Erwin Schrödinger

Father of Quantum Chemistry
The Nobel Prize in Physics 1933

In 1952,

*… we would never experiment with just **one** electron, atom, or molecule …*

E. Schrödinger, *Br. J. Philos.* (1952), p. 233.

# Lecture 8: STM Manipulation and Organization of Single Atoms and Molecules on Surface

Part I:

- Significance of atomic manipulation, and their lateral organization;
- Typical examples of fabrication and manipulation of single atoms on surface --- proven feasibility;
- mapping single atoms or molecules on surface: *physisorption vs. chemisorption;*
- growth of atomic scale nanostructures on surface.

Part II:

- Overview of molecular self-assembly *(examples, implications, applications);*
- Molecular interactions in self-assembly;
- Atomic fabrication of self-assembly*;*
- Tuning the epitaxy of molecular packing on surface .

Atom and molecule manipulation by low-temperature STM
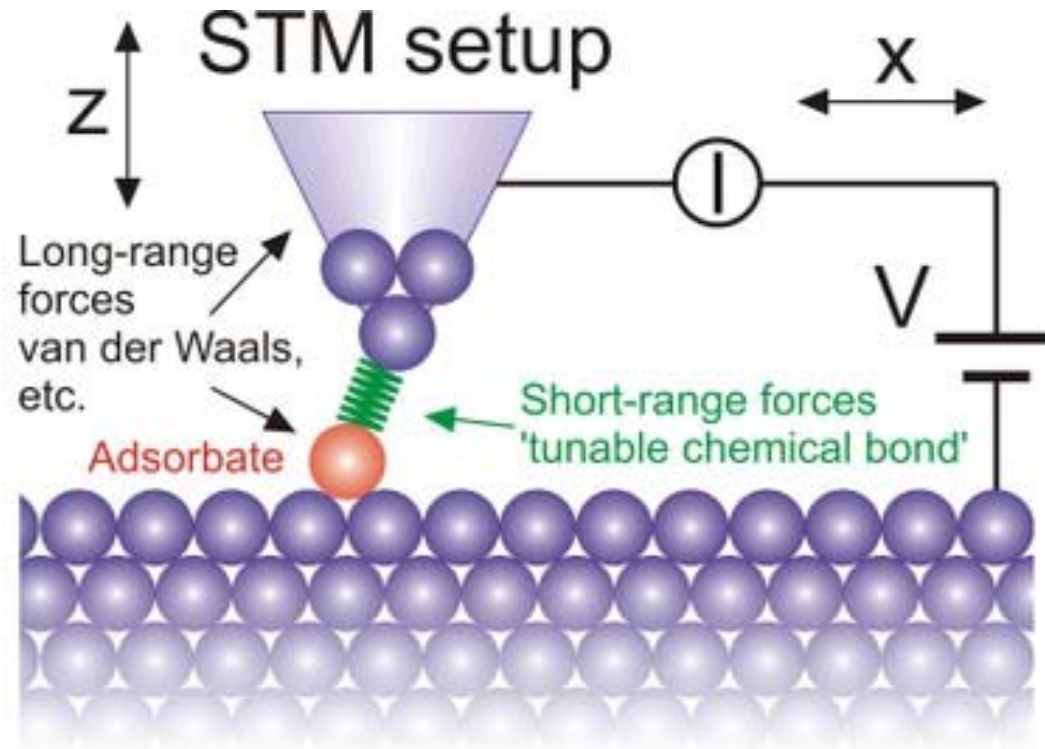
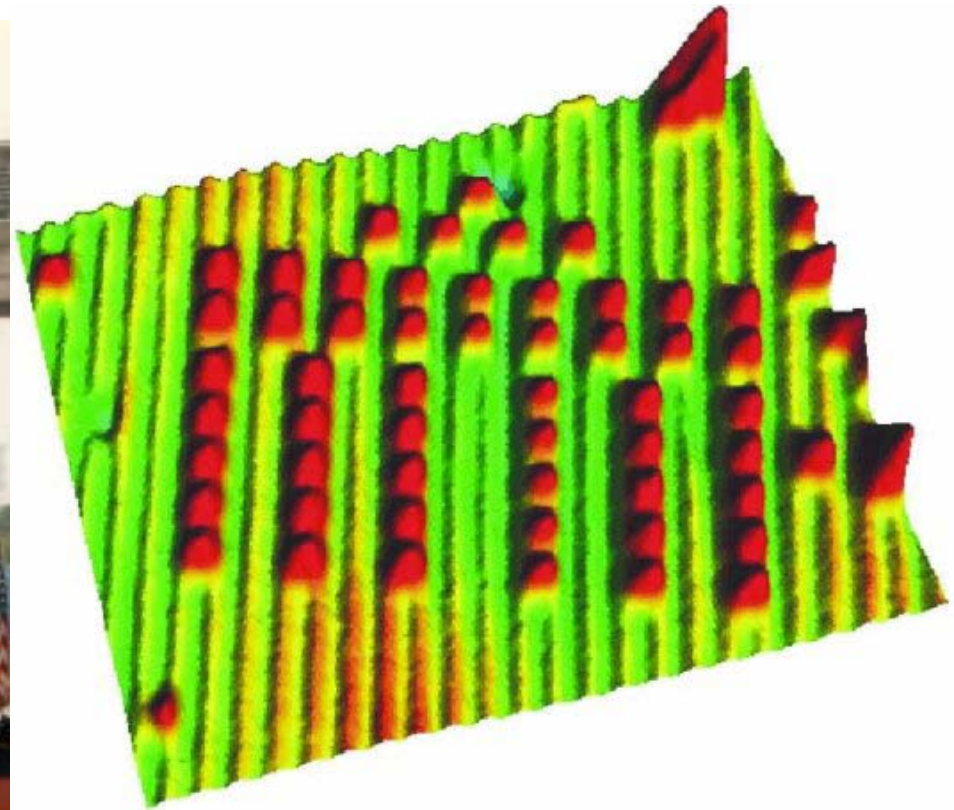**Lateral manipulation:** Moving atoms/molecules along the surface

