π-Conjugated Polymers

OUTLINE

Lect. 1:

Conjugated polymers: The use of a Band Model, Geometry, Excited States.

Lect. 2:

Conjugated Polymers: Bandgap Engineering.

Lect. 3:

Synthetic Methods toward Conjugated Polymers.

Outline Part 2

- **Introduction**
- **Bandgap determination**
- **Band Gap Engineering**
- **Intermolecular effects on Bandgap**

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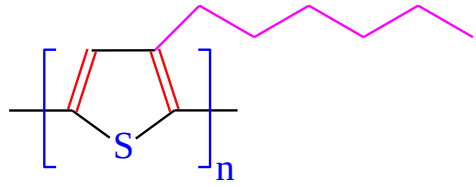
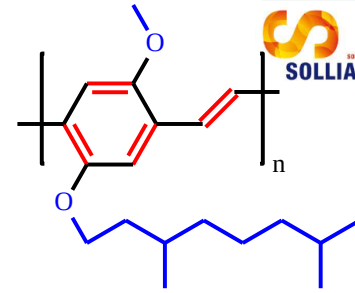
HyMaD HYBRID MATERIALS DESIGN

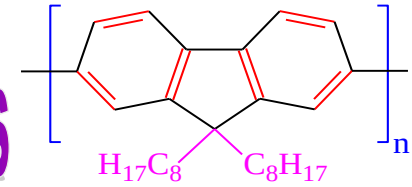
Applications as Semi-Conductor



Poly(Hexyl Thiophene) (PHT)



OC_1C_{10}-PPV



Poly(DiOctyl-Fluorene) (PDOF)

Plastics Electronics

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Organic Electronics

- Emerging key technology for the 21st century
- Variety of applications : LEDs, transistors, electrochromic windows, (bio-)sensors, solar cells,..

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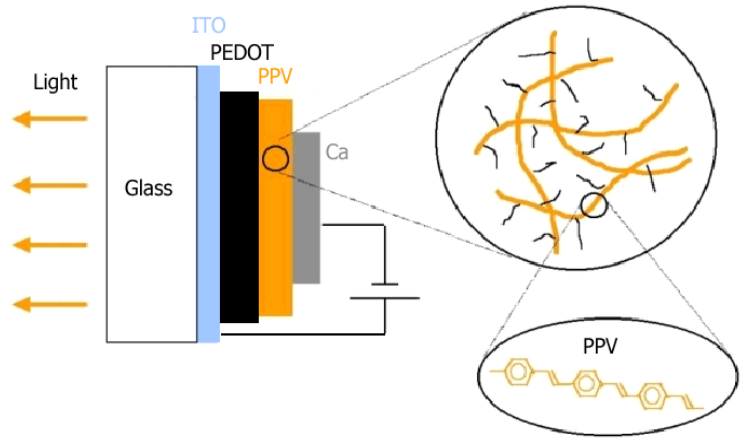
Applications as Semi-Conductor

Polymer LED

1990



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Applications as Semi-Conductor

Source Philips

Text

Video

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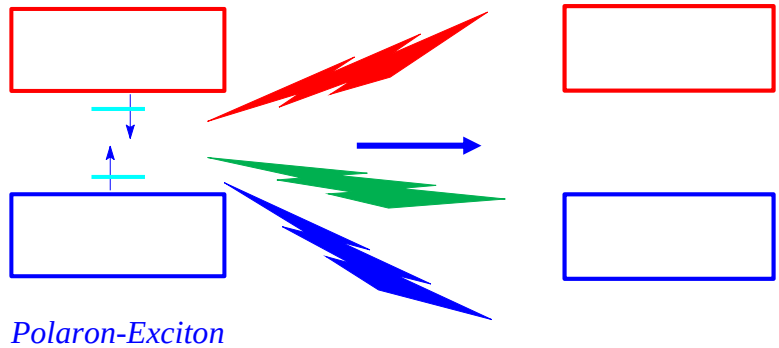
Bandgap and Excitons



Polaron-Exciton

LED

$E_g < E_g < E_g$

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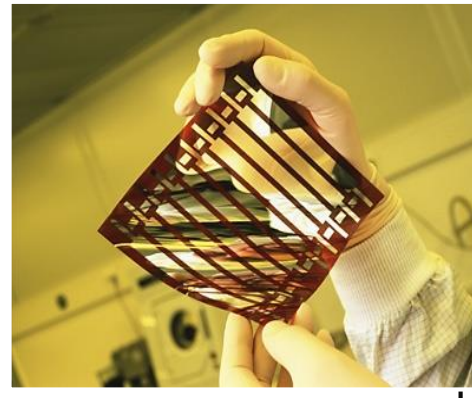
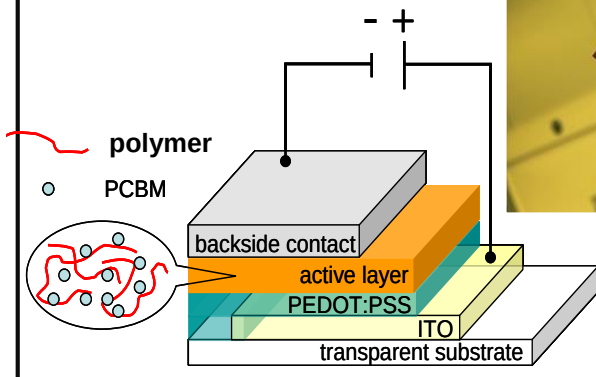
Organic Electronics

Plastic Solar Cell





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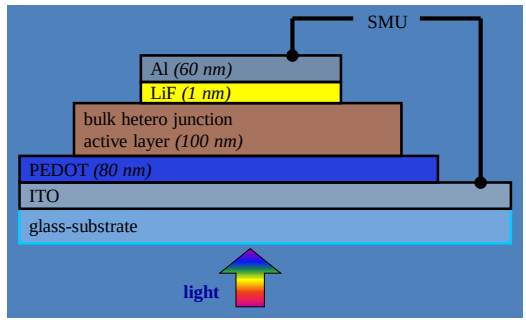
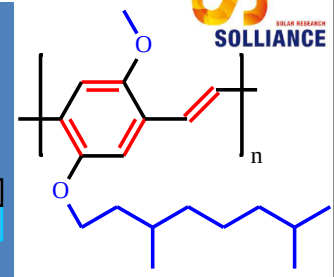
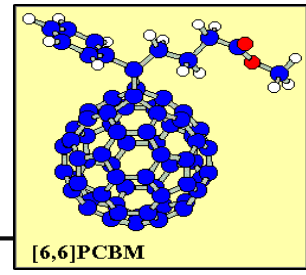
Applications of Conjugated Polymers



