Week 6

Electronic Properties 2

Ohmic and Space Charge Conduction

Doping

Recombination

Heterojunctions

Chapter 4.3-4.6

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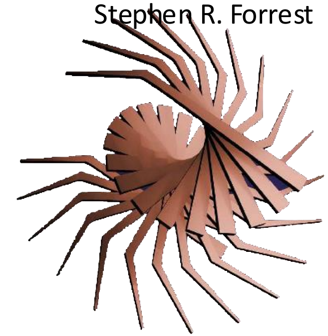


Current and Conductivity

1. **Ohm's Law** (gives DC mobility).

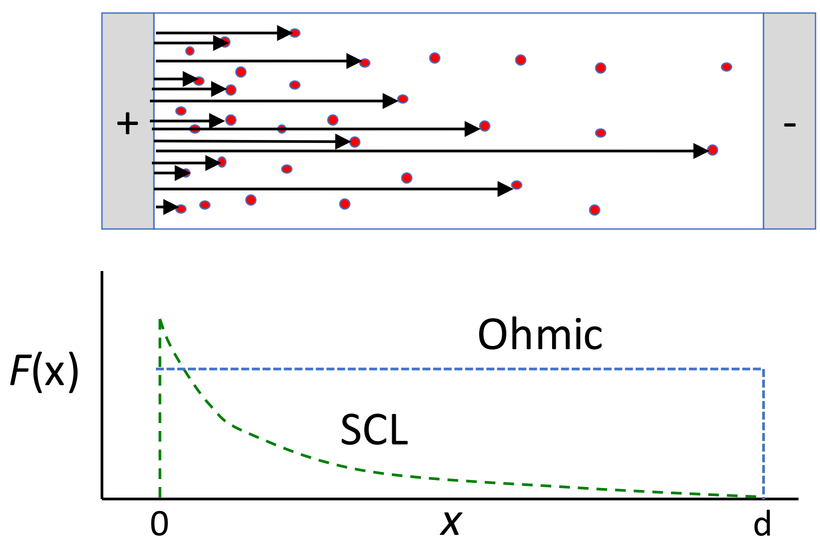
- For a single carrier (holes in this case) in a uniform electric field:

$$j = qp\mu F = qp\mu\frac{V}{d}$$

- Gives the product $p\mu \Rightarrow$ requires independent determination of charge density.
- *Ohmic regime* identified by *linear* relationship between *j* and *V.*

2. **Space charge limited current** (gives DC mobility).

- When the injected carrier density $p_{inj} > p_0$ (the background charge density), charge accumulates at electrodes:



Space Charge Limited Current

- In the space charge regime, we make the following assumptions to solve *j* vs. *V* :
  - $p_{inj} > p_0$
  - Only one carrier type is present
  - $\mu \neq \mu(F)$ (Field-independent mobility)
  - Free carrier distribution follows Boltzmann statistics
  - Trapped charge occupation defined by Fermi statistics
  - *F* is large enough for drift (and not diffusion) to dominate
  - Field not so large that field emission is important

- In 1D, Gauss says: $\dfrac{dF}{dx} = \dfrac{q\left(p_{inj}(x) + p_t(x) + p_0\right)}{\varepsilon} \approx \dfrac{qp_{inj}(x)}{\varepsilon}$ (trap free case)
  - $\varepsilon = \varepsilon_0 \varepsilon_r$
  - Current in the absence of trapped charge, p_t(x): $j(x) = q\mu_p p_{inj}(x) F(x)$
  - Now: $$\frac{dF^2(x)}{dx} = 2F(x)\frac{dF(x)}{dx} = \frac{2qp_{inj}(x)F(x)}{\varepsilon} = \frac{2j(x)}{\varepsilon\mu_p}$$
  - Since *j* is constant across layer $\Rightarrow F^2(x) = \dfrac{2jx}{\varepsilon\mu_p}$ (This is current continuity)

j-V in the SCL regime

$$F^2(x) = \frac{2jx}{\varepsilon\mu_p} \Box \quad F(x) = \sqrt{\frac{2jx}{\varepsilon\mu_p}}$$

Note: $F(x) \sim x^{1/2}$ vs. $F(x)$= constant for Ohmic

Now potential is: $$-\frac{dV}{dx} = F(x)$$

Integrating between $0 < V < V_a$ and $0 < x < d$

We obtain: $$V_a = \frac{2}{3}\sqrt{\frac{2jd^3}{\varepsilon\mu_p}}$$

Giving the **Mott-Gurney relationship**:

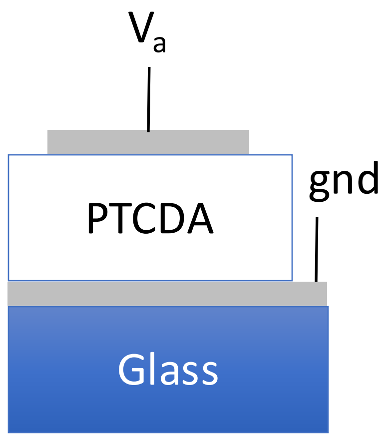
$$\boxed{j = \frac{9}{8}\mu_p \varepsilon \frac{V_a^2}{d^3}}$$

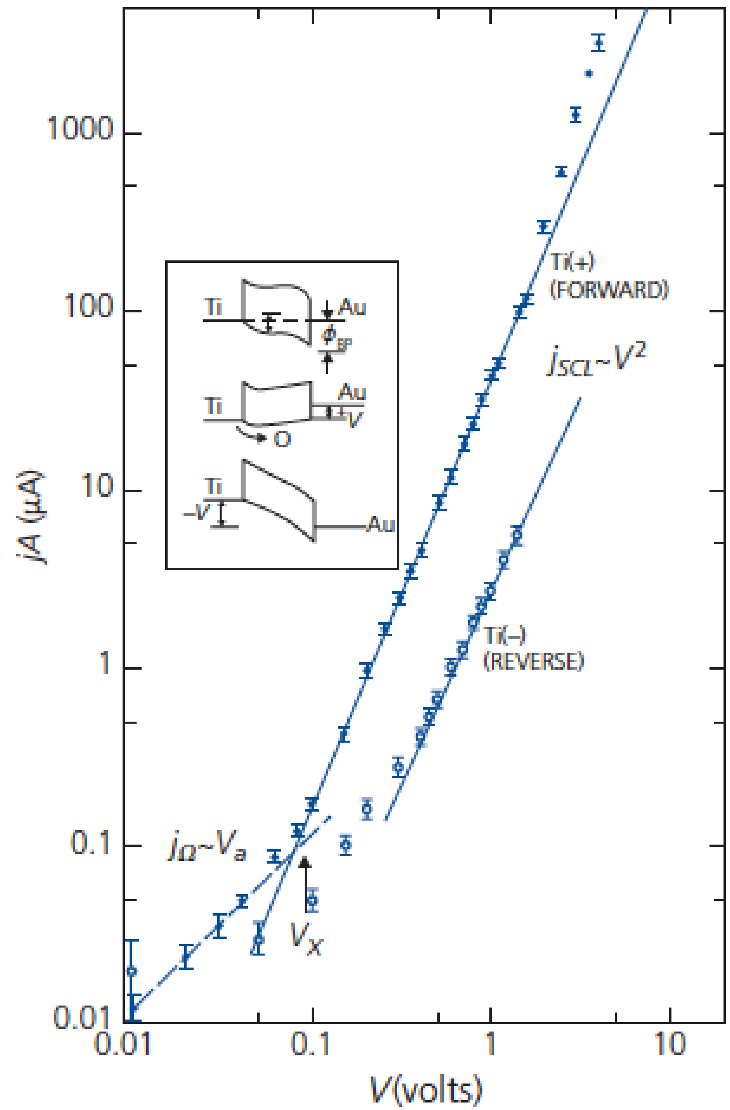
Note the absence of p!

⇒ Only need the dielectric constant and the film thickness to find μ.

Use the Ohmic region of the j-V curve to determine p_0.

SCL Current in PTCDA





To find background carrier density:

At V_x: j(ohmic)=j(SCL)

$$\Rightarrow qn\mu\frac{V_x}{d} = \frac{9}{8}\mu\varepsilon\frac{V_x^2}{d^3}$$

$$\Rightarrow n = \frac{9}{8}\frac{\varepsilon}{q}\frac{V_x}{d^2}$$

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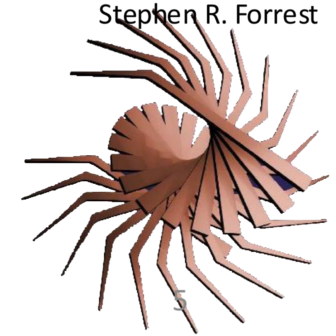
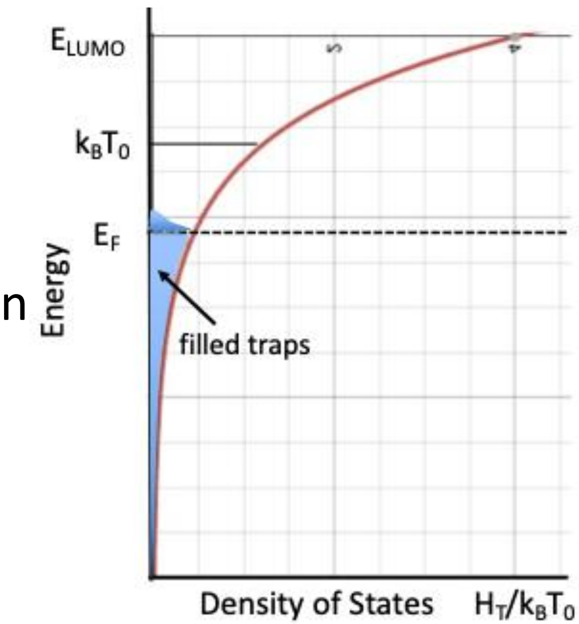


Forrest, S. R., Kaplan, M. L. & Schmidt, P. H. *J. Appl. Phys.*, **55,** 1492 (1984).

But what happens if things aren't so simple?

- We have assumed no traps. In organics, this is not often the case due to ***static disorder***.
- Simplest case: A single discrete, shallow trap where $\frac{p_{inj}}{p_t} = \Theta \ll 1$
- Then <u>you</u> can show: $j = \frac{9}{8}\left(\Theta\mu_p\right)\varepsilon\frac{V_a^2}{d^3}$
  - ➢ That is, the mobility is now reduced by Θ
- More often there is an exponential distribution of traps, in which case we have trap-filled limited conduction:

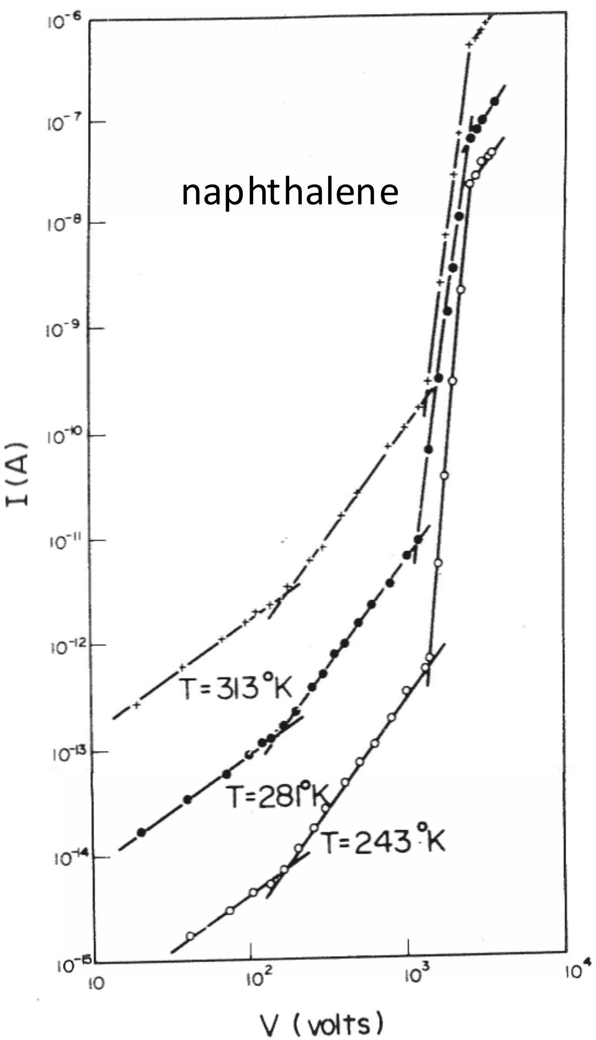
$$\boxed{j_{TFL} = q\mu N_{HOMO}\left[\frac{\varepsilon m}{q(m+1)N_t}\right]^m \left[\frac{2m+1}{m+1}\right]^{m+1} \frac{V_a^{m+1}}{d^{2m+1}}}$$



