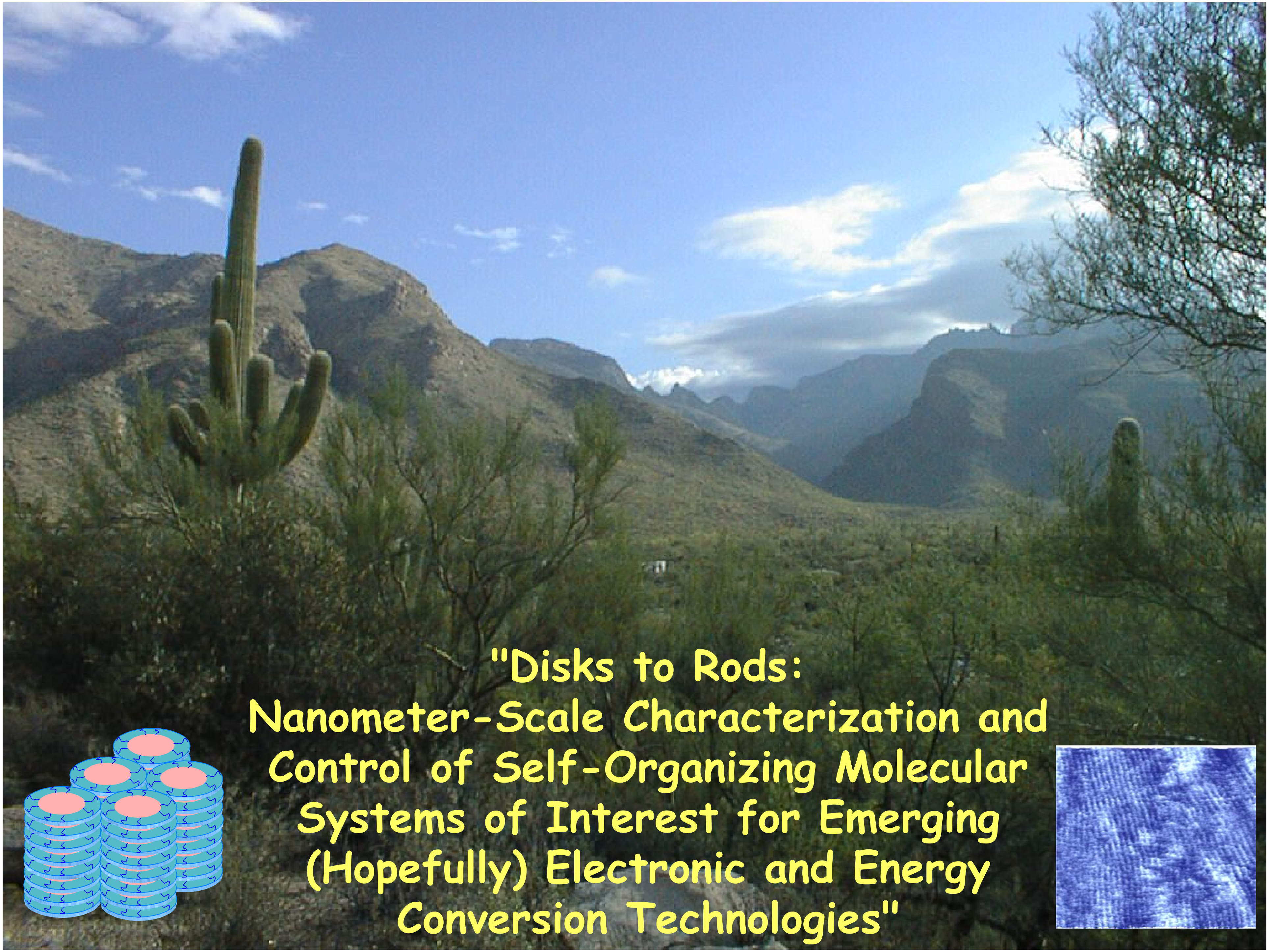

"Disks to Rods:
Nanometer-Scale Characterization and
Control of Self-Organizing Molecular
Systems of Interest for Emerging
(Hopefully) Electronic and Energy
Conversion Technologies"

Organic Field-Effect Transistors are Coming (Here!)

$$I_d=(W/L)\mu C_i[(V_g-V_T)^2-(1/2)V_d^2]$$

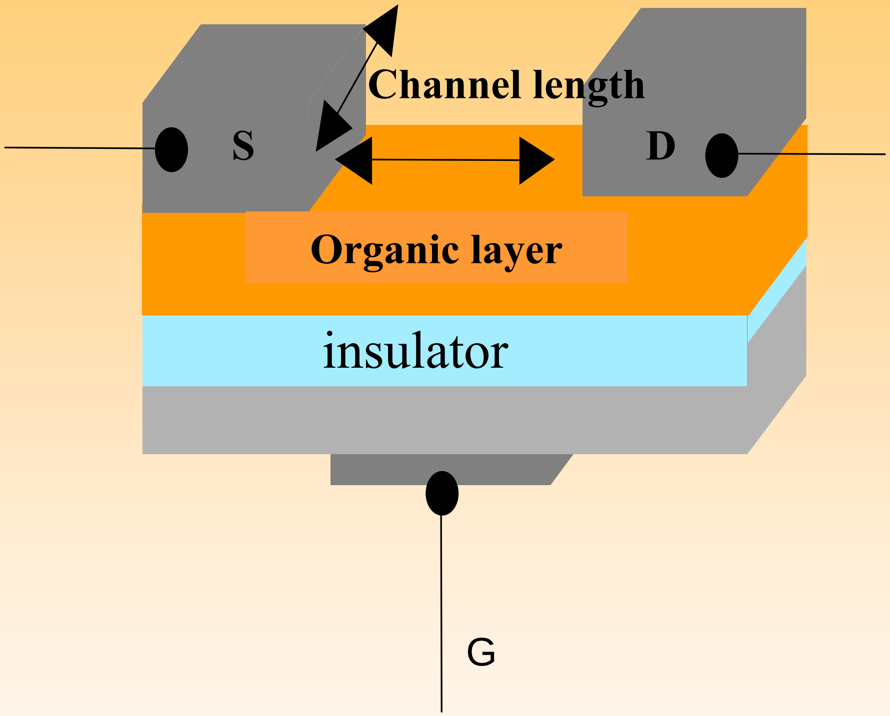
W=width of the channel

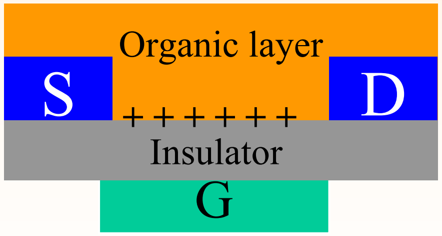
L=length of the channel

C_i=Capacitance of the insulator

V_T=Threshold voltage

μ= charge mobility $cm^2V^{-1}sec^{-1}$



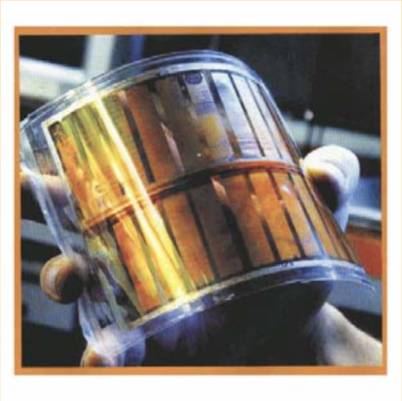


"on state"

For example:
Howard Katz, Zhenan Bao, *J. Phys. Chem. B.*, 104, 671 (2000).

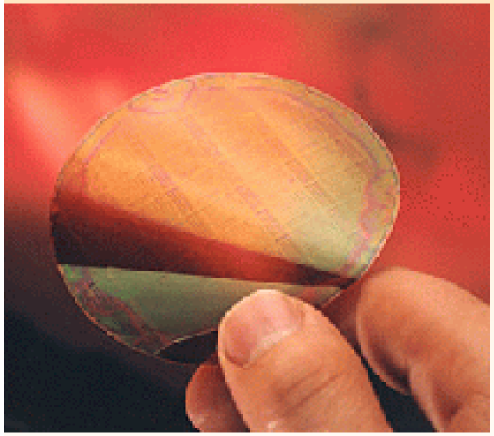
Emerging Technologies Based on Organic Thin Film Materials

Organic Light Emitting Diodes



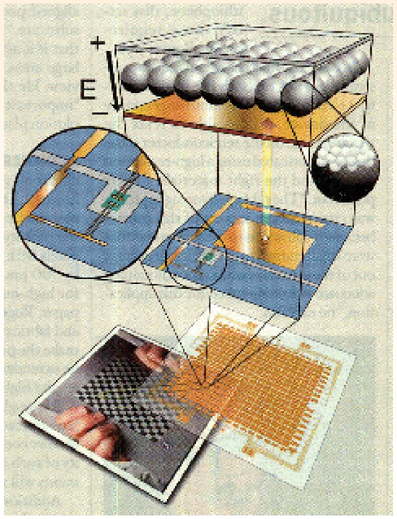
Organic Solar Cells

Flexible Displays



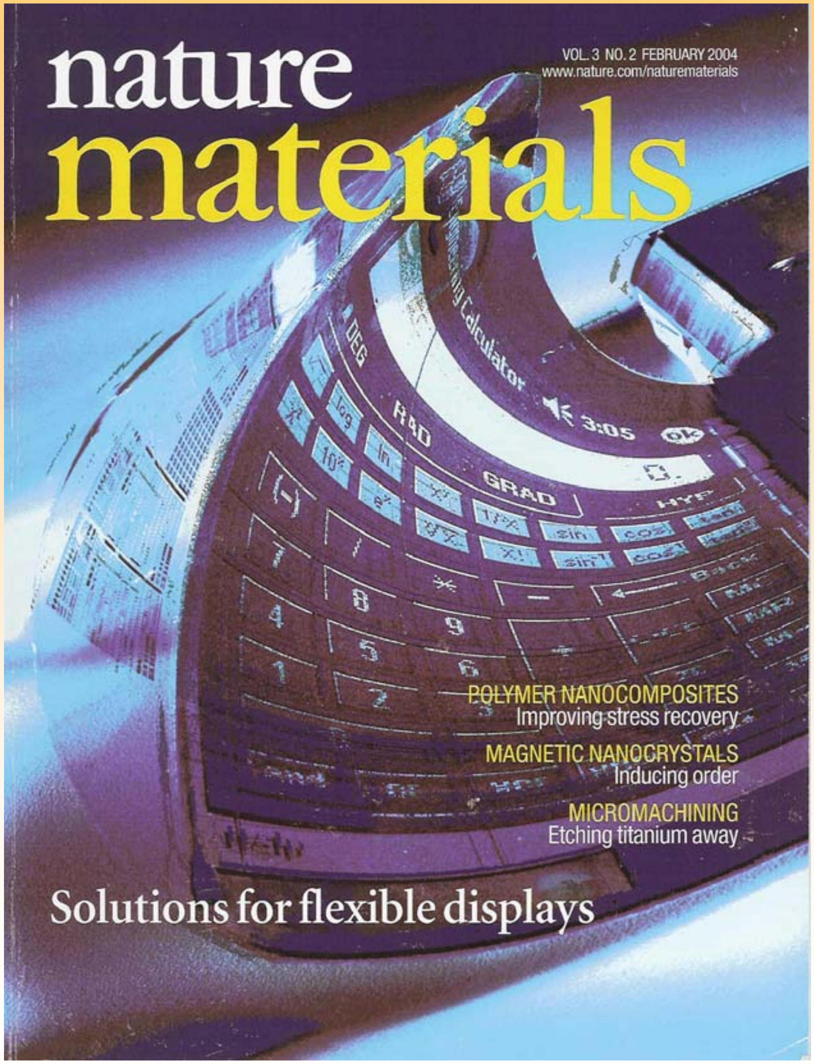
Organic Field-Effect Transistors

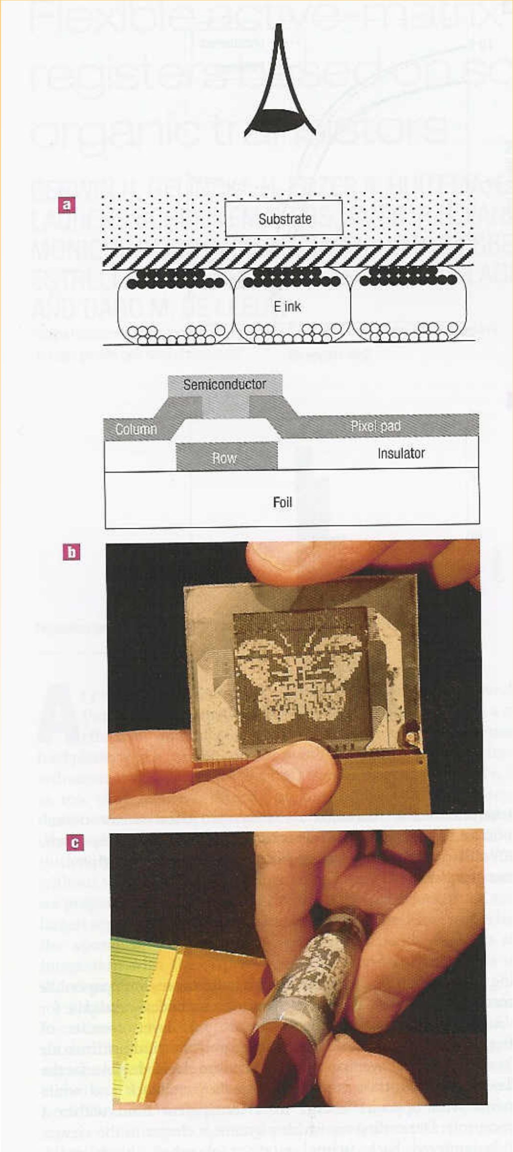
"Paper 2.0"
E-Ink/Lucent



http://www.research.phillips.com

"Paper 2.0" E-Ink – Recent Updates





February 2004

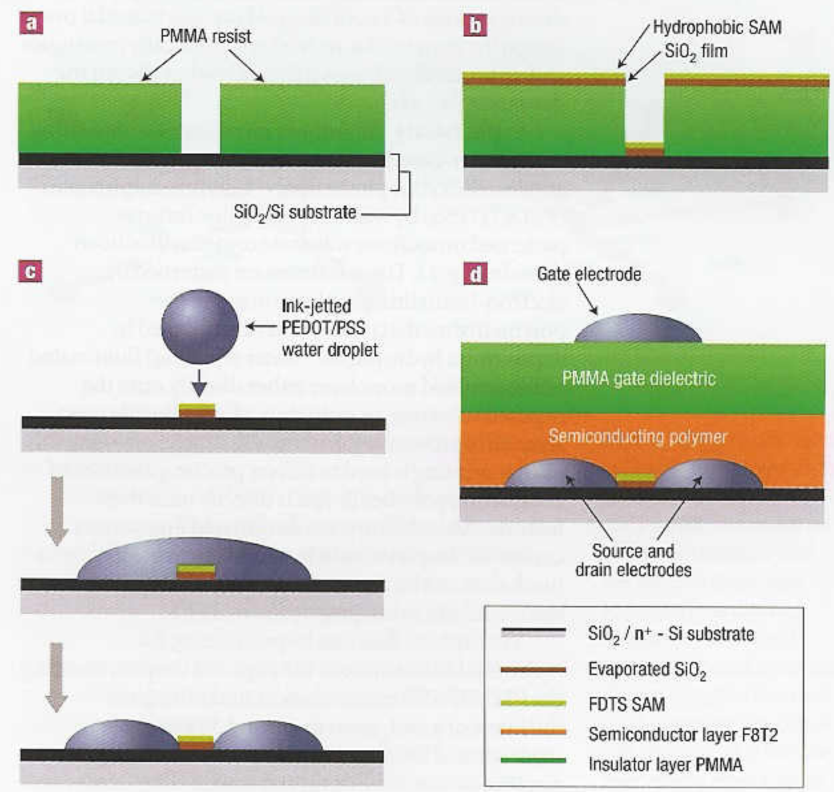
Inkjet Printing/Self-Organization >> New Electronic Technologies

CONDUCTING POLYMERS

Fine printing

nature materials

VOL. 3 NO. 3 MARCH 2004
www.nature.com/naturematerials

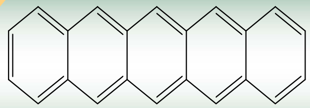


March 2004

Dewetting of conducting polymer inkjet droplets on patterned surfaces

J. Z. WANG[1], Z. H. ZHENG[1], H. W. LI[2], W.T.S. HUCK[2] AND H. SIRRINGHAUS[1*]
[1]Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, UK
[2]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK
*e-mail: hs220@phy.cam.ac.uk

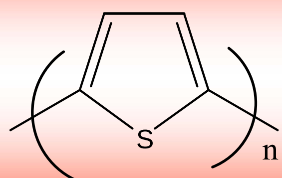
Materials of Interest



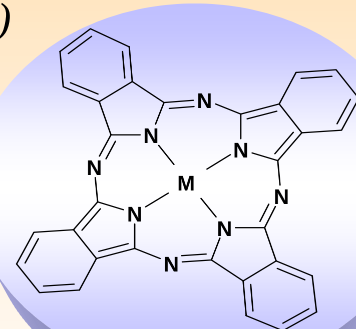
Pentacene
$\mu = 3.4\ cm^2V^{-1}S^{-1}$
Kelly et al
J.Phys.Chem .B (107) **2003** 5877

Amorphous silicon

$\mu = 1.0\ cm^2V^{-1}S^{-1}$



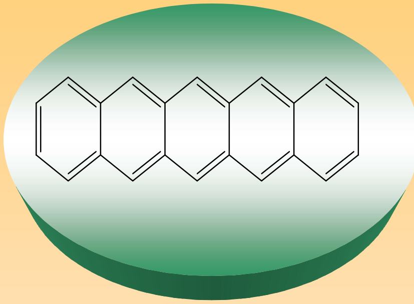
Poly thiophene
$\mu = 0.1\ cm^2V^{-1}S^{-1}$
Sirringhaus et al
Science 280 **1998** 1741

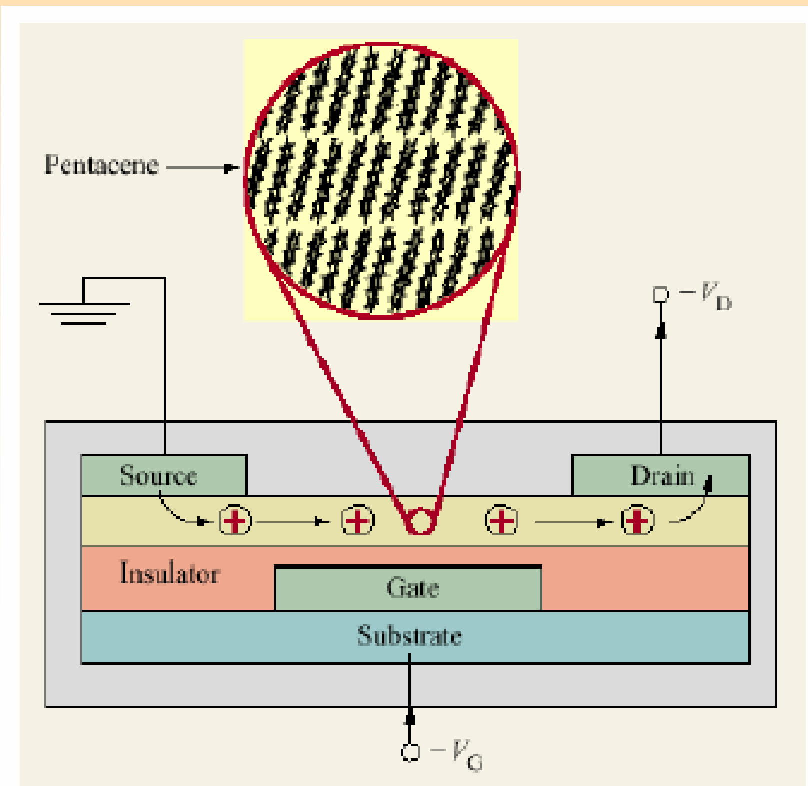


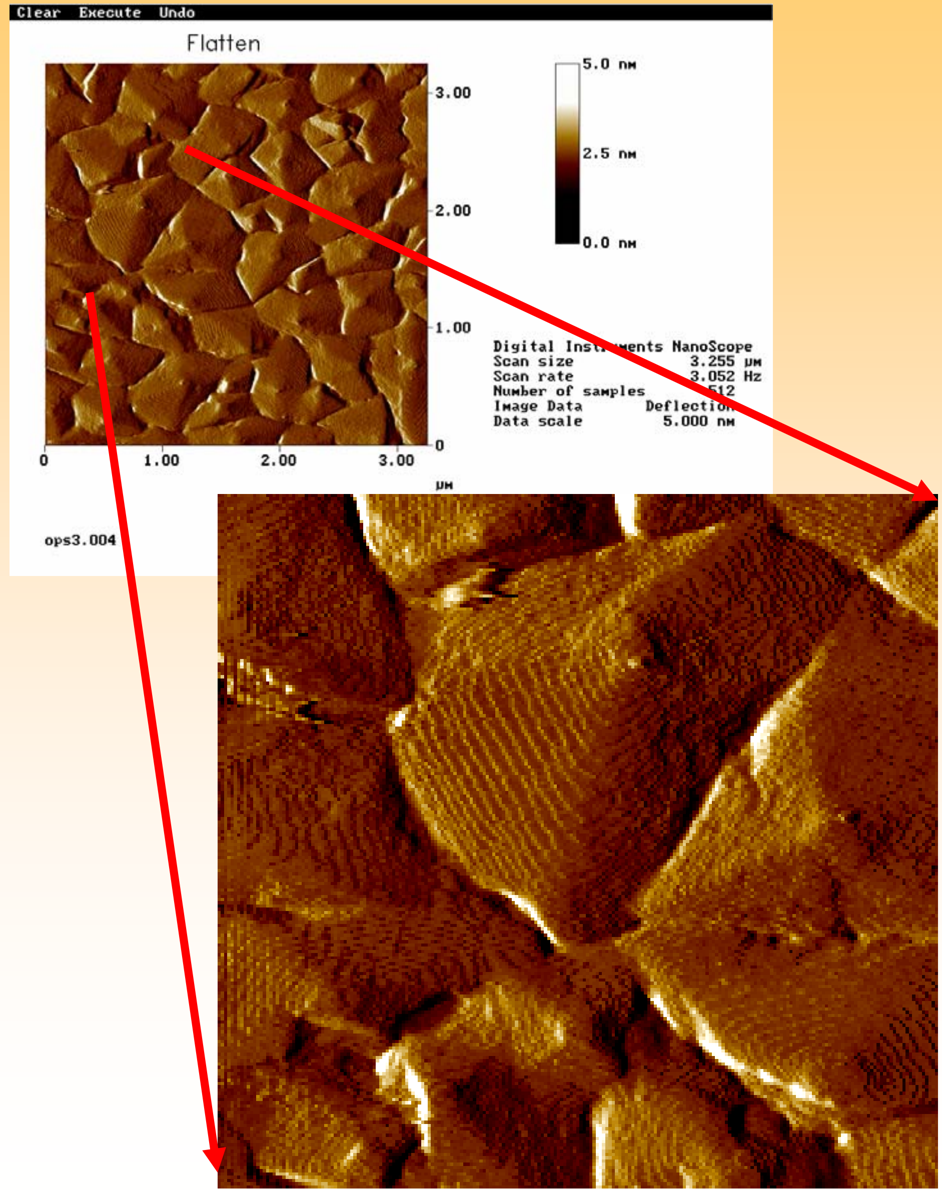
Phthalocyanine
$\mu = 0.02\ cm^2V^{-1}S^{-1}$
Dodabalapur et al
App.Phys.Lett.69 **1996** 3066

Oligothiophene
α-6T $\mu = 1.1\ cm^2V^{-1}S^{-1}$
Dodabalapur et al
Science (290) **2000** 963

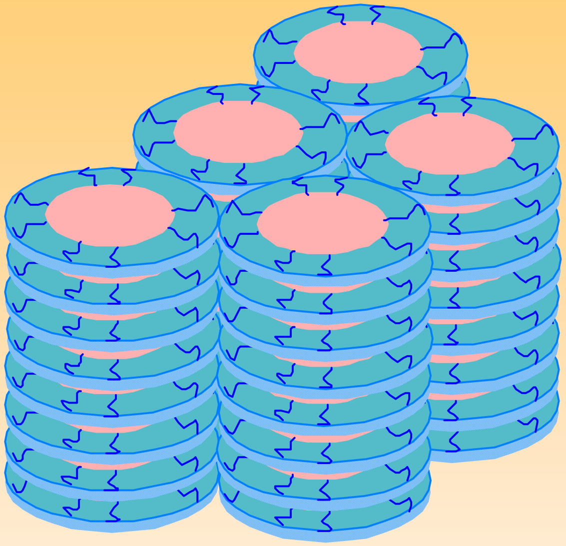
State-of-the-Art: Pentacene OFETs

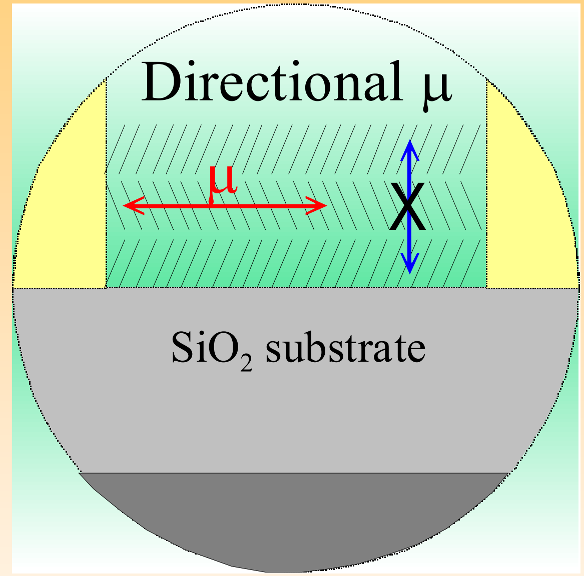


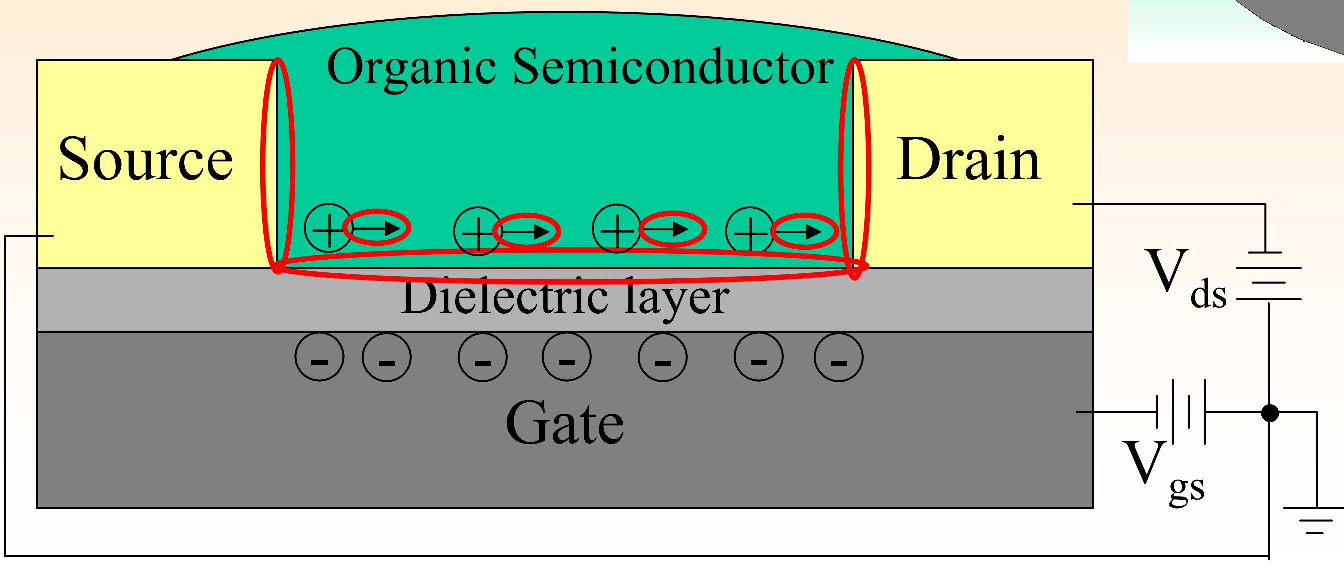




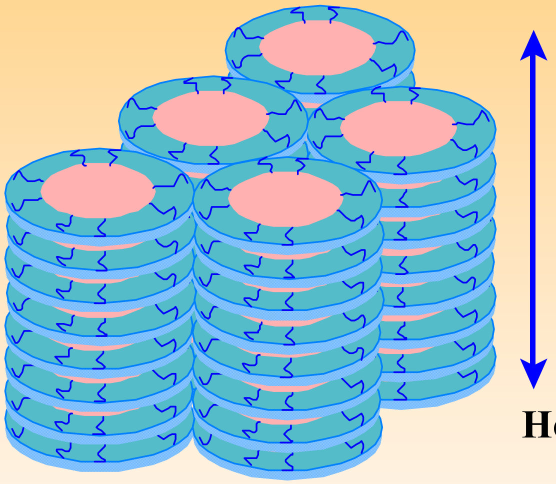
Discotic Mesophase Materials in Organic Field Effect Transistors



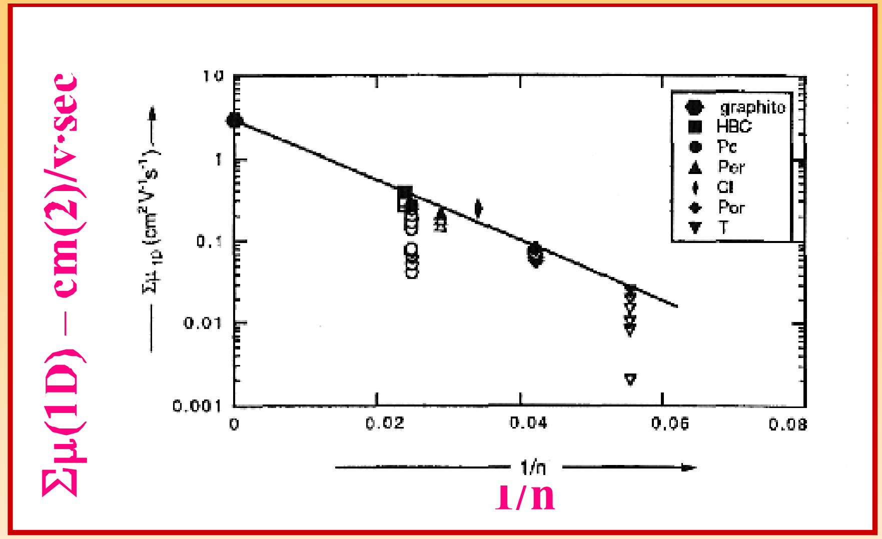




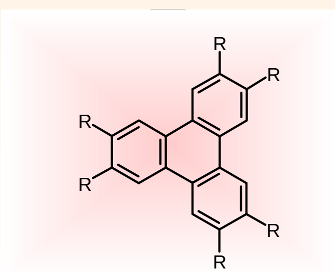
Charge Mobilities in Discotic Mesophase Materials



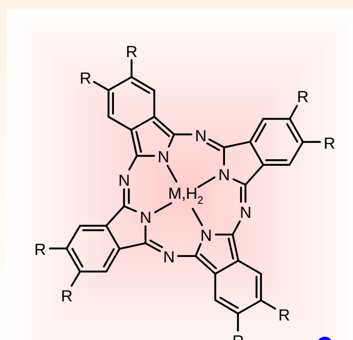
Hole transport



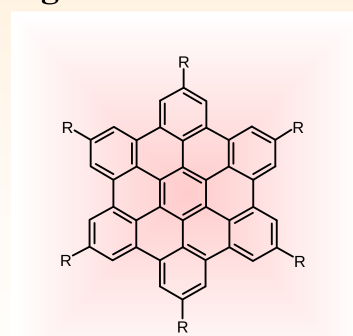
Warman – Adv. Mater. 13(2001)131
Pulsed-radiolysis transient microwave conductivities – measurement
coherence length = ca. 100 nm



$\mu = 0.1\ cm^2 V^{-1} s^{-1}$
Adam, et.al.
Nature 371(1994)141

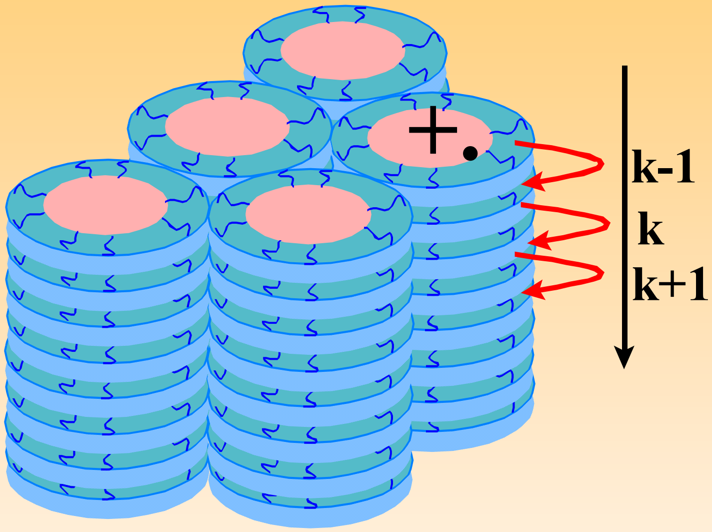


$\mu = 0.02 \rightarrow 0.2\ cm^2 V^{-1} s^{-1}$
e.g. Gattinger, et. al.
JPC-B 103(1999)3179.



$\mu = 0.5 \rightarrow 1.0\ cm^2 V^{-1} s^{-1}$
van de Craats, et.al.
Adv. Mater. 11(1999)1469

Charge hopping in van der Waals solids



<u>Polaronic model:</u>

$$k_{ET} = f_0 \exp [-(E^p_{k+/-1} - E^p_k + 2\lambda_p)^2/8k_BT\, \lambda_p]$$

e.g.: Schouten, Warmen, et. al.,
***J. Amer. Chem. Soc.*, <u>114</u>, 9028 (1992).**

<u>Simplified Marcus model:</u>

$$k_{ET} = (4\pi^2/h)\, [1/(4\pi\lambda k_BT)^{1/2}]\, (t^2)\exp(-\lambda/4k_BT)$$

e.g. Brédas and coworkers,
***Proc. Nat'l. Acad. Sci.*, <u>99</u>, 5804 (2002);**
***Advanced Materials*, <u>13</u>, 1053 (2001);**
***Chem. Phys. Lett.*, <u>327</u>, 13 (2000).**

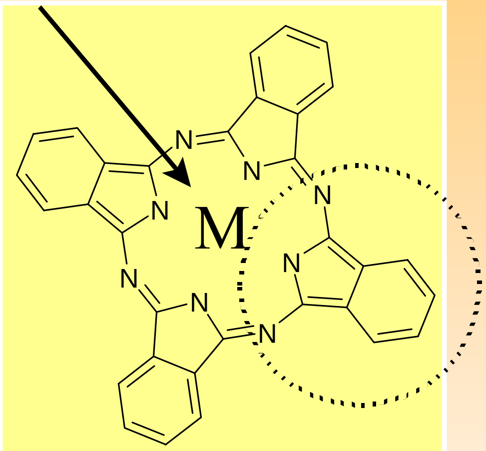
Hole/Electron mobilities related to:

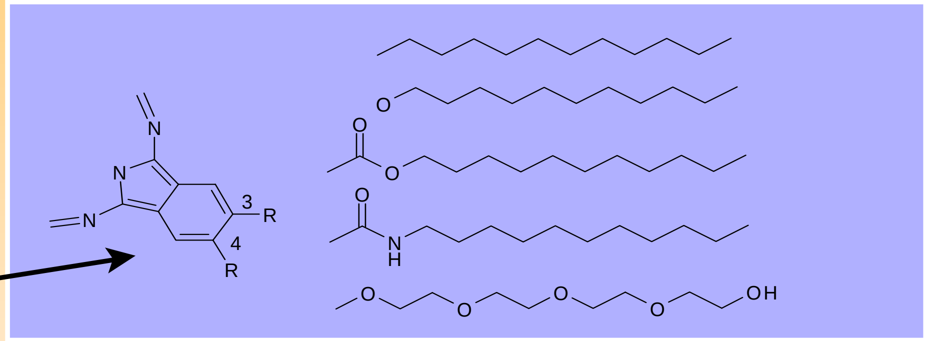
a) **(+./-.) stabilities,**
b) **low reorganization energies for charge movement (λ),**
c) **large electronic transfer integrals (t).**

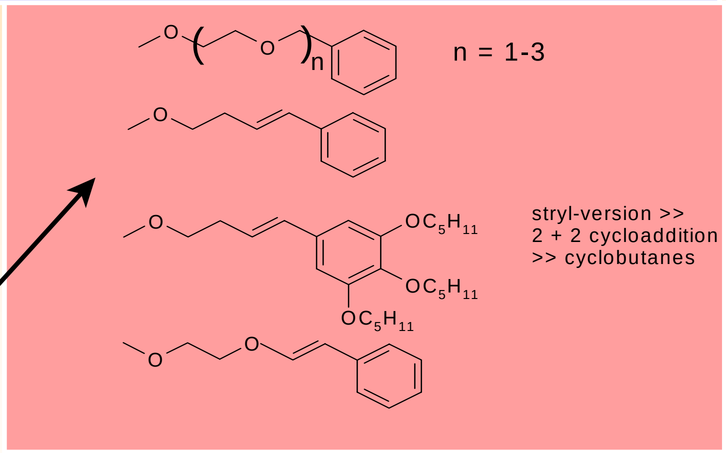
New Self-Organizing Materials

Building a discotic mesophase Pc

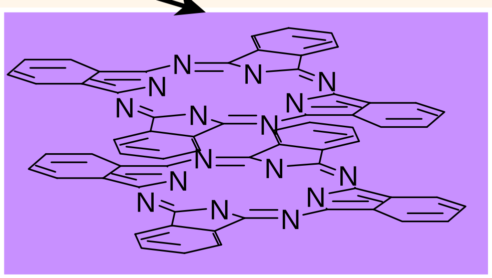
Central metal selection







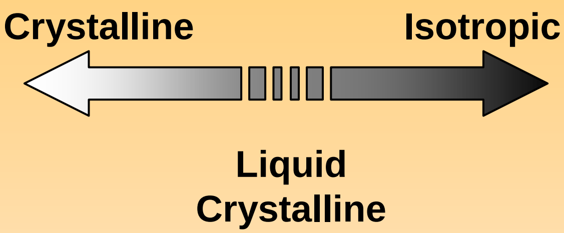
Pc-Pc interactions – "polymorphism"

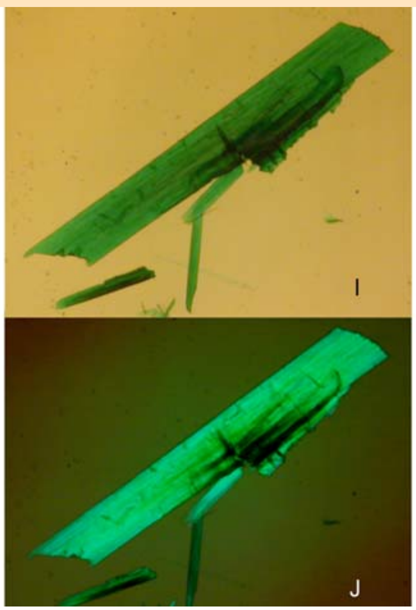


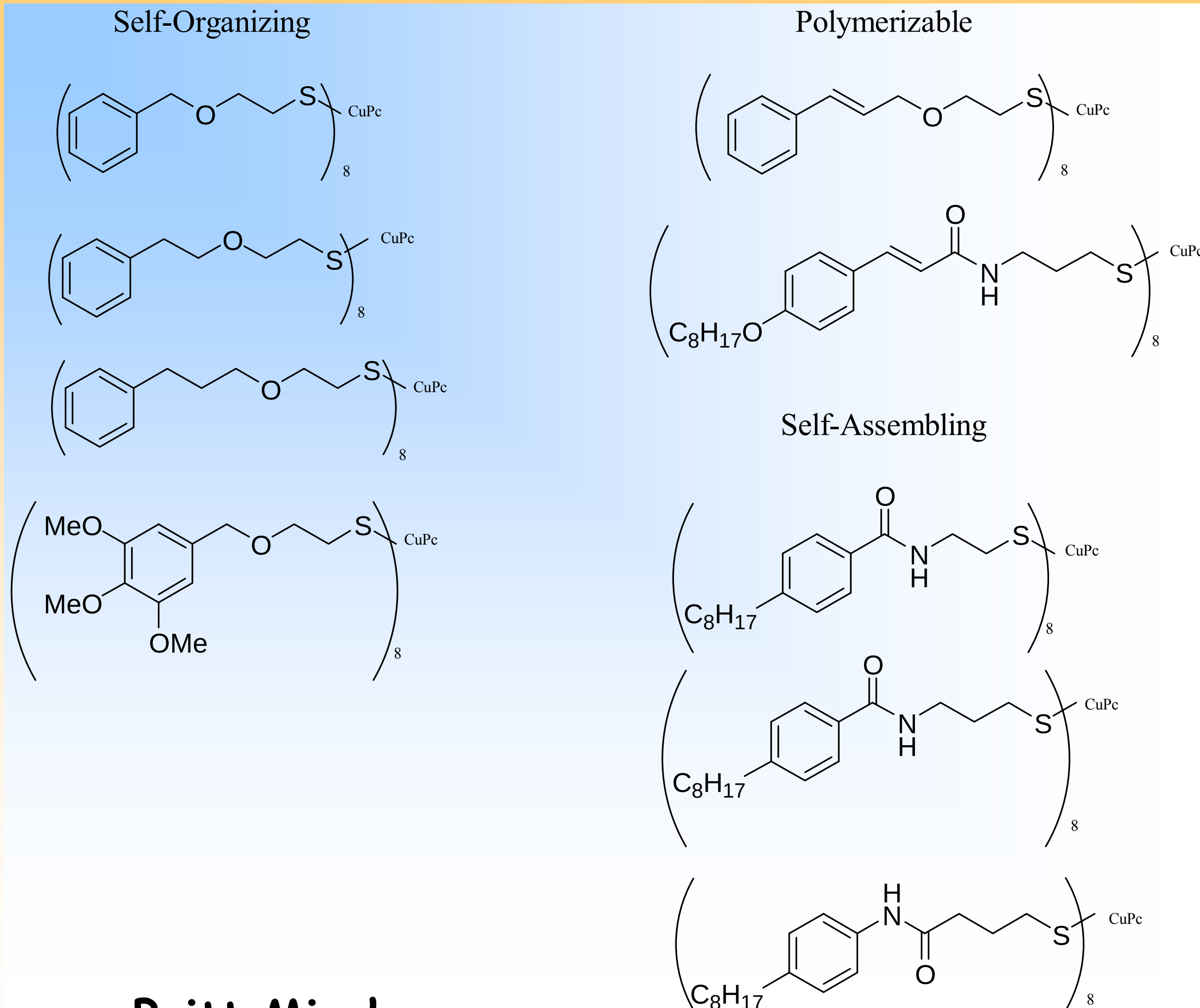
Side chain interactions – electron withdrawing, electron donating, site of attachment, length of side chain, branching, polymerizable groups, terminal groups

Drager, O'Brien, *J.Org. Chem.* 2001

Recent Targets

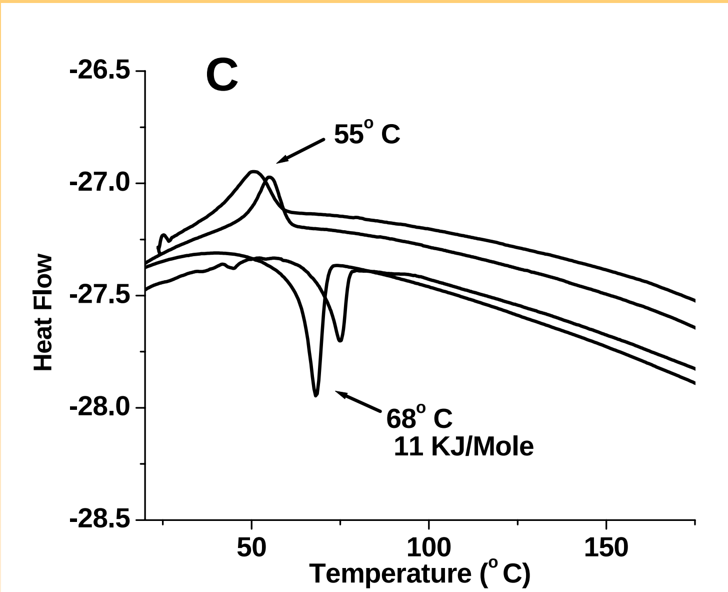


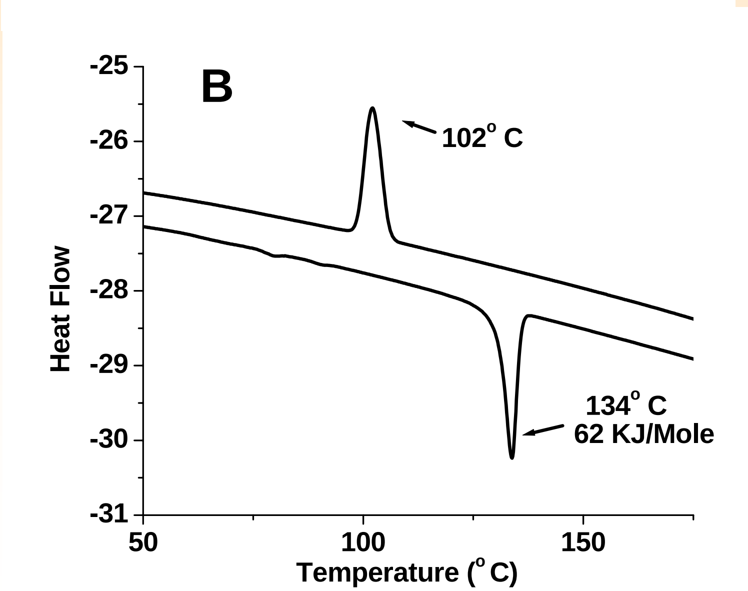


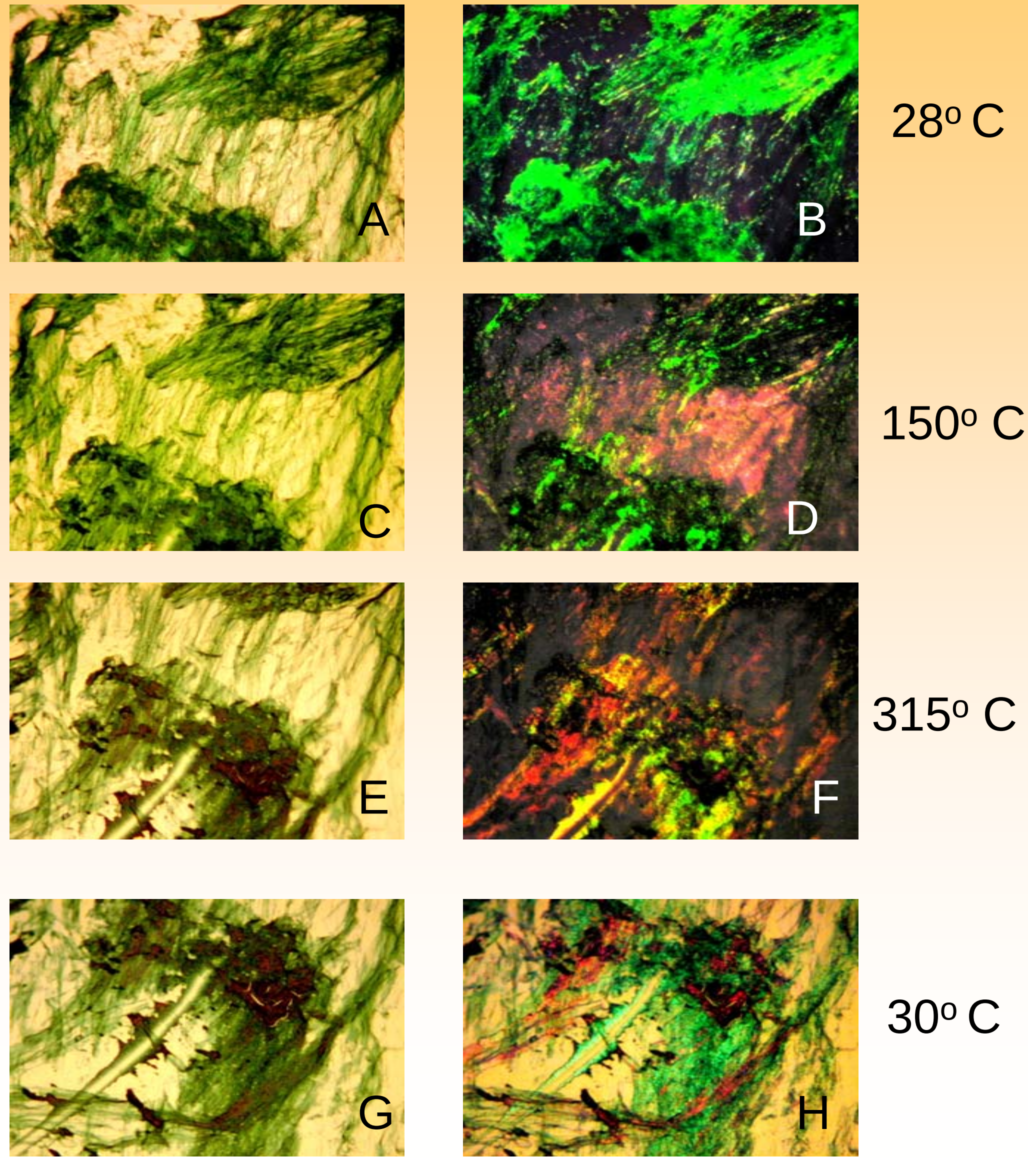


Britt Minch,
Ryan Hernandez

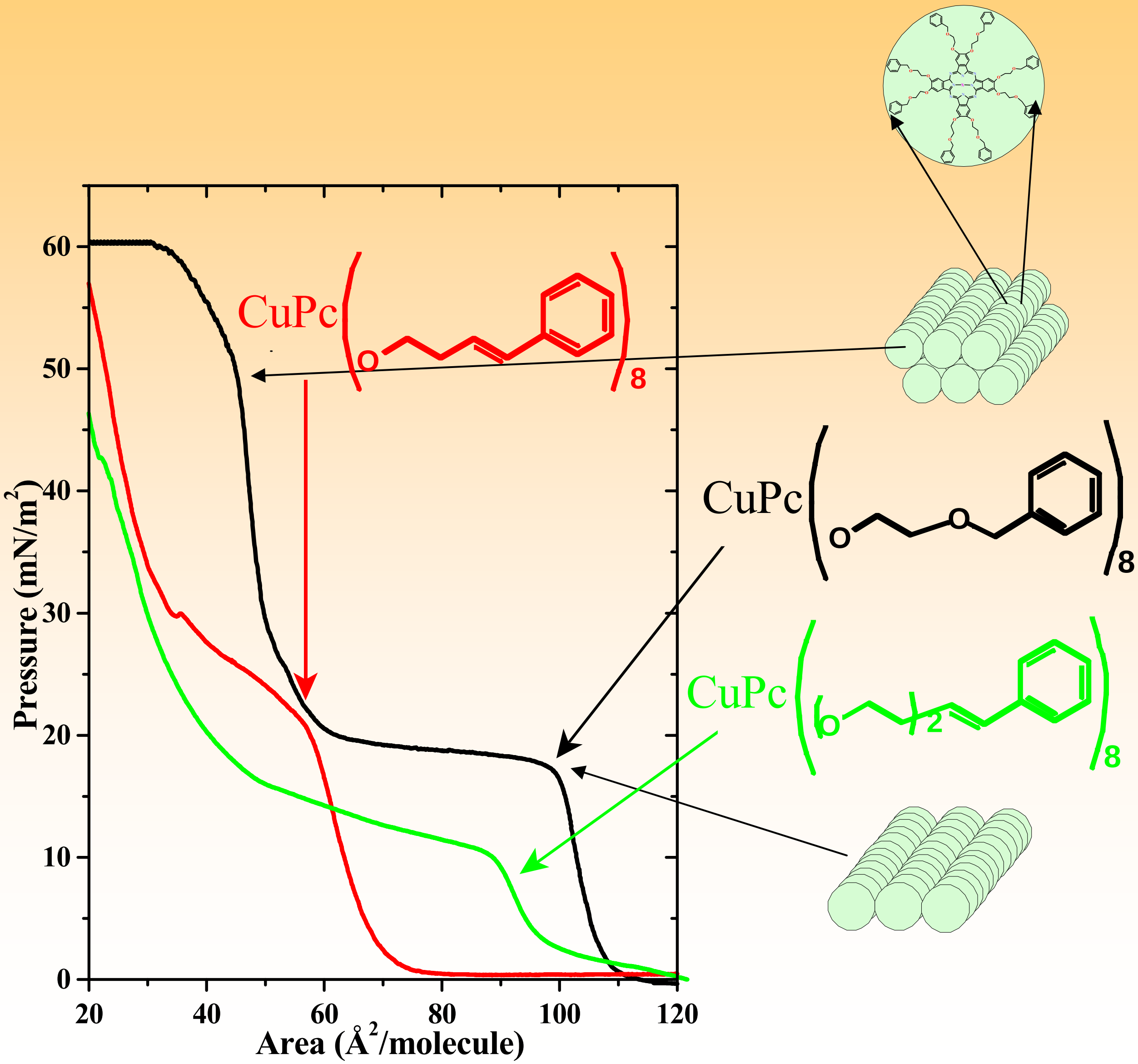
Thermal properties of new Pcs (K → LC) transitions

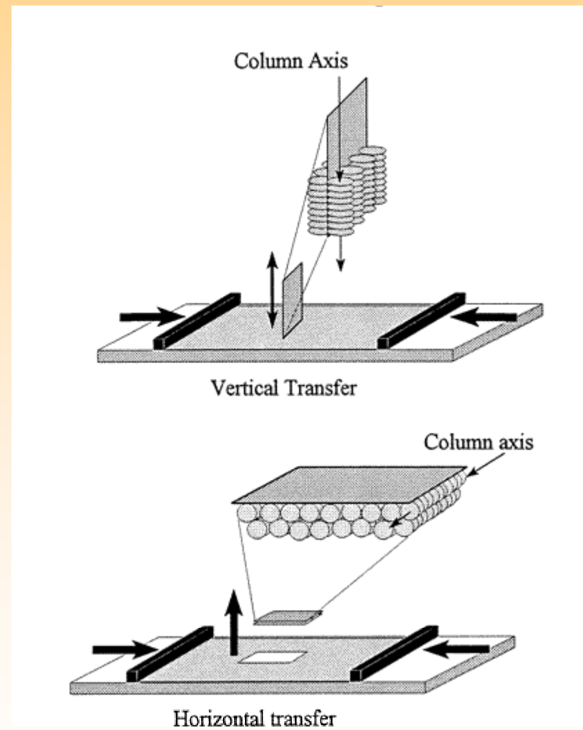




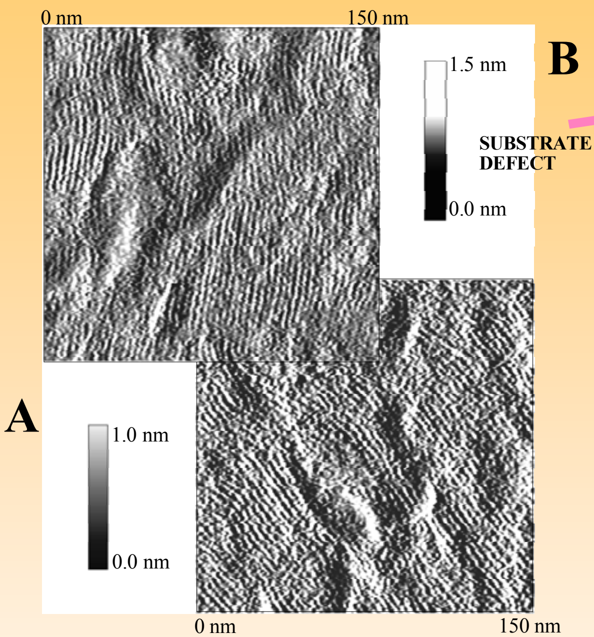


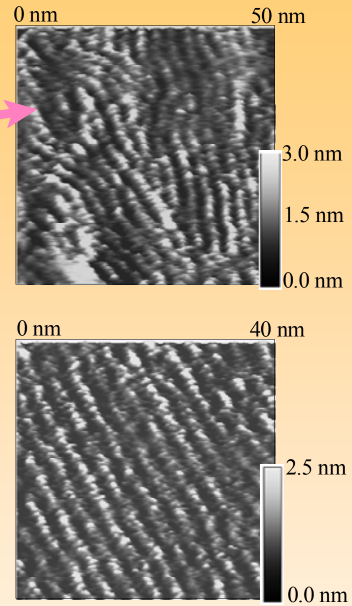
Horizontally Transferred Monolayers/Bilayers from LB Films

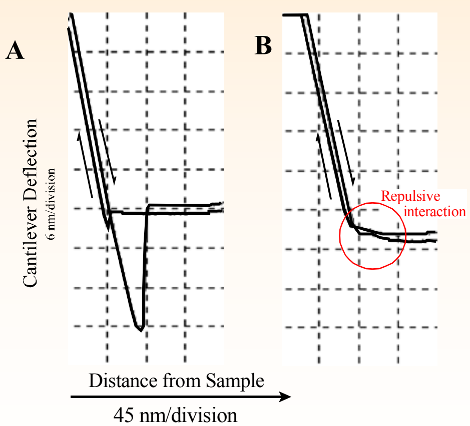




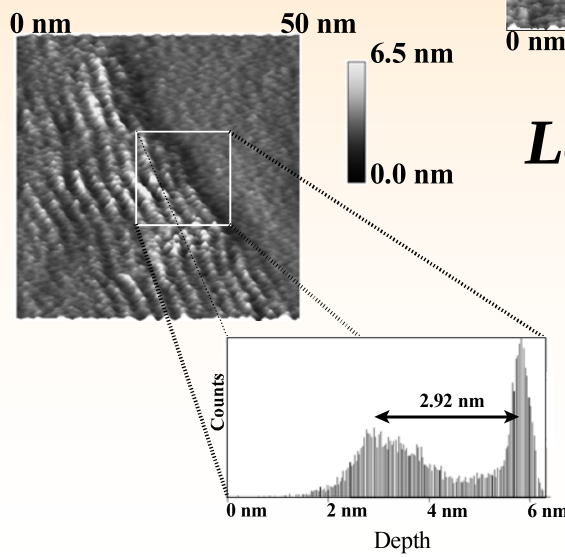
Tapping Mode AFM (solution) Single Bilayers/Si(100)

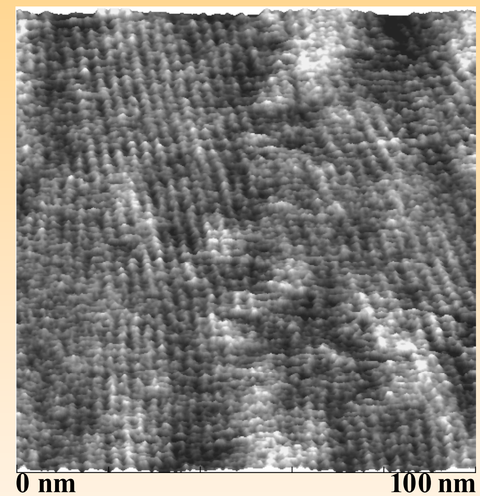






***JACS*, 1999**

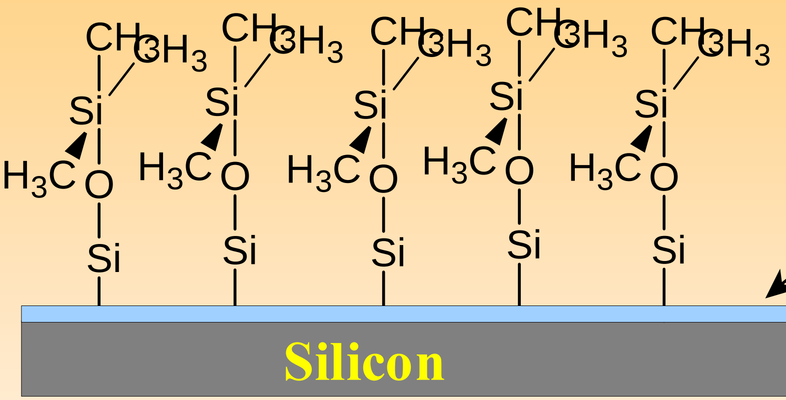




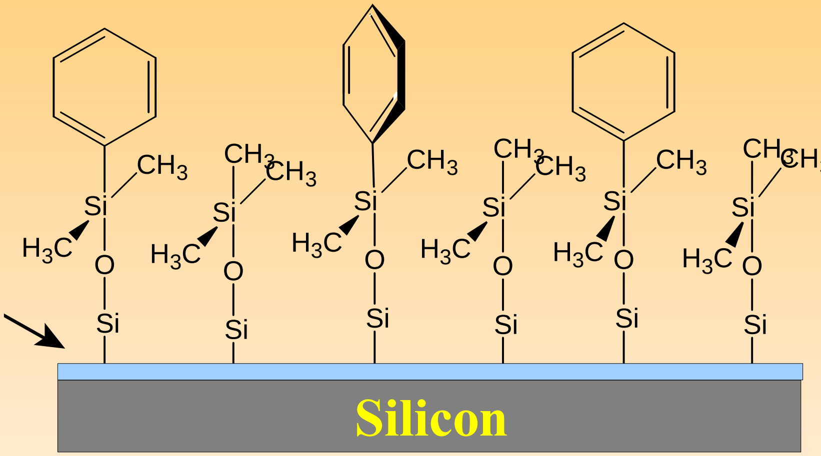
***Langmuir*, 2001**

Interface Modification >> Macroscopic/Microscopic Order

Methyl

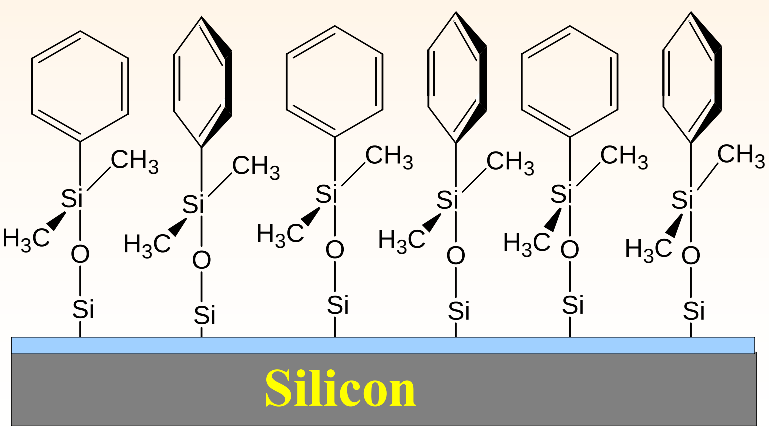


Phenyl/Methyl

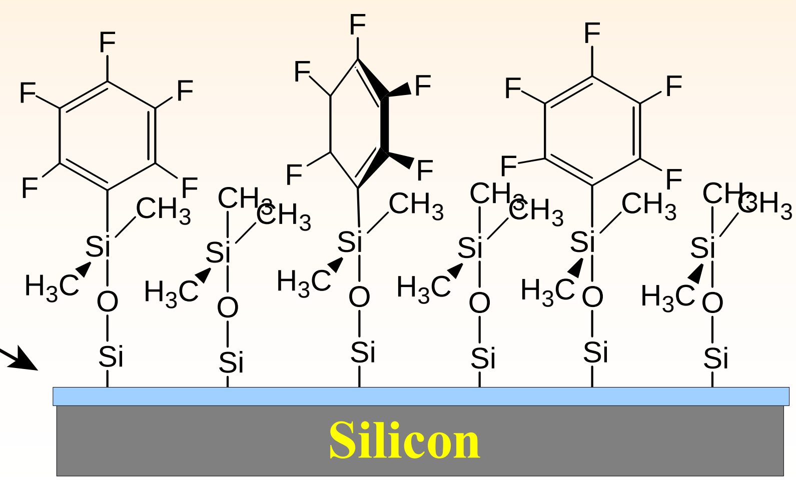


Oxide

Phenyl

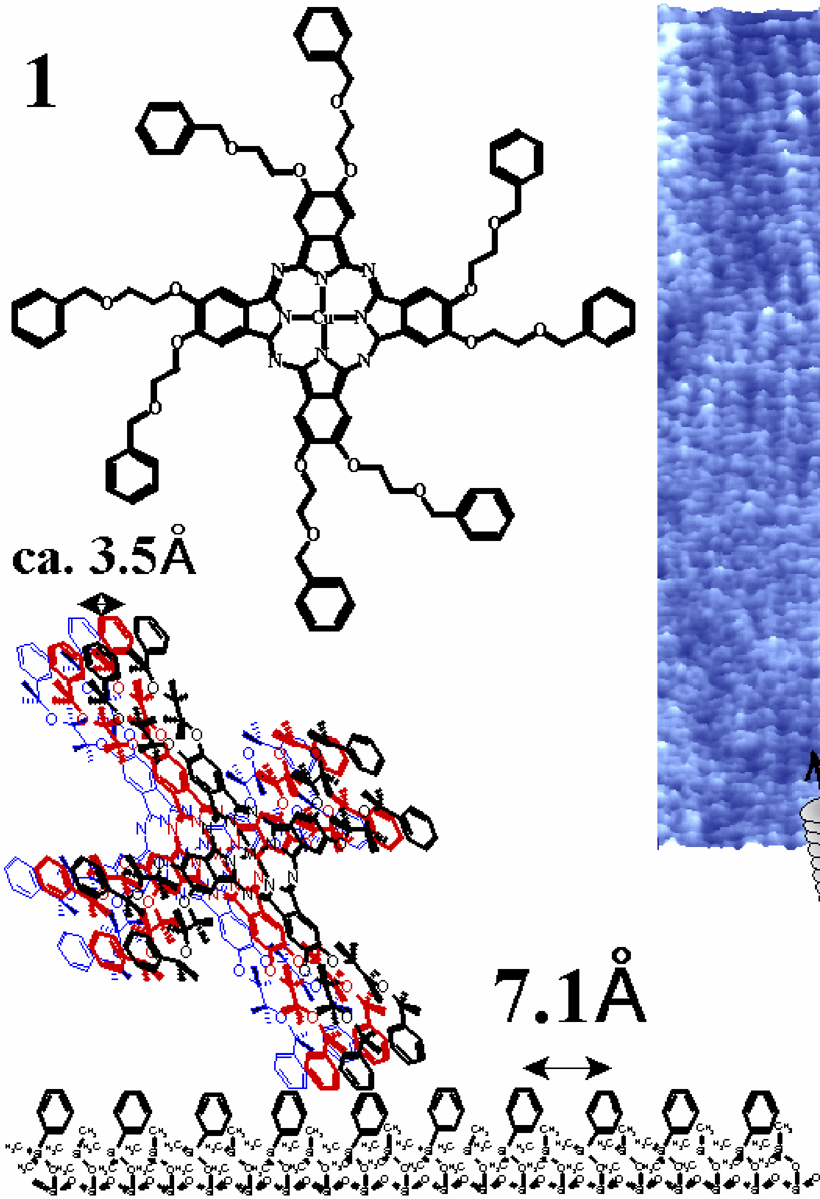


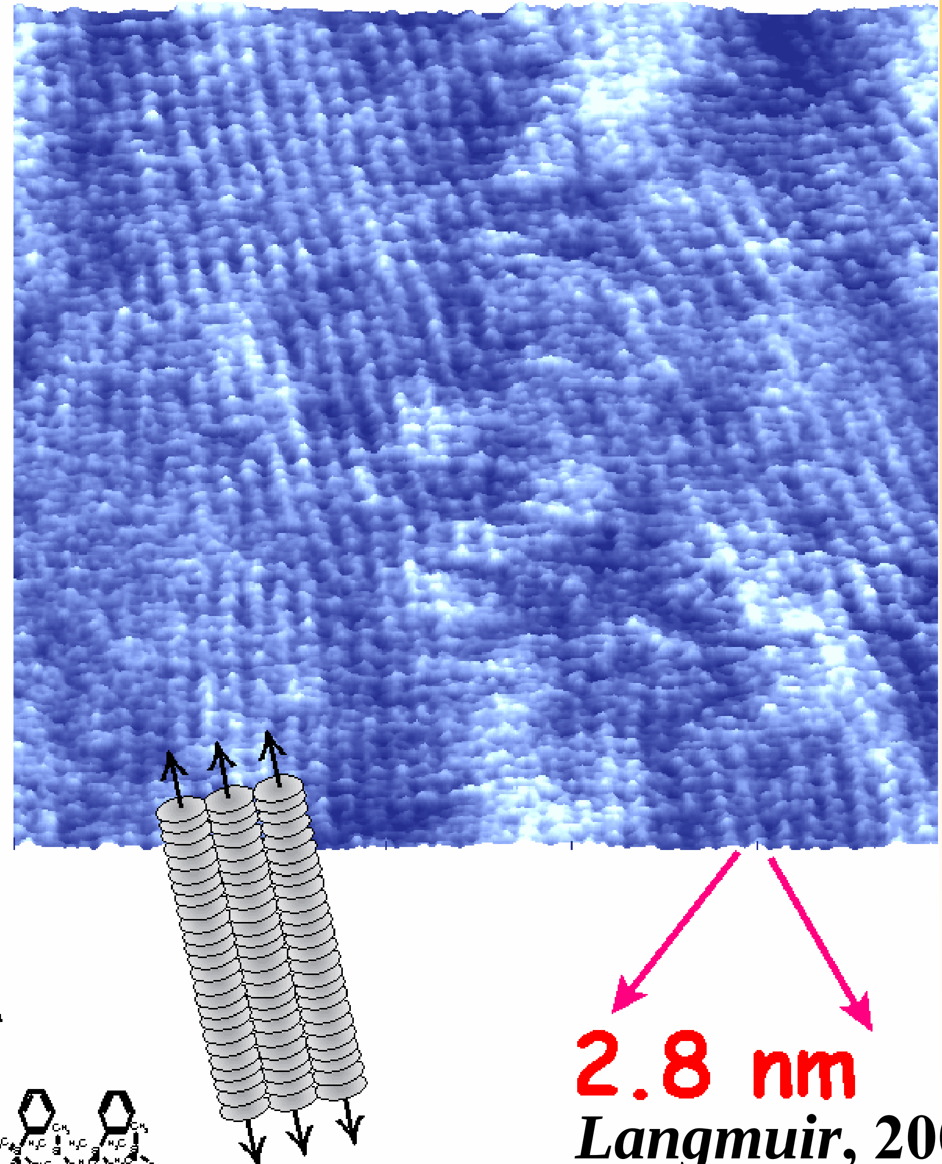
Fluorophenyl/Methyl



Oxide

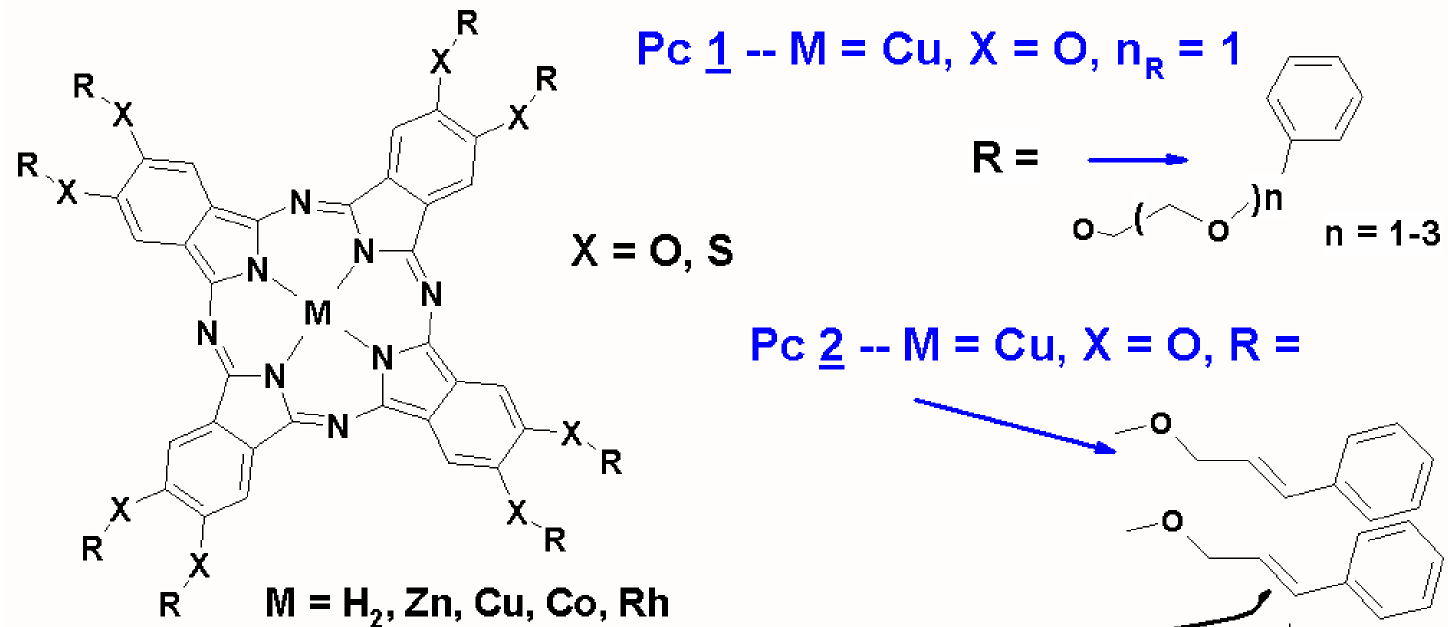
Coherence of Rod-Like Aggregates of 100-300 nm

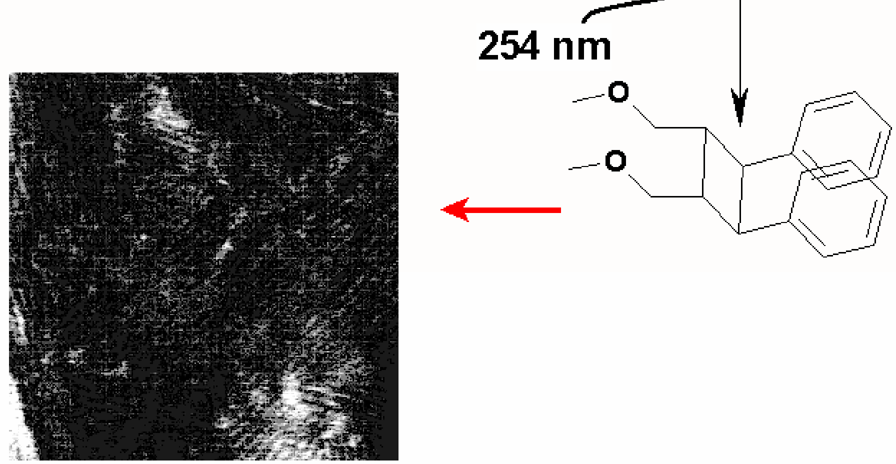




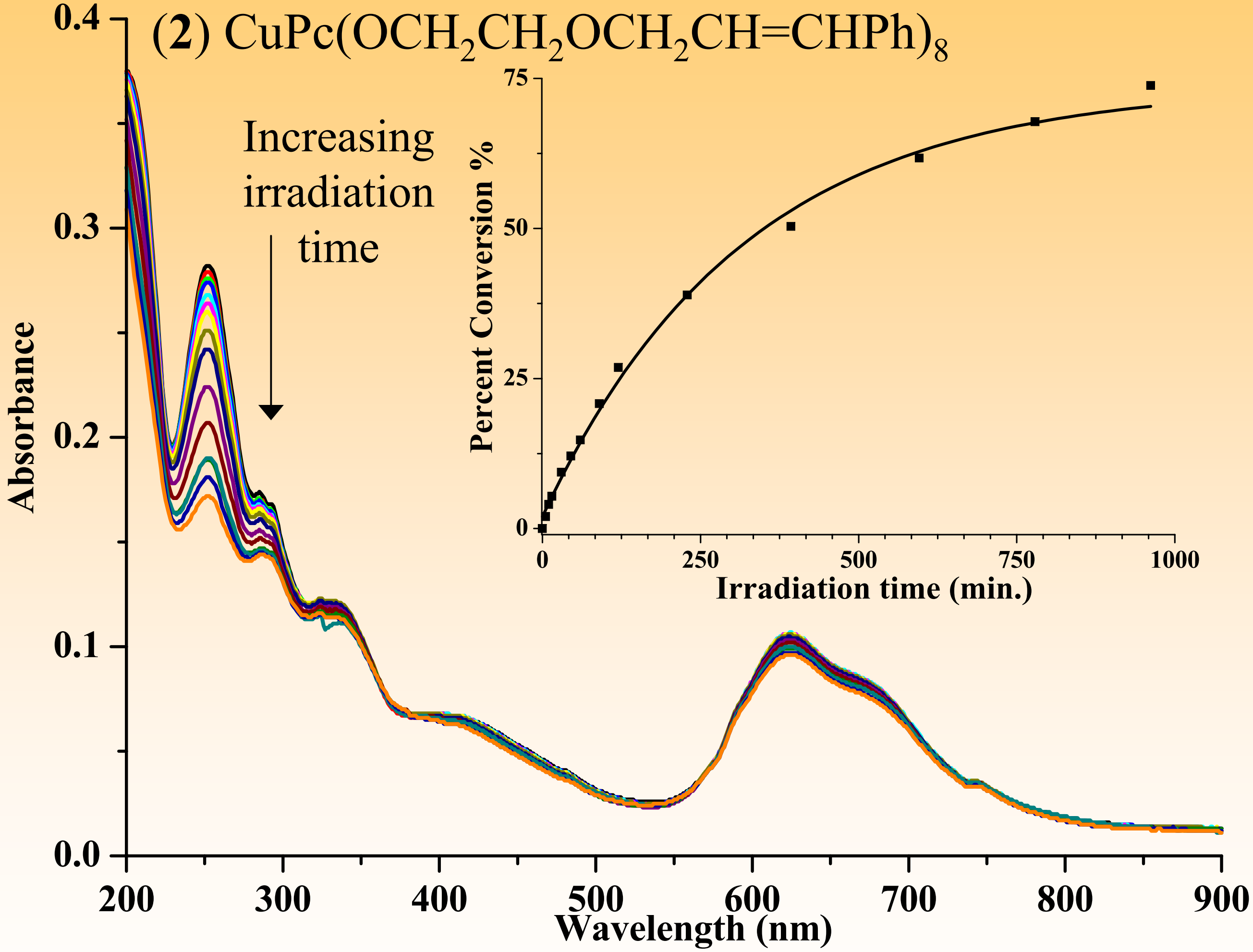
Langmuir, 2001

Other processing strategies – photopolymerization of rod-like aggregates





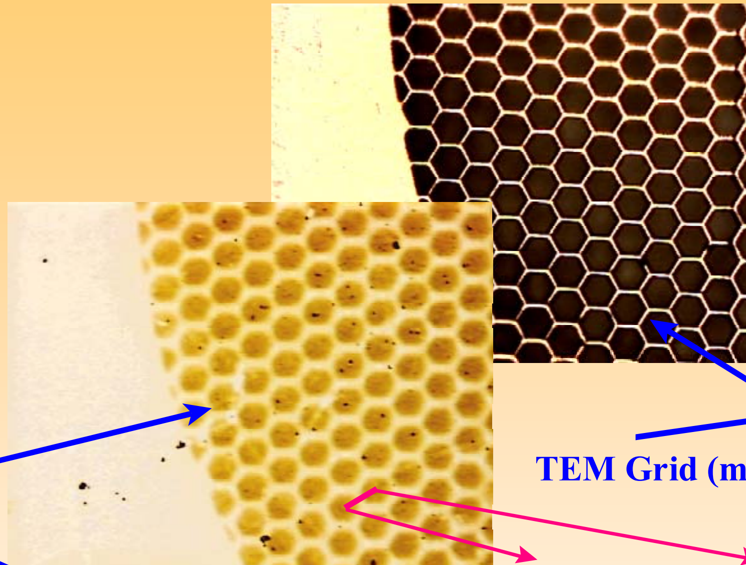
Conversion efficiency = ca. 75% -- Strongly Cross-linked



Drager, Zangmeister, Armstrong, O'Brien – *JACS* 2001

Donley, Xia, Minch, Zangmeister, Armstrong, O'Brien – *Langmuir* 2003

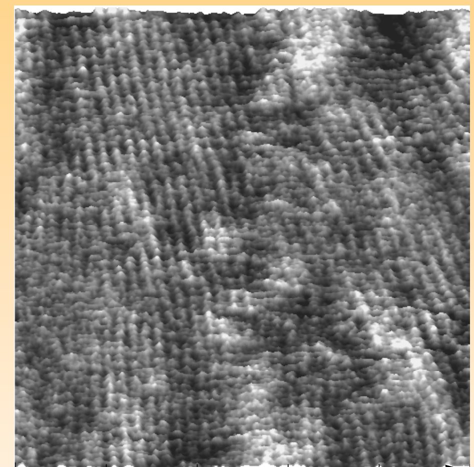
Photolithography Down to 2 micron Features

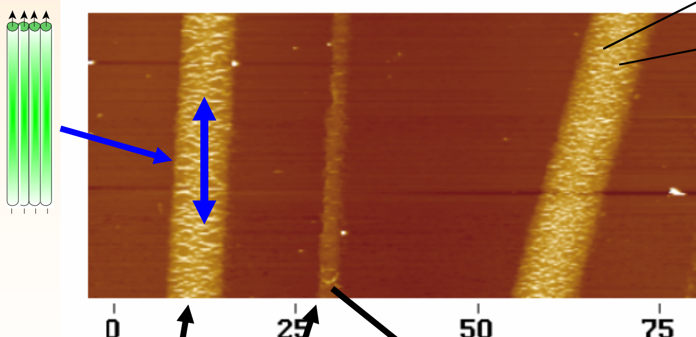


TEM Grid (mask)

40 micron spacing

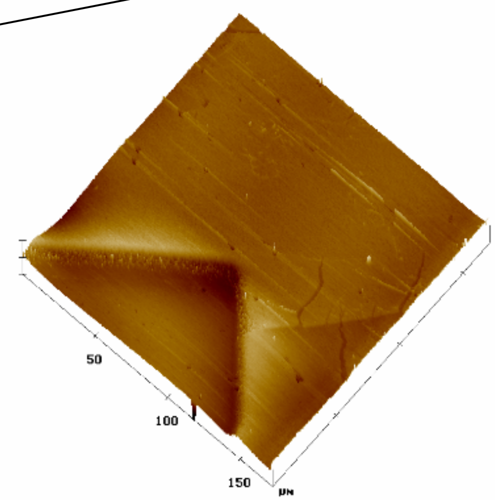
Patterned Pc (10 bilayers/Si(100), 254 nm exposure, followed by solvent wash.





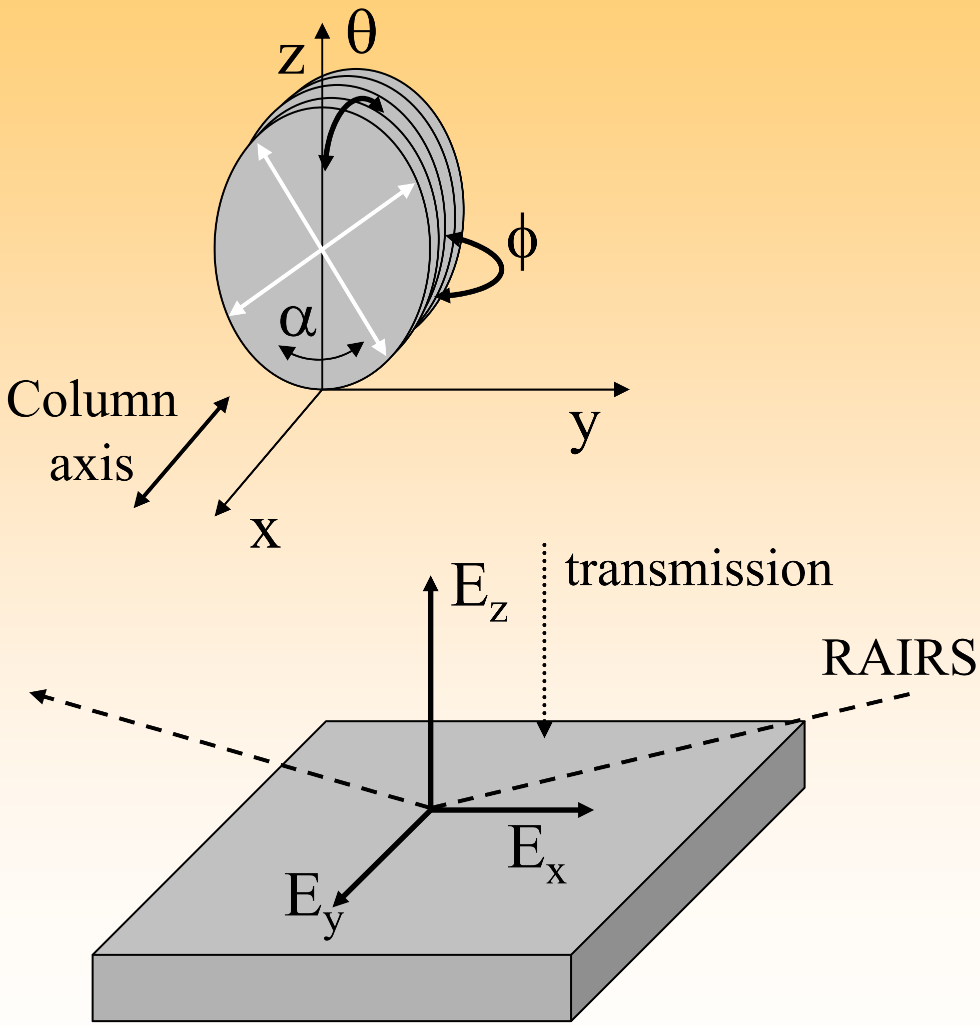
8μ 2 μ

>> sub-micron?

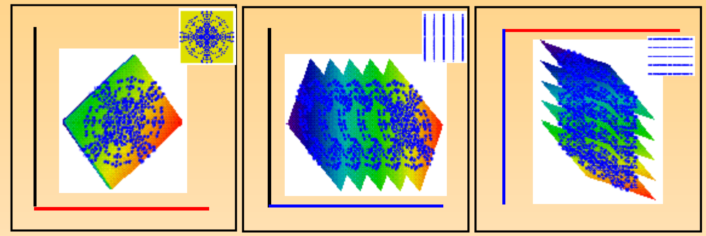


Donley, Xia, Minch, Zangmeister, Armstrong, O'Brien – *Langmuir* 2003

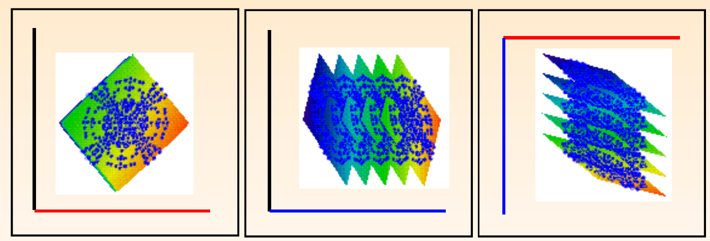
Microstructure: RAIRS and Transmisison FT-IR



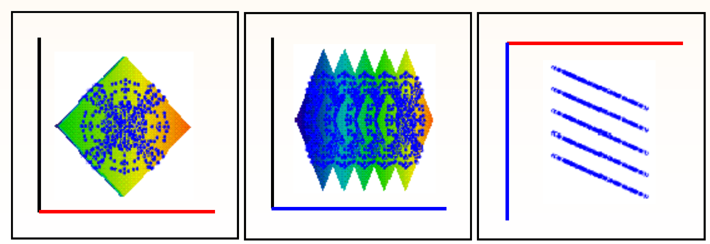
(A) Before annealing:
α = 45°, θ = 74°, ϕ = 55°



(B) After annealing:
α = 45°, θ = 77°, ϕ = 63°

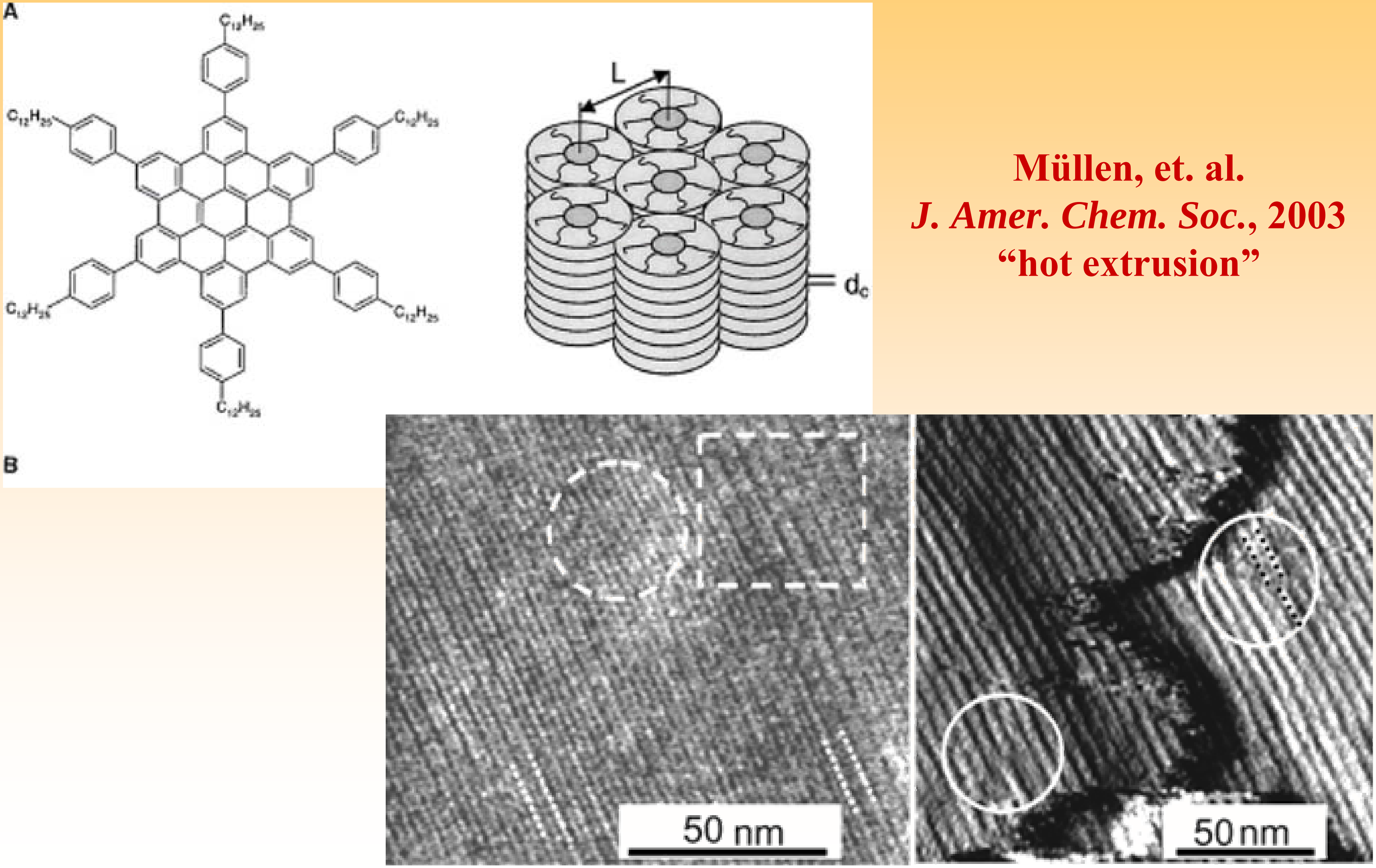


(C) After polymerization:
α = 45°, θ = 90°, ϕ = 66°



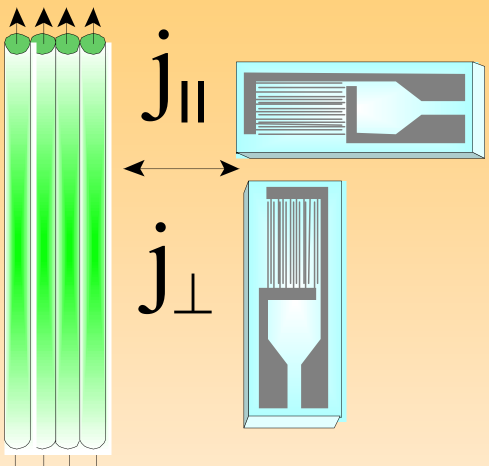
Carrie Donley, Sergio Mendes, in preparation

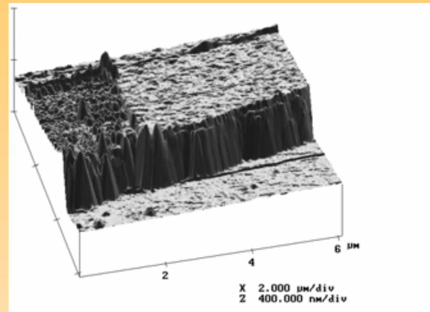
Other Appealing Discotic Mesophases: Hexa-benzocoronene -- HBC



Müllen, et. al.
***J. Amer. Chem. Soc.*, 2003**
“hot extrusion”

d.c. Conductivities – Interdigitated Array Microelectrodes



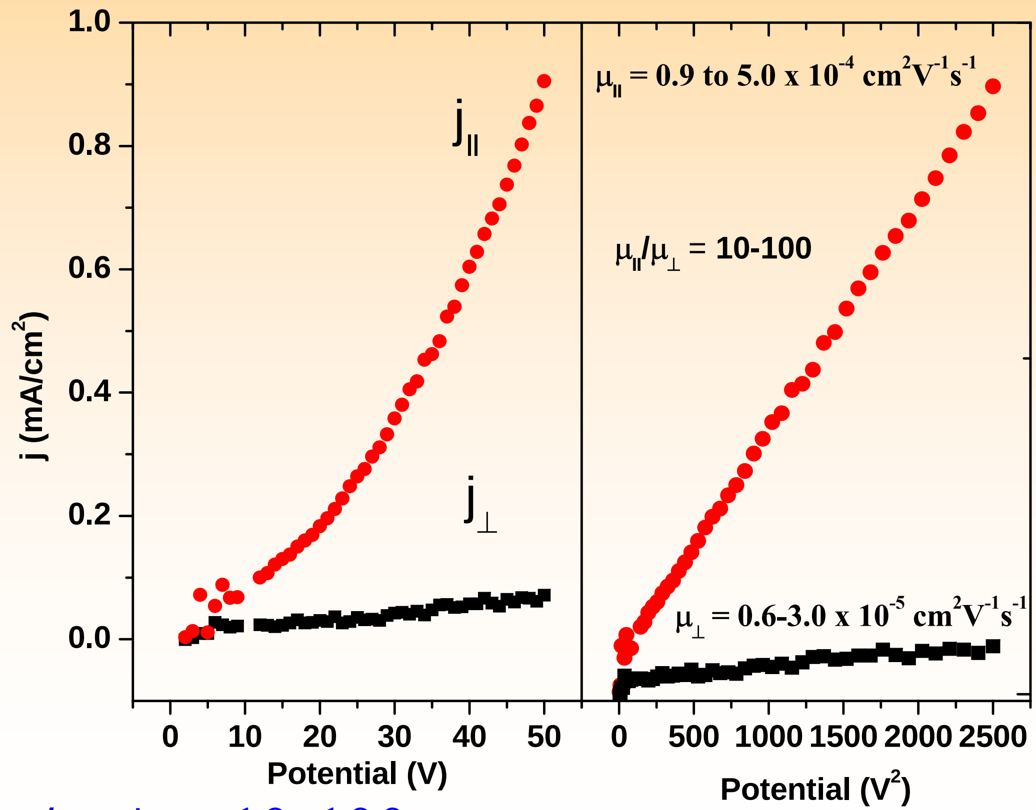


$$j_{\Omega} = ne\mu \frac{\mathrm{V}}{\mathrm{L}}$$

"ohmic" region

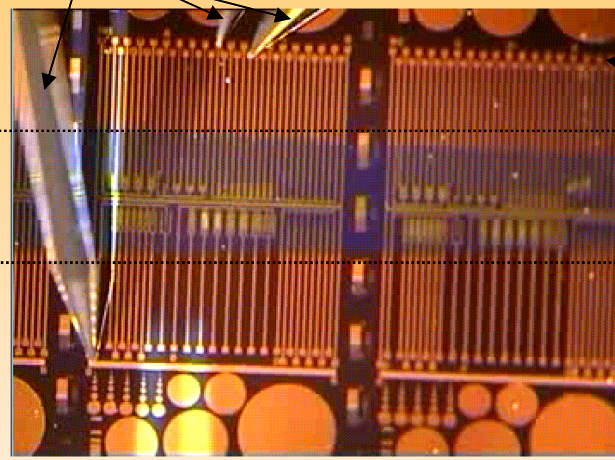
$$j_{\mathrm{SCLC}} = \frac{9}{8}\varepsilon_{o}\varepsilon\mu\frac{V^{2}}{d^{3}}$$

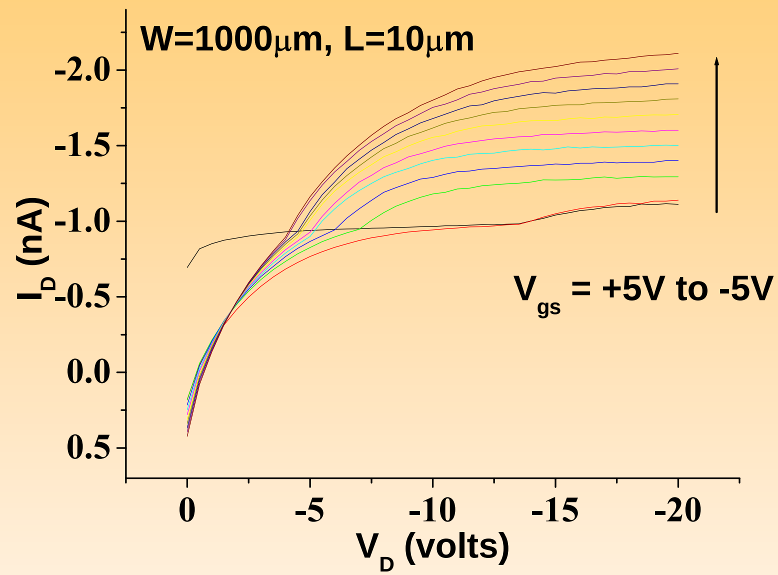
"SCLC" region

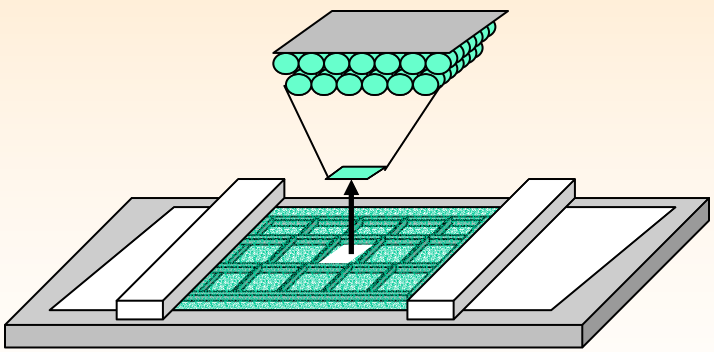


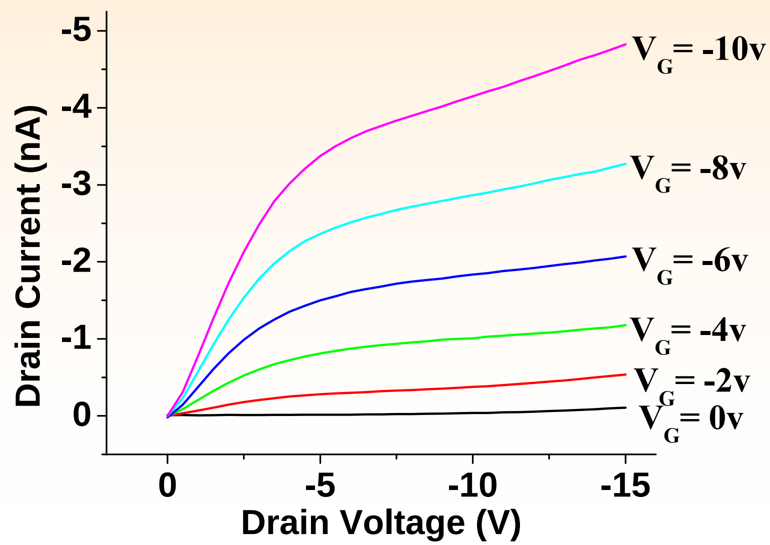
$\mu_{\|} \approx$ 5 x 10^{-4} cm^2/volt·sec; $\mu_{\|}/\mu_{\perp}$ = 10-100

Preliminary OFET Measurements – Anisotropies in Charge Mobilities









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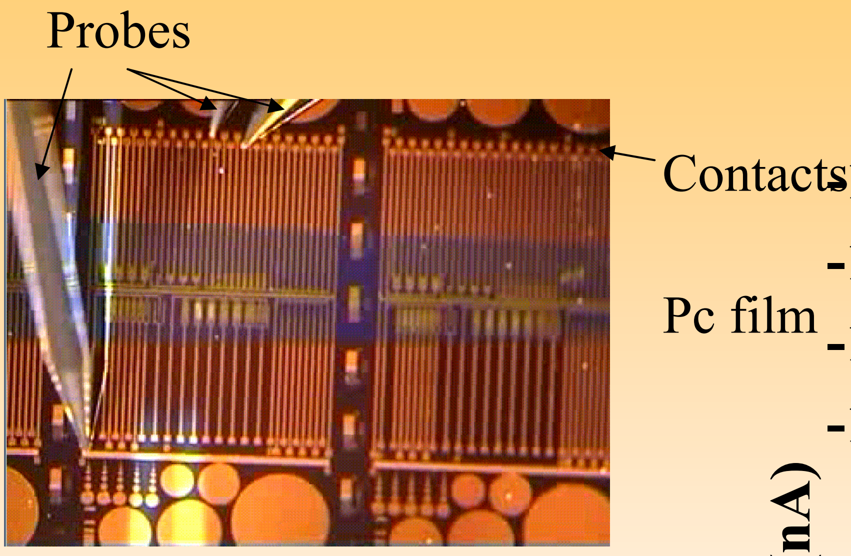
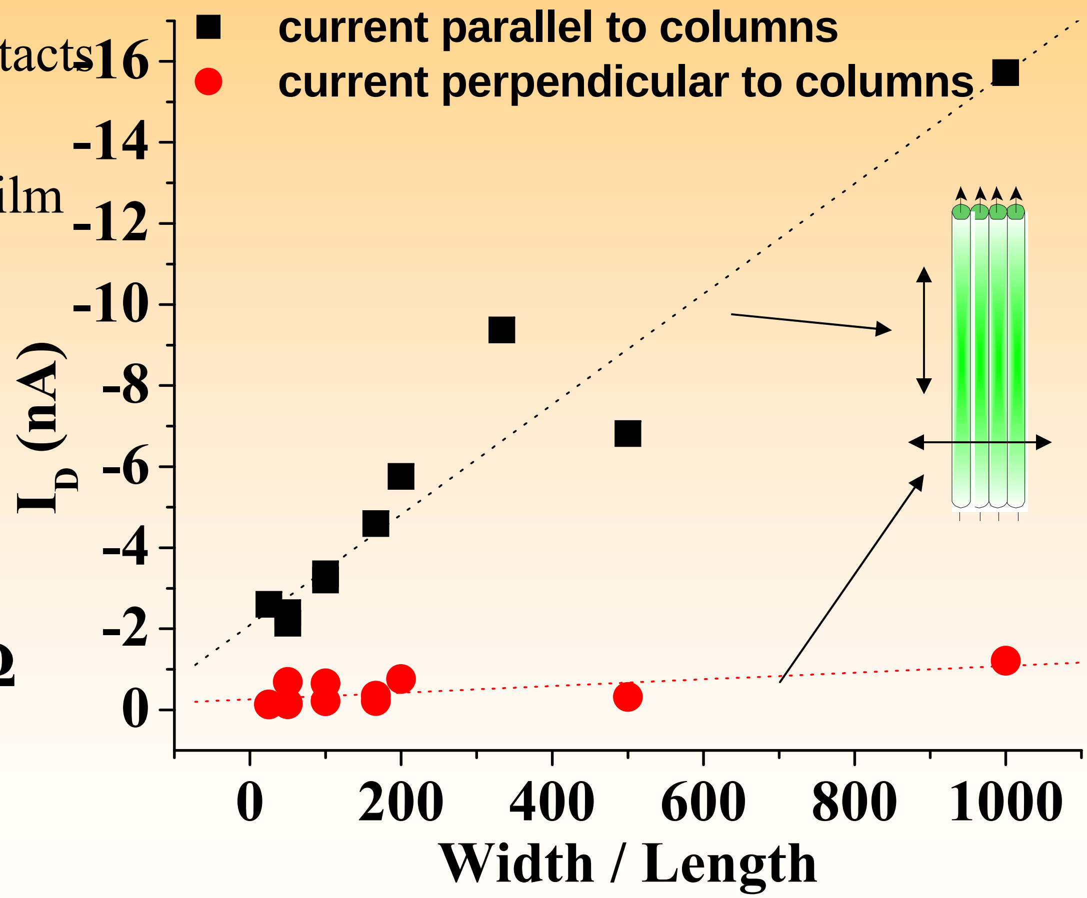
Preliminary OFET Measurements – Anisotropies in Charge Mobilities

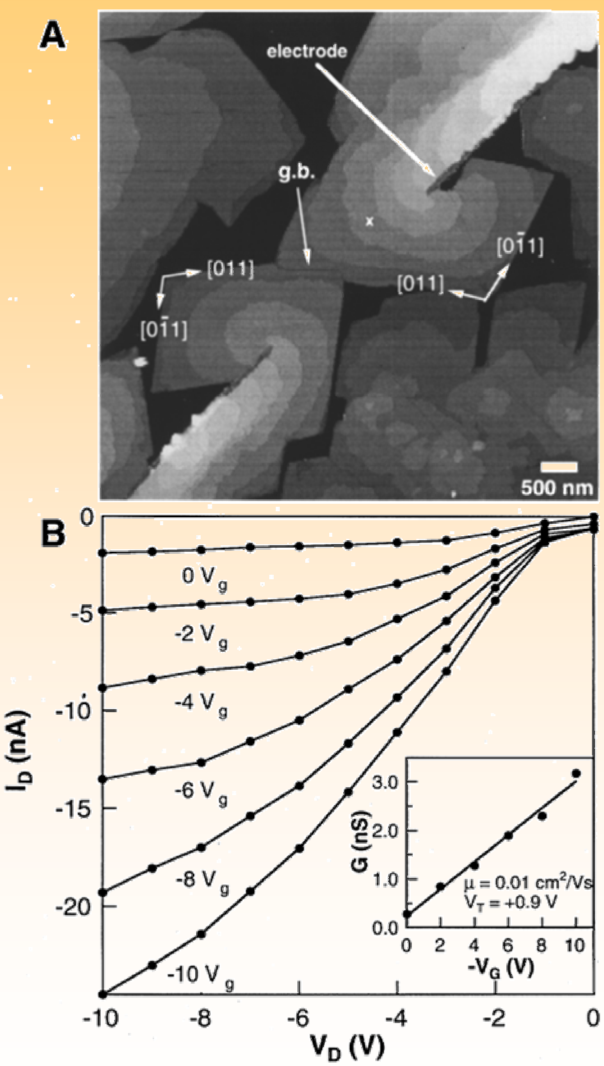


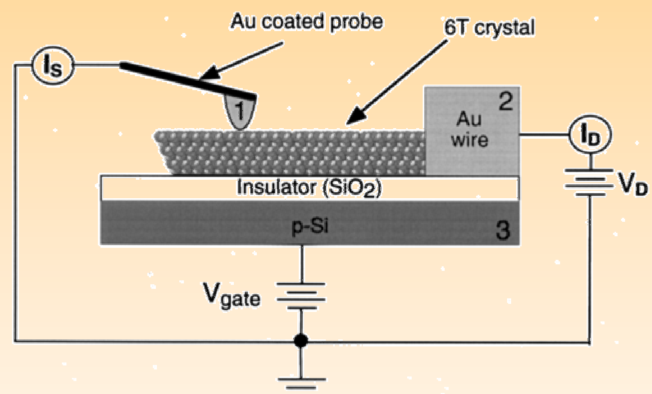


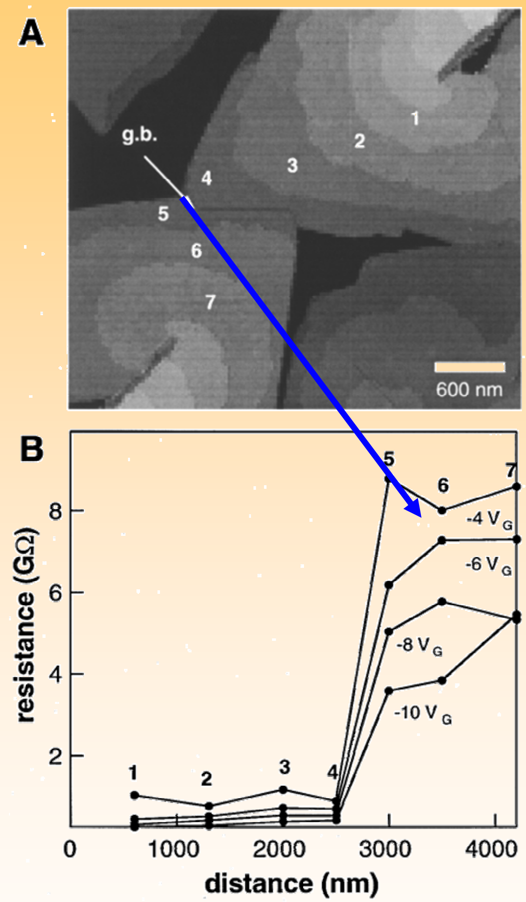
$$\mu_{\parallel} \approx 10^{-6}\ \mathrm{cm^2/volt \cdot sec};$$

$$\mu_{\parallel}/\mu_{\perp} = 10;\ R_{contact} = 10^{9}\ \Omega$$

Grain boundaries and defects control electrical properties



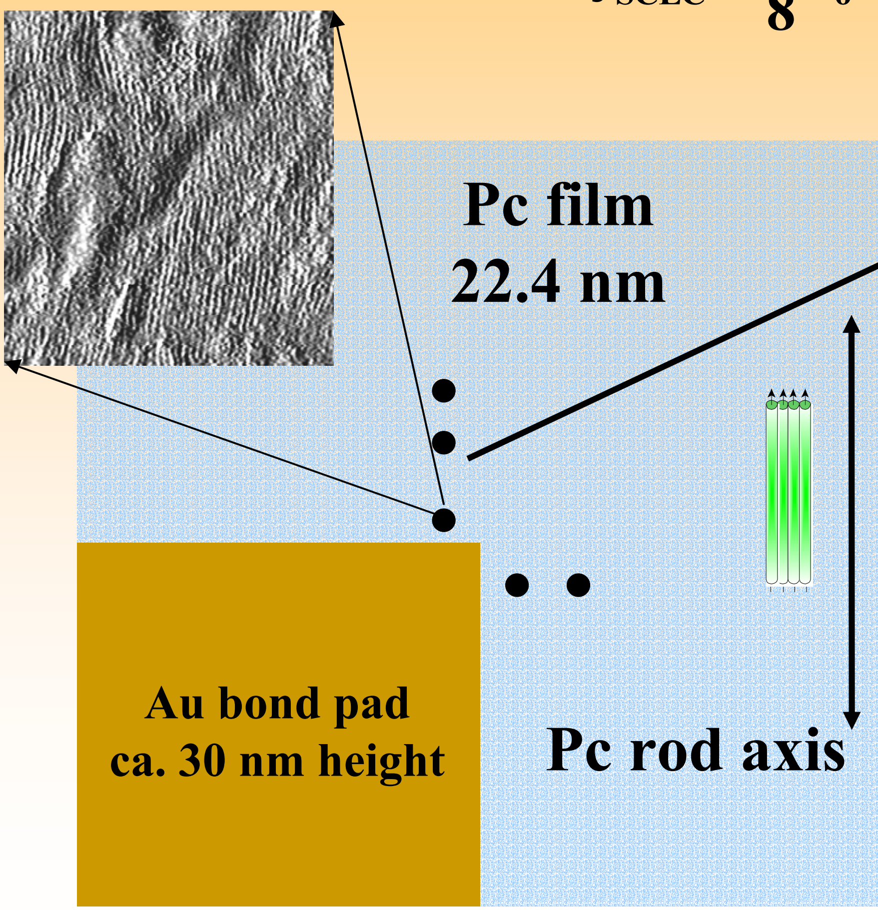


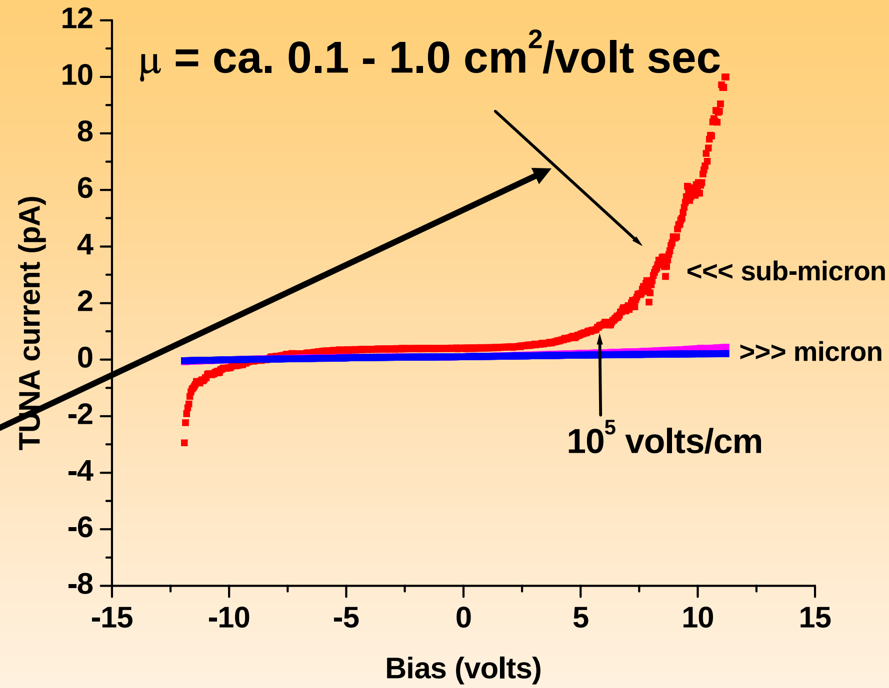


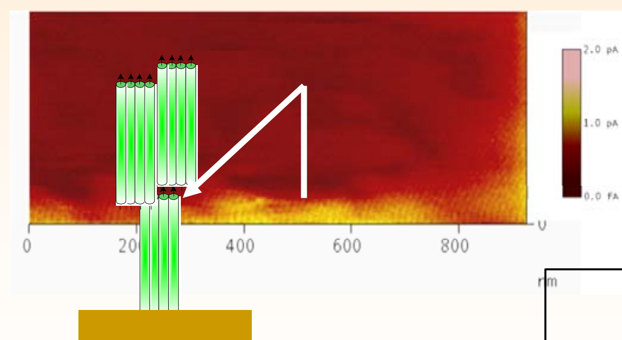
T. W. Kelley & C.D. Frisbie
"Gate voltage dependent resistance of a single organic semiconductor grain boundary,"
J. Phys. Chem. B **2001, *105*, 4538-4540.**

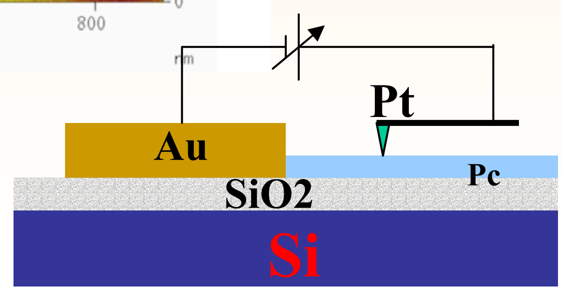
Tunneling AFM – ca. 500 nm from Au bond pad

$$j_{SCLC} = \frac{9}{8}\varepsilon_o \varepsilon \mu \frac{V^2}{d^3}$$









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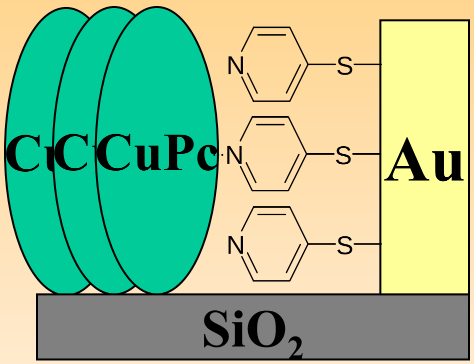
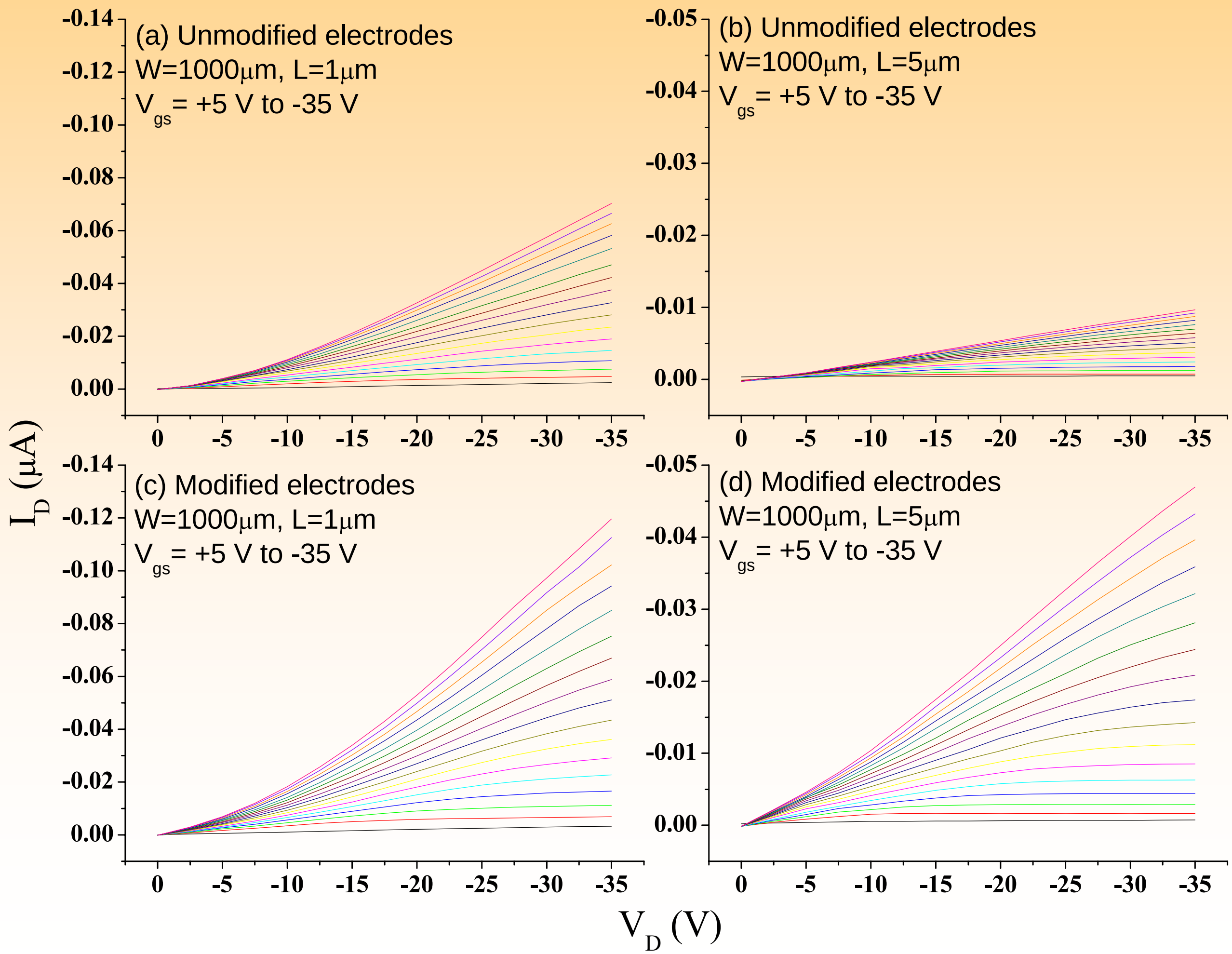
S/D Contact Chemical Modification – Normal and Unusual SAMs





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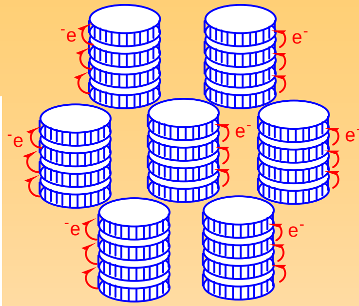
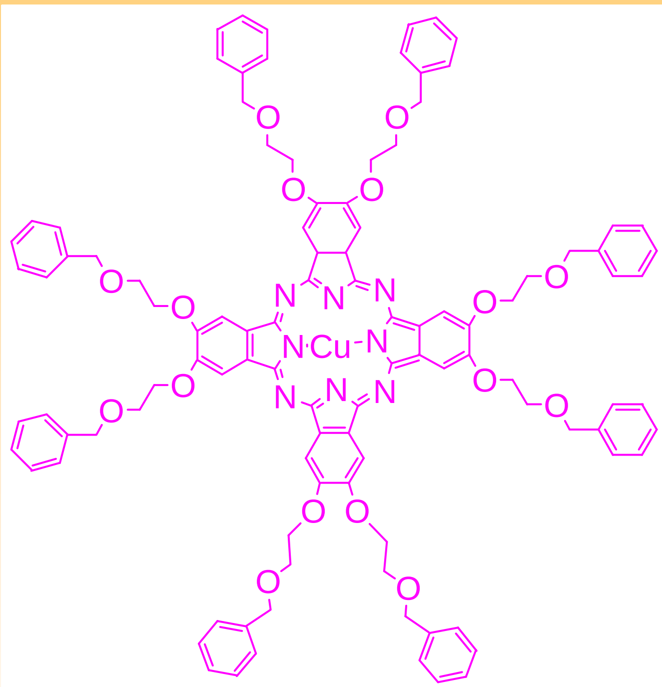
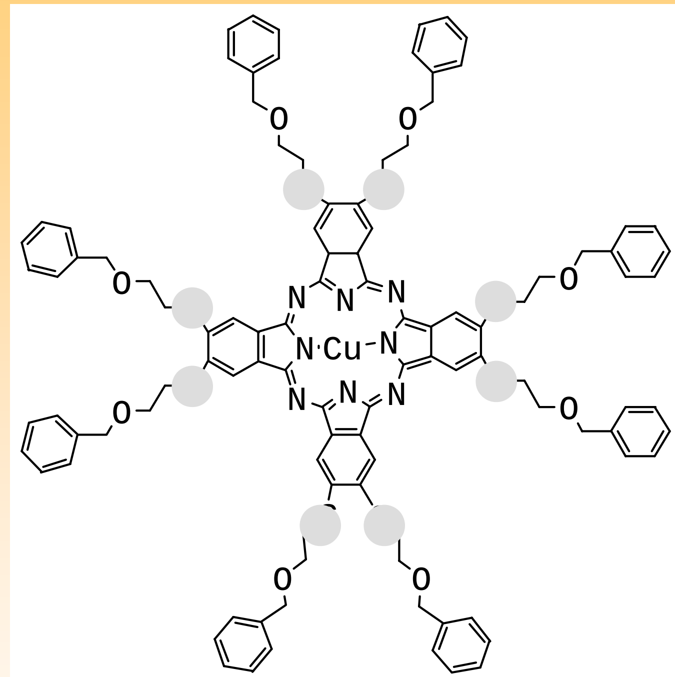
Wei Xia,
Dave Mathine

Optimization of Pc Photoreceptors





O-Et-O-Bz CuPc



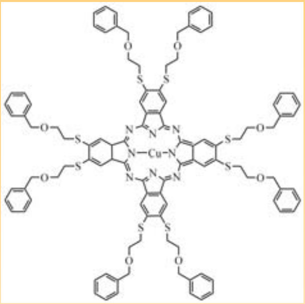
X-Et-O-Bz CuPc

K↔D_h 111°C; D_h↔I > 400°C; difficult to process as spin-cast thin films

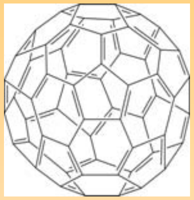
K↔D_h 134°C; D_h↔I 320°C; easy to process into thin films by spin-coating (chloroform)

