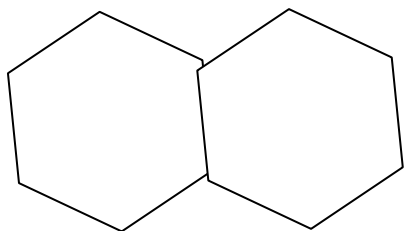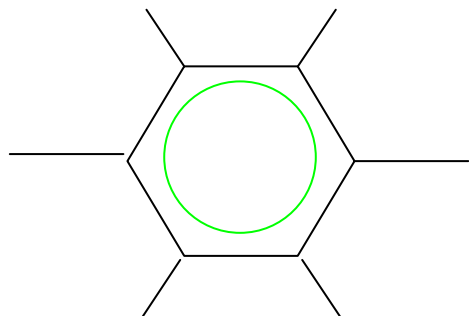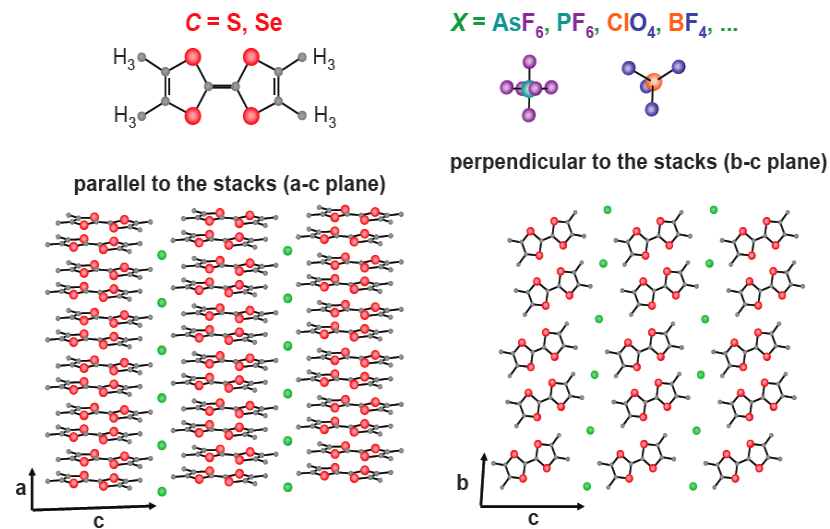# Optics of conducting polymers.

N. Kirova

LPS, Université Paris-Sud, 91405 Orsay, France

Molecular crystal

C = S, Se

X = AsF$_6$, PF$_6$, ClO$_4$, BF$_4$, ...

H$_3$C ... O ... O ... CH$_3$
H$_3$C ... O ... O ... CH$_3$

parallel to the stacks (a-c plane)

perpendicular to the stacks (b-c plane)
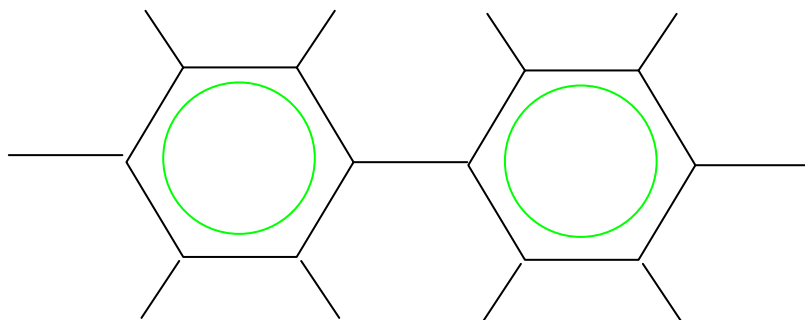
Organic crystal

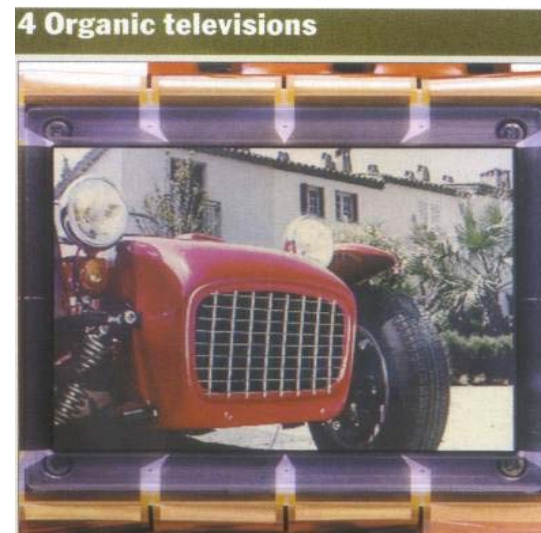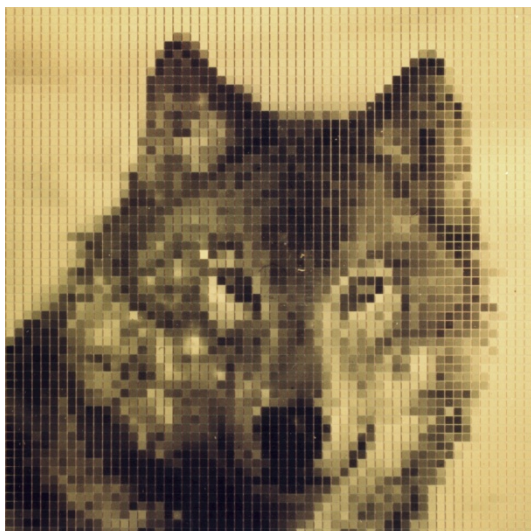**Polymer**

?

2

Conducting polymers: today's applications

LED display and microelectronic chip made by Phillips Research Lab

Tsukuba, LED TV.

Devices produced by UNIAX, the former company of A. Heeger

Optical pumping:

creation of electron-hole pairs under illumination

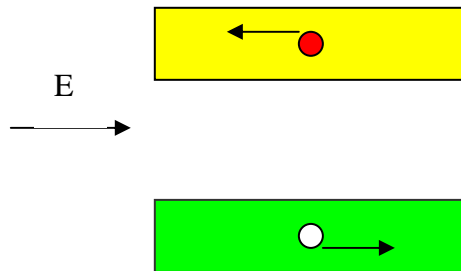Created electrons and holes are either free, or bound

EXCITON : electron-hole pair, bound by long range Coulomb forces
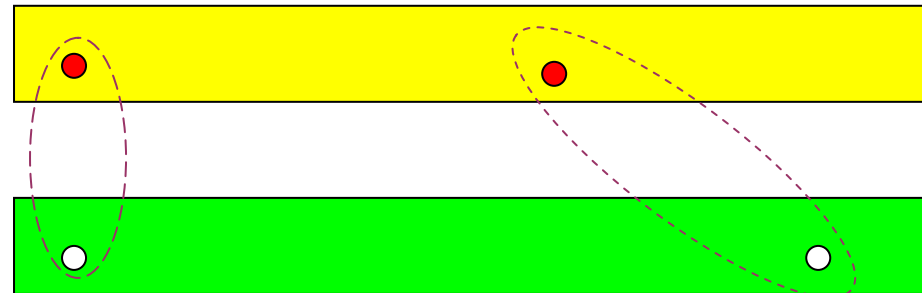Compare – the atom of positronium

Important question – what kind of particles are created:
band electrons and holes, or excitons?

Band electrons and holes give
the photoconductivity

Excitons give the
photolumunescence

E

4

What is the exciton binding energy?

E_b	Experiments
0.1eV or less	Photoconductivity + optics Moses et al
0.1 - 02 eV	Charge injection (Campbell , Pei, Brédas)
0.3 eV -0.4 eV	STM + optics, Bradley et al, electroluminiscence
0.8 - 1 eV 0.25eV - ?	PA (Leng et al , Frolov et al, Vardeny)

Different theoretical approaches:
Computational studies
(Bredas et al,
Mazumdar et al,
Mukamel et al)
vs.
analytical studies
(N.K. et al, Gartstein et al).

Molecular crystal or solid state physics ?
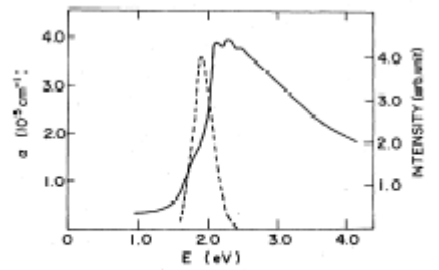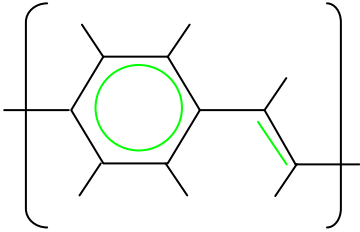
Optical absorption spectra of (CH)x and PPV

FIG. 2. Comparison of the photoluminescence spectrum (- - - -) and the interband absorption spectrum (solid curve) for *cis*-(CH)$_x$.
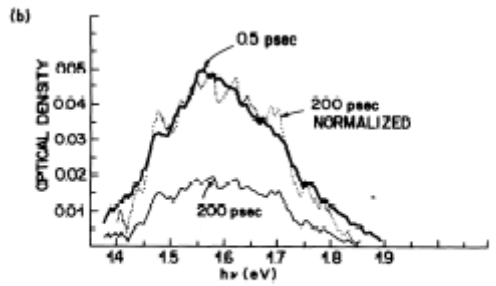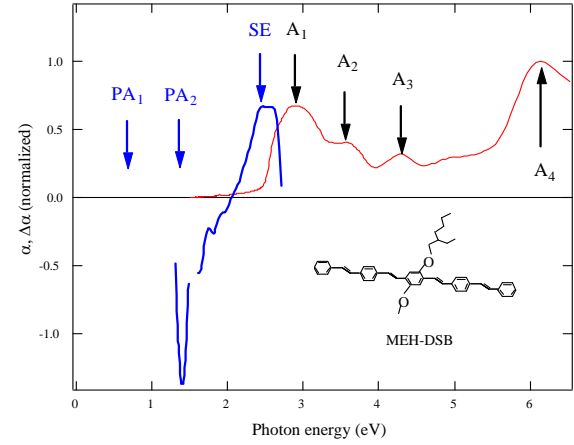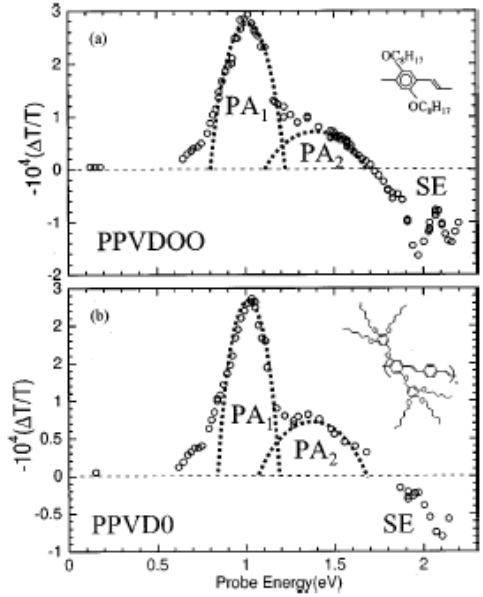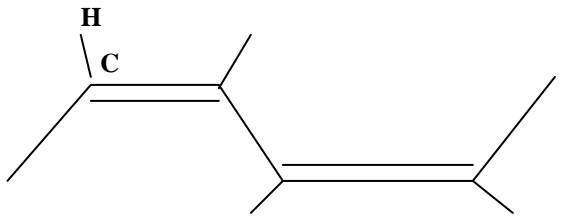

FIG. 1. Photoinduced difference spectra at 0.5 and 200 psec (a) for *trans*-polyacetylene and (b) for *cis*-polyacetylene, excited at 2.0 eV.