- ***m* = *T*$_t$/*T*** where T_t is the characteristic trap temperature
  - Define $p_t = N_t \exp\left(-\left(E_{Fp} - E_{HOMO}\right)/k_BT_t\right)$
  - Leading to: $p = N_{HOMO}\exp\left(-\left(E_{Fp} - E_{HOMO}\right)/k_BT\right) = N_{HOMO}\exp\left(-\left(E_{Fp} - E_{HOMO}\right)/k_BT_t\left[T_t/T\right]\right)$

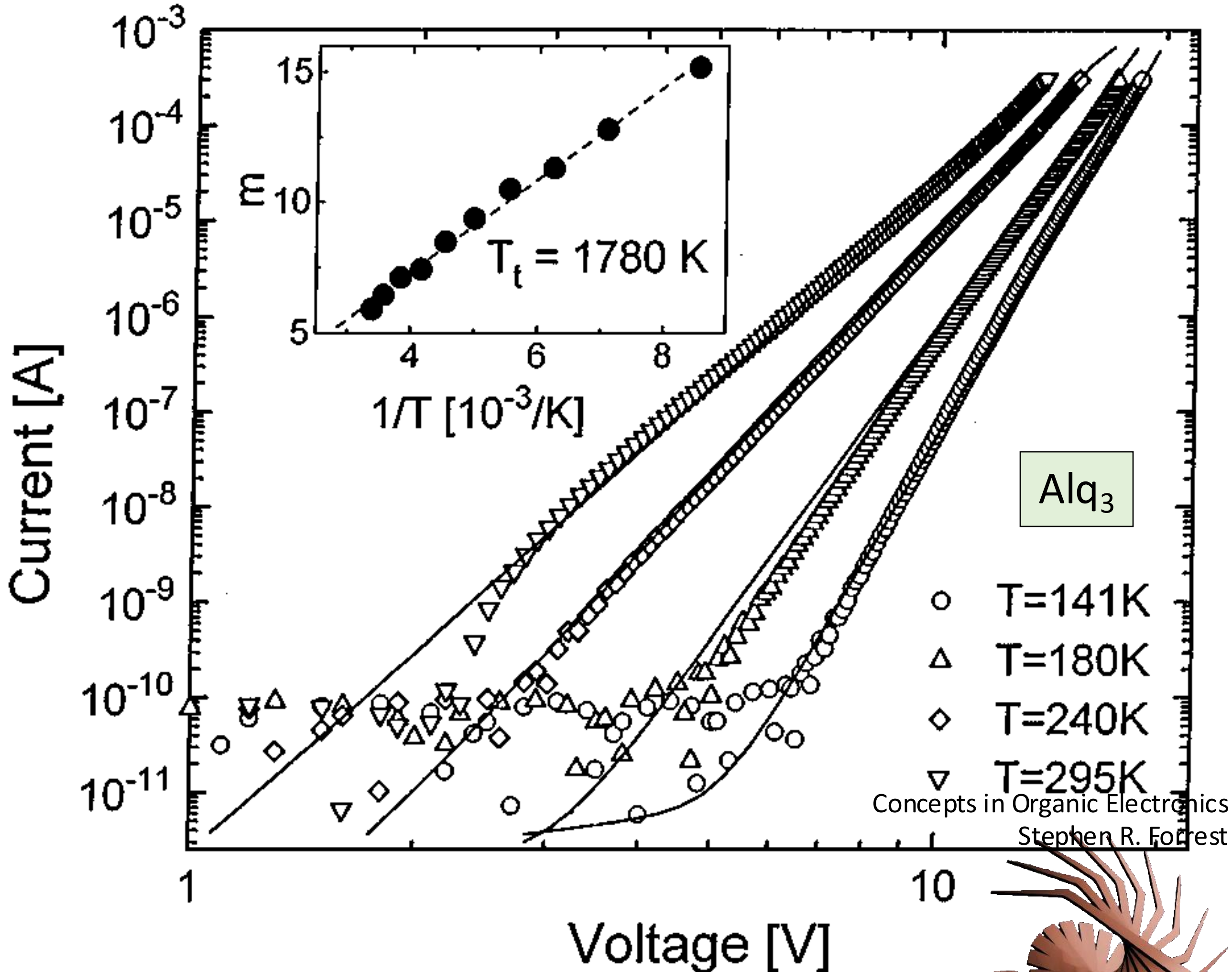
$$p = N_{HOMO}\left(\frac{p_t}{N_t}\right)^{T_t/T} \Rightarrow p_t = N_t\left(\frac{p}{N_{HOMO}}\right)^{1/m}$$

Examples of TFL-SCL



Multiple ohmic, SCL and TFL regions

M. Campos, Mol. Cryst. Liq. Cryst. **18**, 105 (1972)



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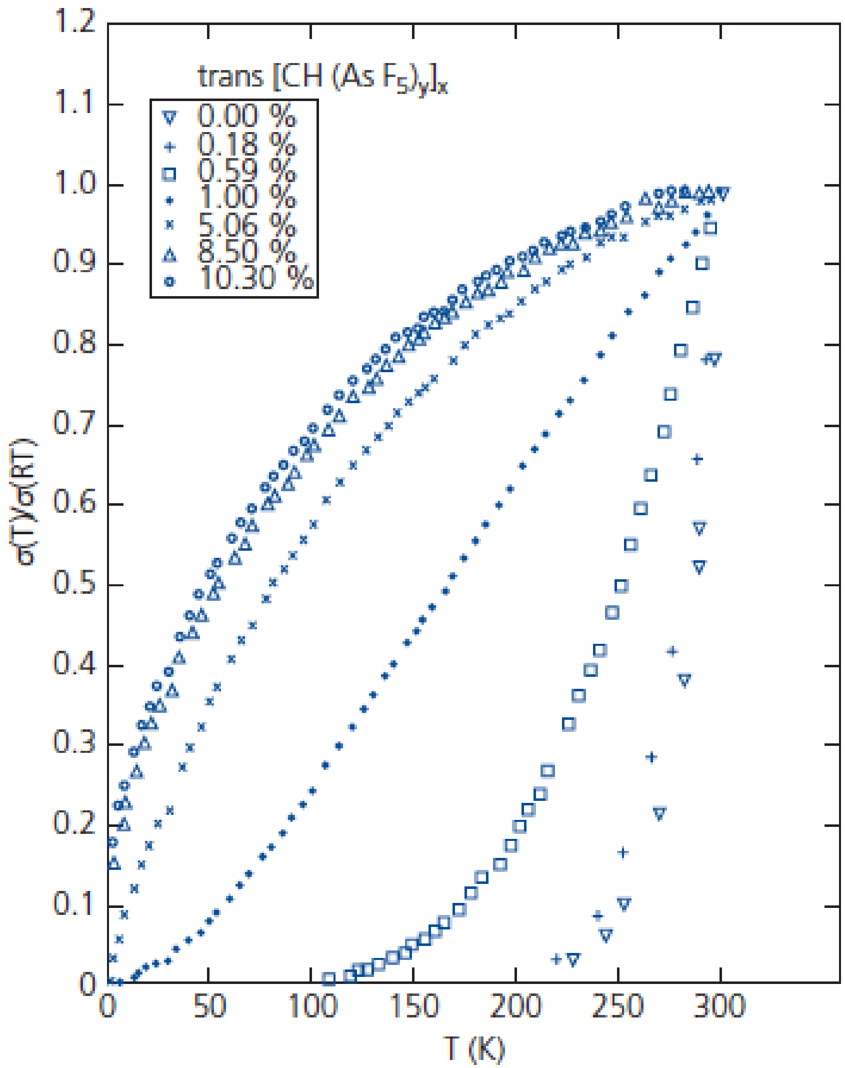
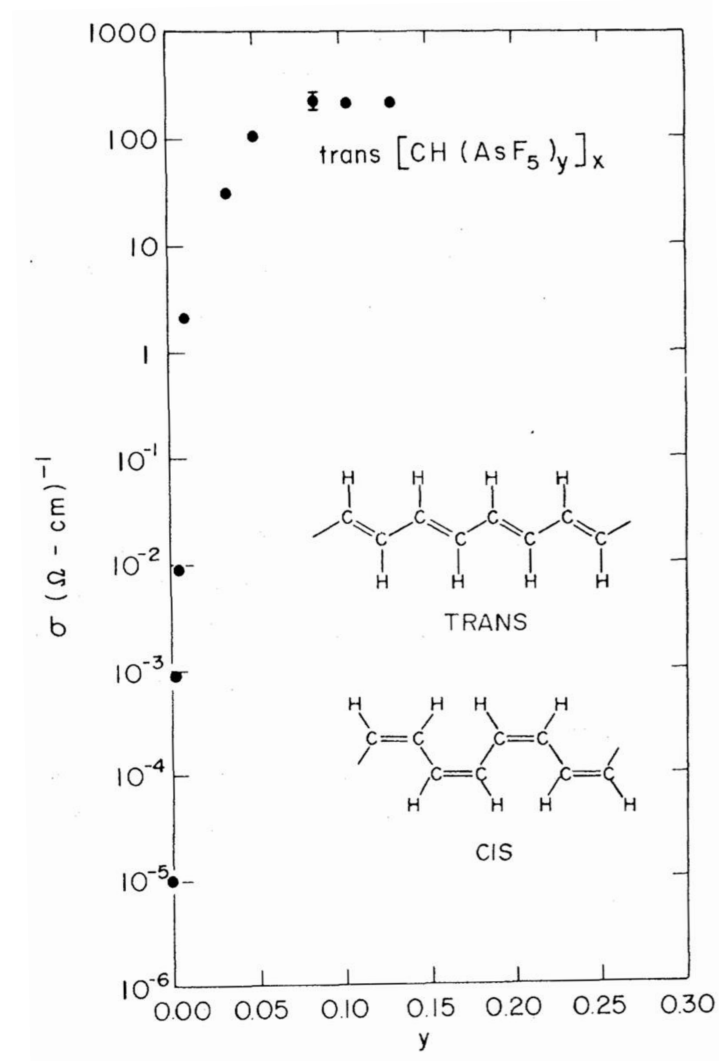
P. E. Burrows, et al., *J. Appl. Phys.*, **79**, 7991 (1996).

