The Development of Organic Conductors, Including Semiconductors, Metals and Superconductors

Lessons from History, Continued

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The Development of Organic Conductors, Including Semiconductors, Metals and Superconductors

Lessons from History, Continued

Organic Conductors and Metals

Organic Superconductors

Conjugated Polymers for Organic Electronics

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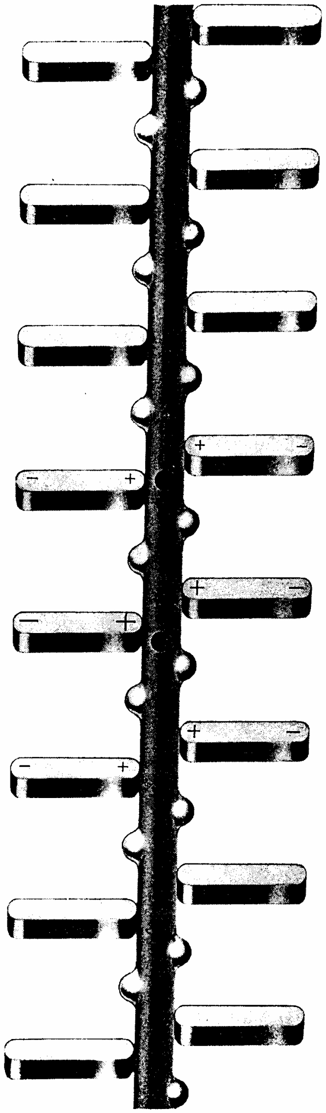
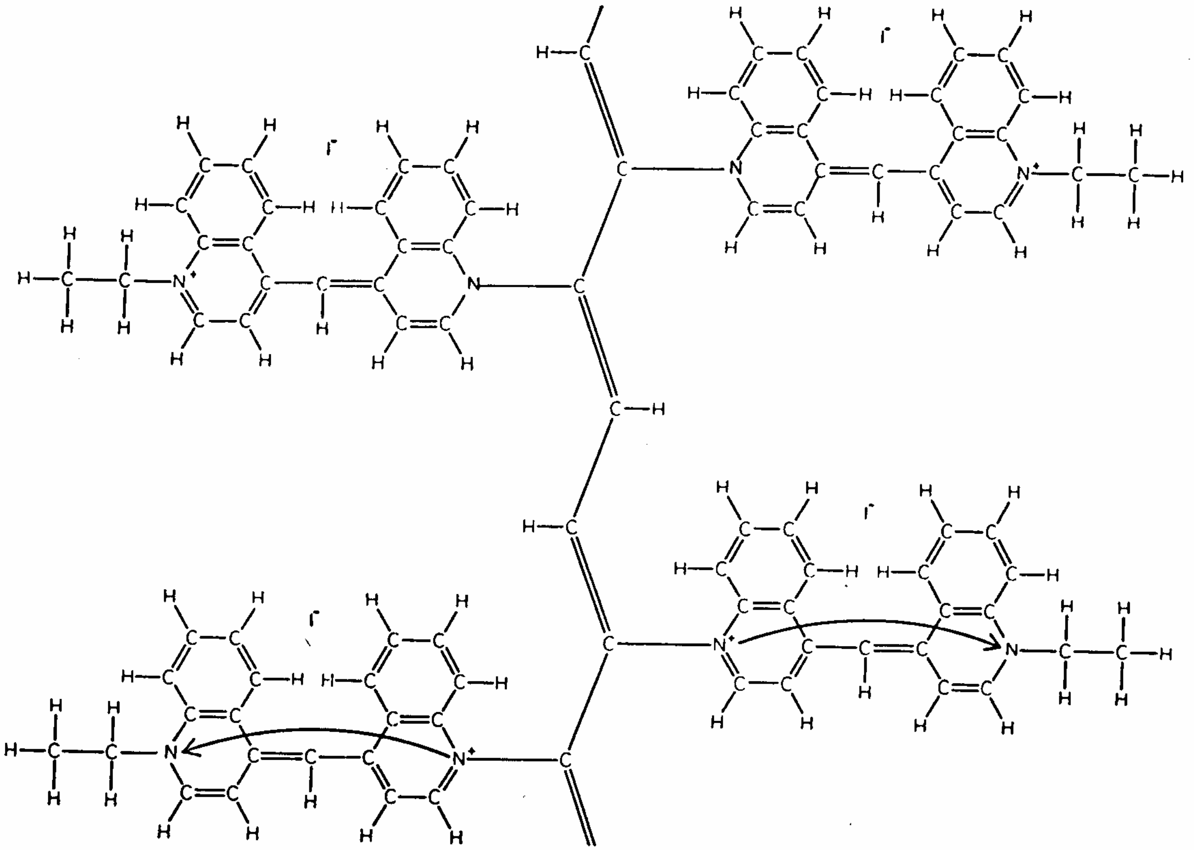
SUPERCONDUCTIVITY AT ROOM TEMPERATURE

IT HAS NOT YET BEEN ACHIEVED, BUT THEORETICAL STUDIES SUGGEST THAT IT IS POSSIBLE TO SYNTHESIZE ORGANIC MATERIALS THAT, LIKE CERTAIN METALS AT LOW TEMPERATURES, CONDUCT ELECTRICITY WITHOUT RESISTANCE

BY W. A. LITTLE

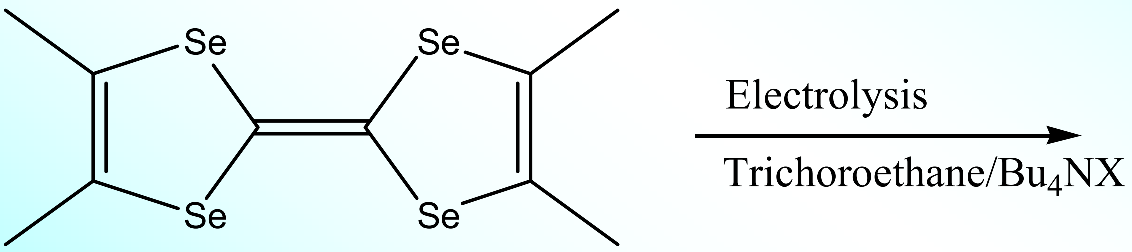


ELECTRON PAIRS are conducted along the spine of a hypothetical superconducting molecule by an attractive mechanism similar to that in a superconducting metal. As an electron passes each side chain its electric field polarizes the side-chain molecule and induces a positive charge at the end nearer the spine. A second electron is attracted to this region of positive charge and is thereby indirectly attracted to the first electron.



HYPOTHETICAL SUPERCONDUCTING MOLECULE is built around a "spine" of carbon atoms connected by alternating single and double bonds. Periodically along the spine a side chain consisting of the common dye diethyl-cyanine iodide extends outward. These side-chain molecules are highly polarizable; that is, an electron can move freely from a nitrogen site close to one end of the molecule to another nitrogen site close to the other end. A colored *N* designates the nitrogen atom that contains the resonating electron in the two possible conditions of polarization. Electrons can also move freely along the spine itself.

The First Organic Superconductors



TMTSF

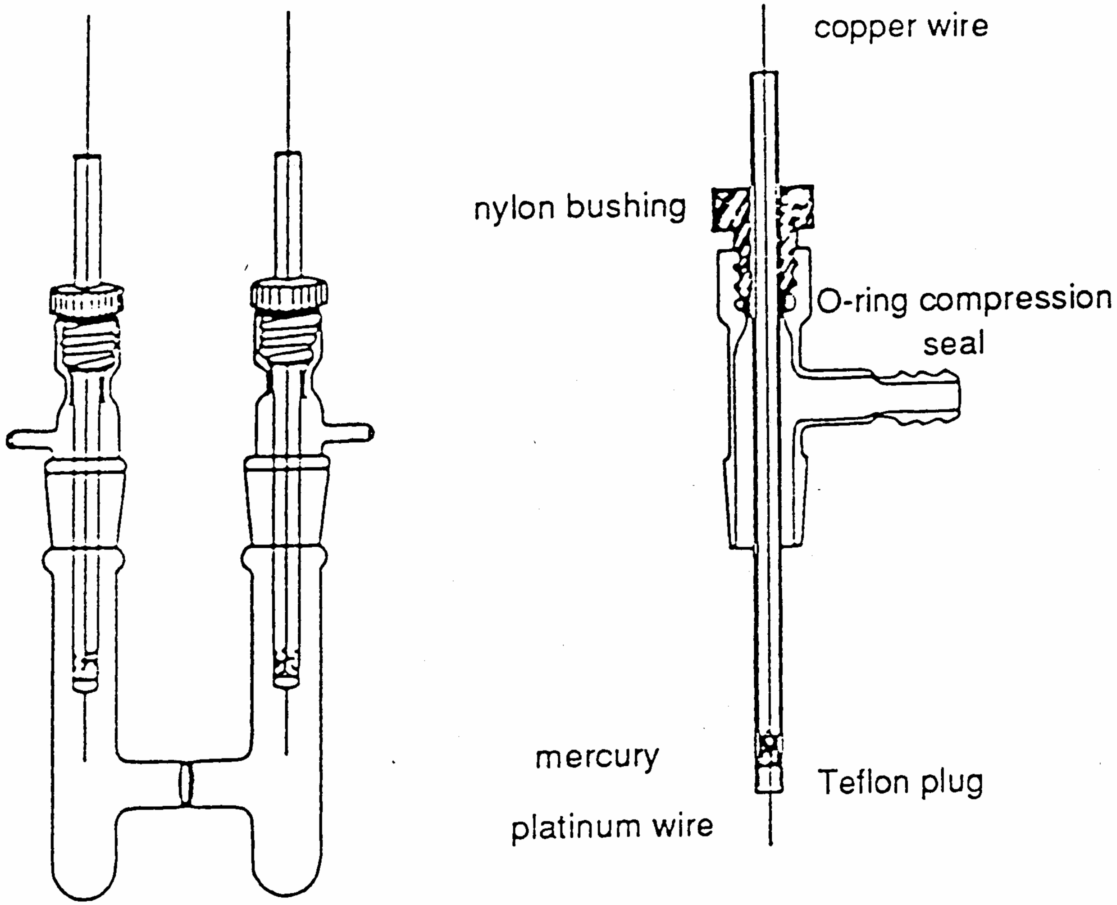
Electrolysis

Trichoroethane/Bu_4NX

$TMTSF_2X$

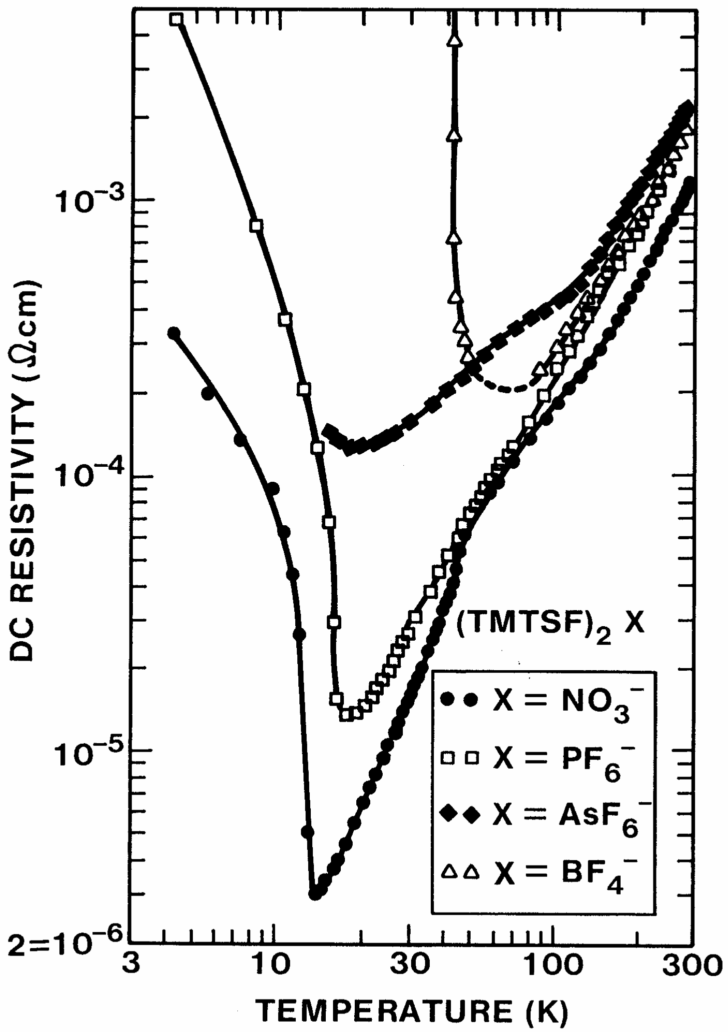
Bechgaard Salts

Electrochemical Synthesis Apparatus



Actual Electrosynthesis

D.C. RESISTIVITY vs TEMPERATURE FOR TYPICAL SAMPLES OF $(TMTSF)_2X$. NOTE THE LOGARITHMIC TEMPERATURE AND RESISTIVITY SCALES.



From Bechgaard, K and Jerome, D., *Scientific American*

Summary of Requirements for Organic Metals and Superconductors

Planar π-donors and/or acceptors

Segregated stacks of π-donors and/or acceptors

Partial charging of **stacks** of π-donors and/or acceptors

The End of the Stack Tyranny: the Kappa Phase

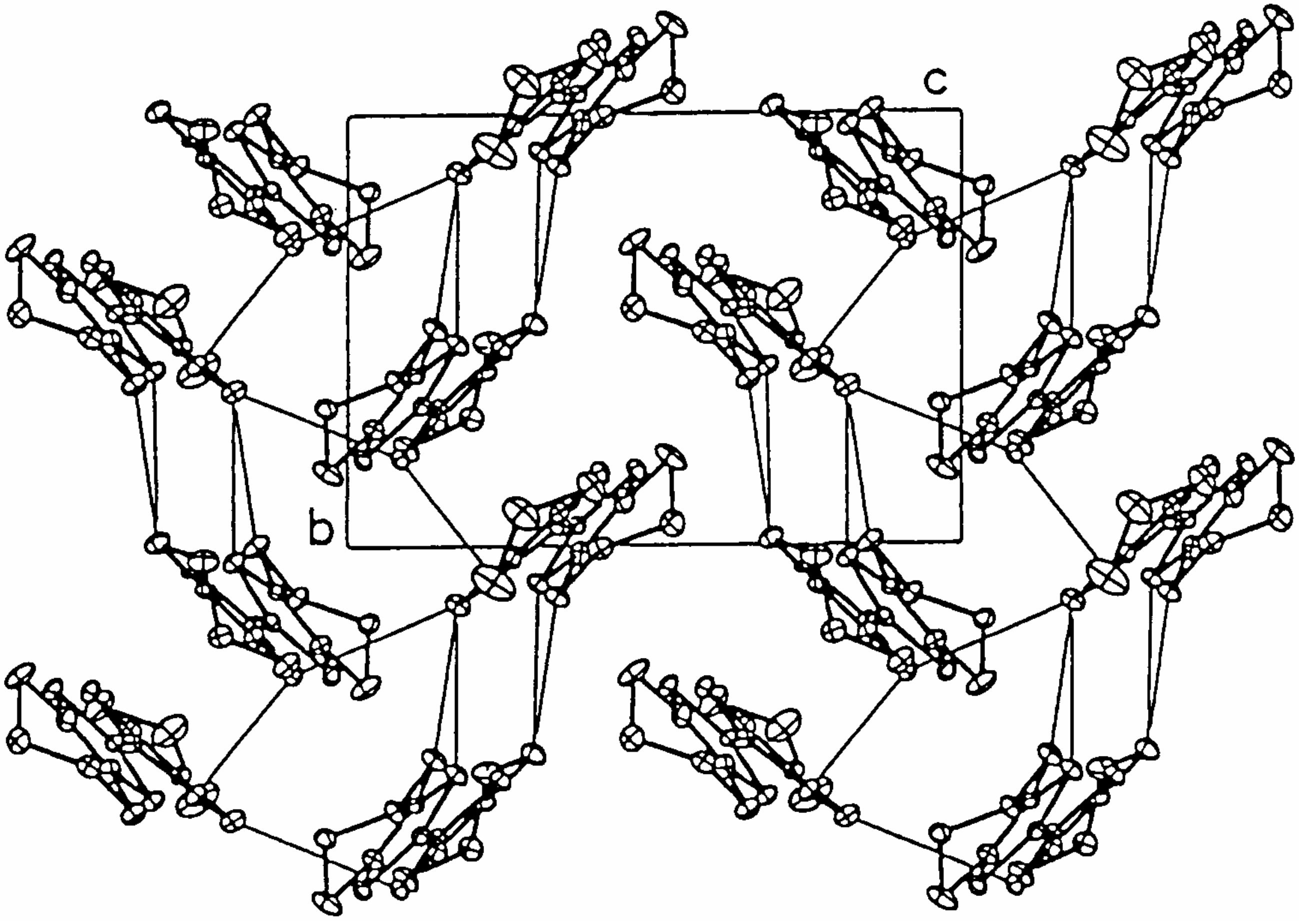


Figure 2.7 Structure of κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$] at 118 K. S ··· S contacts shorter than 3.6 Å are indicated by thin lines. (From Ref. 43.)

A Polymeric Anionic Layer

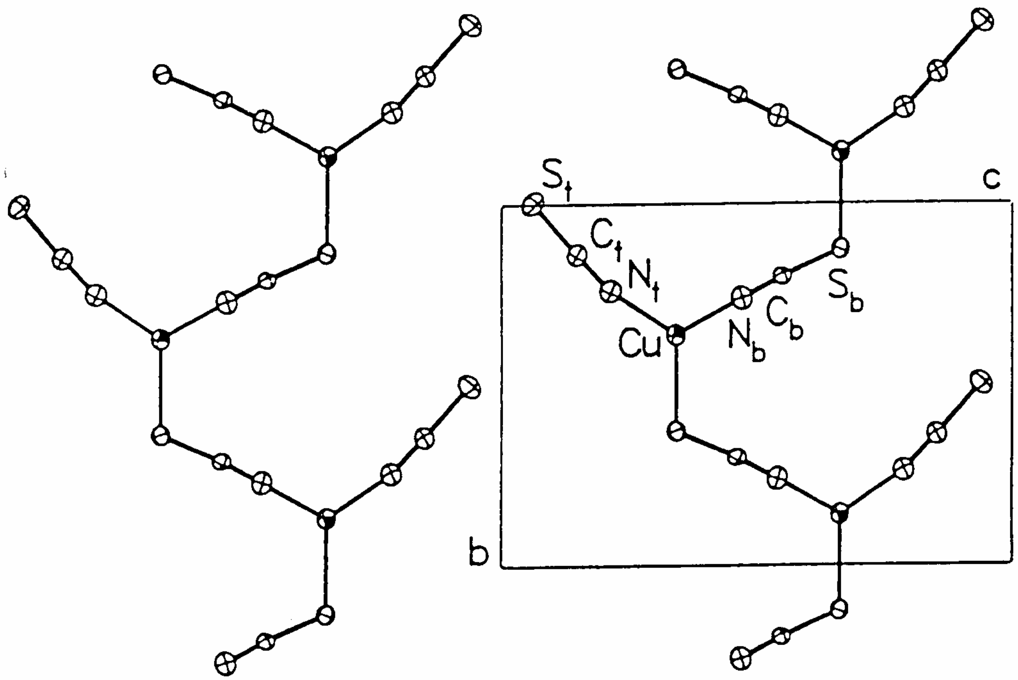


Figure 2.8 Polymeric $[Cu(NCS)_2]^-$ anion in κ-(BEDT-TTF)$_2$[Cu(NCS)$_2$]. (From Ref. 43.)

Other Organic Superconductors

Buckminsterfullerene-Derived Solids

BEDT-TTF, etc superconductivity WITH magnetism

Organic Conductors and Metals

Organic Superconductors

Conjugated Polymers for Organic Electronics

Organic Electronics: Organic Semiconductors

Polymeric Light Emitting Diodes (PLEDs)

Polymeric Photovoltaics (P-PVs)

Polymeric Electrochromics

Organic Light Emitting Diodes (OLEDs)

Organic Field Effect Transistors (OFETs, OTFTs)

Organic Memory Devices (OMDs)

Organic Semiconductors: Key Parameters

Semiconductor gap, Eg [E(π- π*)]

Relative HOMO vis a vis electrode material

Relative LUMO vis a vis electrode material

Nature of the charge-carrier (h$^{(+)}$ or e$^{(-)}$)

Charge-carrier mobility (μ)

Processing and morphology

Conjugated Polymers in 1987

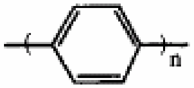
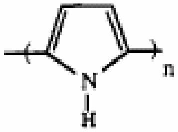
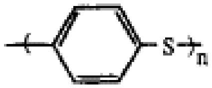
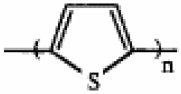
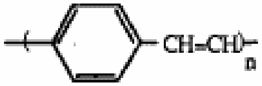
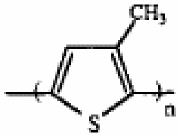
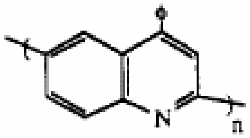
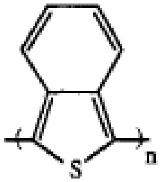
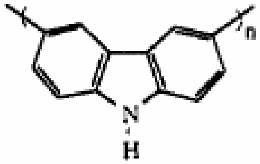
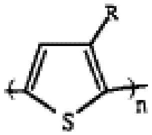
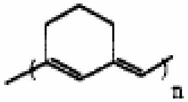
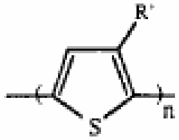
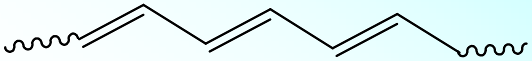
Polymer	Structure	Polymer	Structure
polyacetylene (PA)		Polyparaphenylene (PPP)	
Polypyrrole (PP)		Polyparaphenylene Sulfide (PPS)	
Polythiophene (PT)		Polyparaphenylene vinylene (PPV)	
Poly-3 methyl thiophene (P3MT)		Polyquinoline (PQ)	
Polyisothianaphene (PITN)		Polycarbazole (PCB)	
Poly-3 alkylthiophene R= Butyl P3BT R= Ethyl P3ET		Poly (1,6-heptadiyne) (PHT)	
Poly-3 alkylsulfonate R'= $CH_2CH_2SO_3Na$ (P3ETSNa) R= $(CH_2)_4SO_3Na$ (P3BTSNa)			

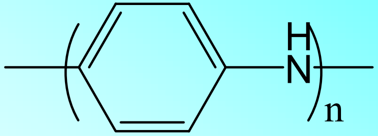
Figure 1. The principal conducting polymers.

The Most Popular Conjugated Polymers

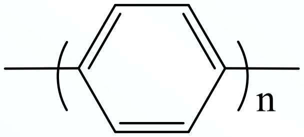


(CH)x

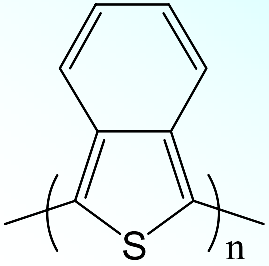
PA



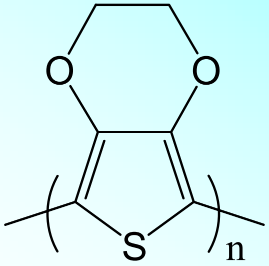
PANI



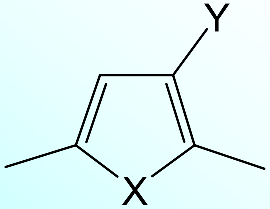
PPP



PITN

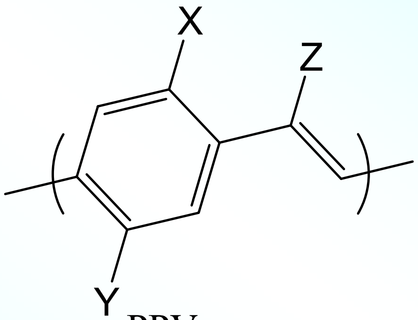


PEDOT

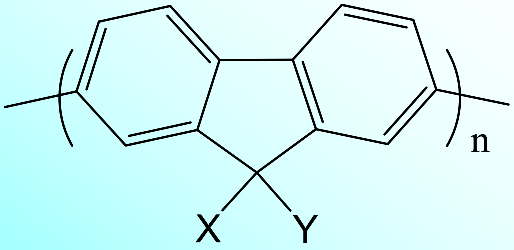


X = S, NH, NR; Y = H, R, Ph, etc

PT, PPy, etc

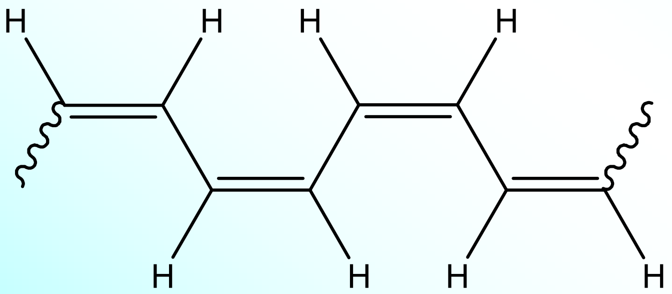


PPVs

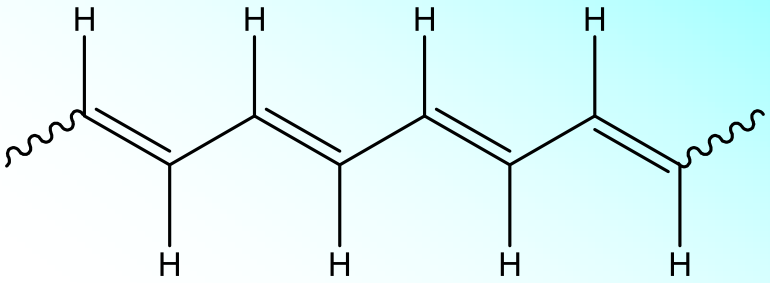


PFs

The Two Configurations of PA



cis



trans

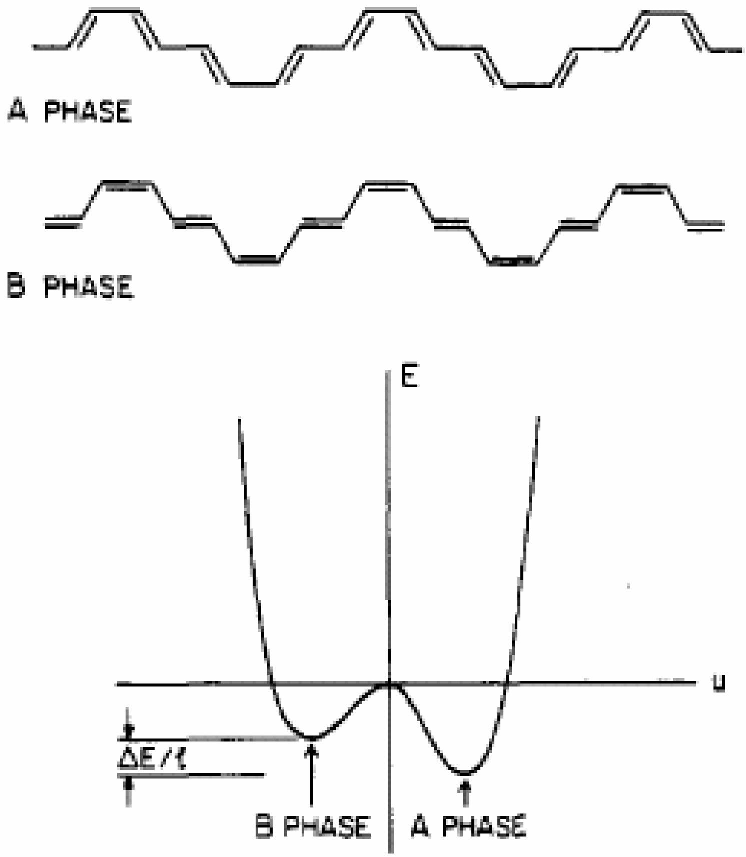
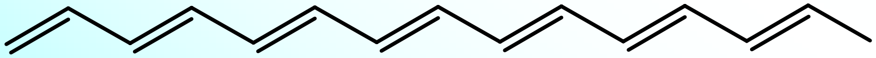


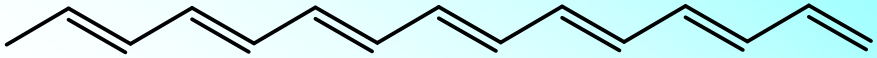
Figure 31. Schematic diagram of polythiophene backbone structure leaving out the sulfur atoms (see Figure 2). The two configurations (A phase and B phase) are nearly (but not precisely) degenerate as shown in the diagram at the bottom of the figure, where we plot energy against the distortion parameter, u ($u = 0$ when the bond lengths are equal).

Optical Properties of Conducting Polymers. Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88,* 183–200

The Degenerate Ground State of PA



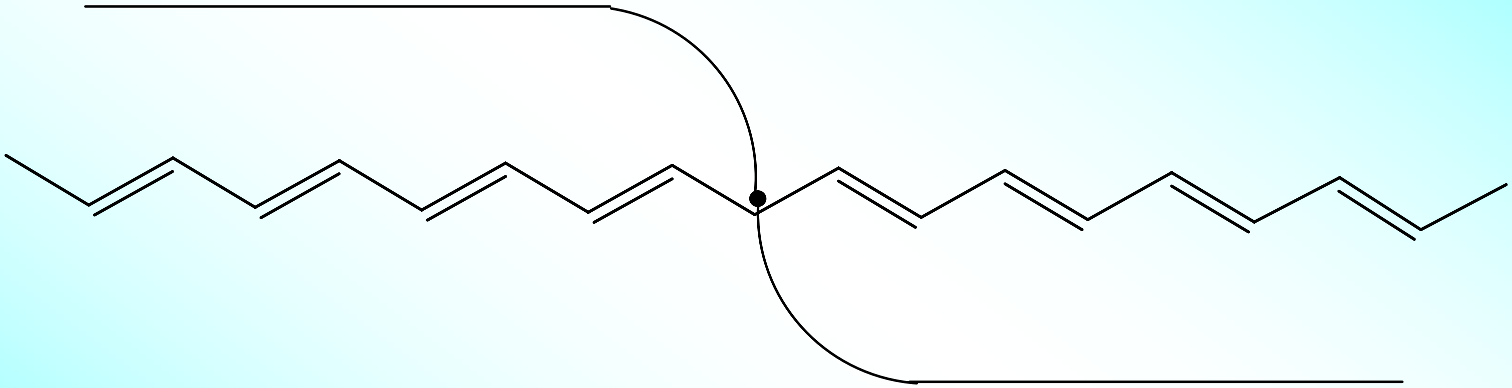
A



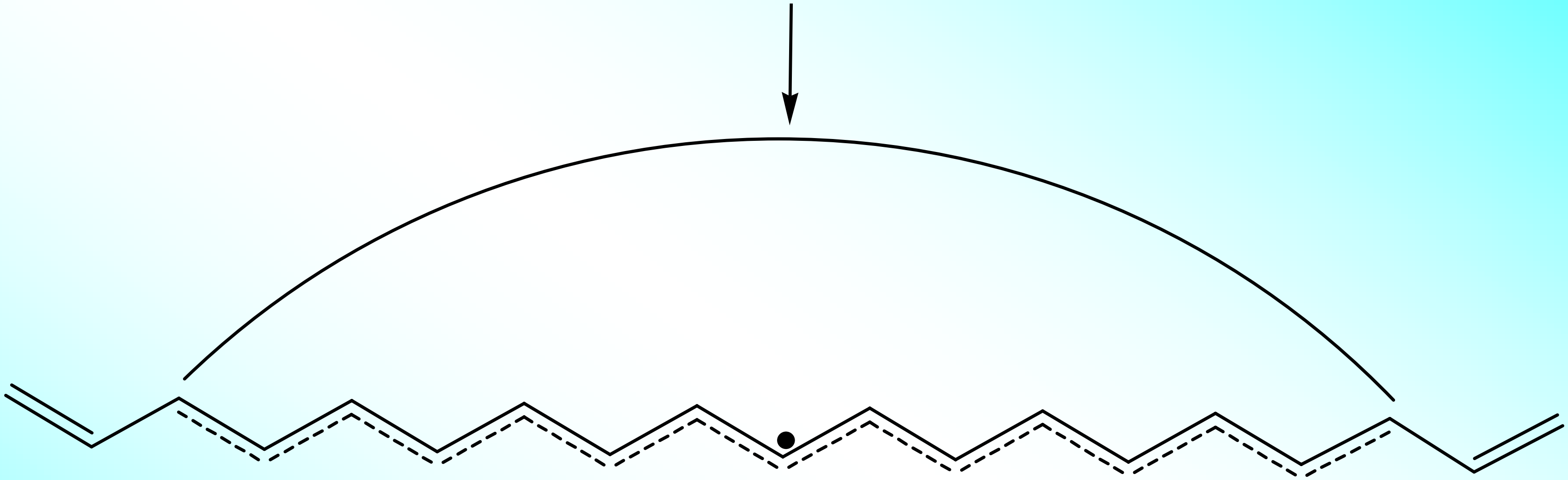
B

$$\mathbf{E}_A = \mathbf{E}_B$$

The Soliton Symmetry of a “Defect” in PA



The Neutral Soliton



Maximum bond equalization

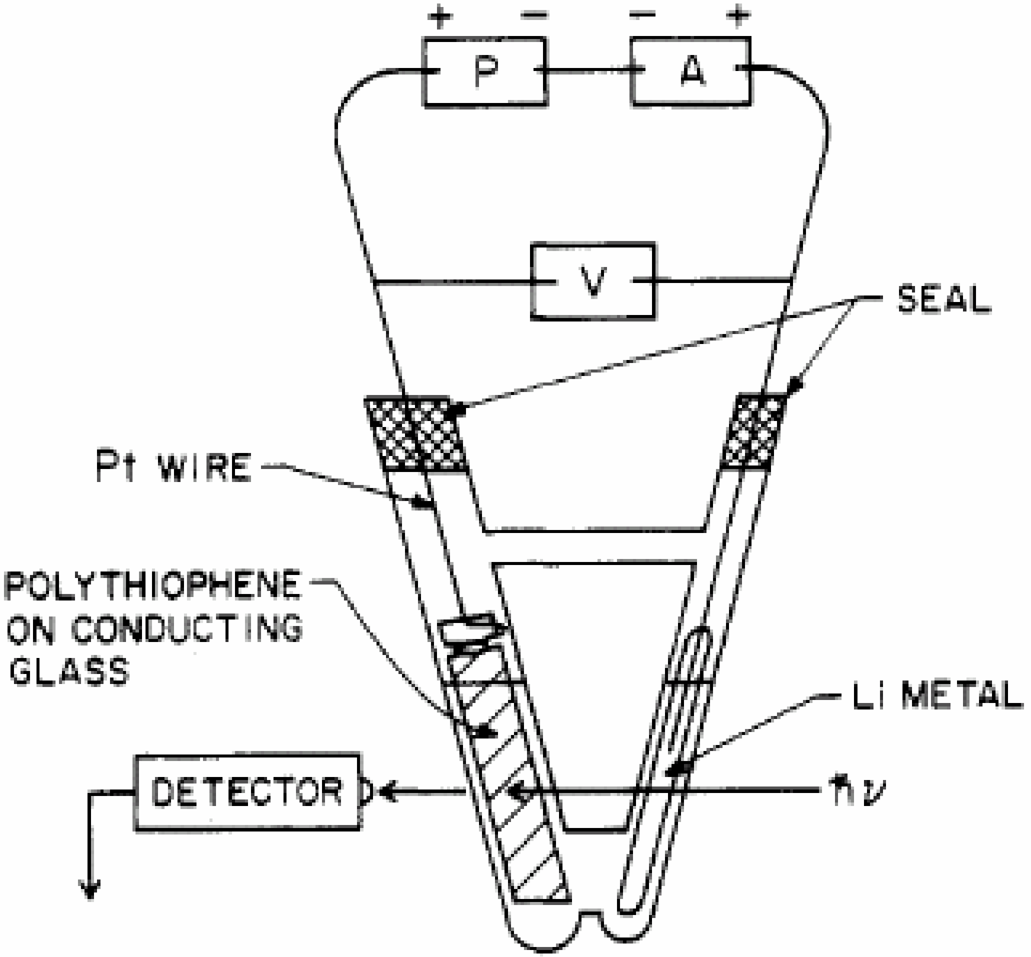


Figure 4. Diagram of apparatus used for in situ visible–IR absorption measurements during electrochemical doping.

Optical Properties of Conducting Polymers. Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88,* 183–200

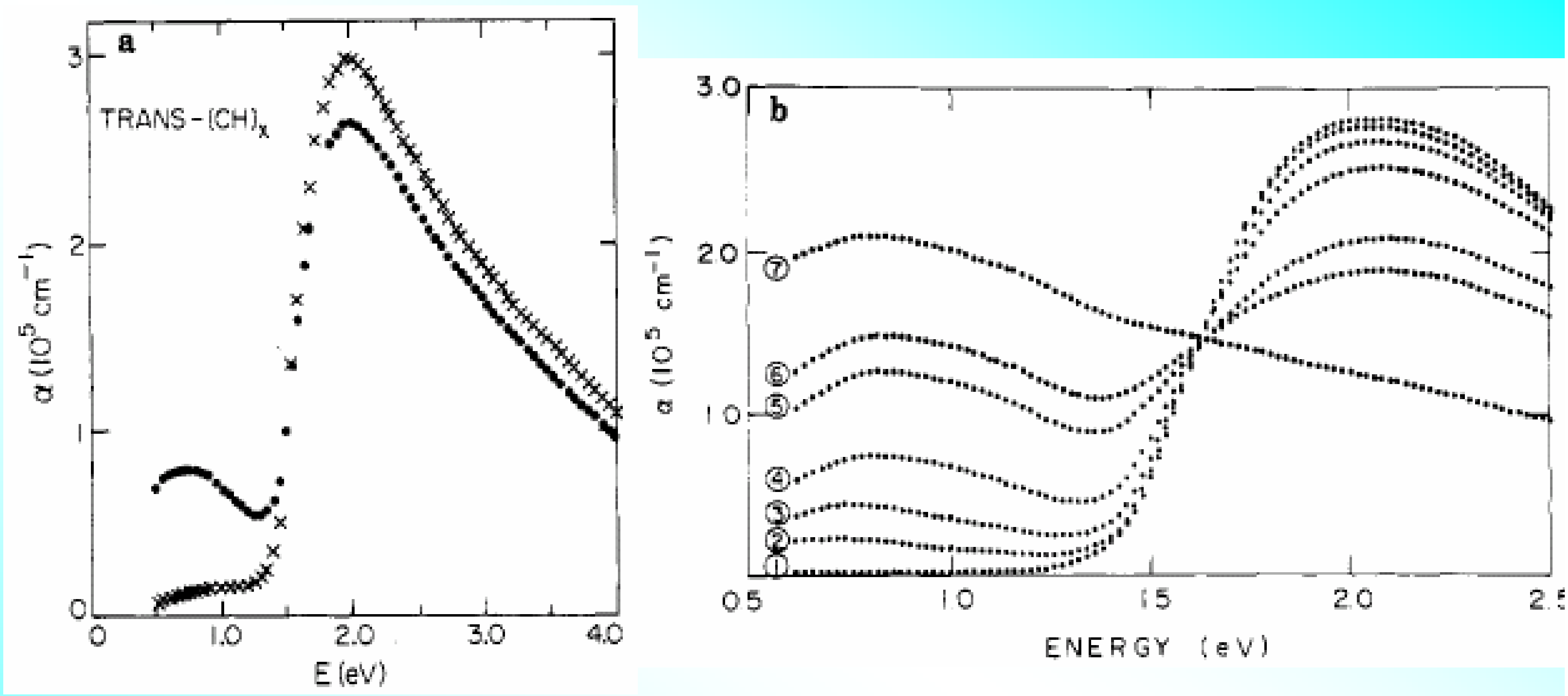


Figure 5. (a) Absorption coefficient of *trans*-$(CH)_x$: (×) before doping; (●) after doping to a fraction of a percent by exposure to AsF_5 vapor. See ref 37. (b) In situ absorption curves for *trans*-$(CH)_x$ during electrochemical doping with ClO_4^-. The applied cell voltages (relative to Li) and corresponding concentrations are as follows: curve 1, 2.2 V ($y = 0$); curve 2, 3.28 V ($y \approx 0.003$); curve 3, 3.37 V ($y \approx 0.0065$); curve 4, 3.46 V ($y \approx 0.012$); curve 5, 3.57 V ($y \approx 0.027$); curve 6, 3.64 V ($y \approx 0.047$); curve 7, 3.73 V ($y \approx 0.078$). See ref 24.

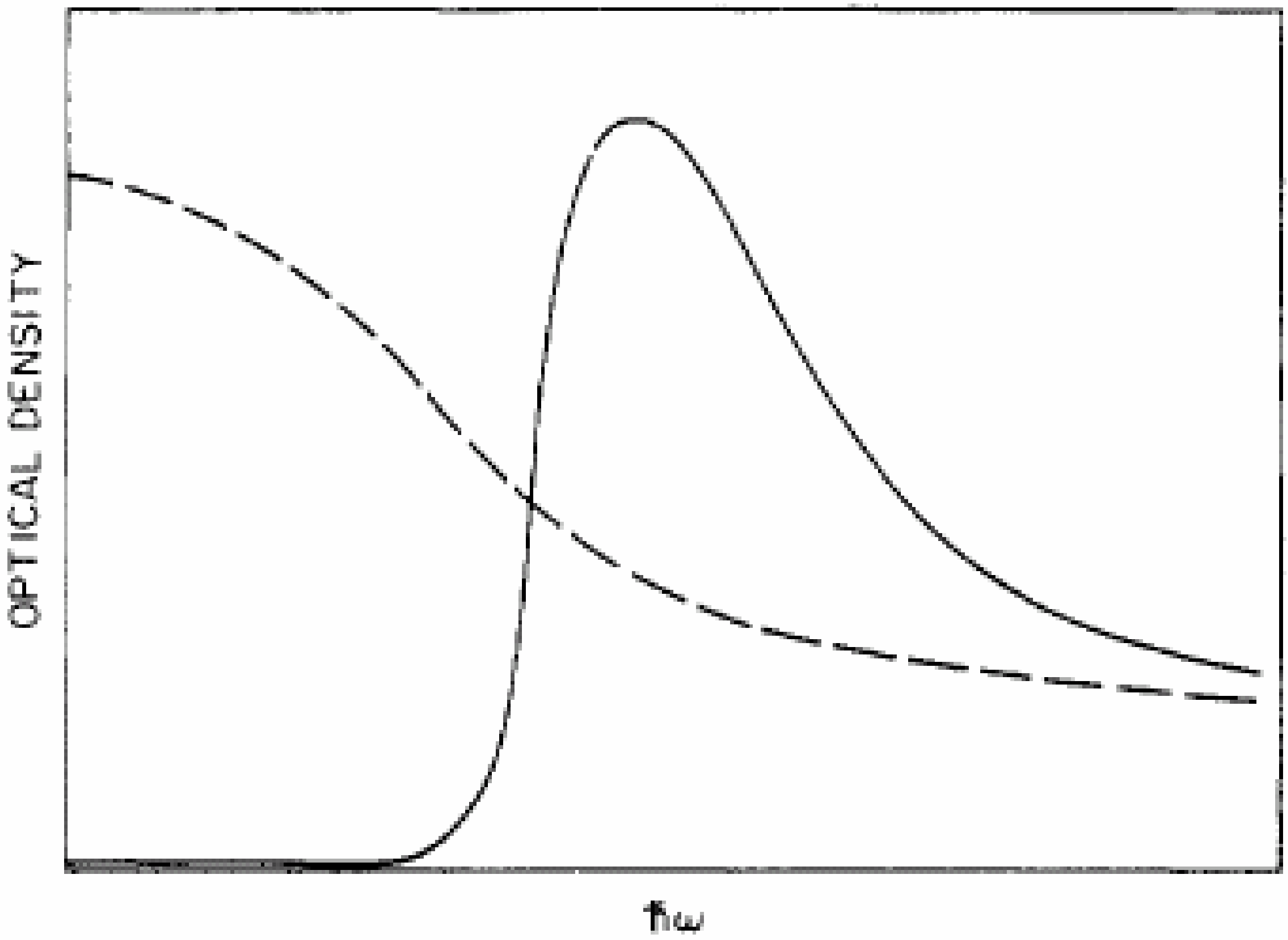


Figure 3. Schematic diagram of optical density of a conducting polymer as a function of photon energy. Solid curve, neutral polymer (semiconductor), which is transparent for $\hbar\omega < E_g$; dashed curve, heavily doped polymer (metallic).

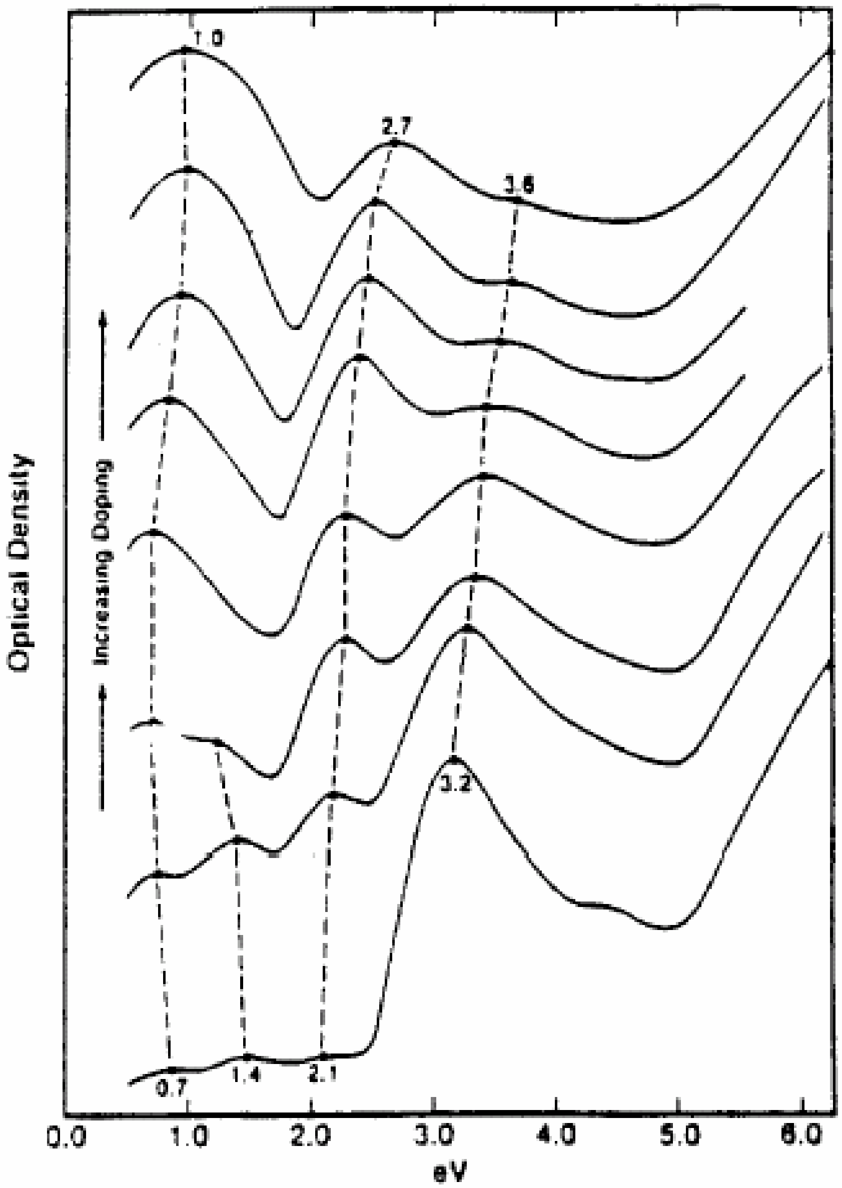


Figure 7. Optical absorption spectra of ClO_4^--doped polypyrrole as a function of dopant concentration. The dopant level increases from the bottom curve (almost neutral polypyrrole) to the top curve (33 mol % doping level).

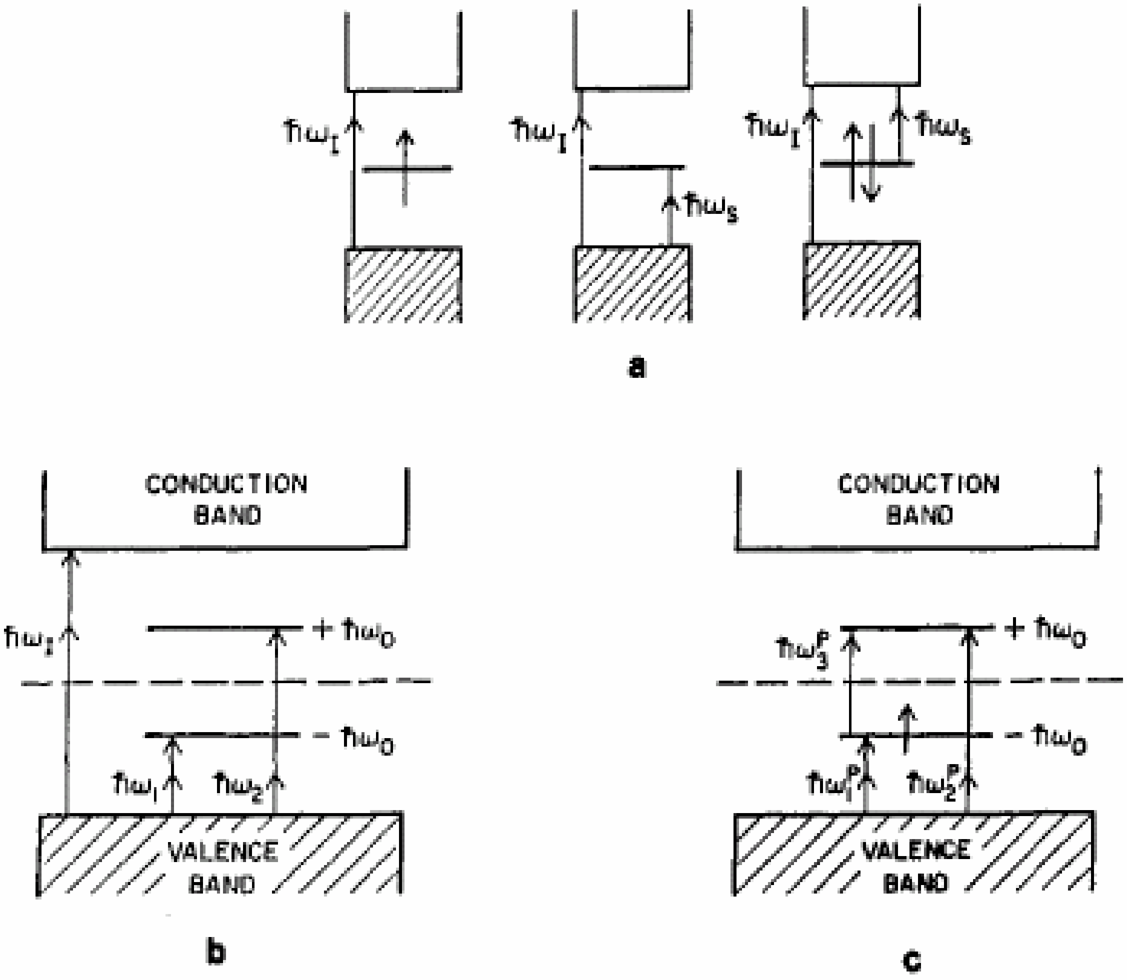
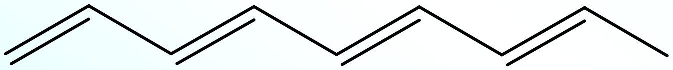
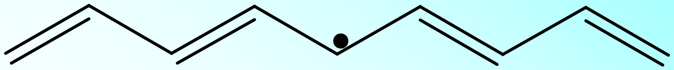


Figure 30. (a) Energy level diagram of the midgap state associated with the soliton where $\hbar\omega_I = 2\Delta$ is the interband transition and $\hbar\omega_S = \Delta$ is the midgap transition; left, neutral soliton; center, positive soliton; right, negative soliton. (b) Energy level diagram for a charged (positive) bipolaron. Because of the splitting of the levels, there are two possible transitions in addition to $\hbar\omega_I$. (c) Energy level diagram for a charged (positive) polaron. Because of the additional occupancy by the unpaired spin, there is an additional transition ($\hbar\omega_3{}^P$).

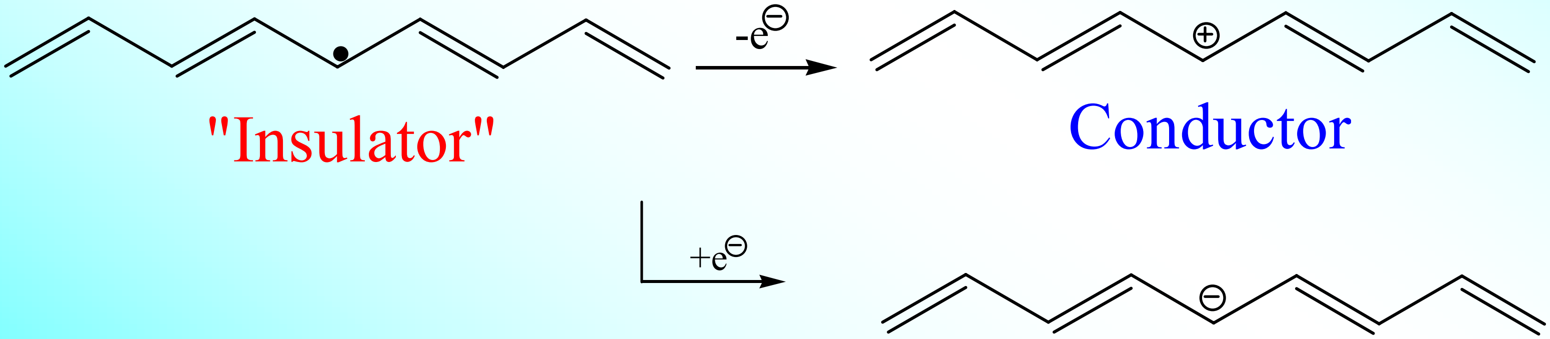
The Purported Coducting and Insulating States of Poly(acetylene)



Ideal



Real

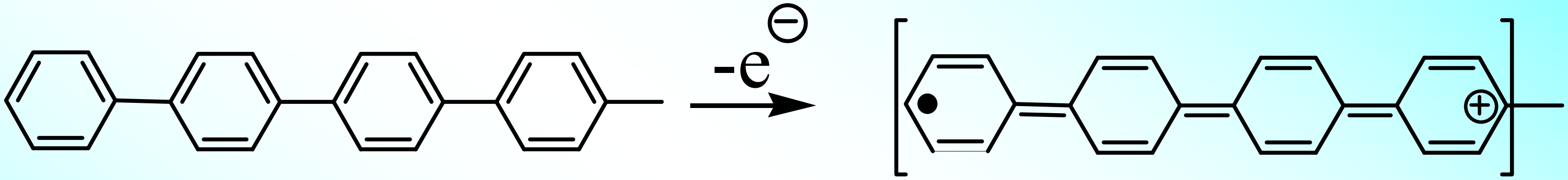


"Insulator"

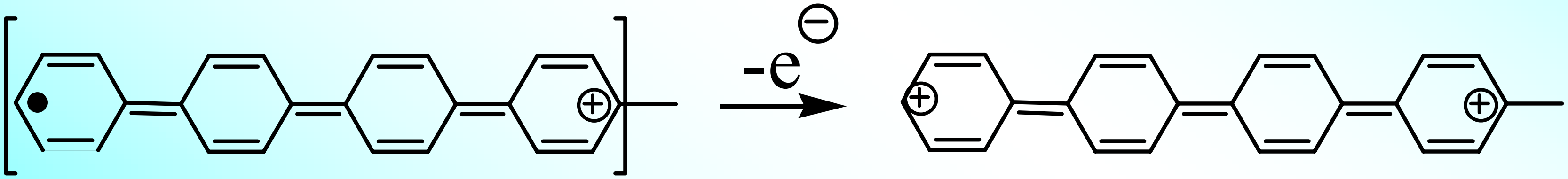
Conductor

Conductor

Conductivity Through Bipolarons (Dications)



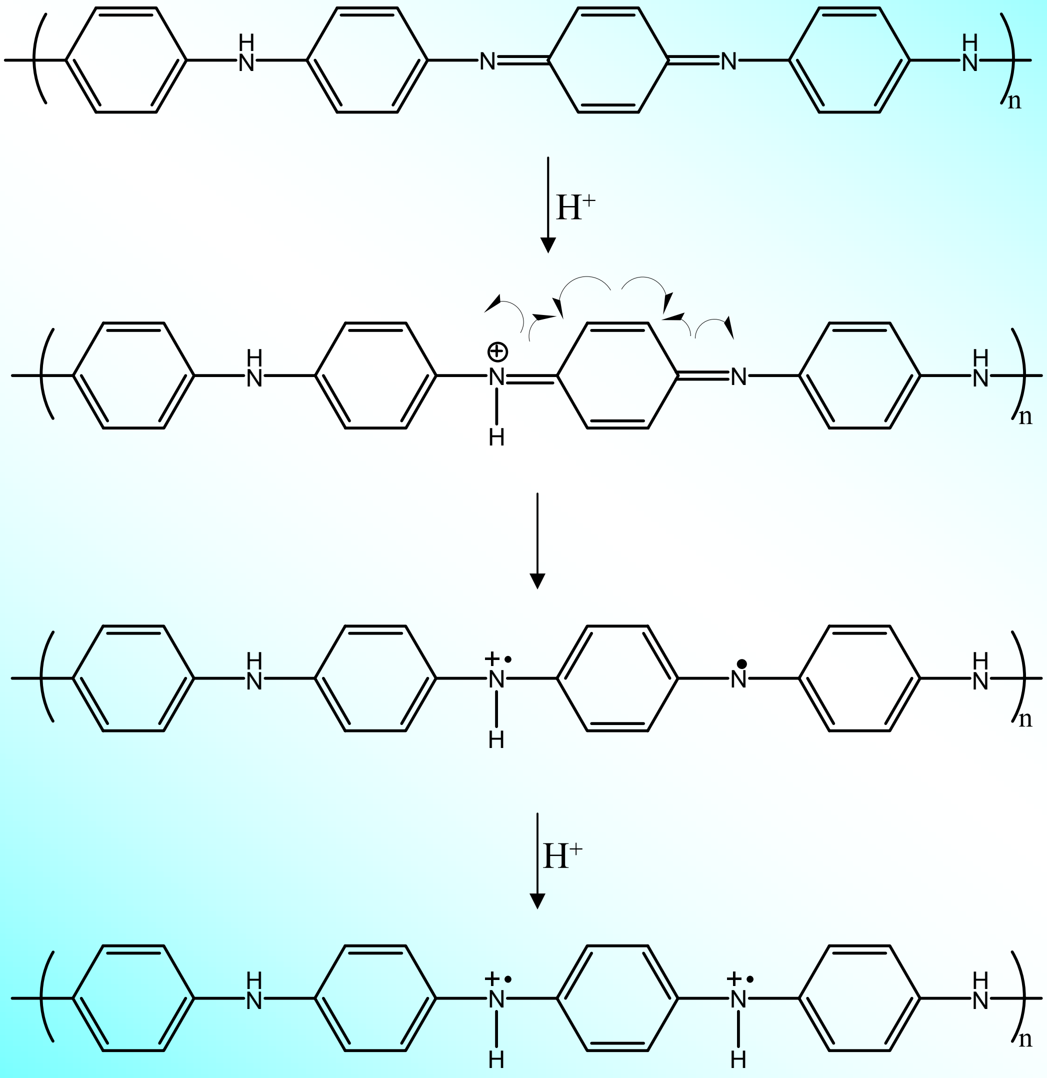
Conductor



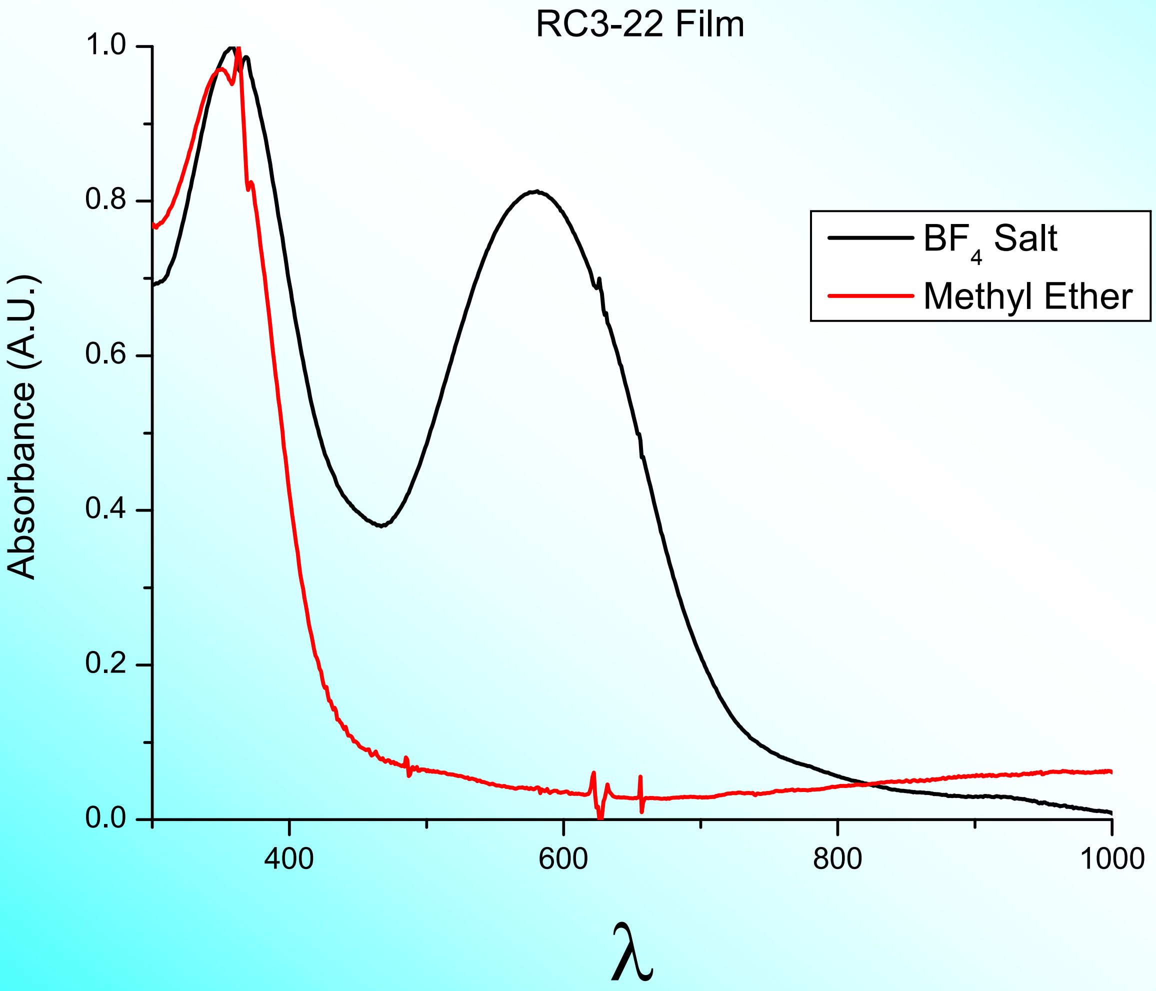
Conductor

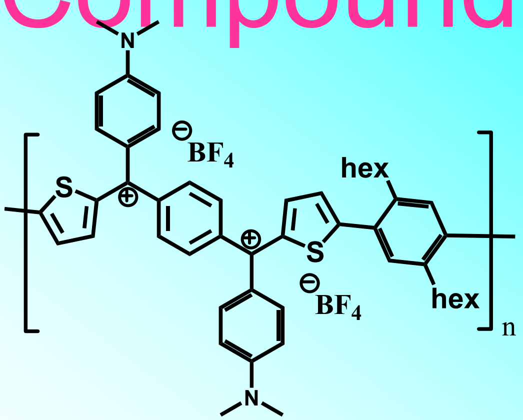
Conductor

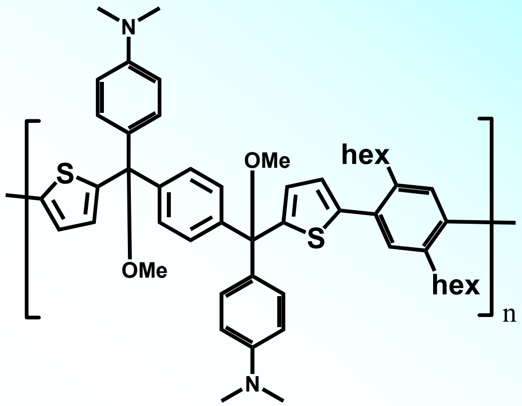
Polyaniline
Proton-Induced Spin Unpairing Mechanism



Another Proteochromic Compound

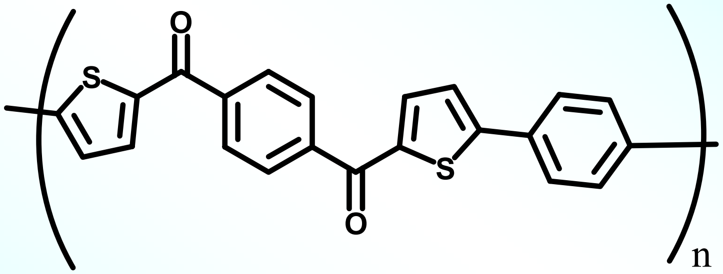




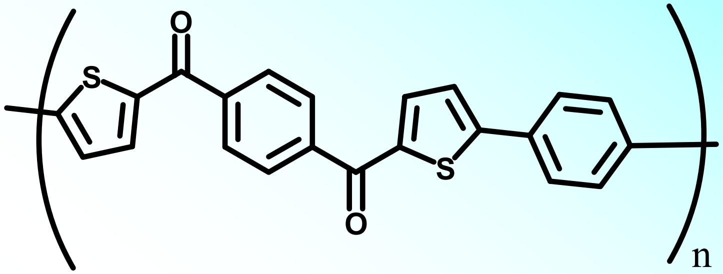


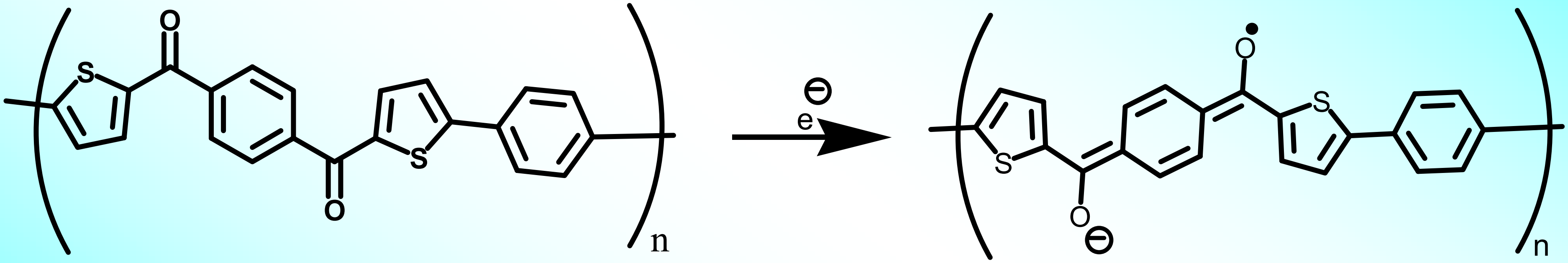
Ryan Chiechi

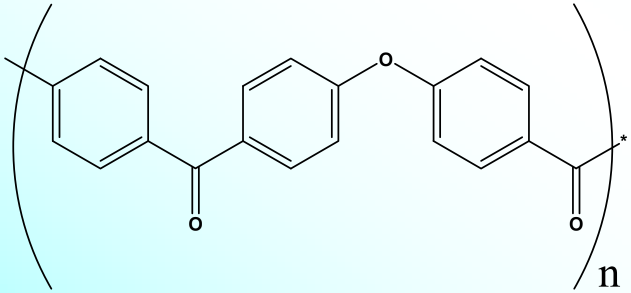
Polyphenylthiophene Ketone (PPTK)



Backbone Ketones for Robust n-Dopable Polymers

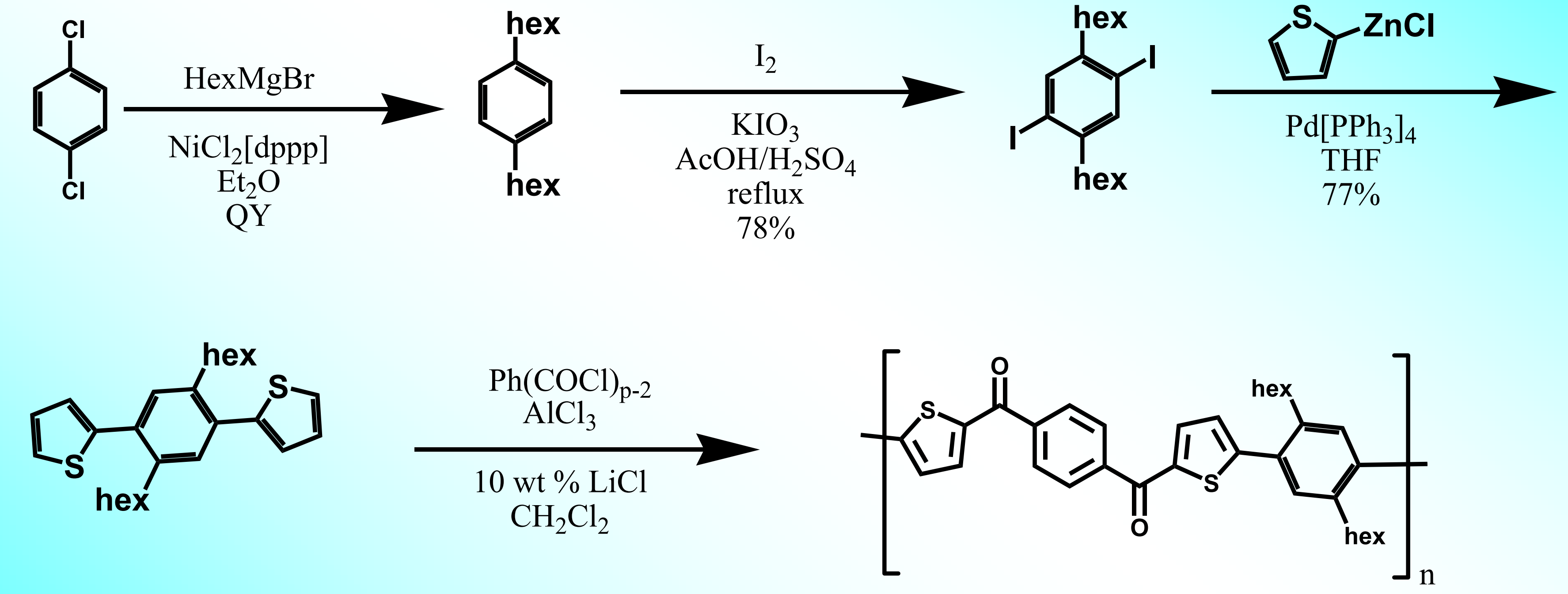




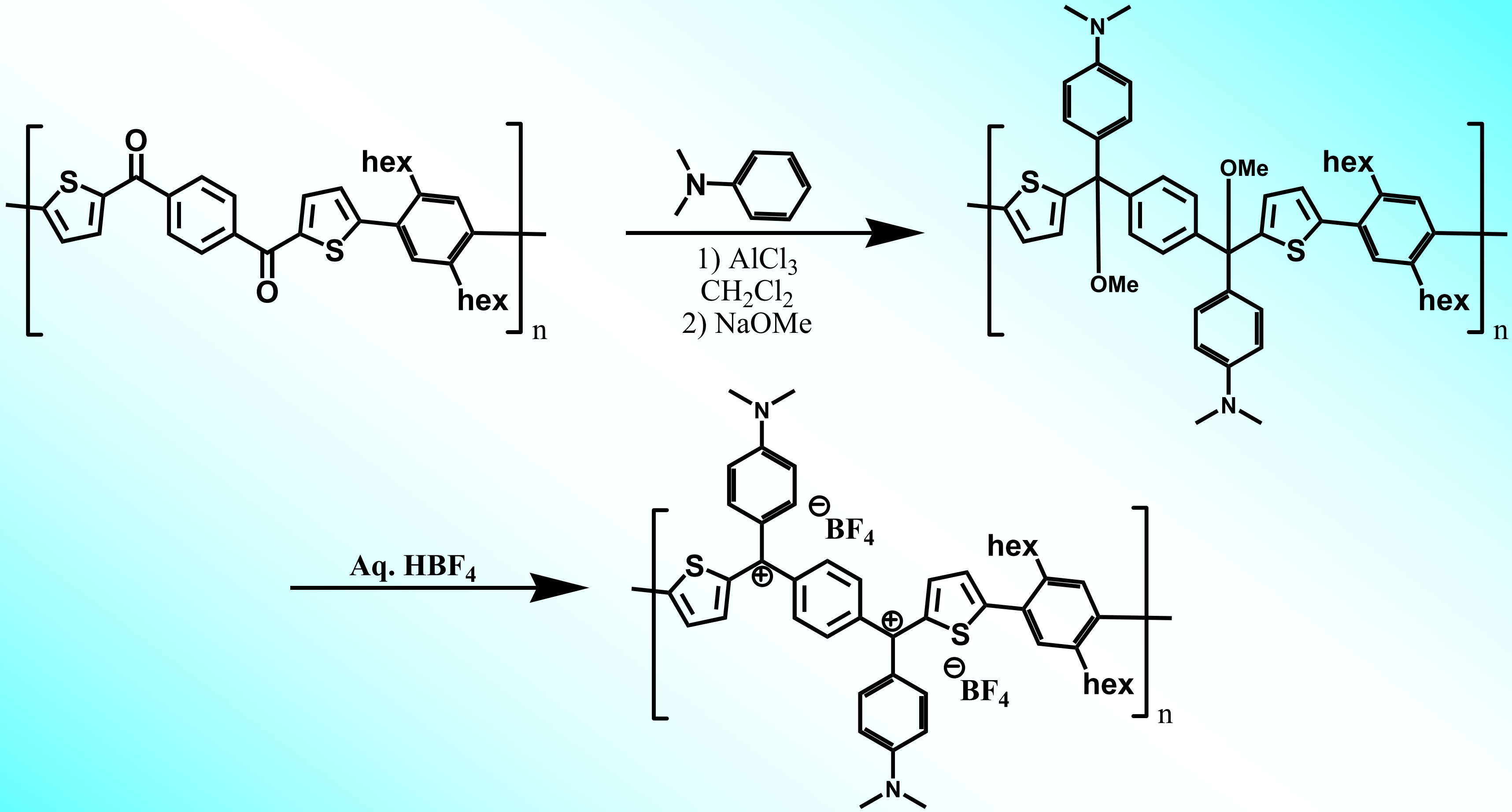


PEK and PEEK, high-performance polymers

Synthesis via Friedel-Crafts Polymerization



Cation Formation



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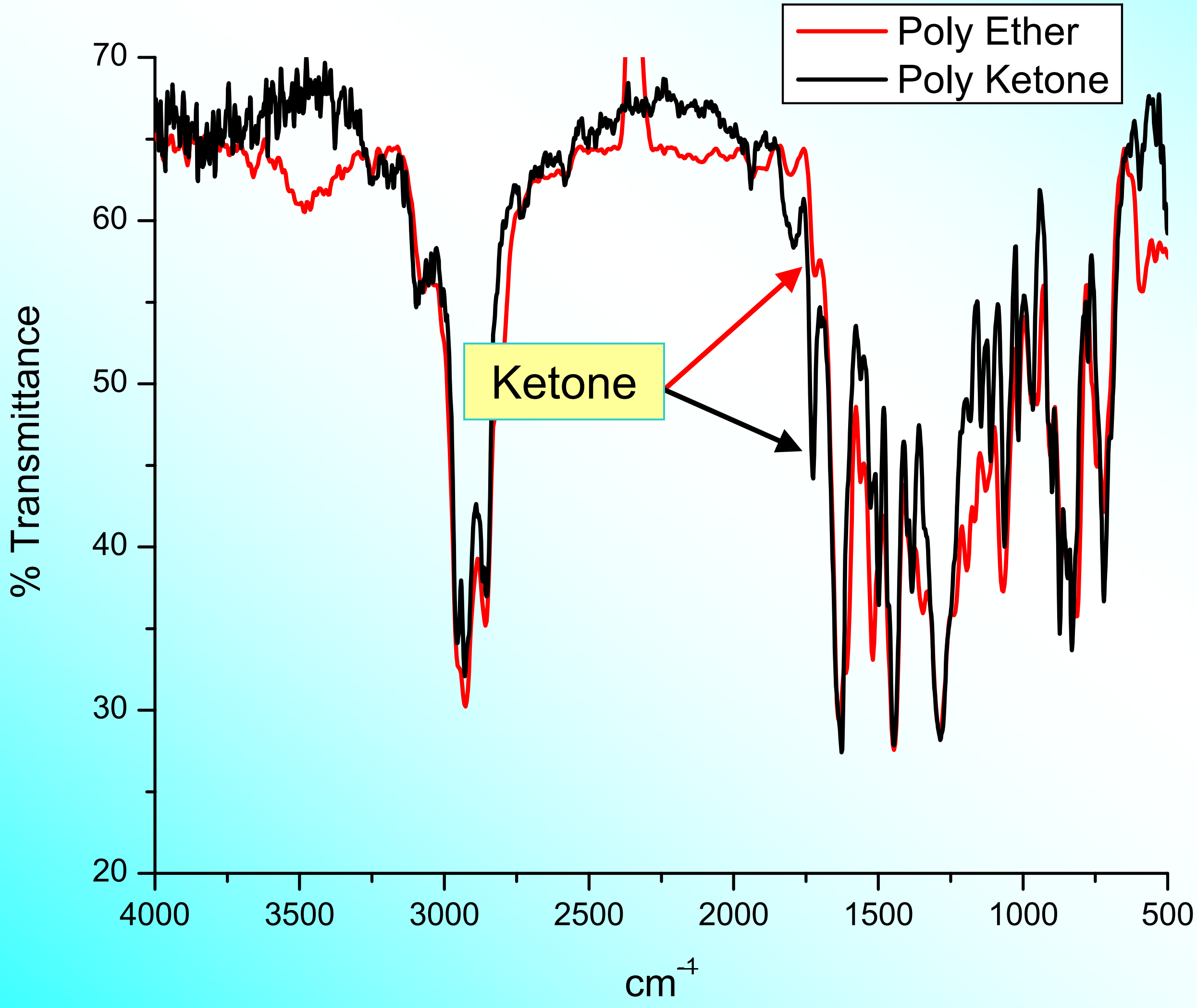
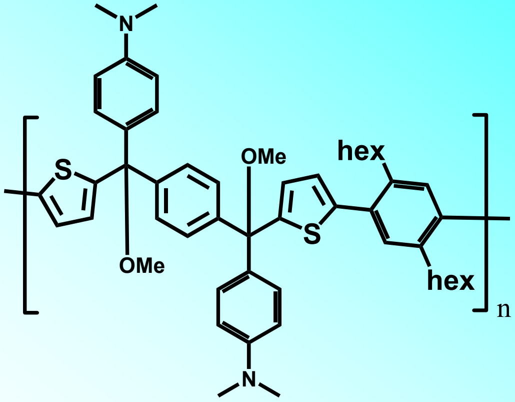
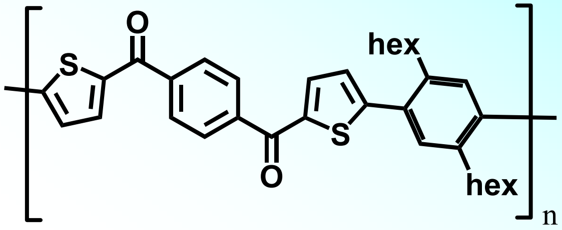
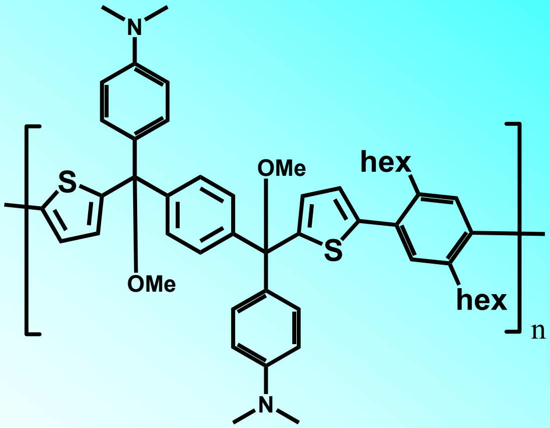
Ketone Conversion

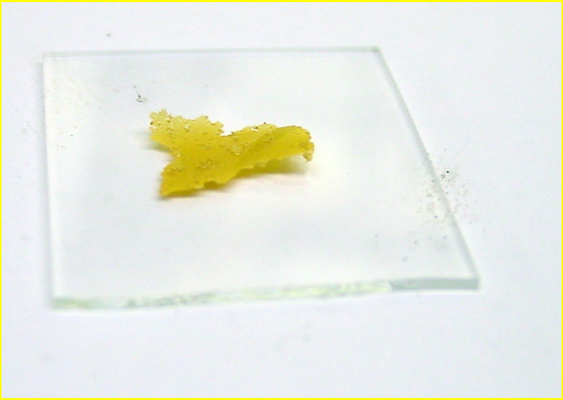




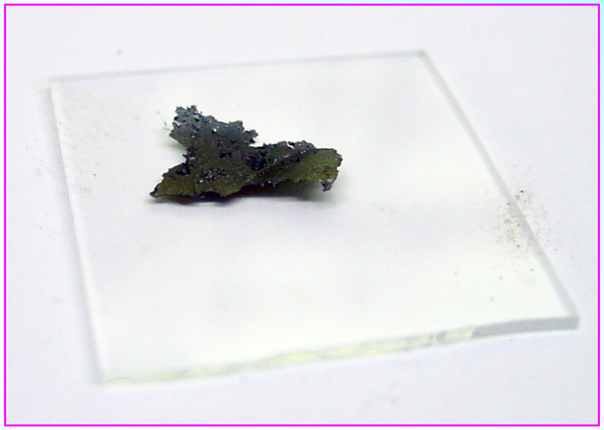


Cation Formation

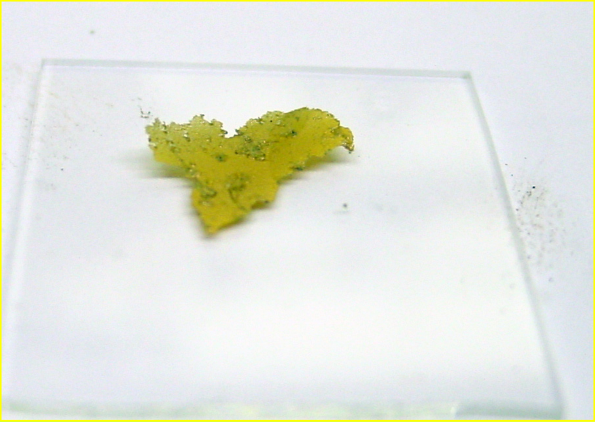




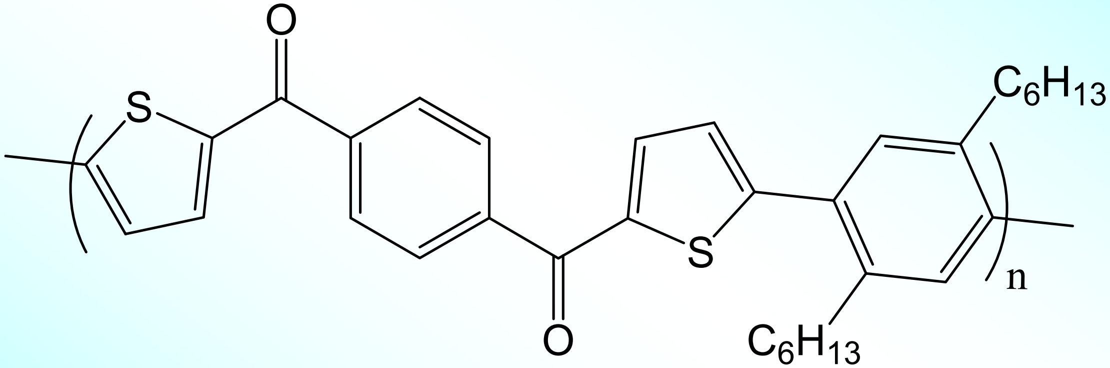
HCl Gas



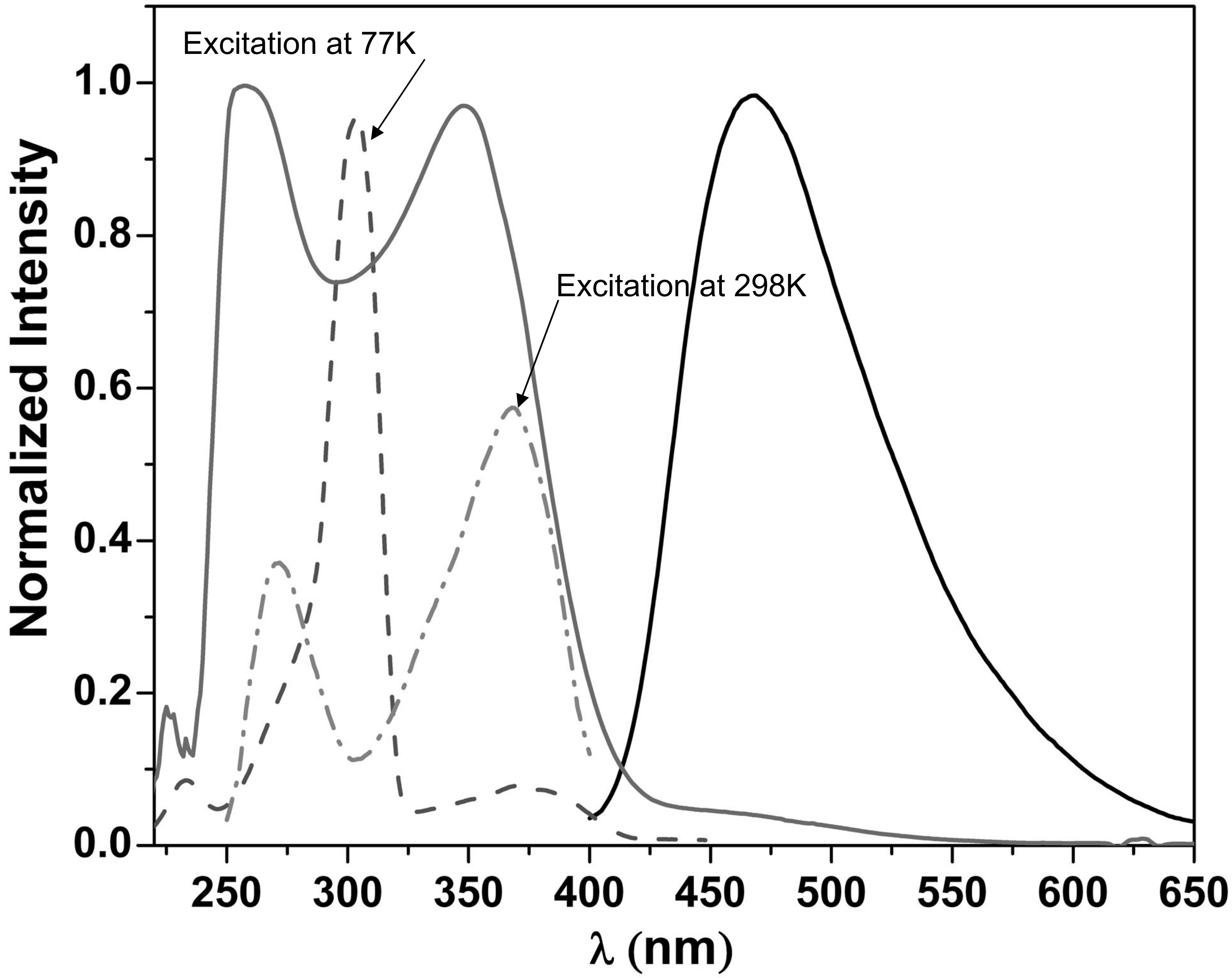
NH_3 Gas



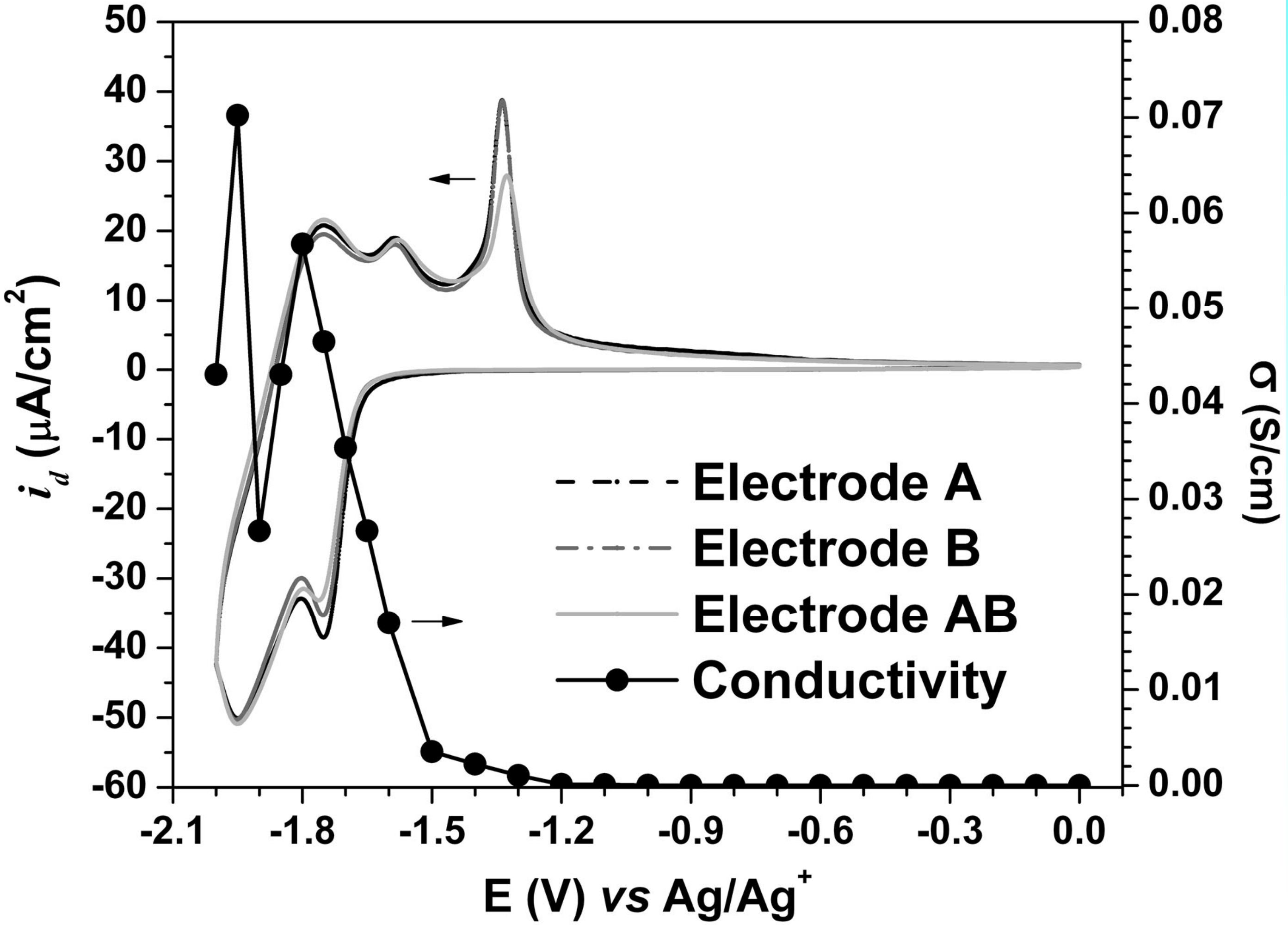
Other Properties of the Poly(ketone)



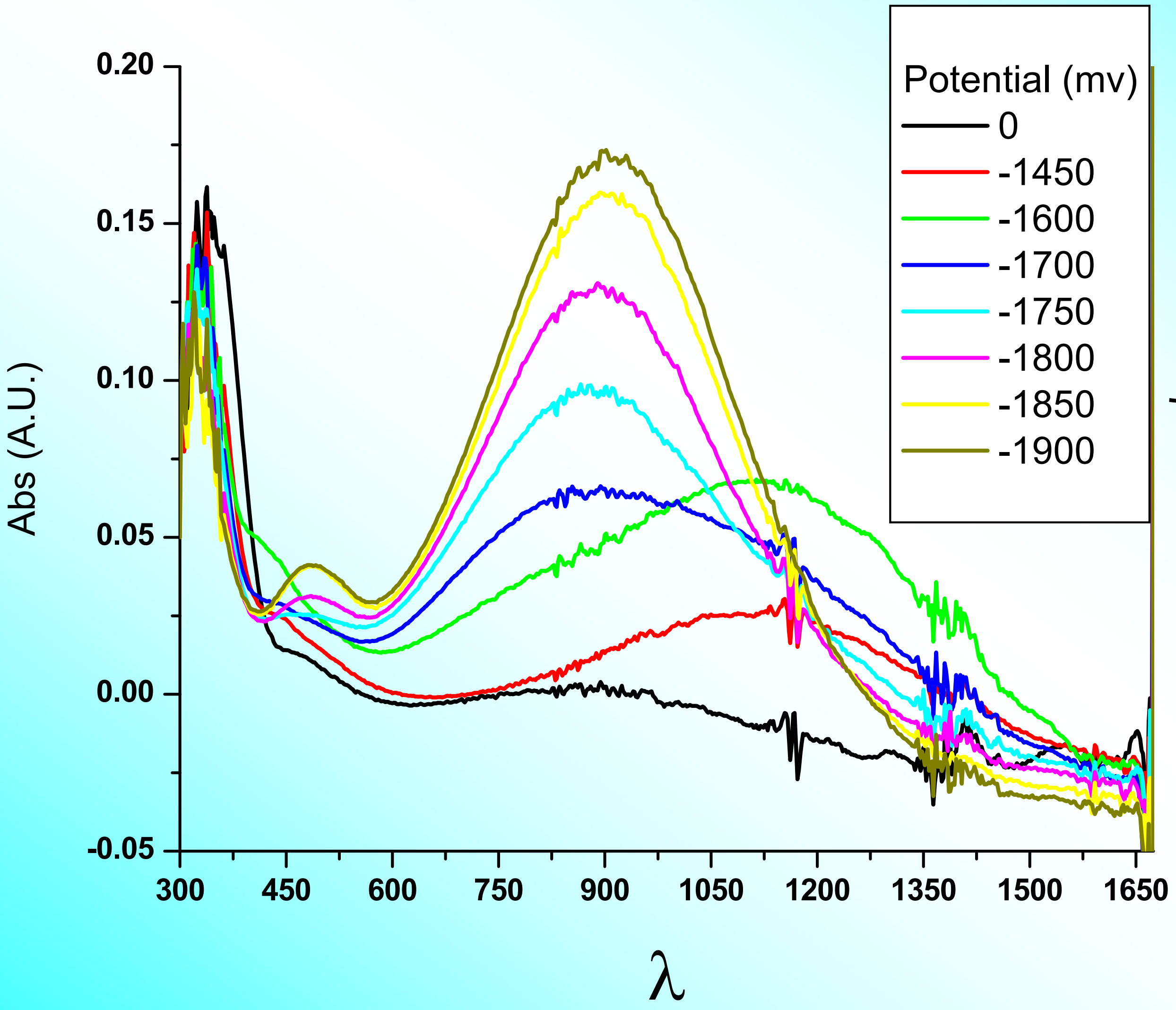
Photophysics

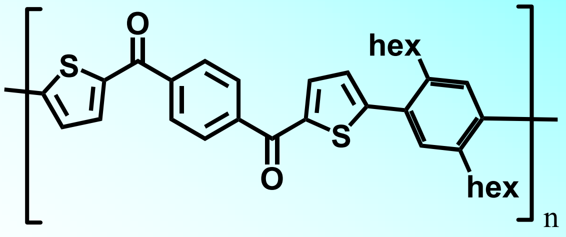


In situ n-Doped Conductivity Measurement

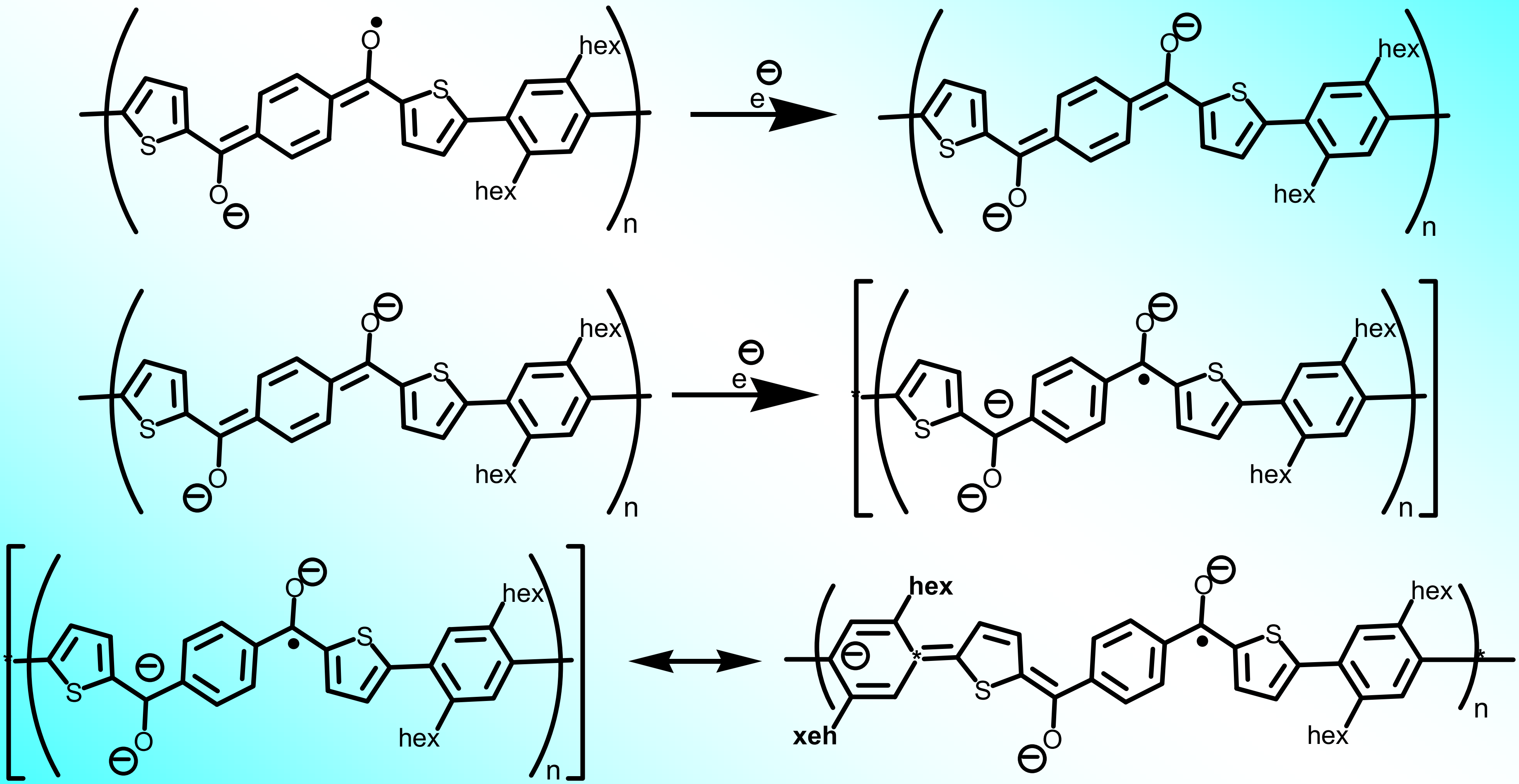


n-Doping Spectroelectrochemistry





Possible Explanation of Conductivity as a Function of *n*-Doping



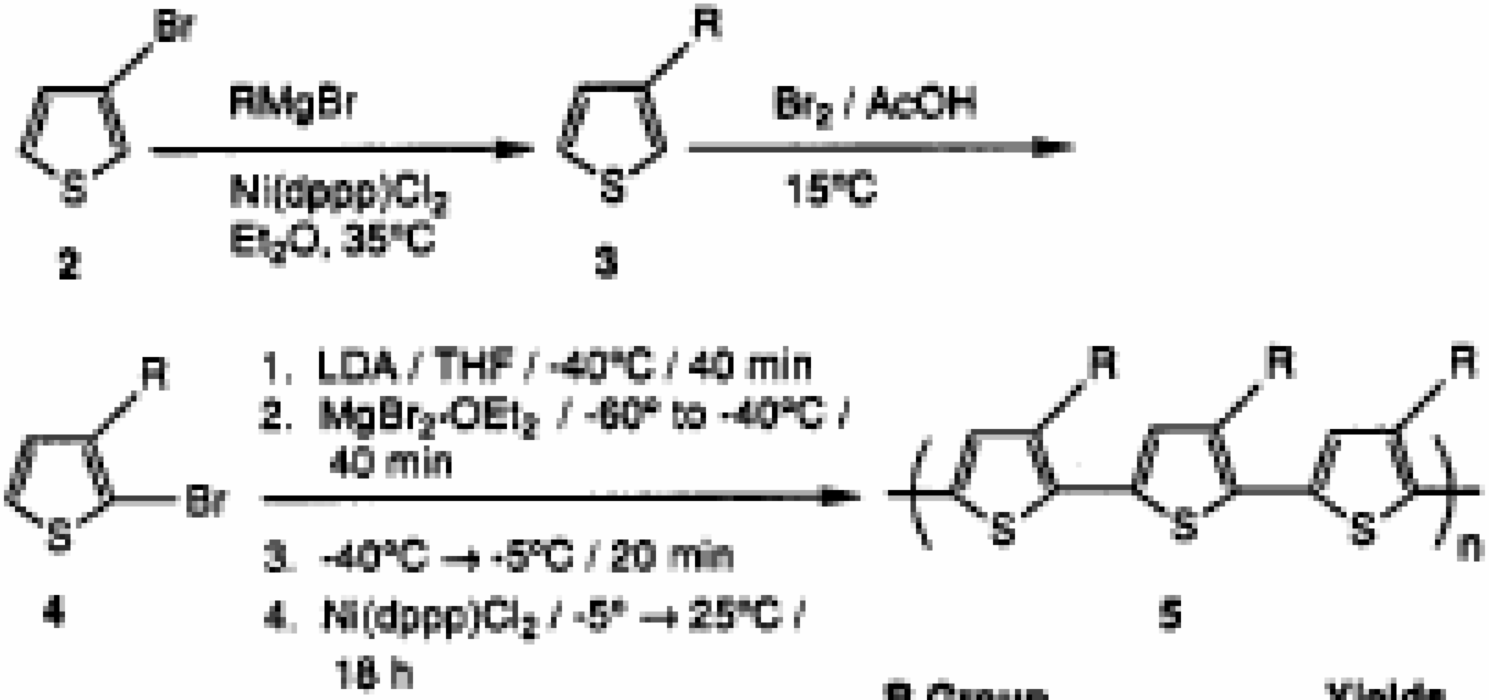
Conclusions:

✓**A high-performance, structural polymer is a robust** *n-dopable* **conducting polymer**

✓ ***n*-Over "doping" creates a conductor from a Mott insulator**

Finally Stereochemistry

Scheme I. Regioselectivity Synthesis of Poly(3-alkylthiophenes)



R Group	Yields
a: *n*-Butyl	69%
b: *n*-Hexyl	36%
c: *n*-Octyl	65%
d: *n*-Dodecyl	33%

Richard D. McCullough,' Renae D. Lowe, Manikandan Jayaraman, and Deborah L. Anderson *J. Org. Chem.* **1993**, *58*, 904-912

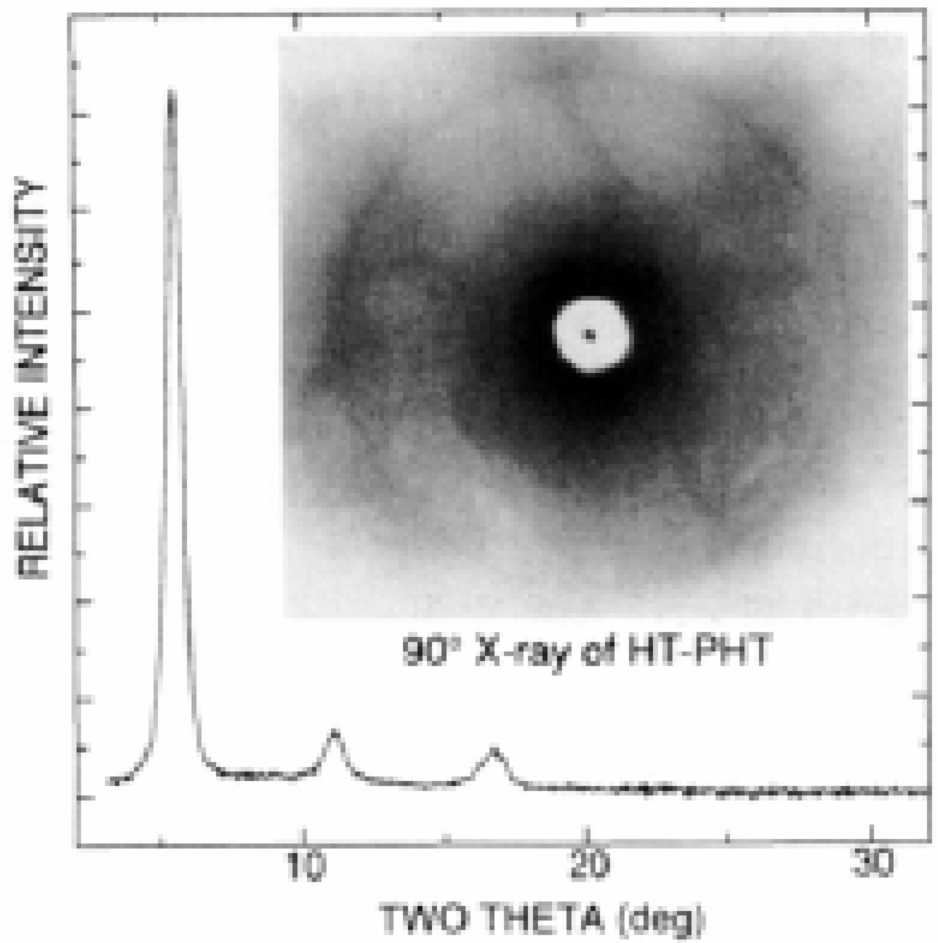


Figure 1. X-ray diffraction pattern of a cast head-to-tail poly(3-hexylthiophene), on a 70-μm coverslip, from scans of intensity of vs 2θ. Inset: X-ray film data taken at a 90° angle of incidence to the coverslip.

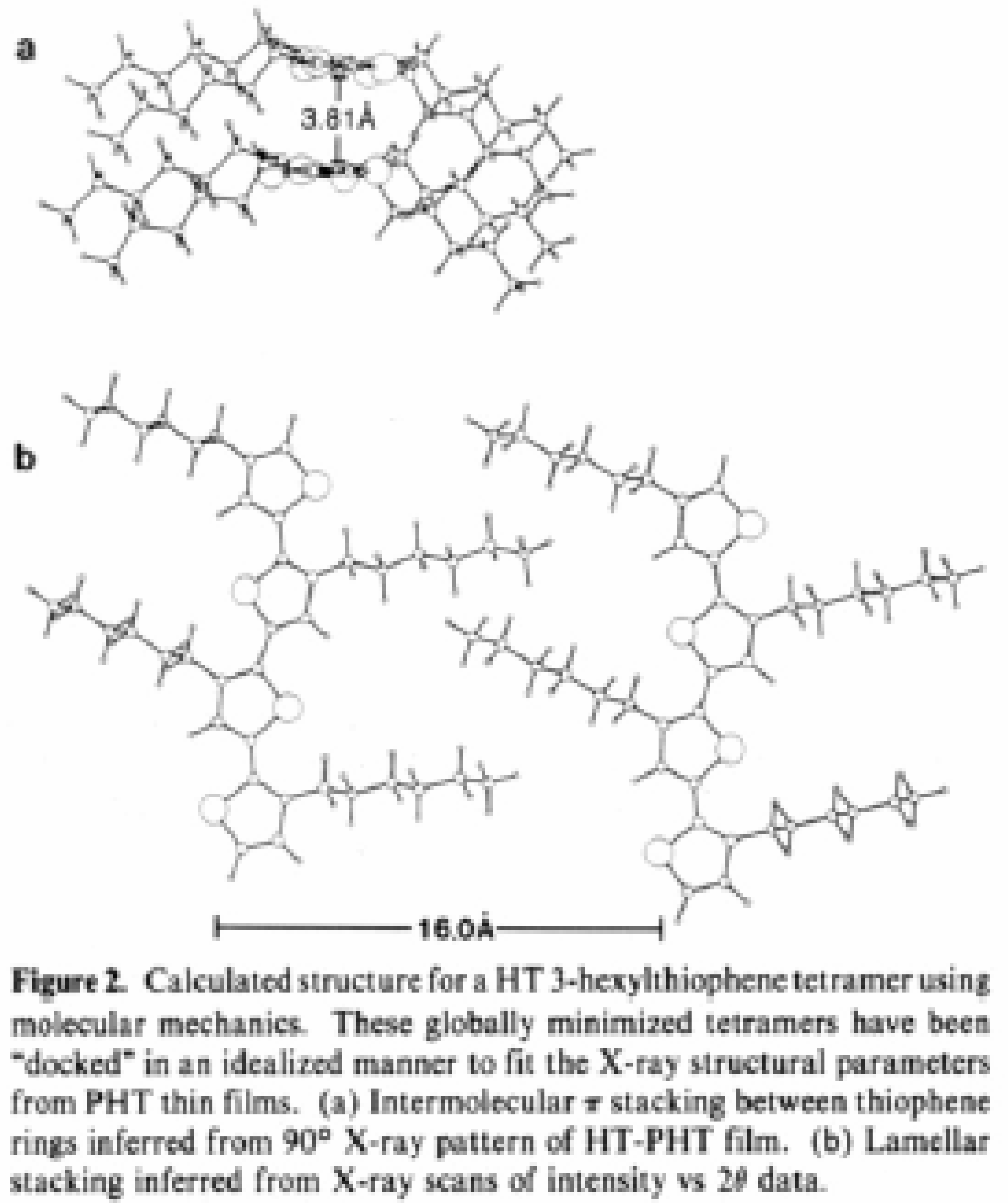


Figure 2. Calculated structure for a HT 3-hexylthiophene tetramer using molecular mechanics. These globally minimized tetramers have been "docked" in an idealized manner to fit the X-ray structural parameters from PHT thin films. (a) Intermolecular π stacking between thiophene rings inferred from 90° X-ray pattern of HT-PHT film. (b) Lamellar stacking inferred from X-ray scans of intensity vs 2θ data.

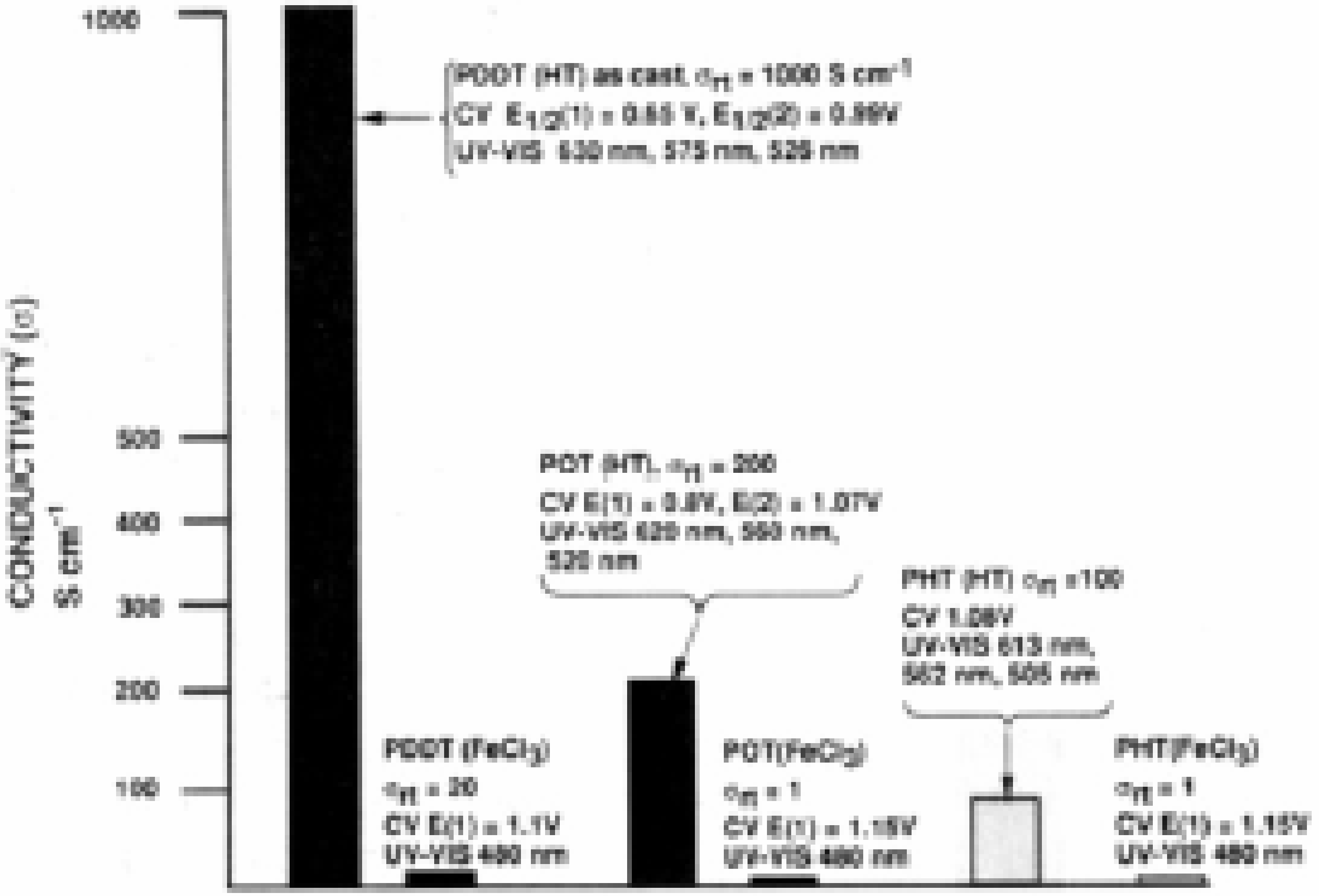
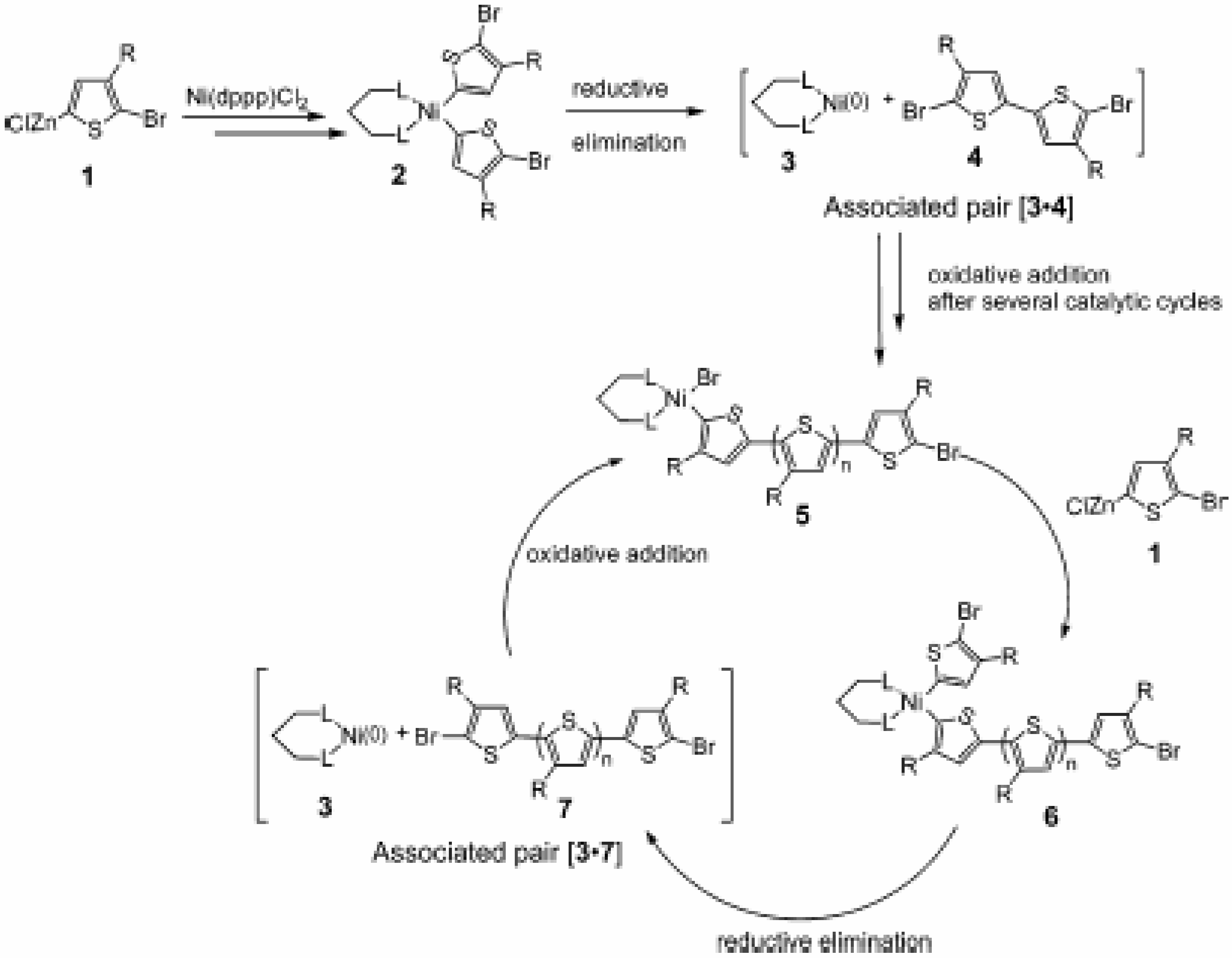


Figure 3. Electrical conductivity and electrochemical and optical absorption data on thin films of HT poly(3-alkylthiophenes).

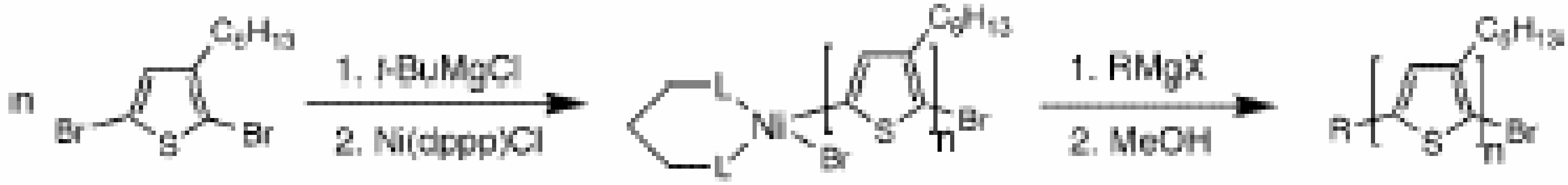
Richard D. McCullough, Stephanie Tristram-Nagle,Shawn P. Williams, Renae D. Lowevt and Manikandan Jayaramant *J. Am. Chem.* Soc. **1993,***115***,** 4910-4911

Scheme 1. Proposed Mechanism for the Nickel-Initiated Cross-Coupling Polymerization



Elena E. Sheina, Jinsong Liu,Mihaela Corina Iovu, Darin W. Laird, andRichard D. McCullough*
Macromolecules **2004,** *37,* 3526-3528

Application of the GRIM Reaction



1 2 3

Scheme 1. Mono-capping of the growing polymer chain by adding RMgX.

Elecrectroemission of Polarized Light

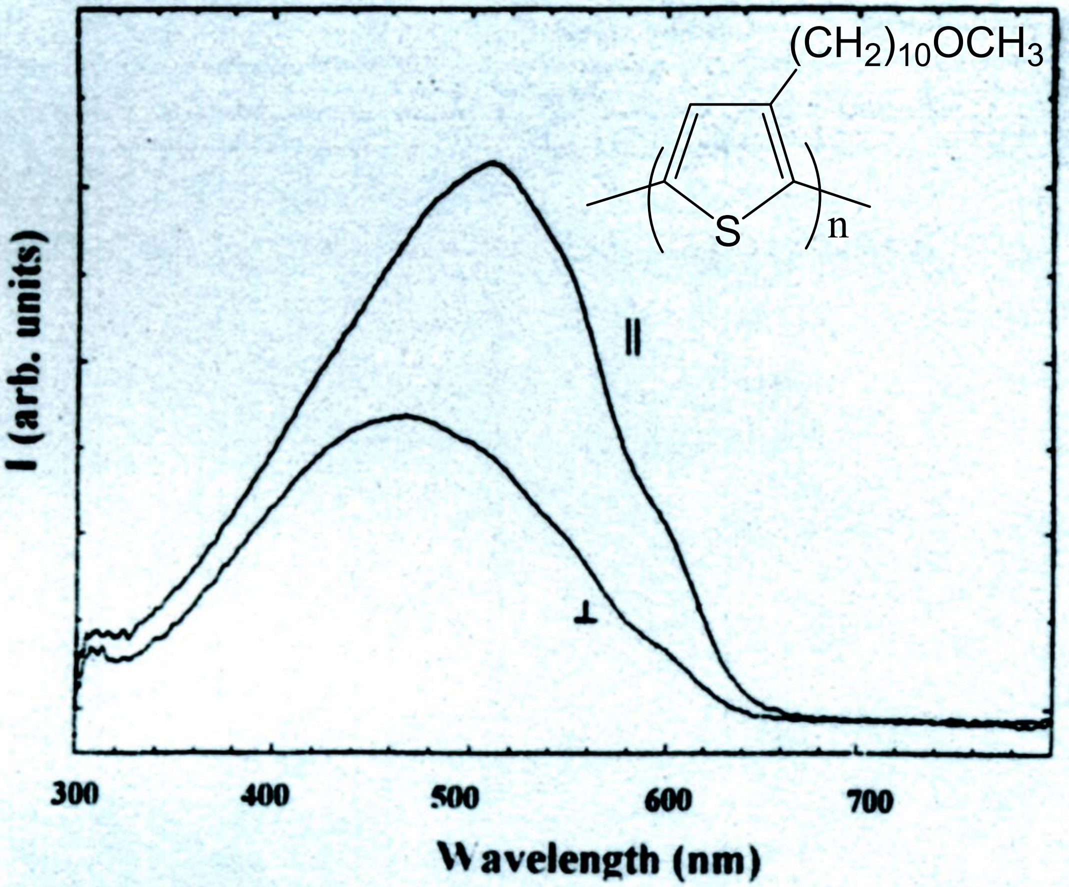


Fig. 2. Adsorption spectra of PDMT LB films. || incident light polarization parallel to the dipping direction: ⊥ incident light perpendicular to the dipping direction.

A. Bolognesi, G. Bajo, J. Palohemio, T. Oestergoerd, H. Stubb *Adv. Mater.* **1997**, *9*, 121-124

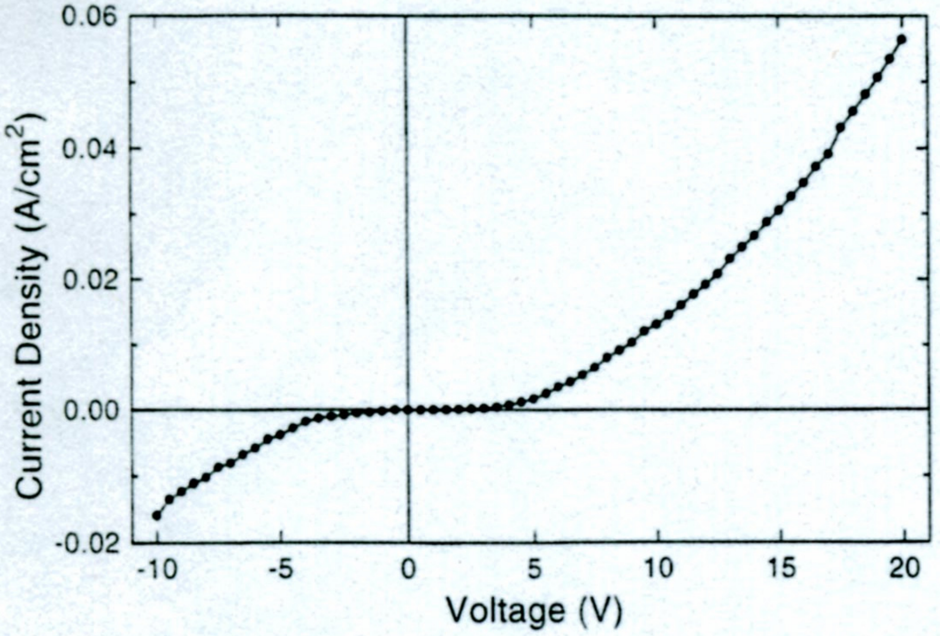
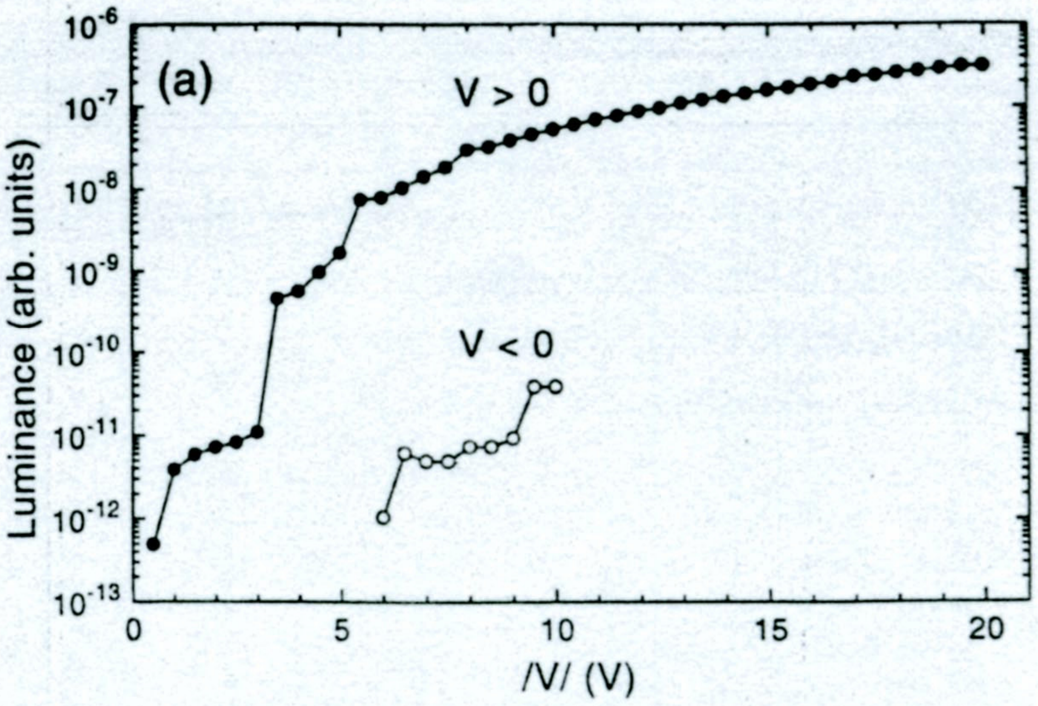


Fig. 3. *I–V* characteristics of the PDMT LED.

Voltage Effect



Current Density Effect

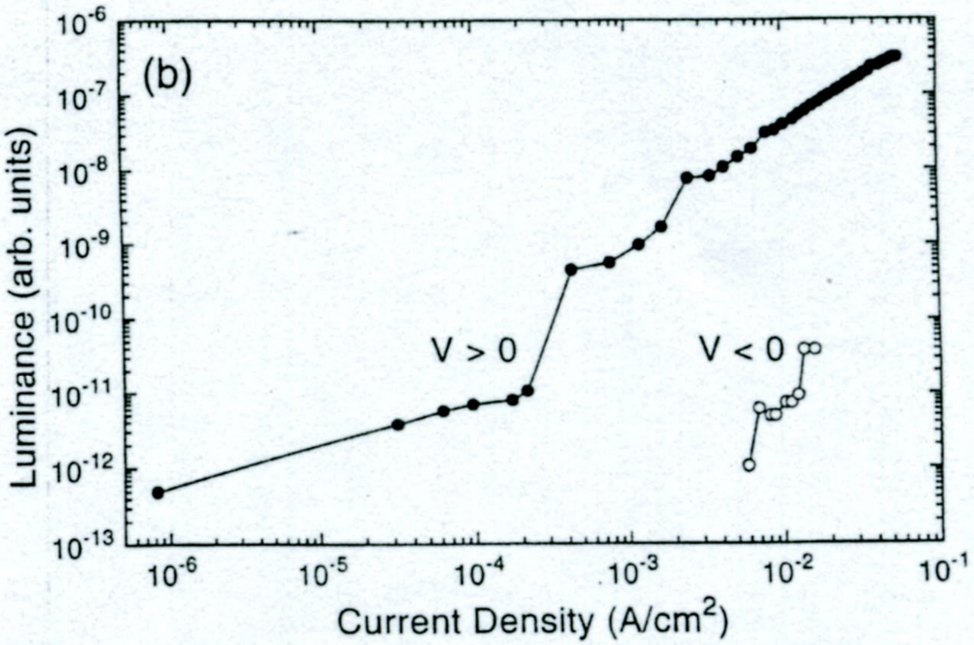


Fig. 4. Luminance of PDMT LED as a function of a) voltage and b) current density.

Polarized Electroemmission!

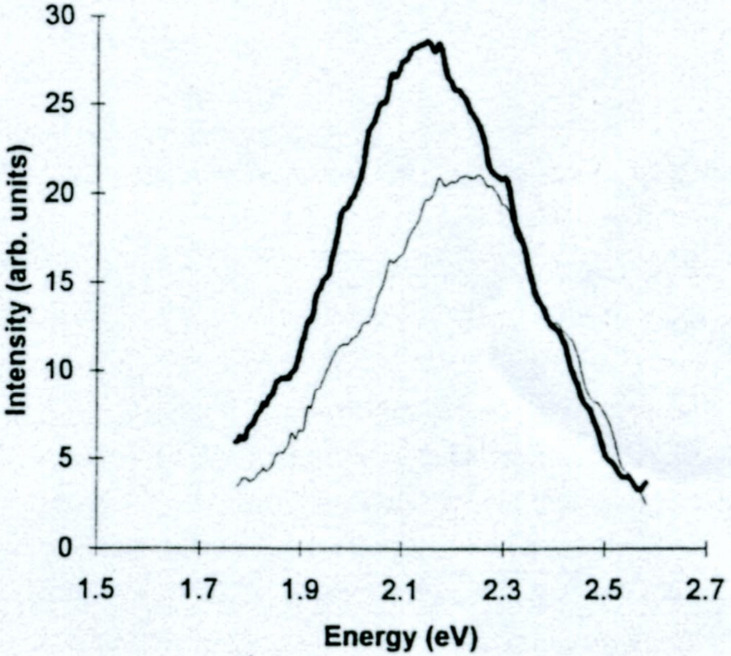


Fig. 5. Polarized EL spectra: the thick line shows parallel emission and the thin line shows perpendicular emission.

Summary

Organic materials based on molecular solids give rise to properties such as metallic conductivity and superconductivity, usually associated with extended solids

Organic conjugated polymers are versatile scaffolds for the development of materials that exhibit a number of exotic properties

The End

Thanks!

Discussion

Jay Siegel