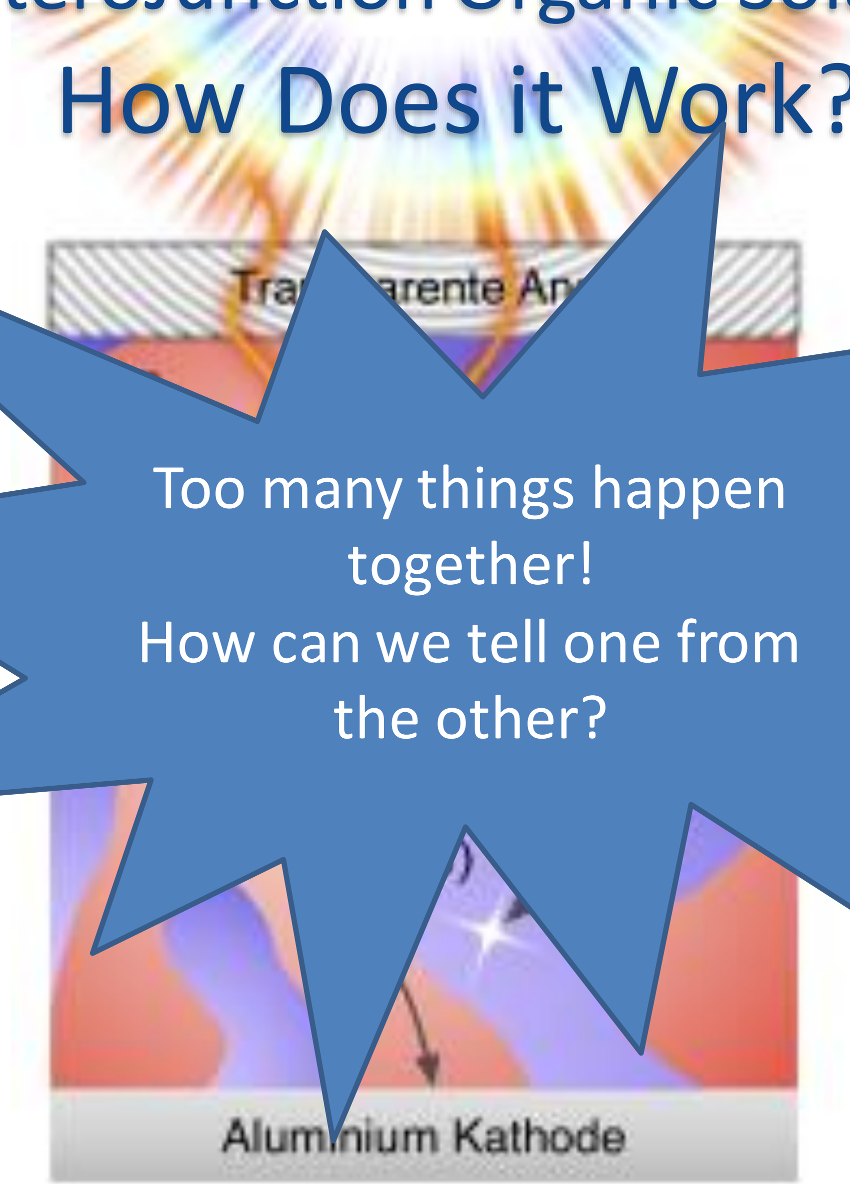
Organic Materials and Devices Lab

Voltage and Intensity Mapping of the Quantum Efficiency of Polymer:Fullerene Solar Cells

L. Tzabari, J. Wang , Y. Lee, J. Hsu and N. Tessler

Technion - Israel Institute of Technology

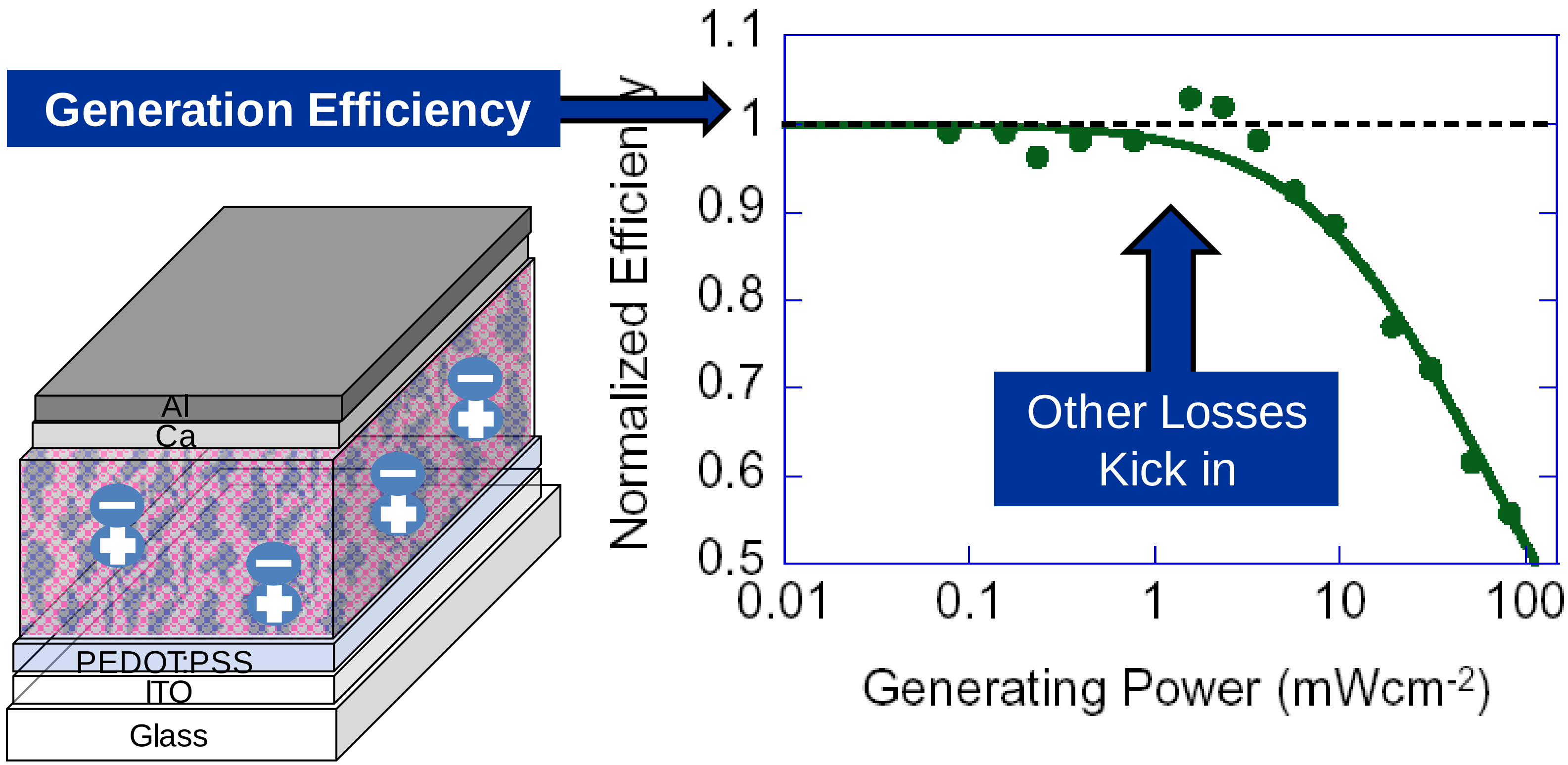
BulkHeteroJunction Organic Solar Cells – How Does it Work?



Too many things happen together!
How can we tell one from the other?

