Organic Electronics:

Fundamental Issues and Emerging Opportunities

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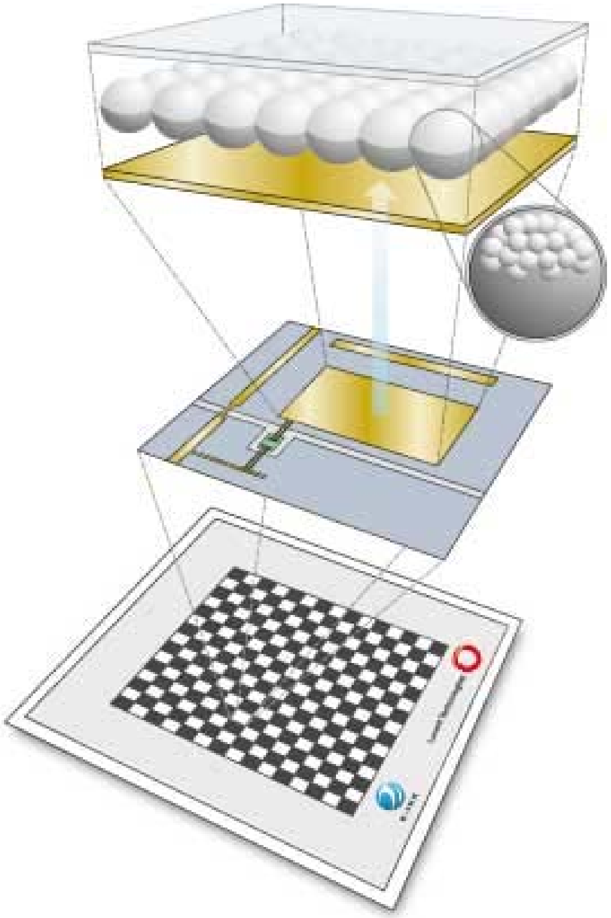
Outline

- Introduction to organic semiconductors
- Interplay between electronic and ionic carriers
  - Electroluminescence in ionic transition metal complexes
- Growth of films from complex materials
  - Evolution of structure and morphology in pentacene films
- Conclusions

Electronics go everywhere

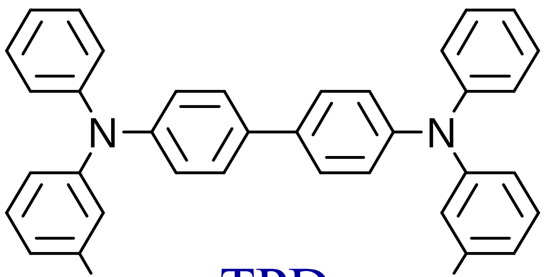
Pioneer



e-Ink & Lucent

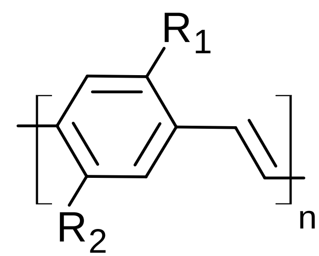
Electrolux

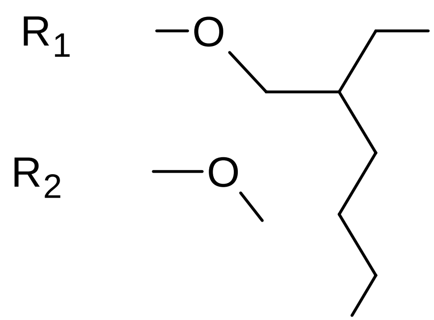
Common organic semiconductors

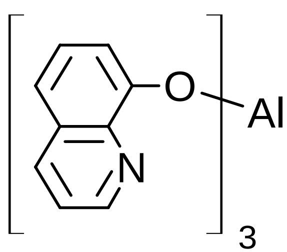


TPD

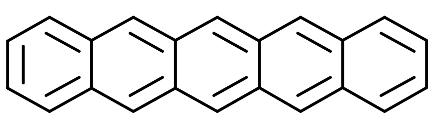
PPV







Alq_3



Pentacene

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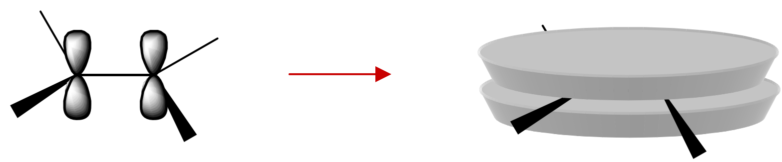
Carbon as a semiconductor

- Hybridization: sp^2 and p_Z

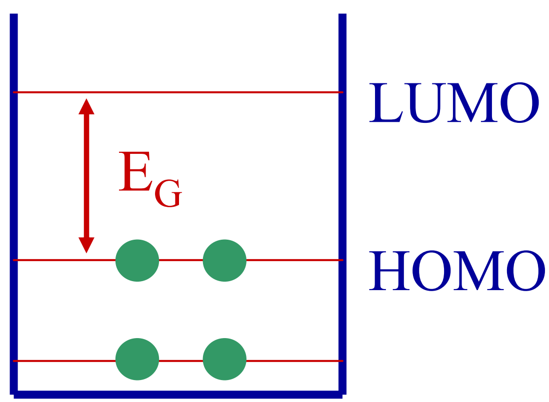
$CH_2{=}CH_2$



- Particle in a box:

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$$

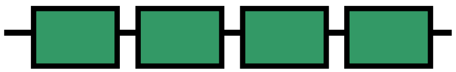
$$n=1,2,3,\ldots$$



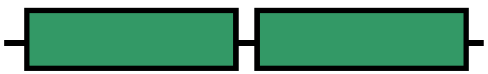
$$E_G \approx \frac{\hbar^2\pi^2}{2maN}$$

Tuning of optical properties

Blue



Red



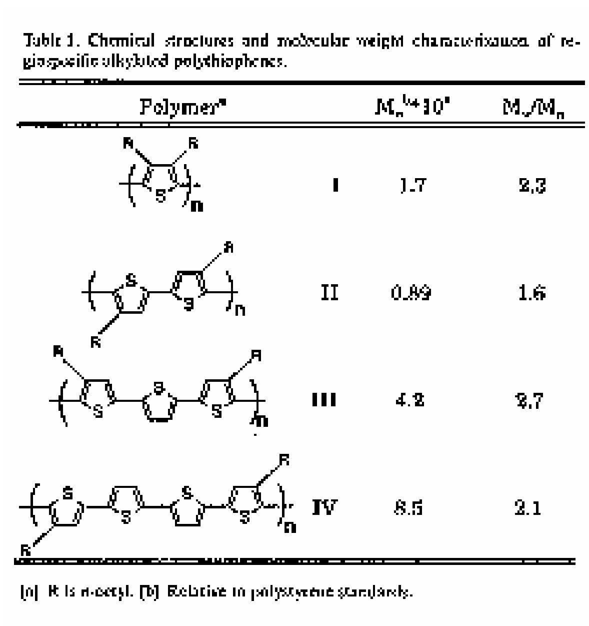


Table 1. Chemical structures and molecular weight characterization of regiospecific alkylated polythiophenes.

Polymer[a]		M_n[b]*10^4	M_w/M_n
	I	1.7	2.3
	II	0.89	1.6
	III	4.2	2.7
	IV	8.5	2.1

[a] R is n-octyl. [b] Relative to polystyrene standards.

R.E. Gill *et. al.*, *Adv. Mater.* **6**, 132 (1994).

Covion

Opportunities and challenges

(+)	Ease of processing

(+)	Tunability of electronic properties

(+)	Integration with biological systems

(-)	Low-end performance

(-)	Stability in devices

Will complement Si, not replace it

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Organic light emitting diodes (OLEDs)

Pioneer
(1997)

Pioneer
(2001 - demo)

Kodak
(2004)

Sony
(2004)

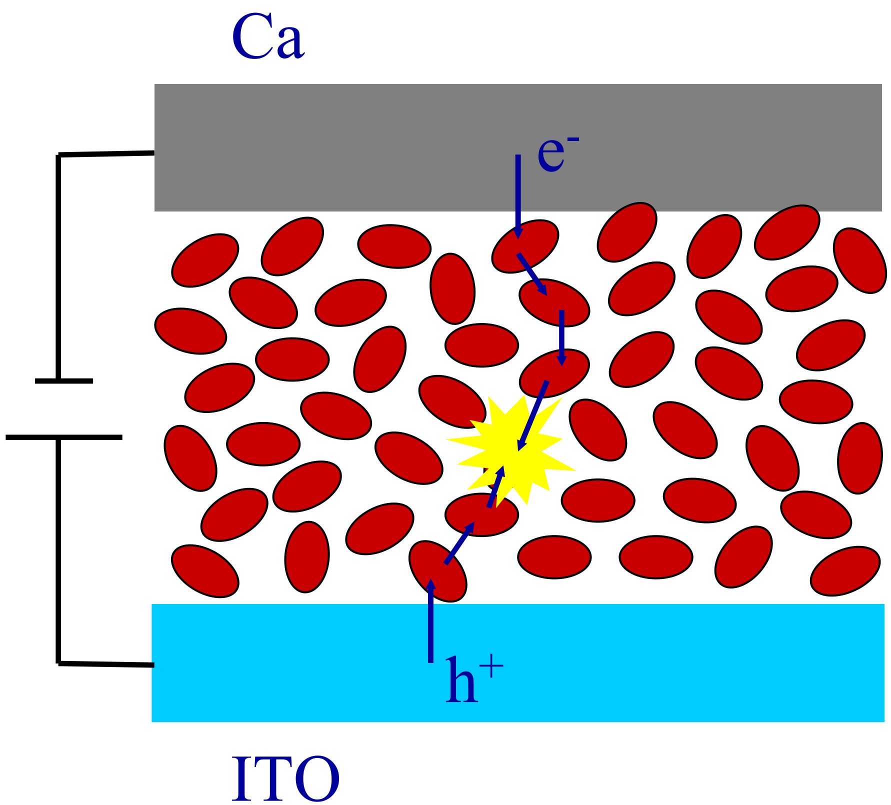
Motorola
(2001)

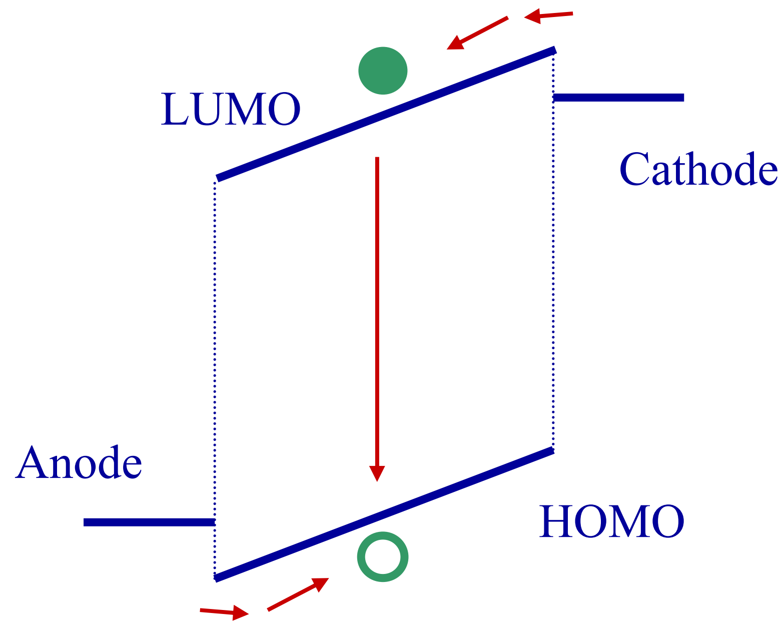
OLEDs vs. liquid crystals

OLEDs for lighting

GE

OLED structure and operation





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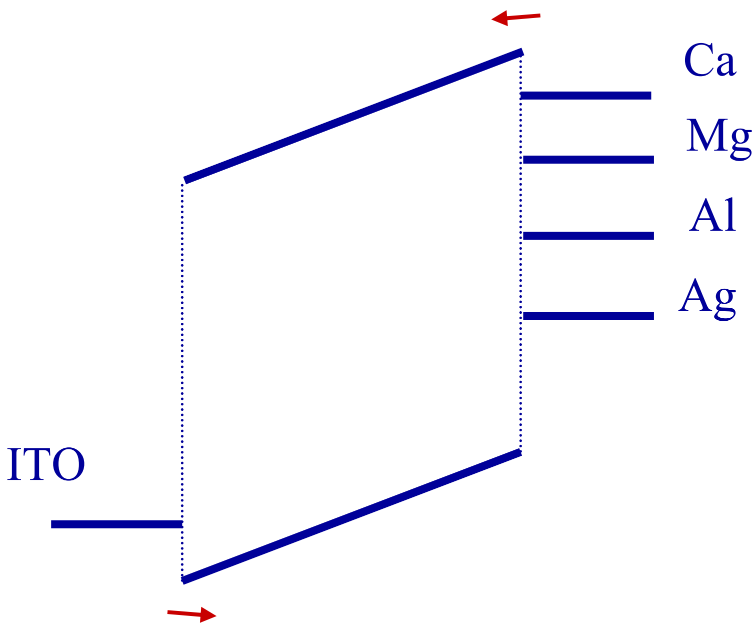
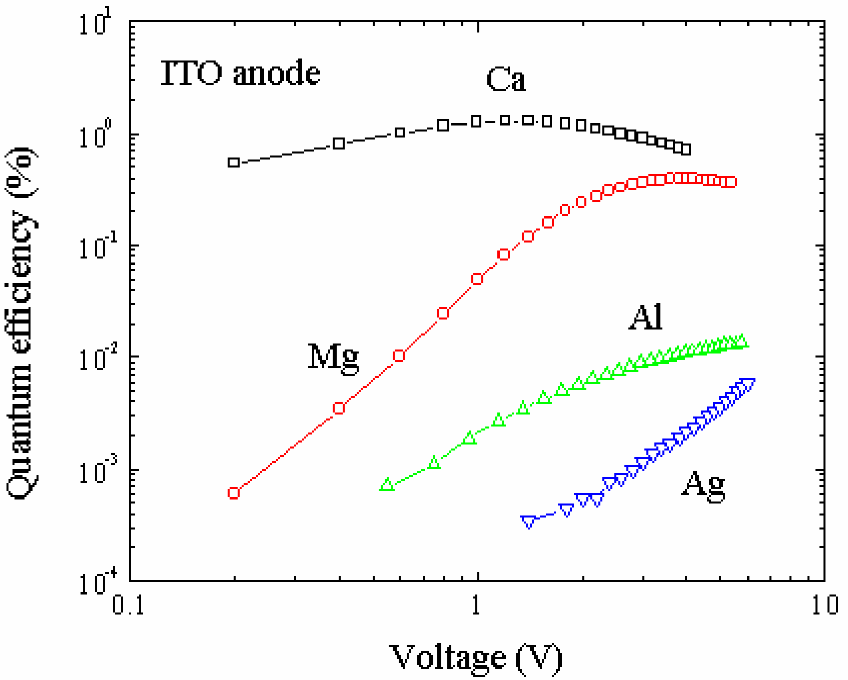
Need for low work function cathode





Low work function cathode required
for efficient electron injection

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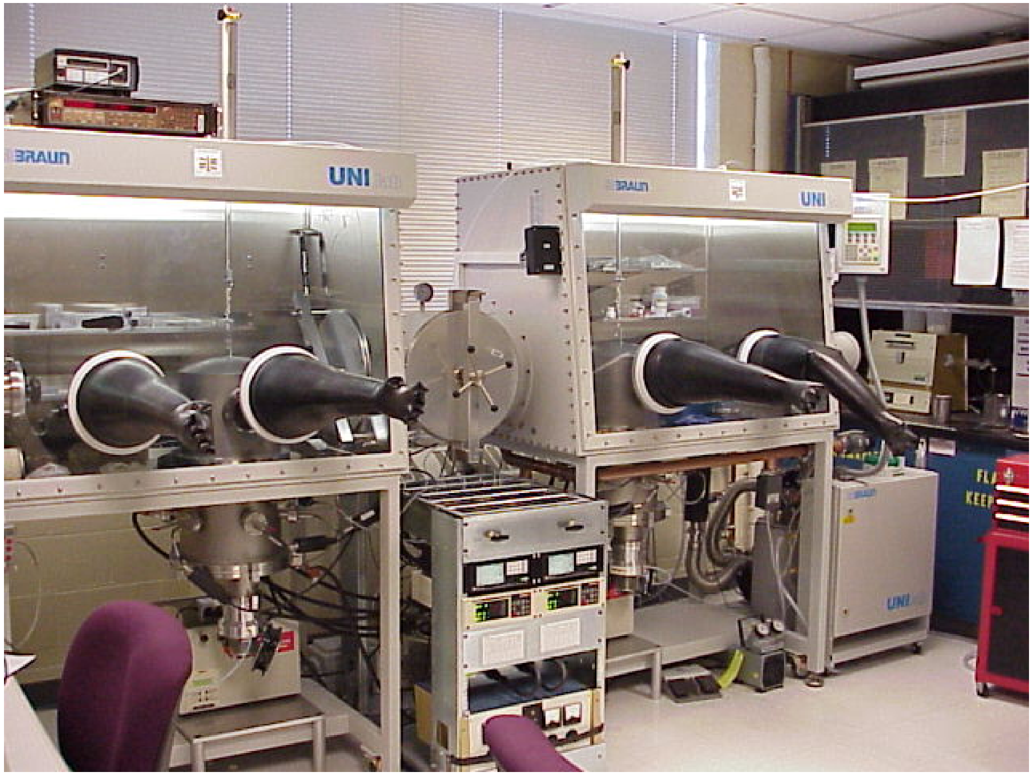
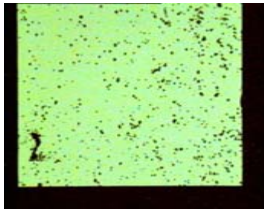
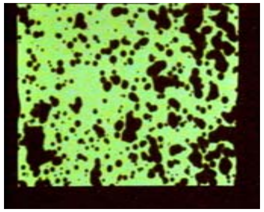
Degradation of the cathode

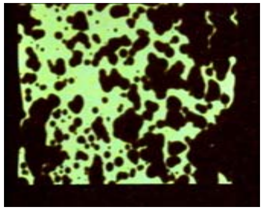




2 min



20 h



40 h

Pictures courtesy of
Dr. Homer Antoniadis.

Can we make OLEDs with air-stable cathodes?

OLEDs with air-stable cathodes

FEATURE ARTICLE: J. Slinker, D. Bernards, P.L. Houston, H.D. Abruña, S. Bernhard and G.G. Malliaras, *Chem. Comm.* **19**, 2392 (2003).

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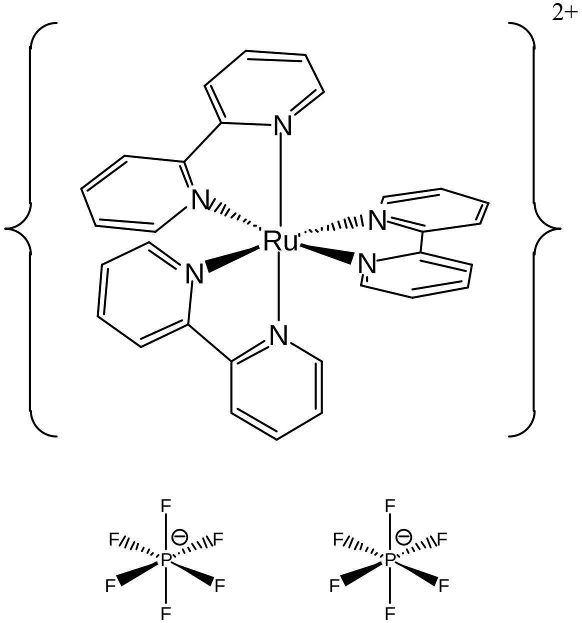
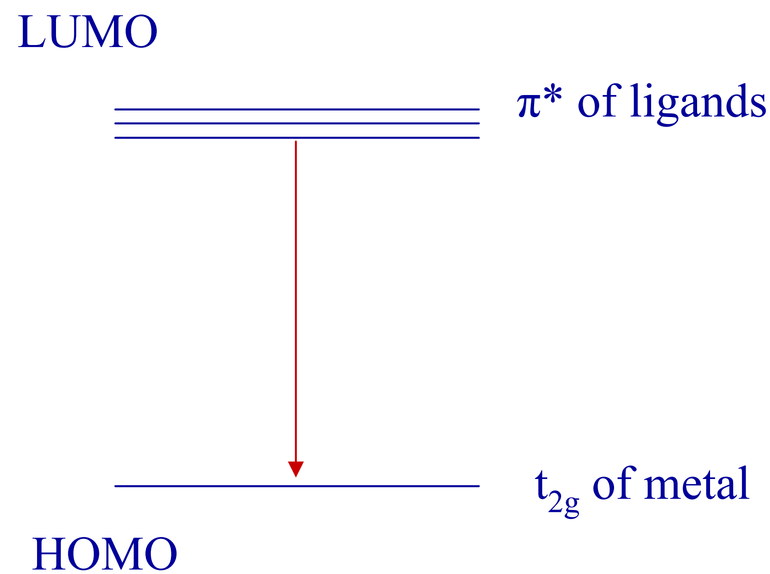
Ionic transition metal complexes

$[Ru(bpy)_3]^{2+}(PF_6^-)_2$





Mixed conductors!

S. Bernhard, X. Gao, G.G. Malliaras, and H.D. Abruña, *J. Am. Chem. Soc.* **124**, 13624 (2002).
Also:
E. S. Handy, A. J. Pal and M. F. Rubner, *J. Am. Chem. Soc.* **121**, 3525 (1999).
M. Buda, G. Kalyuzhny and A.J. Bard, *J. Am. Chem. Soc.* **124**, 6090 (2002).

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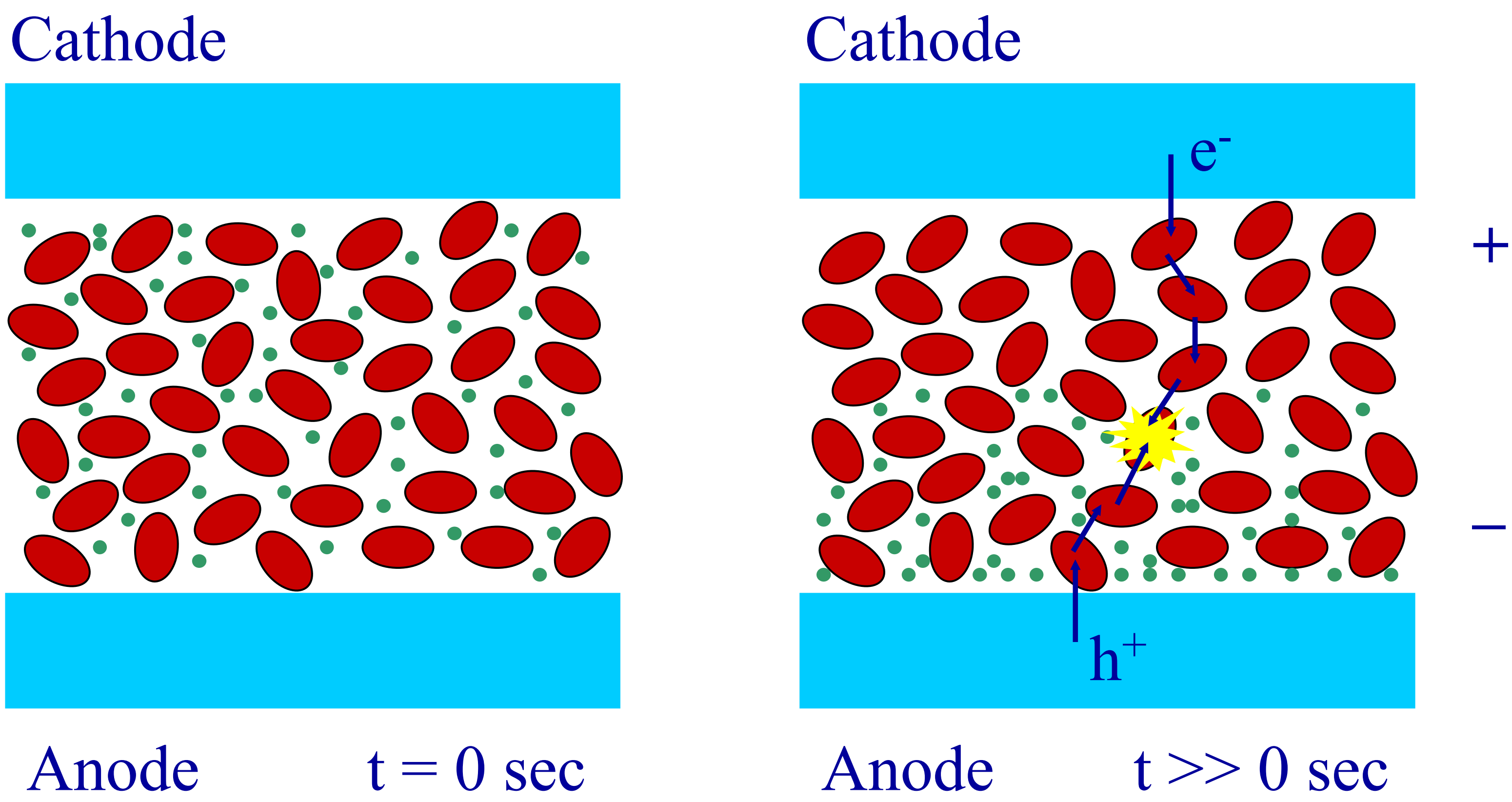
Device model



Also:
J.C. deMello, N. Tessler, S.C. Graham and R.H. Friend, *Phys. Rev. B.* **57**, 12951 (1998).
Q.B. Pei, G. Yu, C. Zhang, A.J. Heeger, *Science* **269**, 1086 (1995).