Doping of Organics to Increase Conductivity

The first demonstration: polyacetylene

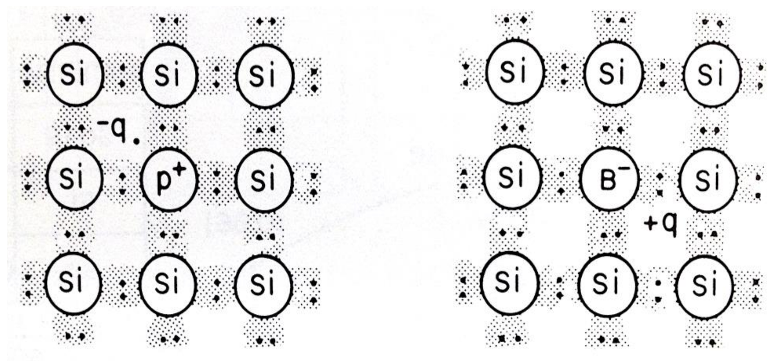




Heeger, Shirakawa, MacDiarmid, et al. Phys. Rev. Lett., **39** 1098 (1977)

Doping in Organics: Not entirely similar to inorganics

Substitutional doping in inorganics



(a) (b)

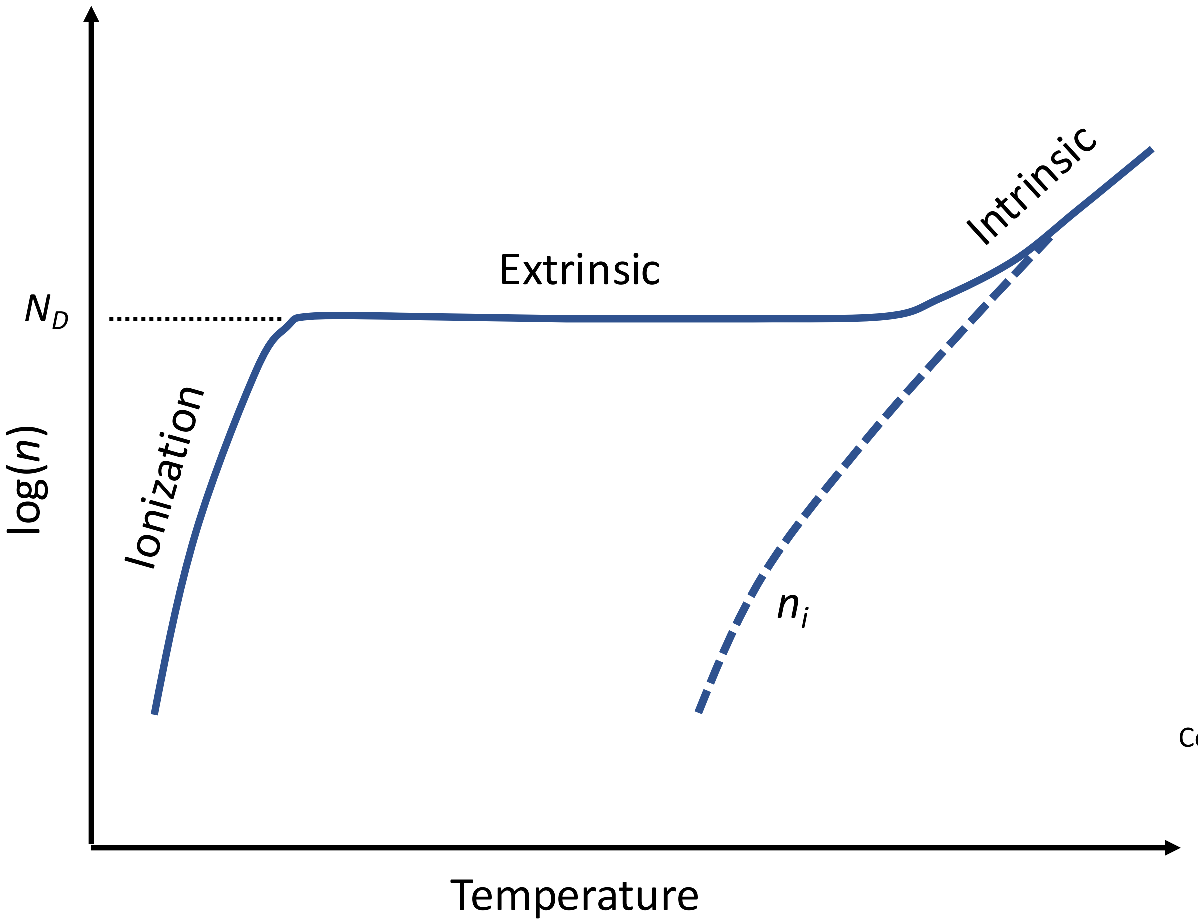
But no shared bonds in organics!

Do not confuse with E_F!

$$n = N_{LUMO} \exp\left(\frac{E_F - E_{LUMO}}{k_B T}\right) \qquad p = N_{HOMO} \exp\left(\frac{E_{HOMO} - E_F}{k_B T}\right)$$

$\Rightarrow$ Law of mass action: $n_i^2 = N_{HOMO} N_{LUMO} \exp\left[-\frac{E_G}{k_B T}\right]$

Doping regimes of an n-type semiconductor



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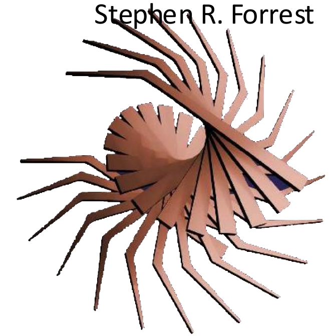
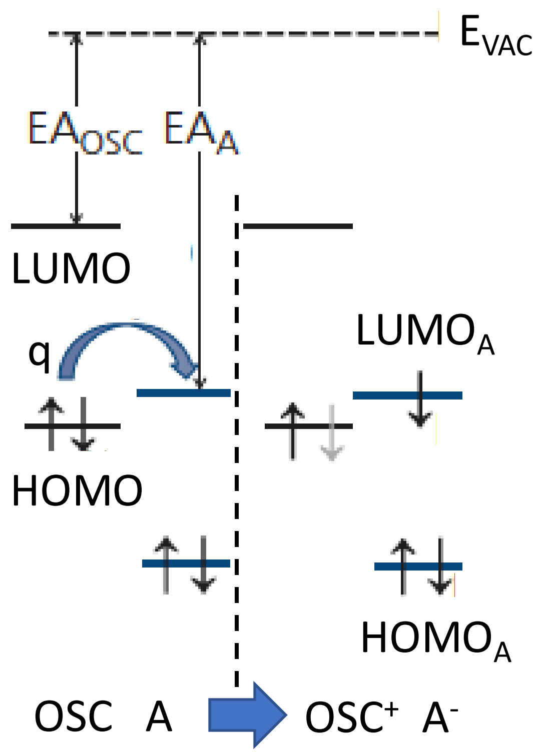
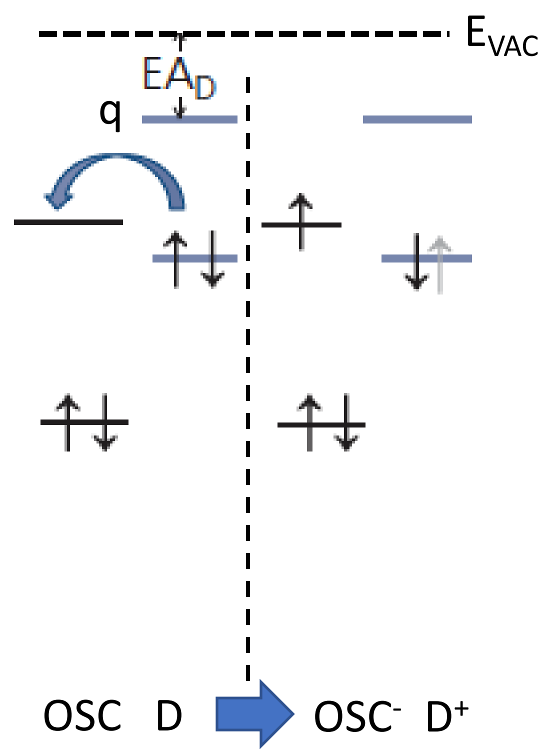


Doping at the molecular level

Involves charge transfer between dopant and host

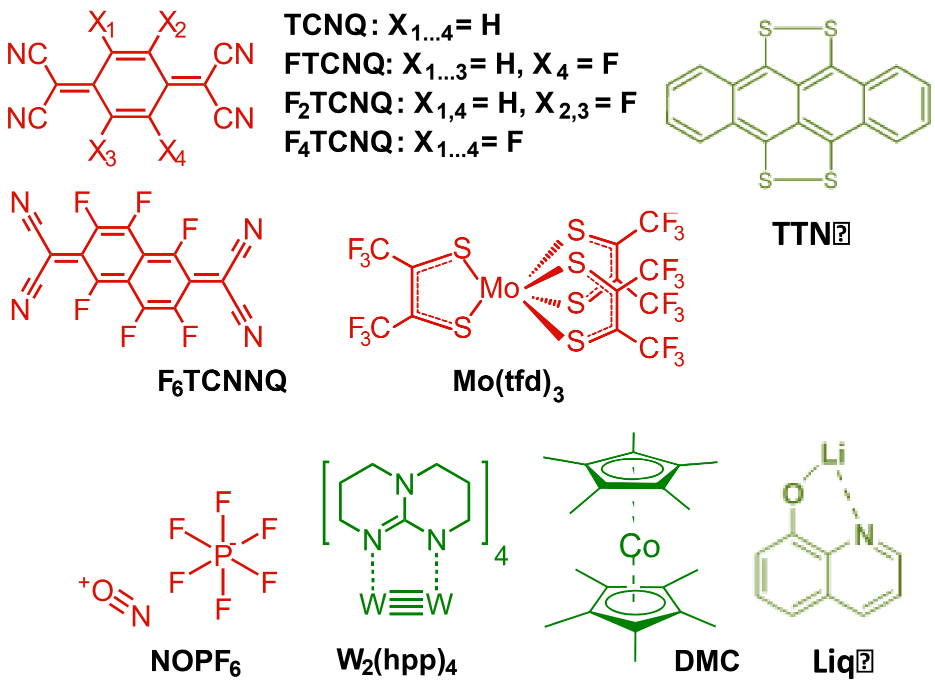


p-type doping



n-type doping

Example *molecular* dopants

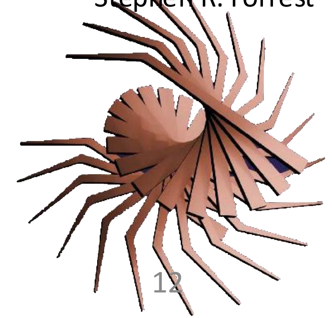


red=acceptors; green=donors

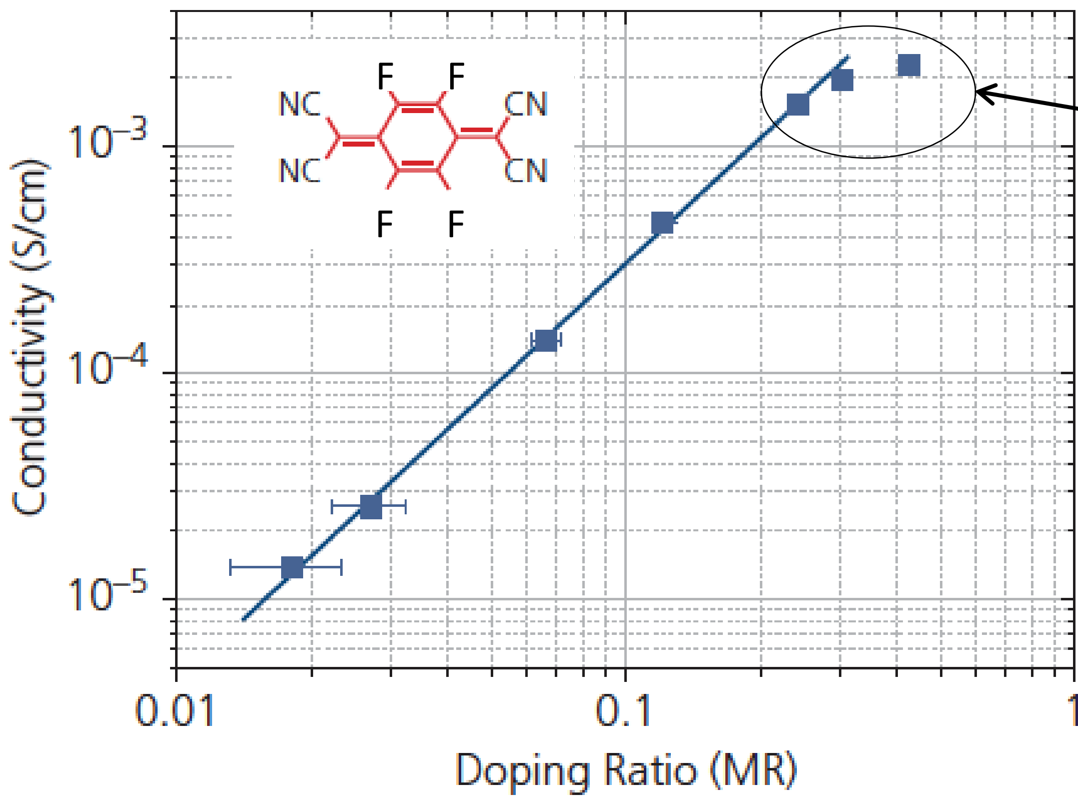
But there are metallic dopants too: Cs, Li, etc.

