Nano-morphology and charge photo-generation in oBHJs based on fullerene and bridged dithiophenes with Carbon and Silicon bridging atoms

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Conversion of Sunlight into Electricity

Three step process

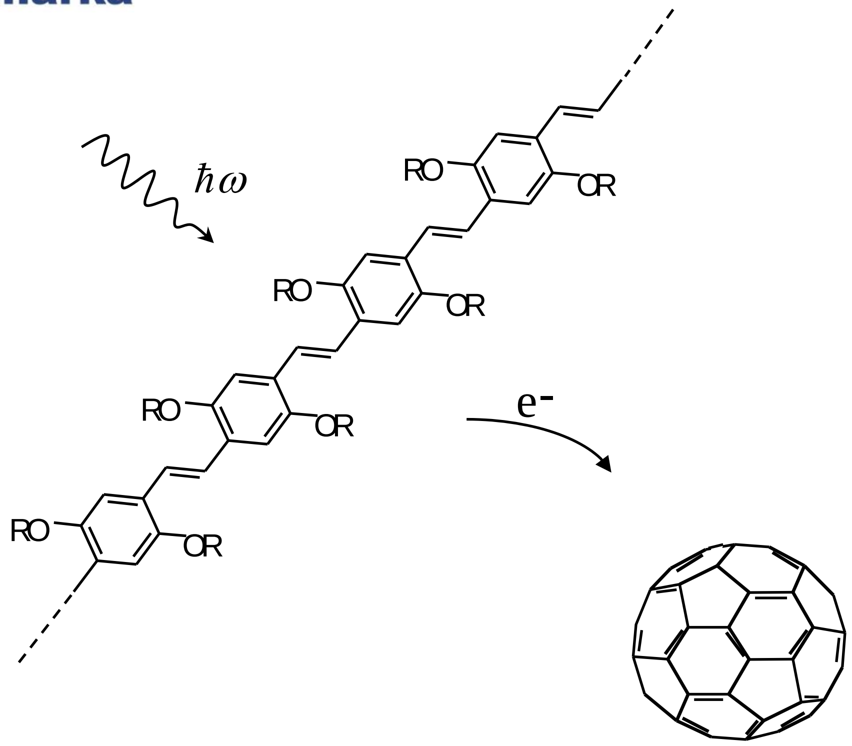
1. Absorption of photons in a material
2. Photo-induced charge separation
3. Collection of charges at electrodes

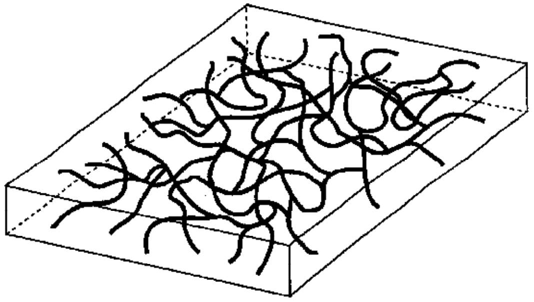
“inks” ---- with electronic functionality!

The Problem:

Semiconducting polymers cast from solution have low mobility with recombination lengths in the 10-20 nm range

The “Idea” ----





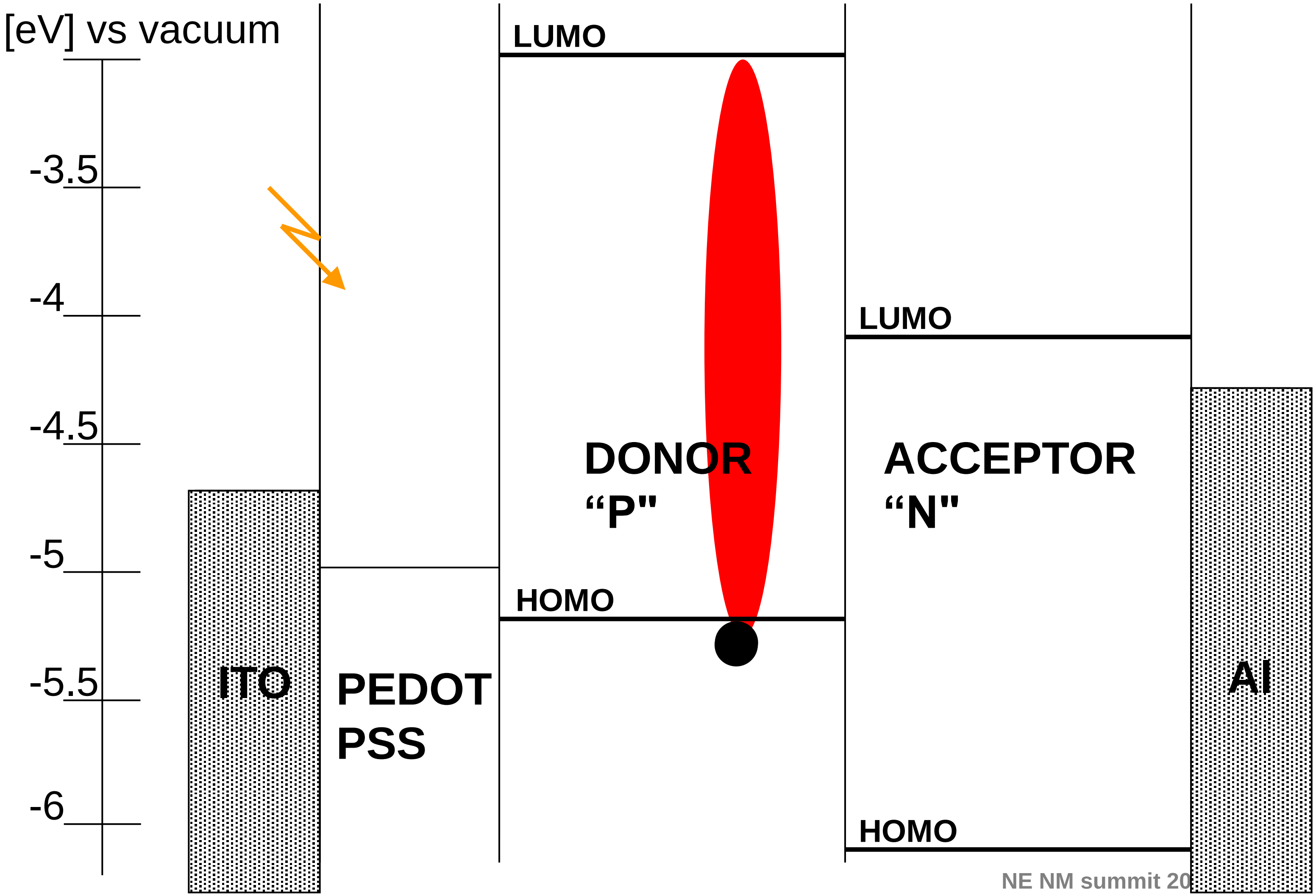
Self-Assembly of
“Bulk Heterojunction” material
by
Spontaneous Phase Separation

Working principle of OPV

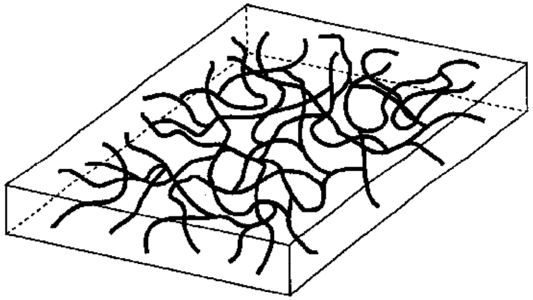
Absorption of a photon and creation of an exciton

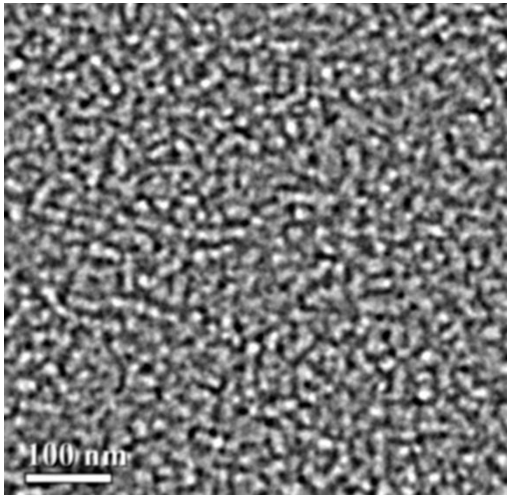
Diffusion of the exciton to the Donor/Acceptor interface

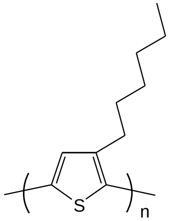
Dissociation of the exciton and charge carriers

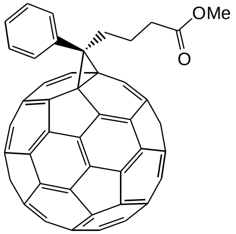


Donor and Acceptor components form charge separating heterojunctions









P3HT **PCBM**

Bulk Heterojunction Material

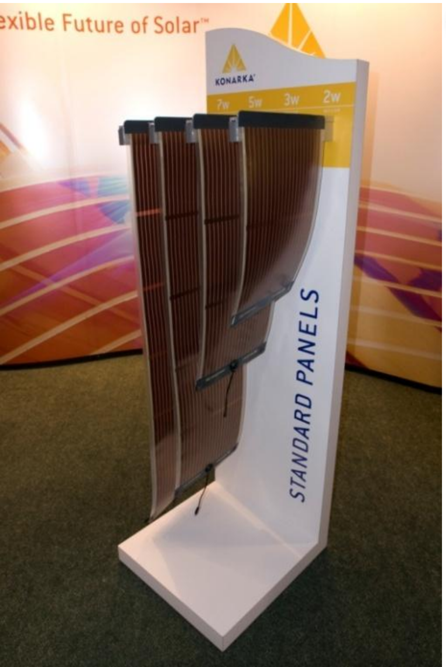
Bicontinuous interpenetrating networks

Self-assembled nanoscale material with charge-separating junctions everywhere!

Low Cost "Plastic" Solar Cells

The Dream →

→



Roll-to-roll manufacturing of plastic solar modules at Konarka facility in New Bedford, MA

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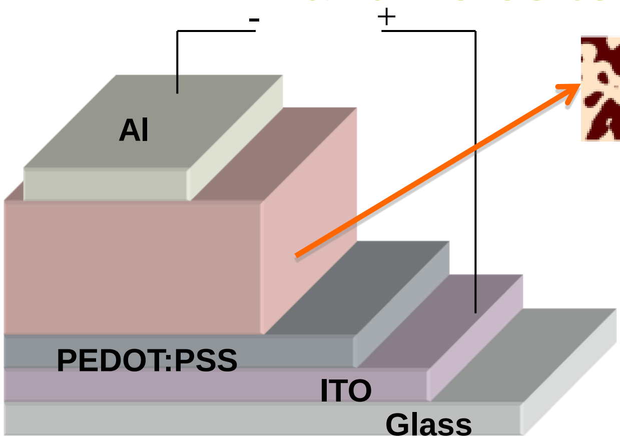
Device architecture

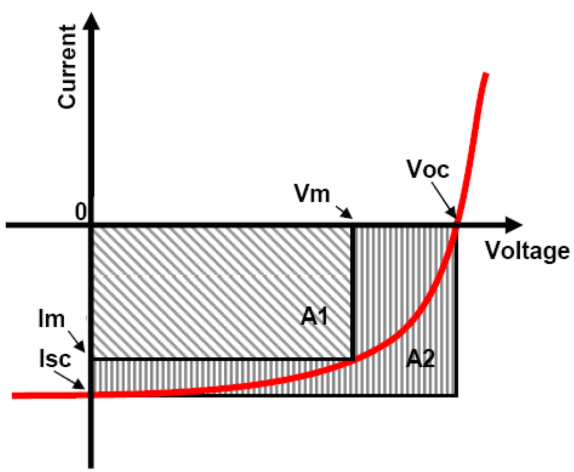
Must break the symmetry ---

Use two different electrodes with different work functions.
Electrons will automatically go toward lower work function contact and holes toward higher work function contact



Thin Film of Phase Separated Bulk Heterojunction Material

Light



Need to improve the efficiency

PCE = Isc Voc FF / Power (input)

How do we control these parameters?