Image is taken from Carsten Deibel's blog

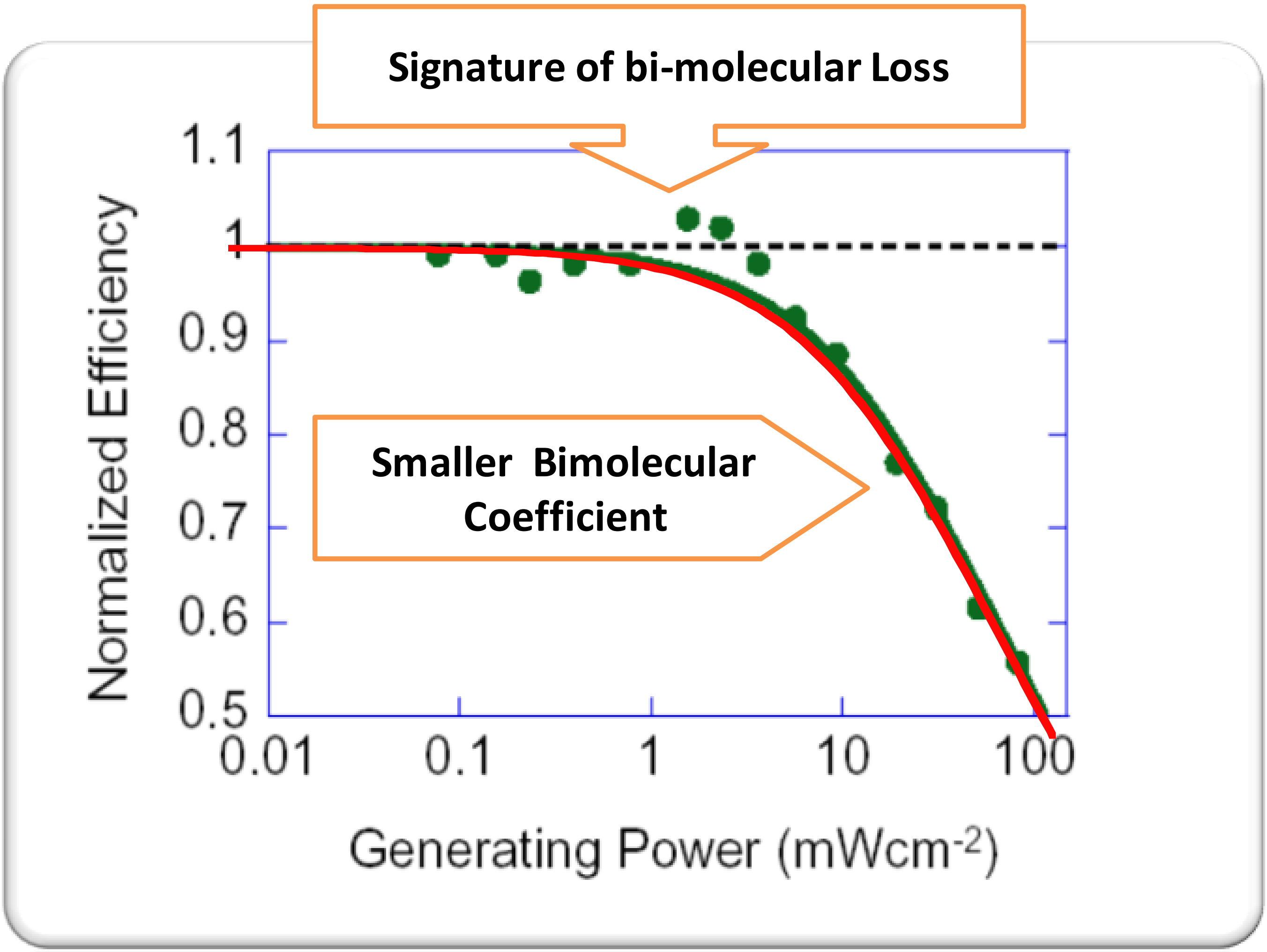
Normalized Quantum Efficiency (QE)



N. Tessler and N. Rappaport, Journal of Applied Physics, vol. 96, pp. 1083-1087, 2004.

N. Rappaport, et. al., Journal of Applied Physics, vol. 98, p. 033714, 2005.

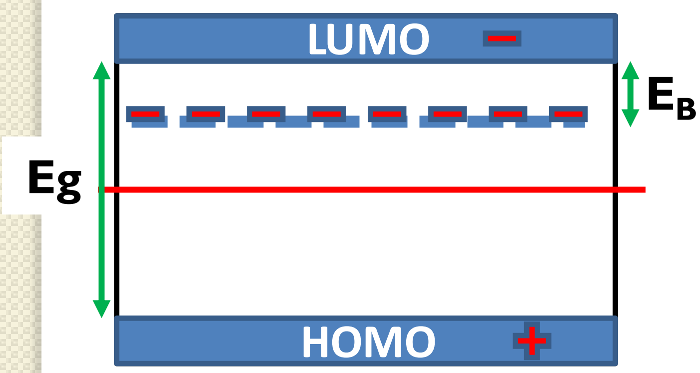
Bimolecular Recombination
- QE as a Function of Light Intensity

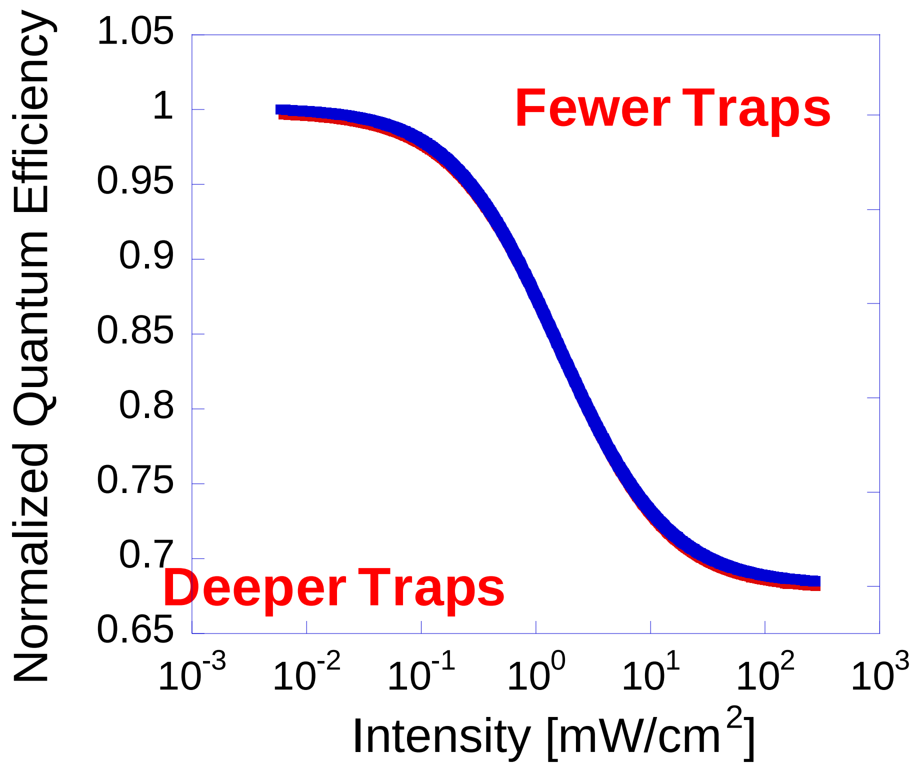


N. Tessler and N. Rappaport, Journal of Applied Physics, vol. 96, pp. 1083-1087, 2004.

N. Rappaport, et. al., Journal of Applied Physics, vol. 98, p. 033714, 2005.

Shockley-Read-Hall (SRH) Recombination - QE as a Function of Light Intensity





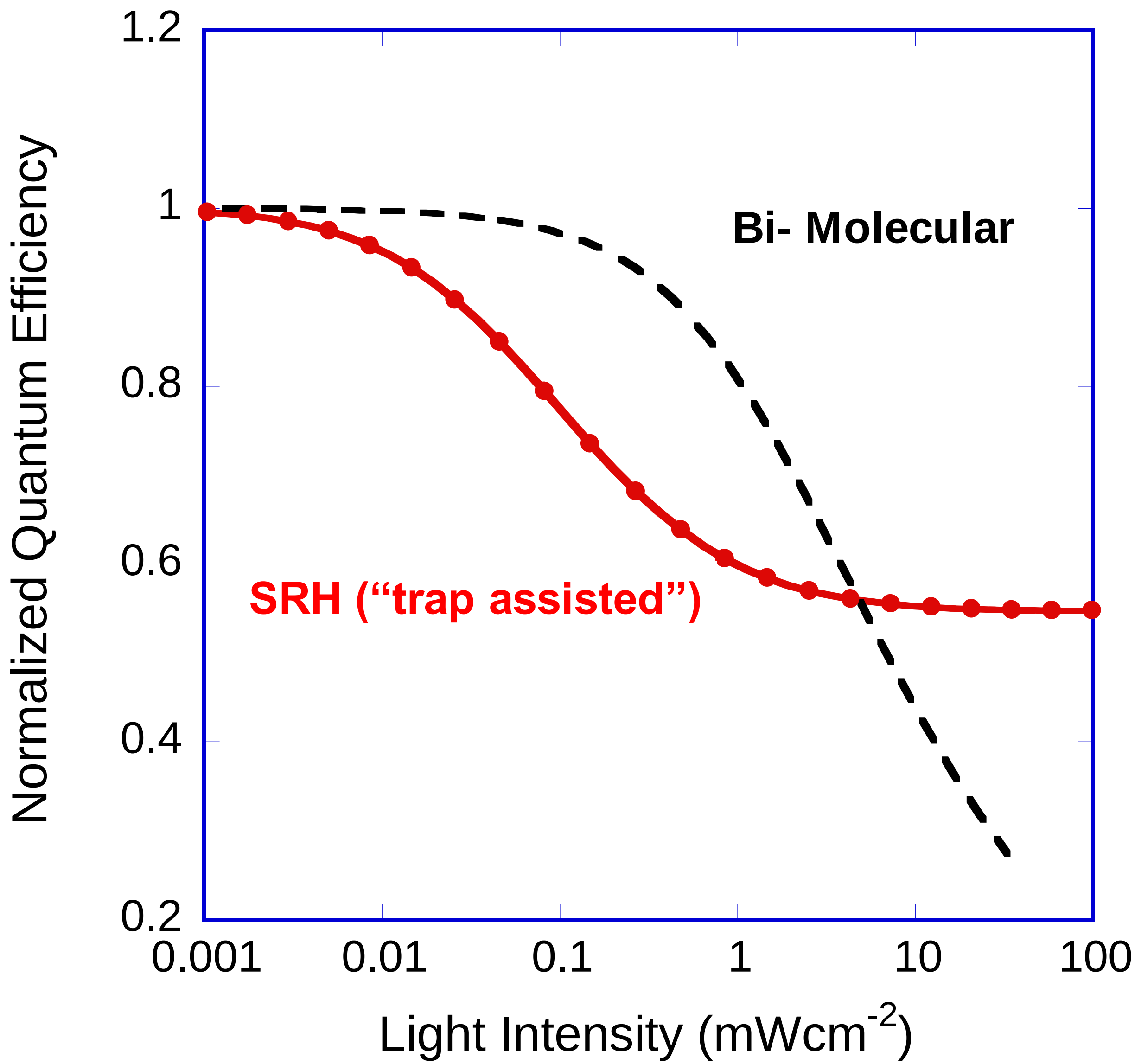
$$R_{SRH} = \frac{C_n N_t \left[n_h n_e - n_i^2 \right]}{\left(n_e + n_h\right) + 2n_i \cdot \cosh\left(\frac{\Delta E_t}{kT}\right)}$$