LiF + Al cathodes common in OLEDs:

$$\mathrm{LiF} + \mathrm{Al} \rightarrow \mathrm{Li}^{+} + e^{-} + \mathrm{AlF}$$



Difficult to get a high conductivity
(it takes *a lot* of dopant)



Scattering/morphological disruption ⇒ saturation

N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine with **F_4-TCNQ**.

Olthof et al., J. Appl. Phys., **106**, 103711 (2009)

Recombination

Charge diffusion equations

$$\frac{\partial n}{\partial t} = \frac{1}{q}\nabla \cdot \mathbf{j}_e - R_e + G_e \qquad \frac{\partial p}{\partial t} = -\frac{1}{q}\nabla \cdot \mathbf{j}_h - R_h + G_h$$

Using Fick's Law

$$\mathbf{j}_e = qD_e\nabla n$$

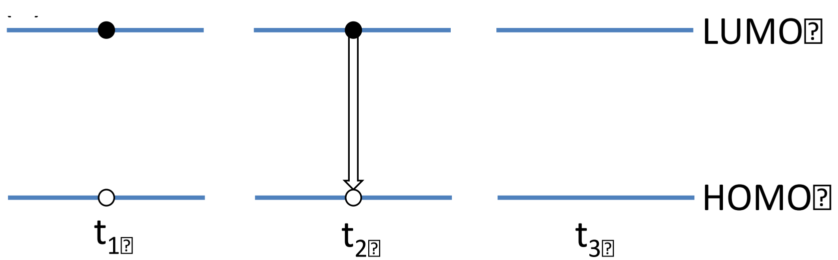
$$\mathbf{j}_h = -qD_h\nabla p$$

Gives:

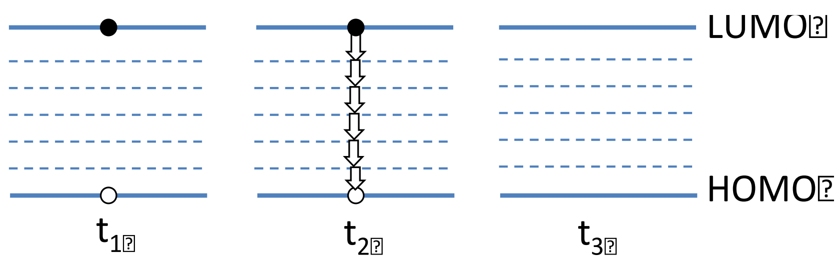
$$\frac{\partial n}{\partial t} = D_e\nabla^2 n - R_e + G_e \qquad \frac{\partial p}{\partial t} = D_h\nabla^2 p - R_h + G_h$$

Direct HOMO-LUMO Recombination and via Midgap States

Direct (Band-to Band) Recombination

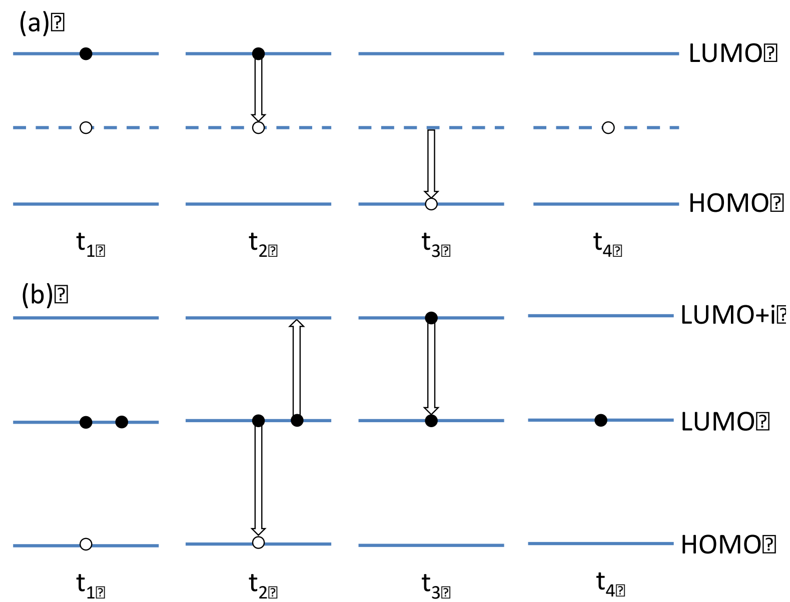


Multiple Step Recombination



$$R_e^{dir} = \frac{n - n_0}{\tau_e} = \frac{\Delta n}{\tau_e}$$

Shockley-Read-Hall Recombination

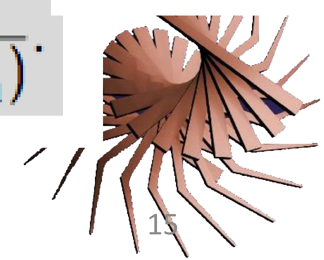


Auger Recombination

Concepts

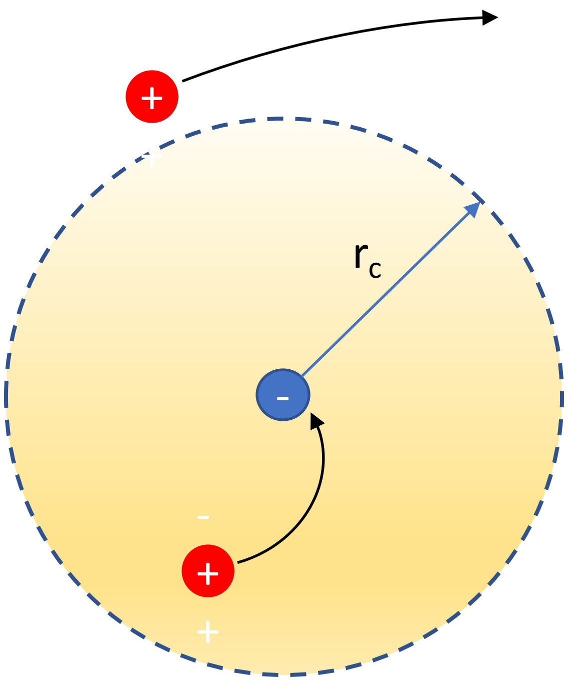
equilibrium restoring force

$$R^{SRH} = \frac{np - n_i^2}{\tau_e (p + p_1) + \tau_h (n + n_1)}.$$



Langevin (Bimolecular) Recombination

- When two carriers meet....



Capture radius: When Coulomb = thermal energy

$$r_c = \frac{q^2}{4\pi \varepsilon_r \varepsilon_0 k_B T}.$$

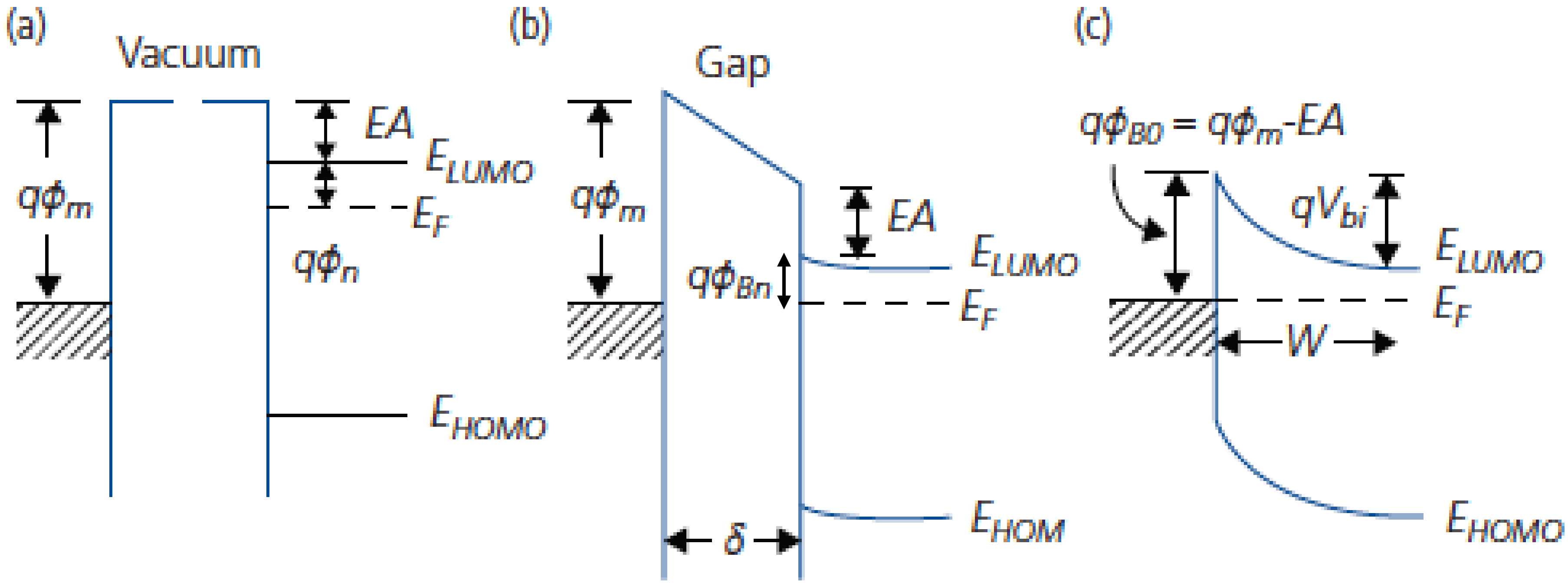
Langevin recombination rate constant:

$$\gamma_L = \frac{q}{\varepsilon_r \varepsilon_0}\left(\mu_e + \mu_h\right) = \frac{q}{\varepsilon_r \varepsilon_0}\mu_T .$$

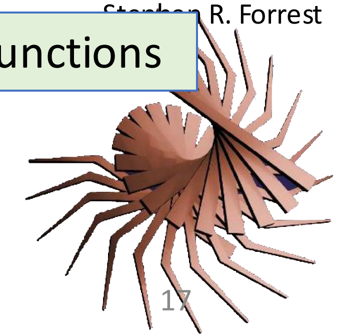
Yielding the recombination rate (and hence current)

$$R^L = \gamma_L \left(pn - n_i^2\right)$$

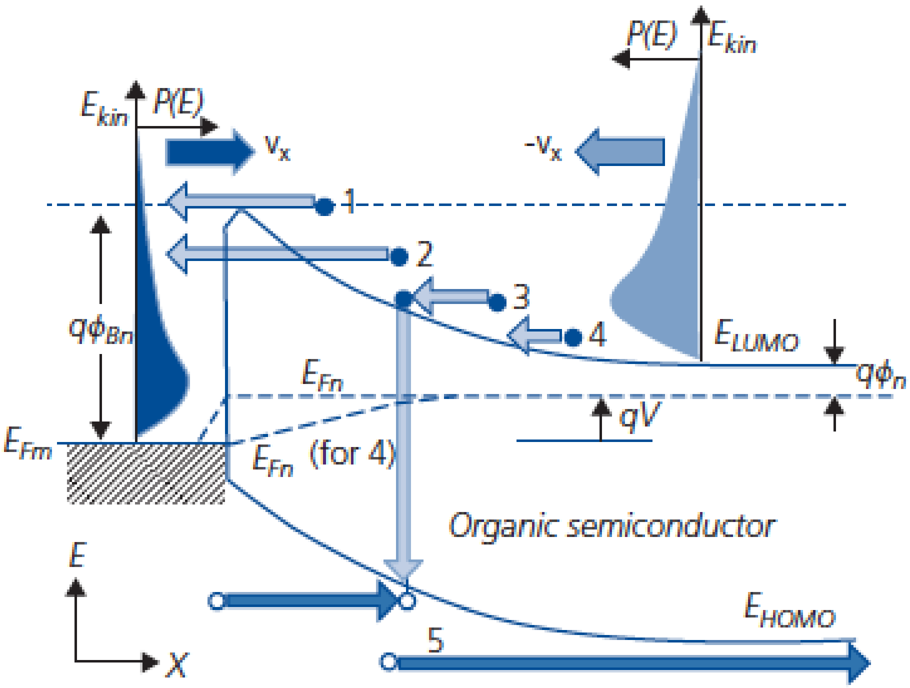
Metal-semiconductor Junctions: Schottky barriers