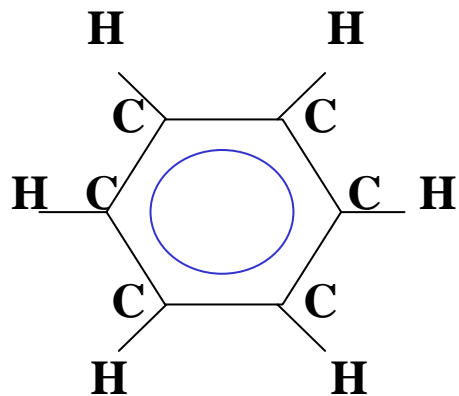**A.J.Heeger, 1982**

MEH-DSB

D. McBranch

Z.V.Vardeny

6

H   H
C   C
H C   C H
C   C
H   H

2T
T
0
-T
-2T
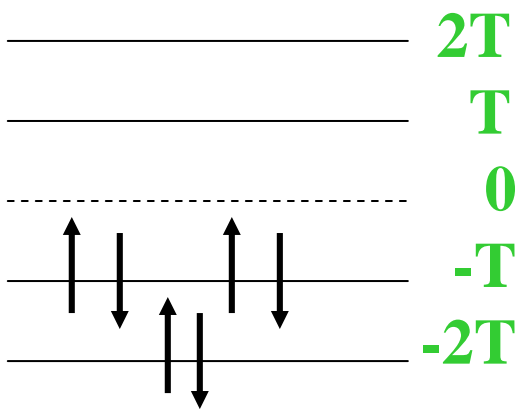
$$E = -2T : \varphi_{-2T}(l) = \frac{1}{\sqrt{6}} \qquad E = 2T : \varphi_{2T}(l) = \frac{(-1)^l}{\sqrt{6}}$$

$$E = -T : \quad g_l = \frac{1}{\sqrt{3}} \cos\frac{\pi l}{3}; \qquad u_l = \frac{1}{\sqrt{3}} \sin\frac{\pi l}{3}$$

$$E = T : \quad g_l^* = -\frac{1}{\sqrt{3}} \cos\frac{2\pi l}{3}; \qquad u_l^* = \frac{1}{\sqrt{3}} \sin\frac{2\pi l}{3}$$

Two types of wave functions with respect to x axis:

+   -   +   +   +   +   +   -
+   **g**   -   - **g*** -   0 **u** 0   0 **u*** 0
+   -   +   +   -   -   -   +

even   **odd**

y
x

7
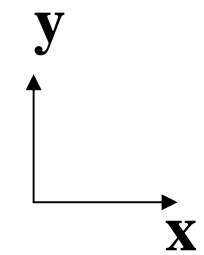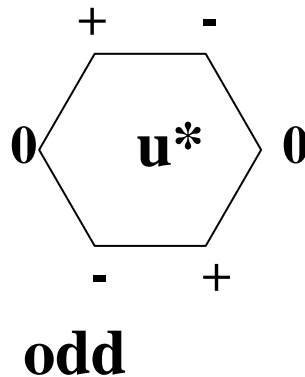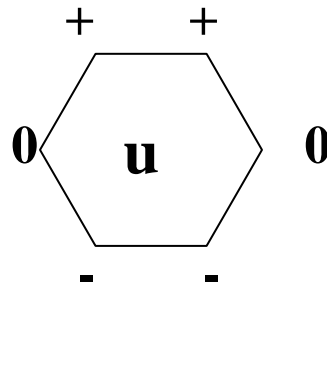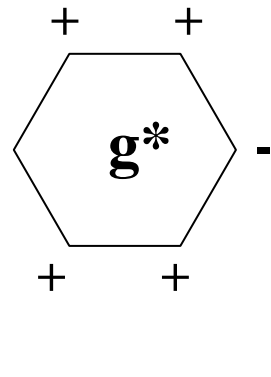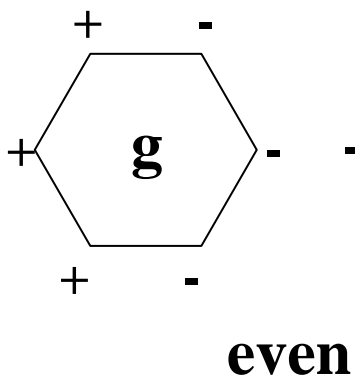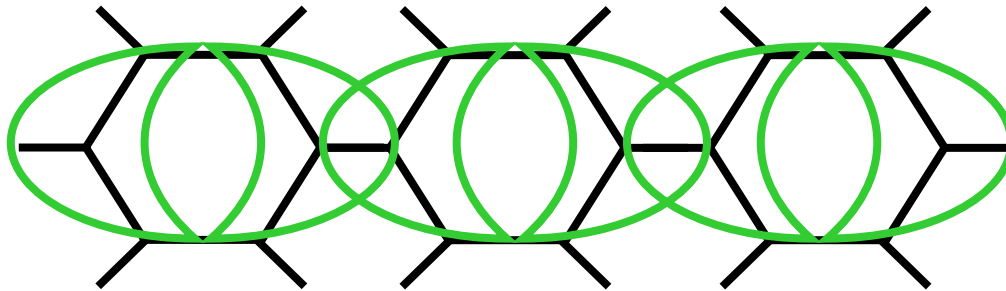
$$g_l = \frac{1}{\sqrt{3}} \cos \frac{\pi l}{3}$$

Even wave functions –
overlap,
traditional dispersive band

$$\mathbf{g} \Rightarrow \mathbf{D}$$
$$\mathbf{g^*} \Rightarrow \mathbf{D^*}$$

$$u_l = \frac{1}{\sqrt{3}} \sin \frac{\pi l}{3}$$
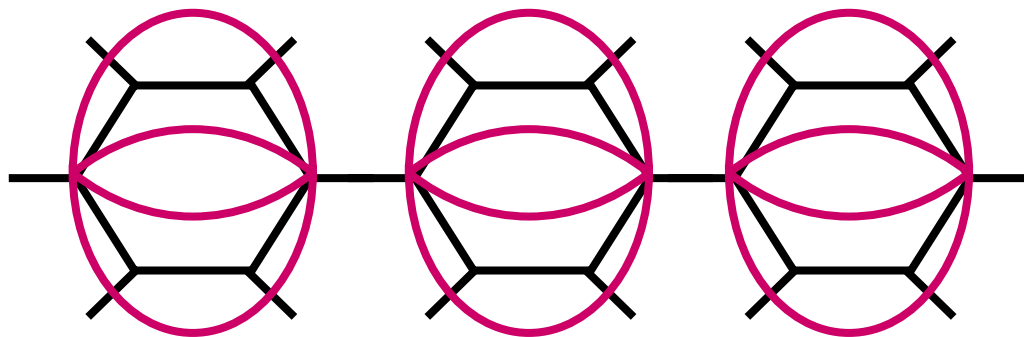
Odd wave functions –
no overlap,
nondispersive flat band

$$\mathbf{u} \Rightarrow \mathbf{L}$$
$$\mathbf{u^*} \Rightarrow \mathbf{L^*}$$

8

Band structure and possible excitons:
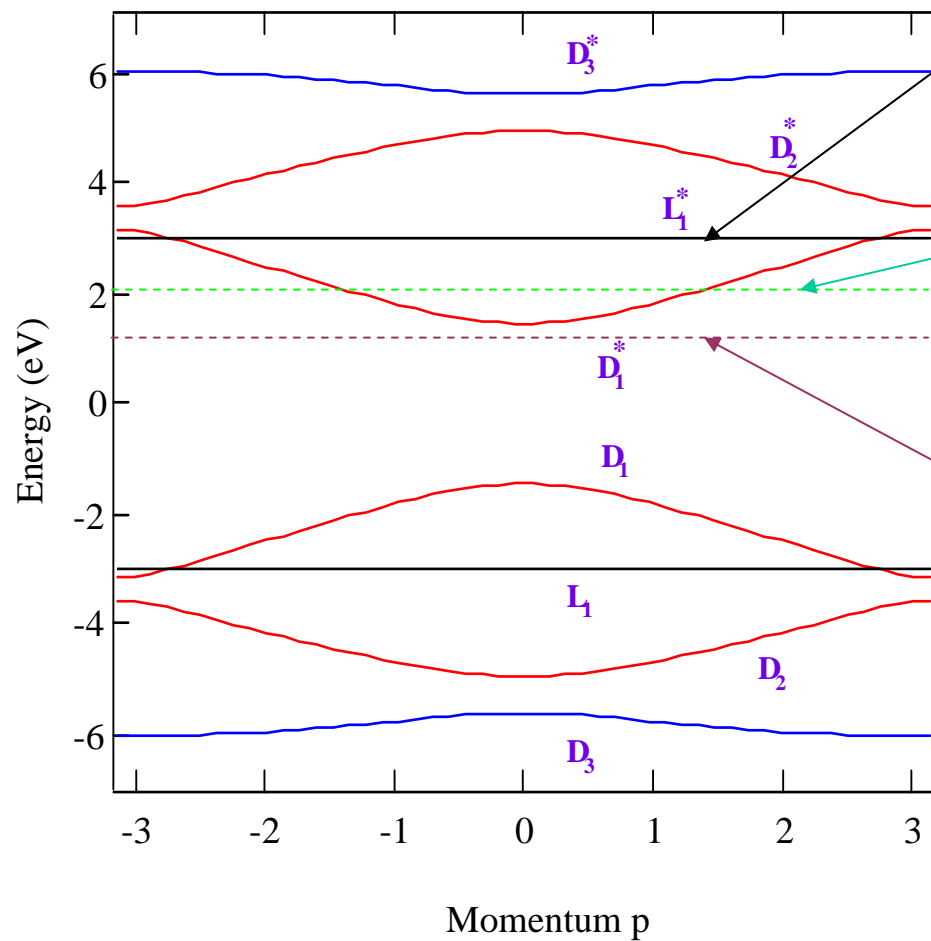
immobile electron + immobile hole
LL* exciton –
the ghost of benzene ring

mobile electron + immobile hole
and vice versa:
DL*±LD* exciton

mobile electron + mobile hole:
DD* exciton

Energy (eV) vs Momentum p

Band labels: D_3^*, D_2^*, L_1^*, D_1^*, D_1, L_1, D_2, D_3

T   t   T*

9

$\Delta p \Delta x \sim \hbar$ W - band width

E

k
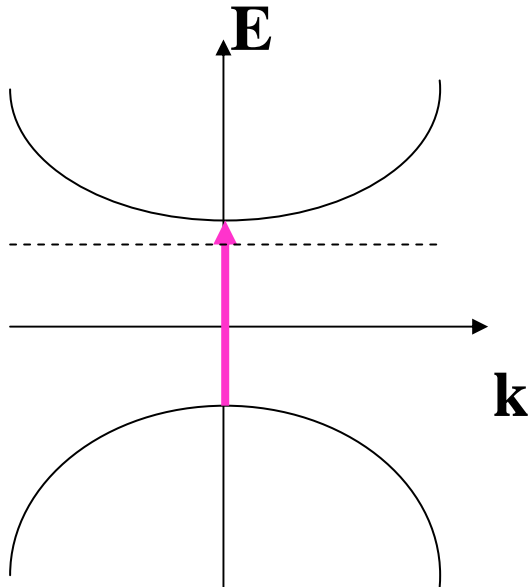
Wannier-Mott exciton: large bands W small energy $E_b << E_g$ large R - basis of the states near the band edge. Kohn-Luttinger effective mass approach. $\Delta E << W$

$$-E_b = -\left\langle \frac{e^2}{\varepsilon |x|} \right\rangle + \frac{p^2}{2m} \qquad \Longrightarrow \qquad -E_b = -\frac{e^2}{\varepsilon R} \ln \frac{R}{a} + \frac{\hbar^2}{2mR^2}$$

$$E_b = \frac{m*e^4}{2\hbar^2 \varepsilon^2} \ln^2 \frac{R}{a} \qquad\qquad R = \frac{\hbar^2 \varepsilon}{m*e^2} \ln^{-1} \frac{R}{a}$$
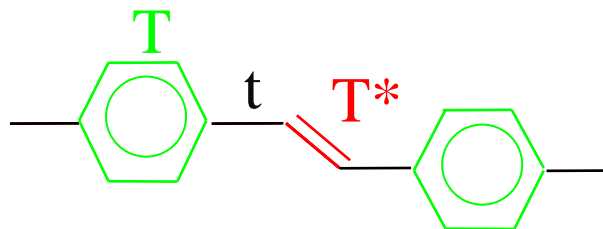
Ln^2 – factor : "capacitance" of elongated cigar of charges