$$R_{SRH} \approx \begin{cases} \dfrac{C_n N_t}{2n_i \cdot \cosh\left(\frac{\Delta E_t}{kT}\right)} \left[n_h n_e - n_i^2 \right] & ;\left(n_e + n_h\right) << 2n_i \cdot \cosh\left(\frac{\Delta E_t}{kT}\right) \\ C_n N_t \dfrac{n_h n_e}{\left(n_e + n_h\right)} & ;\left(n_e + n_h\right) >> 2n_i \cdot \cosh\left(\frac{\Delta E_t}{kT}\right) \end{cases}$$

L. Tzabari, and N. Tessler, Journal of Applied Physics 109, 064501 (2011)

What Can We Learn Using Simple Measurements

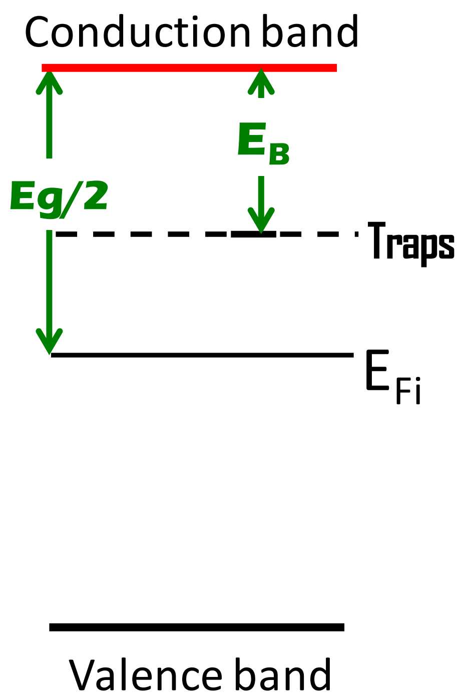
(intensity dependence of the cell efficiency)



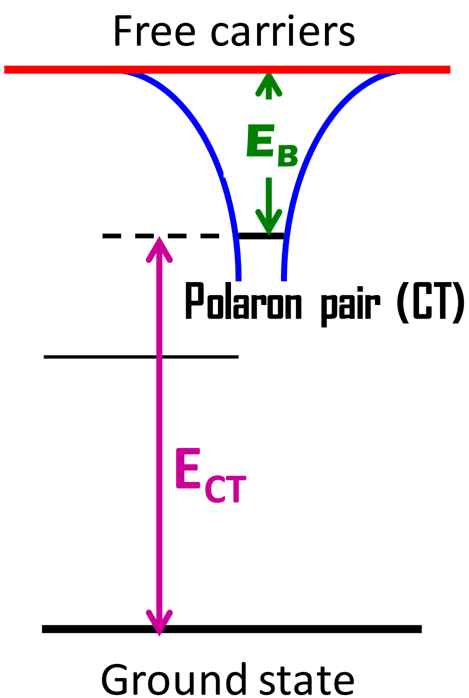
L. Tzabari, and N. Tessler, Journal of Applied Physics 109, 064501 (2011)

SRH in BHJ OPV's???

