7th edition

ORGANIC ELECTRONICS
Principles, devices and applications

Organic TFT II

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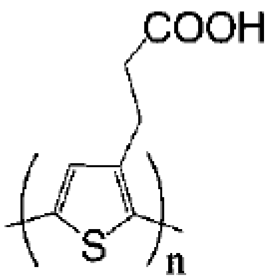
Milano, 24-27 Novembre 2015

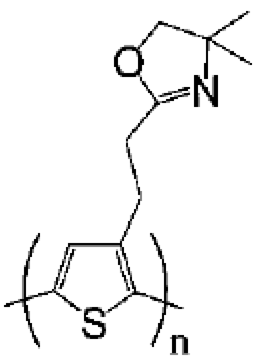
Outline

- Materials (case studies):
  - Polymers (thiophene based and others)
- Single Crystal TFT
- N-type TFT
- Device issues
  - Injection
  - Dielectrics
  - Bias stress
- SAMfet
- Ambipolar TFT
- CMOS strategy

Polythiophenes

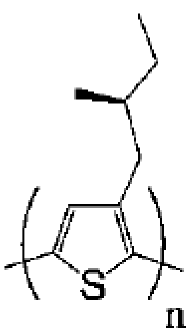
Polythiophene derivative: role of side chain





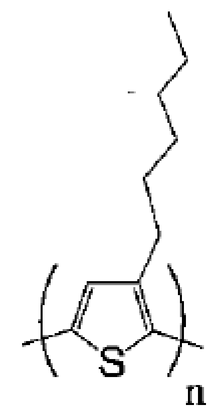
Bulky side chian -> low crystallinity

μ= 10^{-4}-10^{-5}

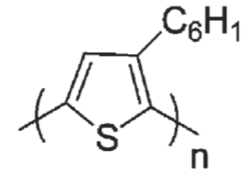


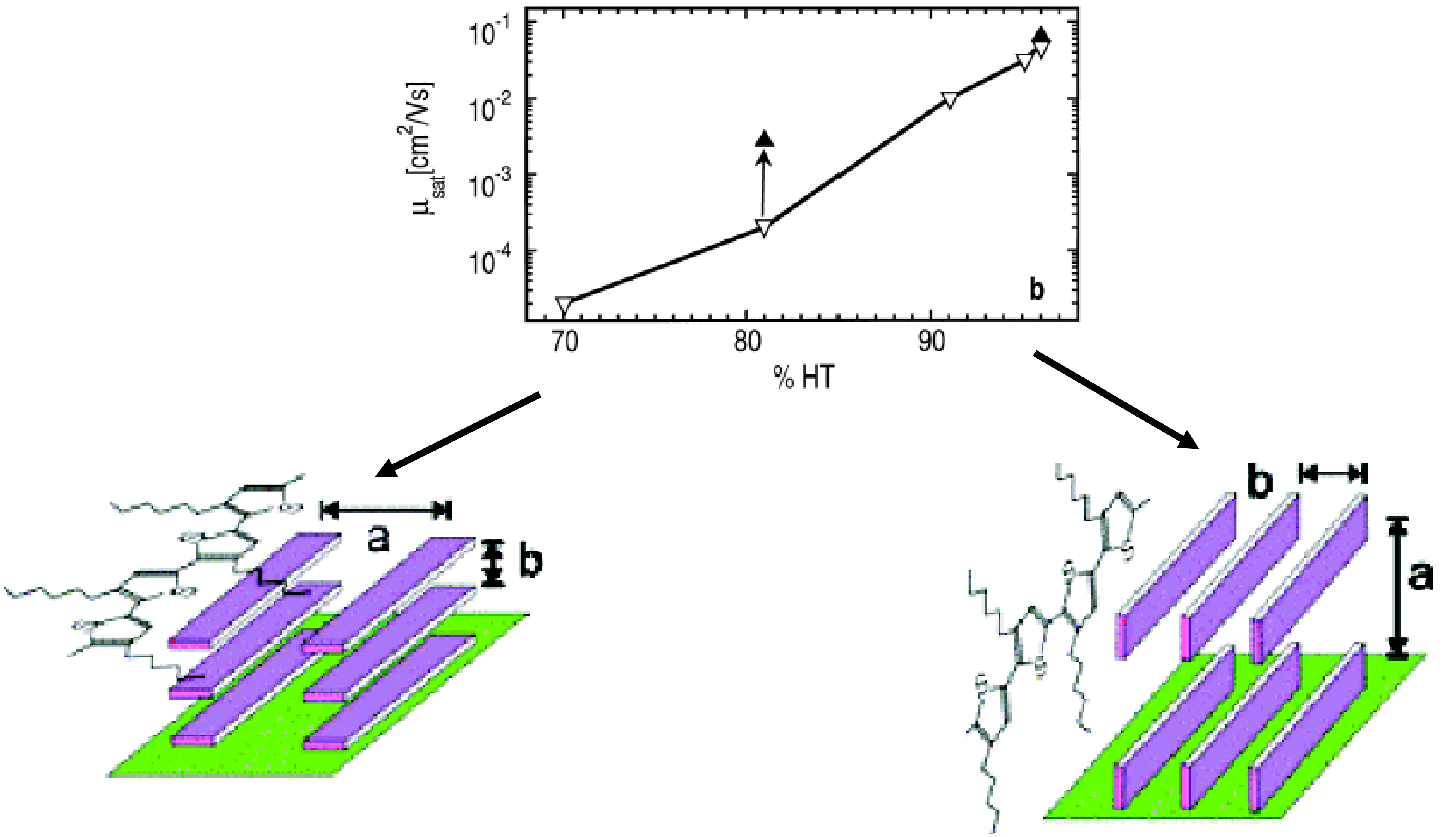
Crystalline but with π-π stacking distance ***larger*** than P3HT

(4.3 vs 3.8 Å)



P3HT: regioregularity

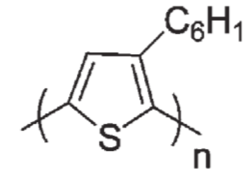


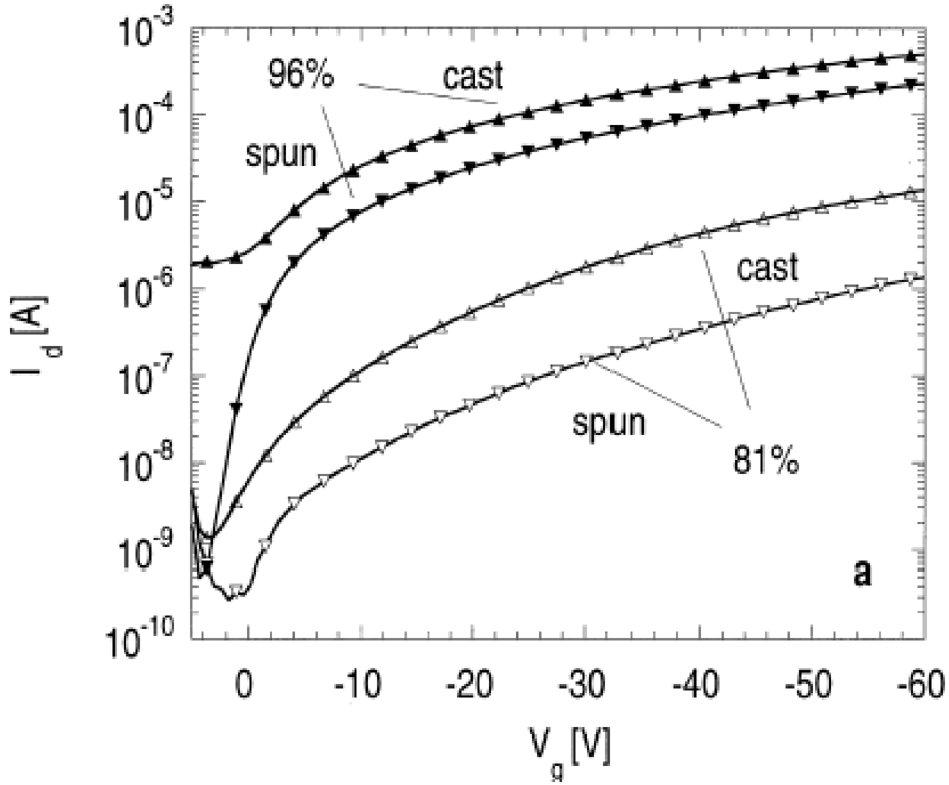


Regioregularity yields more ordered parallel π-stacked domains

Sirringhaus Synth.Met. 111–112 2000 129–132

P3HT: casting vs spin coating

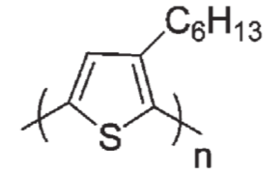




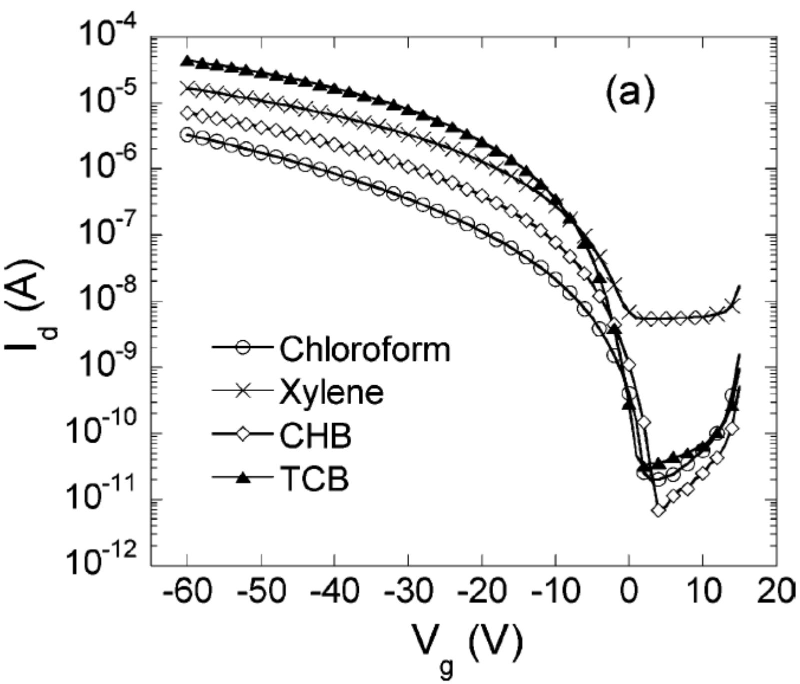
Drop casting yields higher mobility:
Higher order due to slower growth of the film

Sirringhaus Synth.Met. 111–112 2000 129–132

P3HT: solvent effect



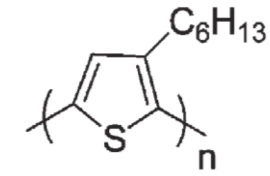
		bp (°C)	mobility ($cm^2/(V\ s)$)	I_{on}/I_{off}
	chloroform	60.5−61.5	0.012	10^5
	thiophene	84		
	xylene	138−139	0.042	10^3−10^4
Bad solvent →	CHB	239−240	0.022	10^6
	TCB	218−219	0.12	10^6

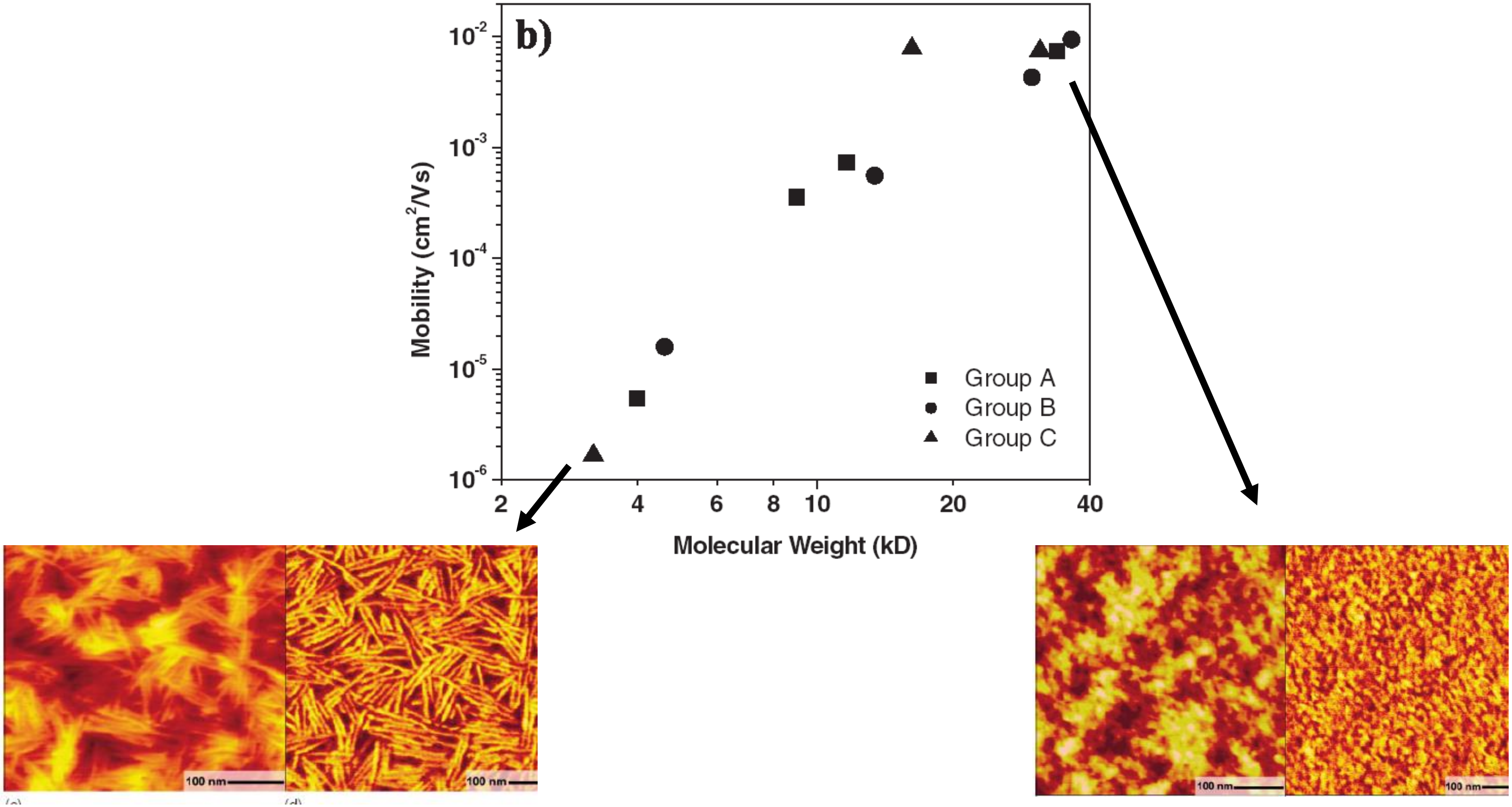


Higher boiling point solvent yields higher mobility retaining high uniformity

Chang *Chem. Mater.;* **2004**; *16*(23); 4772-4776

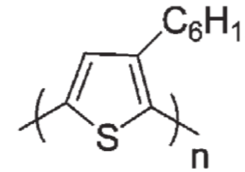
P3HT: molecular weight and morphology

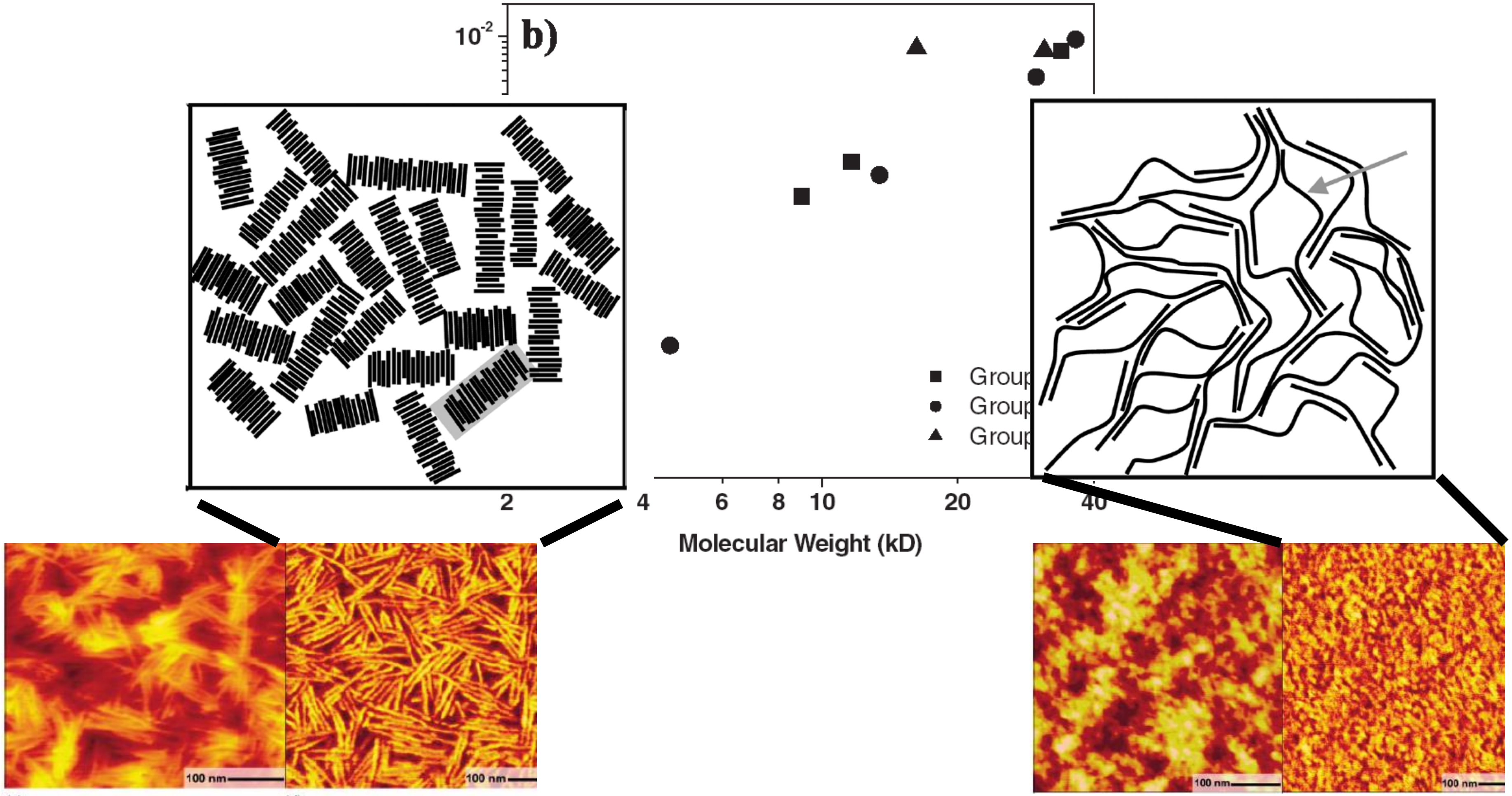




Kline Adv.Mat. 15 2003 1519, Polymer Reviews, v 46, n 1, Jan 1, 2006, p 27-45

P3HT: molecular weight and morphology



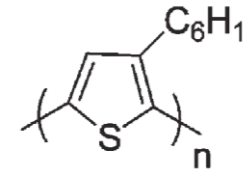


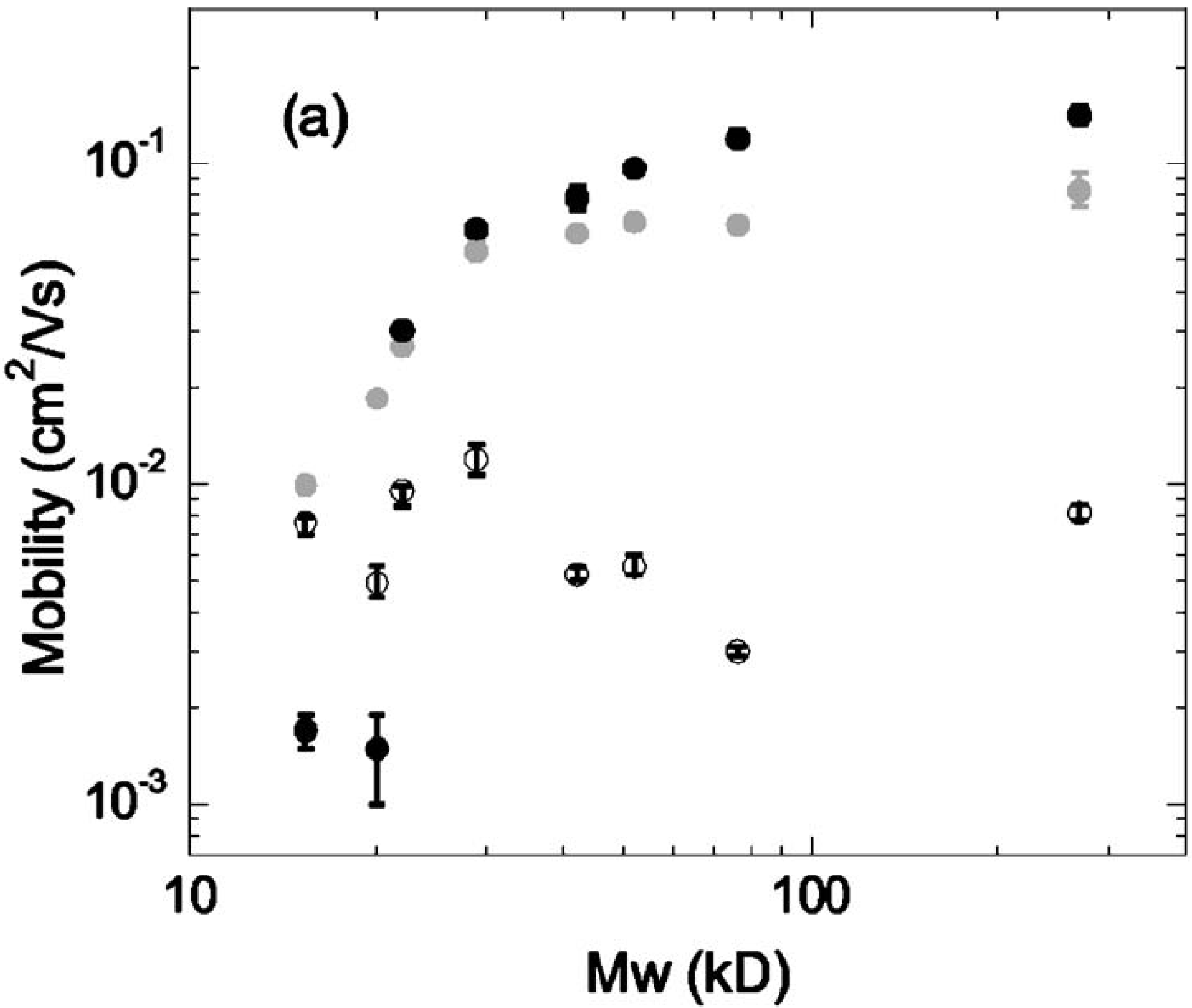
Low MW more crystalline more grain boundaries

High MW less crystalline but with bridging molecules

Kline Adv.Mat. 15 2003 1519

P3HT: MW



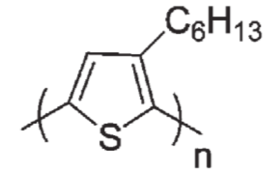


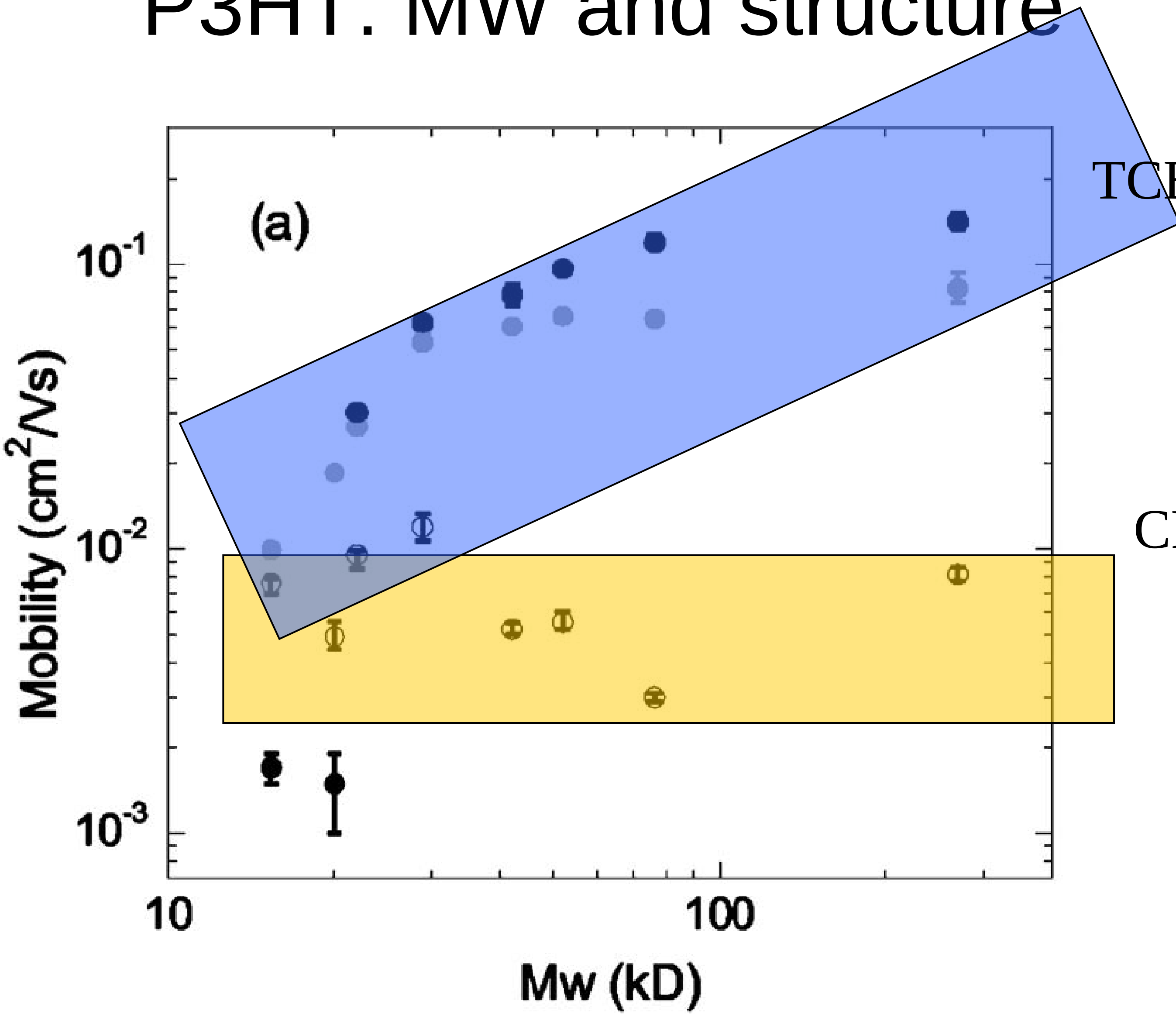
TCB

CF

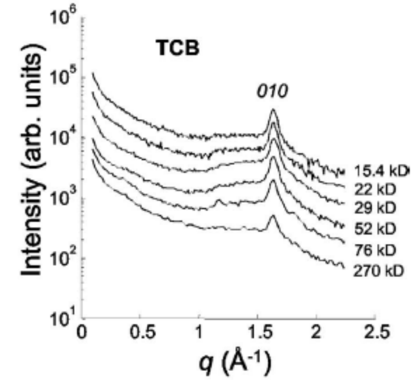
Sirringhaus PHYSICAL REVIEW B **74**, 115318 2006

P3HT: MW and structure

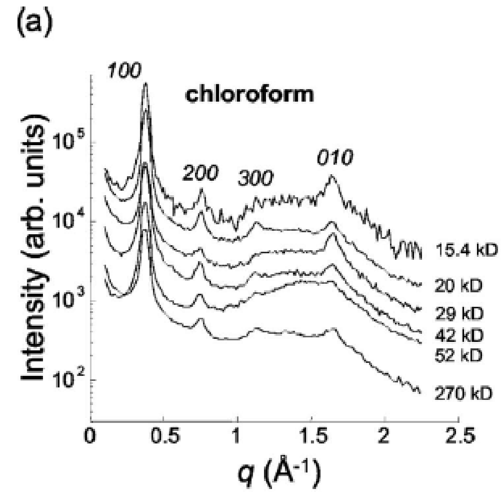




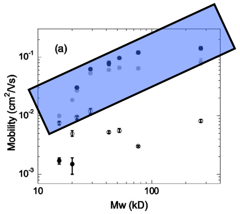
TCB



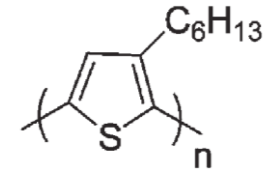
CF

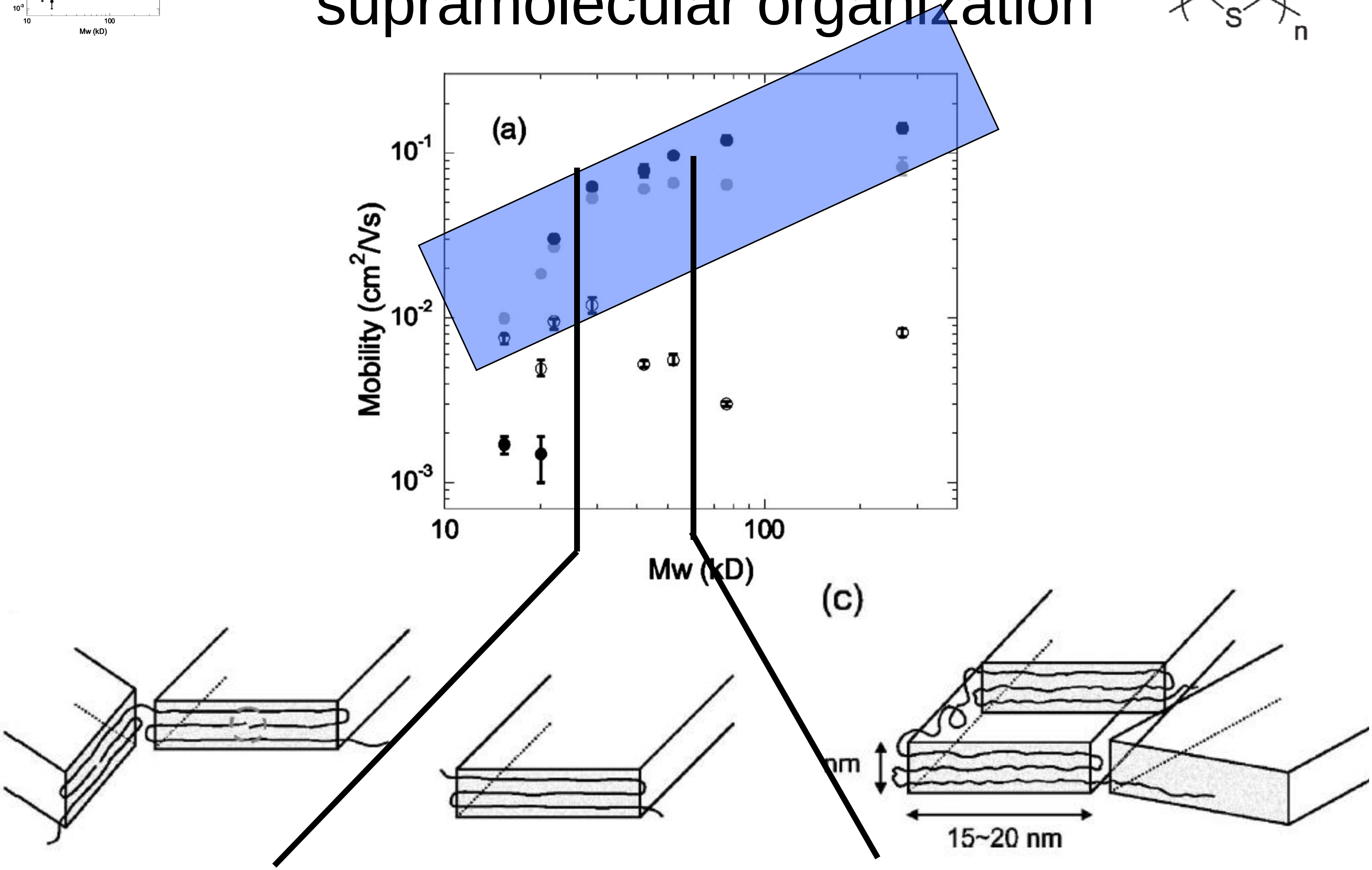


Sirringhaus PHYSICAL REVIEW B **74**, 115318 2006

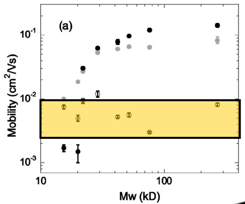


P3HT: MW and supramolecular organization

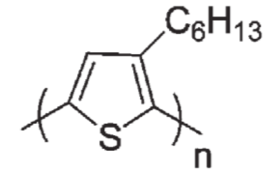




Sirringhaus PHYSICAL REVIEW B **74**, 115318 2006



P3HT: MW and electrical characteristics



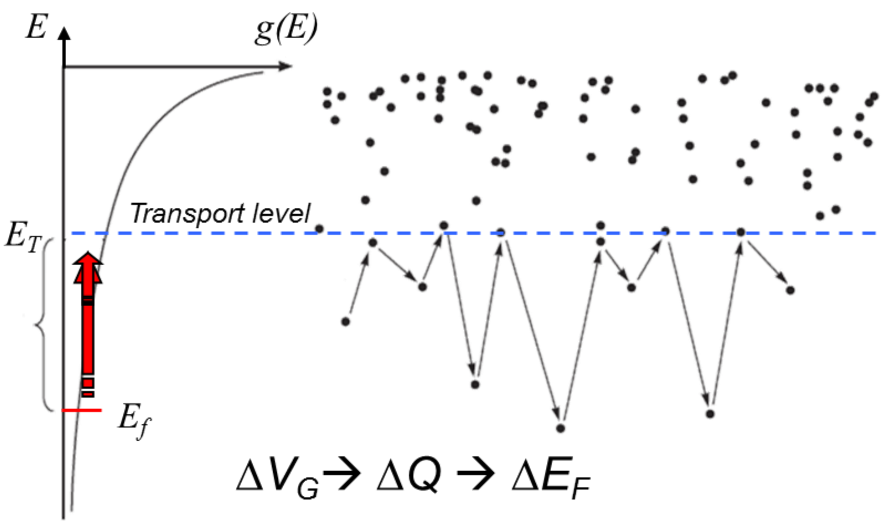
Charge transport modeling

Hopping between localized states (VRH)

$$\mu = k' \cdot Q^{\gamma} \Rightarrow \mu = k \cdot (V_{OV})^{\gamma}$$

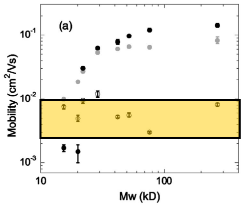
DOS broadening → Energetic disorder

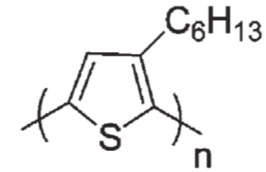
α^{-1} → Wavefunction overlap (morphology)



$\Delta V_G \rightarrow \Delta Q \rightarrow \Delta E_F$

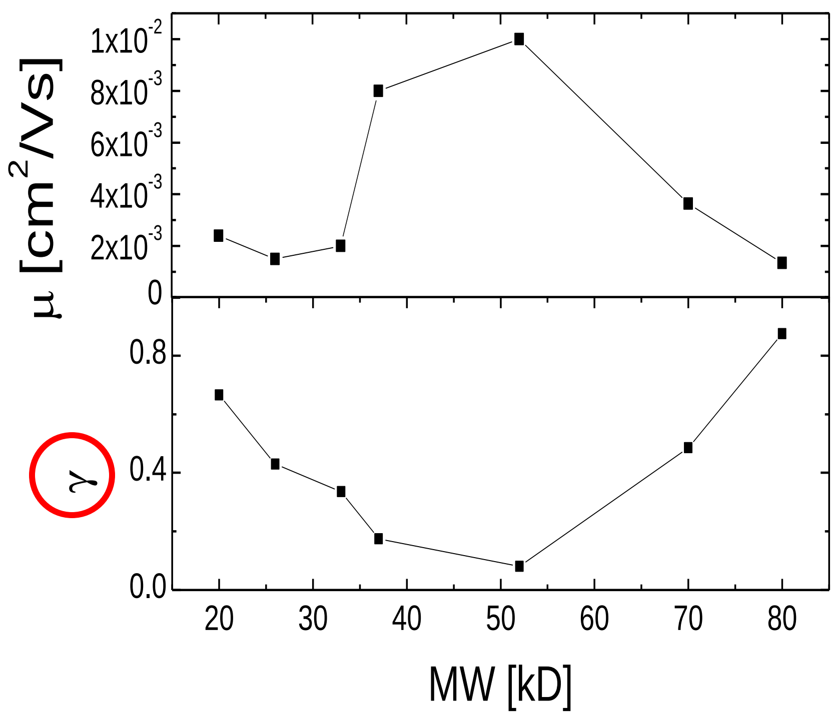
P3HT: MW and electrical characteristics

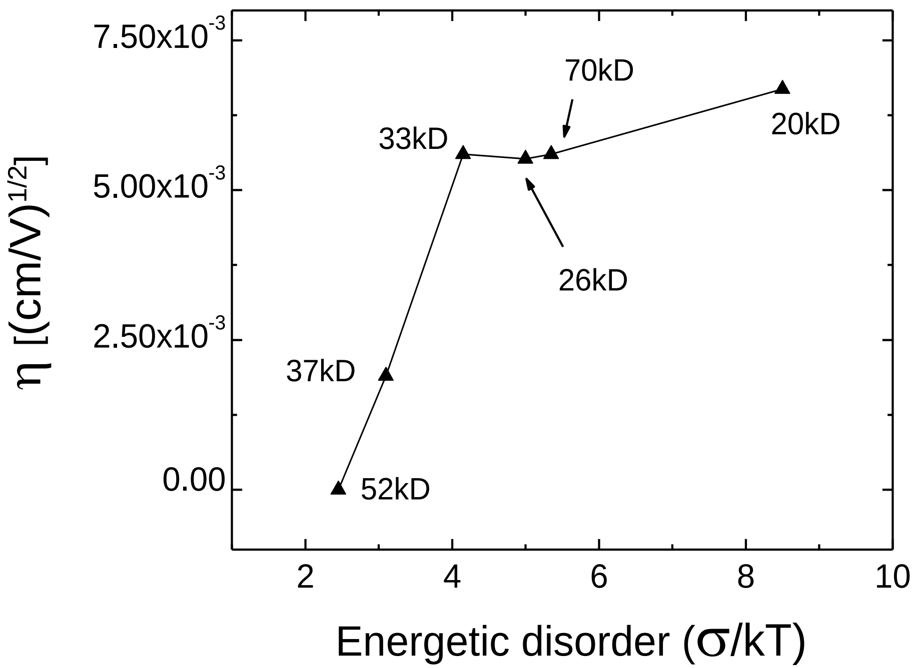




$$\mu = k(V_{OV})^{\gamma}$$

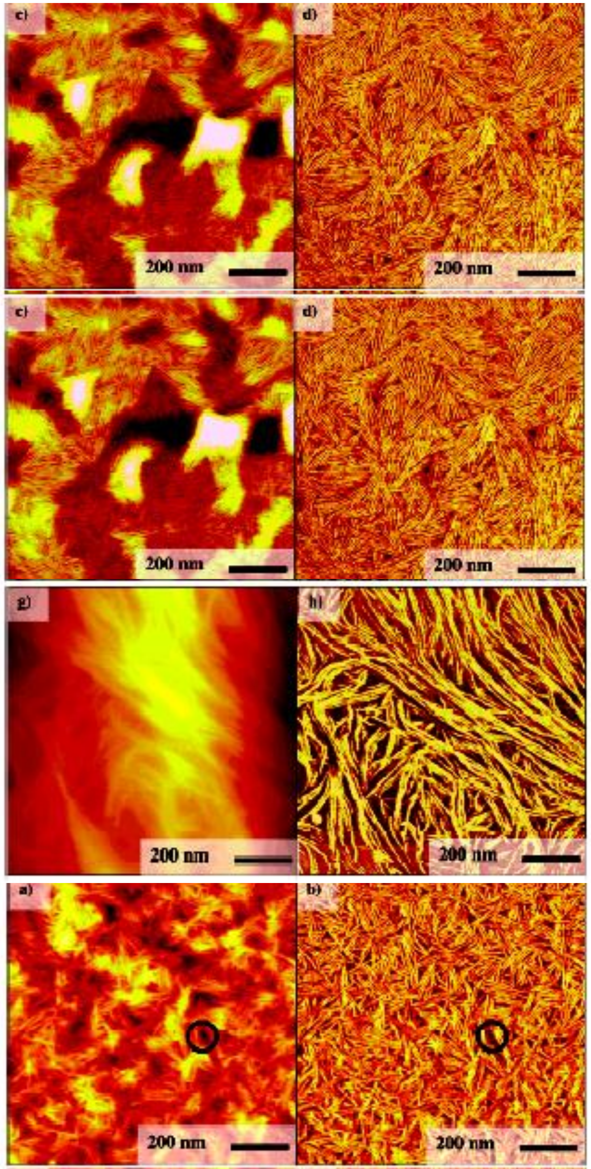
$$\begin{cases} \mu(E) = \mu_0 & \text{for } E < E_0 \\ \mu(E) = \mu_0 \exp\left[\eta\left(\sqrt{E} - \sqrt{E_0}\right)\right] & \text{for } E > E_0 \end{cases}$$