Frenkel exciton:
narrow bands, $E_b \sim E_g$
we need the states from
the whole band W,
small R

electron   hole

10

Visualization of exciton by electric field (field induced exciton dissociation)
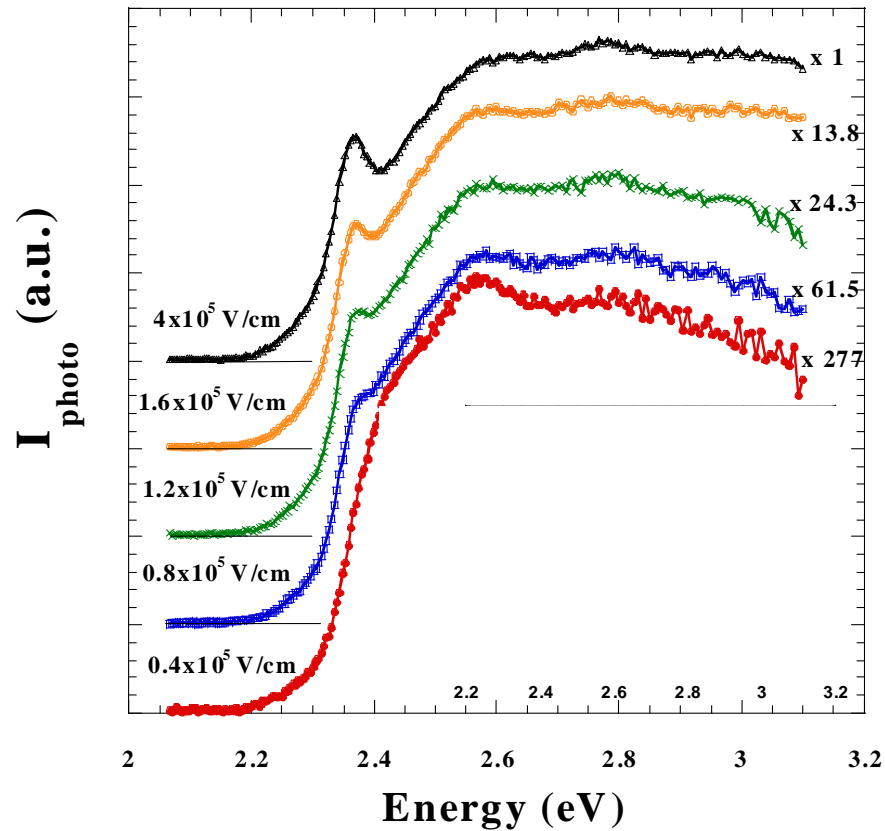
$$\Gamma = \frac{E_b}{\hbar} \exp\left(-\frac{4}{3} \frac{E_b^{3/2} m^{*1/2}}{e\hbar F} \right)$$

D. Moses, A.J. Heeger,
S.Brazovskii, N.Kirova, 2000

11
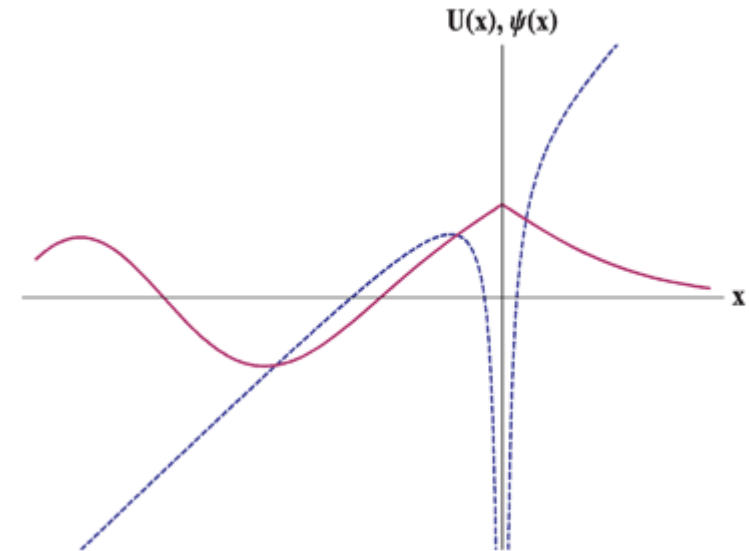
Mystery of triplet excitons and some unresolved questions

• The reduction of benzene ring scales ≈5-6 eV of transition energies to the level of ≈2-3 eV in the polymer is the effect of electronic delocalization.

• The common attempts to build a strongly localized exciton to gain the Coulomb attraction oppositely face the losses of the kinetic energy and push the exciton energy upwards the high intra-molecular values, 4.8eV for S and 3.6eV for T exciton.

But:

• Too small energy of the exciton

• A drastic discrepancy between the low binding energy of S exciton in compare to the strong S - T splitting. Within the usual theory of shallow excitons they are of the same order.

• The origin of the *1/N* dependence of E_{ex} in oligomers (n is the number of monomer units)

• The origin of A_g–B_u exciton level crossing in nonluminescent polymers

Benzene ring, optical transitions

In reality

Without Coulomb correlations

gg*-uu*
gu*+ug* — 6.76 eV

T
0   **4.8 eV**
-T

gg*+uu* — 5.96 eV

gu*-ug* — 4.71 eV

T
0
-T
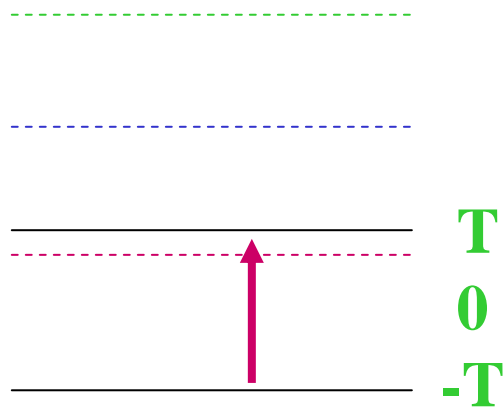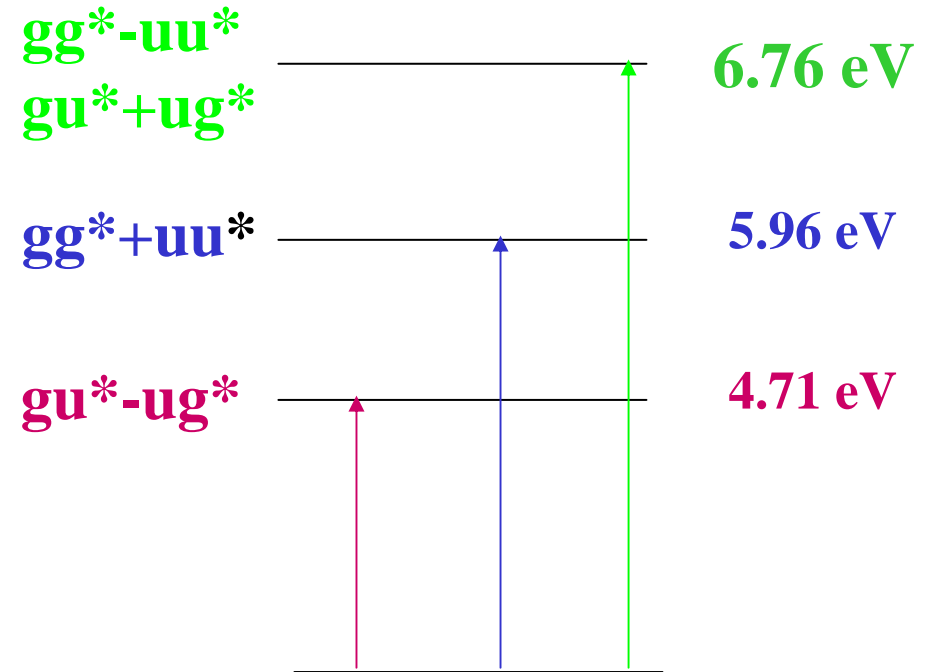
Exciton energy is higher then the energy of free e+h on the molecule,
e-h binding energy is positive effective on-site e-h repulsion! [13]

Electronic correlations

$$\left(\frac{\hat{p}^2}{2m^*} - \frac{e^2}{\varepsilon |x|} + U(x) \right) \psi = -i\hbar \frac{\partial \psi}{\partial t}$$

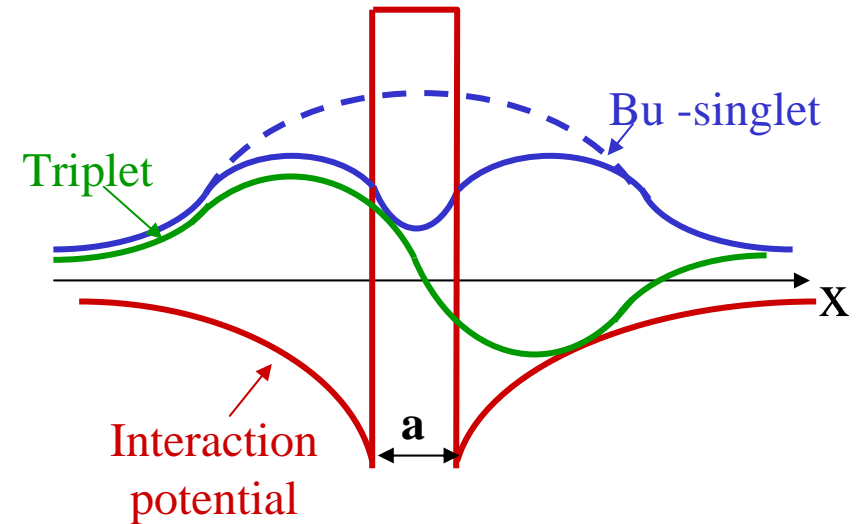Bu -singlet

Triplet

Interaction potential

a

X

Exciton energy

$$E_b = E_0 \left(2 Ln \frac{R}{a} - \frac{a}{a_B} \varepsilon \frac{U_0}{E_0} \right)^2$$

Exciton radius

$$\frac{a_B}{R_{ex}} = \frac{m^*}{m_e} \frac{2}{\varepsilon} \left(Log \frac{R_{ex}}{a} - \frac{a}{a_B} \frac{U_{S,T}}{4E_0} \right)$$

U_0 depends on overlap between quantum states of free band particles (*e,h*) and exact correlated intra-molecular states. It differs for various excitons.

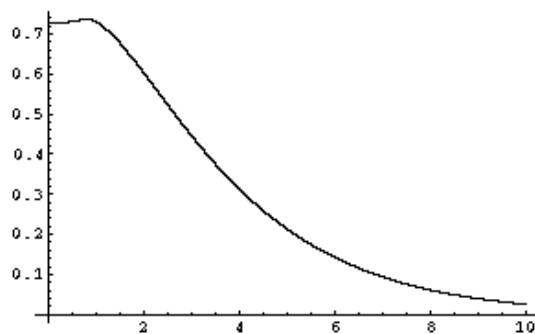**U_S-U_T** - effective exchange interaction

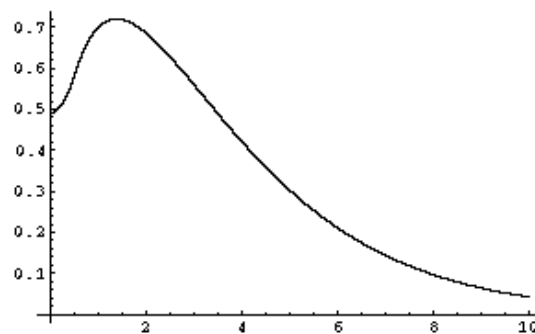**INTYRA-MONOMER COULOMB REPULSION**
The exciton binding energy goes down!!!
Correlations result in lightly bound excitons!

14

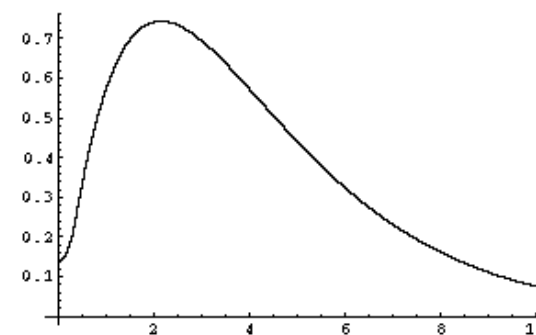**Exciton wave functions for various intra-monomer repulsion potential**

$\varepsilon=2.5$

U=0

U=1eV

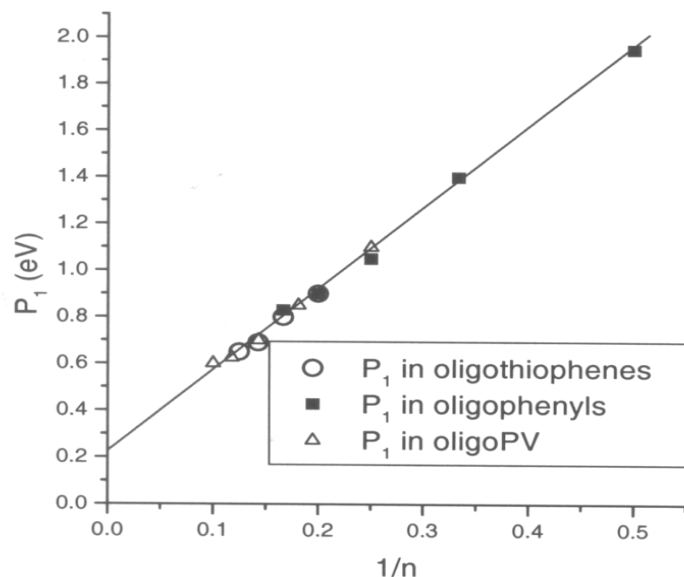**U=4eV**

1/N dependence for triplet/singlet excitons

FIG. 3. The peak photon energy of low energy polaron transition, P_1 in singly oxidized oligomers as a function of the inverse conjugation length (CL). The number n denotes a CL that corresponds to an oligothiophene with n rings. The data for the different oligomer classes were taken from [20]. The line through the data points is a linear fit.

