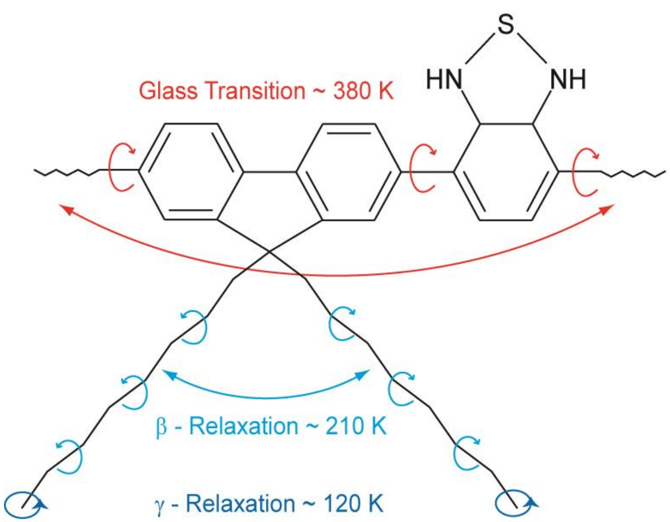
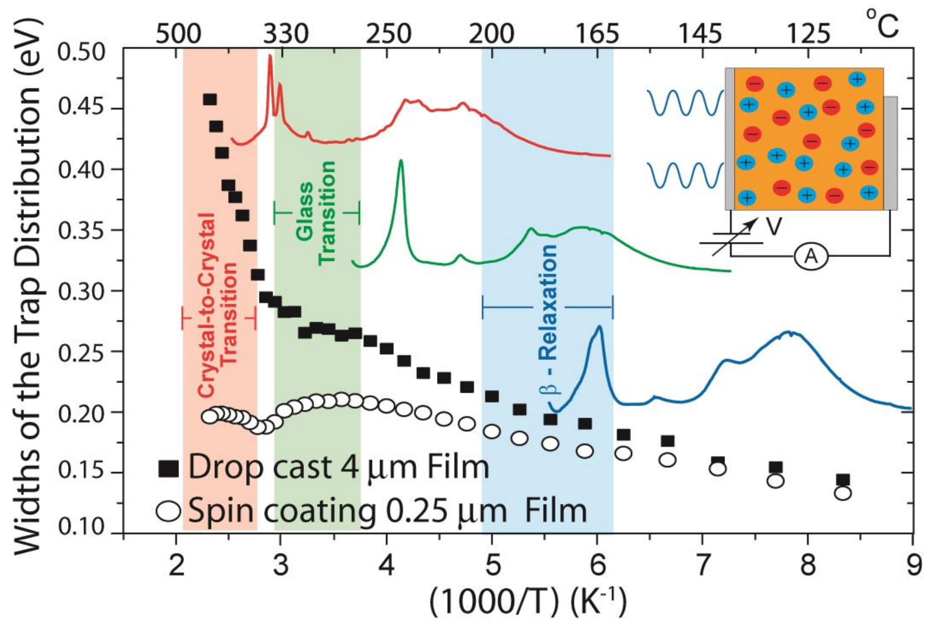
"Café com Física"
São Carlos, 07th of August/2013

TECHNISCHE UNIVERSITÄT DARMSTADT

Importance of Structural Modification and Molecular Dynamics on the Electrical Properties of Organic Electronic Devices





Gregório Couto Faria

São Carlos Physics Institute – University of São Paulo/Brazil

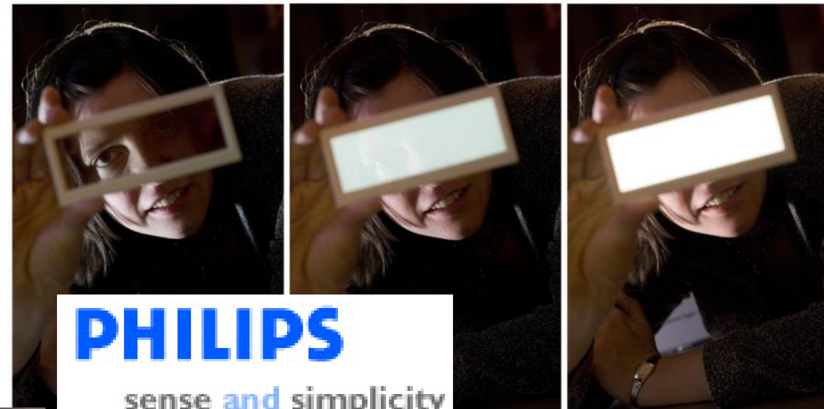
Motivation: Why Organic Electronics?

Synthesis and optical properties of a novel polyfluorene derivative

C. Vijila [a,1], H.-K. Kyyrönen [b], M. Westerling [a], R. Österbacka [a,*], T. Ääritalo [b], J. Kankare [b], H. Stubb [a]

Semiconducting polyfluorenes as materials for solid-state polymer lasers across the visible spectrum[☆]

Ruidong Xia, George Heliotis, Donal D.C. Bradley*



PHILIPS

sense and simplicity

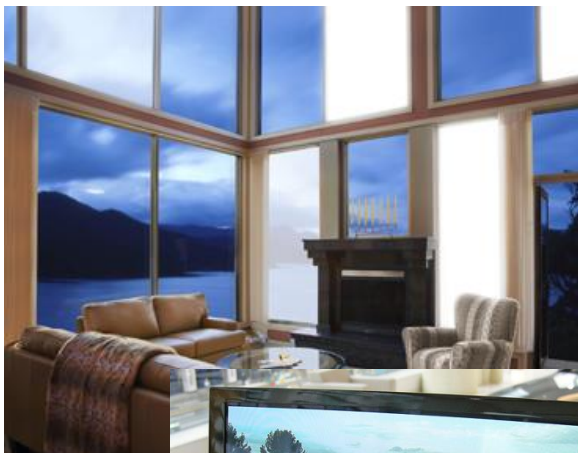
SONY

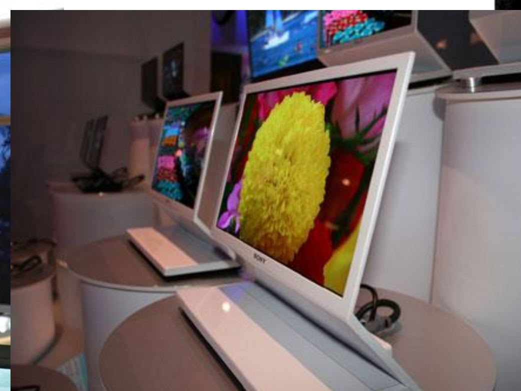
SAMSUNG

Pioneer

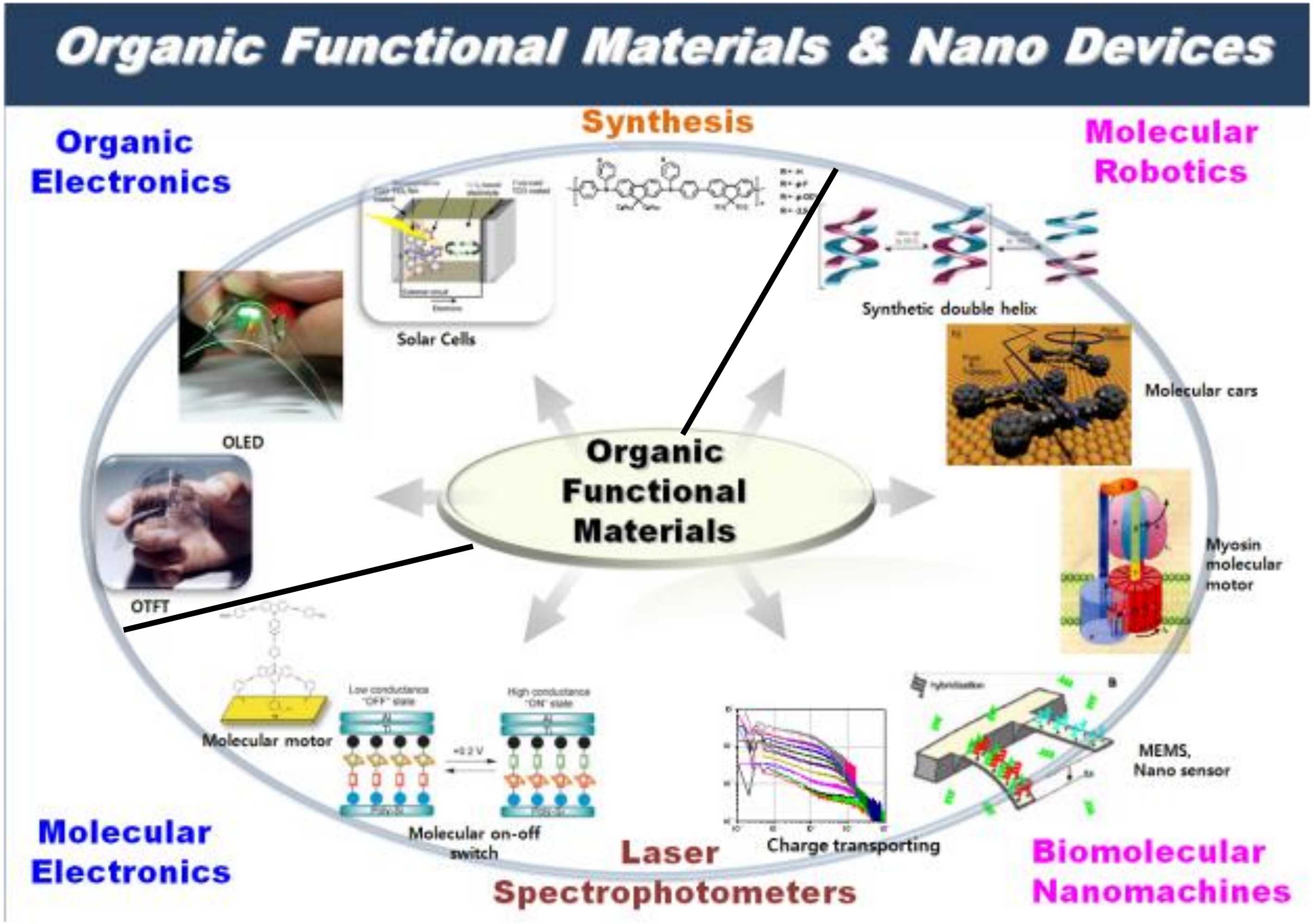
Sumitomo Corporation

CDT





Motivation: Why Organic Electronics?



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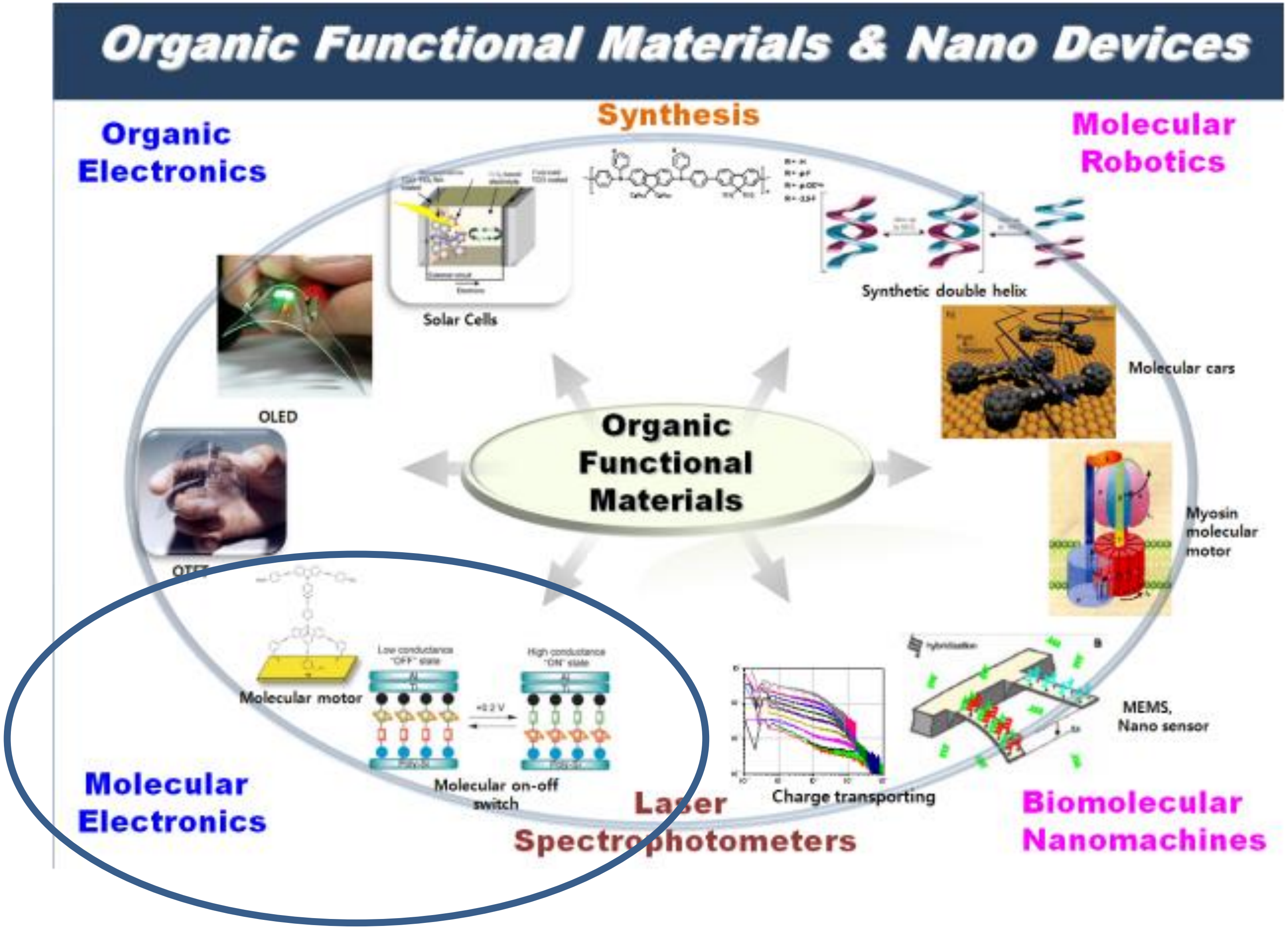

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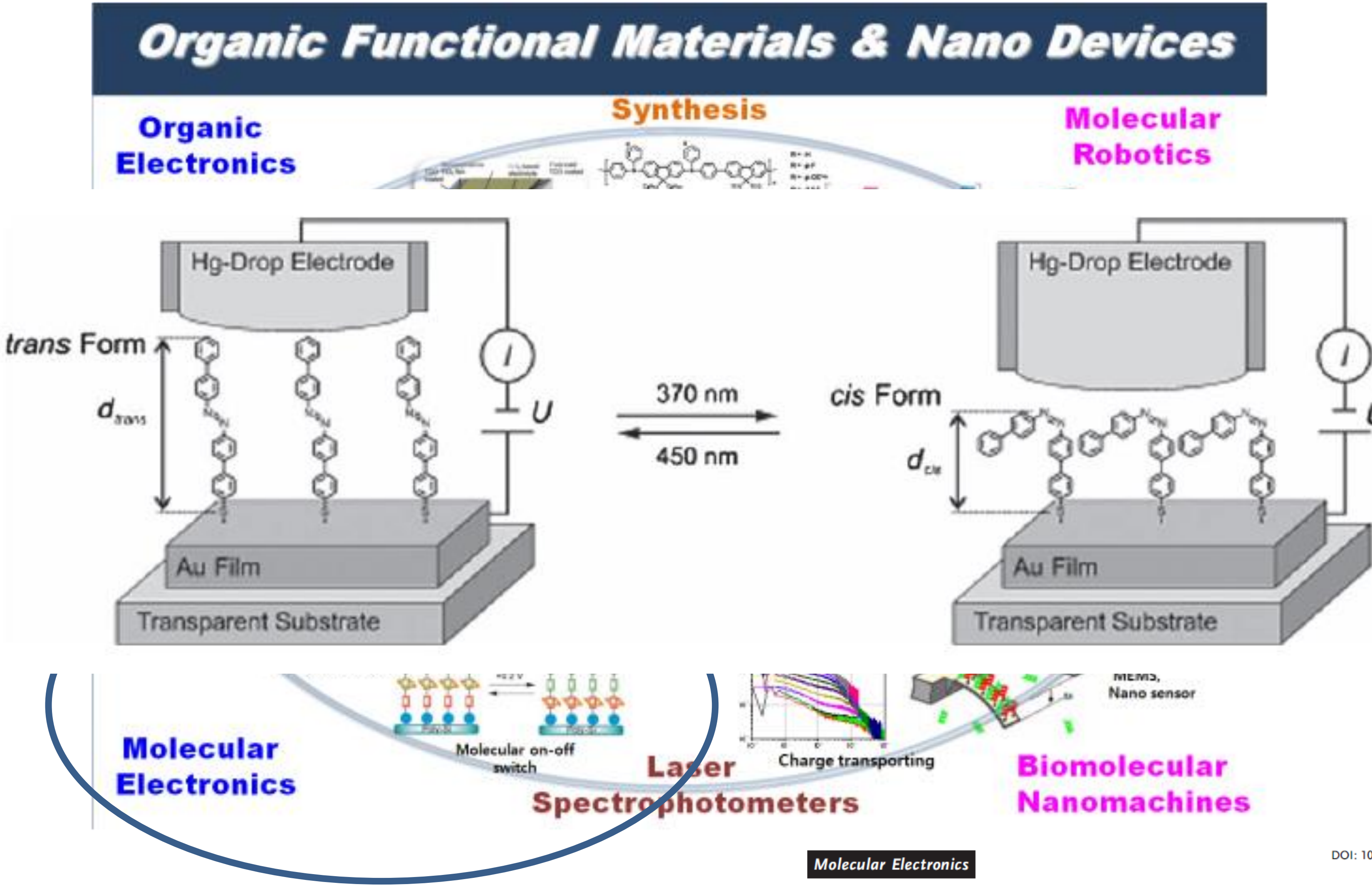


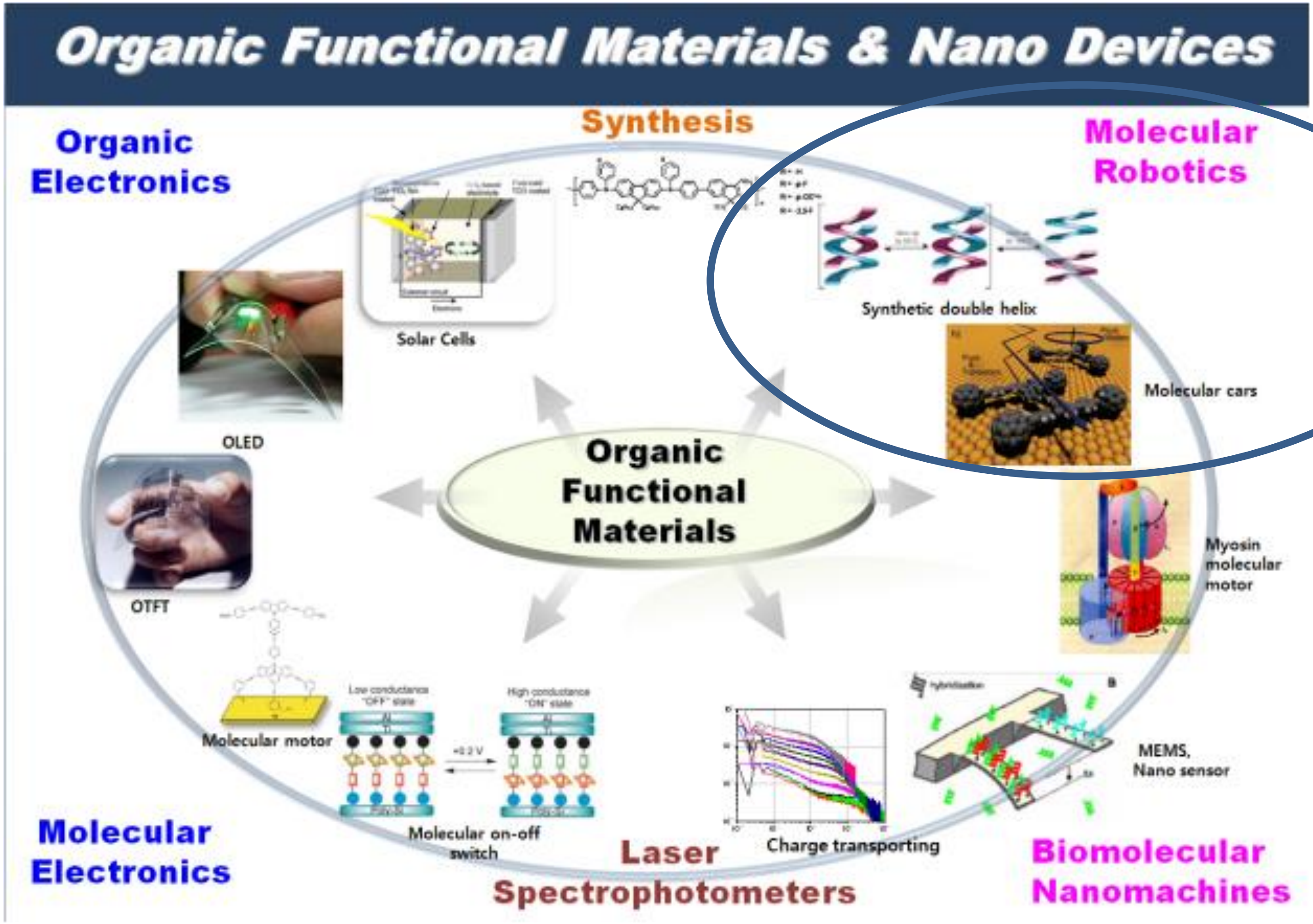
Molecular Electronics

DOI: 10.1002/anie.200705339

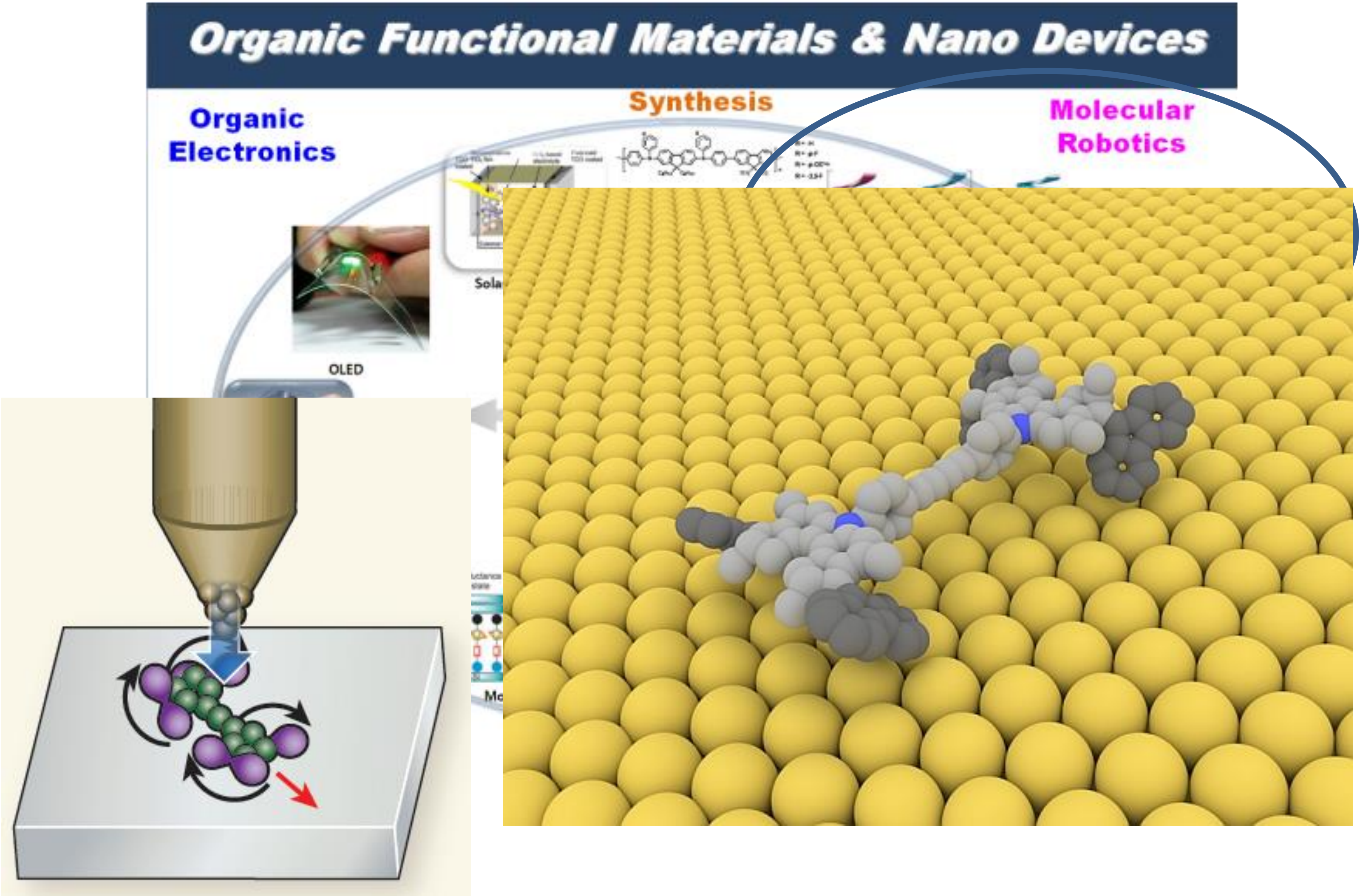
Light-Powered Electrical Switch Based on Cargo-Lifting Azobenzene Monolayers

Violetta Ferri, Mark Elbing, Giuseppina Pace, Michael D. Dickey, Michael Zharnikov, Paolo Samorì, Marcel Mayor,* and Maria Anita Rampi**

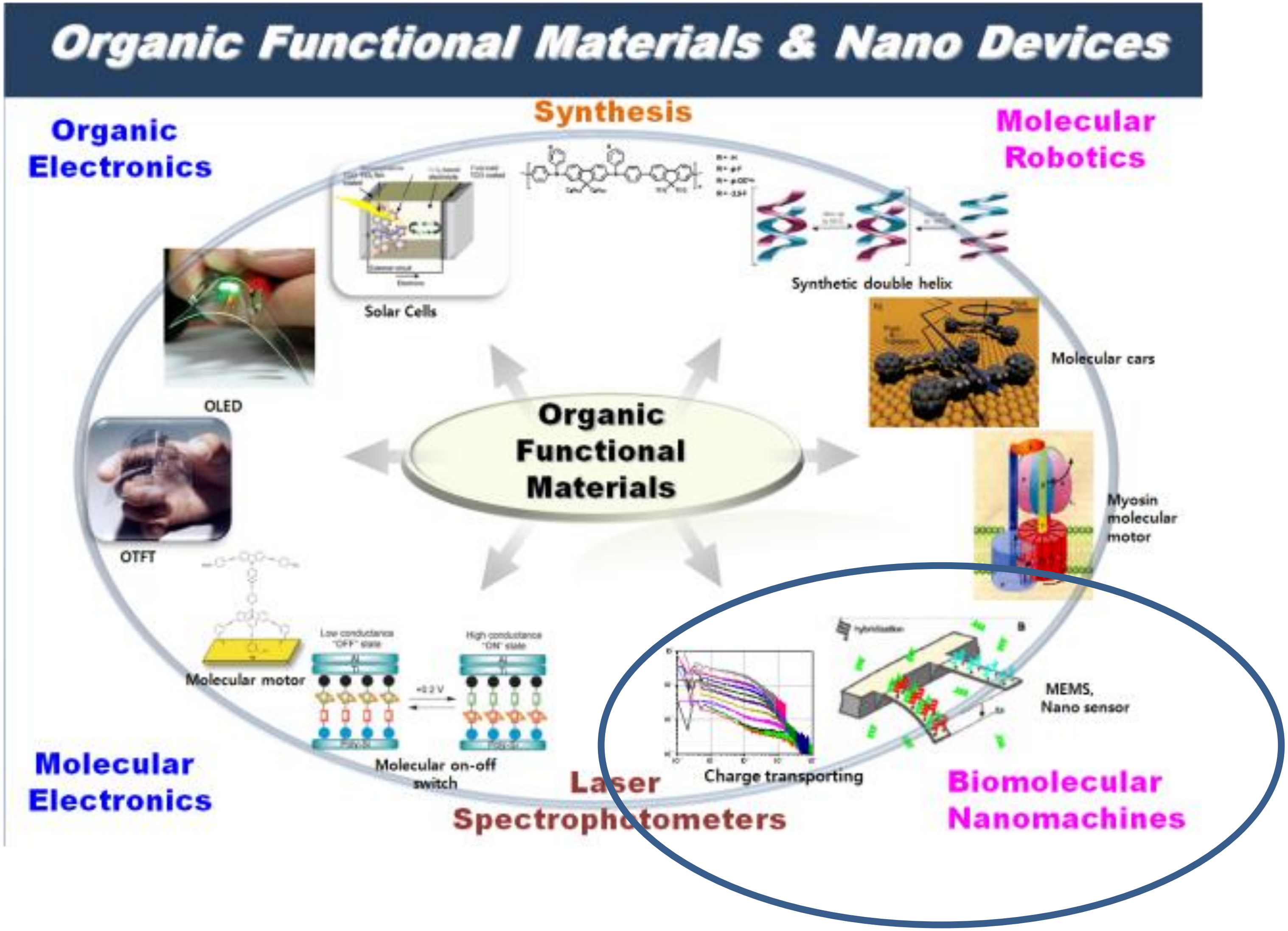
Motivation: Why Organic Electronics?