Voc =[Efull(LUMO) – Epol(HOMO)]

Synthesize polymers with deep HOMO
New Acceptors ---- so that Voc $\rightarrow$ Eg/e

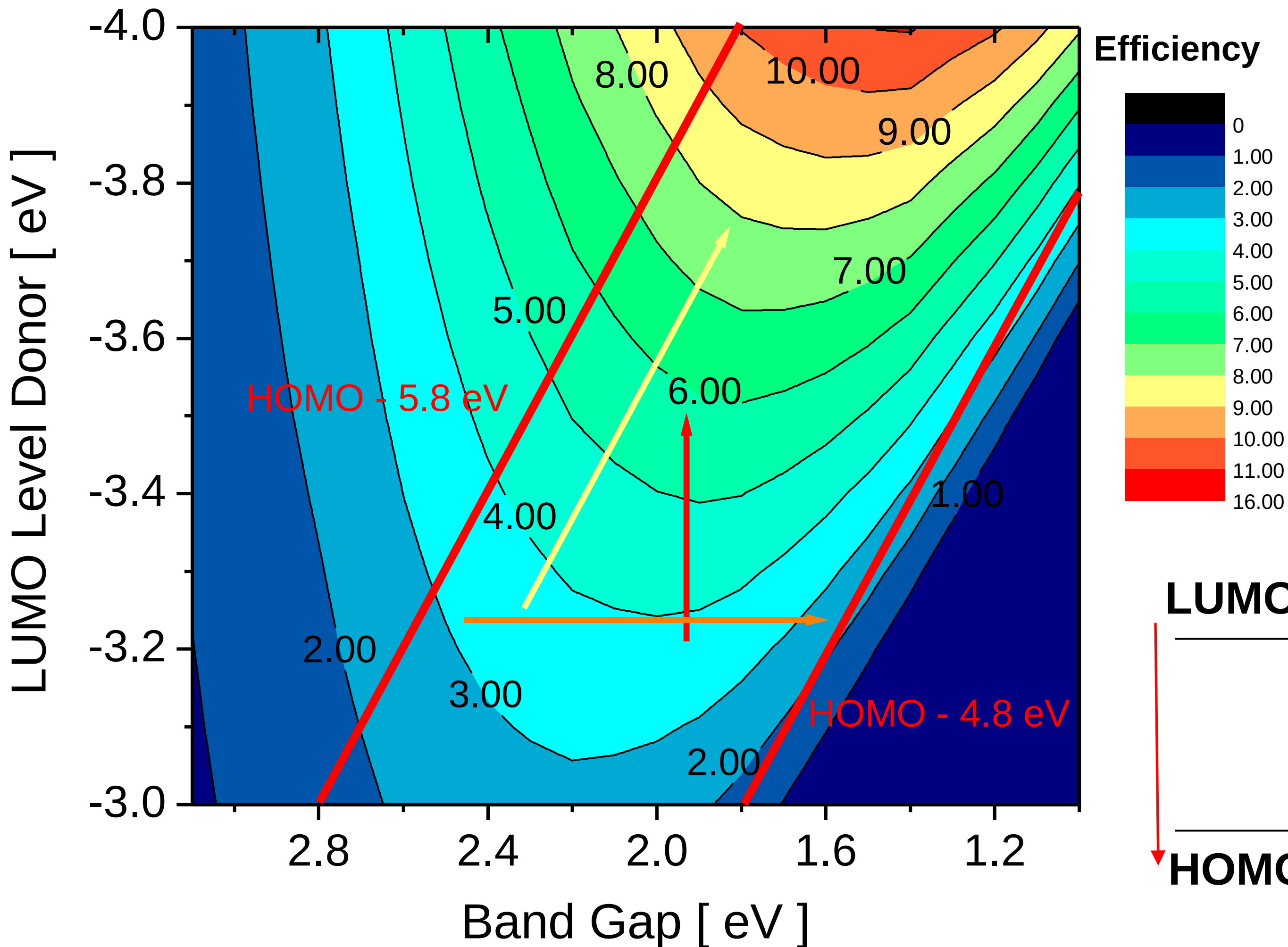
Jsc

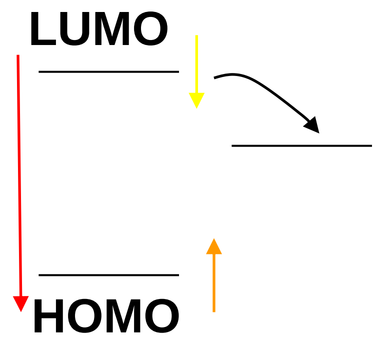
Smaller band gap
Control nano-morphology

FF

Recombination
Reduce density of interfacial traps and increase $\mu\tau$R

Efficiency Prediction OPV





- Assuming fullerenes as acceptors

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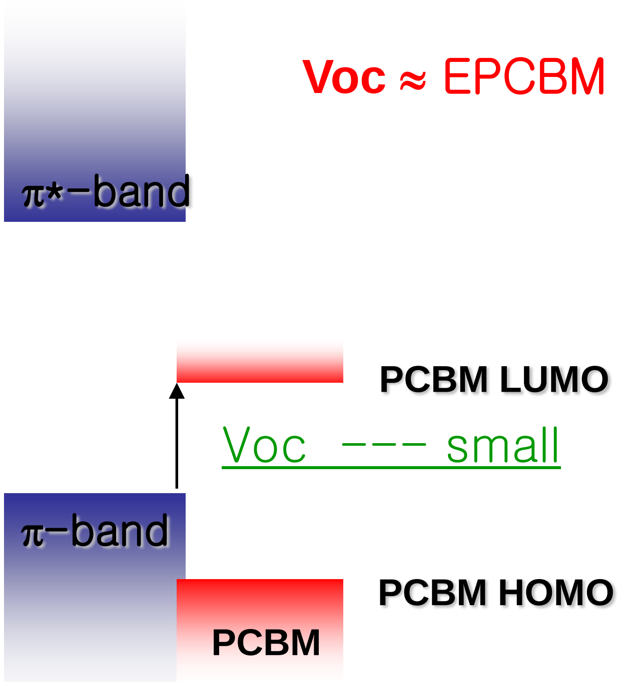
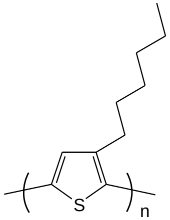
Origin of Voc

When irradiated with high light intensity,
Fermi levels must be equal (holes in the π-band and electrons in PCBM LUMO)

Voc ≈ EPCBM LUMO − Epolymer homo

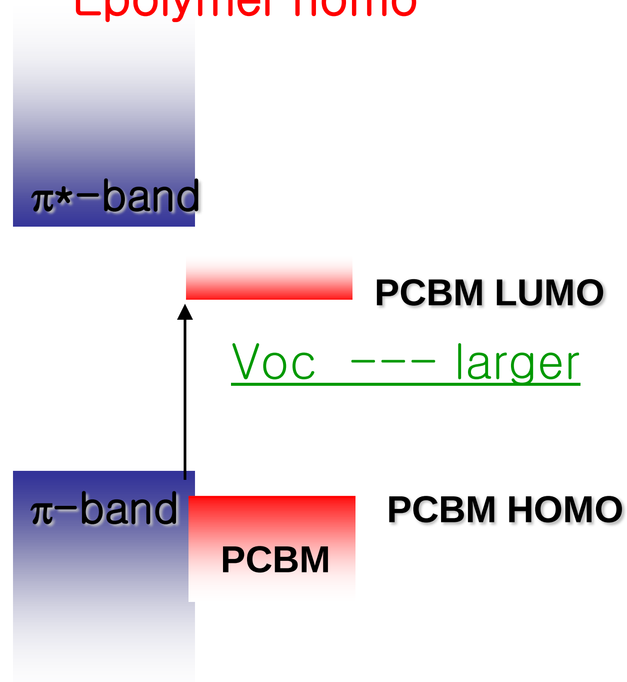


semiconducting polymer



P3HT

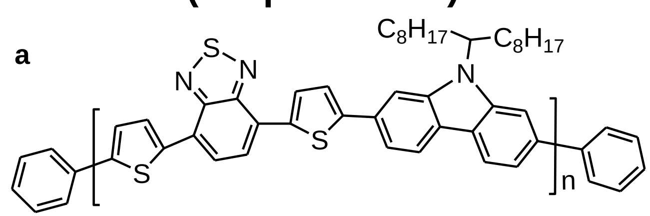
VOC = 0.6 V



semiconducting Polymer (deeper HOMO)

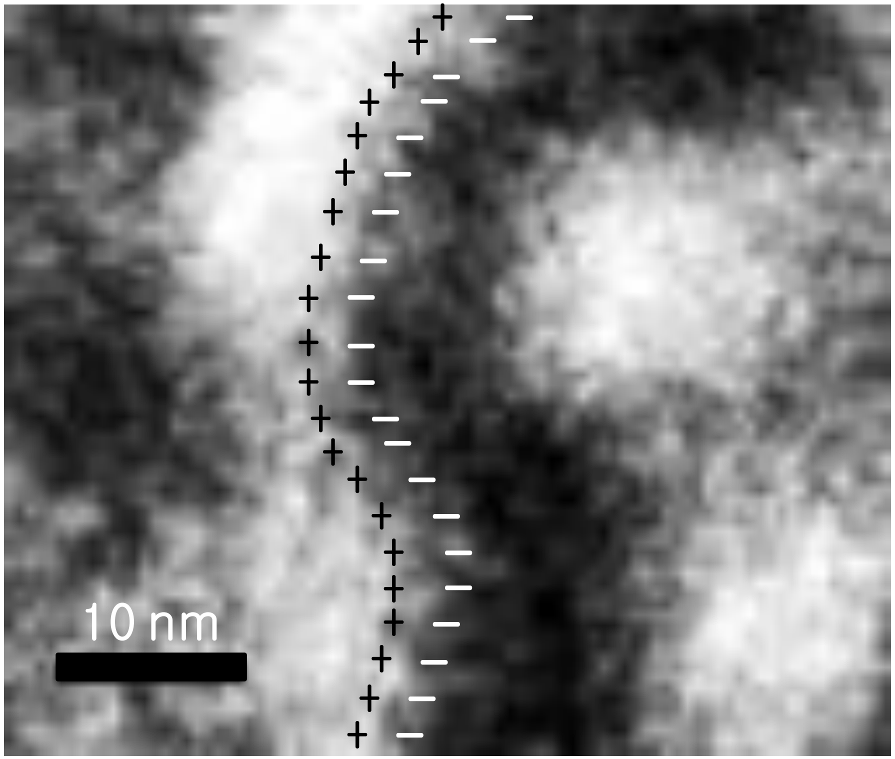
VOC = 0.9 V

a



Simulated image showing the formation of a "parallel plate capacitor" at the Polymer:Fullerene interface.

Light on --- at V =Voc



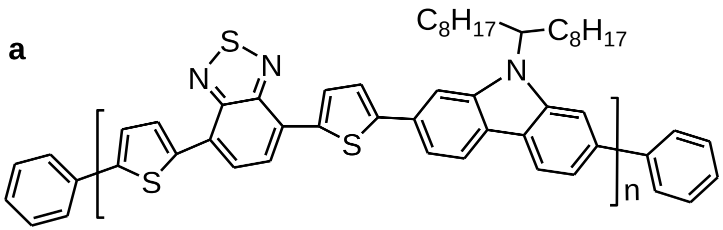
VOC ≈ Ea(LUMO) – Ed (HOMO)

ΔV"capacitor" = Voc

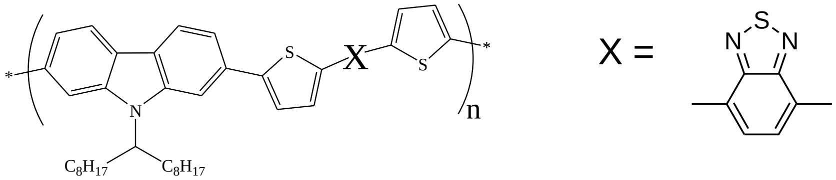
Alternating donor-acceptor co-polymer

poly[N-9′′-hepta-decanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)