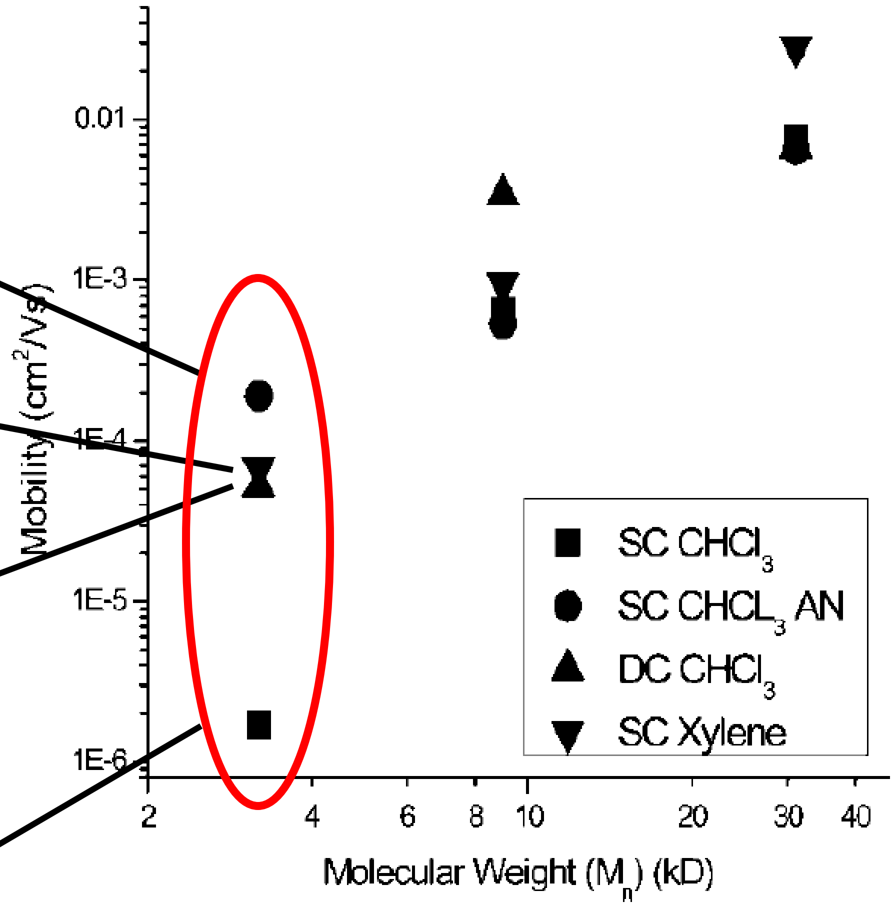




Sampietro et al. J. Appl. Phys., Vol. **104**, 084513, 2008

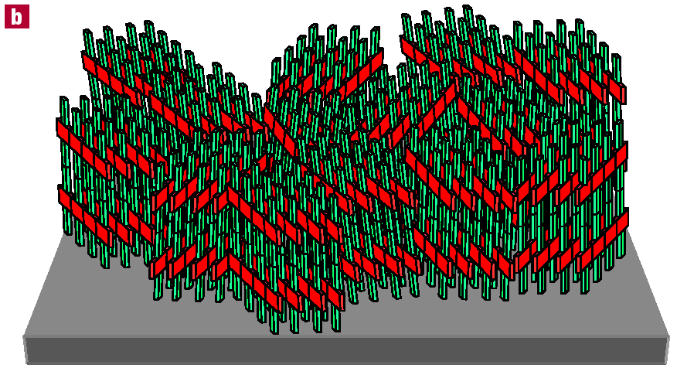
P3HT: MW and processing

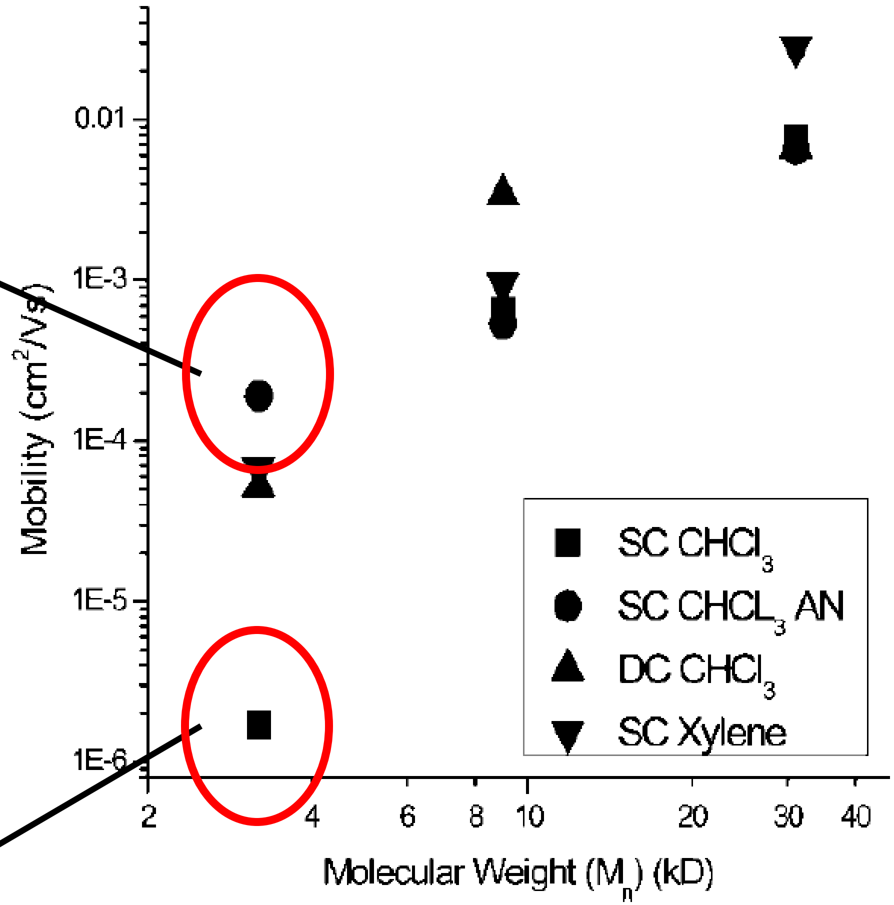


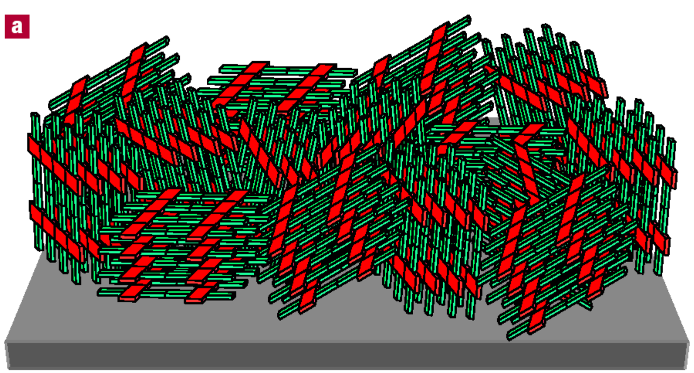


Low MW More affected by processing
-> morphology limited

P3HT: MW and processing

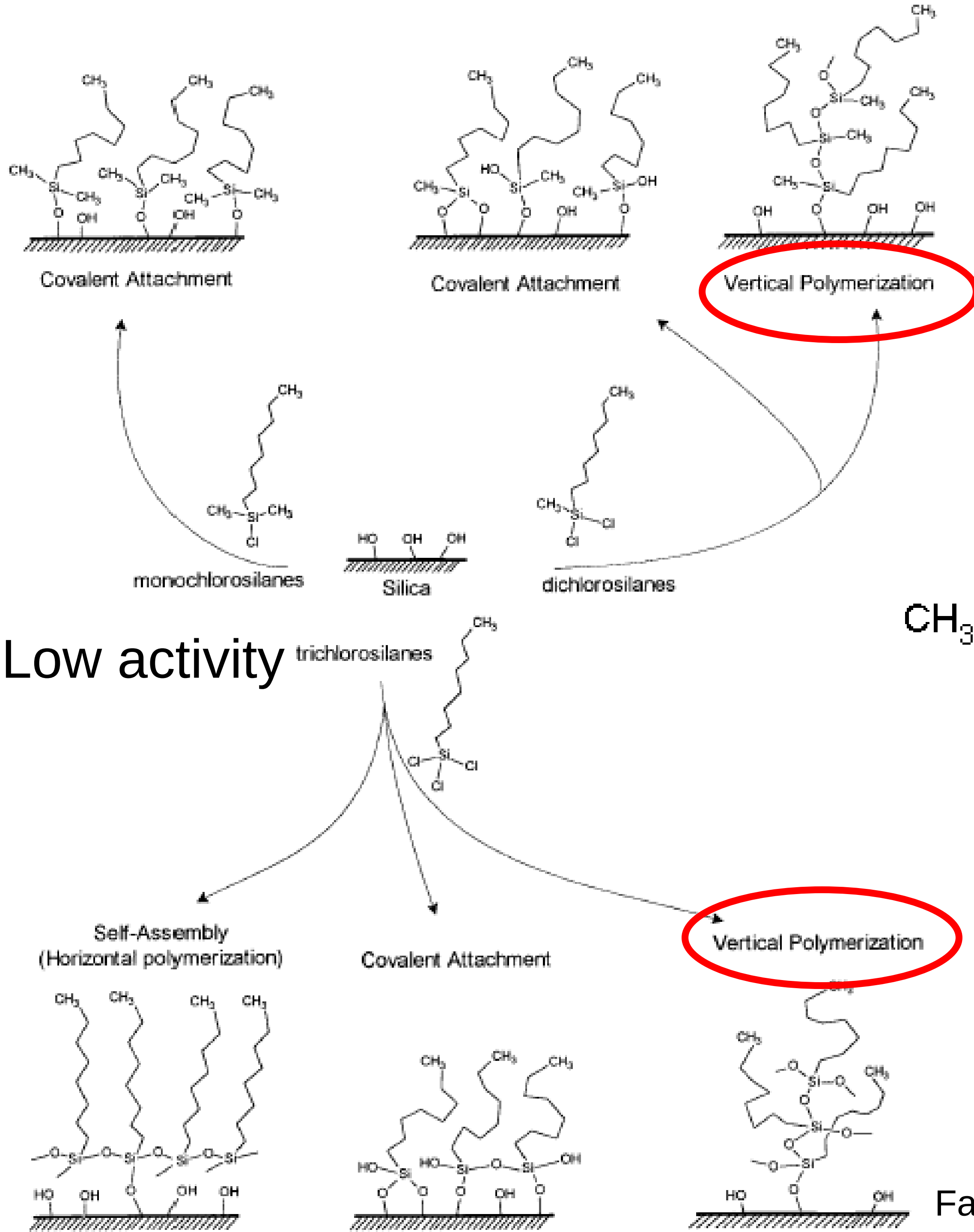




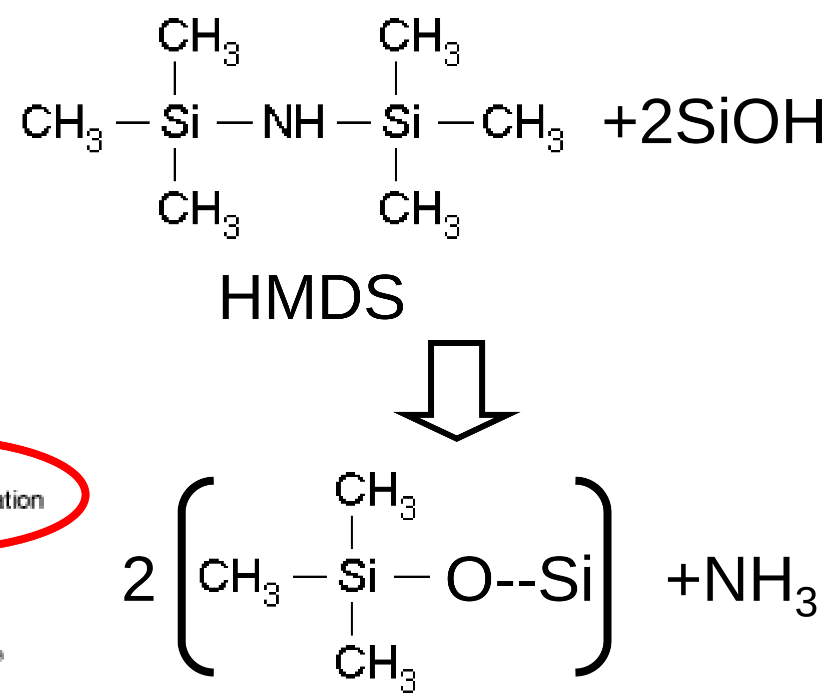


Low MW More affected by processing
-> morphology limited

SiO2 Surface Modification

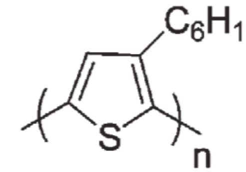


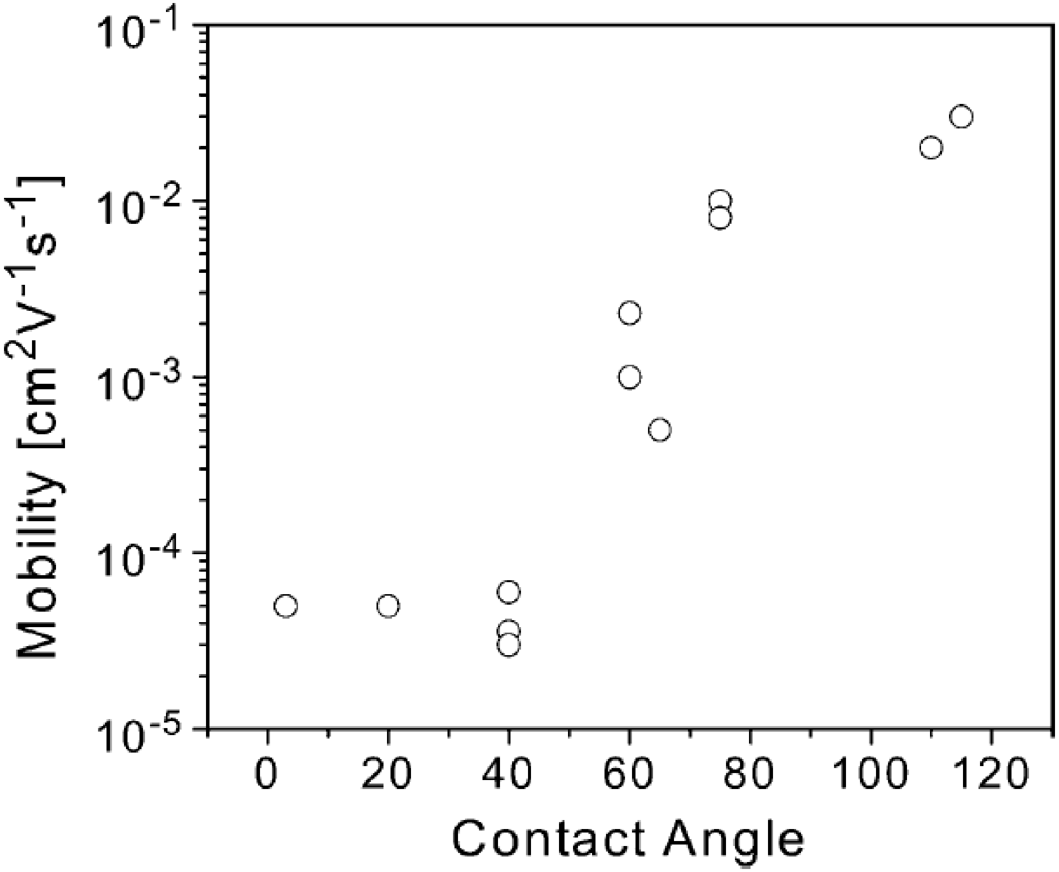
Low activity



Fadeev *Langmuir* **2000,** *16,* 7268-7274

P3HT: surface effect (1)

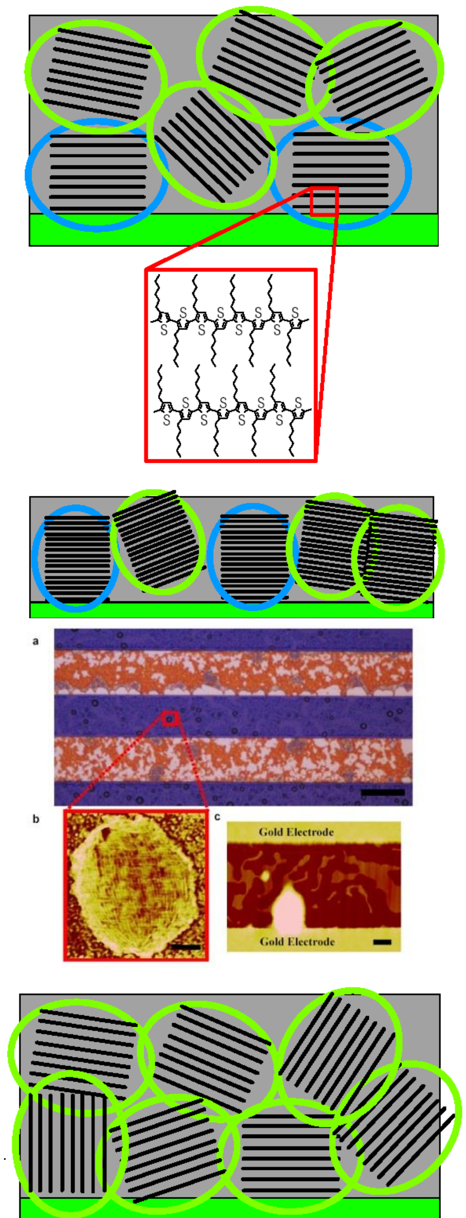


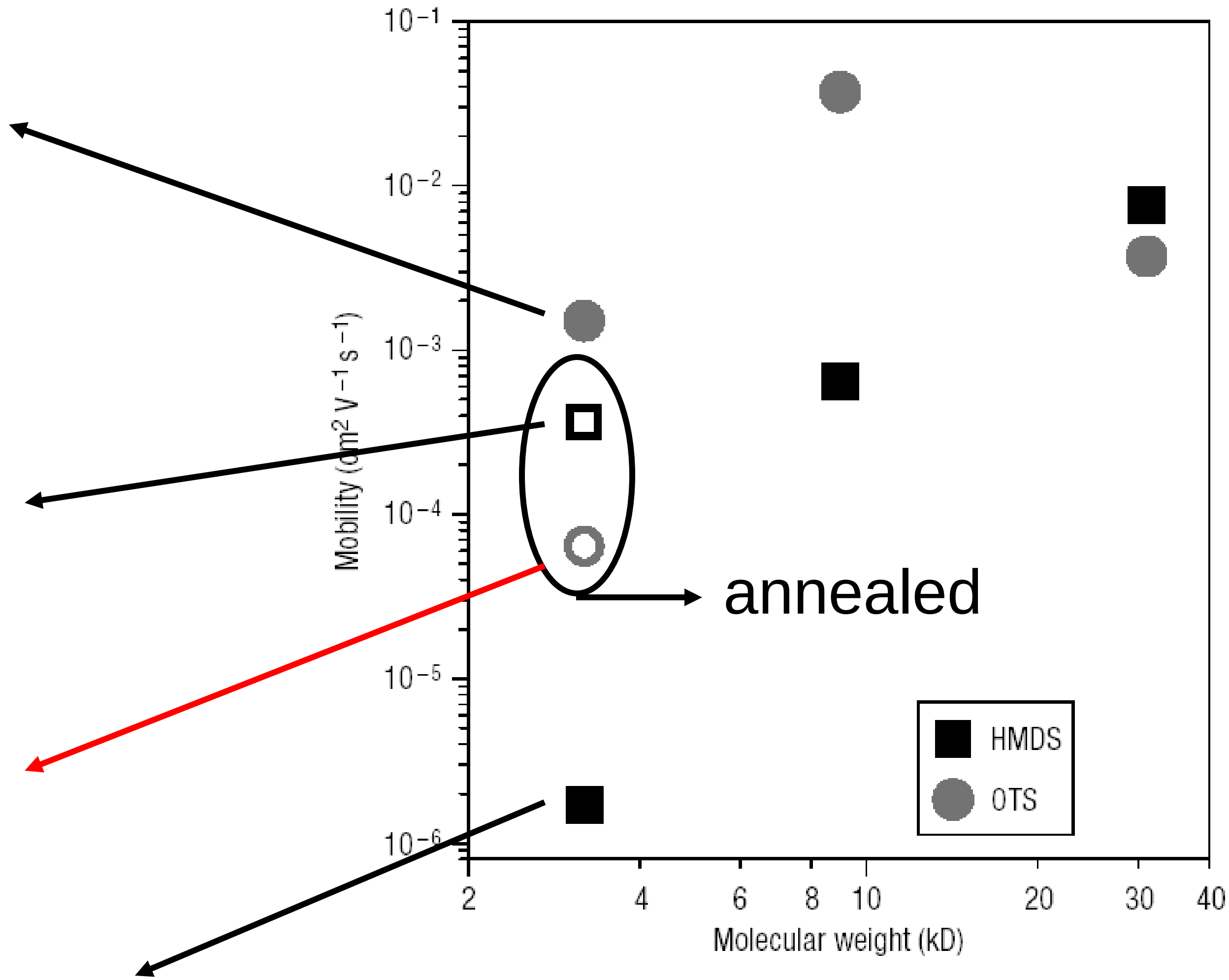


Surface roughness? Surface energy?

Veres Chem.Mater. *16*(23); 2004 4543-4555

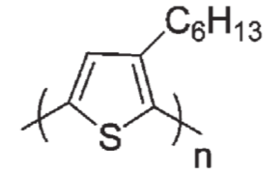
P3HT: MW & surface treatment

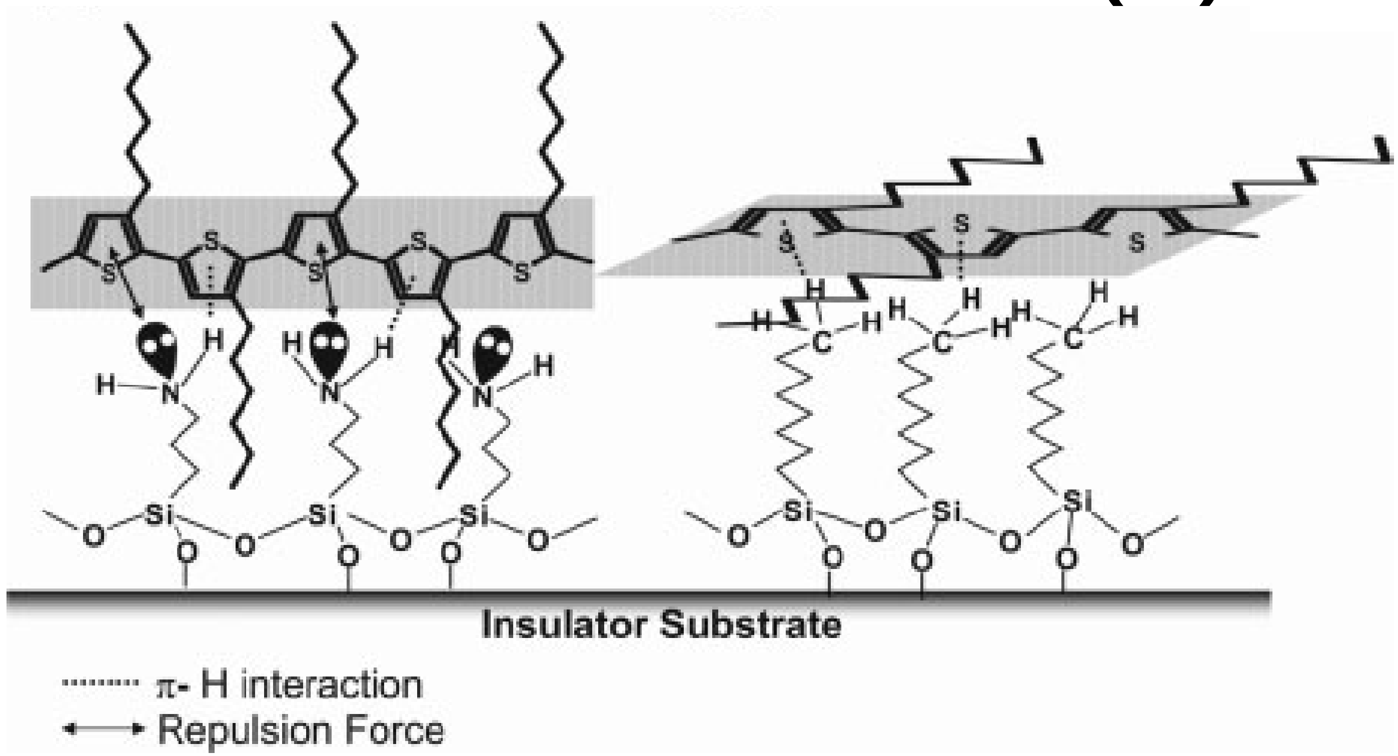




Kline Nature Materials, v 5, n 3, Mar 17, 2006, p 222-228

P3HT:surface effect (2)





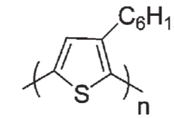
10^{-2} –**(240C 20min)** –> 2.8×10^{-1} 10^{-2} –**(240C 20min)** –> 0.8×10^{-1}

Unshared N e^- pairs repulsion ***Vs*** π-H interaction

Alkane chain interdigitation…

Kim Adv.Funct.Mat. 15 2005 77

P3HT: directional epitaxial solidification

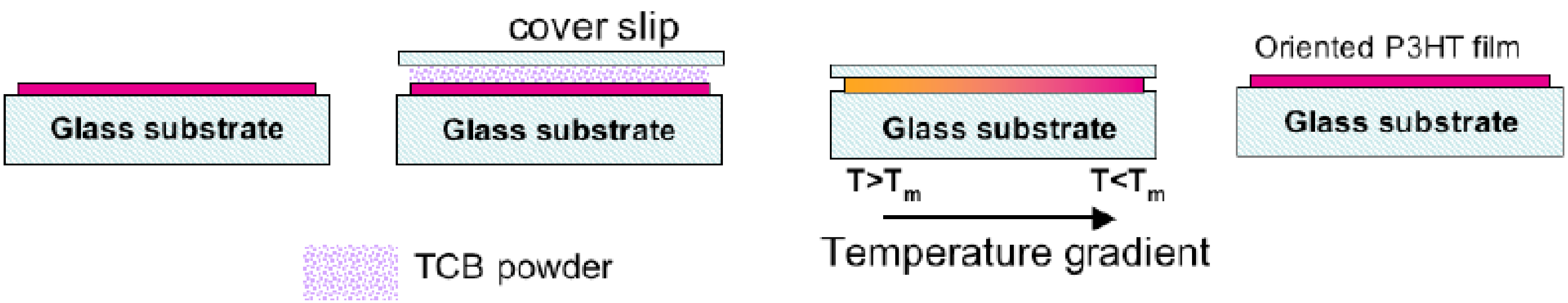


STEP 1
Spin-coat
or dip coat
a P3HT film

STEP 2
Sandwich TCB
powder between
glass slide and
cover slip

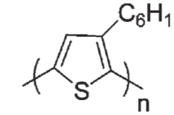
STEP 3
Directional
crystallization
of P3HT on TCB
crystals

STEP 4
Remove cover slip
Sublimation of
TCB (primary
Vacuum)

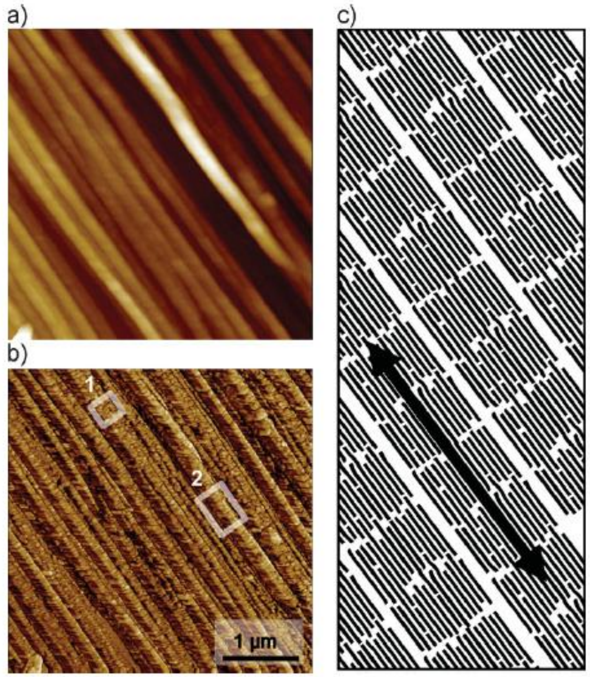


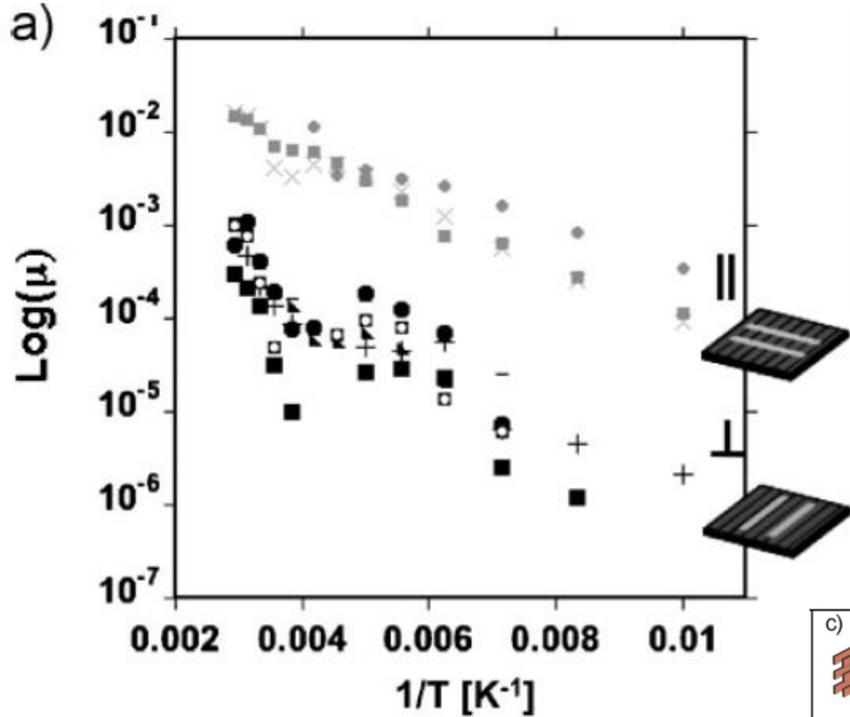
$T>T_m$: uniform dispersion
of P3HT in liquid TCB

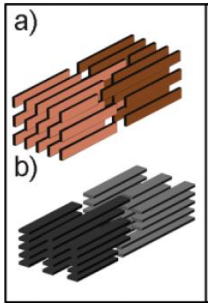
Brinkmann Adv. Funct. Mater. **2007**, *17*, 101–108

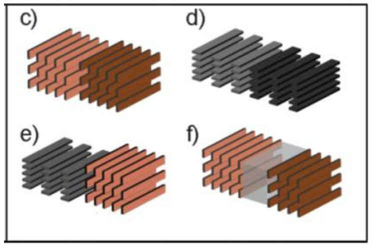


P3HT: directional epitaxial solidification



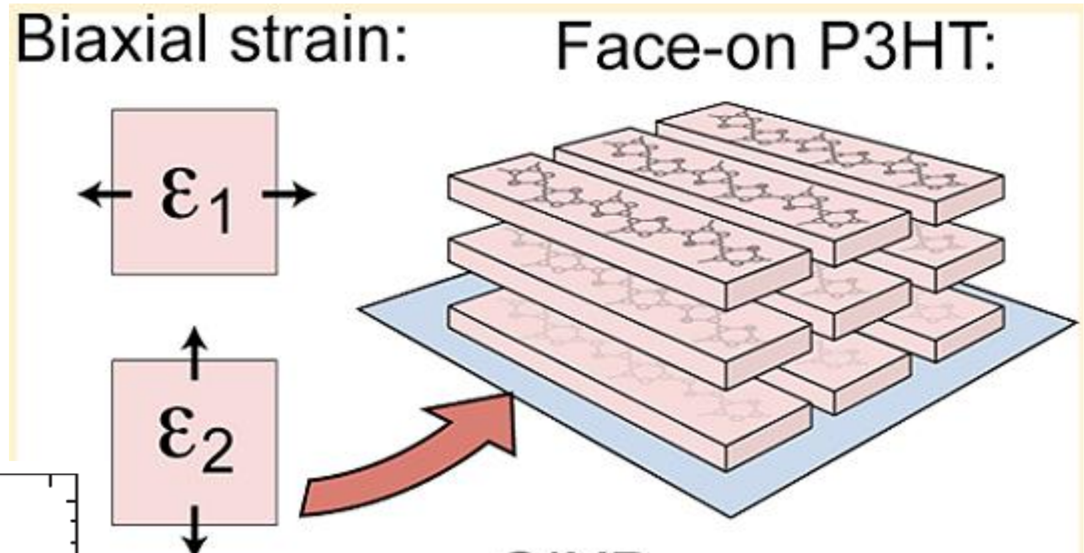


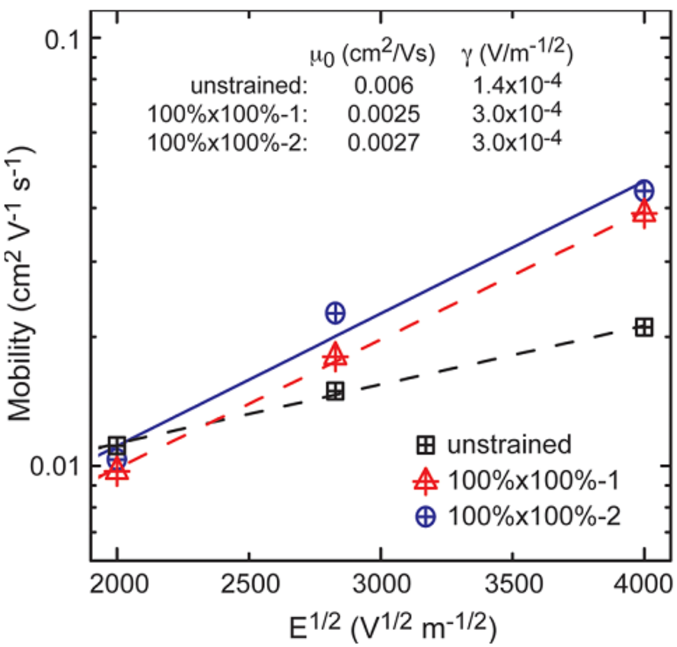


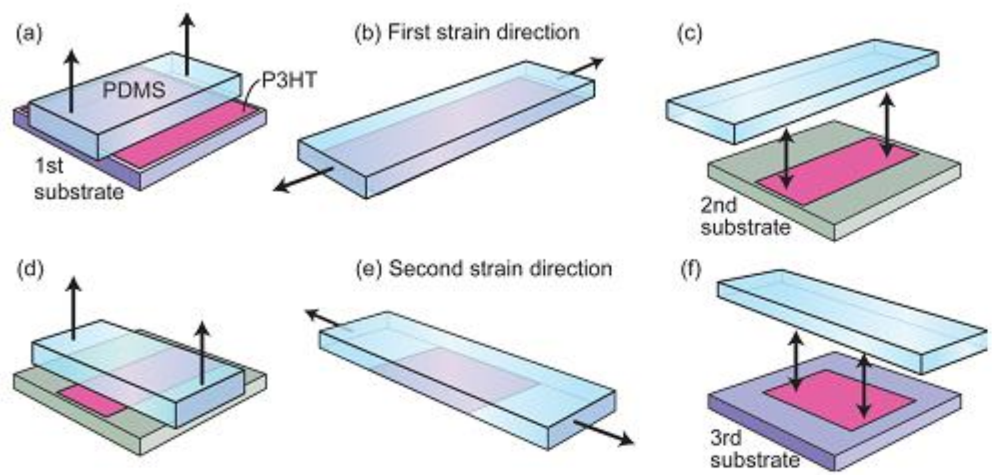


Salleo Adv. Mater. 2009, 21, 1568–1572

The face-on paradigm at trial







Gargi et al.10.1021/jp4050644| J. Phys. Chem. C2013, 117, 17421−17428

Environmental stability: doping

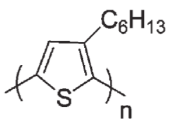


TABLE I. μ_{fet} and σ under various operating conditions.

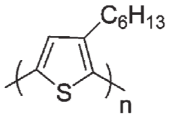
Condition	μ_{fet}[a] (10^{-4} $cm^2/V\ s$)	σ[b] (10^{-3} S/cm)
Vacuum	1.25	0.58
Air		7.16
N_2	1.23	0.78
N_2 (wet)		6.00
O_2 (after 4 h)	0.94	1.49

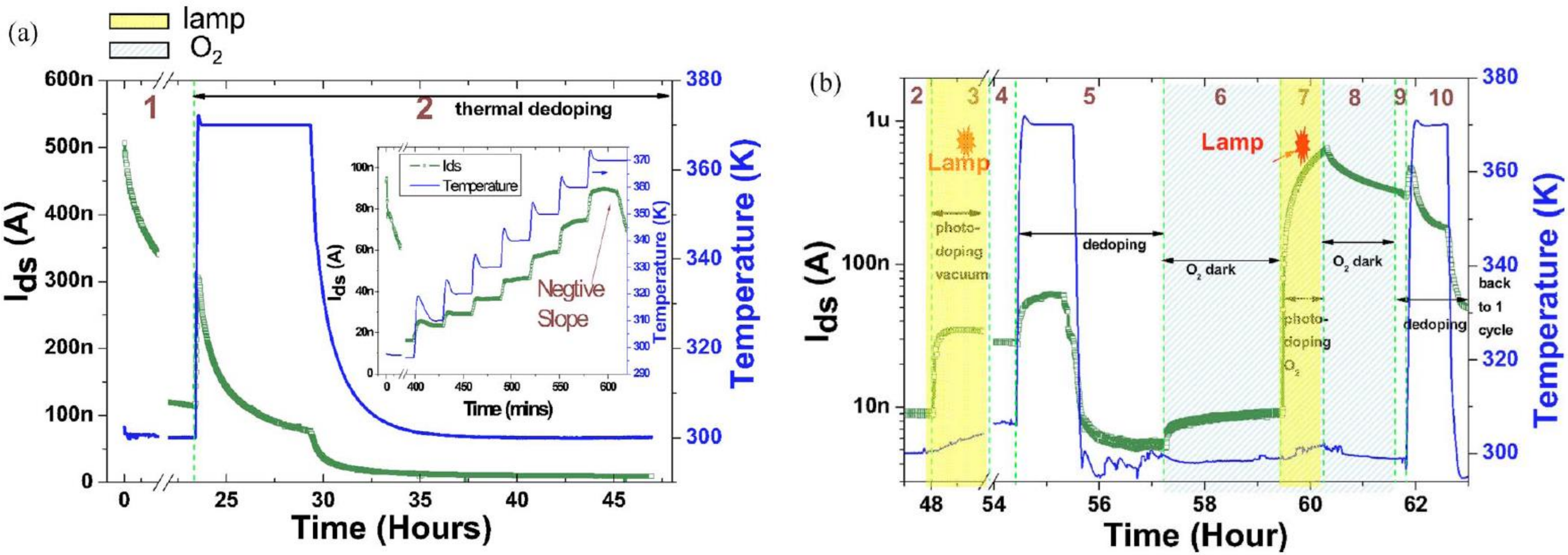
[a]Calculated from the $I_d - V_g$ response at $V_d = -30$ V.
[b]Calculated from the I_d values at $V_g = -30$ V.

