

A microscopic image showing a complex crystalline structure. The central feature is a large, multi-pointed star-like shape with a textured, faceted surface. This central shape is surrounded by a network of smaller, interconnected crystalline regions, creating a porous or interconnected lattice-like appearance. The overall color palette is muted, consisting of various shades of grey, blue, and white, highlighting the geometric and structural complexity of the material.

Crystallisation at Interfaces

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Introduction

Crystal growth at interfaces fundamental to biological crystal growth

Complex \Rightarrow look at **model systems**

- Langmuir Monolayers
- Self Assembled Monolayers (SAMs)
- Patterned SAMS

Precipitation of CaCO_3 under Langmuir Monolayers

Monolayers spread on supersaturated calcium bicarbonate solution.
 CaCO_3 precipitates under the monolayer on loss of CO_2



Range of long-chain amphiphilic monolayers examined:

Stearic Acid (SA)	Octadecylamine (ODA)	Eicosyl Sulphate (ES)	Eicosyl Phosphonate (EP)
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$	$\text{CH}_3(\text{CH}_2)_{19}\text{OSO}_3\text{Na}$	$\text{CH}_3(\text{CH}_2)_{17}\text{OPO}_3\text{H}_2$

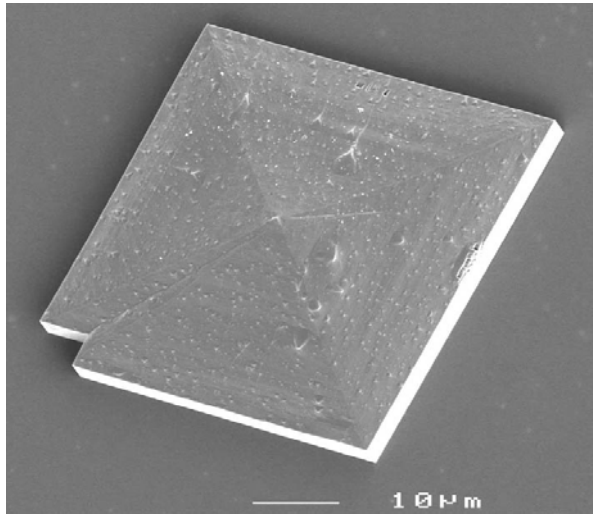
The crystal polymorph and orientation was selected according to the monolayer structure

Stearic acid (SA) Monolayers

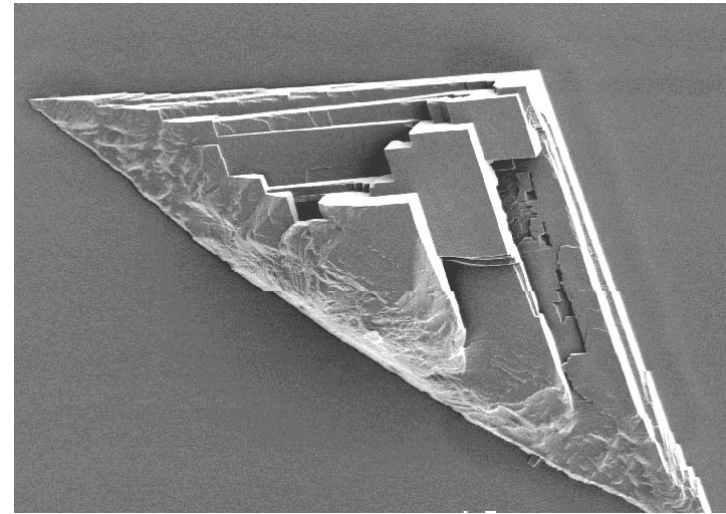
$[Ca^{2+}] = 9 \text{ mM}$, oriented calcite formed

2 morphological forms \Rightarrow Type-I and Type-II

Both plate-like at early stages, nucleated from (1-1.0) plane \Rightarrow realignment occurred during growth



Type I - capped rhombohedral plates



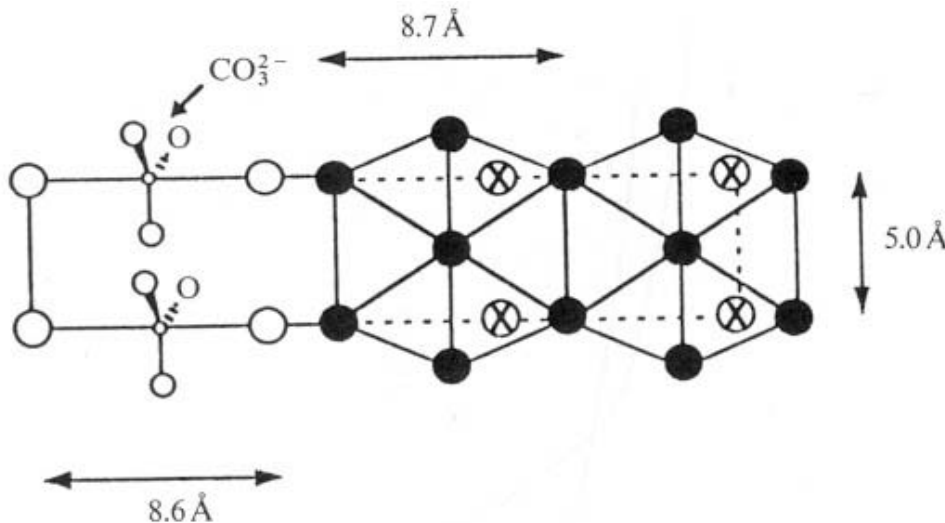
Type II - related triangular morphology

$[Ca^{2+}] = 4.5 \text{ mM}$ \Rightarrow oriented Type-I vaterite crystals were produced

Crystal Orientation:

- Orientation of crystals under SA monolayers due to stereochemical and geometric matching

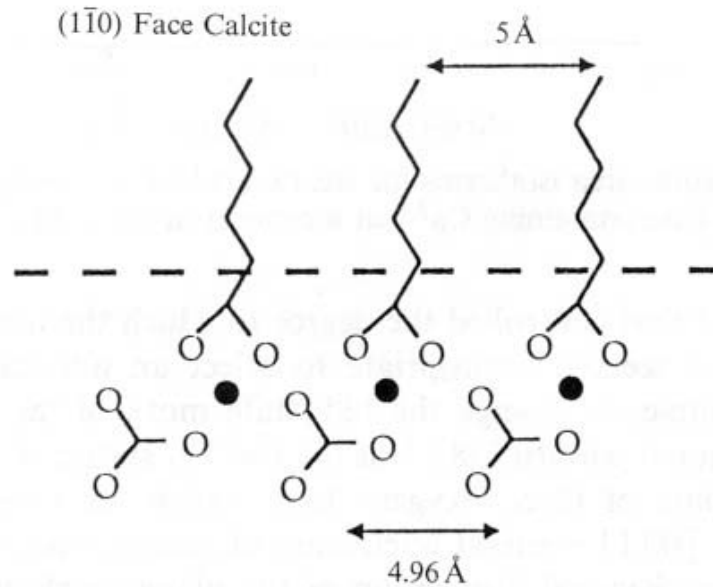
- The monolayer has a hexagonal lattice with $a \approx 5 \text{ \AA}$ \Rightarrow the carbonate-carbonate spacing is 4.69 \AA in the (1-1.0) face of calcite and a close epitaxial match occurs in two directions



