Polymer materials

Lecture 11

Conductive polymer

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Nobel Chemistry prize (2000)

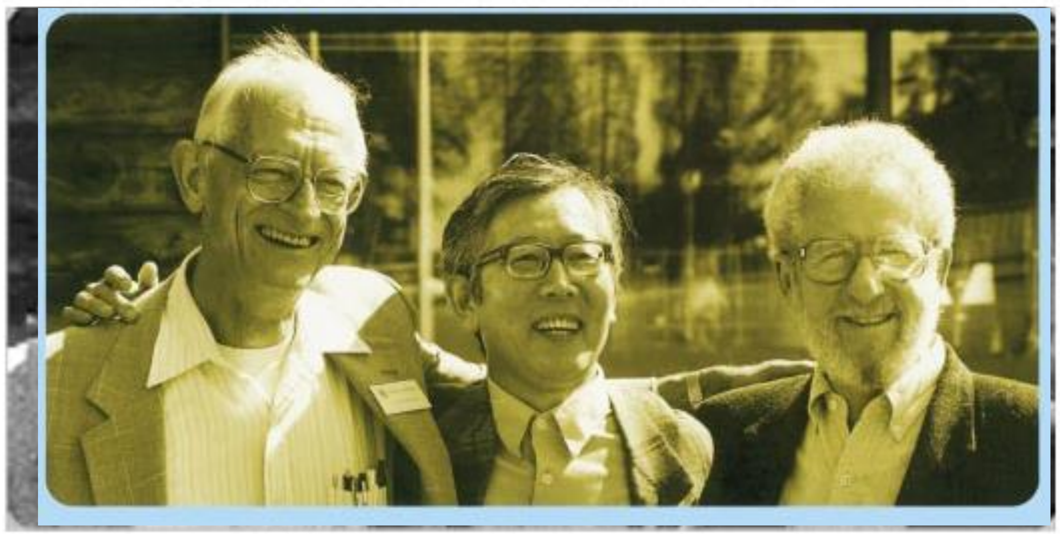
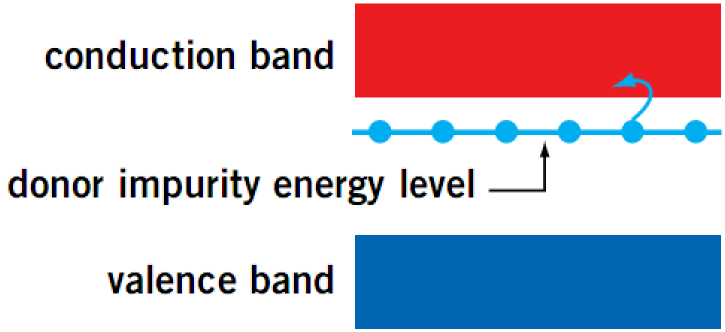


Figure 1.2 Photograph of three awardees of the Nobel Chemistry Prize in 2000
Alan G. MacDiarmid (left) Prof. at the Univ. of Pennsylvania, USA
Hideki Shirakawa (middle) Prof. Emeritus, Univ. of Tsukuba, Japan
Alan J. Heeger (right) Prof. at the Univ. of California at Santa Barbara, USA

Electrical Conductivity of Materials

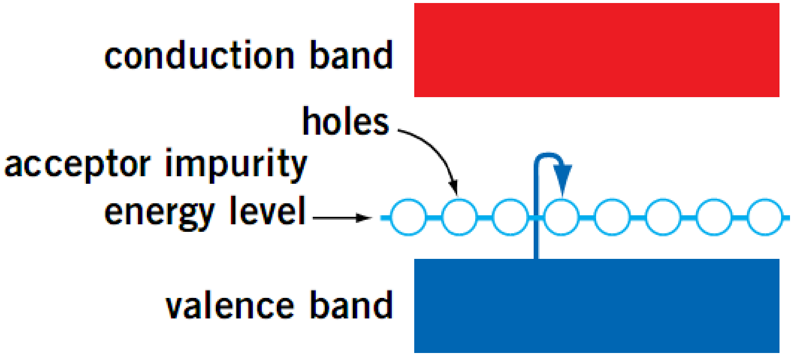
- Insulators
  - $\sigma \sim 10^{-7}$ S cm^{-1}
- Semiconductors
  - $\sigma \sim 10^{-7}$ to 10^{2} S cm^{-1}
- Metals
  - $\sigma > 10^{2}$ S cm^{-1}
- Units are expressed as resistivity (Ω cm) or conductivity (Ω^{-1} cm^{-1} or S cm^{-1})

Energy gaps of n-type and p-type semiconductors



n > p

Energy-band diagram of an n-type semiconductor



p > n

Energy-band diagram of a p-type semiconductor

Element	Gap energy (eV)
Ge	0.66
Si	1.11

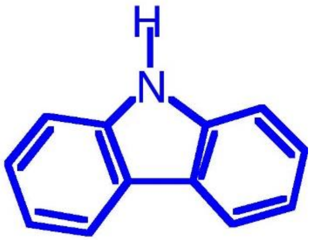
TABLE 18-7 *The donor and acceptor energy gaps (in electron volts) when silicon and germanium semiconductors are doped*

	Silicon		Germanium	
Dopant	E_d	E_a	E_d	E_a
P	0.045		0.0120	
As	0.049		0.0127	
Sb	0.039		0.0096	
B		0.045		0.0104
Al		0.057		0.0102
Ga		0.065		0.0108
In		0.160		0.0112

Semiconducting Polymers

- Some are characterized by their photoconductivity when exposed to light
- Example: polymer with 5-atom ring group
- Poly(*N*-vinylcarbazole) (PVK)

PVK



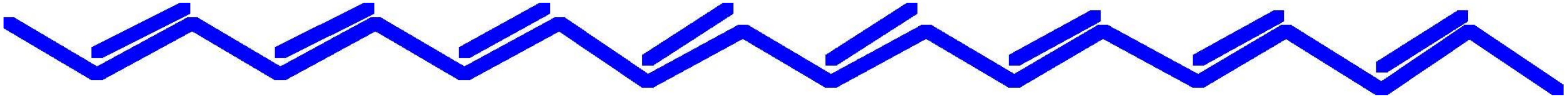
carbazole

Pure PVK is a *hole* conductor with dark conductivity of ~ 10^{-14} S cm^{-1}

It is a very common *photoconducting* materials

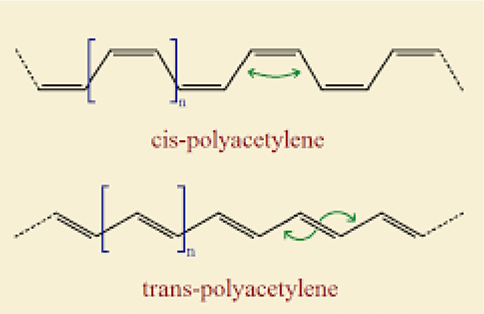
Polymers with Unsaturated (Conjugated) backbone structure