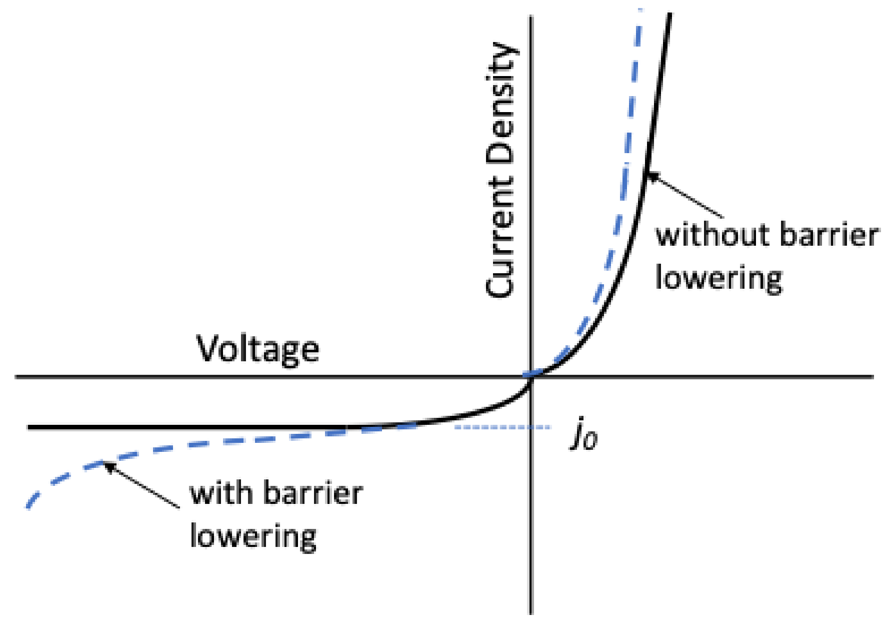


Traps Play a Big Role in Determining Barrier Heights at Metal-Semiconductor Junctions



Current sources across M-O Junctions





$$\boxed{j = j_0\left(\exp\left(qV/k_BT\right)-1\right)}$$

$$j_0 = j_{0TE} = A^*T^2\exp\left(-q\phi_{B0}/k_BT\right) \qquad A^* = \frac{4\pi q m^* k_B^2}{h^3} \qquad \text{(Richardson Constant)}$$

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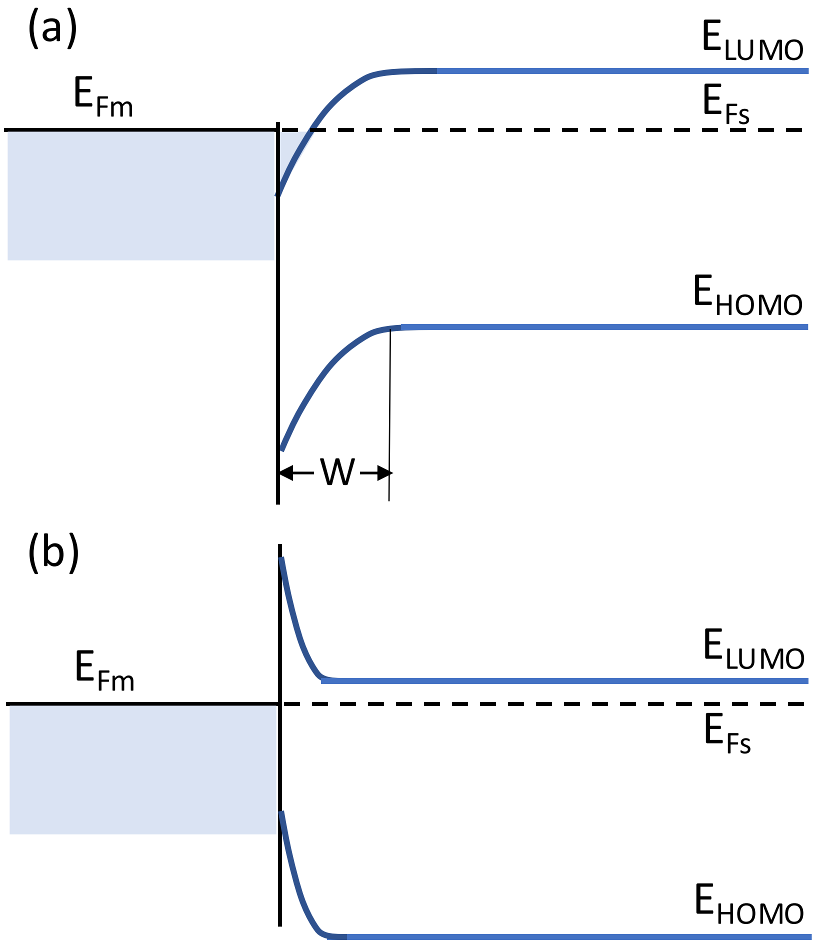
Metal-organic junctions can be low resistance (Ohmic) if the semiconductor is highly doped at the surface

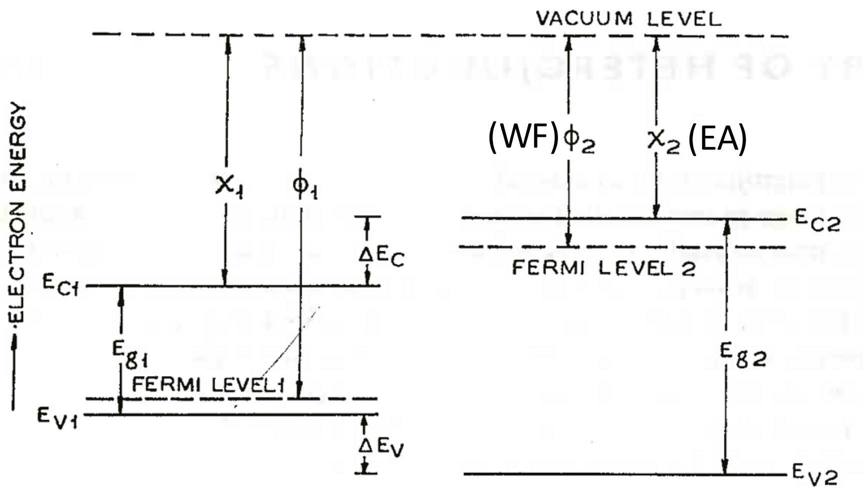


Depletion width at the interface:

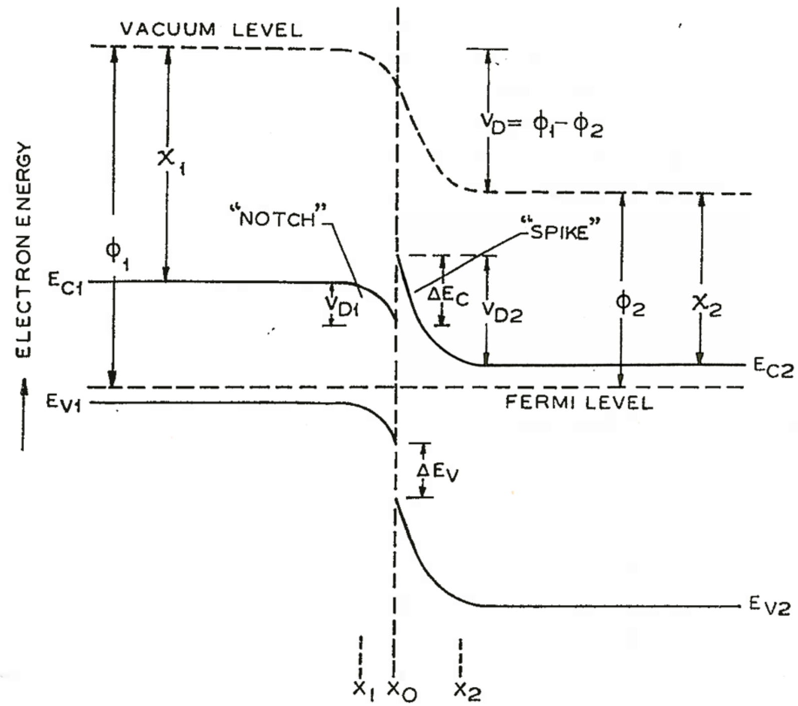
$$W = \sqrt{\frac{2\epsilon(V - V_{bi})}{qN_D}}$$

Heterojunctions: Organic-organic contacts

- A heterojunction is a contact between two dissimilar materials (typically semiconductors)
- HJs play a vital role in almost all photonic devices, and many electronic devices too.
- Some definitions:



Anisotype HJ



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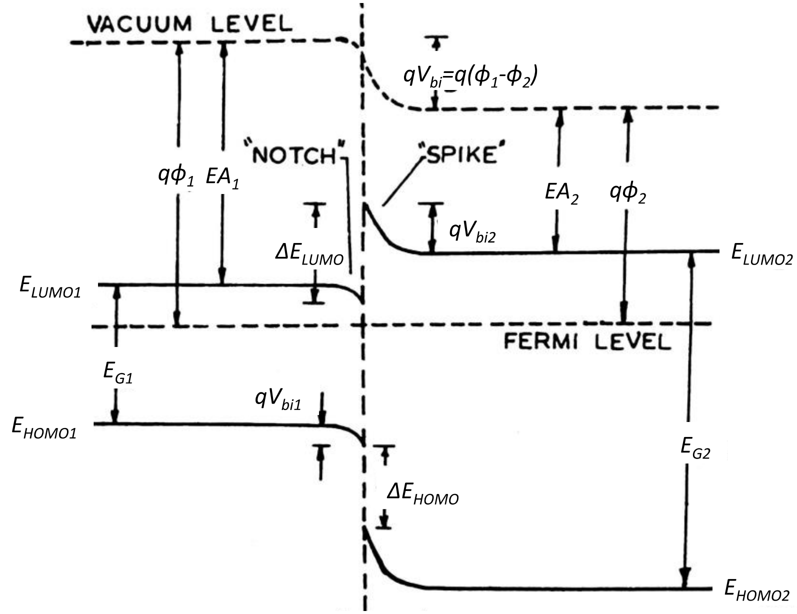
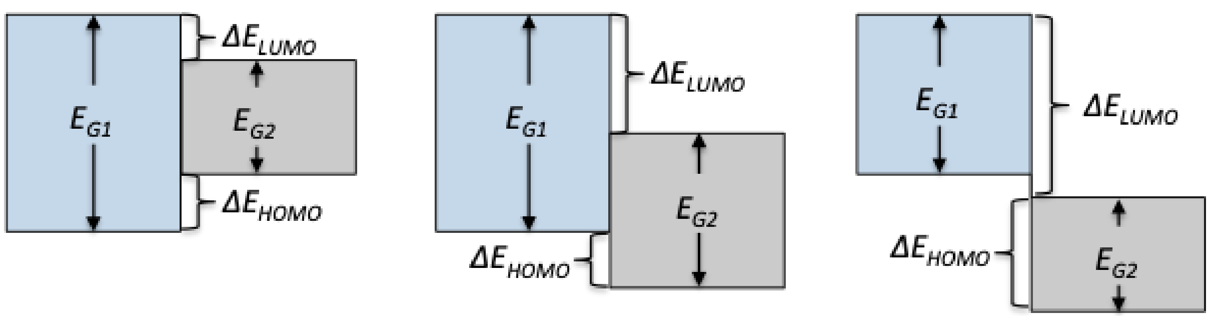
- Anderson's rule: $\Delta E_c = |\chi_1 - \chi_2|$ (doesn't work so well for inorganics due to charge transfer; better for organics)
- $\Delta E_v = \Delta E_g - \Delta E_c$
- Band bending due to free charge: organics tend toward flat bands

