Week 1-11

Electronic Properties 5

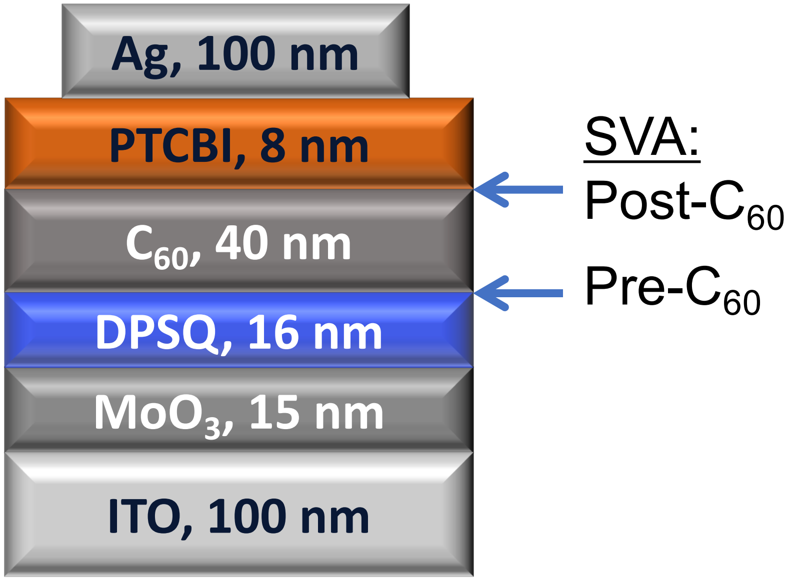
Organic Heterojunctions, cont'd

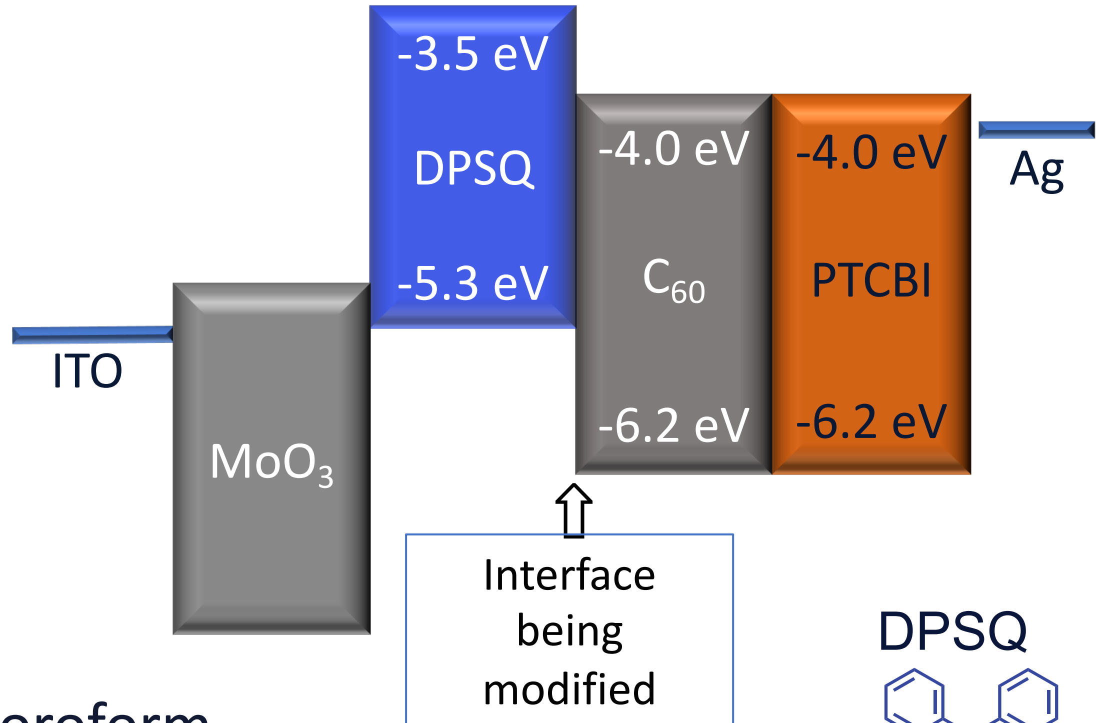
Organic-Inorganic Heterojunctions

Chapter 4.7.2-4.8

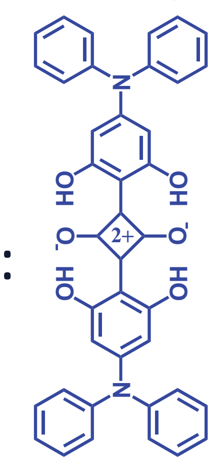
A Test of the Ideal Diode Theory

The role of order





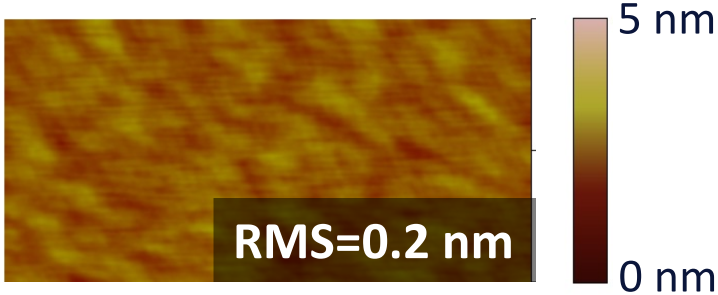
DPSQ



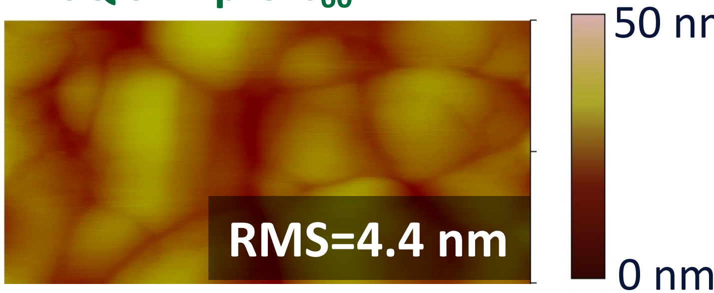
- DPSQ is spun cast from chloroform.
- Other layers deposited by thermal evaporation.
- **Vary D-A interface order via solvent vapor annealing** (SVA):
  - 10 min exposure to dichloromethane vapor to “anneal” squaraine component.

