Electronic and Optoelectronic Polymers
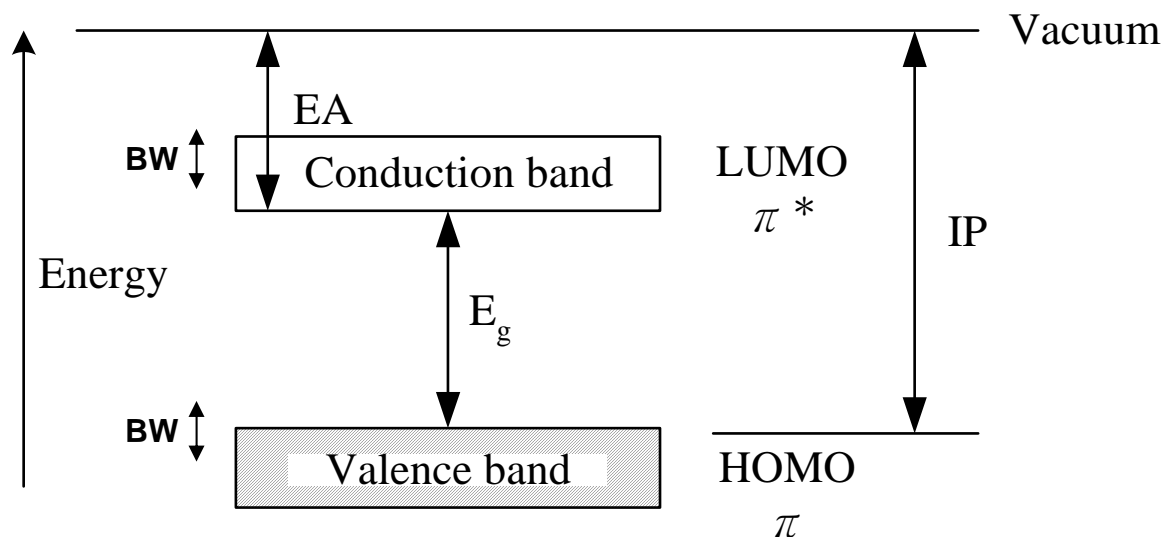
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Institute of Polymer Science and Engineering

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Outlines

Electronic Parameters of Conjugated Polymers

Eg: Band gap = IP - EA

IP: Ionization potential

EA: Electron affinity

BW: Bandwidth

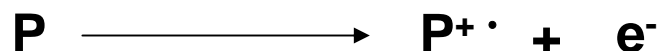LUMO: **L**owest **U**noccupied **M**olecular **O**rbital

HOMO: **H**ighest **O**ccupied **M**olecular **O**rbital

Electronic Parameters of Conjugated Polymers

Ionization Potential (IP)

**The energy required for the ionization reaction. The minimum energy needed to remove an electron from the top of the valence band to vacuum level**

$$P \longrightarrow P^{+\cdot} + e^-$$

Thus, the IP values for a polymer indicate the susceptibility or ease of removing electrons from the polymer by a suitable electron acceptor. IP values measure the dopability of a polymer to a p-type conductor or ease of hole injection .

Electron Affinity (EA)

The energy needed to add an electron to the bottom of the conduction band or LUMO level from the vacuum level.

$$P + e^- \longrightarrow P^{-\cdot}$$
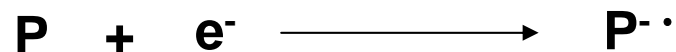
EA measures the ease of electron injection or n-type dopability
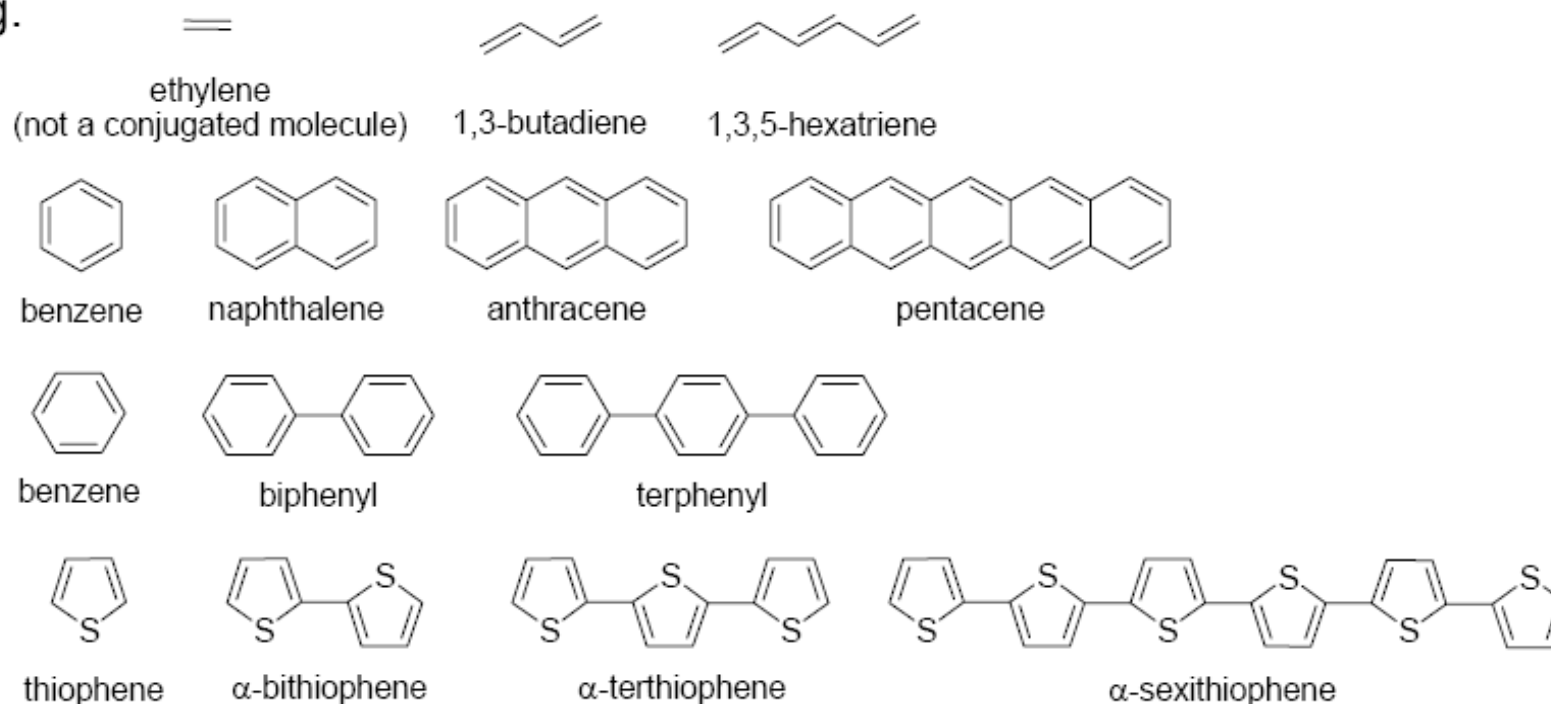
Bandgap or energy gap (E_g) = the smallest energy gap transition between π and π^* bands = HOMO-LUMO energy gap

π-Conjugated Molecules

Have been around a long time with numerous examples from organic and biological chemistry
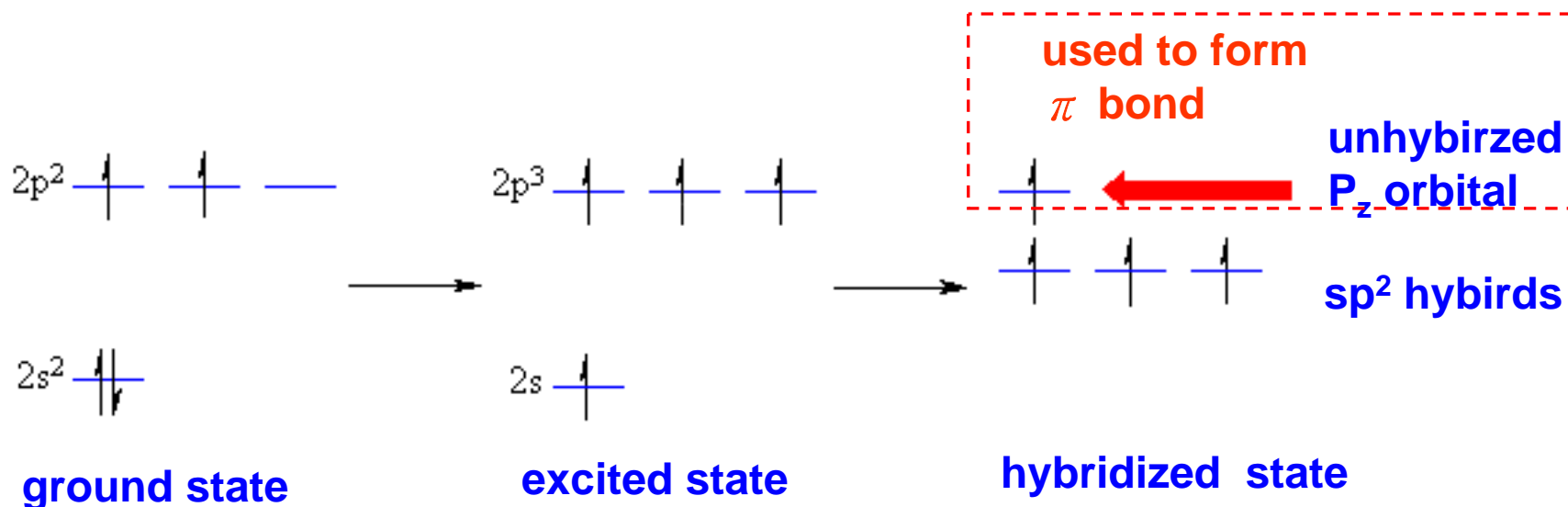
Molecules composed of alternating single and double bonds

e.g.