PCDTBT

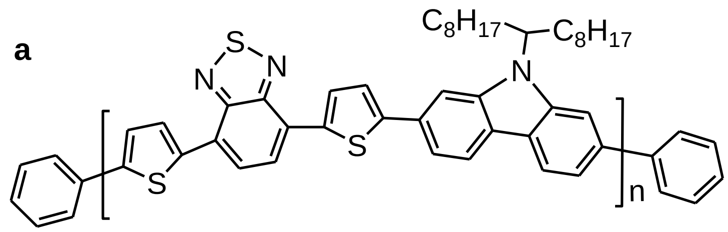


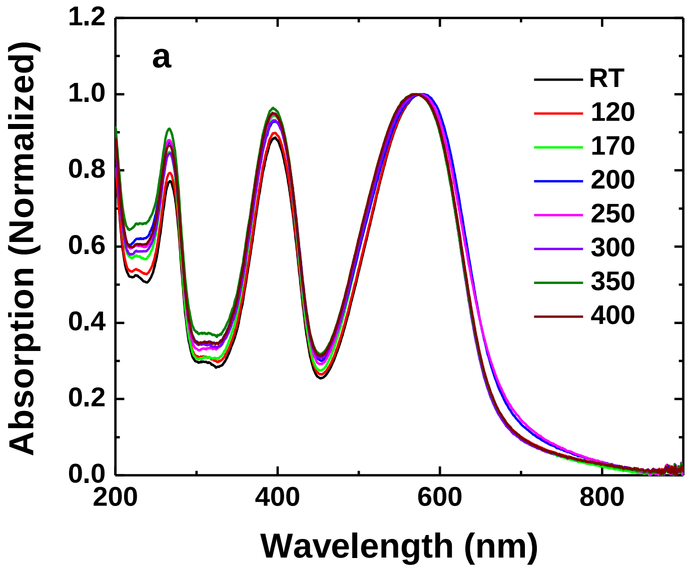
Flexible Chemistry

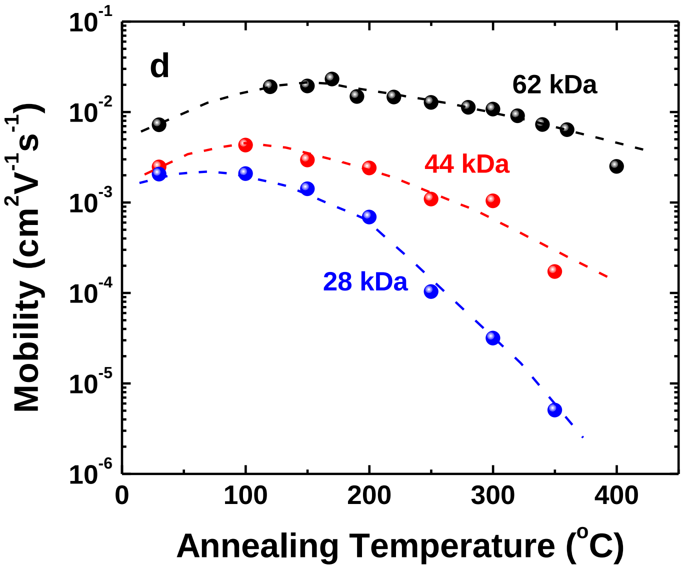


Mario Leclerc and colleagues
Université Laval
Quebec City

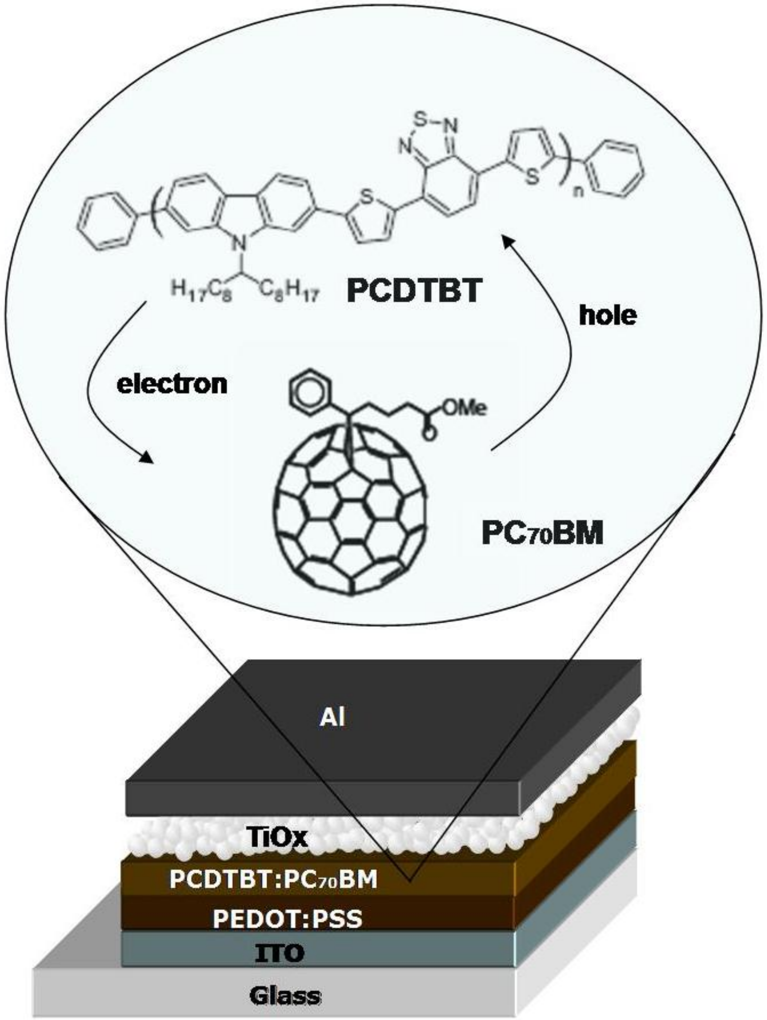
PCDTBT: Stable Semiconducting Polymer

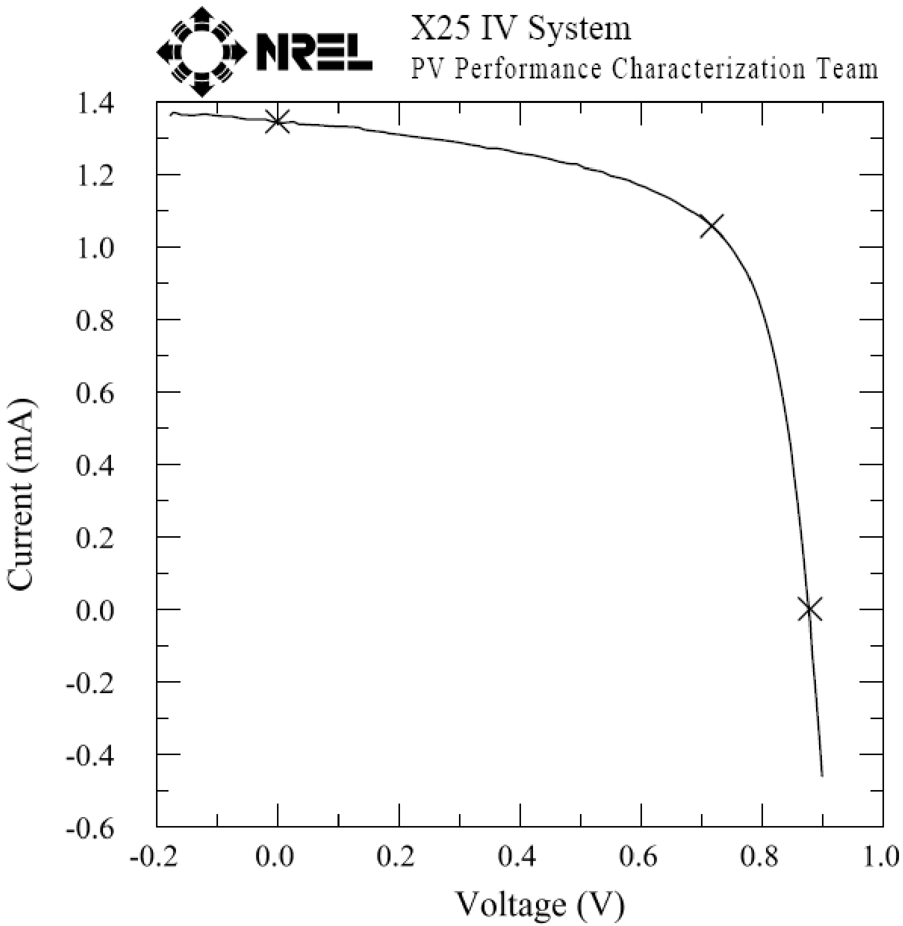






Shinuk Cho

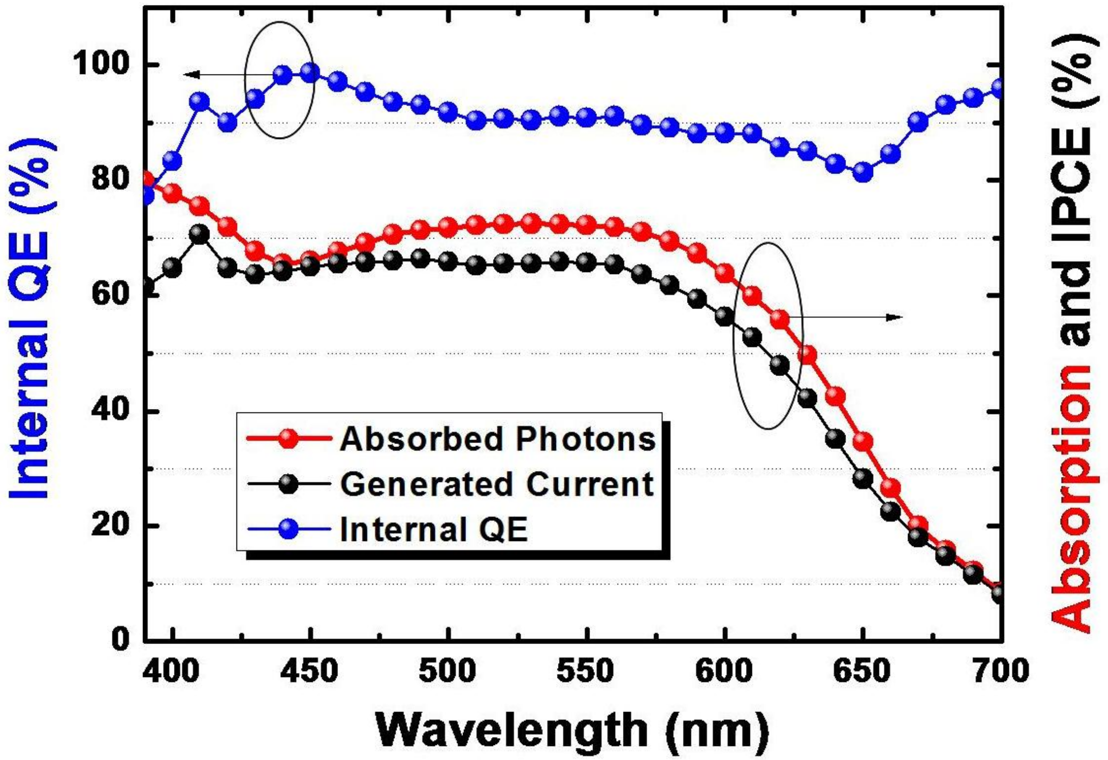




VOC = 0.88V
FF = 64%
Power Conversion Efficiency = 6 %

Sung Heum Park

Potential for high efficiency



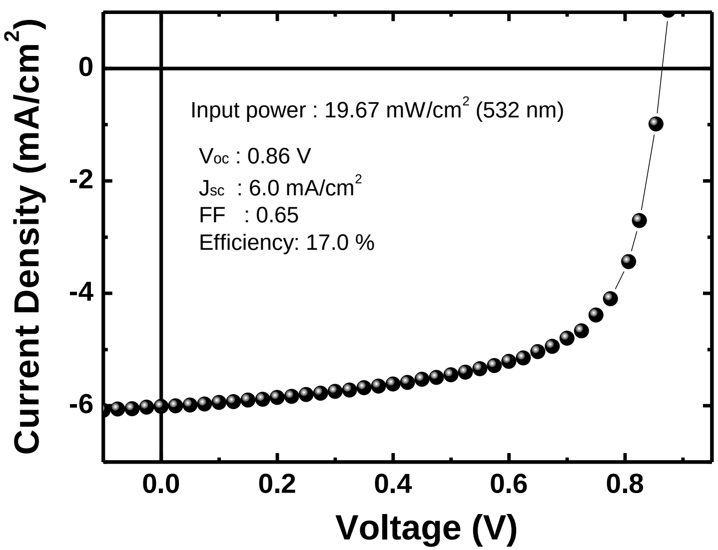
Internal Quantum efficiency approaches 100%.

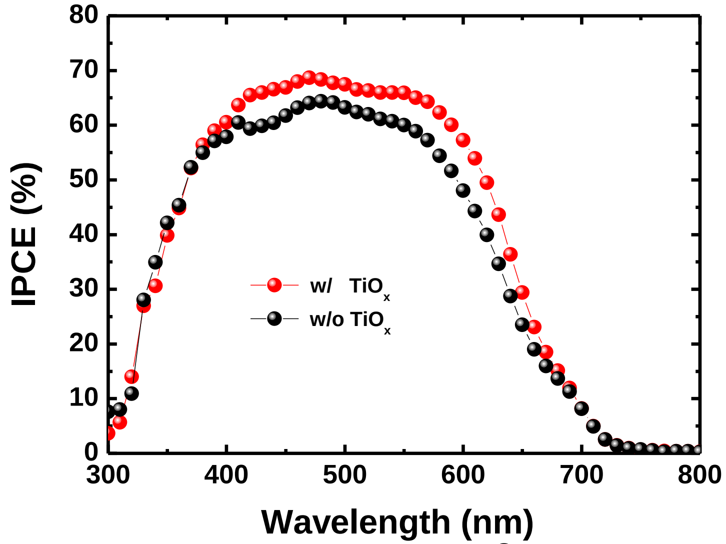
Nearly every photon yields one “e-h” polaron pair and
all photo-generated carriers are collected at the electrodes.

