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

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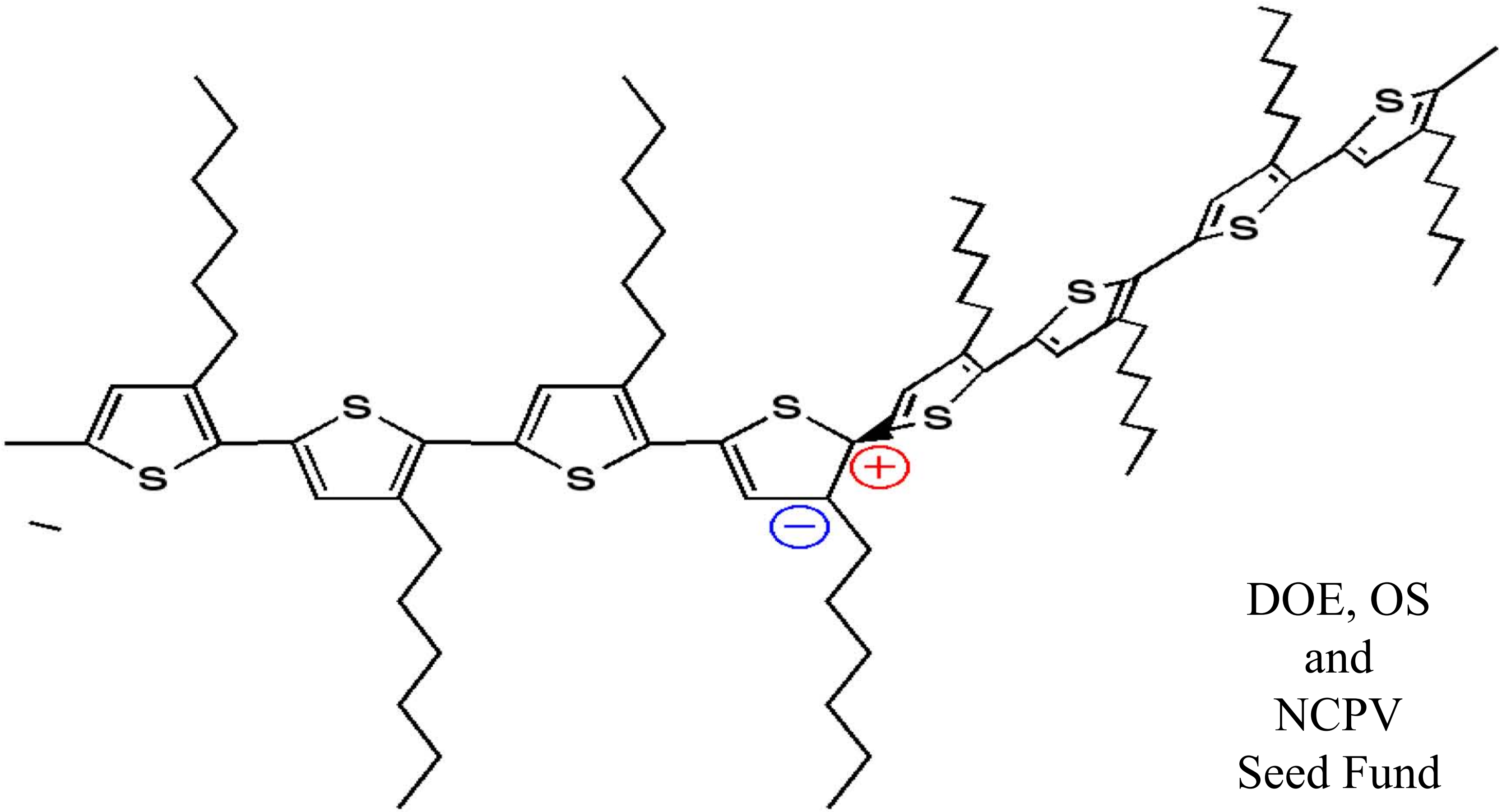

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Free carrier density at zero field, p_{f0} or n_{f0}