ethylene
(not a conjugated molecule)   1,3-butadiene   1,3,5-hexatriene

benzene   naphthalene   anthracene   pentacene

benzene   biphenyl   terphenyl

thiophene   α-bithiophene   α-terthiophene   α-sexithiophene

Towards Organic Semiconductors

Electronic Structures of Atomic Carbon in Conjugated Molecules

$2p^2$ ↿ ↿ —

$2p^3$ ↿ ↿ ↿

used to form π bond

↿⇂ ⬅ **unhybirzed P$_z$ orbital**

↿⇂ ↿⇂ ↿⇂ **sp^2 hybirds**

$2s^2$ ↿⇂

$2s$ ↿

ground state   **excited state**   **hybridized state**

- mix 3 orbitals, get a set of 3 sp^2 orbitals

- the other p orbital remains unaffected

- each sp^2 hybrid and p orbital contains a single unpaired electron

2s + **2p$_x$+2p$_y$** → **3 sp^2 orbitals**
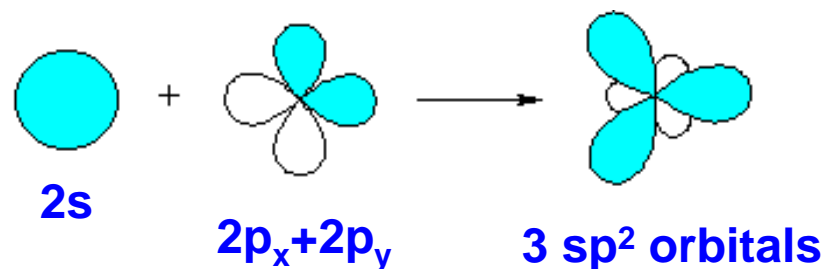
Molecular Orbital (MO) Theory of Conjugation
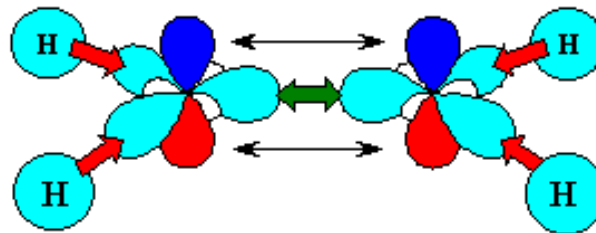
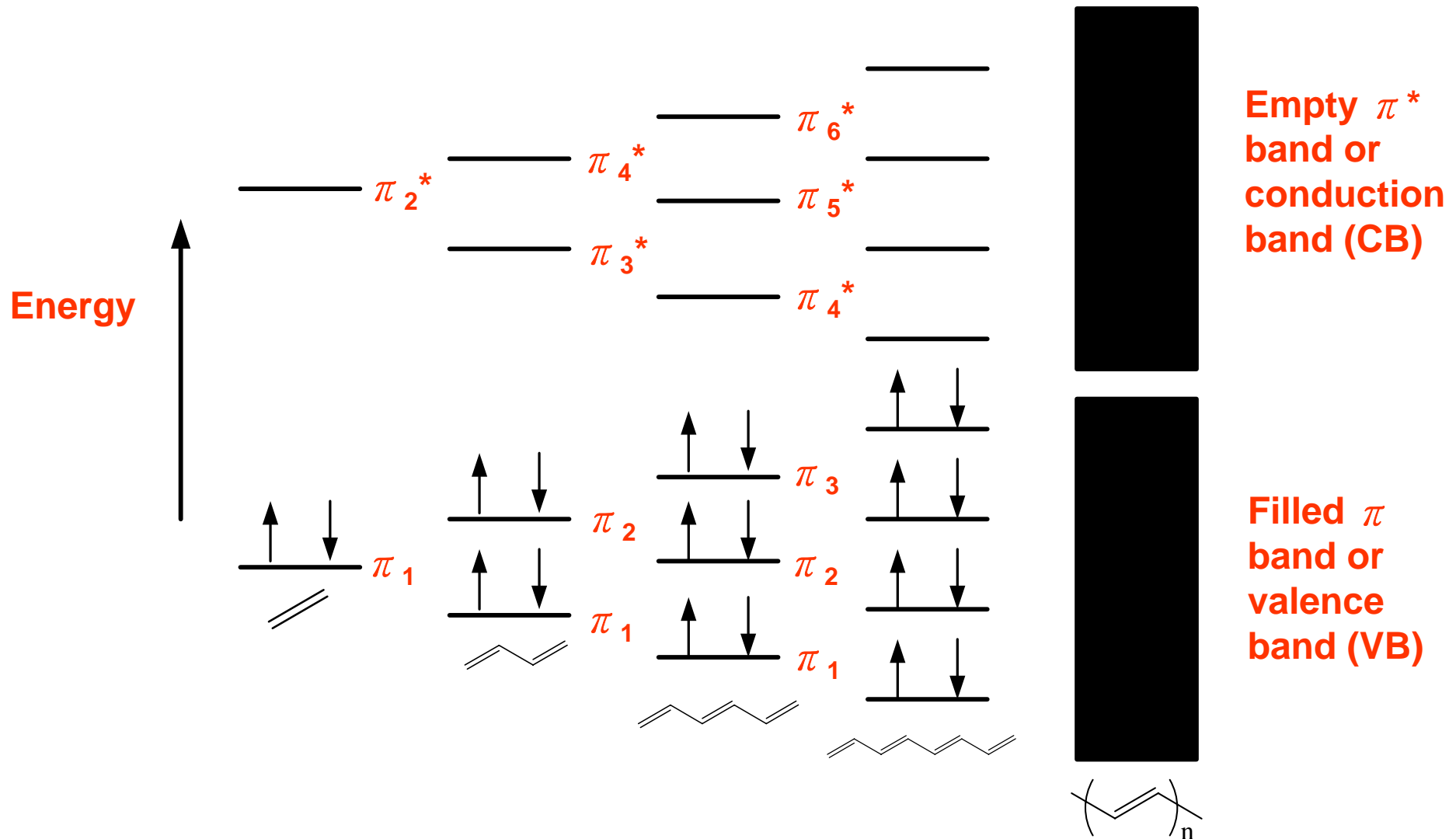- both C are sp2 hybridized.
- 4 **C-H** s bonds are made by the interaction of C sp^2 with H1s orbitals (see **red** arrows)
- 1 **C-C** s bond is made by the interaction of C sp^2 with another C sp^2 orbital (see **green** arrow)
- 1 **C-C** p bond is made by the interaction of the C p with the other C p orbital (see **black** arrows

Formation of the Molecular Orbitals for ethylene
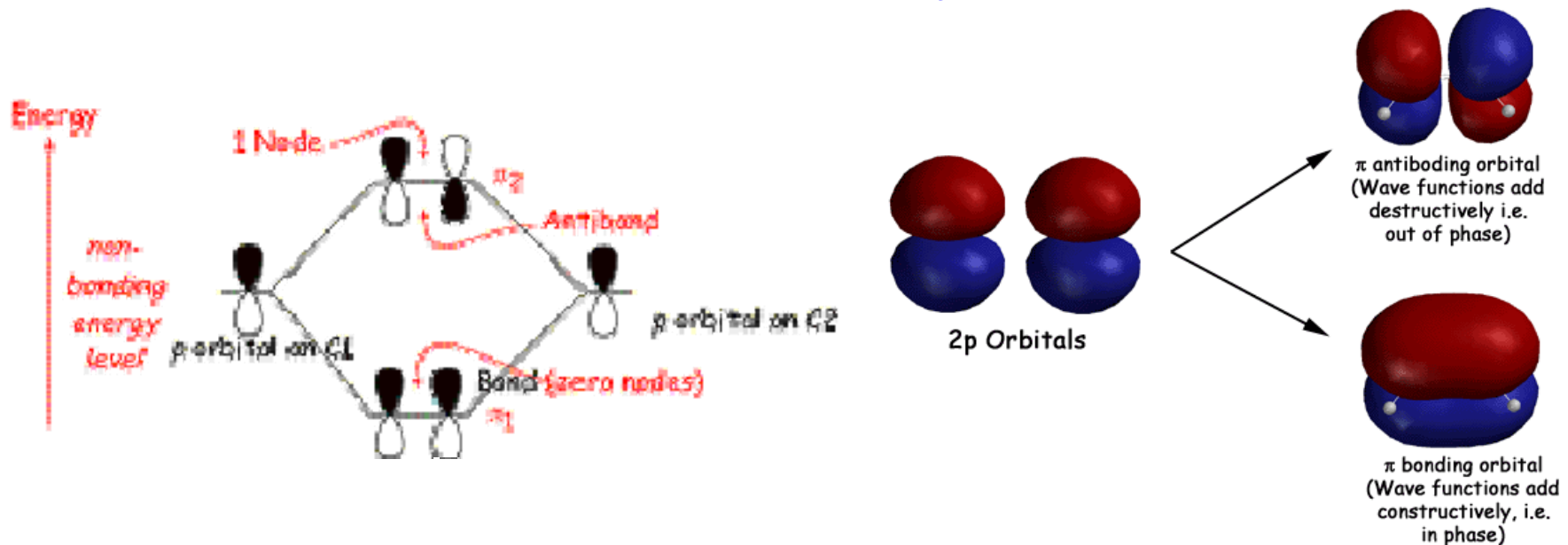
# Evolution of a Semiconductor Bandgap with Increasing Chain Length

π to π^* Energy Gap in a Series of Polyenes of Increasing Chain Length
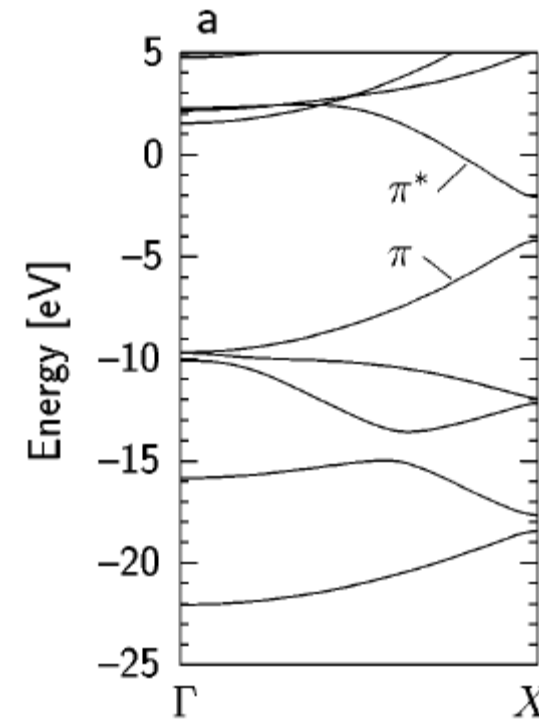
Energy