Vertical manipulation: Transfer of atoms/molecules between surface and STM tip

Part I: Atomic manipulation (laterally)

- <u>Significance of atomic manipulation</u>: ultimate resolution of lithography; direct imaging of atomic wave interaction; building up single-atom electronic device (transistor); atomic investigation of chemical reaction (pre-bonding).

- *STM*, was initially invented to image surfaces down to atomic scale (see last lecture).

- It has been further developed later to an operative tool --- atoms and molecules can be manipulated at *low substrate temperatures* to create and investigate artificial structures.

- These possibilities give rise to starting new opportunities for physical and chemical experiments on the single atom and single molecule level --- not just imaging, but beyond, for manipulating and fabiricating.

# Building **Brandenburg gate** at atomic scale using CO molecules

STM-image of the Brandenburg Gate constructed on Cu(211) with atomic precision using 48 CO-molecules using the technique of lateral manipulation.

L.Bartels *et al., Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al., ibid*. 77, 2133 (1996)

Lateral manipulation and build-up of artificial structures

- The figure shows the <u>first example</u> of an artificial structure on atomic scale.
- The Brandenburg gate has been formed with 48 CO molecules by laterally manipulating them into the proper positions with atomic accuracy.
- In lateral manipulation an ad-particle at the surface is moved with the tip along the substrate surface to the desired place <u>without loosing contact</u> to the substrate.
- This is achieved by bringing the tip very close to the ad-particle, so that besides the ever present <u>van der Waals</u> interactions also <u>chemical forces</u> between tip and particle are coming into play.
- These forces can be tuned to be large enough to surmount the surface diffusion barriers, so that the ad-particle comes along with the tip, if the tip is moved parallel to the surface to the desired end point.
- It is fascinating that even at the level of the very atoms, a distinction can be made between different manipulation modes, namely **pulling**, **pushing** and **sliding** (see next slide).

Attractive and repulsive modes in STM manipulation
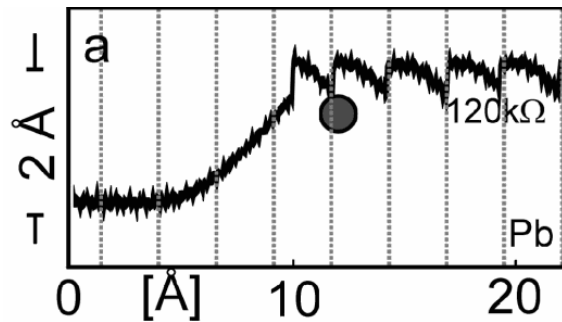
(a) and (b) a **Pb**-atom