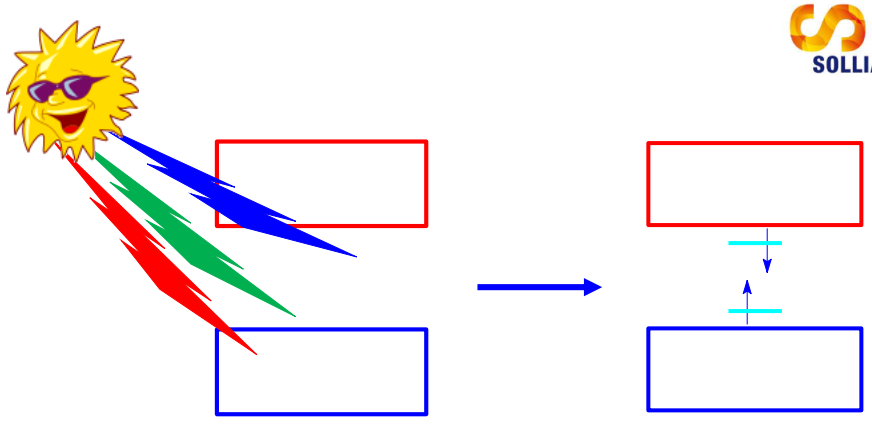
Plastic solar cell



OC_1C_{10}-PPV



Bandgap and Excitons



Solar Cell

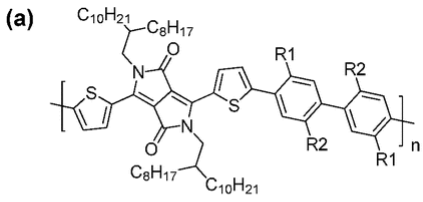
Polaron-Exciton

$E_g < E_g < E_g$

Outline Part 2

- Introduction
- Bandgap determination
- Band Gap Engineering
- Intermolecular effects on Bandgap

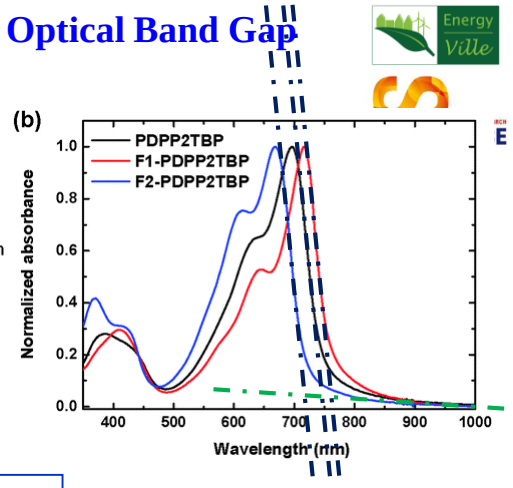
Determining Optical Band Gap



PDPP2TBP: R1 = R2 = H

F1-PDPP2TBP: R1 = F and R2 = H

F2-PDPP2TBP: R1 = H and R2 = F



E_g (eV) = 1240/(λ_{onset} in nm)

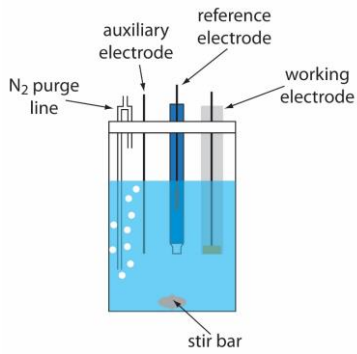
E_g (eV) = 1240/760 = 1.63 eV

E_g (eV) = 1240/750 = 1.65 eV

E_g (eV) = 1240/720 = 1.72 eV

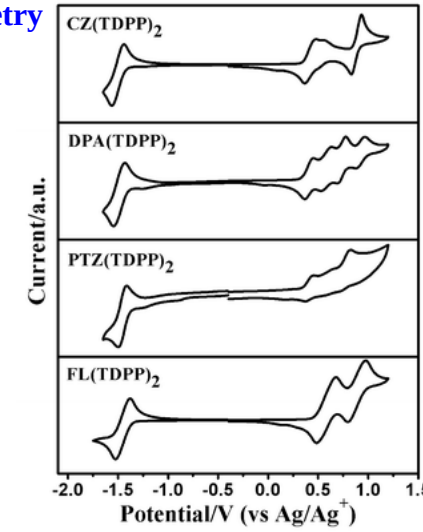
Determining Electrochemical Band Gap

Cyclic Voltammetry

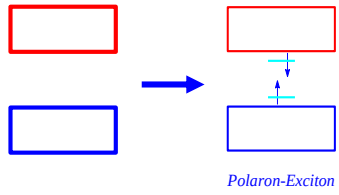


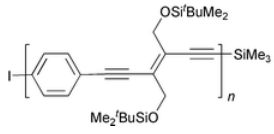
$$E(HOMO) = -((E_{ox})_{on} + 4.4)\,eV$$

$$E(LUMO) = -((E_{red})_{on} + 4.4)\,eV$$

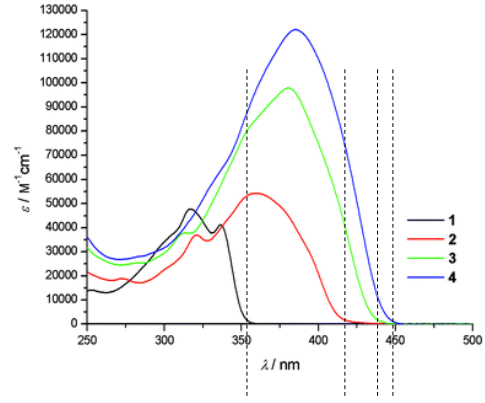


Effective Conjugation Length



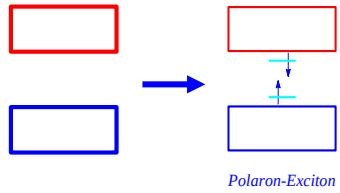


1 $n = 1$
2 $n = 2$
3 $n = 3$
4 $n = 4$



N. F. Utesch and F. Diederich, *Org. Biomol. Chem.* (2003) 1, 237-239

Effective Conjugation Length

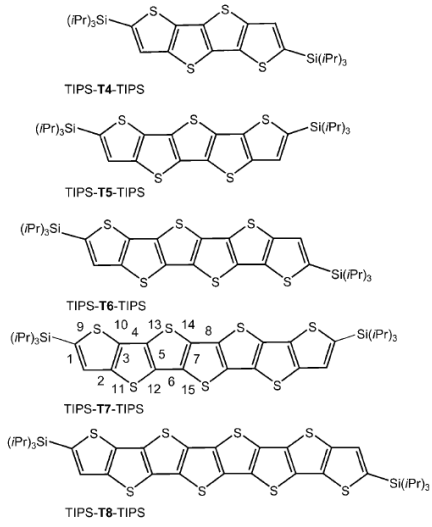


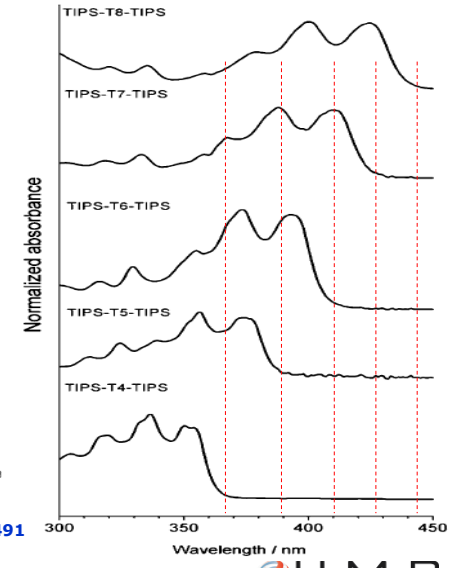
Conjugation length =
length in number of uninterrupted π-bonds in a conjugated system

Effective Conjugation length =
length in number of uninterrupted π-bonds at which the optical absorption onset saturates in the conjugated system

