ASSEMBLY AND PROCESSING OF ORGANIC NANOSTRUCTURES

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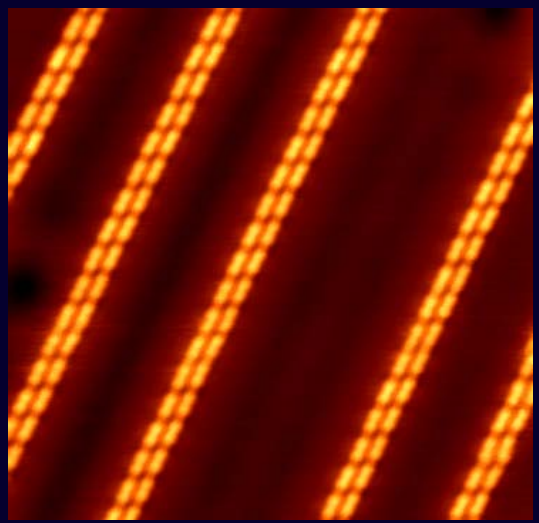
Outline

- Introduction
- H-bonding induced self-assembly
- Organic micro- and nano-crystals on PMMA/SiO_2
- Summary

Molecular organisation using weak intermolecular interactions

highly directional interactions - dipolar coupling, metal co-ordination, H - bonding used for supramolecular assembly

H bonding

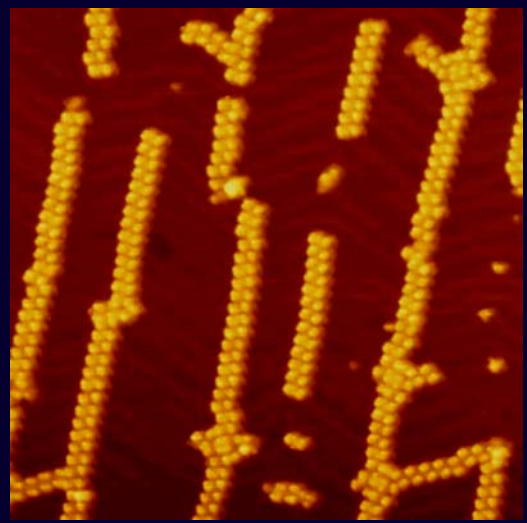


20nm x 20nm

benzoic acid derivatives (PVBA) on Ag(111)

J.V. Barth et.al., Angew. Chem. (2000)

Dipolar interaction

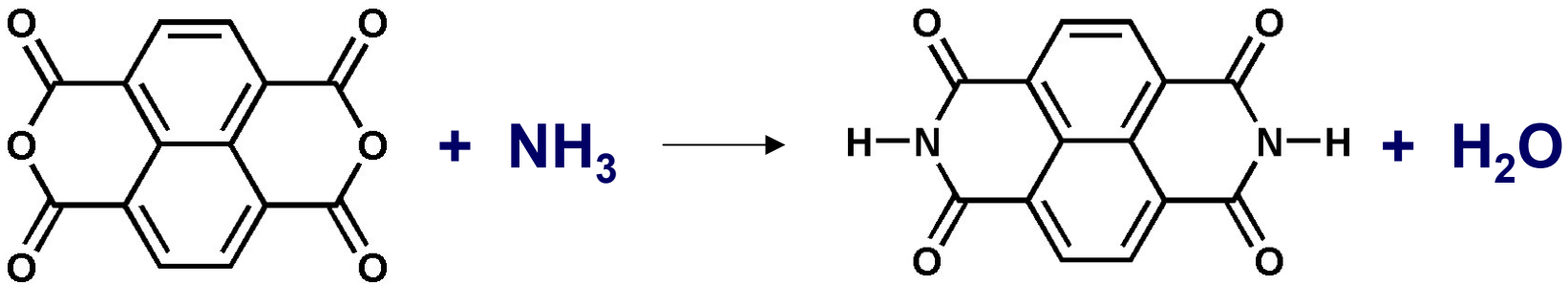


70nm x 70nm

formation of dimers, trimers and chains from functionalised porphryns

Yokoyama et.al. Nature (2001)

