Wake Forest Nanotechnology Conference
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Conjugated Polymers Based on Benzodithiophene for Organic Solar Cells

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Current Industry Leader: Si Solar Cells

Modules

- 12 % efficiency
- $350/m^2$
- $\$3/W_p$ (from manufacturer)
- $\$6/W_p$ (installed)

$\$1/W_p$ ~ $0.05/kWh

Comparison

DOE numbers

Average cost of PV cell electricity
(based on single crystal Si): $.27/kWh
Today's grid electricity: $0.06/kWh

$1/$W_p$ ~ $0.05/kWh

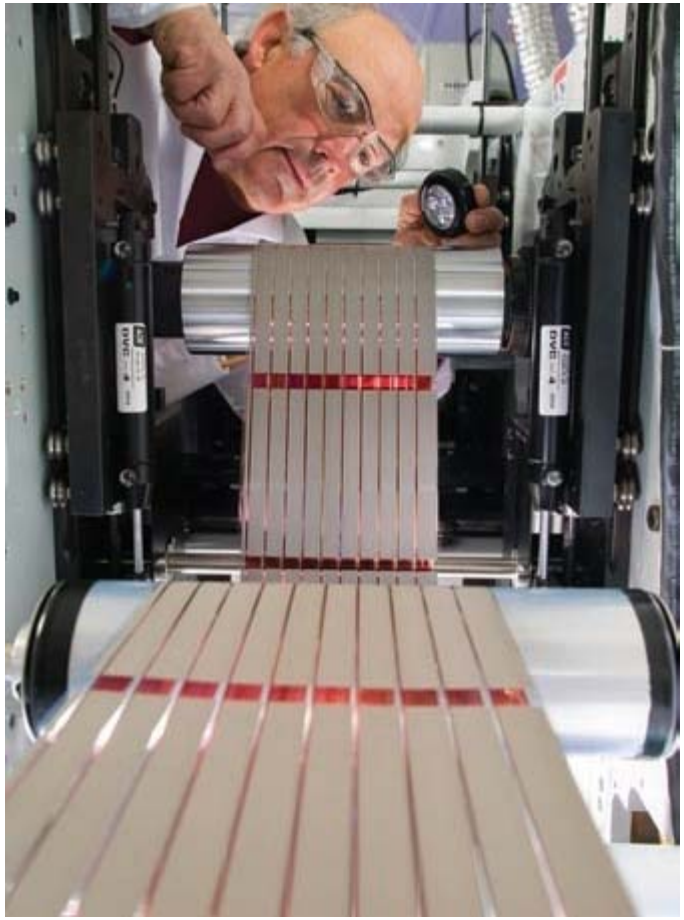
Materials	Efficiency	Materials Cost	Installed Cost	$/kWh
Poly Si	12-14%	Expensive	$4-6/$W_p$	$0.20-0.30
CIGS	10-11%	Cheap	$4/$W_p$	$0.20
Organic	**5-6%**	Cheapest	$3/$W_p$ or lower	$0.15 or lower

If the efficiency could be further increased, the $/$W_p$ would be even lower!

Low Cost Alternative: Organic Solar Cells

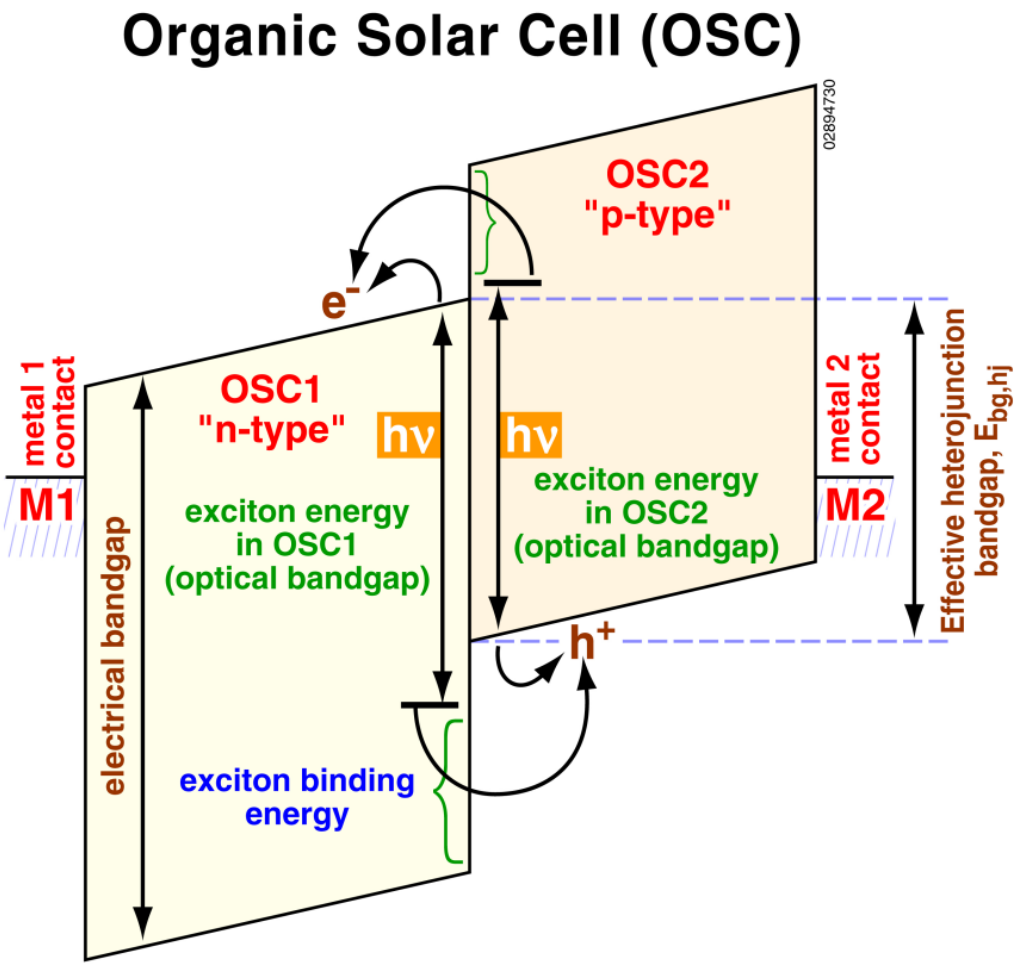
Advantages of Organic Semiconductor (OSC) Based Photovoltaics Over Inorganic

- Low cost
- Light weight
- Compatible with plastic substrate and can be fabricated using high-throughput printing techniques (large area; flexible)
- High optical absorption coefficients
- Band gap & energy levels can be fine-tuned through molecular design



Konarka

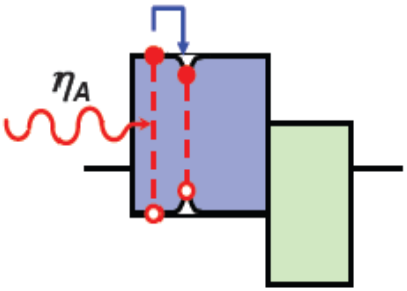
Excitonic Solar Cell: Donor-Acceptor Interface



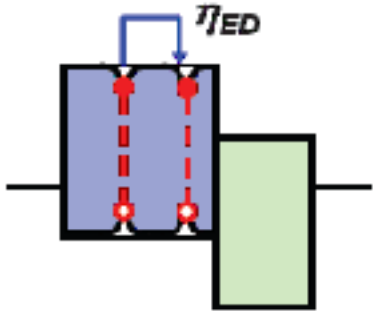
Fundamental Physical Processes in OPV

It's All about Exciton!

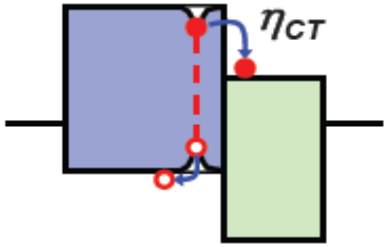
Light absorption (Exciton generation)



