Charge injection and transport in organic semiconductors

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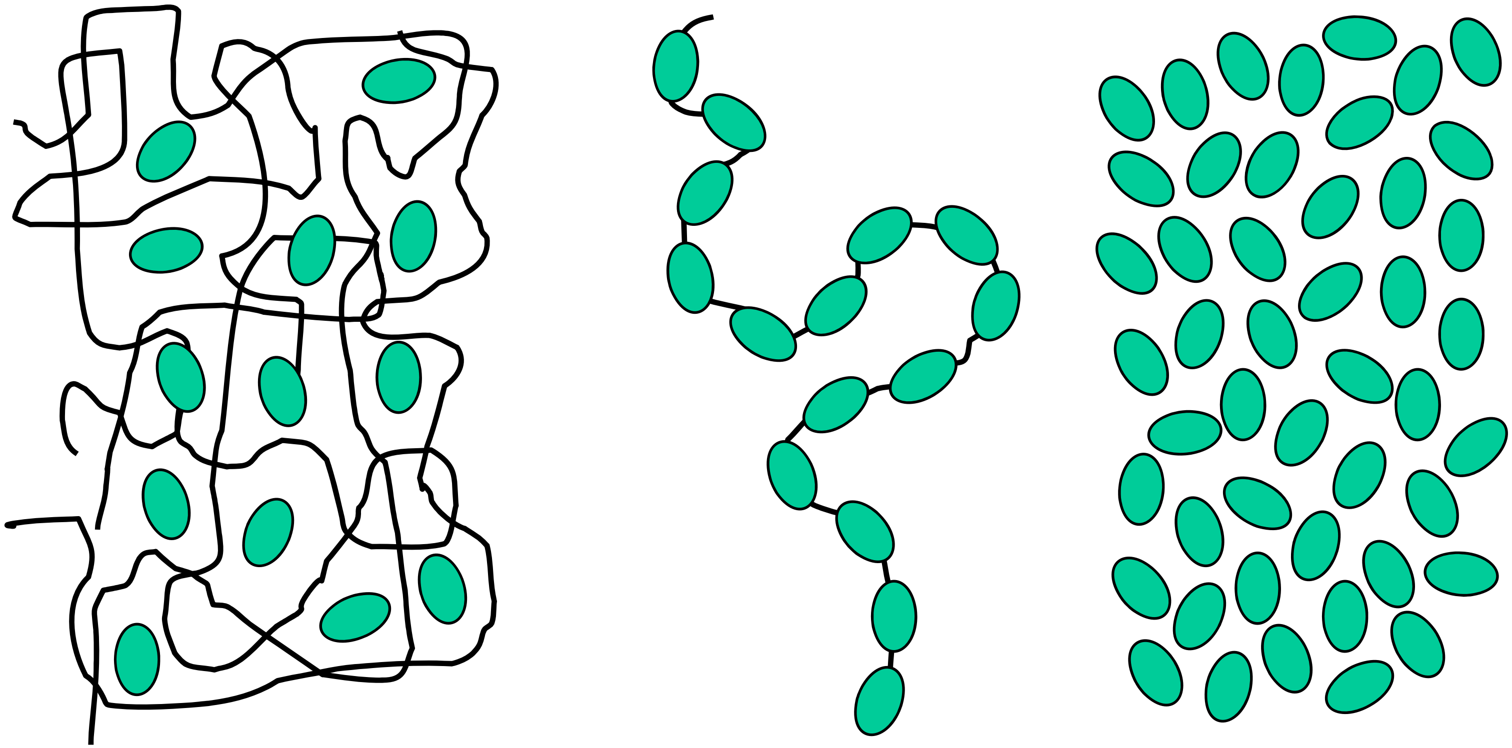
Outline

- Organic semiconductors and devices
- Charge injection and transport processes
- Charge transport in organic semiconductors
- Charge injection in organic semiconductors
- Conclusions

Organic semiconductor families

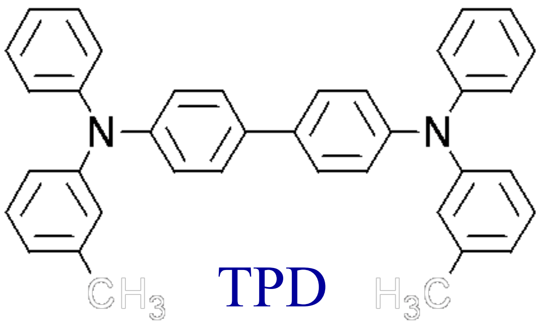


Molecularly Dispersed Polymers (MDPs)

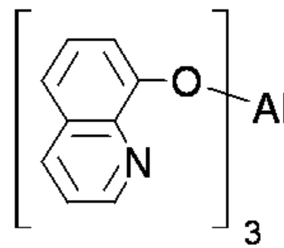
Functional Polymers

Small Molecules

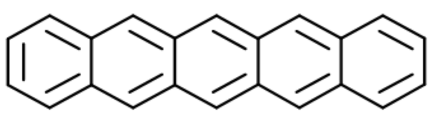
Examples of conjugated small molecules



TPD

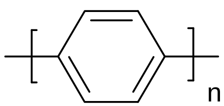


Alq_3

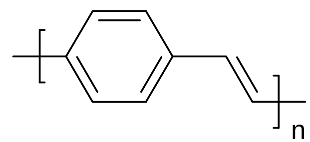


Pentacene

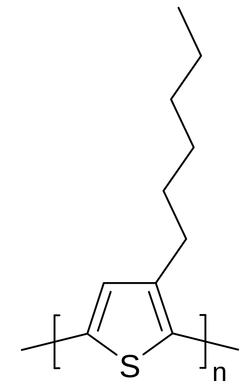
Examples of conjugated polymers



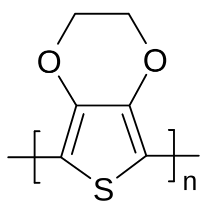
PPP



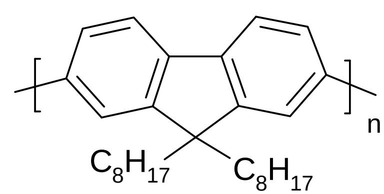
PPV



P3HT



PEDOT

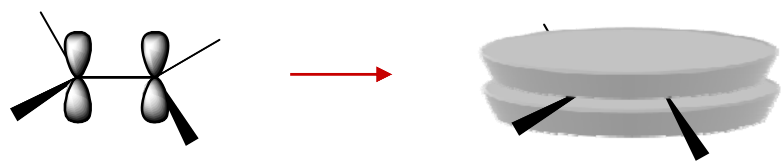


PFO

Carbon as a semiconductor

- Hybridization: sp^2 and p_Z

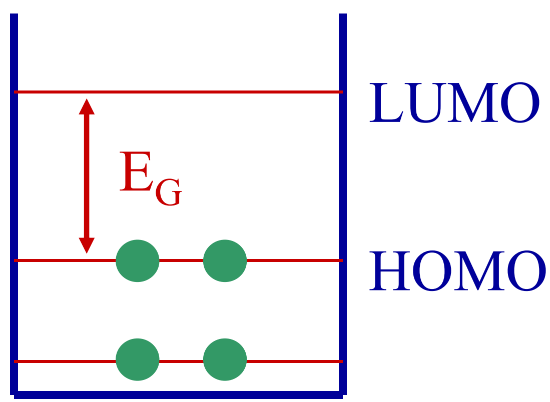
$CH_2{=}CH_2$



- Particle in a box:

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

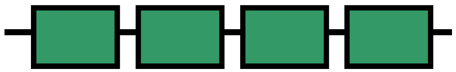
$$n = 1, 2, 3, \ldots$$



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

Tuning of optical properties

Blue



Red

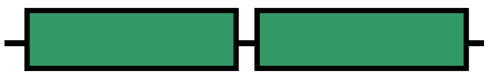
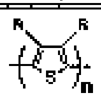
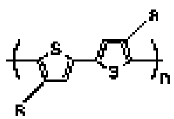
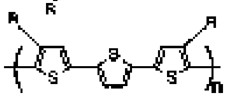
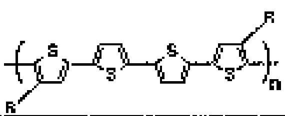
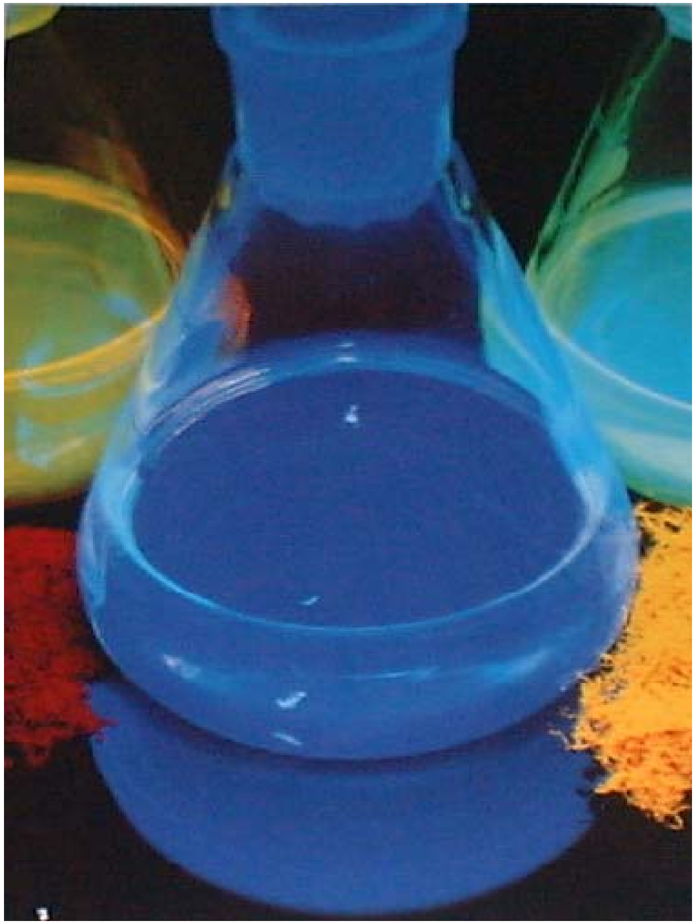


Table 1. Chemical structures and molecular weight characterization of regiospecific alkylated polythiophenes.

Polymer[a]		M_n[b] * 10[illegible]	M_w/M_n
	I	1.7	2.3
	II	0.89	1.6
	III	4.2	3.7
	IV	8.5	2.1

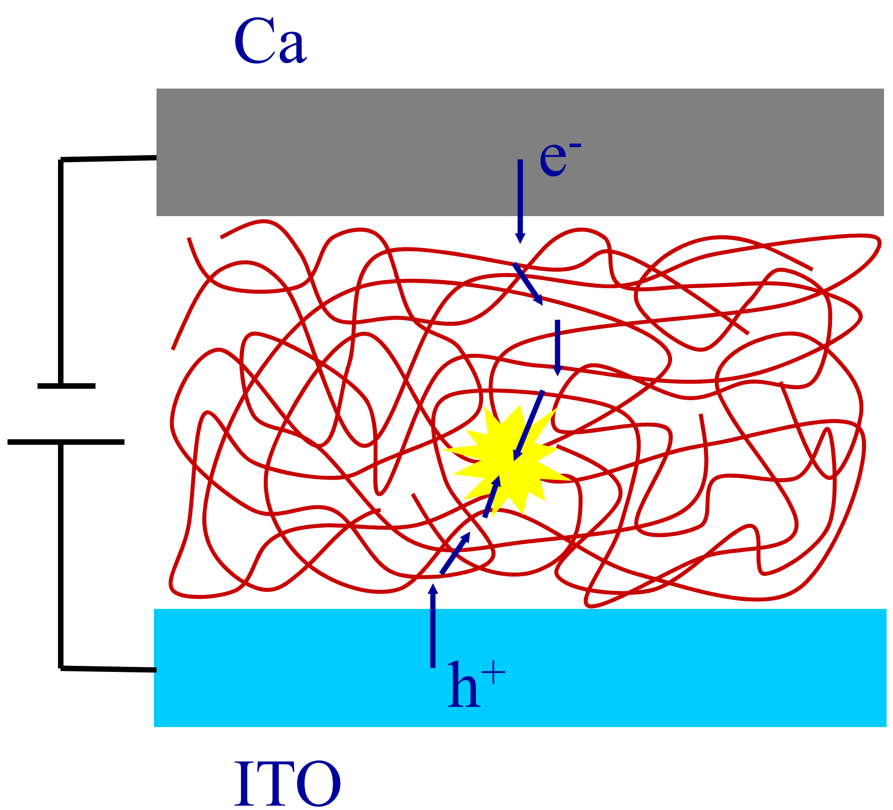
[a] R is n-octyl. [b] Relative to polystyrene standards.

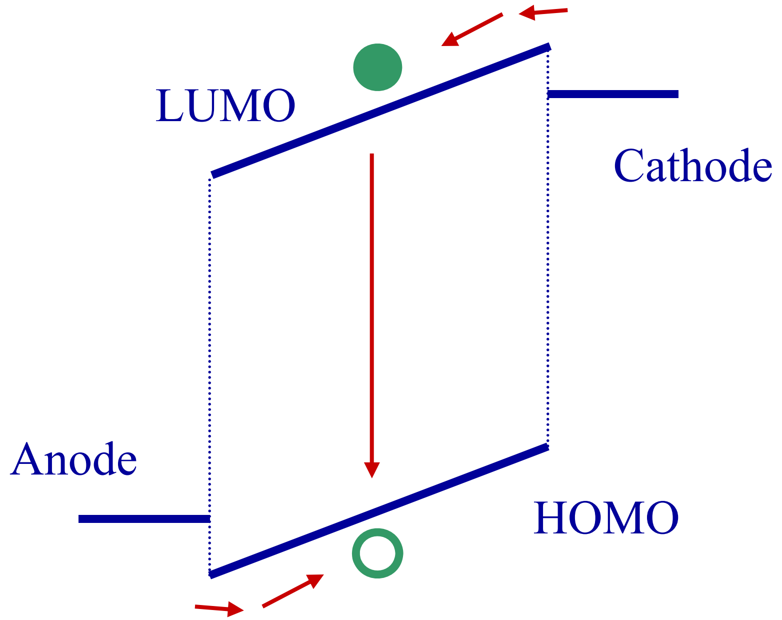


Covion

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

PLED structure and operation





Electroluminescence: <u>charge injection</u>, <u>charge transport</u>, recombination

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Charge transport in semiconductors

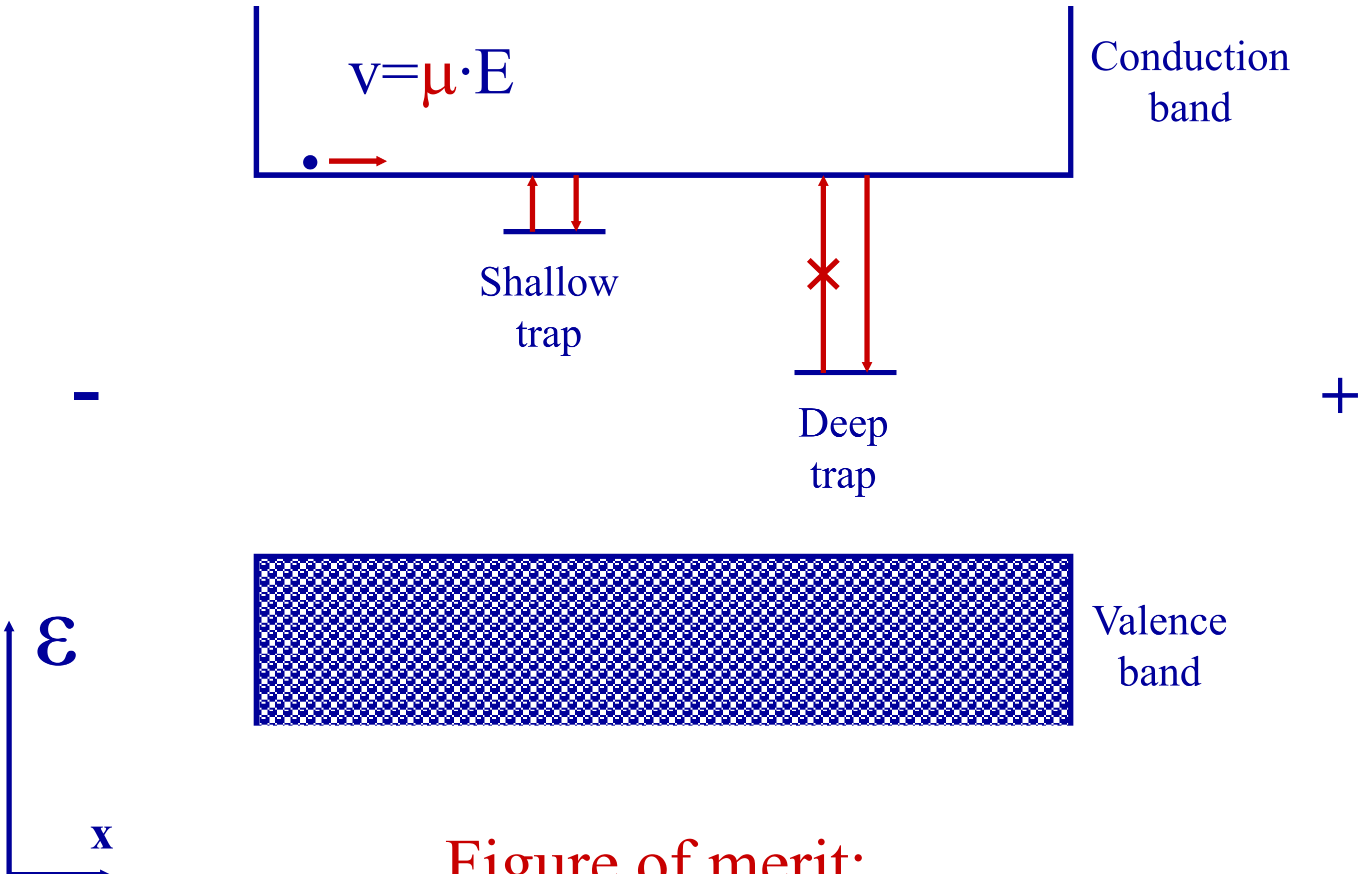
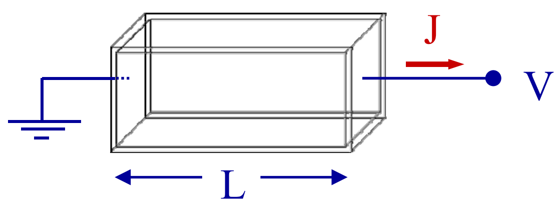
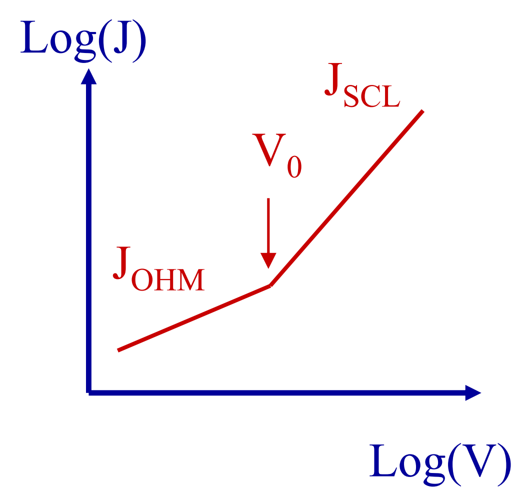


Figure of merit:
mobility, μ ($cm^2/V\cdot sec$)

Charge transport in semiconductors (II)

Question: What is the maximum current that can flow through a (trap-free) semiconductor?