Intrinsic SC, $E_{bg} = 2.0$ eV $p_{f0} = n_{f0} \approx 10^4$ cm^{-3}

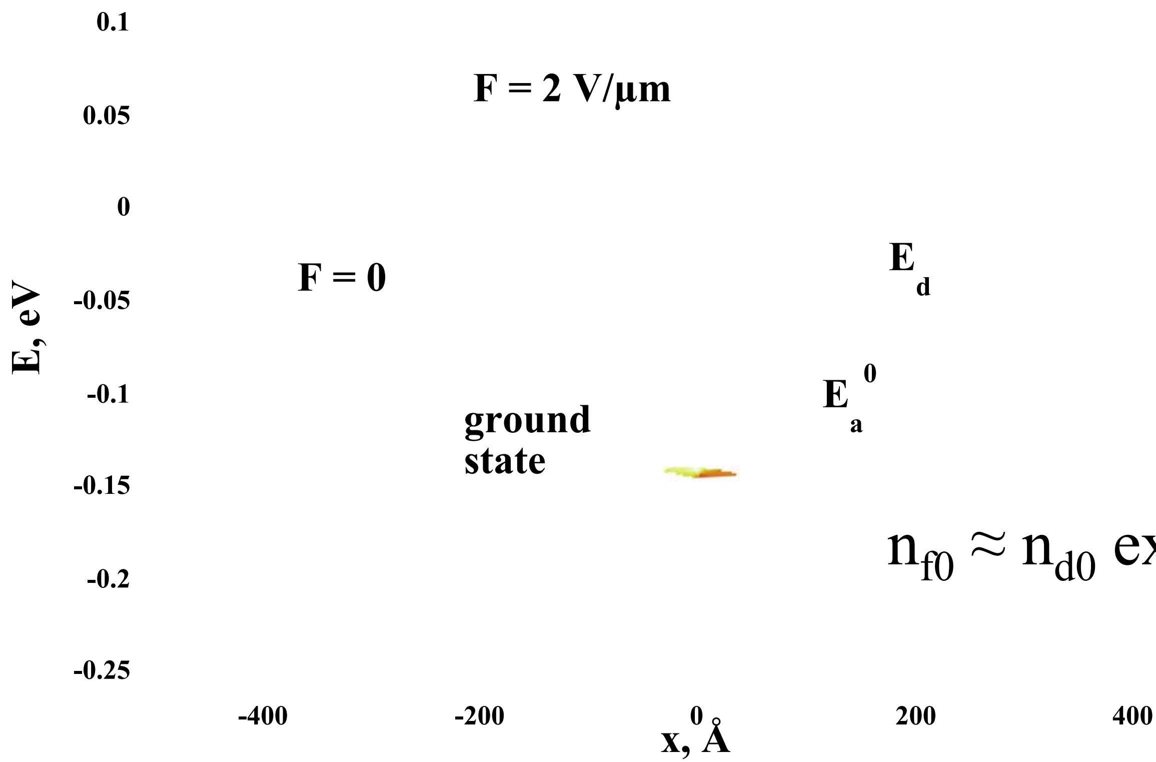
Molecular SCs (e.g., porphyrins, perylenes, phthalocyanines) $10^{11} - 10^{14}$ cm^{-3}

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., P3HT, MDMO-PPV) $10^{15} - 10^{17}$ cm^{-3}

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.; Bässler, 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

