Lecture 3:

Electronic structure of organic semiconductors

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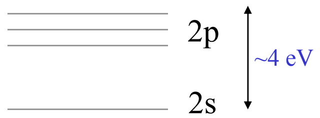
Carbon and Hybridization

Electronic Configuration of carbon: C=$1s^22s^22p^2$

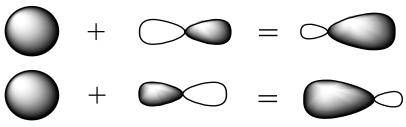


Covalent bonding energy for the s orbital:
3~4 eV per bond

→ hybridization: sp, sp^2 , sp^3

"In carbon, three possible hybridizations occur: sp, sp^2 , and sp^3 ; other group IV elements such as Si, Ge exhibit primarily sp^3 hybridization. Carbon differs from Si and Ge insofar as carbon does not have inner atomic orbitals except for the spherical 1s orbitals, and the absence of nearby inner orbitals facilitates hybridizations involving only valence s and p orbitals for carbon."

Ref. R. Saito *et al.* "Physical Properties of Carbon Nanotubes" (Imperial College Press, 1998, Singapore) p.5.



$$\varphi_1 = \frac{1}{\sqrt{2}}(\phi_s + \phi_{p_x})$$

$$\varphi_2 = \frac{1}{\sqrt{2}}(\phi_s - \phi_{p_x})$$

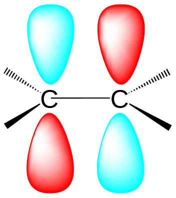
$$\text{Orthonormality}: \langle \varphi_1 | \varphi_1 \rangle = 1,\ \langle \varphi_2 | \varphi_2 \rangle = 1, \langle \varphi_1 | \varphi_2 \rangle = 0,\ \langle \varphi_2 | \varphi_1 \rangle = 0$$

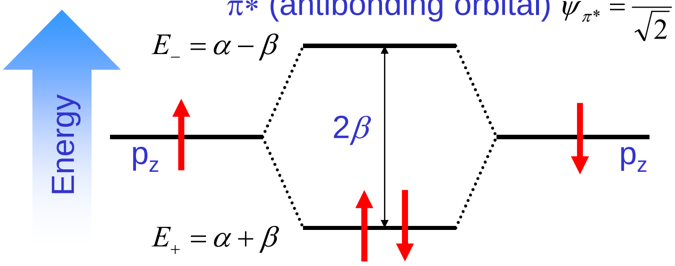
sp hybridization

Molecules: Chemical Bonds

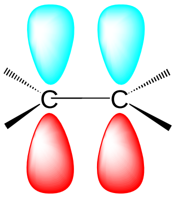
Ethylene (C_2H_4)

π* (antibonding orbital) $\psi_{\pi*} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$





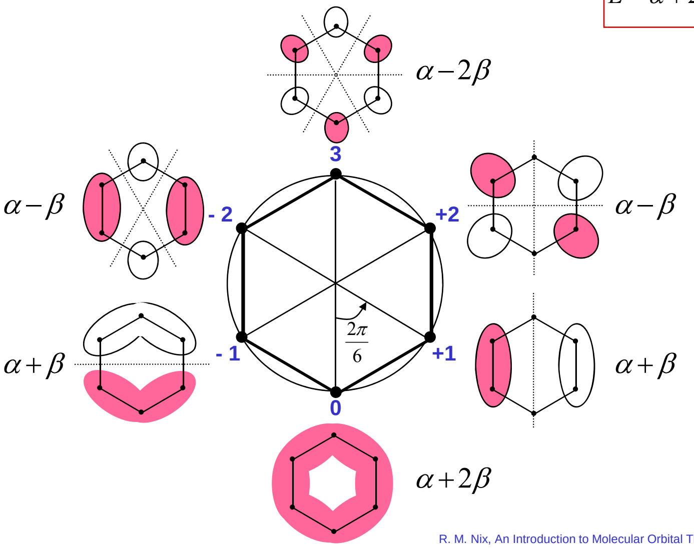
π (bonding orbital) $\psi_{\pi} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$

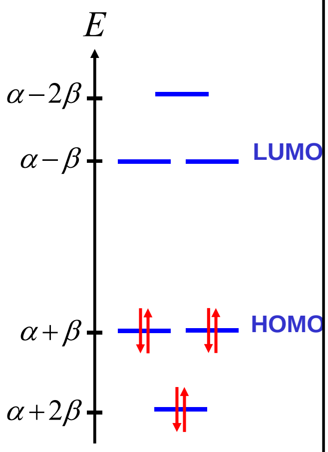


Benzene Molecule

Number of π-electrons: N=6

$$\boxed{E = \alpha + 2\beta\cos\left(\frac{2\pi n}{6}\right),\ (n = 0, \pm 1, \pm 2, 3)}$$

