Conducting Polymers and their Composites for Microbial Fuel Cells

Shilpa N Sawant

Chemistry Division
Bhabha Atomic Research Centre
Trombay, Mumbai- 400 085
email: stawde@barc.gov.in

Workshop on Hydrogen Energy and Fuel Cells, IITB, Apr.4, 2009

Outline

Part I **Microbial Fuel Cells**

- Introduction
- Factors affecting MFC performance

Part II **Conducting polymers**

- Introduction
- Applications
- Biosensors & MFC

Part III **Self assembled films**

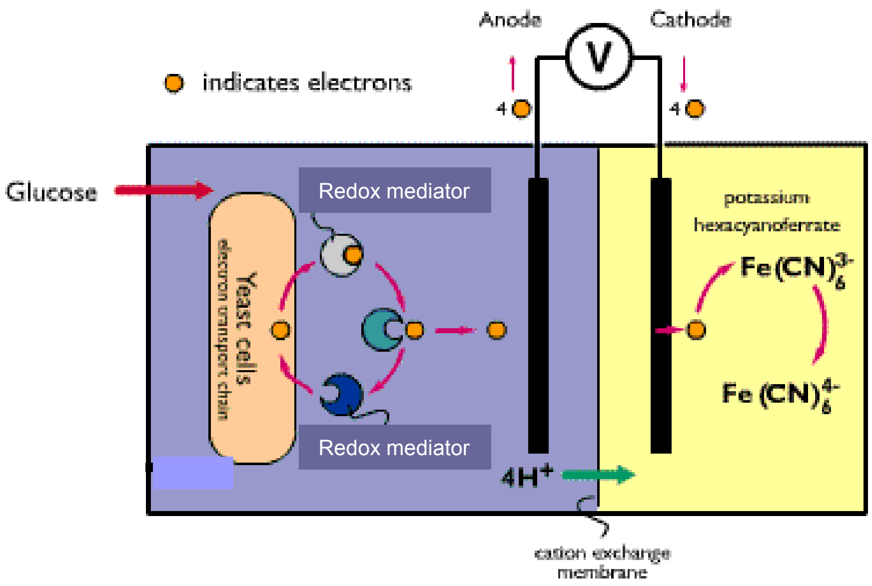
- Self assembled monolayer
- Langmuir-Blodgett films

Biomolecule immobilization

Dye / redox mediator

Microbial Fuel Cells

Systems that harvest electrons produced during microbial metabolism
-channels them for electric current generation



http://www.ncbe.reading.ac.uk/ncbe/materials/MICROBIOLOGY/fuelcell.html

Energy generation + Waste disposal

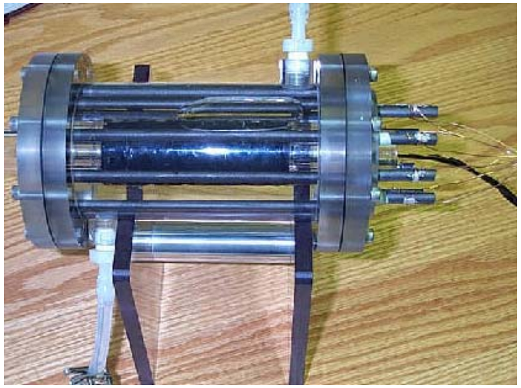
Factors Affecting Microbial Fuel Cell Operation

Cell geometry

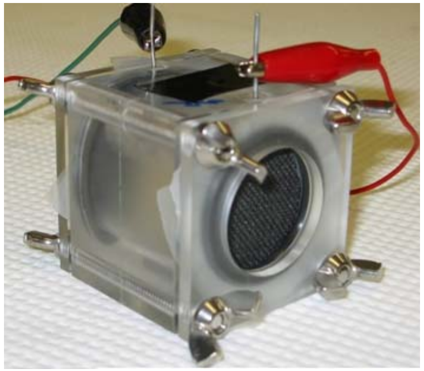
Cell geometry optimization

Distance between the electrodes & PEM

Area of the PEM



http://www.parts.mit.edu



Factors Affecting Microbial Fuel Cell Operation

Cell geometry

Anode chamber

- Anode material
- Redox mediators
- Microorganism- cells/ enzymes
  -immobilisation

Cathode chamber

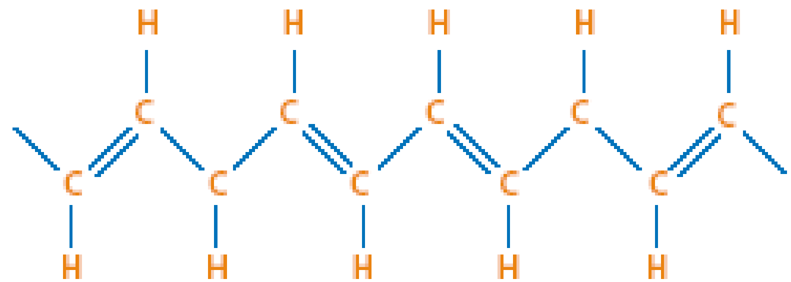
- Cathode material
- Redox mediator
- Microorganism/ enzymes

Membrane

- Proton exchange membrane

Conducting Polymers – An overview

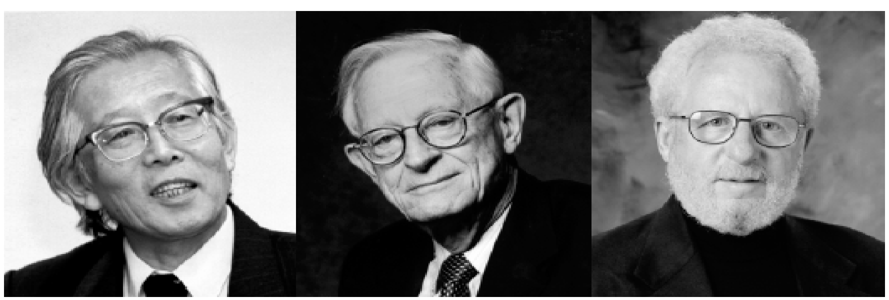
Polymers: insulating
Recent advances: conducting polymers

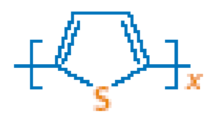


Trans-polyacetylene

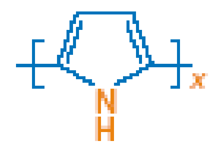
Nobel prize awarded in 2000

Shirakawa, MacDiarmid and Heeger

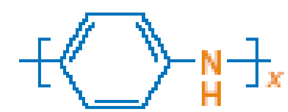




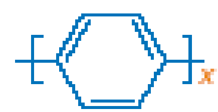
Polythiophene



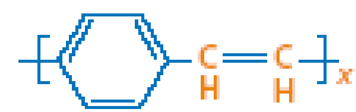
Polypyrrole



Polyaniline



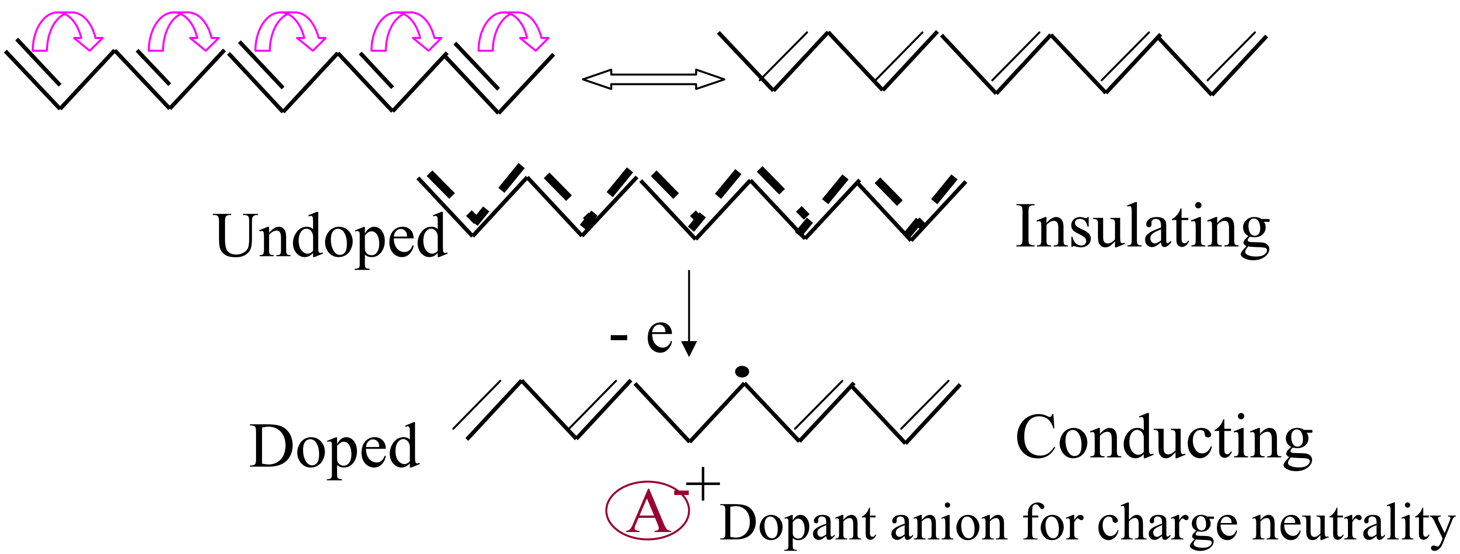
Poly(*p*-phenylene)



Poly(*p*-phenylenevinylene)

Why Conducting?

Conjugation of π-electrons



Doping of conducting polymers

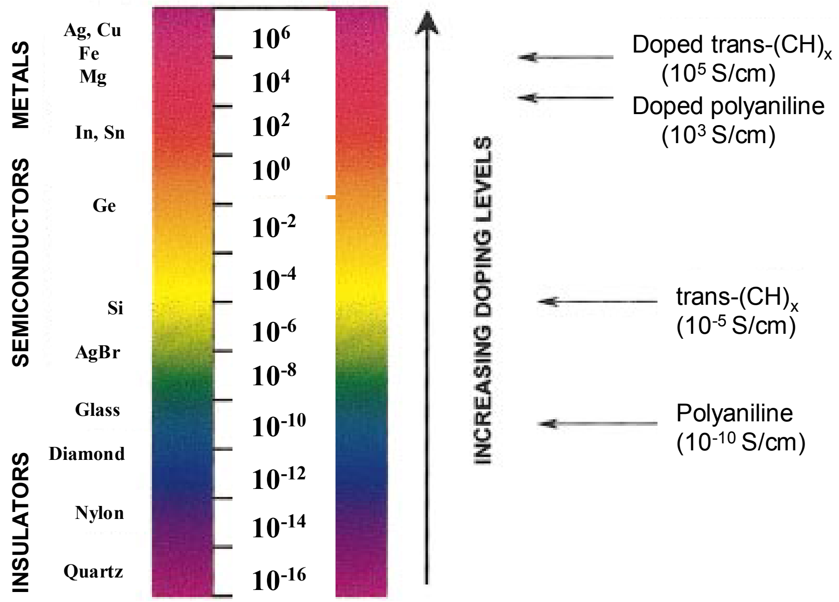
p-doping: $[CH]_n + 3x/2\ I_2$ -----→ $[CH]_n^{x+} + xI_3^-$ (oxidation with halogen)

n-doping: $[CH]_n + xNa$ ---→ $[CH]_n^{x-} + xNa^+$ (reduction with alkali metal)

p- or n- doping can be achieved by chemical or electrochemical method.