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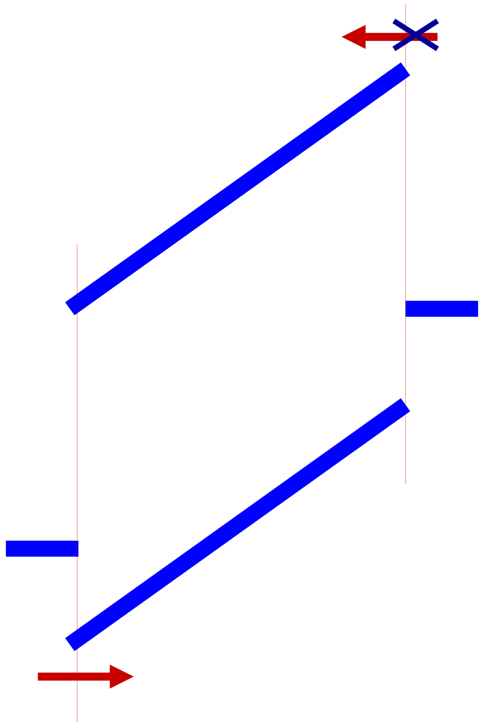
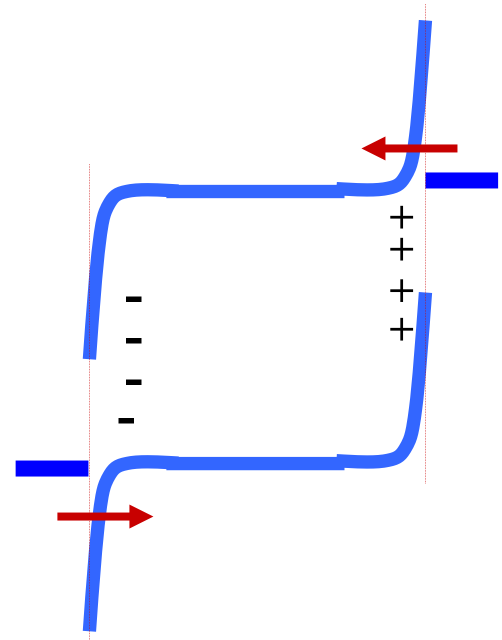
Device model (II)



Traditional OLED



Ionic transition metal complexes

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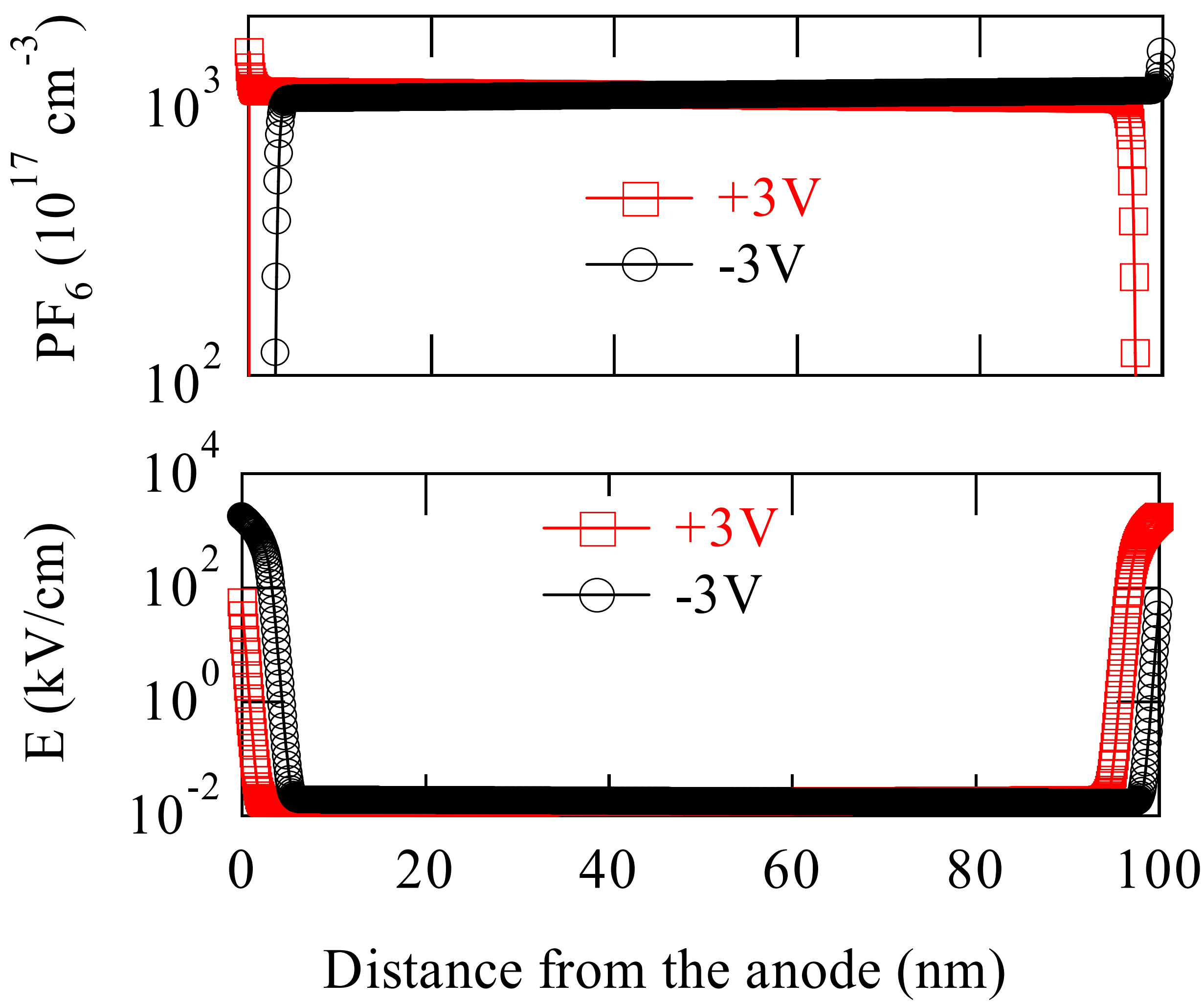
Device model (III)



Key prediction:

Contacts become ohmic

Every injected charge will form an exciton (b=1)

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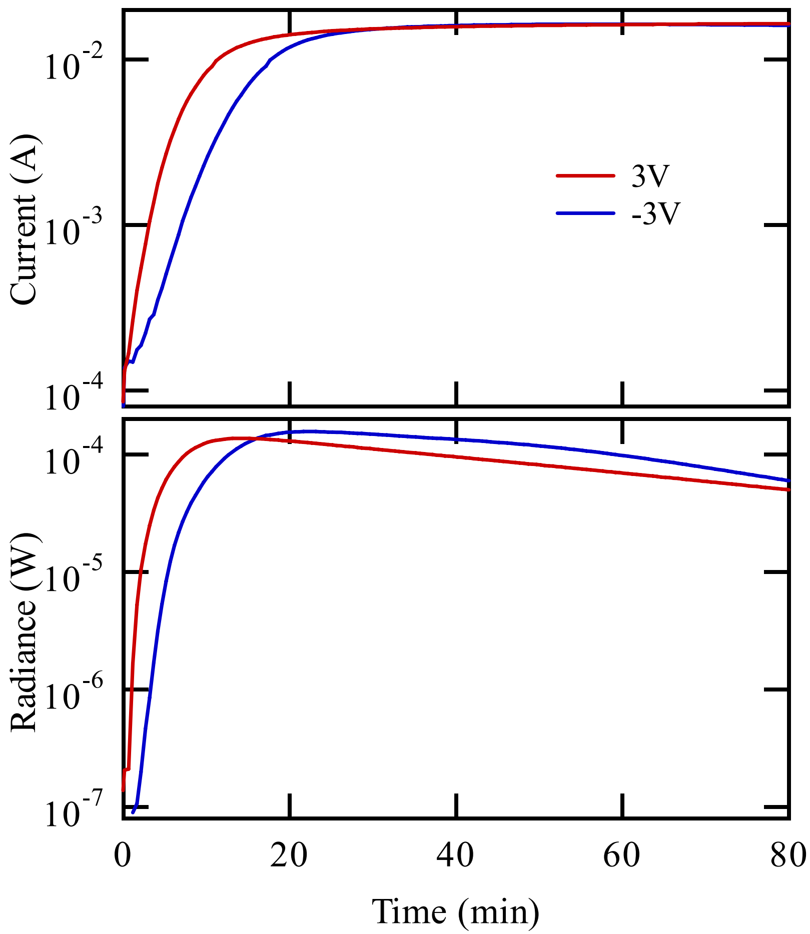
Device model (IV)



A. Gorodetsky, S. Parker, J. Slinker, D. Bernards, M.H. Wong, S. Flores-Torres, H.D. Abruña, and G.G. Malliaras, *Appl. Phys. Lett.* **84**, 807 (2004).

No rectification. These are light emitting resistors!

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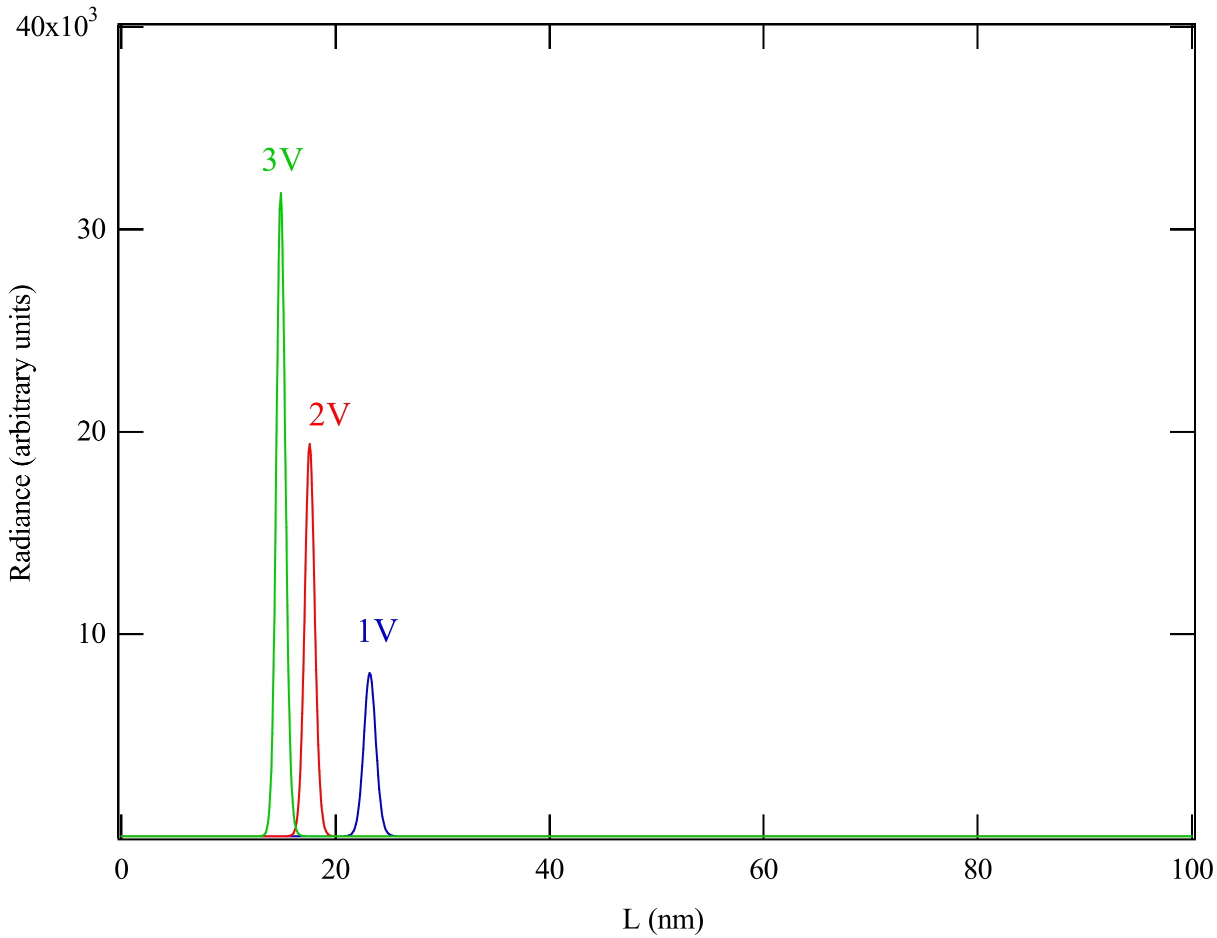
Device model (V)



Narrow recombination zone

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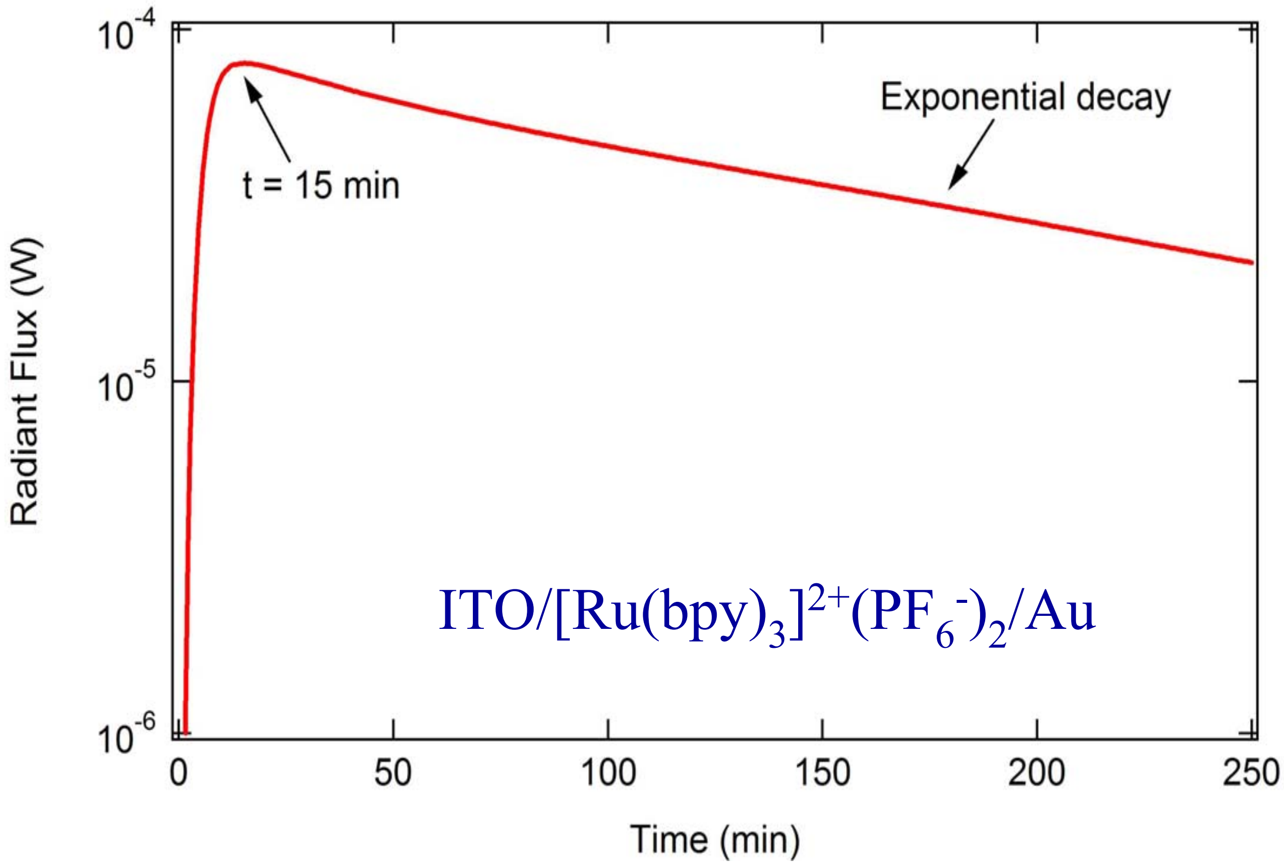
Device characteristics



$ITO/[Ru(bpy)_3]^{2+}(PF_6^-)_2/Au$

At 3V:

>300 cd/m^2

Slow turn-on, followed by decay

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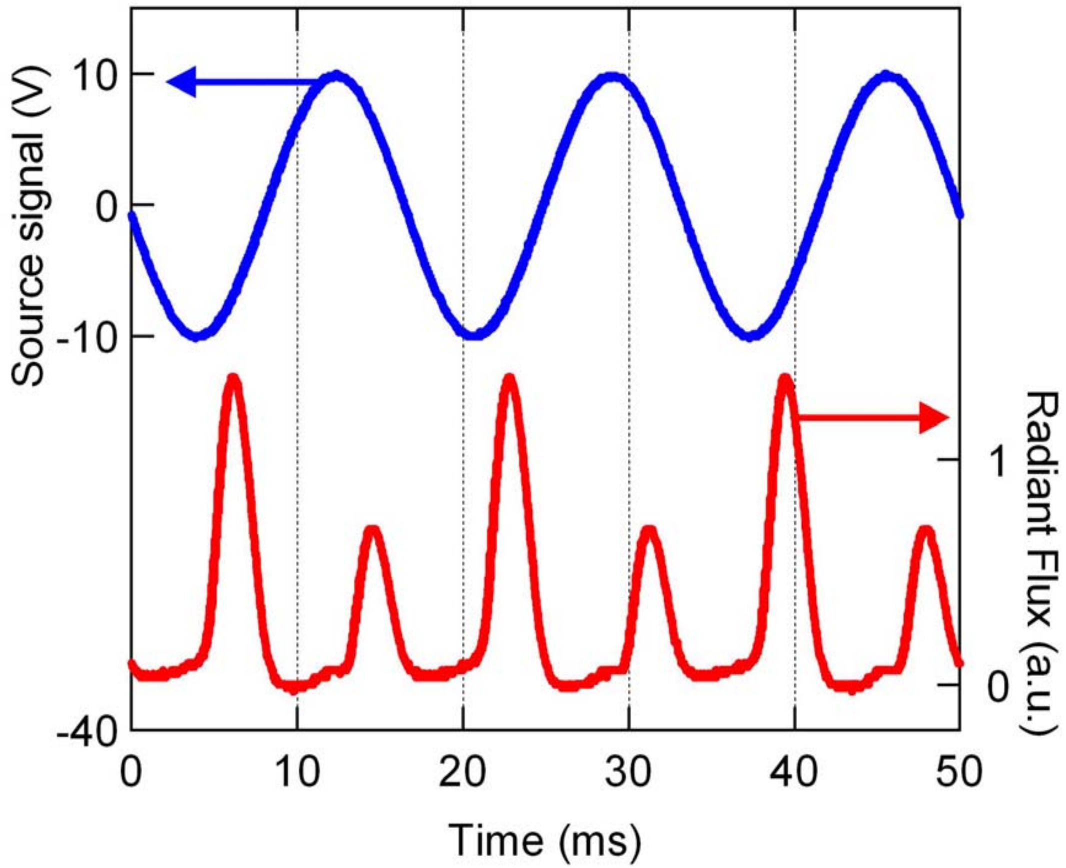
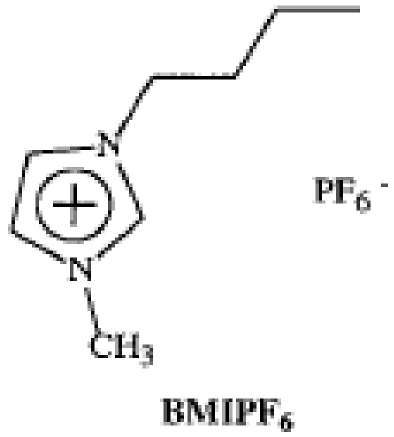
Turn-on time





S.T. Parker, J.D. Slinker, M. Lowry, M.P. Cox, S. Bernhard, and G.G. Malliaras, *Chem. Mater.* **17**, 3187 (2005).

Addition of ionic liquids improves turn-on time

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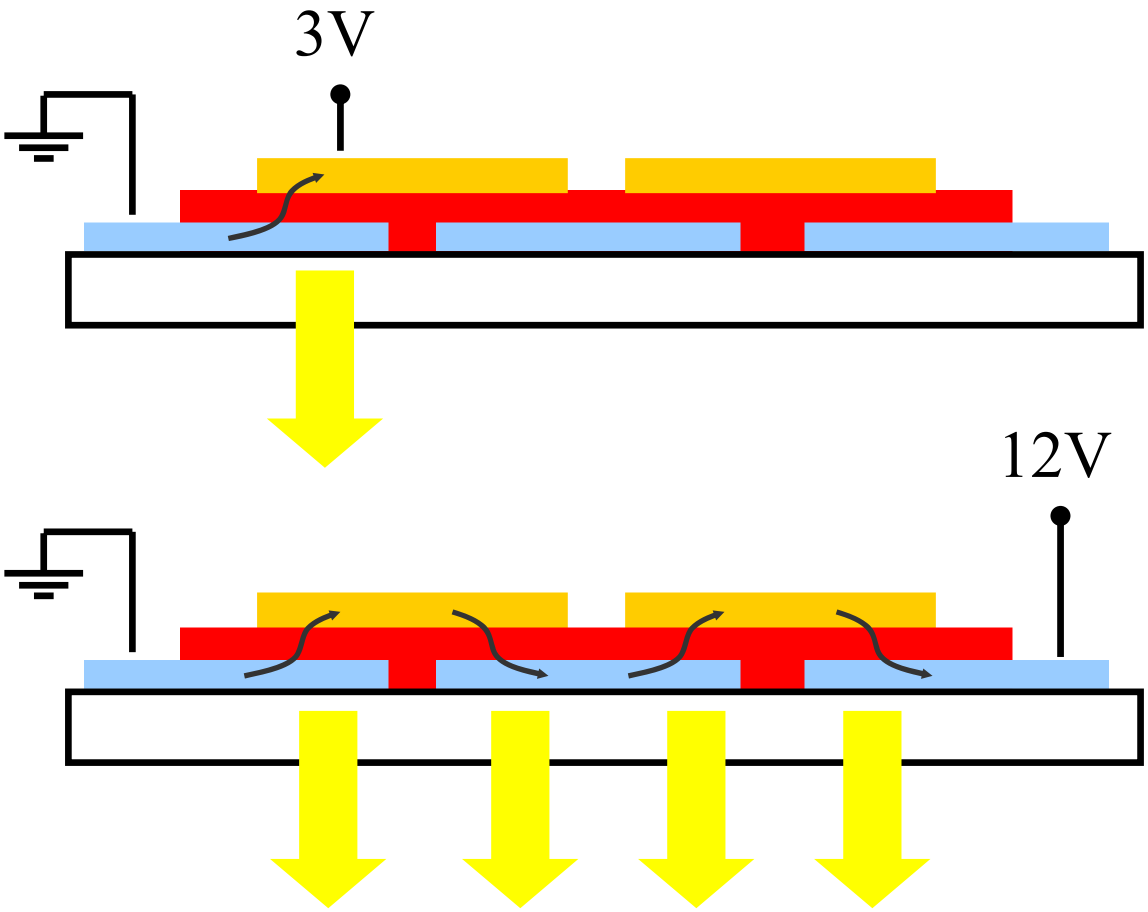
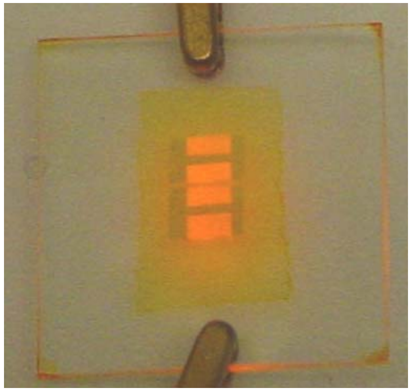
Cascaded devices





D.A. Bernards, J.D. Slinker, G.G. Malliaras, S. Flores-Torres, and H.D. Abruña, *Appl. Phys. Lett.* **84**, 4980 (2004).

