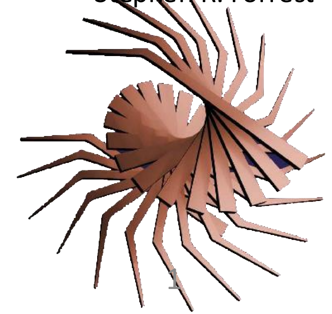
Week 12

Organic Photvoltaics 1

Measuring solar cell efficiency
OPV Architectures
Morphologies and Materials
Transparency

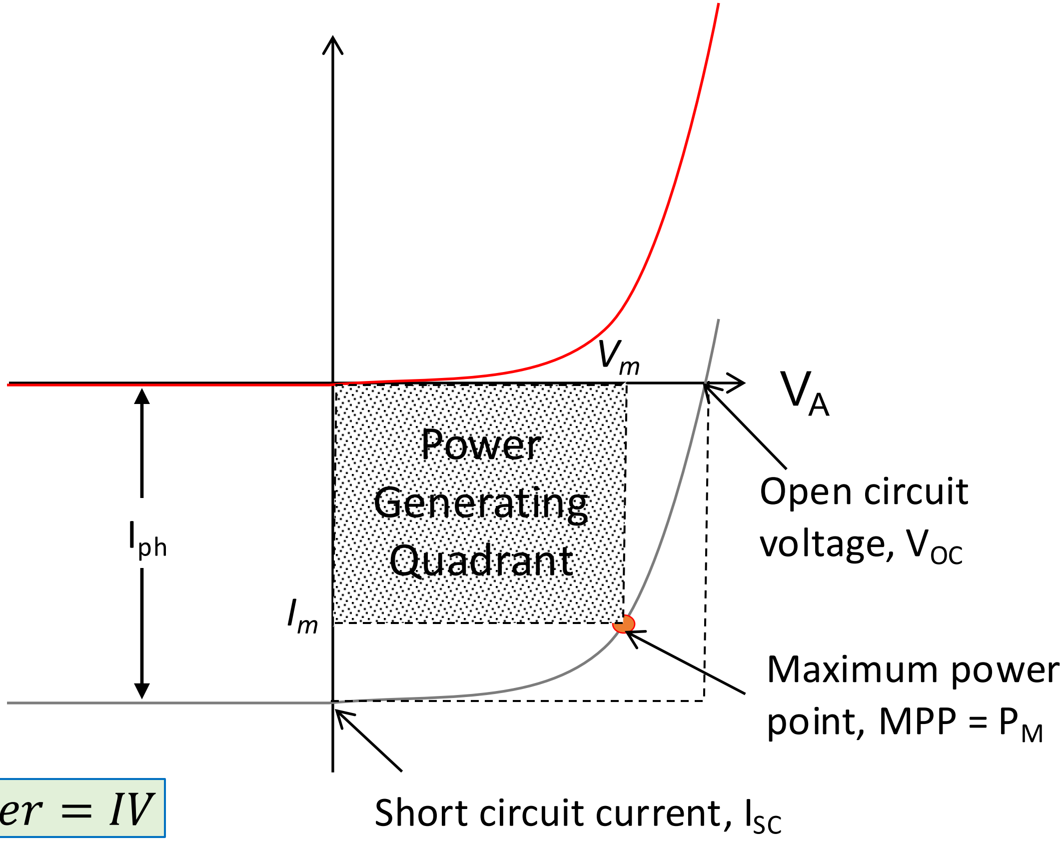
Chapter 8.1-8.5



Solar Cell Basics

Power Conversion Efficiency, η_P:

- $I_{SC} \propto$ number of photons absorbed
- V_{OC} determined by material
- Fill factor (FF) related to device resistance

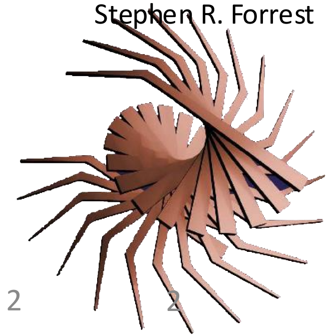


$$\boxed{Power = IV}$$

Maximum power generated: $P_M = I_M V_M = FF I_{SC} V_{OC}$

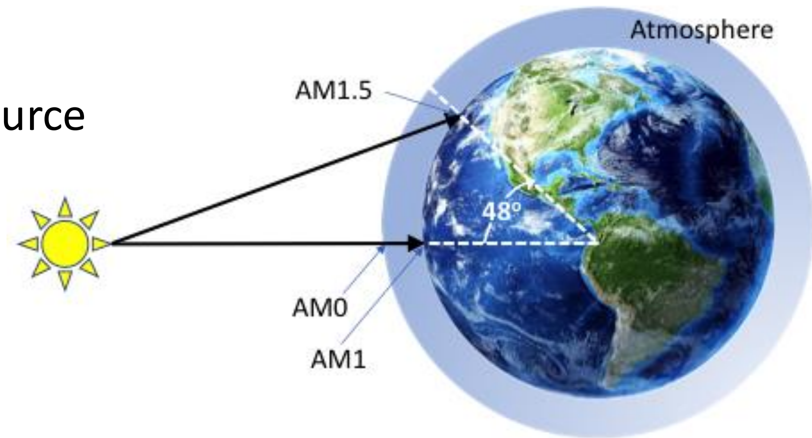
Fill Factor: $FF = \dfrac{V_M I_M}{V_{OC} I_{SC}}$

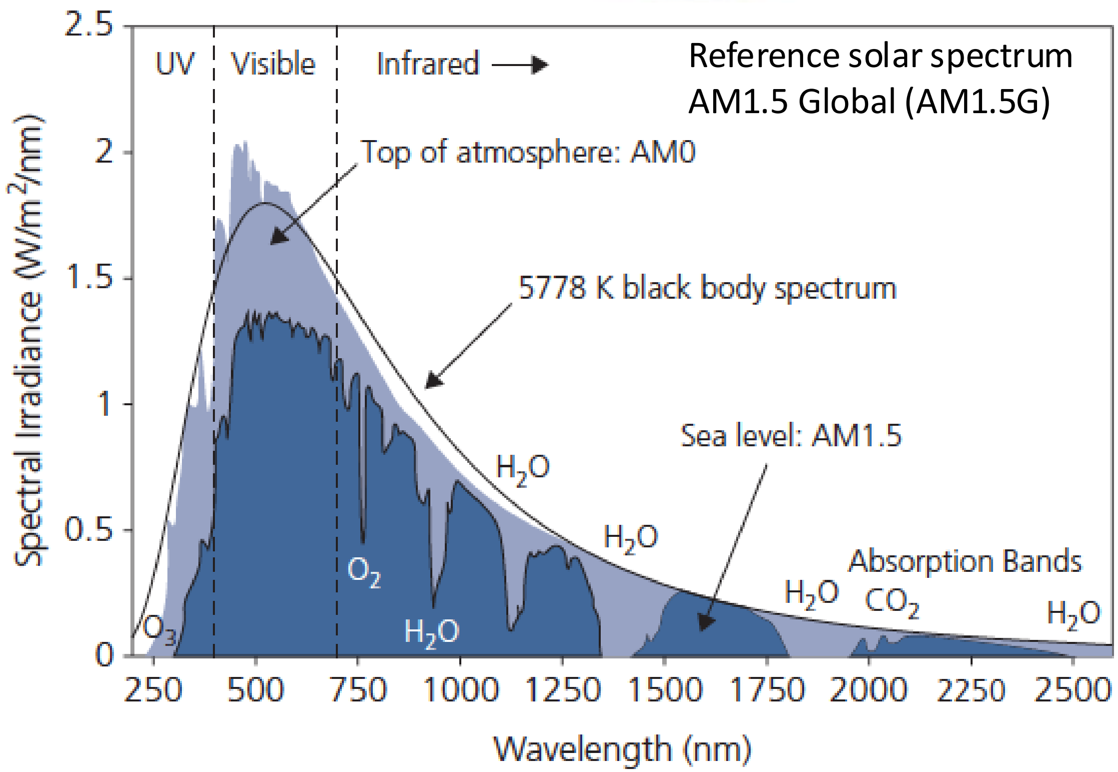
$$\boxed{\eta_P = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{inc}}}$$



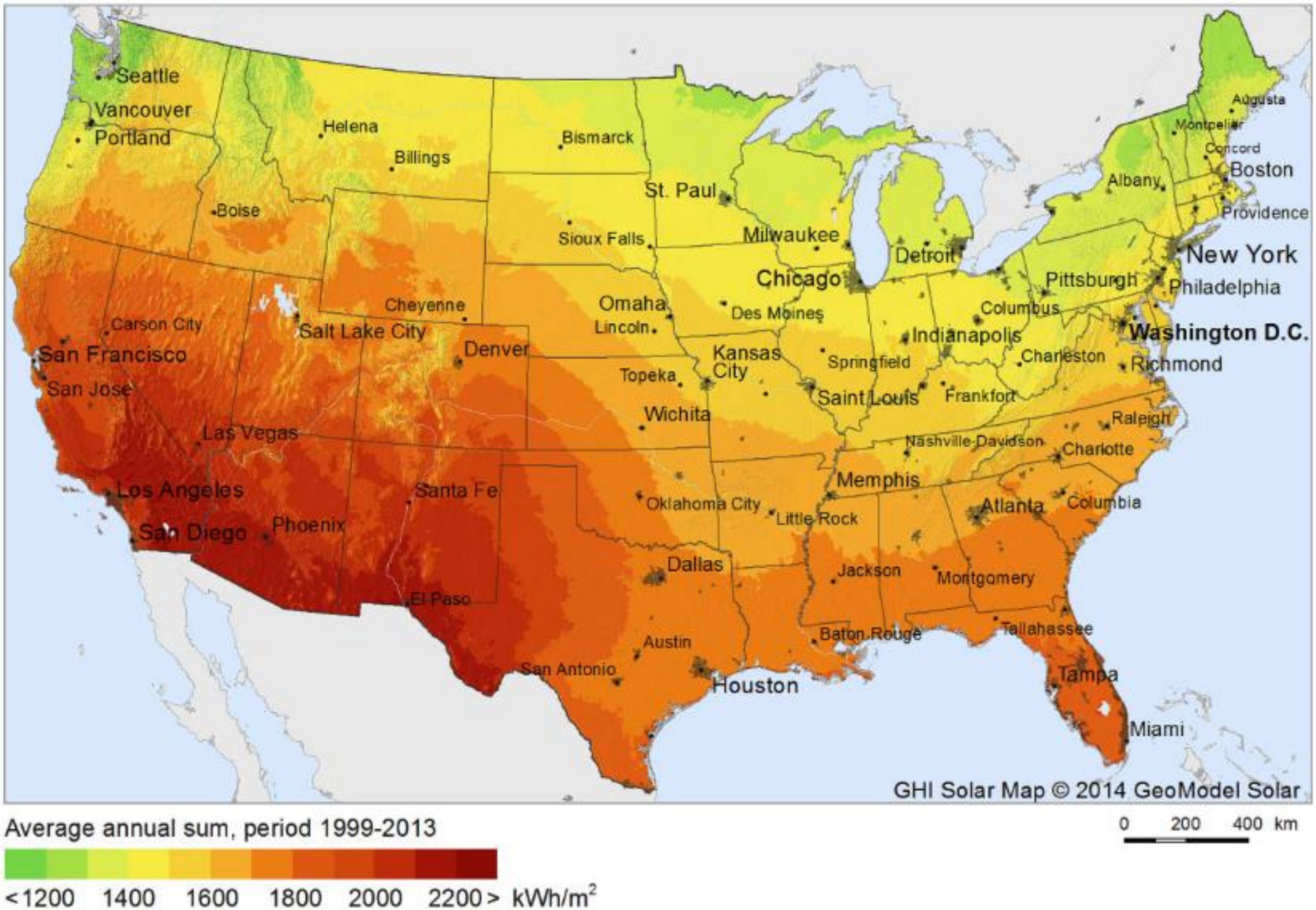
Understanding Solar Cell Efficiency Limits

Consider the Source





Annual Solar Insolation: US



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Solar Cell Facts

- Solar power at Earth's surface on sunny day: 1 kW/m^2
- Power conversion efficiency of a solar cell: electrical power generated per Watt of sunlight in units of W/W or %

Technology	Max. PCE	Pros & Cons
Single junction solar cell thermodynamic limit	31%	-
Multijunction solar cell record under concentrated sunlight	47%	Very efficient & expensive (100X Si)
Silicon solar cell	27%	-
Silicon cell when installed	18-20%	Competitive w. fossil fuel wide deployment
GaAs single junction cell	29%	Very expensive, useful for space applications
Perovskite cells	>26%	Unstable, toxic materials, potentially low cost, flexible
Organic cells	>20%	Potentially low cost, flexible, transparent

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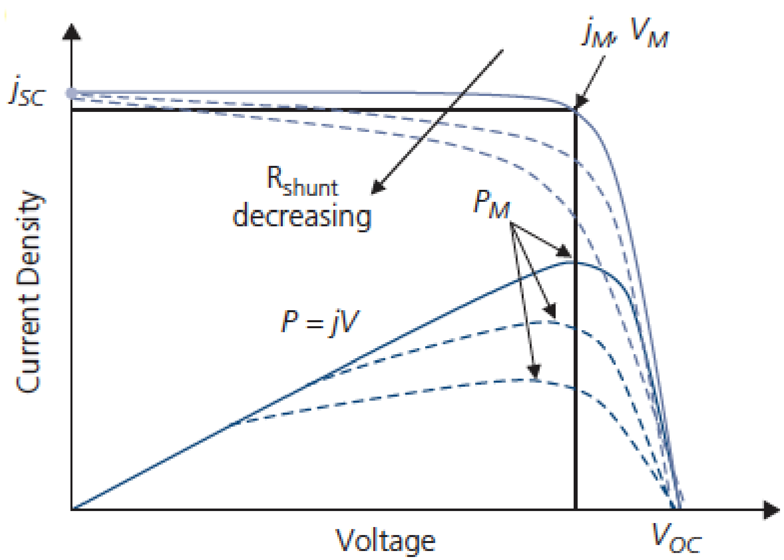
No Cell is Ideal

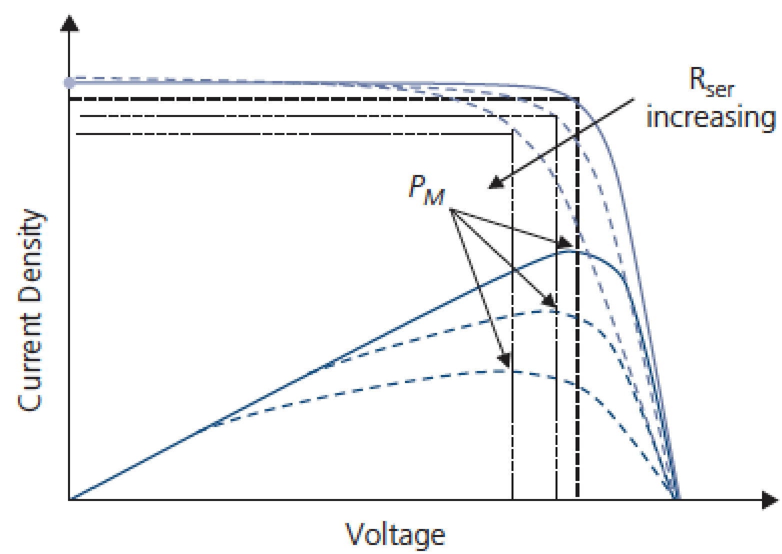
(see Ch. 4.7)

