Charge Injection and Transport in Conjugated Polymers

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CNF Cornell NanoScale Science and Technology Facility

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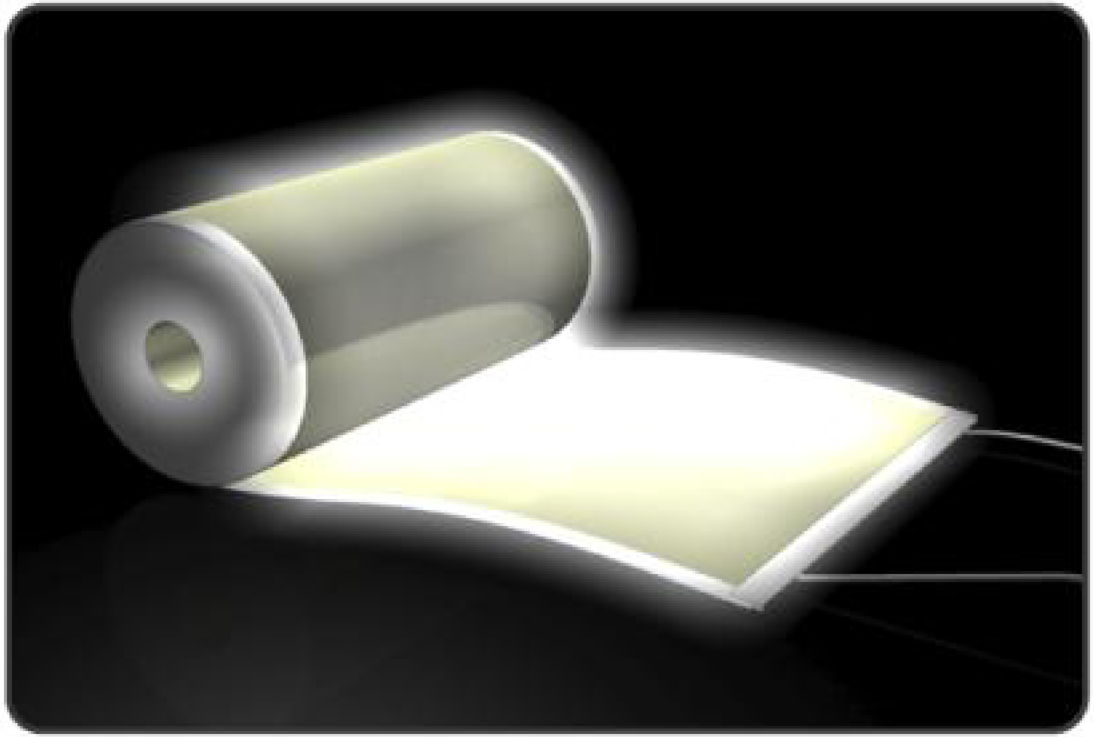
Outline

- Brief introduction to PLEDs
- Charge transport: theory and experiments
- Charge injection: theory and experiments
- Outlook

GE OLED Vision

"Lighting Wallpaper"



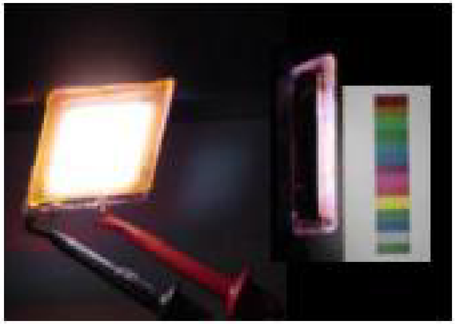
- Energy Efficient
- Low Cost
- Thin and Flexible

New design possibilities could change the way we think about lighting!

imagination at work

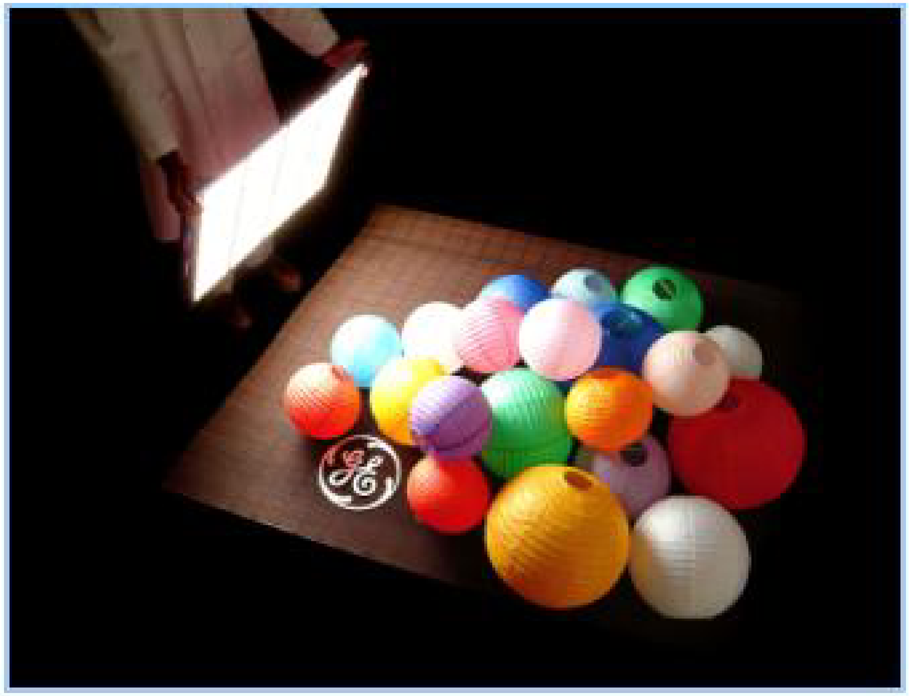
Early Progress

2001 – Illumination-Quality Light Possible



2002 – Scalable Large Area Architectures.

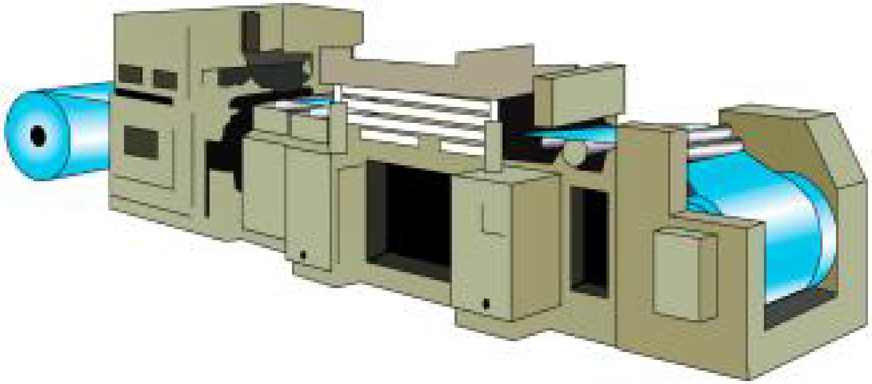
2003 – Incandescent Milestone

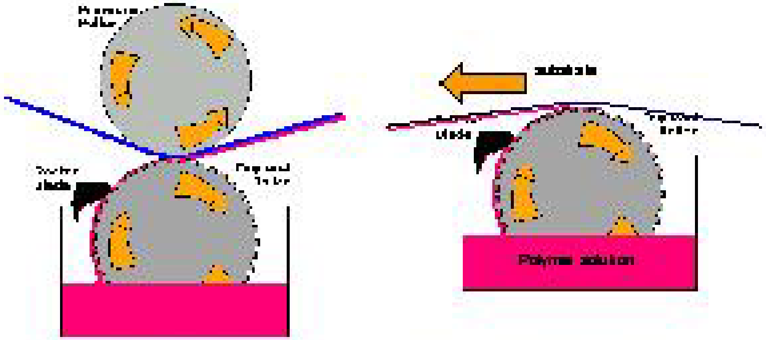


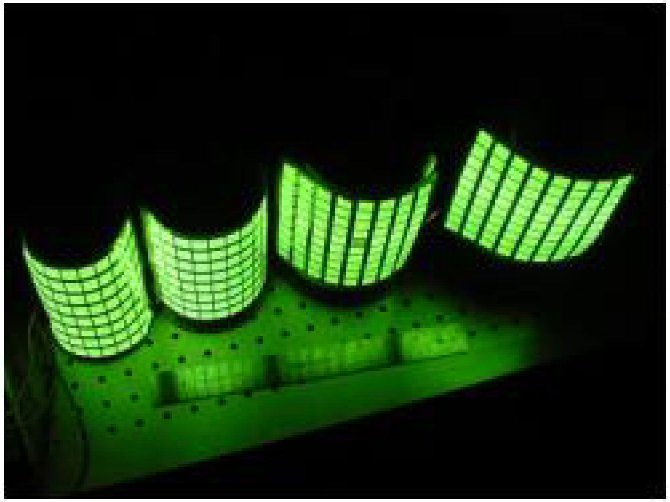
imagination at work

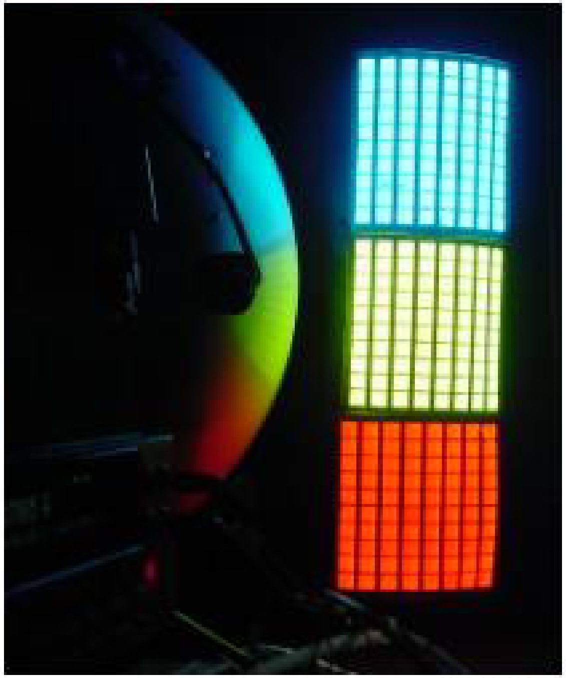
Current GE Focus

Developing Low Cost Manufacturing Infrastructure

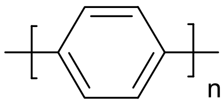




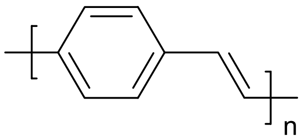




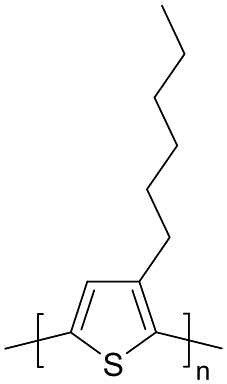
Chemical structure of conjugated polymers



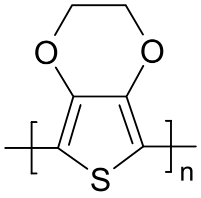
PPP



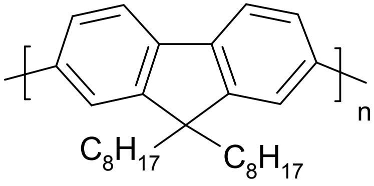
PPV



P3HT



PEDOT

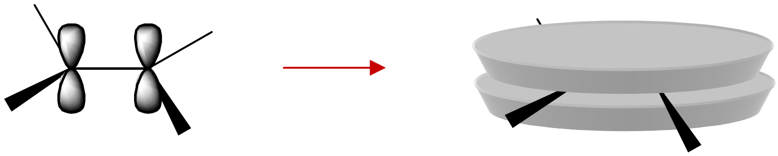


PFO

Carbon as a semiconductor

- Hybridization: sp^2 and p_Z

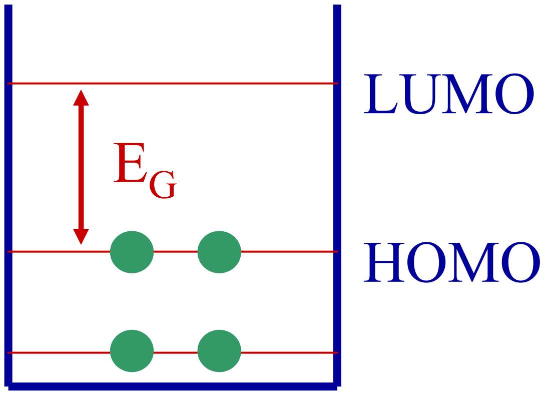
$CH_2{=}CH_2$



- Particle in a box:

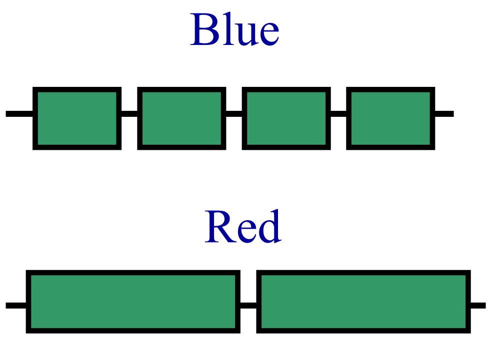
$$E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$$

$$n=1,2,3,\ldots$$



$$E_G \approx \frac{\hbar^2\pi^2}{2maN}$$

Tuning of optical properties



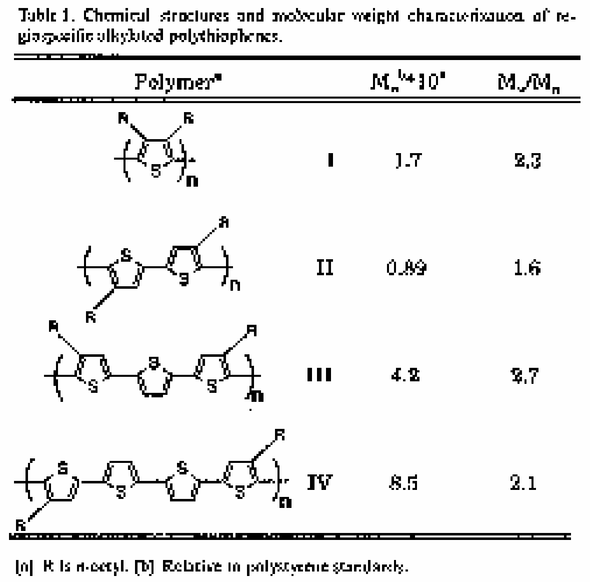
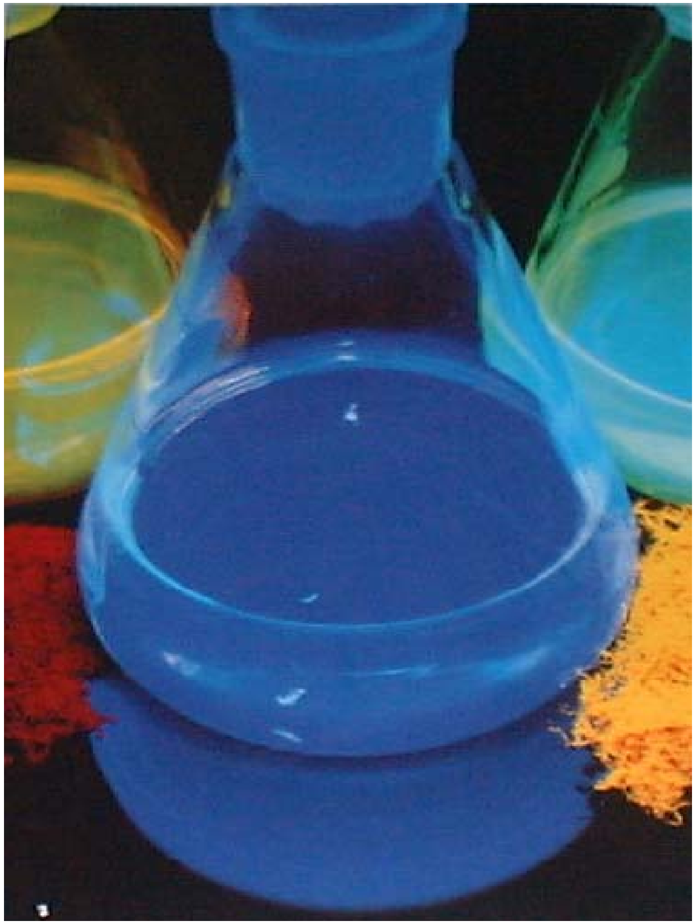


Table 1. Chemical structures and molecular weight characterization of regiospecific alkylated polythiophenes.