Semiconductor Picture

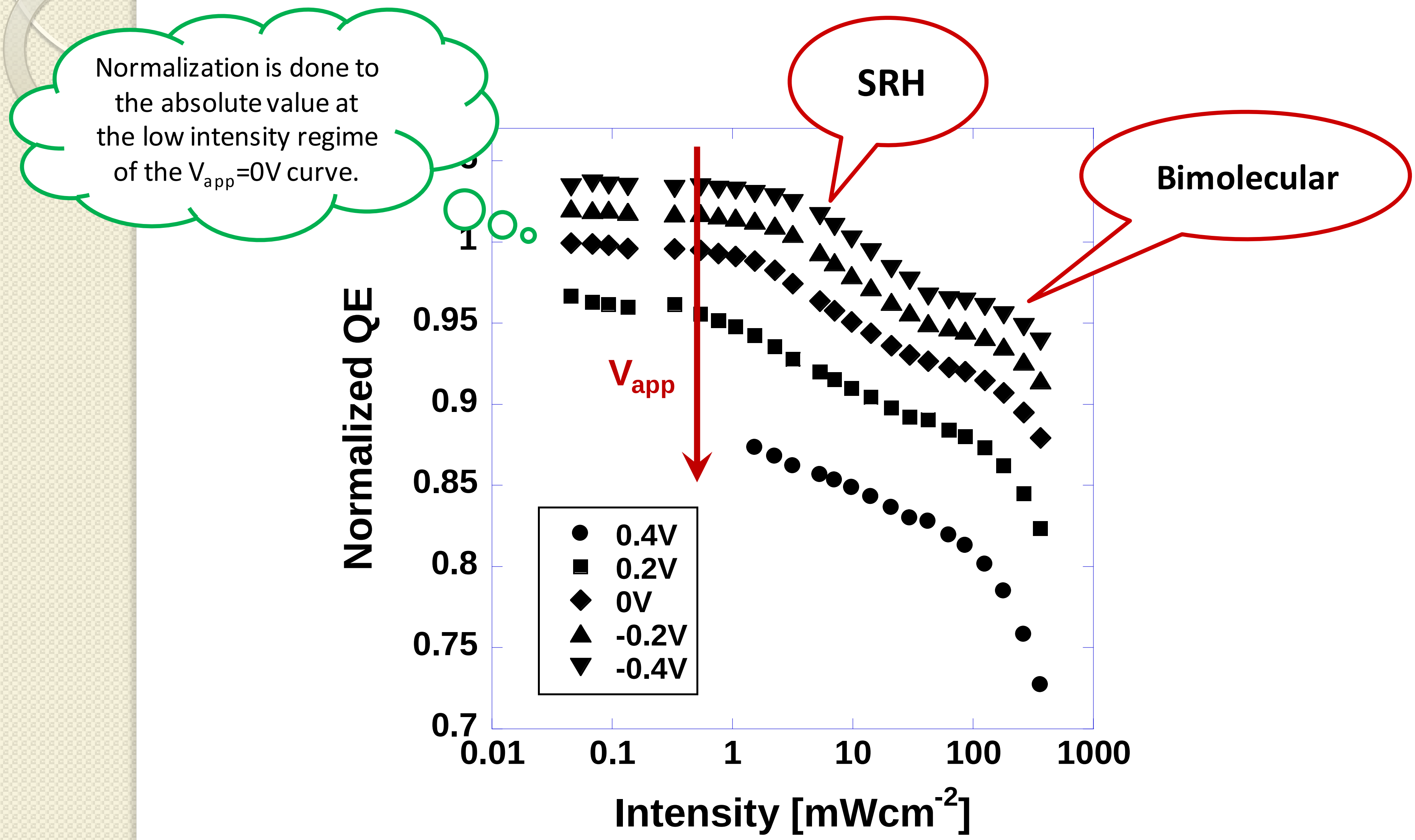


Molecular Picture

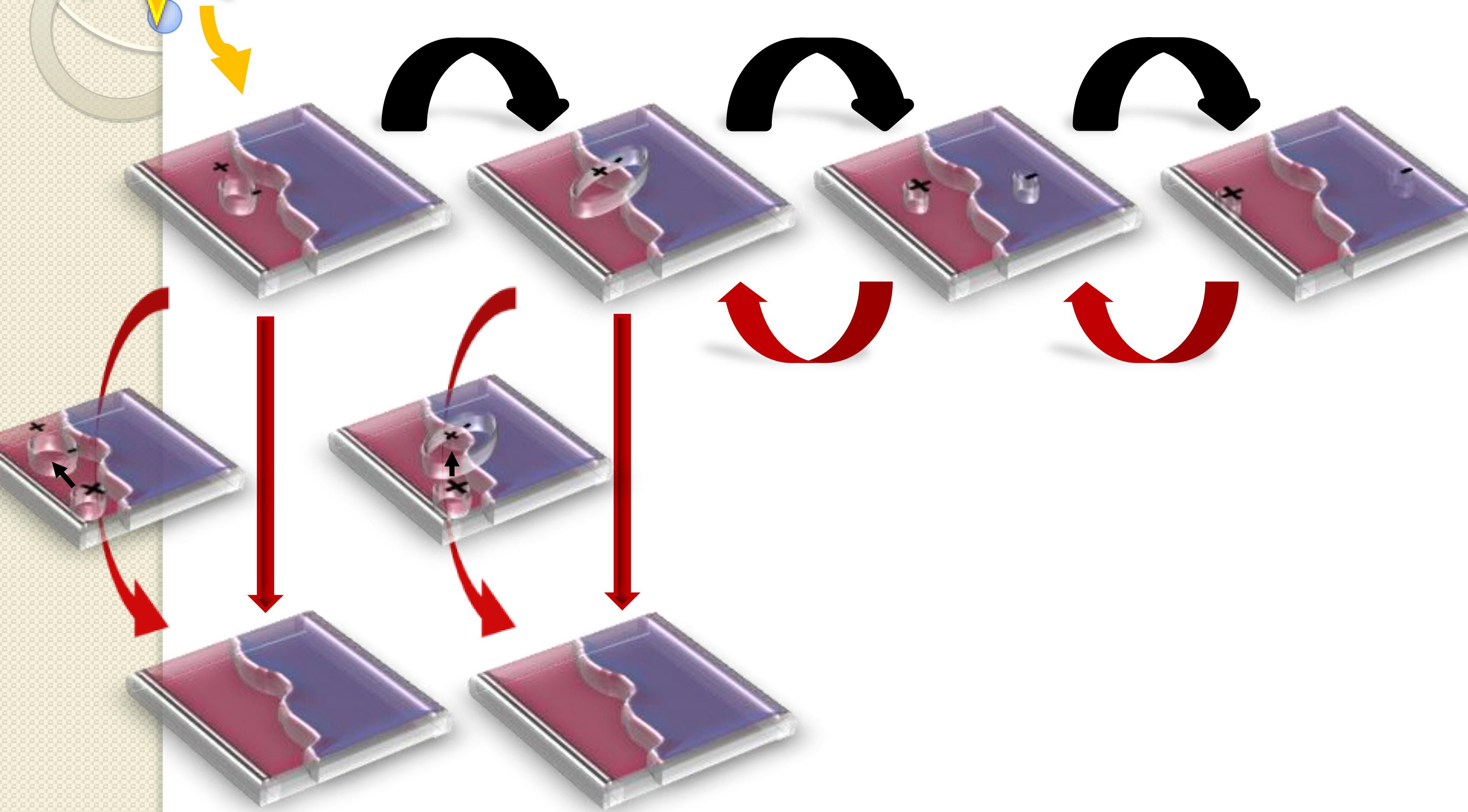


L. Tzabari, J. Wang , Y. Lee, J. Hsu and N. Tessler; J. Phys. Chem. C, 118 (48), 27681 (2014)

Fitting procedure

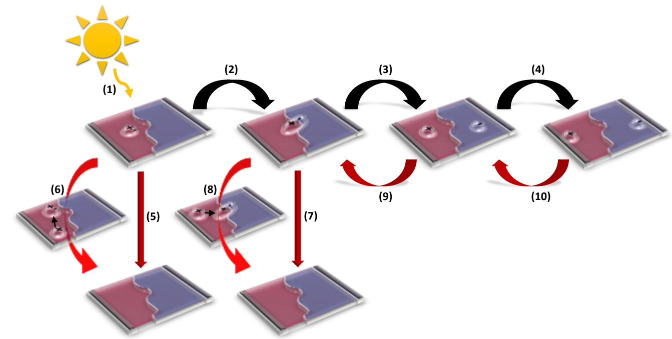


The Physical Framework we built



L. Tzabari, V. Zayats and N. Tessler; J. Appl. Phys. 114, 154514 (2013)

Model's Equations



Excitons:

$$\text{(I)}\quad \underbrace{G}_{\text{Generation}} = \underbrace{K_{ct}(n_{ct}-n_{ct\text{-}ex})\times n_{ex}}_{\text{Exciton}\rightarrow\text{CT-exciton}} + \underbrace{K_{gs}\times n_{ex}}_{\text{Exciton's decay}} + \underbrace{K_{ep}\times n_{ex}\times p}_{\text{Exciton annihilation}}$$

Polarons:

$$\text{(II)}\quad \underbrace{K_{cd}\times n_{ct\text{-}ex}}_{\text{CT-exciton dissociation}} + \underbrace{K_{dark\_inj}}_{\text{Injection}} = \underbrace{\frac{\mu V p}{d^2}}_{\text{Drift out}} + \underbrace{\frac{C_n(n_{ct}-n_{ct\text{-}ex})(p^2-n_i^2)}{2p+2n_i\cosh(\frac{\Delta E_t}{KT})}}_{\text{Free carriers}\rightarrow\text{CT-exciton}}$$

CT-excitons:

$$\text{(III)}\quad \underbrace{K_{ct}(n_{ct}-n_{ct\text{-}ex})\times n_{ex}}_{\text{Exciton}\rightarrow\text{CT-exciton}} + \underbrace{\frac{C_n(n_{ct}-n_{ct\text{-}ex})(p^2-n_i^2)}{2p+2n_i\cosh(\frac{\Delta E_t}{KT})}}_{\text{Free carriers}\rightarrow\text{CT-exciton}} = \underbrace{K_{cd}\times n_{ct\text{-}ex}}_{\text{Dissociation}} + \underbrace{\frac{n_{ct\text{-}ex}}{\tau}}_{\text{Relaxation}} + \underbrace{K_{ct\text{-}p}\times n_{ct\text{-}ex}\times p}_{\text{Annihilation}}$$

Notation:
- n_{ex} - exciton density
- P - polaron density
- n_{ct} - CT density
- $n_{ct\text{-}ex}$ - CT-exciton density

Model's parameters

Parameter	Meaning	Process number
G	Exciton generation rate $\left[\sec^{-1}\text{cm}^{-3}\right]$	(1)
n_{ex}		
n_{ct}		
n_{oct}	Occupied CT density $\left[\text{cm}^{-3}\right]$ (with a polaron pair)	
p	Polaron density $\left[\text{cm}^{-3}\right]$	
V		
K_{ct}		
K_{ct-p}		
$K_{dark\_inj}(p_{inj}, p_{dark,sc})$	Contact injection rate $\left[\sec^{-1}\text{cm}^{-3}\right]$	(10)
$p_{dark,sc}$		
$2n_i \cosh(\frac{\Delta E_t}{KT})$	Density of free charges for which the Fermi level coincides with the trap level for	
$N_{eff} \exp(-\frac{E_{LUMO,D}-E_t}{KT})$		
$N_{eff} \exp(-\frac{E_B}{KT})$		

Parameter	Meaning	Value	Reference	Process number
K_{gs}	Rate of Exciton decay in the bulk	10^9 [1/sec]	[21]	(5)
K	Exciton polaron recombination	10^{-8}	[13]	(6)
			[22][23]	(3)
			[24]	
C_n	Charge capture coefficient	$q\mu/\varepsilon$ [cm³/sec]	[25]	
τ	CT lifetime	10^{-9} [1/sec]	[16][26]	(7)
			-	
	…rom a …ic drift- …mulation		[15]	

n_{ct} - CT density, correlates with electrically active interfacial area between the different phases