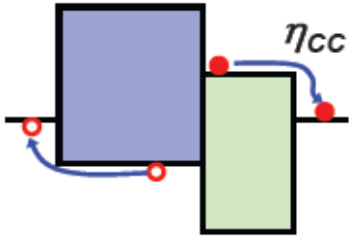
Exciton diffusion



$$\eta_{EQE} = \eta_A * \eta_{ED} * \eta_{CT} * \eta_{CC}$$

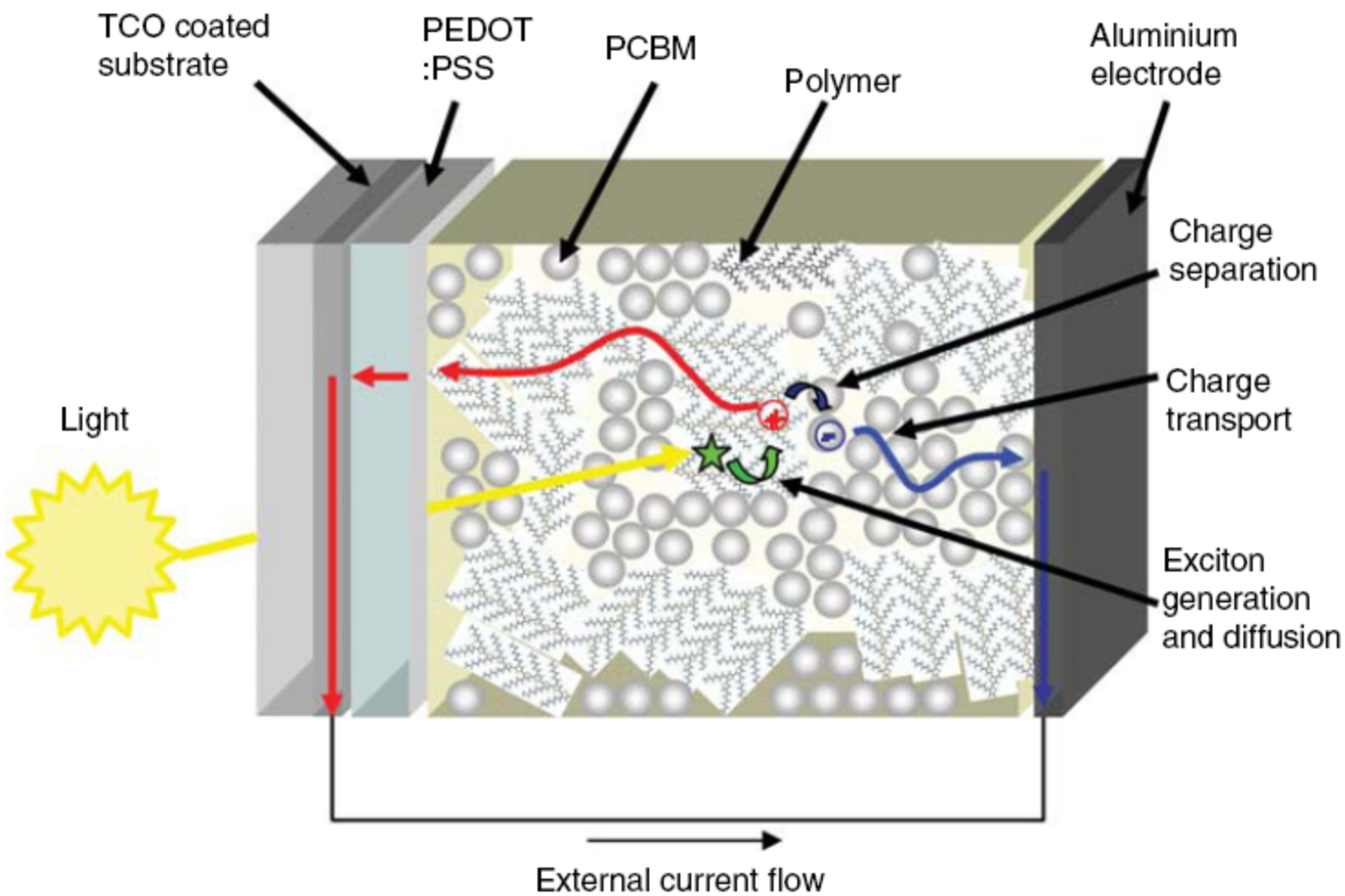


Charge transfer (Exciton dissociation)



Charge collection

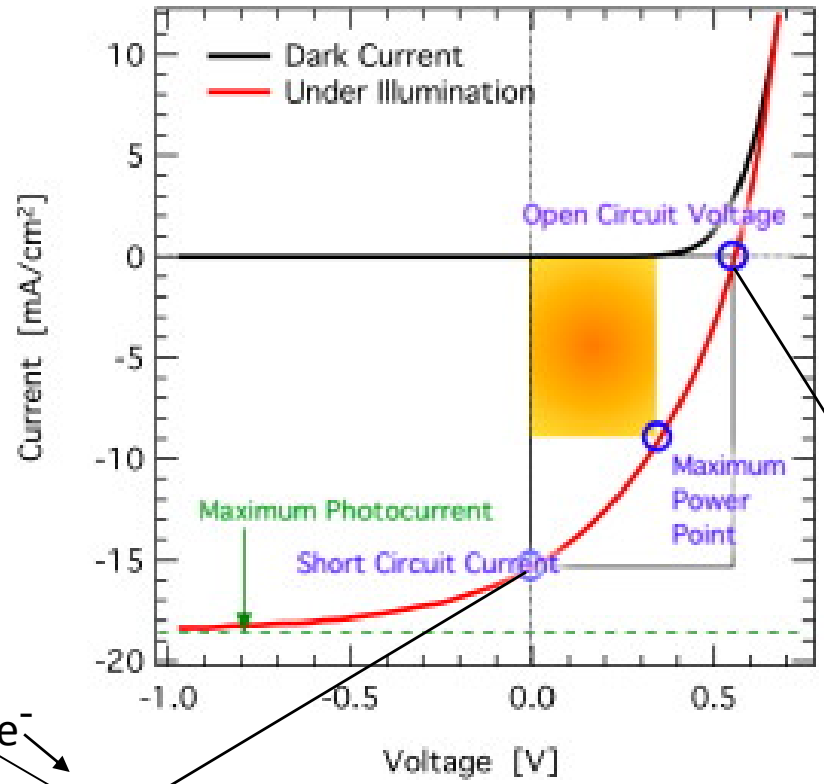
Bulk Heterojunction (BHJ) Polymer Solar Cells

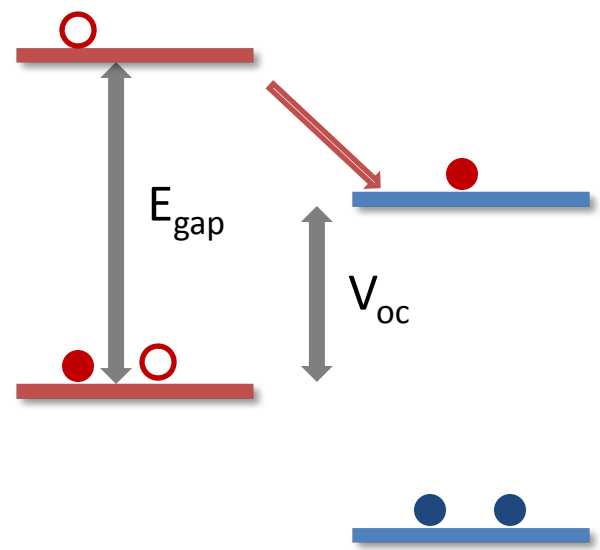


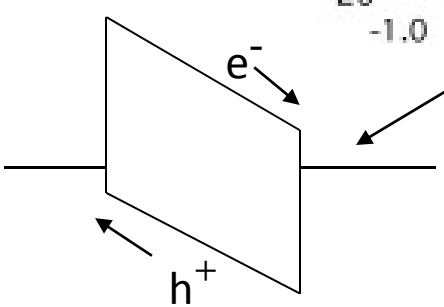
Brabec, C. & Durrant, J. *MRS Bulletin* **2008,** *33,* 670

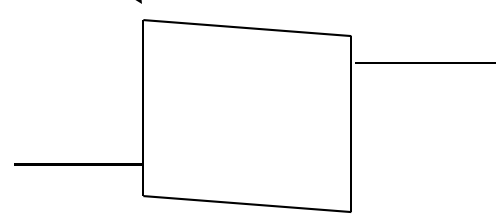
Characterizing Solar Cells

Fill factor = $P_{max}/J_{sc}V_{oc}$









J_{sc} = short circuit current

V_{oc} = open circuit voltage

J_{sc} is determined by how many charge carriers reach the electrodes before recombination occurs

V_{oc} is determined primarily by the energy levels in the system.

Efficiency Definitions

External quantum efficiency *(h_e)*

- Also known as IPCE (incident photon to converted electron) efficiency
- Electron out/photons on the device

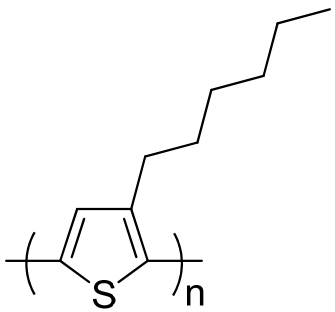
Internal quantum efficiency *(h_i)* = Electrons out/photons absorbed

h_i can be very high in a thin device because the electric field is high and the charge carriers don't have far to go, but h_e is low because not many photons are absorbed.

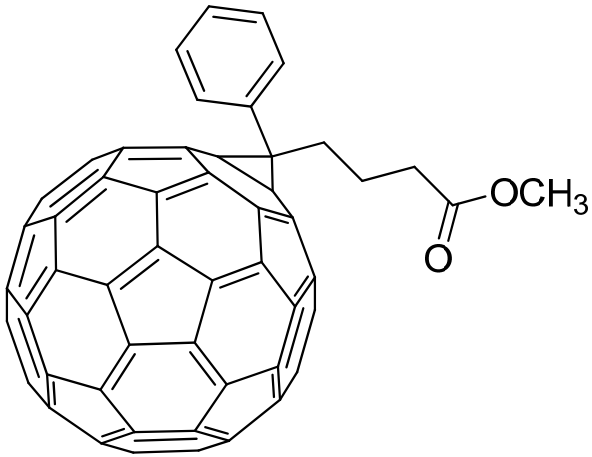
Energy conversion efficiency $= \dfrac{\text{electrical power generated}}{\text{incident optical power}}$