Conjugation length ≥ Effective Conjugation Length

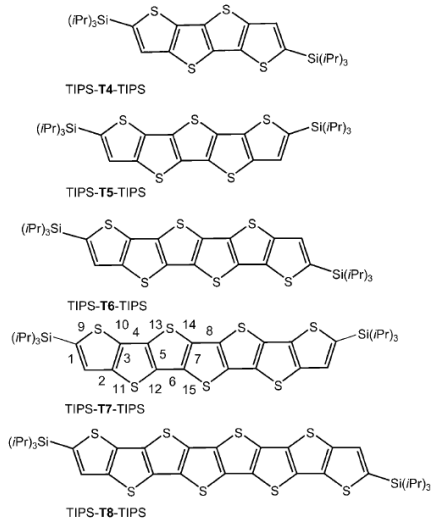
Effective Conjugation Length

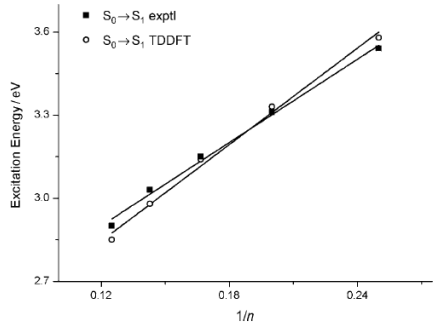




Arago J et al., Chem. Eur. J. (2010) 16, 5461-5491

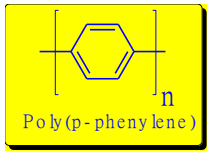
Effective Conjugation Length

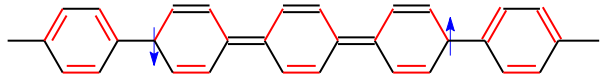




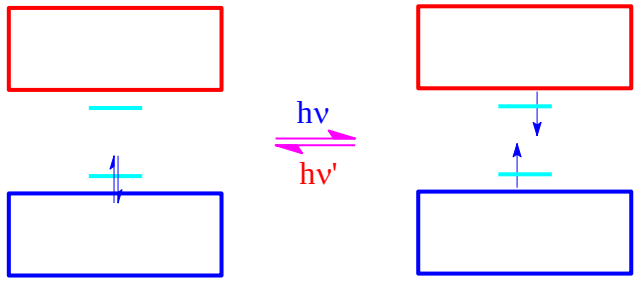
Arago J et al., Chem. Eur. J. (2010) 16, 5461-5491

Effective Conjugation Length





Soliton-anti-Soliton pair



Polaron-Exciton

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Outline Part 2

- Introduction
- Bandgap determination
- Band Gap Engineering
- Intermolecular effects on Bandgap

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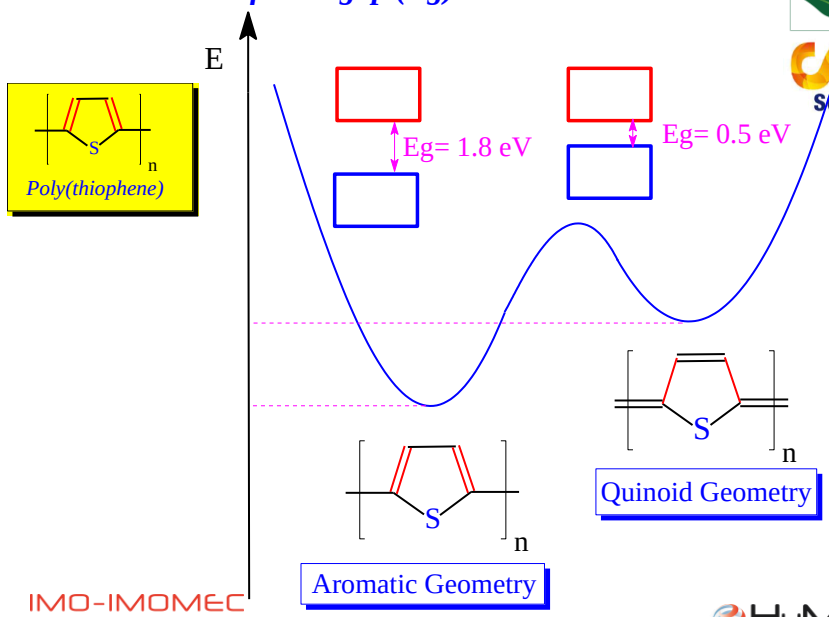
Relation of Bandgap (Eg) vs Molecular Structure



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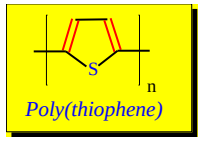
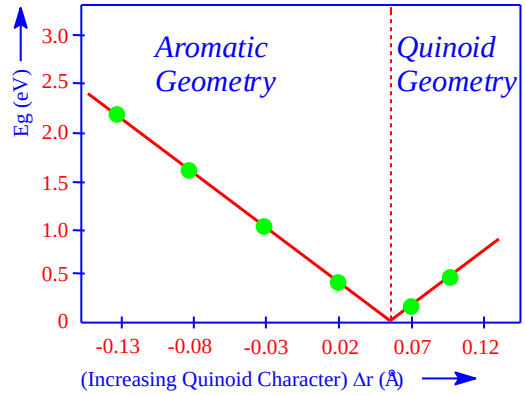
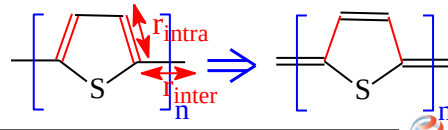
Bond Length Alternation

J. L. Brédas, Synth. Met., 17, 115-121 (1987)





$\Delta r = r_{intra} - r_{inter}$



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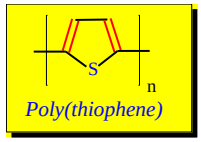
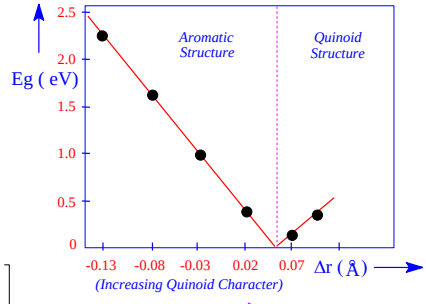
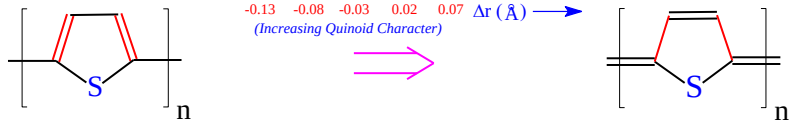
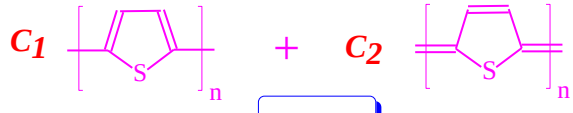
Relation of Band Gap (Eg) vs Δr







J. L. Brédas, Synth. Met., 17, 115-121 (1987)



$C_1 > C_2$

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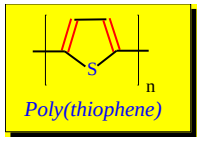
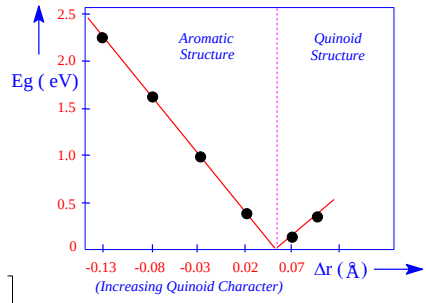
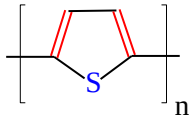
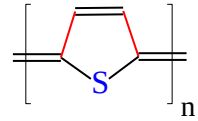
22

Relation of Band Gap (Eg) vs Δr









Quality of Intrachain Delocalisation

|||

Δr_{BLA} = Bond Lenght Alternation (BLA)