Open circles: Ca ions in (1-10) face calcite

Filled circles: close-packed stearic molecules

Stereochemical Effects

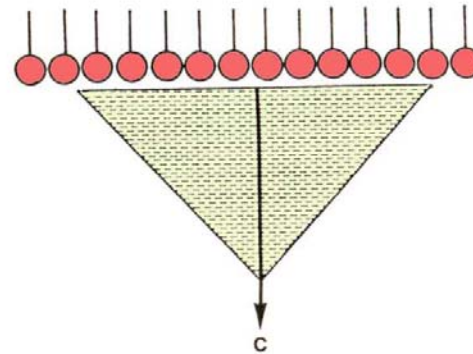
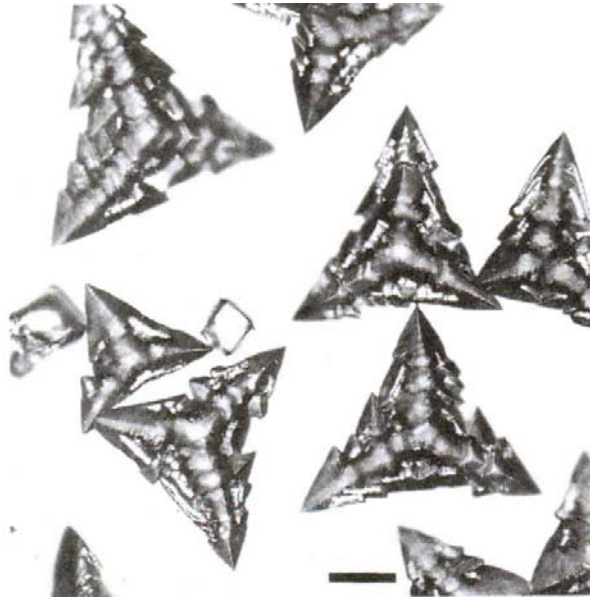


- The stereochemistry of the monolayer headgroups is also essential in directing nucleation \Rightarrow other planes eg. (0001) offer a similar geometric match

The orientation of the carboxylate groups in the SA monolayer mimics the rows of perpendicular carbonate ions in the (1-1.0) calcite face, but not in the (0001) face

n-Eicosyl Sulphate and n-Eicosyl Phosphonate Monolayers

- Sulphate and phosphonate headgroups have a trigonal symmetry
- Sulphate monolayer, immature crystals were pseudo-hexagonal in form, **nucleated from a (0001) face**
- ⇒ developed to a trigonal pyramidal morphology
- Phosphonate gave similar results



Orientational Effect of Monolayer ?

Approximate geometric match between:

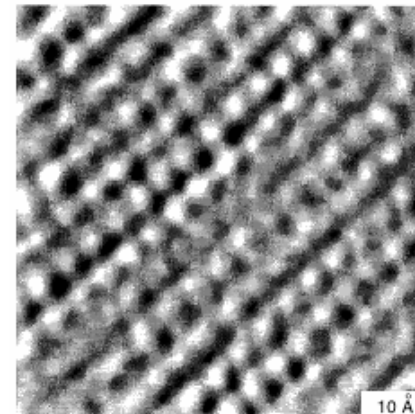
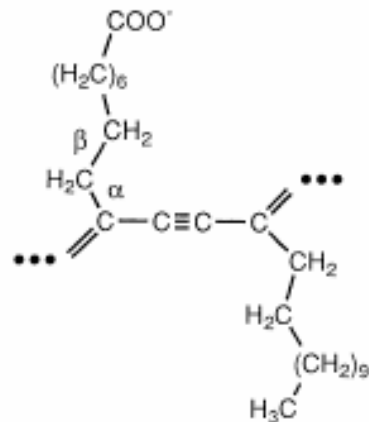
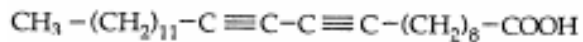
- Hexagonal array of Ca^{2+} ions in the (0001) calcite face,
 $a = 4.96 \text{ \AA}$,
- Hexagonal packing of the headgroups in the sulphate,
 $a = 5.5 \text{ \AA}$
- Hexagonal packing of the headgroups in the phosphonate
 $a = 5.2 \text{ \AA}$

However, **STEREOCHEMICAL RECOGNITION** is probably the overriding factor determining the orientation.

The monolayer headgroups have a **trigonal symmetry** \Rightarrow mimics the **planar carbonate ions in the (0001) face of calcite**

Calcite Precipitation under Acidic Polydiacetylene Films

- Previous monolayers showed control of CaCO_3 crystal orientation normal to the monolayer
→ no control in the plane of the monolayer
- Langmuir-Schäfer films of acidic polydiacetylene - highly organised and structure well defined - carboxyl groups exposed



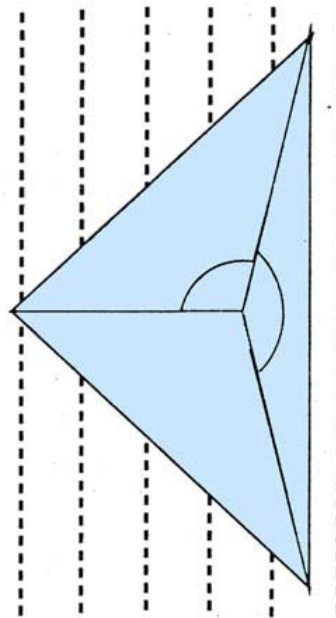
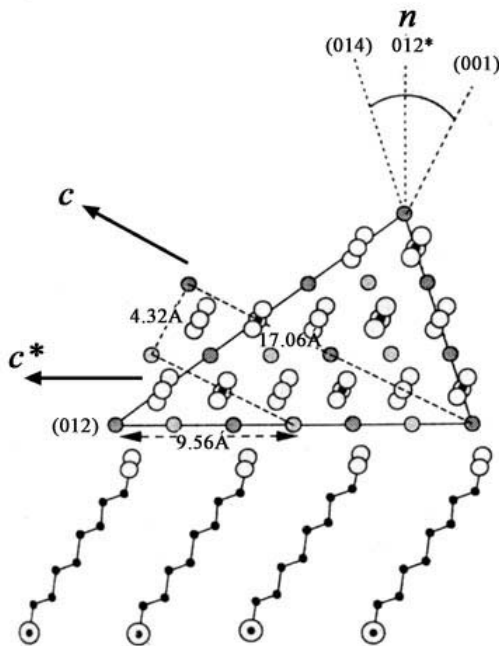
AFM image of p-PDA film



- Calcite crystals with either rounded or triangular morphologies formed \Rightarrow co-aligned within single domains of the PDA films.

- Crystals nucleated from an (01.2) plane

- a -axis parallel to the polymer backbone direction.



Both the crystal and p-PDA polymer have a periodicity of $\approx 5\text{\AA}$ along the a -axis

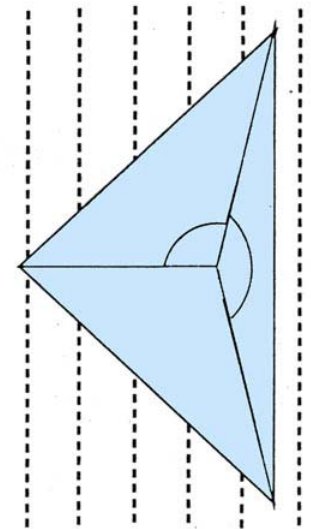
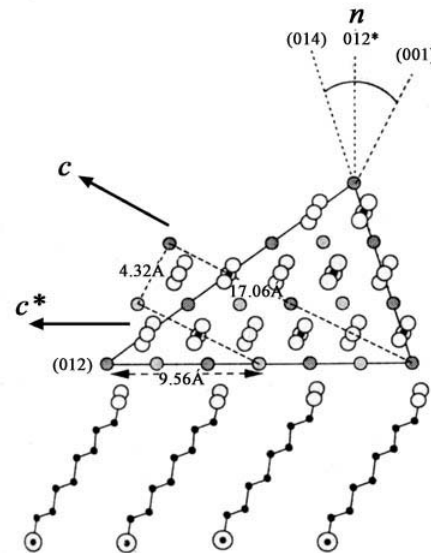
\Rightarrow the carboxy groups along the polymer backbone fit closely to the calcite crystal structure.