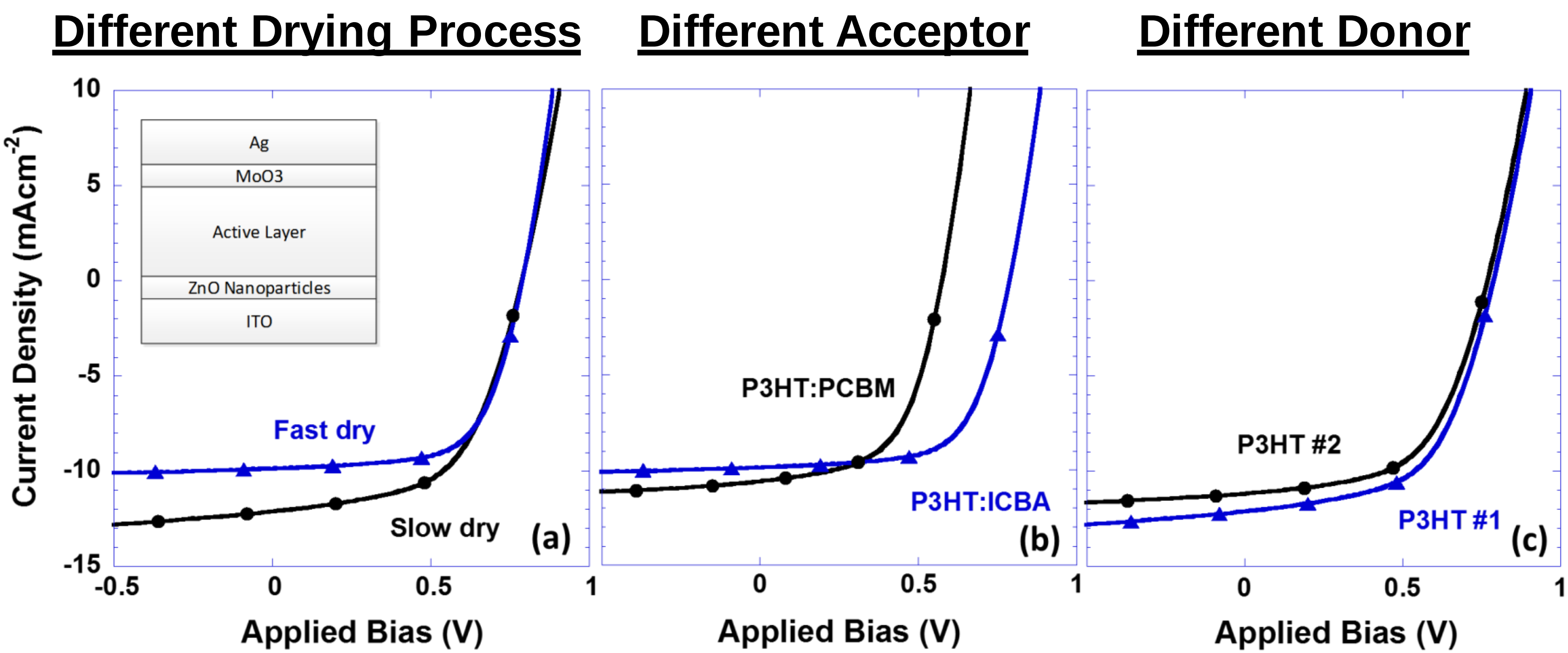
$\frac{K_{ct}}{K_{ct-p}}$ - CT-exciton creation to annihilation ratio. How efficient is the exciton to free carriers conversion

$P_{dark,sc}$ - Dark carrier density at Vapp=0V

E_{CT} - The CT state energy

Experimental Results

Our BHJ cells (P3HT:fullerene)



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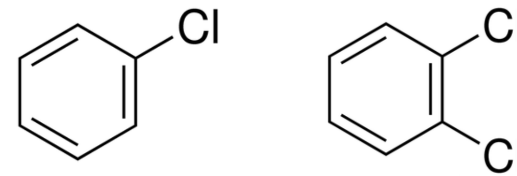
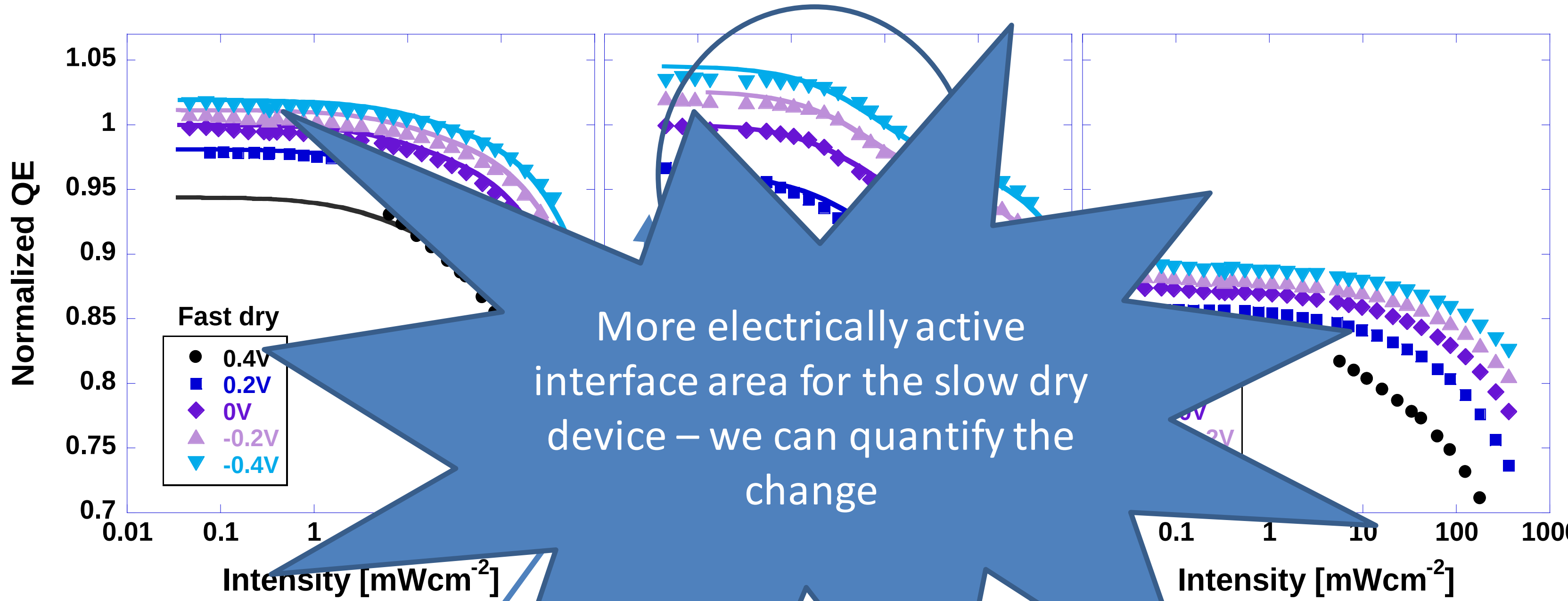


Fast Dry vs. Slow Dry (CB vs. DCB)



More electrically active interface area for the slow dry device – we can quantify the change

	N_{CT} [cm^{-3}]	E_{CT} [eV]	$\frac{K_{CT}}{K_{CT-p}}$	$p_{dark,sc}$	V_{OC} [V]	J_{SC} [mA/cm^2]	FF	PCE
Slow dry	$9.5\cdot10^{15}$	1.3	$3\cdot10^{4}$	$7.5\cdot10^{14}$	0.79	12.1	57%	5.4%
Fast dry	$5.2\cdot10^{15}$	1.31	$0.6\cdot10^{4}$	$25.7\cdot10^{14}$	0.79	9.9	65%	5%

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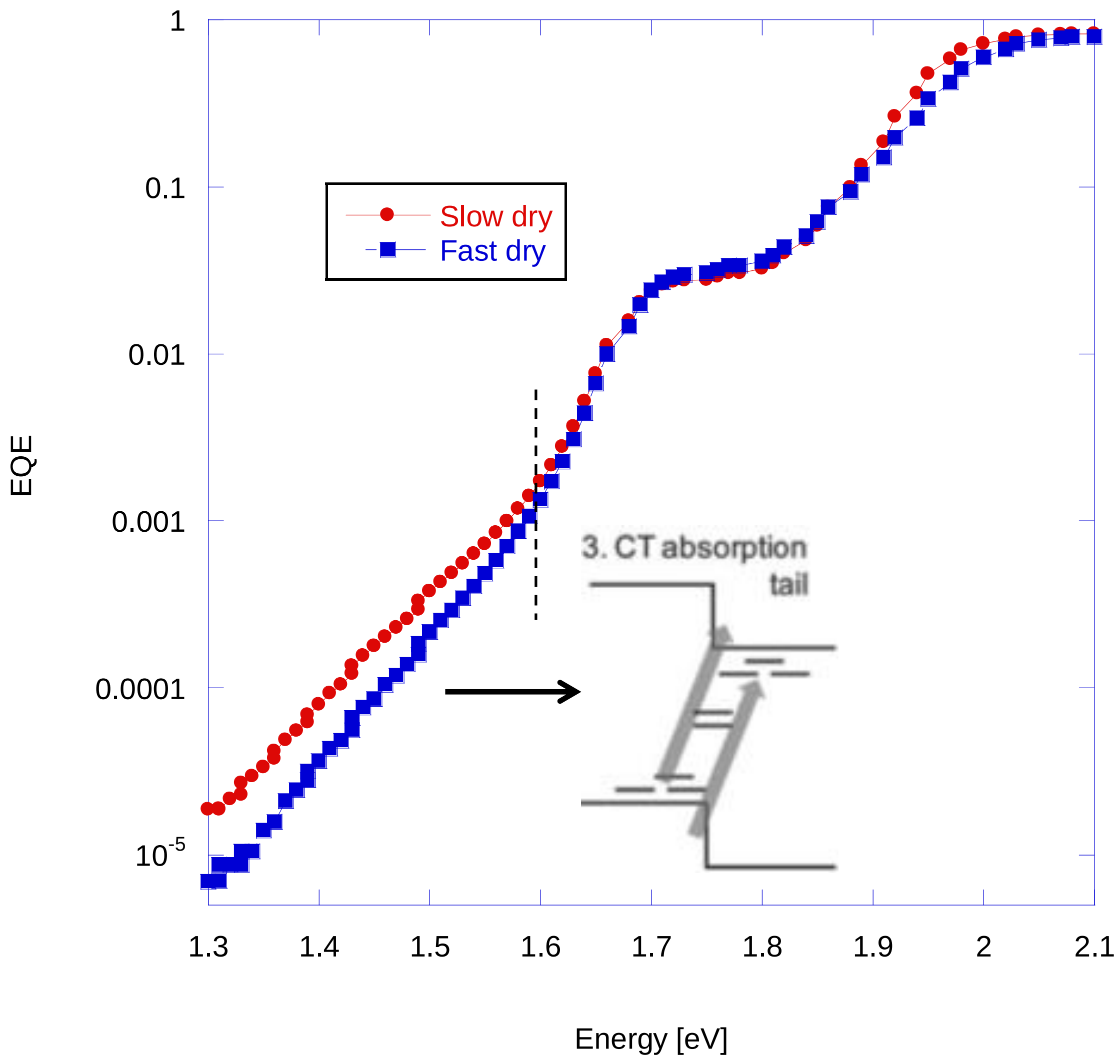
Fast Dry vs. Slow Dry – Direct Measurement of the CTs

