Lecture 6: Conjugated Polymers

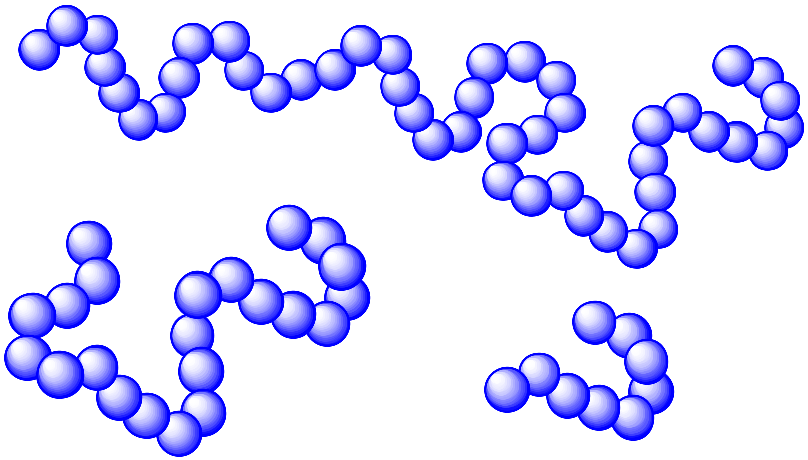
Modern Topics in Polymerization

SNU Fall 2011

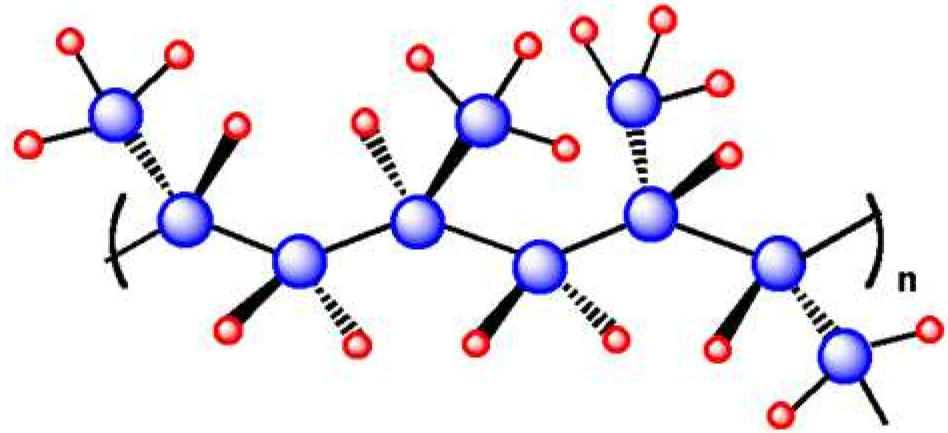
Prof. Pyun

Structural Heterogeneity in Polymers

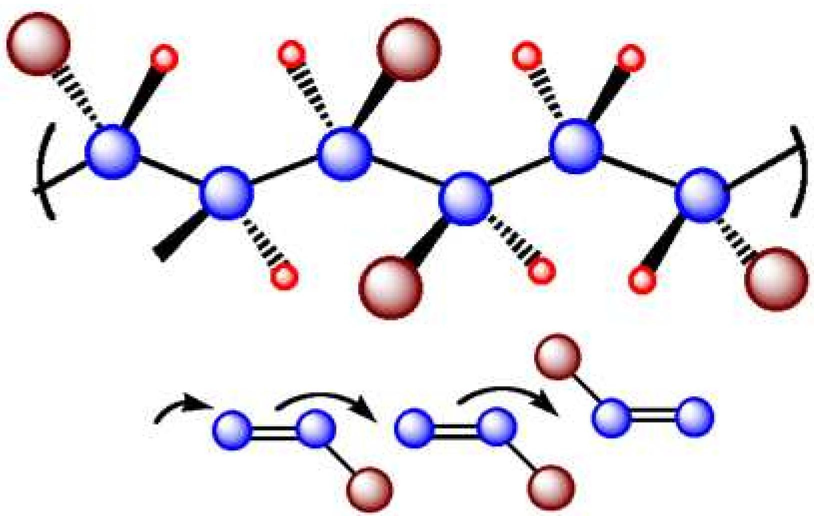
Molecular Weight



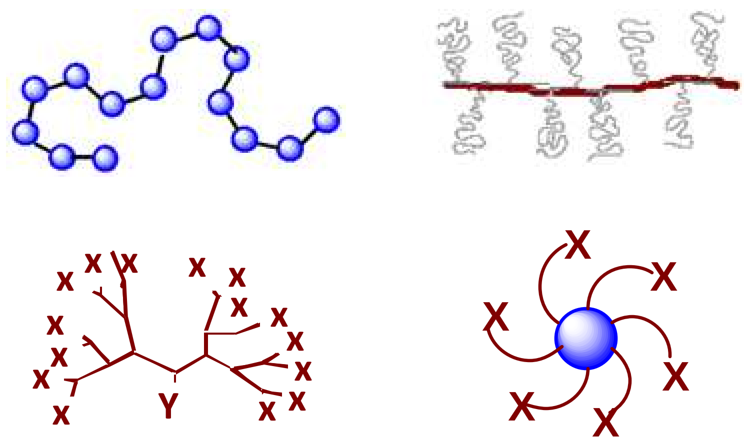
Tacticity



Regioregularity

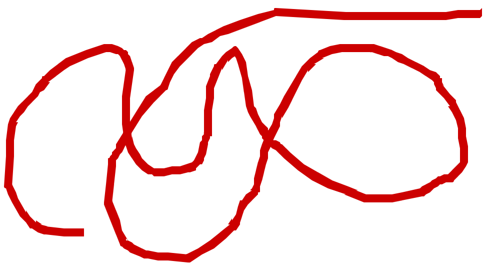


Architecture

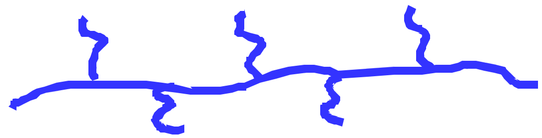


Examples of Synthetic Polymer Architecture

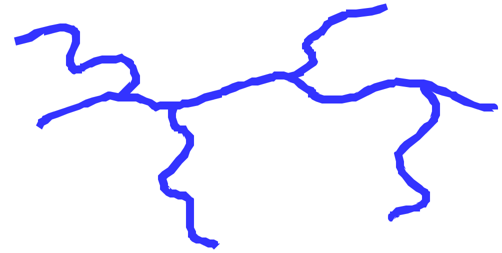
Linear polymers



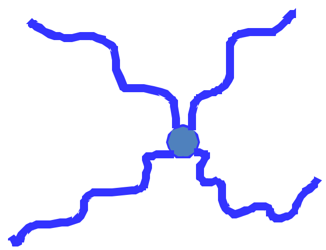
Branched polymers



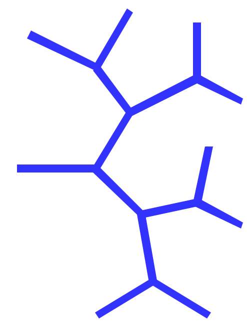
Short branched/graft copolymer



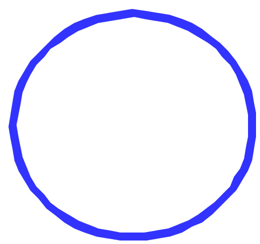
Long chain branches



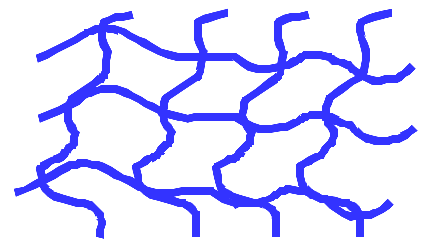
Star Polymers



Dendrimers, Hyperbranched



Cyclic Polymers



Network/Crosslinked

Thermoplastics:

Can be reversibly melt processed

Can be dissolved

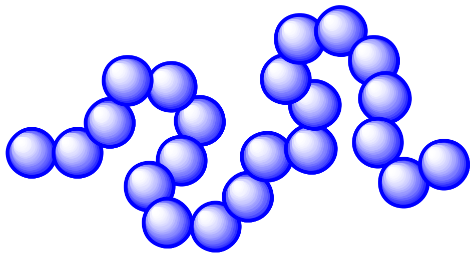
Elastomers

Lightly crosslinked rubbery polymer network: highly elastic

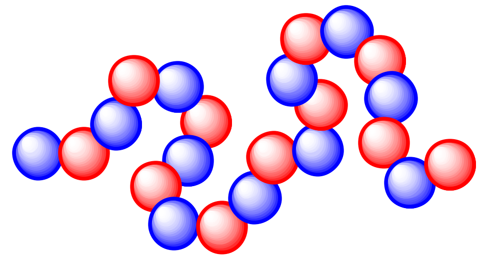
Thermosets

Form insoluble, highly crosslinked networks of higher mechanical integrity relative to uncrosslinked analogue

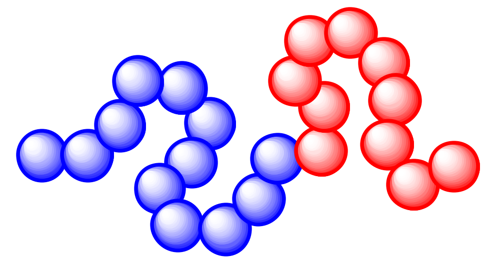
Classification of Statistical and Segmented Copolymers



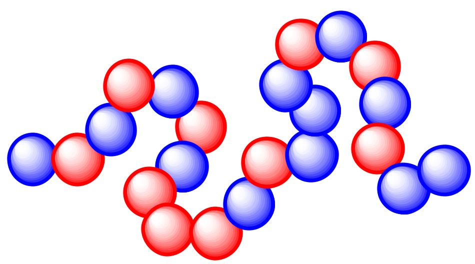
Homopolymers



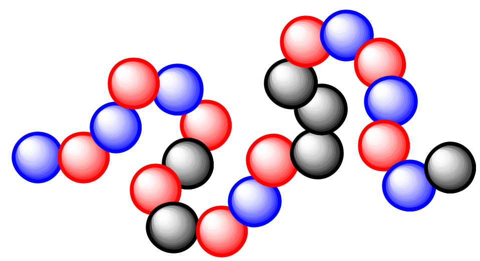
Alternating Copolymers



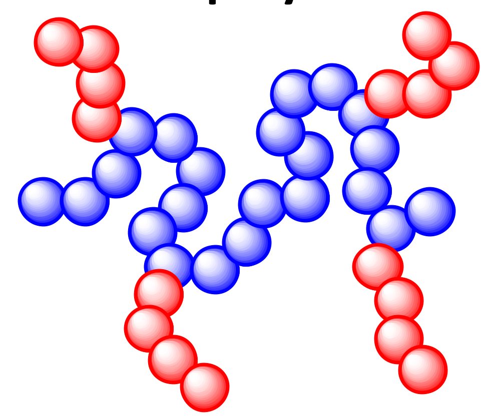
Block Copolymers[+]



Random Copolymers*

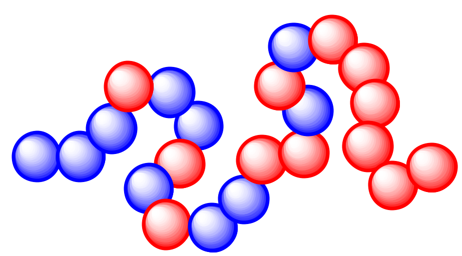


Random terpolymers*



Graft Copolymers[+]

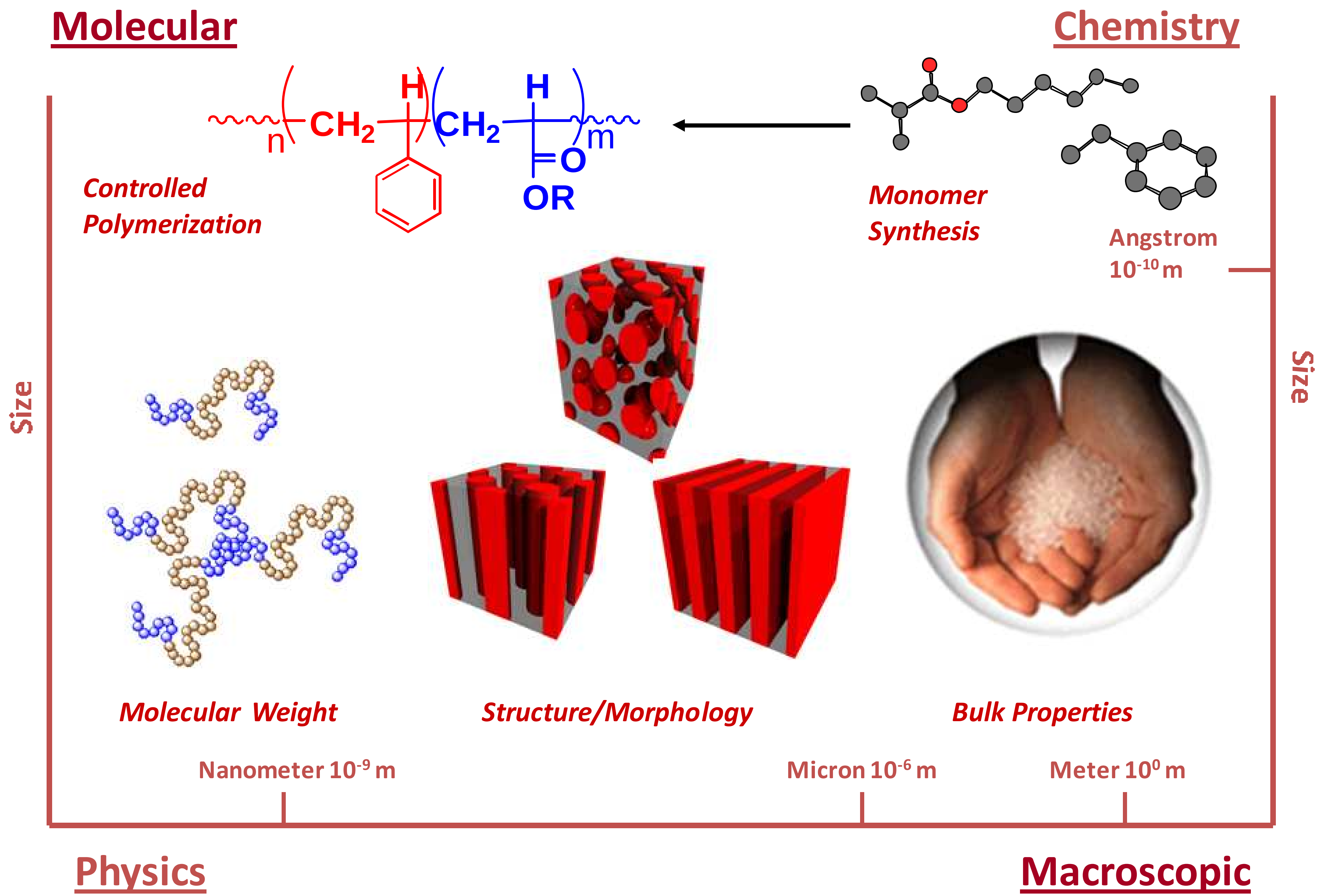
*** = statistical copolymers**
+ = segmented copolymers



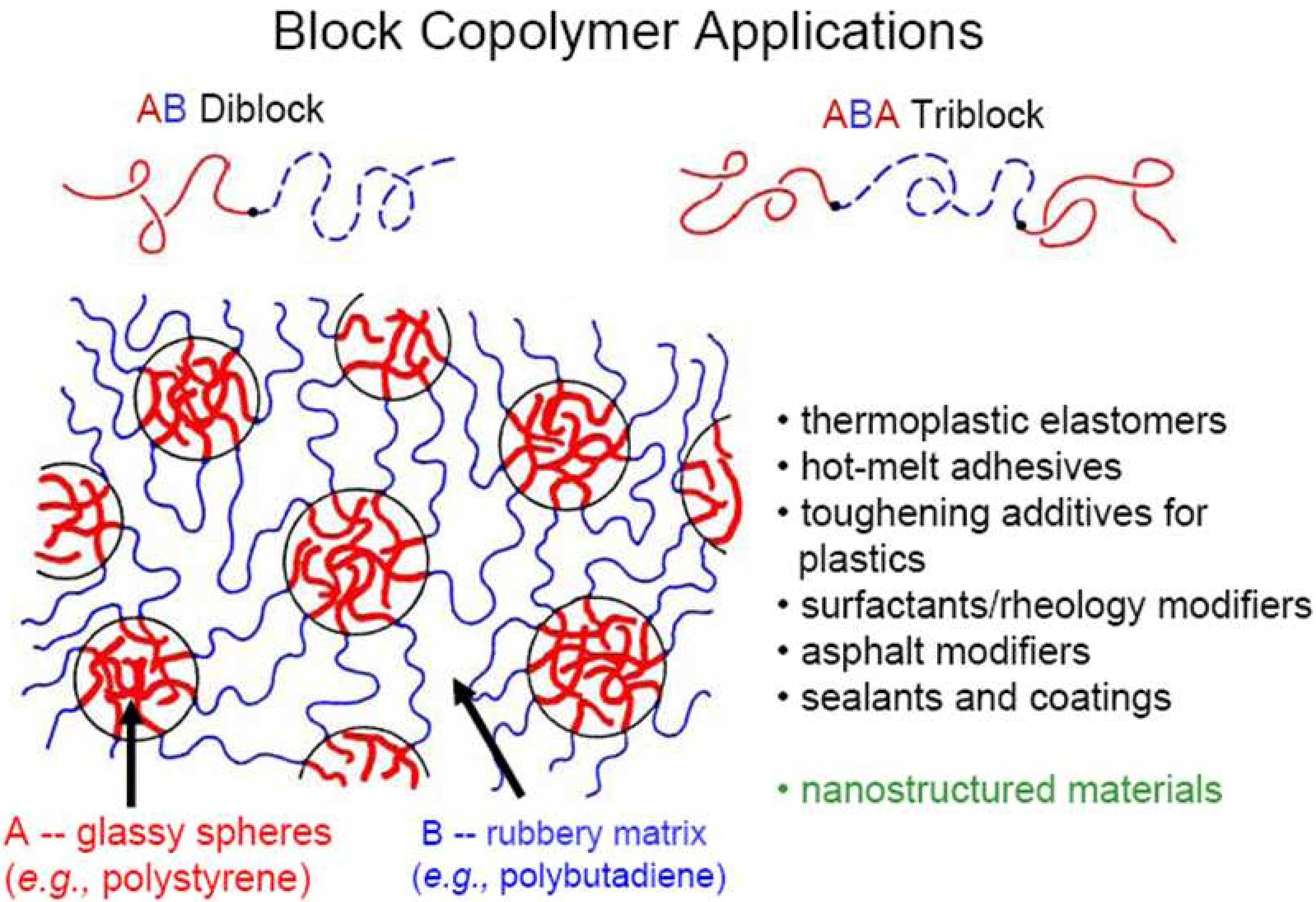
Gradient Copolymers*

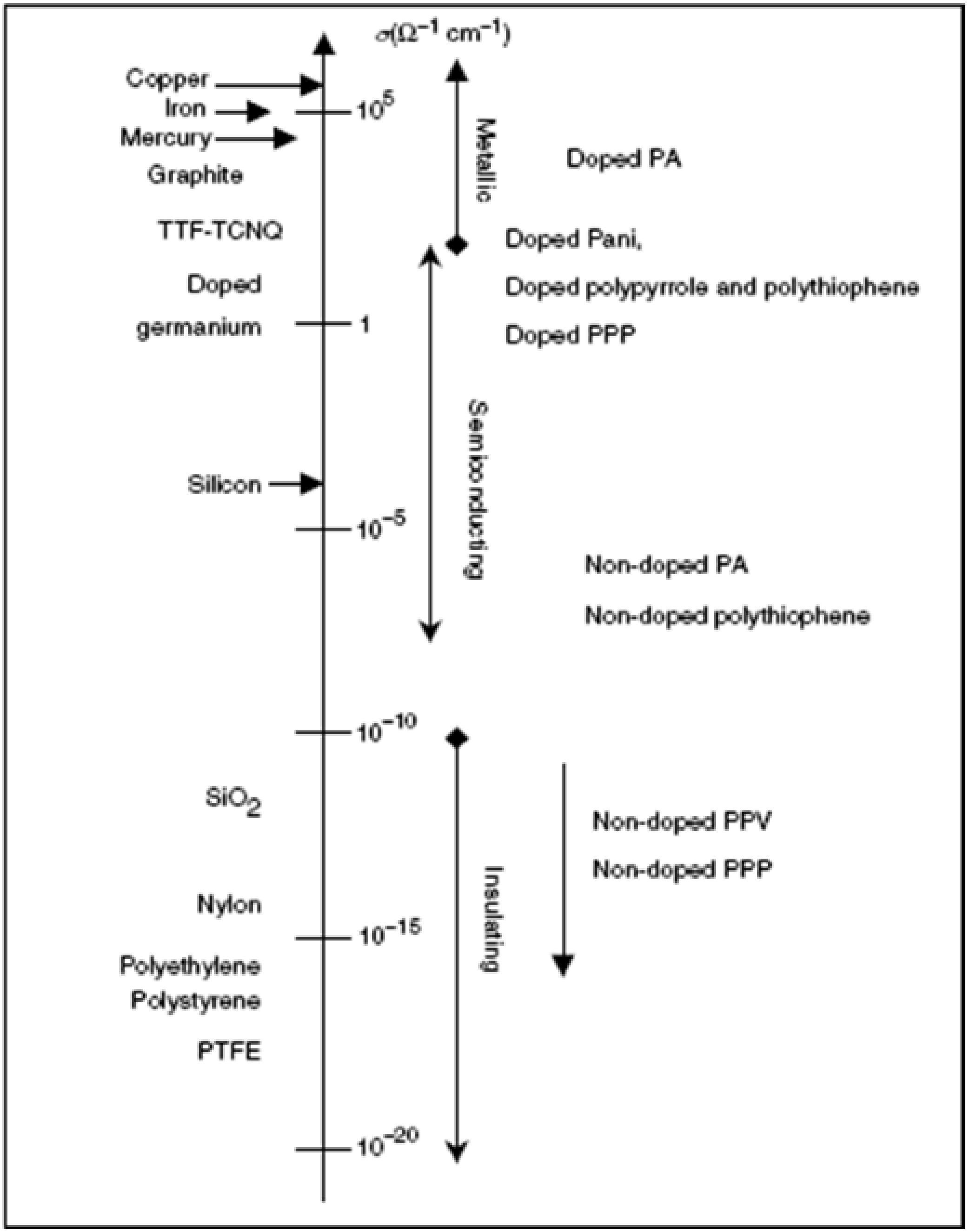
What factors affect copolymerizations?
Control MW?
Composition?

