Introduction to Organic Electronics

Organic Thin-film Transistors

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History of organic thin-film transistors (OTFTs)

1970's --- the first world energy crisis launched interests in organic semiconductor (for solar cells)

1983 --- the first OTFT based on polyacetylene

Air-sensitive, low mobility (10^{-5} $cm^2V^{-1}s^{-1}$)

1990 --- the OTFT based on sixithiophehe

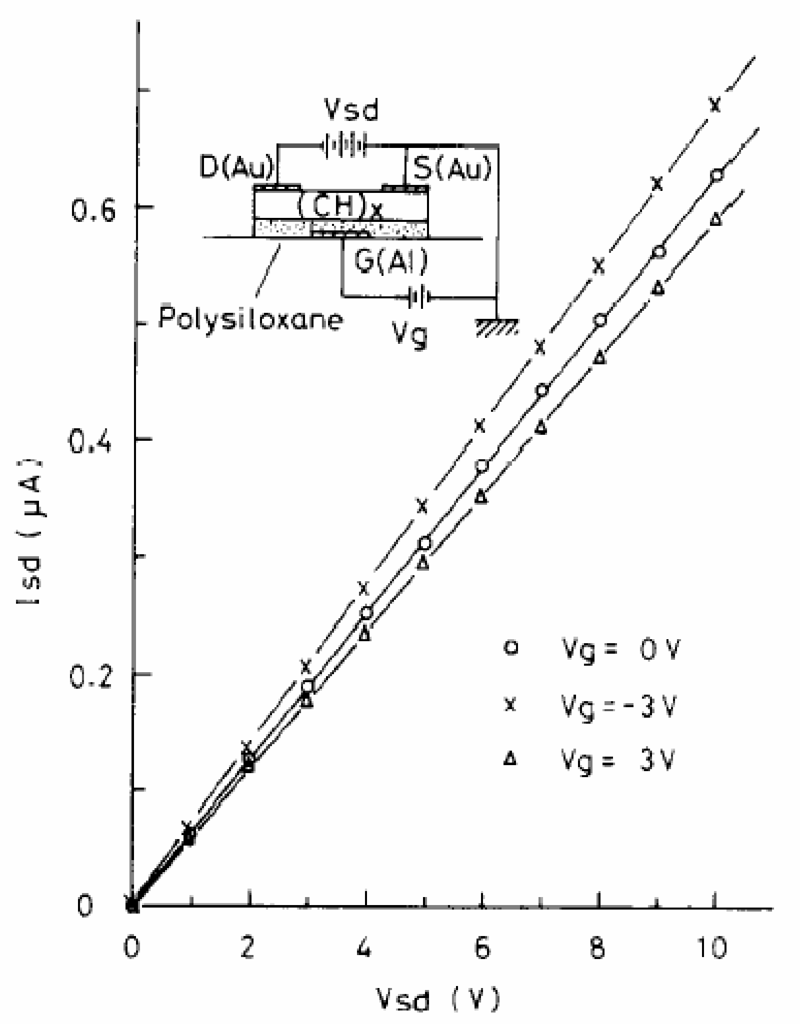
mobility ~ 0.1 $cm^2V^{-1}s^{-1}$ (comparable with a-Si:H)

1997 --- the OTFT based on pentacene

mobility ~ 1 $cm^2V^{-1}s^{-1}$

F. Garnier, Thin-film Transistors, Chapter 6

The First OTFTs



polyacetylene/polysiloxane

Very low mobility (10^{-5})
Nonexistence of pinch-off

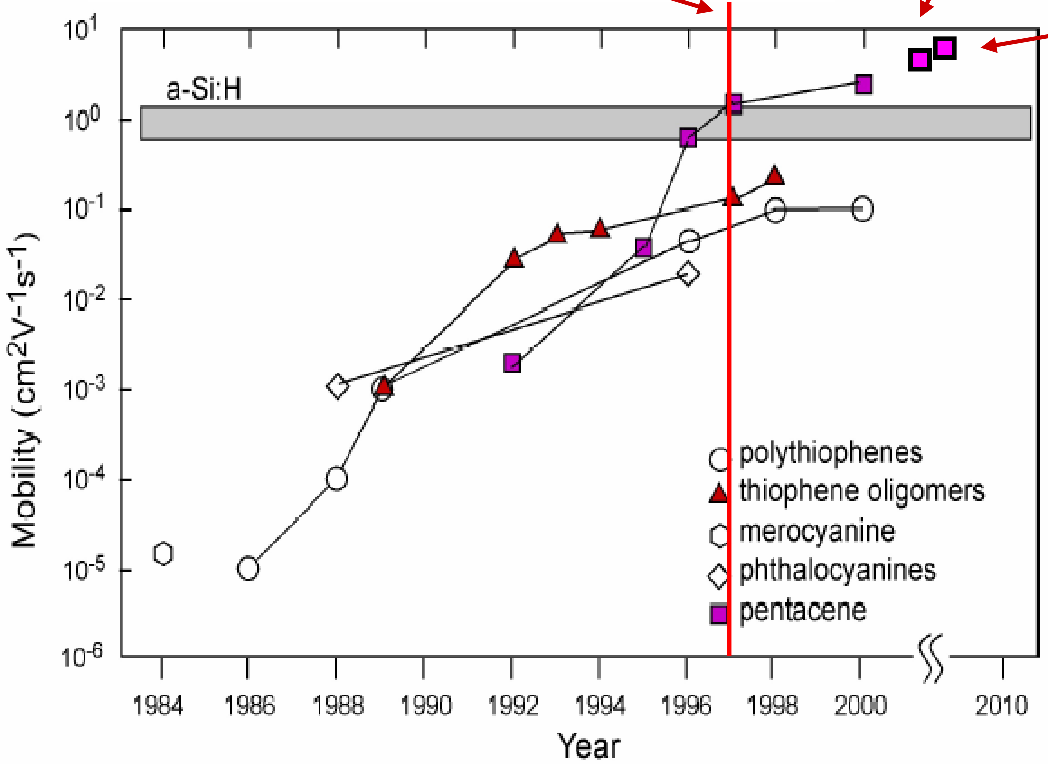
F. Ebisawa, J. Appl. Phys., 54, 3255 (1983)

Evolution of OTFT hole mobility

SAM insulator surface treatment **(1997)**

5 cm²/V.s **(2004) by 3M**

7 cm²/V.s **(2005) by Samsung (SID'05)**



C. D. Dimitrakopoulos, and P. R. L. Malenfant Adv. Mater., 14, 99 (2002)

Challenges of OTFTs

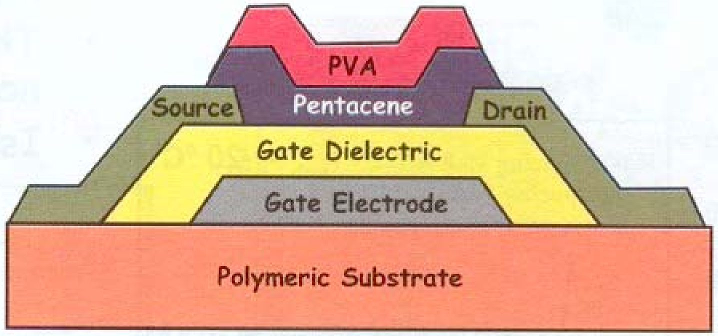
Low mobility

High threshold voltage

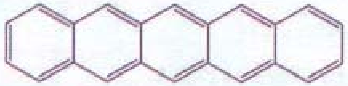
Organic thin-film transistors (OTFTs)

·Low temperature processing allows arbitrary substrates and flexible processing

·Simple device fabrication



Pentacene:

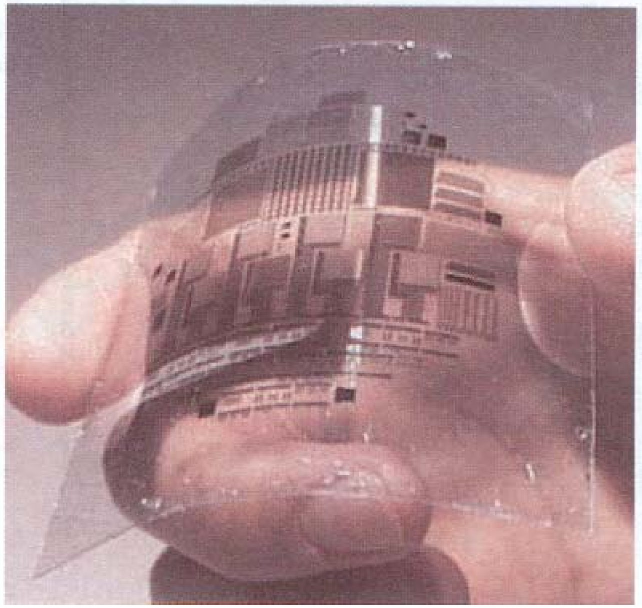

pentacene

·Small molecule organic semiconductor

·Thin film mobility > 3 cm^2/V-s, ~ 1 cm^2/V-s typical

·Simple low-temperature vacuum deposition

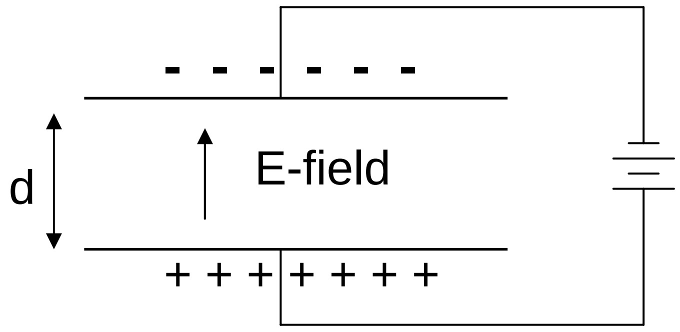
·Strong tendency to form well-ordered molecular crystals

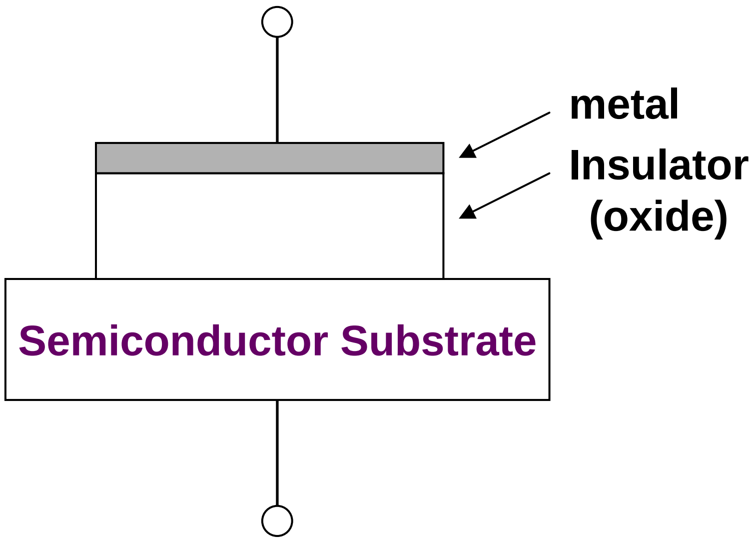


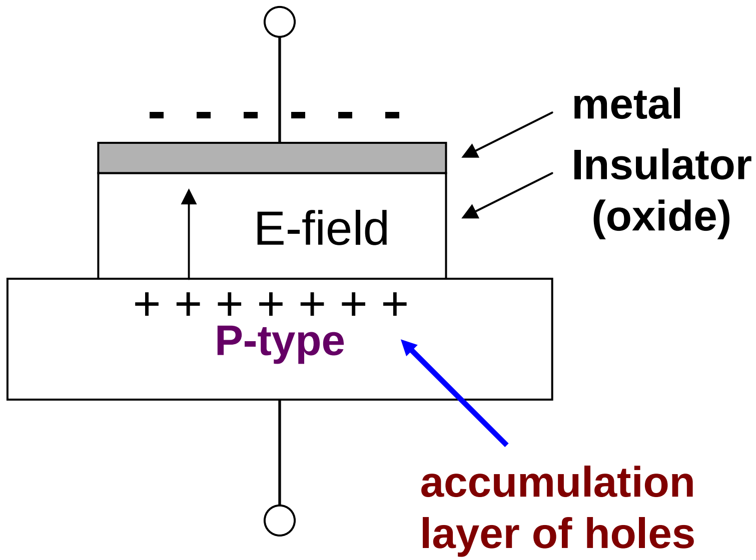
T. N. Jackson, 2004 SID seminar lecture notes.

Metal-Insulator-Semiconductor (MIS)

$C = \varepsilon A/d$

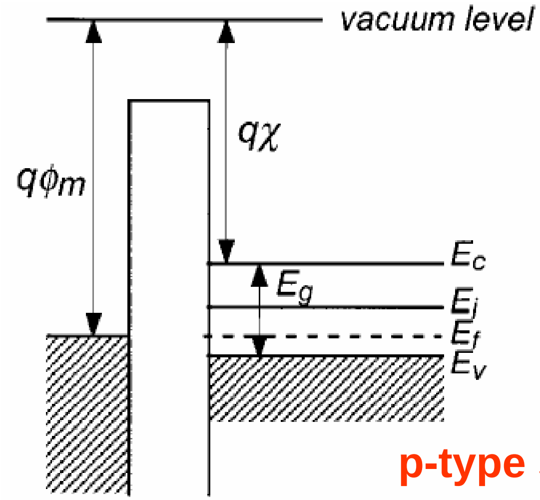




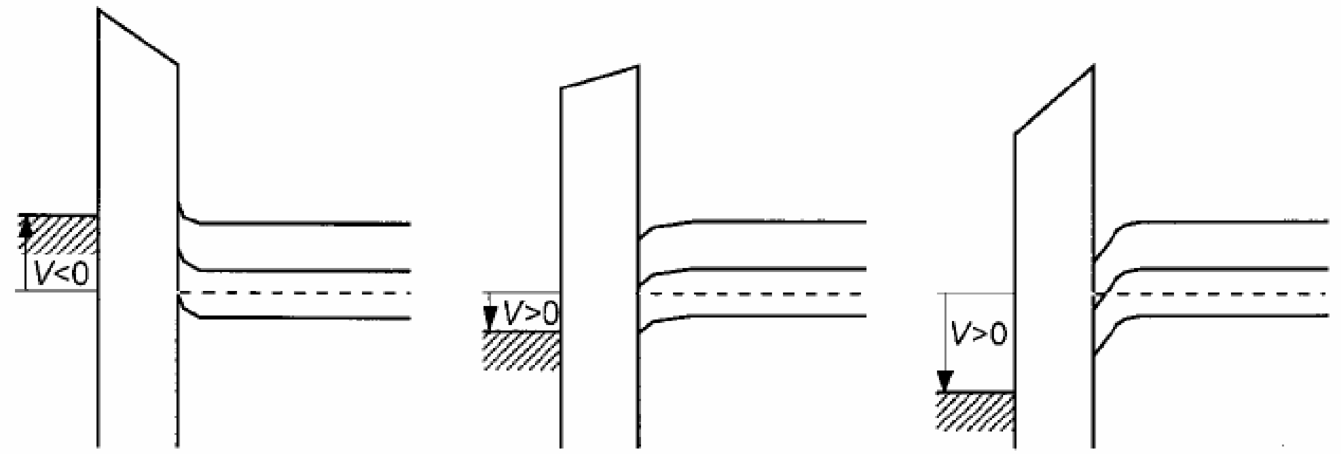


Metal-Insulator-Semiconductor Junction

Ideal MIS band diagram



p-type semiconductor

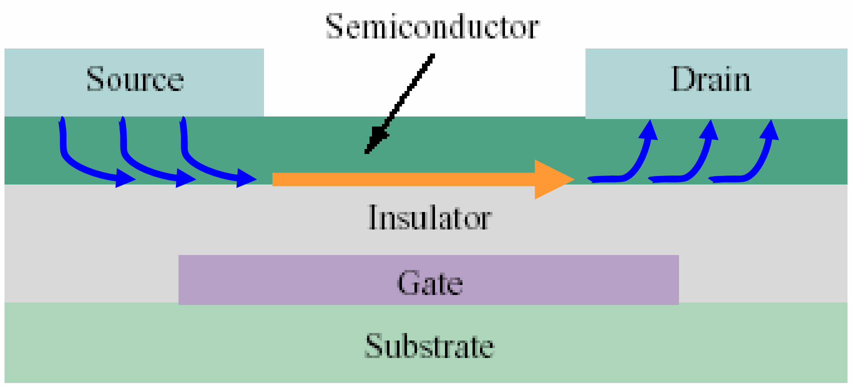


(a) **accumulation** (b) **depletion** (c) **inversion**

G. Horowitz, Adv. Mater., 10, 365 (1998)

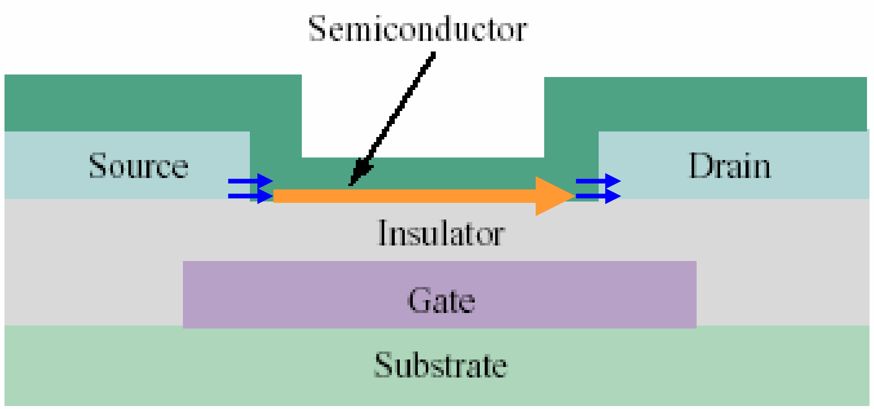
OTFT device configurations

Staggered or
Top-contact (TC) Device



(a)

Coplanar or
Bottom-contact (BC) device



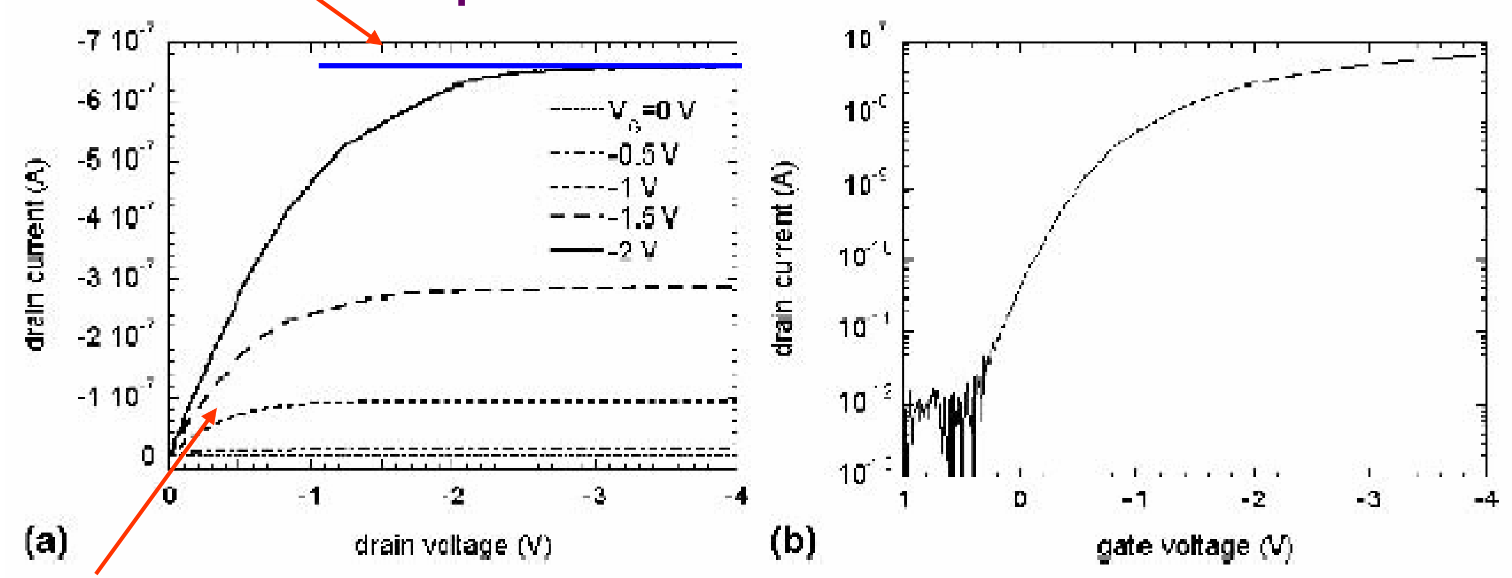
(b)

TC OTFT Rc < BC TFT Rc

Typical OTFT I-V characteristics

saturation regime

Output **Transfer**



Ohmic's law

When the drain voltage is compared to gate voltage, the voltage drop at drain Contact falls to zero and the conducting channel is pinched off

