POLITECNICO
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Molecules for plastic electronics: *structure and electronic properties*

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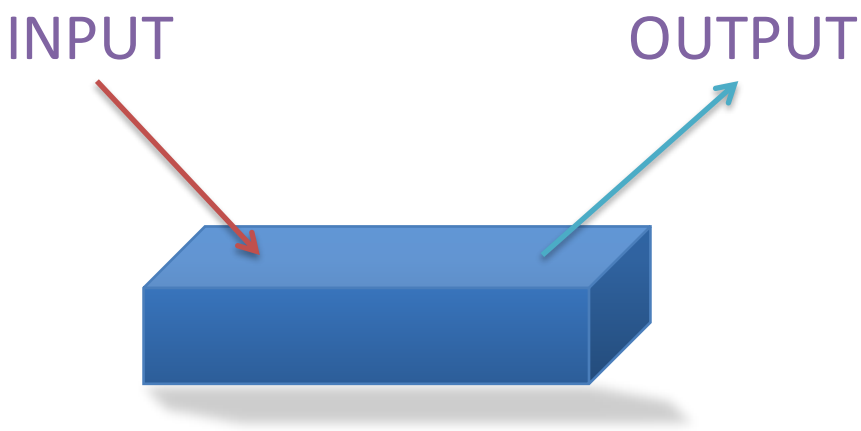
SMART MATERIAL



- INPUT:
  - Light
  - Voltage
  - Environment
  - Pressure
  - Heat

- OUTPUT
  - Electrical
  - Light
  - Optical
  - Mechanical
  - Electrical

- ✓ The change of properties in the bulk reflects a modification at the molecular level.
- ✓ The output has to be easily detected
- ✓ Reversibility to feature a working function.
- ✓ Fatigue resistance → device lifetime.

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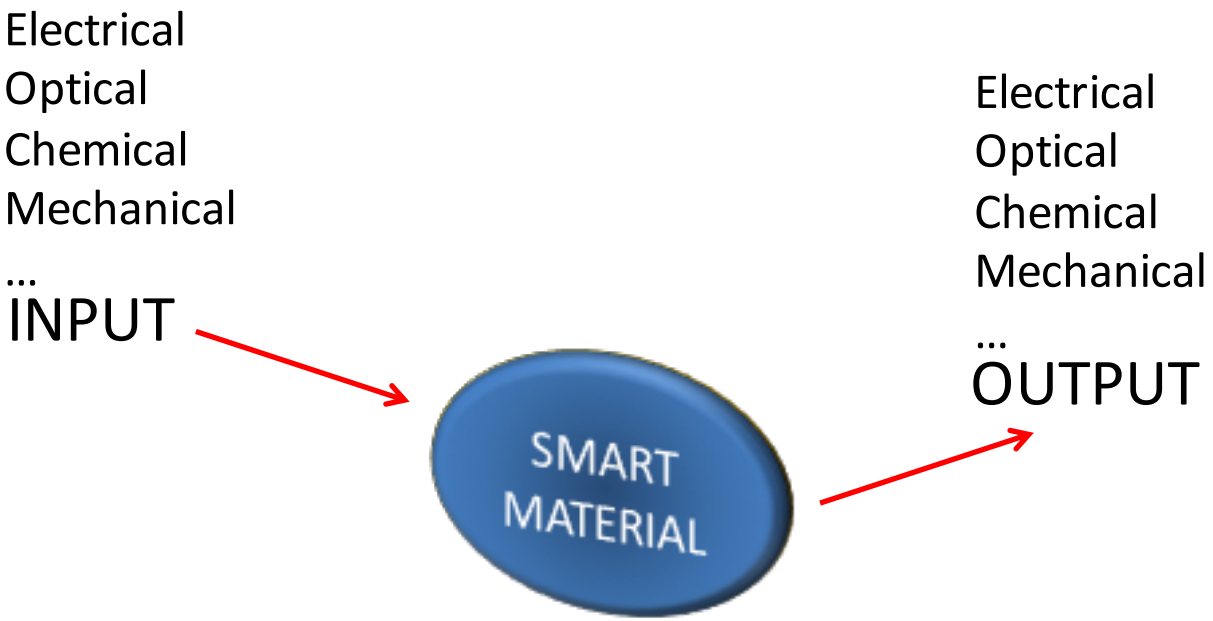

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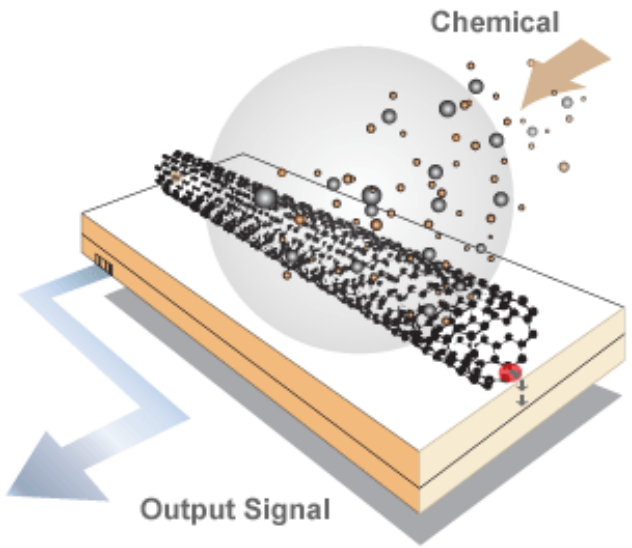
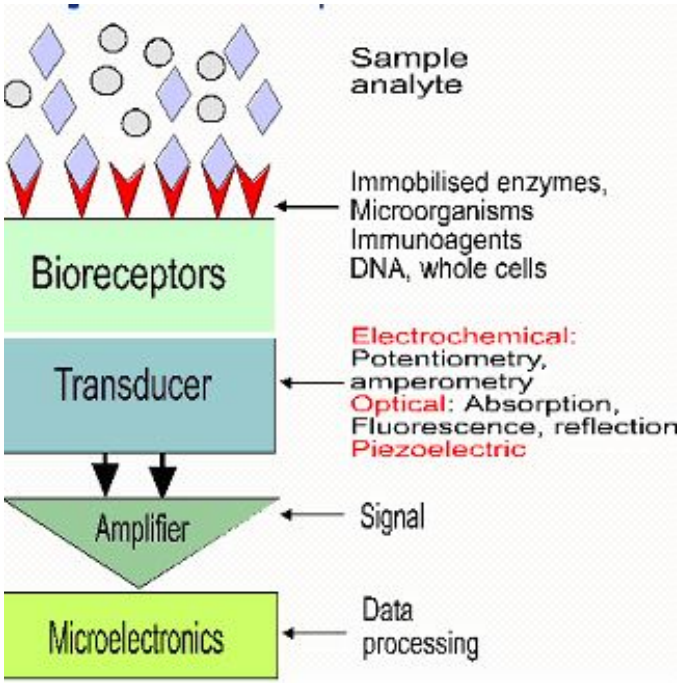
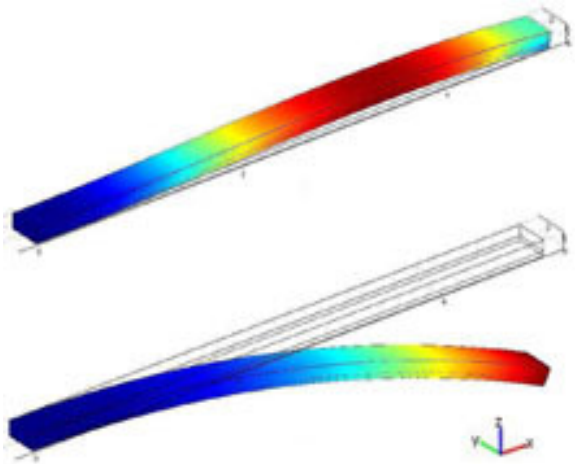
analyte → SMART MATERIAL → Optical, Electrochemical

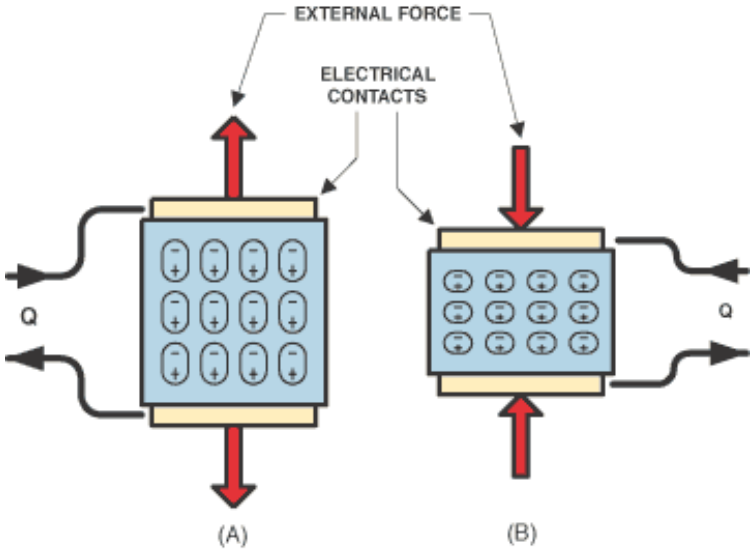
Sensors/Biosensors



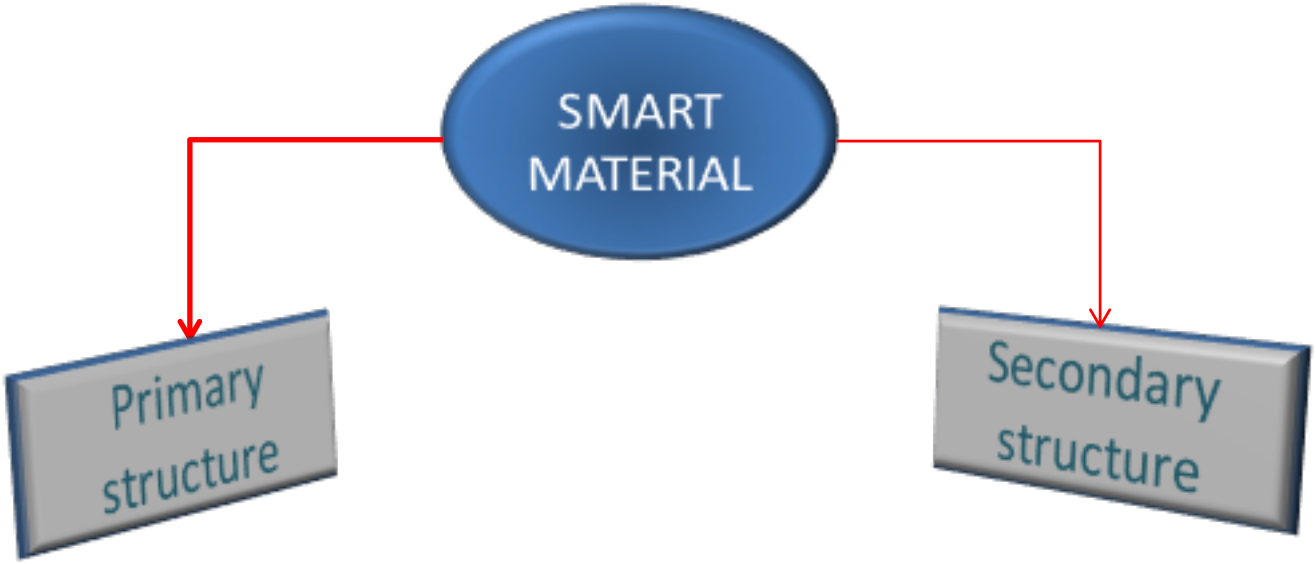


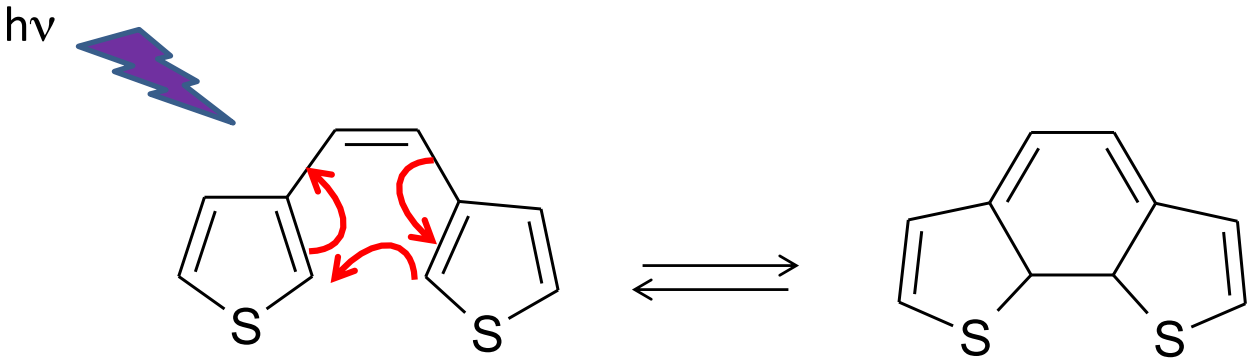
Piezoelectric materials

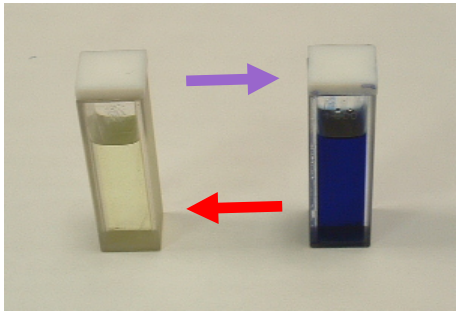




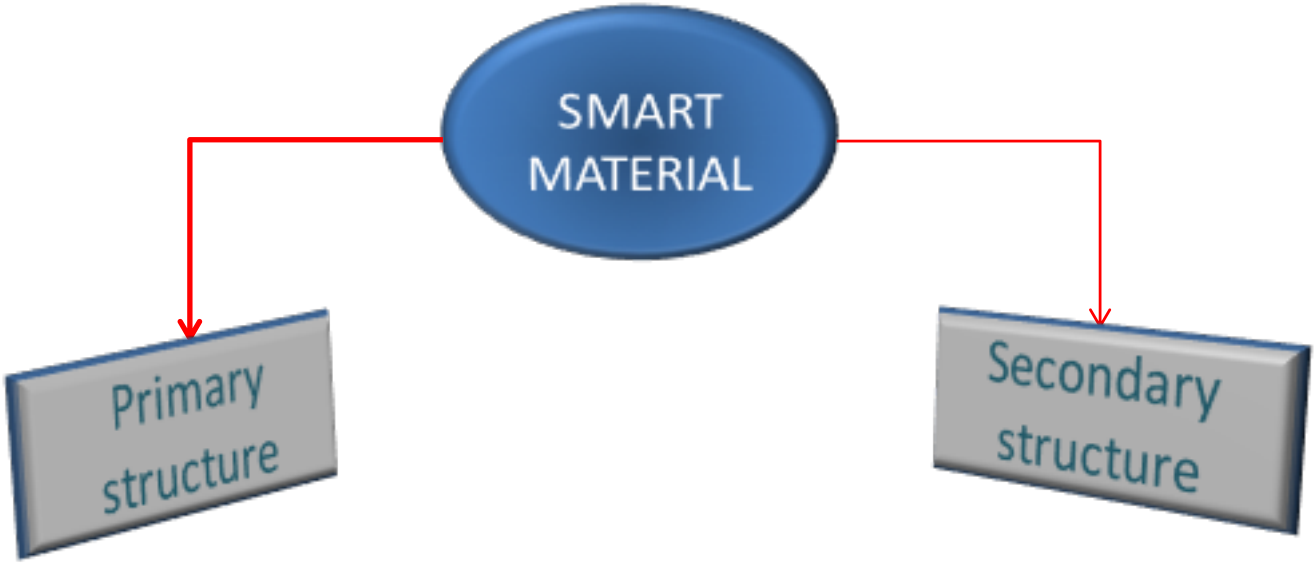
Smart material modification upon stimulus

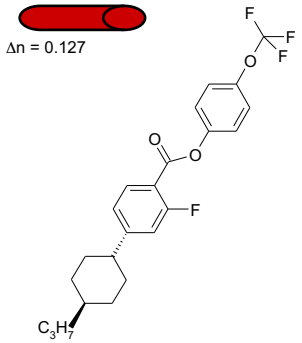


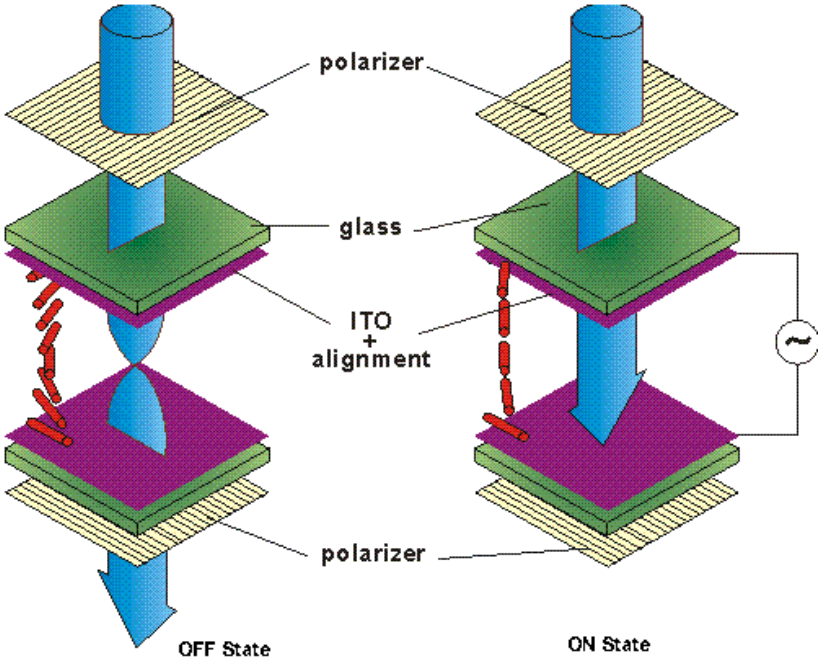




Smart material modification upon stimulus







Fundamentals of molecular design of materials for molecular electronics/organic optoelectronics