Moisture and Oxygen related doping!!!

Hoshino J. Appl. Phys., Vol. 95 2004 5088

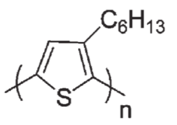
Oxygen doping

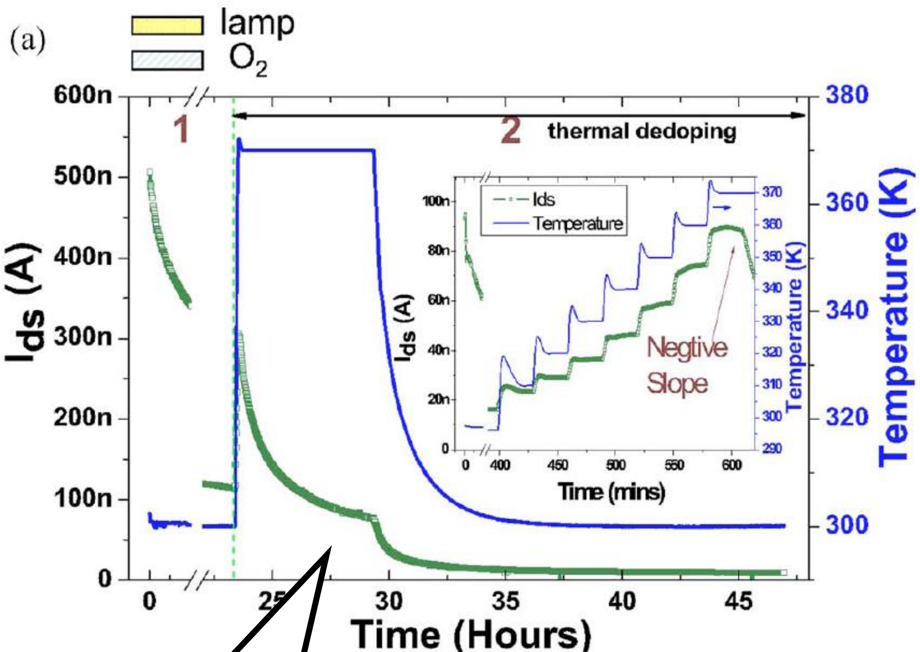


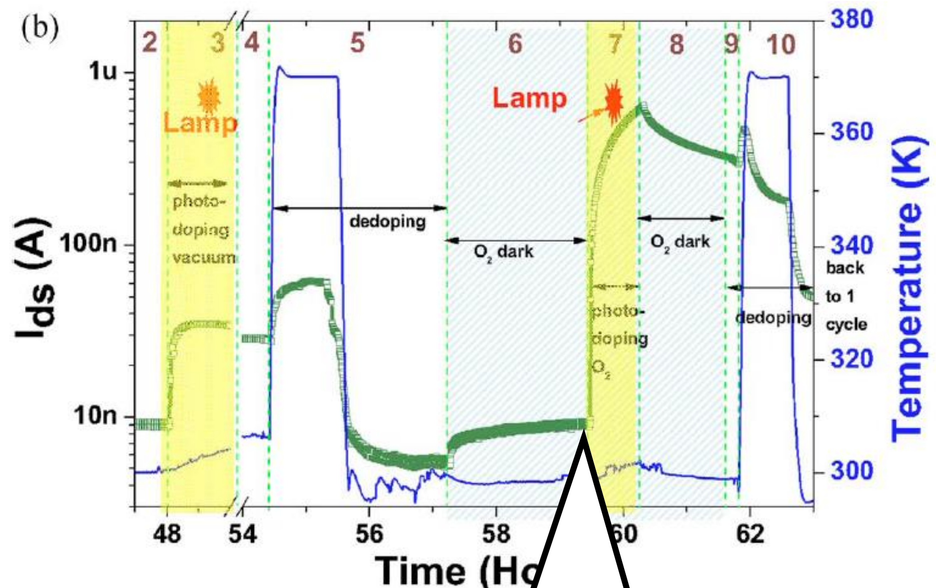


Liao JOURNAL OF APPLIED PHYSICS **103**, 104506 2008

Oxygen doping







Dedoping faster at higher T

Doping faster with light!

Liao JOURNAL OF APPLIED PHYSICS **103**, 104506 200

Oxygen doping

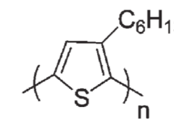
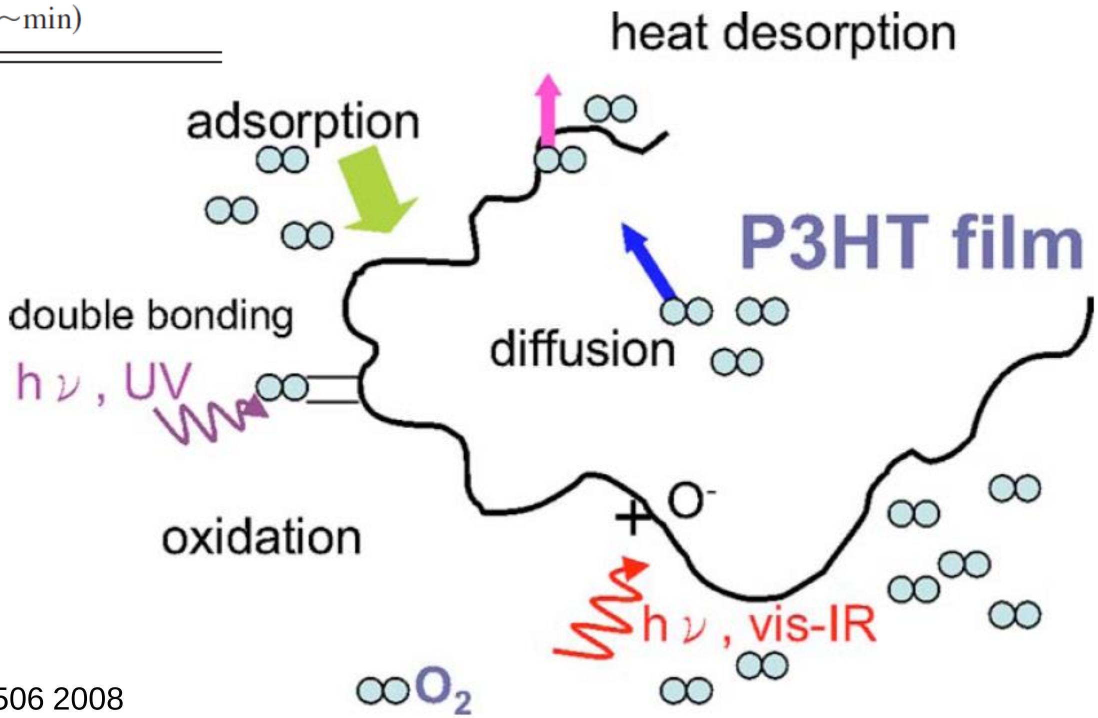


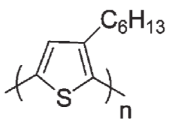
TABLE II. The oxygen doping and de-doping rate at different experimental environments.

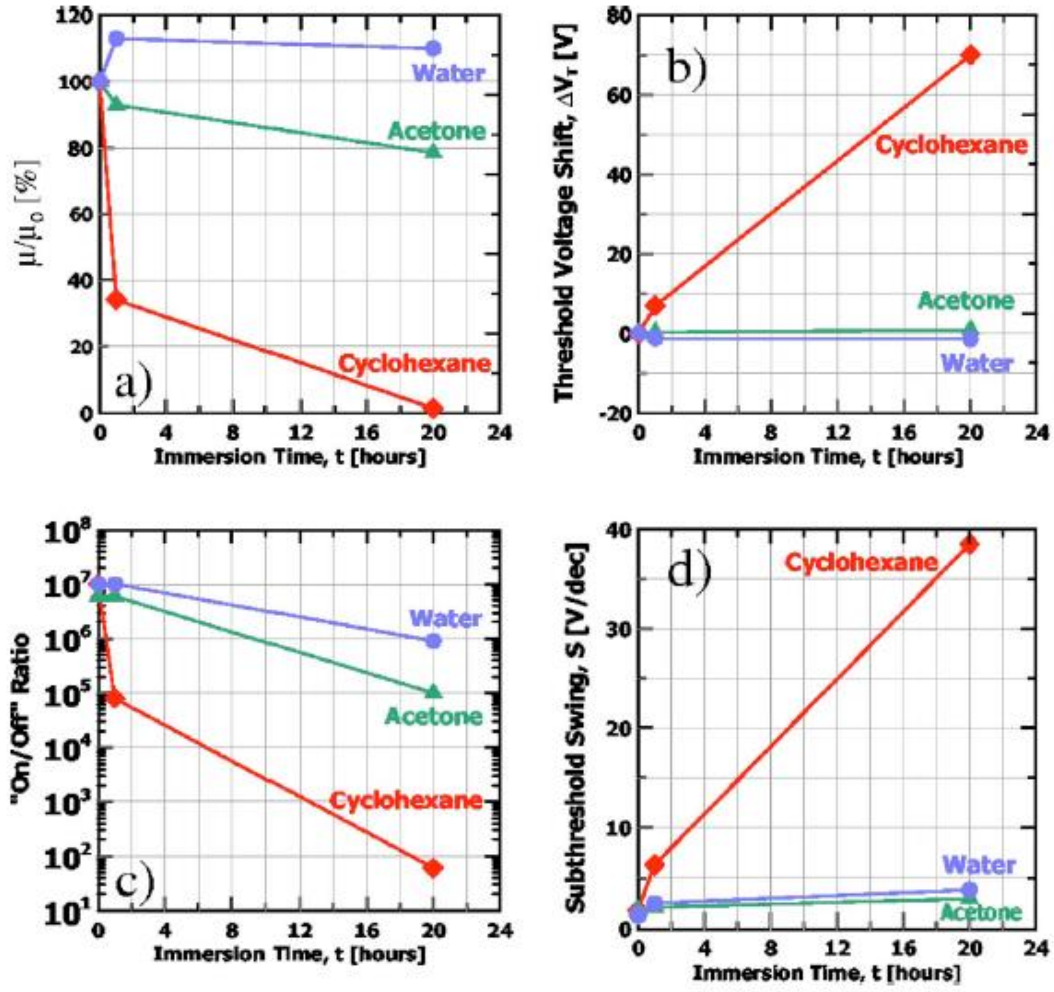
Doping condition	Rate
Light+Vacuum	Moderate (∼min)
O_2, dark	Slow (∼h)
O_2, Light	Fast (∼s)
De-doping condition	Rate
300 K+Vacuum+Dark	Very slow (∼days to weeks)
370 K+Vacuum+Dark	Moderate (∼min)



Liao JOURNAL OF APPLIED PHYSICS **103**, 104506 2008

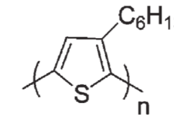
Environmental stability: storage

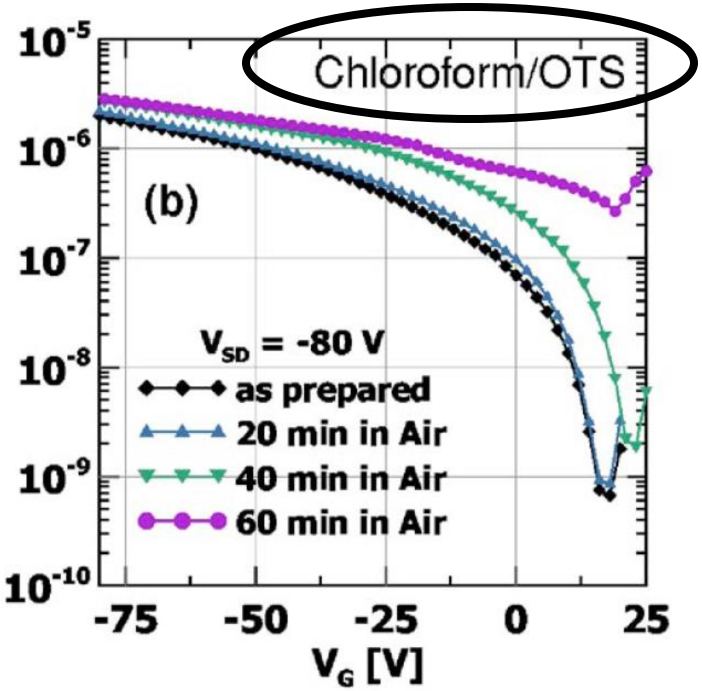


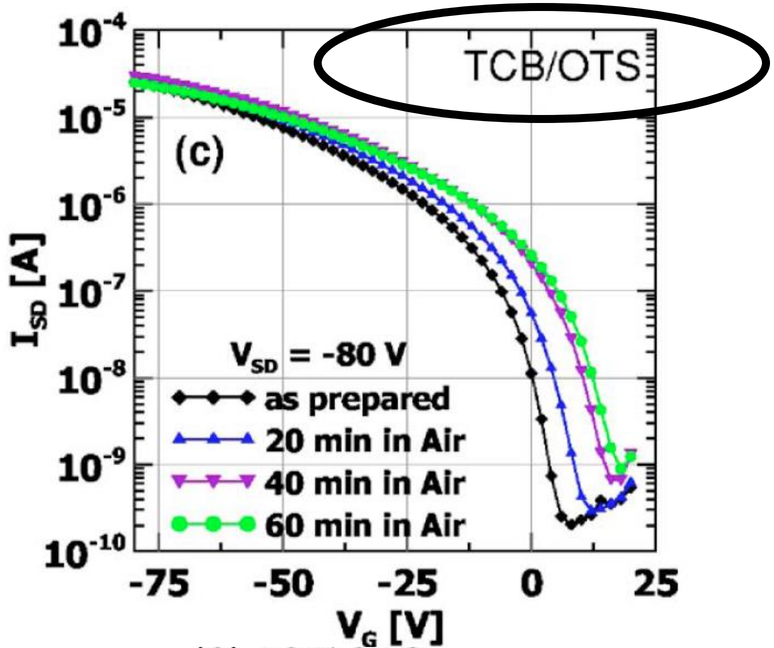


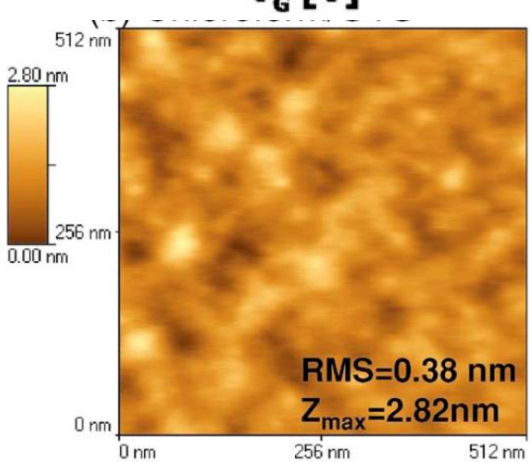
Majewski J. Appl. Phys. **102**, 074515 2007

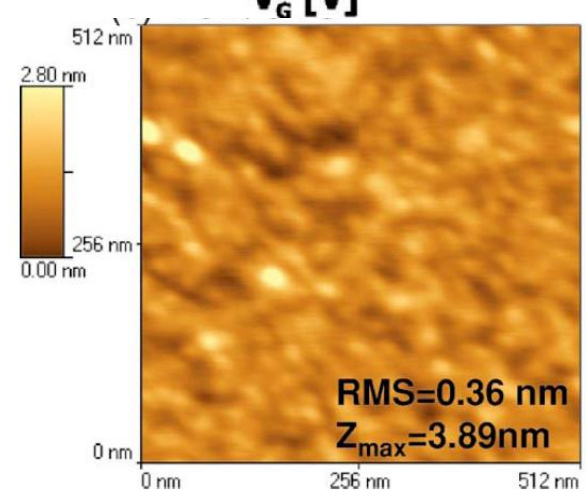
Environmental stability: role of processing





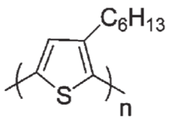






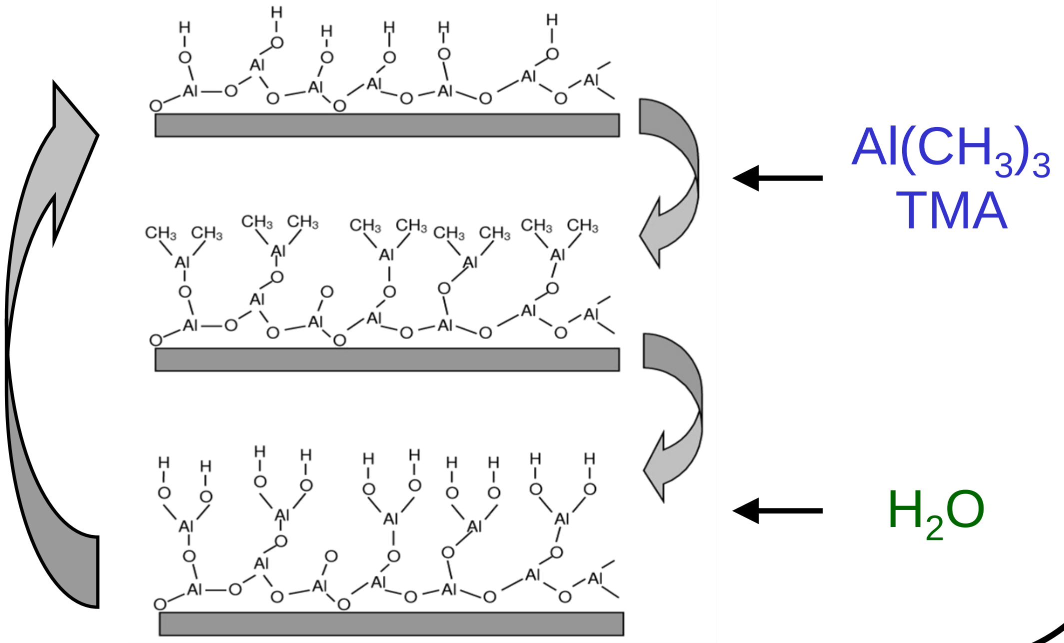
Majewski APPLIED PHYSICS LETTERS **88**, 222108 2006

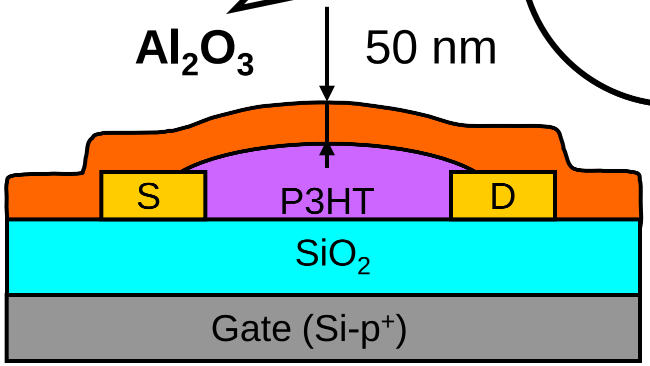
Air stability & capping



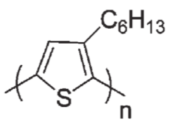
Al_2O_3 deposited by means of

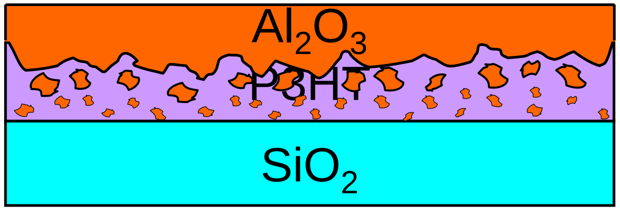
Atomic Layer Deposition (ALD)[@125C, few mbar]





Air stability & capping

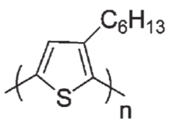


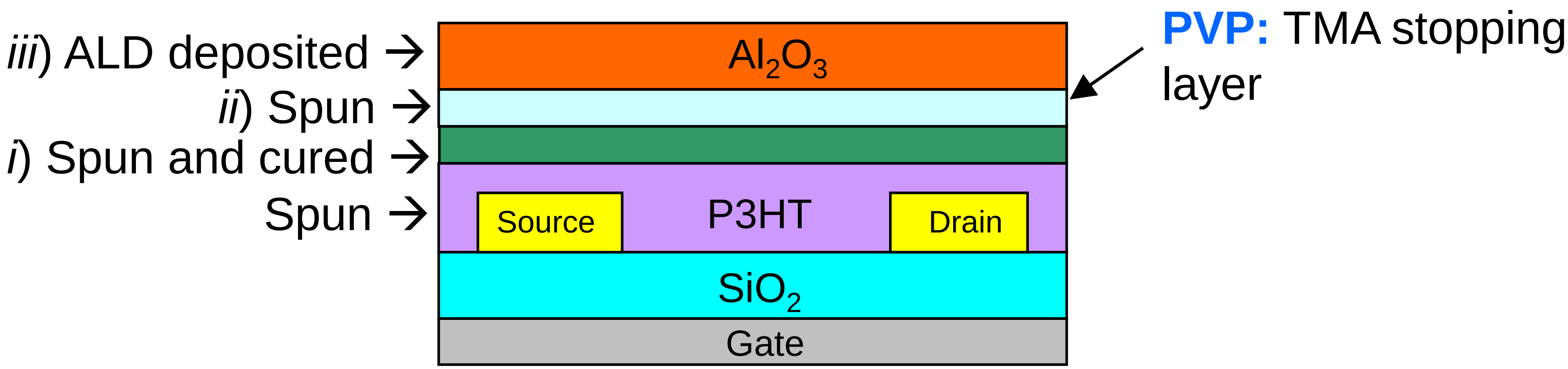


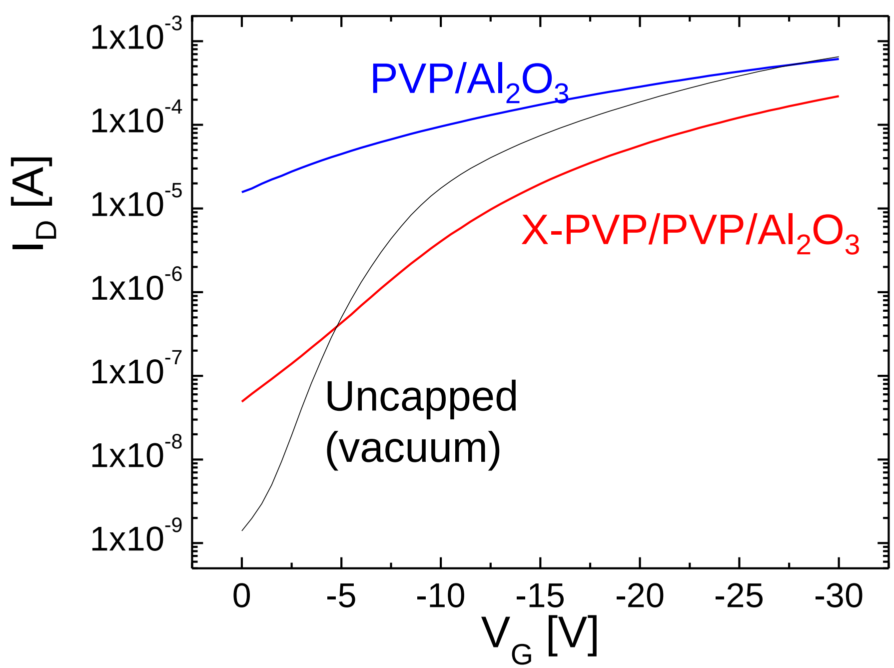
Need stopping layer to prevent **damage**! ← $Al(CH_3)_3$ TMA

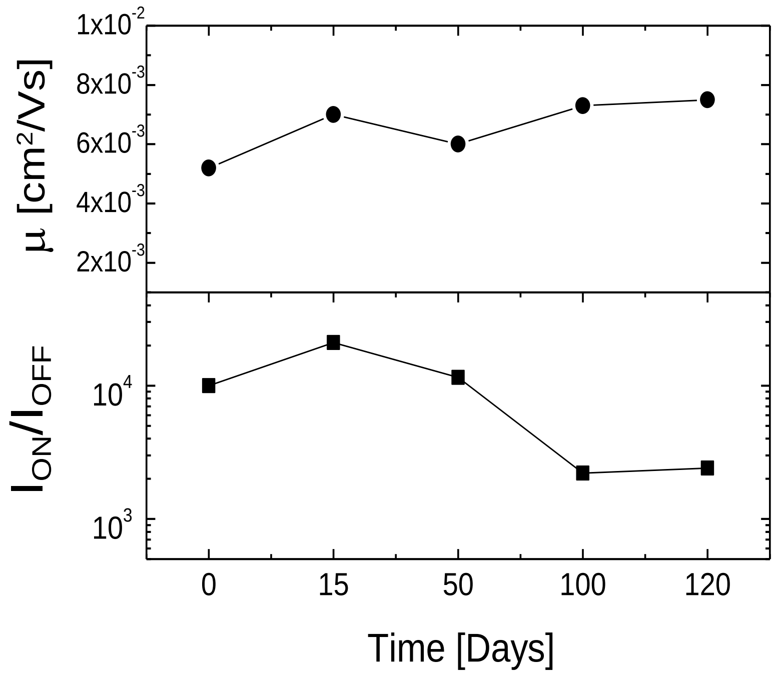
Need stopping layer to prevent **doping**! ← H_2O

Air stability & capping





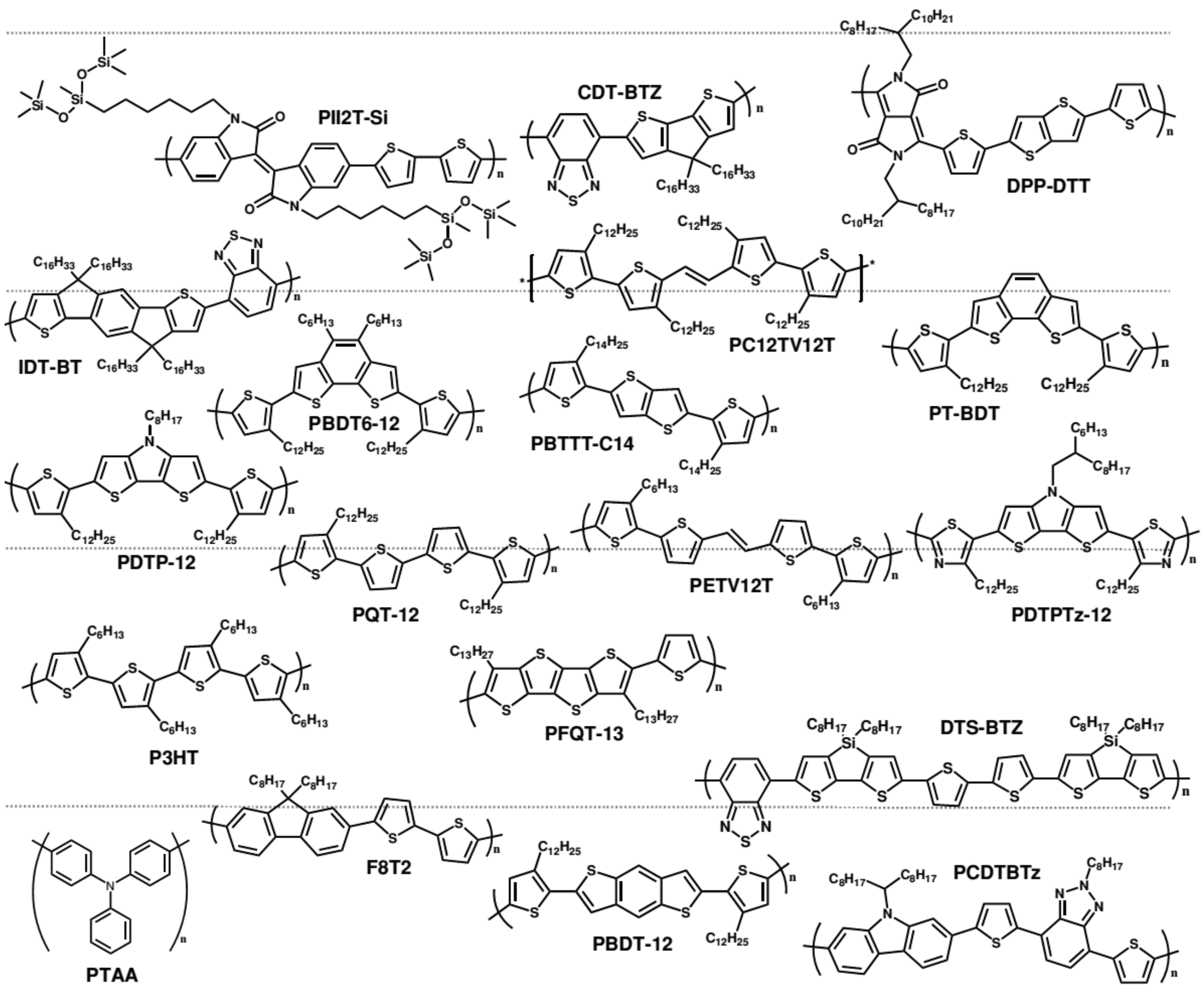




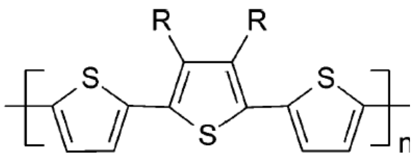
Sampietro Organic Electronics 2007 8 407-414 - Organic electronics in press 10.1016/j.orgel.2009.03.003

New gen. materials

aka the tongue-breaking era



Polyalkylthiophenes: scheme of substitution(1)



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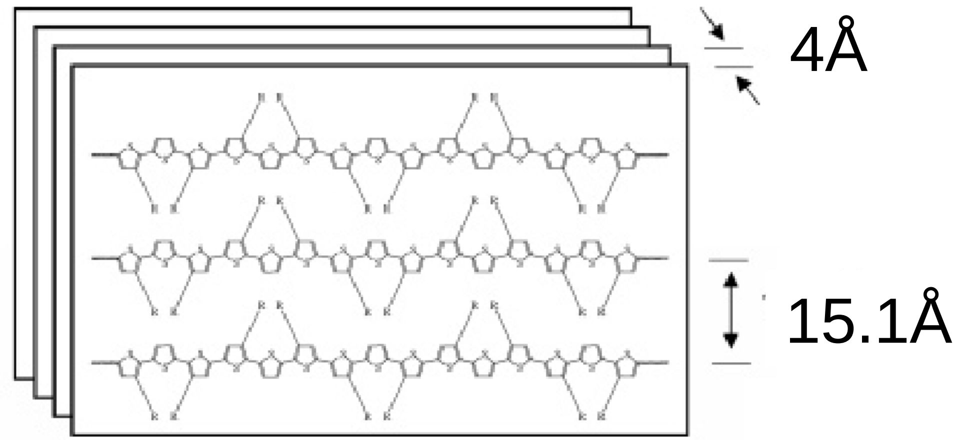
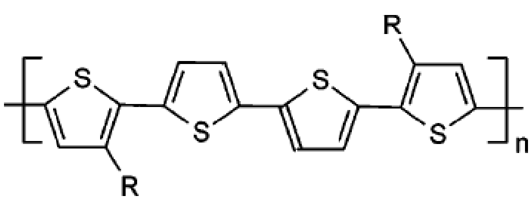
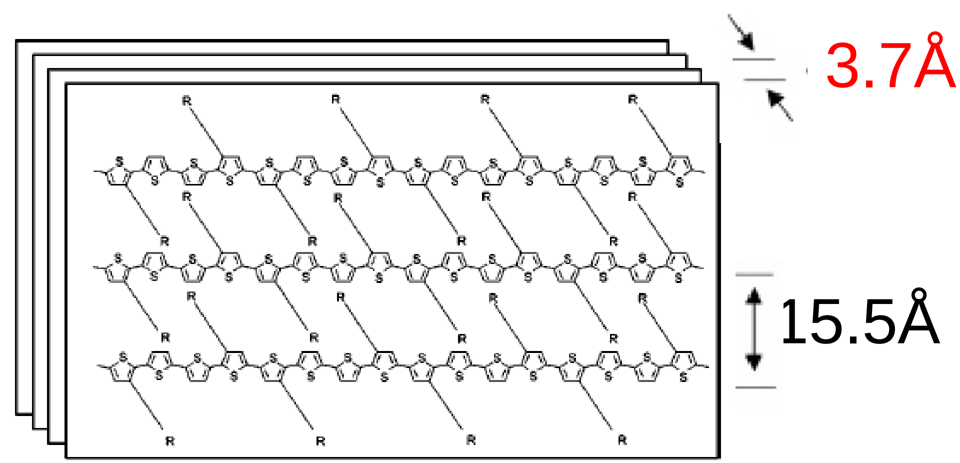


$3\times10^{-2} cm^2/Vs$

Ong Synth.Met. 142 (2004) 49–52

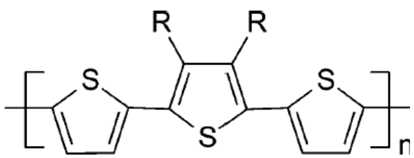




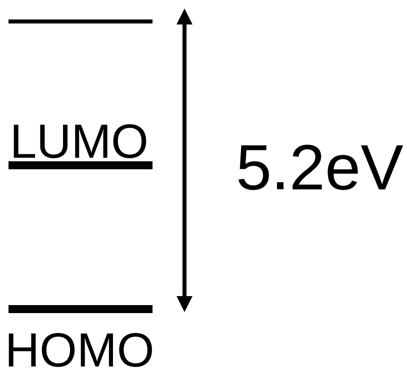
$10^{-1} cm^2/Vs$

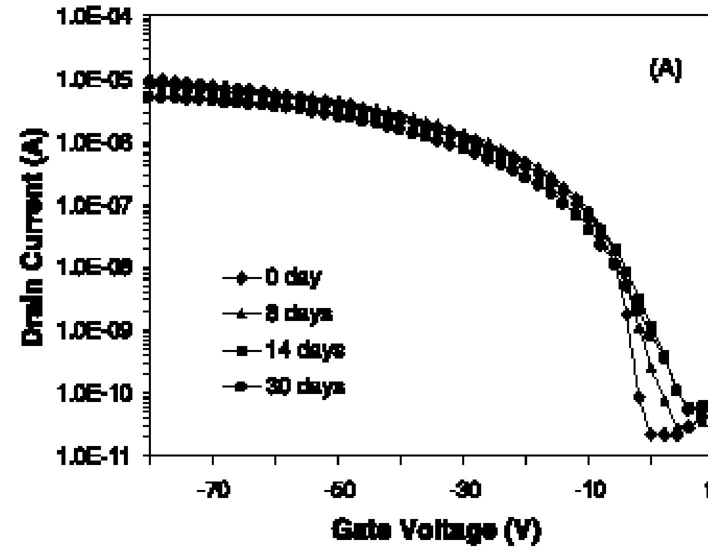
Ong J. AM. CHEM. SOC. 2004, 126, 3378-3379

Polyalkylthiophenes: scheme of substitution(2)

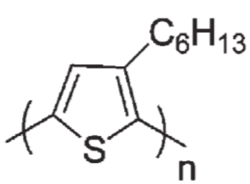


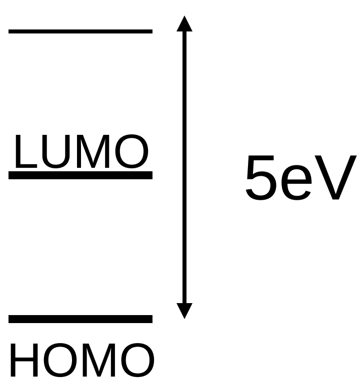
2

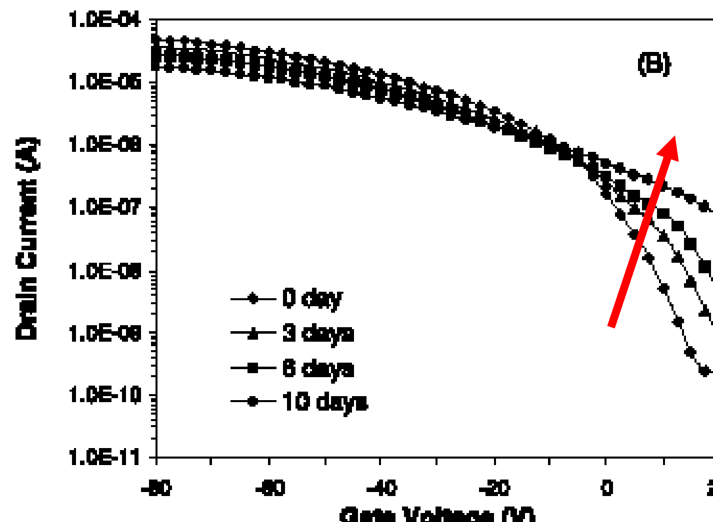




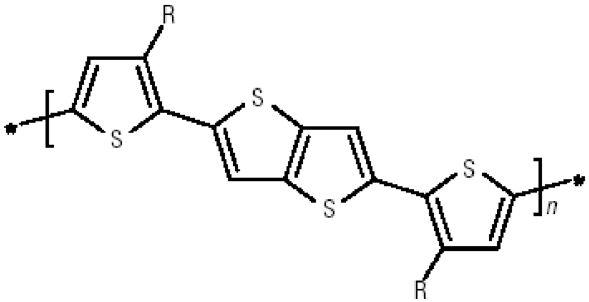
Torsional deviation gives lower lying HOMO and hence higher stability

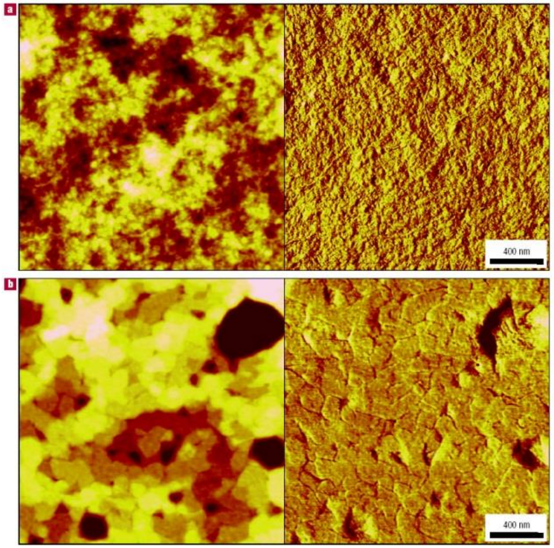






Fused thiophene based polymer





HOMO lowered by competition between Delocalization and resonance without interfering with crystallinity

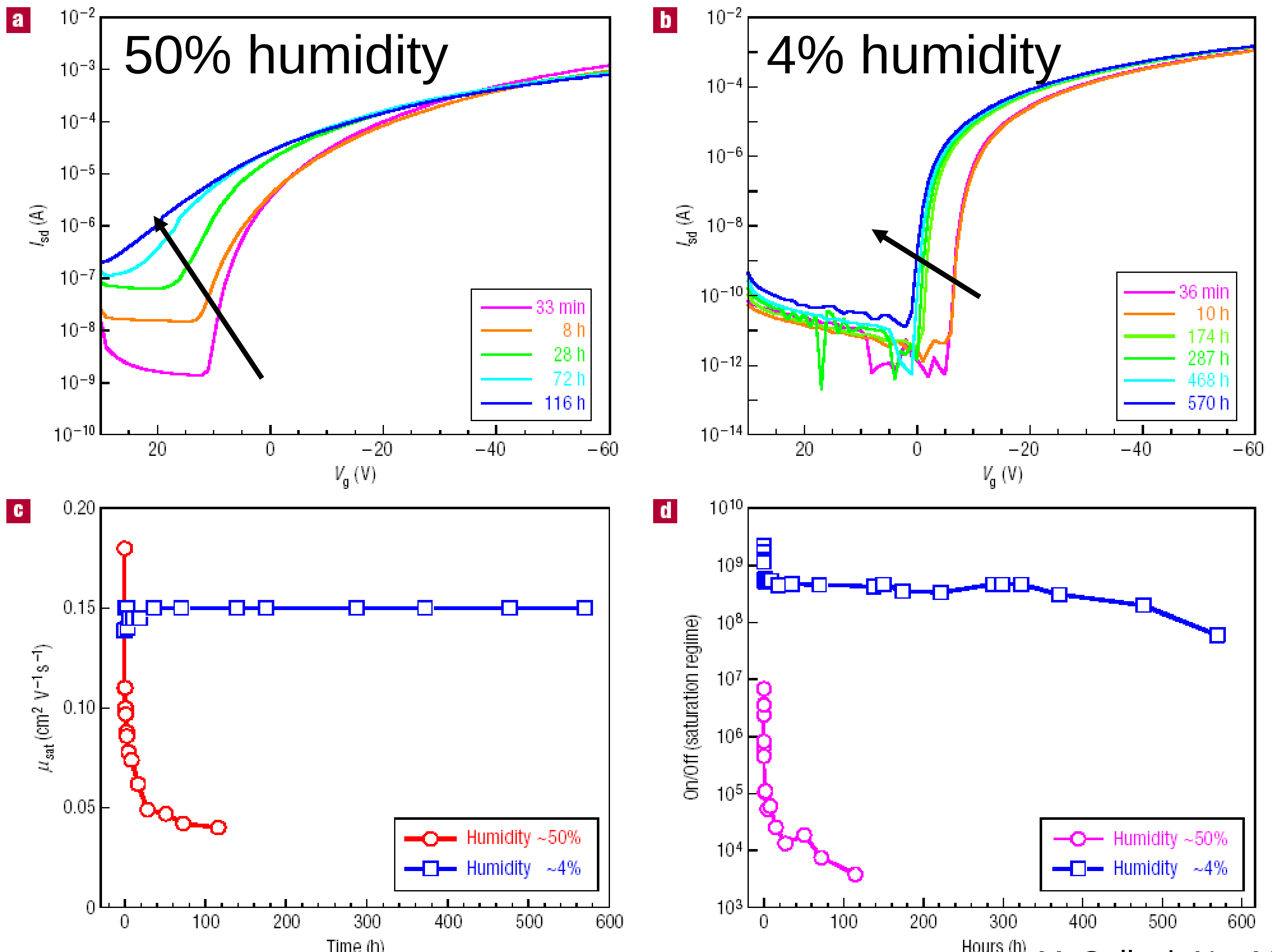
Table 1 Polymer properties. *T*1↑ and *T*2↑ correspond to the low- and high-temperature endotherms on heating (at 10 °C min^{-1}) respectively, and *T*2↓ and *T*1↓ correspond to the high- and low- temperature exotherms on cooling (10 °C min^{-1}) respectively. IP was measured by an ambient ultraviolet photoelectron spectroscopy (UPS) technique.