What Factors Control the Crystal Orientation ?

- Stereochemistry of the carboxylate groups also important in selecting the (01.2) crystal face.

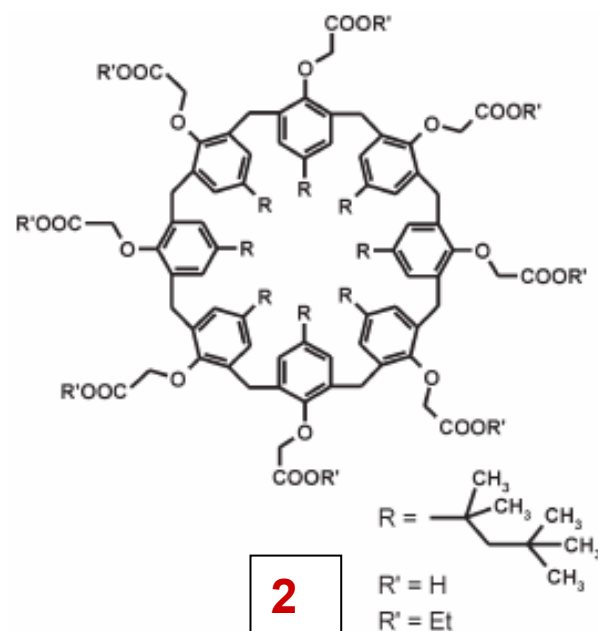
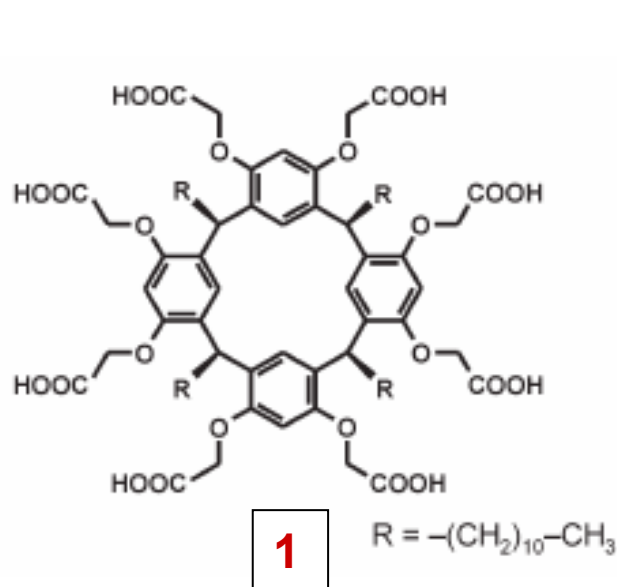
- The (01.2) face comprises alternating planes of Ca^{2+} ions and CO_3^{2-} ions that are tilted 28° to the normal of the (01.2) plane.

- This orientation is closely matched by the 30° tilt of the side chains and carboxylate groups on the polymer.

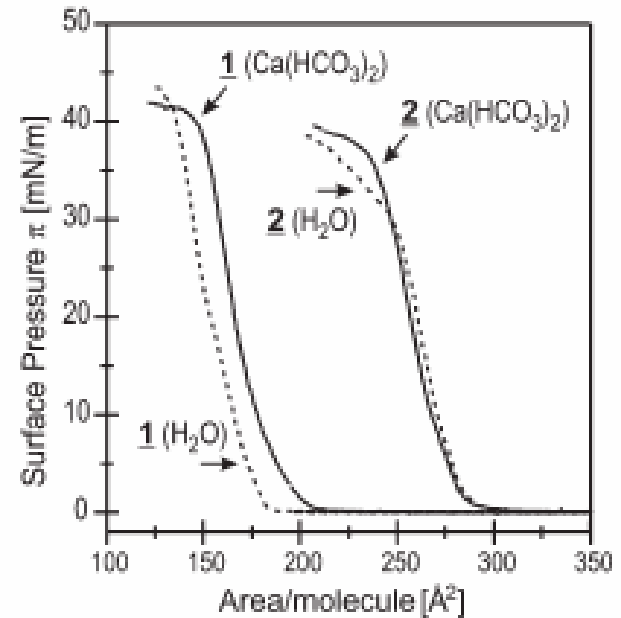
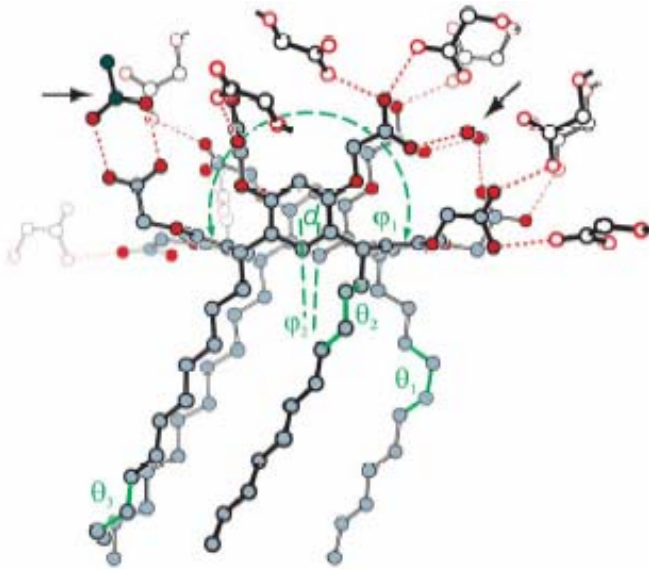


The stereochemical match thus uniquely selects for the (01.2) plane, rather than, eg. the (0001) face, which offers a similar geometric, but poor stereochemical match.