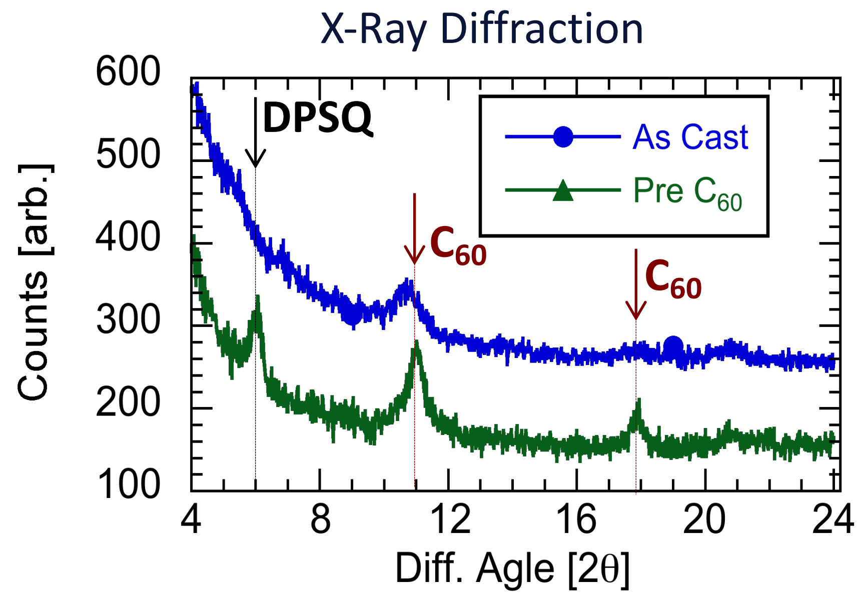
SVA Pre-C_{60}

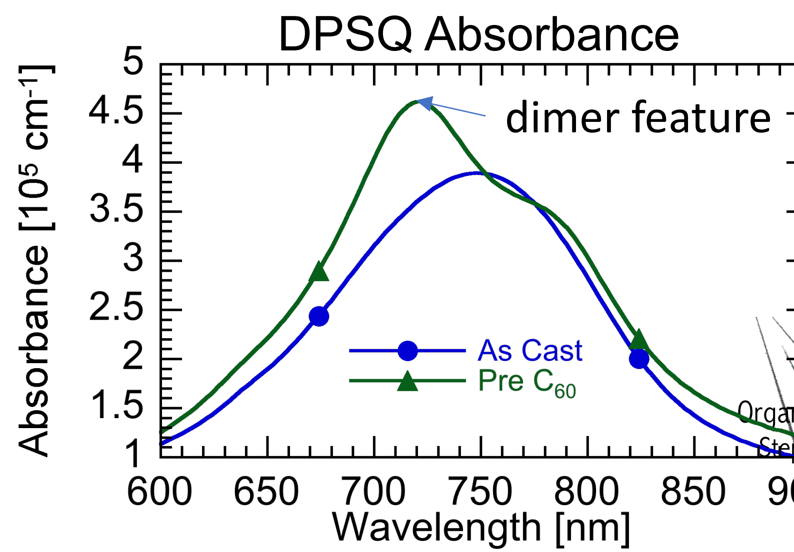
As Cast DPSQ



DPSQ SVA pre-C_{60}



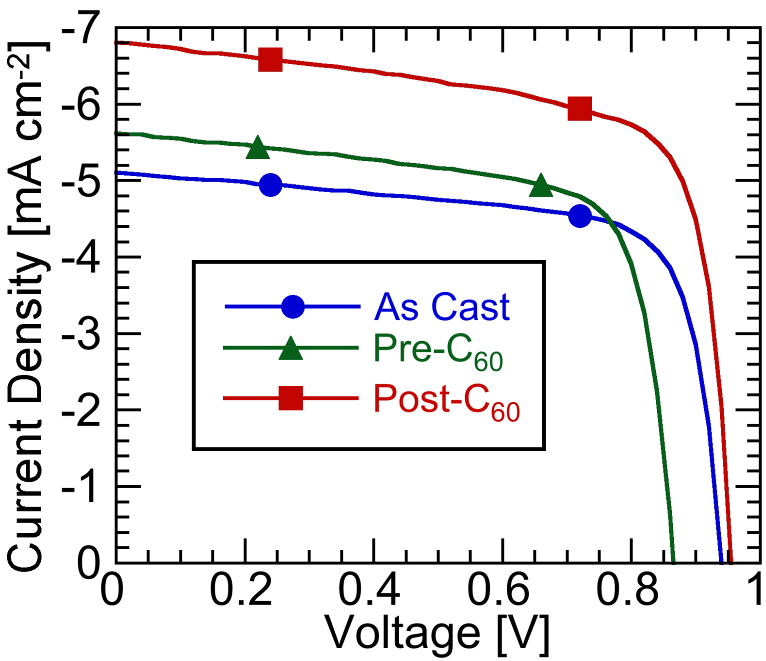


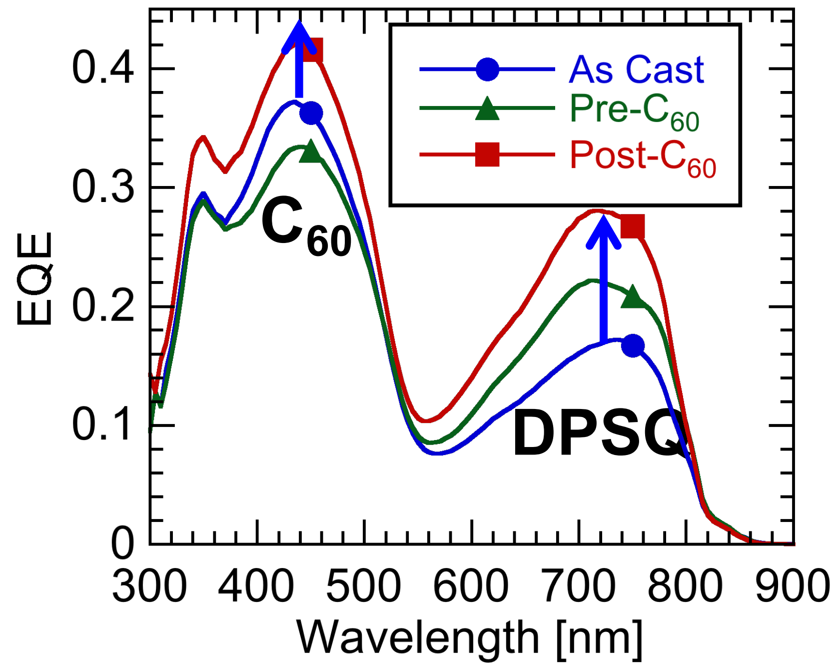


- SVA Pre C_{60}:
  - Crystallizes and roughens DPSQ.
  - Crystalline DPSQ templates *quasi-epitaxial* C_{60} growth.

J. D. Zimmerman, et al. Nano Lett. 12, 4366 (2012)

Devices with SVA Post-C_{60}



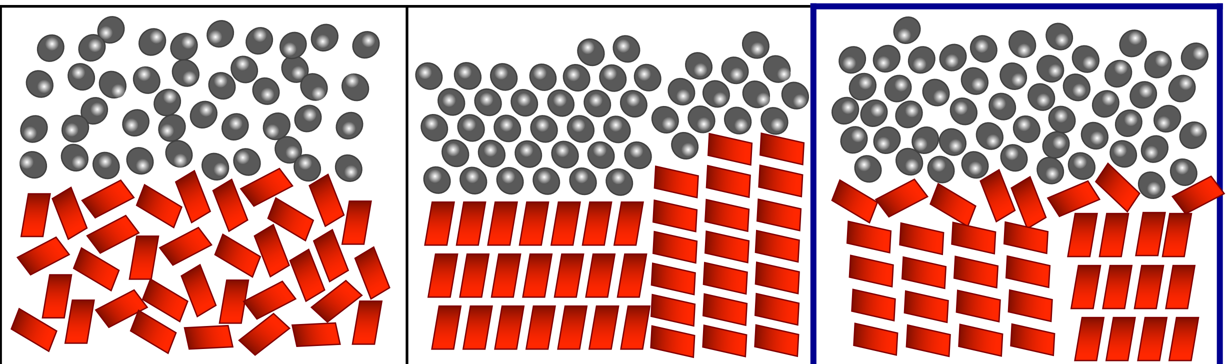


- SVA post-C_{60}
  - DPSQ EQE ⇑ 80%.
  - J_{SC} ⇑ 25%.
- No loss in V_{OC}
  - k_{PPr} unchanged.