Sidechain	Mn/Mw	λ_{max} (nm)	IP (eV)	*T*1↑ (°C)	*T*2↑ (°C)	*T*2↓ (°C)	*T*1↓ (°C)	Cooling enthalpy *T*2↓ ($J\ g^{-1}$)	Cooling enthalpy *T*1↓ ($J\ g^{-1}$)	$\mu_{max\ sat}$ (N_2) ($cm^2\ V^{-1}\ s^{-1}$)	$\mu_{max\ lin}$ (N_2) ($cm^2\ V^{-1}\ s^{-1}$)	ON/OFF ratio (N_2)
C10	28,500/51,300			171	251	237	142	13.1	18.5	0.30	0.22	10^6
C12	29,600/54,000	547	5.1	143	244	233	115	10.1	20.5	0.30	0.11	10^6
C14	33,000/59,600			141	248	233	102	11.3	26.5	0.63	0.39	$>10^7$
										0.72*	0.20*	$>10^{6*}$

* Different device geometry ($W = 2{,}000\ \mu m$, $L = 5\ \mu m$) and dielectric thickness (200 nm).

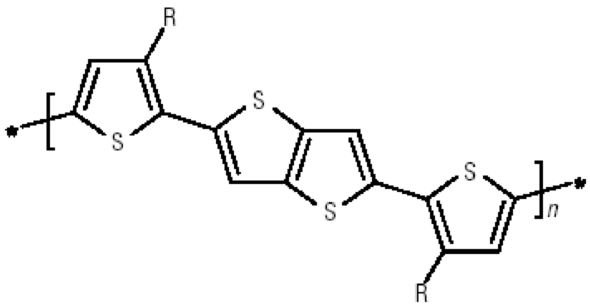
McCulloch Nat.Mat. 5 2006 328

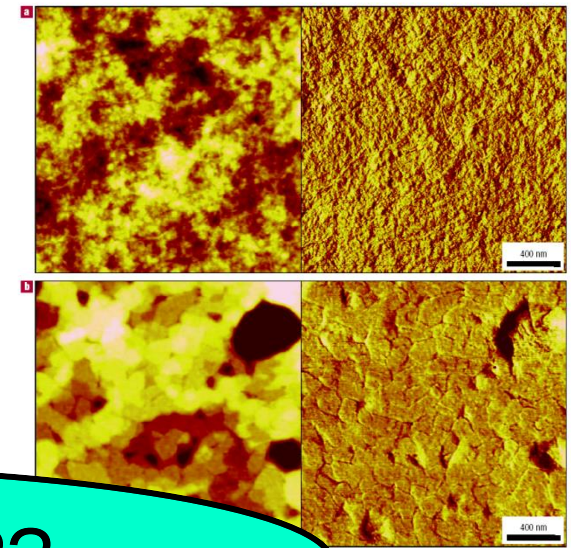
Fused thiophene based polymer



McCulloch Nat.Mat. 5 2006 328

Fused thiophene based polymer





HOMO lowered by competition between
Delocalization and resonance
without interfering …

Why so high???

Table 1 Polymer properties. *T*1↑ and *T*2↑ correspond to the low- and high-temperature endo… (at 10 °C min^{-1}) respectively, and *T*2↓ and *T*1↓ correspond to the high- and low- temperature exotherms on cooling (10 °C min^{-1}) respectively. IP was … by an ambient ultraviolet photoelectron spectroscopy (UPS) technique.

Sidechain	Mn/Mw	λ_{max} (nm)	IP (eV)	*T*1↑ (°C)	*T*2↑ (°C)	*T*2↓ (°C)	*T*1↓ (°C)	Cooling enthalpy *T*2↓ (J g^{-1})	Cooling enthalpy *T*1↓ (J g^{-1})	$\mu_{max\ sat}$ (N_2) (cm^2 V^{-1} s^{-1})	$\mu_{max\ lin}$ (N_2) (cm^2 V^{-1} s^{-1})	ON/OFF ratio (N_2)
C10	28,500/51,300			171	251	237	142	13.1	18.5	0.30	0.22	10^6
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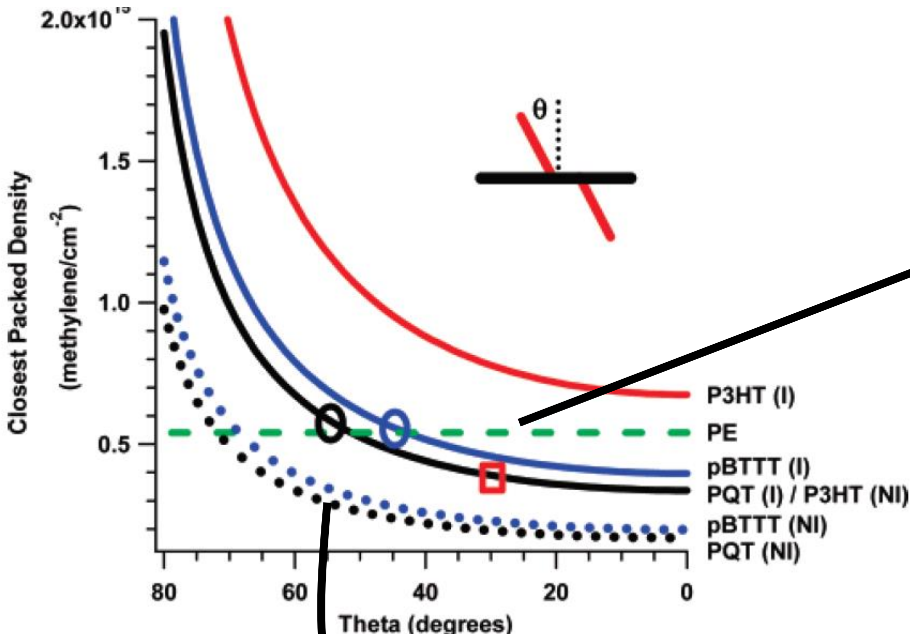
C14	33,000/59,600			141	248	233	102	11.3	26.5	0.63	0.39	$>10^7$
										0.72*	0.20*	$>10^{6*}$

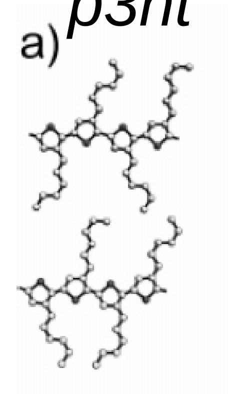
* Different device geometry ($W = 2{,}000$ μm, $L = 5$ μm) and dielectric thickness (200 nm).

McCulloch Nat.Mat. 5 2006 328

Side chain density role!!

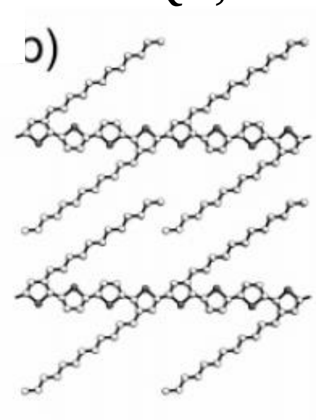


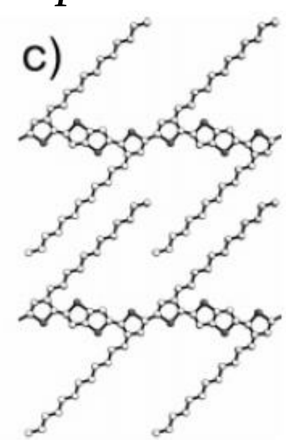
p3ht



Interdigitate
Unphysical!
2D ordering only

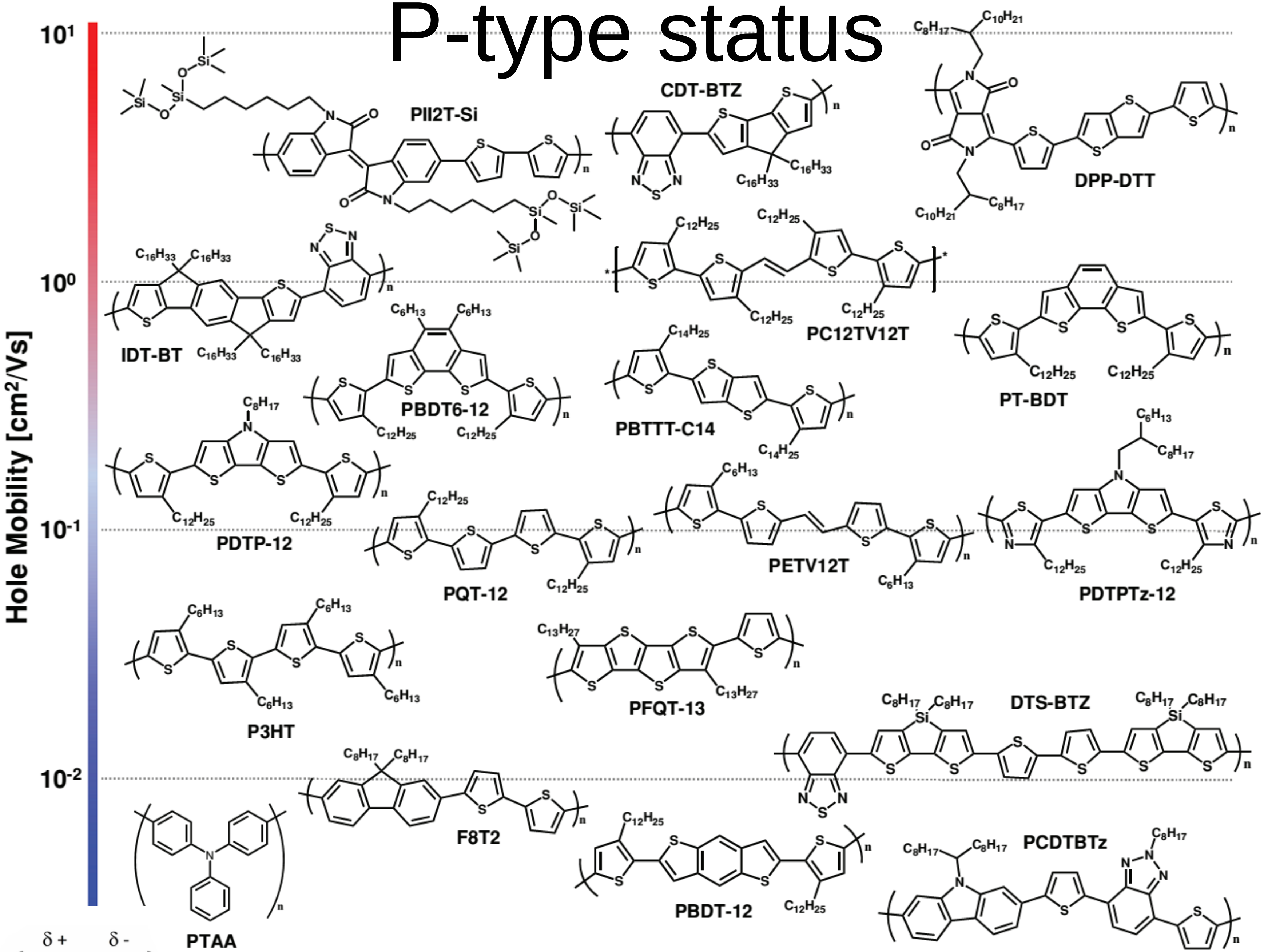
PQT, *pBTTT-C12*

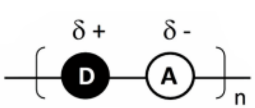




Chabinyc *Macromolecules*, **2007**, 40 (22), 7960-7965

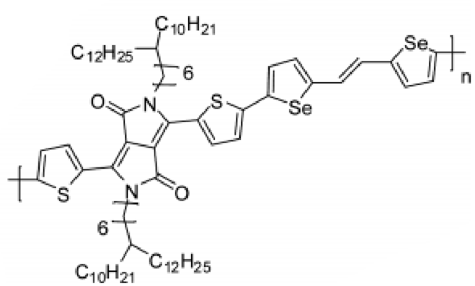
P-type status

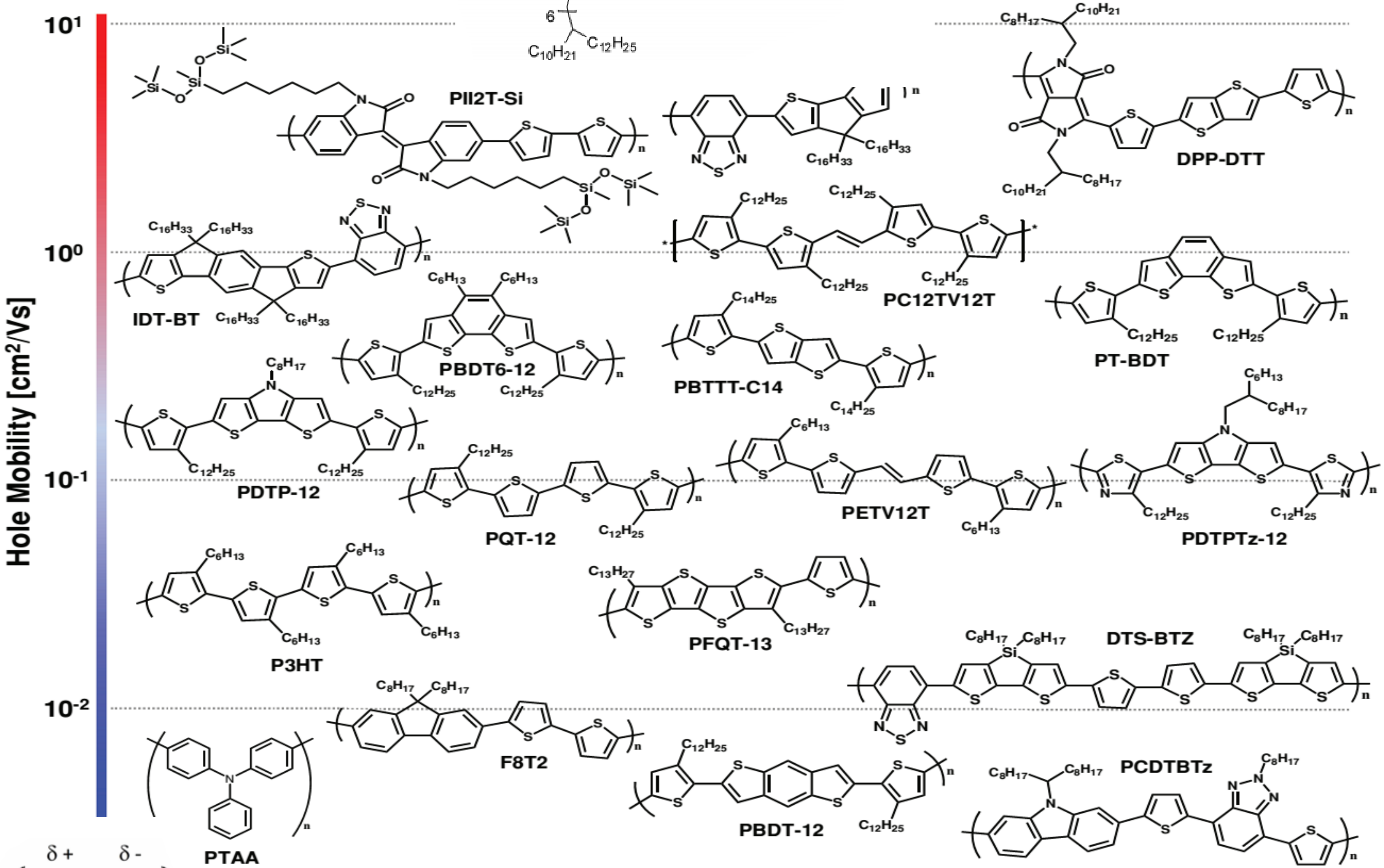


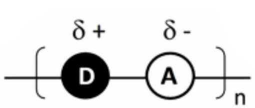


D/A strategy increasingly popular!

Caironi et al., Adv. Mater. 2013, 25, 4210–4244

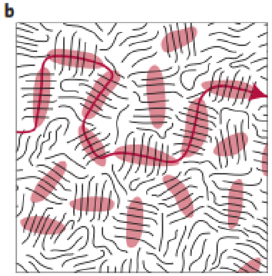
Record:  12 cm^2/Vs



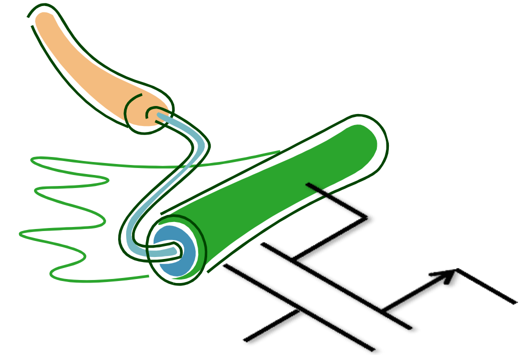


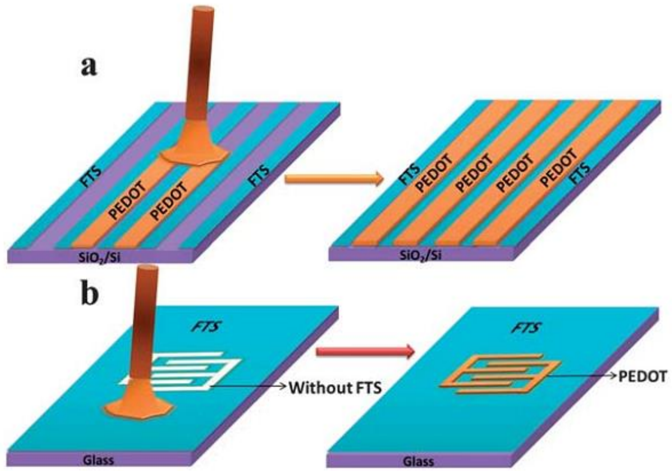
D/A strategy increasingly popular!

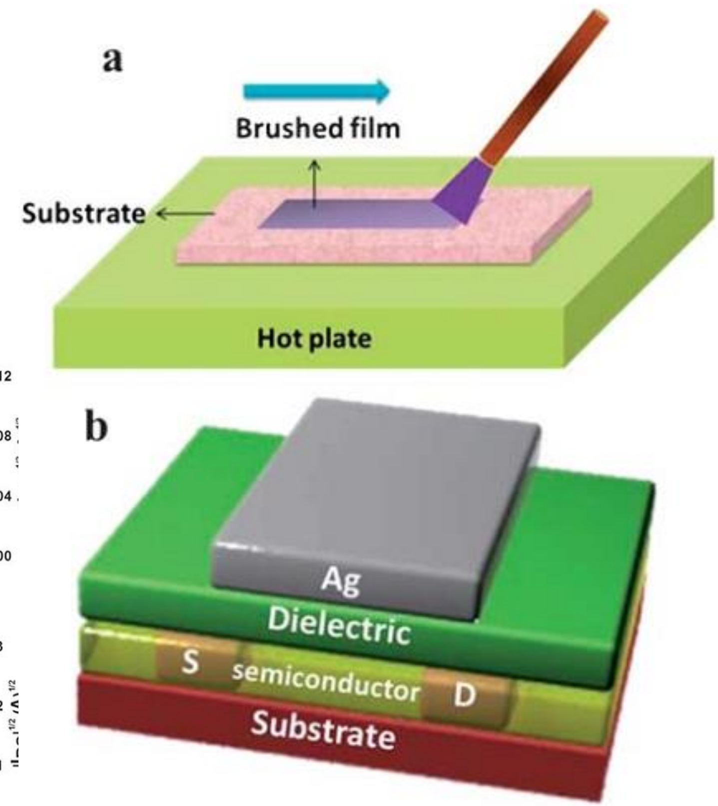
J. Am. Chem. Soc.2013, 135, 14896–14899

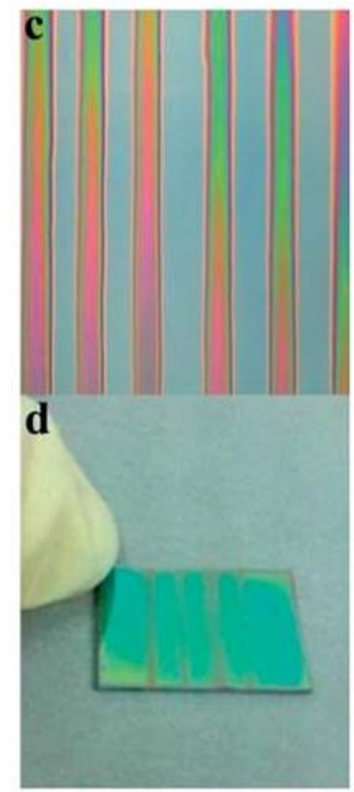


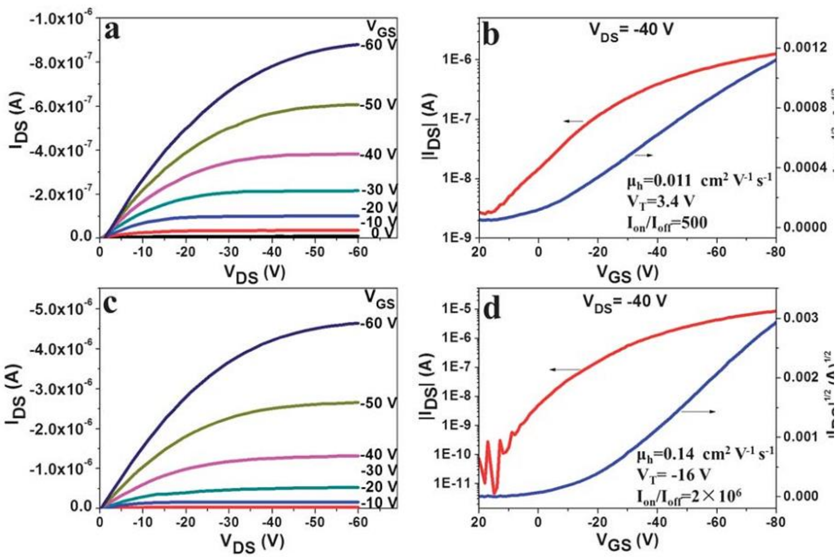
Paint your own!





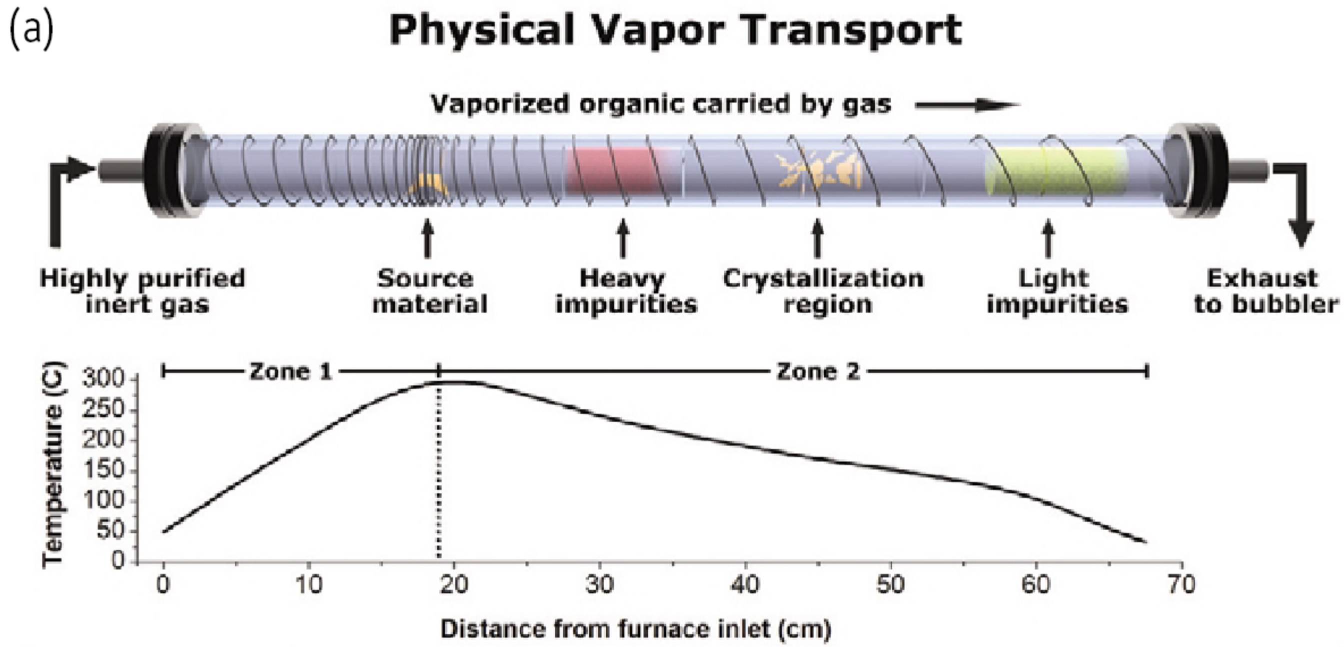


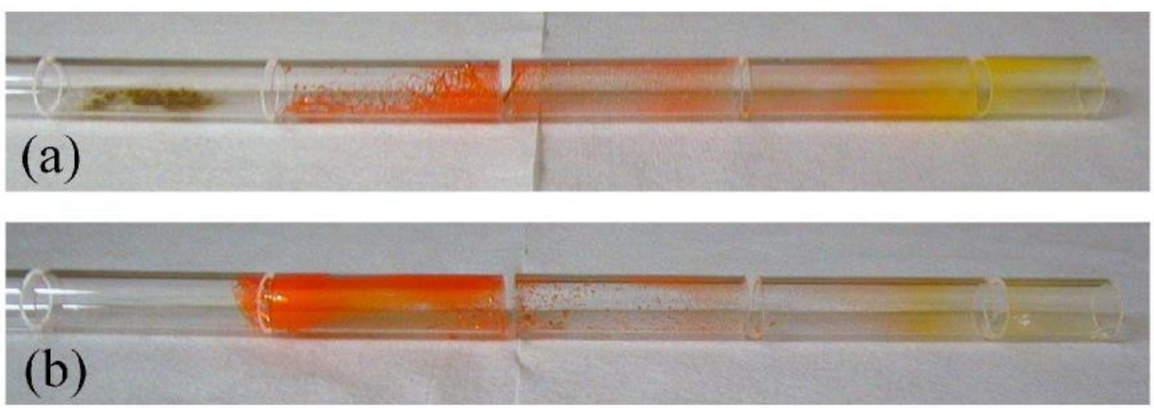




J. Mater. Chem. C, 2013, 1,3072

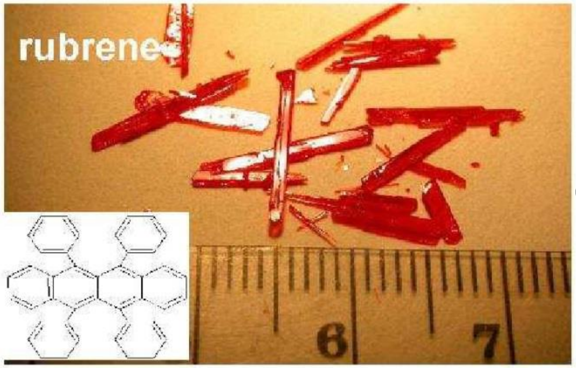
Single Crystal FET(1)

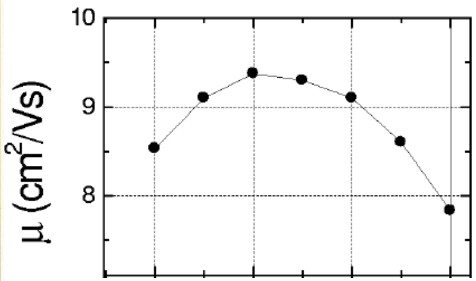


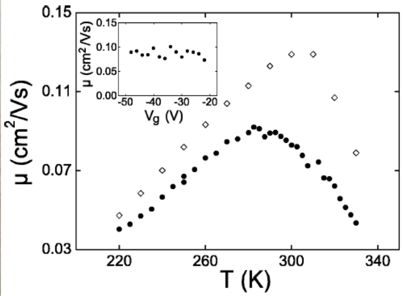


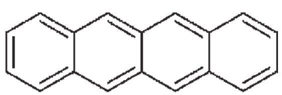
deBoer, *Physica Status Solidi (A)* 201, 2004 p 1302-1331, Bao Mat.Today 10 2007 20

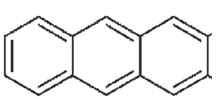
Single Crystal FET(2)

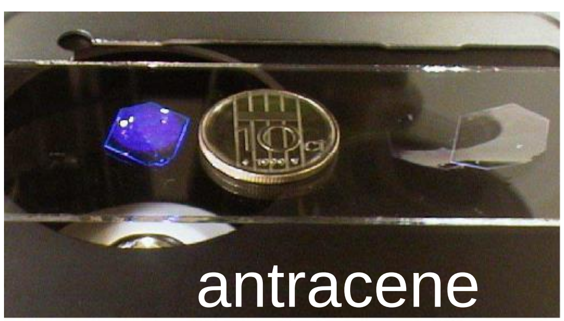


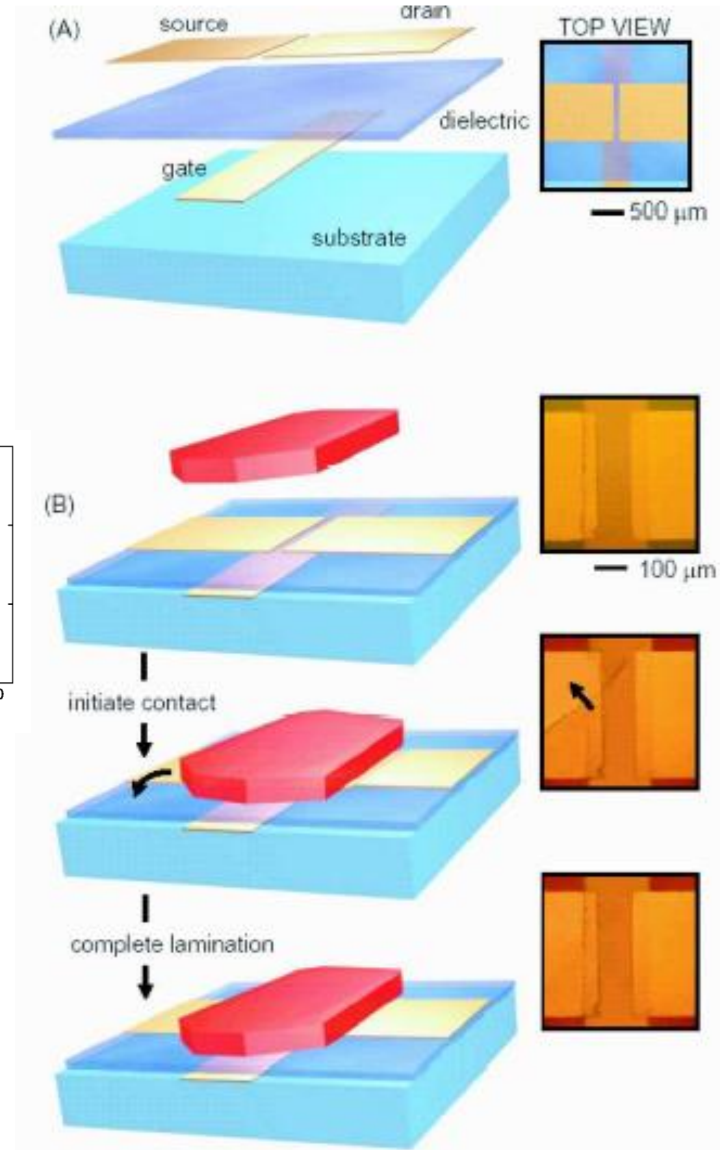




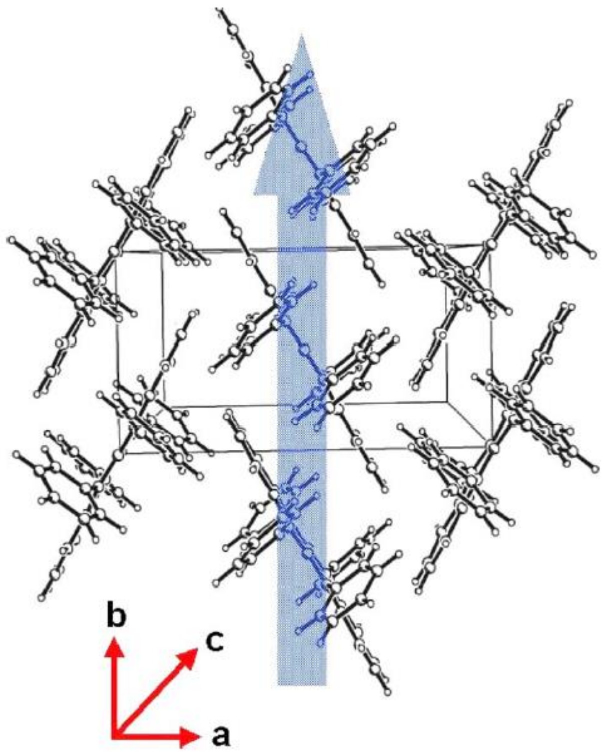


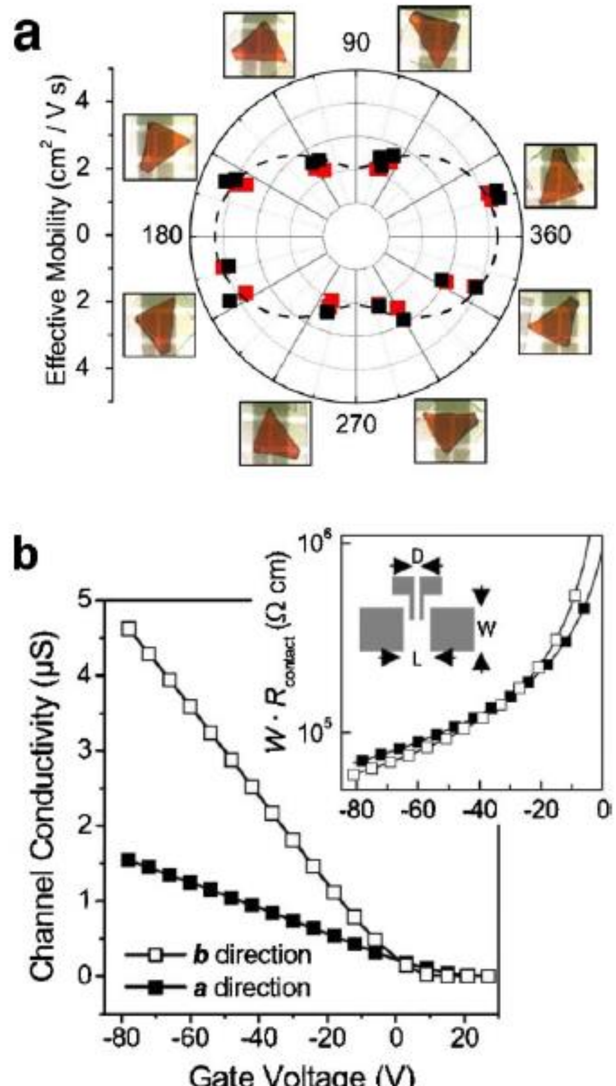






Single Crystal FET(3)

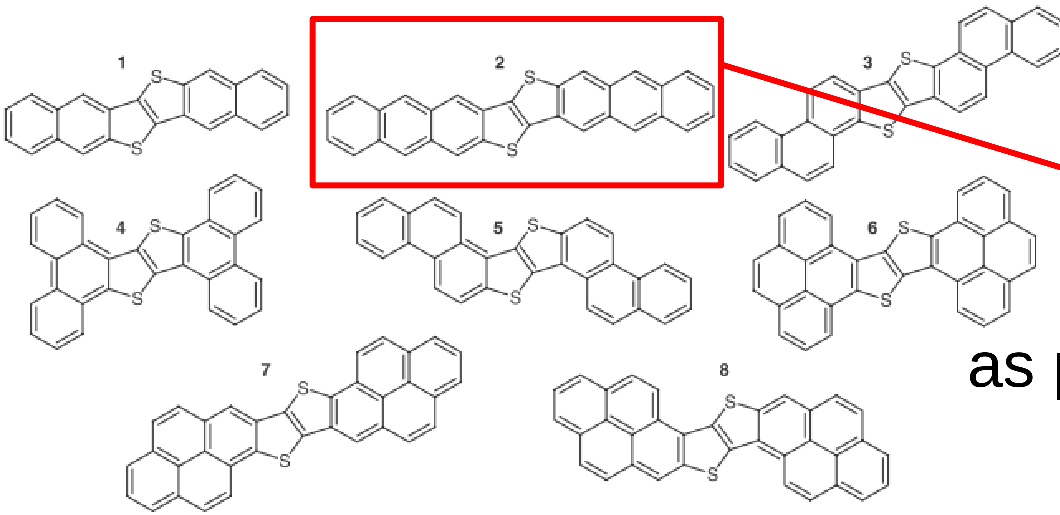




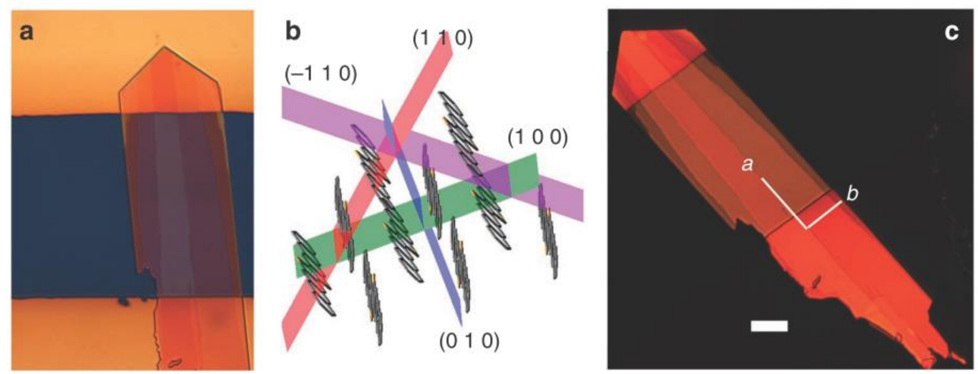
Transport anisotropy

Morpurgo Rev. Mod.Phys 78 2006 973

Record: 12.3 cm^2/Vs

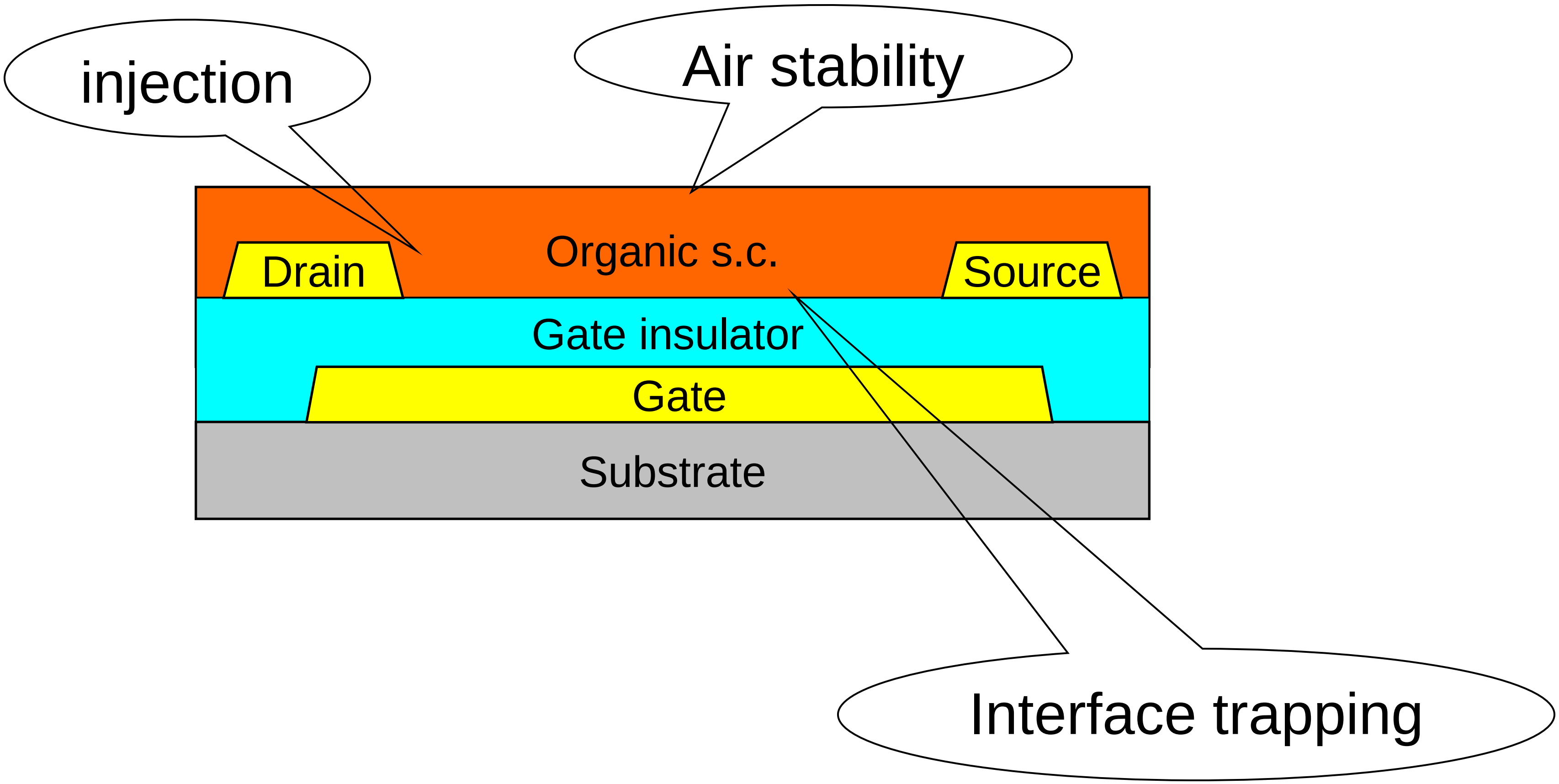


The best one
as predicted by **computation**!