- A conjugated main chain with alternating single and double bond
- First example of conjugate polymer:
  - Polyacetylene

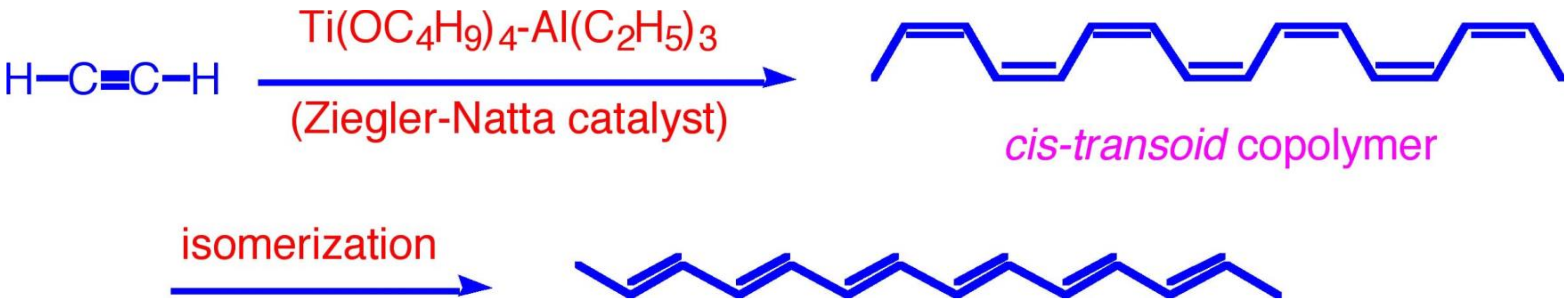


Pure polyacetylene: $\sigma \sim 10^{-9}$ (*cis*) and 10^{-5} (*trans*) S cm^{-1}
High electrical conductivity was observed when the polymer was "***doped***" with oxidizing or reducing agents

Synthesis of Polyacetylene

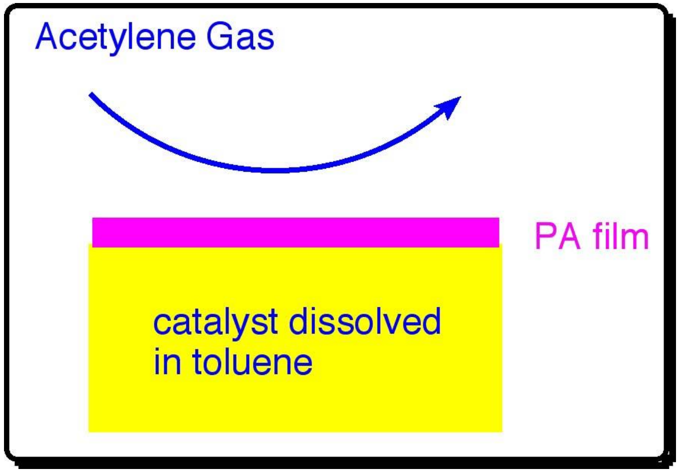


By Ziegler-Natta Catalyst



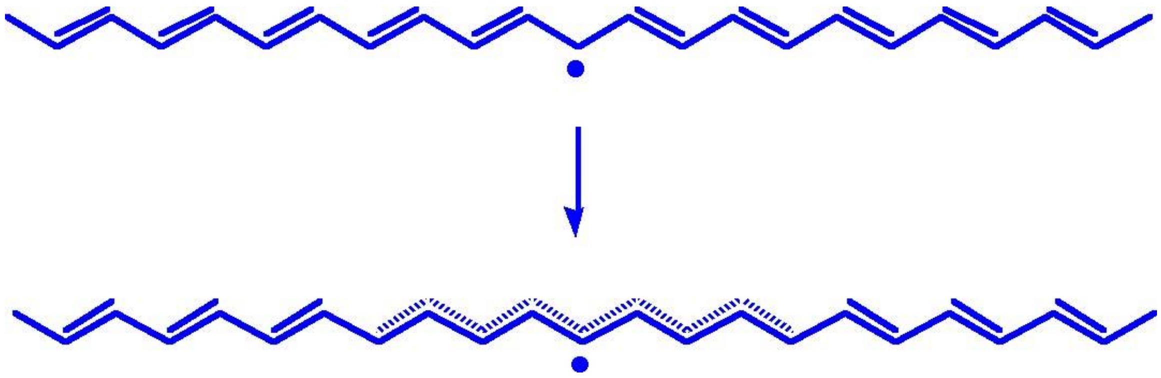
Effect of Temperature:

At -78 °C or below: all-*cis* PA
At 180 °C or higher: all-*trans* PA



The Conduction Process in Conjugate Polymers

- **Soliton**: a defect/ charge in every 5 to 9 repeating units

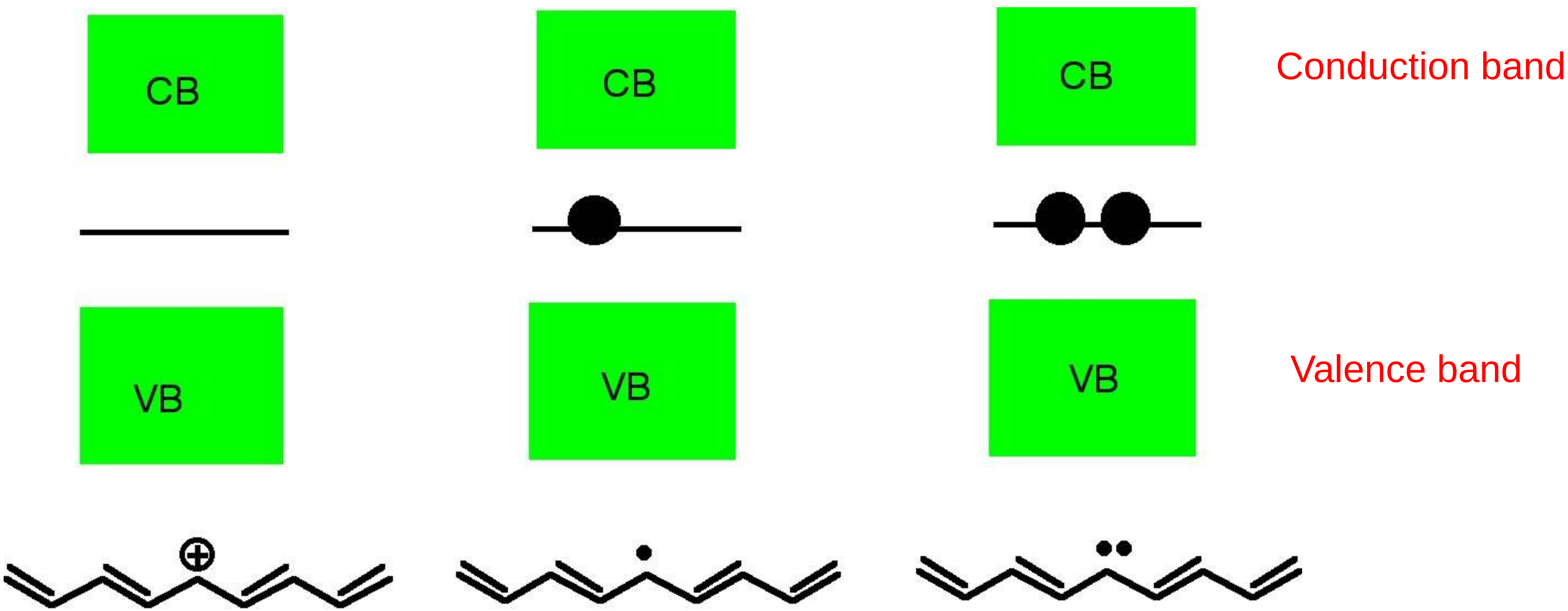


- The charge formed by adding iodine I_2
- get an electron from the polymer and forms I_3^-

Positively charged Soliton S^+

Neutral soliton S^0

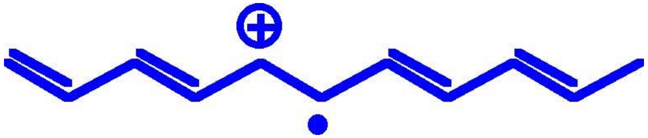
Negatively charged Soliton S^-



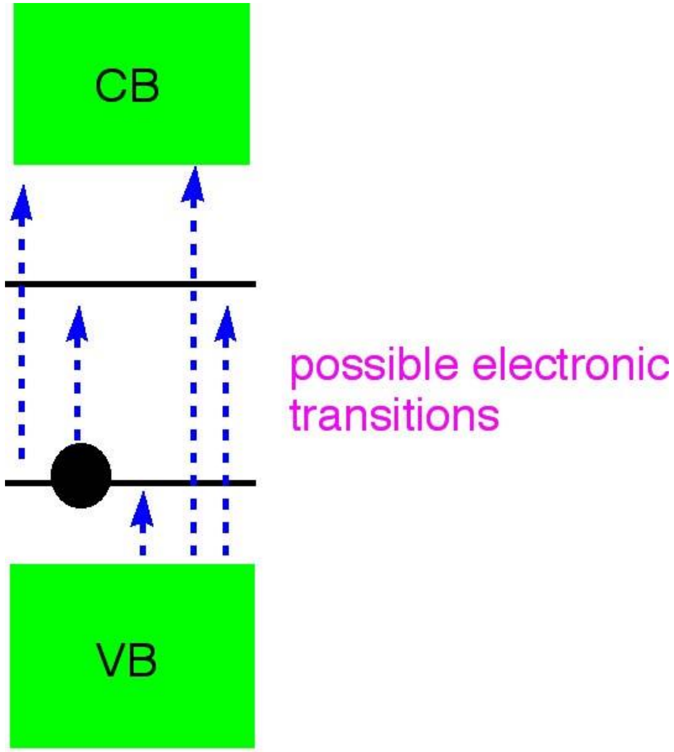
- The C become charge (+ or -) or radical

Isolated solitons are not stable in polymers, charge exchange and form **polaron (a pair)**