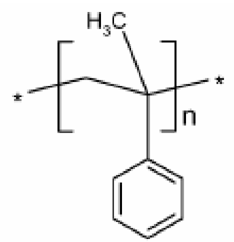
G. Horowitz, J. Mater. Res., 19, 1946 (2004)

3M's high mobility OTFTs

3M

High Mobility Pentacene Devices

- Surface treatments
- Controlled deposition conditions
- Top contact construction

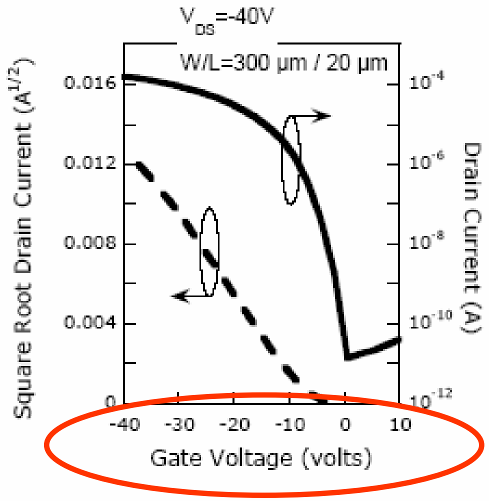


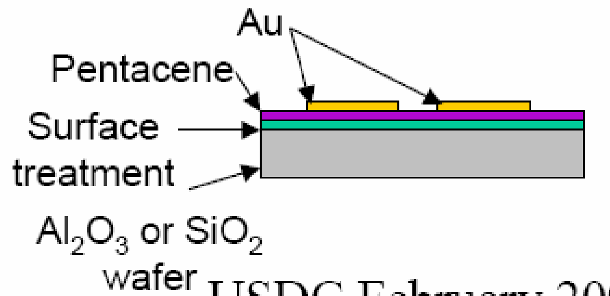
Poly-α-methylstyrene

Average μ - pentacene on Al_2O_3

Without surface treatment
~ 1 cm^2/Vs

With (AMS) surface treatment
~ 5 cm^2/Vs





3M Corporate Research Materials Lab

USDC February 2004

Charge Transport

For conventional semiconductor,

Delocalized states, and is limited by the scattering of carriers, Mainly phonons

$$T \downarrow \longrightarrow \mu \uparrow$$

$$\mu = a\, T^{-n}$$

$(n \sim 1)$

For Organic semiconductor,

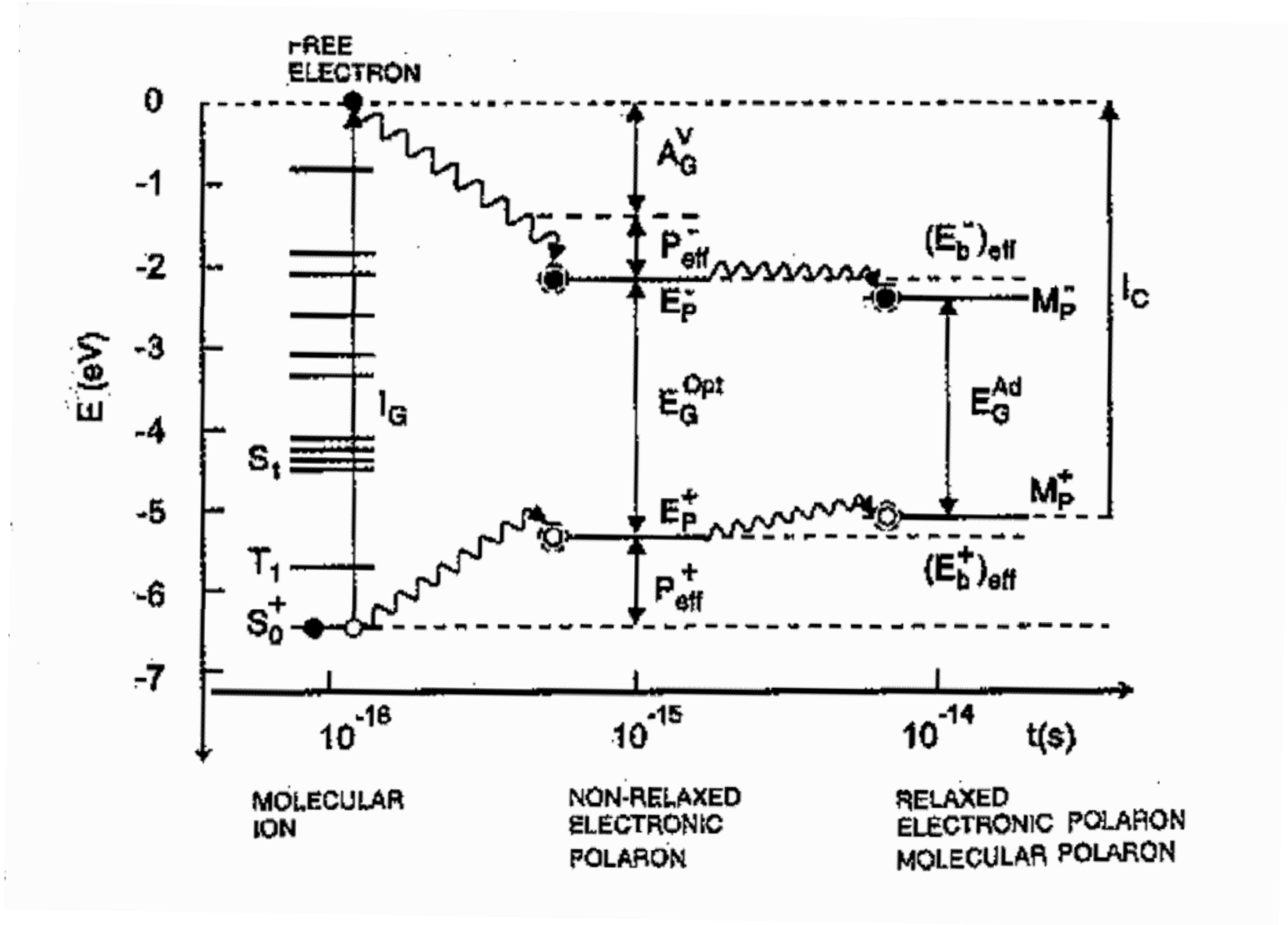
Hopping between localized states, phonon assisted (the mean free path of carriers < atomic distance)

$$T \uparrow \longrightarrow \mu \uparrow$$

$$\mu = \mu_o \exp -(E_a/kT)$$

G. Horowitz, Adv. Mater., 10, 365 (1998)

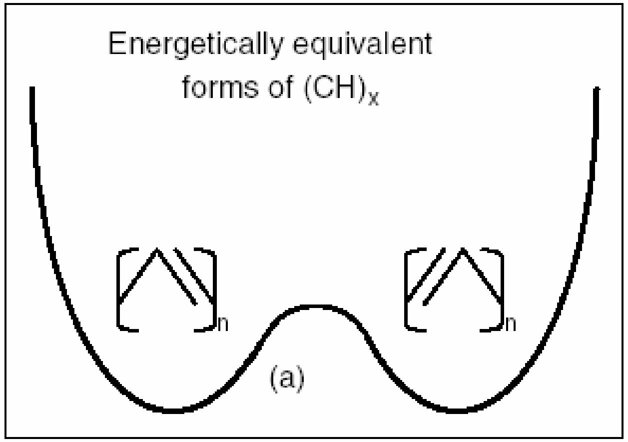
Electronic Polarons vs Molecular Polarons

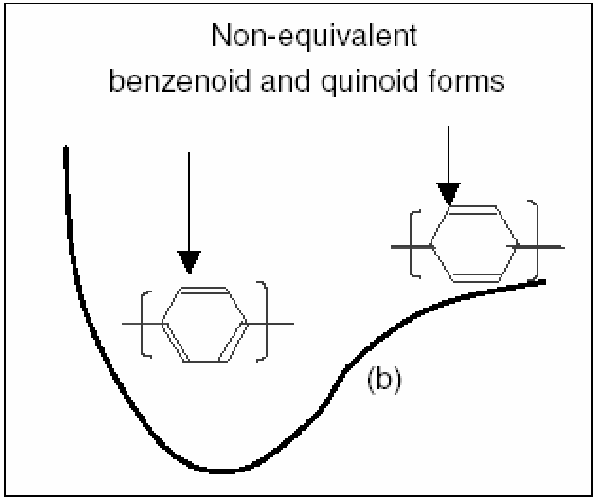


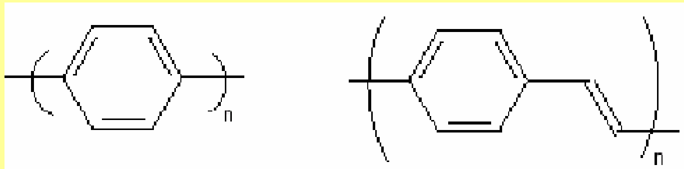
E_p^- & E_p^+ : **non-relaxed electronic polaron** states
P_{eff}^- & P_{eff}^+ : effective electronic polarization energies
M_p^- & M_p^+ : **molecular polaron** conductivity levels
$(E^-)_{eff}$ & $(E^+)_{eff}$: effective formation energies of a molecular polaron (due to vibronic polarization)

R. Farchioni & G. Grosso, Organic Electronic Materials (Wiley, New York, 1981)

Degenerate PA and non-degenerate PPP

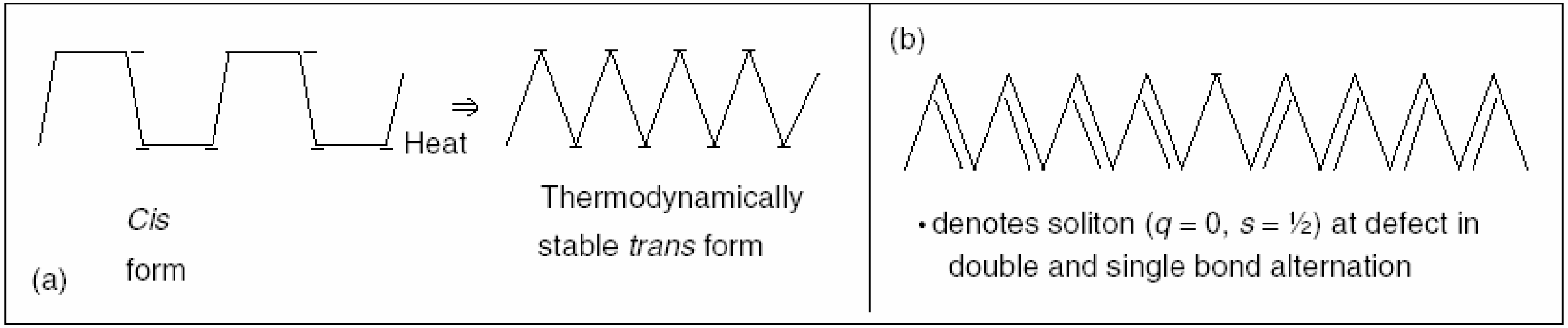






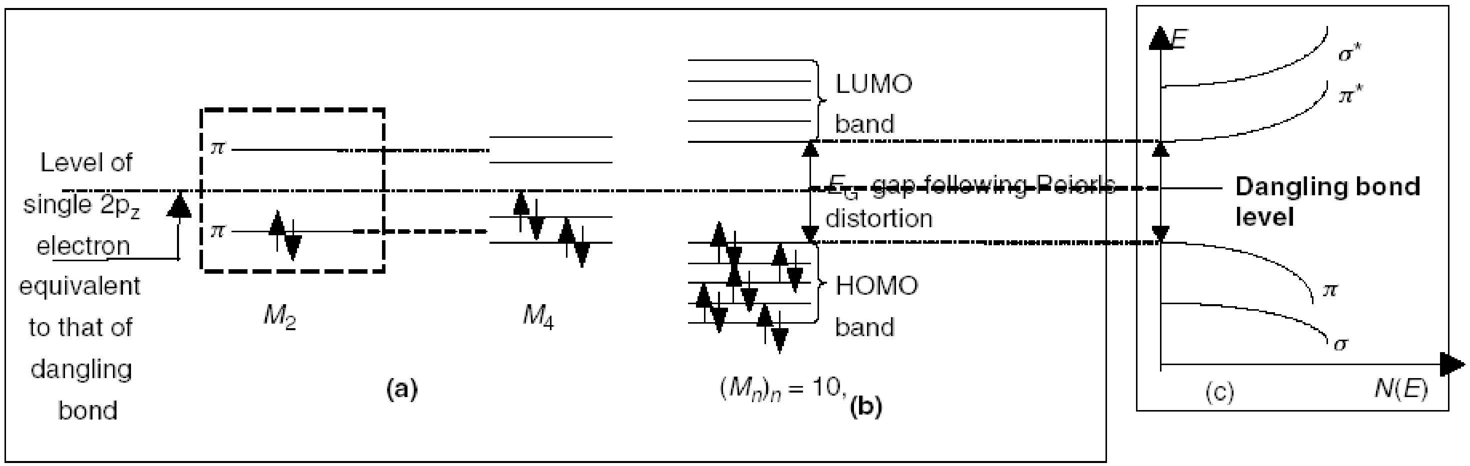
Structure of PA and PPV

Soltion defect and energy level



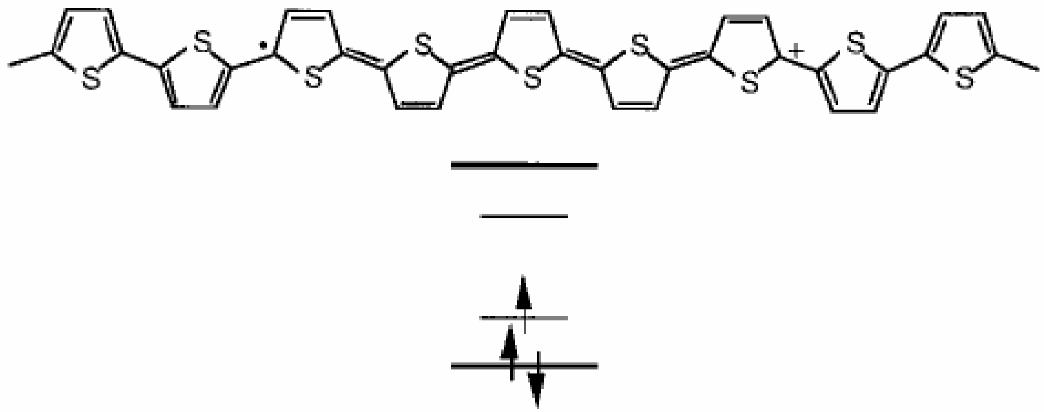
Soliton defect in PA

Soliton: structure defect, a stable free radical
can propagate along the chain, may not carry any charge itself



The small polaron

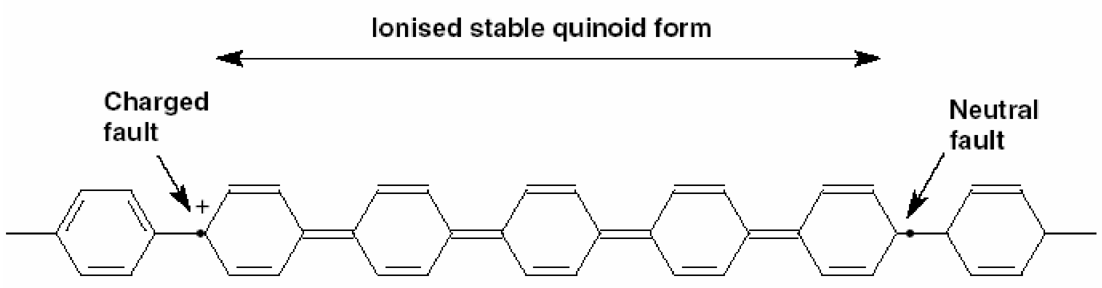
A polaron results from the deformation of the conjugated chain under the action of the charge.
The charge is "self-trapped" by the deformation it induced in the chain.

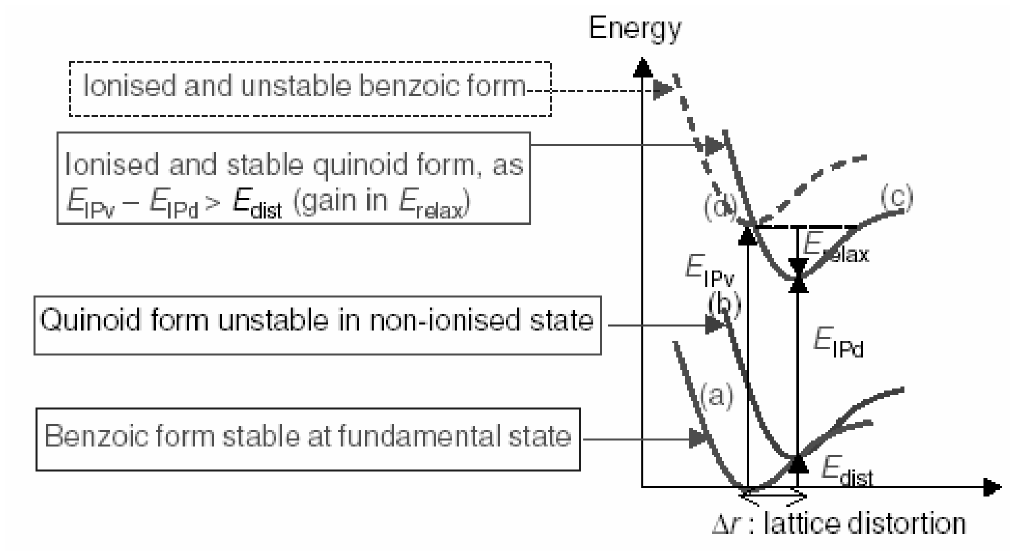


A polaron in polythiophene

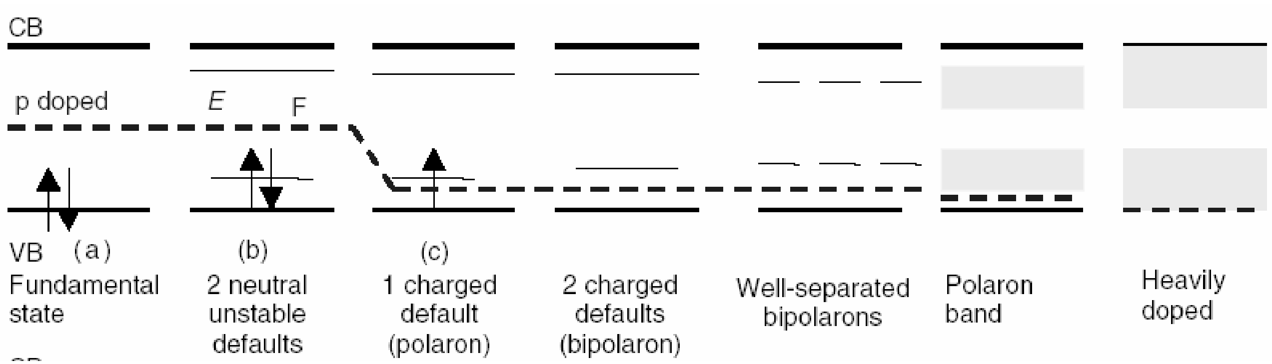
G. Horowitz, Adv. Mater., 10, 365 (1998)

Charge storage in conjugated polymers





p-doped



The small polaron model : Holstein's model

The total energy : (three terms)

The lattice energy E_L,

$$E_L = \sum_{n=1}^{N} \frac{1}{2M}\left(\frac{\hbar}{i}\frac{\partial}{\partial u_n}\right)^2 + \frac{1}{2}M\omega_0^2 u_n^2$$

N harmonic oscillators vibrates at frequency, ω_0

The energy dispersion of the electron,

$$E_k = E_0 - 2J\cos(ka)$$

(J : the electron transfer energy)

The electron-lattice coupling

$$\varepsilon_n = -Au_n$$

Important parameter : polaron binding energy E_b : = $A^2/(2M\omega_0^2)$

"Small" polaron : electronic bandwidth 2J < E_b, (perturbation)

High temperature limit :

$$\mu = \sqrt{\frac{\pi}{2}}\frac{ea^2}{\hbar}\frac{J^2}{\sqrt{E_b}}(kT)^{-3/2}\exp\left(-\frac{E_b}{2kT}\right)$$

~ 1 $cm^2V^{-1}s^{-1}$ ($ea^2/\hbar$)