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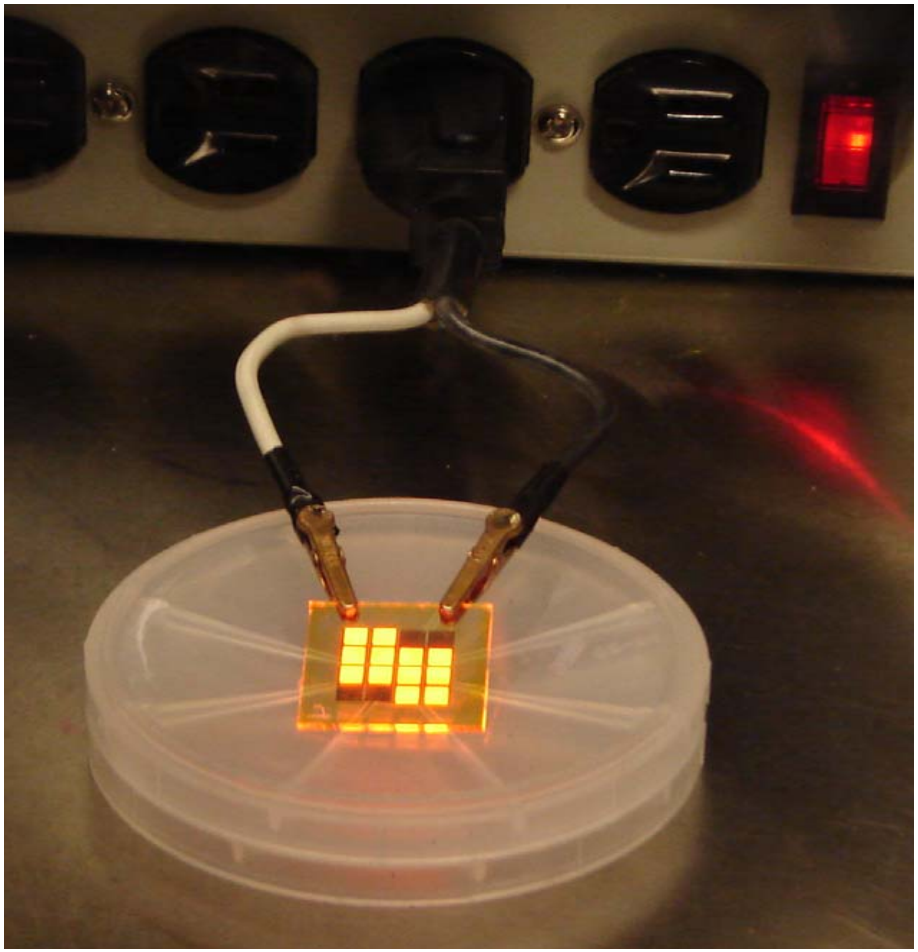
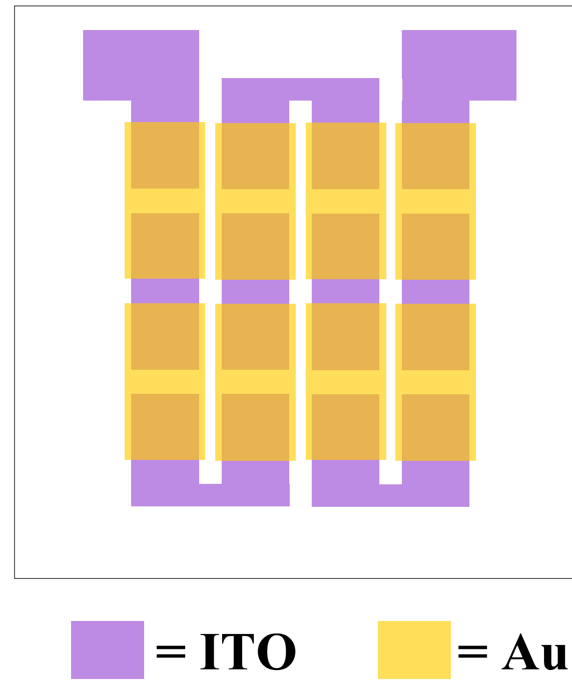
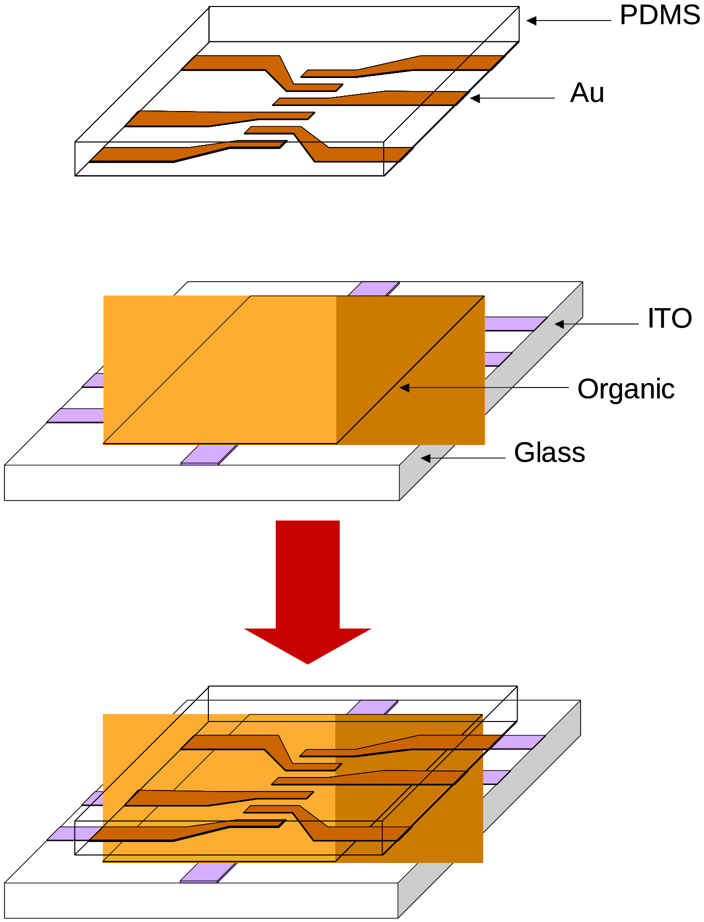
Operation straight from the outlet

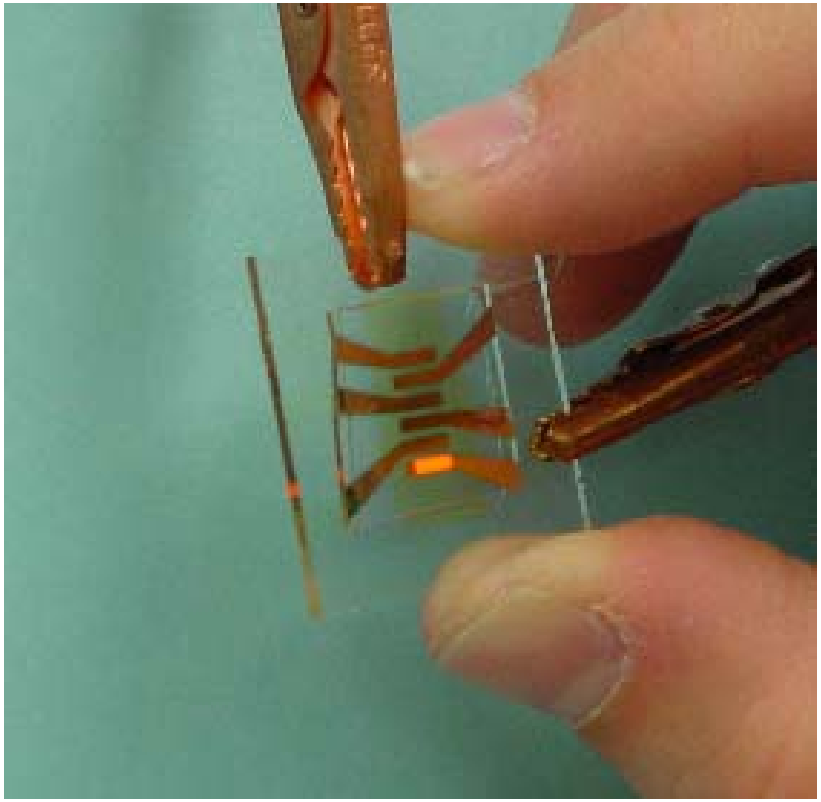




J. D. Slinker, J. Rivnay, J.A. DeFranco, D.A. Bernards, A. Gorodetsky, S.T. Parker, M. Cox, R. Rohl, S. Flores-Torres, H.D. Abruña and G.G. Malliaras, *J. Appl. Phys.* **99**, 074502 (2006).

Devices with laminated contacts





D.A. Bernards, T. Biegala, Z.A. Samuels, J.D. Slinker, G.G. Malliaras,
S. Flores-Torres, H.D. Abruña, and J.A. Rogers, *Appl. Phys. Lett.* **84**, 3675 (2004).

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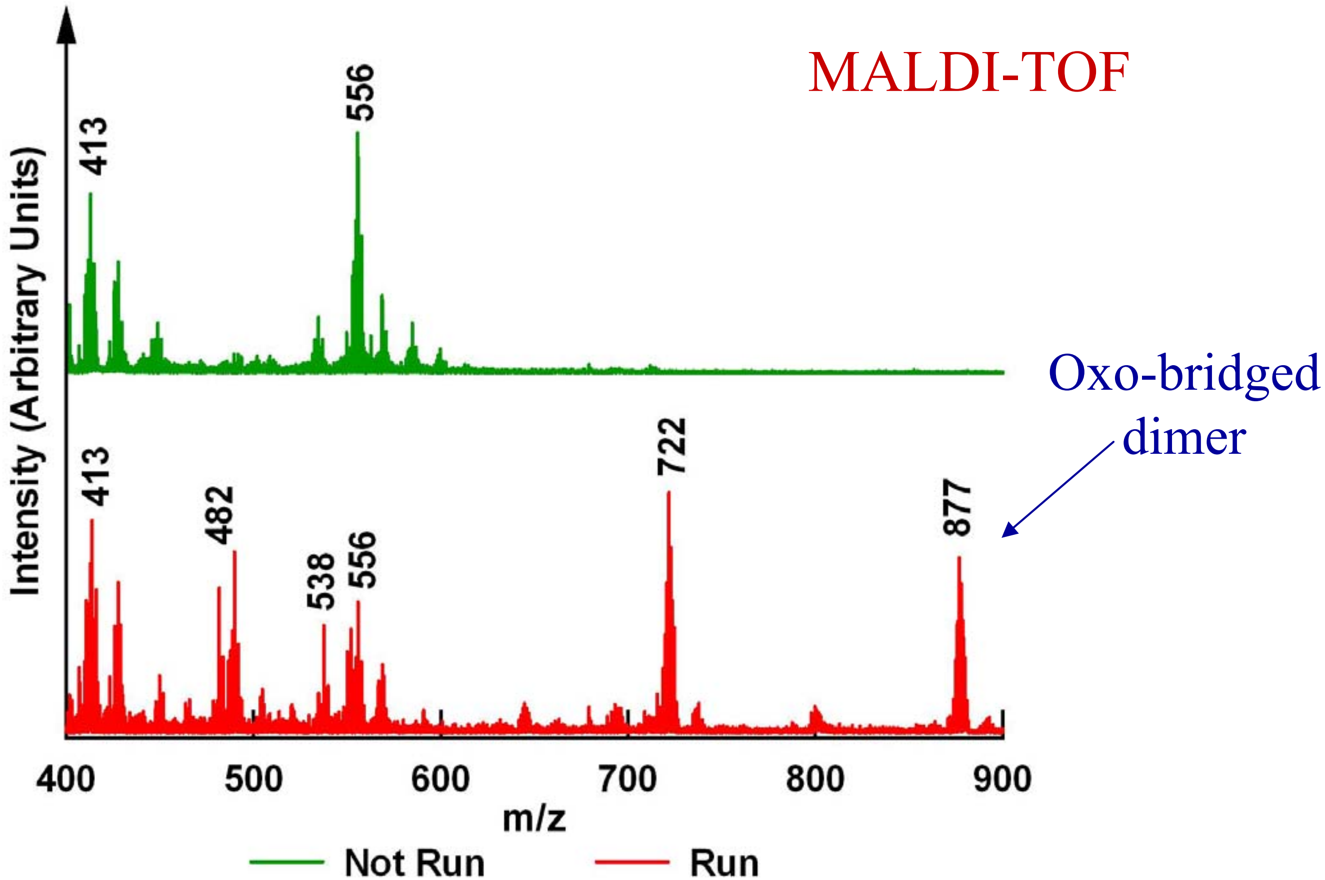
Lifetime



New peaks appear in degraded device

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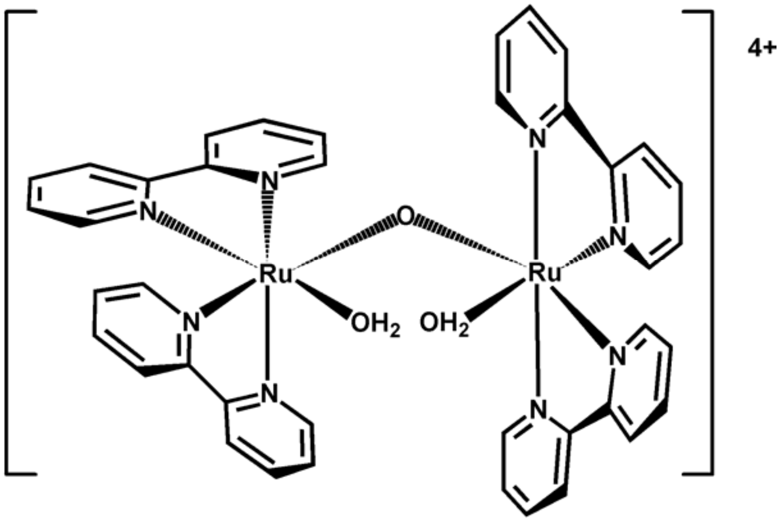
Lifetime (II)

$[(bpy)_2(H_2O)RuORu(OH_2)(bpy)_2]^{4+}$
Oxo-bridged dimer



Dimer identified in degraded devices

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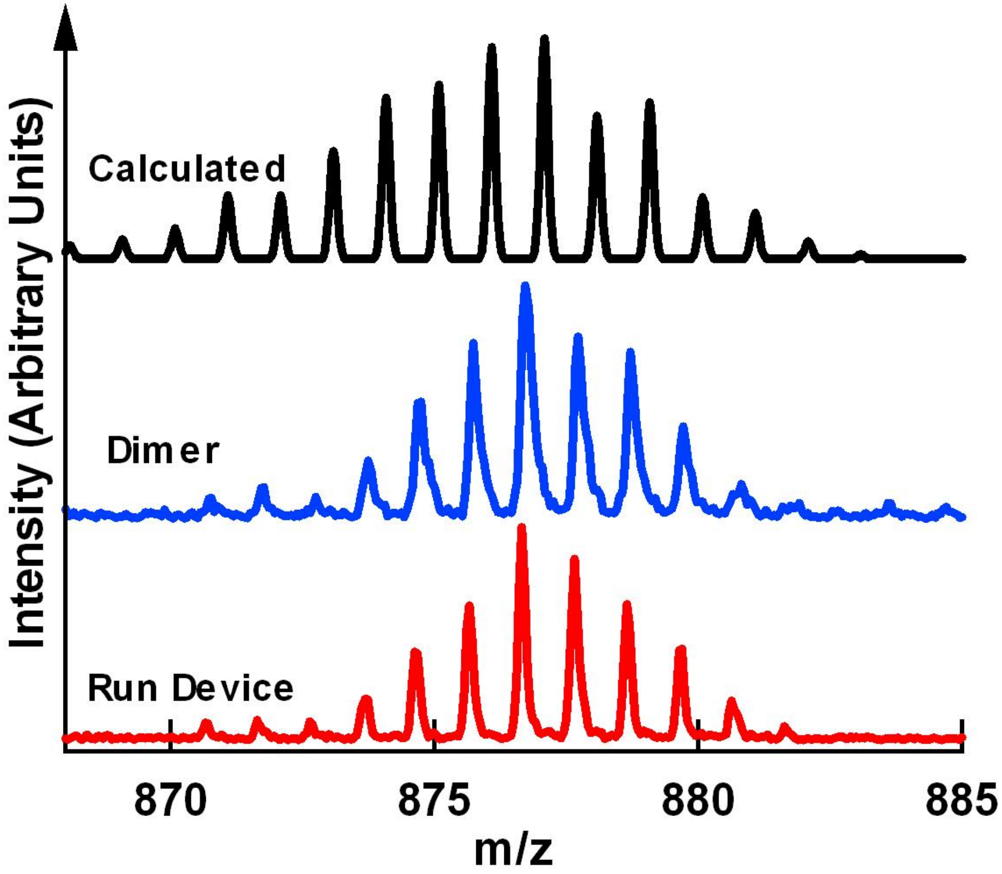
Lifetime (III)



L. Soltzberg, J.D. Slinker, S. Flores-Torres, D.A. Bernards, G.G. Malliaras, H.D. Abruña, J.S. Kim, R.H. Friend, M. Kaplan and V Goldberg, *J. Am. Chem. Soc.*, in press.

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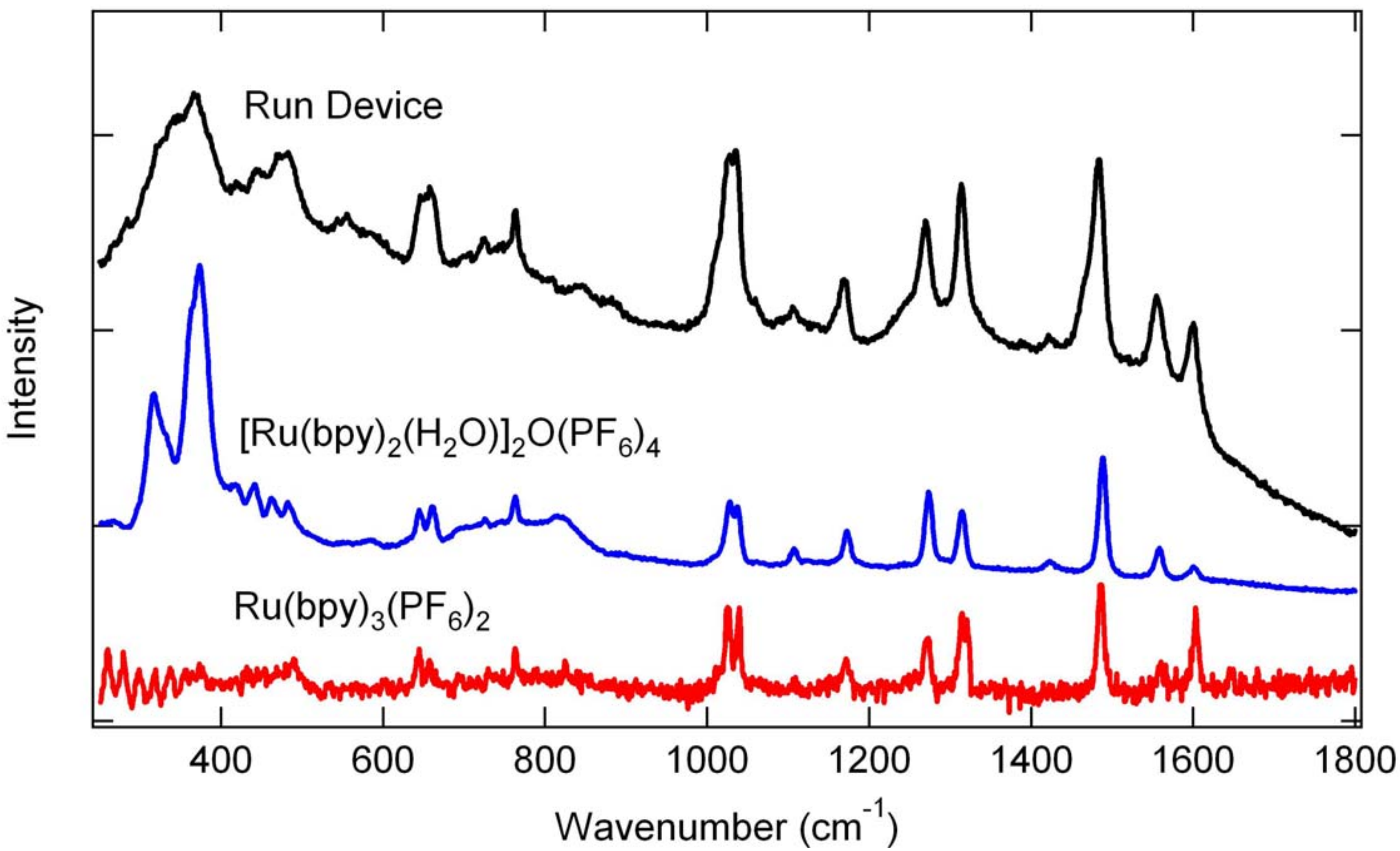
Lifetime (IV)



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Raman also shows dimer in degraded devices

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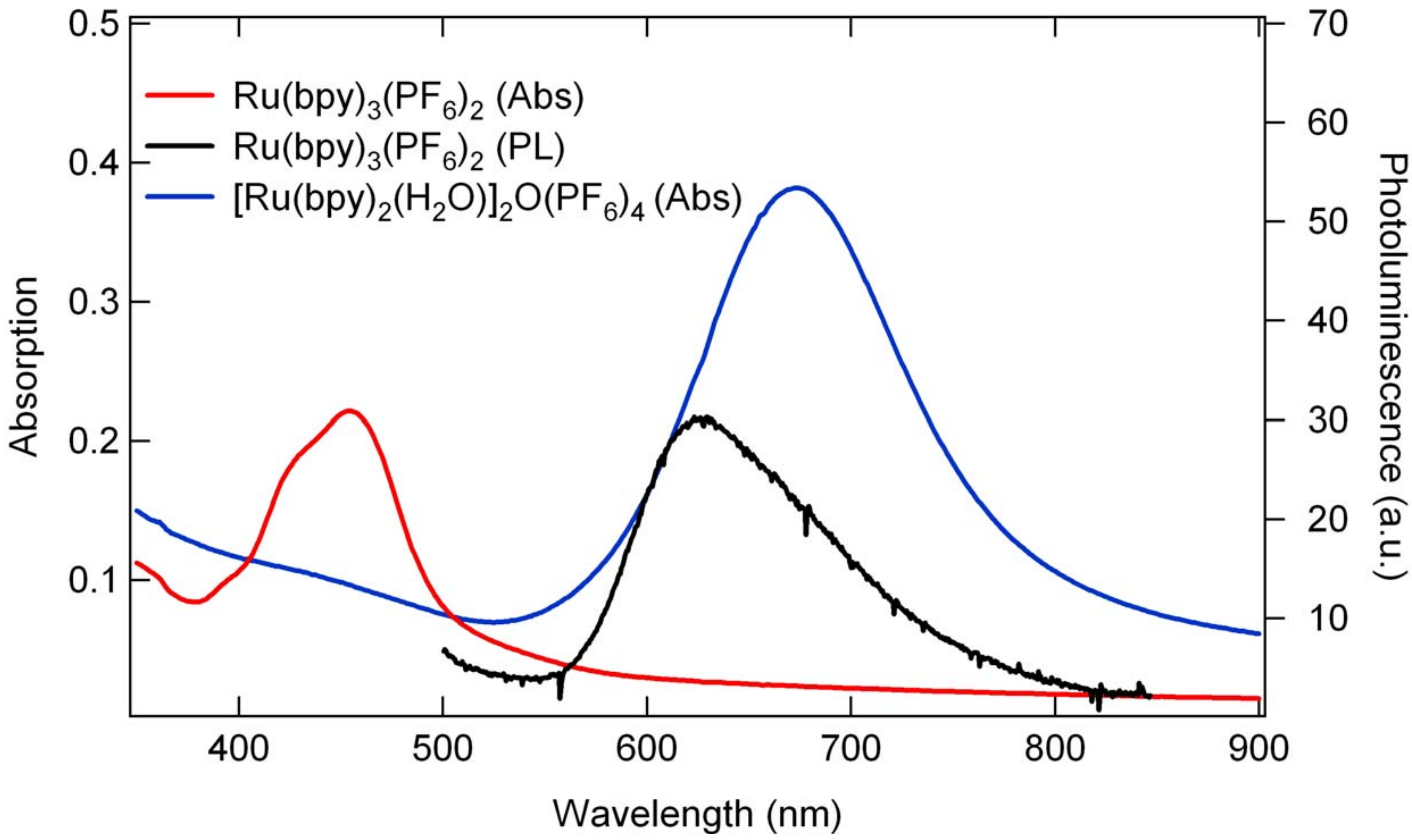
Lifetime (V)