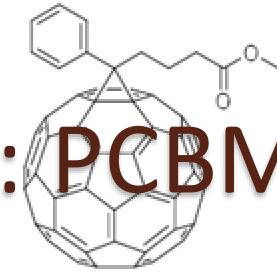


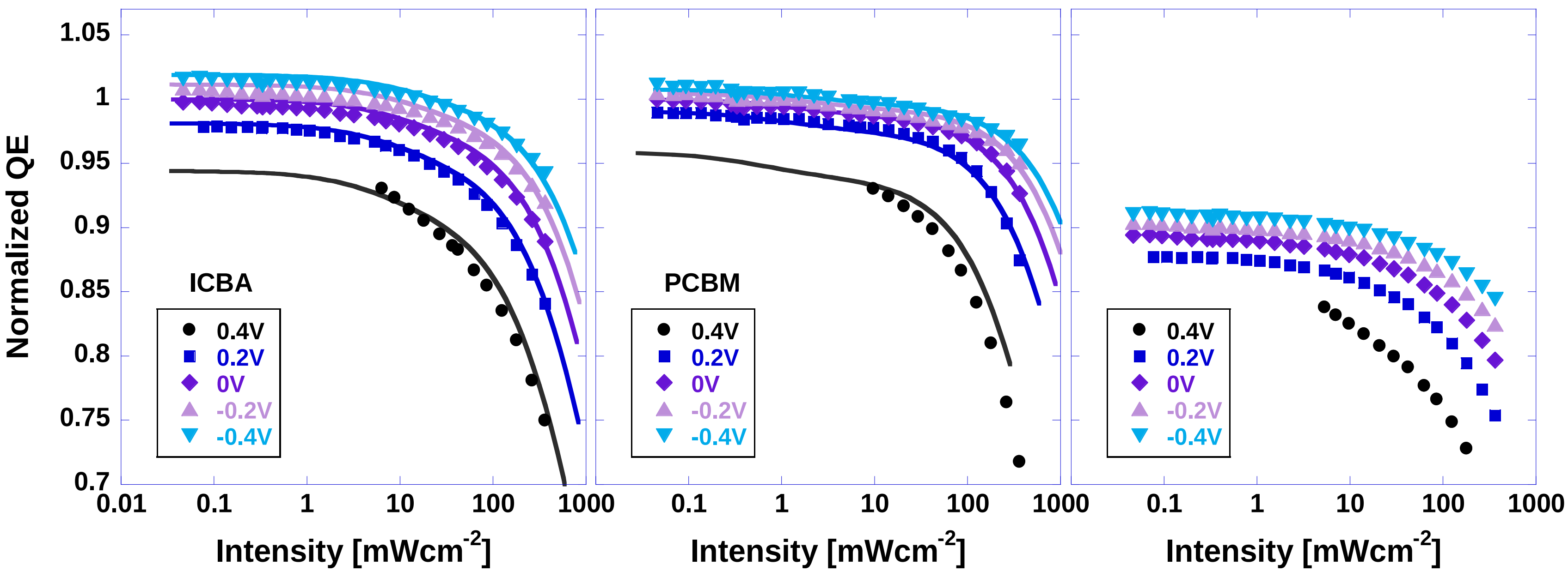
- P3HT HOMO: ~5.2eV
- ICBA LUMO: ~-3.5eV

=> CTs below 1.6eV

- *Street, R. A., Krakaris, A. and Cowan, S. R, Adv. Funct. Mater., 22: 4608–4619* (2012)
- *L. Tzabari*, J. Wang , Y. Lee, J. Hsu and N. Tessler; J. Phys. Chem. C, 118 (48), 27681 (2014)

Different Acceptor: PCBM vs. ICBA





	N_{CT} [cm^{-3}]	E_{CT} [eV]	$\frac{K_{CT}}{K_{CT-p}}$	$p_{dark,sc}$	V_{OC} [V]	J_{SC} [mA/cm^2]	FF	PCE
PCBM	$1 \cdot 10^{15}$	1.06	$15 \cdot 10^{4}$	$2.8 \cdot 10^{14}$	0.57	10.6	57%	3.5%
ICBA	$5.2 \cdot 10^{15}$	1.31	$0.6 \cdot 10^{4}$	$25.7 \cdot 10^{14}$	0.79	9.9	65%	5%

