Charge transport along conjugated polymer chains and DNA

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www.dct.tudelft.nl/om

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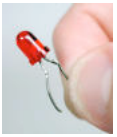
Electronic equipment based on inorganic semiconductors (e.g. Si, GaAs)

- **communication:** radio, TV, telephone, satellite

- **sound/images:** CD, MP3, photo/video camera

- **lighting/ signaling:** light-emitting diodes



- **data handling:** computers

- **energy conversion:** solar cells

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Inorganc semiconductors (e.g. silicon)

Advantages:

- fast switching (electrons very mobile)
- stable
- small devices possible (now micro-, future nano-scale)

Disadvantages:

- expensive (production of Si at high temperature)

- brittle
- heavy

('clean rooms' needed)

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Disadvantages of inorganic semiconductors:

- EXPENSIVE
- BRITTLE
- HEAVY

Opposite

- CHEAP
- FLEXIBLE
- LIGHT

Plastic electronics?

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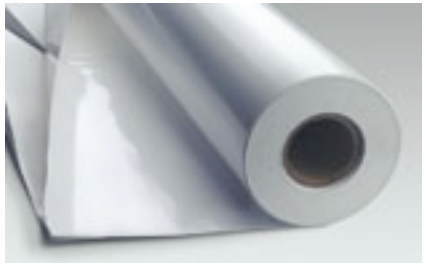
Plastics known as insulators

Polyethylene not conducting



Teflon or PVC as insulator

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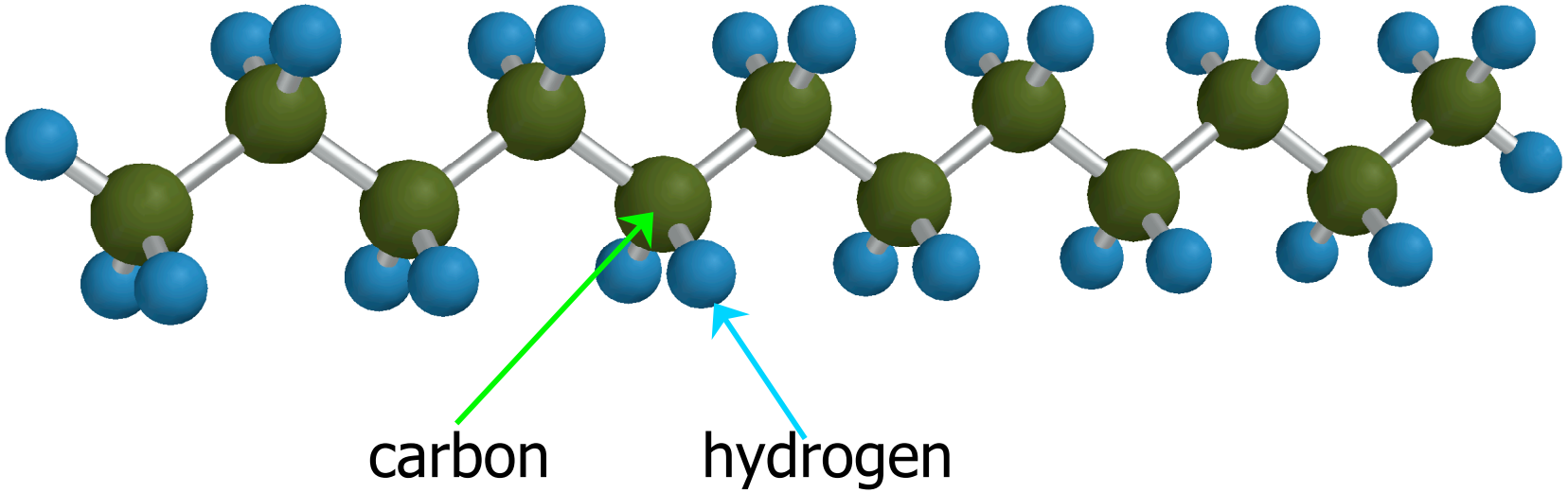
Plastics known as insulators

Polyethylene is insulator



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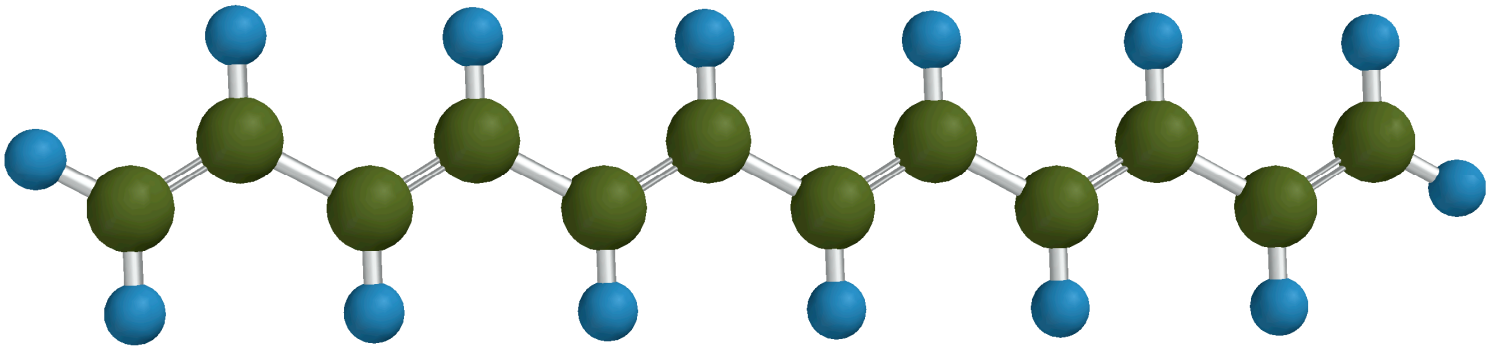
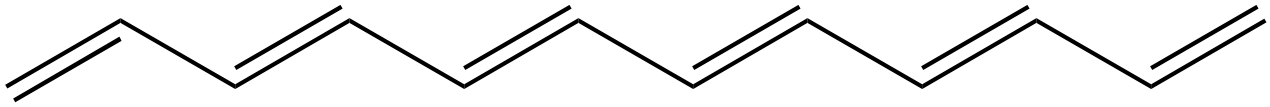
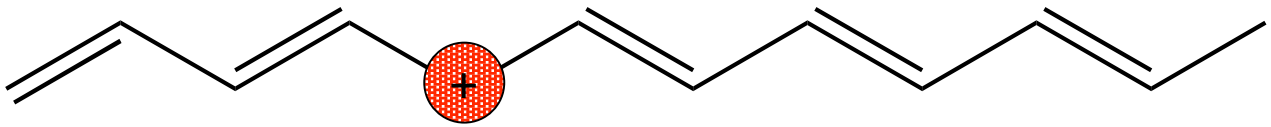
Conjugated polymers can become conducting

polyacetylene





insulating



conducting

I_3^-

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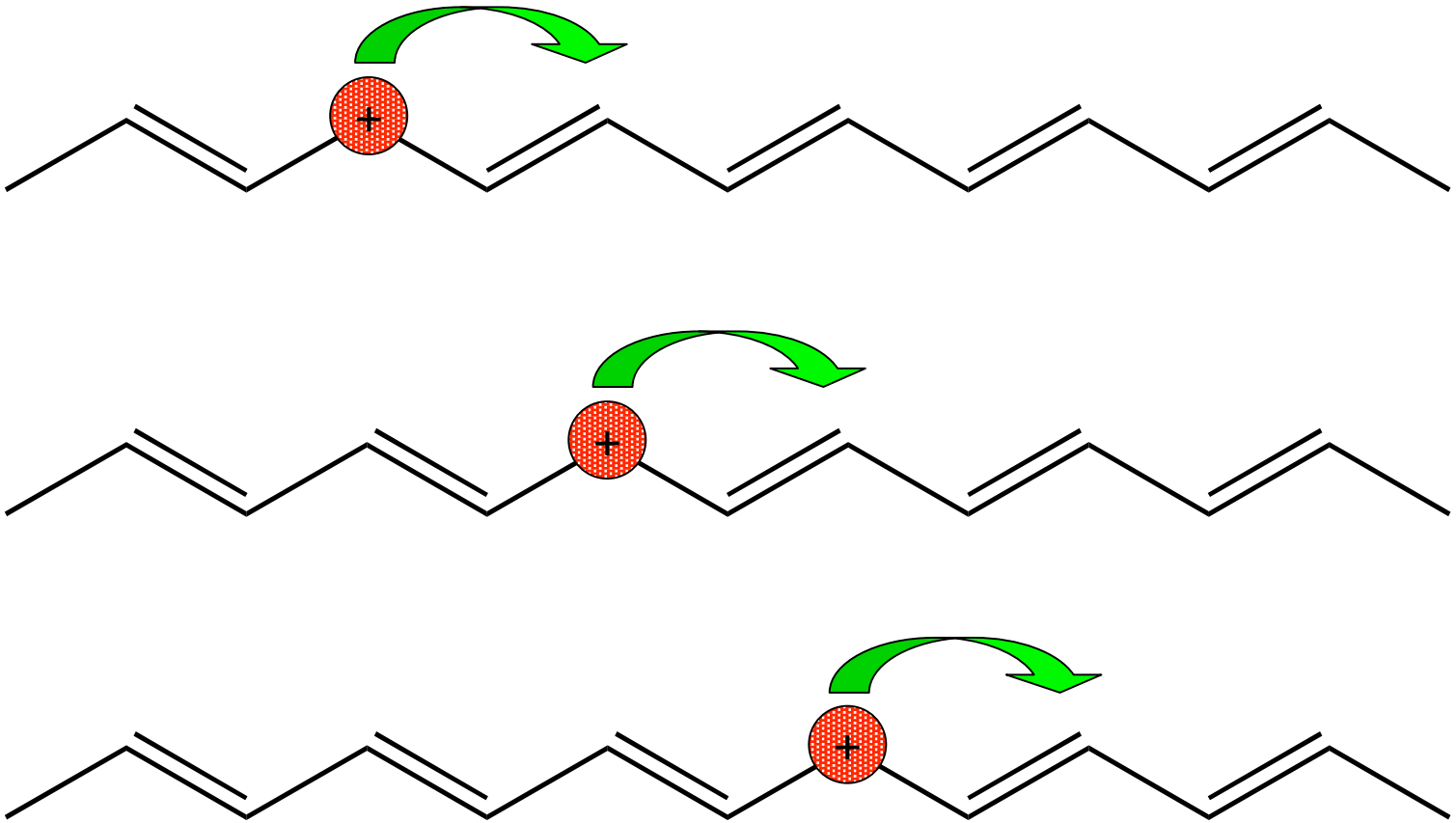
Charge can move along polymer chain



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Polymers can be made conducting by:

- chemical doping

- charge injection from electrodes

- photo-excitation

Nobel Prize Chemistry 2000

"Discovery and development of conducting poymers"

MacDiarmid Shirikawa Heeger

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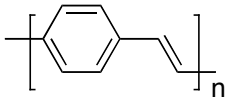
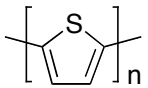
Conjugated polymers:

different colors, soluble, easy processing

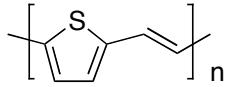
Merck OLED Materials GmbH



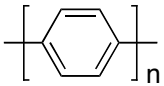
poly(p-phenylene vinylene) (PPV)



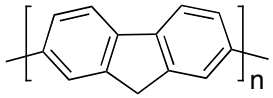
polythiophene



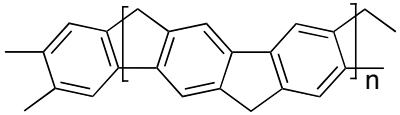
poly(thienylene vinylene) (PTV)



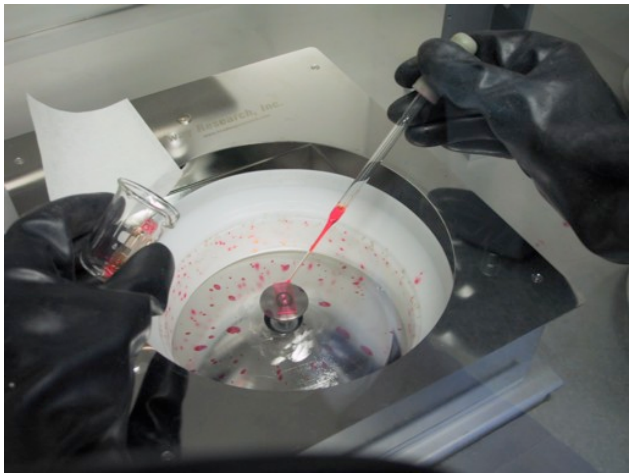
poly(p-phenylene)(PPP)

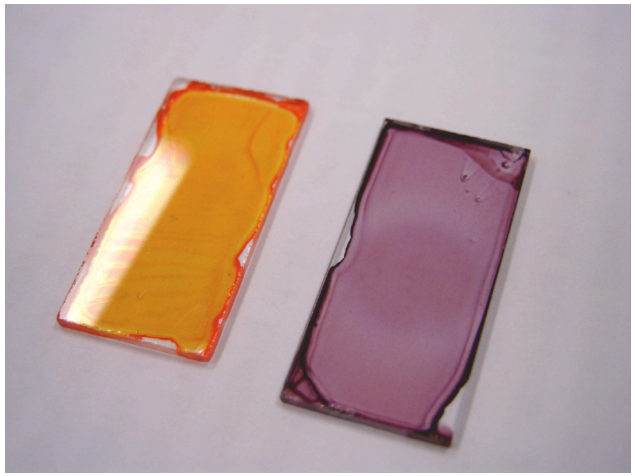


polyfluorene



ladder-type PPP





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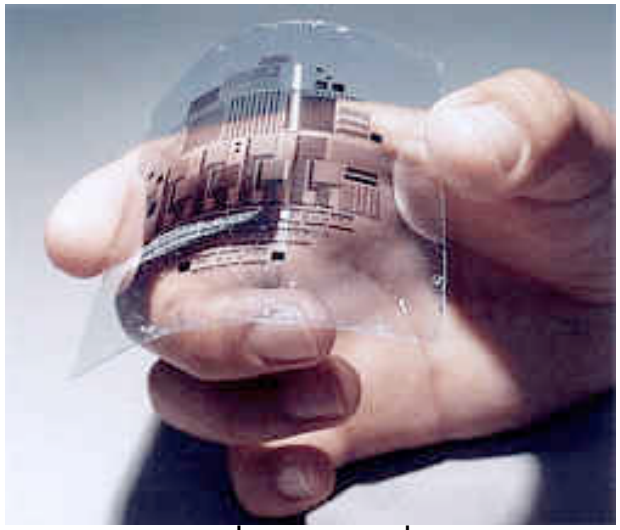
Currently world-wide research on plastic electronics

Prototype circuits of plastic transistors



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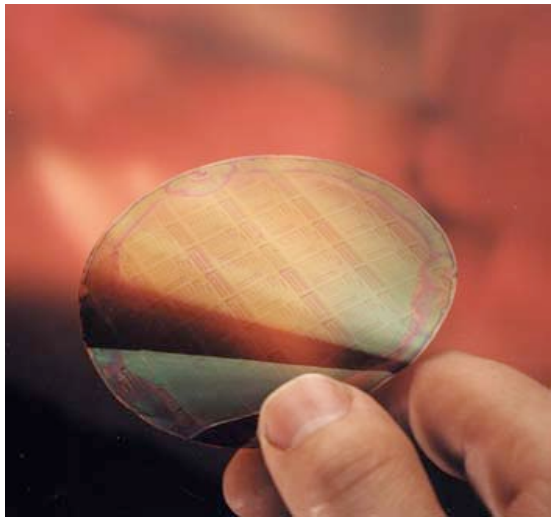

physicsweb.org (D.M. de Leeuw, Philips)

1st commercial application of plastic LED in 2002 (Philips)

Future: solar cells, flexible display, flexible rechargeable newspaper, electronic tags (identification)

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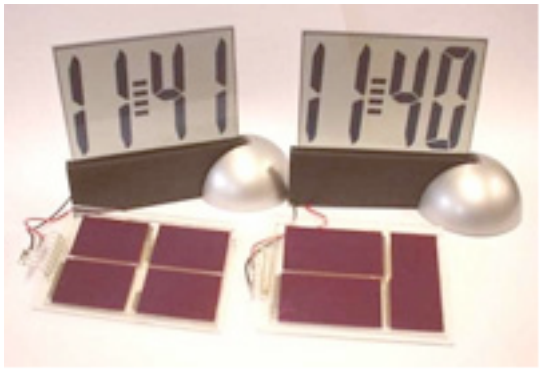
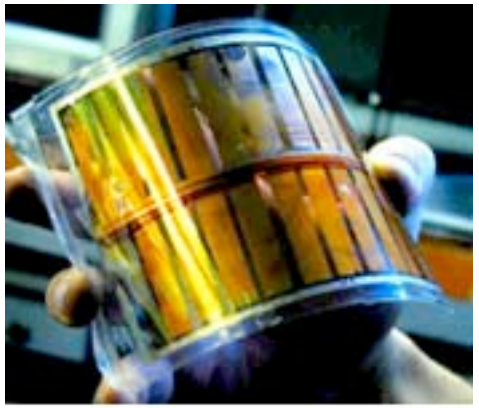
Plastic solar cells

Digital clocks powered by CDT's polymer solar cells





Concept image of Organic/Nanosolar manufactured product from Nanosolar.com

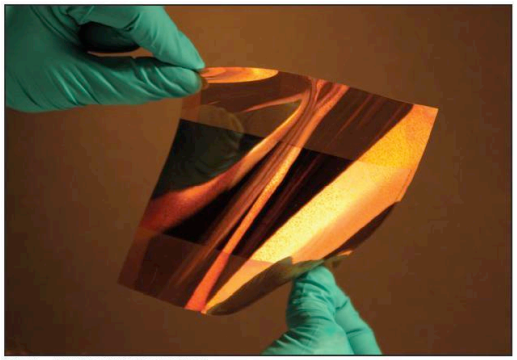


Figure 1. A flexible, organic-based solar cell

Efficiency < 5 %

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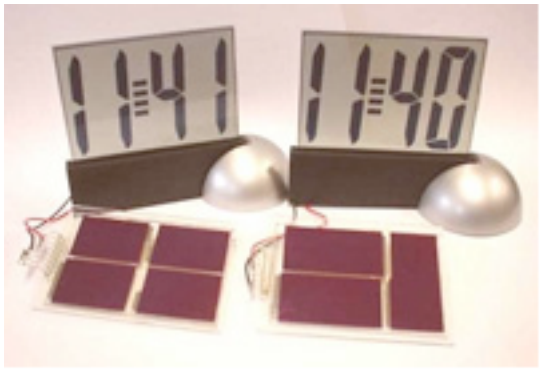
Plastic solar cells

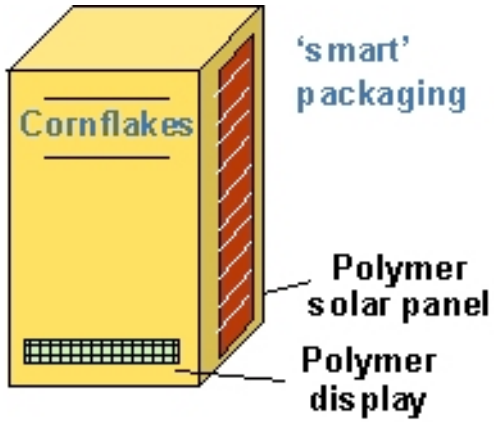
Digital clocks powered by CDT's polymer solar cells



Tents with solar cells

© NREL, USA

Smart package with plastic solar cell and display



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Philips - Products

1999

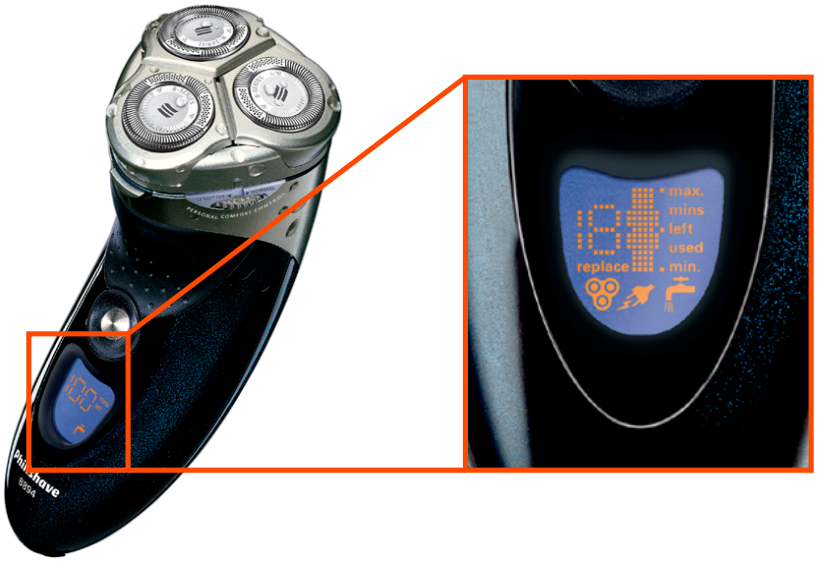
Segmented displays

2000

Monochrome graphic displays

2002

First to bring PLED technology to the consumer market



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Philips : full color screen with OLEDs

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Electronic paper

Plastic Logic, Cambridge UK
Philips, Eindhoven

- Lightweight
- Thin
- Flexible
- Unbreakable

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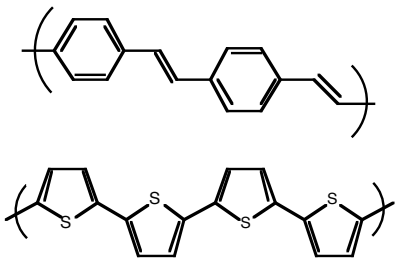
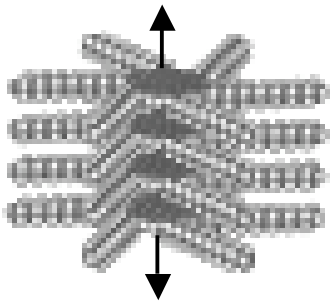
Opto-electronic properties of materials

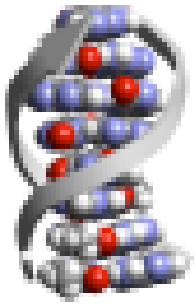
conjugated polymers



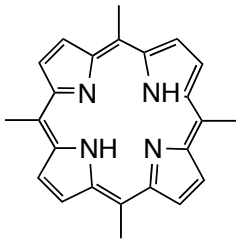
supramolecular materials



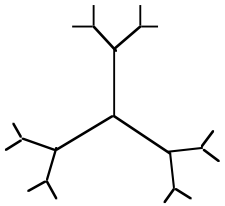
self-assembling
discotic molecules



DNA



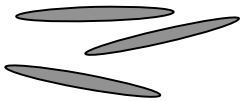
porfyrins



dendrimers

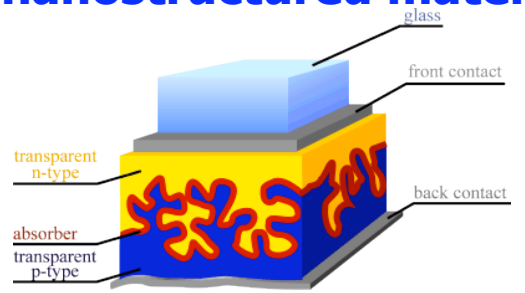
inorganic nanoparticles

spherical



elongated

nanostructured materials



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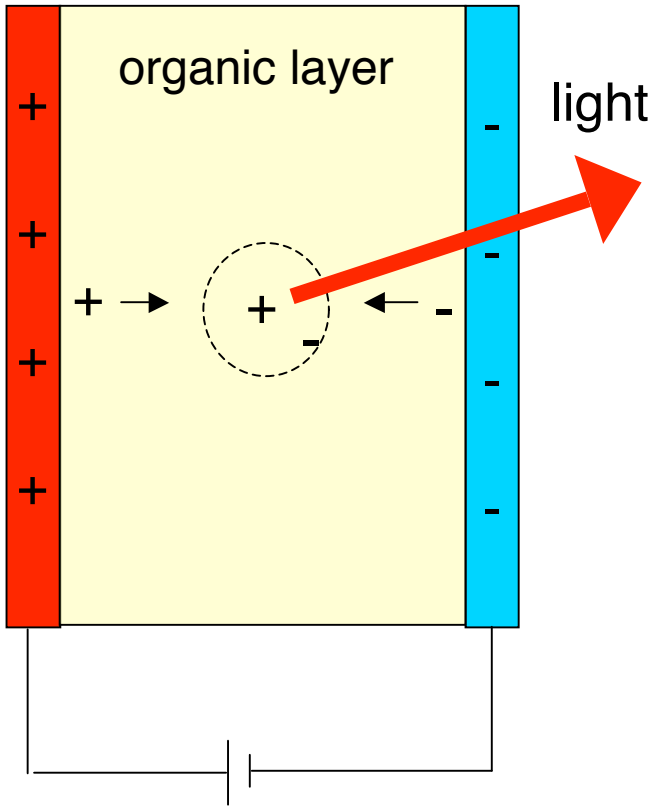
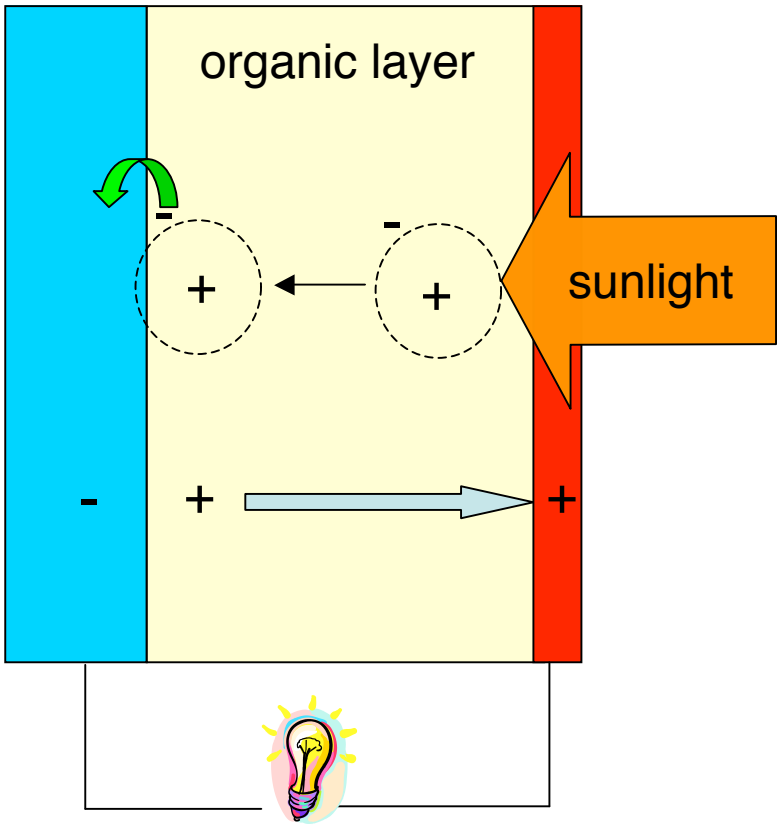
Organic materials in opto-electronic devices

Light-emitting diode



Solar cell



Charge carrier mobility must be high

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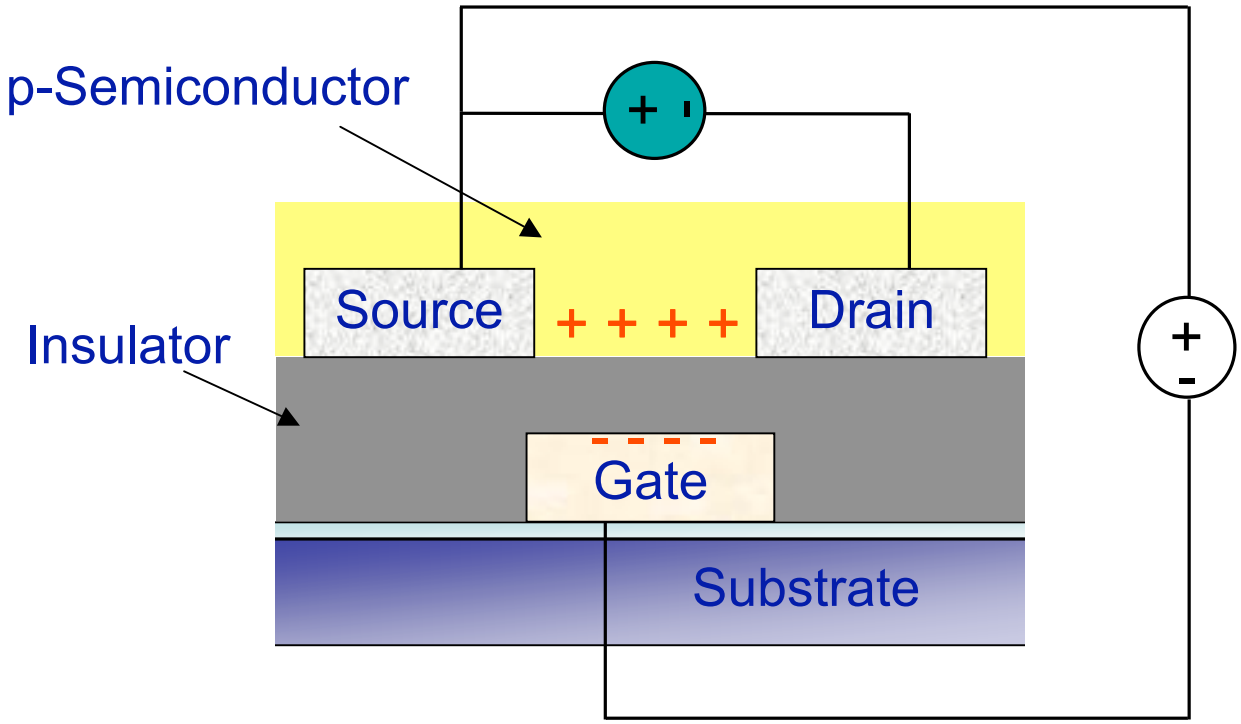
Unipolar *p*-type field-effect transistor



Crucial question: What is charge carrier mobility ?