Motivation: Why Organic Electronics?



Motivation: Why Organic Electronics?



Motivation: Why Organic Electronics?

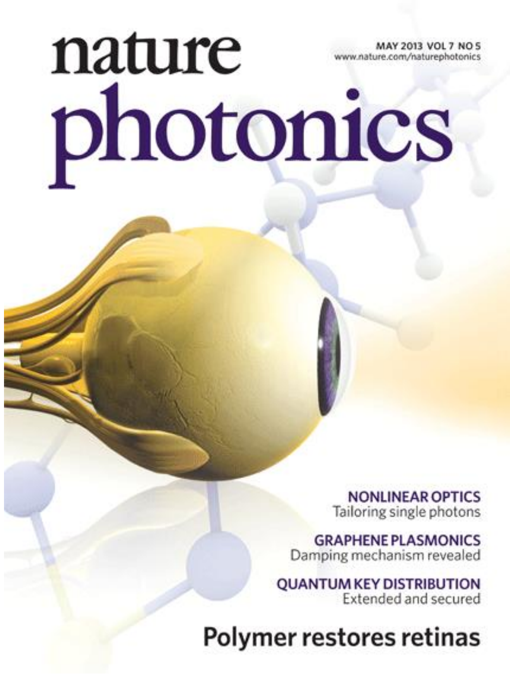
Organic Bioelectronics:

NATURE PHOTONICS | ARTICLE

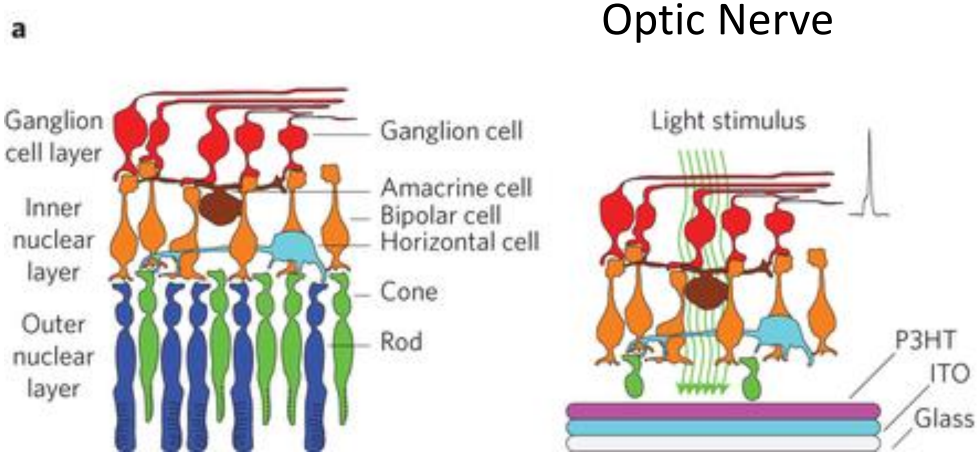
A polymer optoelectronic interface restores light sensitivity in blind rat retinas

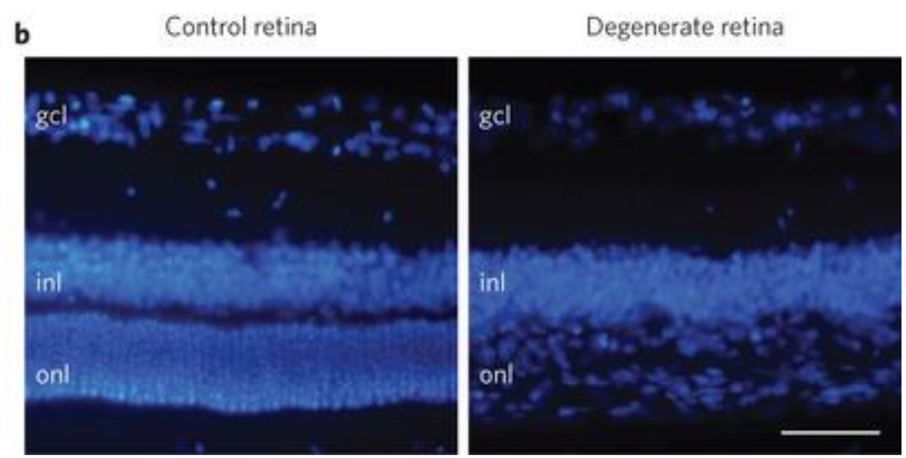
Nature Photonics **7**, 400–406 (2013) | doi:10.1038/nphoton.2013.34

Diego Ghezzi, Maria Rosa Antognazza, Rita Maccarone, Sebastiano Bellani, Erica Lanzarini, Nicola Martino, Maurizio Mete, Grazia Pertile, Silvia Bisti, Guglielmo Lanzani & Fabio Benfenati



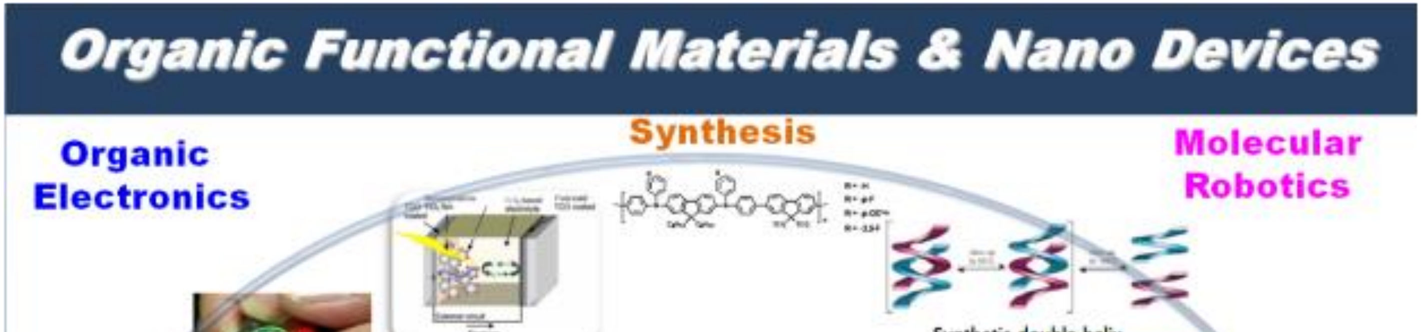
Optic Nerve

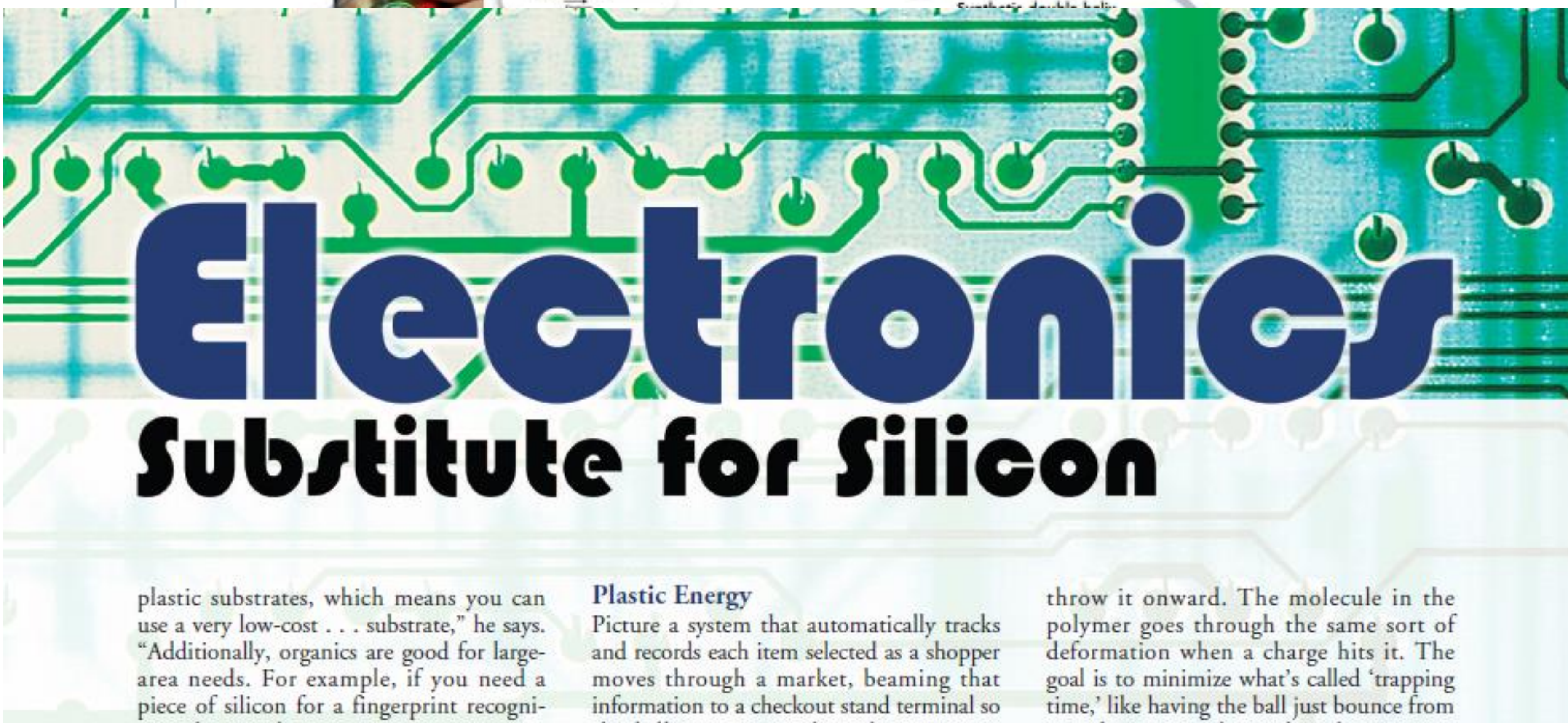




Replace Retina by P3HT/PCBM:

Motivation: Why Organic Electronics?





Electronics

Substitute for Silicon

plastic substrates, which means you can use a very low-cost . . . substrate," he says. "Additionally, organics are good for large-area needs. For example, if you need a piece of silicon for a fingerprint recogni-

Plastic Energy

Picture a system that automatically tracks and records each item selected as a shopper moves through a market, beaming that information to a checkout stand terminal so

throw it onward. The molecule in the polymer goes through the same sort of deformation when a charge hits it. The goal is to minimize what's called 'trapping time,' like having the ball just bounce from

Motivation: Organic versus Inorganic?

"

Safer, Cheaper, Lighter

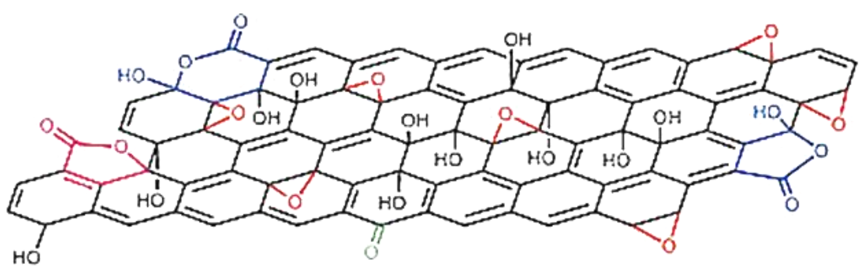
Schen says organic electronics involves a much smaller set of hazardous compounds and materials than more traditional technologies. Gone are the arsenic (used in

"

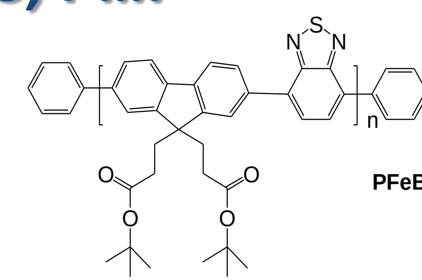
Safer: Highly toxic organic solvents for solution and synthesis ;

Possibility of usage of heteroatom: Se, S, P….

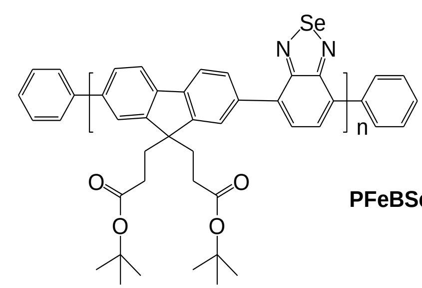
Acids are used during synthesis…



Oxygenated functional groups in Graphene:
Usage of $KMnO_4/H_2SO_4$



PFeBT



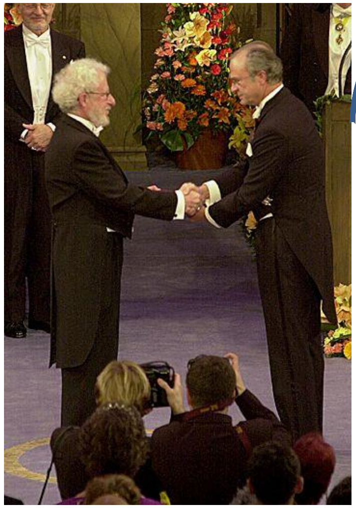
PFeBSe

Motivation: Organic versus Inorganic?

> **Safer, Cheaper, Lighter**
>
> Schen says organic electronics involves a much smaller set of hazardous compounds and materials than more traditional tech-nologies. Gone are the arsenic (used in

Cheaper : It is not the price!!! But it initially was…

2009: Average price for silicon photovoltaic: 450 €/kg!



KONARKA®

Motivation: Organic versus Inorganic?

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Safer, Cheaper, Lighter

Schen says organic electronics involves a much smaller set of hazardous compounds and materials than more traditional technologies. Gone are the arsenic (used in
"

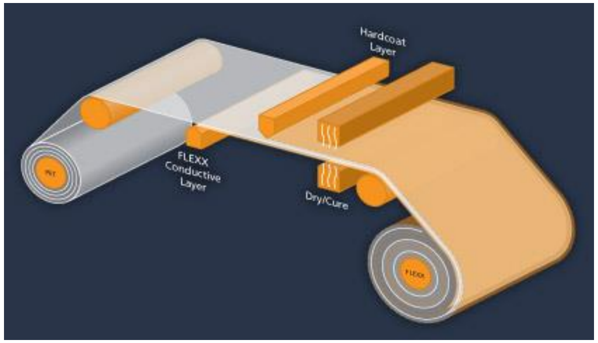
Cheaper : It is not the price!!! But it initially was…

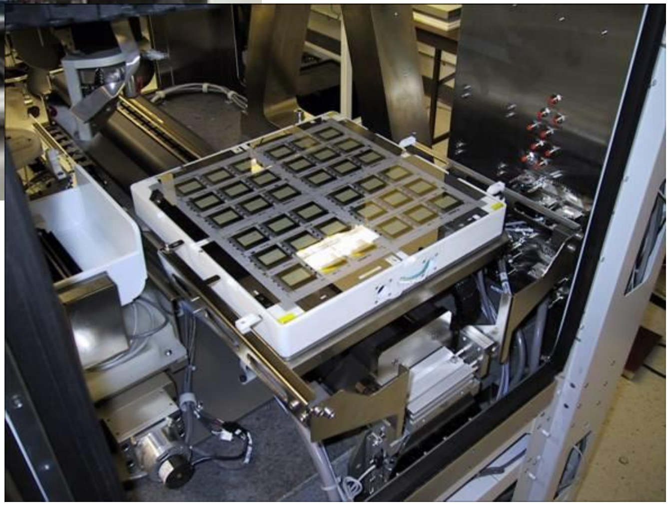
2012 – China dropped the price to 20 €/kg….

Organics: Where is the advantages?

Yes, OE still presenting great advantages…

1) Solution processing: Ease and priceless deposition methods.





Organics: Where is the advantages?

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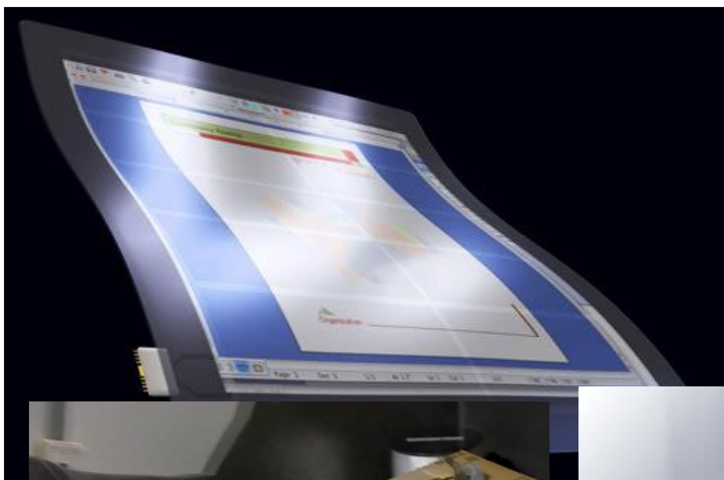
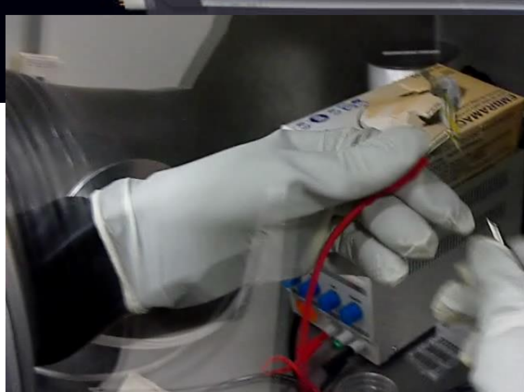
2) Flexible Application: Deposition on flexible substrates.





Organics: Where is the advantages?

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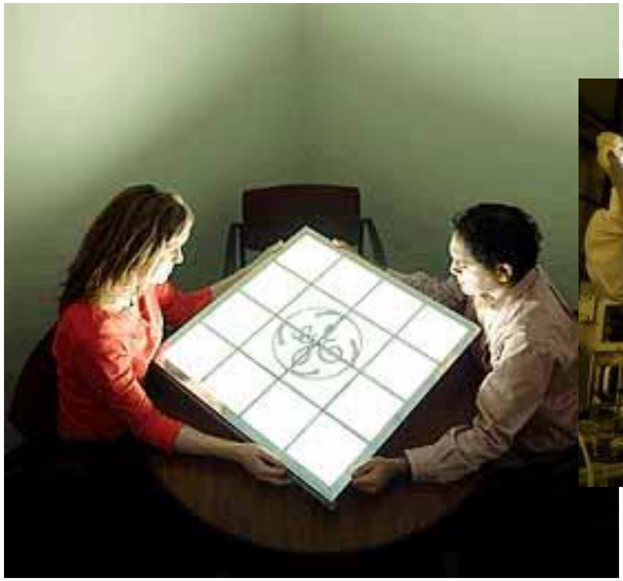
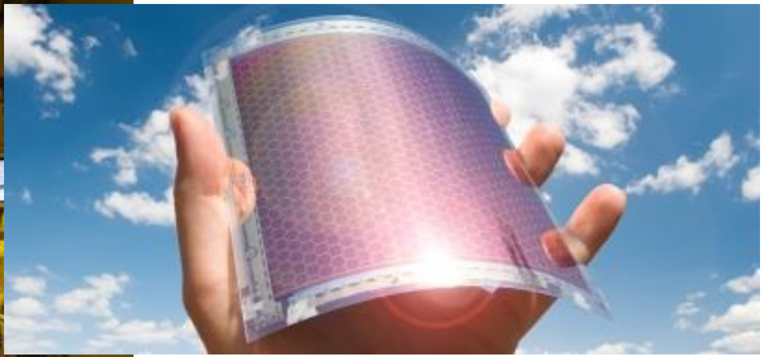




Organics: Where is the advantages?

Yes, OE still presenting great advantages…

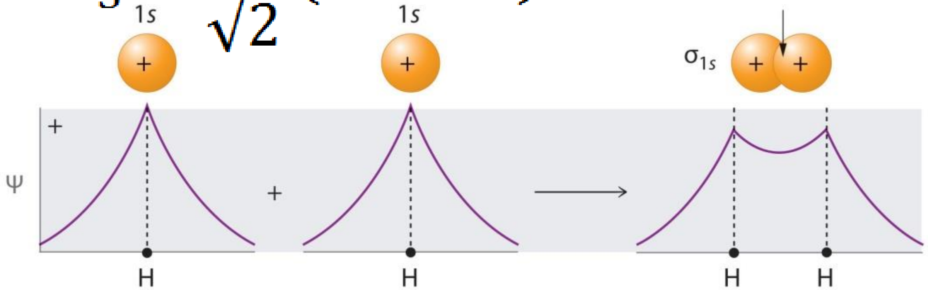
1) Solution processing: Ease and priceless deposition methods.
2) Flexible Application: Deposition on flexible substrates.
3) Large area devices: Illumination panel/Large area photovoltaic.
4) Transparent materials: Windows-lighting application.

Yes, OE deserves attention!

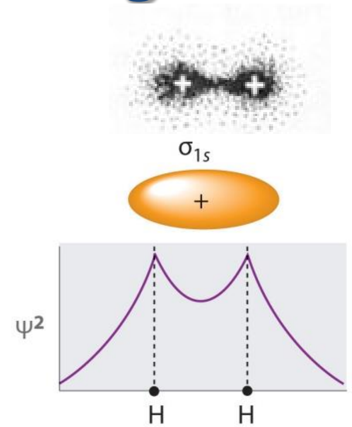
Principles of Semiconducting Conjugated Molecules

Origin of bonding and anti-bonding orbital:

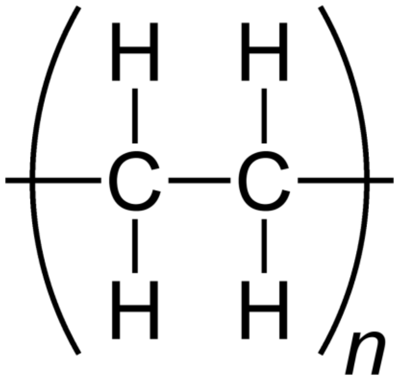
$$\Psi_S = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$$

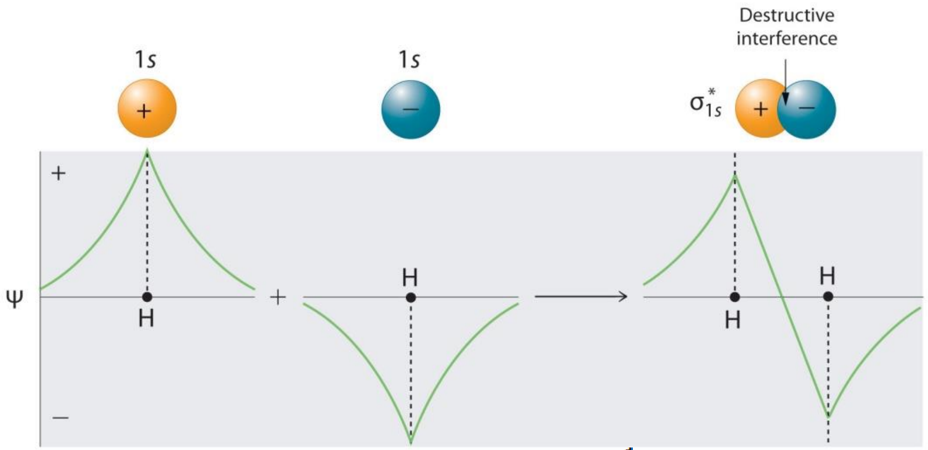


(a) Wave functions combined for σ_{1s}



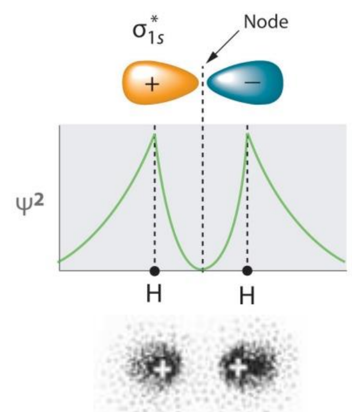
(b) Bonding probability density



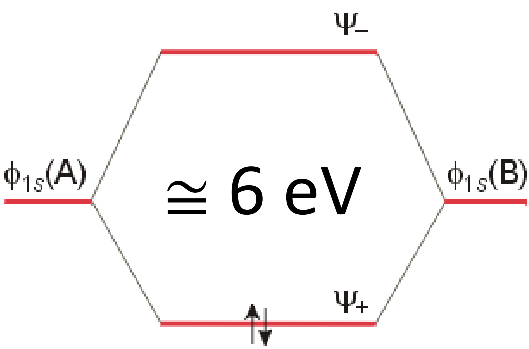


(c) Wave functions combined for σ^*_{1s}

$$\Psi_A = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

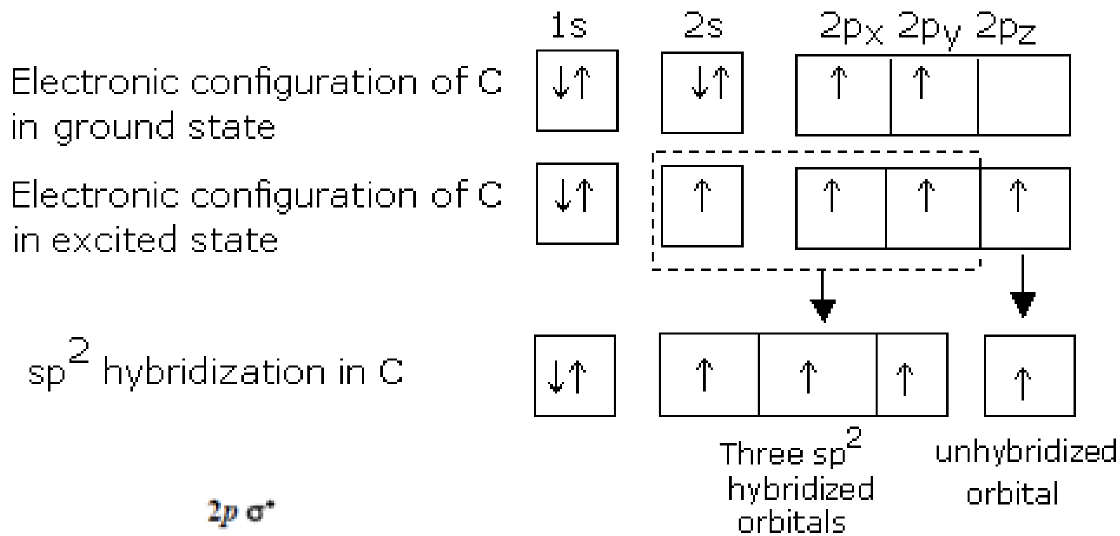


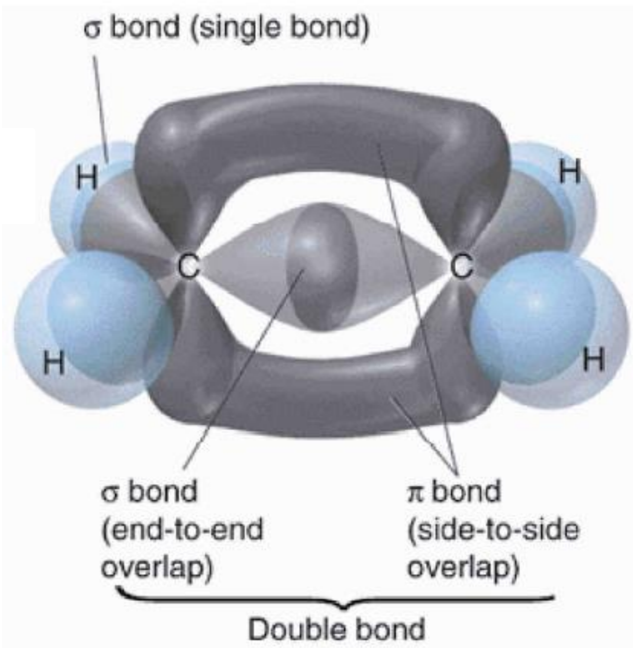
(d) Antibonding probability density

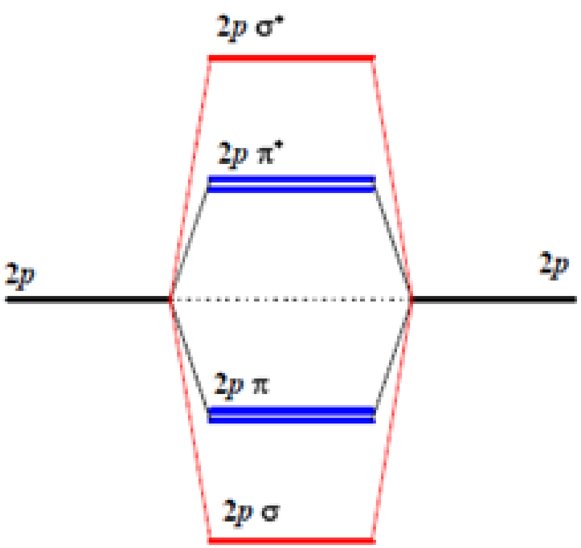


Principles of Semiconducting Conjugated Molecules

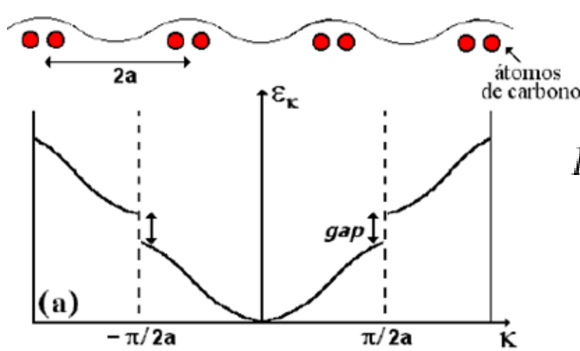
Conjugated systems → sp² Hybridization





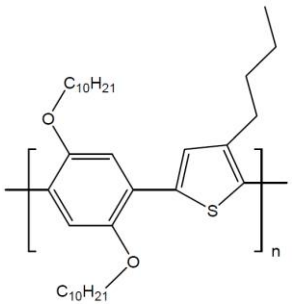


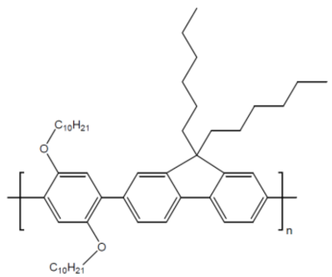
Dimerization (HOMO and LUMO)