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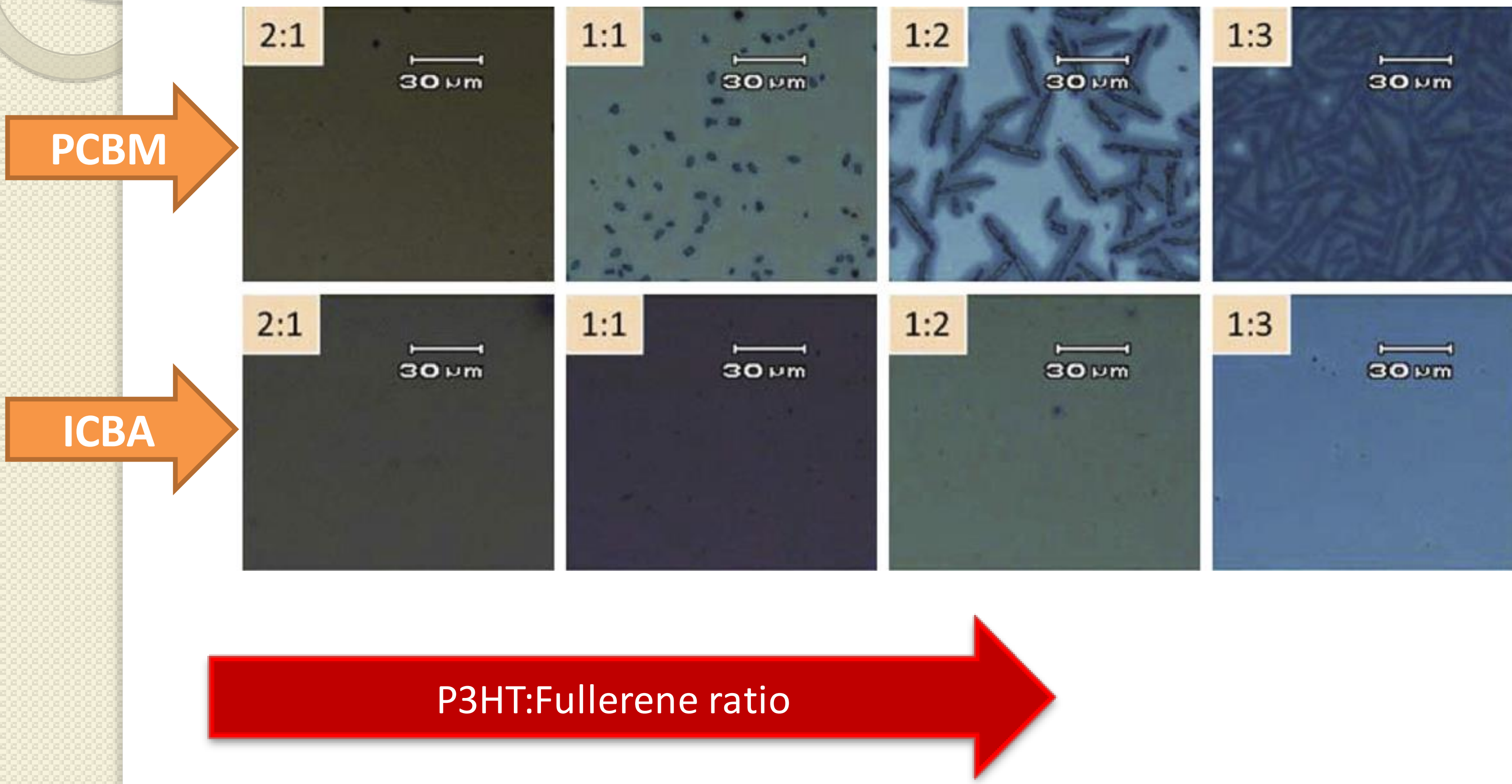
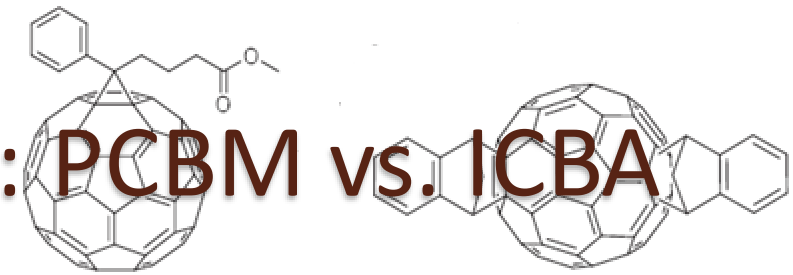
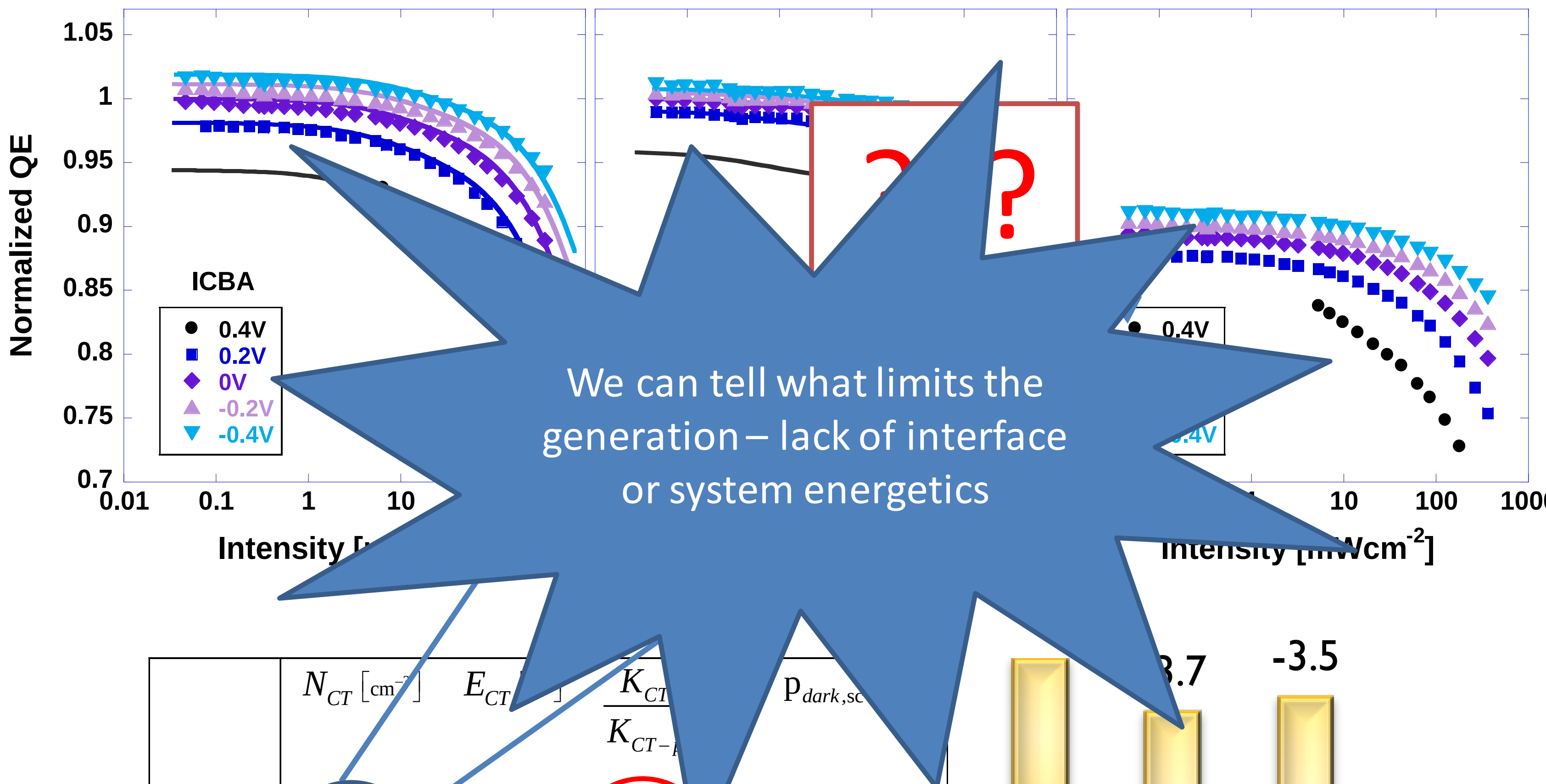
“ICBA is less crystalline than PCBM.”



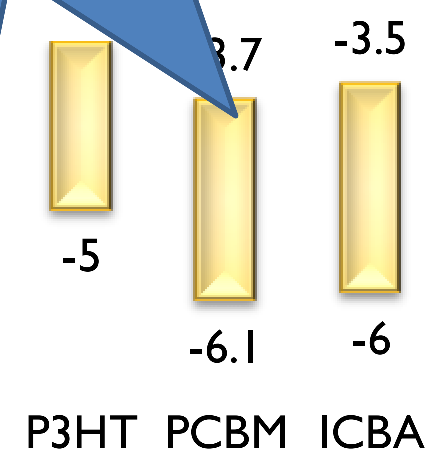
D Gao et al., ACS Appl. Mater. Interfaces 5, 8038 (2013)

Different Acceptor: PCBM vs. ICBA





	N_{CT} [cm^{-3}]	E_{CT} [ ]	$\frac{K_{CT}}{K_{CT-}}$	$p_{dark,sc}$
PCBM	$1\cdot10^{15}$	1.06	$15\cdot10^{4}$	$2.8\cdot10^{14}$
ICBA	$5.2\cdot10^{15}$	1.31	$0.6\cdot10^{4}$	$25.7\cdot10^{14}$



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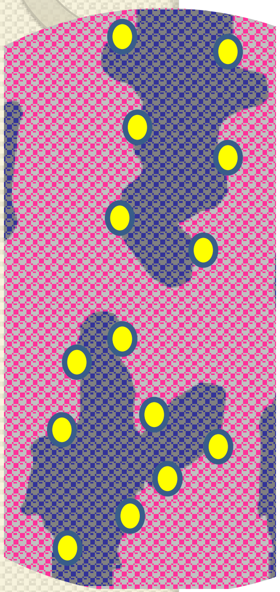
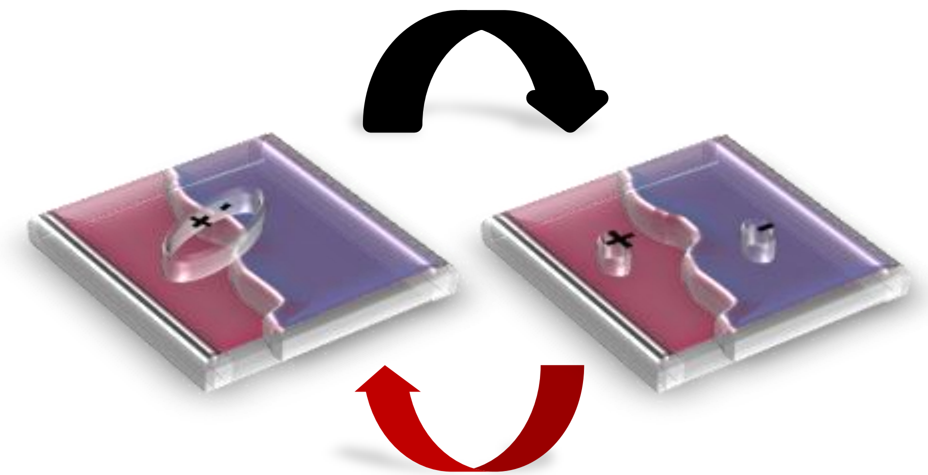
Conclusions

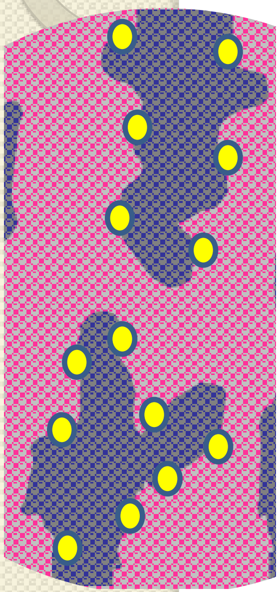
- Free carrier recombination is done through the interface using the SRH mechanism.