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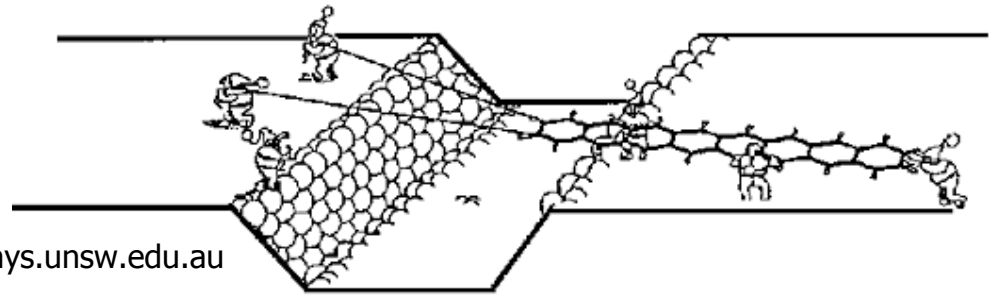
Molecular Electronics



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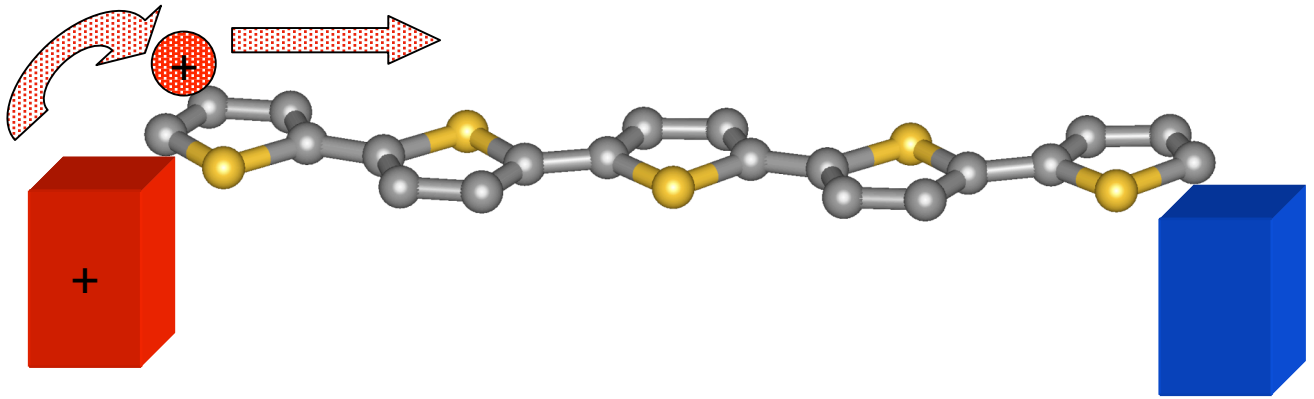
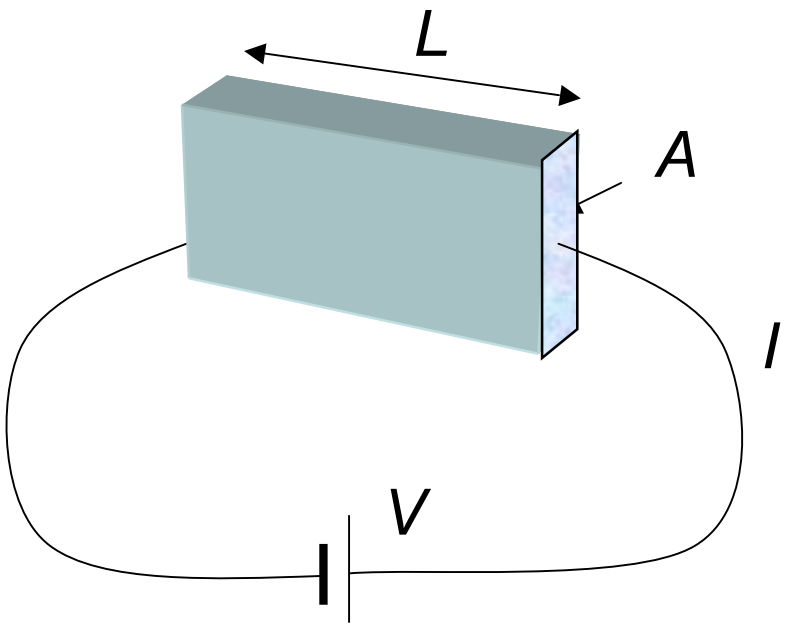
Molecules as building blocks for electronic circuits



- charge transport through single molecule (Ohm's law not valid)
- good contacts
- self-assembling (otherwise too elaborate)

What determines charge carrier mobility?

Mobility from device measurements (LED, solar cell, transistor)



Ohm's law:

$V = I R$

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Charge transport measurement

$V = I\,R$

$I = V/R$

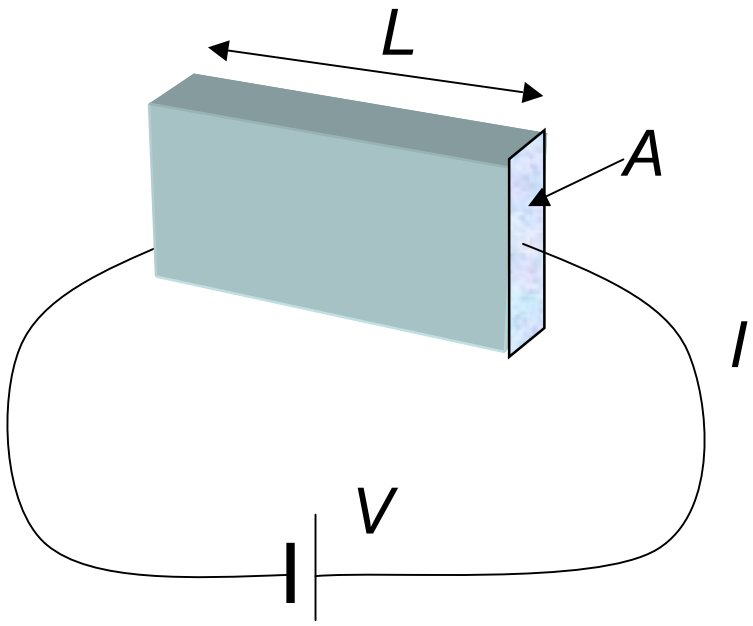
$j = I/A = V/(RA)$ (current density)

use $V = \mathcal{E}\,L$

$j = I / A = (L/(RA))\,\mathcal{E} = \sigma\mathcal{E}$

$\sigma = 1/\rho$ σ conductivity

ρ resistivity



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Definition of mobility μ

Current density: amount of Coulomb per unit area and unit time

$$j = \sigma \mathcal{E} = e\, n\, v = e\, n\, \mu\, \mathcal{E}$$

$$\sigma = e\, n\, \mu$$

$$v = \mu\, \mathcal{E}$$ **mobility is velocity per unit field strength**

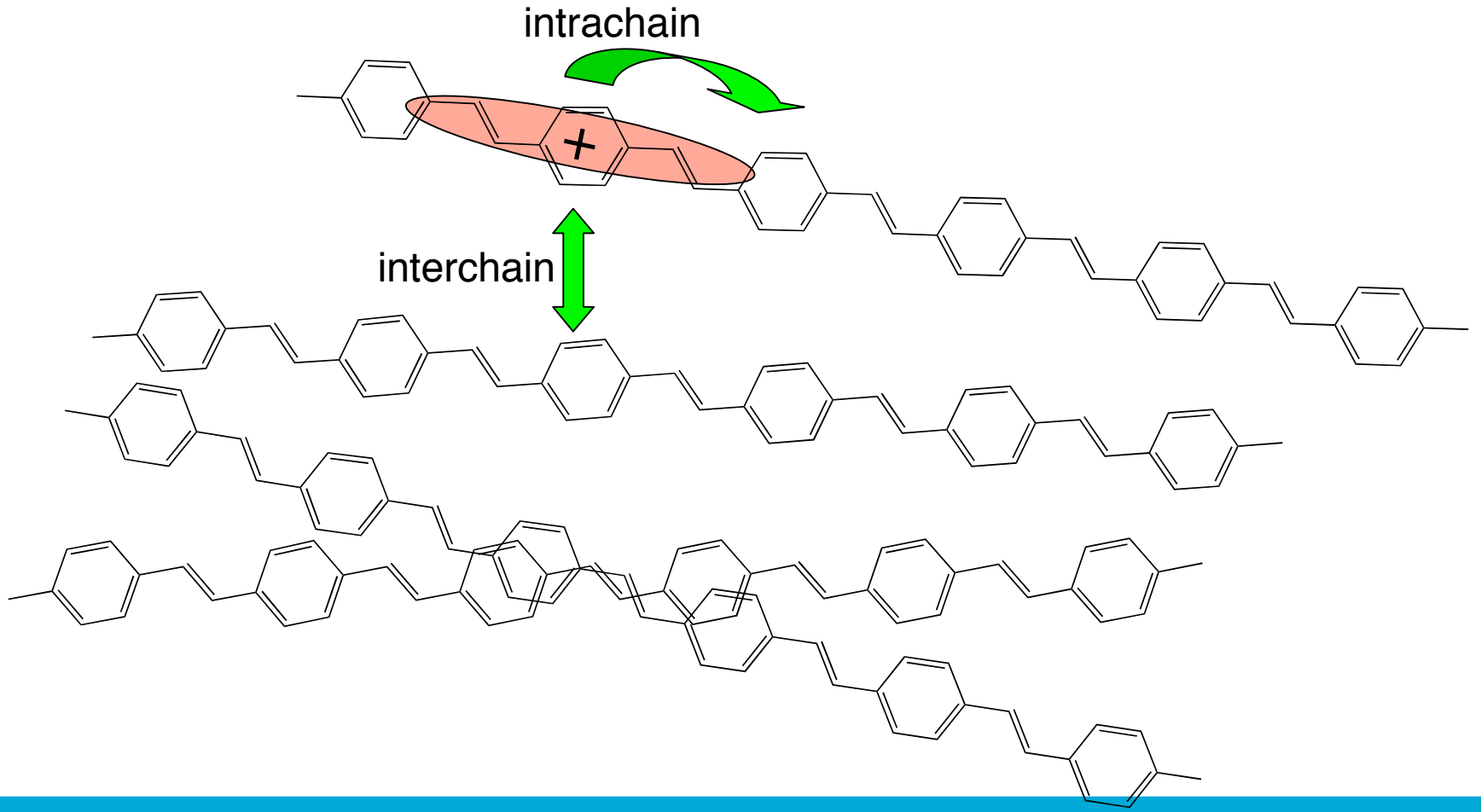
metal	μ ($cm^2V^{-1}s^{-1}$)
Al	43
Cu	39
Au	16

semi-conductor	μ electron ($cm^2V^{-1}s^{-1}$)	μ hole ($cm^2V^{-1}s^{-1}$)
Si	1500	450
GaSb	5000	850
InAs	33000	460

μ = 1 $cm^2V^{-1}s^{-1}$ --> v = 1 cm/s in field of $\mathcal{E}$ = 100 V/m

What is mobility for organic polymers?

Intra- and interchain charge transport



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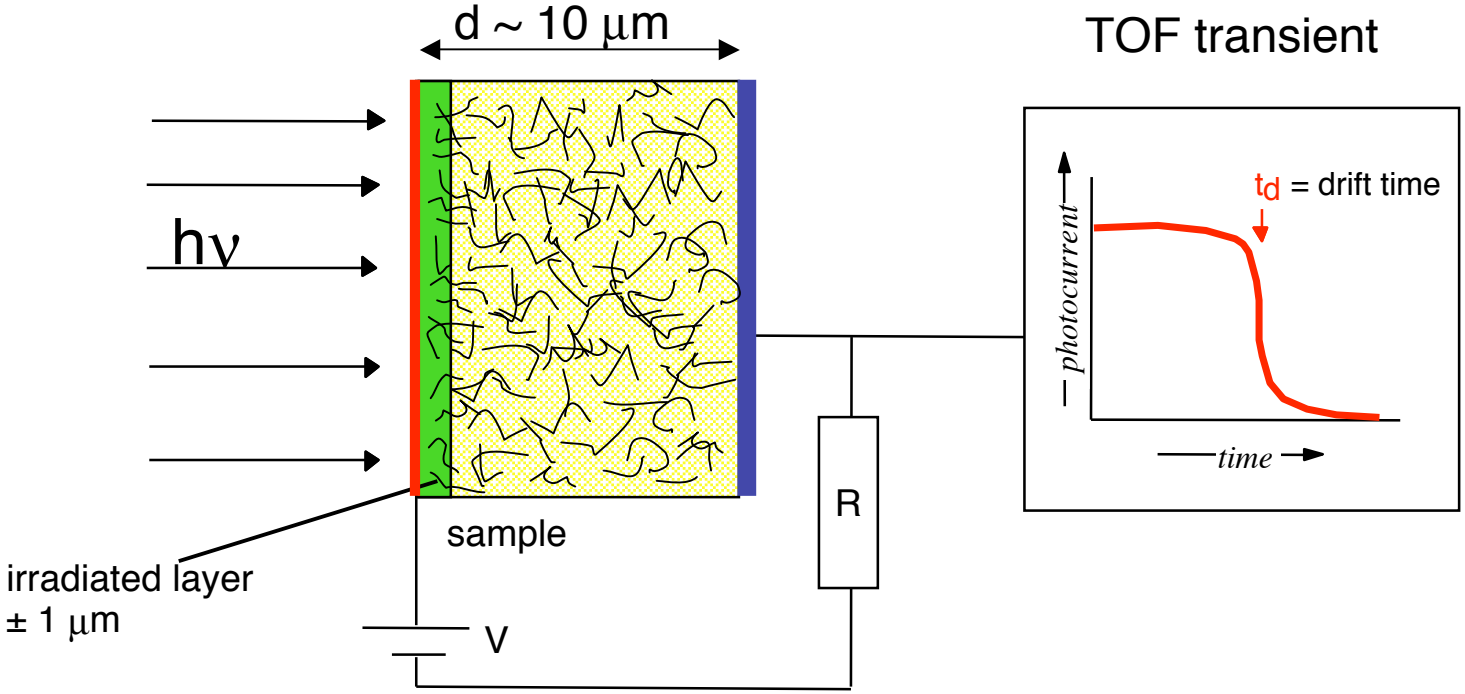
Typical time-of-flight measurement of mobility



$$\mu_{TOF\ (DC)} = \frac{d^2}{V\ t_d} = 10^{-7} - 10^{-1}\ cm^2\ V^{-1}\ s^{-1}\ \text{for polymers}$$

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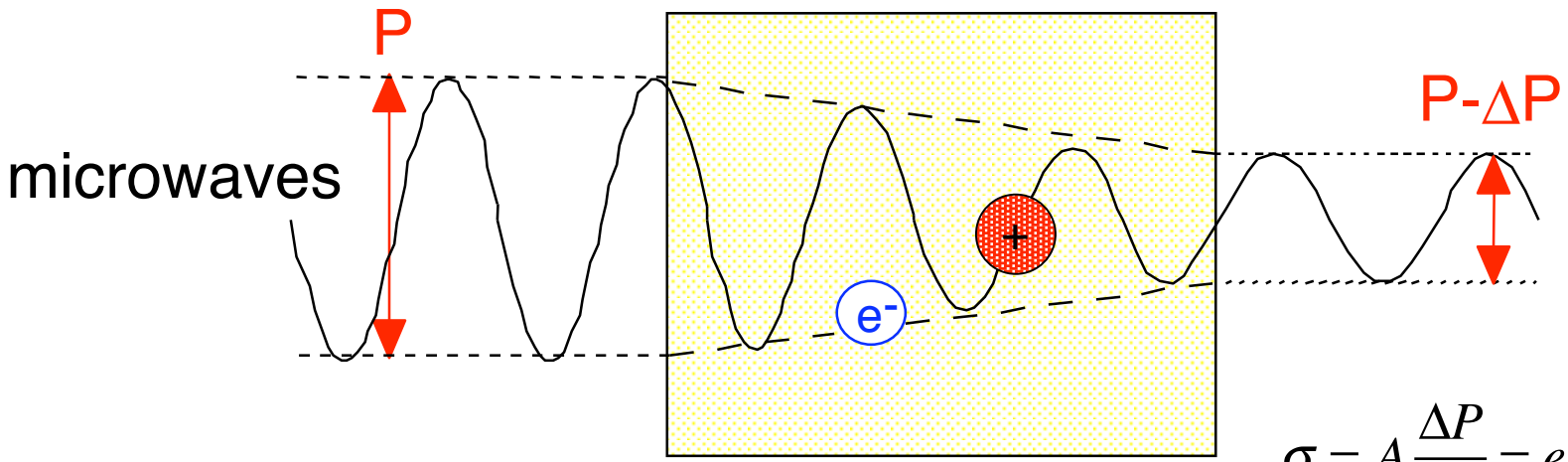
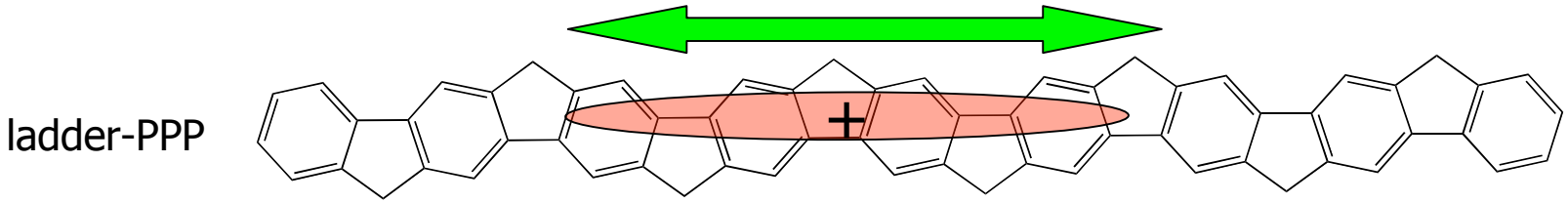
Intrachain mobility from AC conductivity measurements:
microwaves (10^{10} Hz), terahertz (10^{12} Hz)



$$\sigma = A\frac{\Delta P}{P} = e\,n\left[\mu_{+} + \mu_{-}\right]$$



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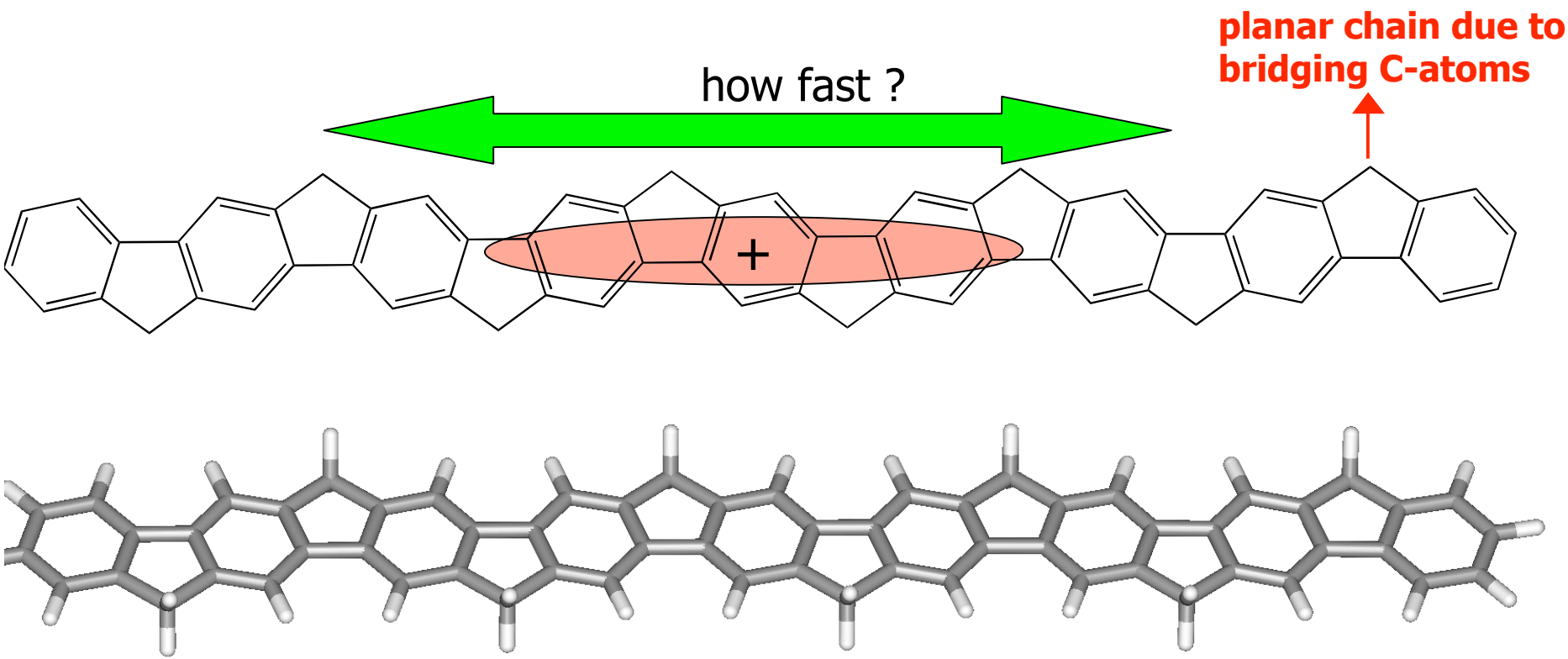
ırge mobility along ladder-PPP polymer: chain of phenyl ring

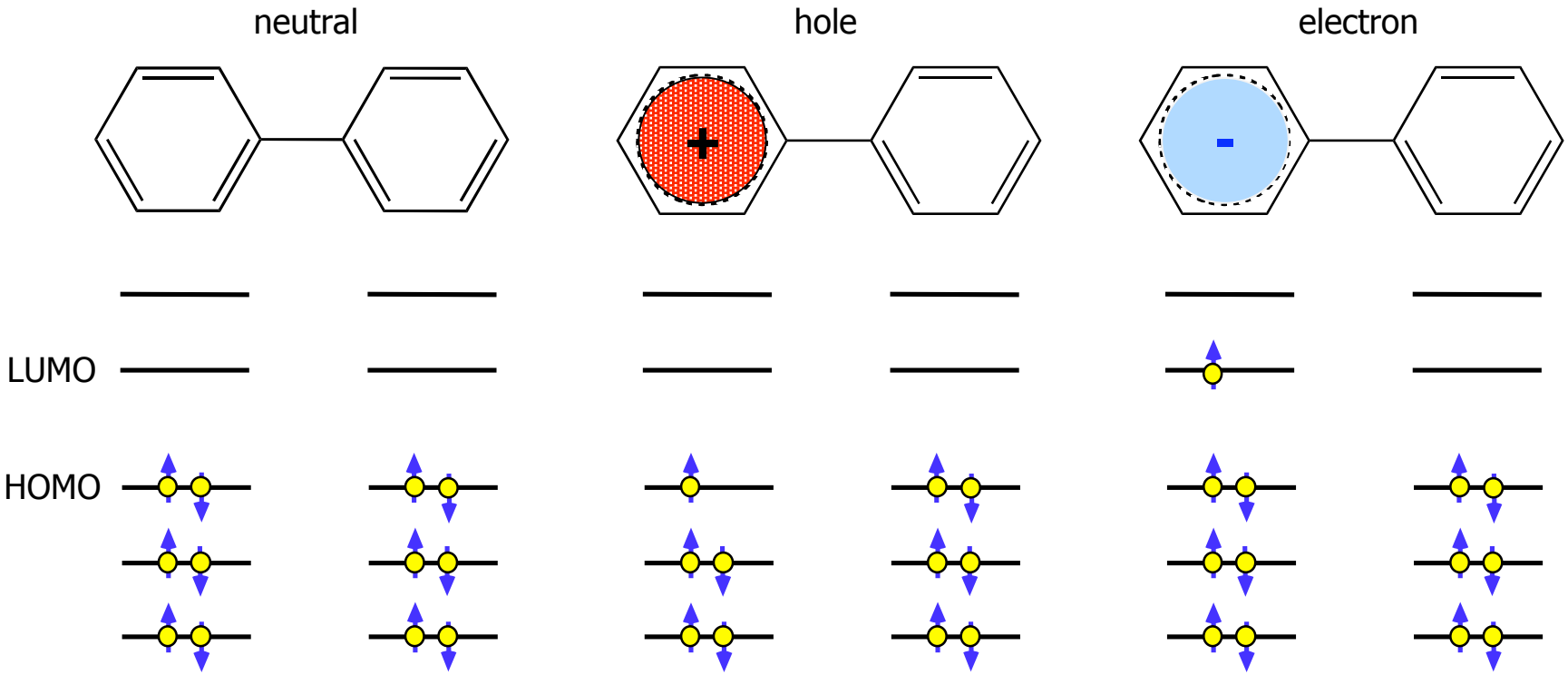


Ladder-PPP: rigid planar conjugated backbone due to bridging C-atoms connecting phenyl rings

Theoretical description of charges

Holes (positive charges): HOMO orbitals on monomers (Koopmans for ionization)

Excess electrons: LUMO orbitals on monomers or SOMO's of anion.



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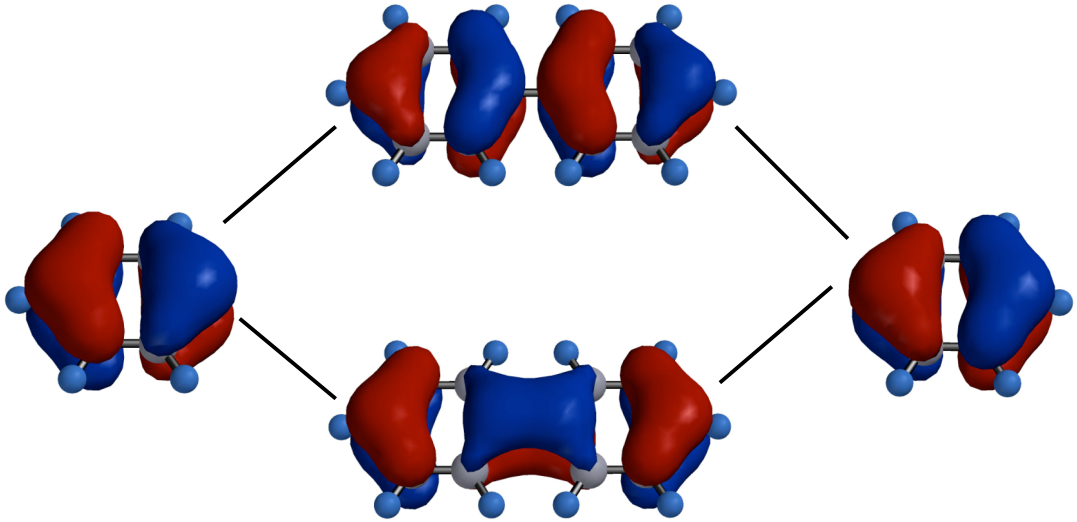
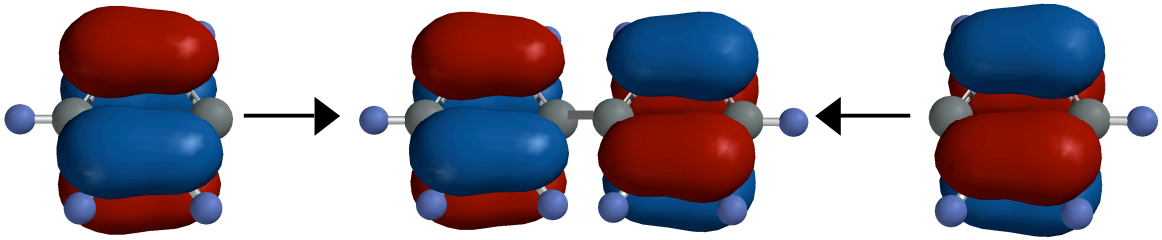
Hole is reperesented by superposition of HOMOs on phenyl rings

phenyl orbitals (almost) degenerate

Coupling



No coupling



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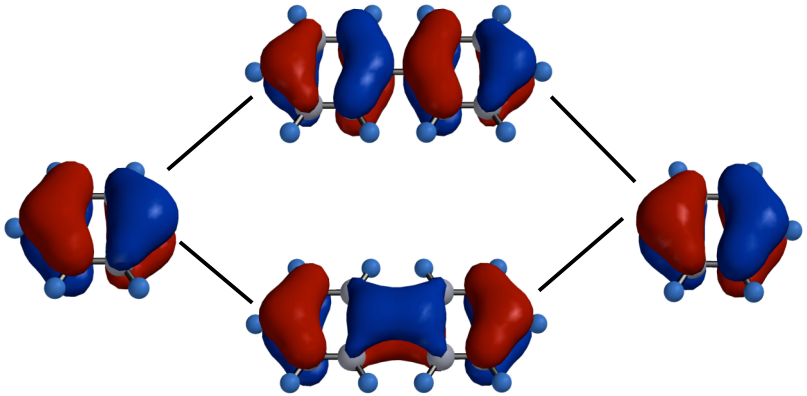
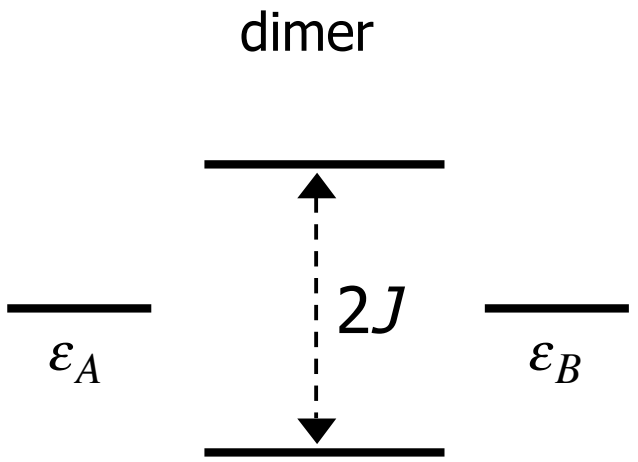
Electronic coupling between two identical units





for S=0 splitting $2J$

$$\left|\Psi^{\pm}_{\text{dimer}}\right\rangle = \frac{1}{\sqrt{2}}\left(\varphi_A \pm \varphi_b\right)$$

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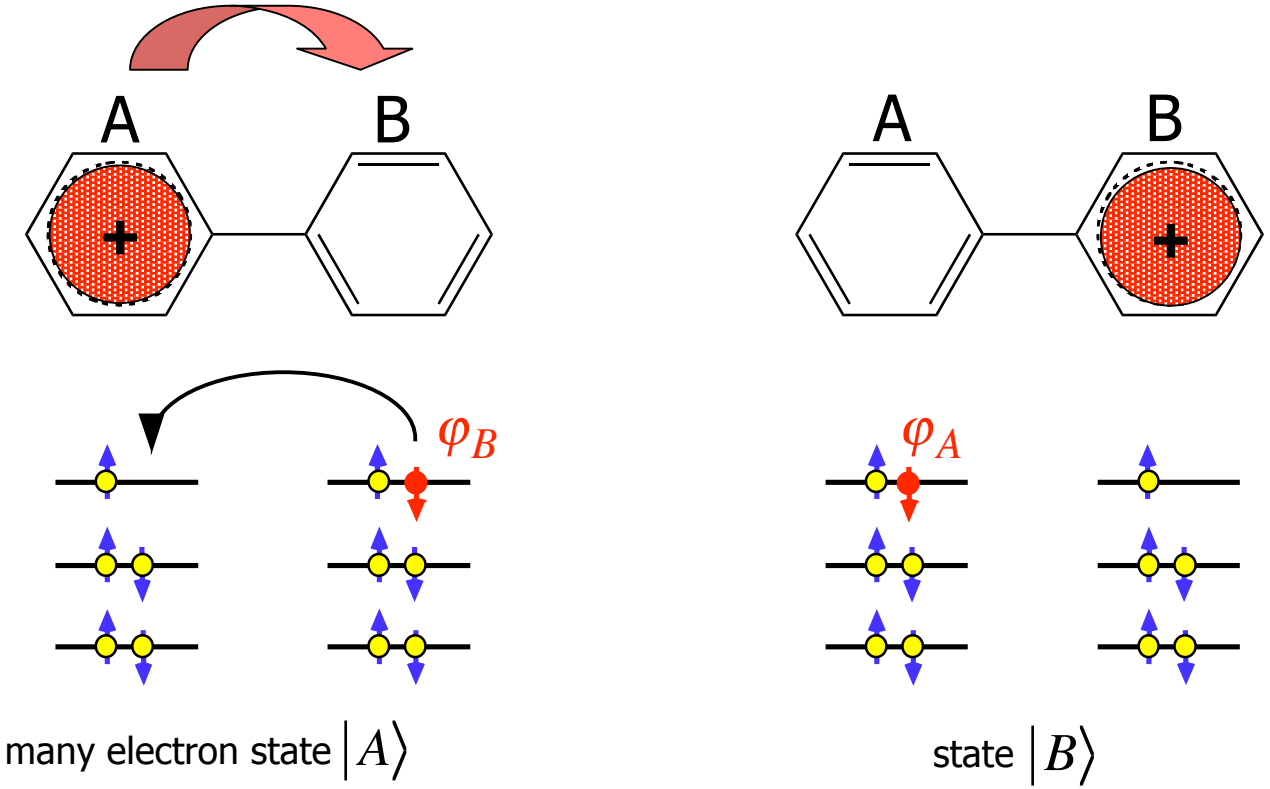
Hole transfer from A to B



many electron state $|A\rangle$

state $|B\rangle$

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Charge transfer from A to B

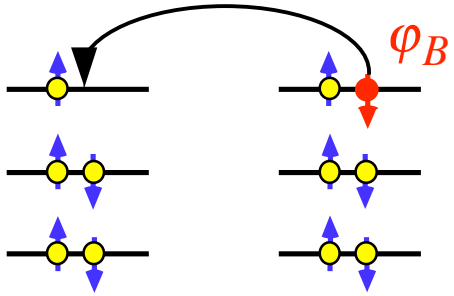
Electronic coupling or charge transfer integral: $J = \langle A | H | B \rangle$

with H the many e^- hamiltonian

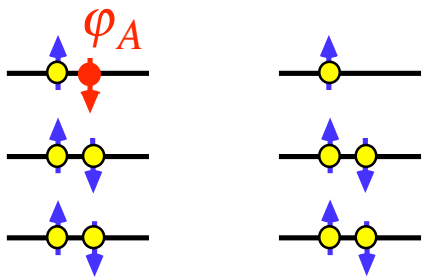
Slater matrix rules for two states differing in one orbital ($\varphi_B \leftrightarrow \varphi_A$) gives

$$J = \langle A | H | B \rangle = \langle \Phi(1,2,..,n-2)) \varphi_B(n-1) | H | \Phi(1,2,..,n-2) \varphi_A(n-1)) \rangle$$

$$= \langle \varphi_B | h | \varphi_A \rangle \quad \text{with } h \text{ the Hartree-Fock or Kohn-Sham operator}$$



many electron state $|A\rangle$



state $|B\rangle$

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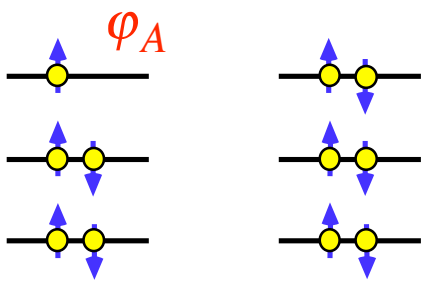
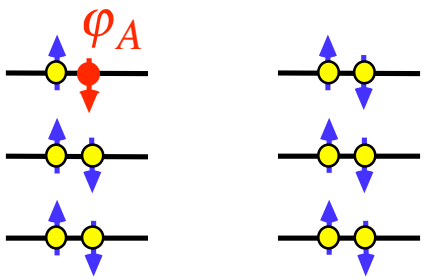
Site-energy of hole on A

With respect to neutral ground state:

$$\varepsilon_A = \left\langle \Phi(1,2,..,n-1) \middle| H \middle| \Phi(1,2,..,n-1) \right\rangle - \left\langle \Phi(1,2,..,n-1)\varphi_A(n) \middle| H \middle| A(1,2,..,n-1)\varphi_A(n) \right\rangle$$



(n-1) e$^-$ hole state $|A\rangle$



(*n*) e$^-$ neutral state

$\varepsilon_A = \langle \varphi_A | h | \varphi_A \rangle$ analogous to Koopman's theorem

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Charge parameters:

site energy $\varepsilon_A = \langle \varphi_A | h | \varphi_A \rangle$

charge transfer integral $J_{AB} = \langle \varphi_A | h | \varphi_B \rangle$

spatial overlap integral $S_{AB} = \langle \varphi_A | \varphi_B \rangle$

Can be obtained from electronic structure calculations:
semi-empirical, Hartree-Fock or Density Functional Theory

Approximated value of *J* from orbital spilitting for identical units,
or directly using fragment orbitals in ADF

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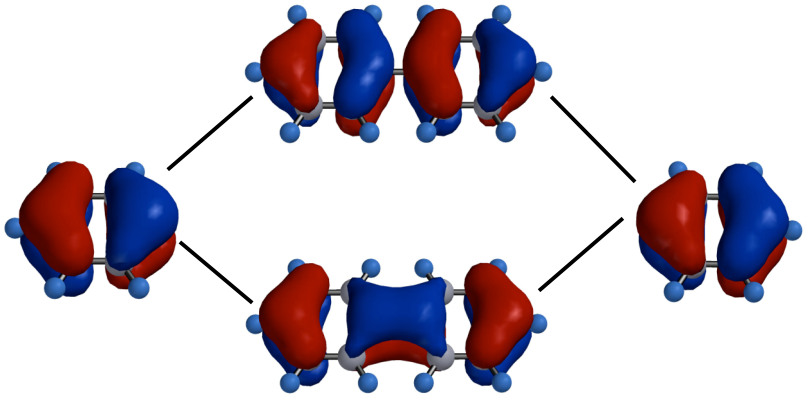
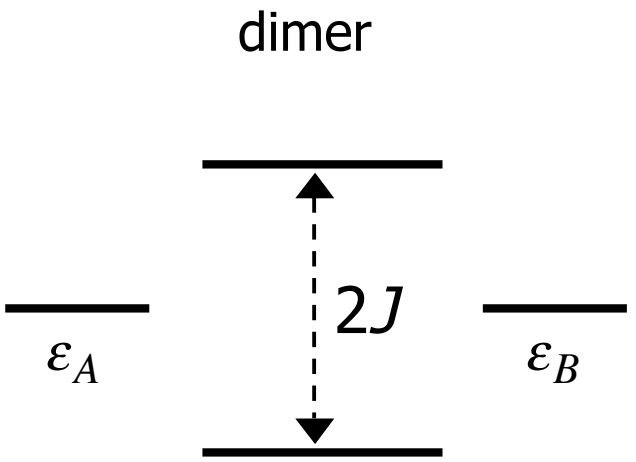
Electronic coupling between two identical units





for S=0 splitting $2J$

$$\left|\Psi^{\pm}_{\text{dimer}}\right\rangle = \frac{1}{\sqrt{2}}\left(\varphi_A \pm \varphi_b\right)$$

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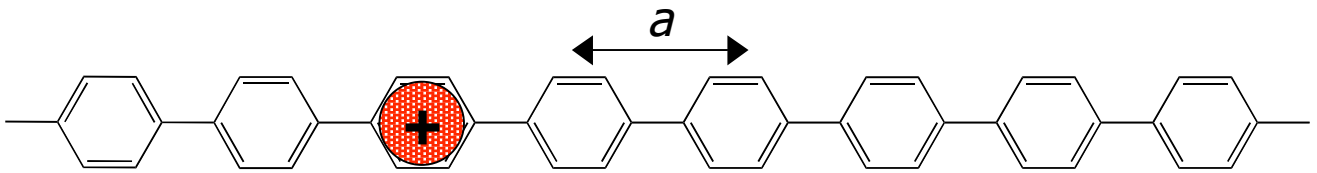
Theoretical description of charges

PPP



Periodic structure with repeat units at distance *a*: Bloch functions for charge

$$\left|\Psi_{\mathbf{k}}(\mathbf{r})\right\rangle = f_N \sum_s \exp\left(i\mathbf{k}\cdot\mathbf{r}_s\right)\left|\varphi\left(\mathbf{r}-\mathbf{r}_s\right)\right\rangle \qquad k = k_x = 0, \pm\frac{2\pi}{L}, \ldots\ldots, \frac{\pi}{a}$$

Only nearest neighbour interactions gives for (*J* real)

$$E_{\mathbf{k}} = \frac{\left\langle\Psi_{\mathbf{k}}\left|H_{el}\right|\Psi_{\mathbf{k}}\right\rangle}{\left\langle\Psi_{\mathbf{k}}\left|\Psi_{\mathbf{k}}\right\rangle\right.} = \frac{\varepsilon + 2J\cos(ka)}{1 + 2S\cos(ka)}$$

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Band energies and effective charge tranfer integral

$$E_k = \frac{\varepsilon + 2J\cos(ka)}{1 + 2S\cos(ka)}$$

For S small Taylor expansion of denominator gives, using $1/(1+S) \approx 1 - S$

$$E_k = \varepsilon + 2(J - S\varepsilon)\cos(ka) \equiv \varepsilon + 2J_{eff}\cos(ka)$$

with the effective charge transfer integral taking into account spatial overlap

$$\left(J_{eff}\right)_{s,s'} = J_{s,s'} - S_{s,s'}\left(\frac{\varepsilon_s + \varepsilon_{s'}}{2}\right)$$

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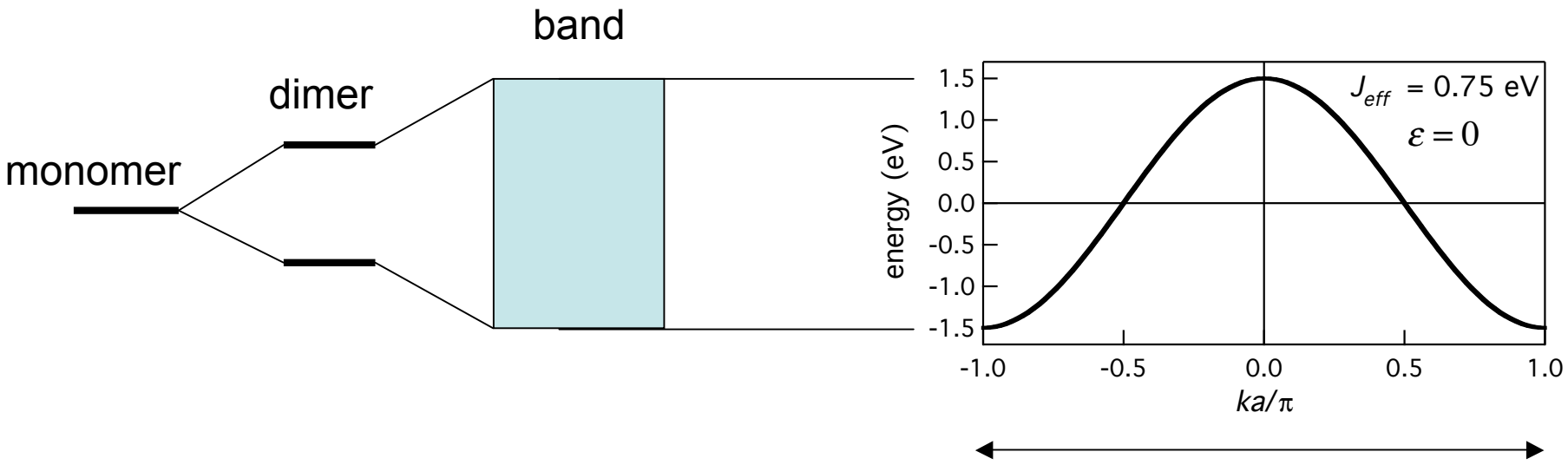
Electronic valence band

$$E_k = \varepsilon + 2J_{eff}\cos(ka)$$



1st Brillouin zone

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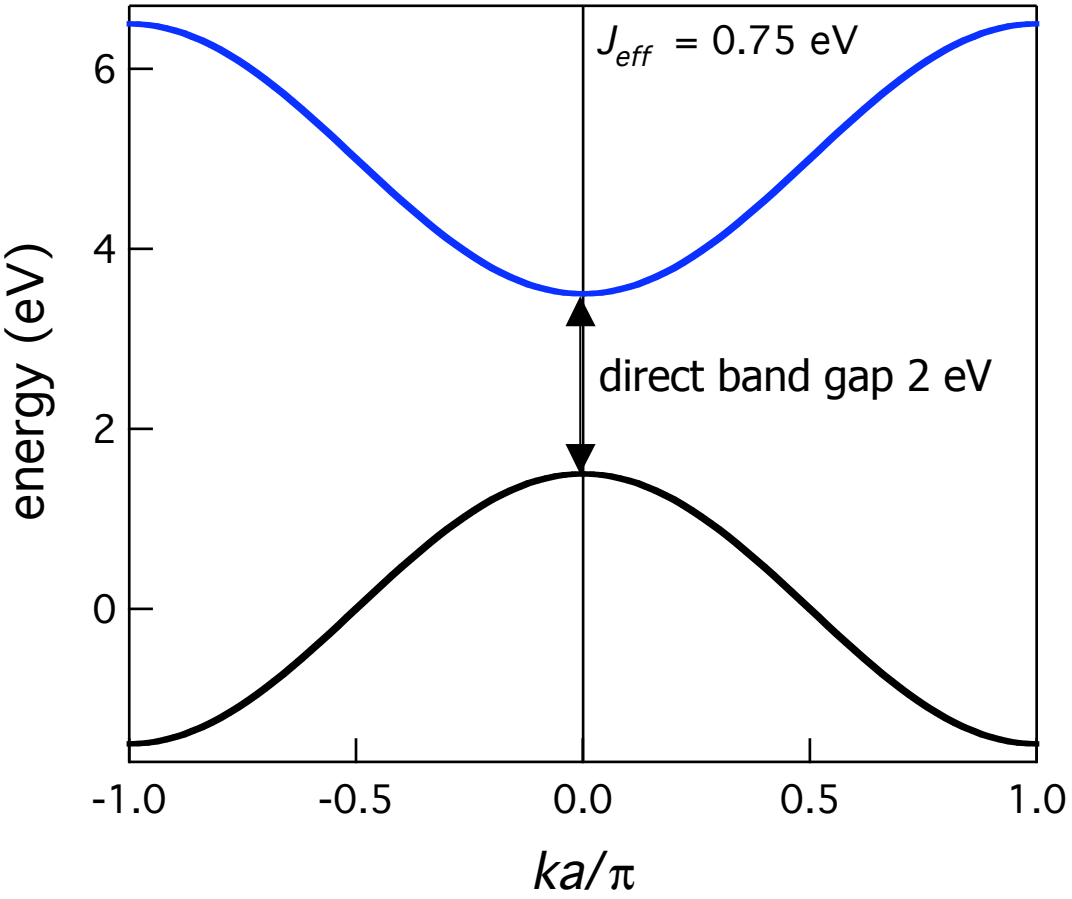
Valence and conduction band



conduction band

valence band

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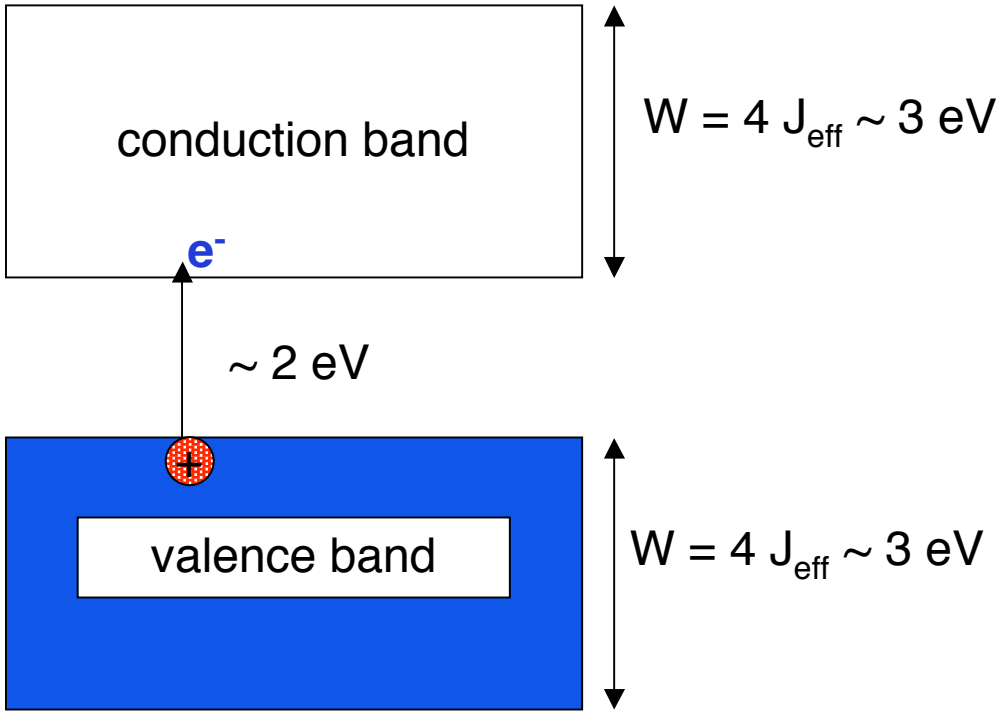
Pristine polymer: filled valence and empty conduction band: insulator

Production of charges: doping, (photo-excitation), injection from electrode



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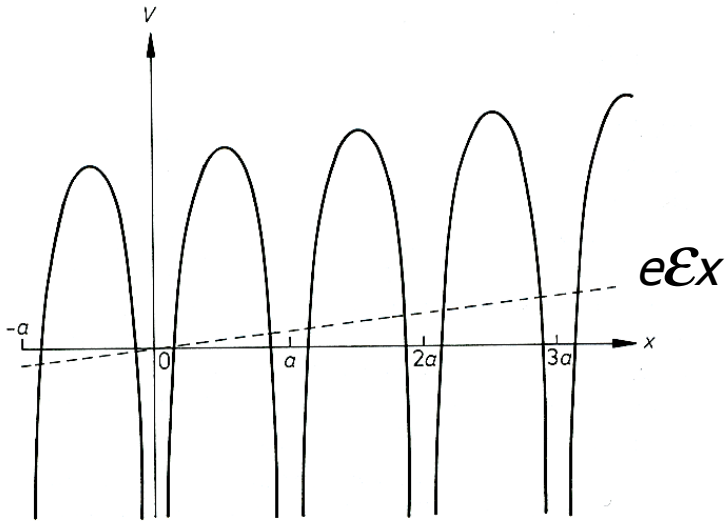
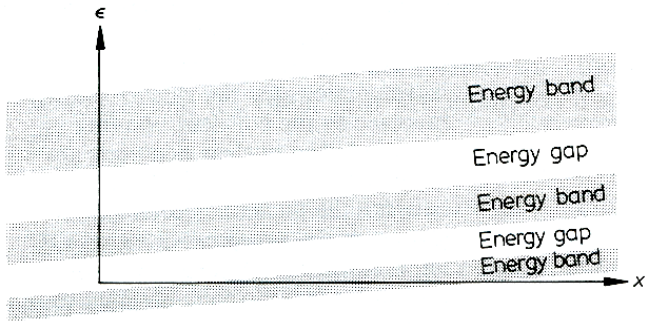
Motion of charges in external electric field



field causes band energy to vary as $e\mathcal{E}x$



Hook and Hall, Sol. State Phys. Fig. 4.13

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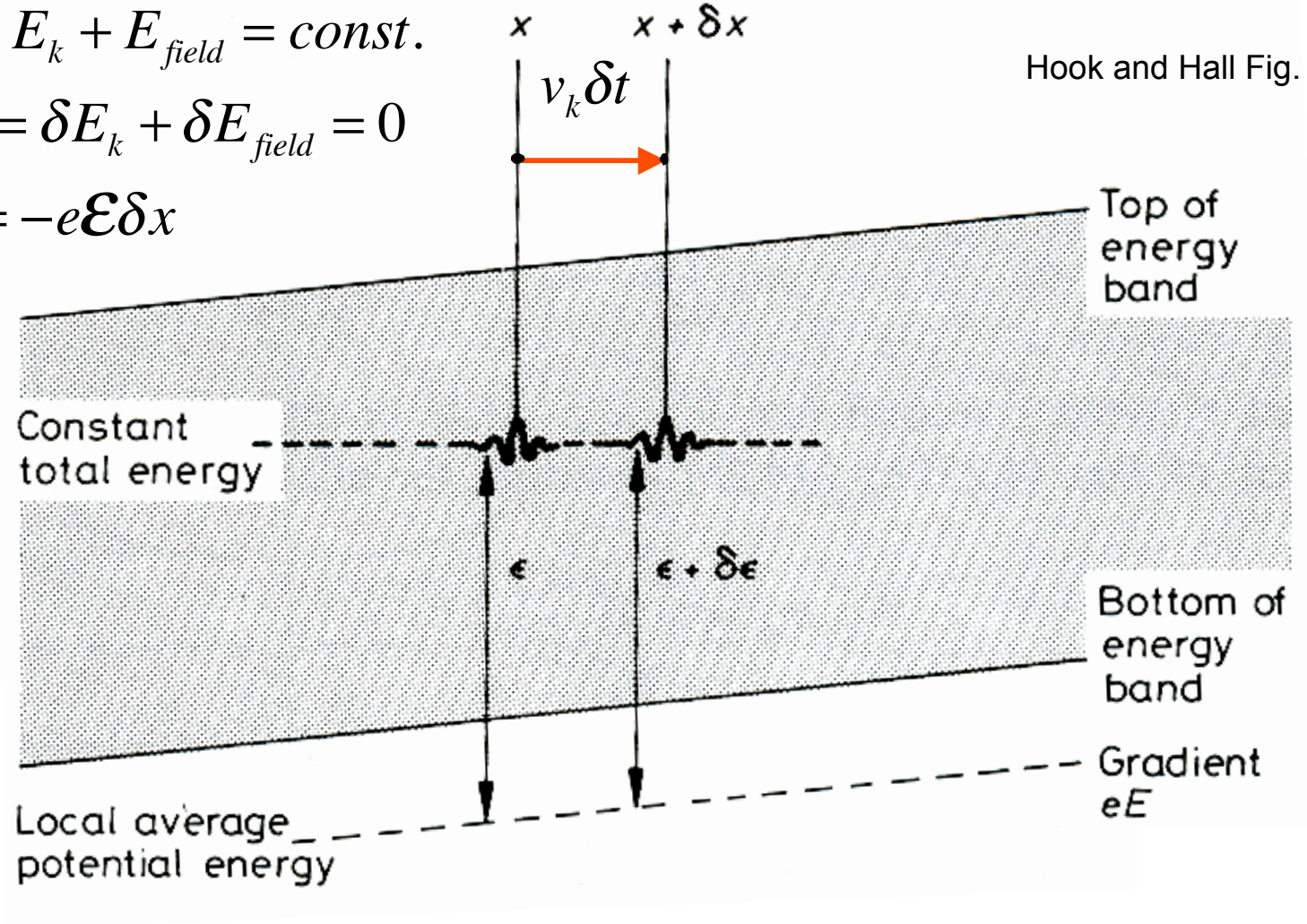
Energy conservation in electric field

$$v_k = \frac{1}{\hbar}\frac{dE_k}{dk}$$ group velocity of wave packet around *k* and *x*

$$E_{tot} = E_k + E_{field} = const.$$

$$\delta E_{tot} = \delta E_k + \delta E_{field} = 0$$

$$\delta E_k = -e\mathcal{E}\delta x$$



Hook and Hall Fig. 4.14

Motion of charges in external electric field

$$\left.\begin{aligned} \delta E_k &= -e\mathcal{E}\,\delta x = -e\mathcal{E}\,v_k\,\delta t \\ \delta E_k &= \left(\frac{dE}{dk}\right)\delta k = \hbar v_k \delta k \end{aligned}\right\} \quad \frac{d(\hbar k)}{dt} = -e\mathcal{E} = \text{Force}$$

Force acts on $\hbar k$

Electric field changes *k*-value and thus velocity; there is acceleration given by

$$a = \frac{dv}{dt} = \frac{d}{dt}\left(\frac{1}{\hbar}\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}(-e\mathcal{E}) = \frac{-e\mathcal{E}}{m^*}$$

Motion of charges in external electric field

$$a = \frac{-e\mathcal{E}}{m^*} = \frac{\text{force}}{\text{effective mass}}$$ with the effective mass $$m^* = \hbar^2 \left(\frac{d^2E}{dk^2} \right)^{-1}$$

For free electrons the effective mass is the free electron mass.

For electrons in solid the effective mass brings effect of periodic potential into account.

Integration of $\frac{dv}{dt} = \frac{-e\mathcal{E}}{m^*}$ gives $v(t) = v(0) - \frac{e\mathcal{E}}{m^*}\, t$

Result physically unrealistic since velocity does not keep increasing during time.

Motion of charges in external electric field

Charge undergoes scattering, analogous to friction force

$$\frac{dv}{dt} = \frac{-e\mathcal{E}}{m^*} - \frac{v}{\tau}$$

τ is scattering time, randomization of velocity direction

$$\langle v(t)v \rangle = \langle v^2 \rangle \exp(-t/\tau)$$

Equilibrium drift velocity of charge

$$\frac{dv}{dt} = 0 \quad \Rightarrow \quad |v| = \frac{e}{m^*}\tau\,|\mathcal{E}| \equiv \mu\,\mathcal{E}$$

Mobility $\mu = \dfrac{e}{m^*}\tau$

- increases with τ
- decreases with m^*

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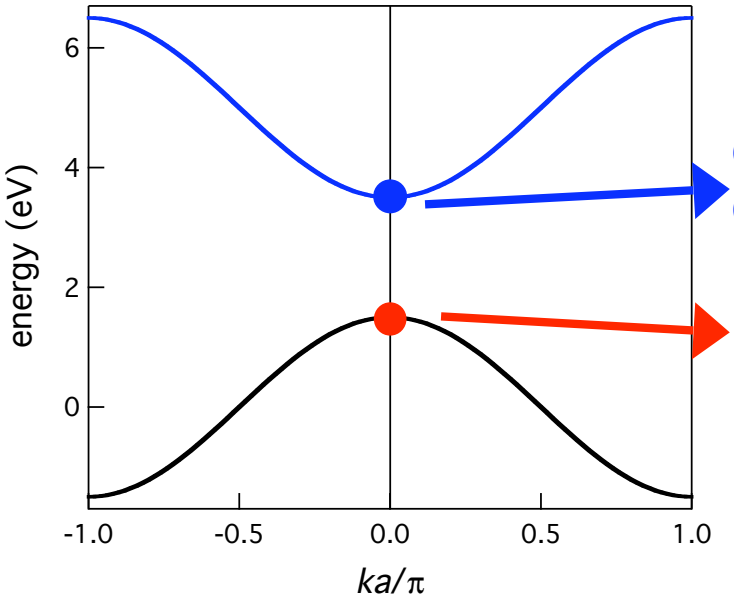
Mobility from m^* and τ



electron at bottom conduction band

hole at top valence band

$k = 0$

Effective mass at $k = 0$

$$m^* = \hbar^2 \left(\left(\frac{d^2 E}{dk^2} \right)_{k=0} \right)^{-1} = \frac{\hbar^2}{2a^2 \left| J_{eff} \right|}$$

larger J_{eff} --> smaller m^* --> higher mobility

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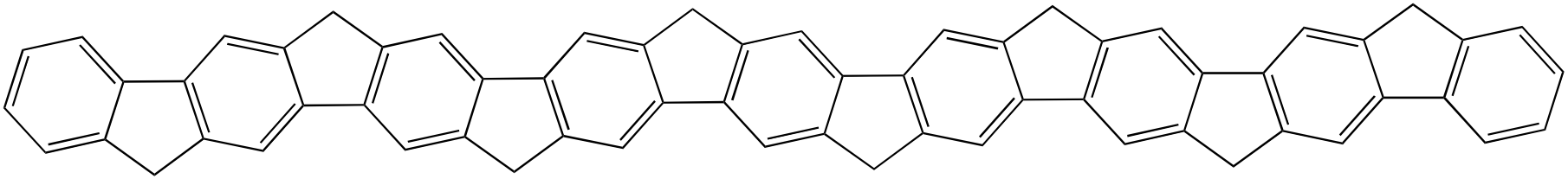
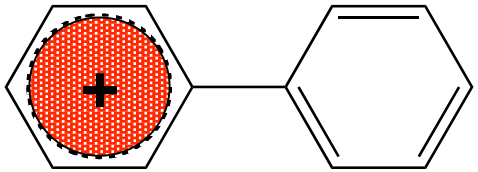
Charge transfer integral for ladder-PPP



Site energies all identical

Electronic coupling calculated with fragment orbitals and ADF program

Planar biphenyl model system



$$J_{s,s\pm1} = \langle \varphi_s \,|\, h_{KS} \,|\, \varphi_{s\pm1} \rangle = 0.8 \text{ eV}$$

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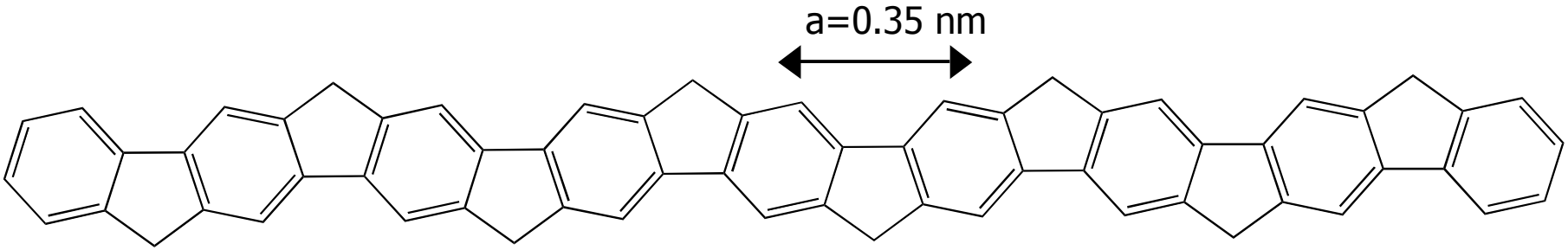
Effective mass for ladder-PPP



$$J_{eff} = 0.8 \text{ eV} \qquad m^* = \frac{\hbar^2}{2a^2 J_{eff}} = 0.4 \text{ m}_0$$

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Mobility for semiconductors

semi-conductor	μ hole ($cm^2V^{-1}s^{-1}$)	m^* (m_0)	τ (fsec)
Si	450	0.2	51
GaSb	850	0.4	193
InAs	460	0.4	105

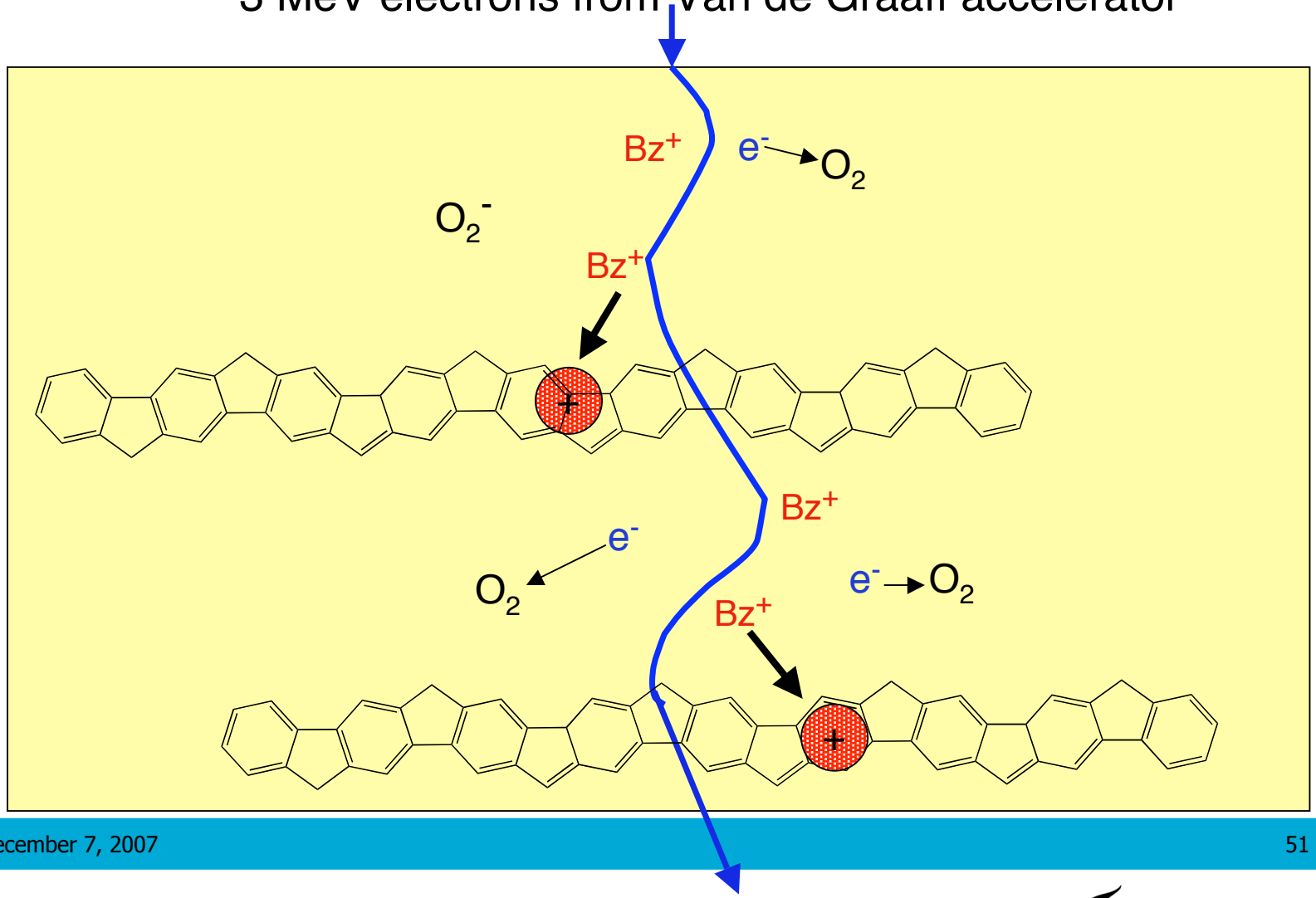
- ladder-PPP $m^* = 0.4\ m_0$
- in case scattering similar to semiconductor: mobility ~ 100 - 1000 $cm^2V^{-1}s^{-1}$

Estimated mobility 3 to 4 orders of magnitude higher than every measured for interchain transport in polymer based device.

Does estimated mobility agree with experiment?

Holes on isolated ladder-PPP chains in dilute solution

3 MeV electrons from Van de Graaff accelerator



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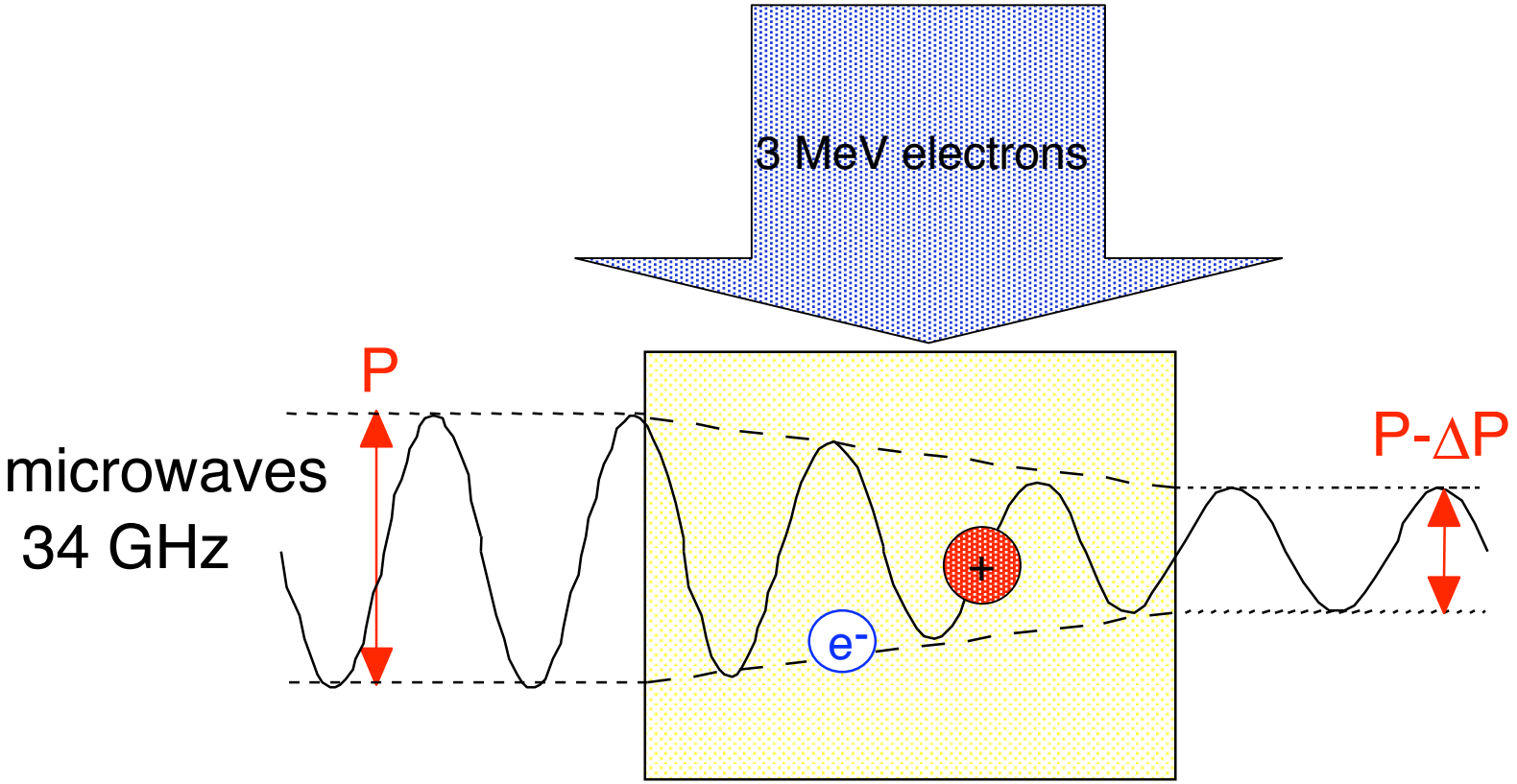
Mobility of charges obtained from microwave absorption



$$\Delta\sigma = A\frac{\Delta P}{P} = en[\mu_+ + \mu_-]$$

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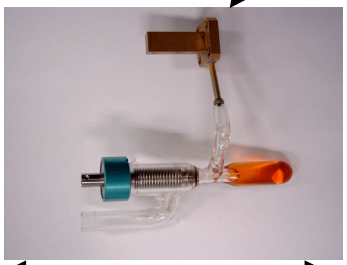
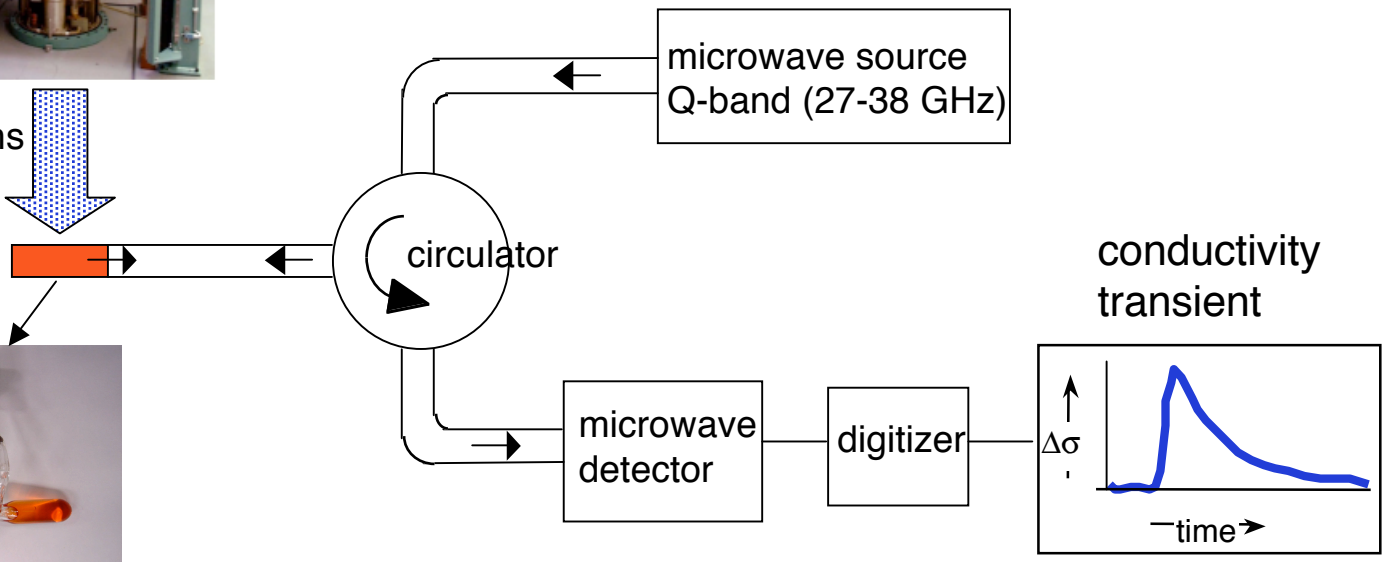
Van de Graaff accelerator

3 MeV electrons
0.5 - 20 ns



~ 10 cm

microwave cell



$$\Delta\sigma = e\, n\, [\, \mu(+) + \mu(-)\,]$$

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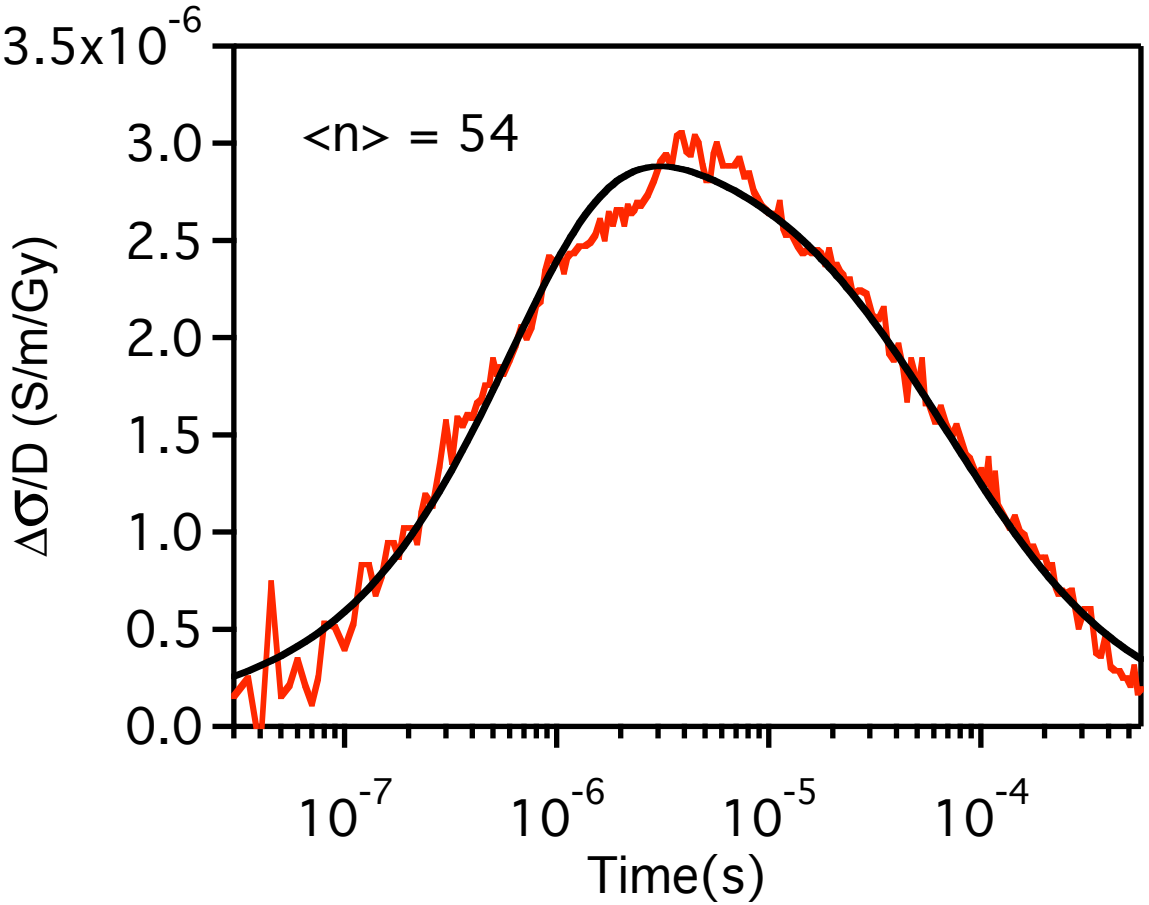
Microwave conductivity due to holes on ladder-PPP chains



Growth:

$Bz^+ + P \longrightarrow P^+ + Bz$

Decay:

$P^+ + O_2^- \longrightarrow P + O_2$

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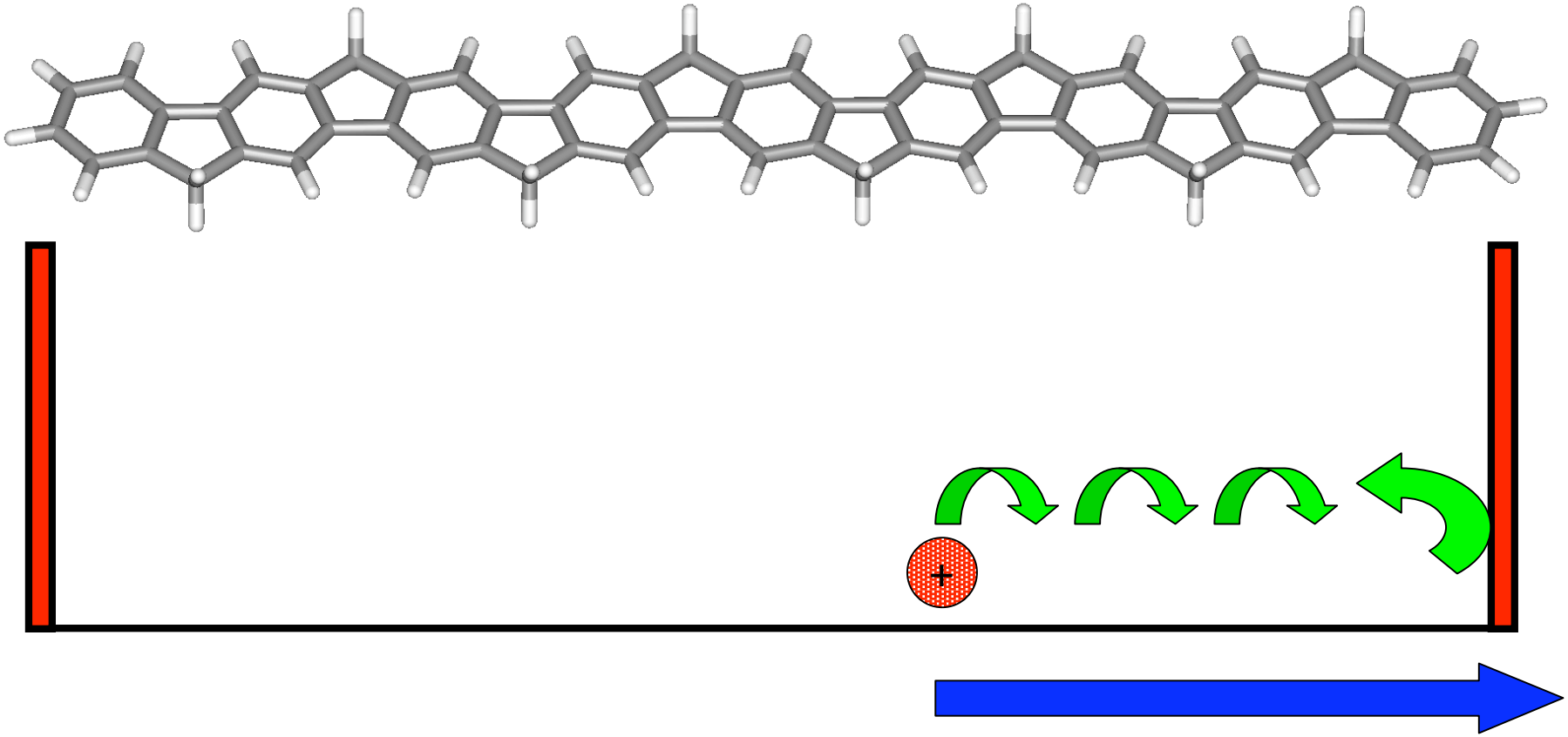
Mobility obtained from analysis of growth and decay kinetics

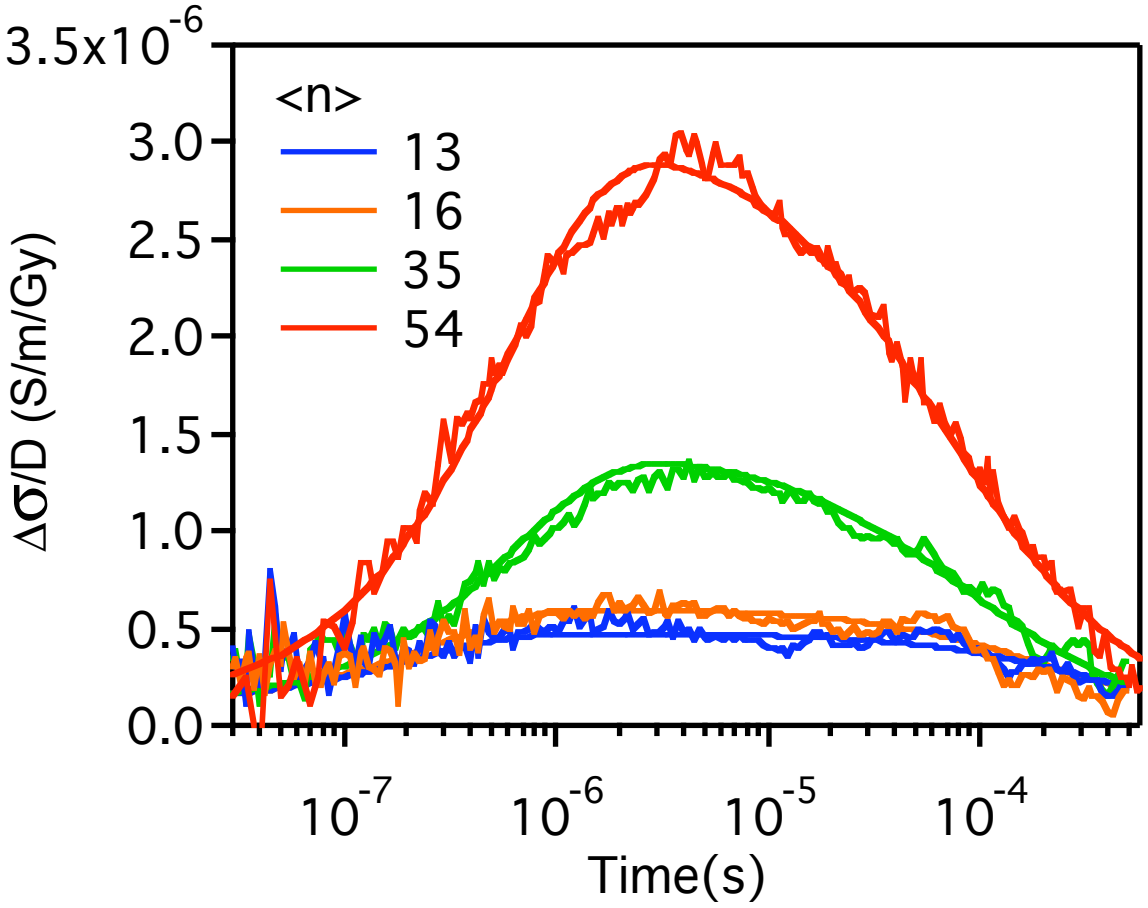
ladder-PPP: $\mu = 0.24\ cm^2V^{-1}s^{-1}$

- Intra-chain mobility is orders of magnitude higher than the value of $10^{-3}\ cm^2V^{-1}s^{-1}$ found from DC time-of-flight measurements! Hertel, D. et al. *Adv. Mater.* **10** , p. 1119 (1998)
- Intra-chain transport for ladder-PPP much faster than chain-to-chain motion

Is 0.24 $cm^2V^{-1}s^{-1}$ the ultimate mobility or limited by chain ends?



Mobility at 30 GHz depends on chain length



<*n*>	μ(30 GHz) $cm^2V^{-1}s^{-1}$
13	**0.030**
16	**0.043**
35	**0.092**
54	**0.24**

- Charge hindered by chain ends for <*n*> ≥ 35
- **Mobility must exceed 5 $cm^2V^{-1}s^{-1}$**

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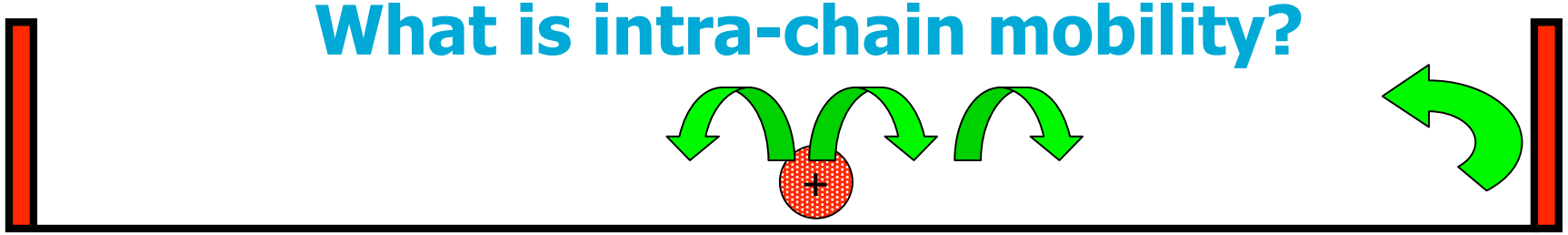
What is intra-chain mobility?



AC mobility: $\mu_{ac} = 8\boldsymbol{D}\frac{e}{k_B T}\sum_{k=0}^{\infty}\frac{[c_k]^{-2}}{\left[\frac{\boldsymbol{D}}{\boldsymbol{L}^2\omega}\right]^2[c_k]^4+1}$ $\qquad c_k = 2\pi\left(k+\frac{1}{2}\right)$

Intra-chain mobility : $\mu_{\text{intra}} = \frac{e}{k_B T}\boldsymbol{D}$ **from comparison of expt. and theory**

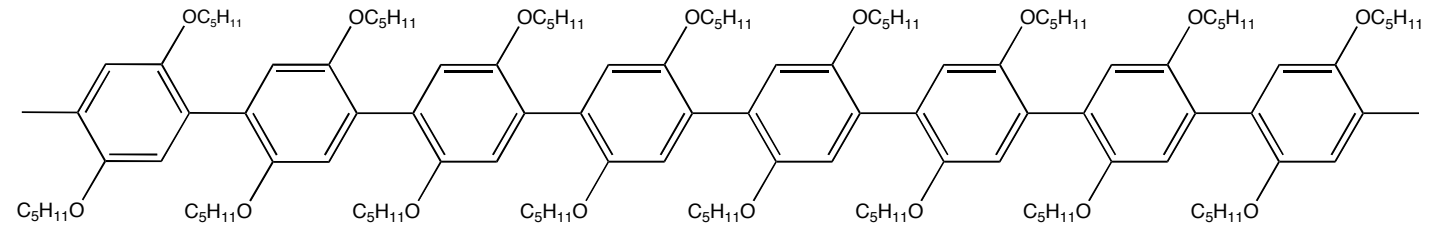
Exptl. data reproduced with μ_{intra} = 600 $cm^2V^{-1}s^{-1}$

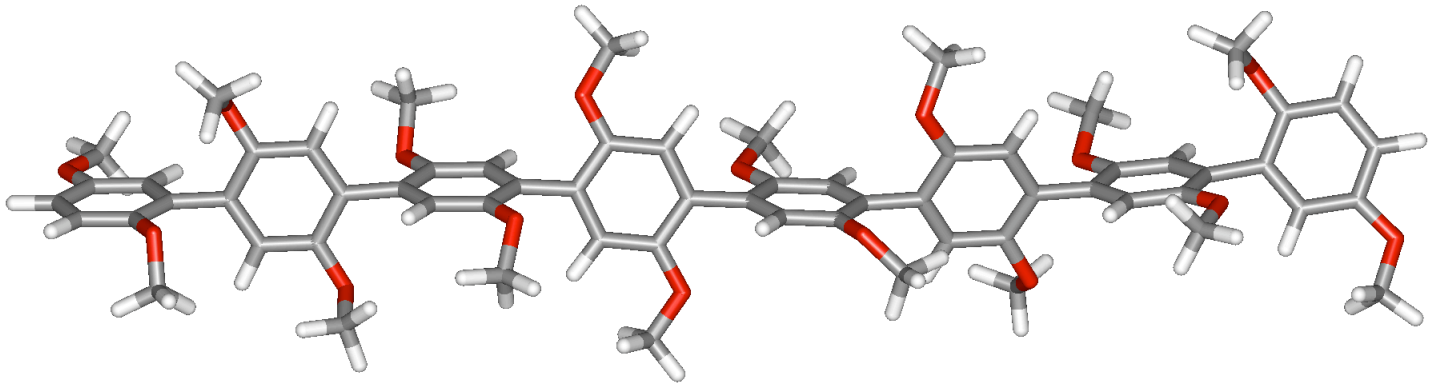
(close to estimate on basis of eff. mass)

P. Prins *et al.*, Phys. Rev. Lett. 73, 045204 (2006)

High mobility for ladder-PPP due to planarity of backbone

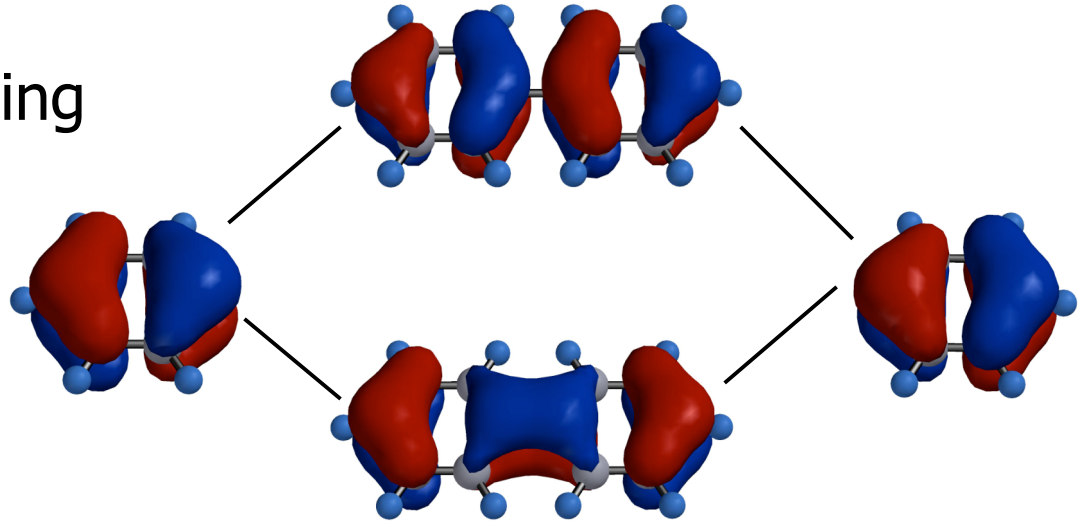
Torsional disorder in PPP leads to lower mobility < 0.01 $cm^2V^{-1}s^{-1}$



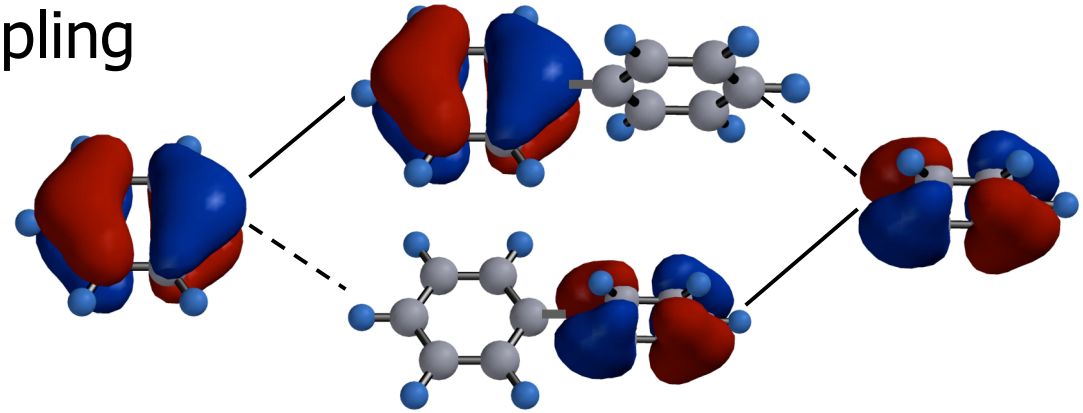


Wavefunction of hole is superposition of HOMOs on phenyl rings

Parallel rings: coupling



Perp. rings: **no** coupling



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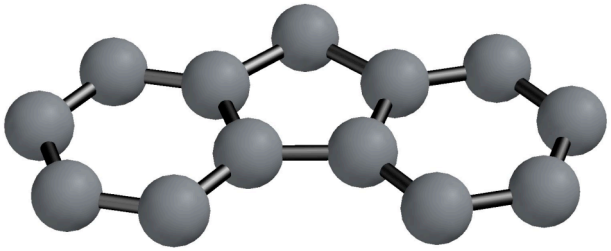
Estimated mobility on basis of assumptions:

- periodic lattice strcuture of polymer
- electron-phonon scattering scattering in polymer weak: Bloch states adequate
- scattering time of charge in polymer similar to inorganic semiconductors

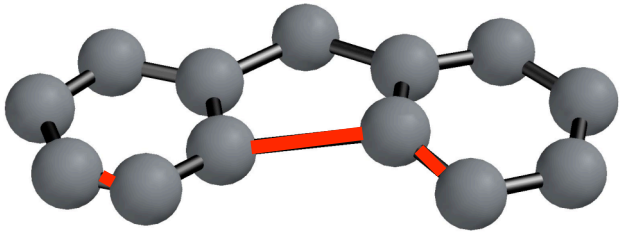
Assumptions may be invalid due to strong dynamic and static structual fluctuations.



equilibrium geomety

$$\varepsilon = \varepsilon_{eq}$$

$$J = J_{eq}$$



vibrations distort geomety

$$\varepsilon(t) = \varepsilon_{eq} + \delta\varepsilon(t)$$

$$J(t) = J_{eq} + \delta J(t)$$

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More general theory for mobility

Previous theoretical framework no longer valid if fluctuations strongly distort periodicity of nuclear lattice.

General framework for mobility based on linear response theory.

Interaction of electrons with external electric field treated as perturbation

$$E(t) = E_0 \cos(\omega t)$$

Drift velocity of charges superimposed on their diffusion

$$v_d(t) = \mu'(\omega) E_0 \cos(\omega t) + \mu''(\omega) E_0 \sin(\omega t)$$

in-phase out-of-phase

More general theory for mobility

General expression for mobility

$$\mu(\omega) = \frac{e}{k_B T} \lim_{b \downarrow 0} \int_0^\infty \left\langle v_x(t) v_x(0) \right\rangle \mathrm{e}^{-i\omega - bt}\, dt$$

convergence factor e^{-bt}

$$= -\frac{e\,\omega^2}{2k_B T} \lim_{b \downarrow 0} \int_0^\infty \left\langle \left(x(t) - x(0) \right)^2 \right\rangle \mathrm{e}^{-i\omega - bt}\, dt$$

Previous result for periodic system with weak electron-phonon scattering is obtained in case

$$\left\langle v_x(t) v_x(0) \right\rangle = \left\langle v_x^2(0) \right\rangle \mathrm{e}^{-t/\tau} = \frac{k_B T}{m^*} \mathrm{e}^{-t/\tau} \quad \Rightarrow \quad \mu(\omega = 0) = \frac{e}{m^*} \tau$$

Note: v_x is thermal velocity in absence of electric field

More general theory for mobility

For normal Gaussian diffusion

$$\left\langle \left(x(t) - x(0) \right)^2 \right\rangle = 2Dt \quad \Rightarrow \quad \mu = \frac{e}{k_B T} D$$

Einstein relation

The mobility (or diffusion constant *D*) can thus be obtained from the mean square displacement (in absence of electric field).

Quantum mechanical theory for mobility

Calculate mean square displacement with time-dependent position operator

$$x(t) = \mathrm{e}^{iHt/\hbar}\, x\, \mathrm{e}^{-iHt/\hbar}$$

full hamiltonian $H = H_e + H_{ph} + H_{e-ph}$

and wavefunction of the charge

$$\left|\Psi_\kappa\right\rangle = \sum_s C_s^\kappa \left|\varphi_s^\kappa\right\rangle \left|\chi_s^\kappa\right\rangle \equiv \sum_s C_s^\kappa \left|s,\kappa\right\rangle$$

with

$\left|\varphi_s^\kappa\right\rangle$ electronic state with charge at unit *s*

$\left|\chi_s^\kappa\right\rangle$ phonon state associated with charge at unit *s*

C_s^κ coefficient of state $\left|s,\kappa\right\rangle$; charge at *s* and *k* labels phonon state+ static defects

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Quantum mechanical theory for mobility

Mean square displacement

$$\left\langle (x(t)-x)^2 \right\rangle == \mathrm{Tr}\left[(x(t)-x)^2 \rho \right] = \sum_{\kappa} P_{\kappa} \left\langle \Psi_{\kappa} \left| (x(t)-x)^2 \right| \Psi_{\kappa} \right\rangle =$$

$$= \sum_{\kappa,\,\kappa"} \sum_{s,\,s',\,s"} P_{\kappa} C_s^{\kappa} \left(C_{s'}^{\kappa} \right)^* a^2 \left[(s")^2 - s"(s+s') \right] \left\langle s',\kappa \left| \mathrm{e}^{iHt/\hbar} \right| s",\kappa" \right\rangle \left\langle s",\kappa" \left| \mathrm{e}^{-iHt/\hbar} \right| s,\kappa \right\rangle$$

$$+ \sum_{\kappa} \sum_{s} P_{\kappa} C_s^{\kappa} \left(C_s^{\kappa} \right)^* a^2 s^2$$

where localized charge states and orthogonal phonon states were assumed, so that

$$\left\langle s,\kappa \left| x \right| s',\kappa' \right\rangle = s\, a\, \delta_{ss'}\, \delta_{\kappa\kappa'}$$

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Quantum mechanical theory for mobility

The factor $\langle s'',\kappa''|e^{-iHt/\hbar}|s,\kappa\rangle$ is

coefficient of state $|s'',\kappa''\rangle$ at time *t*, for a charge which was in state $|s,\kappa\rangle$ at *t*=0.

The factor $\langle s',\kappa|e^{iHt/\hbar}|s'',\kappa''\rangle\langle s'',\kappa''|e^{-iHt/\hbar}|s,\kappa\rangle$ is the product of coefficients for motion from a common initial site (*s*'') to different final sites *s*, *s*'.

Averaging this factor over different realizations of polymer chains with different structural fluctuations causes vanishing of the terms for which $s \neq s'$.

Quantum mechanical theory for mobility

The mean square displacement then becomes

$$\left\langle \left(x(t)-x\right)^2 \right\rangle = \sum_{\kappa,\,\kappa"} \sum_{s,\,s"} P_\kappa \left| C_s^\kappa \right|^2 a^2 \left(s"-s\right)^2 \left| \left\langle s",\kappa" \right| \mathrm{e}^{-iHt/\hbar} \left| s,\kappa \right\rangle \right|^2$$

with

$$p_{s",s} = \left| \left\langle s",\kappa" \right| \mathrm{e}^{-iHt/\hbar} \left| s,\kappa \right\rangle \right|^2$$

the probability that the charge moves from *s* to *s*" during time *t*.

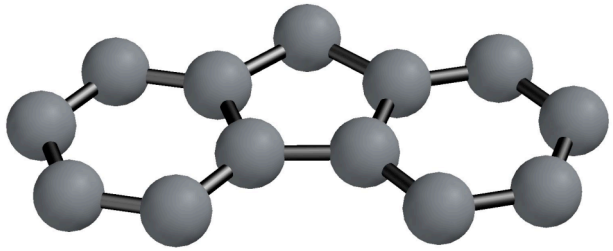
The expressions above show that localized initial states $\left| s,\kappa \right\rangle$ must be progated during time.

Structural fluctuations: electron-phonon scattering

Quantum mechanical description of electron-phonon scattering is tremendous task.

Slow nuclear motions can be described classically (e.g. MD simulations).

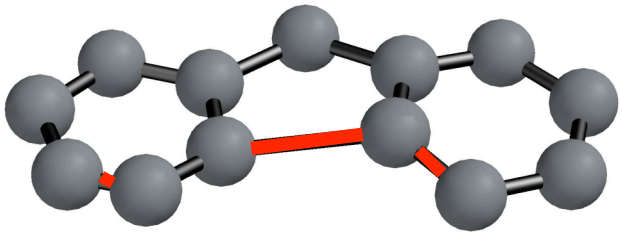
Phenomenological description of phonons in terms of time-dependent fluctuations of site energies and charge transfer integrals.



equilibrium geomety

$$\varepsilon = \varepsilon_{eq}$$

$$J = J_{eq}$$



vibrations distort geomety

$$\varepsilon(t) = \varepsilon_{eq} + \delta\varepsilon(t)$$

$$J(t) = J_{eq} + \delta J(t)$$

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Structural fluctuations: electron-phonon scattering

$$H_{el} = \sum_s \varepsilon_s(t) a_s^+ a_s + \sum_{s,s'=s\pm 1} J_{s,s'}(t) a_s^+ a_{s'}$$

$J_{s,s'}$ is effective charge transfer integral, subscript *eff* dropped

In Hamilton matrix for system of 4 units is

$$H_{el} = \begin{pmatrix} \varepsilon_1(t) & J_{12}(t) & 0 & 0 \\ J_{21}(t) & \varepsilon_2(t) & J_{23}(t) & 0 \\ 0 & J_{32}(t) & \varepsilon_3(t) & J_{34}(t) \\ 0 & 0 & J_{43}(t) & \varepsilon_4(t) \end{pmatrix}$$

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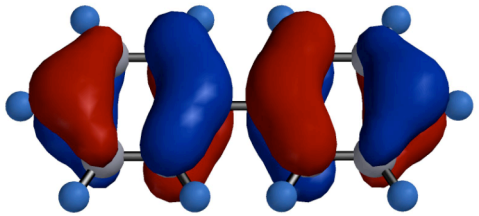
Structural fluctuations: electron-phonon scattering

$$H_{el} = \sum_s \varepsilon_s(t) a_s^+ a_s + \sum_{s,s'=s\pm 1} J_{s,s'}(t) a_s^+ a_{s'}$$

$J_{s,s'}$ is effective charge transfer integral, subscript *eff* dropped

Wavefunction of hole described by of HOMOs on phenyls:



Phenomenological description of fluctuations: e.g.

$$\langle \delta\varepsilon(t)\delta\varepsilon(0)\rangle = \frac{1}{3}\left(\Delta_\varepsilon\right)^2 \exp\left(-\frac{t}{\tau_\varepsilon}\right)$$

$$\langle \delta J(t)\delta J(0)\rangle = \frac{1}{3}\left(\Delta_J\right)^2 \exp\left(-\frac{t}{\tau_J}\right)$$

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Hybrid quantum/classical description of mobility

$$H_{el} = \sum_{s} \varepsilon_s(t) a_s^{+} a_s + \sum_{s,s'=s\pm 1} J_{s,s'}(t) a_s^{+} a_{s'}$$

$$\left\langle (x(t)-x)^2 \right\rangle = \sum_{\kappa,\,\kappa''} \sum_{s,\,s''} P_\kappa \left| C_s^\kappa \right|^2 a^2 (s''-s)^2 \left| \langle s'',\kappa'' | e^{-iHt/\hbar} | s,\kappa \rangle \right|^2$$

In case of classical or phenomenological description of e$^-$-phonon interaction this reduces to

$$\left\langle (x(t)-x)^2 \right\rangle = \left\langle \sum_{s'',\,s} f(s) a^2 (s''-s)^2 \left| c_{s''}(t;s) \right|^2 \right\rangle$$

$f(s)$ initial population of site *s*

$c_{s''}(t;s)$ coefficient of state *s*'' for charge initially at *s*.

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Hybrid quantum/classical description of mobility

Simulation of motion of charge carrier on dynamic chain using time-dependent self-consistent field (TD-SCF) approach.

Propagate wavefunction of charge during small time step:

- nuclear degrees of freedom fixed
- site energies and charge transfer integrals kept constant

Propagated nuclear degrees of freedom during same time step

- wavefunction of charge is kept fixed

Monte-Carlo simulation of charge motion

- initially charge is localized on a single monomer unit *s*

- Schrödinger equation solved numerically

$$i\hbar\frac{\partial\psi(t;s)}{\partial t}=H_{el}(t)\psi(t;s) \qquad \left|\psi(t;s)\right\rangle=\sum_{s''}c_{s''}(t;s)\left|\varphi_{s''}\right\rangle$$

$$c_{s''}(t;s)=\left\langle\varphi_{s''}\left|e^{-iH_{el}(t)t/\hbar}\right|\varphi_{s}\right\rangle$$

- mean-square displacement by averaging over initial sites *s* and realizations of fluctuations (Monte-Carlo sampling of site energies and couplings:

$$\left\langle x^2(t)\right\rangle=\left\langle\psi(t)\left|\Delta s^2\right|\psi(t)\right\rangle a^2=\sum_{s}\sum_{s''}\left|c_{s''}(t)\right|^2(s-s'')^2a^2=\frac{2kT}{e}\mu t$$

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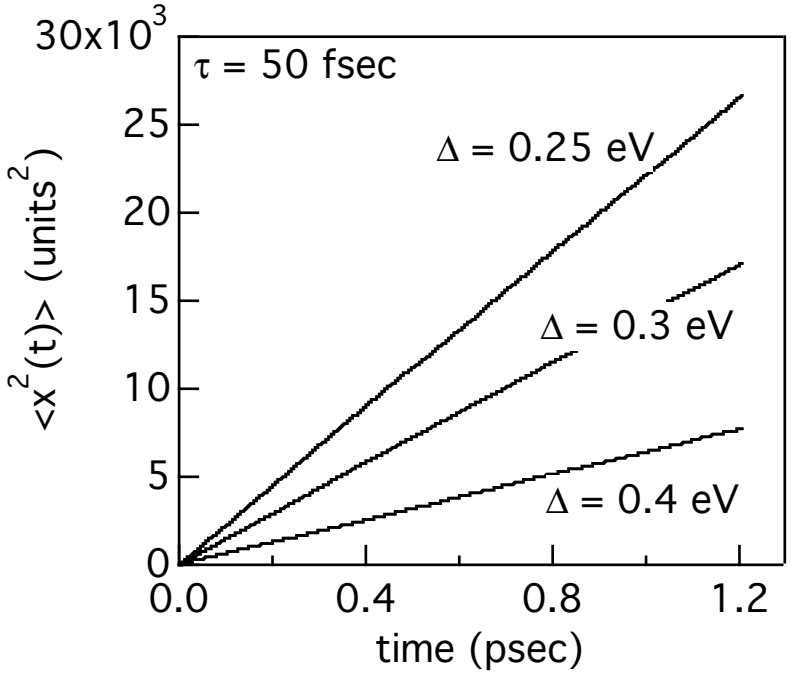
Monte-Carlo simulation of charge motion

Simulated mean-square displacement for different degrees of ddynamic disorder:



$$x^2(t) = \frac{2kT}{e}\mu t$$

$$\langle \delta\varepsilon(t)\delta\varepsilon(0)\rangle = \frac{1}{3}\left(\Delta_\varepsilon\right)^2 \exp\left(-\frac{t}{\tau_\varepsilon}\right)$$

Exptl.mobility of 600 $cm^2V^{-1}s^{-1}$
Reproduced with dynamic fluctuations
Δ_ε = 0.25-0.3 eV, τ_ε ~ 20-100 fs

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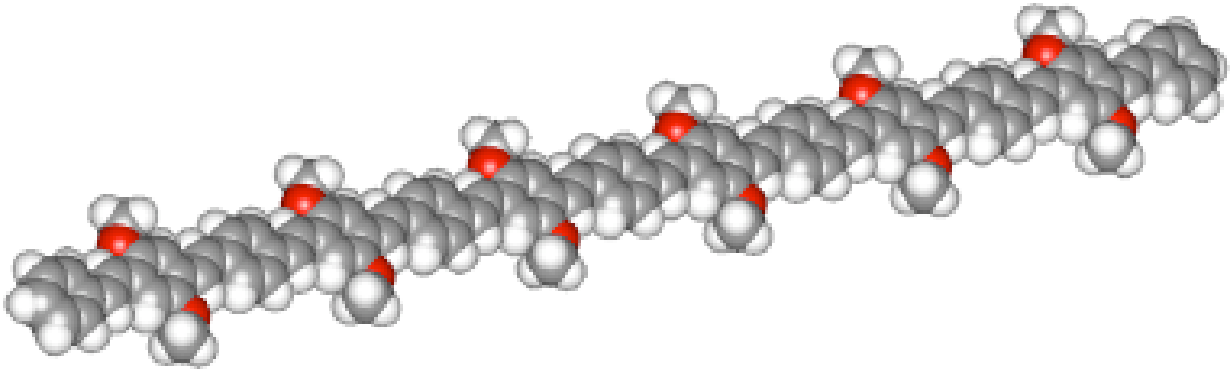
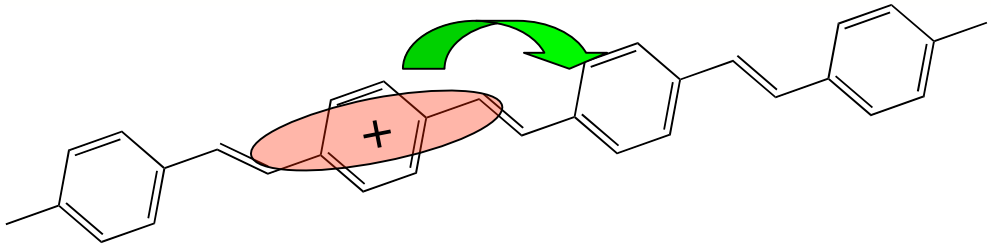
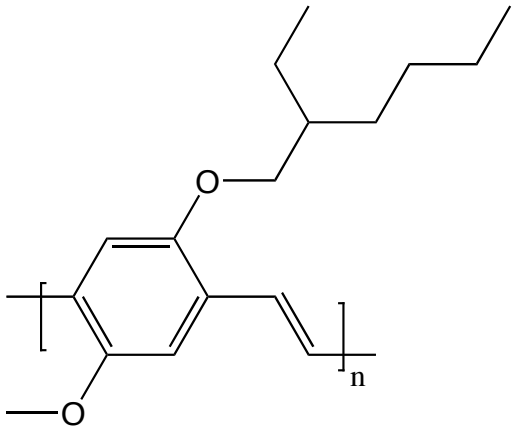
MEH-PPV with (potential) applications in LEDs, solar cells..







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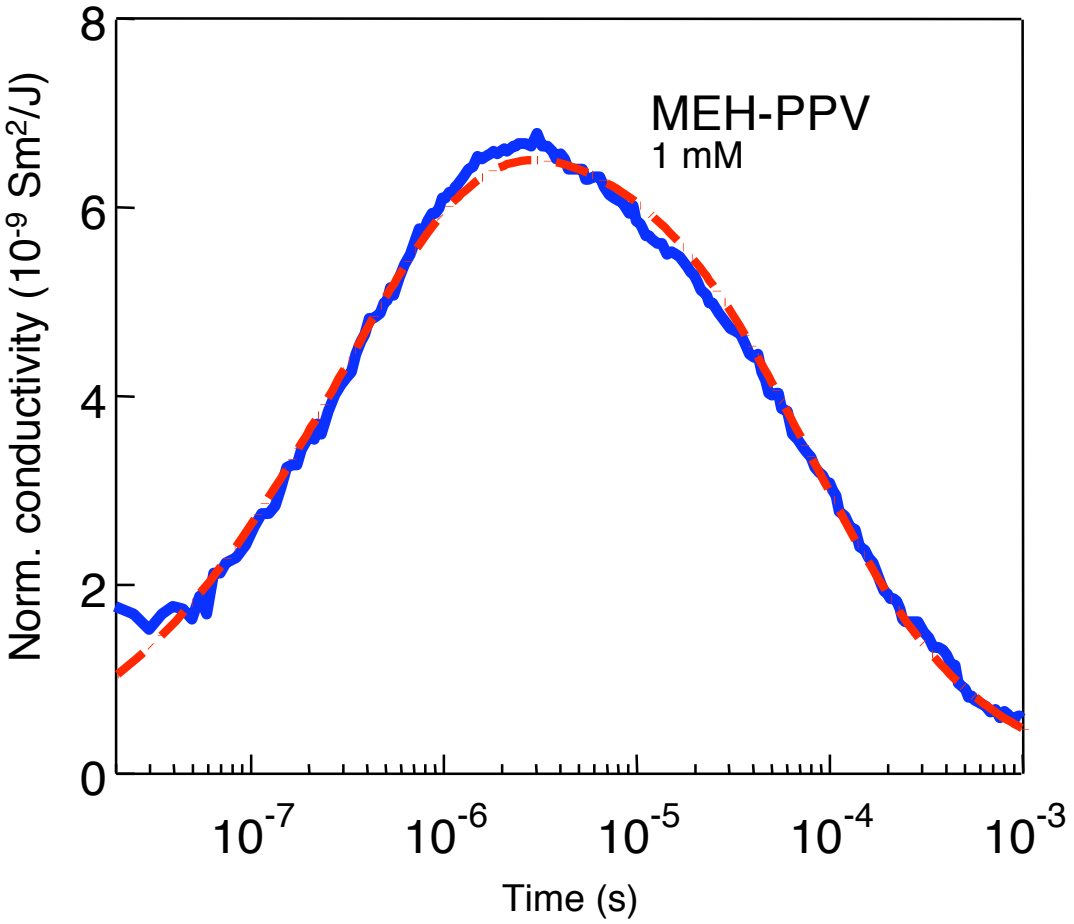
Microwave conductivity due to holes on MEH-PPV chains



Growth:

$Bz^+ + P \longrightarrow P^+ + Bz$

Decay:

$P^+ + O_2^- \longrightarrow P + O_2$

$\mu = 0.43\ cm^2V^{-1}s^{-1}$

Hoofman et al., Nature, **392** 54 (1998)
Grozema et al., Adv. Mat. **14** 228 (2002)
Prins et al. Adv. Mat. **17** 718 (2005)
Siebbeles et al. Rad. Phys. Chem. **72**, 85 (2005)
Prins et al. Mol. Sim. **32** 695 (2006)
Prins et al. J. Phys. Chem. B, **110** 14659 (2006)

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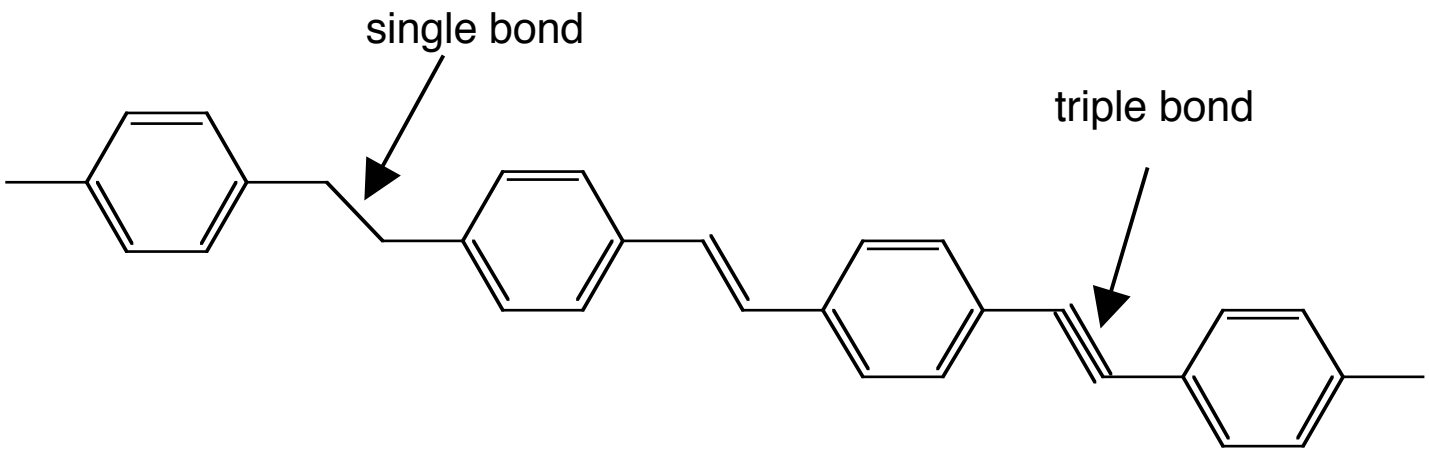
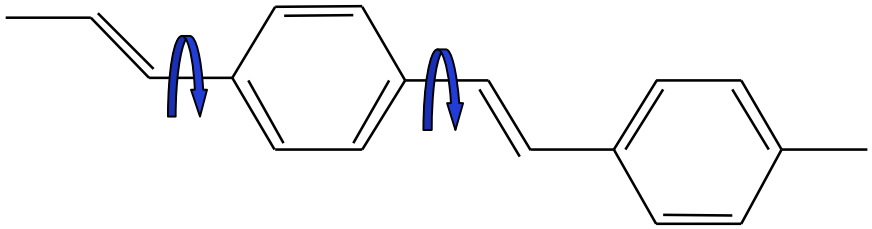
Is 0.43 $cm^2V^{-1}s^{-1}$ the ultimate mobility or limited by defects?

- single and triple bonds hinder charge transport



- torsional disorder reduces mobility



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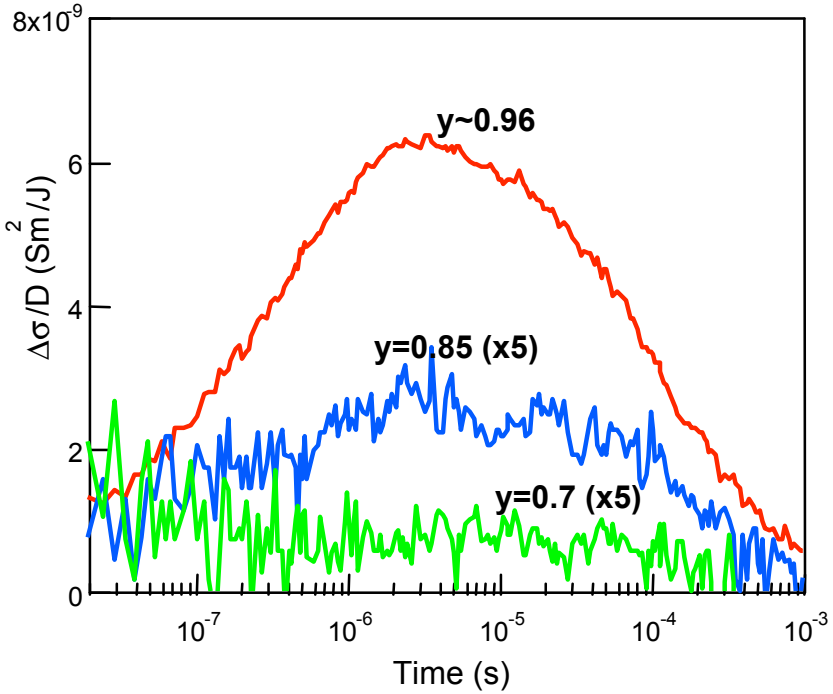
Effect of conjugation breaks in MEH-PPV

Shorter conjugation length: larger band gap due to quantum confinement

Effect of conjugation breaks

- MEH-PPV with broken conjugation



y ~ 0.96 : 0.46 cm²/Vs

y = 0.85 : 0.03 cm²/Vs

y = 0.70 : < 0.01 cm²/Vs

Candeias et al., J. Phys. Chem. B **107**, 1554 (2003)

- Conjugation breaks have dramatic effect on charge carrier mobility

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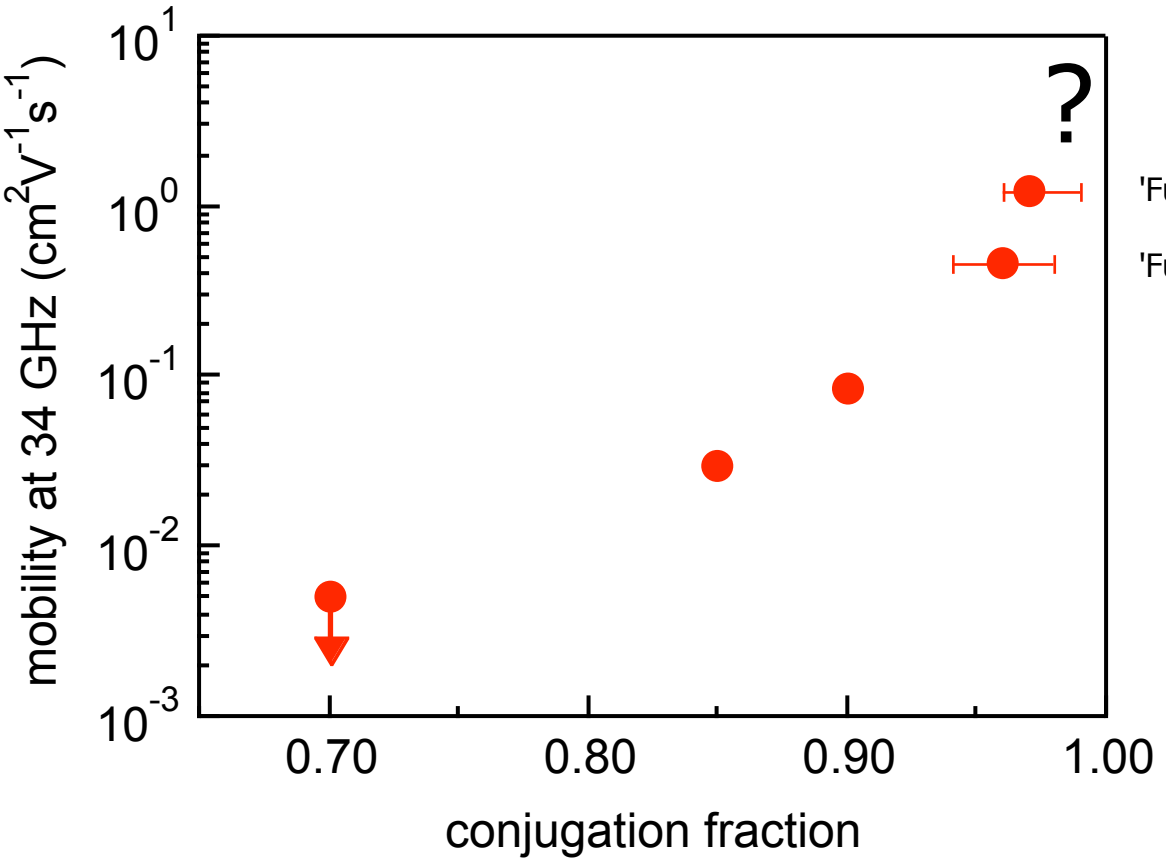
What would mobility be for infinite chains with y=1?



'Fully conjugated' Sulfonyl, IMEC/LUC

'Fully conjugated', Gilch, Sigma Aldrich

Motion of charges hindered by barriers (even for y~96%)

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Theoretical modeling of mobility

- tight-binding Hamiltonian for charge carrier:

$$H_{el} = \sum_s \left[\varepsilon_s a_s^+ a_s - J_{eff}(\Delta\Theta_{s,s+1}) \left(a_{s+1}^+ a_s + a_s^+ a_{s+1} \right) \right]$$

- wavefunction is time-dependent superposition of HOMOs: $\left|\psi(t;s)\right\rangle = \sum_{s''} c_{s''}(t;s) \left| s'' \right\rangle$

  initially localization on a single monomer unit *s*

- Schrödinger Eq. num. solved: $i\hbar \frac{\partial \psi(t;s)}{\partial t} = H_{el}(t)\psi(t;s)$

- mean-square displacement: $\left\langle x^2(t) \right\rangle = \left\langle \psi(t) \right| \Delta s^2 \left| \psi(t) \right\rangle a^2$

Mobility $\mu(\omega) = -\frac{e\omega^2}{2kT} \int_0^\infty \left\langle x^2(t) \right\rangle \exp(-i\omega t)\, dt$

Grozema et al. J. Phys. Chem. B, **106**, 7791-7795 (2002)

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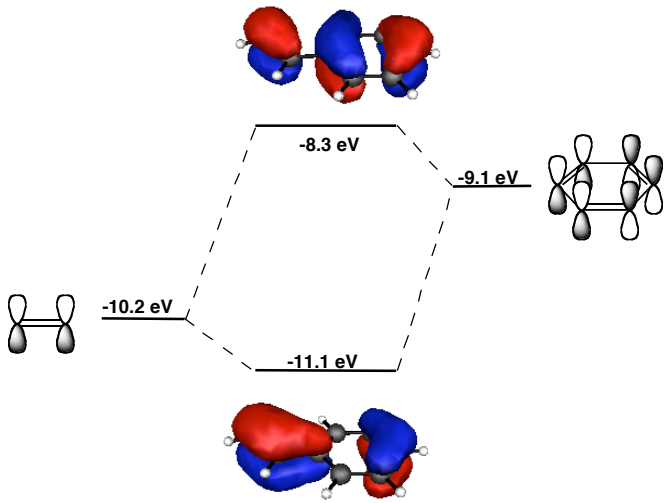
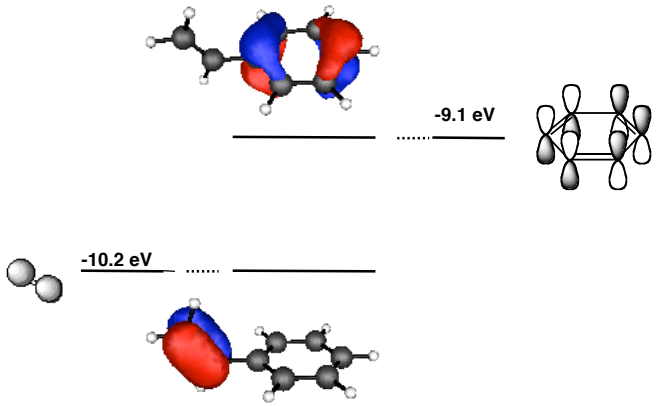
Angles between units determine charge transfer integral and mobility

planar good coupling



perpendicular no coupling



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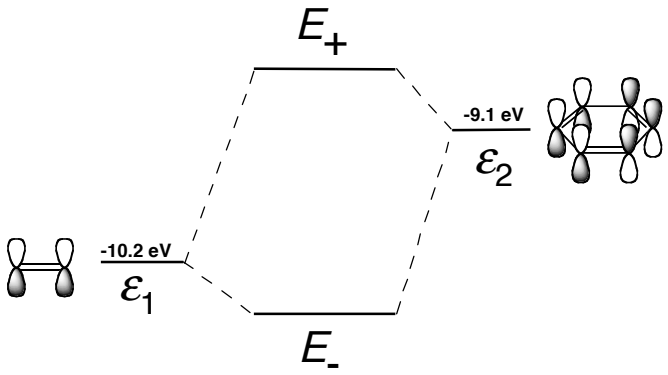
Charge transfer integral for HOMOs: $$\left|J_{eff}\left(\Delta\Theta_{n,n+1}\right)\right| = \frac{1}{2}\sqrt{\left(E_+ - E_-\right)^2 - \left(\varepsilon_2 - \varepsilon_1\right)^2}$$



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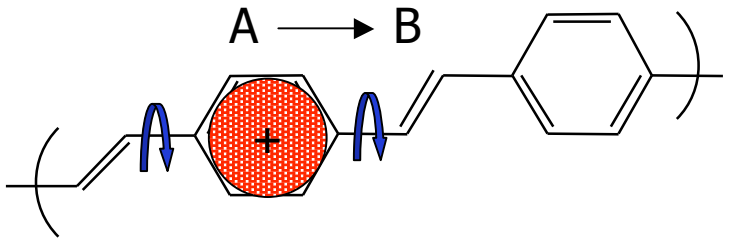
Phenyl rings rotate, thus charge tranfer integrals $J_{eff}(\Delta\Theta_{n,n+1})$ vary with time

$$J = \langle \varphi_A | h(\Theta) | \varphi_B \rangle$$



Diffusional rotation of phenyl rings:

$$\langle \Delta\Theta^2 \rangle = 2Dt \qquad D = \frac{1}{2\tau_{rot}} \qquad \tau_{rot} = 200 \text{ psec}$$

$$\Delta\Theta = \frac{D}{kt}\left(-\frac{\partial V(\Theta)}{\partial\Theta}\right)\Delta t + \sqrt{24\,D\Delta t}\,R \qquad R \in \langle -0.5, 0.5]$$

drift in potential diffusion

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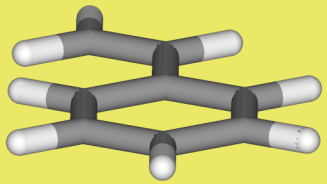
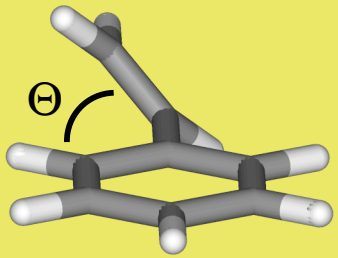
Information about torsional potential needed



$\Theta = 0$



$\Theta \neq 0$

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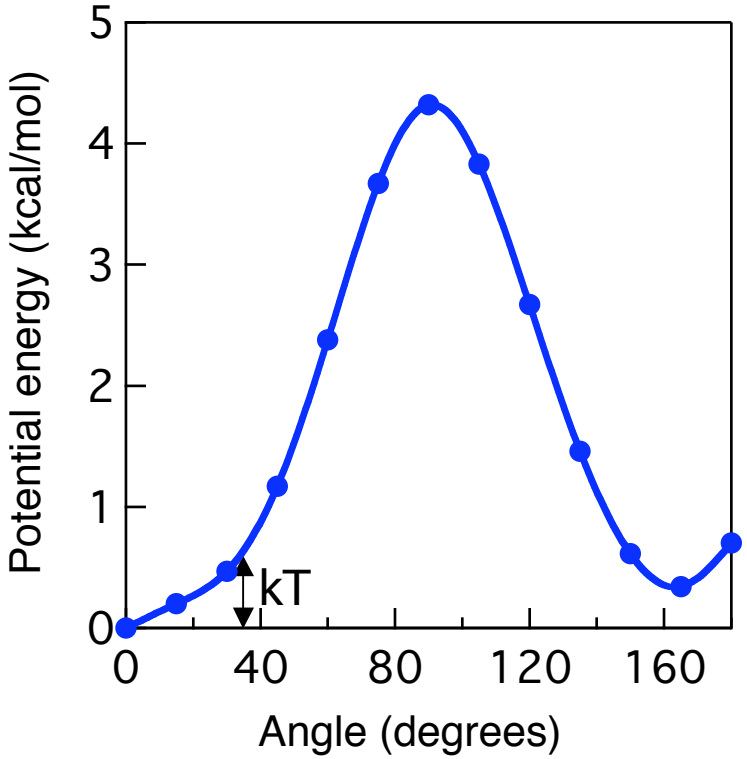
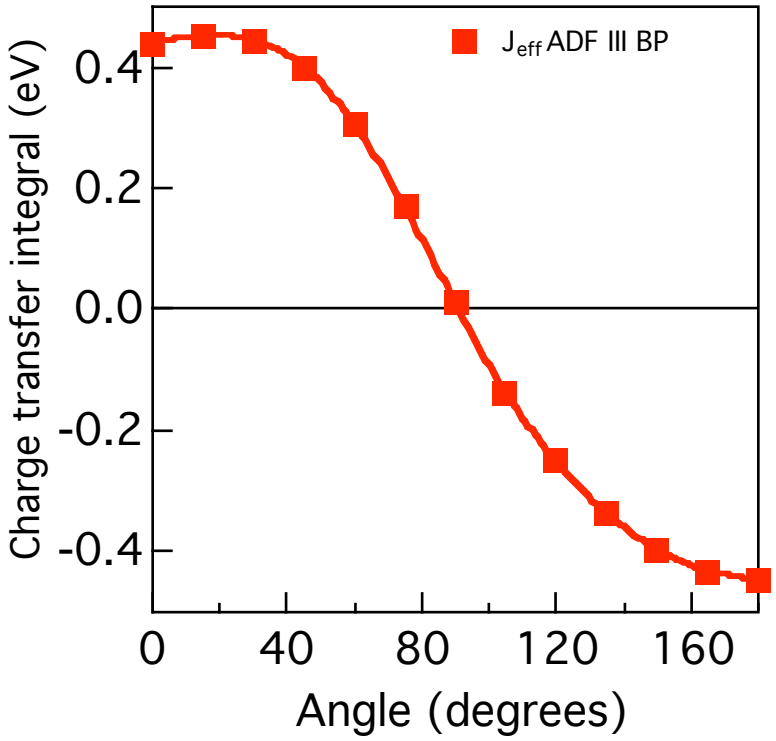
Torsional potential (MP2/cc-pVDZ) and charge transfer integral (DFT) for dialkoxy substituted PV from *ab initio* calculations





Grozema et al. J. Phys. Chem. B, **106**, 7791-7795 (2002)

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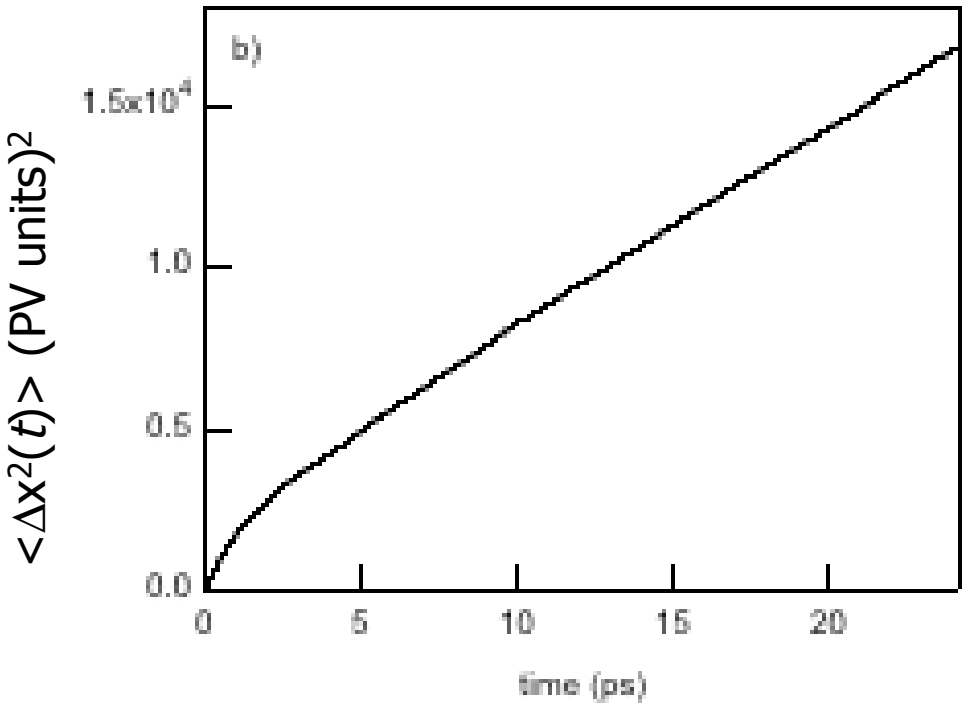
Simulation of motion of charge carrier on dynamic chain using
time-dependent self-consistent field (TD-SCF) approach:

- wavefunction of charge propagated during small time step, while angles are fixed

- angles propagated during same time step assuming wavefunction fixed

Mean-square displacement for infinite PPV chain



From slope: μ = 59 $cm^2V^{-1}s^{-1}$

~ 150 times higher than measured!

$$x^2(t) = 2Dt$$

$$\mu = \frac{e}{kT} D$$

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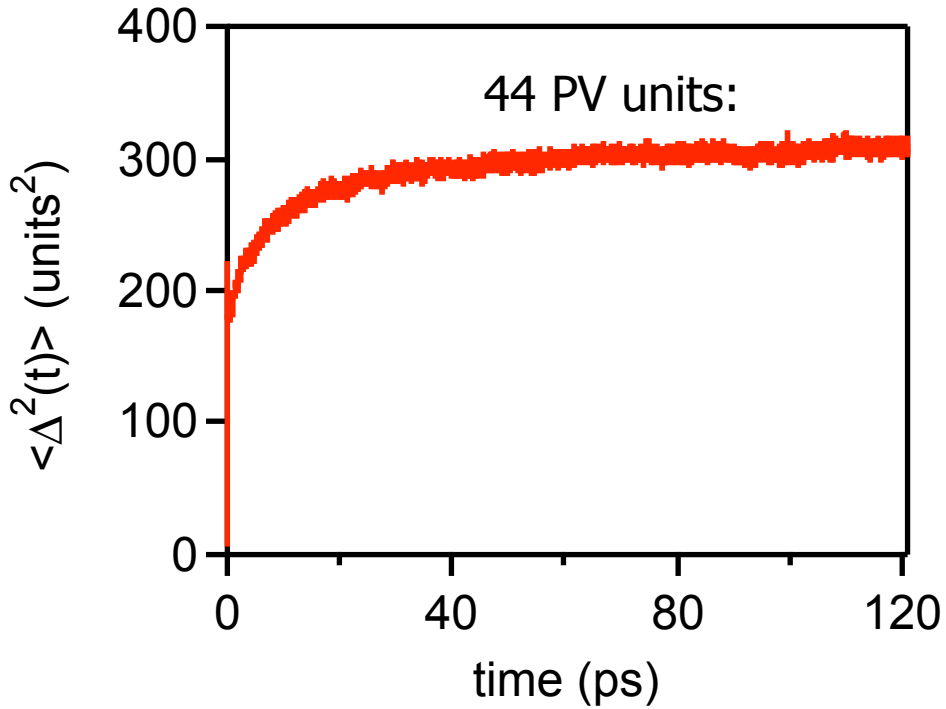
Effect of conjugation breaks: assume reflecting barriers

Calculations of mobility for chains with finite length (*n* PV units)

Averaged over Flory distribution: $P_n = y^n(1-y)$ and $\langle\mu\rangle = \sum_n P_n \mu_n$



$$\mu(\omega) = -\frac{e\omega^2}{2kT}\int_0^\infty \langle x^2(t)\rangle \exp(-i\omega t)\,dt$$

μ(34 GHz) = 0.9 cm^{2}V^{-1}s^{-1}

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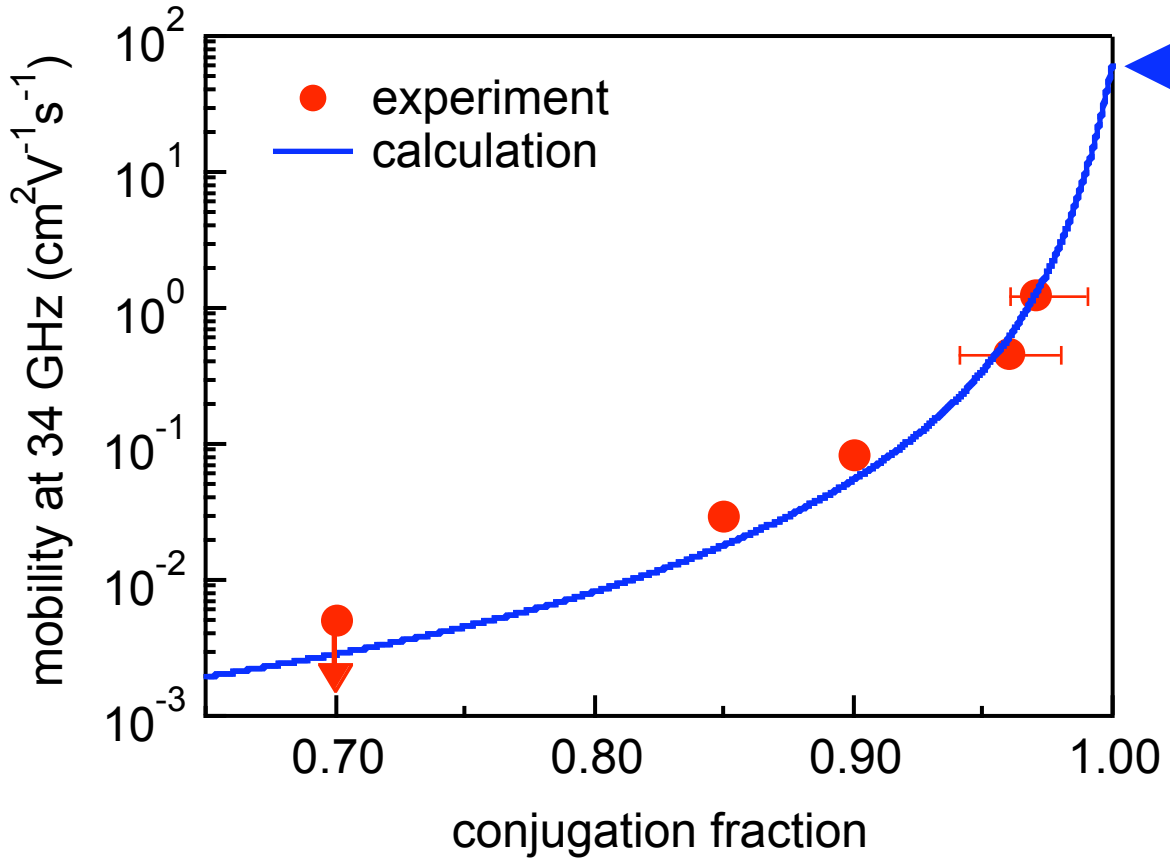
Calculated mobility agrees with experiment

Theory helps to predict the ultimate mobility on defect free chain



Calct. mobility for infinite PPV chains is 59 $cm^2V^{-1}s^{-1}$

Exptl. results for oligomers OPV12 and OPV16 also agree with calcs.

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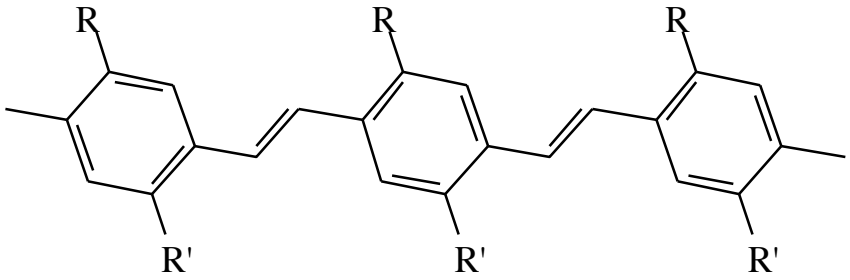
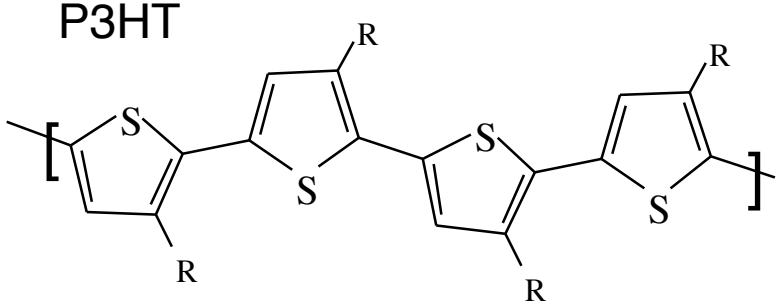
MEH-PPV



R = methoxy

R’ = 2’-ethyl-hexyloxy

P3HT



R = hexyl

chains of ~ hundred monomers

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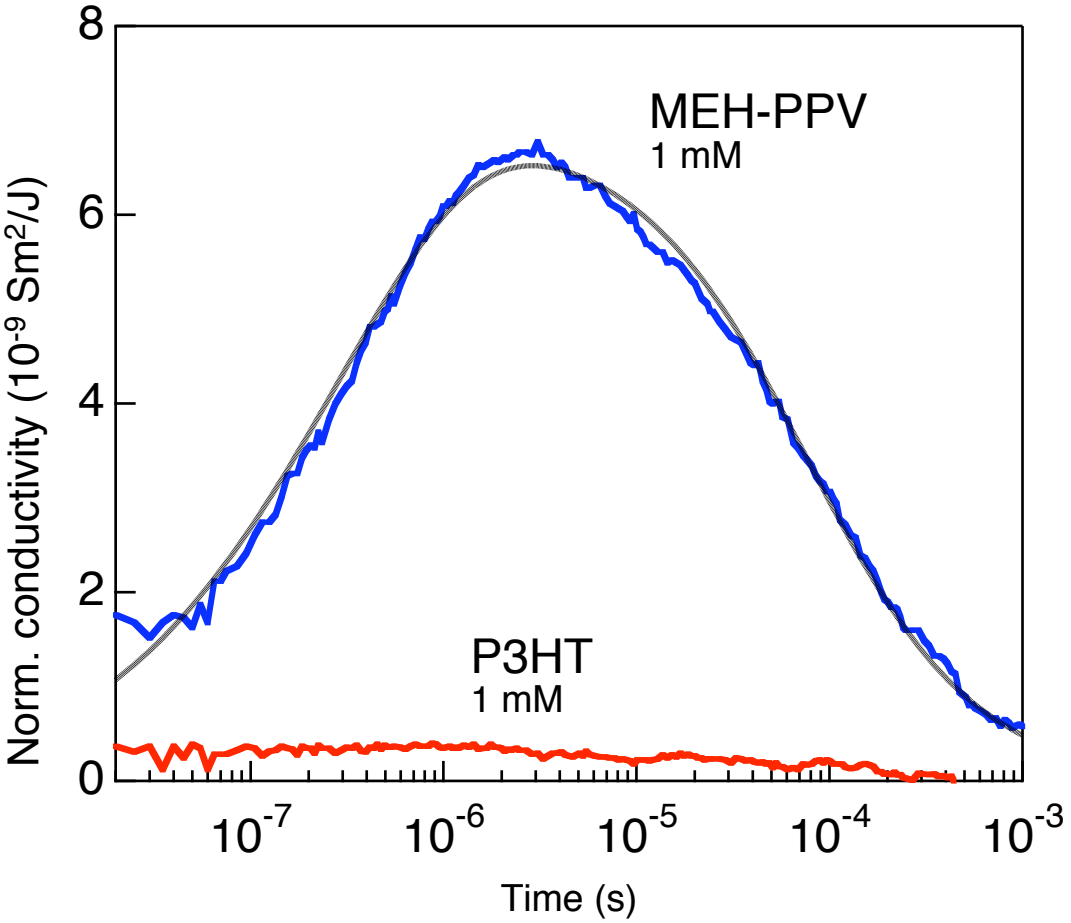
Mobility on MEH-PPV much higher than on P3HT



Growth:

$Bz^+ + P \longrightarrow P^+ + Bz$

Decay:

$P^+ + O_2^- \longrightarrow P + O_2$

Mobilities

MEH-PPV: 0.43 $cm^2V^{-1}s^{-1}$

P3HT: < 0.02 $cm^2V^{-1}s^{-1}$

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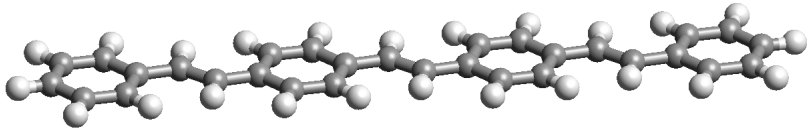
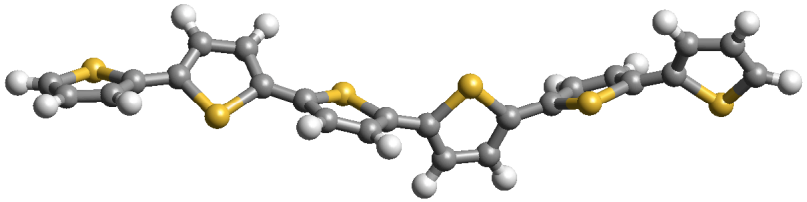
idealized planar PPV



More torsional disorder in thiophene?



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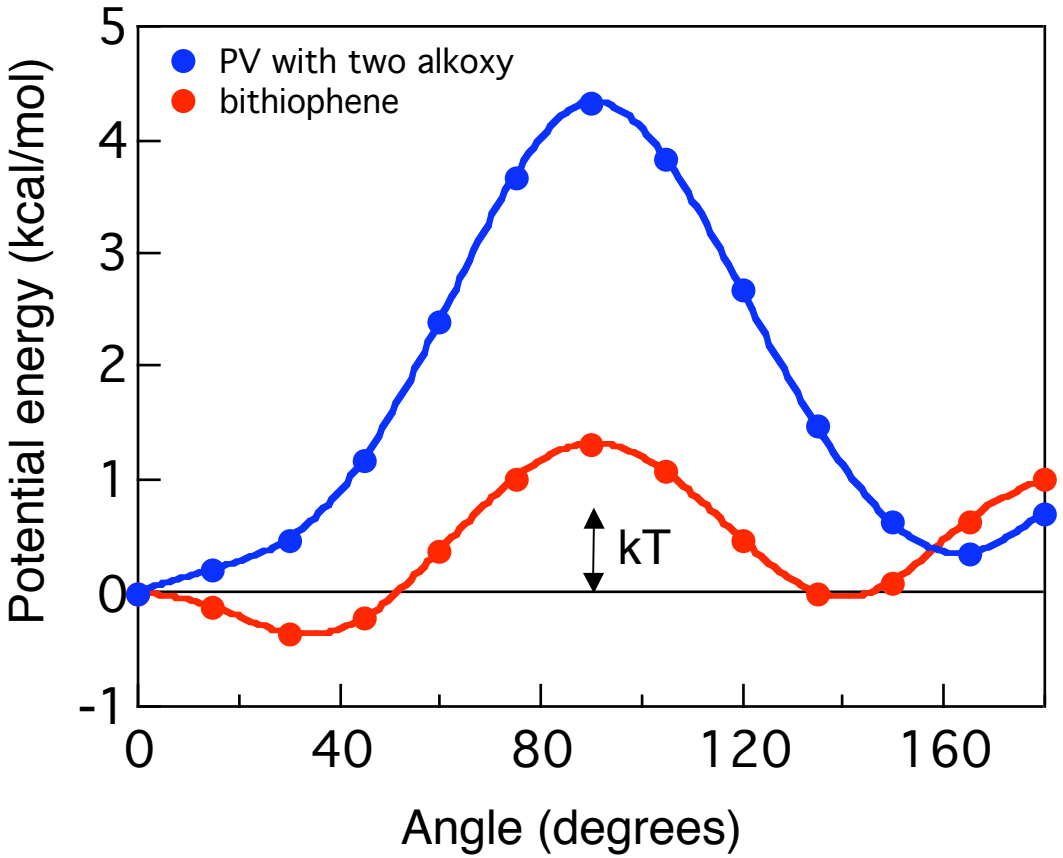
Torsional potential from *ab initio* calculations (MP2/cc-pVDZ)

Torsional barrier in PPV much higher than in thiophene



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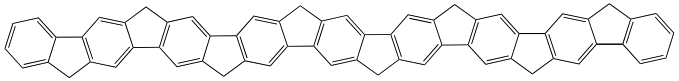
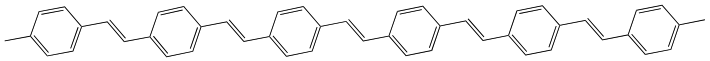
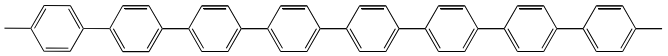
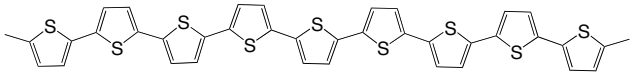
Summary

- Theory has helped to determine ultimate mobility along mocular wires
- Mobility depends on backbone planarity

ladder-PPP  600 $cm^2V^{-1}s^{-1}$

PPV  59 $cm^2V^{-1}s^{-1}$

PPP 

PT  < 0.02 $cm^2V^{-1}s^{-1}$

- Ladder-PPP is a promising molecular wire
- Device performance can be improved by using planar backbones and avoiding chain-to-chain transport

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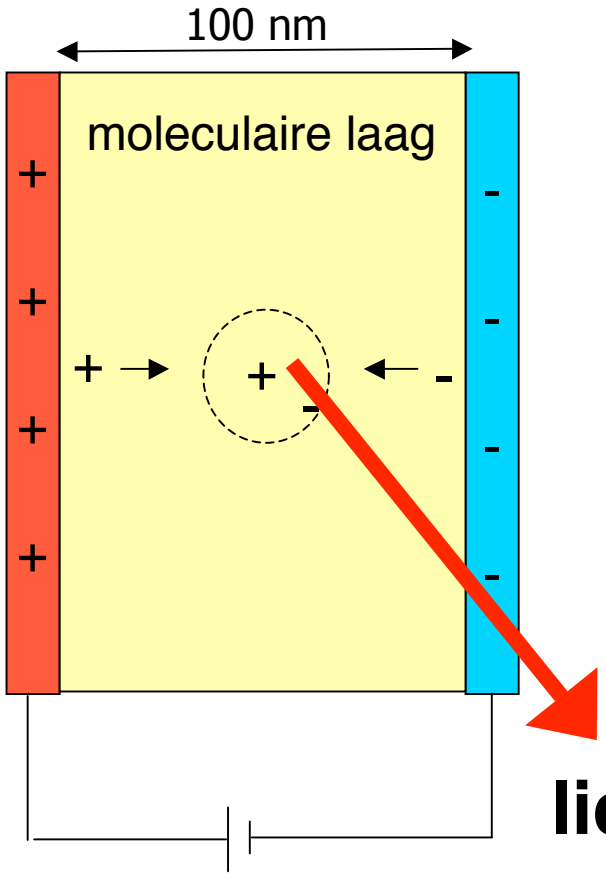
Elektronische processen in devices: LED



licht

- efficiënte injectie (afhankelijk v. interface)
- beweeglijke + en e^- (e^- vaak niet mobiel)
- lading-recombinatie (S/T verhouding?)
- emissie van licht (exciton vervalt stralingsloos)
- stabiel materiaal (instabiel)
- verschillende kleuren (blauw instabiel)

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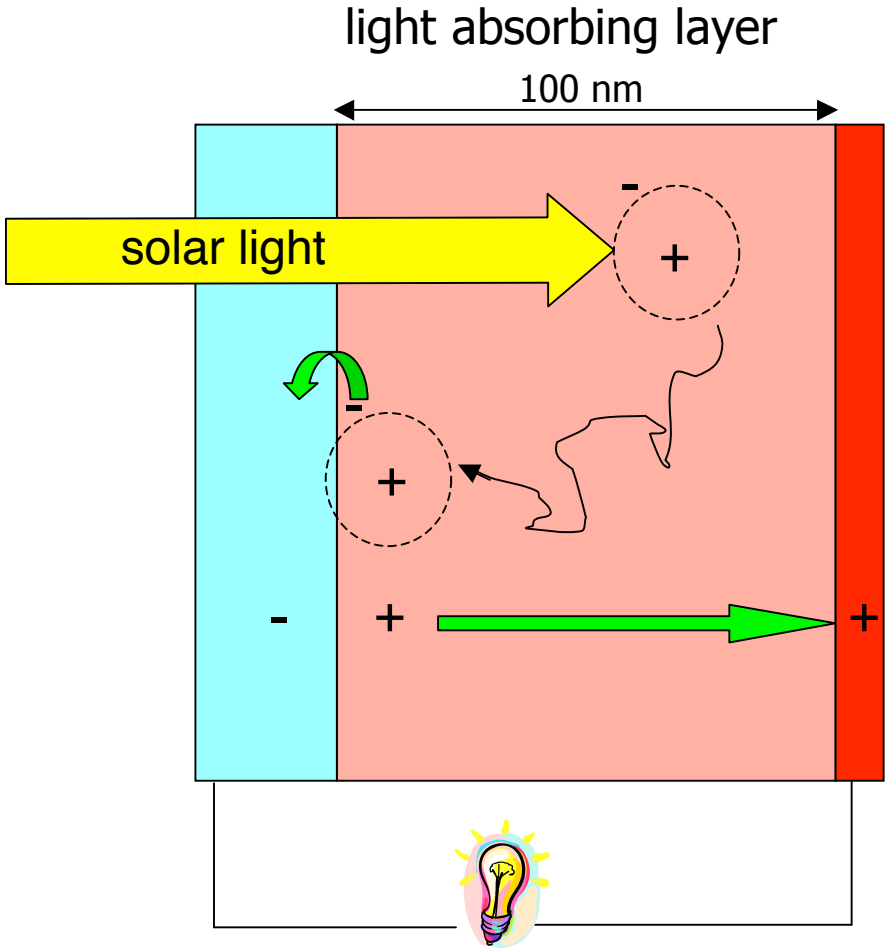
Electronic processes in devices: solar cell



- veel lichtabsorptie (rood licht slecht)
- stabiele excitonen (verval)
- beweeglijke excitonen (korte afstand)
- ladingsscheiding (recombinatie)
- beweeglijke lading (niet erg mobiel)

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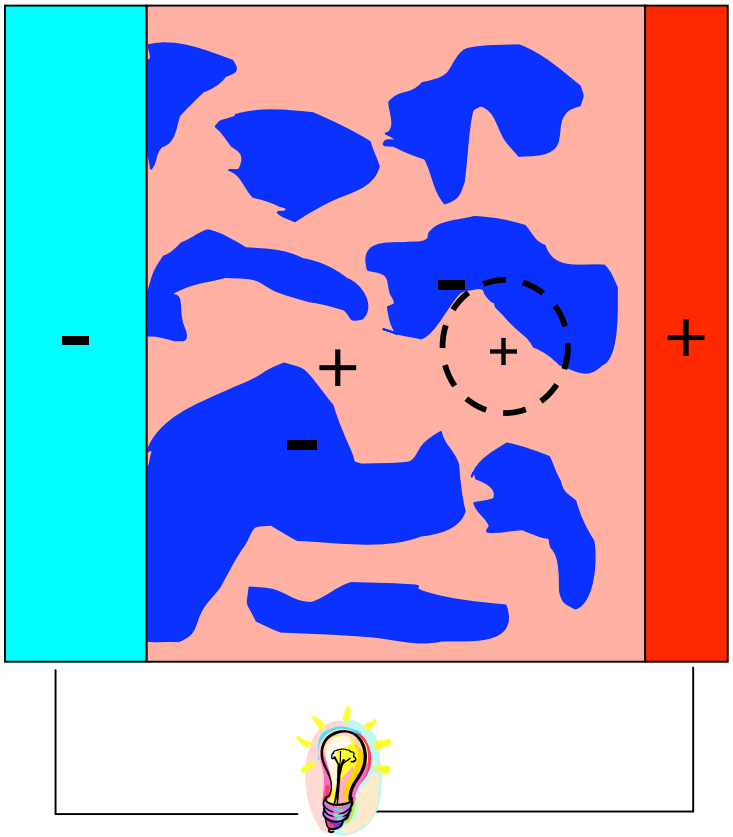
Heterogeneous nanostructured materials because of short exciton diffusion length



Nadelen:

- ladingstransport moeilijker
- ladingsrecombinatie
- excitonen vervallen op vastzittende ladingen

Efficiëntie

- organische zonnecel: < 4 %
- Si zonnecel 15-20 % (record 24%)