Lower voltages: Ohm's law

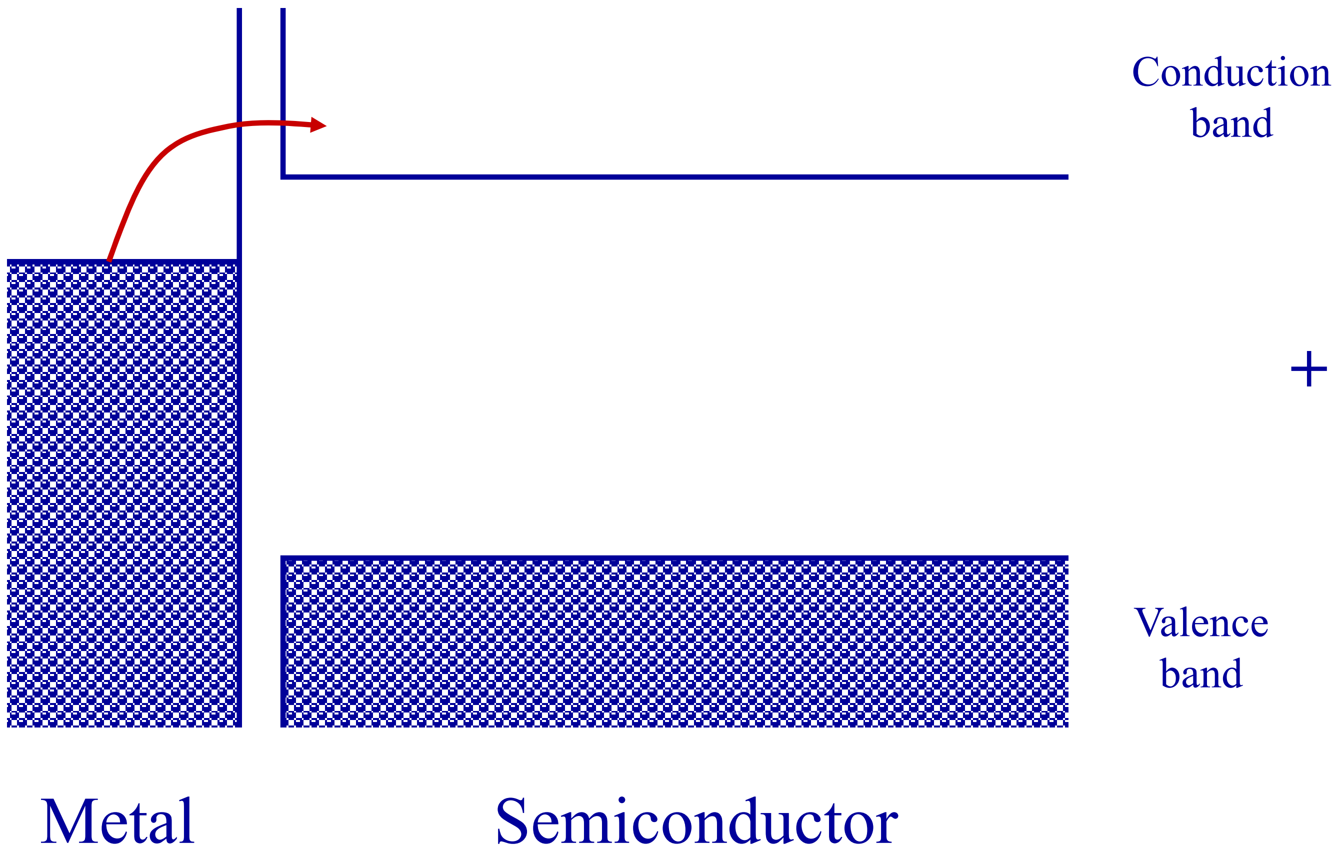
$J_{OHM} = e \cdot N_0 \cdot \mu \cdot V/L$

Higher 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).

Charge injection in semiconductors

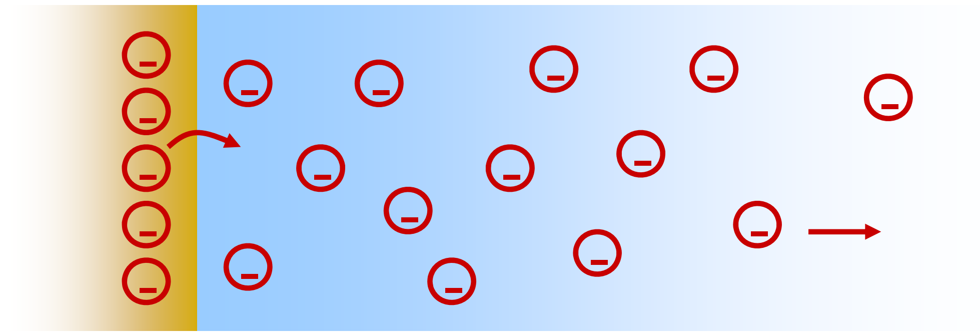


Mechanisms: Thermionic emission or tunneling

Injection vs. transport

Water hose and valve

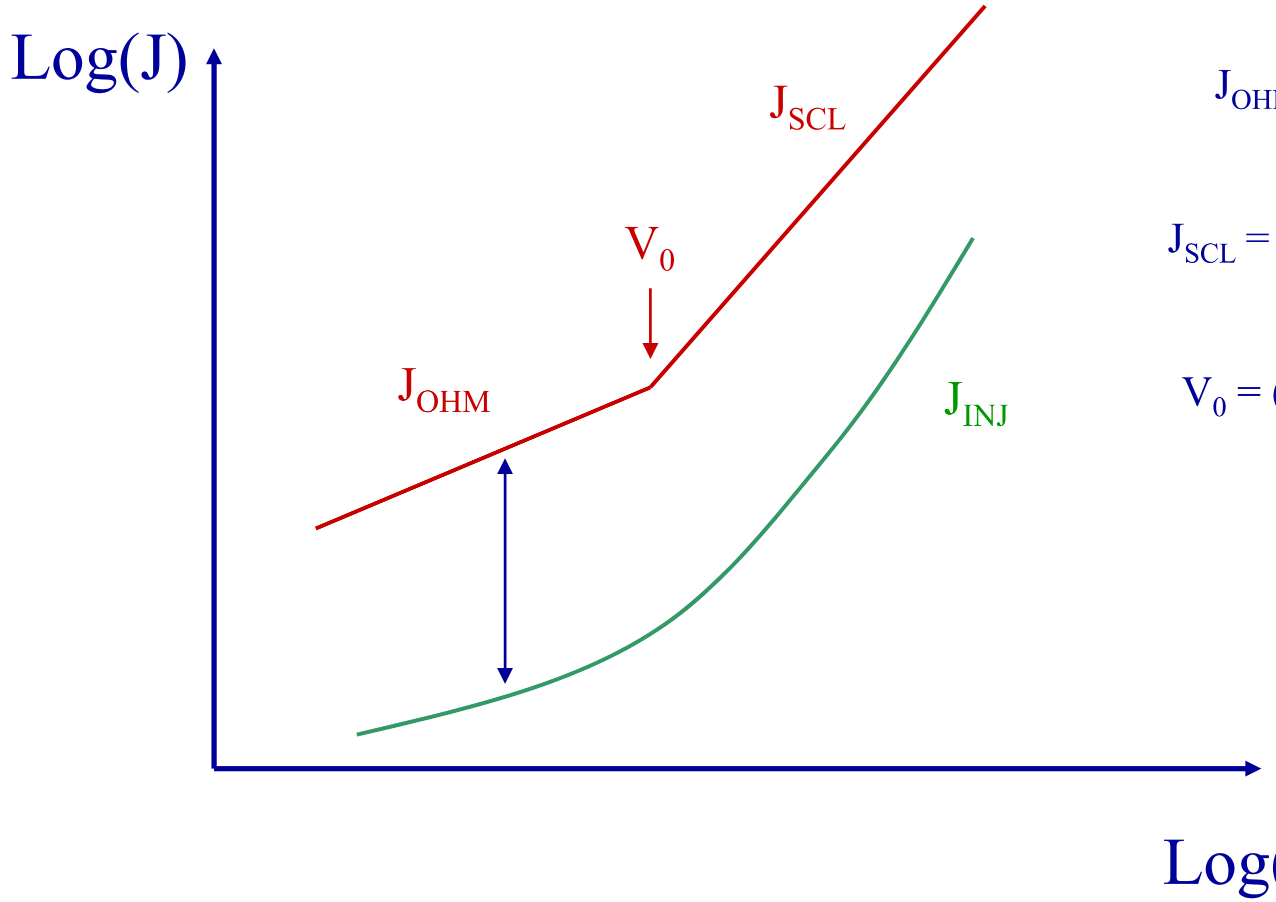
Is the flow limited by the valve or the hose?



Semiconductor contacts

Is the current limited by injection or transport?

Injection vs. transport (II)



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

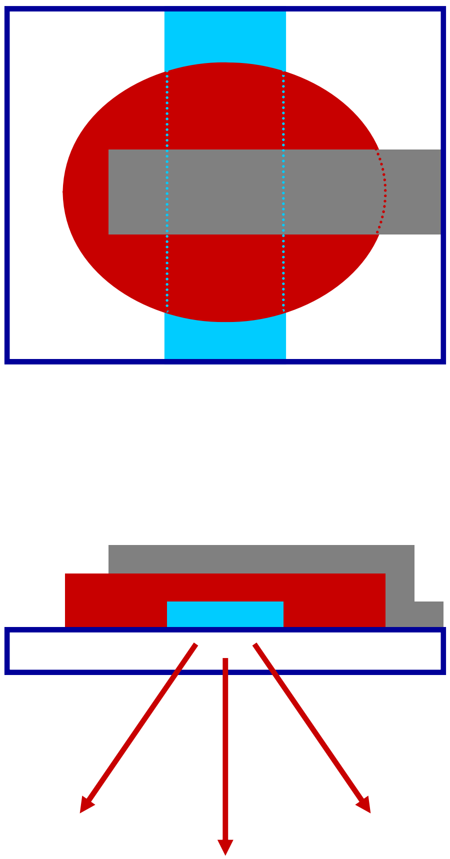
$J_{SCL} = (9/8) \cdot \varepsilon \cdot \varepsilon_0 \cdot \mu \cdot V^2/L^3$

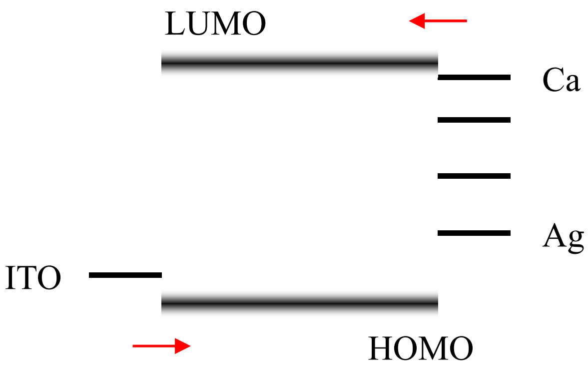
$V_0 = (8/9) \cdot e \cdot N_0 \cdot L^2/\varepsilon \cdot \varepsilon_0$

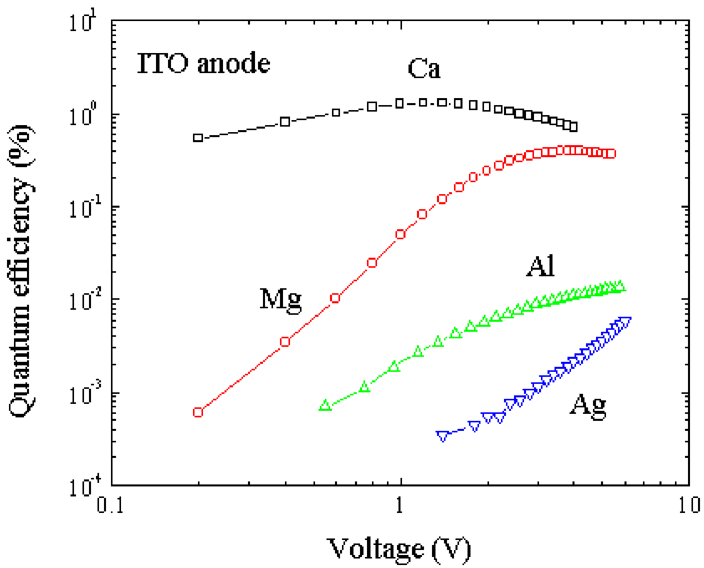
J_{INJ} = ???

Figure of merit: $\eta = J_{INJ} / J_{MAX}$

Example: Injection-limited performance







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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:

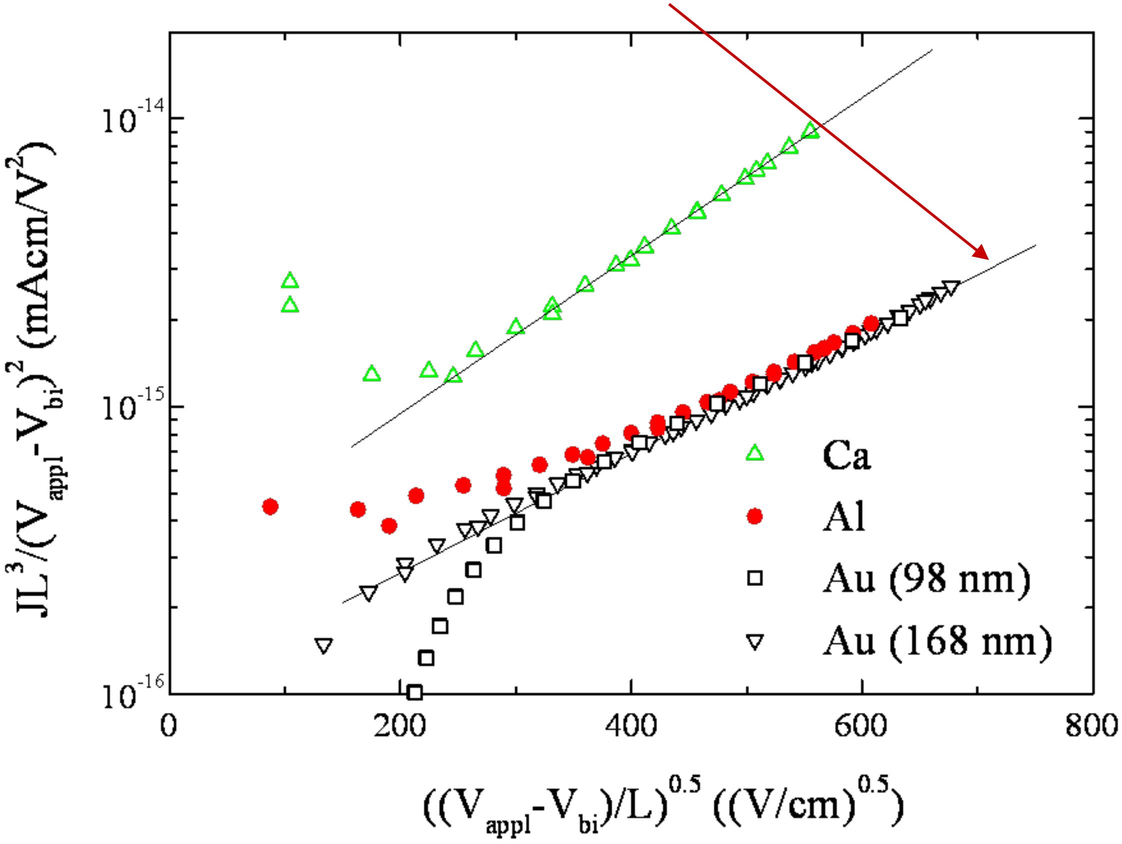
Charge density dependence of mobility — $\mu = \mu(n)$

Charge generation:

Electric field dependence of charge density — $n = n(E)$

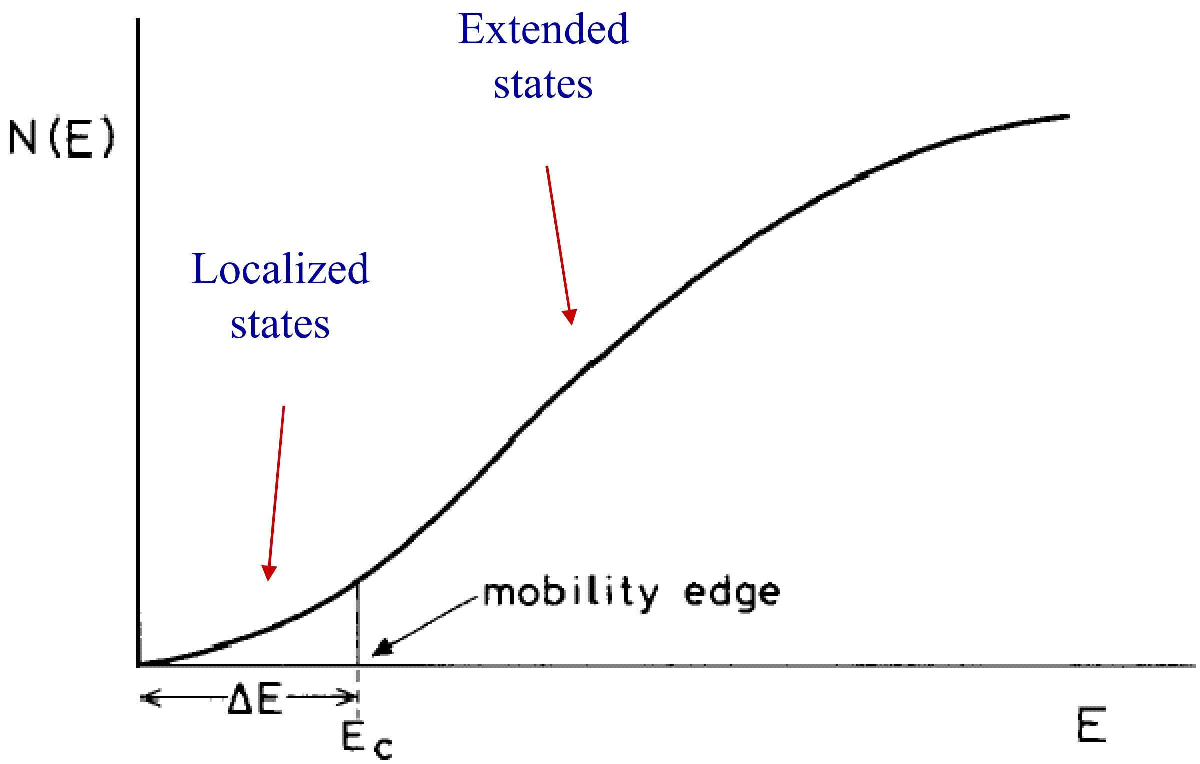
Space charge limited current in organics

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



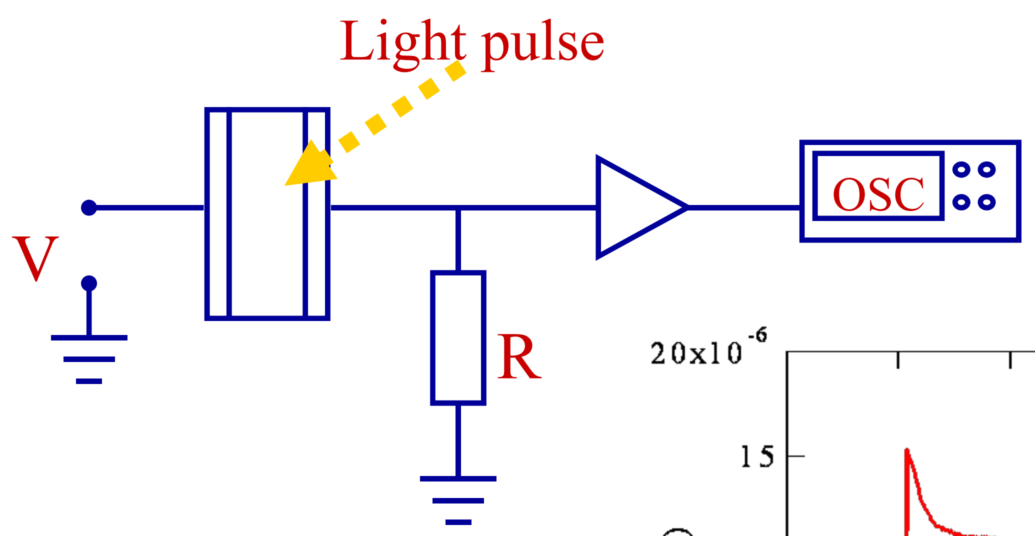
G.G. Malliaras, J.R. Salem, P.J. Brock, and J.C. Scott, *Phys. Rev. B*. **58**, R13411 (1998).

