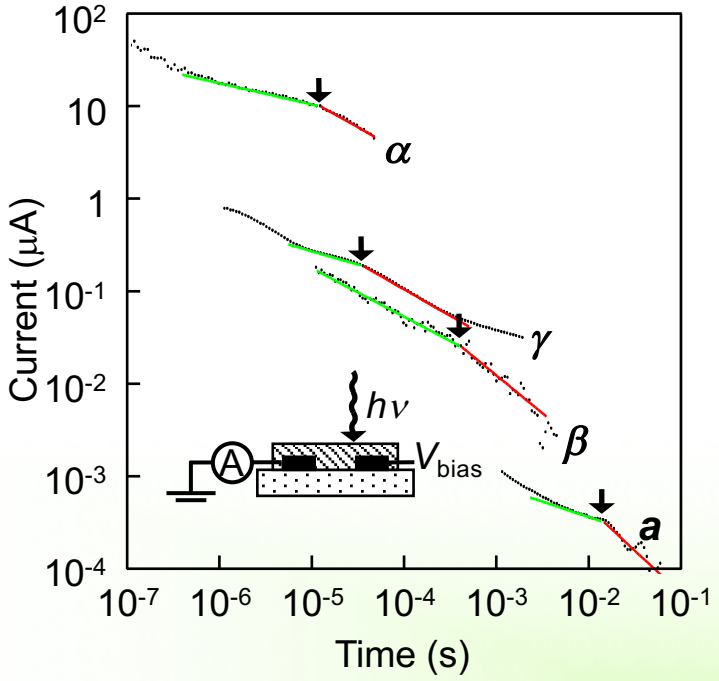



$$\mu_{TOF} = {}^{v}/_{E} \qquad E = {}^{V_B}/_{L} \qquad v = {}^{L}/_{t_{tr}}$$

# TES-ADT polymorphs

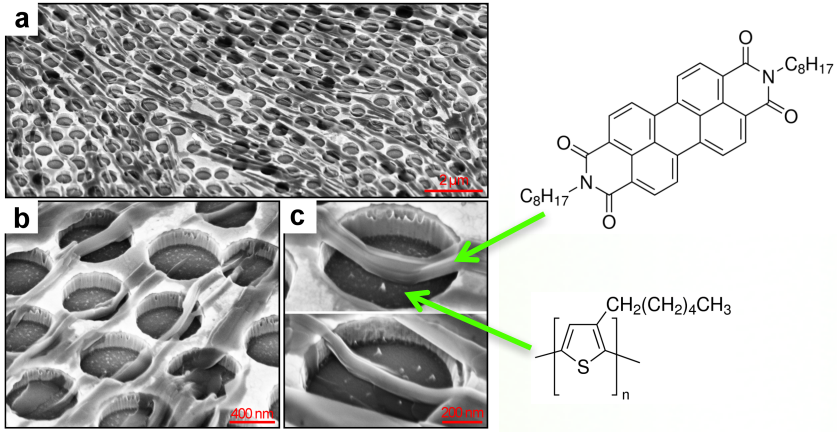


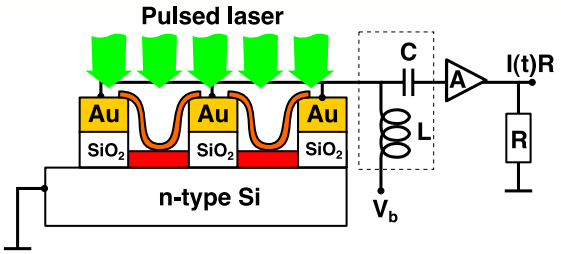



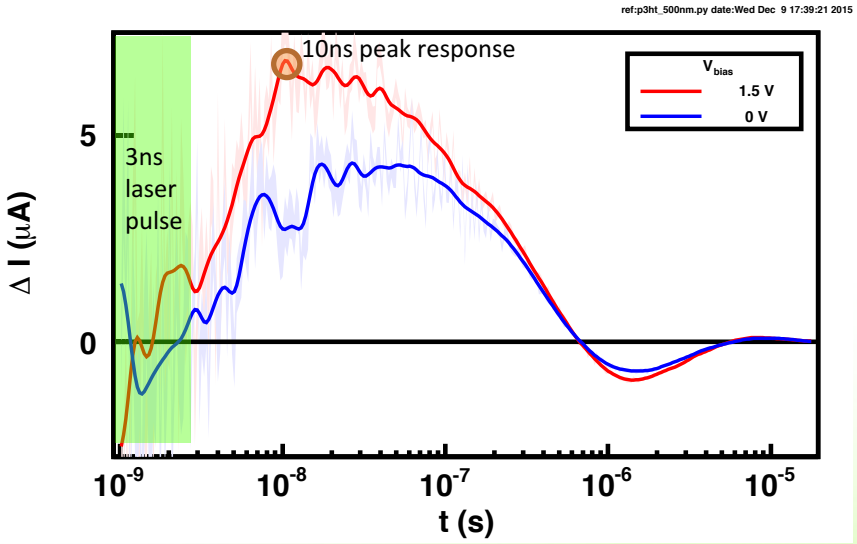

*Liyang Yu et al, Chem. Mater.* ***25****, 1823 (2013)*

# Single Crystal vertical channel p-n junctions

- Perylenedicarboximide (PTCDI-C8) single-crystal nanowires (n-type)