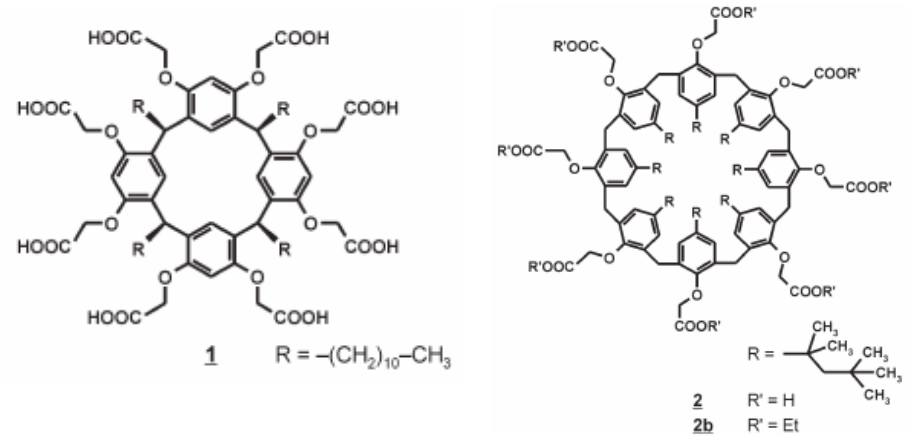
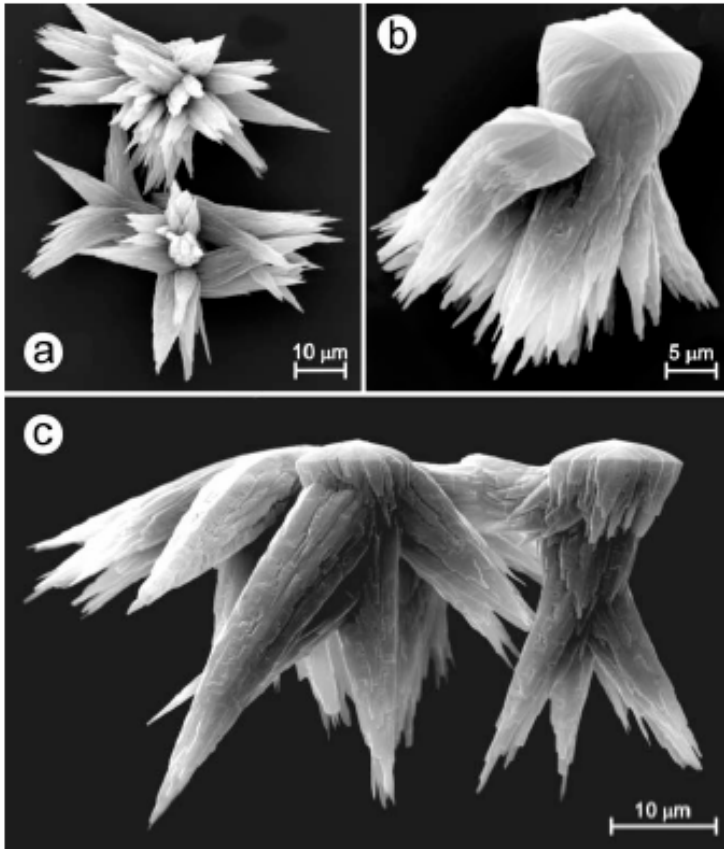
Interfacial Electrostatics Guiding the Crystallization of CaCO_3 under Monolayers of Calixarenes and Resorcarenes



Monolayers of above macrocyclic compounds offer **different surface charge densities** - investigate CaCO_3 growth under these



- Both macrocycles form **monolayers** on water and Ca^{2+} containing subphases
- At zero pressures show **coexistence of LC/LE phases**
- Featureless isotherms suggest **no long range order**



Aragonite crystals precipitate under a compressed monolayer of (1), $\pi = 20 - 25 \text{ mN m}^{-1}$

At low pressures, $p = 0 - 2 \text{ mN m}^{-1}$, fraction of vaterite and (1-10) oriented calcite increases

Monolayers of (2) support uniformly (012) oriented calcite at low pressures, non-oriented calcite crystals at higher pressures

How can the Orientational Effect of the Monolayer be Interpreted?

- Macrocycles (1) and (2) differ greatly in the molecular surface area
- Molecular structures vary greatly
- Oriented calcite growth occurs at low pressures where monolayer is in a liquid condensed phase

Any geometric match seems very unlikely...

• Monolayers of (2), and many other *structurally different* amphiphiles support (012) oriented calcite:

⇒ Occurs at a surface pressure where the average density of carboxylate residues is 2.00-2.44 $\text{CO}_2^- \text{ nm}^{-2}$

Monolayers of (1), support aragonite formation

⇒ Occurs at surface pressures where the average density of carboxylate residues is 4.65-5.00 $\text{CO}_2^- \text{ nm}^{-2}$

⇒ also in keeping with other studies

Results strongly indicate that non-directional interfacial electrostatics is the dominant effect in template-directed CaCO_3 growth under Langmuir monolayers

Summary

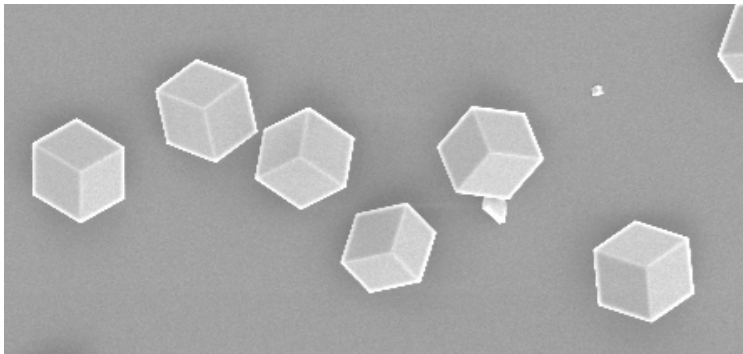
EPITAXIAL MECHANISMS CAN operate to provide orientation of crystals

⇒ see **TOTAL orientation effects** by highly organised p-PDA monolayers

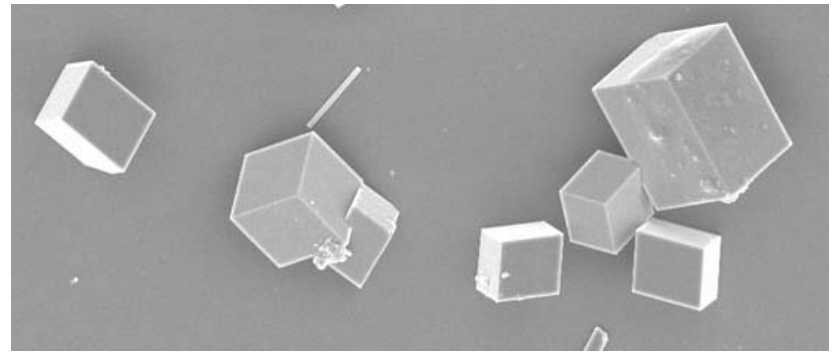
⇒ **Geometric matching is NOT ESSENTIAL** for oriented growth

INTERFACIAL ELECTROSTATICS - ion binding and dipole moments
- appear to be important

STEREOCHEMISTRY - can be a dominating effect. Can observe orientation where **NO** ordering of monolayer

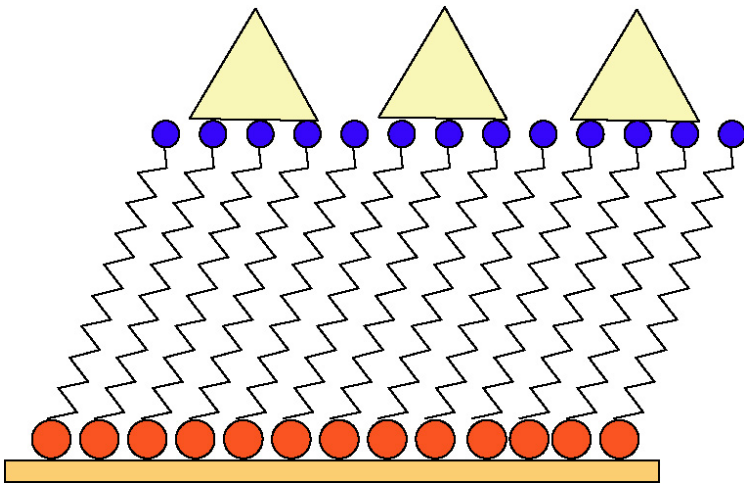


(001) oriented calcite on PAH/PSS film



(104) (NON) oriented calcite on glass

Crystallisation on Self Assembled Monolayers (SAMs)