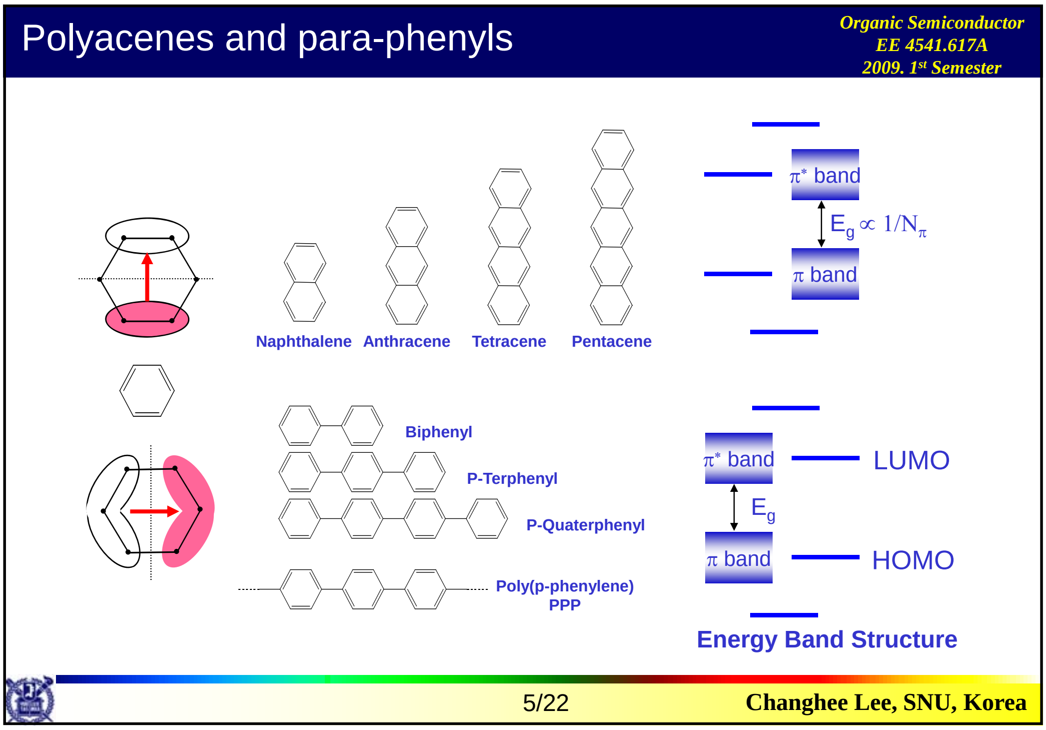




Energy states

R. M. Nix, An Introduction to Molecular Orbital Theory, (http://www.chem.qmul.ac.uk/software/download/mo/)

Molecular orbitals



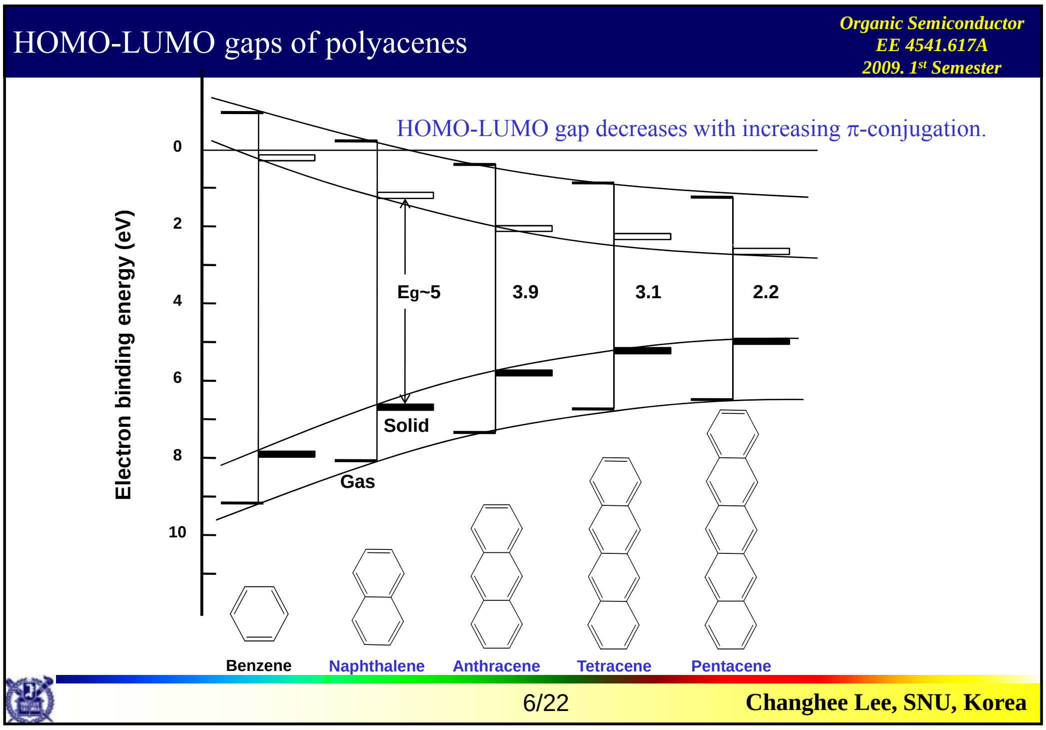
Polyacenes and para-phenyls

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

Energy Band Structure

5/22

Changhee Lee, SNU, Korea



HOMO-LUMO gaps of polyacenes

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

HOMO-LUMO gap decreases with increasing π-conjugation.

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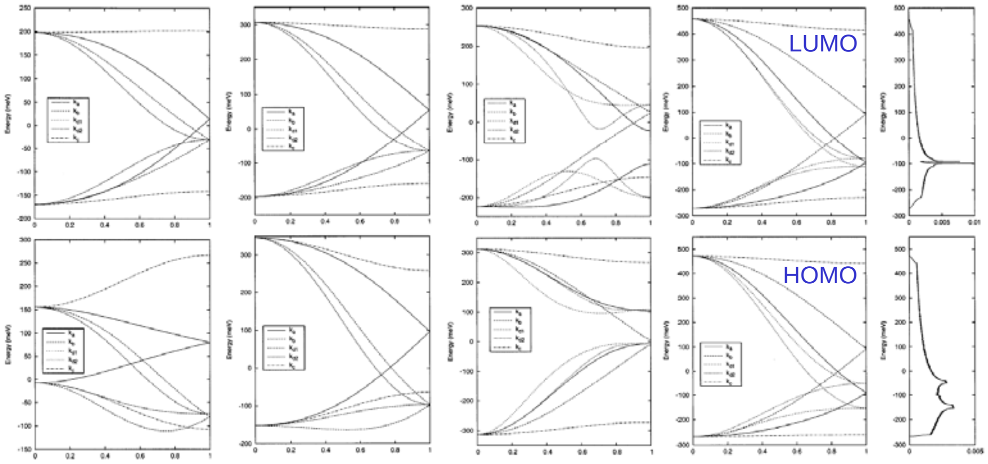
Changhee Lee, SNU, Korea

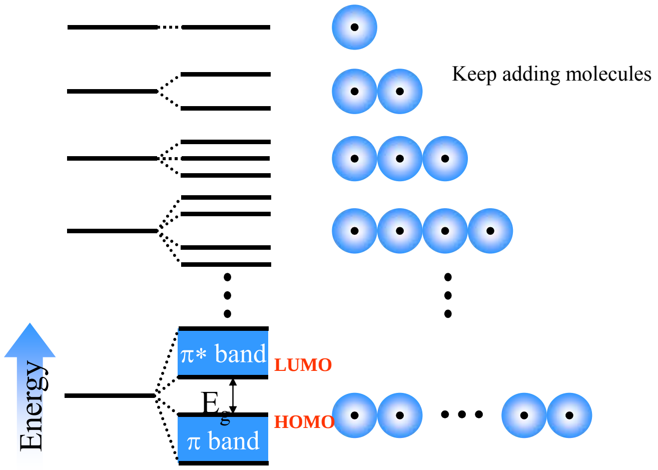