Process	J_{SC}[mA cm^{-2}]	V_{OC} [V]	FF [%]	η_P [%]
As Cast	5.3±0.3	0.94	73	3.6±0.2
Pre-C_{60}	5.6±0.3	0.86	70	3.4±0.2
Post-C_{60}	7.0±0.4	0.96	71	4.8±0.3

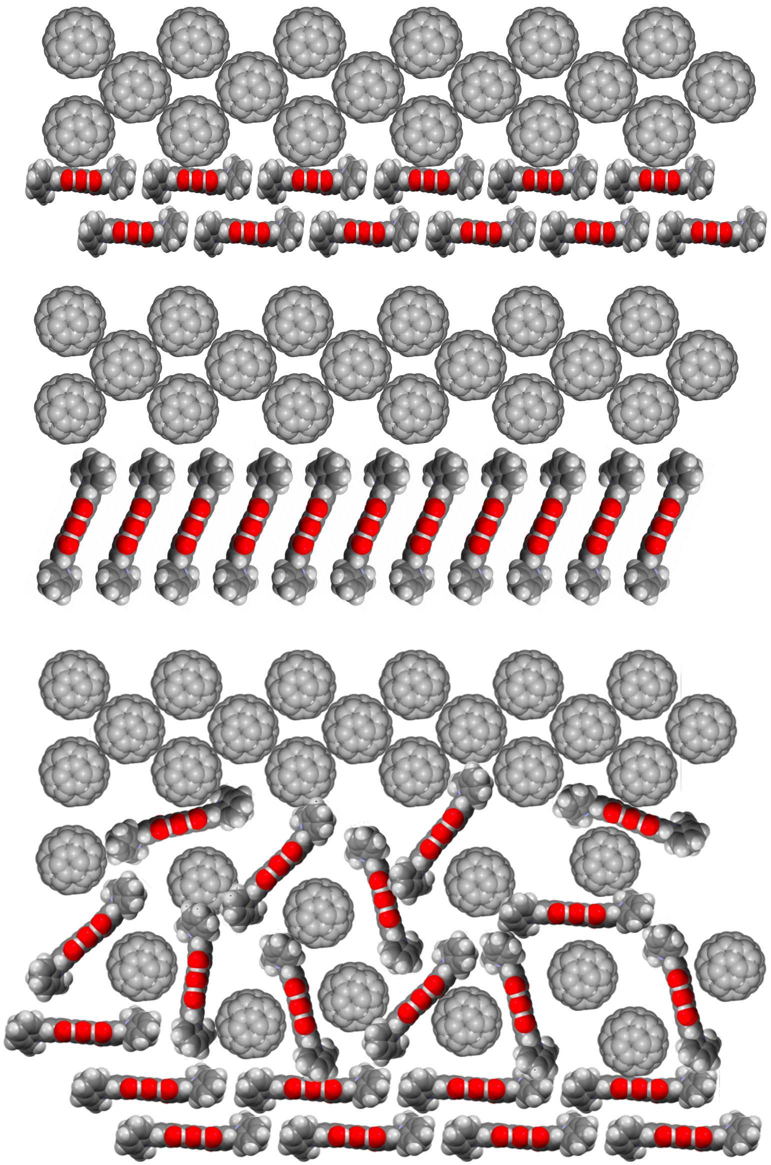
J. D. Zimmerman, et al. Nano Lett. 12, 4366 (2012)

Achieving the Ideal Morphology



	As Cast	Pre C_{60}	Post C_{60}
Bulk DPSQ	Amorphous	Ordered	Mod. Order
Bulk C_{60}	Weak order	Ordered	Weak Order
Interface	Disordered	Ordered	Disordered
Surface	Smooth	Rough	Smooth
k_{PPr}	Low	High	Low
V_{OC}	High	Low	High
J_{SC}	Low	Moderate	High

Morphology vs. V_{OC}



$$qV_{OC} = \Delta E_{HL} - nk_B T \ln\left[\frac{k_{PPr}}{k_{PPd}} \frac{k_{rec} N_L N_H}{J_X / \alpha_0}\right]$$

$$k_{rec} = \gamma = \frac{q}{\varepsilon}(\mu_e + \mu_h)$$

- Worst case scenario: perfectly ordered crystalline interface and bulk, Face-on .
  - High k_{PPr} and k_{rec}
- Better Scenario I: Perfectly crystalline and end-on orientation
- Even Better Scenario II: crystalline bulk, intermixed interface
  - Poor coupling between like-molecules (C_{60}-C_{60} and SQ-SQ) reduces PP formation (k_{rec}) probability.
  - Overcomes enhanced k_{ppr} due to facial contact

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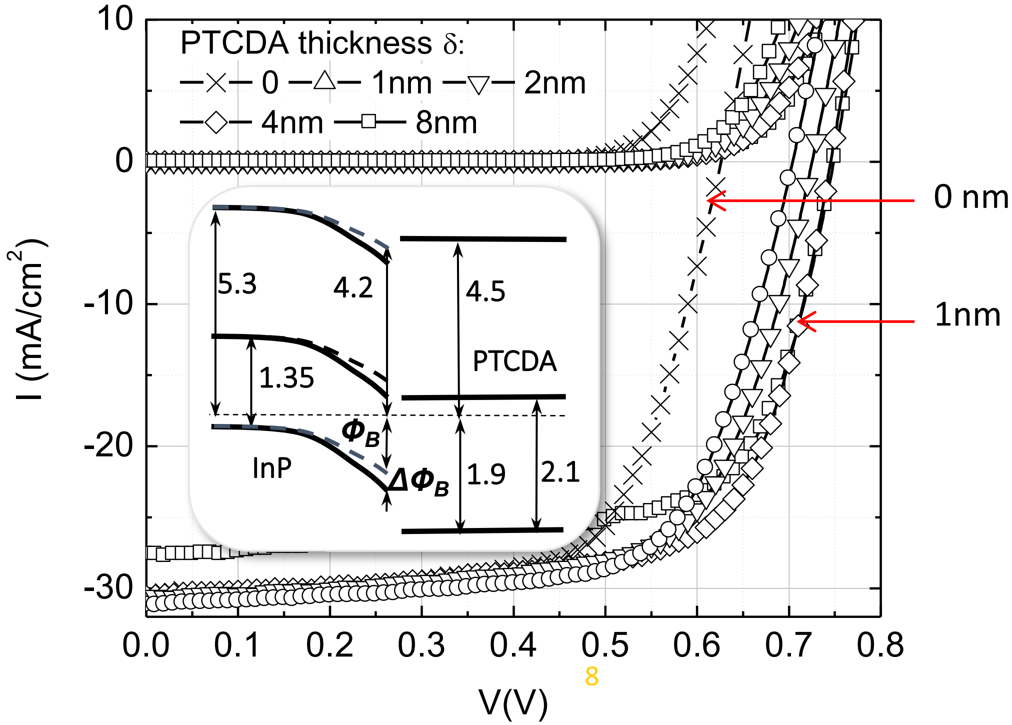
Organic-Inorganic HJs

- The dynamics at organic HJs are based on exciton transport and recombination
- The dynamics of inorganic HJs are based on free charge transport and recombination
- Can we understand hybrid materials systems based on a combination of these two pictures?

Organic-Inorganic HJs: Motivation

- Organic surface passivation of III-V Schottky barrier PV
  - Increase PCE from 13% to 15% in p-InP SB-PV
- Charge transfer between an organic dye and inorganic semiconductor is a critical process in DSSCs
- Nanostructured inorganics for PVs and PDs
- Bridge the gap between inorganic/inorganic and organic/organic junction models, to describe the o/i junction.