Polymer[a]	$M_n{}^{[b]}*10^4$	M_w/M_n
I	1.7	2.3
II	0.89	1.6
III	4.2	2.7
IV	8.5	2.1

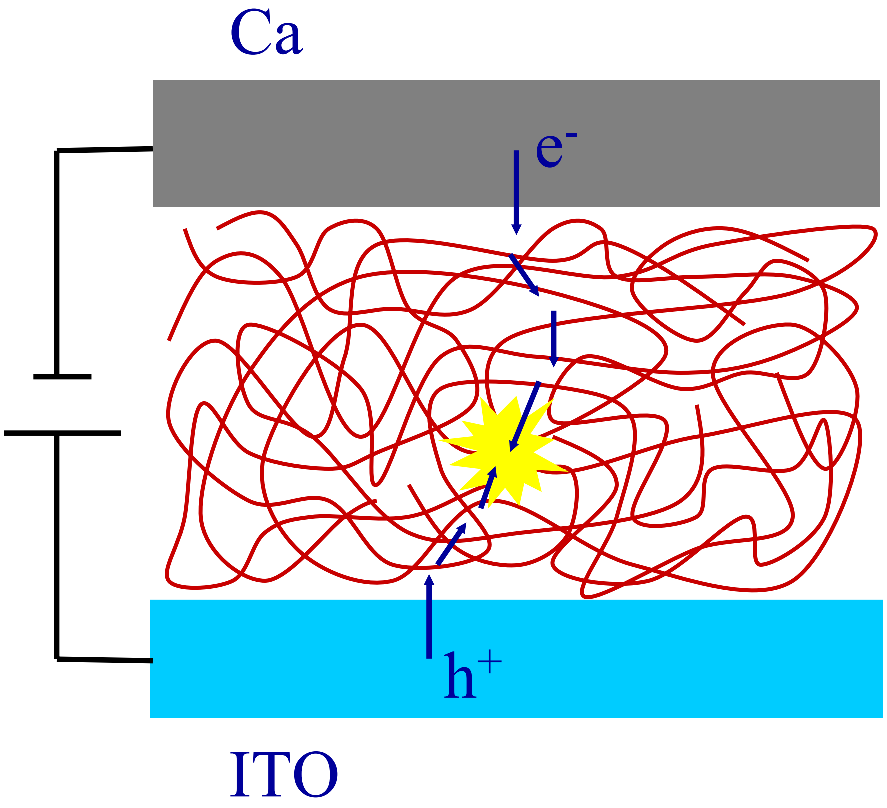
[a] R is n-octyl. [b] Relative to polystyrene standards.

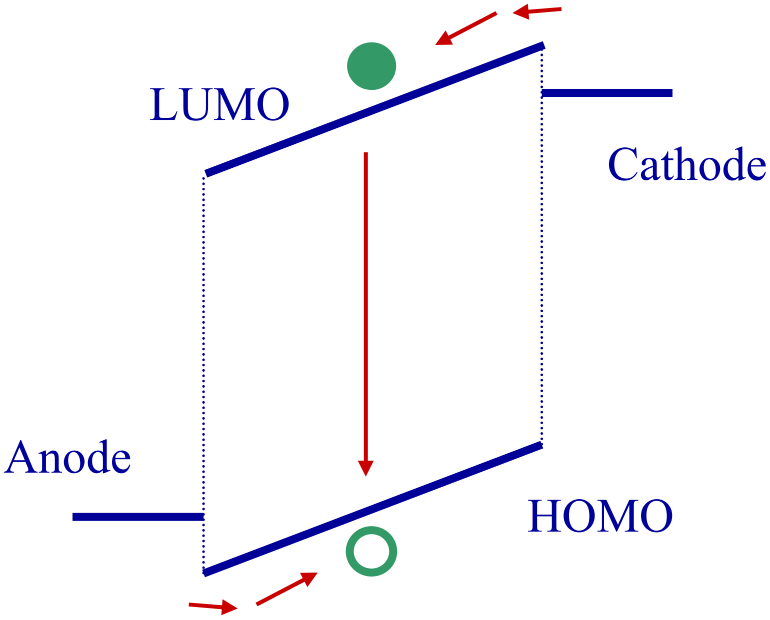
R.E. Gill *et. al.*, *Adv. Mater.* **6**, 132 (1994).



Covion

PLED structure and operation





Electroluminescence: charge injection, charge transport, recombination

Outline

- Brief introduction to PLEDs
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- Charge injection: theory and experiments
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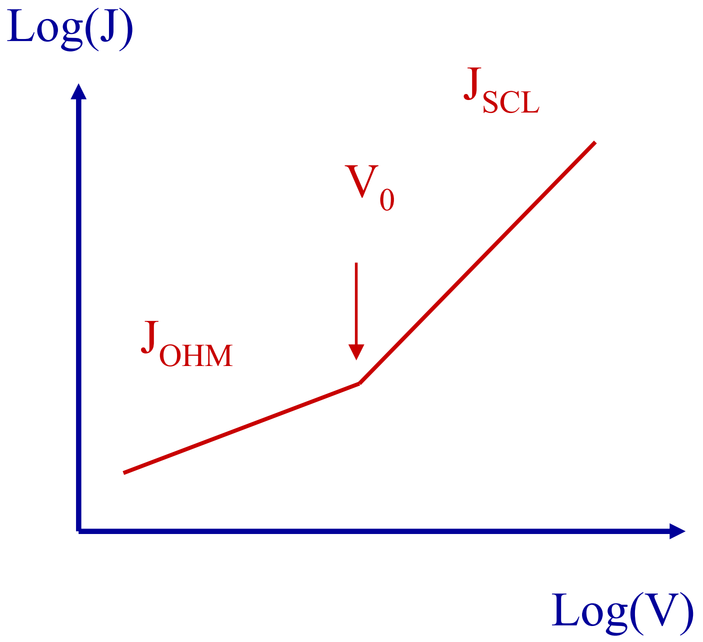
Hierarchy of transport models

$$J = e \cdot n \cdot \mu \cdot E + e \cdot D \cdot dn/dx$$

First order correction:	
Space charge effects	$J = (9/8) \cdot \varepsilon \cdot \varepsilon_0 \cdot \mu \cdot V^2/L^3$
Disorder:	
Energetics	Localized states
Influence on mobility	$\mu=\mu(E,T)$
Manifold filling:	
Charge density dependence of mobility	$\mu=\mu(n)$
Charge generation:	
Electric field dependence of charge density	$n=n(E)$

Space charge effects

$V_0 = (8/9)\cdot e\cdot N_0\cdot L^2/\varepsilon\cdot\varepsilon_0$



Low voltages: Ohm's law

$J_{OHM} = e\cdot N_0\cdot\mu\cdot V/L$

High voltages: Space charge limited current

$J_{SCL} = (9/8)\cdot\varepsilon\cdot\varepsilon_0\cdot\mu\cdot V^2/L^3$

Lampert and Mark, *Current Injection in Solids* (Academic Press,1970).

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Energetics of semiconductors

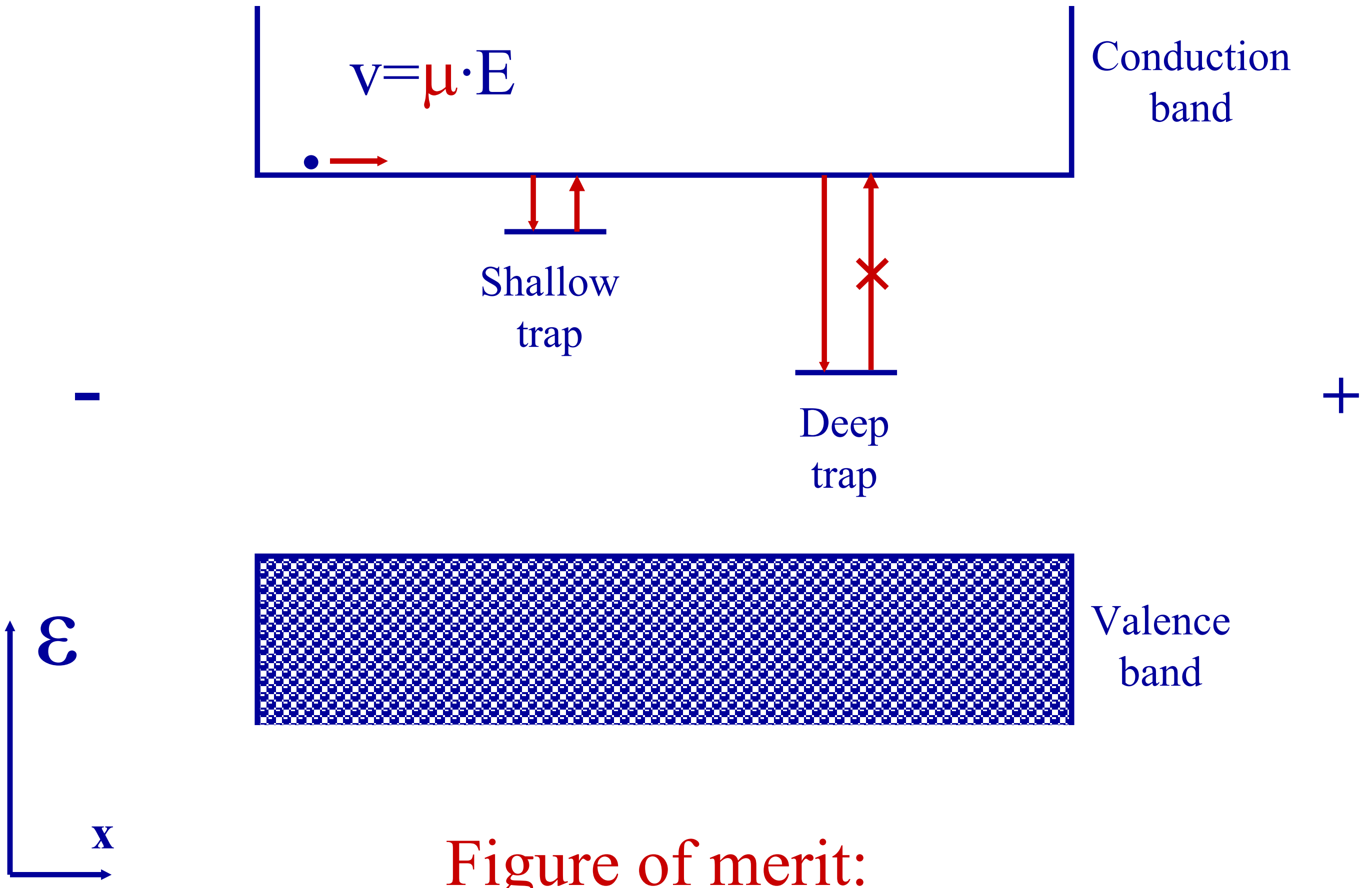

Figure of merit:
mobility, μ ($cm^2/V \cdot sec$)

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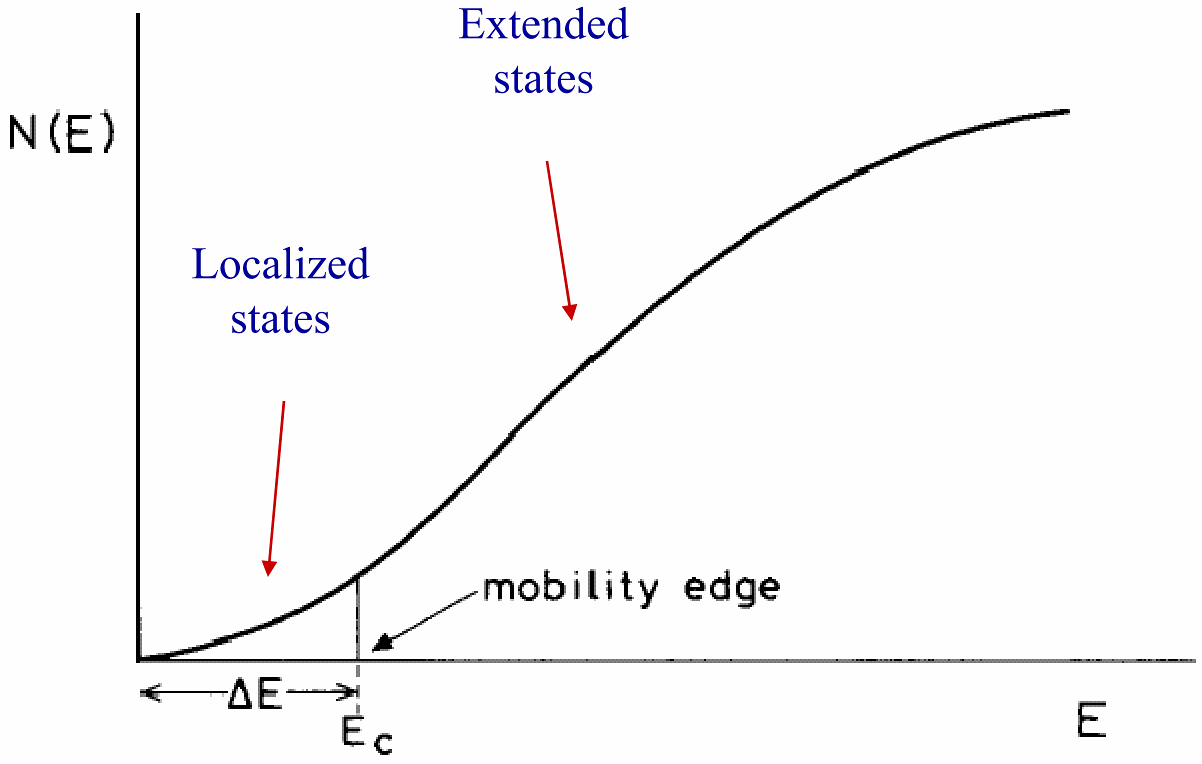
Energetics of amorphous semiconductors



N. Mott, *Nobel Lecture* (1977)

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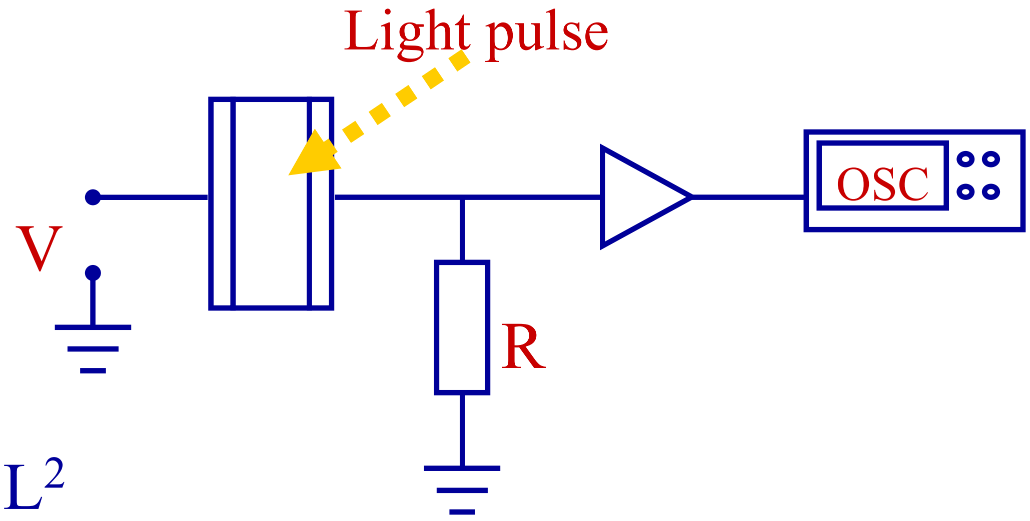
Time-of-flight (TOF)