17% Power Conversion Efficiency

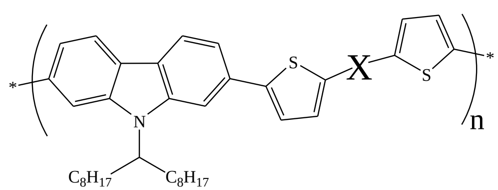
for wavelengths within the absorption band

ITO/PEDOT:PSS/PCDTBT:$PC_{70}BM/TiO_x$/Al

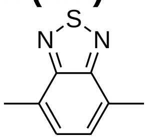




Important progress ---



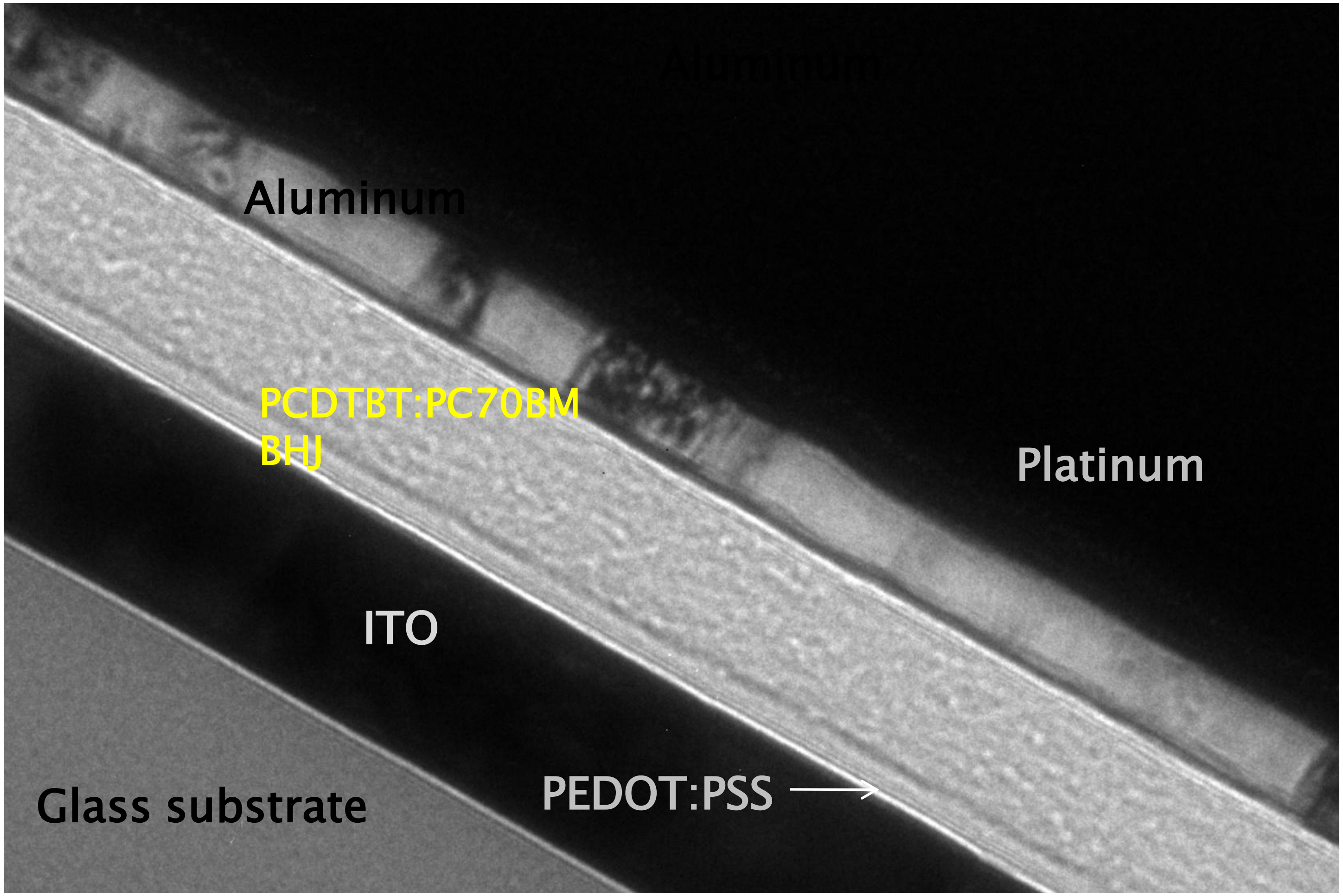
PCDTBT, X =



Demonstrates the potential of BHJ technology for high PCE

- Reduce the band gap
- Increase the FF ($\mu\tau$-product).

Cross-sectional TEM Image of the PCDTBT:PC70BM BHJ

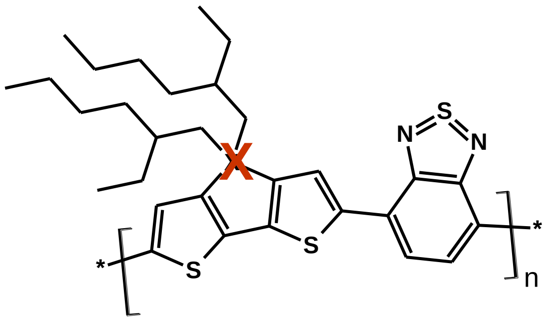


PCDTBT:PC70BM=1:4
Image was obtained under defocus

It’s all about Morphology

Control of morphology a case study

Alternating D/A low-bandgap copolymers:
dithiophenes-benzothiadiazole



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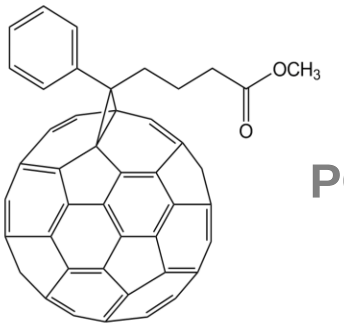


PCBM

X=Si **X=C** (PCPDTBT)

"Si-bridged (Si-b)" vs. "C-bridged (C-b)"

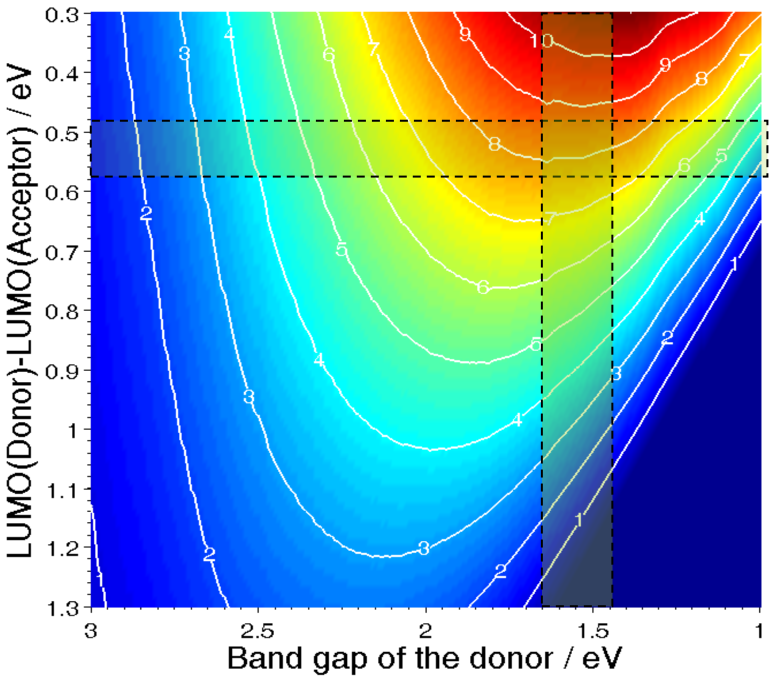
A case of study because:

- **Minimal structural changes**
- **Maximum impact on oBHJ nanomorphology**

Power conversion: potential

	HOMO	LUMO	Vbi ($HOMO_{poly}$-$LUMO_{PCBM}$)
C-b	-5.3 eV	-3.55 eV	1.3V
Si-b	-5.3 eV	-3.6 eV	1.3V

OFETs	Polymer	Blend (1:2)	
	μ_h [cm^2/Vs]	μ_h [cm^2/Vs]	μ_e [cm^2/Vs]
C-b	$5x10^{-3}$	$3x10^{-4}$	$4x10^{-4}$
Si-b	10^{-2}	10^{-3}	10^{-3}
rr-P3HT	10^{-3}	$5x10^{-4}$ (1:1)	$4x10^{-4}$ (1:1)



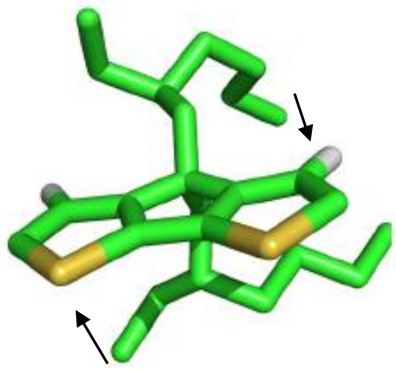
Assuming "full" Voc, FF=0.65, max EQE=65%

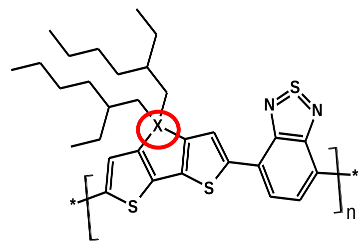
Max estimated PCE in the range 7-8%

Structural considerations

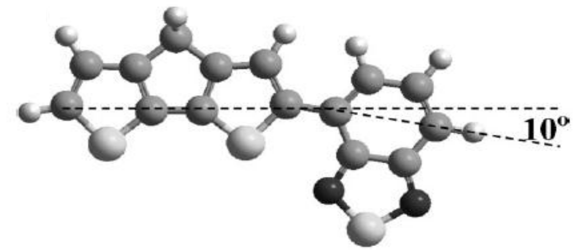
Side chain arrangement

"helicopter effect"

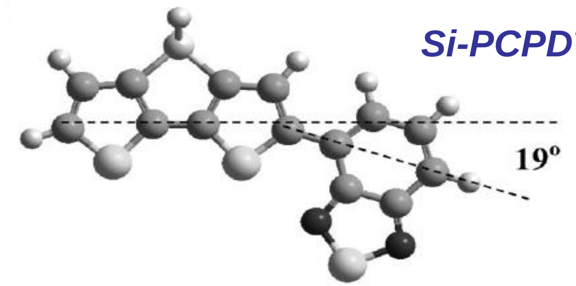


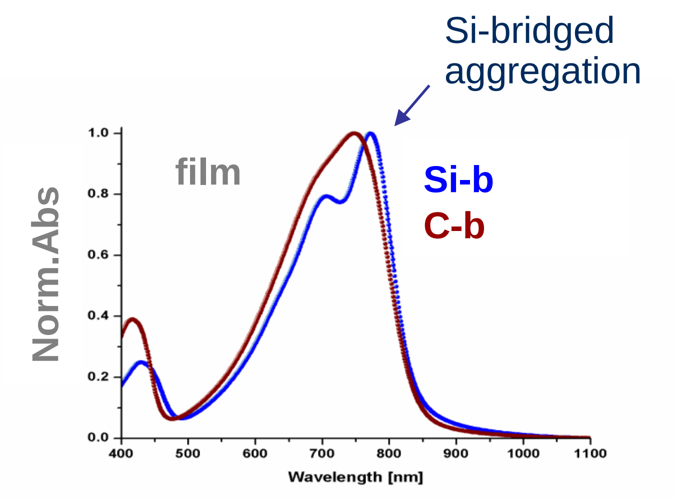


C-PCPDTBT



Si-PCPDTBT





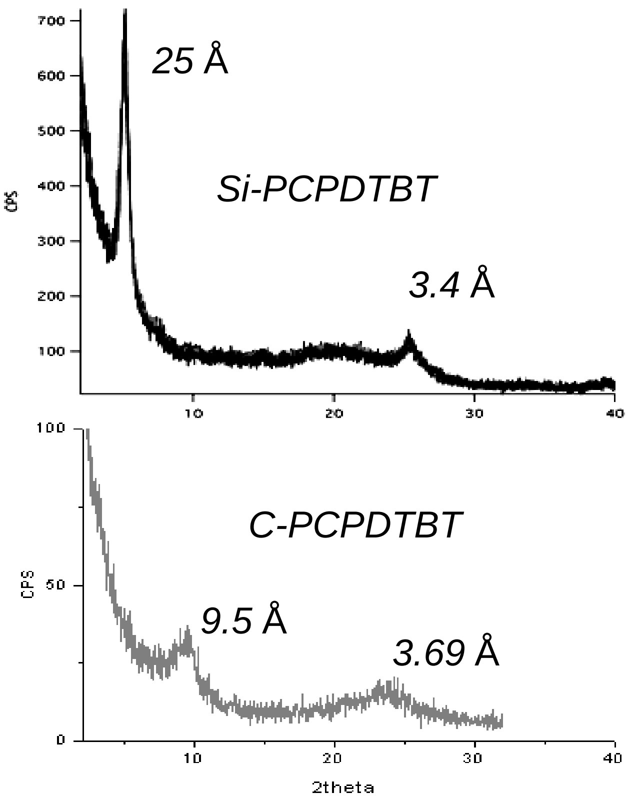
AM1 calculations predict:
- **rather flat backbone**
- **additional distortion in the Si-b backbone**

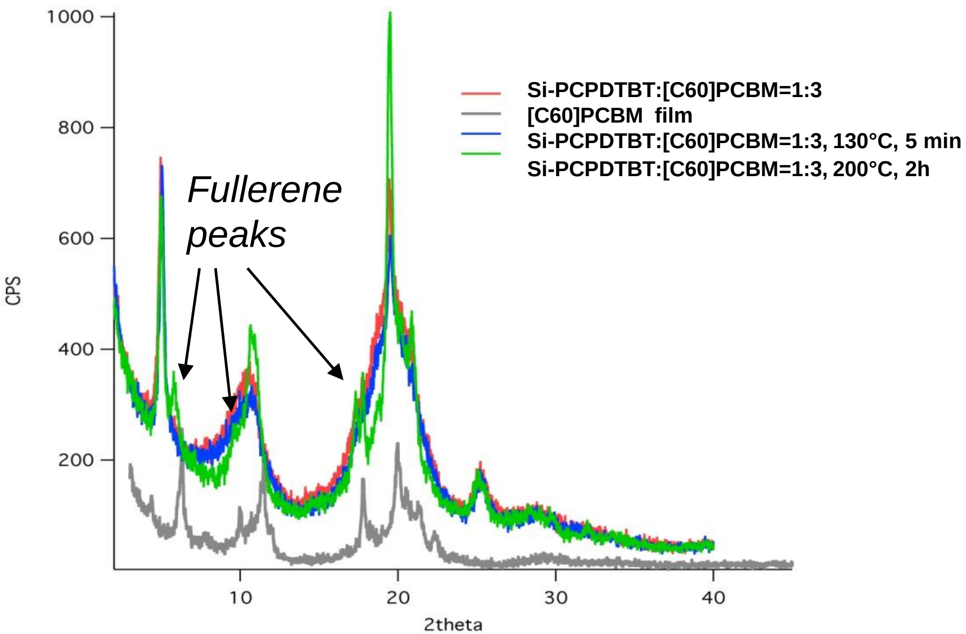
Just a shoulder…

X-Ray diffraction analysis

- Enhanced pi-pi stacking, in Si-PCPDTBT, the stacking distance (3.4 A) is <u>shorter</u> than what found in C-PCPDTBT and P3HT.

