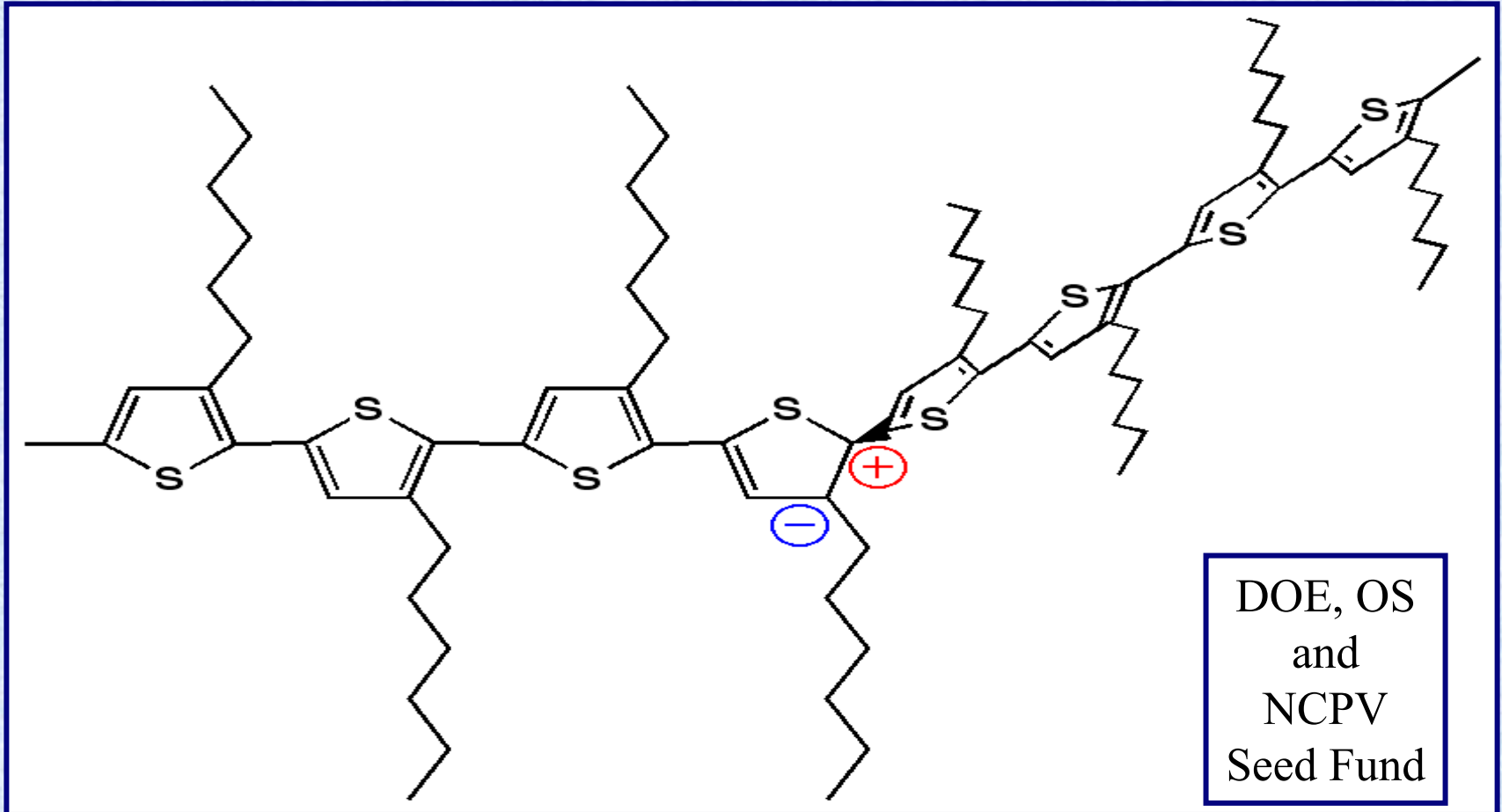


Do the Defects Make it Work? Defect Engineering in π -Conjugated Polymer Films and Their Solar Cells

Brian A. Gregg*, Dong Wang, Matthew O. Reese and Nikos Kopidakis
National Renewable Energy Laboratory



NREL/PR-270-43277

Presented at the 33rd IEEE Photovoltaic Specialist Conference held May 11-16, 2008 in San Diego, California

Free carrier density at zero field, p_{f0} or n_{f0}

Intrinsic SC, $E_{bg} = 2.0$ eV

$$p_{f0} = n_{f0} \approx 10^4 \text{ cm}^{-3}$$

Molecular SCs (e.g., porphyrins,
perylene, phthalocyanines)

$$10^{11} - 10^{14} \text{ cm}^{-3}$$

Peumans, P.; Yakimov, A.; Forrest, S. R., *J. Appl. Phys.* **2003**, 93, (7), 3693.

Gregg, B. A.; Chen, S.-G.; Cormier, R. A., *Chem. Mater.* **2004**, 16, (23), 4586.