$$= \frac{V_{oc} J_{sc} FF}{P_{in}}$$

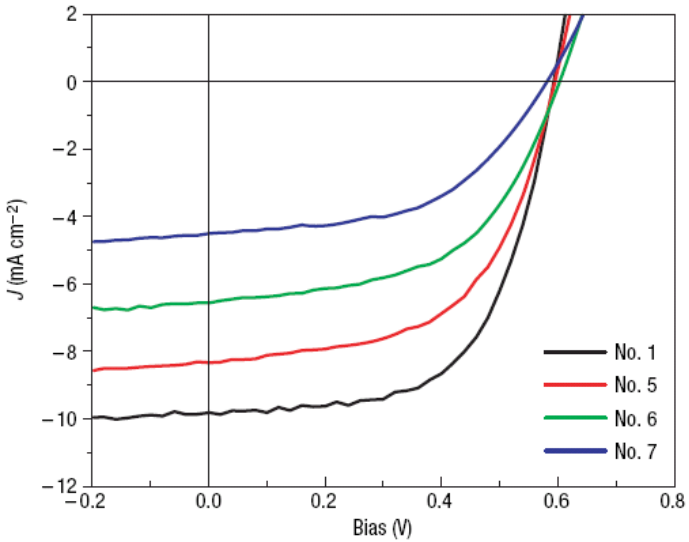
State-of-the-art P3HT/PCBM

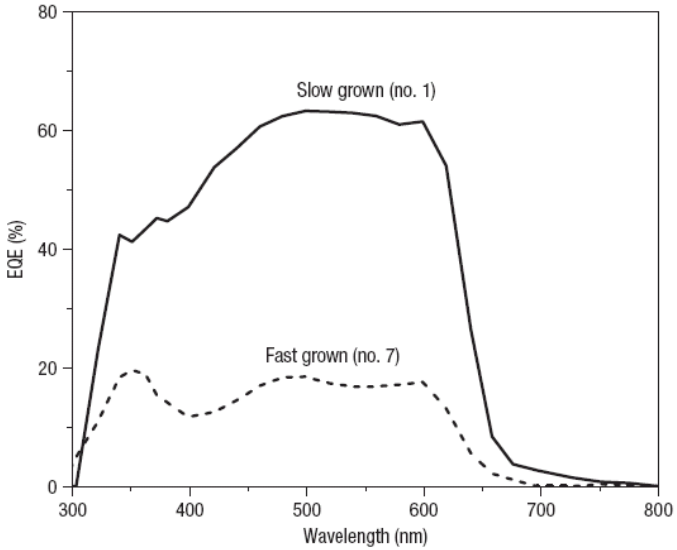


P3HT



PCBM





J_{sc} > 10 mA/cm^2

V_{oc} > 0.6 V

FF > 65%

Efficiency ~ 5%

Yang, Y. *et. al. Nature Mater.* **2005**, *4*, 864

Heeger, A. J. *et. al. Adv. Funct. Mater.* **2005**, *15*, 1617

A Bandgap Challenge

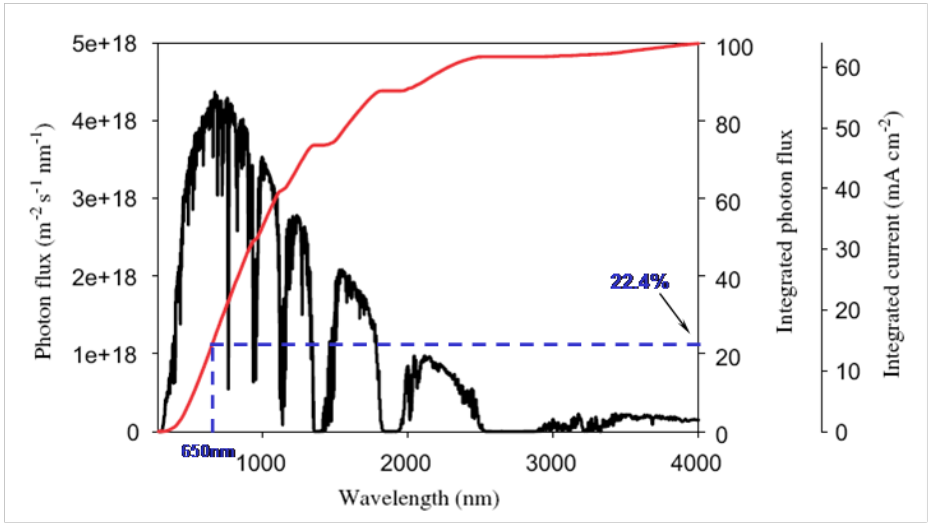
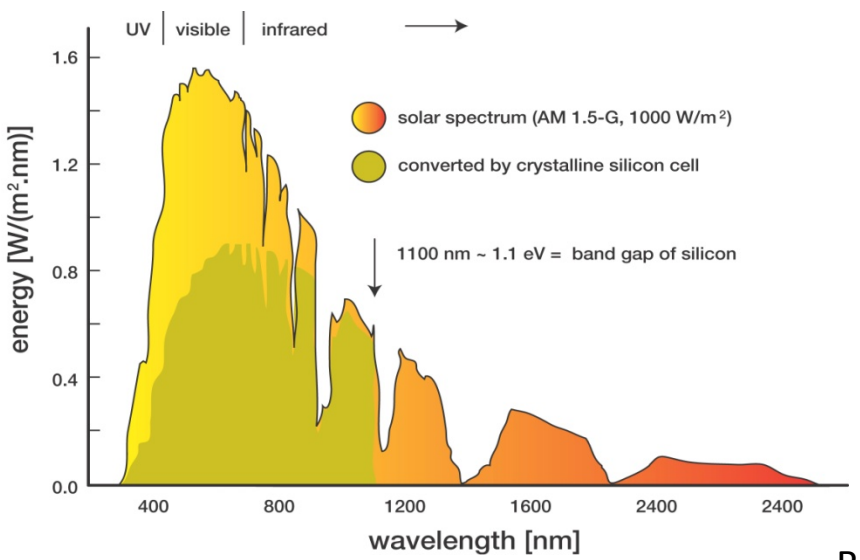


Table 1
The integrated photon flux and maximum current density available for a PV that harvest light from 280 nm up to the wavelength quoted assuming that every photon is converted into one electron in the external circuit

Wavelength	Max. % harvested (280 nm →)	Current density (mA cm^{-2})
500	8.0	5.1
600	17.3	11.1
650	22.4	14.3
700	27.6	17.6
750	35.6	20.8
800	37.3	23.8
900	46.7	29.8
1000	53.0	33.9
1250	68.7	43.9
1500	75.0	47.9

The current density may increase if the polymer is applied in a bulk heterojunction device, due to the absorption of the acceptor beyond the band gap of the donor.



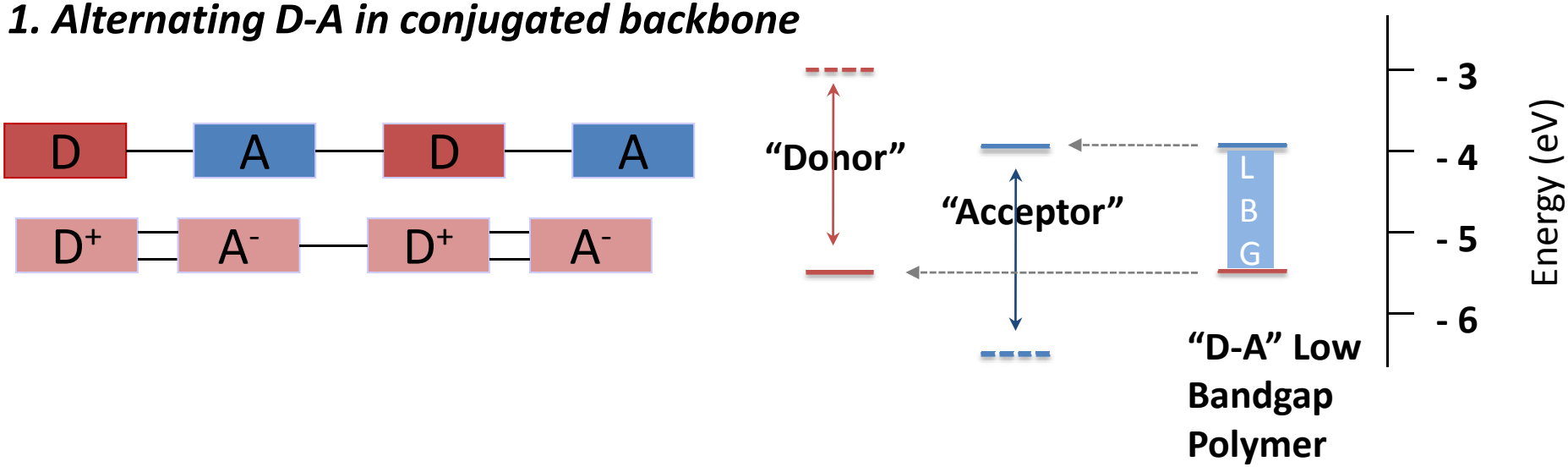
Factors:

- Band gap
- HOMO, LUMO energy level
- Morphology

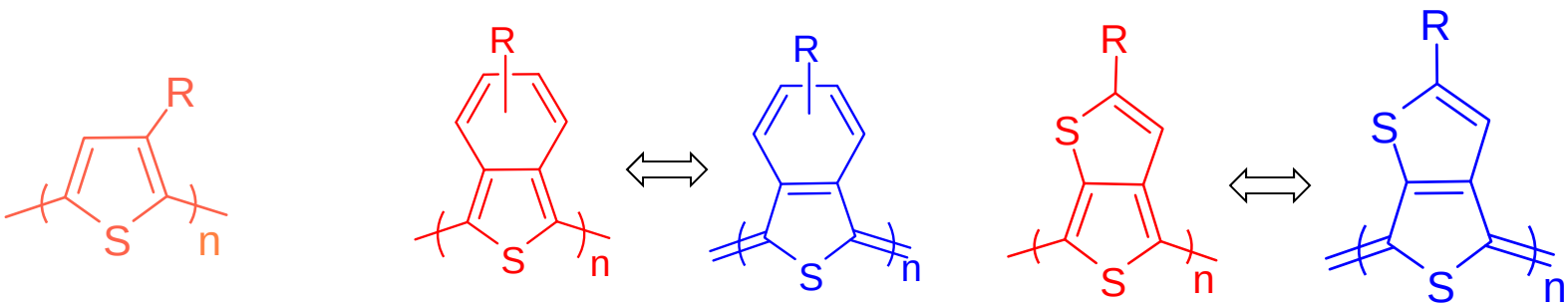
Bundgaard, E. *et. al. Solar Energy Materials and Solar Cells* **2007**, *91*, 954-985.

Controlling Bandgap of Conjugated Polymers

1. Alternating D-A in conjugated backbone



2. Incorporating more stable quinoid resonance structures in the ground state



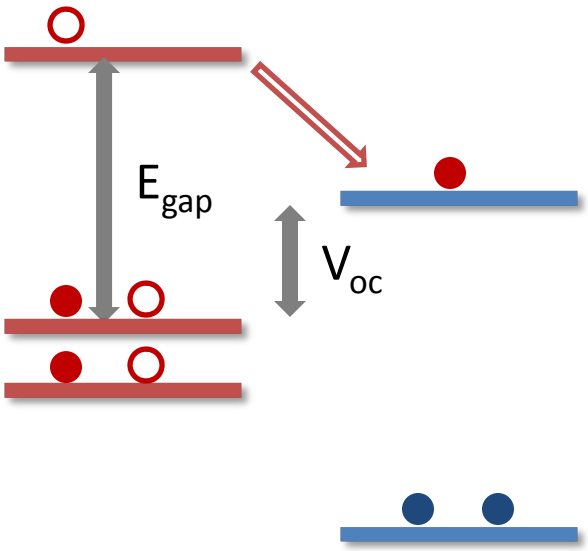
1.7-1.9 eV

1.0-1.3 eV

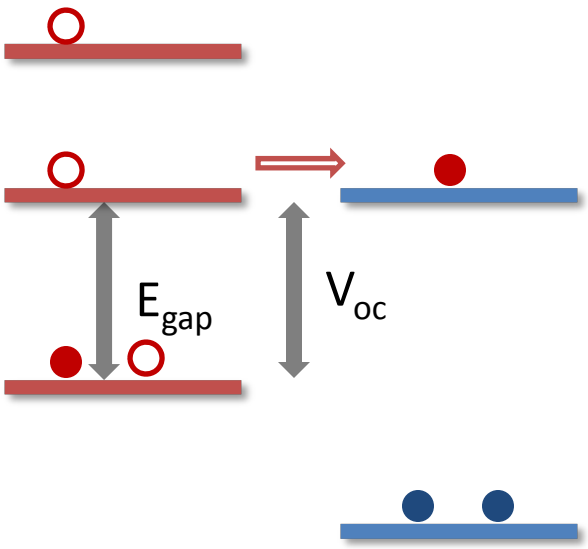
0.9-1.0 eV

Different Types of Low Bandgap Polymers

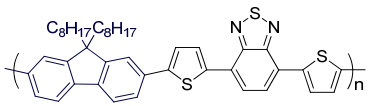
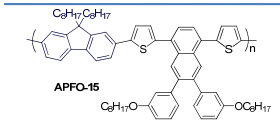
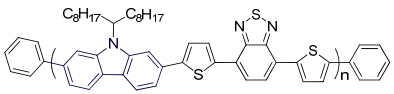
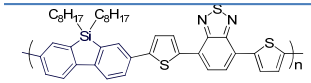
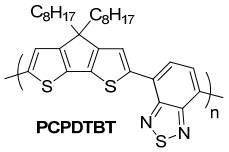
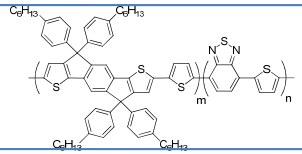
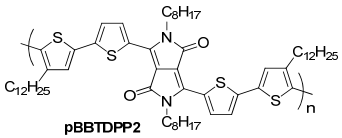
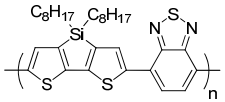
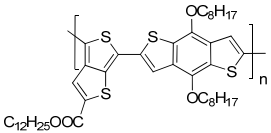
Type A