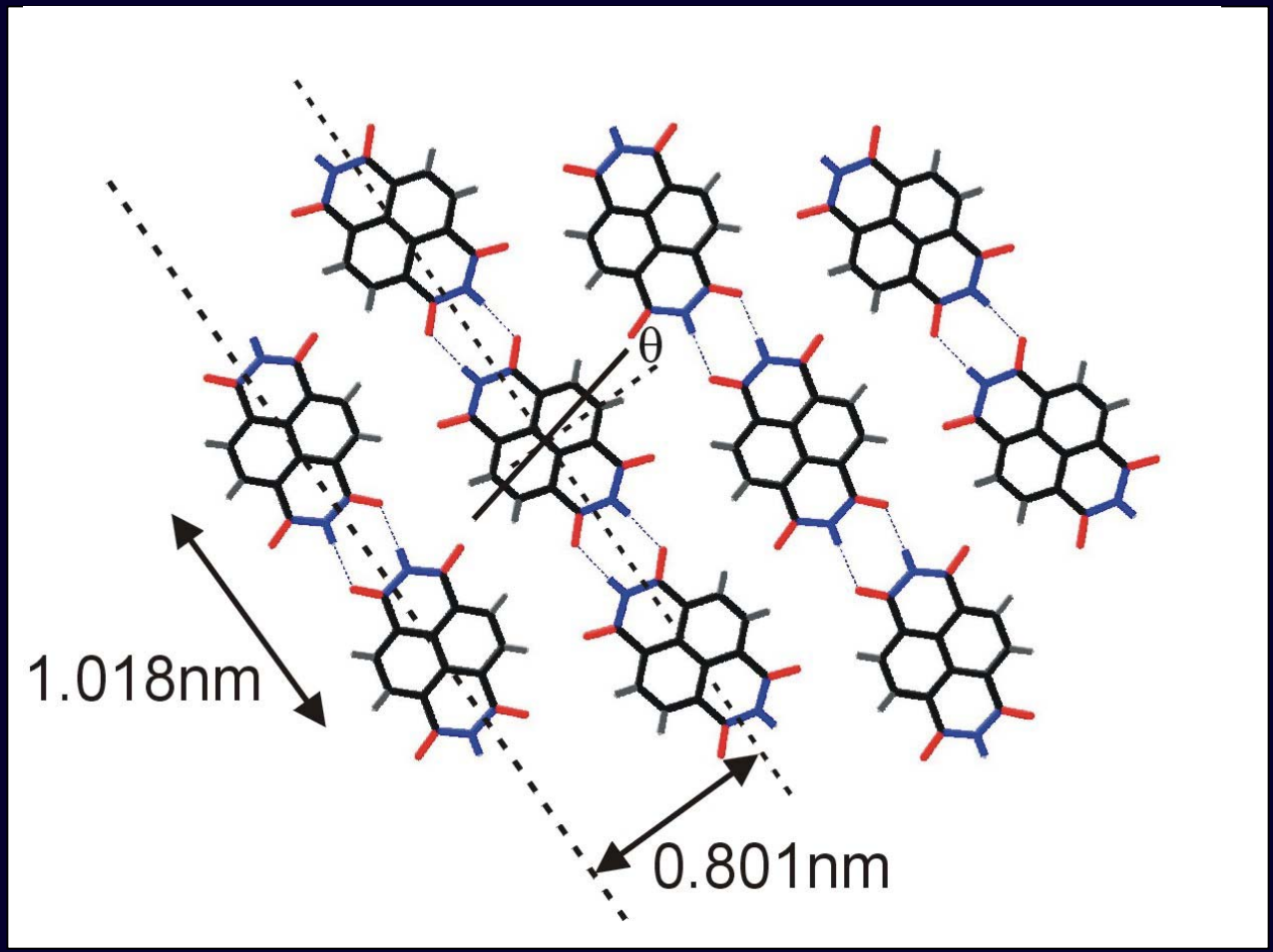
NTCDI and NTCDA



NTCDA NTCDI

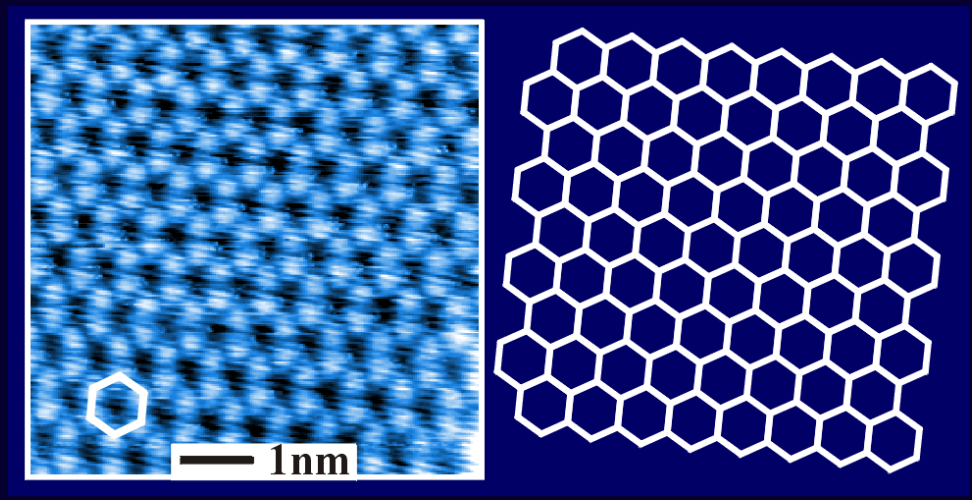
Crystal structure of NTCDI

H-bonded molecules canted through $\theta = \pm 13^{O}$ in alternate rows



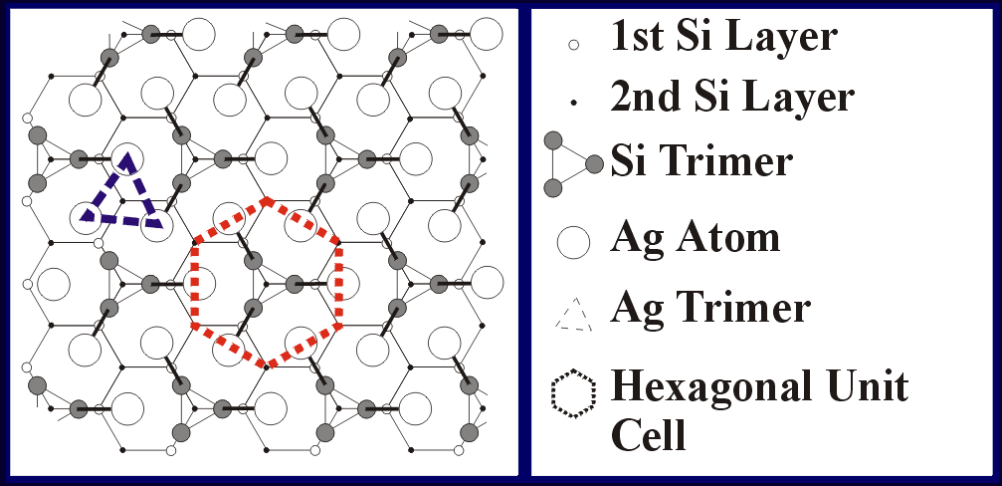
Ag/Si(111)-(√3 x √3)R30° surface

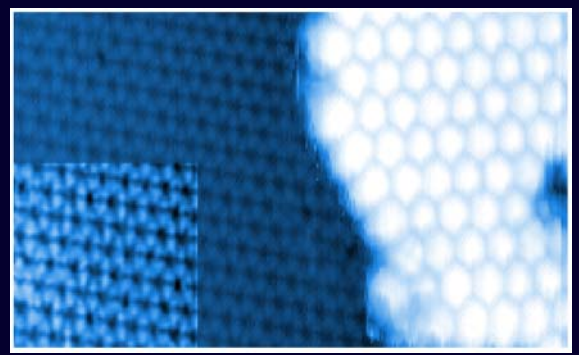
prepared and imaged in UHV



lattice constant a = 0.665nm

dangling bonds only present at step edges and surface defects



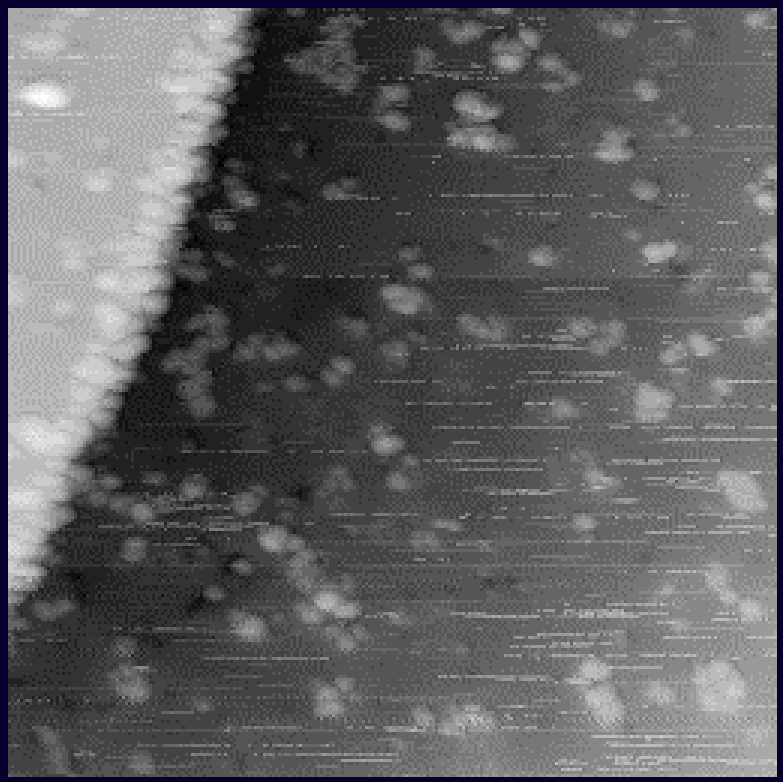


C_{60} island on Ag/Si(111)

T. Takahashi et al., Japn. J. Appl. Phys. 27, l753 (1988)

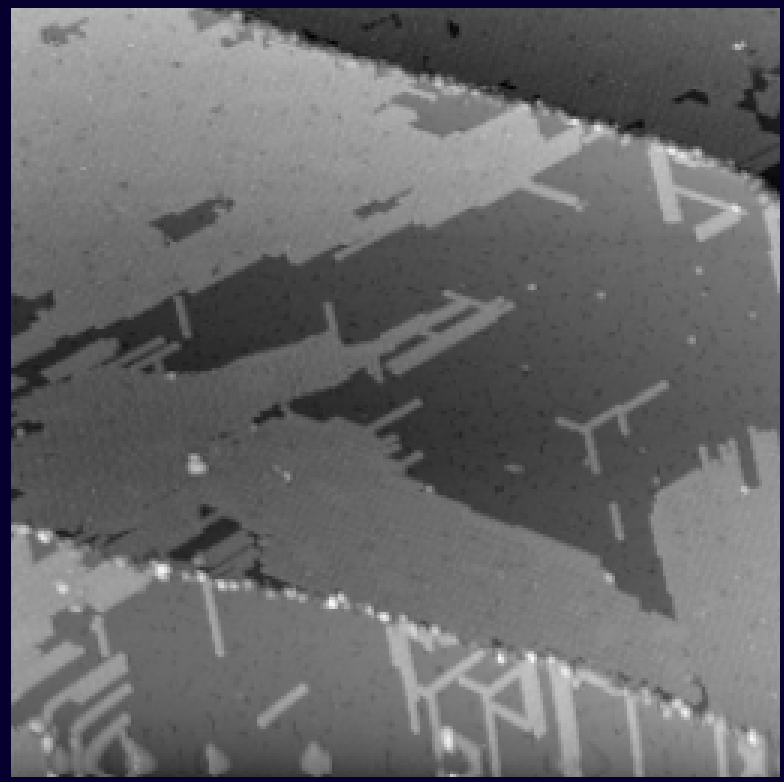
NTCDI and NTCDA on Ag/Si(111) - (√3 x √3)R30°