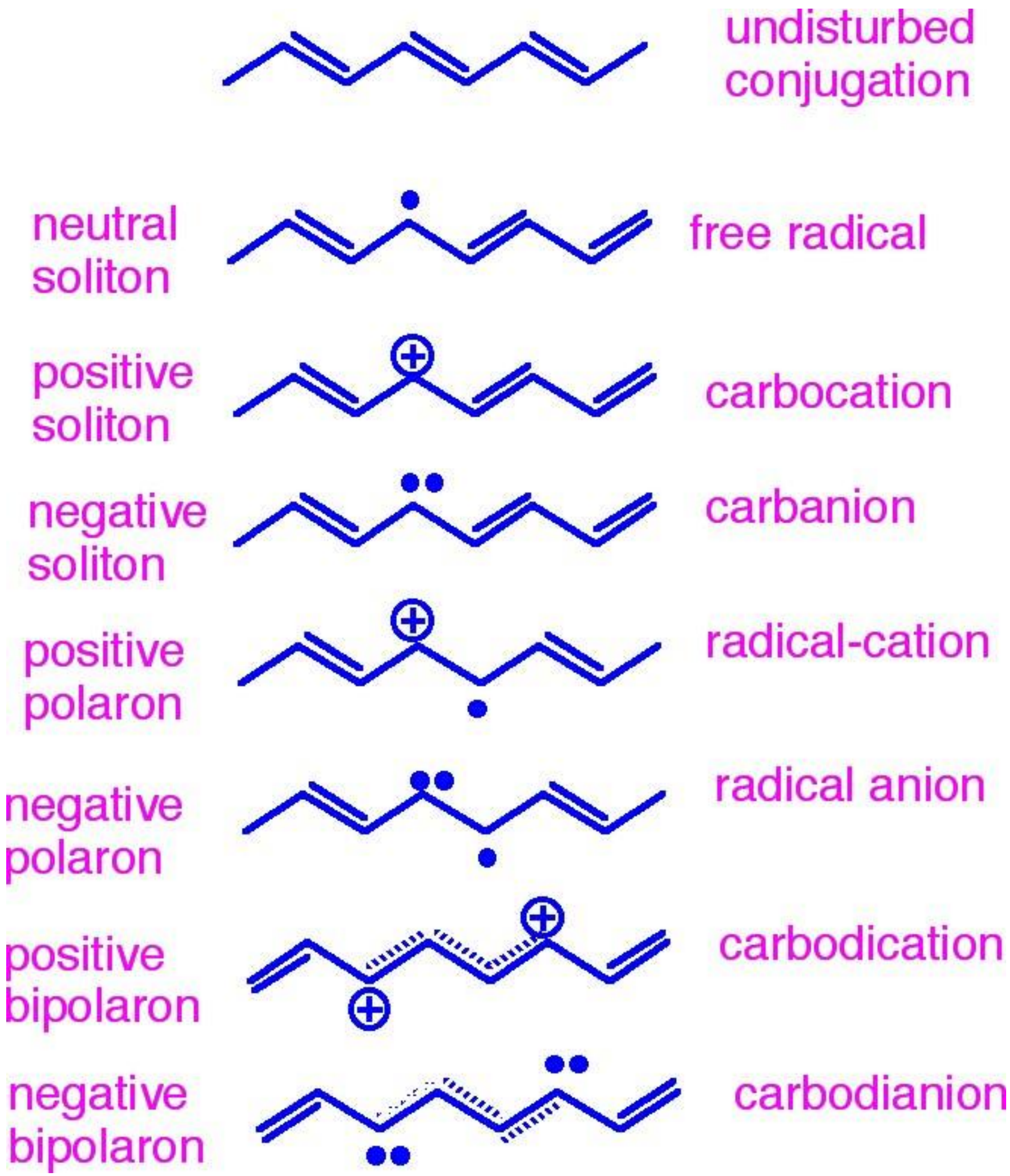
If the hole or electron go to **conductive band → conductive**



The polaron is mobile along the polymer chain



In chemical terms:



Doping polymer

The mobility of a polaron along the polyacetylene chain can be high and charge is carried along the *backbone*.

Hence, high **dopant** concentration is necessary.

Dopants:

Oxidative: AsF_5, I_2, Br_2, $AlCl_3$, $MoCl_5$ (p-type doping)

Reductive: Na, K, lithium naphthalides (n-type doping)

Electrical Conductivity of Some Doped Polyacetylenes

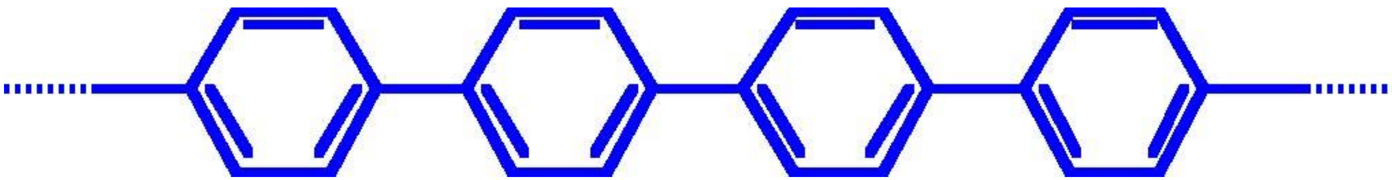
Dopant	Conditions	Conductivity (S cm^{-1})
I_2	Vapor	360
IBr	Vapor	120
HBr	Vapor	7×10^{-4}
AsF_5	Vapor	560
SeF_6	Vapor	180
$FeCl_3$	CH_3NO_2	897
	Toluene	9.0
$MoCl_5$	Anisole	563
	Toluene	356
WCl_6	Toluene	365
	Anisole	8.48

Note: PA is insoluble and labile to atmospheric oxygen

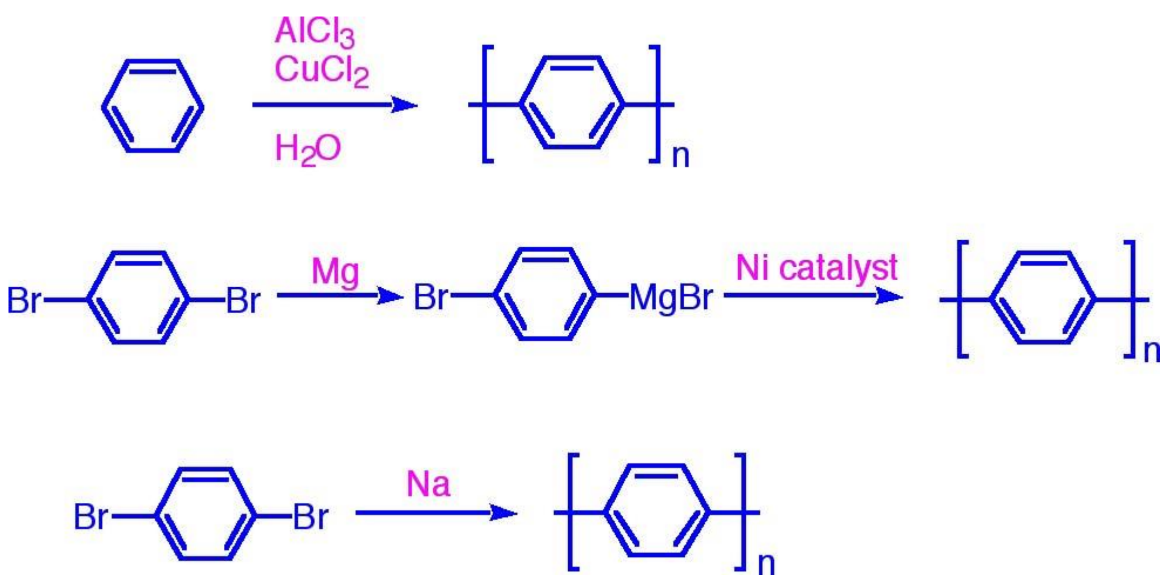
Other possible Polymers

Poly(1,4-phenylene) or Poly(*p*-phenylene) (PPP)