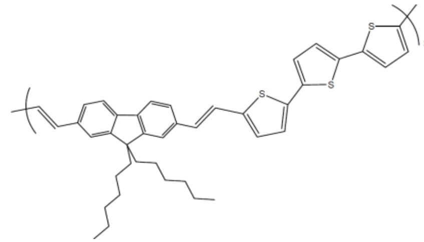


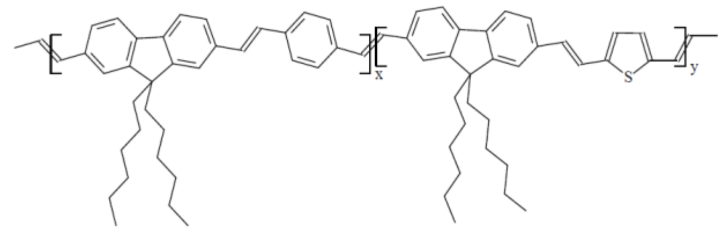
$$H_{\mathrm{SSH}} = -\sum_{i,s} t_{i,i+1}\left(c^{\dagger}_{i,s}c_{i+1,s} + c^{\dagger}_{i+1,s}c_{i,s}\right) + \frac{1}{2}K\sum_i (u_{i+1}-u_i)^2 + \frac{1}{2}M\sum_i \dot{u}_i^2,$$

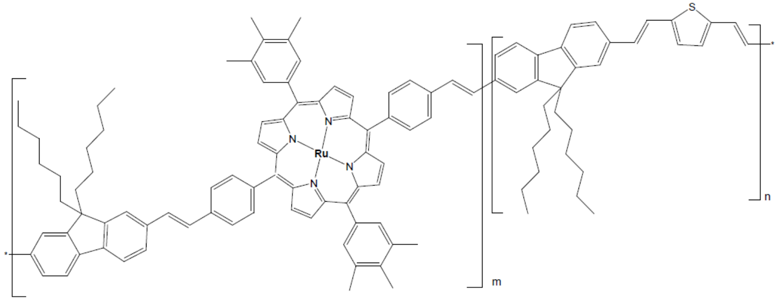
Examples of Conjugated Polymers

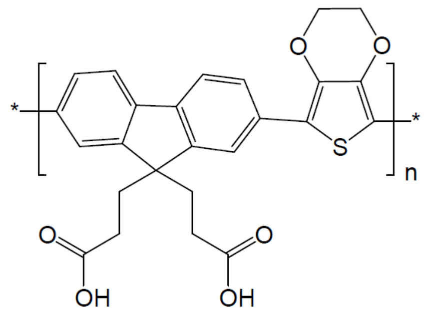


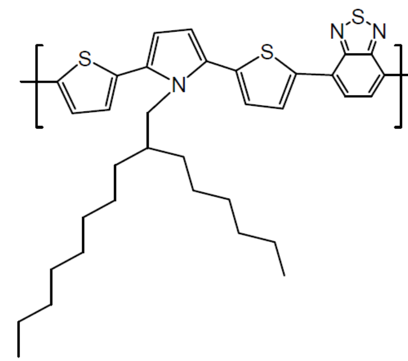


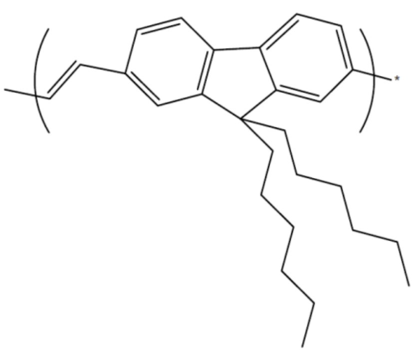


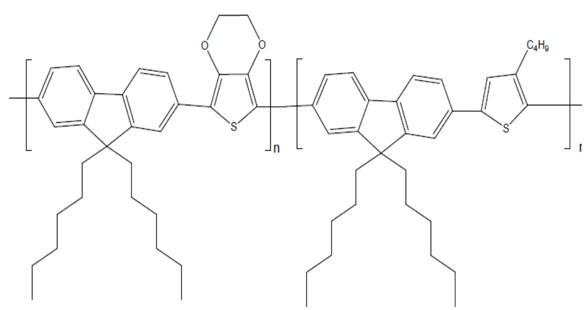


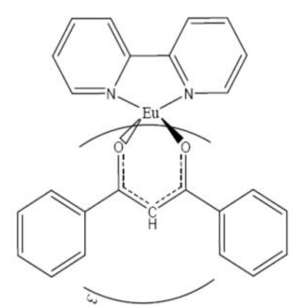


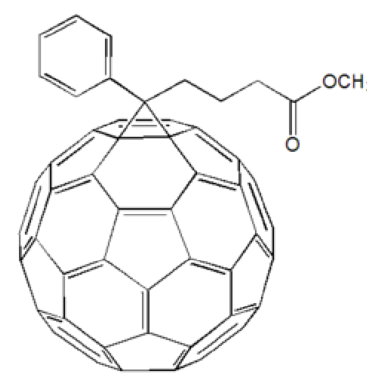












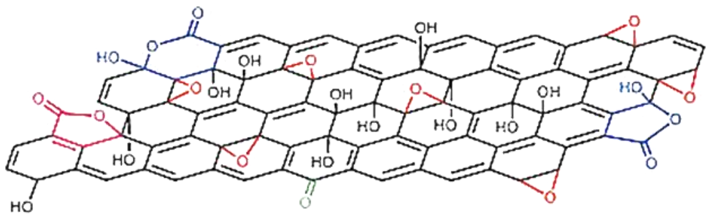
What can be done with those molecules?

Overview of recent results obtained at Bernhard Gross Polymer Group

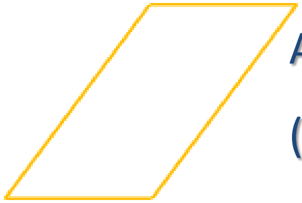
IFSC - USP

Bernhard Gross Grupo de Polímeros

Memory with Graphene Oxide (GO)

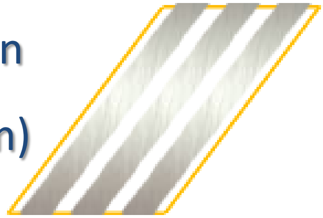


Exfoliation by modified Hummer's method:
- Graphite (powder) in $KMnO_4/H_2SO_4$

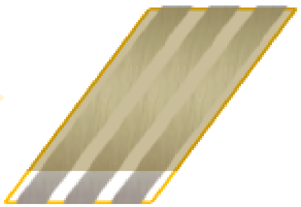


Al thermal evaporation

(70 nm, under vacuum)



GO spray deposition



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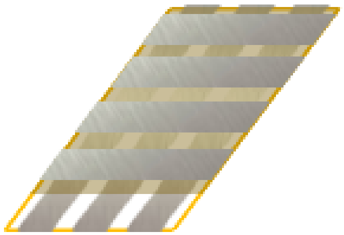
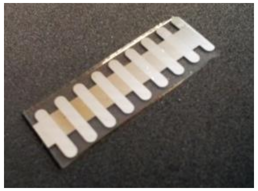
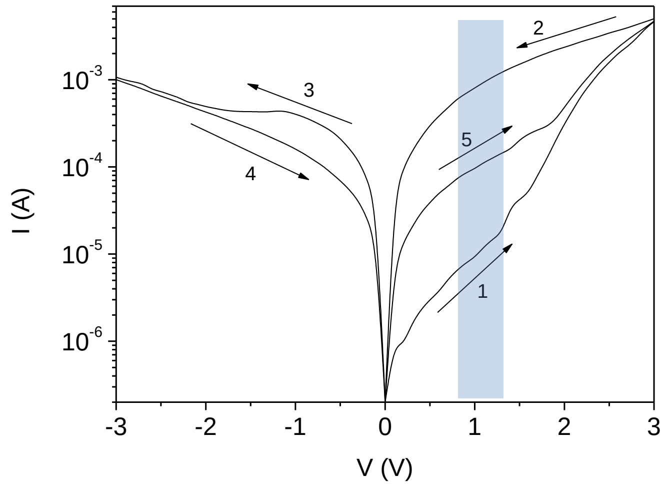
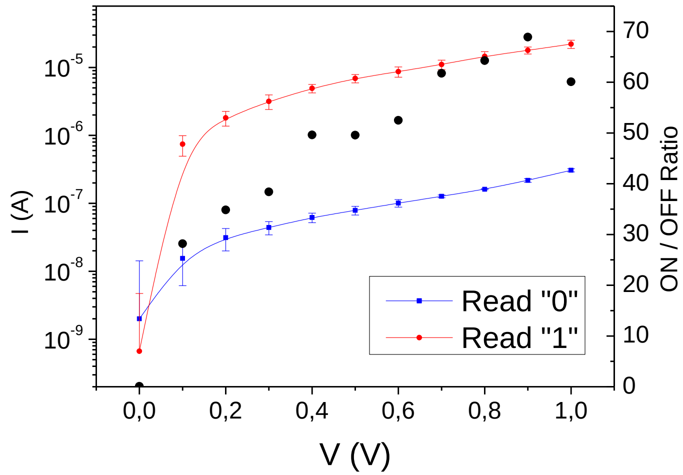




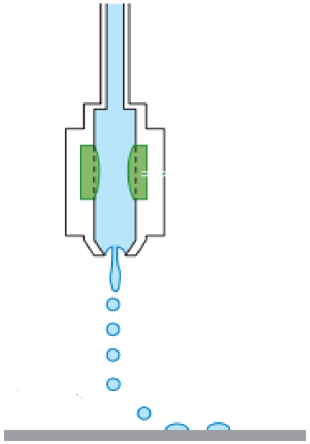


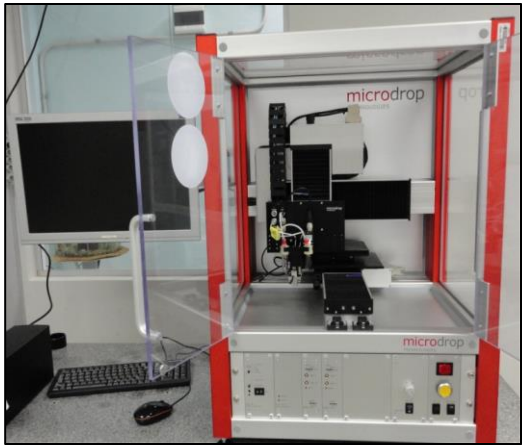


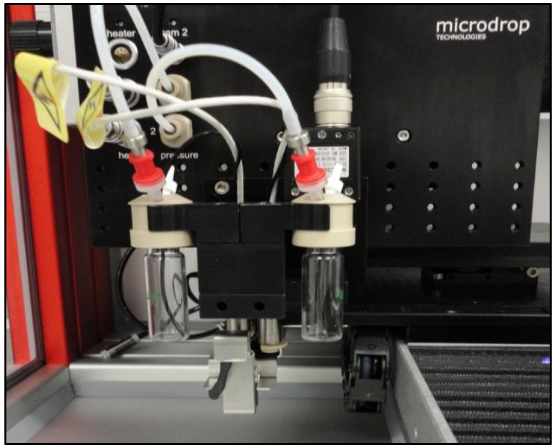
*Lucas Mouta

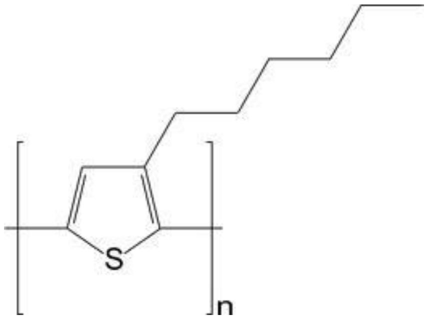
*Bruno Torres

Printed OFET

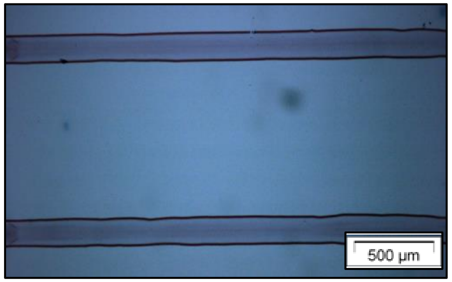


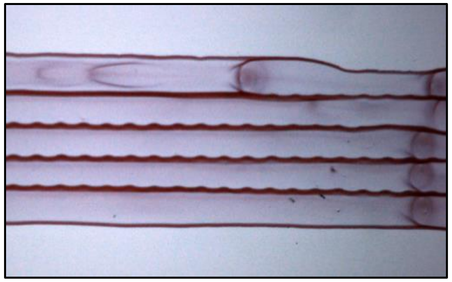


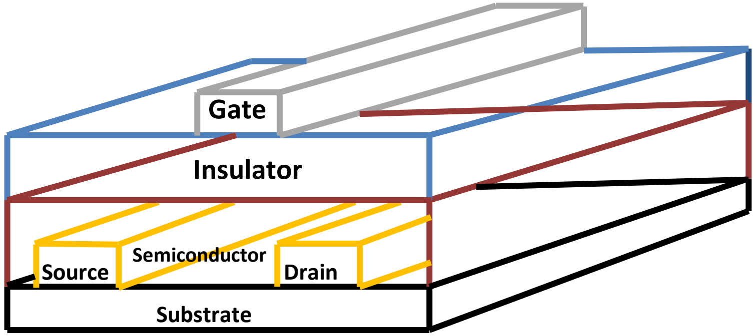


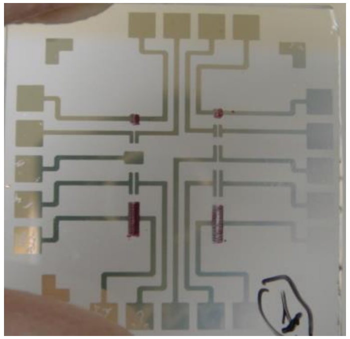


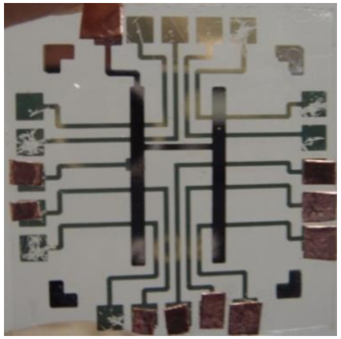
Poly(3-hexylthiophene)





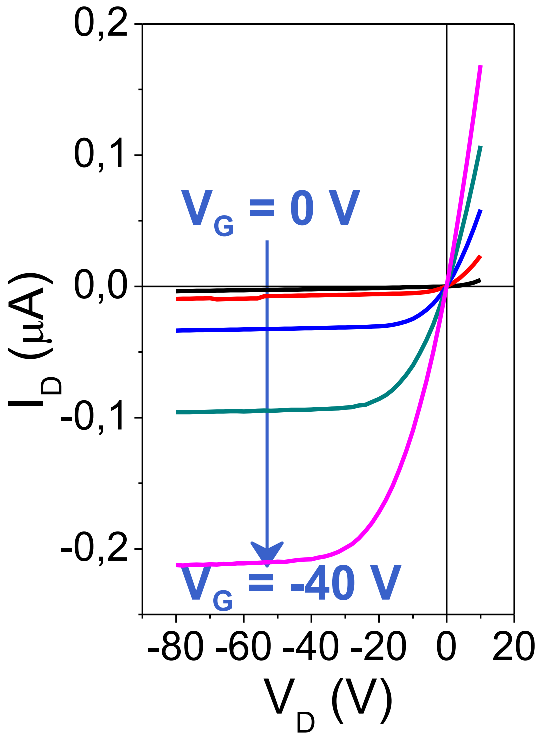


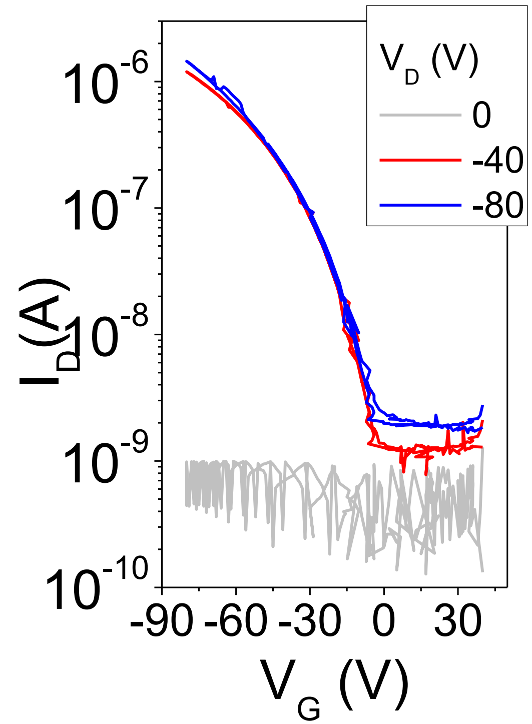


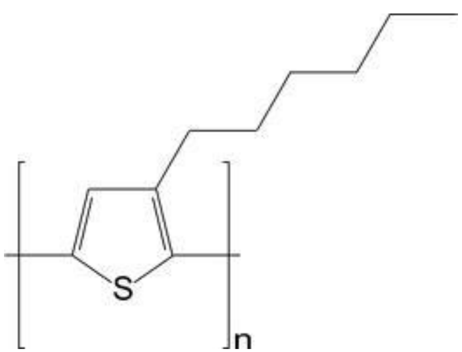


*Josiani Stefanelo

Printed OFET







	on/off ratio	μ_{sat} (cm^2/V.s)	Leakage current
Spin casting	94	3,6 x 10^{-3}	10^{-7}
Inkjet	570	6,5 x 10^{-3}	10^{-9}

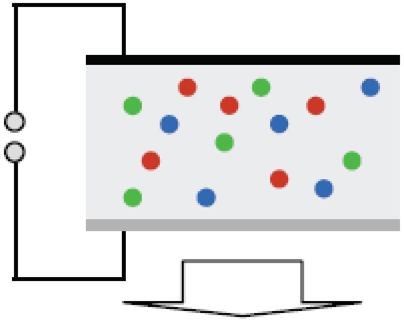
*Josiani Stefanelo

New approach for WLED

How to get white emission?

1) Blending polymer emitting at different colors:

Drawback: Right amount of each/Learning by doing.
Phase separation...



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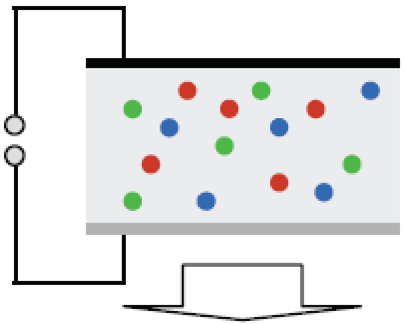
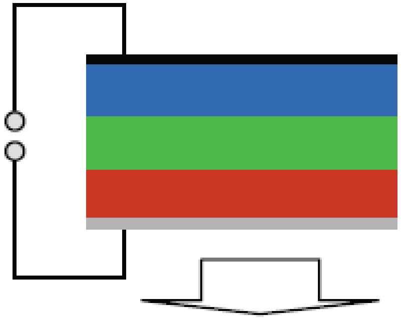


Drawback: Right amount of each/Learning by doing.
Phase separation...

2) Using single device stack with multicolor emitting layers:



Drawback: Previously deposited layers are dissolved by subsequent ones!

New approach for WLED

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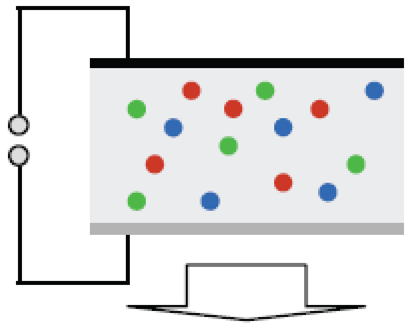
1) Blending polymer emitting at different colors:



Drawback: Right amount of each/Learning by doing.
Phase separation...

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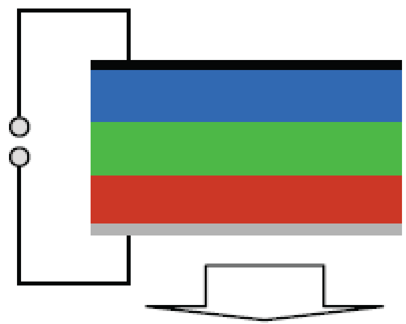
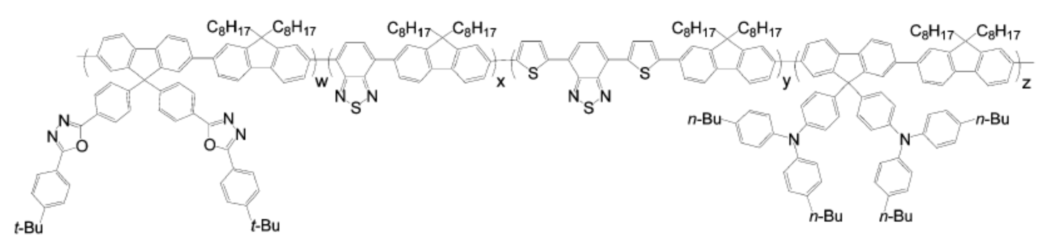


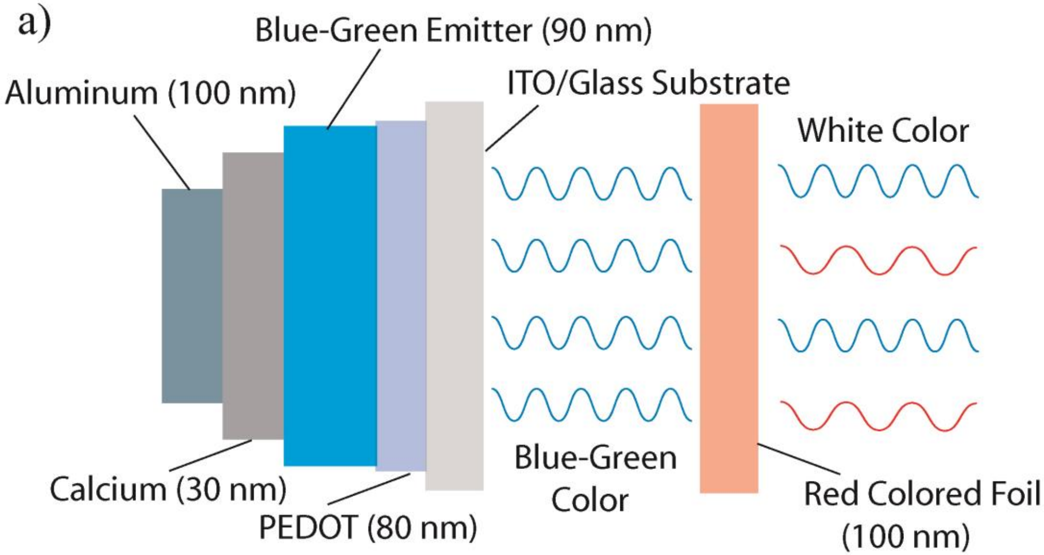
Drawback: Previously deposited layers are dissolved by subsequent ones!

3) Synthetizing single molecules that exhibits white emission!

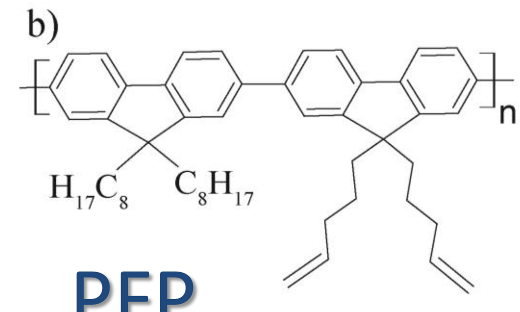
Drawback: Extremely challenging!