Polymeric Materials: Molecular to Macroscopic



Schematic for Spherical Phase Separated Morphology in AB Diblock Copolymer



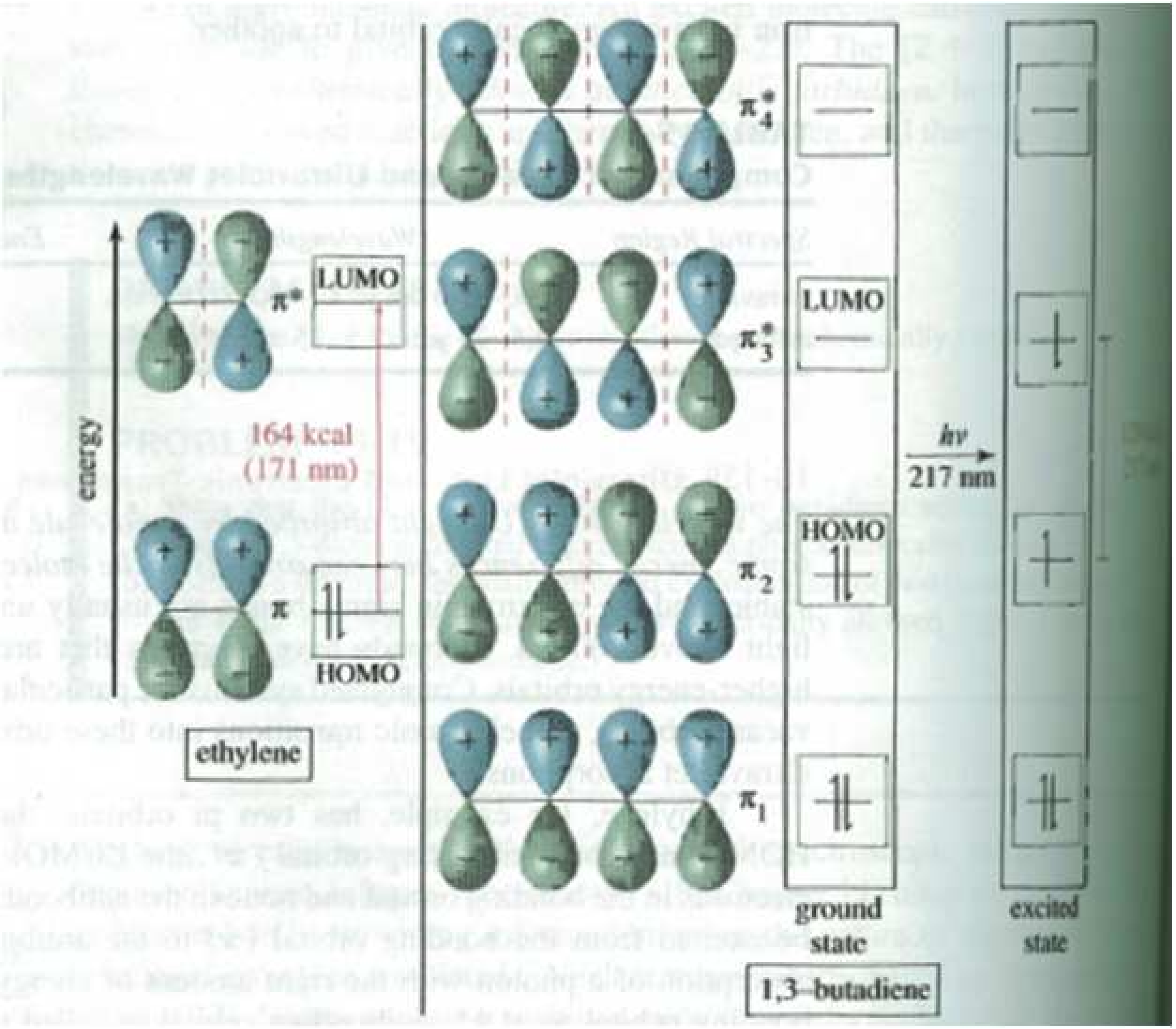


Metallic materials: good electrical conductors, compromised With higher T

semiconductors: moderate electrical conductors, excellent conductors with doping, Conductivity increases with T

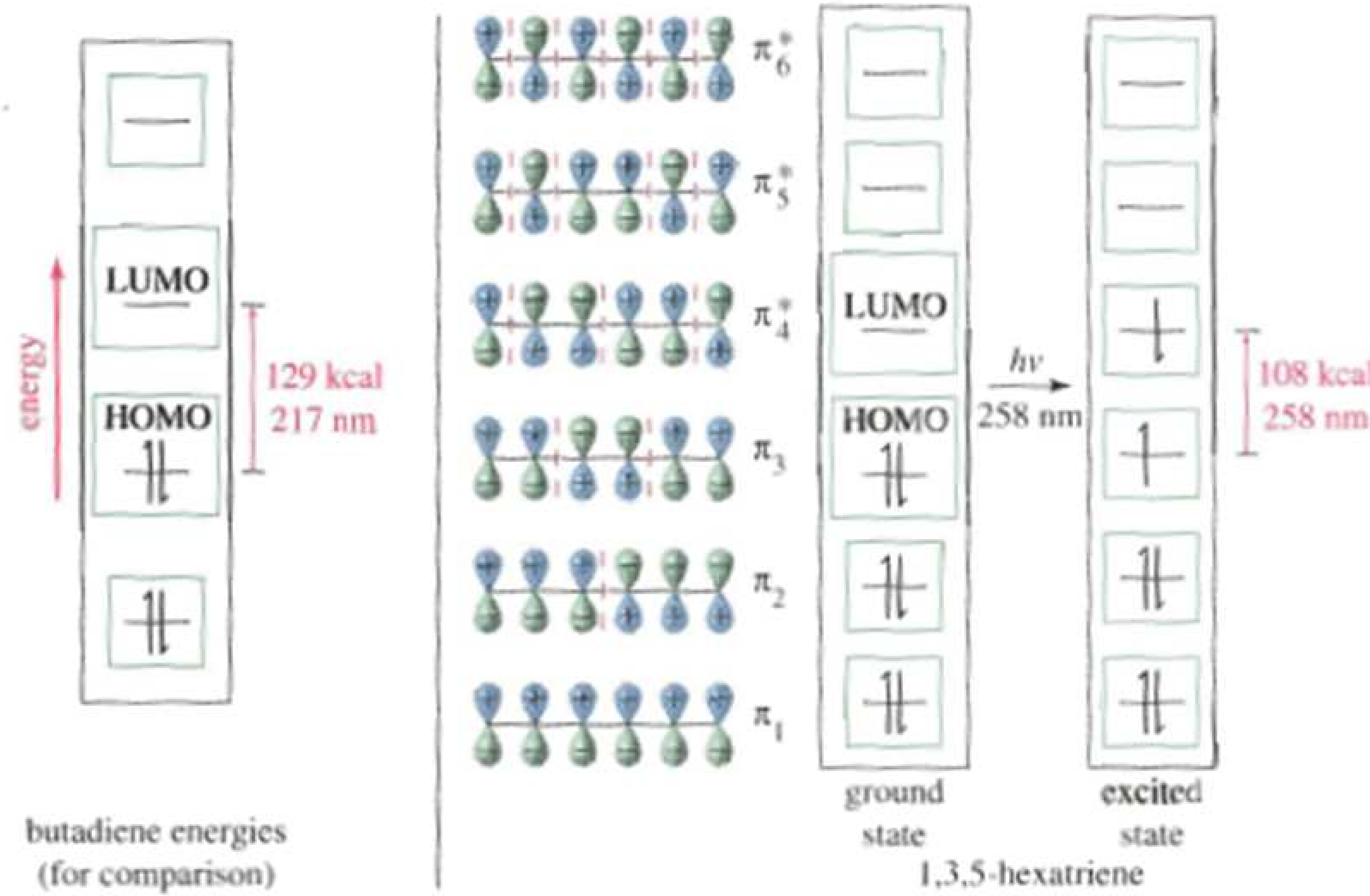
insulators: poor electrical conductors

Conjugation Lengths and HOMO-LUMO gaps



Wade, "Organic Chemistry," 3rd Ed. Prentice Hall, 1995

Conjugation Lengths and HOMO-LUMO gaps



Wade, “Organic Chemistry,” 3rd Ed. Prentice Hall, 1995

Conjugated Polymers: Historical and Current Applications

Initial interest heavily in electrical conductivity of doped conjugated polymers as material substitutes to metallic materials

Availability of high purity conjugated polymers prompted interest in semiconducting properties of these materials for:

Light emitting diodes

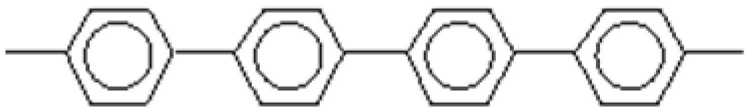
Photovoltaic Devices

Field effect transistors

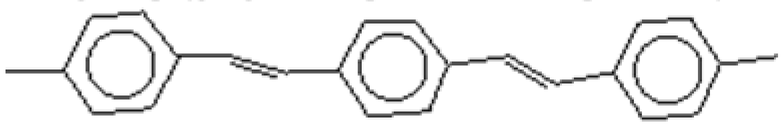
Friend, R.H. *Pure and Applied Chemistry* **2001**, *73*, 425

Examples of Conjugated Polymers

a) poly(*p*-phenylene)

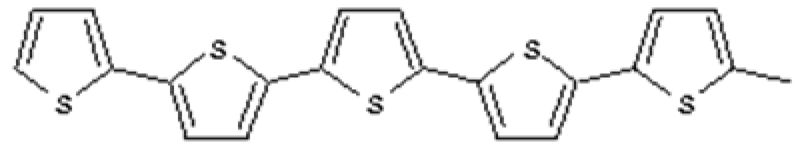


b) poly(*p*-phenylene vinylene)

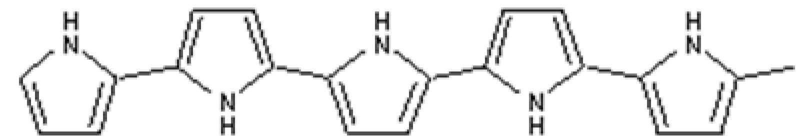


c) *trans*- polyacetylene

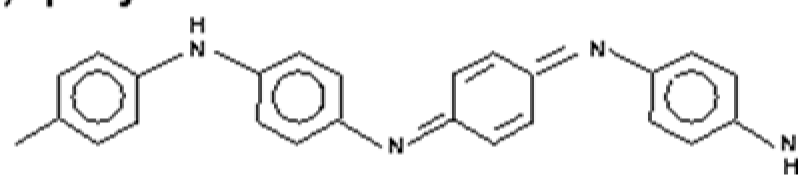
d) polythiophene



e) polypyrrole



f) polyaniline



Prepared using: electropolymerization, soluble precursor/prepolymer

Intractable materials – attractive electronic/optical properties

Side Chain Functionalization: enhance processing characteristics, new materials
compromise in electronic properties

Polyacetylene and Nobel Prize

- Shirakawa, Heeger, Macdiarmid, 2000
- Accidental discovery that doping of polyacetylene yielded highly conductive material (too much catalyst!) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci. Chem. Ed.* **1974,** *12,* 11

Trans and cis forms of polyacetylene

Electrical Conductivity in Doped Polyacetylene

C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
and
H. Shirakawa,[a] E. J. Louis, S. C. Gau, and Alan G. MacDiarmid
Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 23 June 1977)

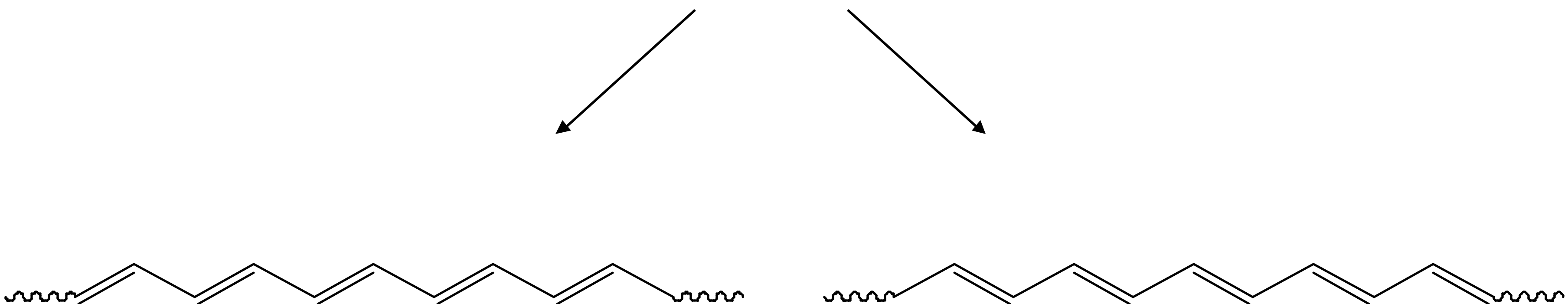
Doped polyacetylene forms a new class of conducting polymers in which the electrical conductivity can be systematically and continuously varied over a range of eleven orders of magnitude. Transport studies and far-infrared transmission measurements imply a metal-to-insulator transition at dopant concentrations near 1%.

Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977,** *39,* 1098.

Polyacetylene and Peierl's Distortion

Idealized structure of *trans*-polyacetylene

Fully delocalized, all equal bond lengths: metallic electronic structures

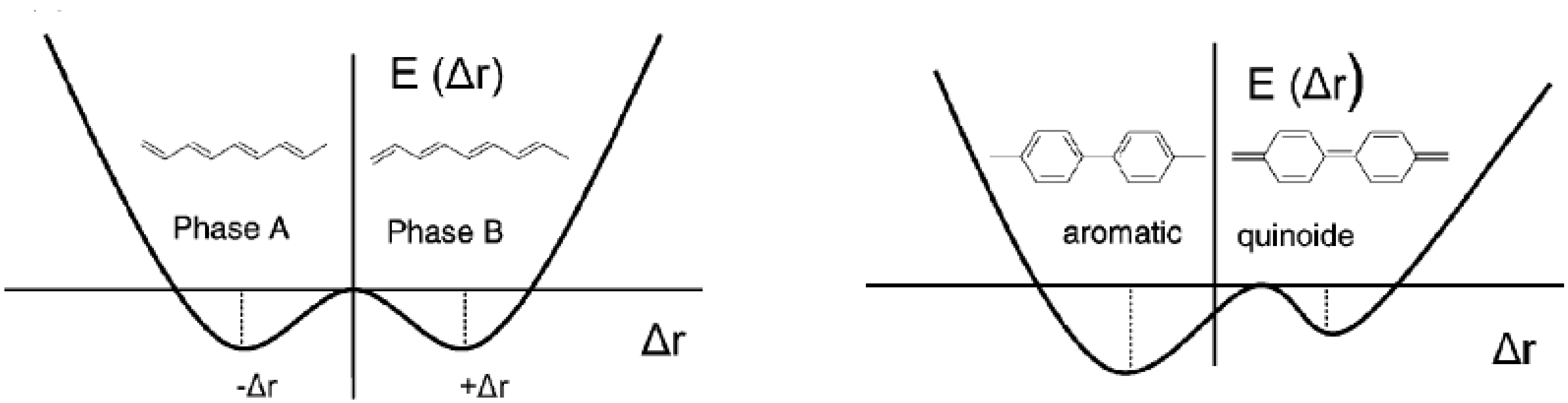


Preferred structure of *trans*-polyacetylene

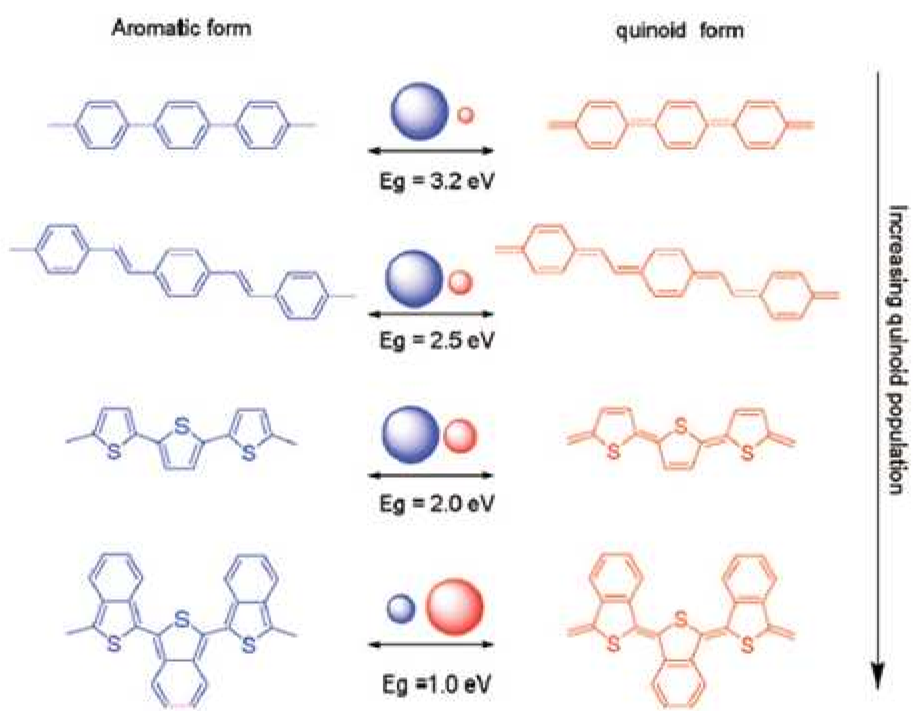
Alternating single-double bonds in polymer chain

Results in larger band gap between π and π^* levels

Aromaticity in Conjugated Polymers: Benzoid vs. Quinoid Forms



Sarifcifti et al., J. Mater. Chem. **2004**, *14*, 1077



Cheng et al., Chem. Rev. **2010**, *109*, 5868

Conductors, Semiconductors, Insulators

The old idea: metals = conductors

metalloids = semiconductors

non-metals (organics) = insulators

New idea:

Organic semiconductors

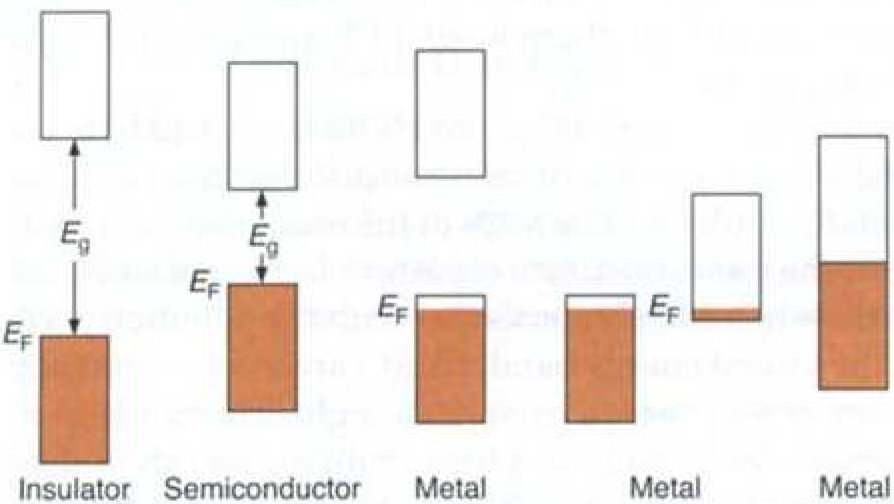
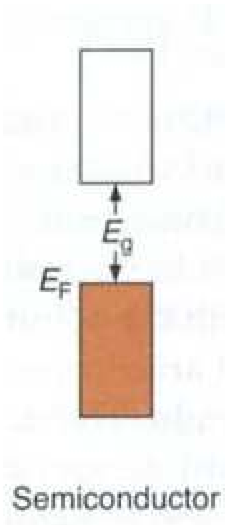


Figure 17.6
Relationships between various aspects of a band structure diagram and the expected electronic properties of a material. An insulator has a very large band gap, while a semiconductor has a small but finite band gap. A metal has a zero band gap, because of an incompletely filled band or because of the overlap of two bands.

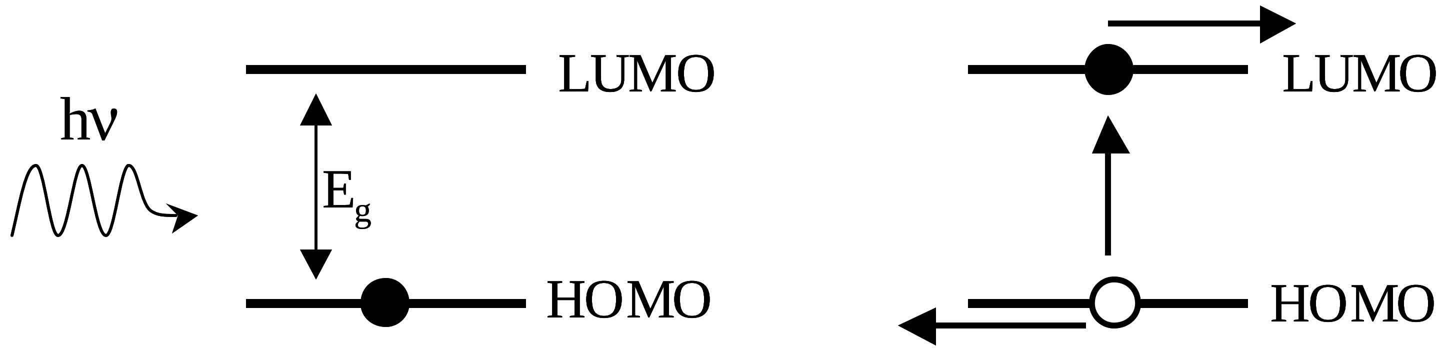
Anslyn and Dougherty. Modern Physical Organic Chemistry. 2006

Organic (Semi-)Conductors III: Band Gaps, Excitons



- Band gap (Eg): energy difference between valence and conduction bands
- Arises from symmetry issues, distortion
- Electrons excited into the conduction band = excitons
- Unoccupied energy levels in the valence band = holes
- Holes and excitons can recombine → no current
- P-type semiconductors → mobile holes
- N-type semiconductors → mobile electrons

Anslyn and Dougherty. Modern Physical Organic Chemistry. 2006



For semiconductors:
Excitation (from energy, Δ, hν), electron transfers into the Conduction Band And leaves behind a “hole.” This electron-hole pair when is close contact before dissociation is referred to as an “exciton.” Charge dissociation of an exciton is important for a number of applications in optoelectronic devices, such as, solar cells.

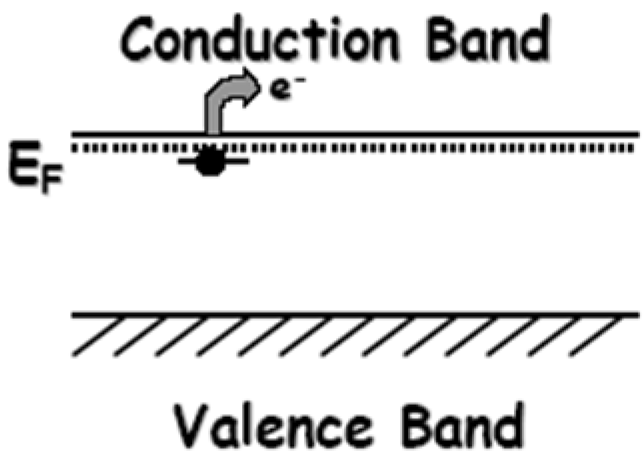
Organic semiconductors possess inferior electron mobility (w/p doping) but possess reasonable hole mobilities

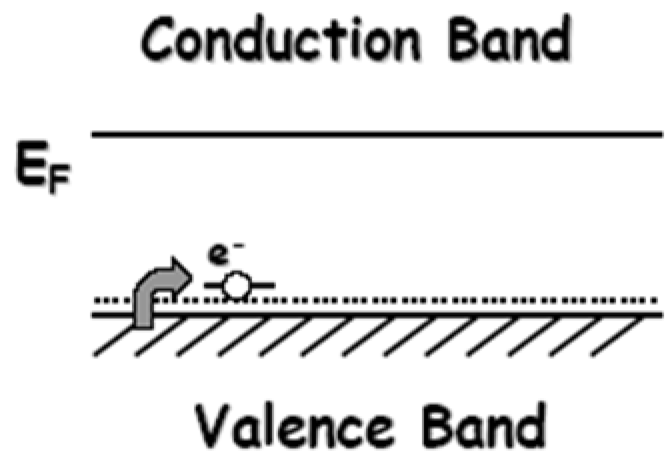
Doping Semiconductors

The Fermi-Dirac function shows that a pure semiconductor with a band gap of more than a few tenths of an eV would have a very small concentration of carriers. Therefore, impurities are added to introduce carriers.

n-doping → Replacing a lattice atom with an impurity (donor) atom that contains 1 additional valence electron (i.e. P in Si). This e^- can easily be donated to the conduction band.

p-doping → Replacing a lattice atom with an impurity (acceptor) atom that contains 1 less valence electron (i.e. Al in Si). This atom can easily accept an e^- from the VB creating a hole.