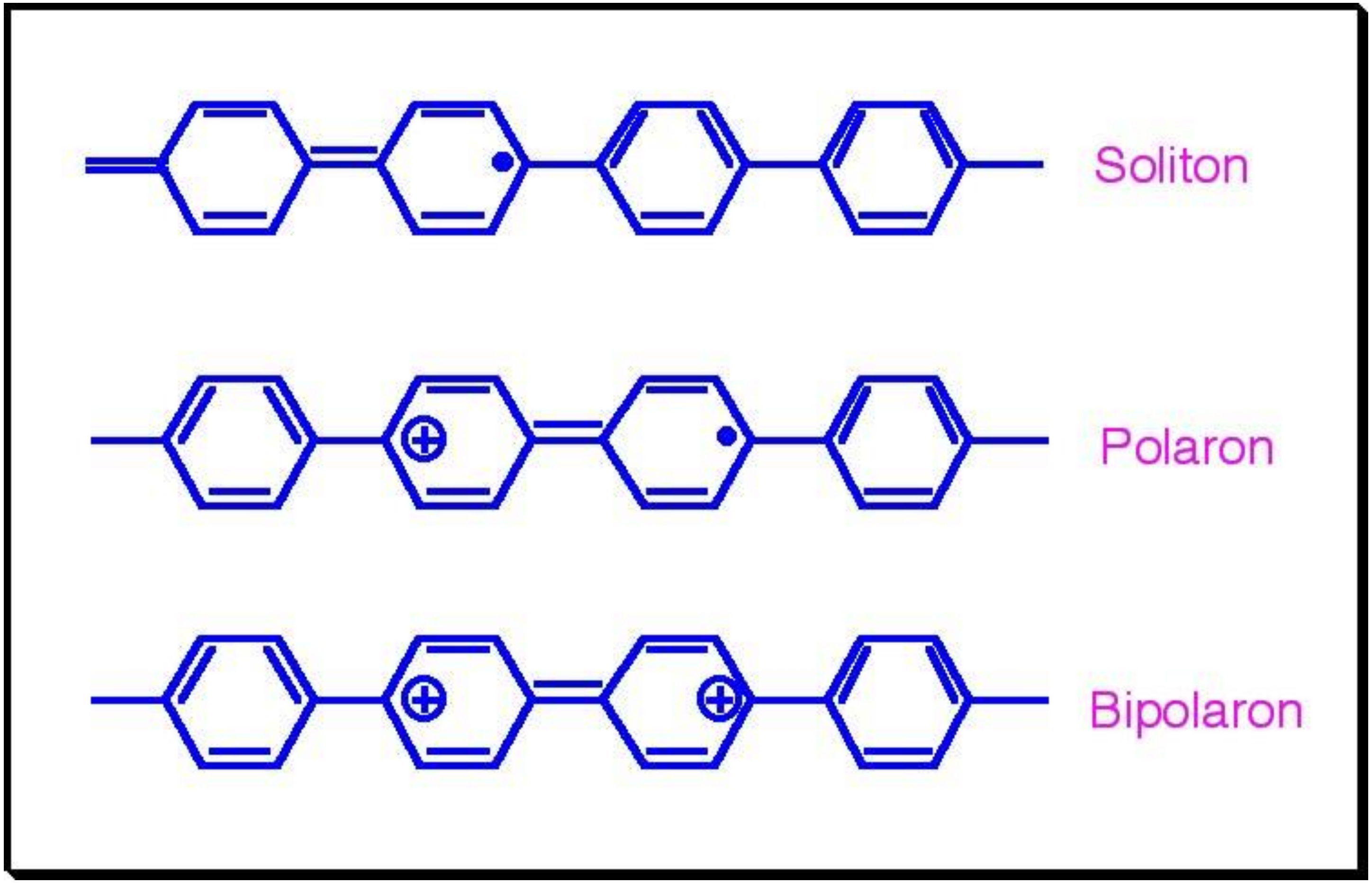
A conjugated polymer based on aromatic units on the main chain



Synthesis



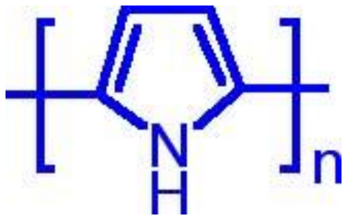
Soliton, polaron, and bipolaron in poly(*p*-phenylene)



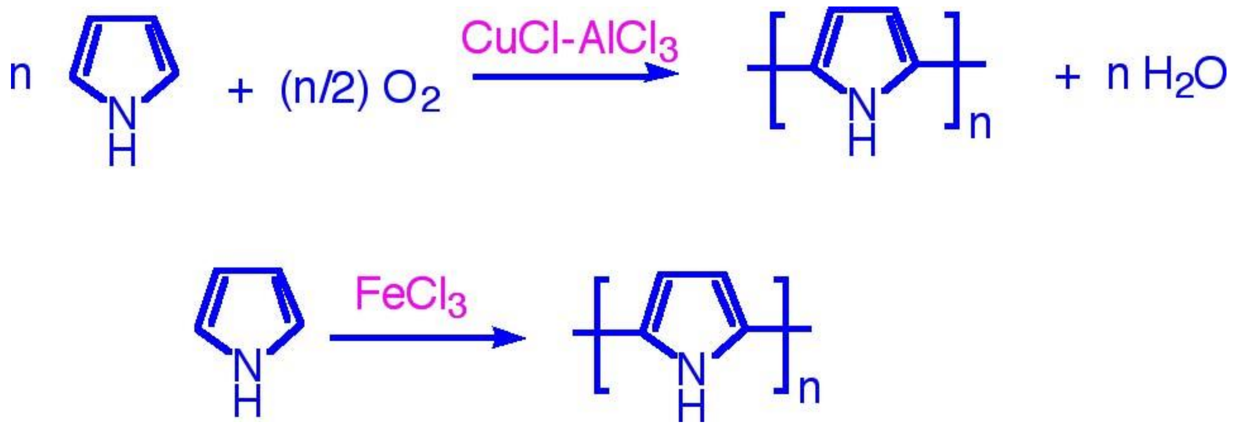
Conductivity of PPP

Dopant	σ (S cm^{-1})
AsF_5	500
$FeCl_3$	0.30
$SbCl_5$	$< 10^{-3}$
I_2	$< 10^{-4}$
SO_3	10^{-1} to 10^{-4}
$AlCl_3$	8.0
$Napht^{-}K^{+}$	50
$Napht^{-}Li^{+}$	5

