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Developing Contacts for Improved Performance and Lifetime in Organic Photovoltaics

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Kuwait, October 17, 2011

People and Support

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U.S. Department of Energy's Solar Energy Technologies Program (SETP) under contract DE-AC36-08GO28308

DOE EERE SETP - AOP
DOE EERE SETP - Seed Fund Program
DOE Center for Energy Efficient Materials (CEEM) EFRC
DOE Center for Interface Science: Solar Electric Materials (CIS:SEM) EFRC

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  - David Ginley
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  - Xerxes Steirer
  - Reuben Collins
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CIS:SEM
Center for Interface Science: Solar Electric Materials

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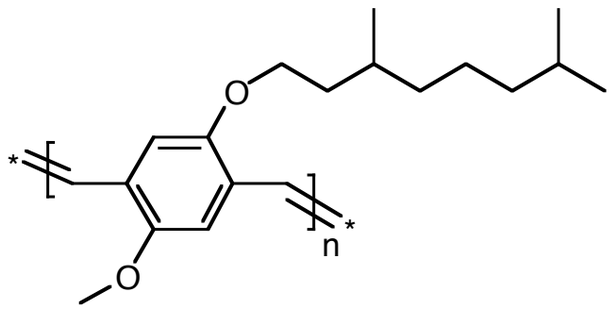
Also:
We would like to thank Konarka and Plextronics for providing materials

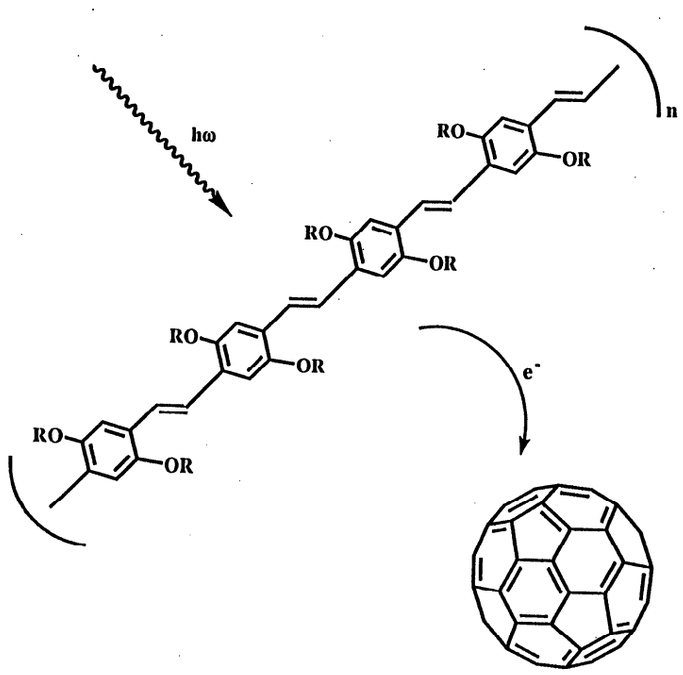
The Basis for Polymer Organic Solar Cells

Ultrafast photoinduced electron transfer between a conjugated polymer and a fullerene was discovered in 1992*.

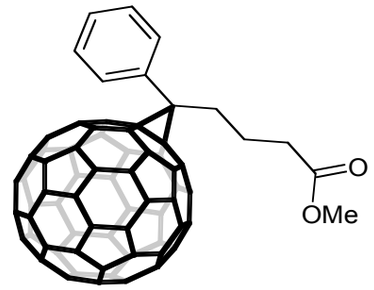
Donor



OC_1C_{10}-PPV
3,7 - dimethyloctyloxy methyloxy PPV



Acceptor



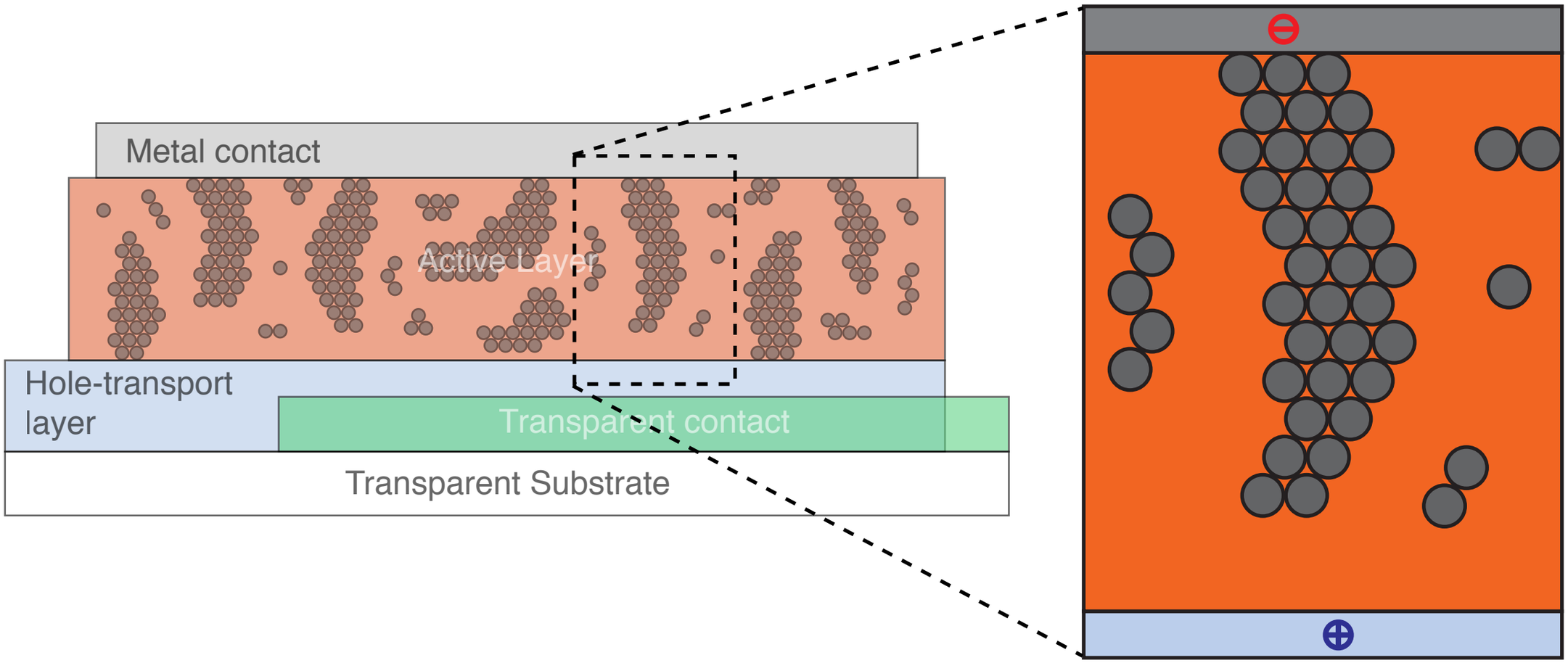
PCBM
1-(3-methoxycarbonyl) propyl-1-phenyl $[6,6]C_{61}$

Forward electron transfer rate: 45 fs†

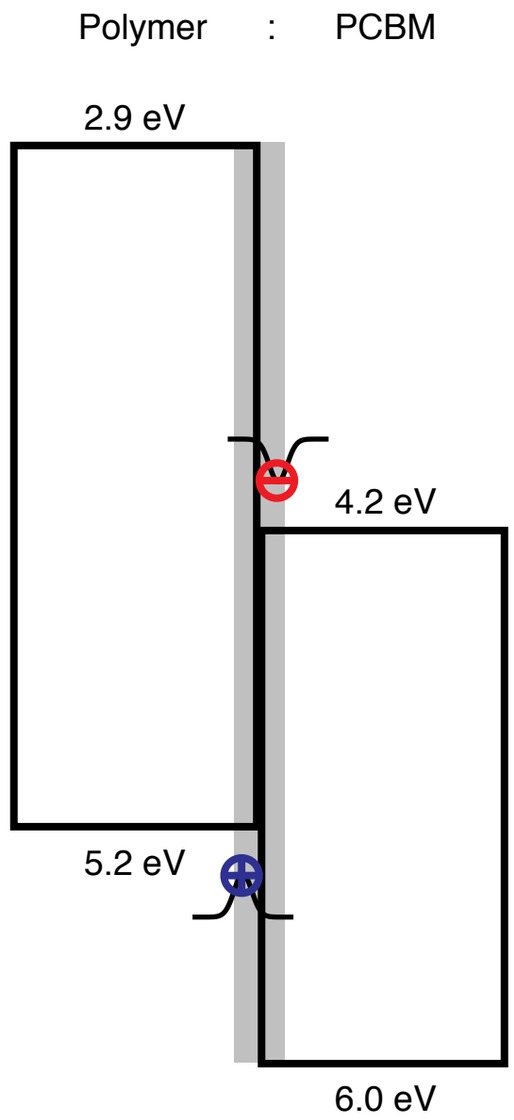
Backward electron transfer rate: ~1 μs

*N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science* **258**, 1474 (1992).
†C. J. Brabec, G. Zerza *et al*., *Chem. Phys. Lett*. **340**, 232 (2001).

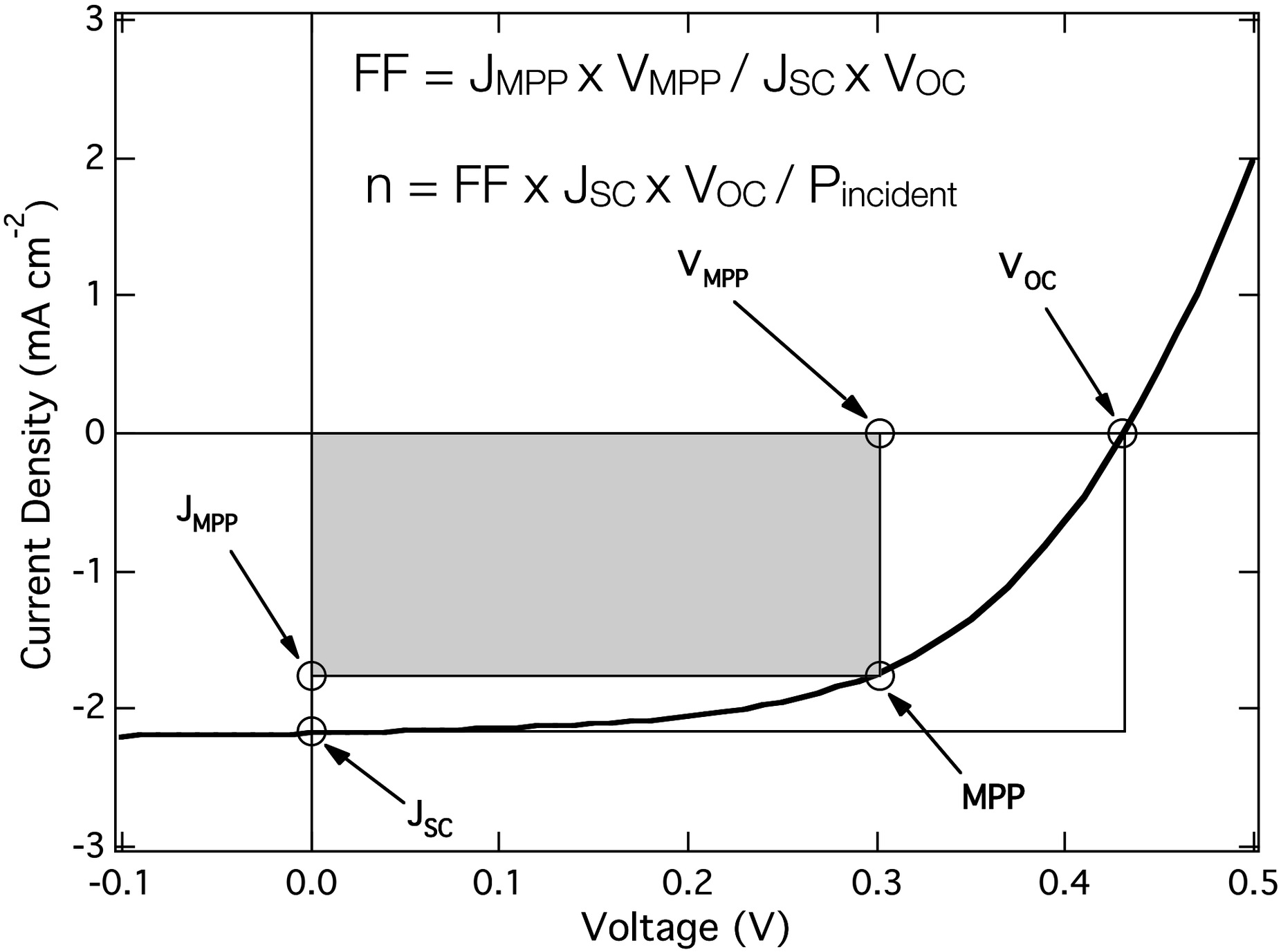
How Do Organic Solar Cells Work?