$$\mu = \frac{L^2}{t_{TR} \cdot V}$$

P. M. Borsenberger, D. S. Weiss, *Organic photoreceptors for Xerography* (Marcel Decker, Inc., New York, 1998).

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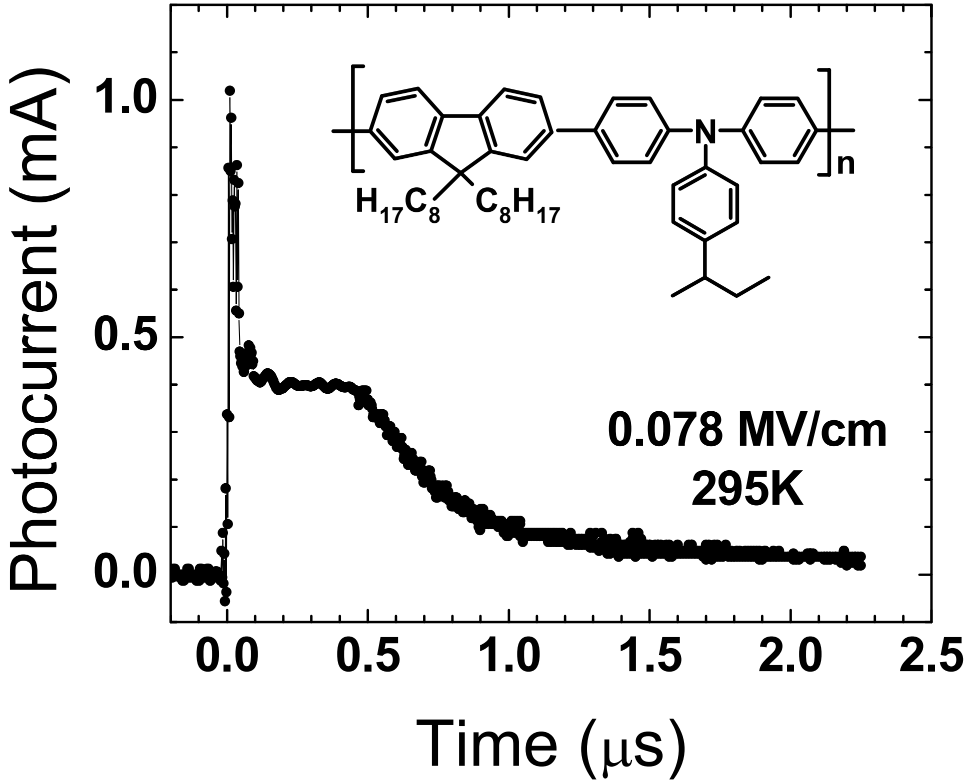
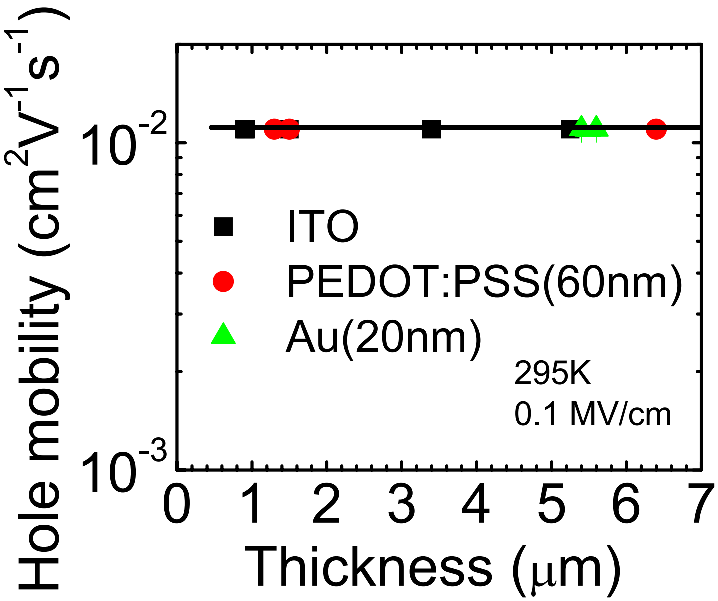
Non-dispersive hole transport in TFB

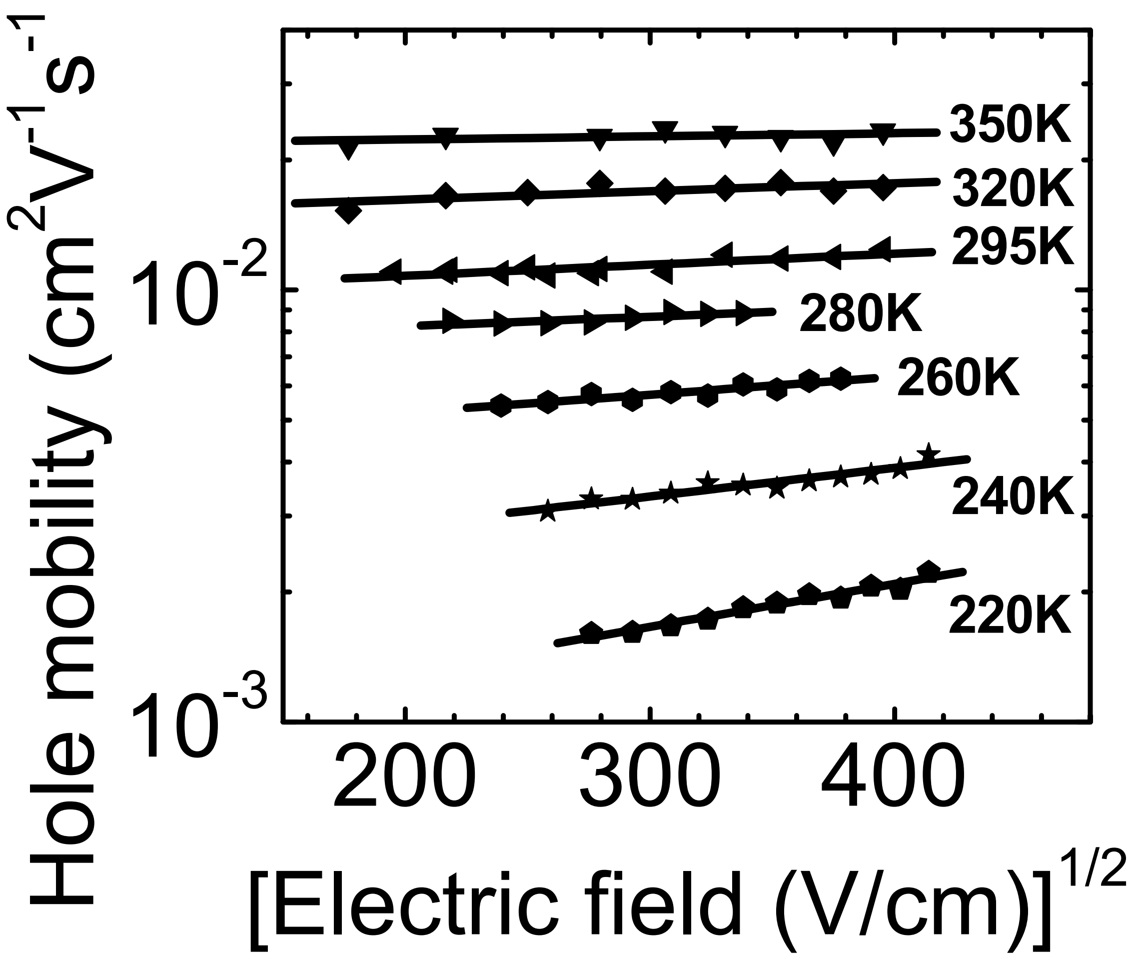
ITO/PEDOT:PSS(CH8000)/TFB(6.4μm)/Al





H.H. Fong, A. Papadimitratos, and G.G. Malliaras, *Appl. Phys. Lett.* **89**, 172116 (2006).

Electric field dependence of mobility



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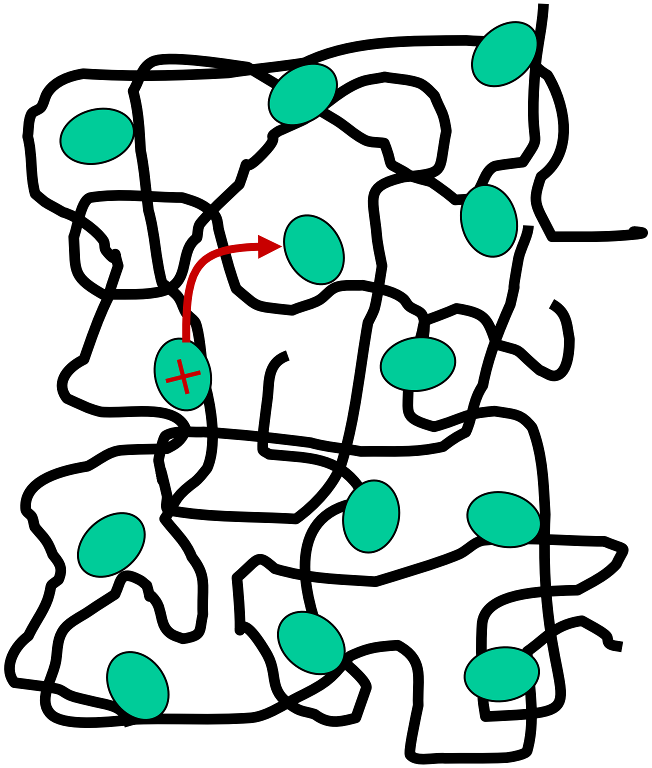
Molecularly dispersed polymers



Solid solutions of conjugated molecules in inert host

Hopping sites are well-defined

Control over the average distance between hopping sites

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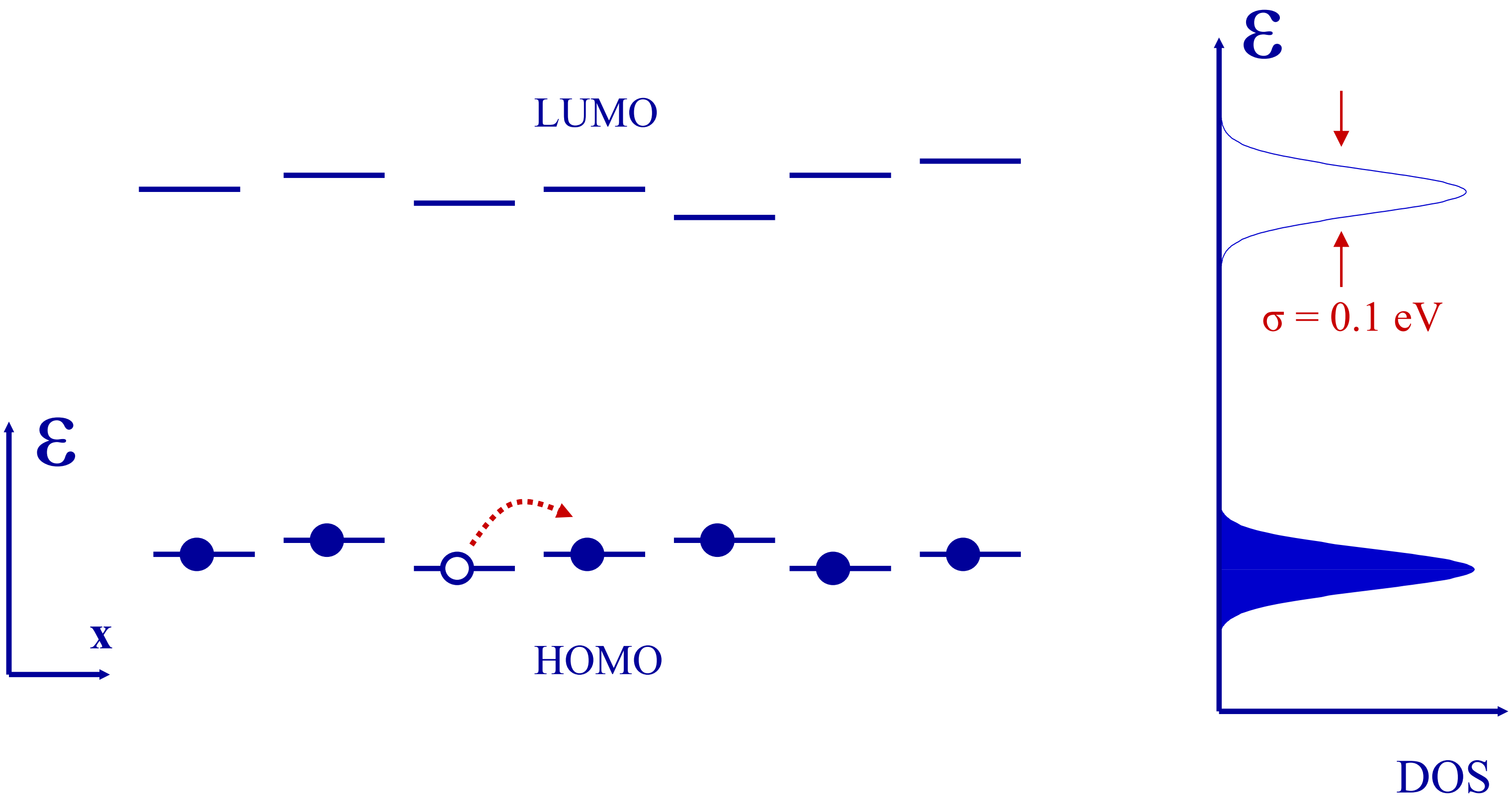
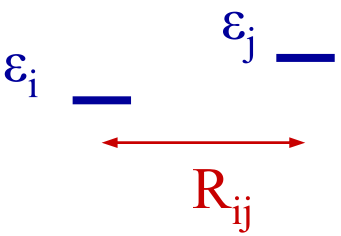
Gaussian disorder model



- Energetic disorder
- Positional disorder

Gaussian disorder model (II)

Density of states:



$$\mathrm{DOS}(\varepsilon) = (2\cdot\pi\cdot\sigma^2)^{-0.5}\cdot exp[-(\varepsilon^2/2\sigma^2)]$$

Hopping rate:

$$\nu_{ij} = \nu_0\cdot exp\text{-}(2\cdot\gamma\cdot a\cdot\Delta R_{ij}/R_{ij})\cdot \begin{cases} exp[-(\varepsilon_j-\varepsilon_i)/kT] & ;\ \varepsilon_j>\varepsilon_i \\ 1 & ;\ \varepsilon_j>\varepsilon_i \end{cases}$$

Mobility:

$$\mu=\mu_0\cdot exp[-(2\sigma/3kT)^2]\cdot exp\{C\cdot[(\sigma/kT)^2-\Sigma^2]\ \cdot E^{0.5}\}$$

H. Bässler, *Phys. Stat. Sol. (b)* **175**, 15 (1993).

Gaussian disorder model (III)

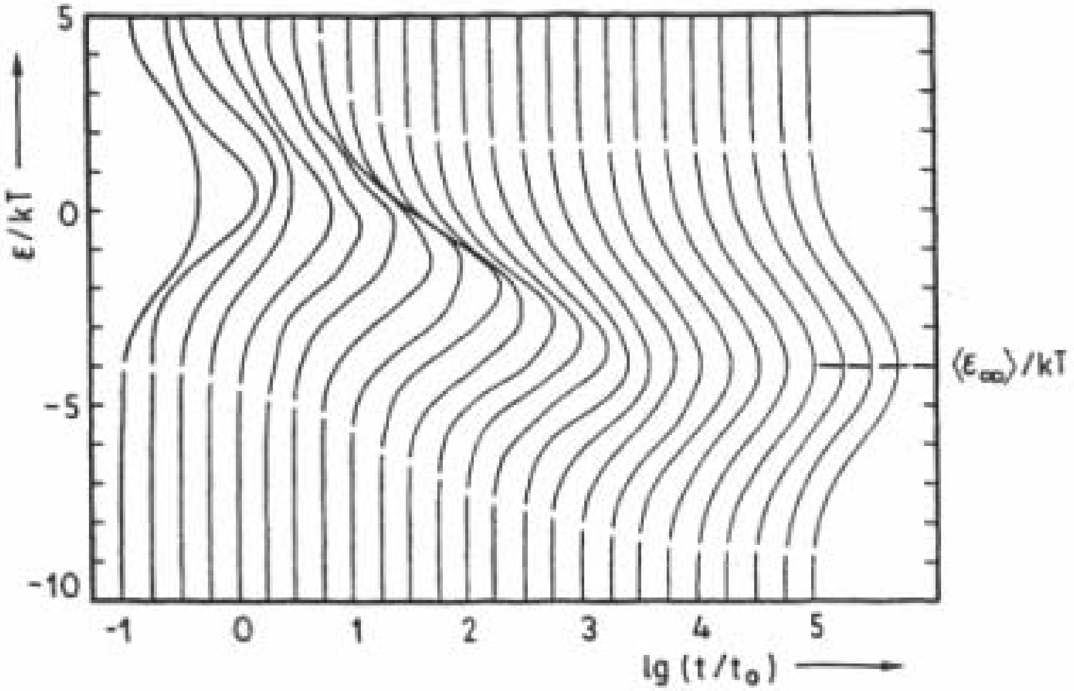


Fig. 2. Temporal evolution of the distribution of carrier energies in a Gaussian DOS of width $\hat{\sigma} = 2$. All profiles are broken at the same carrier density illustrating the different relaxation patterns for mobile and immobile carriers. ε_∞ denotes the theoretical mean energy in the long-time limit