New approach for WLED

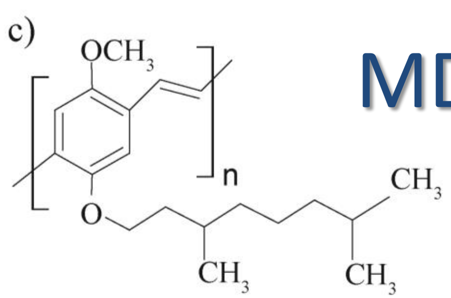


Greenish **EL-polymer**

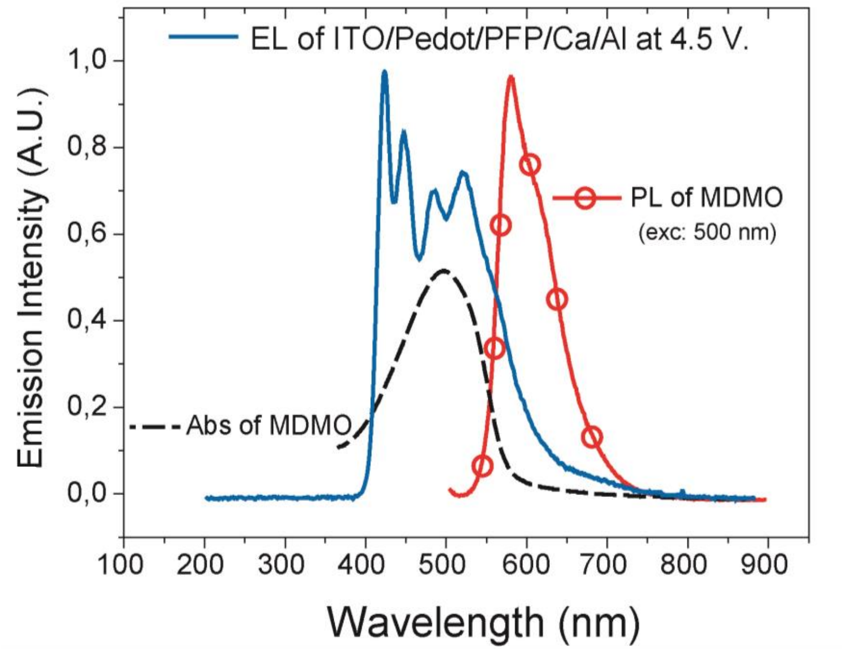


PFP

Red **PL-polymer**

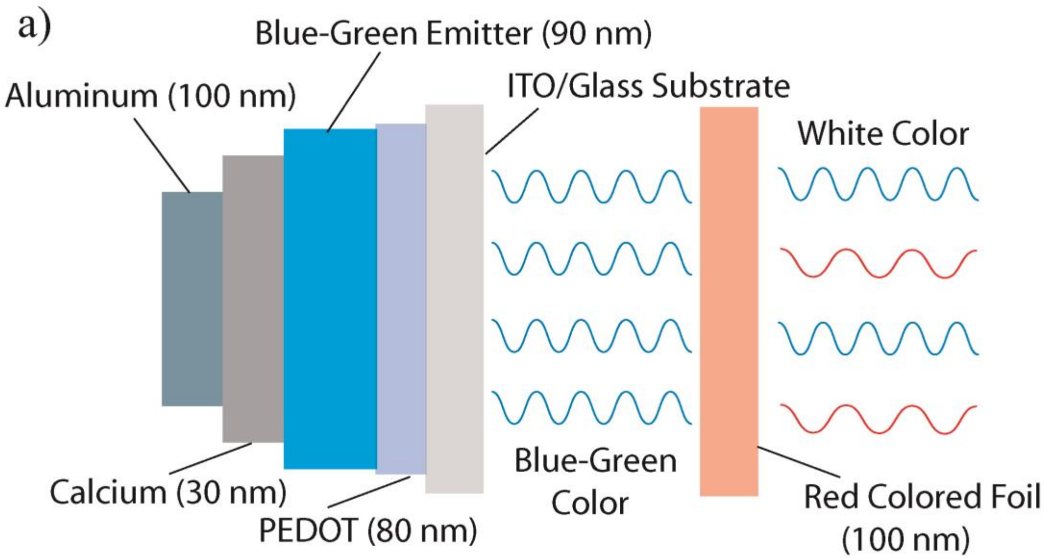


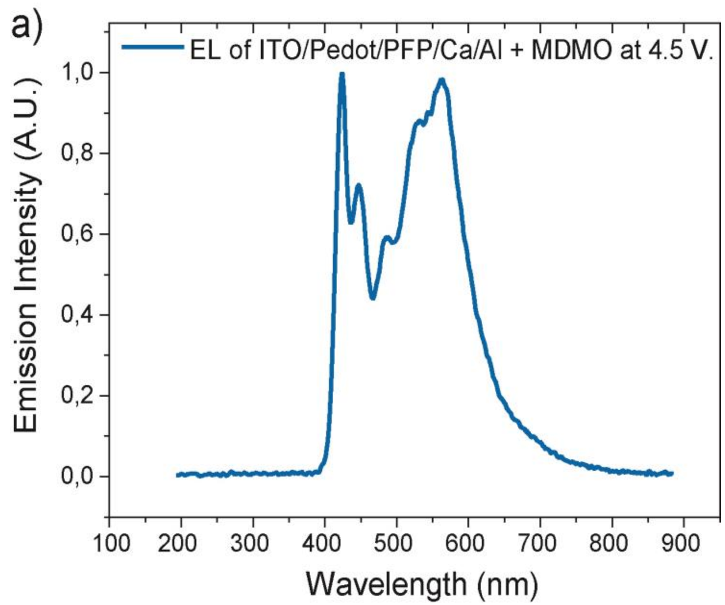
MDMO

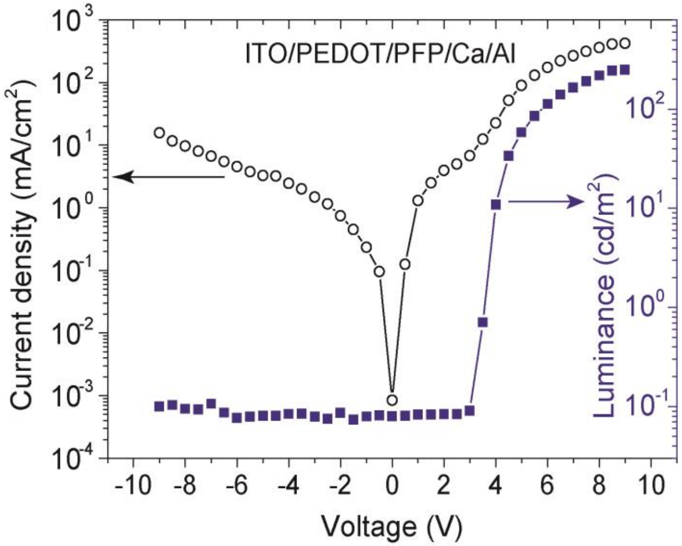


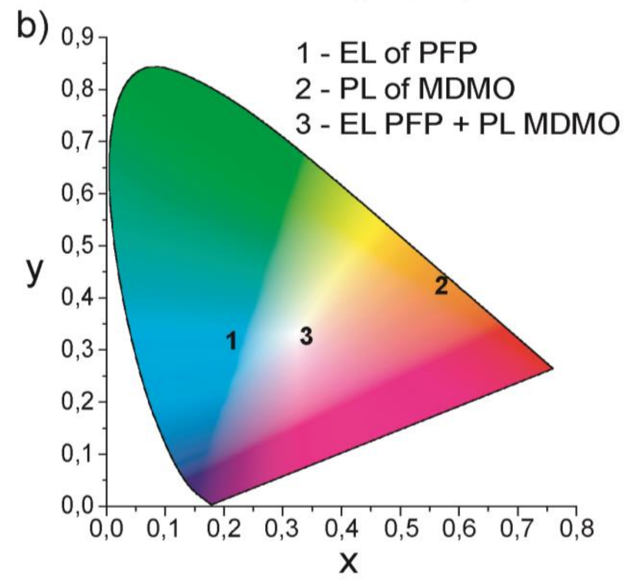
*Fernando Quites

New approach for WLED









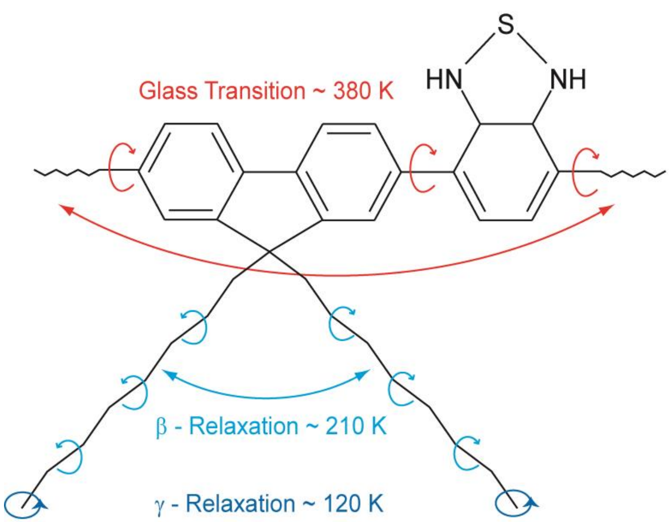
*Fernando Quites

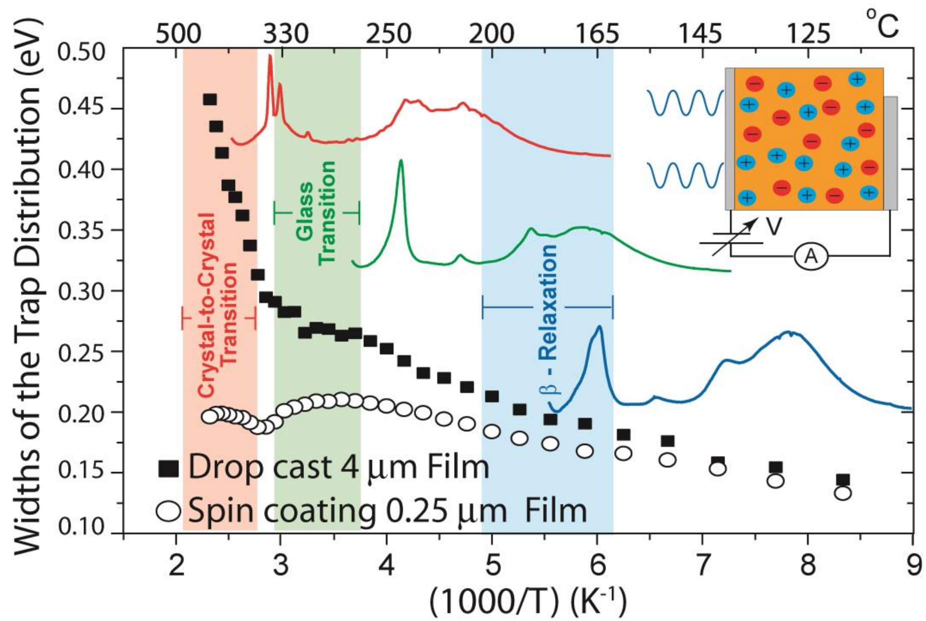
“Café com Física”

São Carlos, 07th of August/2013

TECHNISCHE UNIVERSITÄT DARMSTADT

Importance of Structural Modification and Morphology on the Electrical Properties of Organic Electronic Devices





Gregório C. Faria[1,2], Eduardo R. deAzevedo[1] and Heinz von Seggern[2]

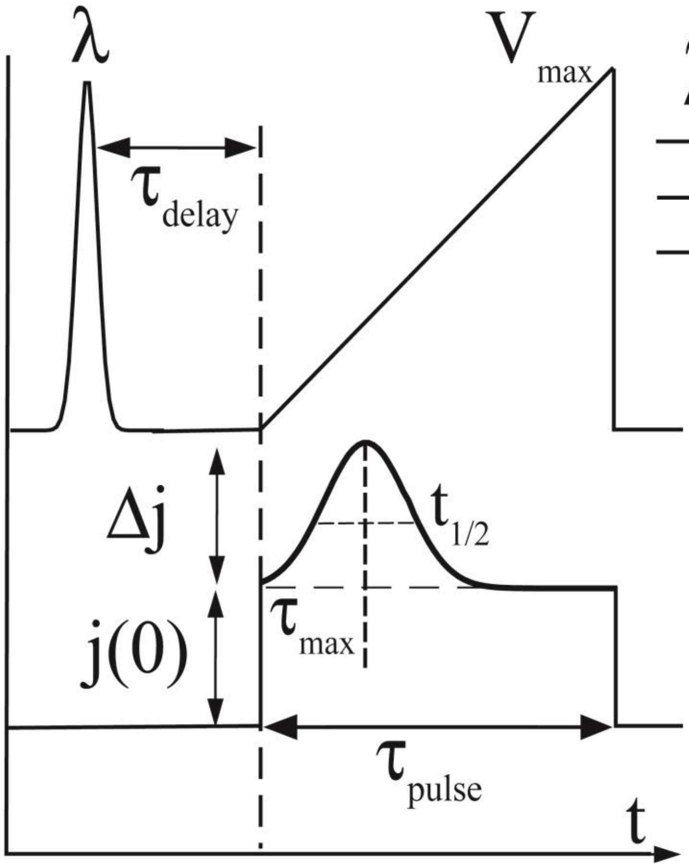
(1) São Carlos Physics Institute – University of São Paulo/Brazil

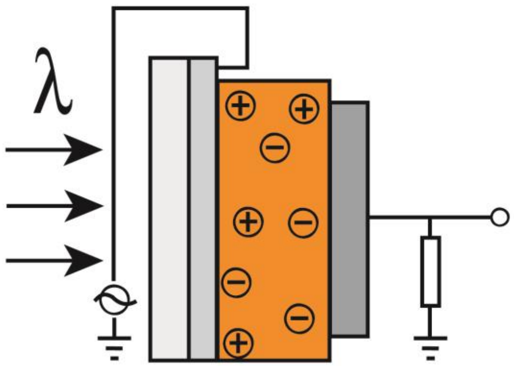
(2) Institute of Material Science – Darmstadt University of Technology/Germany

Mobility Measurement: Photo-CELIV

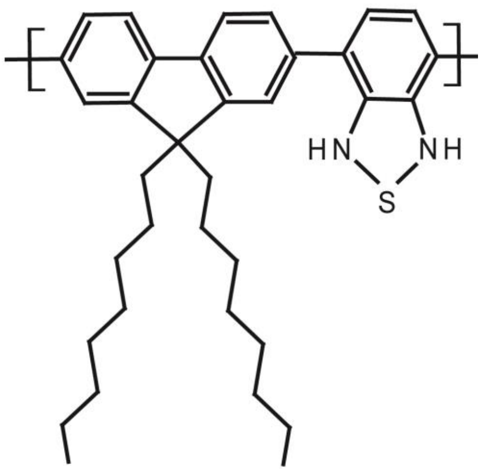
- How does CELIV work?

$$j(0) = (\varepsilon\varepsilon_0 A)/d$$





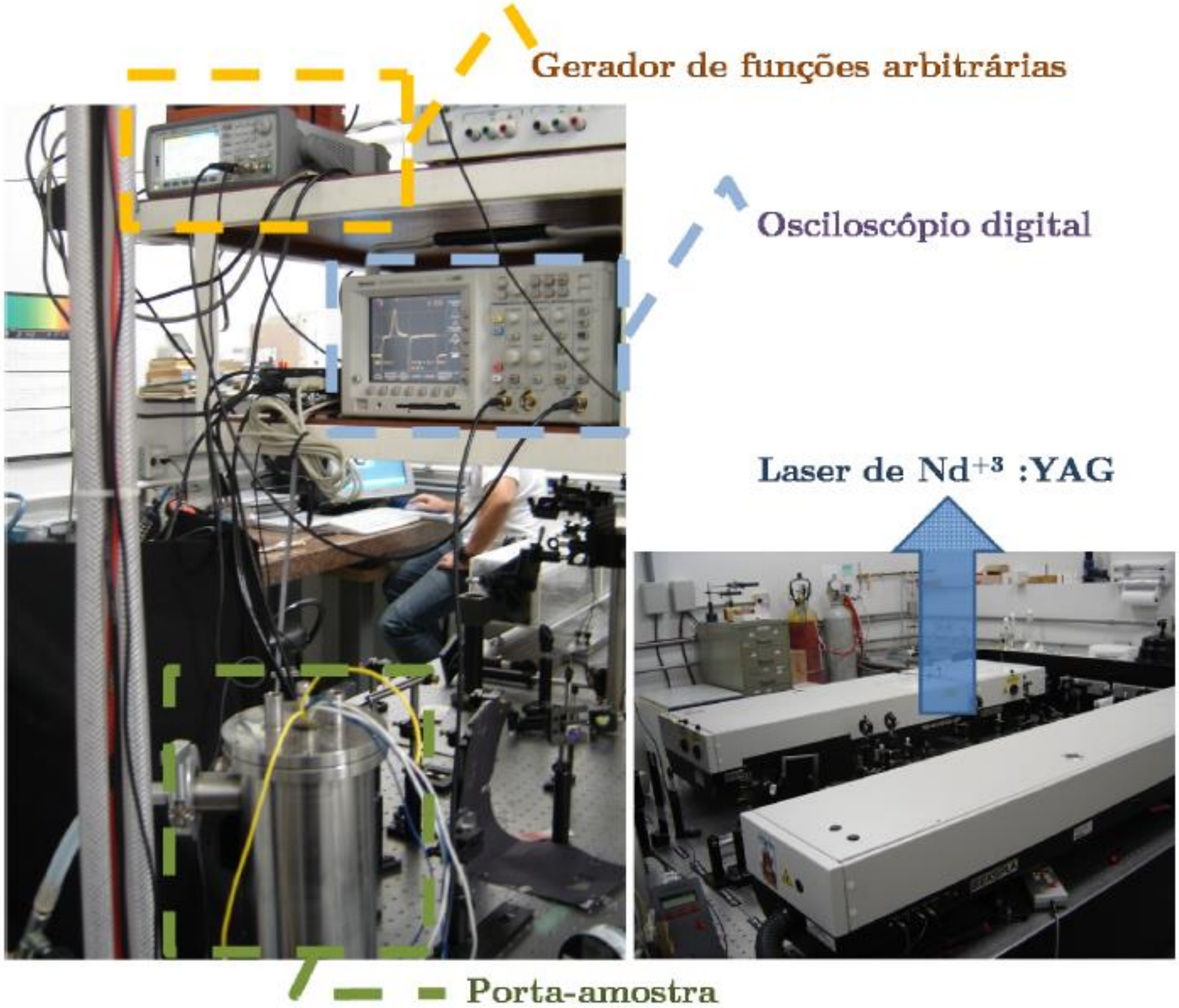
$$\mu = \frac{2d^2}{3At_{max}^2\left[1 + 0.36\frac{\Delta j}{j(0)}\right]}$$



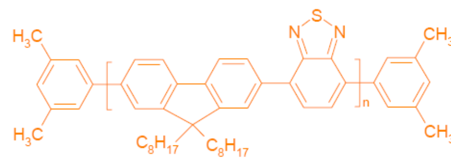
Dispersiveness Parameter:

$$\text{ratio } t_{1/2}/t_{\max}$$

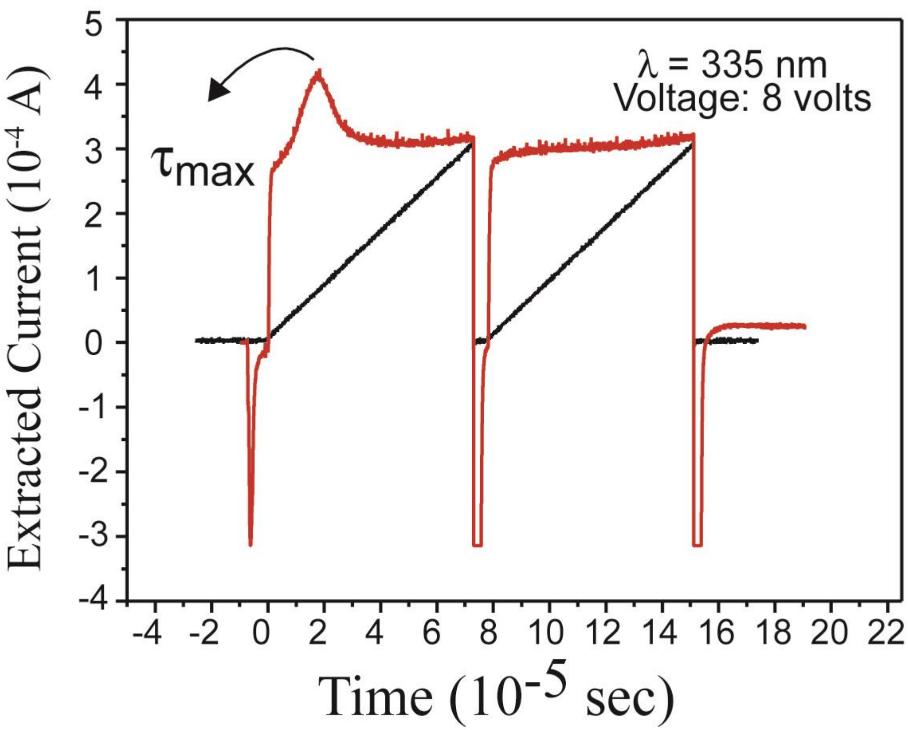
Mobility Measurement: Photo-CELIV



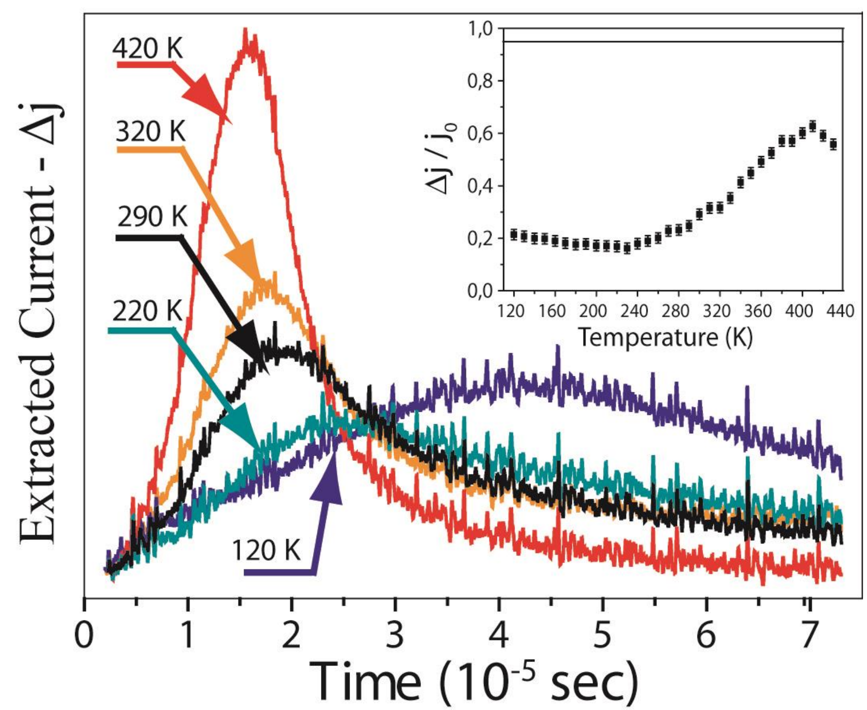
Mobility Measurement: Photo-CELIV



Full Photo-CELIV response:



Extracted Current (Δj):

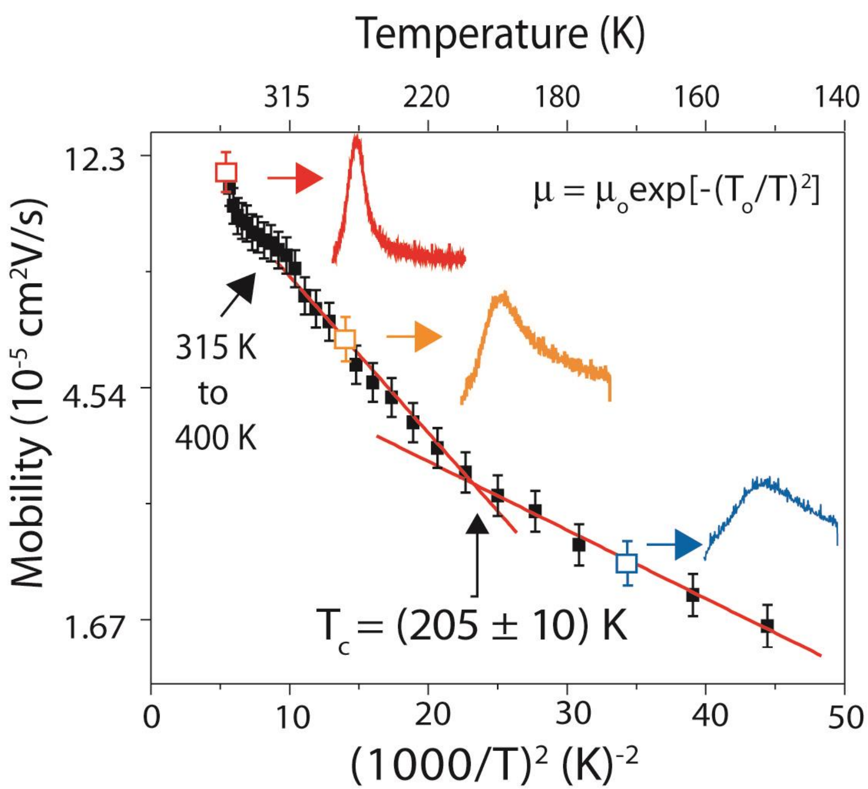


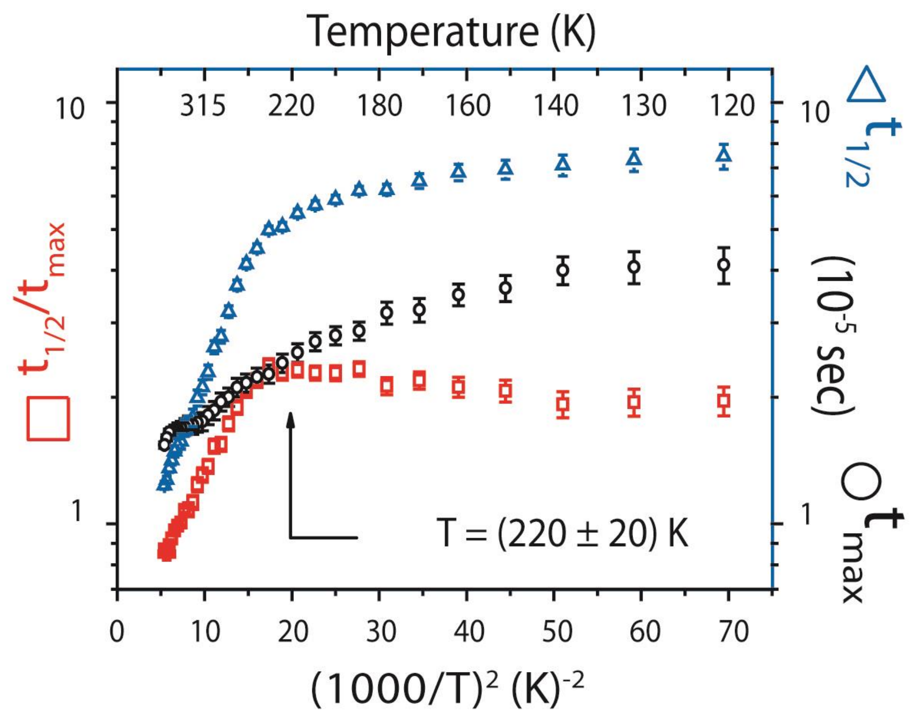
$$\mu = \frac{2d^2}{3At_{\max}^2\left[1 + 0.36\frac{\Delta j}{j(0)}\right]}$$