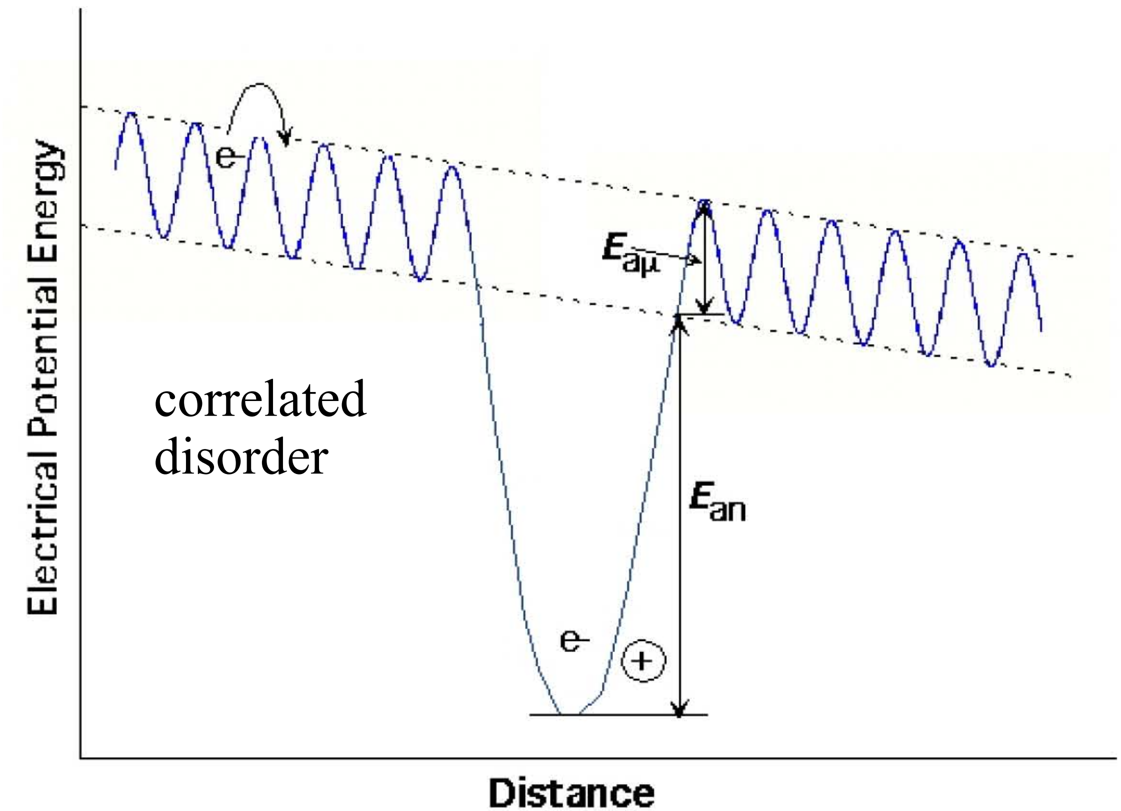


$$n_{f0} \approx n_{d0} \exp(-E_{bind}/kT)$$

Poole-Frenkel currents

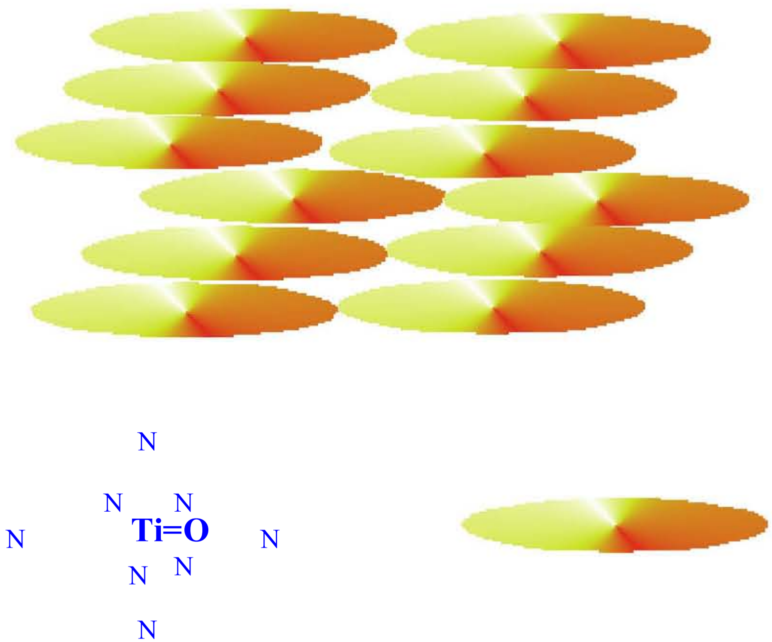
$$J = q\, \mu^0\, F\, n_d\, exp((-E_a{}^0 + (q^3/\pi\varepsilon_0\varepsilon)^{1/2}\, F^{1/2})/kT)$$

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)