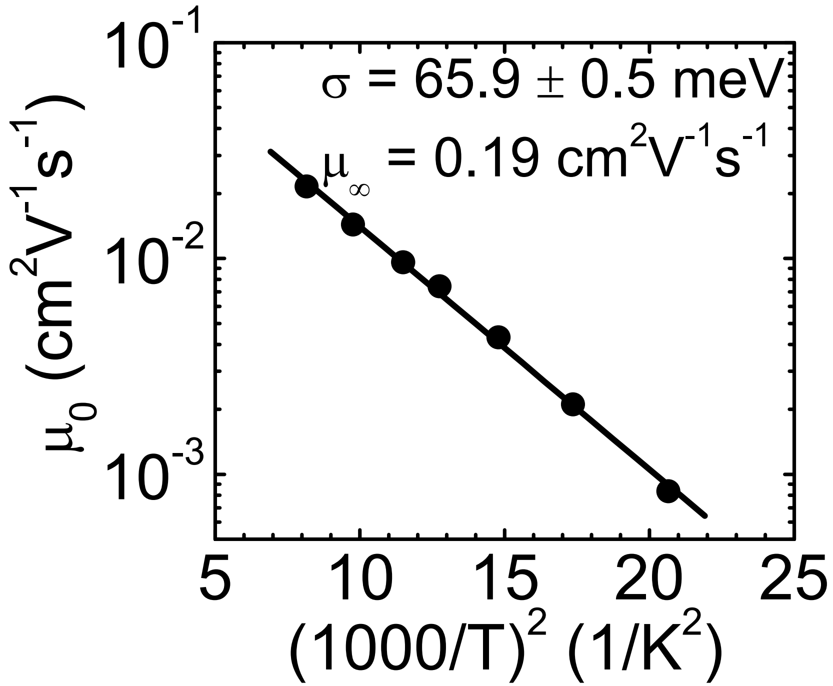
Carriers relax at:

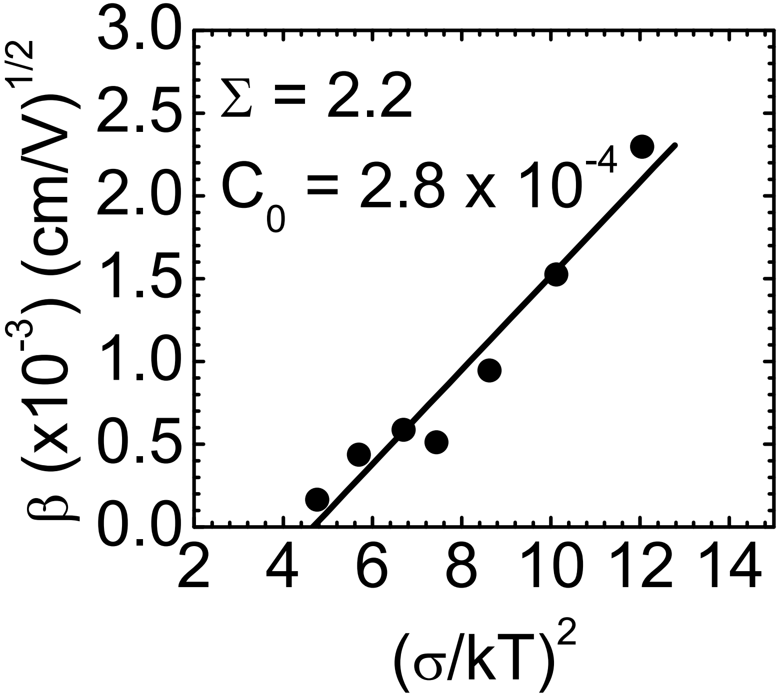
σ^2/kT

$\mu \sim exp[-(\sigma/kT)^2]$

H. Bässler, *Phys. Stat. Sol. (b)* **175**, 15 (1993).

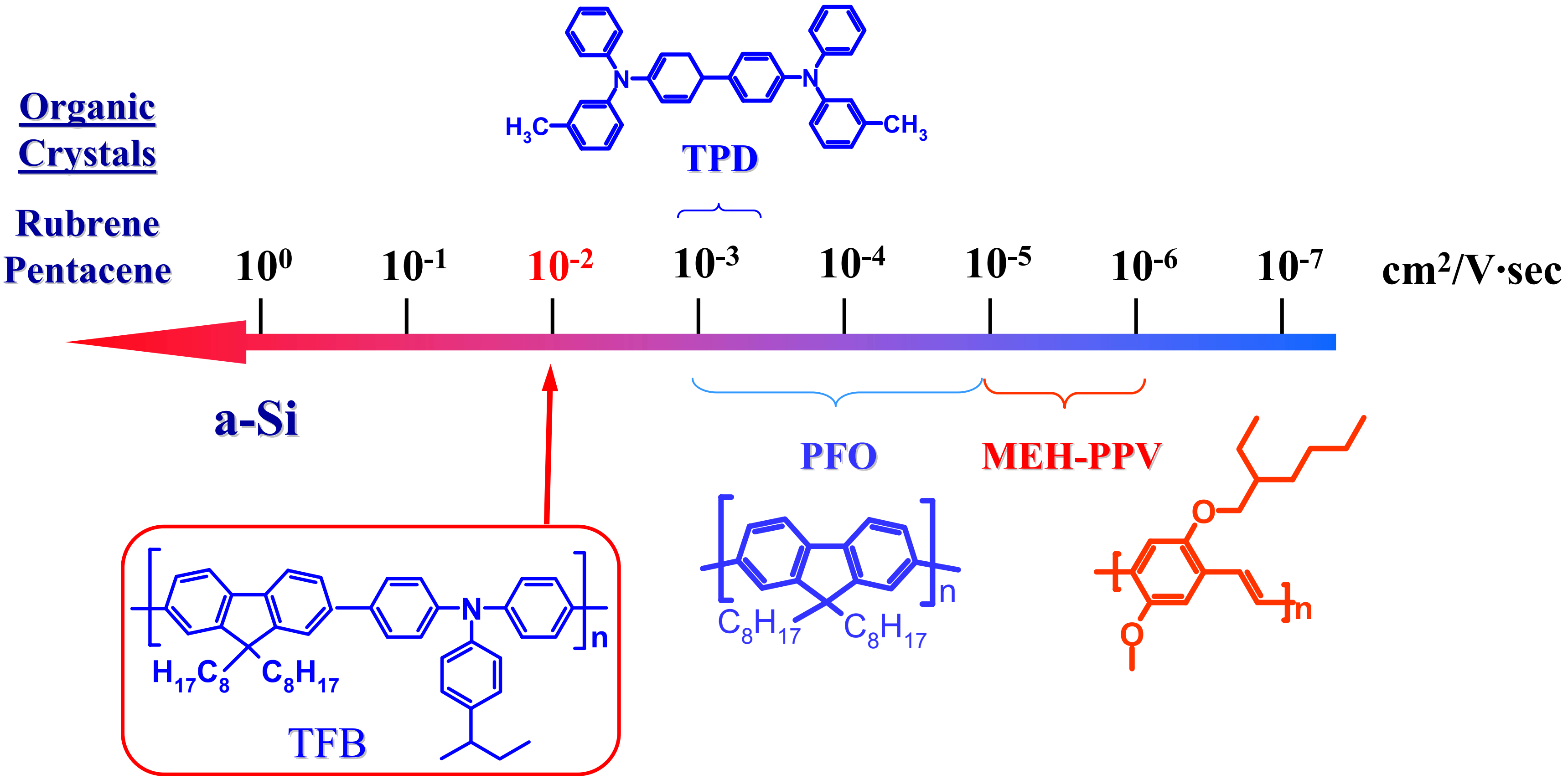
Electric field dependence of mobility (II)





$\mu=\mu_0\cdot exp[-(2\sigma/3kT)^2]\cdot exp\{C\cdot[(\sigma/kT)^2-\Sigma^2]\cdot E^{0.5}\}$

High mobility in conjugated polymers



Organic Crystals

Rubrene
Pentacene

10^0 **10^{-1}** **10^{-2}** **10^{-3}** **10^{-4}** **10^{-5}** **10^{-6}** **10^{-7}** **$cm^2/V\cdot sec$**

a-Si

TPD

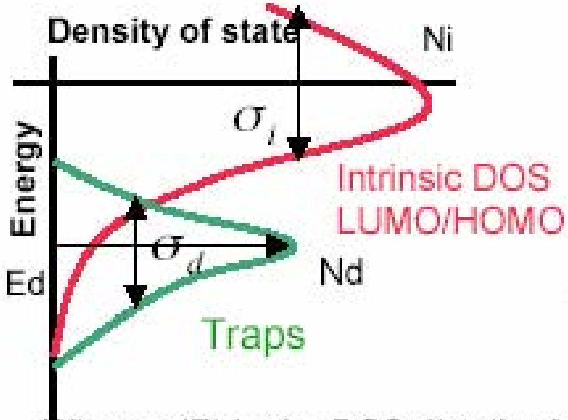
PFO

MEH-PPV

TFB

Physical Models for Analysis of Electrical Characteristics for Organic Devices

- Hopping Model
  - Effective Transport Energy
    - The effective carrier transport energy (Etr) is calculated from[1,2]:



$$\int_{-\infty}^{E_{tr}} g(E)(E_{tr} - E)^3 \, dE = \frac{6\beta}{\pi}(\gamma kT)^3$$

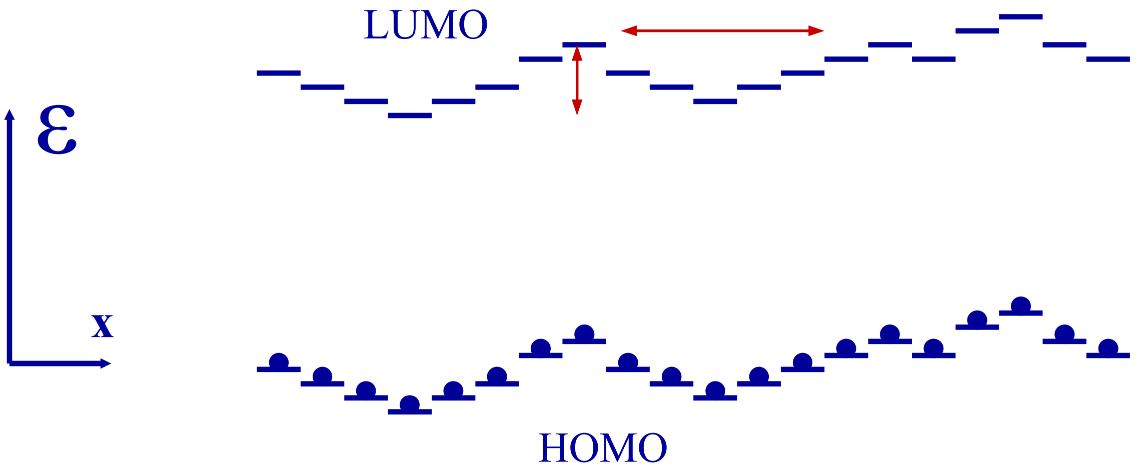
$$g(E) = \frac{N_i}{\sqrt{2\pi}\sigma_i}\exp\left(\frac{-E^2}{2\sigma_i^2}\right) + \frac{N_d}{\sqrt{2\pi}\sigma_d}\exp\left(\frac{-(E+E_d)^2}{2\sigma_d^2}\right)$$

Where g(E) is the DOS distribution, N_i is the total intrinsic state density, N_d is the total dopant state density, σ_i is the intrinsic Gaussian DOS width, s_d is the dopant Gaussian DOS width, E_d is the energy shift, γ is 1/carrier localization radius, β is the percolation constant, E is the band energy, k is Boltzmann's constant and T is the lattice temperature

[1] "Charge carrier mobility in doped disordered organic semiconductors" - V.I. Arkhipov, P. Heremans, E.V. Emelianova, G.J. Adriaenssens, H. Bassler, Journal of Non-Crystalline Solids, 338-340, pp 603-603, 2004.

[2] "Charge carrier mobility in doped semiconducting polymers" - V.I. Arkhipov, P. Heremans, E.V. Emelianova, G.J. Adriaenssens, H. Bassler, Applied Physics Letters, Vol. 82, No. 19, pp 3245-3247, 2003.

Correlated disorder model

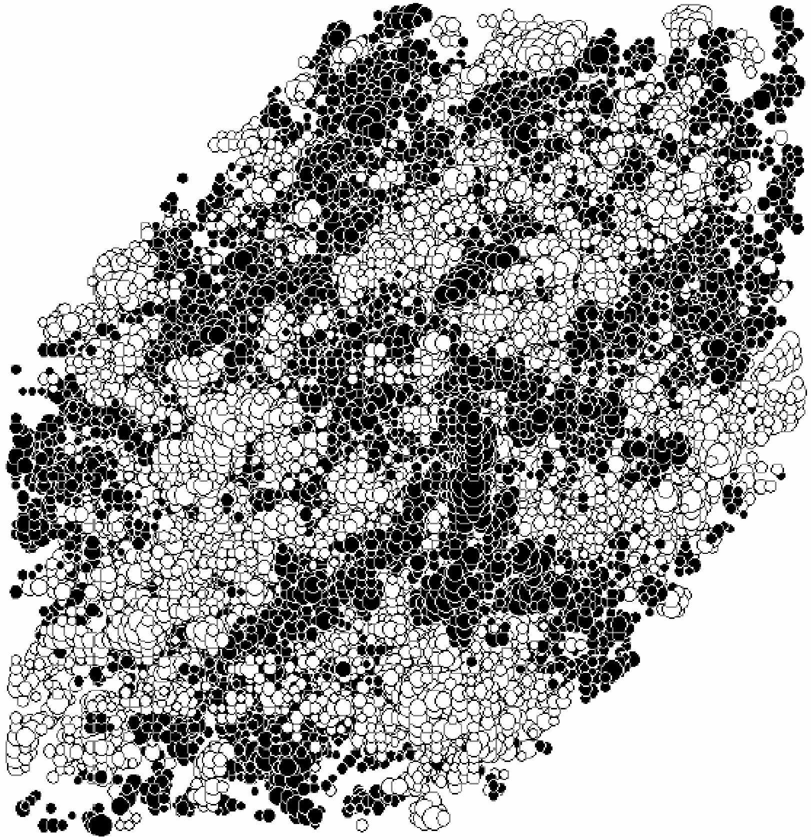


Deeper valleys are also wider.

$$\mu=\mu_0\cdot exp[-(\sigma/kT)^2 + 2\cdot(\sigma/kT)\cdot(e\cdot a\cdot E/kT)^{0.5}]$$

D.H. Dunlap, P.E. Parris and V.E. Kenkre, *Phys. Rev. Lett.* **77**, 542 (1996).

Correlated disorder model (II)



Black/white:
sites with energy
above/below the
mean.

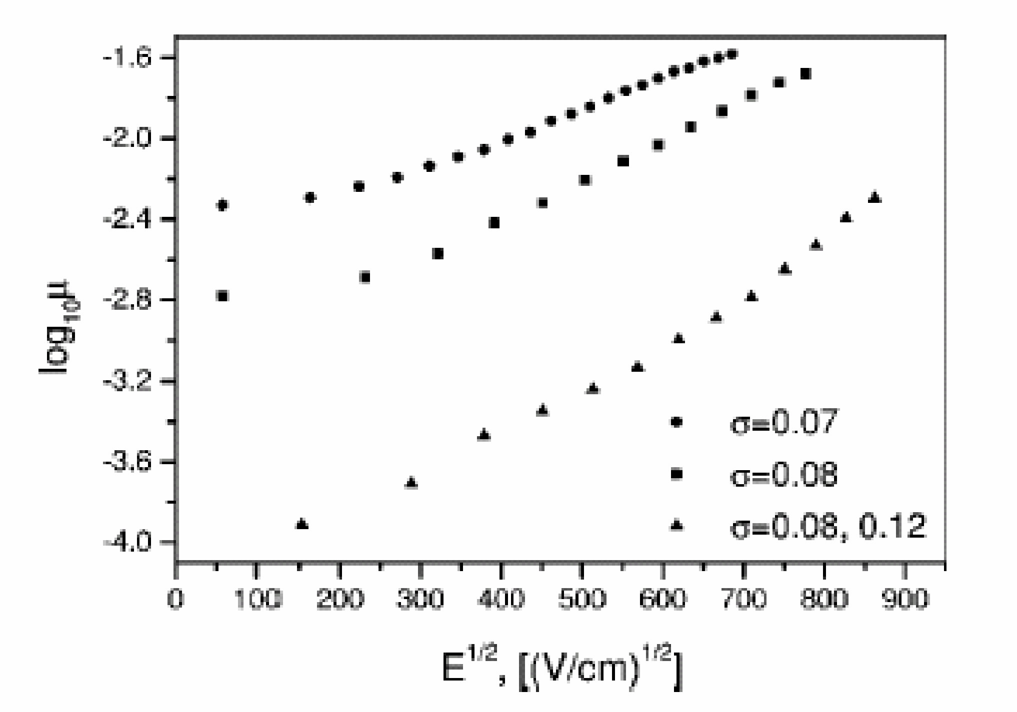
S.V. Novikov, *J. Polym. Sci. Part B: Polym. Phys.* **41**, 2584 (2003).