NTCDA



50nm x 50nm

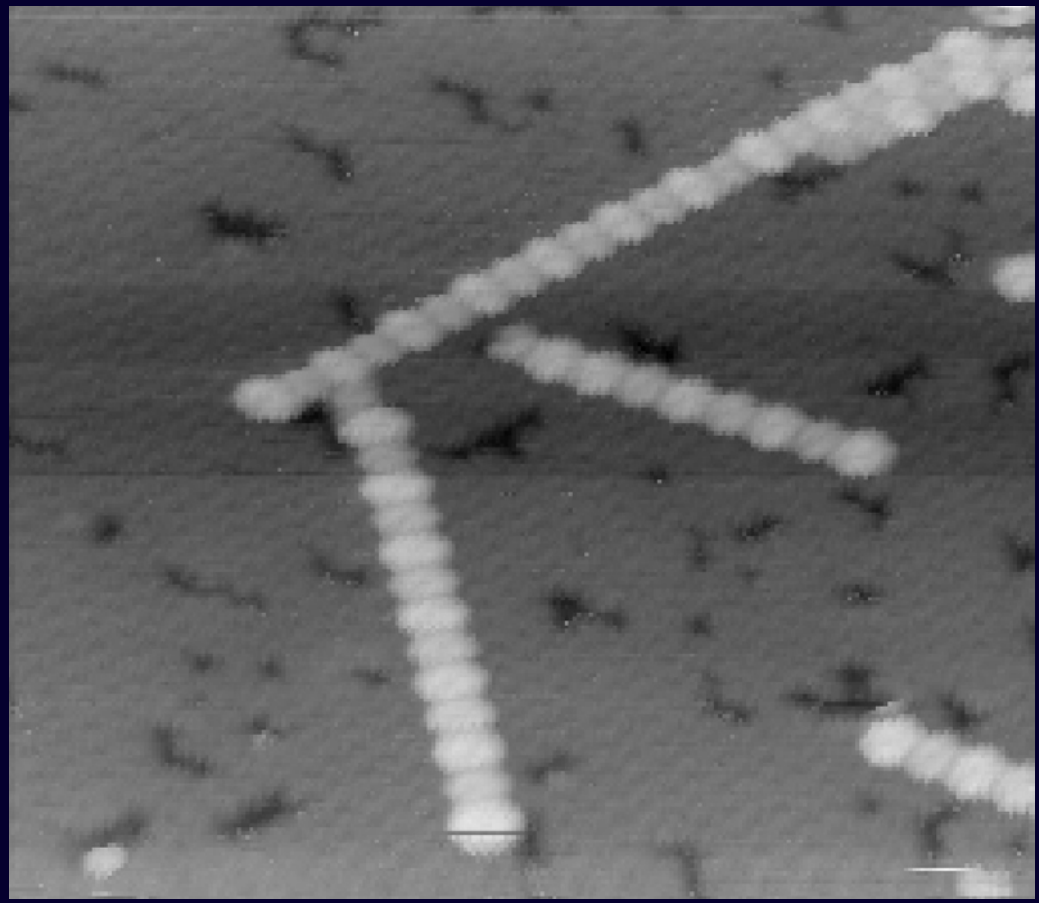
NTCDI



150nm x 150nm

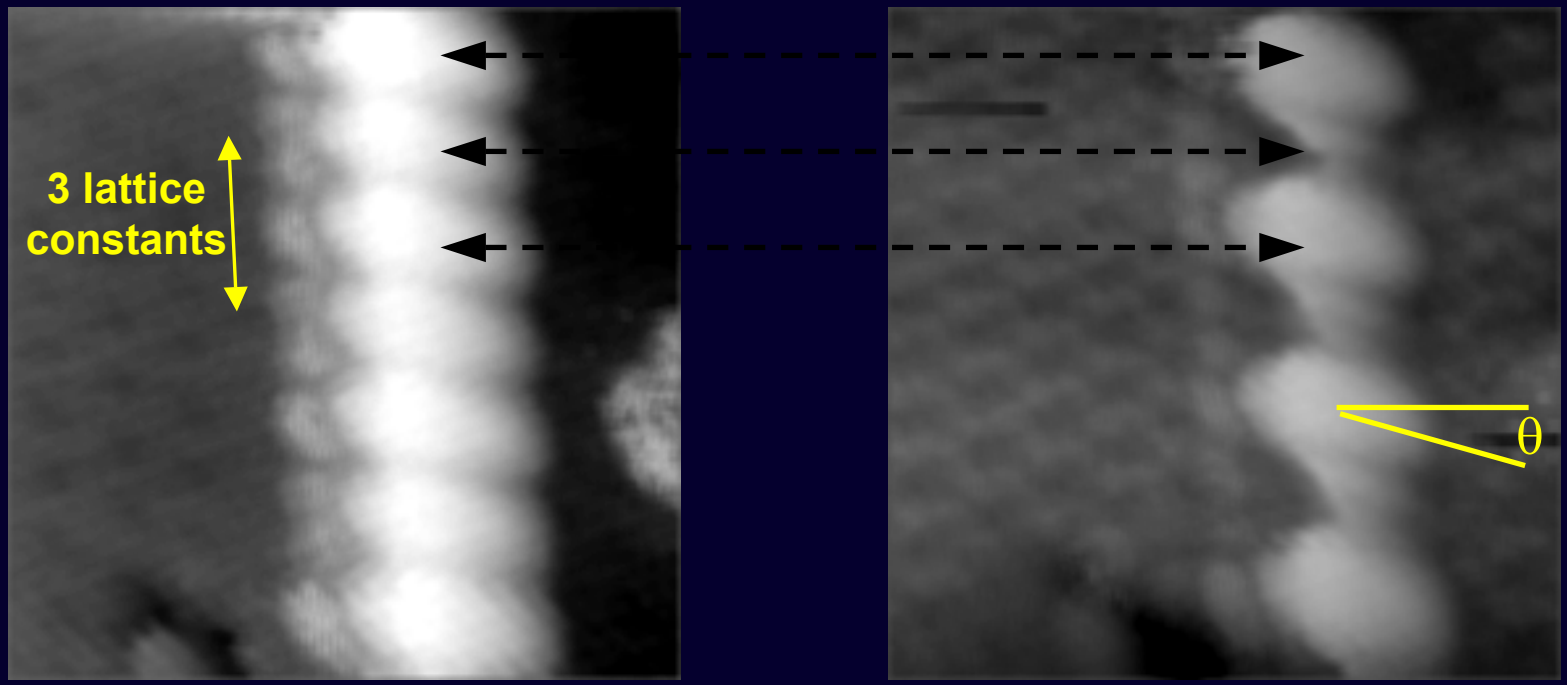
islands and rows of NTCDI running
along principal crystallographic directions

H bonded chains



chains up to 25nm
assembled from 1nm building blocks

Row adsorption sites

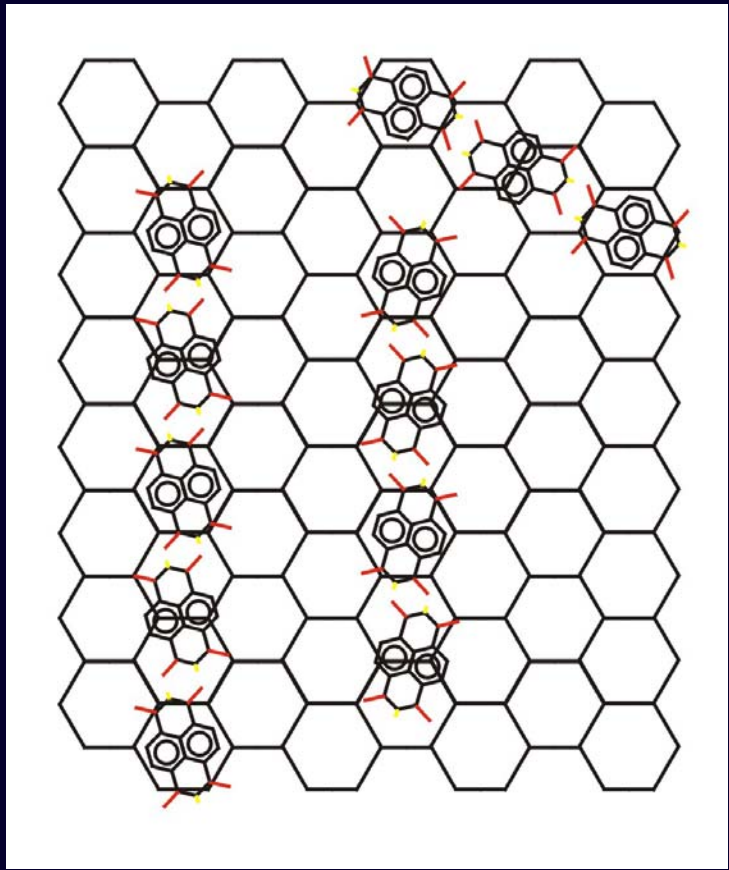


6.4nm × 6.4nm, -1V, 0.1nA

6.4nm × 6.4nm, +1.2V, 0.1nA

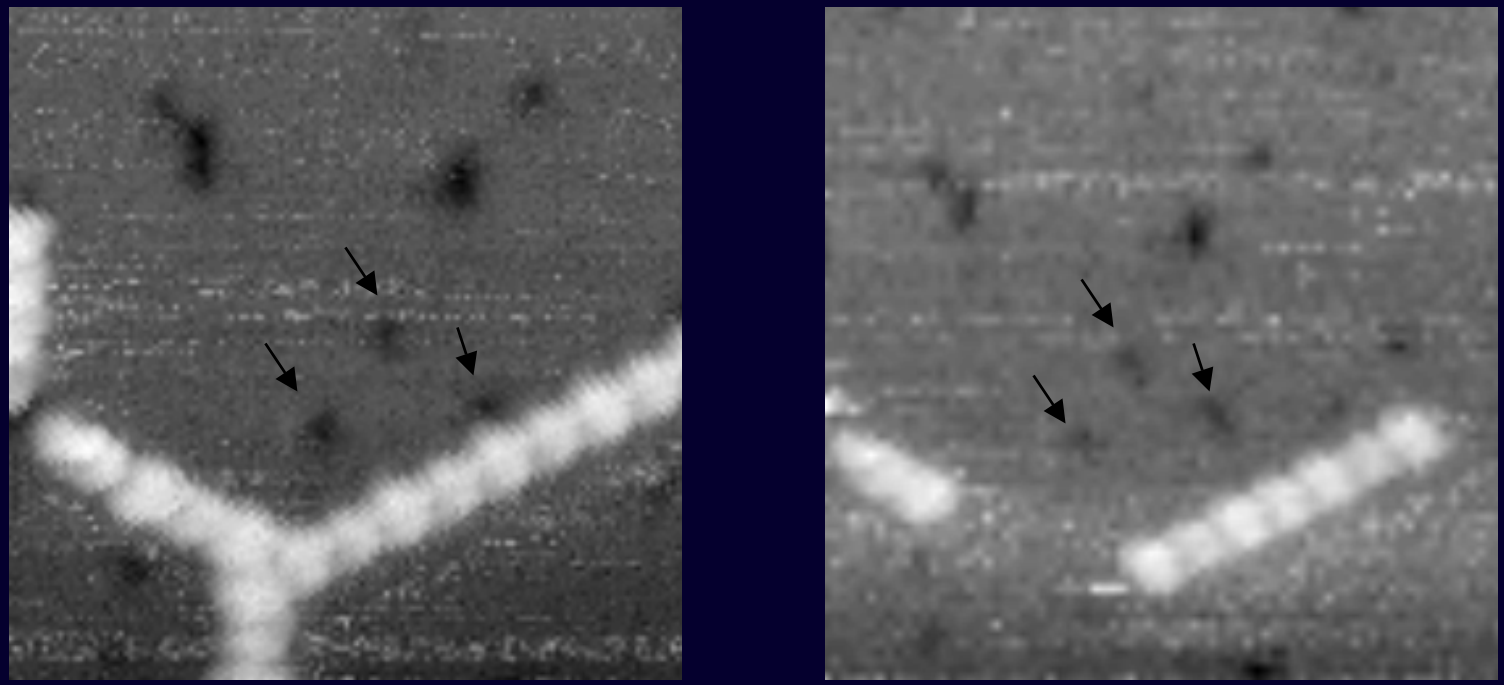
intermolecular separation = 3a/2 = 0.998nm
bulk spacing of NTCDI molecules 1.018nm
alternate molecules adsorbed at different sites
canting angle $\theta = 13 \pm 1^{O}$