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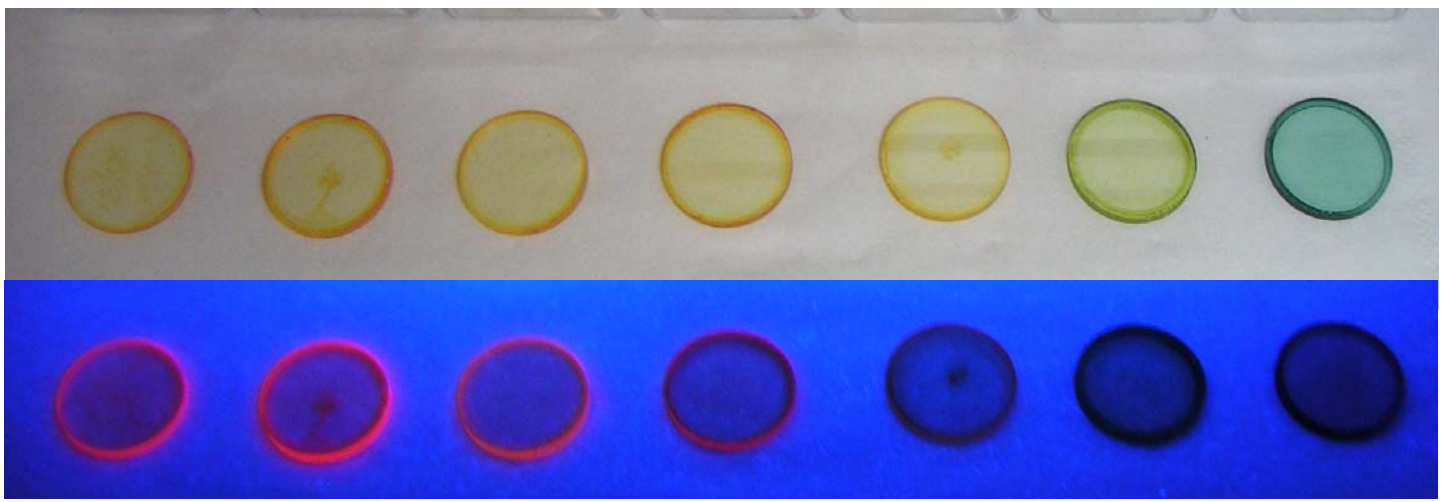
Lifetime (VI)

	Pristine $Ru(bpy)_3$	1:10000	1:1000	1:333	1:100	1:10	Pristine Dimer



Normalized PL Yield:	1	≈1	0.74	0.05	0.01	≈0	≈0

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Dimer quenches emission

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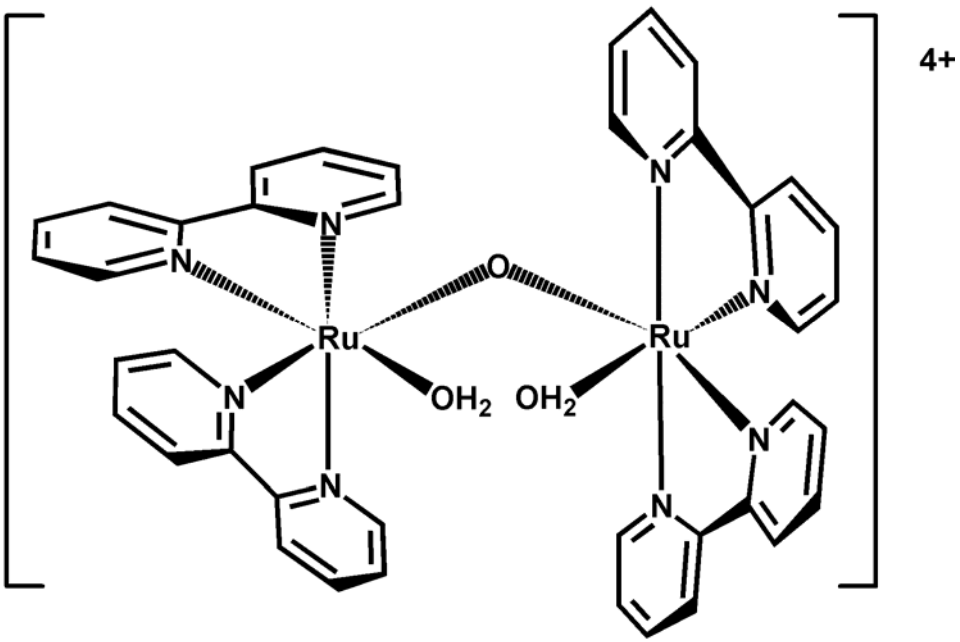
Lifetime (VII)



Can we synthesize intrinsically stable materials?

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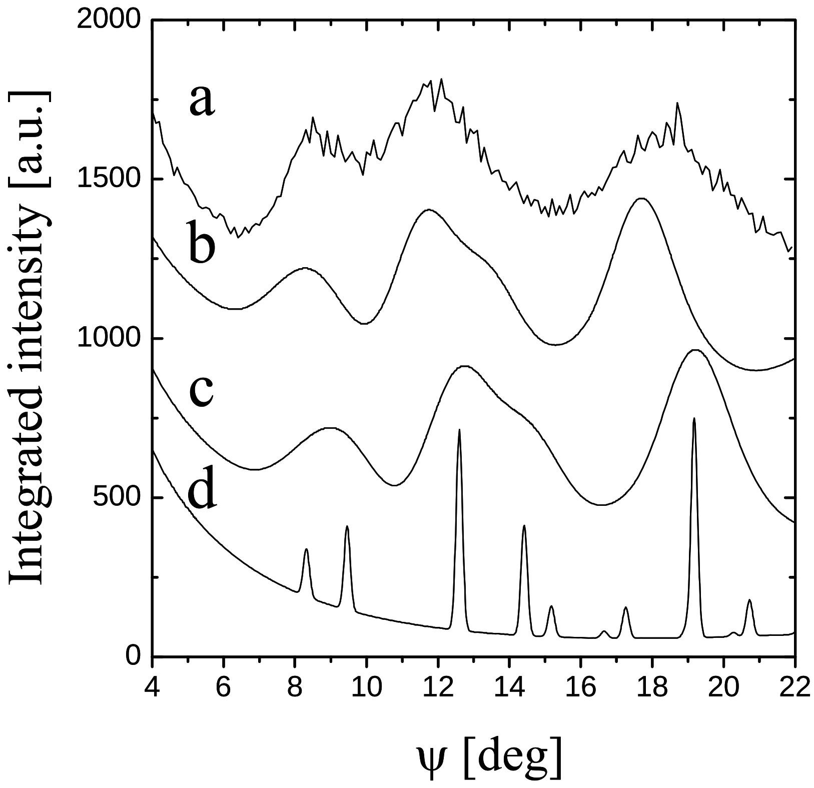
Lifetime (VIII)



D.R. Blasini, D.-M. Smilgies et al.

See poster

Intermediate range order – changes with exposure to ambient

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Take home message (1)

Interplay between ionic and electronic charges in mixed conductors creates exiting opportunities for electroluminescent devices

- Structure of these materials/ how is it modified by ion motion?
- Changes in chemistry/structure during operation?

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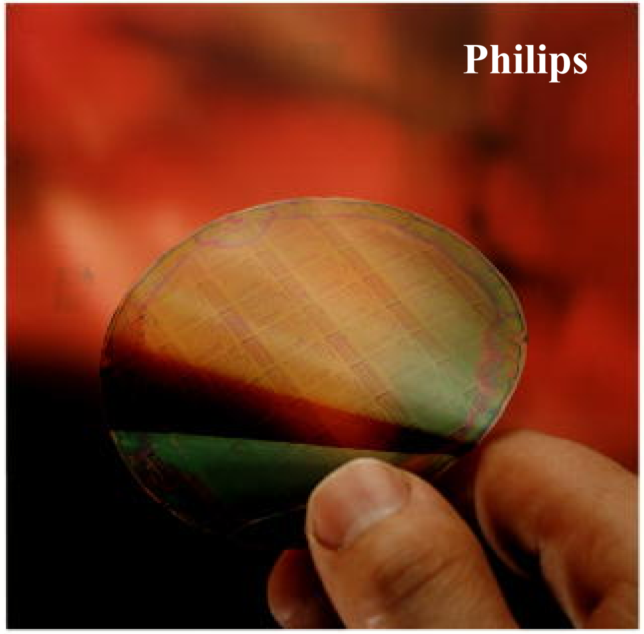
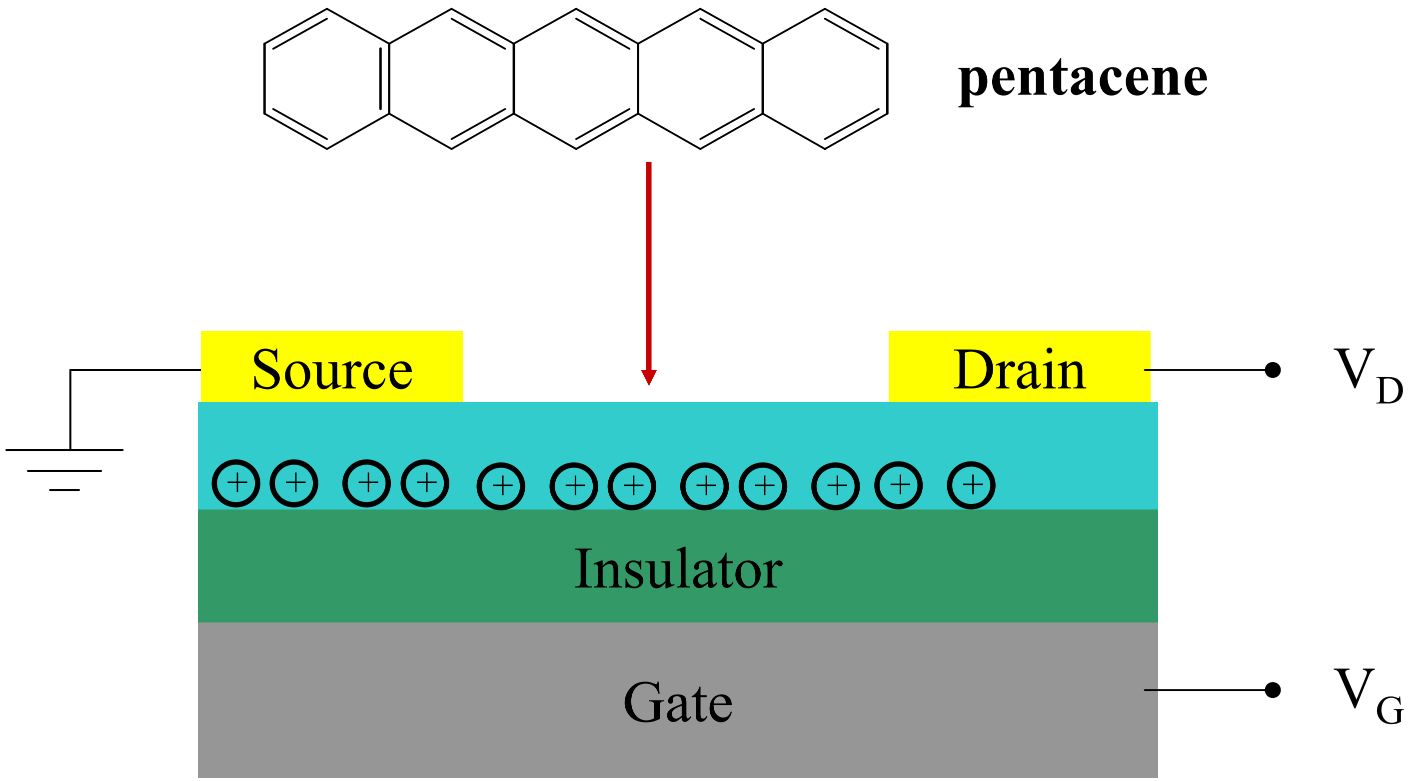
Organic thin film transistors (OTFTs)



Organic thin film transistors (II)



Side view

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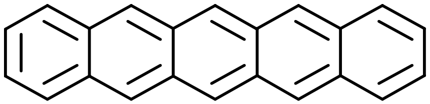
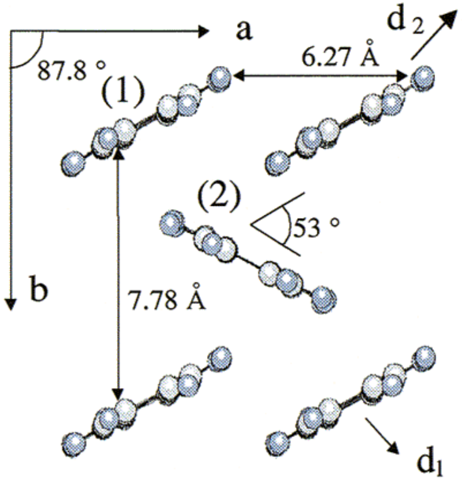
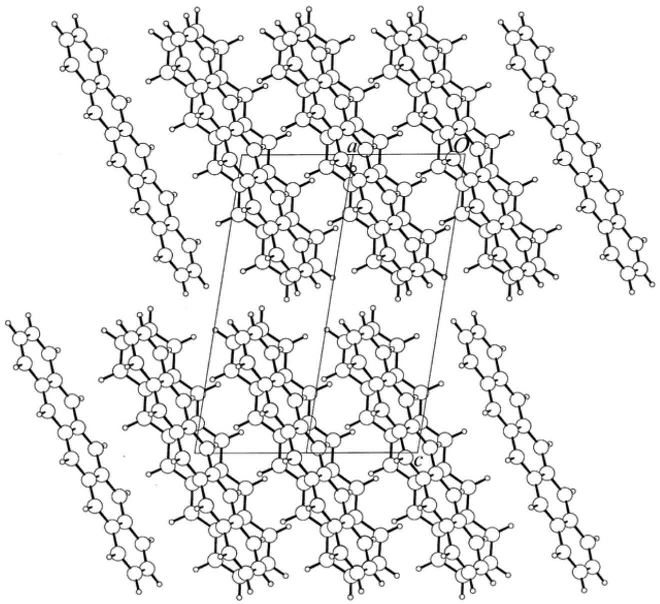
Pentacene crystal structure



Pentacene

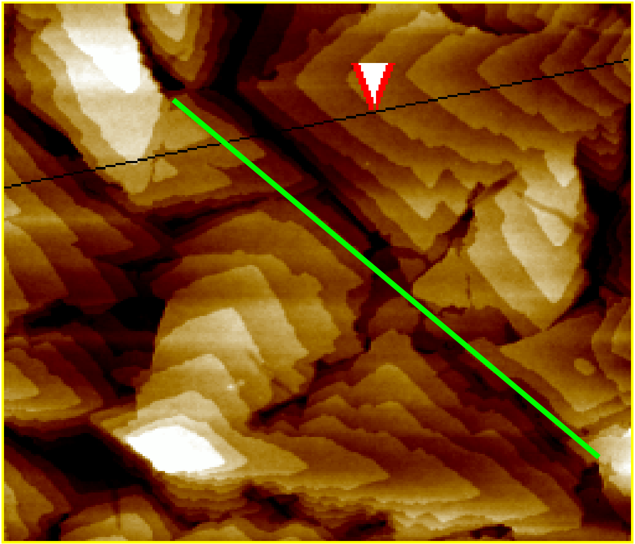


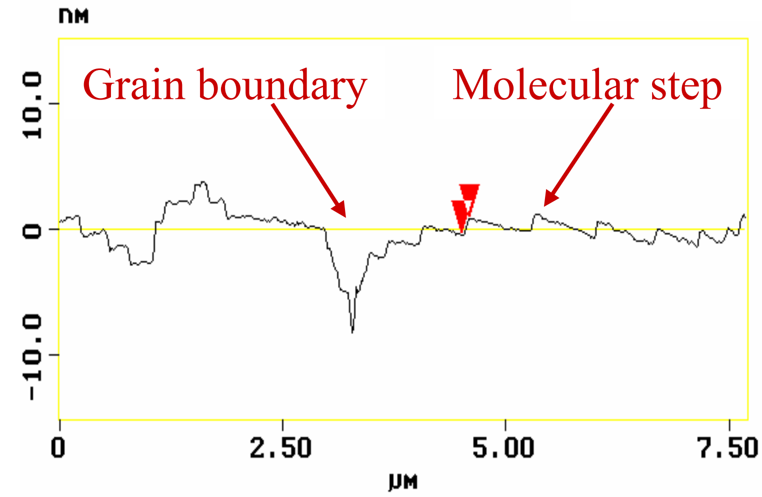
J. Cornil *et al.*, *J. Am. Chem. Soc.*, **123**, 1250 (2001).



C.C. Mattheus *et al.*, *Acta Cryst.* C**57**, 939 (2001).

Morphology of evaporated films





Coherence among seemingly different grains

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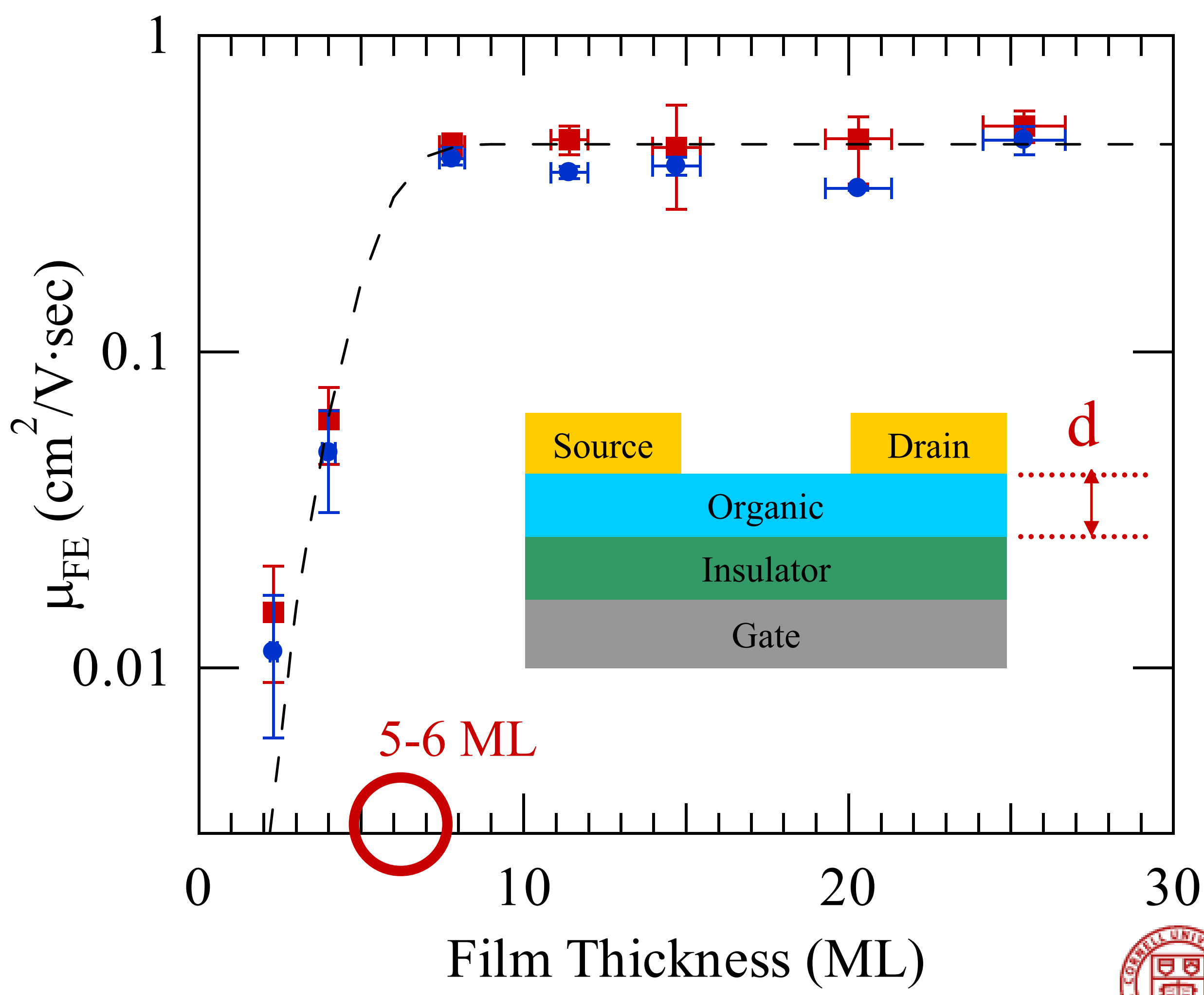
Dependence of mobility on thickness



R. Ruiz, et al., *Adv. Mater*. **17**, *1795* (2005).

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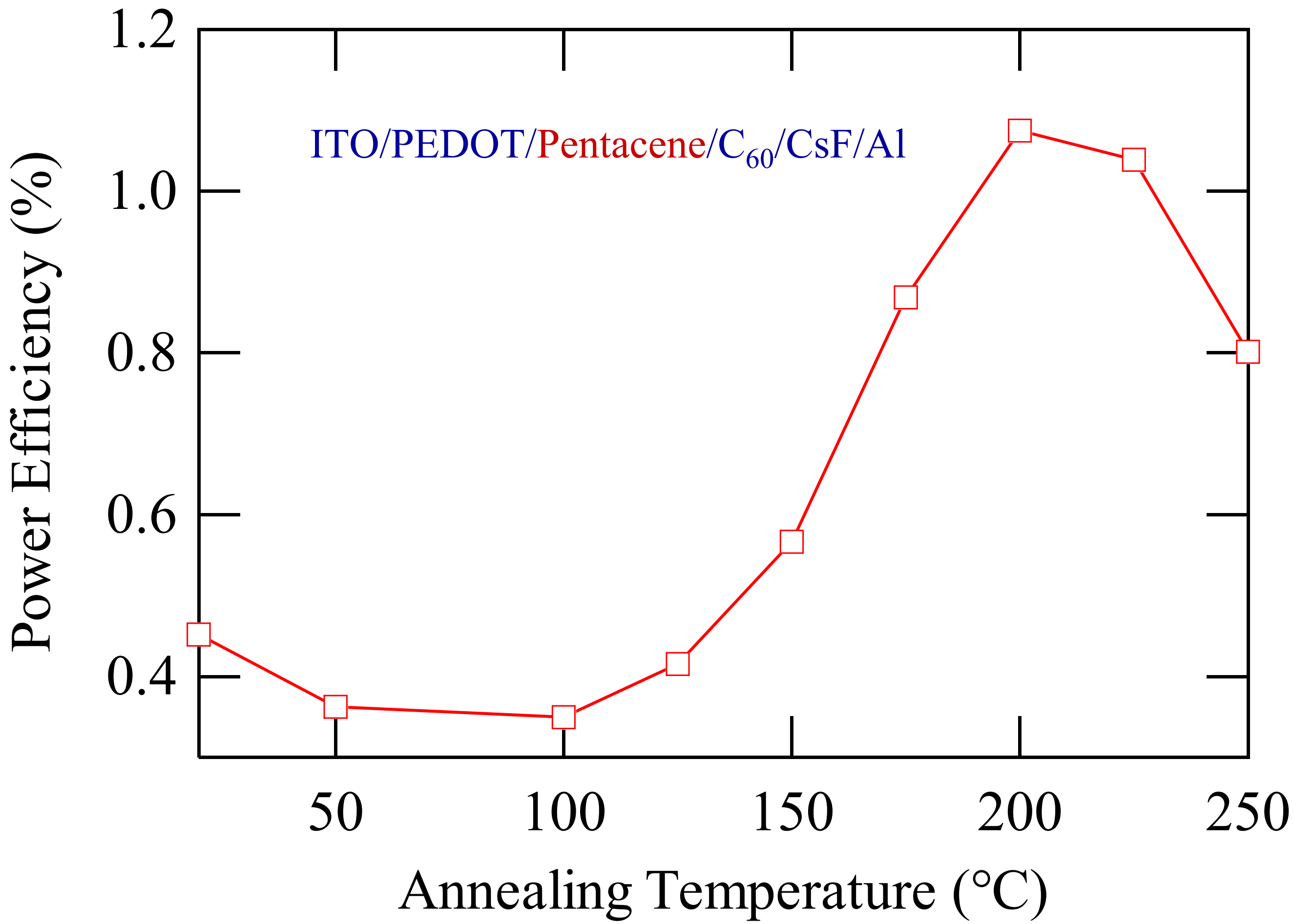
Pentacene also for photovoltaic cells



A.C. Mayer et al., Appl. Phys. Lett. **85**, 6272 (2004).