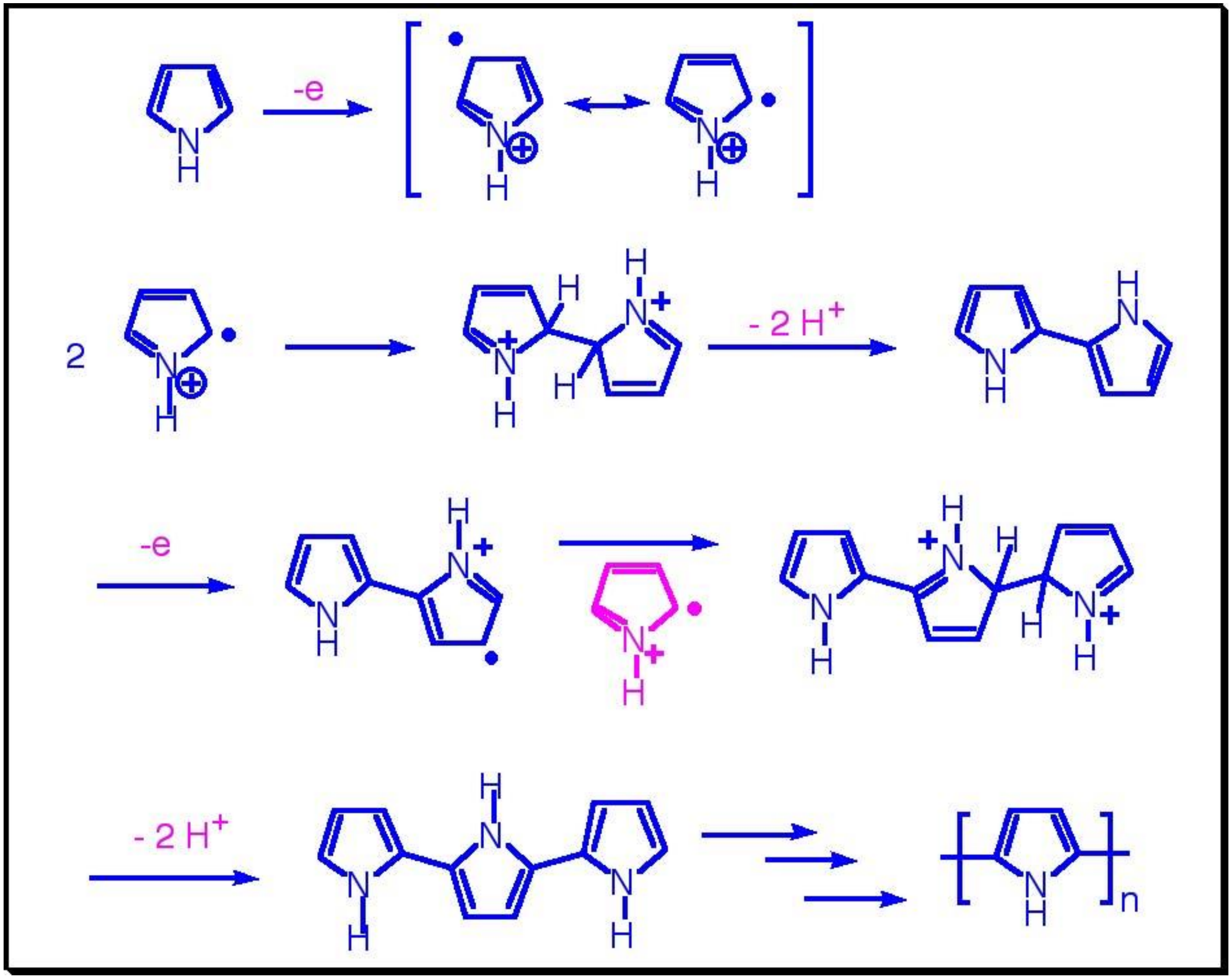
Polypyrrole



- A conjugated polymer based on heterocyclic aromatic units on the main chain
- Synthesized by chemical or electrochemical polymerization from pyrrole
- Mechanism: oxidative coupling reaction