- Neither the presence of PCBM nor annealing significantly affects the crystallinity of the polymer.



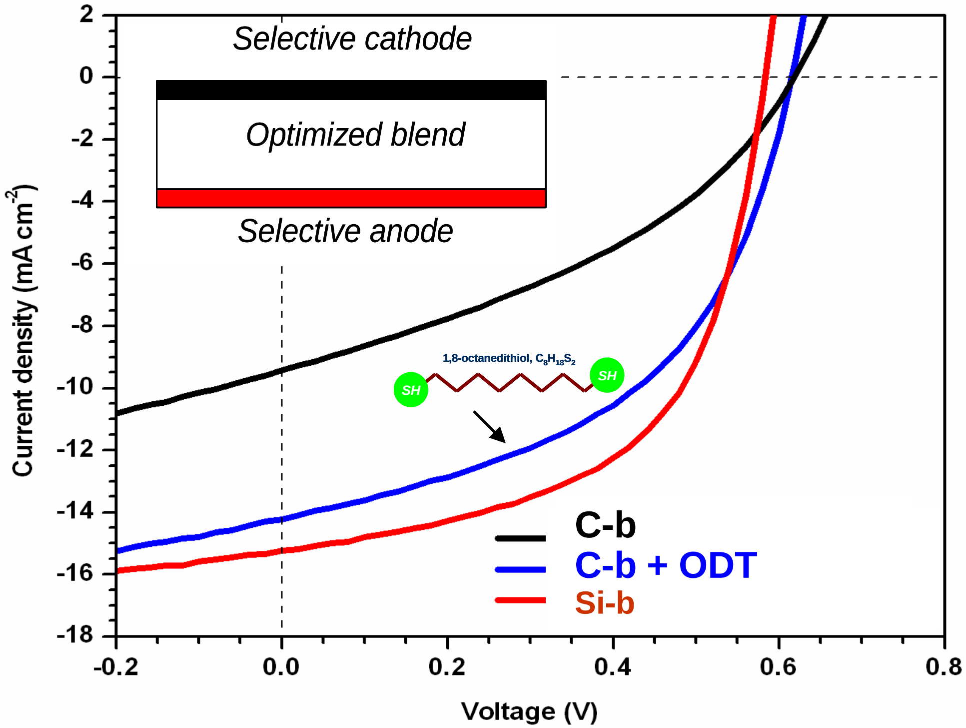


Puddle-cast films of Si-PCPDTBT:PC70BM annealed at 25°, 130° and 200°C

Films of pristine Si-PCPDTBT as cast and annealed (red line).

ok, some crystallinity..

Photovoltaic devices



- **C-b:**
  solar cells dominated by losses
- **ODT:**
  reduces losses (& bad flavour..)
  <u>The effect seems to be partial!</u>
- **Si-b:**
  ΔJsc ~ +6mA/cm^2
  ΔFF ~ +50%

we LOOK INTO…

	Jsc (mA/cm^2)	FF	Voc (V)	Eff(%) corrected
C-b	9.4	0.37	0.62	2.2 (up to 3.5%)
C-b + ODT	14.2	0.49	0.62	4.3 (up to 5%+)
Si-b	15.2	0.57	0.58	5 (up to 6%+)

2D TEM: overlay

Ideal TEM Bright-Field mode

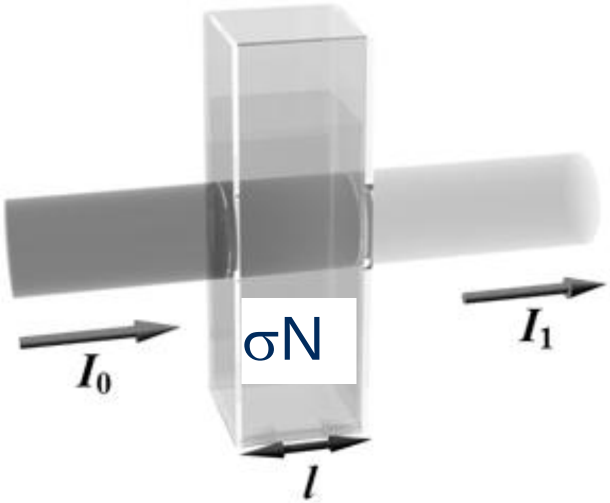
Beer-Lambert law

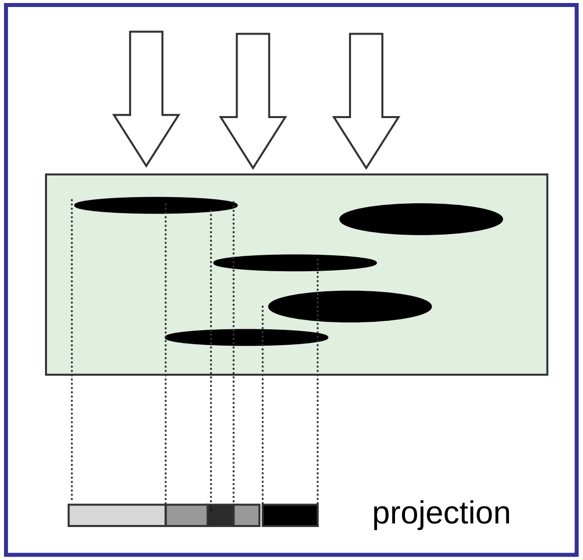
$$T = I/I_0 = 10^{-\sigma N l}$$

σ=absorption cross section

N=density of absorbers

l=film thickness





Generally: density$_{polymer}$ <density$_{fullerene}$

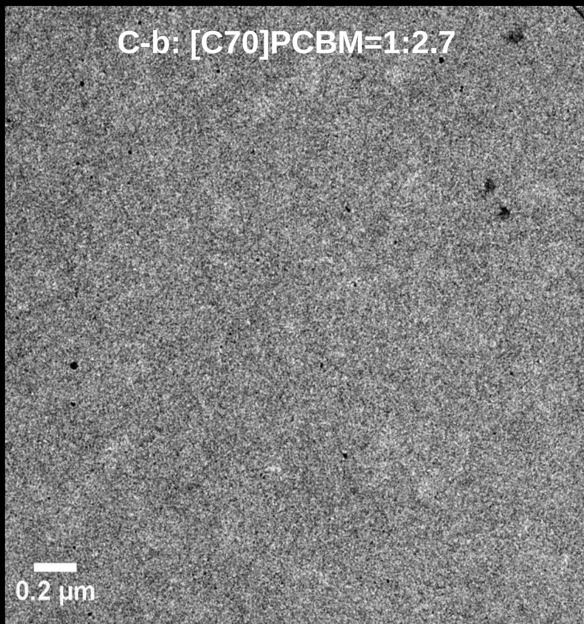
• Ideally BF TEM should produce a grey scale image with local intensity reduced by the number of fullerene molecules along the beam path

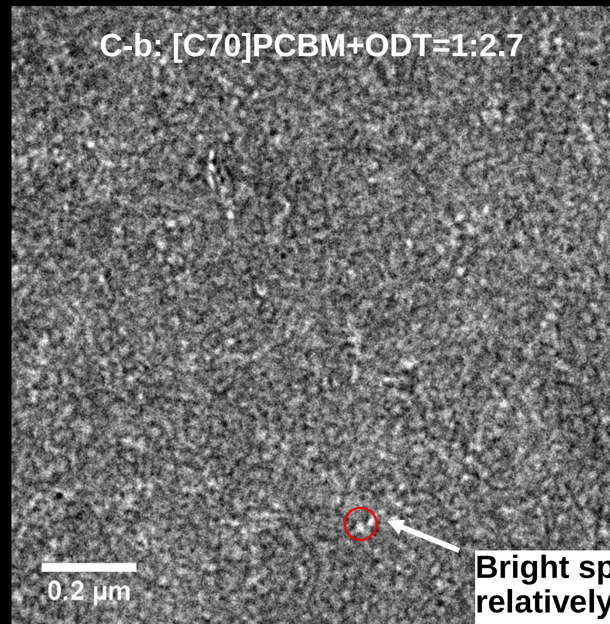
•ratio between the fullerene size/ film thickness determines the relatively low contrast in highly intermixed systems

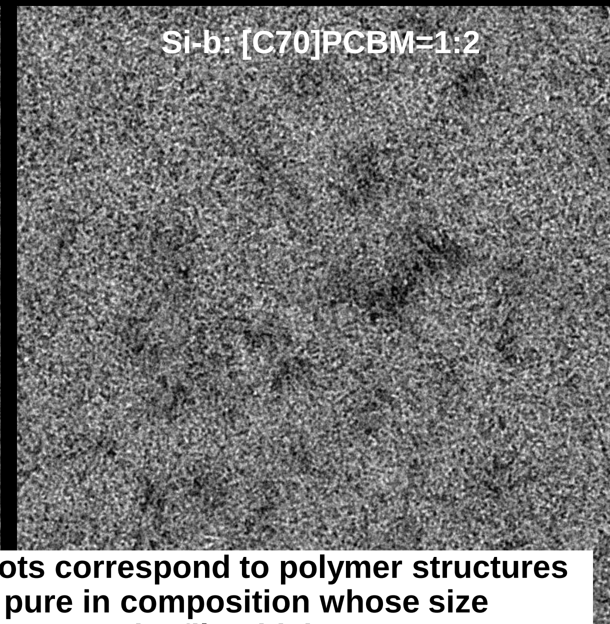
• Diffraction contrast due to crystallinity may add

Bright Field TEM

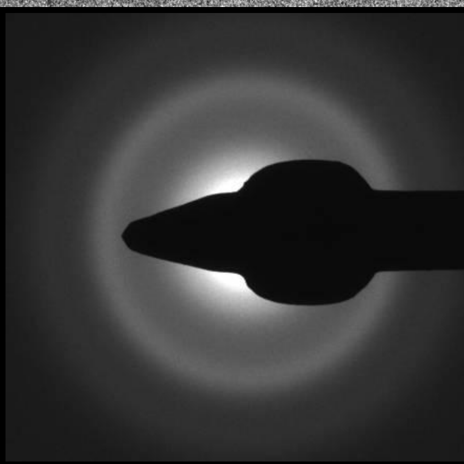
Films prepared as for solar cells on PEDOT:PSS, thickness 90-120nm

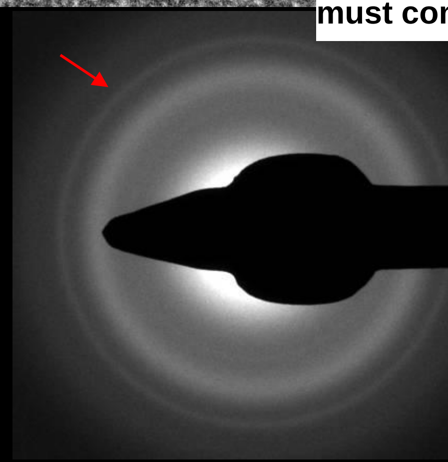


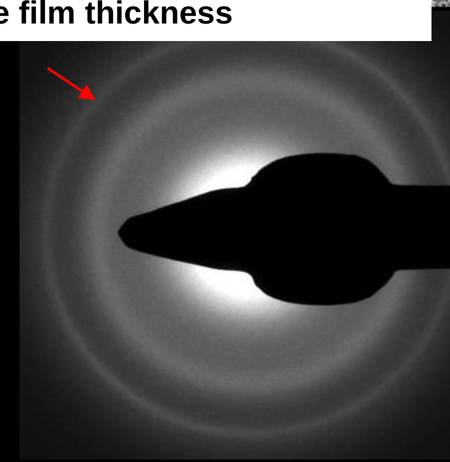




Bright spots correspond to polymer structures relatively pure in composition whose size must compare to the film thickness



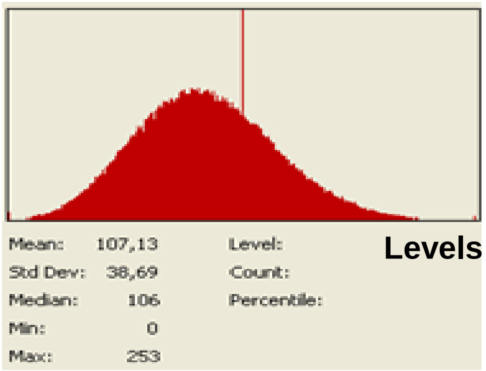




Rms roughness of all films 1<r<5nm

TEM microscope resolution < 1nm

BF-TEM - DFT analysis



Typical image size: 1024x1024 pixels

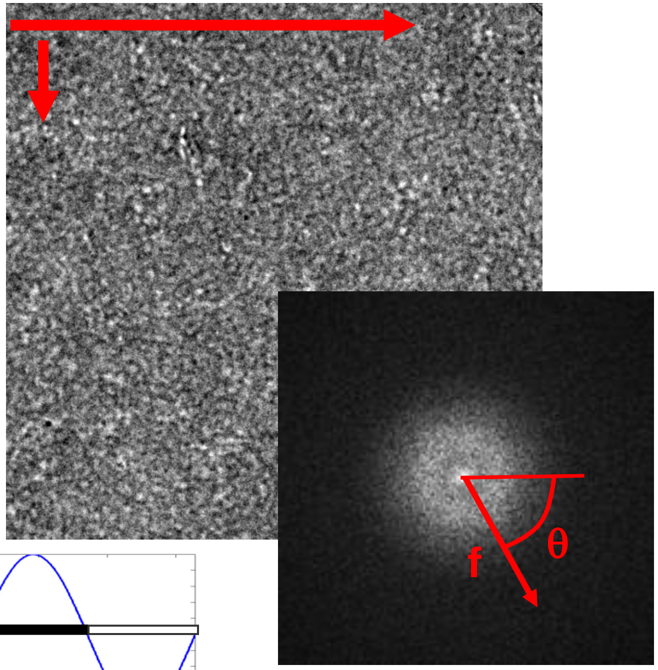
256 grey levels (8 bits)

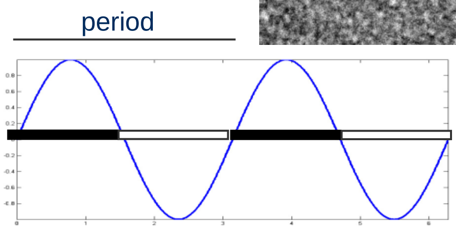
Human eye can distinguish <100 grey levels
(maybe ties on white shirt under ideal illumination..)