Correlated disorder in polymers

Correlations in site energy arise from fluctuations in:

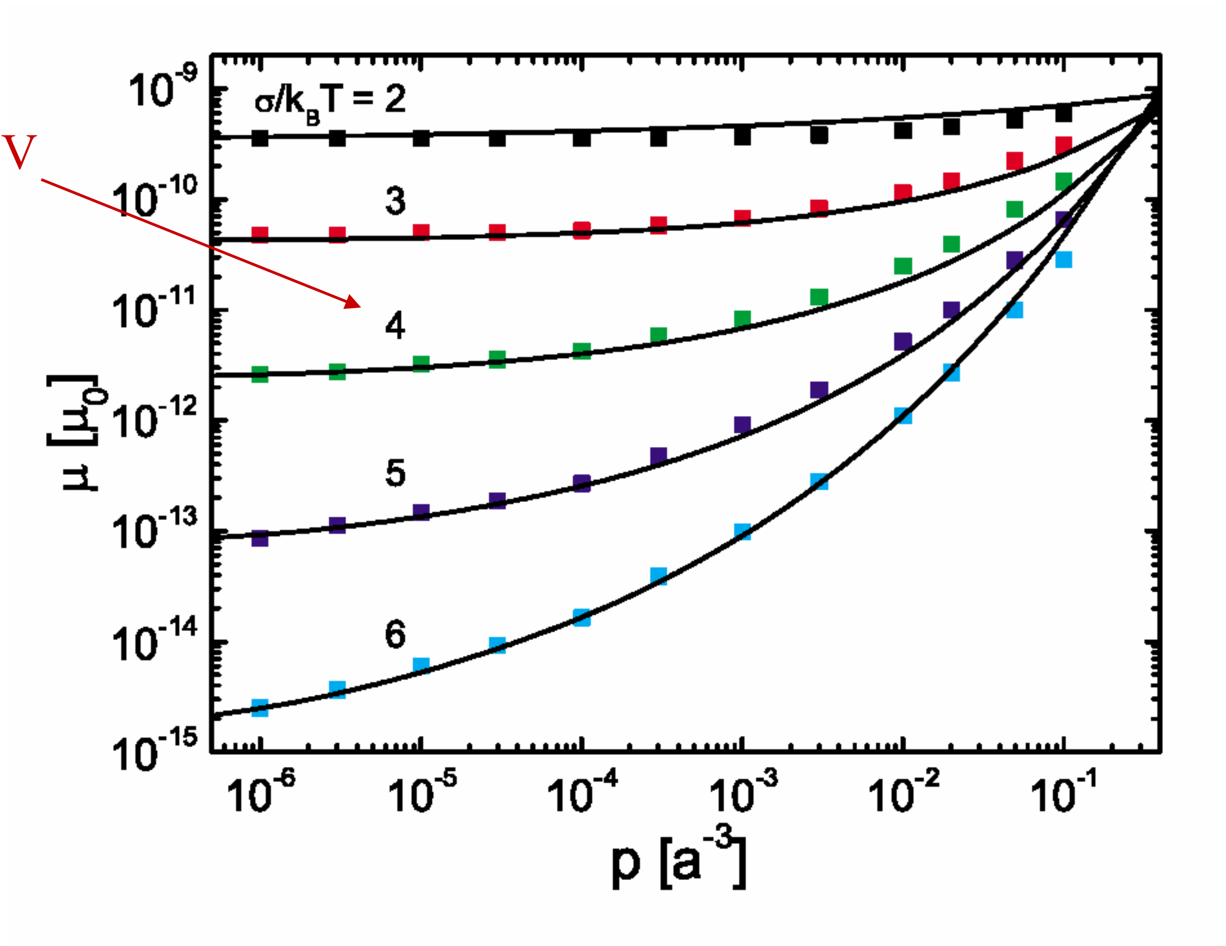
-Conjugation length

-Density



S.V. Rakhamanova and E.M. Conwell, *Appl.Phys. Lett.* **76**, 3822 (2000).

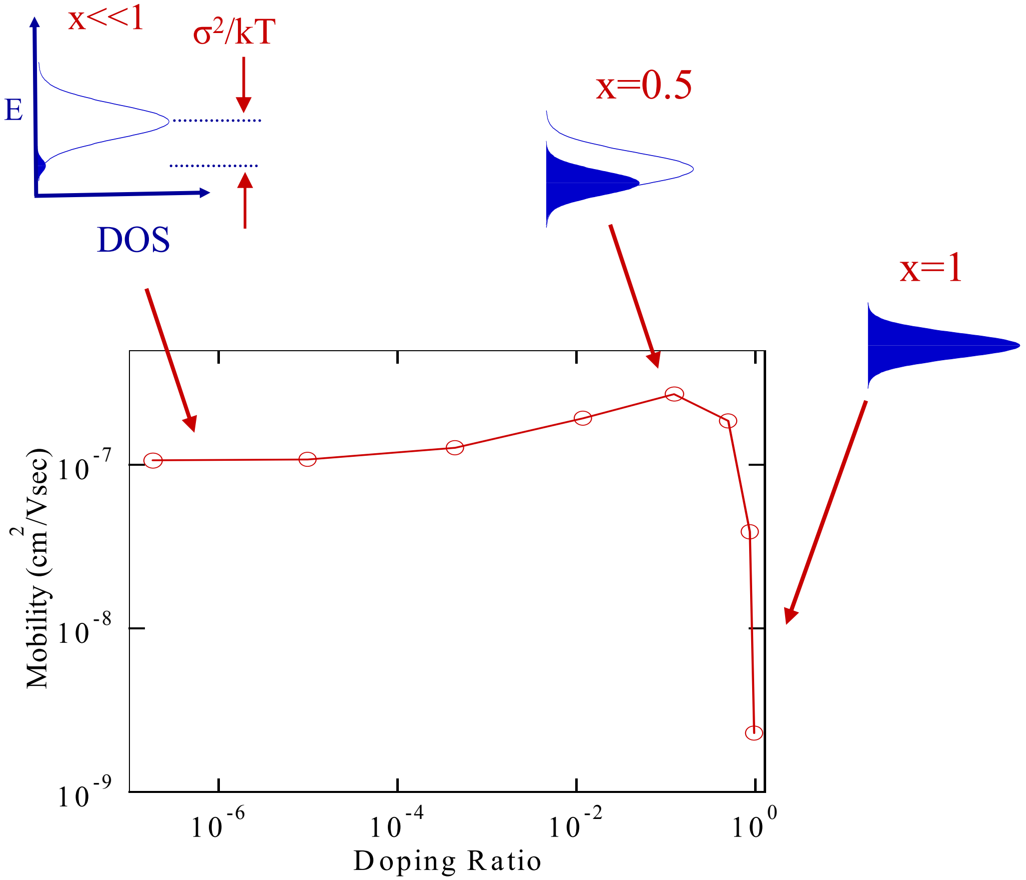
Mobility vs. change density

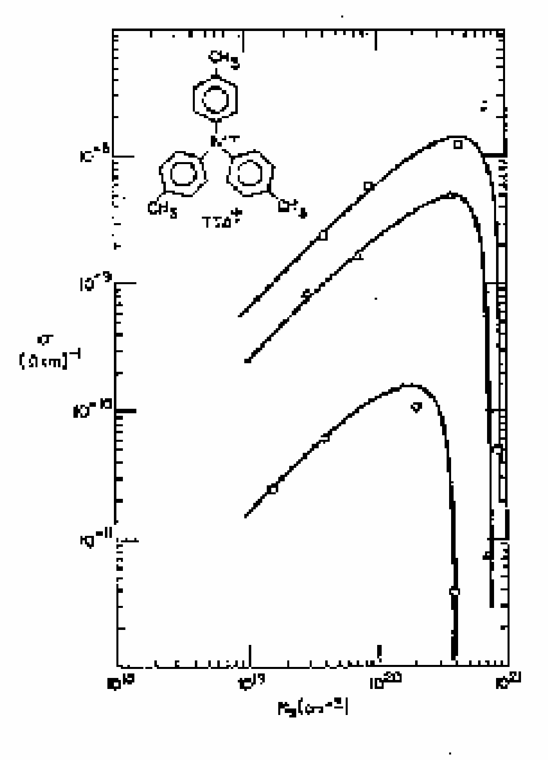


σ=0.1eV

W.F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P.A. Bobbert, P.W.M. Blom, D.M. de Leeuw, and M.A.J. Michels, *Phys. Rev. Lett.* **94**, 206601 (2005).

Manifold filling

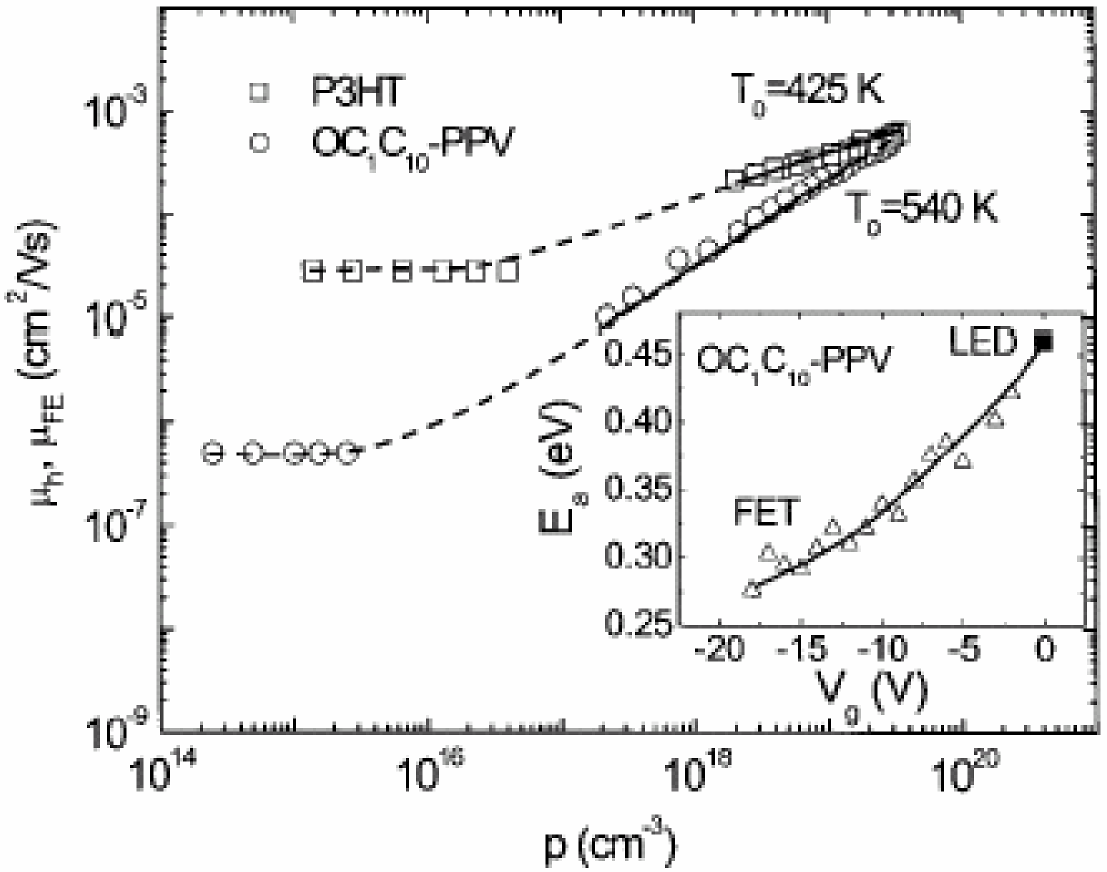




A. Troup *et al.*, *J. Non-Crystalline Solids* **35**, 151 (1980).

Y. Shen, K. Diest, M.H. Wong, B.R. Hsieh, D.H. Dunlap, and G.G. Malliaras, *Phys. Rev. B.* **68**, 81204(R) (2003).

Mobility vs. charge density (II)

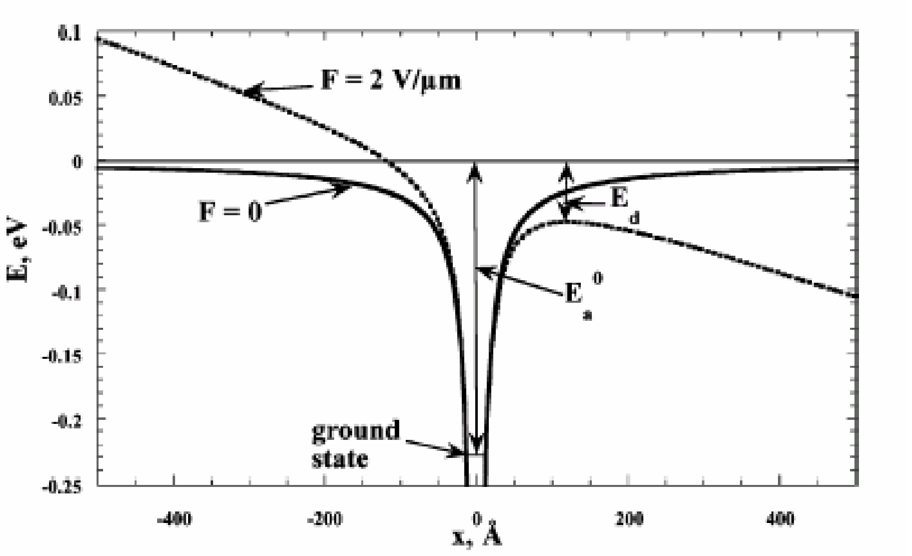


C. Tanase, E.J. Meijer, P.W.M. Blom, and D.M. de Leeuw, *Phys. Rev. Lett.* **91**, 216601 (2003).

Charge density vs. electric field

Field ionization of impurities leads to n=n(E)

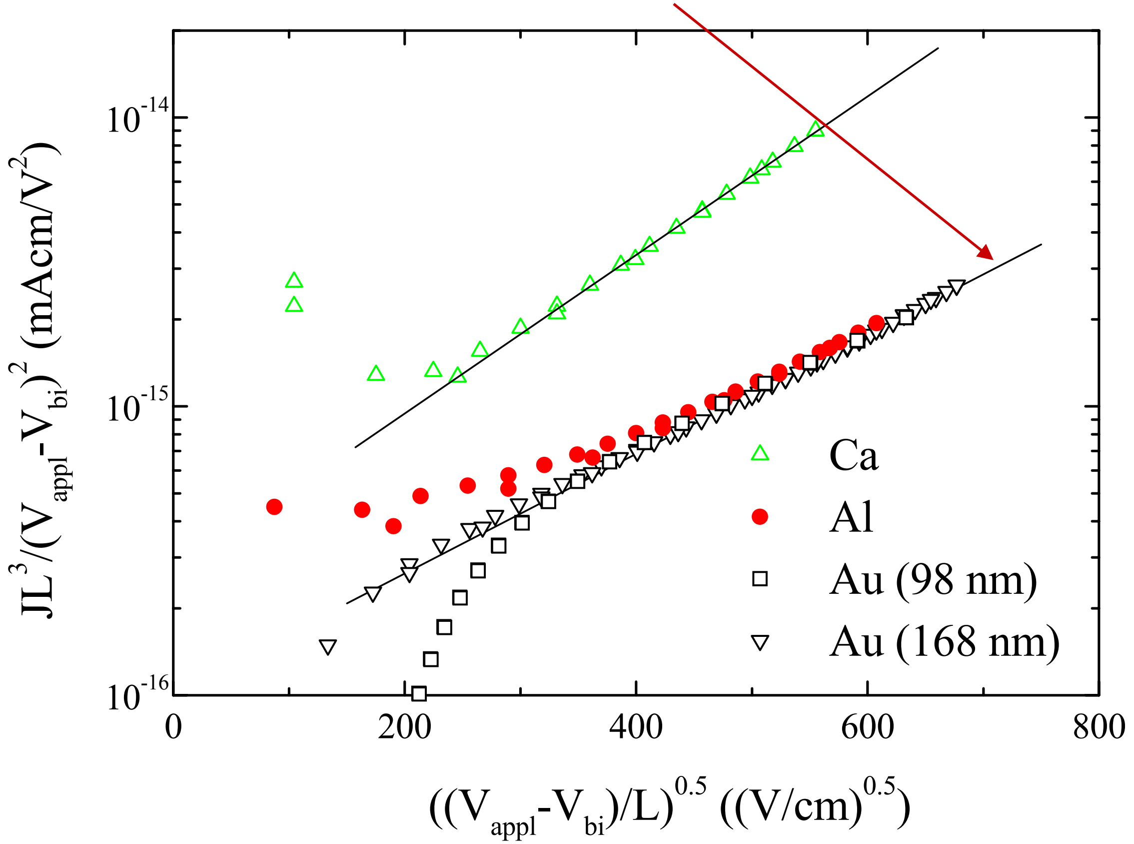
$$J = q\,\mu_n F n_d \exp\left(\frac{\left(-E_a^{\,0} + \left(\frac{q^3}{\pi\epsilon_0\epsilon}\right)^{1/2} F^{1/2}\right)}{kT}\right)$$



B.A. Gregg, *J. Phys. Chem. B* **108**, 45 (2004).