Widths of HOMO and LUMO Bands



naphthalene anthracene tetracene pentacene

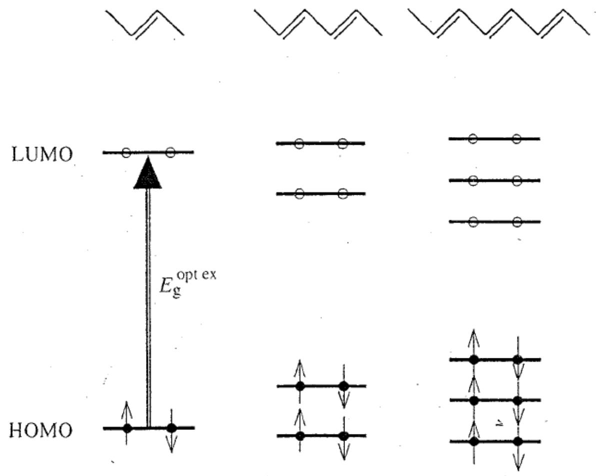
Y. C. Cheng, et al., J. Chem. Phys. 118,3764 (2003)

Molecules → Macromolecules: HOMO, LUMO and Bands

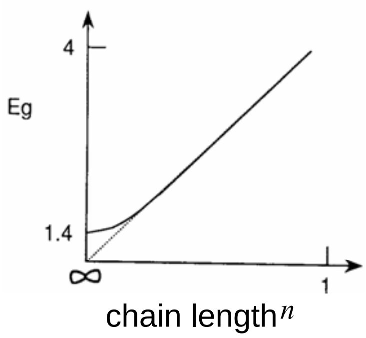


- The average energy separation between MOs decrease as n increases → Formation of bands.
- The HOMO-LUMO separation, ΔE = EHOMO – ELUMO, decreases as n increases.
- Energetically favored electron excitation is from the HOMO to the LUMO
- The interchain transfer integral (t) expresses the ease of charge transfer between two interacting chains: The larger the band-width (the magnitude of transfer integral), the higher the mobility.