I(x,y)=amplitude contrast intensity

$$PSD(f_x,f_y) = \frac{1}{L^2}\left|\int_0^L\int_0^L e^{-i2\pi x f_x} e^{-i2\pi y f_y} I(x,y)\,dx\,dy\right|^2$$

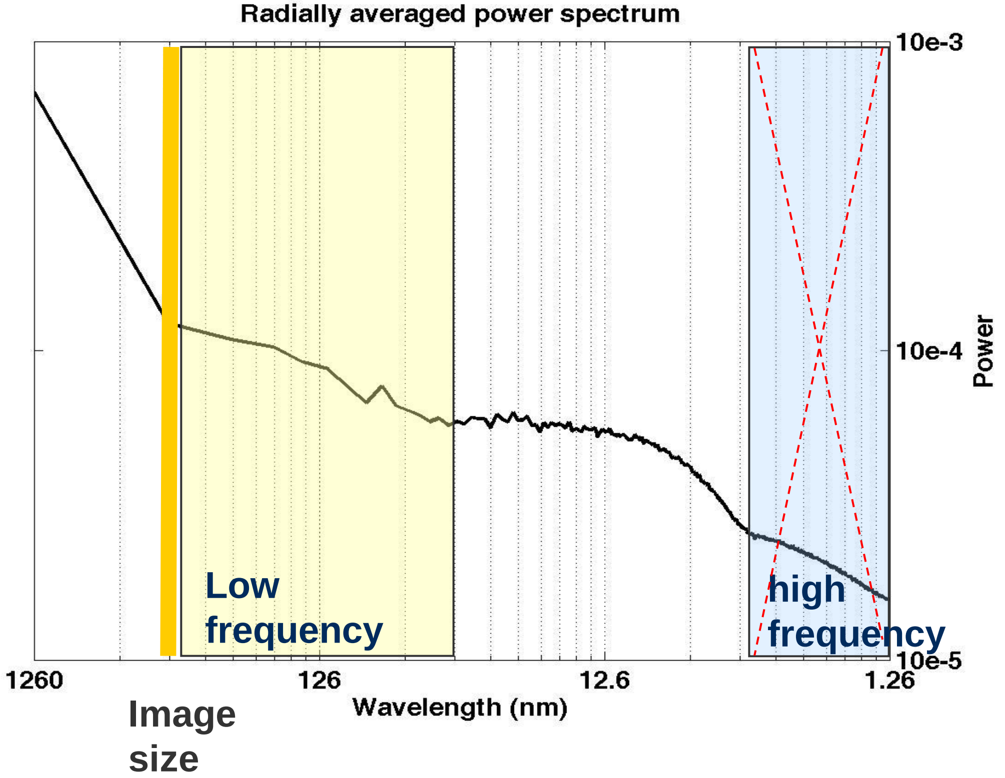
$$PSD(f) = \frac{1}{2\pi}\int_0^{2\pi} PSD(f,\theta)\,d\theta$$





BF-TEM – 1D image analysis

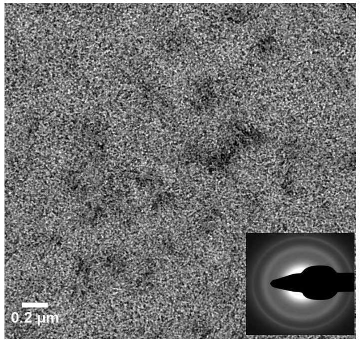
Si-b:PCBM



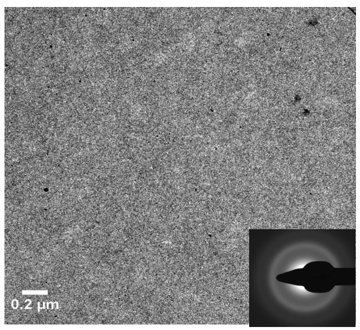
PSD analysis

SFS = Smallest Feature Size

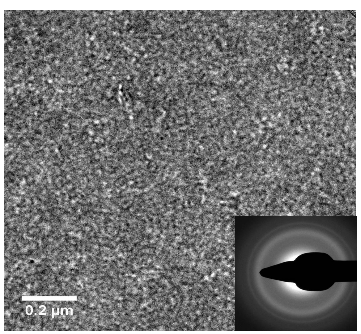
Si-b blend

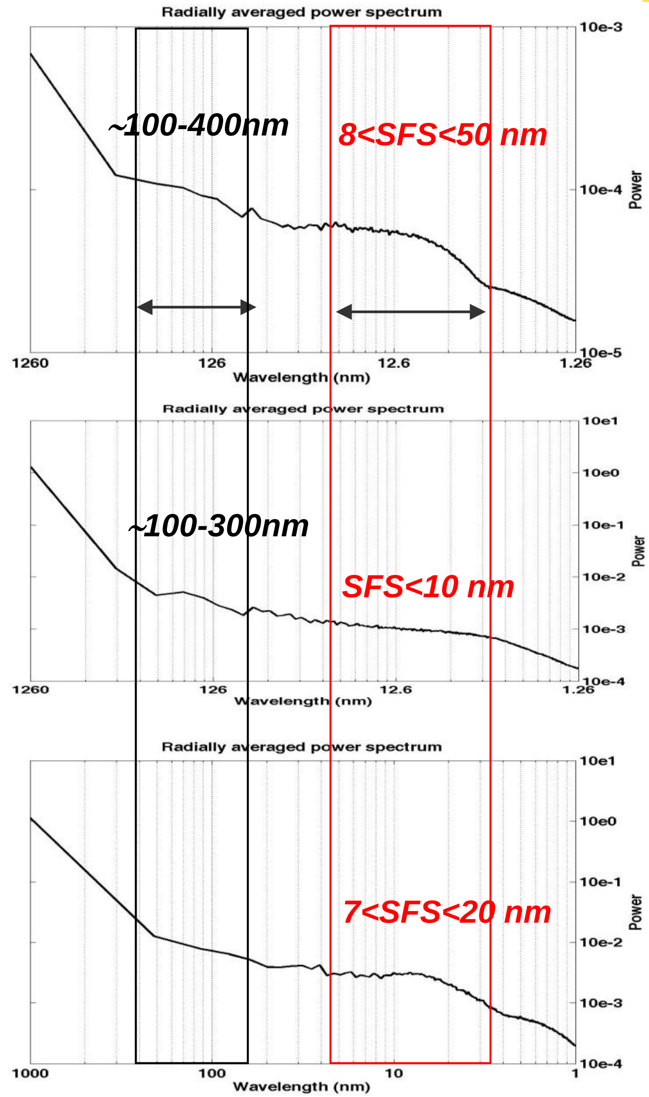


C-b blend



C-b blend+ODT





Meso and nanoscale phase separation

Molecularly dispersed

Regular features, no mesoscale

But low resolution images do not help…

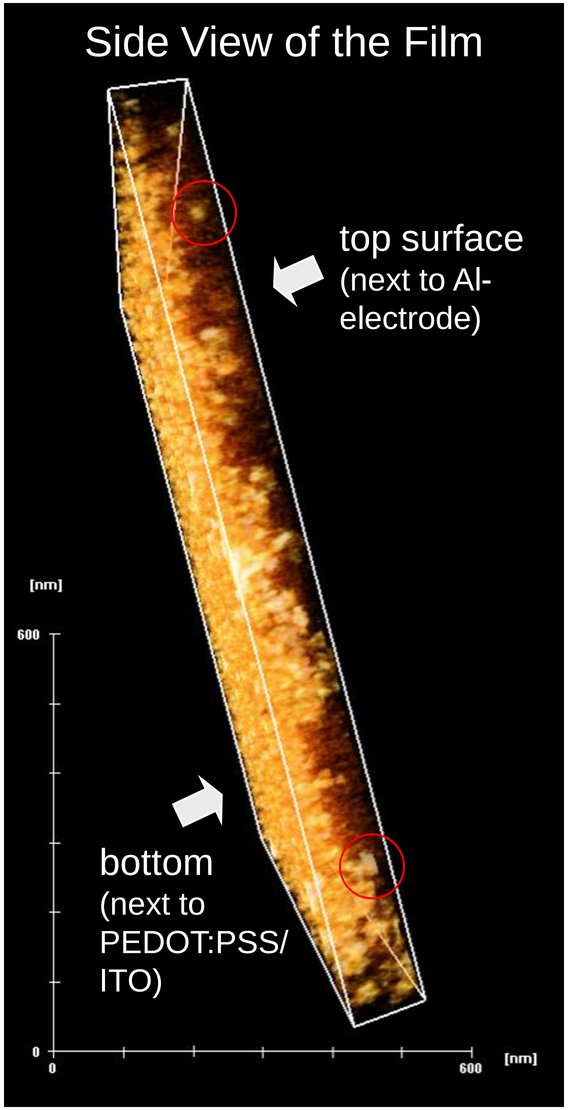
TEM on floated films – PSD analysis

What can we deduce from TEM/PSD analysis?

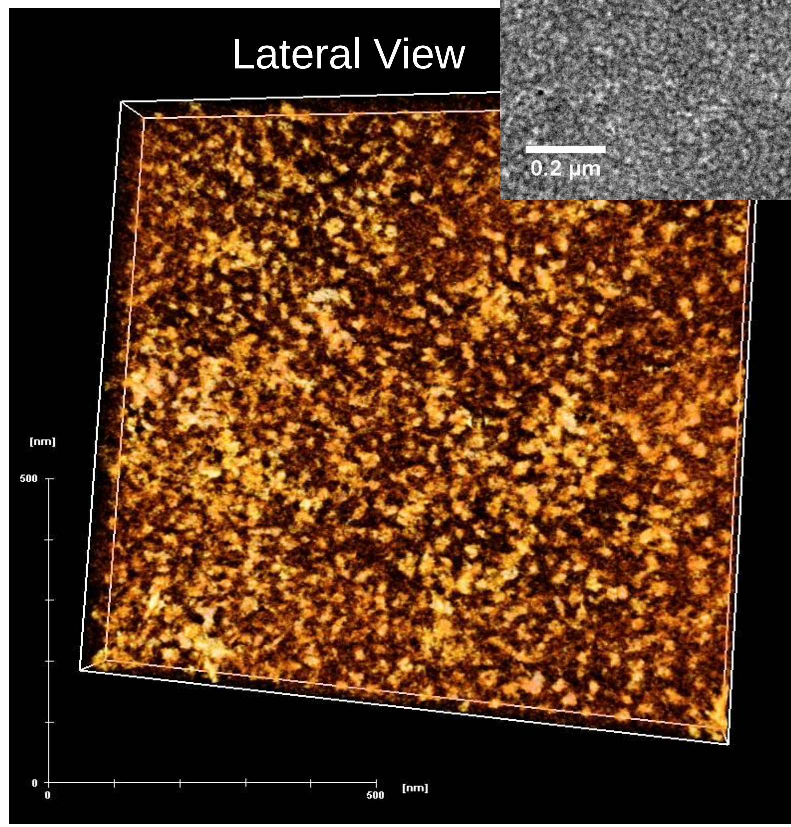
- large features in TEM have generally depth comparable to the lateral size
- C-b blends tend to be amorphous and molecularly dispersed even at high fullerene loads, FS<10nm
- ODT induces phase separation and produces regularly distributed structures with charactersitic size of FS ~ 10-20nm
- Si-b blends phase separate at the meso and nanoscale, with averaage FS >>10nm