Type B

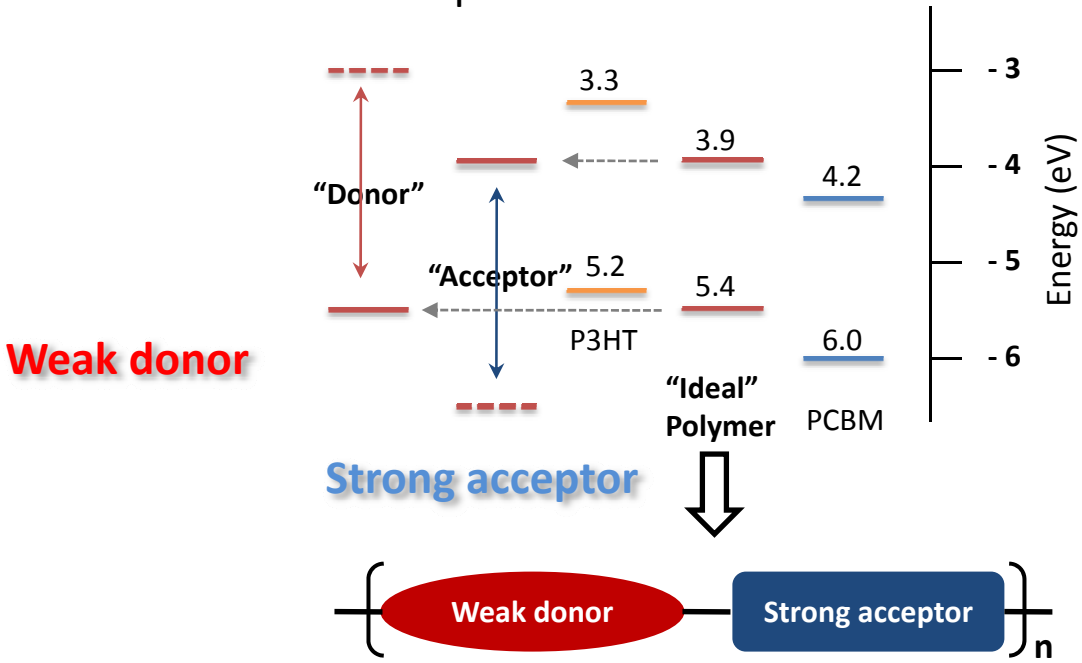


Best Performing Low Bandgap Polymers

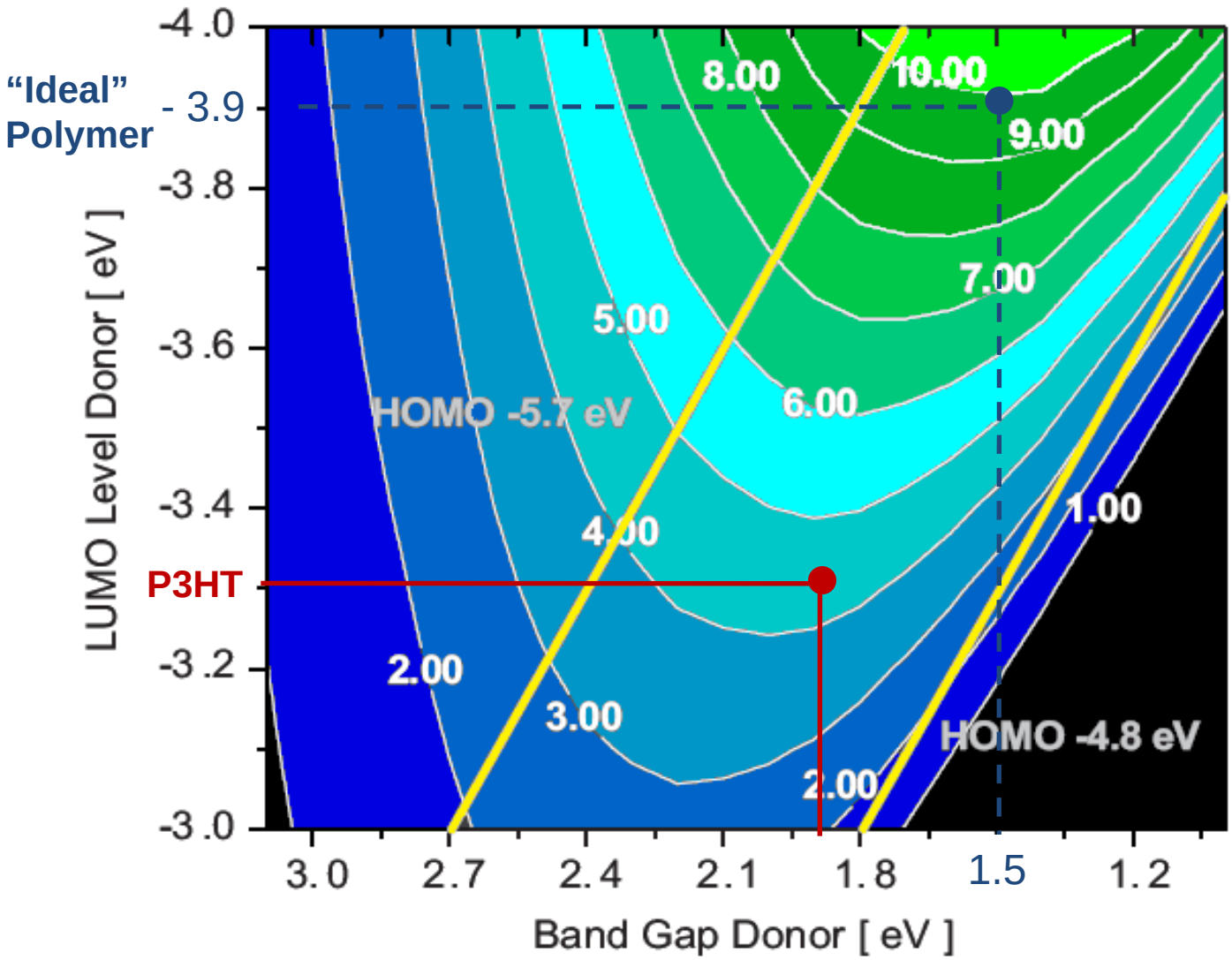
	HOMO (eV)	LUMO (eV)	Egap (opt)	V_{oc}	J_{sc}	FF	η %	Note
 APFO-3	- 5.80	- 3.5		1.03	6.3	0.43	2.8	*Adv. Funct. Mater.* **2006**, *16*, 667; *APL* **2007**, *91*, 071108 (3.5%)
 APFO-15	- 6.30	- 3.6		1.0	6.0	0.63	3.5	*Adv. Funct. Mater.* **2007**, *17*, 3836 (3.5%)
 PCDTBT	- 5.5	- 3.6	1.88	0.89 0.88	6.92 10.6	0.63 0.66	3.6 6.1 (C70)	*Adv. Mater.* **2007**, *19*, 2295. *JACS* **2008**, *130* ,732. *Nat. Photon.* **2009**, *3, 297* (6%)
 PSiF-DBT	- 5.39		1.82	0.90	9.5	0.507	5.4	*APL* **2008**, *92*, 033307.
 PCPDTBT	- 5.3	- 3.57	1.40	0.7	9 11	0.47	2.8 3.2 (C70)	*Adv. Mater.* **2006**, *18*, 2884. *Nat. Mater.* **2007**, *7*, 497. Jsc 16.2, Voc 0.62, FF 0.55, efficiency 5.5%, IPCE over 50%
	- 5.43	- 3.66	1.70	0.80 0.80	6.2 10.1	0.51 0.53	2.5 4.3 (C70)	*JACS* **2008**, *130*, 12828.
 pBBTDPP2	- 5.1	- 3.4	1.7 (film)	0.66 0.61	9.4 11.3	0.47 0.58	2.9 4.0 (C70)	*Adv. Mater.* **2008**, *20*, 2556.
 PSBTBT	- 5.05	- 3.27	1.45	0.68	12.7	0.55	5.1 (C70)	*JACS* **2008**, *130*, 16144.
	- 4.90	- 3.20	1.62 (film)	0.58 0.56	12.5 15.0	0.654 0.633	4.76 5.30 (C70)	*JACS* **2009**, *131,* 56. *JACS* **2009**, *131,* 7792 (6.1%)

"Ideal" Polymer?