Energetics of amorphous semiconductors

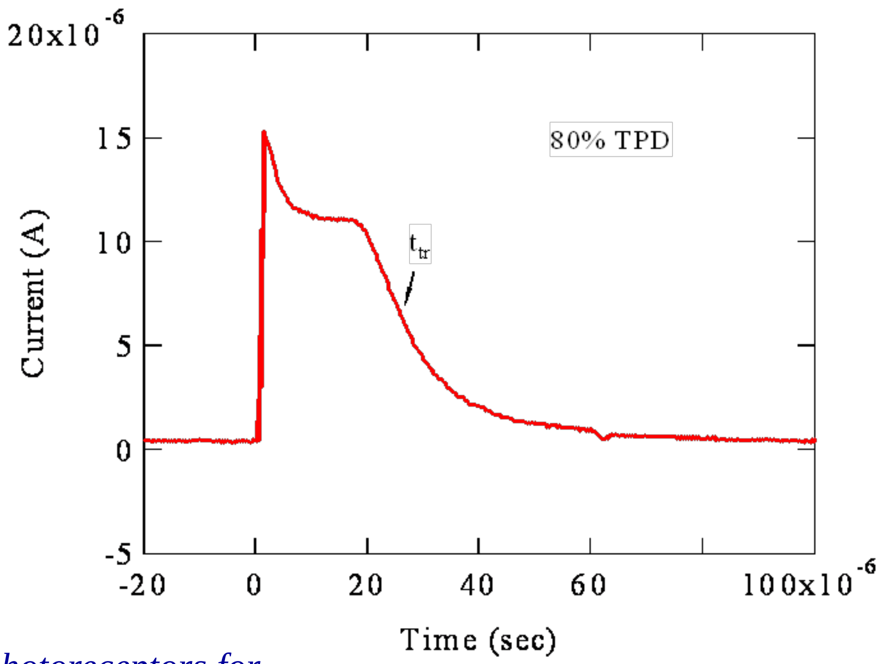


N. Mott, *Nobel Lecture* (1977)

Time-of-flight (TOF)



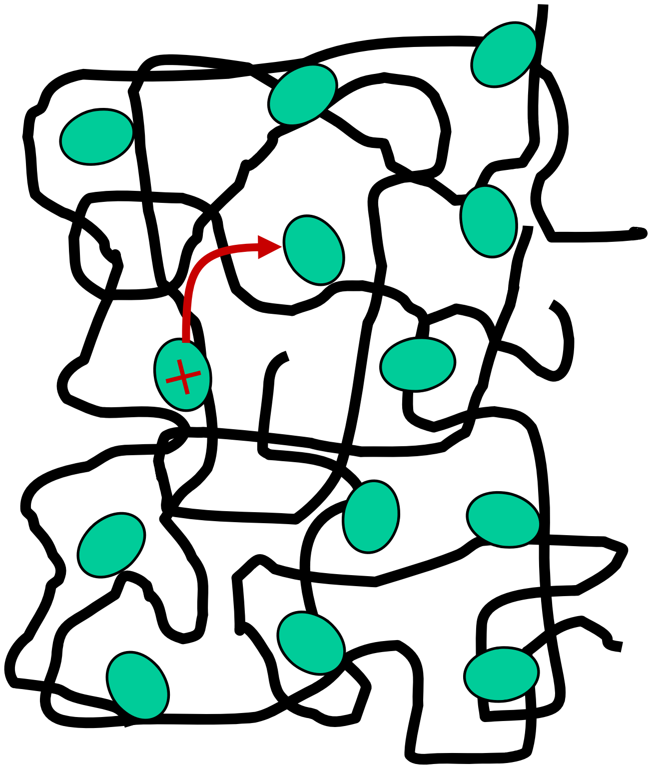
$$\mu = \frac{L^2}{t_{TR} \cdot V}$$



Great book on transport:

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

Molecularly dispersed polymers

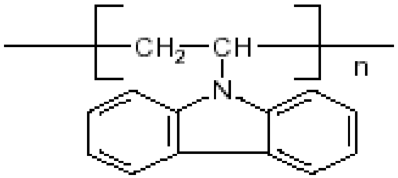


Solid solutions of conjugated molecules in inert host

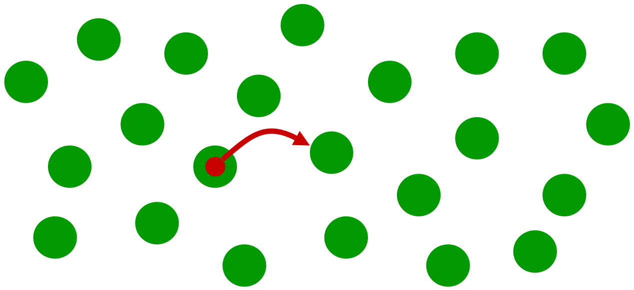
Hopping sites are well-defined

Control over the average distance between hopping sites

Hopping transport



poly(*N*-vinylcarbazole) (PVK)



$\nu_{ij} \sim exp\text{-}(R_{ij})$

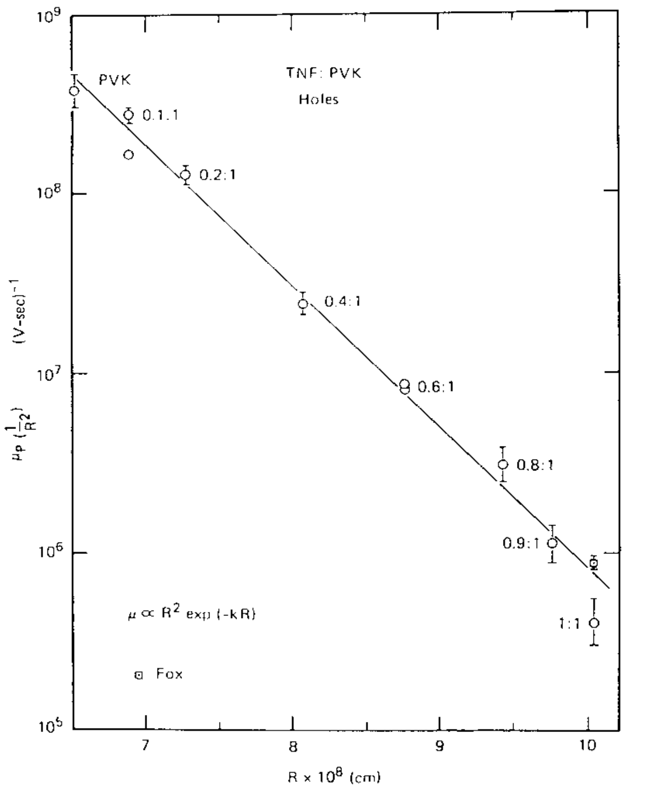
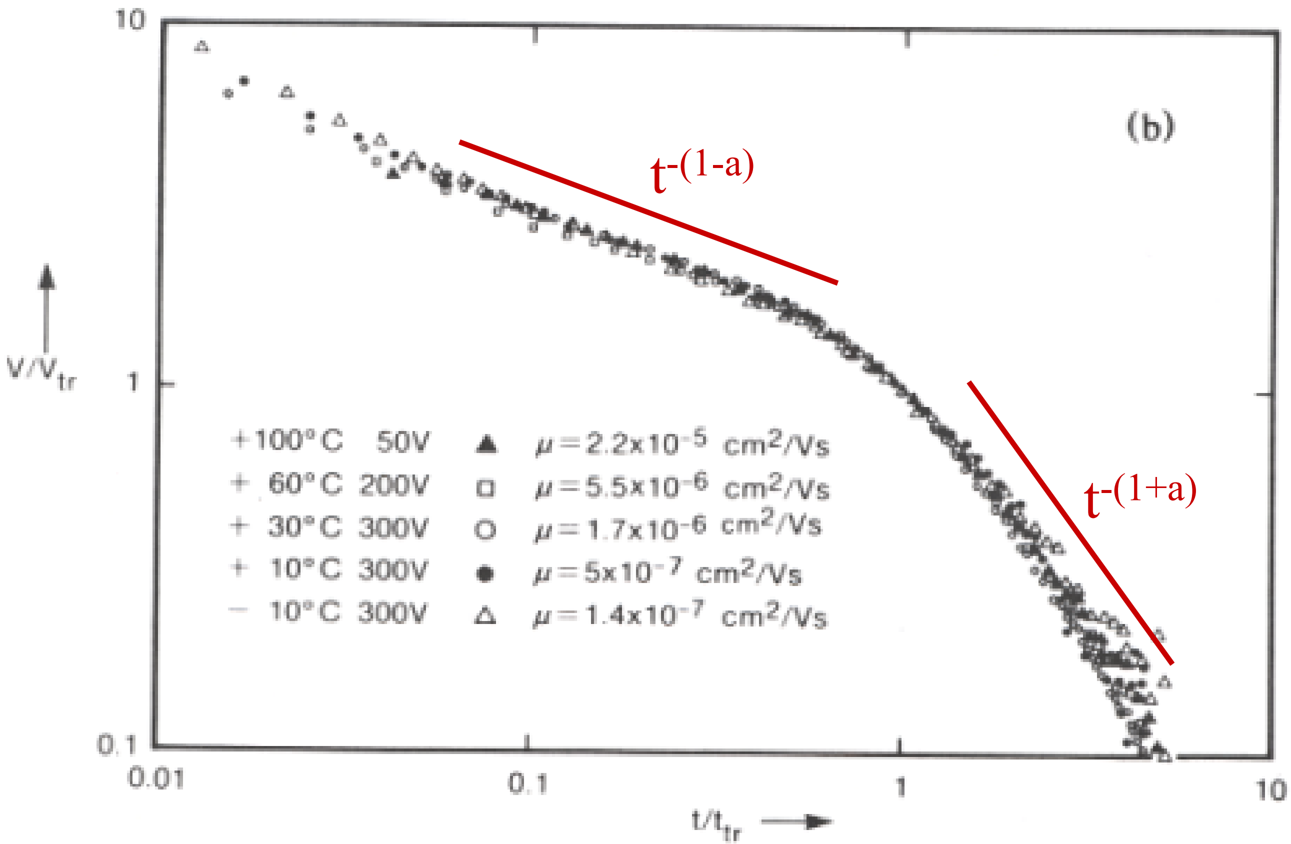


FIG. 9. Hole mobility plotted as a function of the average separation of uncomplexed vinylcarbazole units. A hopping mechanism for hole transport is indicated by the good fit to the functional form of Eq. (3).

W.D. Gill, *J. Appl. Phys.* **43**, 5033 (1972).

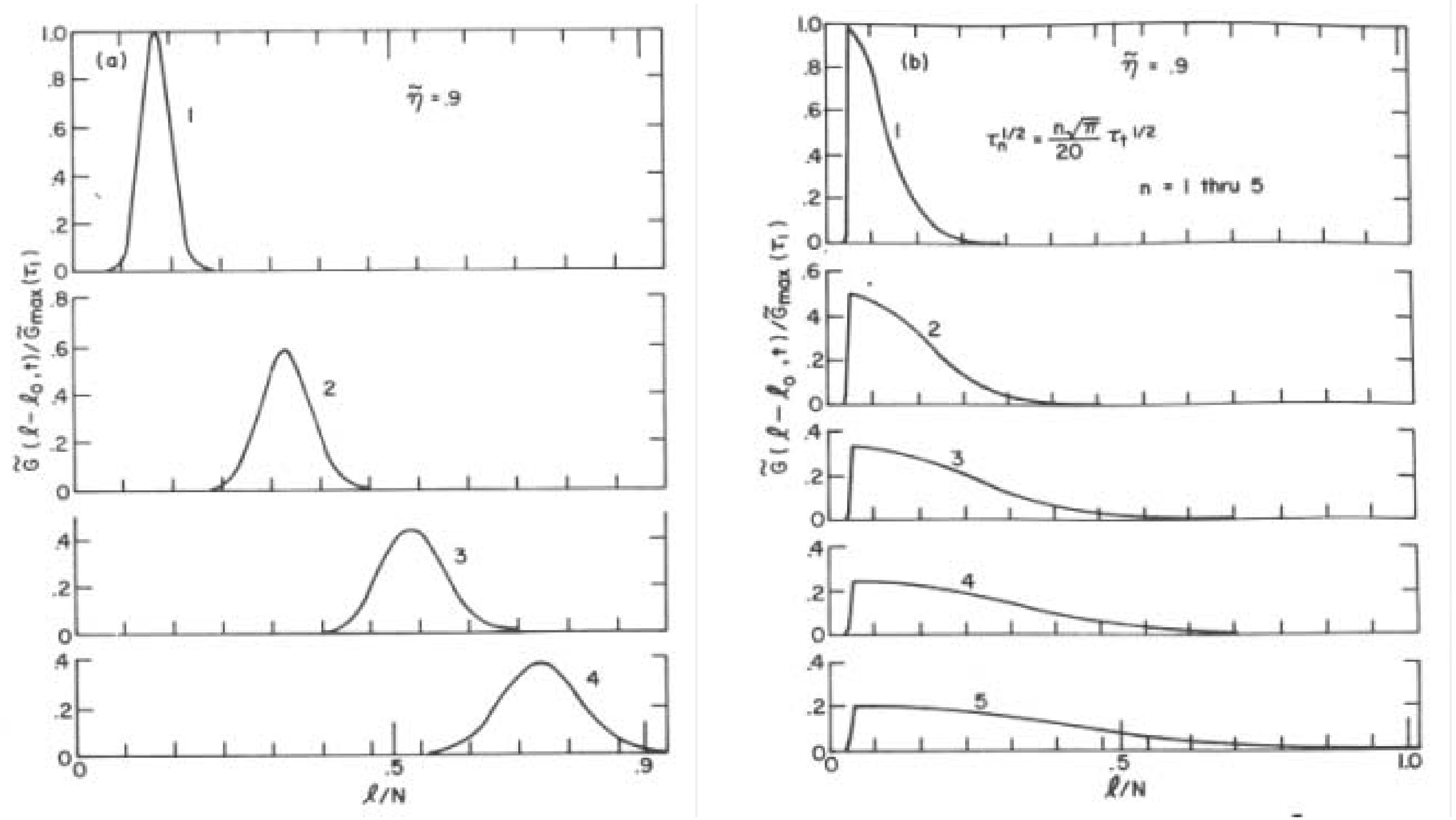
Dispersive transport and universality



a=0.66

F.C. Bos and D.M. Burland, *Phys. Rev. Lett.* **58**, 152 (1987).

Disorder formalism (I)



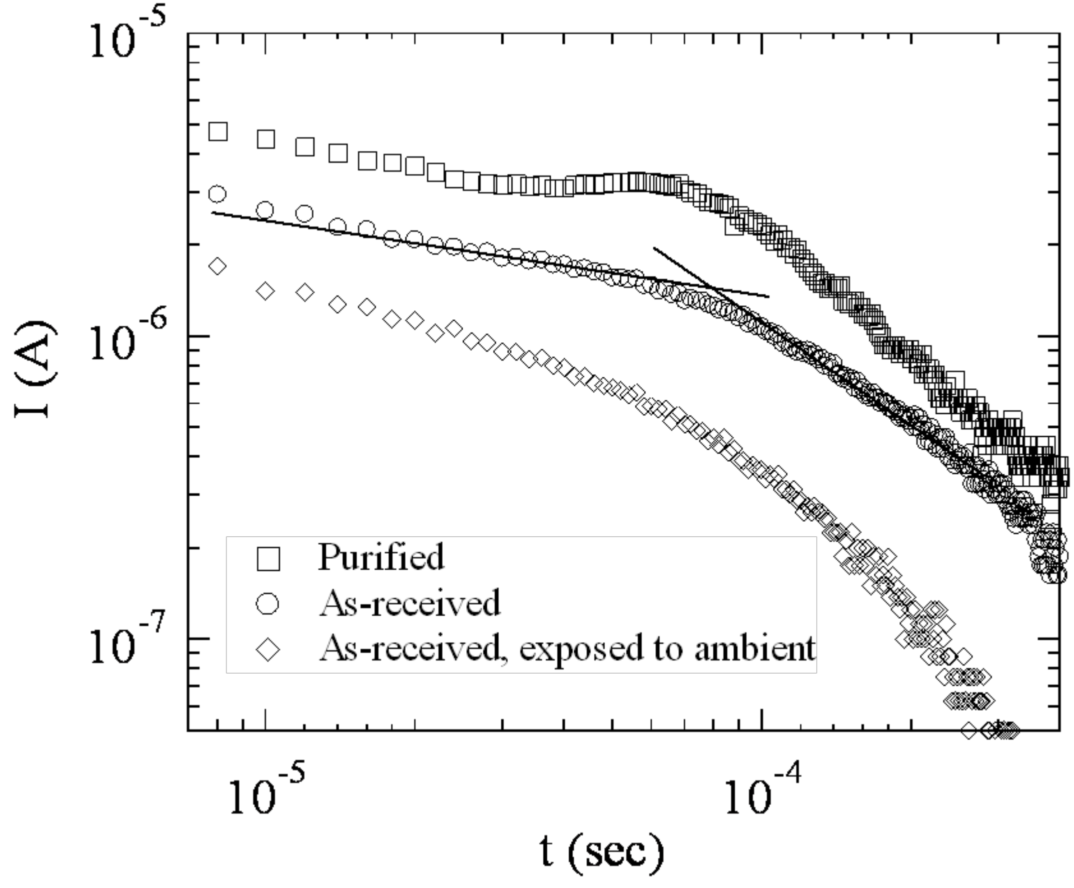
H. Scher and E.W. Monrtoll, *Phys. Rev. B* **12**, 2455 (1975).