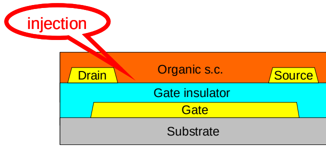
Bao Nature Communications | 2:437 | DoI:10.1038/ncomms1451

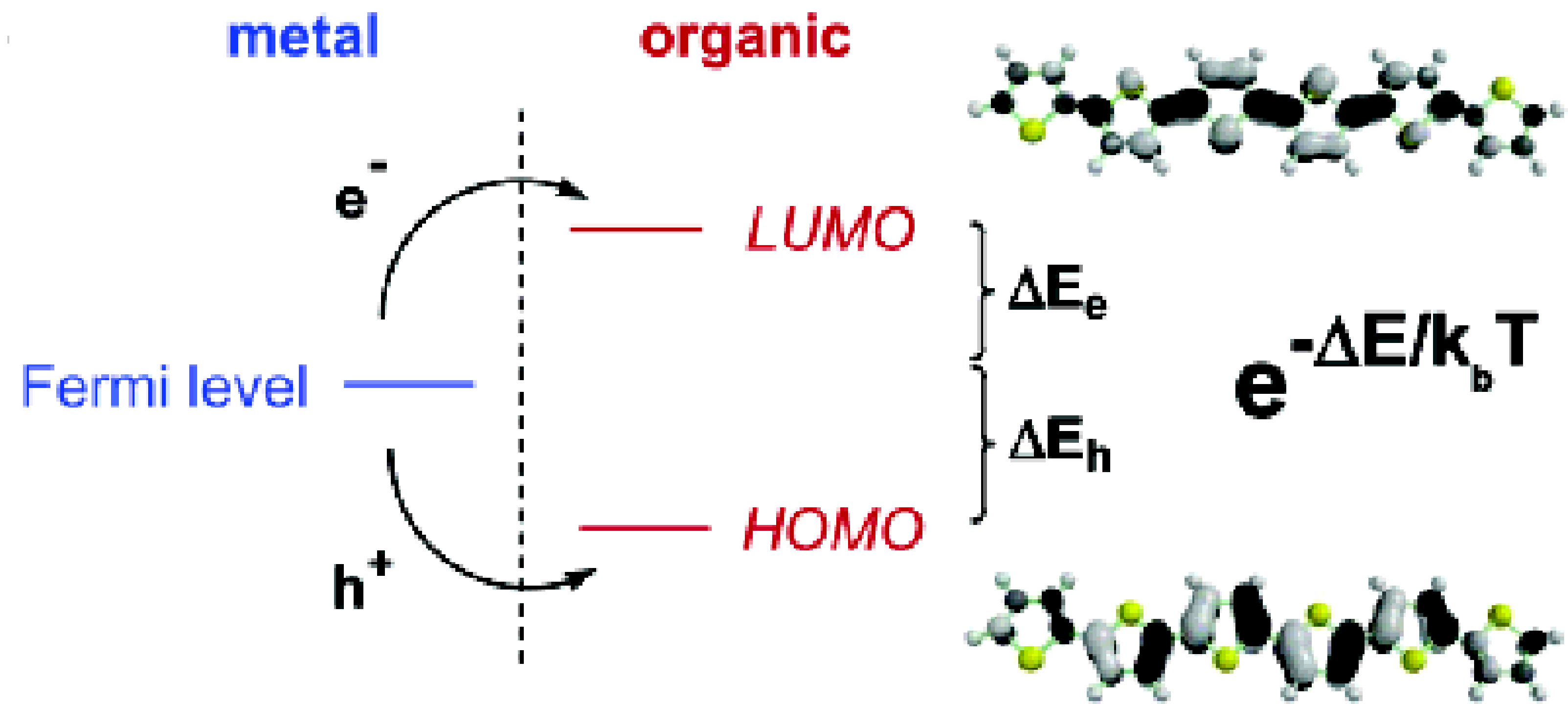
N-type semiconductors



Facchetti J.Am.Chem.Soc. 2004 *126*(42); 13859-13874

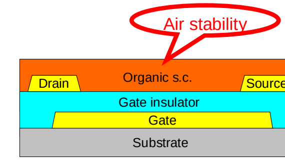
N-type semiconductors

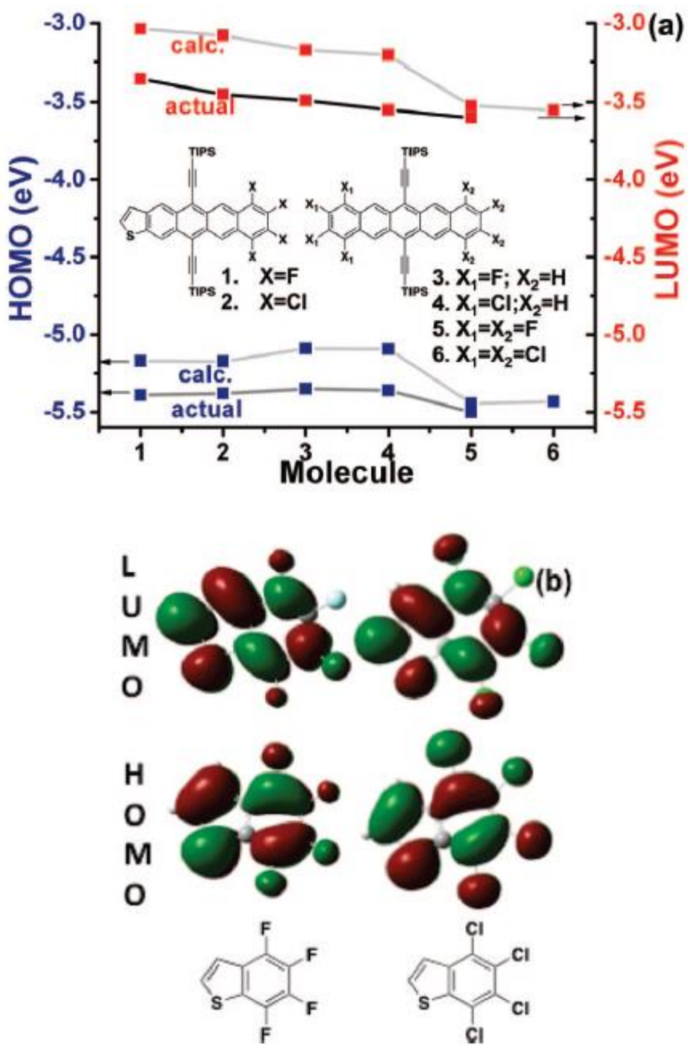


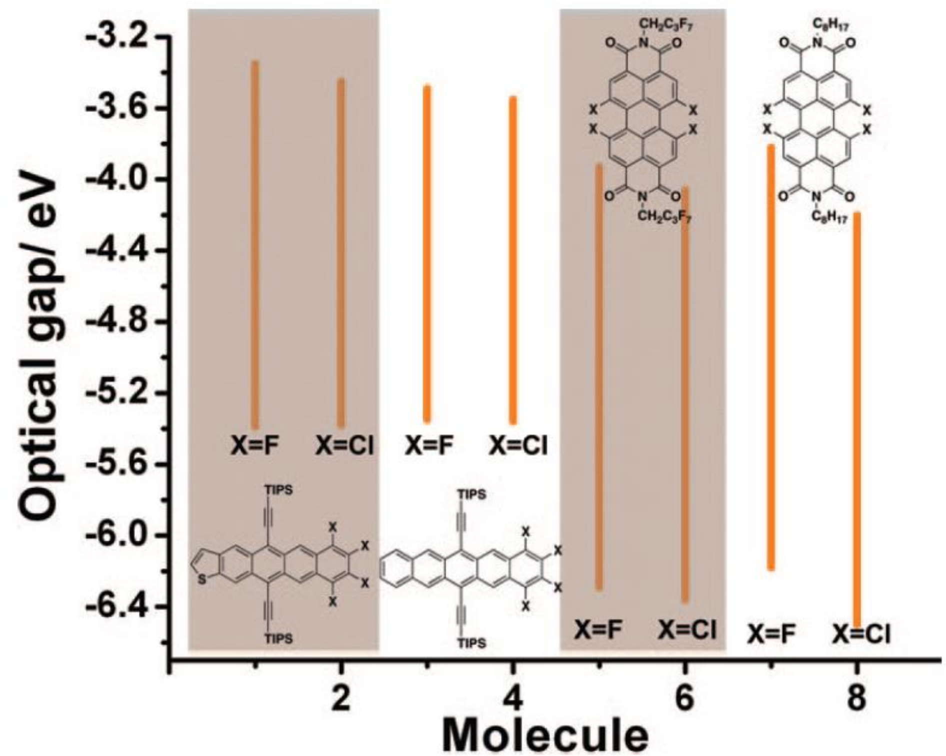


Facchetti J.Am.Chem.Soc. 2004 *126*(42); 13859-13874

Chlorination:
a Route toward Electron Transport

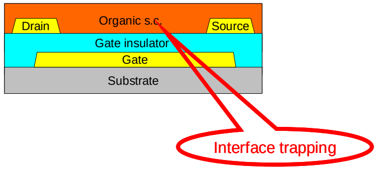


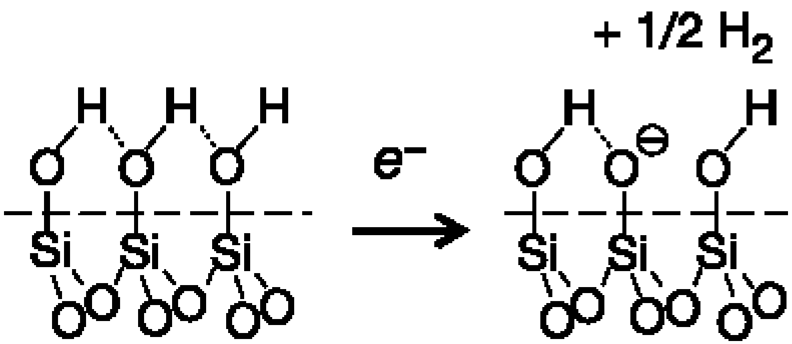




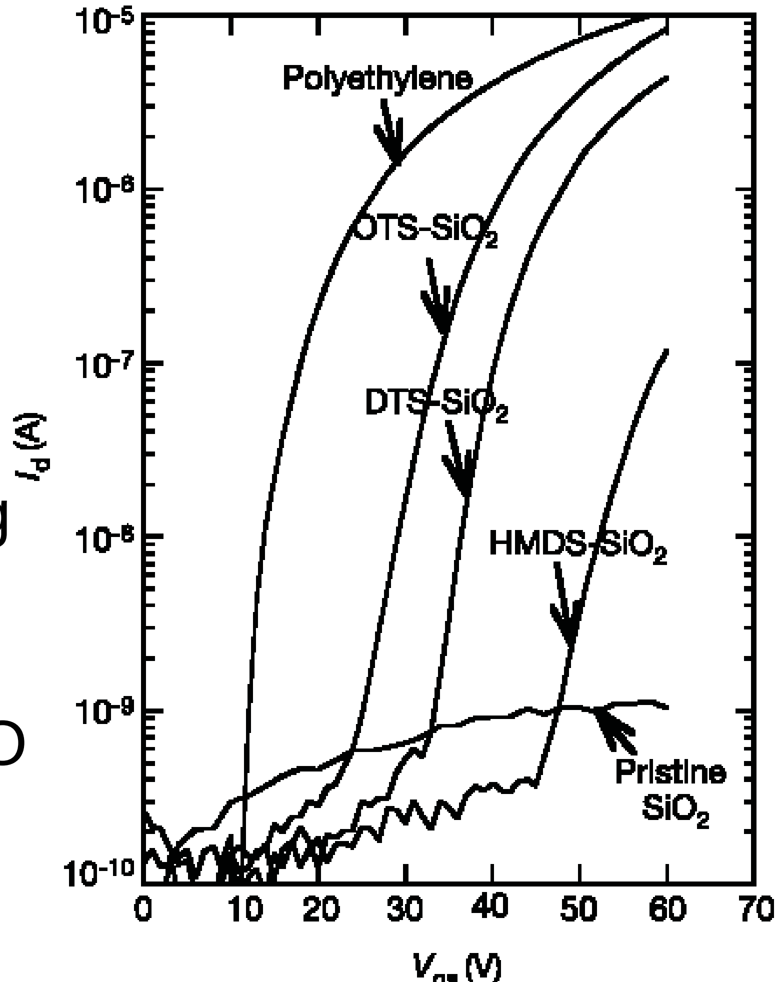
Bao J. Am. Chem. Soc., **2009**, 131 (10), 3733-3740

N-type: role of dielectrics

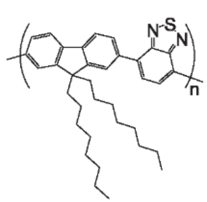




Interfacial electron trapping at SiOH silanol groups
Quenching *n-activity* for not enough low lying LUMO
(LUMO<-3.85eV)

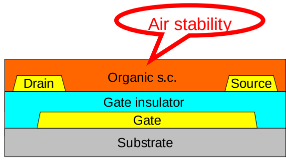


progressively Shorter alkyl chain



Chua NATURE 434 2005 194

Air stability



THEORY

vacuum

-3.74eV H2O oxidation

$2H_20 + 2e^- = H_2 + 20H^-$

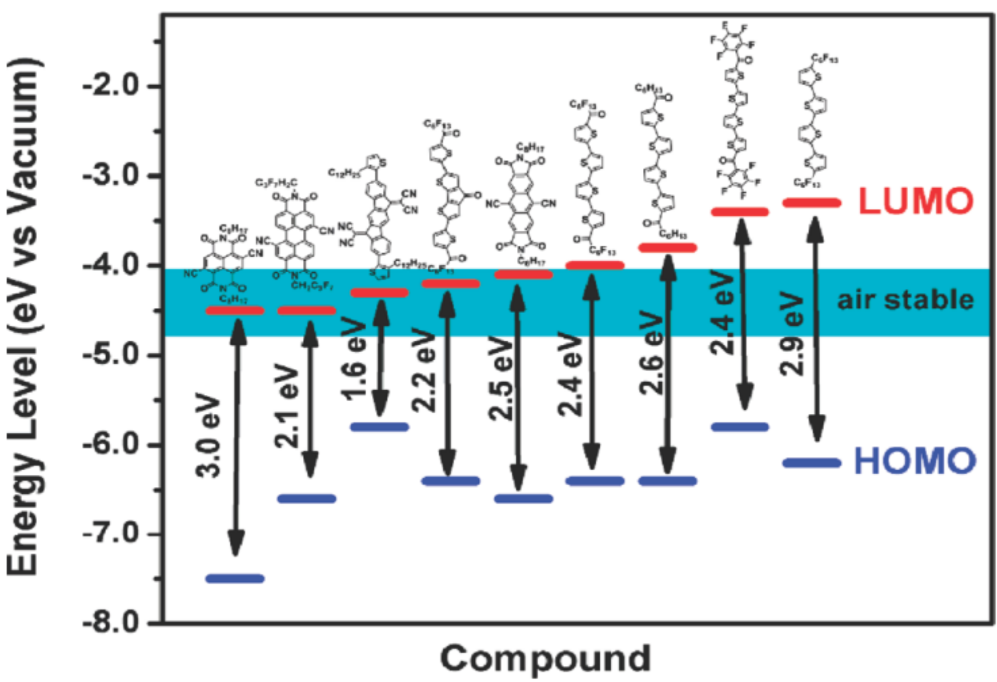
-4.97eV O2 oxidation

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Safe operating LUMO area(?!?)

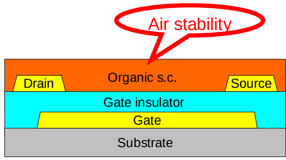
De Leuuw Synthetic Metals 87 (1997) 53-59

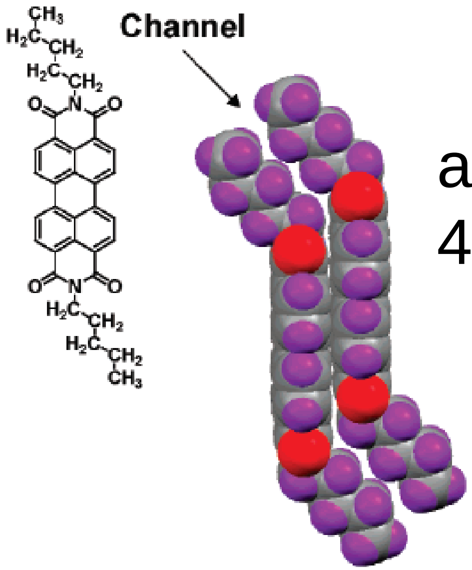
PRACTICE



Facchetti Vol. 44, No. 7 ' 2011 ' 501–510 '
ACCOUNTS OF CHEMICAL RESEARCH

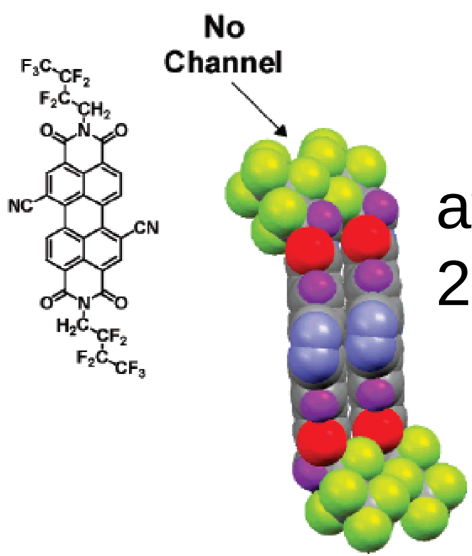
Air stability:barriers





available spacing
4 Å

a steric barrier to atmospheric penetration created by the densely packed Fluorinated groups



available spacing
2 Å

Facchetti J. Am. Chem. Soc., **2007**, 129 (49), 15259-15278\

Ntype status

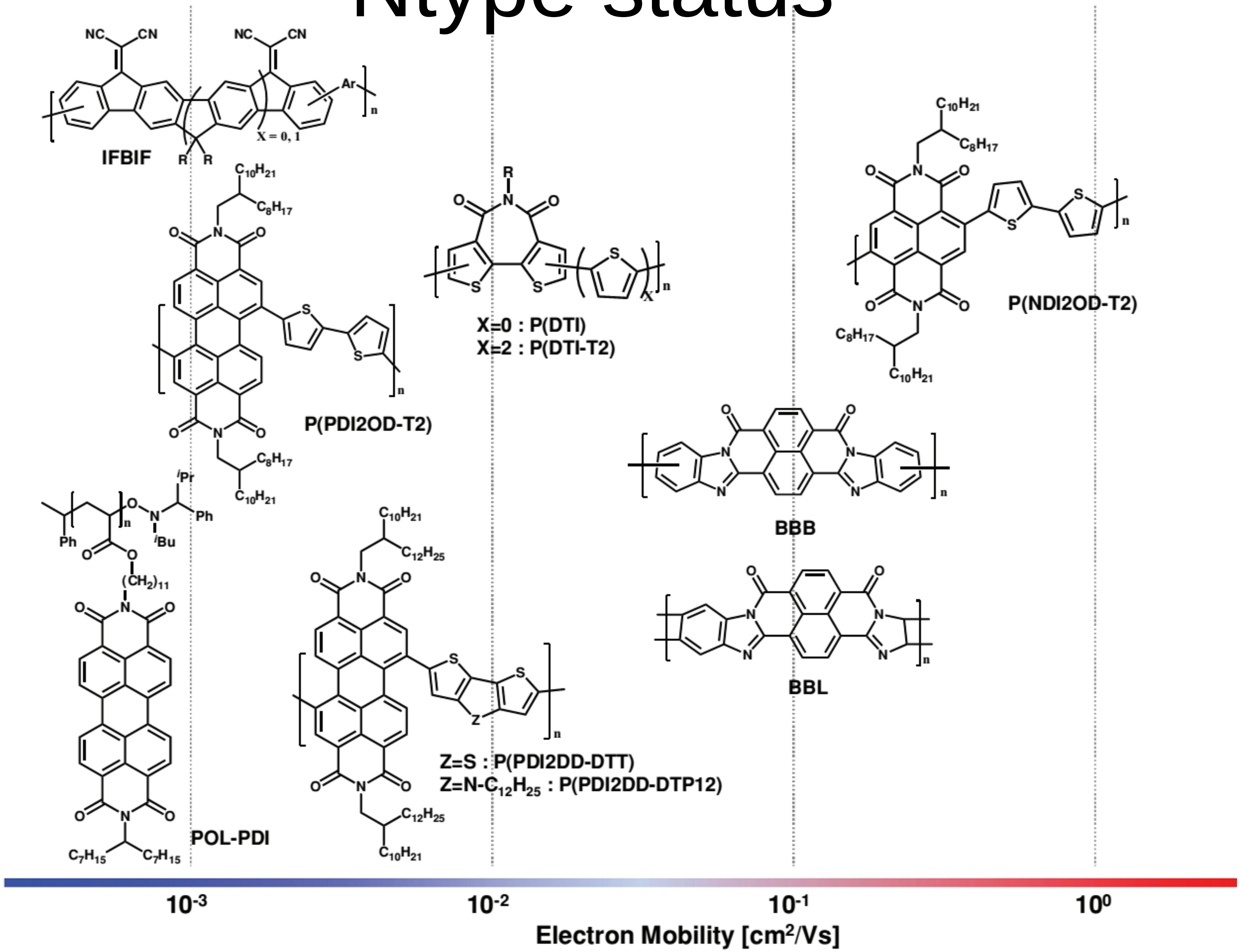
TABLE 1. Summary of the Field-Effect Mobilities (μ), Threshold Voltages (V_T), Current I_{on}/I_{off} ratios, Electrochemical Reduction Potentials (E_{red-1}), and OFET Device Structure/Film-Deposition Method for *n*-Channel Semiconductors

semiconductor	E_{red-1}(V)	μ ($cm^2/V\ s$)[a]	I_{on}/I_{off}	V_T (V)	device structure (deposition technique)[b]	ref
DFH4T	−1.53	0.24 (vacuum)	10^8	20−30	BG-TC (vacum dep.)	27
DFHCO-4T	−0.88	0.32−0.6 (vacuum)	10^5	38	BG-TC (vacum dep.)	33
		1.7 (vacuum)	10^9	24	BG-TC (SiO_2/PS dielectric, vacum dep.)	34
DHCO-4T	−1.06	0.12 (e^-, vacuum)	10^7	35	BG-TC (vacum dep.)	33
		0.01 (h^+, vacuum)	10^7	−54		
		0.67 (e^-, vacuum)	10^7	50	BG-TC (SiO_2/PS dielectric, vacum dep.)	34
		0.002 (h^+, vacuum)	10^3	−60 to −70		
DFHCO-4TCO	−0.65	0.08 (vacuum)	10^7	9	BG-TC (vacum dep.)	33
		0.005−0.01 (air)	10^5−10^6	10−20		
FTTTTF	−1.51	0.43 (vacuum)	10^8	30−40	BG-TC (vacum dep.)	34
DFO-PTTP	NA	0.03−0.07 (vacuum)	10^6−10^7	50−55	BG-TC (vacum dep.)	30
DFCO-4T	−1.05	0.45 (vacuum)	10^8	30	BG-TC (vacum dep.)	35
		0.21 (vacuum)	10^5	50−70	BG-TC (solution dep.)	
DFCO-TQT	−0.45	0.02 (air)	10^5 −10^6	25−30	BG-TC (vacum dep.)	35
NDI-8CN2	+0.08	0.15 (vacuum)	10^3	−37	BG-TC (vacum dep.)	40
		0.11 (air)	10^3	−55		
ADI-8CN2	−0.33	0.03 (vacuum)	10^6−10^7	10	BG-TC (vacum dep.)	41
		0.01 (air)	10^6−10^7	15		
PDI-8CN2	−0.06	0.06−0.1 (air)	10^7	0−10	BG-TC (vacum dep.)	40
		0.01−0.06 (air)	10^5−10^7	0−10	BG-TC (solution dep.)	
PDI-FCN2	+0.04	0.64 (air)	10^4	−20 to −30	BG-TC (vacum dep.)	40
NDI-T	−0.65	0.35 (vacuum)	10^6	28	BG-TC (vacum dep.)	47
		0.10 (air)	10^7	50		
TPDM	−0.53	0.02 (vacuum)	10^6	20	BG-TC (vacuum dep.)	52
TIFDMT	−0.12	0.16 (air)	10^7−10^8	0−5	BG-TC (solution dep.)	49
TTIFDMTT	−0.20	0.001 (e^-, air)	10^5	20	BG-TC (solution dep.)	52
		10^{-4} (h^+, air)	10^5	−25		
P(BTI)	−1.11	0.01 (vacuum)	10^7	75	BG-TC (solution dep.)	57
P(IFDMT4)	−0.29	2×10^{-4} (e^-, air)	10^4	5 (e^-)	BG-TC (solution dep.)	52
		2×10^{-4} (h^+, air)	10^4	−10 (h^+)		
P(NDI2ODT2)	−0.49	0.01−0.08 (air)	10^6−10^7	−20	BG-TC (solution dep.)	59
		0.45−0.85 (air)	10^6−10^8	0−5	TG-BC (solution dep.)	60

[a]Vacuum, measured in a vacuum probe station; air, measured in air. [b]BG-TC, bottom-gate/top-contact; TG-BC, top-gate/bottom-contact; PS, polystyrene.

Facchetti Vol. 44, No. 7 ’ 2011 ’ 501–510 ’ ACCOUNTS OF CHEMICAL RESEARCH

Ntype status

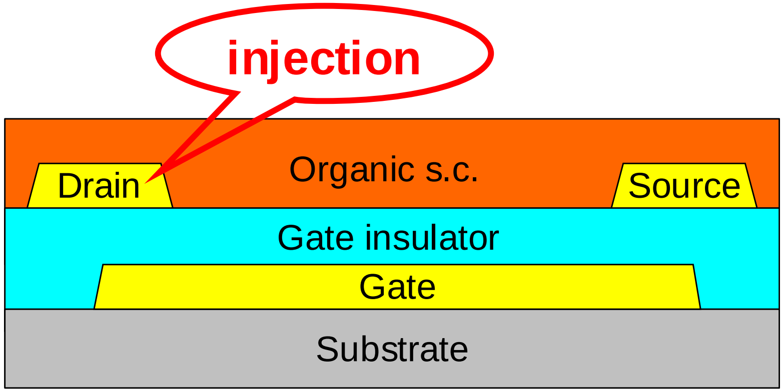


Caironi et al., Adv. Mater. 2013, 25, 4210–4244

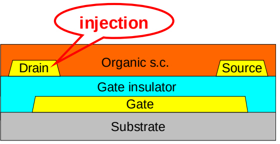
Device issues

- Injection
- Bias stress
- Dielectrics

Contact Resistance

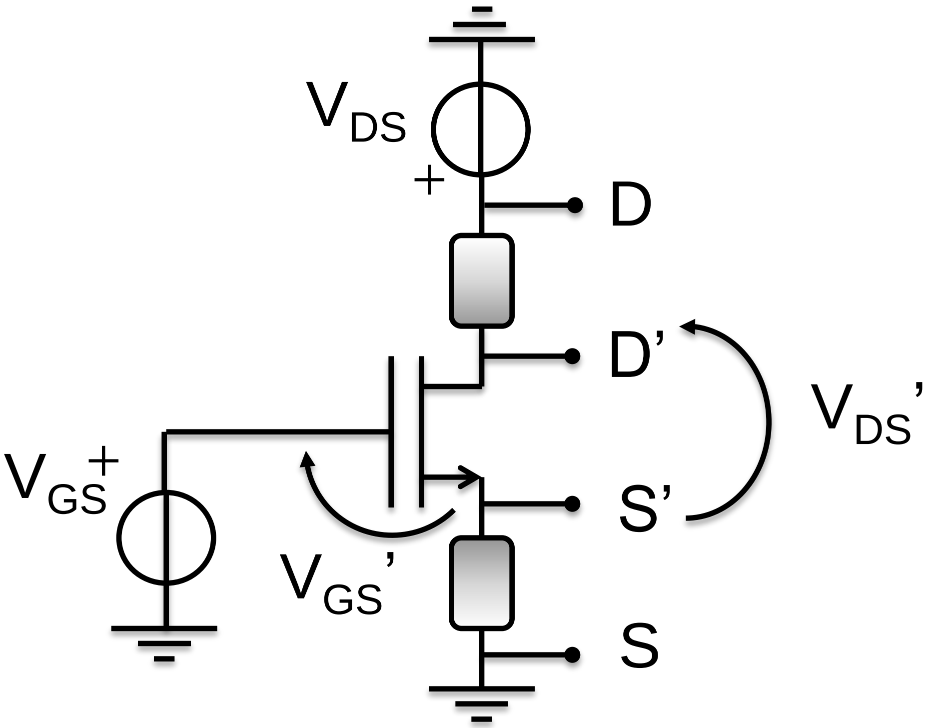


Caironi&Natali, Adv. Mat. 2012 Volume 24, Issue 11, pages 1357–1387



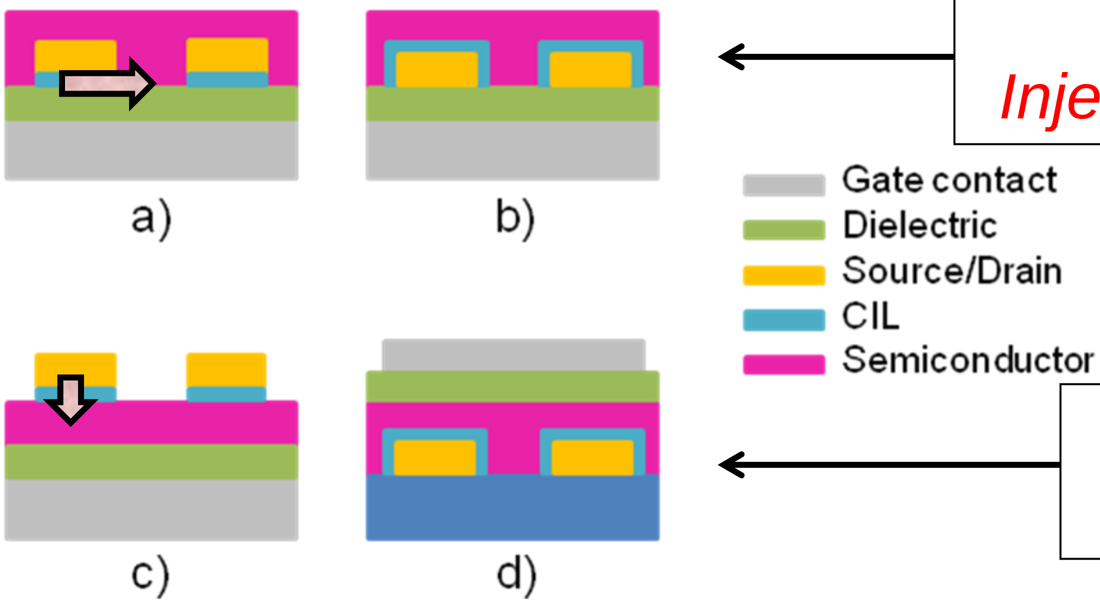
Effect of contact resistances

Only a fraction of applied voltages drop on the actual channel!



- Less current flows!
- Downscaling less effective
- Mobility is *apparent* and *L-dependent*

Contact resistance & topology

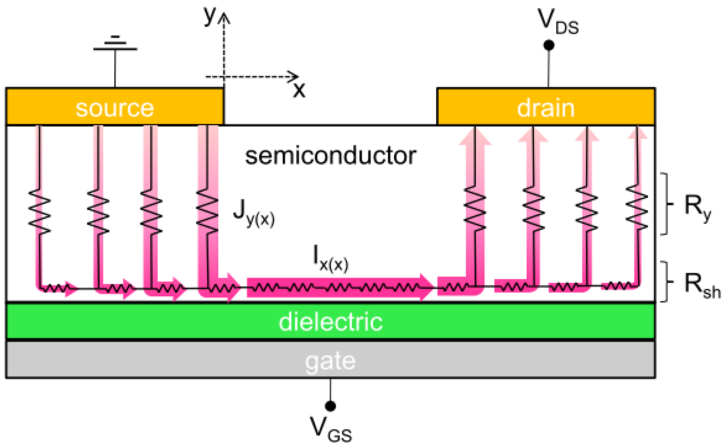


Coplanar
*Injection **into** nm-thick channel*

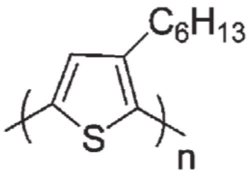
Staggered
*injection **onto** the channel*

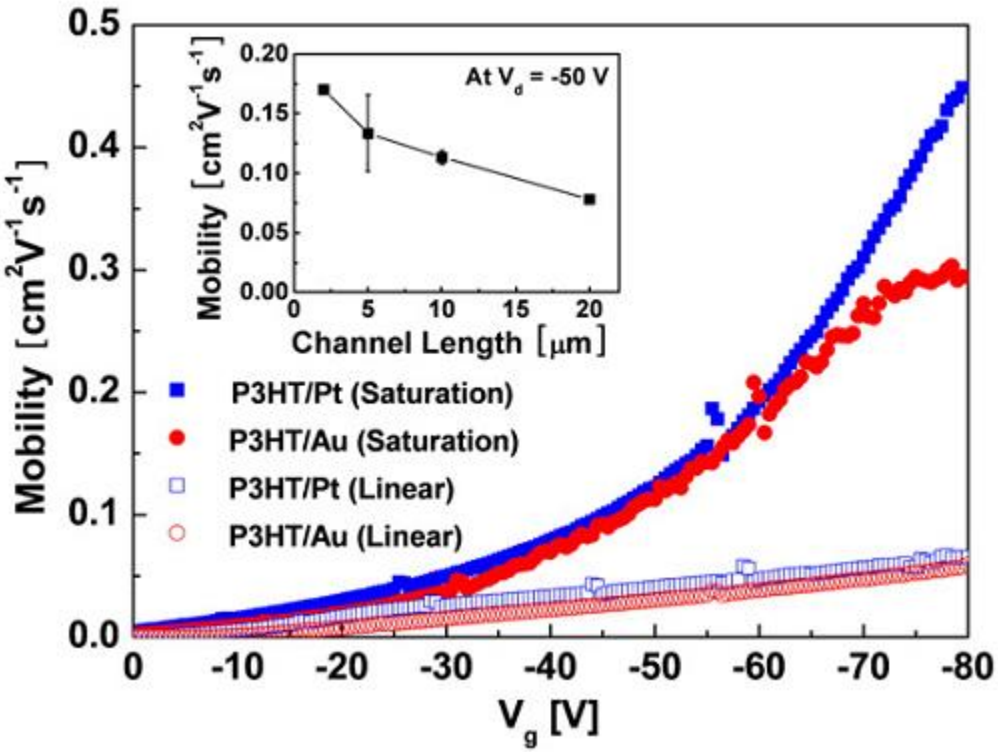
$$R_S = [\sqrt{R_y \times R_{sh}(V_{GS})}]$$

R_{sh} *channel sheet resistance*= $[\mu C_{ox}(V_{GS} - V_T)]^{-1}$



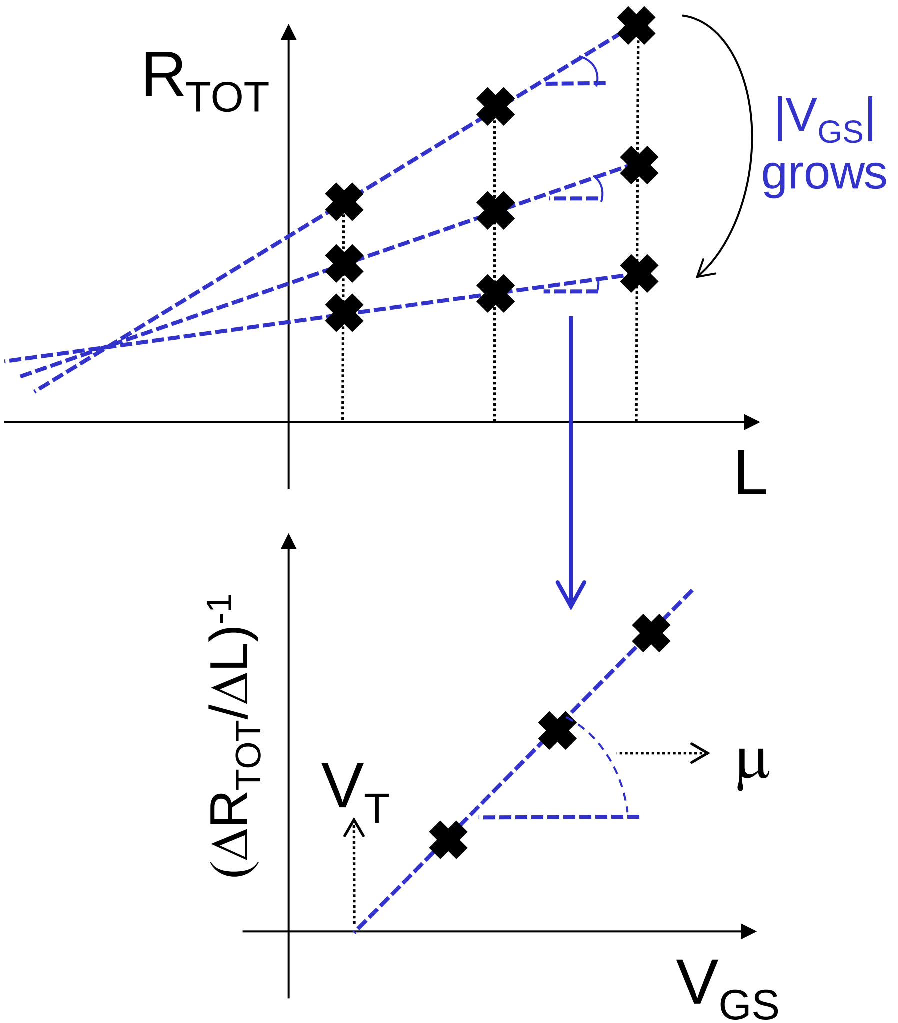
Contact resistance & S/D material



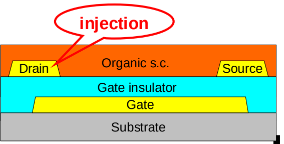


K.-J. Baeg et al. / Thin Solid Films 518 (2010) 4024–4029

Transfer line method



Highly susceptible to sample-to-sample variation!!!