- Absorption → • Low band gap • Broad absorption → J_{sc} (upper limit)
- Energy Level → • Low HOMO level • Minimize voltage lost at electrodes → V_{oc}
- Morphology → • Maximize D/A interface • High mobility & balanced • Biphasic → J_{sc} (attainable) *FF*



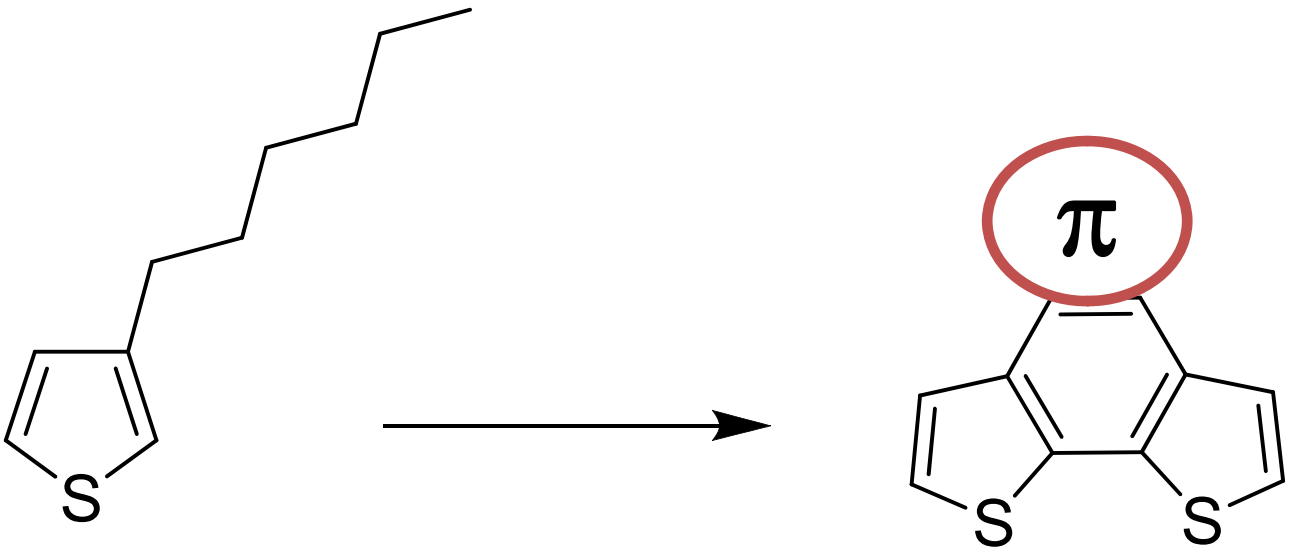
10% Possible?



FF: 0.65
IPCE: 65%

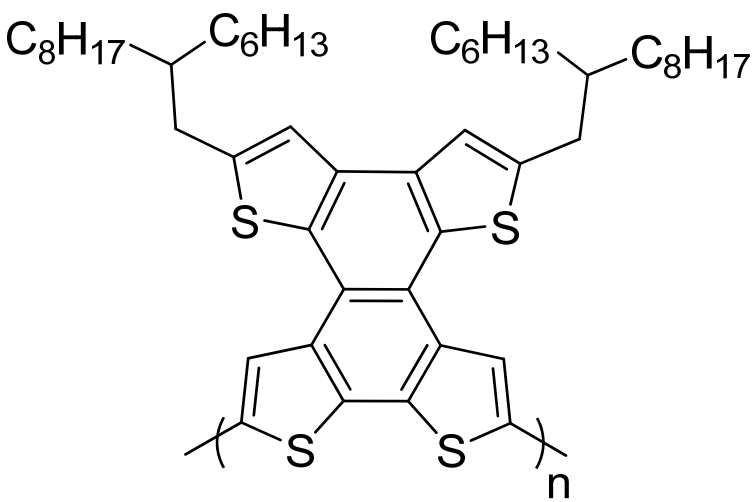
Scharber, M. C. *et.al. Adv. Mater.* **2006**, *18*, 789-794

Fused Thiophenes

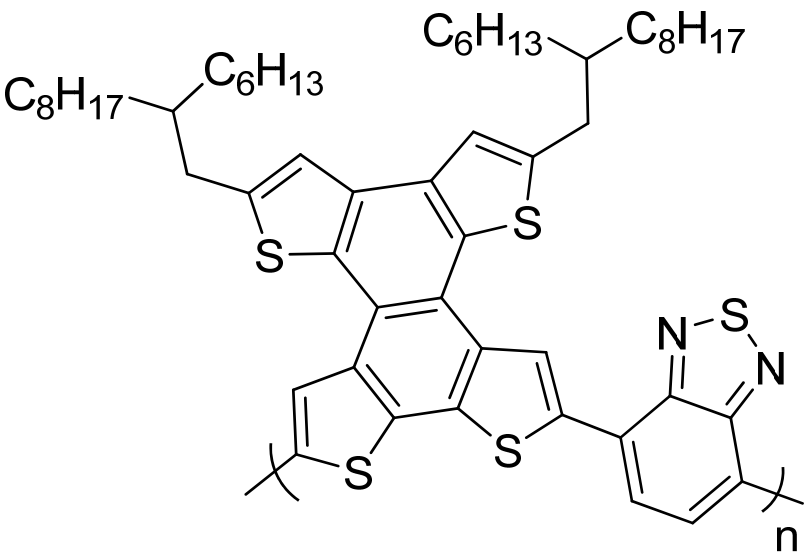


- Fused ring: Increased π conjugation
- π - π stacking: mobility
- Tuning HOMO level!