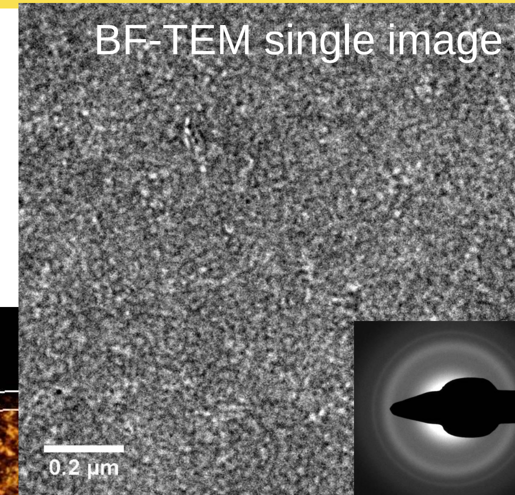
Feature size:
C-b < C-b+ODT< Si-b

TEM Tomography



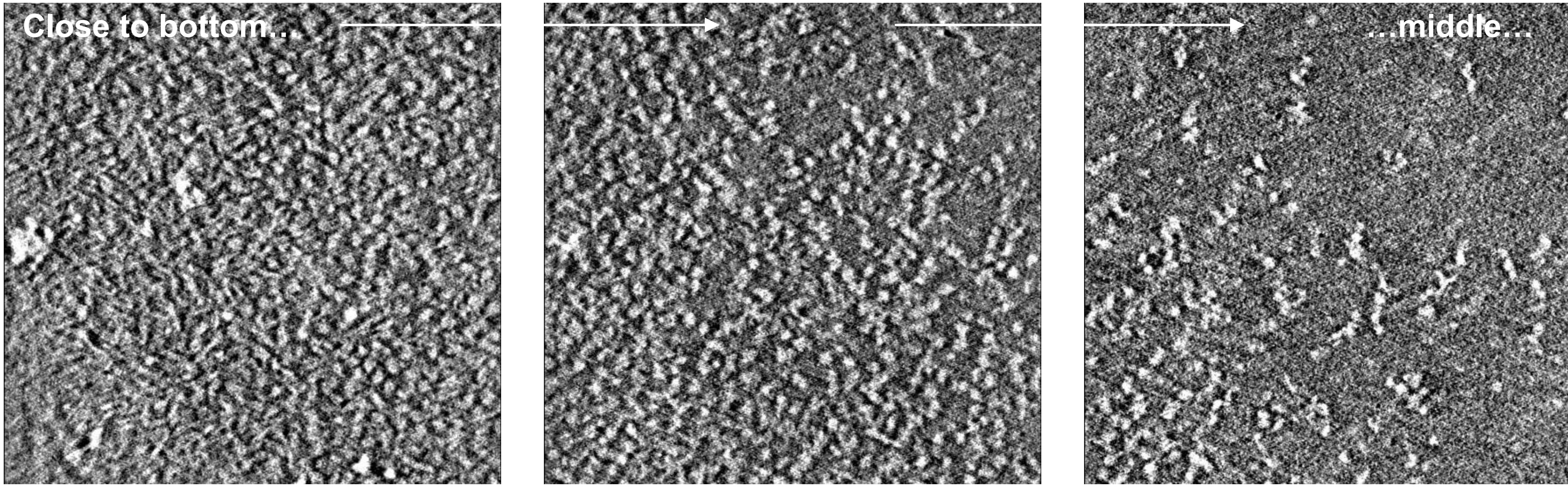
C-PCPDTBT:PC70BM +ODT



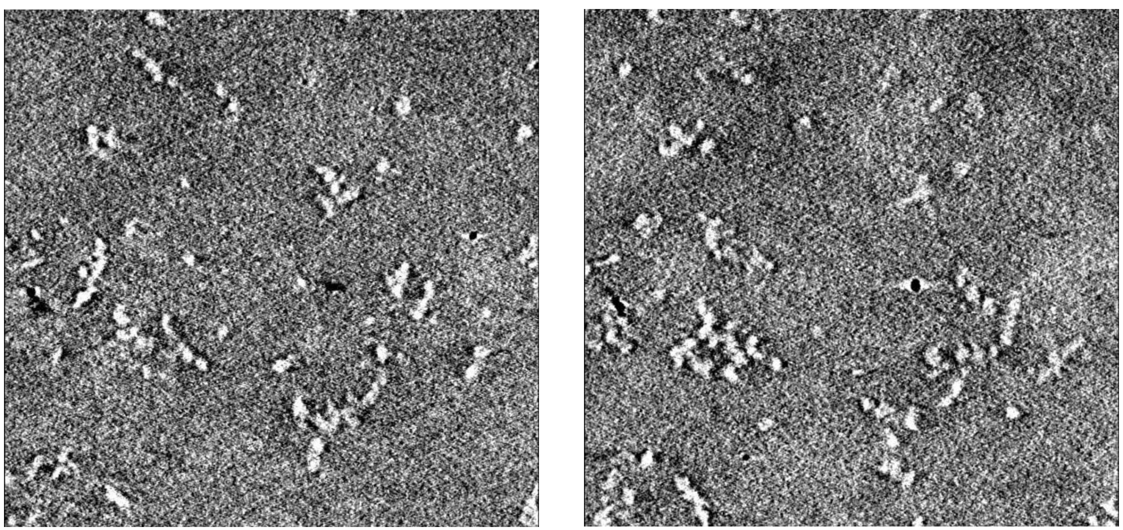


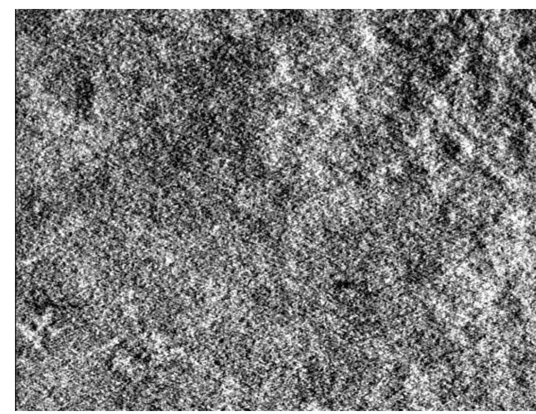
Polymer-rich areas are visualized as bright orange spots

Outcome of electron tomography: slices out of the 3D data stack



…middle… …top of the film





The gradient in composition/morphology confirms that the ODT action is incomplete across the film

Polymer-rich areas look brighter. Slice dimensions are 1082 nm x 1082 nm.

Confinement?

For ε=3-4, the capture radius ~ 16nm

$$r_c = \frac{q^2}{4\pi\varepsilon_0\varepsilon_R kT},$$

SFS = Smallest Feature Size	Max EQE
SFS C-b << r_c	35%
SFS C-b +ODT ~ r_c	55%
SFS in Si-b is distributed around r_c	63%

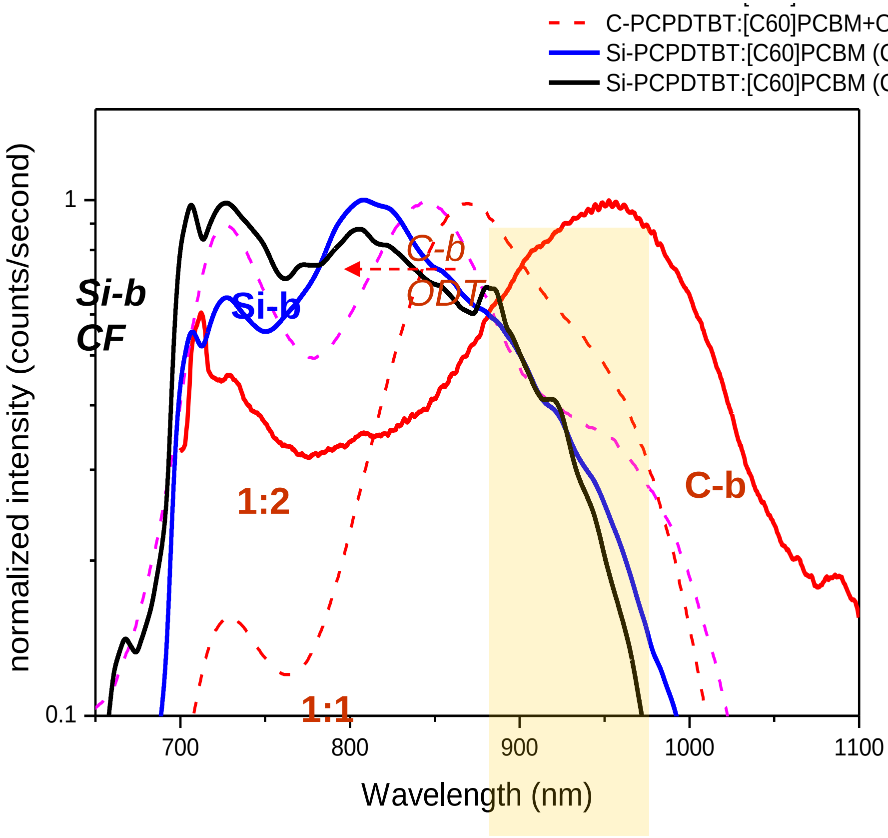
- Losses in C-b blends appear related to the isolated fullerene molecules/nanoclusters

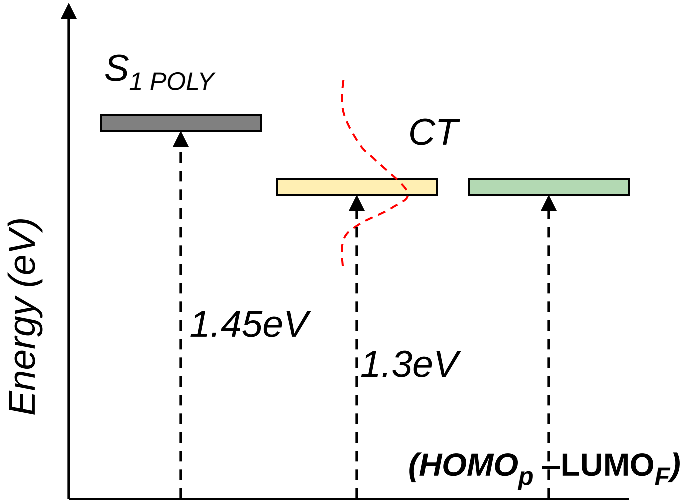
- in C-b blends, ODT helps the fullerene to demix leading to the formation of small polymer-rich clusters

- Si-b forms an optimal phase separation due to a strong tendency to aggregate/crystallize and to a favourable hierarchy of domain size

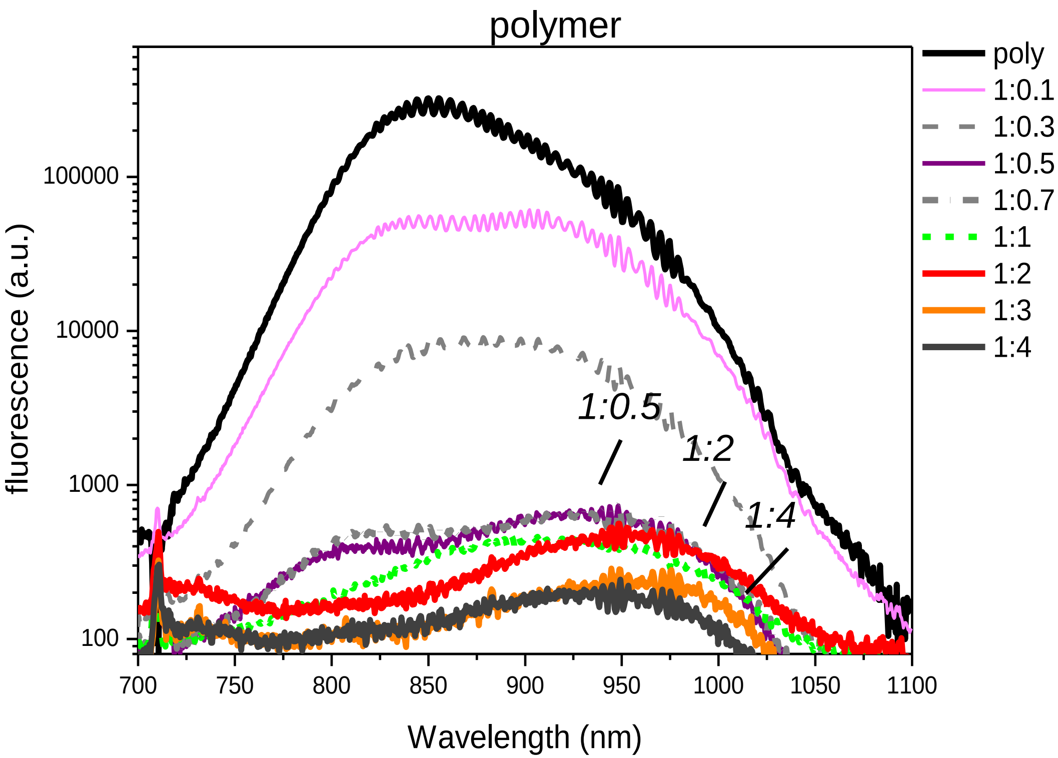
CT emission

- An emissive CT (1.3eV) is present as decay path in C-b. The width of the emission correlates to a distribution of CT energies related to D/A distances
- films prepared with ODT show a quenched CT emission, quenching increases with the fullerene content
- The main emission peak of CTC is increasingly blue-shifted by adding fullerene