(c) a **CO**-molecule on Cu(211).
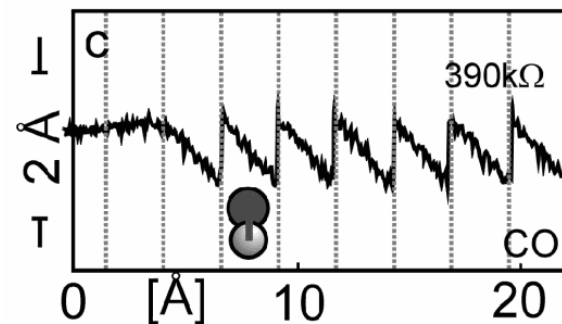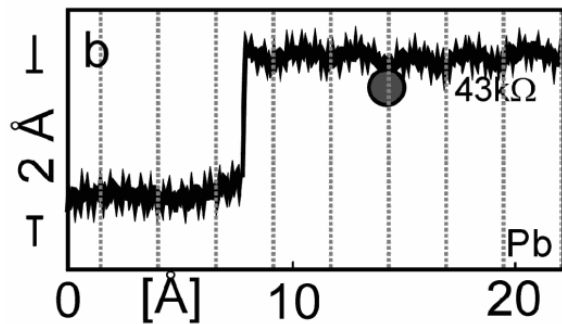
Tip-height curves measured during manipulation of atoms. The tip is moved from left to right and respective tunneling resistances are indicated as qualitative measures of the tip-ad-particle force. The vertical dotted lines correspond to fcc sites next to the intrinsic step edges. The initial sites of the manipulated particles are indicated. Note that in the attractive manipulation modes (a: pulling and b: sliding) the particles first hop towards the tip and then follow it, whereas in the repulsive mode (c: pushing) the CO-molecules perform hops away from the tip.

L.Bartels *et al.*, *Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al.*, *ibid*. 77, 2133 (1996)

Attractive and repulsive modes in STM manipulation

- The figure shows tip height curves obtained in the STM <u>constant current</u> mode during manipulation of metal atoms and CO-molecules.
- A) displays the pulling behaviour of a metal adatom: The atom follows the tip in regular *jumps* from one adsorption site to the next due to attractive tip-particle forces.
- B) Applying larger forces (measured by smaller tunneling resistivities) a sliding motion is induced, in which the ad-particle is trapped under the tip and follows the tip motion <u>continuously</u>, so that the tip height curve yields a picture of the substrate corrugation.
- C) In contrast to metal adatoms, CO molecules are usually pushed: The molecules move <u>discontinuously</u> in front of the tip due to repulsive forces. On <u>close packed</u> surfaces like <u>Cu(111),</u> pushing is not very reliable, as the particles tend to move to the side of the tip and get lost.
- The successful buildup of artificial structures like that in the first figure is all due to the proper choice of the substrate surface: <u>Cu(211),</u> on which CO adsorbs at the upper part of the intrinsic step edges, which act as <u>"railway trails" upon pushing</u>.