N. Li, et al., *Appl. Phys. Lett.*, **98**, 053504 (2011)

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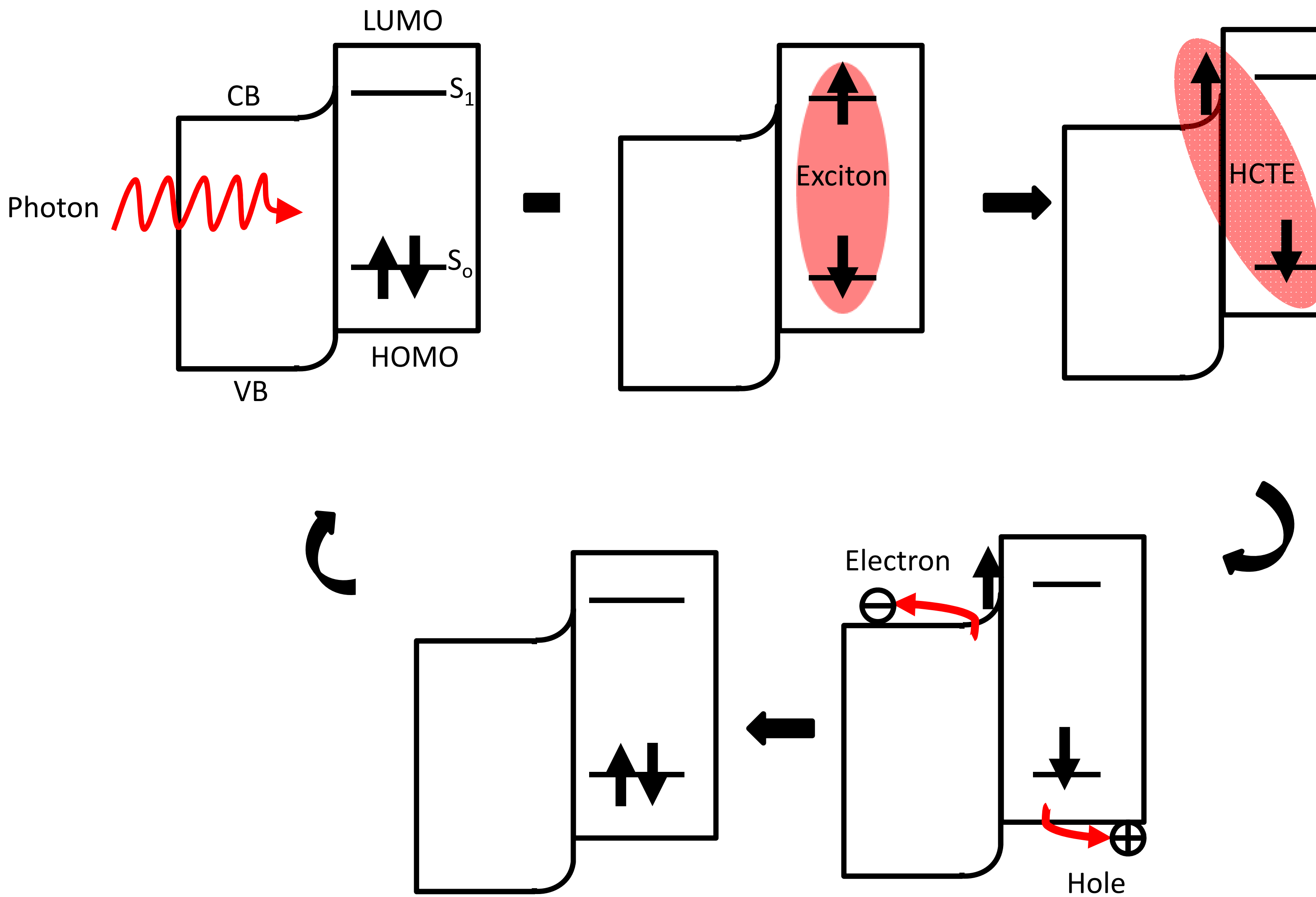
Photocharge Generation at the OI-HJ



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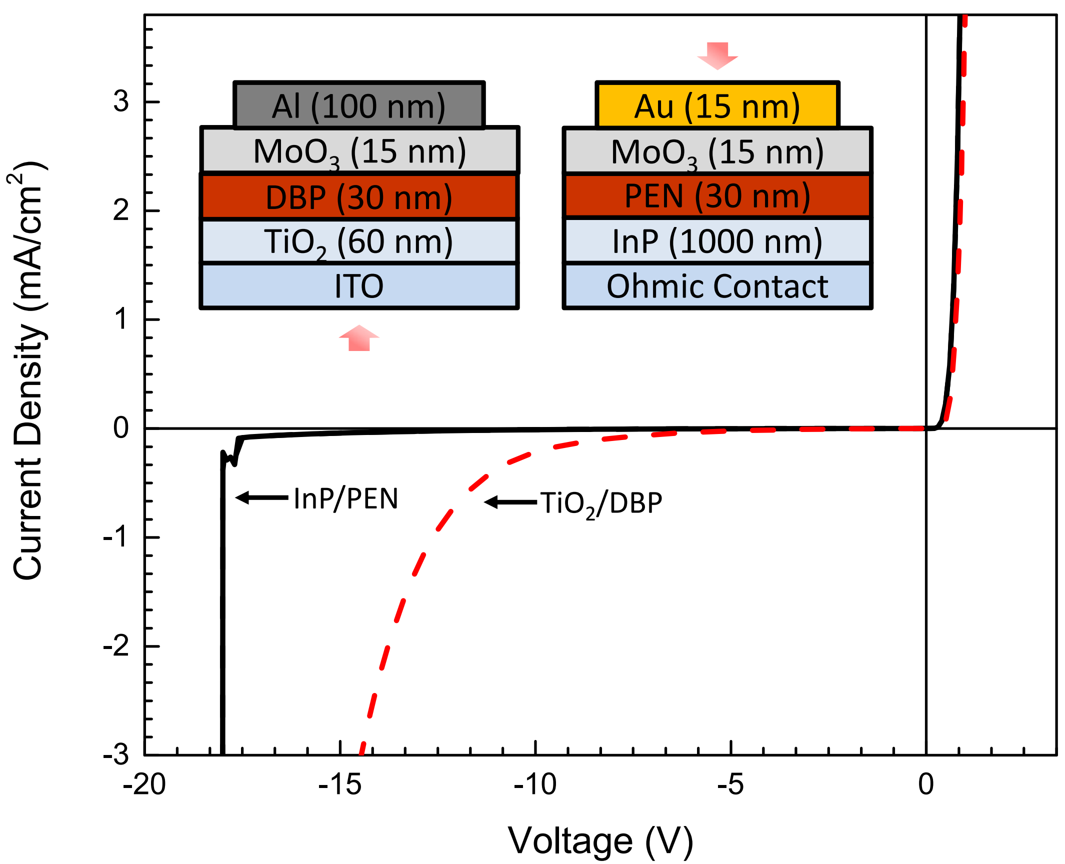
Two Archetype IO-HJs