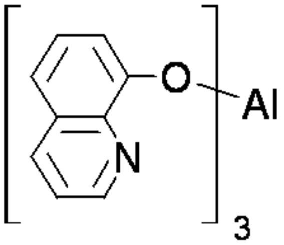
Disorder formalism (II)

Gaussian transport	Disorder formalism
$\psi(t) \sim e^{-t/\tau}$	$\psi(t) \sim t^{-(1+a)}$ $(0<a<1)$
$<l> \sim t$	$<l> \sim t^{a}$
$\sigma \sim t^{1/2}$	$\sigma \sim t^{a}$
$\sigma/<l> \sim t^{-1/2}$	$\sigma/<l> \sim$ const.
	Universality!

H. Scher and E.W. Monrtoll, *Phys. Rev. B* **12**, 2455 (1975).

Effect of traps



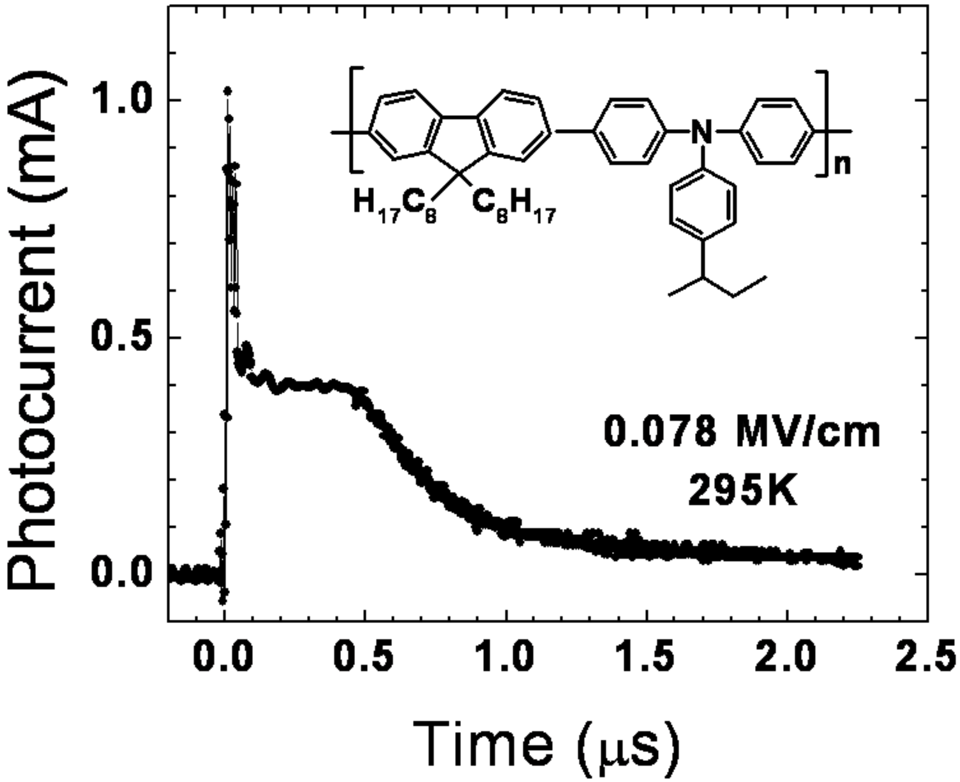


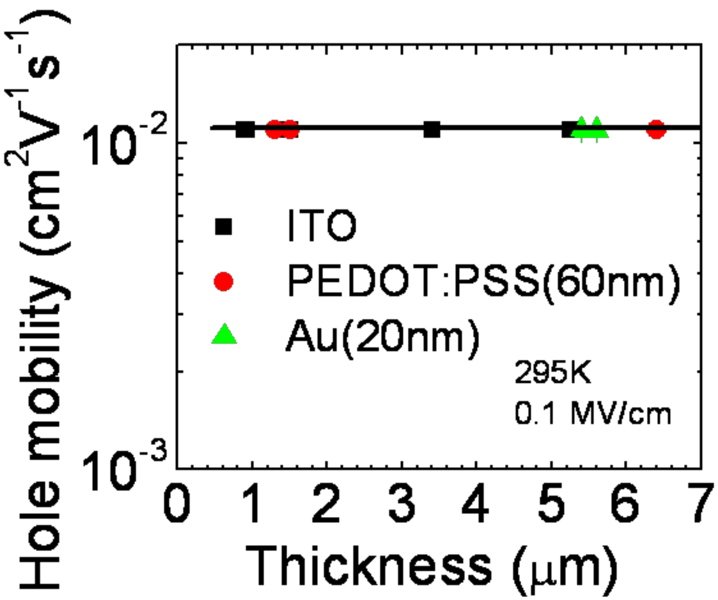
Alq_3

G.G. Malliaras *et.al.*, *Appl. Phys. Lett.* **79**, 2582 (2001).

Non-dispersive hole transport in TFB

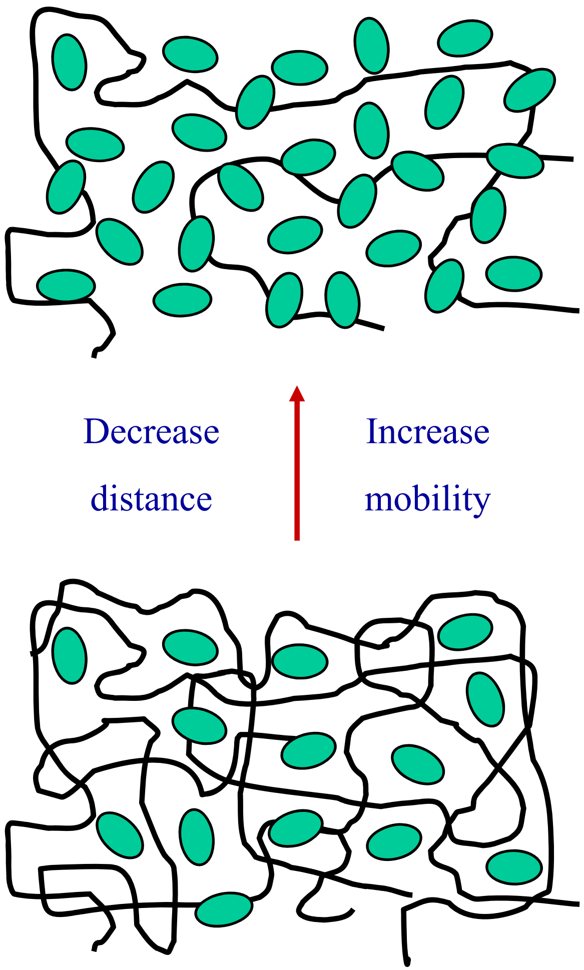
ITO/PEDOT:PSS(CH8000)/TFB(6.4μm)/Al





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

Transport in MPDs



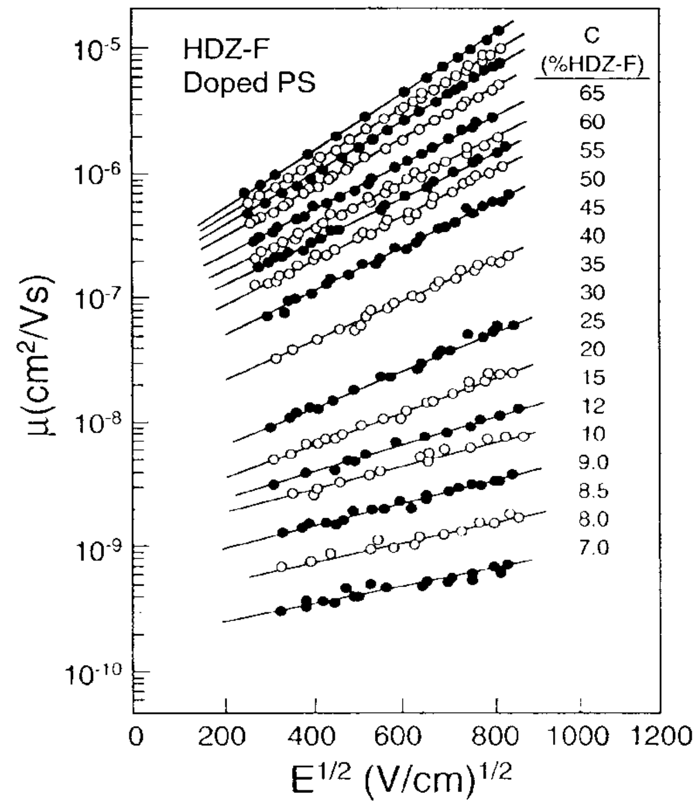
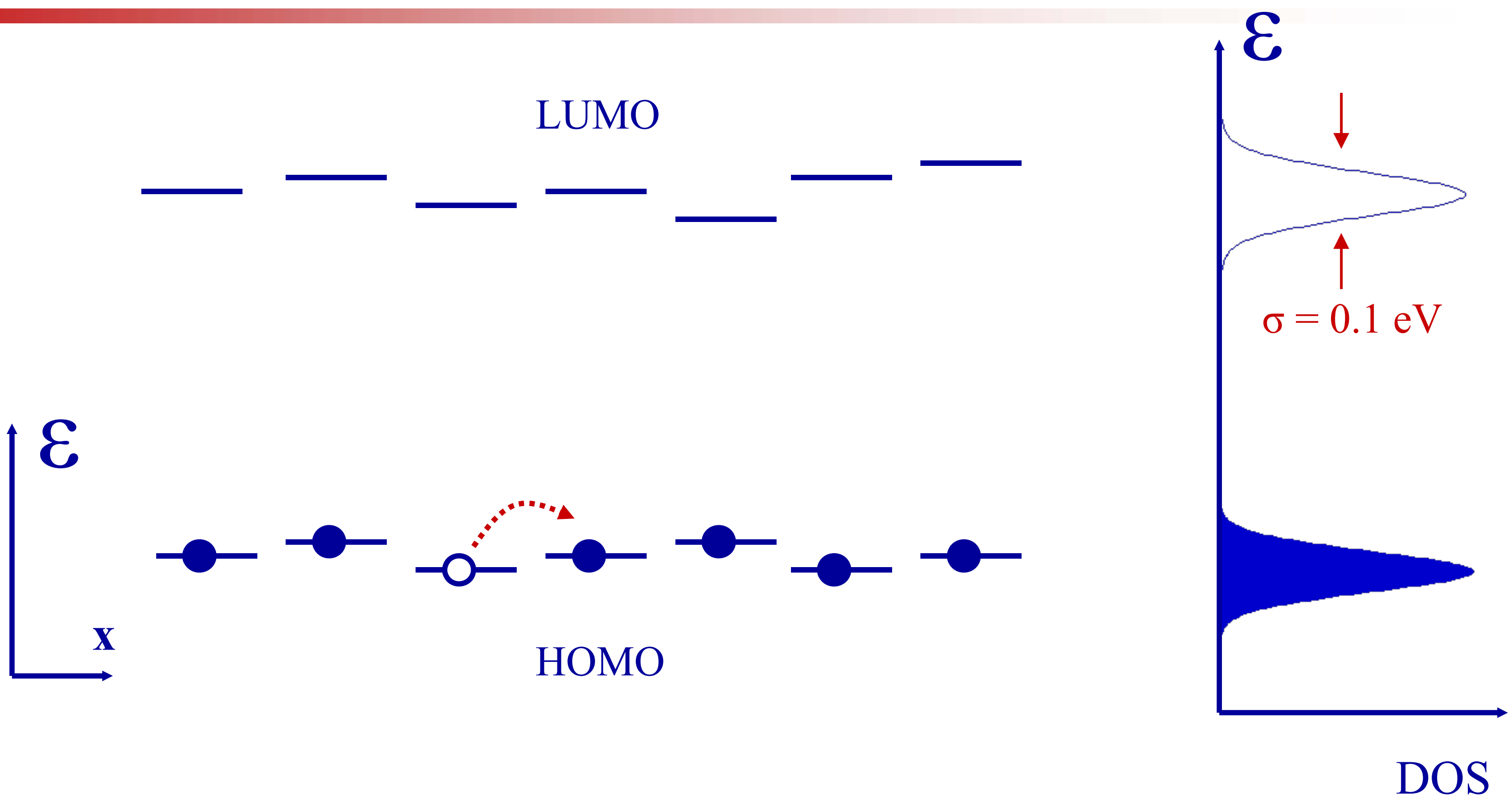


Fig. 2. The field dependencies of the room temperature mobilities for different HDZ-F concentrations.

P.M. Borsenberger *et al.*,
Jpn. J. Appl. Phys. **37** (1998)

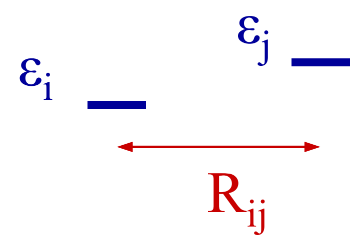
Gaussian disorder model



- Energetic disorder
- Positional disorder

Gaussian disorder model (II)

Density of states:



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

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)

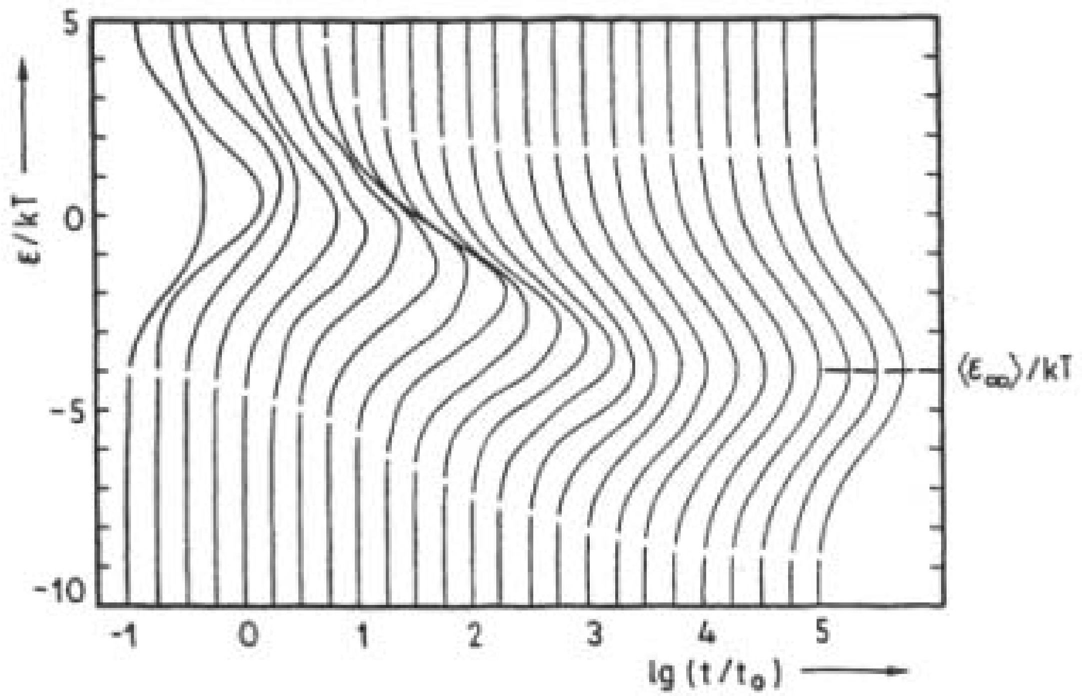


Fig. 2. Temporal evolution of the distribution of carrier energies in a Gaussian DOS of width $\hat{\sigma} = 2$. All profiles are broken at the same carrier density illustrating the different relaxation patterns for mobile and immobile carriers. ε_∞ denotes the theoretical mean energy in the long-time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

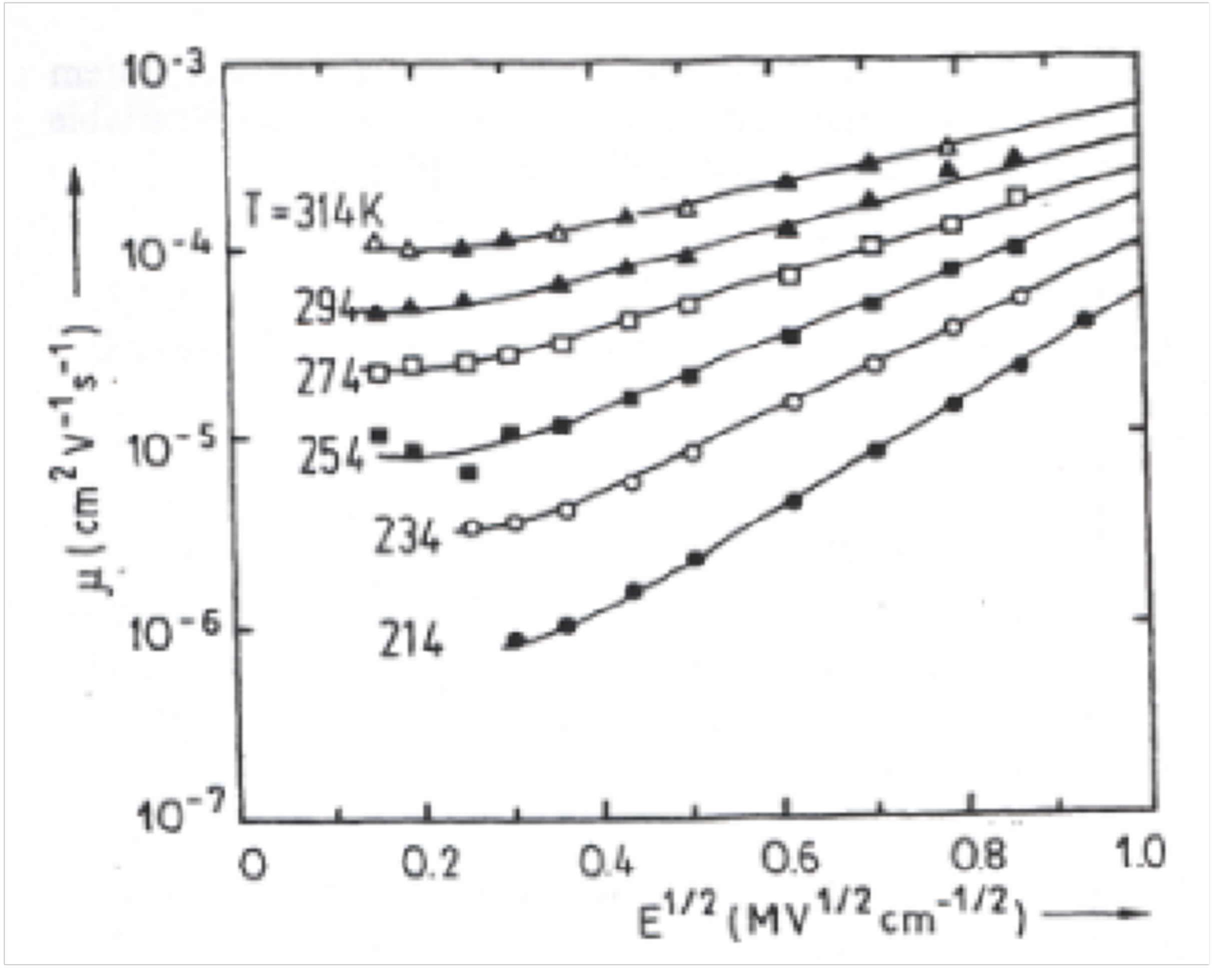
Carriers relax at:

σ^2/kT

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

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

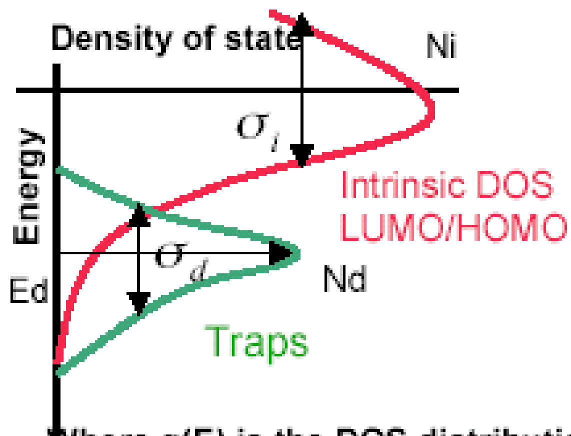
Comparison with experiment



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

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]:



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

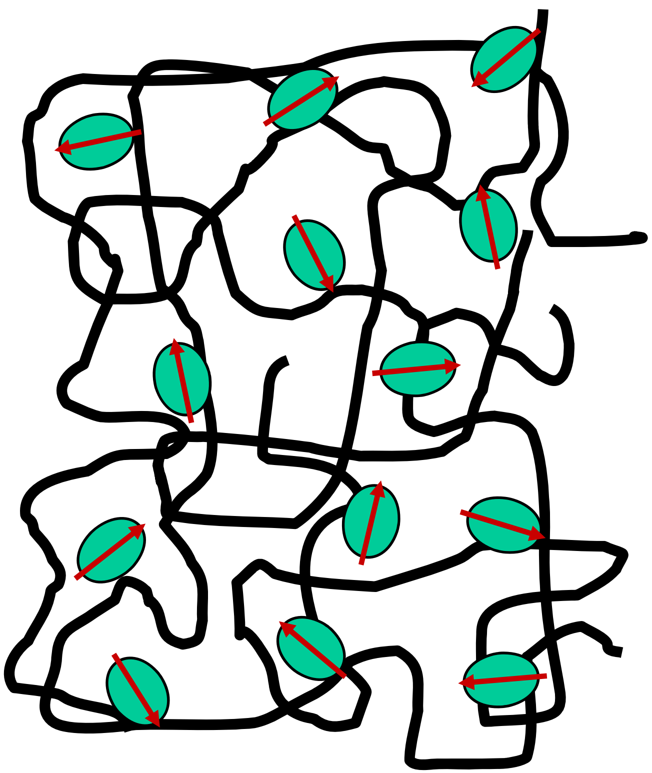
$$g(E) = \frac{N_i}{\sqrt{2\pi}\sigma_i}\exp\left(\frac{-E^2}{2\sigma_i^2}\right) + \frac{N_d}{\sqrt{2\pi}\sigma_d}\exp\left(\frac{-(E+E_d)^2}{2\sigma_d^2}\right)$$

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.

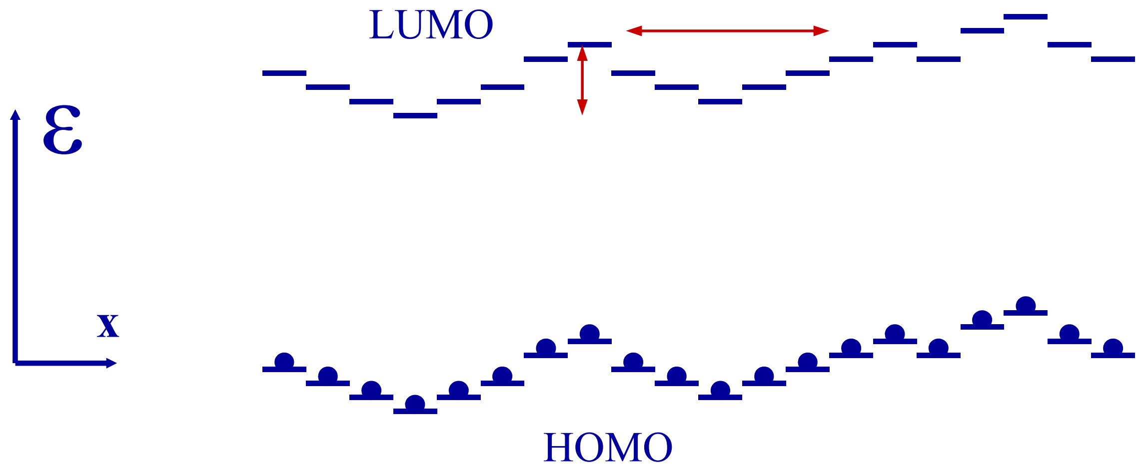
Correlated disorder (I)



Molecules carry a large dipole moment.

Charge dipole interaction causes spatial correlation in the energy of hopping sites.

Correlated disorder (II)

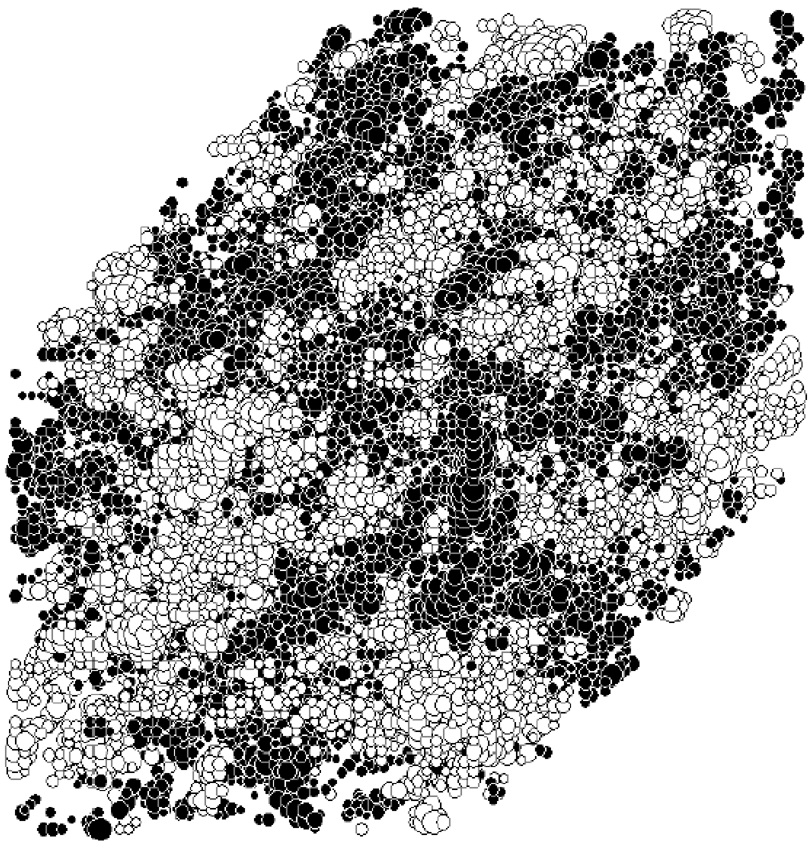


Deeper valleys are also wider.

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

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

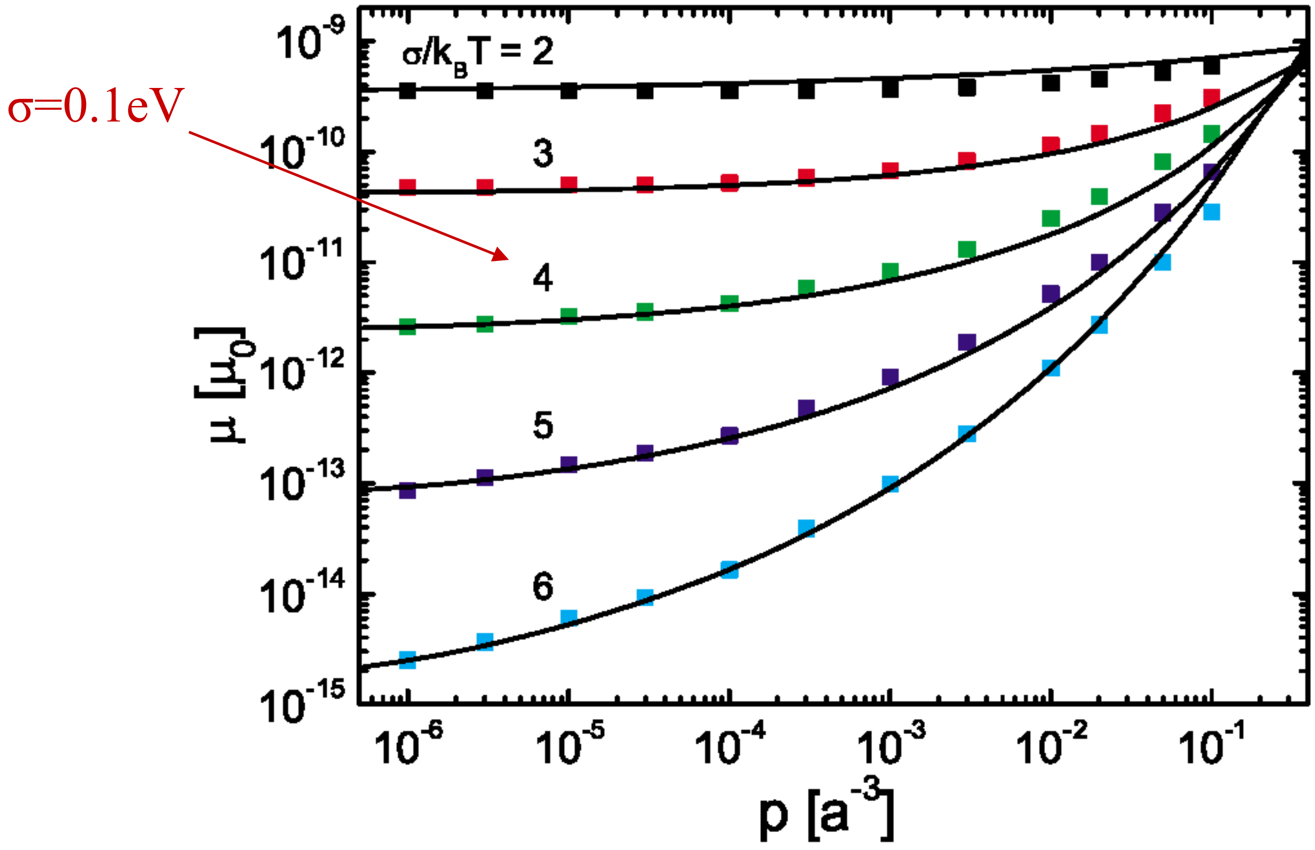
Correlated disorder (III)



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

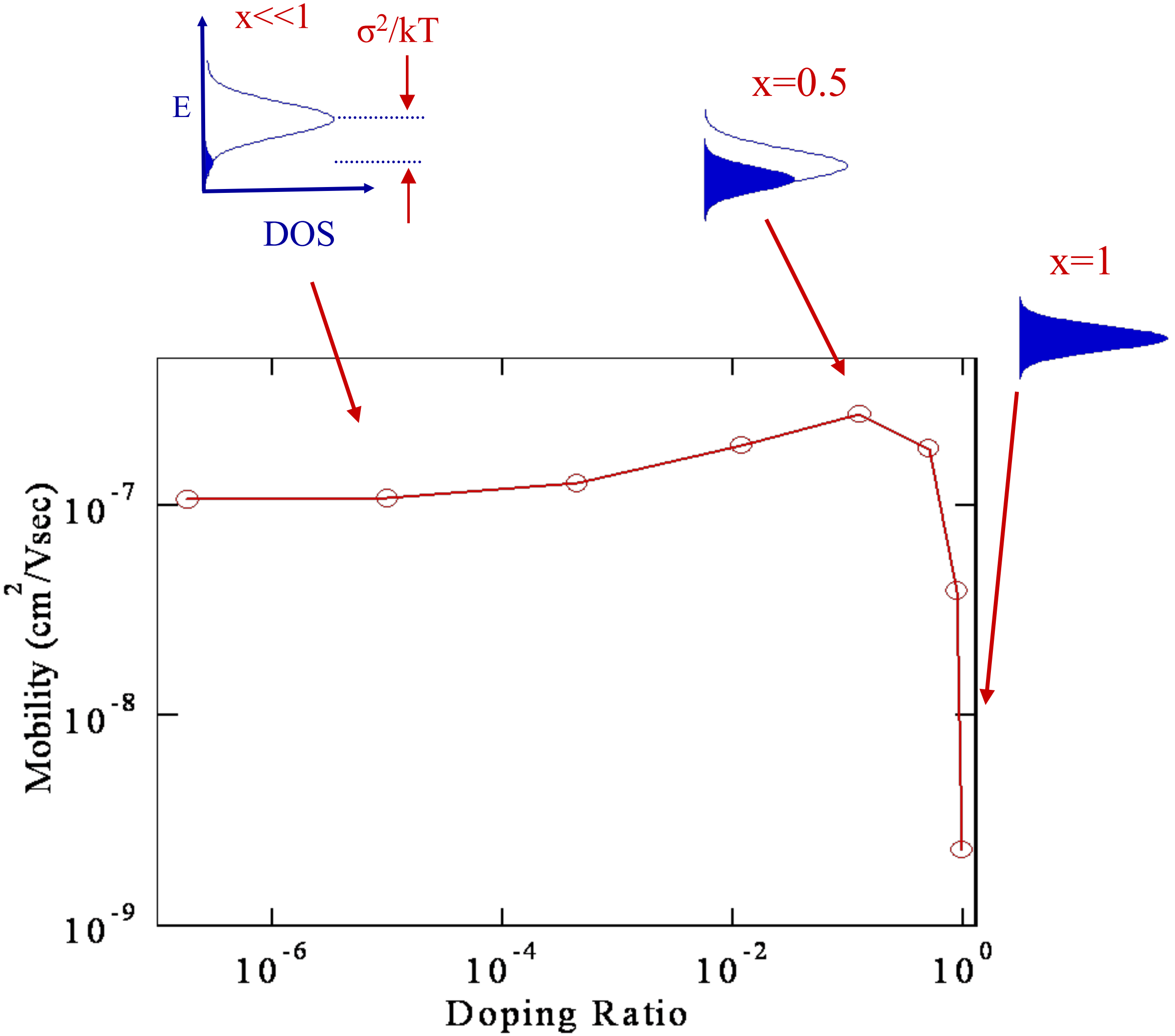
S.V. Novikov, *J. Polym. Sci. Part B: Polym. Phys.*, to appear.

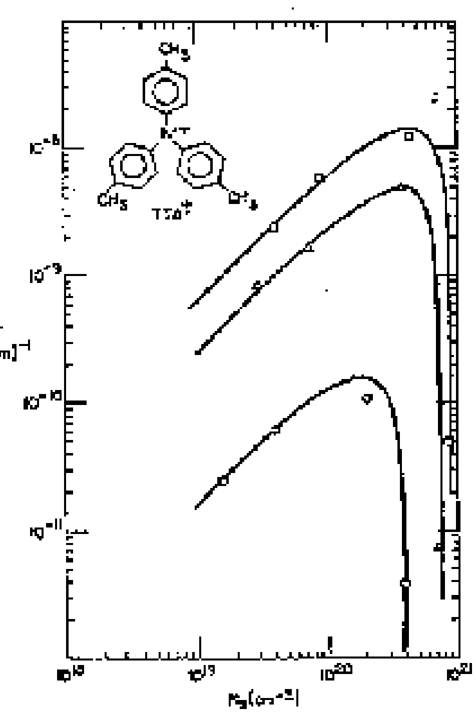
Mobility vs. change density



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).

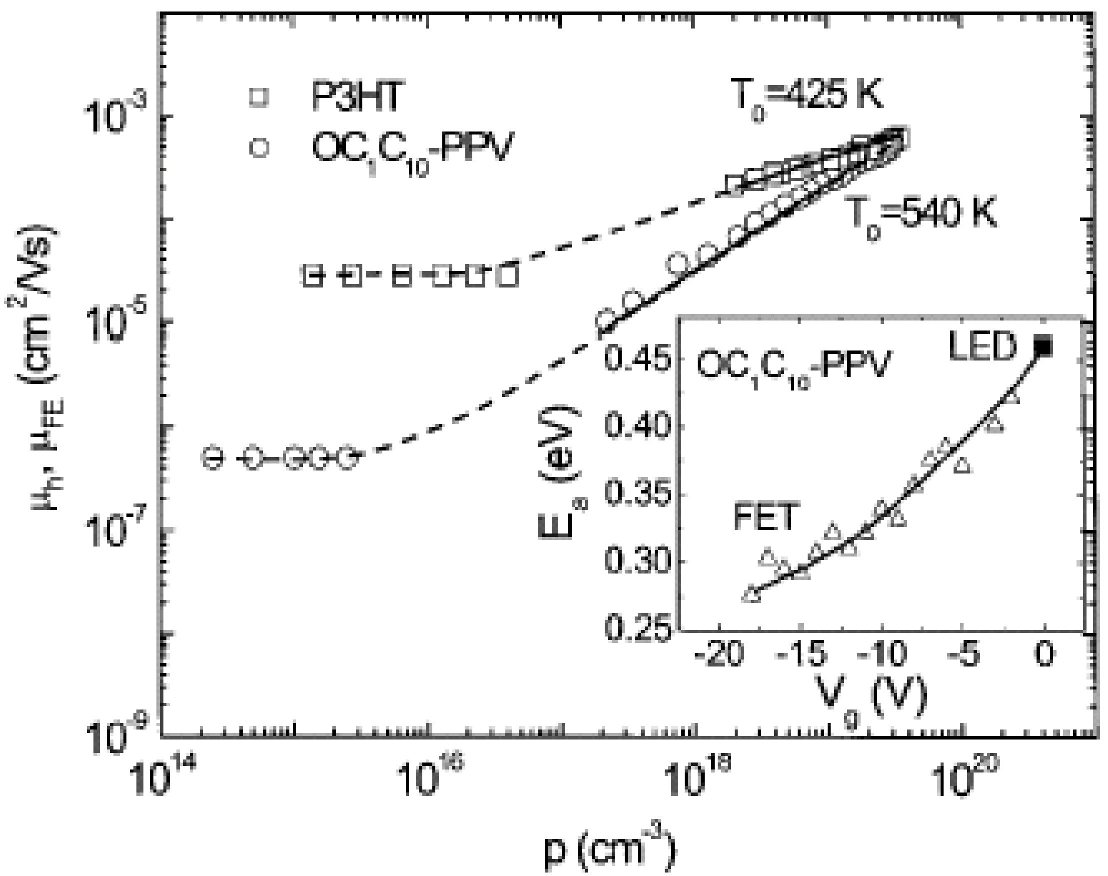
Manifold filling





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

Mobility vs. charge density (II)

