Can theory help in understanding photoexcitations in organic semiconductors? An experimentalist's perspective

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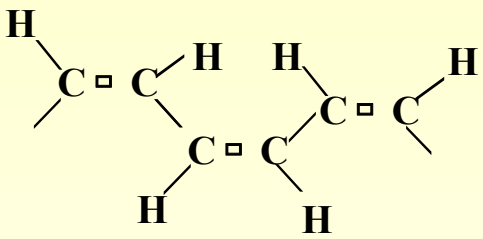
Outline

- Brief introduction to optical processes in organic materials
- Some highlights of utilizing triplet-enhanced conjugated polymers in solar cells
- Theoretical challenges

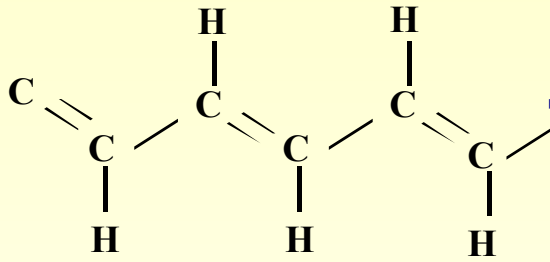
- Raman spectra calculations in polyfluorene
- A simple phenomenological model-bond polarizability model

Conjugated polymers/molecules

Prototype of a conducting polymer: polyacetylene*

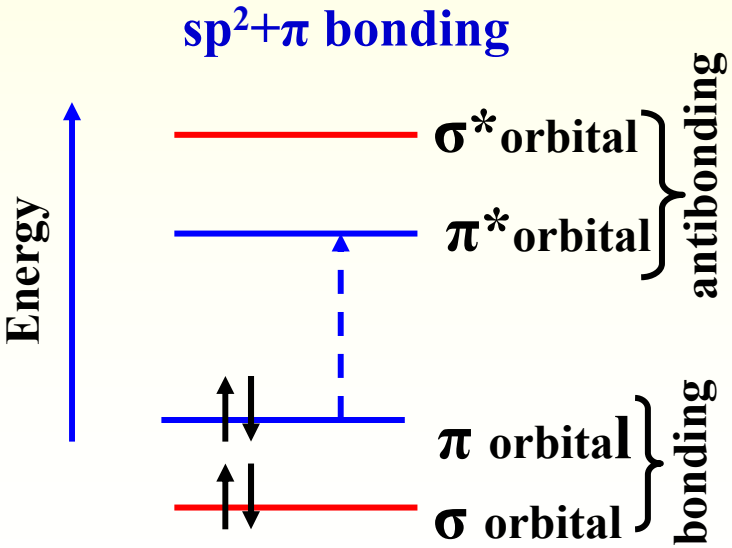


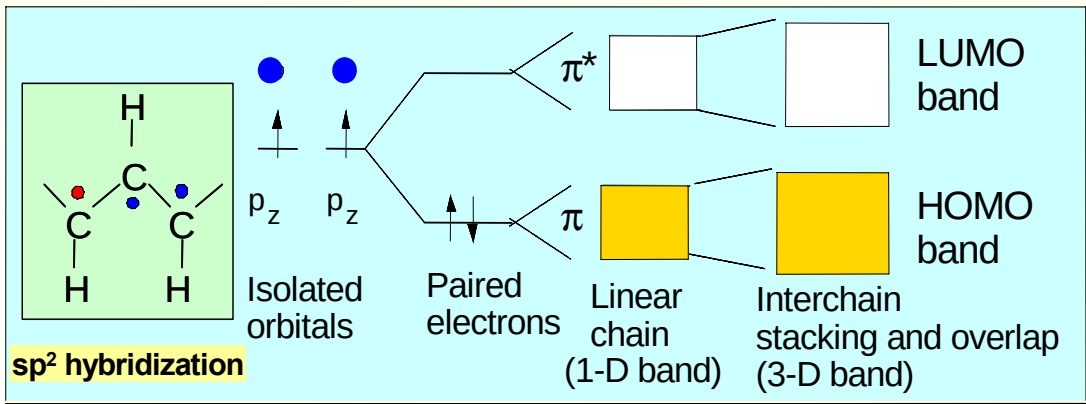
Cis-$(CH)_x$



Trans-$(CH)_x$

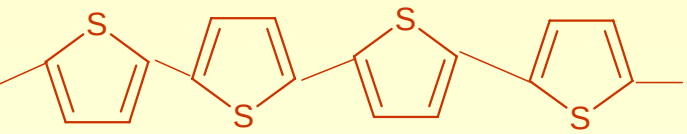
*C. K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, A. G. MacDiarmid, Phys. Rev. Lett. **39**, 1098 (1977).



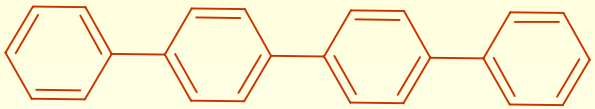


(M.J. Winokur- online tutorial)

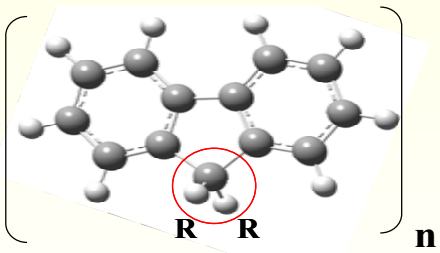
Other prototypes/charge excitations



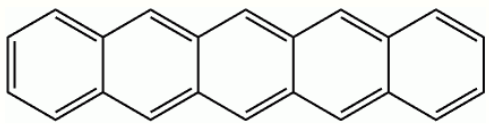
polythiophene



poly-p phenylene

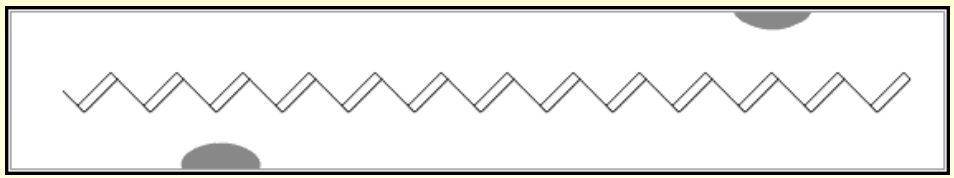


polyfluorene



pentacene

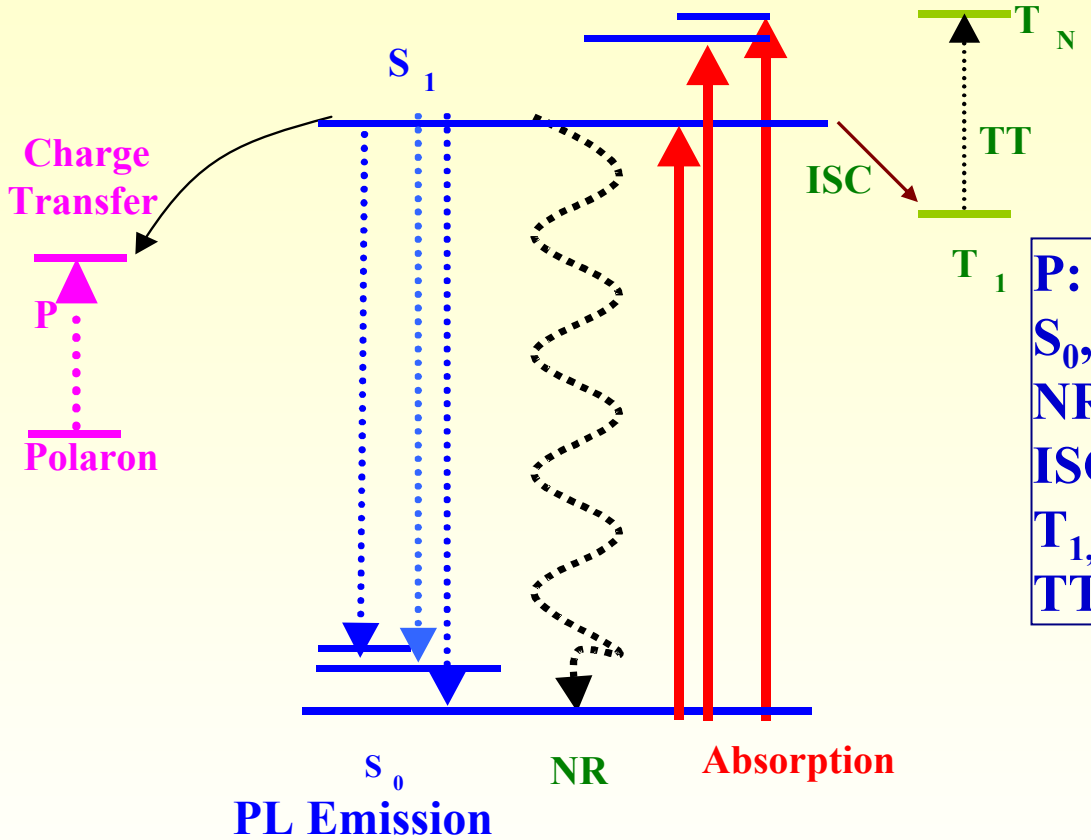
Conducting polymers exhibit fundamentally different charge excitations



http://nobelprize.org/nobel_prizes/chemistry/laureates/2000/public.html

1. Iodine molecule attracts an e- from PA to form I_3^-
2. PA is positively charged (radical cation/polaroan/soliton)
3. The lone e- of the double bond can move along the chain
4. Positive charge (is fixed on the iodide ion) does not move that easily.
5. If PA chain is heavily oxidized, polarons condense pair-wise (solitons).

Scheme of electronic states and transitions

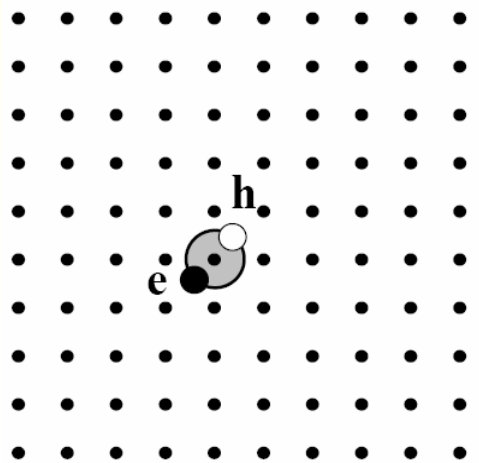


P:	Polaron absorption
S_0, S_1:	Singlet states
NR:	Nonradiative recombination
ISC:	Intersystem crossing
T_1, T_N:	Triplet states
TT:	Triplet-triplet absorption

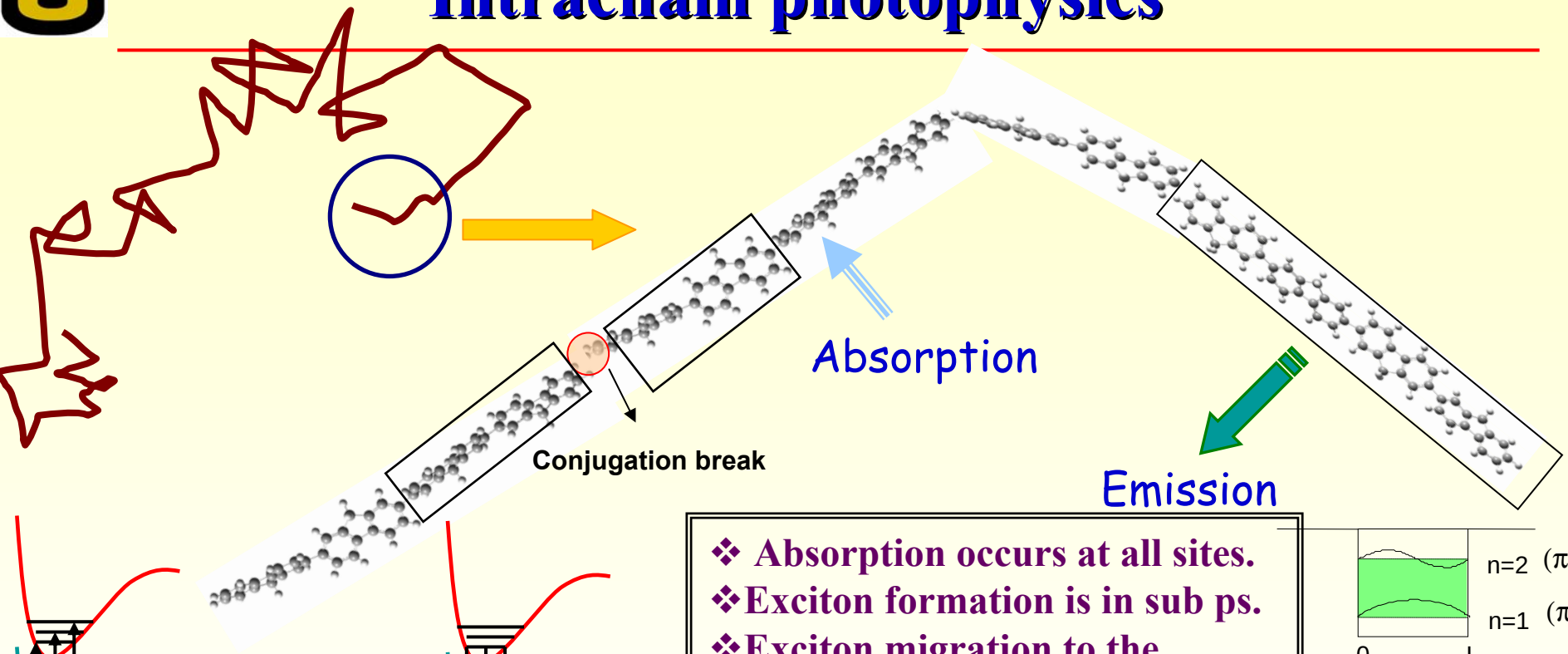
Frenkel exciton

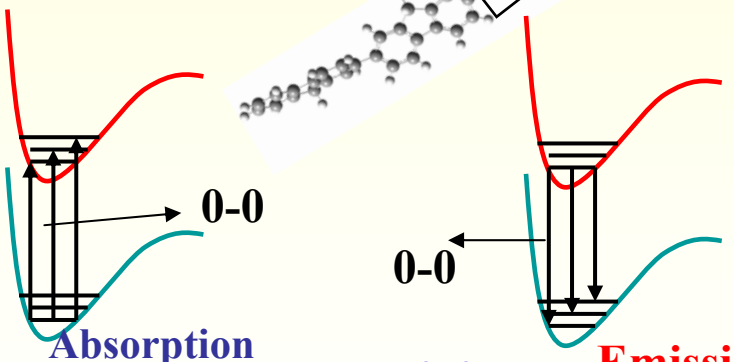
Binding energy ~ 0.5-1 eV

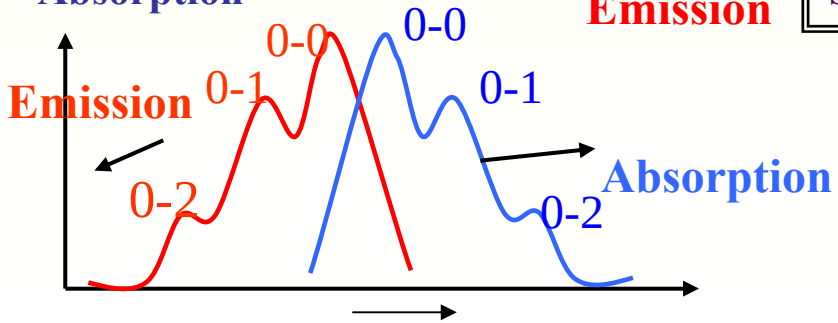
Radius ~10Å



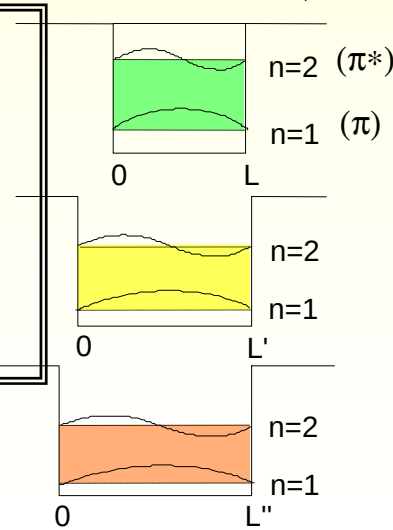
Intrachain photophysics





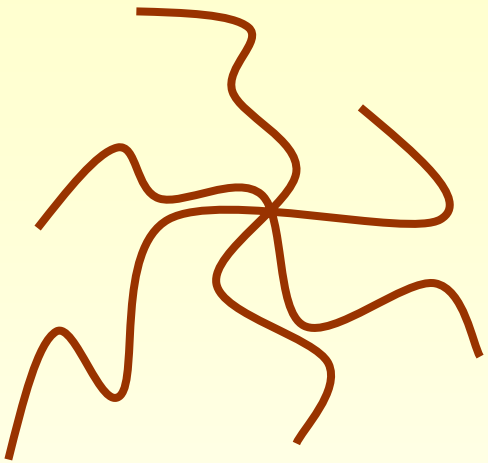


- Absorption occurs at all sites.
- Exciton formation is in sub ps.
- Exciton migration to the longest chain segment.
- PL from the longest chain segment.

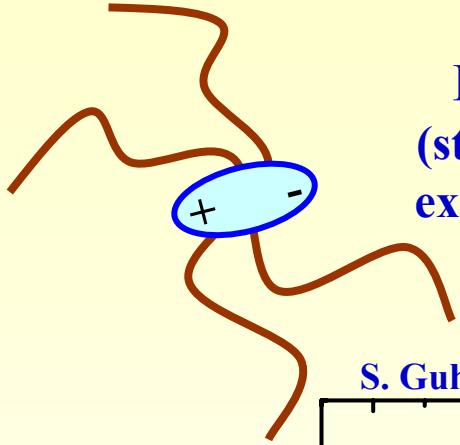


Energy eigenvalues are proportional to L^{-2}

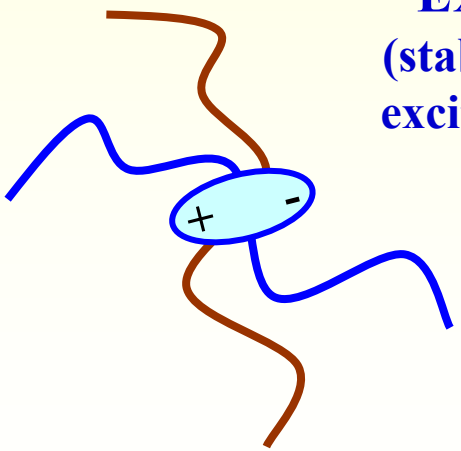
Interchain photophysics



Aggregation (stable in the ground state)



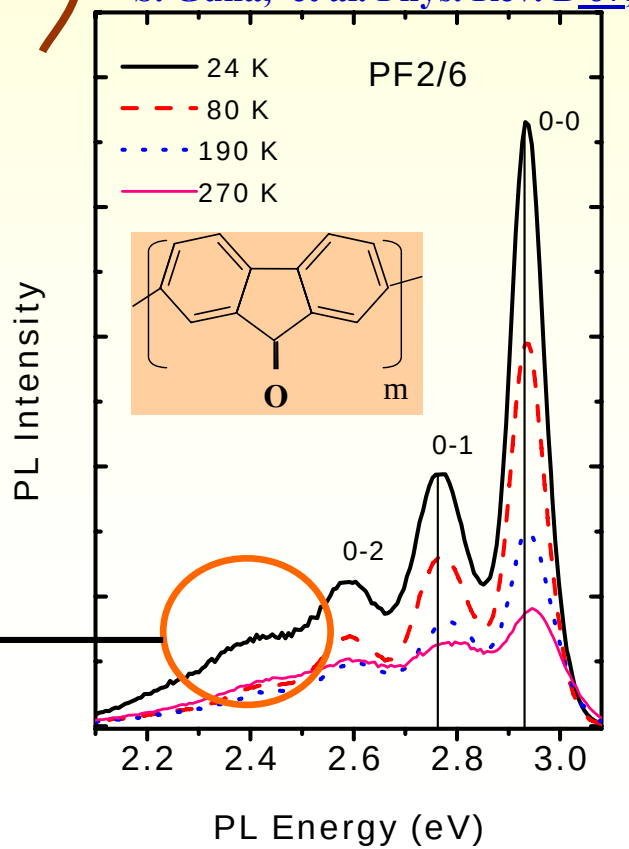
Excimer (stable in the excited state)



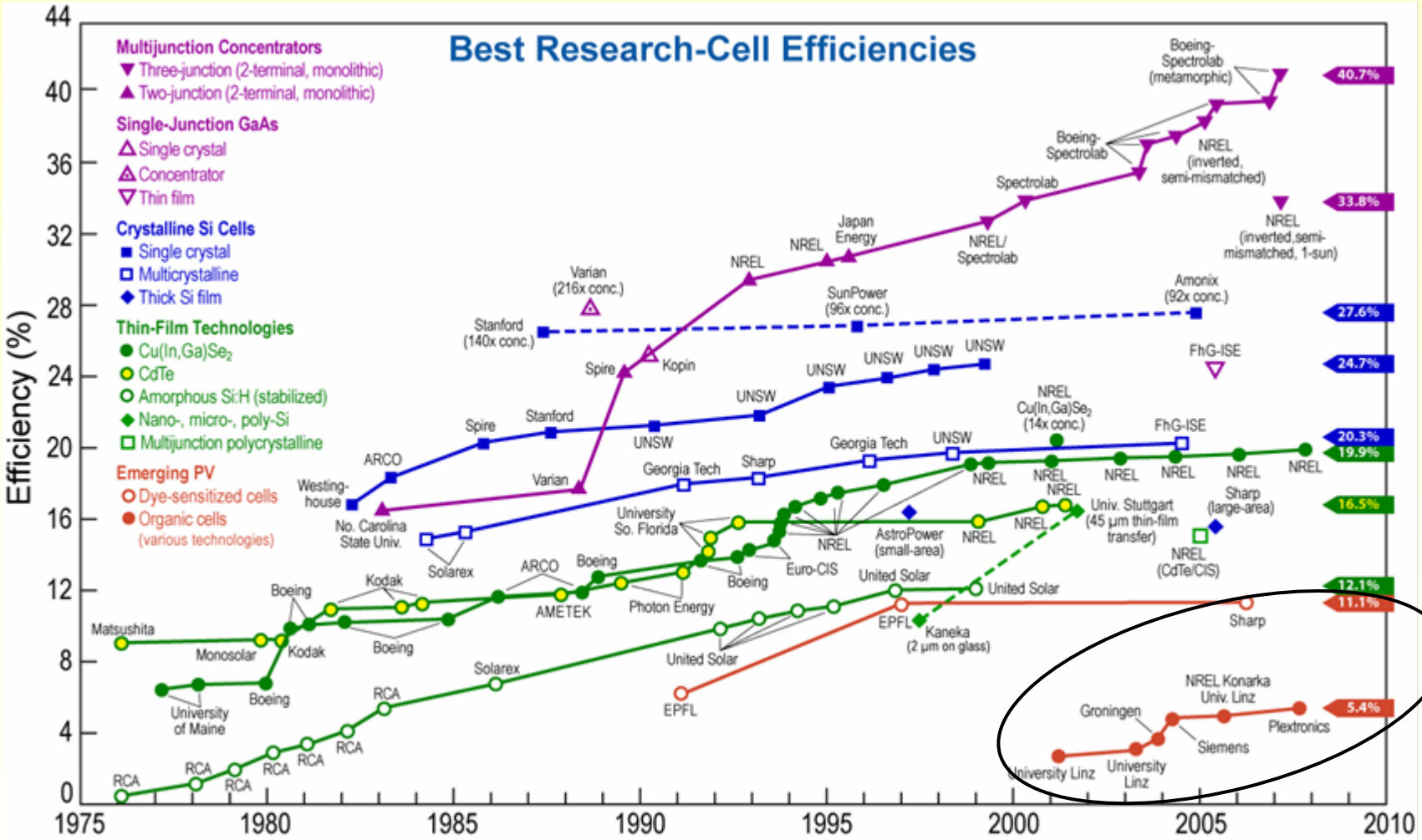
Exciplex (stable in the excited state)

Aggregation
Excimer
Defects (oxygen)

S. Guha, et al. Phys. Rev. B 67, (2003).



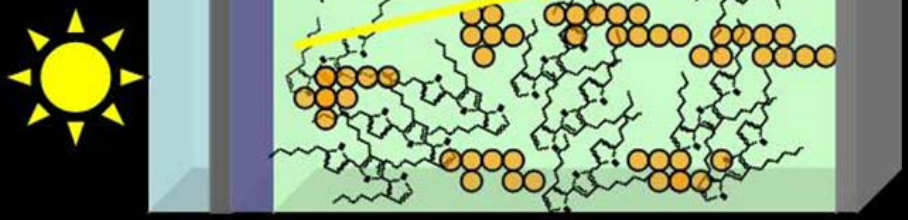
Solar cell efficiencies



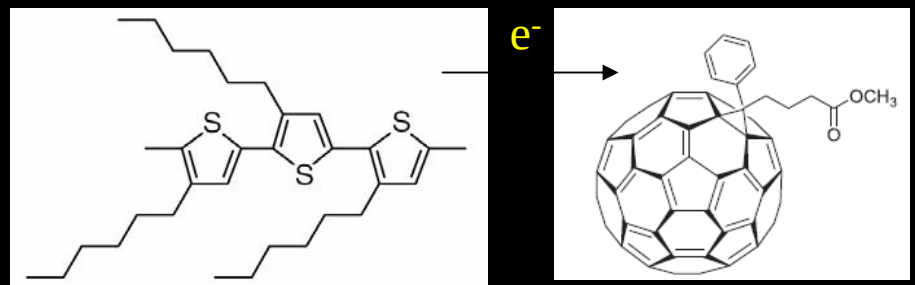
Progress of research-scale photovoltaic device efficiencies, under AM1.5 simulated solar illumination

How does a polymer solar cell work?

Bulk heterojunction solar cell



Need a bi-continuous network with an optimum distance between the two components ~ 10 nm



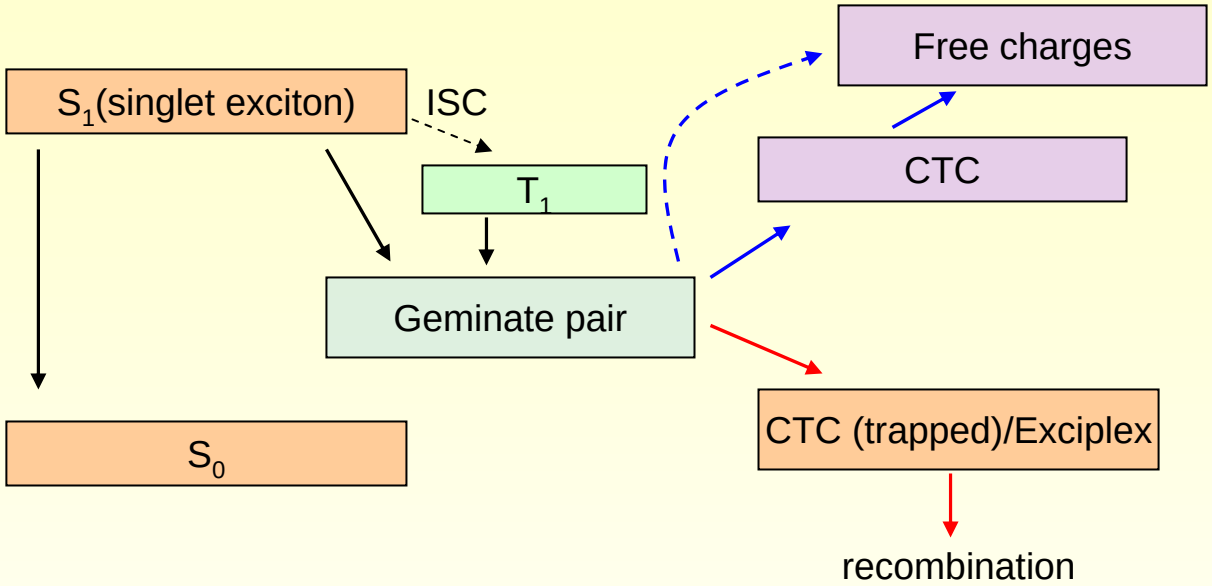
Semiconducting polymer (donor)

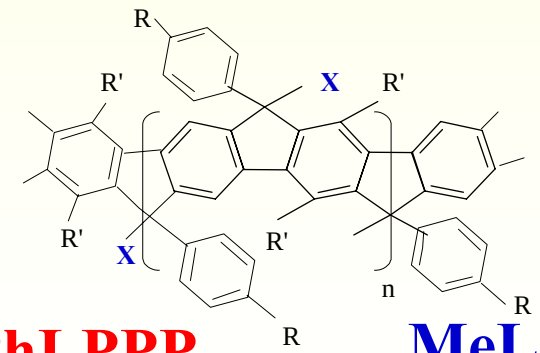
Fullerene (acceptor)

Asymmetry between forward transfer and back transfer (recombination), which is very fortuitous!

One of the fastest photo-induced transfer rates ~ 50 fs (~ 1/100 ps)

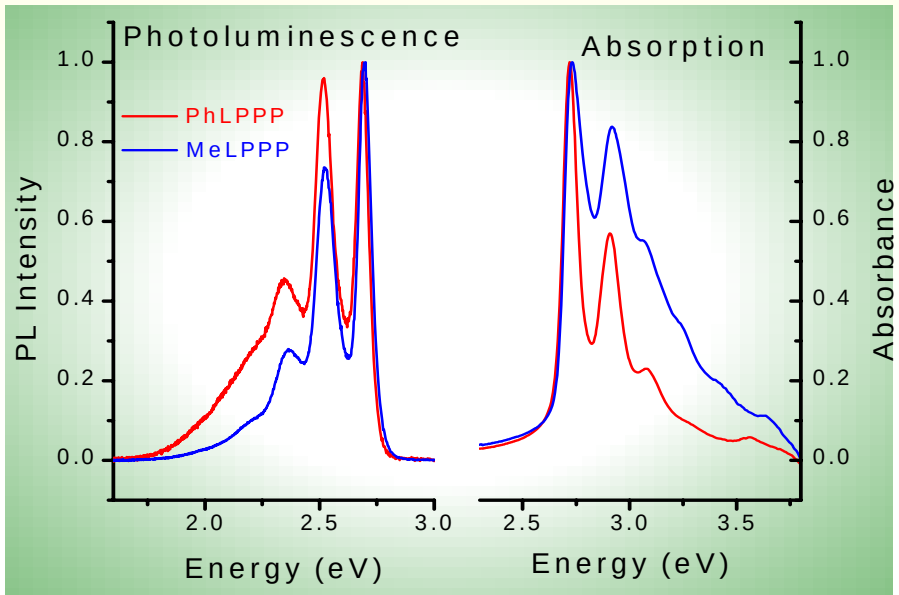
Can triplet excitons contribute?



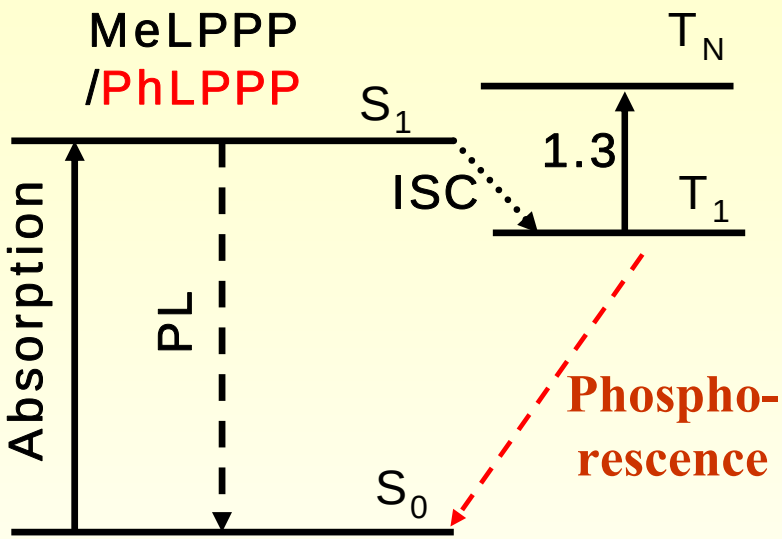


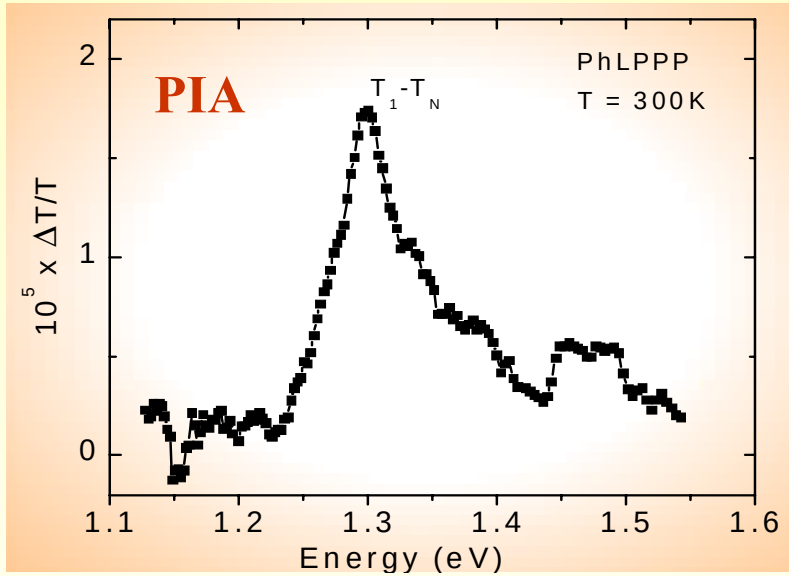
PhLPPP **MeLPPP**

Trace concentration of covalently bound Pd atoms (~100 ppm)

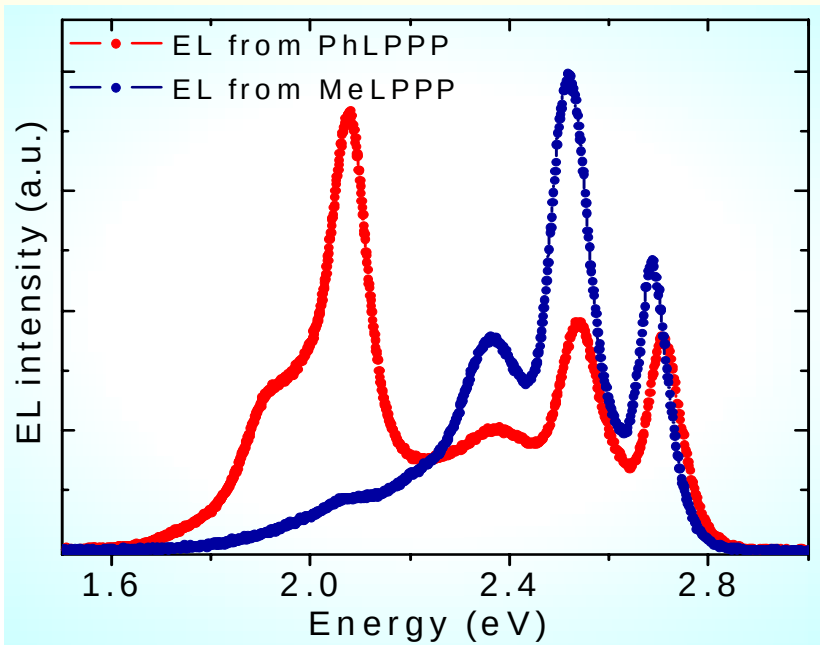


Evidence of triplet excitons

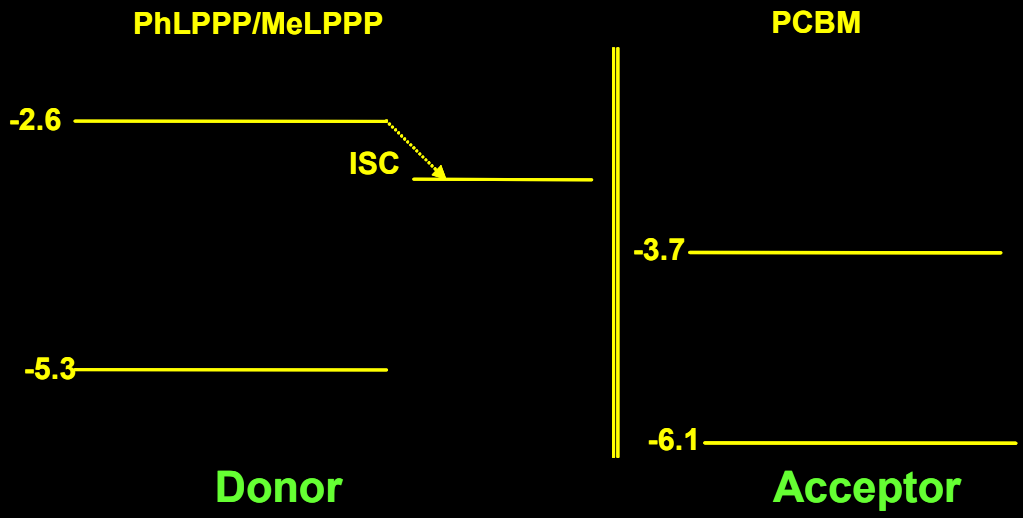


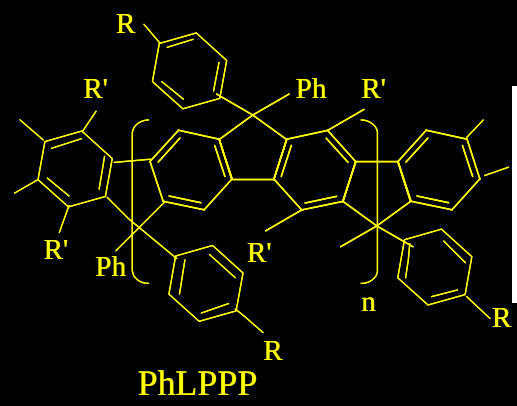


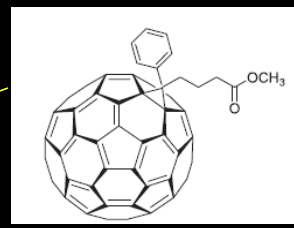
Electroluminescence

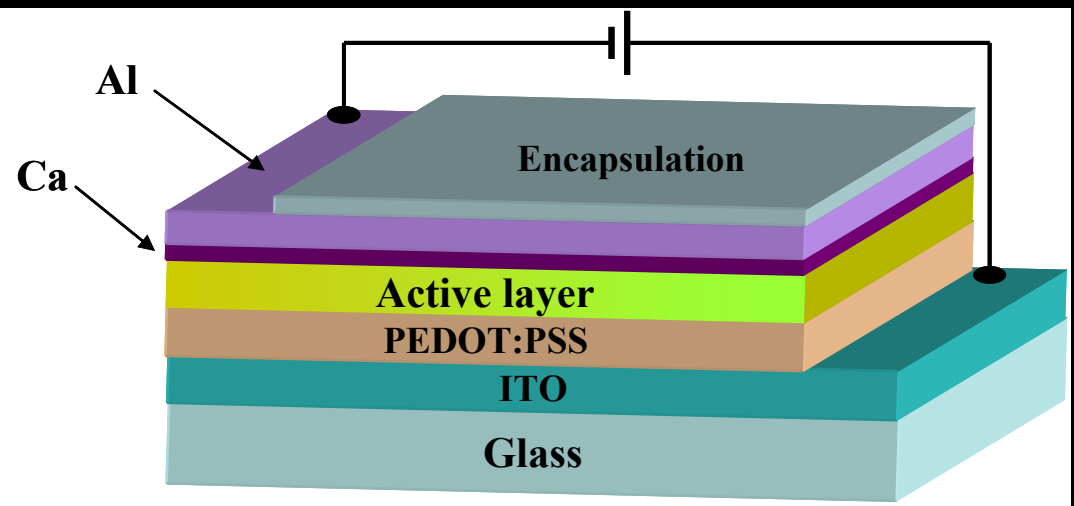


Solar cell fabrication





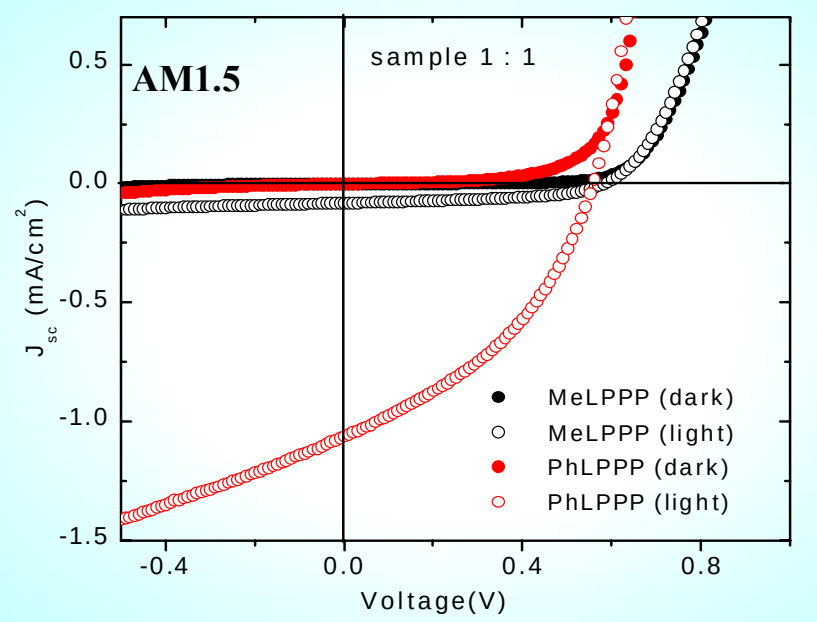




Device with active layer	PCBM conc.
polymer/PCBM(2:1)	33 wt%
polymer/PCBM(1:1)	50 wt%
polymer/PCBM(1:2)	67 wt%

M. Arif et al. Appl. Phys. Lett. 94, 063307 (2009)

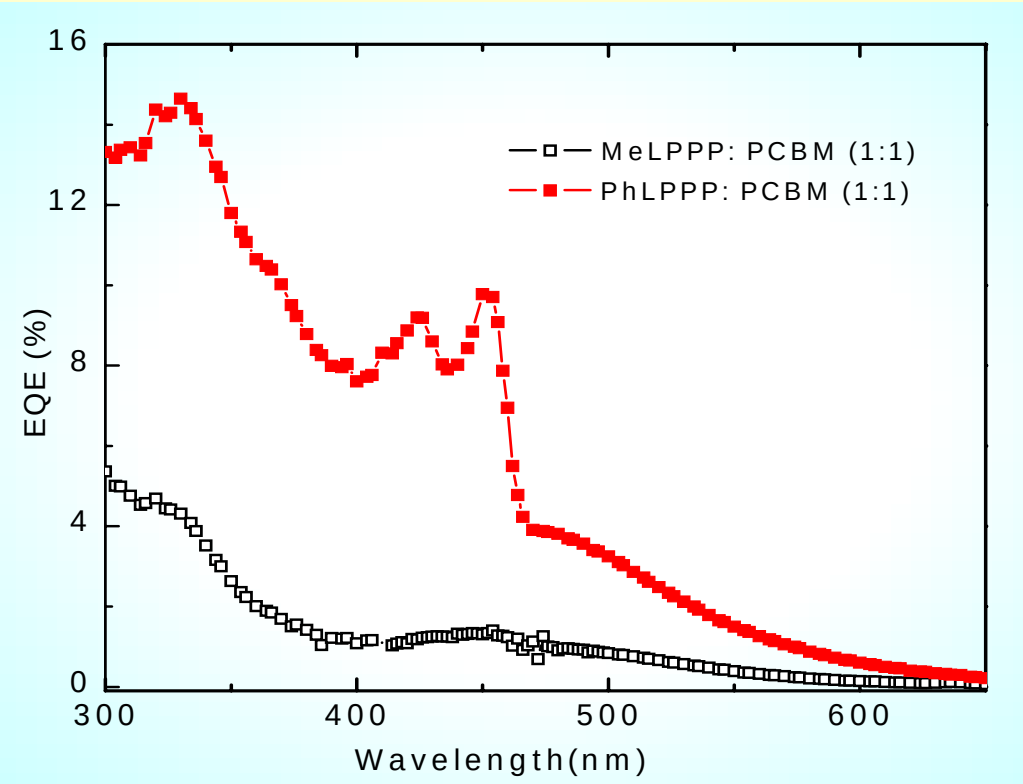
Current-voltage characteristics



$$\eta = \frac{FF \times V_{OC} \times I_{SC}}{P_{in}}$$

Device with active layer	PCBM conc.	Thickness	FF	Voc (V)	Jsc (mA/cm^2)	PCE (%)
MeLPPP/PCBM(2:1)	33 wt%	80-90 nm	0.29	0.35	0.085	0.008
PhLPPP/PCBM (2:1)			0.35	0.55	0.44	0.09
MeLPPP/PCBM(1:1)	50 wt%	50-60 nm	0.46	0.57	0.08	0.02
PhLPPP/PCBM (1:1)			0.41	0.55	1.05	0.23
MeLPPP/PCBM(1:2)	67 wt%	80-90 nm	0.34	0.63	0.33	0.07
PhLPPP/PCBM (1:2)			0.37	0.59	1.07	0.23

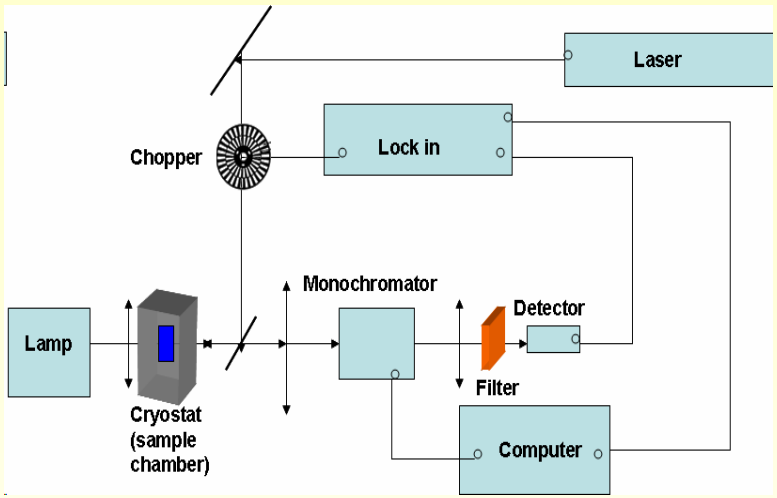
External quantum efficiency

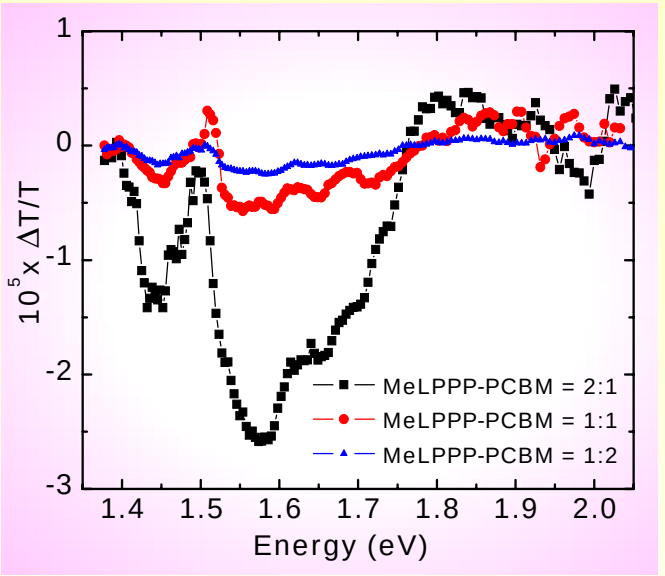


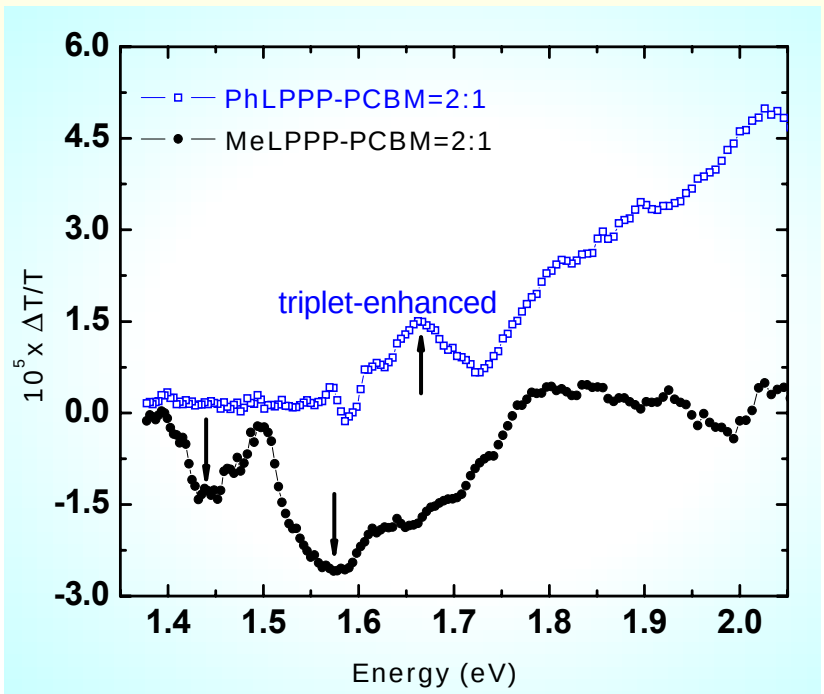
$$EQE = \frac{N_e}{N_{ph}(\lambda)} = \frac{hc}{e}\frac{PR(\lambda)}{\lambda}$$

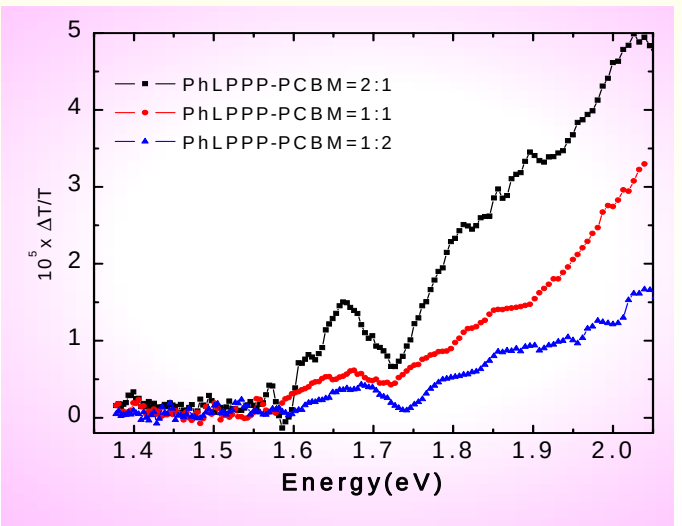
Compared to MeLPPP, EQE of the PhLPPP device is enhanced by a factor of 8. Enhanced PV efficiency and EQE are attributed to the mobile long-lived triplets.

Photo-induced absorption studies

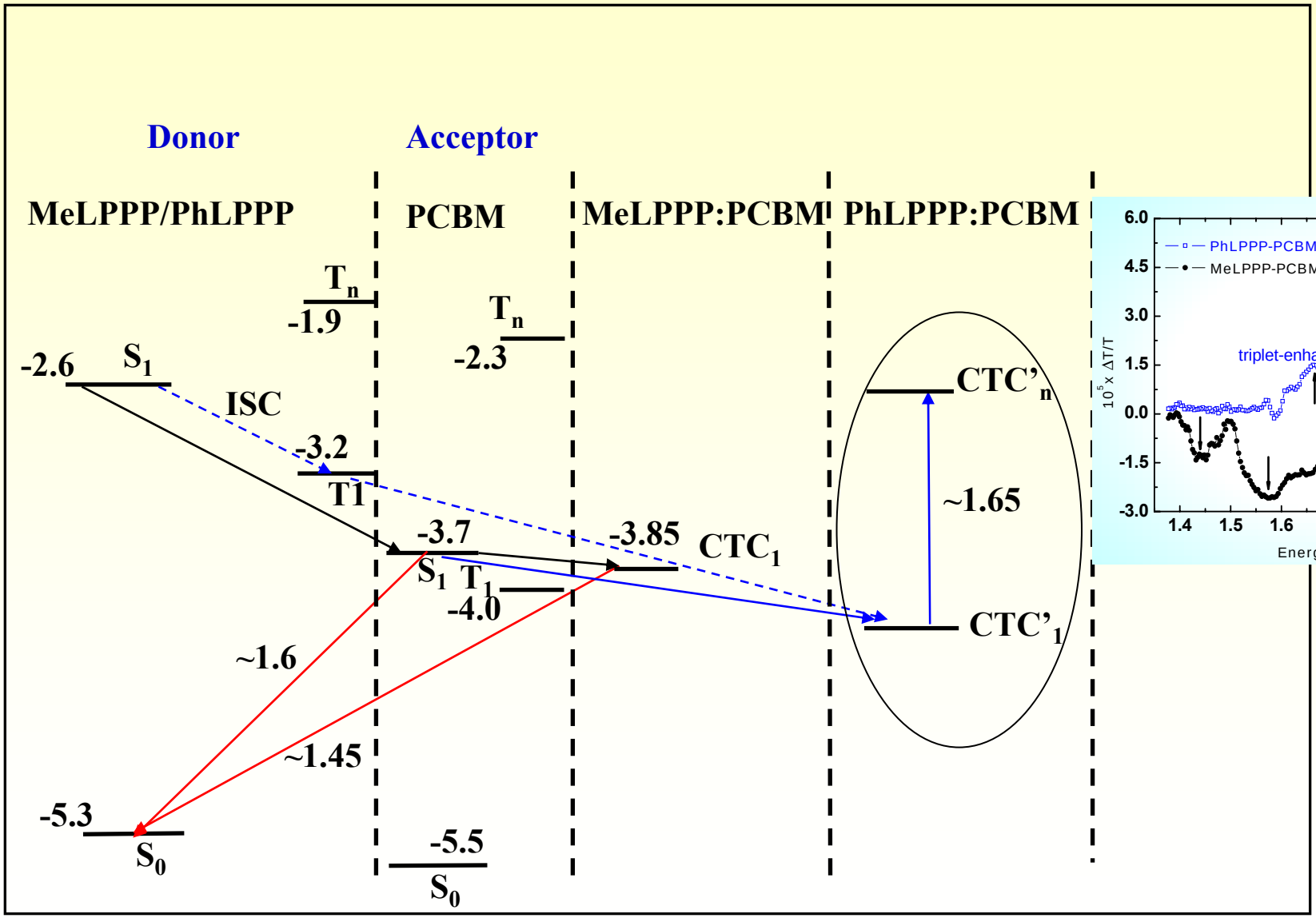








What can we infer about CTCs?



Can ab-initio theory help?

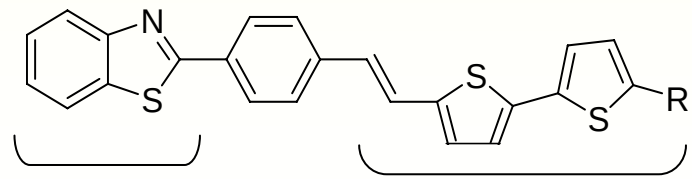
Unfortunately "simple" theoretical models cannot be experimentally verified!

We need a theory that handles large systems with long range charge transfer excitations along with the coupling of the electronic and nuclear degrees of freedom.

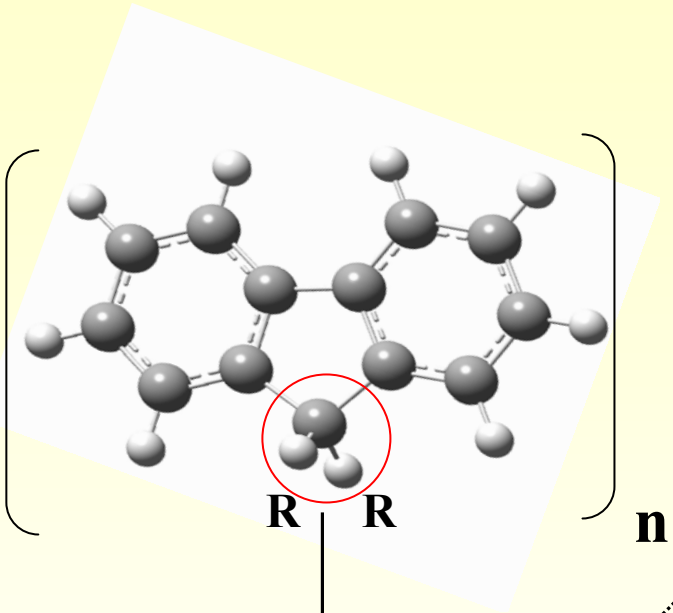
1. How well does theory predict the diffusion lengths for singlet/triplet excitons?

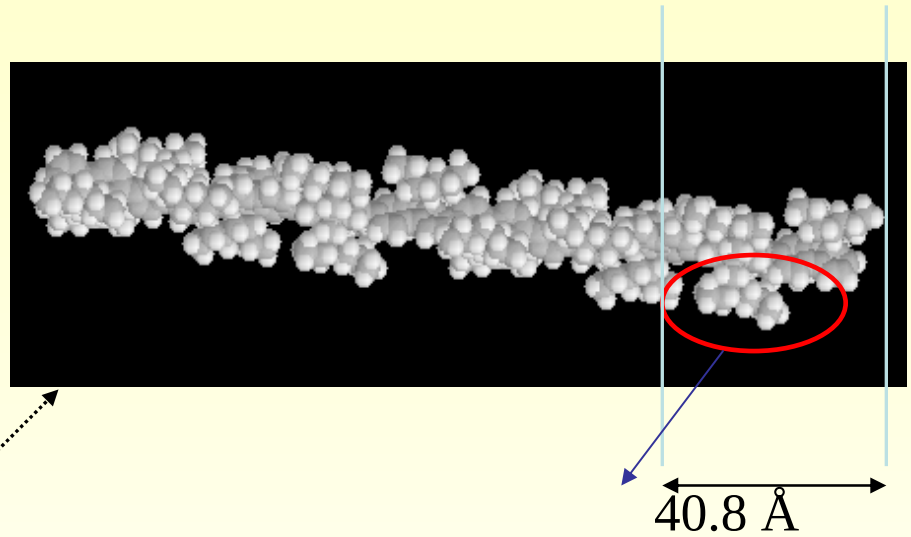
2. How well does theory predict the energy levels of CTCs in donor-acceptor heterojunctions?

3. Is the PV process different when the D-A molecules are on the same chain.

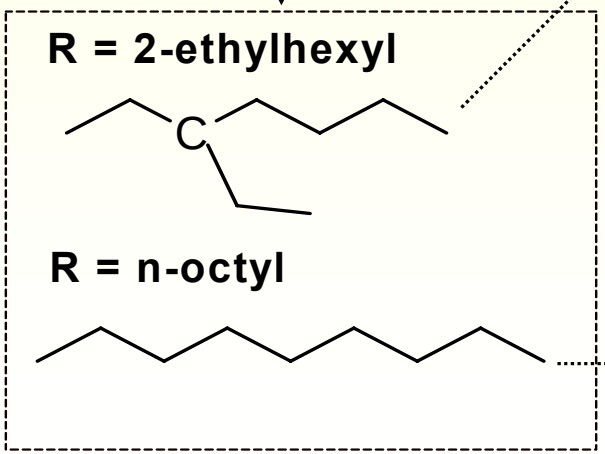


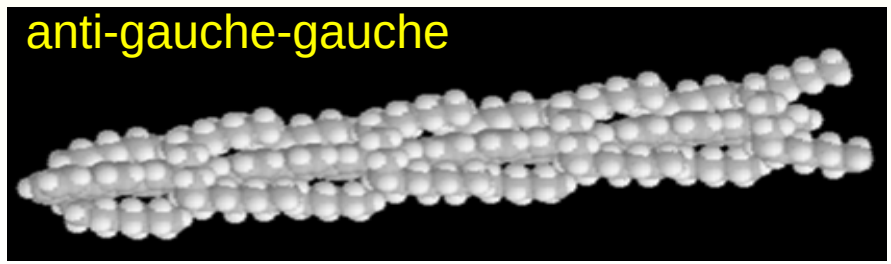
Polyfluorenes





Pair-wise ordering of alkyl side chains.



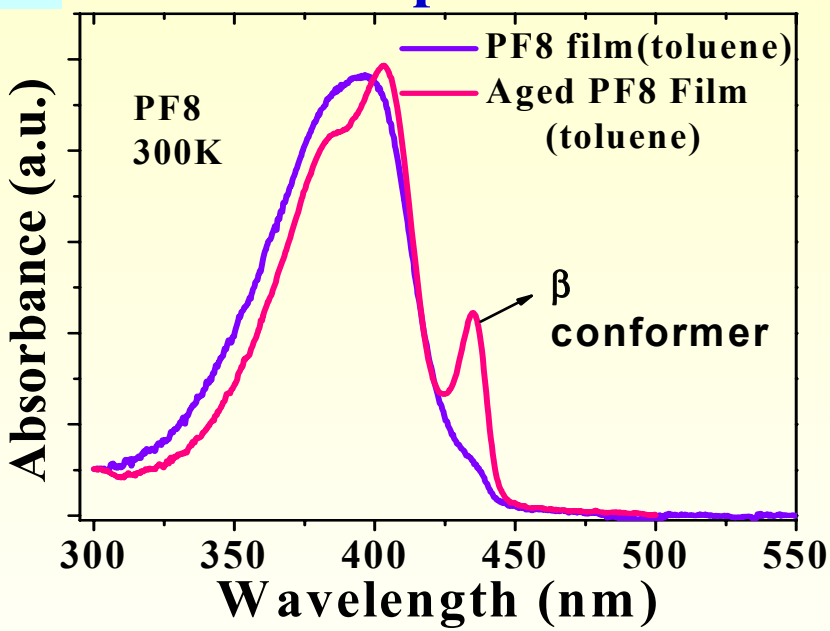


Tanto, Guha, Winokur et al., Macromolecules 37, 9438 (2004).

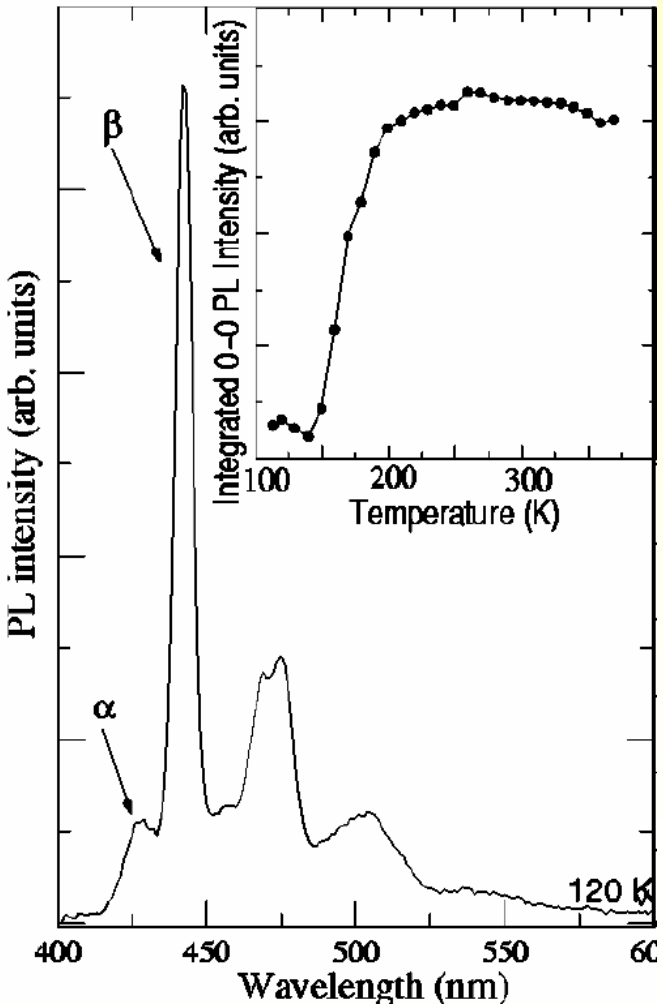
Structure controls optical/electrical property

PF8

Absorption



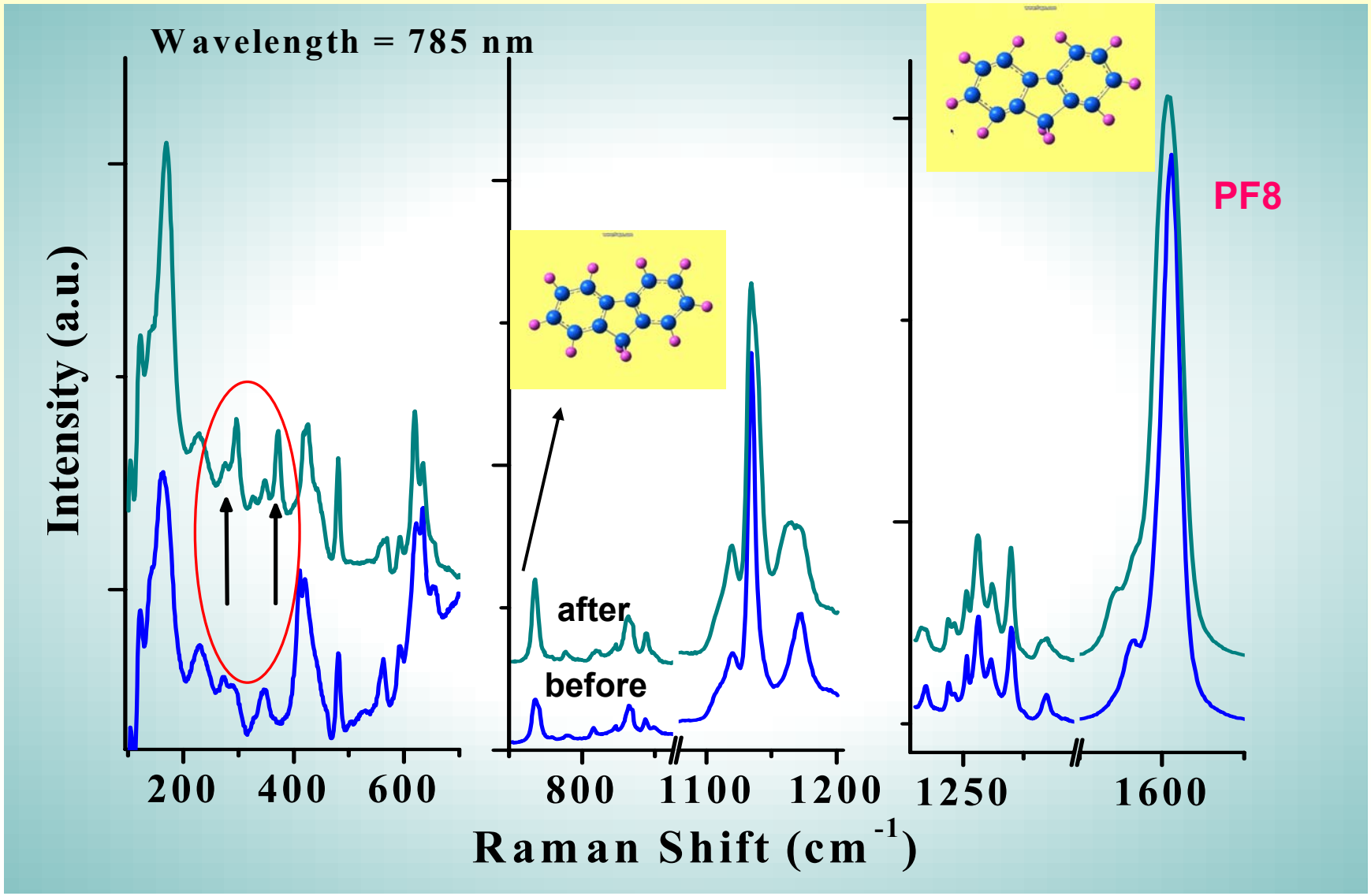
Photoluminescence



Distinct thermochromism with two or more backbone conformations

Cheun et al. Appl. Phys. Lett. (2004)

Raman spectra: PF8



Theoretical methodology

Raman spectra calculations

Gaussian 03: B3LYP density-functional with a 3-21G* basis set.

Gaussian©

$$Raman\ Intensity \propto \sum_{f=1}^{3N} \frac{\left\langle n(\omega_f)+1 \right\rangle}{\omega_f} \left| \sum_{\alpha\beta} \eta'_\alpha \eta_\beta P_{\alpha\beta,f} \right|^2 \times \delta(\omega - \omega_f)$$

$\omega = \omega_L - \omega_S$ (Raman shift)

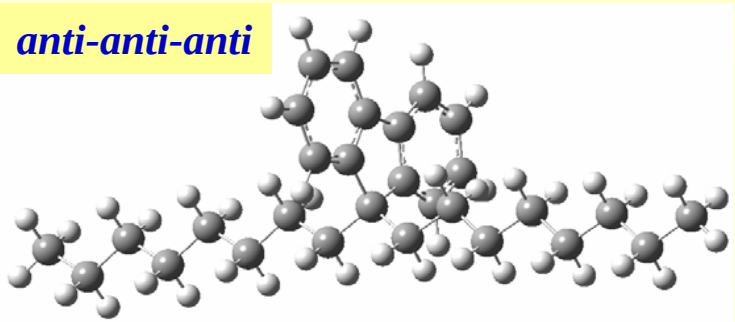
$P_{\alpha\beta f}$ = derivative of the electronic polarizability tensor with respect to the normal coordinate of the mode *f*.

$\left\langle n(\omega_f) \right\rangle \equiv \left[\exp(\beta\hbar\omega_f) - 1 \right]^{-1}$ **is the average occupation number of mode *f*.**

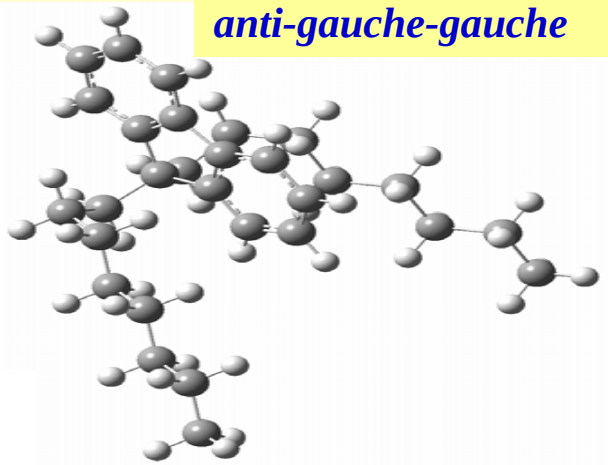
F8 oligomers

Monomer: 3 limiting conformation

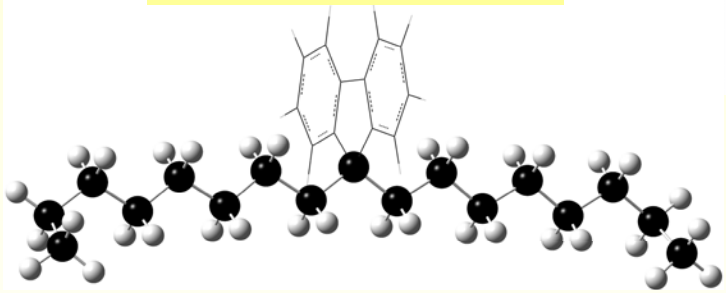
anti-anti-anti



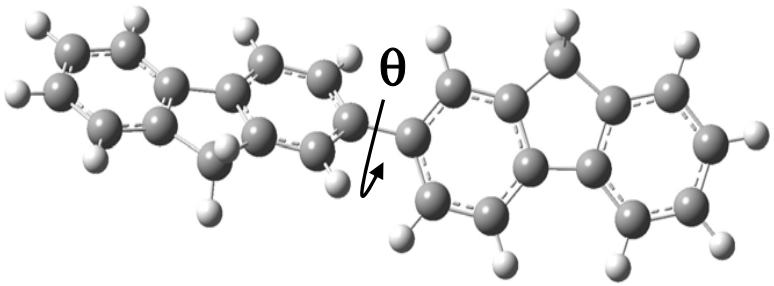
anti-gauche-gauche



anti-anti-gauche



Oligomers: dimer, trimer and tetramer



Torsional angle

C_β conformer: ~180°

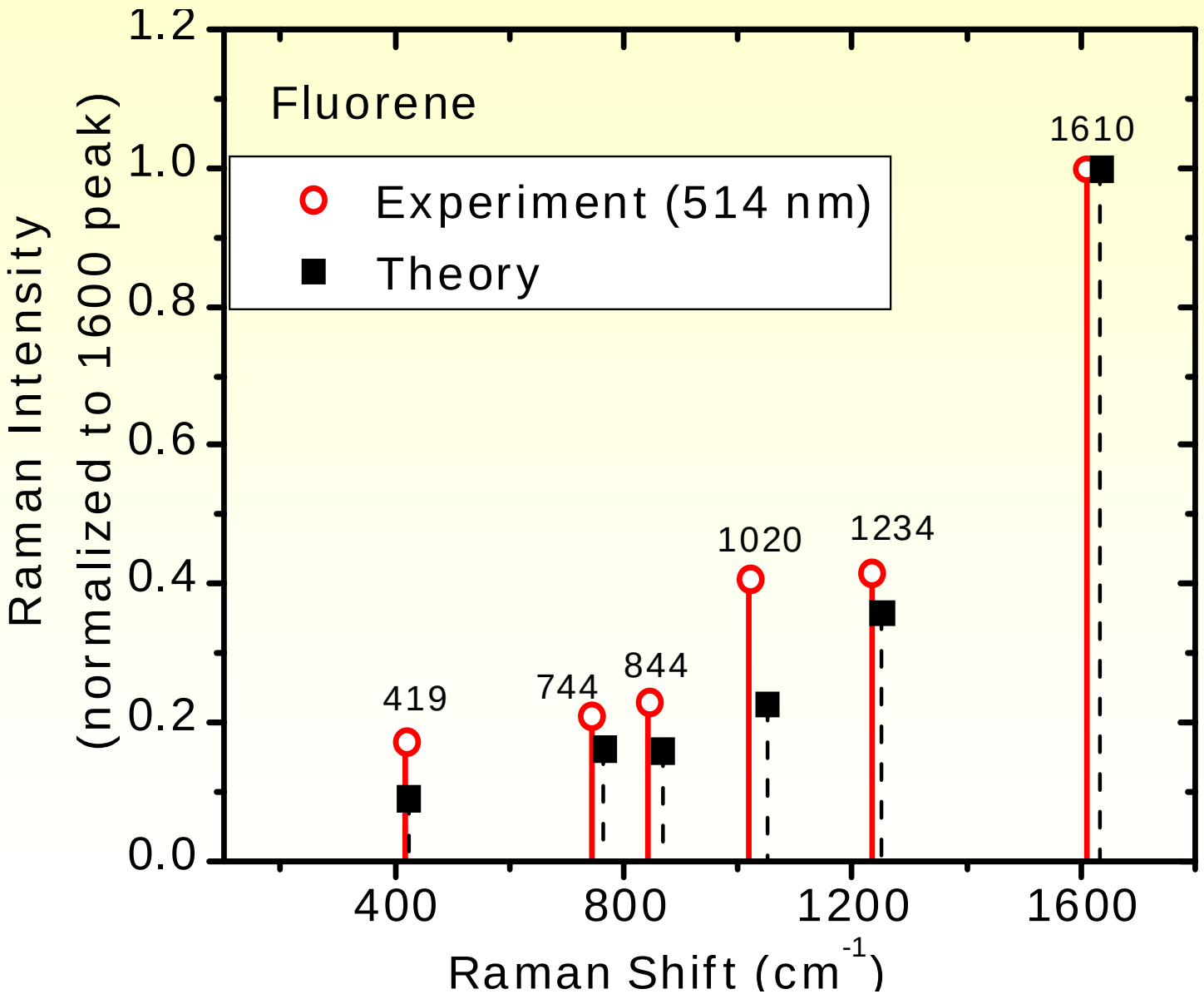
C_γ conformer: ~155°

C_α conformer: ~135°

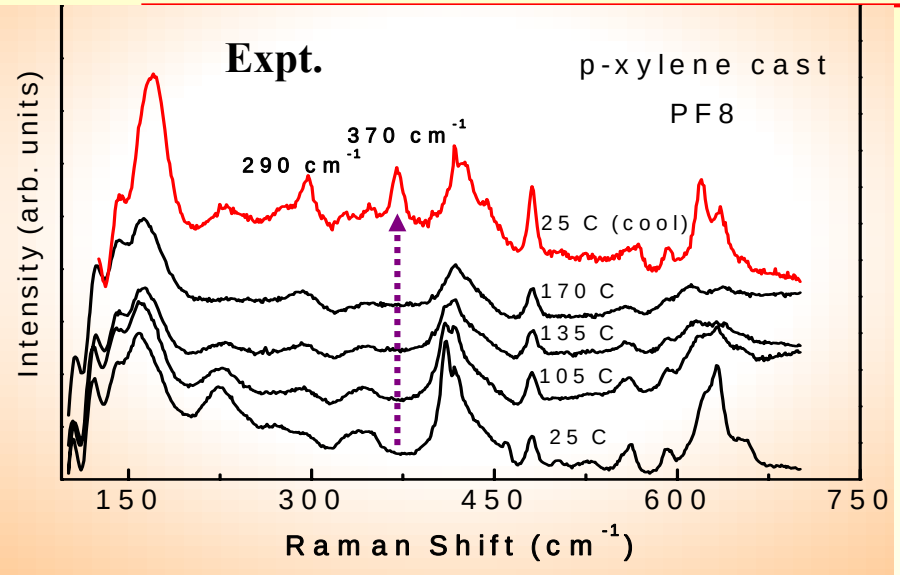
Raman Frequencies-Fluorene

	B3LYP		HF	MPW1 PW91
Expt. Freq (cm^{-1})	3-21G*	6-311G*	3-21G*	3-21G*
1610	1634	1650	1760	1660
1478	1483	1484	1473	1486
1234	1251	1261	1336	1271
1022	1051	1047	1095	1062
738	765	763	804	771

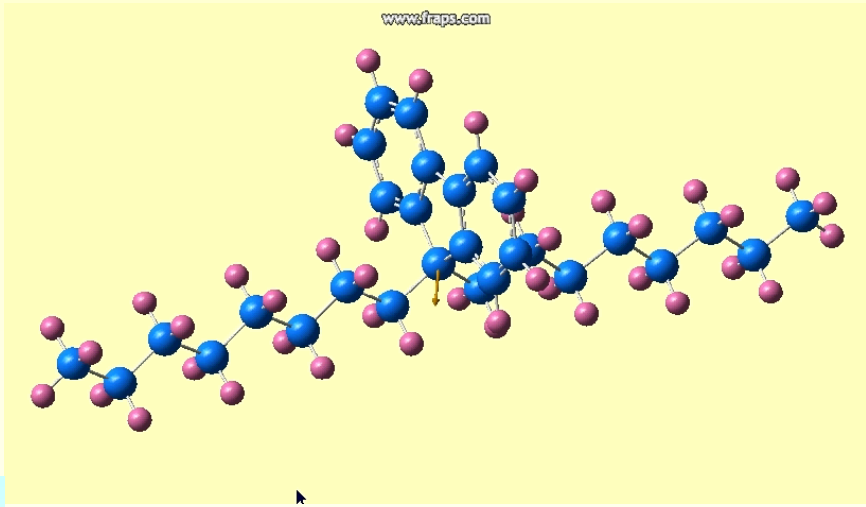
Fluorene (calculation vs. expt.)

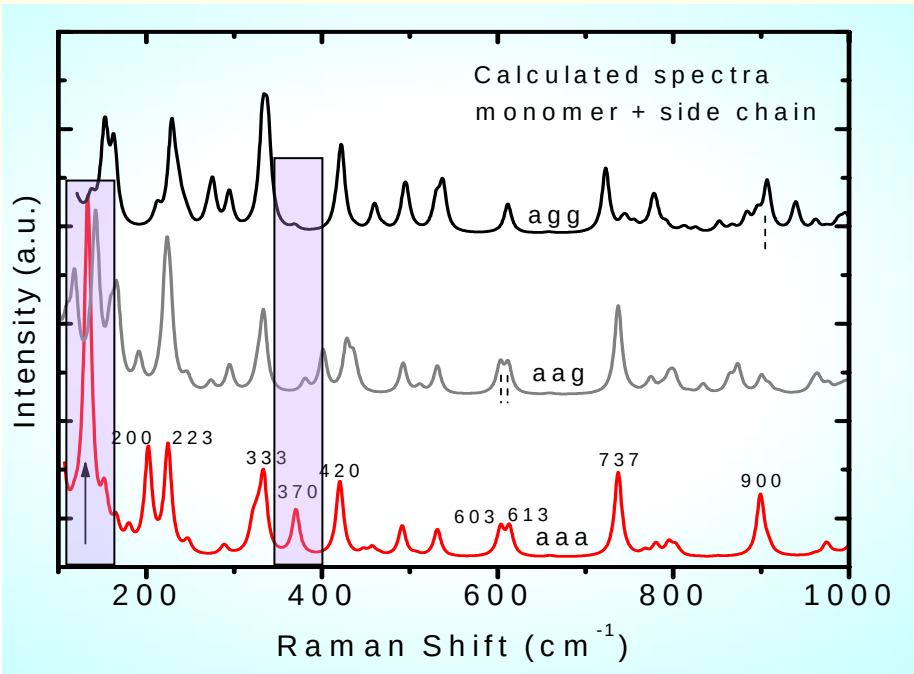


Alkyl side chains: low frequency region



LAM



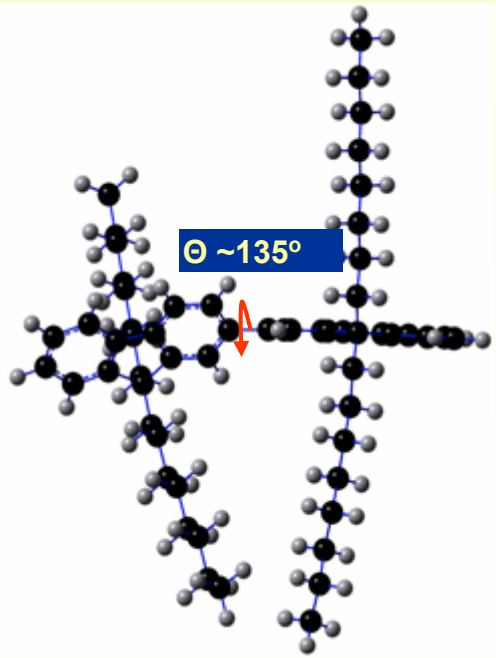


•Arif, Volz, & Guha, Phys. Rev. Lett. 96, 025503 (2006).

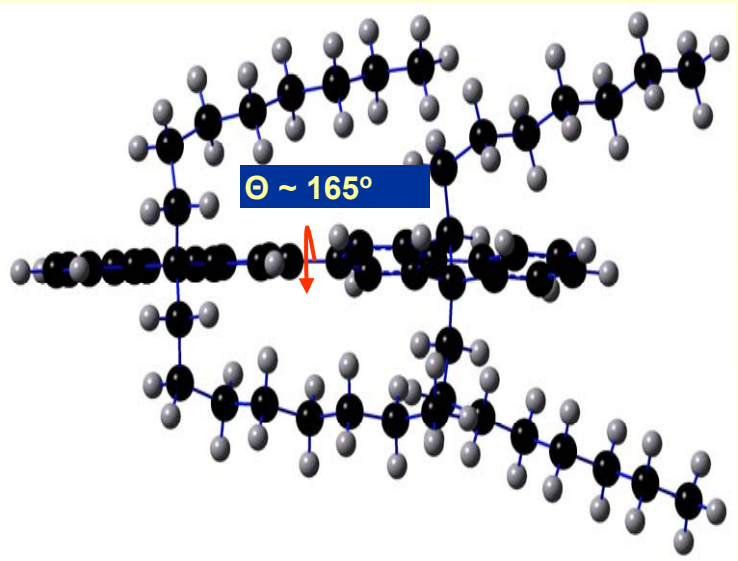
•Volz, Arif & Guha, J. Chem. Phys. 126, 064905 (2007).

Side chain conformations and torsional angle

MM3 calculations



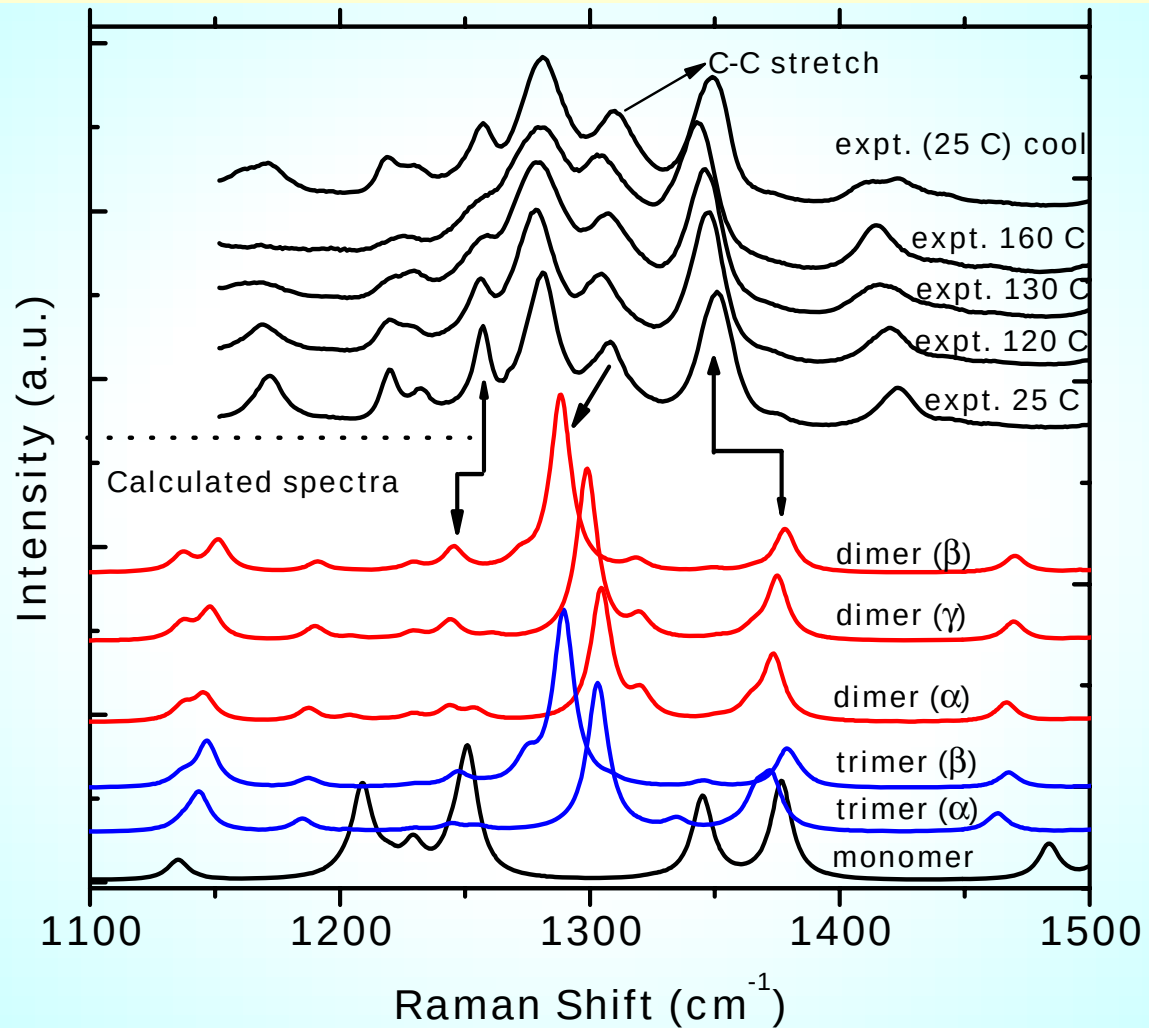
Dimer with *aaa* side chain conformation has an α conformation.



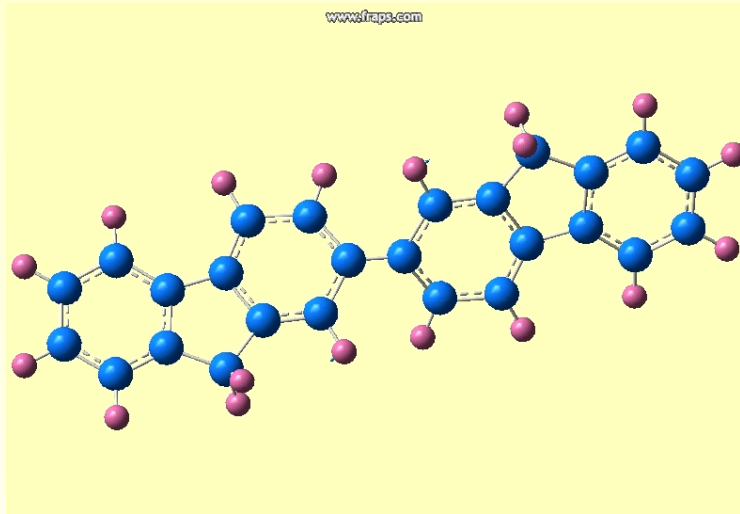
Dimer with *agg* side chain conformation has a β conformation .

Chunwaschirasiri *et al.*, PRL 94, 107402 (2005).

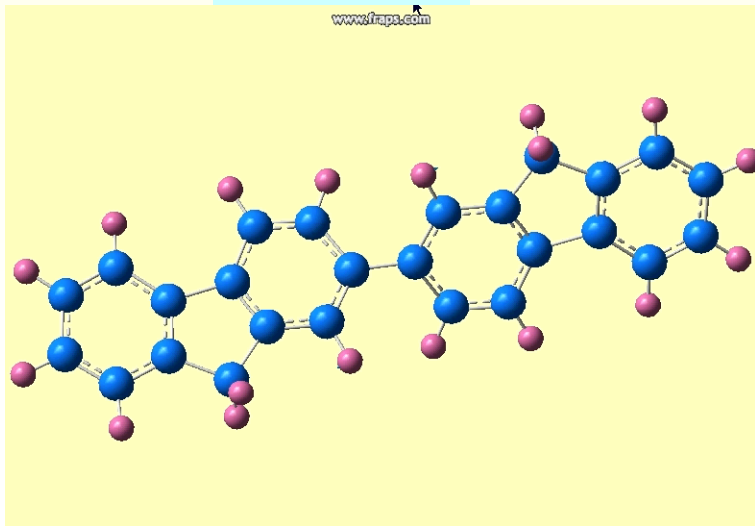
Raman spectra: 1300 cm^{-1} region



1307 cm^{-1}



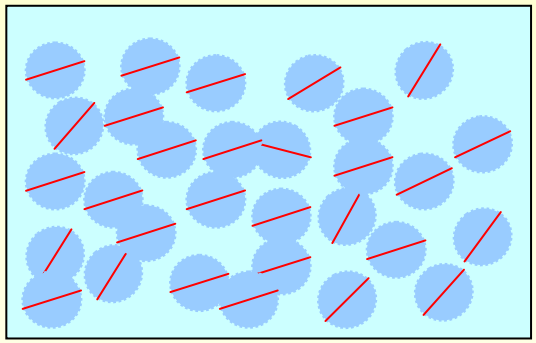
1257 cm^{-1}



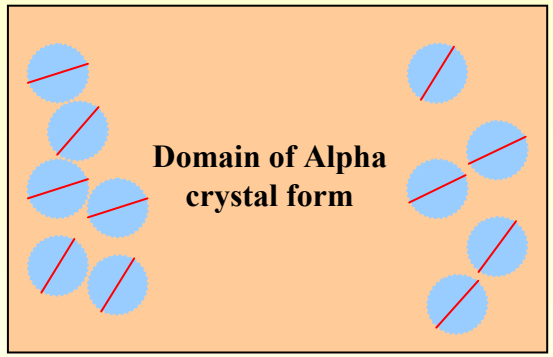
Arif et al. Phys. Rev. Lett. 96, 025503 (2006).

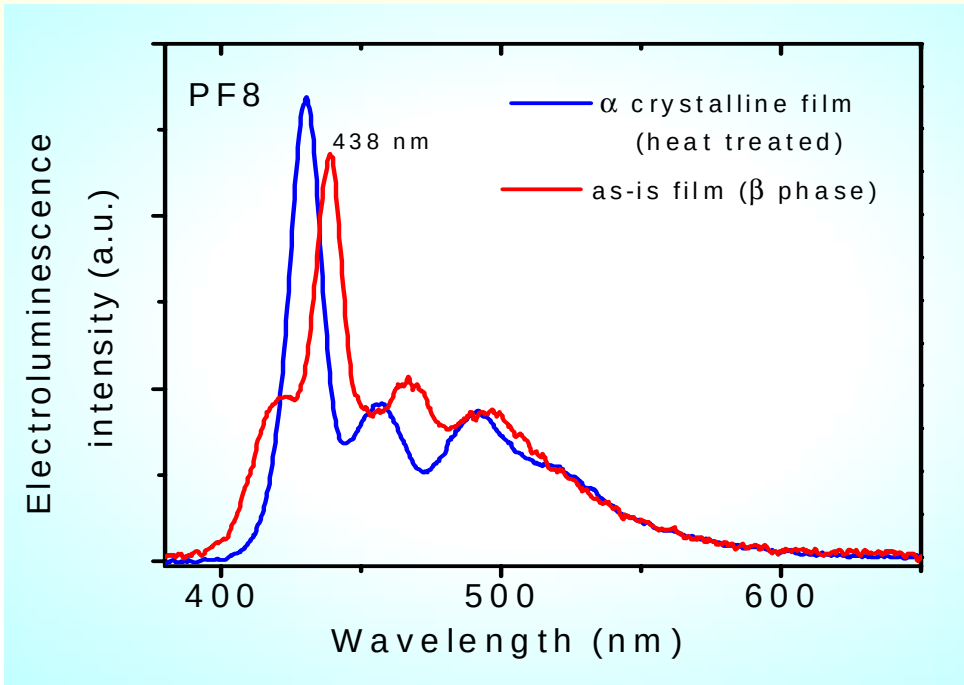
Electroluminescence: PF8-based LED

Before thermal cycling to n-LC mesophase



After cycling from n-LC mesophase



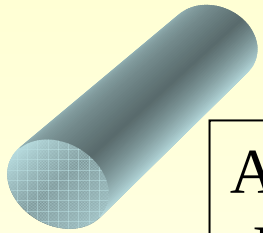


Bond polarizability model

molecular polarizability =sum of the bond polarizabilities

The polarizability of a bond is given by:

$$\Pi^j = \begin{bmatrix} \alpha_{\parallel}^j & 0 & 0 \\ 0 & \alpha_{\perp}^j & 0 \\ 0 & 0 & \alpha_{\perp}^j \end{bmatrix}$$



Assumptions:
- Isolated bonds
- Cylindrical symmetry
- Zero-order approx

($\alpha_{\parallel}$ and $\alpha_{\perp}$ are functions of the bond length)

The bond polarizability for a pair of given atoms is given by

$$\Pi_{\alpha\beta} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})\delta_{\alpha\beta} + (\alpha_{\parallel} - \alpha_{\perp})\left(\frac{\hat{R}_{\alpha}\hat{R}_{\beta}}{R^2} - \frac{1}{3}\delta_{\alpha\beta}\right)$$

R is a vector connecting two atoms.

Bond polarizabilities are transferable between different compounds*

*D. Bermejo *et al.* Solid State Commun. **42**, 153 (1982).

Static polarizability and Raman intensities of fullerenes can be predicted very well.

Raman intensity

$$Raman\ Intensity \propto \sum_{f=1}^{3N} \frac{\langle n(\omega_f)+1 \rangle}{\omega_f} \left| \sum_{\alpha\beta} \eta'_\alpha \eta_\beta P_{\alpha\beta,f} \right|^2 \times \delta(\omega - \omega_f)$$

$$\boldsymbol{P}_{\alpha\beta,f} = -\sum_{\ell} \sum_{\text{Bonds}} \left[\left(\frac{\alpha'_{\parallel} + 2\alpha'_{\perp}}{3} \right) \hat{\mathbf{R}}_0(\ell) \cdot \vec{\chi}(\ell \mid f) \delta_{\alpha\beta} \right.$$

Bond stretching: isotropic

$$+ \left(\alpha'_{\parallel} - \alpha'_{\perp} \right) \left(\hat{\boldsymbol{R}}_{0\alpha}(\ell) \hat{\boldsymbol{R}}_{0\beta}(\ell) - \frac{1}{3} \delta_{\alpha\beta} \right) \hat{\mathbf{R}}_0(\ell) \cdot \vec{\chi}(\ell \mid \boldsymbol{f})$$

Bond stretching:anisotropic

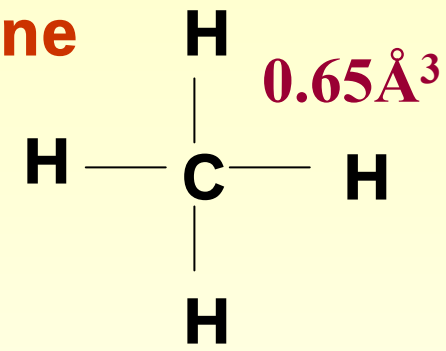
$$\left. + \left(\frac{\alpha_{\parallel} - \alpha_{\perp}}{\boldsymbol{R}_0(\ell)} \right) \left(\begin{array}{l} \hat{\boldsymbol{R}}_{0\alpha}(\ell) \chi_\beta(\ell \mid \boldsymbol{f}) + \hat{\boldsymbol{R}}_{0\beta}(\ell) \chi_\alpha(\ell \mid \boldsymbol{f}) \\ -2 \hat{\boldsymbol{R}}_{0\alpha}(\ell) \hat{\boldsymbol{R}}_\beta(\ell) \left[\hat{\mathbf{R}}_0(\ell) \cdot \vec{\chi}(\ell \mid \boldsymbol{f}) \right] \end{array} \right) \right]$$

Bond rotation

In C_{60} there are 2 types of bonds- 6 parameters

Static polarizability

Methane

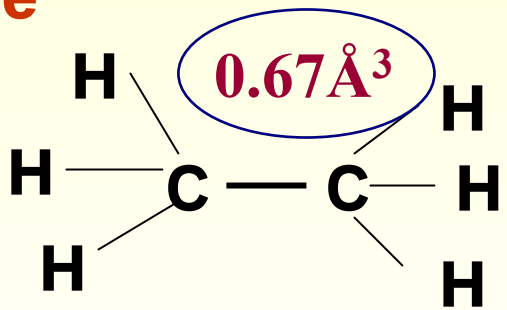


$$\overline{\alpha} = \frac{1}{3}\left(\alpha_{\parallel} + 2\alpha_{\perp}\right)$$

$$\overline{\alpha}_{CH_4} = 2.59\ \mathring{A}^3$$

$$\frac{1}{3}(\alpha_{\parallel} + \alpha_{\perp})^{C-H} = \frac{1}{4}(2.59)\ \mathring{A}^3$$

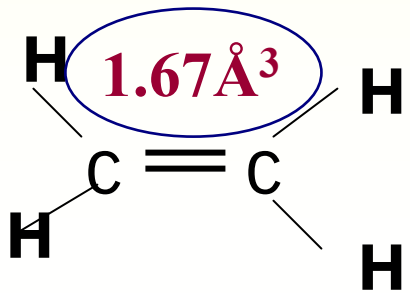
Ethane



$$\overline{\alpha}_{C_2H_6} = 4.56\ \mathring{A}^3$$

$$\frac{1}{3}(\alpha_{\parallel} + \alpha_{\perp})^{C-C} = (4.56 - 6\times 0.65)\ \mathring{A}^3$$

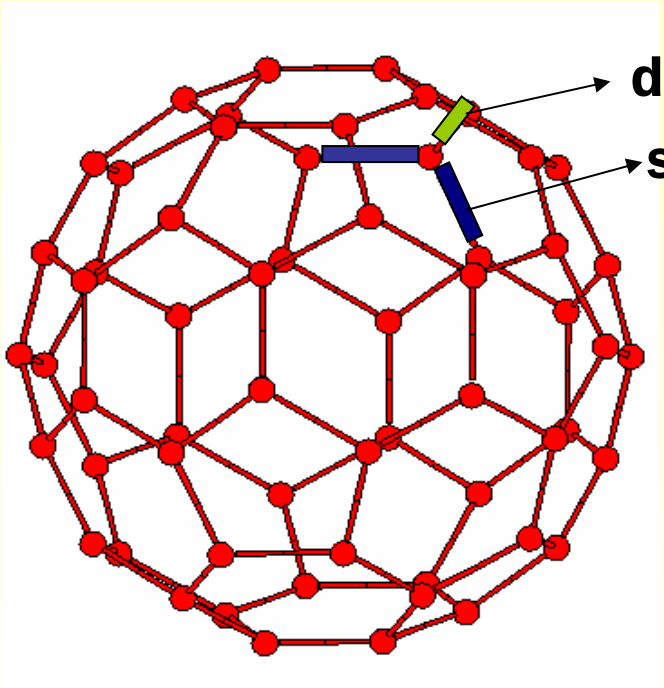
Ethylene



$$\overline{\alpha}_{C_2H_4} = 4.22\ \mathring{A}^3$$

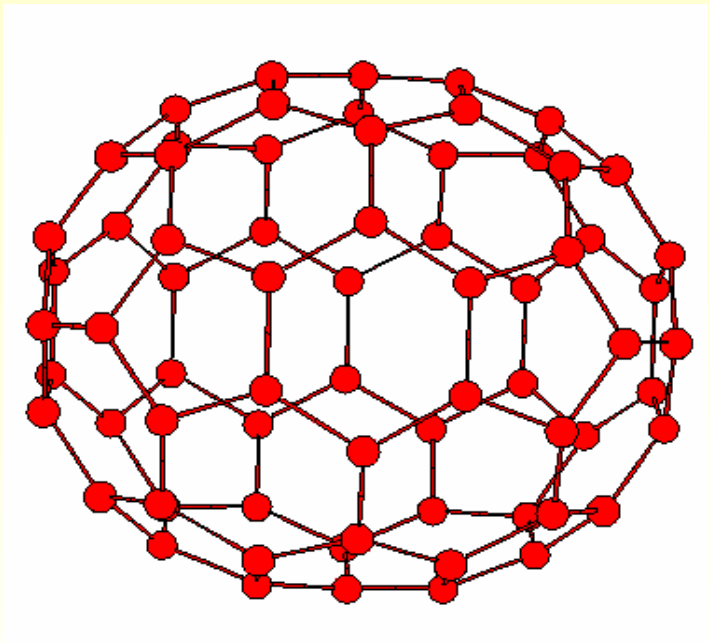
$$\frac{1}{3}(\alpha_{\parallel} + \alpha_{\perp})^{C=C} = (4.22 - 4\times 0.65)\ \mathring{A}^3$$

Using hydrocarbon polarizabilities



C_{60}: 60 single bonds
30 double bonds

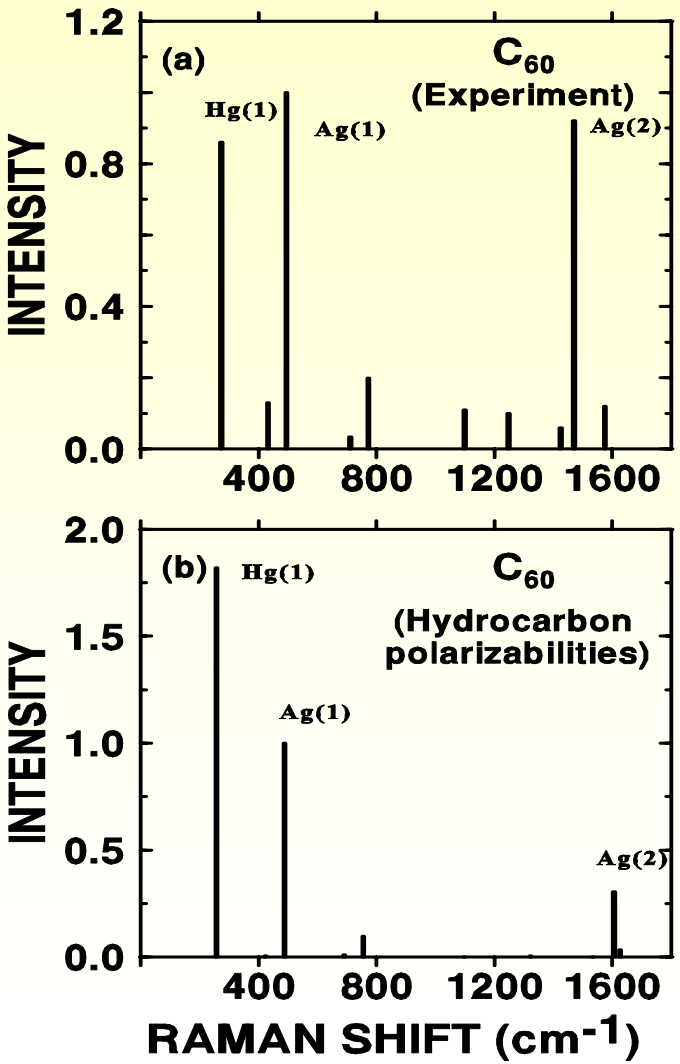
α(cal.)=89.2 Å^3
α(expt.)=83-85 Å^3

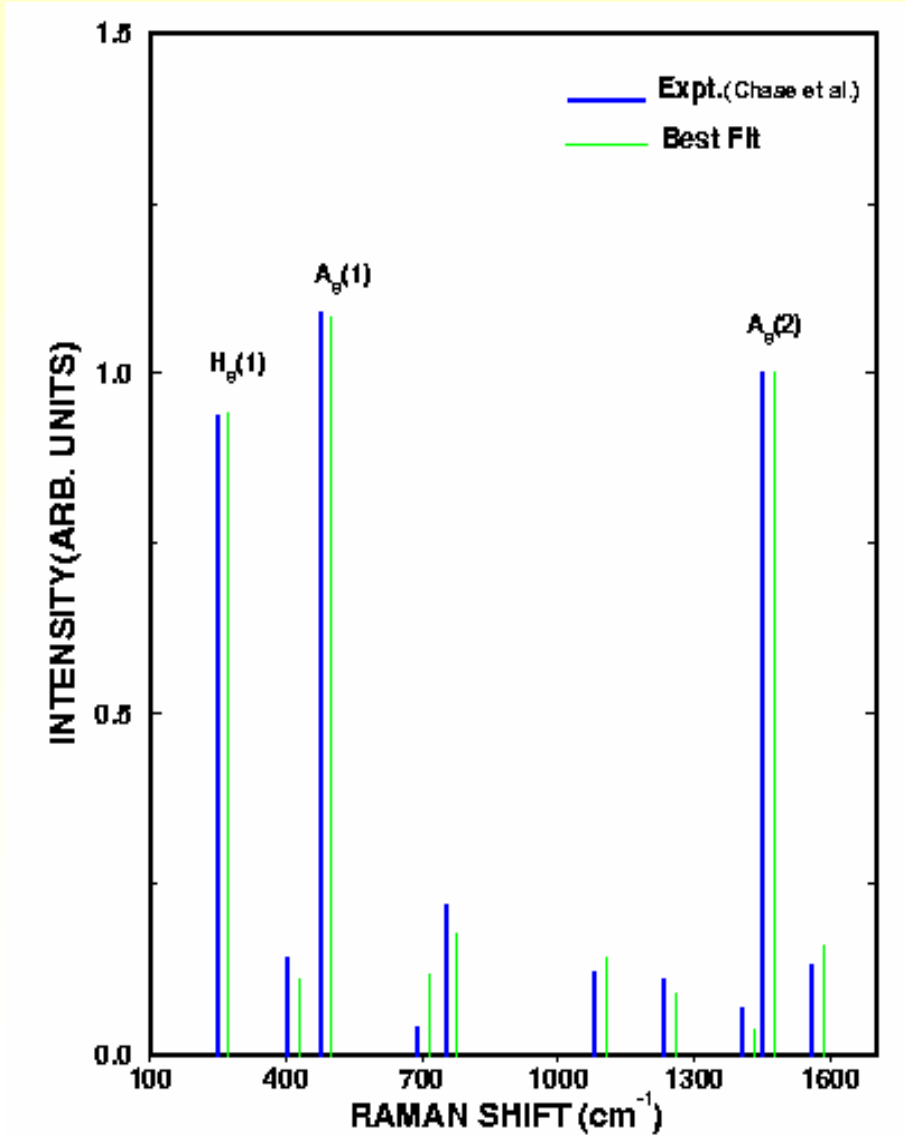


C_{70}: 8 different bonds
1.40-1.45Å
Cutoff: 1.425Å

α(cal.)=109.2 Å^3
α(expt.)=94Å^3

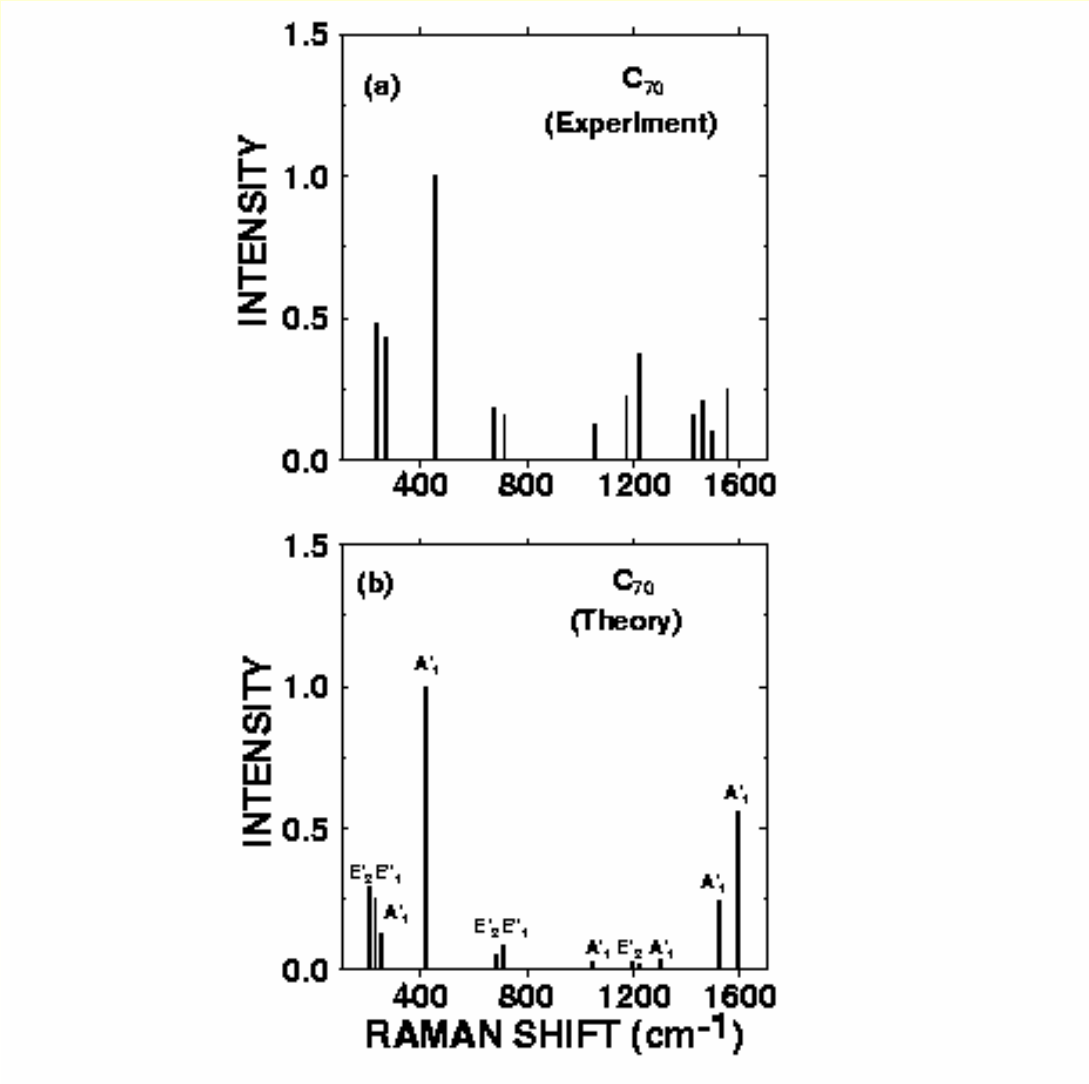
C_{60}: Raman intensity





Guha *et al.* Phys. Rev. B 53, 13106 (1996).

Transferability of parameters: C_{70}



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- **José Menéndez (Arizona State University)**
- **John Page (Arizona State University)**

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Your thoughts….

How does one theoretically handle large systems with long range charge transfer excitations along with coupling of the electronic and nuclear degrees of freedom?

What methodology should we use for calculating the Raman spectra of conjugated polymers?