Organic Photovoltaics: Overview and Aspects of Theory, Modeling, and Simulation

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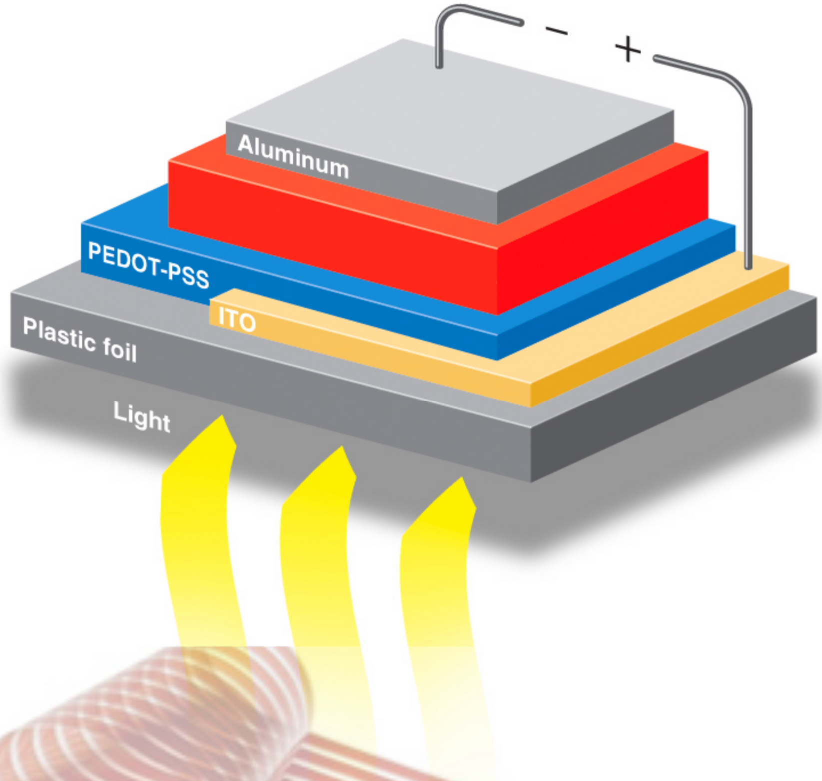
NREL



NSF Challenges in PV Science, Technology, and Manufacturing: The Role of Theory, Modeling, and Simulation

Purdue University

August 2, 2012

Progress in organic photovoltaic efficiencies

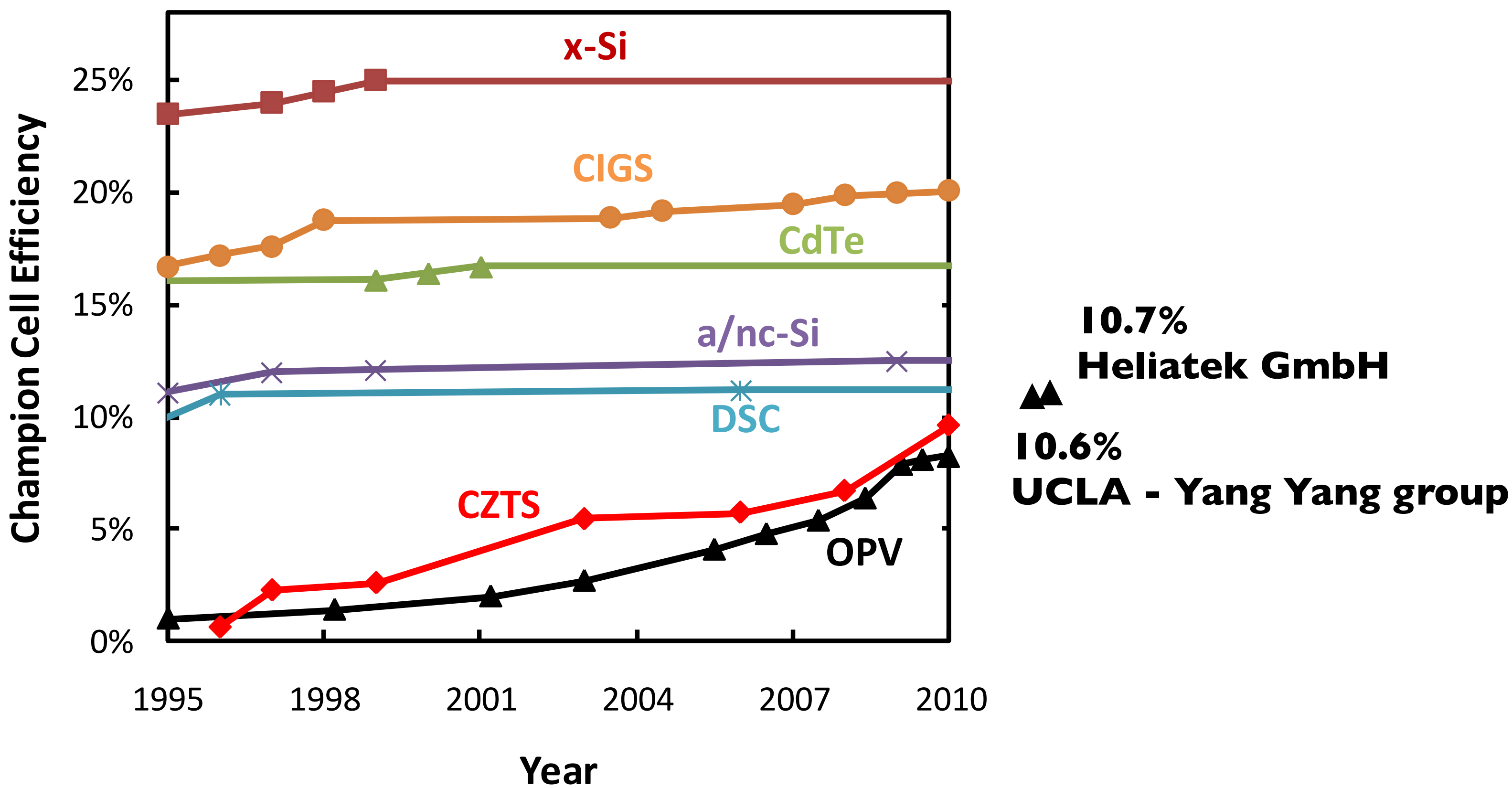
UNIVERSITY of DENVER

Early days of OPV:

- 1958: first reported organic photovoltaic device (Kearns and Calvin, UC Berkeley)
- 1960's - 70's: early work with tetracene, phthalocyanine, and polyvinylcarbazole
- 1986: two-layer cell from phthalocyanine-perylene (CW Tang)
- 1990's: development of pi-conjugated polymers and fullerenes (Friend, Heeger, others)

Recent progress in efficiencies:

*The evolution of champion cell single-junction efficiency since 1995 for various PV technologies**



*C. A. Wolden, J. Kurtin, J. B. Baxter, I. Repins, S. E. Shaheen, J. T. Torvik, A. Rockett, V. Fthenakis, E. S. Aydil, "Photovoltaic Manufacturing: Present Status and Future Prospects", *Journal of Vacuum Science and Technology A*, **29** (3) 030801 (2011).

Companies working on OPV (partial list)

10.7% efficiency
(tandem device)

heliatek
Organic based Photovoltaics
http://www.heliatek.com

10.1% efficiency
(single junction)

MITSUBISHI CHEMICAL
http://www.m-kagaku.co.jp/english/aboutmcc/RC/special/feature1.html

Polyera
http://www.polyera.com

9.1% efficiency
(inverted device)

SOLARMER Energy, Inc.
http://www.solarmer.com/

PLEXTRONICS Light. Power. Circuitry.™
http://www.plextronics.com/

BOSCH
http://www.bosch.com/en/com/innovation/insidebosch/solar_energy_innovation/solar-energy.html

BASF The Chemical Company
http://www.basf-futurebusiness.com/en/projects/organic-electronics/organic-photovoltaics.html

Eight19
http://www.eight19.com

SolarPress Solar Power For Everyone
http://www.solar-press.com/

molecular solar
http://www.molecularsolar.co.uk/

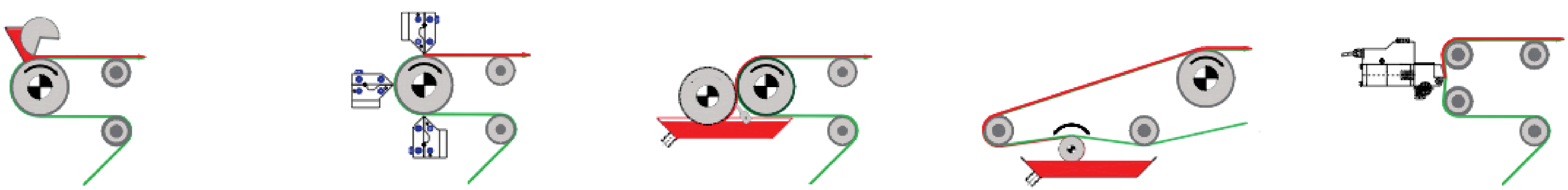
Ossila
http://www.ossila.com/

Industrial manufacturing capability being developed

Coating plant for flexible electronics (*Holst Centre*):

http://www.holstcentre.com/

http://www.coatema.de



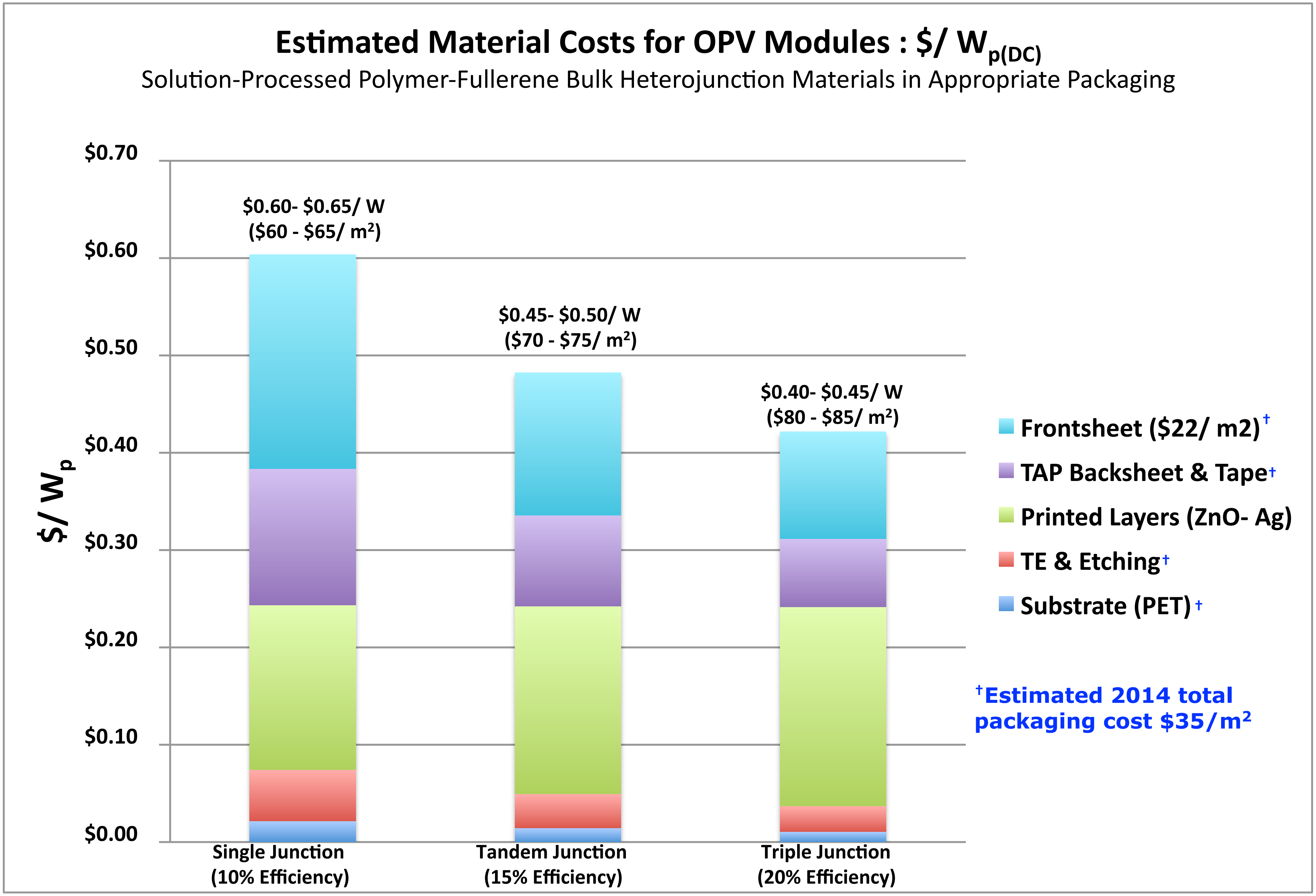
Industrial manufacturing capability being developed