- Polythiophene (P3HT) (p-type)
- **10 ns response**
- S/N ratio $10^7$, EQE > 50%

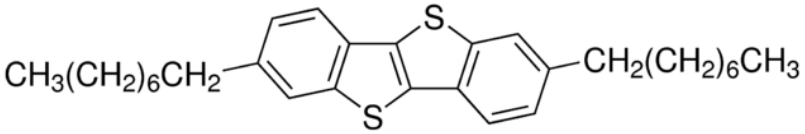


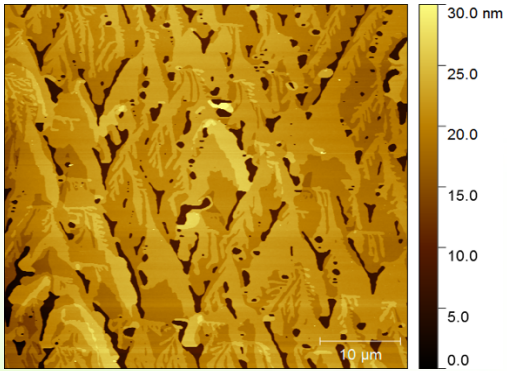



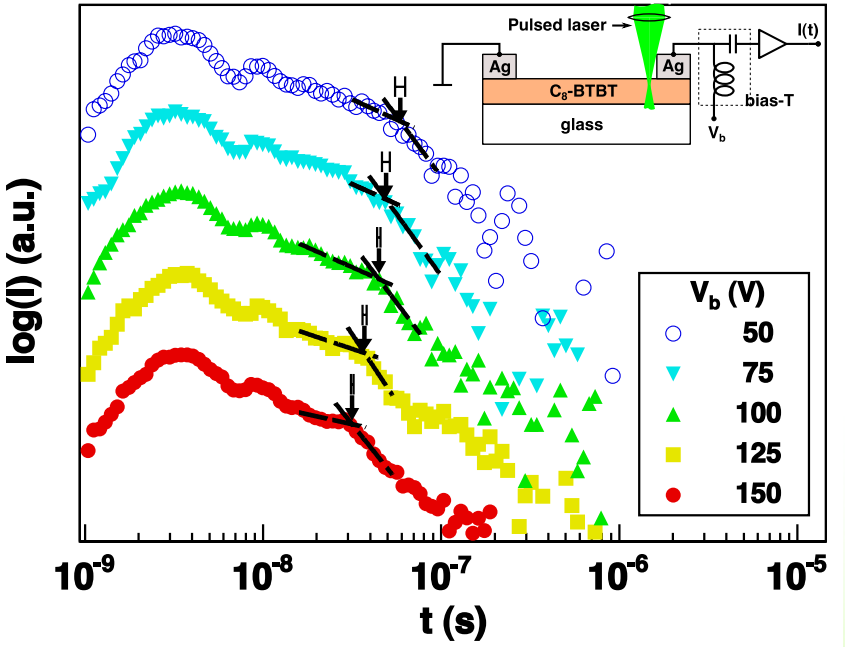

*L. Zhang et al, Nat Nano (2016)*

# Photoresponse of single crystal thin-films




- Benzothieno-benzothiophene (C8-BTBT)
- millimeter-size single crystal
- Measured hole **mobility up to 100 cm$^2$/Vs**