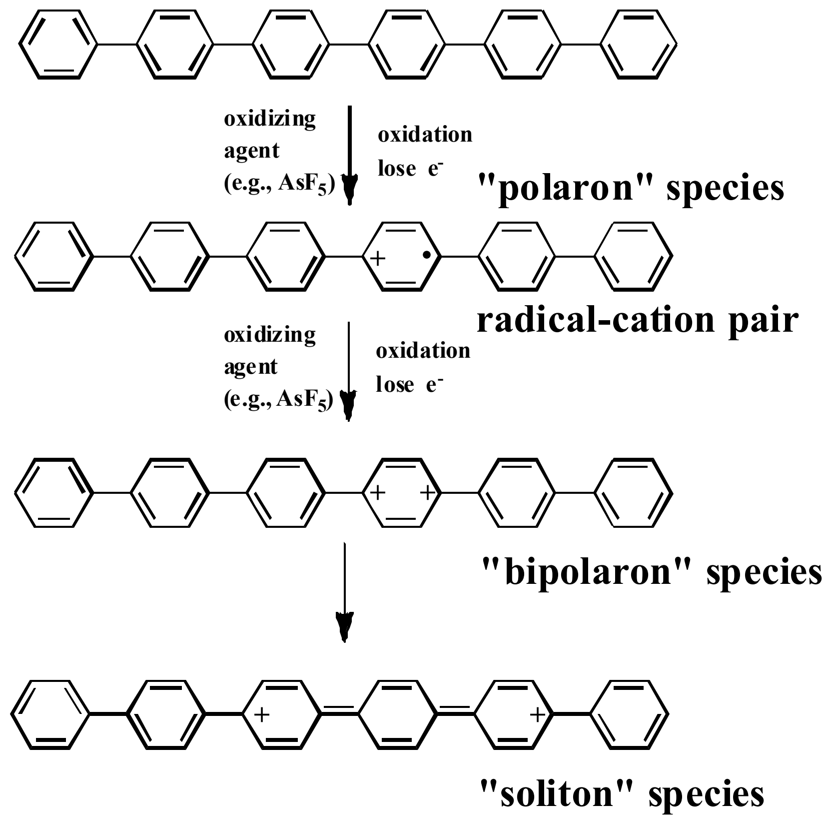
Electrical Conductivity of Conjugated Polymers Upon Doping

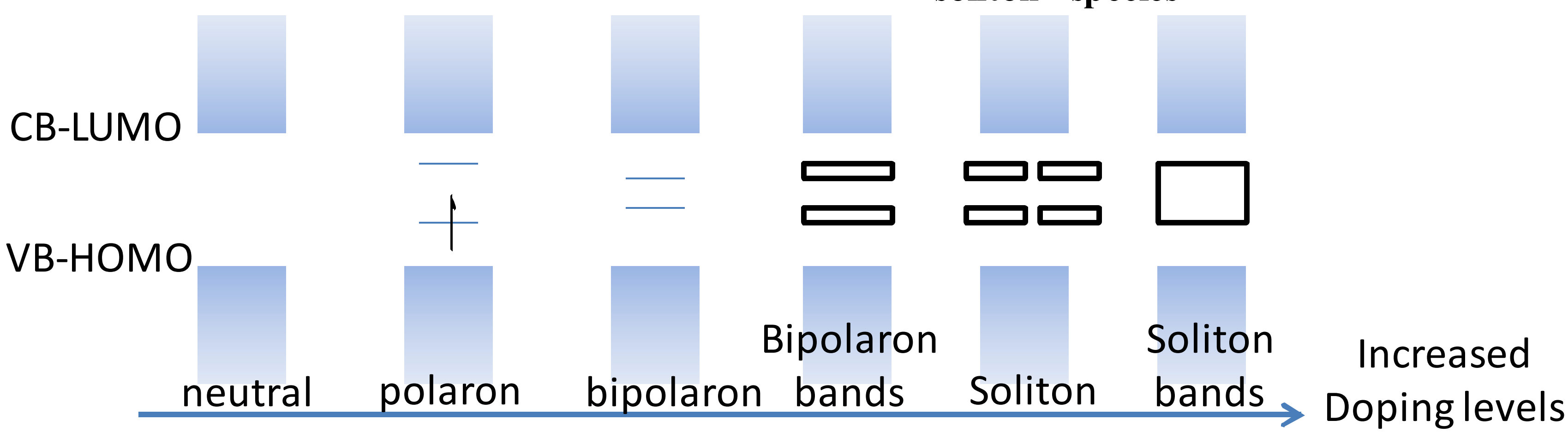
"doping" of conjugated
Polymers different than
In inorganic semiconductors

Referred to as "spinless defects"
since excitons are not the main
conductive species

Oxidizing/reducing agent do
Remove/add electrons from
polymer chain

Creates states in band gap
More doping becomes bands





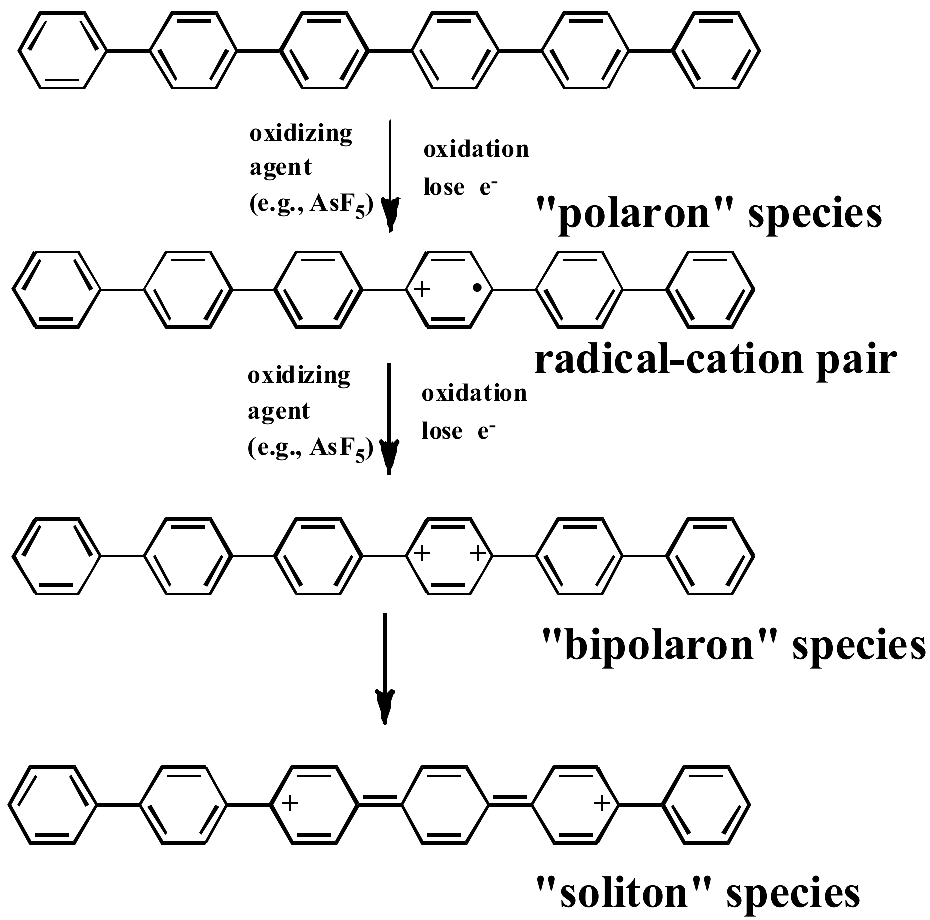
Electrical Conductivity of Conjugated Polymers Upon Doping

“doping” of conjugated
Polymers different than
In inorganic semiconductors

Referred to as “spinless
defects” since excitons are not
the main conductive species

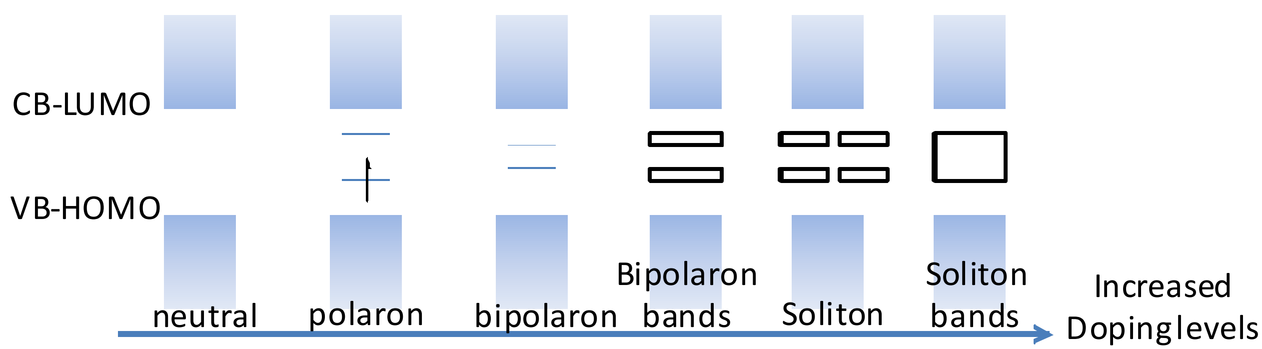
Oxidizing/reducing agent do
Remove/add electrons from
polymer chain

Creates states in band gap
More doping becomes bands
Which eventually enable
significant
Accessible of VB electrons into
CB (metallic behavior)

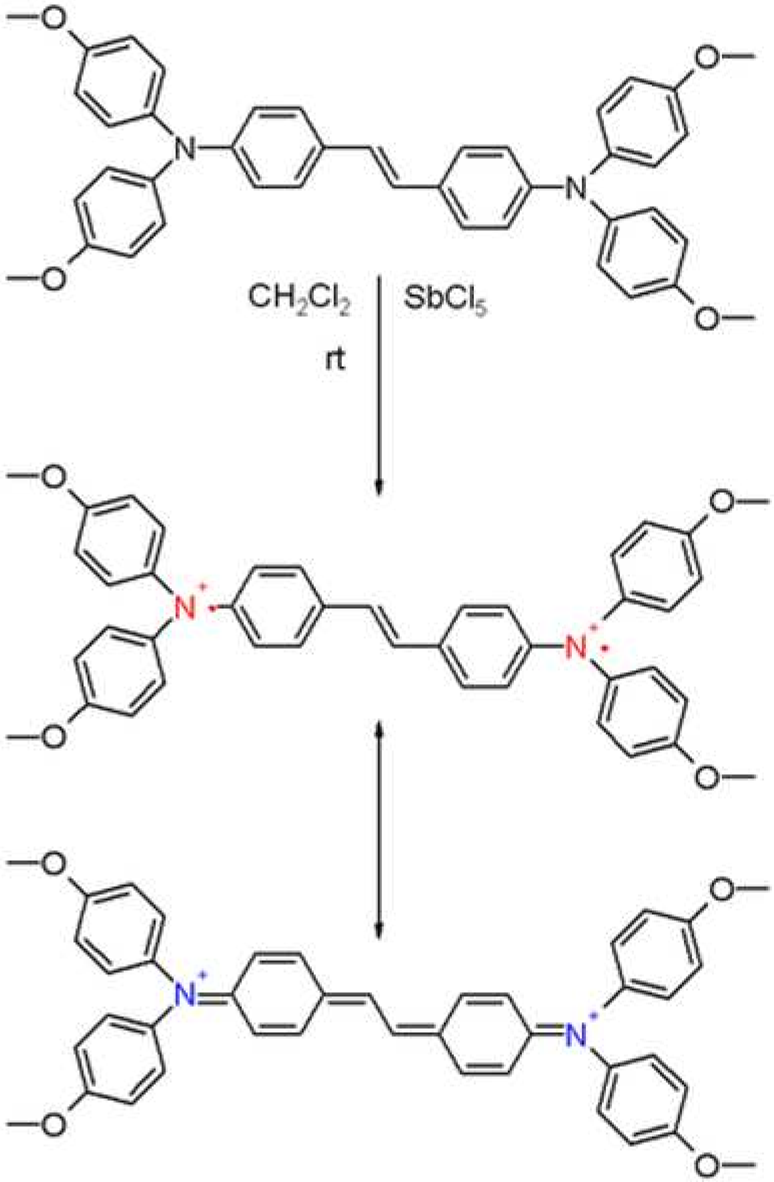


Neutral
Oligophenylene
$10^{-14}\ \Omega^{-1}\ cm^{-1}$

Doped
Oligophenylene
$5 \times 10^{2}\ \Omega^{-1}\ cm^{-1}$



“Molecular” Bipolarons



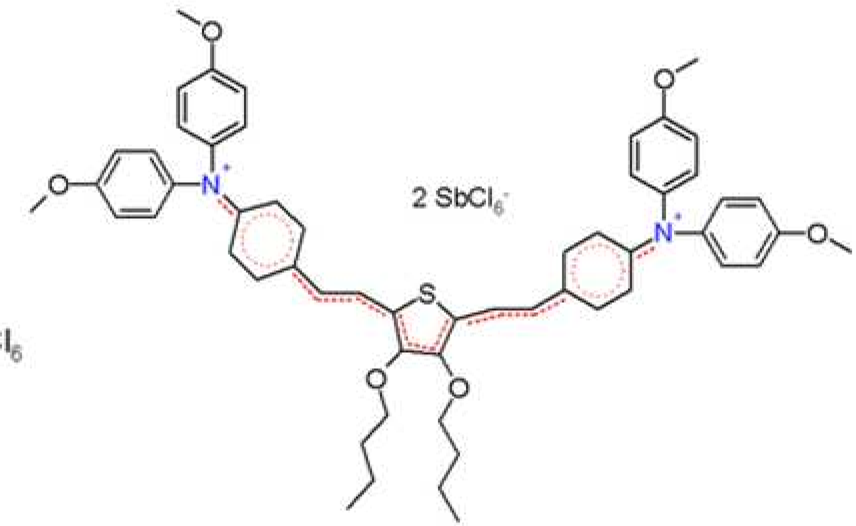
1

2a

2 $SbCl_6$

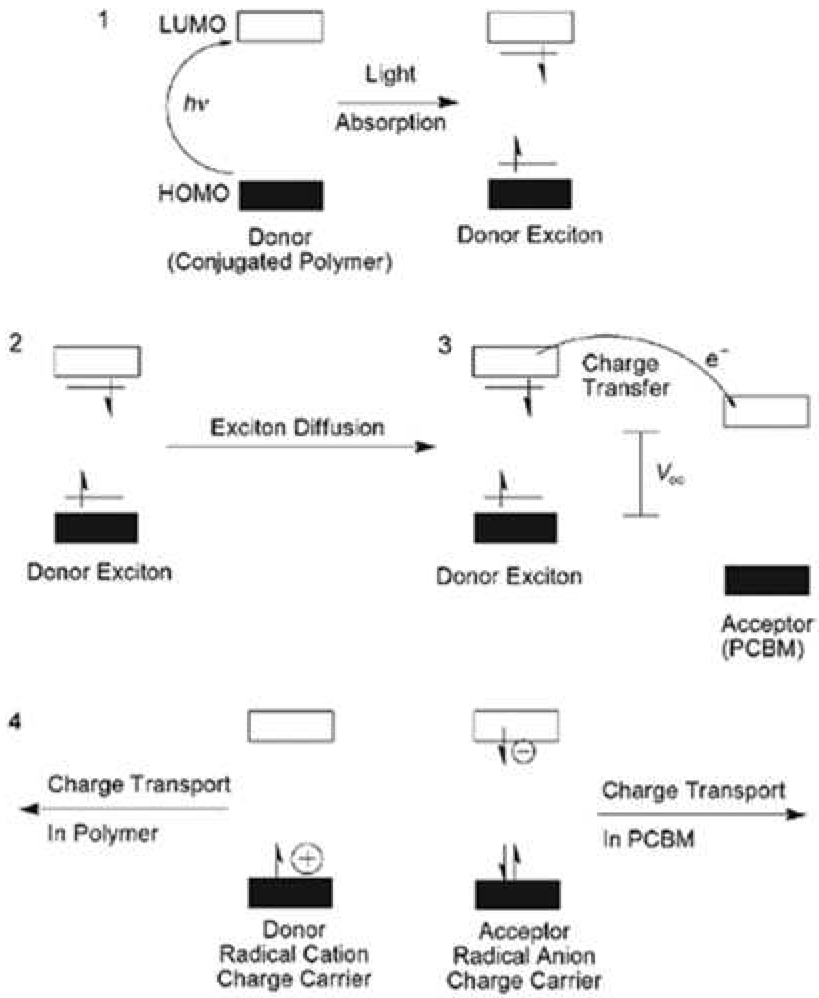
2b

2 $SbCl_6^-$



Barlow et al., J. Am. Chem. Soc. **2006**, *128*, 1812

Photogenerated Charges in Semicoducting Polymers



Fréchet et al., Angew. Chem. Int. Ed. **2008**, *47*, 58

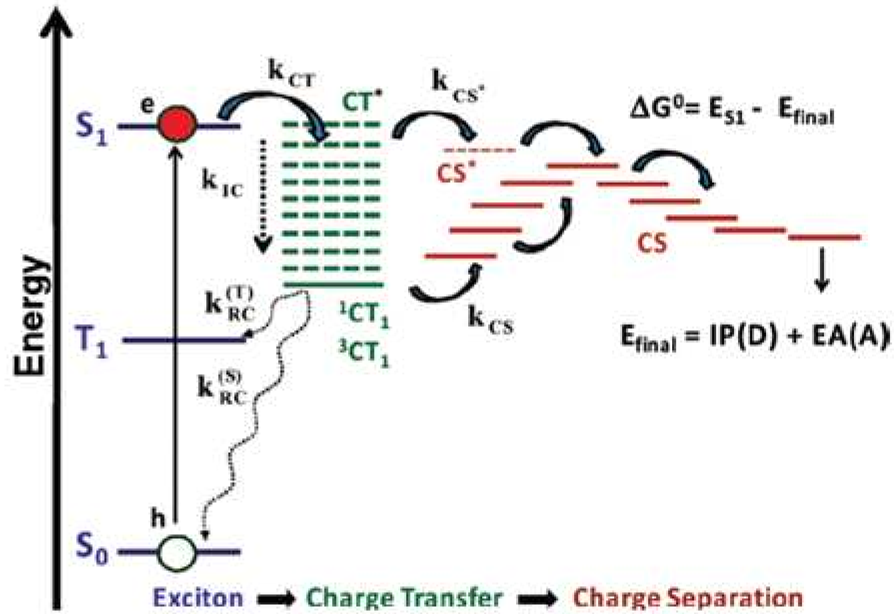
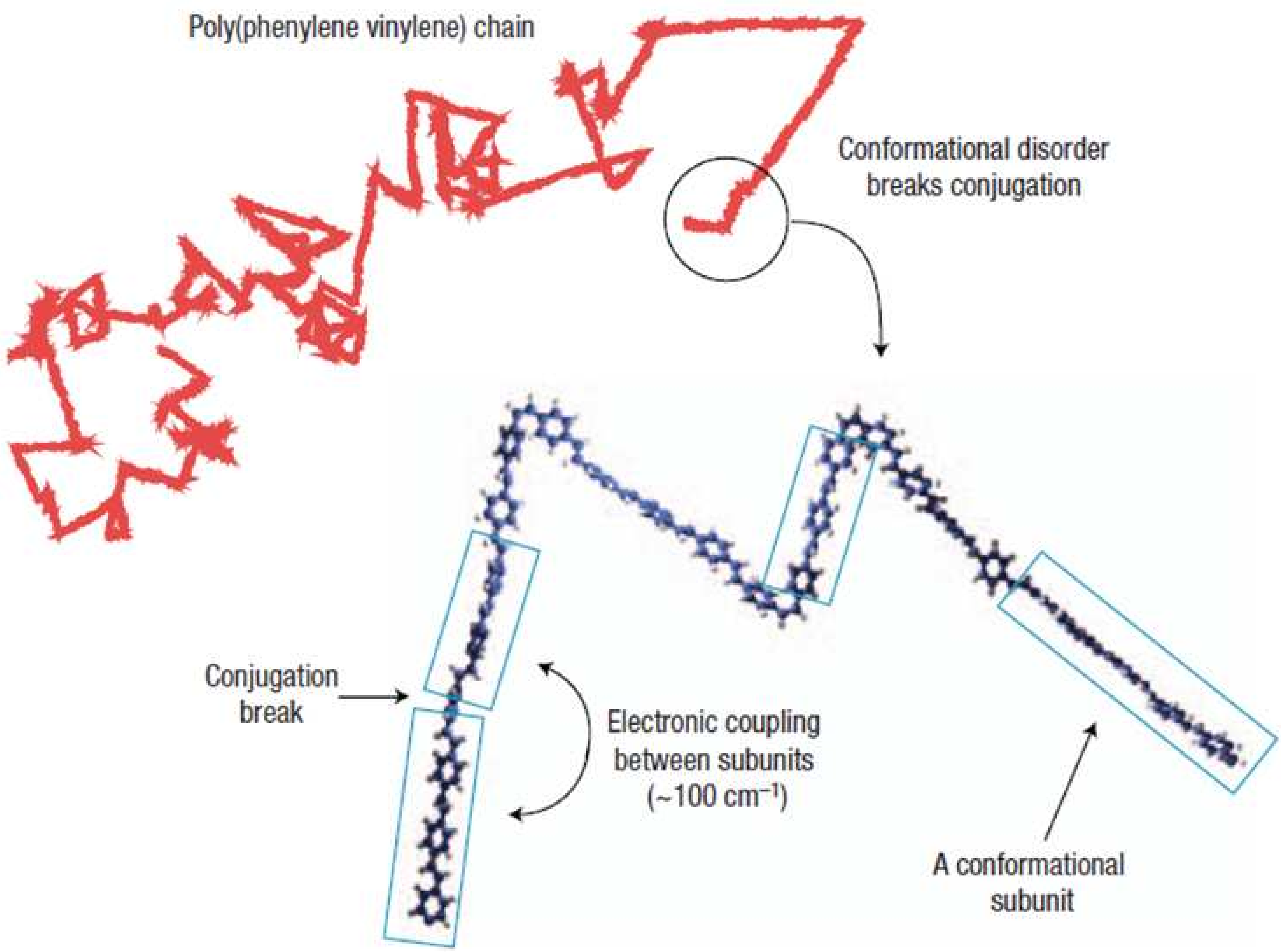


FIGURE 1. Electronic state diagram describing the photo-induced charge-carrier formation mechanism in an organic solar cell: S0 denotes the singlet ground state of the donor or the acceptor, and S1 denotes the first singlet excited state (excitonic state). At the D/A interface, intermolecular charge transfer leads to charge-transfer (CT) states, where the hole is on donor molecule(s) and the electron is on acceptor molecule(s). CT1 is the lowest energy charge-transfer state. CT* represents excited ("hot") levels28-30 of the CT/CS manifolds. The final state is a charge-separated state (CS), where the hole in the donor layer and the electron in the acceptor layer are free from one another. The *ki terms indicate various competing* relaxation and electron-transfer rates. Note that in the simple molecular orbital picture, which is often used in the literature and is based on HOMO-LUMO diagrams, the S0-S1 transition, S1-CT1 transition, and *Efinal would correspond to the HOMO (D)-LUMO (D),* LUMO (D)-LUMO (A), and HOMO (D)-LUMO (A) energy differences, respectively.