π-conjugated Polymers: Energy bandgap

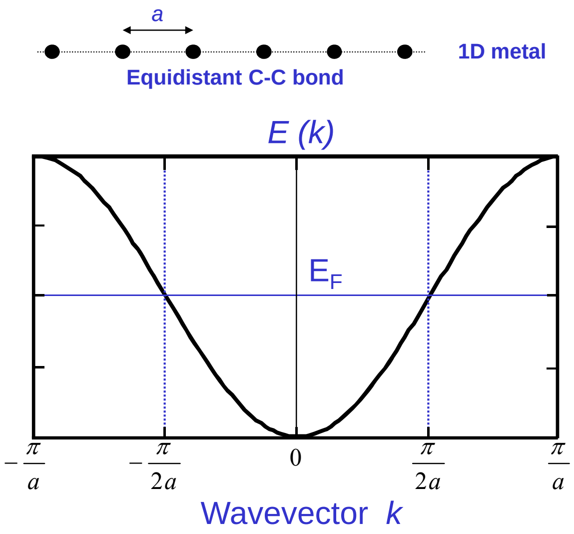


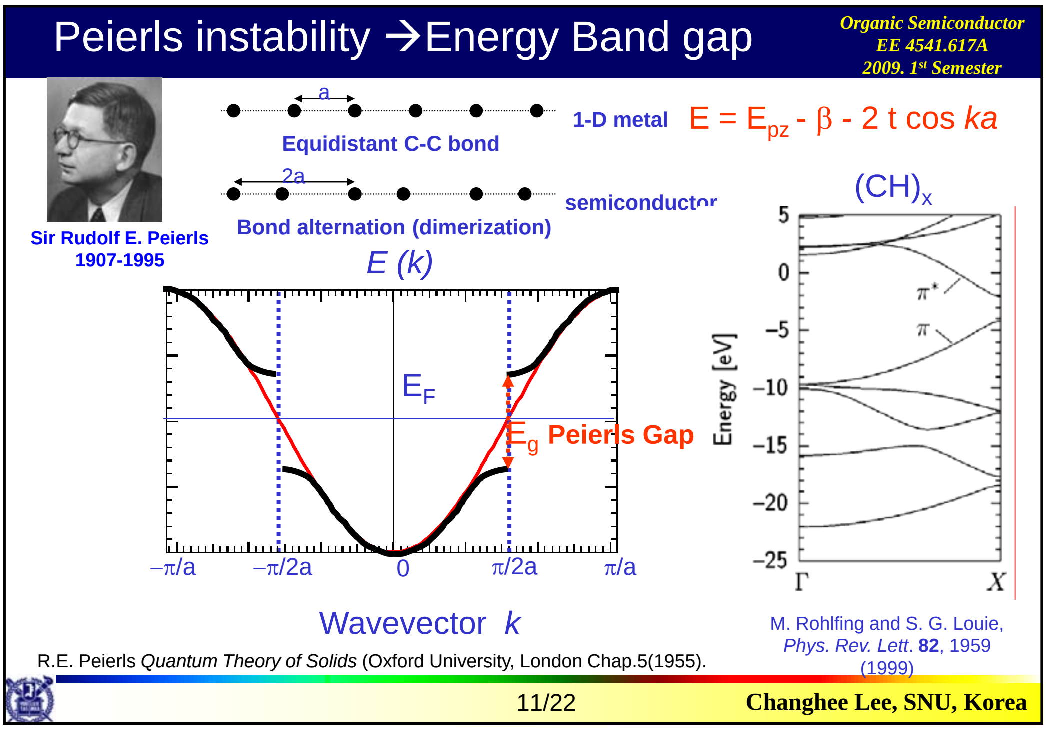
$$E_g^{\;opt}(n) = E_g^{\;opt}(\infty) - \frac{K}{n}$$



Energy gap (HOMO-LUMO) decreases with increasing π-conjugation.