Dispersiveness Parameter:

$$\text{ratio } t_{1/2}/t_{\max}$$

Mobility Measurement: Photo-CELIV

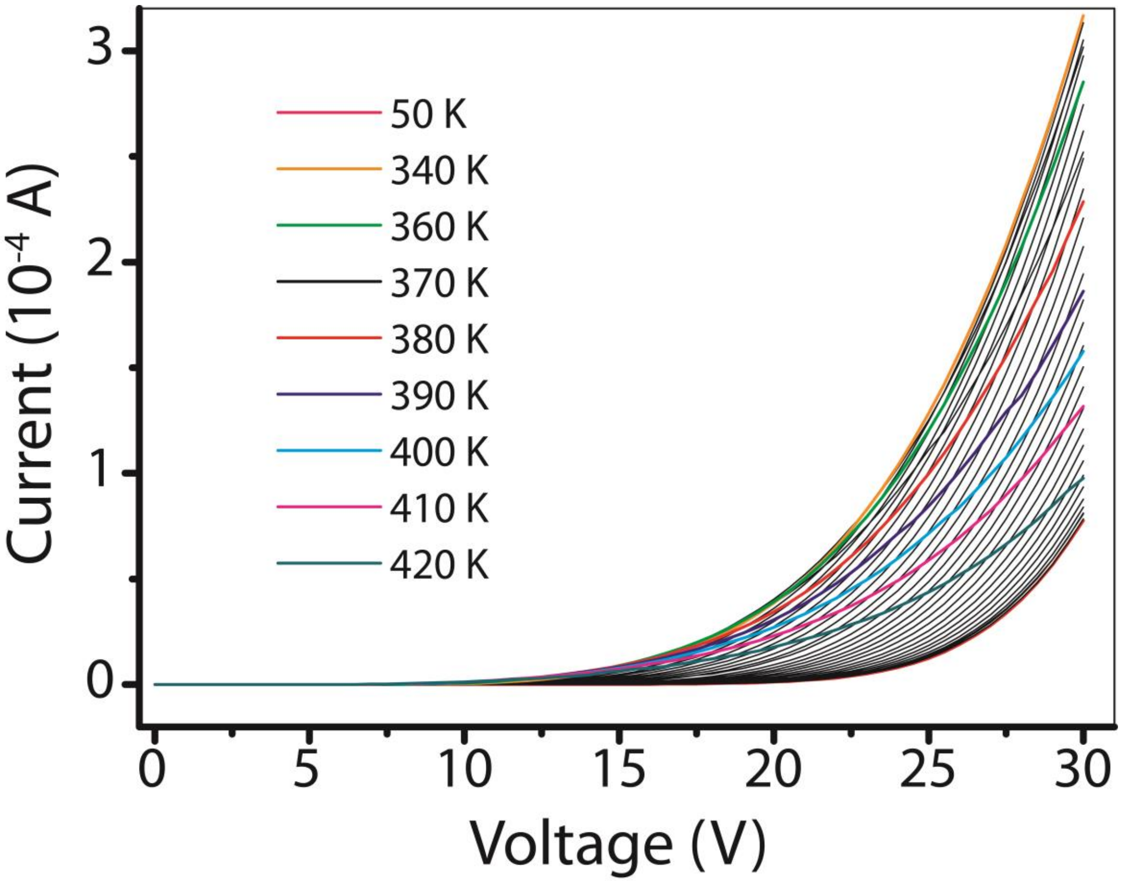




Mobility vs. Temperature: Kinks and modulations…

Is it real? – Move to standard techniques…

Mobility Measurement: Current-Voltage



Modeling

$$J = p(x) e \mu_p [E(x)] E(x),$$

$$\frac{\epsilon}{e} \frac{dE(x)}{dx} = p(x),$$

$$\mu(E) = \mu_0 e^{\gamma \sqrt{E}}$$

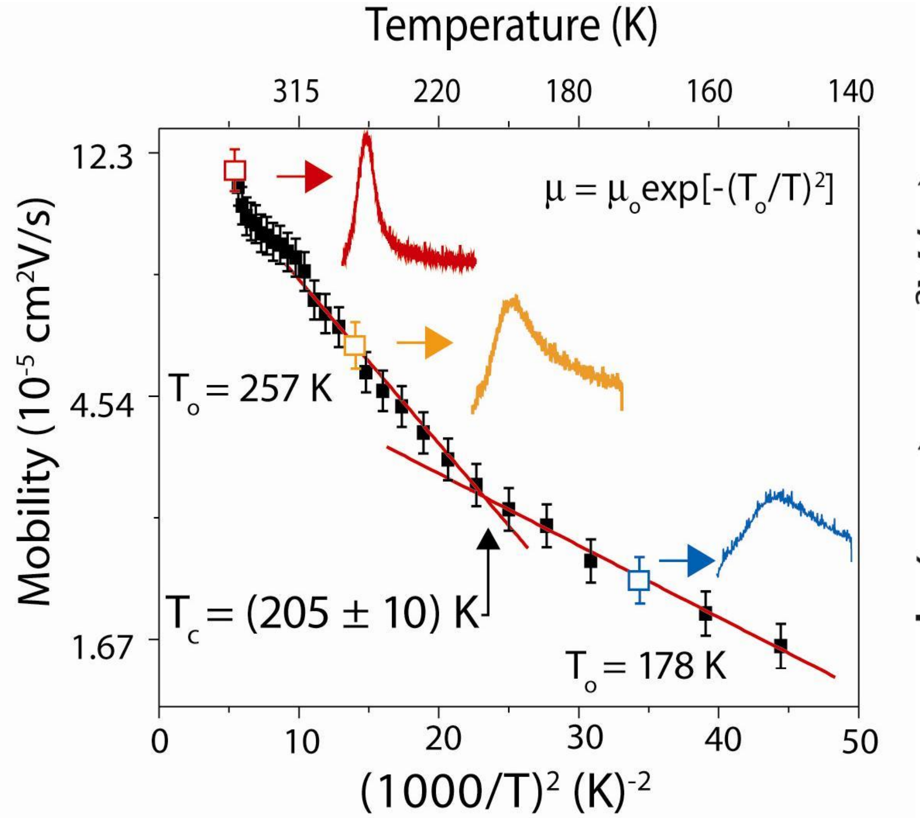
Electric-field and temperature dependence of the hole mobility in poly(*p*-phenylene vinylene)

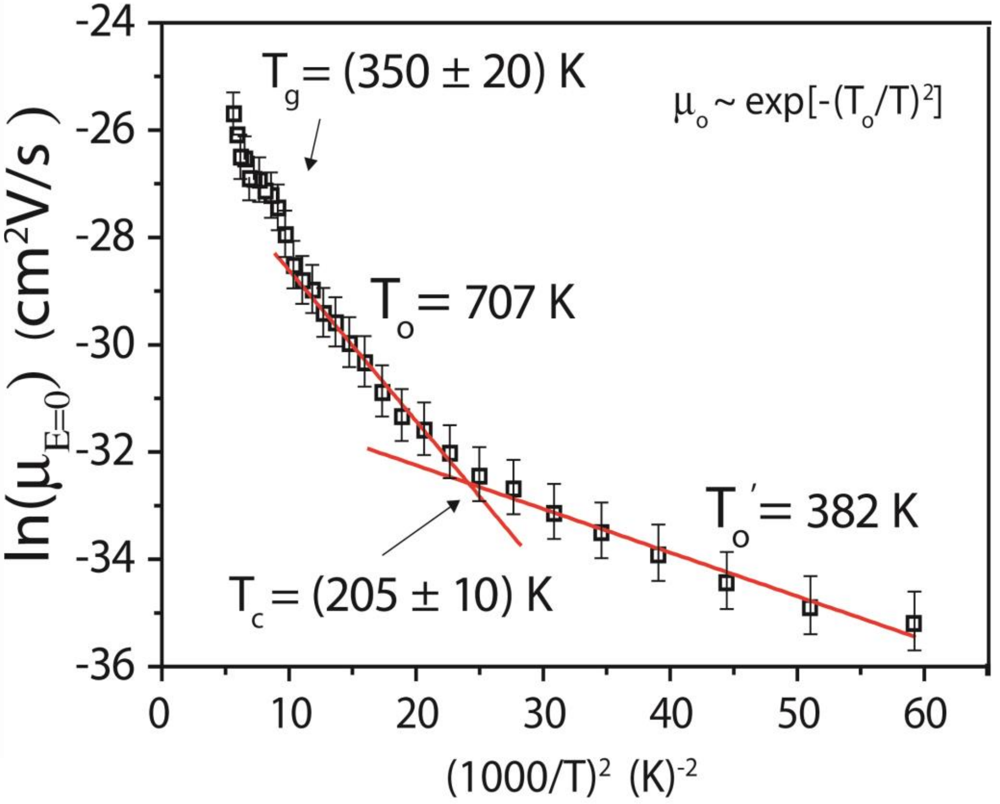
P. W. M. Blom, M. J. M. de Jong, and M. G. van Munster
Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands

(Received 3 September 1996)

Mobility: Photo-CELIV vs IxV

Remarkable similarity



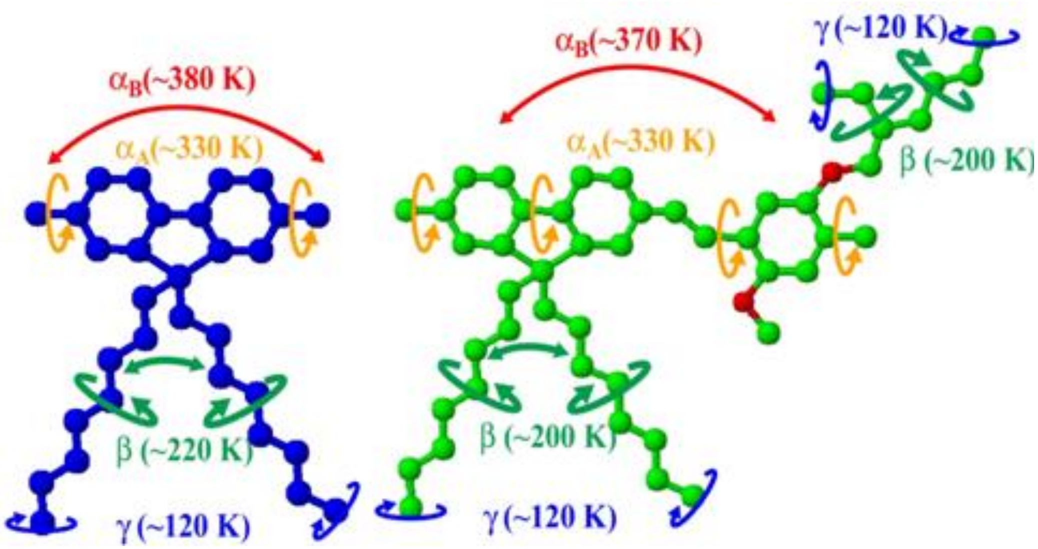


Mobility vs. Temperature: Kinks and modulations…

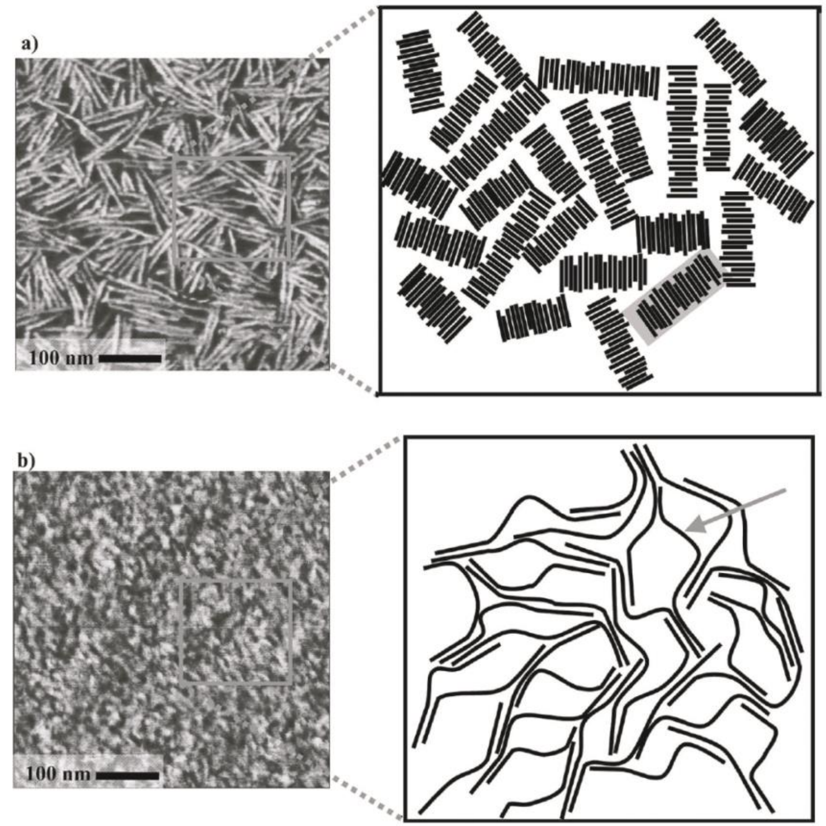
Why??

Motivation

- **Polymer Materials has mobile segments:** ⟶ Rich and Unstable



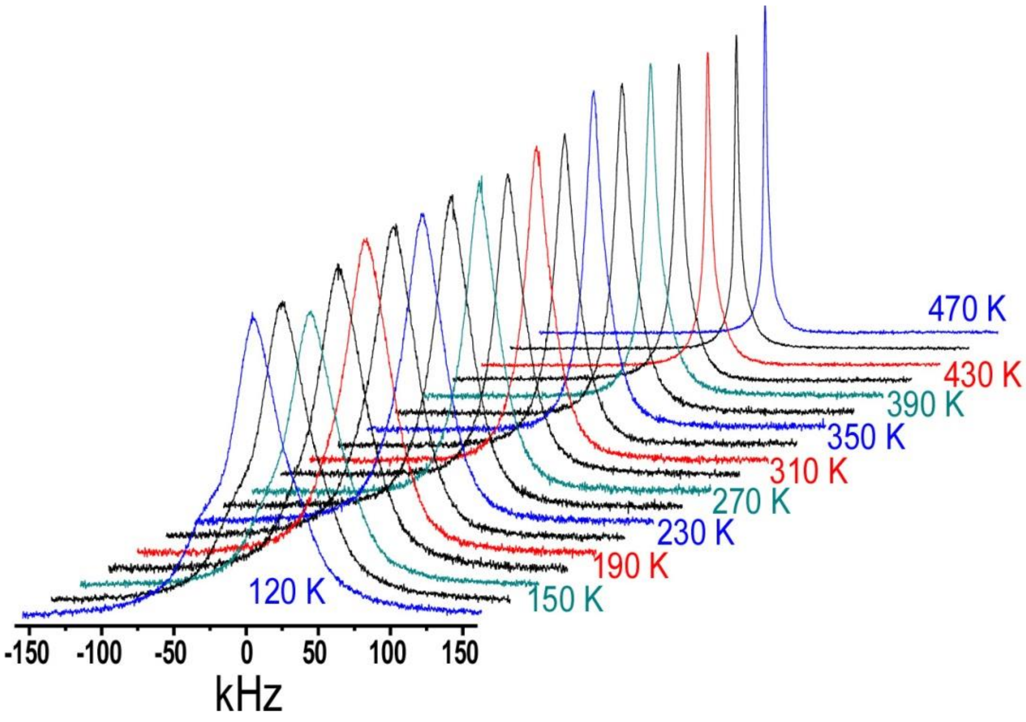
J. Phys. Chem. B **2009**, *113*, 11403–11413

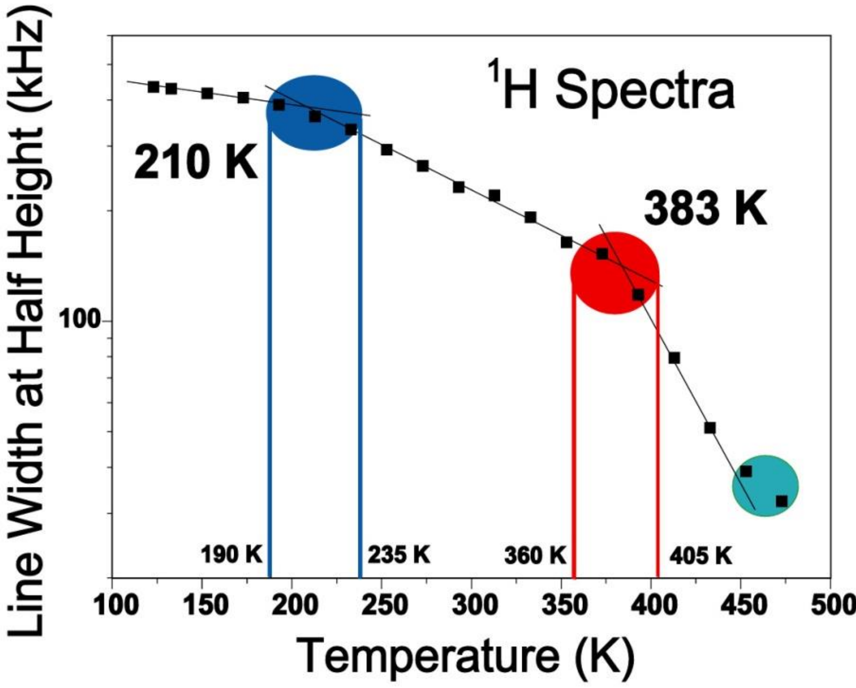


Strongly affect its Electrical and Optical Properties

Molecular Characterization

Static ^1H NMR Experiment – Line Shape Analysis





Colaboração: Prof. Eduardo Ribeiro de Azevêdo – RMN/IFSC

J. Phys. Chem. B **2009,** *113,* 11403–11413

High Resolution ss-NMR Techniques

✓ **DIPSHIFT**

✓ **Exchange Methods**

ELSEVIER

Progress in Nuclear Magnetic Resonance Spectroscopy 47 (2005) 137–164

PROGRESS IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

www.elsevier.com/locate/pnmrs

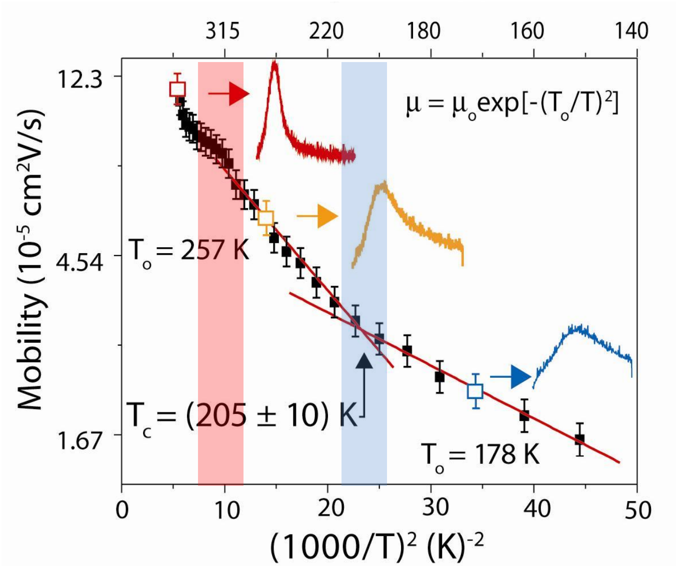
Molecular dynamics in solid polymers

Eduardo Ribeiro deAzevedo[a], Tito José Bonagamba[a], Detlef Reichert[b,*]

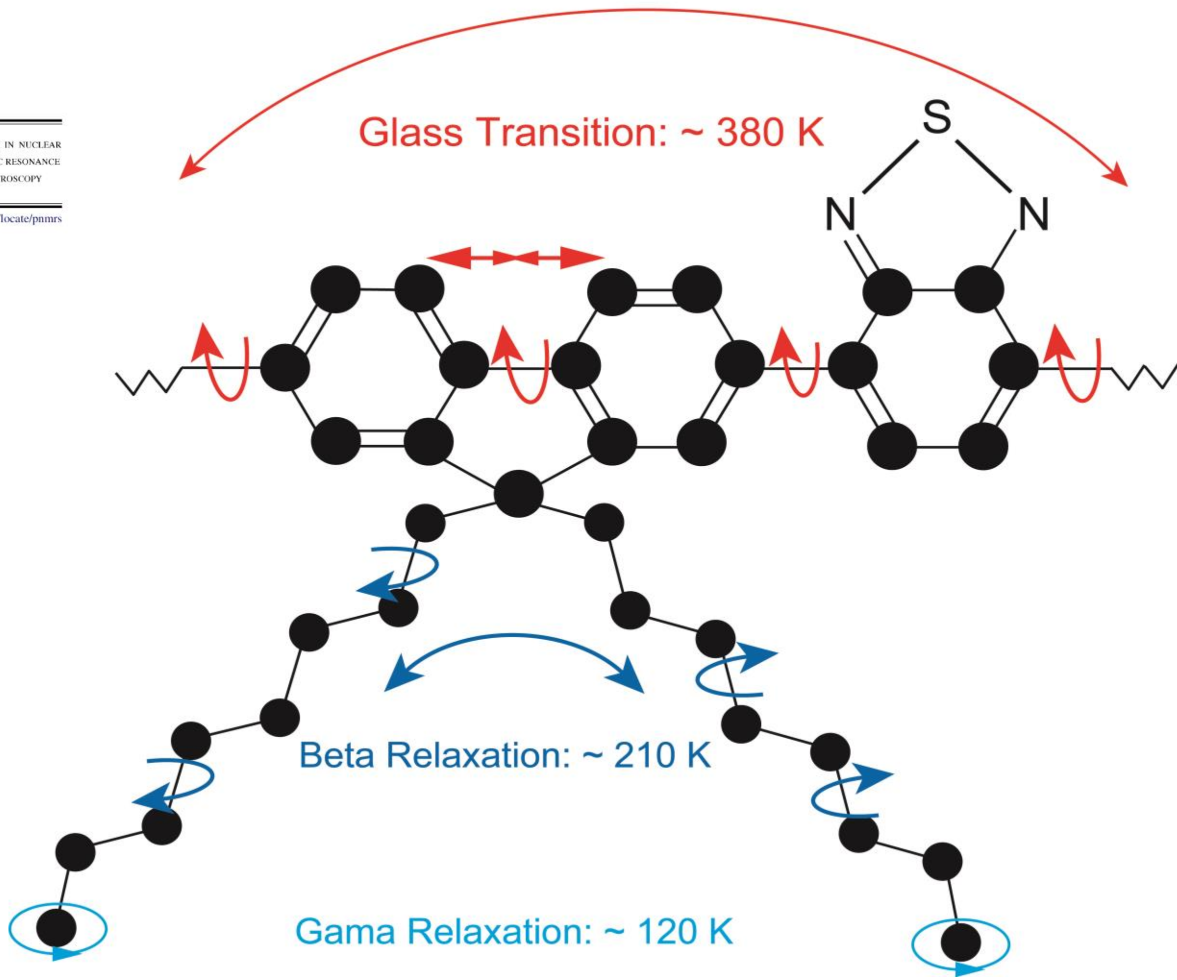
[a] Instituto de Física de São Carlos, USP, Caixa Postal 369, CEP: 13560-970, São Carlos, SP, Brazil

[b] Department of Physics, Halle University, Friedemann-Bach-Platz 6, 06108 Halle, Germany

Received 20 May 2005

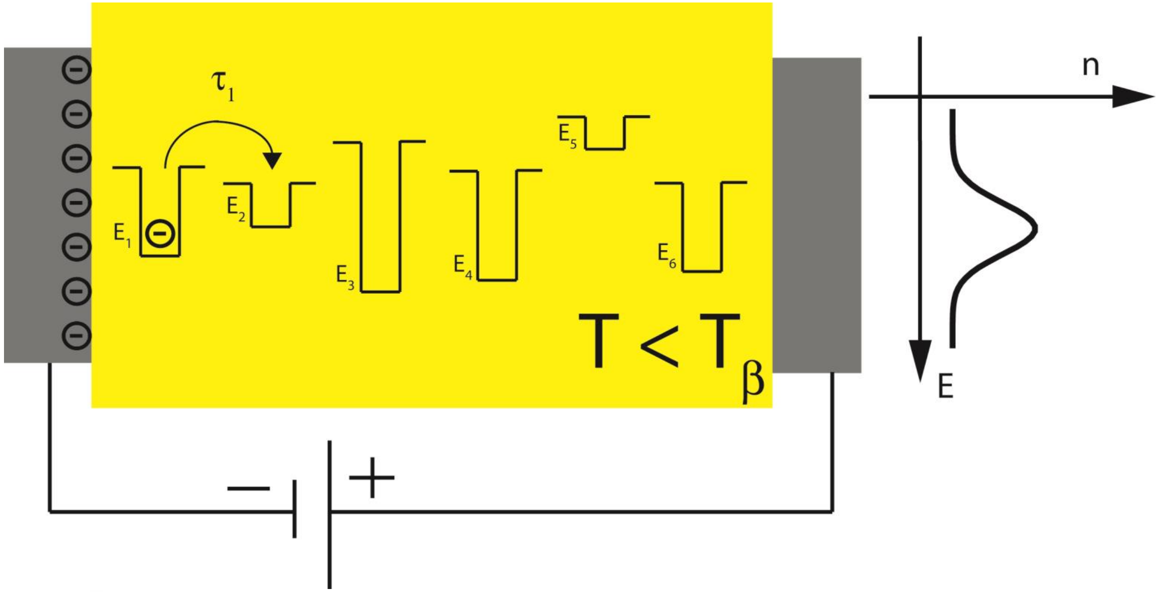


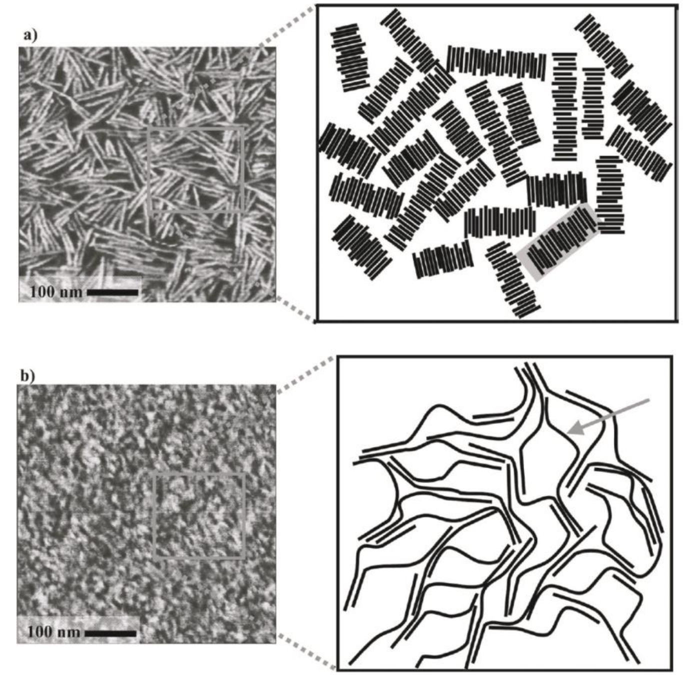
F8BT: Molecular Relaxation Overview

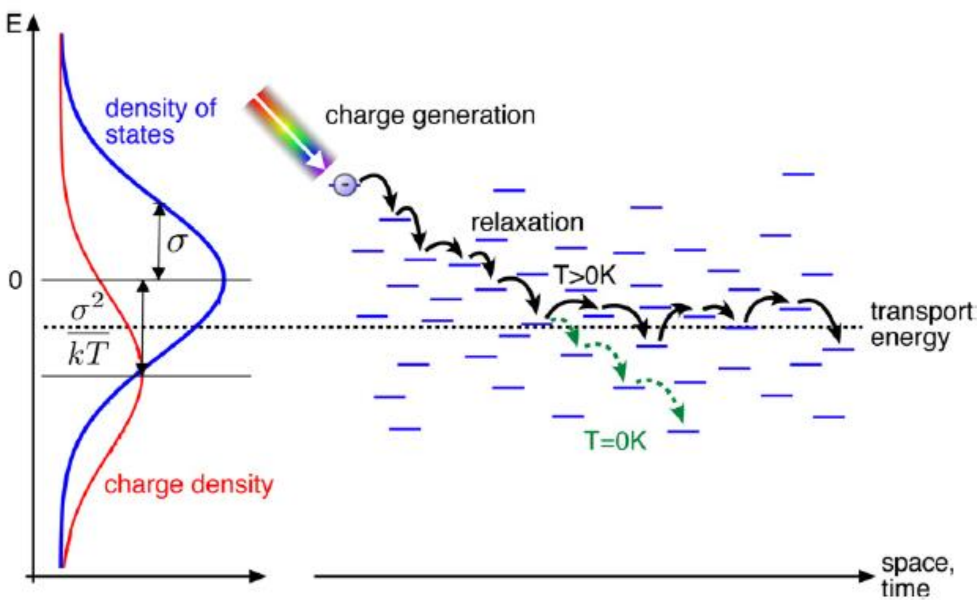


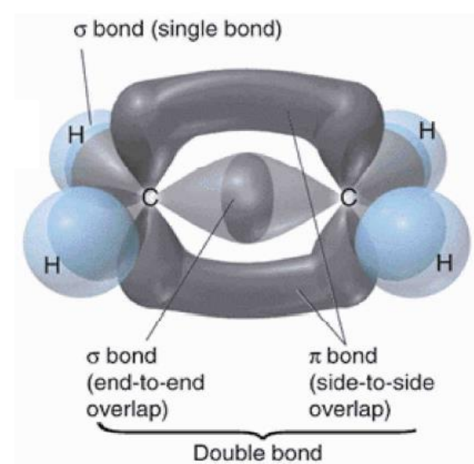
E.R. deAzevedo et al. / Progress in Nuclear Magnetic Resonance Spectroscopy 47 (2005) 137–164

How to interpret?