H-bonded rows of NTCDI



intermolecular spacing within 0.02nm of bulk rows
two inequivalent binding sites

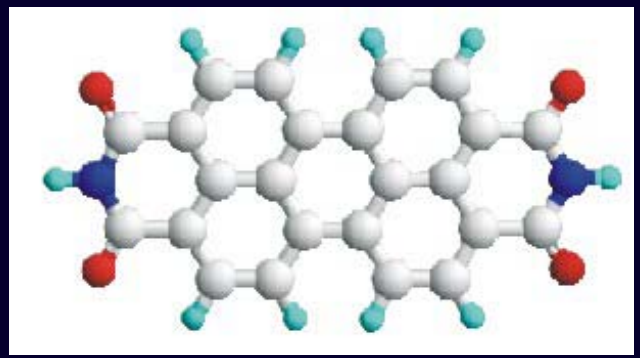
STM induced modifications



12.5nm × 12.5nm, -1.2V 0.1nA

PTCDI on Ag/Si(111)

short chains - kinetically unstable

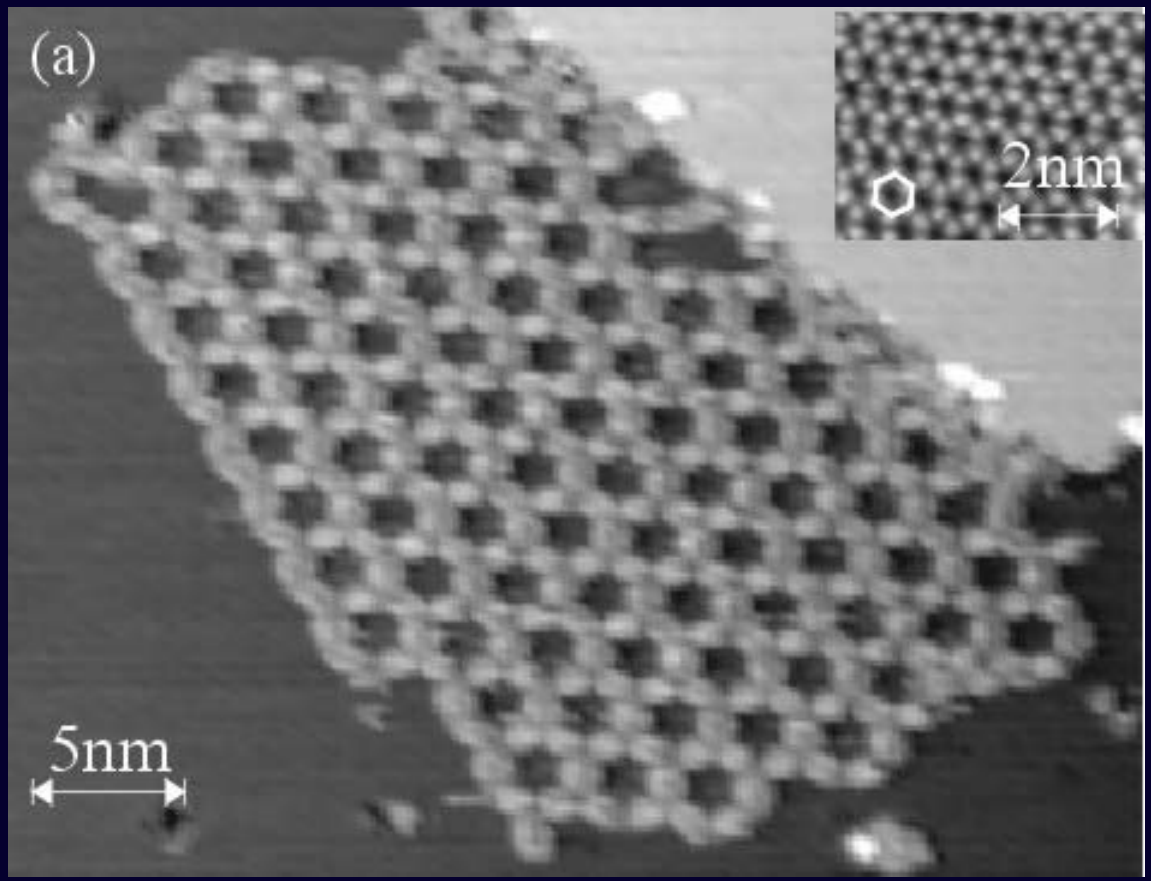


bulk spacing - 1.44nm

surface spacing - 2a = 1.33nm

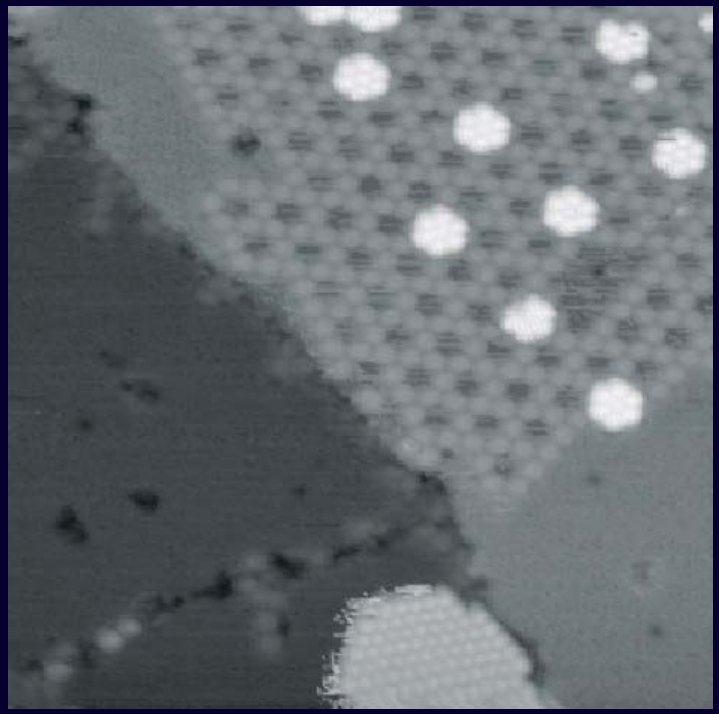
incommensurability leads to **compressive strain**

PTCDI on Ag/Si(111) - honeycomb network



lattice constant $3\sqrt{3}a = 3.46$nm

PTCDI on Ag/Si(111) - honeycomb network

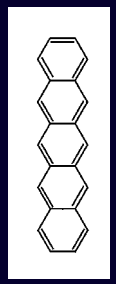


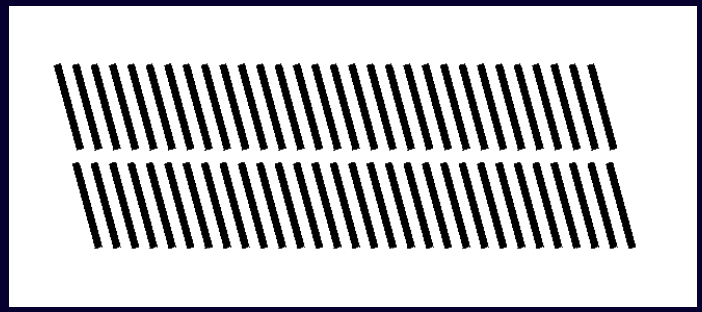
40nm x 40nm

6nm x 6nm

C_{60} molecules trapped in pores
stabilisation of heptameric clusters

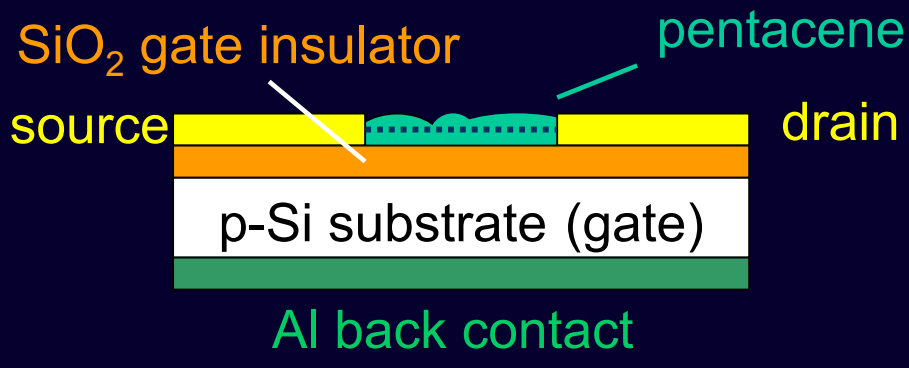
Pentacene thin films and single crystals



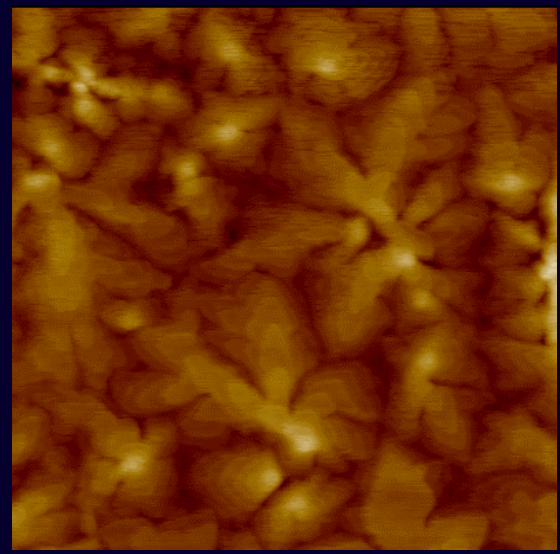


vacuum sublimation

(Dimitrakopoulos, Gundlach et.al.)



μ_h = 0.1 - 1.5 cm^2/Vs



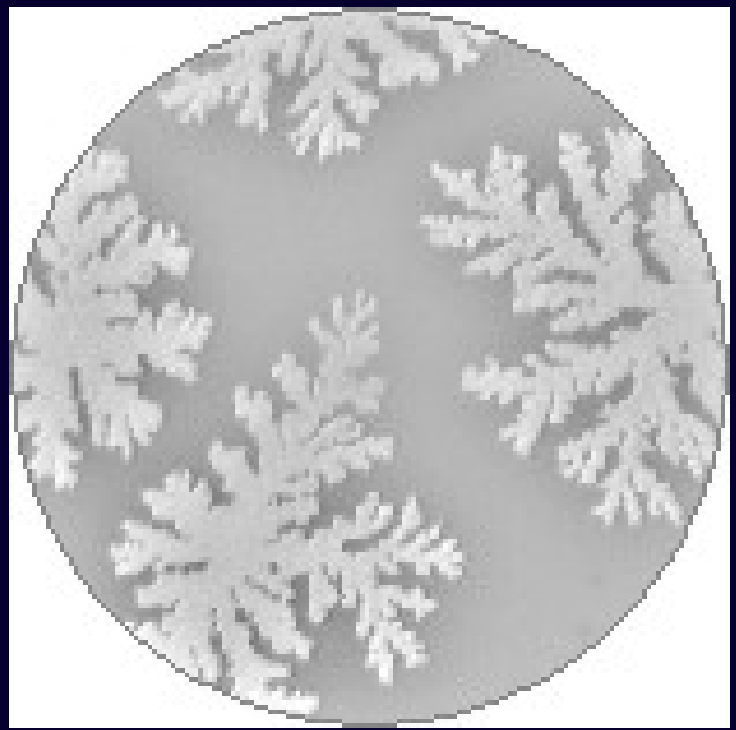
pentacene on PMMA/SiO_2
(13nm) scan size 3 x 3 μm^2

can large single crystals be grown on substrates using sublimation?