By judiciously controlling the doping level,
a whole range of properties from insulator to metal can be obtained.

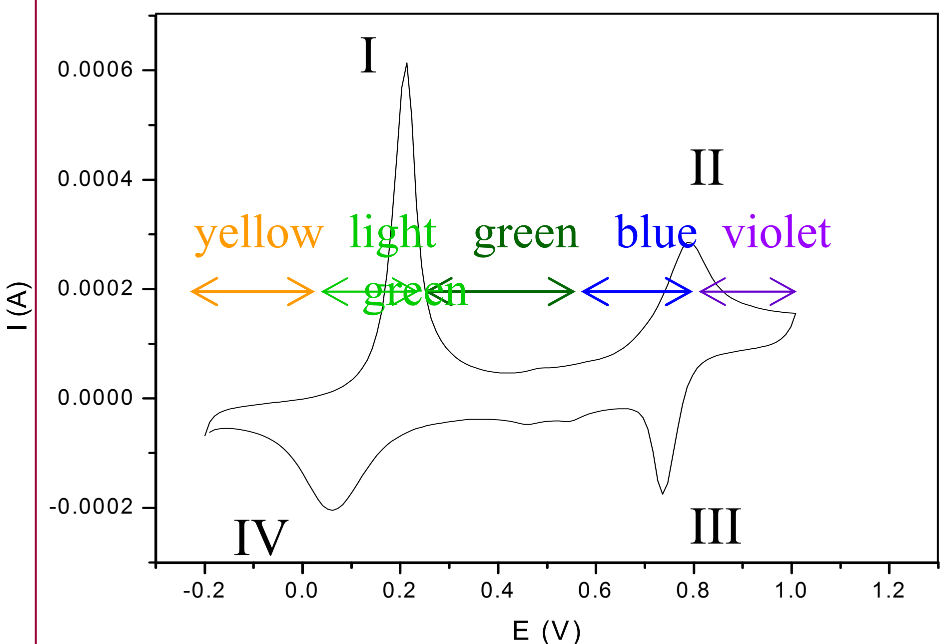
Conductivity increases with increased doping



Redox properties

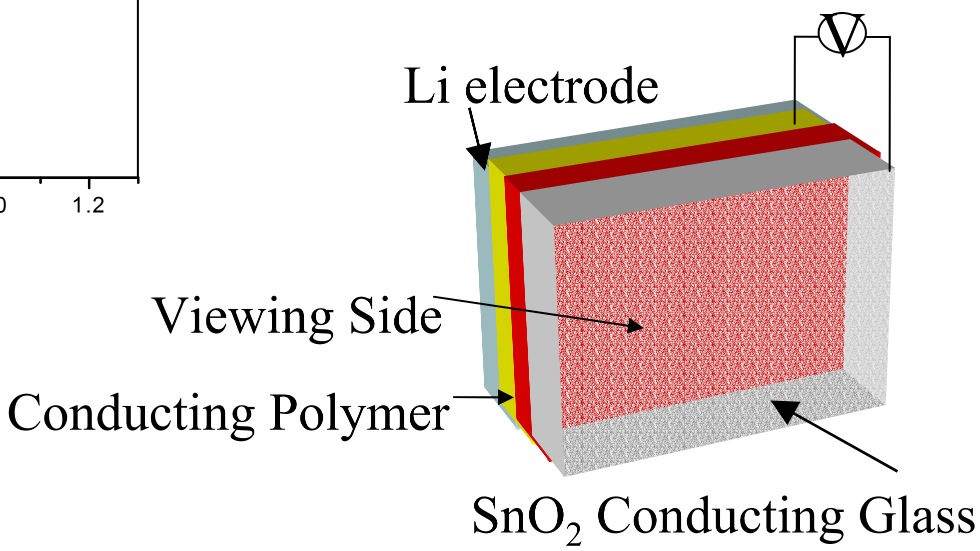
Electrochromism:

CP films change colour under the influence of applied potential

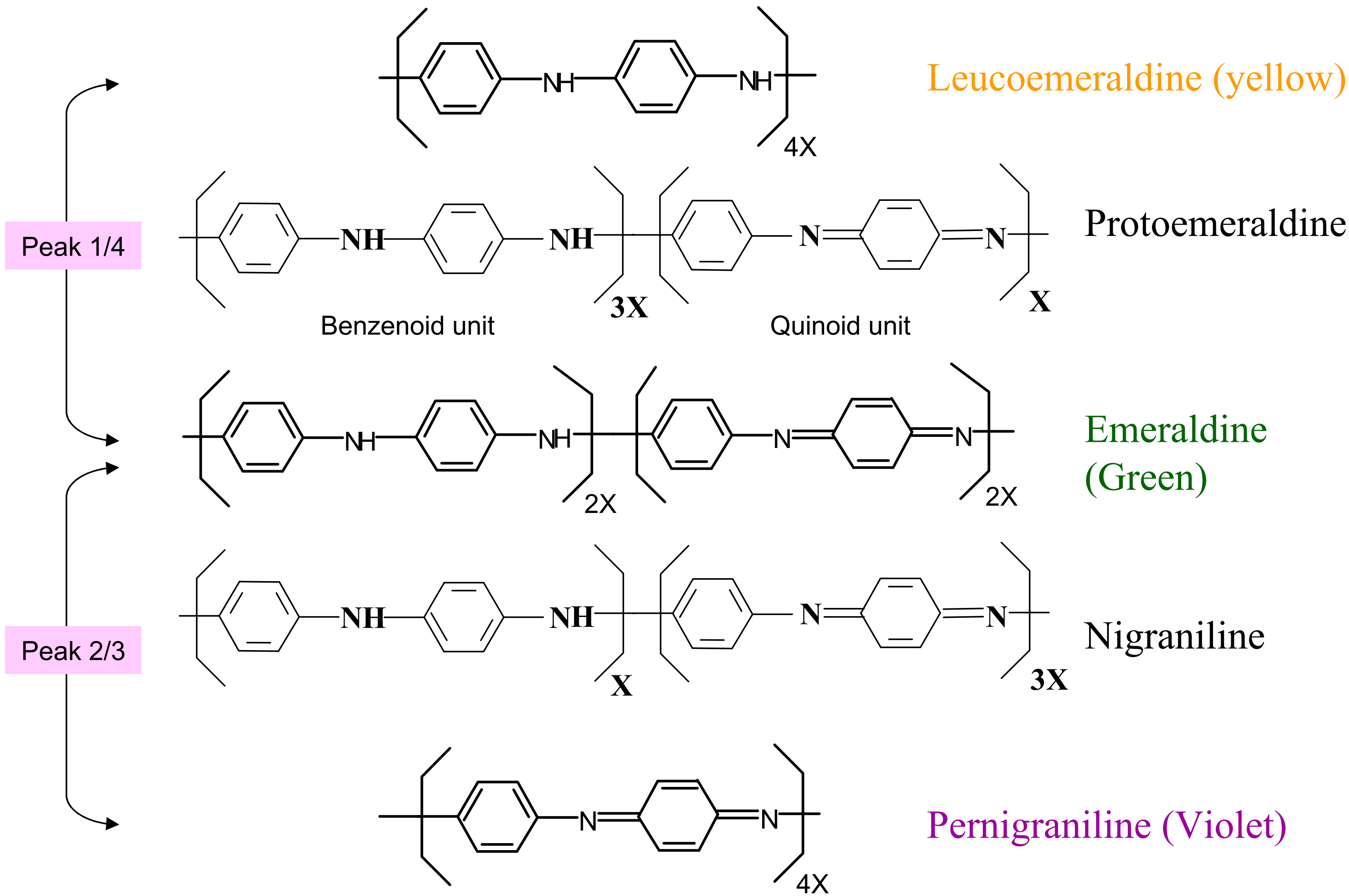


CV of PANI in 0.1M H_2SO_4

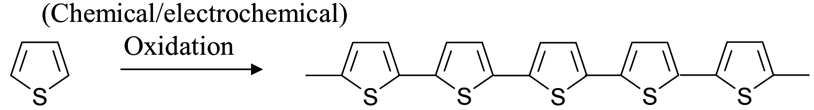
Electrochromic displays



Oxidation states of Polyaniline (PANI)



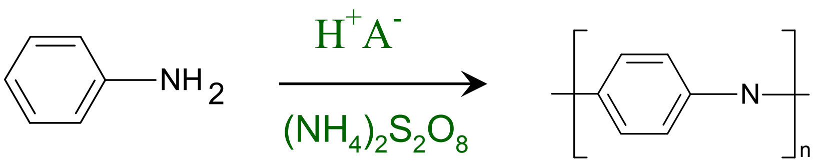
Synthesis



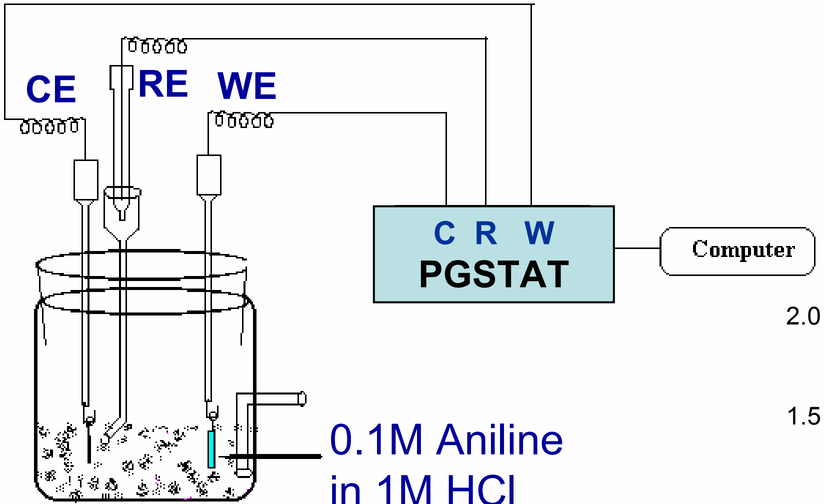
Thiophene Polythiophene

Chemical synthesis of polyaniline

Chemical polymerization: oxidant such as Ferric chloride ($FeCl_3$) or ammonium per sulphate $(NH_4)_2S_2O_8$ are used.