L.Bartels *et al., Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al., ibid*. 77, 2133 (1996)
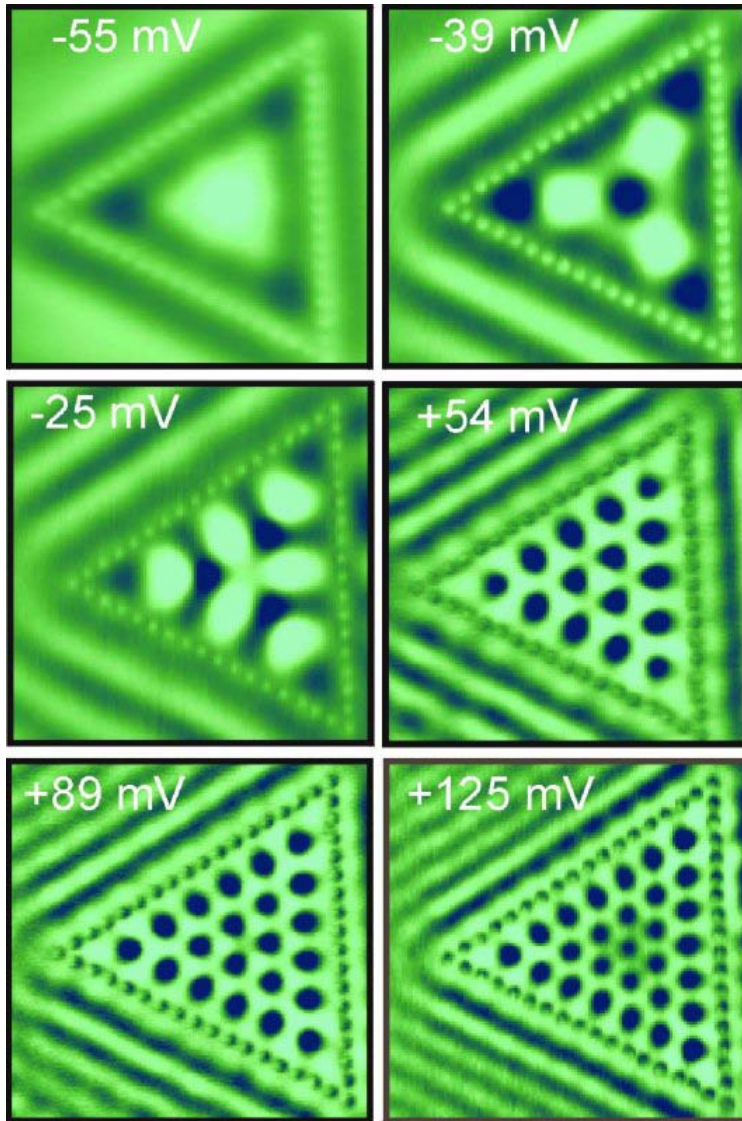
Building up an atomic triangle corral of silver
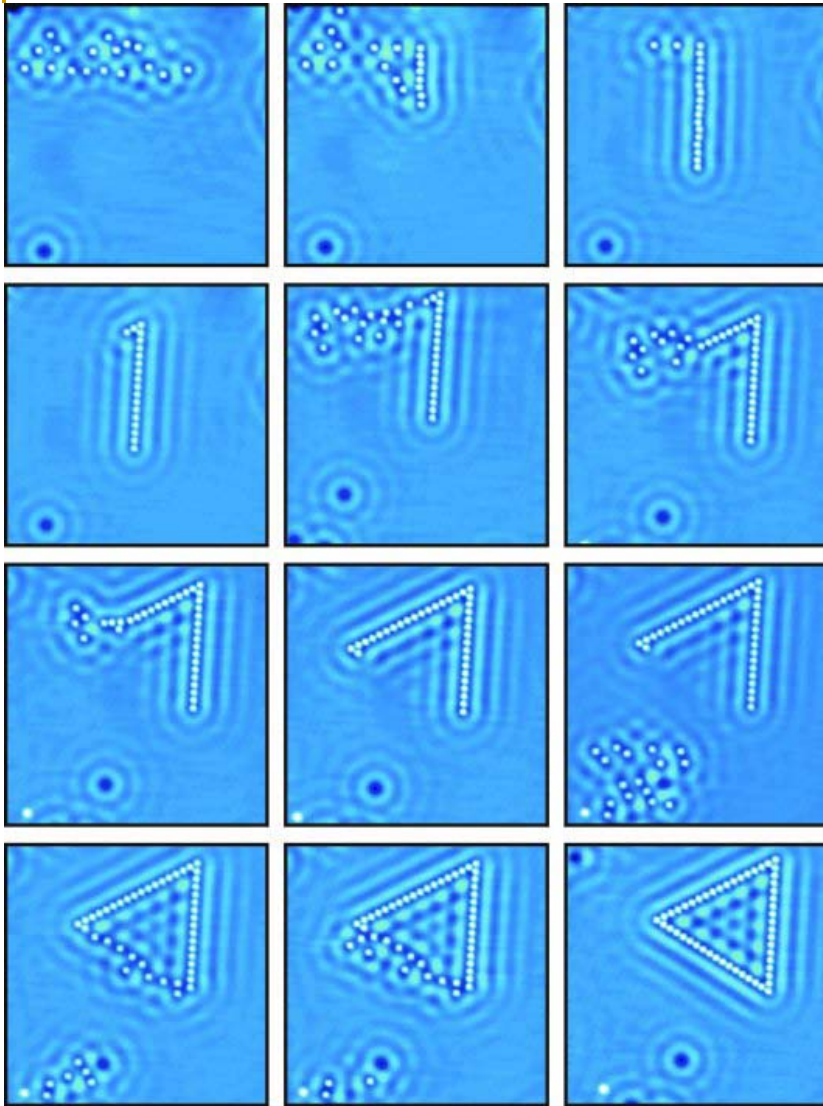
Series of images demonstrating the build-up of a regular triangle consisting of 51 Ag atoms on a Ag(111) surface.

L.Bartels *et al., Phys. Rev. Lett.* 79, 697 (1997); G.Meyer *et al., ibid.* 77, 2133 (1996)

Building up an atomic triangle corral of silver

- The artificially created regular triangle whose buildup is shown in the figure.
- It was made by pulling Ag atoms on a Ag(111) surface.
- With sufficiently stable and nevertheless sharp tips it is even possible to remove native substrate atoms from highly coordinated defect step sites and even from regular step sites of high index surfaces in a one by one manner.

L.Bartels *et al., Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al., ibid*. 77, 2133 (1996)

Building up an atomic triangle corral of silver

-55 mV -39 mV -25 mV +54 mV +89 mV +125 mV

Spectroscopic dI/dV maps measured with the triangle of the last figure displaying the local density of states at energies where the wavelength of the electrons are in resonance with the triangular quantum corral.