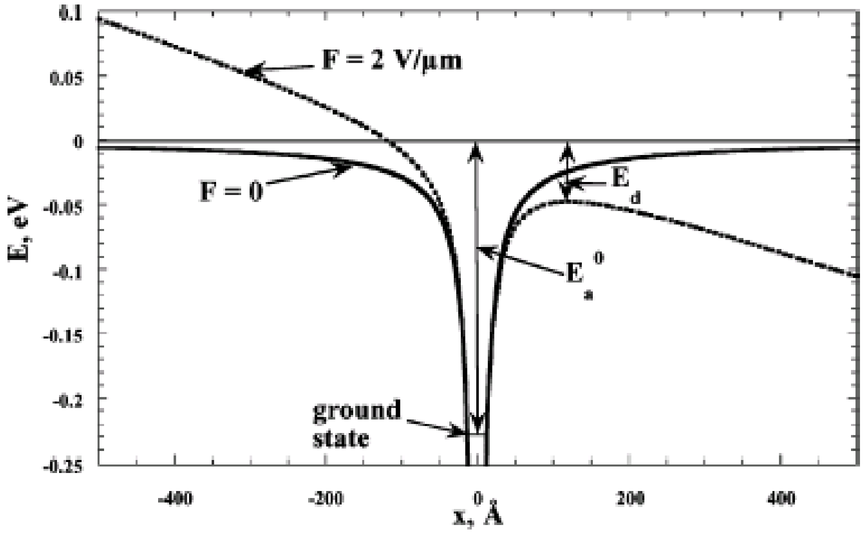


C. Tanase, E.J. Meijer, P.W.M. Blom, and D.M. de Leeuw, *Phys. Rev. Lett.* **91**, 216601 (2003).

Charge density vs. electric field

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

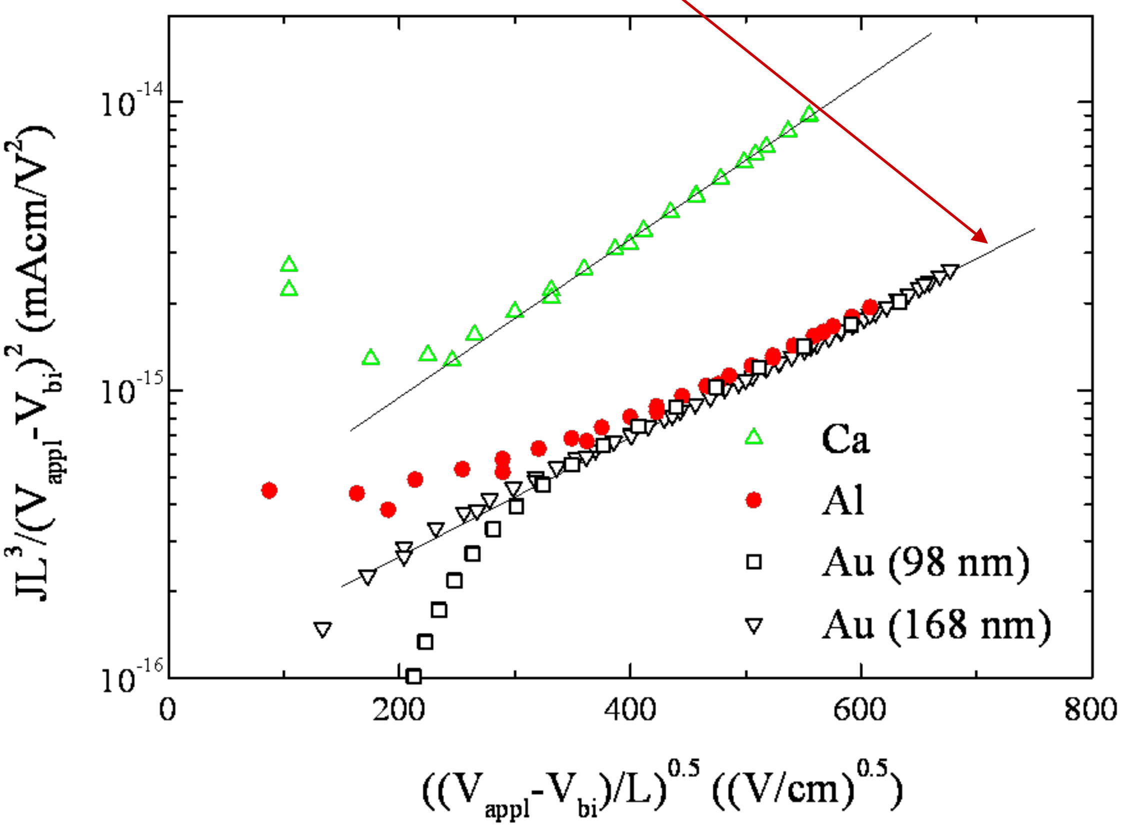
$$J = q\,\mu_n F n_d \exp\left(\frac{\left(-E_a^{\;0} + \left(\frac{q^3}{\pi\epsilon_0\epsilon}\right)^{1/2} F^{1/2}\right)}{kT}\right)$$



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

Charge density vs. electric field (II)

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



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

Cornell University

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	$\mu=\mu(n)$	√

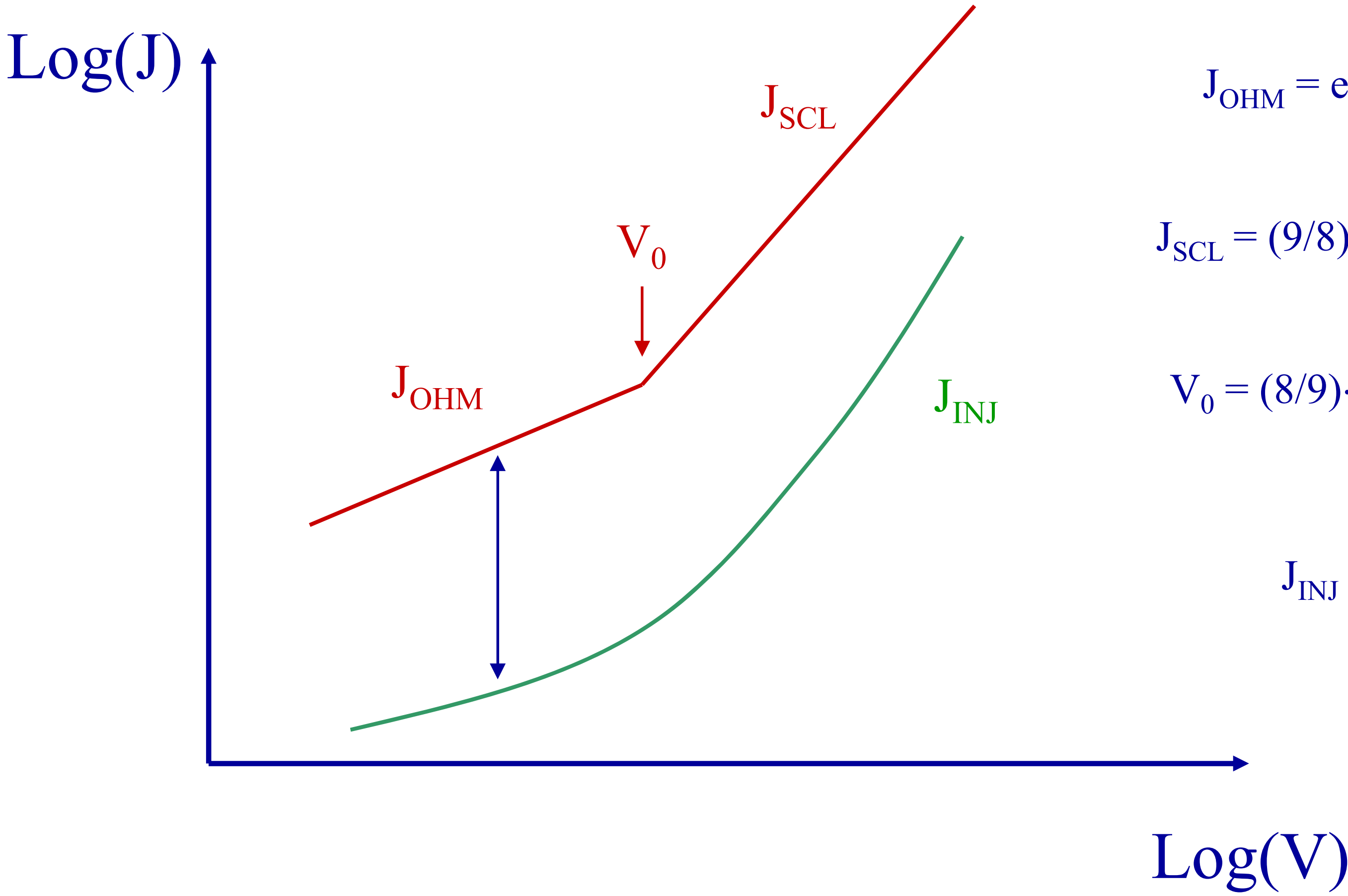
Charge generation:

Electric field dependence of charge density	$n=n(E)$	?

Outline

- Organic semiconductors and devices
- Charge injection and transport processes
- Charge transport in organic semiconductors
- Charge injection in organic semiconductors
- Conclusions

Injection vs. transport



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

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

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

$J_{INJ} = ???$

Figure of merit: $\eta = J_{INJ} / J_{MAX}$

Definition of an ohmic contact

A contact that satisfies the

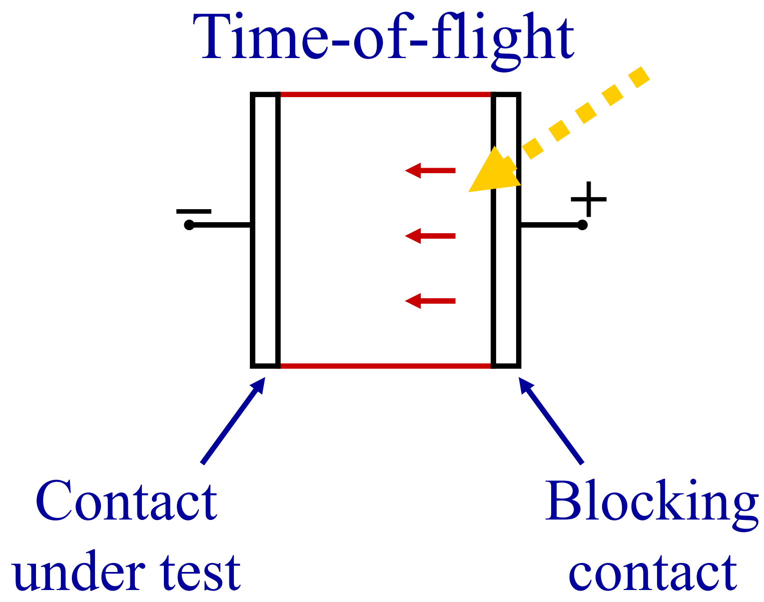
demands of the bulk for current.

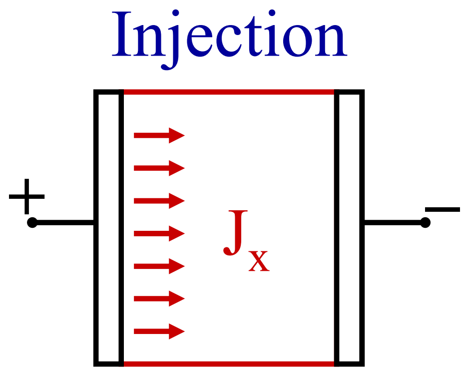
$$\eta = 1$$

See: Y. Shen, A. Hosseini, M.H. Wong, and G.G. Malliaras, "How to make ohmic contacts to organic semiconductors", *ChemPhysChem*. **5**, 16 (2004).

Separation of injection and transport (I)

- Trap-free hole transporter
- Measure mobility → Calculate J_{SCL} $(= (9/8)\cdot\varepsilon\cdot\varepsilon_0\cdot\mu\cdot V^2/L^3)$
- Measure injected current J_{INJ}





$$\eta = J_{INJ} / J_{SCL}$$

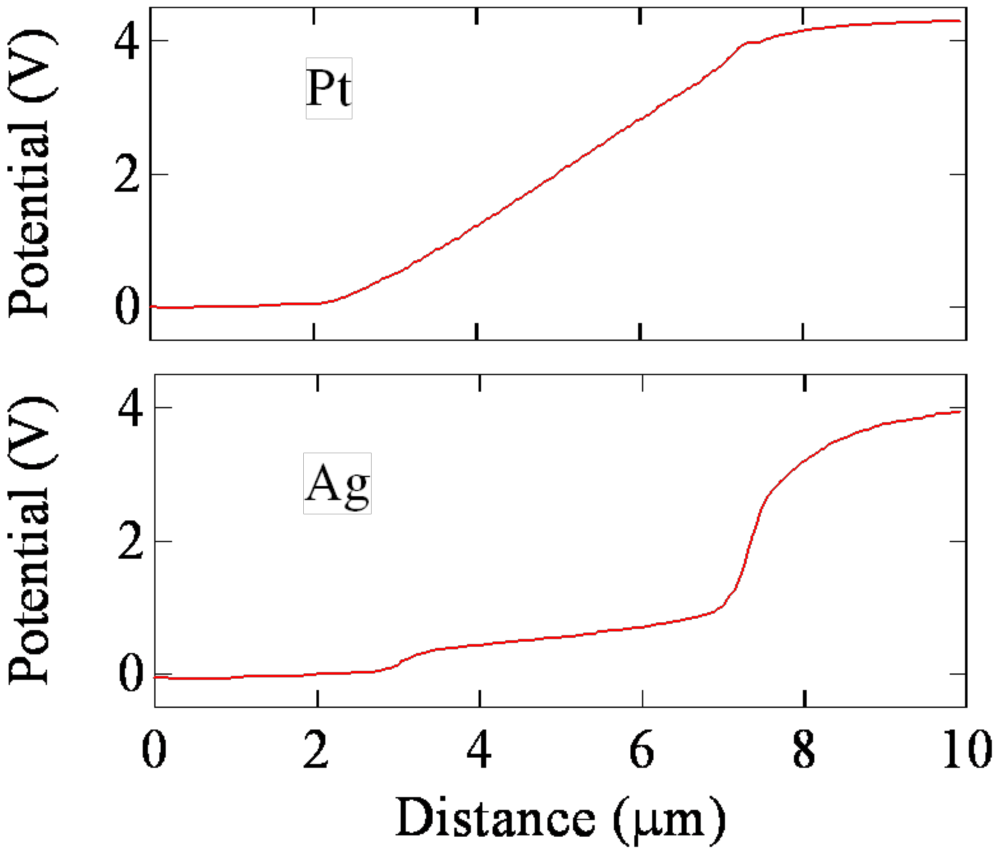
M. Abkowitz *et.al.*, *J. Appl. Phys.* **83**, 2670 (1998).

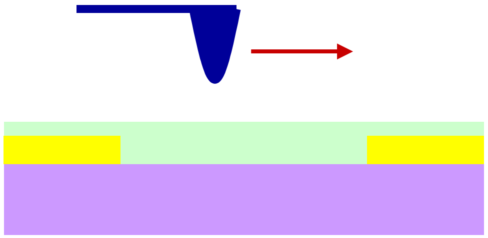
Separation of injection and transport (II)

- Measure J_{OHM} using Ohmic contact
- Compare with current from unknown contact

$$\eta = J_{INJ} / J_{OHM}$$

Separation of injection and transport (III)





Pt makes an ohmic contact to PC:TPD. Ag does not.

Hierarchy of injection models

Mechanism:

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

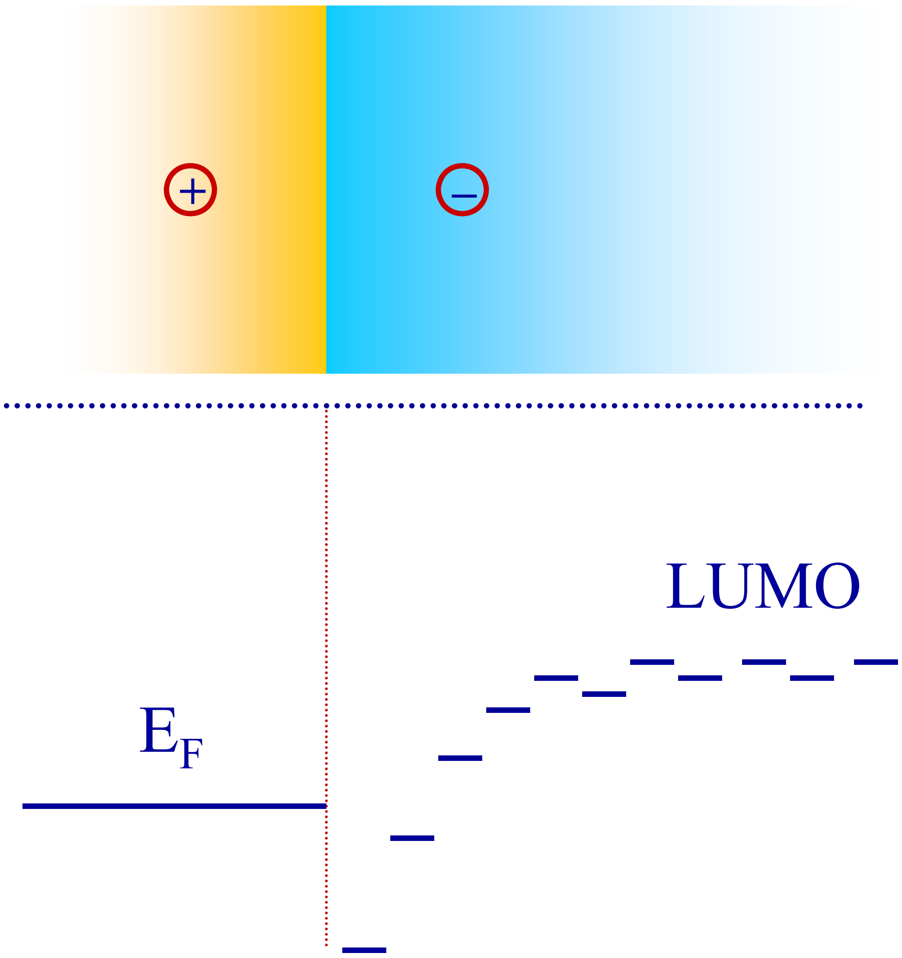
First order corrections:

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

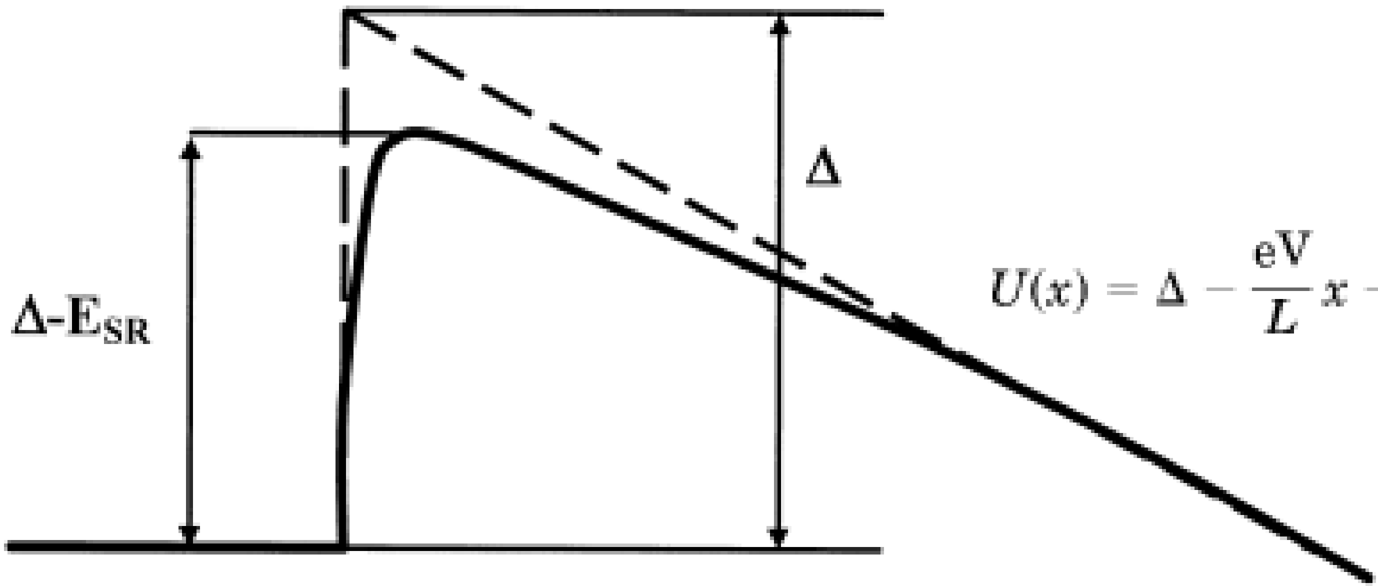
Disorder:

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

Image force



Barrier lowering



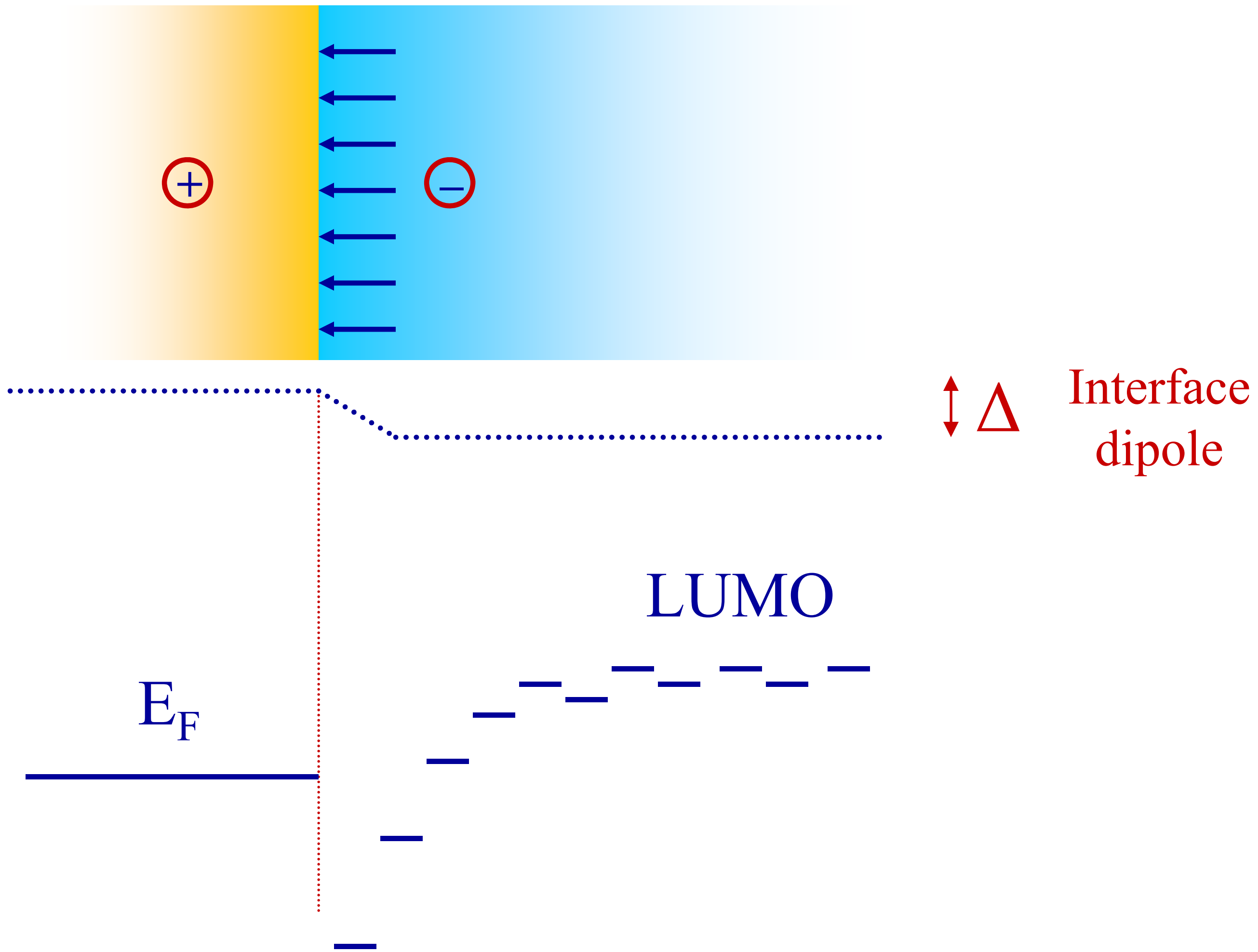
$$U(x) = \Delta - \frac{eV}{L}x - \frac{e^2}{16\pi\varepsilon\varepsilon_0 x}$$

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

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

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

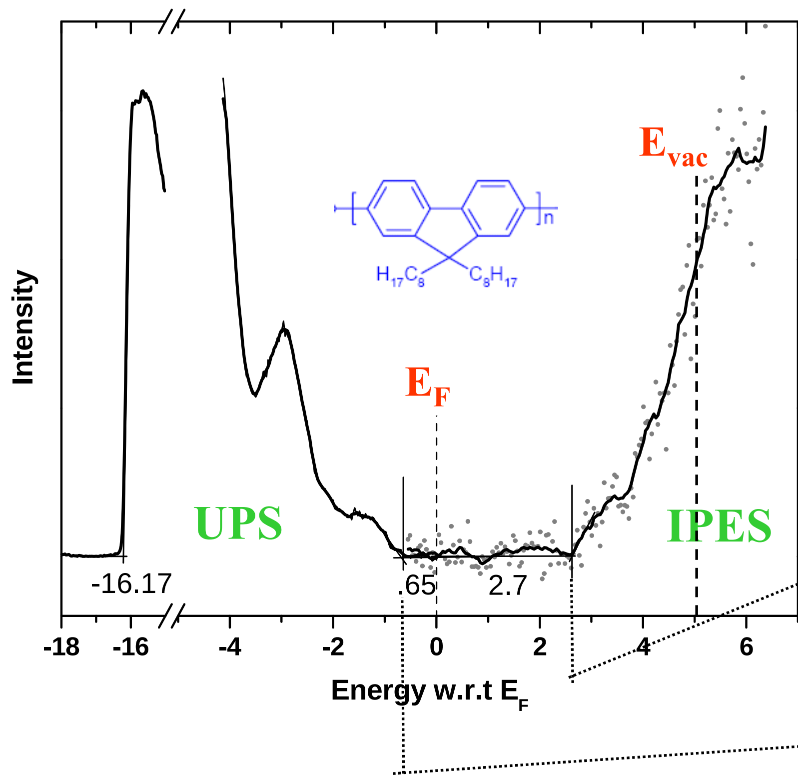
Interface dipole

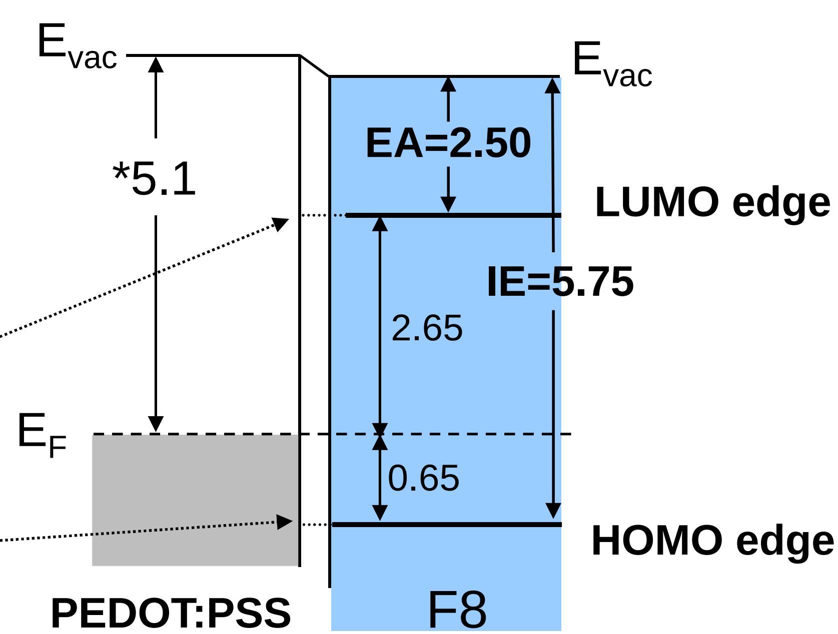


X. Crispin *et.al.*, *J. Am. Chem. Soc.* **124**, 8131 (2002).

Energetics at the contact

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



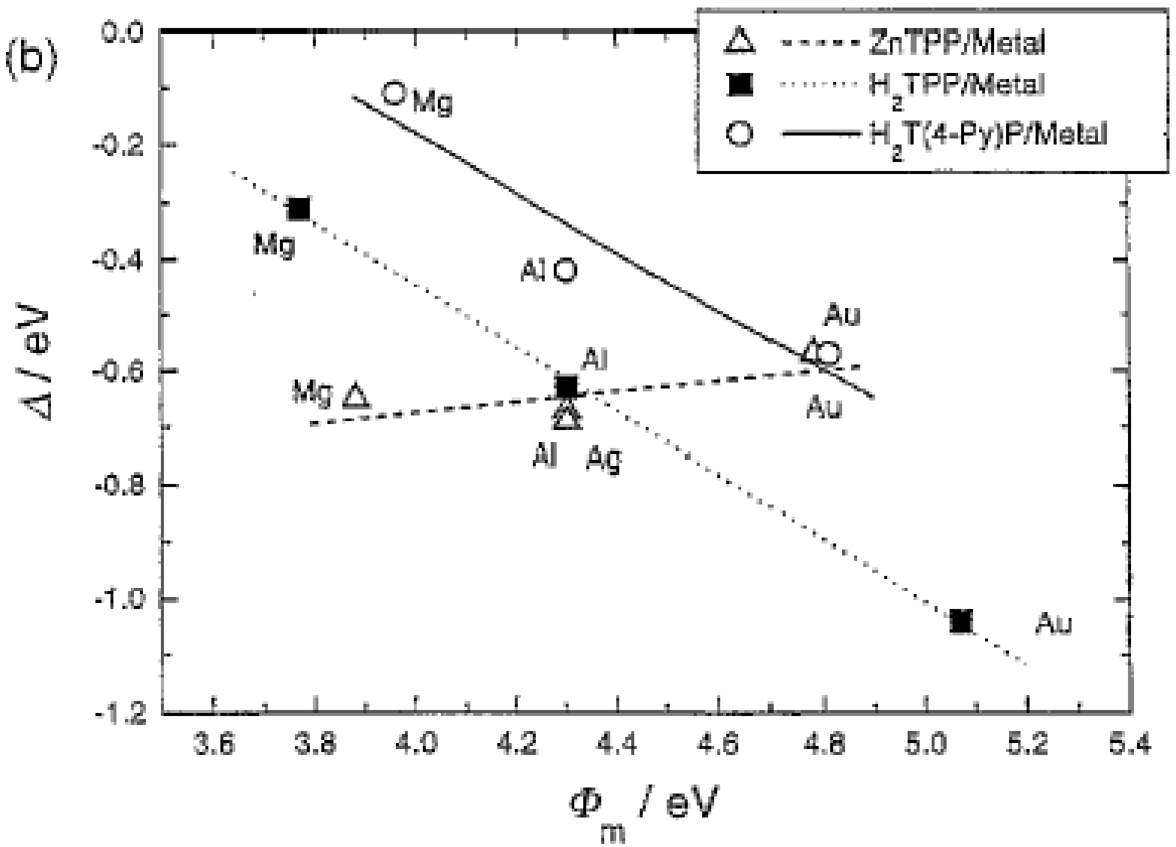


(energies in eV)

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

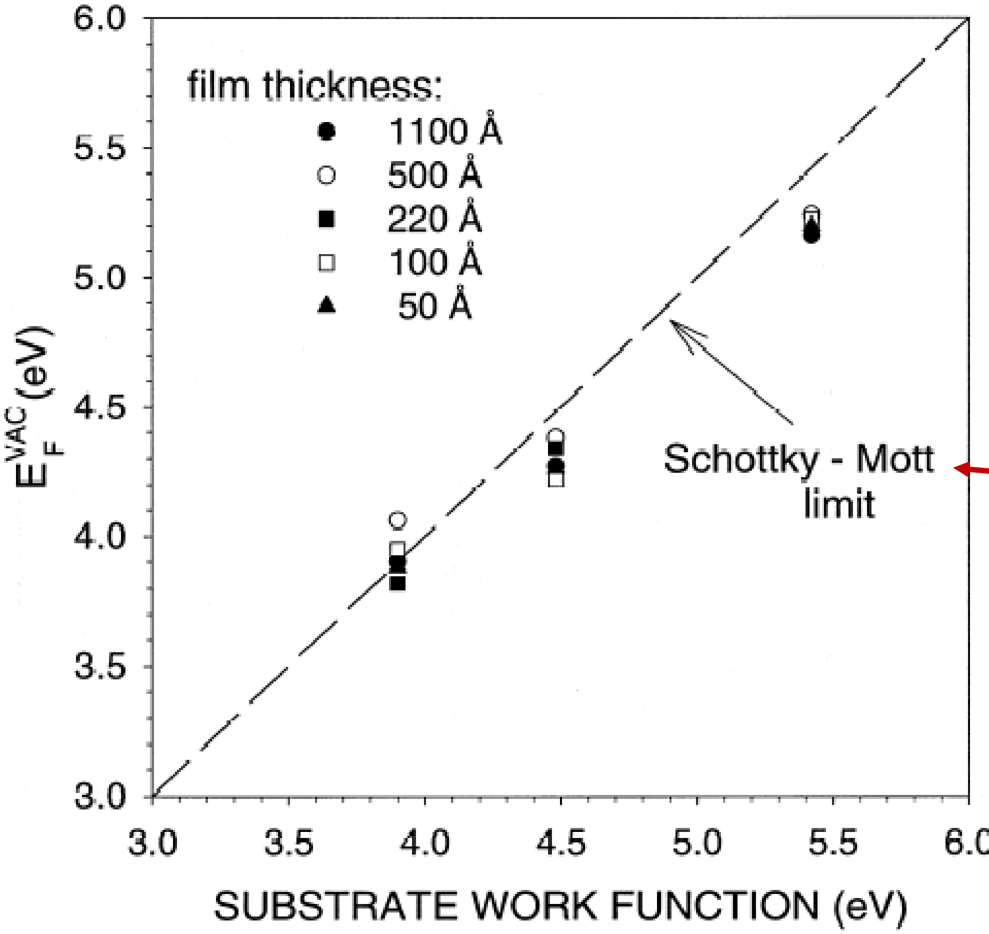
Kahn group - Princeton

Magnitude of the dipole



K. Seki *et.al.*, *Synth. Metals* **91**, 137 (1997).
Also: I.G. Hill *et.al.*, *Appl. Phys. Lett.* **73**, 662 (1998).

Magnitude of the dipole (II)



$\Delta = 0$

G. Greczynski *et. al.*., *Chem. Phys. Lett.* **321**, 379 (2000).

Observation

"Surface science" vs. "realistic manufacturing conditions":

Interfaces prepared under UHV show large dipoles

(*i.e.* barrier cannot be calculated if E_F, LUMO is known)

Interfaces prepared in ambient show negligible dipoles

(*i.e.* barrier scales with metal work function)

Influence on injection

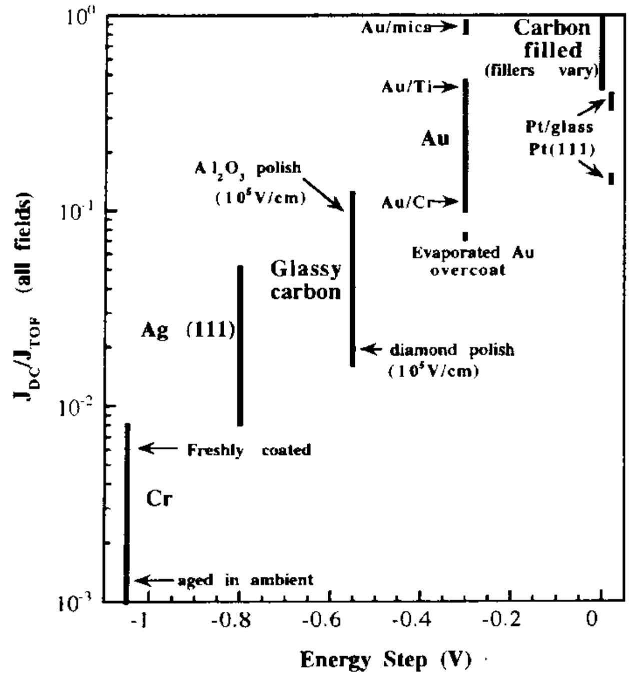
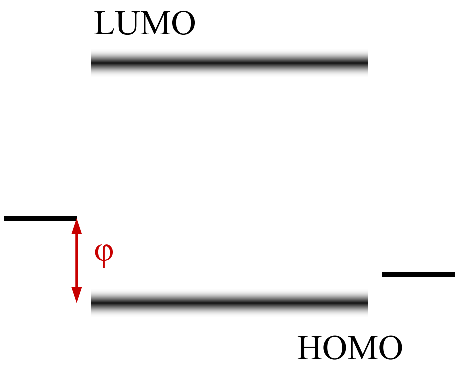


FIG. 6. Hole injection efficiency figure of merit for substrate contacts of varying work function vs. energy step across the contact polymer interface estimated from published work function data and electrochemical redox potential data. The height of each bar reflects the variability in injection efficiency due primarily to variation in substrate surface pretreatment and for the particular case of Au, diffusion to the interface of metal atoms from underlying binder layers.