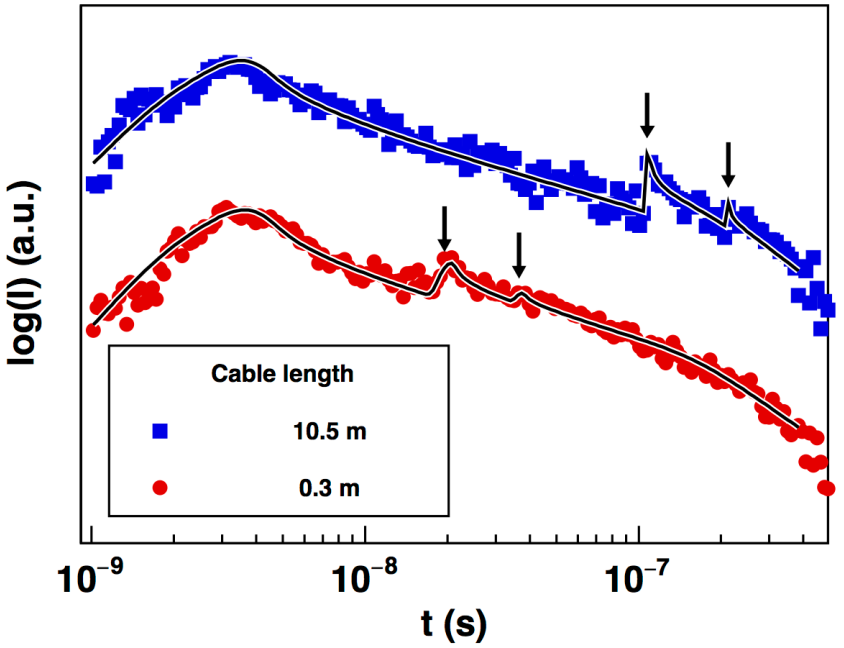



*F. Tong et al, collaboration with KULeuven and IMEC*

# Different cable length

- Sample-amplifier distance
- Reflection peaks equidistant



# Modeling of measured photocurrent

Authentic photocurrent model:

$$I_M(t) = I_0 t^{\alpha-1}\left[1+\left({}^{t}/_{t_{tr}}\right)^{a}\right]^{-\frac{k}{a}}$$

Laser pulse model:

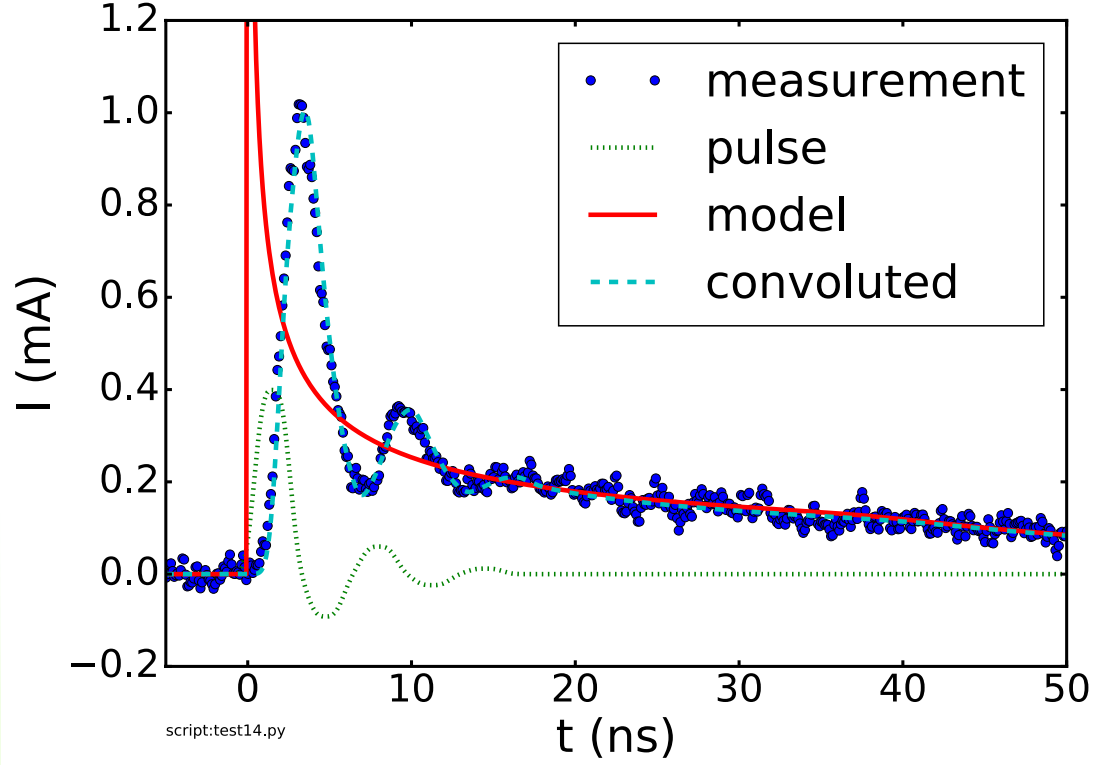
$$g(t,t_0) = \frac{1}{\sqrt{2\pi}\sigma} exp\left[-\frac{1}{2}\left(\frac{|t-t_0|}{\sigma}\right)^{\chi}\right]$$