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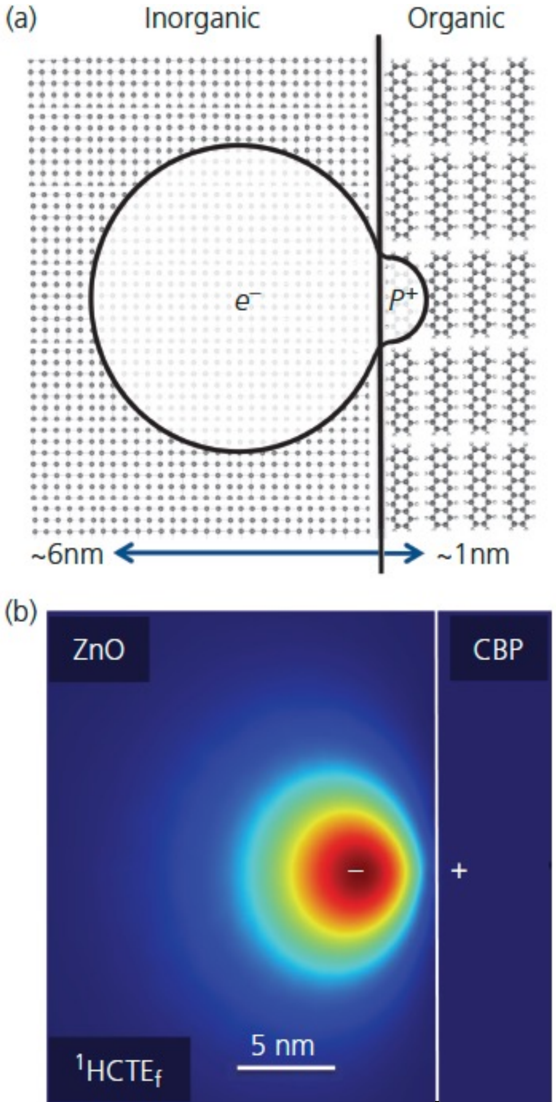
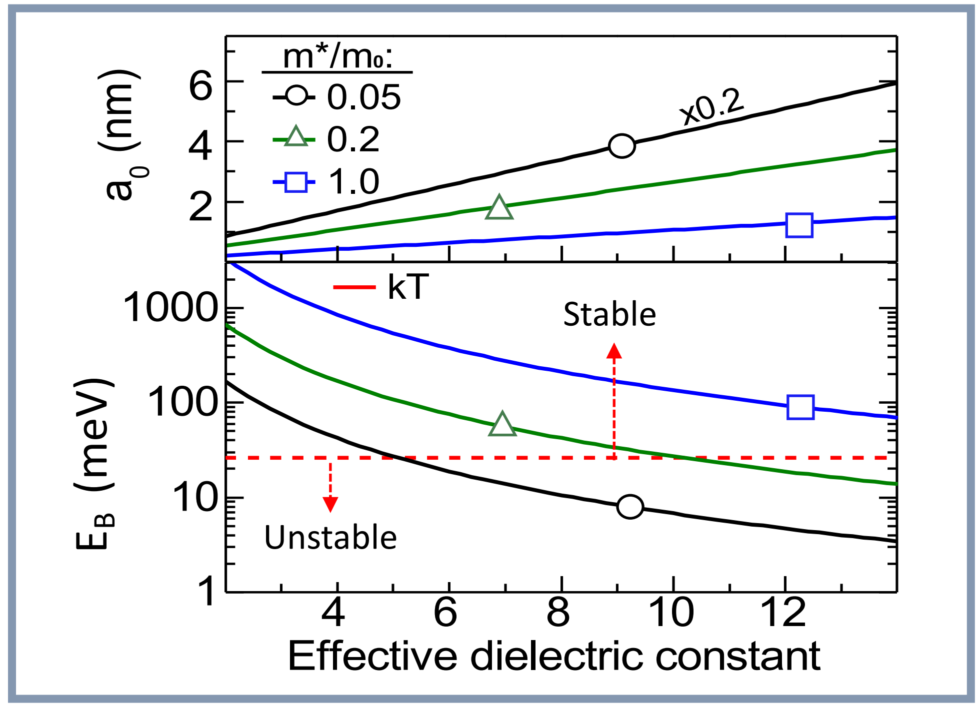
Hybrid Charge Transfer Exciton



inorganic ← → organic

Electron density distribution

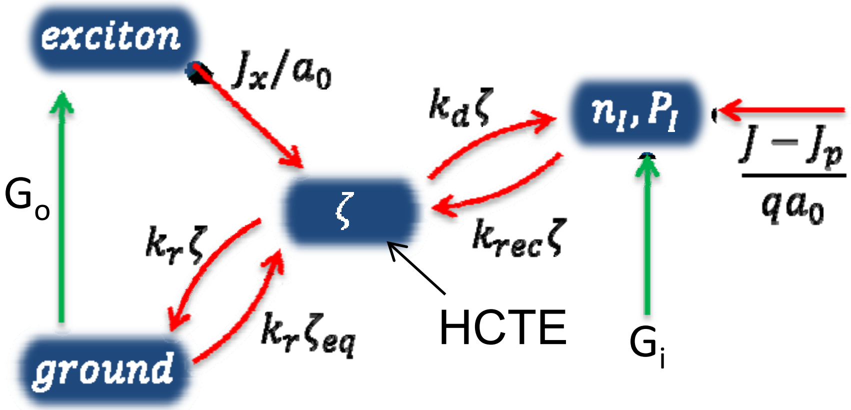


$$\langle a \rangle = a_I + a_O = \frac{8\pi \langle \varepsilon_r \rangle \hbar^2}{m^* q^2},$$

$$\langle \varepsilon_r \rangle = (a_I \varepsilon_I + a_O \varepsilon_O)/(a_I + a_O),$$

C. K. Renshaw, and S. R. Forrest, *Phys. Rev. B*, **90**, 045302 (2014).

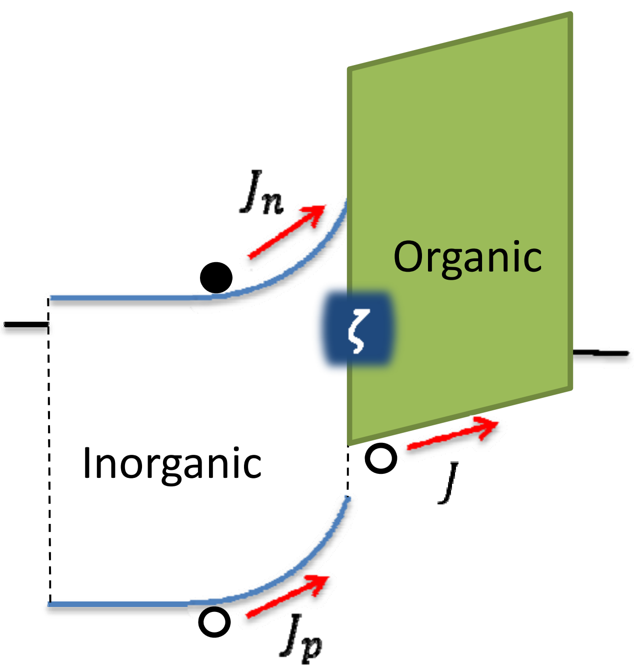
The Hybrid Charge Transfer Exciton Picture