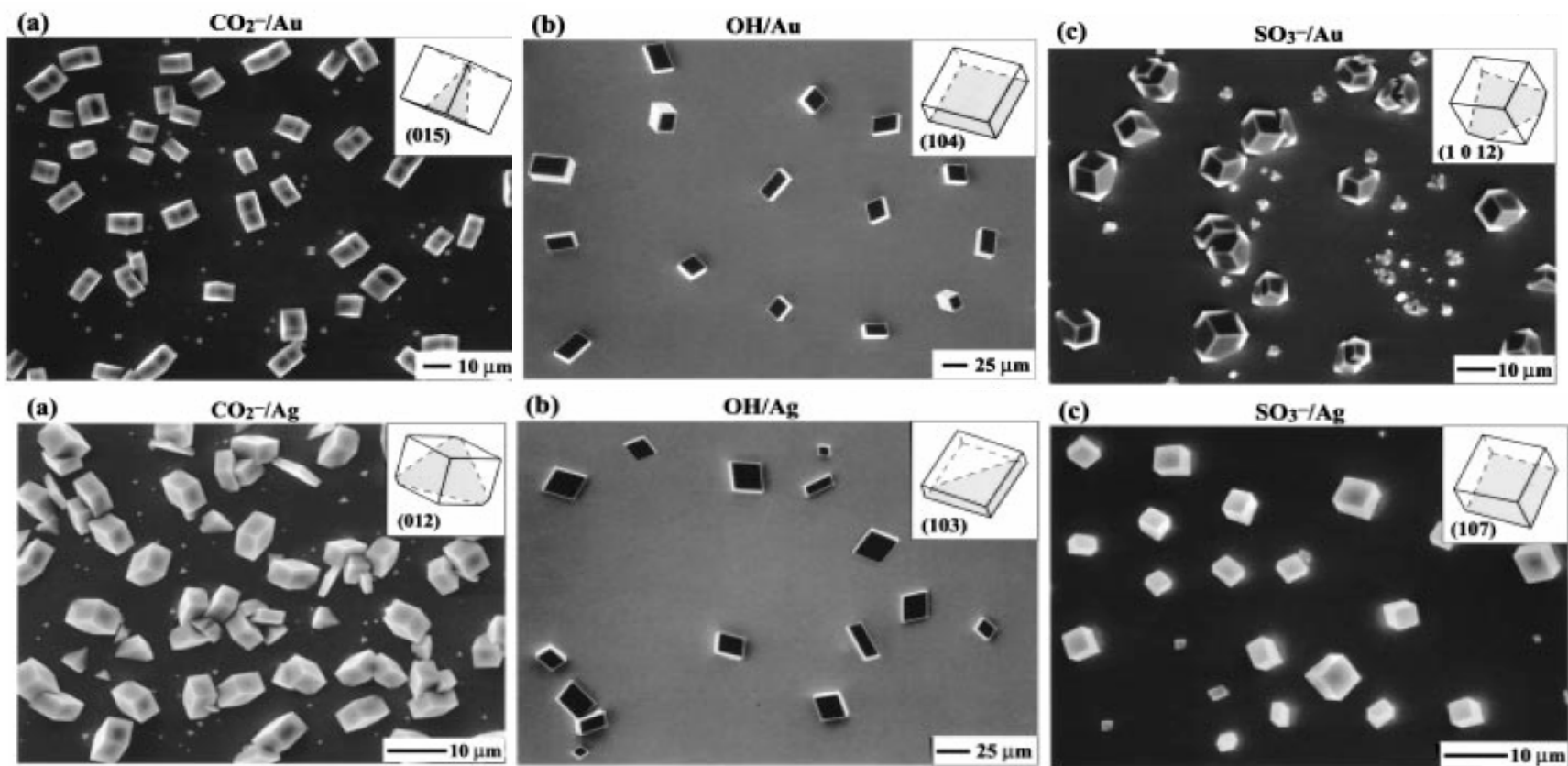
- Offer a simple and flexible method to produce a solid state organic thin film
- The surface chemistry is defined by the SAM terminal group
- Demonstrated to offer high degree of control over crystal nucleation and orientation

SAMs can be easily patterned to direct crystal growth on to designated areas

CaCO₃ Deposition on Functionalised SAMs

ω -terminated alkanethiols on gold and silver thin films

⇒ highly effective in controlling the orientation of deposited calcite crystals,

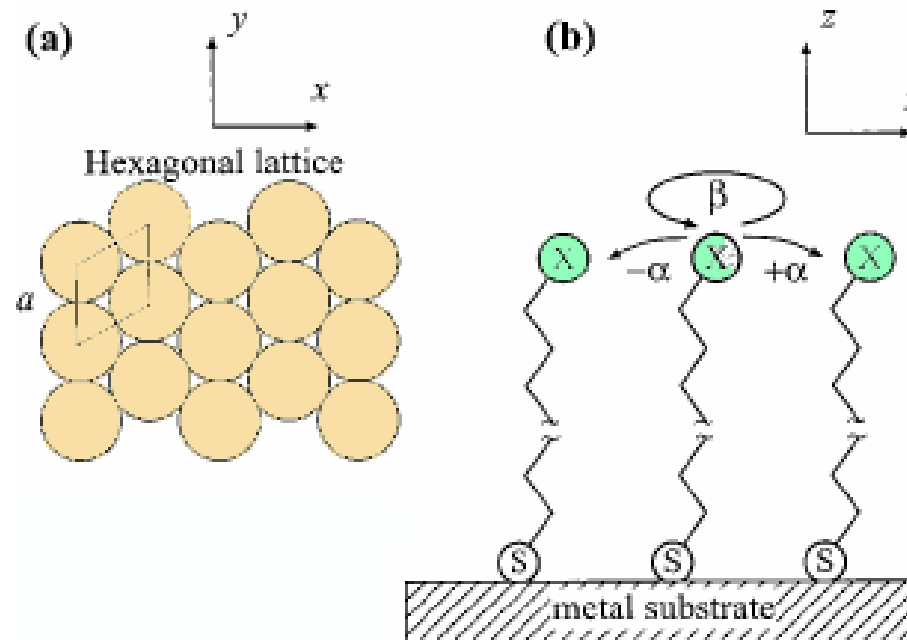


Orientation Effects

Thiol	Au	Ag
$\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$	(015)	(102)
$\text{HS}(\text{CH}_2)_{11}\text{OH}$	(104)	(103)
$\text{HS}(\text{CH}_2)_{11}\text{SO}_3\text{H}$	(10 12)	(107)
$\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$	planes oriented at 24° with respect to the c -axis	planes oriented at $\approx 40^\circ$ to the c -axis
$\text{HS}(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Cl}$	non-oriented/ inhibited crystallisation	non-oriented/ inhibited crystallisation
$\text{HS}(\text{CH}_2)_{15}\text{CH}_3$	non-oriented/ inhibited crystallisation	non-oriented/ inhibited crystallisation

- The CO_2H , OH and SO_3H SAMs selectively nucleate calcite from one plane only
- For the PO_3^- headgroup, the monolayer selects only the angle that the c -axis makes with the substrate.