π_2^*

π_4^*

π_6^*

π_3^*

π_5^*

π_4^*

Empty π^* band or conduction band (CB)

π_1

π_2

π_1

π_3

π_2

π_1

Filled π band or valence band (VB)

The Hypothesis of Alternation -Peirels Instability

Why is Eg≠0 as n ⟶ ∞

The reason of a finite band gap in is instability of the ground state of a chain of equal bonds with respect to nuclear shifts that create a configuration having alternating lengths. Bond length alternations is due to gain in electronic energy that compensates the loss of elastic energy.
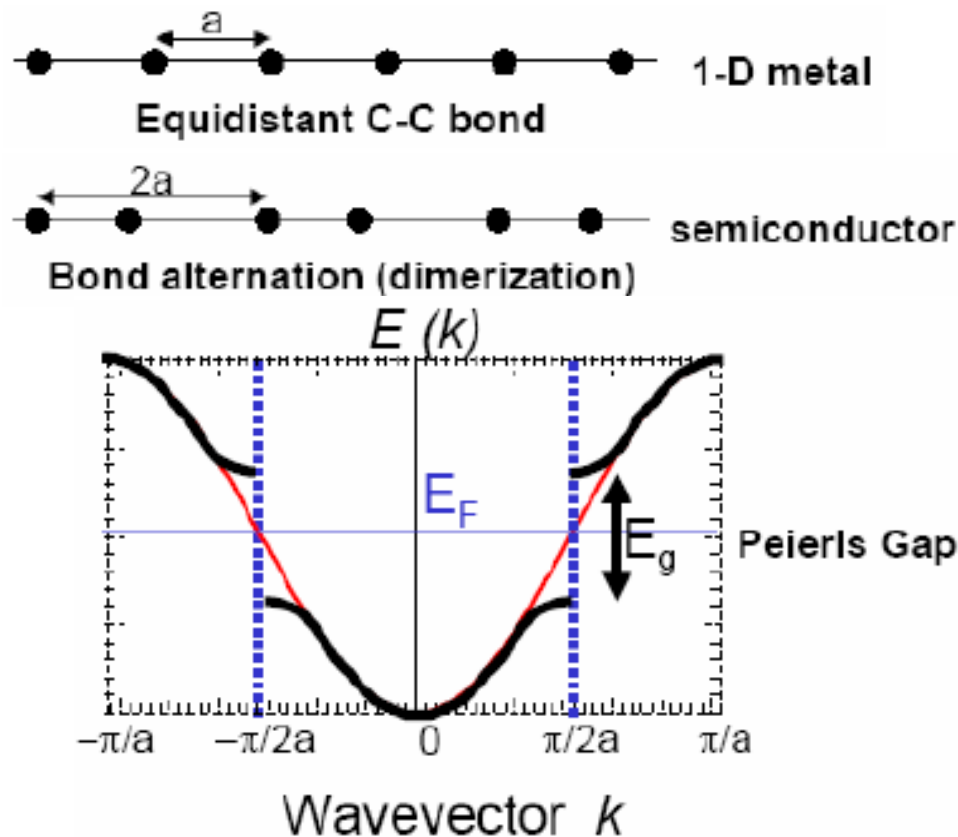

Band structures of trans-polyacetylene

# Five Main Contributions to Electronic Structures of Conjugated Polymers

$$Eg = E^{\delta r} + E^{\theta} + E^{Res} + E^{Sub} + E^{Int}$$

- $E^{\delta r}$: the energy related to **Bond Length Alternation (BLA)**.
- E^{θ}: the mean deviation from **planarity**.
- E^{Res}: the **aromatic resonance energy** of the cycle.
- E^{Sub}: the inductive or mesomeric electric effects of eventual **substitution**.
- E^{Int}: the **intermolecular** or **interchain coupling** in the solid state.

E^{Sub} E^{Res}

$E^{\delta r}$ $\theta°$

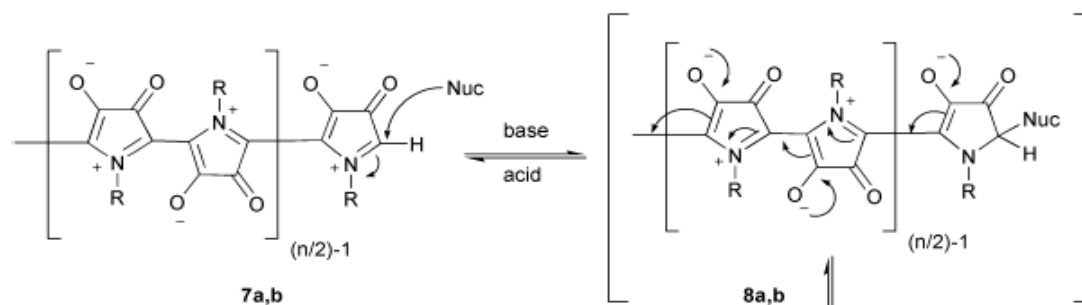E^{Int} E^{θ}

X = S, NH, CH=CH
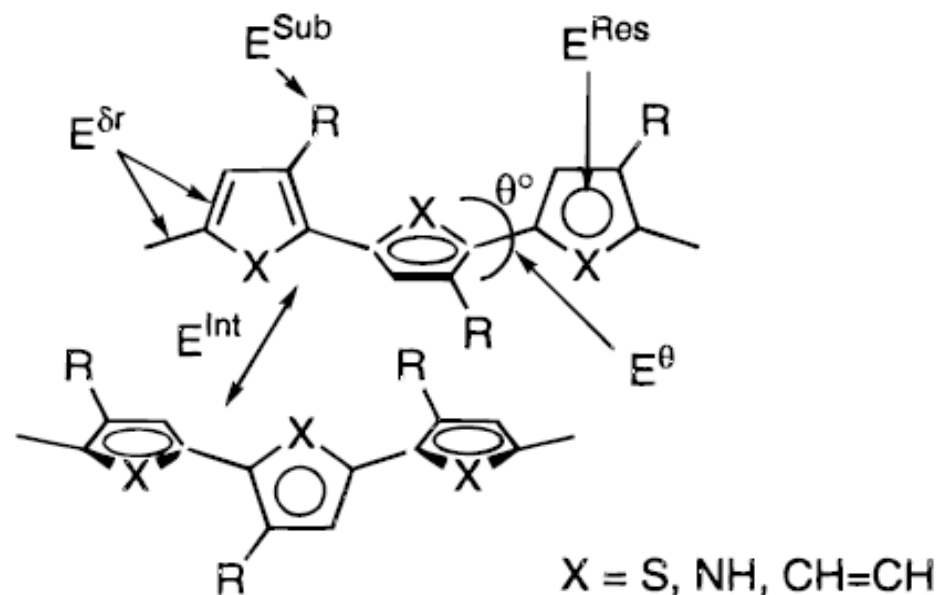
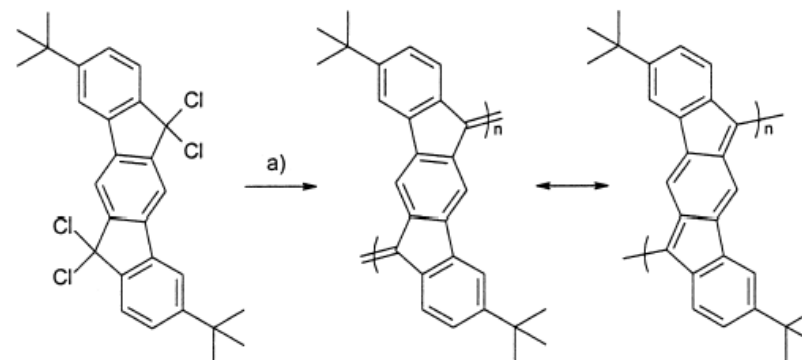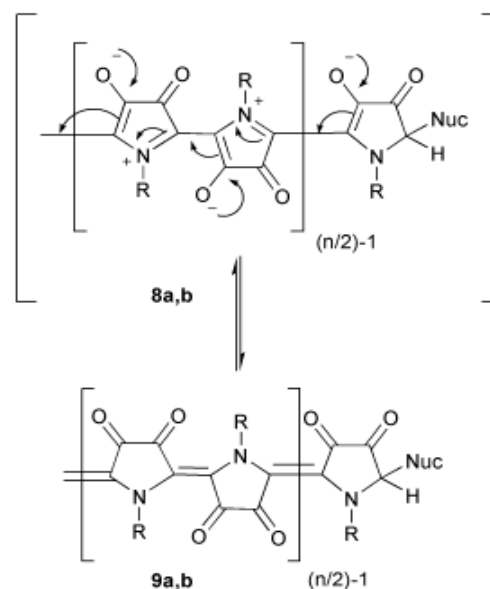# How to Minimize the BLA Along the Backbone for Small Eg?

- Mesomeric structures
- Fused six-membered ring
- Ladder polymers
- Zwitterionic structures
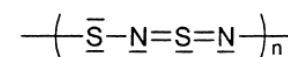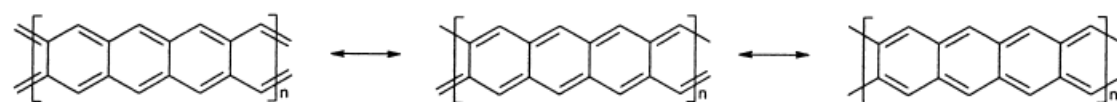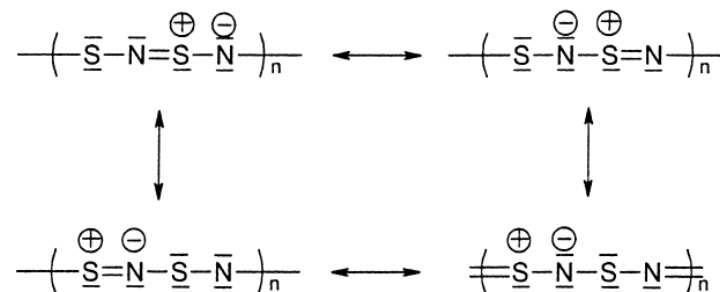
Polysulfur nitride, shows metallic conductivity

$Eg^{opt}(solution) = 1.1$ eV

$Eg^{opt} = 1.55$ eV

Ajayaghosh, *Chem. Soc. Rev.*, **2003**, 32, 181.

van Mullekom et al., *Mater. Sci. Eng. A*, **2001**, 32, 1.