A Case Study of Benzodithiophene Series

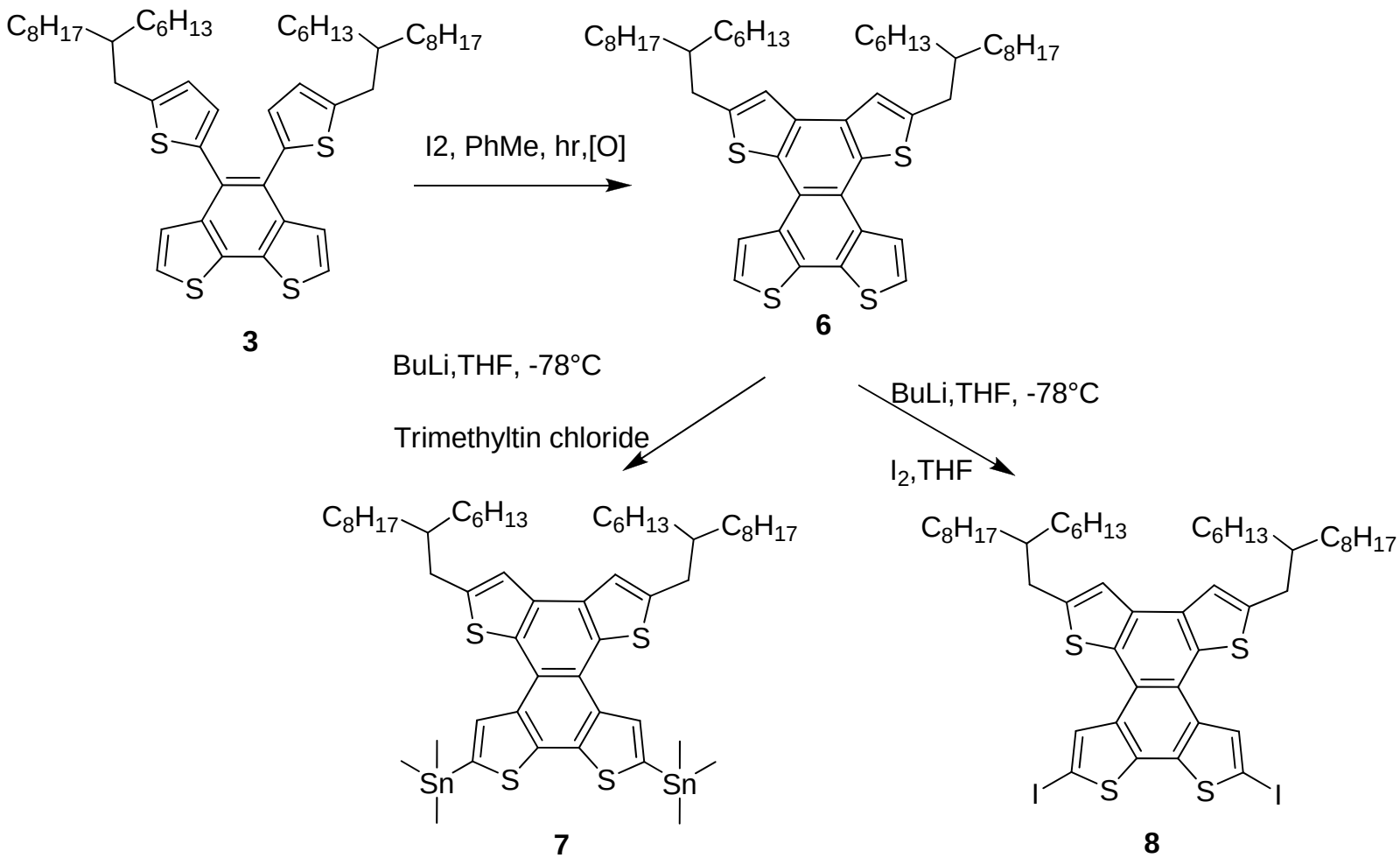


HMPQTN

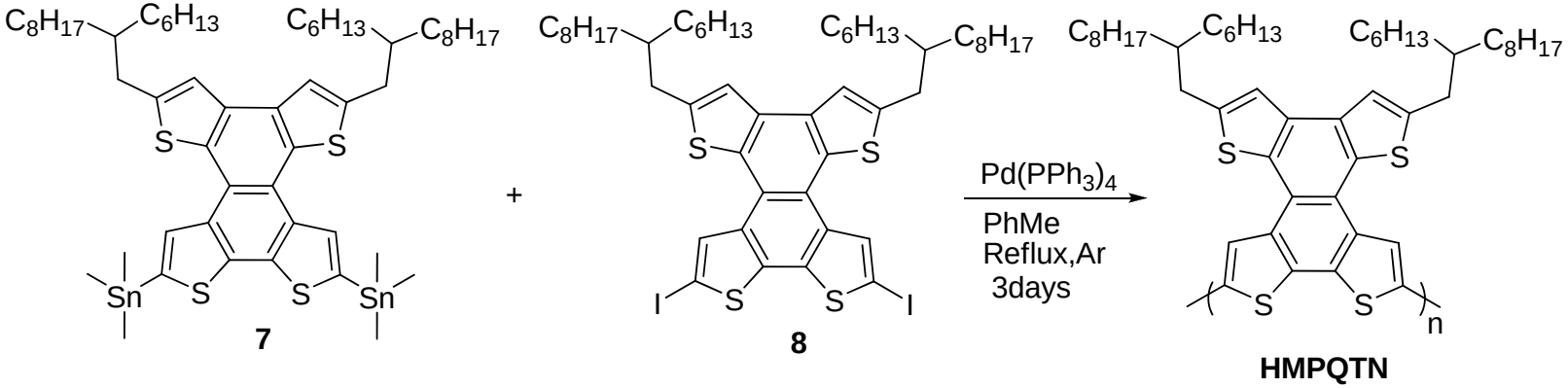


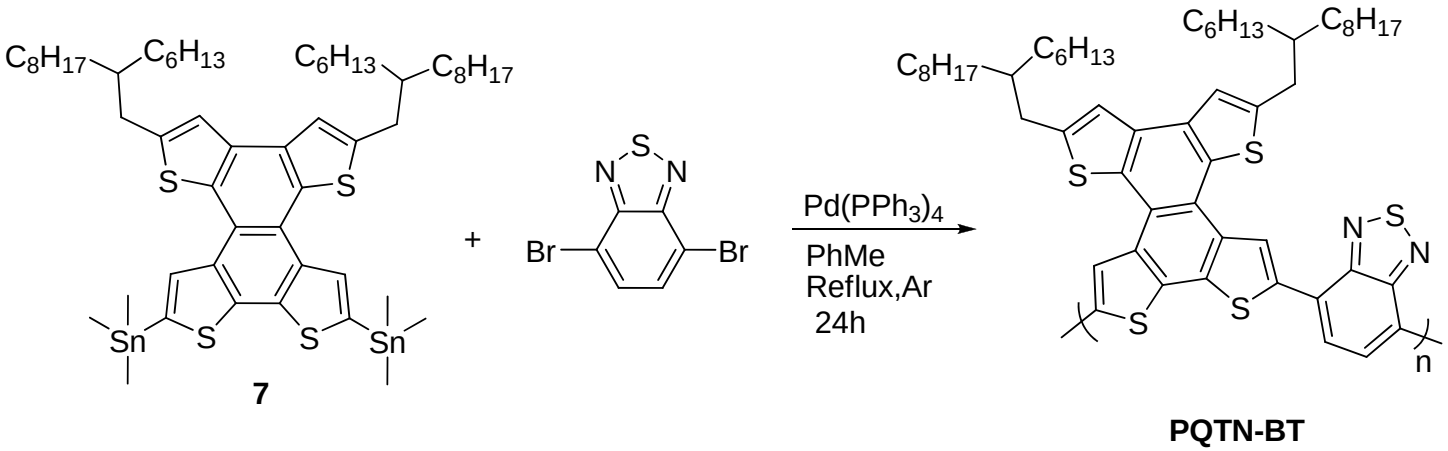
PQTN-BT

Simple Chemistry

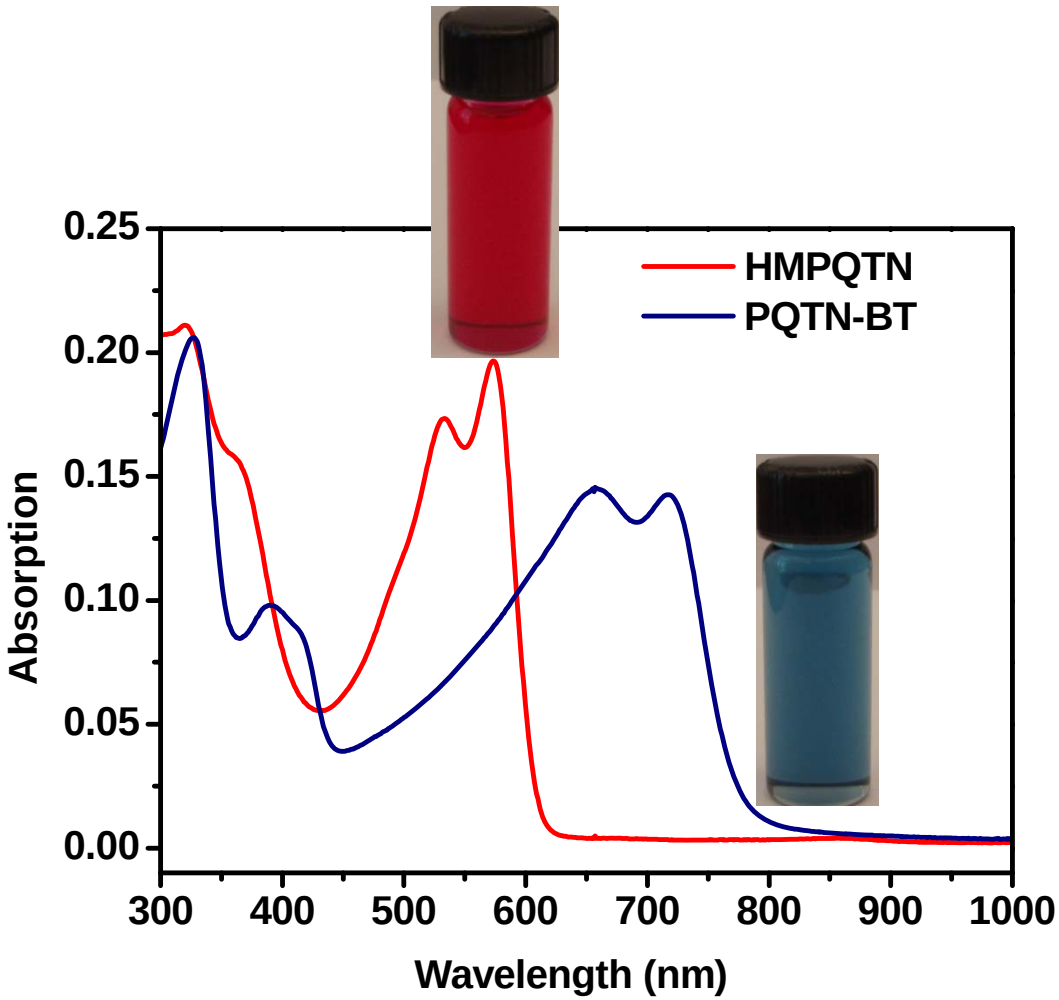


More Polymers



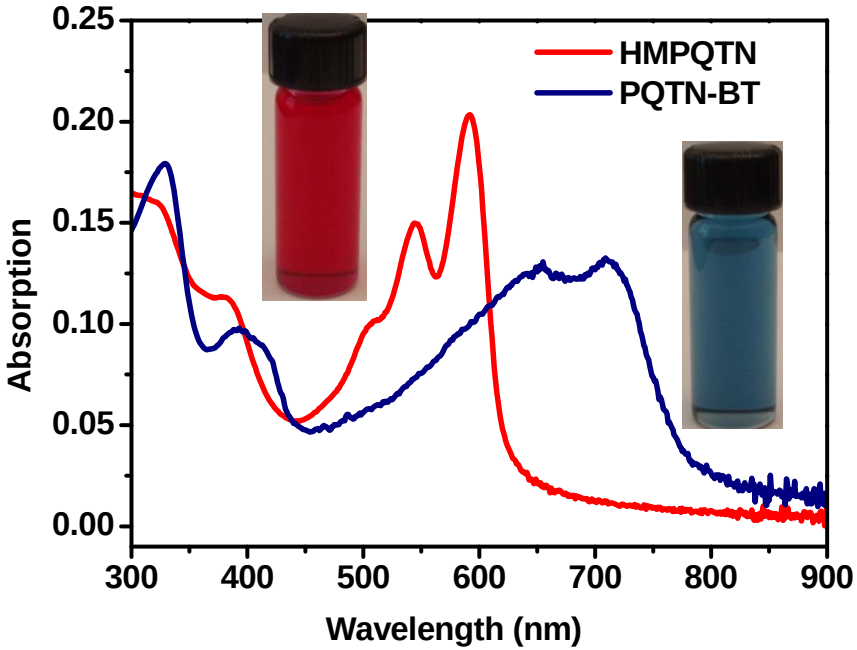


Solution Absorption



0.005mg/mL in $CHCl_3$ at room temperature

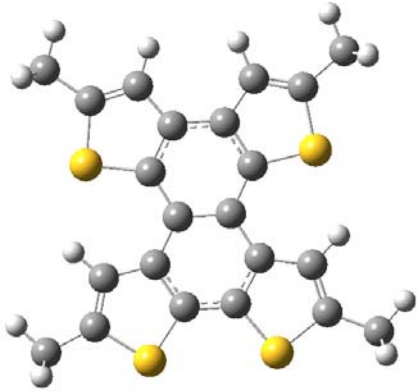
Film Absorption



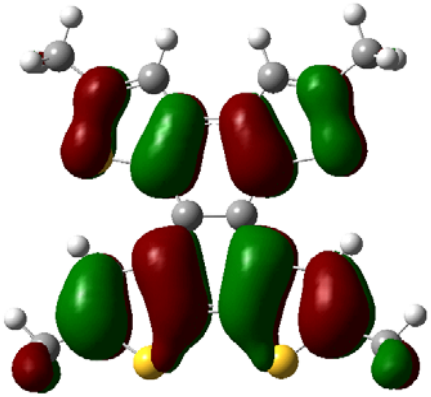
Films of polymers from the solutions in $PhCl_3$ at room temperature with thickness around 40-60nm.