Growth of fractal microcrystals

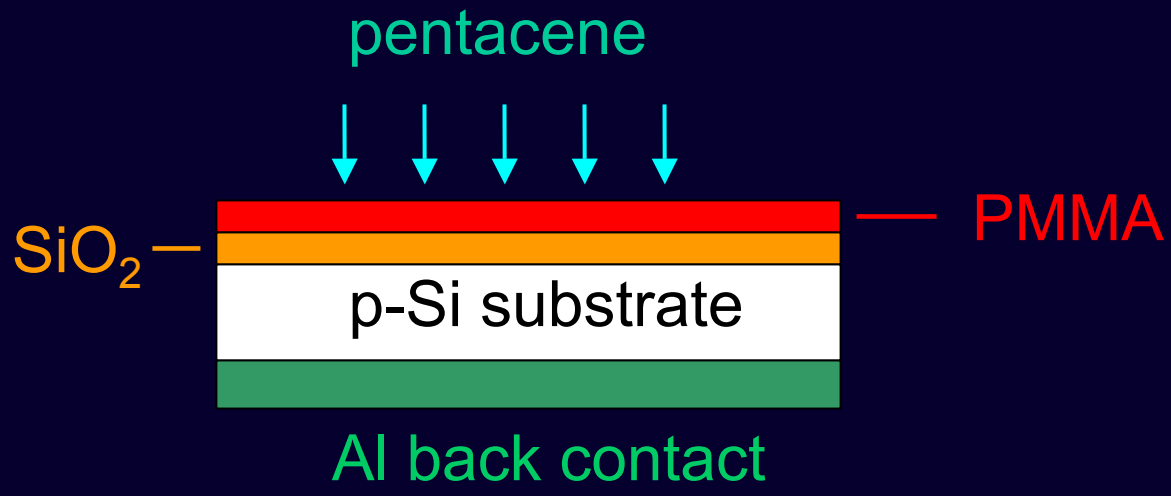
LEEM images of pentacene growth on hydrocarbon terminated passivated Si(100)

fractal islands
separated by ~100μm



Meyer zu Heringdorf et.al. Nature (2001)

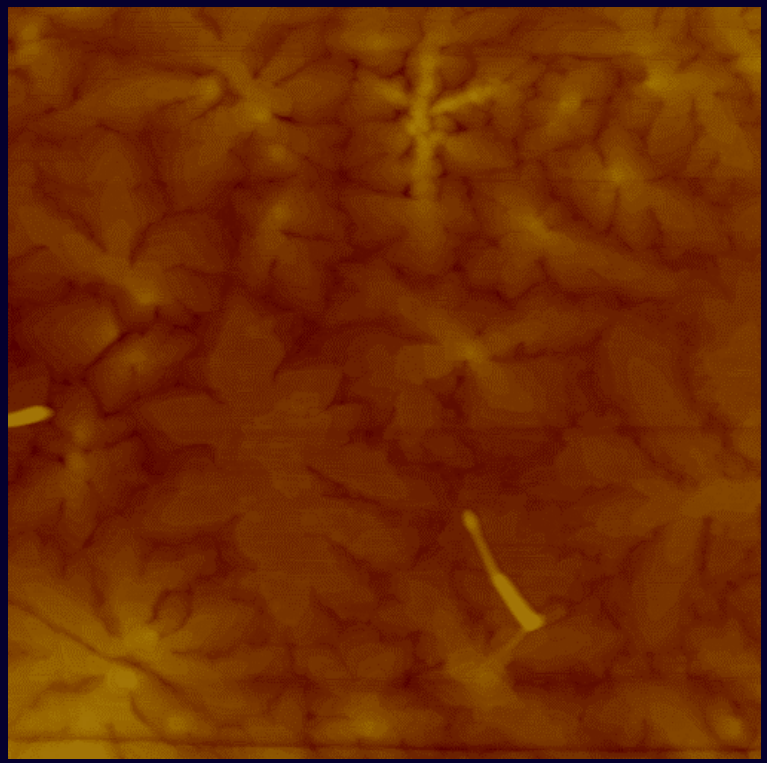
Growth of pentacene on PMMA



- PMMA spin coated and baked at 180°C
- film thickness 100 - 200nm
- low pinhole density
- smooth surface