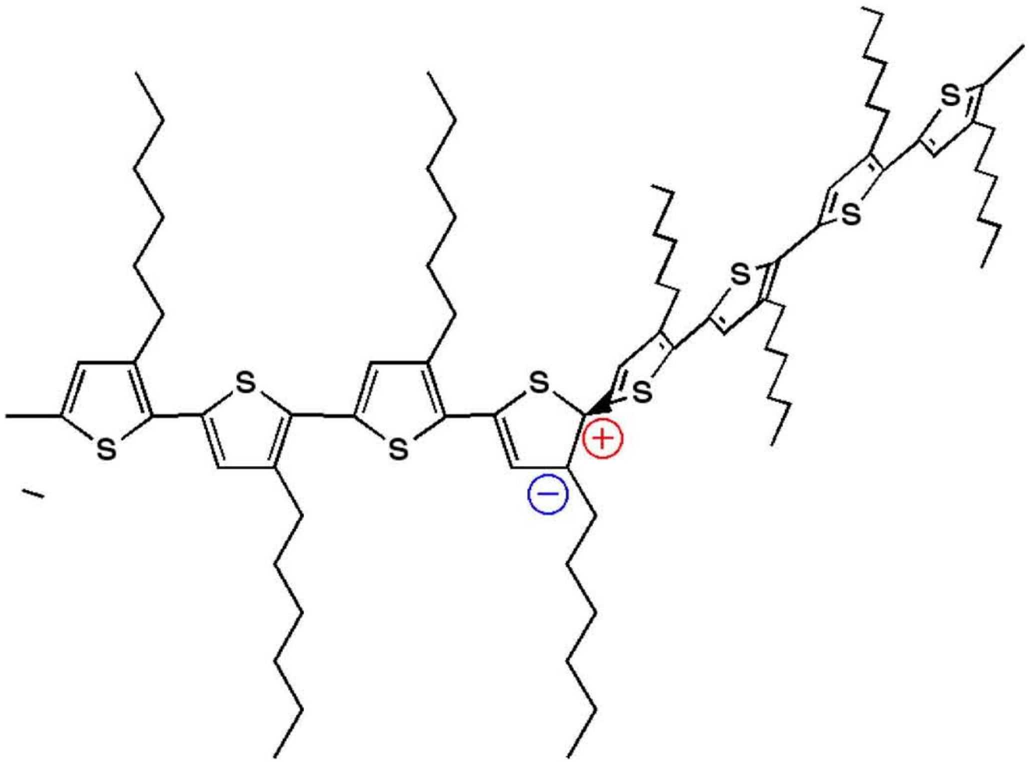


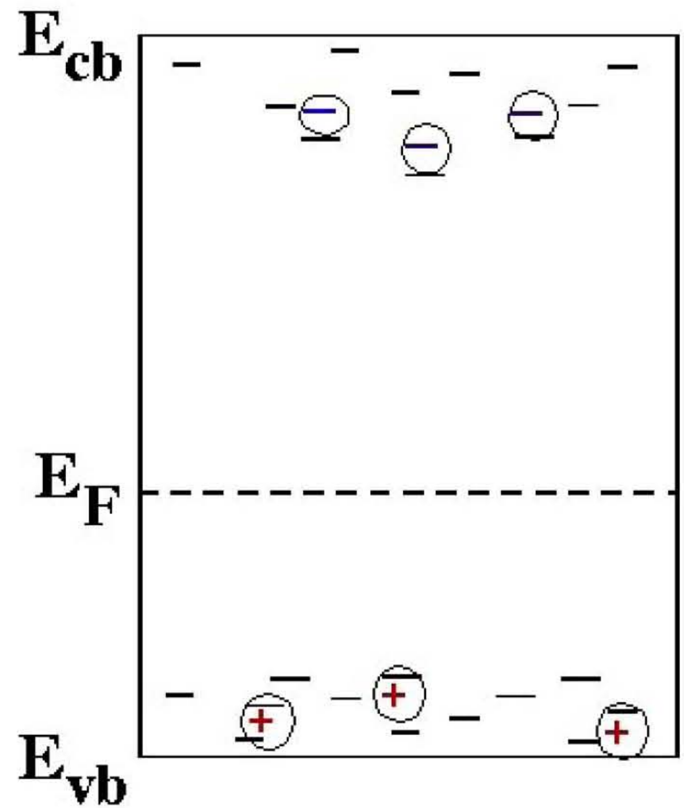
E_{cb} reduction potential

E_F

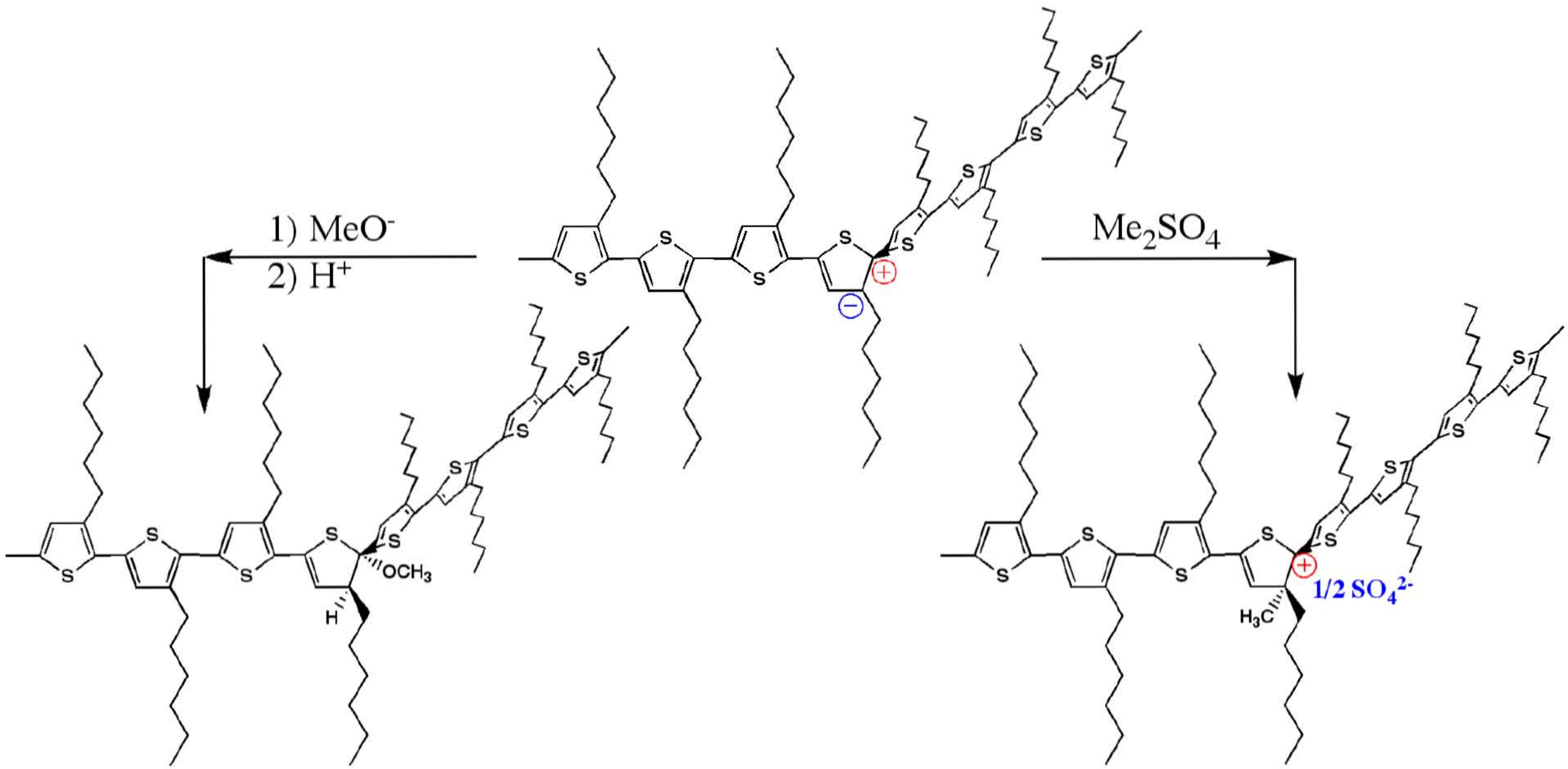
E_{vb} oxidation potential