	Uv-Vis absorption data						Cyclic Voltammetry		TD-DFT
	$CHCl_3$ solution			Film			E^{ox}_{onest}[V]	E^{red}_{onest}[V]	
polymer	λ_{max} [nm]	λ_{onset} [nm]	E_g [eV]	λ_{max} [nm]	λ_{onset} [nm]	E_g [eV]	HOMO [eV]	LUMO [eV]	Calculated HOMO [eV}
HMPQTN	573,530	612	2.04	592,545	620	2.0	0.58/-5.38	NA/-3.34	-5.38
PQTN-BT	716,657	770	1.61	714,652	775	1.61	0.58/-5.38	NA/-3.77	-5.33

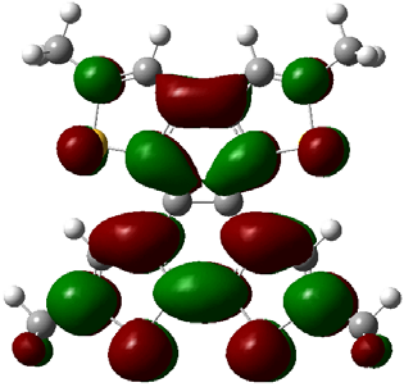
Calculated HOMO/LUMO



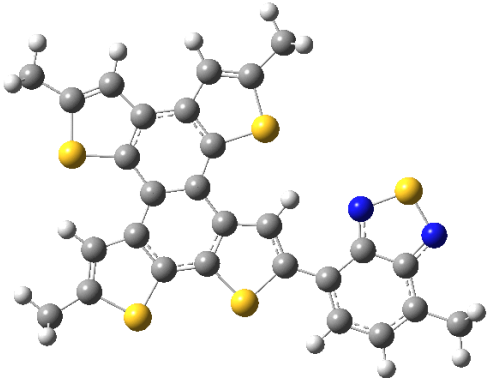
HMPQTN



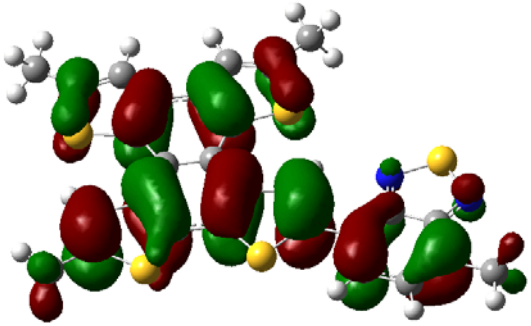
HOMO



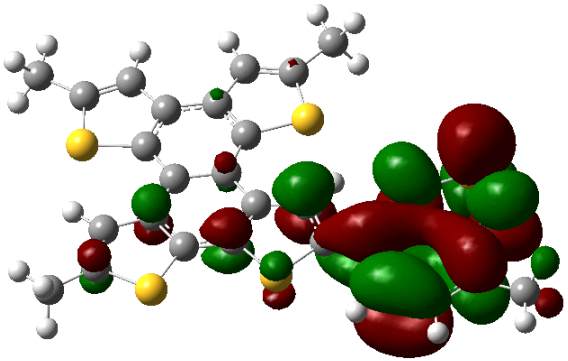
LUMO



PQTN-BT

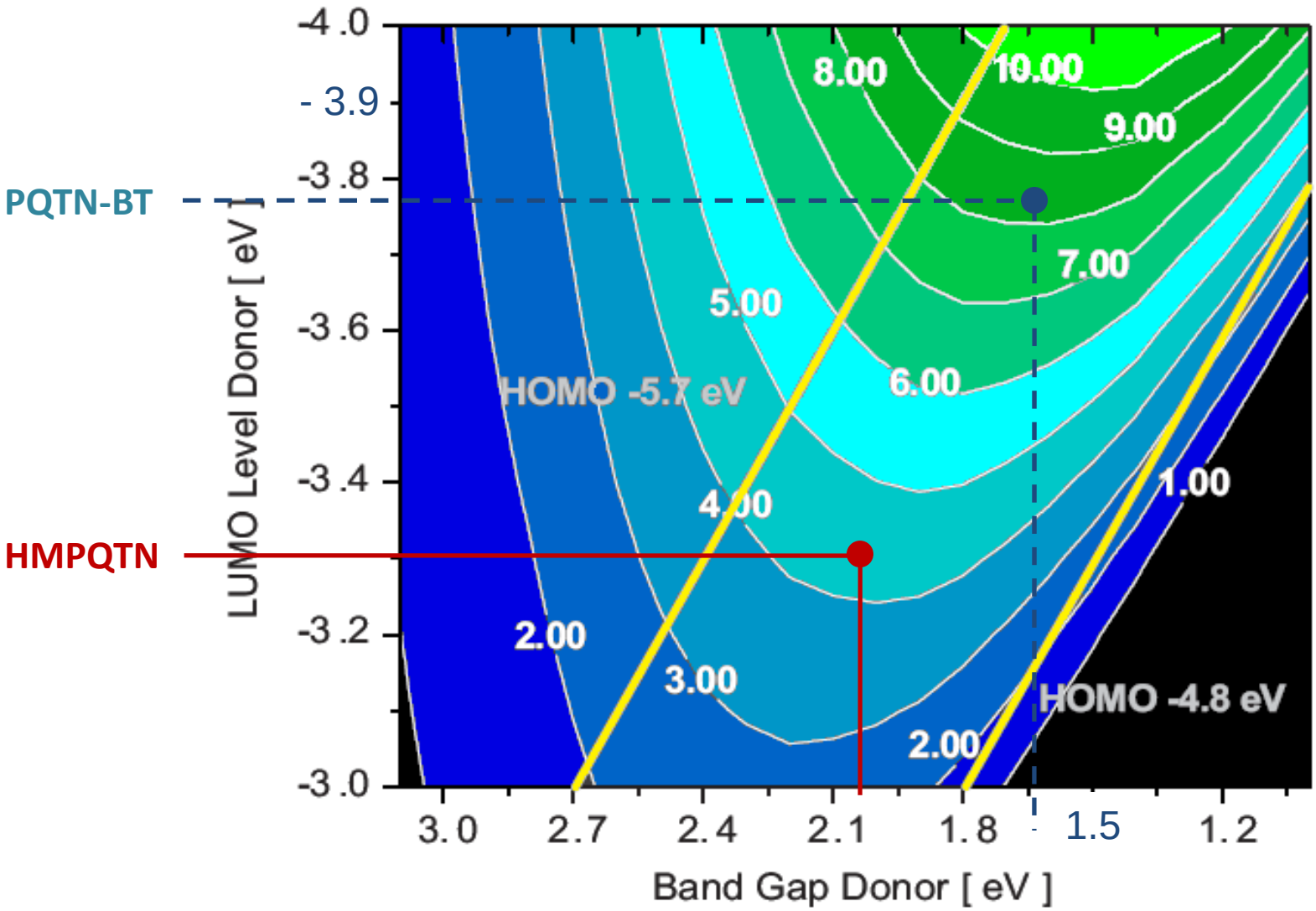


HOMO



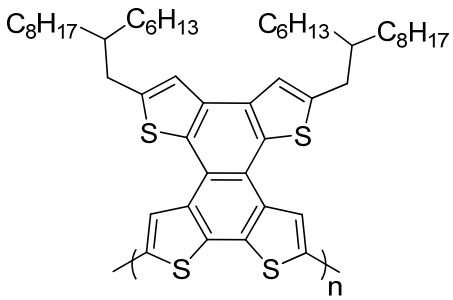
LUMO

What Might Be Achievable?