Charge Generation



Basic Characterization of Solar Cell Performance

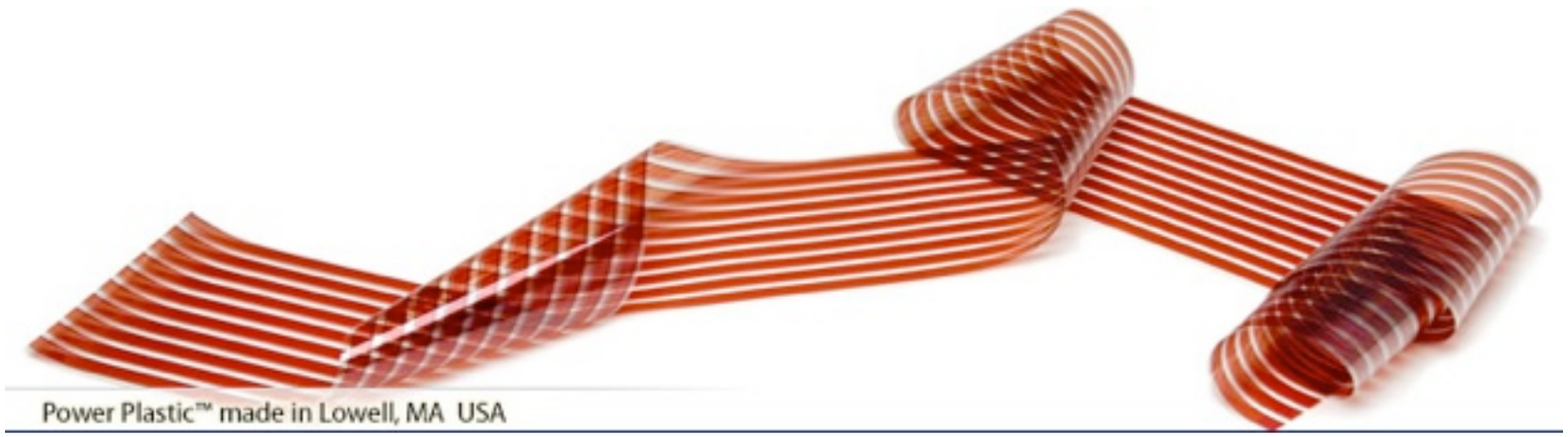


Outlook for Organic Solar Cells

- Low cost organic photovoltaic (OPV) devices
  - Printed or solution processed at high speed on flexible substrates
  - Using roll-to-roll processing for dramatic reduction in capital and production costs
  - Low materials and balance of systems costs

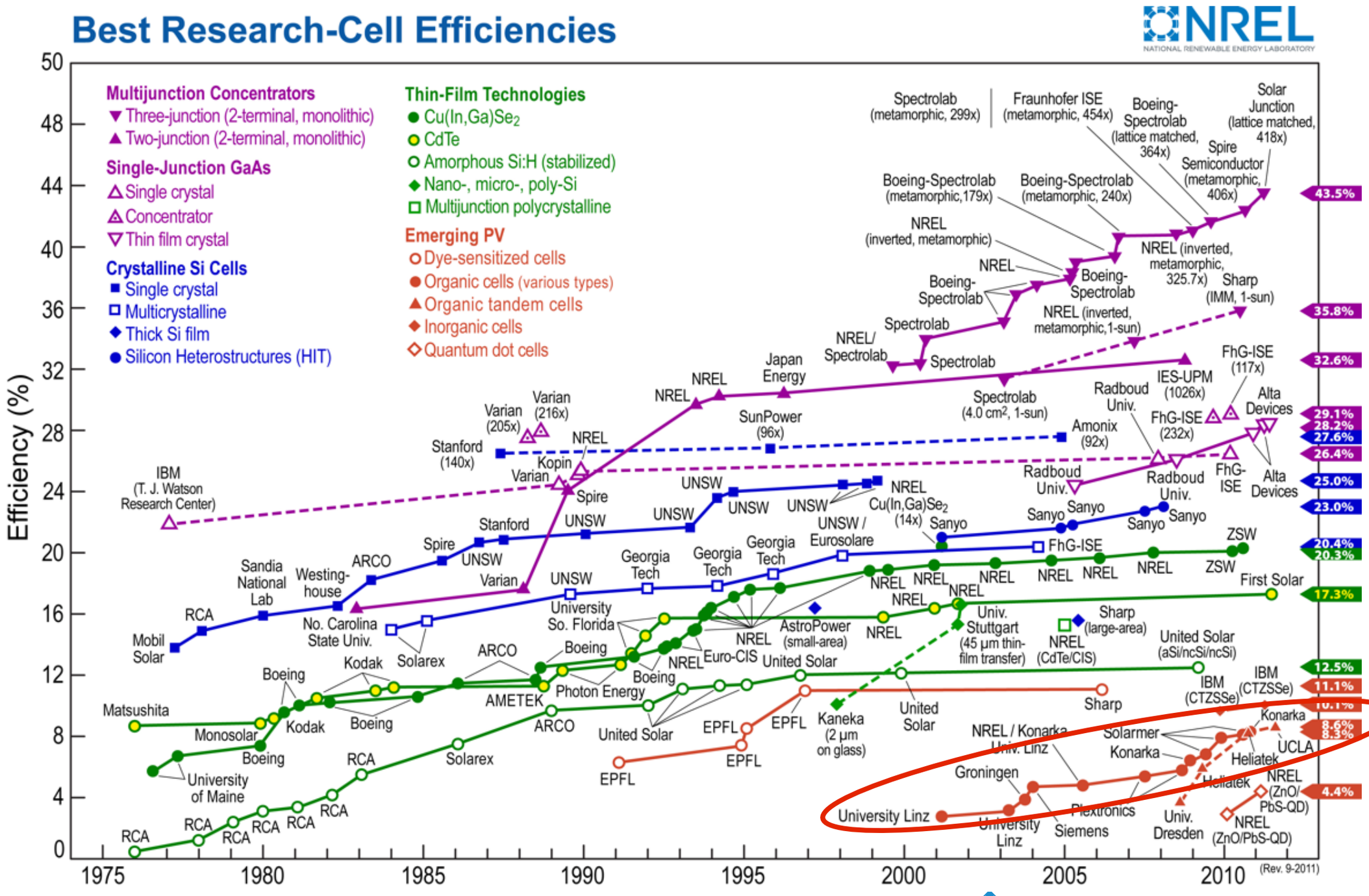
- Near term: > 10% efficiency, lifetime > 10,000 hours
  - Applications in building integrated PV (BIPV) consumer electronics, etc.

- Long term goal: > 15% efficiency, lifetime > 15 years
  - Grid connected - roof top power generation & solar farms
  - Large scale power generation to meet the terawatt challenge



Konarka Technologies, http://www.konarka.com/

Solar Cell Technologies - World Records



First Products and Cost Outlook

- Consumer electronics
- BIPV applications
  - Semitransparent
- Excellent low intensity and diffuse light performance
- Low cost materials and processing

KONARKA®

First Products and Cost Outlook

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- Excellent low intensity and diffuse light performance
- Low cost materials and processing

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LIFE-CYCLE ASSESSMENT OF ORGANIC SOLAR CELL TECHNOLOGIES

Annick Anctil[1,2], Callie Babbitt[1], Brian Landi[2,3] and Ryne P. Raffaelle[4]
[1]Golisano Institute for Sustainability, RIT, Rochester, NY, USA
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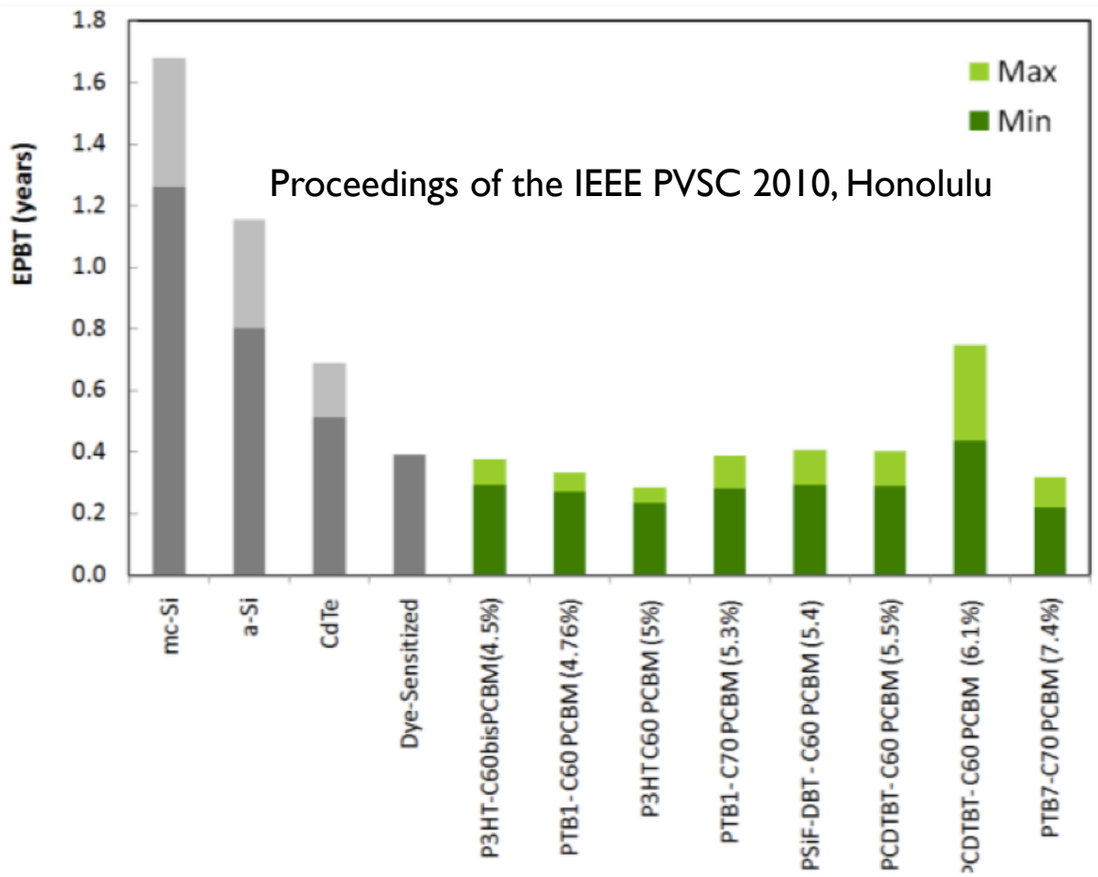
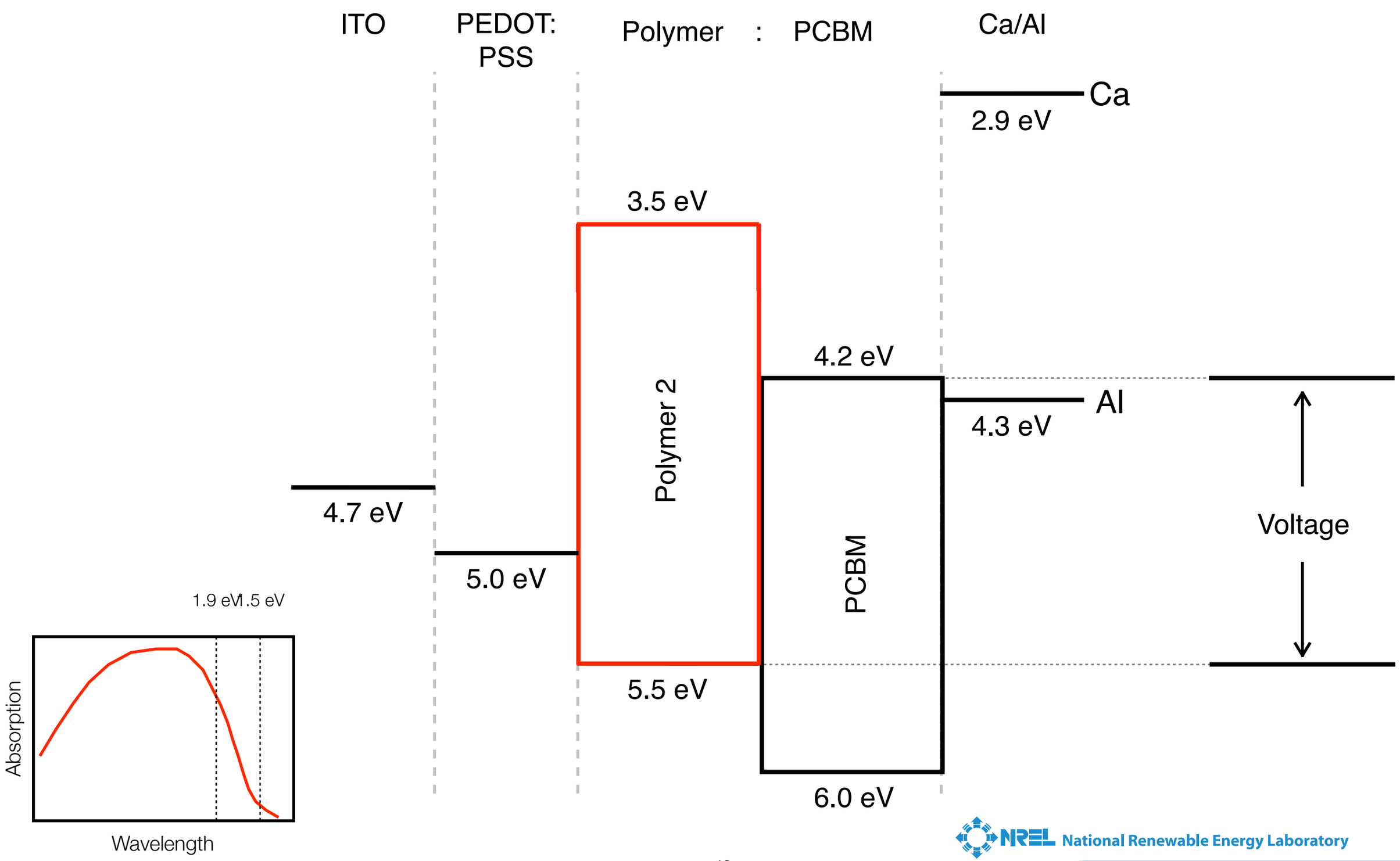
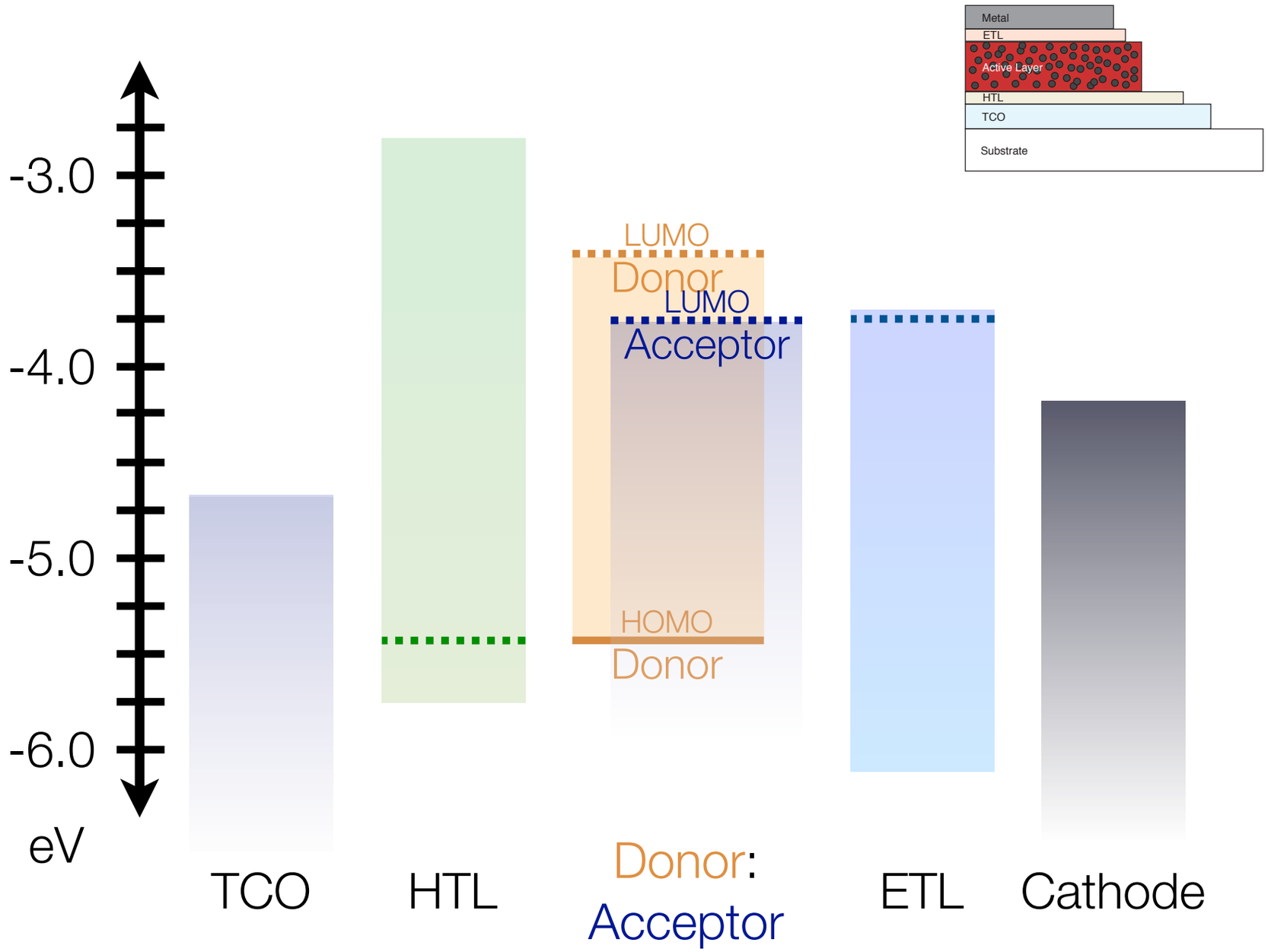