Electrochemical synthesis of polyaniline

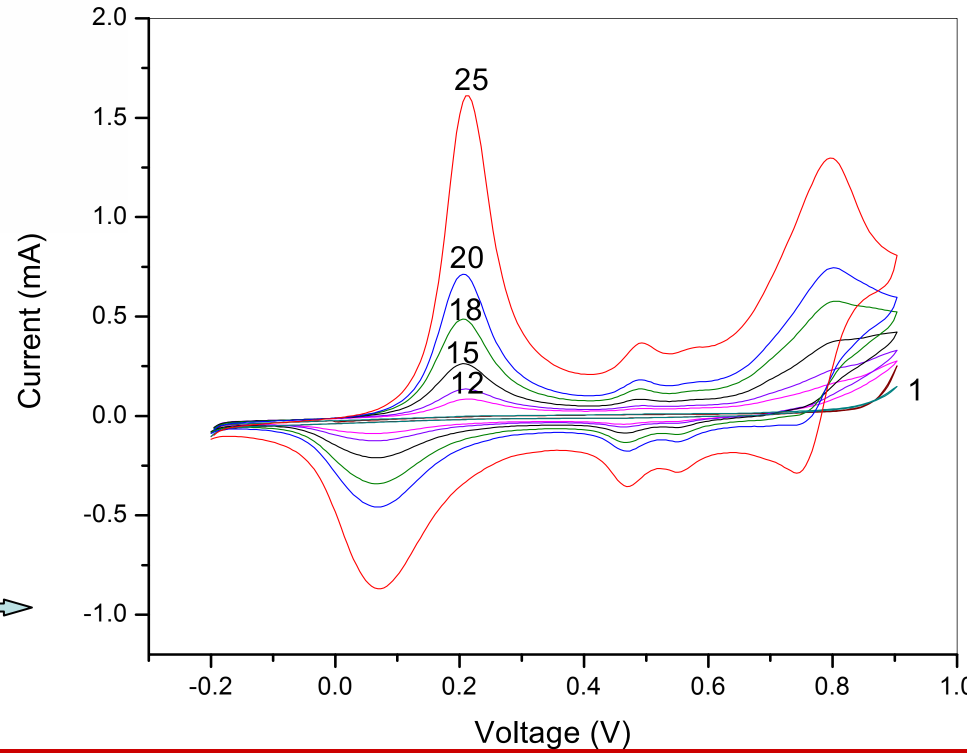


0.1M Aniline
in 1M HCl

Potentiostatic: constant potential applied
Potentiodynamic: potential scanned repeatedly

Method: Potentiodynamic
Scan range: -0.2V to 0.9V
Scan rate: 50mV/sec

Cyclic voltammogram recorded during electropolymerisation of aniline in HCl



Applications of conducting polymers based on:

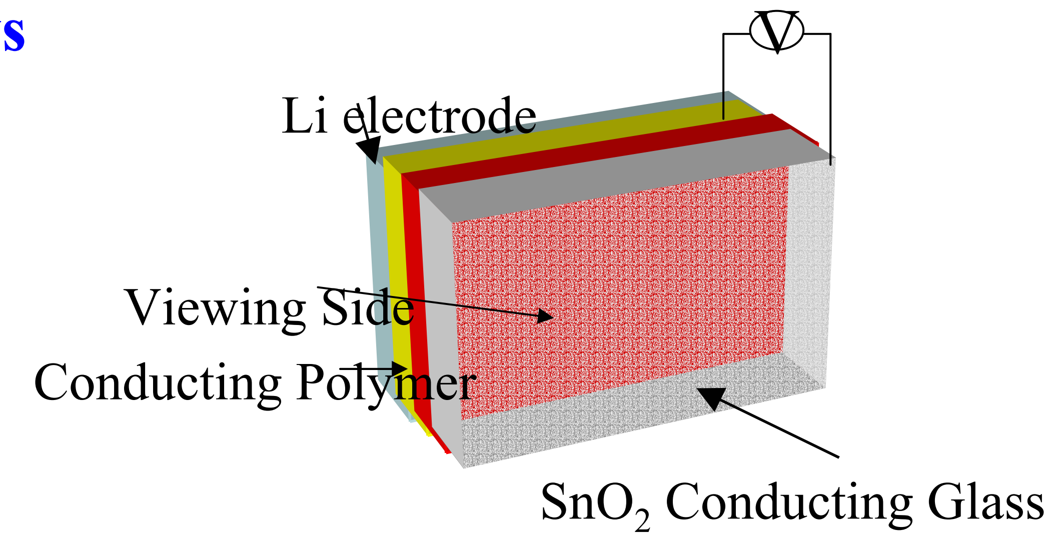
Conductivity

Electrostatic materials
Conducting adhesives
Electromagnetic shielding
Printed circuit boards
Artificial muscles
Antistatic clothing
Piezoceramics
Active electronics
(diodes, transistors)

Electroactivity

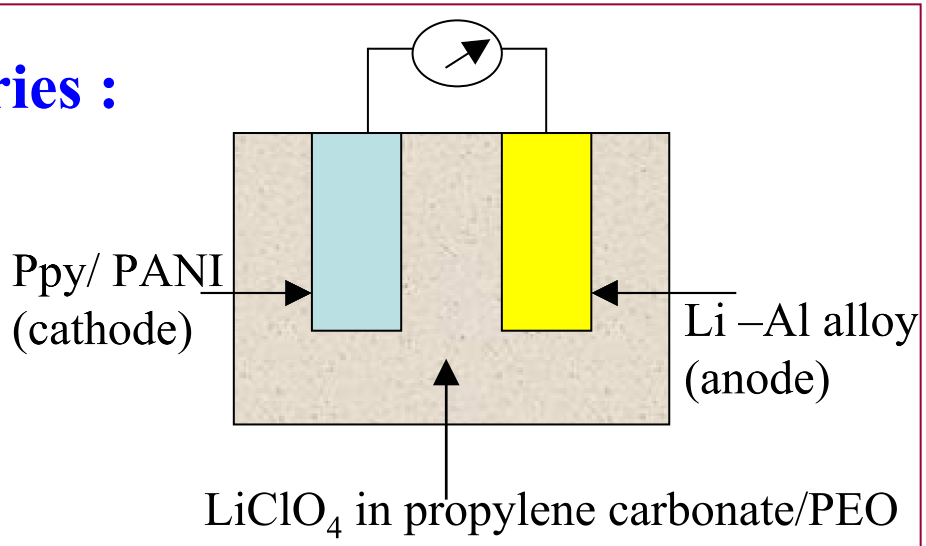
Molecular electronics
Electrical displays
Chemical, biochemical and thermal sensors
Rechargeable batteries and solid electrolytes
Drug release systems
Optical computers
Ion exchange membranes
Electromechanical actuators
'Smart' structures Switches

Electrochromic displays



	Undoped	doped
Polythiophene	Red	Blue
Polypyrrole	Yellow-green	Blue-Black
Polyaniline	Yellow	Green-Blue
Polyisothianaphthene	Blue	Light Yellow

Rechargable polymer batteries :



Pb, Hg toxic,
Environmental hazard for disposal

∴ Polymer Batteries

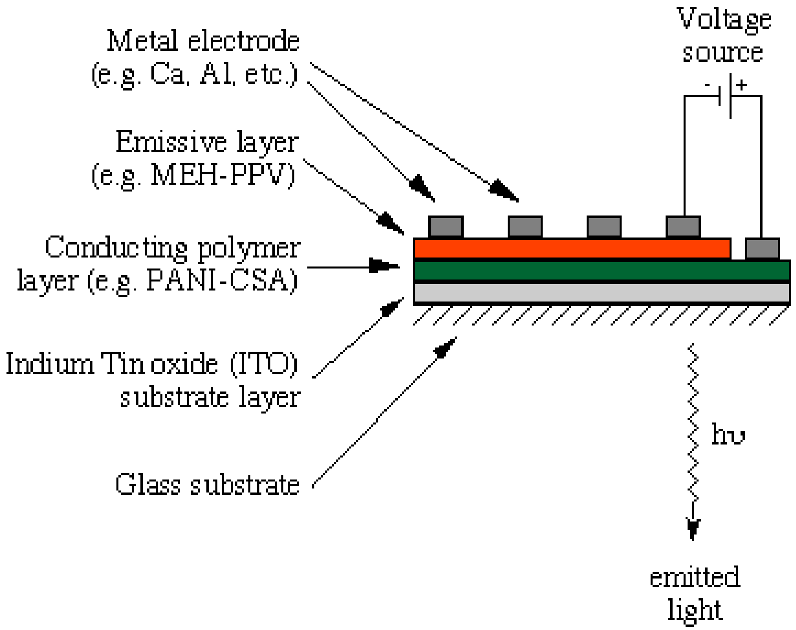
Charging: Neutral polymer at cathode oxidised back to p-fprm

Discharging: + vely charged polymer accepts electrons from Li

Advantages: Light weight, low cost, long life cycle
High energy density 176Watthour/Kg for polymer batteries
30 Watthour/Kg for Lead acid batteries

All polymer batteries

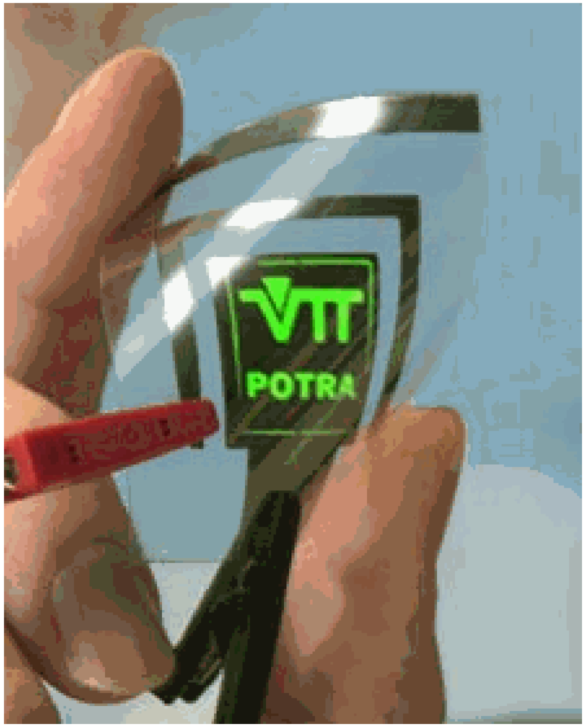
Polymer Light Emitting Diodes (LED)



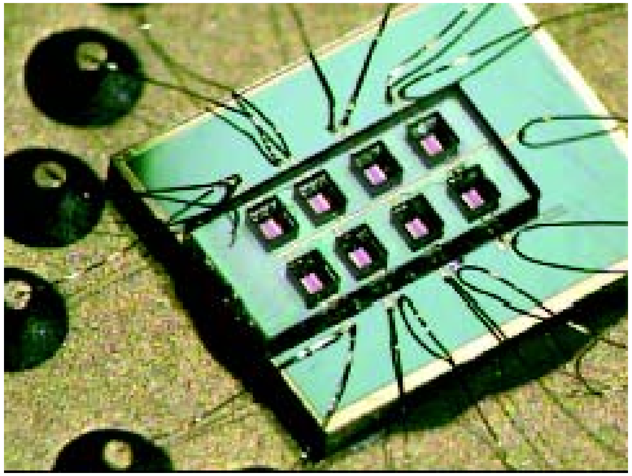
1990 discovery of LEDs, in Cambridge by Richard Friend and his collaborators

Benefit of a PolymerLED:

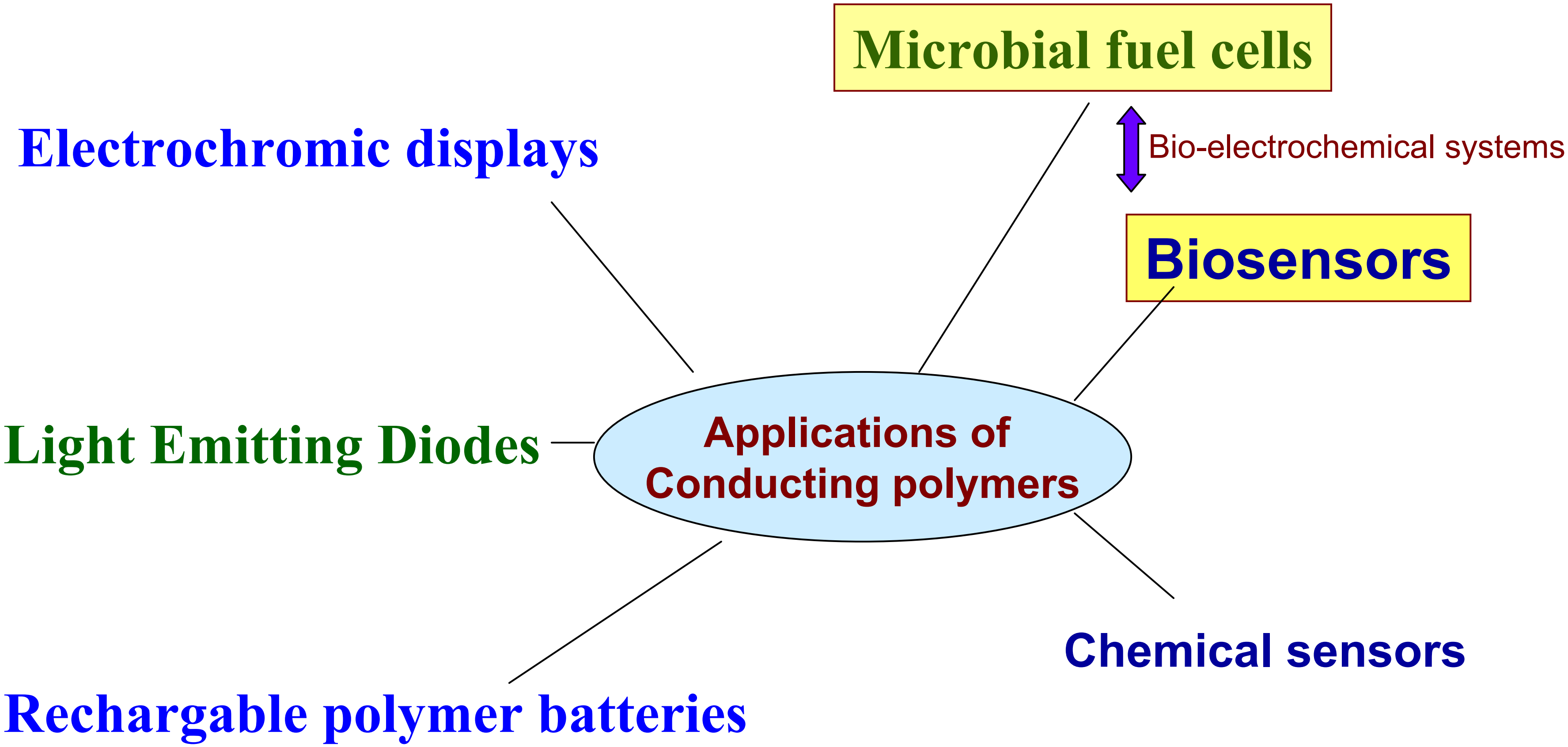
- High contrast and brightness
- Read easily in both bright and dark environments
- No restriction on viewing angle as in LCD
- No need of backlight
- Much less power
- Flexibility



Chemical sensors

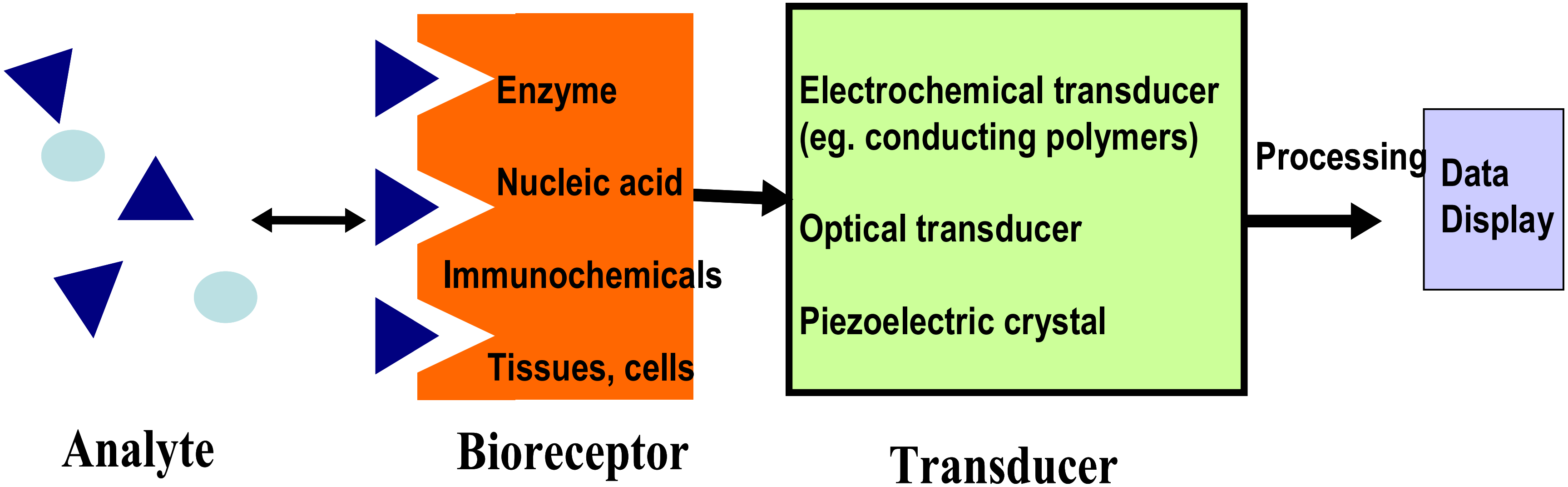


Biosensors


Microbial fuel cells
Bio-electrochemical systems
Electrochromic displays
Biosensors
Light Emitting Diodes
Applications of Conducting polymers
Chemical sensors
Rechargable polymer batteries

Biosensors

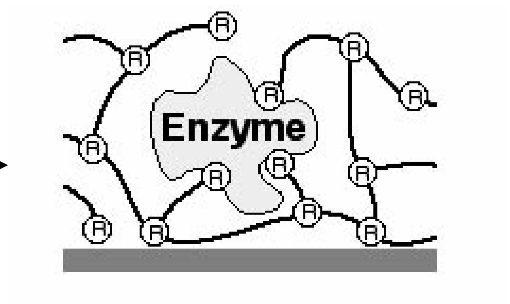
analytical biochemistry + microelectronics



Schematic of a biosensor showing its various components

Why conducting polymers for biosensors / MFC ??

- Entrapment medium

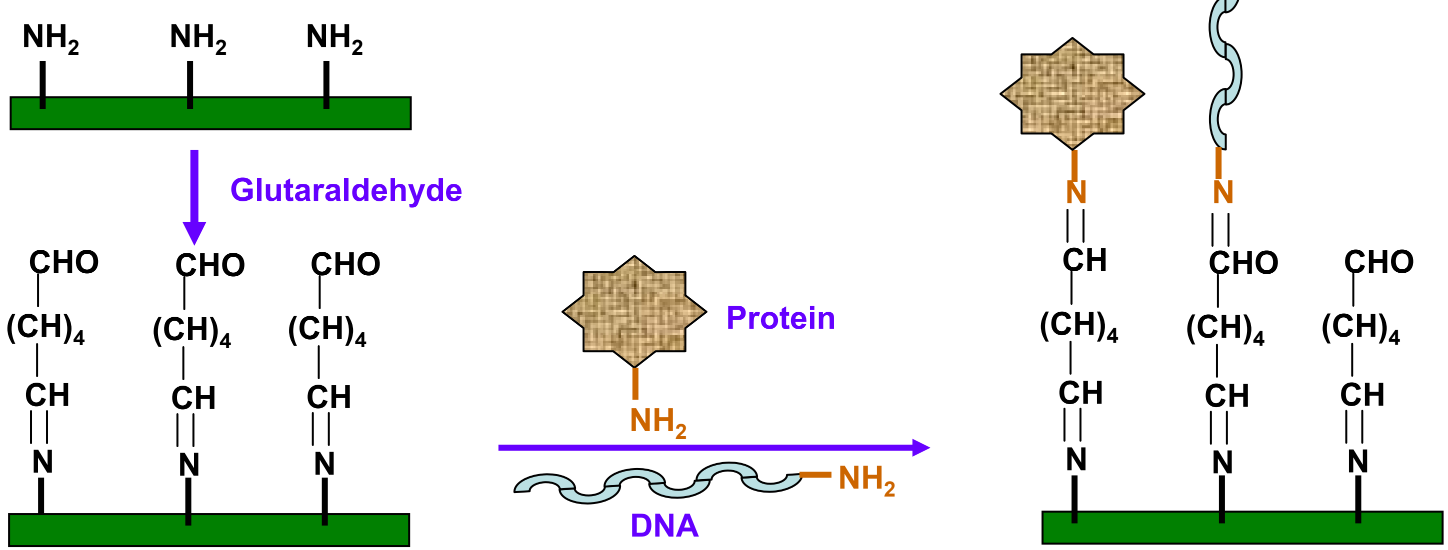


Enzyme entrapped in polymer matrix

Immobilization

During polyn.- physical entrapment / electrostatic

After polyn. – appln. of pot, covalent immobilisation



Polyaniline based sensor for Pesticide

- Agricultural insecticide

- neurotoxin
- carcinogen
- Endocrine disruptor

- **Banned in several countries**
- **Persistent organic pollutant – low water solubility**
- **Bioaccumulates in food chains**

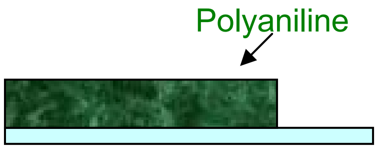
Detection of pesticide in ground water, milk, beverages important

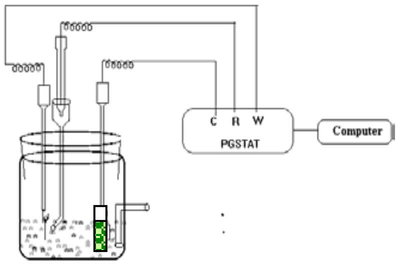
Gas Chromatography

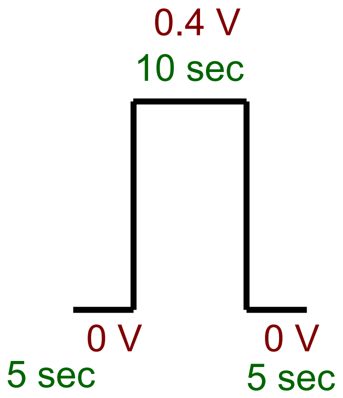
- Expensive, - involves solvent extraction of samples
- ppb level