How to Maintain the Planarity Along the Backbone for Small Eg?

Orbital overlap varies nearly with the cosine of the twist angle, any departure from coplanarity will result in an increase of Eg (Eθ).

- Ladder type → twist inhibition
- Avoid steric hindrance
- Aromatic versus quinoid form (sp^3 versus sp^2)
- Intermolecular hydrogen bonding

PTPI

H
C PTTI
N
S
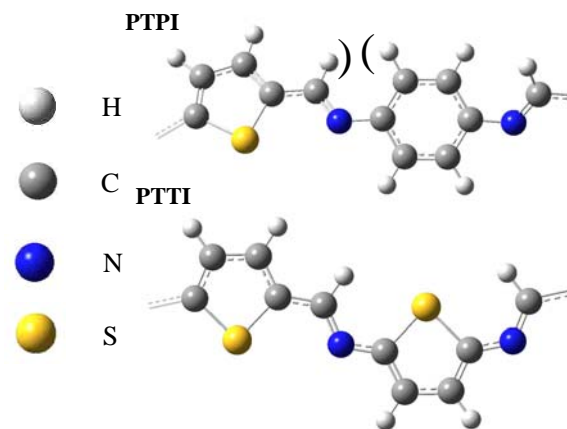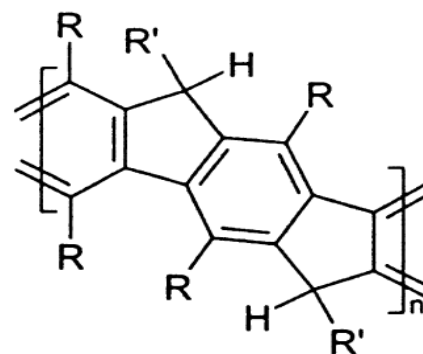
Twist angle: 24°

Eg = 2.35 eV

Twist angle: 0.5°

Eg = 1.42 eV
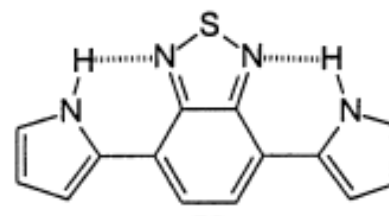
How to Control the Aromaticity Along the Backbone for Small Eg?

- **Aromaticity** results in a competition between π - electron confinement within the rings and delocalization along the chain.

- **Aromatic** and **quinoid** forms are not energetically equivalent.

X = -CH=CH-, NH, S
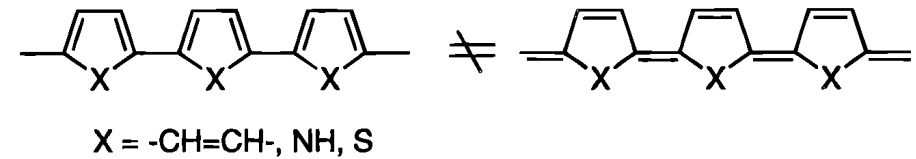
Aromatic form
Eg^{cal} = 2 eV

Quinoid form
Eg^{cal} = 0.26-0.47 eV

a   b   c   d

E r = 1.56 eV

E r = 1.26 eV
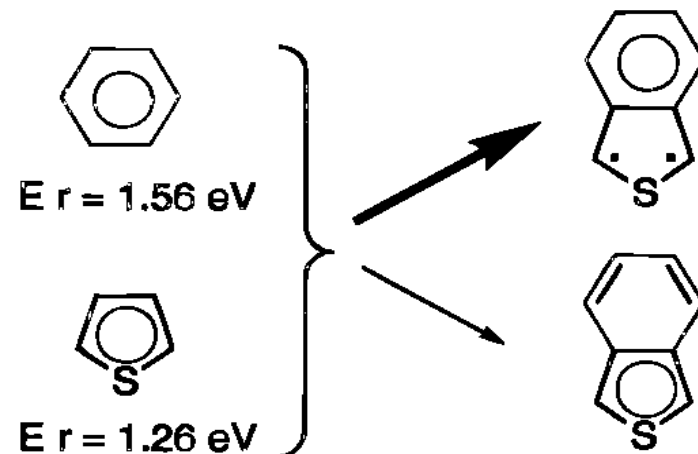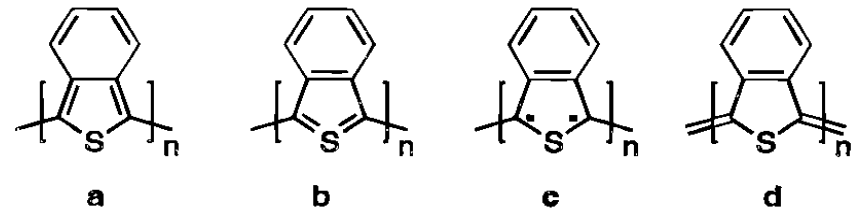
How to Control the Substituents for Small Eg?

Structure (IP, EA, Eg) eV
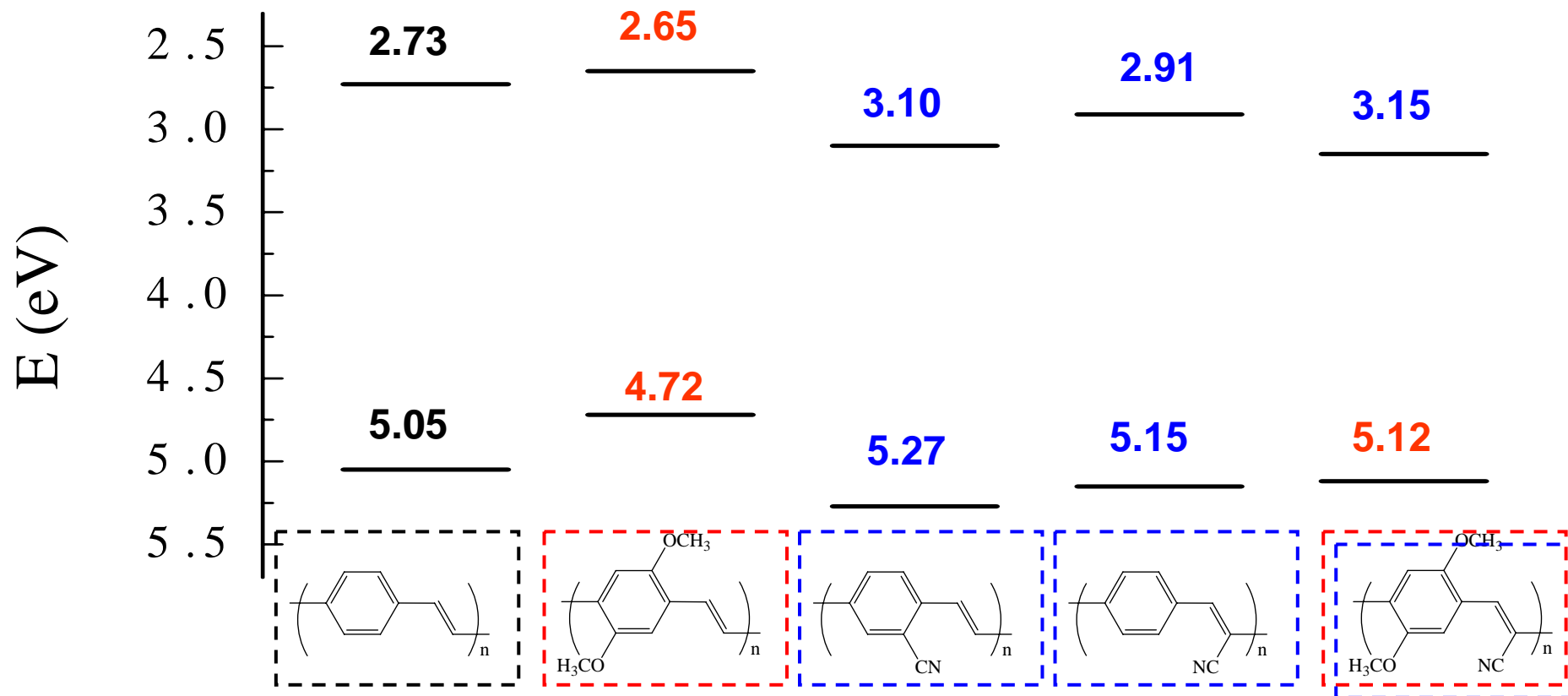
methoxy group will decrease the IP (destabilization of VB)

cyano group will increase the EA (stabilization of CB)

JL Bredas, AJ Heagger *Chem. Phys*. Lett, **1994**, 217, 507.

Experimental Measurements of Electronic Structure Parameters of Conjugated Polymers

Bandgap (Eg)

Optical absorption spectrocopy (UV-Vis-NIR)

λ_g (nm) = 1240 / E_g (eV)

Electrochemical redox potential (cyclic voltammetry)

Reduction wave

E^{ox}_{onset}

E^{red}_{onset}

Oxidation wave
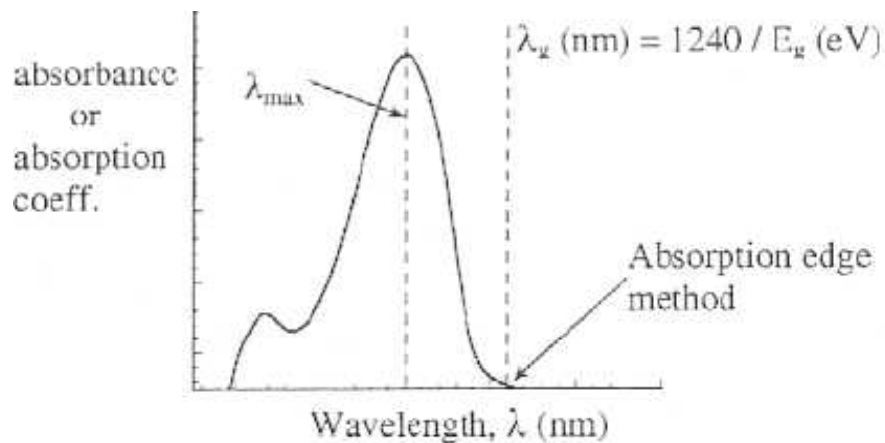
IP & EA

Photoelectron spectroscopy

- **Need ultrahigh vacuum techniques**
- **UPS (from UV)**
- **XPS (ESCA, from X-ray)**
- **Accurate but more difficult to do**
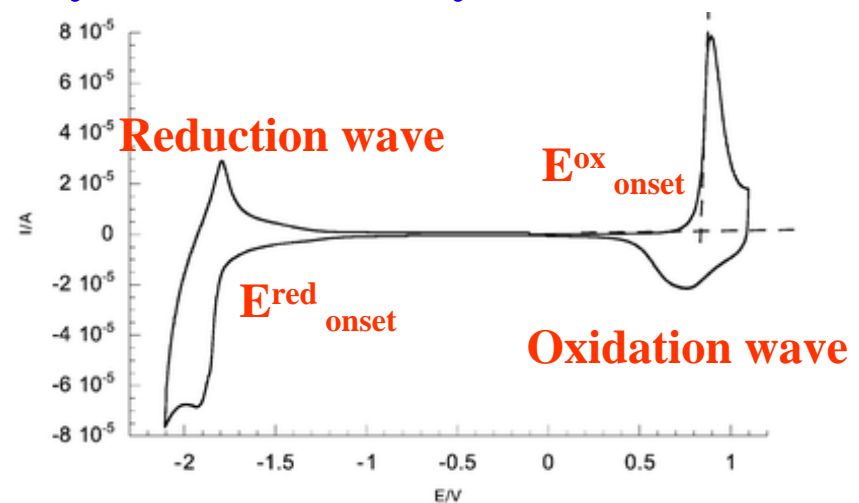
Estimate from electrochemical redox potential

- **IP = E^{ox}_{onset} + 4.4 eV**
- **EA = E^{red}_{onset} + 4.4 eV**

Computational Techniques for Conjugated Polymers

Employ for the study of the electronic structure of π-conjugated ploymers should be :

- **Applicable to such complex conjugated systems**

- **Amenable to geometry optimization and should yield good calculation geometrical parameters**

- **Able to produce good electronic structure characteristics, such as bandgap, ionization potential (IP), electron affinity (EA), charge distribution and wave functions**

- **Capable of yielding good results for other calculated physical observables , such as force constants, transition dipole, etc**

Computational Techniques for Conjugated Polymers

Molecular (Oligomer) method

Extrapolating the linear curve of the HOMO-LUMO gap of the conjugated oligomer against the reciprocal of the number of monomer units (1/n) affords a prediction of the band gap

PBC (periodic boundary condition

Single, infinite, gaseous state, one-dimensional polymer chain was treated.

HOMO-LUMO gap (eV) vs 1/n

2nd order polynomial

$Y = 1.88 + 4.96Y$

$R^2 = 0.999$

2.05

1.88

Linear prediction
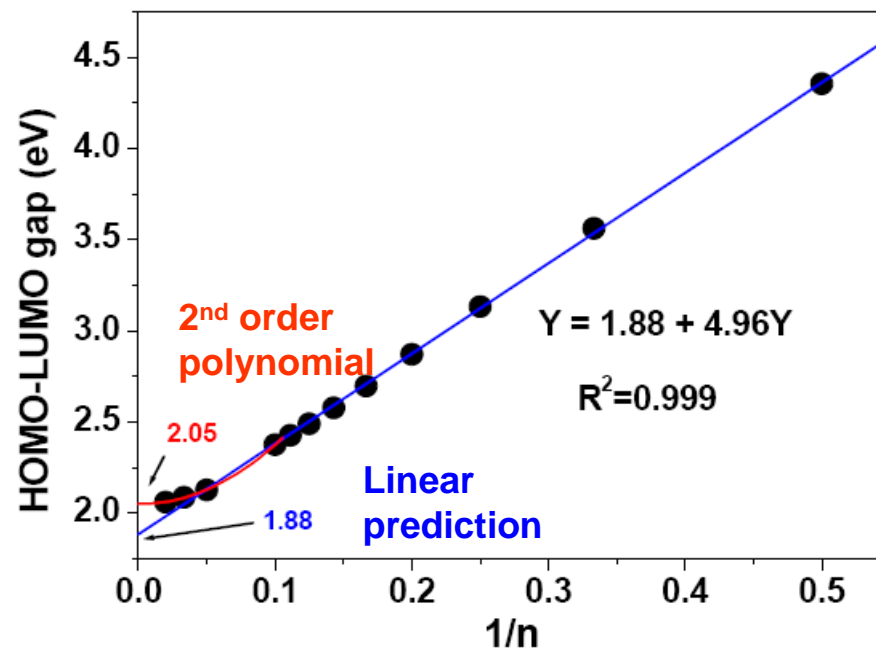
Unit cell for polythiophene
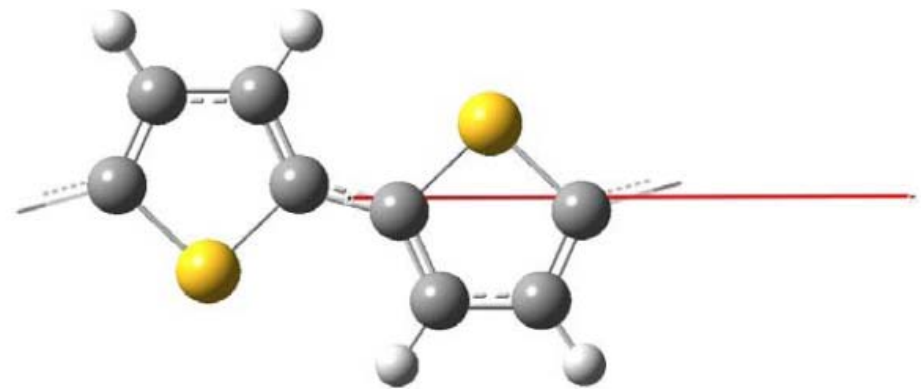
Computational Techniques for Conjugated Polymers

Methodology

DFT/B3LYP/6-31G*

DFT: density functional theory
reliable for the non-planar structures
giving reasonable gap values for most conjugated
polymer system
B3LYP: hybrid functional
6-31G*: basis set
Performed on **Gaussion 03** program

Analyzed Geometry Parameters and Properties

Bridge length (L_B) = length between two conjugated units

Bond length alternation (BLA) = L(C-C)- L(C=C)

Torsional angle = tilt between two conjugated planes

Intramolecular charge transfer = net Mulliken charge distribution

Electron effective mass
$$m^* = \eta^2 \left(\frac{d^2 \varepsilon}{d\kappa^2} \right)$$

Theoretical Analysis on New Conjugated Poly(azomethine)s

For Thin Film Transistors

Cheng-Liang Liu,[1] Fu-Chuan Tsai,[1] Chao-Chung Chang,[1] Wen-Chang Chen,[1,2] and Hsi-Hsin Shih[3]

1: Department of Chemical Engineering and 2: Institute of Polymer   Science and Engineering, National Taiwan University

3: Union Chemical Laboratory, Industrial Technology Research Institute

Optoelectronic Polymer Lab, NTU

Research Objectives

- **Discuss the relationships among the optimized geometries, electronic structures and polymer structures of conjugated polymers**
  - Influences of different linkage on electronic structures
  - Influences of replacement of phenyl ring on PPI by thiophene
  - Influences of electron Donor/Acceptor six-member ring on the electronic properties of poly(azomethine)s
  - Influences of electron Donor/Acceptor five-member ring on the electronic properties of coplanar poly(azomethine)s

- **Molecular designs of coplanar poly(azomethine)s for OTFT applications**

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Theoretical Analysis

■ Methodology

unit-cell
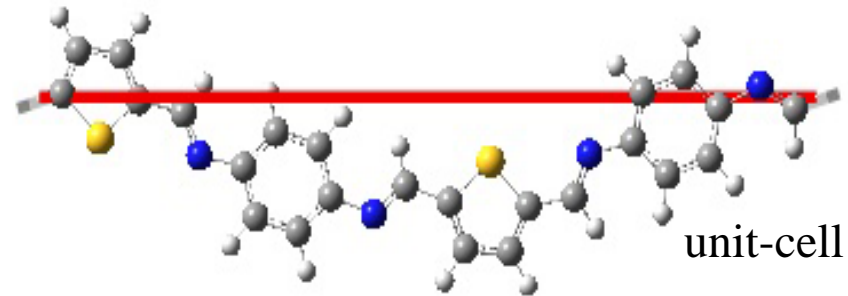
□ **Periodic Boundary Condition (PBC)**

– Single, infinite, gaseous state, one-dimensional polymer chain was treated.

□ **DFT/B3LYP/6-31G**

DFT: density functional theory

● reliable for the non-planar structures

● giving reasonable gap values for most conjugated polymer system

B3LYP: hybrid functional

6-31G: basis set

□ **Performed on Gaussion 03 program**

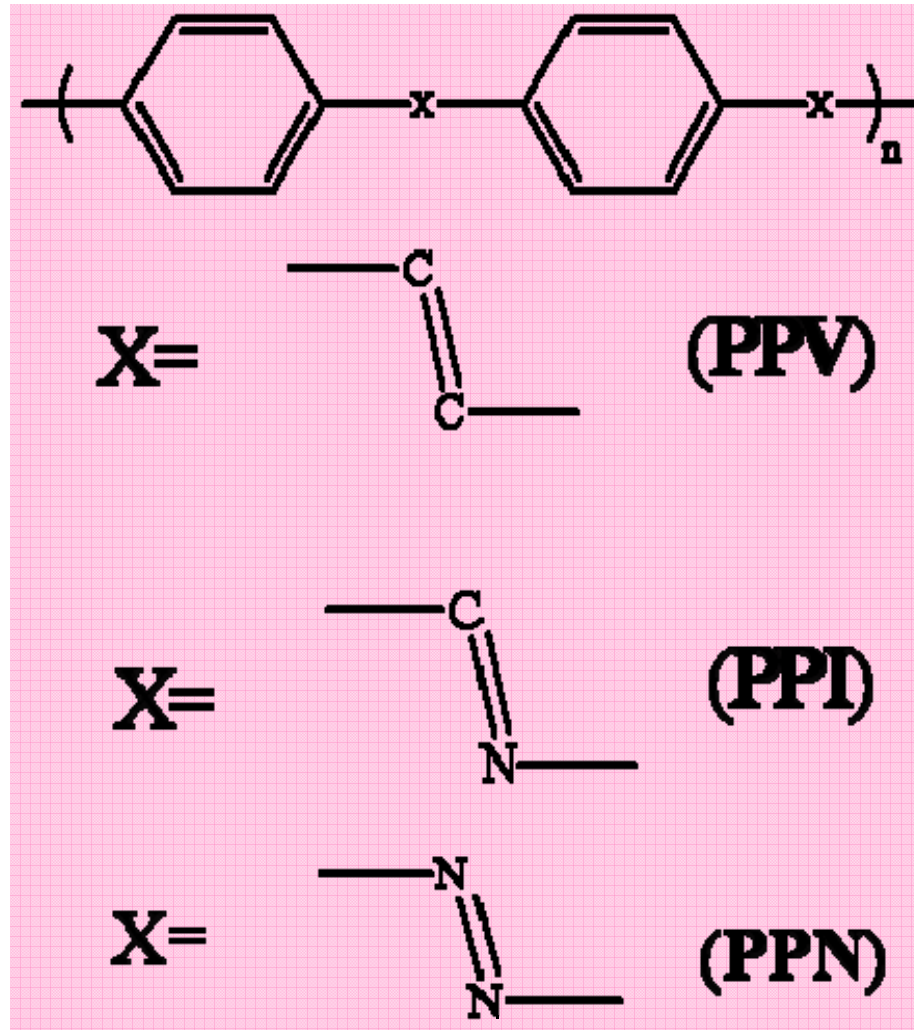widely used for the calculation

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Geometry of Azomethine model compound

■ Twisted nature of azomethine model compound:
the *X*-ray diffraction results of the small molecule
trans-*N*-benzylideneaniline
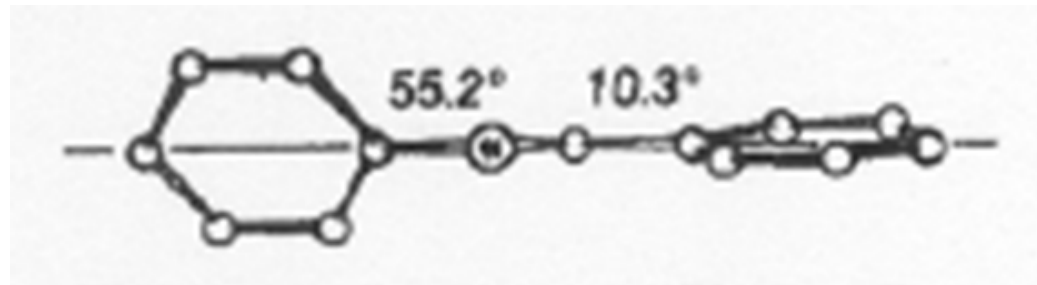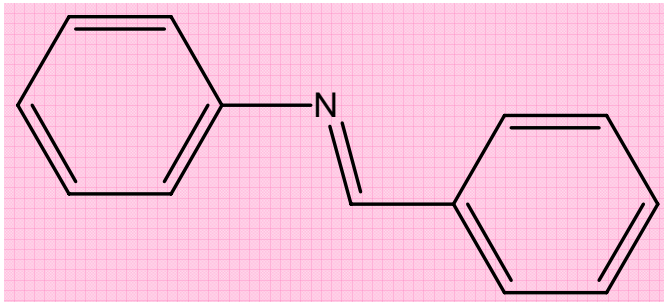
Influences of Linkages on Electronic Structures

Geometries & Electronic Structures of PPV, PPI and PPN
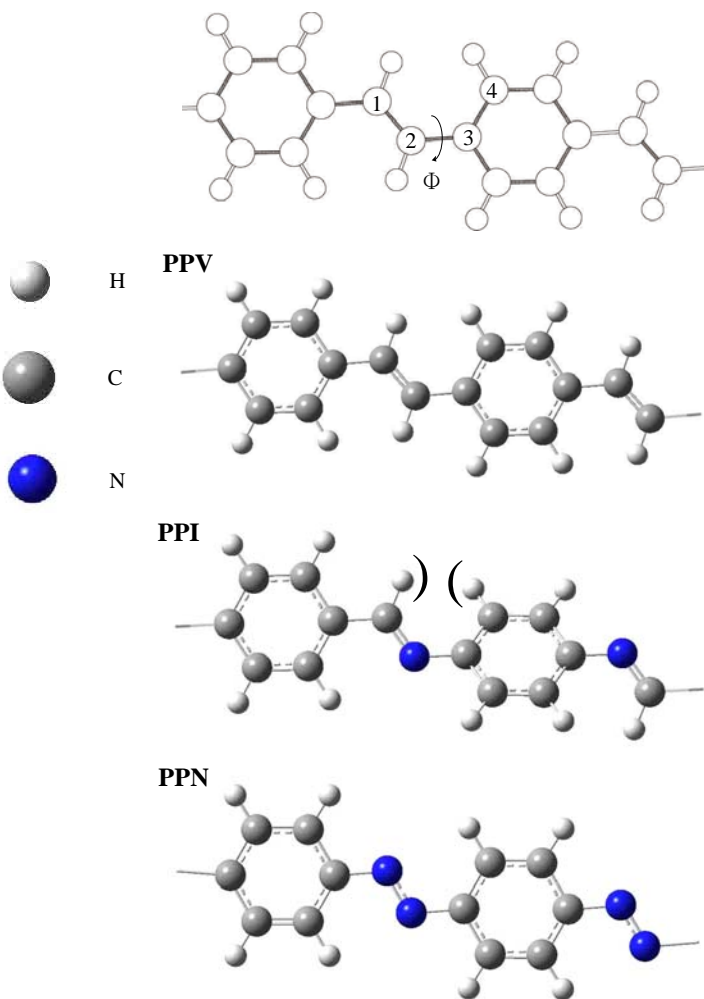
r (1,2)	r (2,3)	θ (1,2,3)	Φ	IP (eV)	EA (eV)	E_g (eV)
C=C 1.355	C-C 1.462	127.0	0.0	4.78	2.31	2.47
C=N 1.293	C-N 1.410	122.5	**31.9**	5.47	2.63	2.83
N=N 1.282	C-N 1.418	115.7	0.0	5.92	3.61	2.31

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Geometries & Electronic Structures

■ **Order of IP/EA :**

e-donating ⟵—————————

$$\mathbf{PPV}\ (C{=}C) < \mathbf{PPI}\ (C{=}N) < \mathbf{PPN}\ (N{=}N)$$

—————————⟶ e-accepting

■ **Order of Eg :**

$$\mathbf{PPN}\ (N{=}N) < \mathbf{PPV}\ (C{=}C) < \mathbf{PPI}\ (C{=}N)$$

planar conformation

twisted conformation

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Ar_1

N ... N

n

$Ar_1 =$ (PPI)

$Ar_2 =$ (PTPI)

S

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PPI

H

C

N **PTPI**

S

r1 (C-C)	r2 (C=N)	Δr (r1-r2)	Φ	IP (eV)	EA (eV)	E_g (eV)
1.463	1.293	0.176	30.4	5.47	2.63	2.83
1.435	1.297	0.138	24.0	5.32 ($\uparrow$)	2.97 ($\downarrow$)	2.35

$\downarrow$: **HOMO/LUMO stabilization**

$\uparrow$: **HOMO/LUMO destabilization**

E_g (**PTPI**) < E_g (**PPI**):

☐ smaller Φ in **PTPI**

∴ ☐ smaller Δr in **PTPI**

☐ extensive π-electron delocalization of thiophene ring in **PTPI**

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Influences of Electron Donor/Acceptor Six-member Ring on Electronic Properties of Poly(azomethine)s