Proceedings of the IEEE PVSC 2010, Honolulu

Enhancing Device Performance

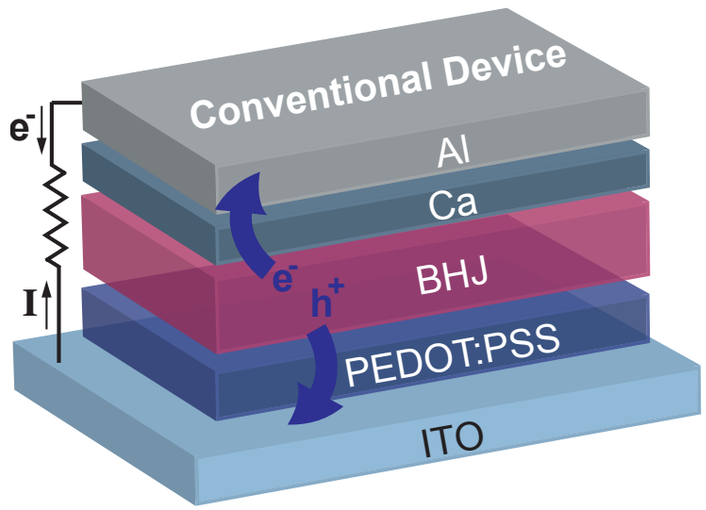


The Contact Layers in Organic Solar Cells

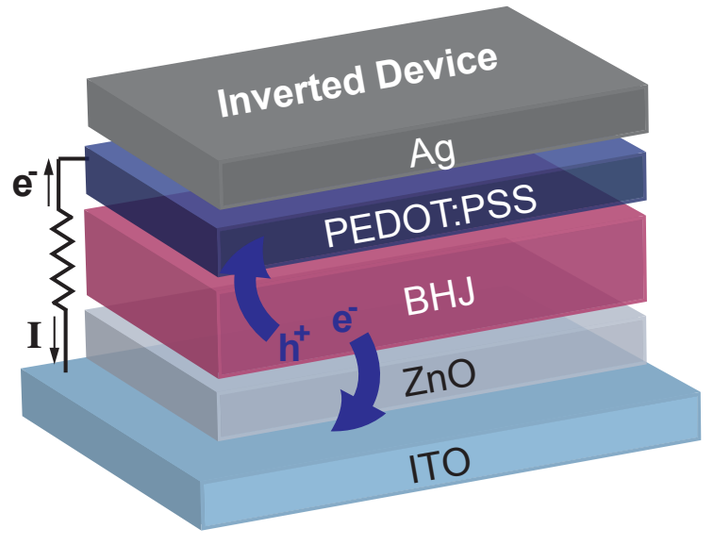


Two Device Architectures

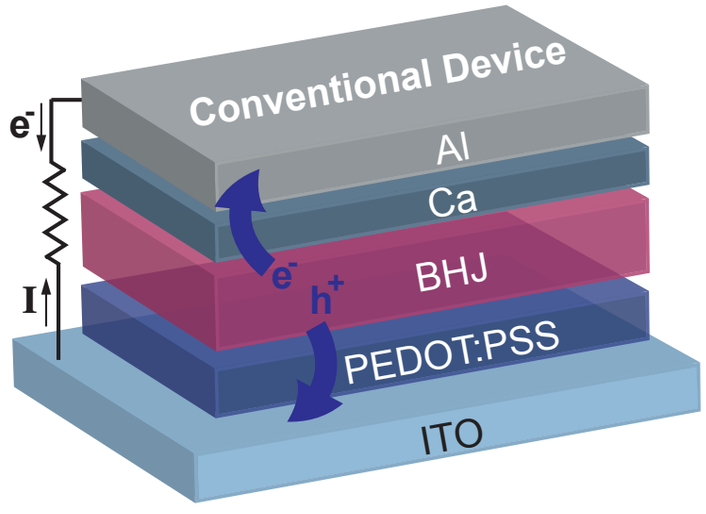
- **Standard architecture**
  - Must be fabricated in an inert atmosphere
  - Employ low work function back metal contacts
  - Susceptible to oxidation



- **Inverted polarity devices**
  - Can be fabricated in air
  - Can use stable high work function metal contacts

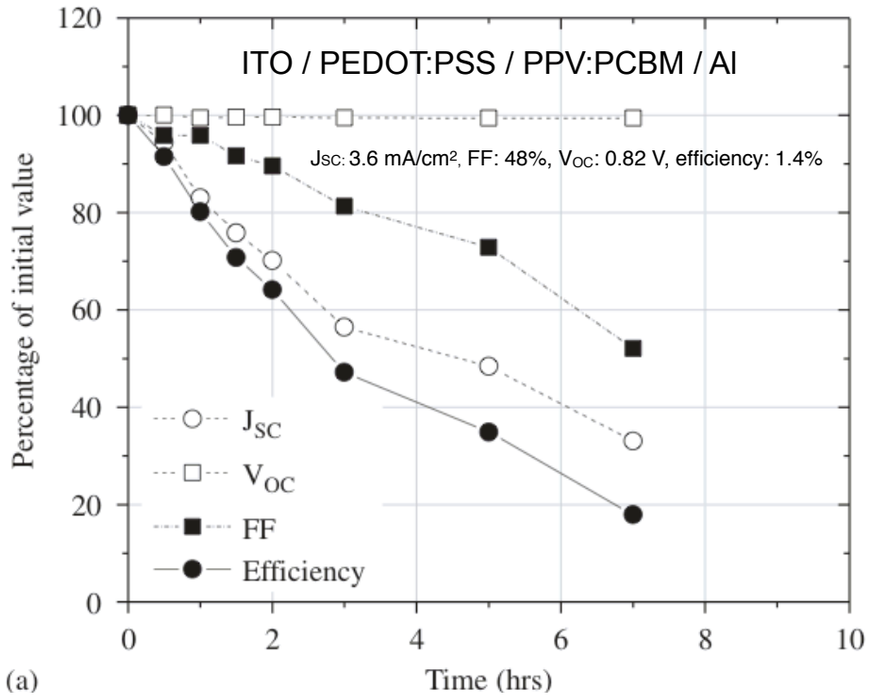


Metal oxides as HTL materials in standard OPV device architectures

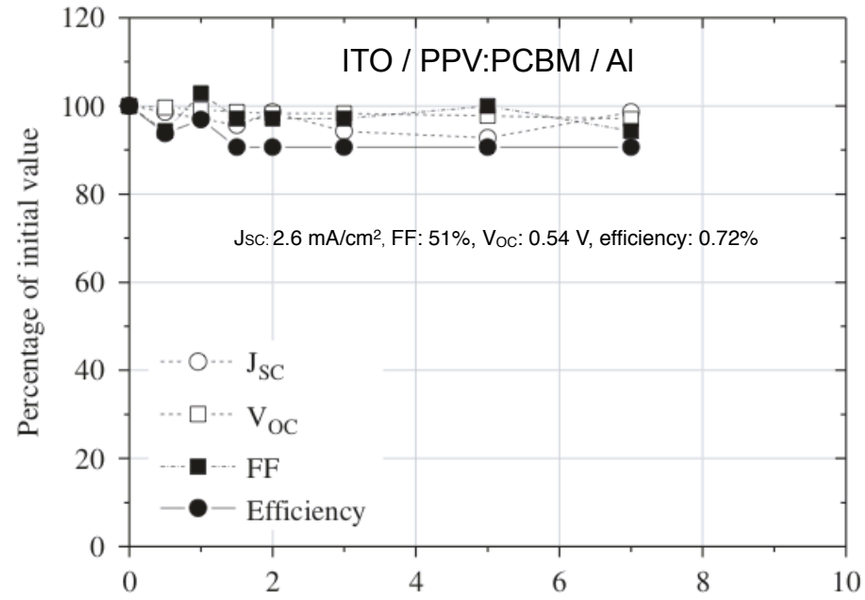


Effects of PEDOT:PSS on OPV Device Performance and Stability

- PEDOT:PSS improves contact between ITO and donor
  - Increases fill factor, photovoltage and efficiency
  - Increases series resistance & decreases photocurrent
- Acidic suspension incompatible with ZnO-based TCO materials
- Reduces device stability due to acidity of ionic salt
  - Etching of ITO by PSS, leaching of In into PEDOT
  - Water adsorption into PEDOT:PSS - formation of insulating domains



(a)



K. Kawano et al. / Solar Energy Materials & Solar Cells 90 (2006) 3520–3530

Metal Oxides as Hole Contact Materials

- PEDOT:PSS has been replaced with thin film metal oxide HTLs
  - n-type: MoO_3, V_2O_5 & WO_3 via thermal evaporation
  - p-NiO deposited via PLD
- Work function of NiO tuned through control oxygen content
- Band offsets allow for hole extraction and proper electron blocking characteristics
- Optimized NiO thickness - 10 nm
  - Enhanced photocurrent
- Stable encapsulated devices in shelf life study

PNAS **105** (2008) 2783

p-Type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells

Michael D. Irwin, D. Bruce Buchholz, Alexander W. Hains, Robert P. H. Chang*, and Tobin J. Marks*

Department of Chemistry, Department of Materials Science and Engineering, and Materials Research Center, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208

Contributed by Tobin J. Marks, December 21, 2007 (sent for review September 12, 2007)

To minimize interfacial power losses, thin (5–80 nm) layers of NiO, a *p*-type oxide semiconductor, are inserted between the active organic layer, poly(3-hexylthiophene) (P3HT) + [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM), and the ITO (tin-doped indium oxide) anode of bulk-heterojunction ITO/P3HT:PCBM/LiF/Al solar cells. The interfacial NiO layer is deposited by pulsed laser deposition directly onto cleaned ITO, and the active layer is subsequently deposited by spin-coating. Insertion of the NiO layer affords cell power conversion efficiencies as high as 5.2% and enhances the fill factor to 69% and the open-circuit voltage (V_{oc}) to 638 mV versus an ITO/P3HT:PCBM/LiF/Al control device. The value of such hole-transporting/electron-blocking interfacial layers is clearly demonstrated and should be applicable to other organic photovoltaics.

interface | photovoltaic | solar energy

In a world of ever-increasing energy demands and the need for renewable energy resources, photovoltaics are becoming an increasingly appealing option for energy production (1). Organic photovoltaic (OPV) cells (2–8) offer a potential alternative to conventional Si solar cells, as exemplified by (*i*) dye-sensitized (9), (*ii*) polymer (10), and (*iii*) small-molecule (11) cells. Of these, polymer cells offer the combined attraction of low cost, light weight, mechanical flexibility, and amenability to manufacture by high-throughput, low-cost, large-area reel-to-reel coating processes. It is estimated that such solar cells could be commercially viable if power conversion efficiencies (PCEs) on the order of ~10% were achieved (12). To date, the highest PCE polymer solar cells have been fabricated with an active layer composed of a blend of regioregular poly(3-hexylthiophene) (P3HT) (13) and the fullerene derivative [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) (14) (Fig. 1). The P3HT + PCBM blend forms a phase-separated "bulk-heterojunction" (BHJ) nanostructure that provides a large interfacial area for exciton dissociation. When photo-excited, the P3HT network acts as an electron donor and transporter of holes to the cell anode, while the PCBM network acts as an electron acceptor and transporter of electrons to the cell cathode (10, 15–19). While one materials limitation of this BHJ design is doubtless the less than optimum match of the narrow P3HT:PCBM optical absorption to the solar spectrum (12), it is also likely that the multiple, poorly understood interfaces represent a significant and generic performance constraint to this type of solar cell.