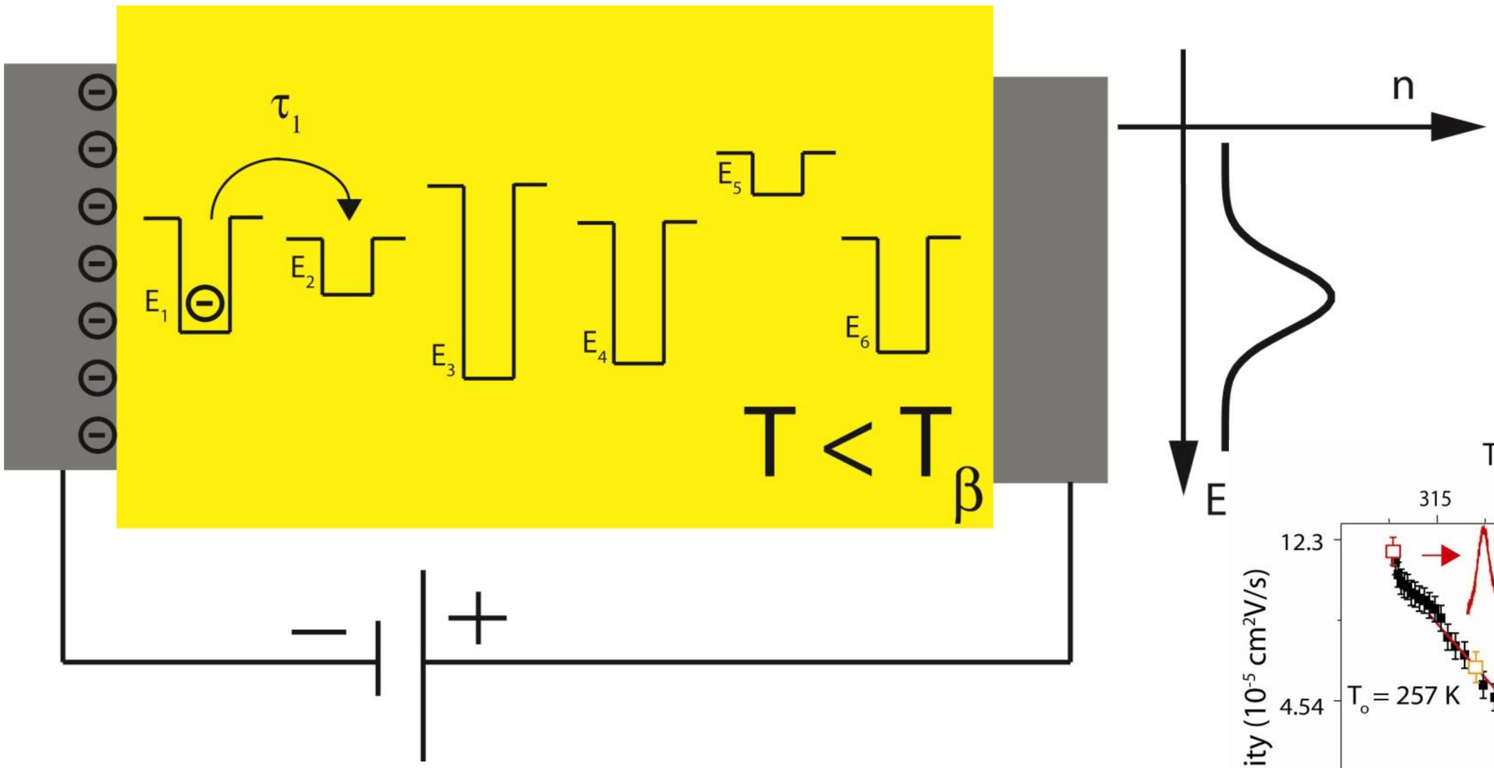


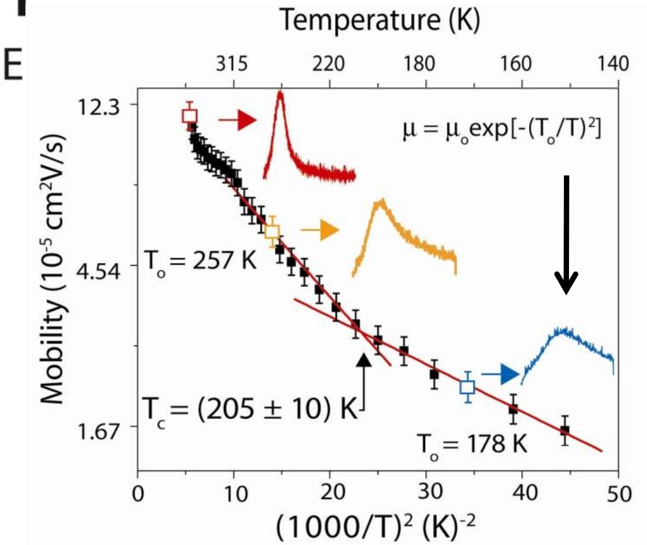




Interpretation

How is this?



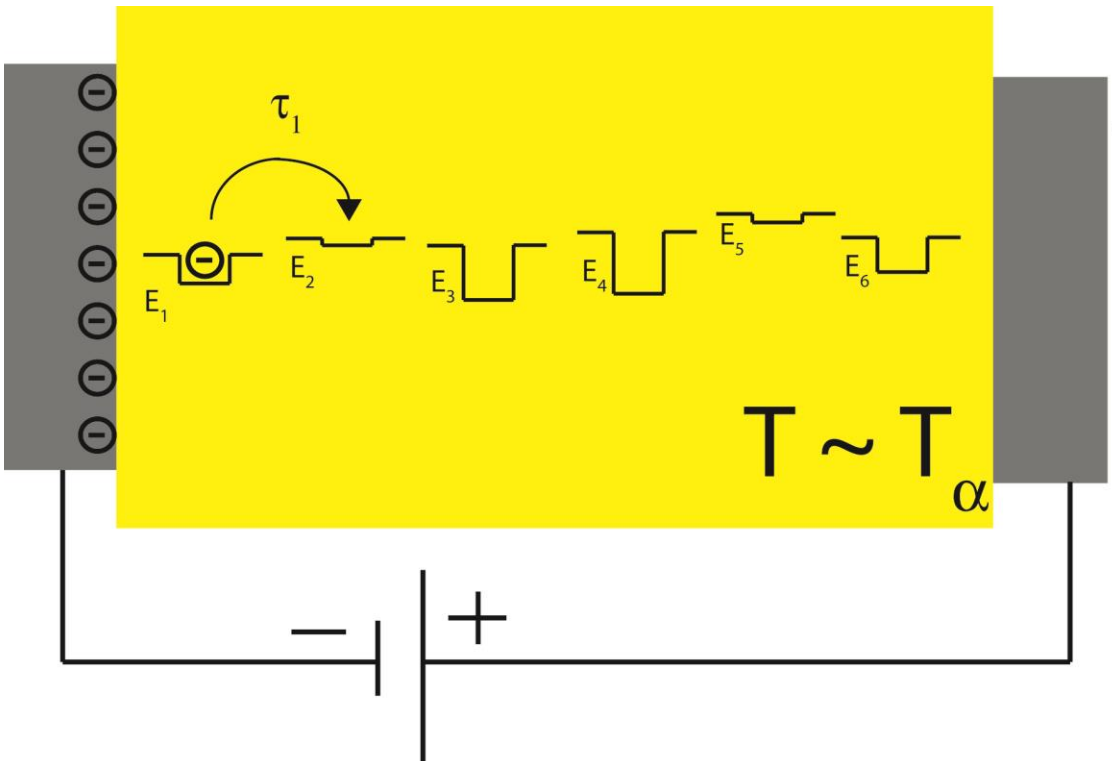


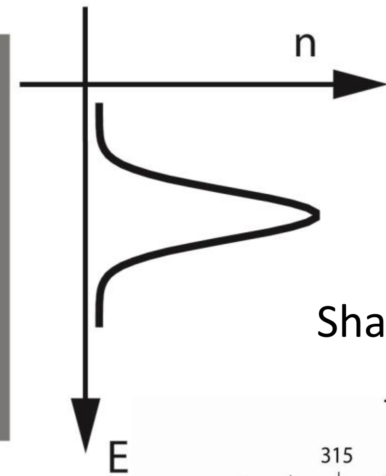
"Trap Controlled" Hopping

Hopping is impeded by deep traps

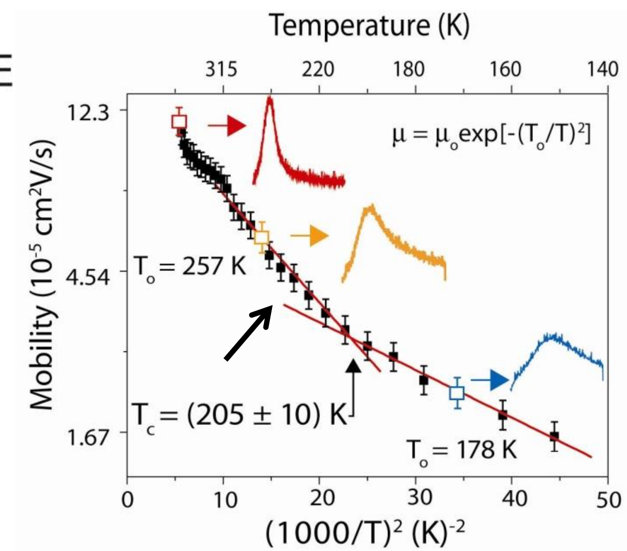
Interpretation

How is this?





Shallower traps.

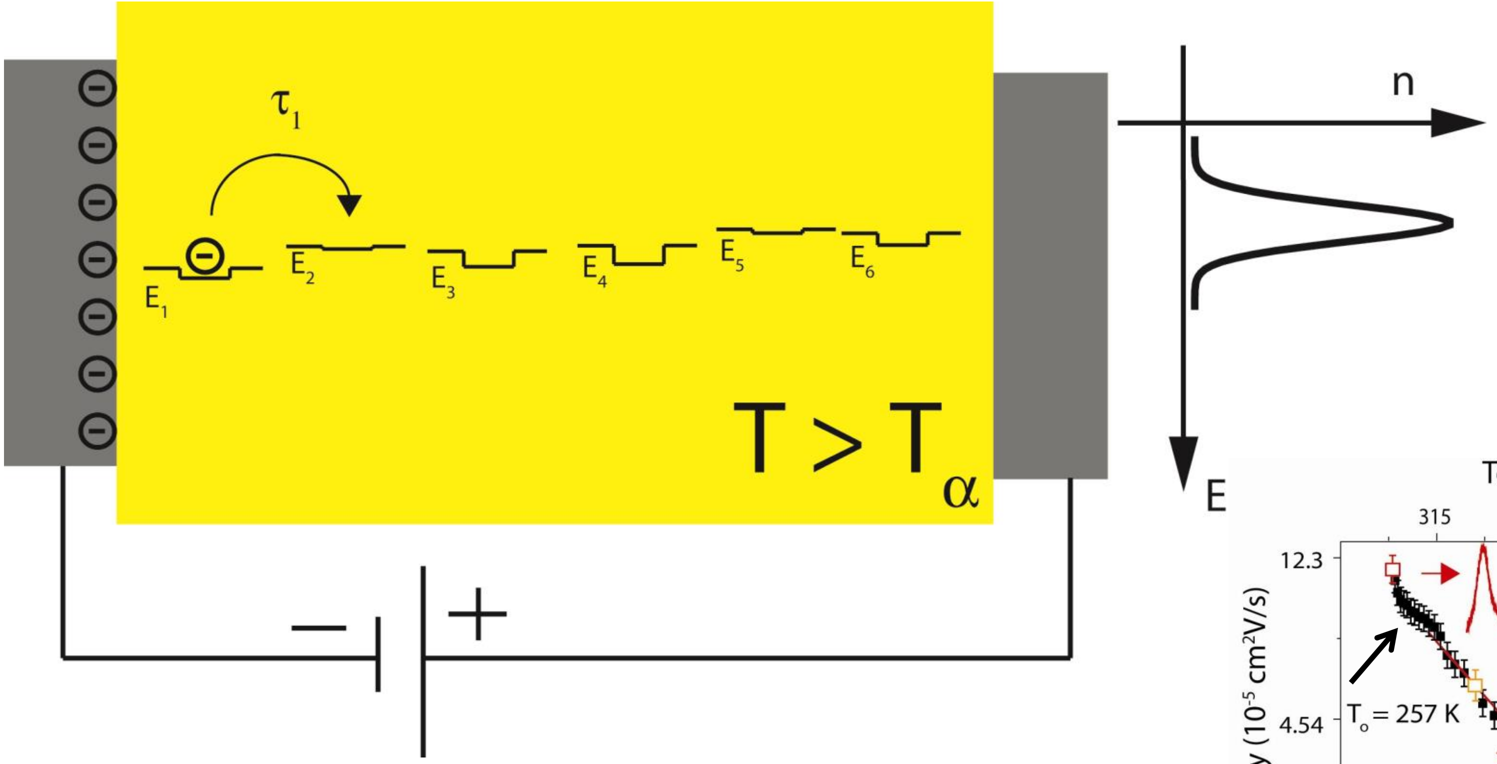


“Trap Controlled” Hopping

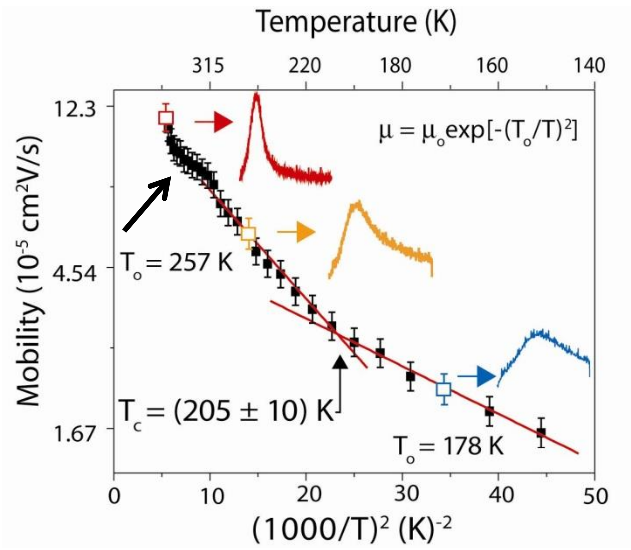
Structural/Motional Detrapping (regime)

Interpretation

How is this?



Hopping occurs free of traps.



Structural/Motional detrapping (regime)

Conclusion

✓ Two main relaxation processes: ~ 210 K (β-relaxation) and ~370 K (glass transition);

✓ β-relaxation: Side Chain Relaxation/ Glass transition: Main Chain Relaxation

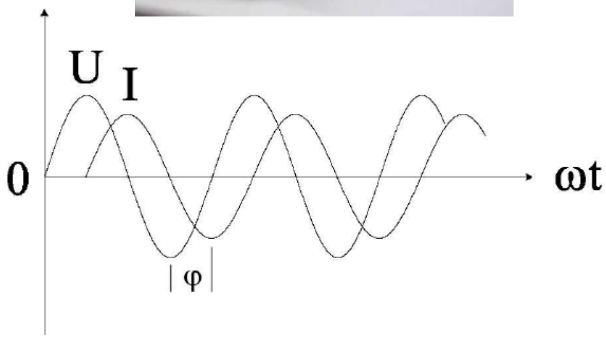
✓Electrical Measurements: strongly influenced by relaxations and crystallization.

✓ Interpretation: trapping and detrapping mechanism together with molecular dynamics – structural/motional detrapping.

IFSC - USP Grupo de Bernhard Gross Polímeros
DAAD
ineo National Institute on Organic Electronics
FAPESP
CNPq Conselho Nacional de Desenvolvimento Científico e Tecnológico

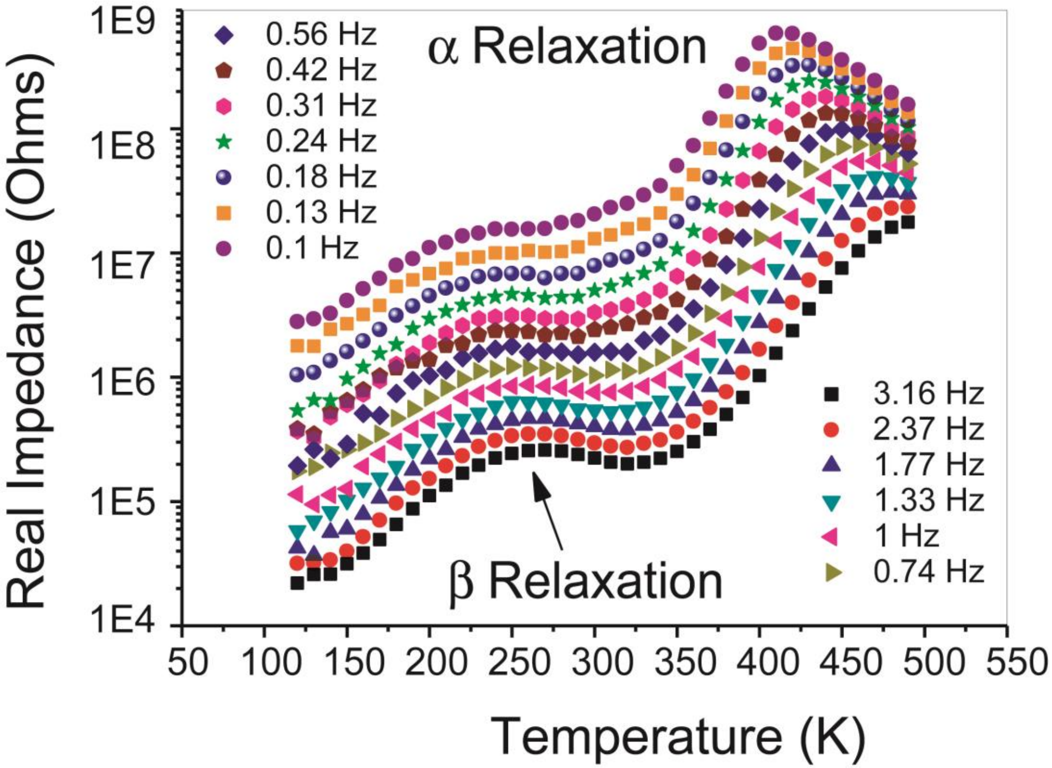
Dielectric Relaxation

Molecular Relaxation detected electrically!!



$$U(t) = U_0 \cdot \sin(\omega t)$$

$$I(t) = I_0 \cdot \sin(\omega t + \varphi)$$



β – Relaxation: ~ 210 Kelvins

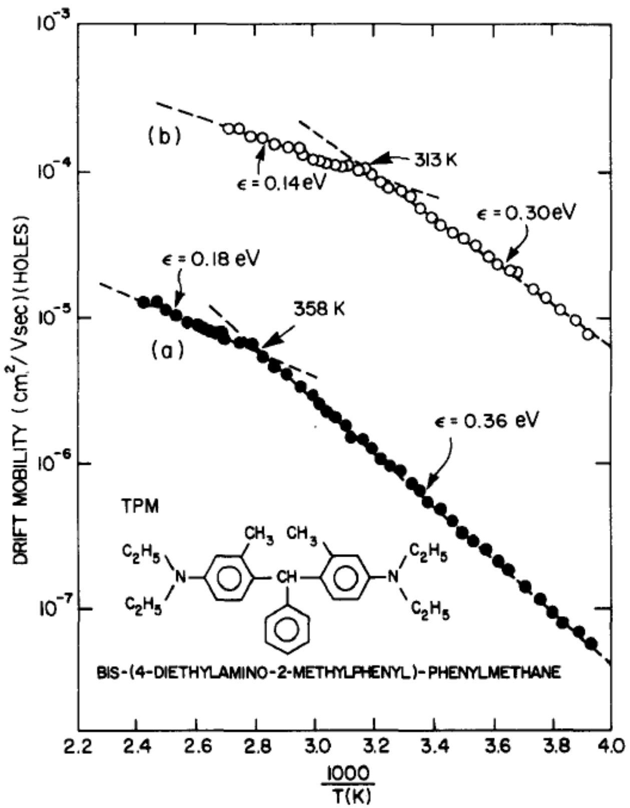
α – Relaxation: ~ 380 Kelvins

Motivation/Goals

- Also, it is very common into the literature:

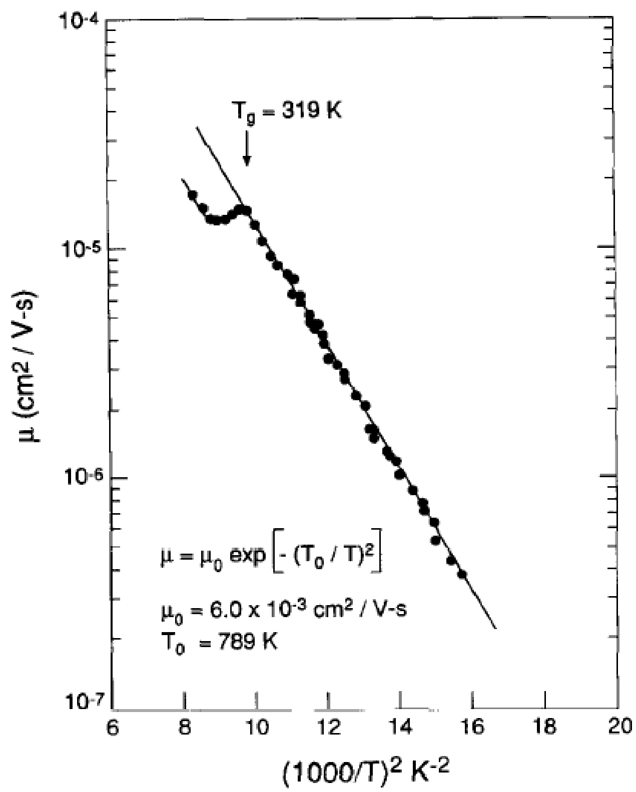
Behavior of the drift mobility in the glass transition region of some hole-transporting amorphous organic films

M. Abkowitz, M. Stolka, and M. Morgan
Xerox Corporation, Webster Research Center, Webster, New York 14580



The transition from nondispersive to dispersive charge transport in vapor deposited films of 1-phenyl-3-*p*-diethylamino-styryl-5-*p*-diethylphenylpyrazoline (DEASP)

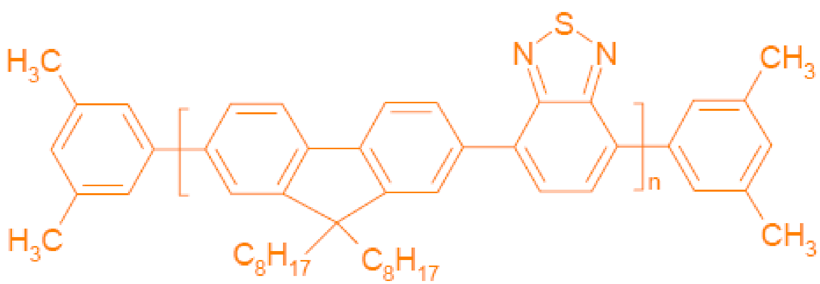
H. Bässler
Fachbereich Physikalische Chemie und Zentrum für Materialwissenschaften der Philipps-Universität, D-35032 Marburg, Germany



- Decided to analyze such futures with more details.

Material and Samples

- Poly(9,9'-dioctylfluorene-co-benzothiadiazole) – F8BT

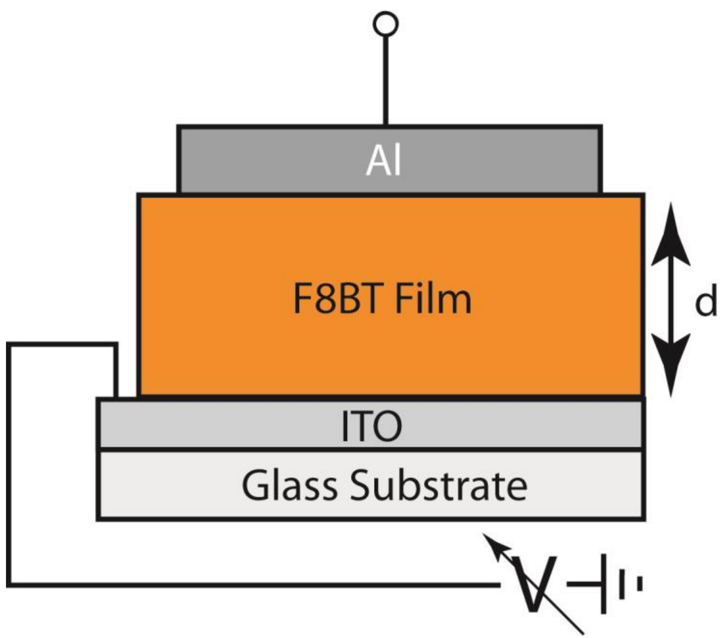


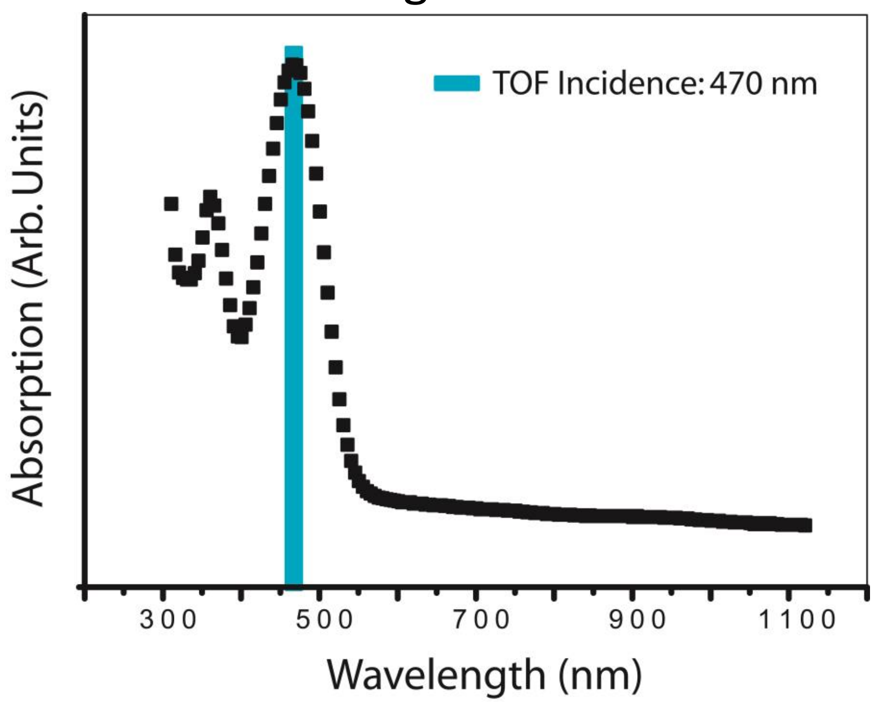
→ Well known material!

We want to measure mobility:

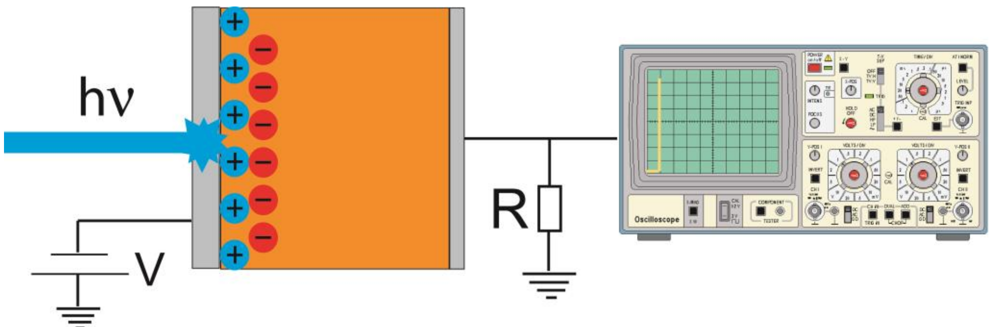
→ Time of Flight Measurements!