Optimum Geometries & Electronic Structures of PTPI, PTPyI and PTNI

PTPI

planar

PTPyI

PTNI

H

C

N

S
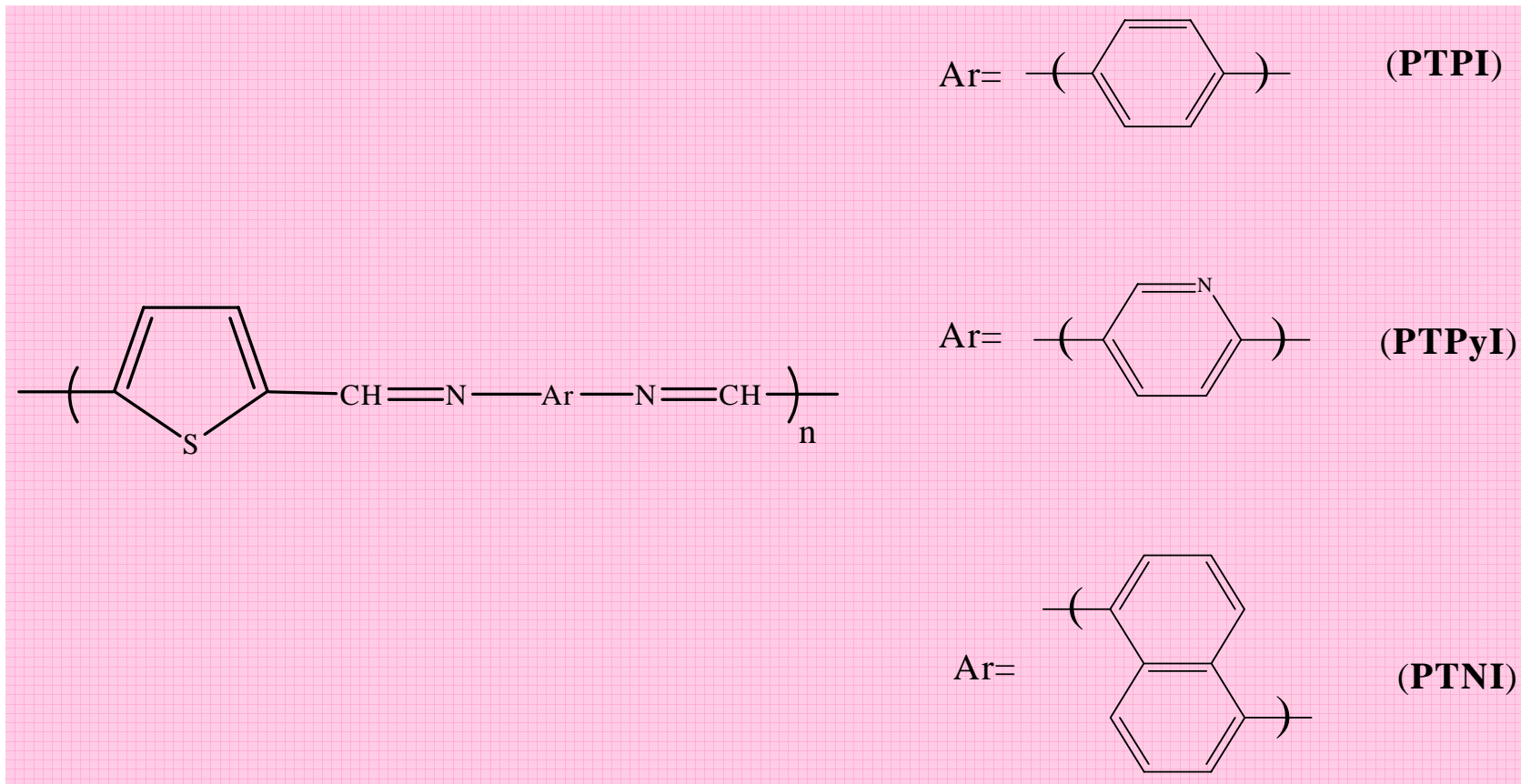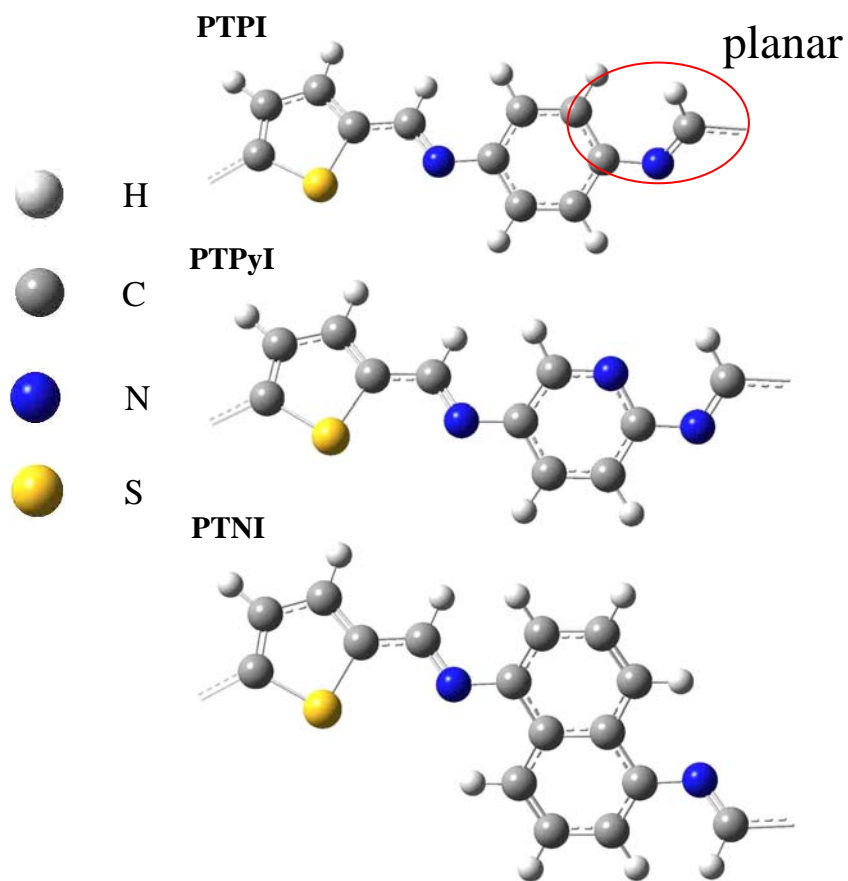
Φ (°)	IP (eV)	EA (eV)	E_g (eV)
24.0	5.32	2.97	2.35
30.2 (↑) (+6.2)	5.57 (↓) (+0.25)	3.16 (↓) (+0.19)	2.40 (+0.05)
30.6 (↑) (+6.6)	5.16 (↑) (-0.16)	2.66 (↑) (-0.31)	2.50 (+0.15)

Optimum Geometries & Electronic Structures of PTPI, PTPyI and PTNI

■ The replacement of phenyl ring either by the e-accepting pyridine or by the e-donating naphthalene leads to more twisted conformation and thus higher E_g obtained.

■ The slightly decreased E_g of **PTPyI** in comparison with **PTNI** is due to the small intra-charger transfer along the polymer chain induced by the e-accepting pyridine.

Influences of Electron Donor/Acceptor Five-member Ring on Electronic Properties of Coplanar Poly(azomethine)s
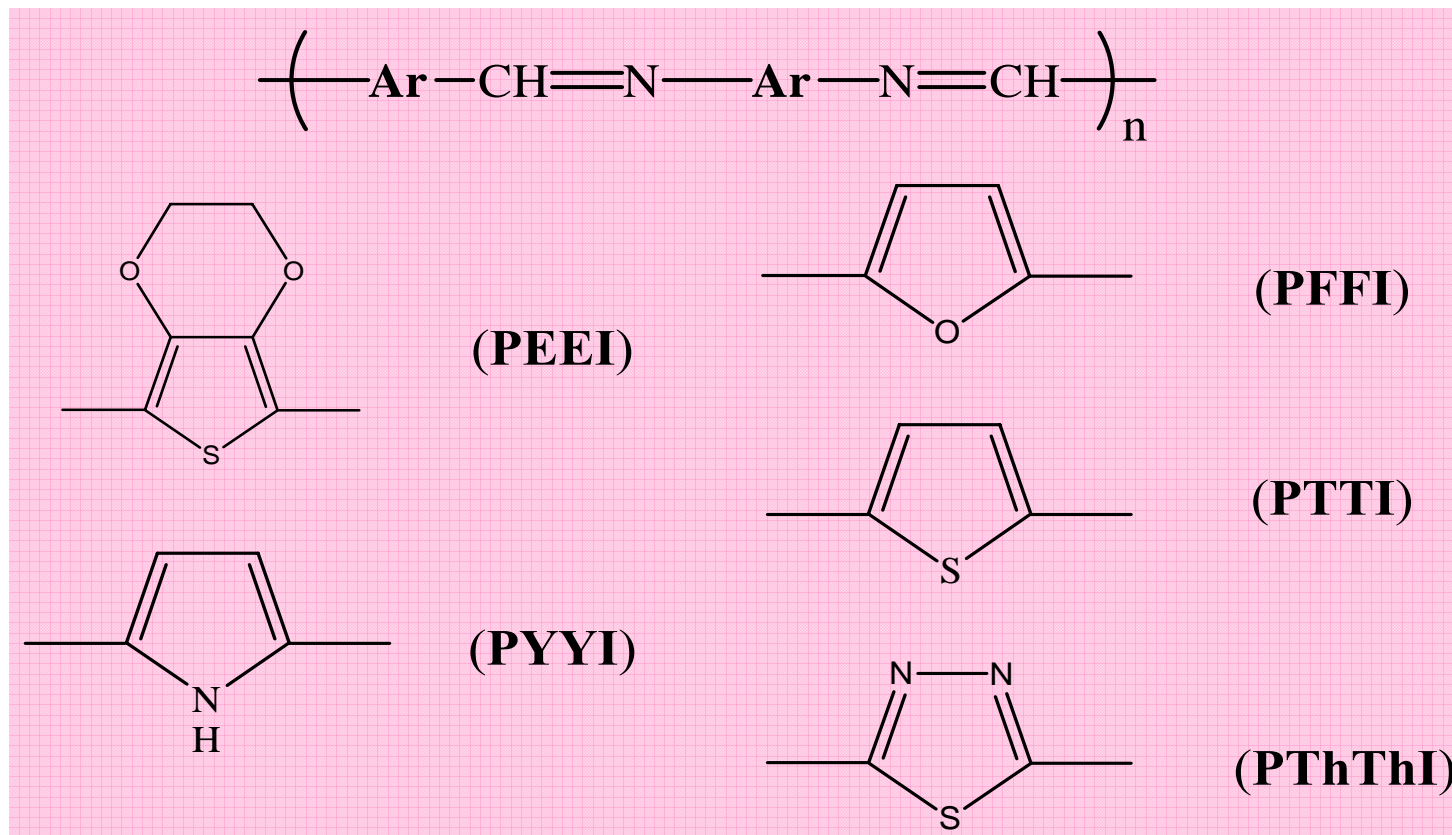
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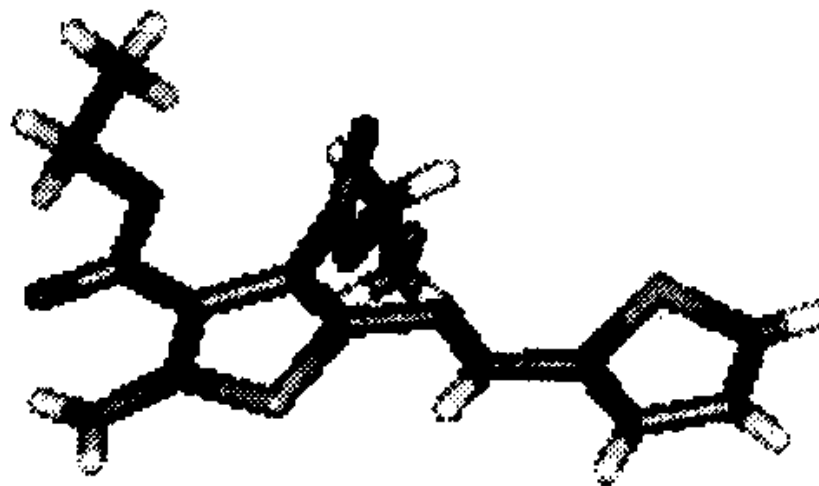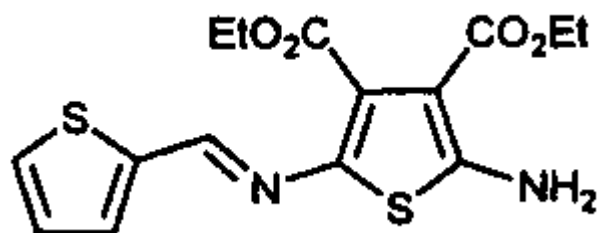- A planar configuration of the monoazomethine showed by X-ray crystal analysis