Isotype vs. Anisotype HJ



n-N isotype HJ

Classification of HJ types



Type I
Nested

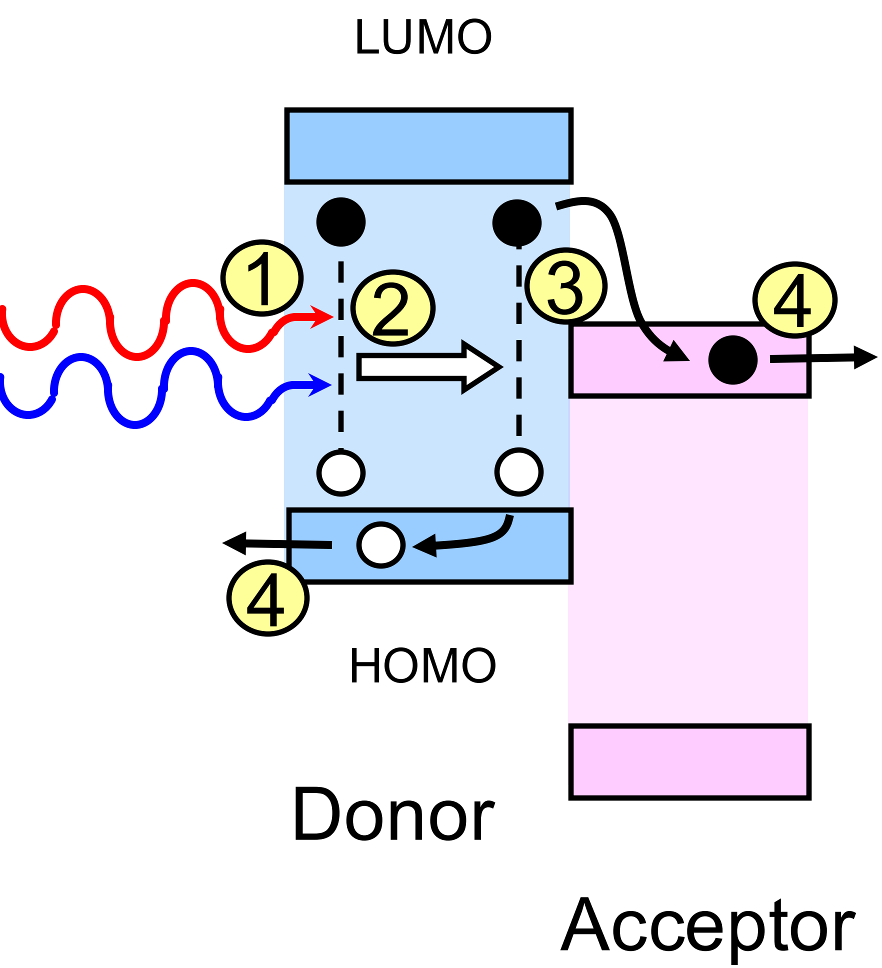
Type II
Staggered

Type III
Broken Gap

Photoinduced Charge-Transfer at a Type II HJ

The Basis of OPV Operation

Processes occuring at a Donor-Acceptor heterojunction



1. Exciton generation by absorption of light ($1/\alpha$)
2. Exciton diffusion over $\sim L_D$
3. Exciton dissociation by rapid and efficient charge transfer
4. Charge extraction by the internal electric field

Typically: $L_D \ll 1/\alpha$

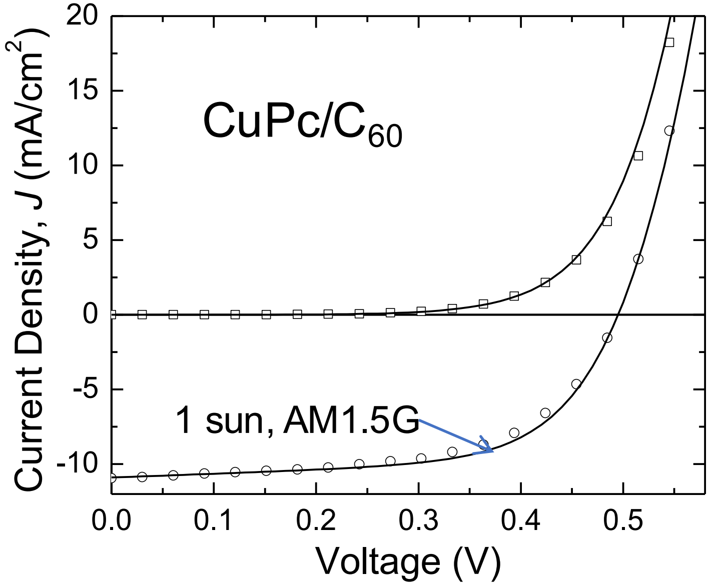
Ideal Diode Equation: Problem Statement

- The Shockley Equation (1949):

$$J = J_o(\exp(qV_a / k_b T) - 1) - J_{ph}$$

has been successfully applied (e.g. Xue and Forrest, 2004) to organic heterojunction cells. But the physics is wrong!

- Why does it "work"?
- Is there a more appropriate relationship for organic (i.e. *excitonic*) HJs?



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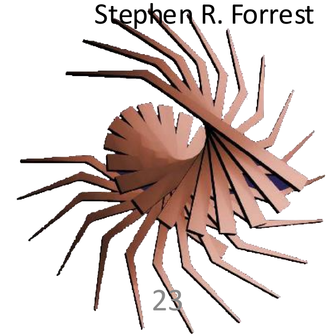

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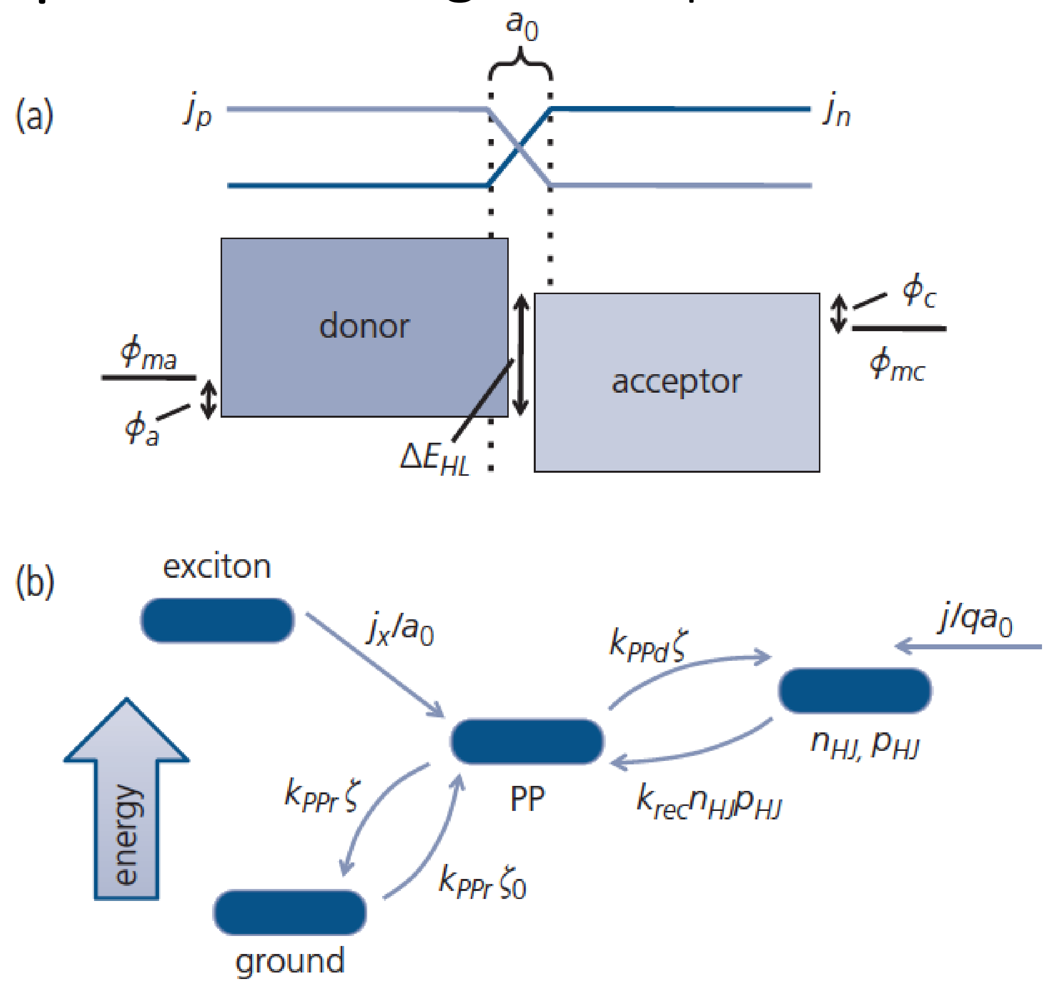
Excitonic Heterojunctions:

Controlled by **energy transport**, *not* charge transport

1. Excitons diffuse with current J_X to HJ
2. Separate into polaron pairs across HJ
3. PP can either dissociate into carriers
4. Or recombine to ground state

ζ=PP density
k_{PPr}=PP recombination rate
k_{PPd}=PP dissociation rate
k_{rec}=charge recombination rate
J=electron current
WF=work function
n_I, p_I=charge at interface

A polaron pair at the interface is equivalent to a charge transfer (CT) state



N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Derivation of the Ideal Diode Eq.

"Just because you have an ideal diode equation does not mean you have an ideal diode"

- The rate equations in steady state:
  - Excitons: $$\frac{J_X}{a_0} - k_{\mathrm{PP}r}(\zeta - \zeta_{eq}) - k_{\mathrm{PP}d}\zeta + k_{rec}n_I p_I = 0,$$
  - Polarons: $$k_{\mathrm{PP}d}\zeta - k_{rec}n_I p_I + \frac{J}{qa_0} = 0,$$

Rate Equations + Fermi Stats:

$$J_0\left\{\exp(qV_a/k_BT) - \frac{k_{PPd}}{k_{PPd,eq}}\right\} - J_{ph}$$

$$\boxed{J = \overbrace{qa_0k_{rec}N_{HOMO}N_{LUMO}\left(1-\eta_{PPd}\right)\exp\left(-\Delta E_{HL}/k_bT\right)}^{J_0}\overbrace{\left\{\exp\left(qV_a/k_bT\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right\}}^{\left\{\exp(qV_a/k_BT) - \frac{k_{PPd}}{k_{PPd,eq}}\right\}} \overbrace{-q\eta_{PPd}J_X}^{-J_{ph}}}$$

electron & hole DOS

PP dissociation efficiency

$$\left(\eta_{PPd} = \frac{k_{PPd}}{k_{PPr} + k_{PPd}}\right)$$

equilibrium dissociation rate

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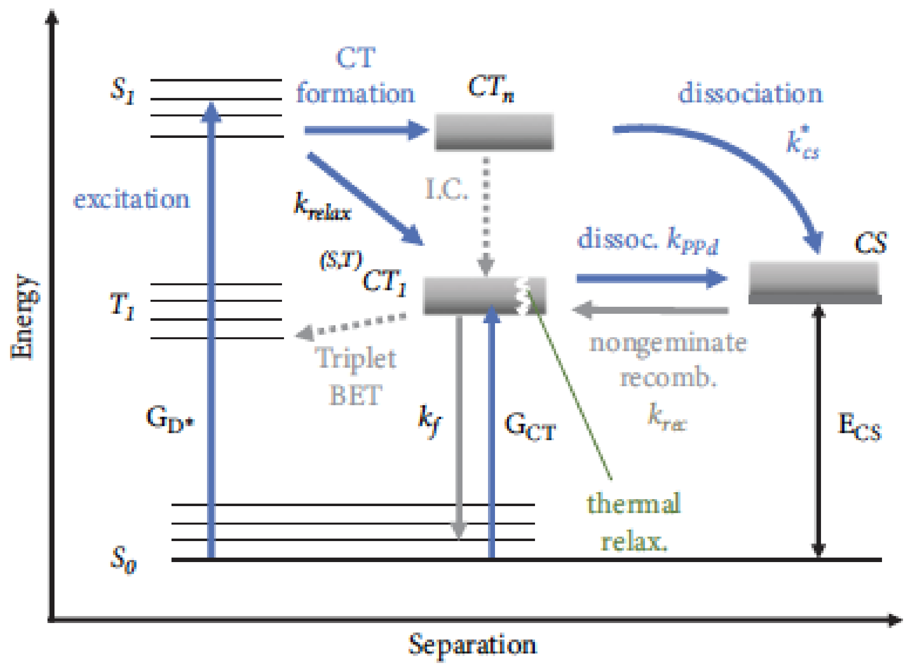
Ideal diode theory suggests the CT state is the precursor to free charge