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



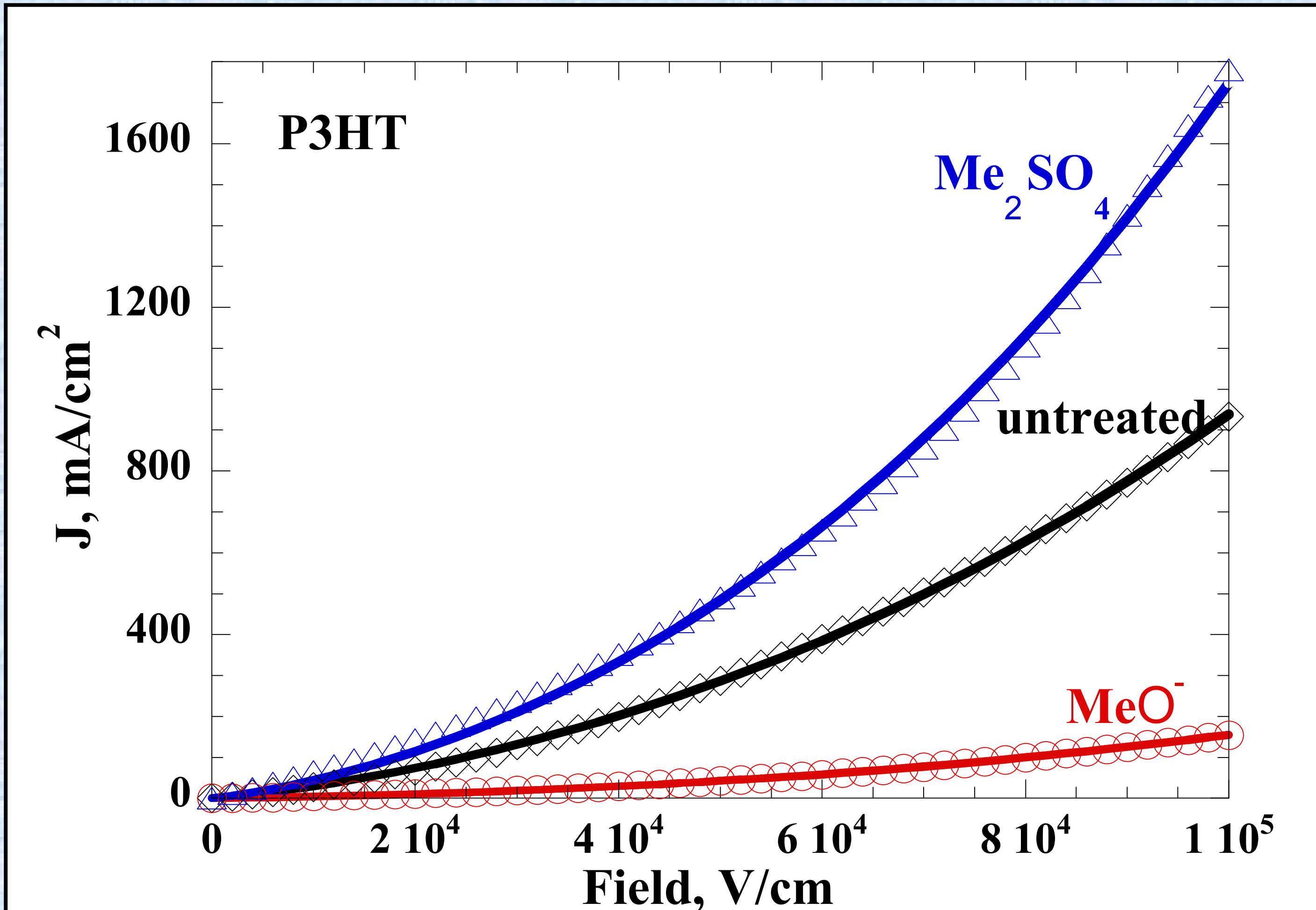


Chemically treating covalent defects in P3HT with nucleophiles and electrophiles