Reflection:

$$P(t) = g(t,t_0) + \sum_{i=1}^{4} R_i \cdot g(t, t_0 + i \cdot \Delta t)$$

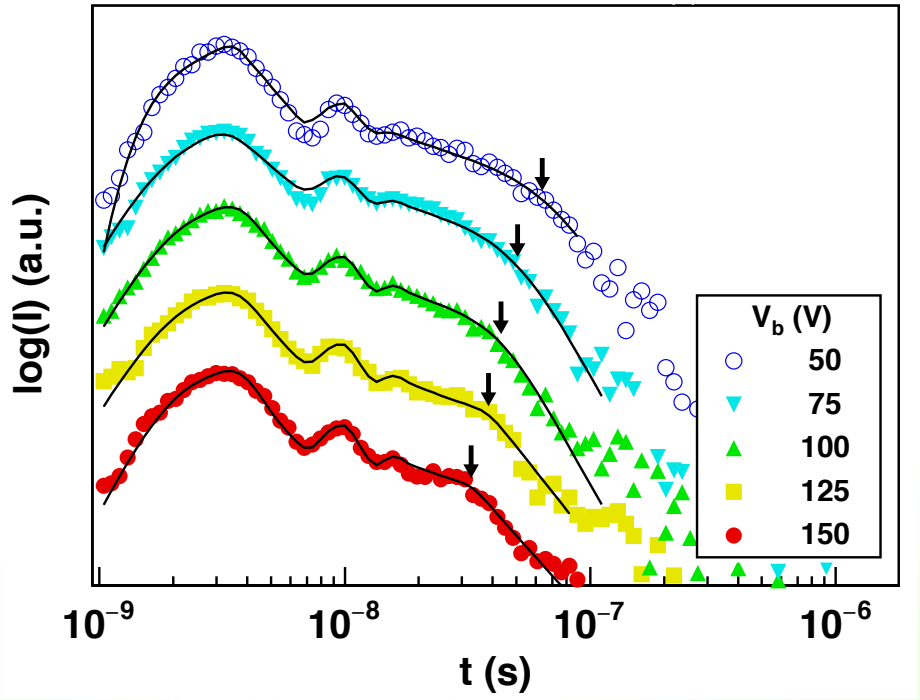
| $i$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $i \cdot \Delta t$ | 3.25 ns | 6.5 ns | 9.75 ns | 13.0 ns |
| $R_i$ | -0.23 | 0.15 | -0.06 | 0.03 |

# Modeling of measured photocurrent



# Modeling of measured photocurrent

- Model reproduces measurements



# Summary

- Transient Current Setup was used to measure charge mobility in organic single-crystal semiconductors
- TOF photocurrent reflects **distribution** of charge carrier transit times
- Authentic photocurrent was ”deconvoluted” using a series of laser pulse and its reflections

# Acknowledgments


- **LFOS**
- **ISIS & icFRC, University of Strasbourg & CNRS**: Paolo Samori, Emanuele Orgiu, Tim Leydecker, Lei Zhang, Arthur Ciesielski, Mirella El Gemayel, Andrea Schlierf
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- *others*