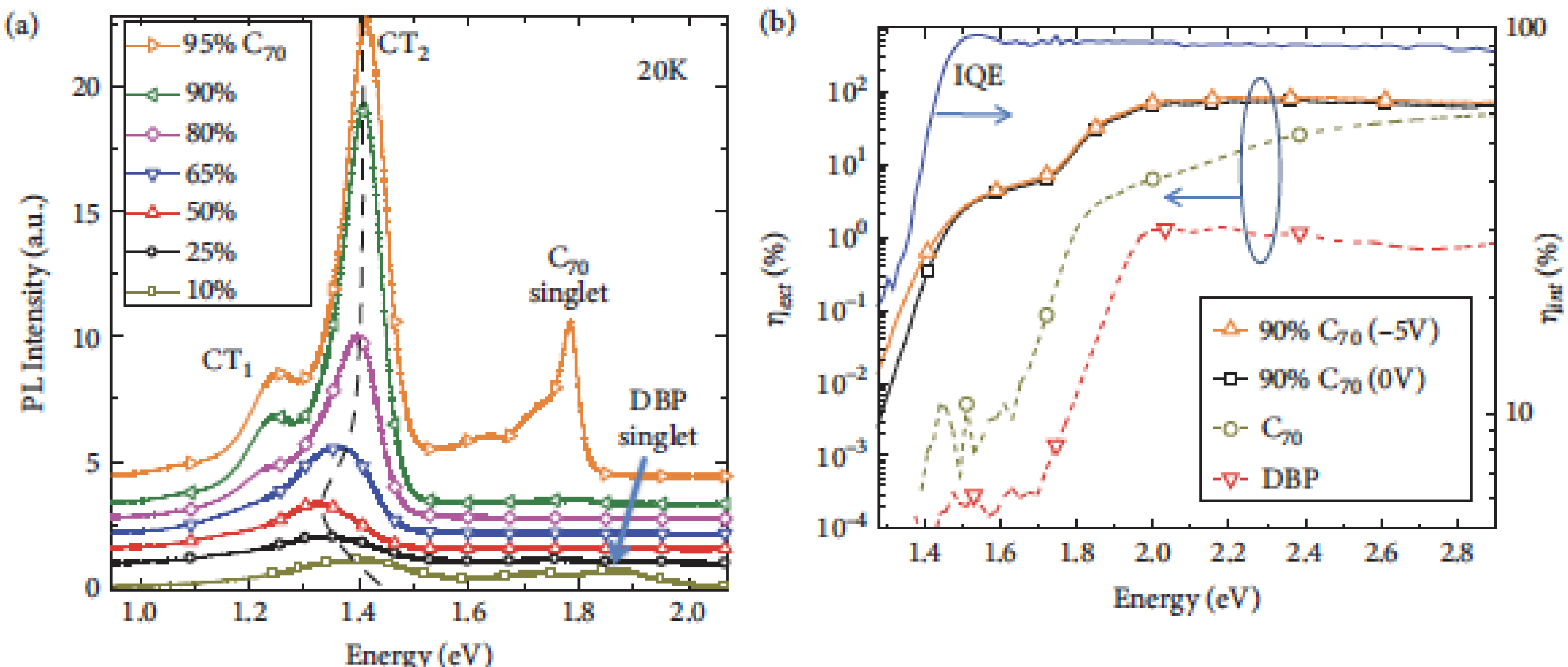
Energy landscape for free charge generation into the charge separated (CS or PP) state



X. Liu, et al. (2019) Trends in Chemistry, **1**, 815.

Back transfer into the triplet is a major source of non-radiative loss of excitons

CT state precursors in the DBP:C_{70} Donor-Acceptor System

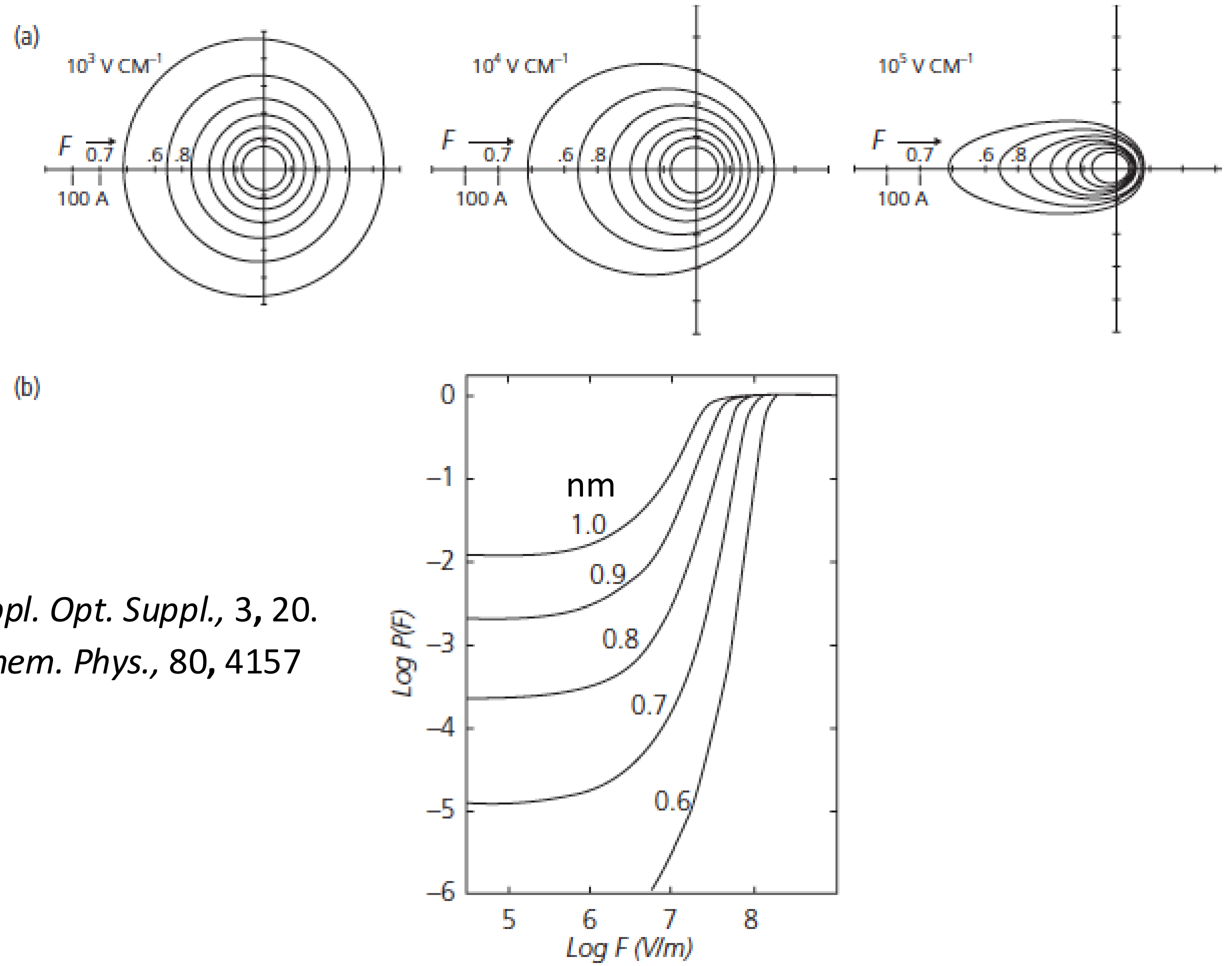


X. Liu, et al. (2016) ACS Nano, **10**, 7619

- PL shows two CT states: one for amorphous and the other for crystalline C_{70} domains
- The shelf in the external efficiency is due to CT state dissociation

Onsager-Braun Exciton Polarization

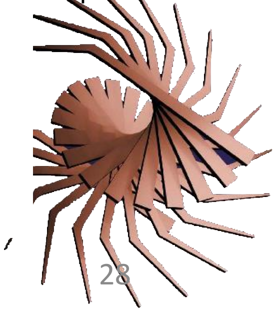
- Why there is a voltage dependence to k_{PPd} that gives *j-V* slope under reverse bias



Probability for exciton ionization

R. Batt, et al. 1969. *Appl. Opt. Suppl.,* 3**,** 20.

C. L. Braun. 1984. *J. Chem. Phys.,* 80**,** 4157

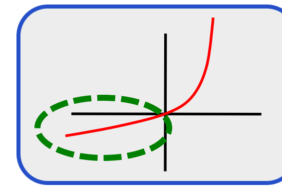


Consequences of the diode equation

$$J_0\left\{\exp(qV_a/k_BT)-\frac{k_{PPd}}{k_{PPd,eq}}\right\}-J_{ph}$$

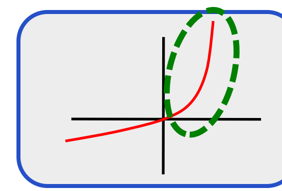
Reverse Bias:

- strong dissociation: $k_{PPd} > k_{PPd,eq}$ → saturation current increases →



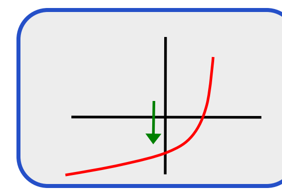
Forward Bias:

- weak dissociation: $k_{PPd} < k_{PPd,eq}$ → exponential diode current →



Illumination:

- photogenerated PPs: $J_X,\ \eta_{PPd} > 0$ → photocurrent addition →



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N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Including traps

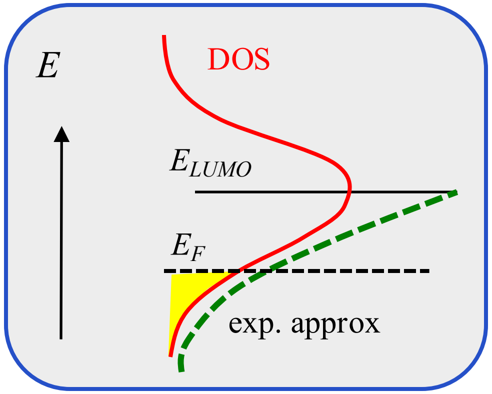
Disordered materials:

- broad density of states (DOS) ⇒ continuous trap distribution:

Trap Distribution Function

$$n_t = H_A exp\left(\frac{E_{Fn} - E_{LUMO}}{k_B T}\right) = H_A \left(\frac{n}{N_{LUMO}}\right)^{1/m_A}$$

where $m_A = T_{t,A}/T \quad \Rightarrow \quad n_A = \dfrac{m_A}{\delta_D(m_A - 1) + 1}$



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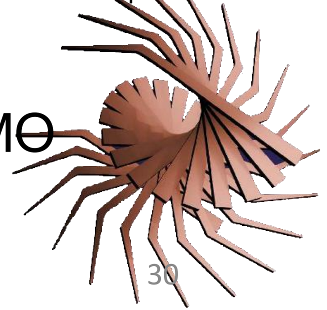
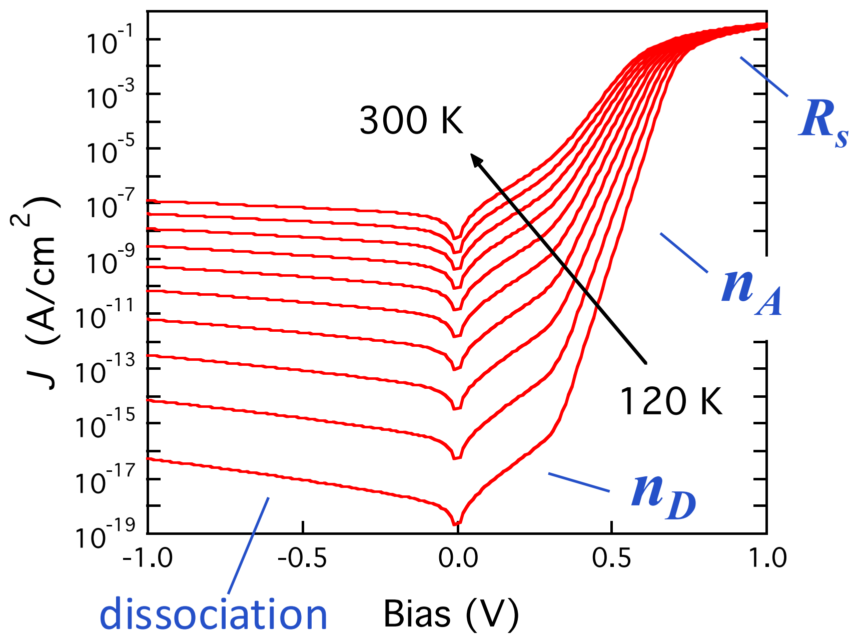
- Ideality factors: n_D, n_A depend on *shape* of trap DOS
  - e.g. n=2 for uniform distribution between HOMO and LUMO