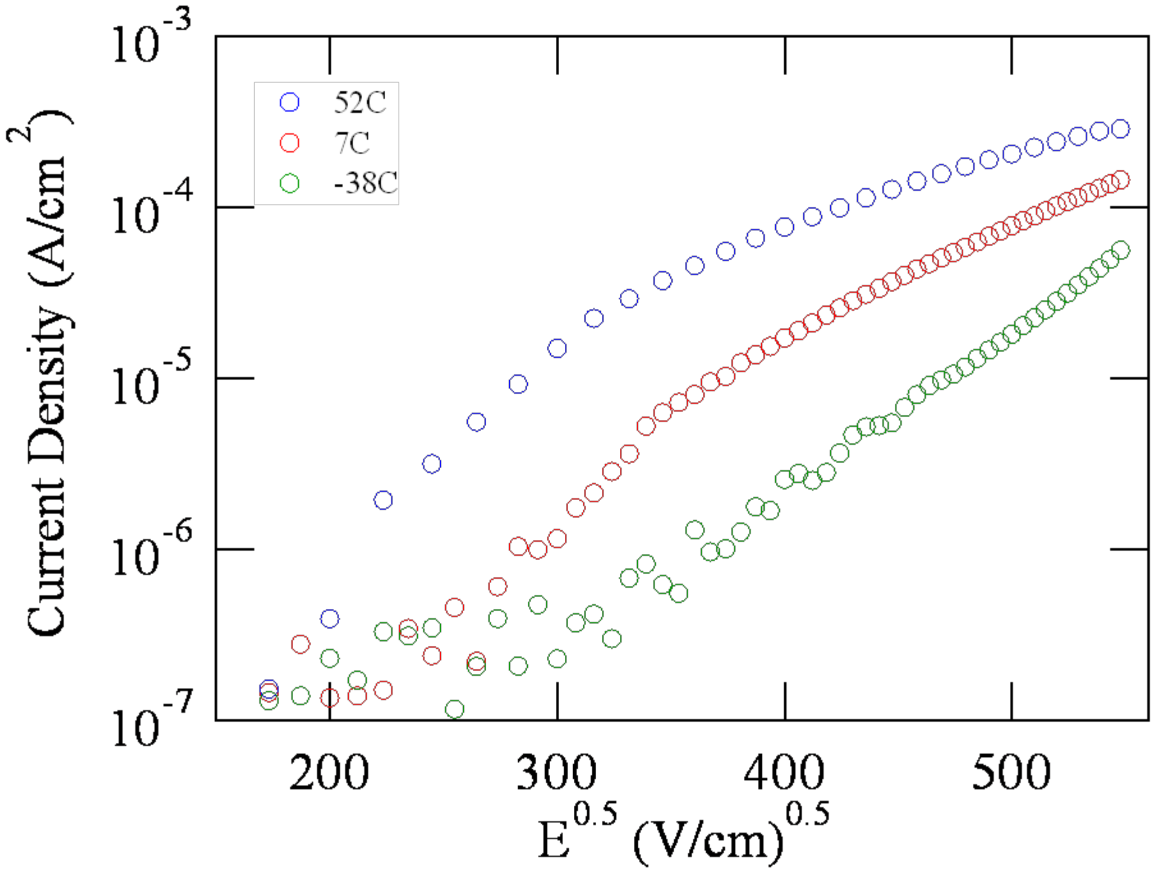
From:

M. Abkowitz *et.al.*,

J. Appl. Phys. **83**, 2670 (1998).

Energetics dominates injection

Field dependence of injection



PEDOT:PSS/PFO

Injection in low mobility materials

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)

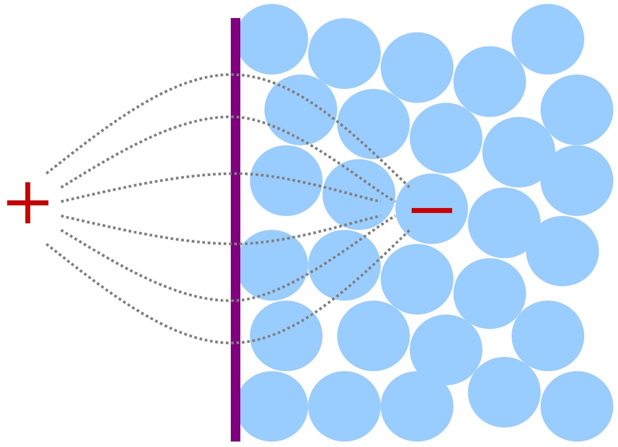
Recombination with image charge

$$J = C\,exp(-\varphi_B/kT) - e n_0 S(E)$$

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

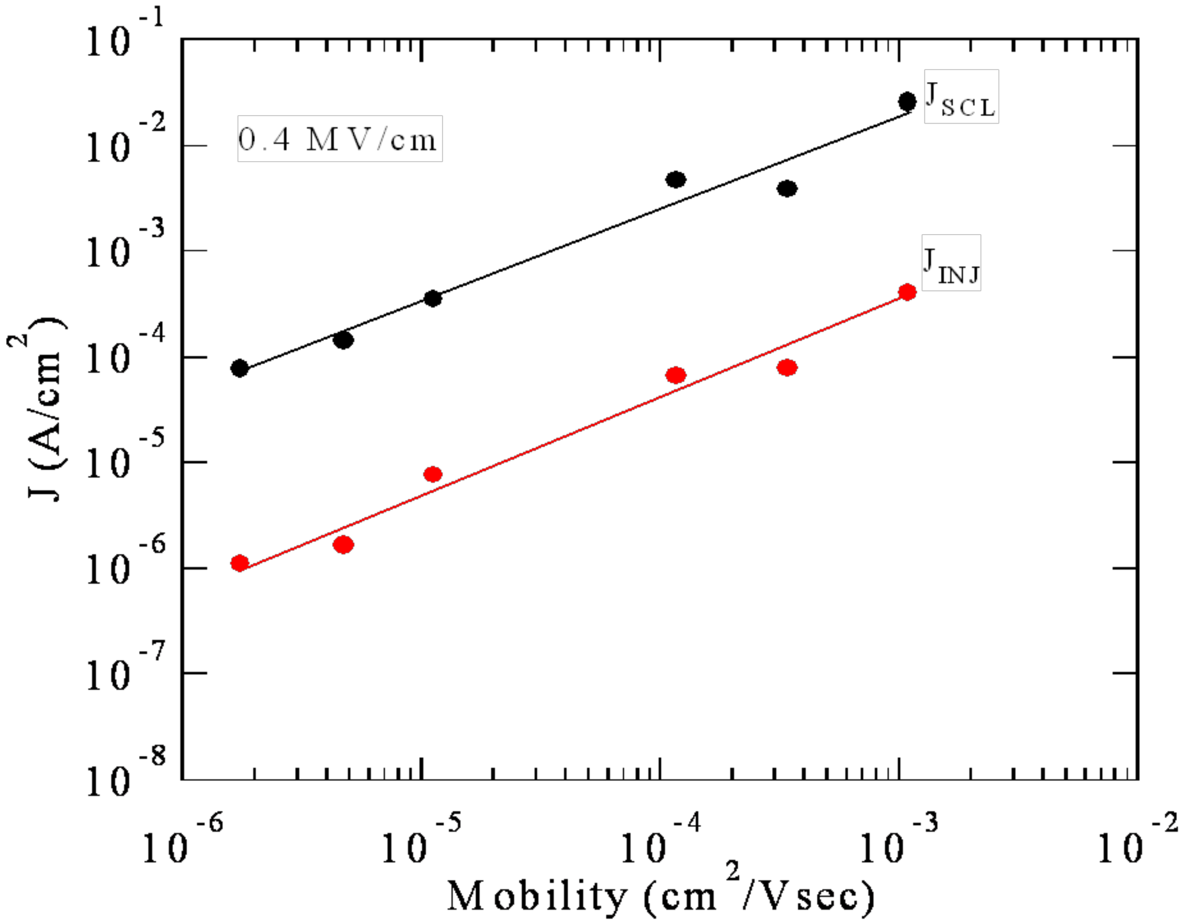
$$C = 16\pi\varepsilon\varepsilon_0 N_0 (kT)^2 \mu / e^2$$

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



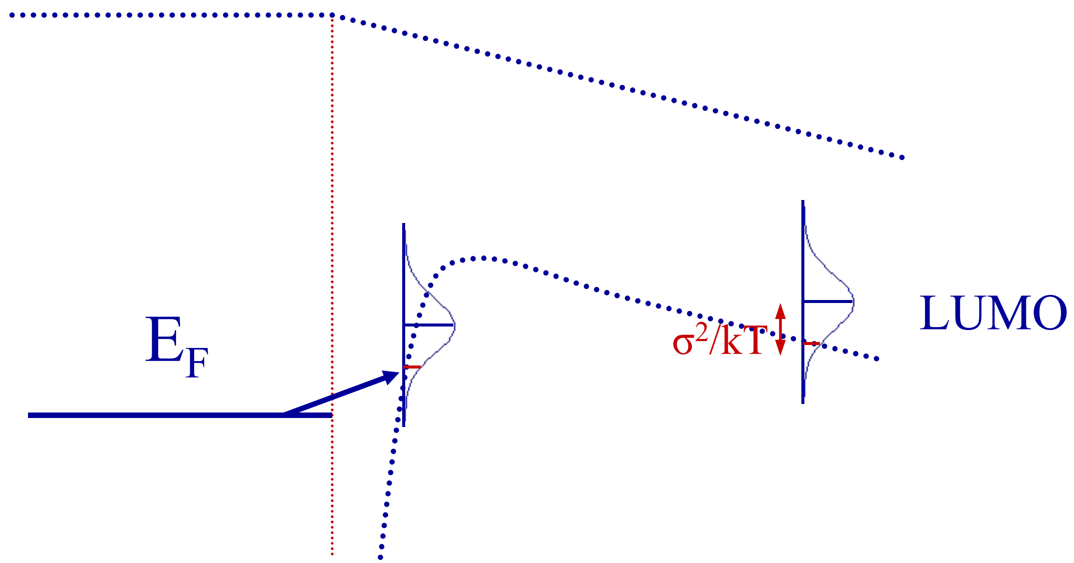
J.C. Scott and G.G. Malliaras, *Chem. Phys. Lett.* **299**, 115 (1999)

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

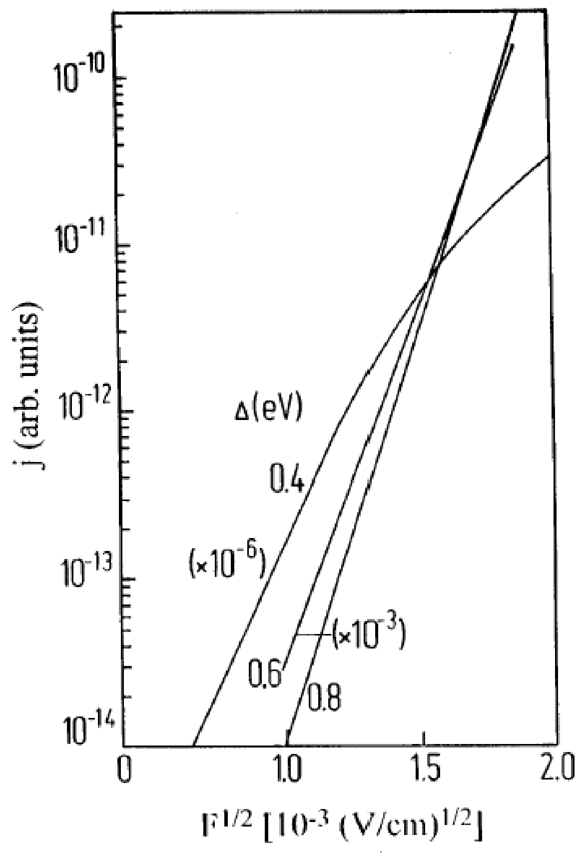


$$J_{Inj} = e \cdot \nu \cdot \int_a^\infty dx_0 \left[\exp(-2 \cdot \gamma \cdot x_0) \cdot w_{esp}(x_0)\right] \cdot \int_{-\infty}^\infty dE \left[Bol(E) \cdot g(U(x_0) - E)\right]$$

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).

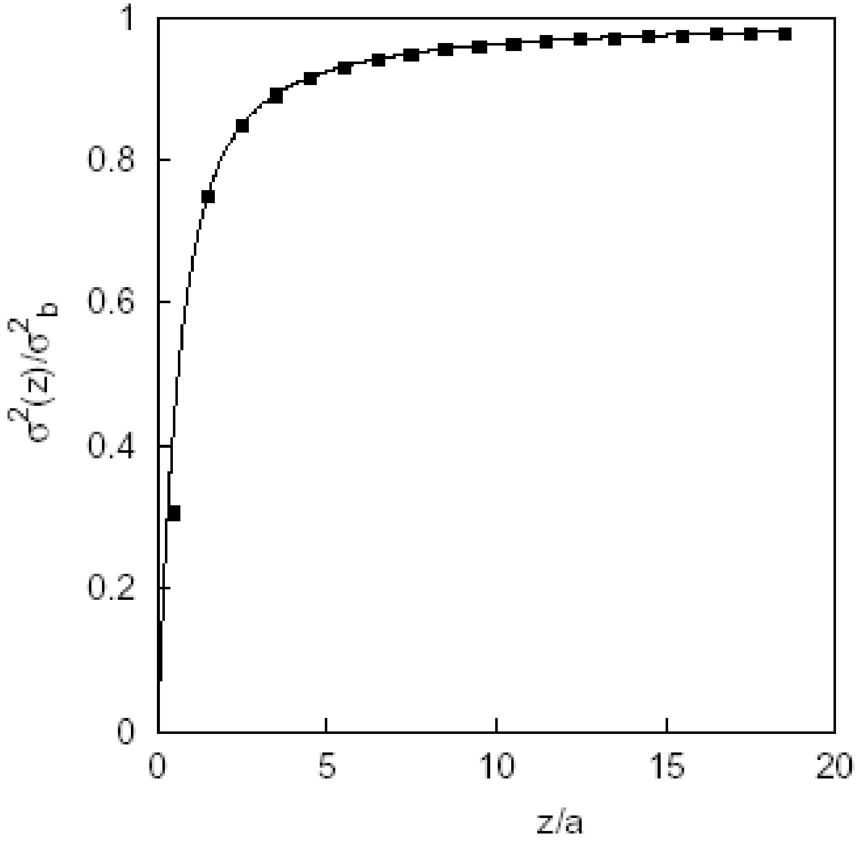
Gaussian disorder (II)



Field dependence resembles thermionic emission

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

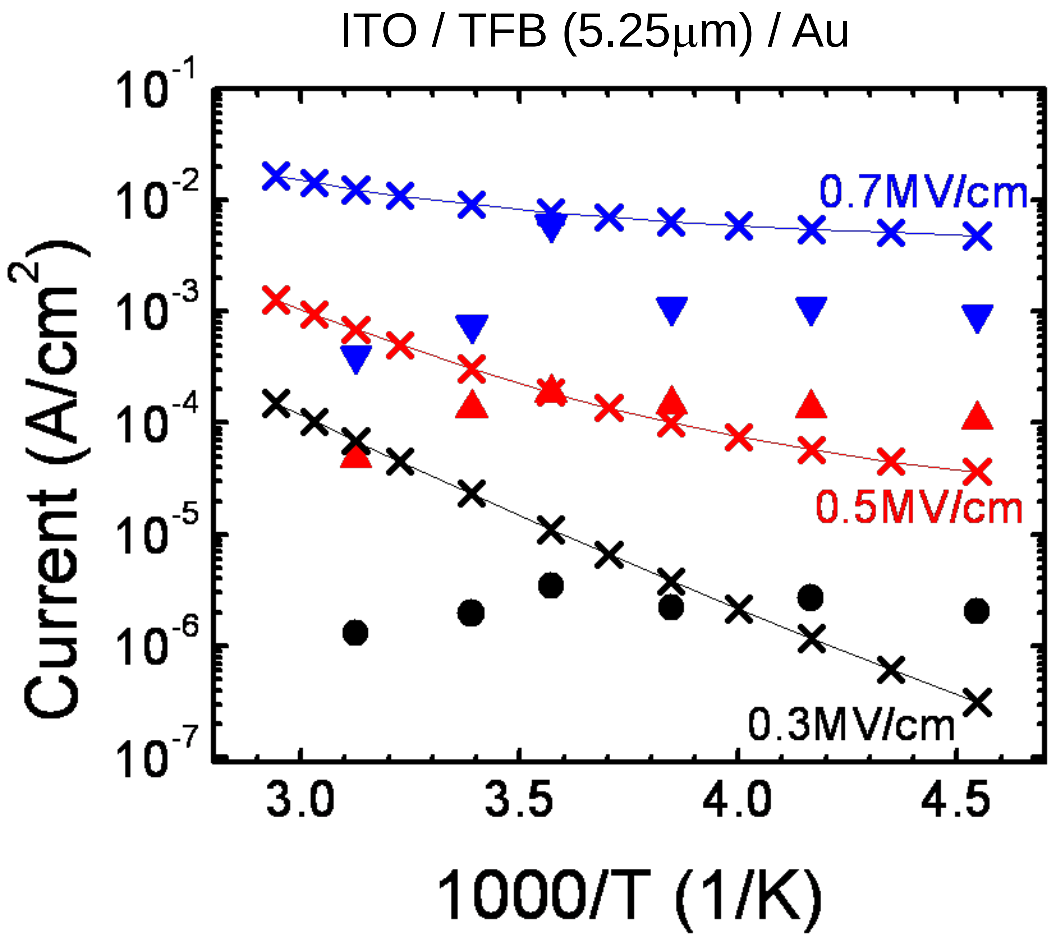
Gaussian disorder (III)



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

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

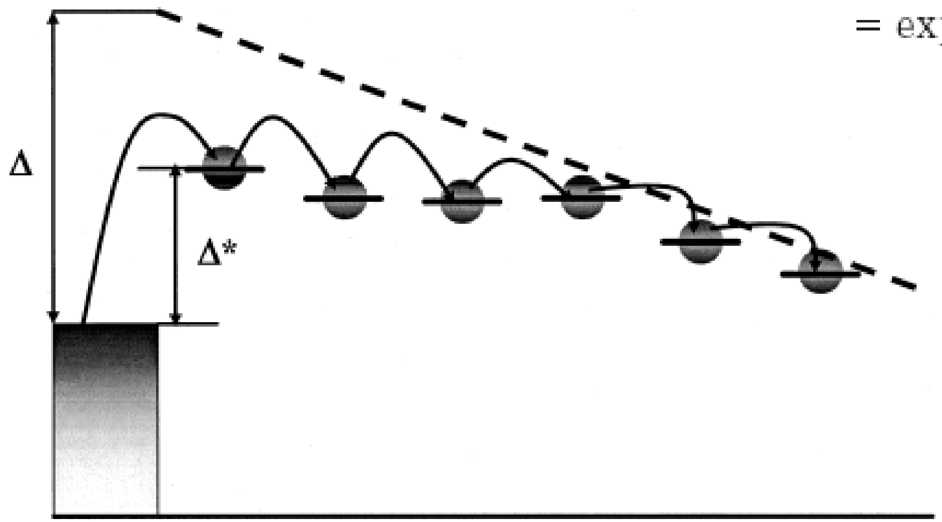
Fit to the data



Preferential pathways model

$$j \propto \exp(-\Delta/(k_B T)) \exp\left[\frac{\varphi_*}{k_B T} - \frac{\varphi_*^3}{6w^2 eEa}\right]$$

$$= \exp(-\Delta/(k_B T)) \exp\left[\frac{2\sqrt{2}}{3}\frac{w}{k_B T}\sqrt{\frac{eEa}{k_B T}}\right]$$



A.L. Burin and M.A. Ratner, *J. of Polymer Sci.: (B): Polymer Phys.* **41**, 2601 (2003).

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 devices
- Organic materials that show ideal transport characteristics and high mobilities have become available
- Charge injection in is often poor (and poorly understood) – opportunity for major improvements in organic device 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