Britt Minch, manuscript in preparation

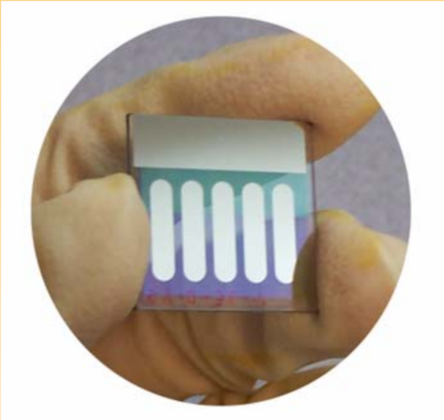
Device Configuration

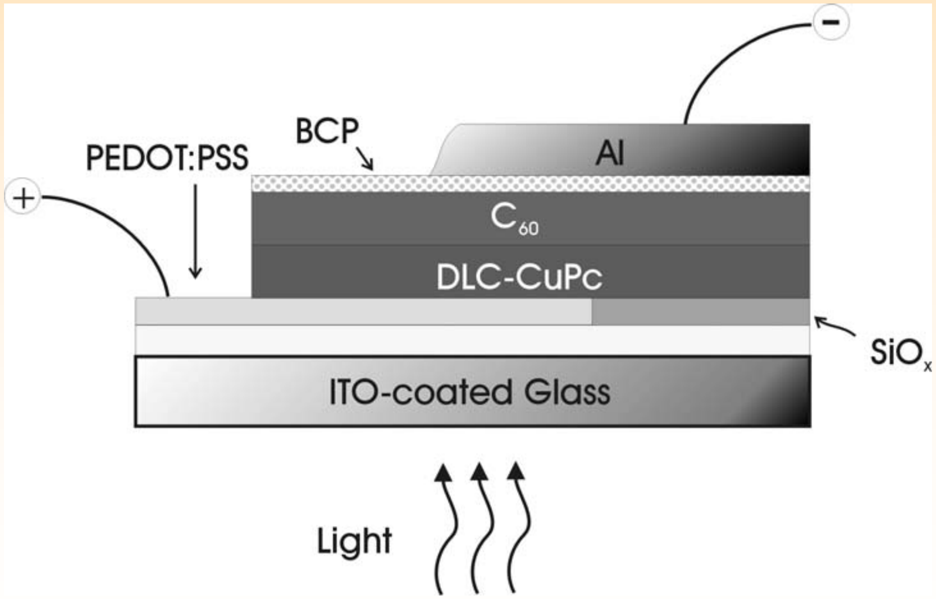


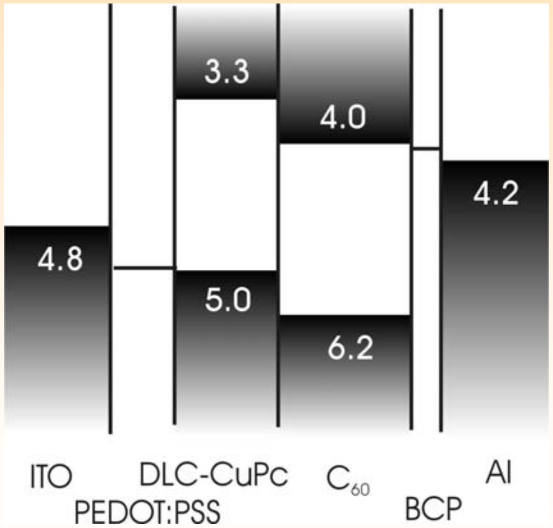
DLC-CuPc



C_{60}

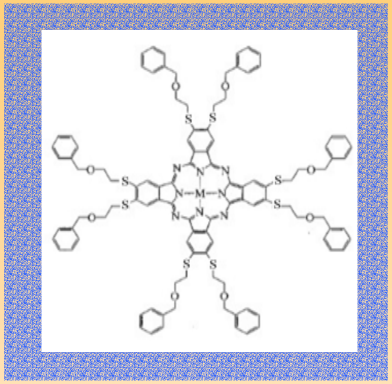


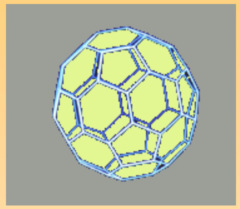


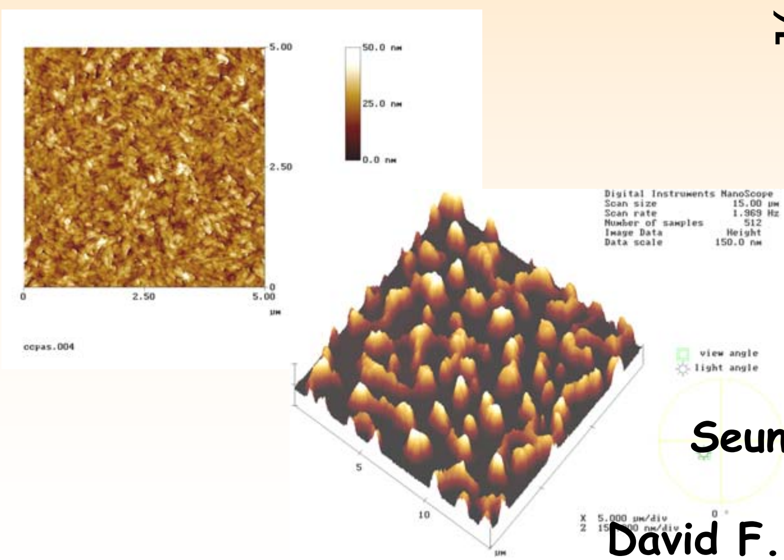


* Energy scale in eV w.r.t vacuum

First-generation OPVs

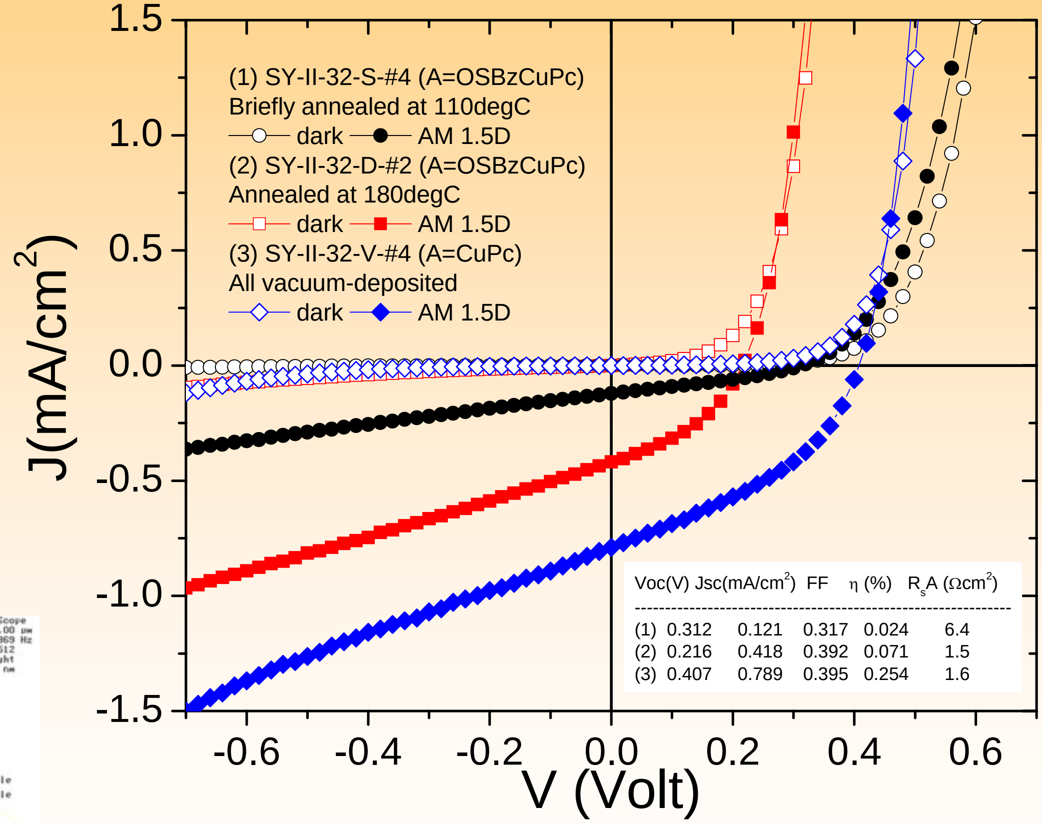






JV-Characteristic of Discotic LC PV Cell

(ITO/PEDOT:PSS(30nm)/'A'(20nm)/C60(40nm)/BCP(12nm)/Al)

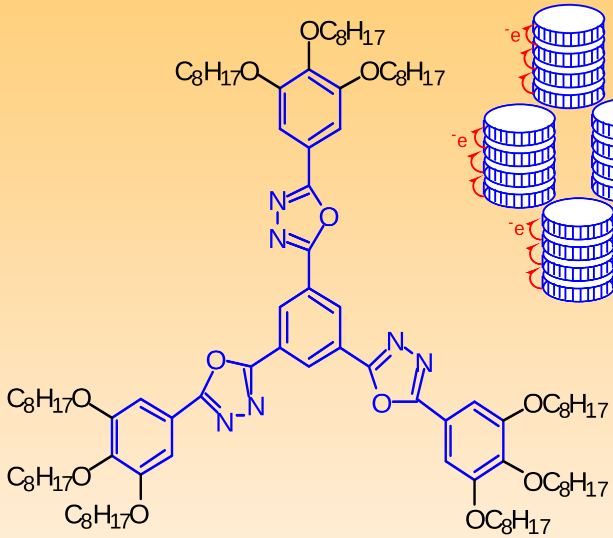


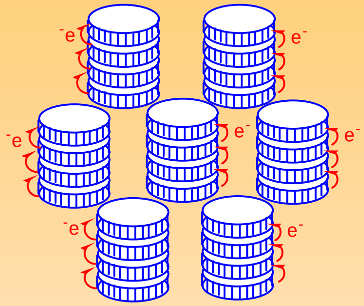
	Voc(V)	Jsc(mA/cm^2)	FF	η (%)	R_sA (Ωcm^2)
(1)	0.312	0.121	0.317	0.024	6.4
(2)	0.216	0.418	0.392	0.071	1.5
(3)	0.407	0.789	0.395	0.254	1.6

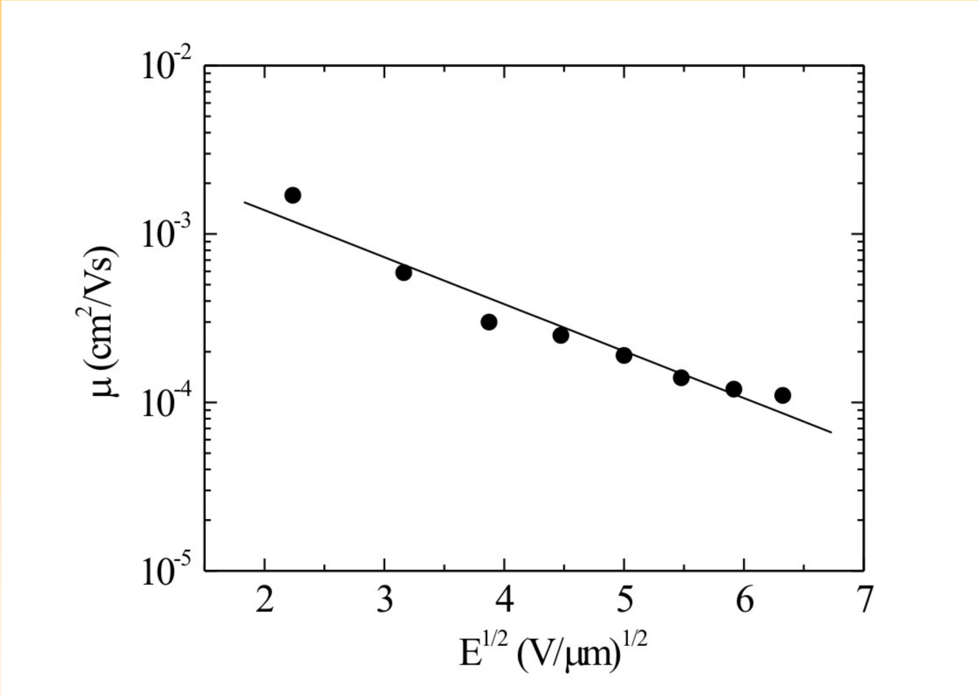
Seunghyup Yoo, Benoit Domercq, Carrie L. Donley, Chet Carter, Wei Xia, Britt A. Minch, David F. O'Brien, Neal R. Armstrong, and Bernard Kippelen

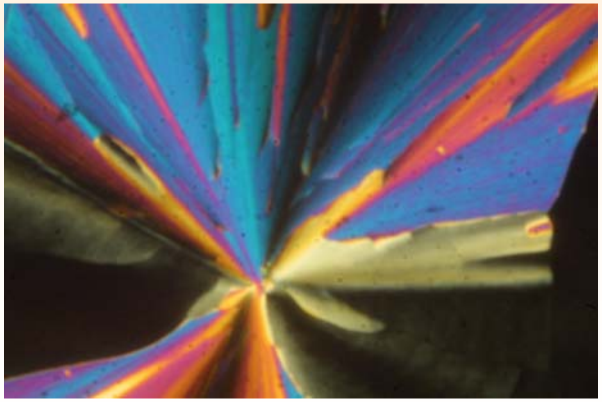
(in-press)

Electron transport materials





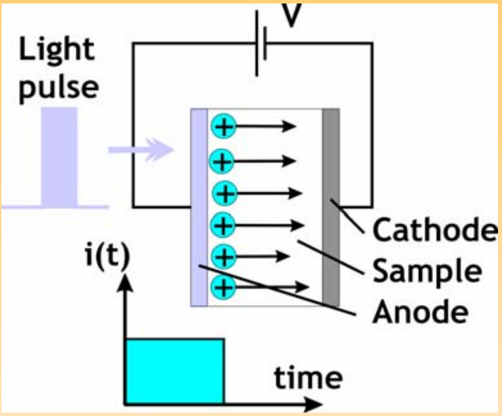


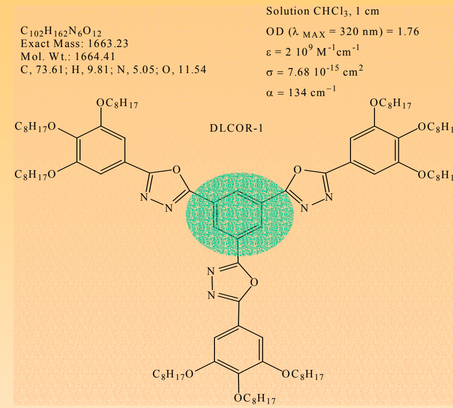


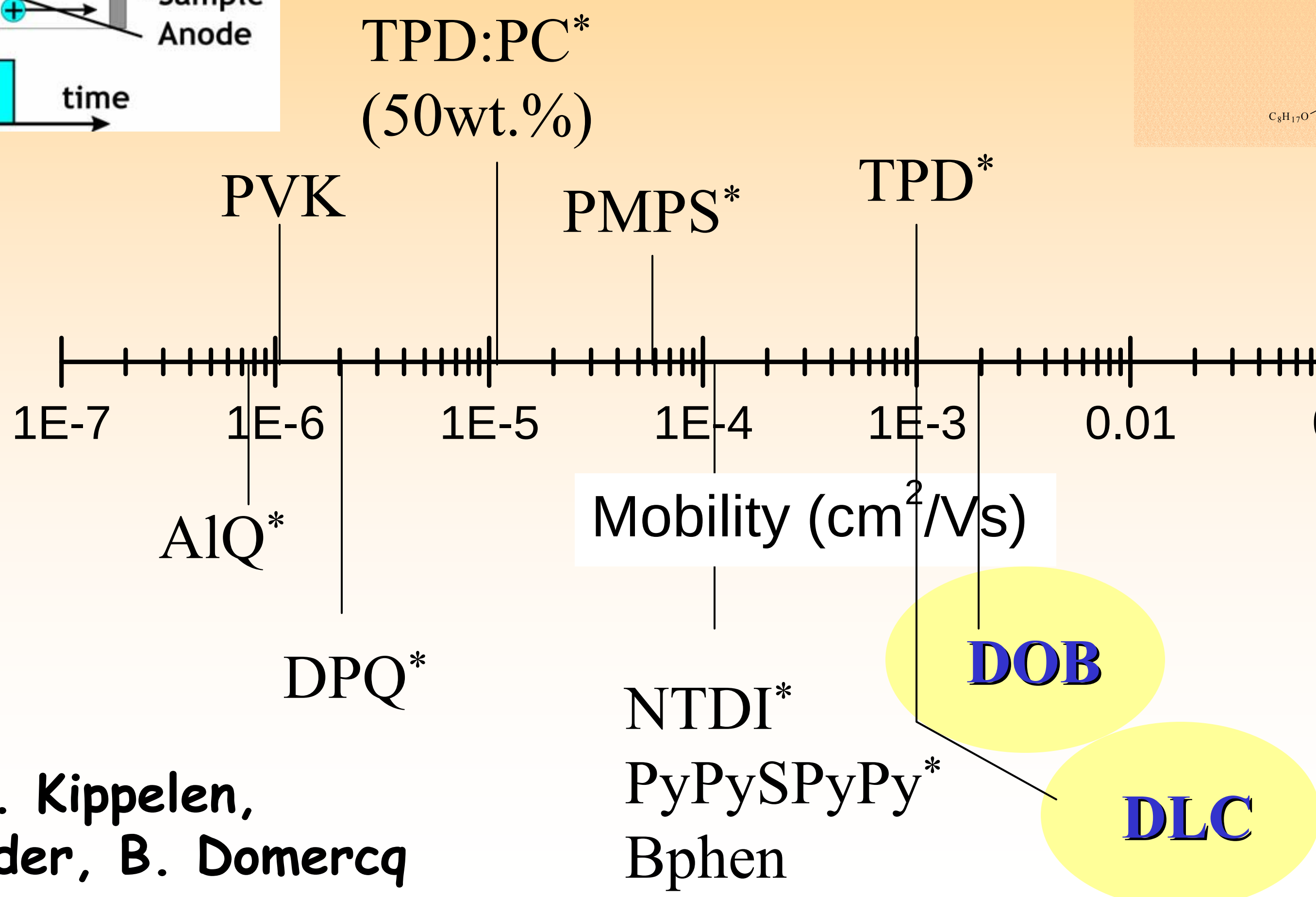
"Star-like" discotic LC oxadiazole materials with high electron mobility

S. Marder and coworkers

Charge Mobilities Through Time-of-Flight Experiments







B. Kippelen,
S. Marder, B. Domercq

Collaborators/Research Support

Carrie Donley (Cambridge Univ.); Britt Minch (MPIP-Mainz); Rebecca Zangmeister (NIST); Tony Drager (Dow); Paul Smolenyak (YCC); Elizabeth Atkinson (Linfield College)

Wei Xia, Samir Cherian; Adam Simmonds; Rick Workman

Dave Mathine, Bernard Kippelen,

Seth Marder; David O'Brien

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