Nanoscale "engineering" of the anode–organic interface has been successfully implemented in organic light-emitting diodes (OLEDs) for enhancing electrode–organic interfacial physical and electrical contact, resulting in reduced turn-on voltage, blocking of misdirected carriers, enhanced thermal durability, and increased current/power efficiency (20–24). In BHJ OPVs, interfacial effects probably limit realization of the maximum theoretical open-circuit voltage (V_{oc}). It is generally thought that the magnitude of V_{oc} parallels the energetic difference between the highest occupied molecular orbital (HOMO) of the BHJ donor material and the lowest unoccupied molecular orbital (LUMO) of the acceptor material (25–28). This difference, less the exciton binding energy, defines the theoretical maximum V_{oc}; however, in actual devices, the output is typically 300–500 mV less than this maximum. The hypothesized source of this loss is the field-driven nature of the devices, the presence of dark current, and Schottky barriers formed at the interfaces (28). One way to enhance OPV performance would then be to suppress these losses to the greatest extent possible. An effective electron-blocking layer (EBL)/hole-transporting layer (HTL) could, in principle, achieve this goal by preventing current leakage and consequent counterdiode formation (29).

In the simplest P3HT:PCBM BHJ cells, a blended solution of P3HT + PCBM in a 1:1 (wt:wt) ratio is typically spin-cast onto tin-doped indium oxide (ITO)-coated glass, which serves as the anode, and is annealed to form the active layer. The cell is then completed and its area defined by the sequential deposition of LiF and Al as the cathode (Fig. 1*A*). Note that inherent to the simplest BHJ cell architecture, the active layer donor and acceptor materials are both in direct contact with the anode, and it is possible for the acceptor material (PCBM) to transfer electrons to the hole-collecting anode, thereby compromising cell efficiency. P3HT:PCBM cells having this architecture typically exhibit PCEs of 2.7–2.9% where PCE is defined in Eq. **1**, with P_{out} the power output of the device, P_{in} the power of incident light source (mW/cm^2), and J_{sc} the short-circuit current density (mA/cm^2).

$$PCE = \frac{P_{out}}{P_{in}} = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad [1]$$

To prevent electron leakage from the BHJ acceptor to the anode, to aid in photogenerated hole extraction, and to planarize the ITO surface, a thin semiconducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) electron-blocking layer (EBL) is typically spin-cast as an aqueous dispersion onto the ITO before active layer deposition (Fig. 1*B*). This device design has achieved confirmed power efficiencies up to 4% (10). Despite these positive characteristics, note that aqueous PEDOT:PSS dispersions are at pH ~ 1 and corrosive to the ITO anode (30, 31). Furthermore, many researchers find that PEDOT:PSS depositions yield inconsistent film morphologies and electrical properties in accord with the demonstrated electrical inhomogeneity of these films (32, 33). Finally, polymer light-

Author contributions: M.D.I., R.P.H.C., and T.J.M. designed research; M.D.I., D.B.B., and A.W.H. performed research; M.D.I., D.B.B., A.W.H., R.P.H.C., and T.J.M. analyzed data; and M.D.I., D.B.B., A.W.H., R.P.H.C., and T.J.M. wrote the paper.

The authors declare no conflict of interest.

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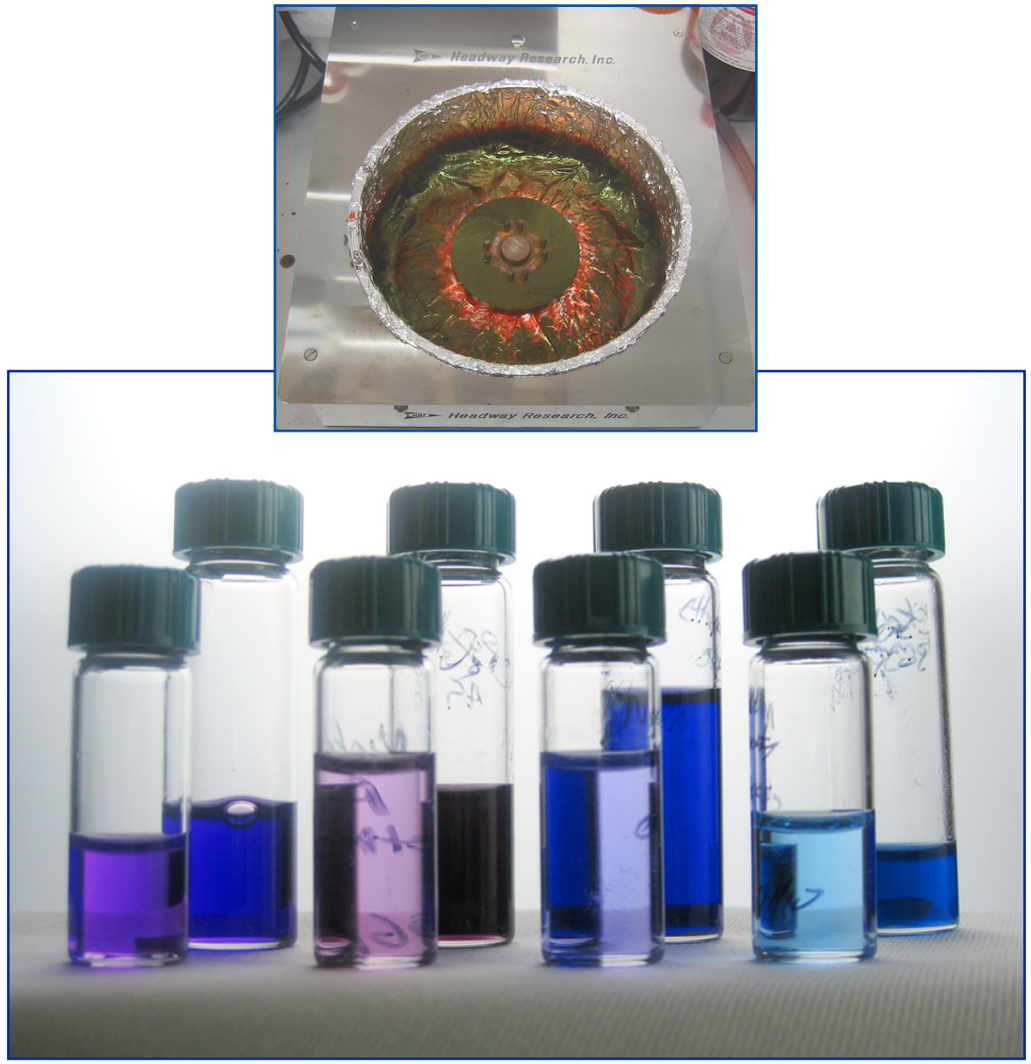
This article contains supporting information online at www.pnas.org/cgi/content/full/0711990105/DC1.

Solution Deposited NiO...

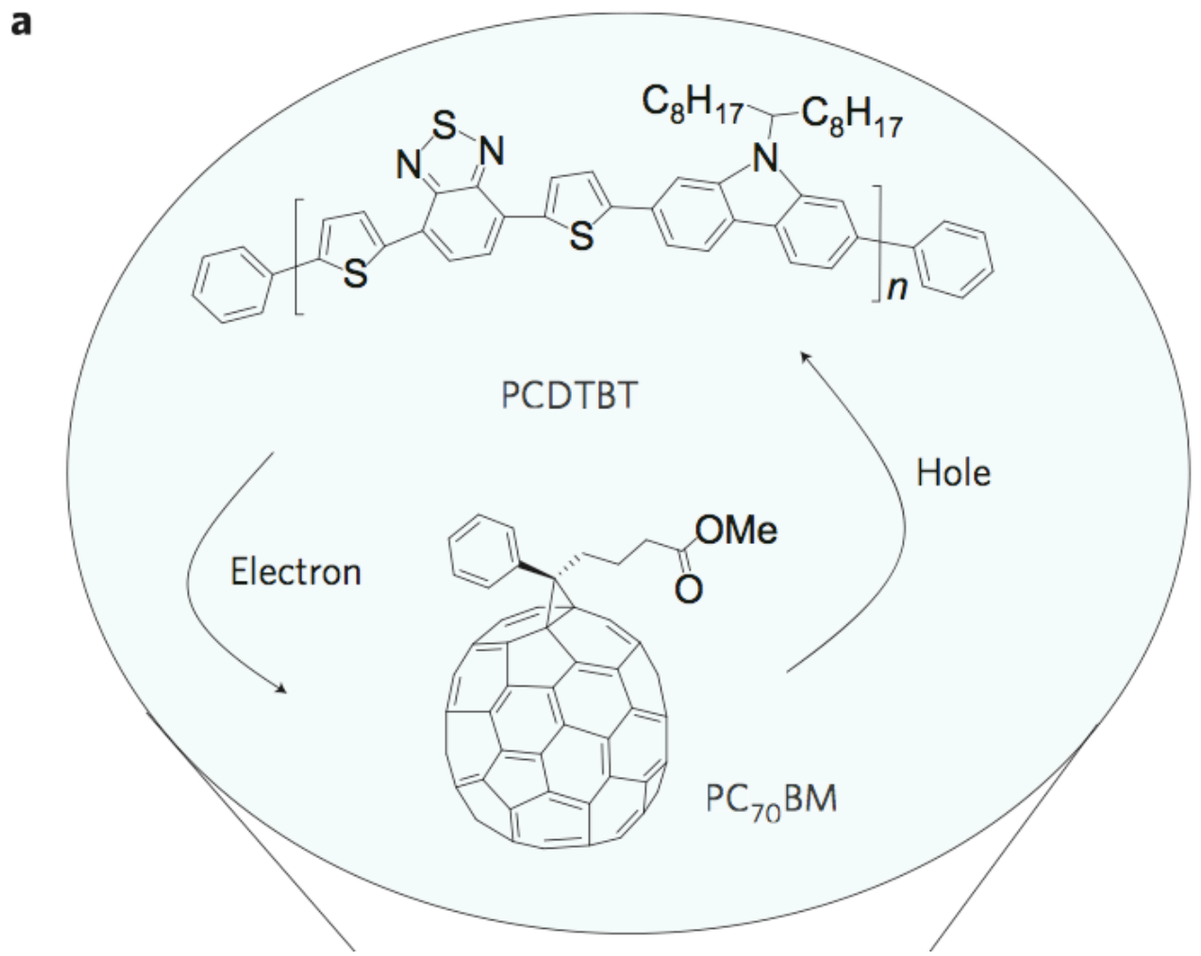
- Nickel metal precursor ink
  - Developed in our group for ink jet printing of Ni metal grid lines
  - Reformulated ink for thin film
- Ni ink is spin coated and annealed in air to form NiO thin film
- NiO films
  - Thin films 5-10 nm
  - Largely amorphous with no observed diffraction in XRD



Steirer, *et. al.*, *Organic Electronics*, **11** (2010) 1414

High Performance Donor System - PCDTBT

- PCDTBT has demonstrated higher V_{OC} due to deeper HOMO level relative to P3HT*



*Park et al. Nature Photonics (2009) vol. 3 (5) pp. 297-303

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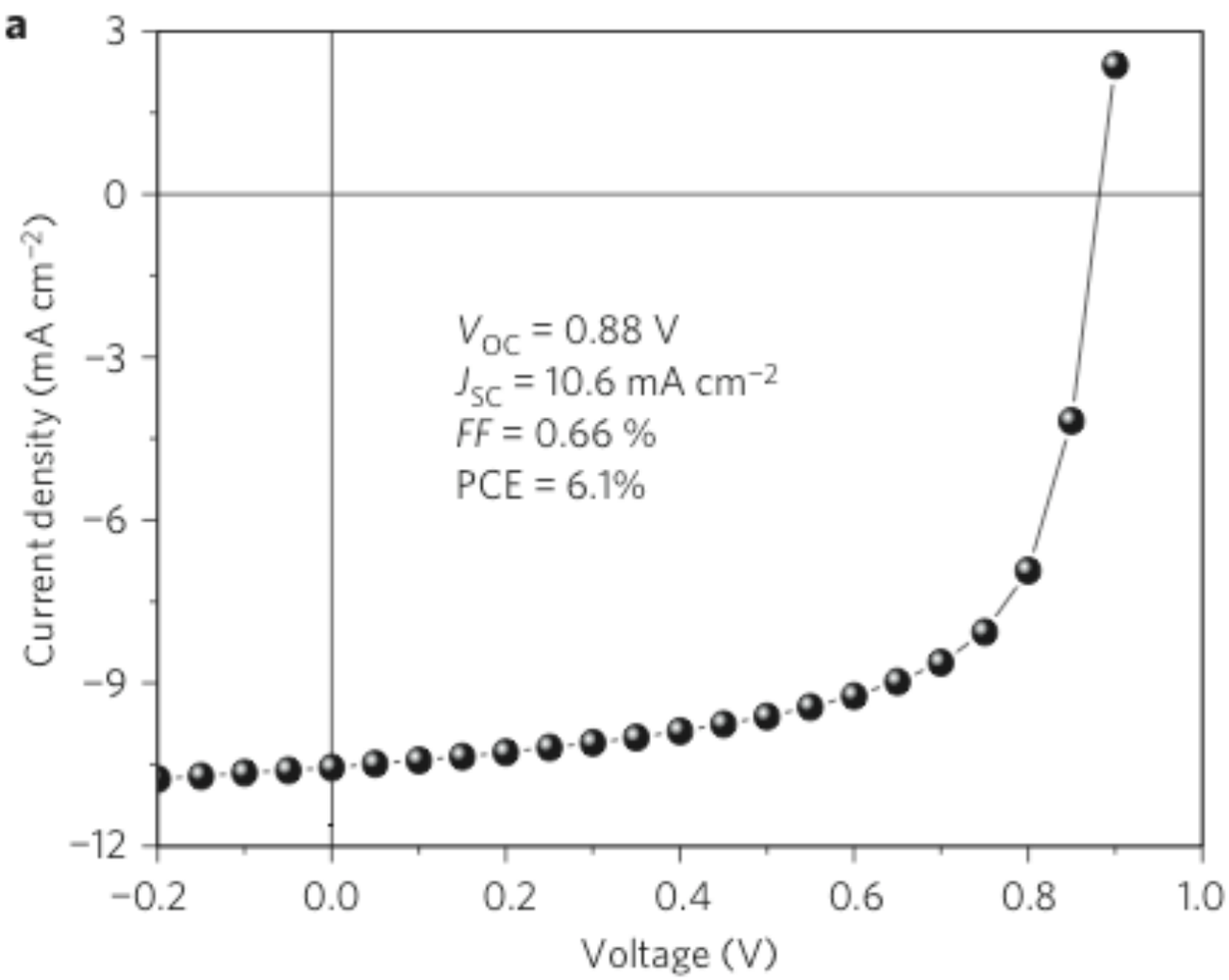
- 6% PCE achieved w/ $PC_{71}BM$ and TiOx optical spacer*