L.Bartels *et al., Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al., ibid*. 77, 2133 (1996)

Physics with artificial structures: electron resonance and interference inside a quantum corral (*quantum confinement*)

- Ad-particles arranged in a <u>closed geometry</u> act as partial confinement for electrons and can be used to determine the <u>electron lifetime</u>.
- By means of lateral manipulation, <u>51 Ag atoms</u> have been precisely positioned at distances of **5** times the nearest neighbour distance to form a triangle with a base length of 245 Å as shown in the figure.
- The electrons of the <u>surface state</u> present on the Ag(111) surface are scattered by these Ag <u>adatoms</u>, resulting in a complex interference pattern.
- Energy resolved data as shown in the figure were taken in the spectroscopic dI/dV-mode.
- The <u>energies in the figure</u> correspond to energies where the wavelength of the electrons is in <u>resonance</u> with the triangle resulting in a strong <u>enhancement</u> of the intensity.
- Calculations of the wave pattern have been performed based on a multiple scattering approach taking into account the <u>phase-relaxation lengths</u> of the electrons, which reflect <u>scattering events</u> inside the triangle influencing their <u>phase coherence</u> and can directly be converted into electron <u>lifetimes</u>.
- Inside of the triangle, <u>electron-electron and electron-phonon</u> scattering determine the electron lifetime and the <u>spatial decay of the interference pattern</u> which has been measured here.
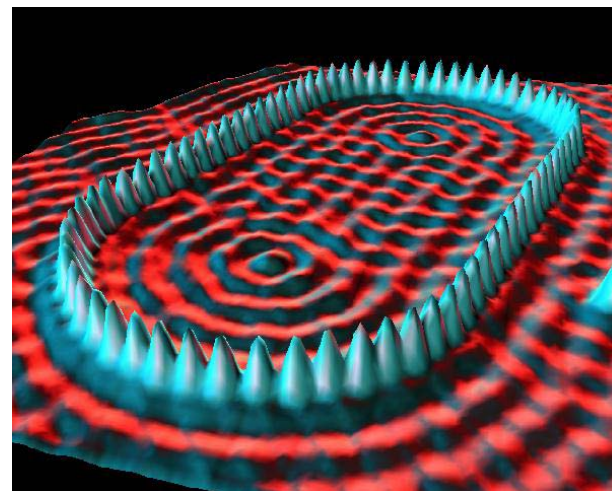
L.Bartels *et al., Phys. Rev. Lett*. 79, 697 (1997); G.Meyer *et al., ibid*. 77, 2133 (1996)

More Atomic arts
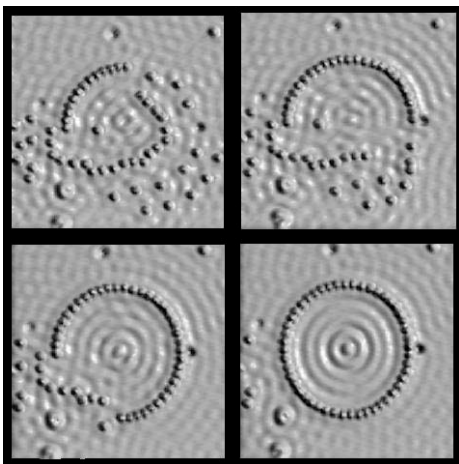
Atomic Circle
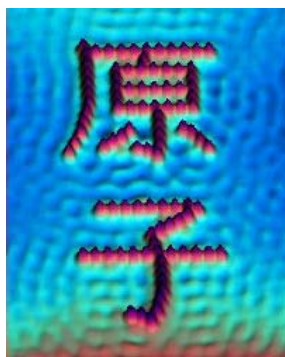(iron atoms on a copper surface)
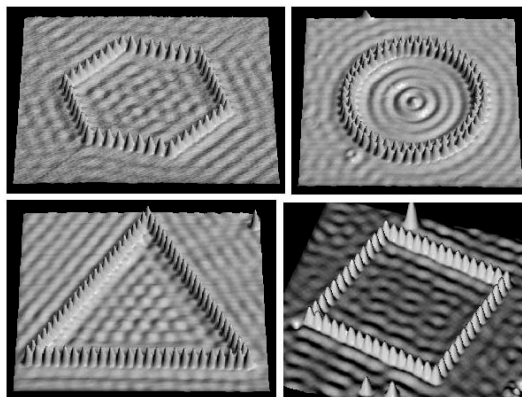
Atomic Polygons