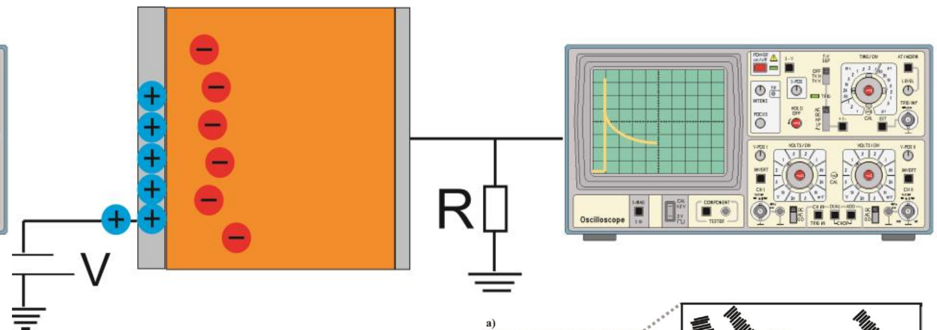
4 µm films obtained by Simple Cast

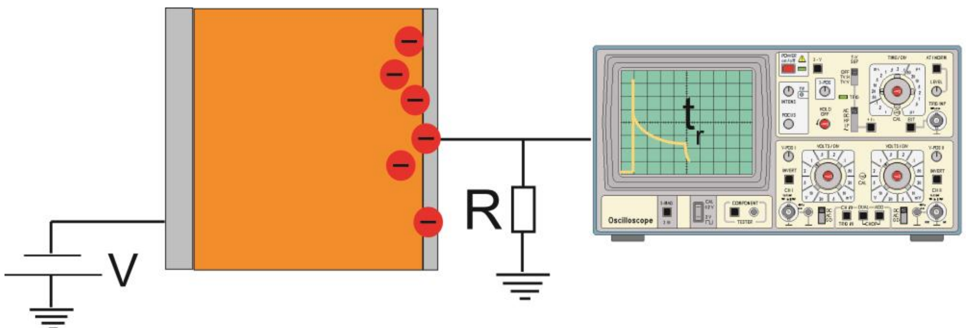


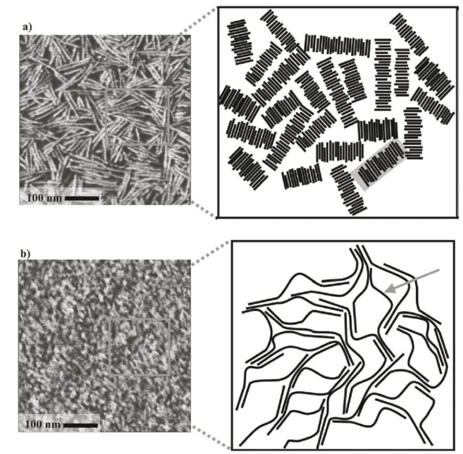


Time of Flight Measurements

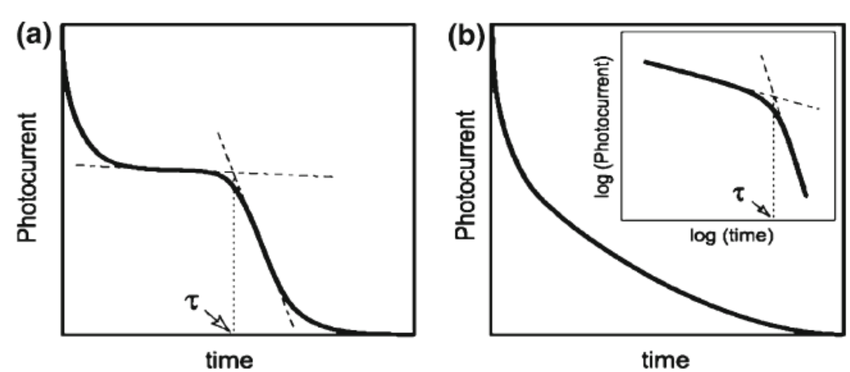






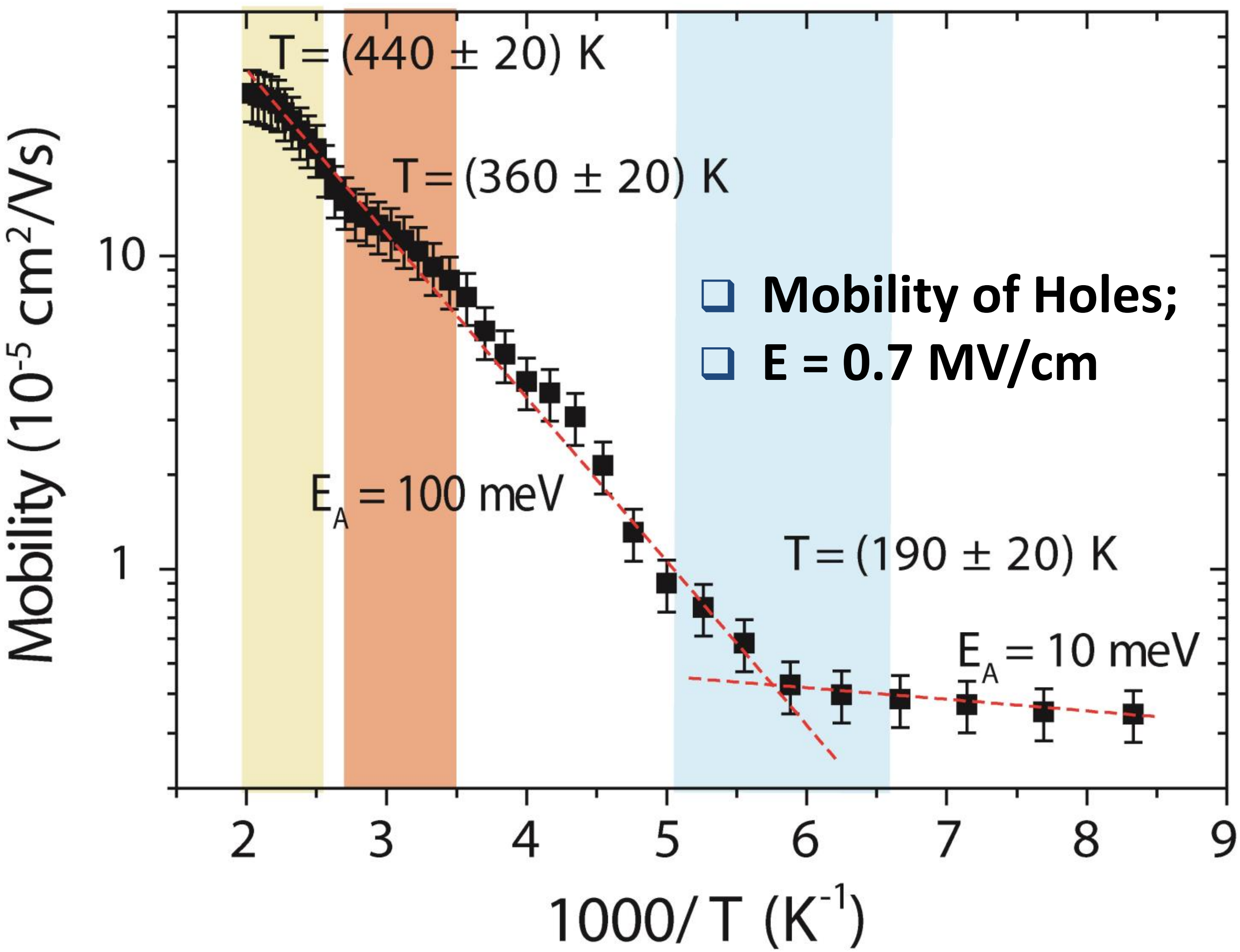


$$\mu = \frac{d}{t_T E}$$



Time of Flight Measurements

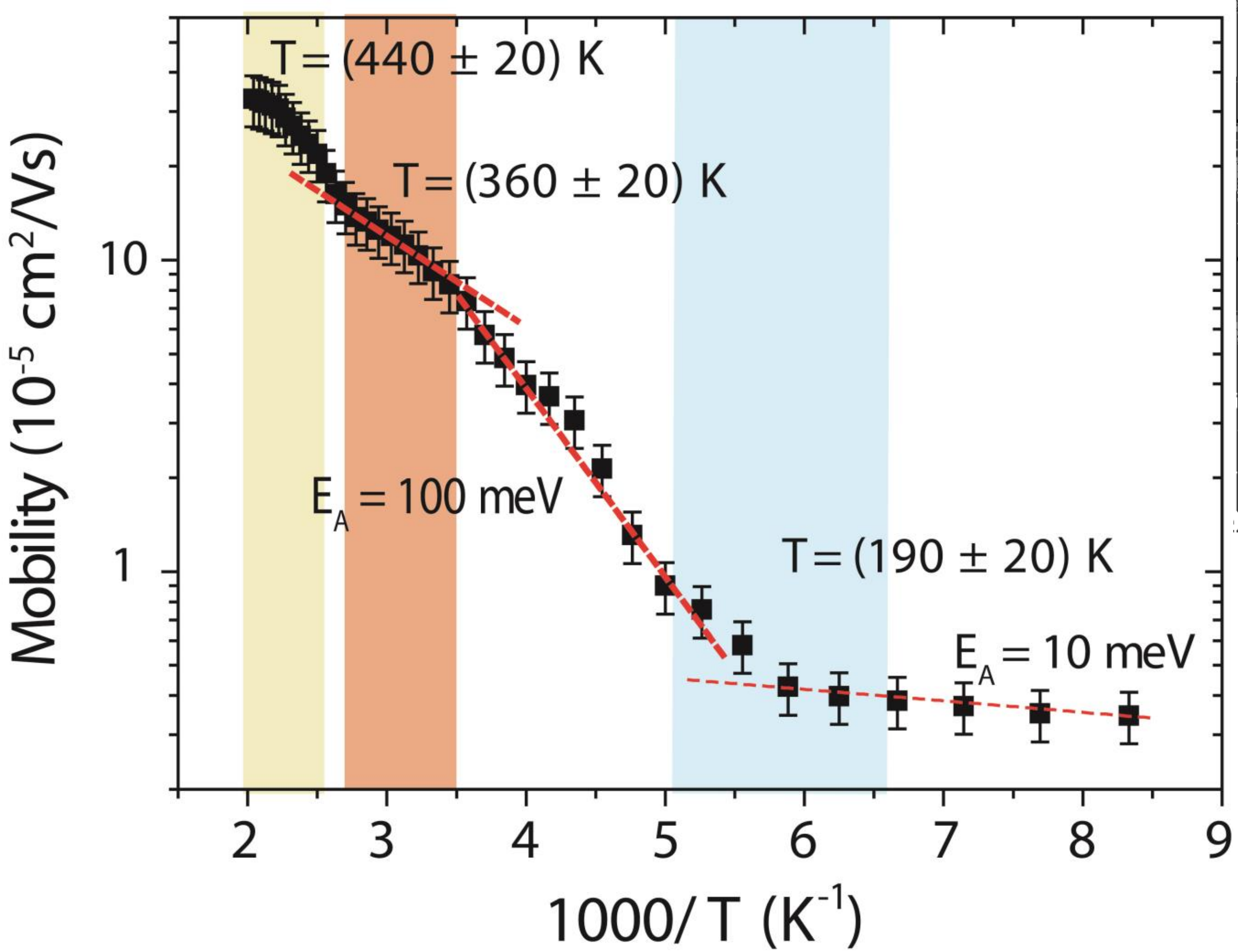
- ❑ **Excitation: 9 ns pulsed laser - λ = 470 nm;**

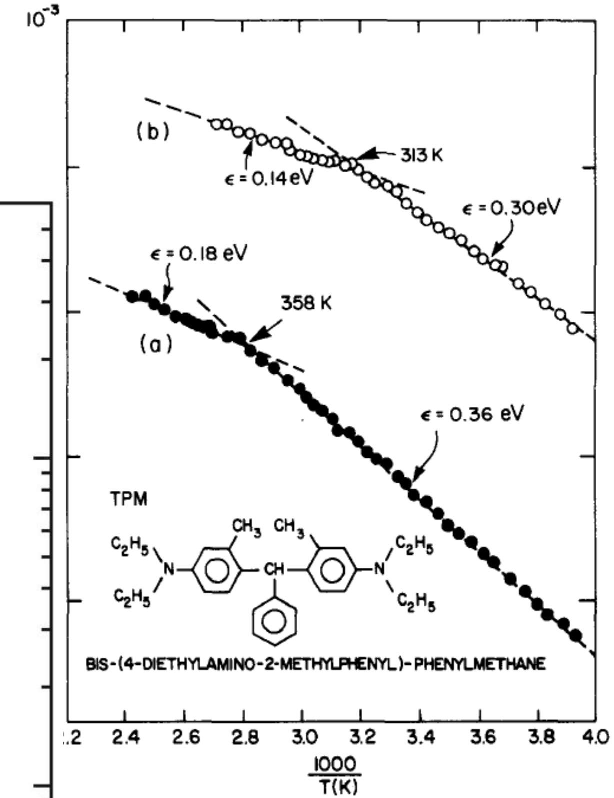


- ❑ **Mobility of Holes;**
- ❑ **E = 0.7 MV/cm**

Time of Flight Measurements

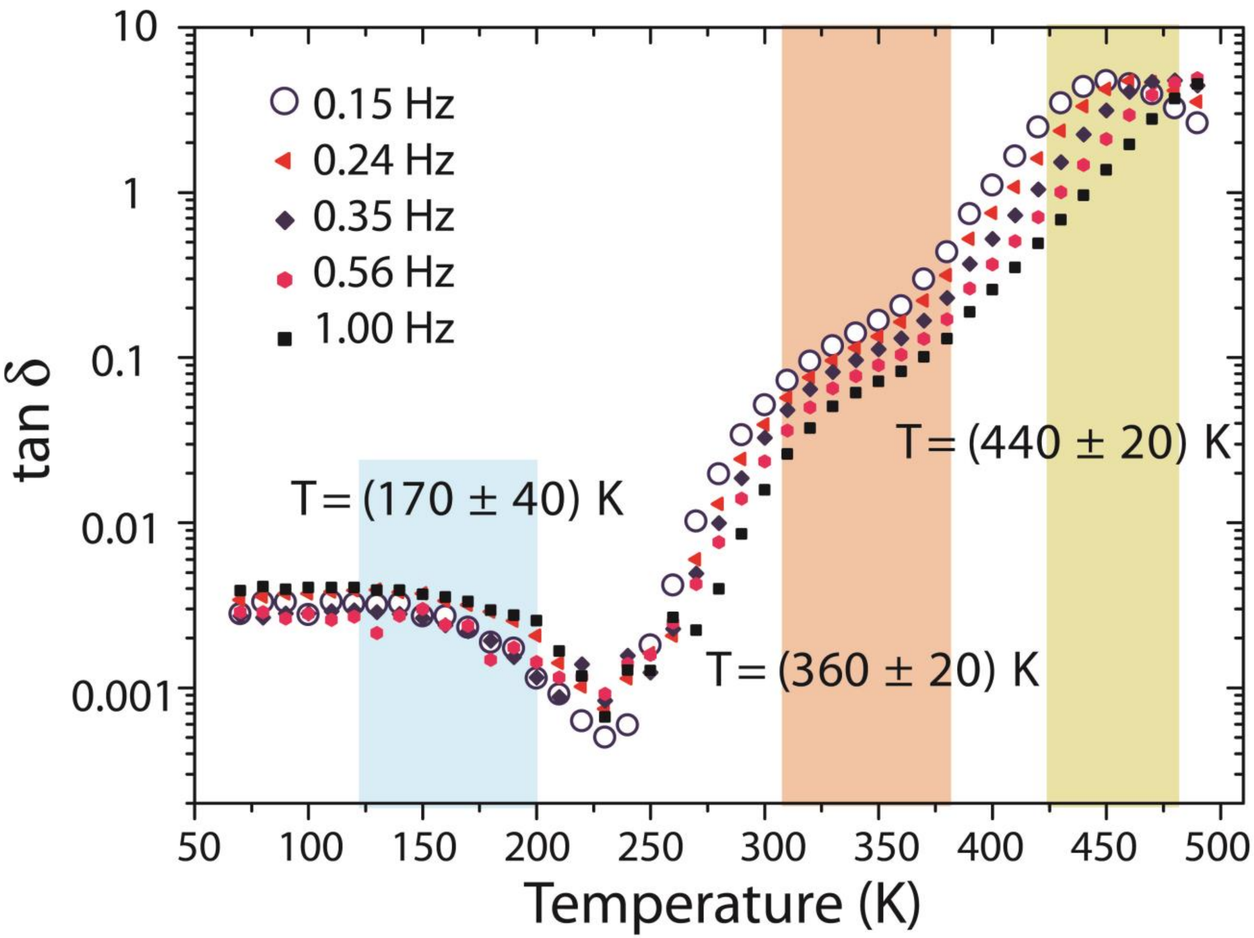
- Excitation: 9 ns pulsed laser - λ = 470 nm;

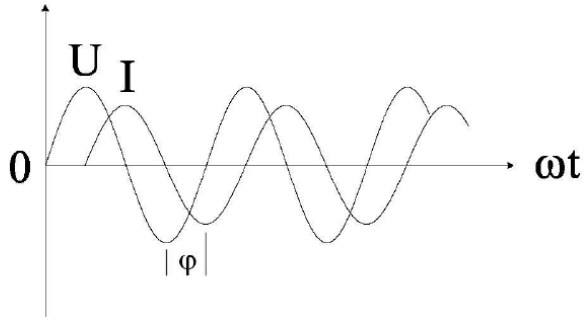




Dielectric Spectroscopy

- **Are those characteristics due to molecular relaxation/structural transition?**



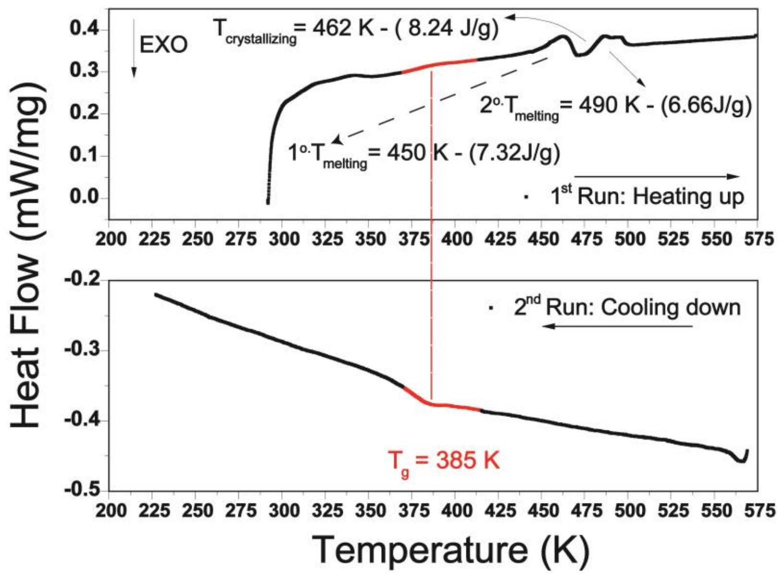


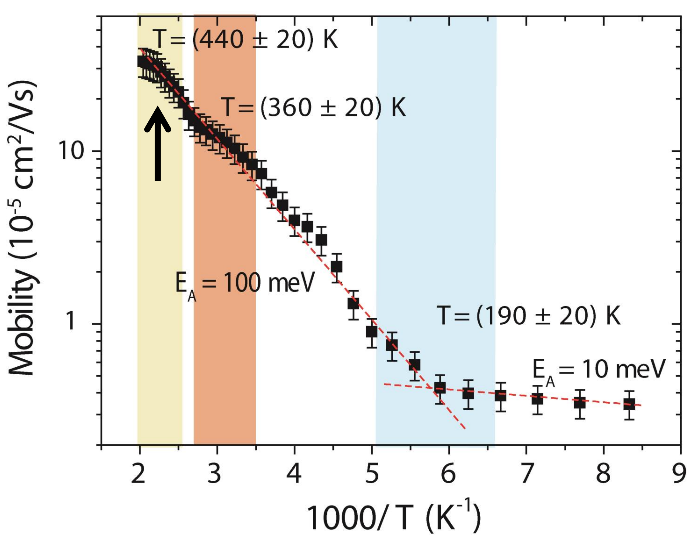
$$U(t) = U_0 \cdot \sin(\omega t)$$

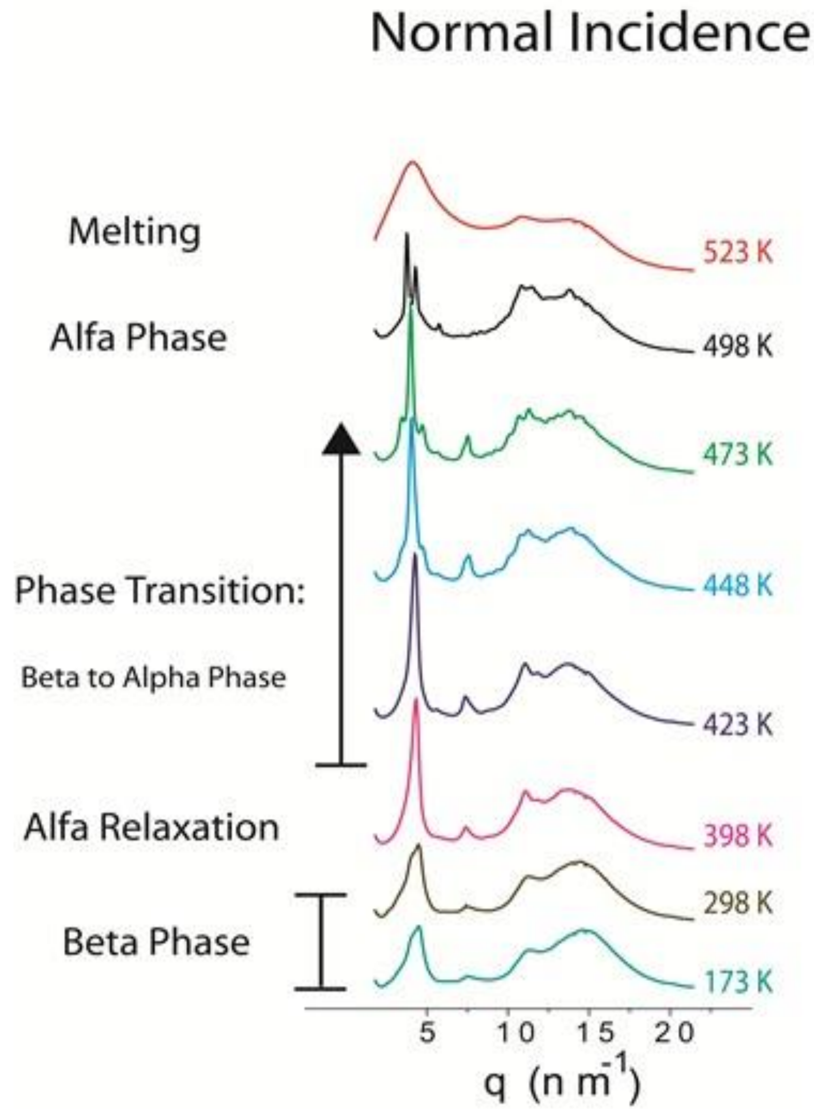
$$I(t) = I_0 \cdot \sin(\omega t + \varphi)$$

Wide Angle X-ray Diffraction vs DSC

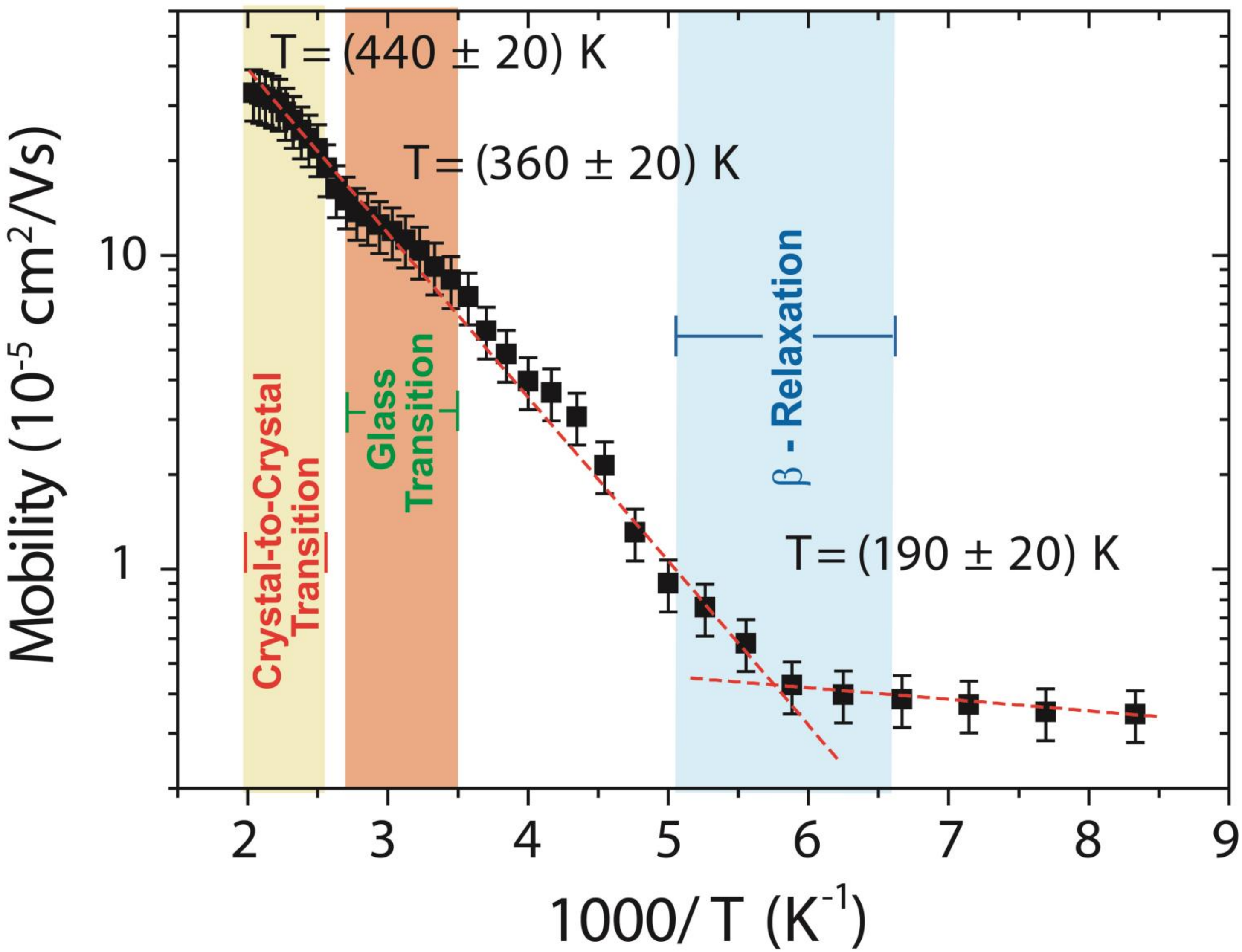
Nice correlations with DSC results:



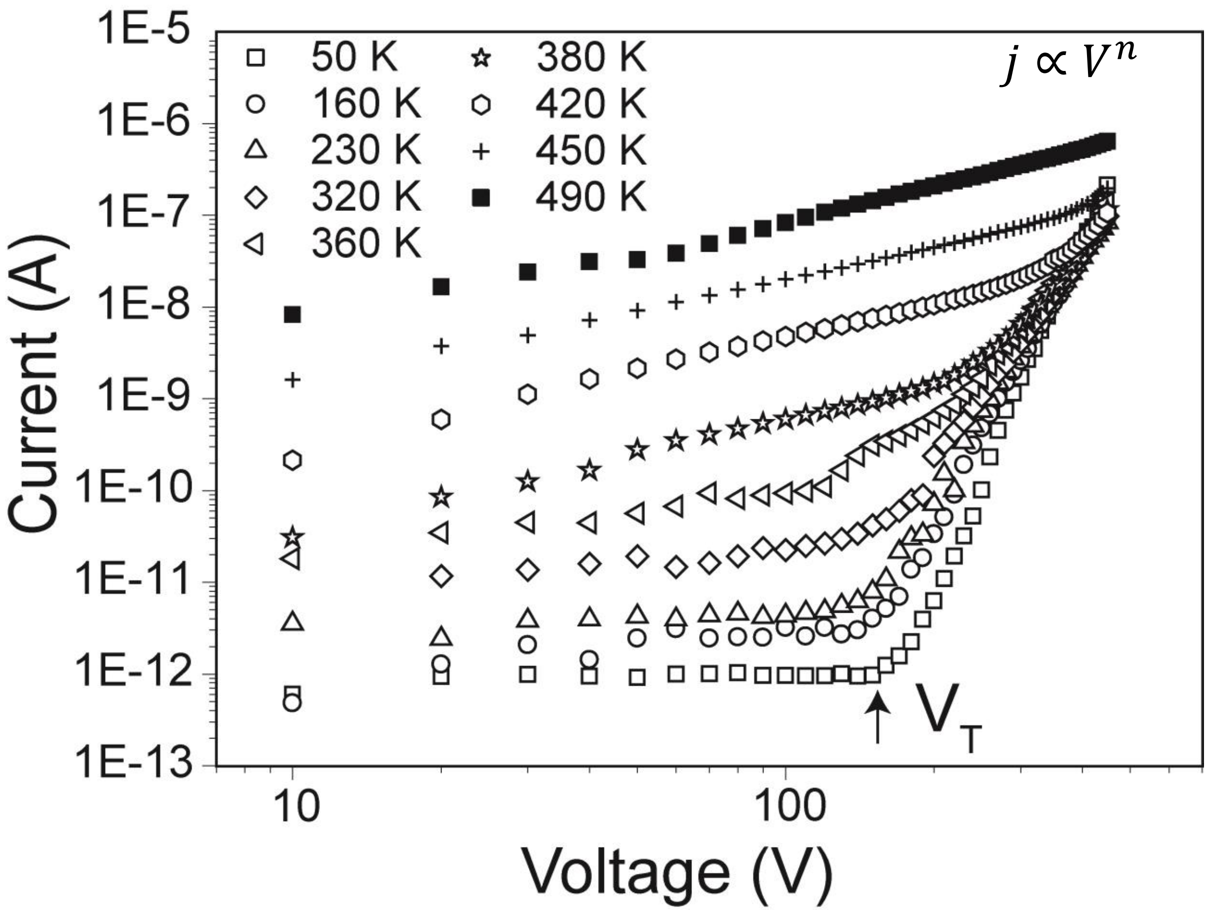




How to interpret the Electrical Data?