<u>Conservation Equations:</u>

$$\frac{d\zeta}{dt} = \frac{J_x}{a_0} - k_r(\zeta - \zeta_{eq}) - k_d\zeta + k_{rec}n_I P_I = 0$$

$$\frac{dn_I(P_I)}{dt} = k_d\zeta - k_{rec}n_I P_I + \frac{J - J_p}{qa_0} = 0$$

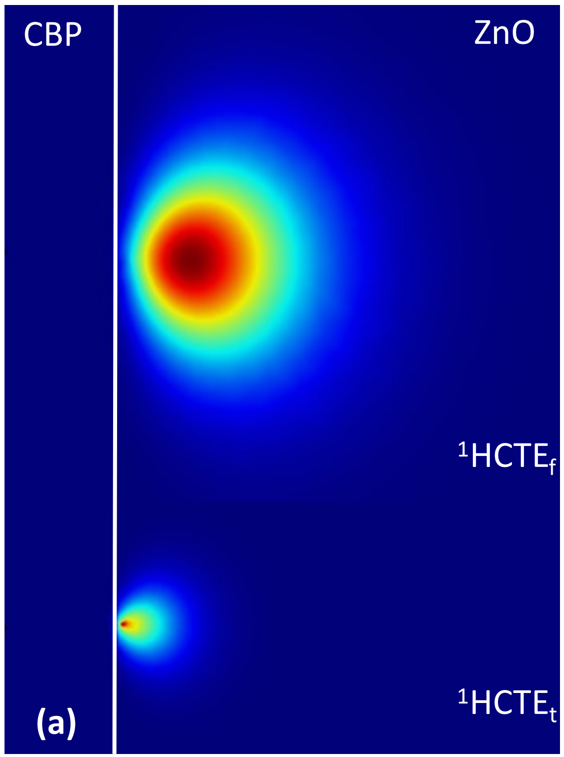


<u>Hybrid Charge-Transfer (ζ) Current:</u>

$$J = qa_0k_{rec}(1-\eta)\left(n_I P_I - \frac{k_{PPd}}{k_{PPd,eq}} n_{I,eq} P_{I,eq}\right) - qJ_x\eta + J_p$$

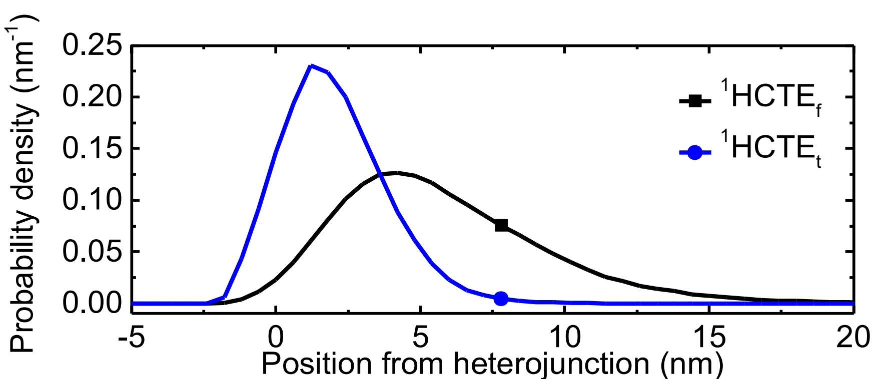
- Current Limiting Mechanisms:
  - Recombination/Generation at interface
  - Injection/Diffusion across interface
- Simultaneous solution yields unique $J(V_a)$

HCTEs Can Be Free, or Trapped at Interface Defects



CBP/ZnO OI-HJ

- Trapped states are smaller and less mobile than free states
- Trapped states can have higher oscillator strength due to improved e-h overlap



Profile of electron density

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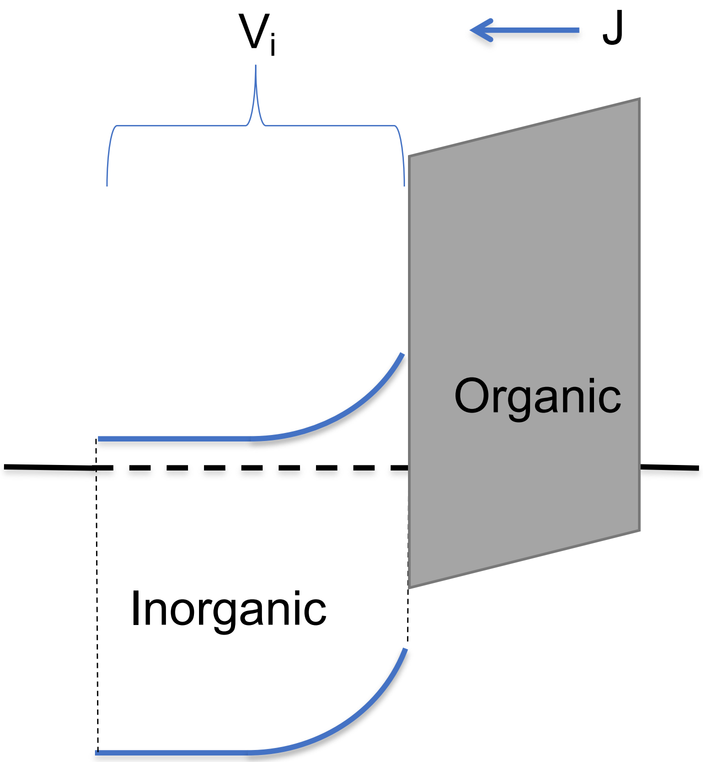
Panda et al., Phys. Rev. B 94, 125429 (2016)

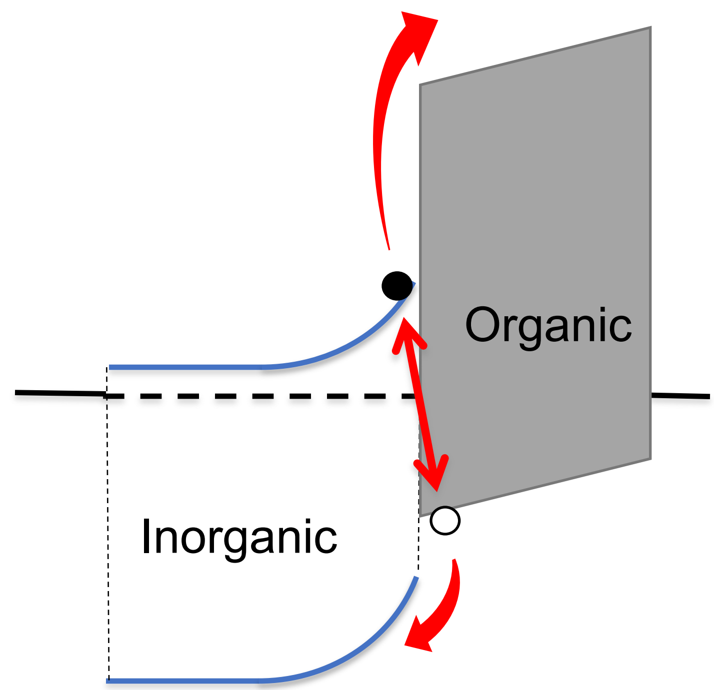
Two Part Device Model of the OI-HJ

Electrostatic



- Solve Drift-Diffusion Eqn. in Organic
- Get (F, p, n, V_o) for given J and V_i
- Not a unique solution

Interface Current



- Current Limiting Mechanism:
  - Recombination/Generation at interface
  - Injection/Diffusion across interface
- Simultaneous solution yields unique $J(V_a)$

OI Diode Equations

Similar (in some important ways) to both I and O junctions

Without Traps:

$$J = qa_O k_{rec} N_{HOMO} N_c \exp\left(-\frac{\Delta E_{IG}}{k_B T}\right)\left(\exp\left(\frac{qV_a}{k_B T}\right)-1\right) - qJ_X + J_i$$

With Traps in Organic Only:

$$J = qa_O\left[k_{rec,n} N_c H_O \exp\left(-\frac{\alpha_O}{k_B T}\right)\left(\exp\left(\frac{qV_a}{n_O k_B T}\right)-1\right) + k_{rec,P} N_{HOMO} H_i \exp\left(-\frac{\alpha_i}{n_i k_B T}\right)\left(\exp\left(\frac{qV_a}{n_i k_B T}\right)-1\right)\right] - qJ_X + J_i$$