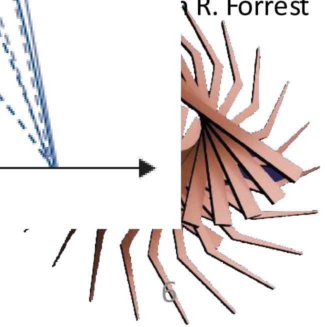
$$\boxed{j = j_0\left[\exp\left(q\left(V_a - jAR_{ser}\right)/n_S k_B T\right) - \frac{k_{PPd}}{k_{PPd,eq}}\right] + \frac{V_a - jAR_{ser}}{R_{shunt}} - j_{ph}}$$

$$V_{OC} = \frac{n_S k_B T}{q}\log\left(\frac{j_{ph}}{j_0} + \frac{k_{PPd}}{k_{PPd,eq}}\right) \approx \frac{n_S k_B T}{q}\log\left(\frac{j_{SC}}{j_0} + 1\right)$$

It is customary to replot power generating *j-V* of the 4th quadrant into the 1st quadrant

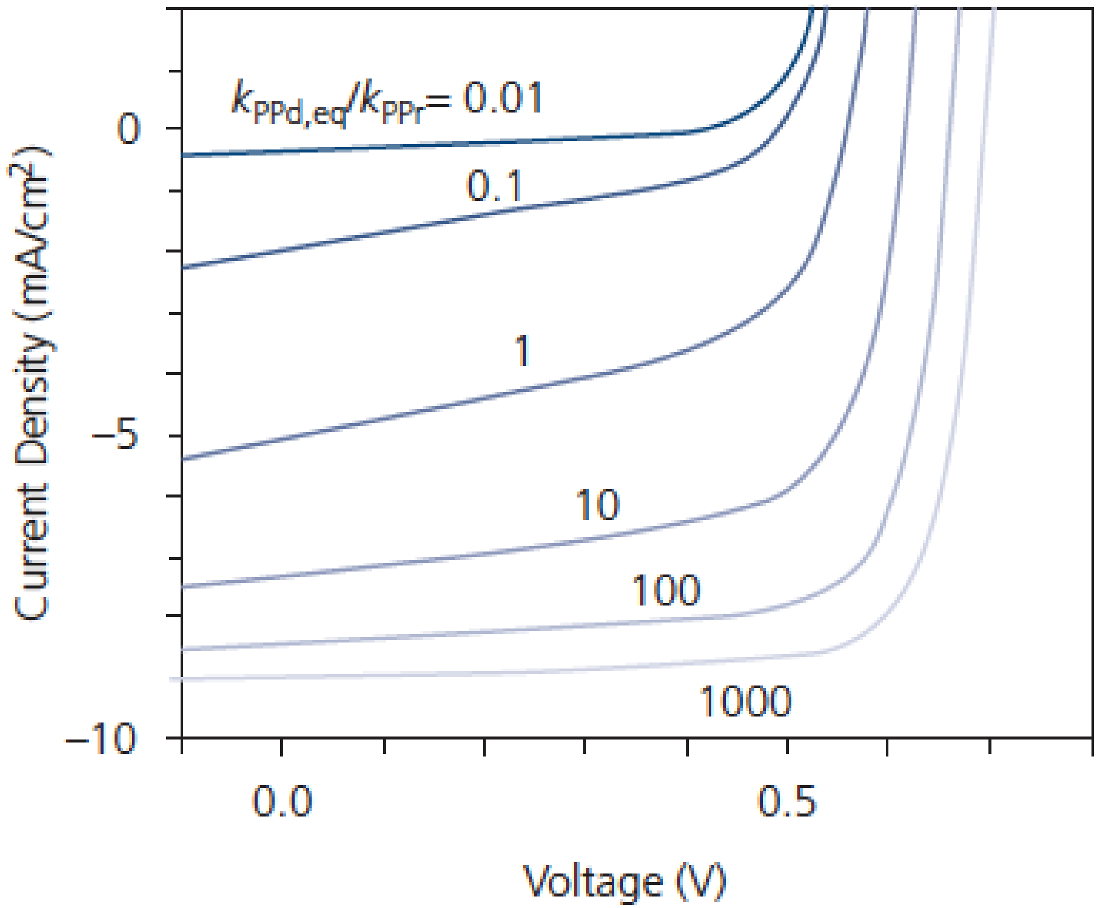






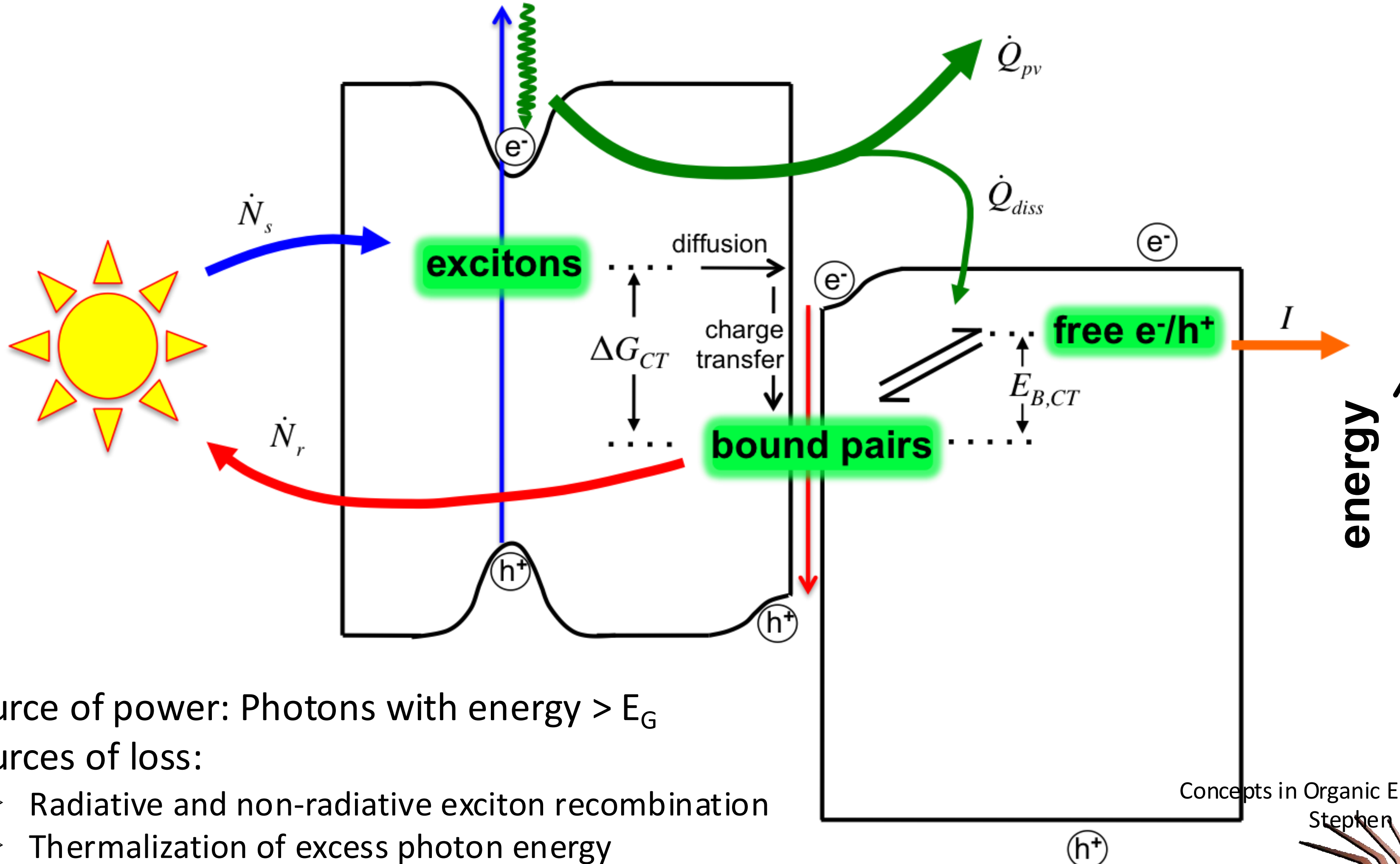
Dependence of V_{OC} on recombination rates

$$qV_{OC} = \Delta E_{HL} - k_B T \log\left[\frac{A}{j_{SC}}\left(\frac{k_{rec}k_{PPr}}{k_{PPd}+k_{PPr}}\right)\right]$$



C. K. Renshaw, et al. 2012. *Phys. Rev. B,* 86**,** 085324

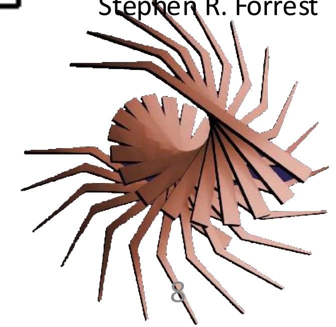
Thermodynamic Limits to OPV cell Efficiency



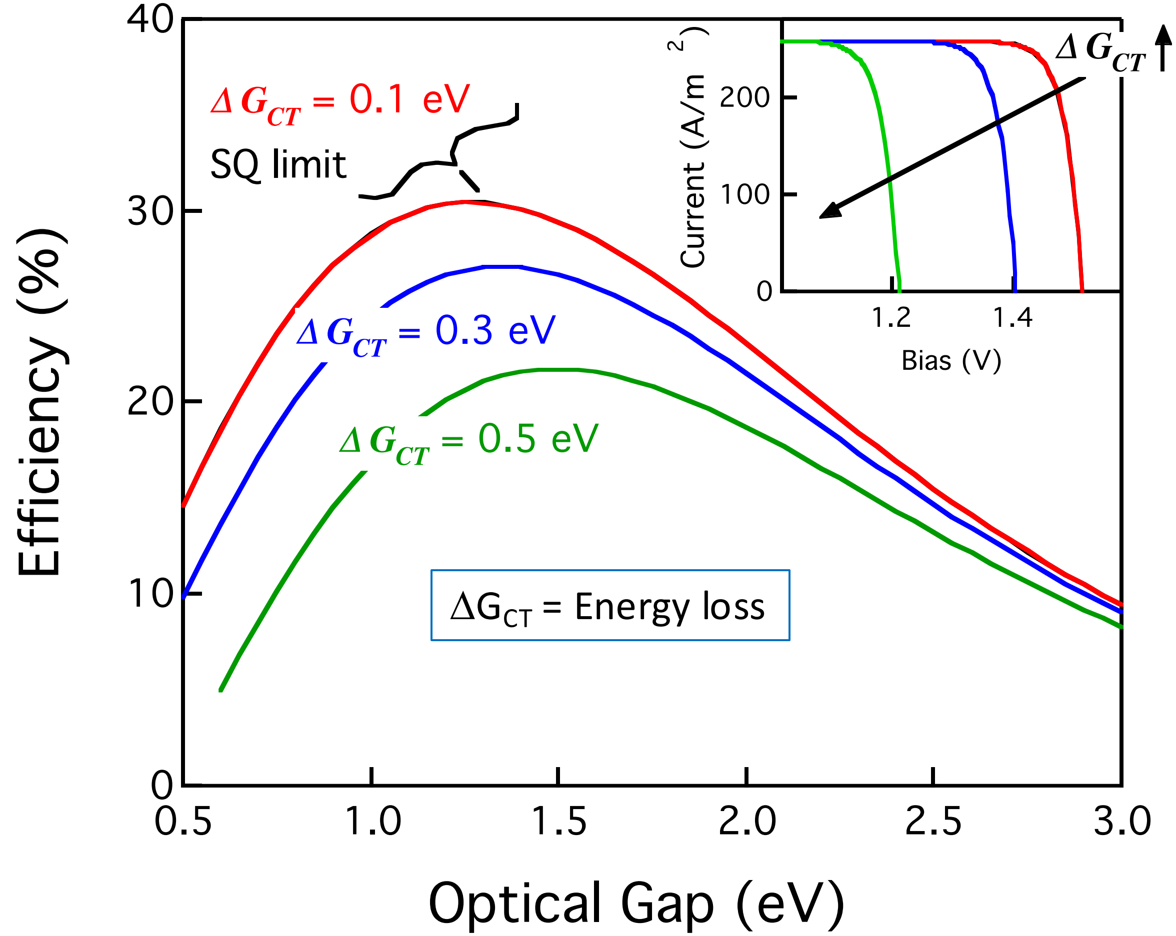
- Source of power: Photons with energy > E_G
- Sources of loss:
  - Radiative and non-radiative exciton recombination
  - Thermalization of excess photon energy
  - Recombination of CT states

Loss in *EXCITONIC* Solar Cells

Giebink, et al., Phys. Rev. B **83**, 195326 (2011)



Single-Junction OPV Efficiency Limit



Assumptions:

- Based on 2nd Law of Thermodynamics
- Sun=Black Body Source at 5770K
- Polaron pairs mediate photogeneration

Observations:

- OPV efficiency limit: 22 - 27%
- Polaron pair energy ⇒V_{oc} redux
- Theory gives SQ limit (⇒ general!)

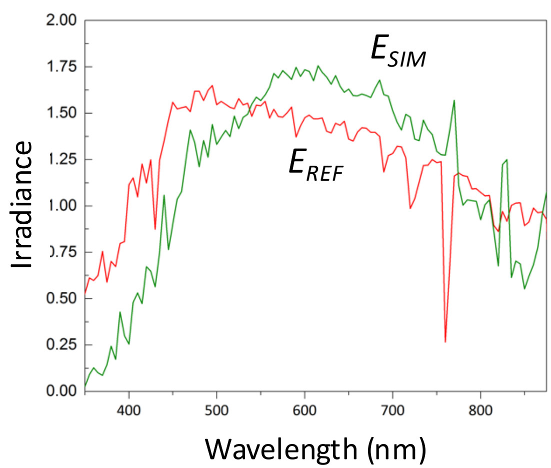
Giebink, et al., Phys. Rev. B **83**, 195326 (2011)

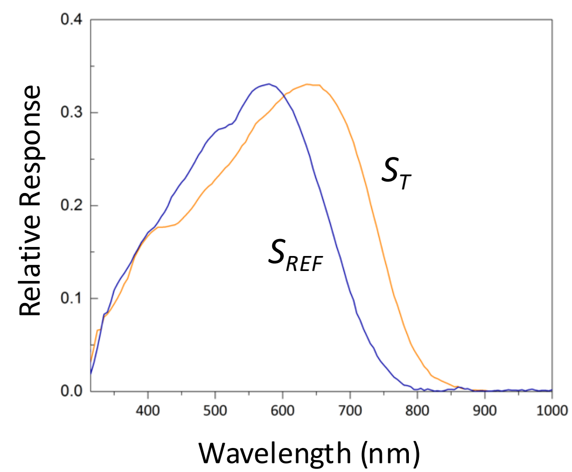
Measuring *Single Junction* Solar Cell Efficiency

Challenges:

- The laboratory spectrum (E_{REF}) is not identically equal to the reference solar spectrum (AM1.5G):
  It is only simulated (E_{SIM})
- Reference detector spectral response (S_{REF}) not identical to the test solar cell (S_T)

Example spectra:





To correct for these differences we calculate the *spectral mismatch factor*

$$M = \frac{j_{SIM}^{T}}{j_{REF}^{T}} \frac{j_{REF}^{REF}}{j_{SIM}^{REF}} = \frac{\int_{\lambda_1}^{\lambda_2} E_{SIM}(\lambda) S_T(\lambda)\, d\lambda \int_{\lambda_1}^{\lambda_2} E_{REF}(\lambda) S_{REF}(\lambda)\, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{REF}(\lambda) S_T(\lambda)\, d\lambda \int_{\lambda_1}^{\lambda_2} E_{SIM}(\lambda) S_{REF}(\lambda)\, d\lambda}$$

$j_{SIM}^{T} = j_{SC}$ of test device using the simulated spectrum at 1 sun

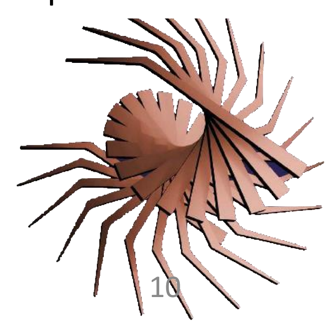
$j_{REF}^{T} = j_{SC}$ of test device using the reference AM1.5G spectrum at 1 sun

… etc.