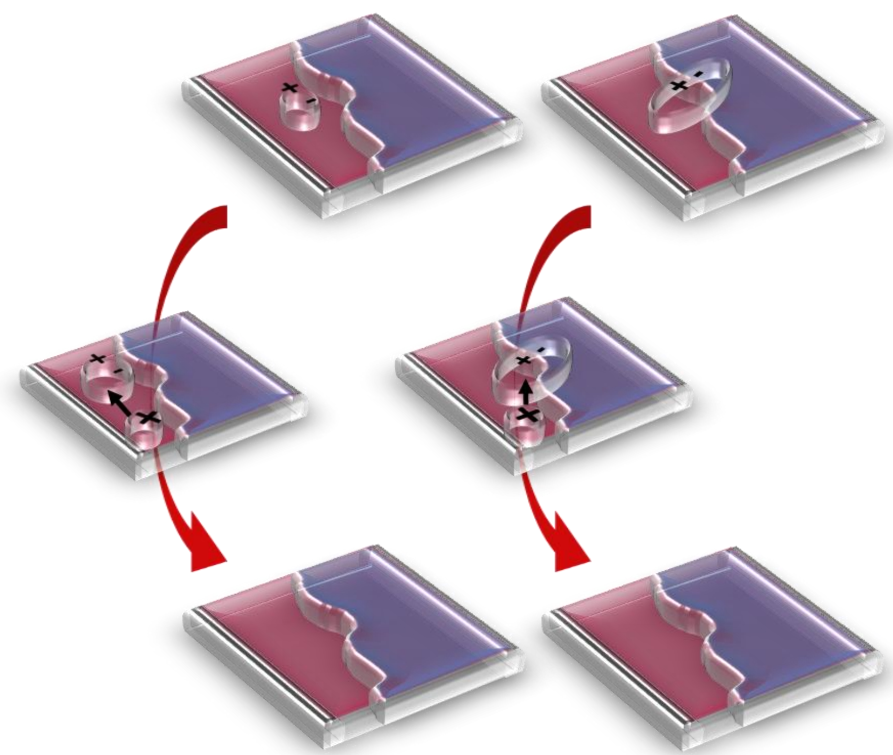


- More interface will enhance the generation efficiency while enhancing the recombination capability at the same time.

Conclusions

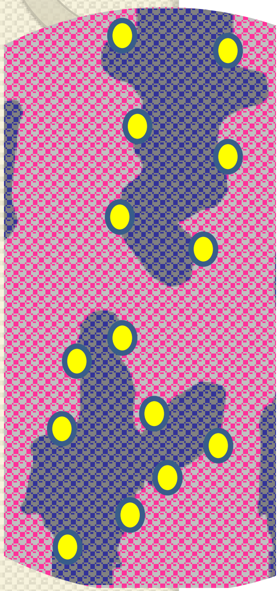


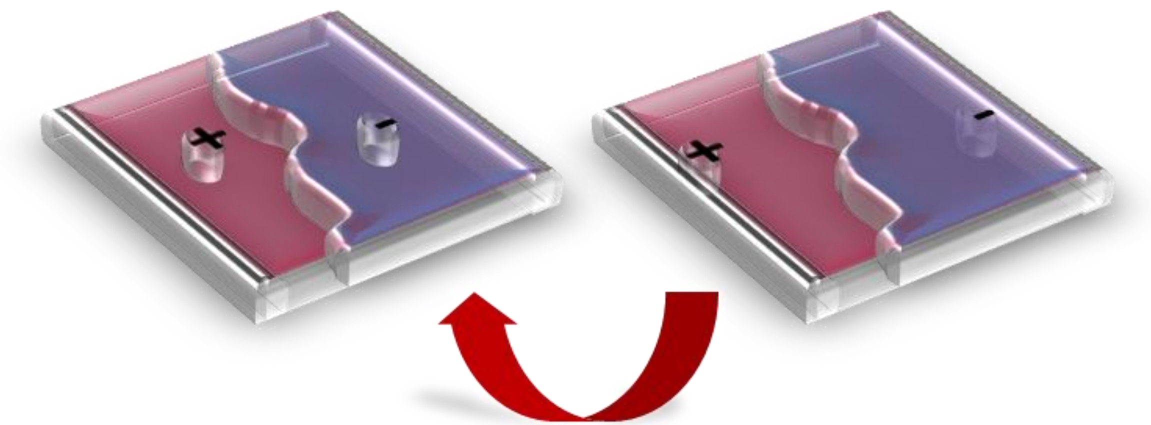
- Under high light intensities, where the different species density increases, other recombination paths as Exciton-Polaron annihilation and CT-Polaron annihilation arise and take over.



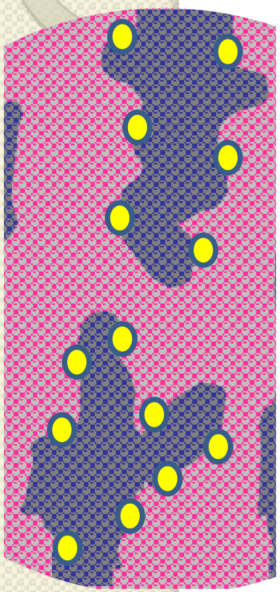
Conclusions

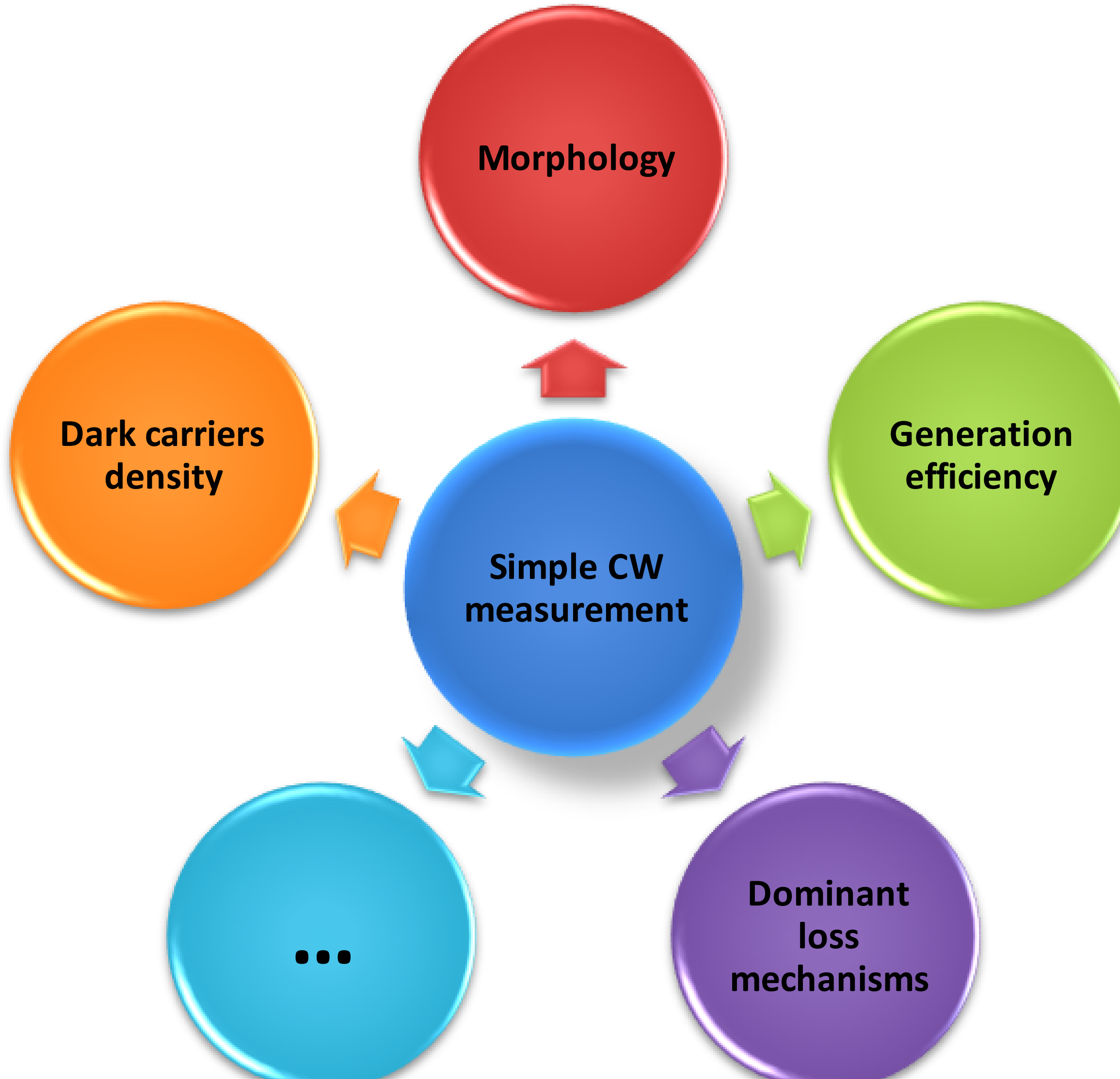
- Dark carriers (injection) are crucial part of solar cell's performance.





What does it all mean





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Thank you!