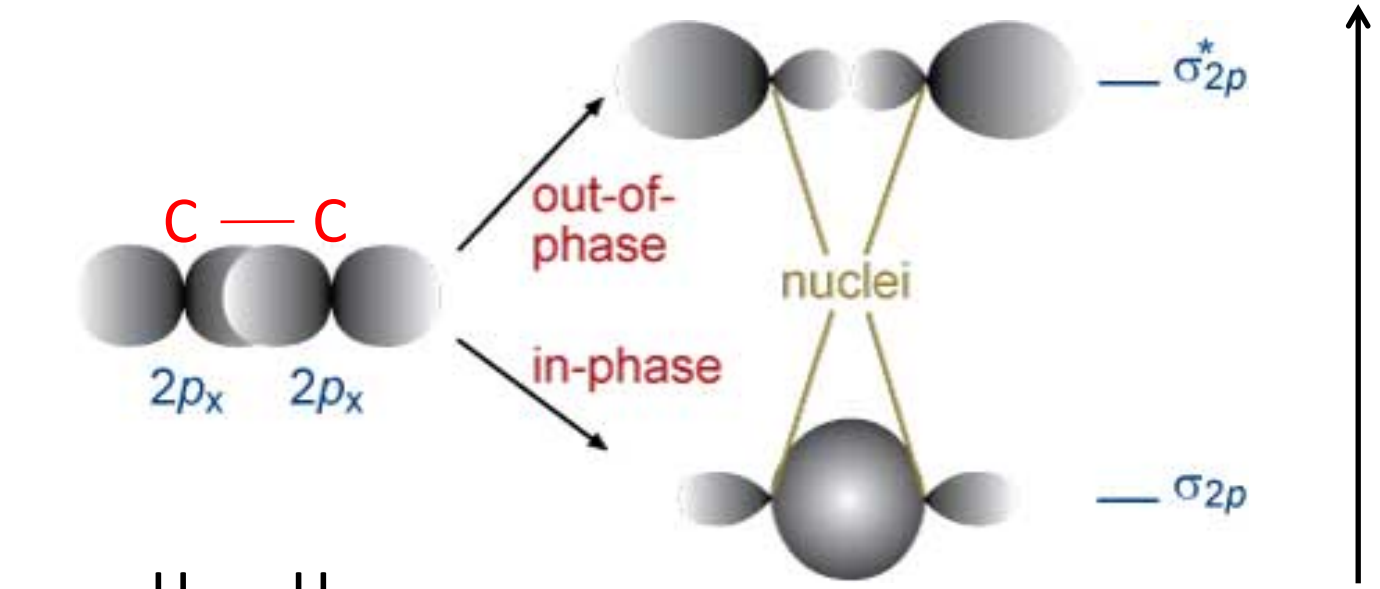
- ✓ Fundamental ingredients: **polarizable electrons**
- ✓ **Molecular design**
  - → main units
  - → substituents (EA, ED)
- ✓ Lego-chemistry as a tool
  - = tuning of properties
- ✓ solubility → material characterization processing
- ✓ ☹ stability → device lifetime

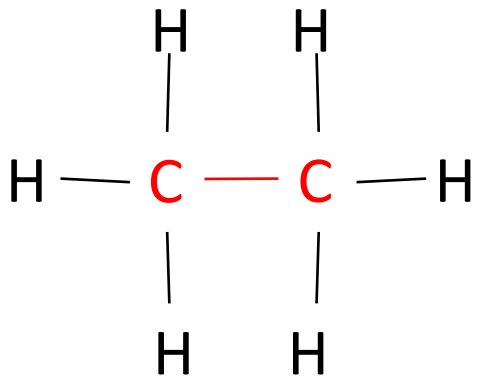
Fundamental requirement: polarizable electrons

- ✓ basics on the C=C double bond
- ✓ delocalized chemical bond: conjugation
- ✓ aromatic rings: benzene
  benzenoid fused rings
  heterocycles
- ✓ substituents: alkyl chains
  electron-donors e electron-acceptors
- ✓ Organic compounds and solubility
- ✓ Aggregation phenomena
- ✓ (Self-)Assembly

Organic functional materials: basic ingredients

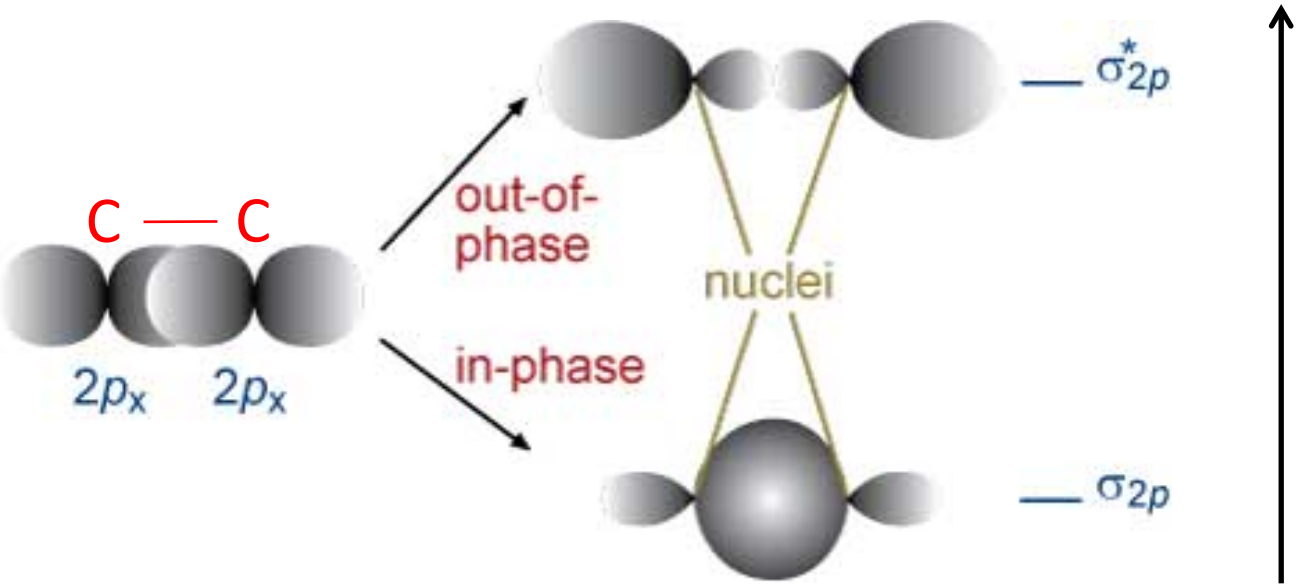
- ✓ σ bonds constitute the skeleton of the molecules
- ✓ usually when σ bonds break, molecule gets degradation

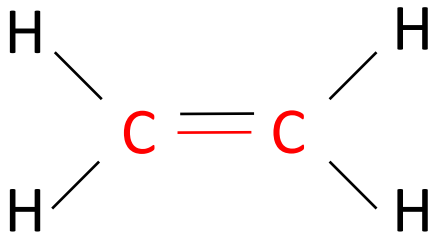




Organic functional materials: basic ingredients

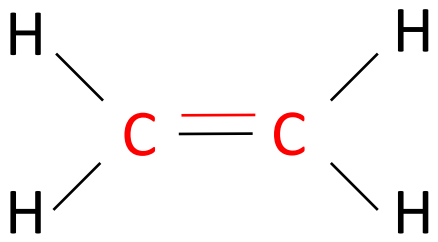
✓ the double bond consists of a part which arises from the formation of a σ bonds…

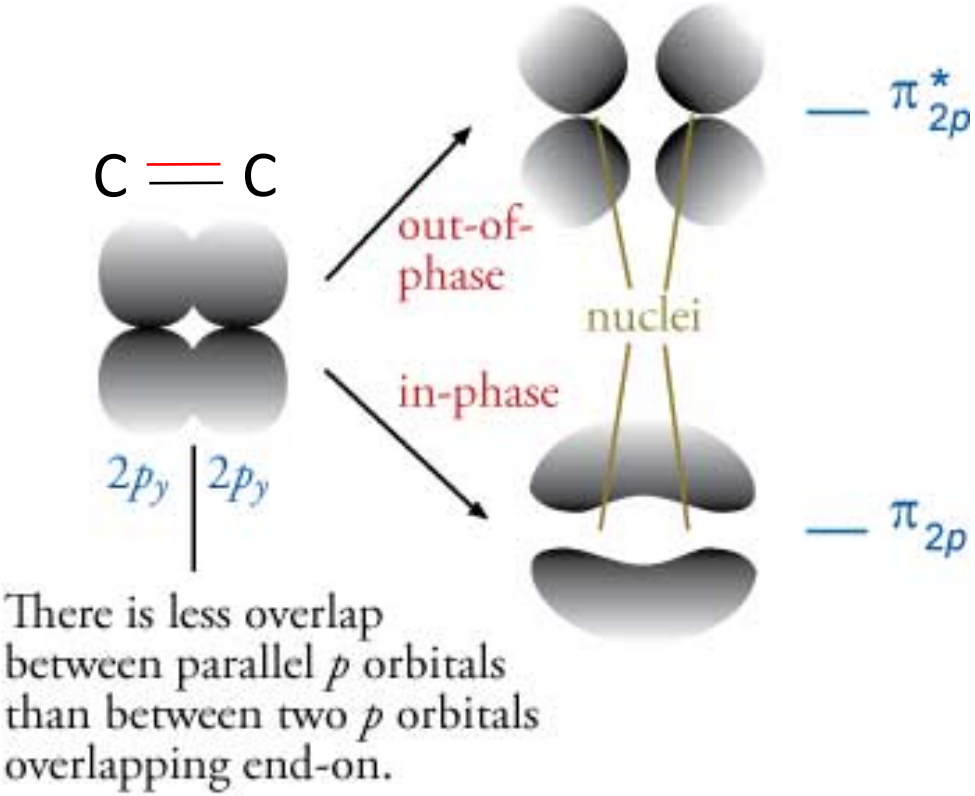




Organic functional materials: basic ingredients

✓ the double bond consists of a part which arises from the formation of a σ bonds…
…. and a part due to the overlapping of the p_z (p_y) atomic orbitals

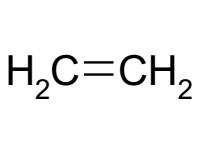




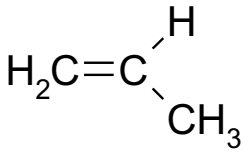
Alkenes: continuous chain of carbon atoms that contains the double bond.

✓General formula: C_nH_{2n} (homologous of cycloalkanes)

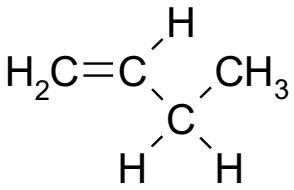
✓The name given to the chain is obtained from the name of the corresponding alkane by changing the ending from -*ane* to ***-ene***.



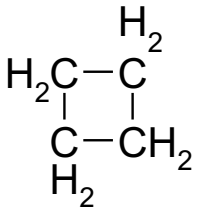
ethene



propene



1-butene



cyclobutane

✓The location of the double bond along an alkene chain is indicated by a prefix number that designates the number of the carbon atom that is part of the double bond and is nearest an end of the chain. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest number prefix.

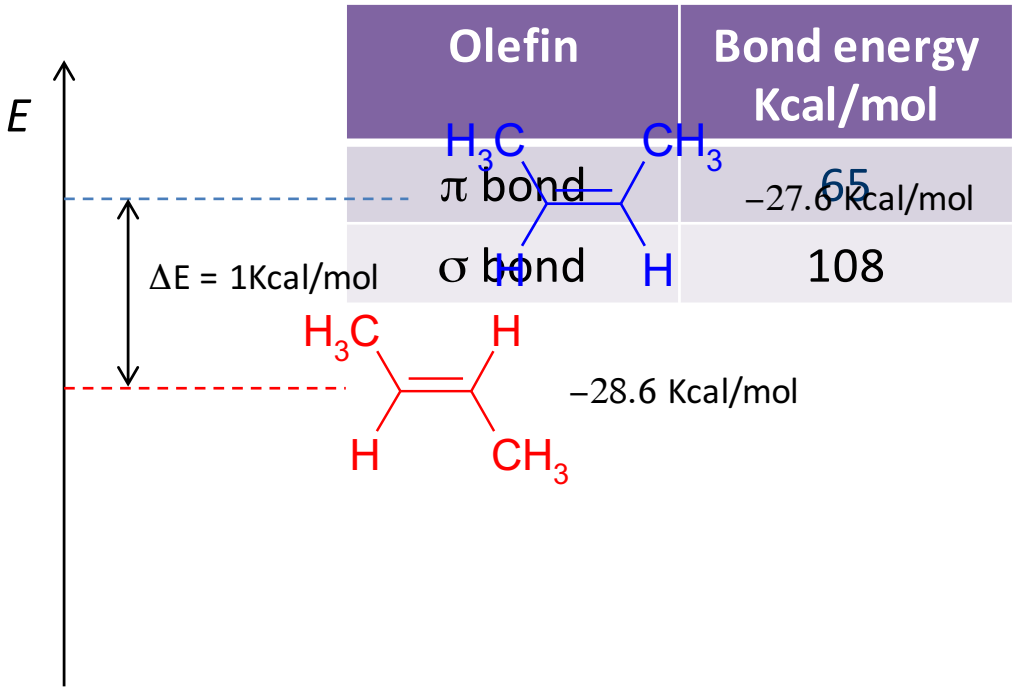
✓In propene the only possible location for the double bond is between the first and second carbons; thus, a prefix indicating its location is unnecessary.

Organic functional materials: basic ingredients

✓ although it is weaker than σ bond, the π bond is strong enough to allows the formation of stable *trans* and *cis* isomers

✓ the relatively low bond energy makes π electrons less bound and more polarizable

Bond	Bond energy, Kcal/mol	Calculated from	Bond length Å	From
C-C	80	C_2H_6	1.53	C_2H_6
C=C	141	C_2H_4	1.34	C_2H_4
C≡C	195	C_2H_2	1.20	C_2H_2



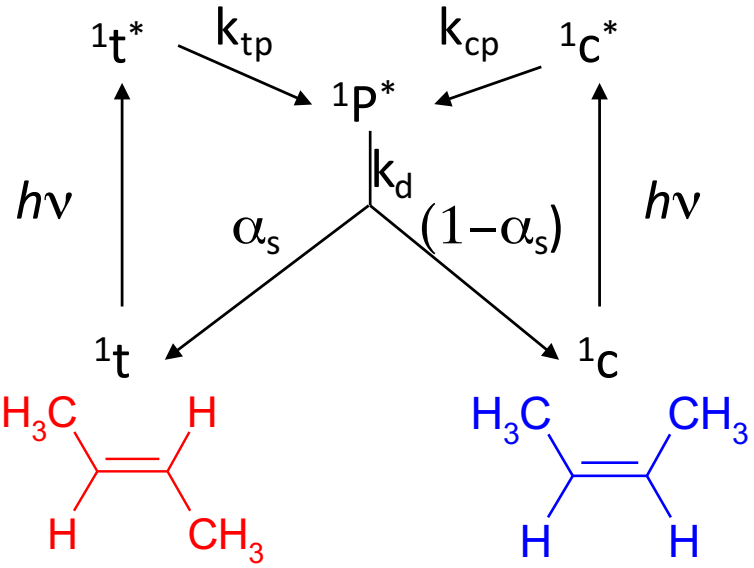
Olefin	Bond energy Kcal/mol
π bond	65
σ bond	108

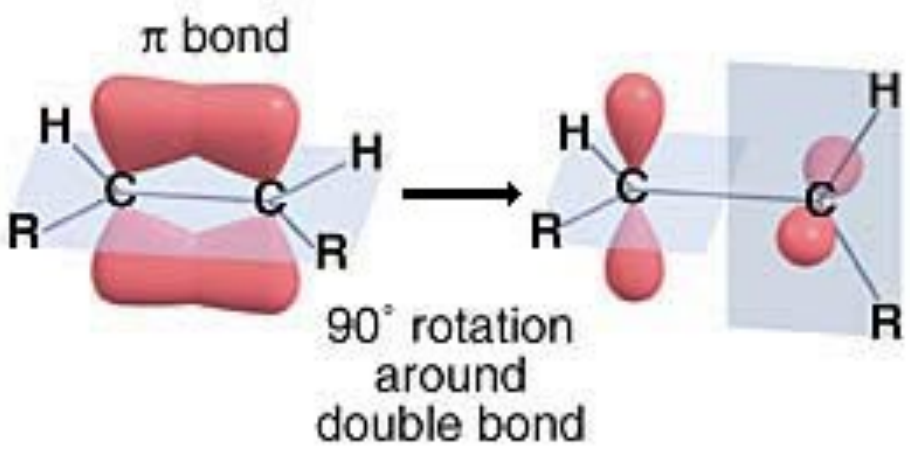
–27.6 Kcal/mol

✓ The *cis-trans* isomerisation of olefin involves 180° rotation about a C,C double bond.

✓ Except in strained cyclic olefins, the reaction is usually highly activated as a thermal process in the absence of catalysts.

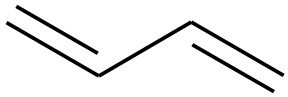
✓On the contrary, it occurs more easily if the molecule is at the first singlet or triplet excited state.



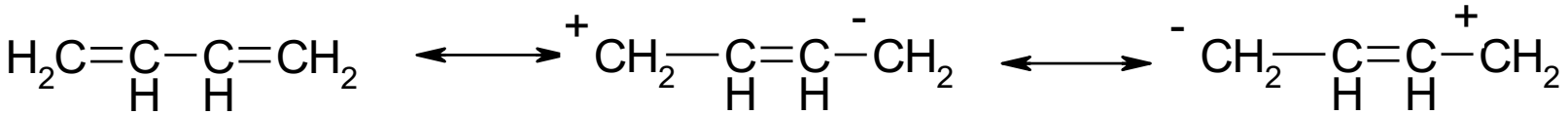


One double bond is not enough…

…the simplest case of 1,3-butadiene



It cannot be represented by a single Lewis formula
There are some possible canonical forms (#3)



The double bonds are not localized between the C1-C2 and C3-C4 carbon atoms, but π molecular orbitals arise from the linear combination of the four p_z orbital, one belonging to each carbon atom.