Heliatek, Dresden (Saxony) plant

- roll-to-roll vacuum processing
- 2 - 3 MW in 2012
- new facility with 50 - 75 MW in 2014

http://www.heliatek.com/

Preliminary analysis of OPV material costs*



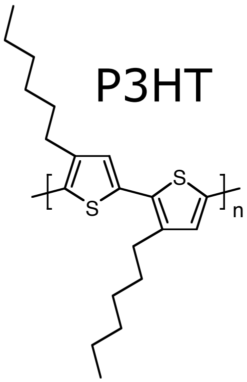
**NREL Energy Analysis team (Michael Woodhouse, Alan Goodrich) and OPV team (Dana Olson,Matthew Reese, David Ginley)*


MRS BULLETIN
Serving the International Materials Research Community
A Publication of the Materials Research Society
January 2005, Volume 30, No. 1
Nanostructured Oxide – Polymer Composites
Top electrode
Polymer
Nucleation layer
TCO
Light
Bulk Heterojunction
Aluminum
PEDOT-PSS
ITO
Plastic foil
Light
Contact
Contact layer
Nano composite layer
Contact layer
Flexible substrate
Donor
Acceptor
π-conjugated polymer
Semiconductor nanoparticles
100nm
Organic Multijunction
Ag
CuPc
Solid-State Dye-Sensitized Cell
Top electrode
TCO
Glass
Light
Dye molecule
TiO2
Fullerene

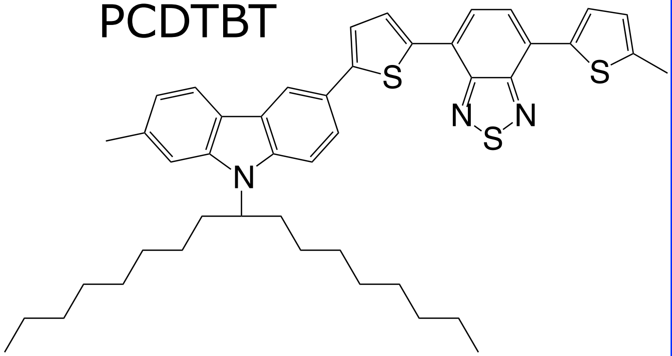
Some typical electron *donor* molecules

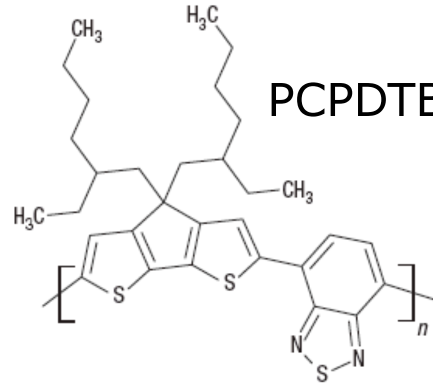
polymers - require solution processing

P3HT



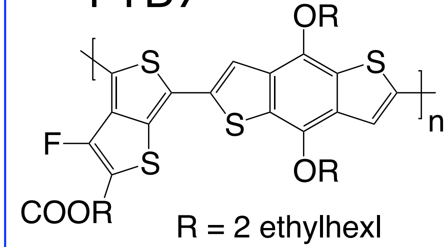
PCDTBT





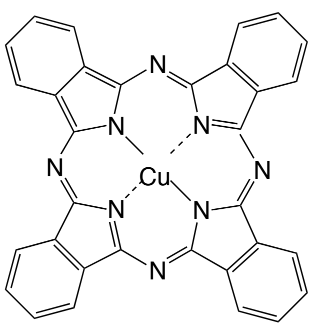
PCPDTBT

PTB7

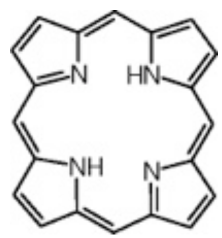


R = 2 ethylhexl

small molecules - require vacuum deposition

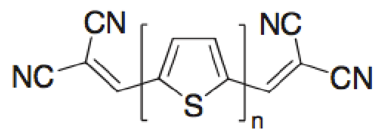


metal phthalocyanine



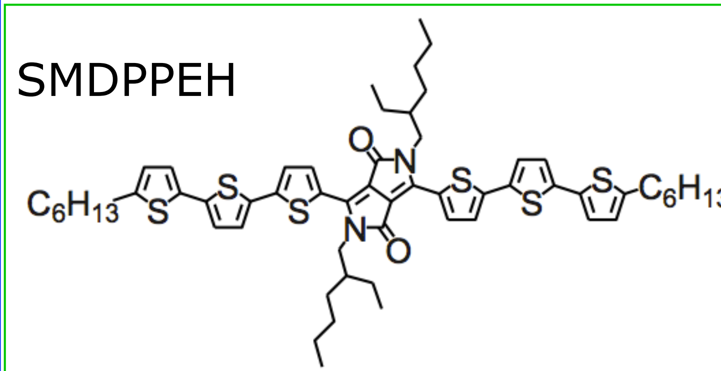
porphyrin

DCV*n*T



1-4 (n=1-4)

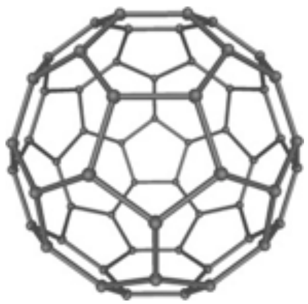
SMDPPEH



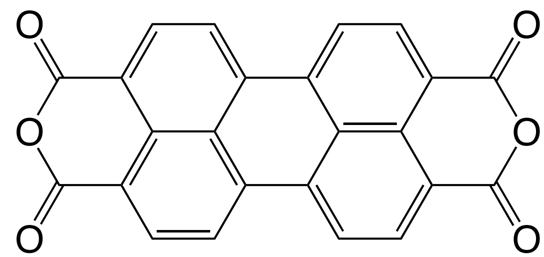
solution processable small molecules

Some typical electron *acceptor* molecules

small molecules - require vacuum deposition

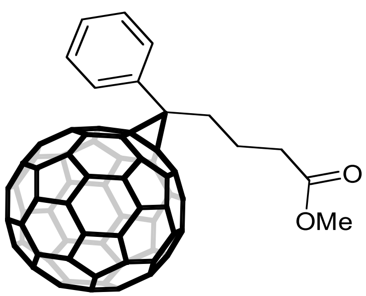


C_{60}

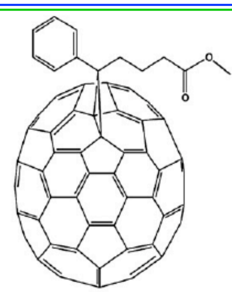


perylene

solution processable small molecules

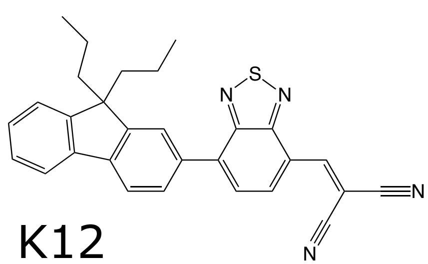


[60]PCBM

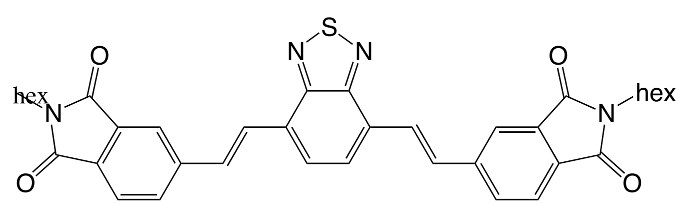


[70]PCBM

ICBA

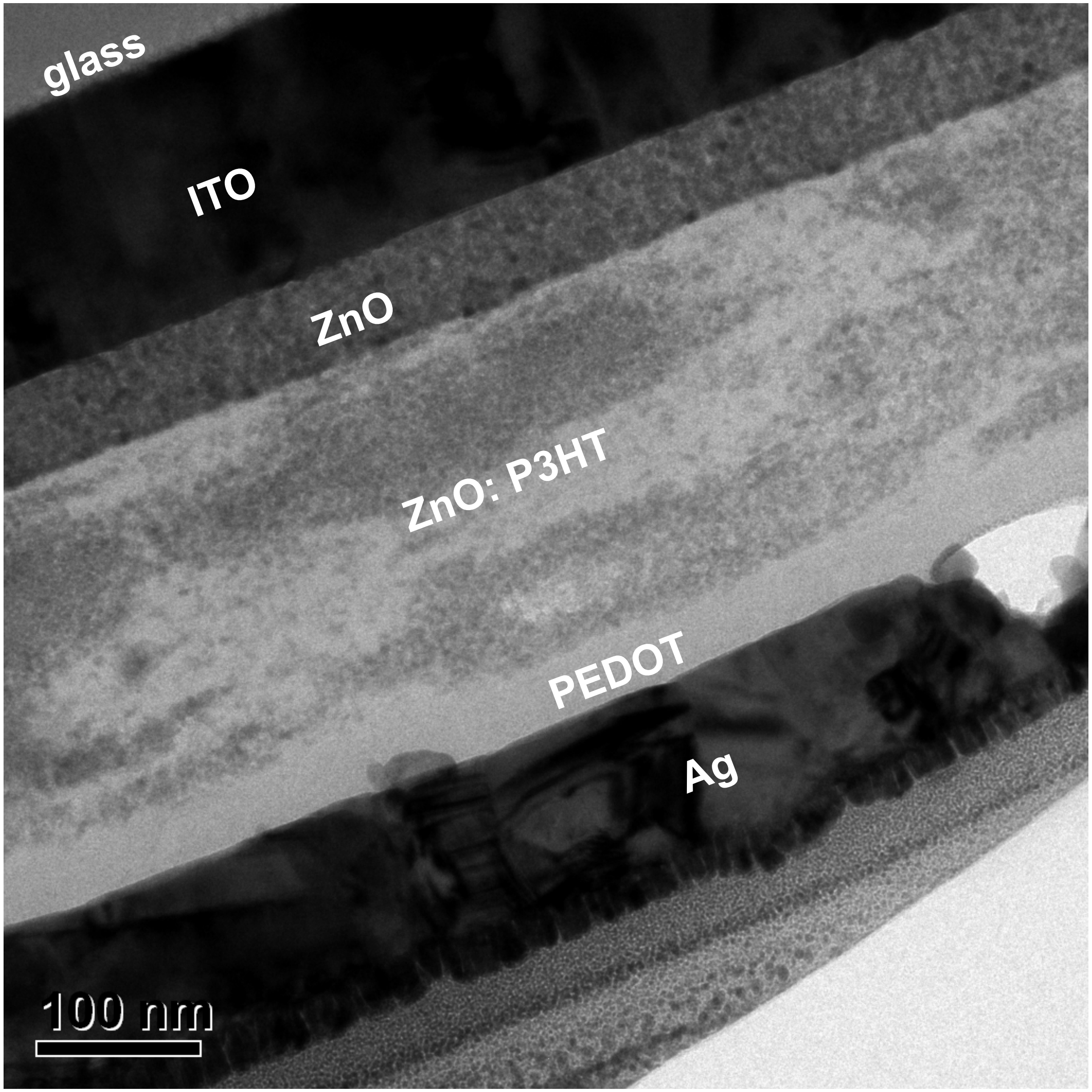


K12



PI-BT

Cross-sectional image of a representative device



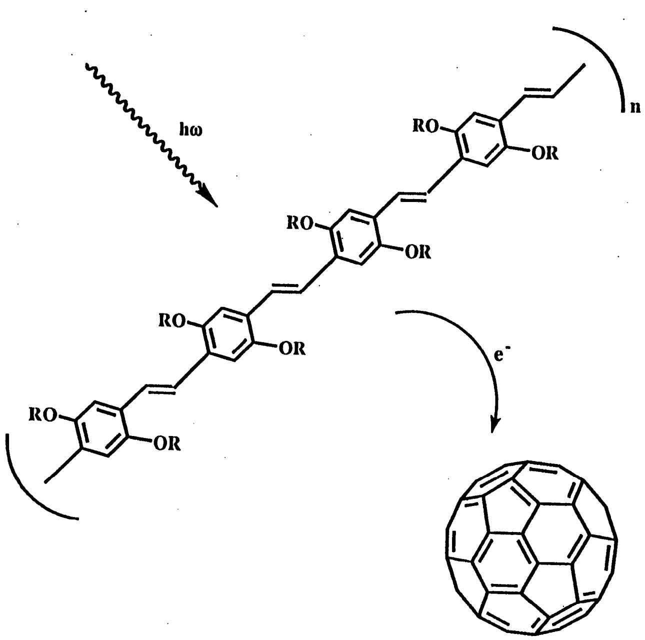
Julia Hsu, UT Dallas

Basic operation of a bulk heterojunction OPV

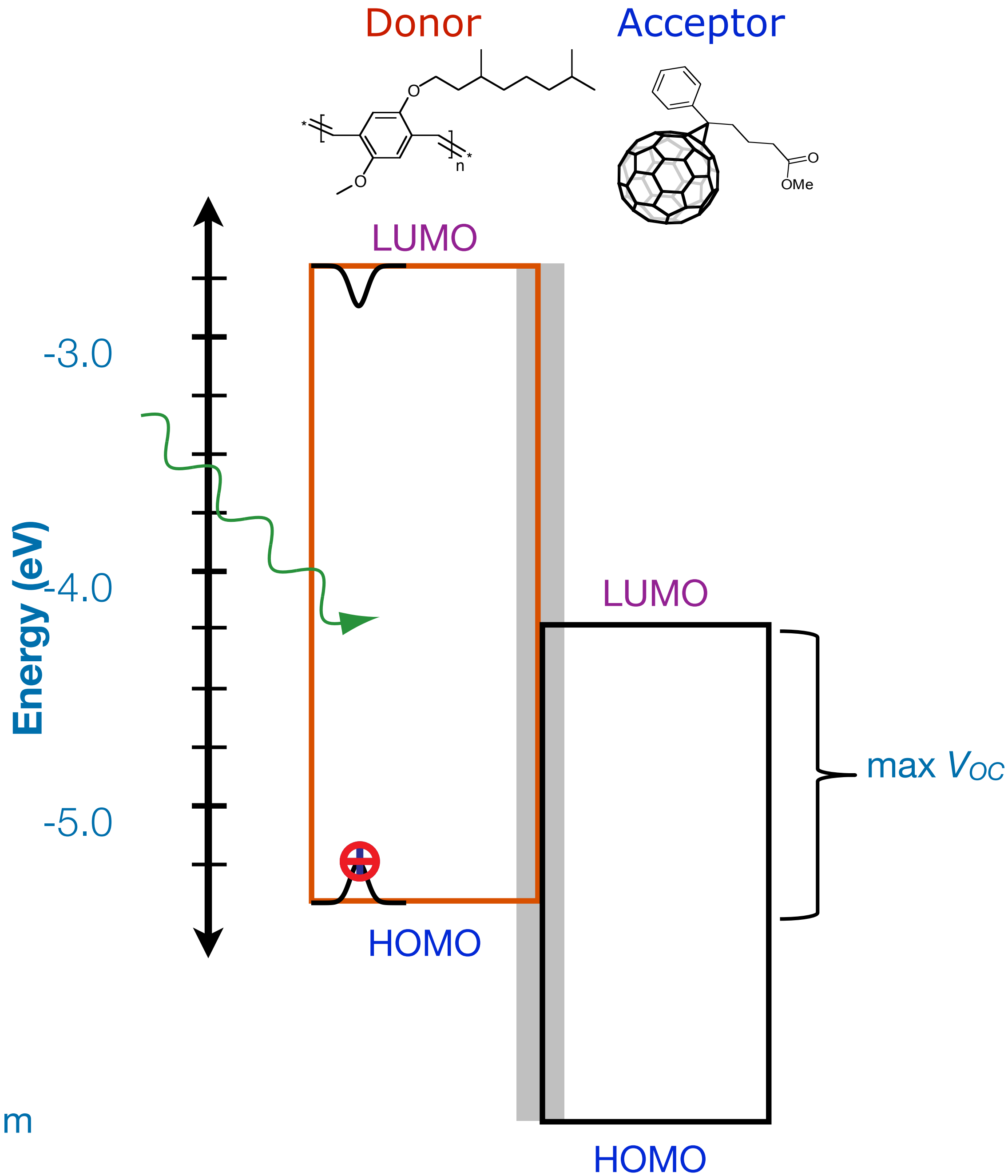
Ultrafast photo-induced electron transfer

Forward rate ~ 45 fs

Backward rate ~ 1μs



100-200 nm

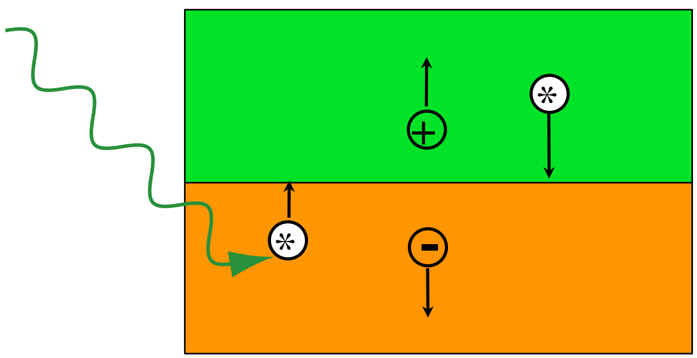


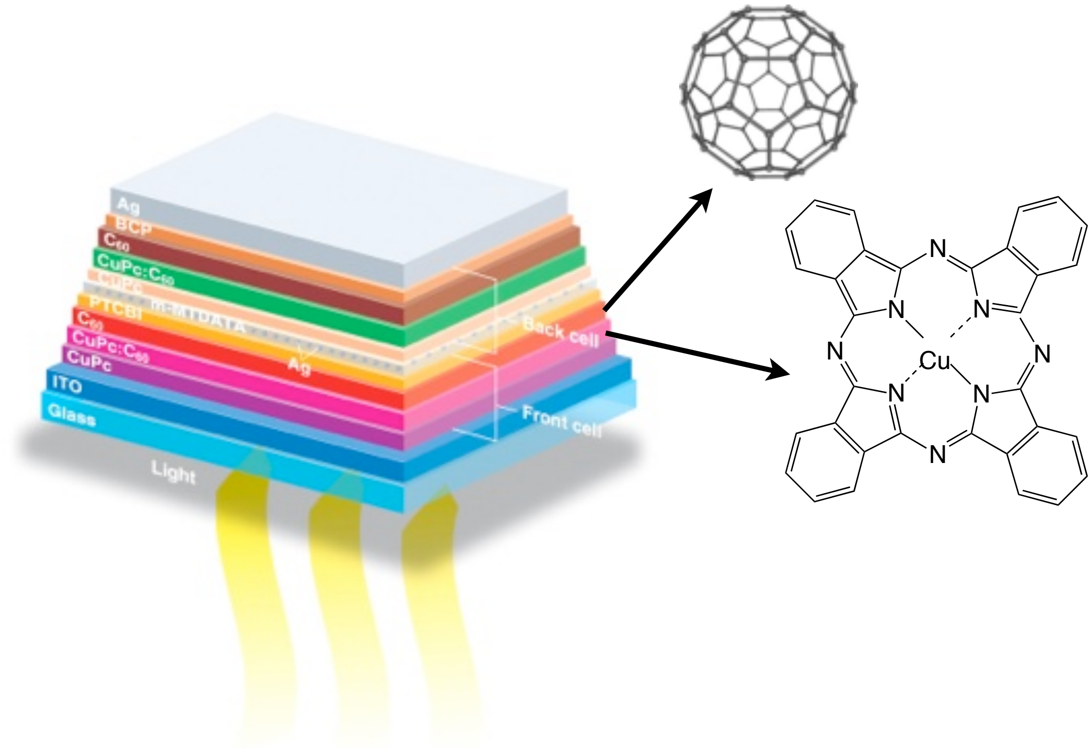
LUMO = Lowest Unoccupied Molecular Orbital / Conduction band
HOMO = Highest Occupied Molecular Orbital / Valence band

Planar versus bulk donor-acceptor heterojunctions

Planar heterojunction

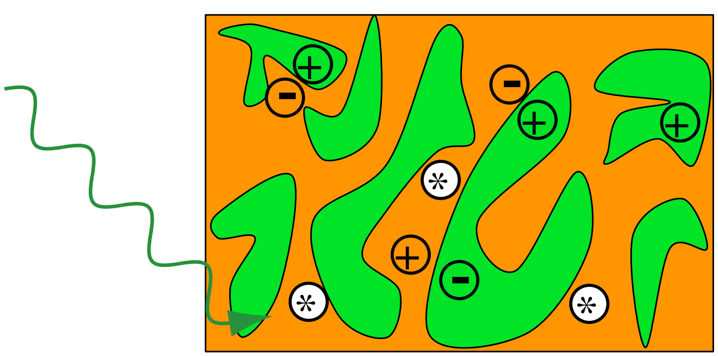
- exciton must diffuse a long distance
- carrier recombination is mitigated

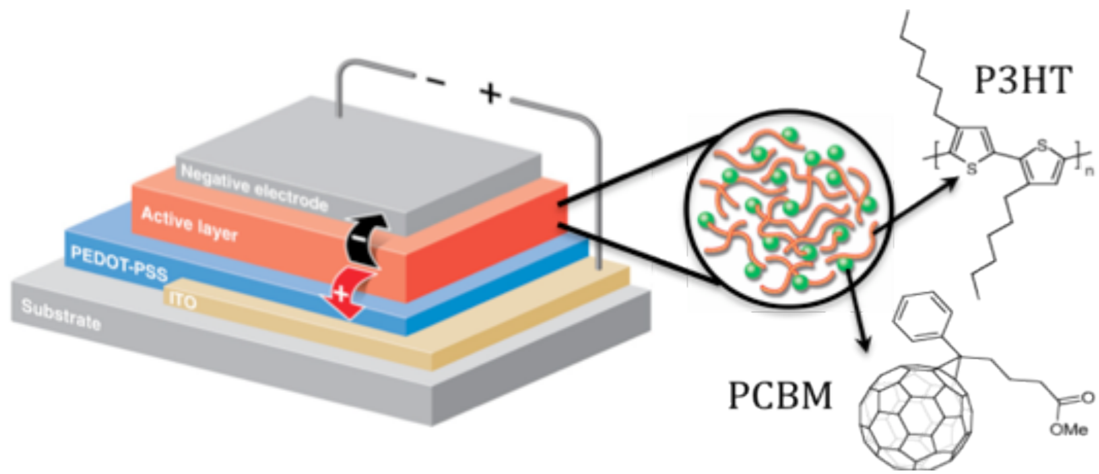




Bulk heterojunction

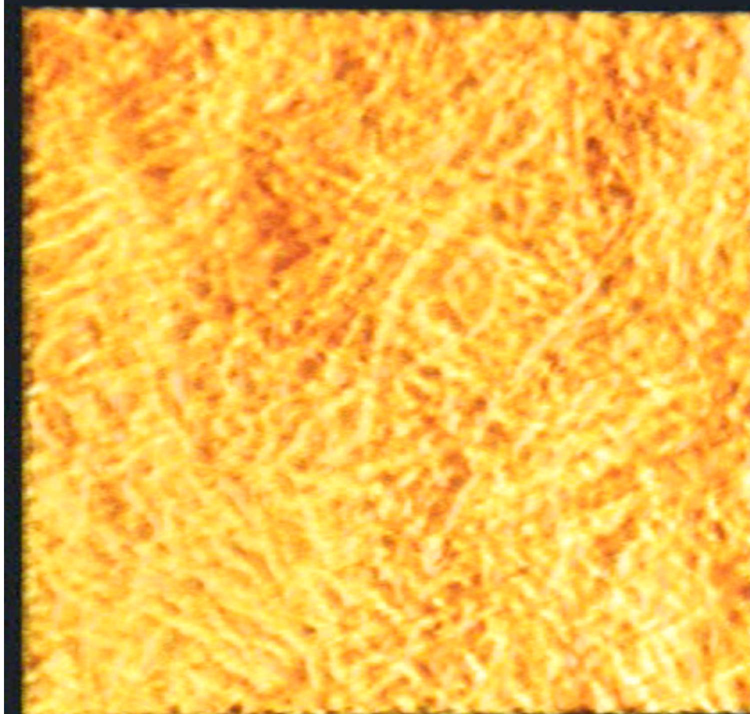
- exciton is easily dissociated
- carrier recombination is enhanced

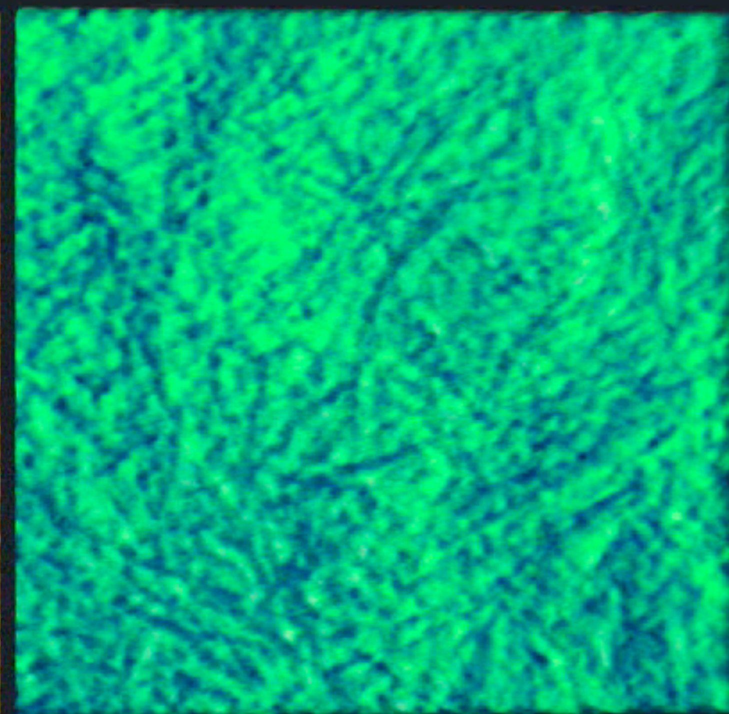




Low Loss EF-TEM

P3HT:PCBM

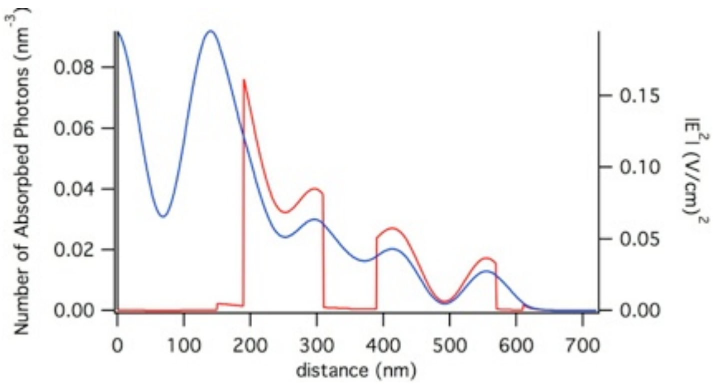




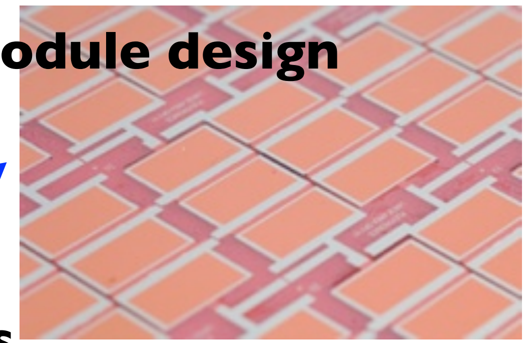
(800 nm field of view)

Dr. Andrew Herzing
Dr. Dean DeLongchamp
NIST OPV Project

OPV is inherently multi-scale

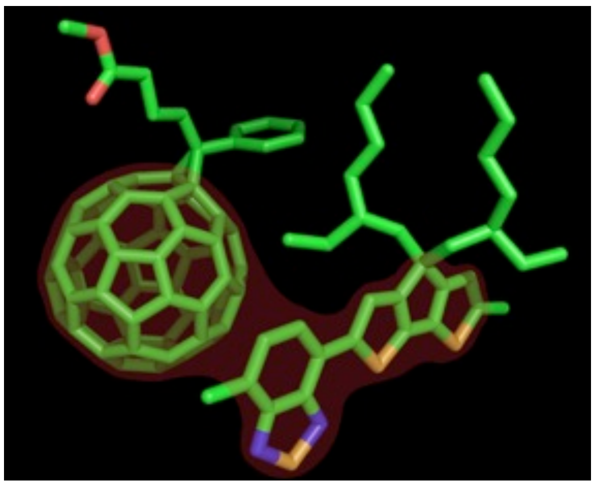


Module design

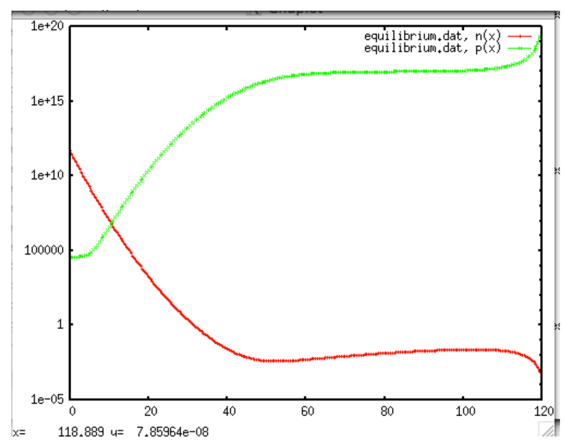


(Plextronics)

Optical considerations and light management

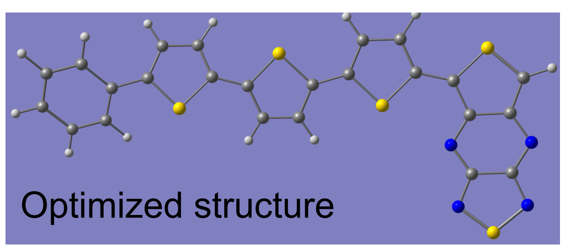


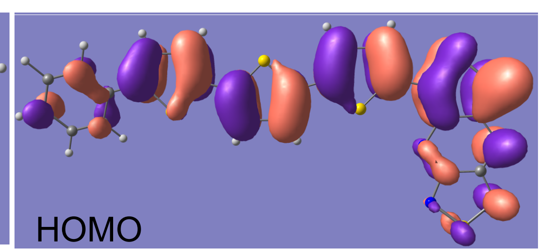
Device physics



Photophysics and charge transport

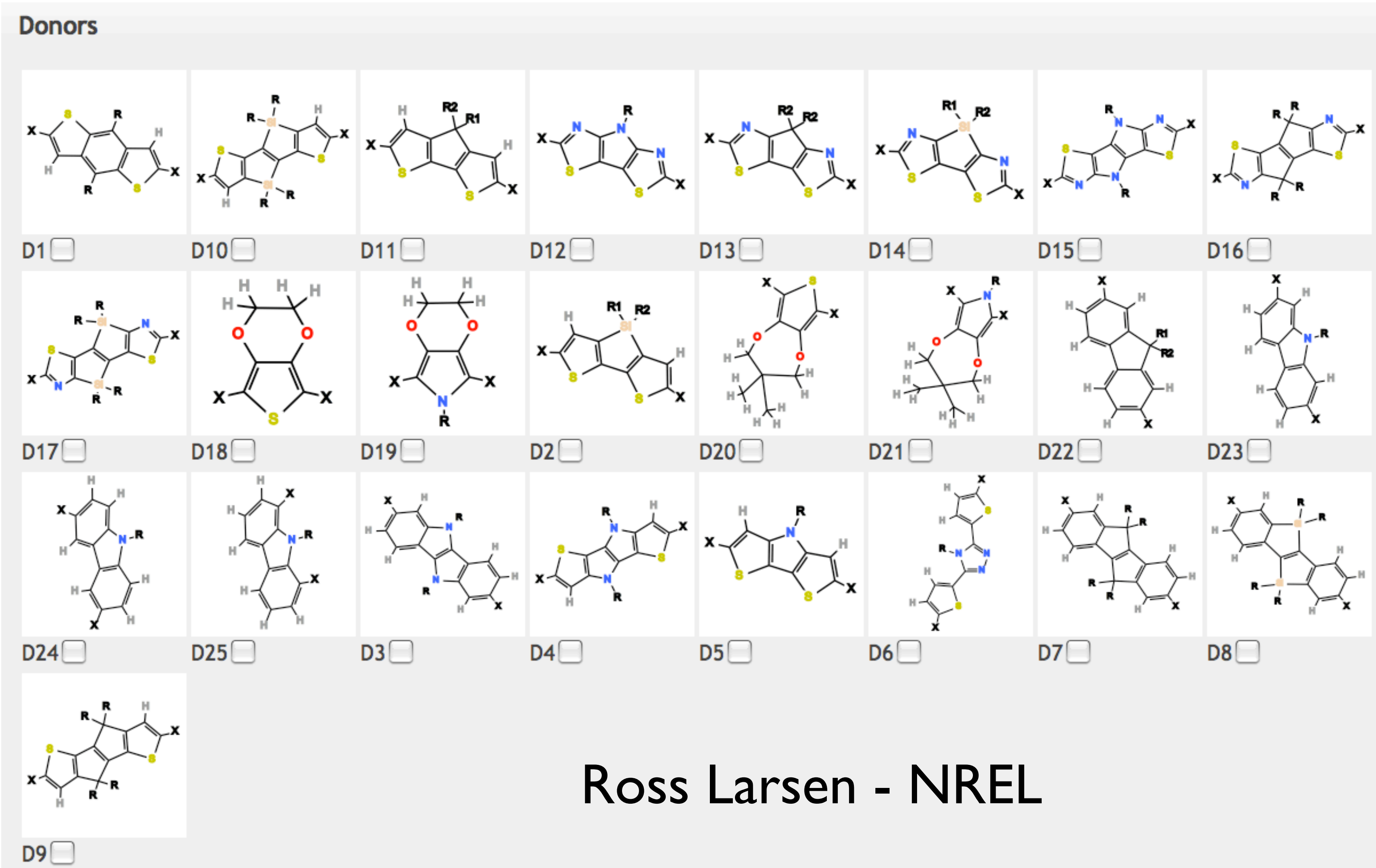
Molecular design





Molecular Design

Examples from donor library



Ross Larsen - NREL

DFT/TD-DFT applied to these for calculating band gap and HOMO/LUMO energies.

Other efforts: Harvard Clean Energy Project (Aspuru-Guzik)
University of Pittsburgh (Hutchinson)

Modeling of OPV device behavior

1-D steady-state drift-diffusion model

Poisson Equation :

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{e}{\varepsilon}(n(x) - p(x) - C(x))$$

Intrinsic, dark carriers

Continuity Equations :

$$\frac{\partial}{\partial x}J_n(x) = eU(x)$$

$$\frac{\partial}{\partial x}J_p(x) = -eU(x)$$

$$J_n = enE + D_n \frac{\partial}{\partial x} n$$

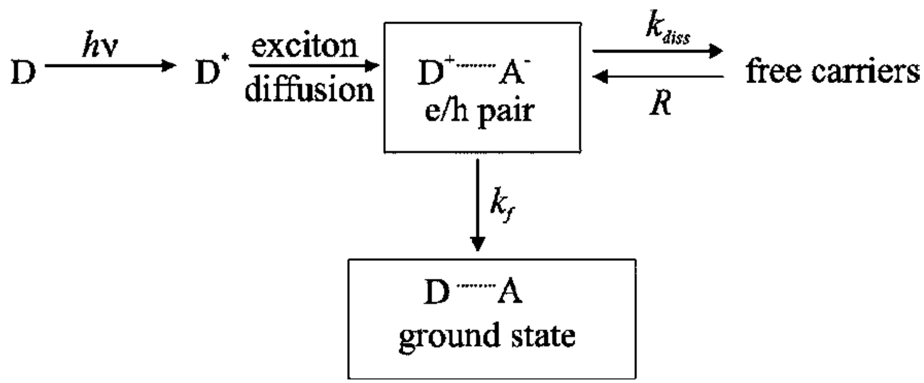
$$D_n = \mu_n k_B T / e$$

$$J_p = epE - D_p \frac{\partial}{\partial x} p$$

$$D_p = \mu_p k_B T / e$$

$$E = -\frac{\partial}{\partial x}\psi$$

U = net generation rate



$$U = PG - (1-P)R$$

$$R = \gamma(np - n_i^2)$$

$$P = \frac{k_d}{k_d + k_f}$$

$$k_d = k_d(x, T, E, E_b)$$

$$k_f = \text{parameter}$$

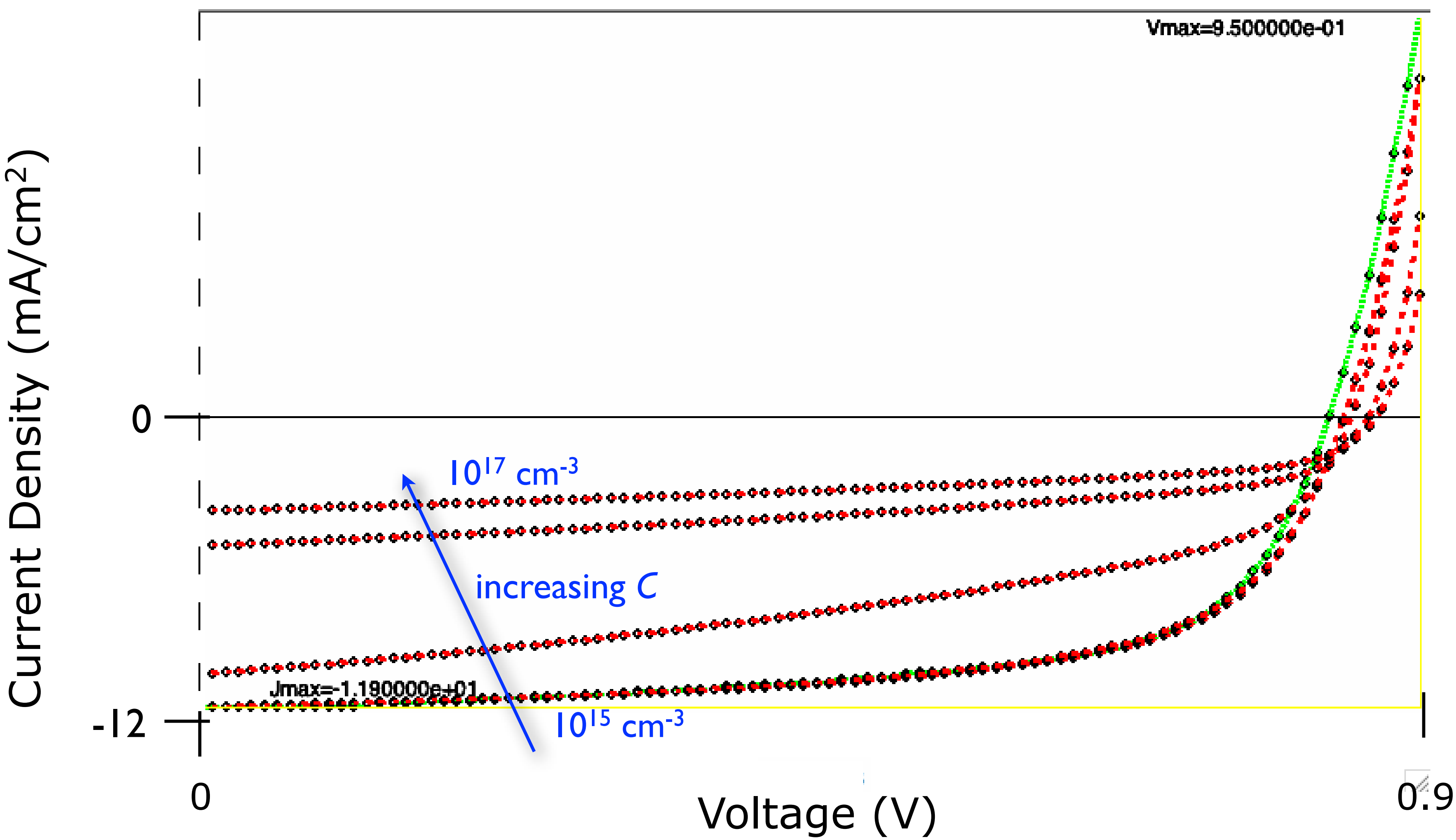
Koster, et al., *Phys. Rev. B* **72** 085205 (2005)

- BHJ + ideal (ohmic) contacts, no other layers (e.g. PEDOT:PSS)
- Bulk heterojunction transport parameterized by $\mu_{n,p}$, K_f

Software (Python) implementation performed by *Peter Graf*, NREL Scientific Computing Center

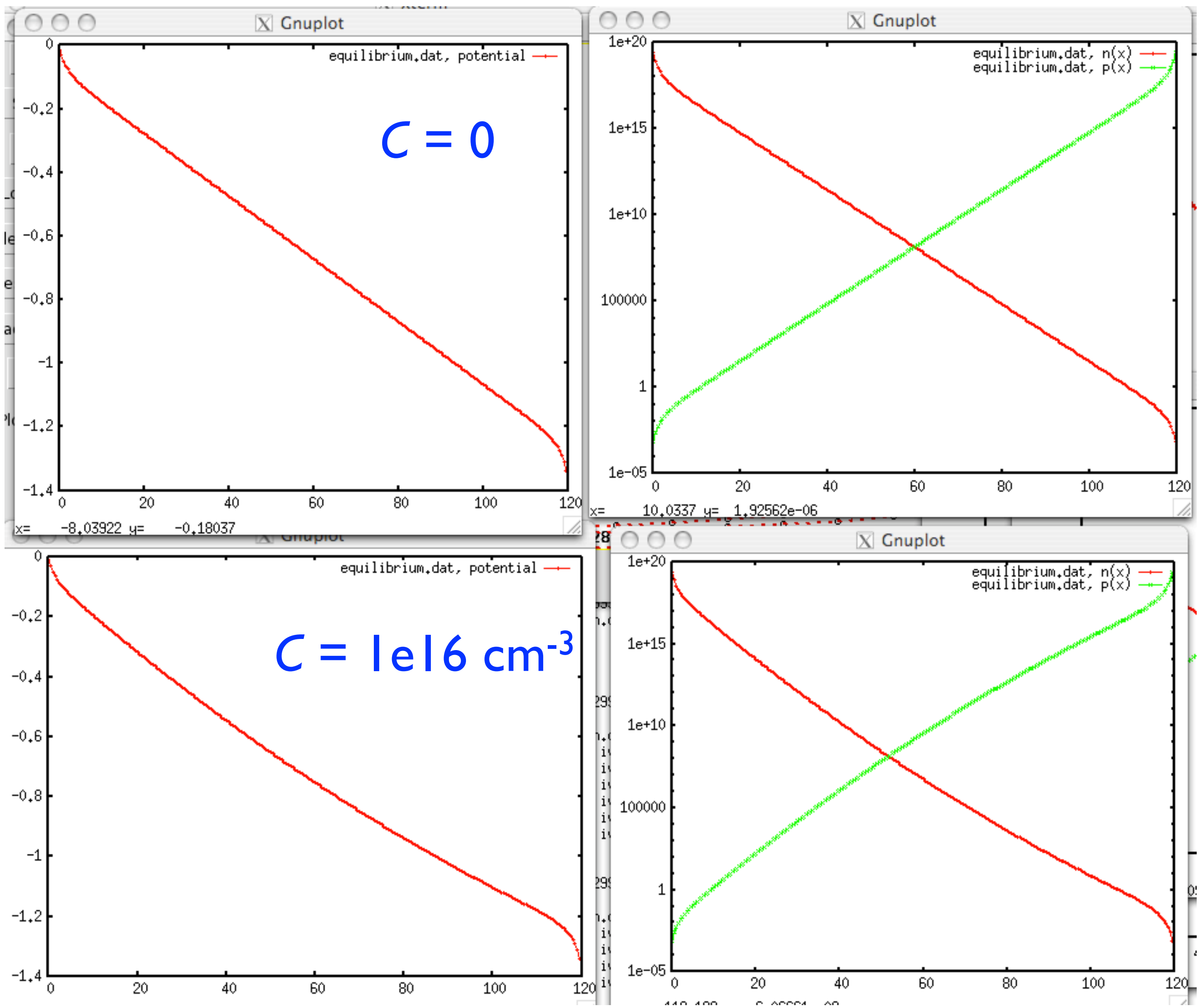
Influence of Dark Carriers

Simulation of the impact of dark carrier density (C) on JV curves.



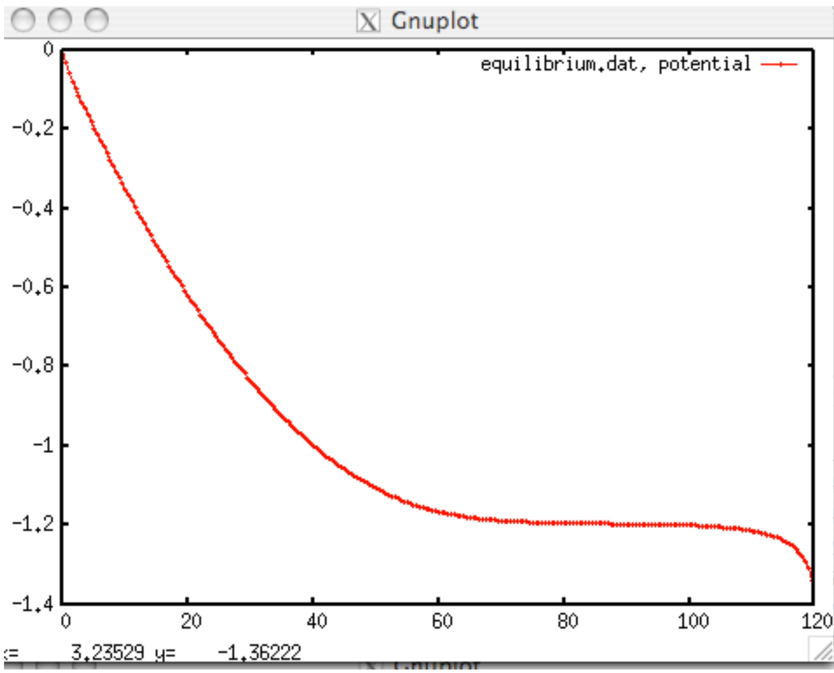
Influence of Dark Carriers

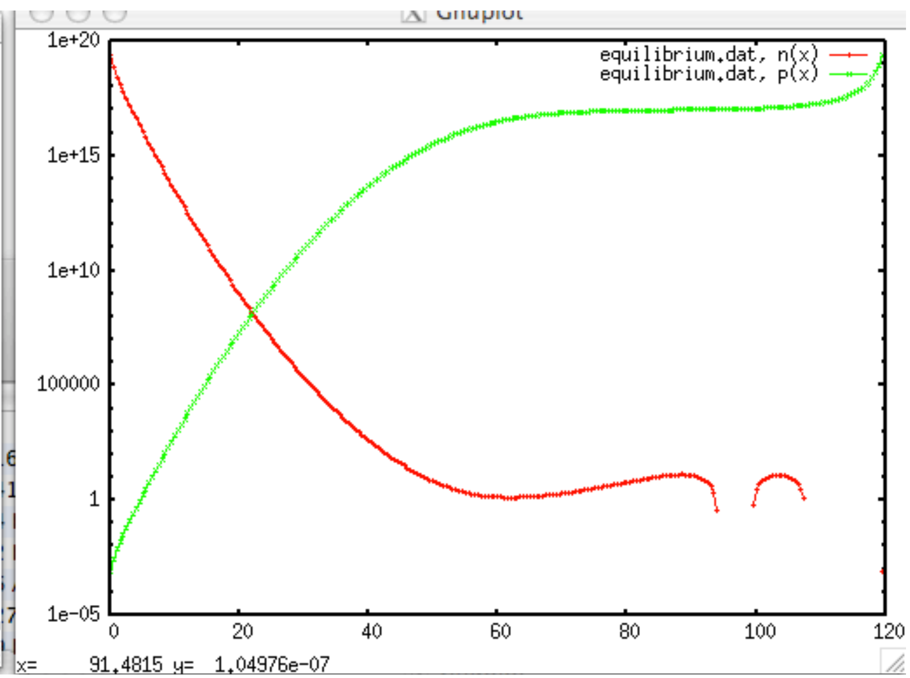
Simulation of the impact of dark carrier density (*C*) on the electric potential and carrier distributions.



Influence of Dark Carriers

C = 1e17 cm^{-3}



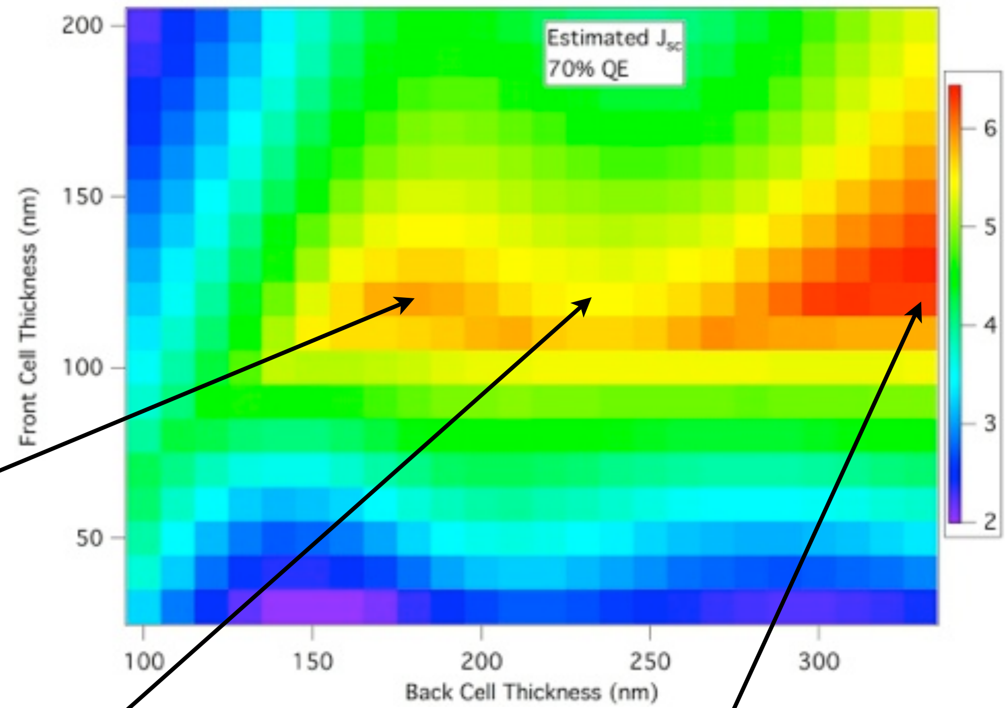


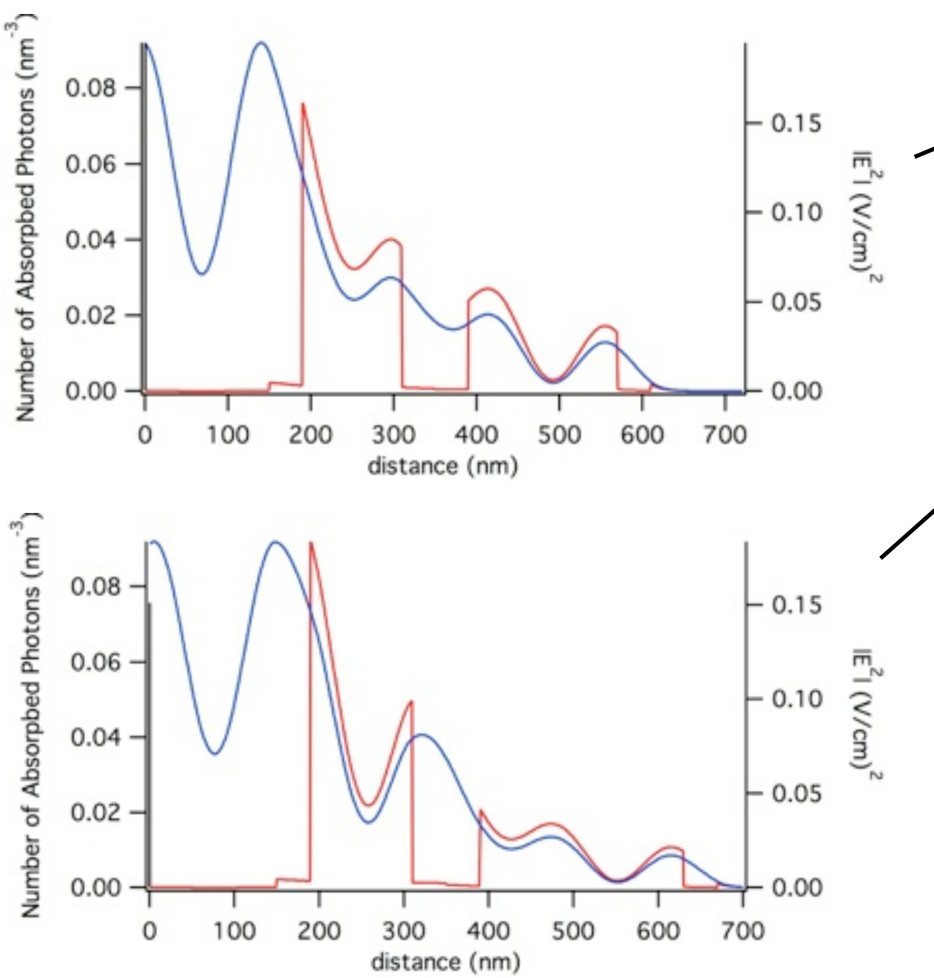
Experiment*: P3HT Na = 5e16 cm^{-3}

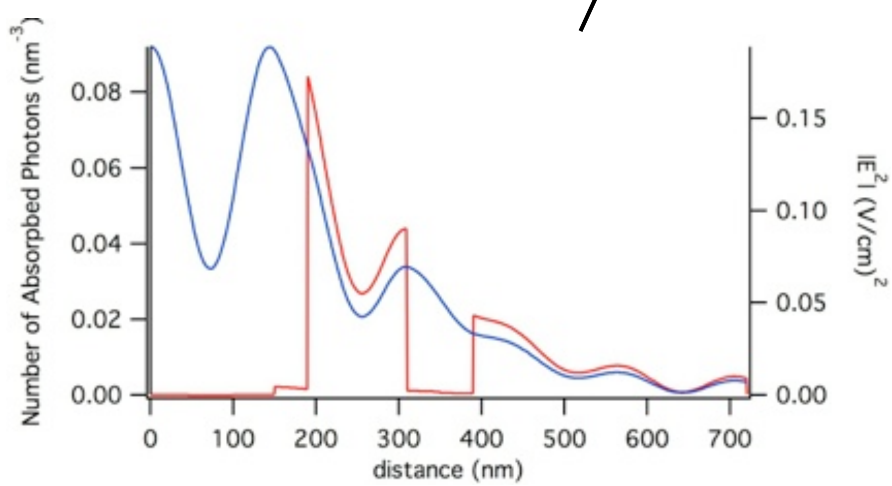
*Ziqi Liang, Alexandre Nardes, Dong Wang, Joseph J. Berry, and Brian A. Gregg, "Defect Engineering in pi-Conjugated Polymers", *Chem. Mater.* 2009, **21**, 4914–4919.

Modeling of optical field strength in tandem devices

Transfer matrix calculations of optical field strength and resulting device current:



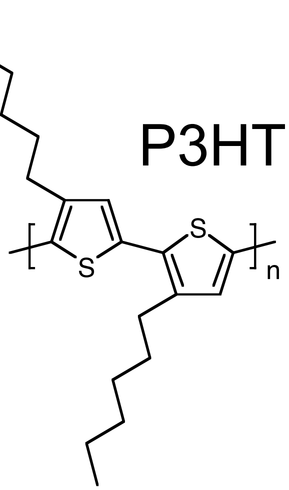




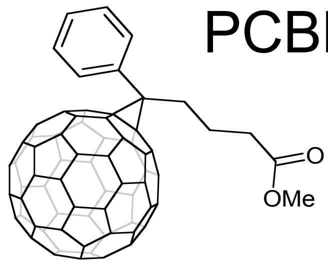
Calculations courtesy Brian Bailey and Sarah Cowan, NREL.

Role of the band offset

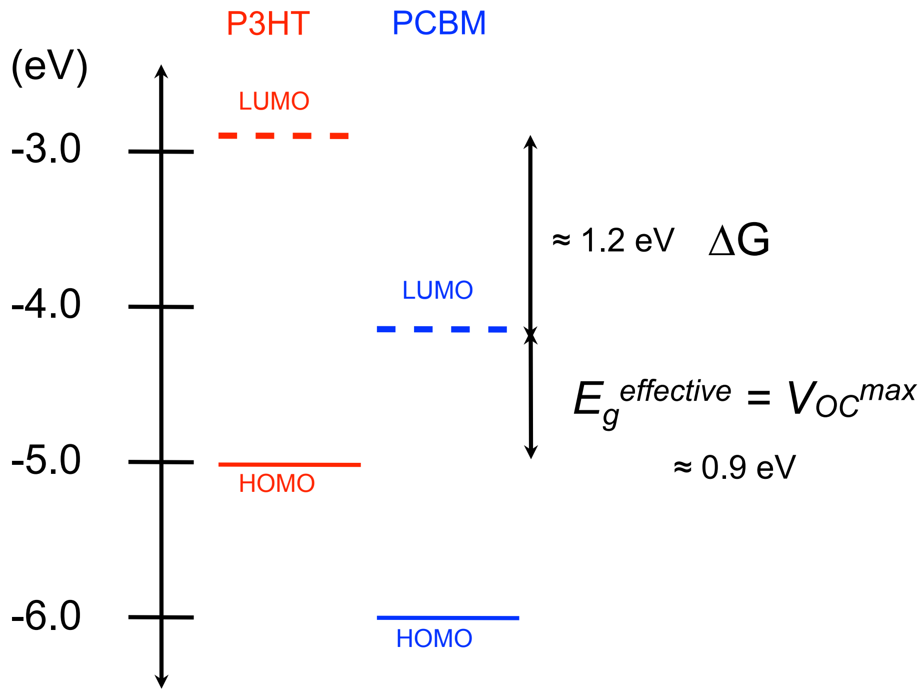
The LUMO-LUMO (δ_{LUMO}) band offset is typically very large



P3HT



PCBM

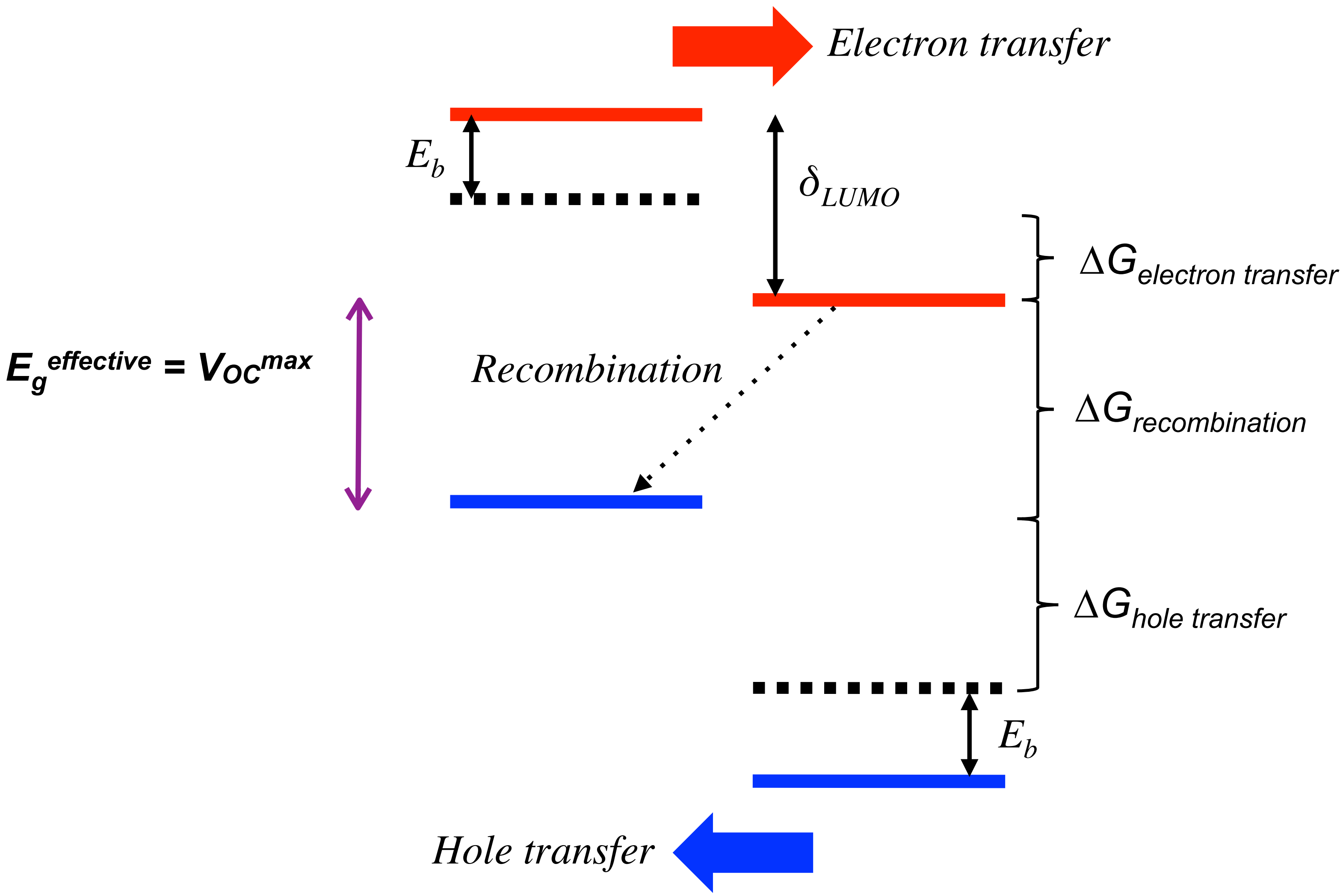


Open Question:

Is the thermal energy gained from a large band offset necessary for efficient charge separation?

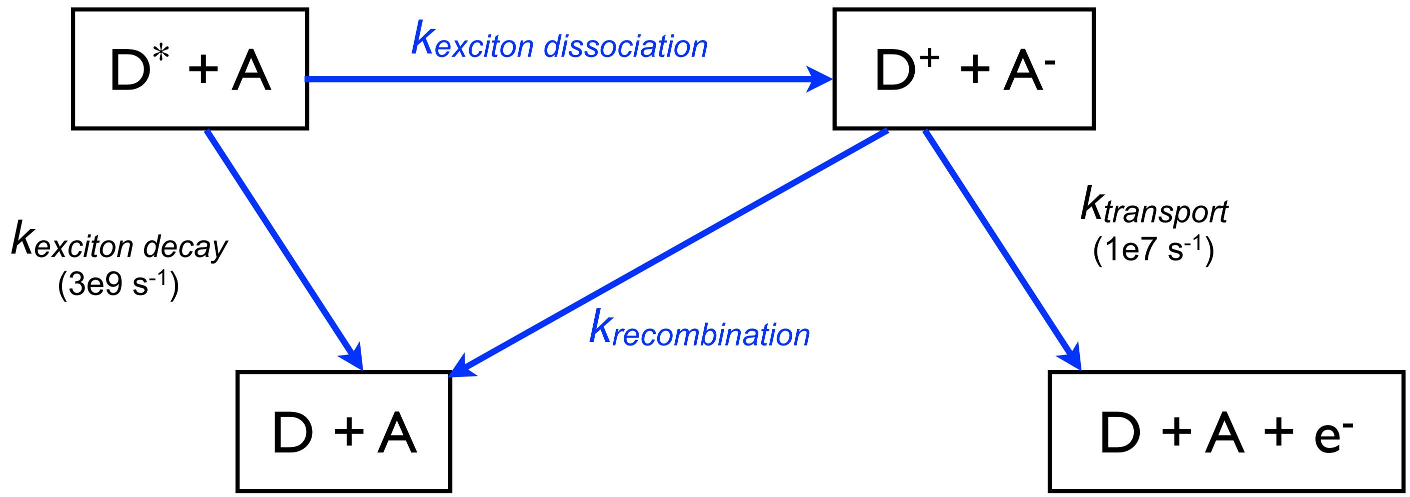
Role of the band offset

A more complete picture



Marcus theory and the influence of reorganization energy

Simplified kinetic scheme for photocurrent production:



(and analogously for excitation of the *acceptor*)

Assume *dissociation* and *recombination* governed by Marcus theory:

$$k = \left(\frac{4\pi^2}{h}\right) V^2 \left(\frac{1}{\sqrt{4\pi\lambda k_B T}}\right) \exp\left(\frac{-(\Delta G + \lambda)^2}{4\lambda kT}\right)$$

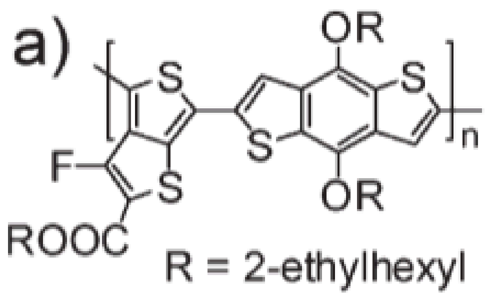
V: ~0.01 eV

ΔG is negative

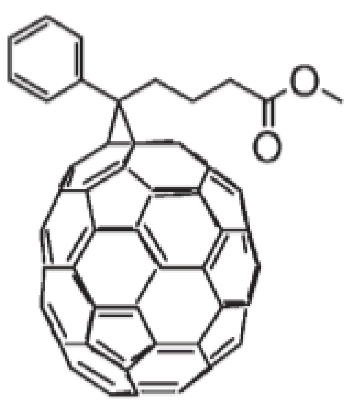
An example, high performance OPV system

Y. Liang et al, *Adv. Mater.* **22**, E135-E138 (2010).

For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%



PTB7



$PC_{71}BM$

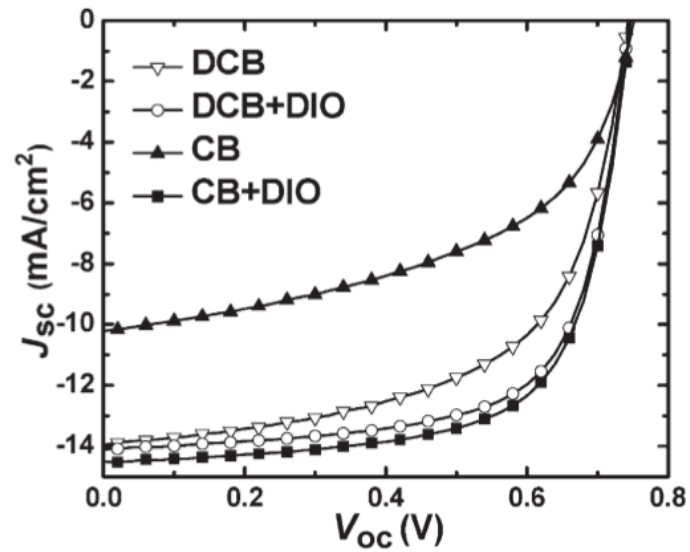


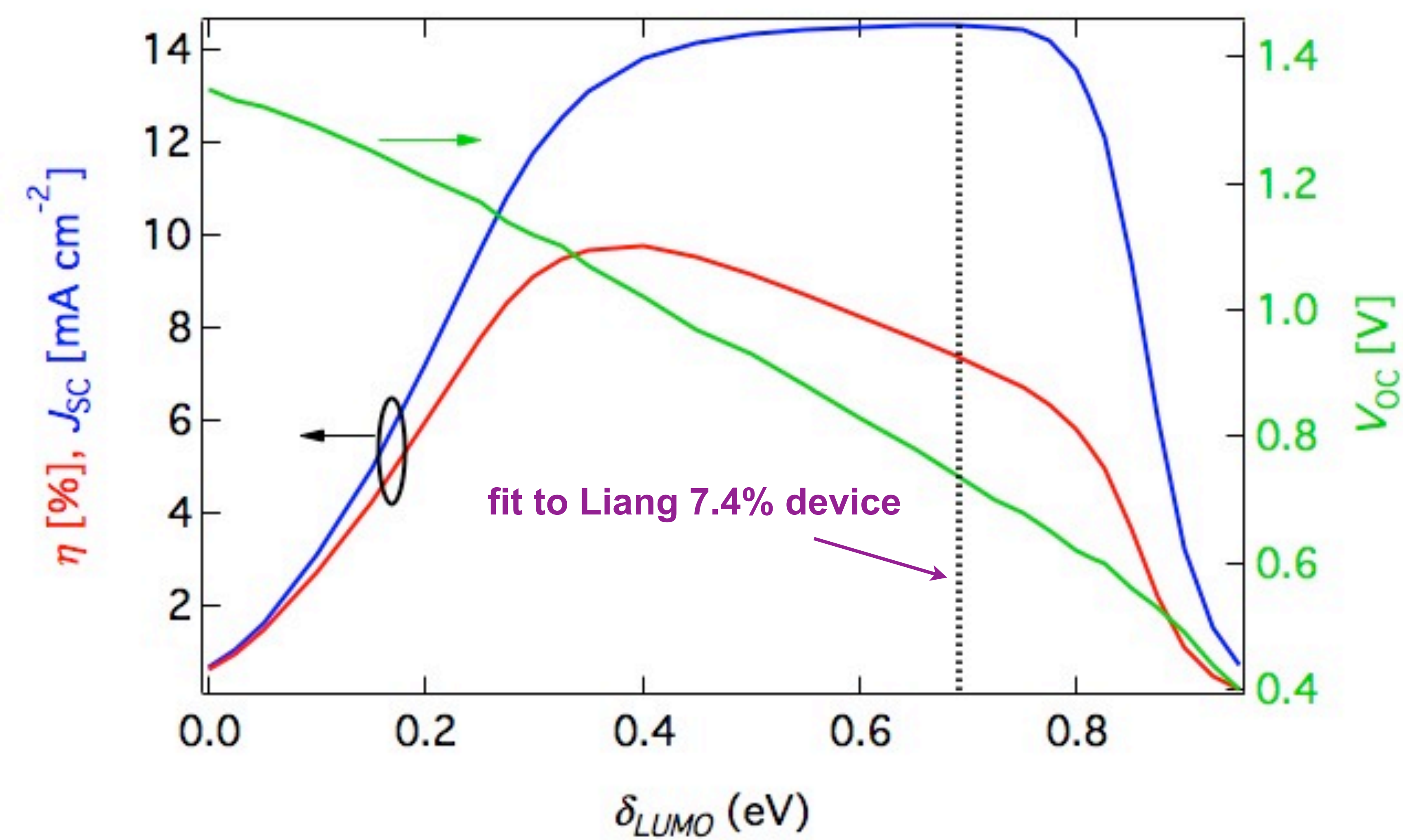
Figure 2. *J–V* curves of PTB7/$PC_{71}BM$ devices using (i) DCB only, (ii) DCB with 3% DIO, (iii) CB, and (iv) CB with 3% DIO as solvents.

	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	J_{sc} (calc.) [mA cm^{-2}]	Error [%]
DCB	0.74	13.95	60.25	6.22		
DCB+DIO	0.74	14.09	68.85	7.18	13.99	0.74
CB	0.76	10.20	50.52	3.92		
CB+DIO	0.74	14.50	68.97	7.40	14.16	2.34

Pathway to higher efficiency: Reducing λ

High reorganization energy regime: λ = 0.75 eV

<u>Model parameters:</u>
E_{gap}(PTB7) = 1.64 eV
peak OD (PTB7) = 0.51
E_{gap}([70]PCBM) = 1.73 eV
peak OD ([70]PCBM) = 0.33
$\lambda_{electron\ transfer} = \lambda_{hole\ transfer}$ = 0.75 eV



L.J.A. Koster, S. E. Shaheen, and J. C. Hummelen, *Advanced Energy Materials* (2012); DOI: 10.1002/aenm.201200103

Pathway to higher efficiency: Reducing λ

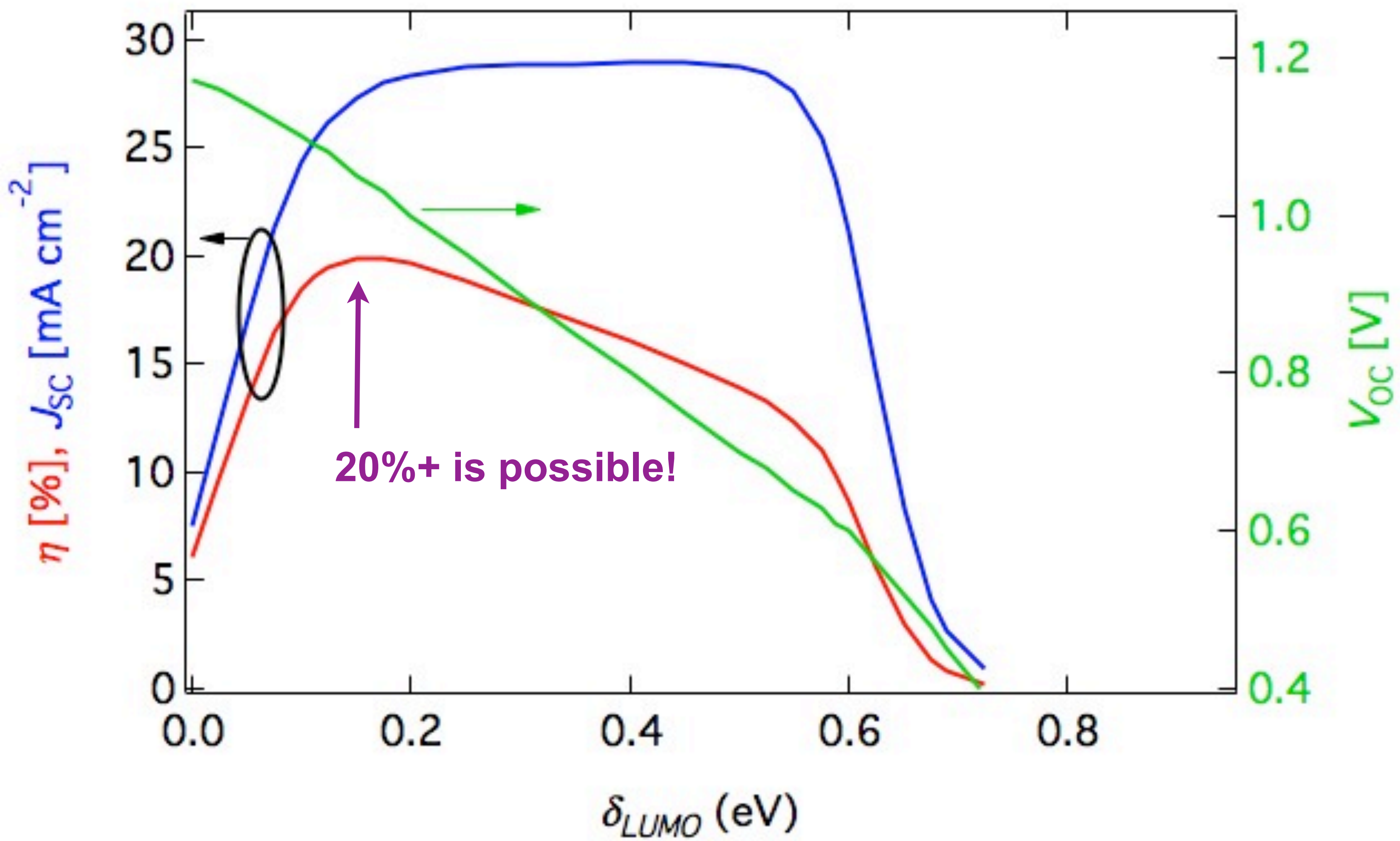
Highly optimized regime: λ = 0.30 eV and high optical density

Model parameters:

E_{gap}(PTB7) = 1.40 eV
peak OD (PTB7) = 1.00

E_{gap}([70]PCBM) = 1.40 eV
peak OD ([70]PCBM) = 1.00

$\lambda_{electron\ transfer} = \lambda_{hole\ transfer}$ = 0.30 eV



L.J.A. Koster, S. E. Shaheen, and J. C. Hummelen, *Advanced Energy Materials* (2012); DOI: 10.1002/aenm.201200103

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