Dark Current With Traps

- General form including series resistance:

$$J = J_{sD}\left[\exp\left(\frac{q\left(V_a - JR_s\right)}{n_D k_b T}\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] + J_{sA}\left[\exp\left(\frac{q\left(V_a - JR_s\right)}{n_A k_b T}\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] - q\eta_{PPd}J_X$$

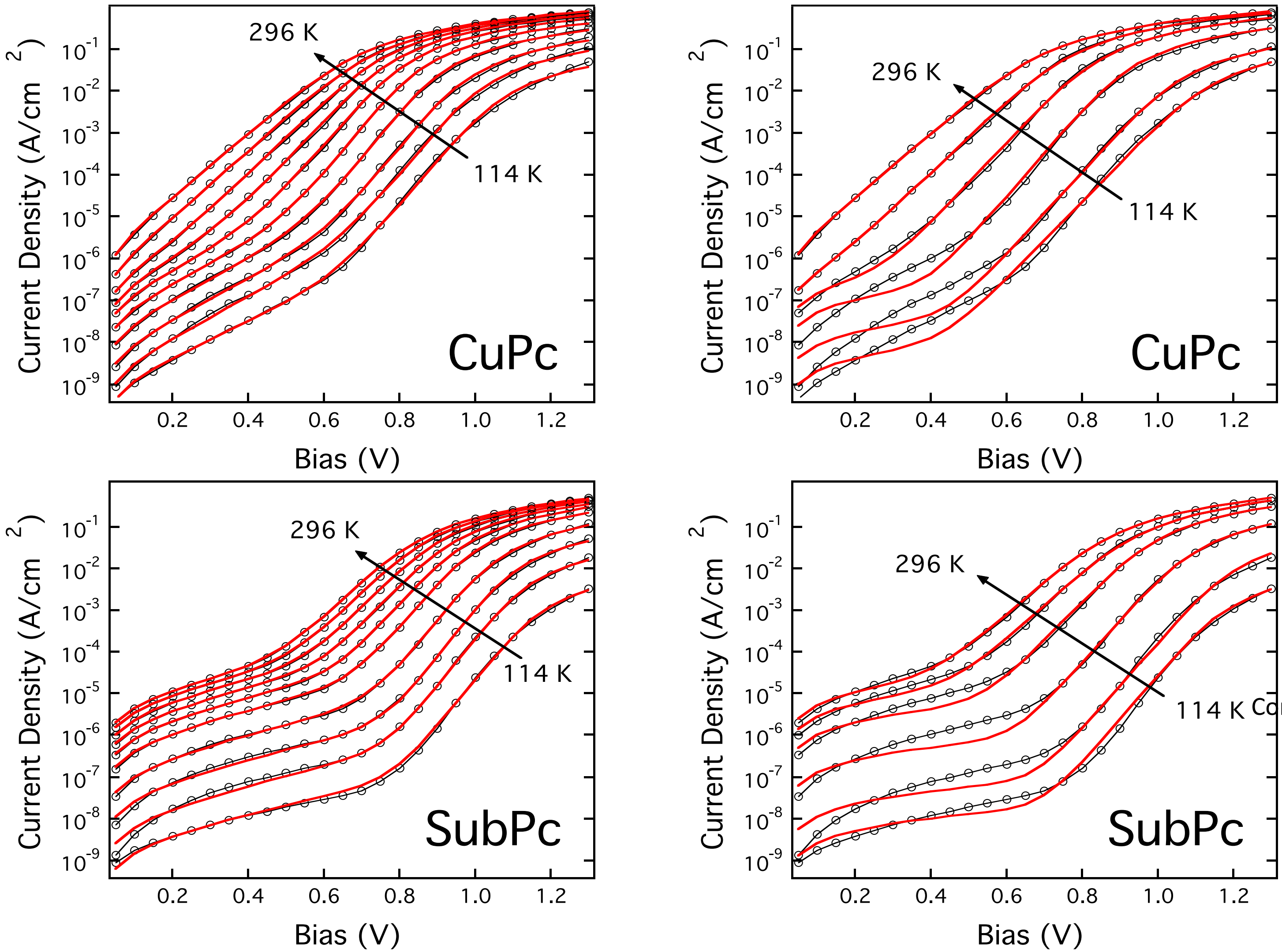


N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

J-V Fits to Diode Eq. with Traps

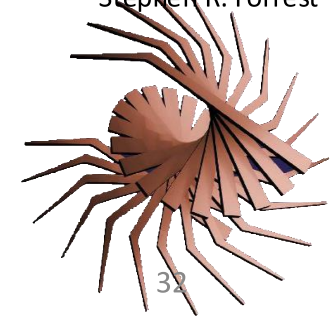
Org. HJ with Traps

Shockley Eq.



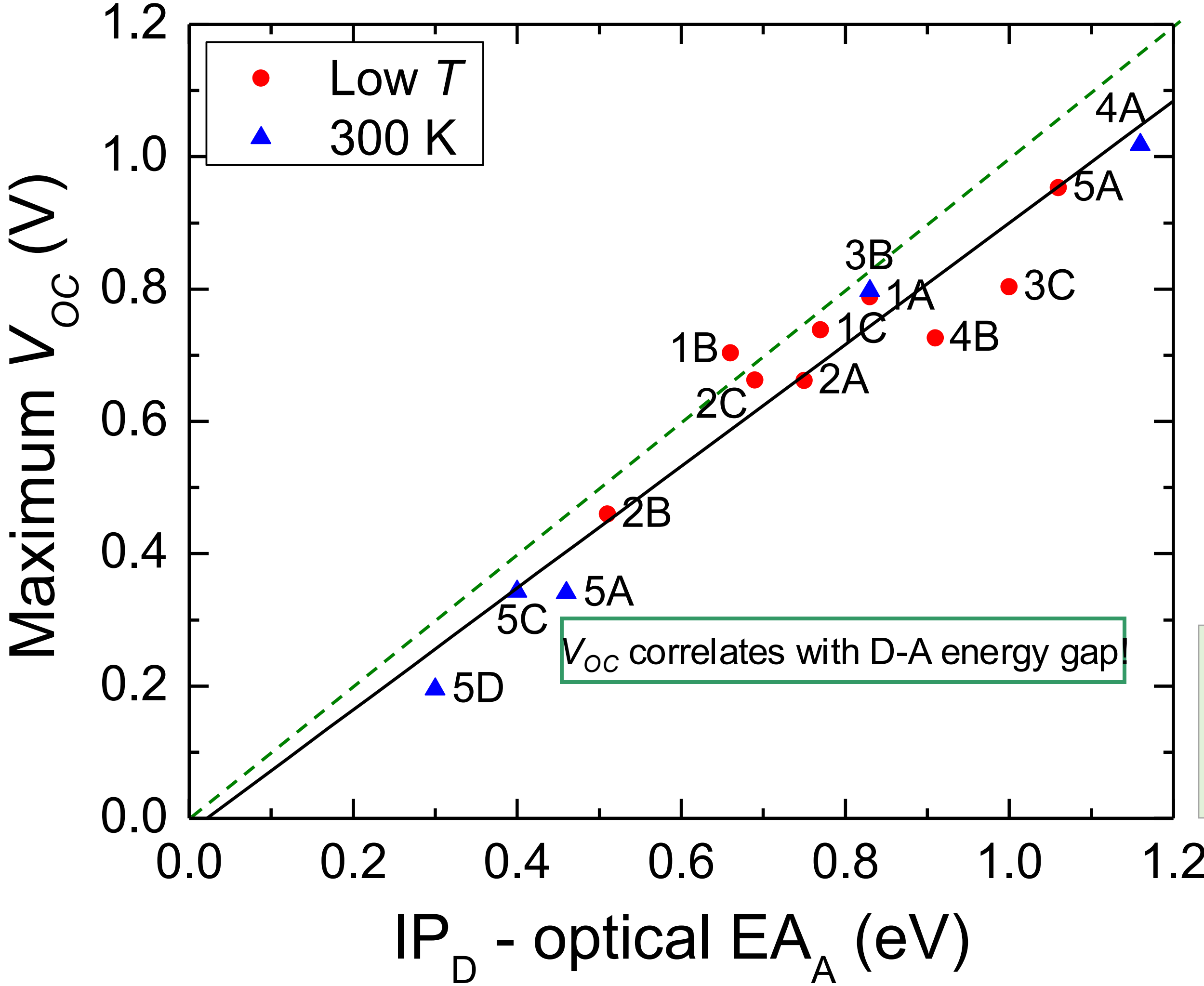
Acceptor

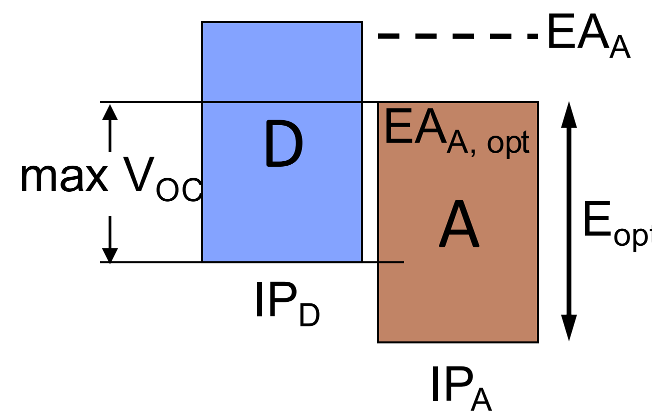
C_{60}



N. C. Giebink, et al. Phys. Rev. B, **82**, 155305 & 155306 (2010).

Dependence of V_{OC} on HJ Energies for Many Different D-A Combinations

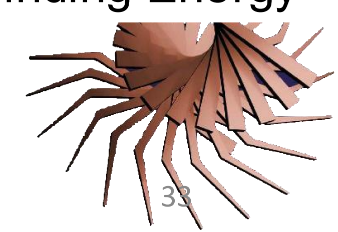




A single rule fits all materials

$$qV_{OC}^{max} = \overbrace{IP_D - EA_A}^{E_{HL}} - \overbrace{\frac{q^2}{4\pi\varepsilon_0\varepsilon_r r_{DA}}}^{-E_B}$$

PP Binding Energy



B.P. Rand, et al., *Phys. Rev. B*, **75**, 115327 (2007).

What the theory tells us

Open Circuit Voltage

$$qV_{oc} = \left(\Delta E_{HL} - E_B\right) - k_b T \ln\left[\frac{k_{PPr} N_{HOMO} N_{LUMO}}{\zeta_{\max} J_X / a_0}\right]$$

- At maximum sustainable power $J_x \sim a_o N_{HOMO} k_{PPr}$

  - More excitons cannot be supported.

Also: $\zeta_{\max} \sim N_{HOMO} \sim N_{LUMO}$

Thus: $qV_{oc} = \Delta E_{HL} - E_B$ ➡ *as observed!* *(E_B=polaron energy)*

- Slope under reverse bias due to PP recombination – eliminates R_p

Electronic Transport in Organics -What we learned

- Origins of electronic band structure
- Concept of polarons (large and small)
- Charge transfer
- Conductivity, effective mass and mobility
- Doping
- Effects of trapped charge
- Schottky Barrier Diodes
- Organic Heterojunctions