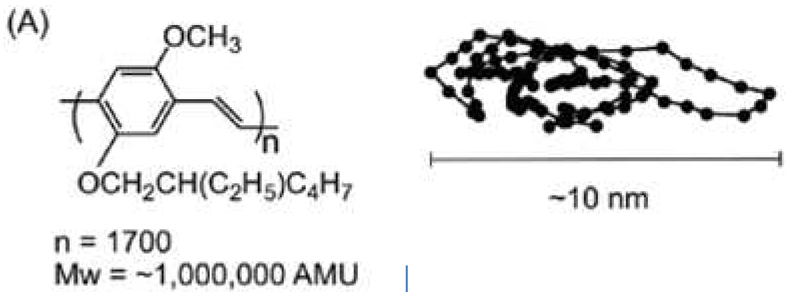
Bredas et al., Acc. Chem. Res. **2009**, *42*, 1691

Conjugated Polymers: Definitely NOT Molecular Wires

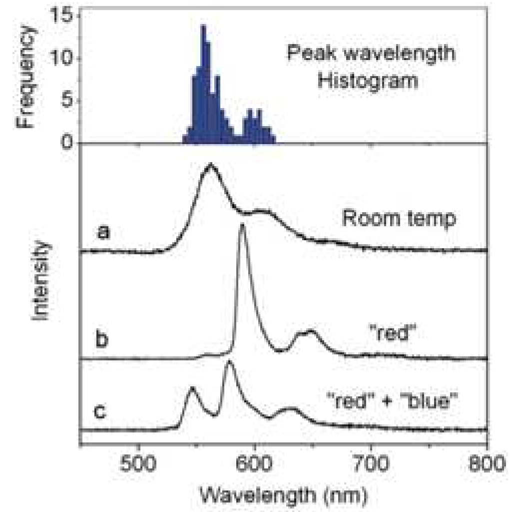


Rumbles et al., Nature Materials **2006**, *5*, 283

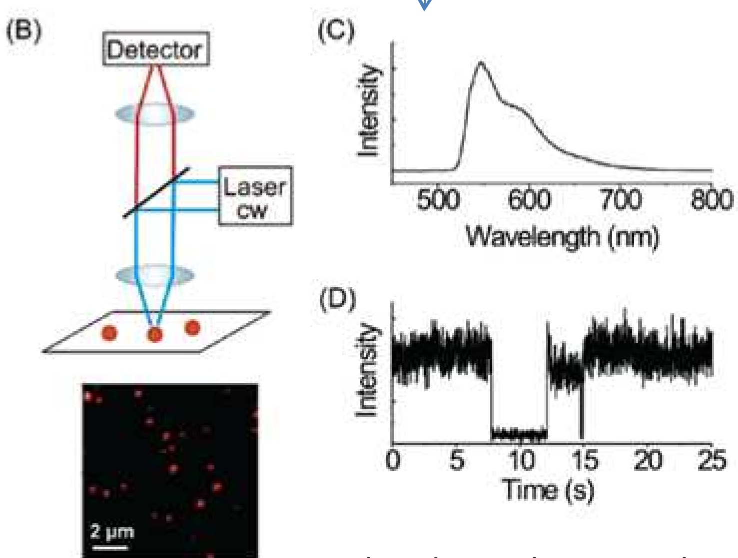
Single Molecule Spectroscopy and Conjugated Polymers: Insights into the Photophysics



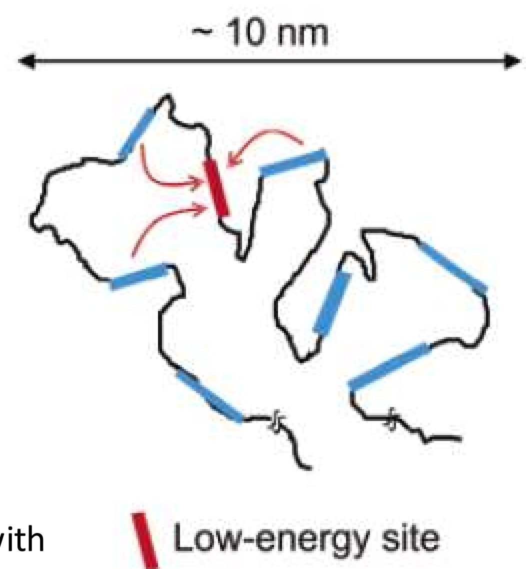
Isolated PPV chains
In transparent
polymer matrix



SMS at 20K
Resolves broad
Spectral emission
characteristics



Isolated PPV chains can be tracked with fluorescence spectroscopy. In bulk films, fluorescence is quenched.



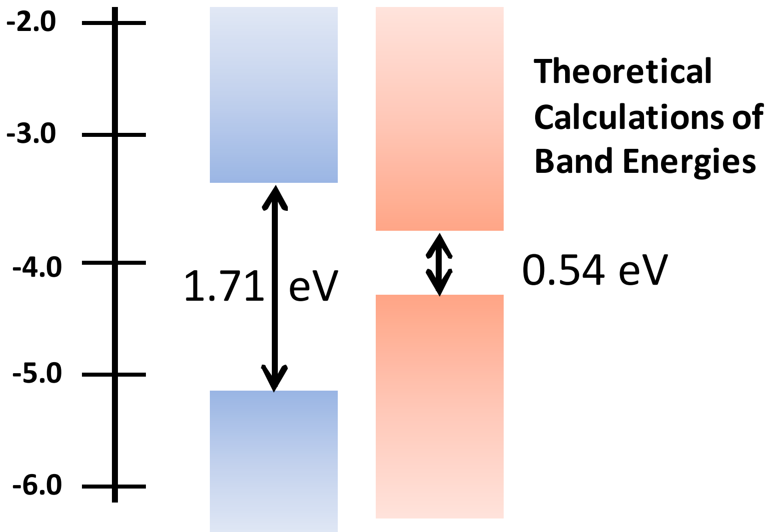
Chain conformational defects break up conjugation lengths to ~ 10 units
Upon excitation, blue subunits energy transfer to lower energy red units
Red units (only a few/one) per chain dominant emission
Some isolate blue units also emit

Barbara et al., Acc. Chem. Res. **2005**, *38*, 602

Structural Factors Affecting the Electronic and Optical Properties of Conjugated Polymers: Band gap engineering

- Peierls distortion: infinite molecular wires do not exist
- Aromaticity: Contribution and non-degenerate energies of benzoid vs. quinoid forms in conjugated polyaromatic macromolecules
  - See example of electrochemically prepared polythiophene vs. polyisothianapthene
- Conjugation length: bandgap tends to decrease with increasing conjugation length approaching a finite value for infinite conjugation length-BUT never approached due to disruption of conjugation from chain torsional strain
  - Ex. MEH-PPV, optically conjugation lengths approximately 10-15 units
- Substituent effects: electron donating groups tends to raise the HOMO; electron withdrawing groups lower the HOMO
- Intermolecular interactions & morphology of polymer solid state

Bandgap Control: The Case of Polyisothianaphtene



Bredas et al., J. Chem. Phys. **1986**, *85*, 4673

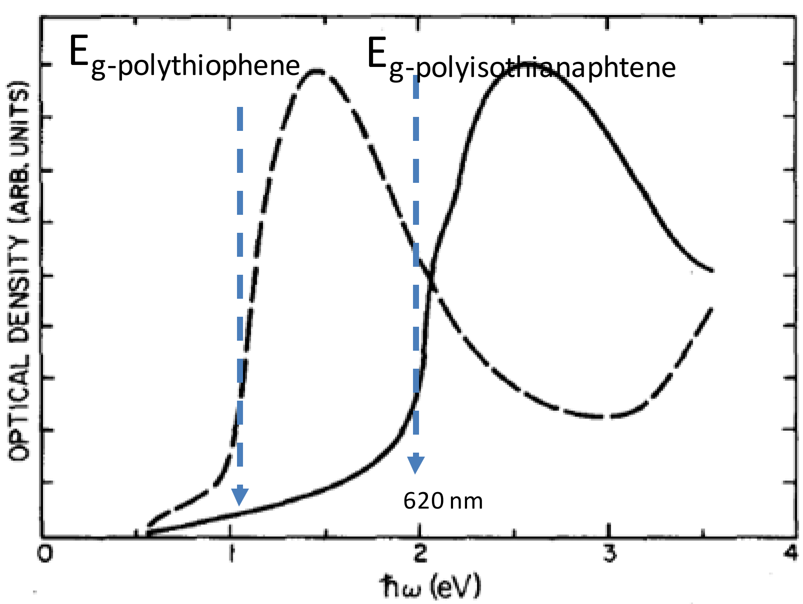
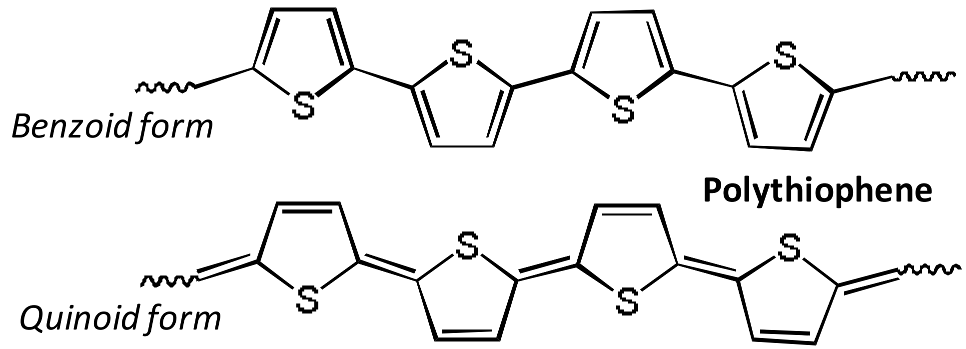
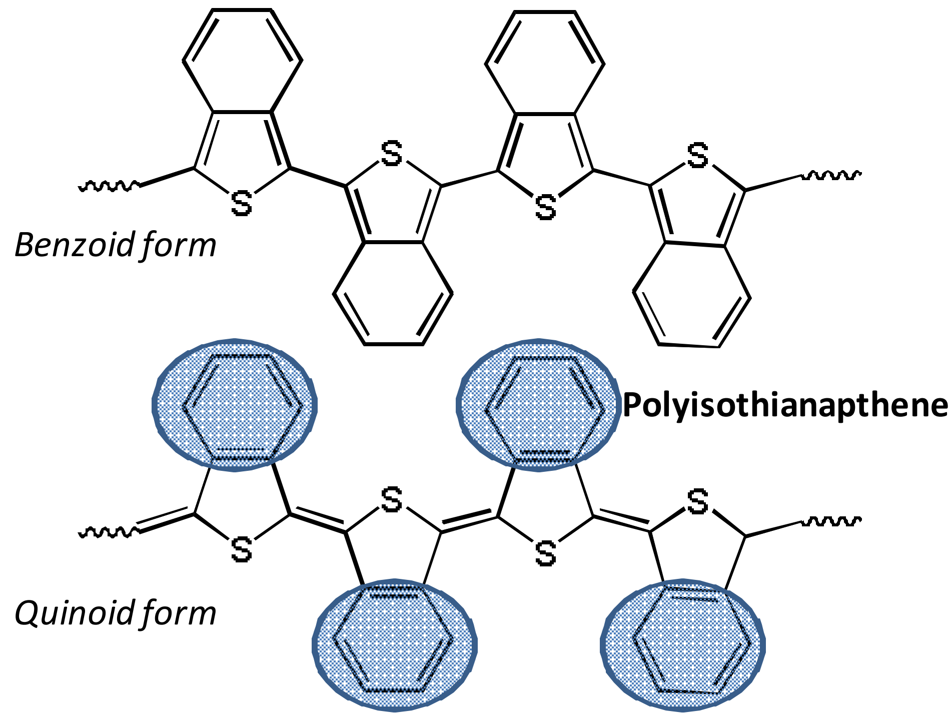


FIG. 5. Absorption coefficients of polythiophene (solid curve) and polyisothianaphthene (dashed curve). Wudl et al., J. Chem. Phys. **1985**, *82*, 5717





Aromatic stabilization of quinoid form

Substituent Effects on the Band Edges in Polythiophenes

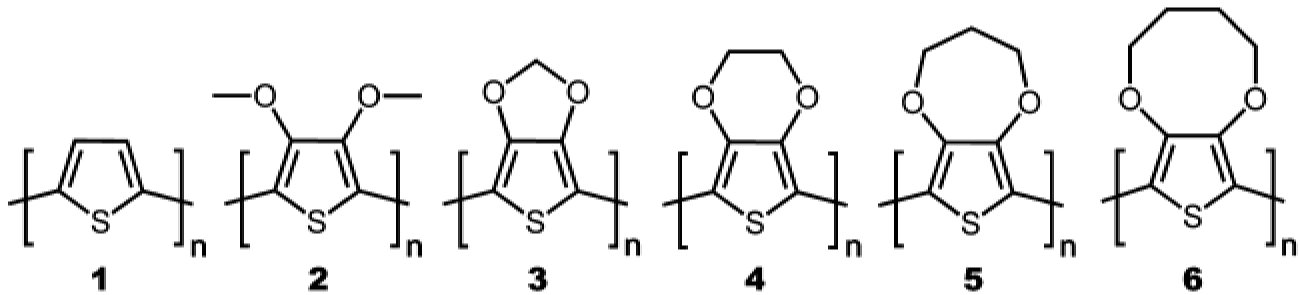
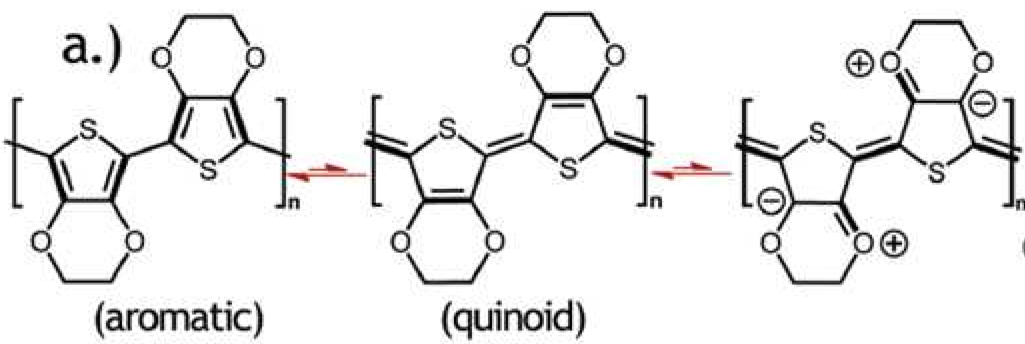
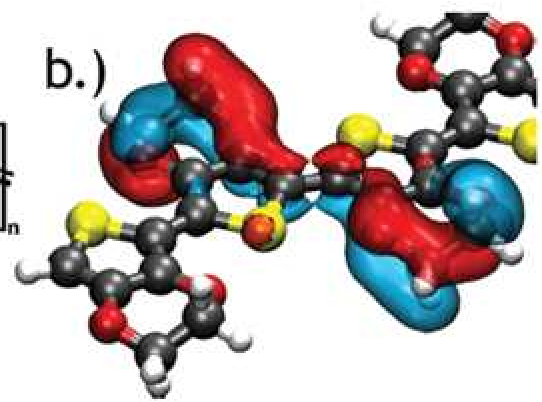


Figure 1. Poly(thiophene) and poly(alkylenedioxythiophene) polymers under study: poly(thiophene) (PTh) **1**, poly(dimethoxythiophene) (PDMTh) **2**, poly(methylenedioxythiophene) (PMeDOT) **3**, poly(ethylenedioxythiophene) (PEDOT) **4**, poly(propylenedioxythiophene) (PProDOT) **5**, and poly(butylenedioxythiophene) (PBuDOT) **6**.

species	substitution	HOMO eigenvalue (eV)
1		−5.28
2	dimethoxy	−4.73
3	methylenedioxy	−5.04
4	ethylenedioxy	−4.44
5	propylenedioxy	−4.64
6	butylenedioxy	−4.50

Polythiophene Eg ~ 2.1 eV
PEDOT Eg ~ 1.5 eV





Abruna et al., J. Phys. Chem. C. **2010**, *ASAP*

Donor-Acceptor Comonomer Units in Conjugated Polymers

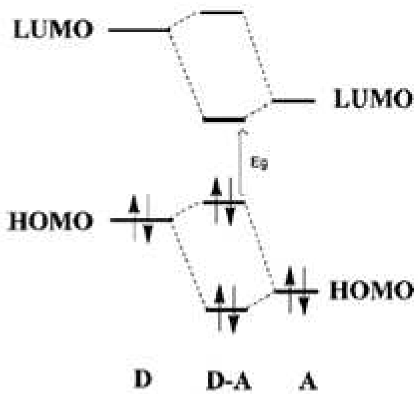


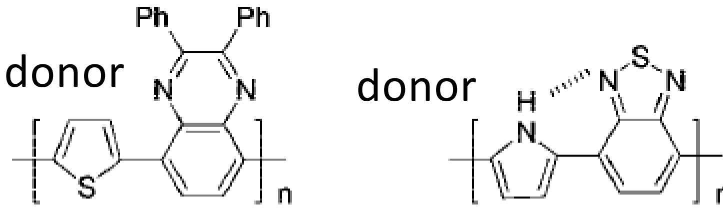
Figure 6. Orbital interactions of donor and acceptor units leading to a smaller band gap in a D−A conjugated polymer.

Electron acceptor

Electron donor

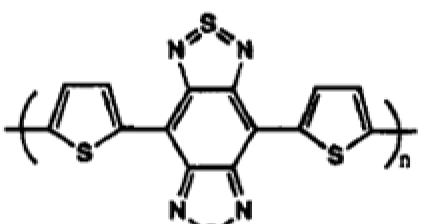
donor

acceptor

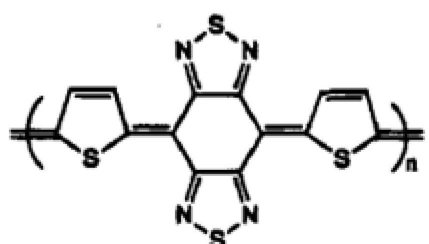


P7	P8
Eg = 1.7 eV	Eg = 1.1 eV

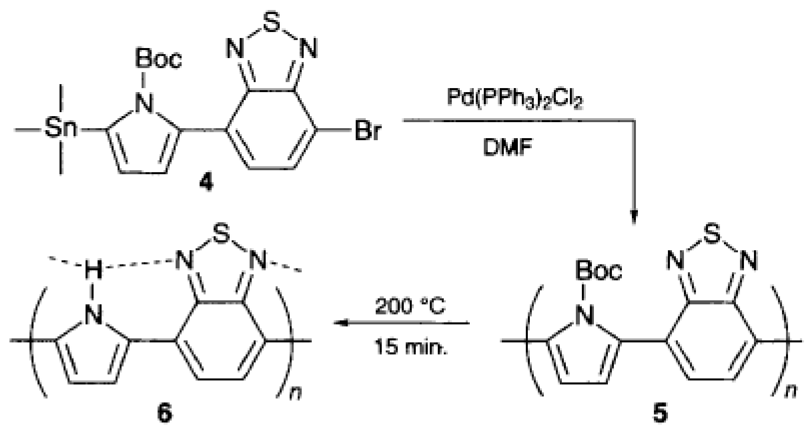
Yamashita et al., J. Am. Chem. Soc. ***1996, 118, 10389.***



1



1'



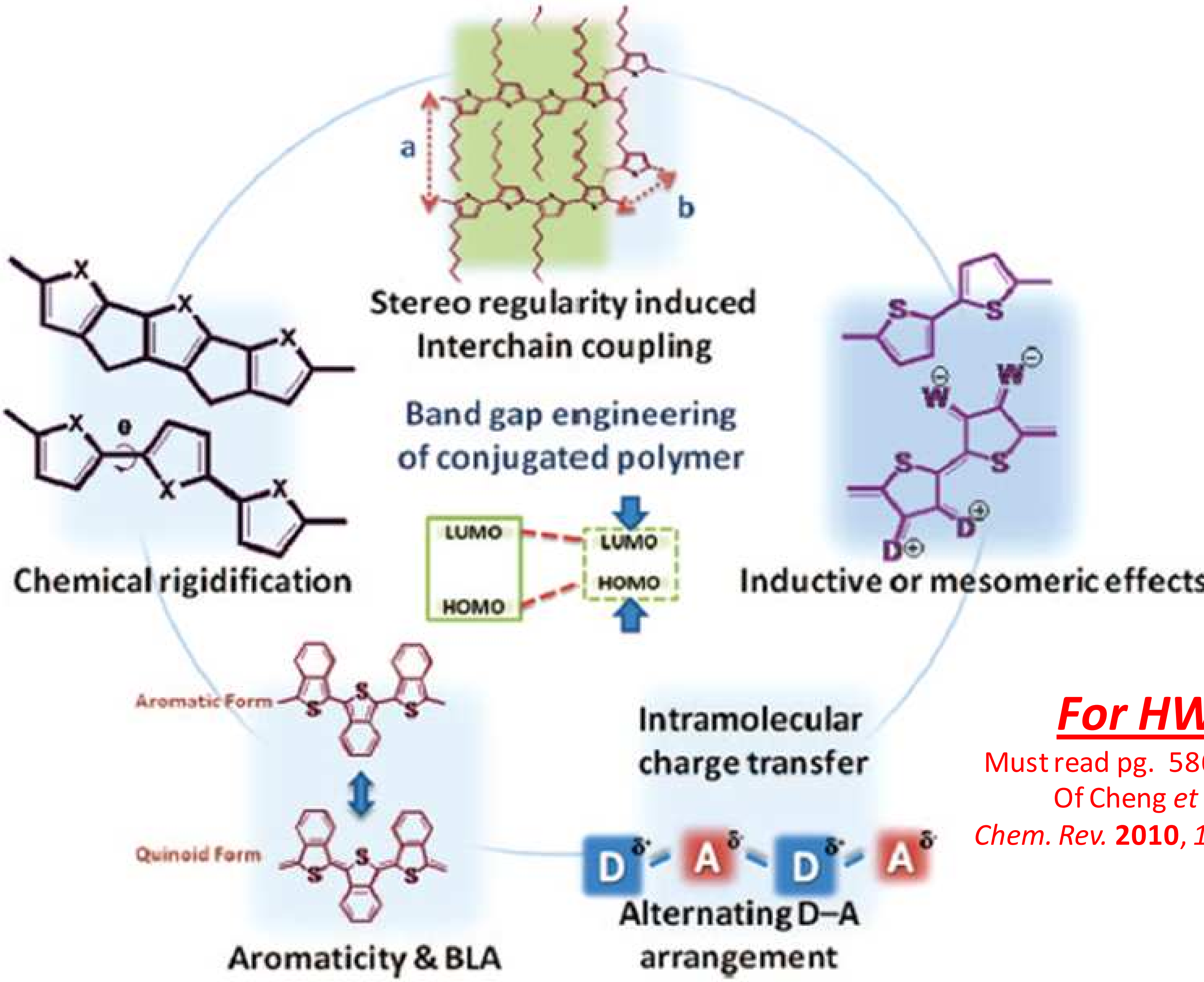
Eg ~ 1.1 eV

Polythiophene Eg ~ 2.1 eV

Yamashita et al., J. Am. Chem. Soc. **1995**, *117*, 6791

Meijer et al., Chem. Commun. **1996**, *2163*

Summary of Bandgap Engineering of Organic Conjugated Polymers



For HW!

Must read pg. 5868-5874
Of Cheng *et al.*
Chem. Rev. **2010**, *109, 5868*

Why Are Most Conjugated Polymers Electron Donors/p-type?

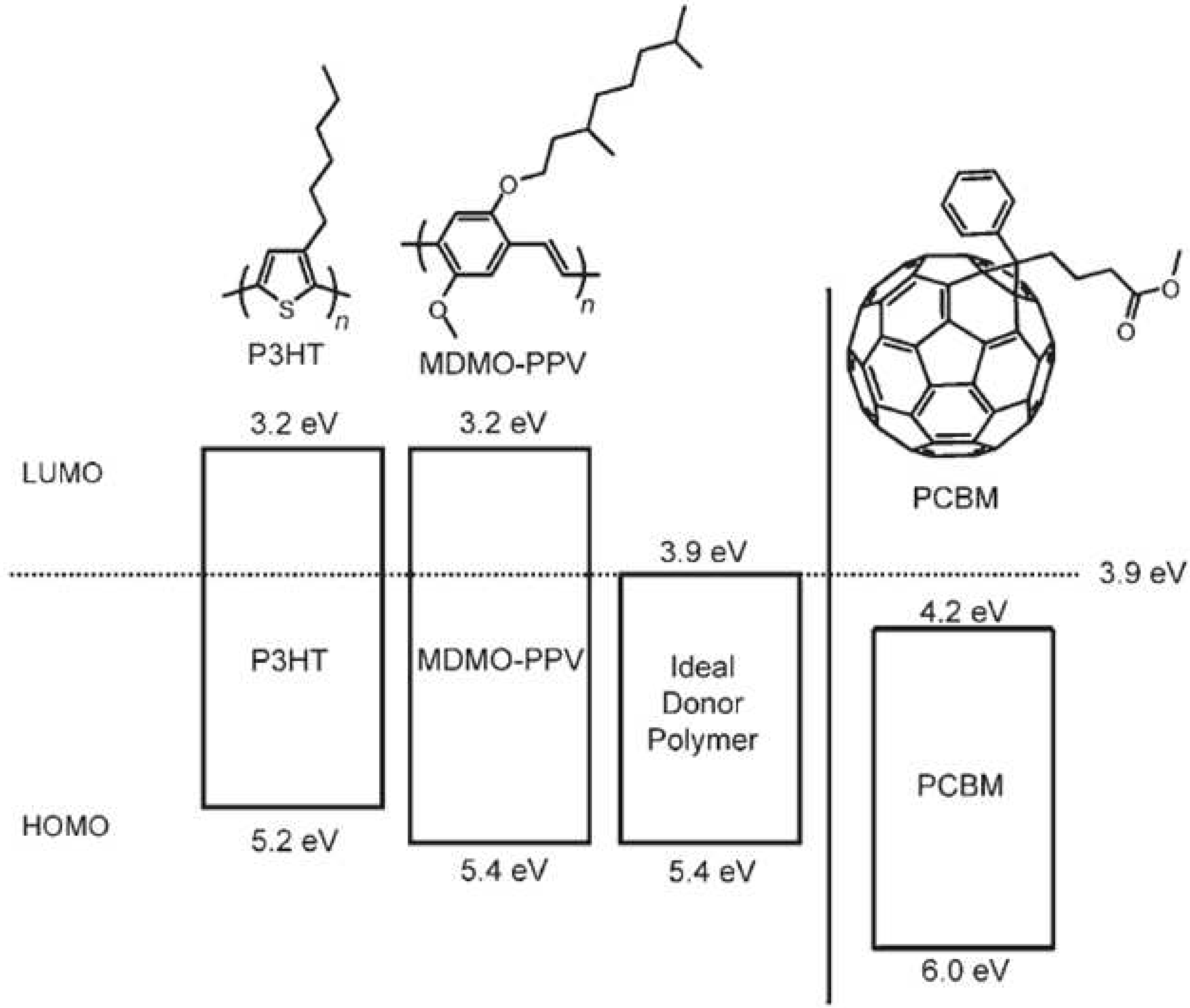
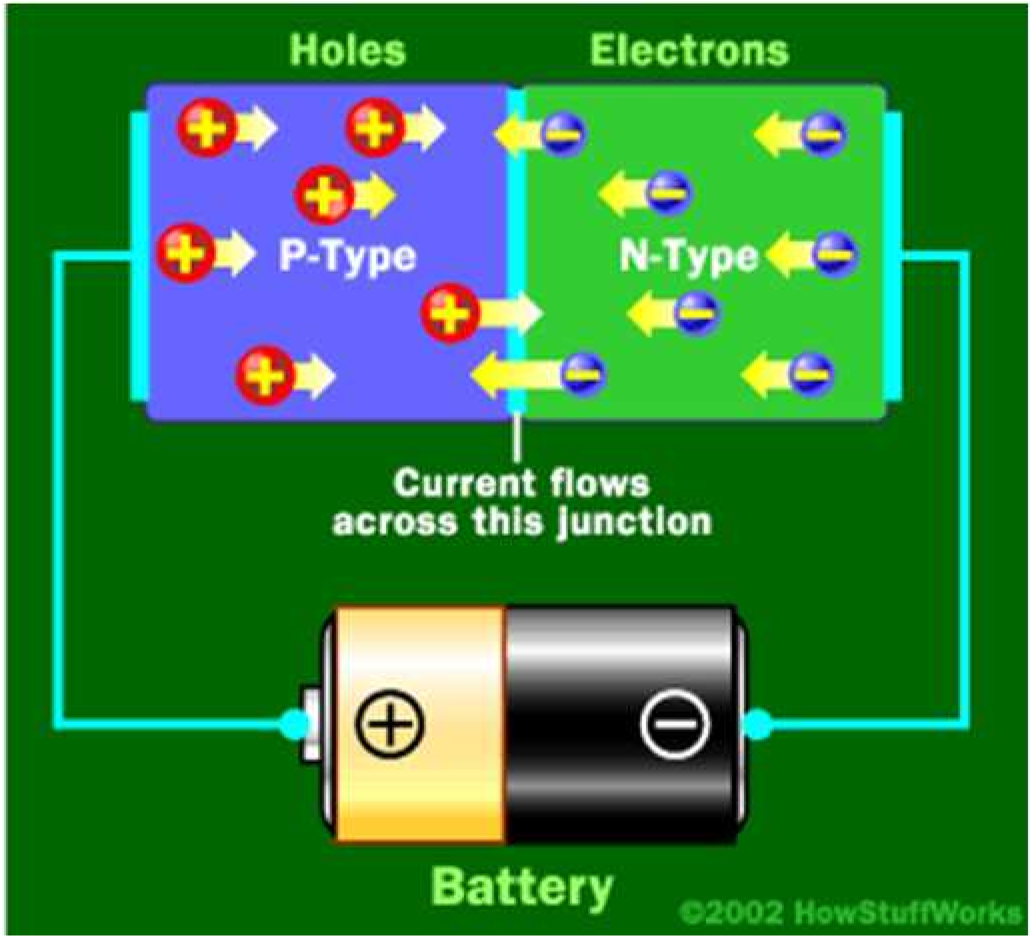


Figure 2. Band structure diagram illustrating the HOMO and LUMO energies of MDMO-PPV, P3HT, and an "ideal" donor relative to the band structure of PCBM. Energy values are reported as absolute values relative to a vacuum.

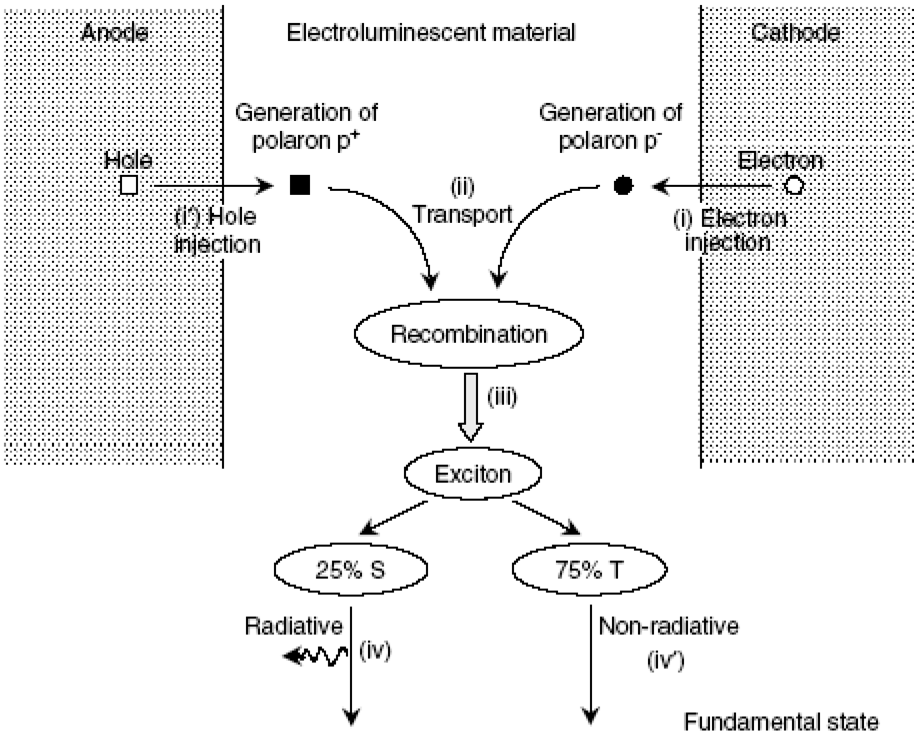
Fréchet et al., *Angew. Chem. Int. Ed.* **2008**, *47*, 58

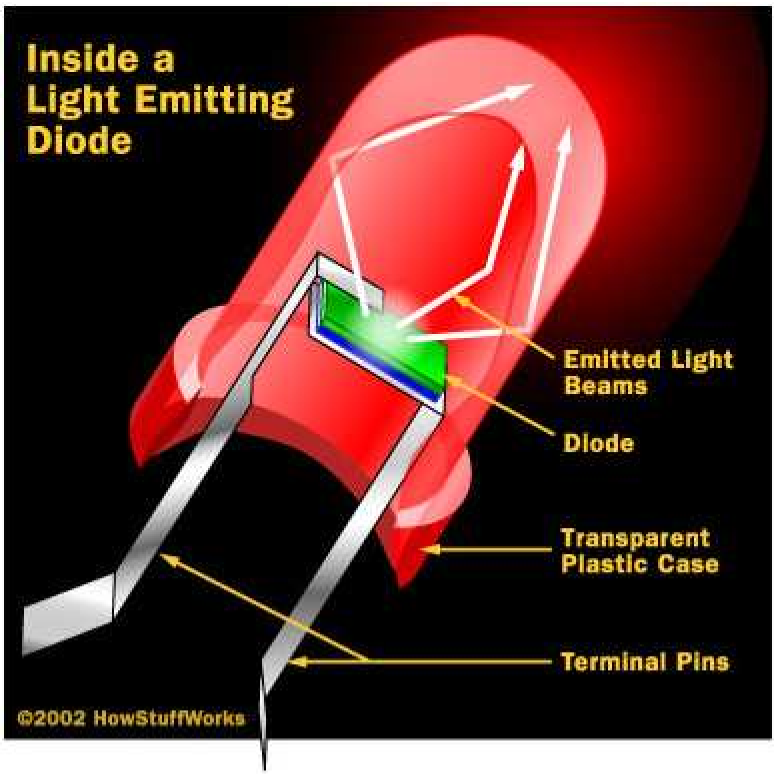
Basic Operation of a Diode



www.howthingswork.com

Organic Light Emitting Diode: Basic Operation





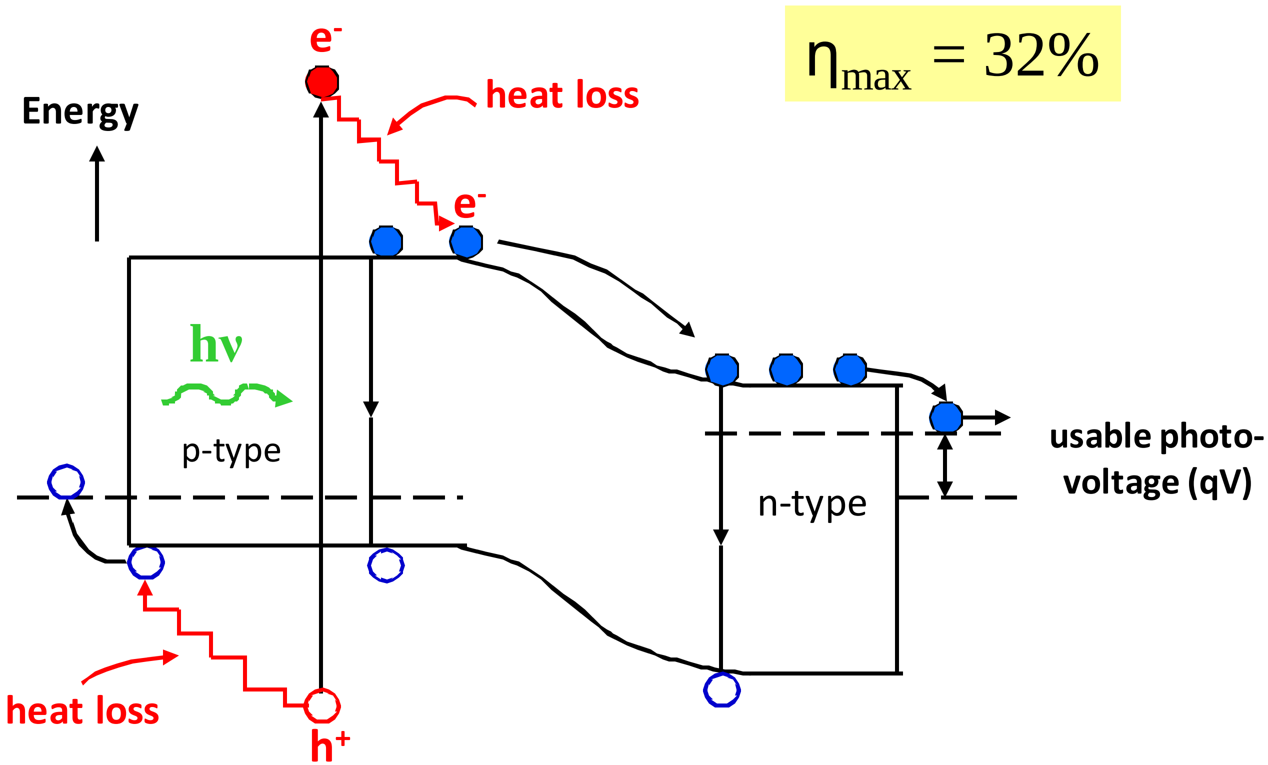
Large emitting areas, high brightness
No bulbs to burn out!
Higher Efficiency relative to incandenscent lamps

www.howthingswork.com

Moliton et al., *Polym. Int.* **2004**, *53*, 1397

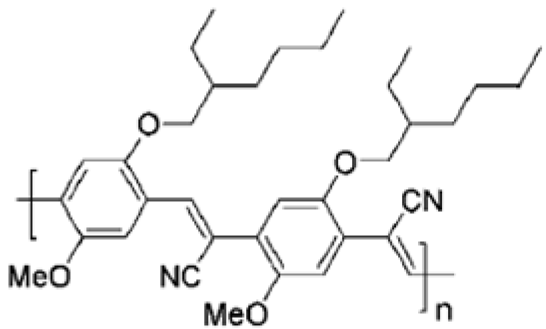
OLED’s and Optical Displays, Plastic Electronics, E-Newspapers

Conventional p-n junction photovoltaic (solar) cell

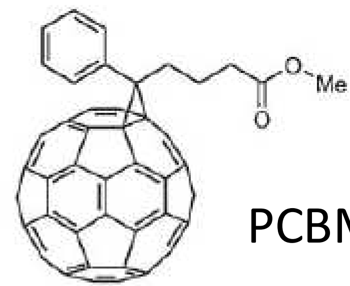


Jenny Nelson, *The Physics of Solar Cells*, 2003.

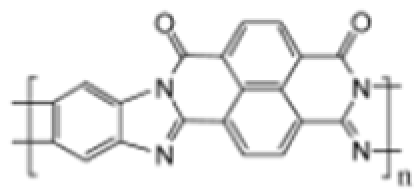
Examples of Conjugated Polymers as Electron Acceptors/n-type



Holmes et al., *Synth. Metals* **1995**, *71*, 2117

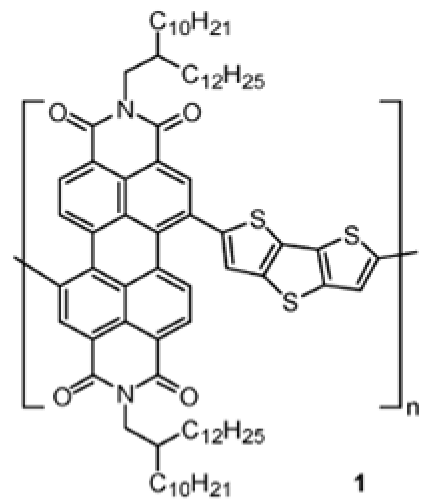


PCBM

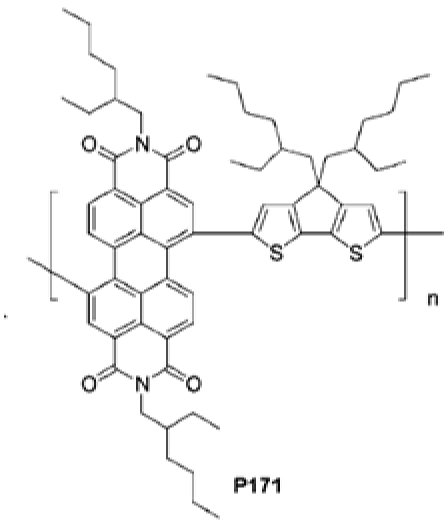


BBL

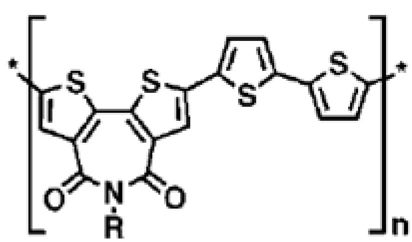
Jenekhe et al., *JACS* **2003** ,125, 13656



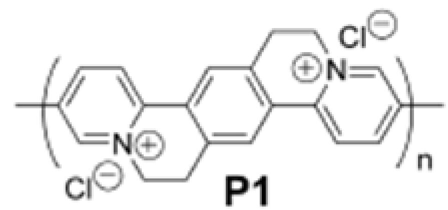
Marder et al., *JACS* **2007**,129, 7246



Yang, Y. *Chem. Commun.* ***2008,*** 6034.

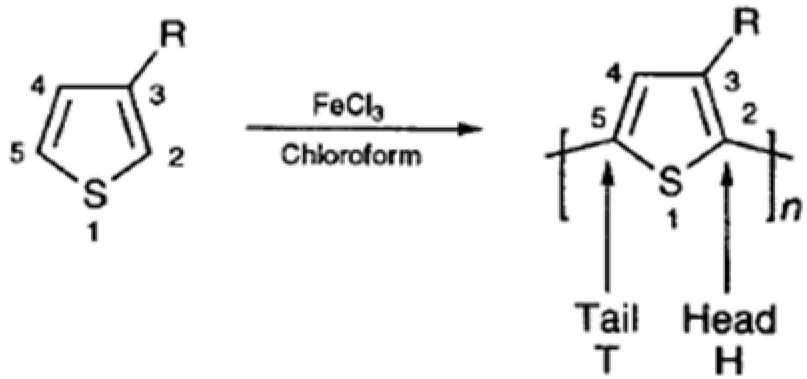


Marder et al., *JACS* **2008**,130, 9679



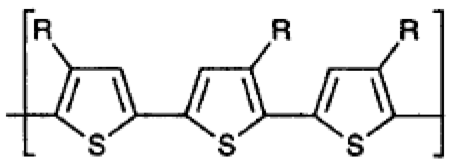
Swager et al., *JACS* **2009**,131, 17724

Regioisomers in the preparation of poly(3-alkylthiophenes)

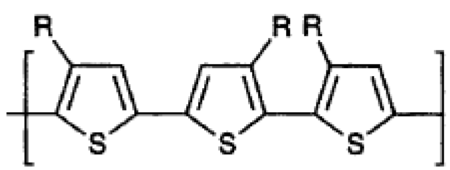


$R = C_6H_{13}$

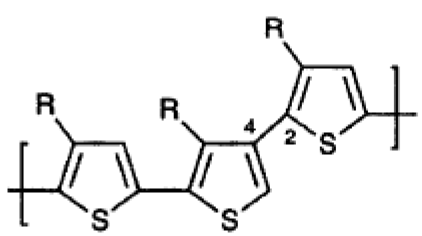
Poly 3-hexylthiophene
1



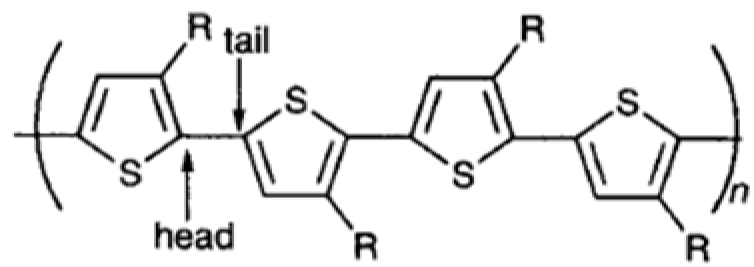
T-T-H-T



T-T-H-H



2-4 linkage

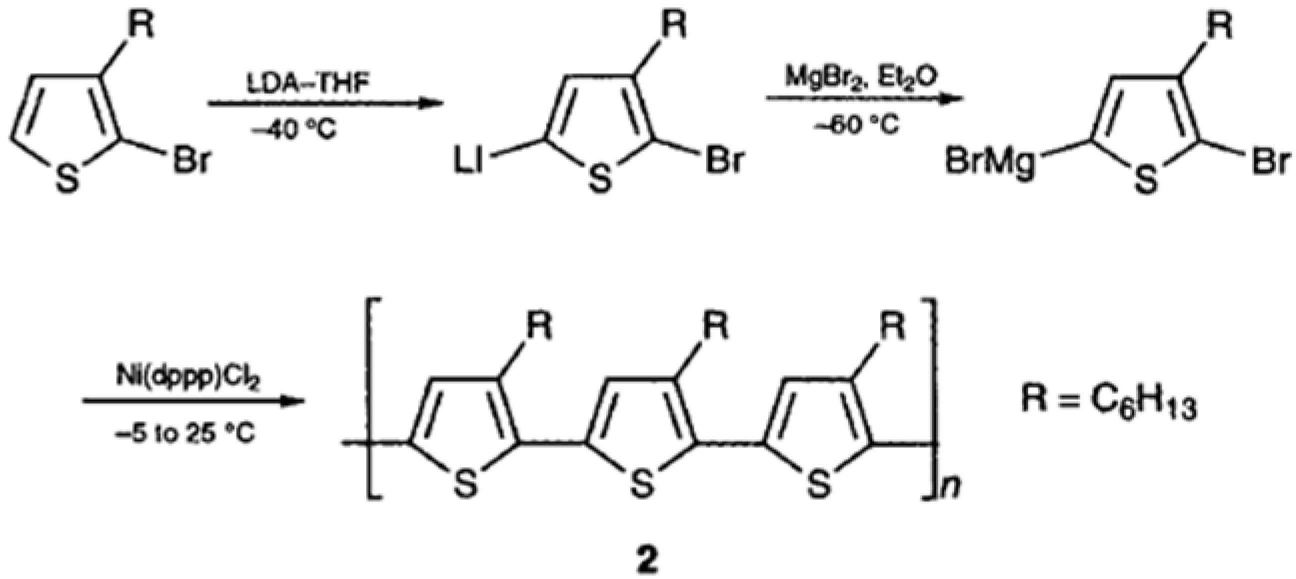


HT-HT-HT

Regioregular poly(3-alkylthiophenes)

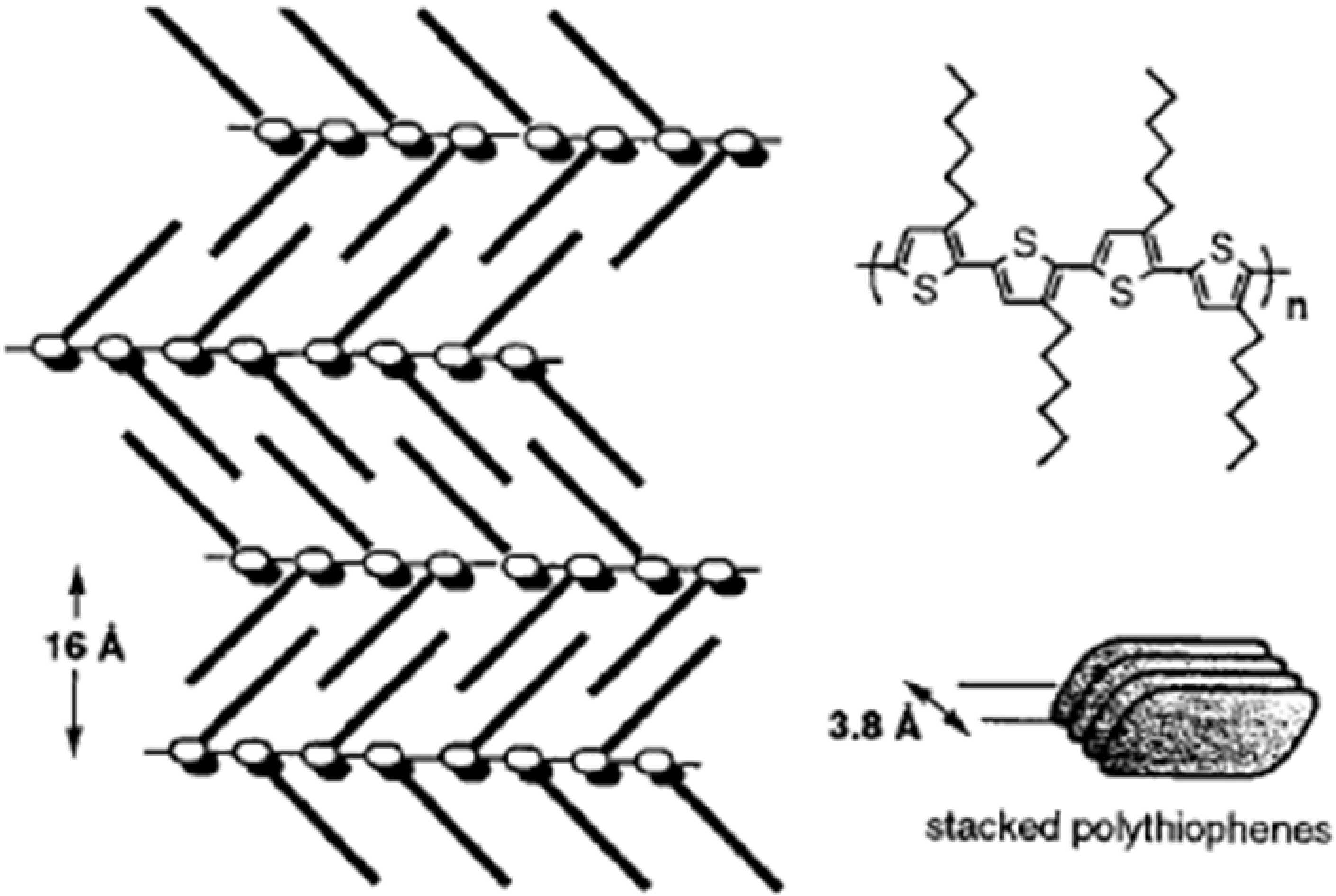
McCullough et al., J. Mater. Chem. **1996**, *6*, 1763

The McCullough Method for the Preparation of poly(3-alkylthiophenes)



McCullough, J. Am. Chem. Soc. **1993**, *115*, 11608
McCullough, Adv. Mater. **1998**, *10*, 93

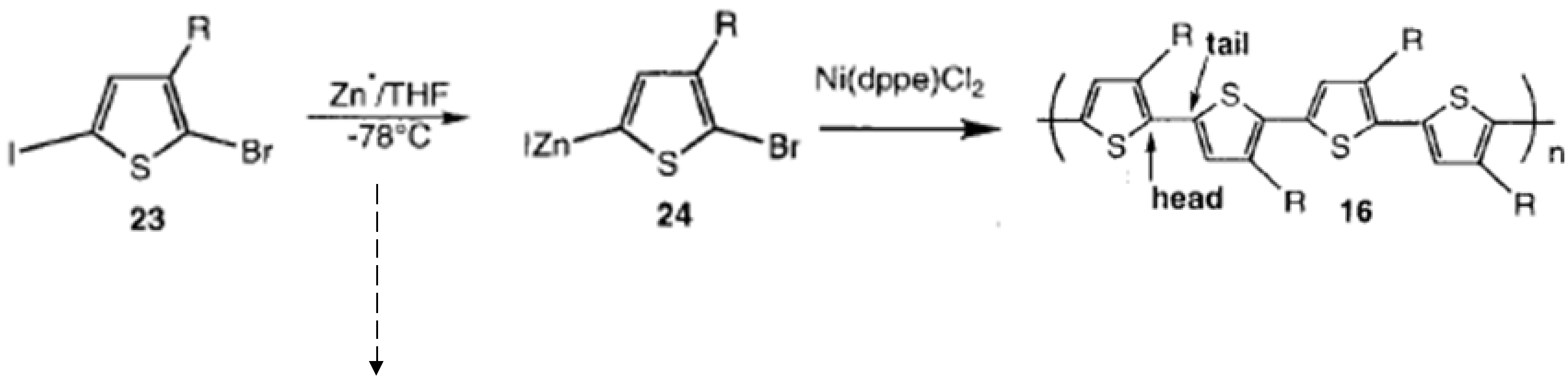
Regioregular Polythiophene



Higher crystallinity = ordered thin films = enhanced charge transport

McCullough, Adv. Mater. **1998**, *10*, 93

Regioregular Polythiophene from the Reike Method



Colloidal zinc

Rieke, J. Am. Chem. Soc. **1995**, *117*, 233

Regioregularity Effects on Thin films of Poly(3-Hexylthiophene)

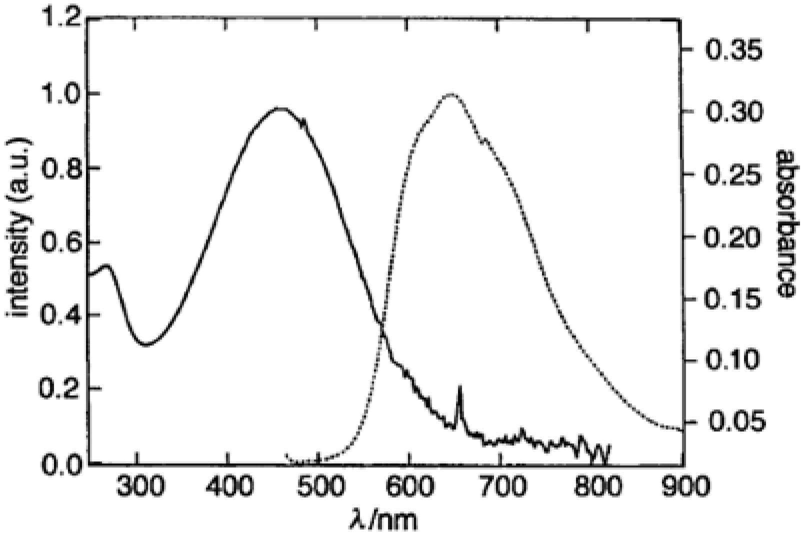
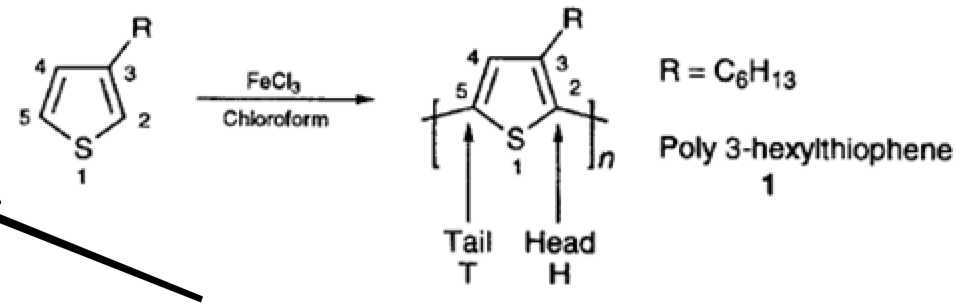
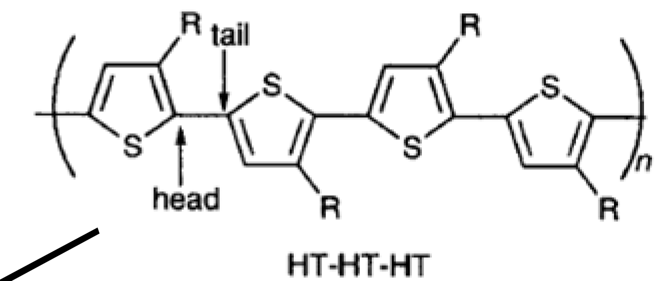


Fig. 3 UV–VIS (left, solid line) and photoluminescence (right, broken line) spectra of thin film of polymer **1**. Excitation wavelength 460 nm, 2.5 nm bandwidth.



Regiorandom poly(3-alkylthiophenes)



Regioregular poly(3-alkylthiophenes)

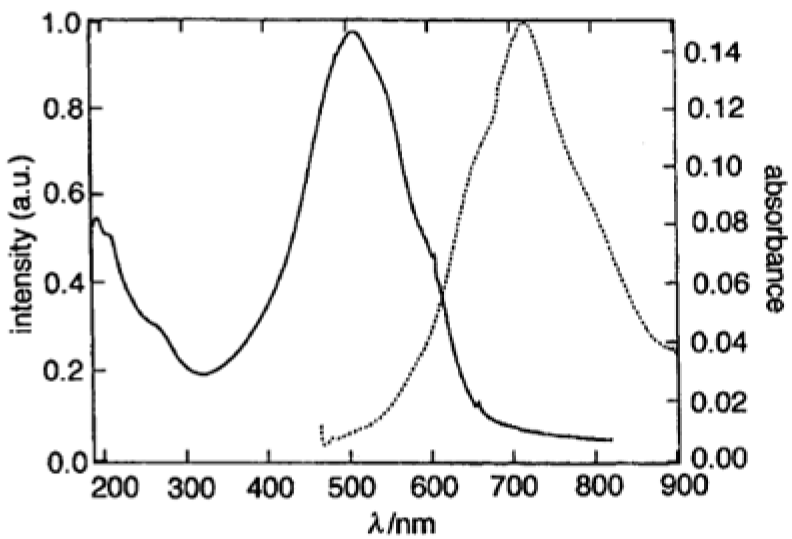


Fig. 4 UV–VIS (left, solid line) and photoluminescence (right, broken line) spectra of thin film of polymer **2**. Excitation wavelength 450 nm, 2.5 nm bandwidth.

Table 1 Photophysical properties of polymers **1** and **2**

polymer	λ_{max}(abs)/ cm^{-1} (nm)	λ_{max}(PL)/ cm^{-1} (nm)	stokes shift/ cm^{-1}
1	21,930 (456)	15,380 (650)	6550
2	19,610 (510)	13,950 (717)	5660

Electronic & Optical Properties of Conjugated Polythiophenes

π-bond overlap along polymer create a number of nearly equivalent Energy levels, forming electronic bands as seen in inorganic semiconductors

Electrons from valence band can be transported into conduction band by excitation by external energy (hν, heat, fields), defined as π-π* transition

Neutral polythiophenes-organic semiconductor, electronic transition Absorbance ~ 300-500 nm & Emission (dependent on structure/band gap)

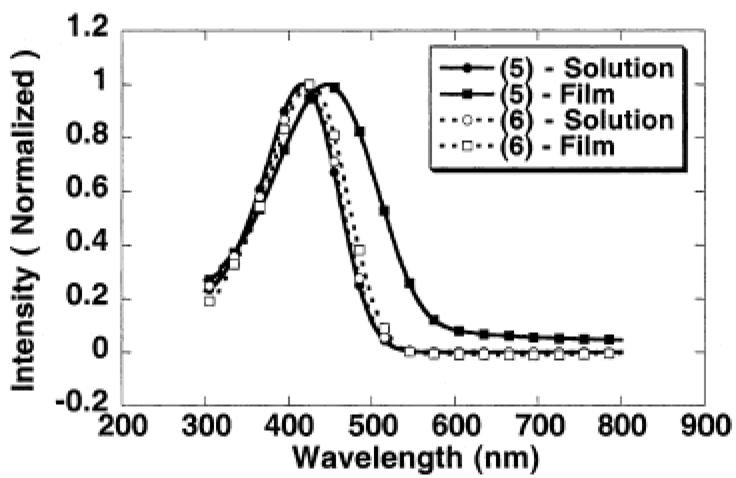
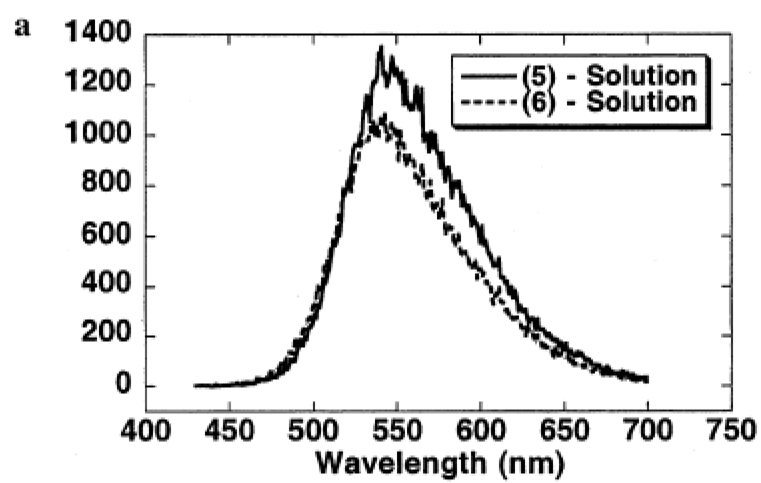


Figure 5. UV/vis analysis (300–700 nm) of **5** and **6** in solution and as cast films.

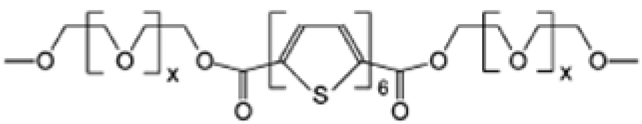


Costanzo et al., *Macromolecules* **2002**, *35*, 6804

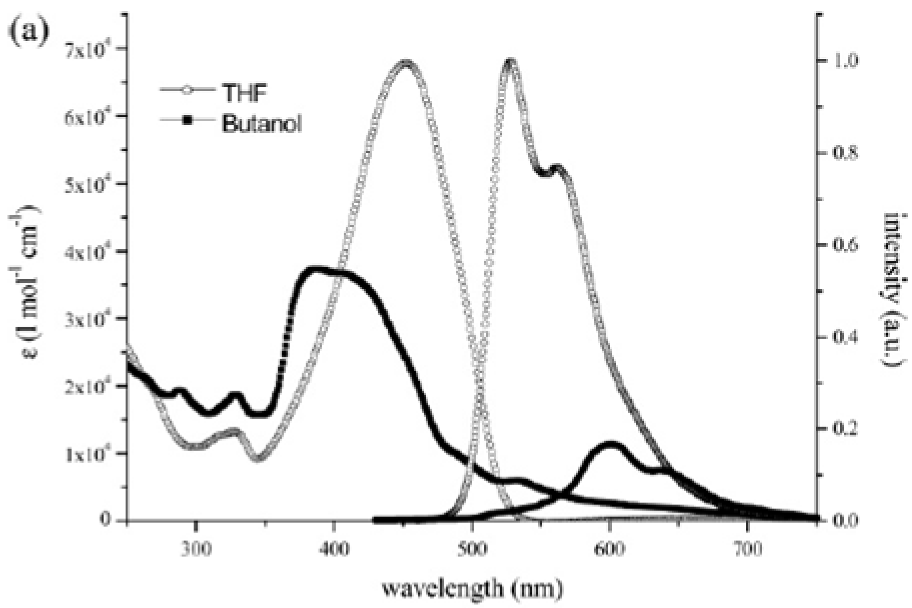
Effect of Optical and Assembly Morphology &Conditions of PT's

Both polythiophenes and oligothiophenes have been used to as materials For device applications

Oligothiophenes prepared as pure substances: structure-property correlations

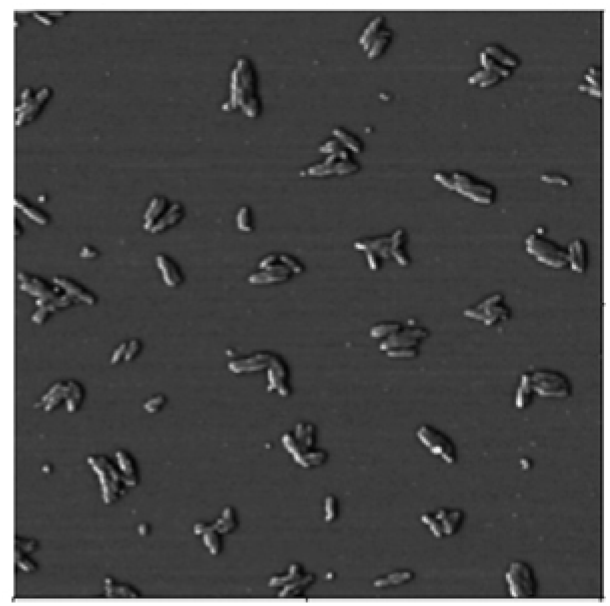


2a: x=4 ; **2b**: x=8 ; **2c**: x=17



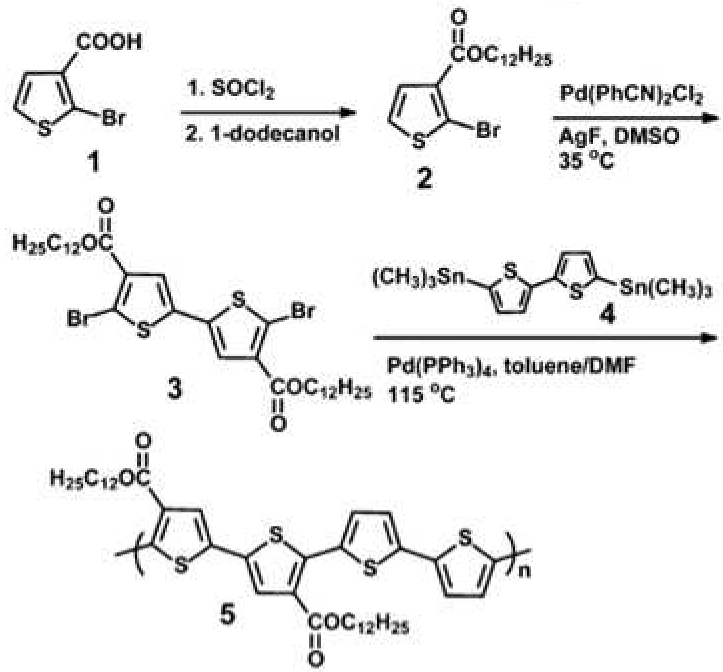
Leclere et al., *Chem. Mater.* **2004,** *16*, 4452

THF-molecular dissolution
n-BuOH-supramolecular aggregates

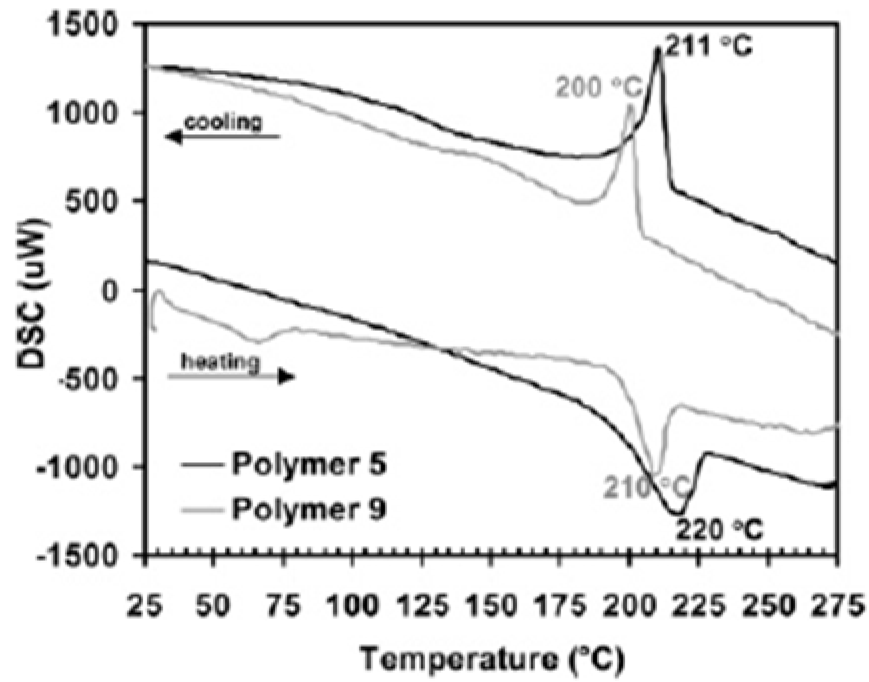


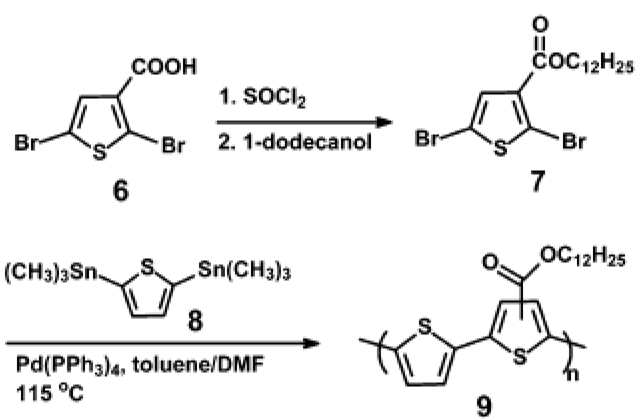
AFM 1 μm x 1 μm of 2a from n-BuOH

Solid State Morphology of Polythiophene Thin Films



Regioregular PT:
Mn = 6,000; M_w/M_n = 1.2





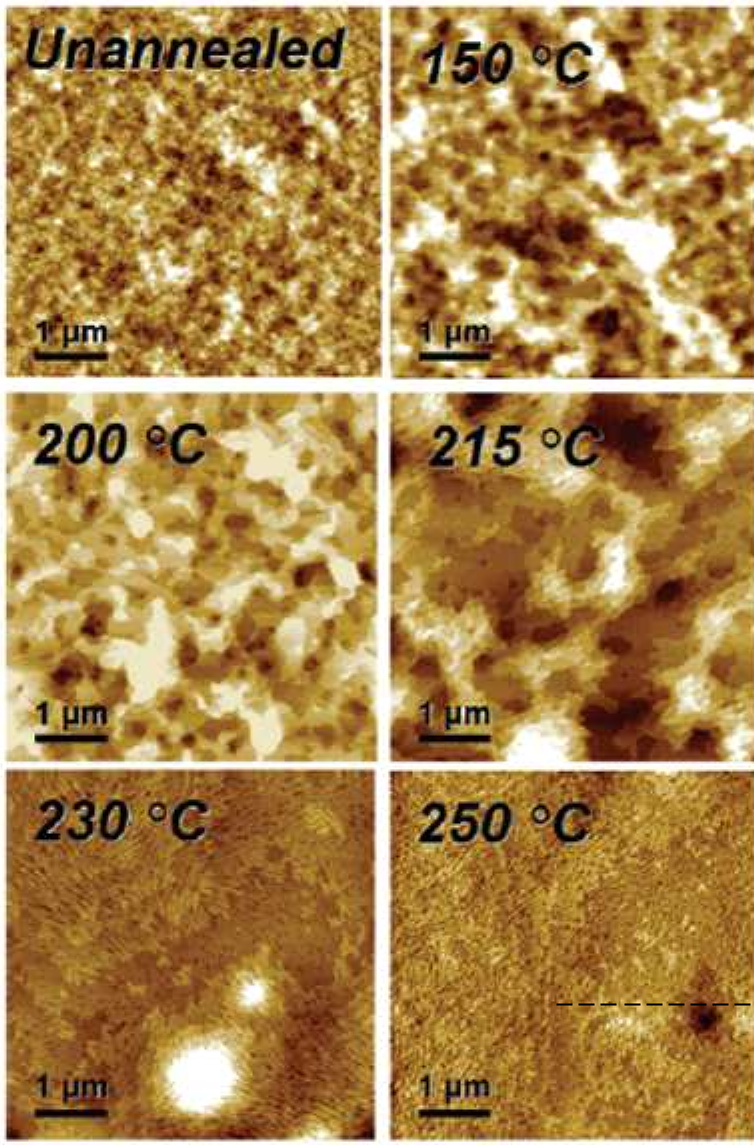
Regiorandom PT:
Mn = 6,000; M_w/M_n = 1.2

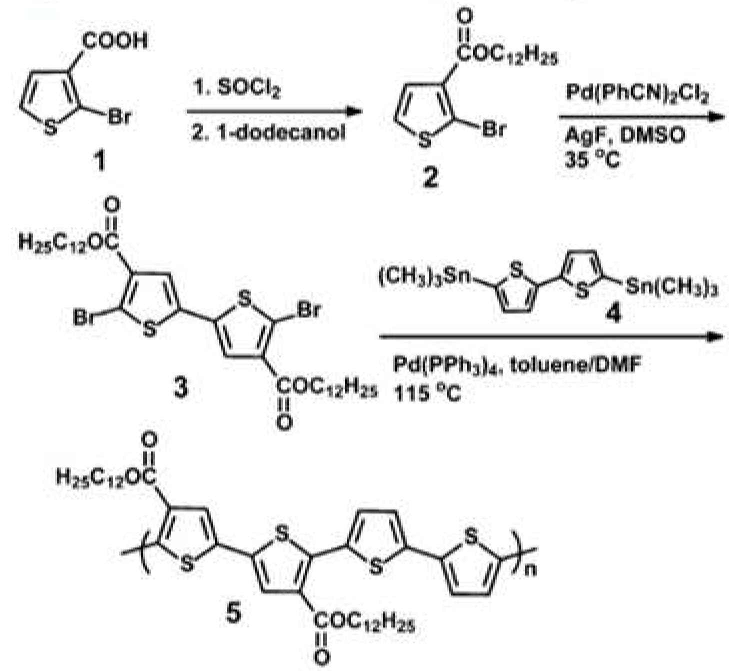
Regioregular PT exhibits Higher T_m & T_c relative to Regiorandom PT of Comparable MW

Fréchet et al, *Chem. Mater.* **2005**, *17*, 4892

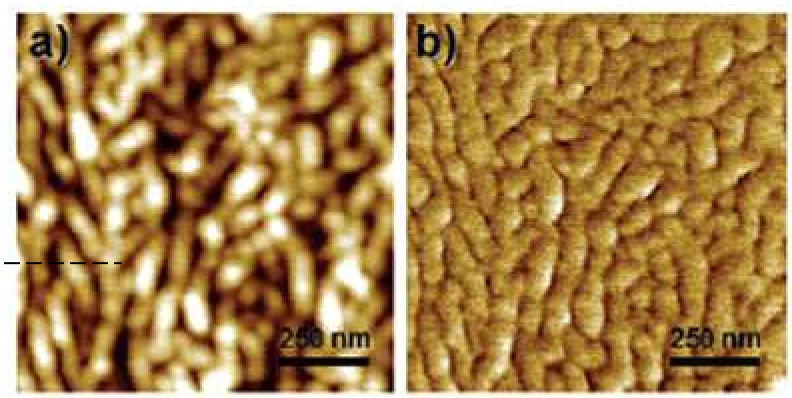
AFM Solid State Morphology of Polythiophene Thin Films

Six-fold Increase In ave. Hole Mobility With Ordered morphology





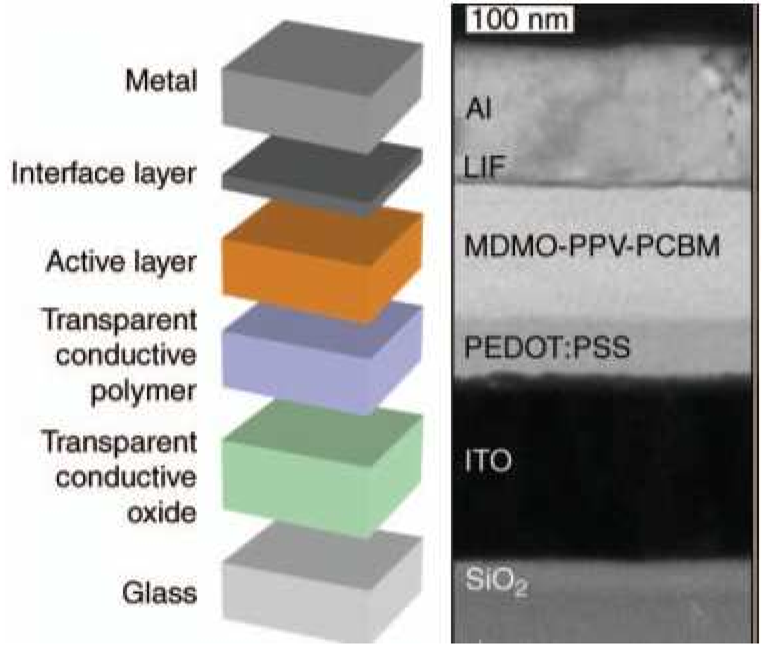
Regioregular PT: Mn = 6,000; M_w/M_n = 1.2



Annealing of PT: formation of ordered lamellar morphology-crystalline

Fréchet et al, *Chem. Mater.* **2005**, *17*, 4892

Modification of ITO Electrodes: An Old Game Revisited



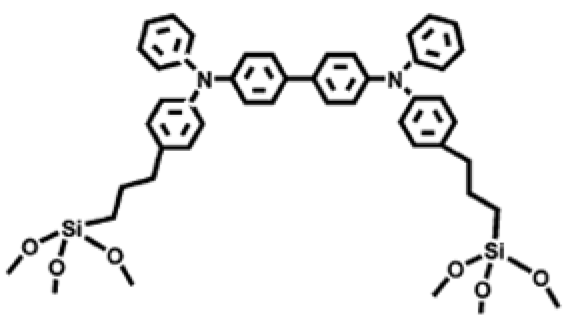
Sariciftci *et al. MRS Bull.* **2005**, *30*, 33

ITO transparent anode for photovoltaic devices
Hole transport layer of PEDOT-PSS

Direct modification of ITO with hole transporting thin films: improved PV devices?

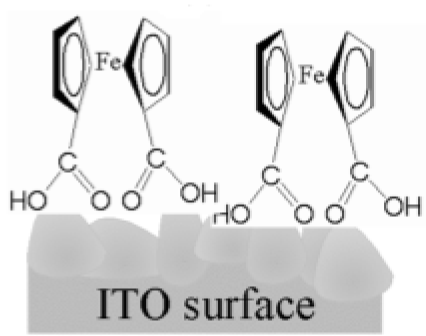
Routes to create conjugated polymer & semiconductor quantum dot thin films on ITO electrodes

Covalent Attachment



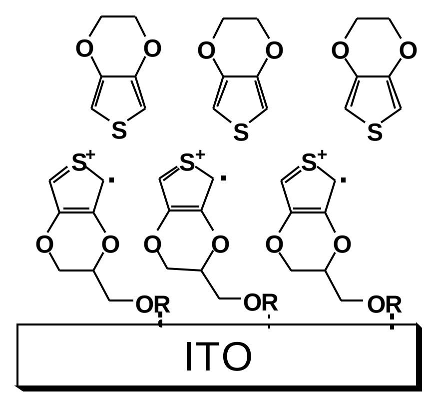
Marks *et al., J. Am. Chem. Soc.* **2005**, *127*, 10227

Ionic Attachment



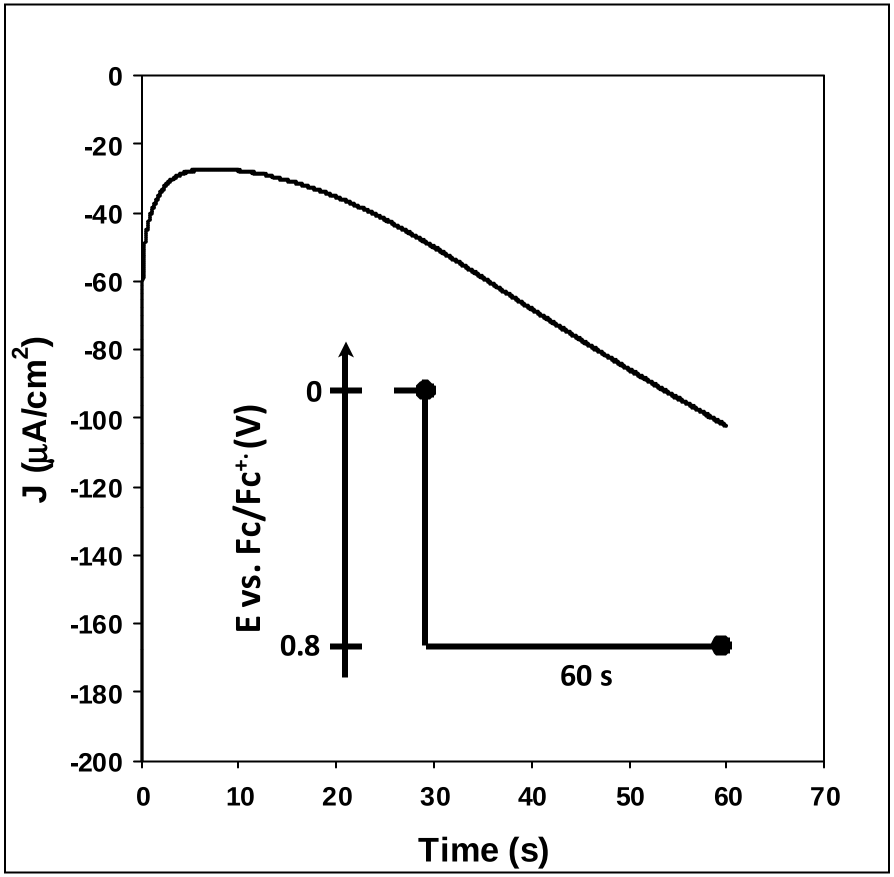
Armstrong *et al., Thin Solid Films* **2003**, *445*, 332

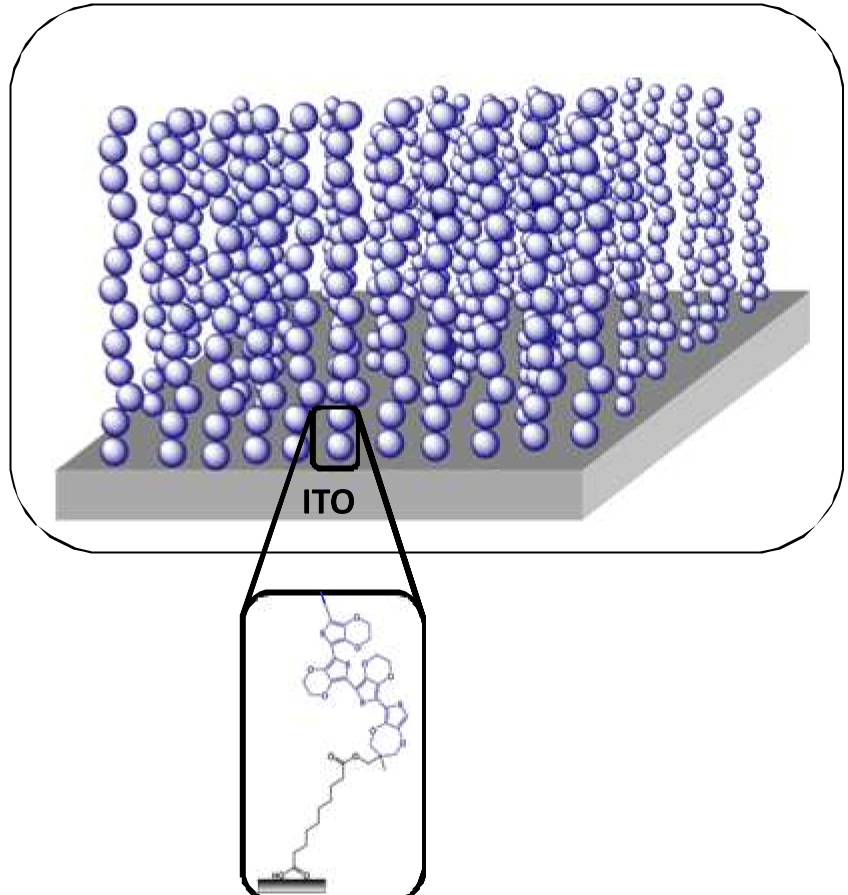
Electropolymerization

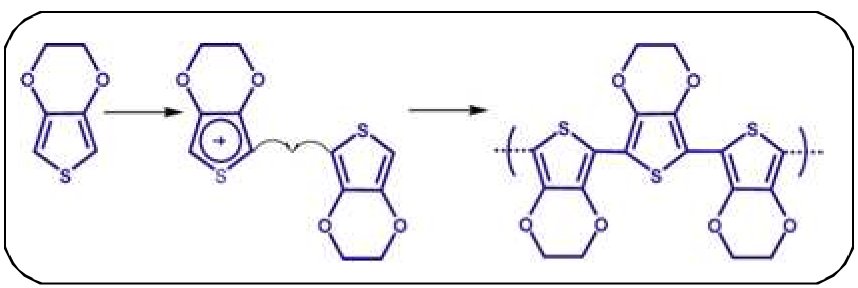


Armstrong *et al., Langmuir* **2007**, *23*, 1530

“Wiring” PEDOT to ITO via Electropolymerization





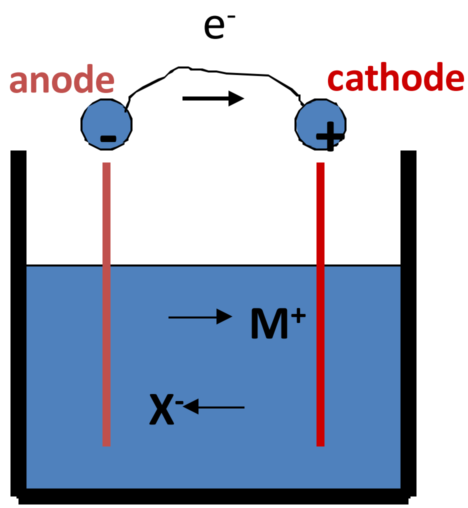


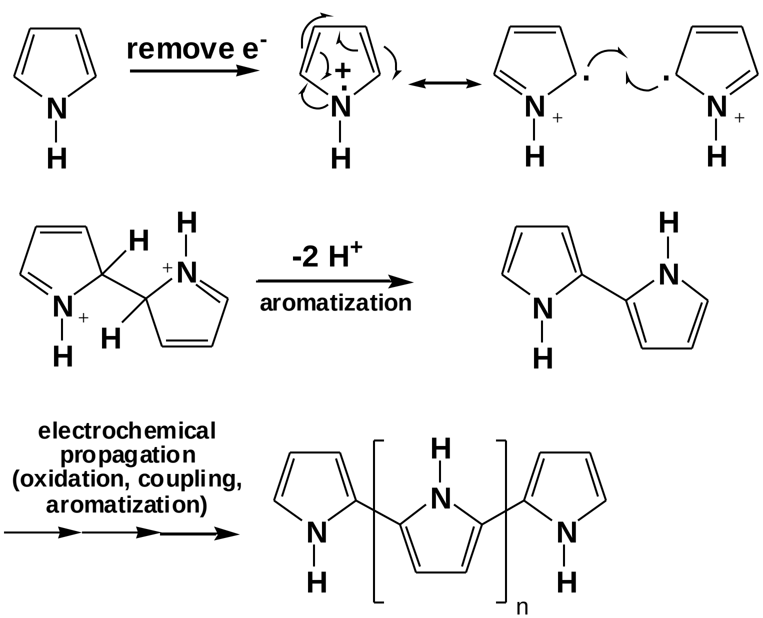
ITO Interface Modification Provides for High ET Rates and Smooth Polymer Films

Armstrong *et al.*, *Langmuir* **2007**, *23*, 1530

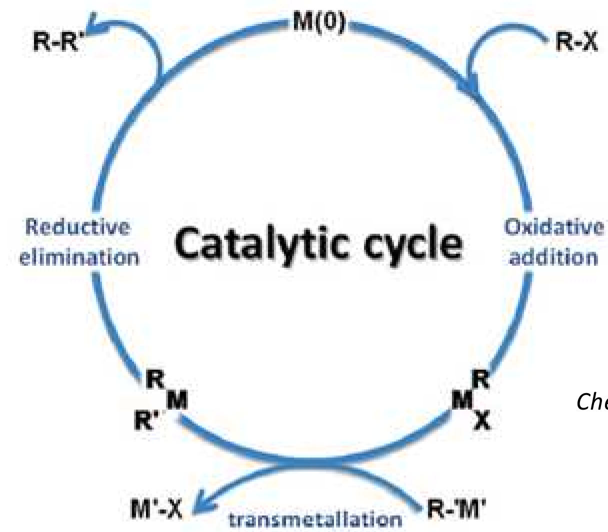
General Approaches for the Synthesis of Conjugated Polymers

Electrochemical Polymerization

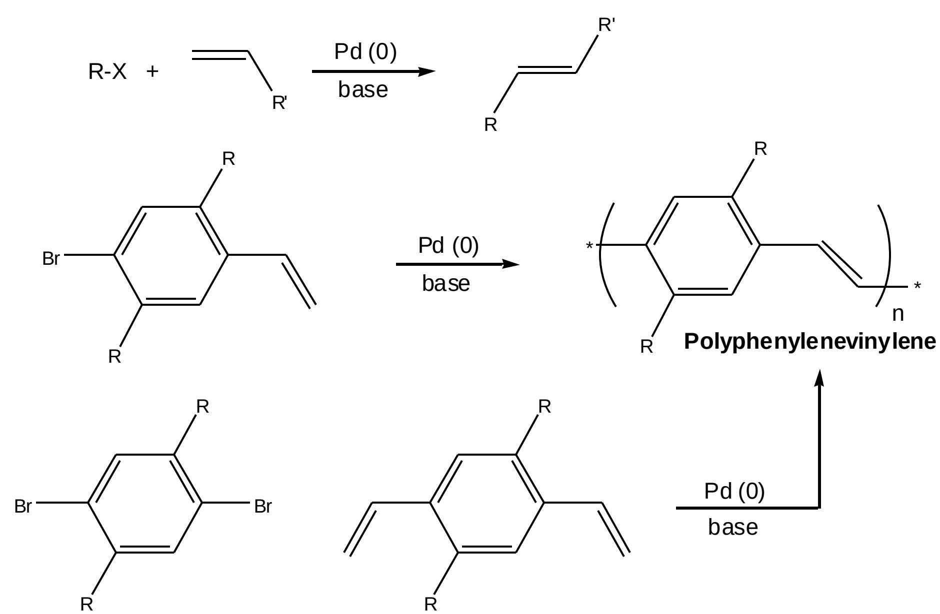




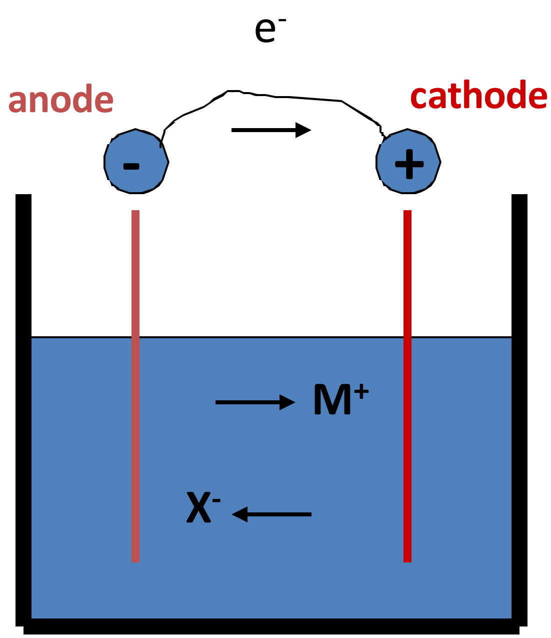
Organometallic Catalytic Rxns



Cheng *et al.*
Chem. Rev. **2010**, *109, 5868*



Electrochemical initiation & Electropolymerization of conjugated monomers onto electrodes

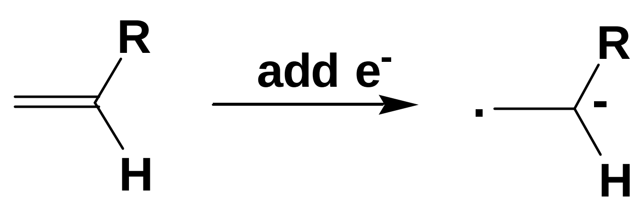


Remember: Red-Cat was stepped on by An-Ox

Cathode: reduction e.g., $Cu^{2+} + 2e^{-} \longrightarrow Cu(s)$

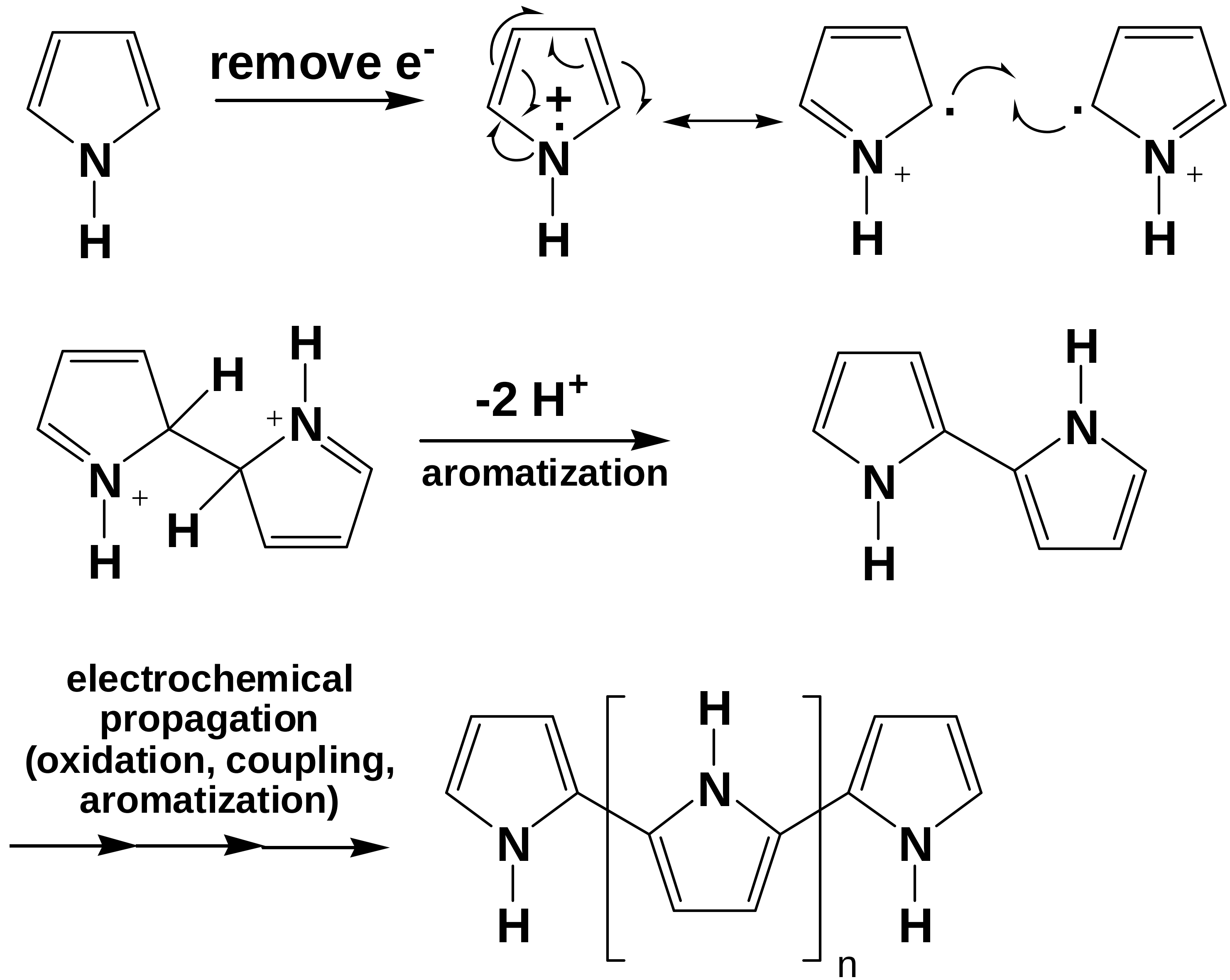
Anode: oxidation, e.g., $Zn(s) \longrightarrow Zn^{+2} + 2e^{-}$

Depending on reduction potential various monomers can be reduced/oxidized to initiate polymerization (e.g., styrene, methacrylates, acrylonitrile



Reduction at cathode

Electropolymerization of Pyrrole and Thiophenes



Moutet, A. *Acc. Chem. Res.* **1989**, *22*, 249

Electrochemical Polymerization of Thiophenes

1. **Solution oxidative Polymerization with $FeCl_3$**

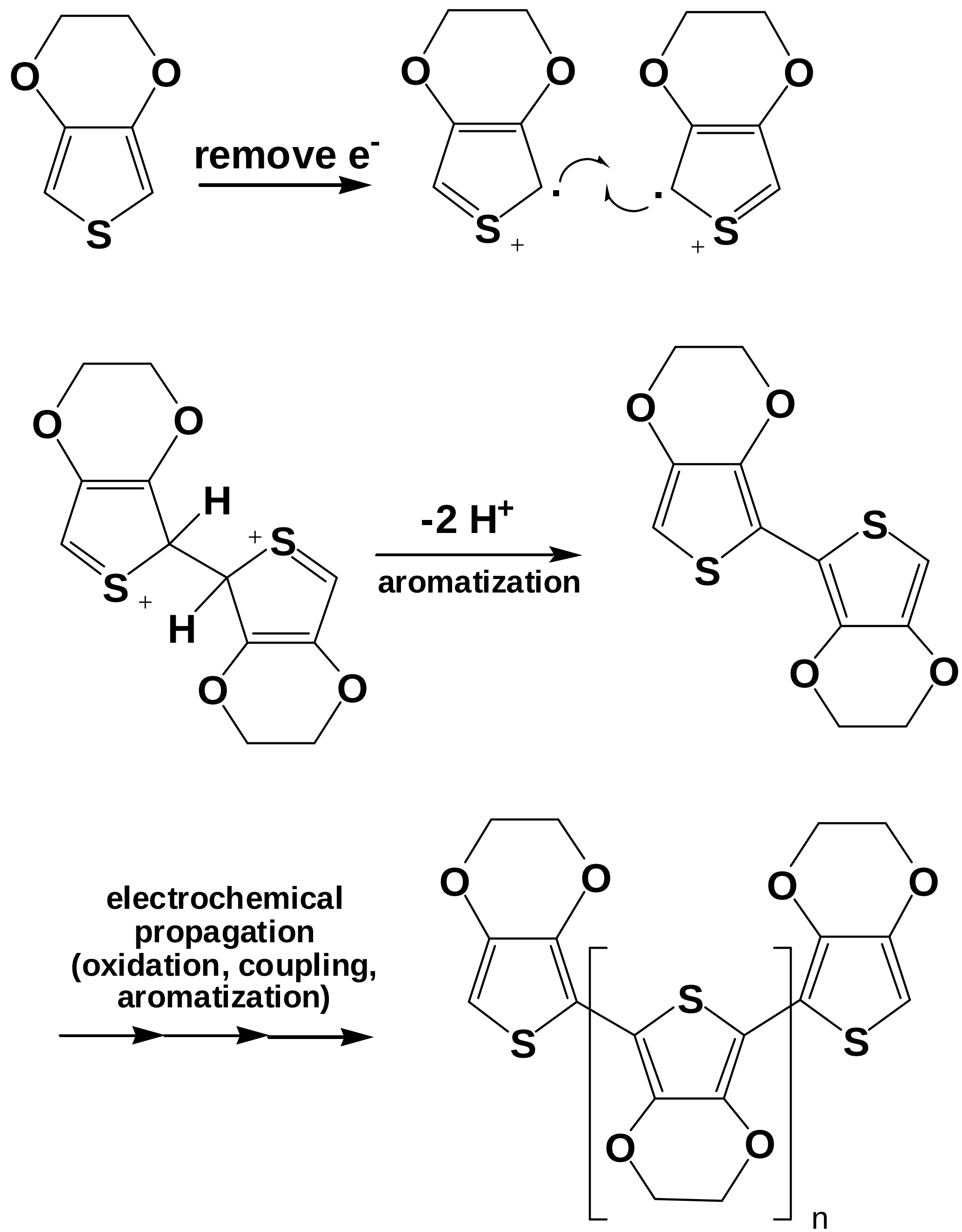
2. **Electropolymerization on electrodes (e.g., ITO) indium tin oxide**

3. **Poly(3,4-diethylene -oxythiophenes)(PEDOT)**

High conductivity (600 S/cm)
Neutral form

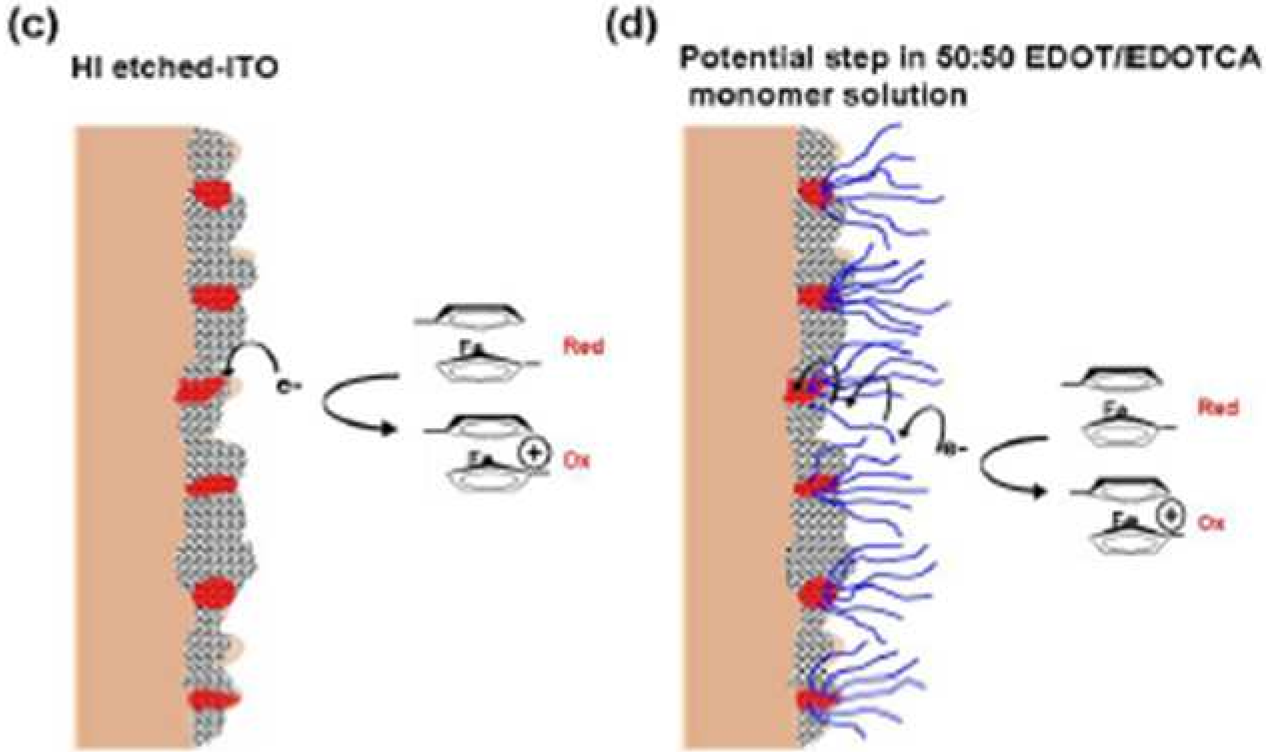
Transparent, highly stable

Electrochromic properties (tunable color with applied field)



Modification of Electrodes with Conjugated Polymers

Extensively investigted with polypyrrole on electrode surfaces by Murray et al., (Acc. Chem. Res. **1980**, *13*, 135)
PEDOT based polymers deposited on transparent conductive semiconductors (e.g., indium-tin oxide (ITO)



Polymer film can be designed to specific Analytes, allow "communication" To surface

Armstrong et al.,
Langmuir **2006** in press

Conjugated polymer film continuous over electrode, possess comparable redox activity as oxide surface, which is difficult to work with.

Electronic & Optical Properties of Conjugated Polythiophenes

Neutral polythiophenes-organic semiconductor, electronic transition
Absorbance ~ 300-500 nm & Emission (dependent on structure/band gap)

Metallic polythiophenes achieved by 1) doping, 2) electrochemical oxidation
Equivalent to p-doping
From semiconductor to metallic state loss of luminescence

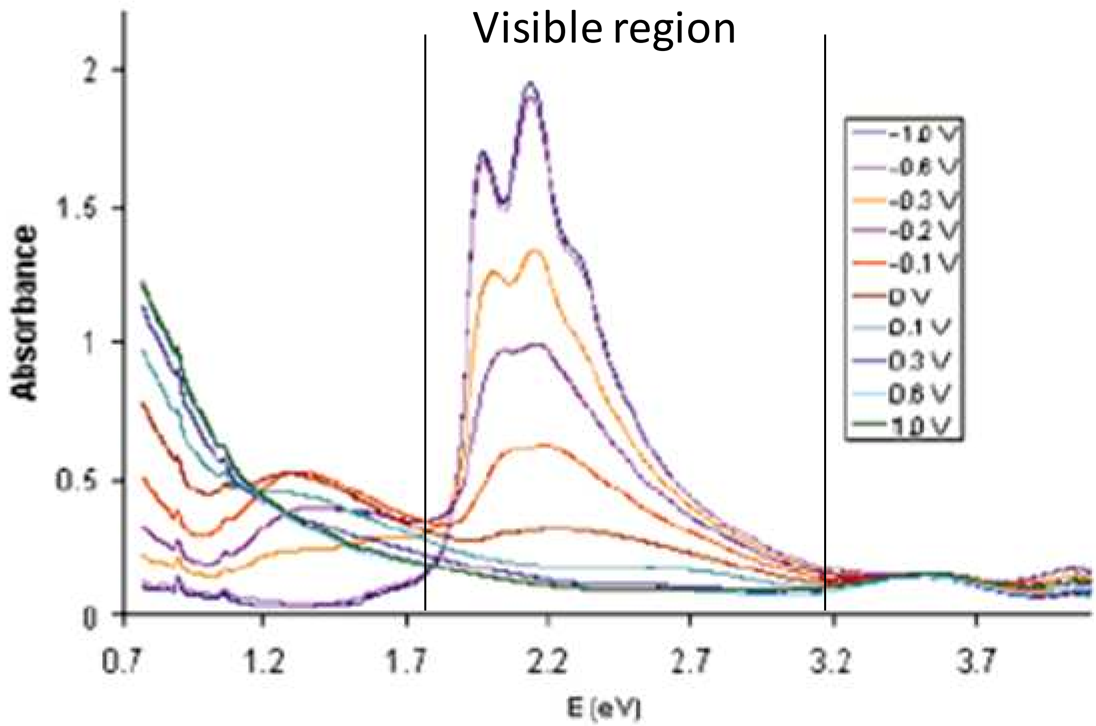


Fig. 5. Spectroelectrochemistry of PProDT–Me_2.

This effect of tunable optical Properties with e-chem "Electrochromism"

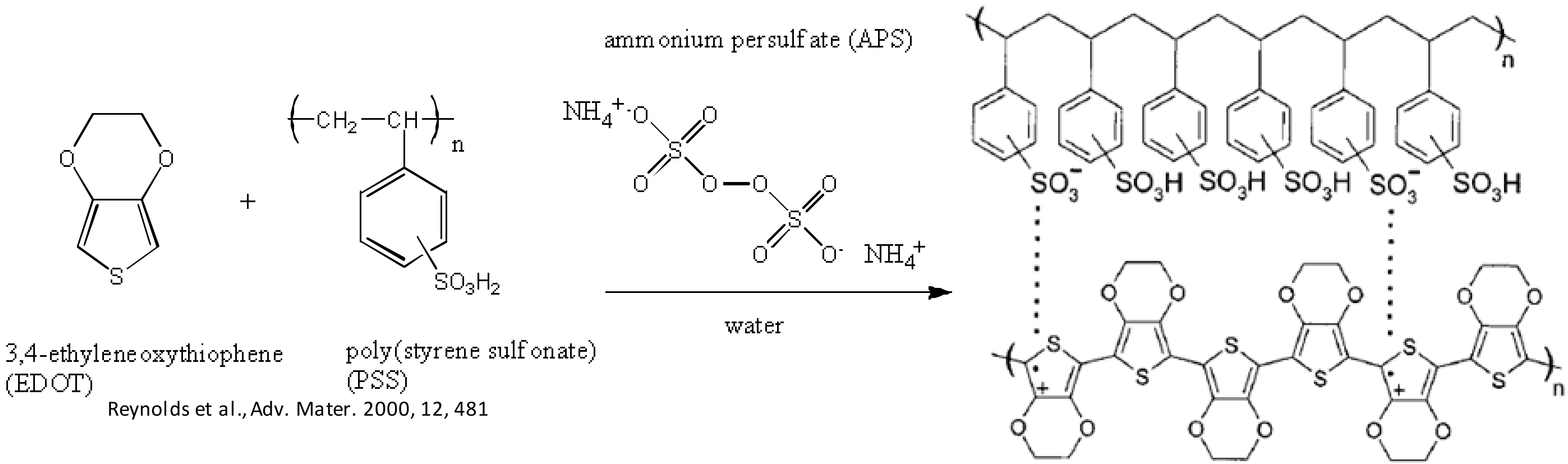
Neutral PEDOT-semiconductor
Blue-opaque

↕

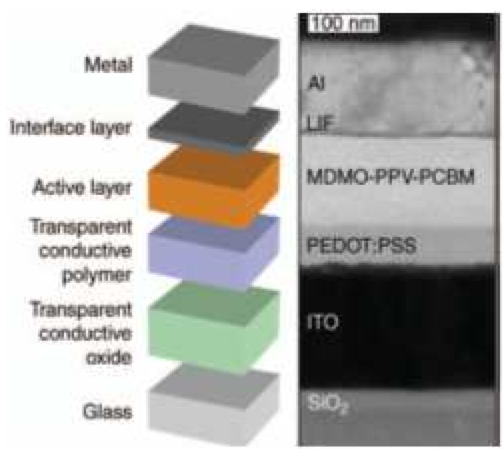
Oxidized PEDOT-metallic
transparent

Reynolds et al., *Adv. Mater.* **2000**, *12*, 481

Modification of ITO with PEDOT:PSS-What is it?



Reynolds et al., Adv. Mater. 2000, 12, 481



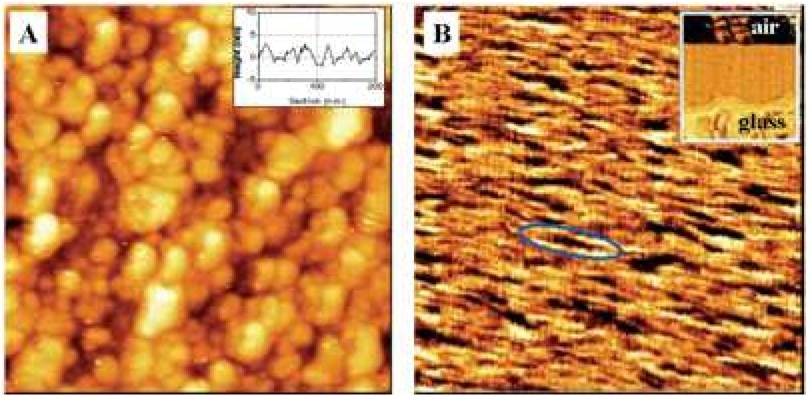
Sariciftci *et al. MRS Bull.* **2005**, *30*, 33

PEDOT-PSS utilized as electron blocking layer-selective for hole transport to ITO anode

PEDOT-PSS comes as aqueous dispersion that can be spin coated into thin films onto ITO

Normally PEDOT is intractable solid
Structure of PEDOT:PSS difficult to determine
Ratio of PEDOT:PSS ~ 1:6, 1:2.5 by wt

On the morphology of PEDOT-PSS and electrical properties



Kemerink et al. Adv. Mater. ***2007.***

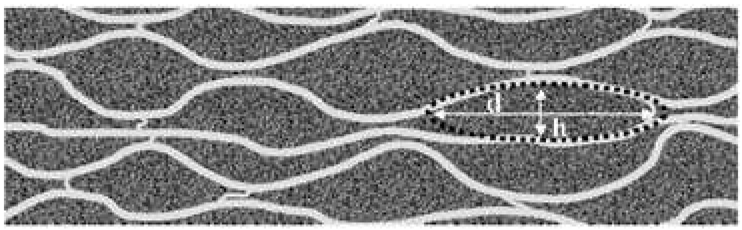
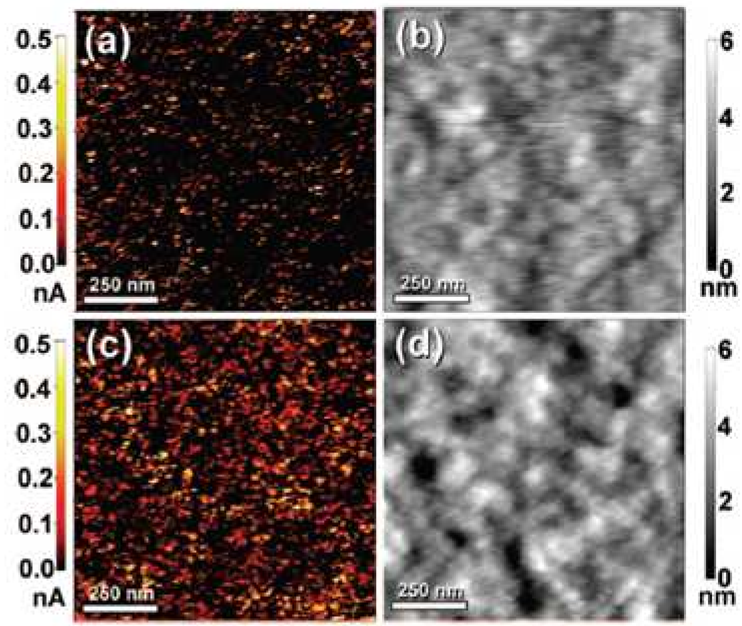


Figure 3. Cross-sectional view of the schematic morphological model for PEDOT:PSS thin films derived from combined STM and X-AFM measurements. PEDOT-rich clusters (dark) are separated by lamellas of PSS (light). The PEDOT-rich lamella is composed of several pancake-like particles as pictured by the dotted lines. The typical diameter *d* of the particles is about 20–25 nm and the height *h* is about 5–6 nm.

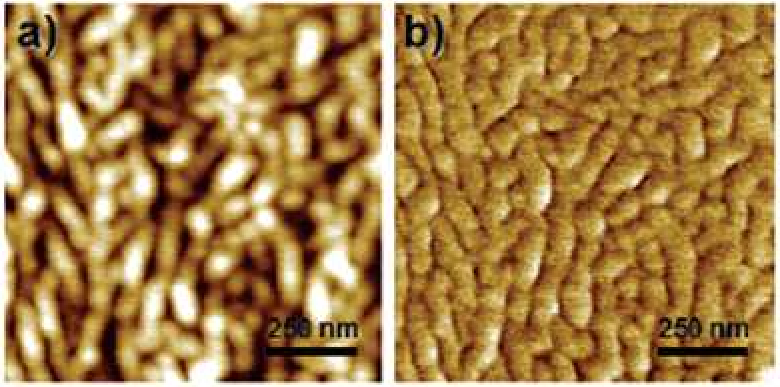


Ginger *et al., J. Phys. Chem. C* **2008**, *112*, 7922

C-AFM studies indicate that surface conducivity Strongly dependent on processing conditions

1) **20 nm conducting PEDOT nanoparticles particles embedded in PSS.**
2) **Order-of-magnitude variations in the film conductivity interpreted in terms of charge transport along percolating path or network, formed by strongly coupled conductive particles.**
3) **Moreover, morphology and conductivity of the top layer differ substantially from those in the bulk attributed to an enhanced PSS content.**

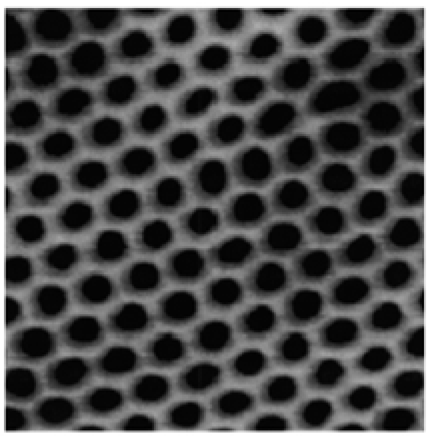
Controllable Alignment of Conjugated Polymers



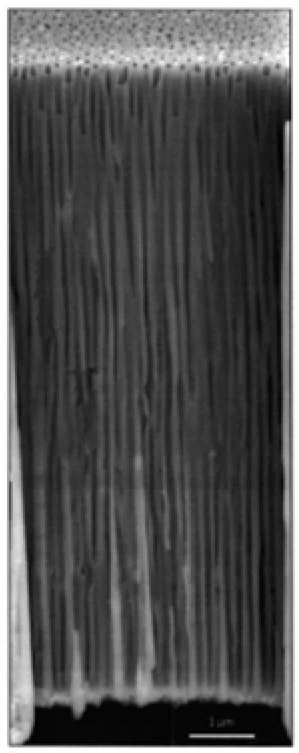
Self-assembled block copolymer morphologies
Exhibit order on 10^{-9} to 10^{-7} m
Defects on larger length scales

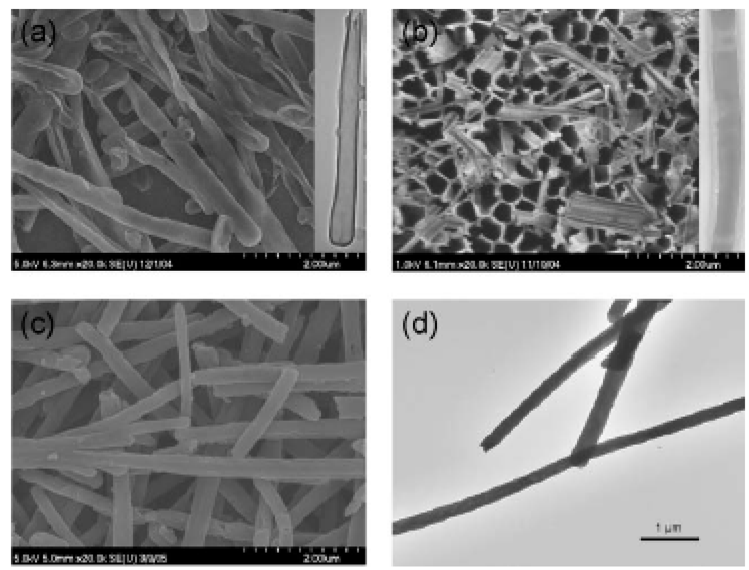
"Bottom up" assembly approaches

"Top-Down Approaches"



Porous membrane
"hard" templates
Polymerize monomer
In pores and degrade
membrane





Martin et al., *Nature* 1994, *369*, 298; Martin et al., *J. Mater. Chem.* **1997**, *7*, 1075-1087; Foulger et al., *Chem. Commun.* **2005**, *3092*