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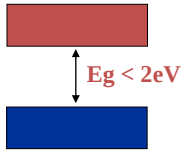
Structure - Band Gap Relationship for Conjugated Polymers

$$Eg = E^{\delta r} + E^{\theta} + E^{res} + E^{sub} + E^{int} \; *$$



Low Band Gap Polymers

$E^{\delta r}$ = bond length alternation
E^{θ} = mean deviation from planarity
E^{res}= aromatic resonance energy

E^{sub} = inductive and mesomeric substituent effects
E^{int} = intermolecular or interchain interactions

* **"Synthetic Principles for Bandgap Control in Linear π-Conjugated Systems", J. Roncali, Chem. Rev., 97, 173-205 (1997)**

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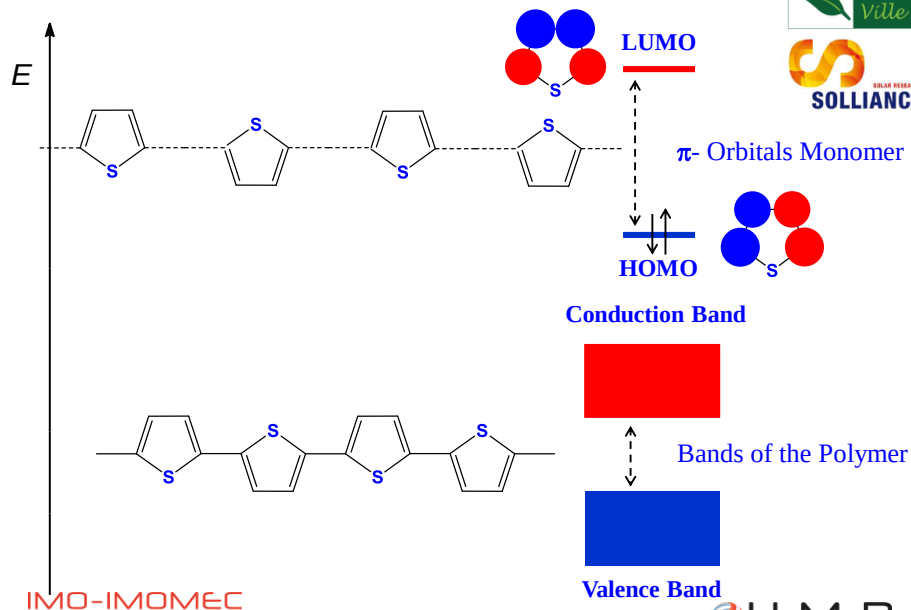
Delocalisation across Contour Length Polymer



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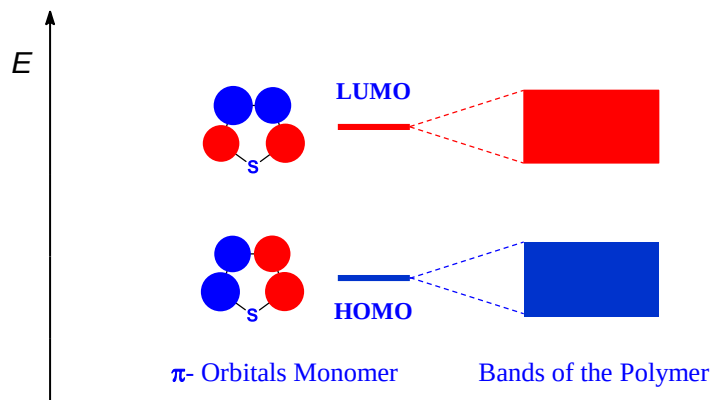
Delocalisation across Contour Length Polymer



Quality of Intrachain Delocalisation

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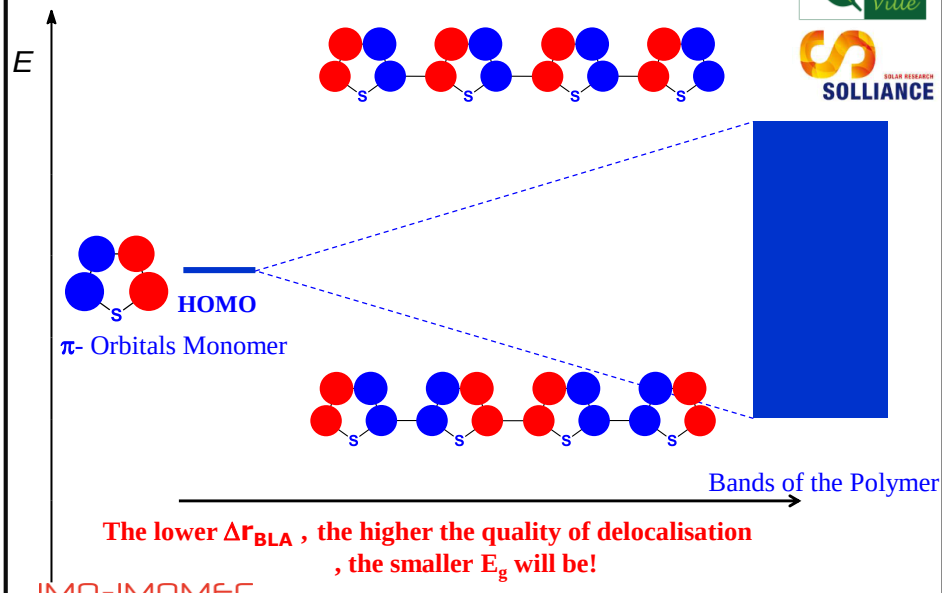
Band Model of Conjugated Polymers



The lower Δr_{BLA} , the higher the quality of delocalisation , the smaller E_g will be!

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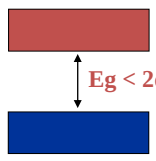
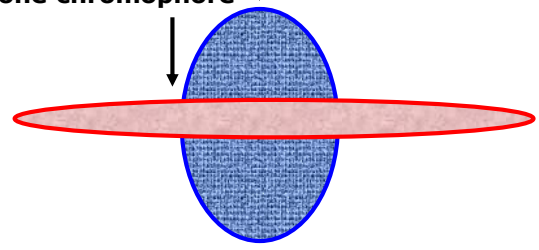
Structure - Band Gap Relationship for Conjugated Polymers

Competition!

Delocalisation localised in the repeating unit

Delocalisation along backbone chromophore





Low Band Gap Polymers

Δr_{BLA} = measure of quality of delocalisation along backbone

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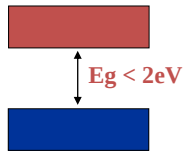
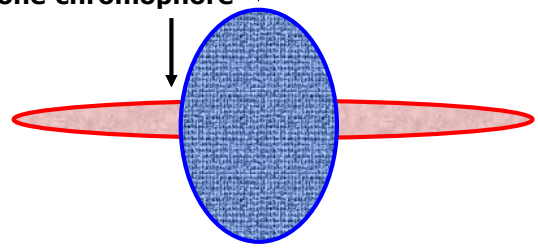
Structure - Band Gap Relationship for Conjugated Polymers

Competition!

Delocalisation localised in the repeating unit

Delocalisation along backbone chromophore





Low Band Gap Polymers

How to engineer Δr_{BLA} , and ultimately engineer the Band Gap?