Pentacene thin films on PMMA

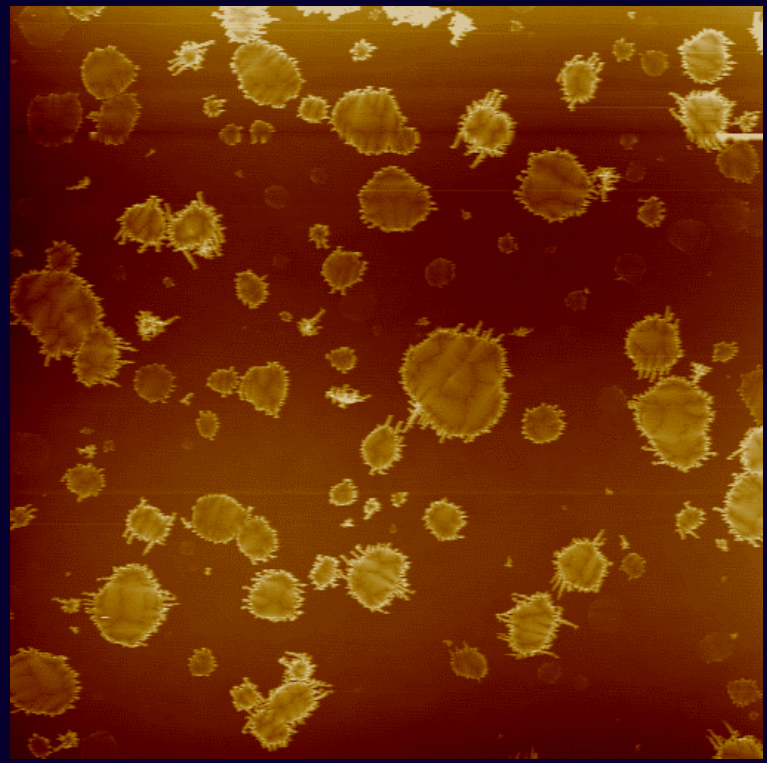
room temperature



5μm x 5μm

island size ~ 2μm

heated substrate T = 80°C

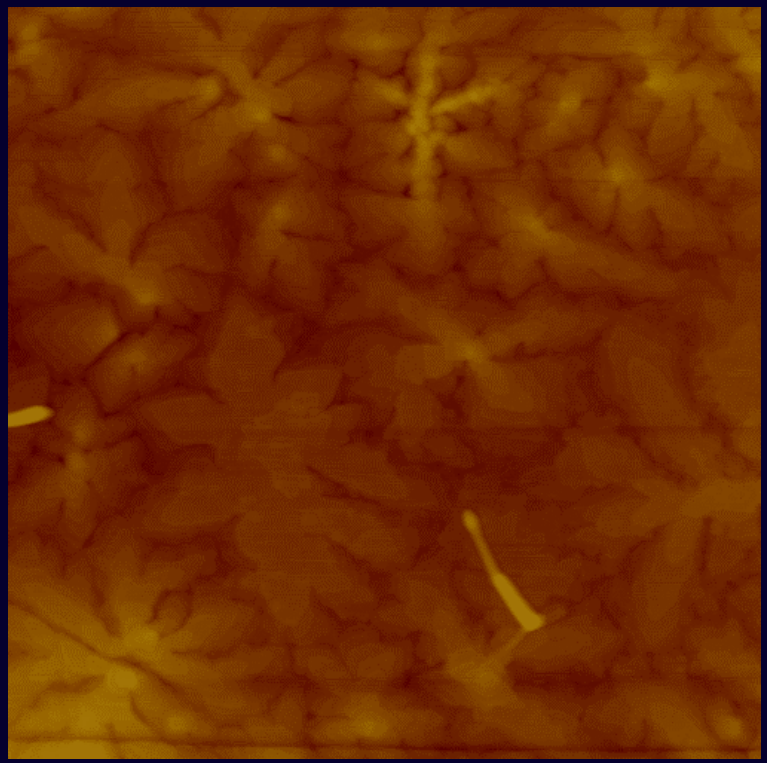


117μm x 117μm

isolated islands up to ~ 20μm

Pentacene thin films on PMMA

room temperature



5μm x 5μm

island size ~ 2μm

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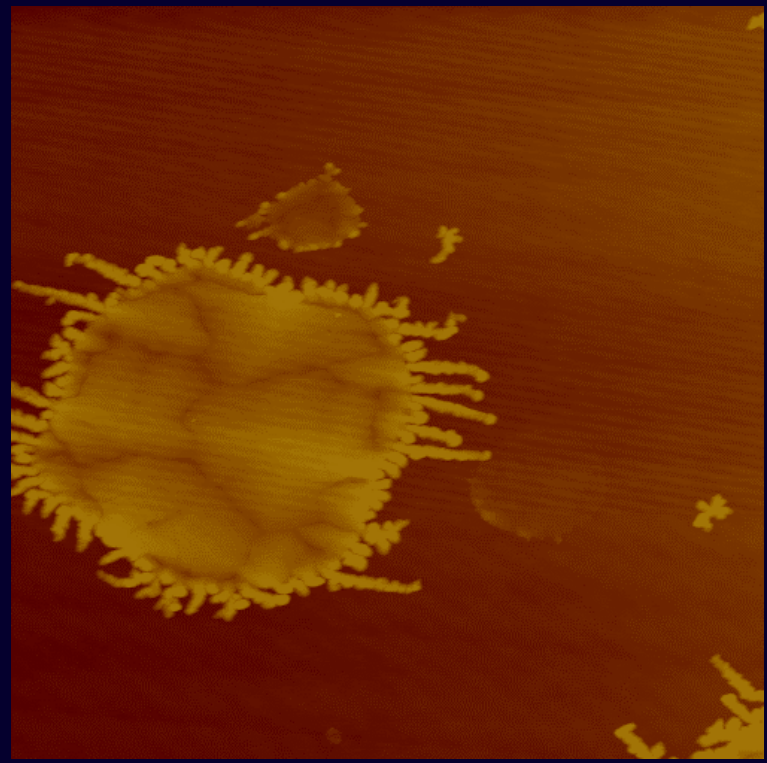
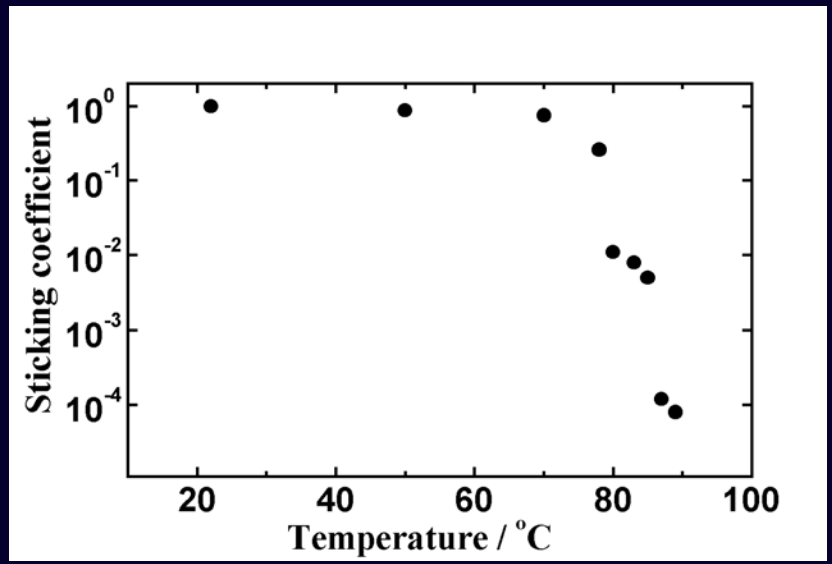
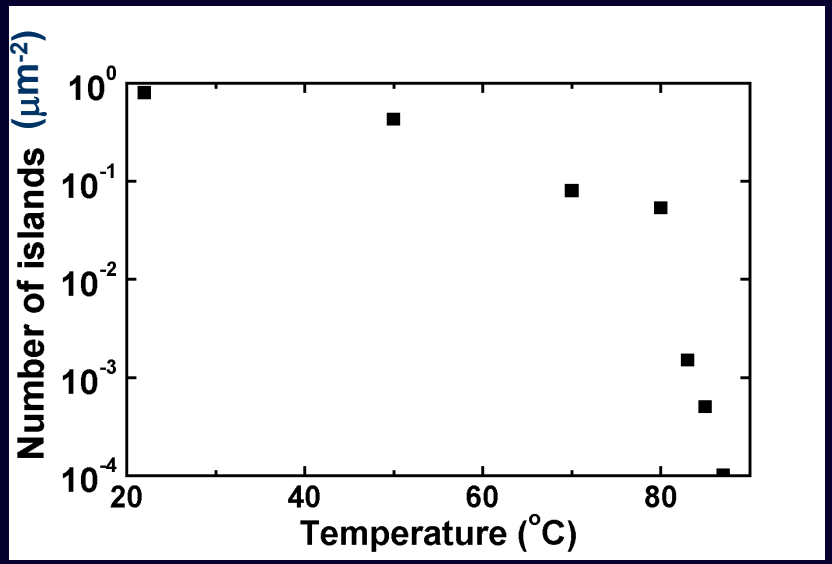


23μm x 23μm

isolated islands up to ~ 20μm

Island density and sticking coefficient

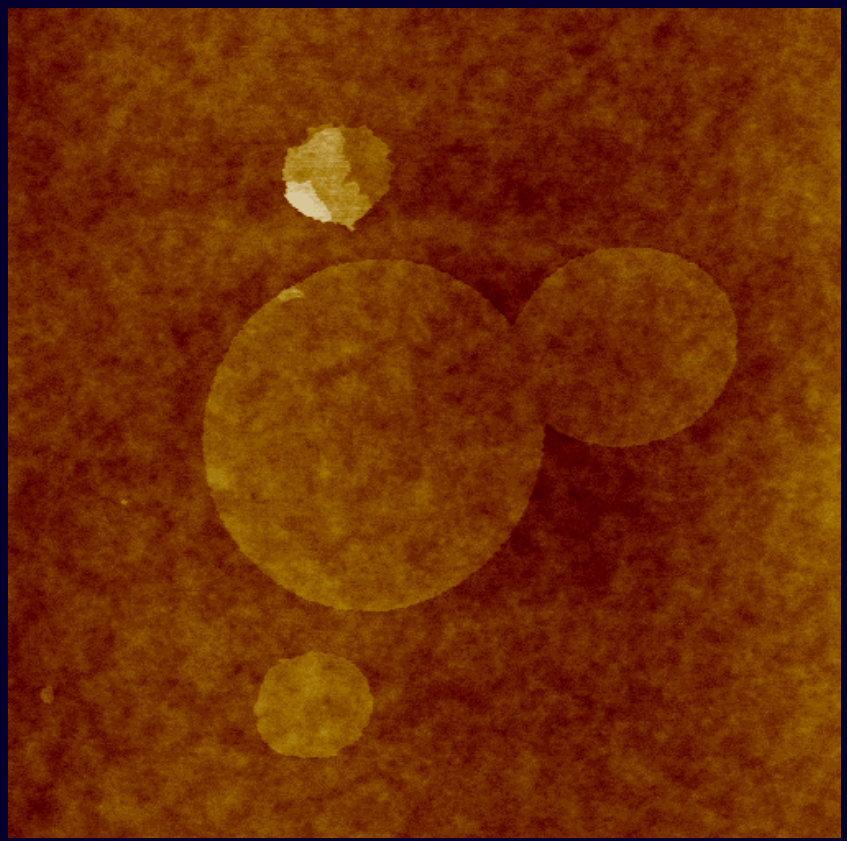




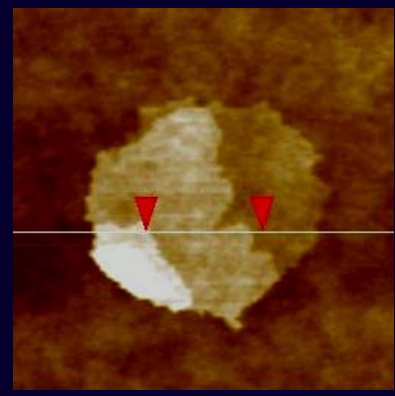
‘extreme incomplete’ growth regime - nucleation still occurring