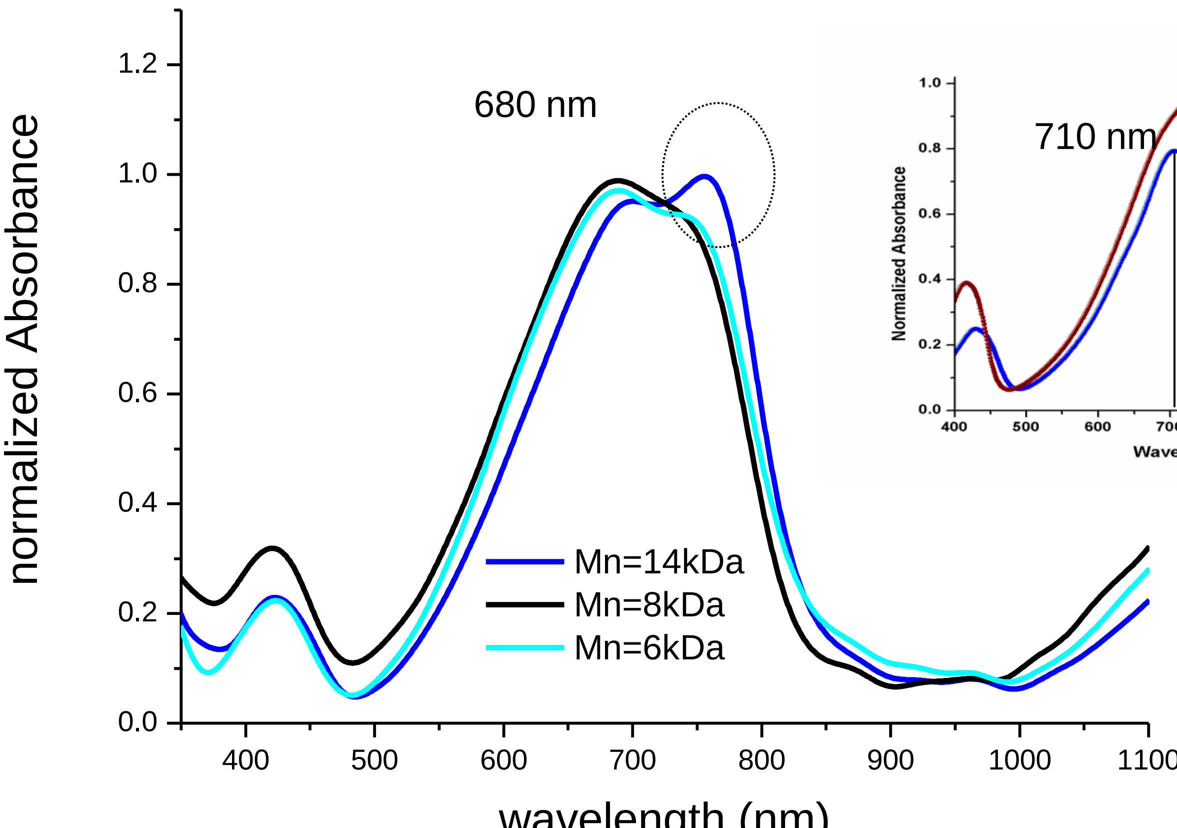
C-b: compositional dependence of CT emission

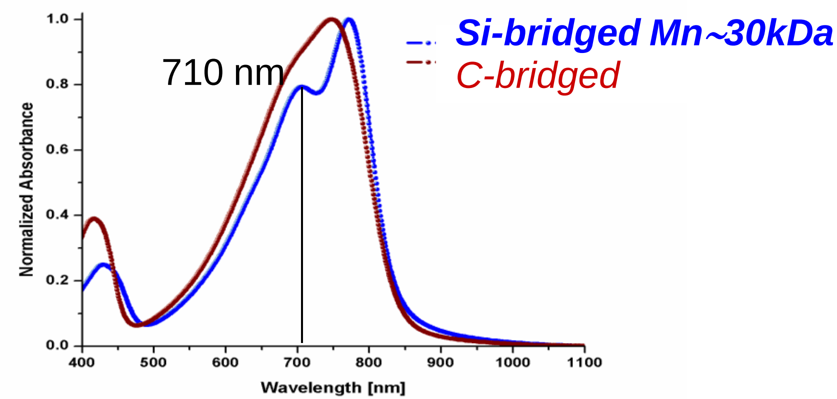


- **in C-b high quenching of the main polymer peak is required to observe CT**
- **at high fullerene content the quenching stays complete**

Nano-morphology vs. moelcular weight in Si-bridged blends

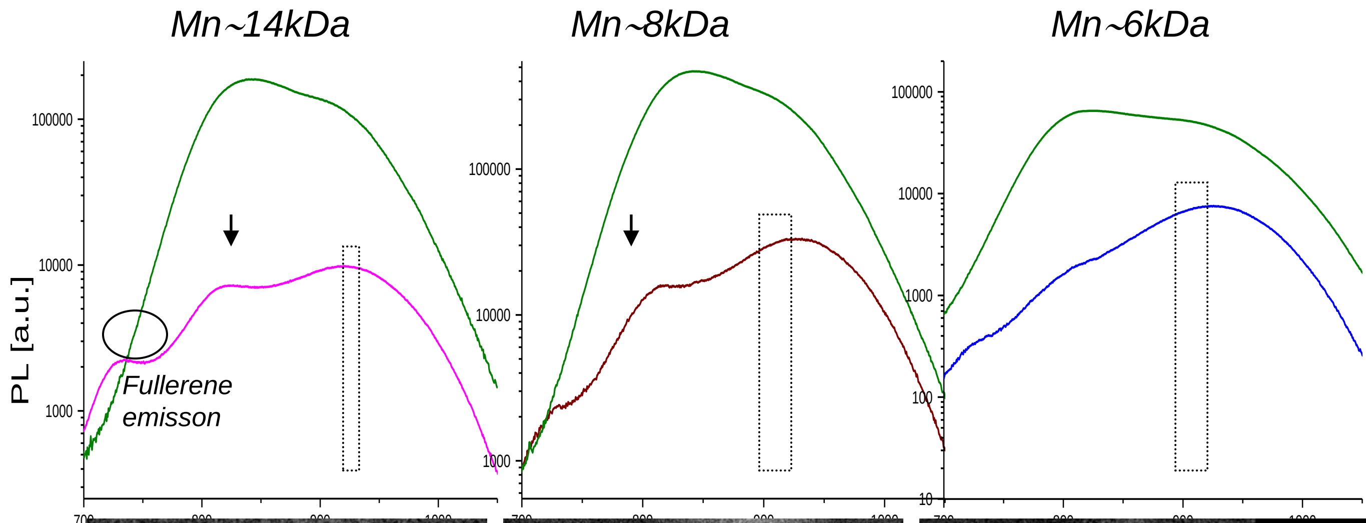
Si-bridged	Mn (Da)	Mw (Da)	PDI
low-1	14324	20357	1.42
low-2	8047	12931	1.61
low-3	6061	9598	1.58

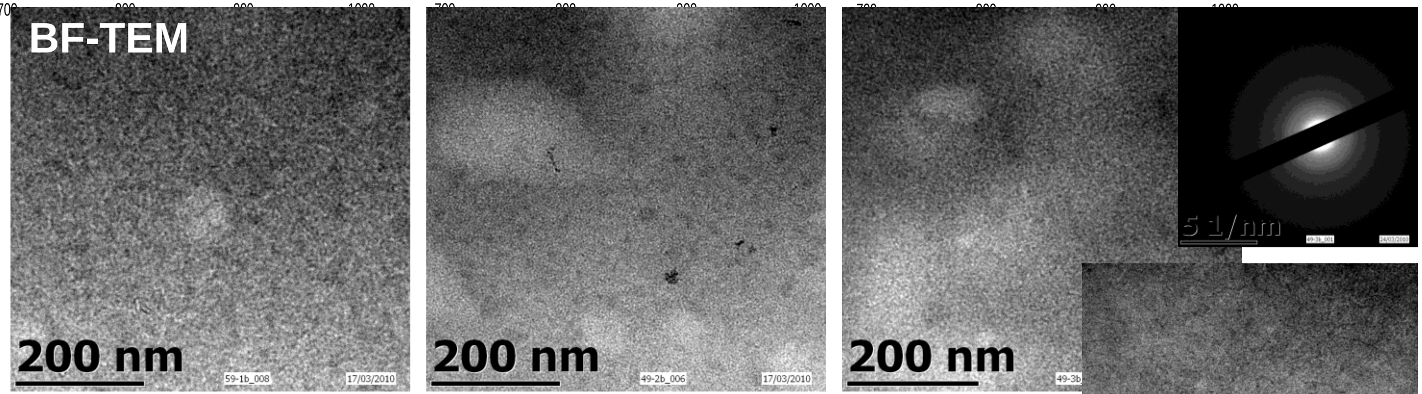


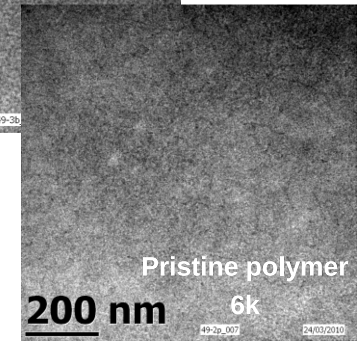


Excitation 405nm,3 mW
Si detector

Low molecular Si-b blends (1:2)

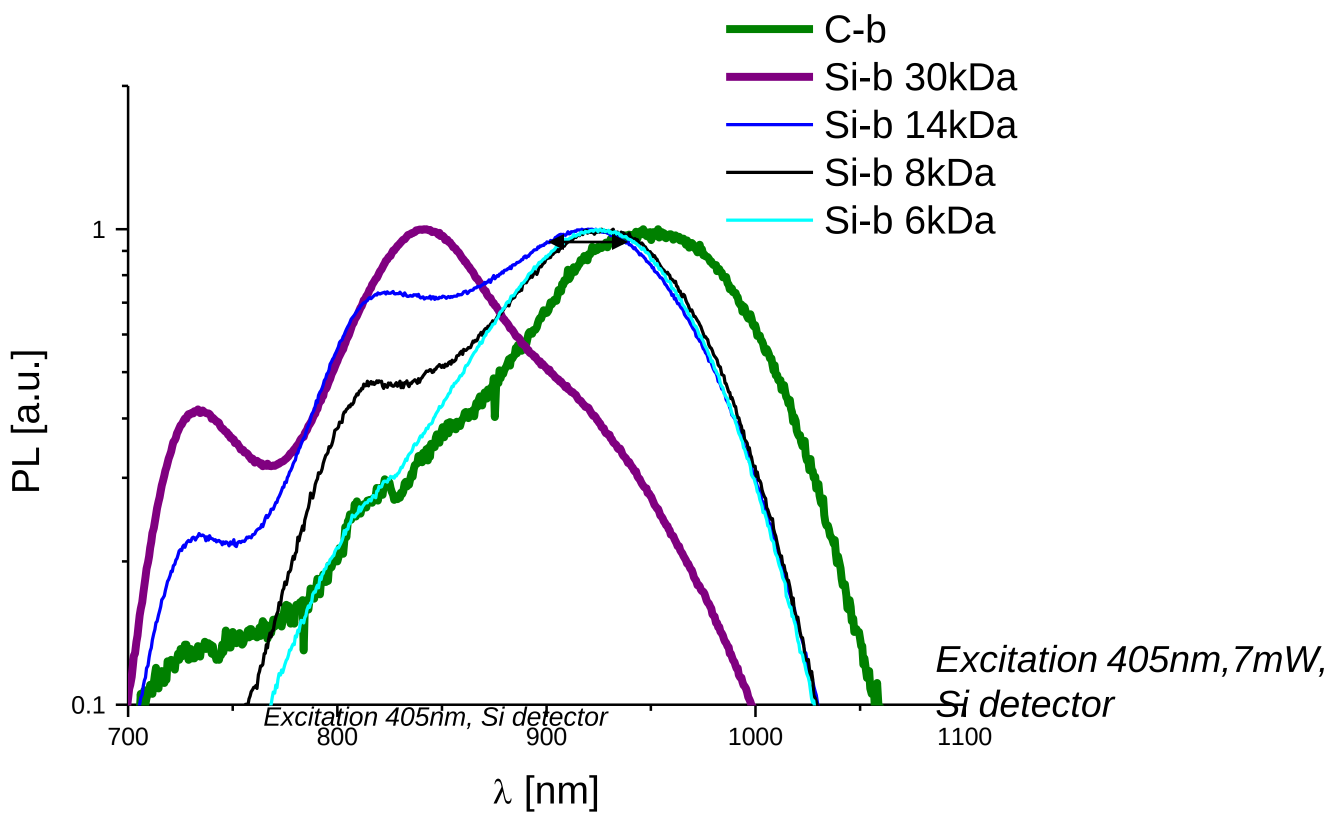






- Large polymer aggregates, likely due to not fully dissolved material, coexist with a highly intermixed morphology
- The quenching of the main polymer emission peak is between 10 and 100 times.
- PCBM emission disappears by reducing Mn. All blends appear amorphous by Electron Diffraction.
- The polymer emission peak at 830 decreases by reducing Mn, revealing a well defined peak at 930-950nm

Nano-morphology vs. moelcular weight in Si-bridged blends



- **by reducing Mn the main polymer emission is progressively quenched, together with the fullerene emission at 710nm**

Conclusions

- The morphological analysis of Si-bridged:[C70]PCBM in comparison to its carbon-bridged analogous leads to correlate the improved photogeneration to slightly larger phase separation.

- Films processed under optimized conditions show in TEM a feature size in the length scale in the range of the exciton diffusion length.

- The higher chain packing and crystallinity of the Si-bridged copolymer is thought to be the driving force for the fullerene demixing

- CT emission in C-PCPDTBT blends shows relation to the losses affecting the system, and may be an indicator of the degree of intermixing in the blend.
- An NIR emission peak was found in well intermixed Si-bridged blends based on very low molecular weight material, indicating a close relation between intermixing and infrared emission

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