Pesticide sensor

- Polyaniline deposited on gold IDE
- Pesticide detected by pulsed amperometry

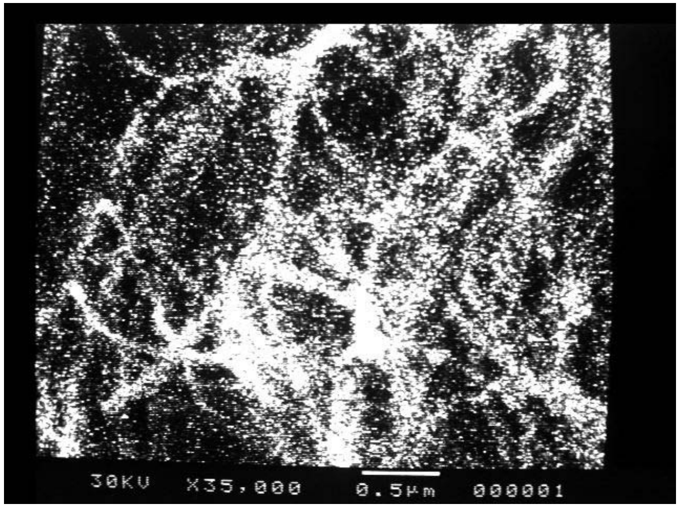




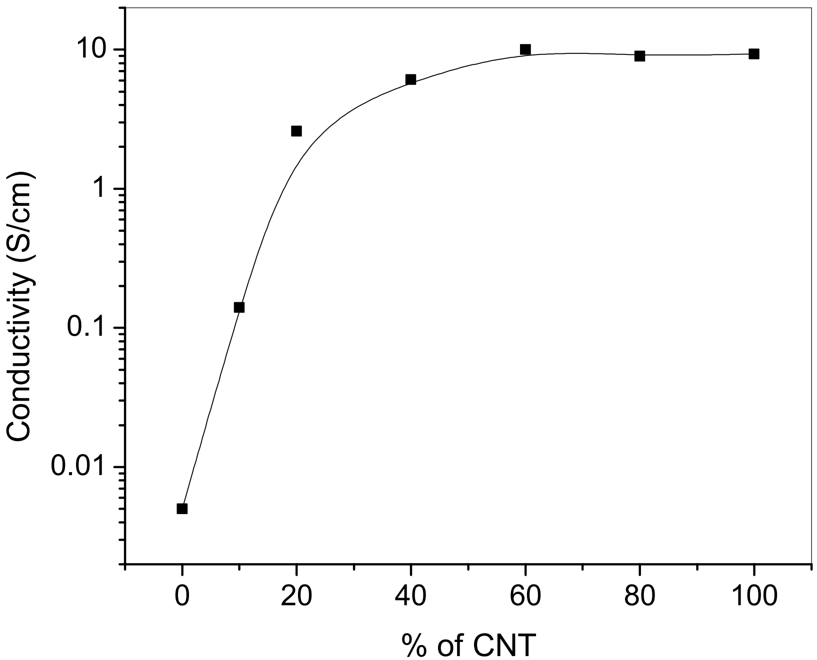


Input pulse

PANI-CNT composites



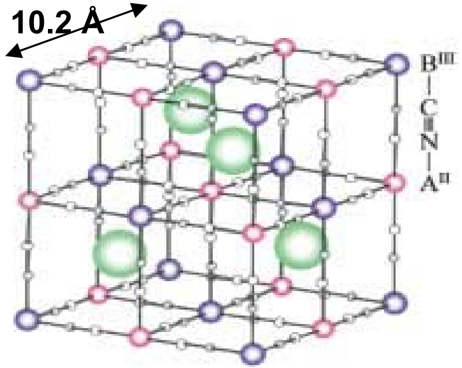
SEM images of PANI-CNT composite



Room-temperature conductivity of PANI-CNT composites as a function of CNT concentration

Organic-inorganic hybrid materials

Polyaniline (PANI) + Prussian Blue (PB)



$Fe_4^{III} [Fe^{II}(CN)_6]_3.15H_2O$

known for optical and magnetic properties

in situ formation of PB via the reaction of $FeCl_4^-$ doped PANI and $K_3Fe(CN)_6$.

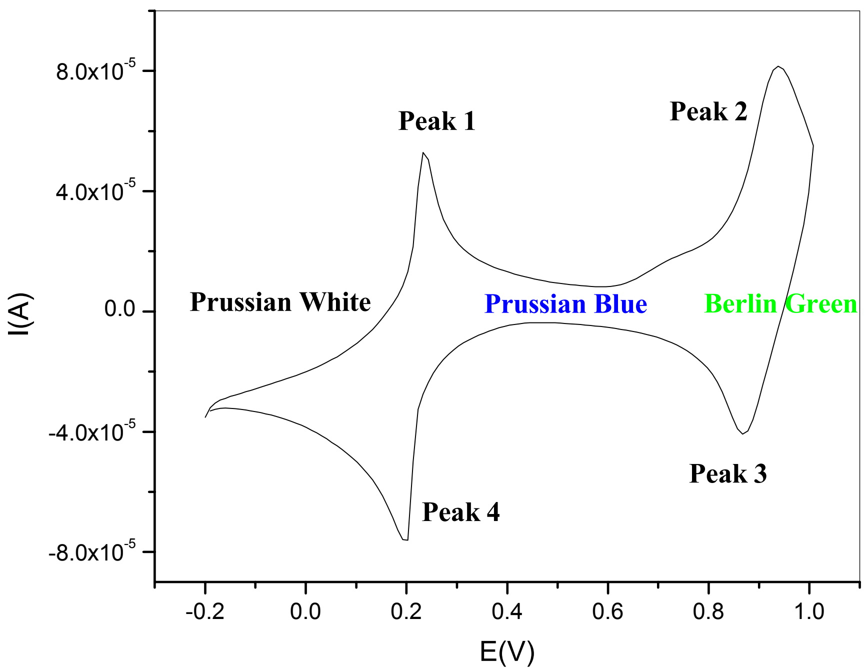
Aim: To prepare bi-functional material using dopant as reaction site

Conductivity	due to PANI matrix
Magnetism	due to PB

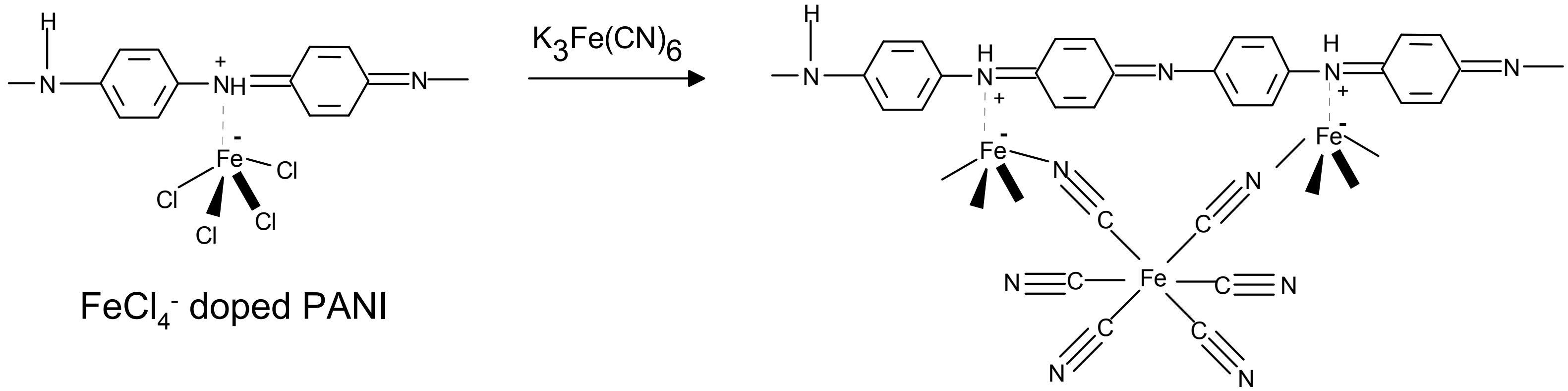
Shilpa *et. al.* Phil. Mag. 2004, 84 (20), 2127

Electrochemistry of PB

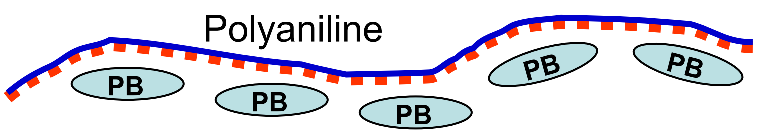
CV of PB in 0.1M KCl



	peak 1		peak 2	
$K_2Fe^{II}[Fe^{II}(CN)_6]$	$\longrightarrow$	$KFe^{III}[Fe^{II}(CN)_6]$	$\longrightarrow$	$Fe^{III}[Fe^{III}(CN)_6]$
	$- K^+ - e$		$- K^+ - e$	
Prussian white		Prussian blue		Prussian green



Schematic of formation of PB in PANI matrix



In the hybrid, PB formed present as small particles along the polymer chain with uniform distribution

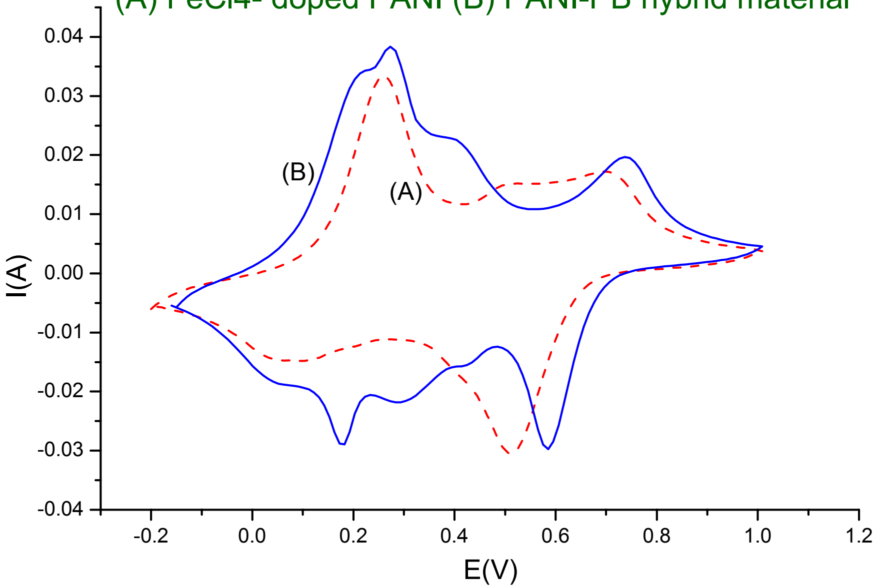
new functionality– add property of magnetism to CP

Electrochemical studies

redox behavior of PANI : H^+ essential

redox behavior of PB independent of H^+, K^+ essential

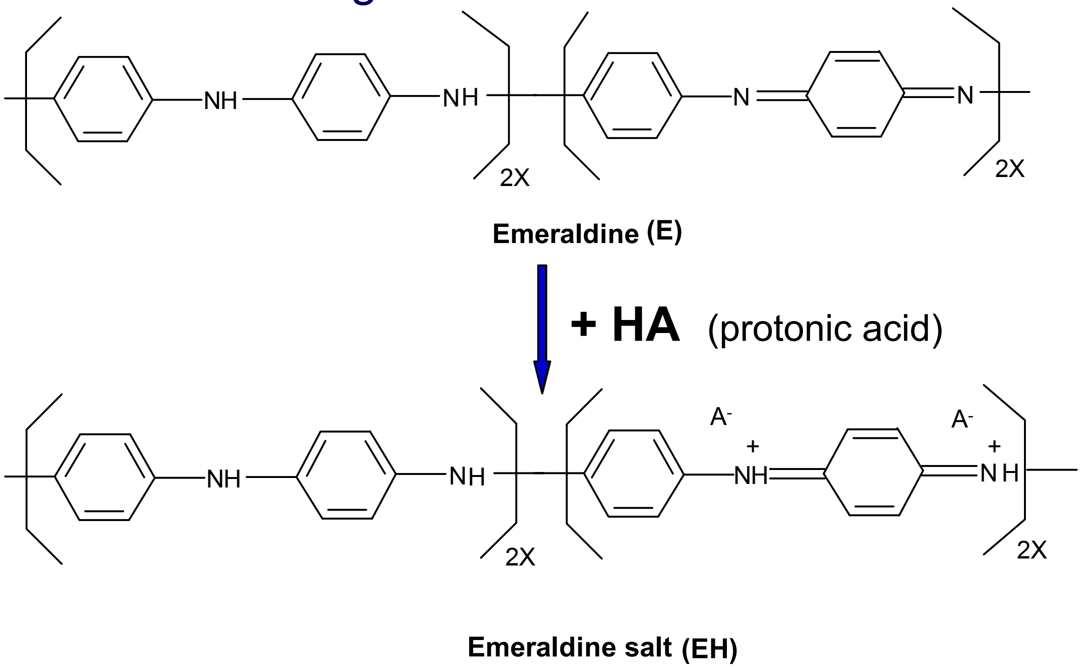
(A) FeCl4- doped PANI (B) PANI-PB hybrid material