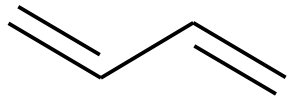
It follows that:

the double bond (C1-C2) and (C3-C4) is longer than a typical double bond
the single bond is longer than a typical single bond (C2-C3)

Nomeclature: conjugated olefines, oligoenes, polyenes

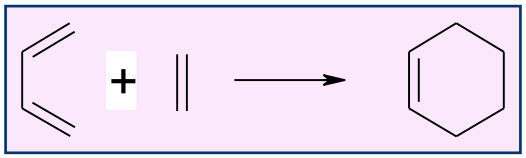
One double bond is not enough…

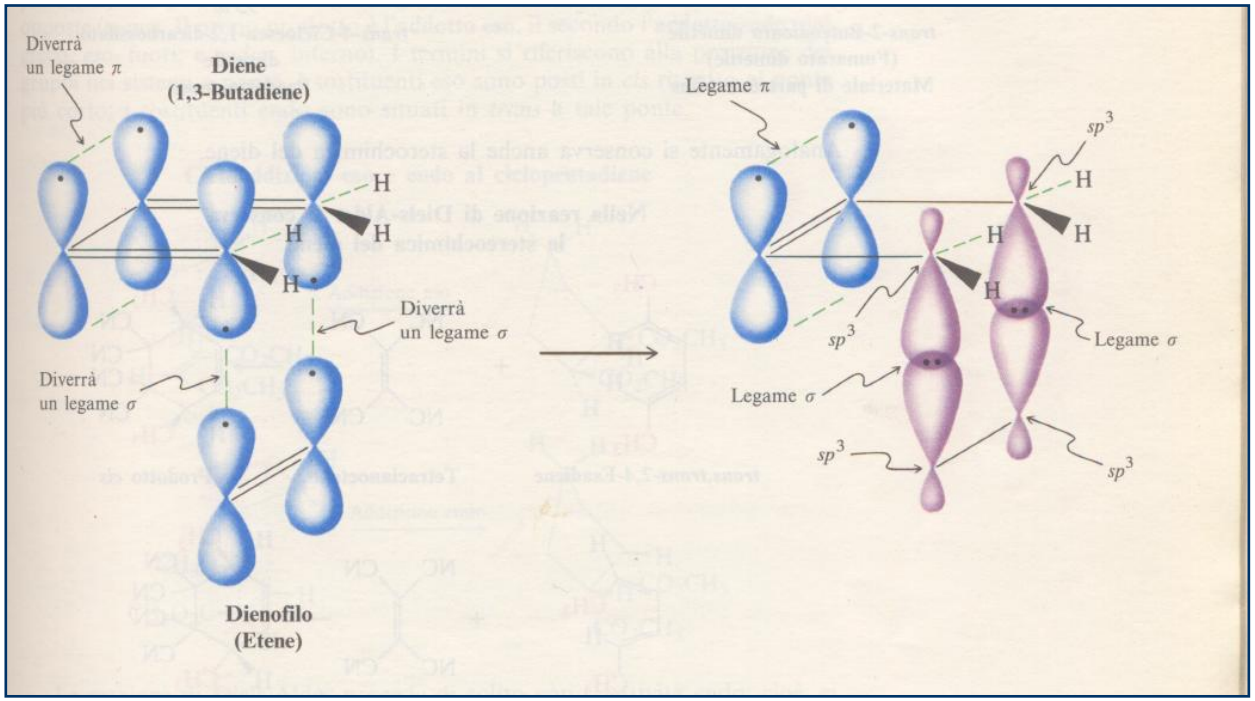
…the simplest case of 1,3-butadiene



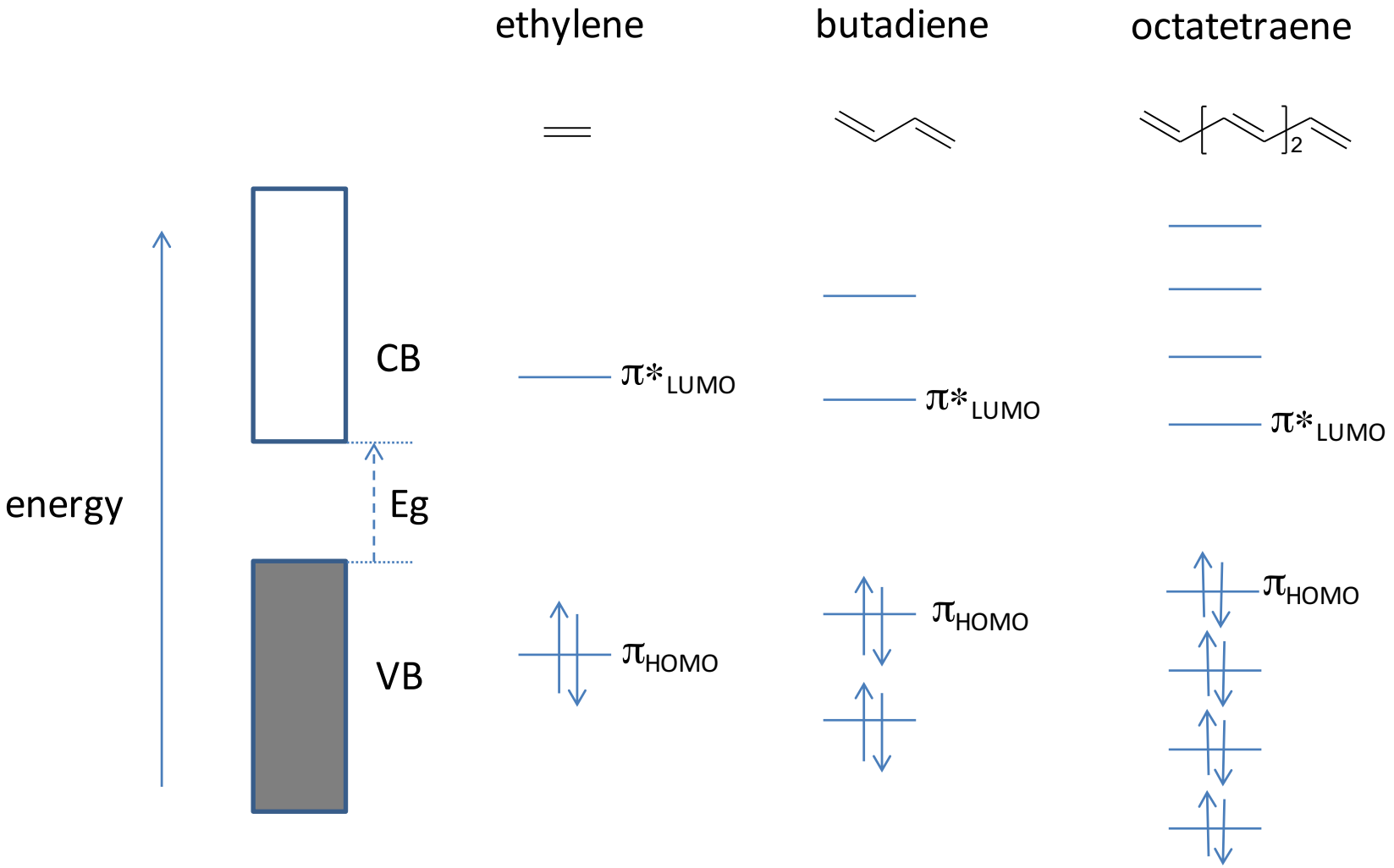
Conjugated systems

Conjugated molecules undergo not only typical reactions of olefins, possibly modified by the extended p overlapping, but also peculiar cycloaddition thermally or photochemically driven.





Giving some other π electrons more…
…the oligoenes



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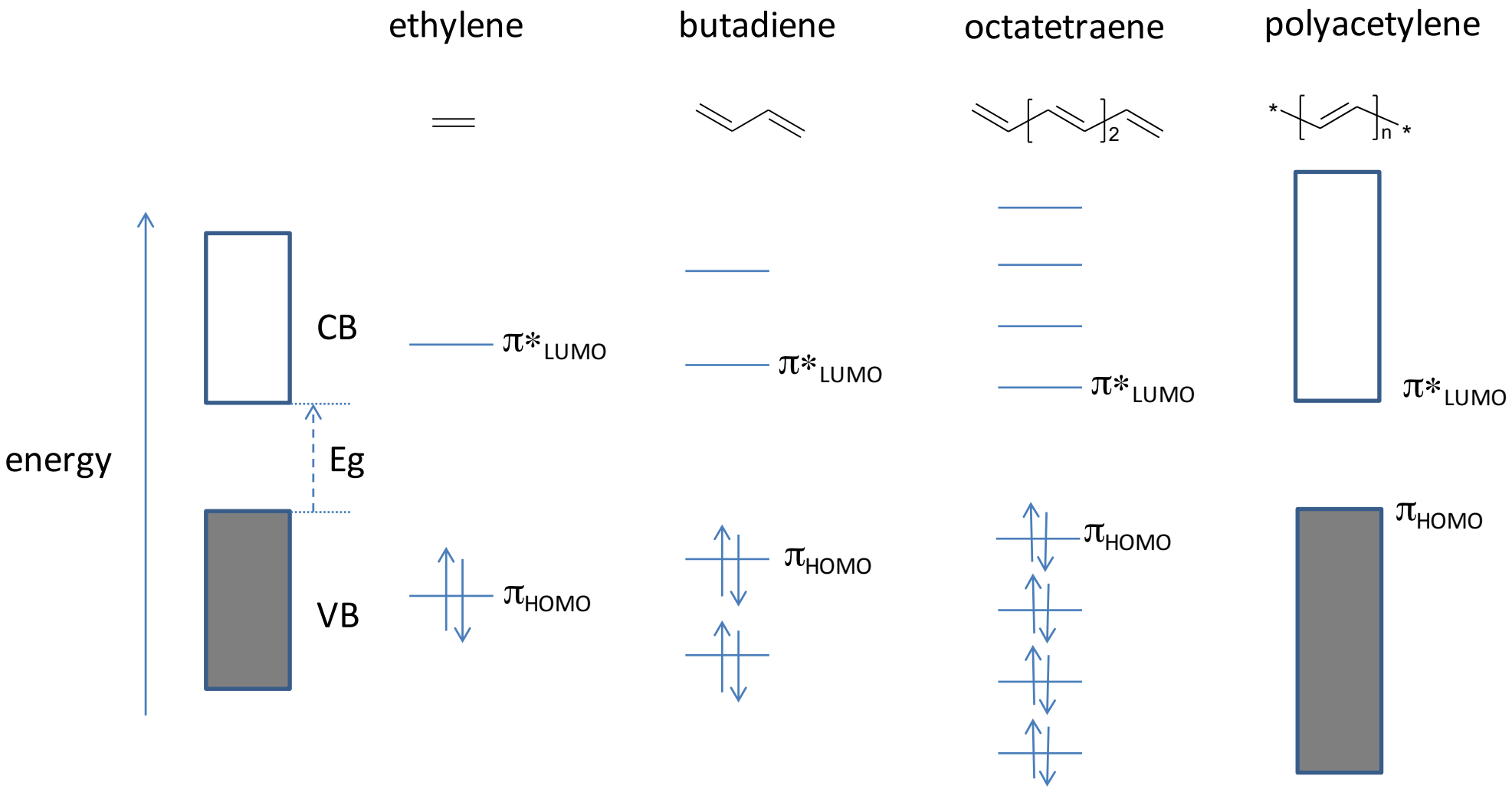

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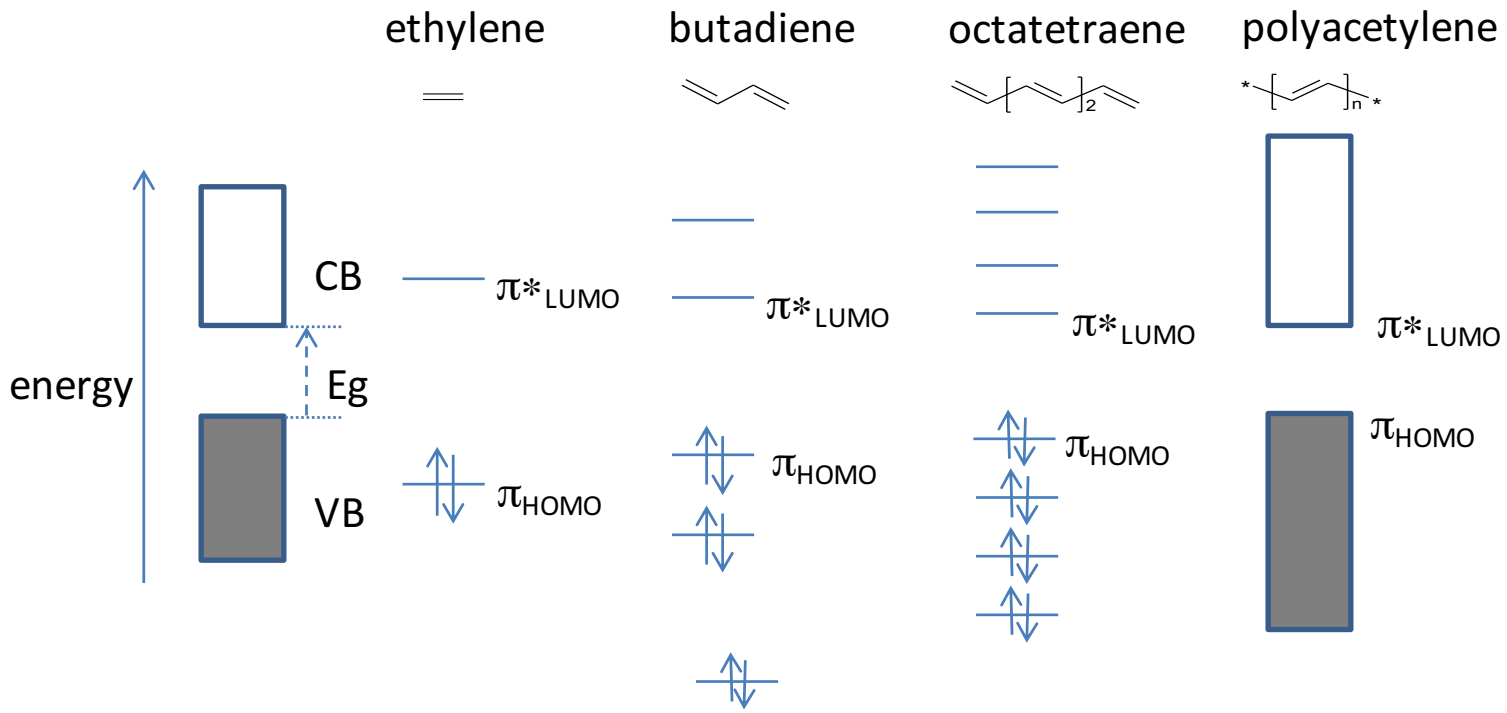


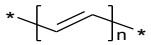
✓The HOMO increases in energy with increasing conjugation length
✓The LUMO decreases in energy with increasing conjugation length
✓The band gap (Eg) is decreases with increasing conjugation length

Properties:

✓Ionization potential gets lower
✓ material gets more susceptible to electrophiles (more reactive, in general)
✓ spontaneous oxidations

Peierls distortion

polyacetylene



π^*_{LUMO}

π_{HOMO}

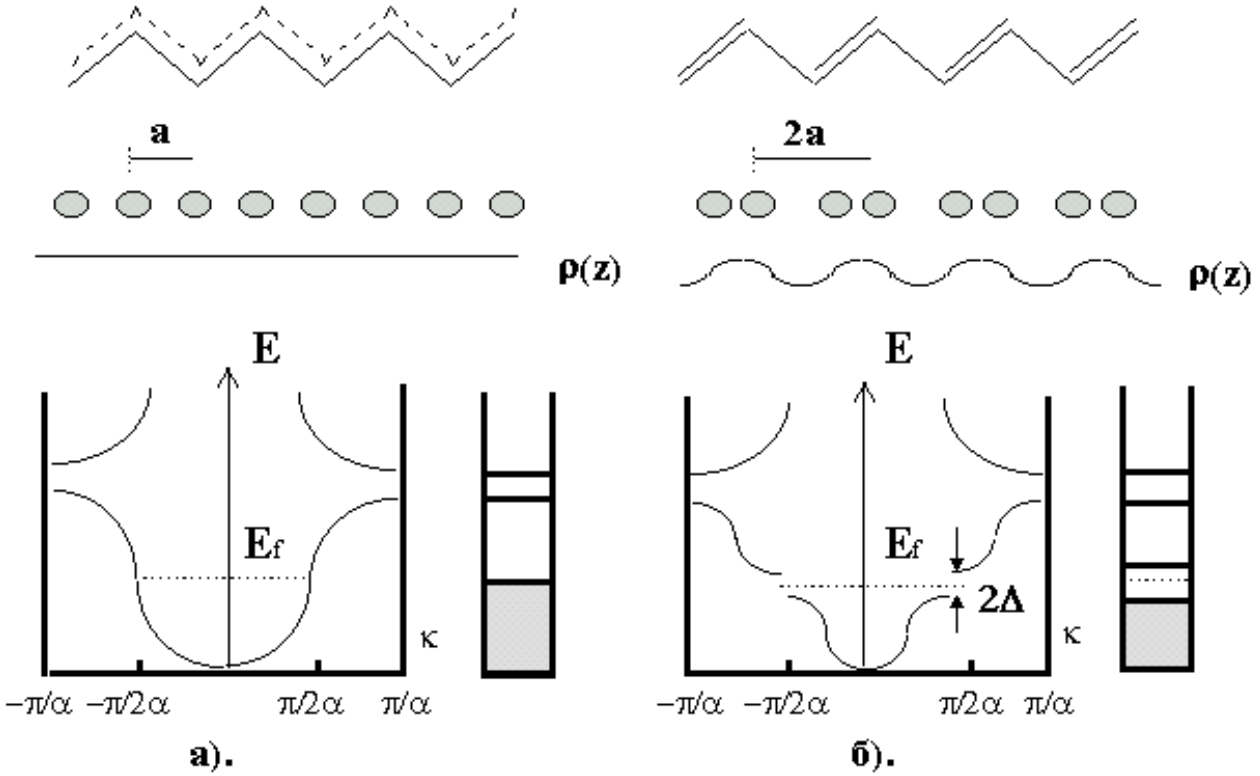
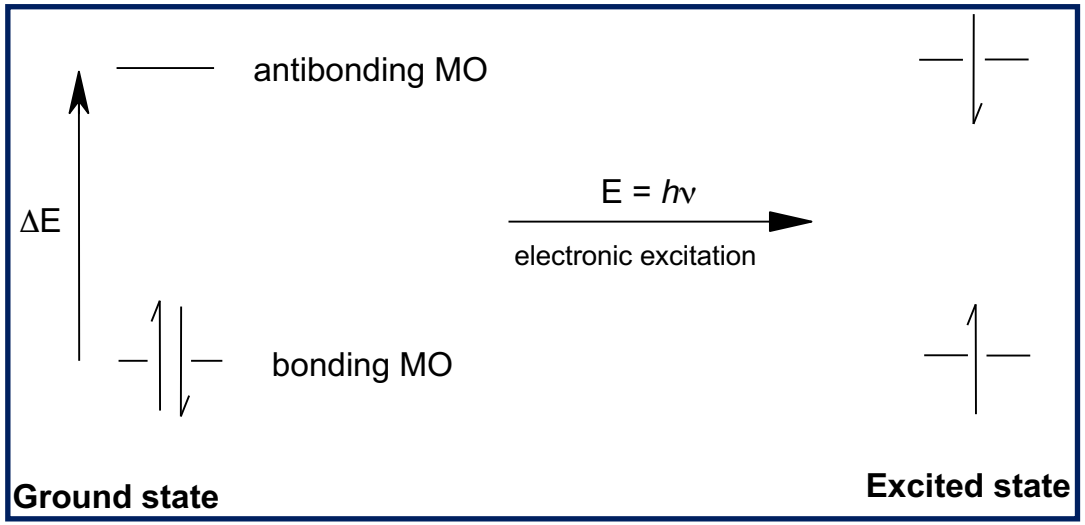
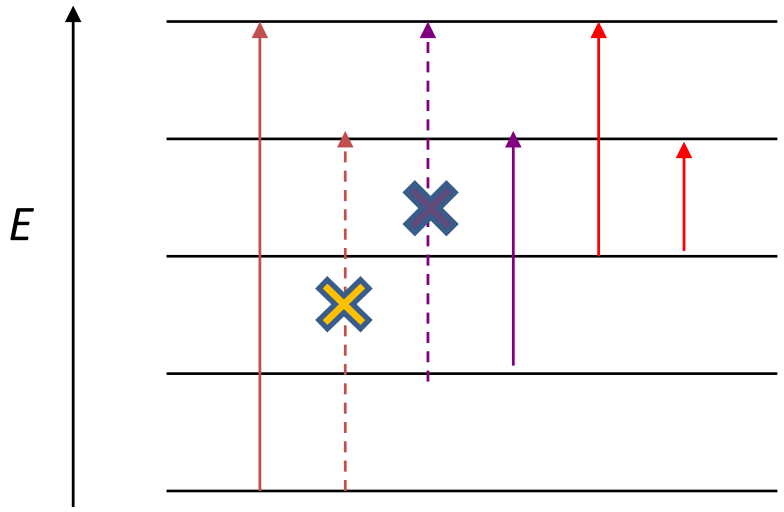


Fig. 1. Electron dispersion and a band pattern of one-dimensional molecular system: a). metallic and b). insulator state, (**ρ(z)**–a electronic density, **a**–a lattice period).

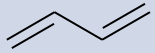
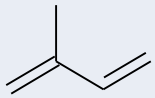
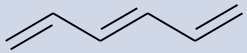
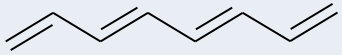
Electronic levels and optical properties: the UV-vis electronic spectra



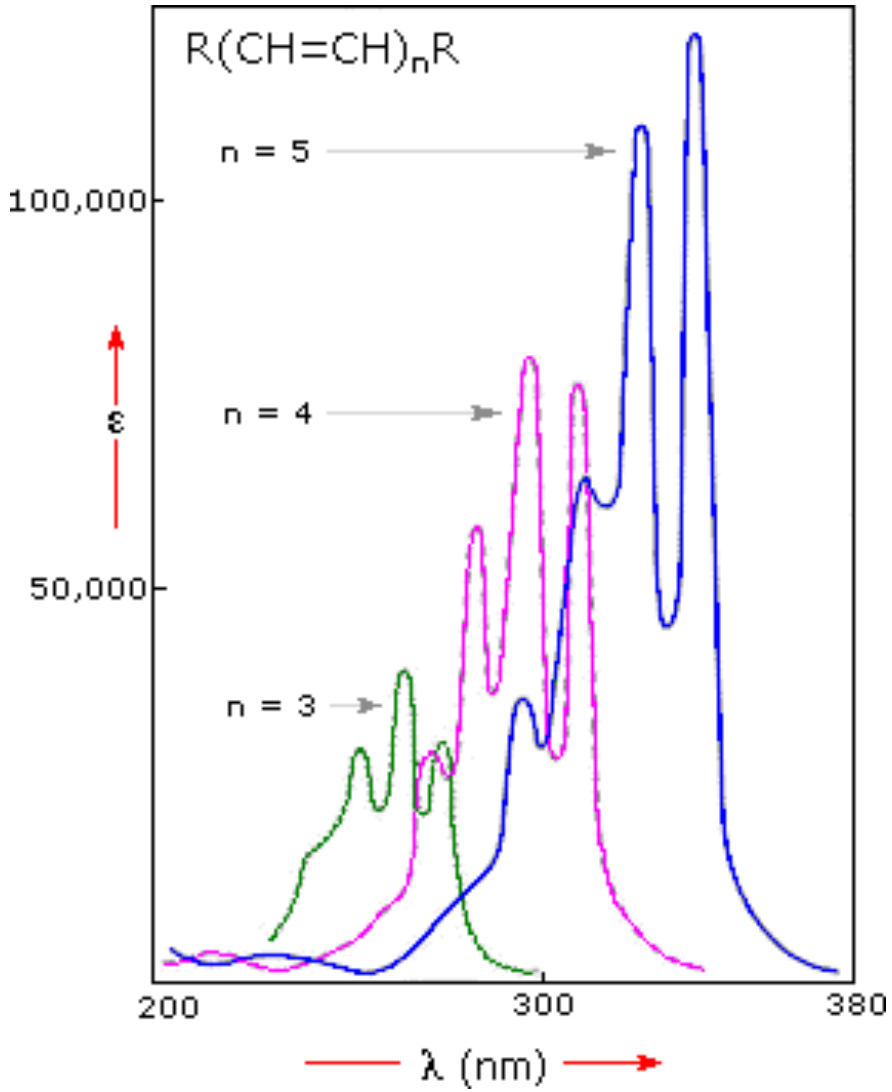
Electronic transitions



σ*	Antibonding (single bonds)
π*	Antibonding (double bonds)
n	Non bonding
π	Bonding (double bonds)
σ	Bonding (single bonds)

Structure	Compound	λ_{max} (nm)	ε
	Ethene	171	15500
	1,4-pentadiene	178	---
	1,3-butadiene	217	21000
	2-methyl-1,3-butadiene	222,5	---
	*trans*-1,3,5-hexatriene	268	36300
	*trans,trans*-1,3,5,7-octatetraene	330	----

The UV-vis electronic spectra of oligoenes



Conjugation:
not only linear double bonds…

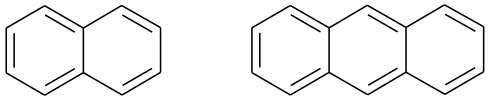
ethene (alk**ene**)

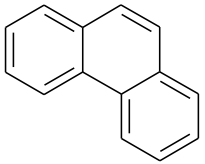
acetylene (alk**ine**)

propylene (allyle)

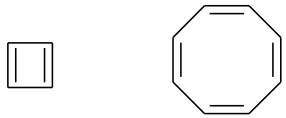
1,3-buta**diene**

BENZENE

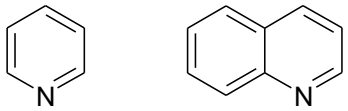




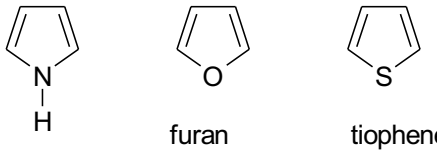
POLYCYCLIC BENZENOID HYDROCARBONS



CYCLIC POLYENES



HETEROCYCLES



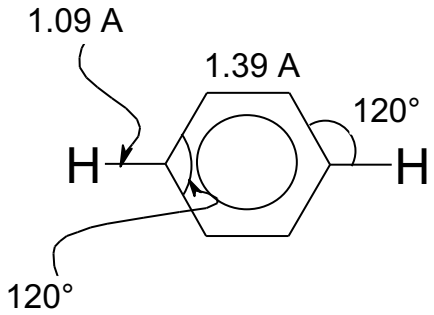
pyrrole

furan

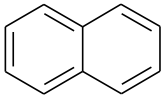
tiophene

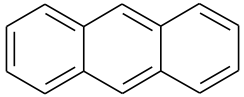
5-MEMBERED HETEROCYCLES

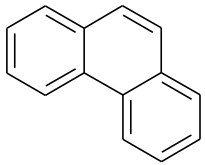
Conjugation:
not only linear double bonds…



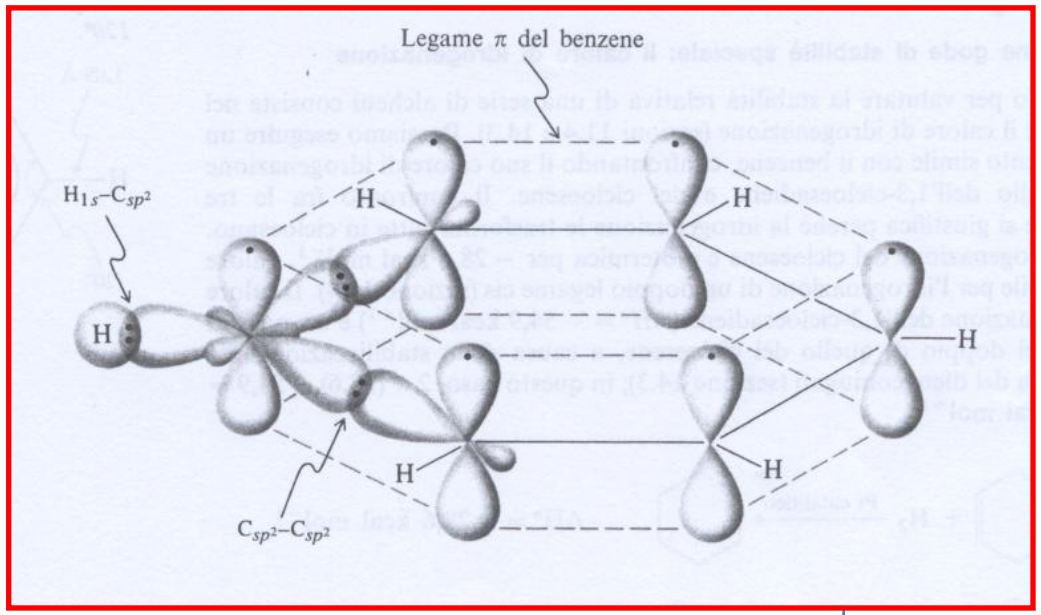
BENZENE



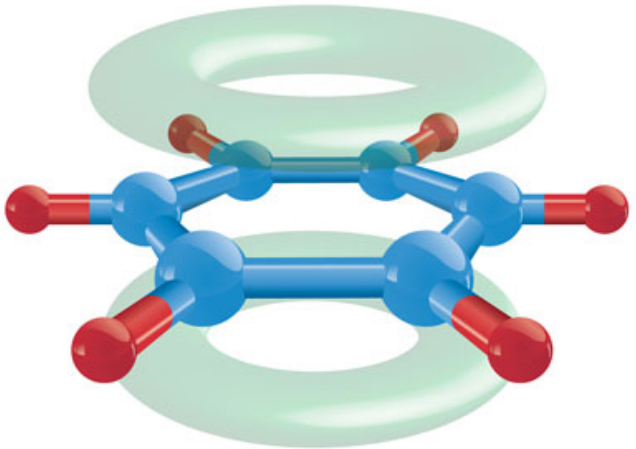


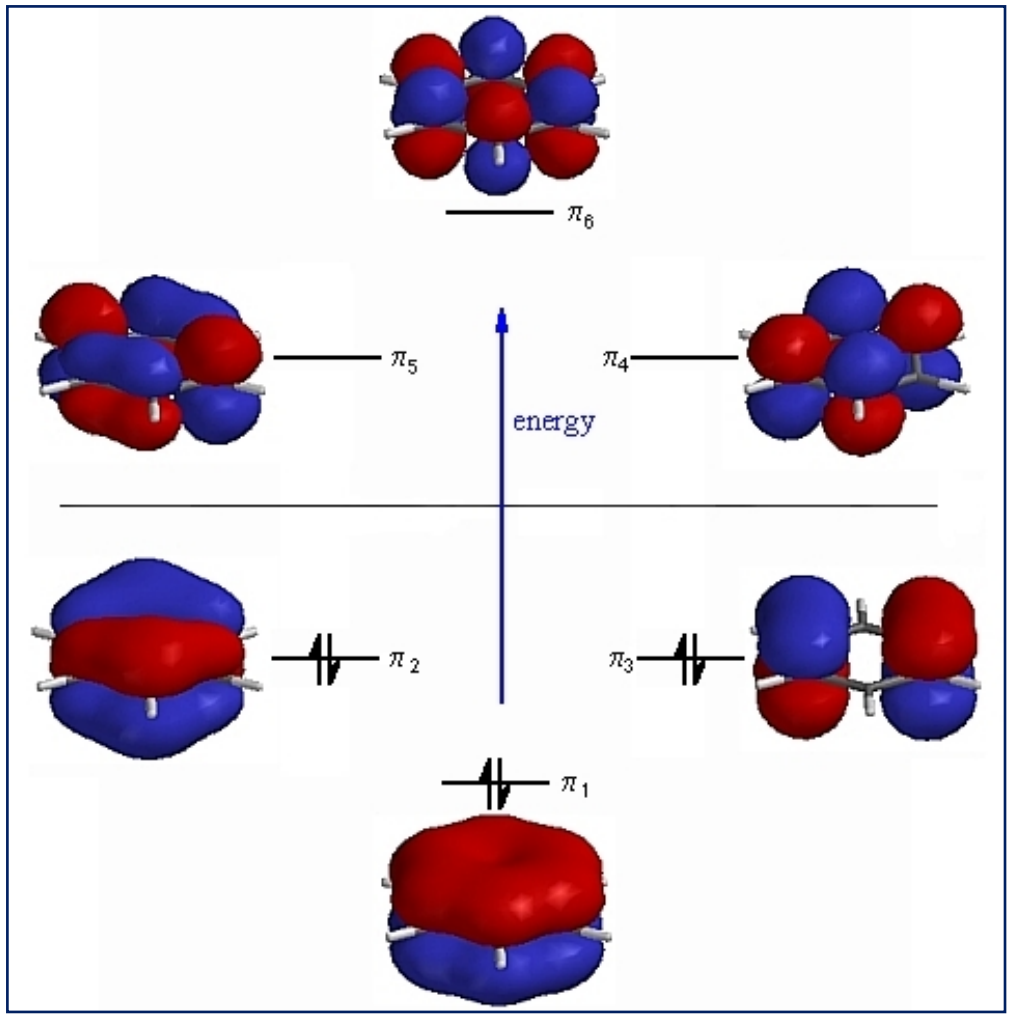


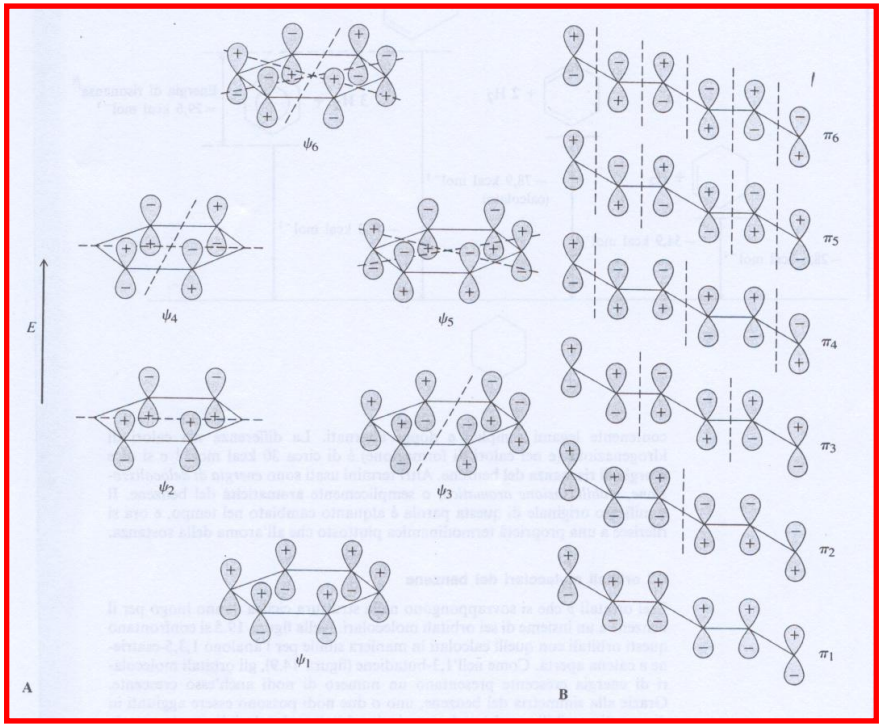
POLYCYCLIC BENZENOID HYDROCARBONS



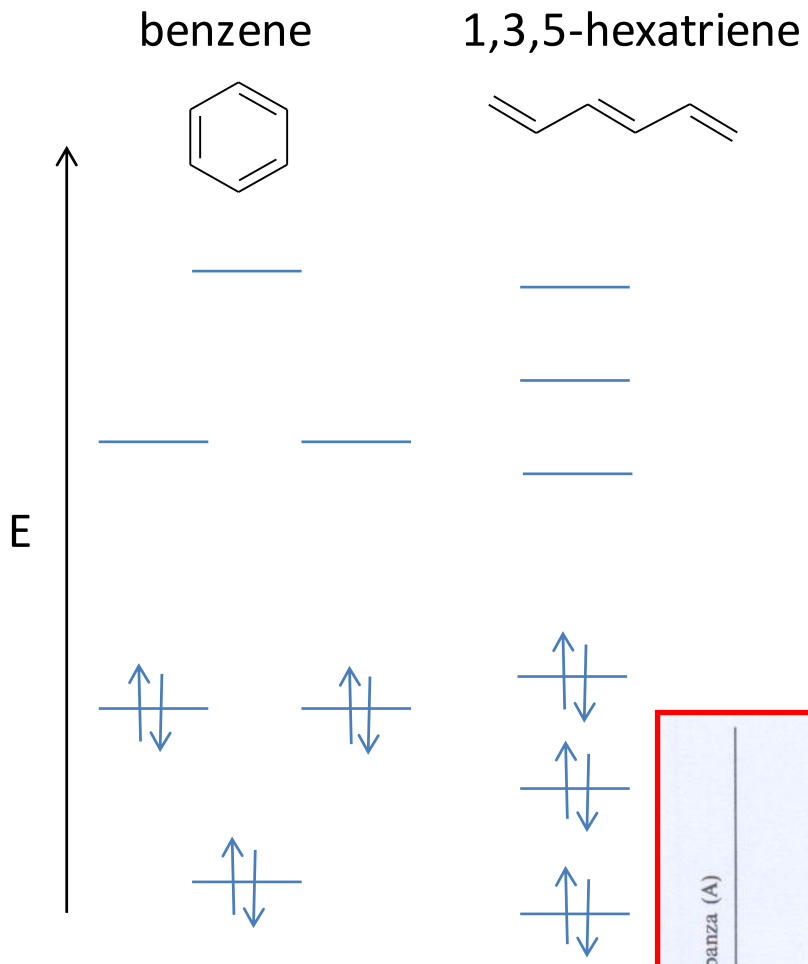
Resonance Energy= 29.6 kcal mol^{-1}

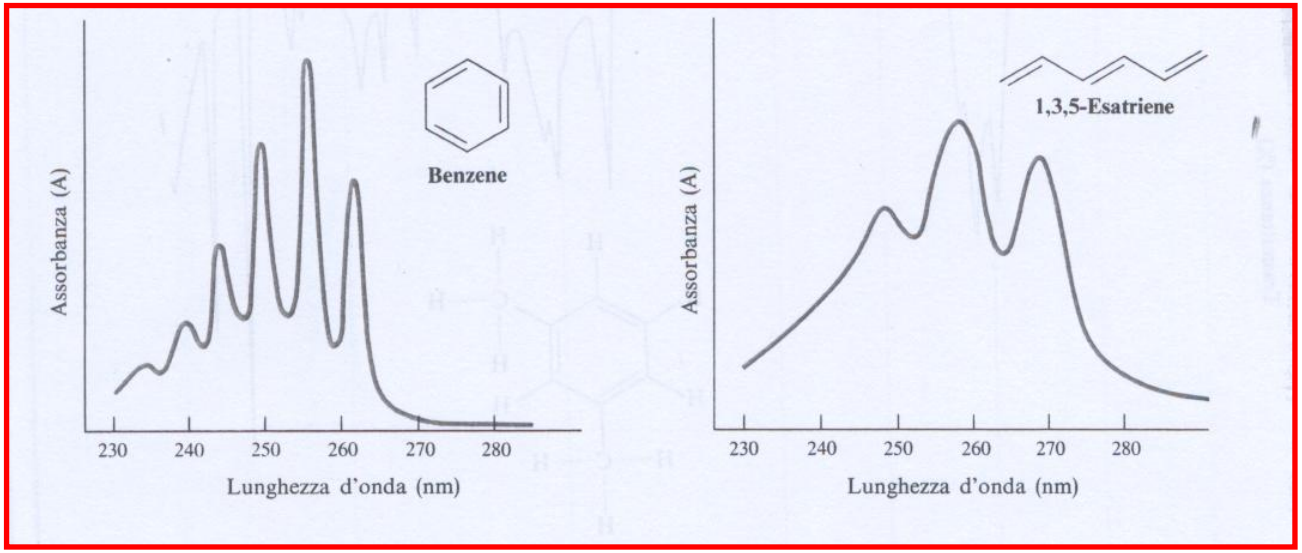



π_6
π_5
π_4
energy
π_2
π_3
π_1


ψ_6
ψ_4
ψ_5
E
ψ_2
ψ_3
ψ_1
π_6
π_5
π_4
π_3
π_2
π_1
A
B

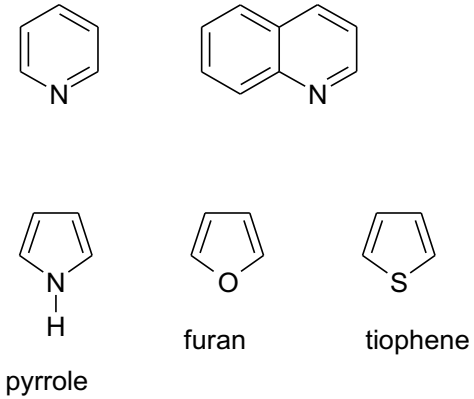
Benzene: cyclic vs homologous linear compound





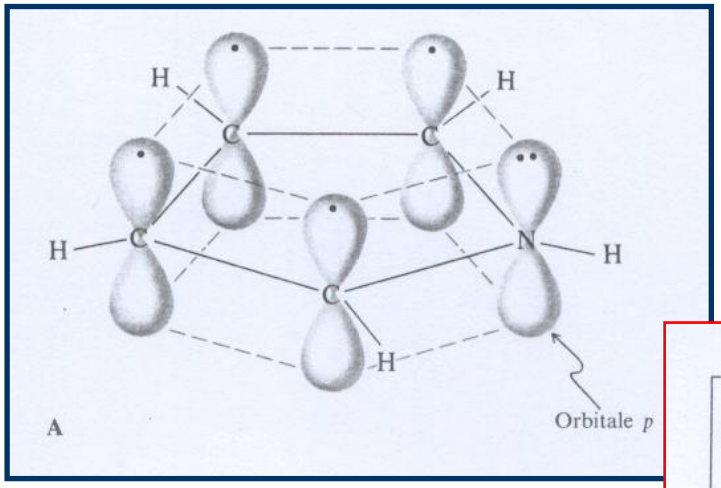
Conjugation:
not only linear double bonds…

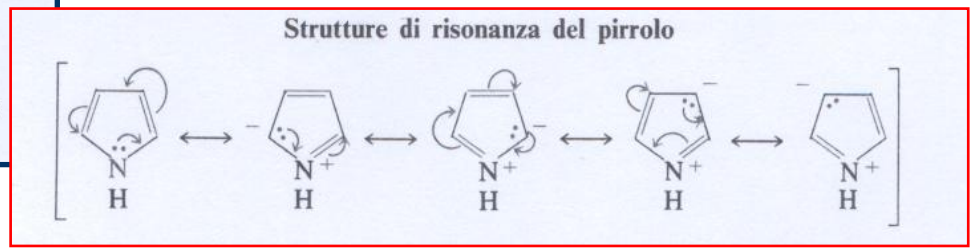
✓Isoelectronic as a benzene (aromatic compounds)
✓ thiophene: relative high chemical stability
✓thiophene: highly versatile in organic chemistry



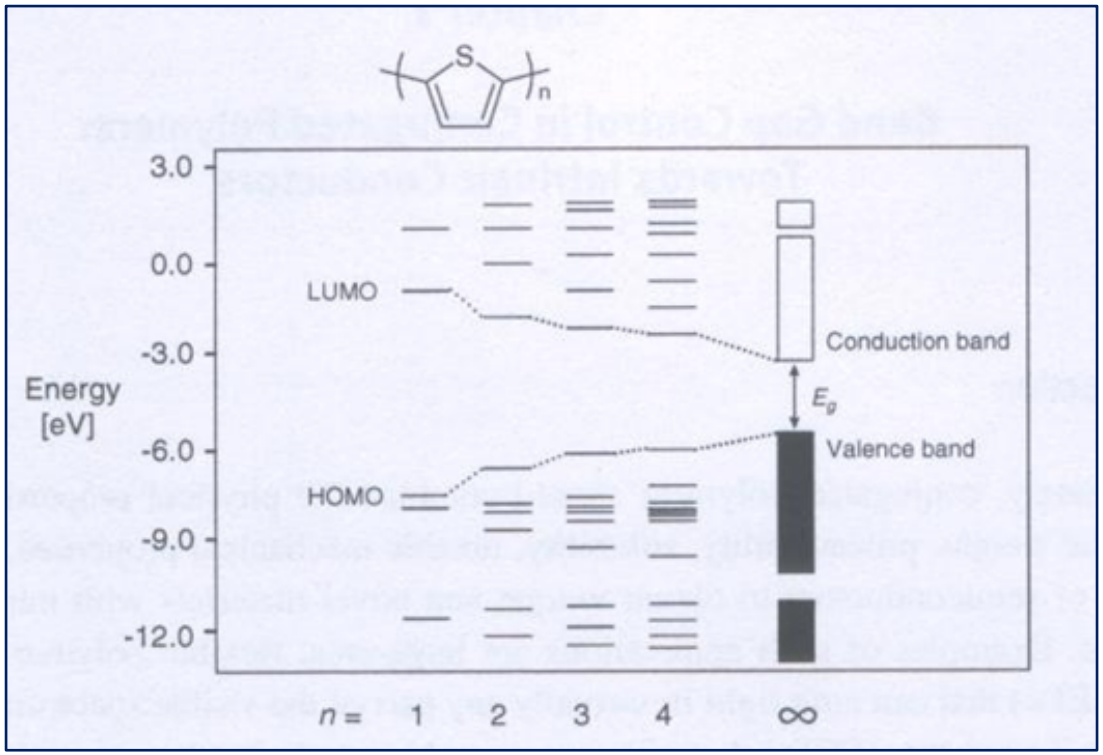
HETEROCYCLES

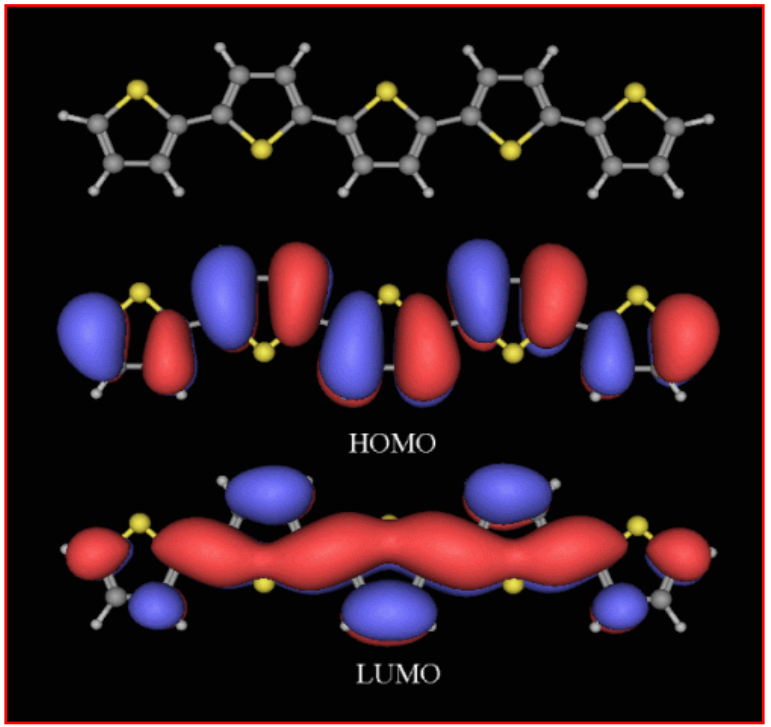
5-MEMBERED HETEROCYCLES



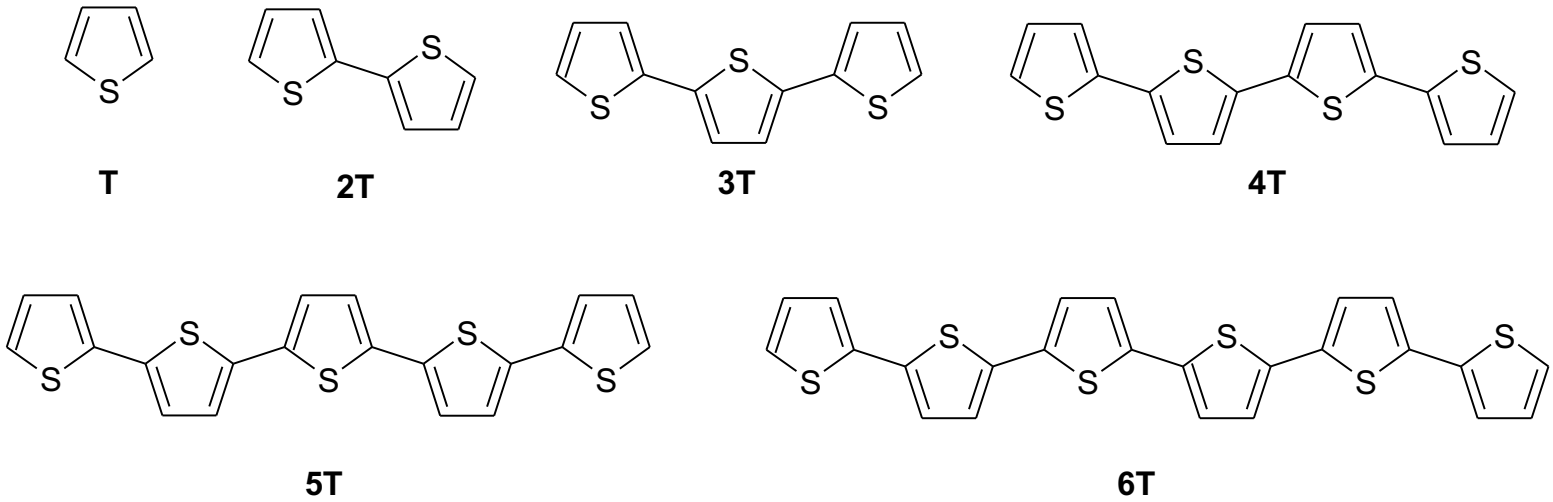


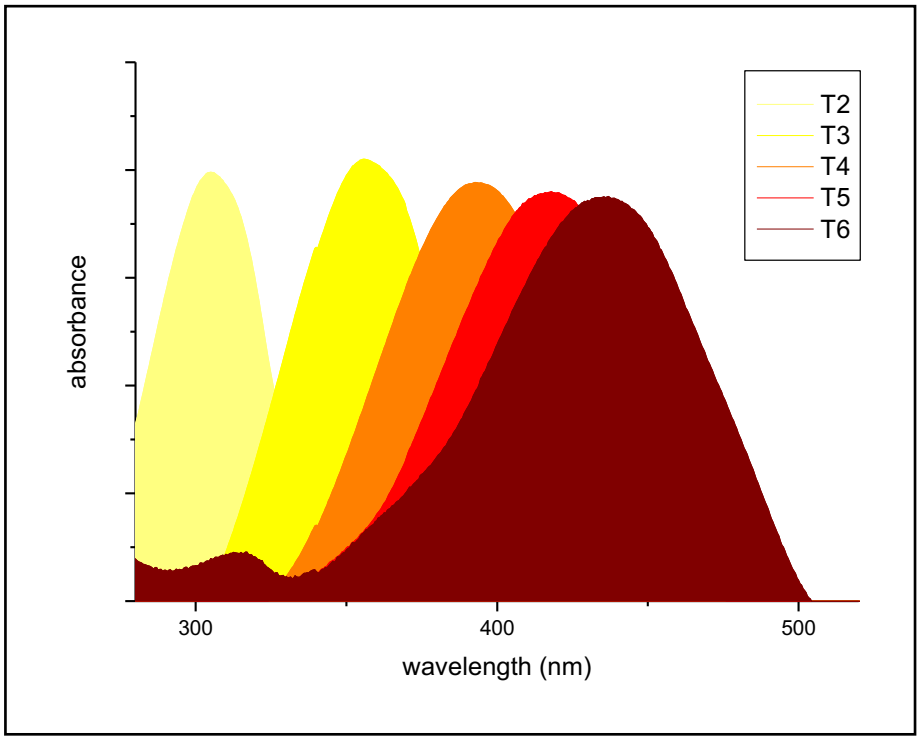
Electronic levels and optical properties: the UV-vis electronic spectra of oligo-/poly-thiophene



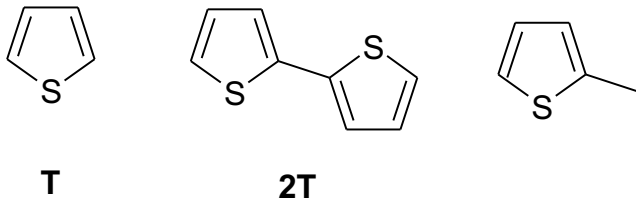


Electronic levels and optical properties: the UV-vis electronic spectra of oligothiophene



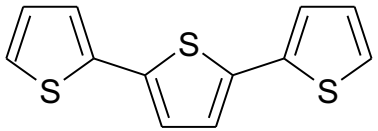


Electronic levels and optical properties: the UV-vis electronic spectra of oligothiophene

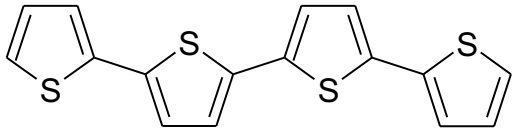


T

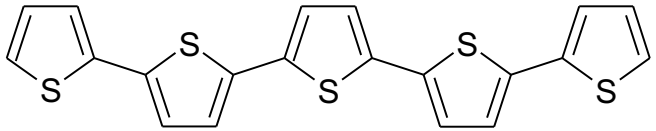
2T



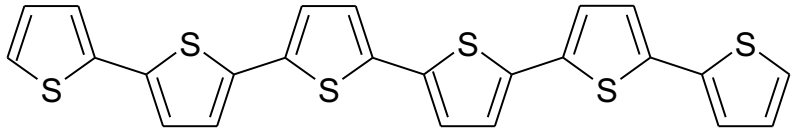
3T



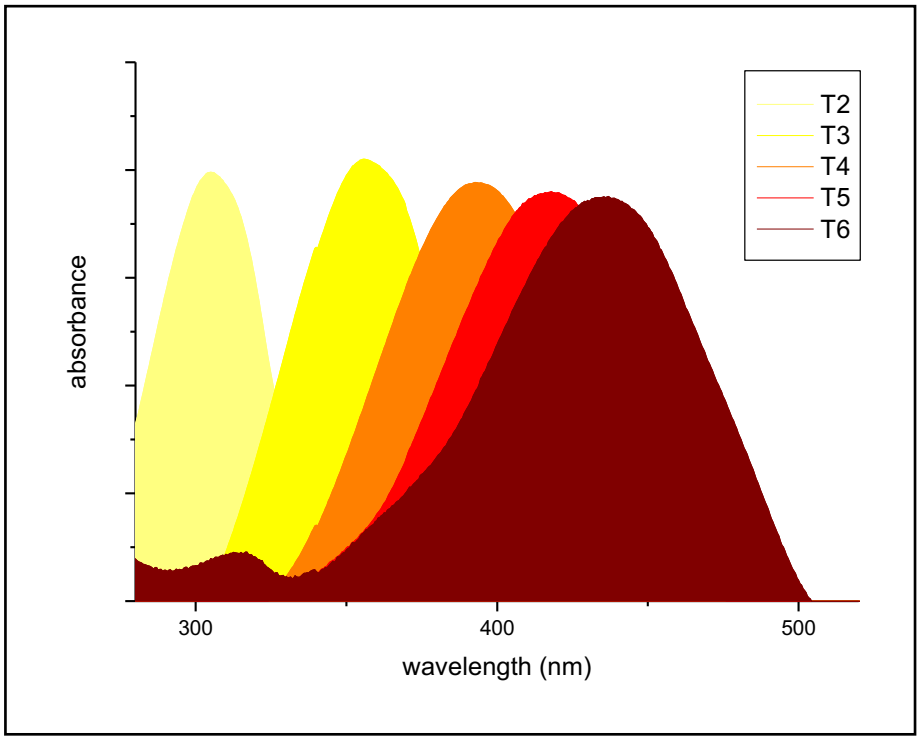
4T

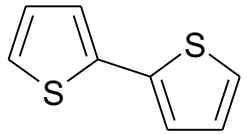


5T



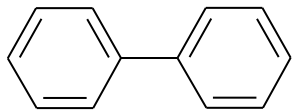
6T





2T

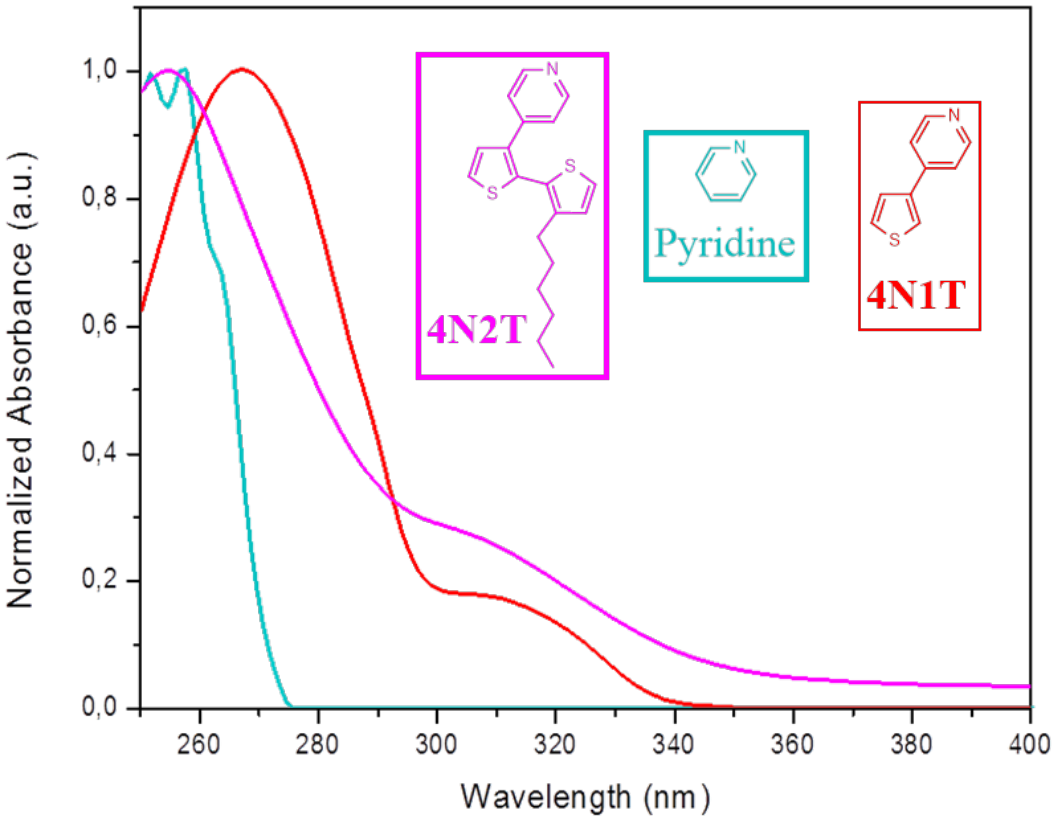
λ_{max} = 305 nm

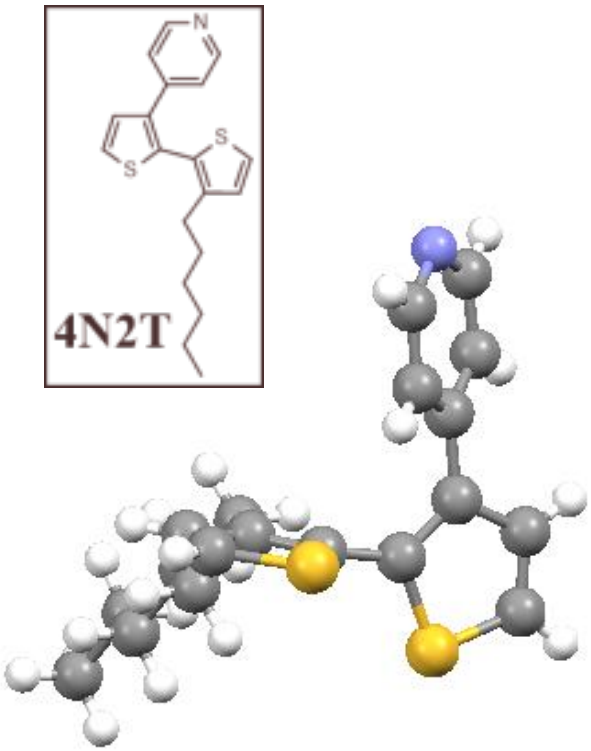


λ_{max} = 245 nm

Thiophene: smaller resonance energy
smaller steric hindrance
H2-H2’

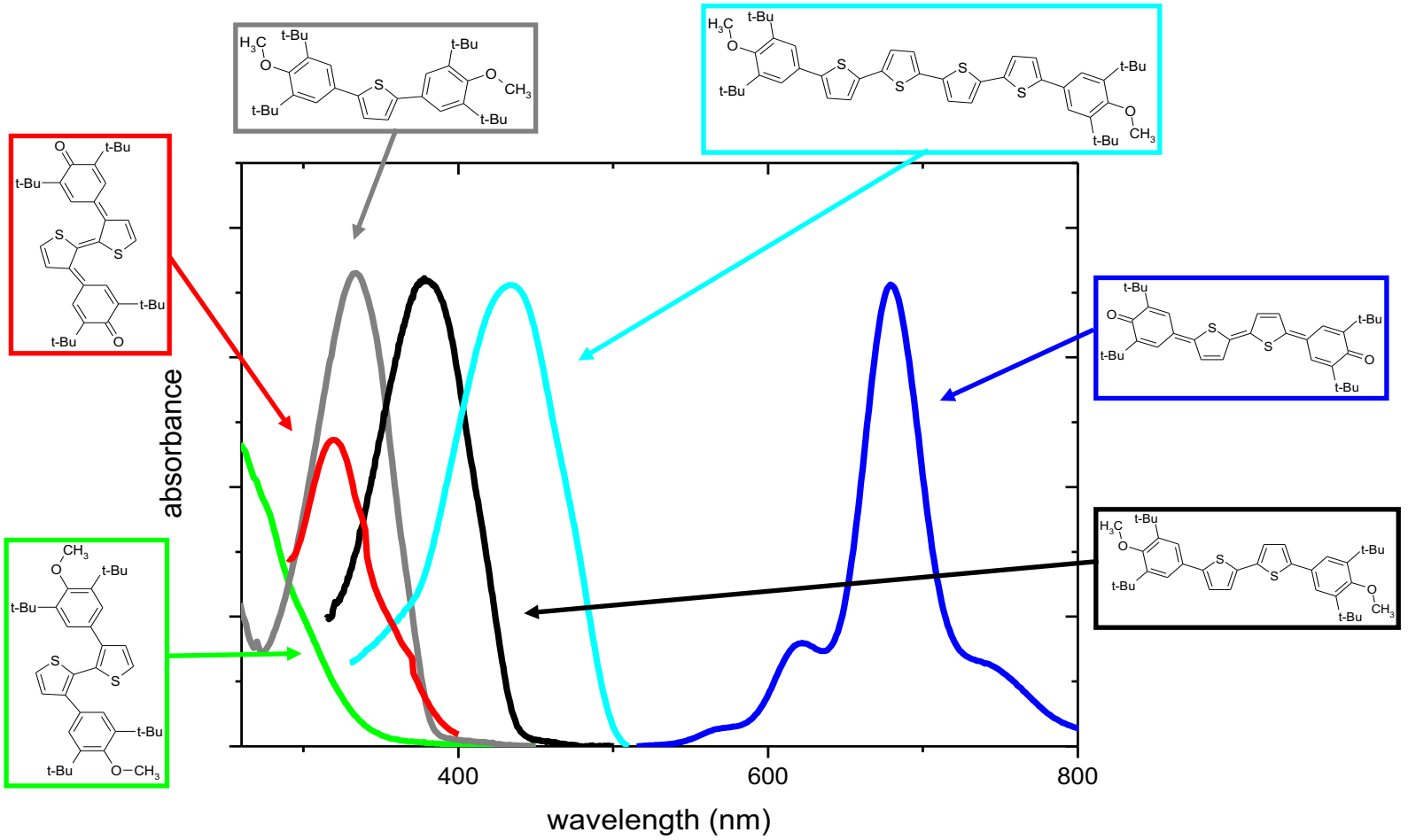
Steric Hindrance





Courtesy of J. M. Rujas

Electronic spectra (UV-vis)

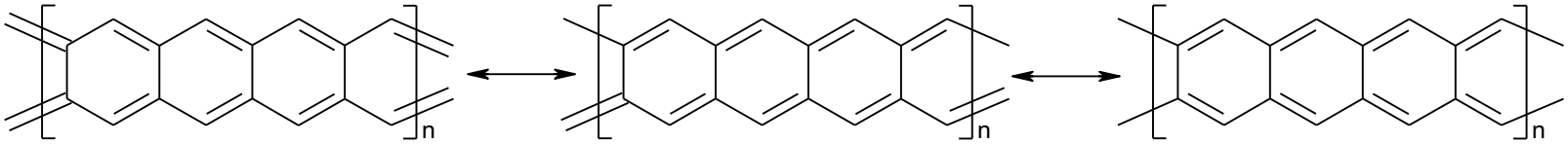


	Z-aromatica	Z-chinoide	Z-aromatica ++	L-aromatica	L-chinoide
fenile-tiofene	40,3	32,1	34,7	21,3	0,0
tiofene-tiofene	65,6	35,5	32,5	19,8	0,0

Fig 3.8 Valori calcolati degli angoli torsionali attorno ai legami tiofene-tiofene e fenile-tiofene per le due classi di molecole: lineari (L) e a "Z".

Ladder polymers

polyacenes



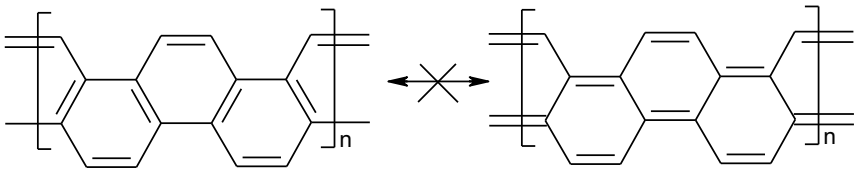
E_{gap} = 0 eV (Bredas, Pomerantz)

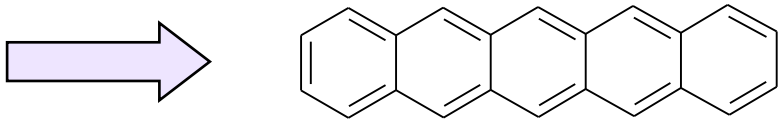
E_{gap} = 0.5 eV (Yamabe)

E_{gap} = 0.2 eV (Kao and Lilly)

n_{max}= 7

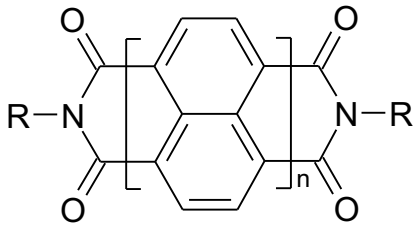
polyphenantrene

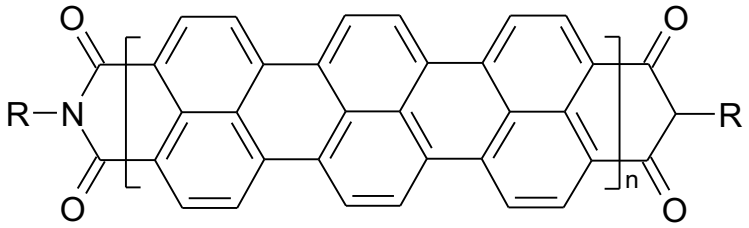


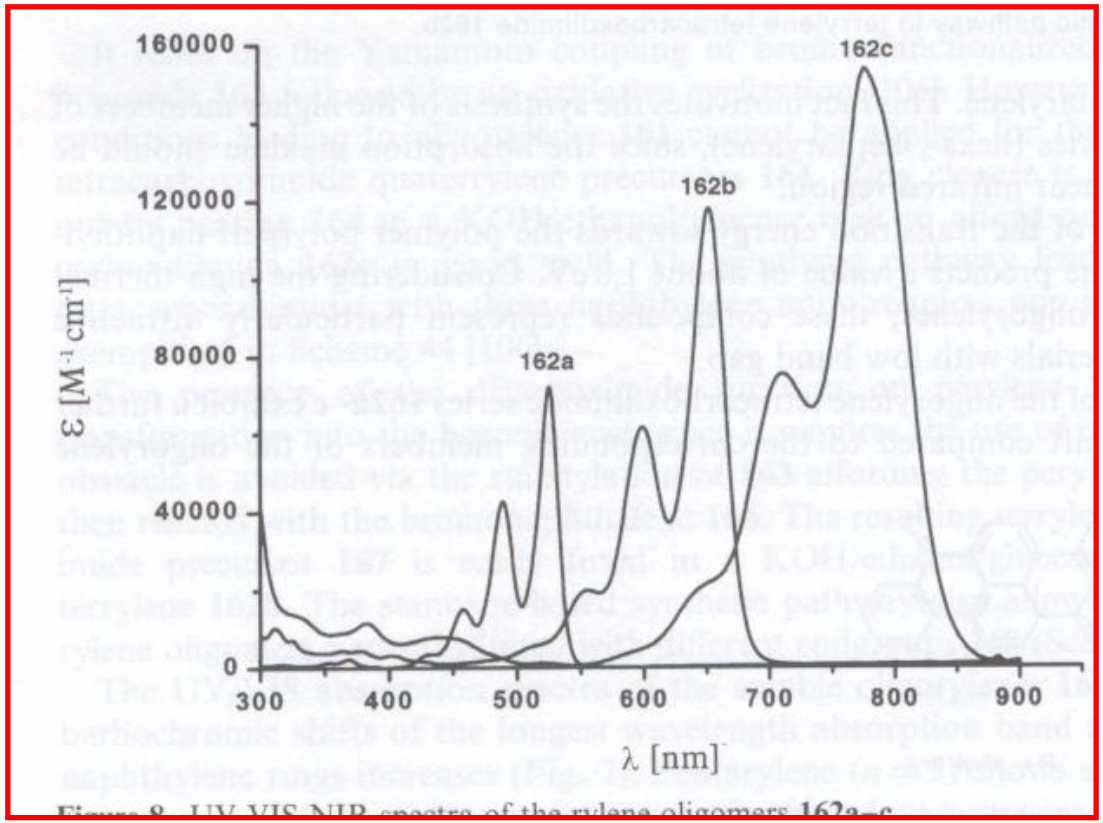


pentacene (OFET)

The electronic spectra (UV-vis): Ladder polymers

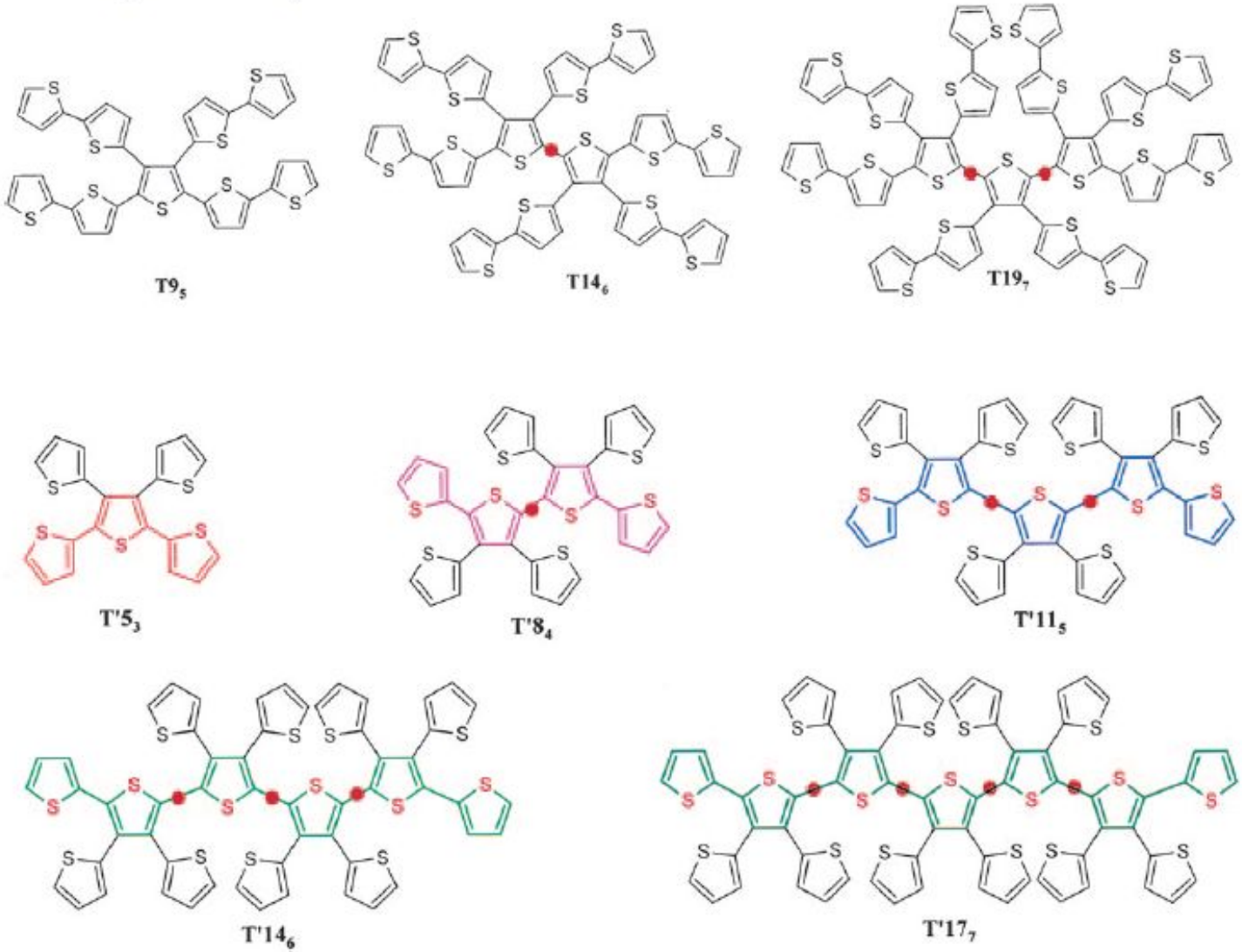






Branched oligoenes

Towards Molecular Design Rationalization in Branched Multi-Thiophene Semiconductors: The 2-Thienyl-Persubstituted α-Oligothiophenes, Chem. Eur. J. 2010, 16, 9086-9098.
T.Benincori, V.Bonometti, ...8... and F.Sannicolo*



Scheme 1. The TX_Y series and the new $T'X_Y$ series. Red circles indicate "nodes" in the main α-conjugated backbone (see text for discussion).

Branched oligoenes

Towards Molecular Design Rationalization in Branched Multi-Thiophene Semiconductors: The 2-Thienyl-Persubstituted α-Oligothiophenes, Chem. Eur. J. 2010, 16, 9086-9098.
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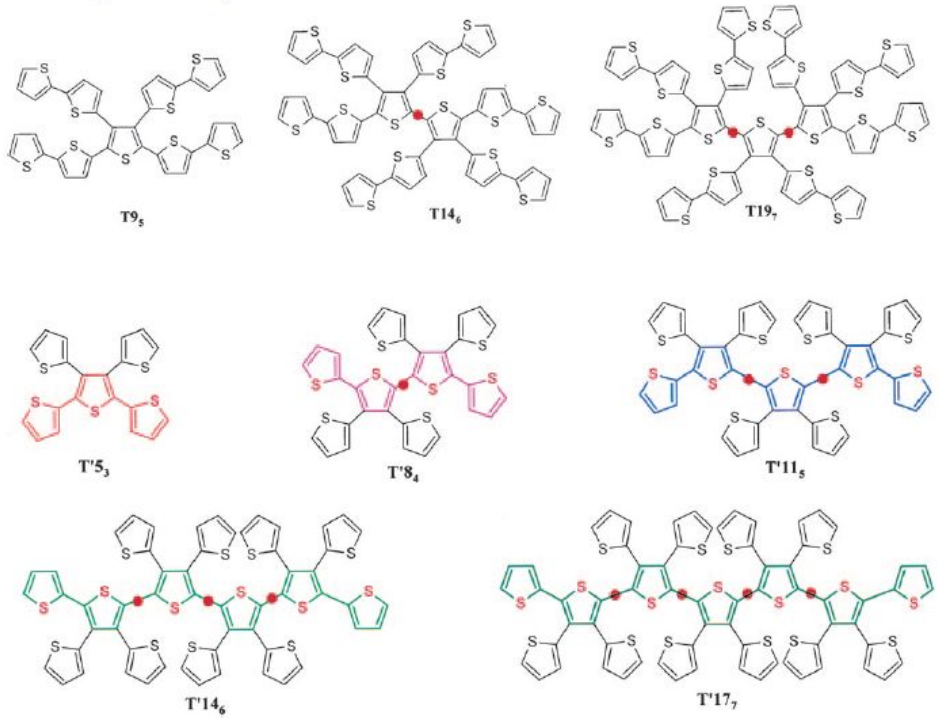


Scheme 1. The TX_Y series and the new $T'X_Y$ series. Red circles indicate "nodes" in the main α-conjugated backbone (see text for discussion).

Table 1. UV/Vis characterization of TX_Y and $T'X_Y$ compounds: UV/Vis absorption maxima and onset wavelengths, λ_{max} and λ_{onset}, and the corresponding bandgap energies, $E_{g,max}$ and $E_{g,onset}$.

Compound	λ_{max} [nm]	λ_{onset} [nm]	$E_{g,max}$ [eV[	$E_{g,onset}$ [eV]
T'5$_3$	362	425	3.42	3.92
T'8$_4$	370	460	3.35	2.69
T9$_5$	419	500	2.96	2.48
T'11$_5$	375	490	3.30	2.53
T14$_6$	420	515	2.96	2.41
T'14$_6$	370	500	3.35	2.48
T'17$_7$	400	510	3.10	2.43
T19$_7$	421	523	2.95	2.37

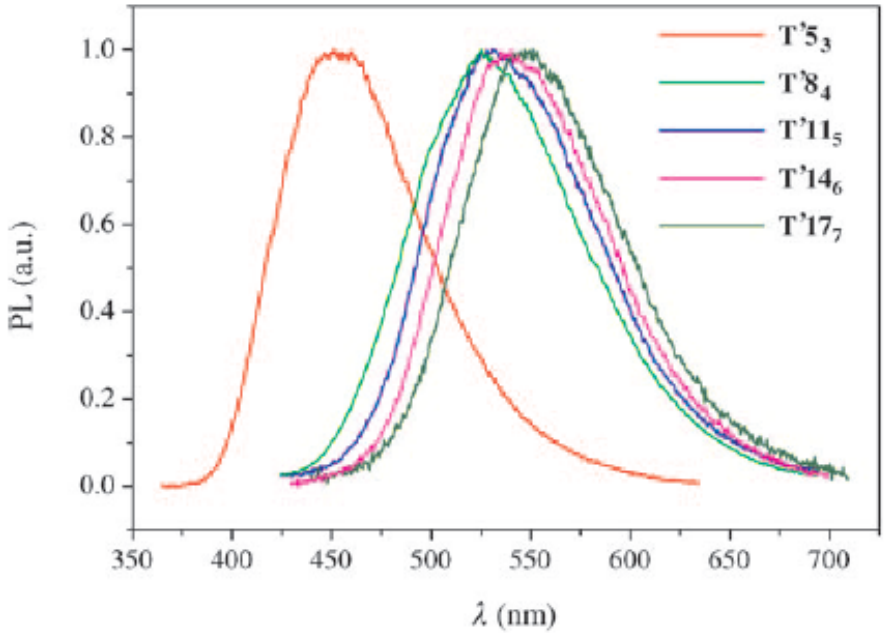
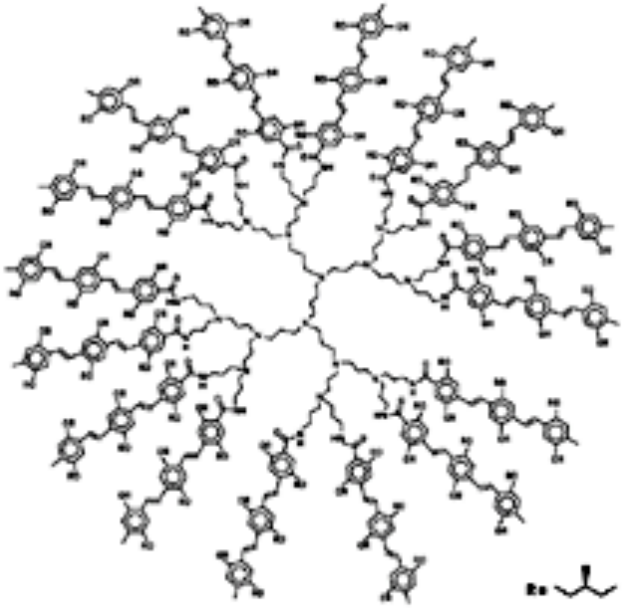
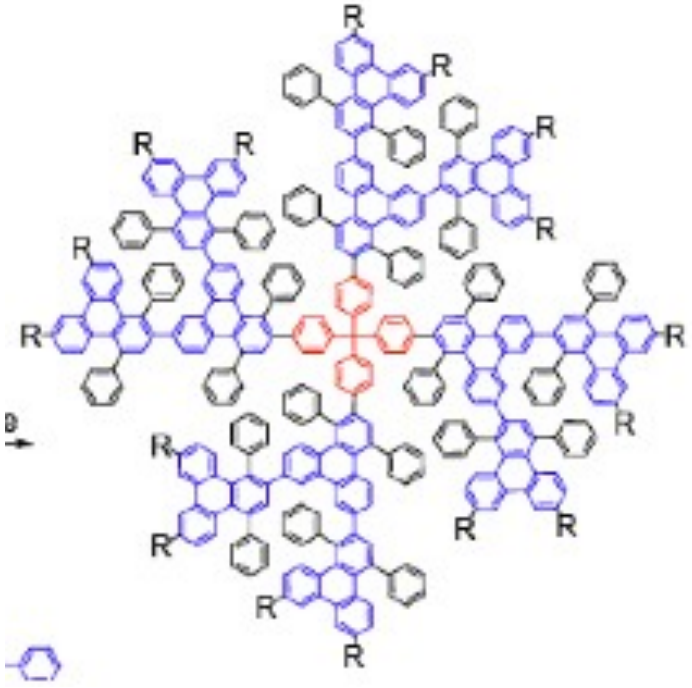


Figure 8. Normalized PL spectra of $T'X_Y$ in 10^{-5} M CH_2Cl_2 solutions.

Dendrimers





The attractive properties of multi-chromophores dendrimers suggested a new approach towards blue light-emitting materials with the following characters:

(i) blue light emission is brought about by the presence of electronically decoupled polycyclic aromatic hydrocarbon (PAH) units;

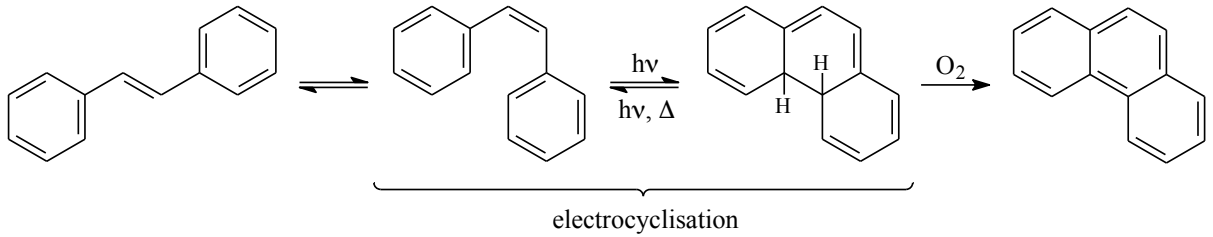
(ii) the units are incorporated into a rigid polyphenylene dendritic structure and thus adopt sterically defined positions and disallow intra-dendrimer chromophore-chromophore interactions;

(iii) amorphous films are obtained due to the lack of intermolecular interactions;

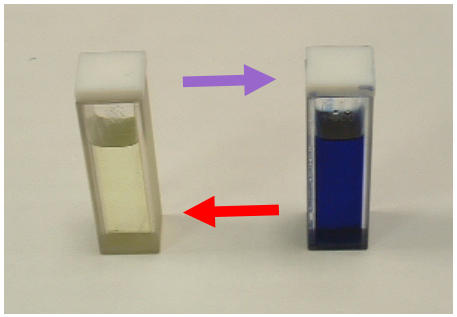
(iv) the amount of "useless" substituent and coupling units is kept at a minimum

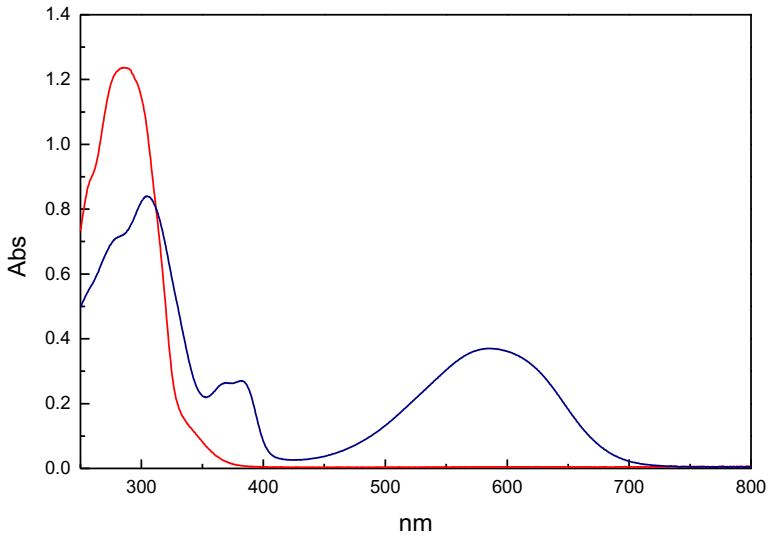
Electronic spectra: electrocyclization

Stilbene:



Analogous dithienylethenes





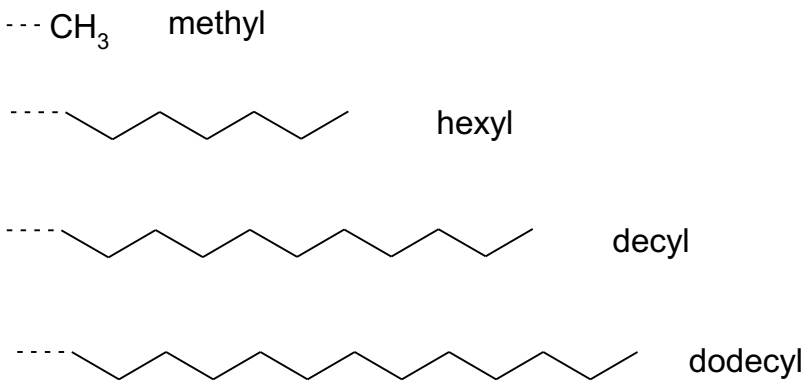
The side groups

Side groups are usually introduced onto the main molecular skeleton :

- ✓ solubility
- ✓ conjugation
- ✓ HOMO/LUMO levels and bandgap
- ✓ intermolecular interactions: solid state packing/self-assembly

#1: alkyl chains

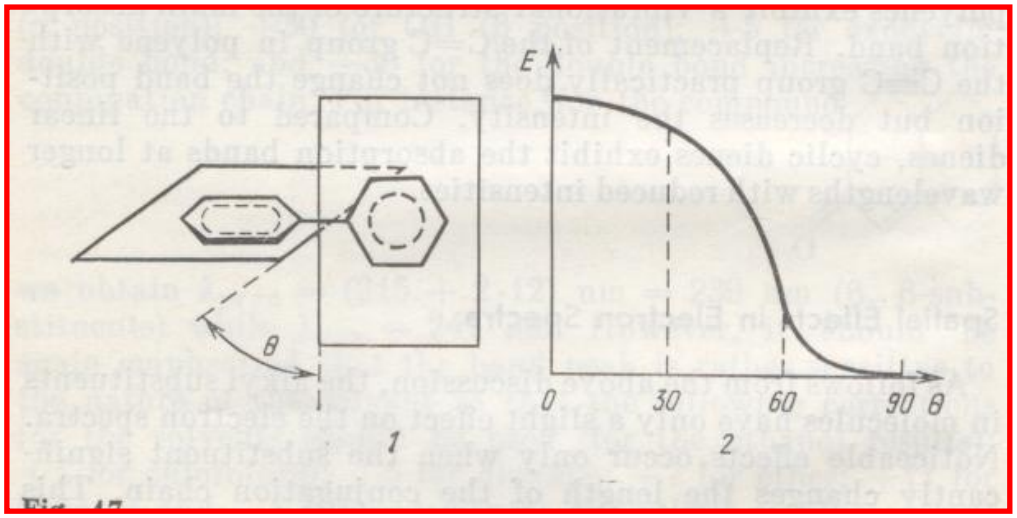
its main role is to increase solubility
cooperate to the intermolecular packing through Van der Waals interactions

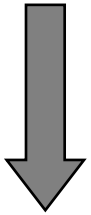


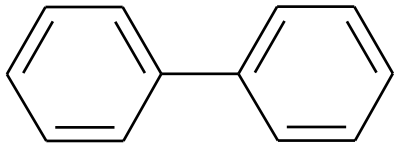
#2: functional groups

selective/specific interactions
post-functionalization
electronic effect

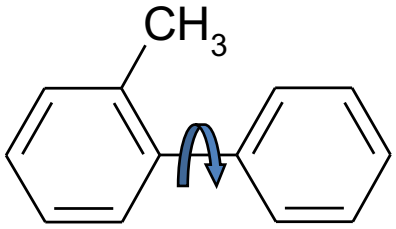
Steric effect of side groups: distortion of the skeleton







θ = 45°

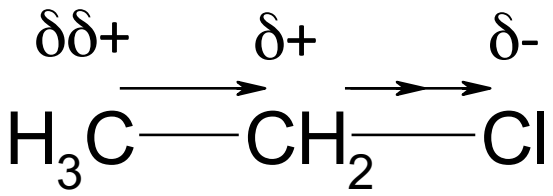


λ_{max} = 245 nm (ε_{max} = 19000)

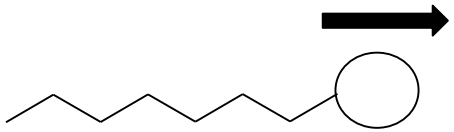
λ_{max} = 236 nm (ε_{max} = 10000)

Electronic effect of side groups: inductive effect

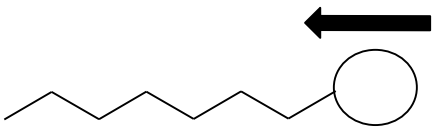
Inductive effect: polarization of a bond caused by the polarization of an adjacent bond



- ✓ Strongly related to electronegativity
- ✓ the effect is greatest for adjacent bonds but may be felt far away
- ✓ The only effect in saturated hydrocarbons



-I Electron-withdrawing



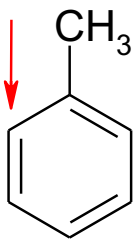
+I Electron-donating

The analogous effect which does not operate through bonds, but directly through space (or solvent molecules) is named field effect. It is often very difficult to separate these two effects.

Electroactive substituents onto aromatic rings

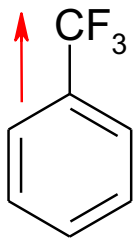
Inductive effect

donor



Ring relatively rich of electrons
(more reactive)

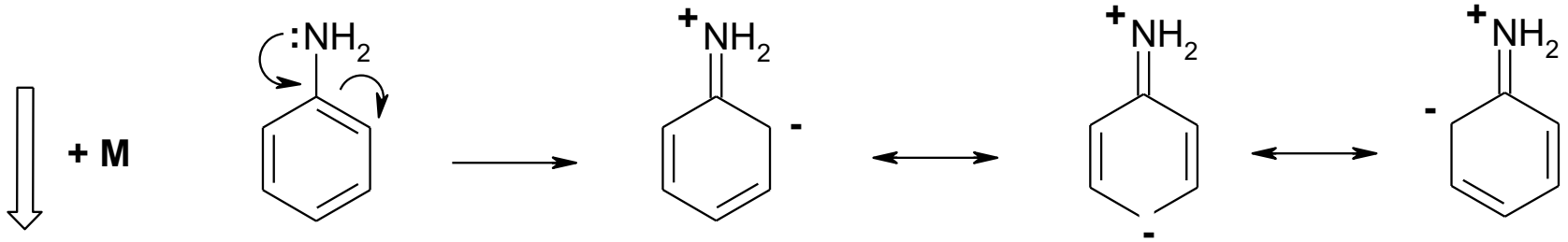
acceptor



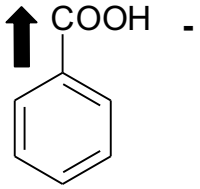
Ring relatively poor of electrons
(less reactive)

Resonance effect (mesomeric effect)

Decrease in electron density in one position (and corresponding increase elsewhere) due to the presence of unshared electrons pair

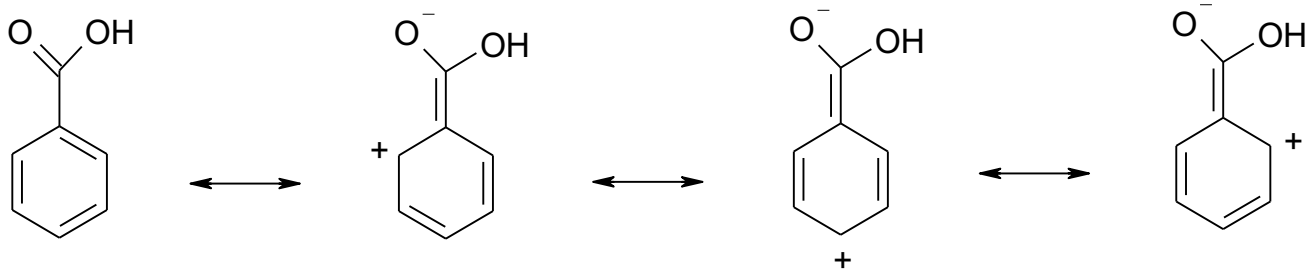


Electroactive substituents onto aromatic rings



Inductive effect

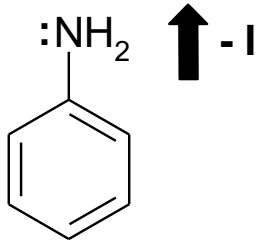
-M



examples **- M**

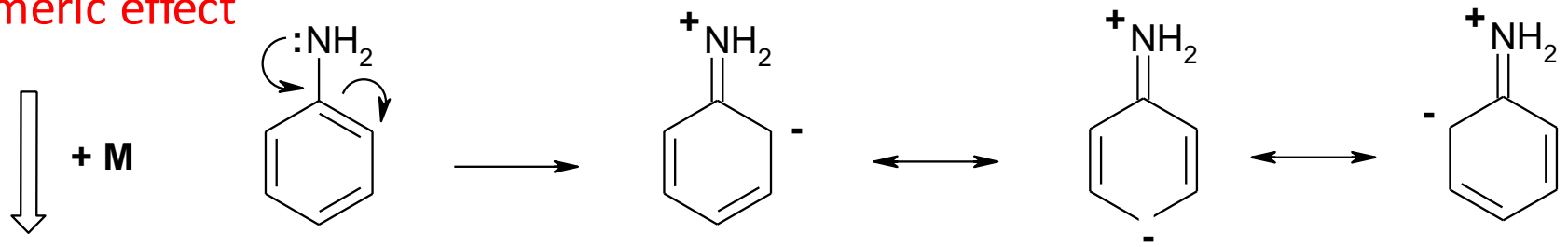
NO_2 CHO COOH CN

Electroactive substituents onto aromatic rings



Inductive effect

Mesomeric effect

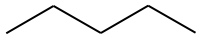
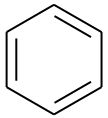


examples

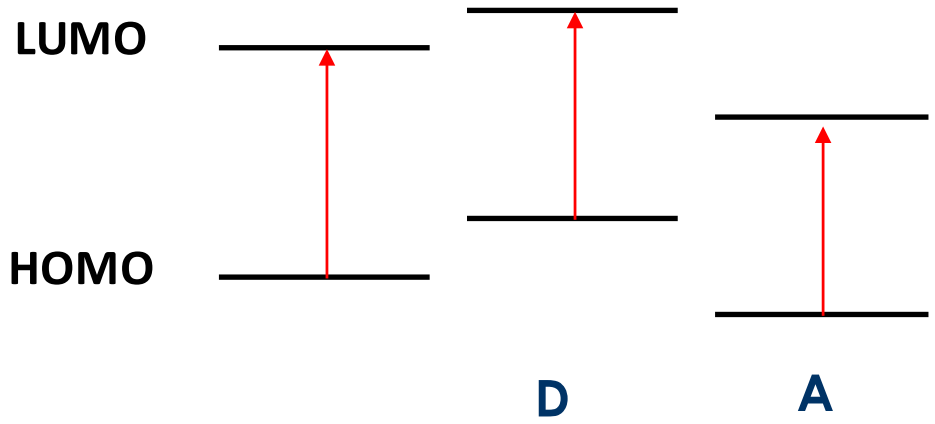
+M

OH OMe —NH2 Alogeni

Electronic effect of side groups: mesomeric and inductive effects

—CH_3	+ I		+
	+ I		+
	- I		-
—$SiMe_3$	+ I		+
—NH_2	- I	+ M	+
—NO_2	- I	- M	-
—OH	- I	+ M	+
—OMe	- I	+ M	+
—COOH	- I	- M	-
—CHO	- I	- M	-
—CN	- I	- M	-
—F	- I	+ M	-
—Cl	- I	+ M	-
—Br	- I	+ M	-

Effect of electo-active substituents on the electronic levels of the skeleton



Introduction of electro-active groups:

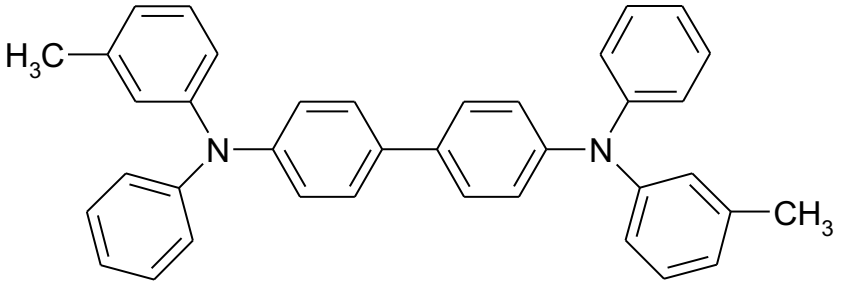
✓ Affects the ionization potential and electron affinity, that is HOMO/LUMO

✓ Affects E_{GAP}

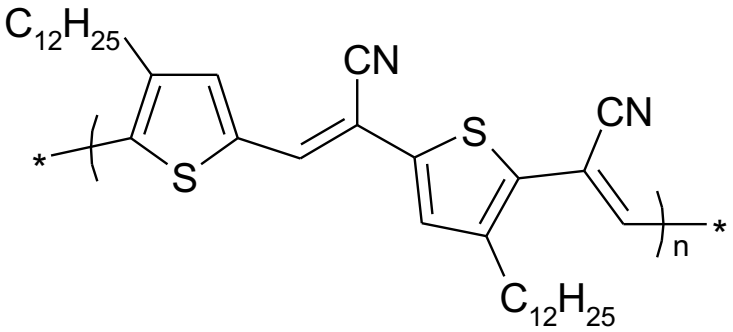
✓Selectively enhances electron vs hole transport

✓ Tunes the barrier org/Mt

Effect of electo-active substituents on the electronic levels of the skeleton

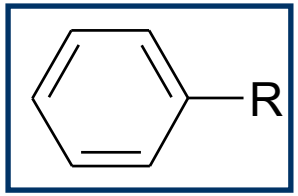


Good hole transporter

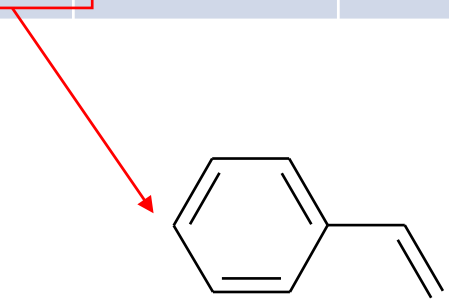


High electron affinity
Good electron transporter

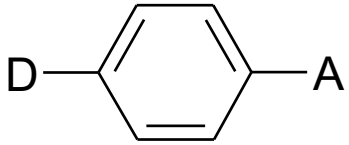
Substituted benzene: Electronic spectra



R	Band at 200 nm		Band at 256 nm	
	λ (nm)	ε	λ (nm)	ε
---	203	7400	256	220
CH3	206	7000	261	225
OH	211	6200	270	1450
SH	236	8000	271	630
NH_2	230	8600	280	1430
CH_2=CH	244	12000	282	750

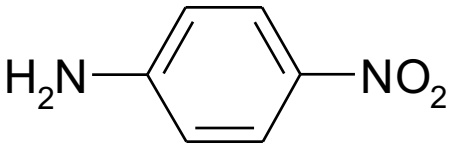


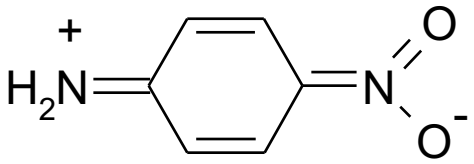
donor-acceptor systems



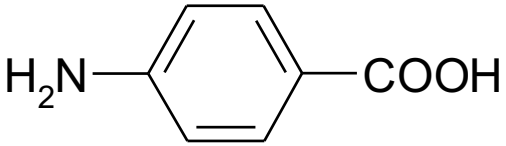
Donor-acceptor

$h\nu \approx I_D\text{-}E_A$

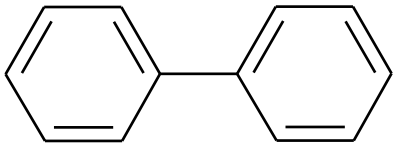




Charge-transfer



λ_{max} = 289 nm (ε_{max} = 18600)



λ_{max} = 245 nm (ε_{max} = 19000)

donor-acceptor systems: effect on the electronic levels

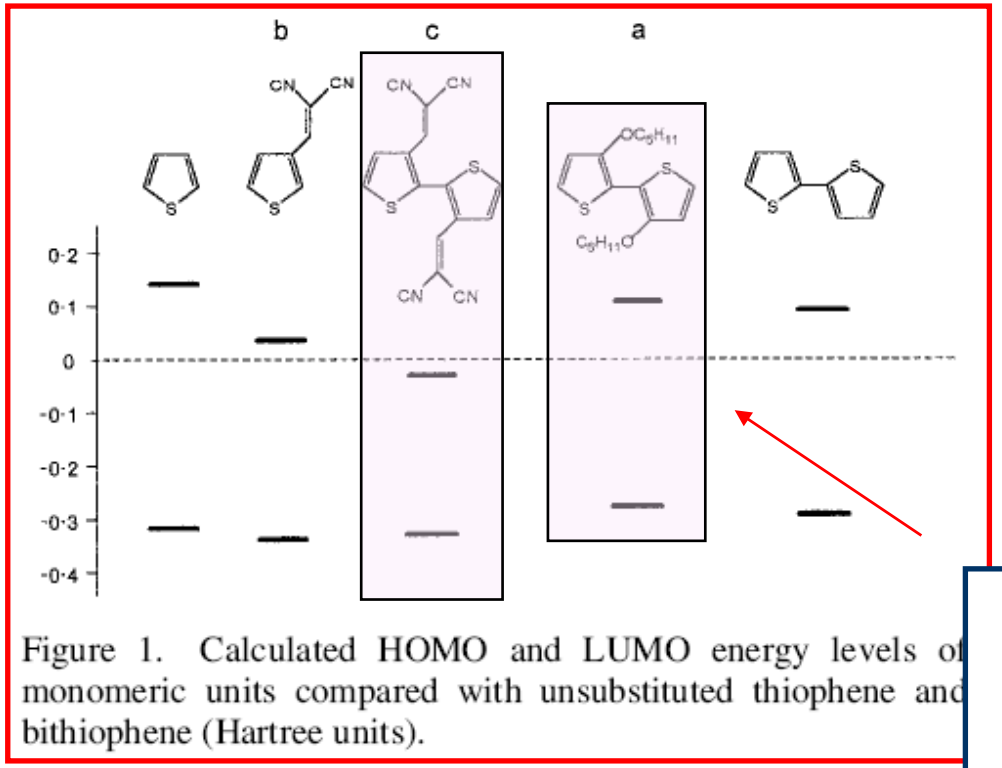
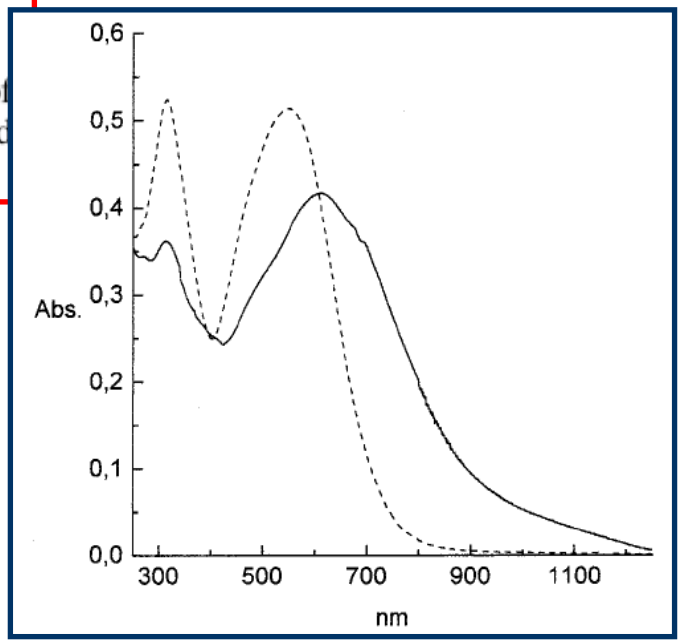


Figure 1. Calculated HOMO and LUMO energy levels of monomeric units compared with unsubstituted thiophene and bithiophene (Hartree units).



E_{gap} (polymer) = 1.2 eV

M.C. Gallazzi *et al.*, *Macromol. Chem. Phys.* 2001, **202**, 2074