π -conjugated polymers (e.g.,
cm⁻³

$$10^{15} - 10^{17}$$

~~SCLC~~

P3HT, MDMO-PPV)

Jarrett, C. P.; Friend, R. H.; Brown, A. R.; de Leeuw, D. M., *J. Appl. Phys.* **1995**, 77,

6289. Chen, S.-G.; Stradins, P.; Gregg, B. A., *J. Phys. Chem. B* **2005**, 109, 13451. Jain, S.

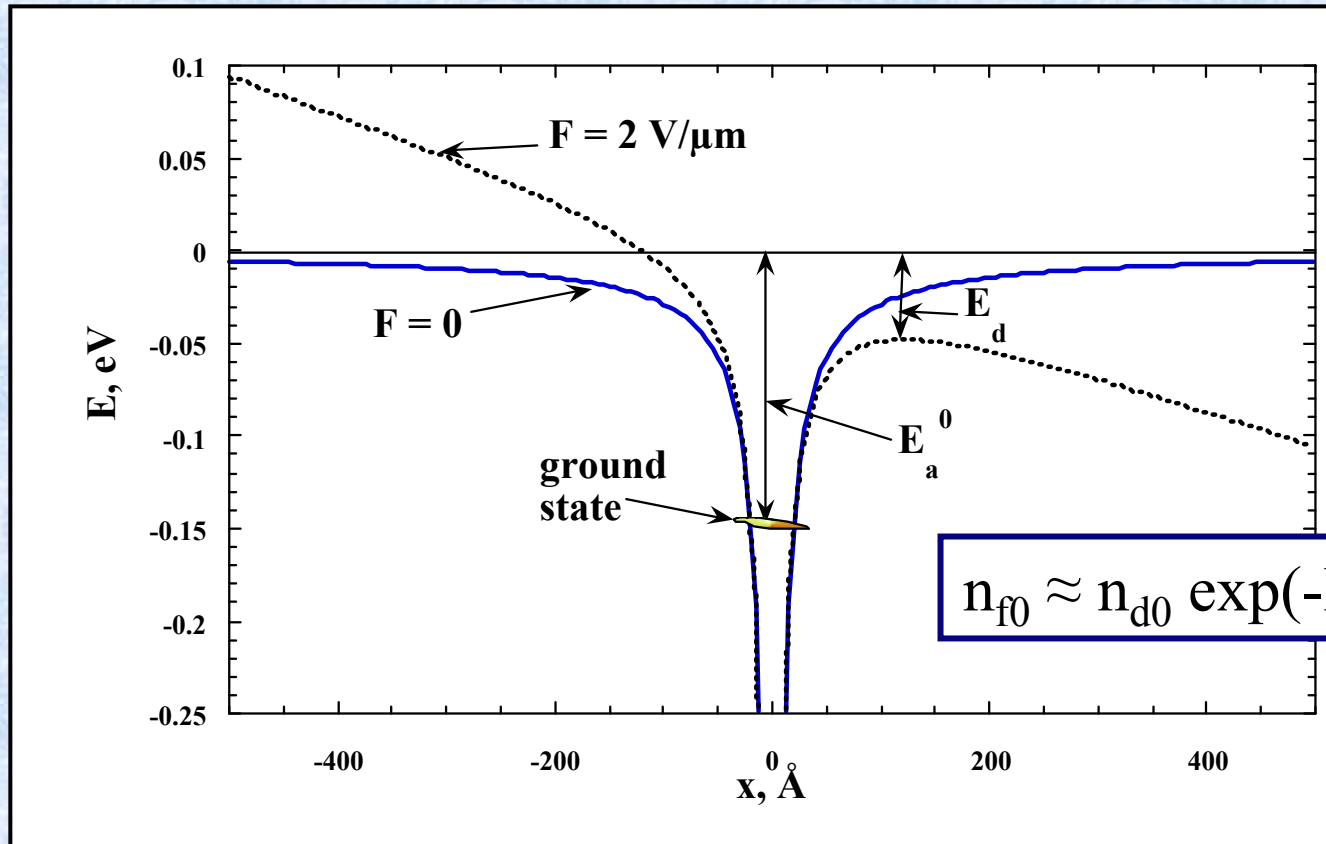
C.; Geens, W.; Mehra, A.; Kumar, V.; Aernouts, T.; Poortmans, J.; Mertens, R.; Willander, M., *J. Appl.*

Phys. **2001**, 89, 3804. Dicker, G.; de Haas, M. P.; Warman, J. M.; de Leeuw, D. M.; Siebbeles, L. D. A.,

J. Phys. Chem. B **2004**, 108, 17818; Mozer, A. J.; Sariciftci, N. S.; Pivrikas, A.; Österbacka, R.;

Juska, G.; Brassat, L.; Bäessler, H., *Phys. Rev. B* **2005**, 71, 035214.

Binding energy between charges $> k_B T$ because of low dielectric constant and localized carrier wavefunctions. Should apply to excitons, doping, charge separation and transport