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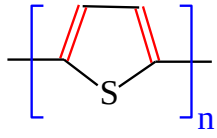
Tuning Aromatic Resonance Energy

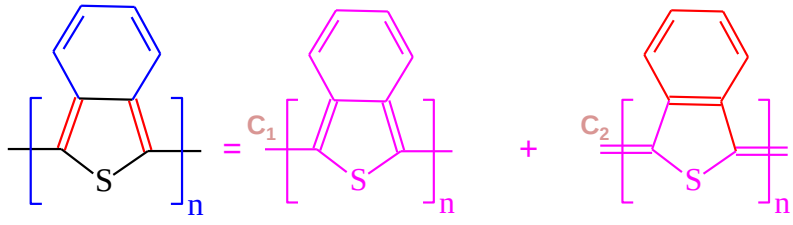


Eg = 1.8 eV

Poly(IsoThiaNaphthene)

Eg = 1.1 eV
Absorption in Red
Transparant on Doping

Assumed Aromatic Geometry



Eg = 0.5 eV

$C_1 > C_2$

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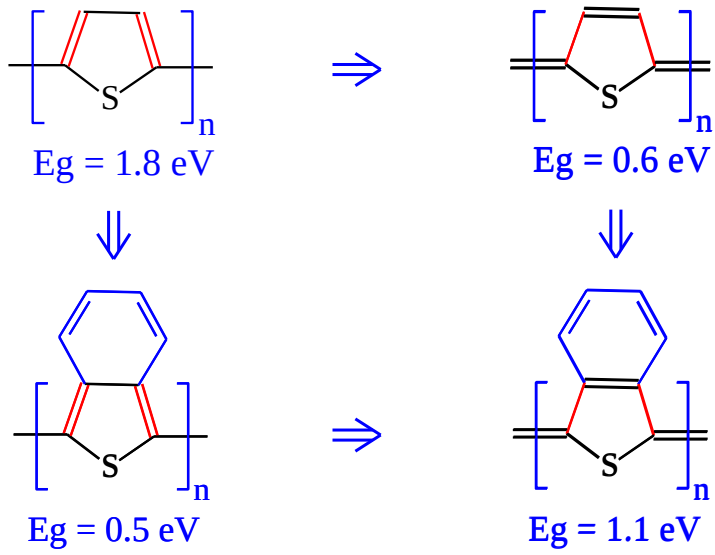
Tuning Aromatic Resonance Energy



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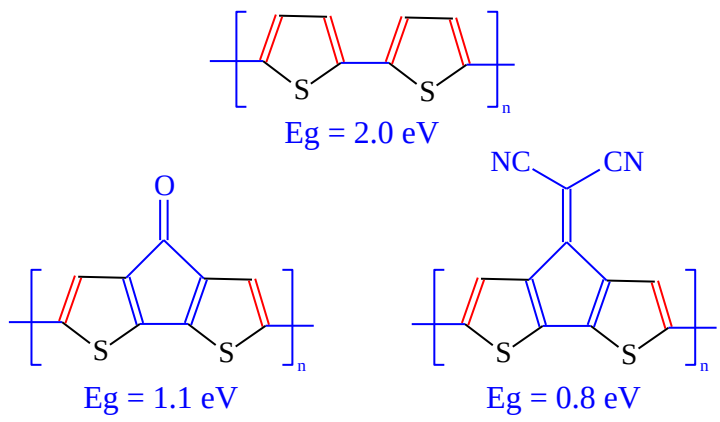
Tuning Aromatic Resonance Energy



Lambert T. M., Ferraris J. P.; J. Chem. Commun.; 752 (1991)

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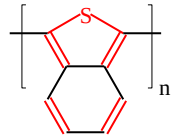
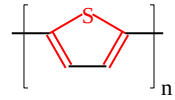
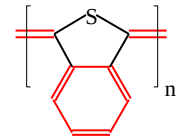
Tuning Aromatic Resonance Energy



Eg = 0.6 eV



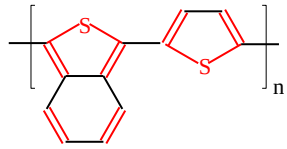
Eg = 1.8 eV



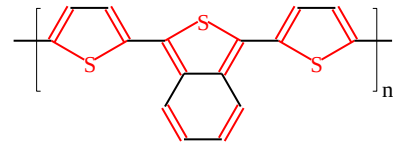
Eg = 1.1 eV

Aromatic Geometry

Quinoid Geometry



Eg = 1.2 eV



Eg = 1.4 eV

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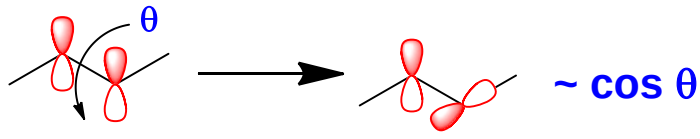
Mean Deviation from Planarity



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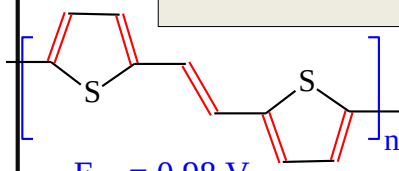
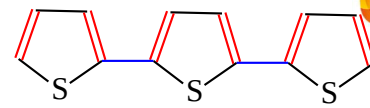
Mean Deviation from Planarity

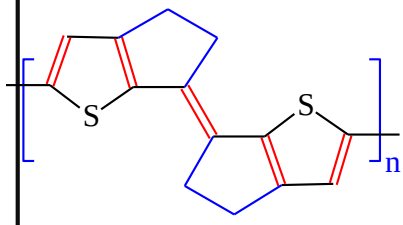


E_{ox} = 0.98 V

Eg = 1.80 eV

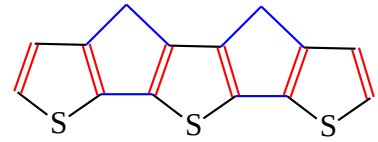


E_{ox} = 1.07 V



E_{ox} = 0.58 V

Eg = 1.40 eV



E_{ox} = 0.60 V

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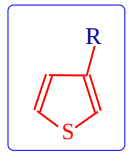
Mean Deviation from Planarity

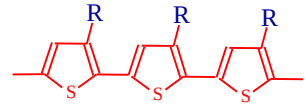
Regio-Regular Conjugated Polymers



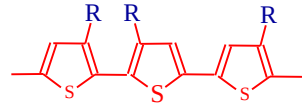
Poly(Alkyl Thiophene) (PAT)

$FeCl_3$ →

75%



25%



E_g = 2 eV

100%

E_g = 1.8 eV

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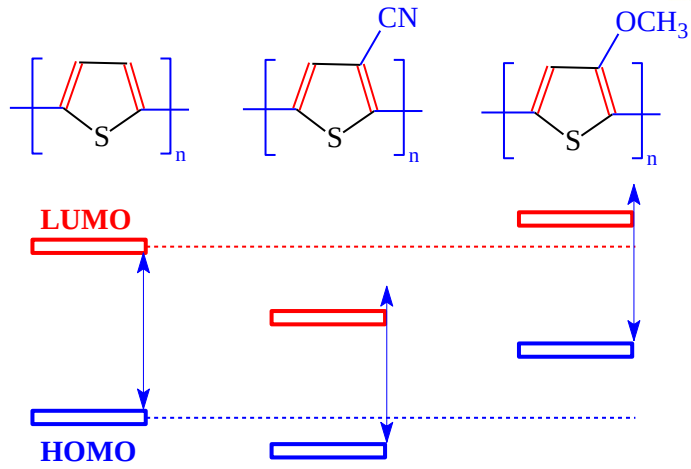
Inductive and Mesomeric Substituent Effects