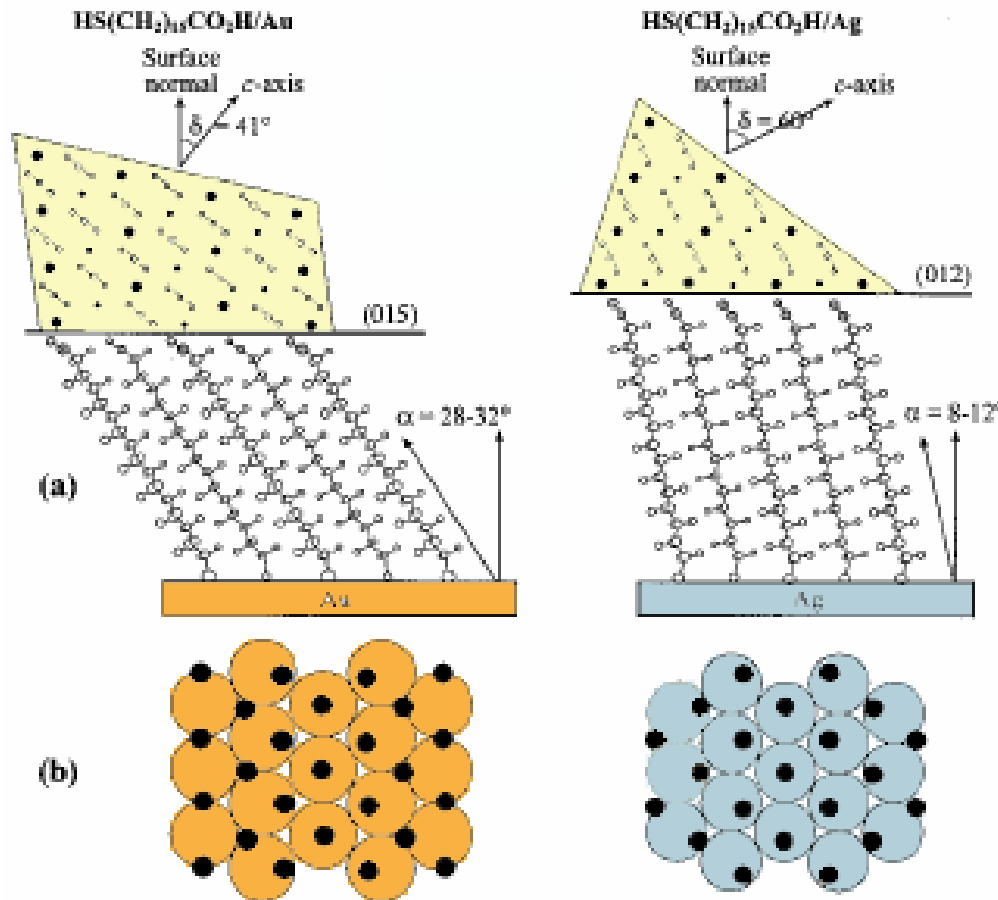
- **Lattice structure** of SAMs is the same for a given metal
- **No lattice match** occurs between the metal lattice and the calcite nucleating plane.



The calcite nucleation face is determined by the structure, chemical character and coordination number of the monolayer headgroup

In all cases of oriented nucleation, the Au and Ag substrates induced nucleation from faces differing in orientation by 15-20°,

⇒ identical to the difference in the tilt angle of the thiol molecules on Au and Ag



Match of CO₂H orientation of SAM headgroup and CO₃-groups in calcite nucleating face

Match of CO₂H groups in SAM and Ca ions

Summary

- Lattice match between SAM and nucleating crystal planes **DOES NOT APPEAR** to be responsible for oriented nucleation
- Orientation of functional groups in the SAM precisely matched the orientation of carbonate groups in the nucleating crystal face
- Matching of symmetry of functional group alone cannot be responsible for orientation - cf. SO_3H^- and PO_3H_2^-

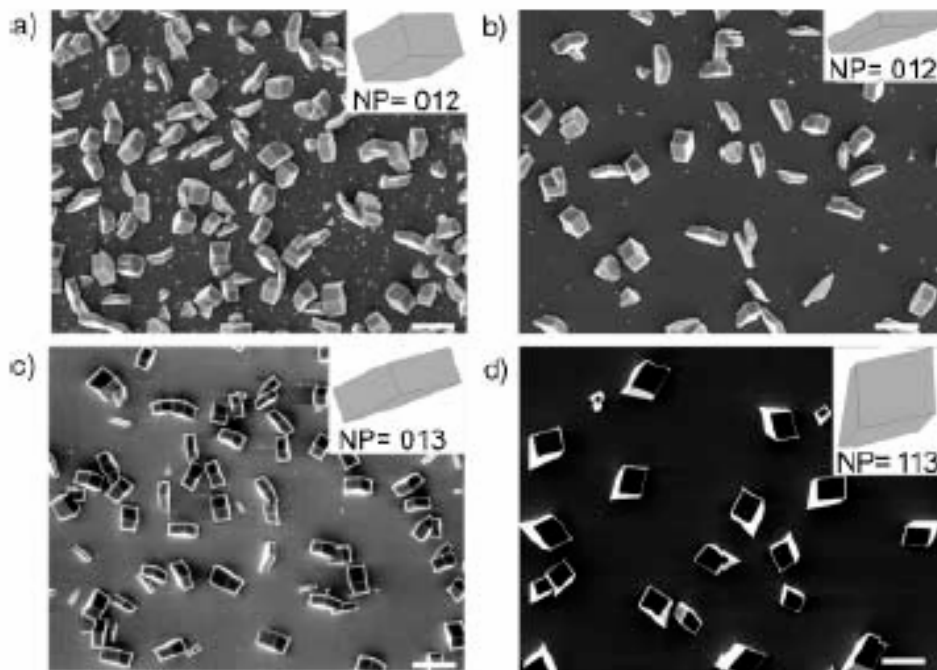
Benefit of SAMs \Rightarrow can selectively nucleate a wide range of orientations \Rightarrow can make systematic changes in the structure

Oriented Nucleation on SAMs with Alkyl Chains of Differing Parity

Calcite grown on $-COOH$ terminated SAMs with odd/even alkyl chains

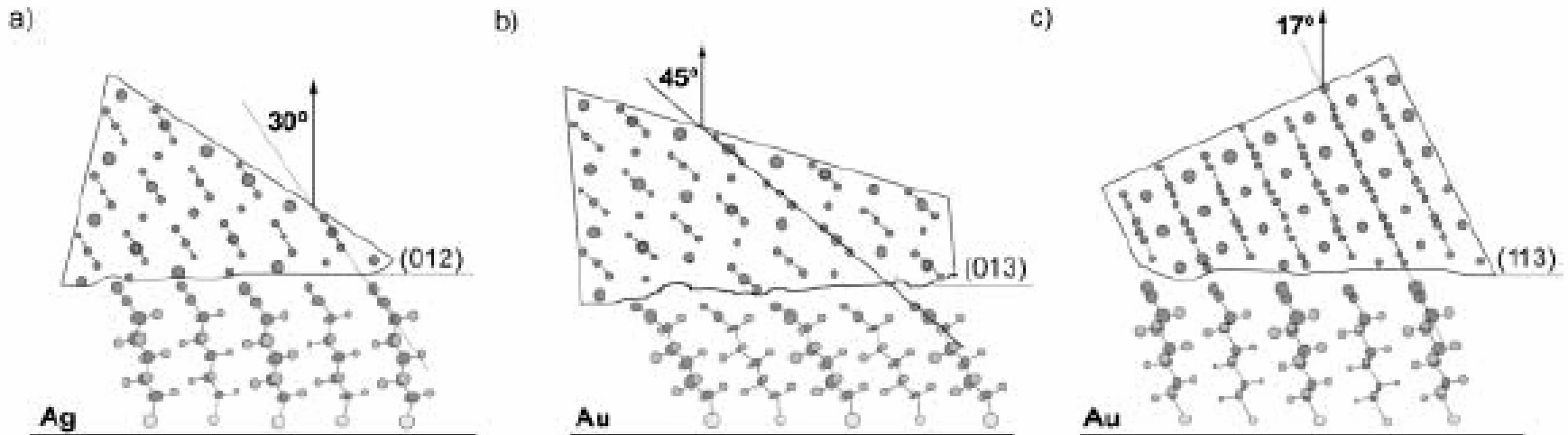
Ag substrates \Rightarrow orientation of terminal group constant

Au substrates \Rightarrow terminal group adopts 2 different orientations for odd and even chains



a) C15-Ag, b) C10-Ag
c) C15-Au, d) C10-Au

- Crystal orientation constant on Ag SAMs (012)
- (013) Oriented on odd-chain SAMs on Au
- (113) Oriented on even-chain SAMs on Au

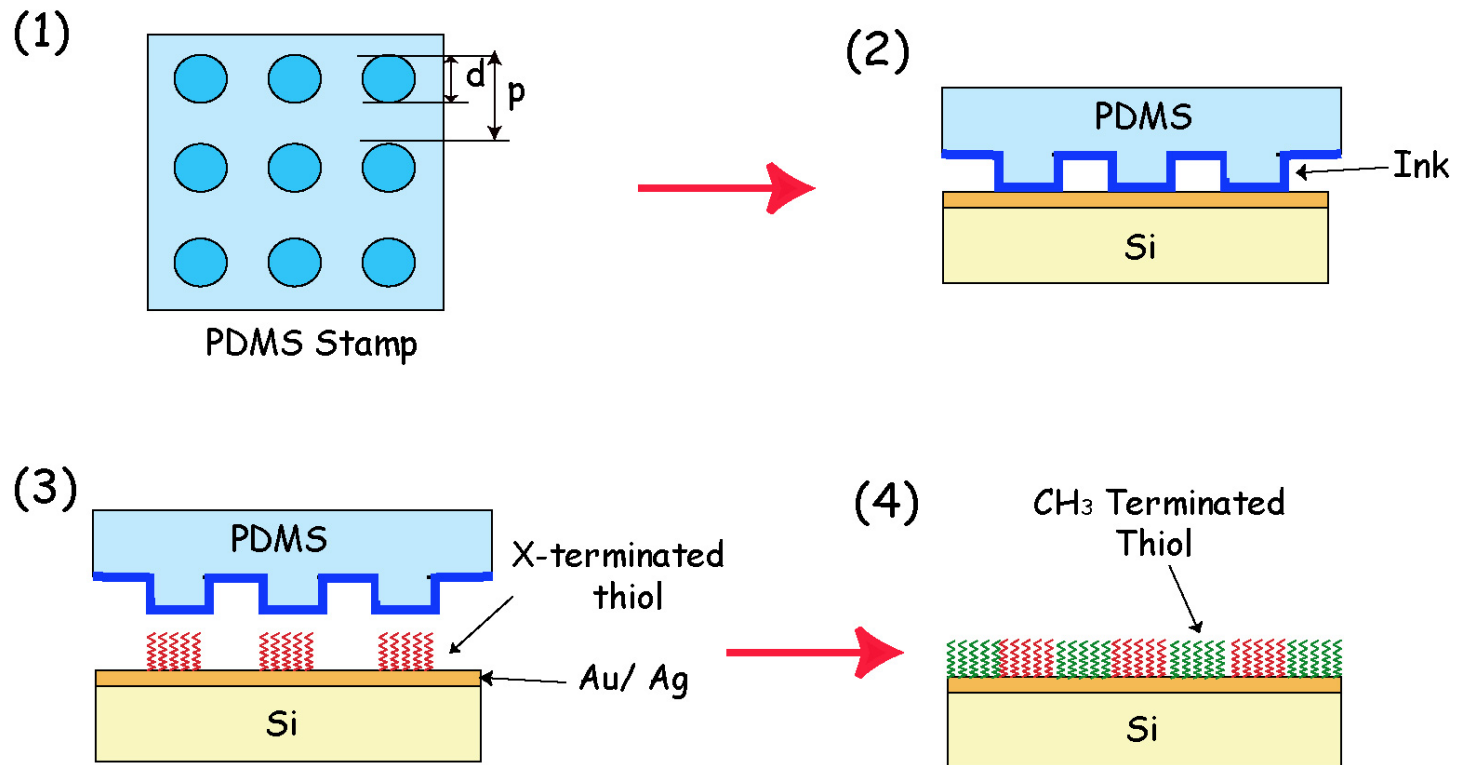


Alignment of $-CO_2H$ groups on SAMs with the carbonate groups in calcite for a) odd (and even) chain length SAMs on Ag, b) odd chain length SAMs on Au, c) even chain length SAMs on Au, NP=(113).

The CO bonds in the surface carboxylate groups are parallel to the CO bonds in the carbonates in the nucleated calcite crystals.

Patterning Crystal Growth

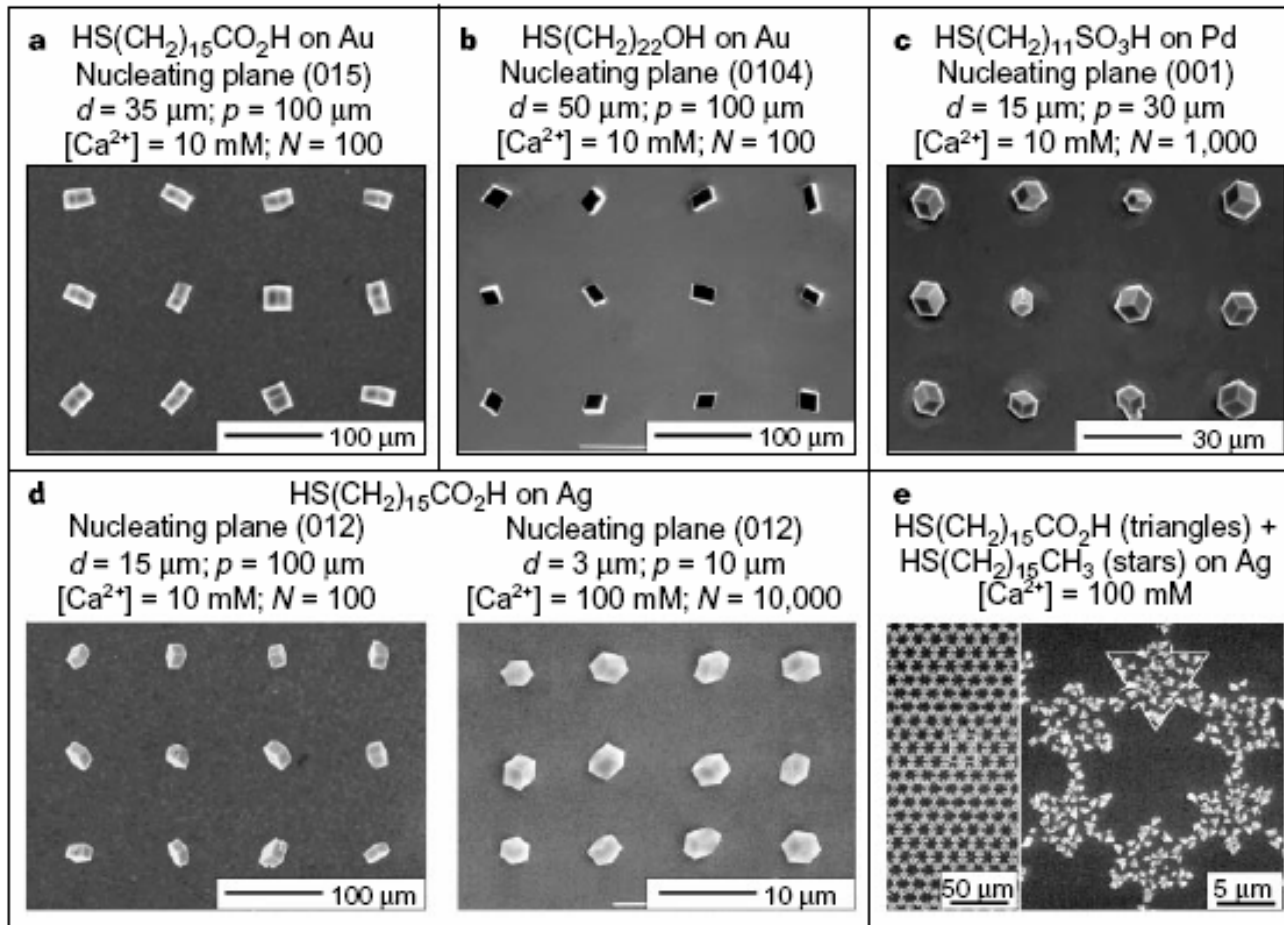
One of major advantages of SAMs \Rightarrow can be patterned in 2D



Generates patterns of SAMs with contrasting endgroups

Oriented Crystal Growth on Patterned SAMs

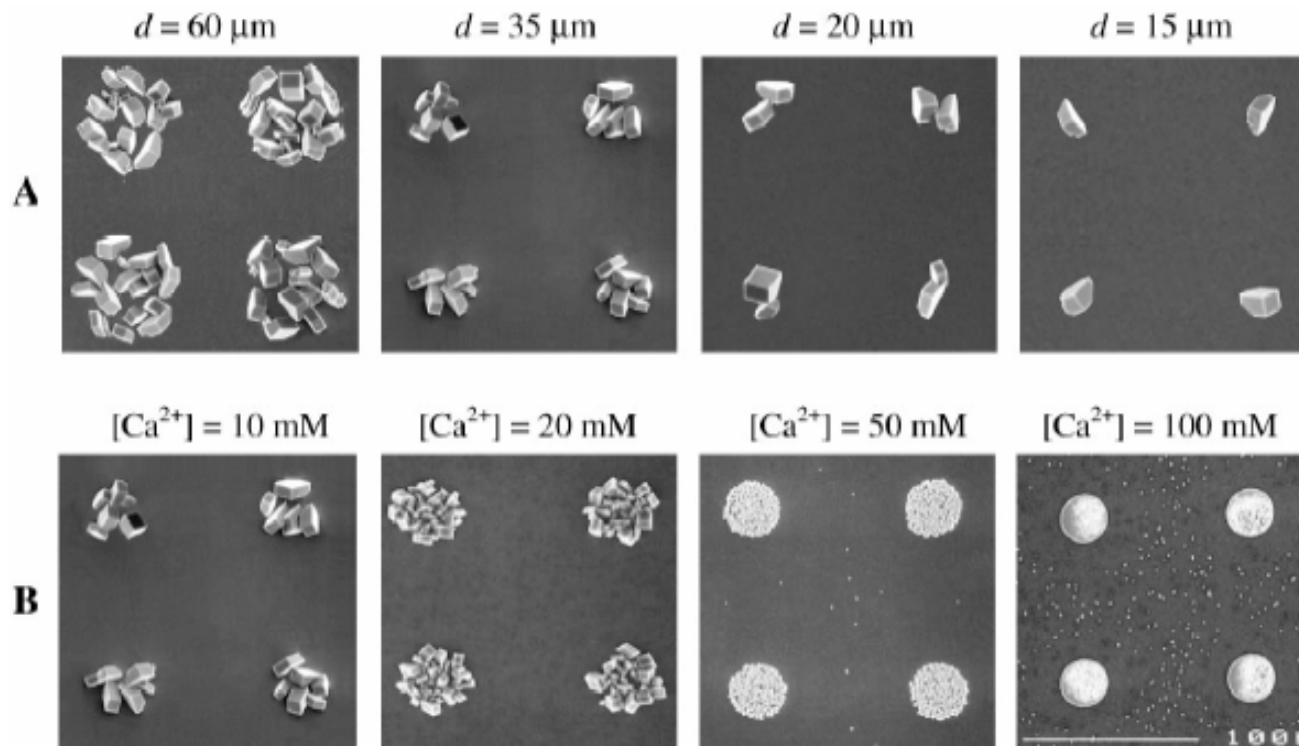
Patterned SAMs enable periodic arrays of discrete crystals with controlled densities, location, size and orientation to be produced



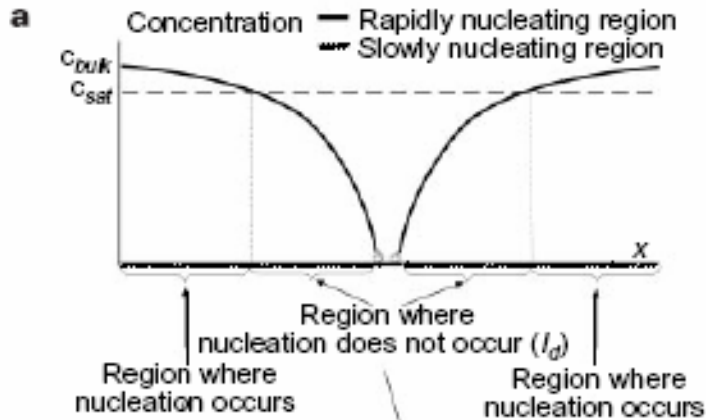
Aizenberg, Black, Whitesides, *Nature* (1999), 398, 495-498.

Variation of the **density** and **sizes** of features on the stamp, the **concentration** of the crystallising solution and the **SAM terminal groups** gives control over the:

- **Location of crystal growth**
- **Density of crystal growth**
- **Number of crystals nucleating within a given region**
- **Orientation of the crystals**



Aizenberg, *Journal of Crystal Growth* 211 (2000), 143-148.



Localised crystallisation occurs due to diffusion-limited nucleation

- Crystals nucleate first on the areas of hydrophilic $-CO_2H$ thiols
- Transport of ions to the growing crystals reduces the concentration of ions in the adjacent hydrophobic areas
 ⇒ prevents non-specific nucleation within a characteristic distance of the interface.
- Variation of the size and periodicity of patterns and the concentration of the crystallising solution therefore offers control over crystal patterning.

Summary

Orientational Control

- **Geometric Match** - doesn't appear to be overriding effect
- **Stereochemical Match** - evidence quite convincing!

Control by SAMs...

- Orientation between Au substrate and crystals indicates the **structural relationship** between the **SAM** and **calcite crystals**
- Match of **CO₂H** orientation of **SAM** headgroup and **CO₃-** groups in calcite nucleating face

Electrostatics...

"Non-directional interfacial electrostatics is the dominant effect in template-directed CaCO₃ growth under Langmuir monolayers"