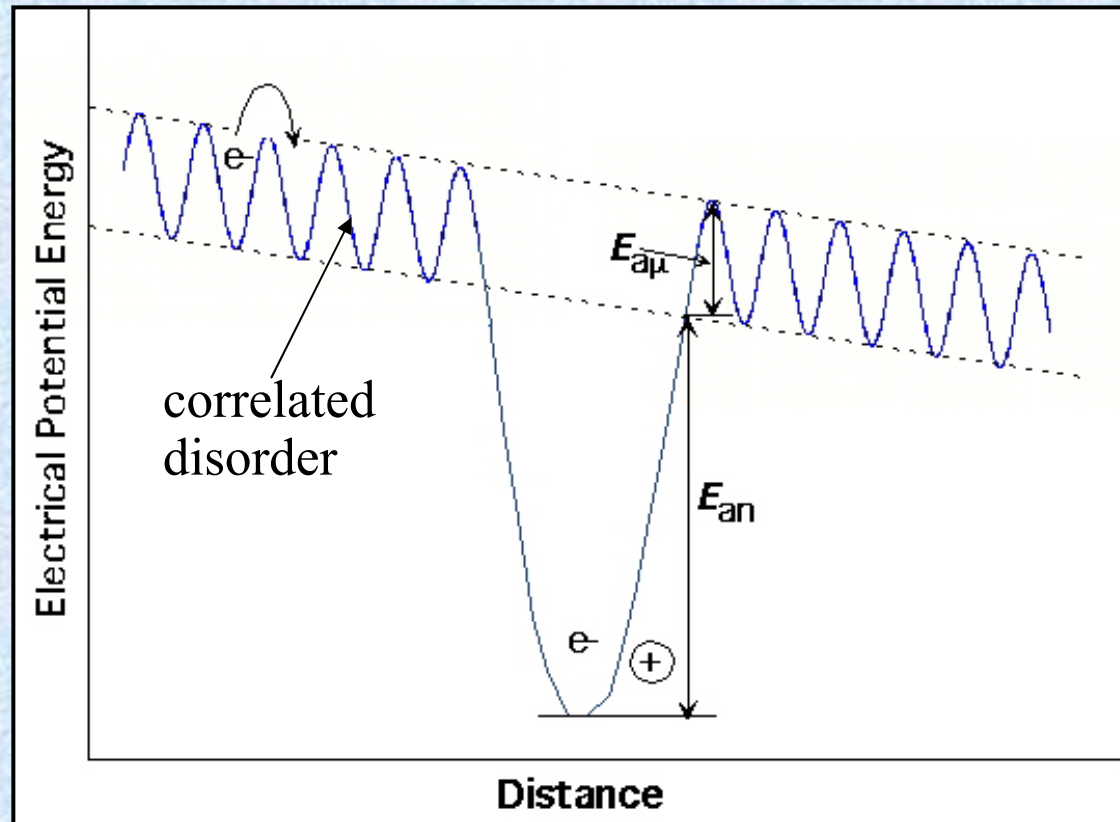


$$n_{f0} \approx n_{d0} \exp(-E_{\text{bind}}/kT)$$

Poole-Frenkel currents

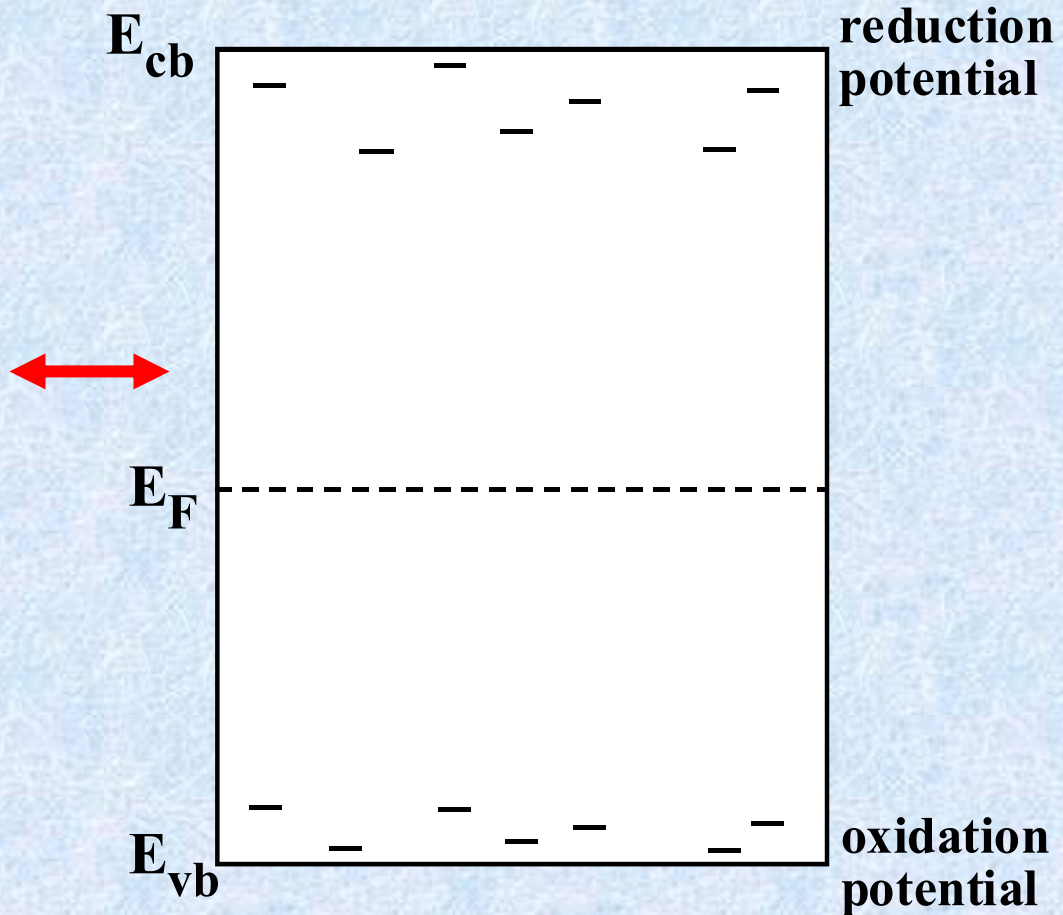
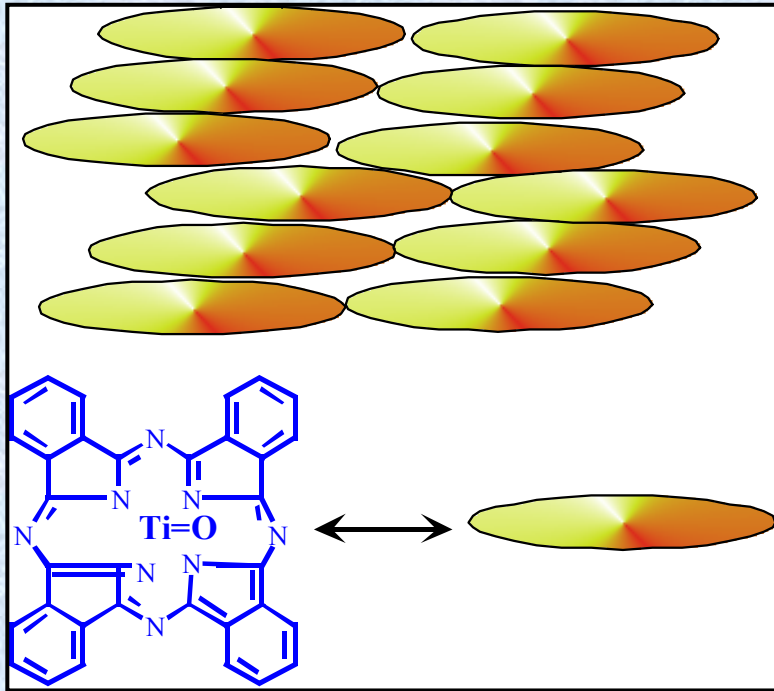
$$J = q \mu^0 F n_d \exp((-E_a^0 + (q^3/\pi\epsilon_0\epsilon)^{1/2} F^{1/2})/kT)$$