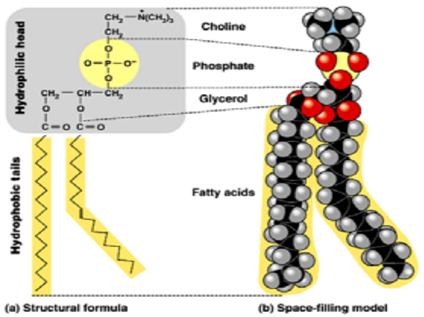
Cyclic voltammogram in 0.5M KCl (pH=0.5)

Polyaniline

Proton exchange membrane

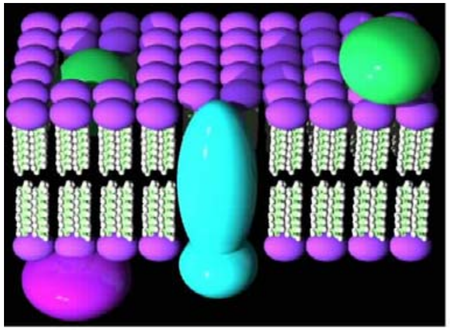


Self-Assembly: The autonomous organization of components into patterns or structures without human intervention



Phospholipids

Self assembly →



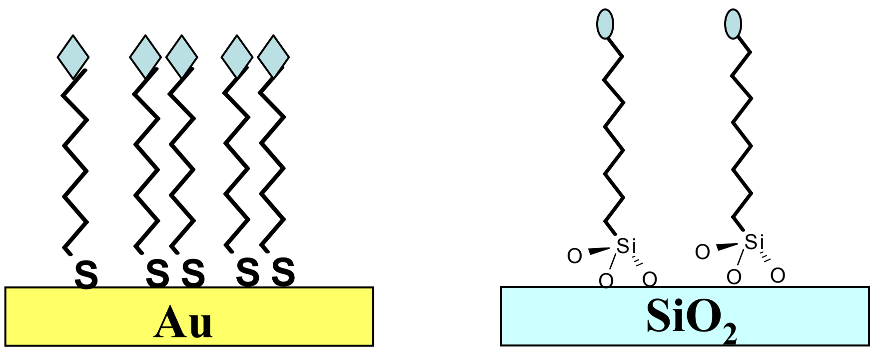
Cell membrane

Why self-assembly??

1. Order appears better
2. Living cells self-assemble – mimic nature
3. Making ensembles of nanostructures

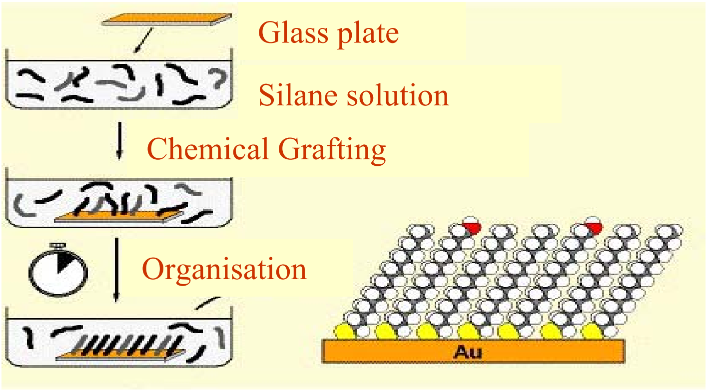
Involves non-covalent interactions –van der Waals, electrostatic, Hydrophobic interactions, H-bonding, coordination bonds

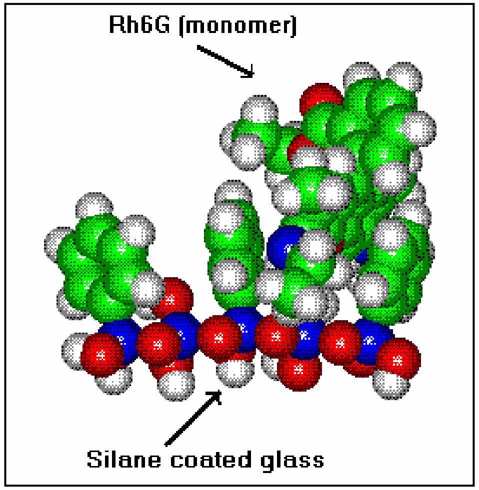
Self-Assembled Monolayers (SAMs) - for surface functionalisation



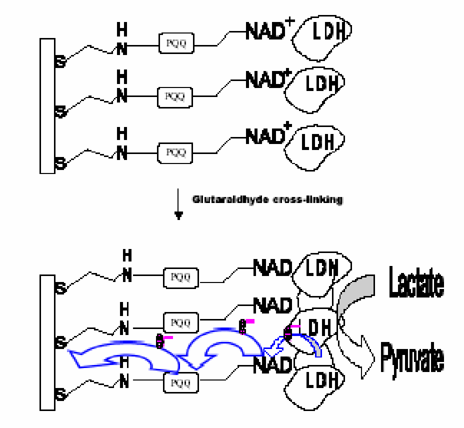
Thiols on gold

Silanes on glass





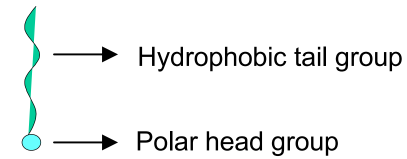
Orientation of dye on silane surface



Shilpa Tawde *et.al.* J. Mat. Chem., 1999, 9, 1847

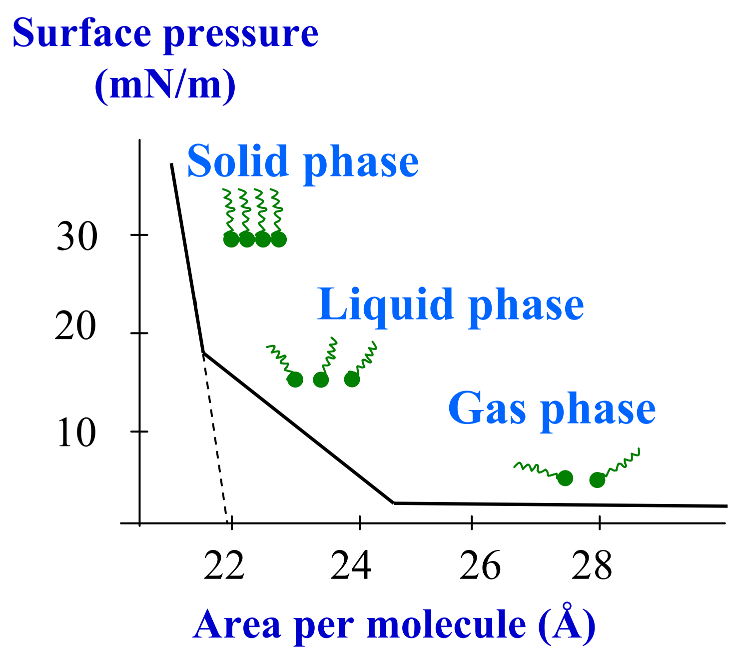
Langmuir-Blodgett (LB) technique enables the preparation of

- ultrathin films
- controlled thickness and
- well defined molecular orientation.