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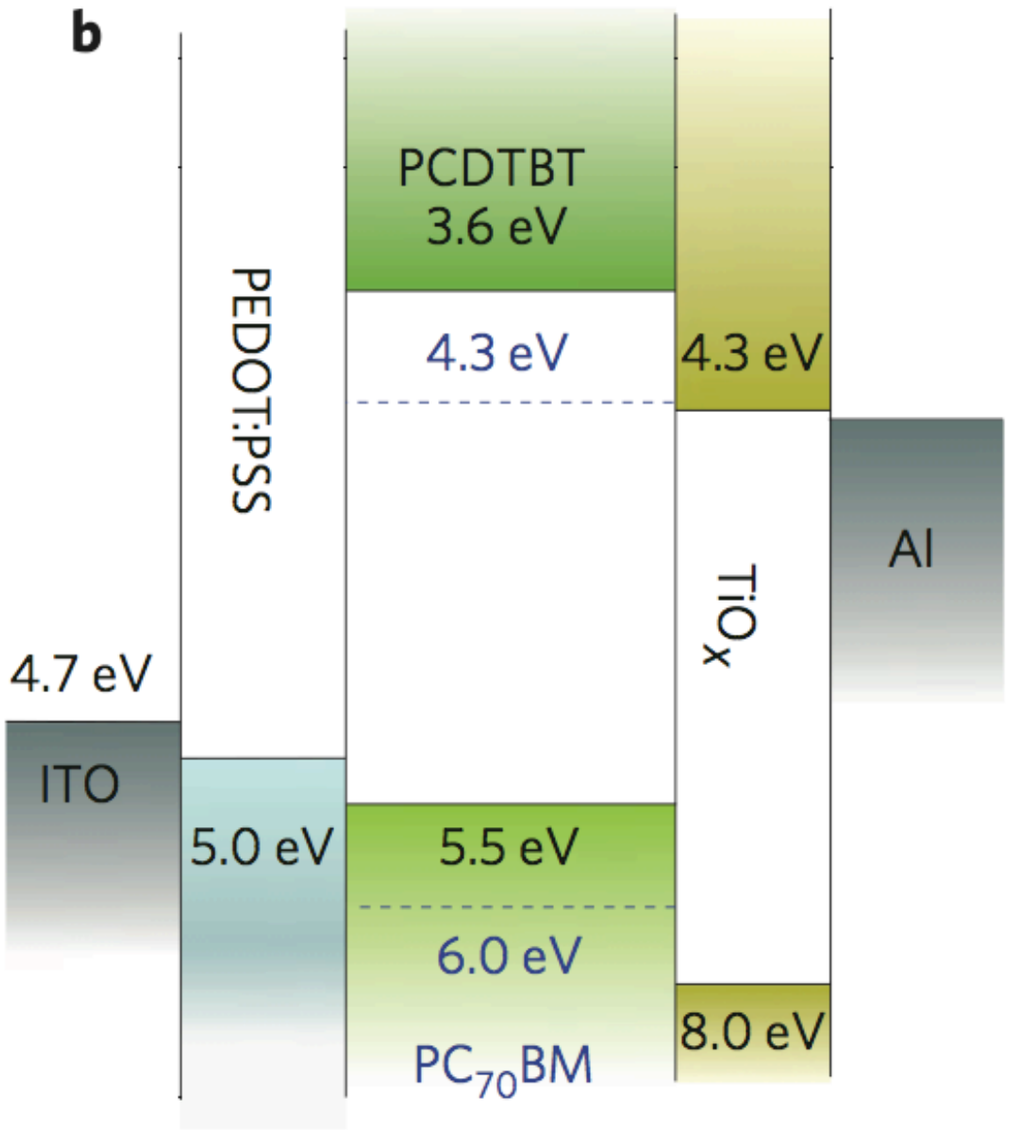

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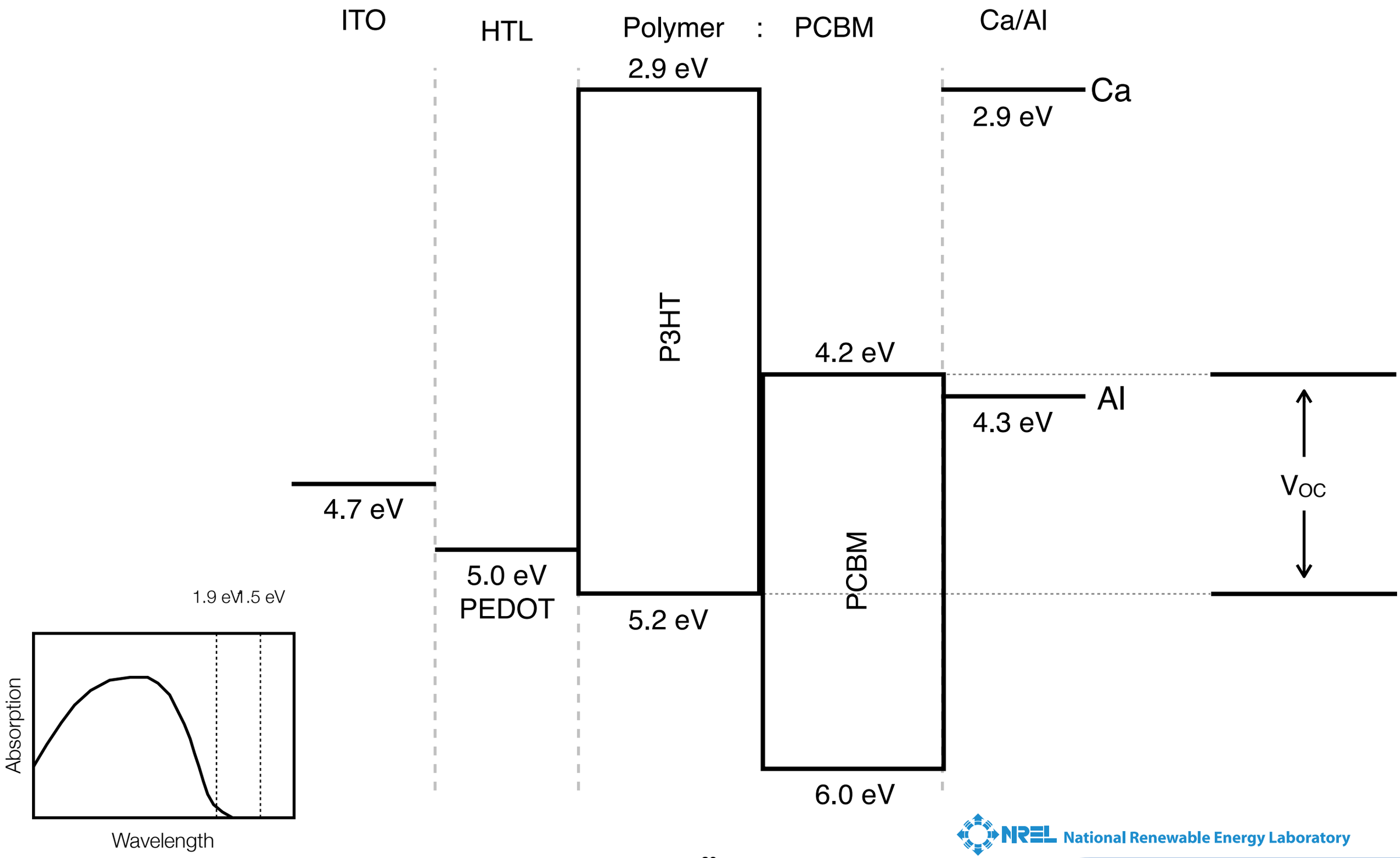
Enhancing Device Performance



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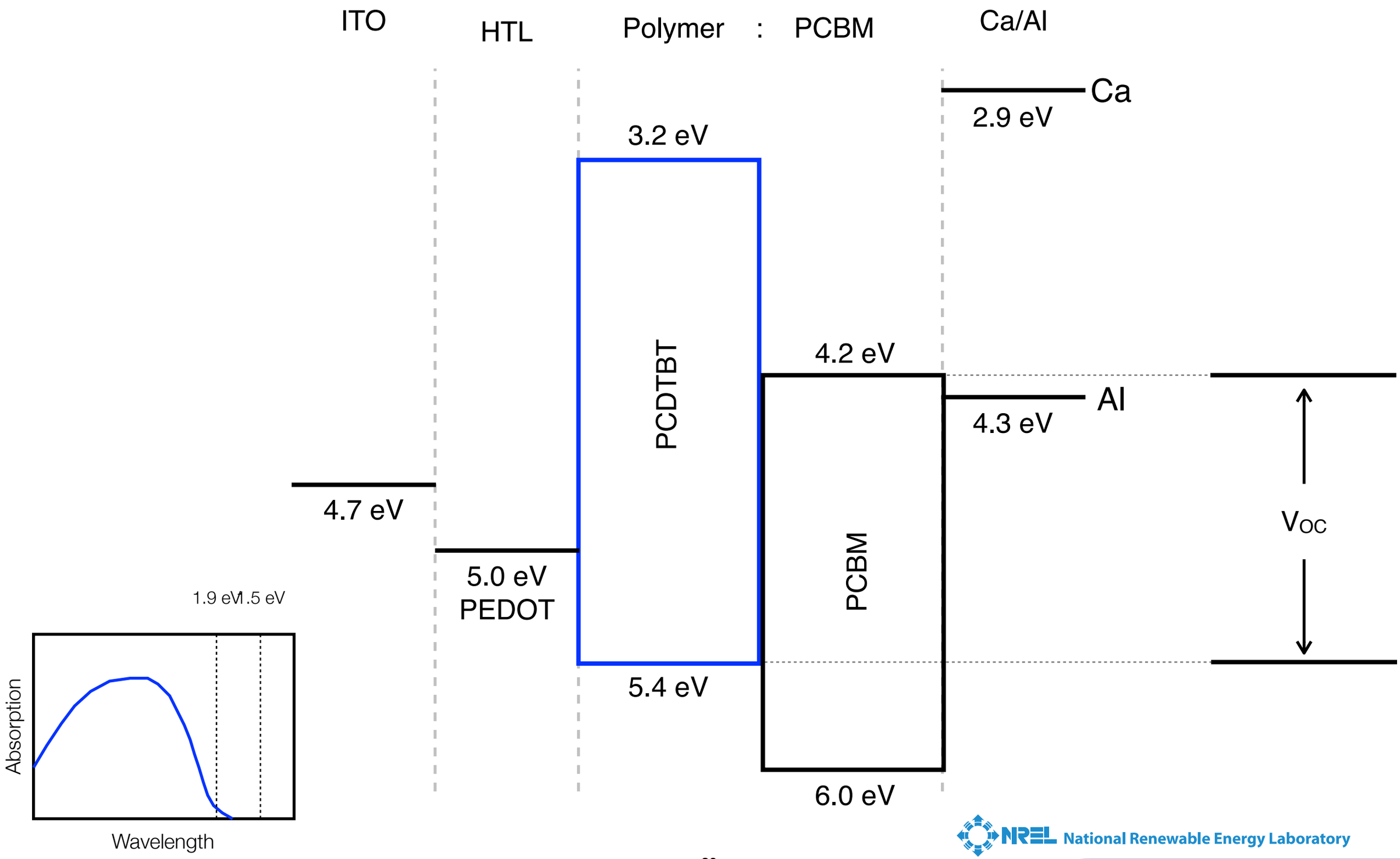