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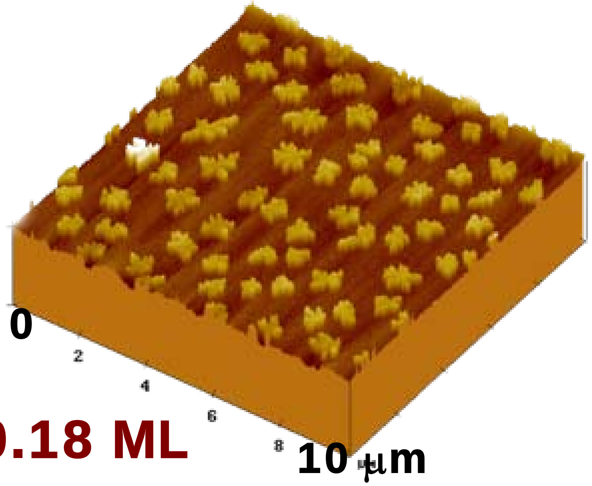
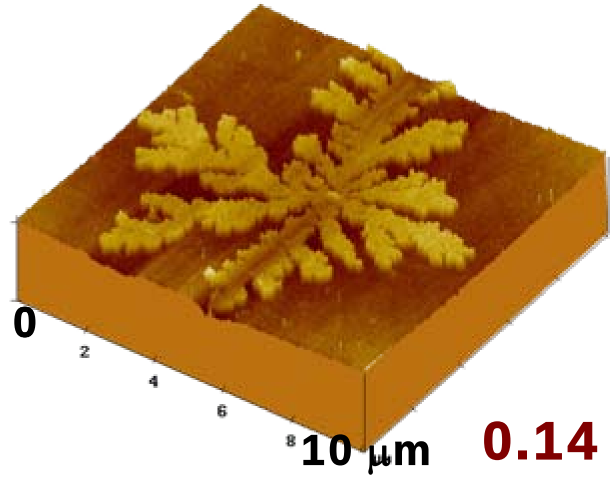
Pentacene nucleation

Silicon oxide
(hydrophilic)



0.18 ML

H-terminated silicon
(hydrophobic)



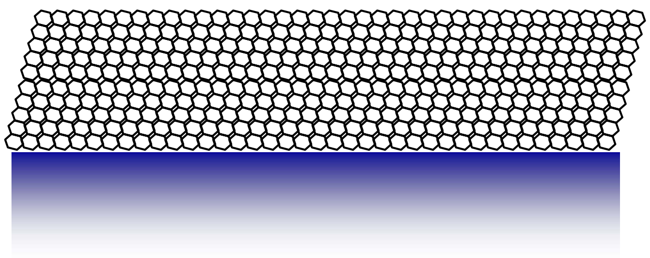
0.14 ML

Ruiz et al, Phys.Rev. B 67, 125406 (2003).

How does the substrate affect film growth?

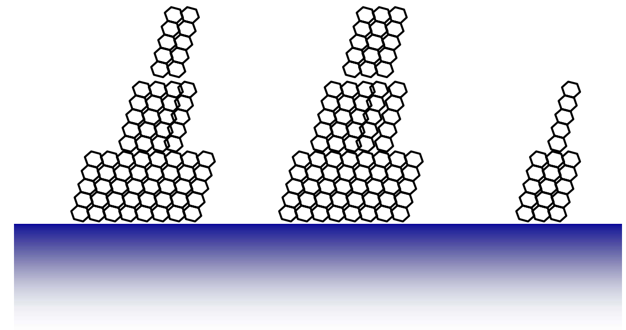
Modes of growth

The two extremes:



Layer by layer (2D)

Good substrate coverage
Good connectivity
Best for OTFTs

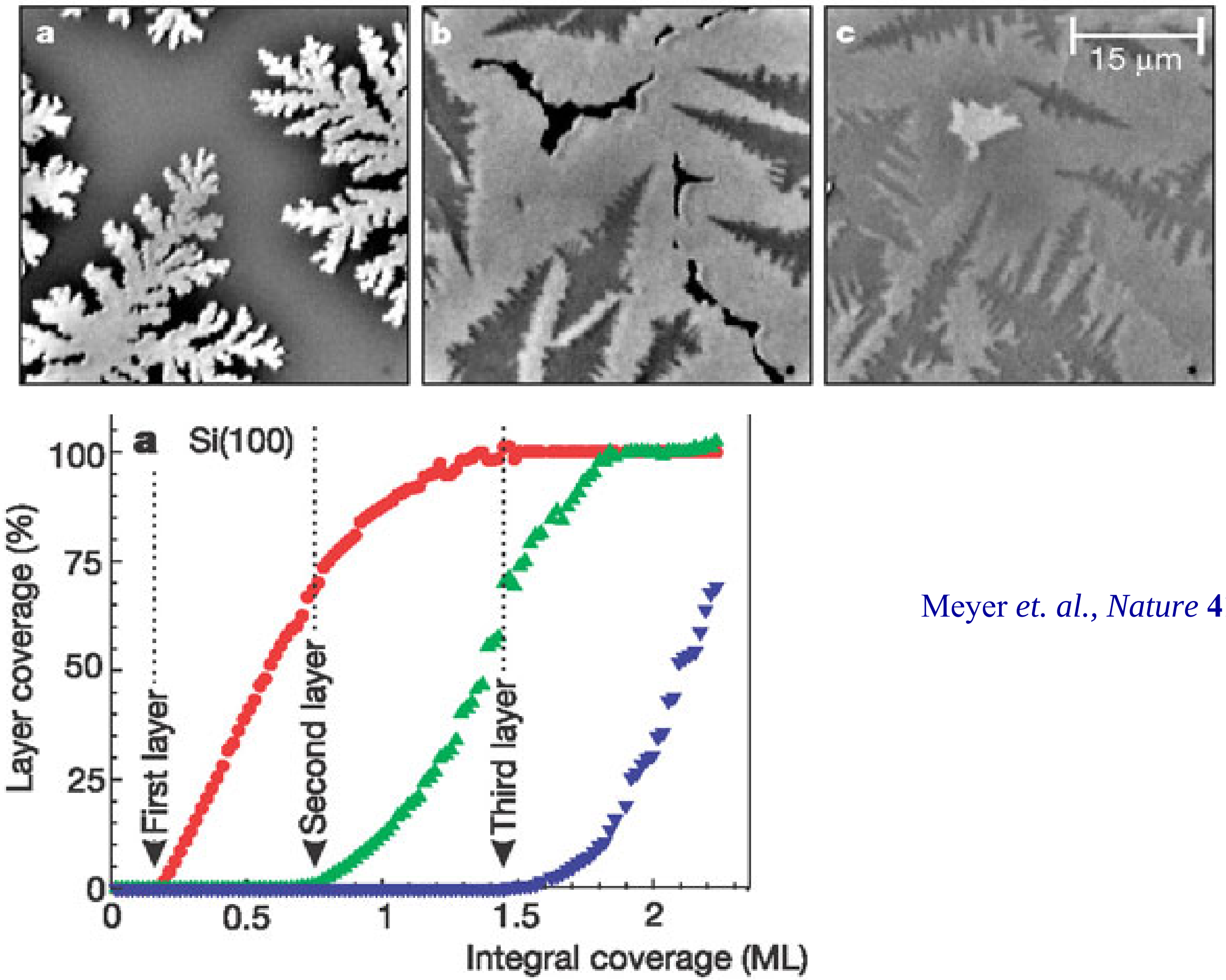


Islands (3D)

Poor substrate coverage
Poor connectivity
Worst for OTFTs

R. Ruiz, et al.,*Chem. Mater*. **16**, 4497 (2004).

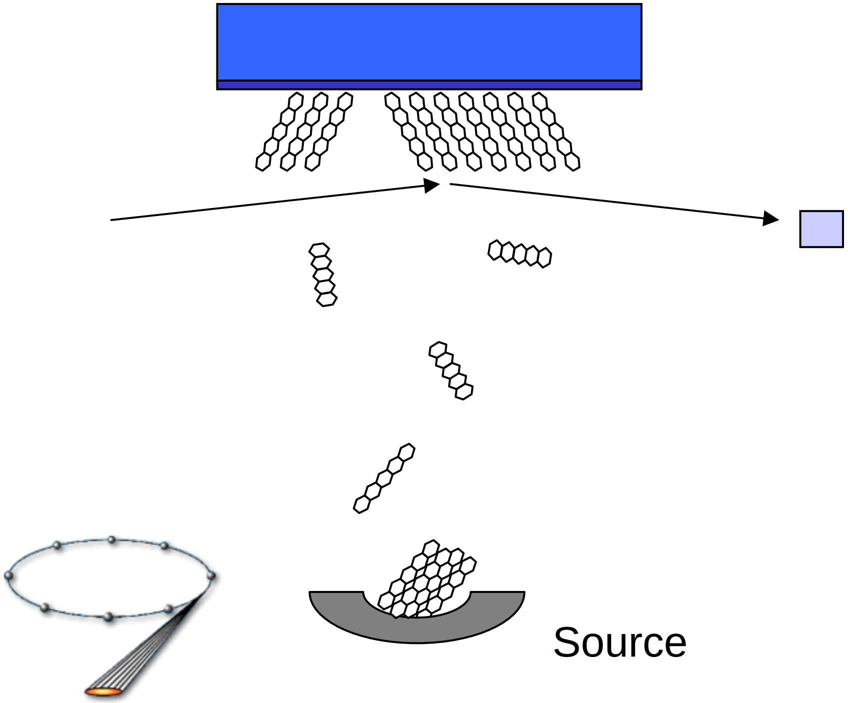
Pentacene on Si (100)

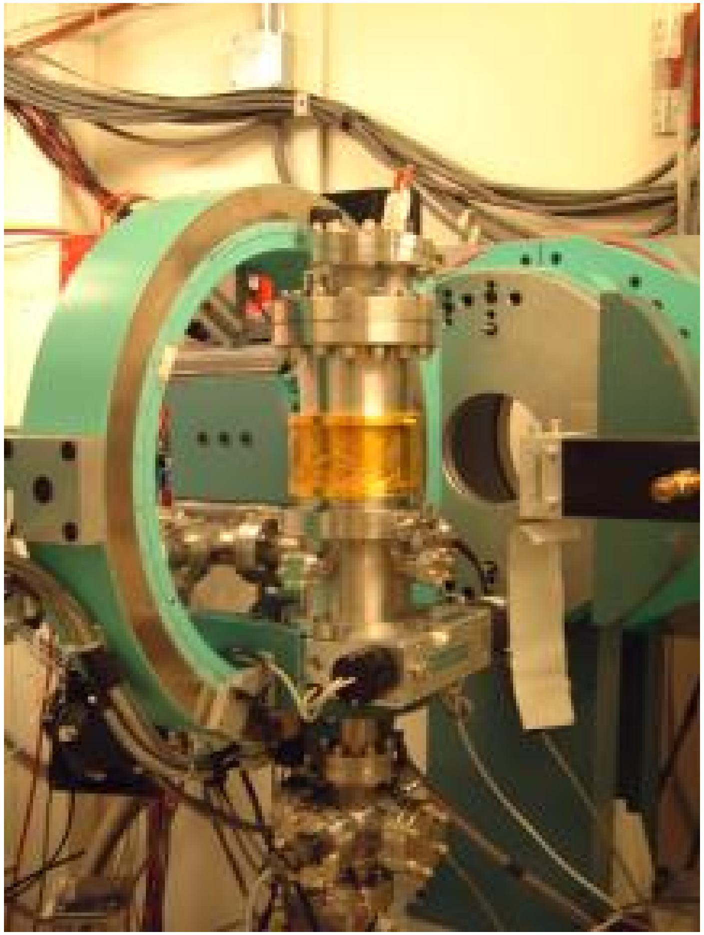


Meyer *et. al.*, *Nature* **412,** 517 (2001).

In situ growth studies

In-situ growth,
morphology and
electrical measurements





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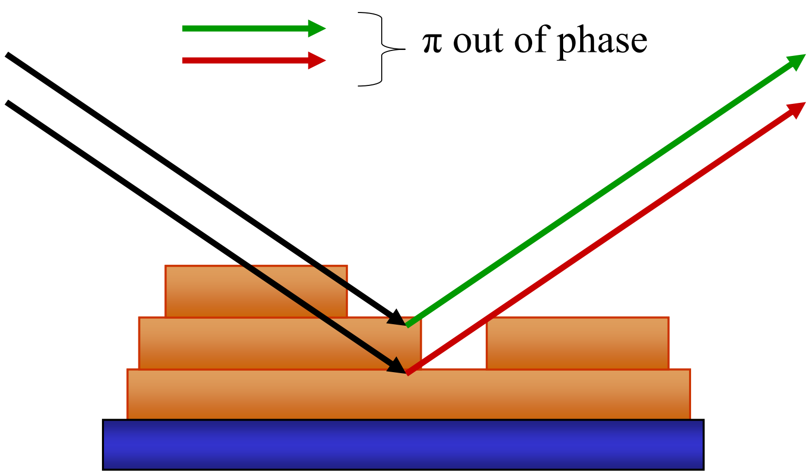
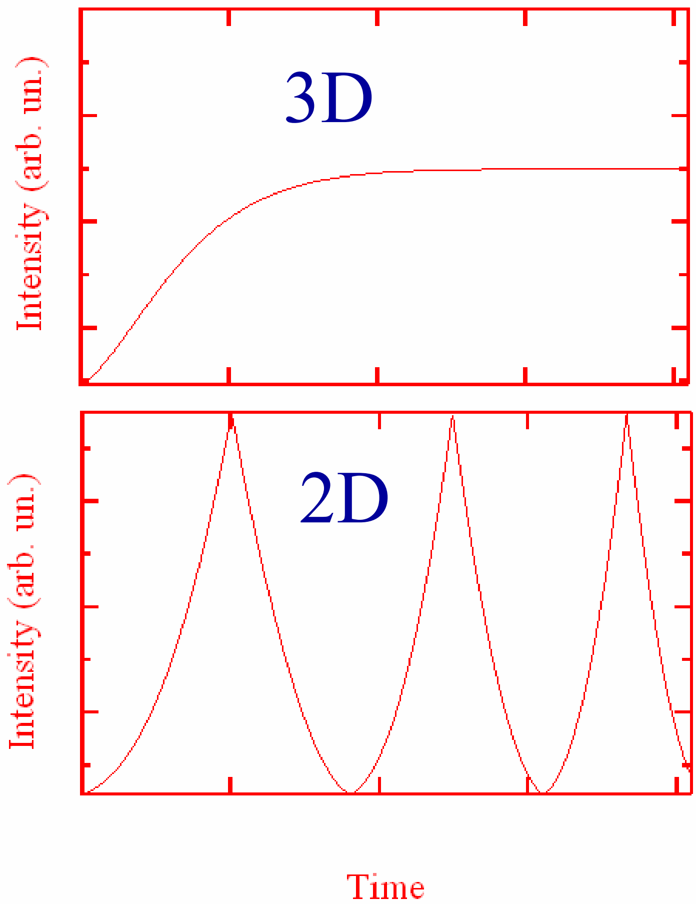
Anti-Bragg x-ray scattering

$$I = \left| r_{sub} e^{-i\varphi} + r_{pen} \sum_n \theta_n e^{-iq_z dn} \right|^2$$





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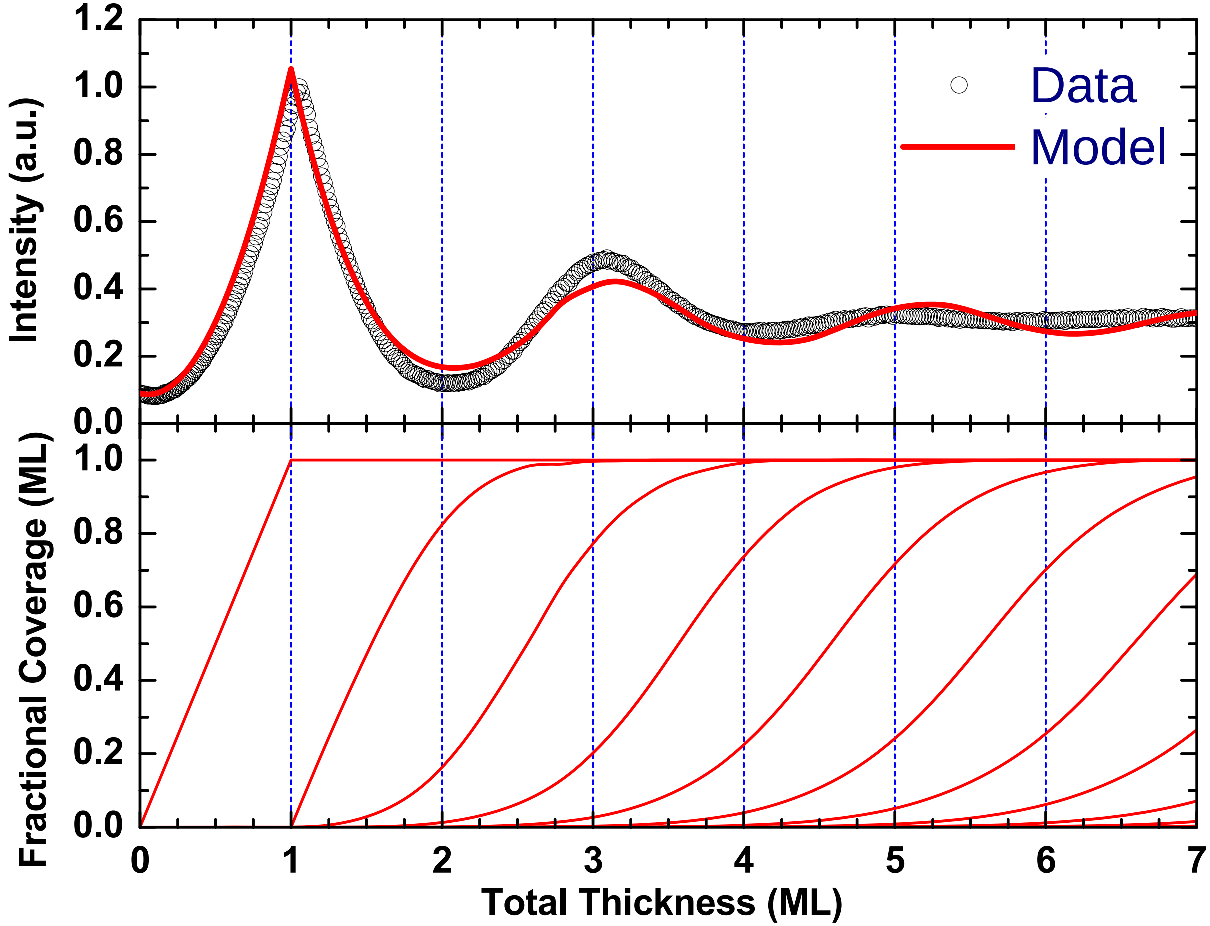
Growth mode of pentacene on SiO_2



A.C. Mayer, et al., *Org. Electr.* **5**, 257 (2004).

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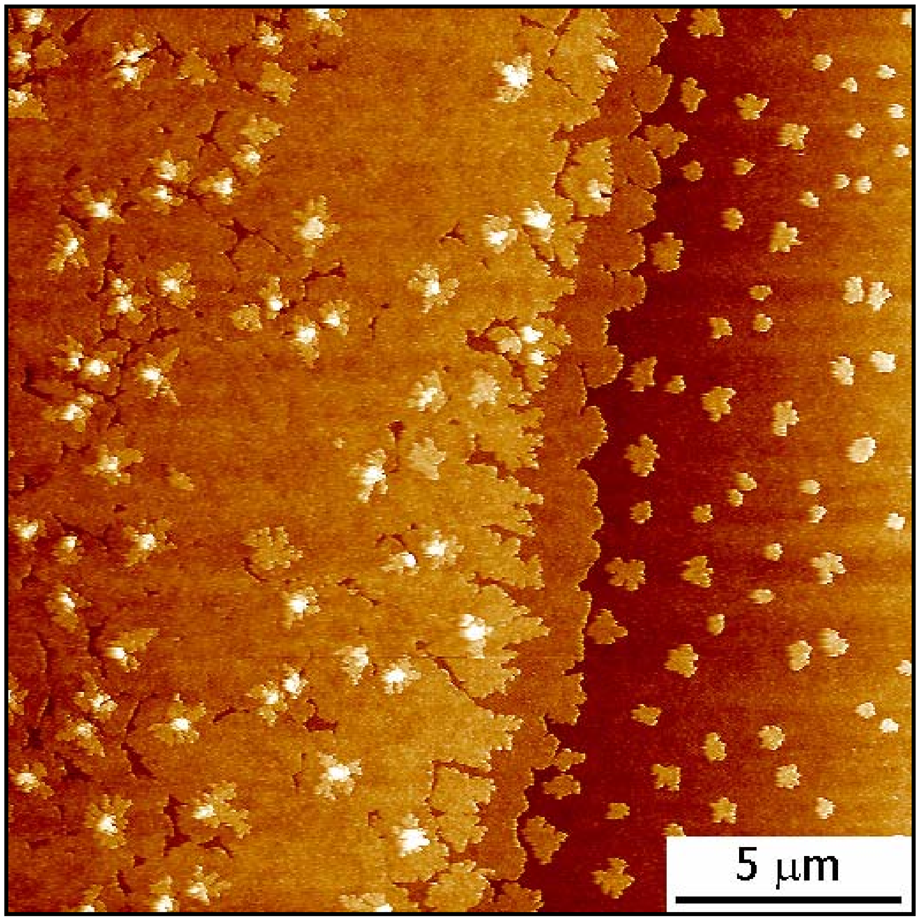
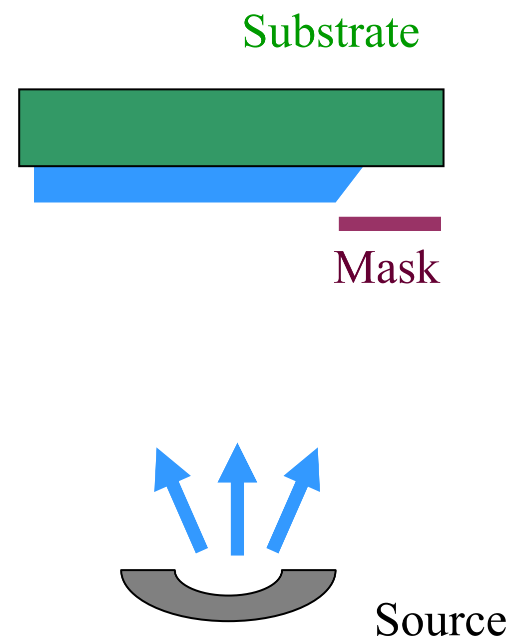
Early growth is layer-by-layer

d = 2.3 ML





Pentacene on SiO_2

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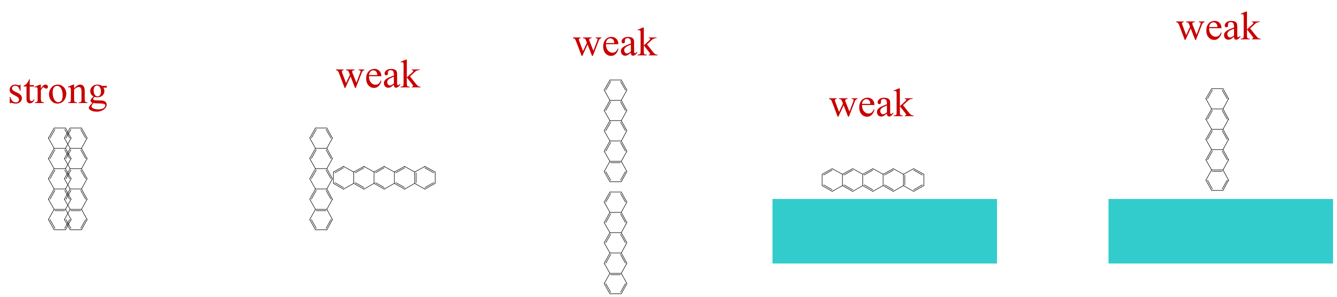
Origin of layer-by-layer growth