Prerequisite : Amphiphilic molecule

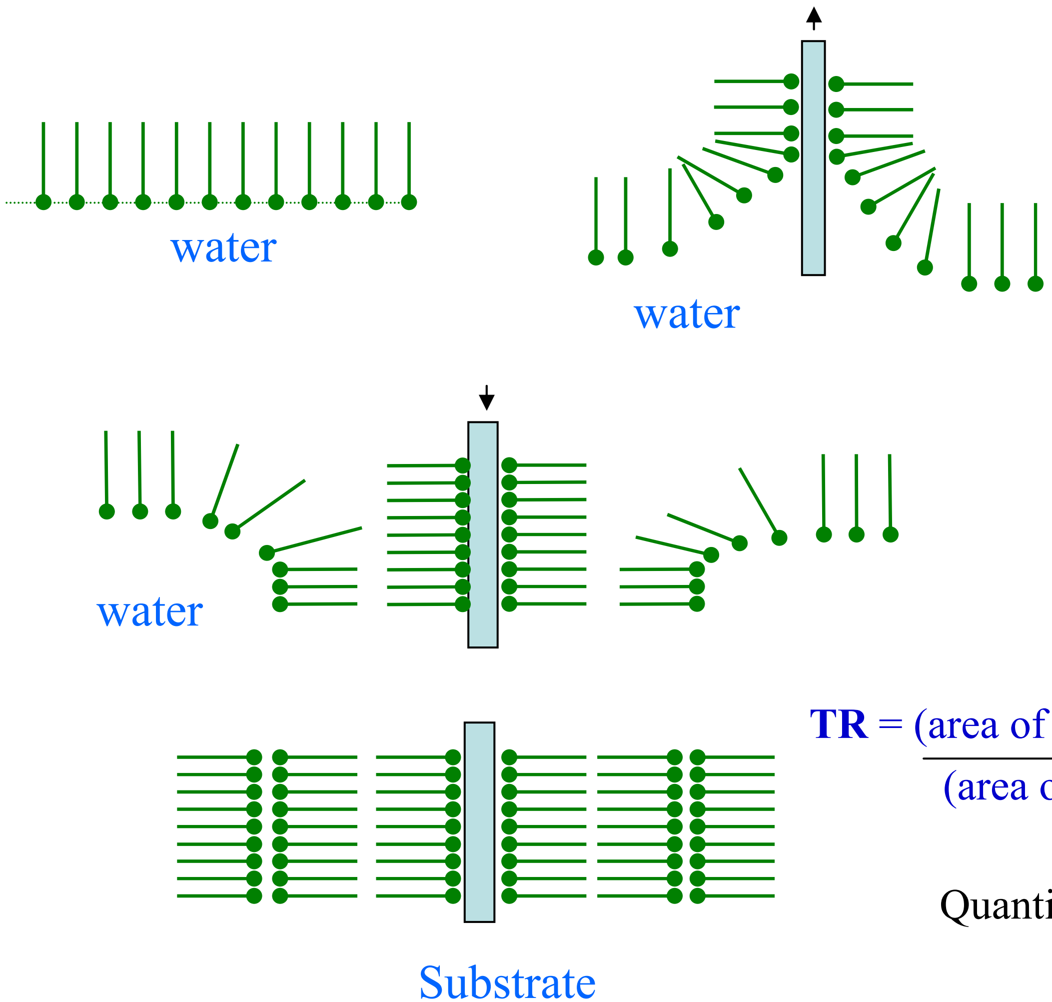
KSV 5000 Langmuir-Blodgett Trough



$\pi = \gamma - \gamma_0$

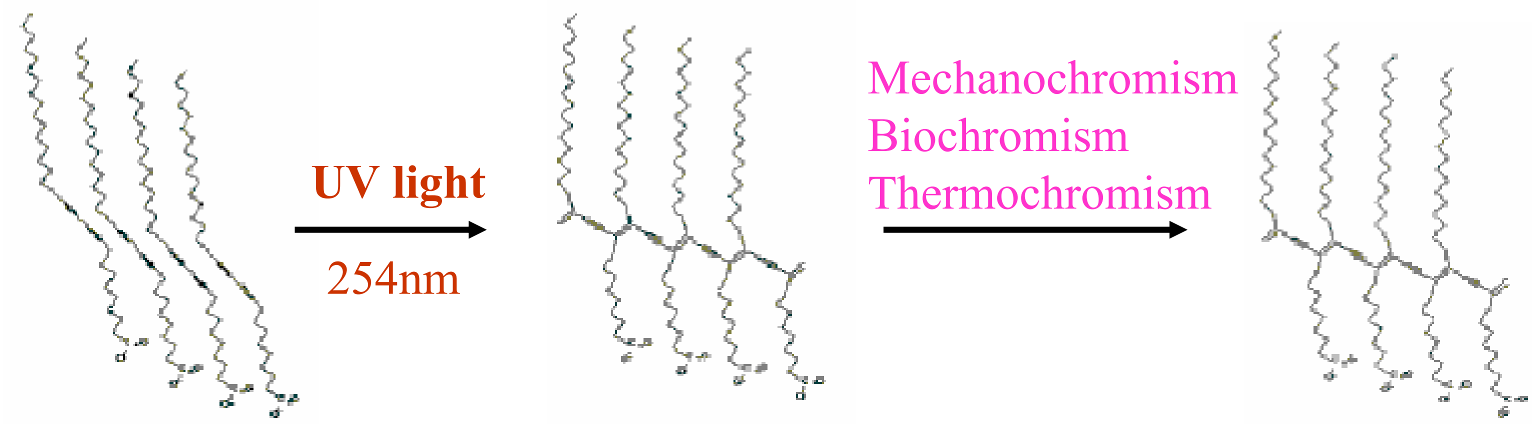
= (ST of pure water) – (ST of water covered with a monolayer)

Deposition of Langmuir-Blodgett film



$$\mathbf{TR} = \frac{\text{(area of monolayer removed from the surface)}}{\text{(area of substrate immersed in water)}}$$

Quantitative estimate of film quality



Long chain
Diacetylene

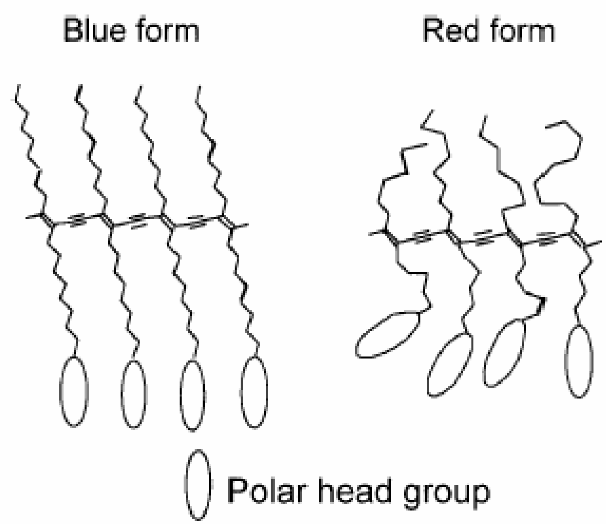
Polydiacetylene (PDA)

λ_{max}= 610-640nm

Blue form

λ_{max}= 520-560nm

Red form

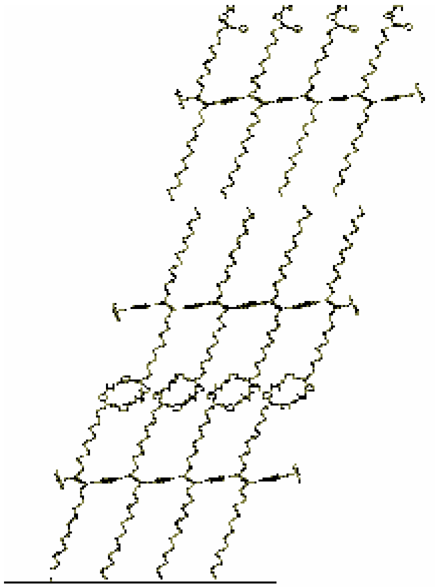


Strong intermolecularH-bonding between polar head groups: Polymer backbone extended chain-like shape

Weak intermolecular H – bonding: Backbone folds to a zig-zag shape

Figure 7. Illustration of the "side chain disorder" model to explain the chromatic property of polydiacetylenes.

(Huo et al. Langmuir,1999)

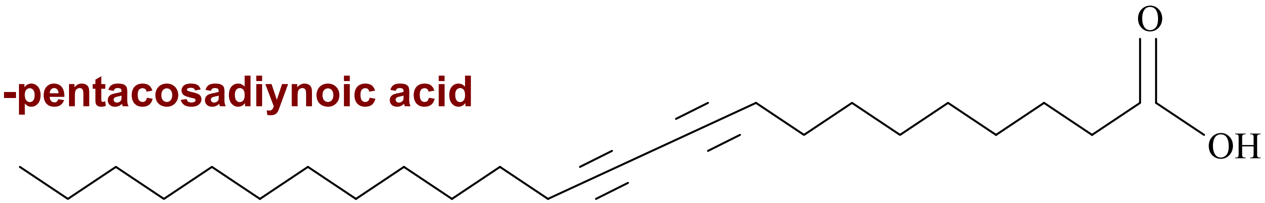


3 layer PDA LB film

To obtain a good response,
- highly ordered
- ultrathin film (1-5 monolayers)

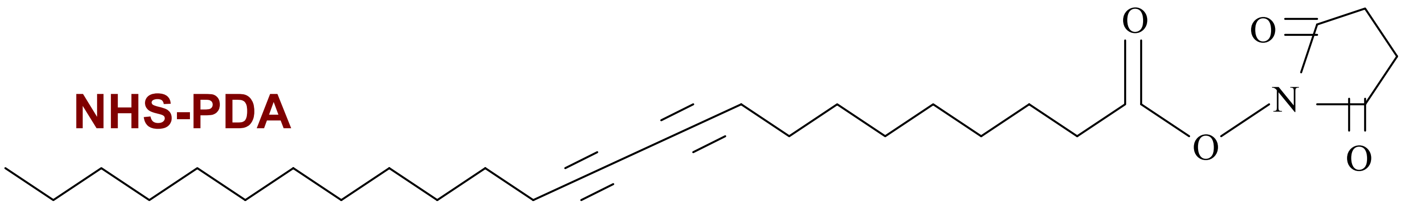
Langmuir-Blodgett technique used

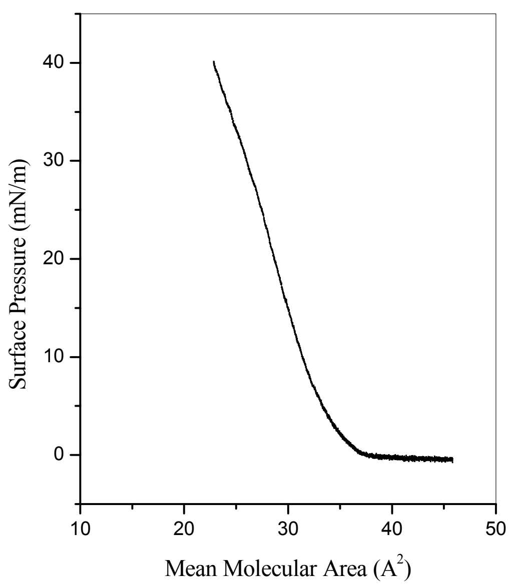
10,12-pentacosadiynoic acid



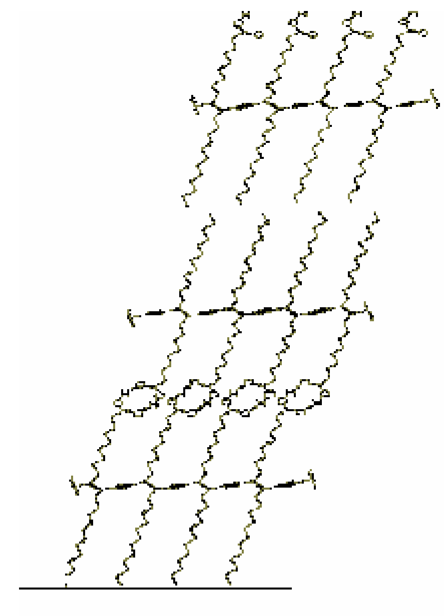
PDA

NHS-PDA



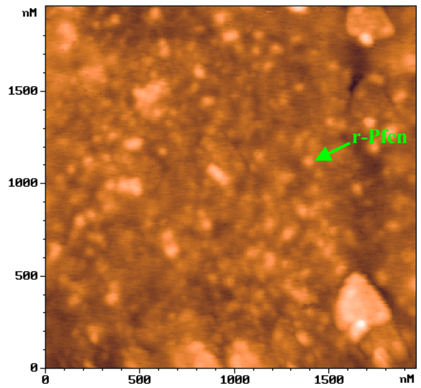


Surface pressure-area isotherm of 1:1 molar mixture of PDA/NHS-PDA

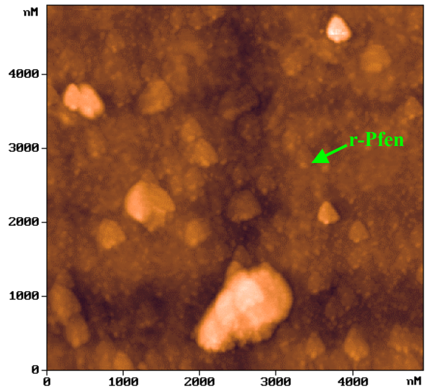


3 layer NHS-PDA LB film

AFM topography of protein immobilized PDA films



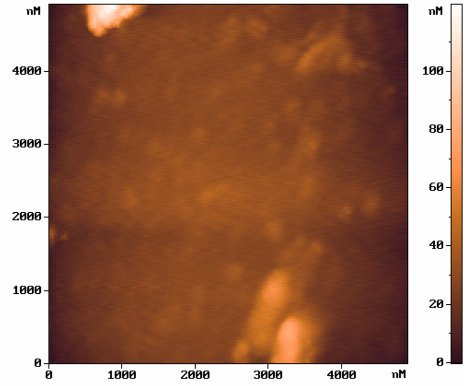
2 x 2 µm



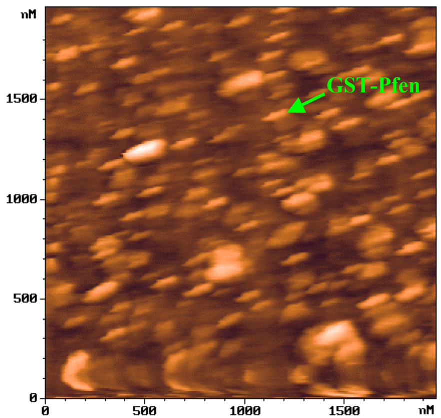
5 x 5 µm.

Images of His6-Pfen immobilized on PDA film

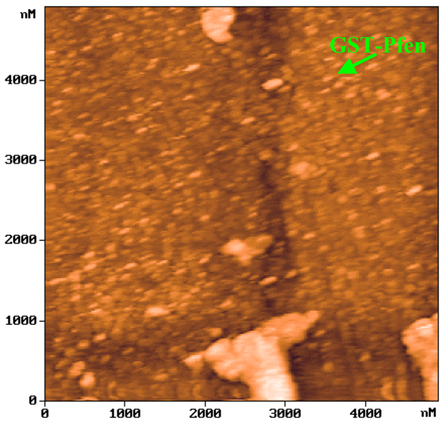
Dia: ~40 nm



Control film



2 x 2 µm



5 x 5 µm.