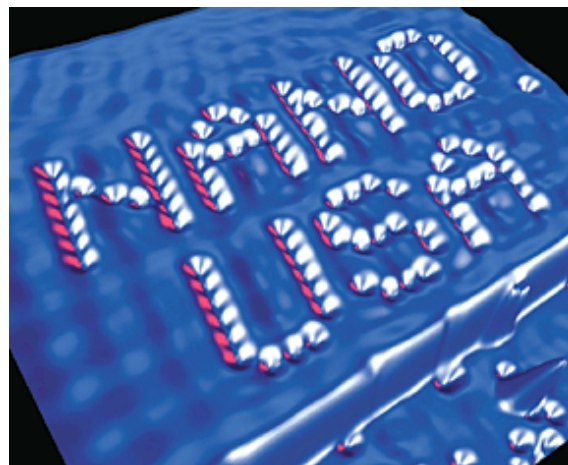### Atomic Stadium
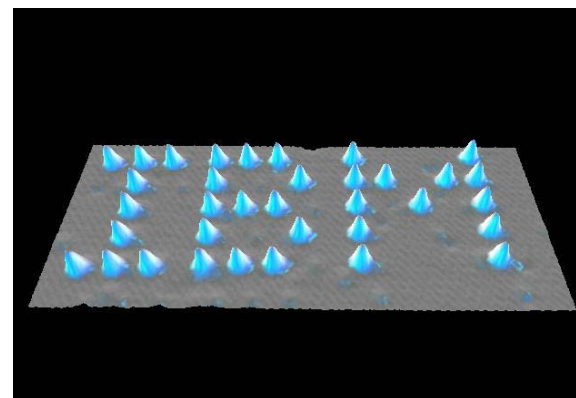(iron atoms on a copper surface)

Atomic Words
(iron atoms on a copper surface)

Molecular Words
(CO on a copper surface)

Atomic Logo
(Xe atoms on a Nickel surface)

Physisorption vs. chemisorption

January 31, 1881 --- August 16, 1957
Nobel Prize in Chemistry, 1932

- Langmuir's early work --- only chemisorption concerned.
- Later work by Morrison and Roberts, and Kisliuk --- considered both physisorption and chemisorption.
- Theoretical work --- support the presence of precursor states in adsorption and desorption processes

Physisorption: weakly bound, mobile on surface, easy to desorb
Chemisorption: strong binding, no lateral mobility, hard to desorb.
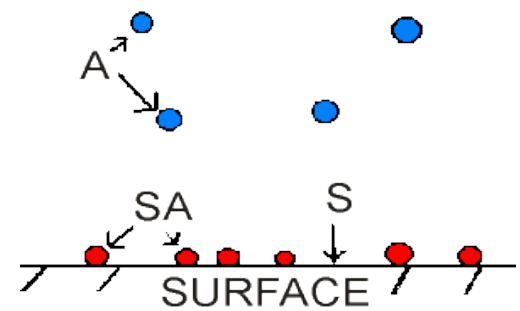
- In Langmuir's early work, a simple scenario was considered in which an impinging species either was chemisorbed when striking an <u>adsorbate-free surface site</u> or was scattered back into the gas phase upon encountering an <u>occupied site</u>, leading to a (reverse) linear dependence of the sticking coefficient (that is, the probability of adsorbing) on surface coverage.

$$\theta = \frac{Kp}{1 + Kp}$$

  Where θ is the percentage coverage of the surface, (number of adsorption sites occupied/number of total adsorption sites available), K is the adsorption coefficient, =ka/kd, and p is the gas pressure.

- Exceptions to this behavior -- <u>systems exhibiting near-unity sticking probability at high coverage</u> -- were noted early on, for example, Cs and N_2 adsorption on tungsten.

- To account for these observations, more sophisticated models by Morrison and Roberts and Kisliuk invoked a <u>weakly bound</u>, <u>mobile intermediate state</u> that allowed incoming adsorbates to search for a free site.

- Later adsorption studies, usually measurements of sticking coefficients, pointed to such a precursor-mediated adsorption mechanism.

- Numerous theoretical papers have modeled the role of precursor states in adsorption and desorption.

# Comments for the combined adsorption model

- Over the past 70 years, numerous gas-surface adsorption studies have indicated the existence of a *weakly bound*, *mobile intermediate* that is a precursor to chemical bond formation.

- Although knowledge of physical interactions between adsorbates and surfaces (physisorption) and of relatively strong chemical interactions (chemisorption) has advanced steadily over the years, important issues remain to be addressed.

- One such issue, central to a discussion of adsorption phenomena and a recurring theme throughout the history of surface science, involves an adsorption intermediate known as a precursor (physi-adsorption state).

- Although no direct observation or characterization has been achieved, numerous observations consistent with precursor-mediated adsorption have led to widespread use of the concept.