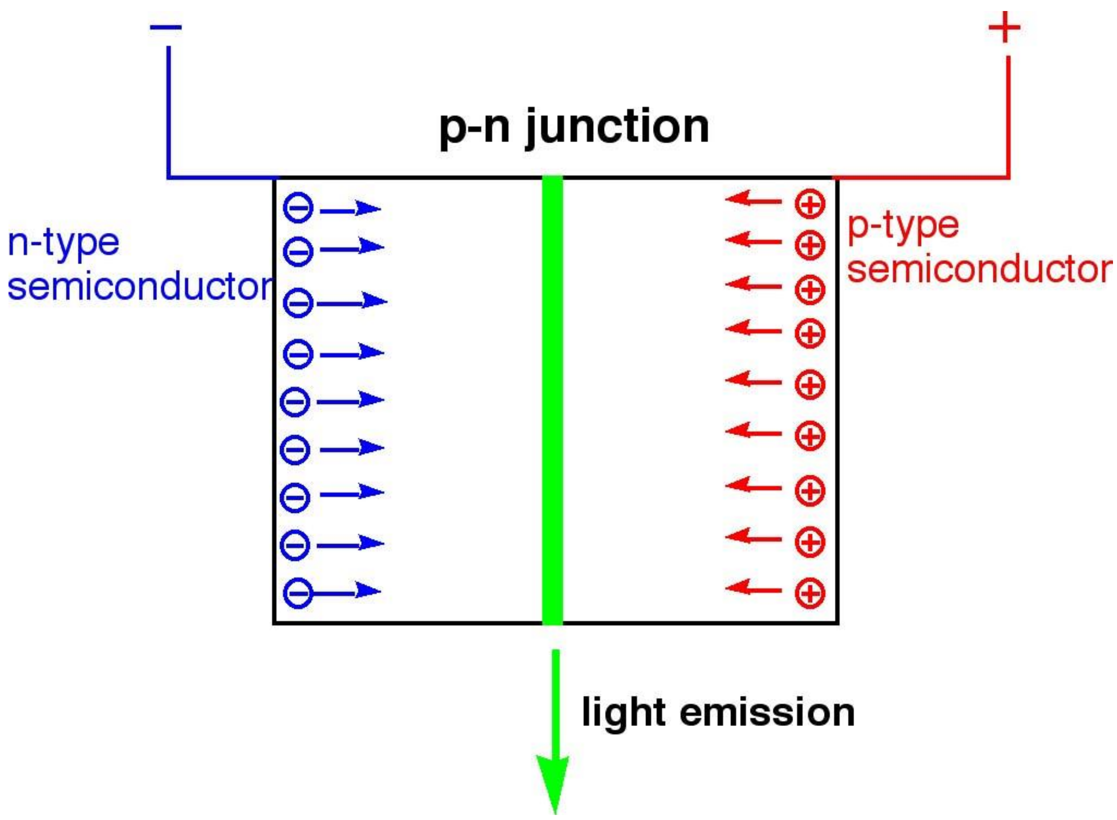


Proposed mechanism for the electrochemical polymerization



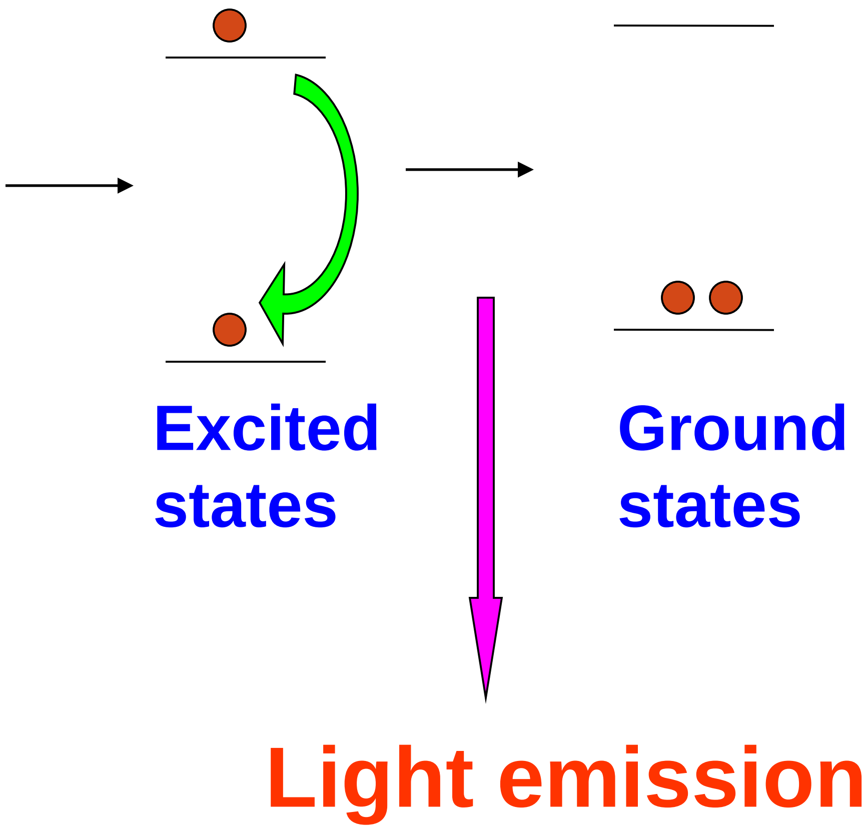
Application:LED Display

- Light emission resulted from the recombination of holes and electrons in a semiconductor



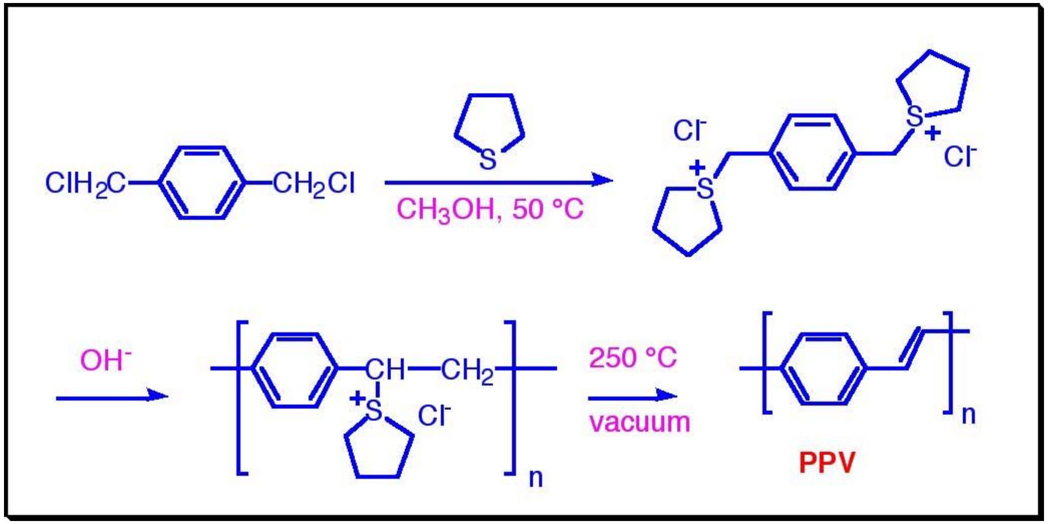
When hole and electron recombine:

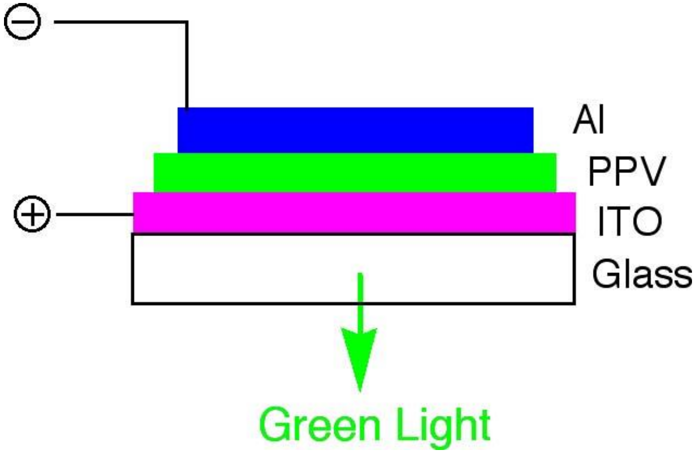
$Hole^{+}$ + $Electron^{-}$



Organic Light Emitting Polymer

- First reported in 1990 (*Nature* **1990**, *347*, 539)
- Based on poly(*p*-phenylenevinylene) (PPV), with a bandgap of 2.2 eV



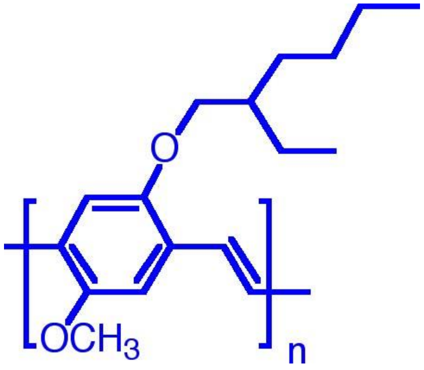


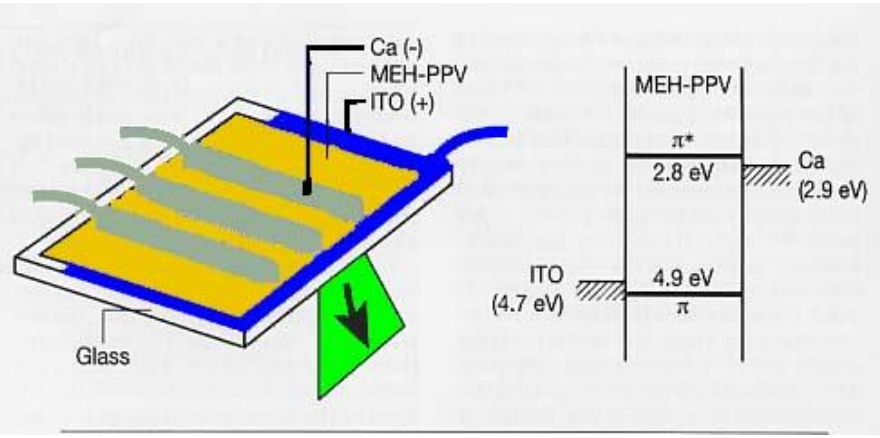
ITO: Indium-tin-oxide
-A transparent electrical conductor

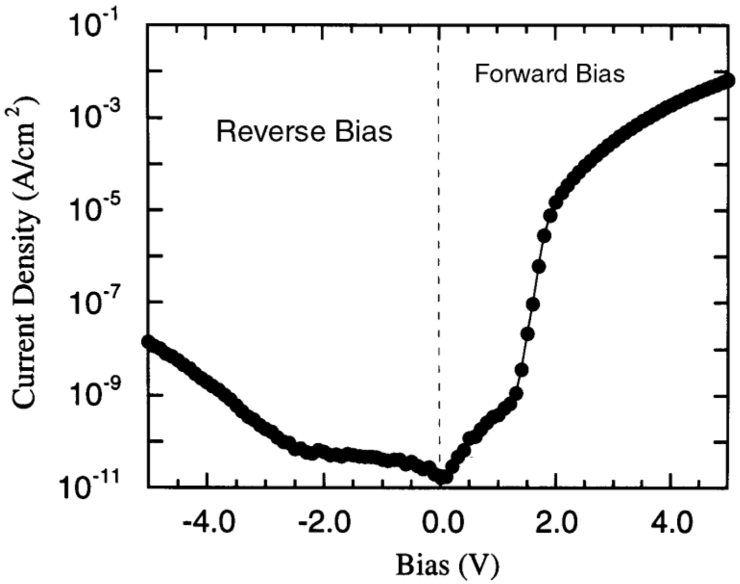
- Threshold for charge injection (turn-on voltage): 14 V (E-field = 2 x 10^6 V/cm
- Quantum efficiency = 0.05 %
- Emission color: **Green**
- Processible ?   No!!
- Polymer is obtained by precursor approach

Other PPV Derivatives

- **MEH-PPV**
- More processible, can be dissolved in common organic solvents (due to the presence of alkoxy side chains)
- Fabrication of *Flexible light-emitting diodes* (*Nature* **1992**, *357*, 477)



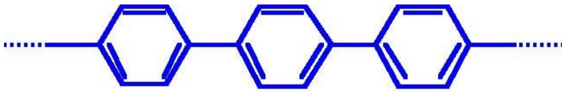




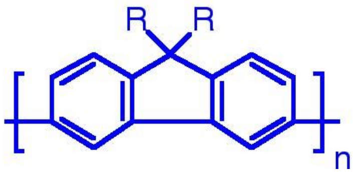
Substrate: poly(ethylene terephthlate) (PET)
Anode: polyaniline doped with acid-a flexible and transparent conducting polymer

EL Quantum efficiency: 1 %
Turn-on voltage: 2-3 V

Other Examples of Light Emitting Polymers

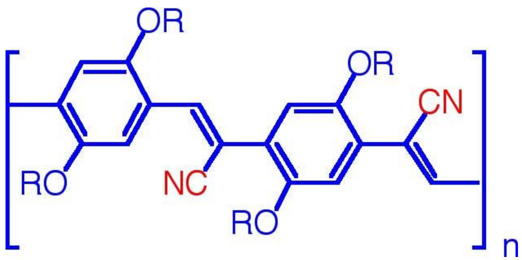


Poly(p-phenylene) (PPP)



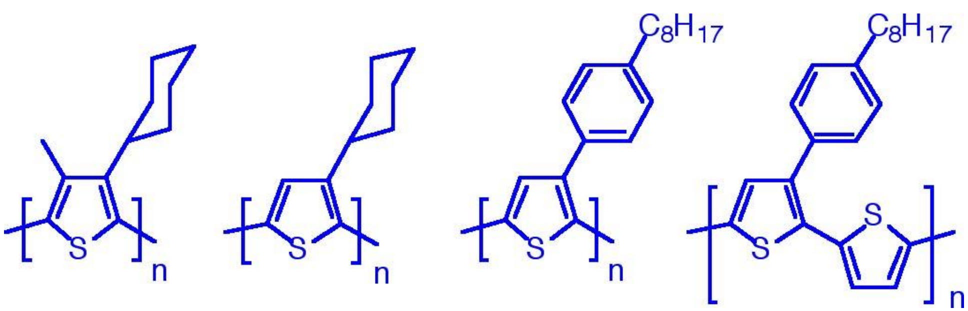
Poly(9,9-dialkyl fluorene)

BLUE light emission



CN-PPV: **RED** light emission

Nature **1993**, *365*, 628



Polythiophene derivatives

A blend of these polymers produced ***variable colors***, depending on the composition

Nature **1994**, *372*, 443