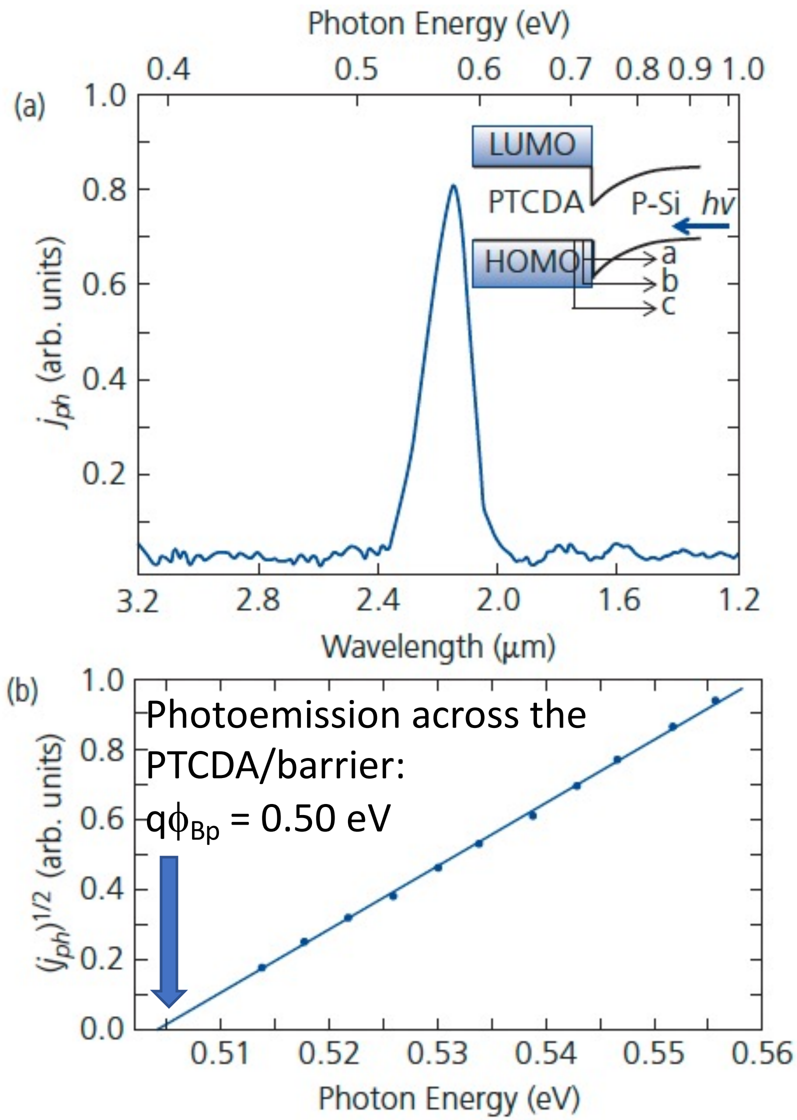
$$n_o = \frac{l_o}{\delta_i(l_o - 1) + 1}, \quad \alpha_o = \frac{\Delta E_{IG}}{n_o} + \frac{l_o - 1}{l_o}(\delta_o \phi_o - \delta_i \phi_i)$$

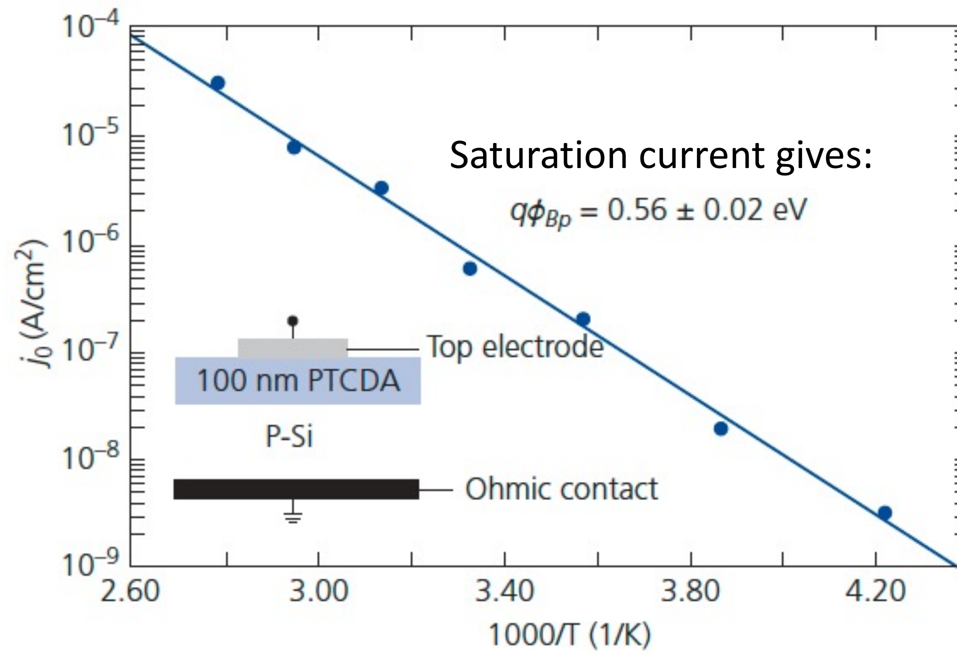
Voltage is divided between sides of the junction

For Hybrid Device:	For Pure Organic Device:
$\delta_o = \frac{1}{1 - \frac{V_i \varepsilon_o}{f(V_i, T) W_o}} = 1 - \delta_i$	$\delta_D = \frac{W_D}{W_D + W_A} = 1 - \delta_A$

C. K. Renshaw, and S. R. Forrest, *Phys. Rev. B*, **90**, 045302 (2014).

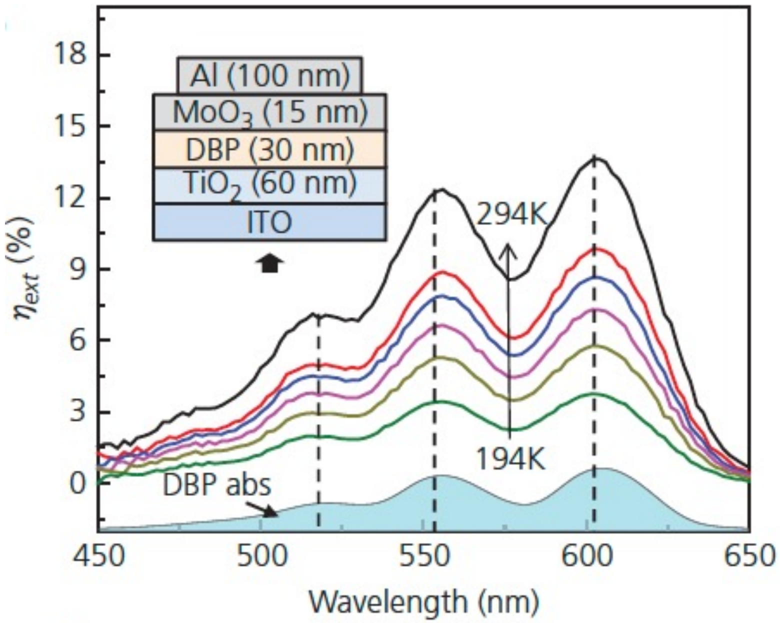
Direct Observation of Transport at an OI-HJ