Charge density vs. electric field (II)

$J_{SCL} \approx (9/8)\varepsilon\varepsilon_0\mu_0 V^2 \mathit{exp}[0.89(V/E_0L)^{0.5}]/L^3$



G.G. Malliaras, J.R. Salem, P.J. Brock, and J.C. Scott, *Phys. Rev. B*. **58**, R13411 (1998).

Charge transport

First order correction:		
Space charge effects	$J = (9/8)\cdot\varepsilon\cdot\varepsilon_0\cdot\mu\cdot V^2/L^3$	√
Disorder:		
Energetics	Localized states	√
Influence on mobility	$\mu=\mu(E,T)$	√
Manifold filling:		
Charge density dependence of mobility	$\mu=\mu(n)$	√
Charge generation:		
Electric field dependence of charge density	$n=n(E)$	?

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- Charge injection: theory and experiments
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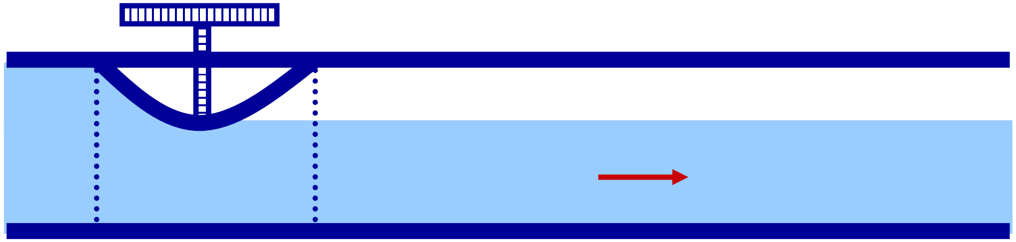
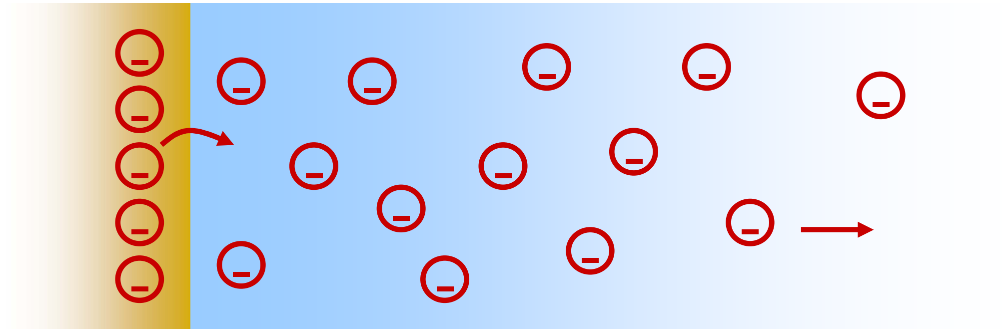
Injection vs. transport



Water hose and valve

Is the flow limited by the valve or the hose?



Semiconductor contacts

Is the current limited by injection or transport?

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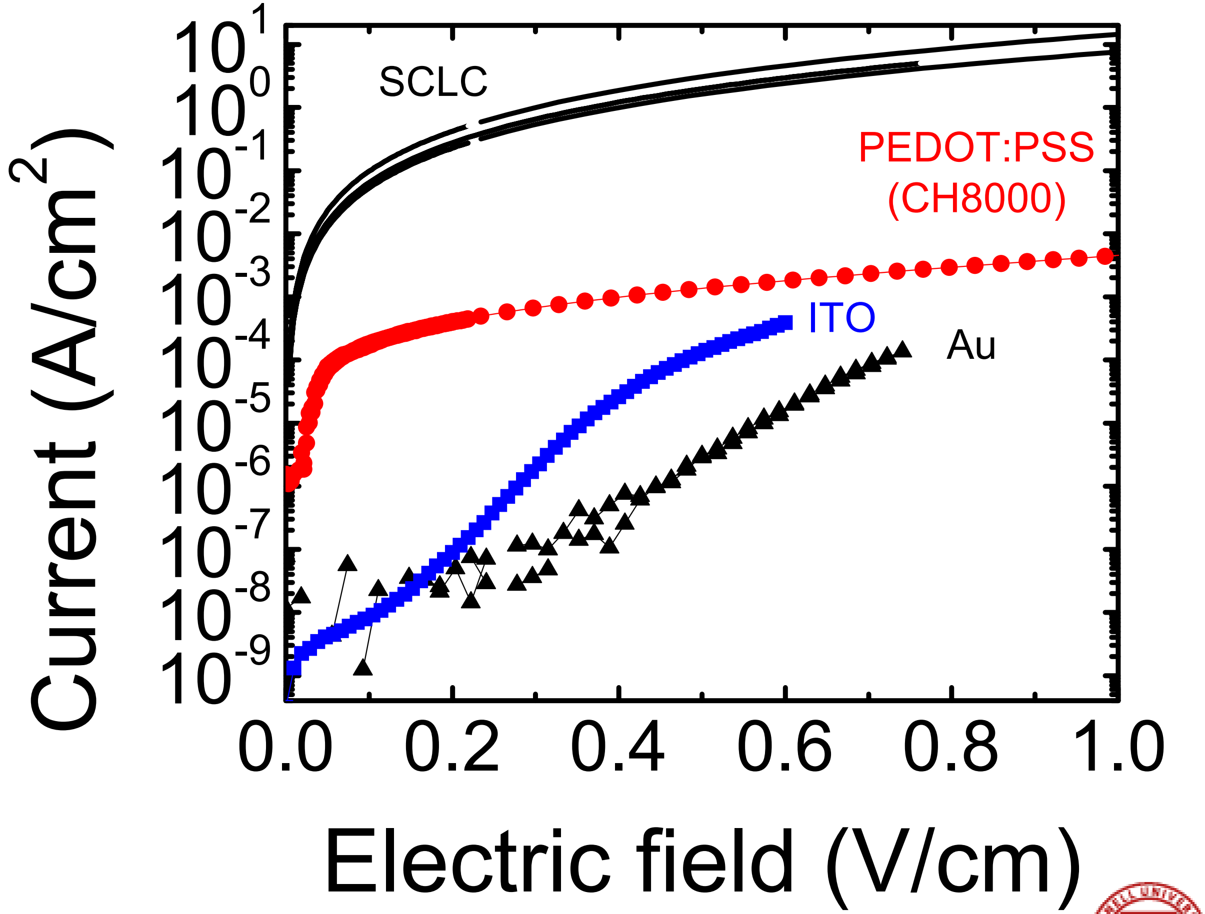
Hole injection in TFB



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Hierarchy of injection models

Mechanism:

Thermionic emission	$J = A\cdot\exp(-\varphi/kT)$
Tunneling	$J = A\cdot E^{2}\cdot\exp(-B\cdot\varphi^{3/2}/E)$

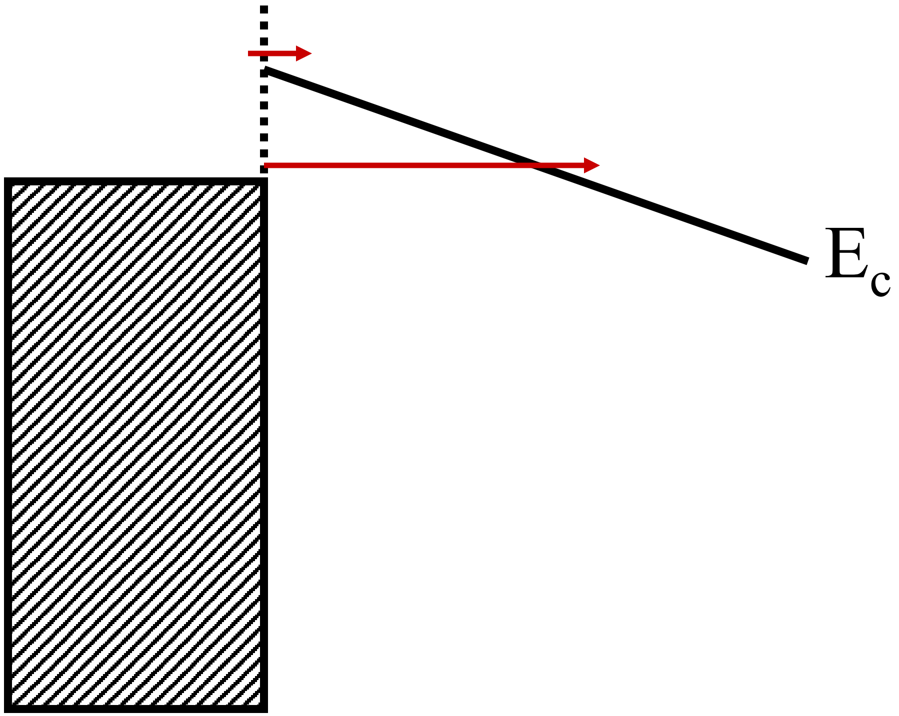
First order corrections:

Barrier lowering	$J \sim \exp(E^{0.5})$
Recombination with image force	$J \sim \mu$

Disorder:

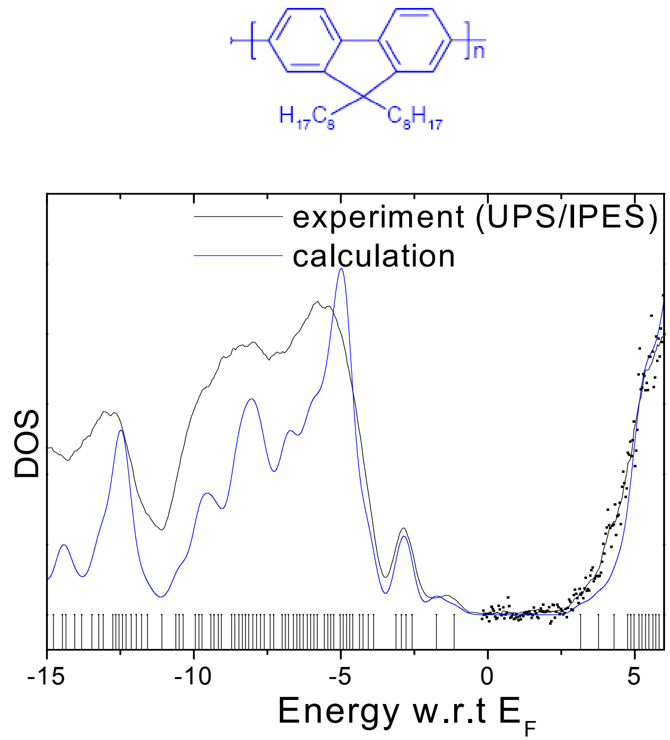
Gaussian disorder	$J \sim \exp(E^{0.5})$

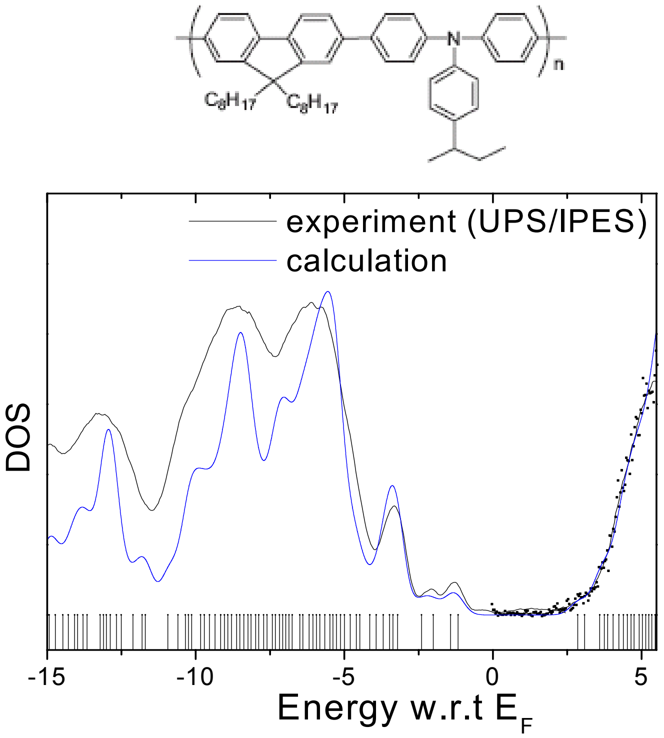
Thermionic emission and tunneling



Lampert and Mark, *Current Injection in Solids* (Academic Press,1970).

Energetics of conjugated polymers

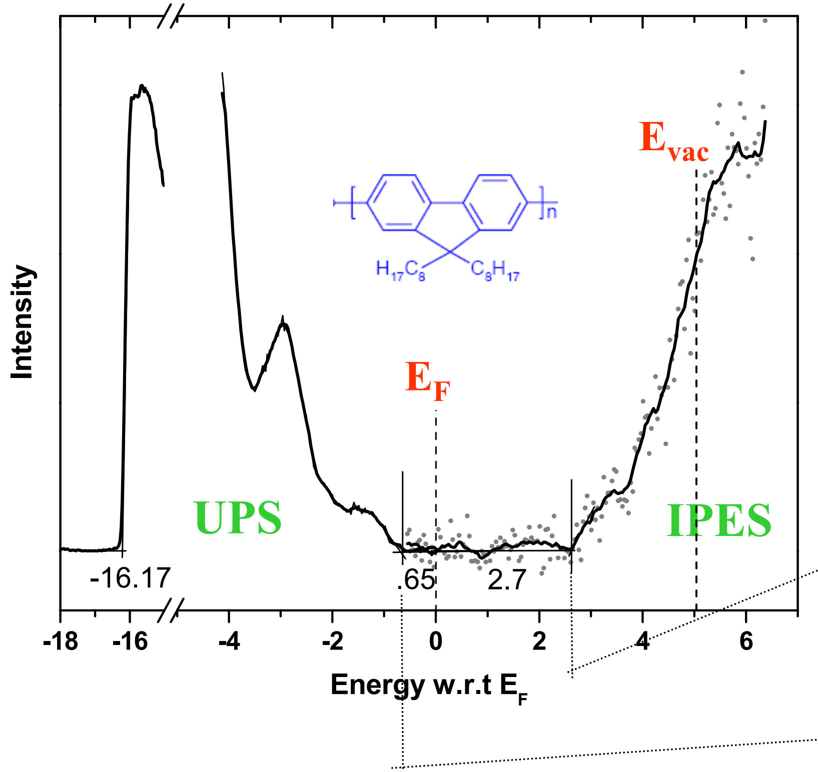


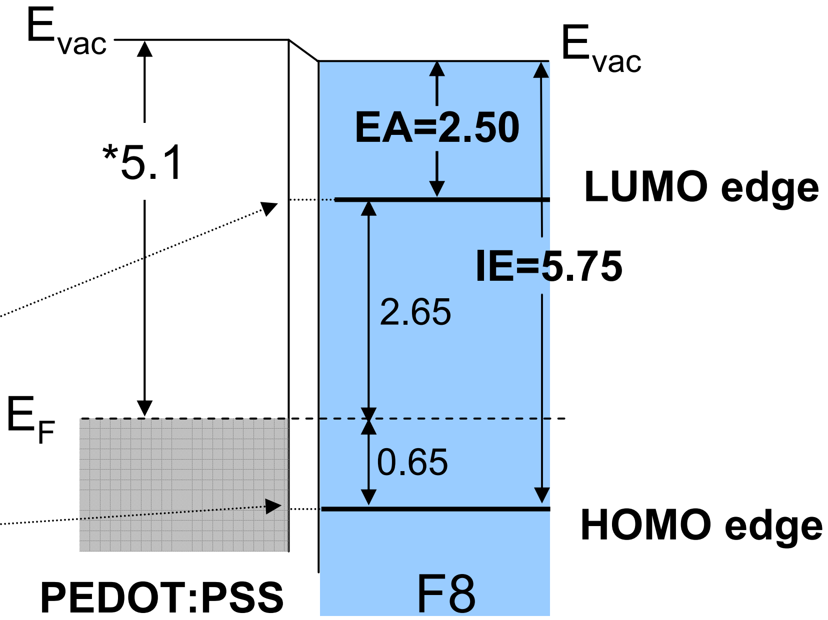


J. Hwang et al., *J. Phys. Chem. C*, in press.

Energetics at the contact

Ionization energy (IE) and electron affinity (EA) measured from HOMO and LUMO edges w.r.t vacuum level