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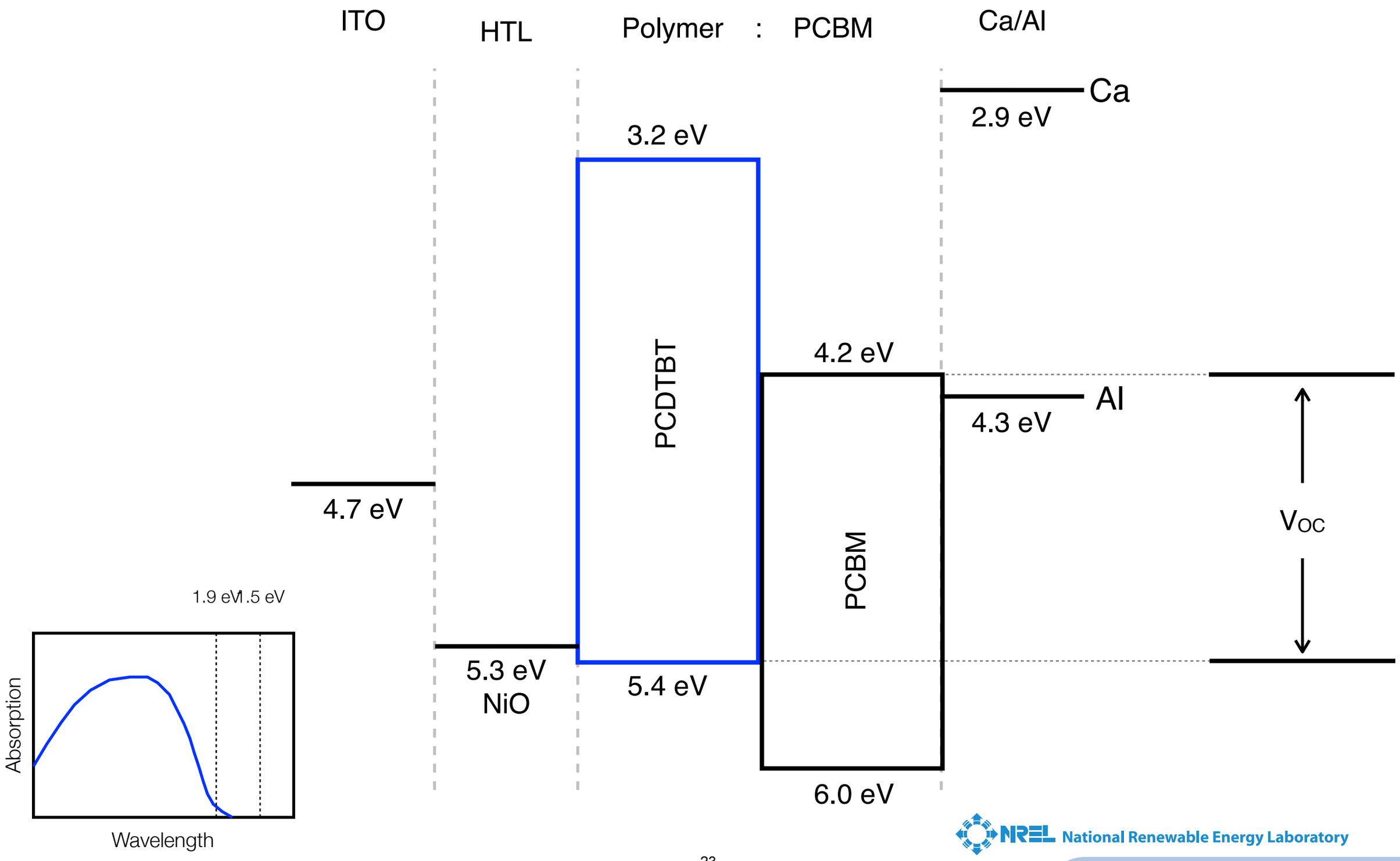
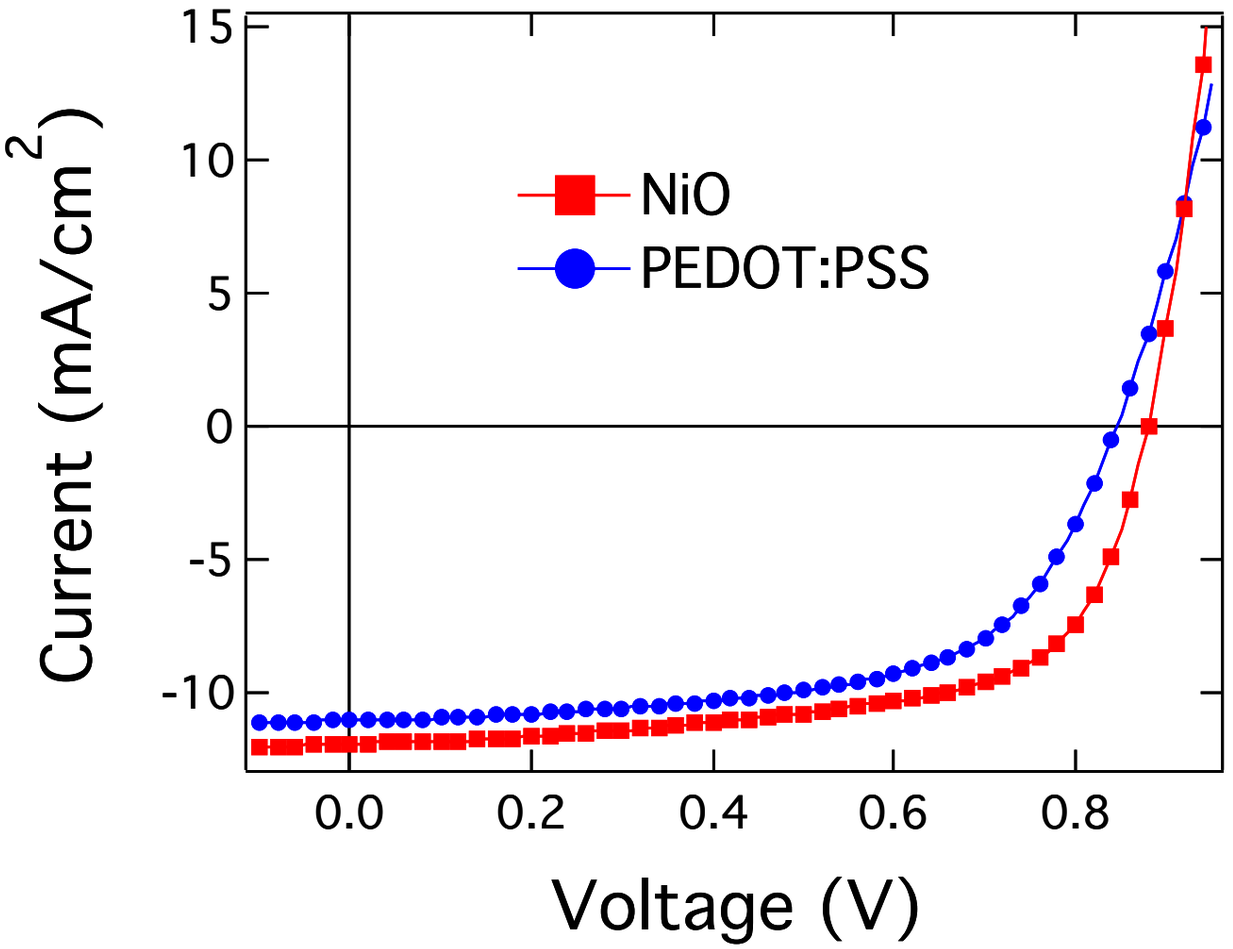


Improved performance with solution NiO and PCDTBT:$PC_{70}BM$ active layer

- PCDTBT has demonstrated higher V_{OC} due to deeper HOMO level relative to P3HT*
  - PEDOT:PSS not well matched to HOMO of PCDTBT
  - Solution NiO after O_2 plasma treatment serves as much better contact to PCDTBT
  - Enhanced lifetime relative to PEDOT



PCDTBT	Voc (mV)	Jsc (mA/cm^2)	FF (%)	PCE (%)	Rp (kΩcm^2)	J_{sat} (nA cm^{-2})
NiO	879	11.5	65	6.7	140±10	2.3±0.1E-3
PEDOT:PSS	845	11.1	60	5.7	15±1.0	2.6±2.0

- Steirer, *et. al. submitted*

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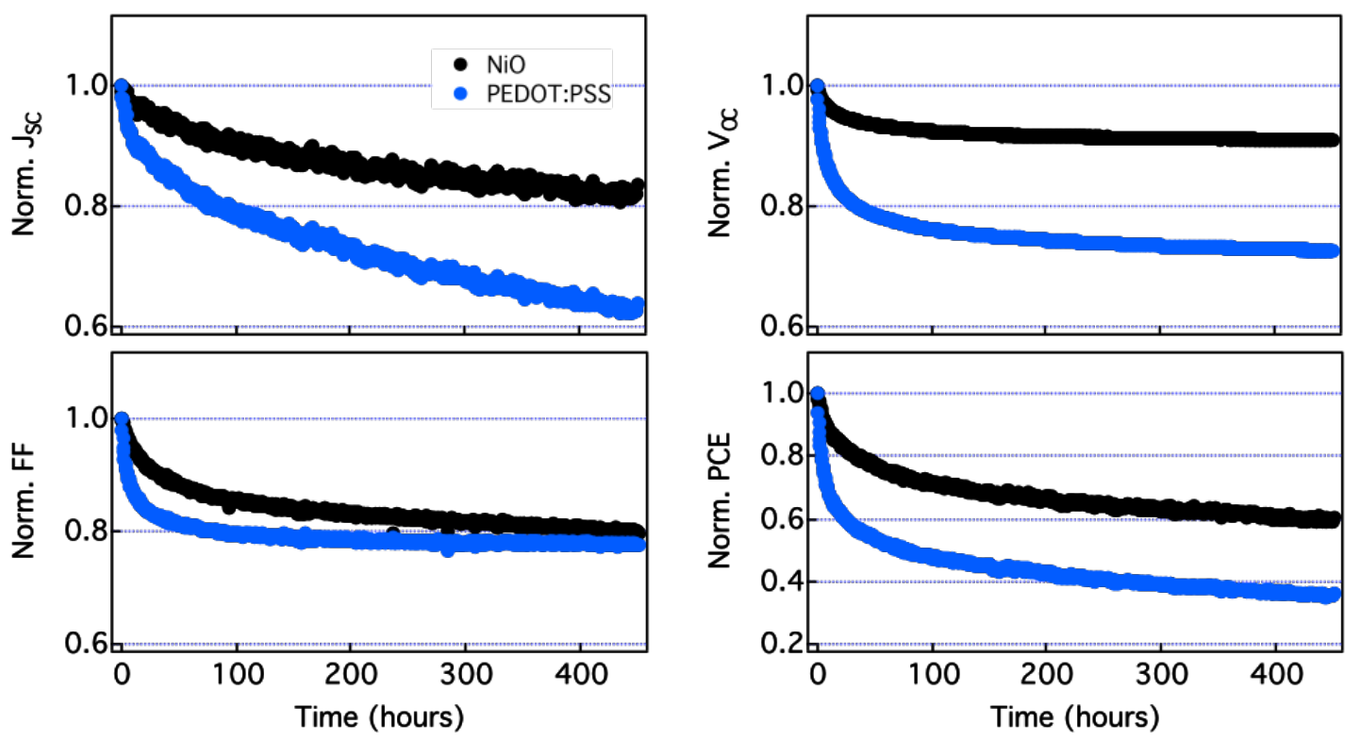

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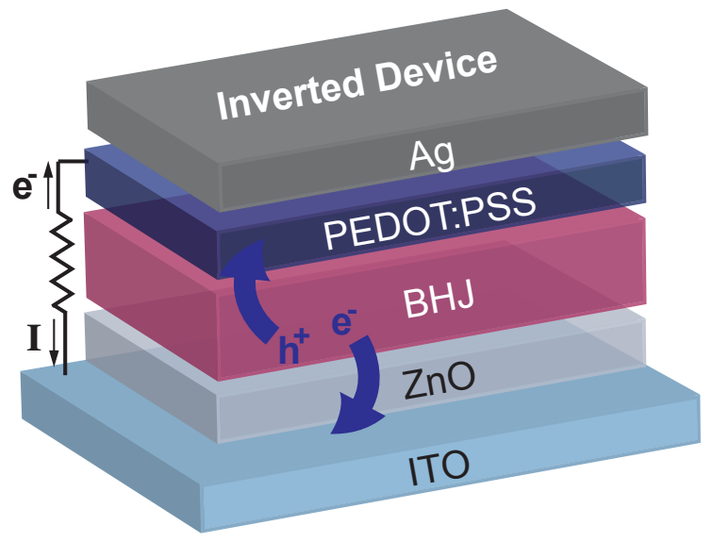
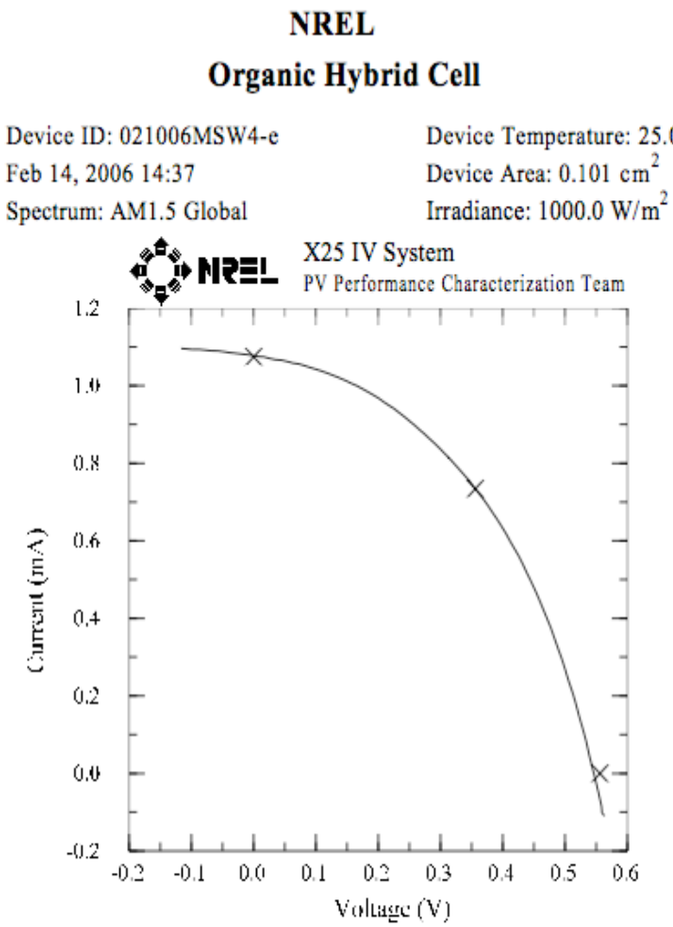
Metal oxides as ETL materials in inverted OPV device architectures