1-d system





Peierls instability →Energy Band gap

Sir Rudolf E. Peierls
1907-1995

Equidistant C-C bond

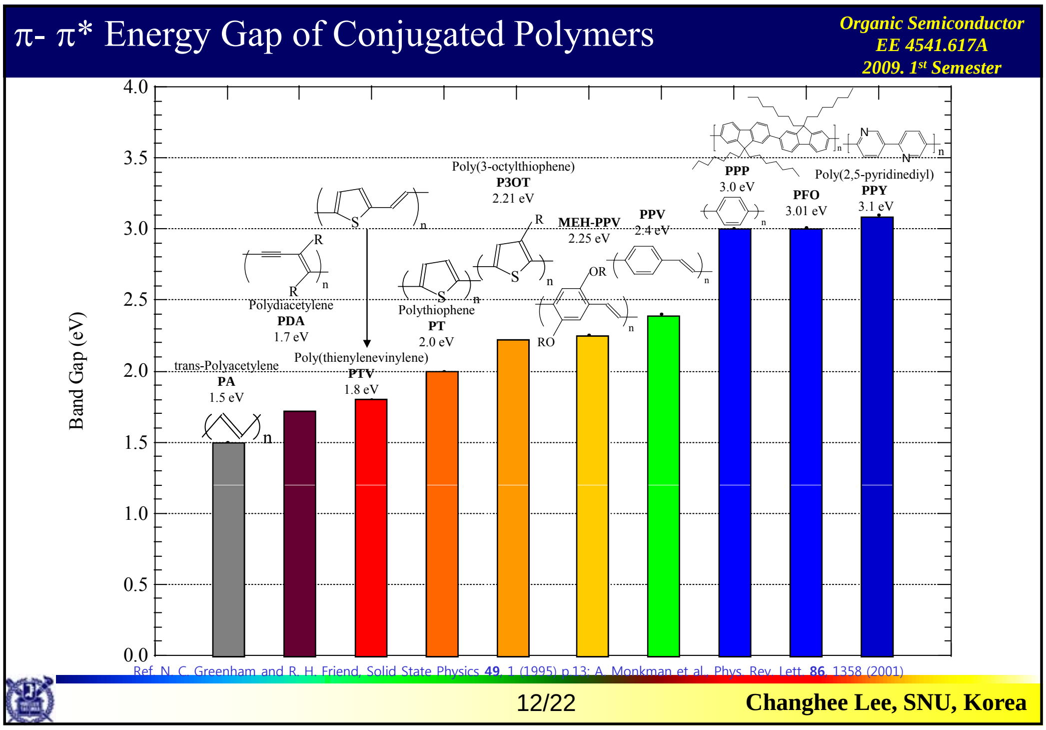
1-D metal $E = E_{pz} - \beta - 2\,t \cos ka$

Bond alternation (dimerization)

semiconductor

M. Rohlfing and S. G. Louie, *Phys. Rev. Lett*. **82**, 1959 (1999)

R.E. Peierls *Quantum Theory of Solids* (Oxford University, London Chap.5(1955).



π- π* Energy Gap of Conjugated Polymers

Ref. N. C. Greenham and R. H. Friend, Solid State Physics **49**, 1 (1995) p.13; A. Monkman et al., Phys. Rev. Lett. **86**, 1358 (2001)

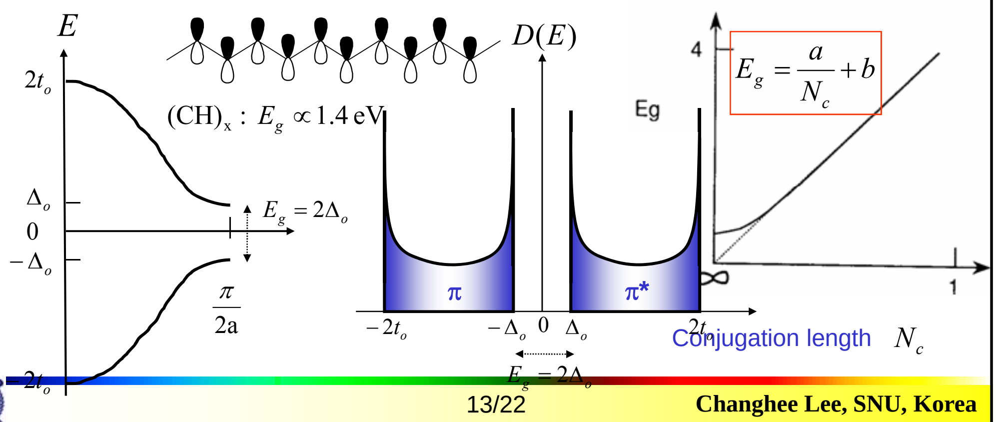
Polyacetylene: SSH Hamiltonian

Su-Schrieffer-Heeger Hamiltonian

$$H = H_{kinetic} + H_{elastic} + H_{electronic}$$

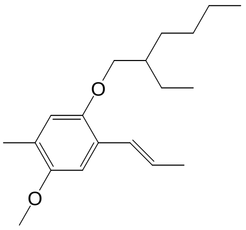
$$= \frac{M}{2}\sum \dot{u}_n^{\,2} + \frac{K}{2}\sum_n (u_n - u_{n+1})^2 - \sum_{n,s}[t_0 + \alpha(u_n - u_{n+1})](c^+_{n+1,s}c_{n,s} + c^+_{n,s}c_{n+1,s})$$

$$\boxed{\text{Peierls gap}: 2\Delta = 16t_o\ \exp[-(1+\frac{1}{2\lambda})],\ \text{where}\ \lambda = \frac{2\alpha^2}{\pi t_o K}.}$$



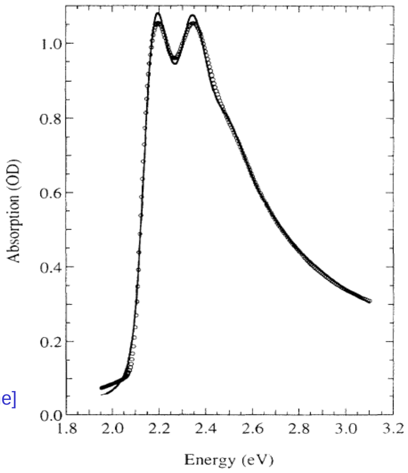
$$\boxed{E_g = \frac{a}{N_c} + b}$$

DOS and Absorption



poly[2-methoxy-5-(2'-ethyl-hexyloxy)-l,4-phenylene vinylene]

MEH-PPV



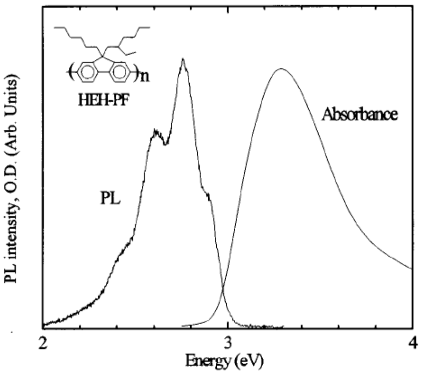
Density of States (DOS):

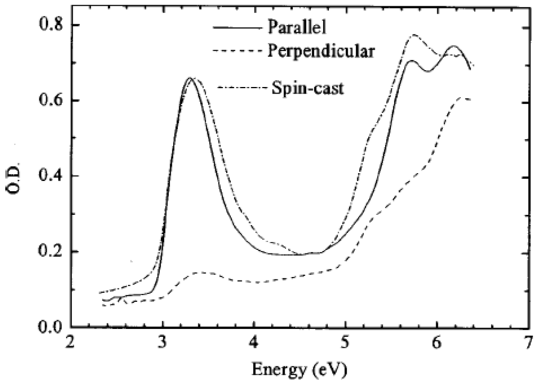
Square-root singularity in 1-d.

$$\boxed{D(E) = \frac{dN(E)}{dE} \propto \frac{1}{\sqrt{E - E_g}}}$$

T. W. Hagler et al., Phys. Rev. B 51, 14199 (1995)

PL and Absorption of Conjugated Polymers



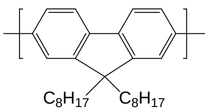


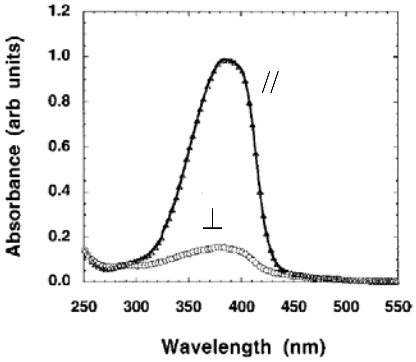
poly (9-hexyl-9-(2'-ethyl-hexyl)-fluorene-2,7-diyl) (HEH-PF)

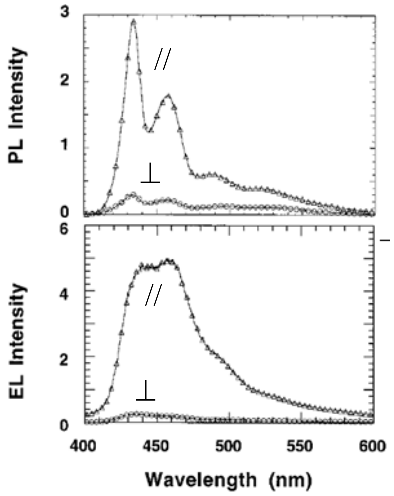
E. K. Miller, G. S. Maskel, C. Y. Yang, A. J. Heeger, Phys. Rev. B 60, 8028 (1999)

Polarized absorption, PL and EL

poly(9,9-dioctylfluorene)
PFO



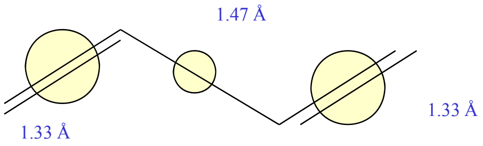




K. S. Whitehead, M. Grell, D. D. C. Bradley, M. Jandke and P. Strohriegl, App. Phys. Lett. 76, 2946 (2000).

Electron-Phonon coupling

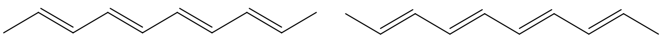
- Strong electron-phonon coupling:
π-electron bond densities directly determine the geometric structure,
e.g., butadiene, C_4H_6.



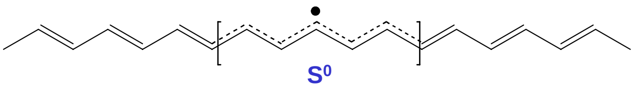
- Vibronic progressions in optical absorption and photoluminescence spectra
- Stokes shift between optical absorption and emssion.
- Polaron formation

* Charge transfer or low energy charge-excitations (via dong or photoexcitation) strongly affects the p-electron bond densities → geometric structure.

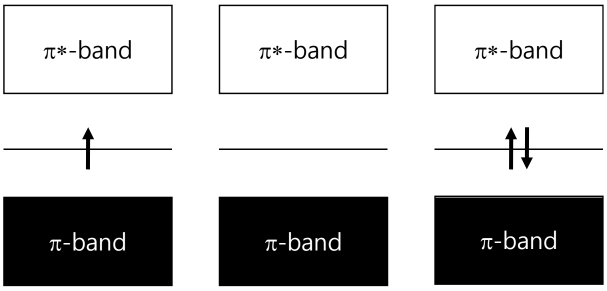
Soliton



A **Polyacetylene $(CH)_x$** B

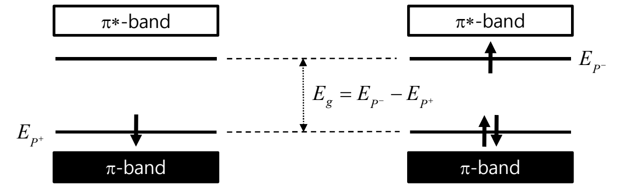


S^0
(neutral Soliton)

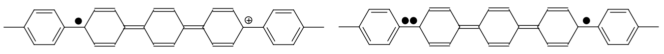


S^0	S^+	S^-
Charge Q = 0	Charge Q = +1	Charge Q = -1
Spin S = 1/2	Spin S = 0	Spin S = 0

Polaron

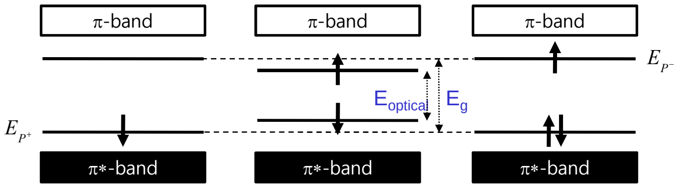


Polaron = charge + lattice distortion



hole polaron (P^+)

electron polaron (P^-)



hole polaron (P^+) Singlet exciton ($P^- \cdots P^+$) electron polaron (P^-)

Exciton Energies of π -Conjugated Polymers

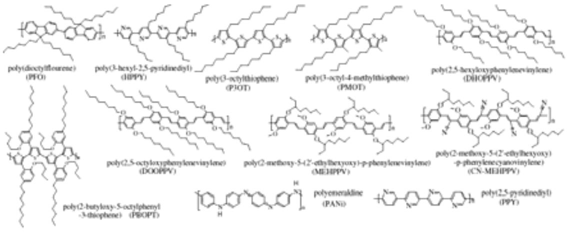


TABLE I. Photophysical data obtained by pulse radiolysis for triplet states in various conjugated polymers; ΔE_{ST} is the energy difference between the $1\,^1Bu$ and the $1\,^3Bu$ states.

	S_0-S_1 energy (eV) (λ/nm)				T_1-T_n (eV)		ΔE_{ST} (eV)	
Polymer	Maximum[b]	Onset[c]	PL	T_1-S_0 (eV)	(λ/nm)	τ_T (μs[a])	Maximum[b]	Onset[c]
PMOT	3.77 (329)	3.22 (385)	2.64 (469)	2.20	1.85 (670)	62	1.57	1.02
P3OT	2.83 (438)	2.42 (512)	2.21 (562)	1.65	1.50 (825)	21	1.03	0.62
PBOPT	2.52 (492)	2.18 (570)	2.17 (572)	1.60	1.38 (900)	57	0.92	0.58
MEHPPV	2.48 (500)	2.23 (556)	2.25 (550)	1.30	1.50 (830)	92	1.18	0.93
PFO	3.22 (385)	3.01 (412)	3.00 (413)	2.30	1.65 (750)	108	0.92	0.71
DOOPPV	2.59 (478)	2.23 (556)	2.28 (544)	1.50	1.55 (800)	134	1.09	0.73
DHOPPV	2.58 (480)	2.13 (581)	2.30 (538)	1.50	1.62 (765)	176	1.08	0.63
PPY	3.35 (370)	3.10 (400)	3.26 (380)	2.40	2.10 (590)	98	0.95	0.70
HPPY	3.90 (318)	3.50 (344)	2.82 (440)	2.50	2.10 (590)	70	1.40	1.00
CN-MEHPPV	2.72 (456)	2.35 (527)	2.28 (544)					
PANi[d]	2.00	1.77 (700)	N/A	<0.9	1.55 (800)	ca. 2.4 ≥ 2000	<1.1	<0.9

[a]Triplet state lifetime in benzene solution; [b]from maximum of absorption band; [c]from onset of absorption band; [d]measured in 80% benzene/20% N-methylpyrrolidone.

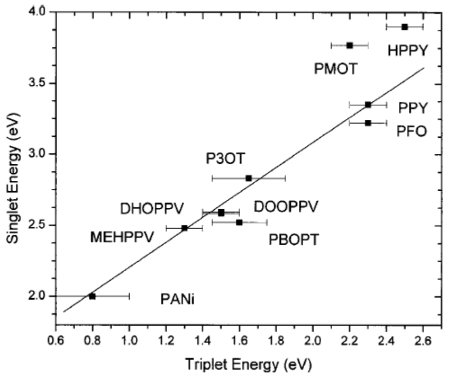
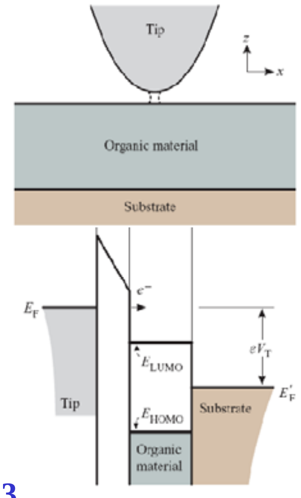
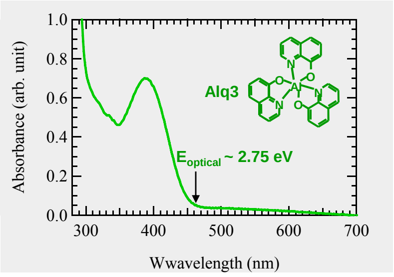


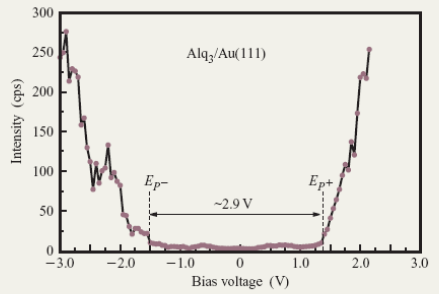
FIG. 2. Plot of triplet energy gap against singlet energy gap for different polymers. Polymer acronyms given in Fig. 1. The line is a guide to the eye.

A. Monkman et al., Phys. Rev. Lett. **86**, 1358 (2001)

Bandgap, Exciton binding energy







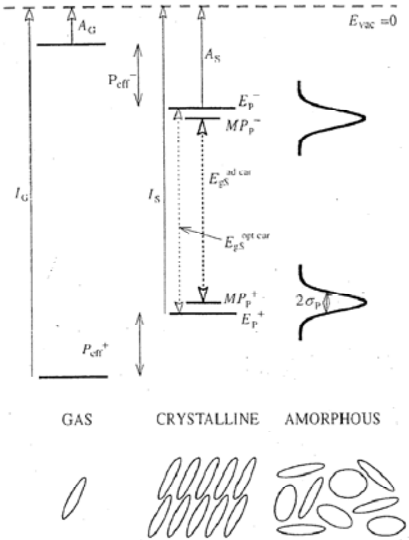
Alq3

From z–V measurements, $E_{gsp} = 2.96 \pm 0.13$ eV.
Threshold for optical absorption: $Ea = 2.75$ eV,
→ $E_b = 220 \pm 130$ meV.

S. F. Alvarado, L. Rossi, P. Muller, P. F. Seidler, W. Riess, IBM J. Res. Dev. **45,** 89 (2001)

Energy levels of π-conjugated molecule in the gas, crystalline and amorphous state

- **Weak van der Waals interaction between molecules** → Each molecule keep its molecular levels which are shifted due to the interaction with surrounding molecules in the solid-state.



Solid-state ionization potential

$$I_S = I_G - P_{eff}^{\ +} - (E_b^{\ +})_{eff}$$

Solid-state electron affinity

$$A_S = A_G + P_{eff}^{\ -} + (E_b^{\ -})_{eff}$$