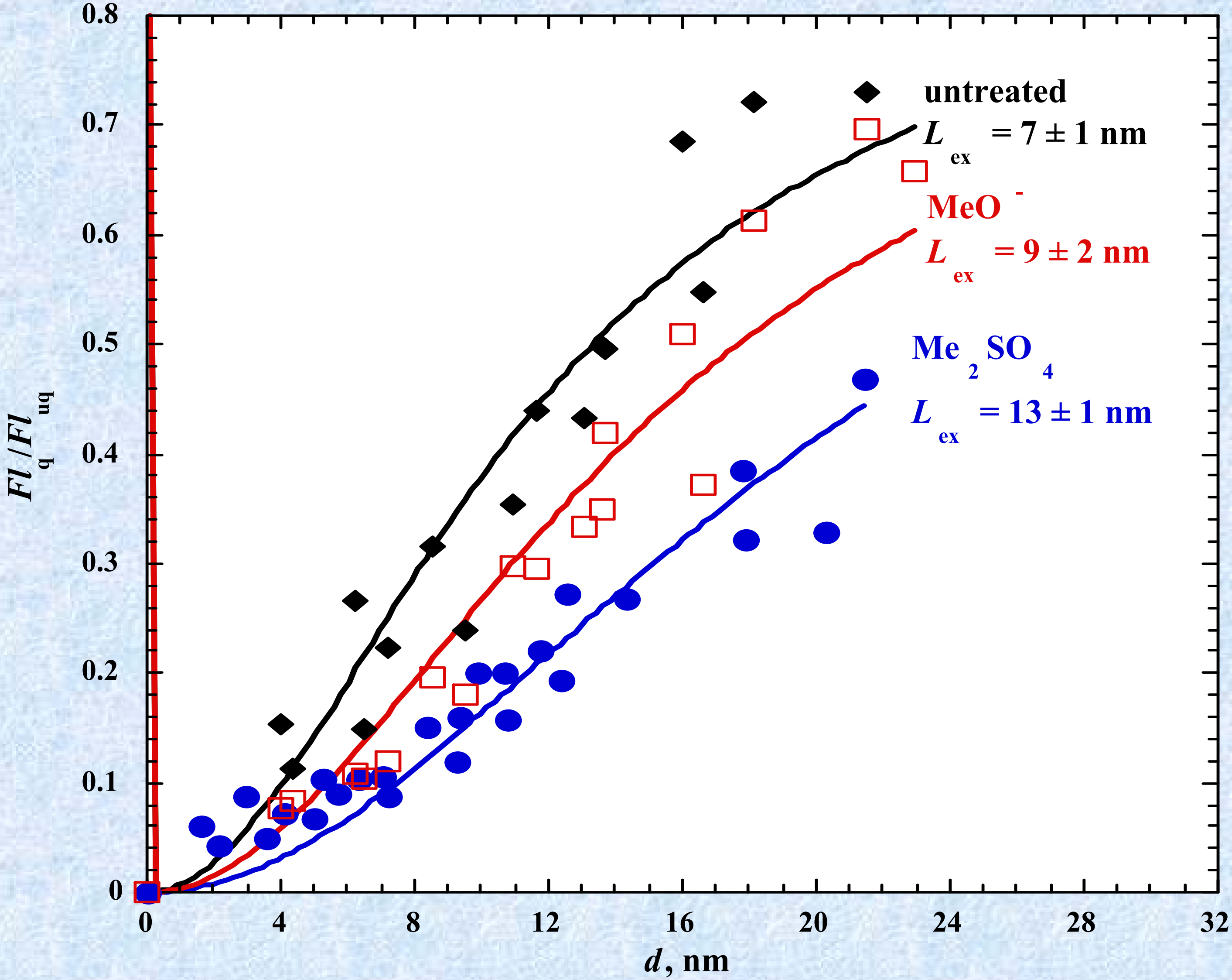


No reaction with pristine materials

Dark current-field curves for treated and untreated P3HT