$M = 1$ if $S_{REF} = S_T$ or $E_{REF} = E_T$

Solar cell calibration is then: $j_{REF}^{T} = \frac{j_{REF}^{REF} \bullet j_{SIM}^{T}}{M \bullet j_{SIM}^{REF}}$

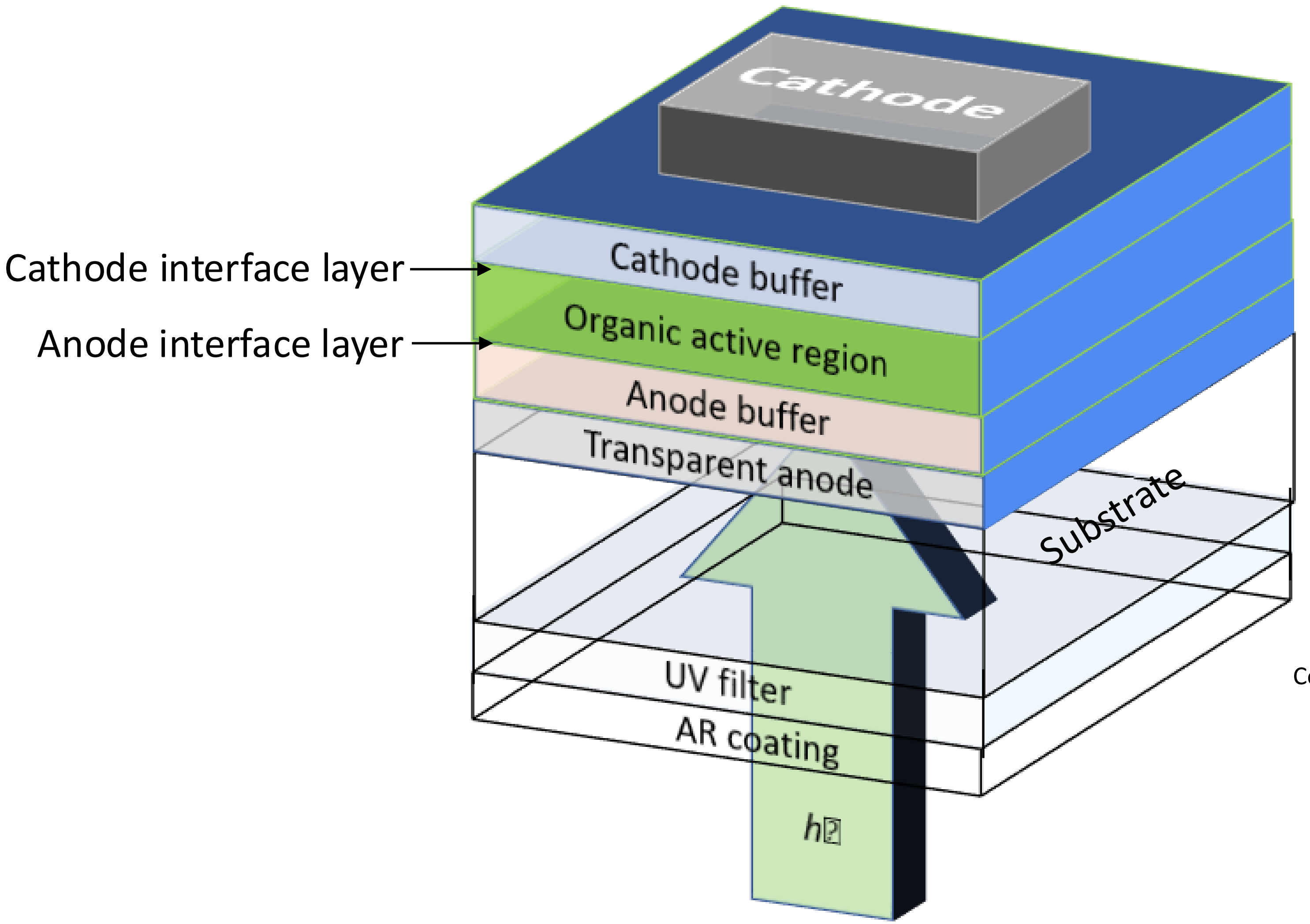
For most accurate calibration: $M \cong 1$



Organic Solar Cell Challenges

- High efficiency (>20%)
- Large Module Size
- High Reliability (>20 years)
- Low Production Cost (<$0.50/Watt)

Basic OPV Design



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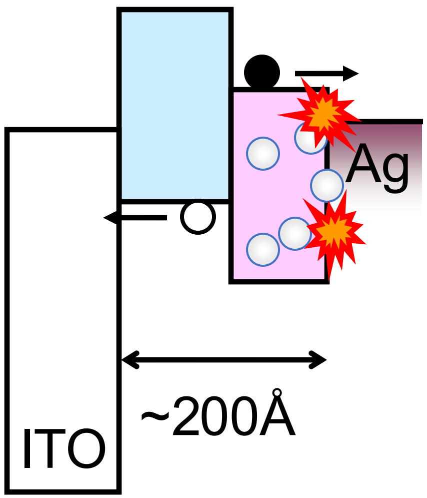
Getting to High Efficiency: The Double Heterojunction

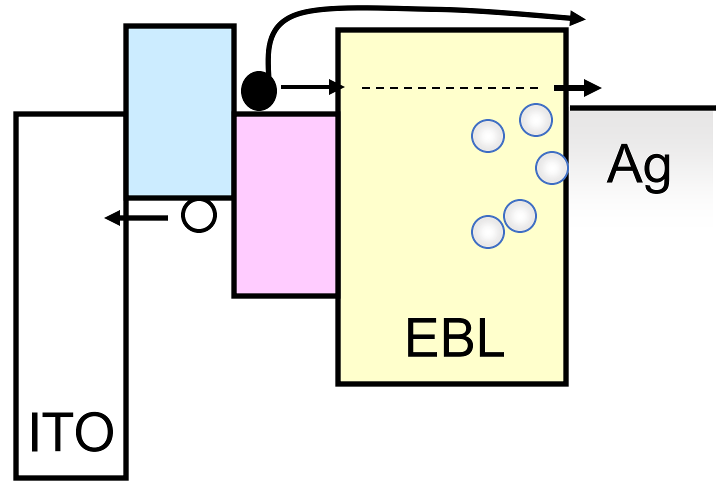
Problem



(Tang cell: 1%)

- cathode metal diffusion
- deposition damage
- exciton quenching
- vanishing optical field
- electrical shorts

Solution

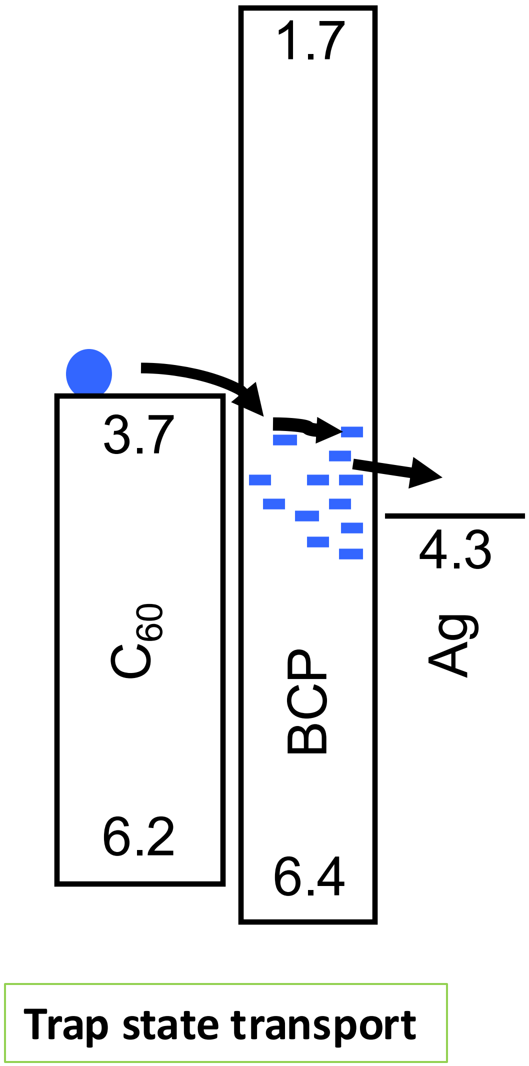


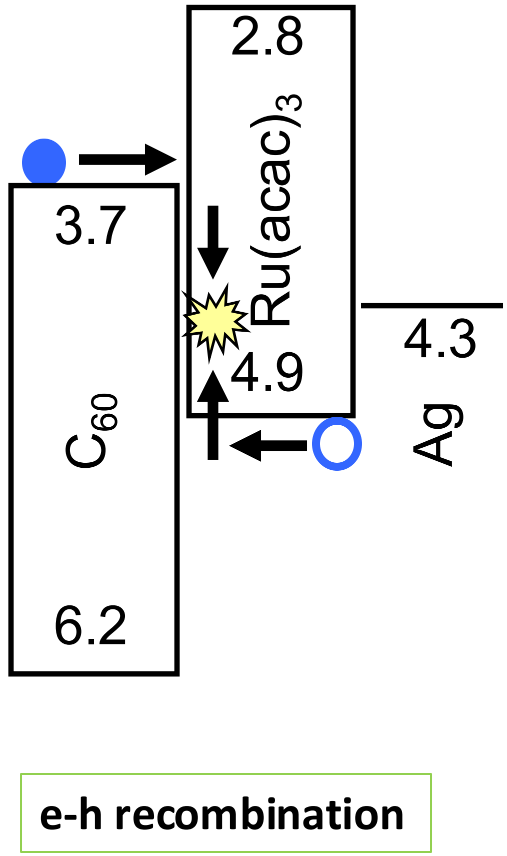
Introduce ‘Exciton Blocking Layer’ (EBL) to:

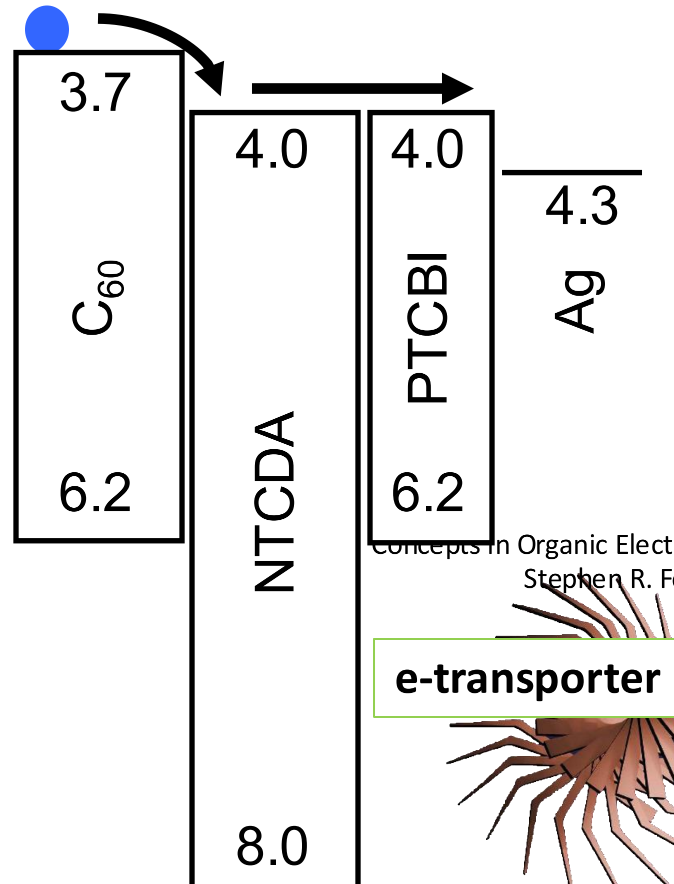
- confine excitons to active region
- separates active layer from metal
- act as a buffer to damage
- EBL thickness determined by depth of damage (if too thick, EBL is insulating)

Species of Exciton Blockers/Cathode Buffers

- Essential for high efficiency
- Transport charge
- Reduce quenching
- Provides optical spacer
- Reduces damage from cathode

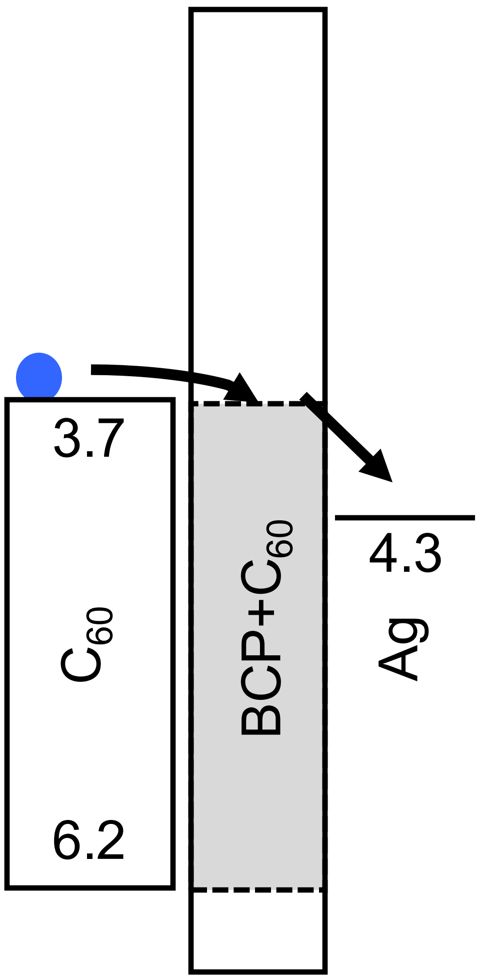


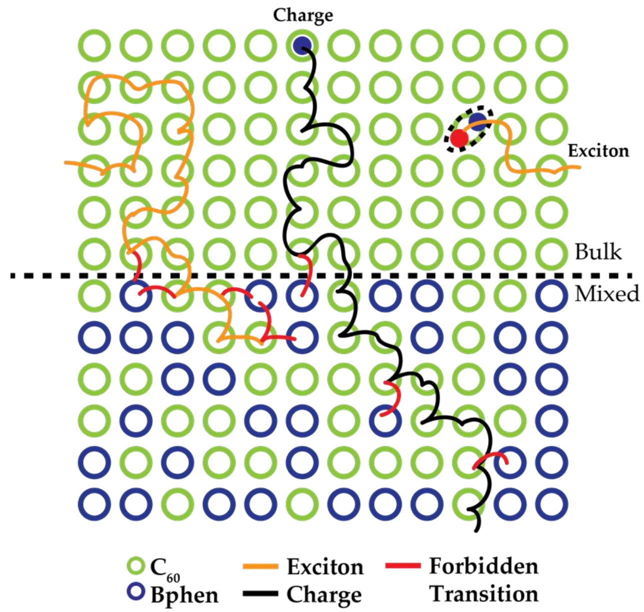




Lassiter et al., Appl. Phys. Lett, **98**, 243307 (2011)

Electron Filtering Buffer Layer





- Highly transparent
- Electron conductivity independent of C_{60} conc. to ~30%
- Compound buffer: C_{60}:Bphen/BPhen
- Active region: DBP:C_{70}