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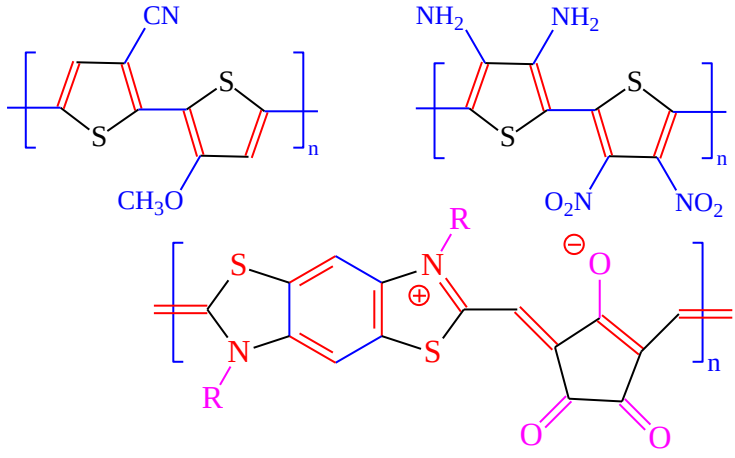
Inductive and Mesomeric Substituent Effects



Havinga, E. E. ; Tenhoeve, W. ; Wynberg, H. "A new class of small band-gap organic polymer conductors": Polymer Bulletin (1992) 29 (1-2) p 119-126

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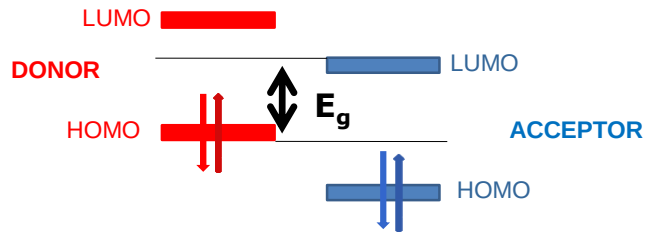
Low bandgap alternating copolymers

Design strategy for low bandgap: DONOR-ACCEPTOR alternant COPOLYMERS

Increase the double bond character of the single bonds

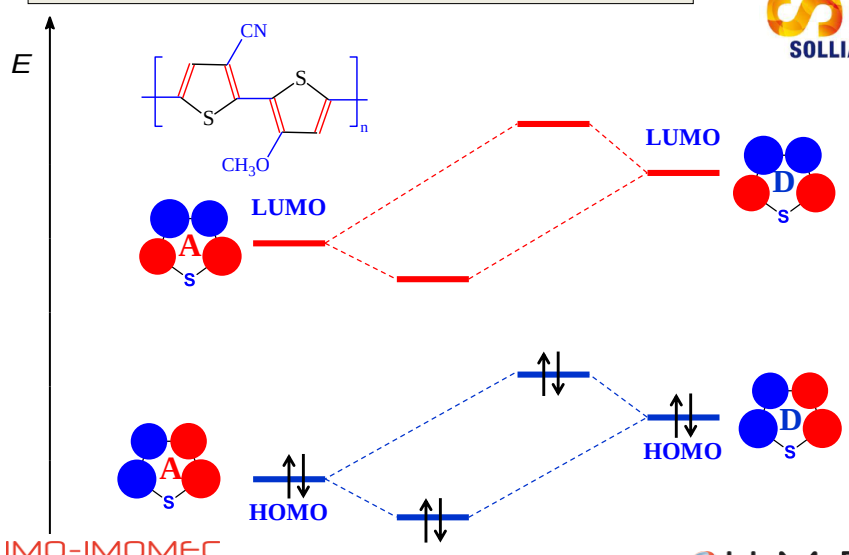
– D – A – D – A – D – A – ⟷ – D^+ = A^- – D^+ = A^- – D^+ = A^- –

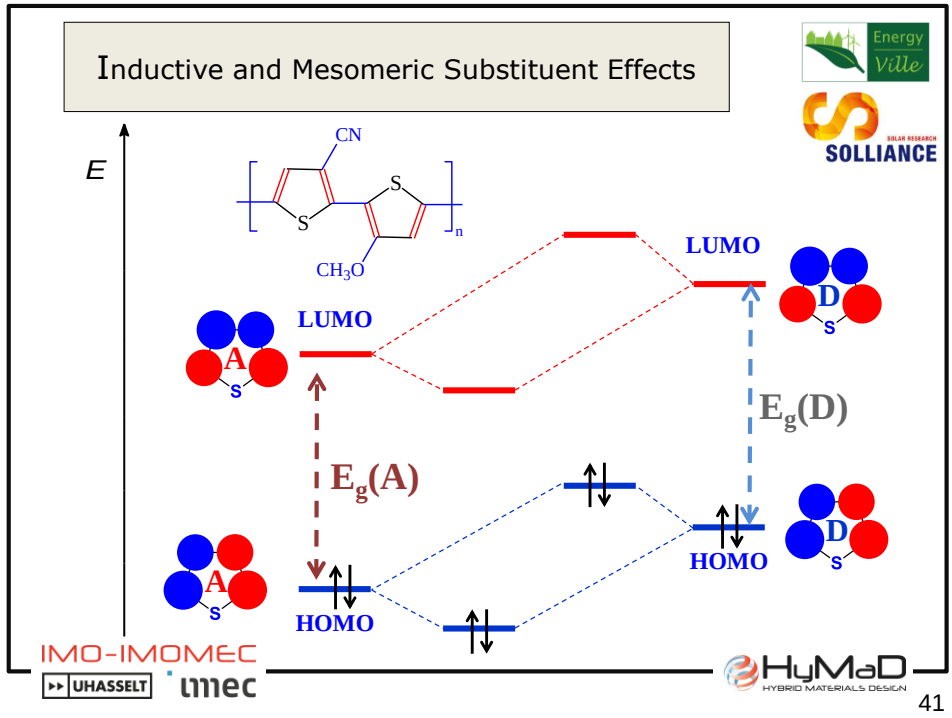
Reduction of the bond length alternation
Lowering of the bandgap E_g



Havinga, E. E. ; Tenhoeve, W. ; Wynberg, H. "A new class of small band-gap organic polymer conductors": Polymer Bulletin (1992) 29 (1-2) p 119-126