- In inorganics, layer-by-layer growth requires strong interaction with the substrate
- In pentacene, it is the strong anisotropic interaction that leads to layer-by-layer growth:



- Organics: building blocks with complex shape (plenty to choose from)

  Anisotropic interactions are important

  Exciting growth physics

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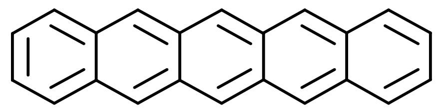
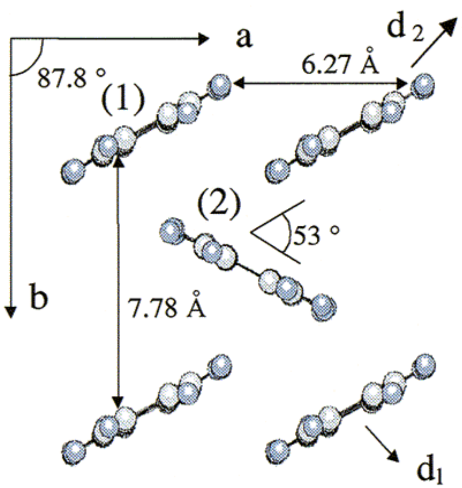
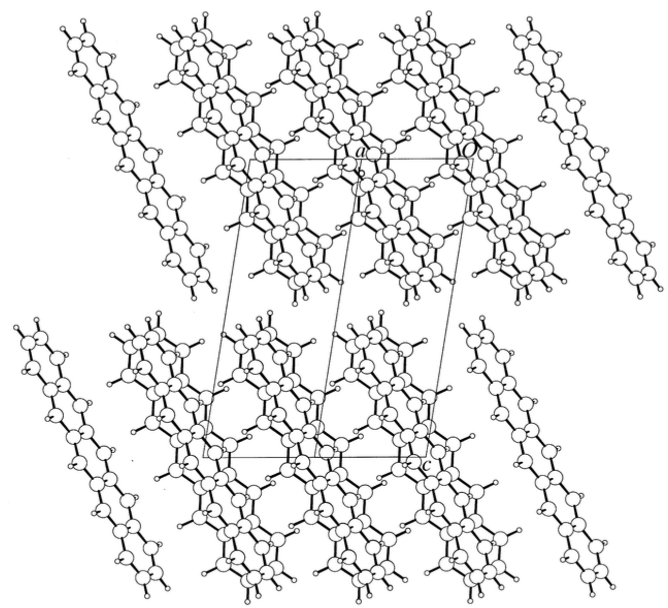
Pentacene crystal structure



Pentacene

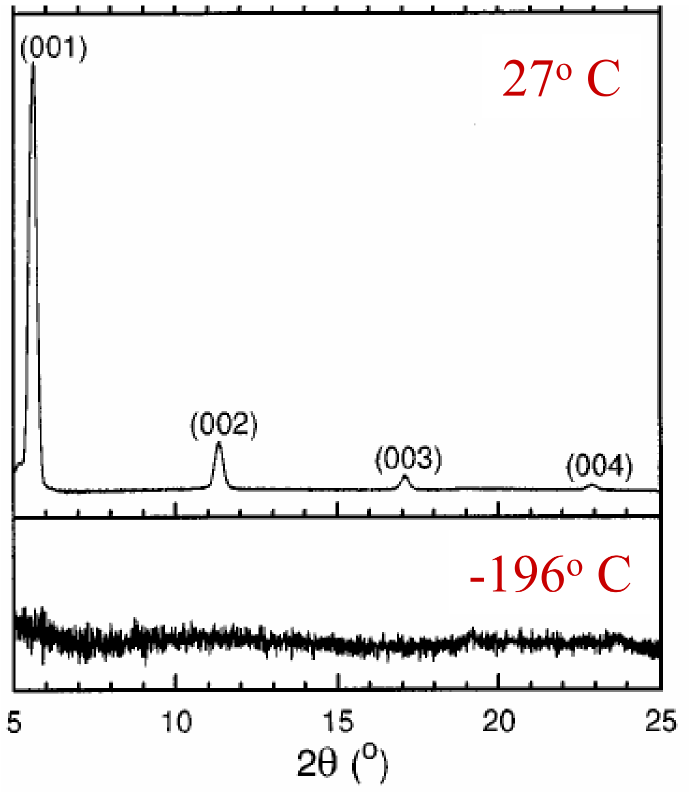


J. Cornil *et al.*, *J. Am. Chem. Soc.*, **123**, 1250 (2001).



C.C. Mattheus *et al.*, *Acta Cryst.* C**57**, 939 (2001).

The "thin-film" phase



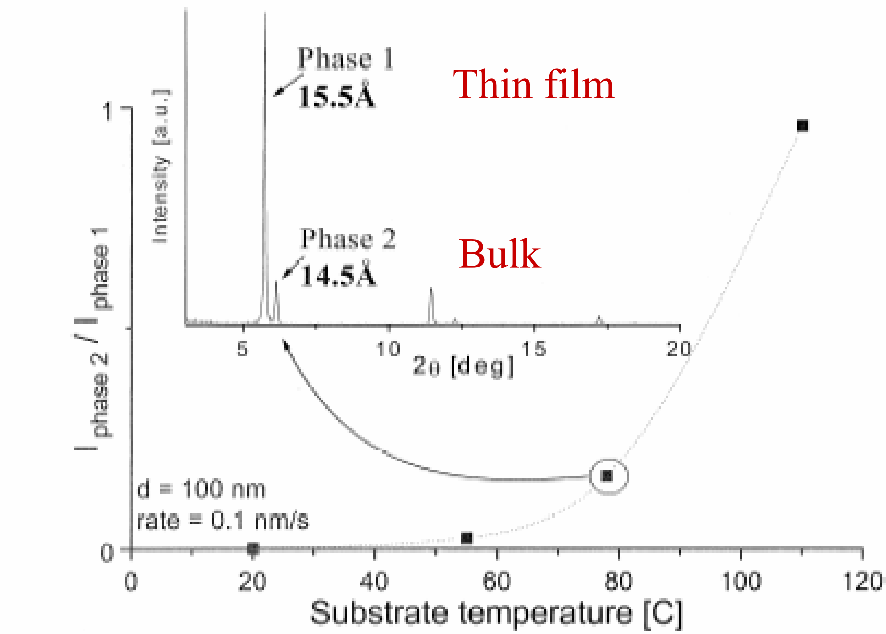
Only (00*l*) reflections: Film has layers that grow parallel to substrate

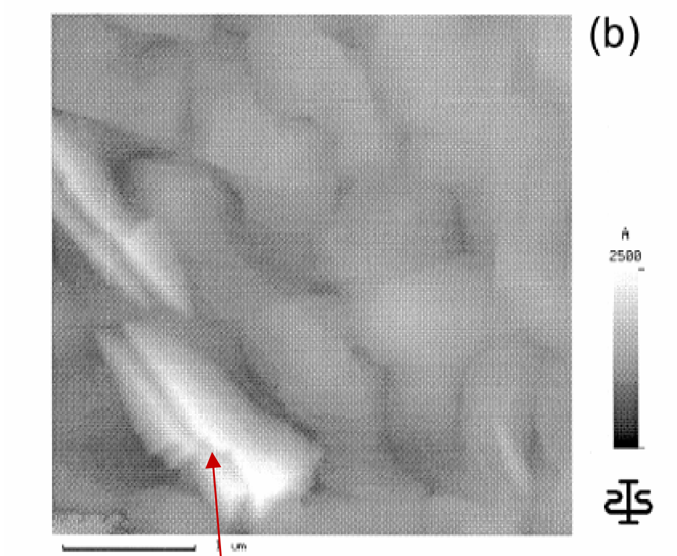
$d_{001} \approx 15.7$Å: "thin film" phase (bulk $d_{001} \approx 14.5$Å)

C.D. Dimitrakopoulos *et al*., *J. Appl. Phys.* **80**, 2501 (1996).

Coexistence of "thin-film" and bulk phases

Bouchoms et al., *Synth. Met.* **104**, 175 (1999)





Bulk ?

Is the thin film phase a strained meta-phase?

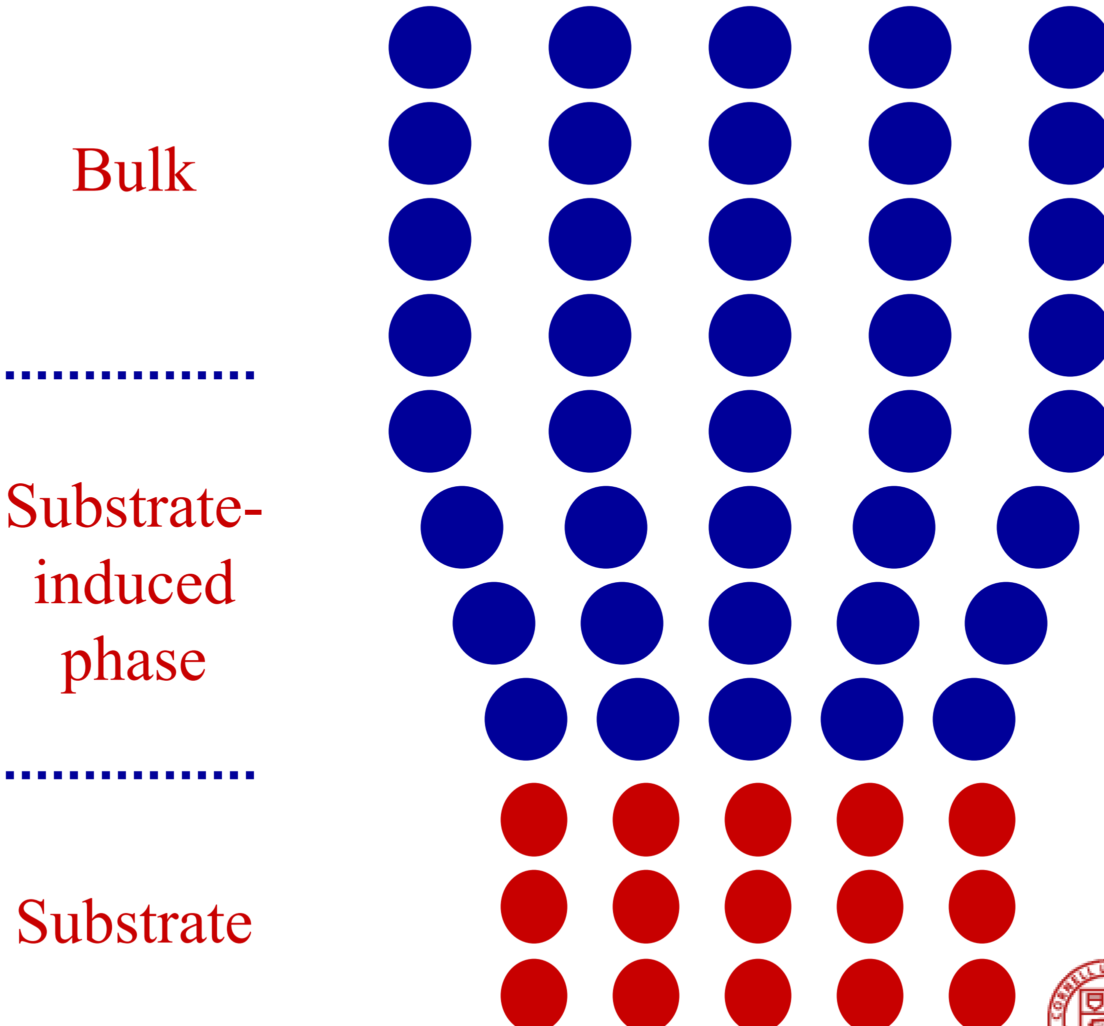
How do the two phases evolve as a function of thickness?

Strain in heteroepitaxy

Bulk

Substrate-induced phase

Substrate



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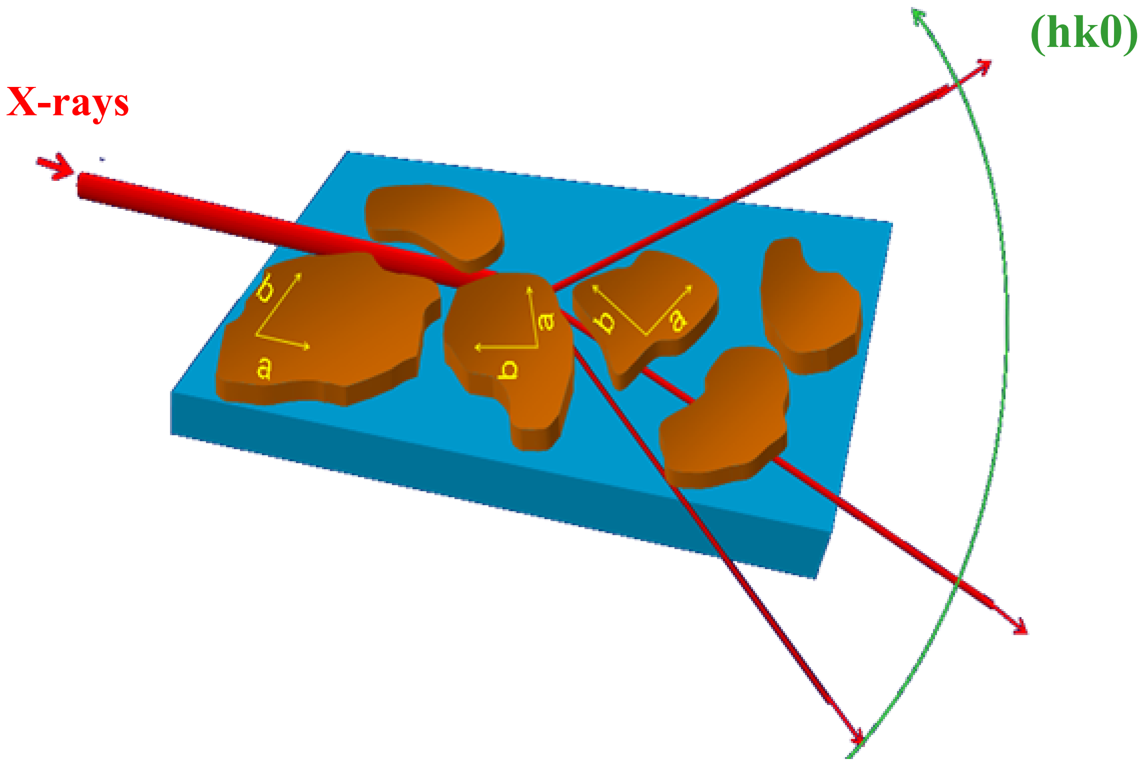
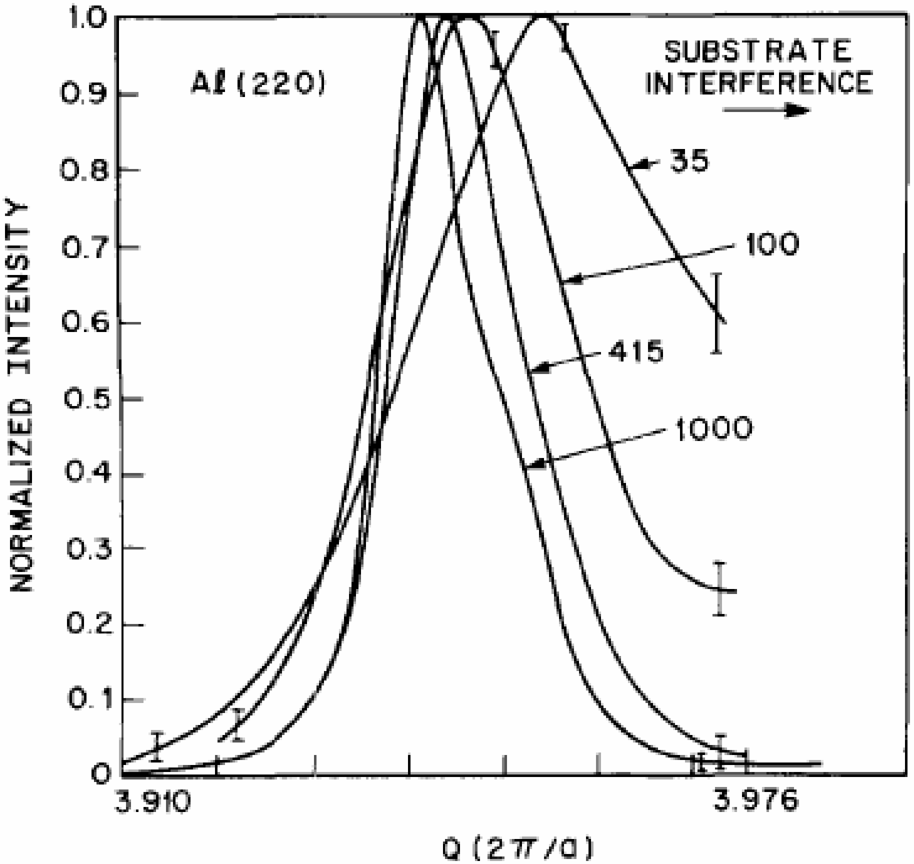
In-plane x-ray diffraction



Is the "thin-film" phase due to strain?

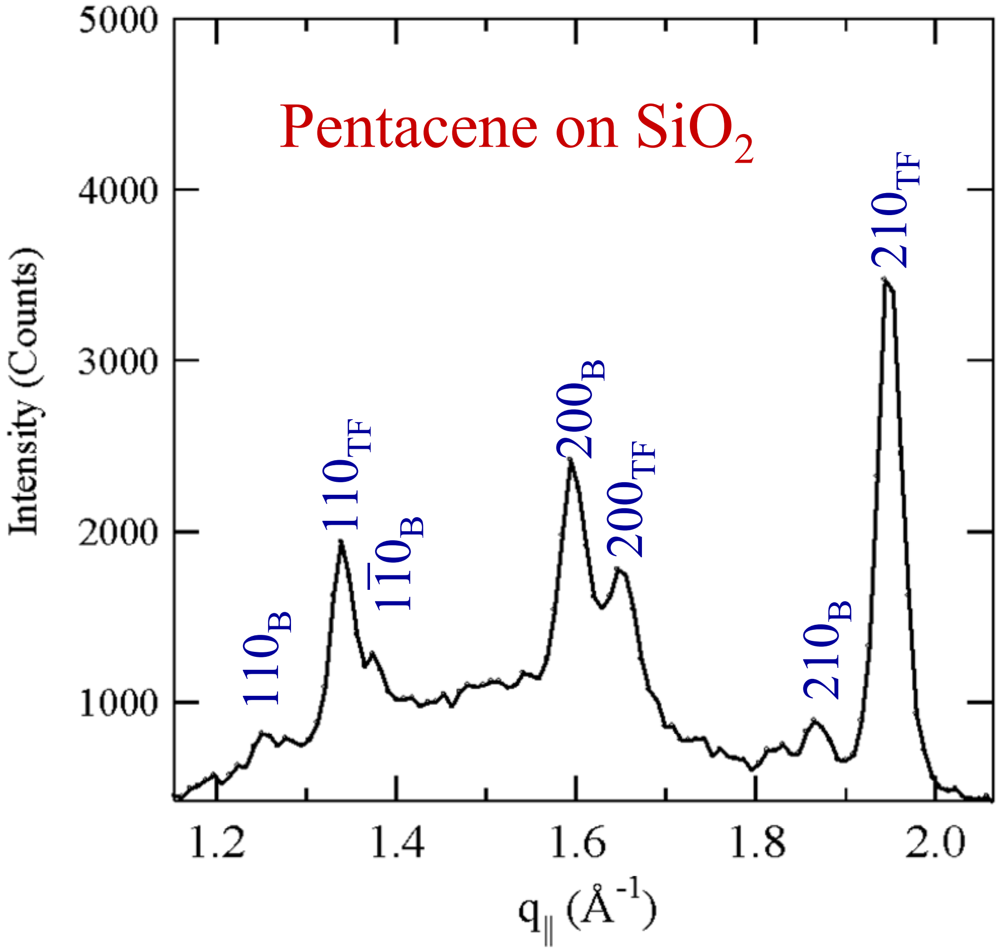


Al on GaAs

In-plane diffraction can reveal effects of strain

W.C. Marra et al., *J. Appl. Phys.* **50**, 6927 (1979).

In-plane diffraction in pentacene films



Two distinct phases that co-exist

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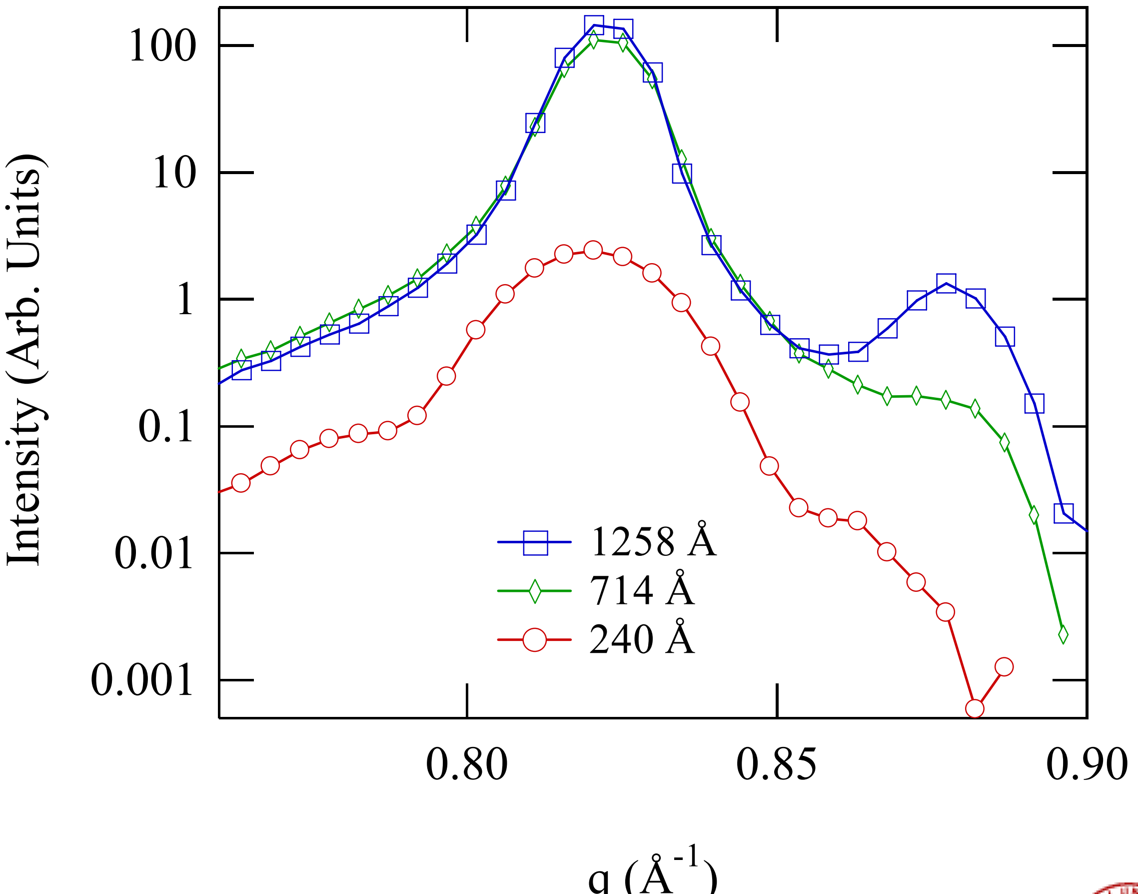
Evolution of bulk phase with thickness



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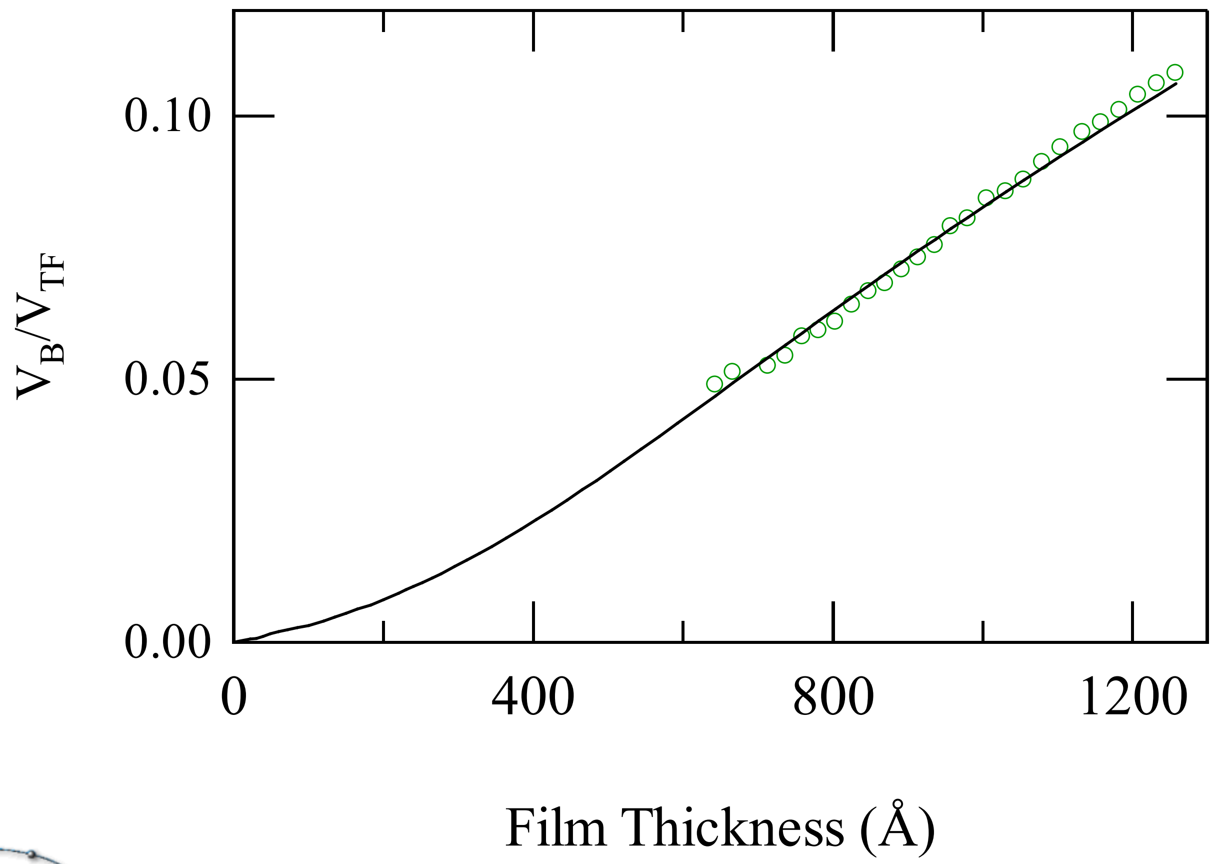
Evolution of bulk phase with thickness (II)



Bulk phase nucleates at the substrate!