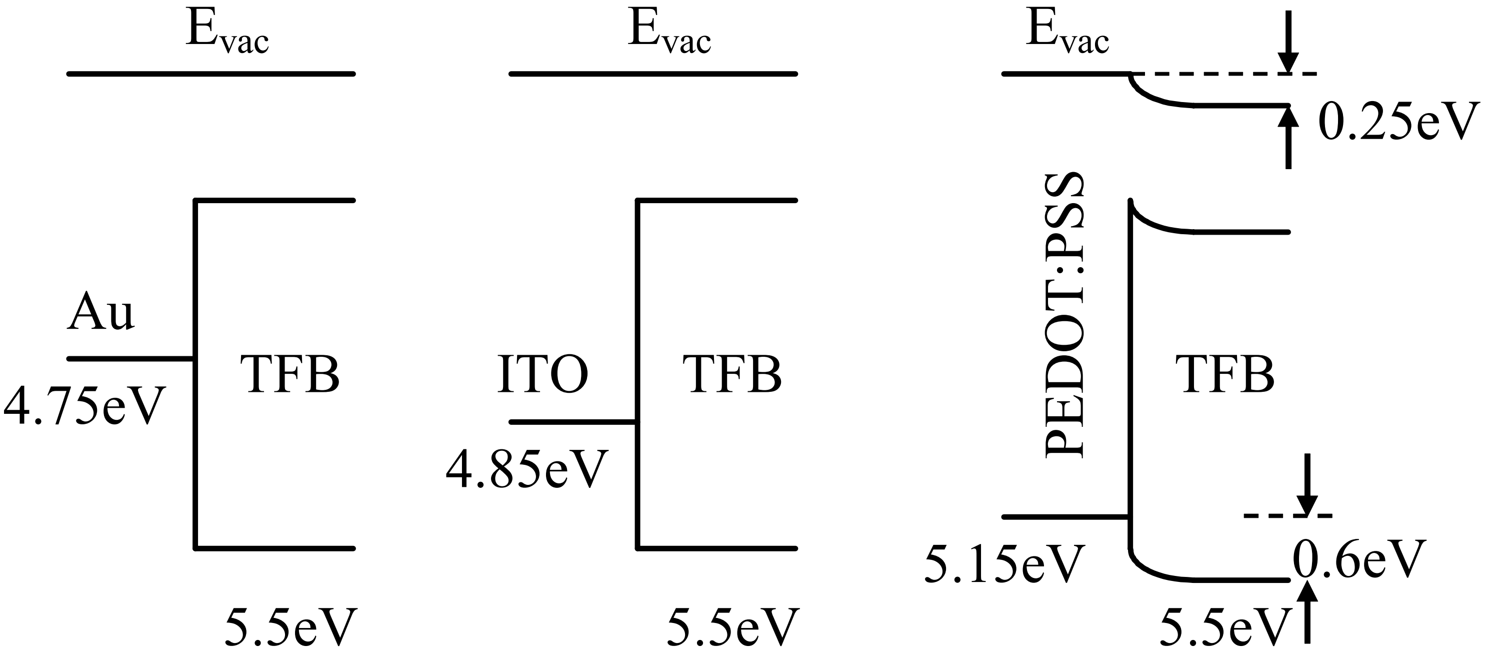




(energies in eV)

* Work function of PEDOT:PSS substrate measured on separate sample produced in same batch.

Hole injection barriers for TFB contacts

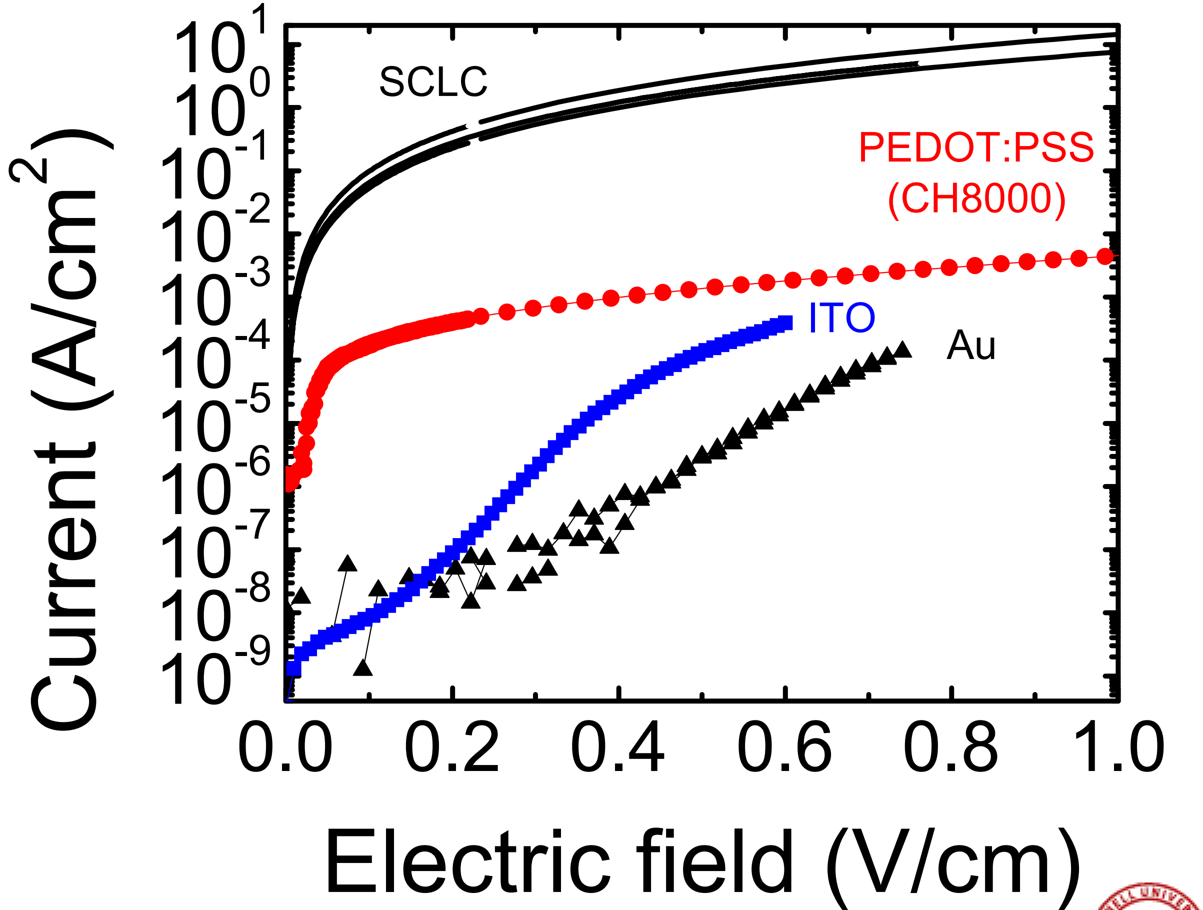


0.75eV

0.65eV

0.6eV

Hole injection in TFB



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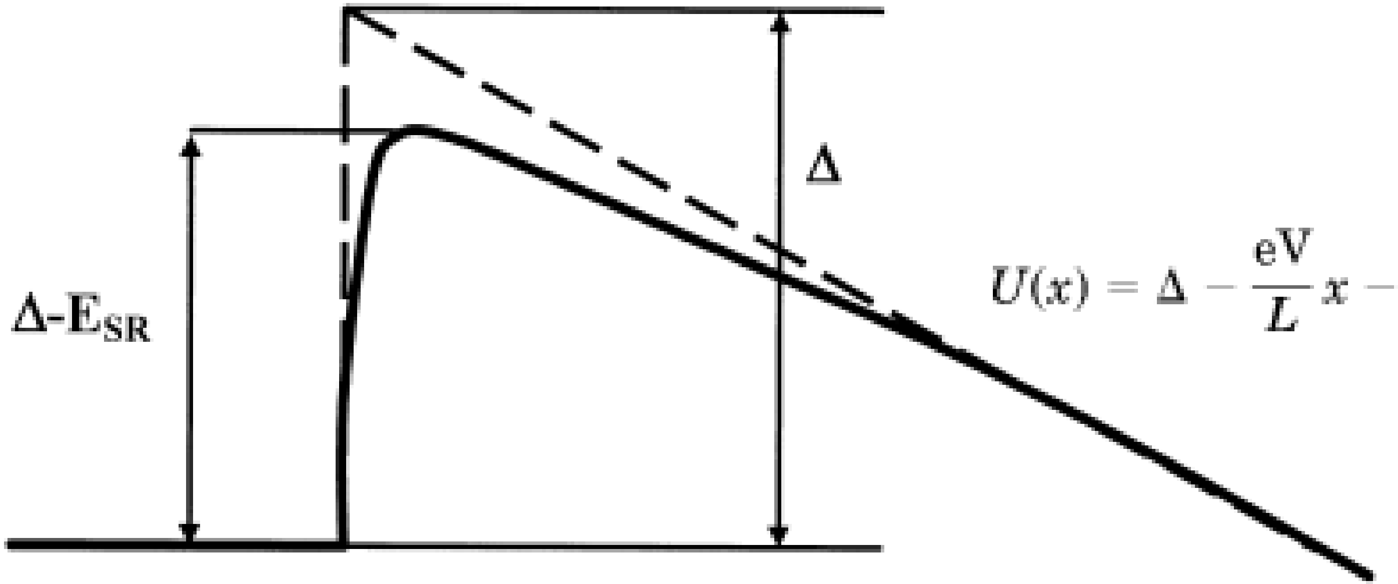
Barrier lowering



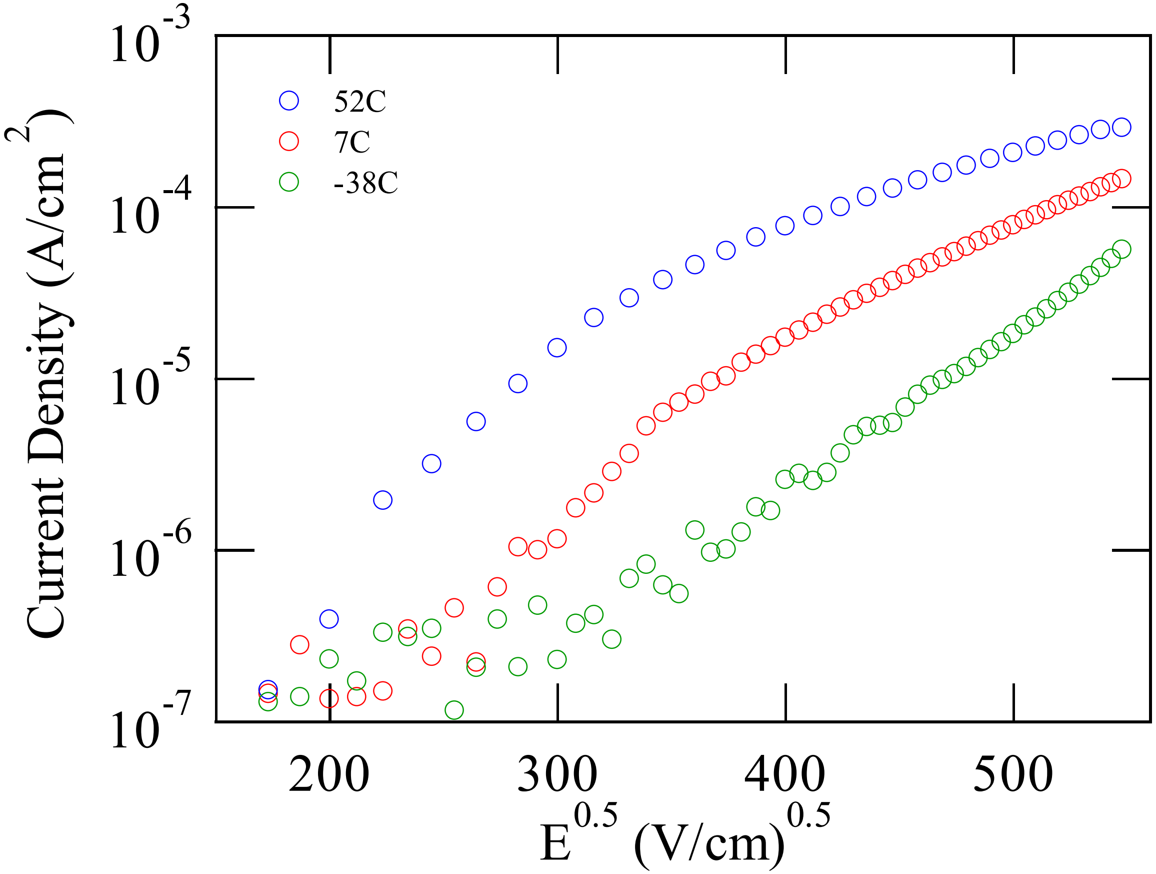
$$U(x) = \Delta - \frac{\mathrm{eV}}{L}x - \frac{e^2}{16\pi\varepsilon\varepsilon_0 x}$$

$$\Delta_{\mathrm{SR}} = \Delta - E_{\mathrm{SR}},$$

$$E_{\mathrm{SR}} = \sqrt{\frac{V}{L}\frac{e^3}{4\pi\varepsilon_0\varepsilon}}$$

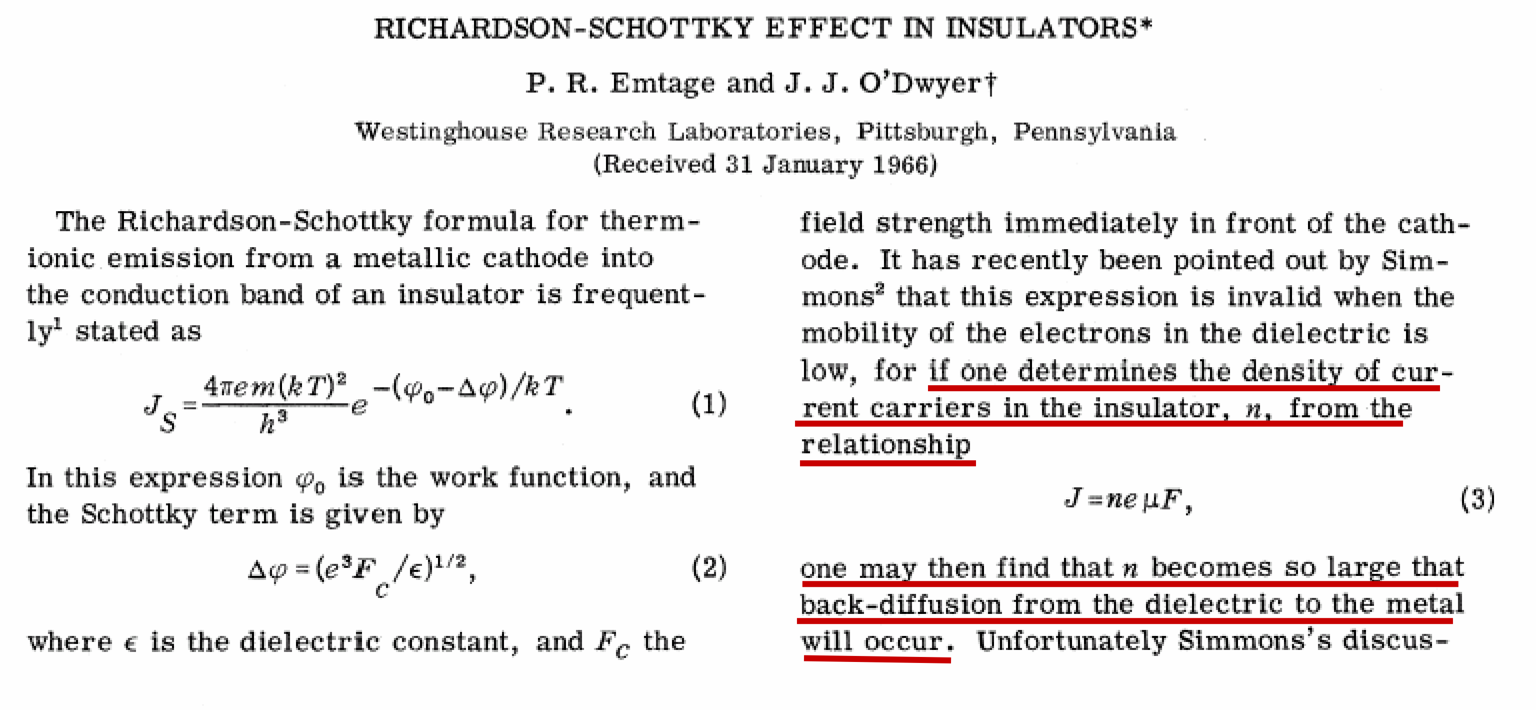
Lampert and Mark, *Current Injection in Solids* (Academic Press,1970).