Inductive and Mesomeric Substituent Effects




Inductive and Mesomeric Substituent Effects
E
CN
S
S
n
CH3O
LUMO
LUMO
A
S
D
S
Eg(D)
Eg(A)
A
S
D
S
HOMO
HOMO
IMO-IMOMEC
UHASSELT
imec
HyMaD
HYBRID MATERIALS DESIGN
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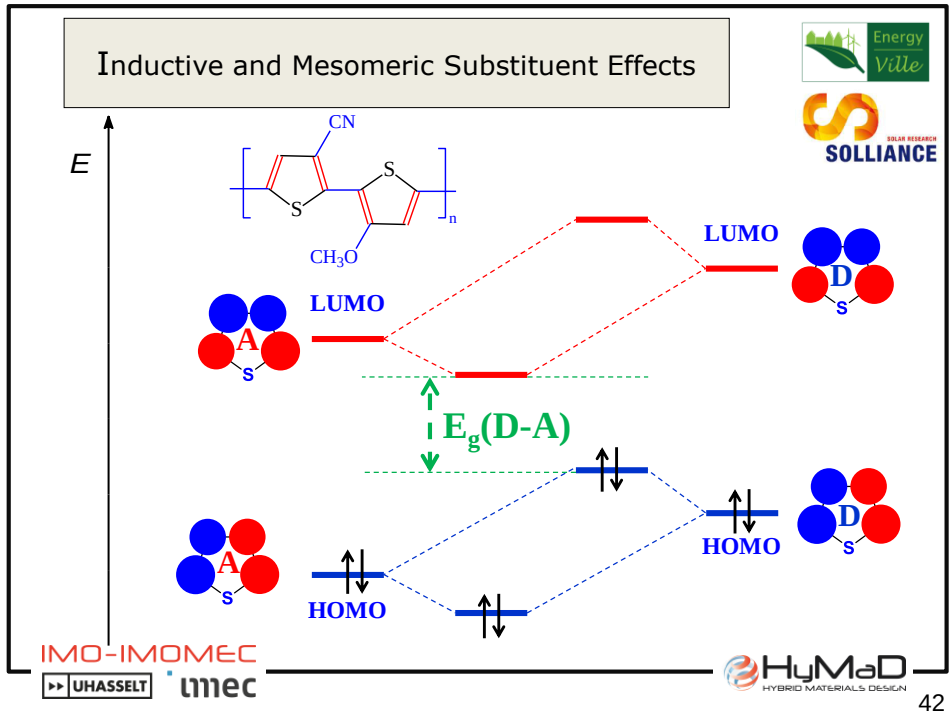
Inductive and Mesomeric Substituent Effects
E
CN
S
S
n
CH3O
LUMO
LUMO
A
S
D
S
Eg(D-A)
A
S
D
S
HOMO
HOMO
IMO-IMOMEC
UHASSELT
imec
HyMaD
HYBRID MATERIALS DESIGN
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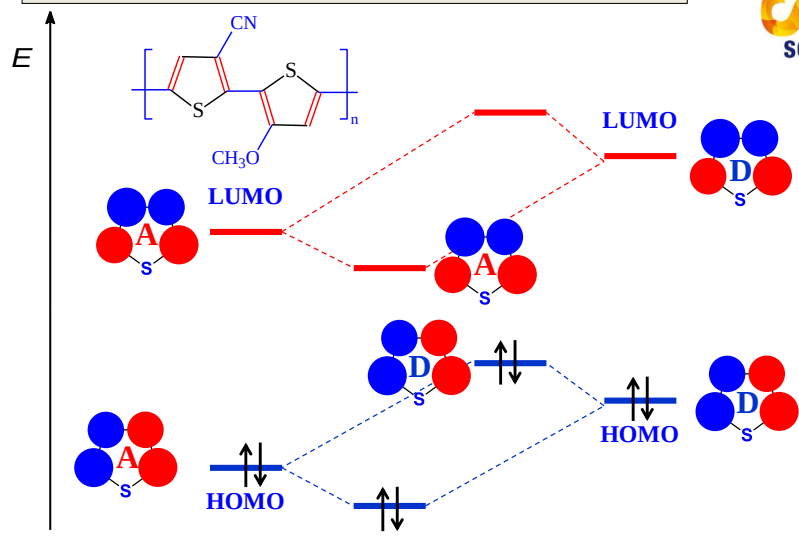
Inductive and Mesomeric Substituent Effects



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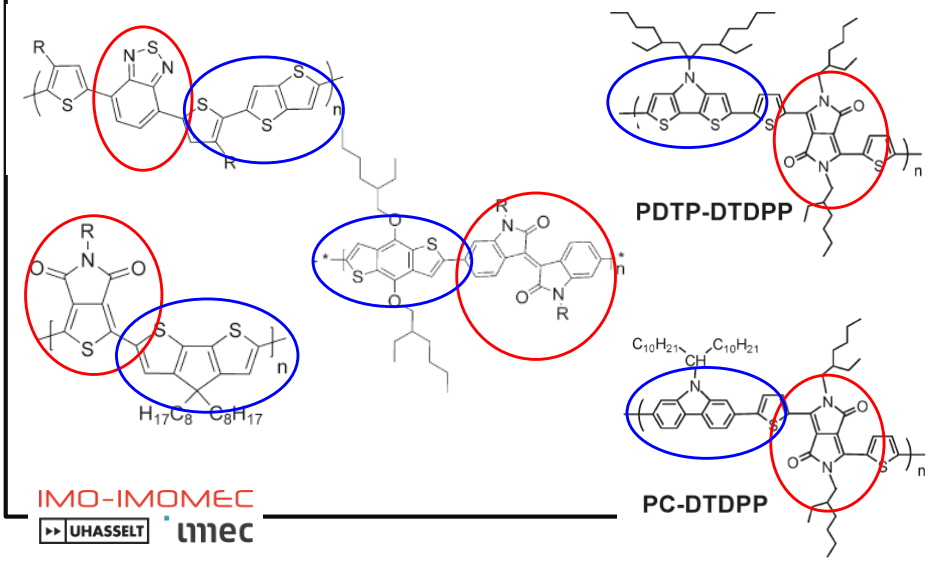
Donor-Acceptor alternating co-polymers



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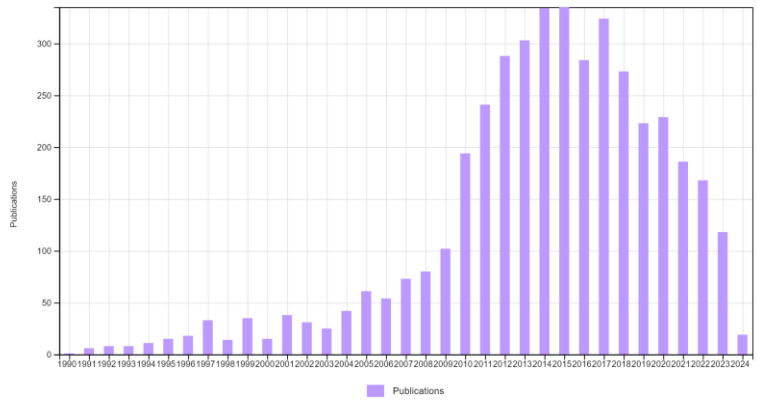
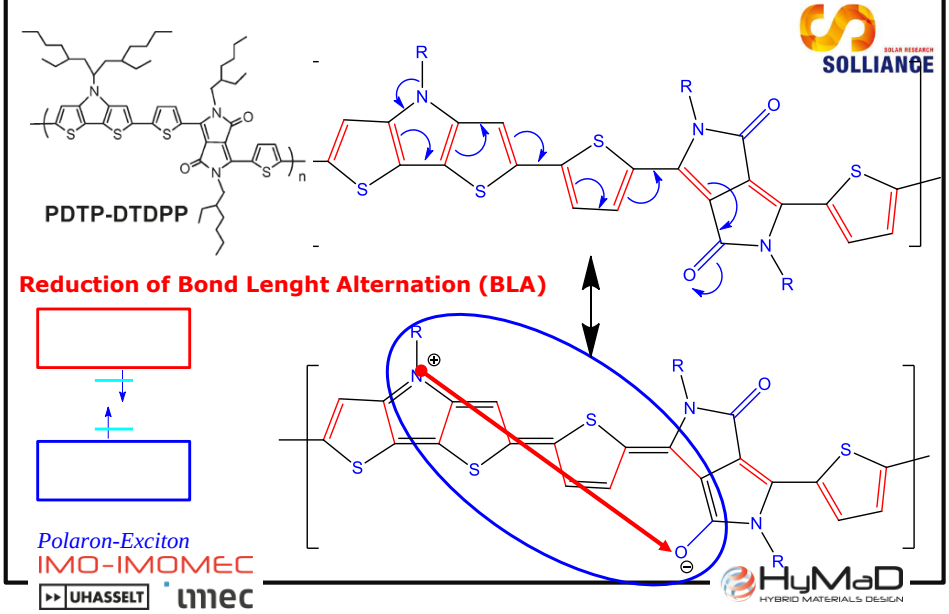
Workhorse materials in plastic electronics
articles