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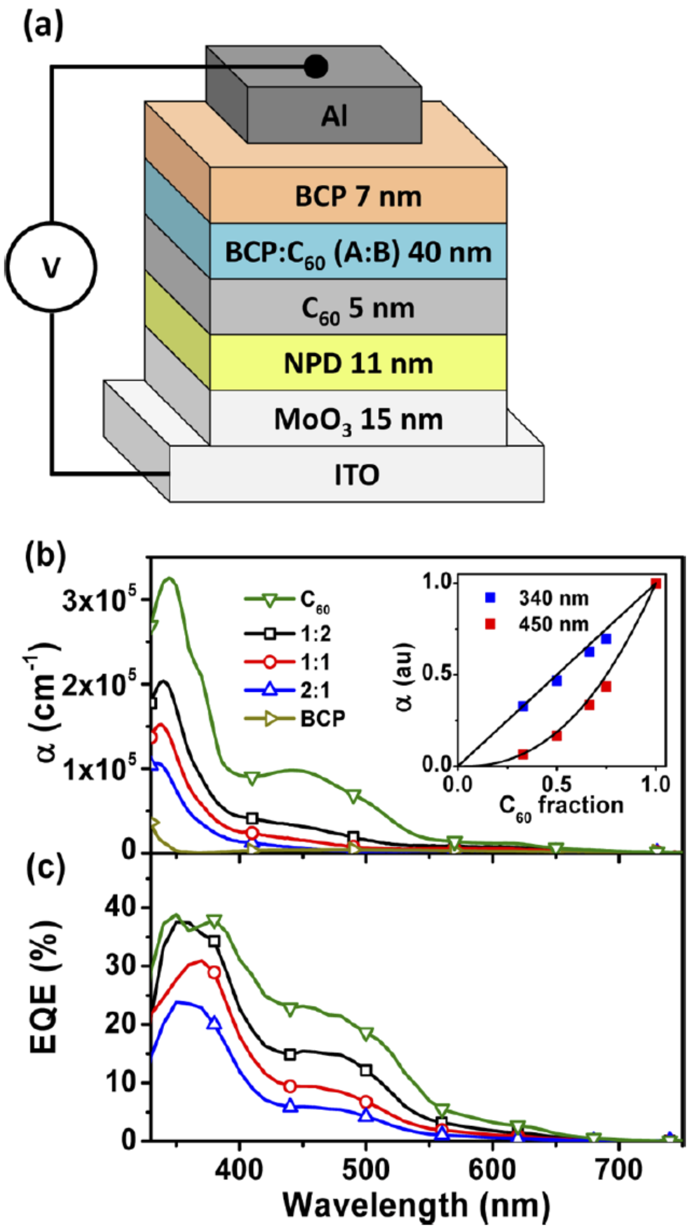
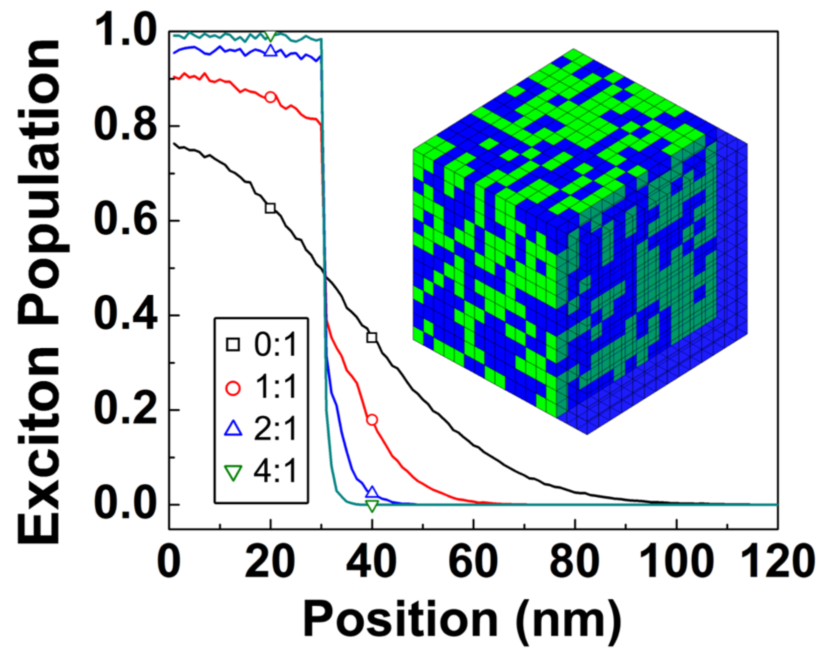
Bartynski, et al., **13**, 3315 Nano Lett (2013)

C_{60}:Bphen Electron Filtering Blockers

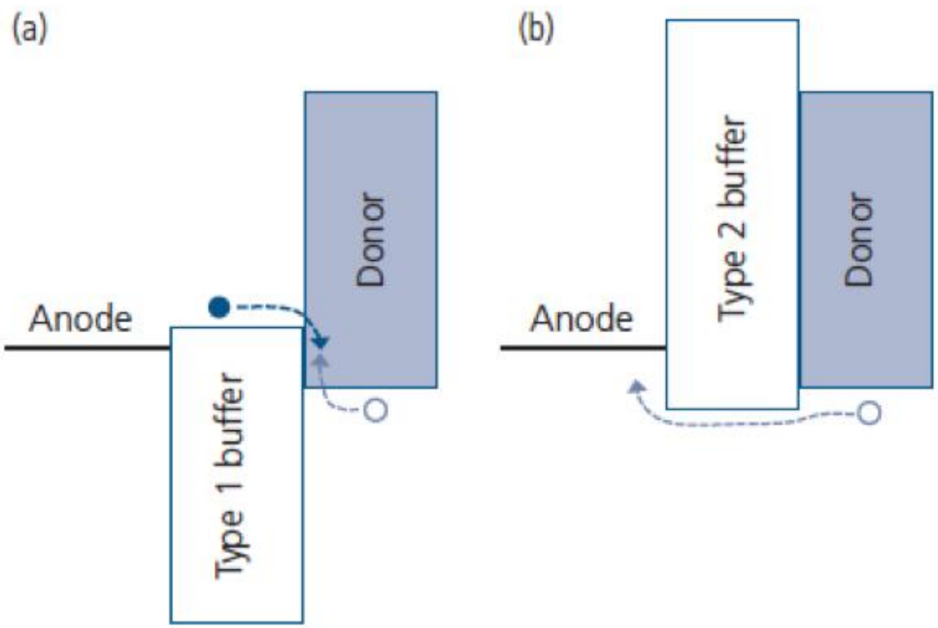




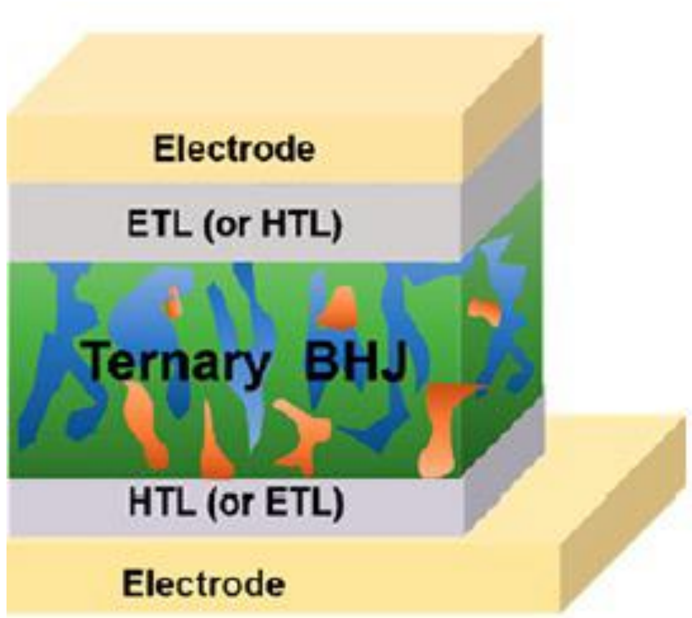
Doping (C_{60}:BCP)	Blocking Efficiency (%)
1:0	49.9 ± 0.8
1:1	81.0 ± 0.6
1:2	94.9 ± 0.6
1:4	98.4 ± 0.6

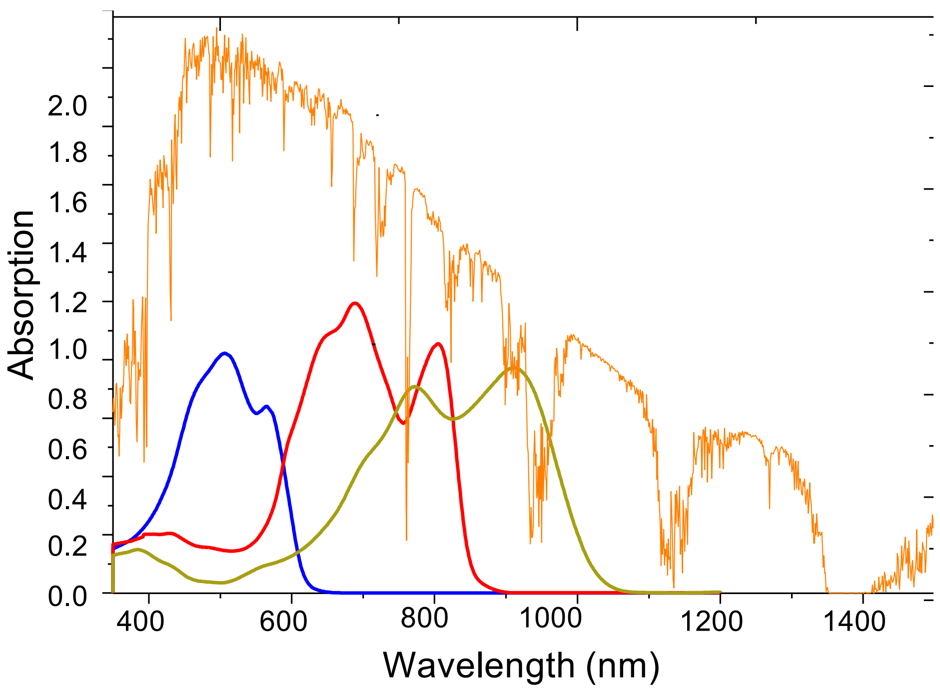
Bartynski, et al., **13**, 3315 Nano Lett (2013)

Anode buffer designs



Ternary Solar Cells Increase Spectral Coverage

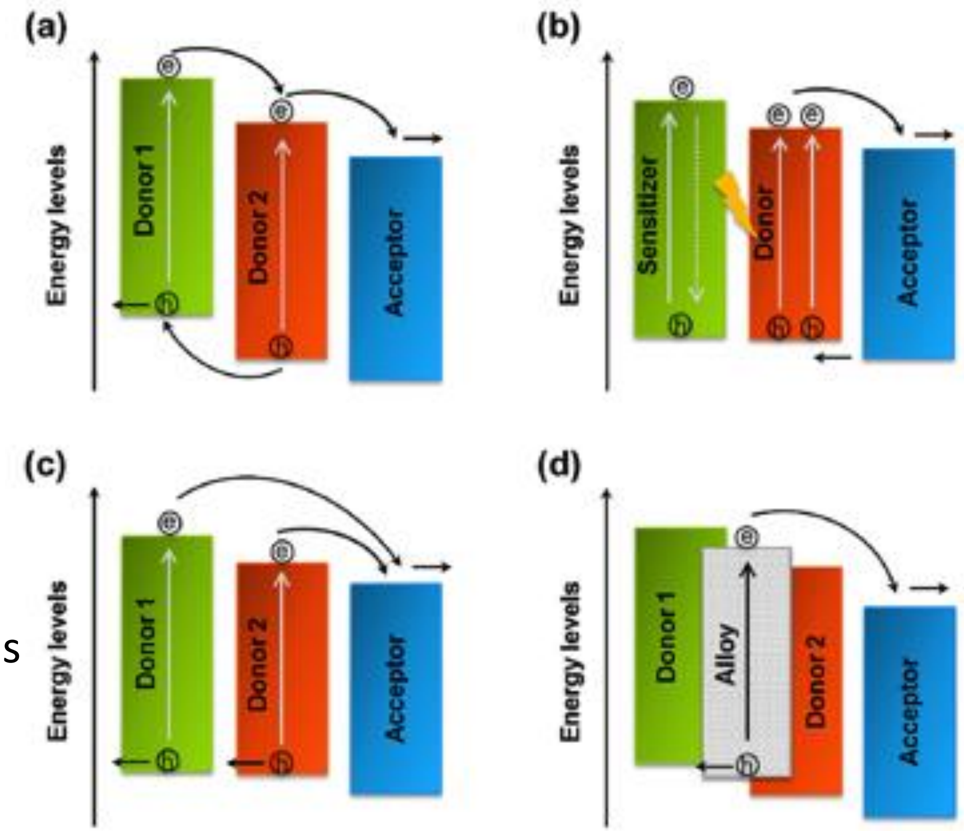




Ternary BHJs Increase Solar Coverage

Charge Xfer

Energy transfer



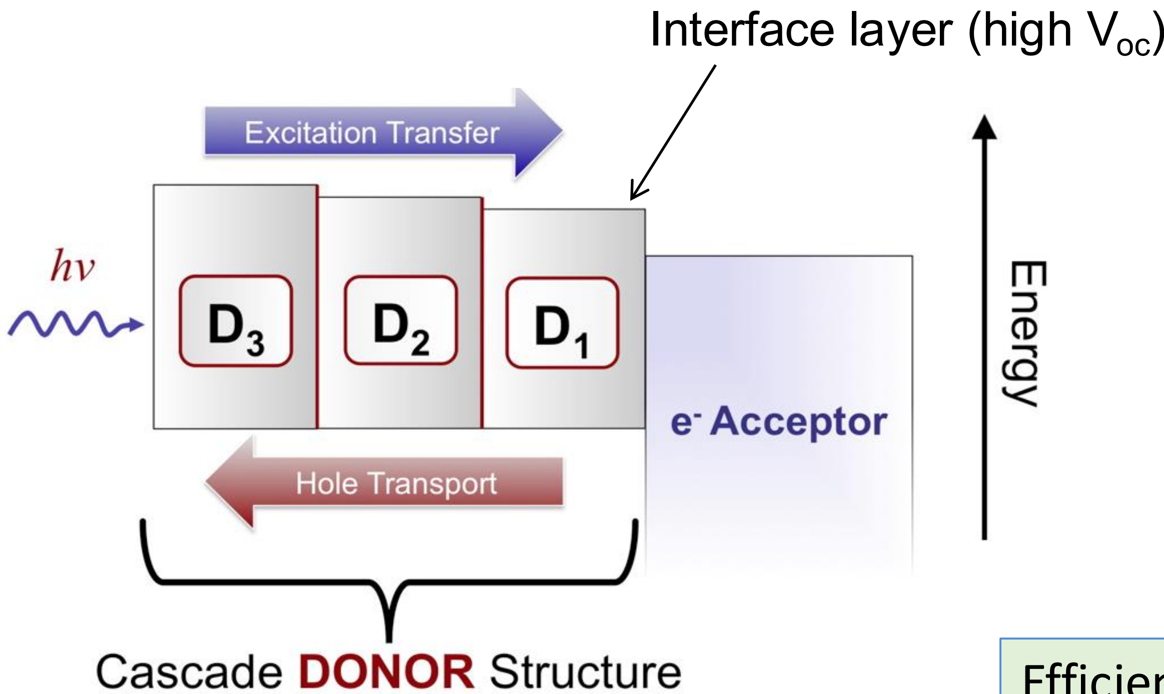
Parallel Junctions

"Alloy" formation

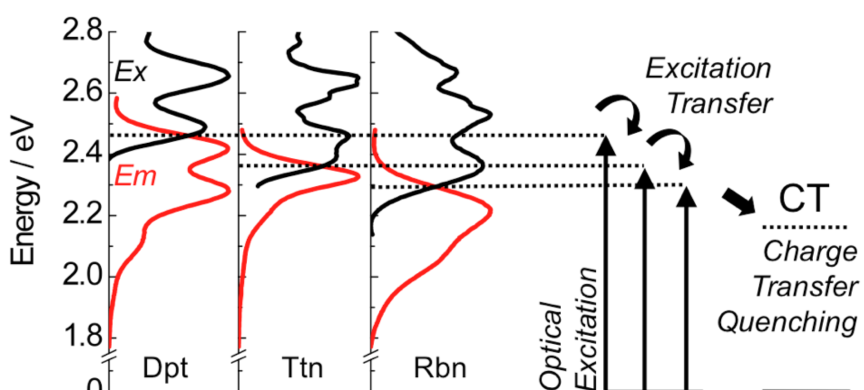
Features of ternary blends:

- V_{OC} of the ternary lies between the extremes of the two subcell junctions
- Materials chosen to cover solar spectrum
- Can be DA_1A_2 or AD_1D_2 junctions
- Morphology is key
- Probably more than one process governs performance
- Molecular alloy formation unlikely

Increasing solar coverage: Exciton Cascades



Efficiency: 7.1%



Schlenker, et al., *Chem. Mater.*, **23**, 4132 (2011).
O. L. Griffith & S. R. Forrest, *Nano Letters*, **14**, 2353 (2014).