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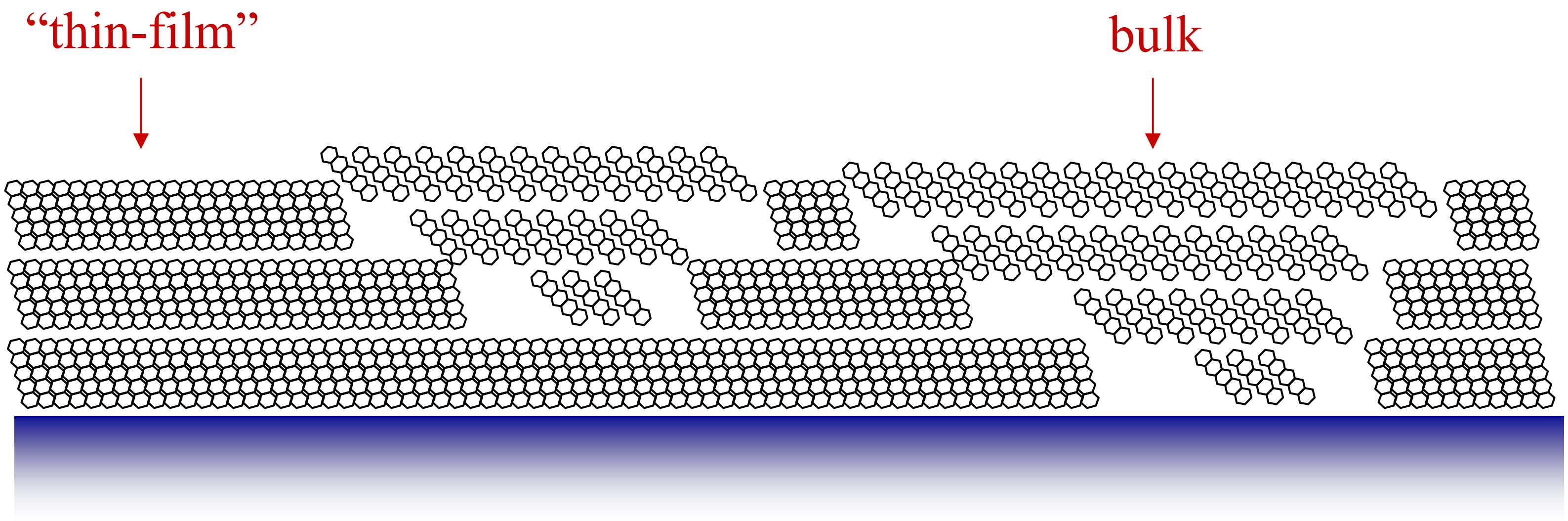
Model for evolution of bulk phase



Bulk phase nucleates at the substrate.
It continues to nucleate as film gets thicker
Bulk islands do not scatter in phase

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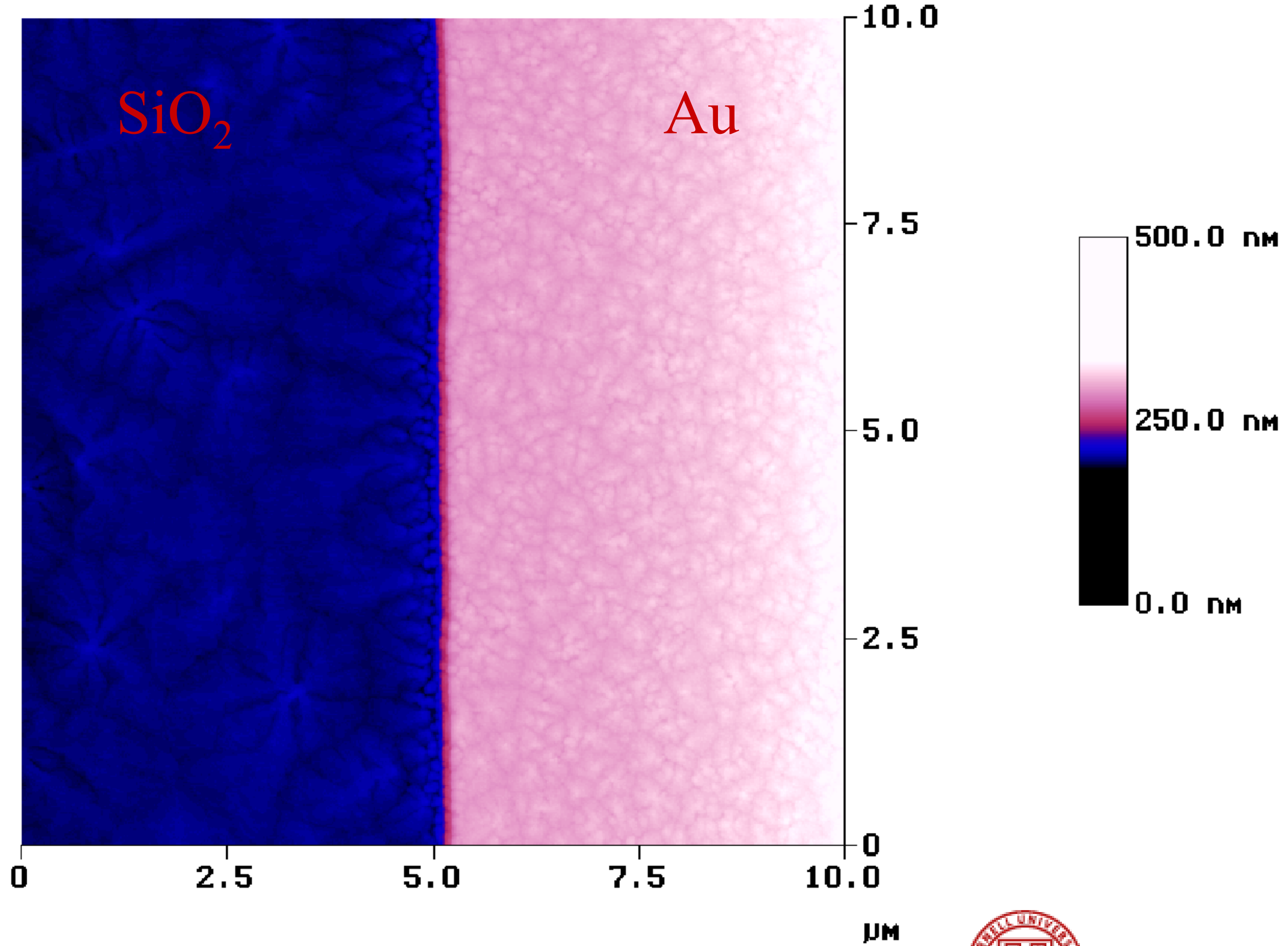
Growth near the electrodes



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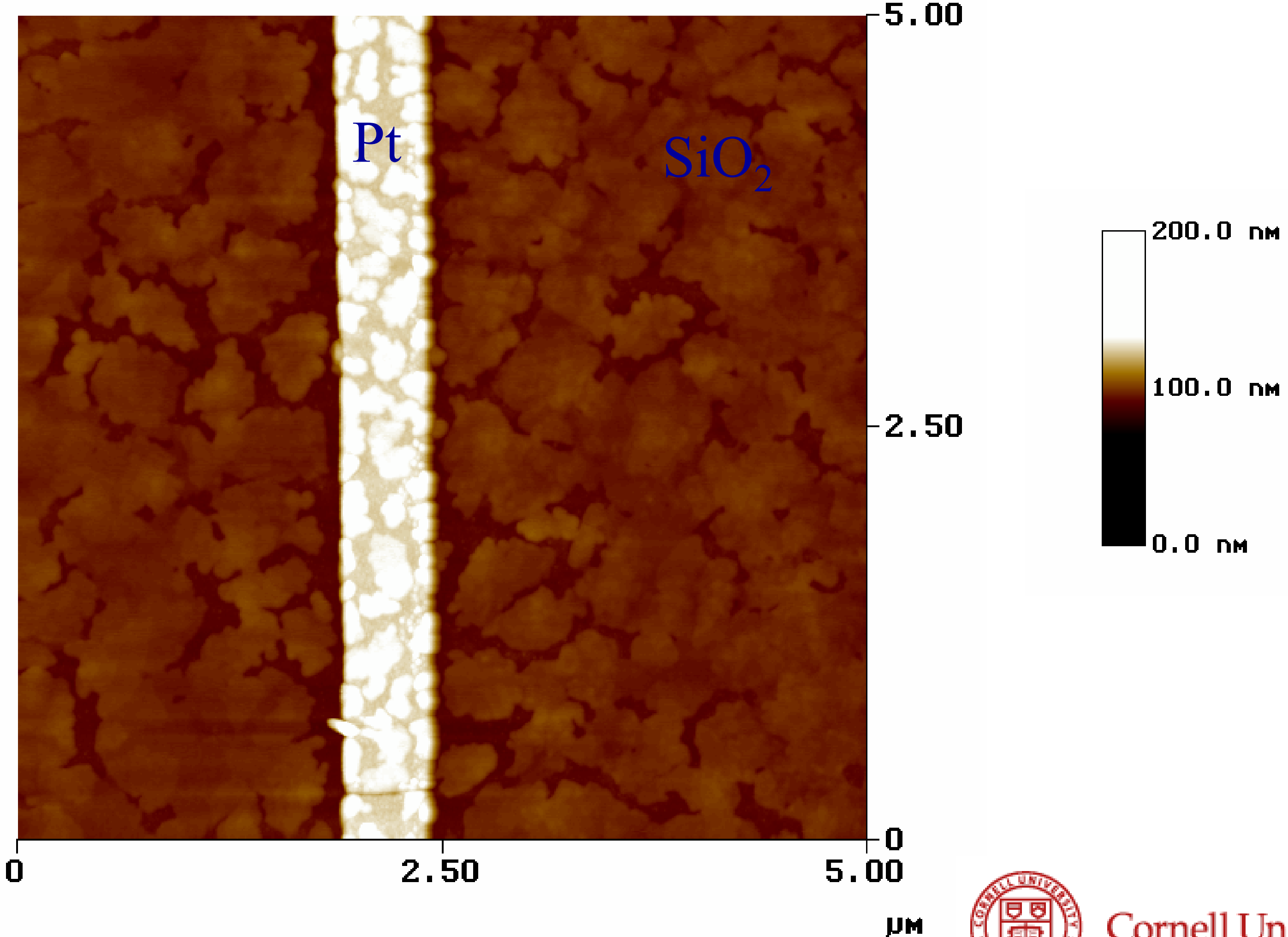
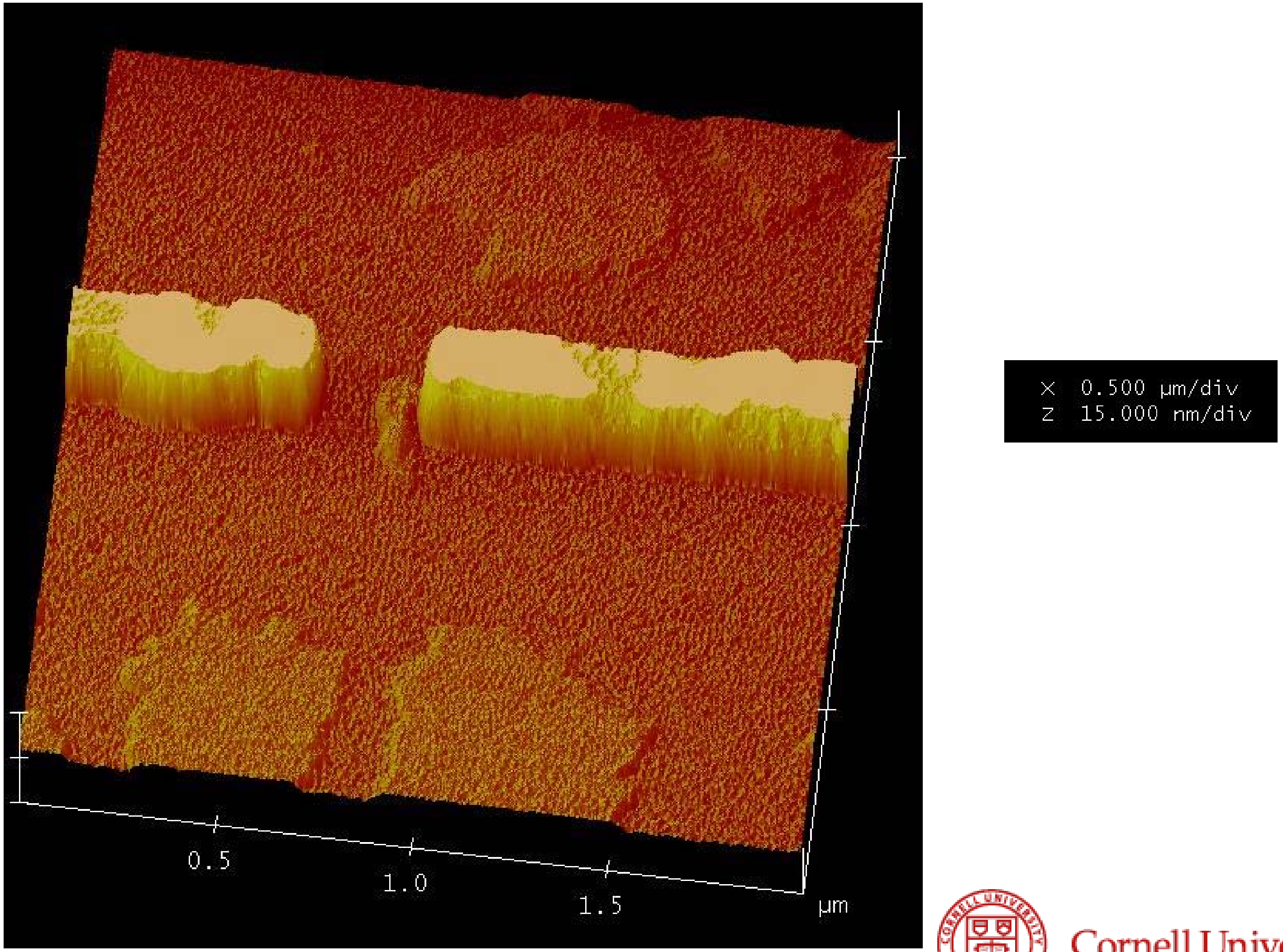
Growth near the electrodes (II)



Growth near the electrodes (III)



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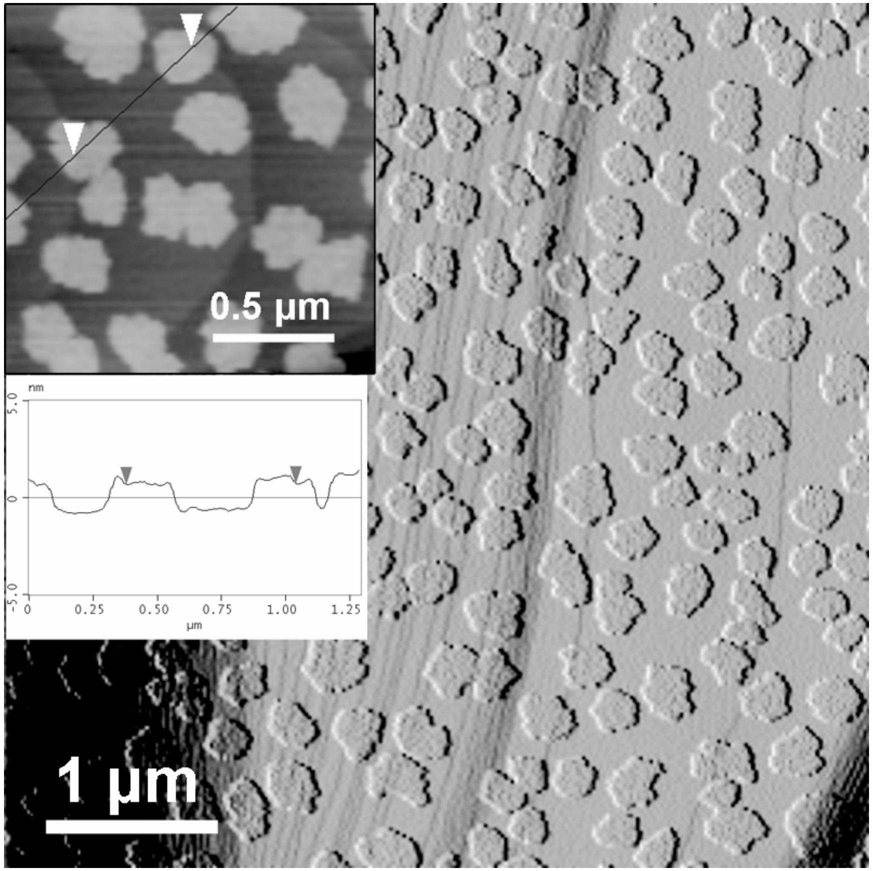
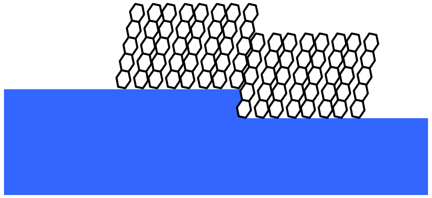
Creating model defects



Pentacene on SiO_2



Pentacene neglects steps on SiO_2
We can use stepped surfaces to create model defects

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Take home message (2)

Organic semiconductors are interesting "building blocks" for studies of thin film growth physics.

- Defects and their influence on charge transport?
- Structure at interfaces?

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Department of Energy · United States of America

Panasonic

NYSTAR

CNF Cornell Nanofabrication Facility

Cornell High Energy Synchrotron Source

Cornell University

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Satoyuki Nomura (Hitachi)
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Jack Blakely (Materials Science)
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Joel Brock (Applied Physics)

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Princeton
Stefan Bernhard (Chemistry)

Simmons College
Velda Goldberg (Physics)
Len Soltzberg (Chemistry)

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Richard Friend

CHESS
Alexander Kazimirov
Detlef Smilgies
Daniel Blasini

University of Vermont
Randy Headrick

University of Kentucky
John Anthony

LMU
Bert Nickel

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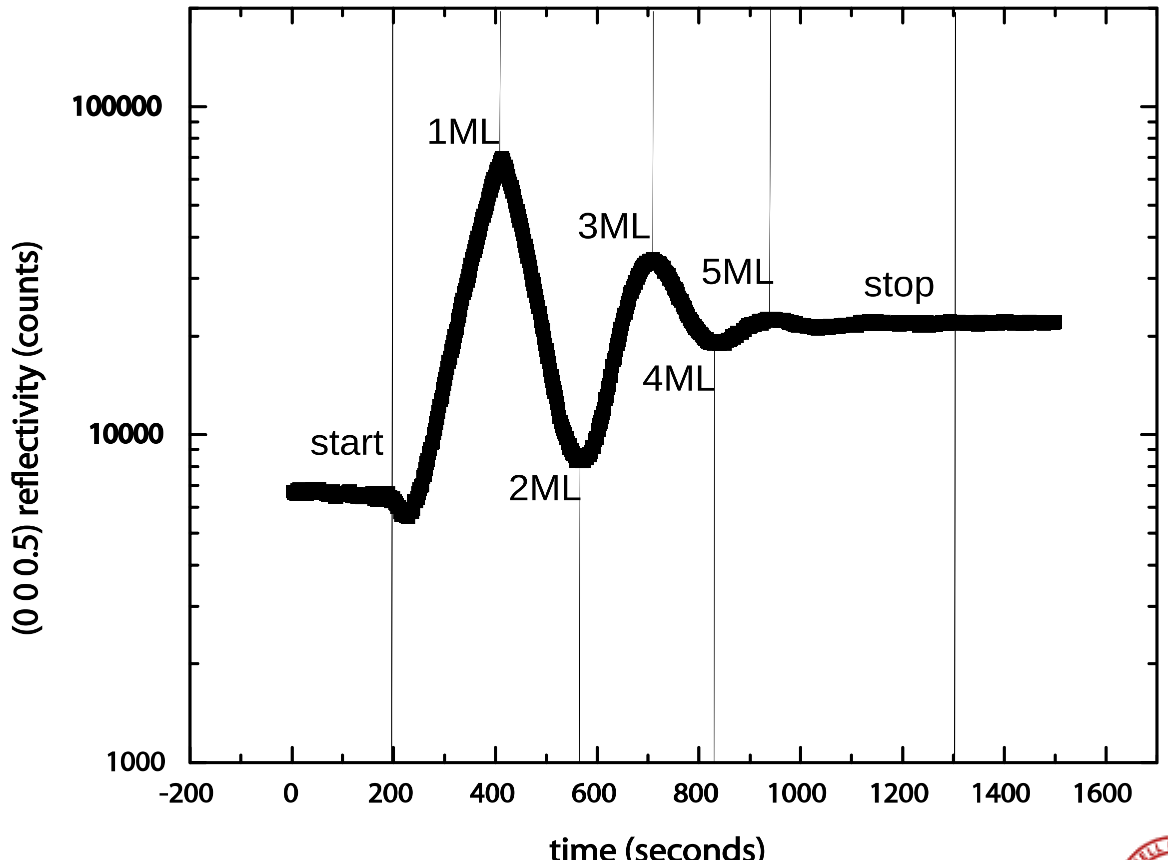
Anti-Bragg from pentacene