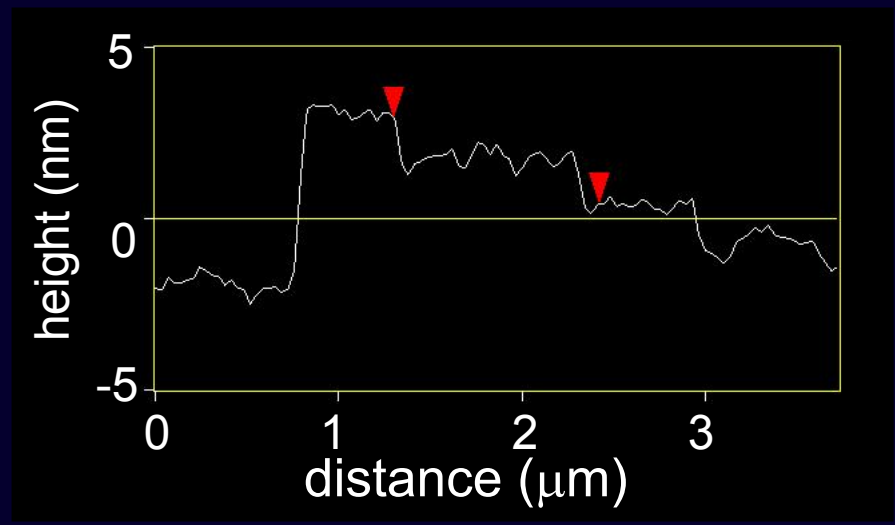
Temporal development of island

T = 83°C



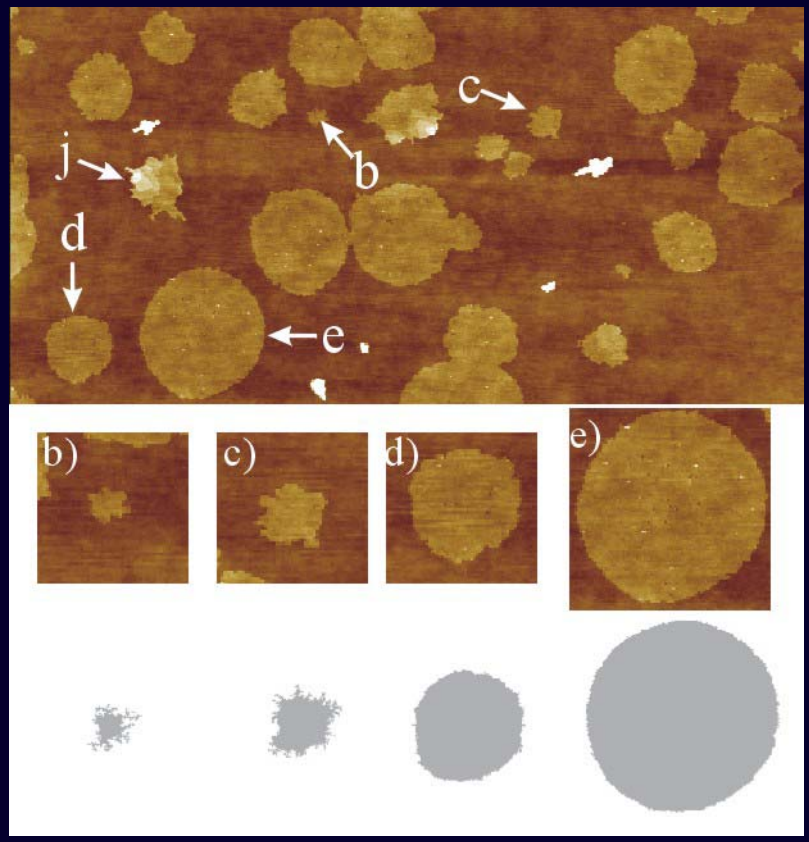
18μm x 18μm

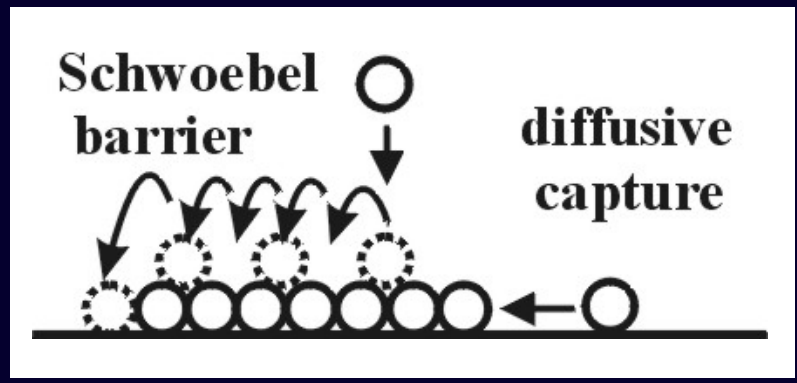


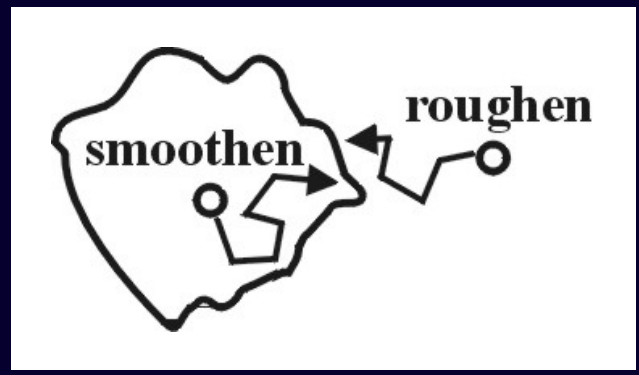


step height ~1.5nm

Monolayer growth







$N_D = 70$

$N_T =$ 1000 3000 10000 30000

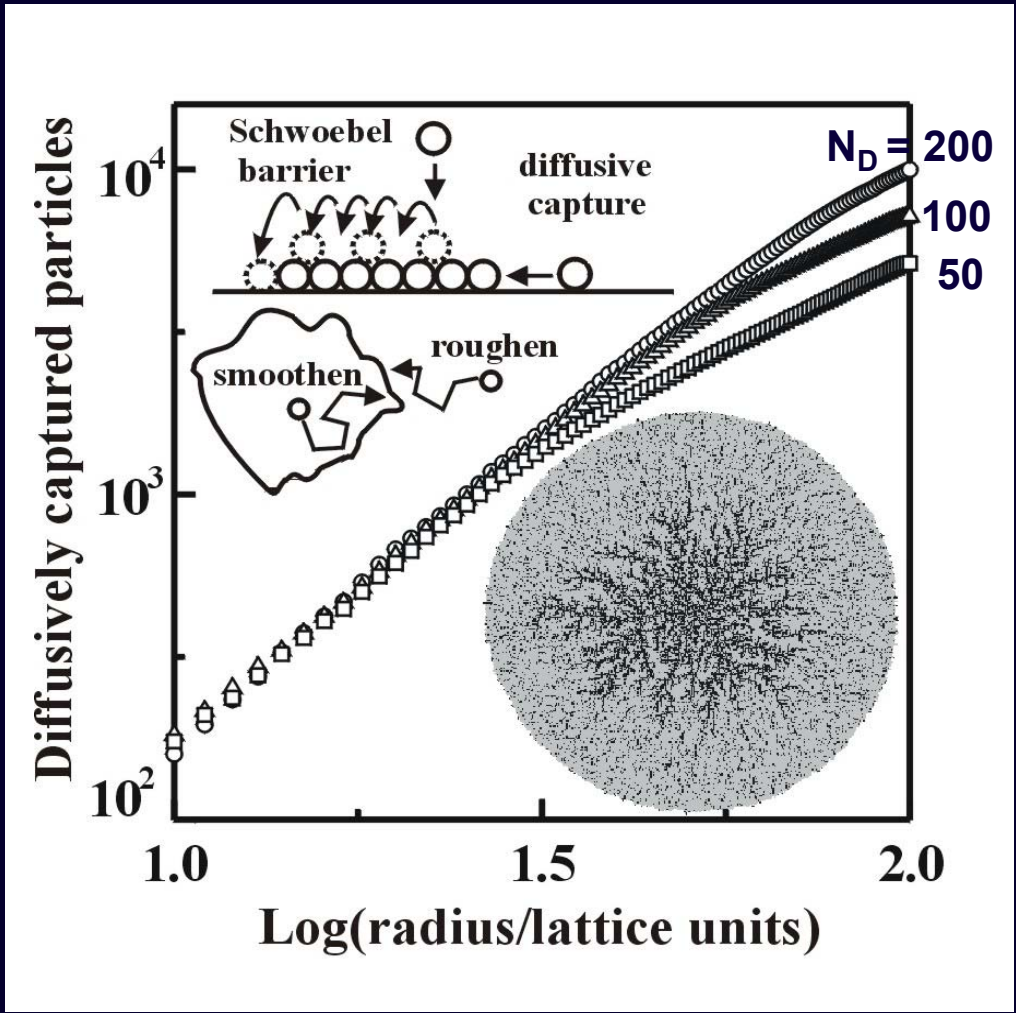
simulations on square lattice

diffusive capture by 'hit and stick' (diffusion limited aggregation)

reduced sticking coefficient on PMMA - molecules removed after N_D hops

diffusive capture growth rate α r direct capture growth rate α r^2

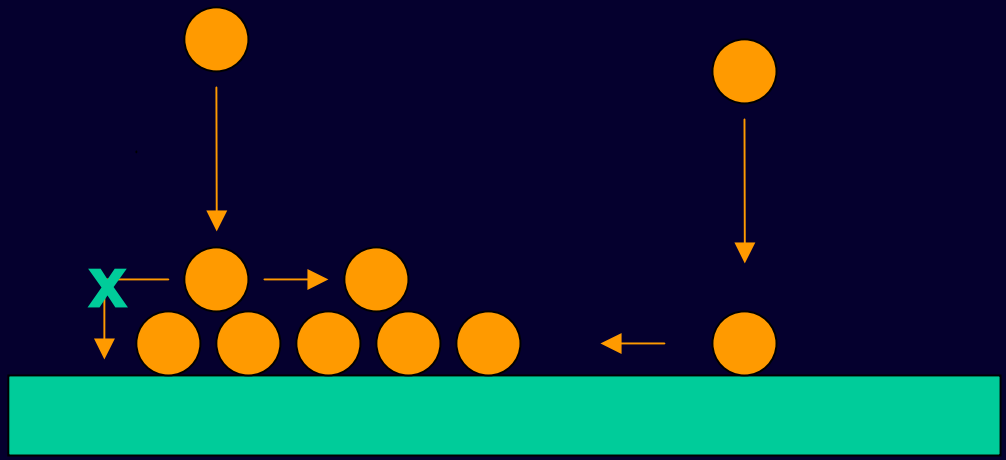
Fractal - compact size dependent transition

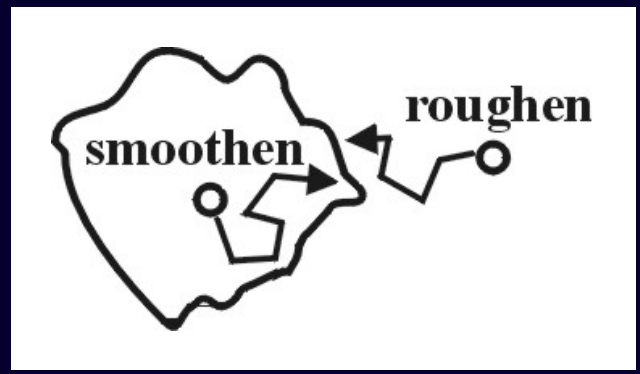


$N_D = 200$, $N_T = 70000$

fractal dimension 1.83

Self limiting island growth





lateral growth continues until 2nd layer nucleates

2nd layer acts as a sink for diffusing molecules - transition from lateral to vertical growth

$$\frac{dn_2}{dt} = R - \frac{n_2}{\tau} - \frac{2a\, n_2}{r\ \tau_{down}}$$

(a - order molecular dimensions)