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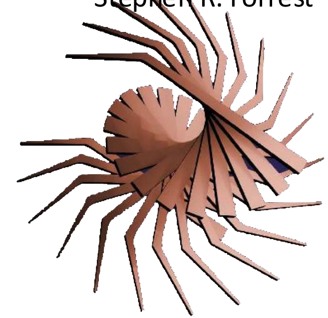
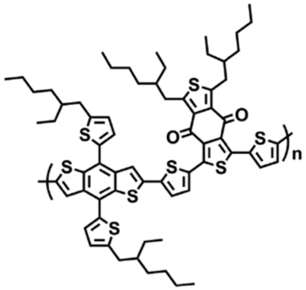
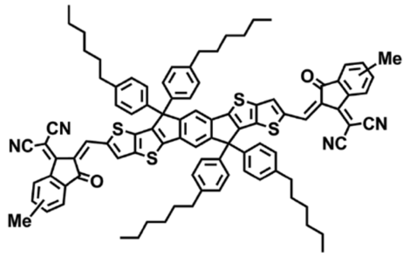


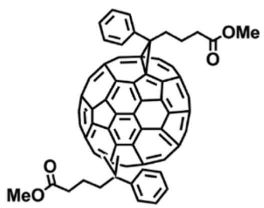
Example DA_1A_2 ternary BHJ



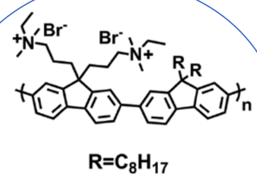
PBDB-T



IT-M



BisPC$_{71}$BM

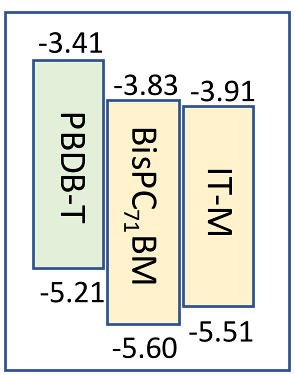


PFN-Br

Exciton blocker

D:A_1:A_2 ratio	V_{OC} (V)	j_{SC}[a] (mA/cm^2)	*FF*	η_P (max) (%)	η_P (ave)[b] (%)
1:1:0	0.937	16.7	0.69	10.80	10.45
1:1:0.2	0.952	17.4	0.74	12.20	11.75
1:0:1	1.02	10.6	0.58	6.25	5.86

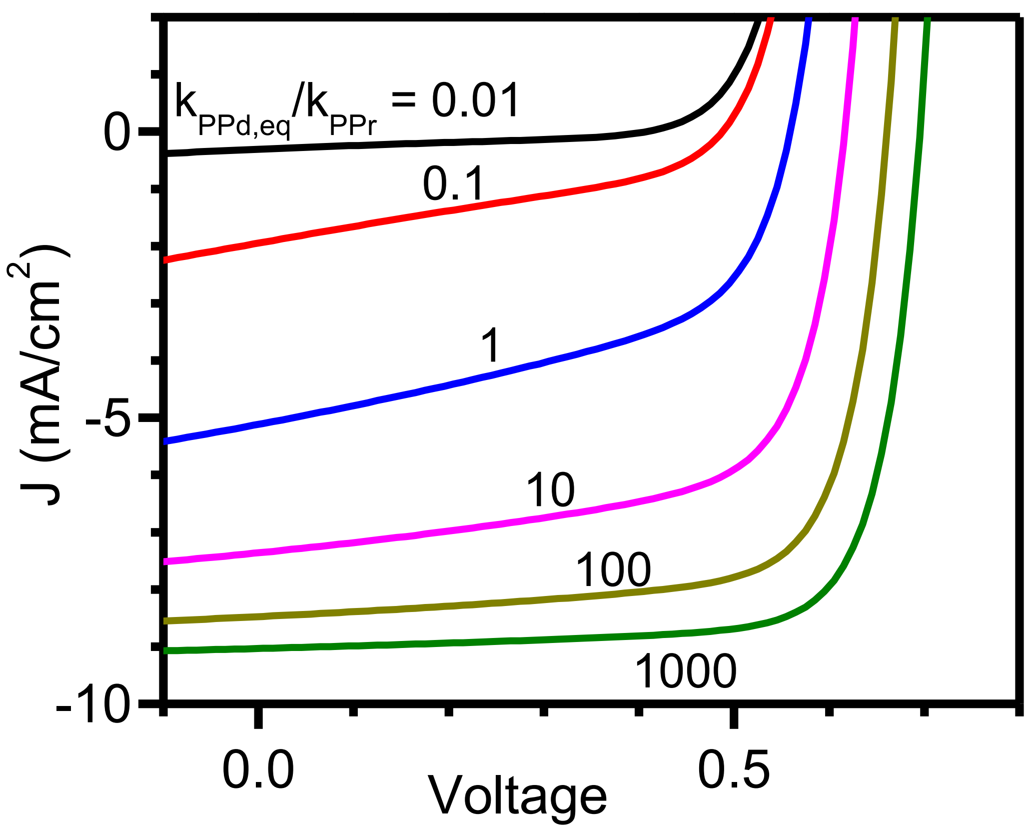
- Cell area = 4 mm^2.
- Sample size = 100 diodes



W. Zhao, et al., *Advanced Materials,* **29**, 2, (2017).

The central importance of morphology

From ideal diode theory



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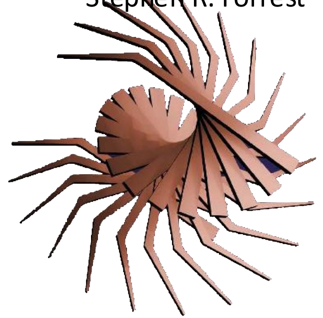


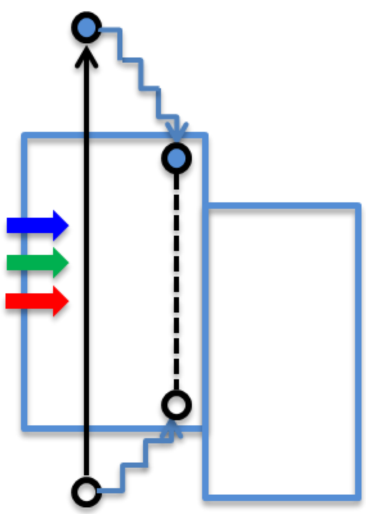
- PP recombination ⇒ Reverse Slope
- Best morphologies limit k_{PPr} at interface:
  - **Steric hindrance**
  - **Disorder at interfaces/order in the bulk**

Multijunction OPV cells: The Most Effective Way to Increase Efficiency

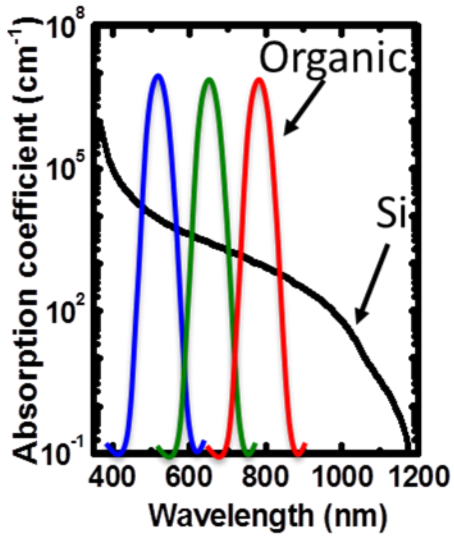
Can significantly exceed the thermodynamic limit of single junction cells

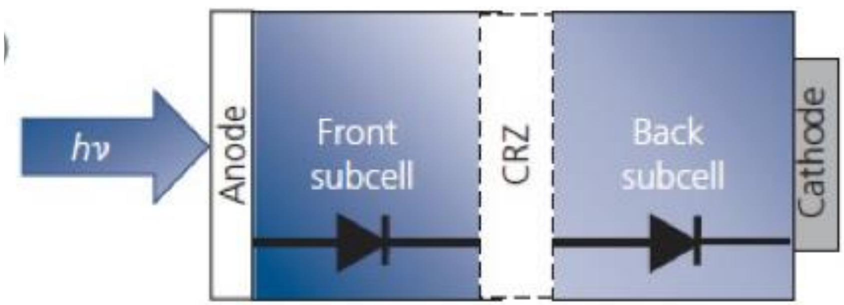
Major issues of single junction OPV:

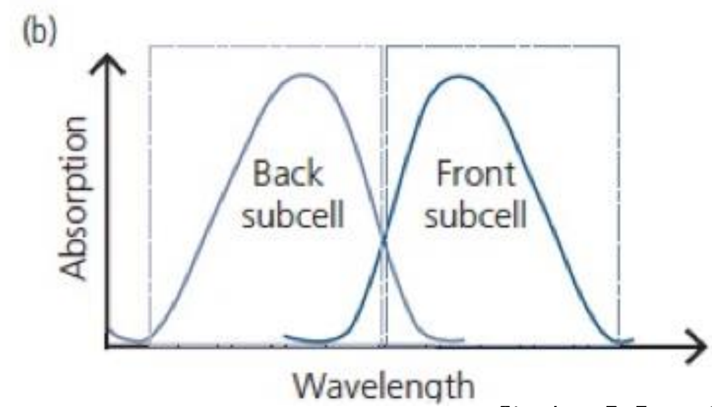
Thermalization loss



Narrow absorption range







Advantages of multijunction cells:

- Decrease thermalization losses
- Cover a broad spectral range

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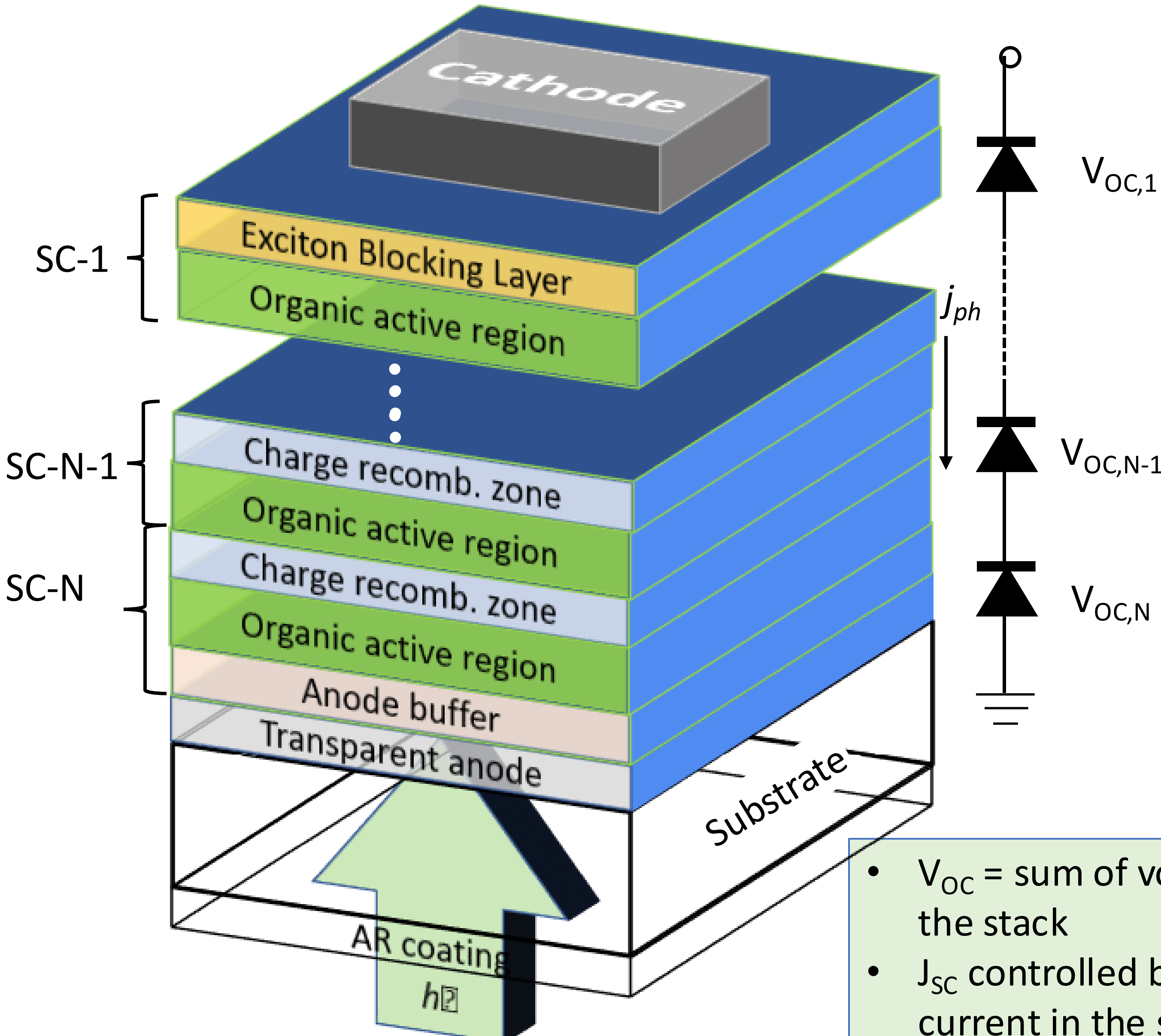
Tandem Cell Designs: Series Stacking



$$V_{OC} = \sum_{i=1}^{N} V_{OC,i}$$

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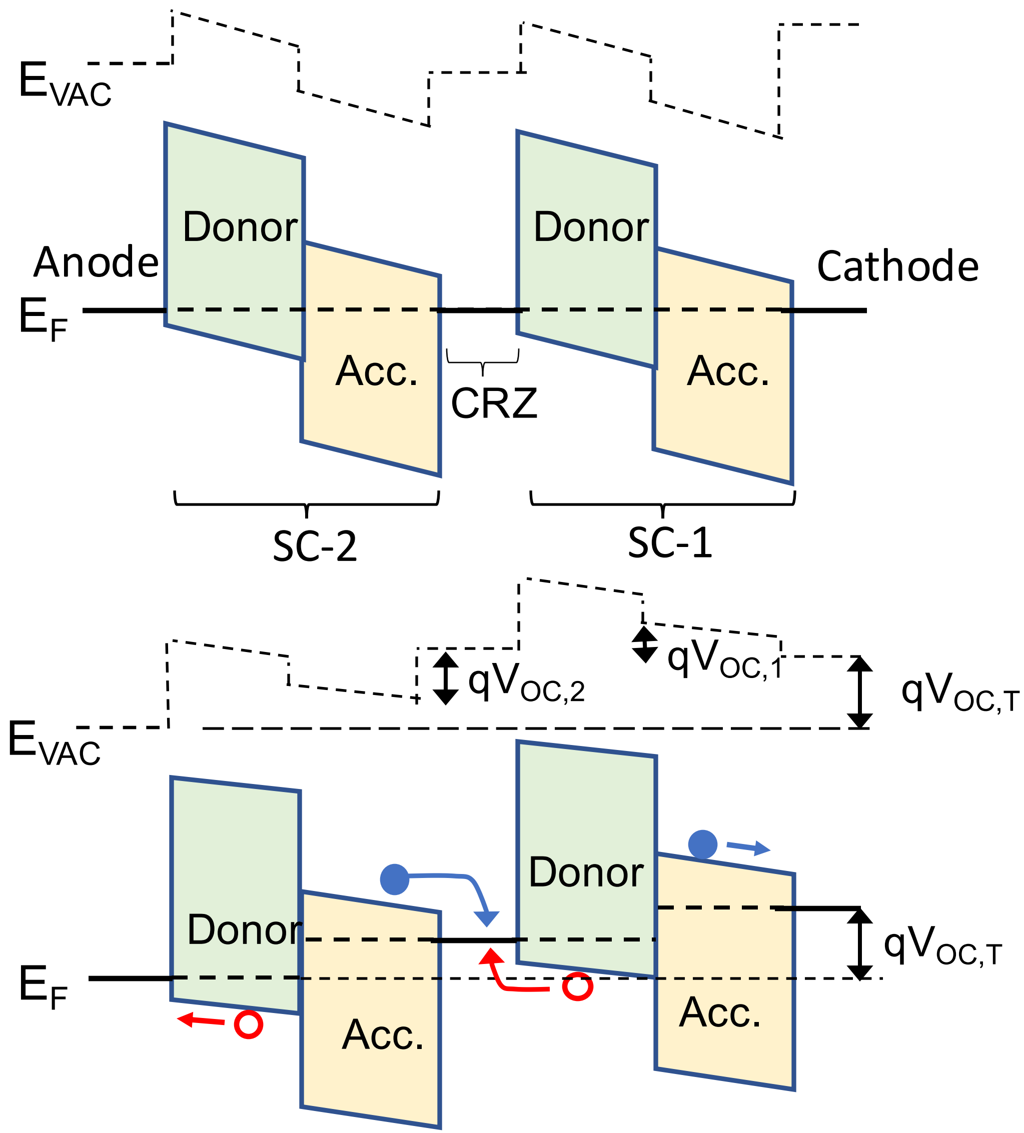
- V_{OC} = sum of voltages of the subcells in the stack
- J_{SC} controlled by the lowest subcell current in the stack