Band diagram with trapped charges and dipole-induced conduction band fluctuations

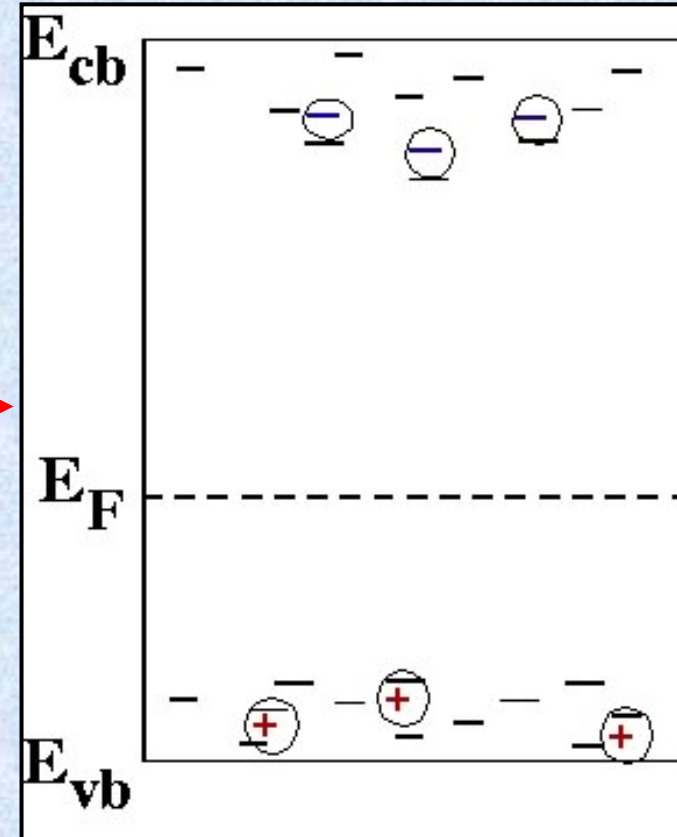
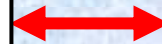
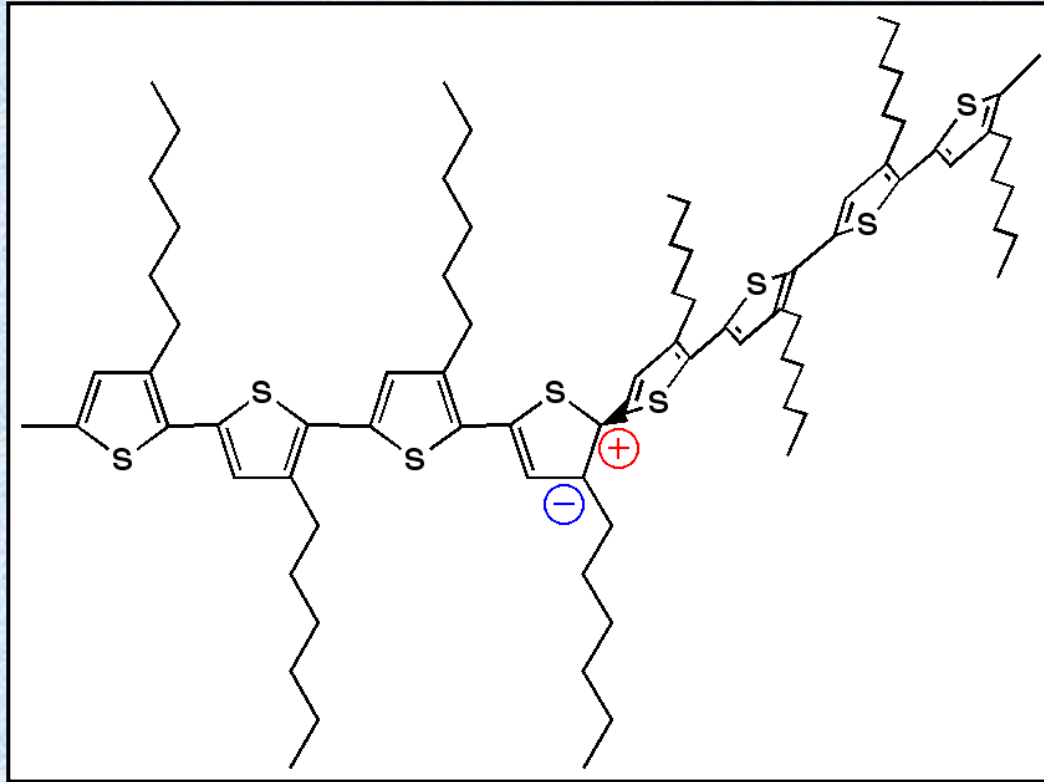


The field-dependence of μ may be similar to that of n_f , this is *not* included in the original PF model—> PF factor/2