Pentacene on SiO_2



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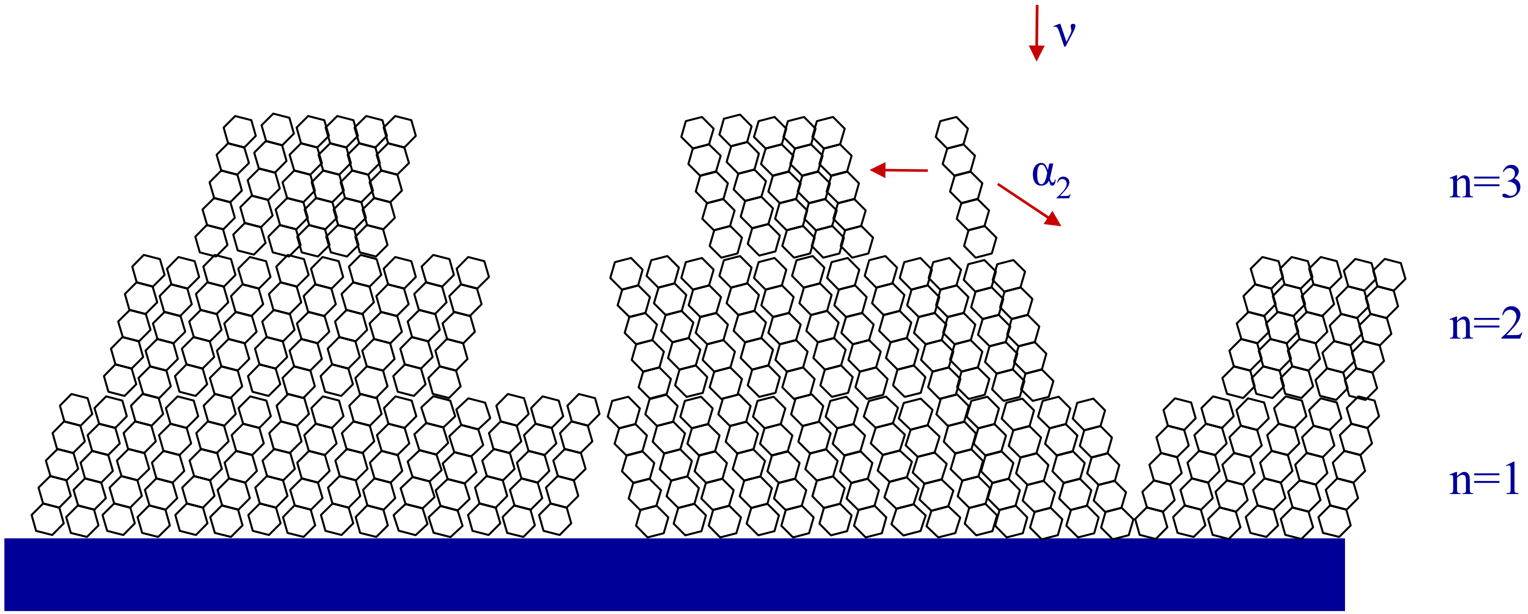
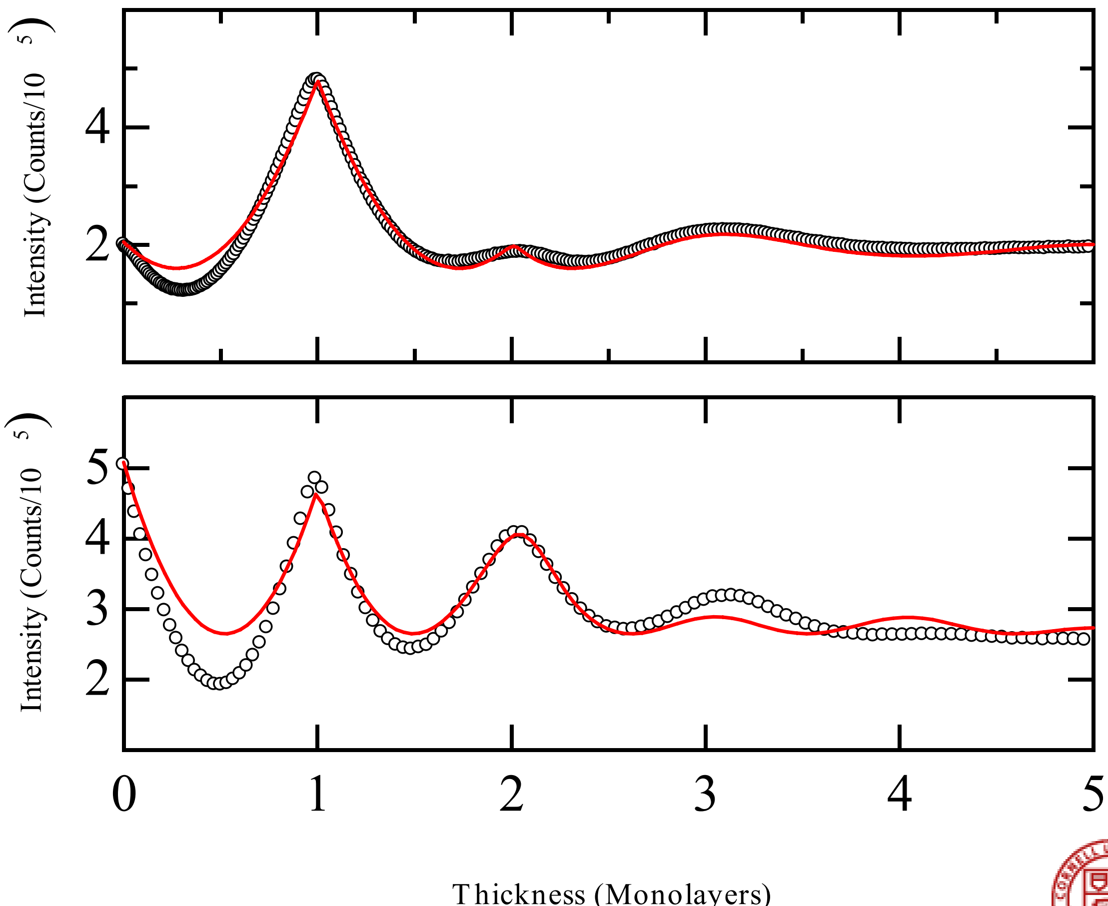
Modeling pentacene growth



$$\frac{d\theta_n}{dt} = \nu\left(\theta_{n-1} - \theta_n\right) + \nu\alpha_n\left(\theta_n - \theta_{n+1}\right) - \nu\alpha_{n-1}\left(\theta_{n-1} - \theta_n\right)$$

Influence of substrate temperature

Pentacene on SiO_2



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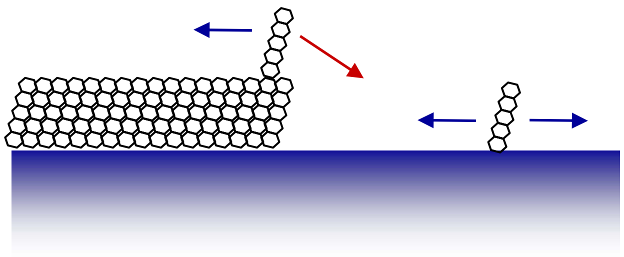
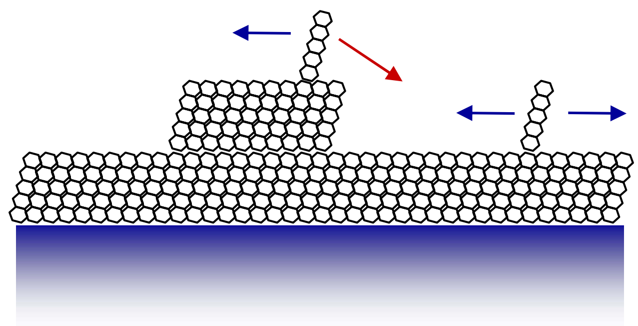
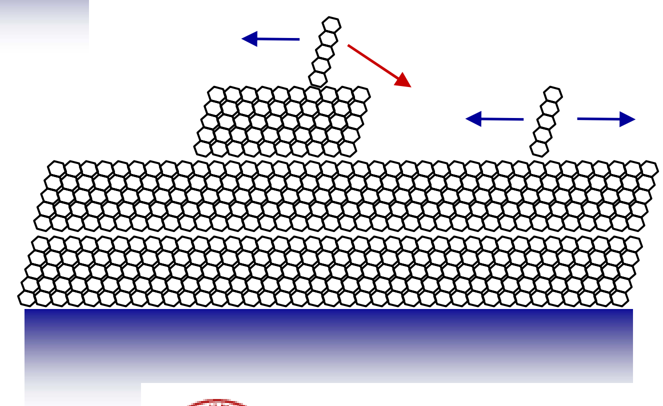
Influence of substrate temperature (II)



Temperature helps overcome the Ehrlich-Schwoebel barrier





$$\frac{A_{T1}}{A_{T2}} = e^{E_{ES}\left(\frac{1}{kT_2}-\frac{1}{kT_1}\right)} \Rightarrow E_{ES} \approx 70 meV$$

A. Mayer, et al.,*Phys. Rev. B.* **73**, 205307 (2006).

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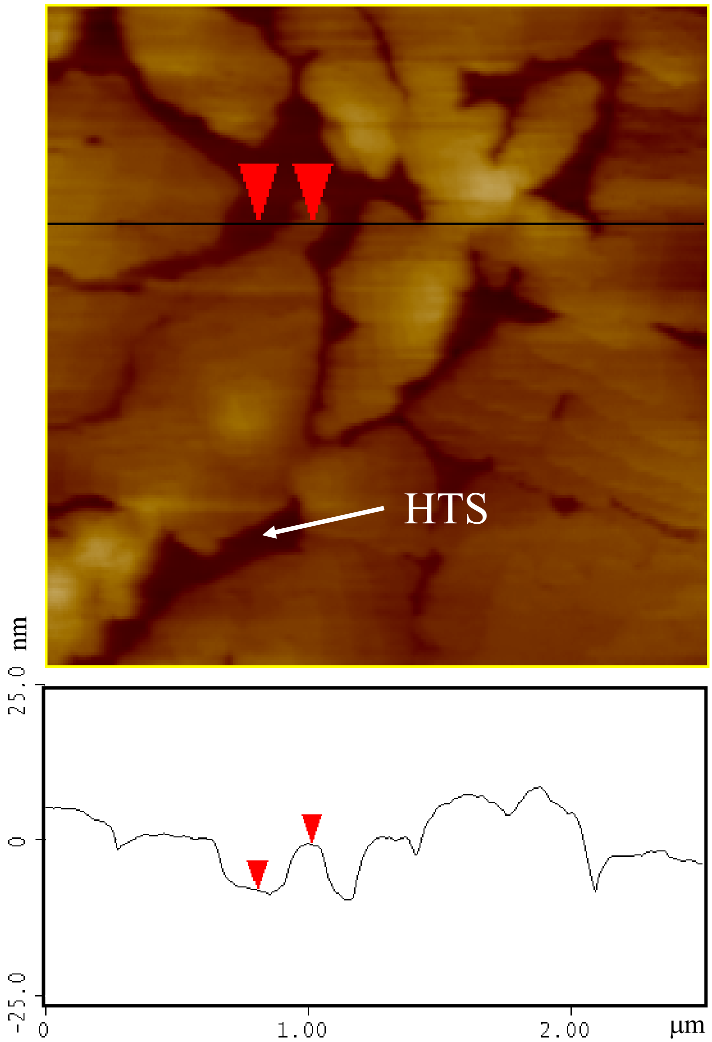
Influence of substrate



Pentacene on HTS

3D growth

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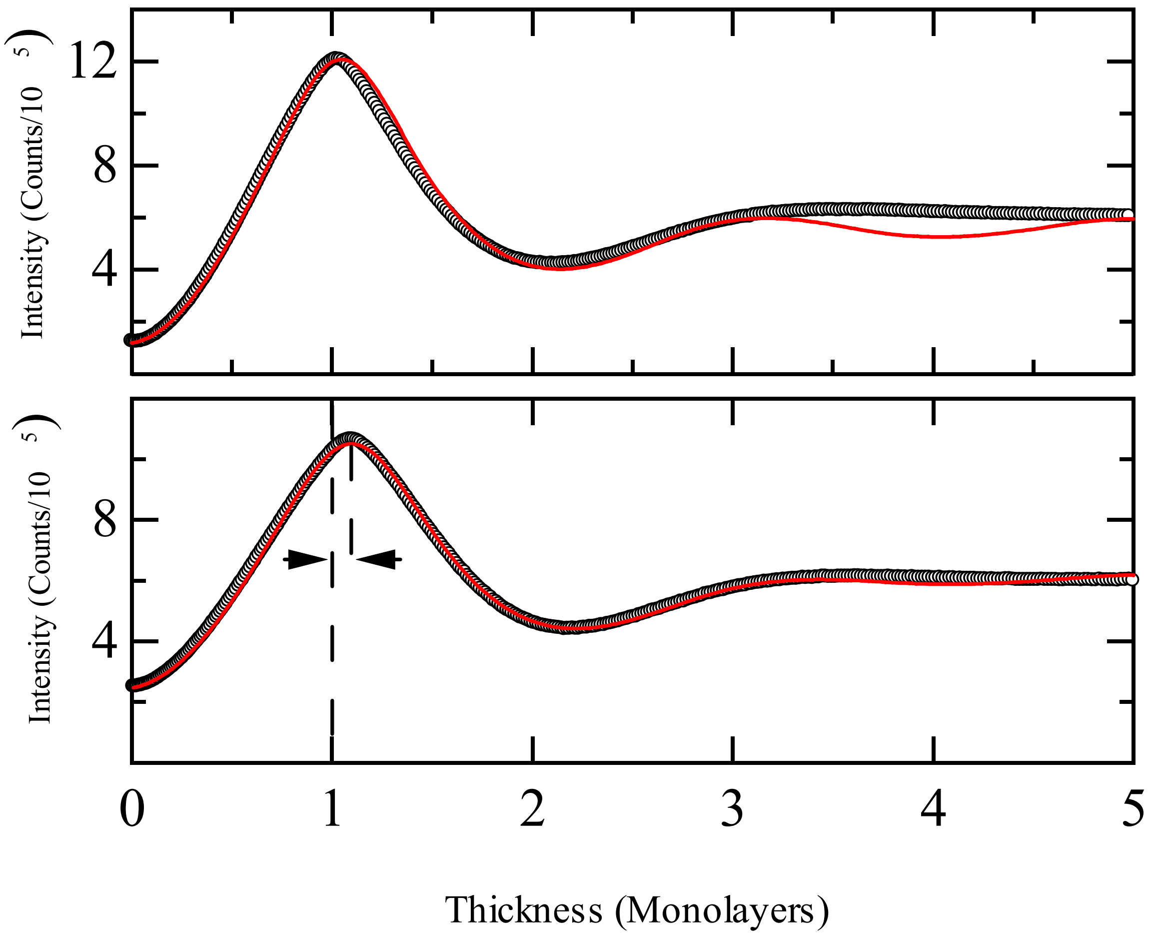
Influence of substrate (II)



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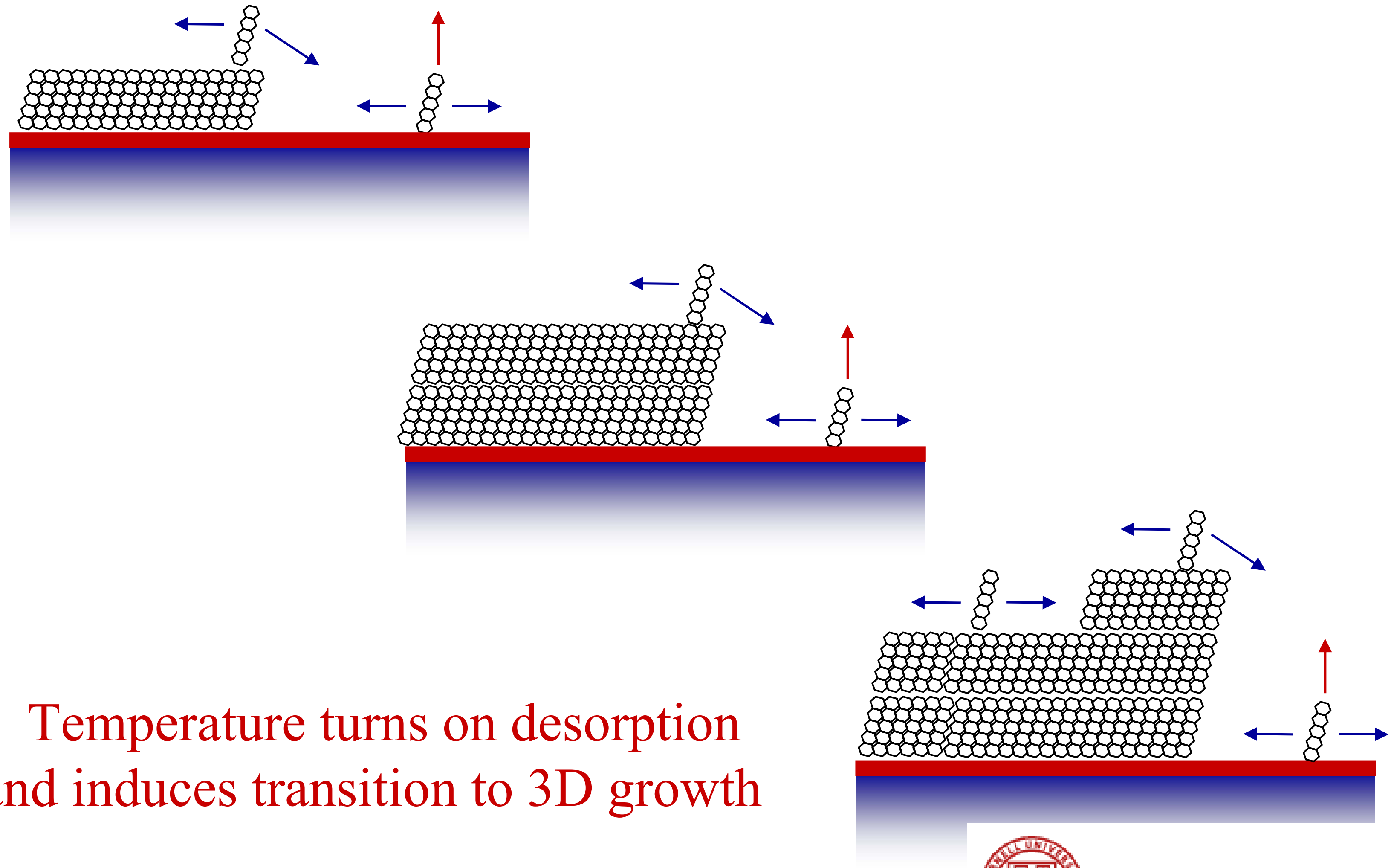
Influence of substrate (II)



Temperature turns on desorption
and induces transition to 3D growth

A. Mayer, et al.,*Phys. Rev. B.* **73**, 205307 (2006).

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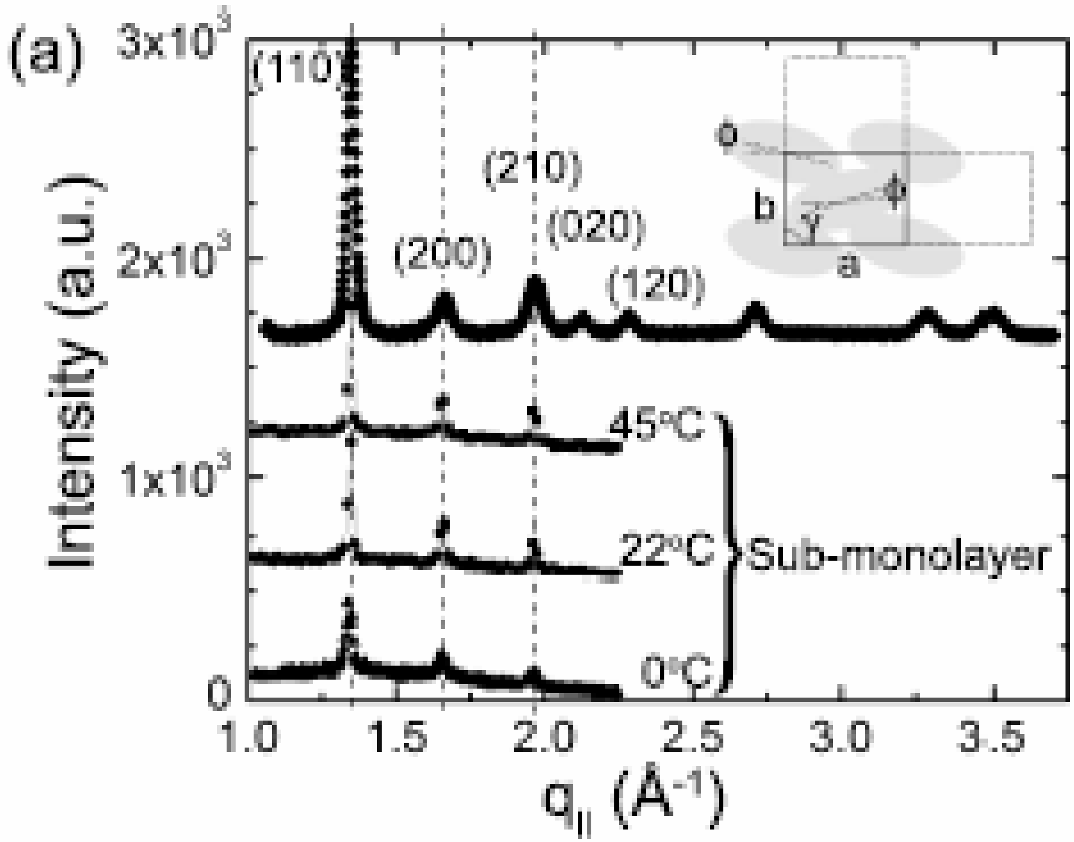
In-plane x-ray diffraction in thin films

Pentacene on SiO_2



R. Ruiz, et al., *Appl. Phys. Lett*. **85**, 4926 (2004).

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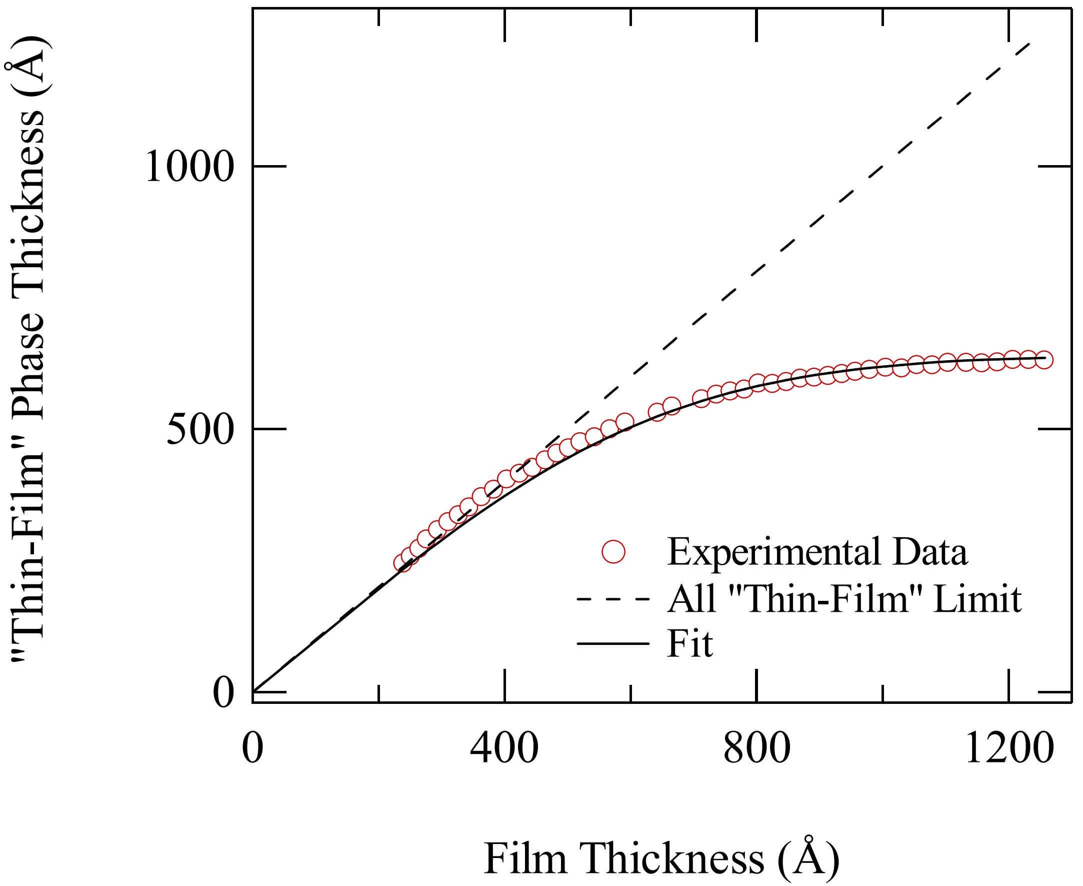
Evolution of bulk phase with thickness (II)

From width of peaks:



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Evolution of bulk phase with thickness (III)

From integrated intensity: