Design of novel conjugated polymers based on fluorene, carbazole and borafluorene

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Regroupement québécois sur les matériaux de pointe

Université de Montréal

Outline

- Motivate the interest in organic material
- Stoke's shift and localized exciton
- Fluorene, Carbazole and Borafluorene
- Ladder Polymers
- Results on non-ladder and ladder polymers
- Interesting candidates…
- Conclusion

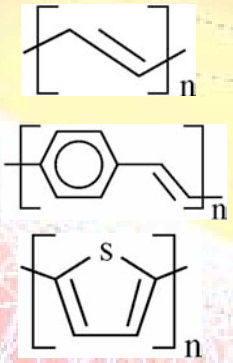
Polymers vs Semiconductors

The semiconductor industry...

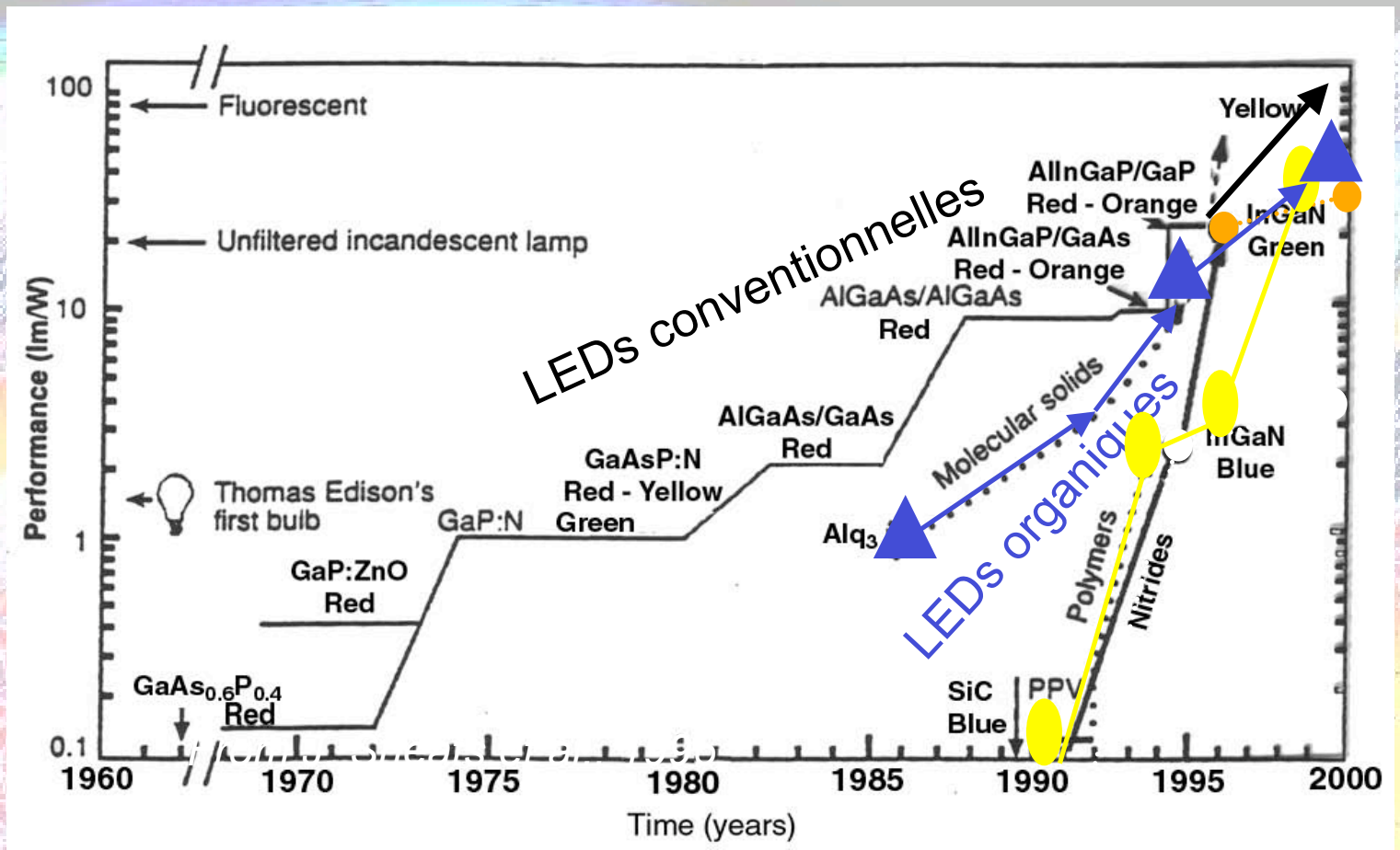
- uses materials with same structure but made out of different elements
  ex: III-V, II-VI,…
- devices are made by combining different materials in order to tailor the electronic properties
  ex: heterostructures, superlattices, quantum wells,...

Polymers...

- different atomic structures of carbon atoms
  ex: polyacetylene,
  p(*p*-phenylenevinylene),
  thiophene, ...



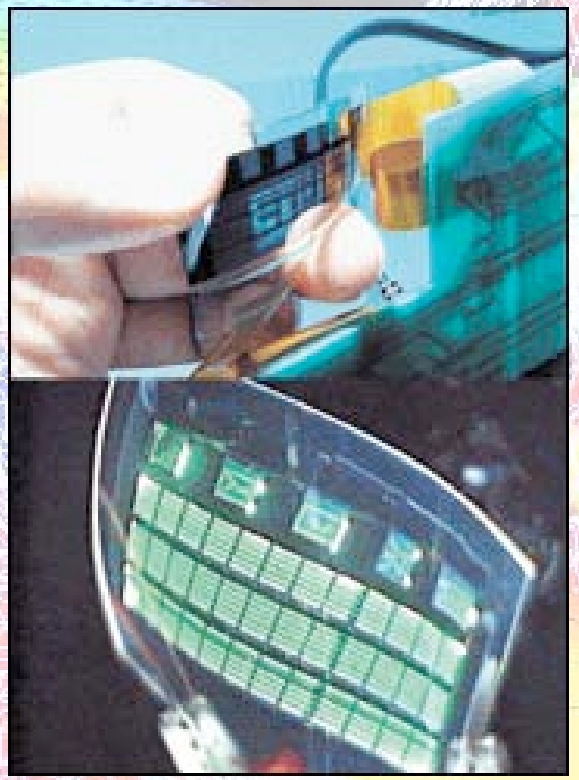
Emergence of organic materials



Advantages of OLED

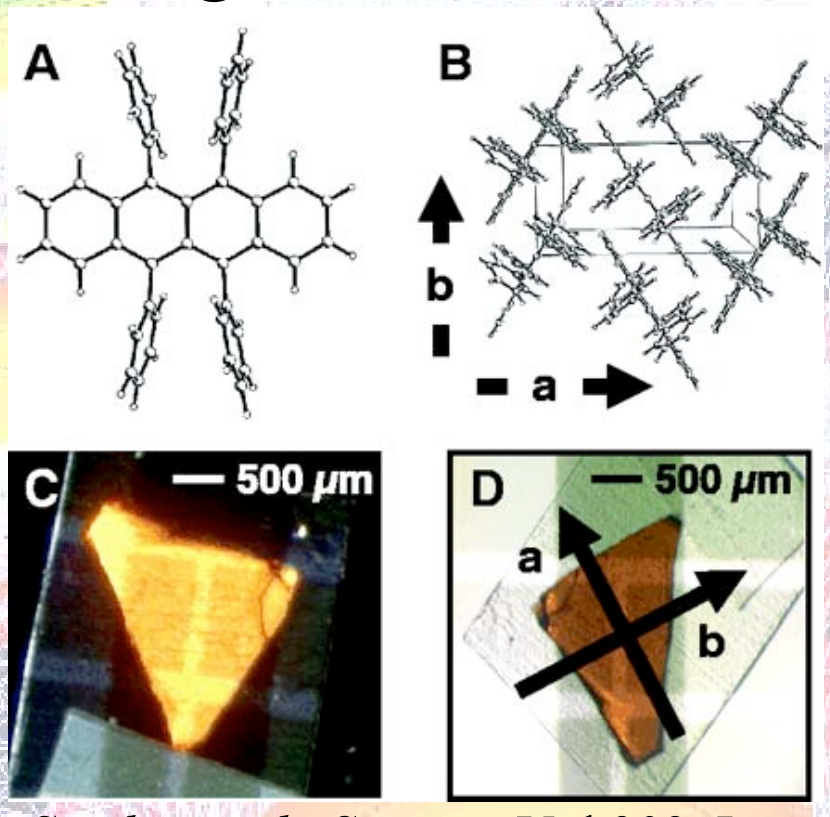
- Wide range of colours
- High performance
- Can cover large surface, low weight
- Low cost of fabrication
- Flexible display
- Still some challenges…life time

Flexible display



…the next step…

Organic Field Effect Transistor (OFTF)



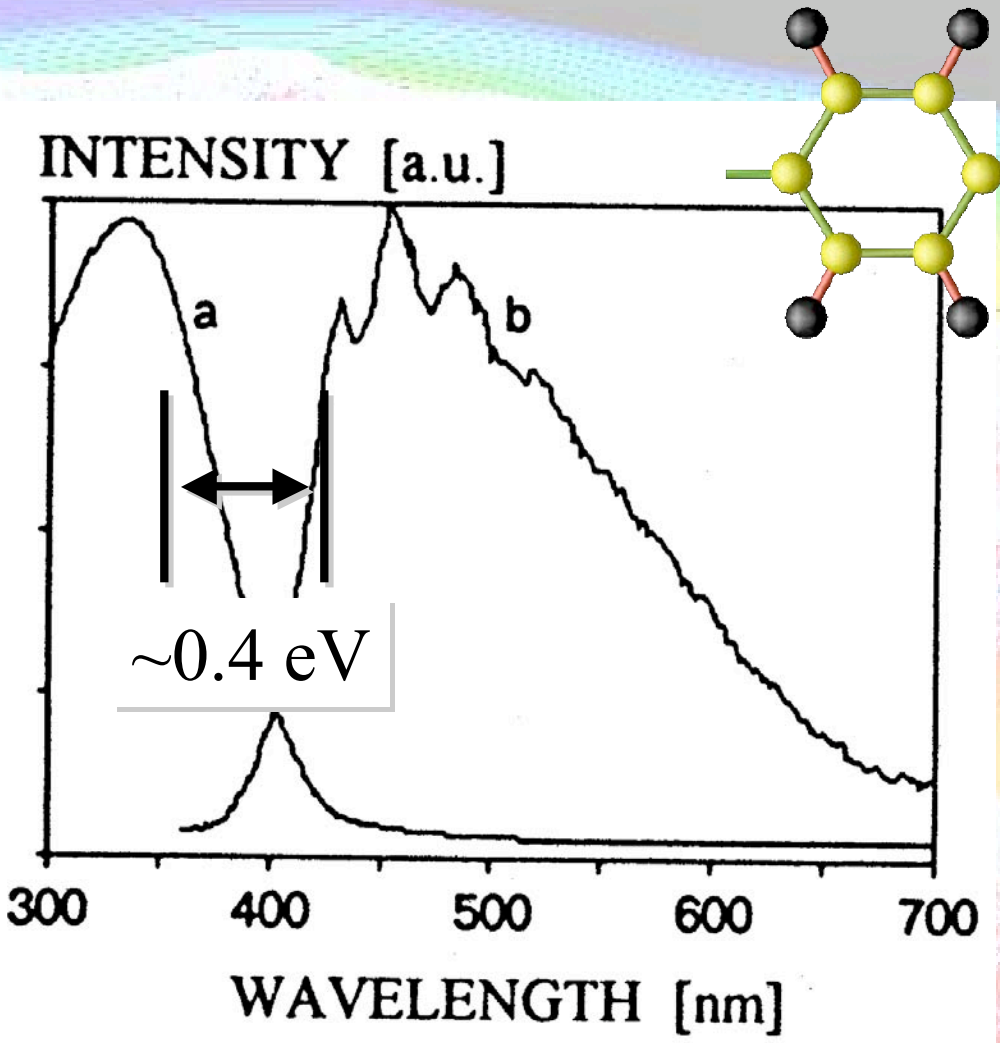
Sundar et al., Science, Vol 303, Issue 5664, 1644-1646 , 12 March 2004

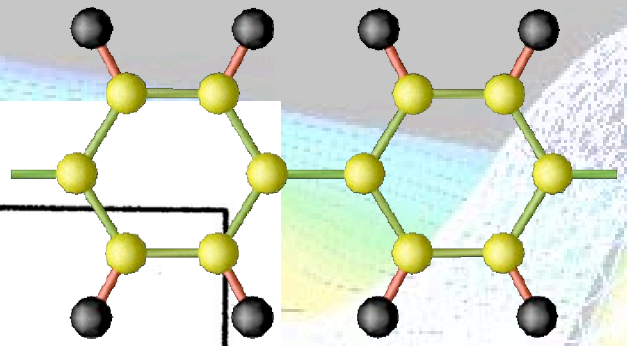
$\mu \sim 15$ V•s/cm^2

Si: ~ 500 V•s/cm^2

But mobility remains low…

Poly(p-phenylene) (PPP)





Stoke`s shift

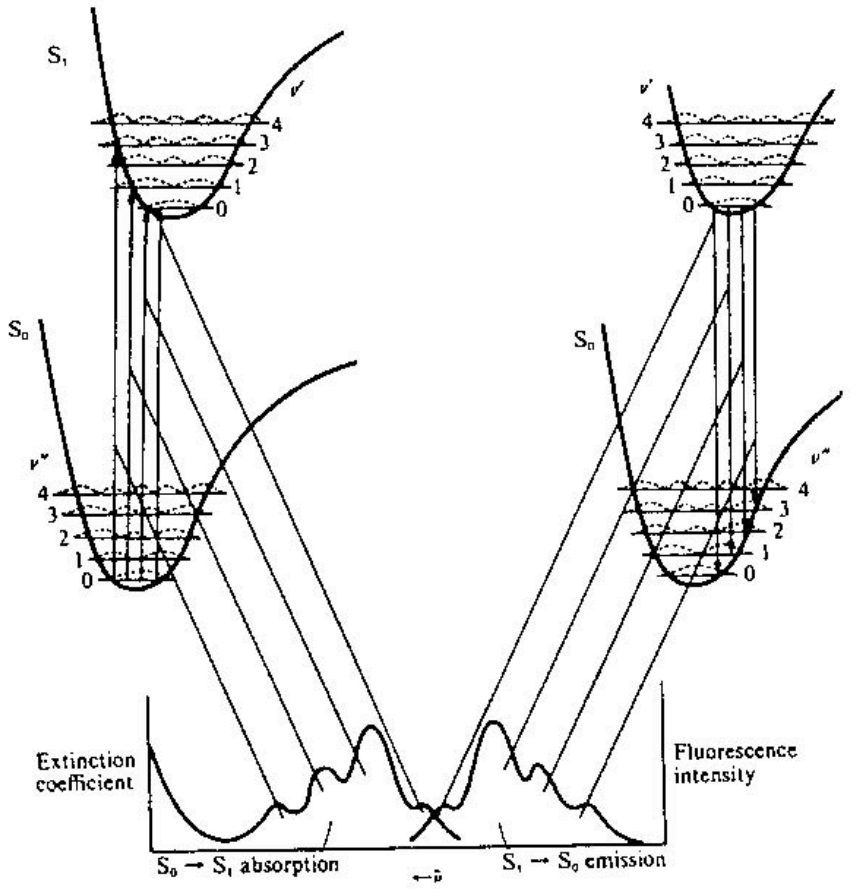
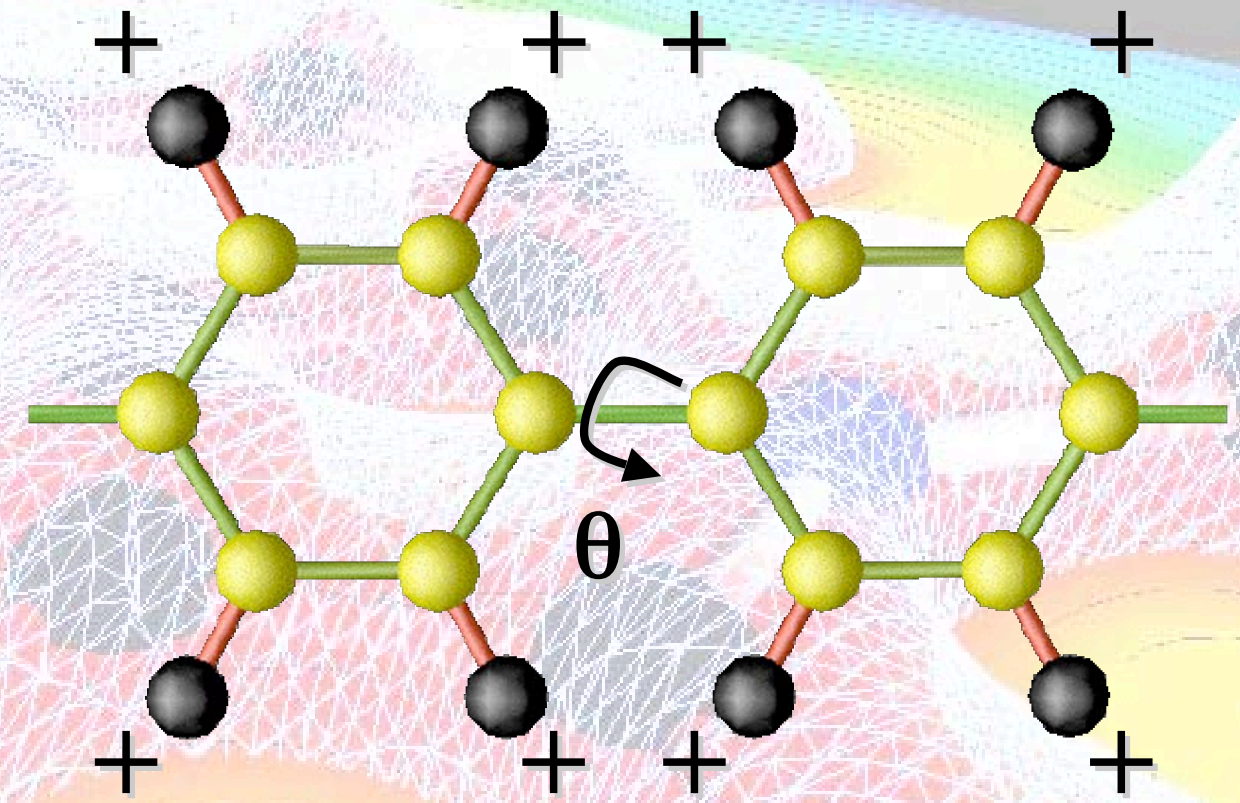
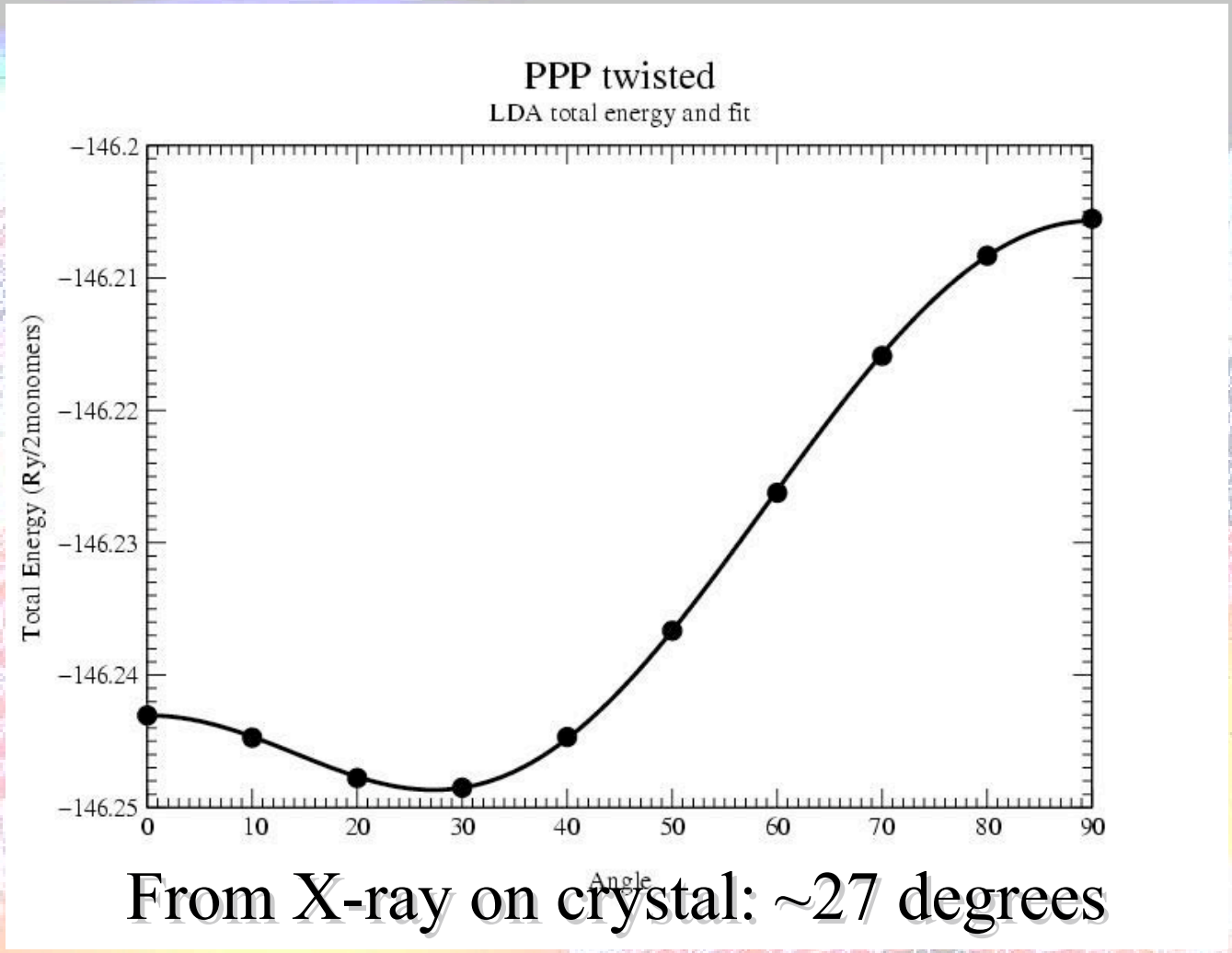


FIG. 26. Absorption and emission processes between the S_0 and S_1 electronic states of an organic molecule. [A. Kearwell and F. Wilkinson, in *Transfer and Storage of Energy by Molecules* (G. M. Burnett and A. M. North, eds.), Vol. 1, Wiley, New York (1969)].

Where does it comes from…

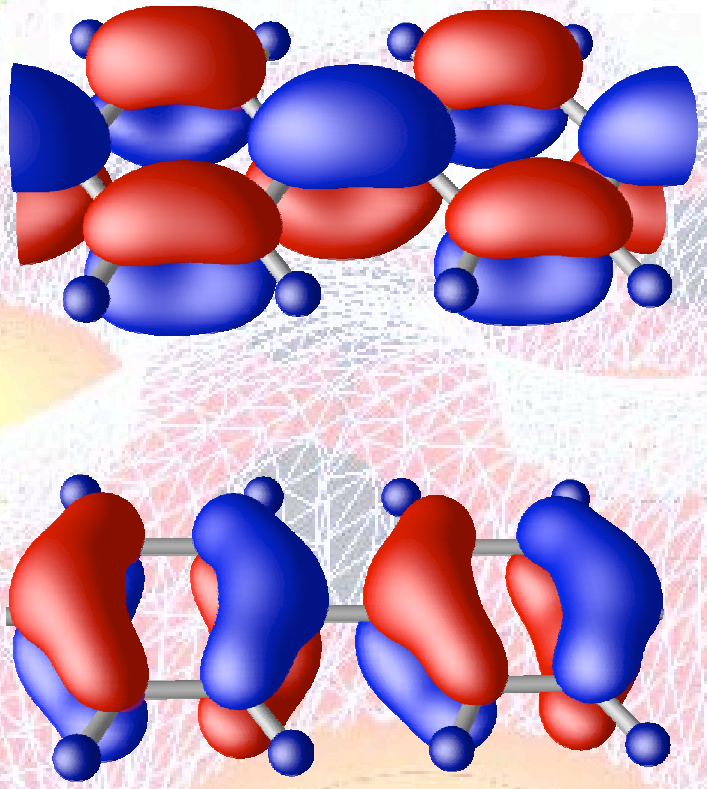


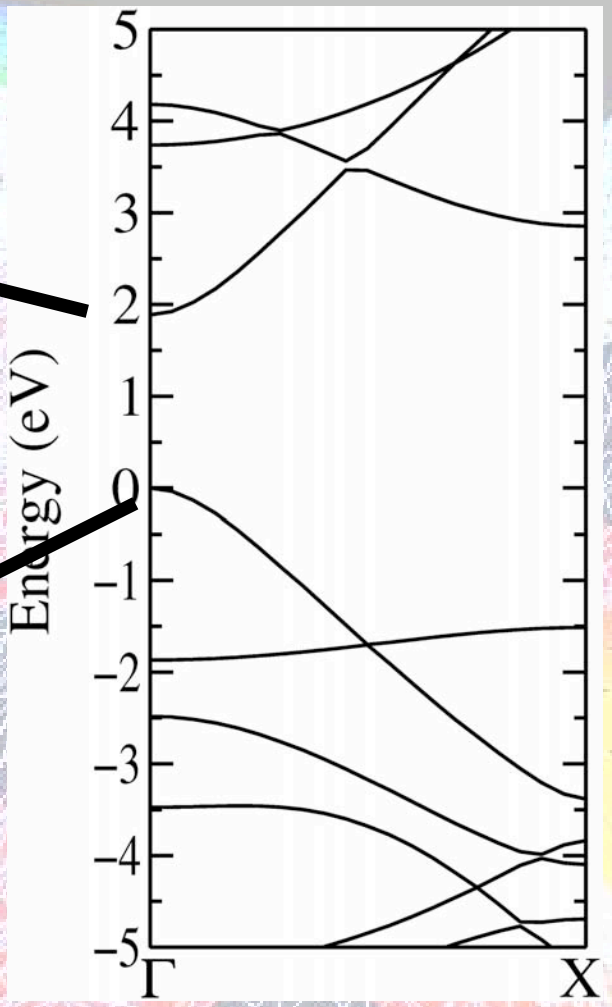
DFT calculations



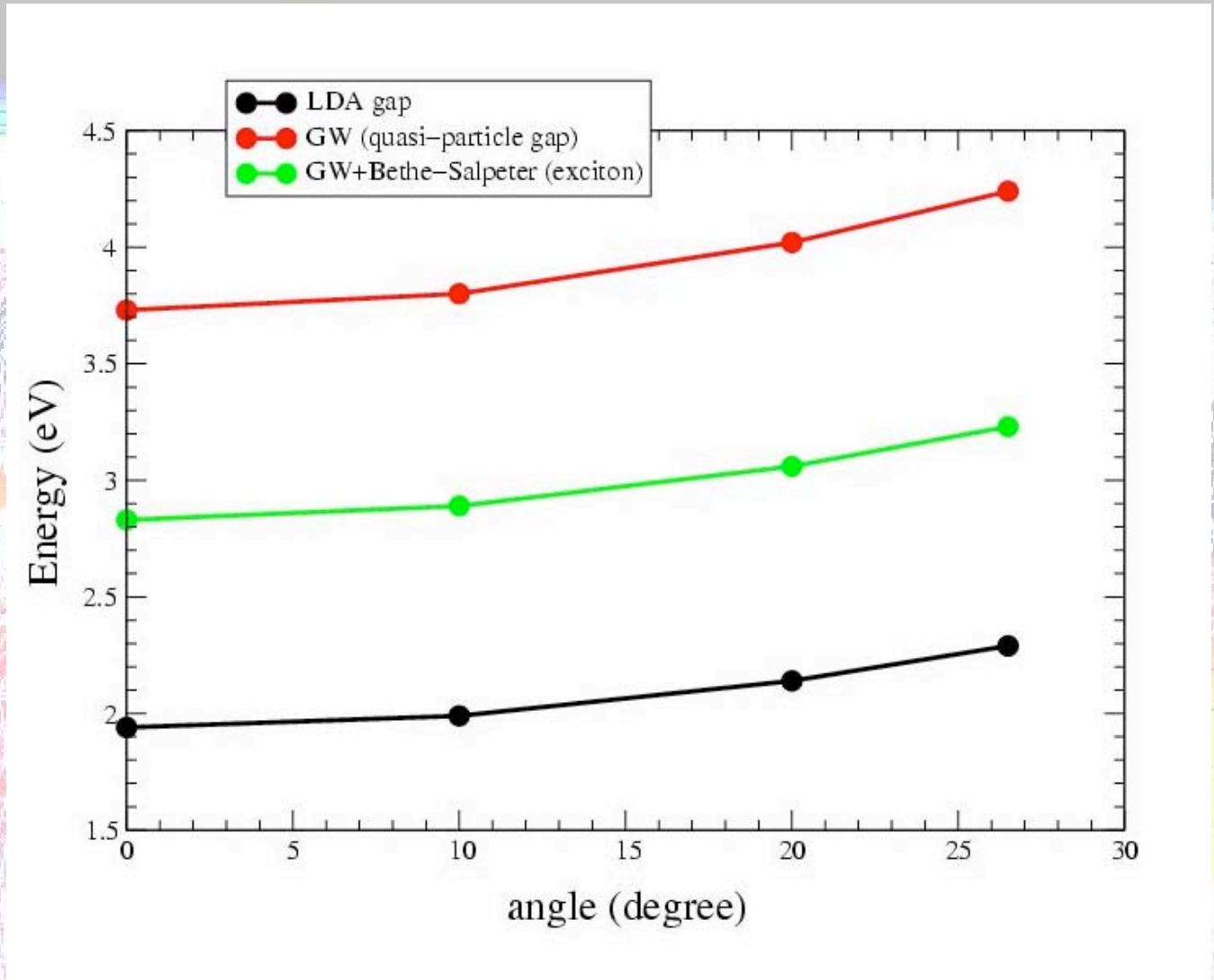
From X-ray on crystal: ~27 degrees

Wavefunctions: PPP

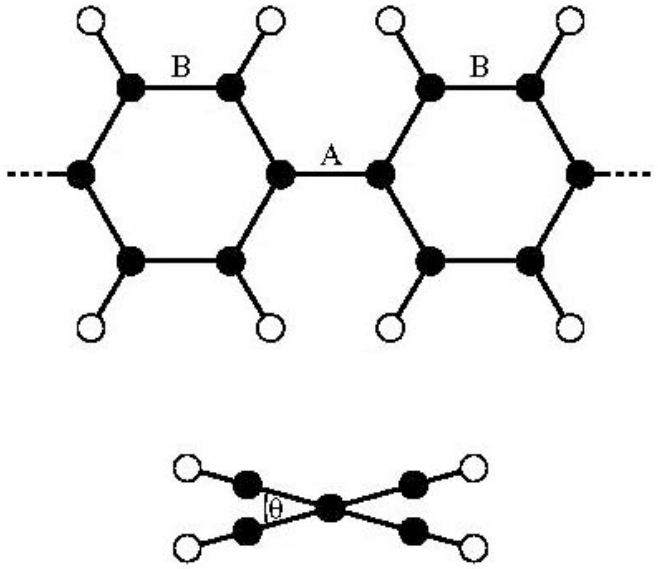


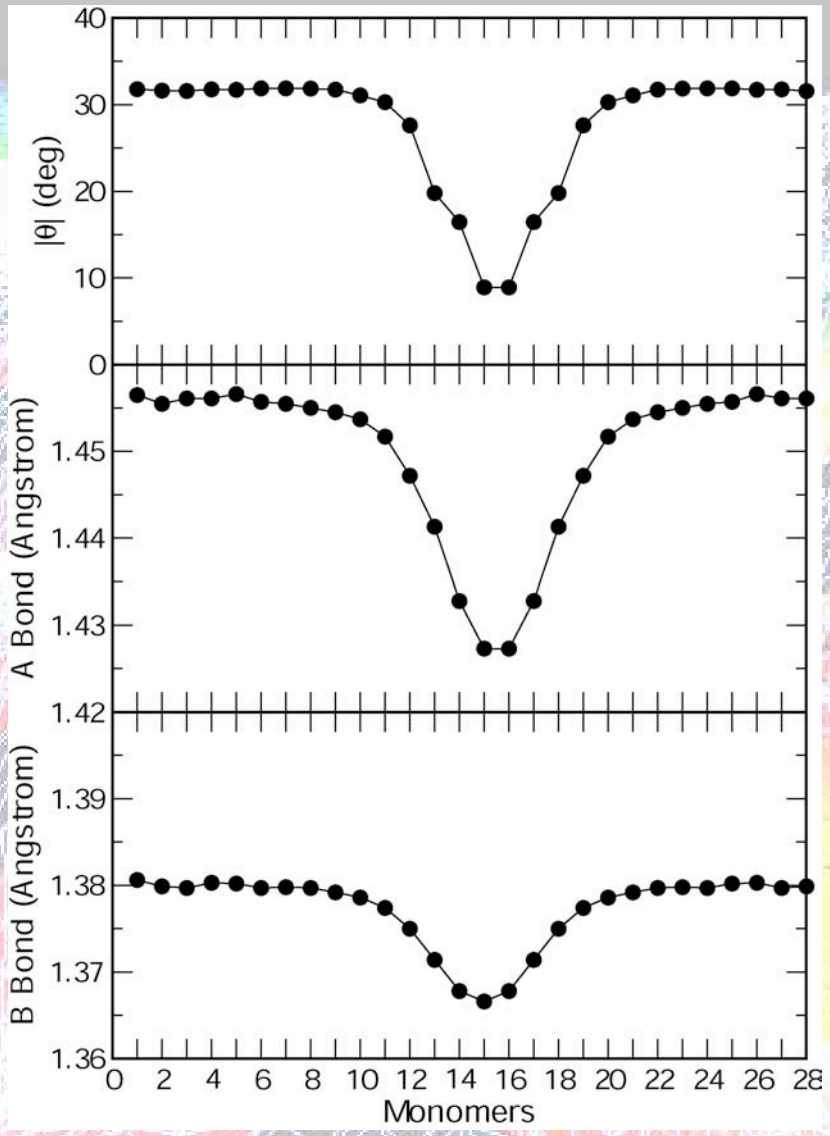


Excited state



Bounded exciton

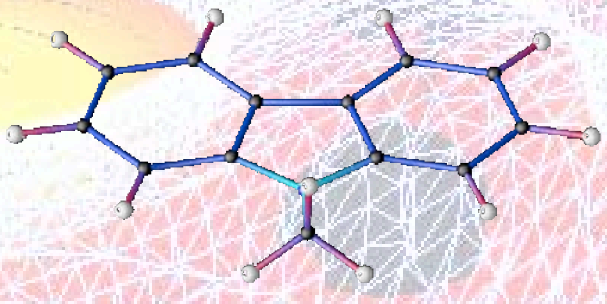




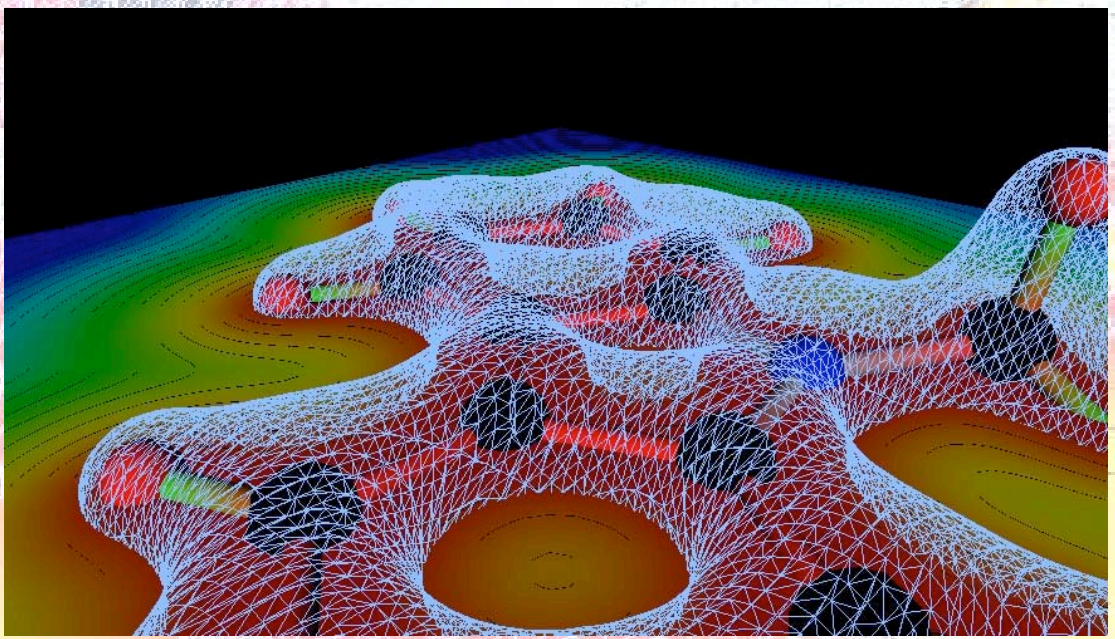
E. Artacho, M. Rohlfing, M. Côté, P. D. Haynes, R. J. Needs, and C. Molteni, submitted (cont-mat/0402197)

Polymers with Carbazole

- Goal is to fabricate polymers for electronic transports
- In collaboration with the experimental group of Mario Leclerc at the University Laval

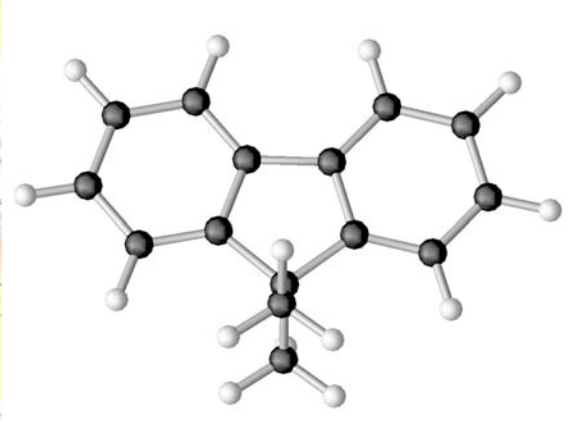


Carbazole molecule



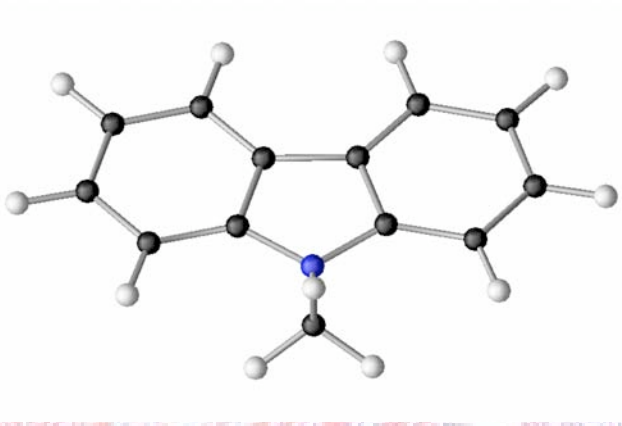
And other molecules…

fluorene



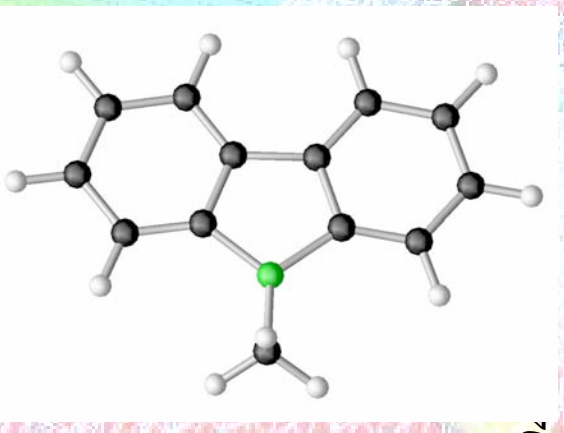
C

carbazole



N

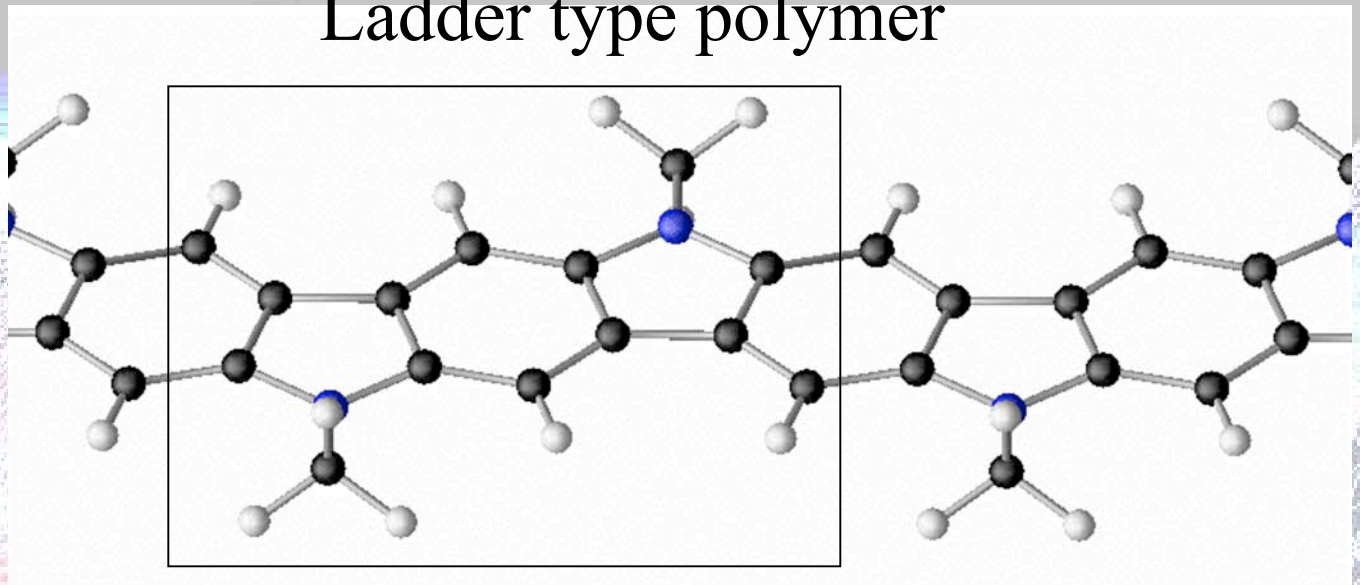
borafluorene



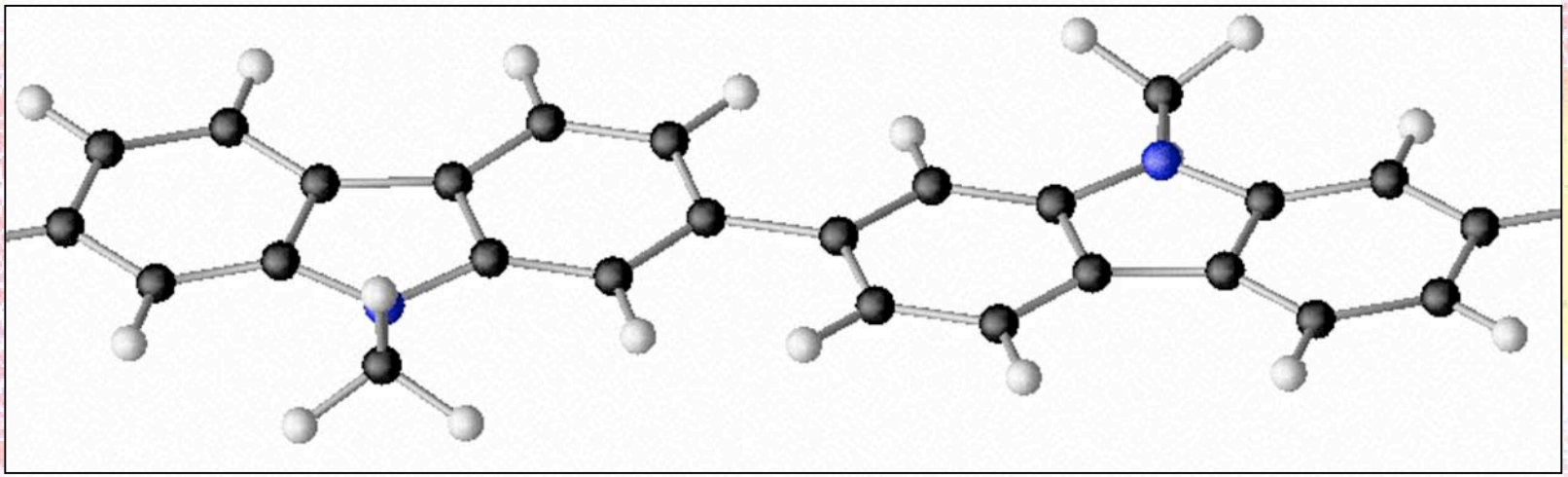
B

Ladder polymers

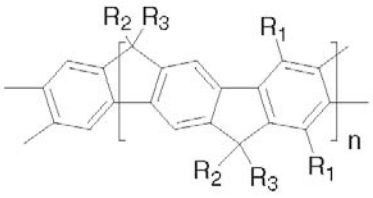
Ladder type polymer



Normal polymer

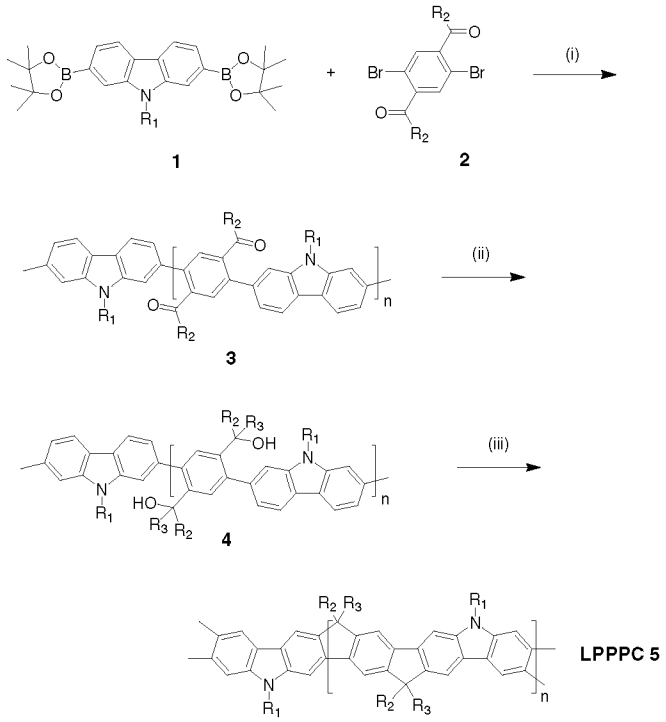


MeLPPP and LPPPC



MeLPPP

S. A. Patil, U. Scherf and A. Kadashchuk, Adv. Funct. Mater, 13, no 8, p. 609, 2003



Scheme 1. Synthesis of ladder poly(*para*-phenylene carbazole) (LPPPC).

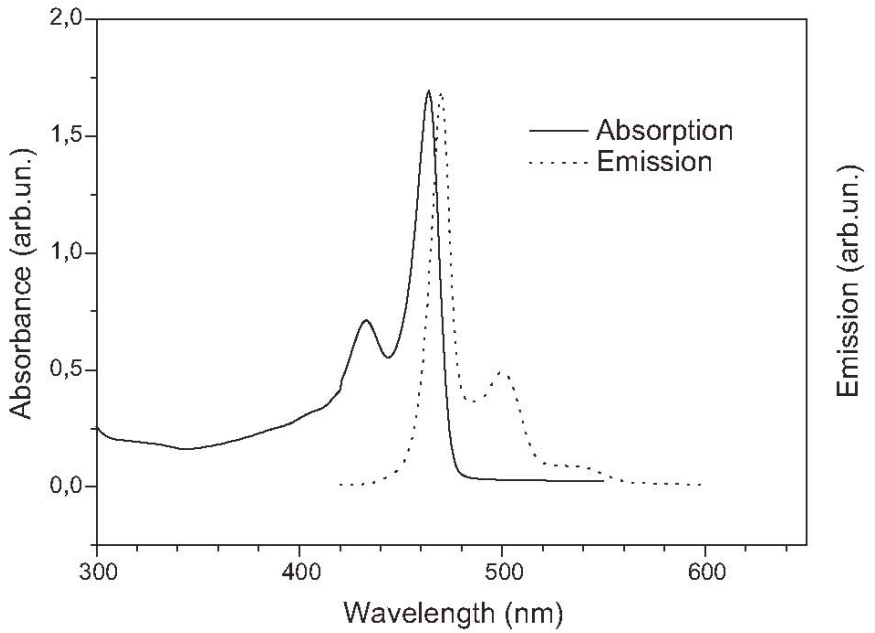
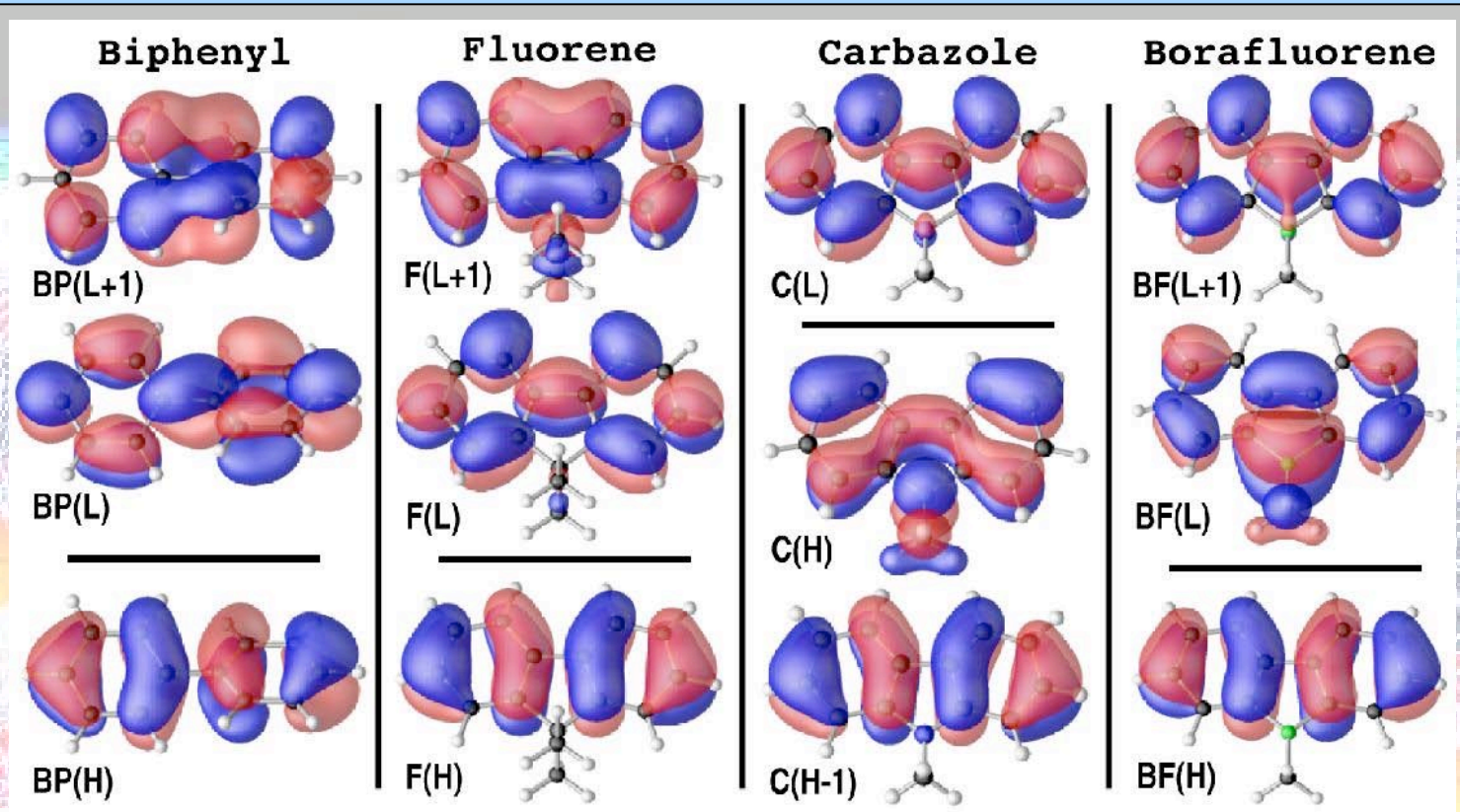


Fig. 1. Absorption and emission spectra of LPPPC ($CHCl_3$, dilute solution).

Abinit Workshop 2004

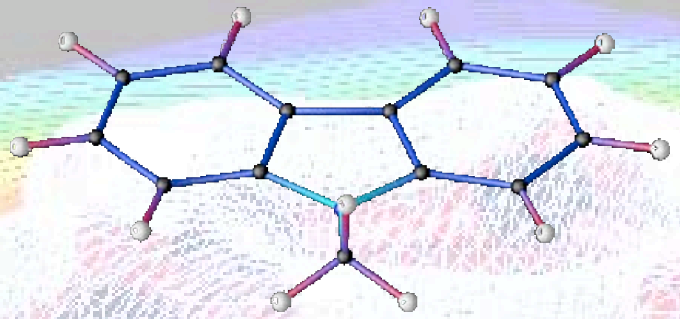
TDDFT on molecules



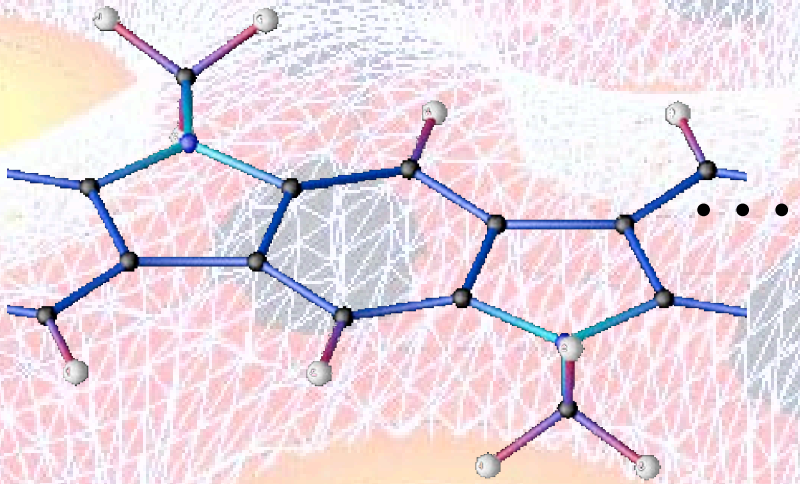
	excitation energy				polarization[h]	
	vapor (eV)	crystal (eV)	DFT (eV)	TDDFT (eV)	exptl	DFT
biphenyl	4.37[a]	4.11[b]	3.84	4.46	L[b]	L
fluorene	4.19[c]	4.07[d]–4.10[e]	3.58	4.24	L[d,e]	L
carbazole	3.81[c]	3.618[f]	3.22	3.66	S[f]	S
borafluorene	3.02[g]		2.46	2.78		L

Brière and Côté,
J. Phys. Chem. B,
108, p. 3123, 2004.

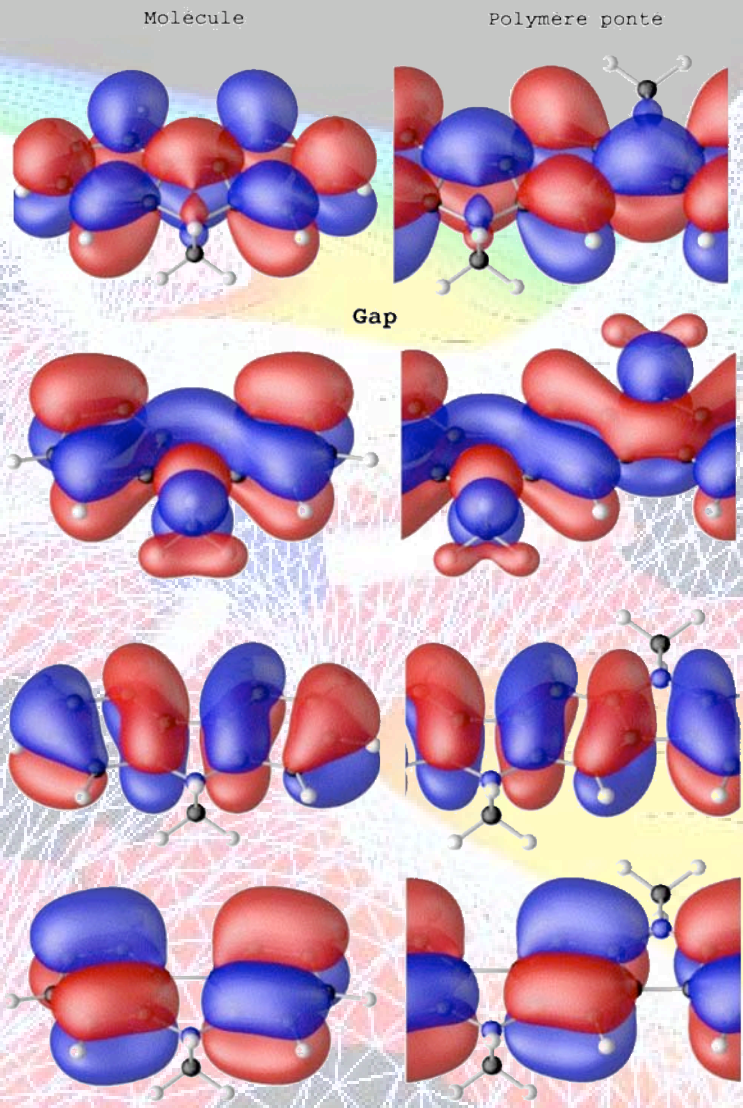
Ladder Polymer with Carbazole



molecule

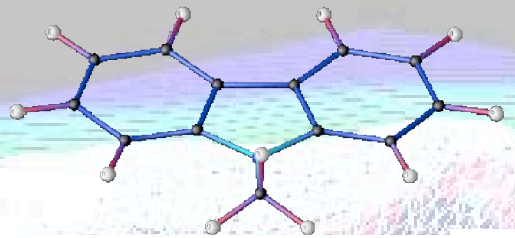


ladder polymer

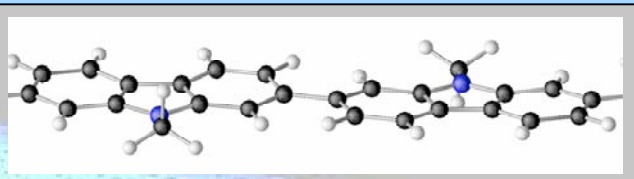


Abinit Workshop 2004

Polymer, not ladder

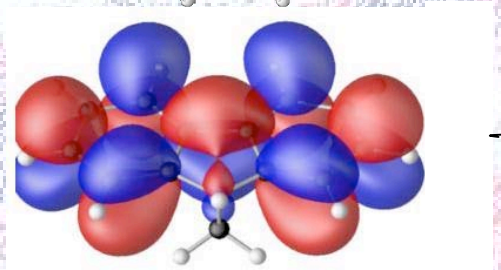


...

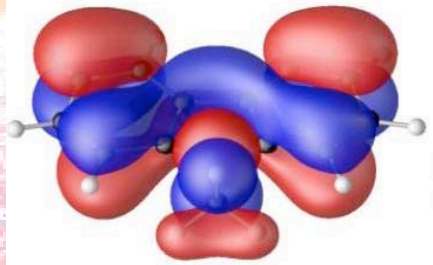


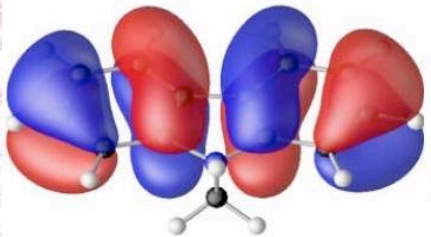
...

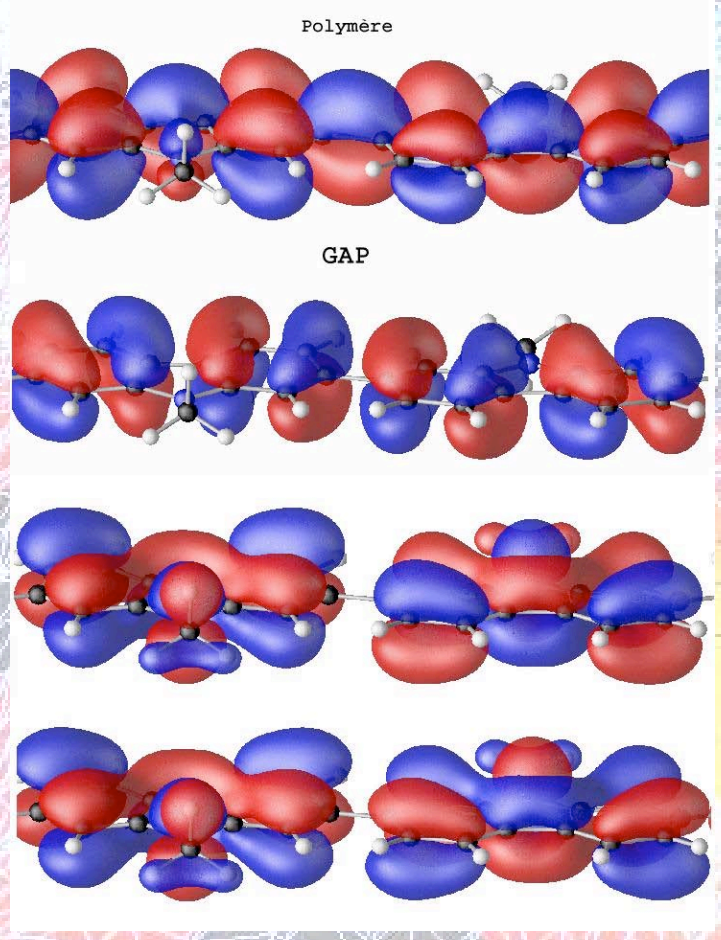
Wavefunctions at Gamma



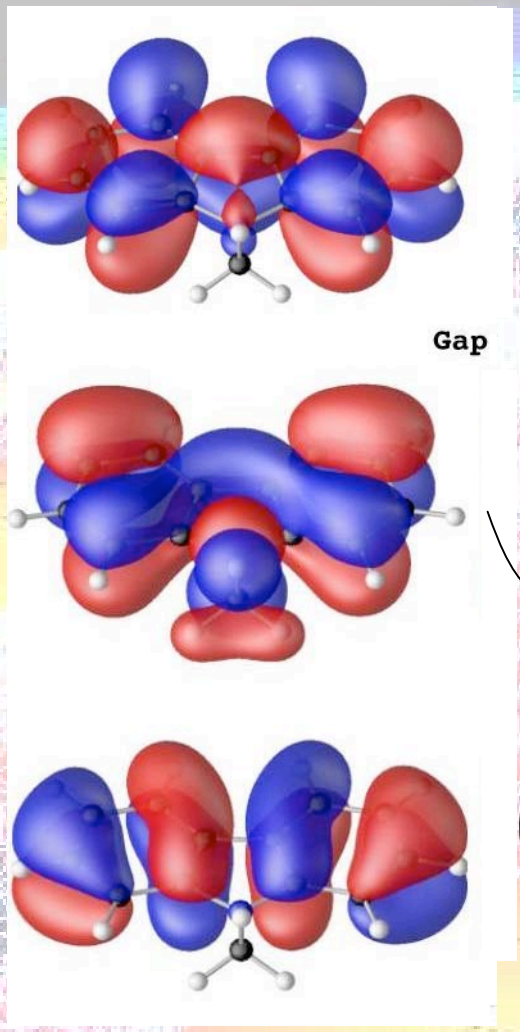
Gap

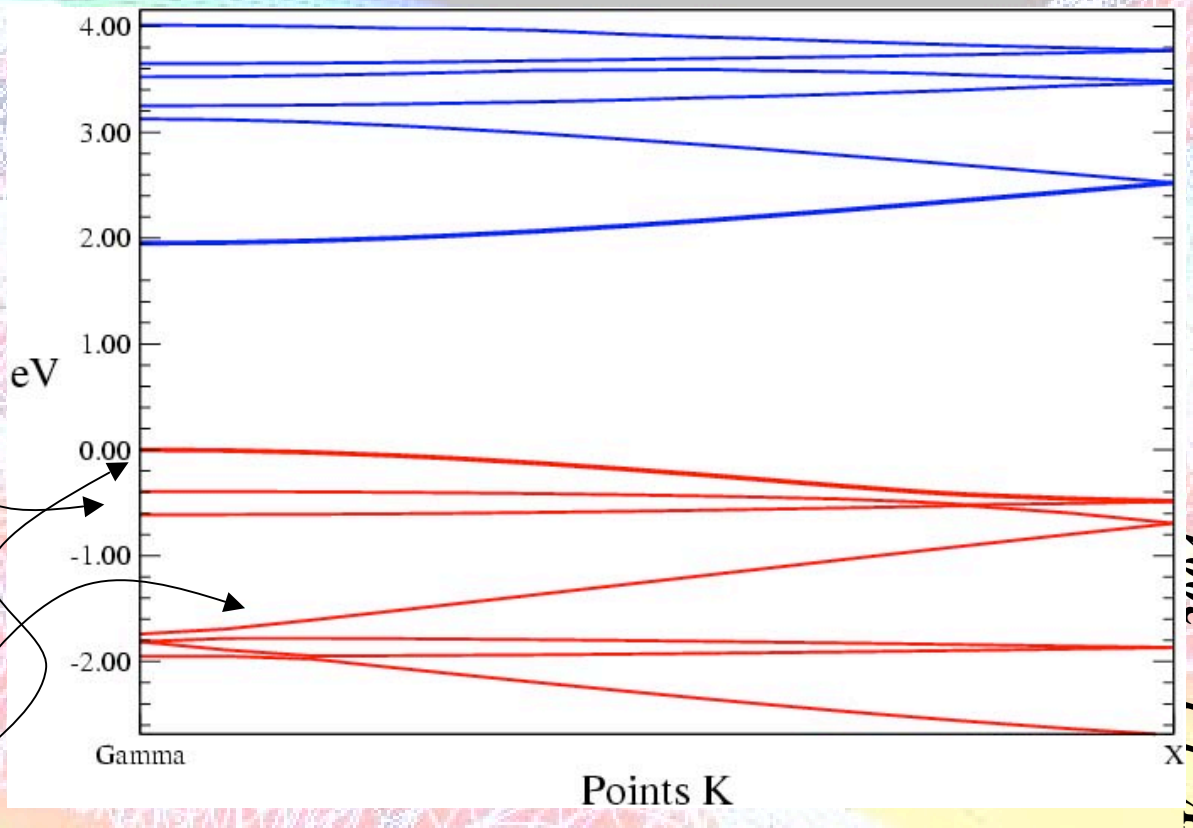






Polymer, not ladder(2)



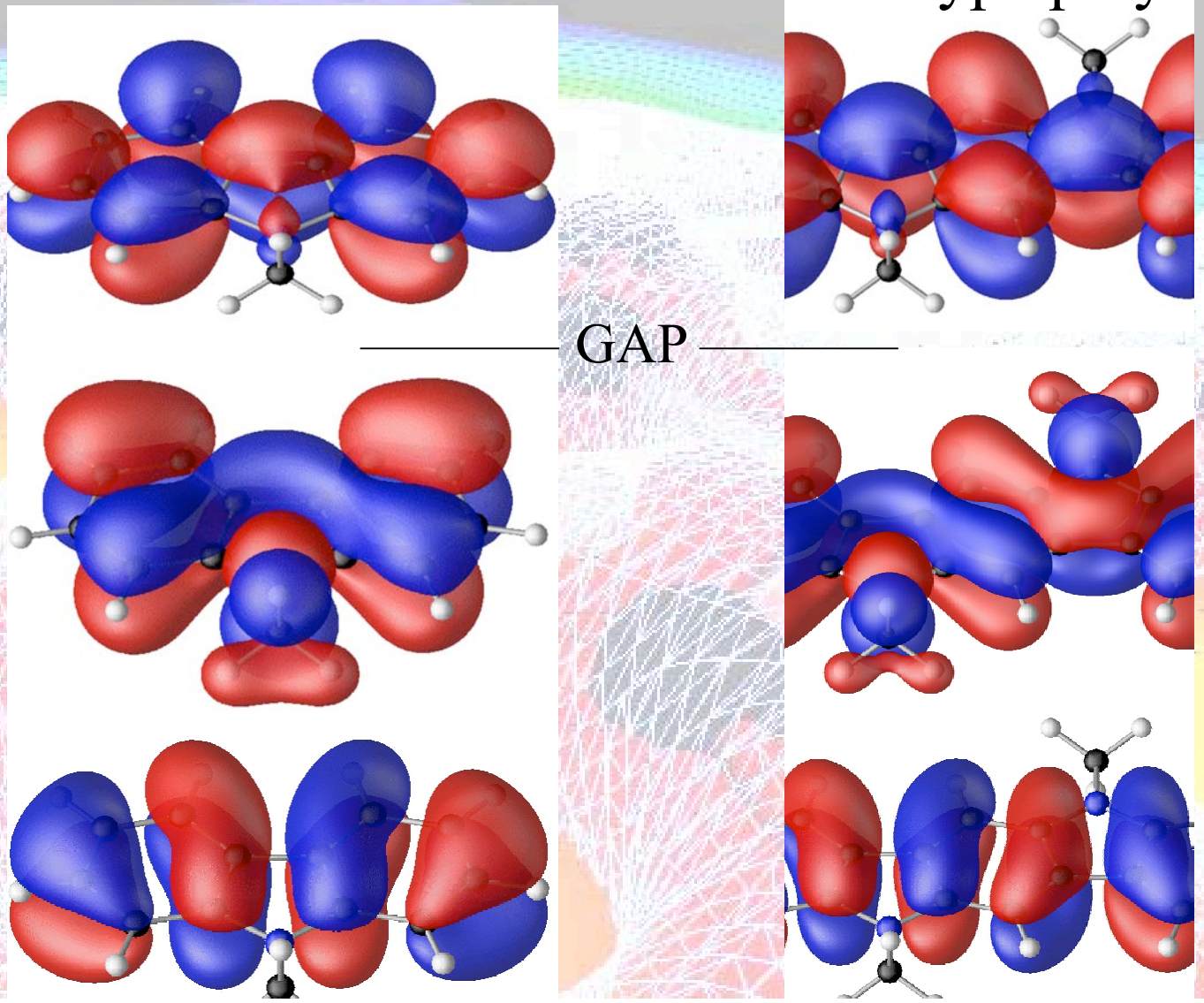


Brière and Côté, J. Phys. Chem. B, 108, p. 3123, 2004.

Wave functions comparison I

Carbazole

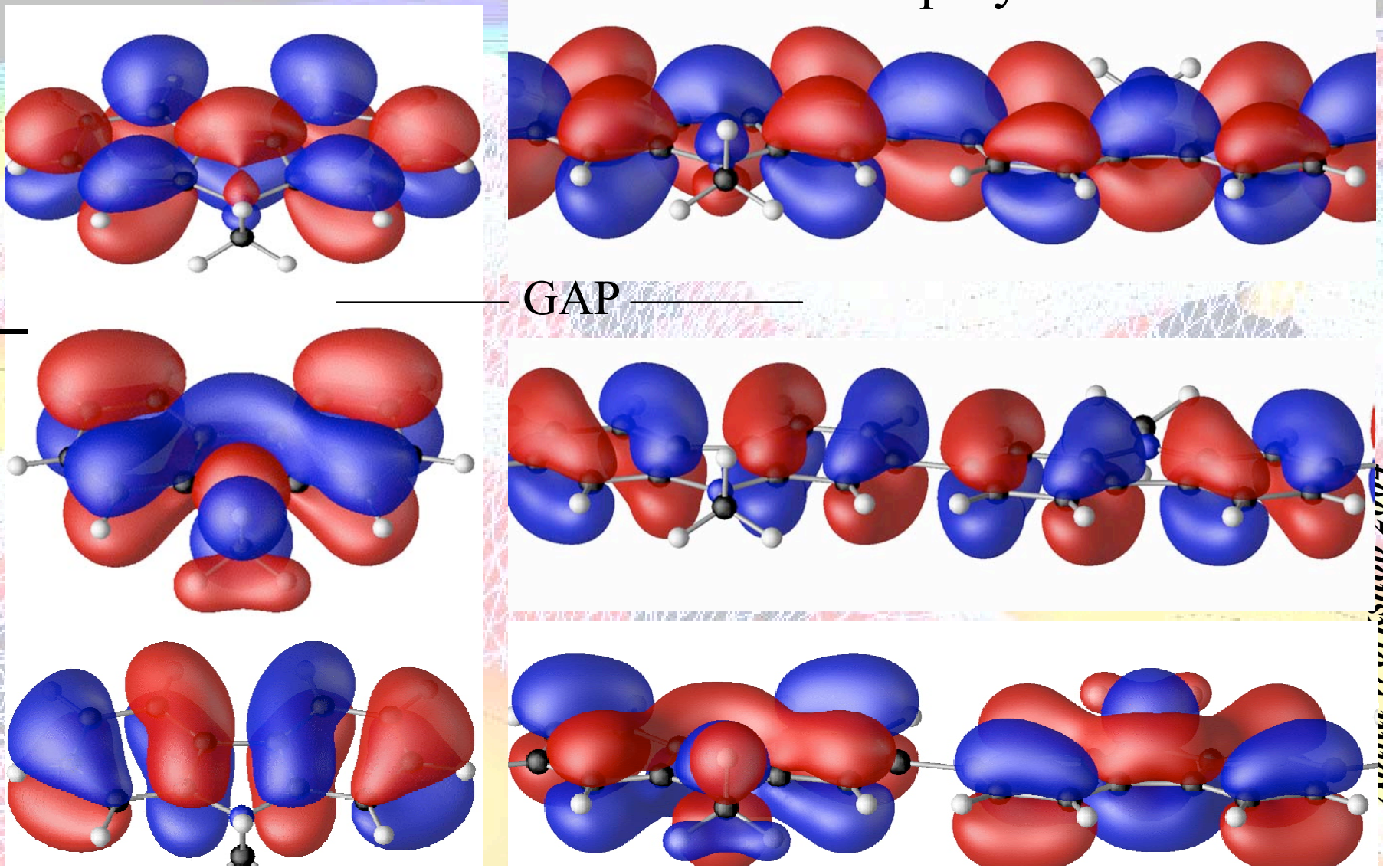
Ladder type polymer



Wave functions comparison II

Carbazole

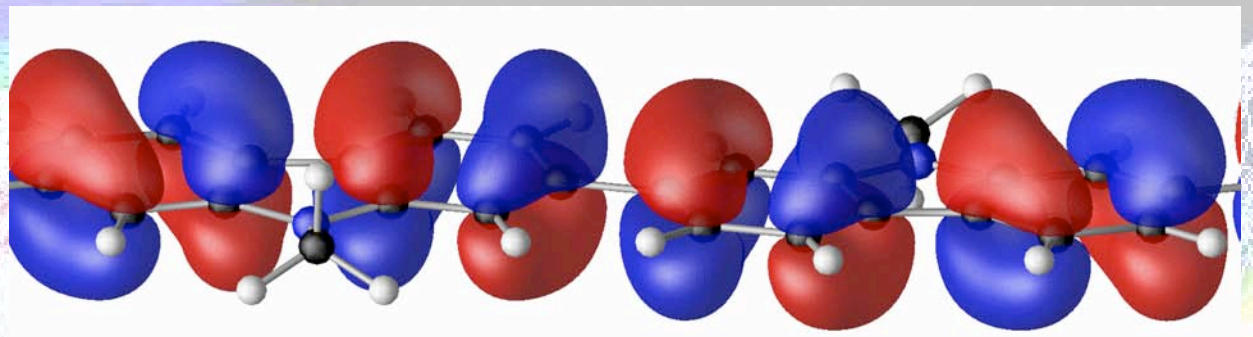
Normal polymer



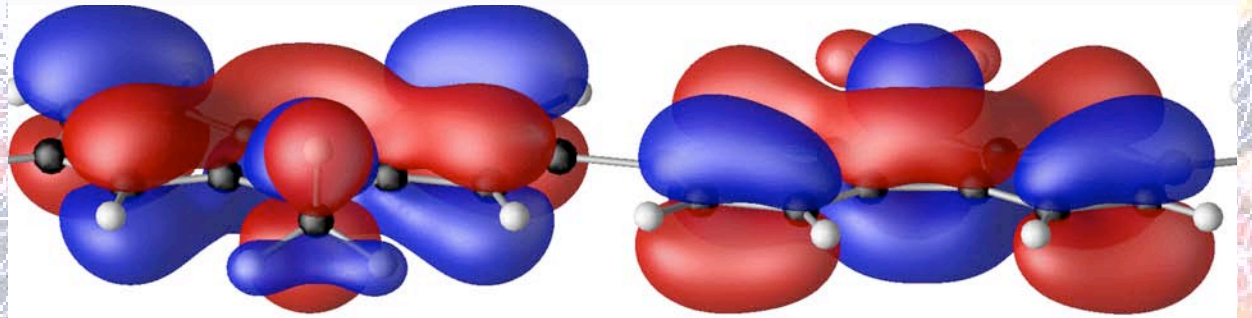
Dispersion

Last valence bands

Strong dispersion



Weak dispersion



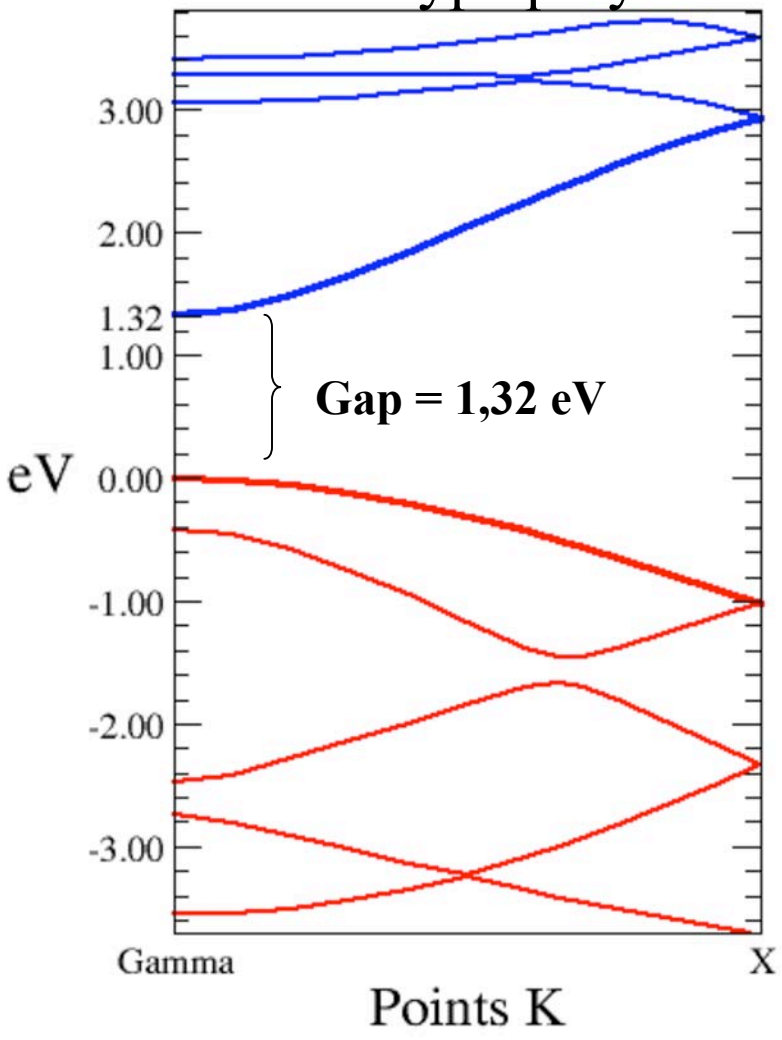
Because of the phase difference, there is two ways to write the polymer wave functions using the molecule ones:

$$\Psi_+ = \varphi_G + \varphi_D$$ Binding state.

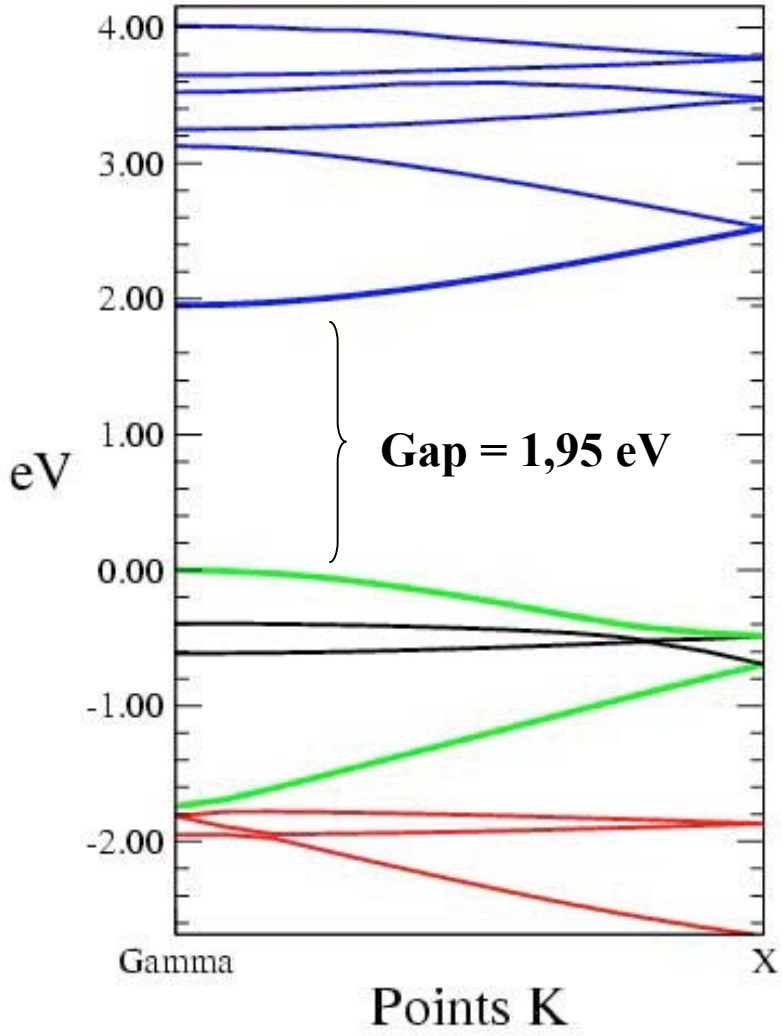
$$\Psi_- = \varphi_G - \varphi_D$$ Anti-binding state.

Band Structure

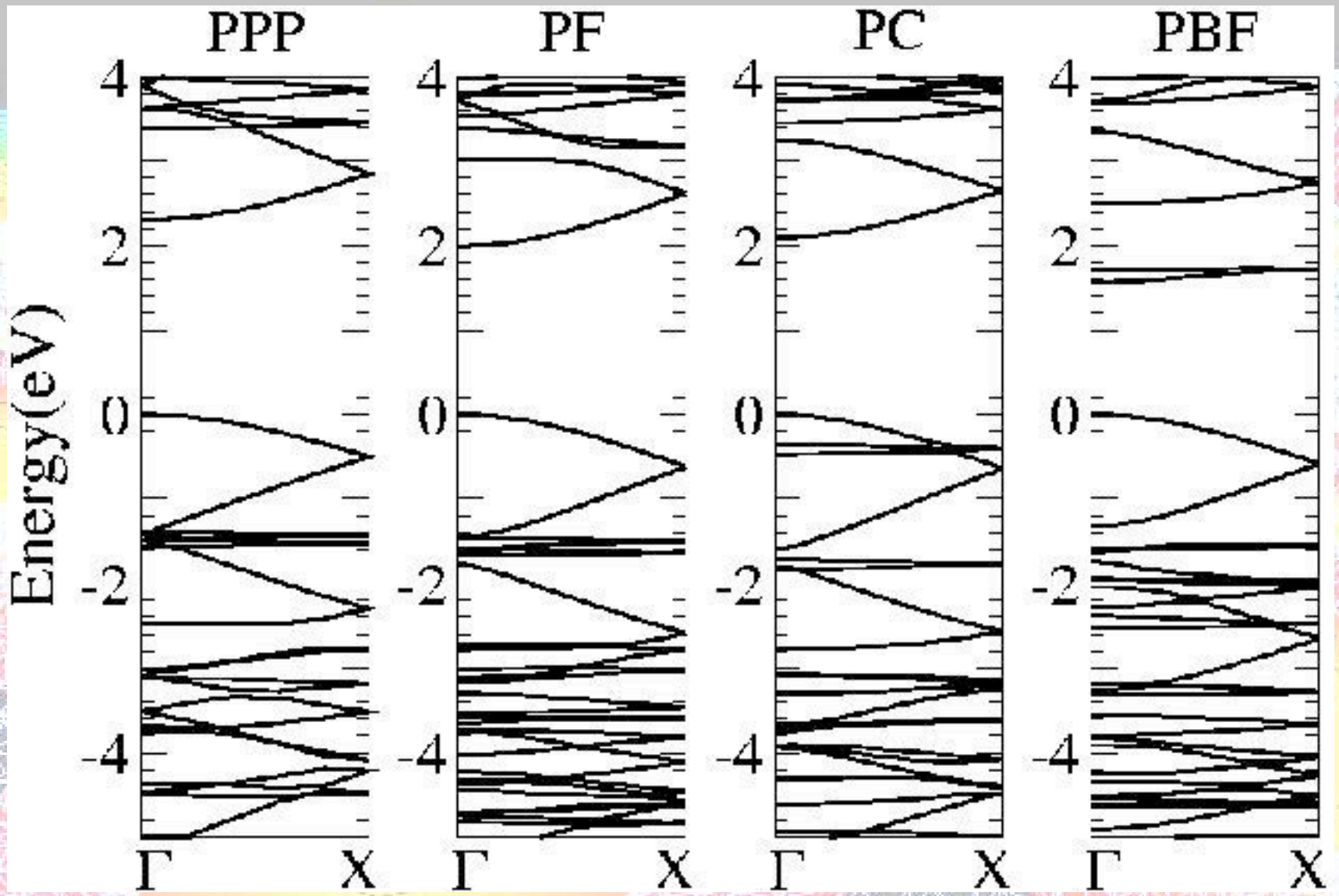
Ladder type polymer



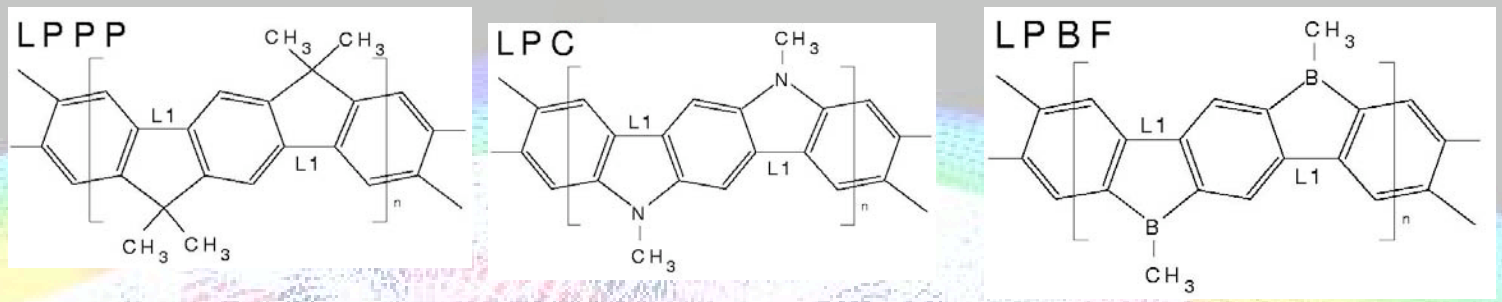
Normal polymer

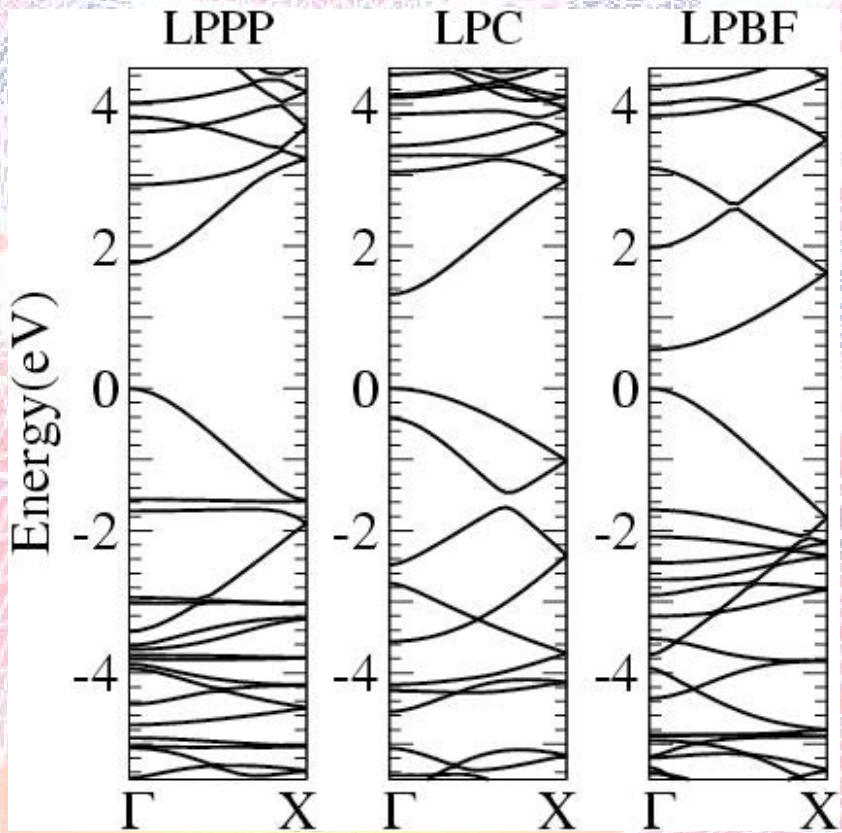


Band Structure: Normal Polymers



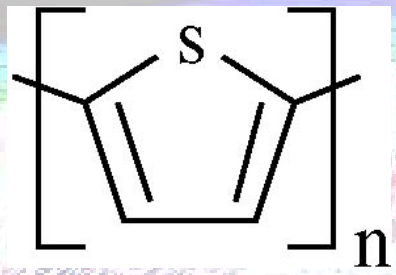
Band Structures: Ladder Polymers





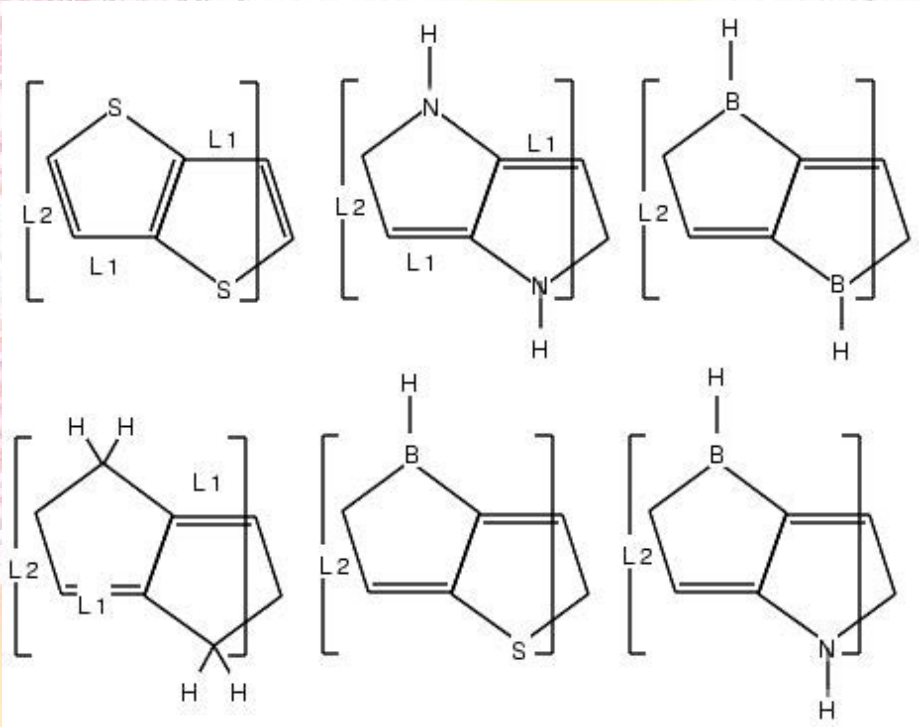
Borafluorene Ladder polymer could have a "small" energy gap!

The dream: metallic polymers

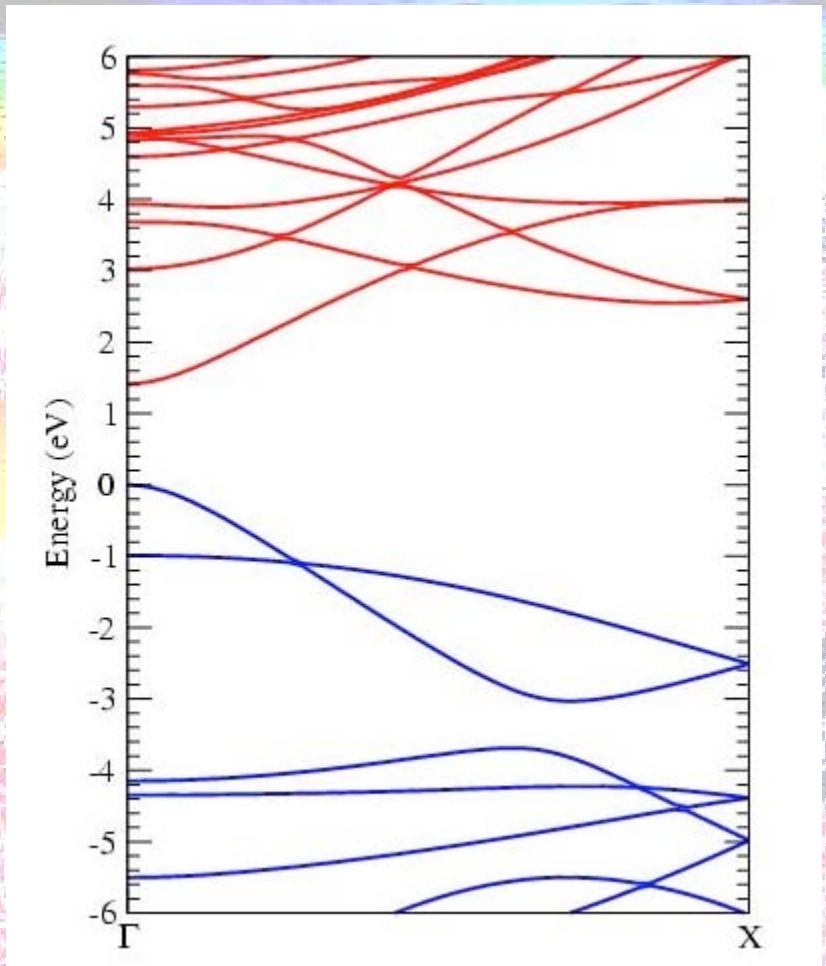


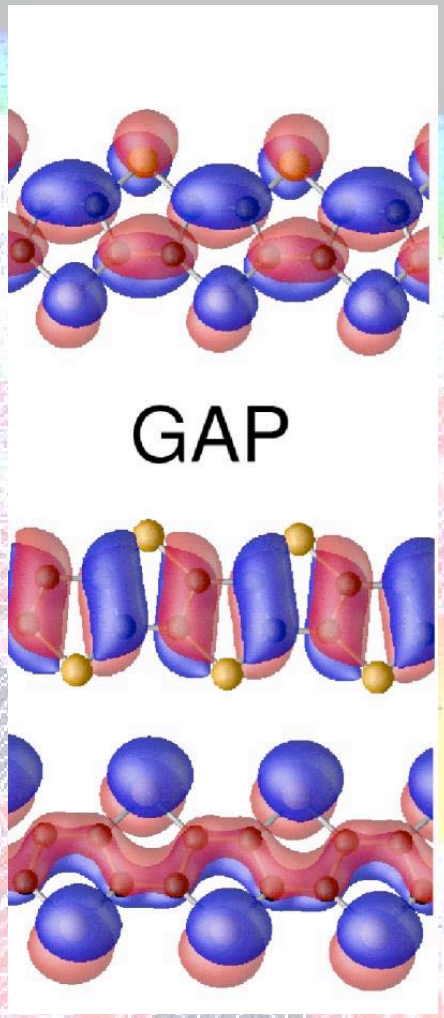
Thiophene …ladder?

Hypothetical Structures…

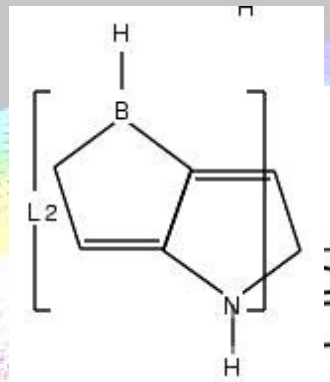


Ladder thiophene…

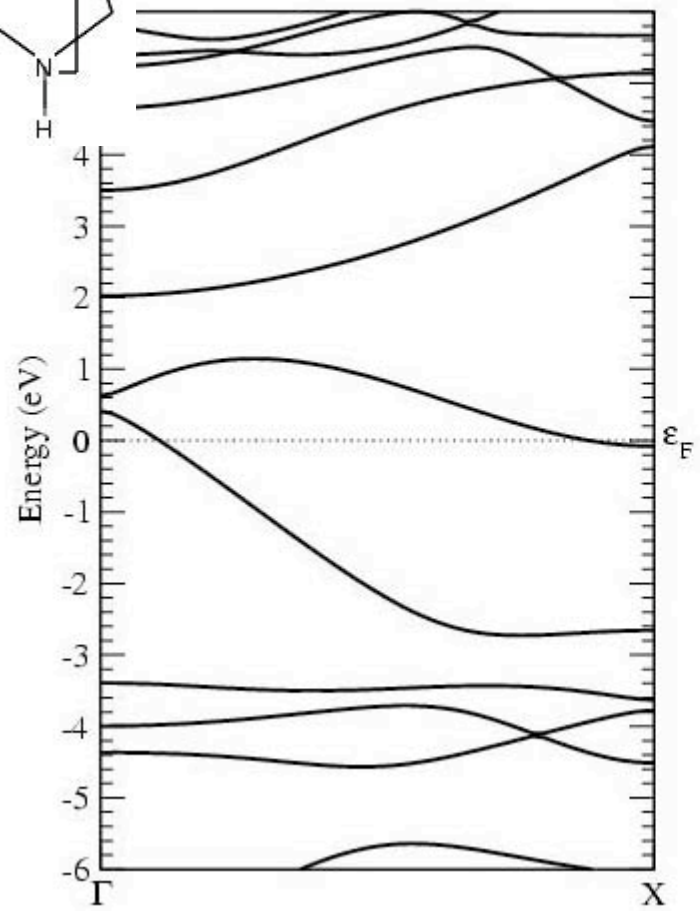




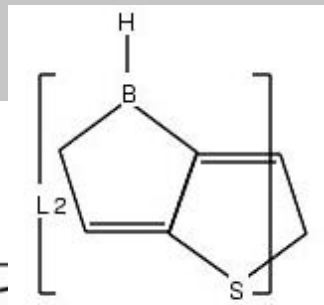
…interesting candidates…

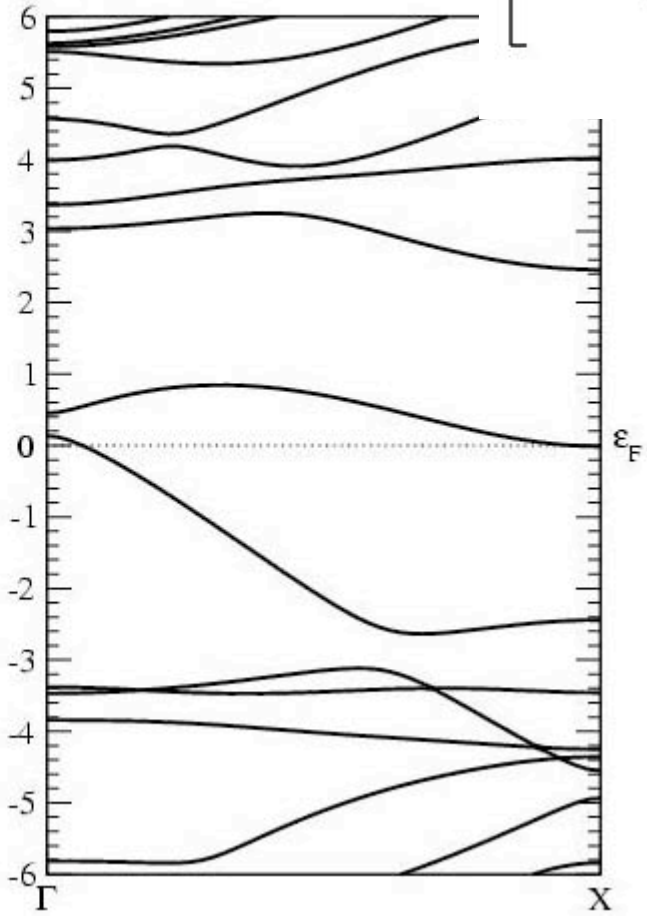


BOA



BOS





Conclusion

- Polymers (chemistry) have a lot of possibilities (nanotechnology?)
- We can use Abinit to predict new materials
- Need excited states for extended systems

Abinit in Montréal

- 2 postdoc:
  - Vladimir Timochevskii (Wien2K, Siesta, Abinit)
  - Sébastien Hamel (Abinit, Octopus, Games, …)
- Graduate students:
  - Jean-François Brière (now at Cornell for Ph.D.)
  - Jean-François Chabot
  - Sébastien Langevin
  - Paul Boulanger (codirection with Matthias Ernzerhof)
  - Simon Pesant
  - Benjamin Tardif

Other professors: Normand Mousseau and Laurent Lewis