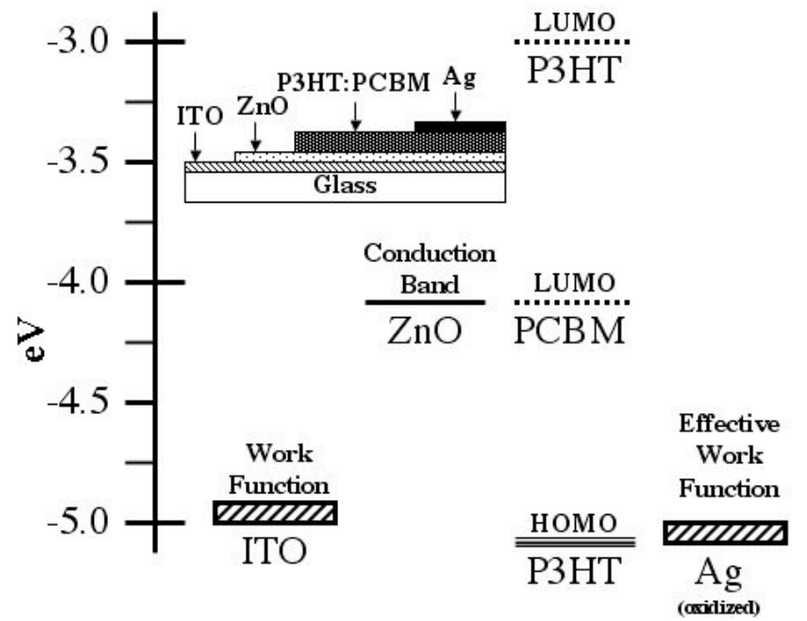


Inverted polarity bulk heterojunction devices



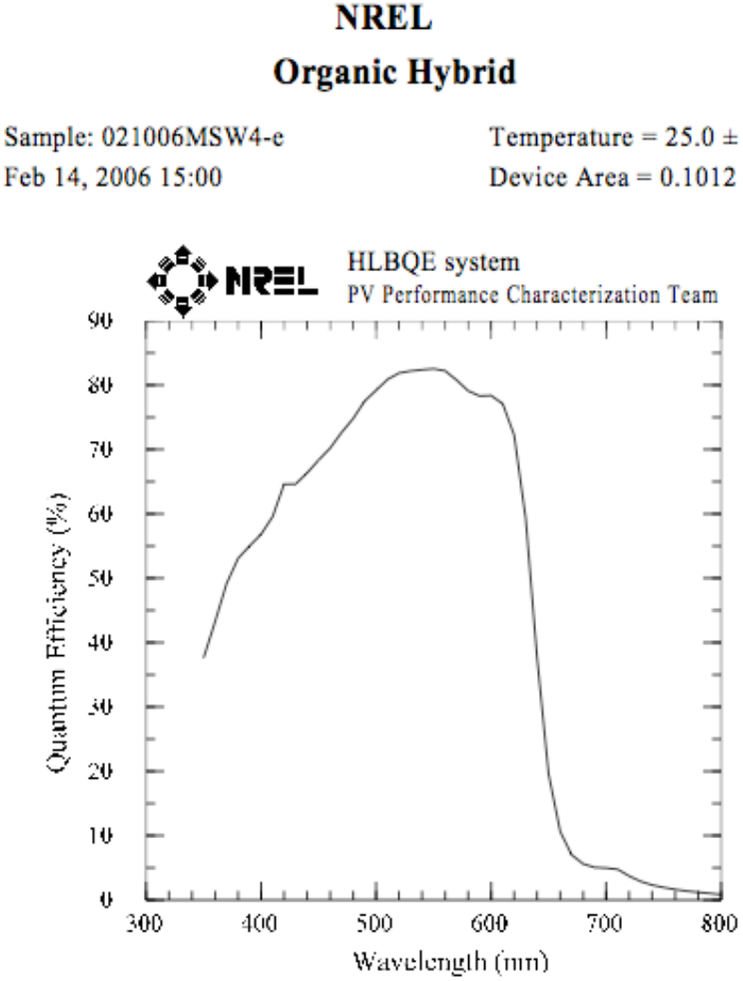
V_{oc} = 0.5560 V
I_{sc} = 1.0738 mA
J_{sc} = 10.612 mA/cm^2
Fill Factor = 43.77 %

I_{max} = 0.73431 mA
V_{max} = 0.3560 V
P_{max} = 0.26140 mW
Efficiency = 2.58 %



ITO / ZnO 50 nm / P3HT:PCBM 250 nm / Ag

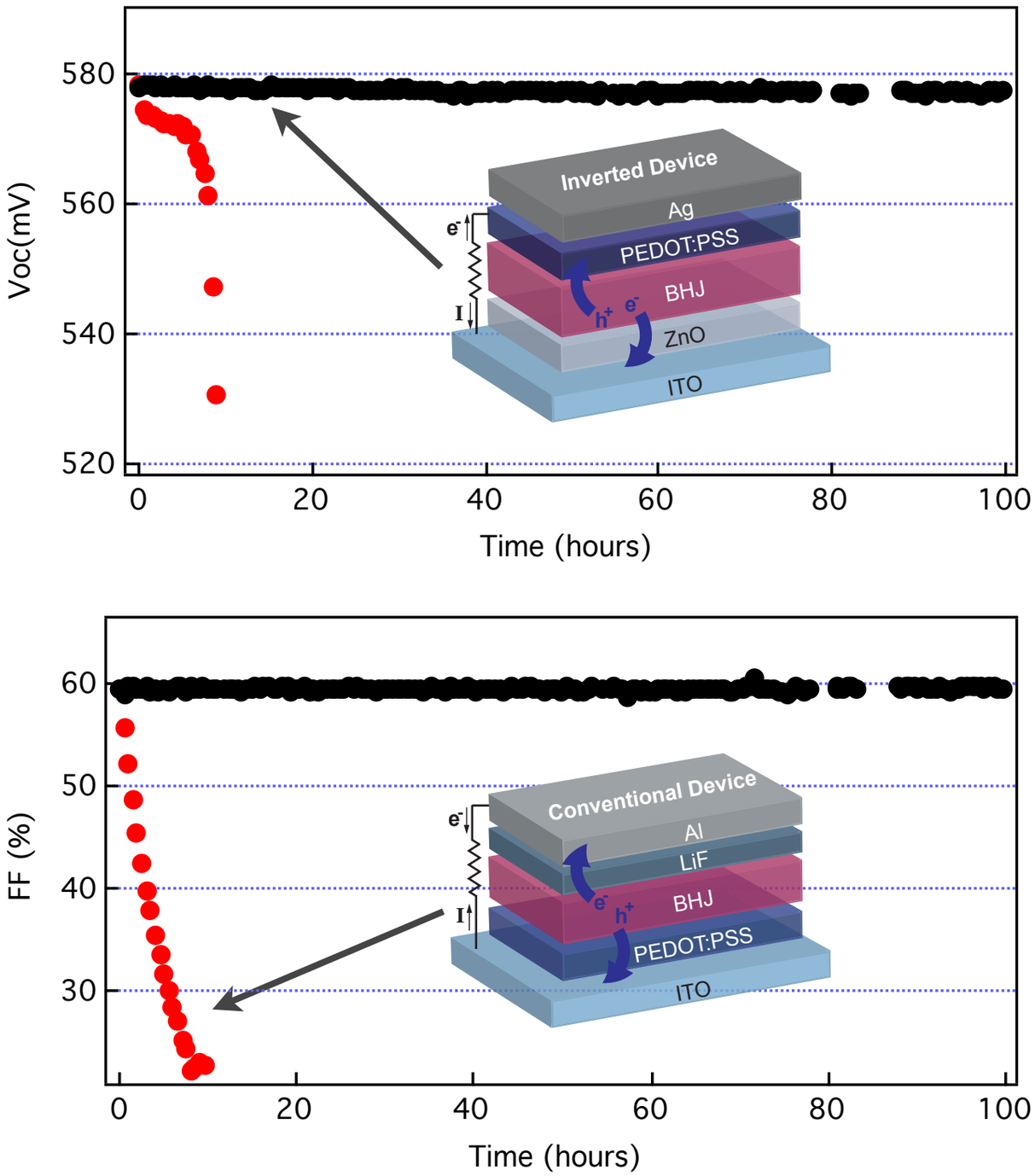
M.S. White, D.C. Olson, et al., *Appl. Phys. Lett.* (2006)

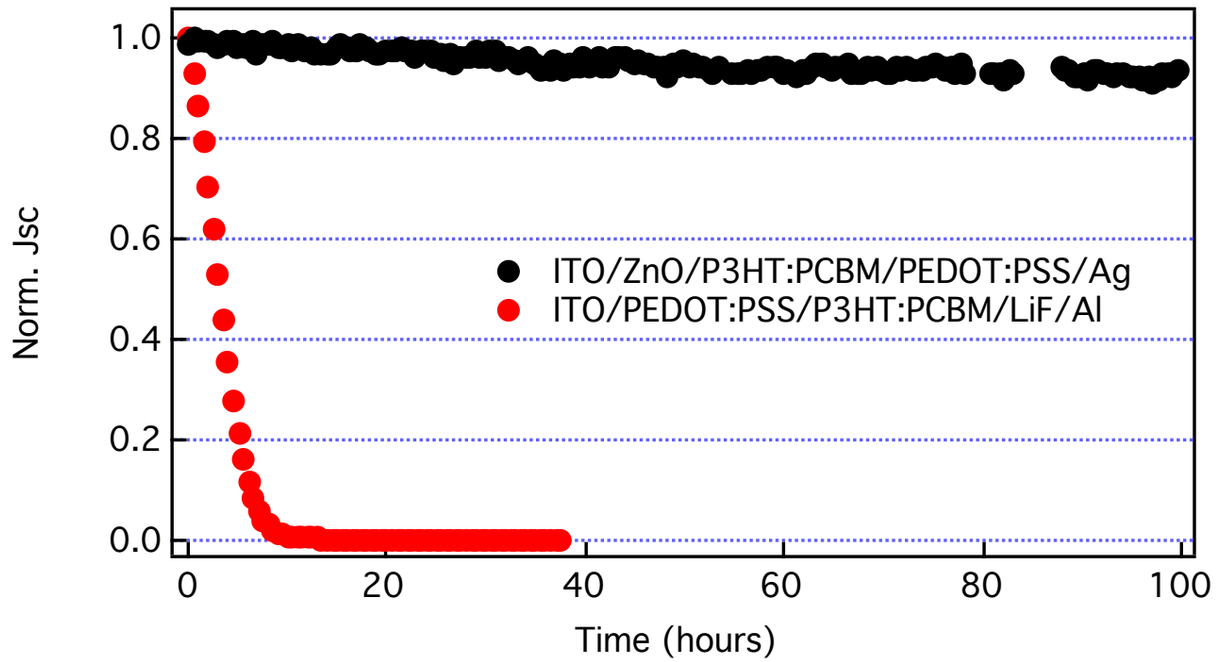


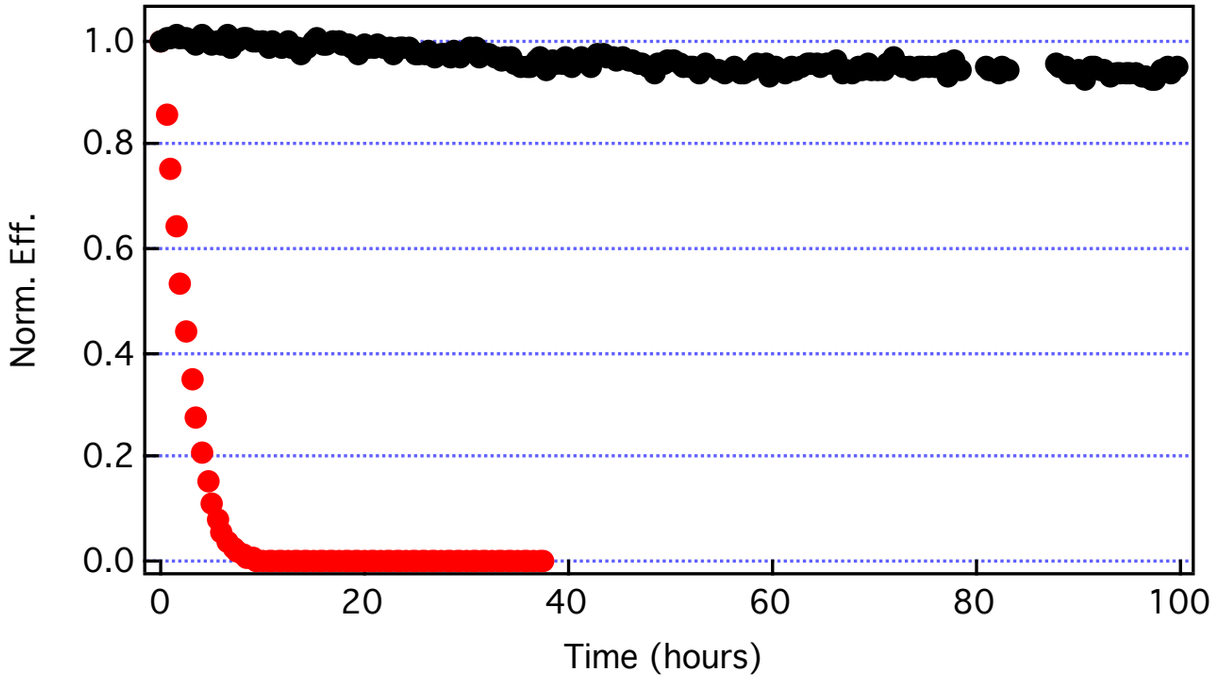
zero voltage bias
Light Bias = 1.00 mA into 0.10 cm^2