Differential method

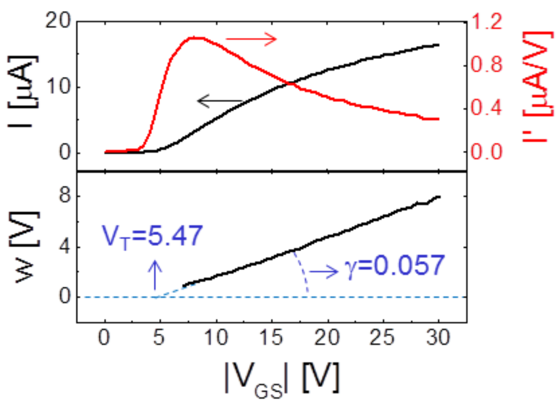
philosophy: decrease the problem complexity

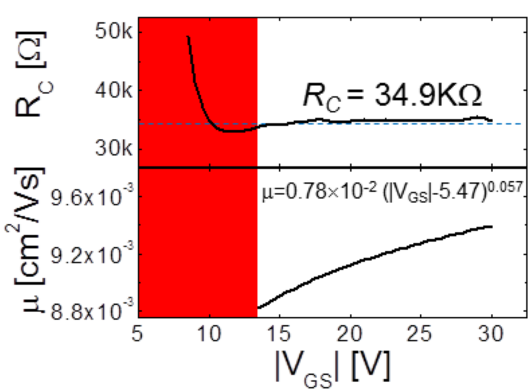
- Current equation: $$I_D = \frac{k V_D (V_G - V_{th})^{\gamma+1}}{1 + k R_{DS} (V_G - V_{th})^{\gamma+1}}$$
- Definition: $$z = \frac{I_D^2}{\mathrm{d}I_D / \mathrm{d}V_G} \Rightarrow z = \frac{K}{\gamma+1} V_D (V_G - V_T)^{\gamma+2}$$

➢ **Z does not depend on R_{DS} !**

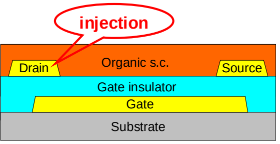
- Definition: $$w = \frac{\int_{Vth}^{V_G} z \mathrm{d}V_G}{z} \approx \frac{\int_{0}^{V_G} z \mathrm{d}V_G}{z} = \frac{1}{\gamma+3}(V_G - V_{th})$$

➢ **Linear in V_G and dependent only on γ and V_{th} !**

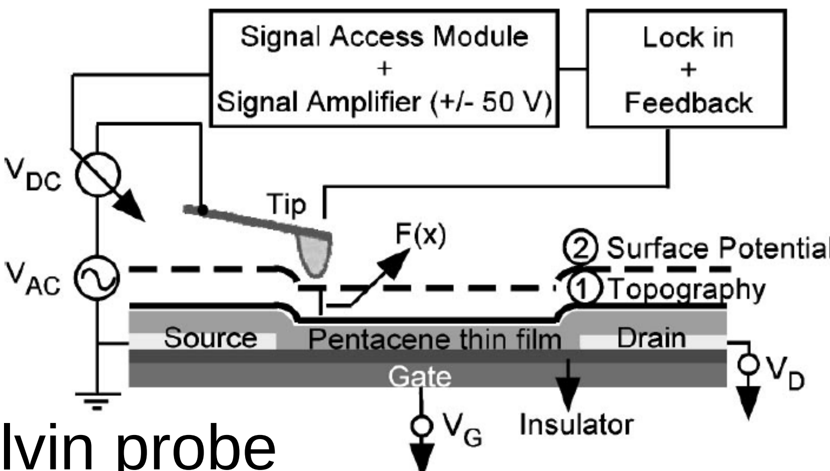




M. Sampietro et al, J. Appl. Phys., Vol. **101**, 2007

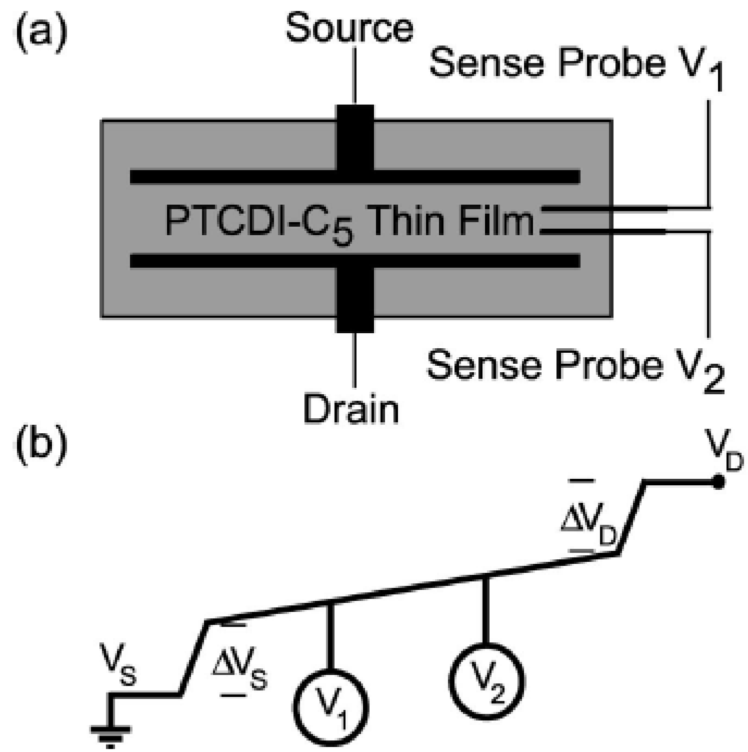


Other methods



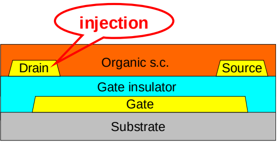
Kelvin probe

Puntambekar APPL.PHY.LETT. 83 2003 5539

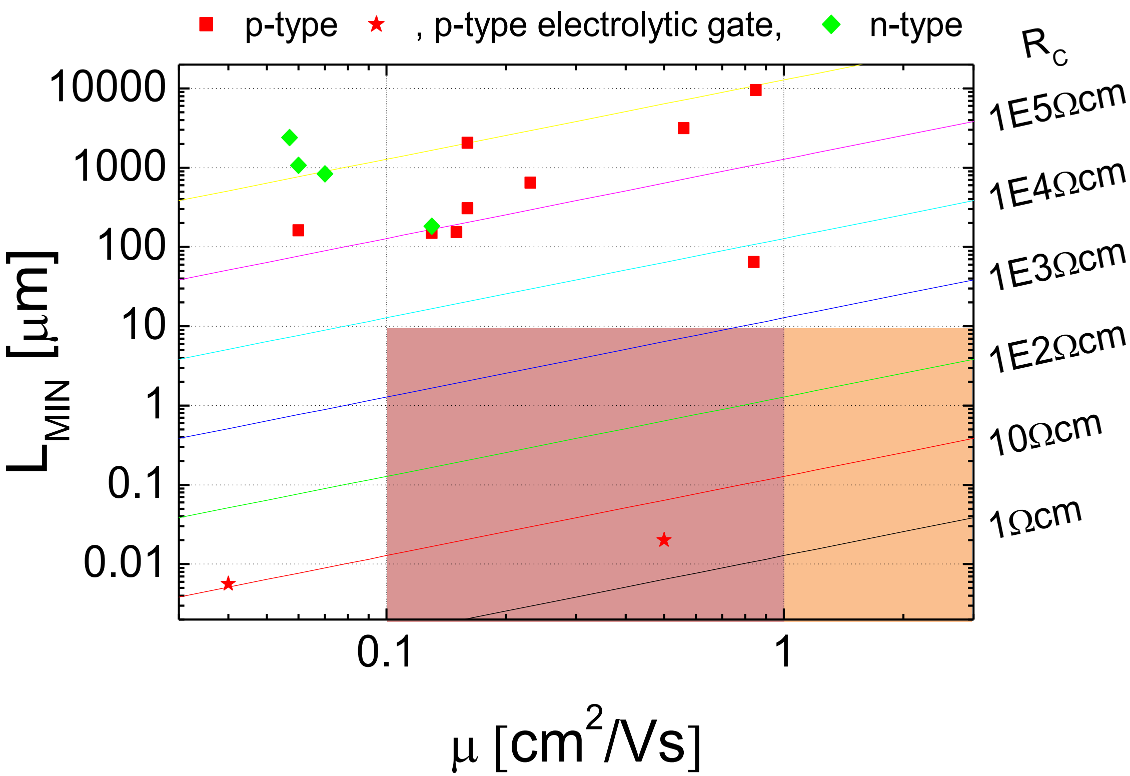


4-point-probe

Chesterfield J.APPL.PHYS. 95 2004 6396

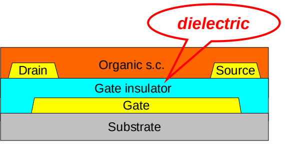


Contact resistance & downscaling: current status

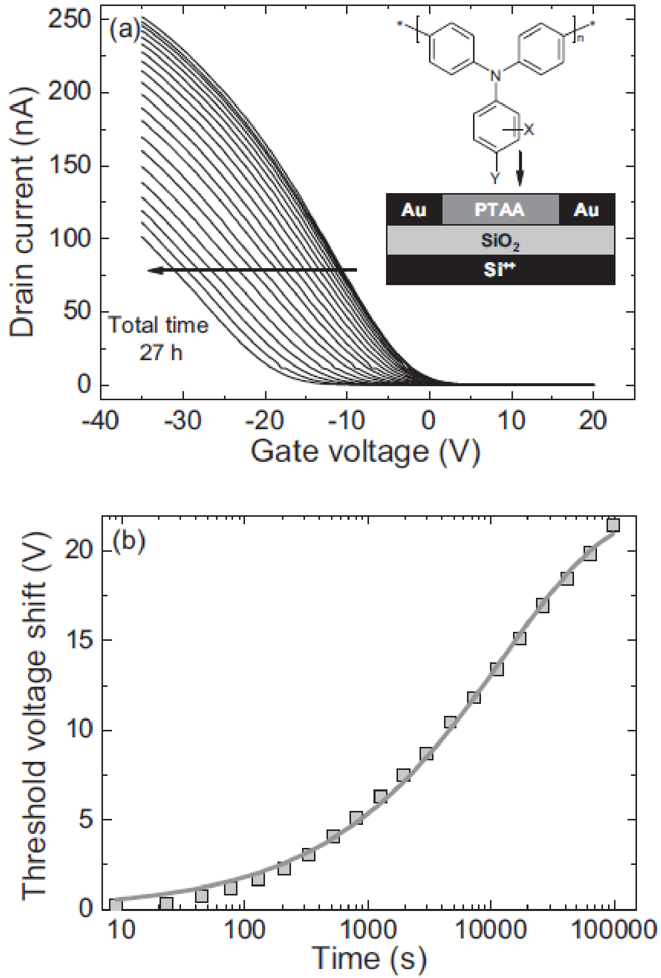


L_{MIN} is the channel length experiencing an halving in the current due to contact resistances for a given technology (μ, Rc)

Caironi&Natali, Adv. Mat. 2012 Volume 24, Issue 11, pages 1357–1387



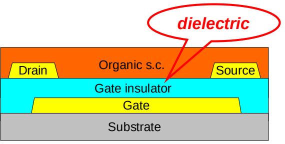
Bias stress



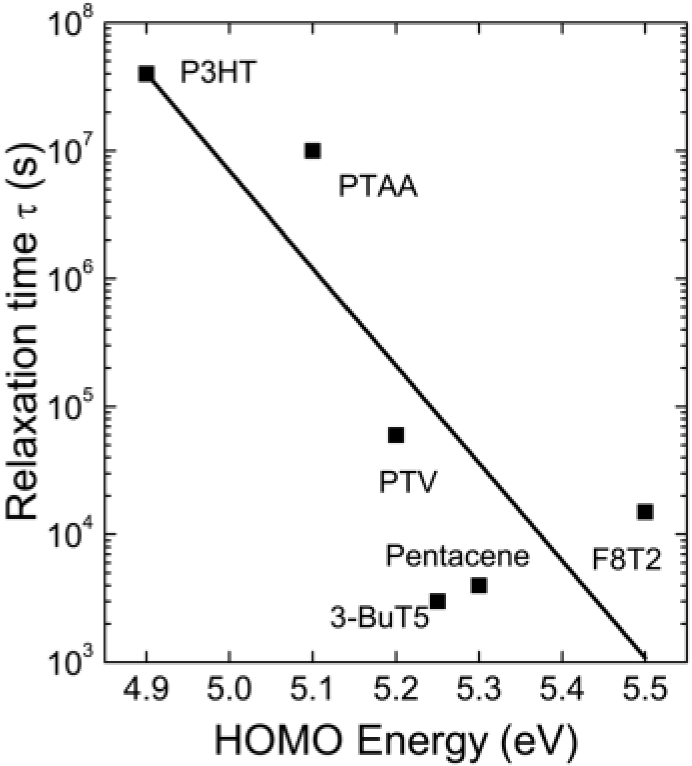
V_T shift!

Charge trapping

de Leeuw Adv. Mater. **2008**, 20, 975–979



Bias stress



$$\Delta V_{\mathrm{th}}(t) = (V_{\mathrm{G}} - V_{\mathrm{th},0})(1 - \exp[-(t/\tau)^{\beta}]),$$

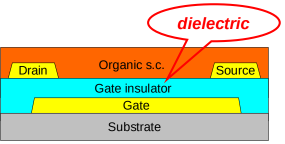
$$\tau = \tau_0 \exp\left(\frac{\epsilon_a}{k_B T}\right)$$

Semiconductor	τ_0 [s]	ϵ_a [eV]	τ ($T = 25\,^\circ$C) [s]
P3HT	3×10^{-3}	0.6 ± 0.1	4×10^{7}
PTAA	8×10^{-4}	0.6 ± 0.1	1×10^{7}
PTV	2×10^{-6}	0.62	6×10^{4}
3-BuT5	3×10^{-7}	0.6 ± 0.1	3×10^{3}
Pentacene (Single crystal)	2×10^{-8}	0.67	4×10^{3}
F8T2	3×10^{-5}	0.52	1.5×10^{4}

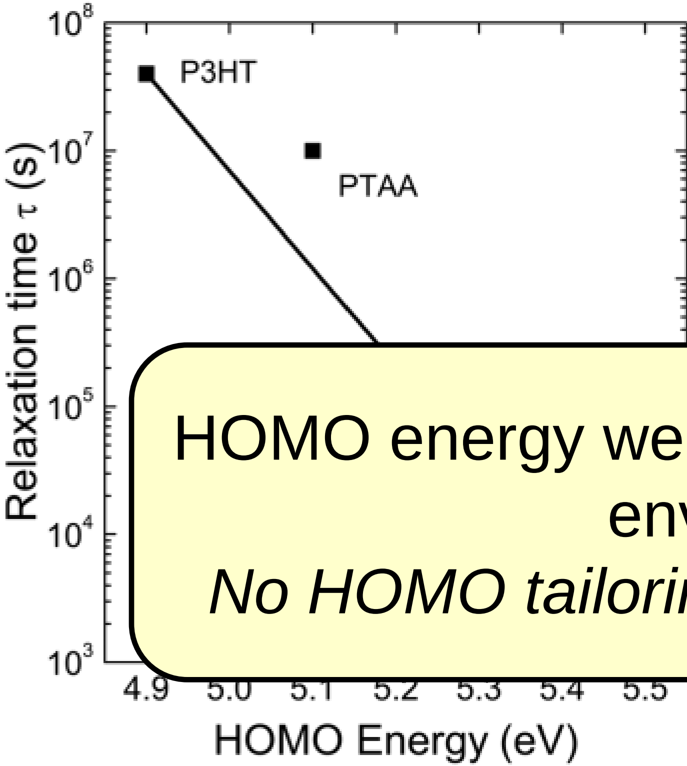
$$\begin{array}{ll} 4H^+ + O_2 + 4e^- \rightleftharpoons 2H_2O & E = 0.57\ \mathrm{V} \\ 4OS^+ + 4e^- \rightleftharpoons 4OS & E = E_{OS} \\ \hline 2H_2O + 4OS^+ \rightleftharpoons 4OS + O_2 + 4H^+. & \end{array} \quad (3)$$

$$\tau \propto \frac{[O_2]^{1/2}}{[H_2O]} \exp\left[-\frac{(\epsilon_{\mathrm{HOMO}} - 4.97\mathrm{eV})}{2k_B T}\right] \exp\left(\frac{\epsilon_d}{k_B T}\right).$$

De Leeuw APPLIED PHYSICS LETTERS 99, 103302 (2011)



Bias stress



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$$\tau = \tau_0 \exp\left(\frac{\epsilon_{\mathrm{a}}}{k_{\mathrm{B}}T}\right)$$

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PTAA	8×10^{-4}	0.6 ± 0.1	1×10^{7}
PTV	2×10^{-6}	0.62	6×10^{4}

HOMO energy well below 5 eV needed, but this implies environmental instability.

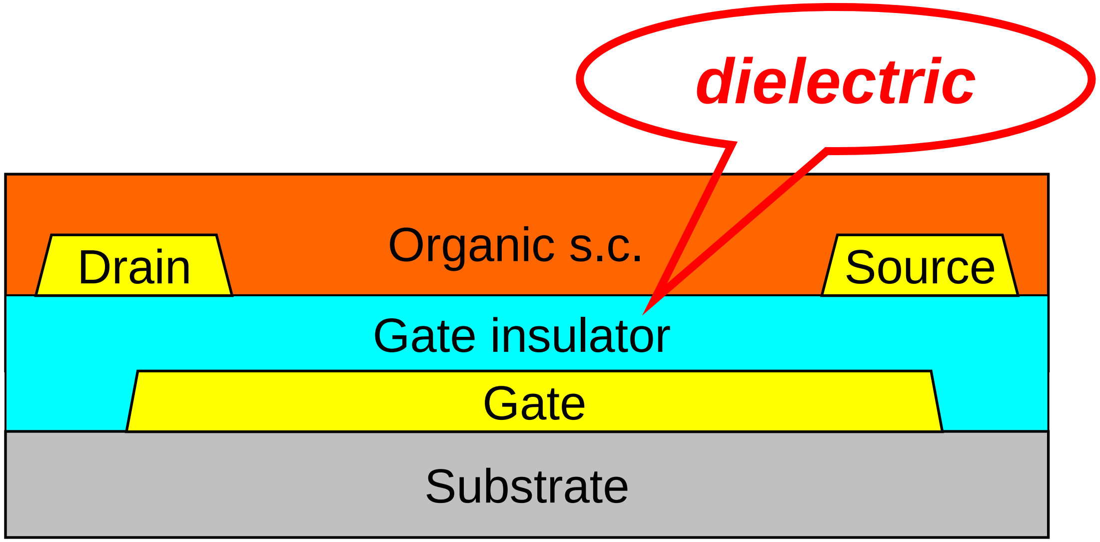
No HOMO tailoring, but water elimination is needed!!

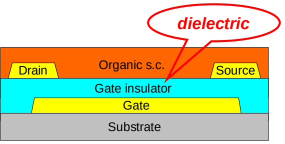
$$\mathrm{OS}^{+} \rightleftharpoons 4\mathrm{OS} + \mathrm{O_2} + 4\mathrm{H}^{+}. \quad (3)$$

$$\tau \propto \frac{[\mathrm{O_2}]^{1/2}}{[\mathrm{H_2O}]} \exp\left[-\frac{(\epsilon_{\mathrm{HOMO}} - 4.97\mathrm{eV})}{2k_{\mathrm{B}}T}\right] \exp\left(\frac{\epsilon_{\mathrm{d}}}{k_{\mathrm{B}}T}\right).$$

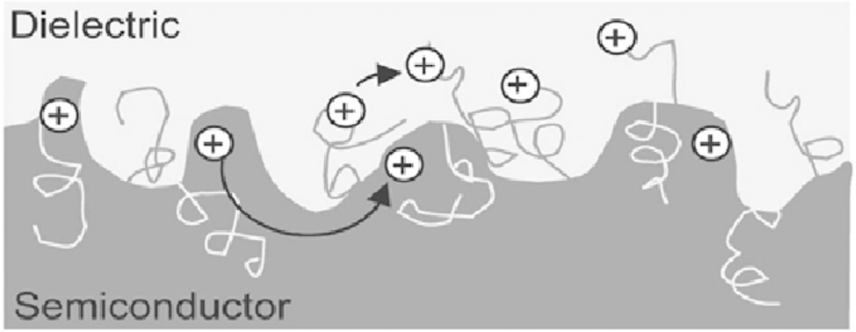
De Leeuw APPLIED PHYSICS LETTERS 99, 103302 (2011)

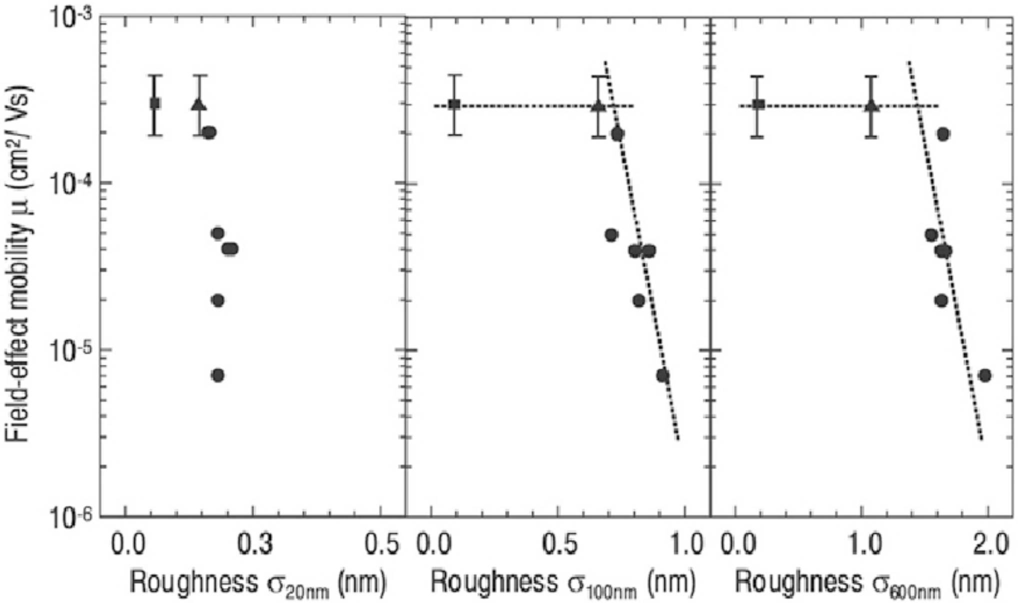
Role of dielectrics





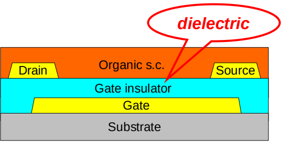
Roughness



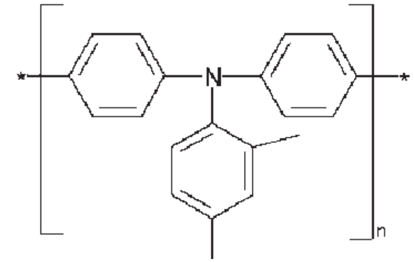


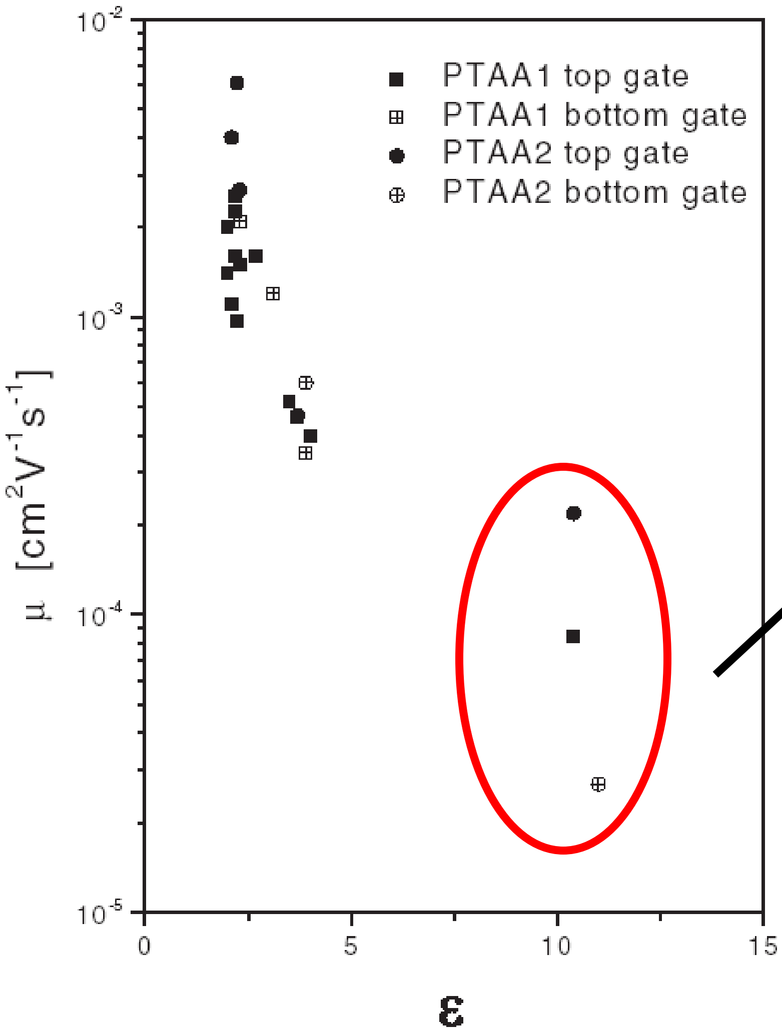
Sirringhaus, Adv.Mat. 2005, 17, 2411-2425

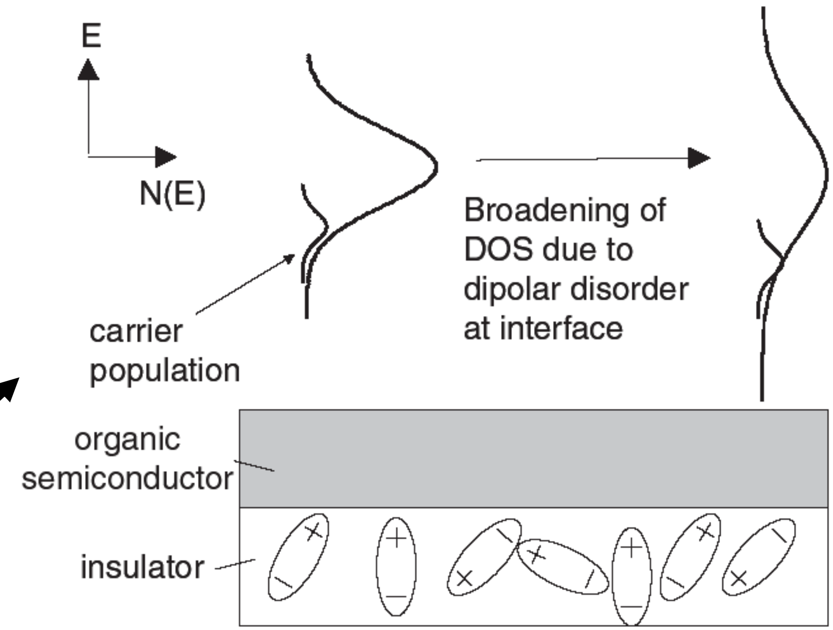
see also Appl. Phys. Lett. 101, 093308 (2012)

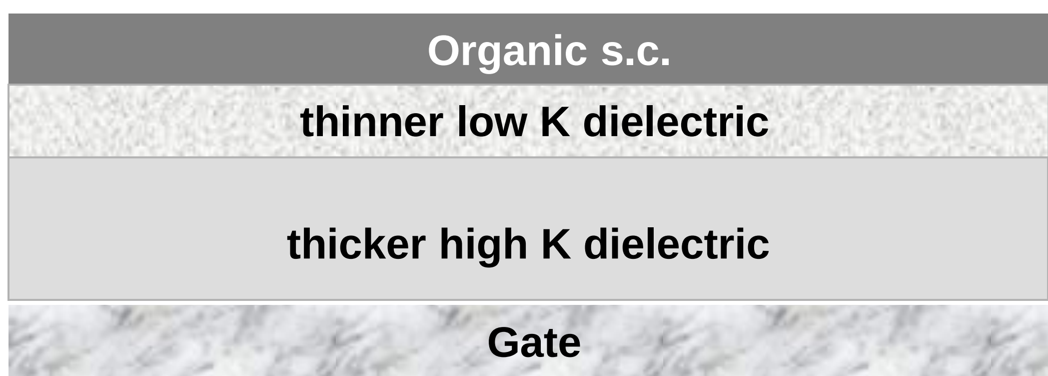


High κ: PTAA

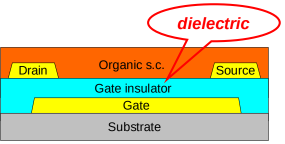




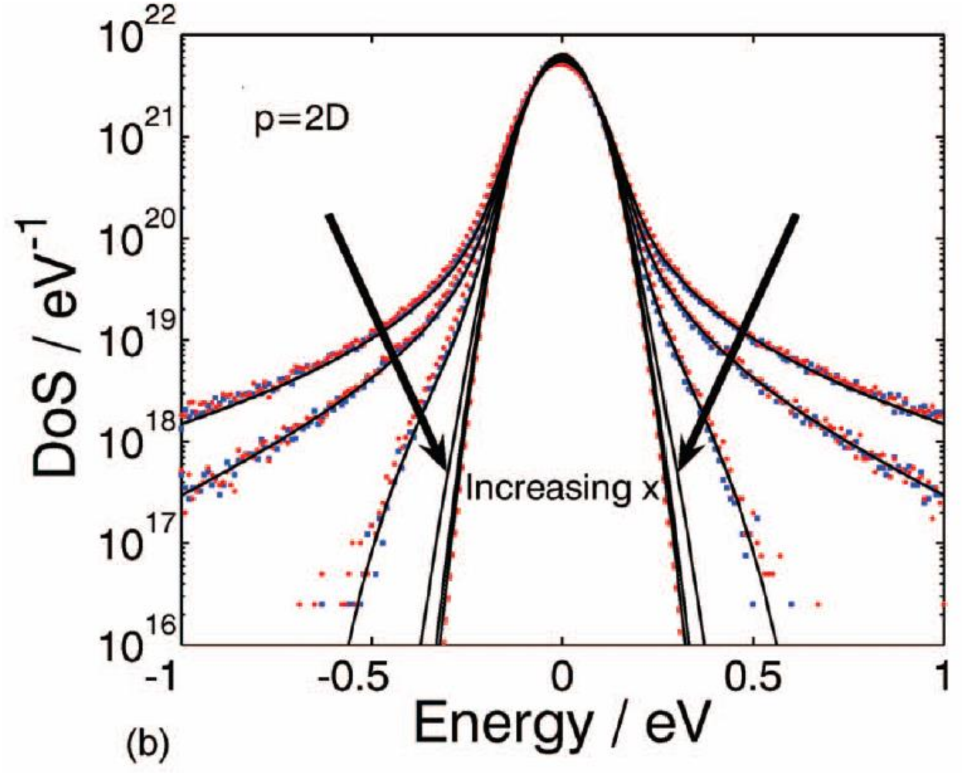




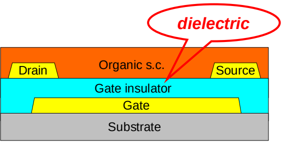
Veres Adv.Funct.Mat 13, 2003 199



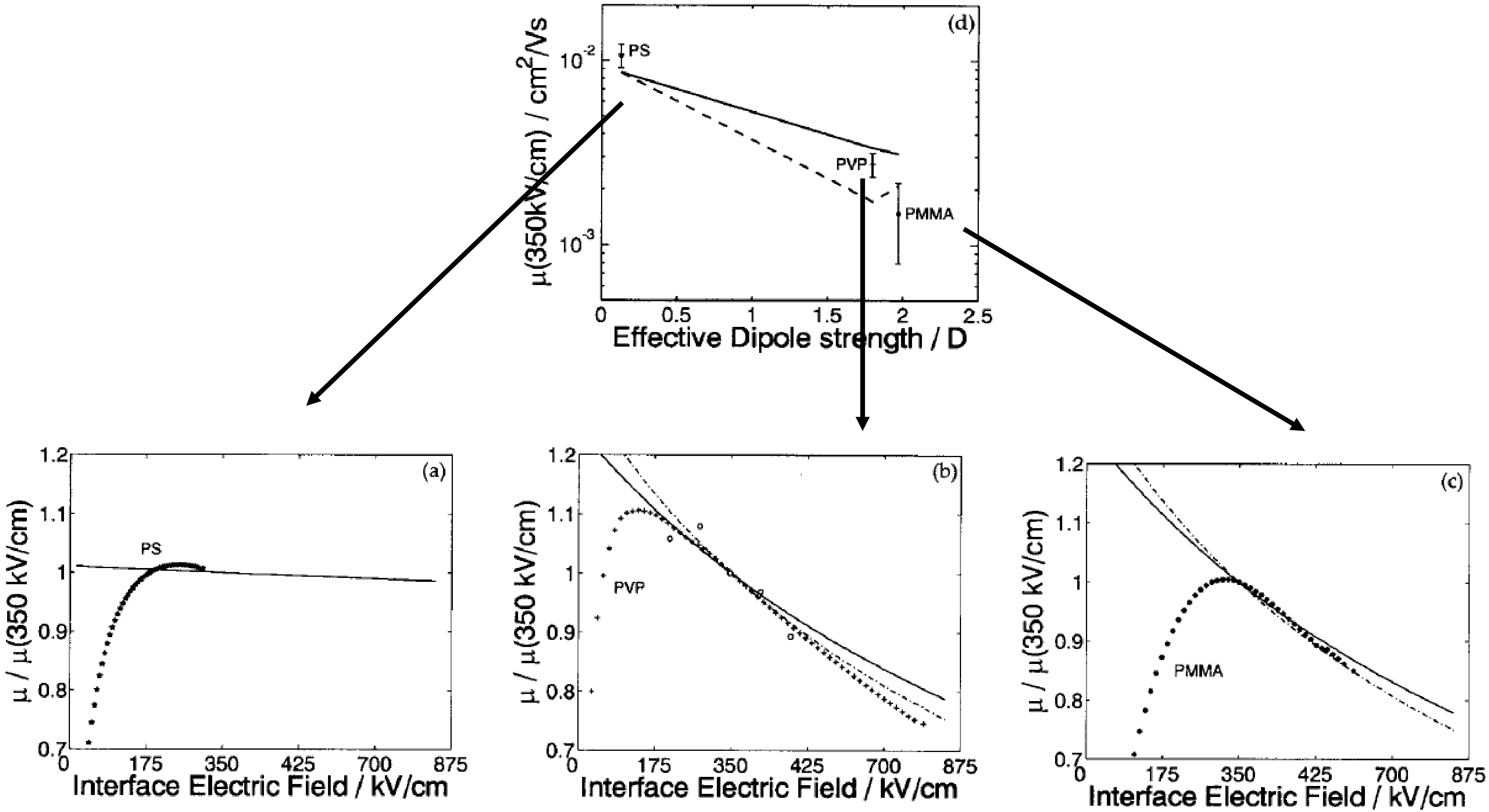
Dipole induced DOS broadening



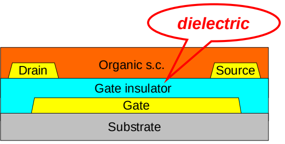
Sirringhaus, THE JOURNAL OF CHEMICAL PHYSICS **128**, 234905 2008



Dipole induced DOS broadening

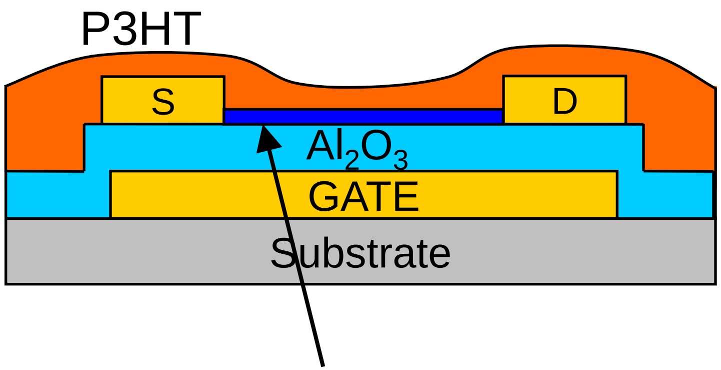


Sirringhaus, THE JOURNAL OF CHEMICAL PHYSICS **128**, 234905 2008

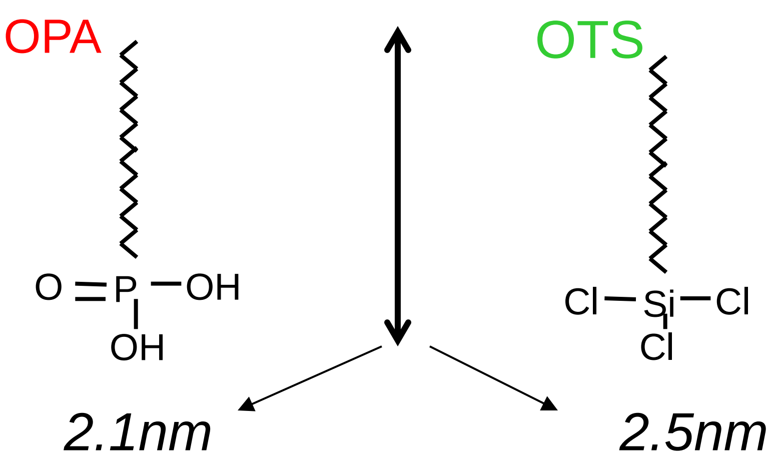


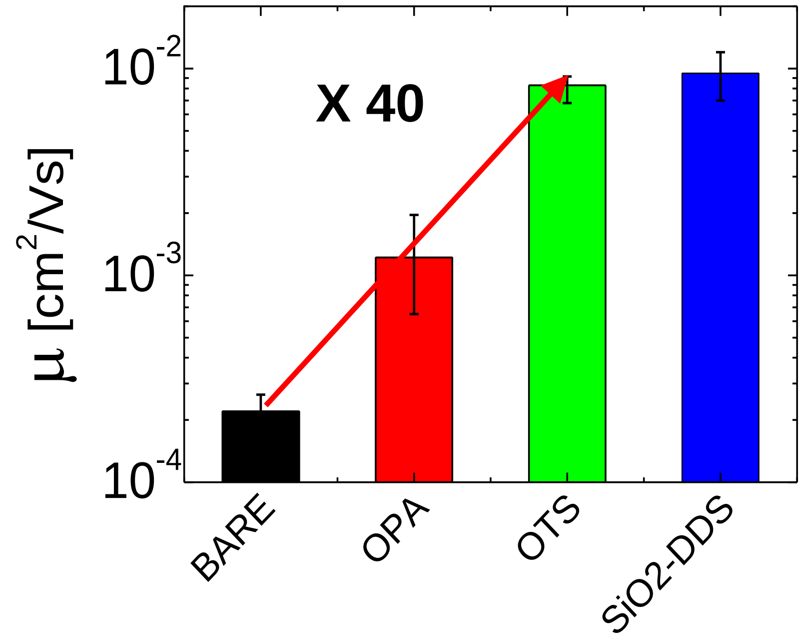
Solution: SAM interlayer

- functionalization of the Al_2O_3 surface by means of different SAMs

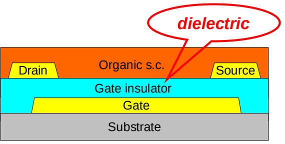


Self Assembly Monolayer (SAM)