- The direct observation and characterization of such a species was reported in 1998 by Robert Wolkow group at Canada.

- **Precursor and chemisorbed benzene on a silicon surface were clearly distinguished, using of a tunable-temperature scanning tunneling microscope.**

Existence of such a barrier allows the long-lived state of physisorption to be detected at low temperatures.

Formation of chemisorption state represents the lowest energy state (the most stable state).
The adsorbate species is thus in the closest proximity of the surface (like chemical bonding)
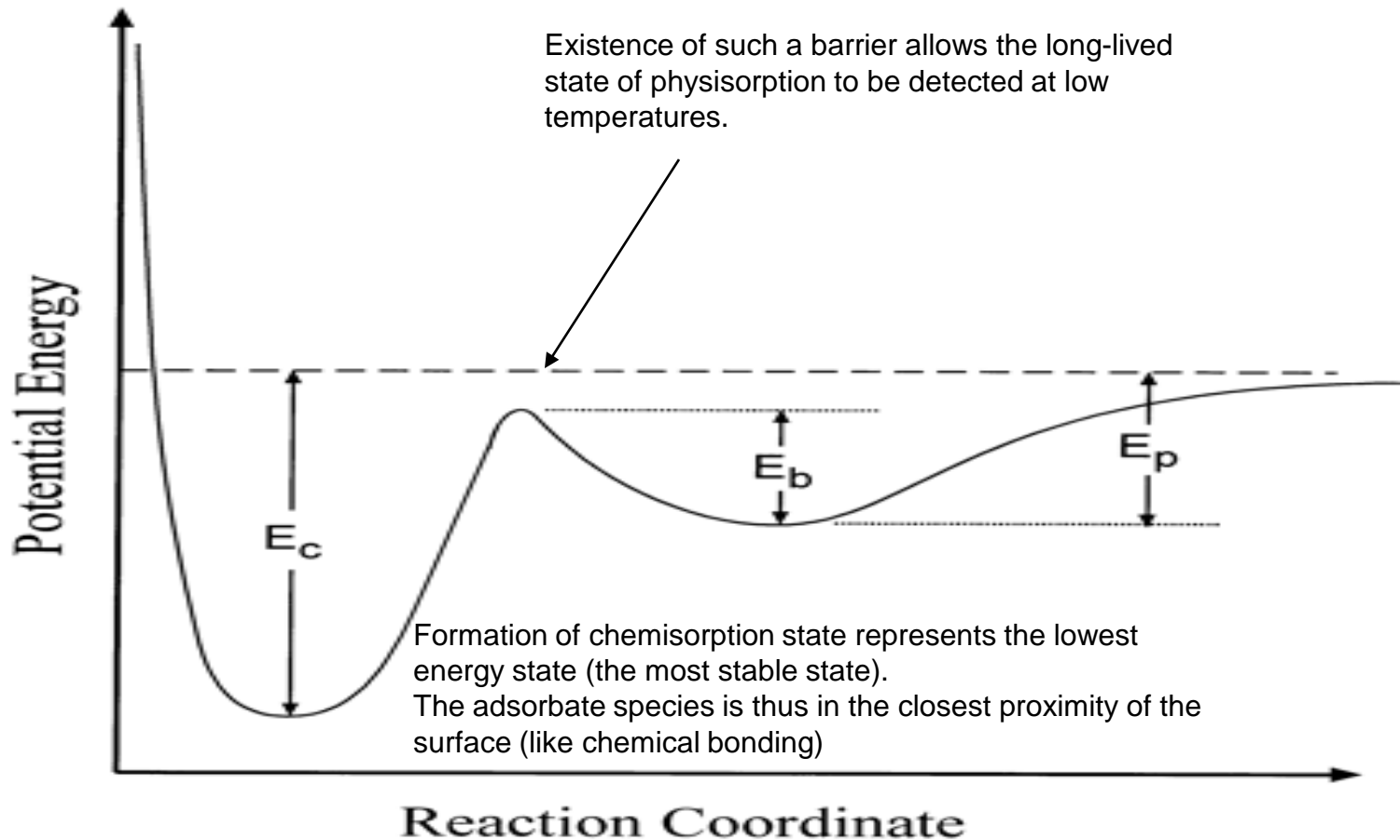
Schematic potential energy diagram describing precursor-mediated adsorption. E_p and E_c are the well depths for physisorption and chemisorption, respectively. E_b is the barrier controlling precursor decay to chemisorption.