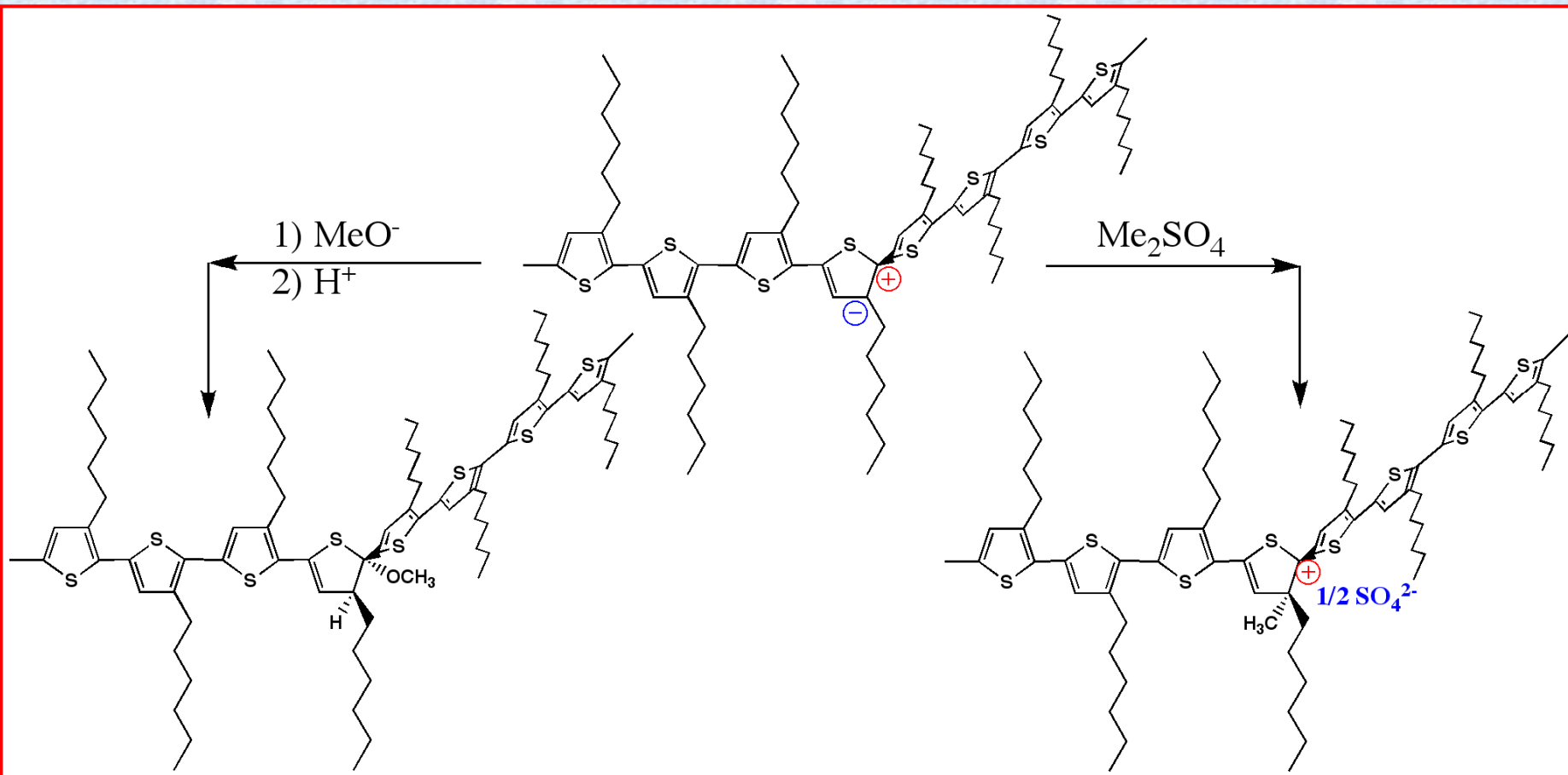
Non-Covalent Defects: Molecular semiconductors have only non-covalent defects (and chemical impurities)



Covalent Defects: π -conjugated polymers have both covalent and non-covalent defects (and chemical impurities)