G. Horowitz, Adv. Mater., 10, 365 (1998)

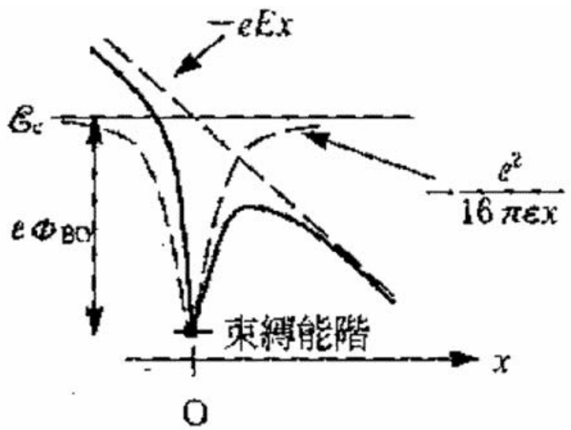
Field-Dependent Mobility

The mobility of organic materials become field-dependent at high field (~ 10^5 V/cm) (a general feature of organic devices)

Poole-Frenkel mechanism,

the coulombic potential near the localized levels is modified by the applied filed in such a way as to increase the tunnel transfer rate between sites.

$$\mu(F) = \mu(0)\exp\left(\frac{q}{kT}\beta\sqrt{F}\right)$$



G. Horowitz, Adv. Mater., 10, 365 (1998)

Multiple Trapping and Release (MTR)

A narrow delocalized band with a high concentration of localized traps
(widely used in a-Si)

Assumptions:

1. Trap probability ~ 1

2. The release of trapped carriers is controlled by a thermal activated process.

$$\mu_D = \mu_0 \alpha \exp\left(-\frac{E_t}{kT}\right)$$

single trap

a single trapping level E_t

α is the ratio of effective density of states between the trap level and the delocalized band edge

G. Horowitz, Adv. Mater., 10, 365 (1998)

Multiple Trapping and Release (MTR)

Gate-bias-dependent mobility

At low gate bias, field-induced charges go to localized levels
⇒ low mobility

At high gate bias, more localized levels are filled, and Fermi level approach the delocalized band, increasing mobility

However, at high field region, the mobility is still too low to correspond to transport in delocalized states

G. Horowitz, Adv. Mater., 10, 365 (1998)

Two general types of organic materials

Two general cases

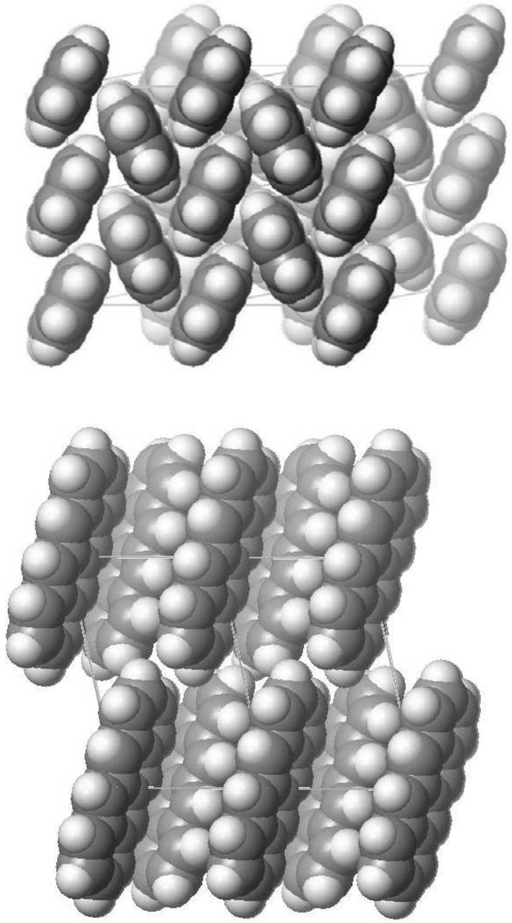
"Low" mobility materials

- **transport via hopping**
- **typical mobility $10^{-6} \sim 10^{-1}$ $cm^2V^{-1}sec^{-1}$**
- **common for polymeric or disorder organic semiconductors**

"high" mobility materials

- **transport via narrow band transport**
- **typical mobility $10^{-1} \sim 10$ $cm^2V^{-1}sec^{-1}$**
- **$\mu(T)$ depends on details (traps, doping, bandwidth, etc.)**
- **common for small molecular crystal organic semiconductors**

Crystal Structure - Anisotropy



Tetracene

Herringbone-Structure

van-der-Waals (attraction)
Pauli-Principle (repulsion)

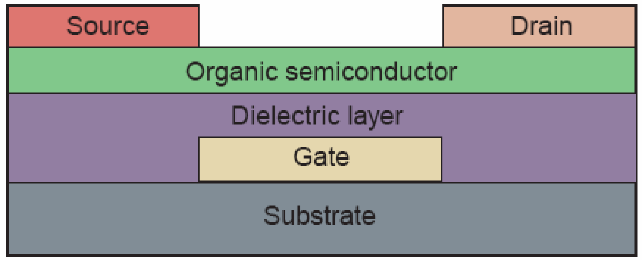
Layered Semiconductor

Anisotropy

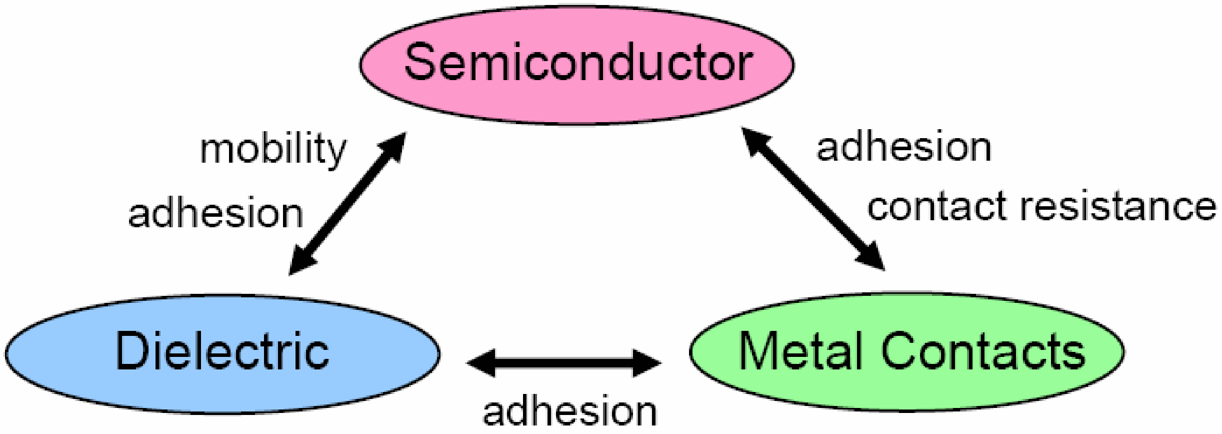
	$\sigma_{par} / \sigma_{per}$	$\sigma_{par1} / \sigma_{par2}$
Thiophenes	~70	~1.5
Acenes	~3	~1.5

Critical Issues of OTFTs

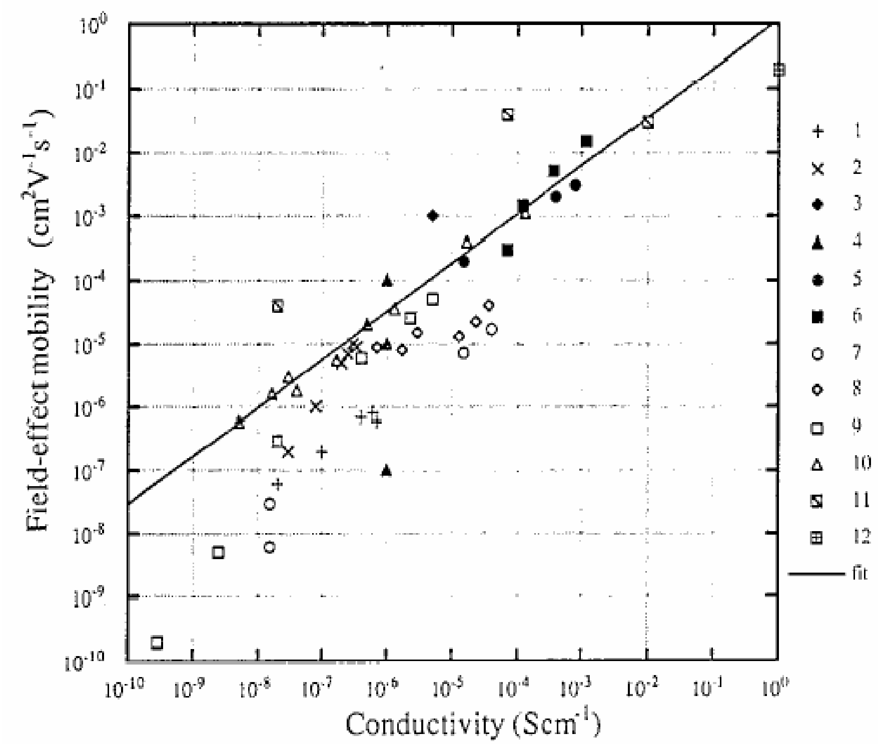
- Mobility
- On/Off Ratio
- Contact Resistance
- Dielectric Compatibility
- (Solvent Compatibility)

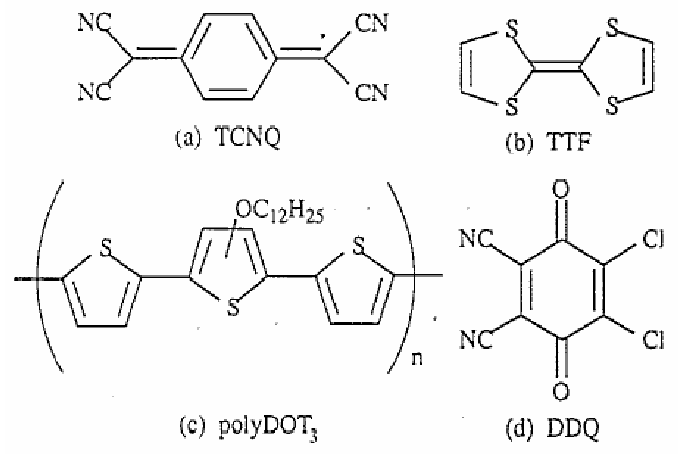


Top contact



Conductivity vs Mobility in doped amorphous organic semiconductor



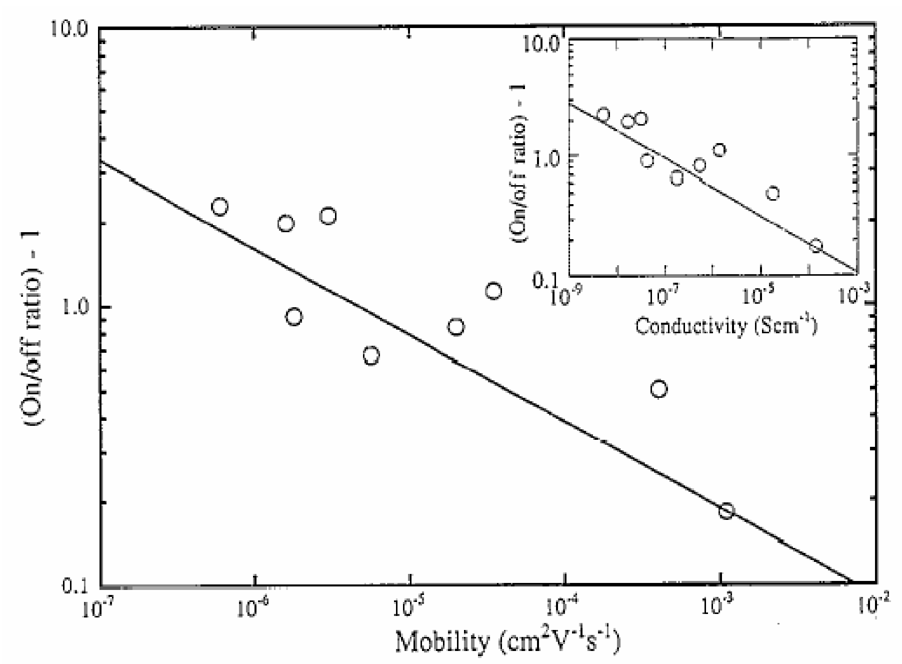


$\mu \sim \sigma^{\delta}$ ($\delta = 0.76$)

Data set	Material	Deposition technique	Ref.
1	PHT AA	Langmuir–Blodgett	[14]
2	QT AA	Langmuir–Blodgett	[14]
3	ScPc2	vacuum-deposited	[15]
4	P3HT	spin-coated	[16]
5	Pc2Lu	vacuum-deposited	[17]
6	Pc2Tm	vacuum-deposited	[17]
7	polyalkylthiophene	spin-coated	[18]
8	polyalkylthiophene	spin-coated	[39]
9	TCNQ	vacuum-deposited	[23]
10	polyDOT$_3$	spin-coated	this work
11	C_{60}	vacuum-deposited	[19]
12	(*N*-octa′)-Ni(dmit)$_2$	Langmuir–Blodgett	[20]

A. R. Brown *et al.*, Synth. Met., 68, 65 (1994)

Conductivity vs Mobility in doped amorphous organic semiconductor

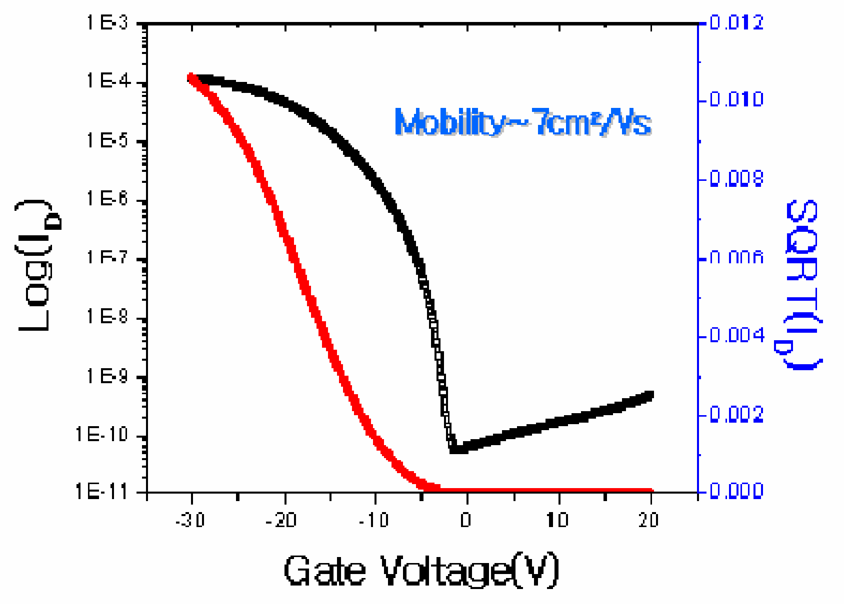


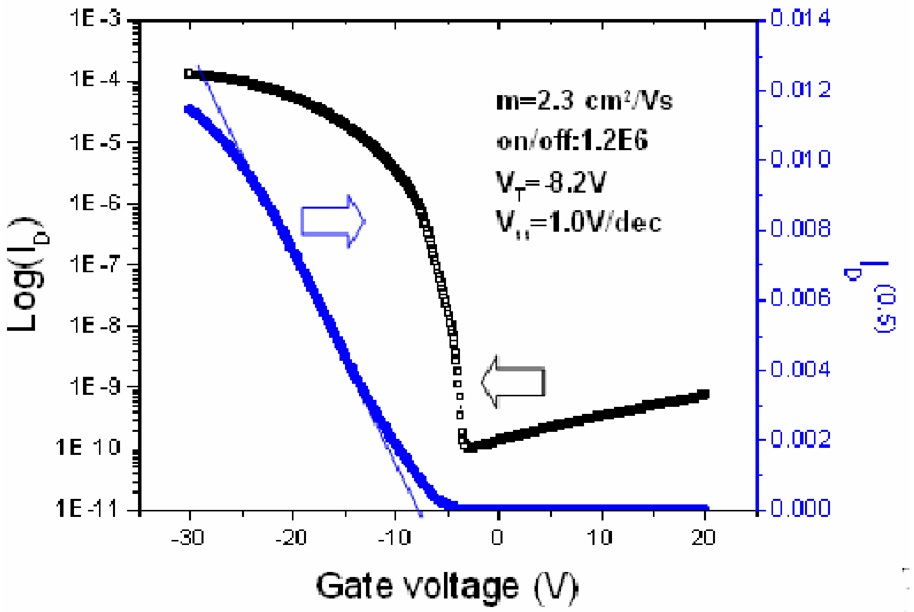
$\mu \sim \sigma^{\delta}$ $(\delta < 1)$

More rapid increase in conductivity with dopant concentration results in decrease of on/off ratio

A. R. Brown *et al*., Synth. Met., 68, 65 (1994)

High performance OTFT array





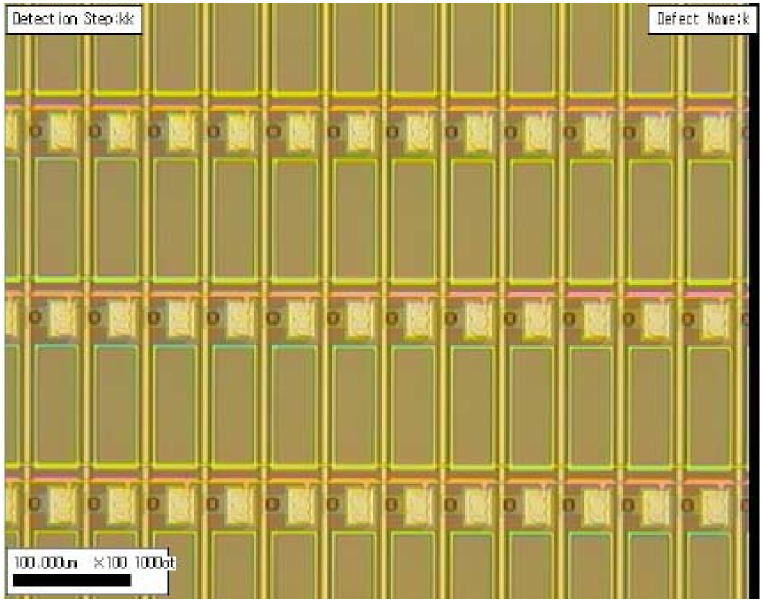
Top contact / Au electrodes
New S4 insulator
(polysilicon-acrylate with titanium complex)

Bottom contact / Au electrodes

M. P. Hong *et al*, SID 05'

High performance OTFT array

Bottom contact / ITO electrodes

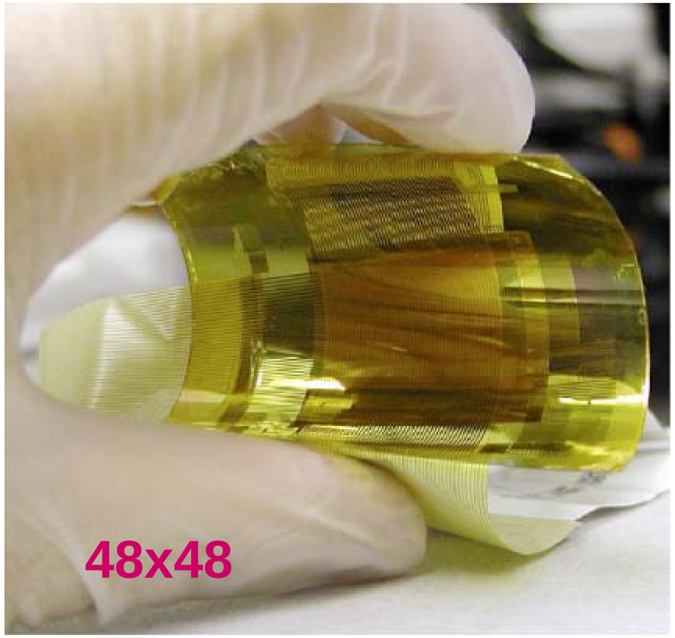


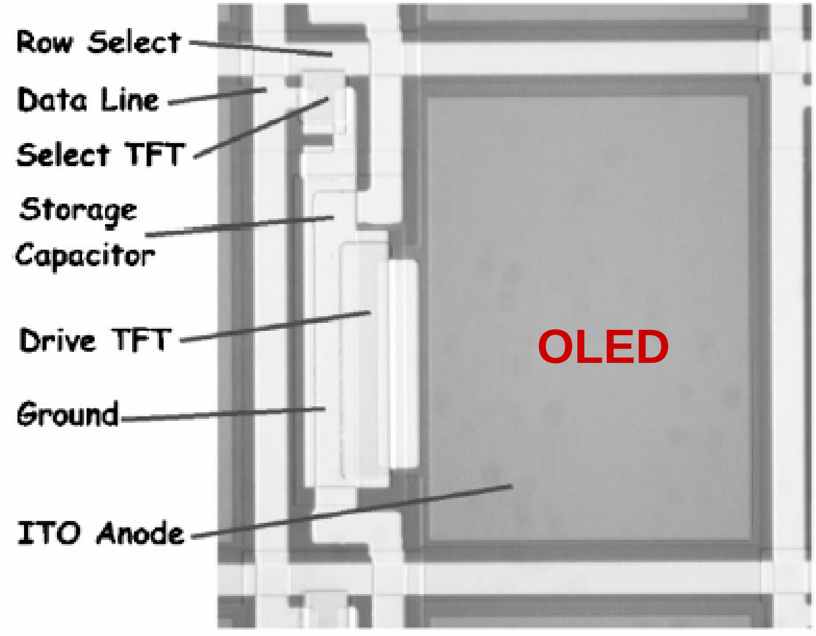
15.0" OTFT array
(Al/Mo gate)

Prototype of 15" XGA OTFT-LCD

M. P. Hong *et al*, SID 05'

All-organic active matrix flexible display

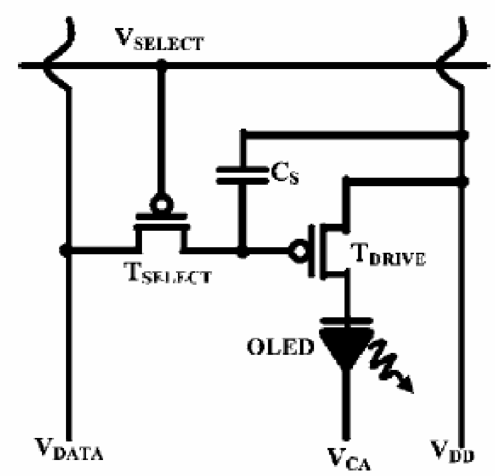




Pixel pitch 500μm; Aperture ratio:52%
Drive Transistor: W/L = 200 μm/20 μm
Select Transistor: W/L = 20 μm/20 μm

SiN/SiO_2 bi-layer gate (PECVD)
Nickel gate electrode
Pt source and drain electrodes

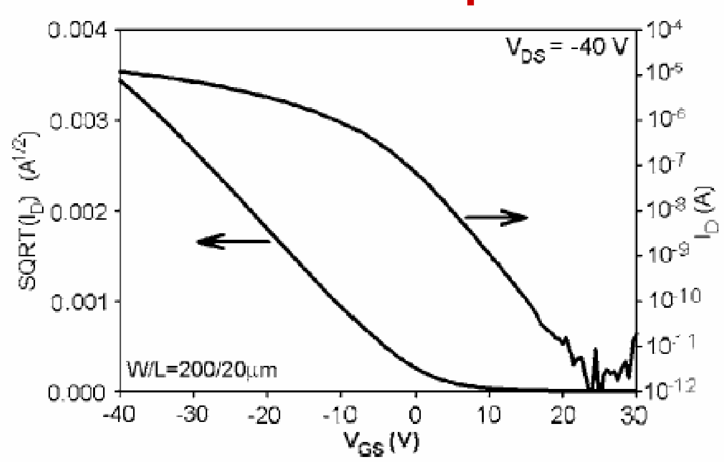
Substrate:
Flexible polyethylene terephthalate (PET)



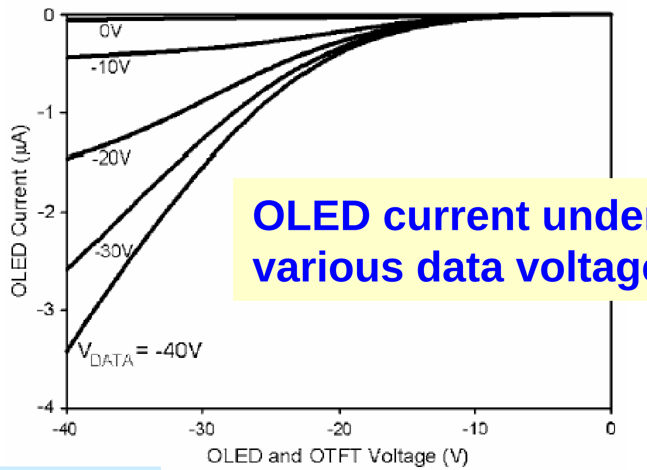
L. Zhou *et al*, **APL**, 88, 083502, (2006)

All-organic active matrix flexible display

Before OLED deposition



mobility : 0.2 cm^2/Vs; V_t = 0.4V
on-off ratio : ~ 10^7



OLED current under various data voltage

Good current modulation

Operating while flexed

A pattern of stripes

L. Zhou *et al*, **APL**, 88, 083502 (2006)

Fabrication of OTFTs

For most OTFTs,

“Inverted” architecture, in which gate electrode is laid down first

1. **Electropolymerization**
2. **Solution-processed deposition**
   - **Spin-coating**
   - **Ink-jet printing**
3. **Vacuum evaporation**

G. Horowitz, Adv. Mater., 10, 365 (1998)

Electropolymerization of polythiophene

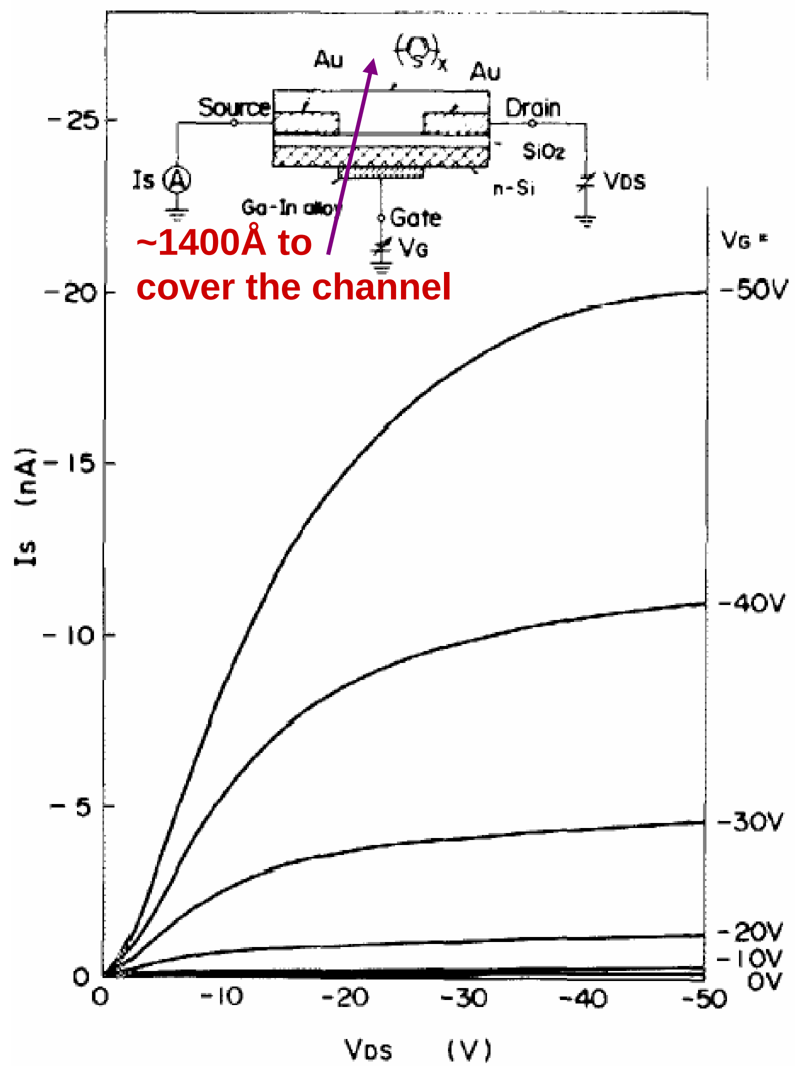
Starting material, 2,2'-bithiophene

For as-grown polythiophehe,
no field-effect was observed
Should be undoped electrochemically firstly

Drawbacks:

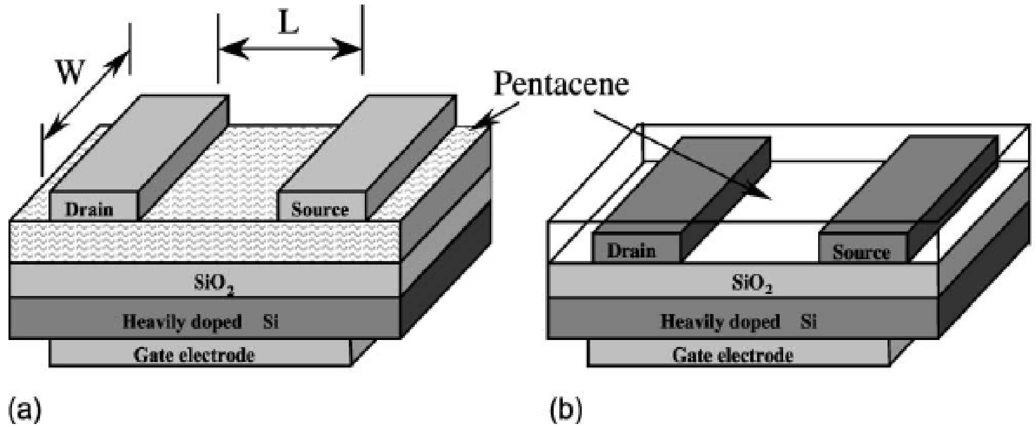
Low mobility, 10^{-5} cm^2/V.sec (high density of structural and conjugation defects)

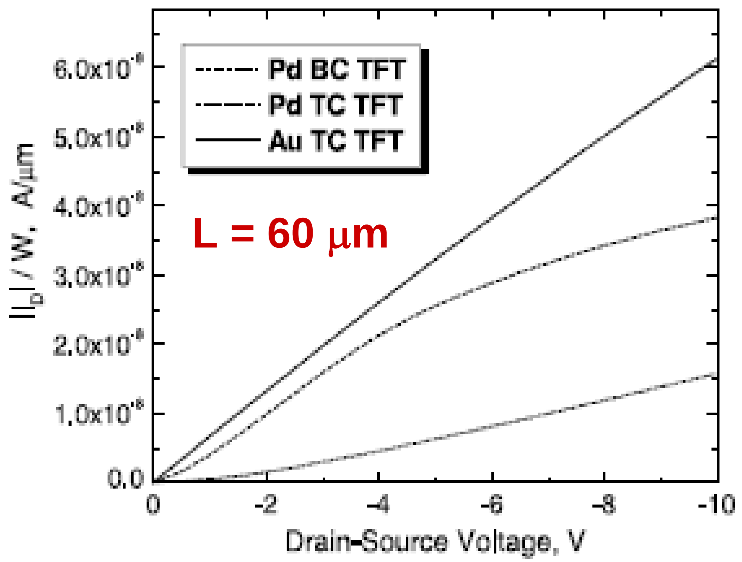
Low on-off ratio 10^2-10^3



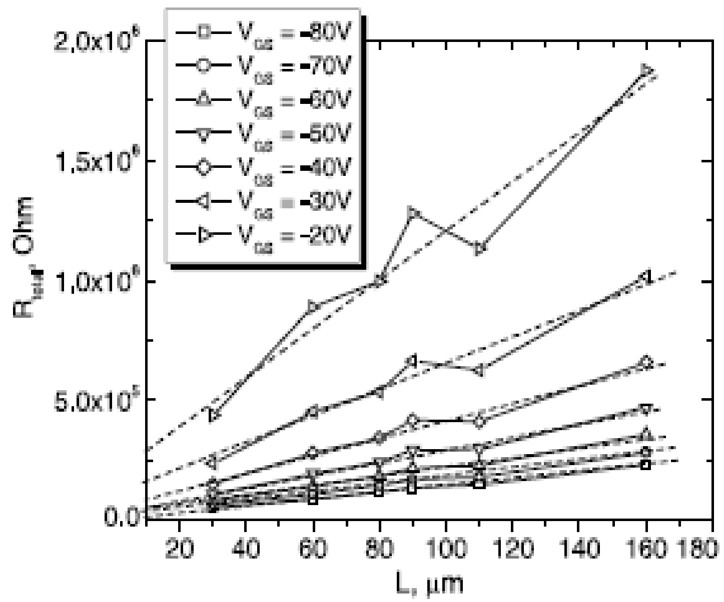
A. Tsumura, and H. Koezuka, and T. Ando, Appl. Phys. Letts., 49, 1210 (1986)

Contact resistance in OTFTs





pronounced non-linearity for Pd TC and BC devices

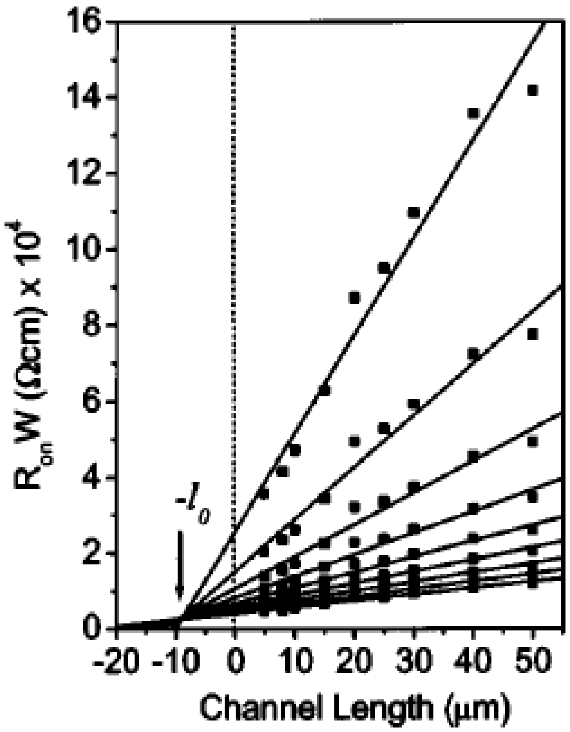


Transfer line method Gold TC TFT

P. V. Necliudov et al. Solid-State Electronics, 47, 259 (2003)

Transfer line method

$$R_{on} = \frac{\partial V_{DS}}{\partial I_{DS}}\Big|_{V_{DS}\to 0}^{V_G} = R_{ch} + R_p = \frac{L}{W\mu_i C_i (V_G - V_{T,i})} + R_p$$

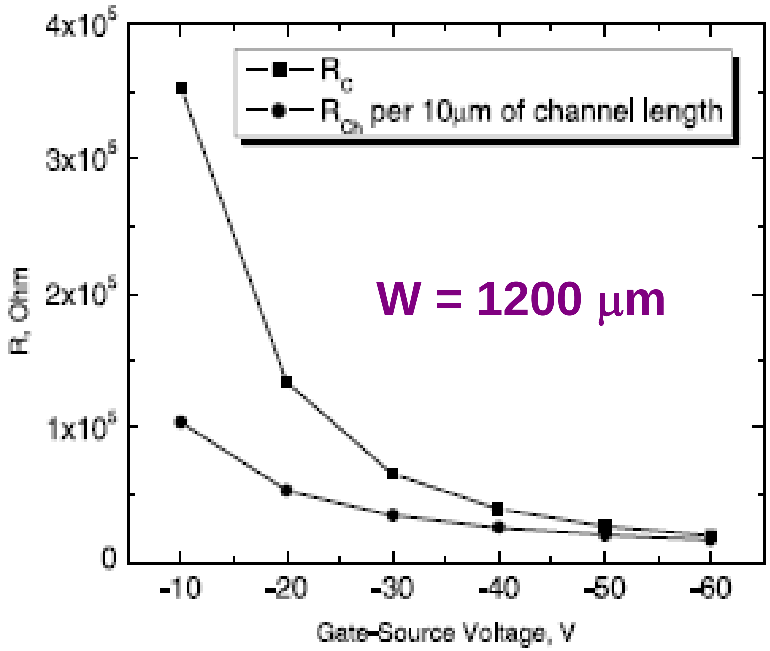


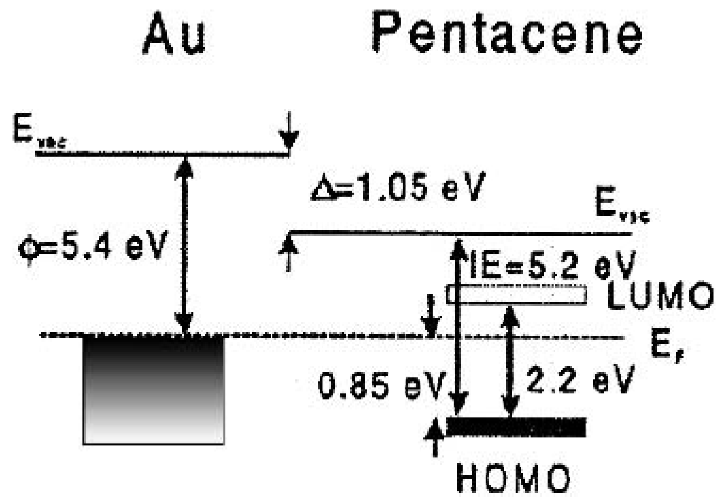
μ_i ,the intrinsic mobility
$V_{T,i}$,threshold voltage
R_p ,parasitic resistance
R_{on} ,device resistance
R_{ch} ,channel resistance

The contact resistance is extracted by plotting the width-normalized resistance (RW) as a function of L

The extrapolation to zero channel length gives the total (S&D) contact resistance

Contact resistance in OTFTs





Channel resistance becomes comparable with the contact resistance at V_{GS} > 40V

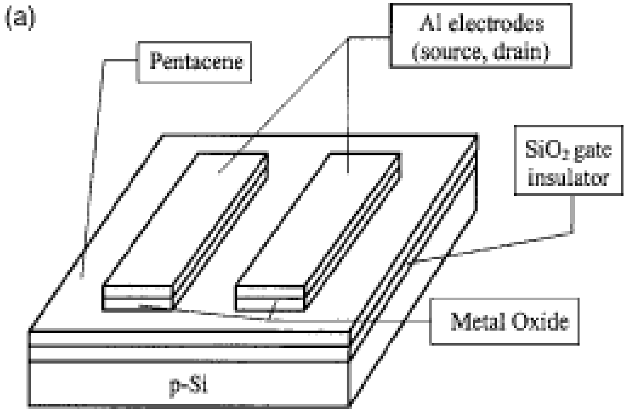
Performance of TFT with L < 10 mm can be limited by contacts

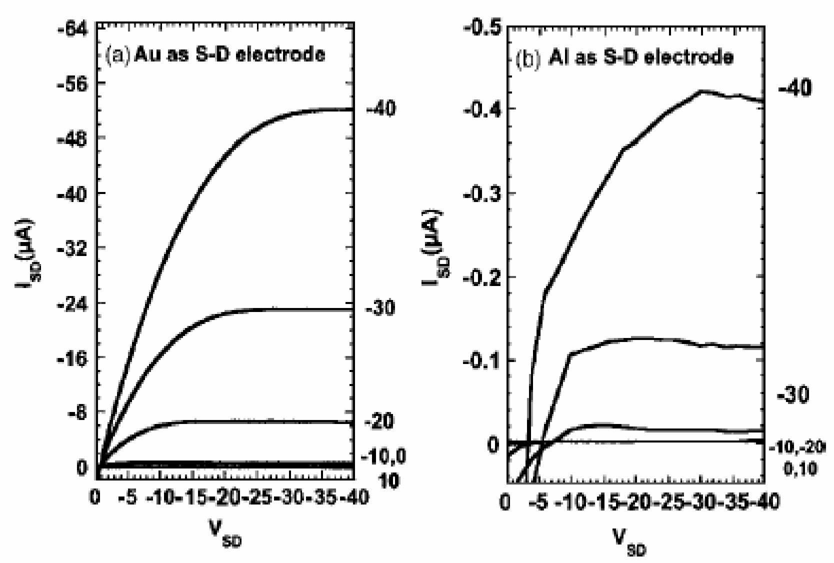
Shottky-Mott model is not followed

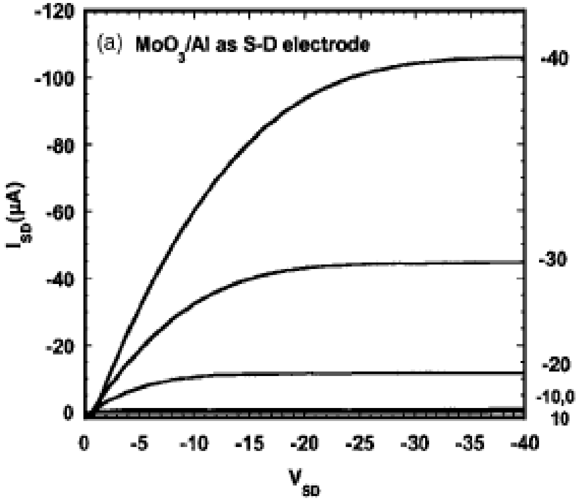
Adsorbed molecules tend to push back the tailing e^- density at the metal surface, thus reducing the surface dipole and decreasing the work function of the metal

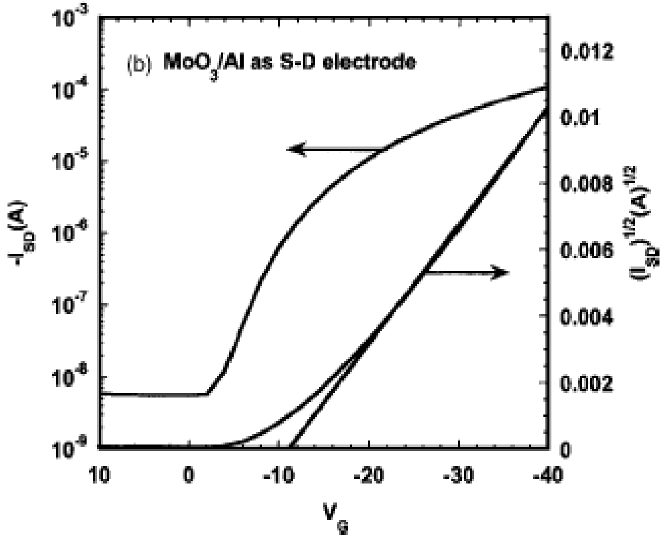
P. V. Necliudov et al. Solid-State Electronics, 47, 259 (2003)

Metal oxide/metal bilayer electrodes for OTFTs









Large injection barrier while Al was used as the electrodes

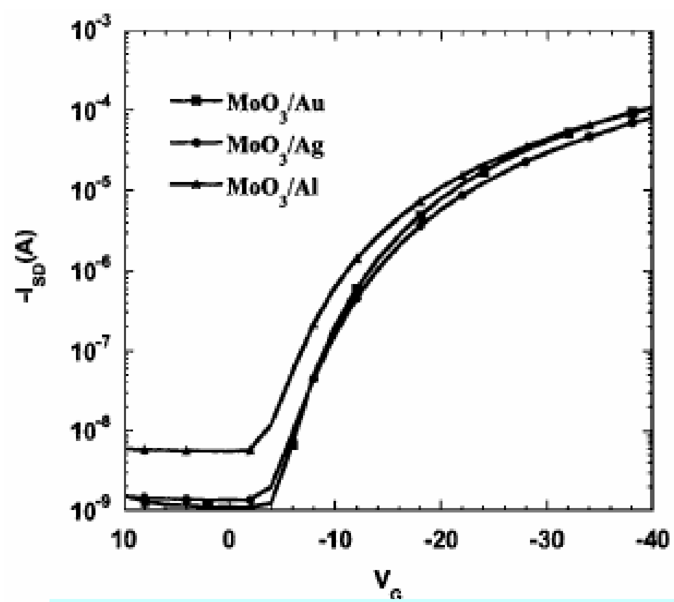
Improved I-V characteristics after MoO_3 is incorporated

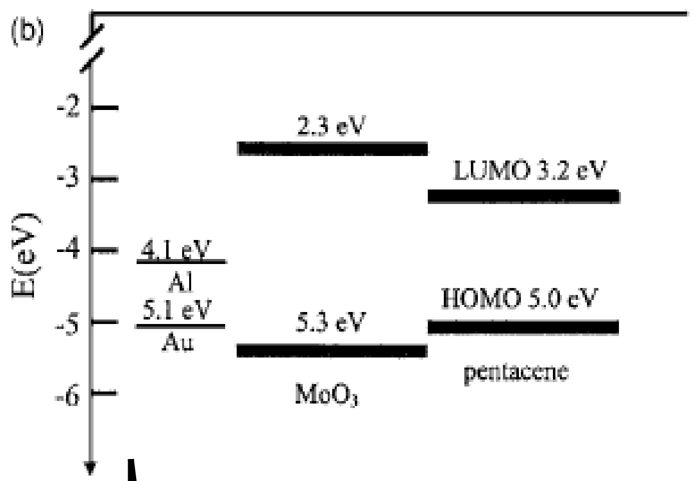
C. –W. Chu et al. Appl. Phys. Lett, 87, 193508 (2005)

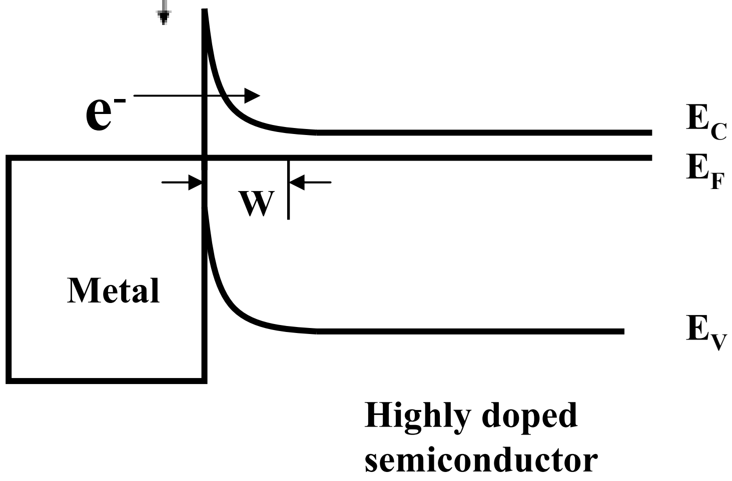
Metal oxide/metal bilayer electrodes for OTFTs

TABLE I. Electrical parameters of the OTFTs in this study.

Drain-source electrodes	Mobility ($cm^2/V\ s$)	Threshold voltage (V)	On-off ratio
Al	2.8×10^{-3}	−16.2	2.3×10^{2}
Au	0.182	−8.75	2.8×10^{4}
MoO_3/Al	0.4	−12.1	3.8×10^{4}
WO_3/Al	0.253	−12.88	4.1×10^{4}
V_2O_5/Al	0.226	−10.43	1.8×10^{4}







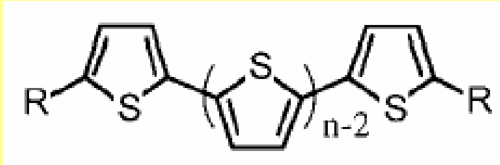
An Ohmic contact is achieved between the metal and MoO_3

MoO_3 yeilds a thin film containing MoO to MoO_3 as well as Mo, resulting in highly doped semiconductor

C. –W. Chu et al. Appl. Phys. Lett, 87, 193508 (2005)

Materials for OTFTs

Oligothiophenes



(R = C_nH_{2n+1})

Mobility is "independent" of the present or absent of alkyl end substitution

The first OTFT made with a small conjugated molecule

Table 1. Typical mobility [$cm^2 V^{-1} s^{-1}$] of recent oligothiophene-based OFETs.

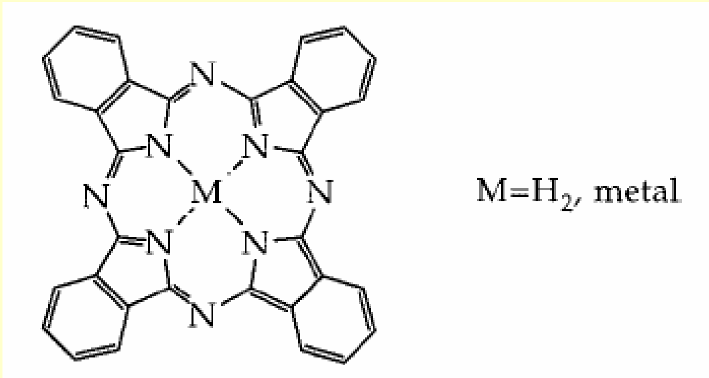
Compound	Unsubstituted	Dihexyl-substituted	Reference
4T	$10^{-4} - 6 \times 10^{-3}$		[35,36]
5T	1.5×10^{-3}		[36]
6T	0.01 – 0.03	0.04 – 0.06	[30–32]
		0.09 – 0.13	[34]
8T	0.01 – 0.03	0.01	[35,37]

G. Horowitz, Adv. Mater., 10, 365 (1998)

Phthalocyanines (PCs)

The first reported organic semiconductors (1948)

Thermally stable up to 400^{o}C and easy to evaporate under vacuum



Mobility : 0.0001 ~ 0.01 $cm^2V^{-1}s^{-1}$

Very sensitive to oxygen

G. Horowitz, Adv. Mater., 10, 365 (1998)

Pentacene

Belong to the family to polyacenes

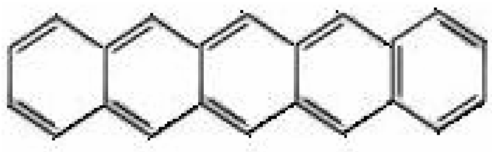
Table 2. Field-effect mobility [$cm^2 V^{-1} s^{-1}$] of pentacene with various modes of deposition and substrate temperature (RT: room temperature).

Deposition mode	Substrate temperature [°C]	Mobility	Reference
Vacuum evaporation	RT	0.002	[48]
Spin-coated precursor		0.001	[51]
Pulsed-laser	RT	0.03	[52]
Vacuum evaporation	RT	0.038	[49]
Vacuum evaporation	85	0.4	[53]
Vacuum evaporation	120	0.62	[50]

On-off ratio : up to 10^8

properties:

*sublime at 290 °C-300 °C
*decompose > 300 °C in air
*do not dissolve in water
*slightly dissolved in organic solvents
*optical band gap : 2.8 eV

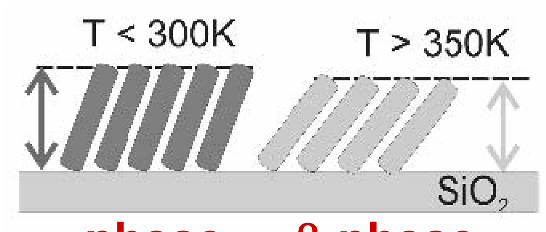


$C_{22}H_{14}$

G. Horowitz, Adv. Mater., 10, 365 (1998)

Pentacene

In bulk, triclinic phase
(β-phase, d_{001} = 14.5Å)



α-phase **β-phase**

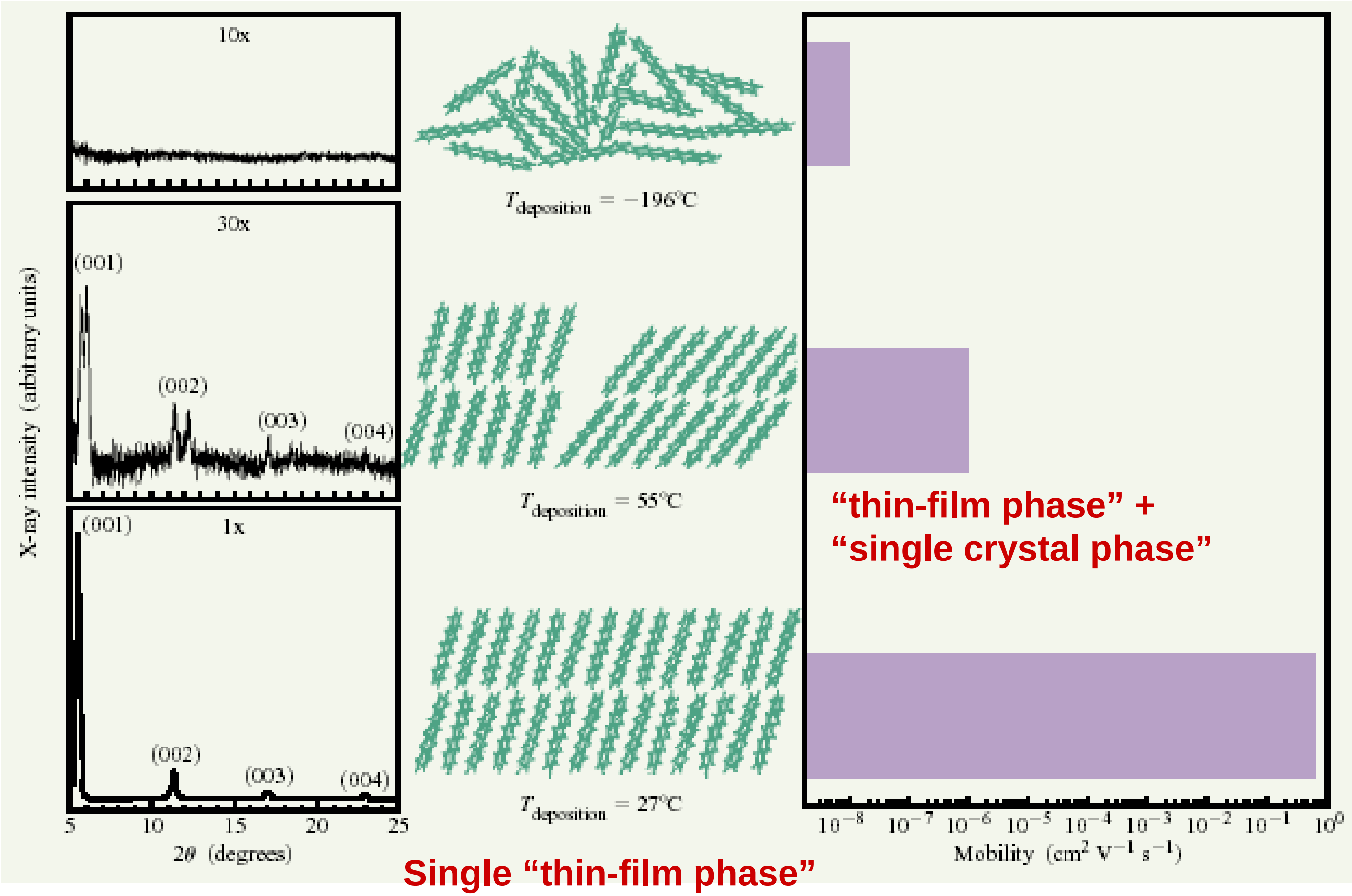
thin-film phase

single crystal phase

On SiO_2 surface
metastable, surface induced structure
(α-phase, d_{001} = 15.5Å)
called "thin-film structure"
(due to the low (001) surface energy)

Length of pentacene = 16 Å
Different of in molecular packing will affect dramatically the electronic properties

Pentacene



X-ray differactograms, and schematic representations of structural order of pentacene at different substrate temperature

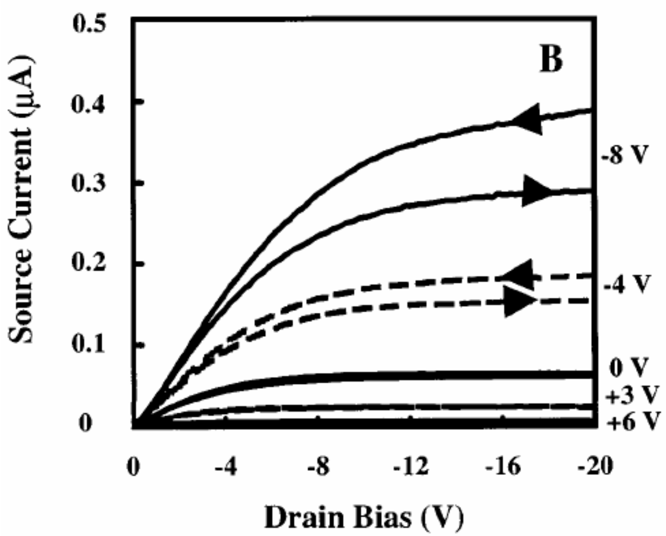
Solution Processed Pentacene

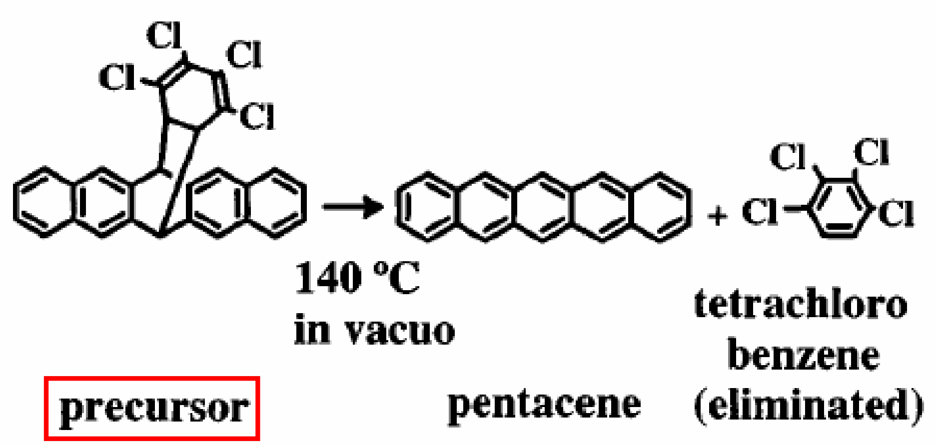
Mobility : 9×10^{-3} cm^2/Vs

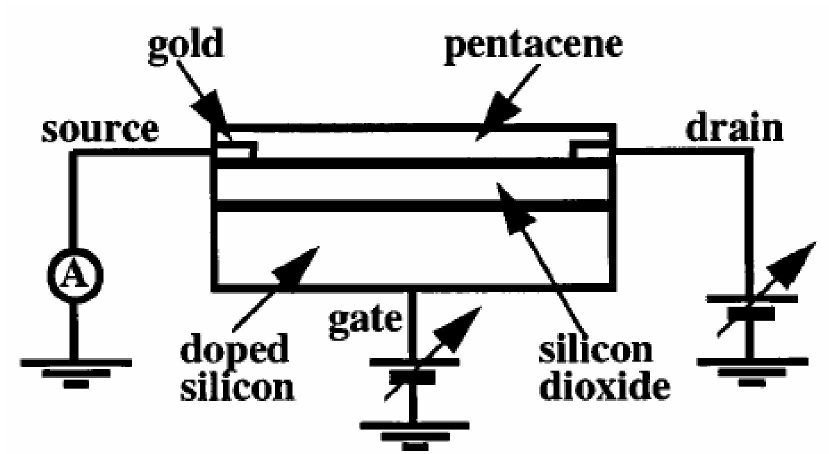
On-off ratio ~ 10^5

Advantages :

- **low temperature process**
- **can be patterned by IJP**

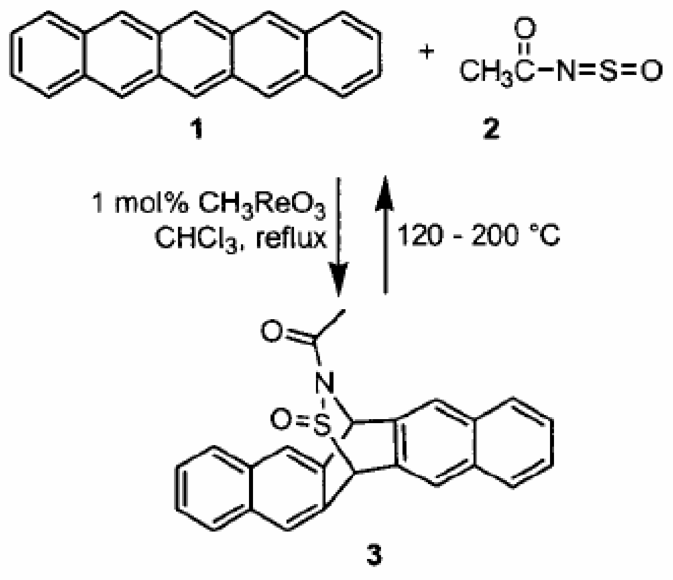






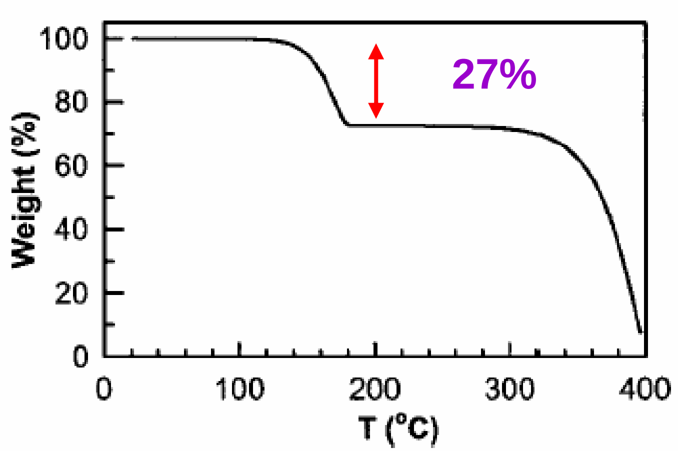
A. R. Brown et al. J. Appl. Phys. 79, 2136 (1996)

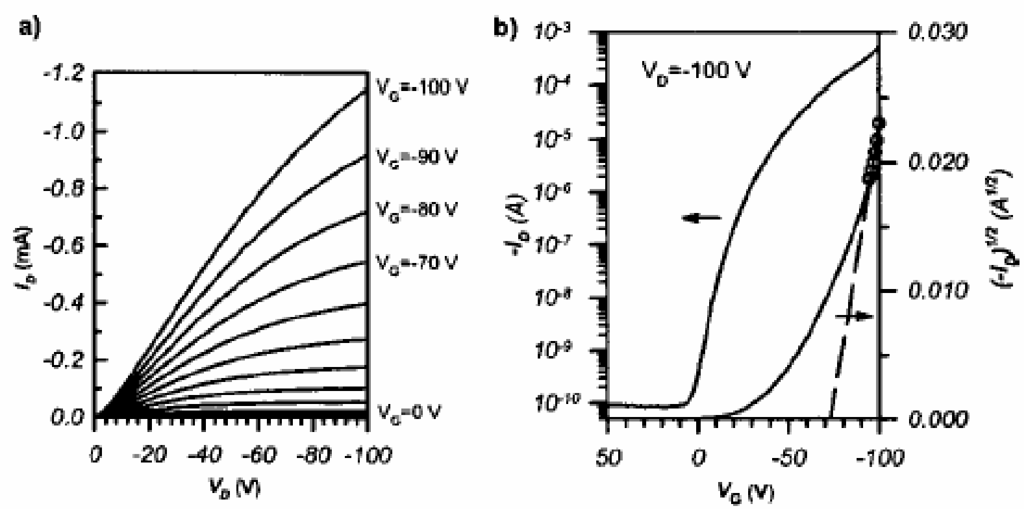
Solution Processed Pentacene



Single step synthesis

Mobility : 0.29 cm^2/Vs (linear region)
0.42 cm^2/Vs (saturation region)
On-off ratio : $2x10^7$

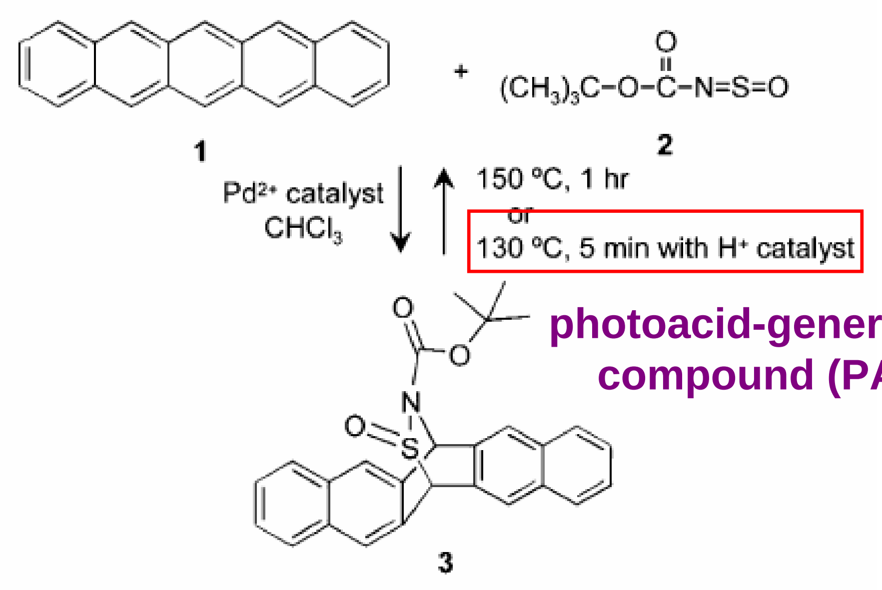




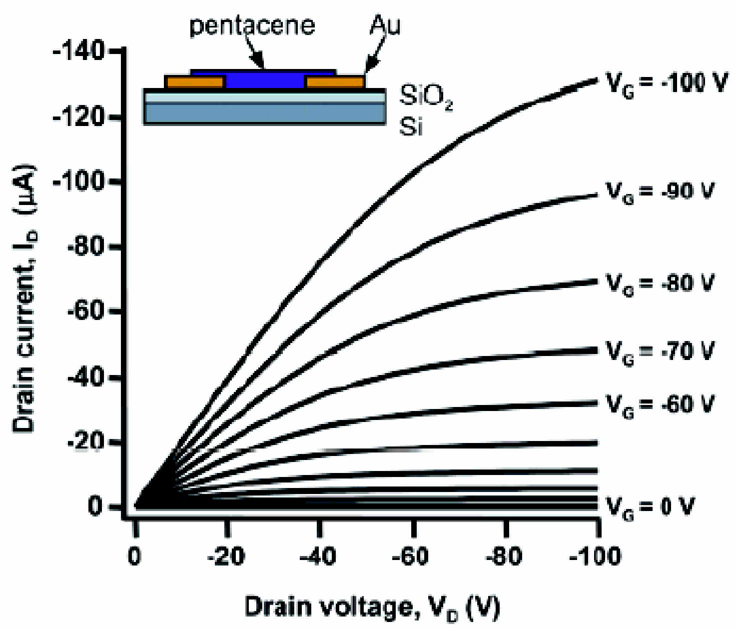
Bottom contact, 200°C 1.5 min under N_2

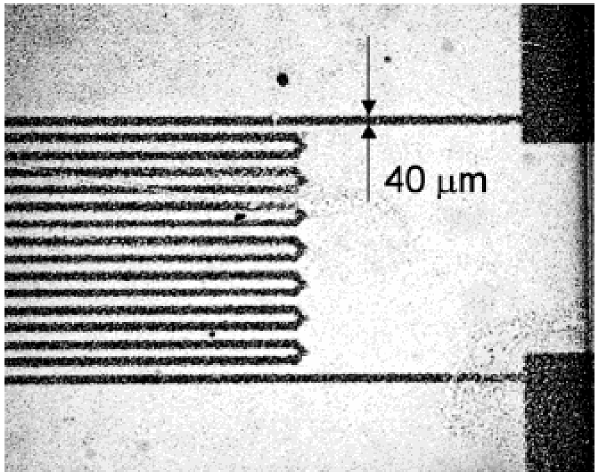
A. Afzali *et al*. J. Am. Chem. Soc., 124, 8812 (2002)

Photopatternable Pentacene



photoacid-generating compound (PAG)





Mobility : 0.13 cm²/Vs (linear region)

0.25 cm²/Vs (saturation region)

On-off ratio : 2x10⁵

Pentacene patterned by UV exposure through a mask and heating in the presence of PAG

K. P. Weidkamp *et al*. J. Am. Chem. Soc., 126, 12740 (2004)

N-type semiconductors

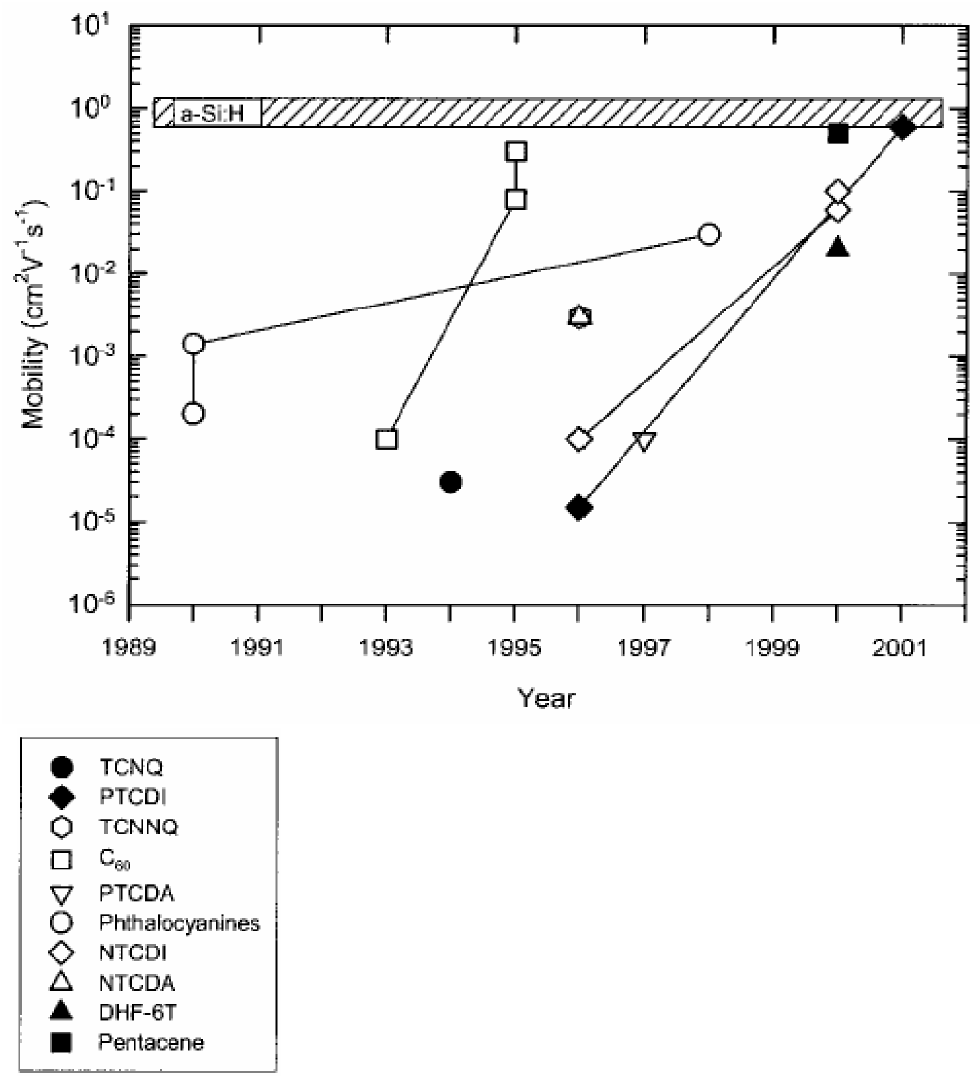
OLED research area introduce the concept of electron and hole transporting materials.
n- and p- type materials are usually characterized by their high electron affinity and low ionization potential, respectively.

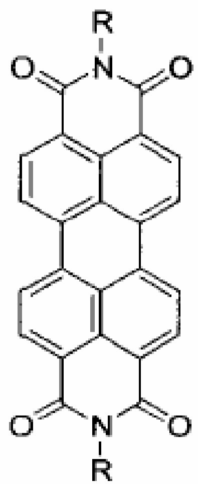
In OTFT, the *accumulation* region is set up for positive gate biases for n- type materials, and for negative gate biases for p-type materials

Problem : strong instability with respective to oxygen and water (act as electron traps)

G. Horowitz, Adv. Mater., 10, 365 (1998)

N-type semiconductors



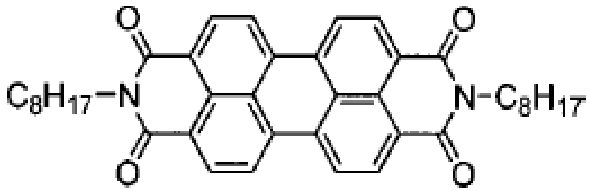


PTCDI-C8

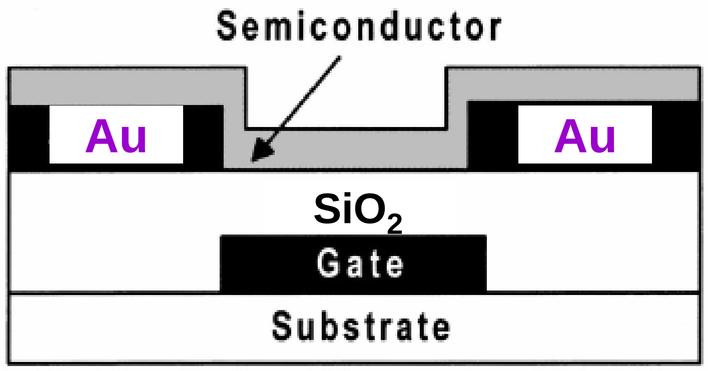
mobility : 0.6 cm^2/Vs
on-off ratio : ~ 10^5

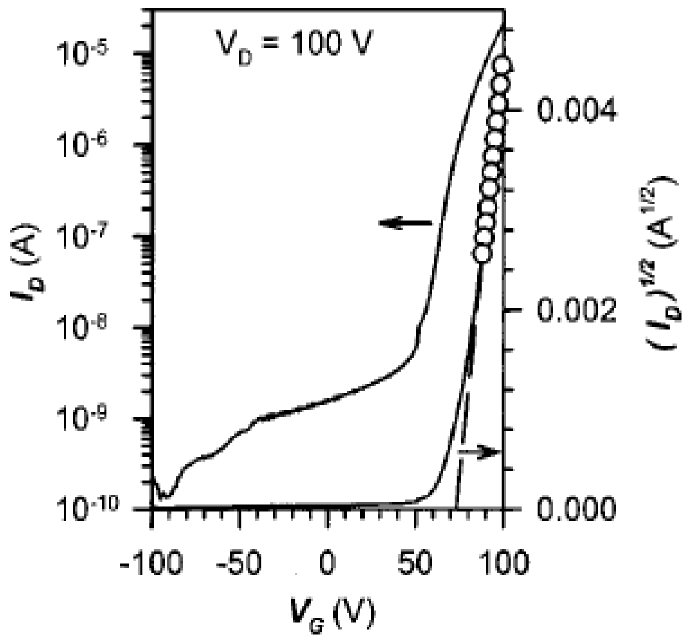
C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater., 14, 99 (2002)

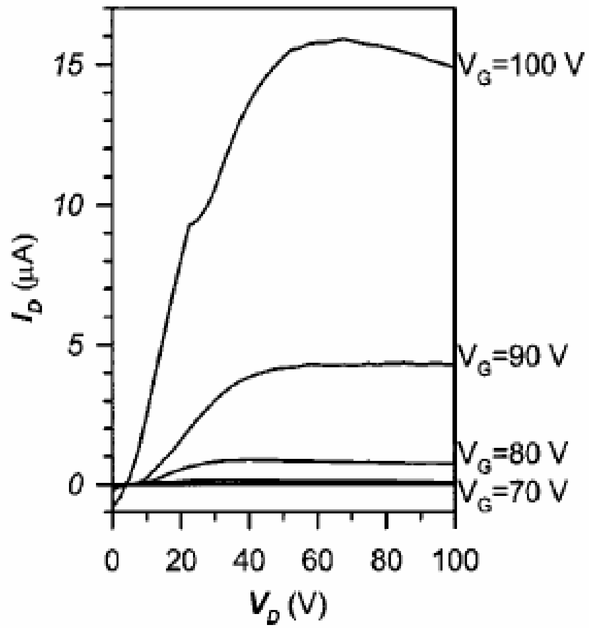
High mobility n-type OTFTs



PTCDI-C8H
Smectic liquid crystalline phases







Mobility : 0.6 cm^2/Vs
V_t = 75V
On-off ratio > 10^5

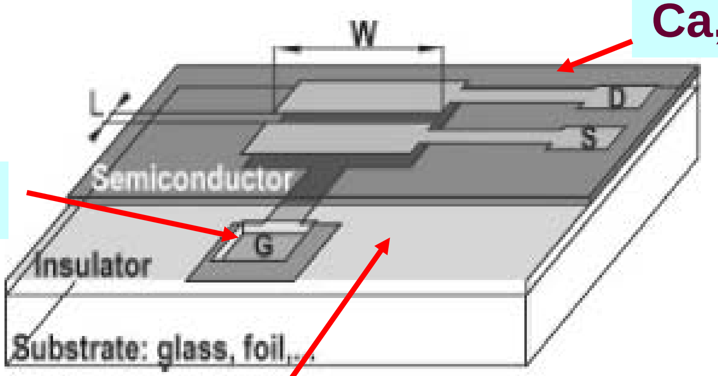
Mobility : 0.3 cm^2/Vs in the linear region

P. R. L. Malenfant *et al*. APL., 80, 2517 (2002)

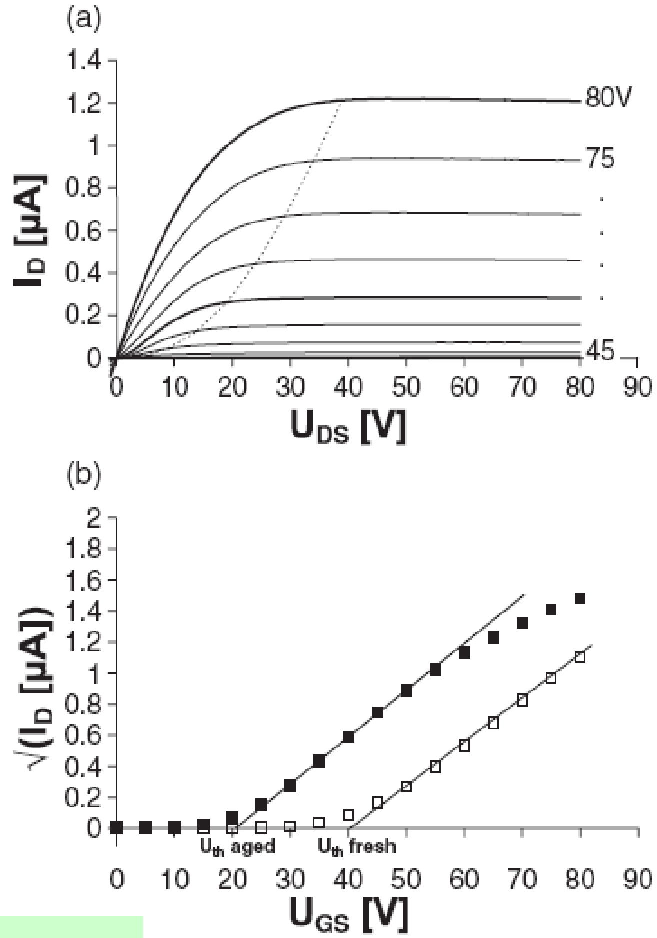
Solution-processed n-type OTFTs

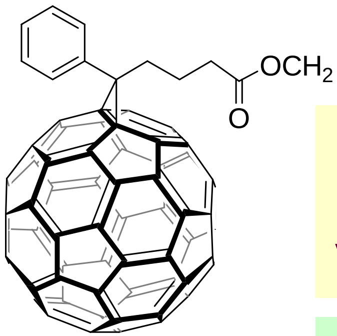
Ca, Al, Au

Au



Organic resin





PCBM
n-type

Mobility : $3.5x10^{-3}$ cm^2/Vs (saturation region)

V_t = 41V

After one work storage

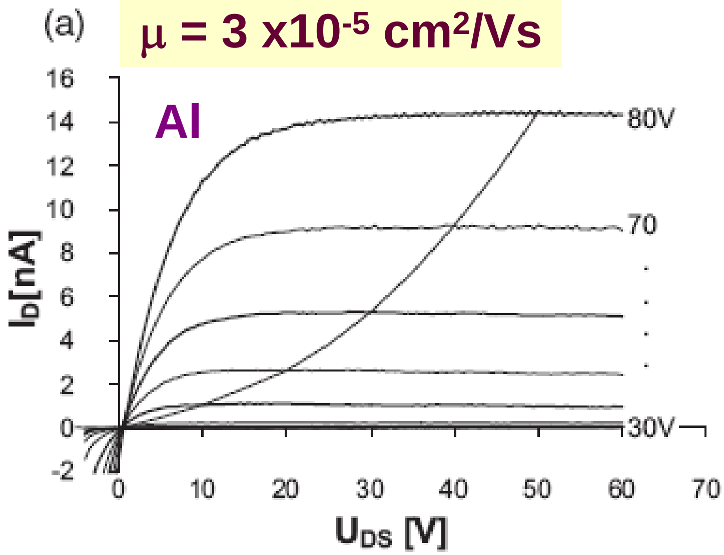
Mobility : $4x10^{-3}$ cm^2/Vs (saturation region)

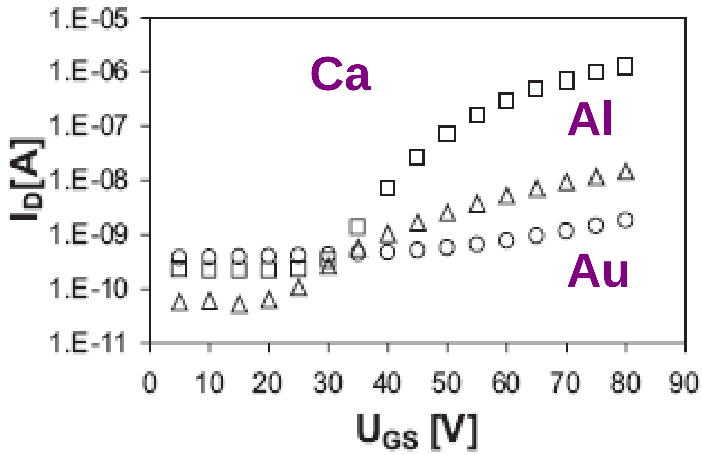
V_t = 21V

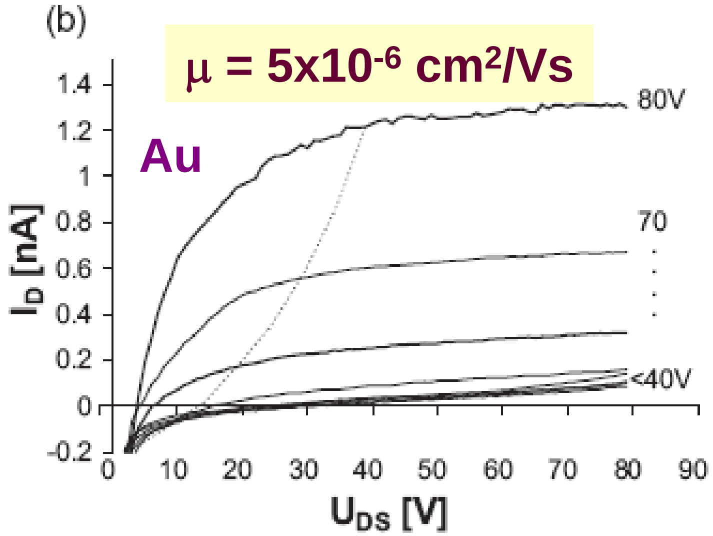
May be due to trap filling by reduction

C. Waldauf *et al*. Adv. Mater., 15, 2084 (2003)

Solution-processed n-type OTFTs







Threshold voltage seems unaffected

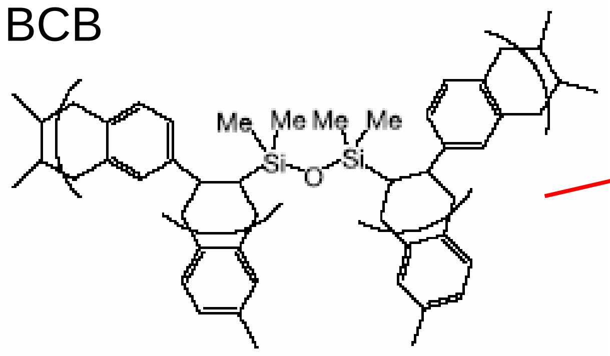
Fermi-level pinning (due to traps)

A higher work function of the contact materials leads decreased injection

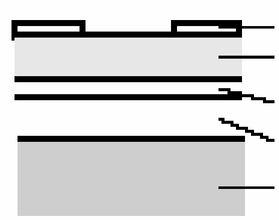
C. Waldauf *et al*. Adv. Mater., 15, 2084 (2003)

General observation of n-type behavior of organic semiconductors

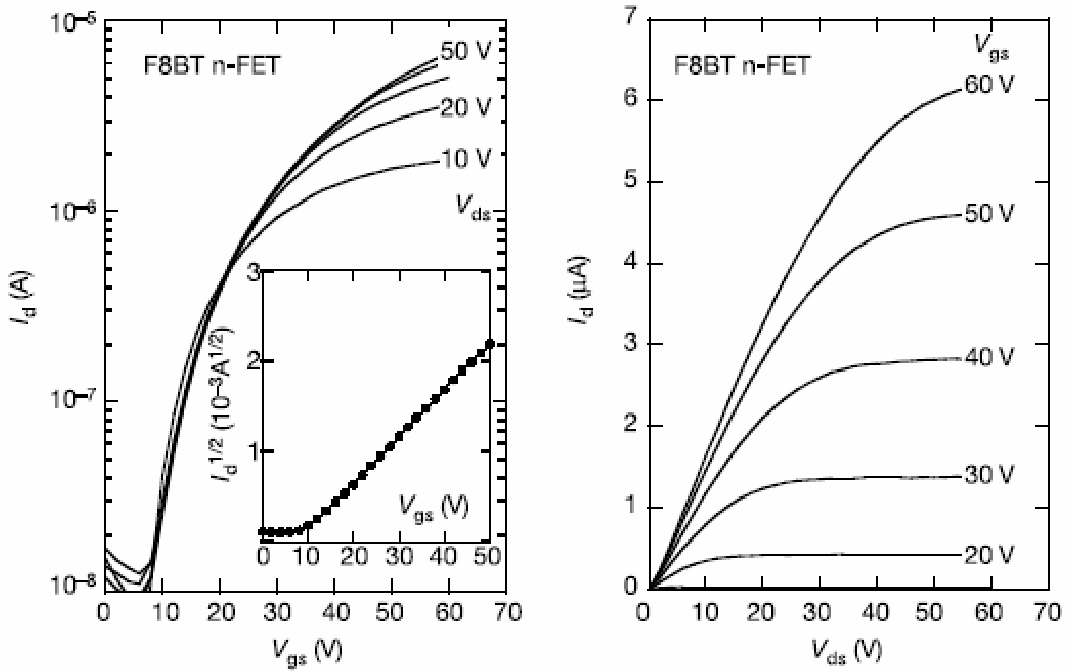
BCB



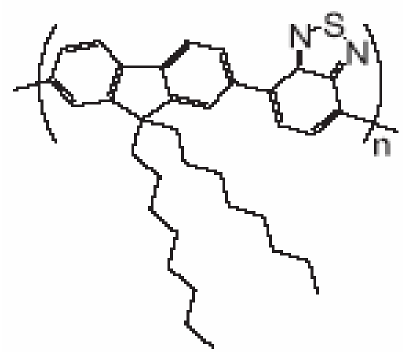
Device Structure



Low-work function (Ca) was used to enable determination of true mobility without correcting for the contact effect



F8BT Poly(9,9-dioctylfluorene-*alt*-benzothiadiazole)



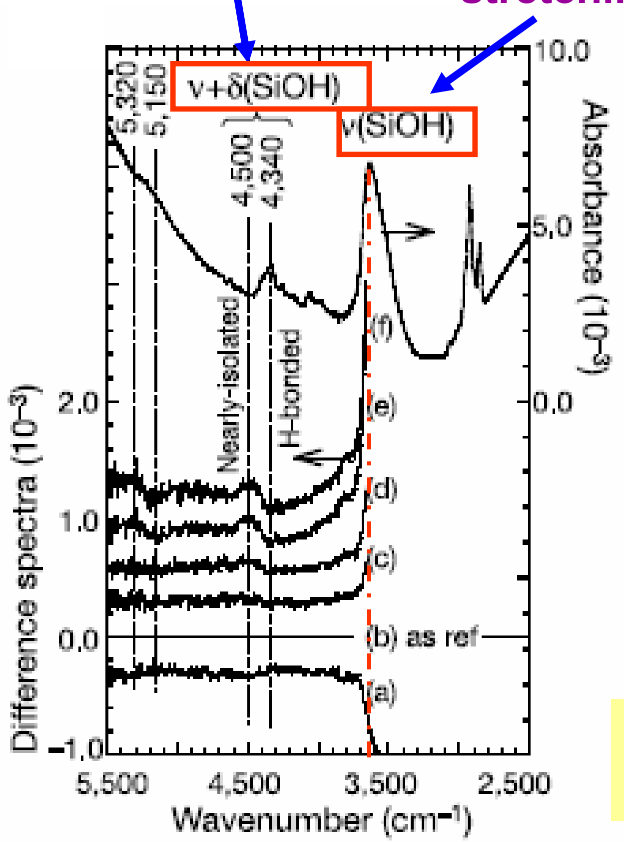
μ_e = 4x10^{-3} (130^{o}C)
= 5x10^{-3} (220^{o}C)

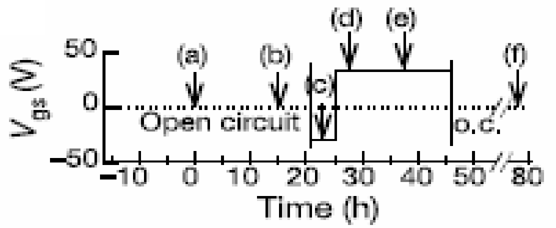
L. L. Chua *et al*., Nature, 434, 194 (2005)

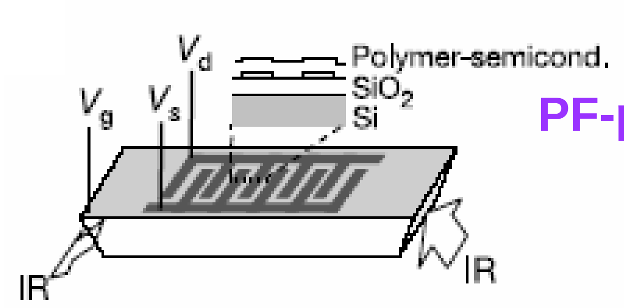
Interfacial electron trapping on standard Si/SiO_2 backgate device

Stretching + Bending

stretching



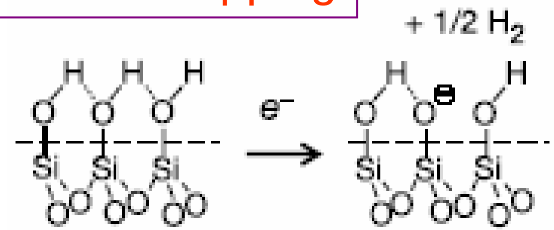




PF-polymer

multiple-reflection attenuated-total-reflection FTIR spectrometry

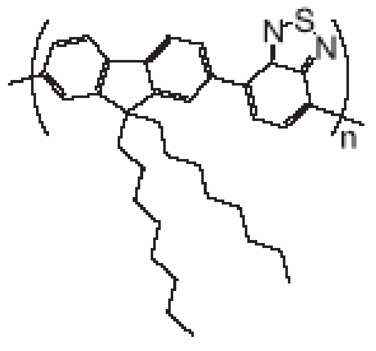
Mechanism of e^- trapping



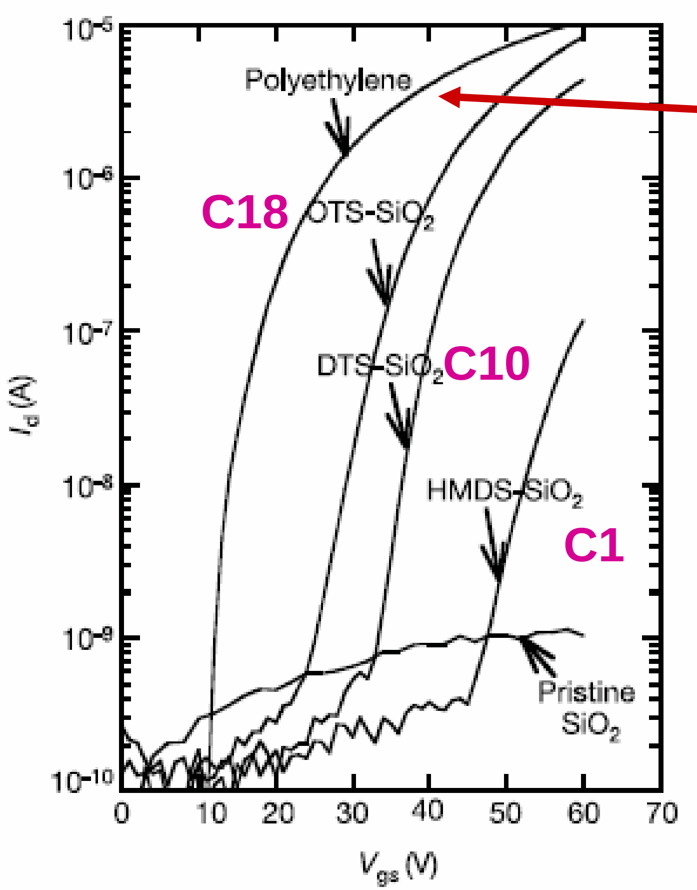
Typical SiOH conc. = ~(3-7)x10^{13} cm^{-2} (6~12% monolayer)
Typical carrier conc. in normal FET operation ~ 10^{13} cm^{-2}

Si-OH intensity shift from H-bonded (4,340cm^{-1}) to nearly-isolated (4,500cm^{-1}) as soon as a positive bias was applied → **e^- trapping**

F8BT n-channel FETs – further evidence



F8BT



Stable n-channel conduction was observed, as is the case with BCB

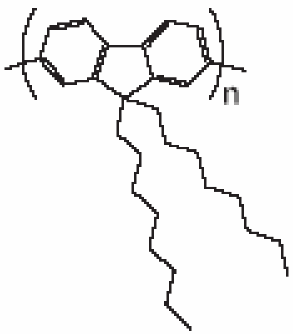
With SAM passivation, n-channel activity can be observed

In the past, SiO_2 or hydroxy-containing polymers, such as poly(vinyl phenol) and polyimides (-COOH), were used as the gate dielectrics, the severe e- trapping supress n-channel conduction

Summary

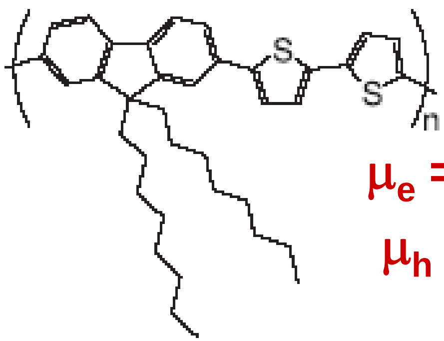
Gate : BCB; electrodes: Ca (n-channel)

F8 Poly(9,9-dioctylfluorene)



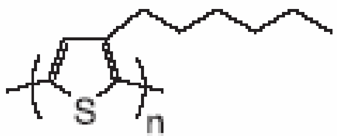
$\mu_e = 5\times10^{-3}$ (130°C)
$= 1\times10^{-2}$ (240°C)
$\mu_h = 3\times10^{-4}$ (200°C)
(HMDS-SiO_2, Au)

F8T2 Poly(9,9-dioctylfluorene-*alt*-bithiophene)



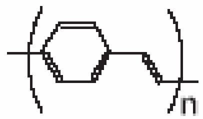
$\mu_e = 6\times10^{-3}$ (130°C)
$\mu_h = 5\times10^{-3}$ (200°C)
(HMDS-SiO_2, Au)

P3HT Regioregular poly(3-hexylthiophene)



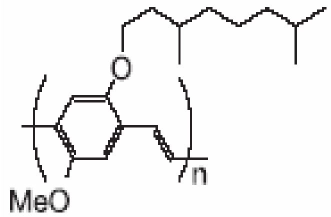
$\mu_e = 6\times10^{-4}$ (100°C)
$\mu_h = 2\times10^{-4}$ (200°C)
(BCB, Ca)

PPV Poly(*p*-phenylenevinylene)



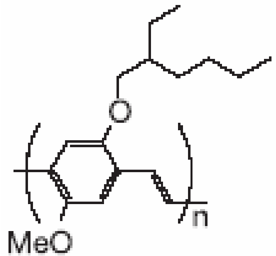
$\mu_e = 1\times10^{-4}$ (250°C)

OC_1C_{10}-PPV Poly(2-methoxy-5-(3,7-dimethyloctoxy)-*p*-phenylene vinylene)



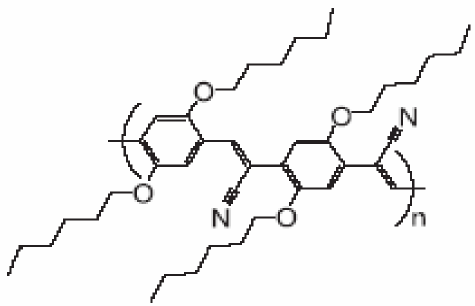
$\mu_e = 8\times10^{-5}$ (130°C)
$= 2\times10^{-3}$ (200°C)
$\mu_h = 5\times10^{-4}$ (200°C)
(BCB, Au)

MEH-PPV Poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene)



$\mu_e = 3\times10^{-5}$ (200°C)
$\mu_h = 5\times10^{-5}$ (200°C)
(BCB, Au)

CN–PPV Poly(2,5-dihexoxy-α,α′-dicyano-*p*-xylylidene-*alt*-2,5-dihexoxy-*p*-xylylidene)



$\mu_e = 4\times10^{-5}$ (130°C)

PF-system has higher mobility than PPV-system

L. L. Chua *et al.*, Nature, 434, 194 (2005)

Polymers

The performance is usually one-order lower than small molecules.

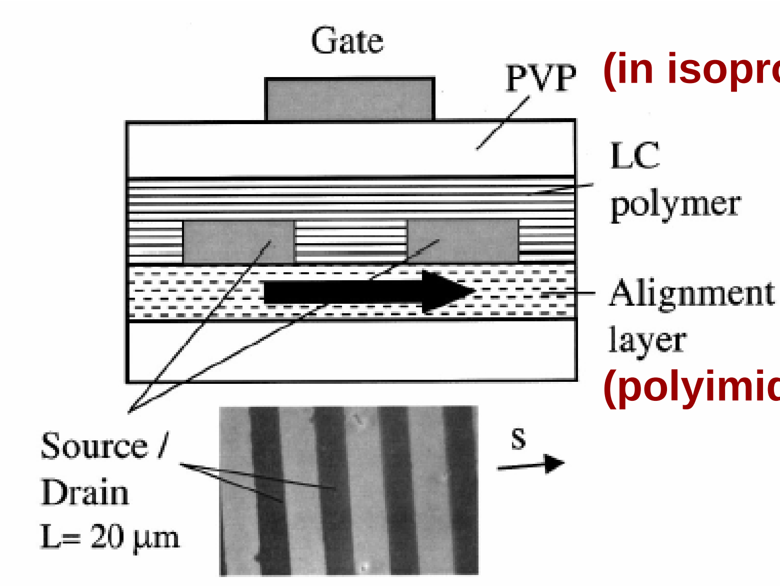
The mobility can be increased by doping, however, at the expense of the on-off ratio

Mobility-conductivity relationship, $\mu \propto \sigma^{\delta}$ ($\delta \sim 0.7$)

Two major materials
polyfluorene and poly(alkyl-thiophene)

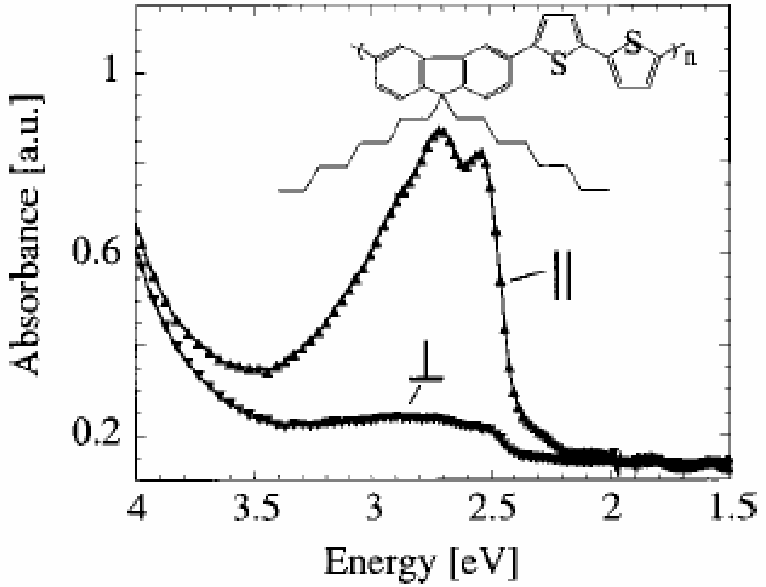
G. Horowitz, Adv. Mater., 10, 365 (1998)

Poly(fluorene)

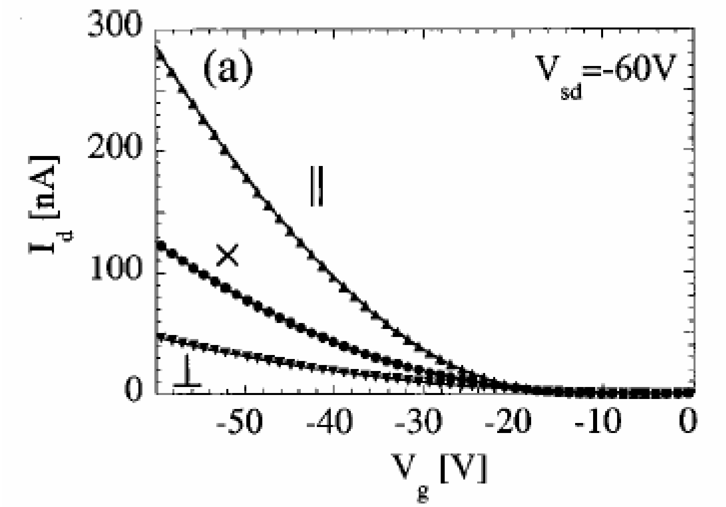


(in isopropanol)

(polyimide)



poly(9,9-dioctyl-fluorene-co-bithiophene) (F8T2)



liquid-crystalline self-organization
in rigid-rod nematic conjugated polymers
(T_m = 265°C)

μ_{II} = 0.009-0.02 cm^2/Vs (linear region)

$\mu_{II} > \mu_x > m_{\perp}$

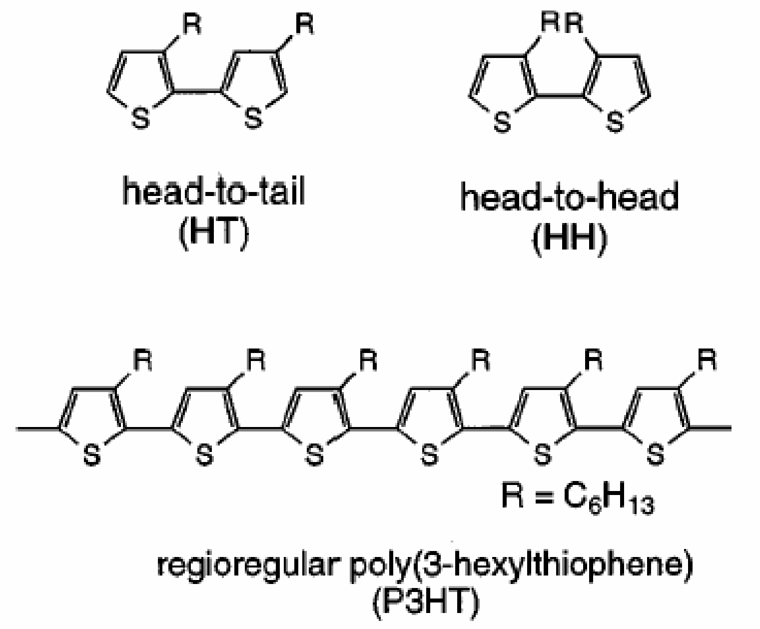
On-off ratio : > 10^5

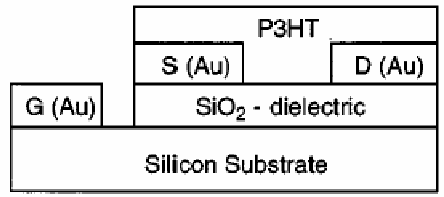
H. Sirringhaus *et al*., APL, 77, 406 (2000)

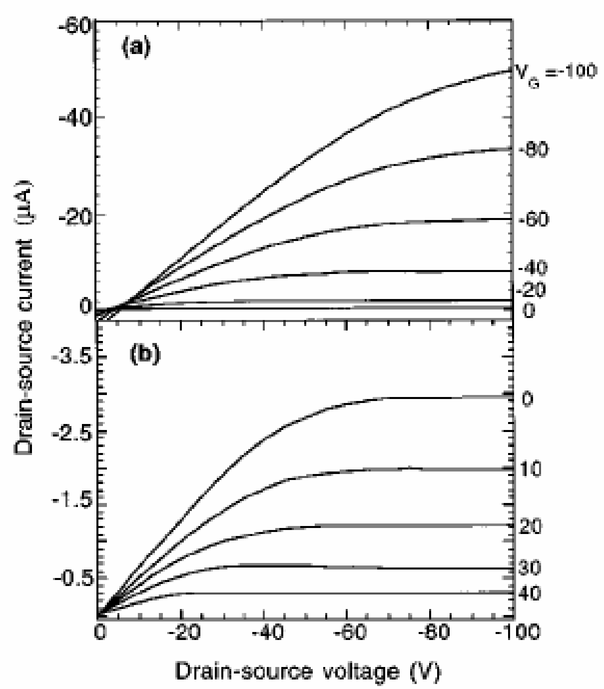
Poly(alkyl-thiophene)

Amorphous films are obtained by spin-coating for regiorandom polymers (both HT and HH)

regioregularity







Regioregular polymer can be obtained via structure-controlled syntheses

→ **Polycrystalline films**

mobility : 0.045 cm^2/Vs in the accumulation mode
0.01 cm^2/Vs in the depletion
on-off ratio : > 10^3

Z. Bao *et al*., APL, 69, 4108 (1996)

Poly(alkyl-thiophene)

TABLE I. Field-effect mobilities and on/off ratios of samples prepared from different conditions. Condition 1, cast, vacuum pumped for 24 h; condition 2, spin-coated; condition 3, treated with NH_3 for 10 h; condition 4, heated to 100 °C under N_2 for 5 min; condition 5, heated to 150 °C under N_2 for 35 min.

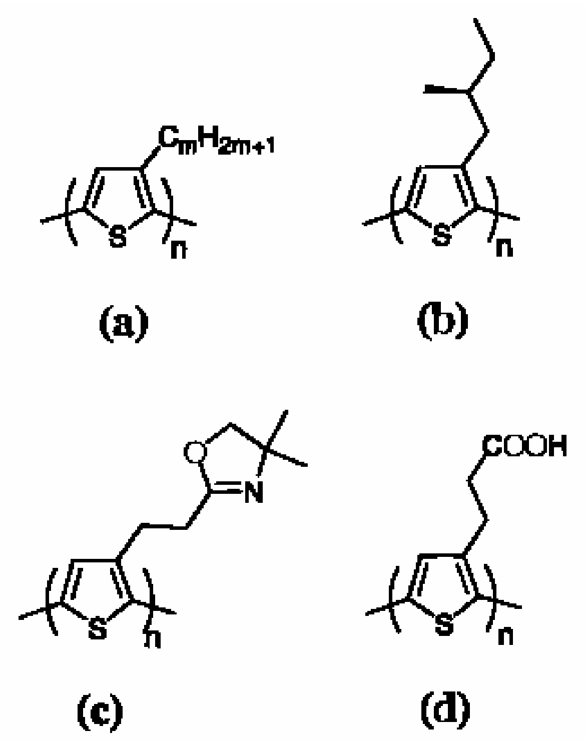
Entry	Solvent	Condition	Mobility ($cm^2/V\ s$)[a]	On/off ratio[b]
1	THF	1	6.2×10^{-4}	10
2	*p*-xylene	1	1.9×10^{-3}	40
3		2	1.9×10^{-5}	2
4	Toluene	1	3.6×10^{-3}	10
5		2	3.2×10^{-3}	25
6	Chlorobenzene	1	4.7×10^{-3}	10
7		entry 6 condition 3	4.7×10^{-3}	80
8		2	6.9×10^{-4}	72
9	1,1,2,2-tetrachloroethylene	1	6.8×10^{-3}	35
10	1,1,2,2-tetrachloroethane	1	2.4×10^{-2}	6
11		entry 10 condition 4	1.4×10^{-2}	35
12		entry 11 condition 5	3.3×10^{-3}	15
13	Chloroform	2	9.2×10^{-3}	80
14		1	4.5×10^{-2}	340
15		entry 14 condition 3	2.1×10^{-2}	9000

[a]Field-effect mobility for the accumulation-mode operation.
[b]On/off ratio is calculated for enhancement-mode operation only, and it is ten times higher for enhancement-depletion operation.

$\mu_{cast} > \mu_{spin\text{-}coating}$, probably due to slower evaporation rate

Z. Bao *et al*., APL, 69, 4108 (1996)

Effect of side chains



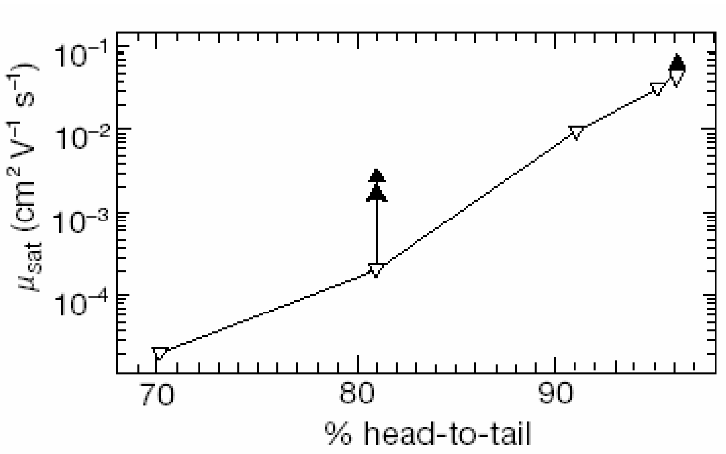
(a) P3HT has the highest mobility (~0.1 cm^2/Vs)
For P3OT (m = 10), mobility (~$1x10^{-6}$ cm^2/Vs)
From diffraction pattern, the degree of π-overlap does not seems to affected by longer side chain.
➡ probably due to higher volume fraction of insulating side chains

(b) π-π overlap distance increase (4.3Å vs 3.9Å for P3HT)
(μ ~ $1x10^{-3}$ cm^2/Vs)

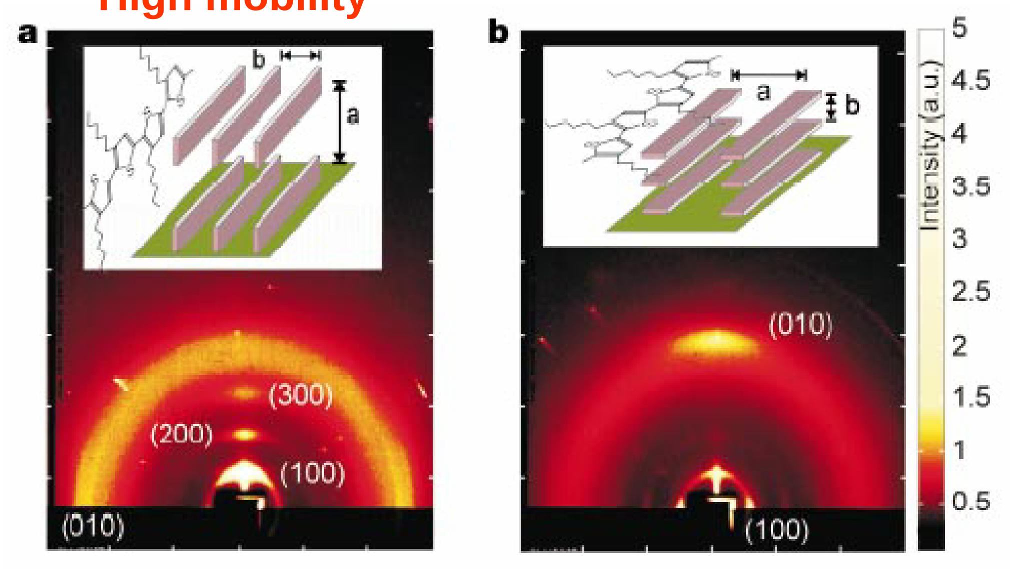
(c) and (d)
(μ ~ $1x10^{-5}$ cm^2/Vs)
Polymers with bulky side chains are difficult to form highly crystalline films

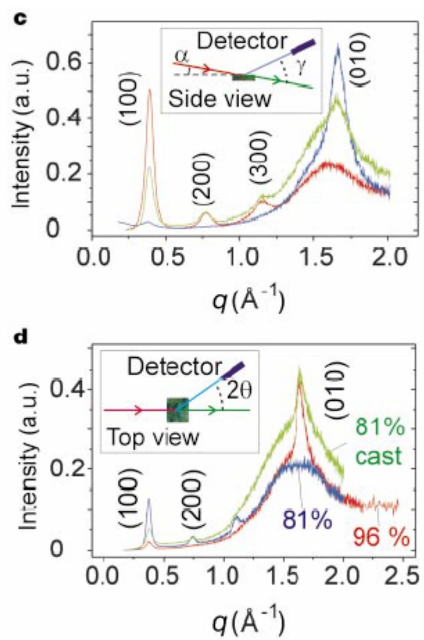
H. E. Katz, and Z. Bao, J. Phys. Chem. B, 104, 671 (2000)

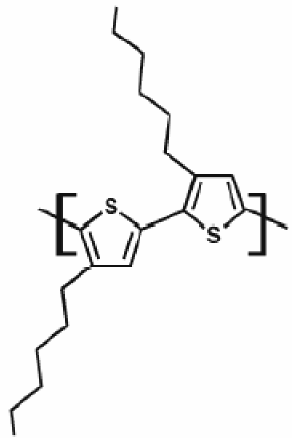
Self-organized polymer TFTs



High mobility







Orientation is also important
High mobility (~0.1 cm^2/Vs) was obtained while the chain edge on

H. Sirringhaus *et al.*, Nature, 401, 685 (1999)

Purification of organic compounds

Methods:

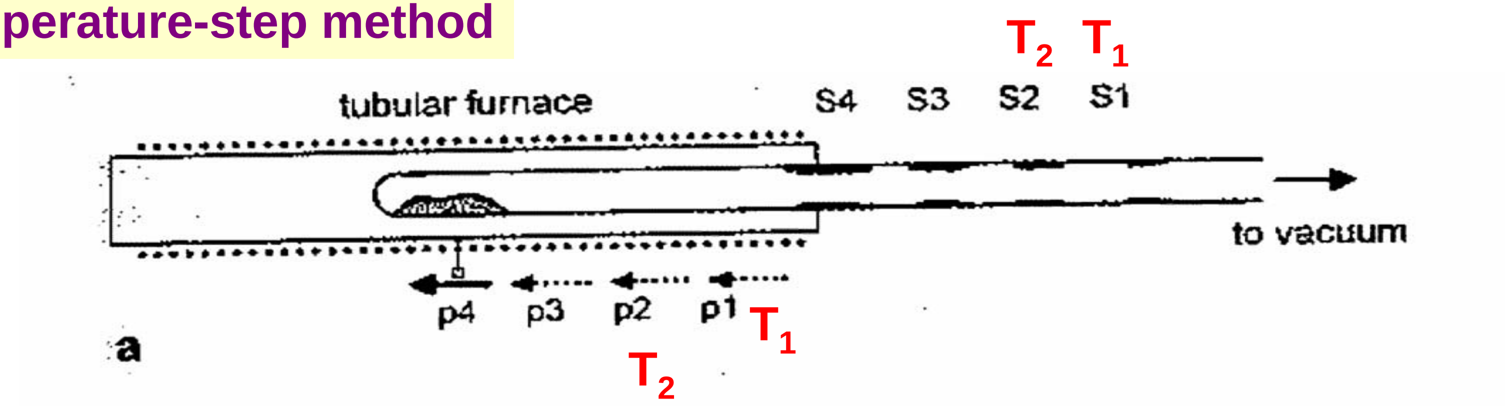
1. Sublimation, applying a temperature-step program or a temperature gradient

2. Recrystallization, from a suitable solvent under slow evaporation or temperature lowering

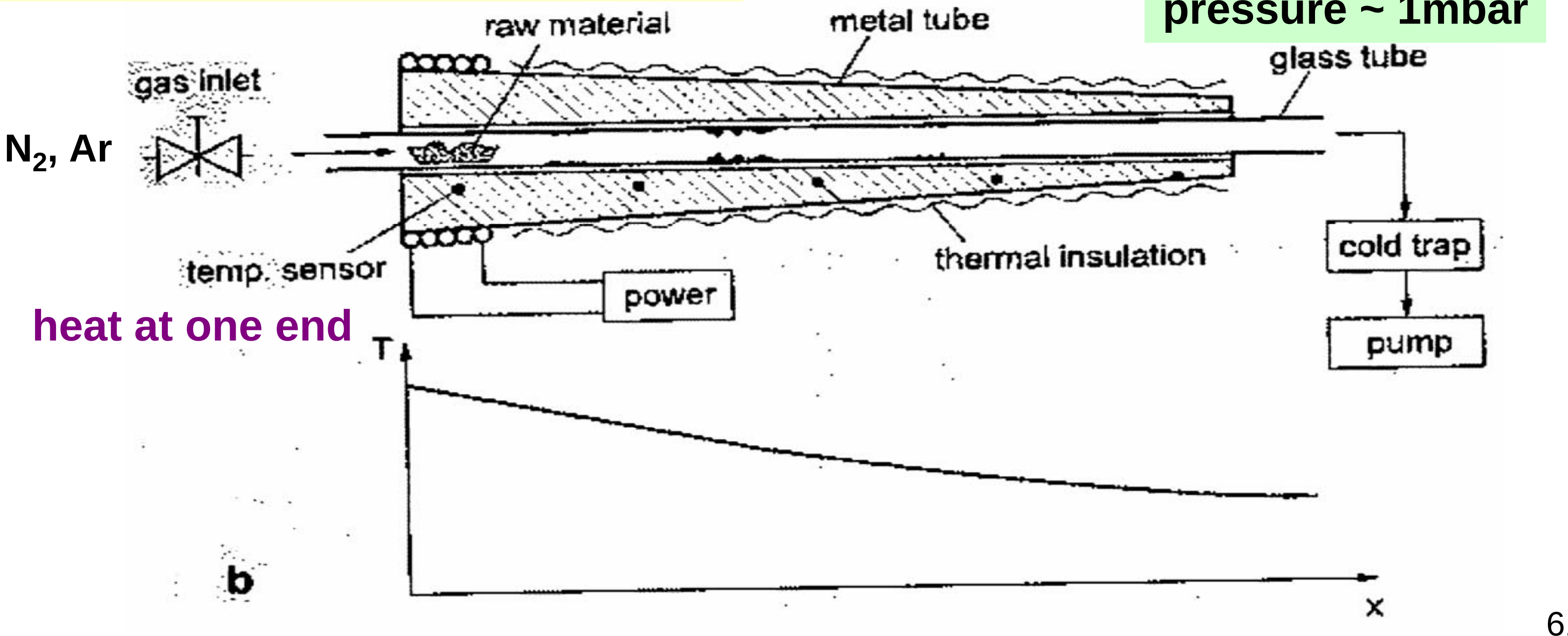
3. Chromatographic methods, a sequence of phase equilibrium between a solution and an adsorptive surface or thin film.

Sublimation

Temperature-step method



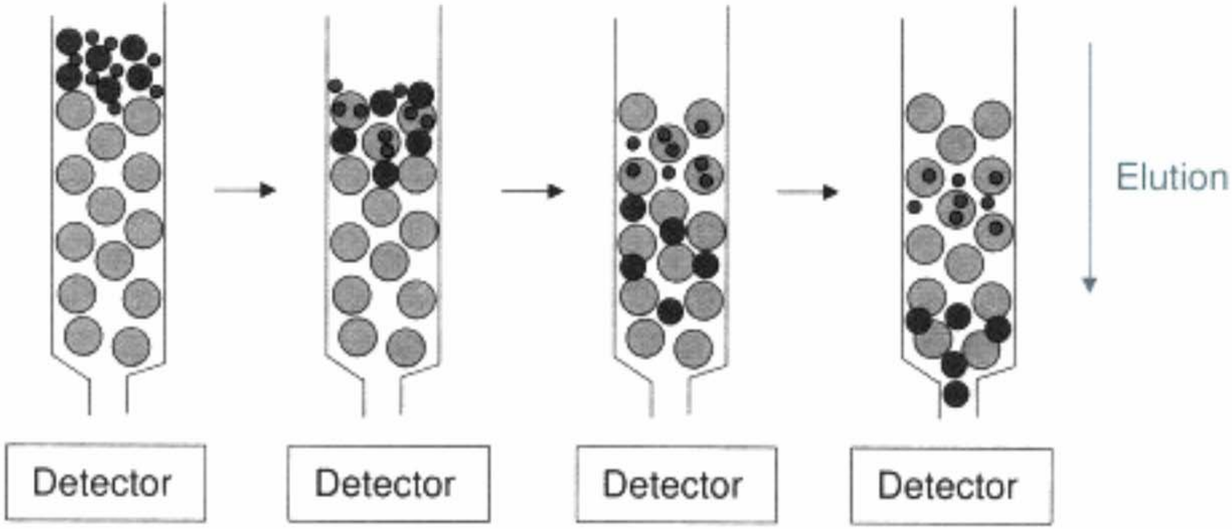
Temperature gradient sublimation



Chromatography

GPC (Gel Permeation Chromatography)

- Separation by size, not by affinity to stationary material
- Results strongly depend on shape of polymer (rod-like polymers are usually overestimated)

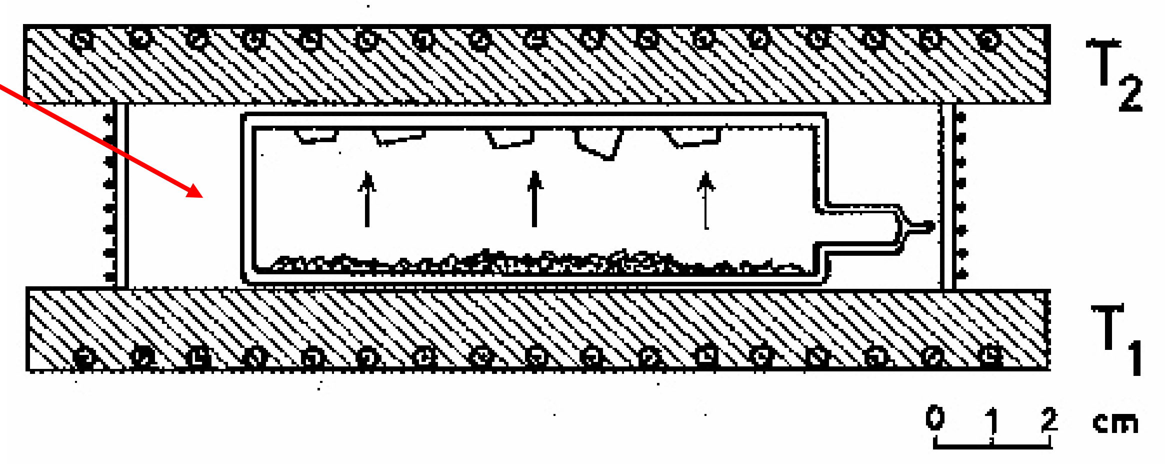


Materials for OLED & PLED SID-Seminar Slide 13

Growth of single crystals

Plate Sublimation Method

Pyrex glass or fused silica ampoule



Vertical temperature gradient ($T_2 < T_1$)