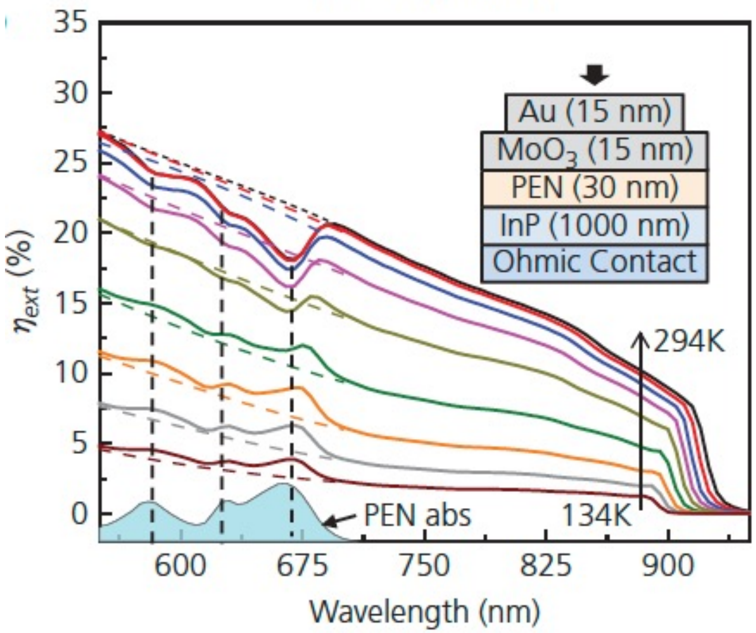


So & Forrest, Appl. Phys. Lett. 52, 1342 (1988).

Spectra from Two Different OI-HJ Diodes



Wide inorganic (TiO_2) band gap: Absorption and quantum efficiency due only to organic (DBP)



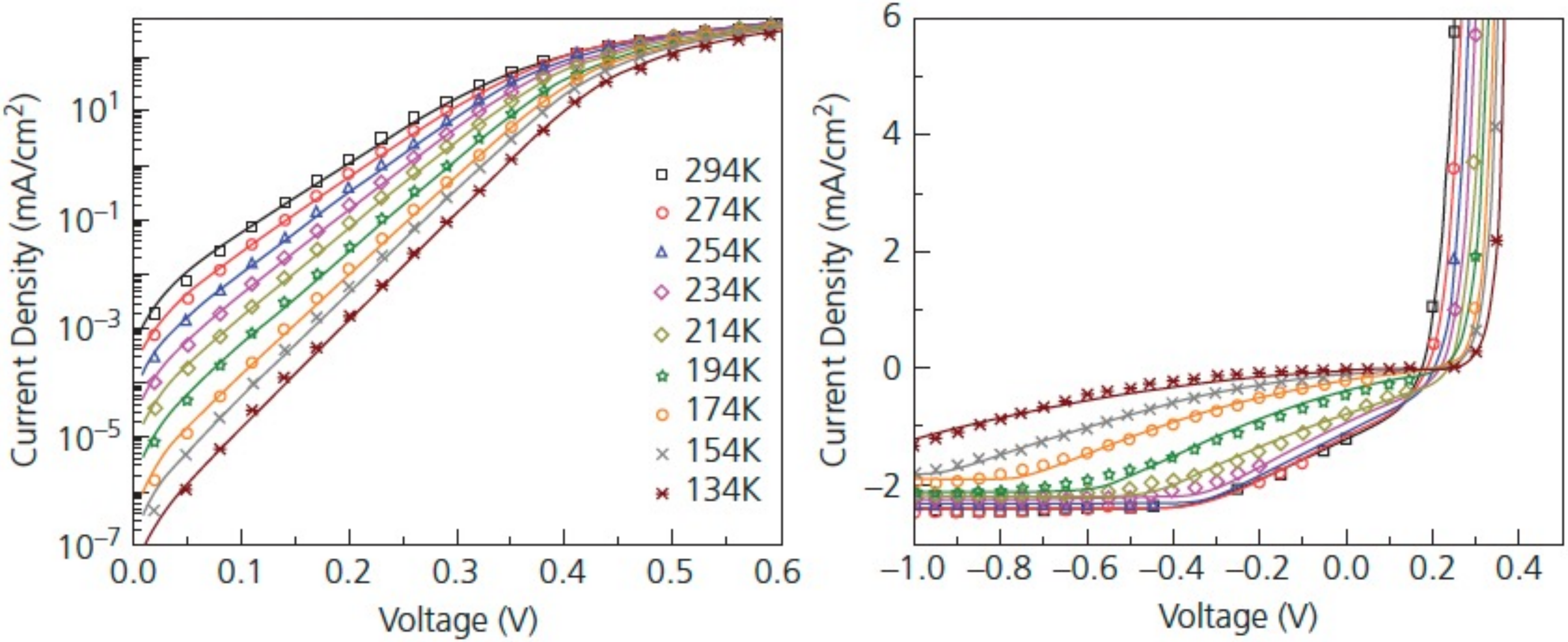
Moderate inorganic (InP) band gap: Absorption and quantum efficiency due only to organic (pentacene)

Note how loss due to absorption in organic converts to gain at low temperature
⇒reduced loss of organic excitons before arrival at heterojunction

A. Panda, et al., *Phys. Rev. B*, **90**, 045303 (2014)

Fit to OI-HJ Theory: DBP/TiO_2

Pentacene/InP



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A. Panda, et al., *Phys. Rev. B*, **90**, 045303 (2014)

Ideal Diode Equations: Why they all look alike!

$$J = J_S\left(\exp\left(\frac{qV}{nk_BT}\right) - \chi\right) - J_{ph}$$

This expression comes from assumption of recombination at the junction

Equation	J_s	J_{ph}	χ	n
Inorganic (diffusion)	$q\left[\frac{D_p n_i^2}{L_p N_D} + \frac{D_n n_i^2}{L_n N_A}\right]$	J_I	1	1
Inorganic[b] (generation, recombination)	$\frac{qn_i}{\tau_t}\left(\frac{k_BT}{q}\frac{2\varepsilon}{qWN_D}\right)$	J_I	$\frac{W}{\left(\frac{k_BT}{q}\frac{2\varepsilon}{qWN_D}\right)}$	2
Organic	$qa_0k_{rec}N_{HOMO}N_{LUMO}(1 - \eta_{PPd})\exp\left(-\frac{\Delta E_{HL}}{k_BT}\right)$	$\eta_{PPd}J_X$	$\frac{k_{PPd}}{k_{PPd,eq}}$	$n_A = \frac{l_A}{\delta_D(l_A - 1) + 1}$
Hybrid	$q\langle a\rangle k_{rec}N_{HOMO}N_c(1 - \eta_d)\exp\left(-\frac{\Delta E_{OI}}{k_BT}\right)$	$\eta_dJ_O + J_I$	$\frac{k_d}{k_{d,eq}}$	$n_O = \frac{l_O}{\delta_I(l_O - 1) + 1}$

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
- Effects of trapped charge: recombination
- Injection from contacts
- Heterojunctions: O-O and O-I

Organic & Inorganic Semiconductor Properties: A Reminder

Property	Organics	Inorganics
Bonding	van der Waals	Covalent/Ionic
Charge Transport	Polaron Hopping	Band Transport
Mobility	<0.1 cm^2/V·s	~1000 cm^2/V·s
Absorption	10^5-10^6 cm^{-1}	10^4-10^5 cm^{-1}
Excitons	Frenkel	Wannier-Mott
Binding Energy	~500-800 meV	~10-100 meV
Exciton Radius	~10 Å	~100 Å

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