Tandem Cell Energetics



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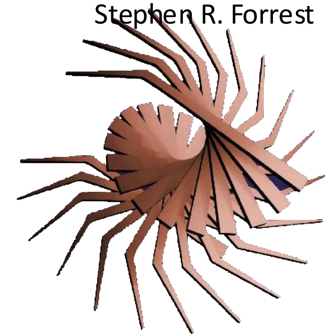
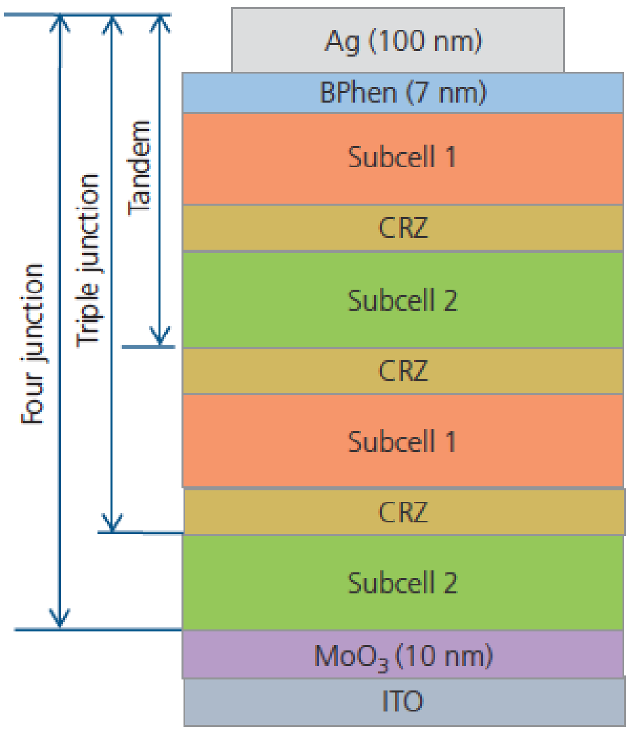
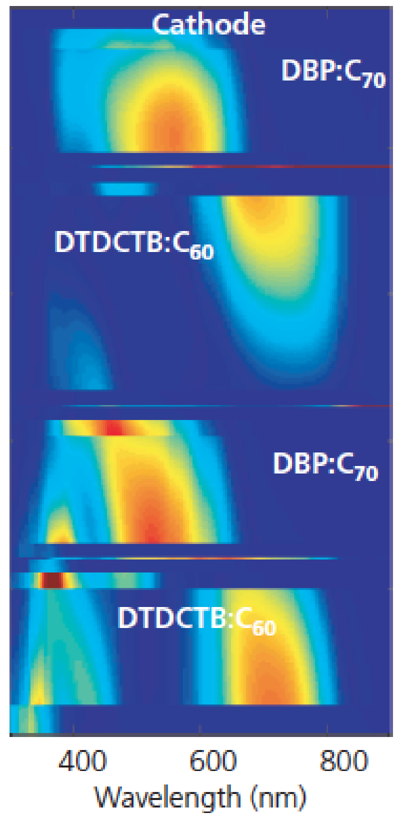


Elements of Multijunction OPVs

Example 4 junction OPV

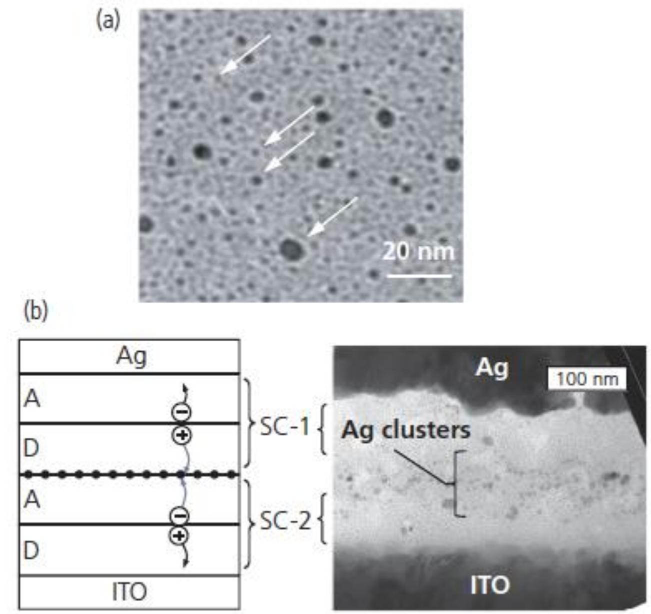


Transfer matrix calculation of the optical field distribution in the cell

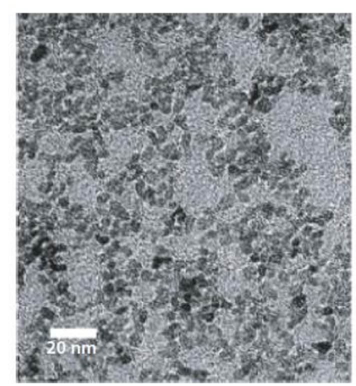


Che, X. 2018. PhD Thesis, University of Michigan

Charge generation layers



VTE deposited Ag NP layer

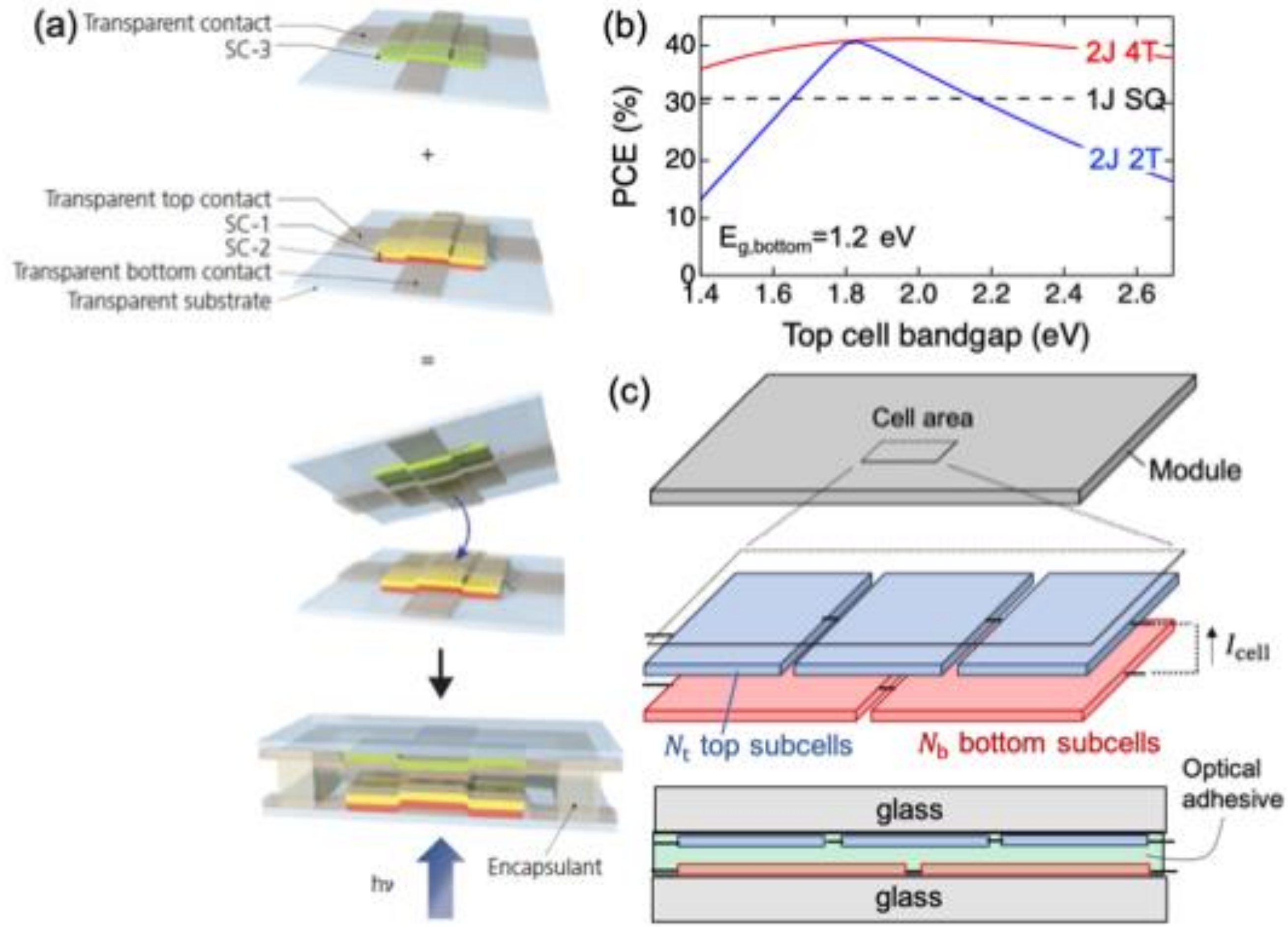


Solution deposited ZnO NPs

B.P. Rand, et al. 2004. *J.Applied Physics,* 96**,** 7519.

W. J, Beek, et al. 2005. J. *Physical Chemistry B,* 109**,** 9505

Mechanical combinations of cells

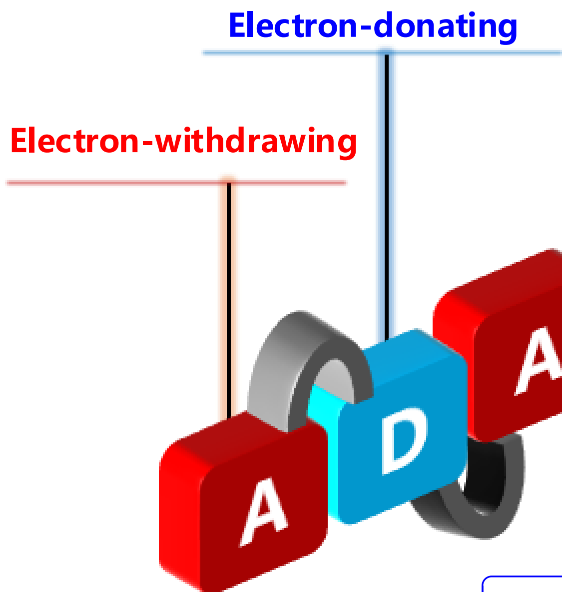


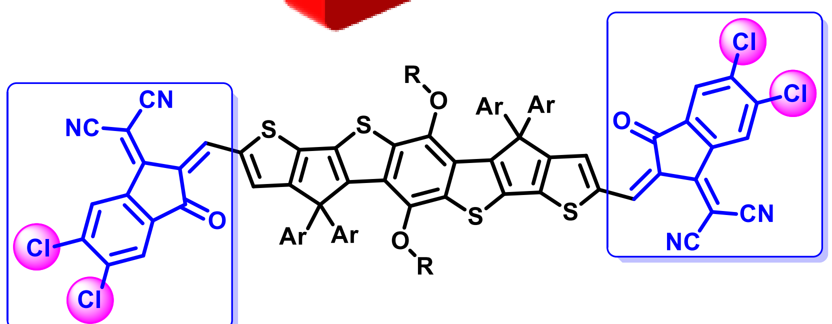
4T tandem cell via mechanical stacking

(b) Thermodynamically-limited efficiency for 2T and 4T two-junction (2J) tandem cells top cell energy gap with a 1.2 eV bottom cell (c) Mechanically stacking top and bottom submodules with different cell areas to achieve the same current.

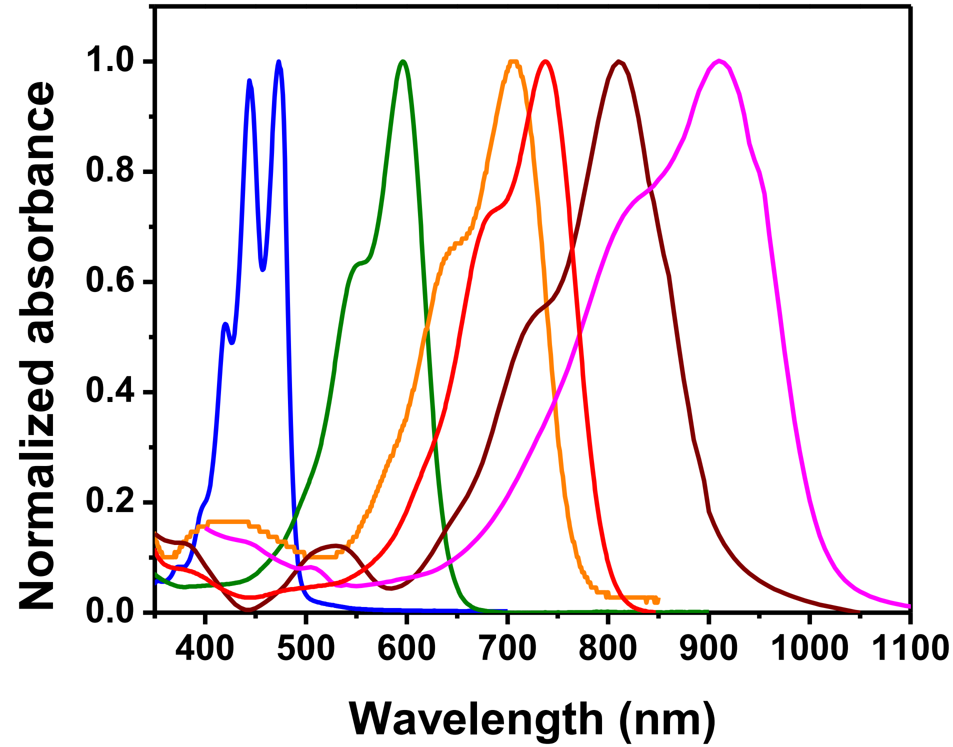
Non-Fullerene Acceptor Molecular Design

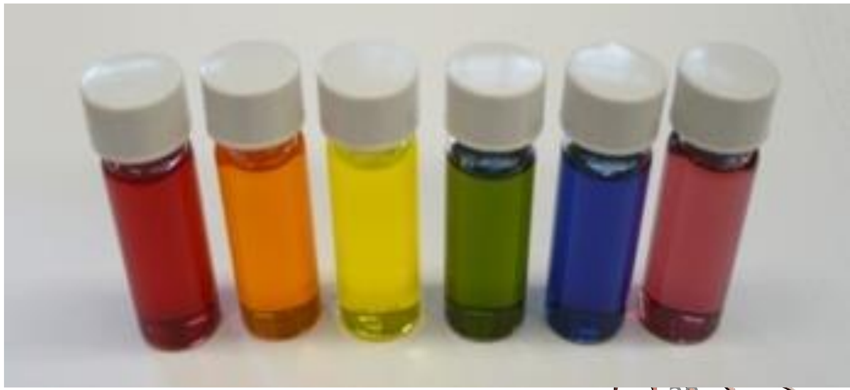
Narrow linewidths enable semitransparent OPVs





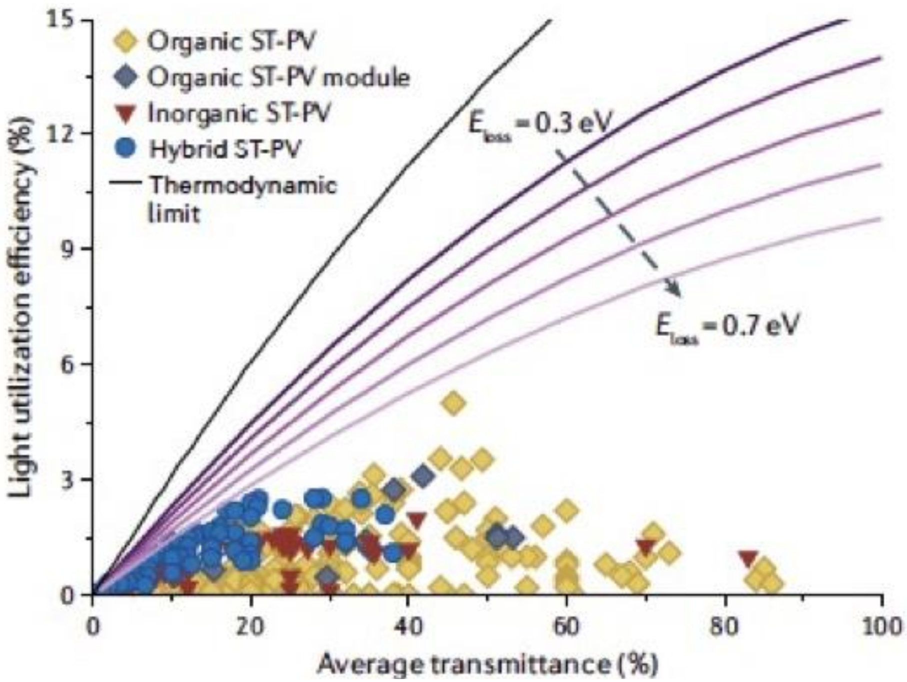
BT-CIC





Absorption tunability presents opportunities unique to OPVs

Wavelength-selective Absorption Can Lead to Semitransparent OPVs



Y. Li, Y., et al. 2023. *Nature Reviews Materials*, 8, 186.

Power generating windows (transparent in the visible, absorbing in the NIR) are a major opportunity unique to OPVs

Transparent OPV Figure of Merit

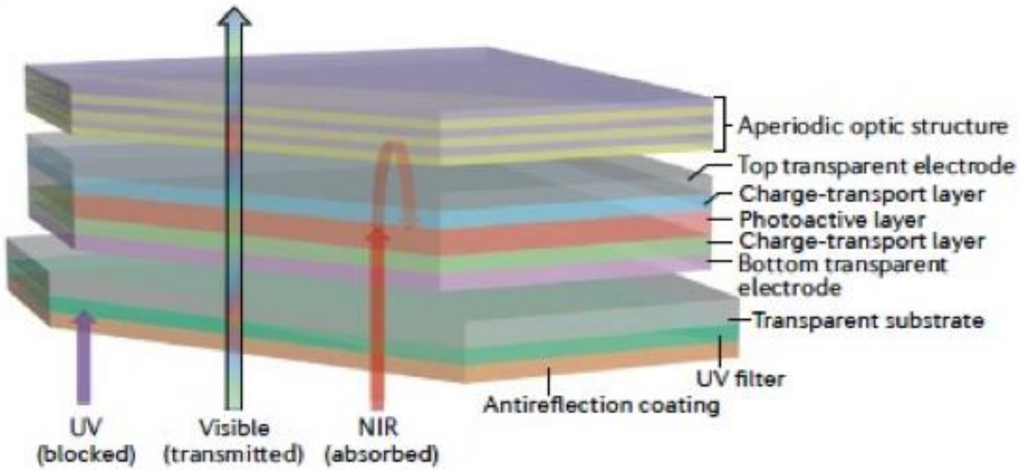
$$LUE = PCE \times APT$$

LUE: light utilization efficiency
PCE: power conversion efficiency
APT: average photopic transmission

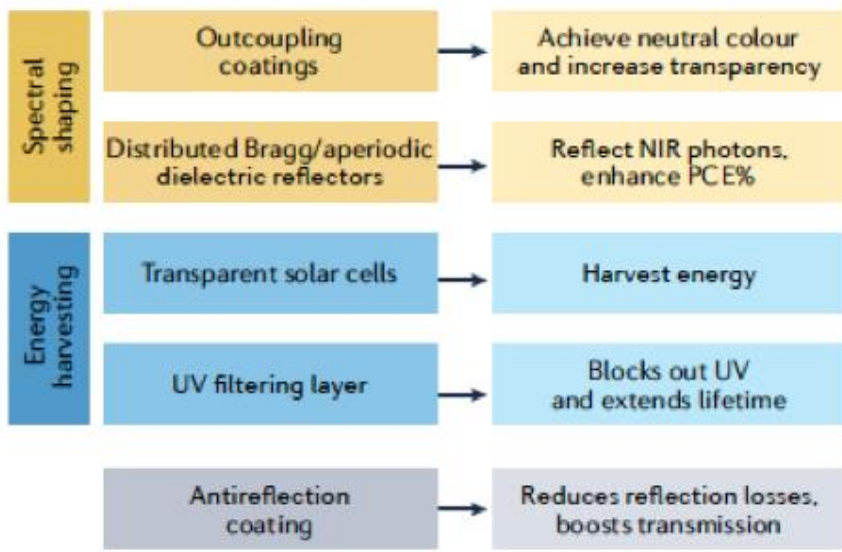
$$\boldsymbol{APT} = \frac{\int T(\lambda)P(\lambda)S(\lambda)d(\lambda)}{\int P(\lambda)S(\lambda)\,d(\lambda)}$$

λ: wavelength; T: transmission
P: photopic response; S: solar photon flux (AM1.5G)

Systematic design of ST-OPVs

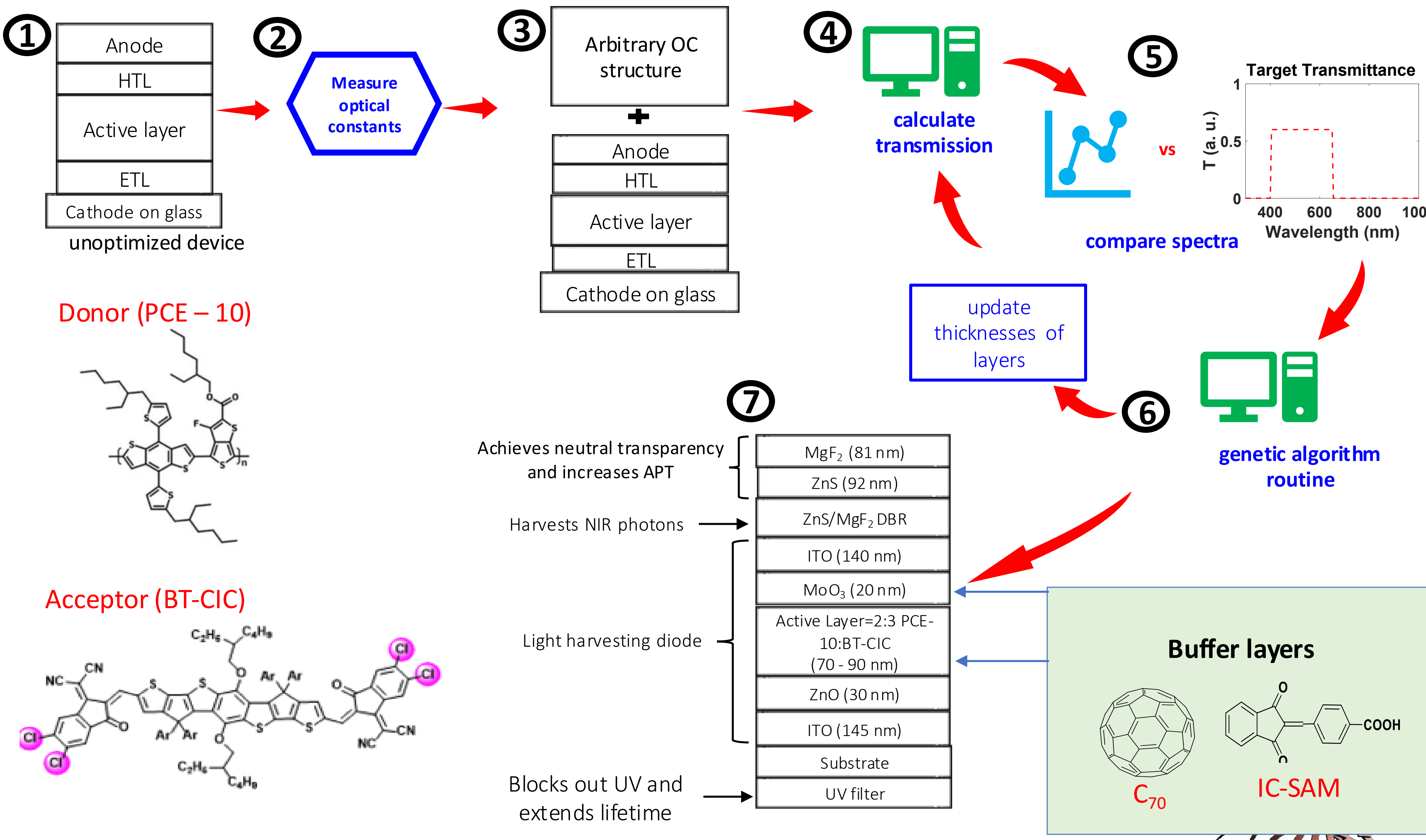


(b)



Y. Li, et al. 2023. *Nature Reviews Materials,* 8**,** 186.

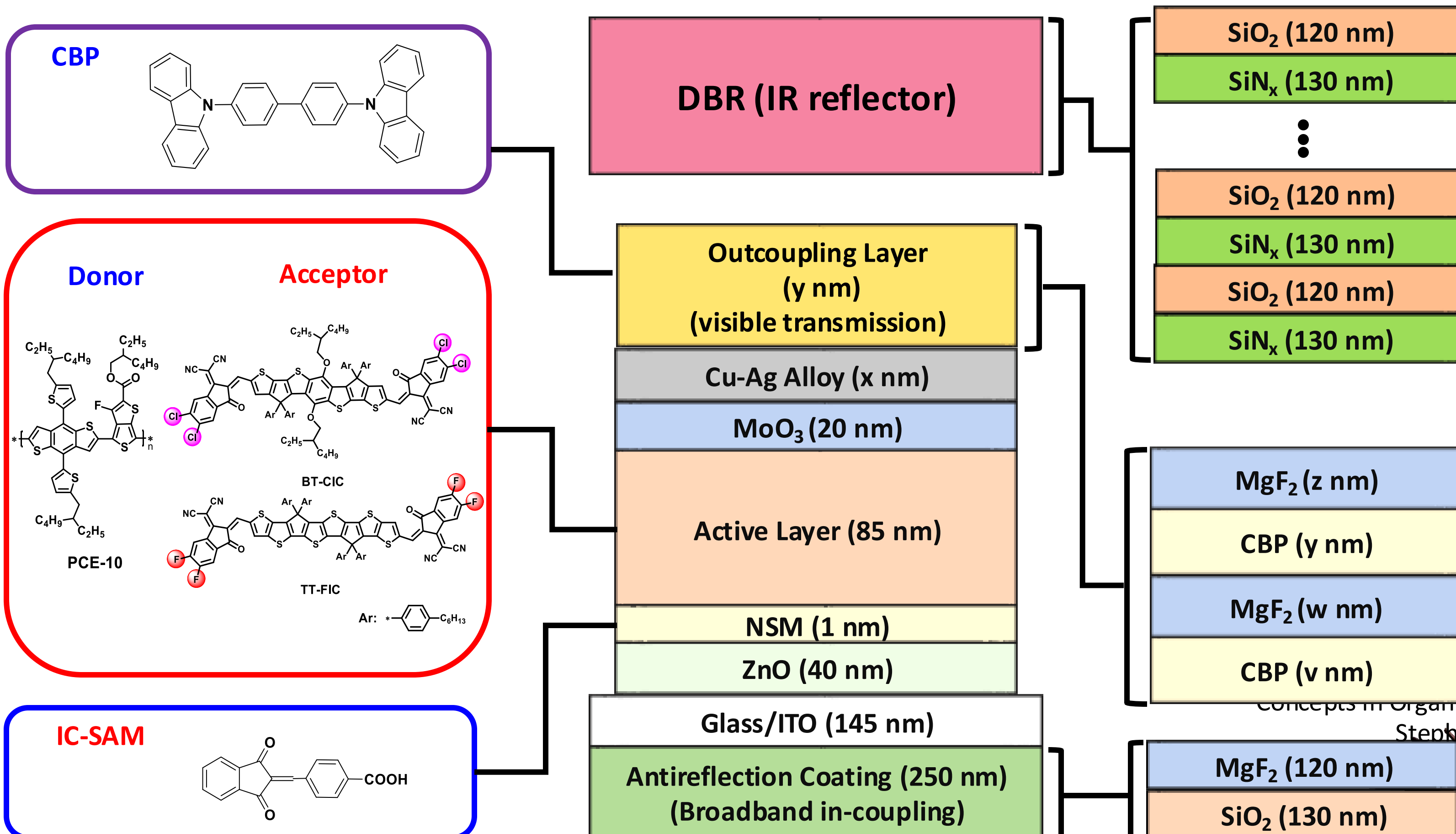
Designing Outcoupling Layers



Sheriff, Jr., H. K. M., et al, *Appl. Phys. Lett.* **118**, (2021).

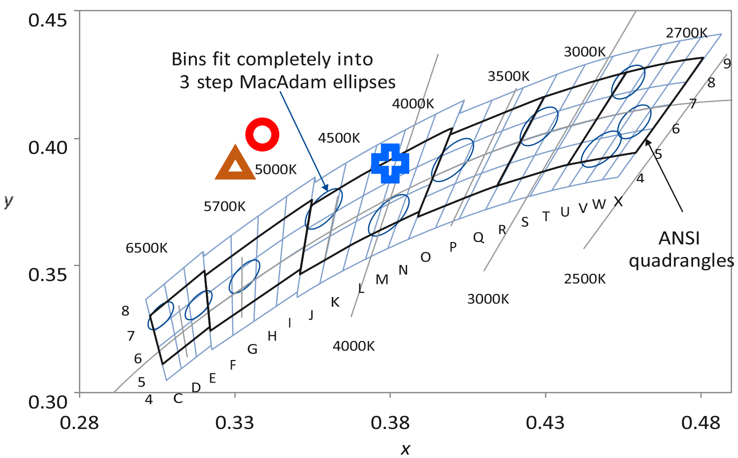
Semi-Transparent Device Materials & Structures

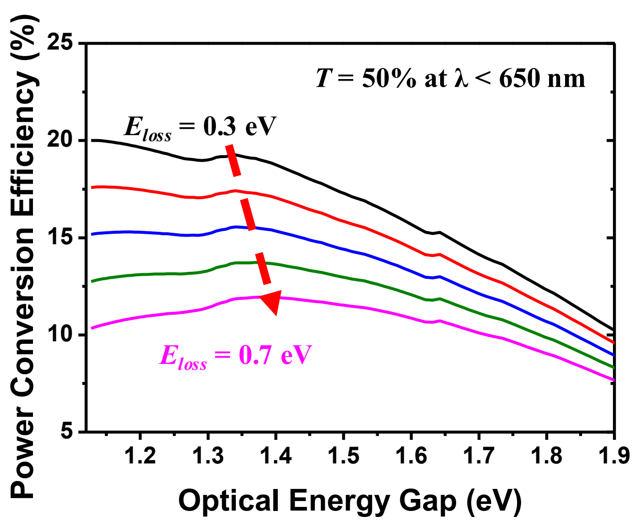
Example of Photon Management

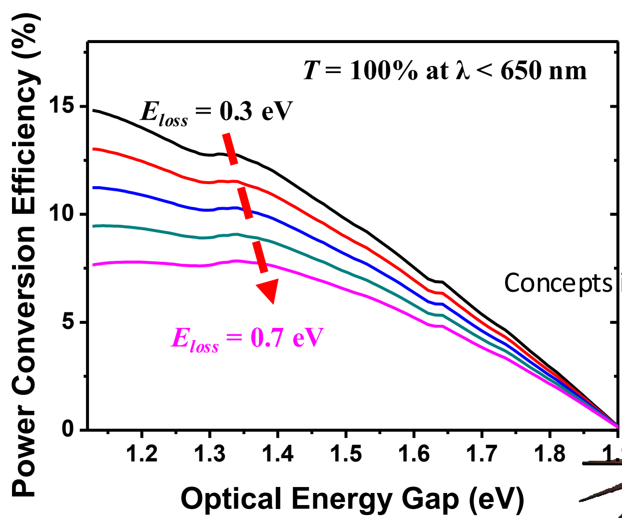


Li, et al. Adv. Mater., **31**, 1903173 (2019)

Color Neutrality Achieved w. ITO Top Contact





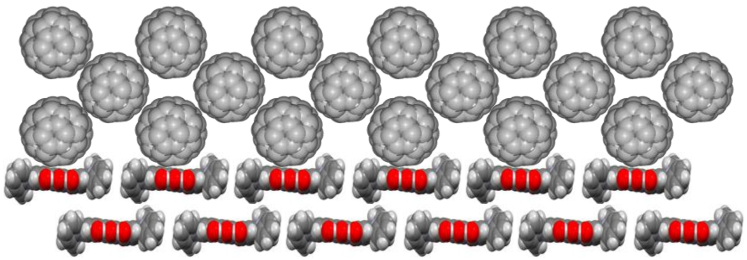


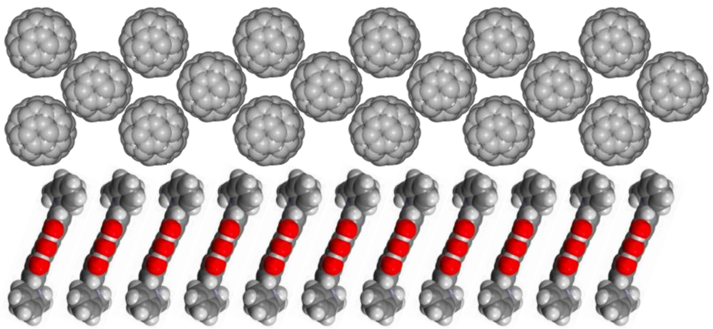
Y. Li, et al. *Proc Nat Acad Sci*, **117** 21147 (2020)

Morphology vs. V_{OC}

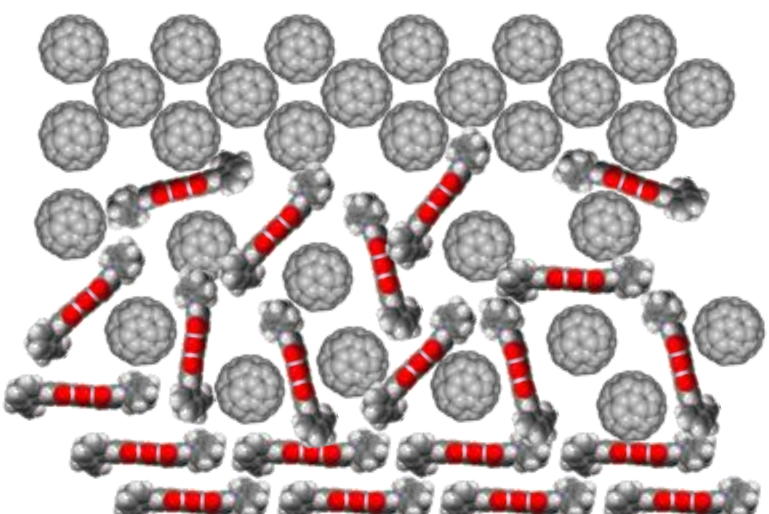
$$qV_{OC} = \Delta E_{HL} - nk_B T \ln\left[\frac{k_{PPr}}{k_{PPd}} \frac{k_{rec} N_L N_H}{J_X / \alpha_0}\right]$$

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



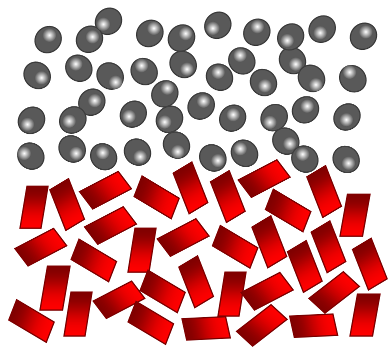
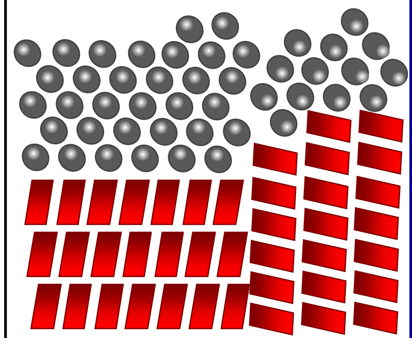
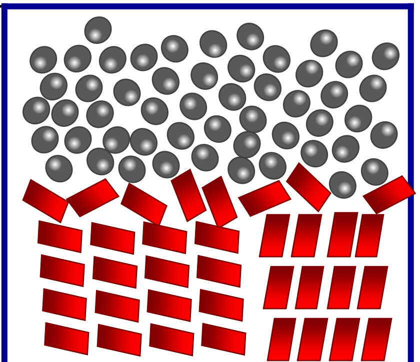


- Worst case scenario: perfectly ordered crystalline interface and bulk, Face-on .
  - High k_{PPr} and k_{rec}

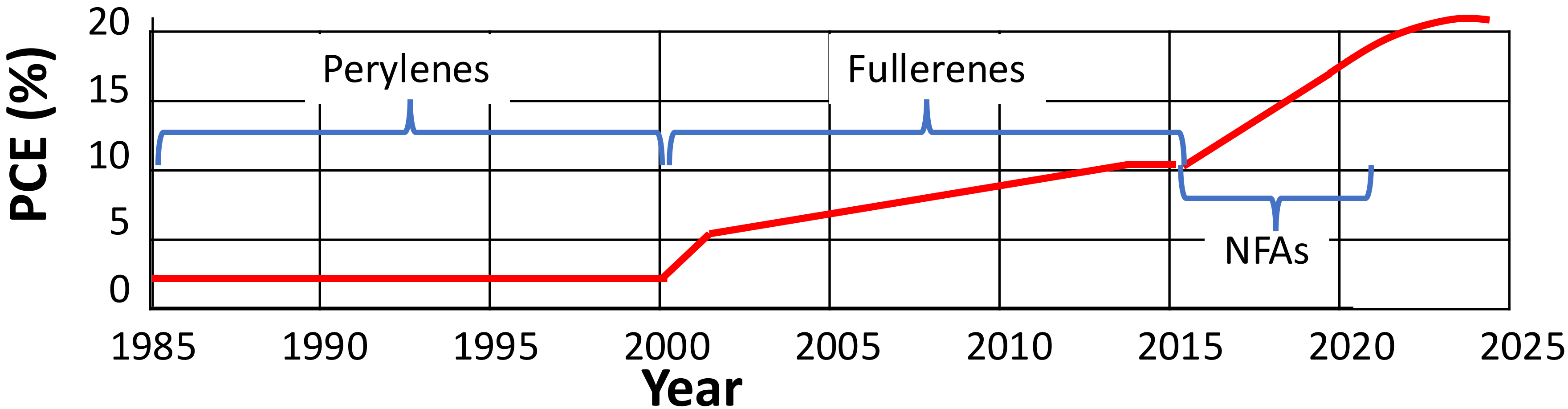


- Better Scenario I: Perfectly crystalline and end-on orientation
- Even Better Scenario II: crystalline bulk, intermixed interface
  - Poor coupling between like-molecules (C_{60}-C_{60} and SQ-SQ) reduces PP formation (k_{rec}) probability.
  - Overcomes enhanced k_{PPr} due to facial contact

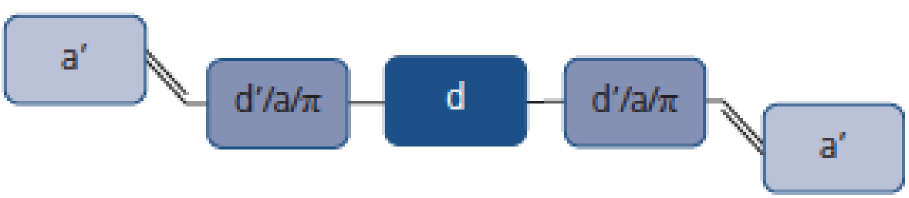
Achieving the Ideal Morphology

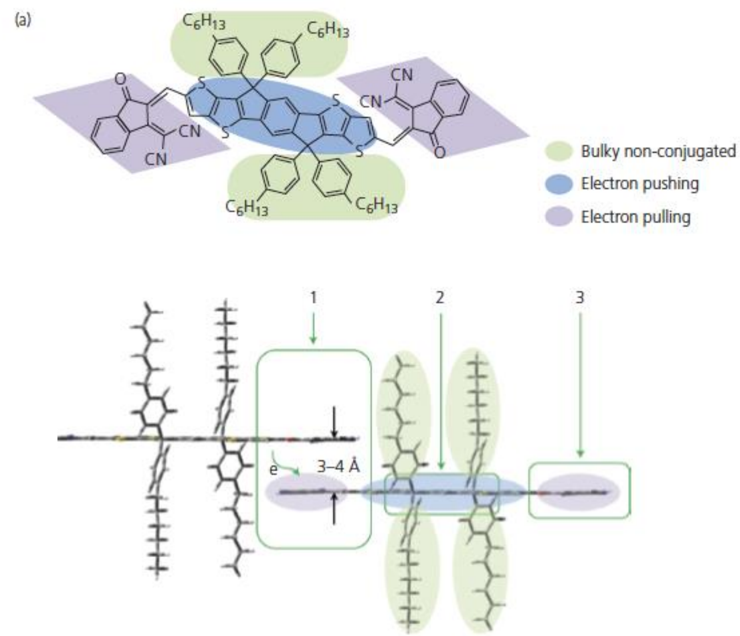
C_{60} **DPSQ**			
	As Cast	**Pre C_{60}**	**Post C_{60}**
Bulk DPSQ	Amorphous	Ordered	Mod. Order
Bulk C_{60}	Weak order	Ordered	Weak Order
Interface	Disordered	Ordered	Disordered
Surface	Smooth	Rough	Smooth
k_{PPr}	Low	High	Low
V_{OC}	High	Low	High
J_{SC}	Low	Moderate	High

Efficiency of OPVs paced by progress of NFAs



Molecular design motif

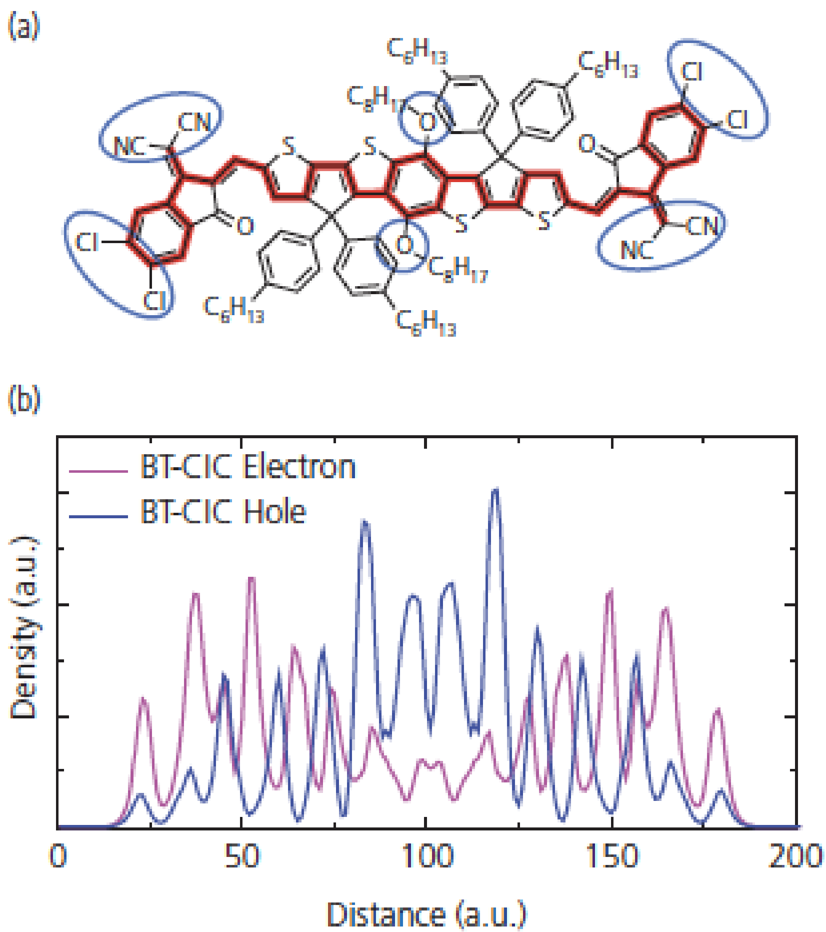


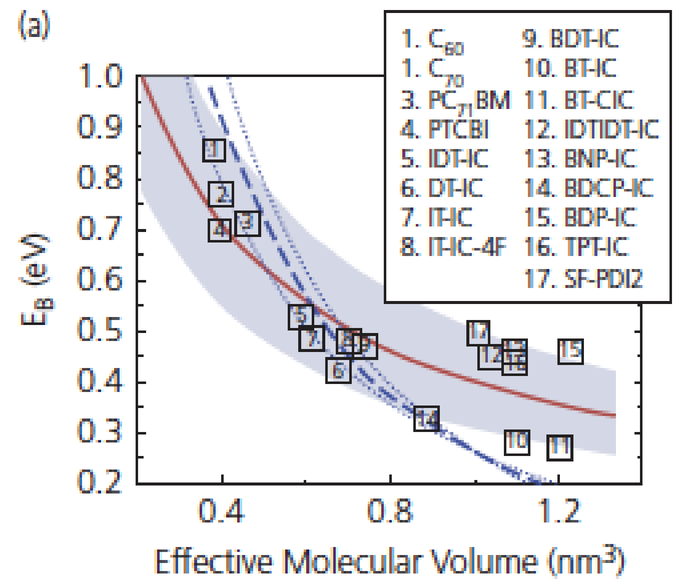


J. Hou, et al., Nature Mater. **17** 119 (2018)

: Electronics
n R. Forrest

NFA's reduce the exciton binding energy via wavefunction delocalization





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X. Liu, et al., Phys. Rev. Applied **11** 024060 (2019)