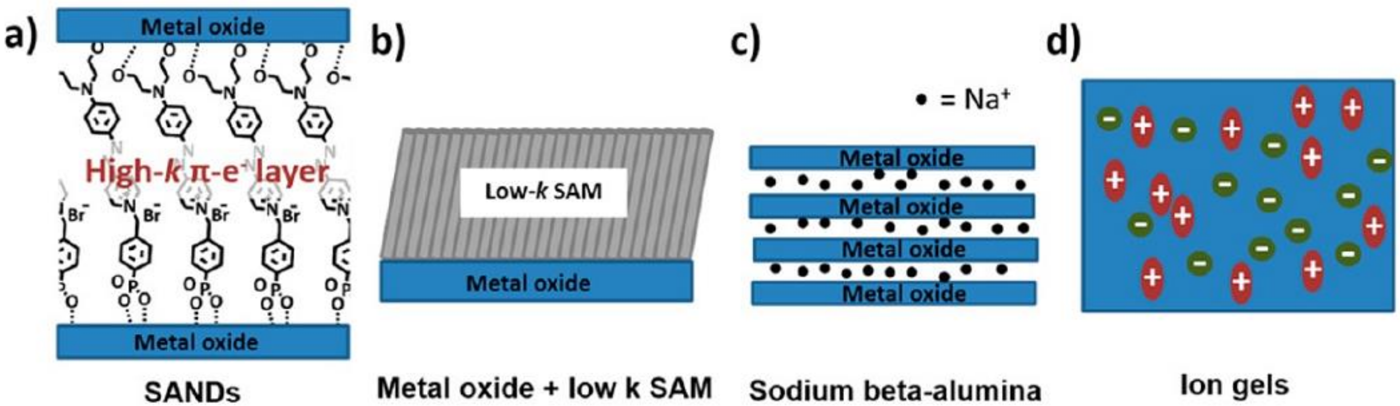


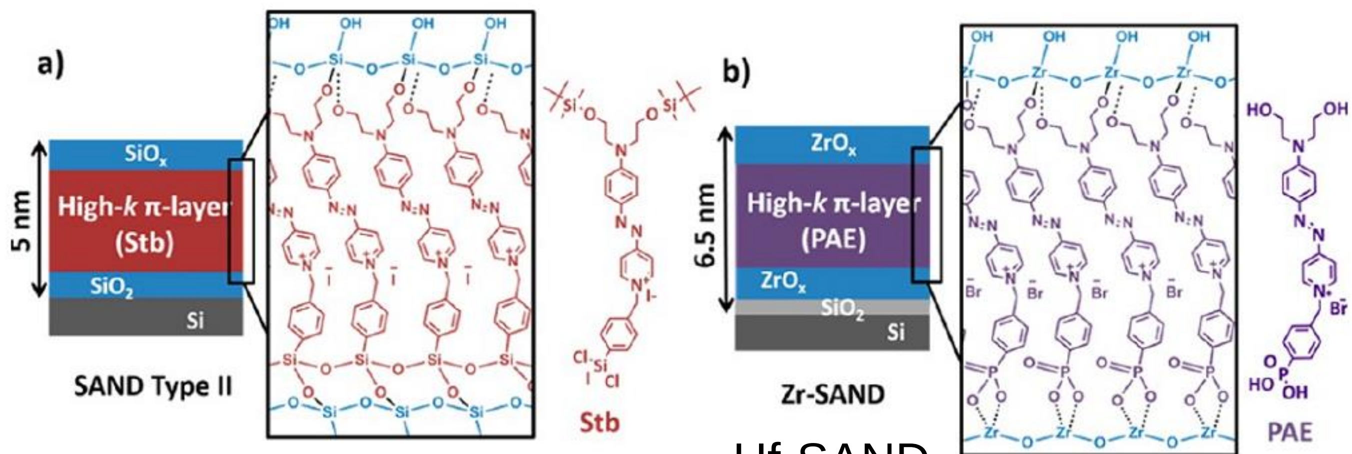


Mobility increases with Al_2O_3 functionalization



Unconventional dielectrics

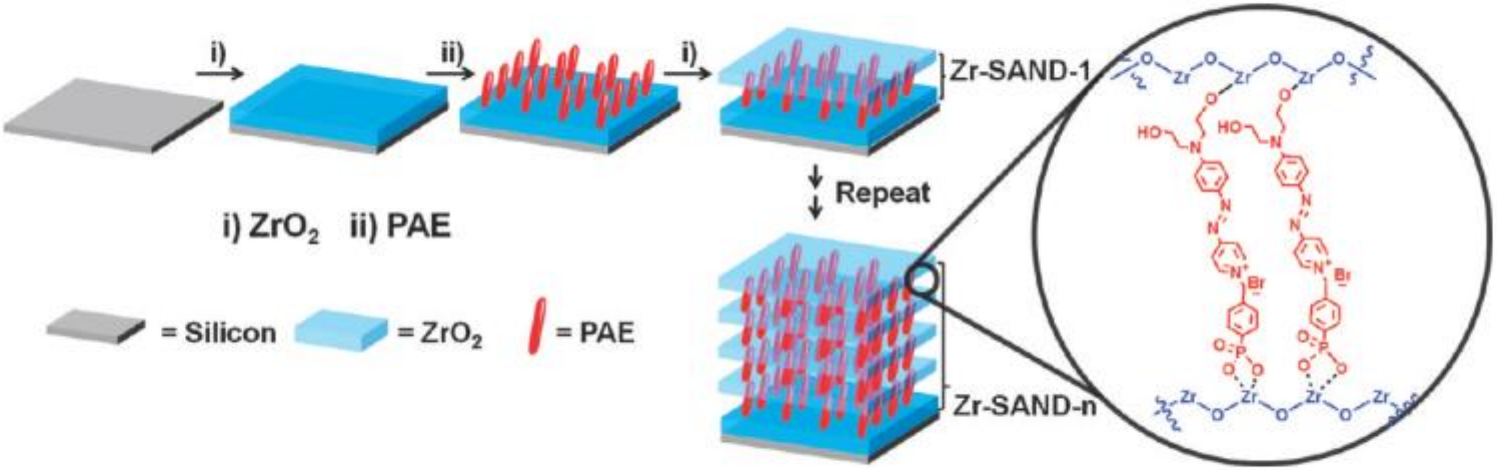


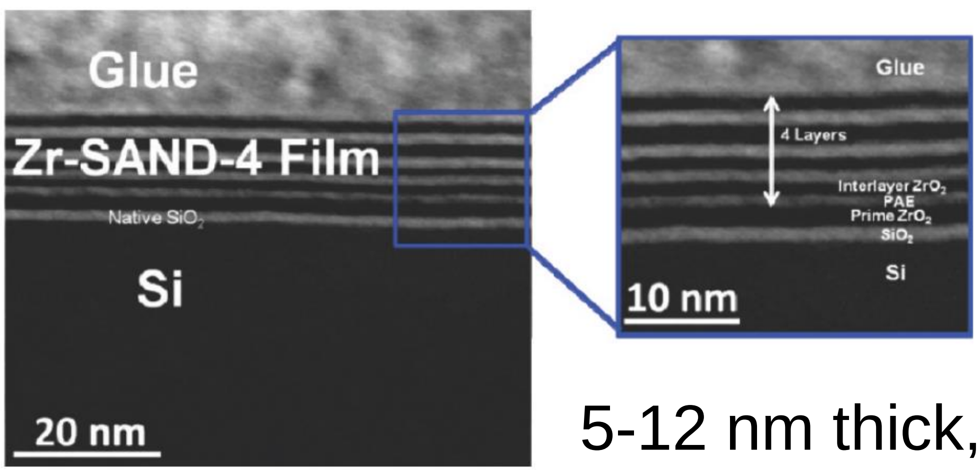


Hf-SAND

J. Am. Chem. Soc.2013, 135, 8926−893

Solution-Deposited Organic-Inorganic Hybrid Multilayer NanoDielectrics



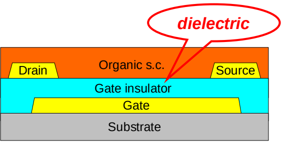


polarizable, phosphonic acid-functionalized **organic precursors** combined with ultrathin layers of **high-k inorganic oxide** materials.

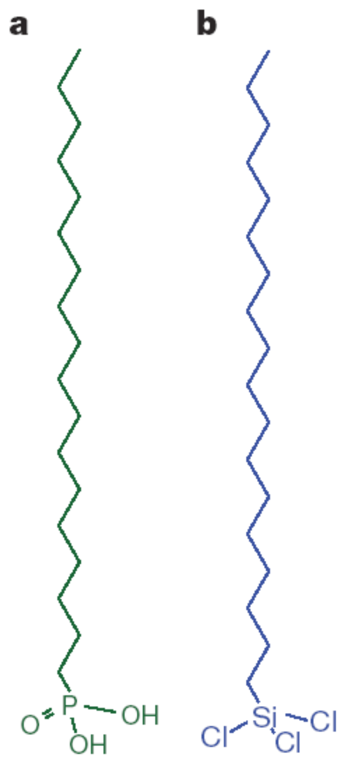
5-12 nm thick, leakage 10^{-7} A/cm^2@2MV/cm, C=750nF/cm^2

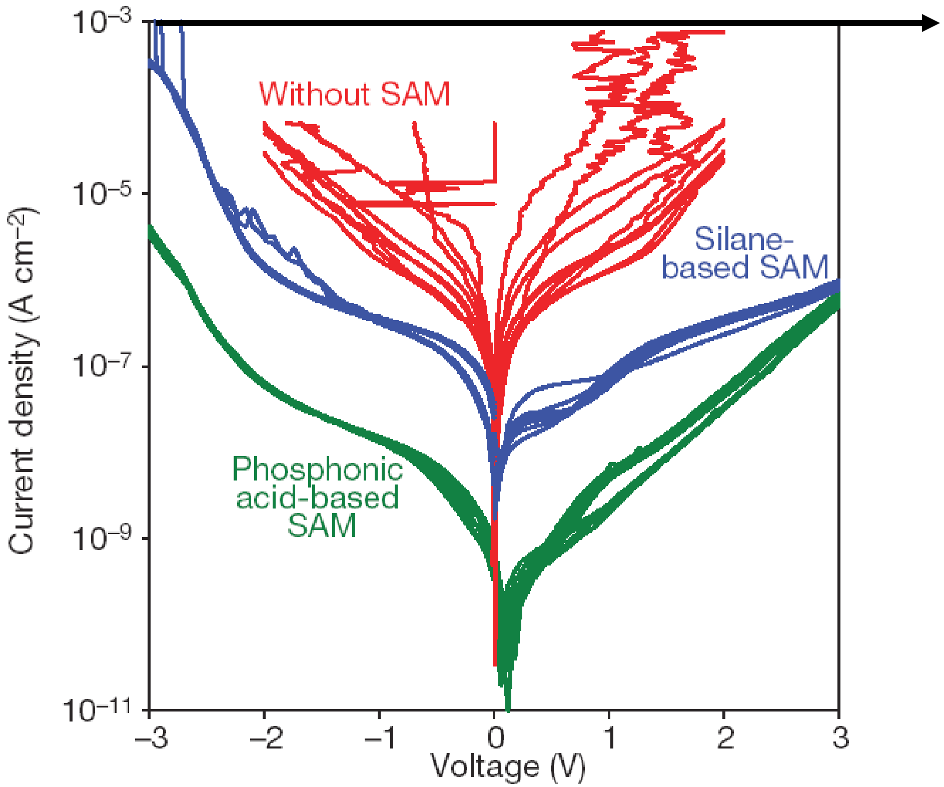
Ambient processible!!!!

Facchetti |J. Am. Chem. Soc. 2011, 133, 10239 – 10250



Ultrathin dielectric: Self Assembled Mono-Layers





2.2nm SiO_2

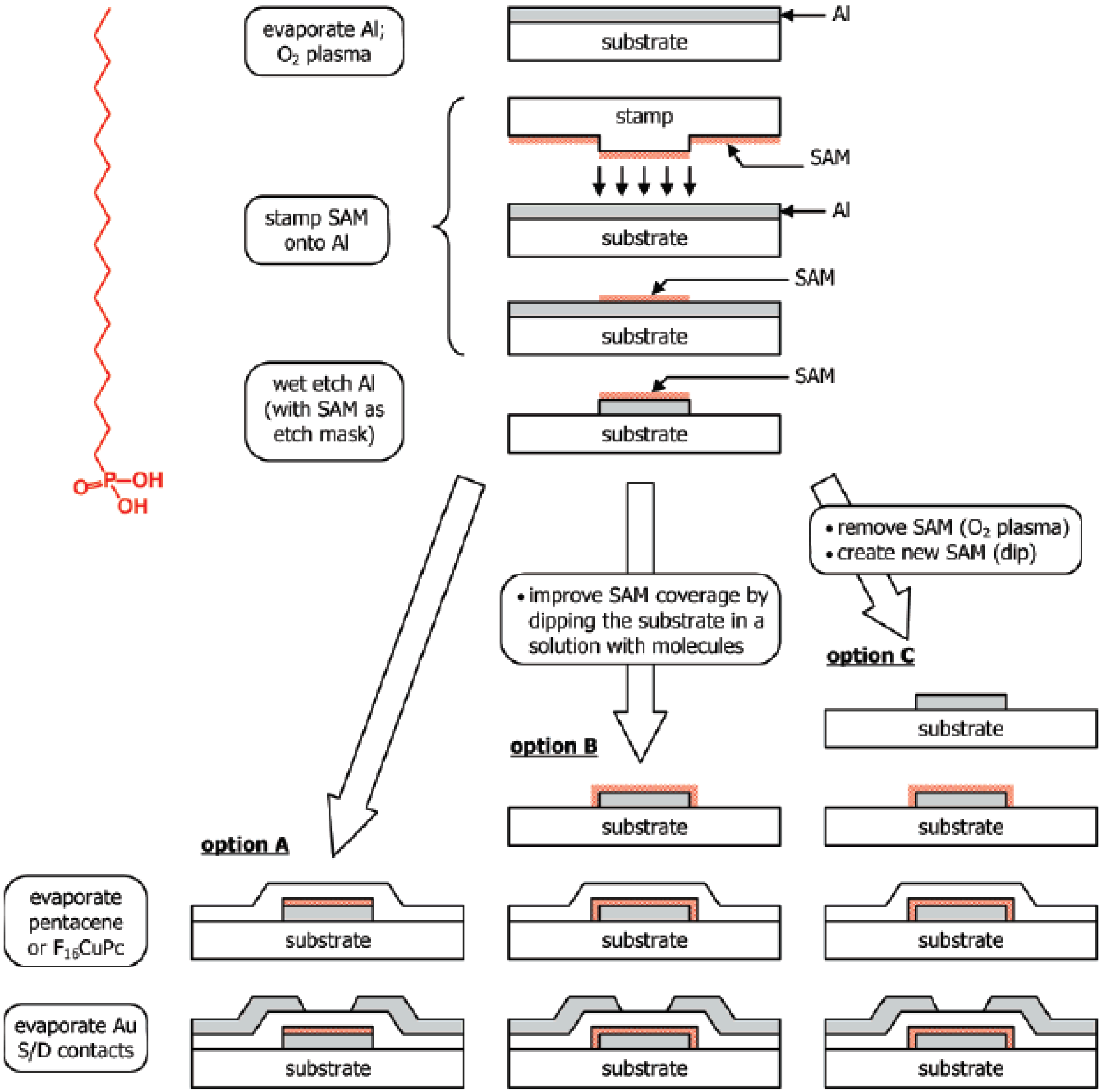
C_{OX}=1.5µF/cm^2

C_{ox}=0.8µF/cm^2

t_{OX}=2.1nm

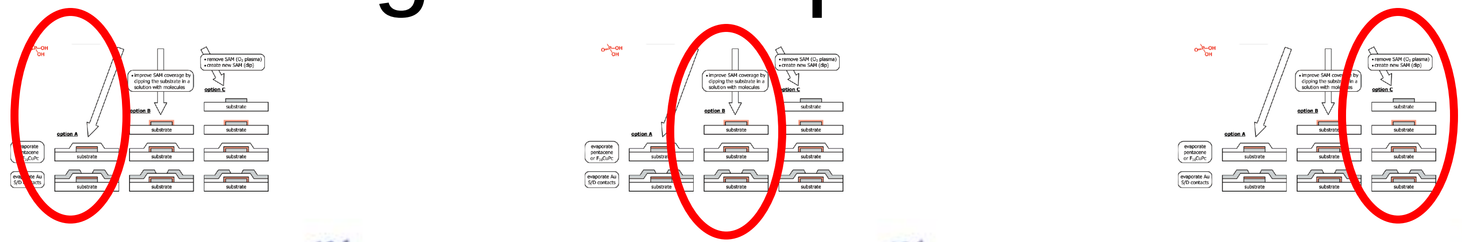
Halik Nature 445 745 2007

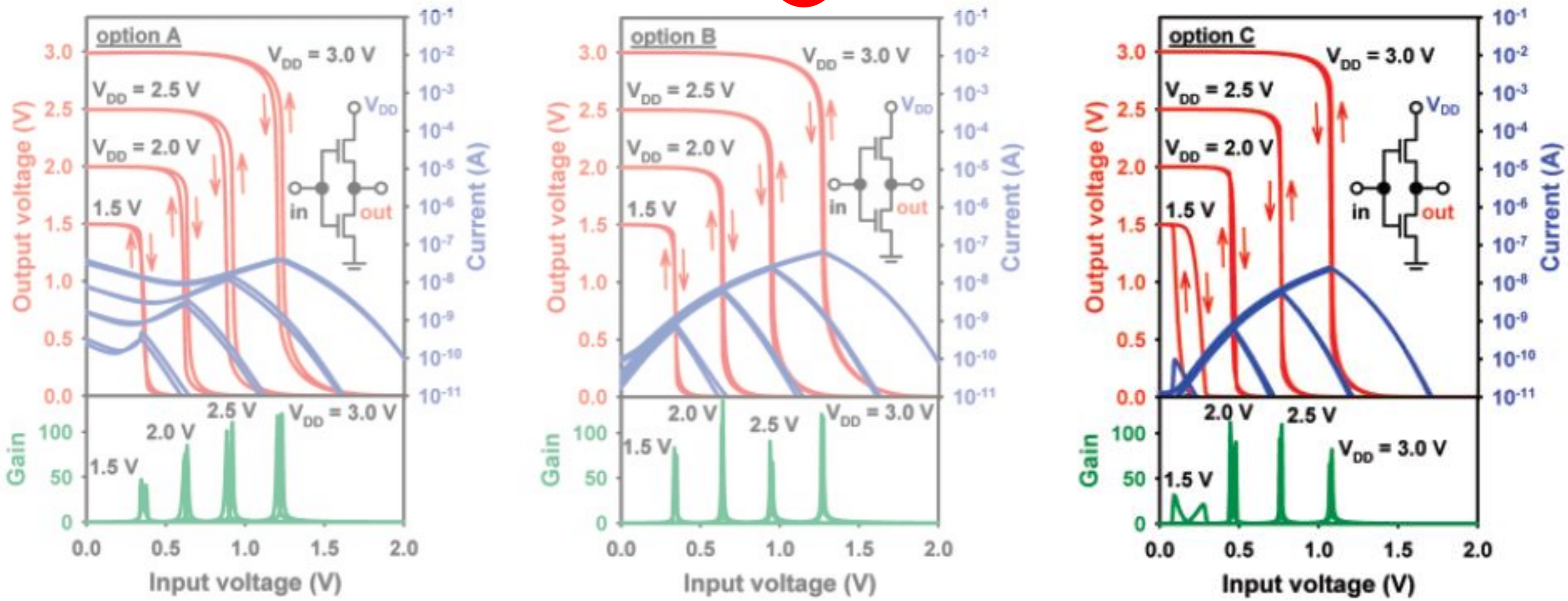
SAM gate: processes

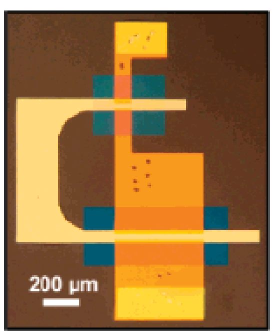


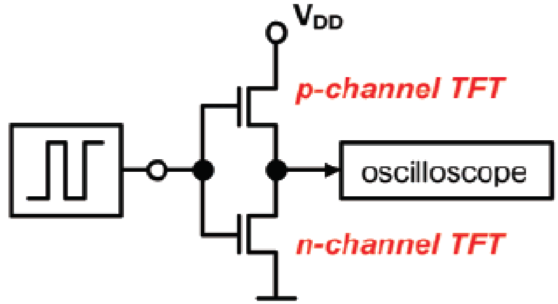
Klauk Langmuir **2008**, *24*, 1665-1669

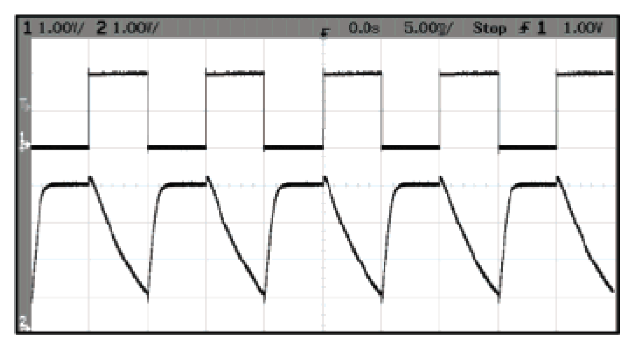
SAM gate: simple circuits







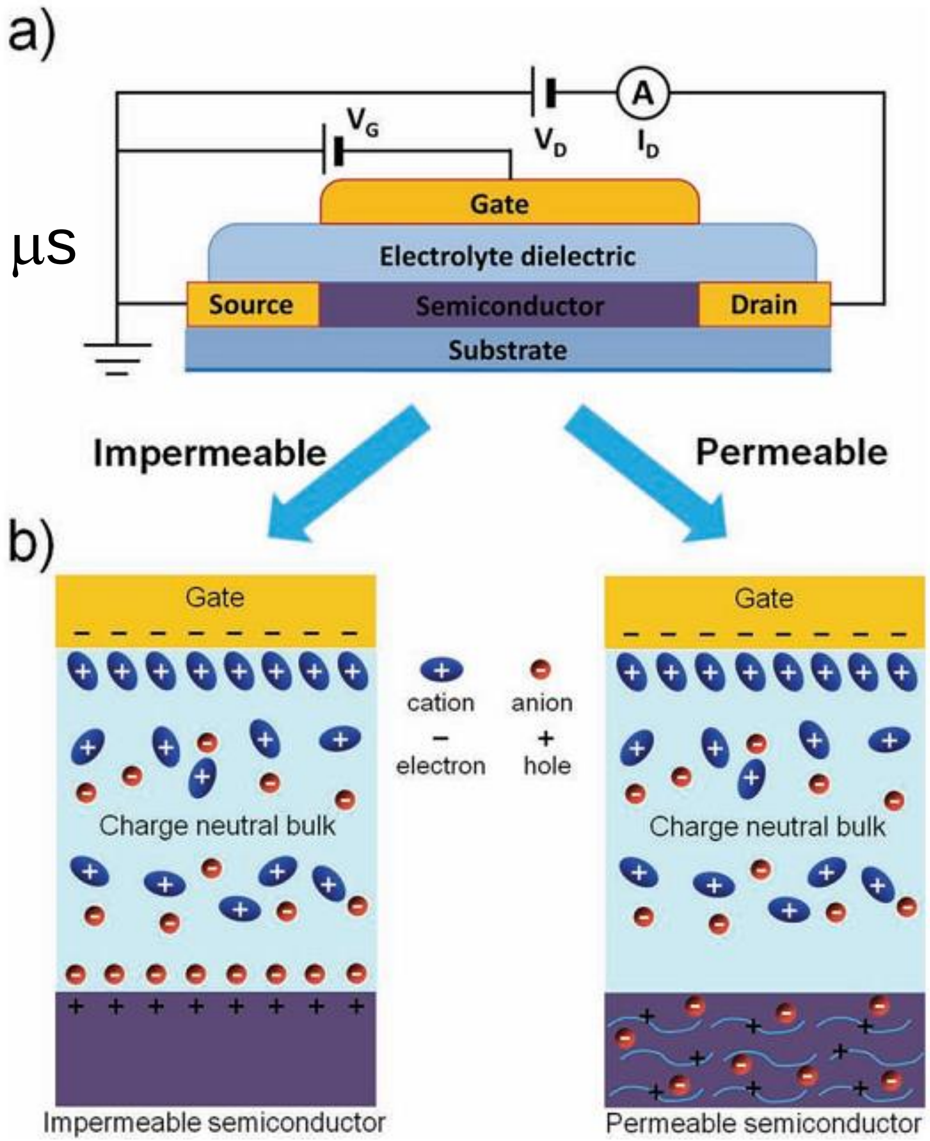




Klauk Langmuir **2008,** *24,* 1665-1669

Electrochemically gatetd TFT

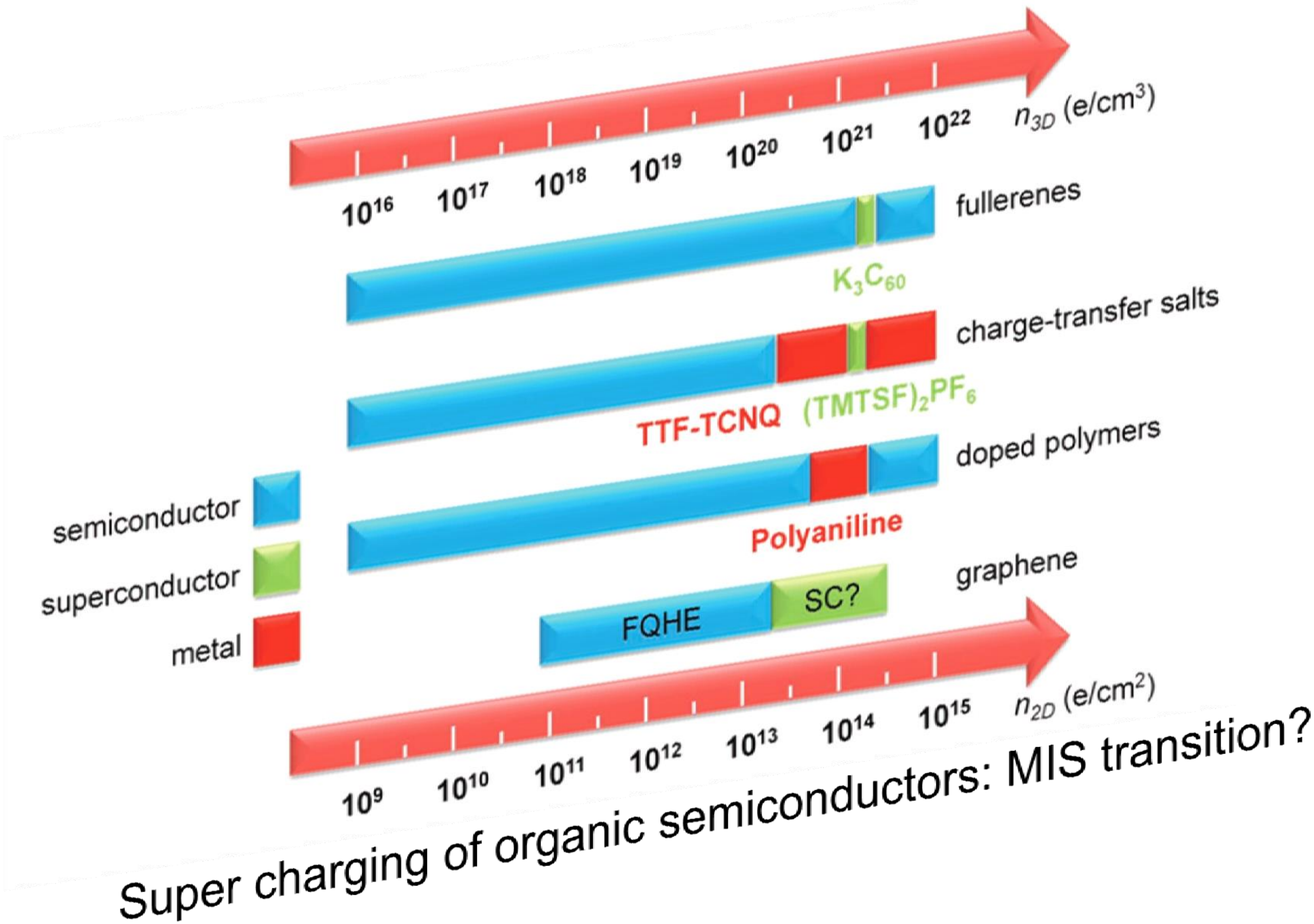
Switching time
potentially below μs
currently <1ms



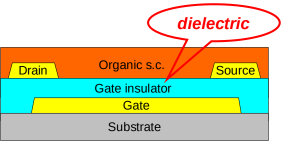
C>1μF/cm²

Frisbie et al. Adv. Mater. 2013, 25, 1822–1846

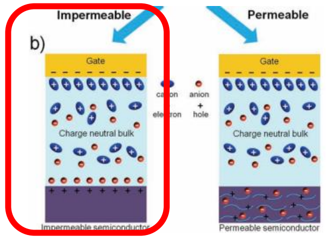
Electrochemically gated TFT

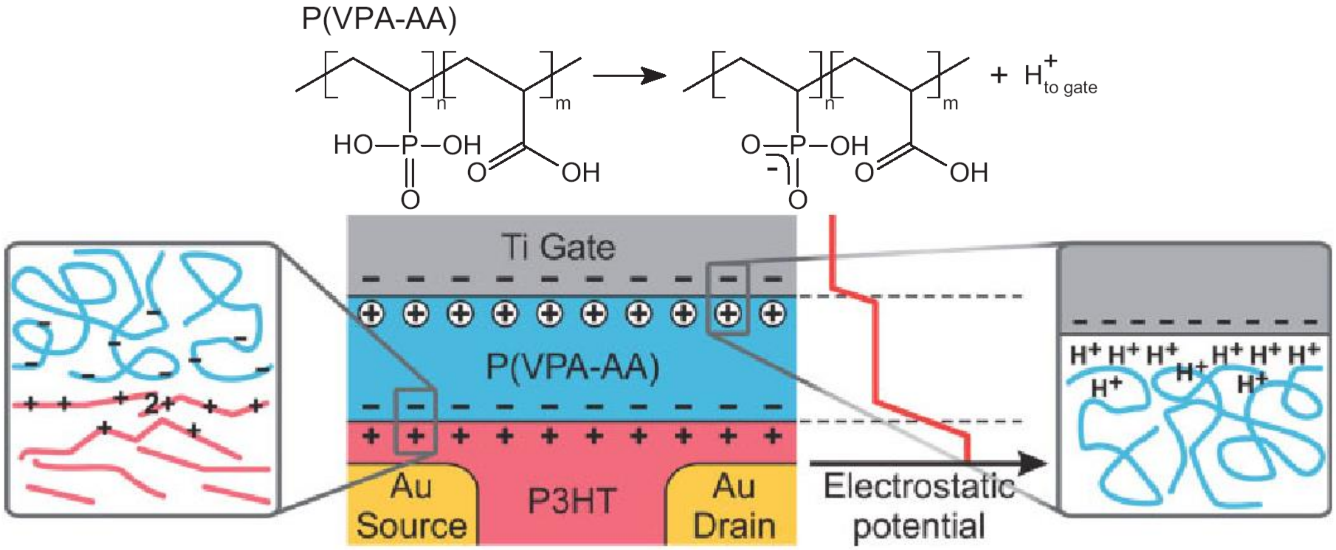


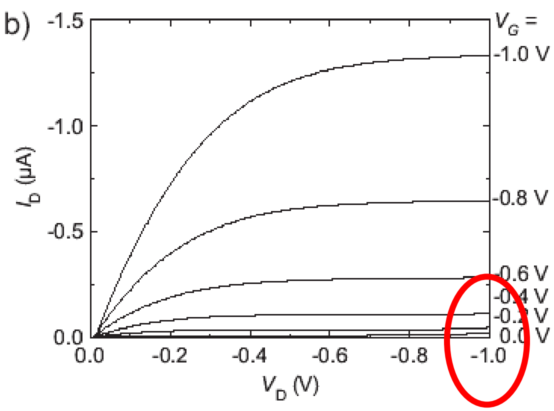
Frisbie et al. Adv. Mater. 2013, 25, 1822–1846

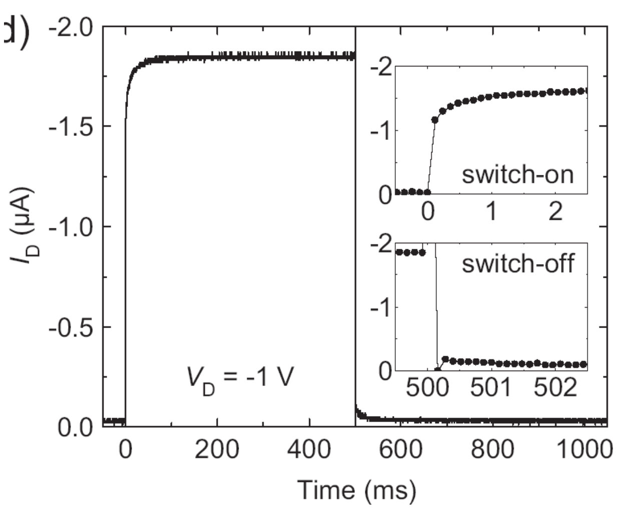


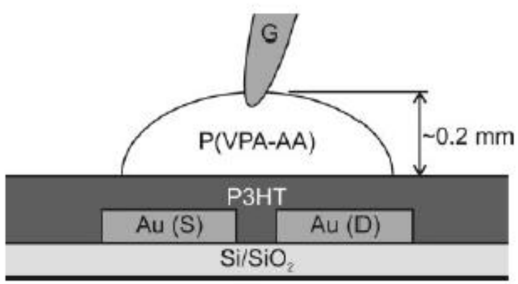
Polyanionic electrolite dielectrics



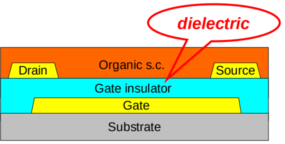




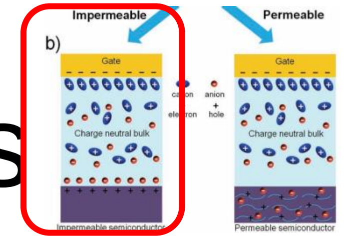


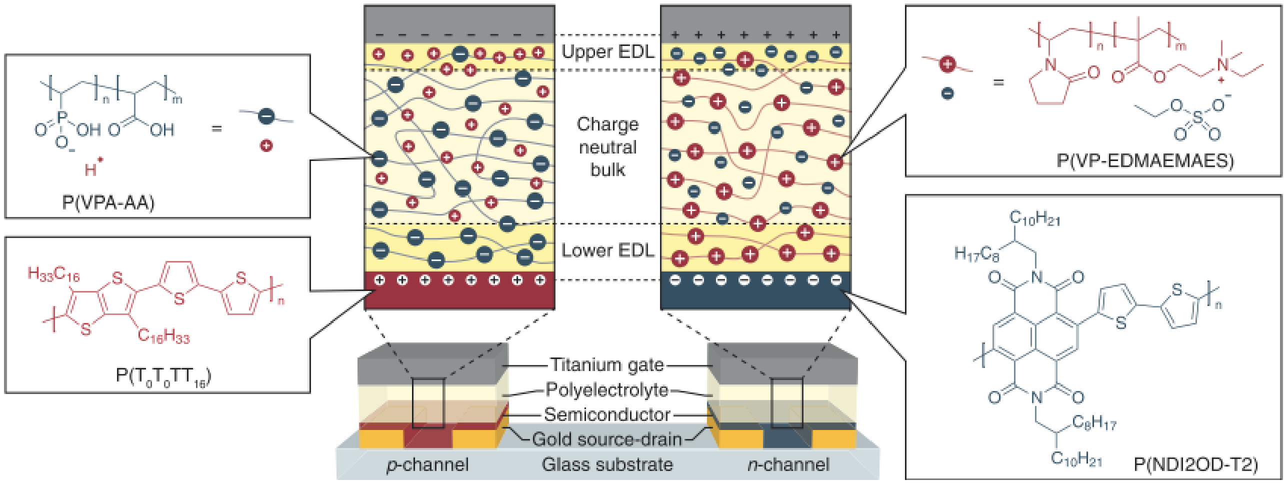


Herlogsson, Adv. Mater. 2007, 19, 97–101



Polyelectroylte dielectrics





Berggren Adv. Mater. 2011, 23, 4684–4689

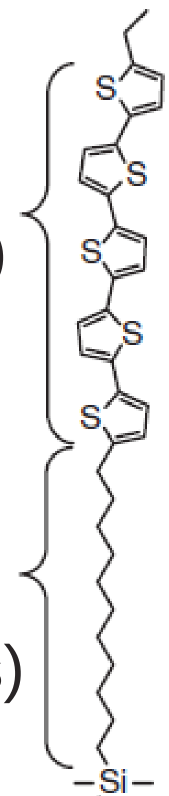
SAM-FET

Thick: 21 Å

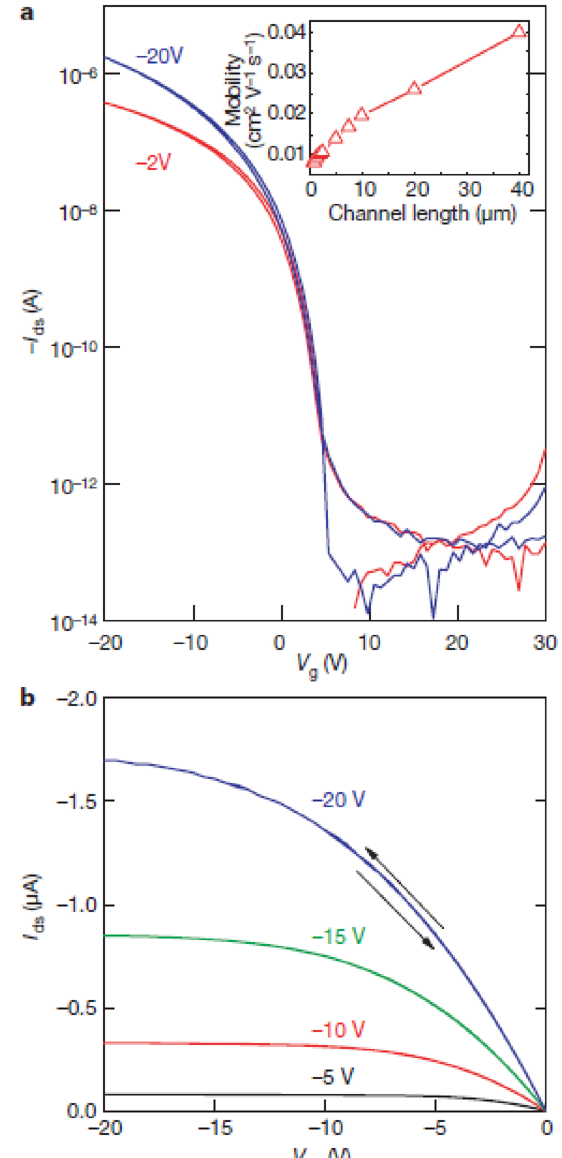
(rough 7.0 Å rms)

Thick: 15 Å

(rough 3.8 Å rms)