Exciton diffusion length before and after chemical treatments



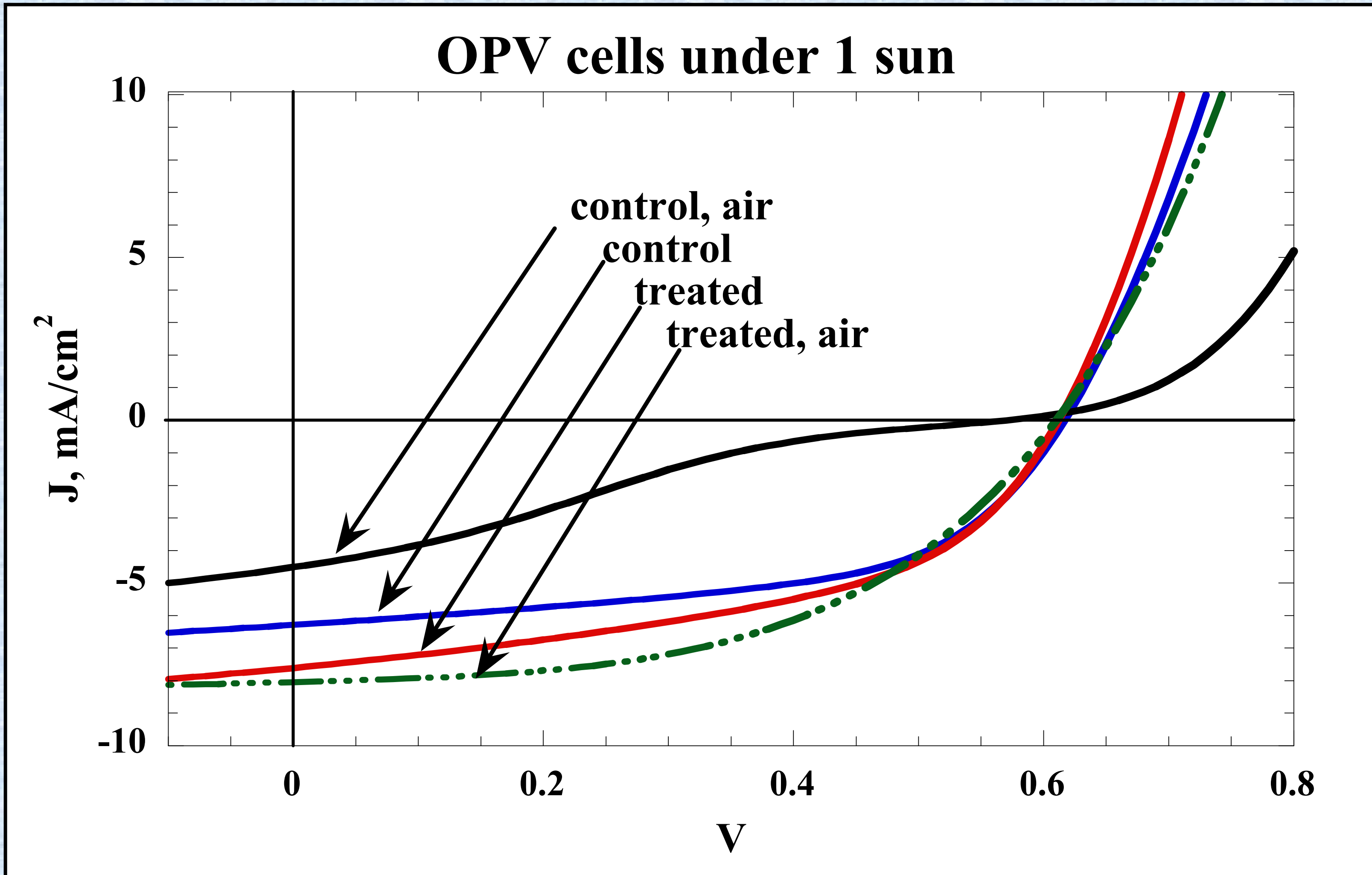
10^{18} cm^{-3} —> ~1 charge every 10 nm

Results of chemical treatments

Table 1.

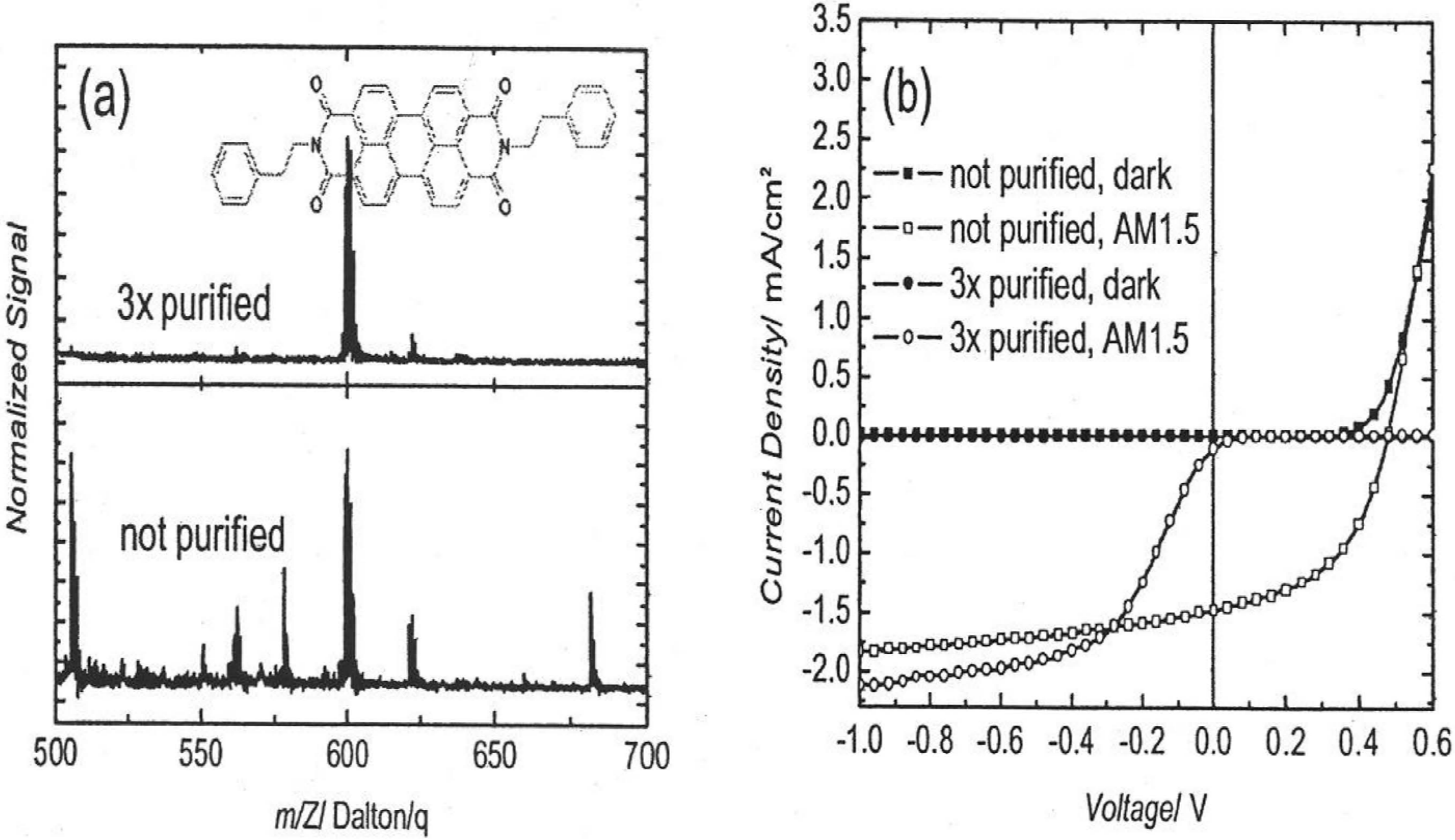
Treatment	Relative PL Quantum Yield	Zero-field conductivity, σ_0, x10^{-7} S/cm	$E_{a,J0}$, meV	PL Lifetime τ_{avg}, ps	L_{ex}, nm	Hole Mobility μ_p, x10^{-4} cm^2/Vs	Free Hole density, p_i, x10^{16} cm^{-3}
P3HT: none	1.00	14	233	401	7	1.2	7.3
MeO	1.35	3	276	579	9	1.8	1.0
MeI	0.92	29	223	354	–	3.5	5.2
Me_2SO_4	0.54	46	210	285	13	4.2	6.8
MDMO-PPV: none	1.00	1.4	280	866	12	–	–
MeO	1.22	0.5	306	1020	14	–	–

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



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} 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