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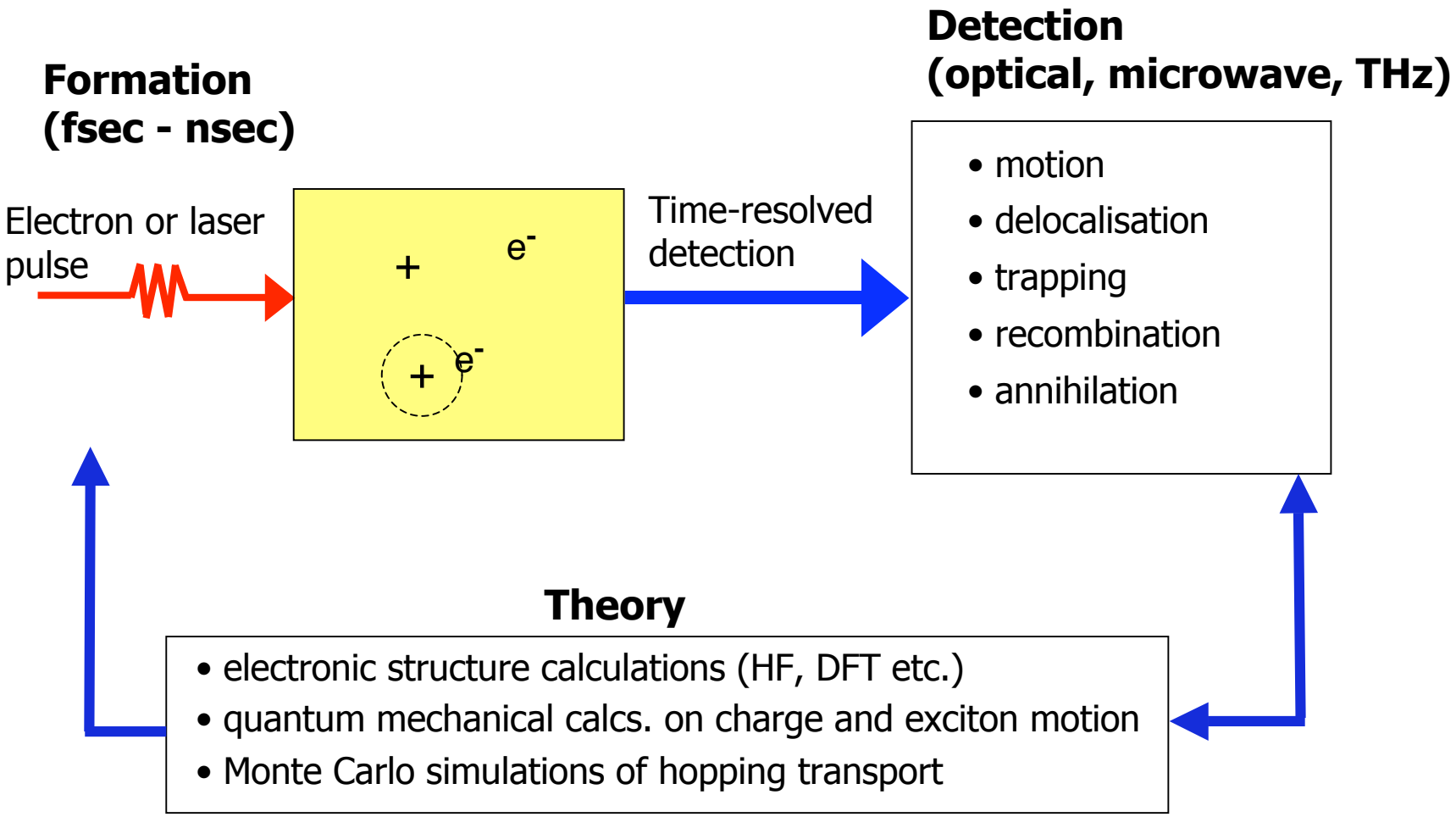
Dynamics of charge carriers and excitons



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Opto-electronic molecular materials

Advantages

- CHEAP
- EASY PROCESSING
- FLEXIBLE
- LIGHTWEIGHT
- LARGE VARIETY
- MOLECULES ARE SMALL
  (MOLECULAR NANO-ELECTRONICS)

Problems

- DISORDERED STRUCTURE
- CONTAIN IMPURITIES
- INSTABLE

Research needed on relation between nano- to mesoscopic material structure and proerties of electrons

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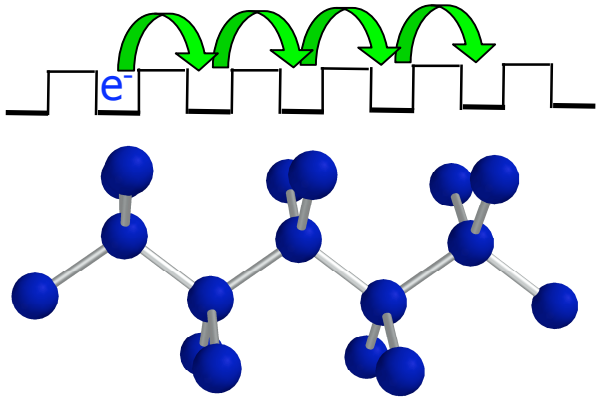
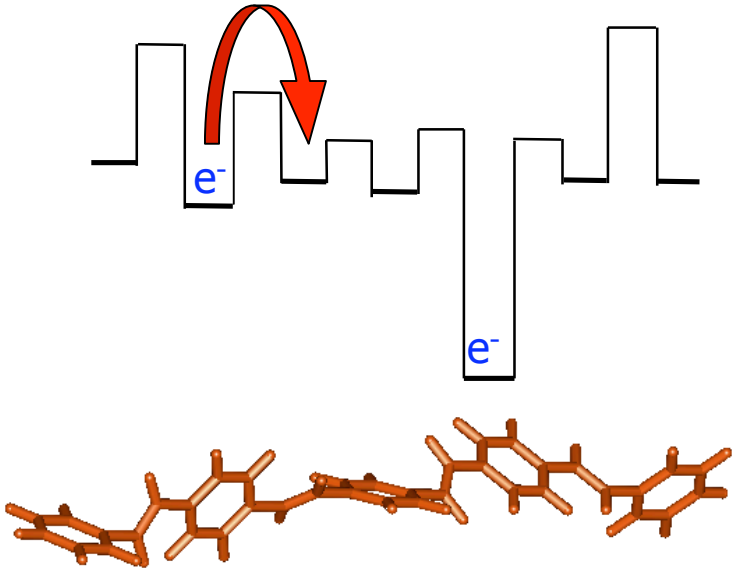
Disorder hinders charge transport

ordered semiconductor:
electrons move fast



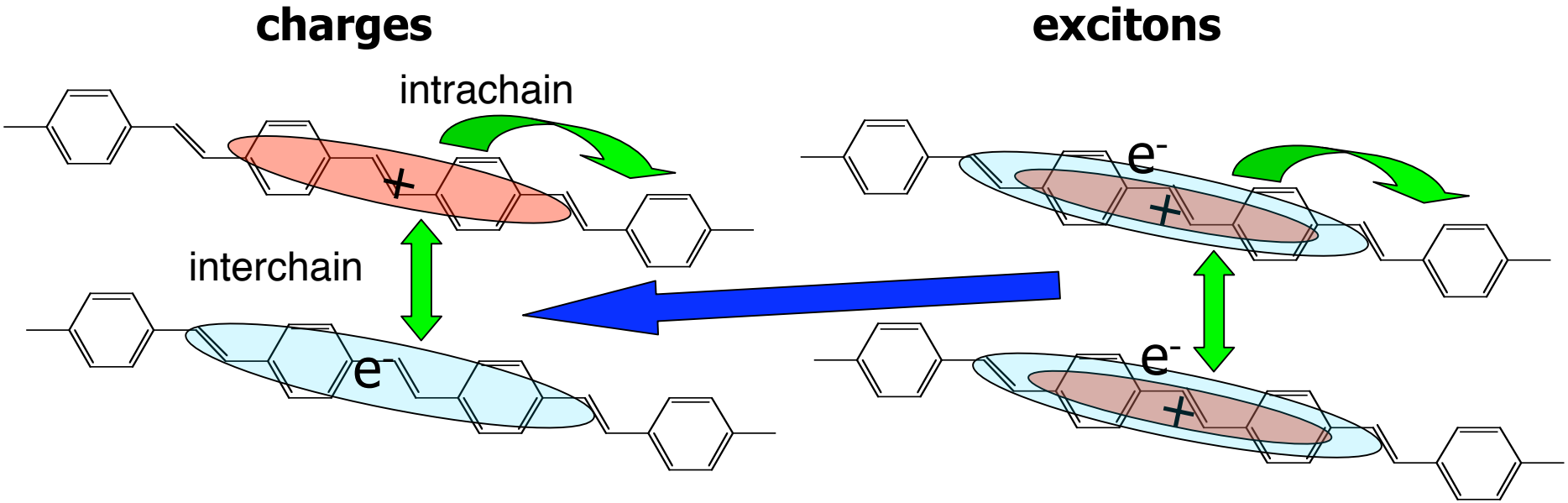
disordered polymer chain:
motion hindered

insight into effects of disorder
provides info about ultimate
mobility



Fundamental knowledge needed for improved device perfomance

- factors governing motion of charges and excitons
- efficiency of charge recombination
- decay channels of excitons: fluorescence, dissociation, annihilation
- quantum yield for photogeneration of charges



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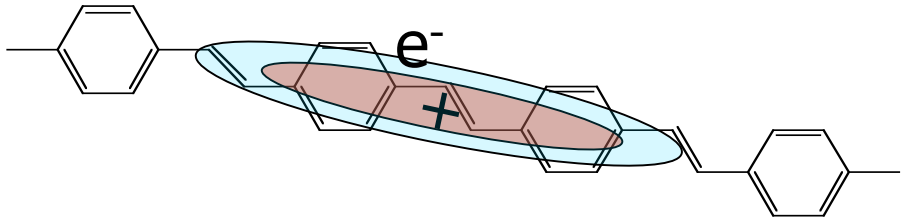
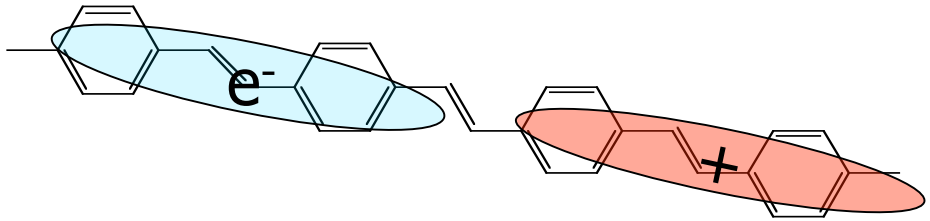
Excitons and free charges

Excitons decay by fluoresence, non-radiative process, econd-order annihilation



Charges decay by recombination, trapping



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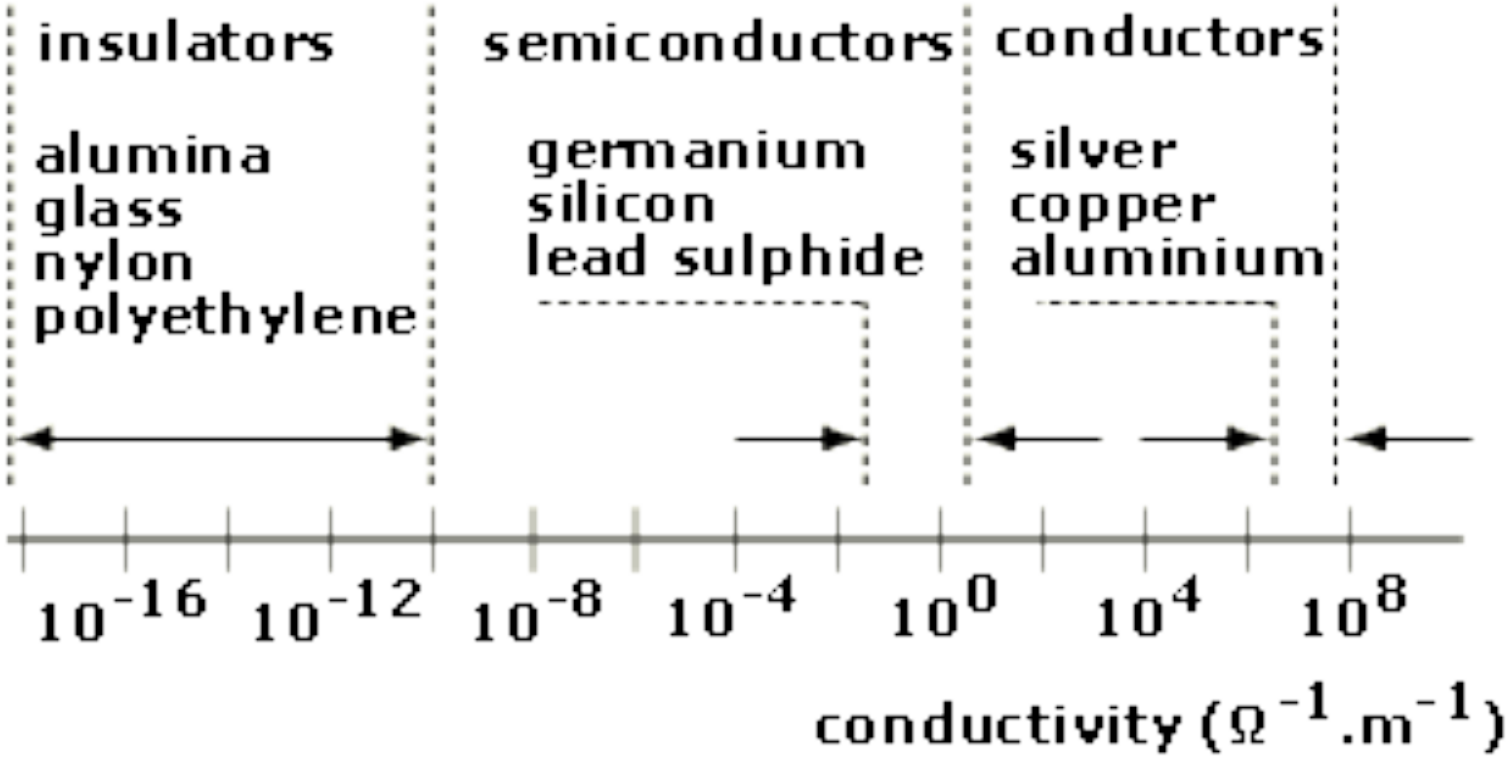


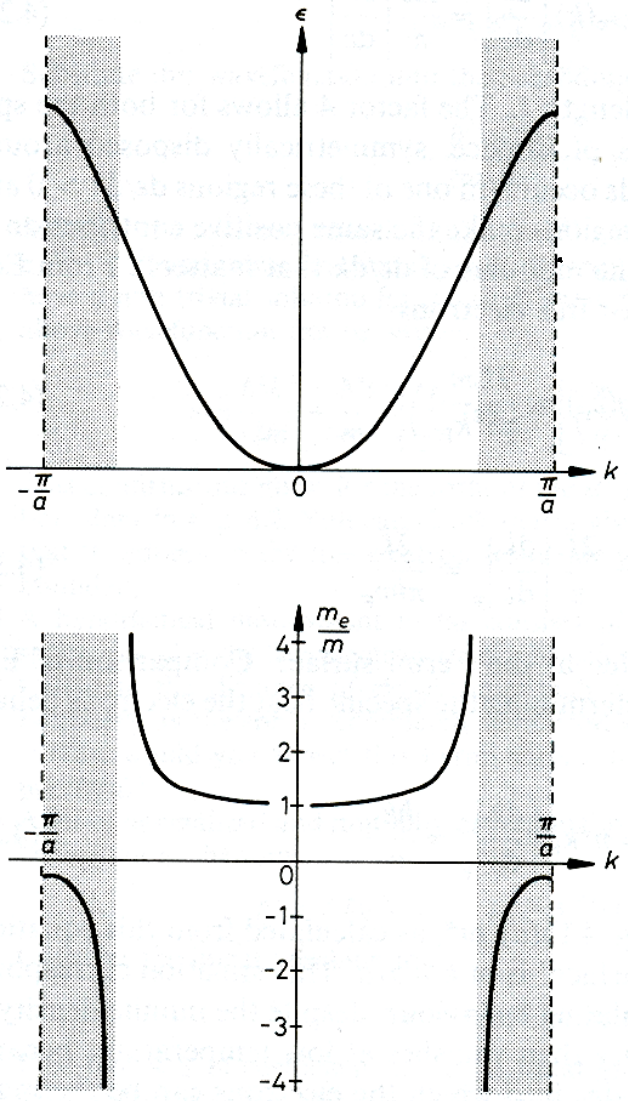
www.ami.ac.uk/courses/topics/0115_cai/images/fc_cai_imga.gif

H&H Fig. 4.15

k-dependent effective masses

$$v_k = \frac{1}{\hbar}\frac{\partial E_k}{\partial k}$$

$$\frac{1}{m_{eff}} = \frac{1}{\hbar^2}\frac{\partial^2 E_k}{\partial k^2}$$



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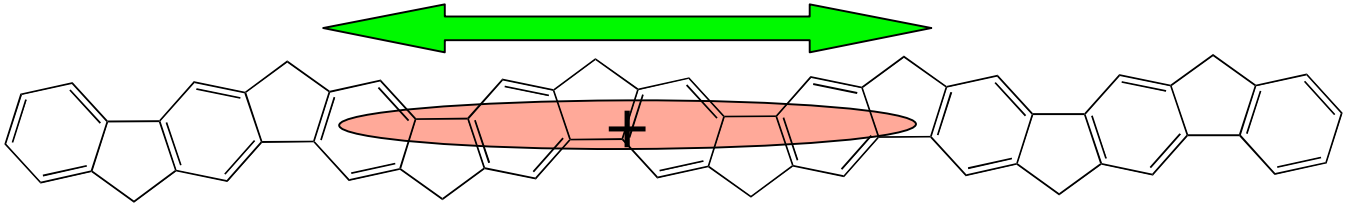
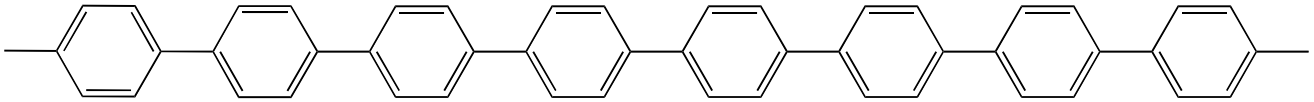
Charge transport along conjugated polymer chains

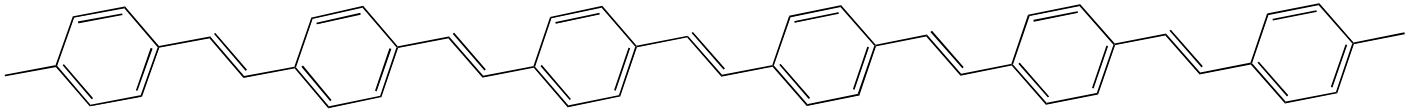
ladder-PPP



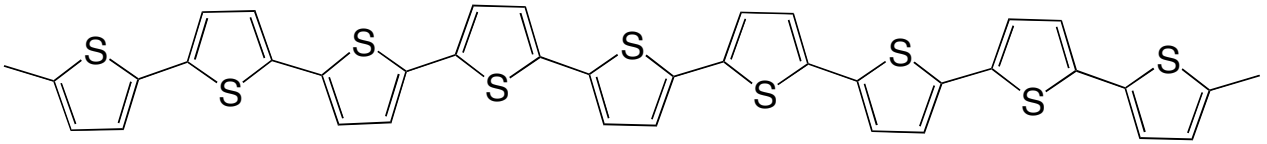
PPP



PPV



PT



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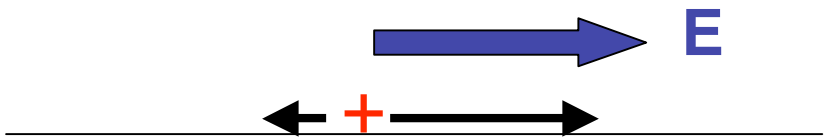
Mobility of charges is key parameter for applications

High mobility essential for fast switching and high current

Mobility is velocity per unit electric field strength:

$$v = \mu E$$



Einstein relation with diffusion coefficient: $\mu = D\,e / kT$

Mean square displacement: $\langle x^2(t) \rangle = 2\,D\,t$

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Effective mass of charge carriers in perfectly ordered polymer

$$m^* = \frac{2\hbar^2}{W d^2} = 0.4\, m_e \qquad \mu = \frac{e}{m^*}\tau$$

Effective mass comparable to that of holes semiconductors such as InAs and GaSb

Hole mobility as high as $\mu = 500 - 900$ cm^2 V^{-1} s^{-1} (velocity in field $F = 1$ V cm^{-1} is 5 m s^{-1})

Until now DC mobilities in conjugated polymers are $10^{-7} - 10^{-1}$ cm^2 V^{-1} s^{-1}

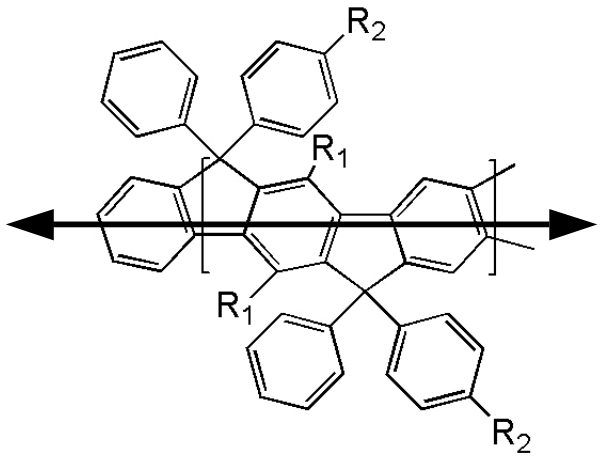
More than 3 orders of magnitude smaller due to:

disorder, chemical defects, inter-chain transport

LPPP chains with different average length

Phe-LPPP

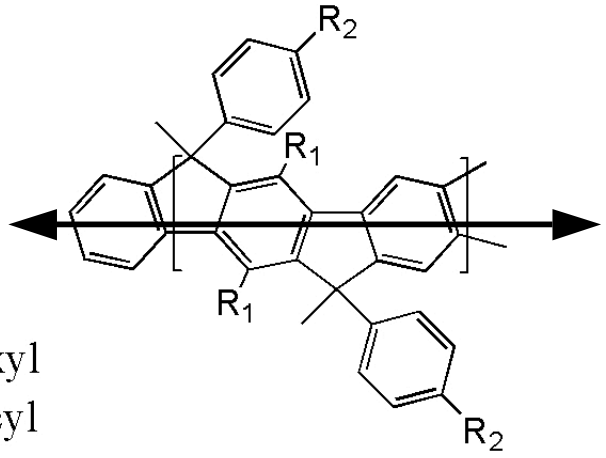
R_1 = *n*-hexyl
R_2 = *t*-butyl



<*n*> = 13, 16, 35

Me-LPPP

R_1 = *n*-hexyl
R_2 = *n*-decyl



<*n*> = 54

Flory distribution of chain lengths 5 ≤ n ≤ 75 $P_n = (1-y)\,y^{n-1}$

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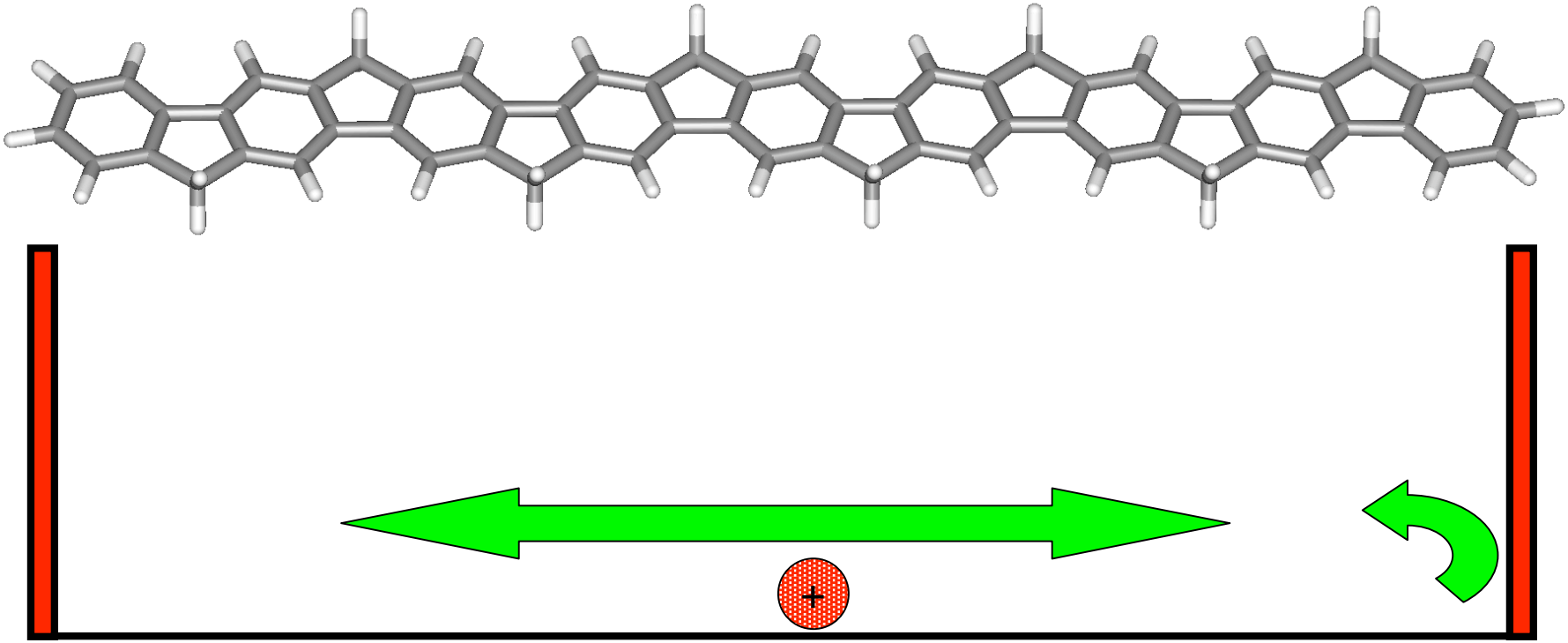
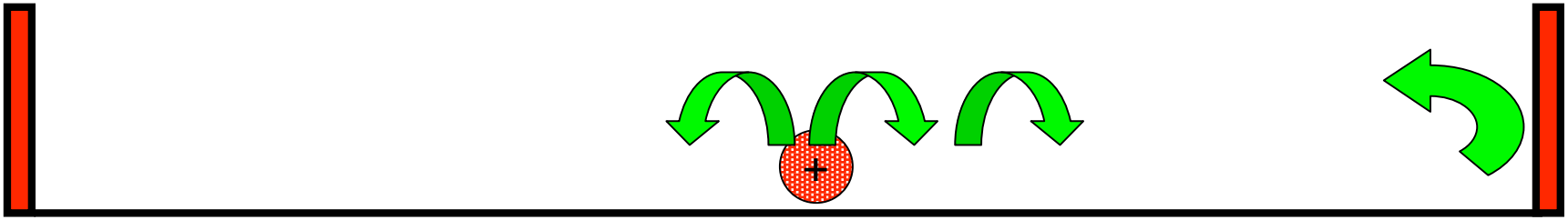
Charge motion hindered by chain ends



Charge moves between reflecting chain ends

What is intra-chain mobility?



Intra-chain diffusion $x^2(\delta t) = 2\boldsymbol{D}\delta t$

Effect of reflecting chain-ends affects $x^2(t)$

Intra-chain mobility $\mu_{\text{intra}} = \dfrac{e}{k_B T}\boldsymbol{D}$