$\mu = 10^{-2} cm^2/Vs$



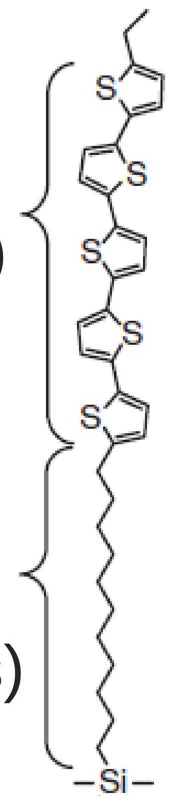
SiO2 gate dielectric

De Leeuw Nature 455 2008 956

SAM-FET

Thick: 21 Å

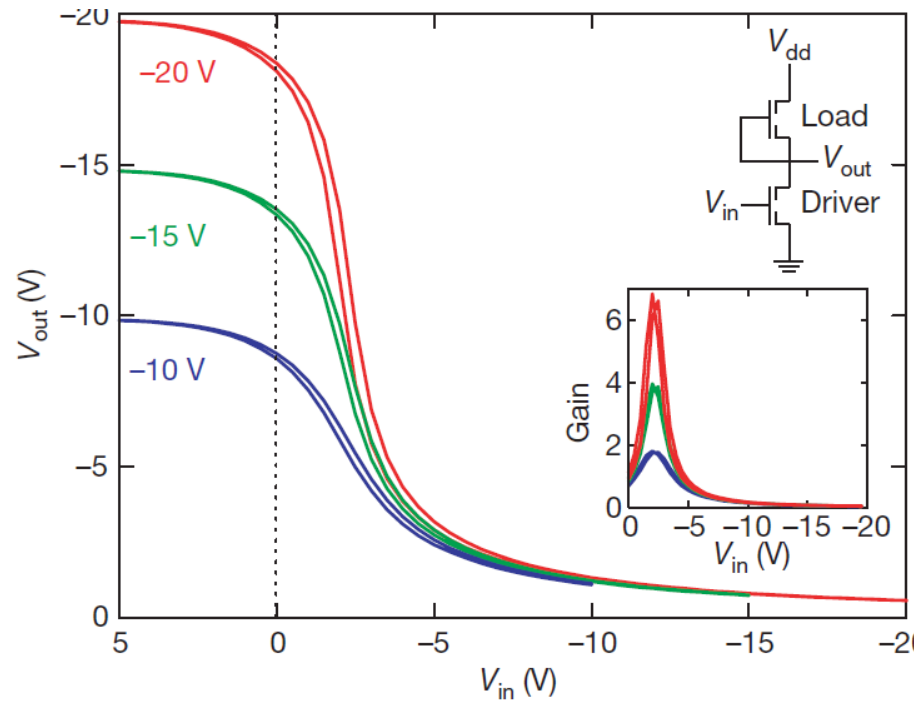
(rough 7.0 Å rms)



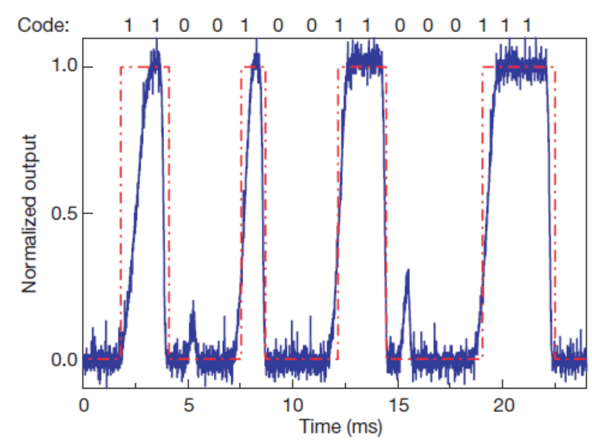
Thick: 15 Å

(rough 3.8 Å rms)

SiO2 gate dielectric

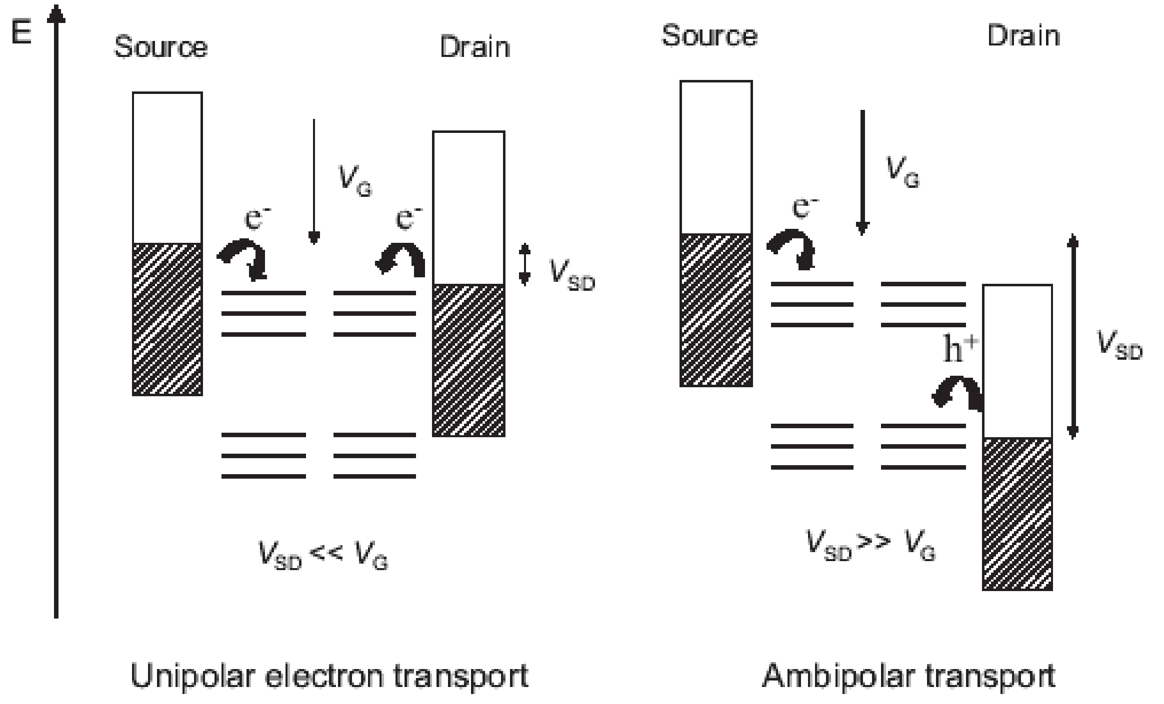


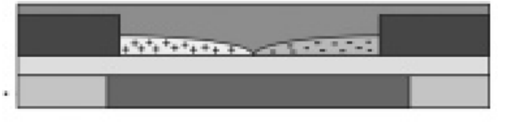
$\mu = 10^{-2} cm^2/Vs$



De Leeuw Nature 455 2008 956

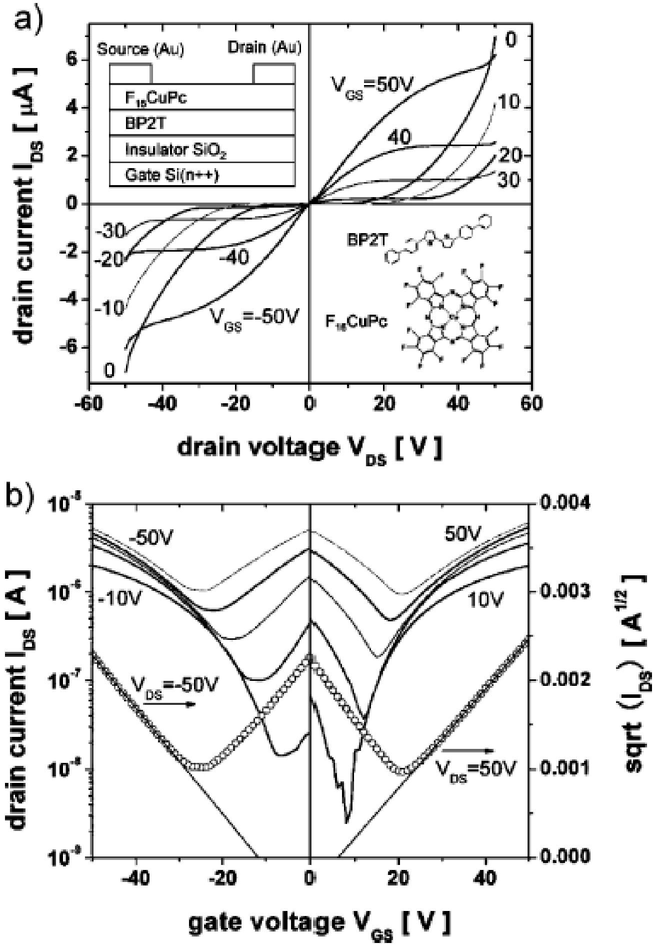
Ambipolar operation

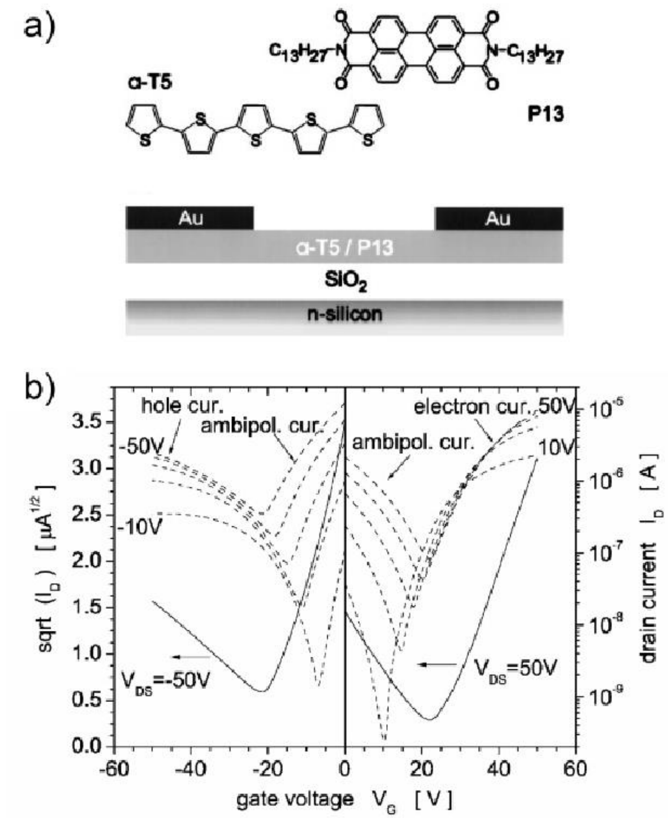




Sirringhaus, Chem. Rev. 2007, 107, 1296, Adv. Mater. **2007**, 19, 1791–1799

Ambipolar operation



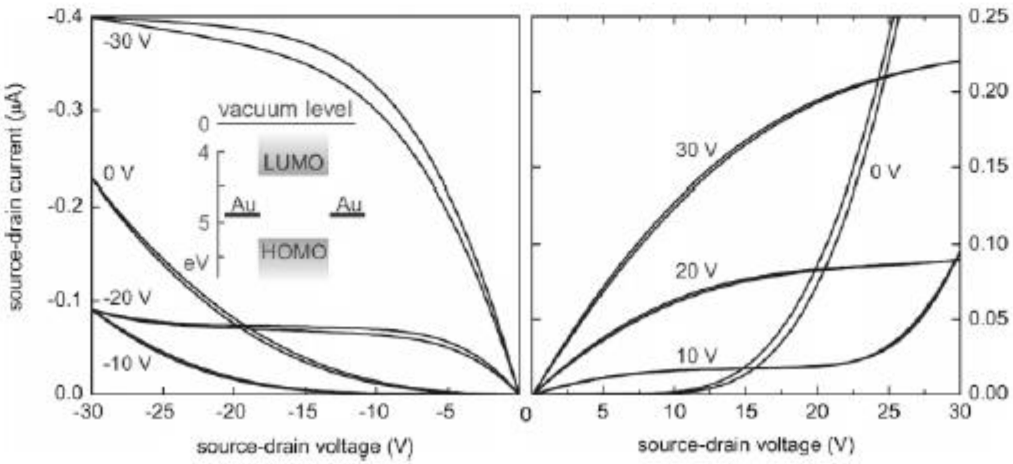


p & n bilayer

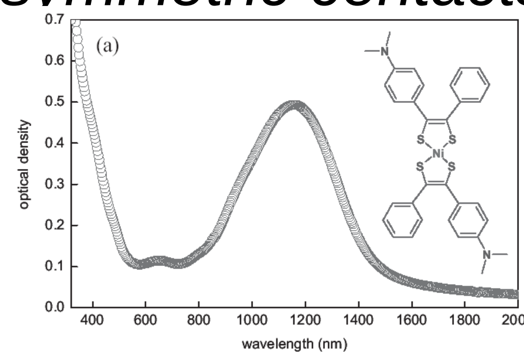
p & n blend

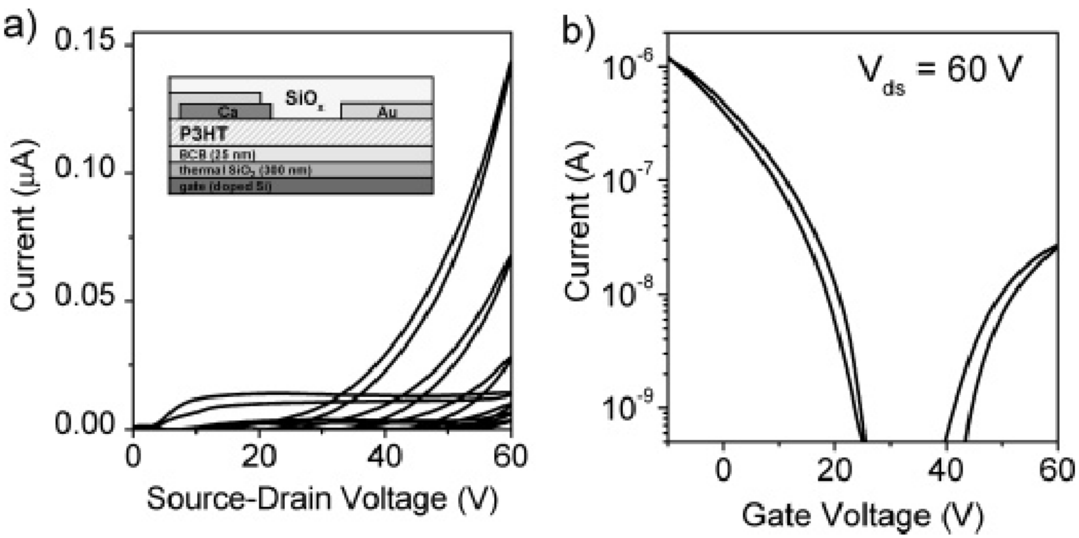
Sirringhaus, Chem. Rev. 2007, 107, 1296, Adv. Mater. **2007**, 19, 1791–1799

Ambipolar operation



Narrow gap
single component
symmetric contacts

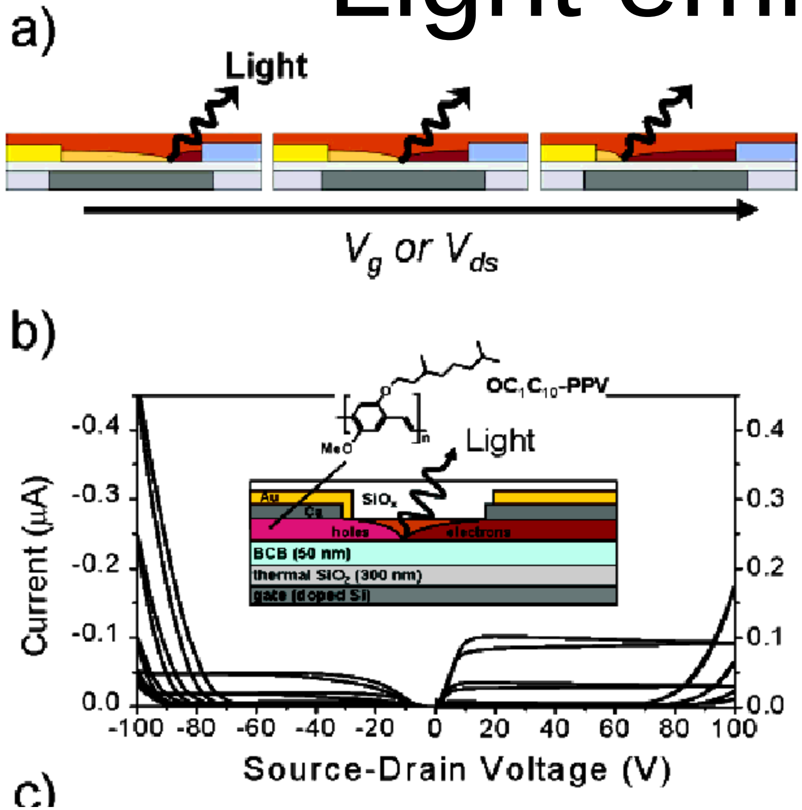


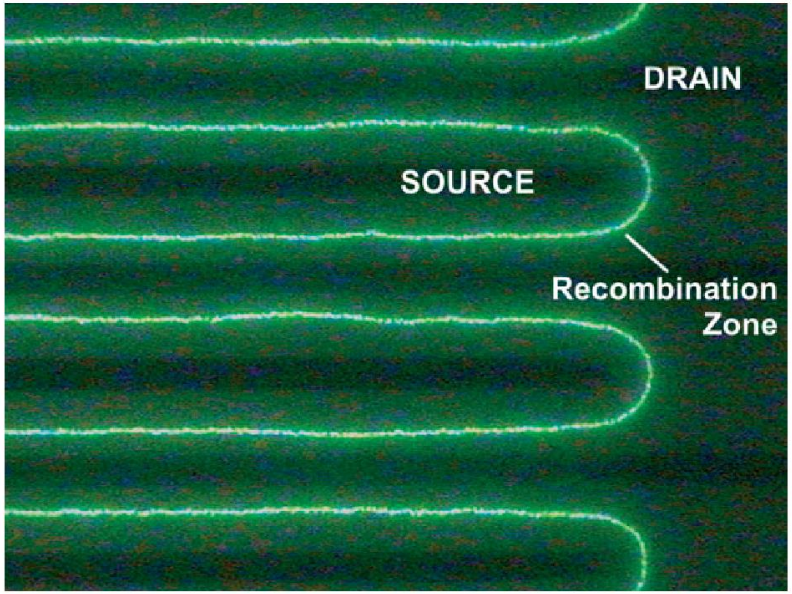


Single component
Asymmetric contacts

See for recent review : Loi et al.10.1002/adma.201304280

Light emitting transistor

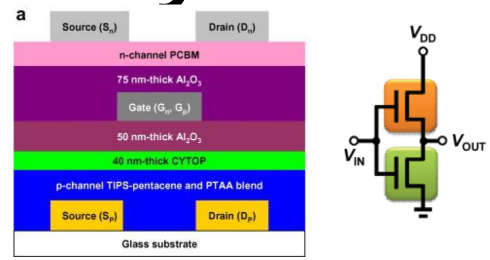




Recombination occurs at pinch-off, charge concentration is low,
Hence low losses due to exciton-polaron quenching
EQE=10%!!!

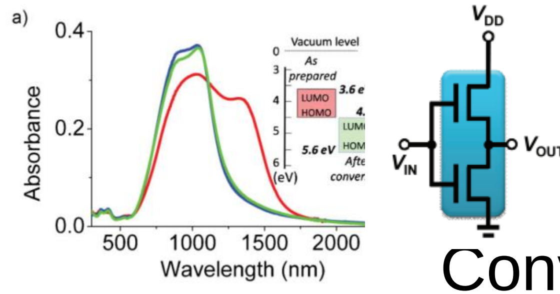
Sirringhaus Nat.Mat 2006 5 69

Complementary circuits



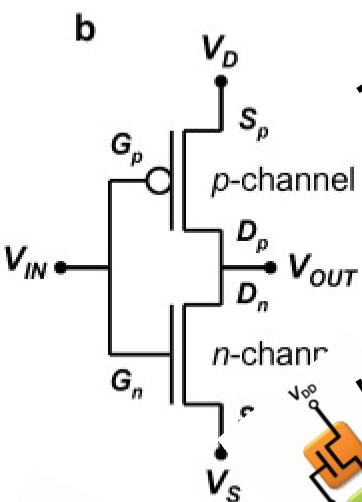
Stacking

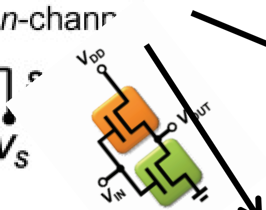
Kippelen Organic Electronics 12 (2011) 1132–1136

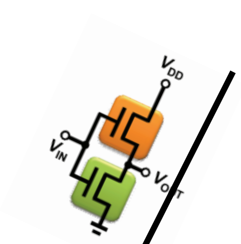


Conversion

Aoyama Adv. Mater. 2010, 22, 1722–1726



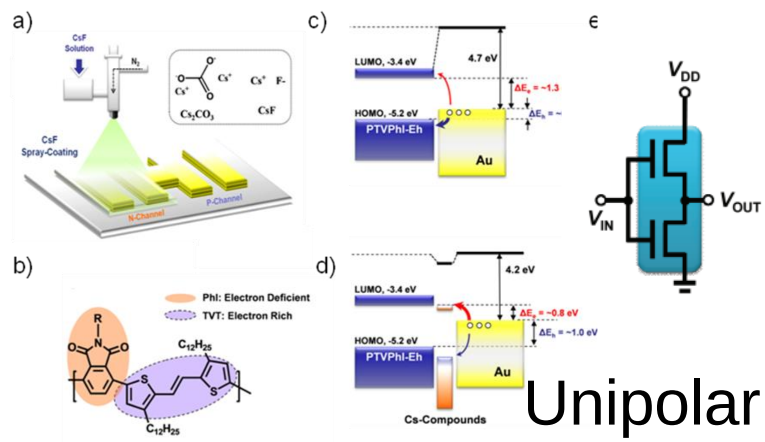




Additive dep.
(eg. inkjet)

Subtractive dep.

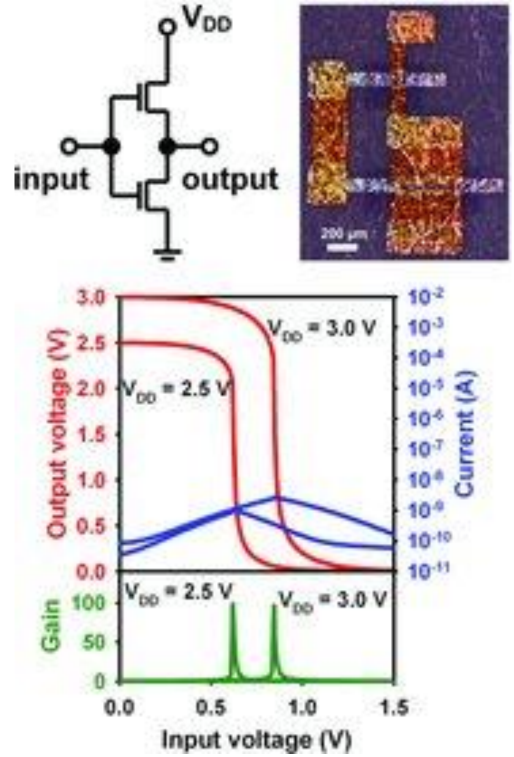
plasma using metal gate as mask



Unipolarization

Caironi *ACS Applied Materials & Interfaces* **2011**, *3*, 3205.

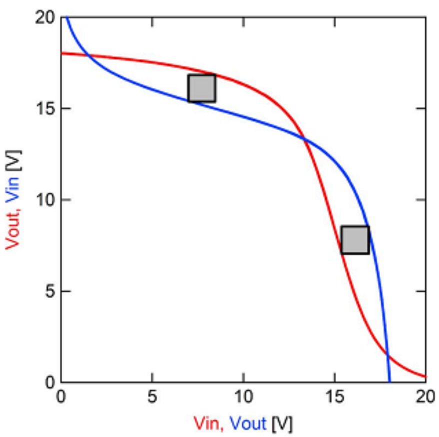
In the end of the day, it's the money

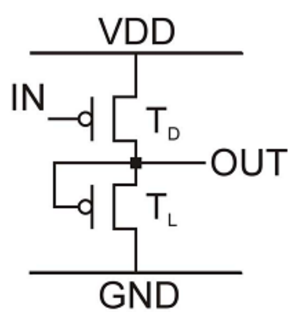


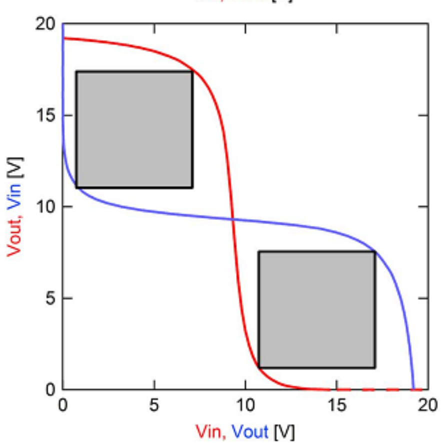
Klauk Advanced Materials Volume 23, Issue 5, pages 654-658, 6 DEC 2010 DOI: 10.1002/adma.201003374

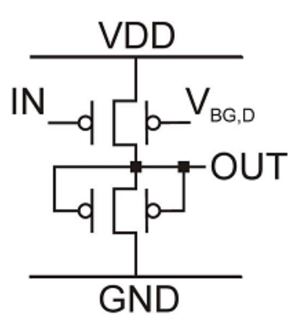
8-Bit, 40-instr/s µprocessor on Plastic

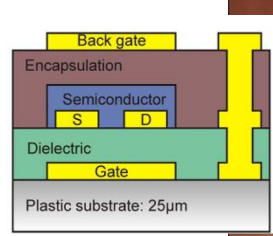
	Plastic microprocessor	Intel 4004
Transistor-count	3381	2300
Area	1.96 x 1.72 cm^2	3 x 4 mm^2
Pin-count	30	16
Power supply voltage	10 V	15 V
Power consumption	92 µW	1 W
Operation speed	40 operations/second	92000 operations/second
Semiconductor	Pentacene	Silicon
P-type mobility	~0.15 cm^2/Vs	~450 cm^2/Vs
Logic family	P-type	P-type
Operation	accumulation	inversion
Technology	5 µm	10 µm
Bus width	8 bit	4 bit
Production year	2011	1971
Wafer scale	6″	2″
Substrate	flexible	rigid

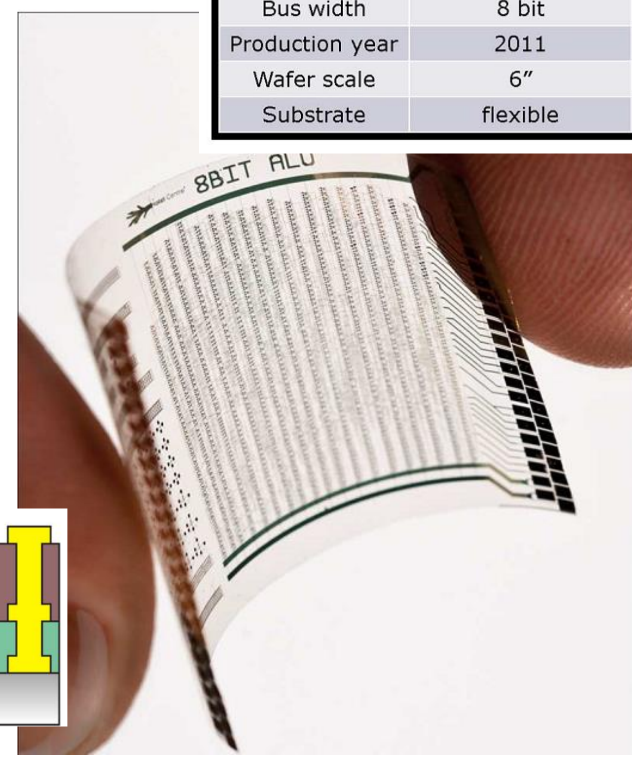








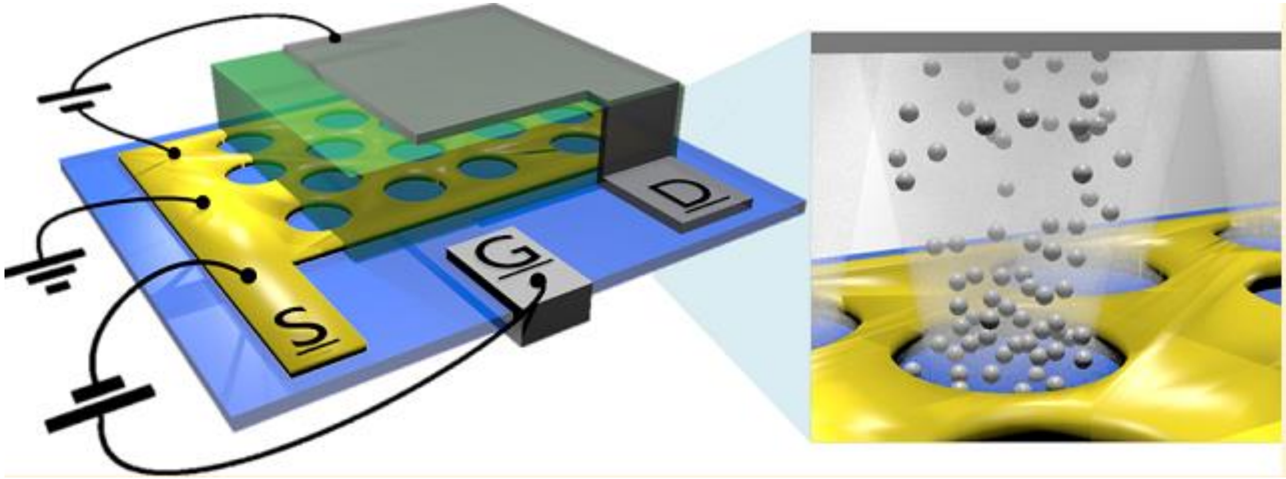


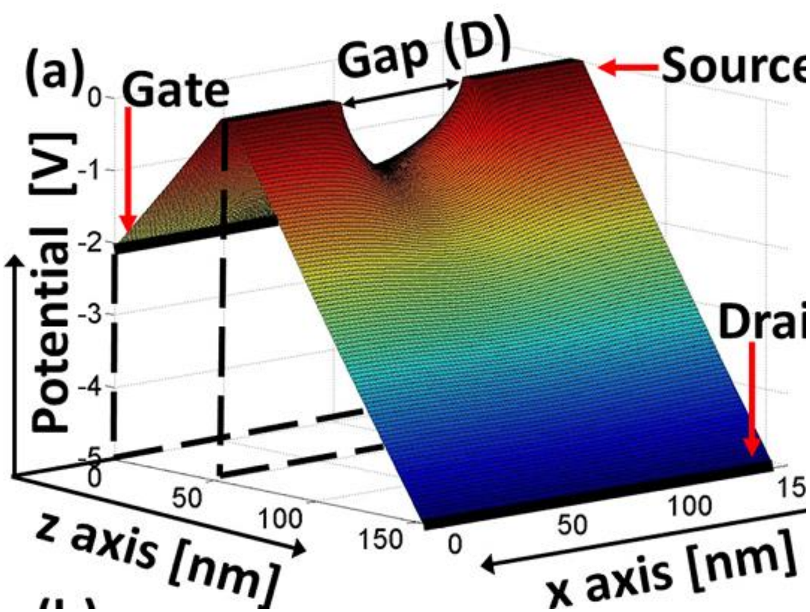


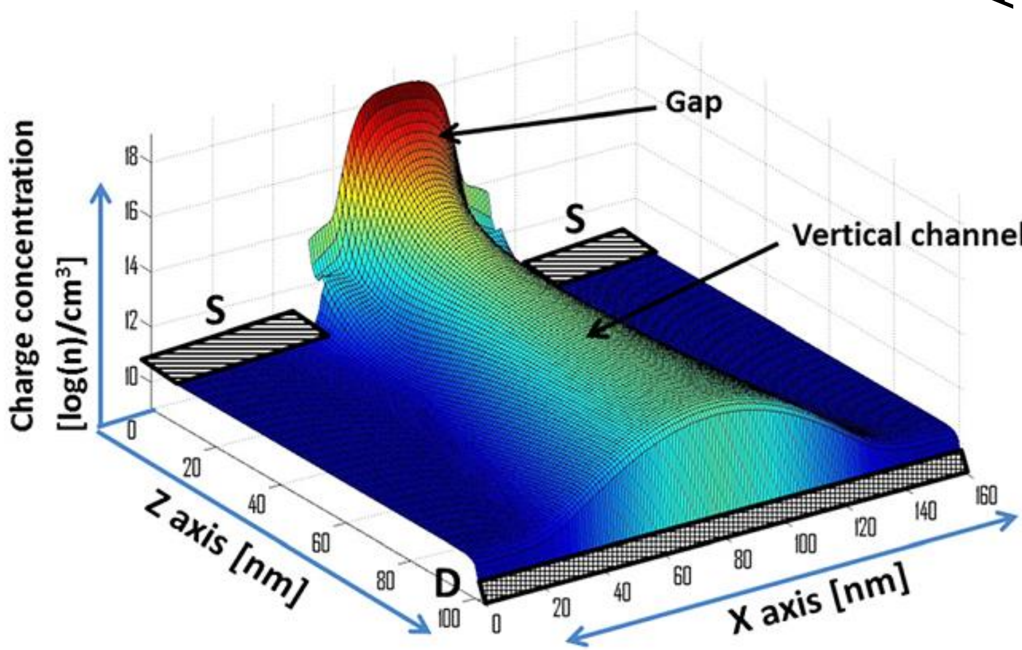
Heremans et al IEEE JOURNAL OF SOLID-STATE CIRCUITS, VOL. 47, NO. 1, JANUARY 2012

Vertical transistor

Gate-induced
tuning
of source
inj. barrier

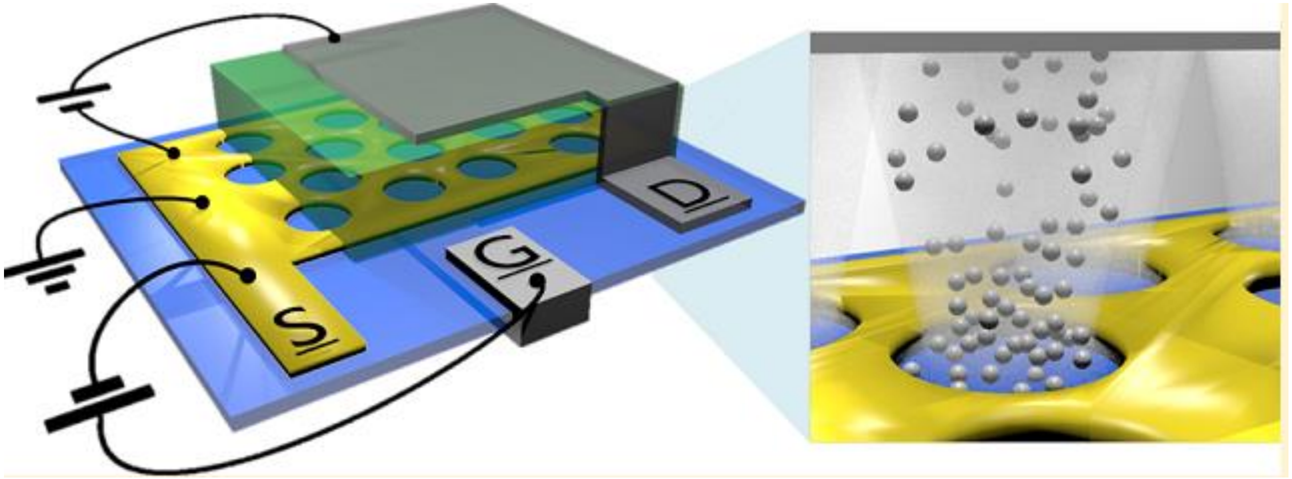


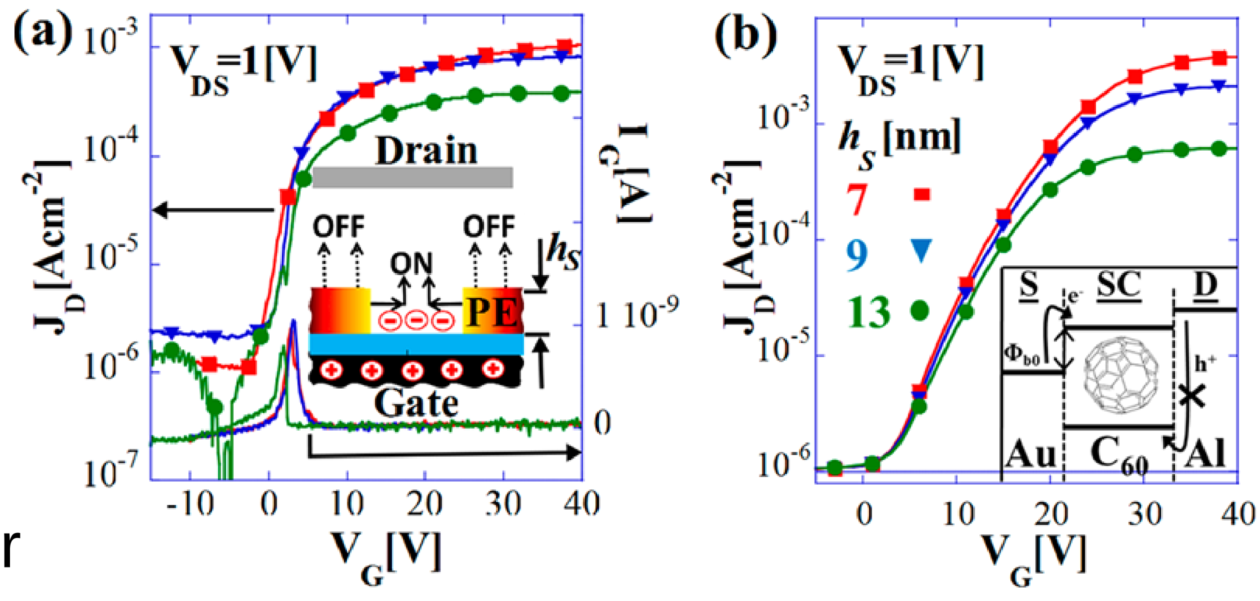




Applied Physics 110, 044501 (2011);

Vertical transistor

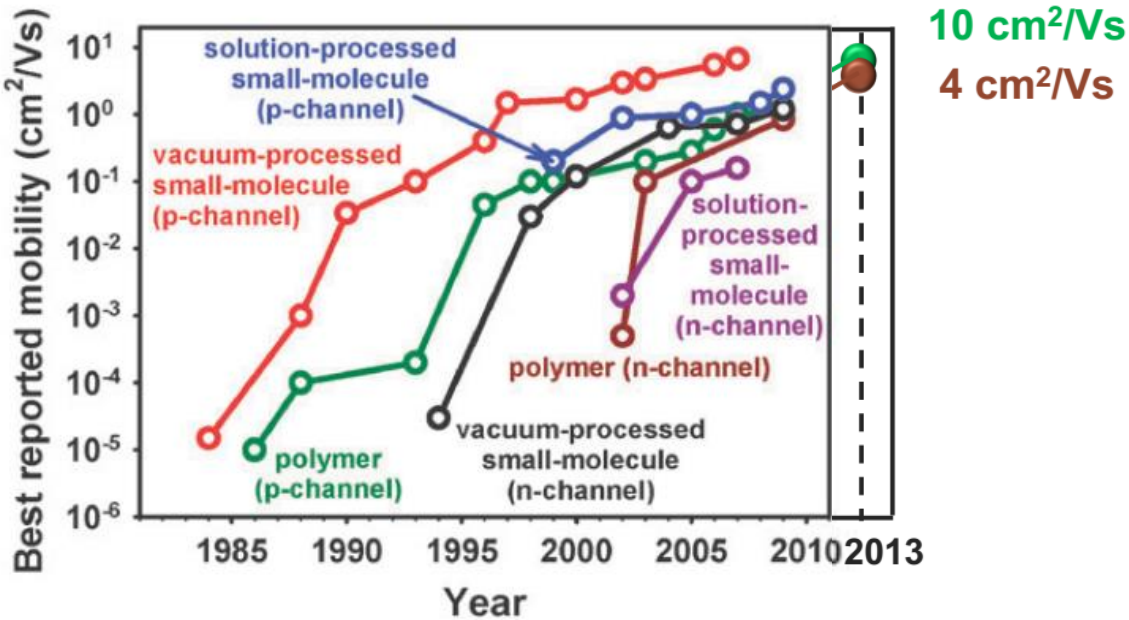




Gate-induced
tuning
of source inj. barrier

Tessler et al 10.1021/nl302163q| Nano Lett.2012, 12, 4729–4733

The End



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