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PEEI

PYYI

PThThI

PTTI

PFFI

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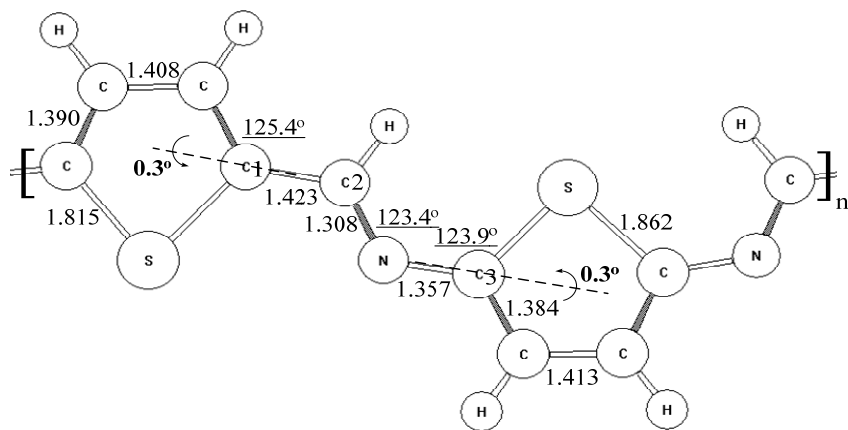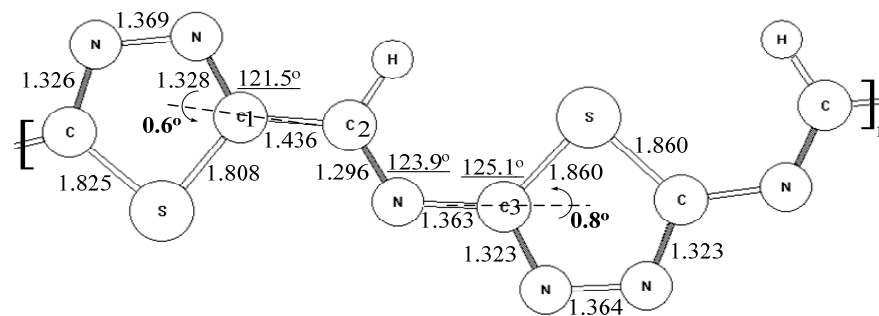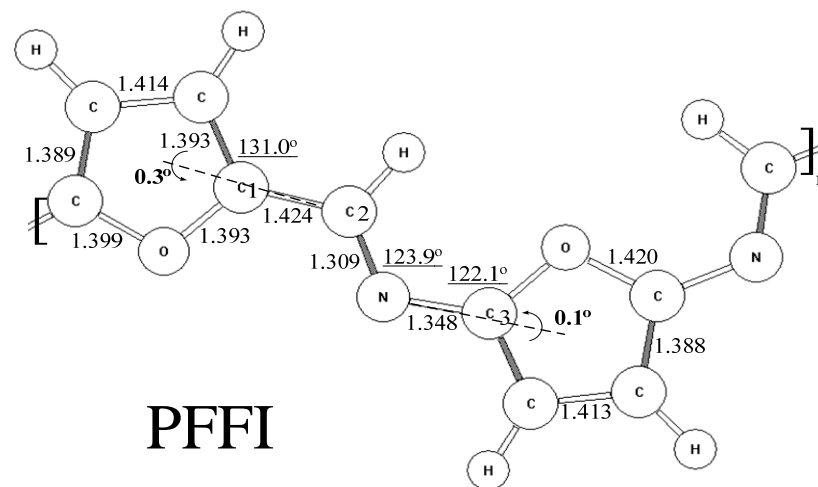
Geometries & Electronic Structures of Coplanar Poly(azomethine)s

	R_{C1-C2} (Å)	$R_{C2=N}$ (Å)	R_{C3-N} (Å)	δ (Å)	Φ_1 (degree)	Φ_2 (degree)	IP (eV)	EA (eV)	E_g (eV)
1 (PPI)	1.463	1.293	1.410	0.021	0.9	**30.4**	5.47	2.63	2.83
2a (PEEI)	1.414	1.314	1.345	0.023	0.2	**0.6**	4.25	3.14	1.11
2b (PYYI)	1.427	1.309	1.371	0.006	1.8	**12.1**	4.40	2.73	1.67
2c (PFFI)	1.424	1.309	1.348	0.025	0.3	**0.1**	4.89	3.33	1.56
2d (PTTI)	1.423	1.308	1.357	0.018	0.3	**0.3**	5.03	3.61	1.42
2e (PThThI)	1.436	1.296	1.363	0.040	0.6	**0.8**	7.19	4.72	2.47

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Electronic Structures of The Studied Poly(azomethine)s

■ IP increases in the following order:

e-donating ⟵————————————

PEEI < PYYI < PFFI < PTTI < PPI < PThThI

■ EA increases in the following order:

PPI < PYYI < PFFI < PEEI < PTTI < PThThI

————————————⟶ e-accepting

■ Eg increases in the following order:

Donor/Acceptor system

PEEI < PTTI < PFFI < PYYI < PThThI < PPI

coplanar conformation   twisted conformation

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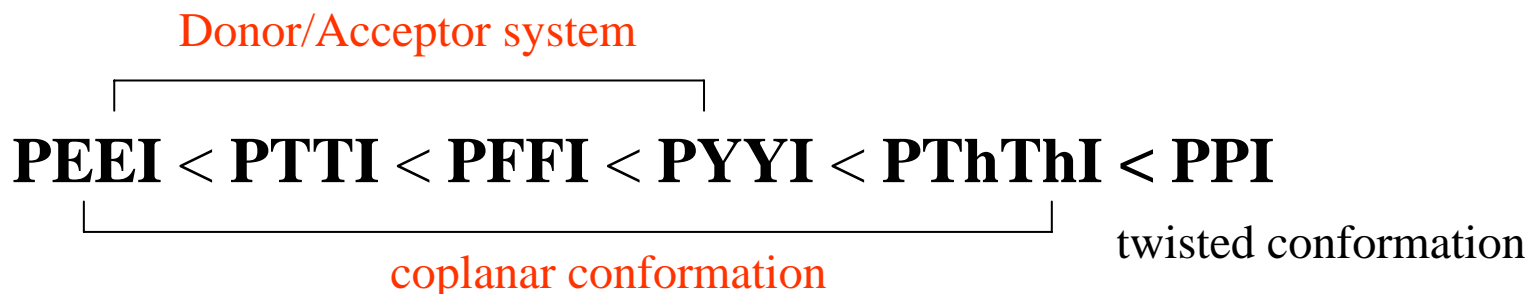
Band Structures of Organic Thin Film Transistor Materials

$$m^* = \eta^2 \left(\frac{d^2 \varepsilon}{d\kappa^2} \right)$$ **effective mass**

$$\mu = \frac{e\tau}{m^*}$$ **Drude form for mobility**

ε energy near the band

κ wavevector

τ life time of the carriers

valance (conductive) band effective mass $\Longleftrightarrow$ hole (electron) mobility
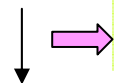
effective mass $\downarrow$ $\Longrightarrow$ π electron delocalization $\uparrow$ $\Longrightarrow$ mobility $\uparrow$

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Band Structures of Coplanar Poly(azomethine)s

	Valence bandwidth (meV) and effective mass	Conduction bandwidth (meV) and effective mass	IP (eV)	EA (eV)	E_g (eV)
1 (PPI)	**247 (0.742 m_e)**	**298 (0.688 m_e)**	5.47	2.63	2.83
2a (PEEI)	**613 (0.233 m_e)**	**644 (0.223 m_e)**	4.25	3.14	1.11
2b (PYYI)	**562 (0.406 m_e)**	**552 (0.403 m_e)**	4.40	2.73	1.67
2c (PFFI)	**590 (0.376 m_e)**	**556 (0.343 m_e)**	4.89	3.33	1.56
2d (PTTI)	**572 (0.278 m_e)**	**583 (0.275 m_e)**	5.03	3.61	1.42
2e (PThThI)	**318 (0.530 m_e)**	**287 (0.504 m_e)**	7.19	4.72	2.47
3 (PPV)	**373 (0.466 m_e)**	**392 (0.446 m_e)**	4.78	2.31	2.47
4 (PAZ)	**347 (0.474 m_e)**	**405 (0.464 m_e)**	5.92	3.61	2.31

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Conclusions

- The twisted conformation of aromatic poly(azomethines) is attributed to the repulsion force between the adjacent hydrogen atoms on the C=N linkage and the *N*-phenylene.

- The coplanar geometry of **PPV** and **PAZ** result in a smaller Eg than that of **PPI**. The **IP** and **EA** of **PPI** are in the intermediate between **PPV** and **PAZ**.

- The coplanar configuration or donor-acceptor intrachain charge transfer resulted in enhanced electronic properties of **PEEI PYYI**, **PFFI**, and **PTTI** in comparison with **PPI**, including lower Eg, higher BW, and lower effective mass.

- The proposed coplanar poly(azomethine)s for OTFT applications.