Inverted P3HT:PCBM devices now
> 3.7% with HTL/Ag contacts

Improved Lifetime with Inverted Device Architecture

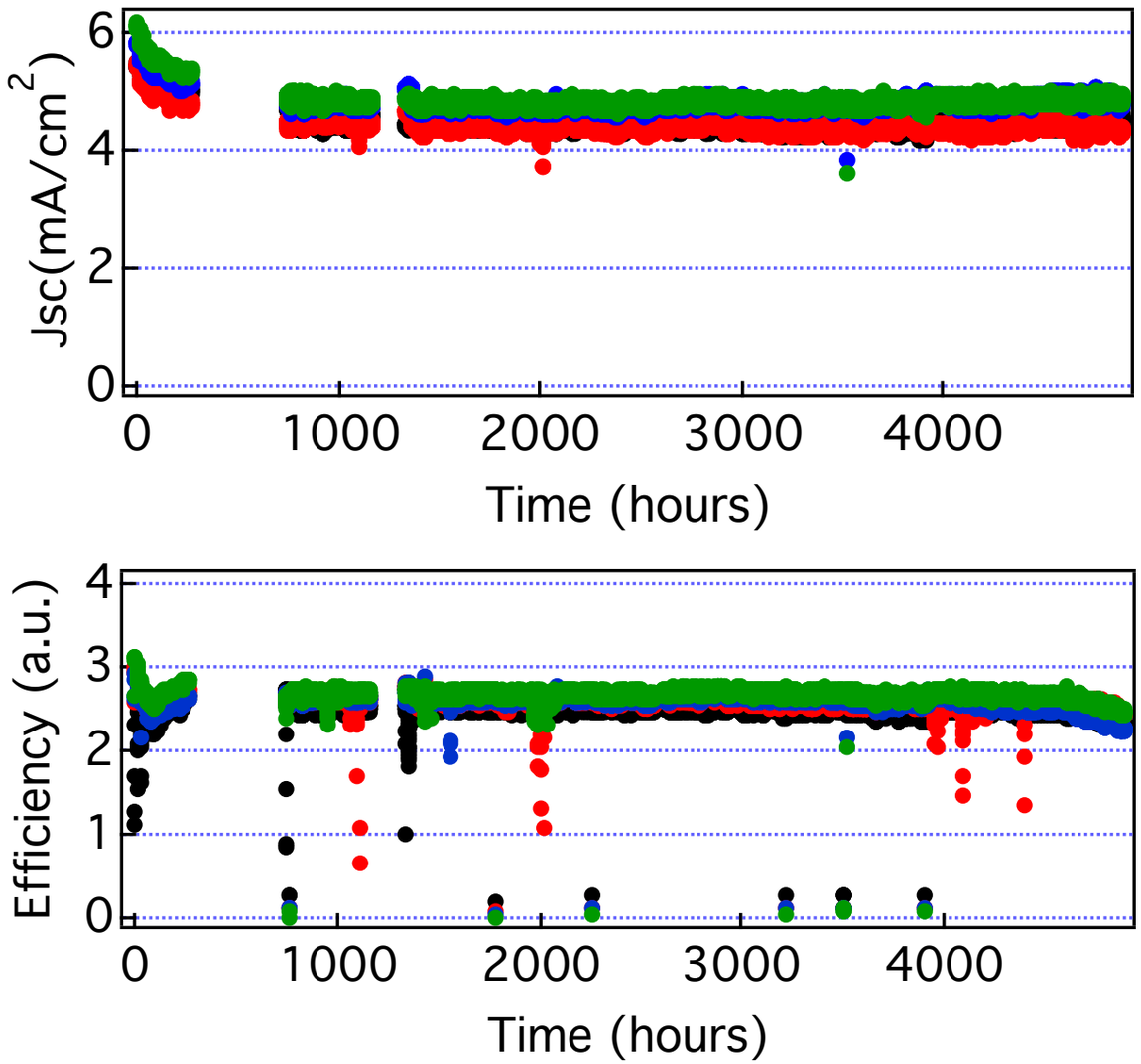


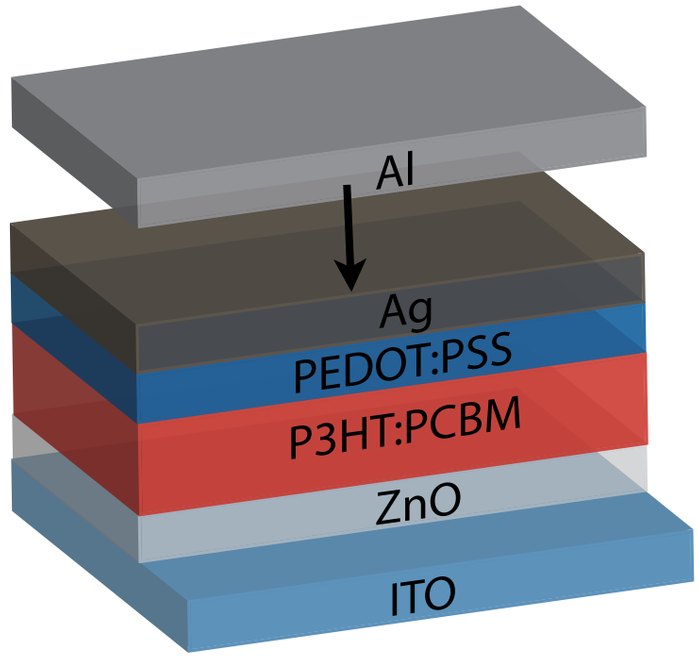




Lloyd, *et.al. in prep.*

Enhanced lifetimes with composite electrodes

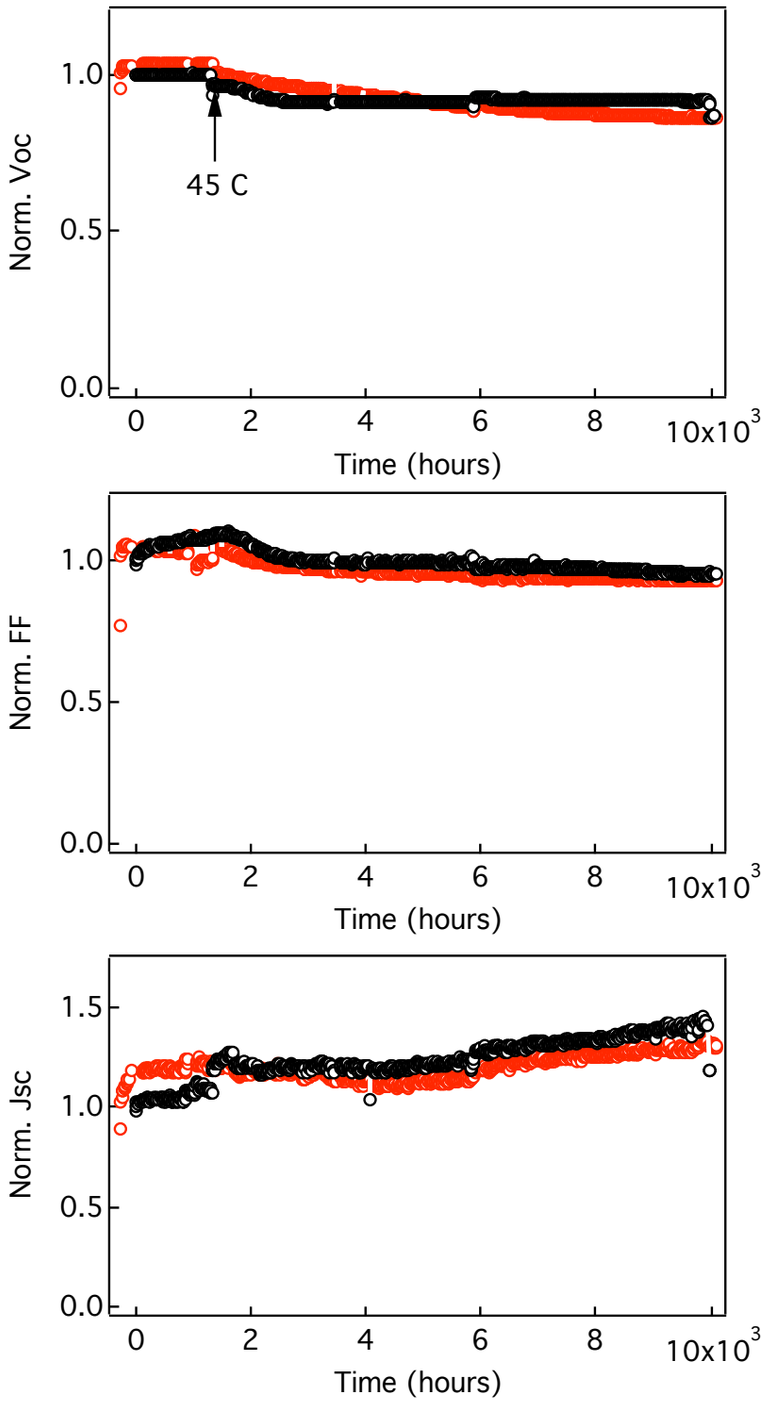


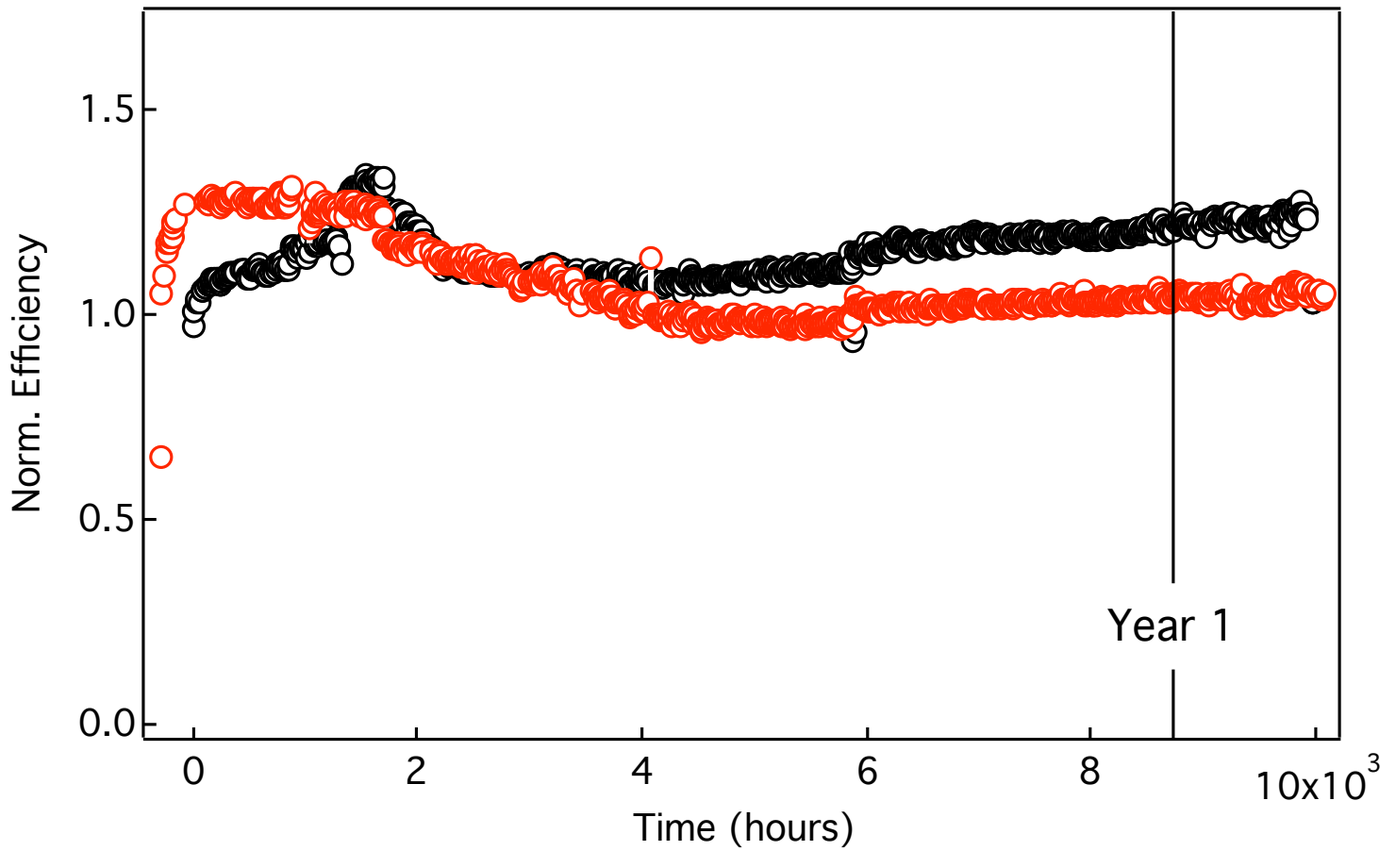


- Composite electrodes show stabilized efficiencies (T_{80}) greater than 5000 hours
- Edge-in diffusion rate < pinhole diffusion rate (not primary lifetime limitation)
- Unencapsulated devices under constant illumination in air
- Al thought to fill pin holes in Ag, form stable oxide barrier

Lloyd, *et.al. in prep.*

Long term stability of encapsulated inverted devices





- Active layers protected from oxygen/moisture ingress
- Glass/epoxy encapsulation, 45 C substrate temp
- >10,000 hours under sulfur plasma illumination
- Cost of such ultra-barriers necessitates development of improved architecture and materials

Conclusions

- Industrial upscaling brings higher efficiencies and better reproducibility
  - Commercial organic solar cells have prospects for very high speed printing/deposition rates of meters/second
- Improving device lifetime is an engineering problem (chemical, electrical, and mechanical)
  - Instability is not an intrinsic property of organic dyes
- Multiple pathways exist to new efficiency regimes
  - OPV is a platform for a myriad of new mechanisms for energy conversion

Support:

CIS:SEM

CENTER for ENERGY EFFICIENT MATERIALS

Also:
We would like to thank Konarka for providing PCDTBT