FF: 0.65
IPCE: 65%

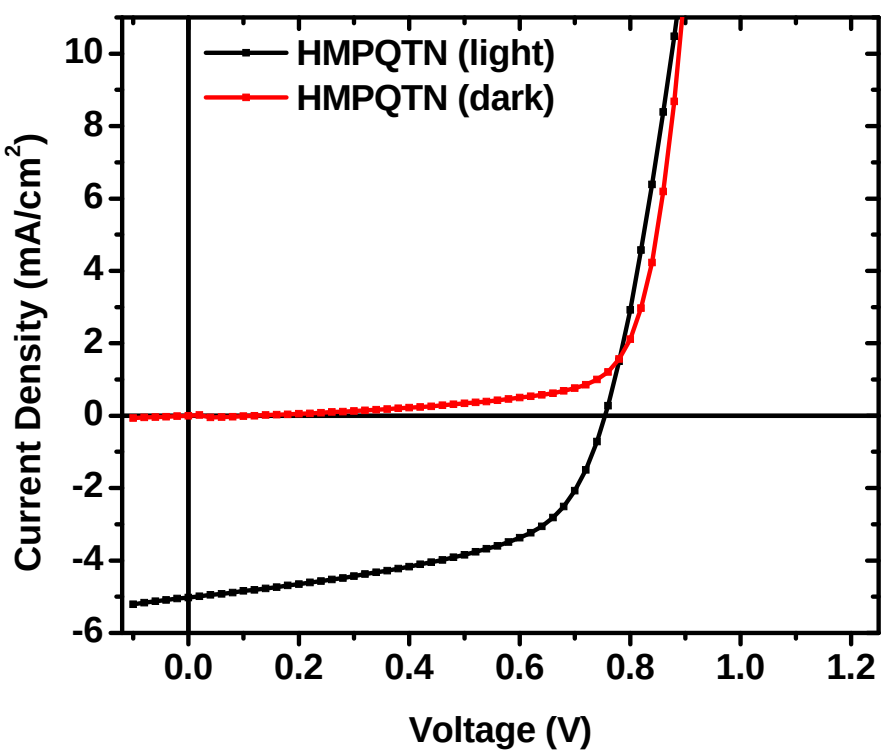
Optimized Devices

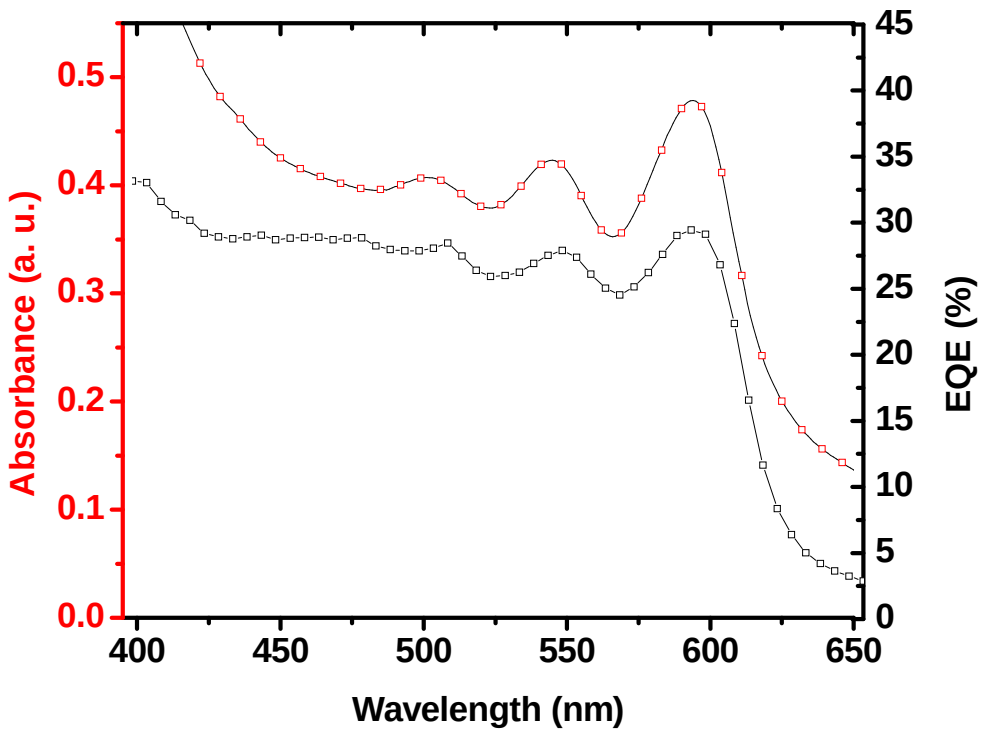


HMPQTN

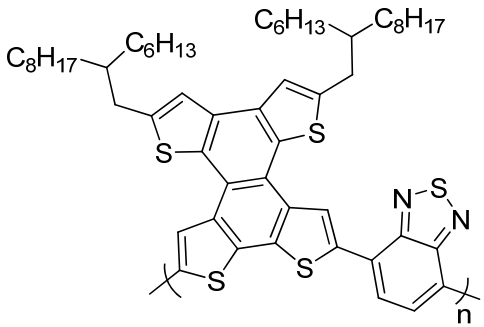
HMPQTN: PCBM = 1:2, 180 nm thick film

V_{oc} - 0.76 V
J_{sc} - 5.02 mA/cm^{-2}
FF - 53.08%
η - 2.03%





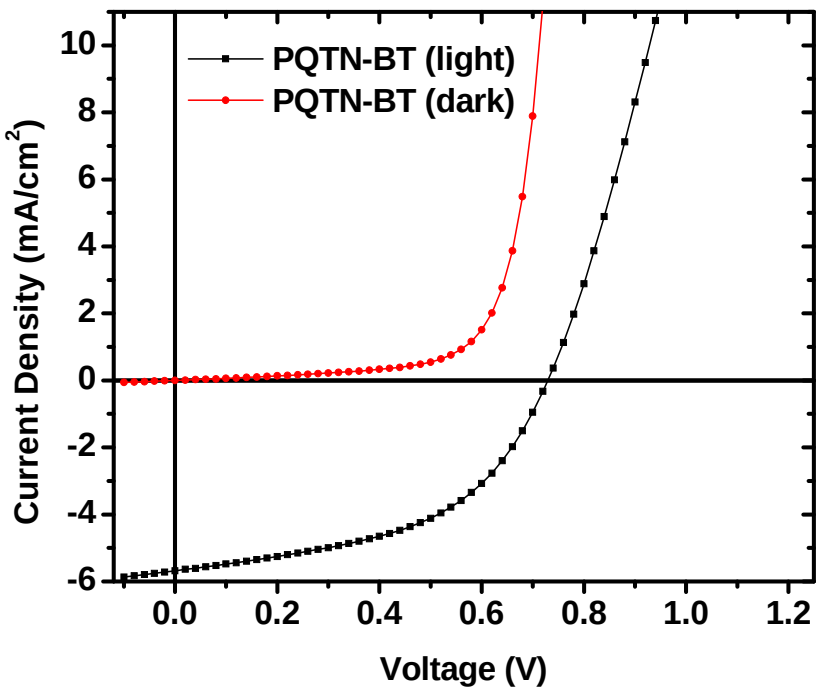
Optimized Devices

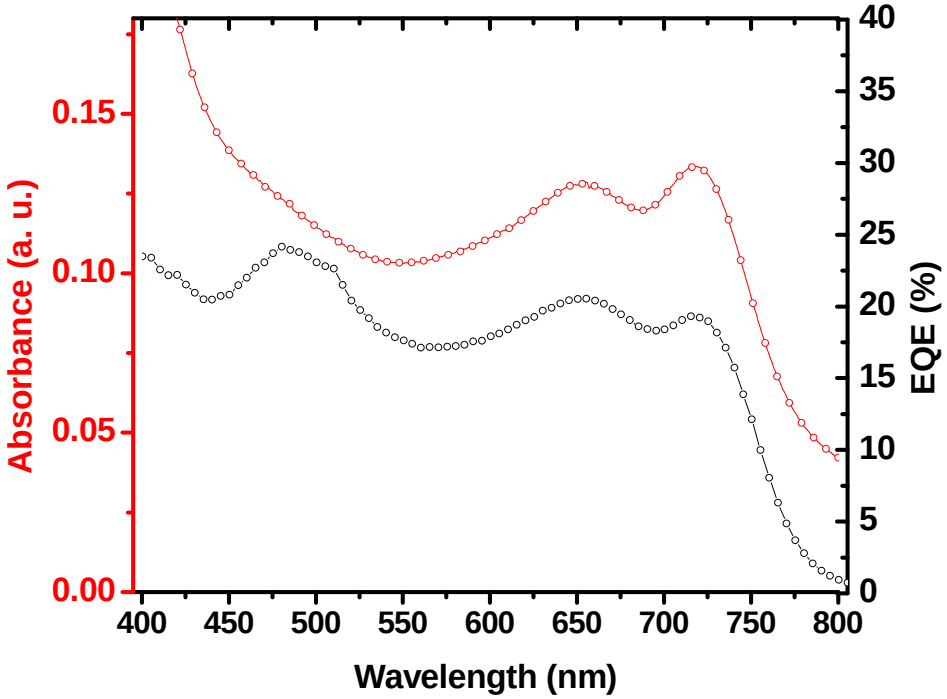


PQTN-BT

PQTN-BT: PCBM = 1:2, 80 nm thick film

V_{oc} - 0.72 V
J_{sc} - 5.69 mA/cm^{-2}
FF - 50.26%
η - 2.06%





Performance vs. Thickness

Polymer	PCBM /Polymer	Film Thickness (nm)	V_{oc} (V)	J_s (mA/cm^2)	*FF*	η (%)	Mobility (cm^2/V·s)
HMPQTN	2:1	55	0.60	2.1	36	0.45	
	2:1	70	0.76	2.42	41	0.76	
	2:1	180	0.76	5.02	53.08	2.03	8.2×10^{-5}
		200	0.72	3.7	50.57	1.35	
PQTN-BT	2:1	45	0.72	3.91	49.06	1.38	
	2:1	55	0.74	5.97	39.52	1.75	
	2:1	80	0.72	5.69	50.26	2.06	1.3×10^{-5}
		115	0.60	2.18	37.46	0.49	

Conclusions

- "Ideal" polymers require **low HOMO** level (maximize V_{oc}) and **low bandgap** (maximize J_{sc}) (when PCBM is used)

- Combining **weak donor** and **strong acceptor** would potentially lead to "ideal" polymers for OSC

- **Mobility** and **morphology** are crucial to approach the theoretical efficiency: attainable J_{sc} and *FF*

- Polycyclic, fused aromatic molecules are excellent building blocks for "ideal" polymers
  (a) effectively lower the HOMO
  (b) improved π-π interactions between polymer chains in thin solid films would enhance the charge carrier mobility

Is 10% Really Achievable?

$$\text{Efficiency} = \frac{V_{oc} \times J_{sc} \times FF}{P_{input}}$$

For example

V_{oc}	0.9 V	1.0 V
J_{sc}	12 mA/cm^2	15 mA/cm^2
FF	0.6	0.70
η	6.5%	10.5%

⇩

ACHIEVED!

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Sarah Stoneking (undergraduate)

Nabil Kleinhenz (undergraduate)

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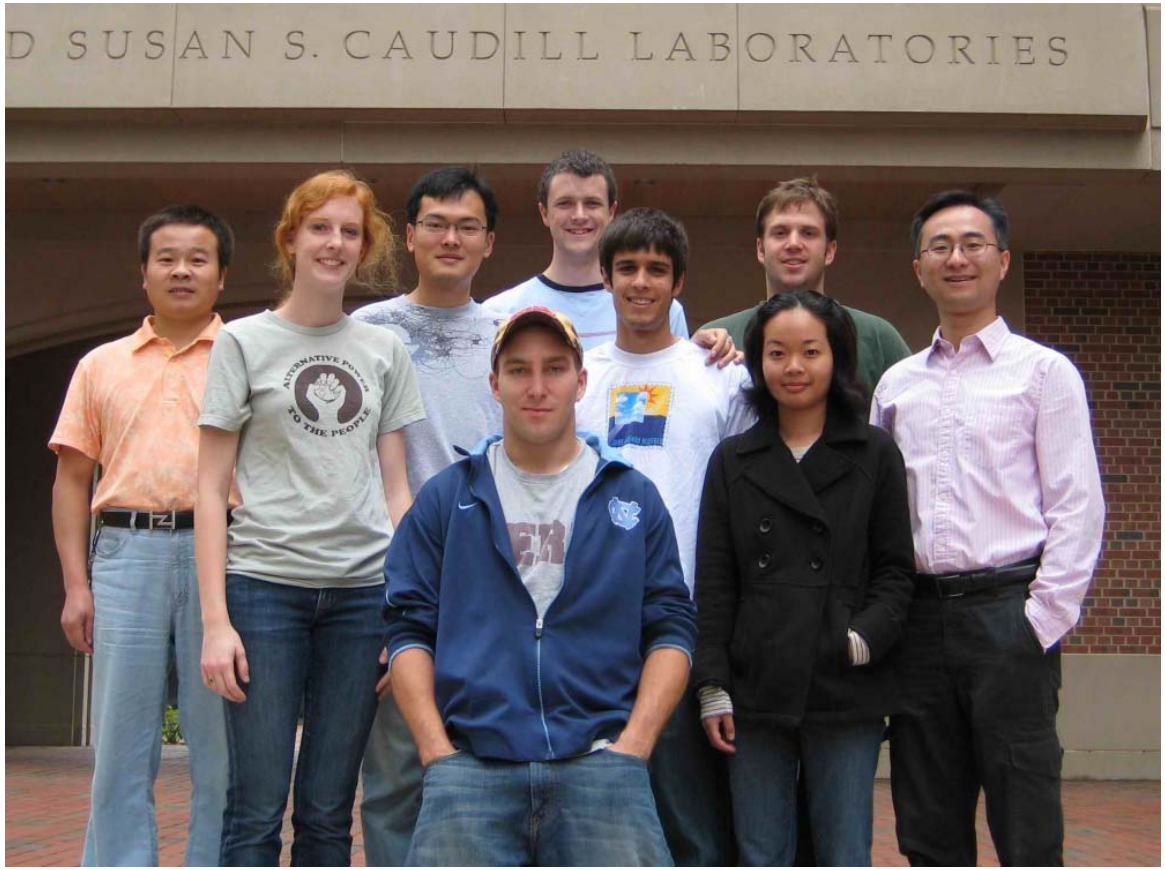

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NSF Science & Technology Center NSF STC Environmentally Responsible Solvents and Processes

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