Figure 3. Comparison between the evolutions of INDO/MRD-CI triplet-triplet vertical energies calculated for the cyano-PPV oligomers (circles, solid line) and the unsubstituted PPV oligomers (triangles, dashed line) with respect to the inverse chain length, 1/m.

J. Cornil, D. Beljonne, J.-L.Bredas, J. Chem. Phys., 103 (1995) 842

M. Wohlgenant, X. M. Jiang V.Vardeny, cond-mat/0112488, 2001.

difference between polaron pair recombination with parallel or antiparallel spins. However the apparent linear dependence of r^{-1} on 1/n remains a mystery.
In summary we have measured the formation cross-

$$W = \sum_{n=1}^{N} \left| \psi_e(x_1) \right|^2 U_0(x_1 - x_2) \left| \psi_h(x_2) \right|^2 = \sum_{n=1}^{N} \frac{1}{N} U_0 \frac{1}{N}$$

$$\boxed{W = \frac{U_0}{N}}$$

Rem.: particle in the box, size quantization

$$W \propto \frac{1}{N^2}$$

What is the exciton binding energy?

E_b	Experiments
0.1eV or less	Photoconductivity + optics Moses et al
0.1 - 02 eV	Charge injection (Campbell , Pei, Brédas)
0.3 eV -0.4 eV	STM + optics, Bradley et al, electroluminiscence
~~0.8 - 1 eV~~ 0.25eV - ?	PA (Leng et al , Frolov et al, Vardeny)

Excitons: effects of the dielectric susceptibility

$$E_b = \frac{\mu e^4}{\varepsilon_\perp^2 \hbar^2} \left(\log \frac{R}{a} - \varepsilon_\perp \frac{a}{a_B} \frac{U_0}{2E_{Ry}} \right)^2$$

**Intrachain exciton,
a - the monomer unit size**

$$E_{CT} = \frac{\mu e^4}{\varepsilon_\perp \varepsilon_\parallel \hbar^2} \left(\log \frac{R_{CT}}{d} \right)^2 \qquad R_{CT} = R^* \frac{1}{\ln(R_{CT}/d)}$$

**Interchain (CT) exciton,
d – the interchain distance**

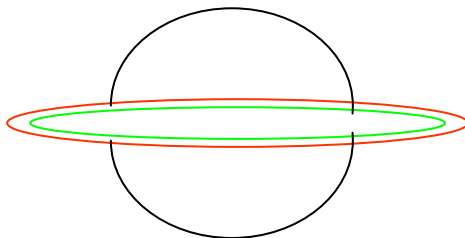$$E_n = \frac{m^* e^4}{2\hbar^2 \varepsilon^2 n^2}$$

Higher excitonic series

$$\boxed{\varepsilon \text{ is } \varepsilon_\perp}$$

Chains on the surface:

$$E_{Bu} = \frac{2m^* e^4}{\hbar^2 \varepsilon^2} \left(\ln \frac{R}{b} \right)^2 \quad \overset{\varepsilon=1}{\boxed{\varepsilon}}$$

$$\varepsilon_{eff} = \frac{\varepsilon}{2} \qquad E_{ex} \Rightarrow 4E_{ex}$$

Isolated chains

(chain loops, gaz bubbles)

$$\varepsilon_{eff} = 1 \qquad E_{ex} \Rightarrow \varepsilon^2 E_{ex}$$

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Inter-chain exciton

EL: 2.65

Steady state photo- and electroluminiscence :
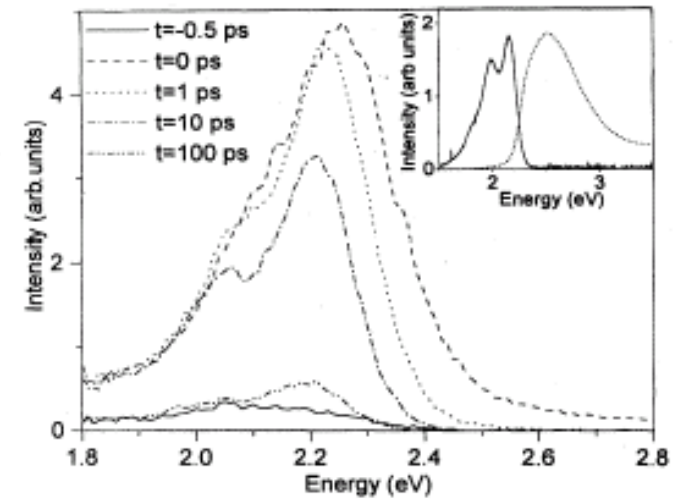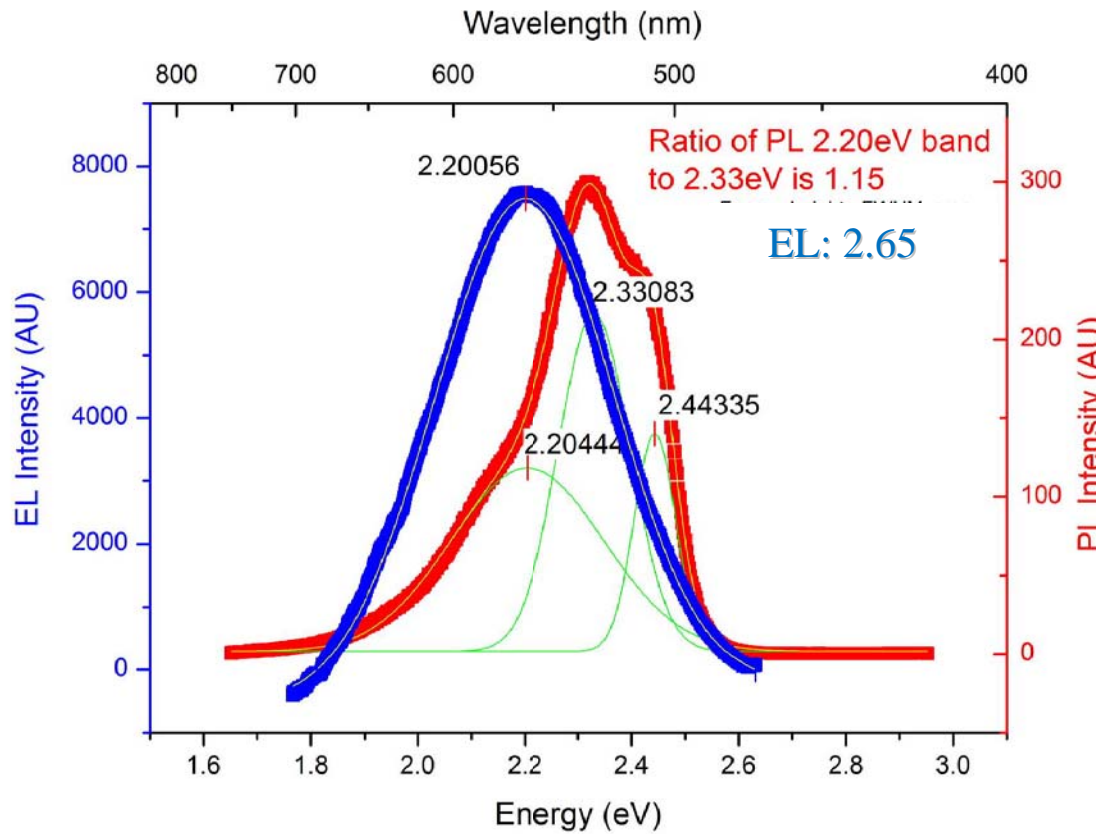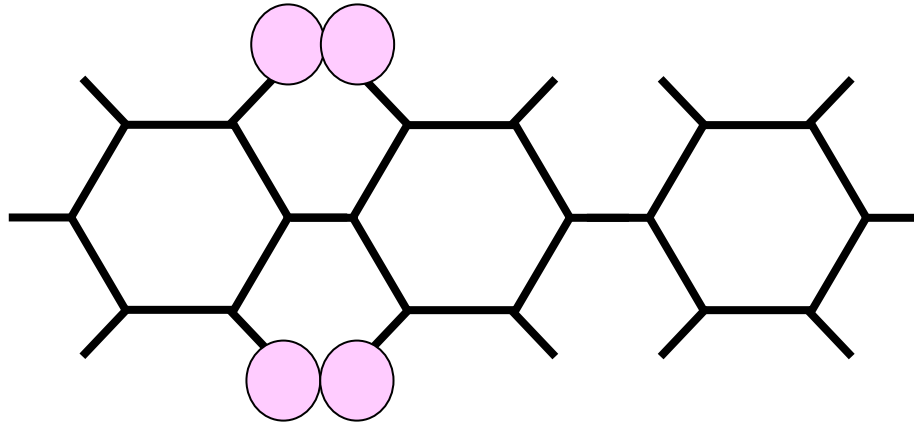D.Lee, Trinity college, Dublin, 2010

FIG. 1. Time-resolved photoluminescence spectra of MEH-PPV after excitation with 200 fs pulses at 3.06 eV. Inset: Solid and dashed lines are the cw emission and absorption of MEH-PPV at room temperature.
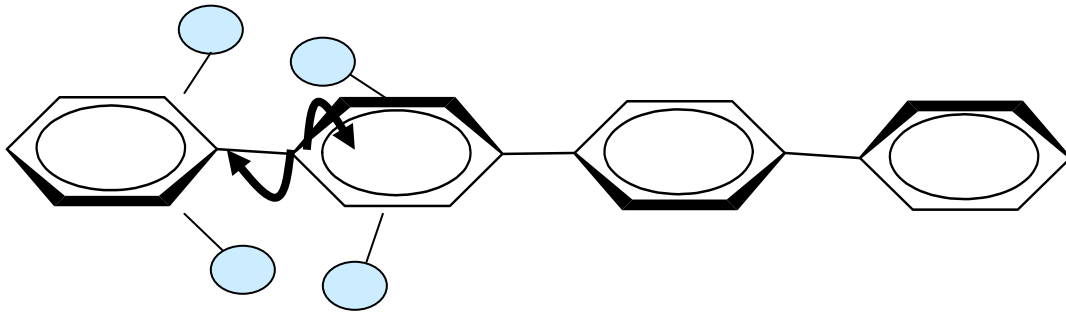
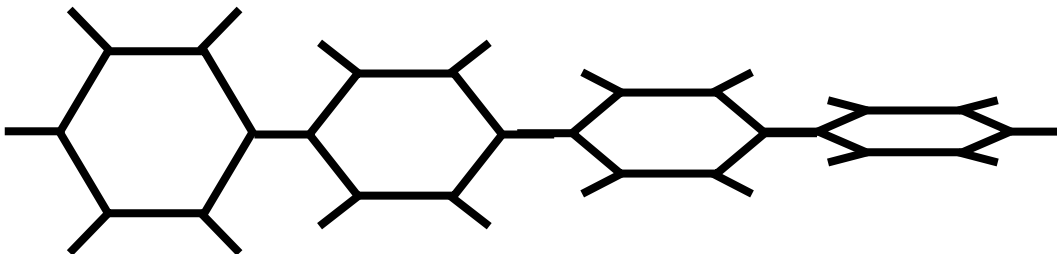Hayes et al, PRB, 52 (1995) 11569
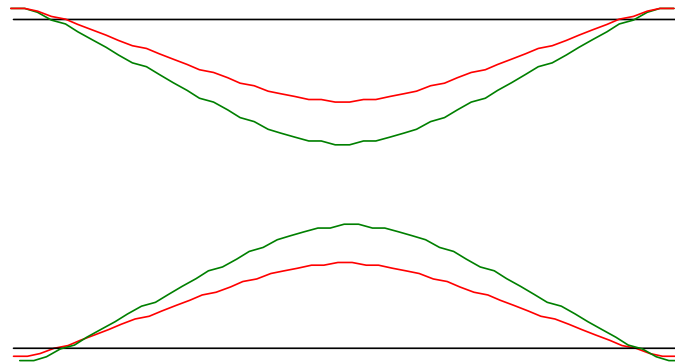
19

Polaronic effects - lattice relaxation

Band gap can be tuned by changing the mutual orientation of the phenyl rings (we change the band dispersion)

PPV: $\varphi \approx 20^o$ Eg ≈ 2.4 e V
PPP: $\varphi \approx 30^o$ Eg ≈ 3.2 e V

Polaronic effects, electronic excitations

The process of the exciton relaxation can be seen in femtosecond optics - red shift of the luminescence during the first 50 ps.

Relaxed exciton has lower energy with respect to created pure Coulomb exciton for about 0.1-0.2 eV
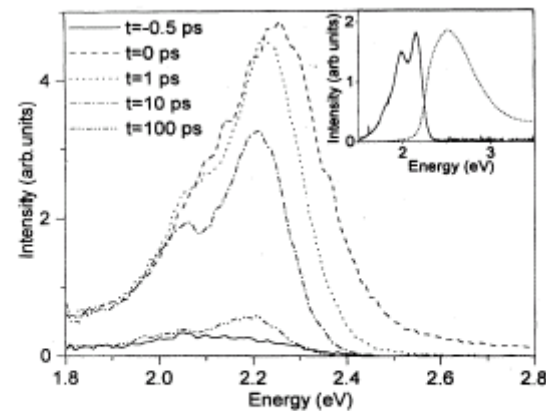

FIG. 1. Time-resolved photoluminescence spectra of MEH-PPV after excitation with 200 fs pulses at 3.06 eV. Inset: Solid and dashed lines are the cw emission and absorption of MEH-PPV at room temperature.
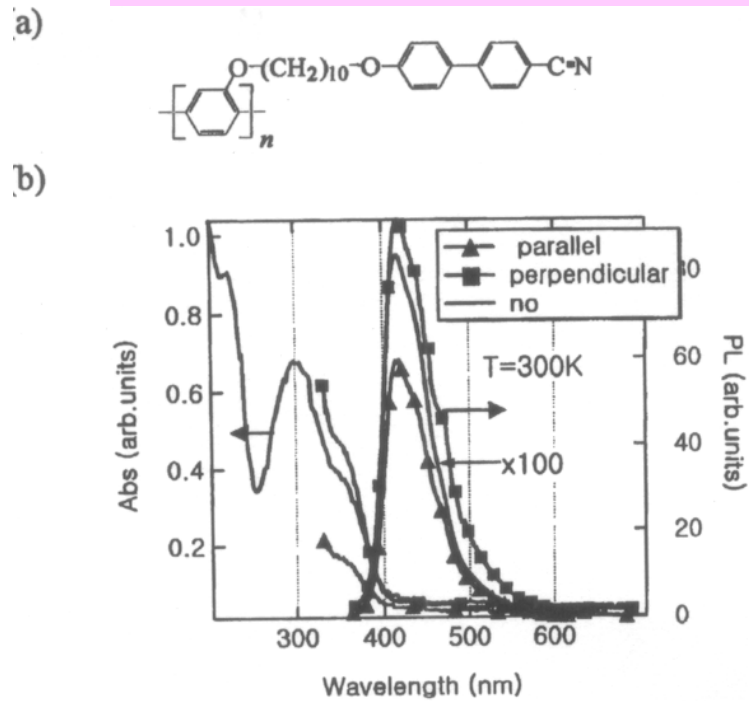
EXCITON LEVEL CROSSING ?

Fig. 1. LC-PPP (a) Molecular structure (b) Polarized absorption and PL.
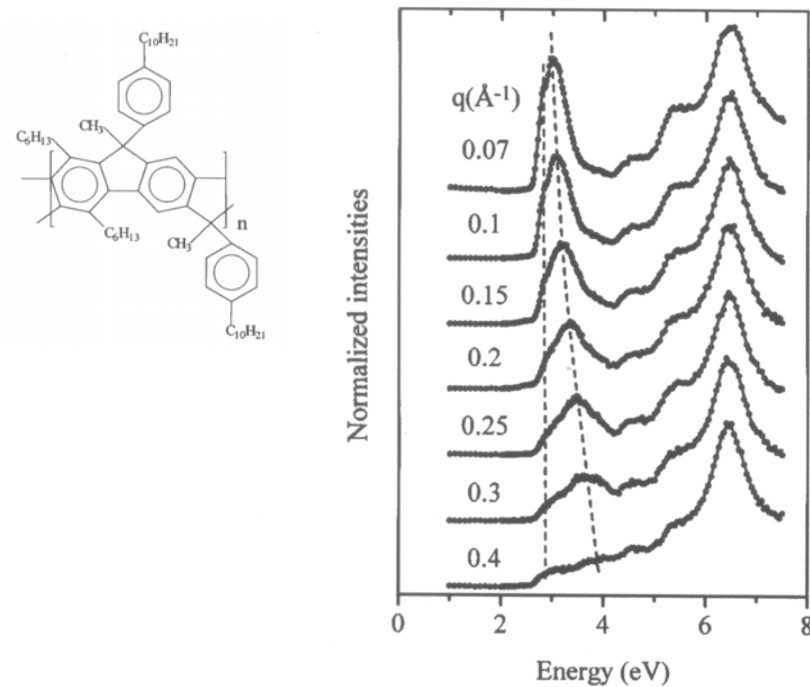
J.H.Park et al,

FIG. 3. Loss function, $Im(-1/\epsilon)$, of mLPPP as a function of the momentum transfer q.

Localized and delocalized singlet excitons….
M. Knupfer et al

Other indirect evidences (for ladder type PPP):
➤ two relaxation times of photoconductivity carriers (Leising et al)
➤ Anti resonance at 0.2 eV in photo-induced absorption (Vardeny et al).
➤ The same peak positions in photo-induced and doping induced absorption

What is the exciton energy ?

Wannier-Mott shallow exciton ($m^* \sim 0.1\, m_e$), with binding energy:

$E_b = 13.6$ eV $(m^*/m_e)(1/\varepsilon^2)S^2 + W_{rel}$

W_{rel} - lattice relaxation energy (typically 0.1 – 0.2 eV)

$\varepsilon = \varepsilon_\perp$, $S = \ln(Rex/a) - U_0$,

U_0 – onsite electron – hole interaction,

Intra-chain exciton in the bulk (PPV)

Eb $\approx 0.1 - 0.2$ eV, relaxed (e.g. PA measurements)

Eb < 0.1eV, non relaxed (PC spectra)

Inter-chain exciton in the bulk

Eb $\approx 0.4 - 0.5$ eV

At the polymer surface:
 increase of the binding energy:

vacuum $\varepsilon = 1$ εeff $= \varepsilon/2$, Eb $\to$ 4Eb

Polymer

Isolated chains (e.g. chain loops, gaz bubbles)

$\varepsilon_{eff} = 1$,   Eb ε^2Eb ≈ 1eV

Practical implementations:
Exciton migration towards low density (hence low ε) regions working as microscopic traps.
This is the only occasion to observe extremely strongly bound excitons (beyond the virtual reality of "configuration interaction")

Conclusion

▪**Delocalization breaks the intraring scheme**

▪**Coexistence of band-like and intra-molecular phenomena due to a particular presence of zero band width carriers, three types of intra-chain excitons**

▪ **Primary intra-chain singlet exciton is strongly affected by electronic correlations.**

▪ **Triplet excitons, relatively deep, are located at energies dictated by the scale of the band theory.**

▪**Interchain exciton is more strongly bound then the intra-chain one**

▪**Band widths are tunable by molecular ring torsions – exciton levels crossing**

•**1/N dependence for oligomers, strong siglet – triplet exciton splitting, B_u-A_g interplay of quantum chemisrty – strong intra-monomer electronic correlations .**

•**Singlet – triplet exciton creation ratio in LED**

•**Exciton migratrion, energy transfer along the chain**

•**Dopants and their effects on the suppression of the luminescence.**

Relations to other systems

- *Low energy triplet excitation* -

  generic feature of the Mott insulator proximity

- *Specific non dispersive electron and exciton* -

  may exist in typical cone sharing compounds (molybdenum oxides)

- *Nonlinear and time resolved optics as challenging tools.*

Luminescent qnd nonluminescent polymers.
Ag - Bu level crossing,

Interaction potential
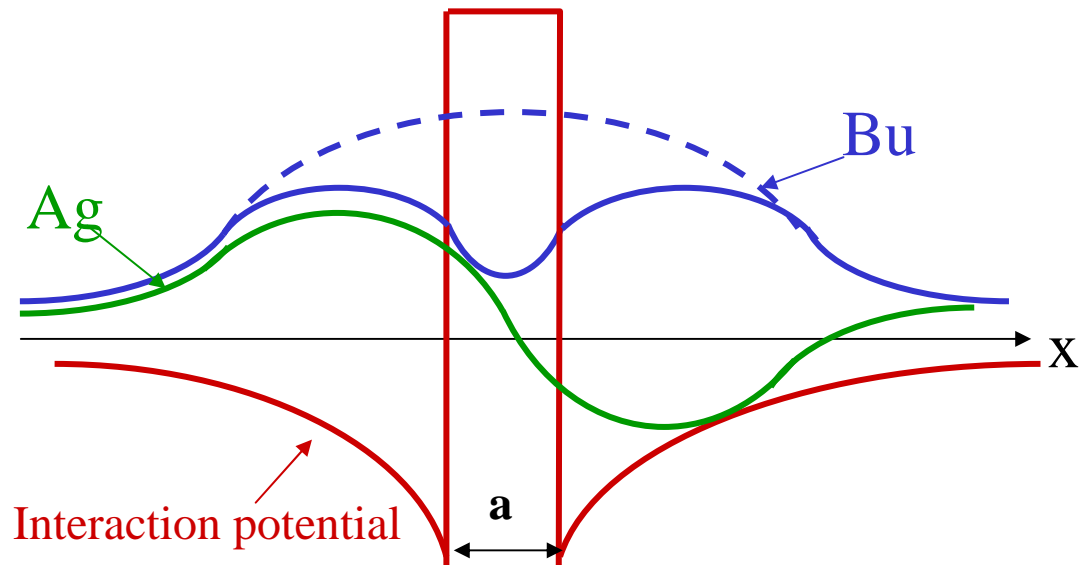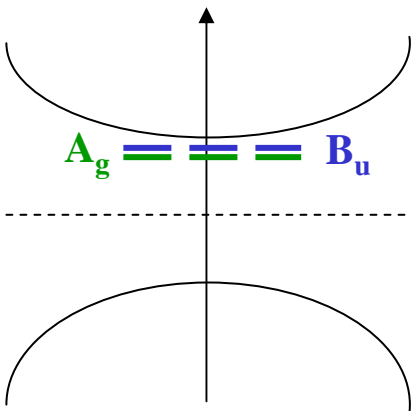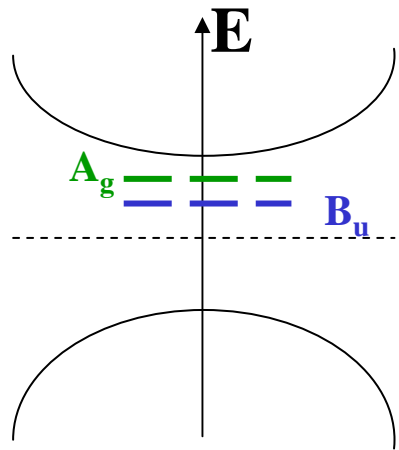
$$R_n = \frac{2n\hbar^2 \varepsilon}{m * e^2}$$

$$E_{Bu} = \frac{m * e^4}{2\hbar^2}\left(\frac{2}{\varepsilon}\ln\frac{R}{a} - \frac{a}{a_B}\frac{U_0}{2E_0}\right)^2$$

$$E_n = \frac{1}{n^2}\frac{m * e^4}{2\hbar^2 \varepsilon^2}$$

$$E_{Ag} = \frac{m * e^4}{2\hbar^2 \varepsilon^2}$$

**Oligomer versus polymer,
size effects in solid state physics.**

•Molecular physics and quantum chemistry domain.

N=1, 2, 3, 4, , 6..

•Solid state physics domain: N=5, , 7,......
•Importance of debated region N=5, 6.
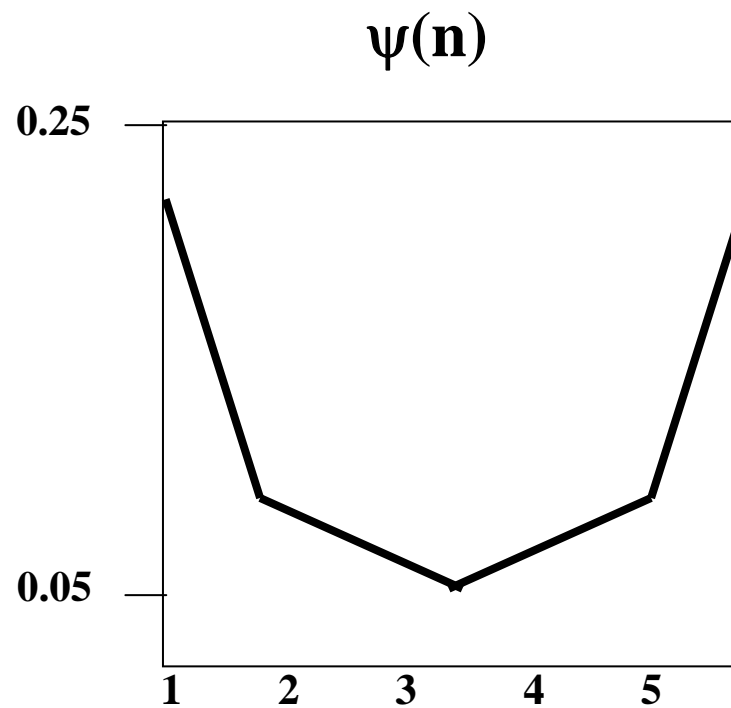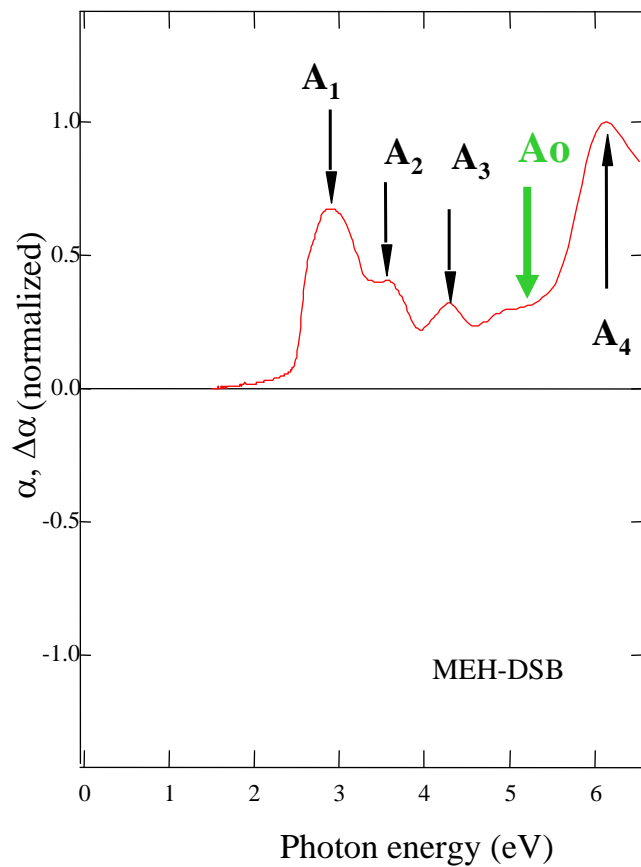•Crossover for method of calculations.
•Importance of soluble oligomers.
•SSPh wise:

  Coulomb continuum
  excitonic bound states
  edge states in oligomers
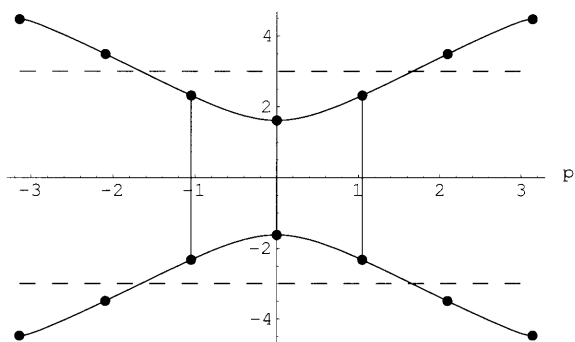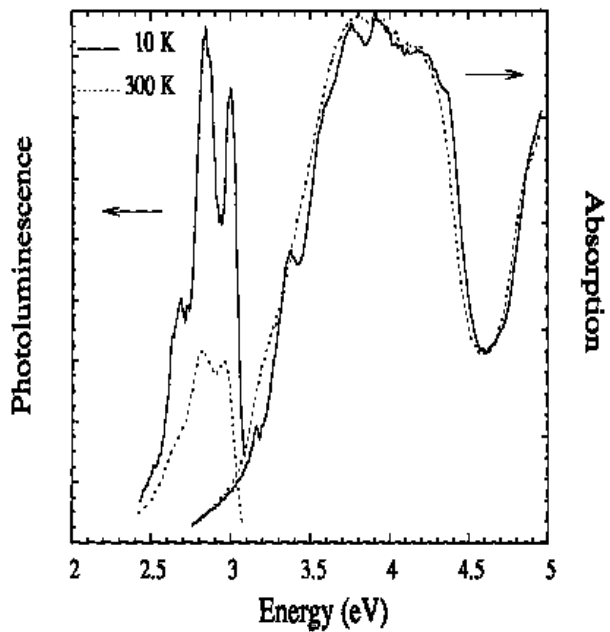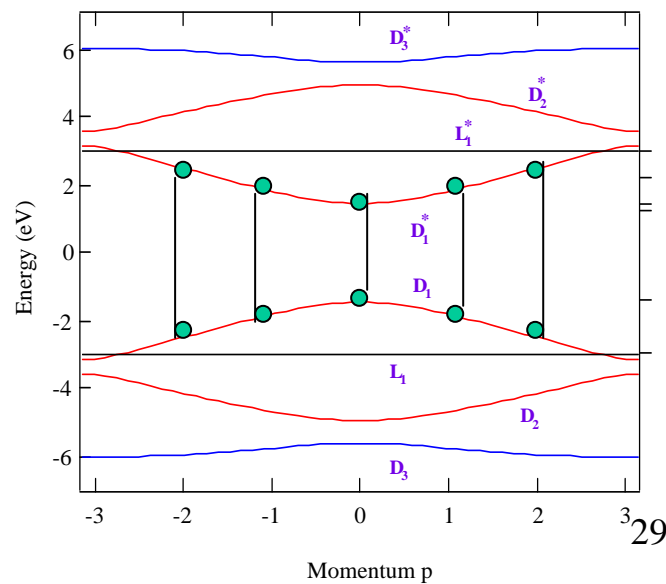
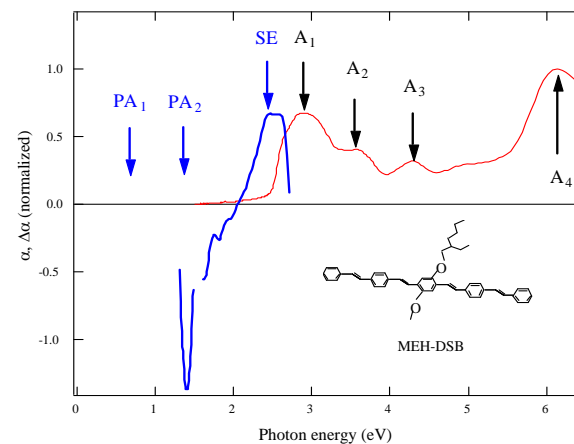# Edge states in PPV-type oligomers.

N.K. et al, 1998

$\psi(n)$

MEH-DSB

McBranch et al, 1997

Five is longer then six, or which oligomer can be considered as a model for polymer

Hexaphenyl

MEH-DSB

Exchange interaction

$$H = H_{kin}(x) + H_{kin}(y) + U(x, y)$$

$$\psi_{S,T}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_{D^*}(x)\psi_D(y) \mp \psi_{D^*}(y)\psi(x)\right]$$

$$\langle H \rangle = E_1 + E_2 + \int dxdy\, U(x-y)\left|\psi_{D^*}(x)\right|^2\left|\psi_D(y)\right|^2$$

$$\mp \int dxdy\, \psi_{D^*}(x)\psi_D(x)U(x-y)\psi_{D^*}(y)\psi_D(y)$$

$$\langle H \rangle_{exch} = \mp \int dx\, dy\, \psi_{D^*}(x)\psi_D(x)U(x-y)\psi_{D^*}(y)\psi_D(y)$$

For the case of exciton

$$\psi_i(x) = \sum_k C_k^v(i)\phi_k^v(x) \quad i = D, D^*$$

$$\phi_k^v(x) = B_0^i(x)e^{ikx}$$

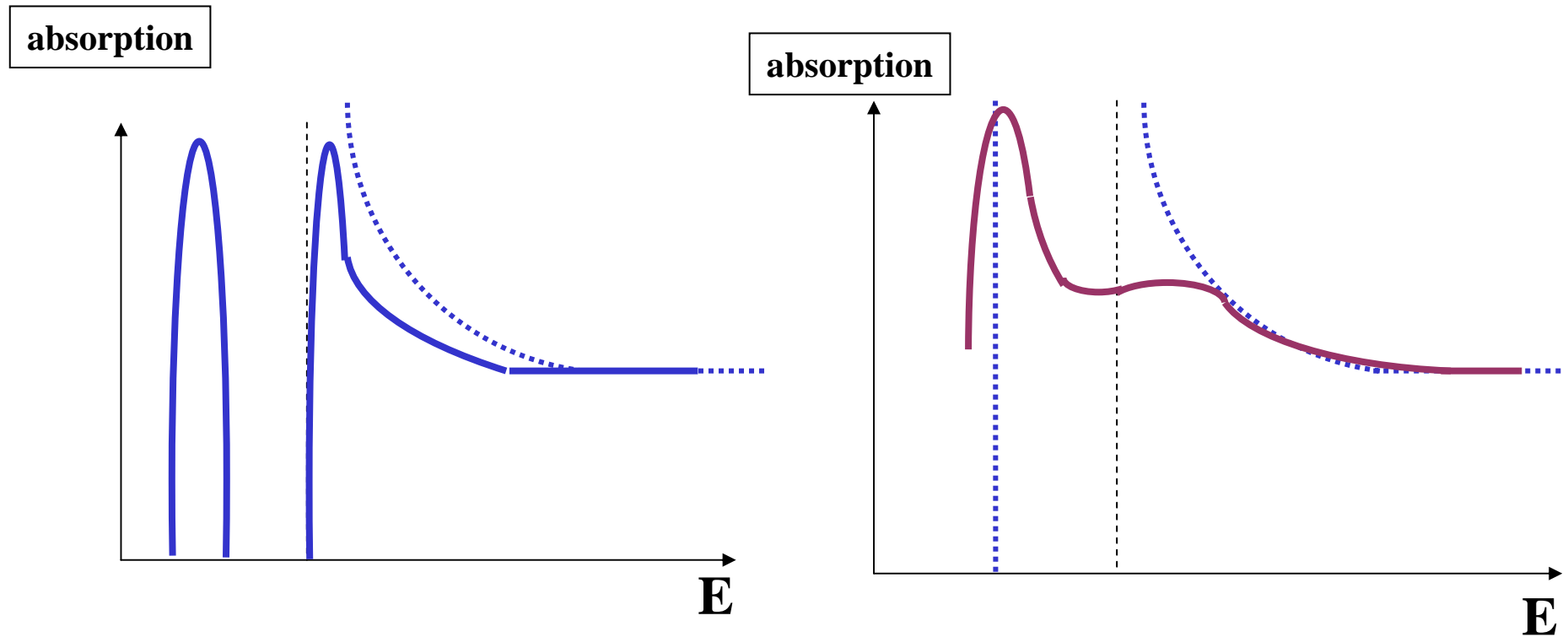$$\psi_i(x) \approx f_i(x)B_0^i(x)$$

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Exchange interaction

$$U(x, y) = -\frac{e^2}{\varepsilon|x - y|};$$

$$H_{\text{int}}(x_1, x_2) = -\frac{e^2}{\varepsilon|x_1 - x_2|}; \quad \psi_{S,T}(x_1, x_2) = \psi_{D^*}(x_1)\psi_D(x_2) \mp \psi_{D^*}(x_2)\psi_D(x_1)$$

$$E_{S,T}^1 = \sum \int \psi_{S,T}^*(x_1) H(x_1 - x_2)\psi_{S,T}(x_2)\, dx_1 dx_2 =$$

$$= -\frac{1}{2}\int \frac{e^2}{\varepsilon|x_1 - x_2|}\left|\psi_{D^*}(x_1)\psi_D(x_2) \pm \psi_{D^*}(x_2)\psi_D(x_1)\right|^2 dx_1 dx_2;$$

$$= -\frac{e^2}{\varepsilon}\int \frac{\left|\psi_{D^*}(x_1)\right|^2 \left|\psi_D(x_2)\right|^2}{|x_1 - x_2|} dx_1 dx_2 \pm \frac{e^2}{\varepsilon}\int \frac{\psi_{D^*}^*(x_1)\psi_D^*(x_2)\psi_{D^*}(x_2)\psi_D(x_1)}{|x_1 - x_2|} dx_1 dx_2$$
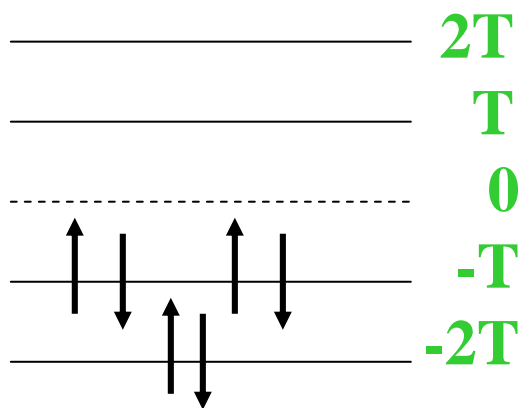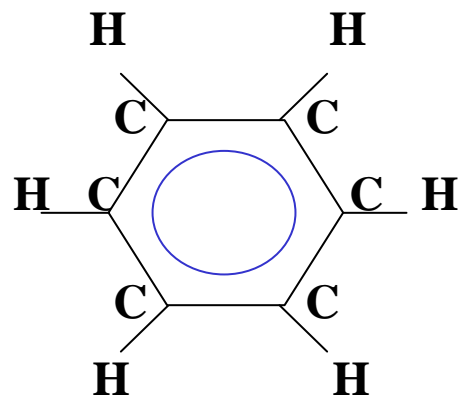
$$\Delta E_{S,T}^1 = 2\frac{e^2}{\varepsilon}\int \frac{\psi_{D^*}^*(x_1)\psi_D^*(x_2)\psi_{D^*}(x_2)\psi_D(x_1)}{|x_1 - x_2|} dx_1 dx_2$$
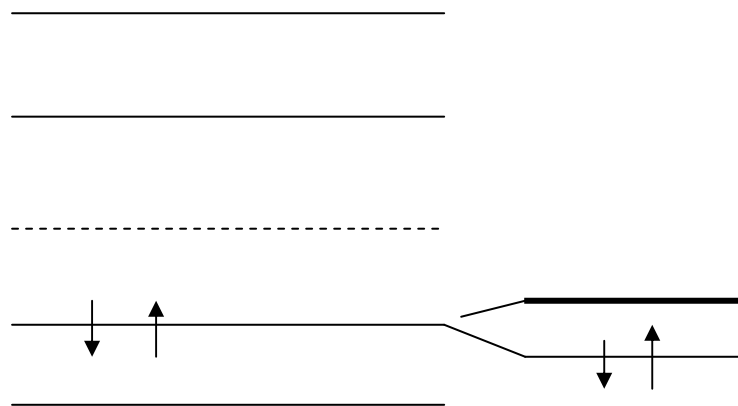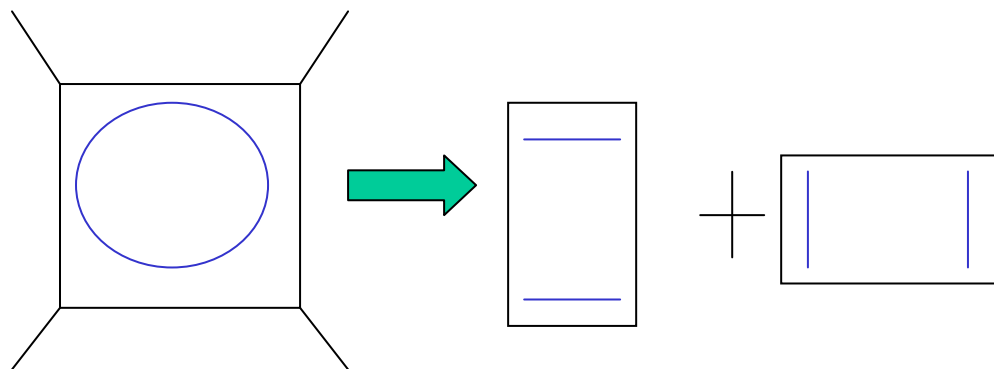
Optical absorption, long rang Coulomb effects

absorption

E

absorption

E

Long range Coulomb interactions
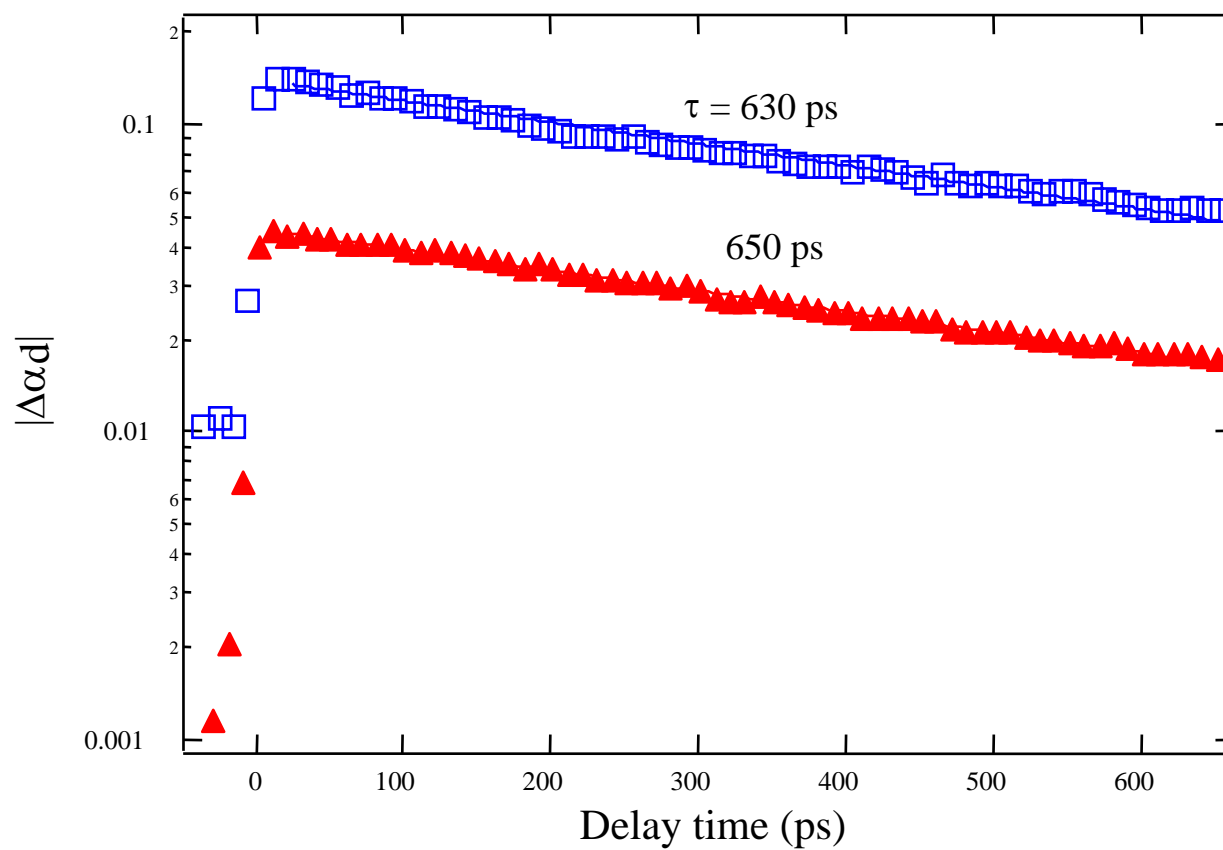
Short range Coulomb interactions

32

$2T$

T

0

$-T$

$-2T$

N=4n+2

Jahn-Teller effect

Dynamics in solution (low intensity excitation):
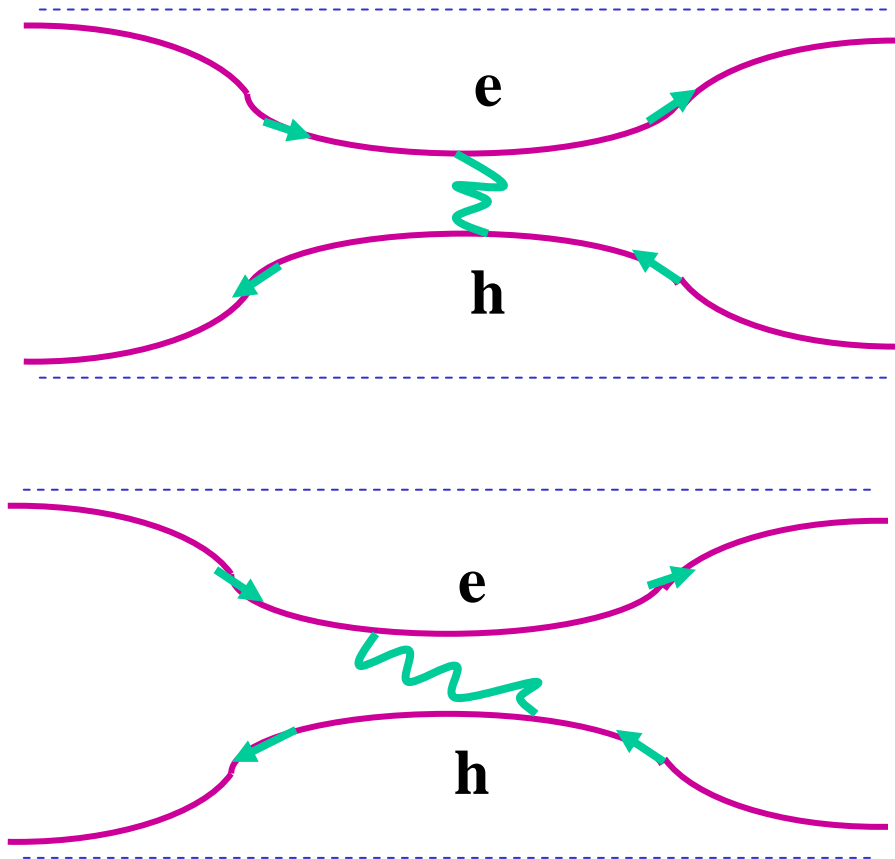
$\tau = 630$ ps

650 ps

SE (2.43 eV)

PA$_2$ (1.46 eV)

McBranch et al,1997

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;;

Suppression of the light emission by the long range Coulomb attraction

Classical intuition: attraction keeps e and h together, thus enhancing their recombination (emission probability)
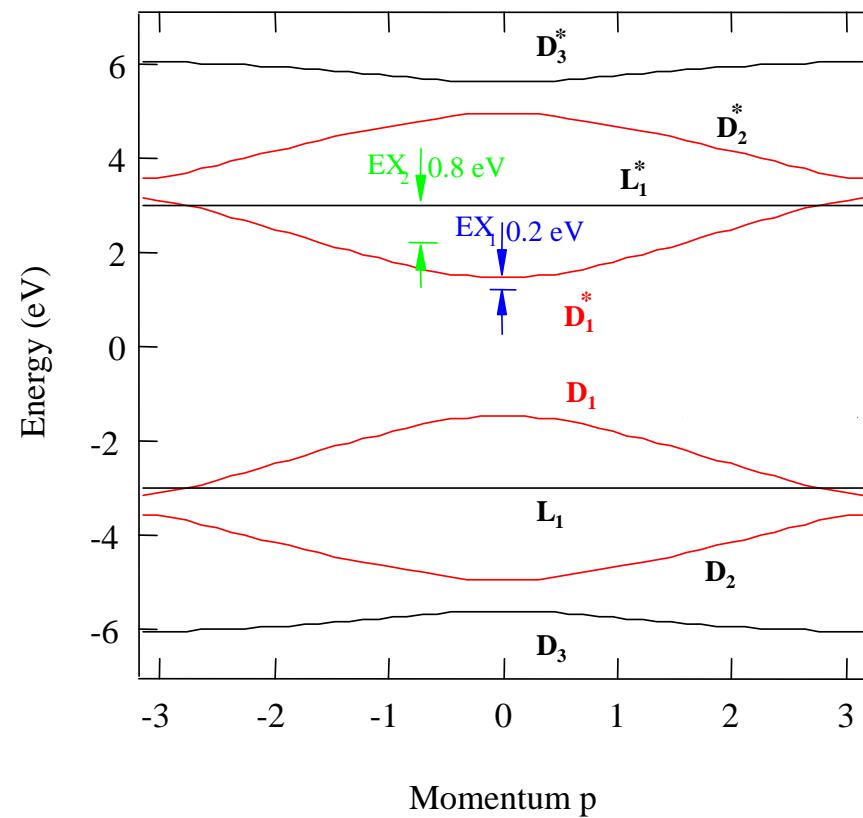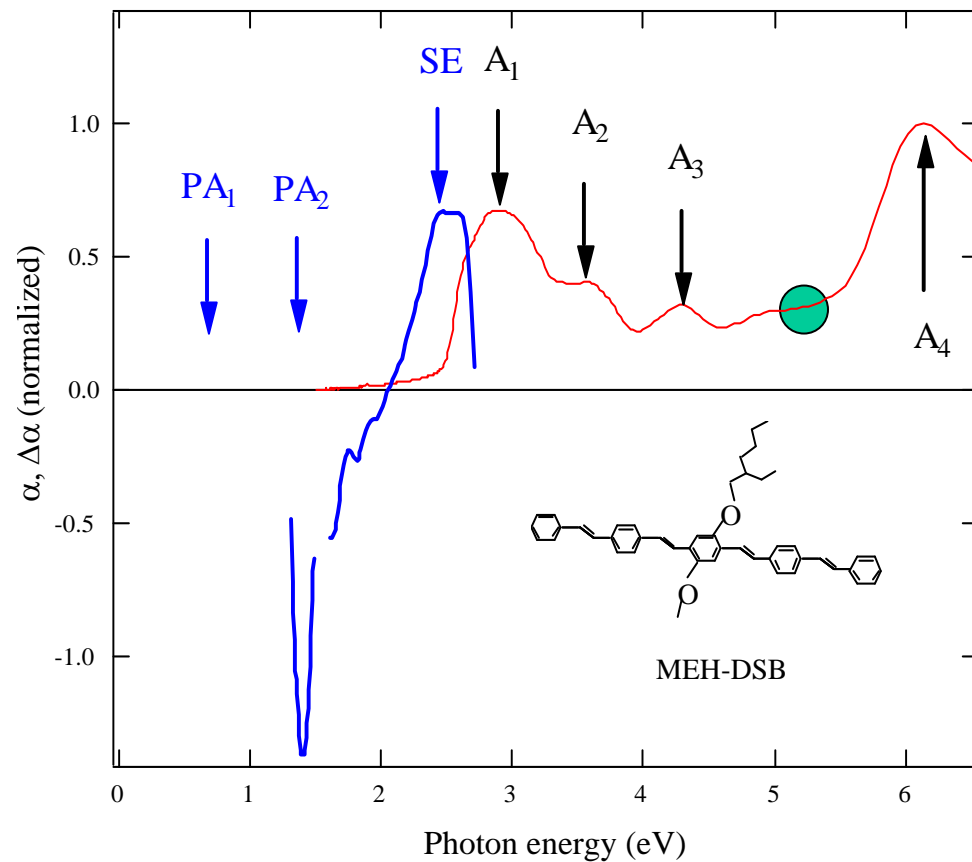
But :

attraction accelerates the zero point velocities and particles pass by without hand shaking

$$\frac{\mu v^2}{2} = E - E_g \qquad \tau_{rec}^0 = \frac{a\sqrt{\mu}}{\sqrt{E - E_g}}$$

$$\frac{\mu v^2}{2} - \frac{e^2}{\varepsilon a} = E - E_g \qquad \tau_{rec} = \frac{a\sqrt{\mu}}{\sqrt{E - E_g + e^2/\varepsilon a}}$$

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Optical transitions and peak assignments for experimental features:

MEH-DSB

McBranch et al, 1997

Overview:

- Light emitting exciton: solid state approach versus molecular physics.
- Band picture and excitons
- Electric field induced ionization of exciton.
- Various types of excitons, possible level crossing
- Mystery of triplet excitons
- Intra-monomer Coulomb correlations.
- 1/L energy dependence for oligomers.
- Polaronic effects.
- Effects of the environment.
- Luminescent and non-luminescent polymers, Ag-Bu level crossing
- Which oligomer becomes the polymer:
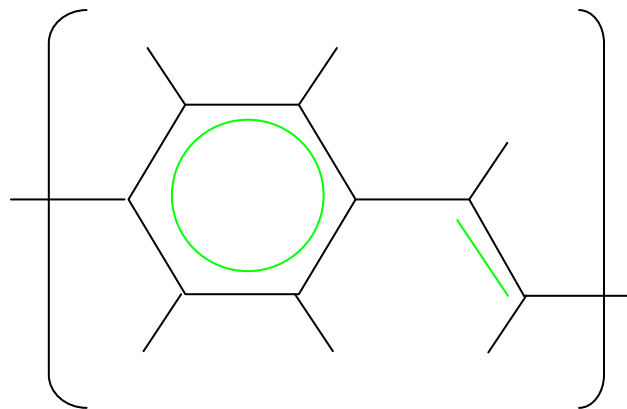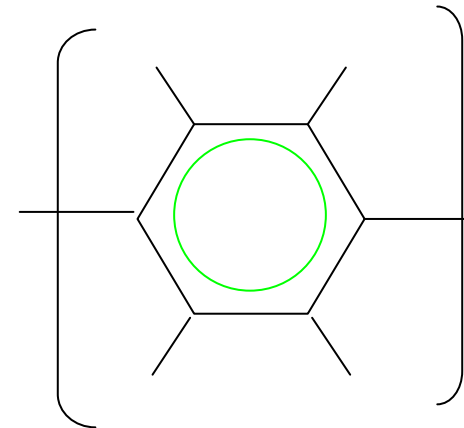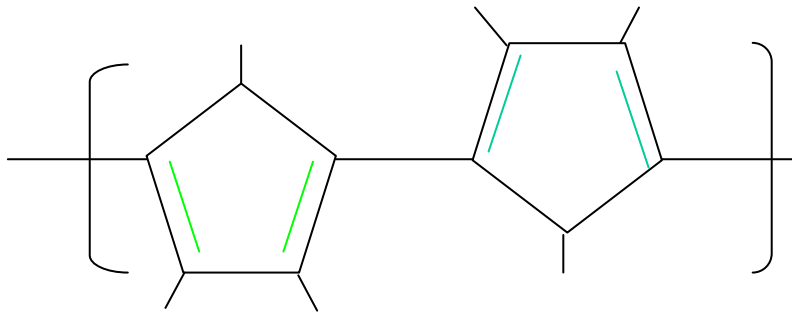
  5 is longer then 6
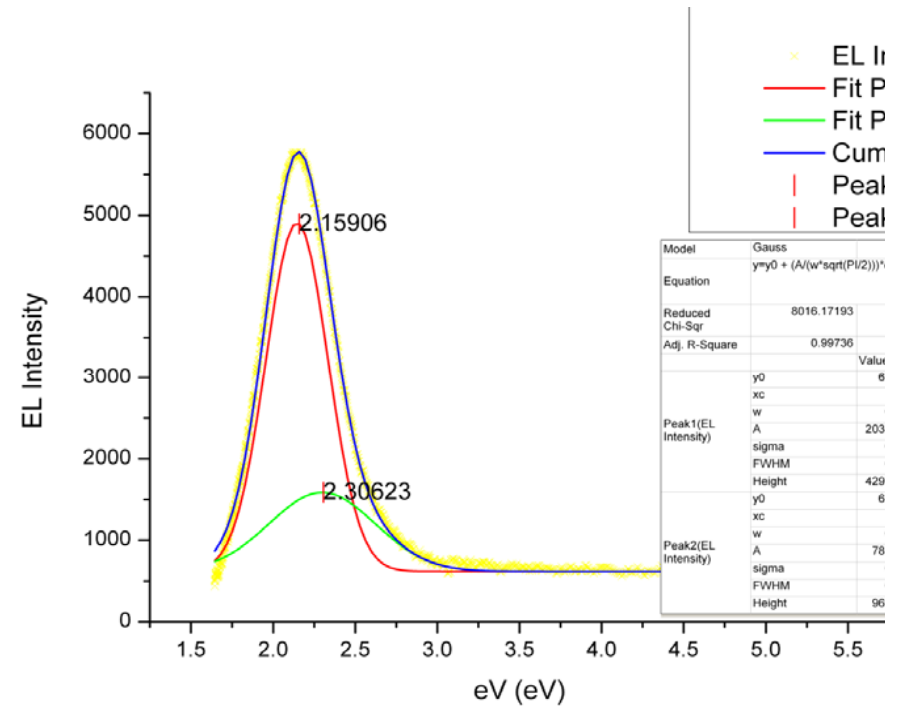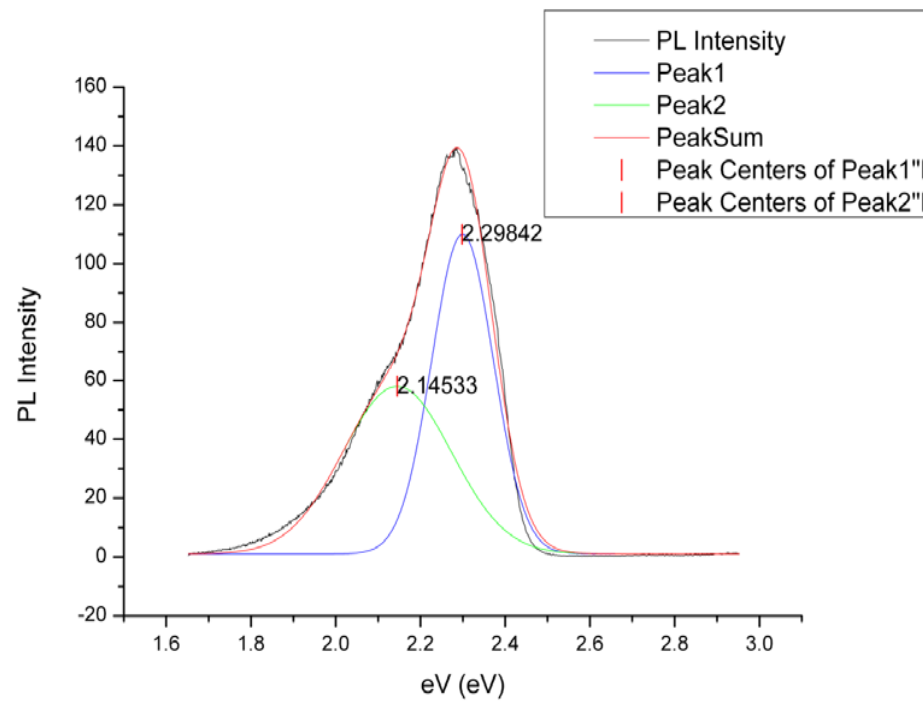
Integrated intensities:

Photoluminiscence

$$P_1/P_2 = 0.92$$

Electroluminiscence

$$P_1/P_2 = 2.65$$

Optically active polymers

Excitons: effects of the dielectric susceptibility

$$E_b = \frac{\mu e^4}{\varepsilon_\perp^2 \hbar^2}\left(\log\frac{R}{a} - \varepsilon_\perp \frac{a}{a_B}\frac{U_0}{2E_{Ry}}\right)^2$$

Intrachain (primary) exciton,
a - the monomer unit size

$$\varepsilon_\perp \frac{m_0}{2\mu}\frac{a_B}{R} = \log\frac{R}{a} - \varepsilon_\perp \frac{a}{a_B}\frac{U_0}{2E_{Ry}}$$

$$E_{Ry} = 13.6 eV$$

$$E_{CT} = \frac{\mu e^4}{\varepsilon_\perp \varepsilon_\parallel \hbar^2}\left(\log\frac{R_{CT}}{d}\right)^2 \qquad R_{CT} = \varepsilon_\perp a_B \frac{m_0}{2\mu}\frac{1}{\ln(R_{CT}/d)}$$

Interchain (CT) exciton,
d – the interchain distance

electron   **hole**

1D exciton, but 3D Coulomb field
mostly out of line,
in perpendicular to the 1D line planes

If U$_0$=0 then $\quad \dfrac{E_b}{E_{CT}} \approx \dfrac{\varepsilon_\parallel}{\varepsilon_\perp} \geq 1$

Electronic correlations, result in

$$\frac{E_b}{E_{CT}} \leq 1$$

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