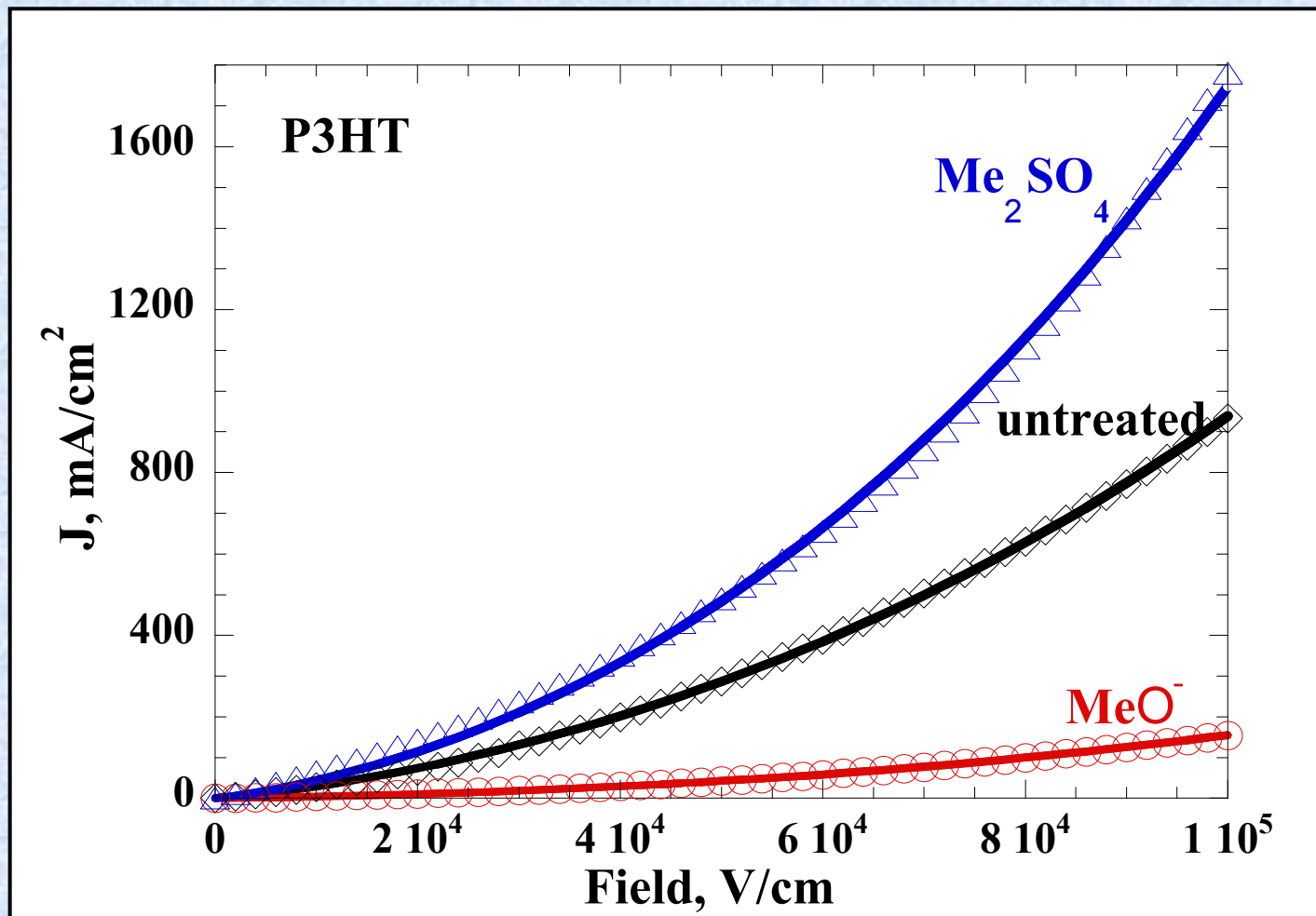


Chemically treating covalent defects in P3HT with nucleophiles and electrophiles

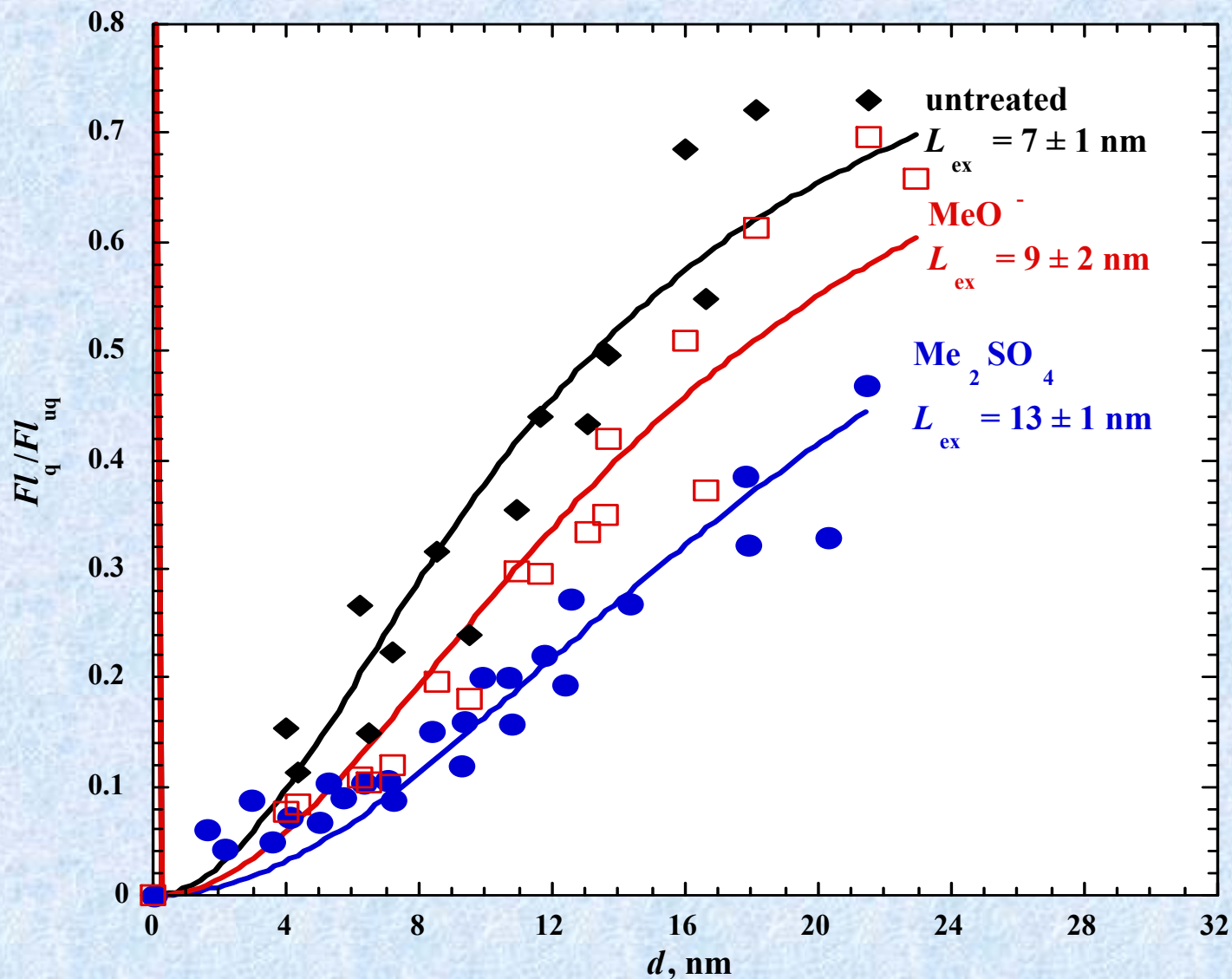


No reaction with pristine materials

Dark current-field curves for treated and untreated P3HT



Exciton diffusion length before and after chemical treatments



$10^{18} \text{ cm}^{-3} \longrightarrow$
 ~ 1 charge
every 10 nm

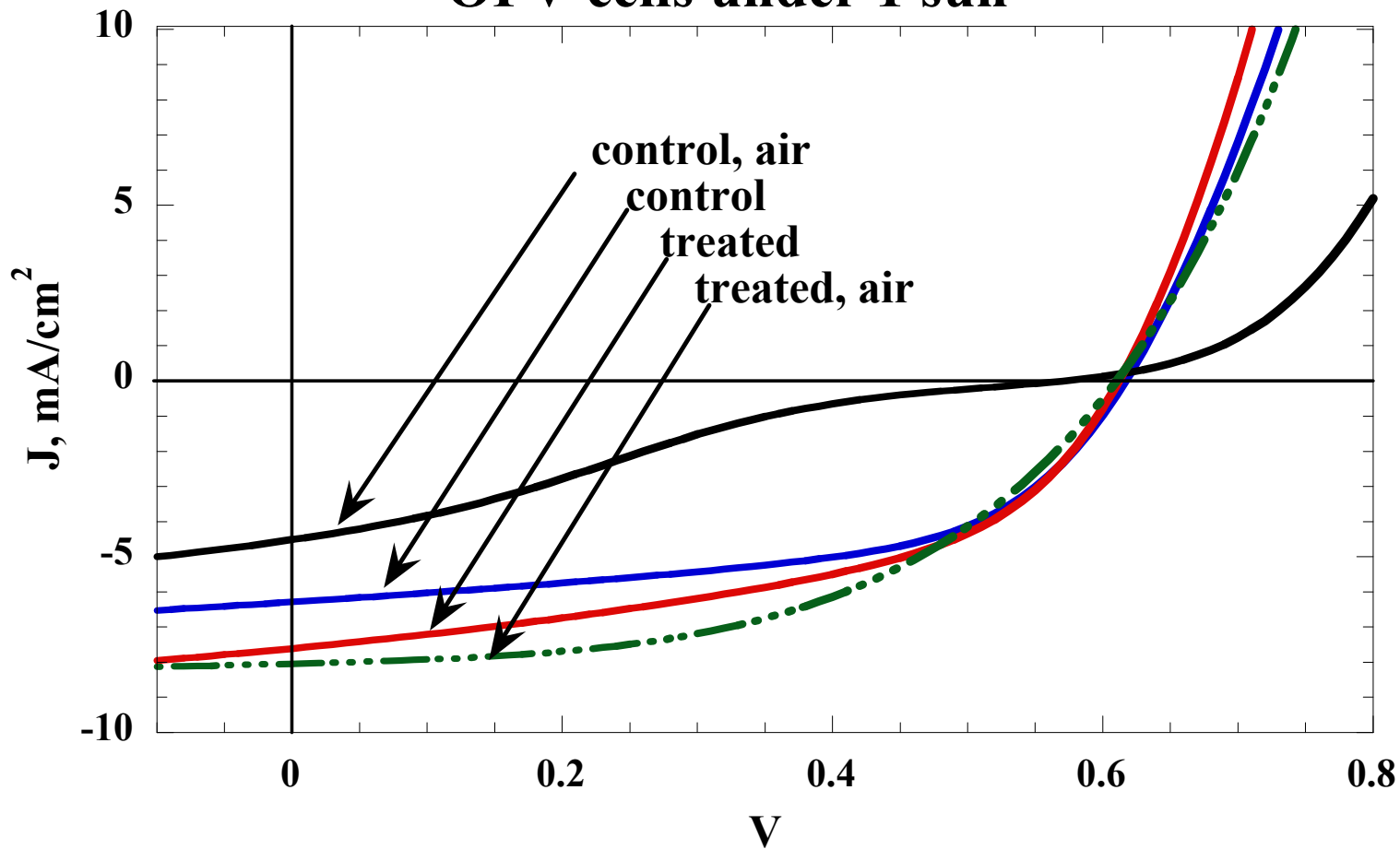
Results of chemical treatments

Tab 1.

Treatment	Relative PL Quantum Yield	Zero-field conductivity, σ_0 , $\times 10^7$ S/cm	E_{AJ0} meV	PL Lifetime τ_{avg} ps	L_{ex} m	Free Hole Mobility, μ_p , $\times 10^4$ cm ² /Vs	Free Hole density, p_f , $\times 10^{16}$ cm ⁻³
P3HT	1.00	14	233	401	7	1.2	7.3
MeO	1.35	3	276	579	9	1.8	1.0
MeI	0.92	29	223	354	—	3.5	5.2
MeSQ	0.54	46	210	285	13	42	6.8
MDMO	1.00	14	280	866	12	—	—
PPV	1.22	0.5	306	1020	14	—	—