Field dependence of injection



PEDOT:PSS/PFO

Low mobility



RICHARDSON-SCHOTTKY EFFECT IN INSULATORS*

P. R. Emtage and J. J. O'Dwyer†

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania
(Received 31 January 1966)

The Richardson-Schottky formula for thermionic emission from a metallic cathode into the conduction band of an insulator is frequently[1] stated as

$$J_S = \frac{4\pi e m (kT)^2}{h^3} e^{-(\varphi_0 - \Delta\varphi)/kT}. \qquad (1)$$

In this expression φ_0 is the work function, and the Schottky term is given by

$$\Delta\varphi = (e^3 F_c/\epsilon)^{1/2}, \qquad (2)$$

where ϵ is the dielectric constant, and F_c the field strength immediately in front of the cathode. It has recently been pointed out by Simmons[2] that this expression is invalid when the mobility of the electrons in the dielectric is low, for if one determines the density of current carriers in the insulator, n, from the relationship

$$J = ne\mu F, \qquad (3)$$

one may then find that n becomes so large that back-diffusion from the dielectric to the metal will occur. Unfortunately Simmons's discus-

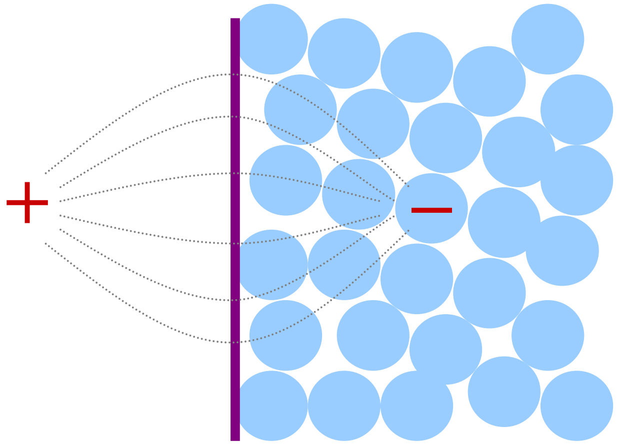
$$J = N \cdot e \cdot \mu \cdot E \cdot \exp(-\varphi_B/kT)$$

P.R. Emtage and J.J. O'Dwyer, *Phys. Rev. Lett.* **16**, 356 (1966)

Recombination with image charge

$$J = C\,exp(-\varphi_B/kT) - en_0 S(E)$$

- Surface recombination as a hopping process in the image charge potential.
- No current flow at zero field.

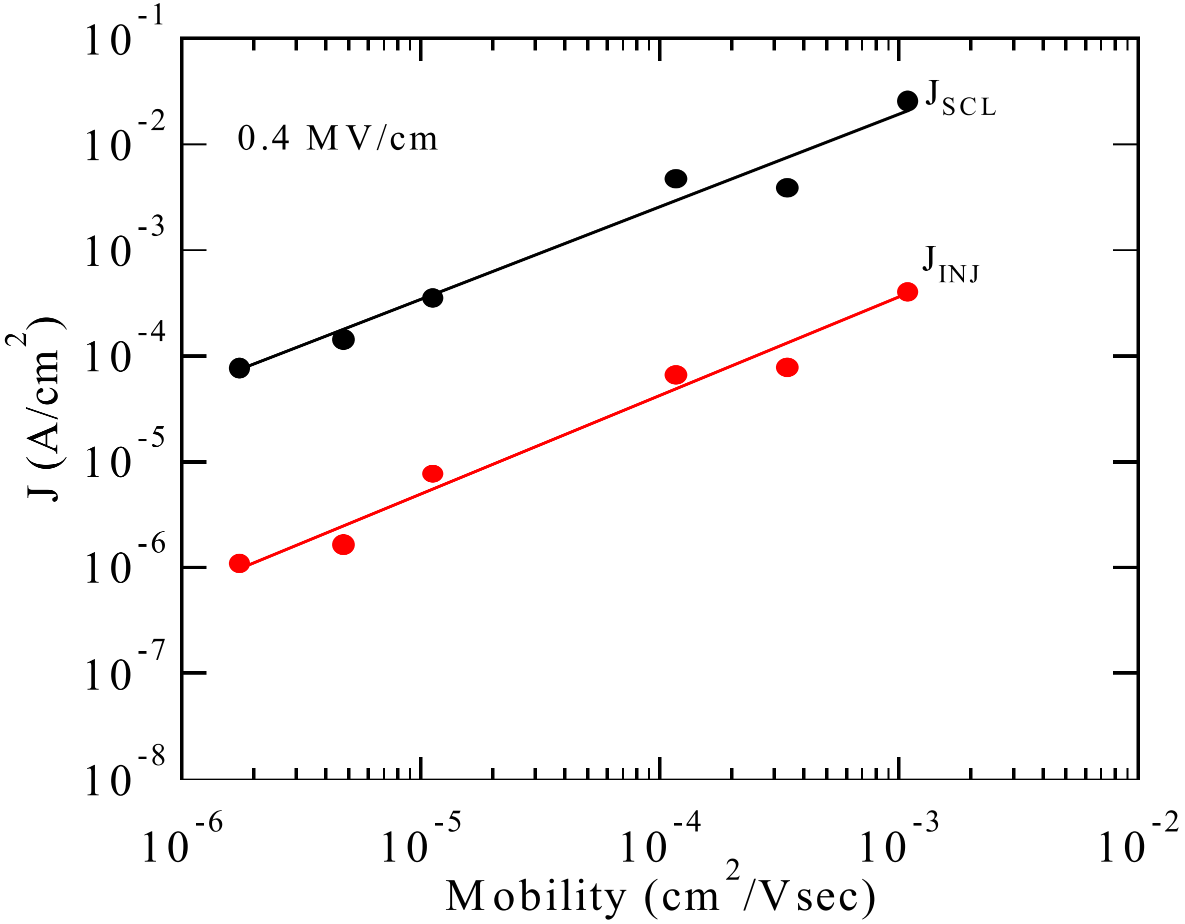


$C = 16\pi\varepsilon\varepsilon_0 N_0 (kT)^2 \mu/e^2$

$S(0) = 16\pi\varepsilon\varepsilon_0 (kT)^2 \mu/e^3$

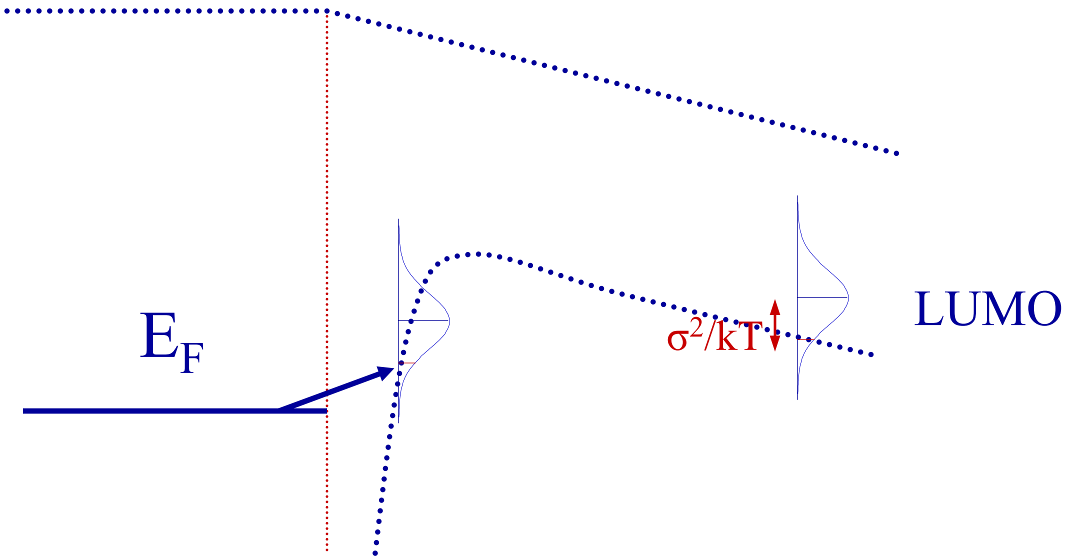
J.C. Scott and G.G. Malliaras, *Chem. Phys. Lett.* **299**, 115 (1999)

Dependence of injection on mobility



Y. Shen, M.W. Klein, D.B. Jacobs, J.C. Scott,
and G.G. Malliaras, *Phys. Rev. Lett.* **86**, 3867 (2001).

Gaussian disorder

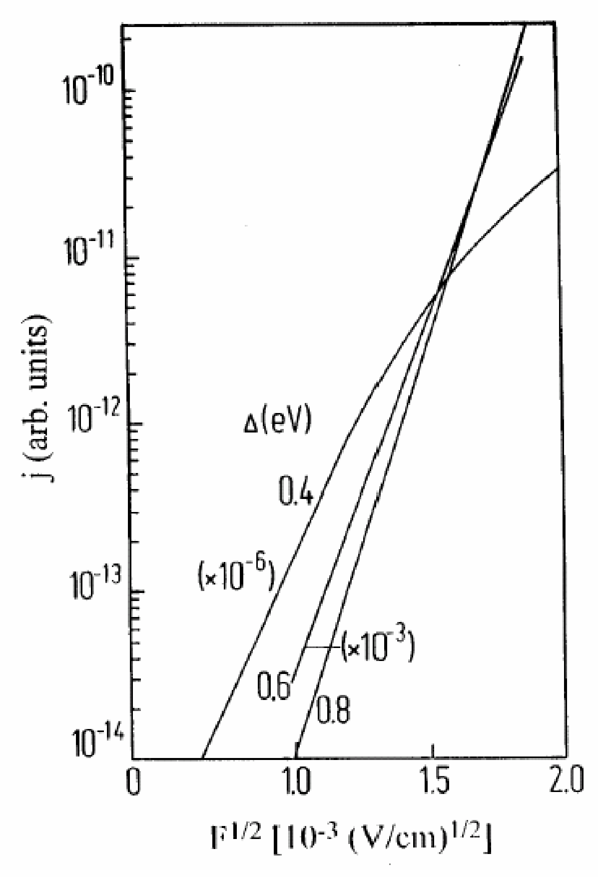


$$J_{Inj} = e \cdot \nu \cdot \int_{a}^{\infty} dx_0 \left[\exp\left(-2 \cdot \gamma \cdot x_0\right) \cdot w_{esp}\left(x_0\right)\right] \cdot \int_{-\infty}^{\infty} dE\left[Bol\left(E\right) \cdot g\left(U\left(x_0\right) - E\right)\right]$$

First hop is the rate limiting step

V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, and H. Bässler, *J. Appl. Phys.* **84**, 848 (1998).

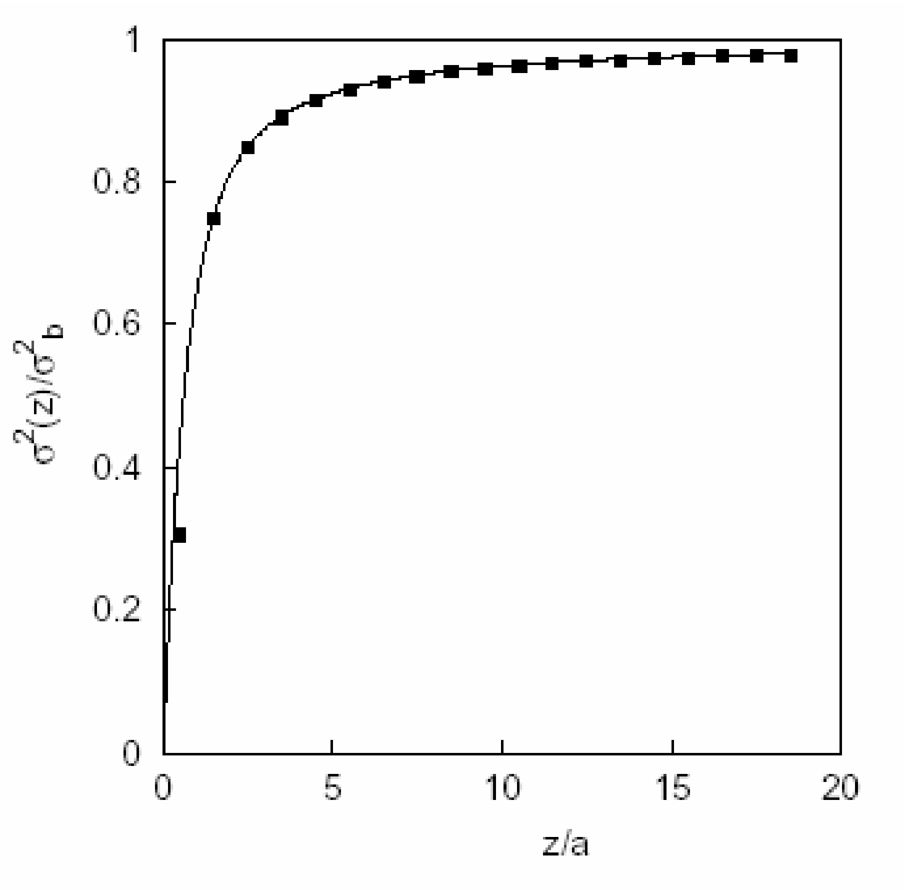
Gaussian disorder (II)



Field
dependence
resembles
thermionic
emission

V.I. Arkhipov, E.V. Emelianova, Y.H. Tak, and H. Bässler, *J. Appl. Phys.* **84**, 848 (1998).

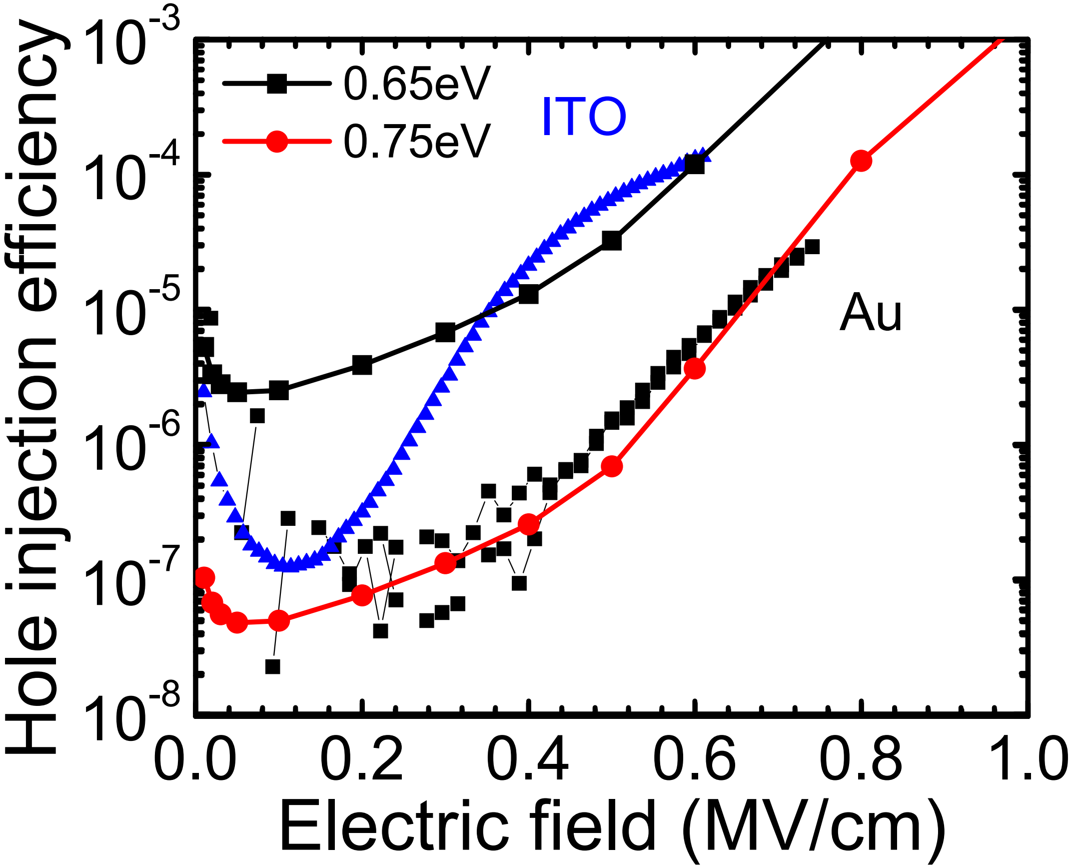
Gaussian disorder (III)



Energetic disorder due to charge-dipole interactions different at the interface

S.V. Novikov, and G.G. Malliaras, *Phys. Rev. B* **73**, 033308 (2006).

Gaussian disorder (III)



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Charge injection

Mechanism:		
Thermionic emission	$J = A \cdot \exp(-\varphi/kT)$	
Tunneling	$J = A \cdot E^2 \cdot \exp(-B \cdot \varphi^{3/2}/E)$	
First order corrections:		
Barrier lowering	$J \sim \exp(E^{0.5})$	√
Recombination with image force	$J \sim \mu$	√
Disorder:		
Gaussian disorder	$J \sim \exp(E^{0.5})$	?

Opportunities

- There is rich physics to be explored in organic light emitting diodes

- Conjugated polymers that show ideal transport characteristics and high mobilities have become available

- Charge injection in TFB is poor (and poorly understood) – opportunity for major improvements in OLED performance

Challenges

- Picture of metal/organic interfaces from spectroscopy is only now getting incorporated in injection models
- Injection expected to be spatially inhomogeneous due to correlated disorder
- $J \sim \exp(E^{0.5})$ ubiquitous, temperature range rather small – need other tests for theories

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