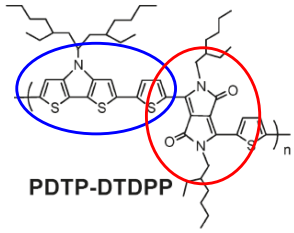


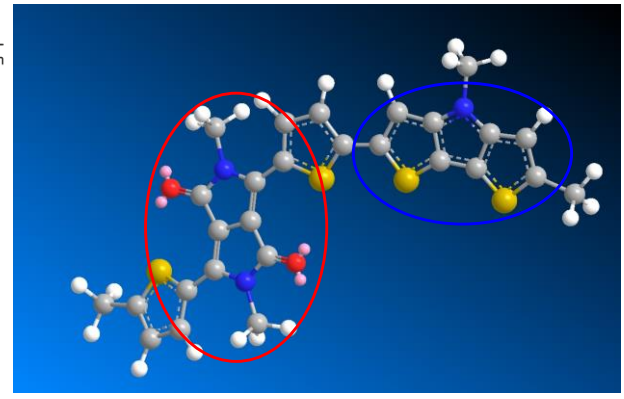
(LBG or low bandgap or low band gap) and conjugated polymer

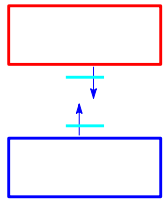
Donor-Acceptor alternating co-polymers



Donor-Acceptor alternating co-polymers







Polaron-Exciton

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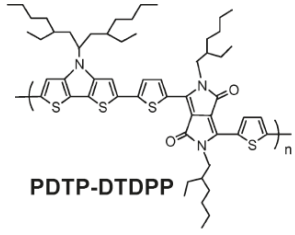
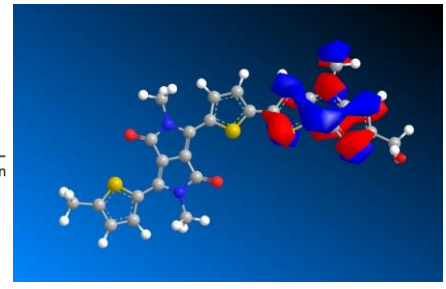
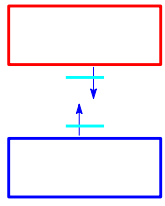
HyMaD HYBRID MATERIALS DESIGN

Donor-Acceptor alternating co-polymers

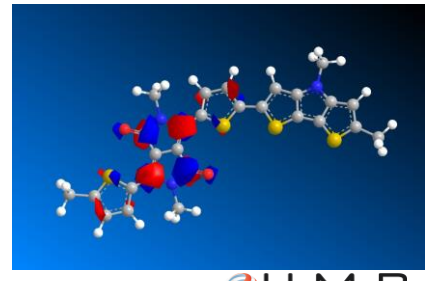




HOMO



LUMO



Polaron-Exciton

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HyMaD HYBRID MATERIALS DESIGN

Outline Part 2

- **Introduction**
- **Bandgap determination**
- **Band Gap Engineering**
- **Intermolecular effects on Bandgap**

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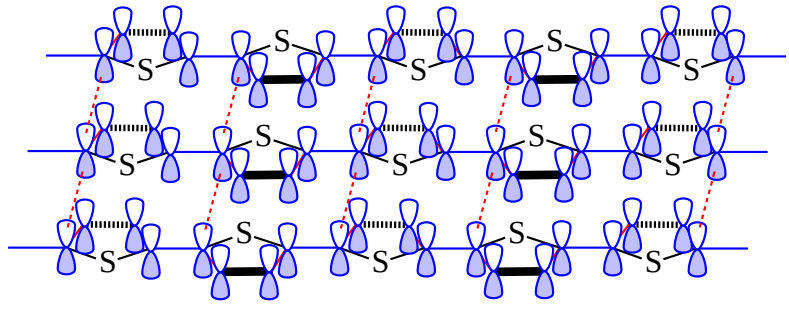
Intermolecular or Interchain Interactions



Deviation from 1-dimensionality

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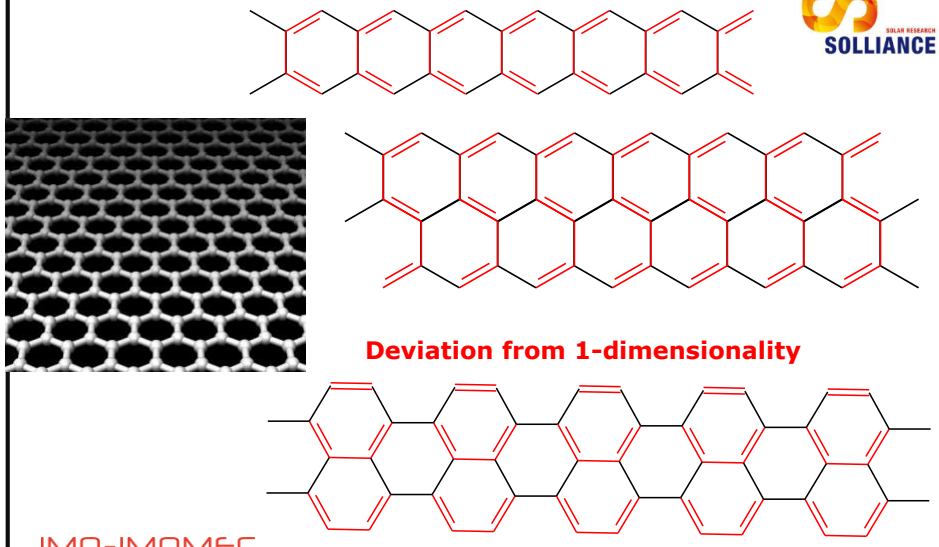
Intermolecular or Interchain Interactions



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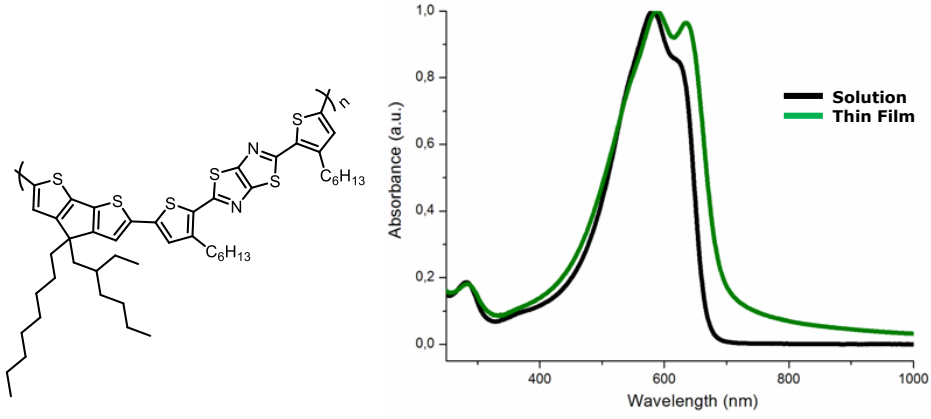
Intermolecular or Interchain Interactions



Van Mierloo, S. *et al.*, *Chem. Mater.* (2012) 24 p587-593

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Lecture Schedule 31th of May 2024

10:15 - 11:00	Lecture 1
11:00 - 11:10	short break
11:10 - 11:55	Lecture 2
11:55 - 12:05	short break
12:05 - 12:50	Lecture 3
12:50 - 13:50	Lunch
13:50 - 14:35	Lecture 4
14:35 - 14:45	short break
14:45 - 15:30	Lecture 5
15:30 - 15:40	short break
15:40 - 16:25	Lecture 6

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