Current vs Voltage Characteristics



Electrical Transport in Solids. With particular reference to organic semiconductors. By K. C. Kao and W. Hwang.

$$7 \leq n \leq 9$$

σ : Width of the DOS

H_d : the trap density

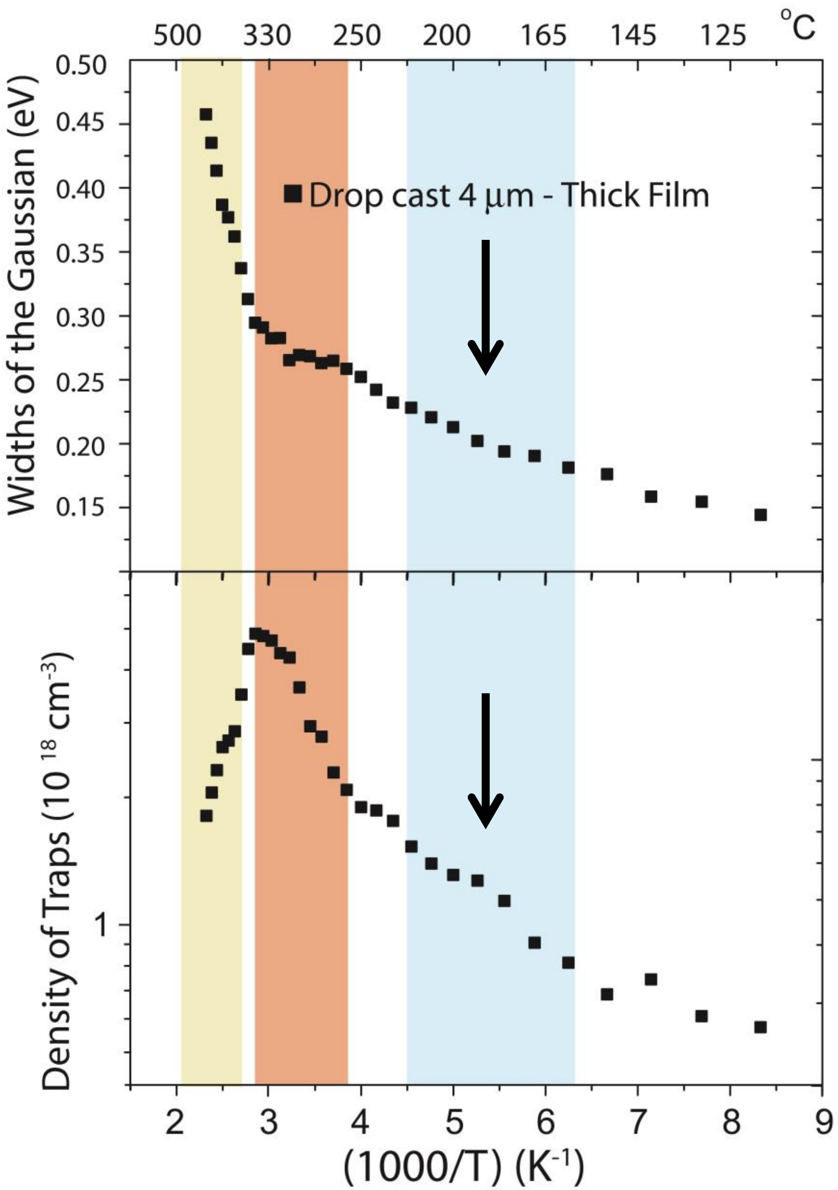
$$m = \left(1 + \frac{2\pi\sigma^2}{16k^2T^2}\right)^{1/2}$$

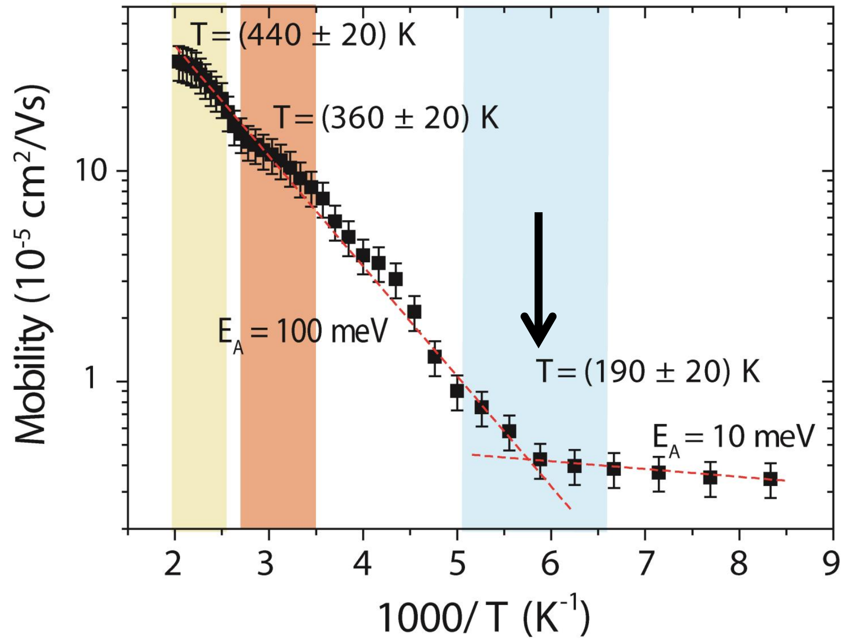
↑

The SCLC regime can be modeled quite well assuming a Gaussian distribution of traps within the forbidden band.

$$J = q^{1-m}\mu_p N_v \left(\frac{2m+1}{m+1}\right)^{m+1} \left(\frac{m}{m+1}\frac{\varepsilon\varepsilon_0}{H_d}\right)^m \frac{V^{m+1}}{L^{2m+1}}$$

Modeled Current vs Voltage

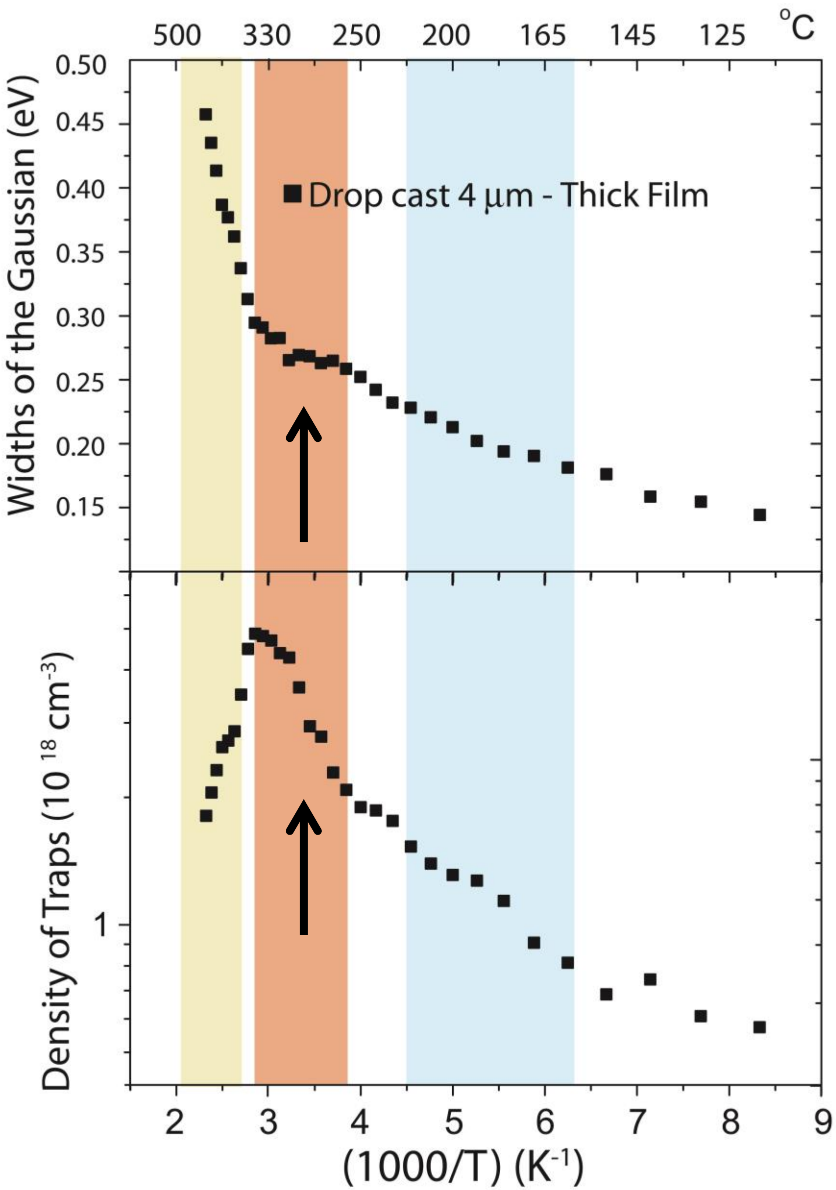


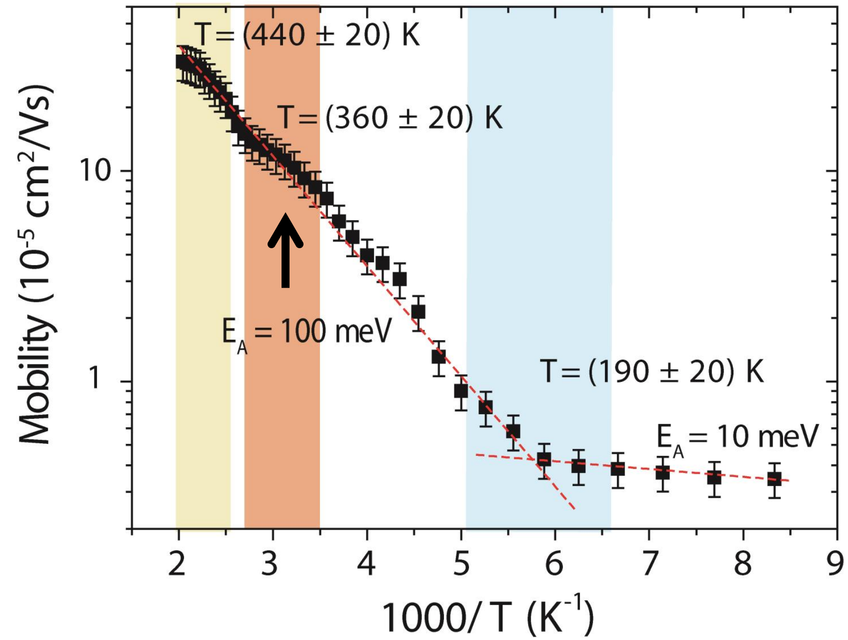


β – Relaxation: Detrapping assisted by the side chain motion!

dx.doi.org/10.1021/jp204893q | *J. Phys. Chem. C* 2011, 115, 25479–25483

Modeled Current vs Voltage

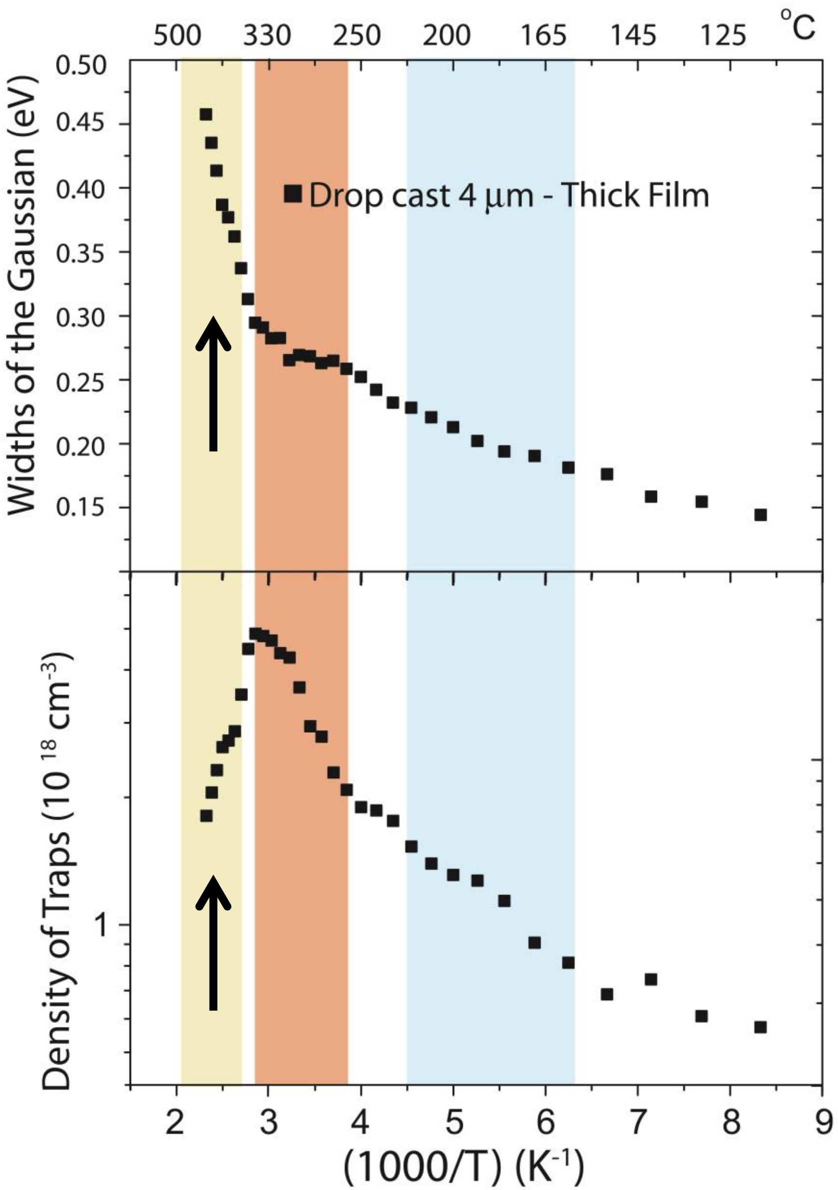


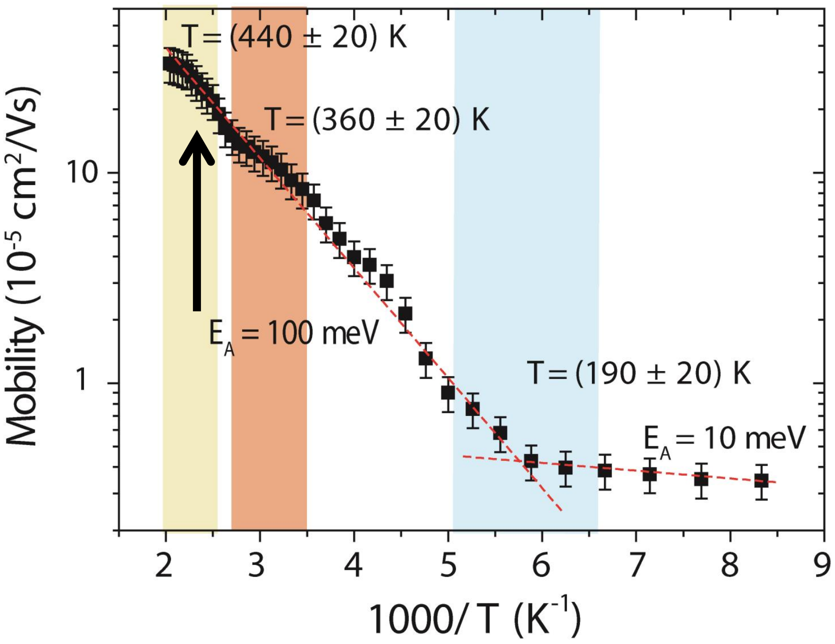


Glass transition: Plateauing of the DOS and Trap-Density increasing!

Increasing torsion of the backbone due to T_g - New trap states!

Modeled Current vs Voltage



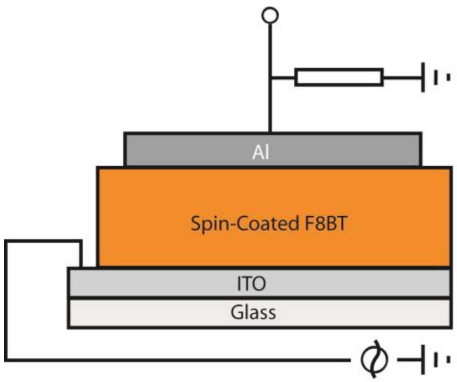


Crystal-to-Crystal: Fast broadening of the DOS' widths; and decreasing of the density of traps.

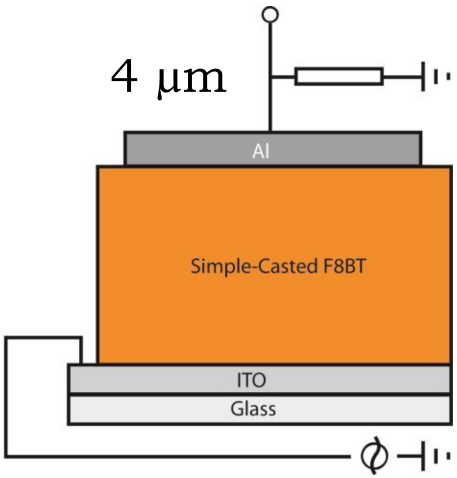
Increasing of crystalline portion: Interface crystal/amorphous broaden the DOS .

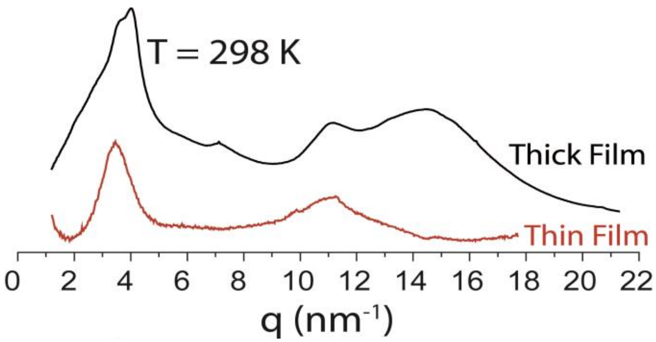
Thin vs Thick films

200 nm

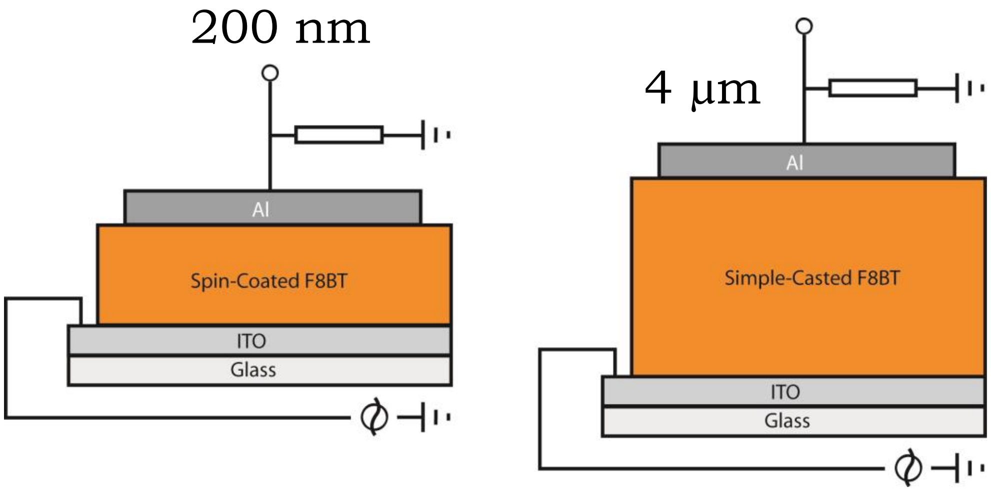


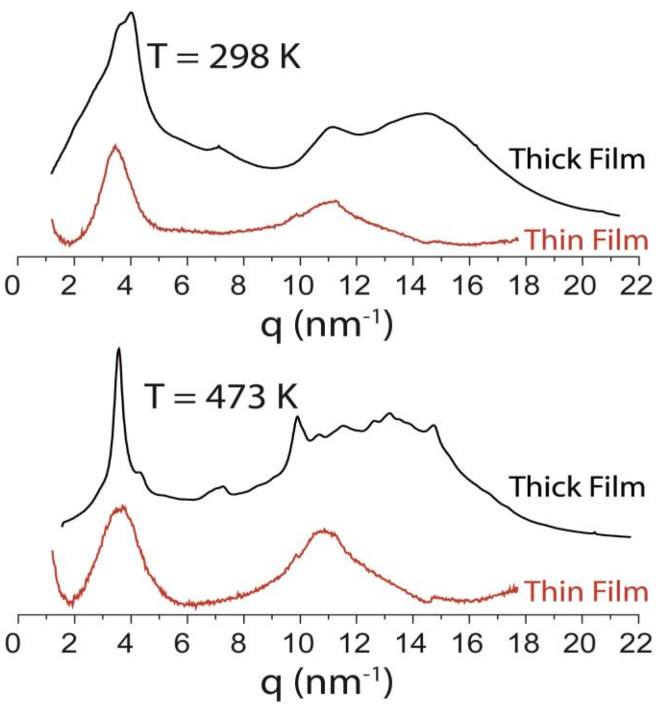
4 µm

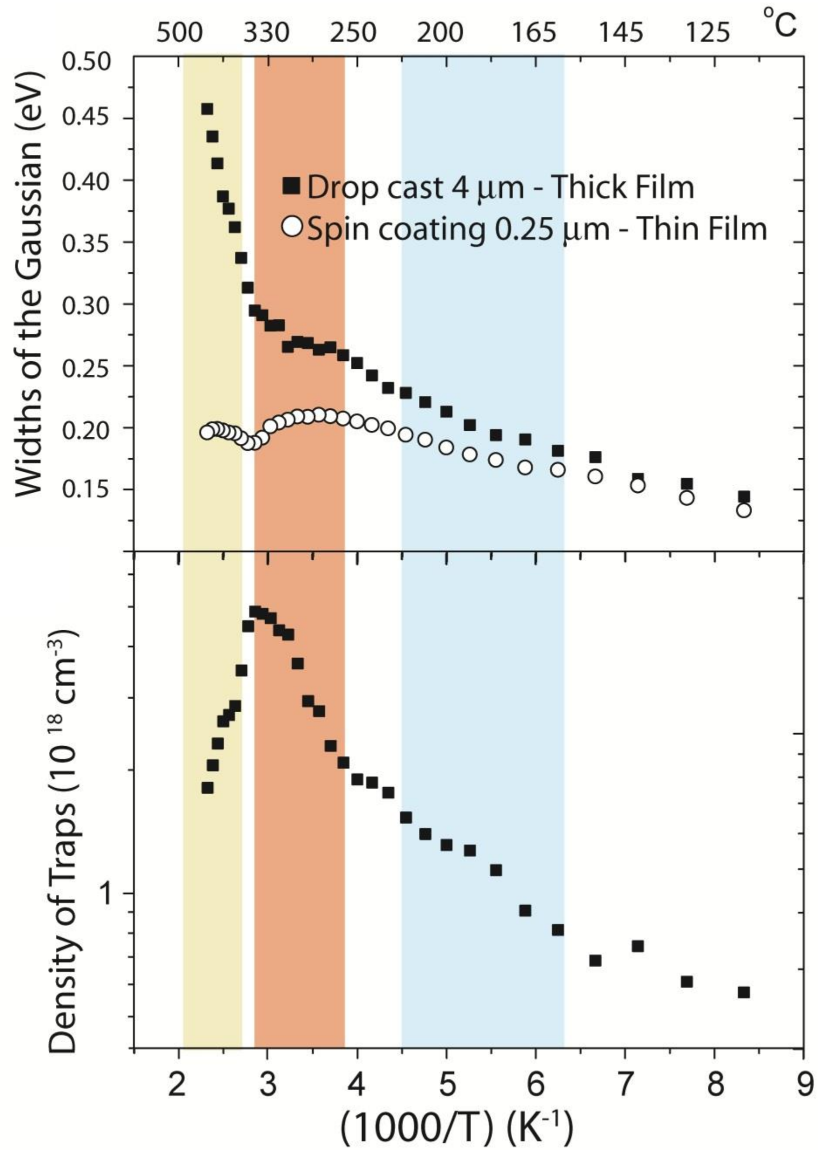




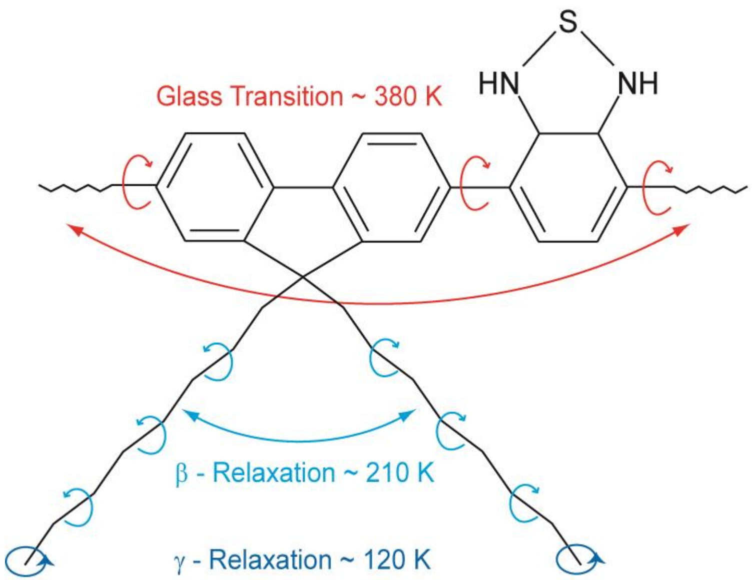
Thin vs Thick films

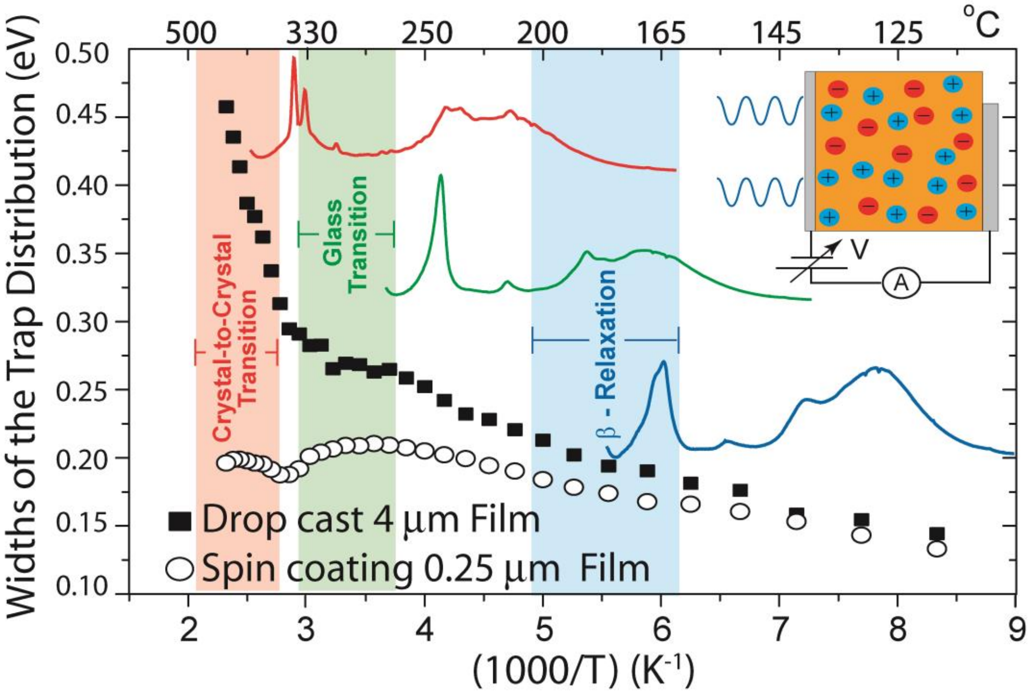






Conclusions





dx.doi.org/10.1021/jp210953m | *J. Phys. Chem. A* 2012, 116, 4285–4295

dx.doi.org/10.1021/jp204893q | *J. Phys. Chem. C* 2011, 115, 25479–25483

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