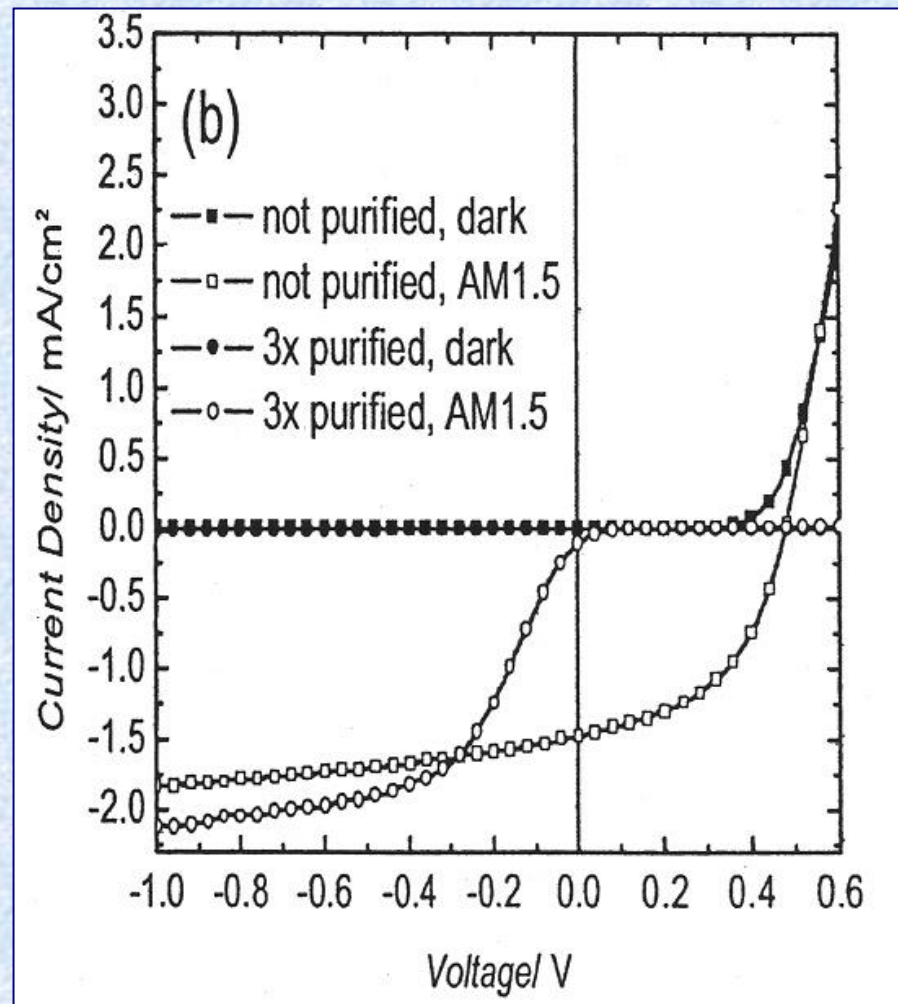
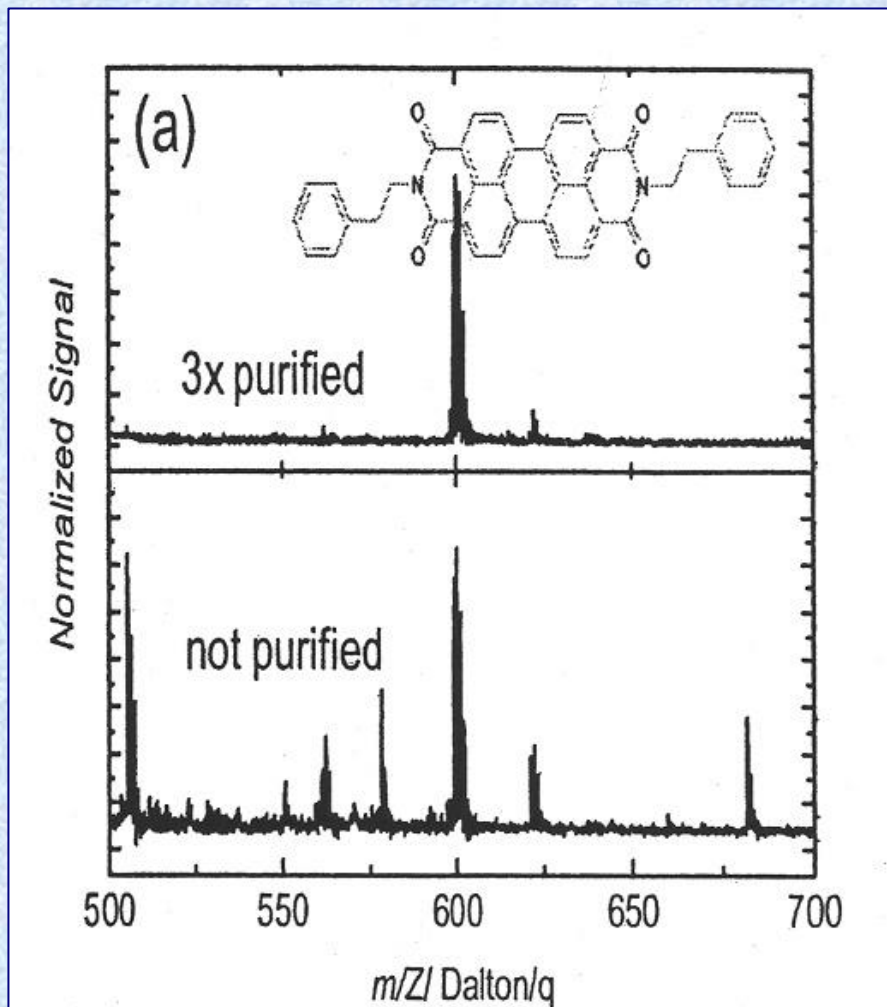
Bulk heterojunction OPV cells made from Me_2SO_4 treated P3HT, and controls

OPV cells under 1 sun



Impurities make it work: a peryene diimide/phthalocyanine cell

P. Peumans, et al, *Adv. Mater.* 2008, 20, 206



Summary

- Charged defects produce $10^{15} - 10^{17} \text{ cm}^{-3}$ *free* carriers
- Treatment with nucleophiles decreases p_f and σ while treatment with electrophiles does not change p_f but increases σ
- Both treatments increase μ_p , L_{ex} and stability against photo-degradation
- Charged defects can improve OPV by increasing conductivity and creating interfacial electric fields
- But they hurt μ_p , L_{ex} and chemical stability
- A better way: synthesize materials without covalent defects and dope with purposely added, bound dopants