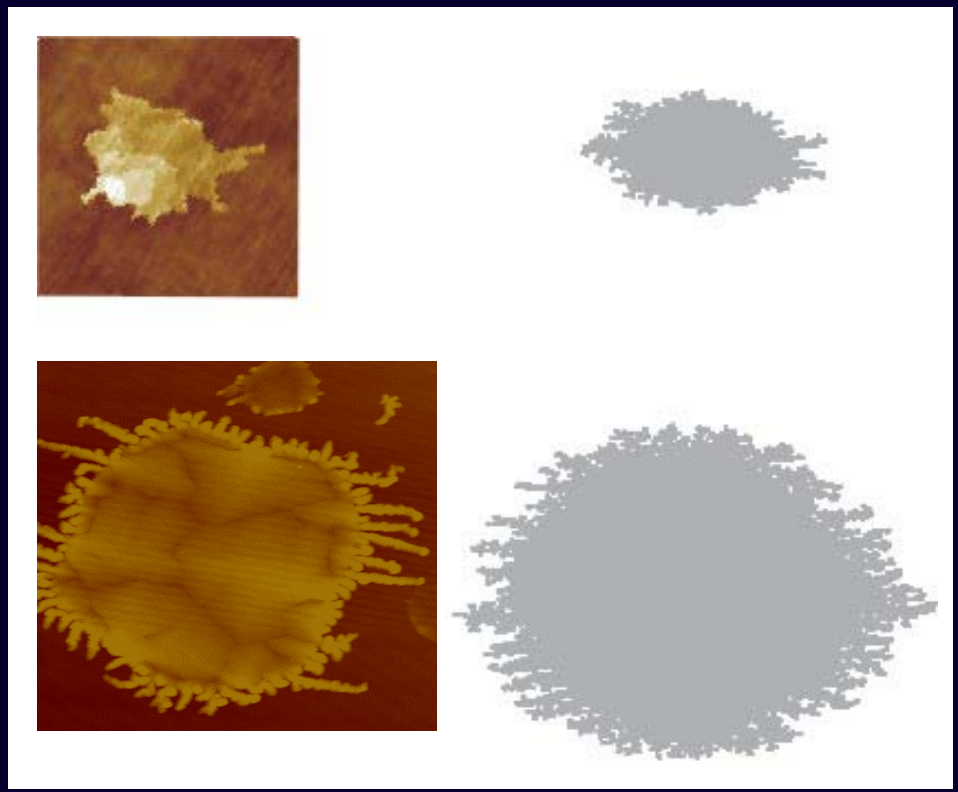
(see Tersoff et.al. PRL 1994)

simple steady state: $n_2 = R\tau_{down} r/2a$

$n_2 \ \alpha \ r$ - nucleation rate $\alpha\ r^m$

Morphology of multilayer islands

direct capture switched off after N_S particles
further lateral growth by diffusive capture only

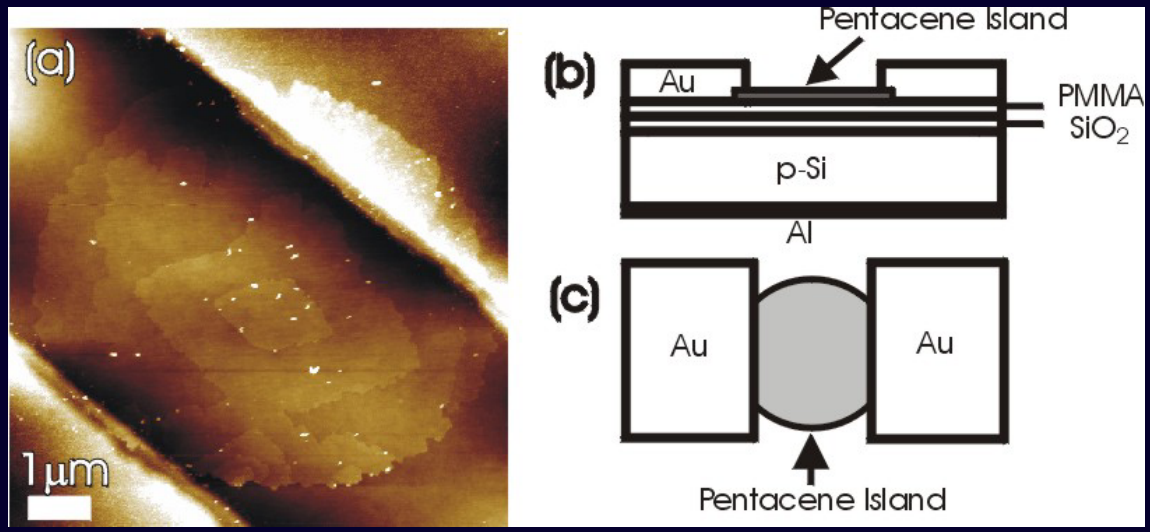


anisotropy incorporated by ascribing probability P to hit and stick success for new bonds oriented along the y direction

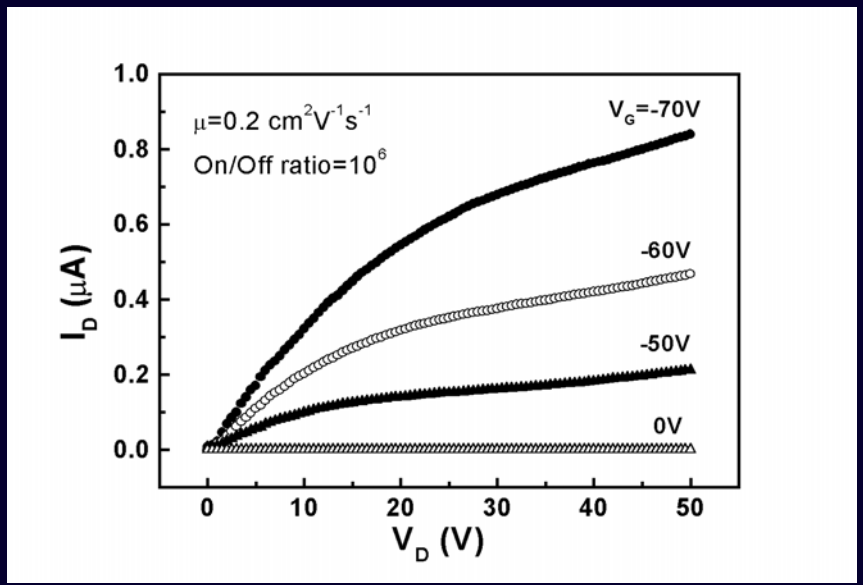
$N_D = 70$, $P = 0.2$, $N_S = 3000$, $N_T = 3500$

$N_D = 70$, $P = 0.2$, $N_S = 15000$, $N_T = 21000$

Single crystal pentacene FET



hole inversion layer



Island height 20nm

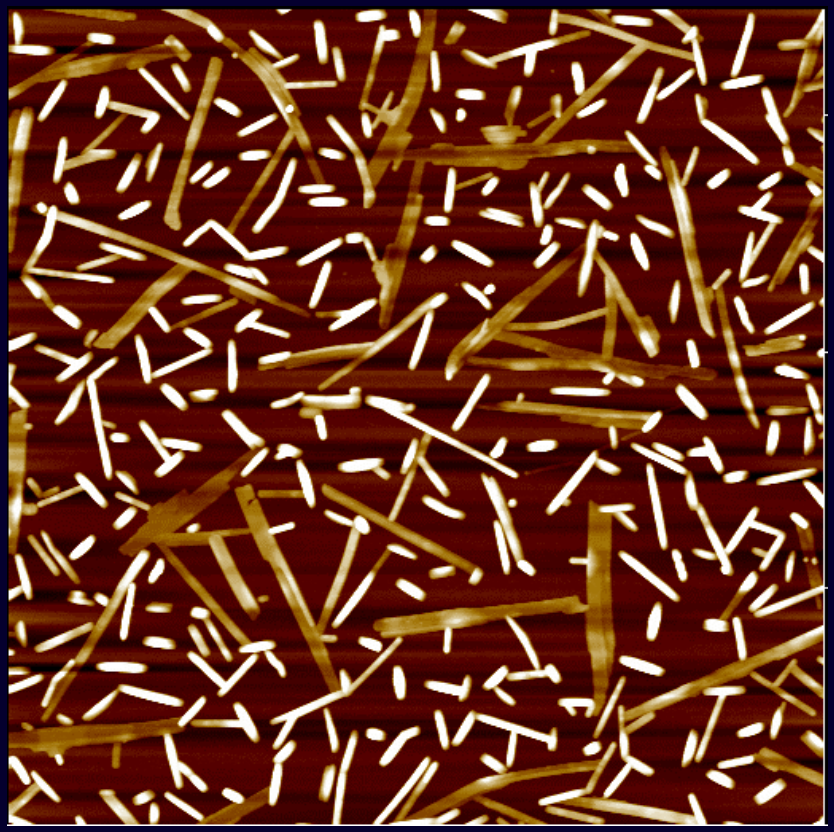
L = 5μm W = 13μm

thickness dependent mobility

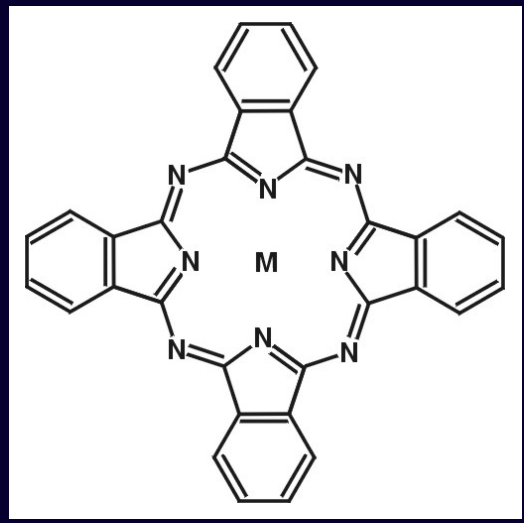
μ ~ 10^{-4} cm^2/Vs for trilayer & bilayers

Cobalt phthalocyanine grown on SiO_2

substrate temperature 85 °C



6.9 μm x 6.9 μm



nanocrystalline rods
height 10-30nm
length ~2μm

see also Katz et.al.

Summary

intermolecular interactions and growth kinetics may be exploited to form:

self assembled rows and networks for use in templating and capture of molecules

ordered monolayers with mesoscopic lateral dimensions

micron and nanometre scale organic crystals

funded by EPSRC
Engineering and Physical Sciences Research Council