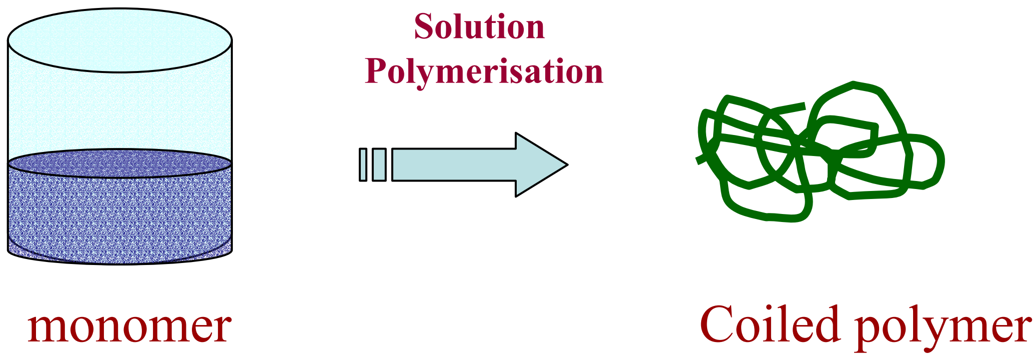
Dia: ~120 nm

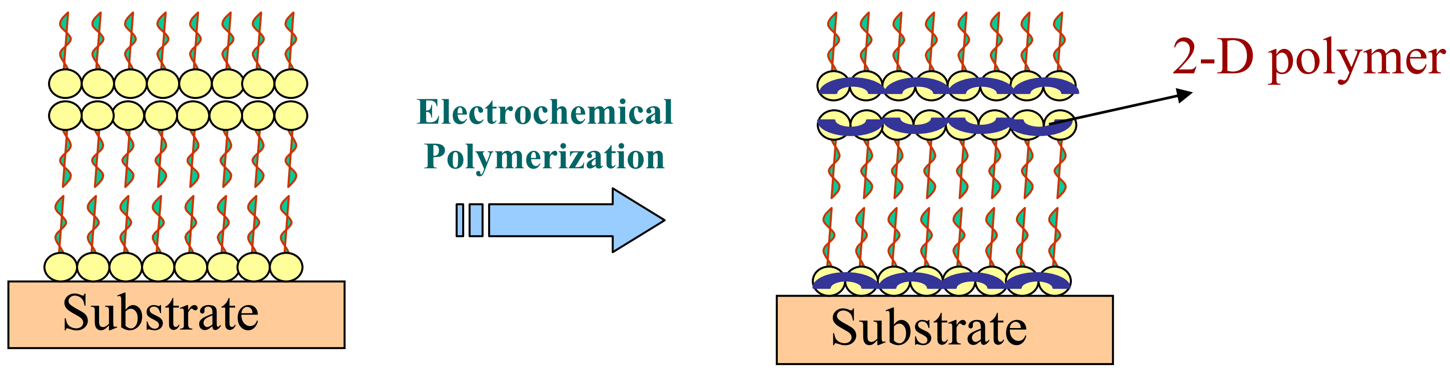
images of GST-Pfen immobilized on PDA film

Self assembled structures

Efficient immobilsation of biomolecules

Motivation

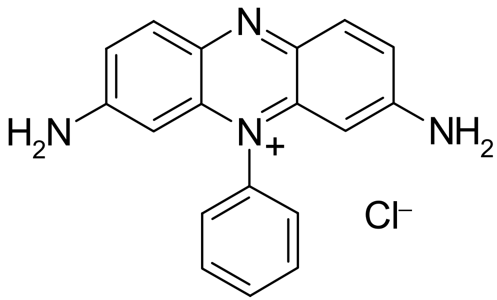




Highly ordered 2D - Polymers thin films can be prepared

Shilpa *et. al.* J. Phys. Chem.B 2006, 110, 24530

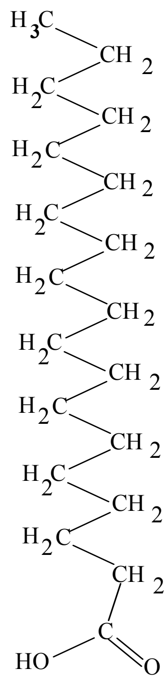
Materials used for LB film formation:



monomer

Phenosafranine dye

Analogous to aniline
Dye : high absorbance



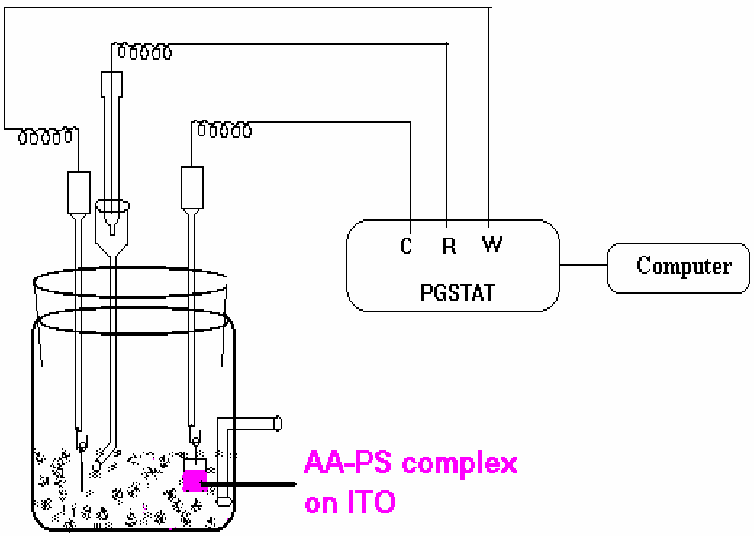
Arachidic acid

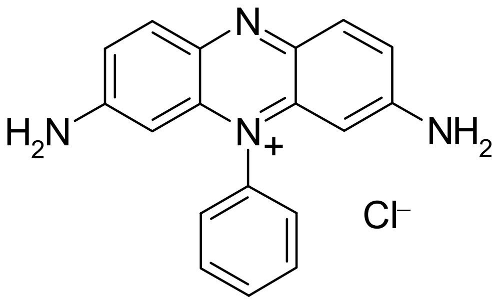
Poly-phenosafranine modified electrodes:

- ✸Electrocatalytic activity for NADH oxidation to enzymatically active NAD^+
- ✸Used for simultaneous detection of ascorbic acid and dopamine

(NADH = β-nicotinamide adenine dinucleotide)

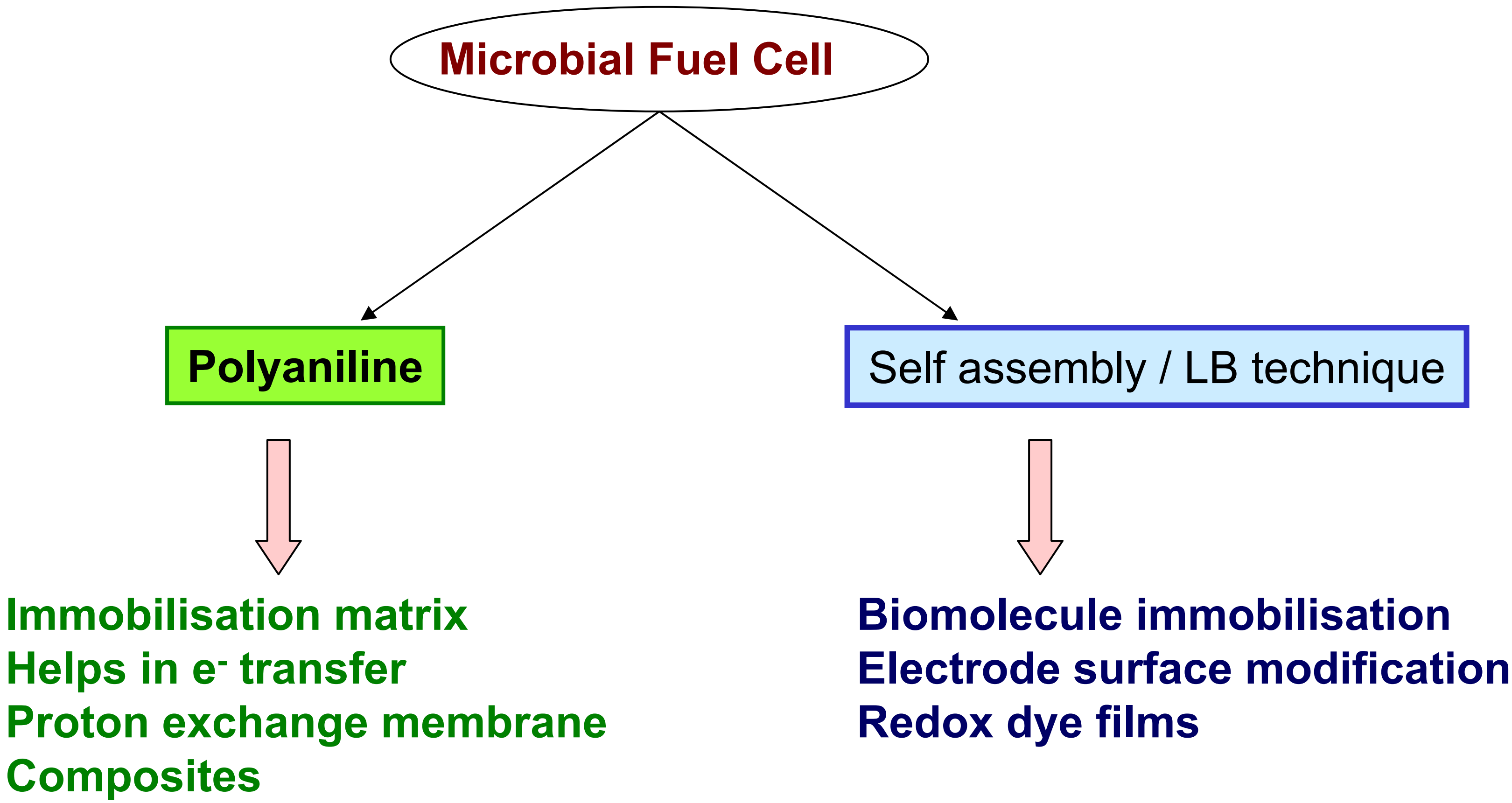
Electropolymerisation of Phenosafranine in AA-PS complex





Phenosafranine dye

Thionine dyes and their polymers
known as redox mediator
Coated on electrode
help to eliminate operational loss of redox mediator


Microbial Fuel Cell
Polyaniline
Self assembly / LB technique
Immobilisation matrix
Helps in e⁻ transfer
Proton exchange membrane
Composites
Biomolecule immobilisation
Electrode surface modification
Redox dye films

Acknowledgements

Dr. D Das
Dr. T. Mukherjee
Dr. J. V. Yakhmi

Collaborators
Dr. G Jarori (TIFR)
Mr. Sadagopan (TIFR)
Dr. Mukesh Doble (IITMadras)

Dr. S. K. Apte (MBD, BARC)
Mr. A Chaurasia (MBD, BARC)

Mrs Vibha Patil (Shivaji Univ)

Team
Anu Prathap
P. Sumesh
Anuradha P R

Thank You !