STM image of single crystal surface of silicon, 7x7 unit cell in diamond shape (12 adatoms in each cell)
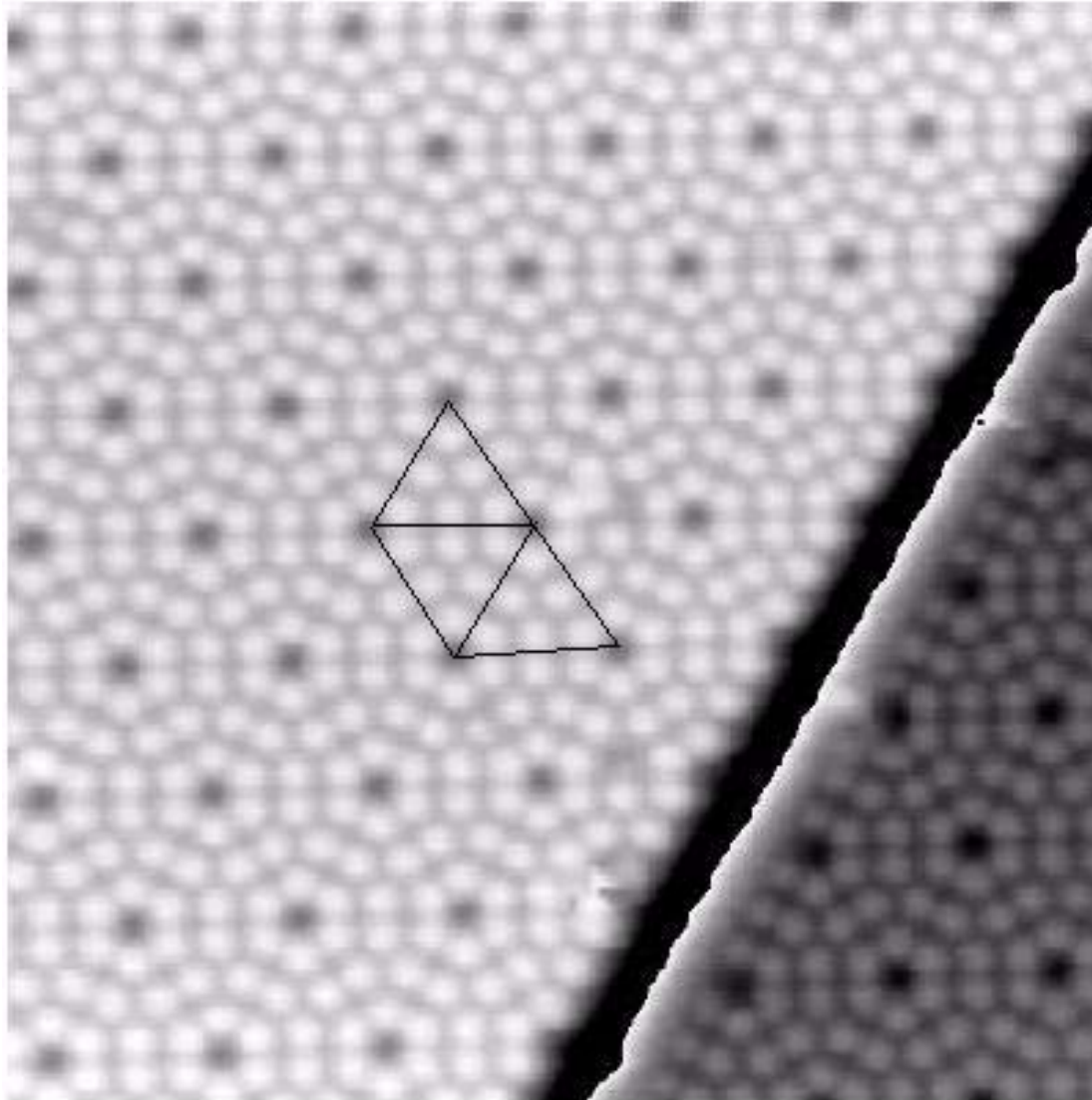
12 adatoms in each diamond shape (7×7) unit cell.

Raina N. Smith, Virginia Commonwealth University

STM image of single crystal surface of silicon, 7x7 unit cell

- One of the Si(111) reconstructions is the 7x7, as shown in *Figure 1*.

- This is the surface which forms when a commercial Si wafer is 'flashed' briefly up to ~1200°C.

- Added to this image is an outline of the <u>unit cell</u>, a diamond shape with seven atoms along each edge, for two different orientations.

- The unit cell is repeated throughout the surface to form the 2-D lattice.

- Note that there is both a long axis and a short axis in the unit cell. The length of the unit cell edge is known as the lattice parameter **a**, and is a defining property of the surface.

Chemisorption at higher T

Physisorption at lower T
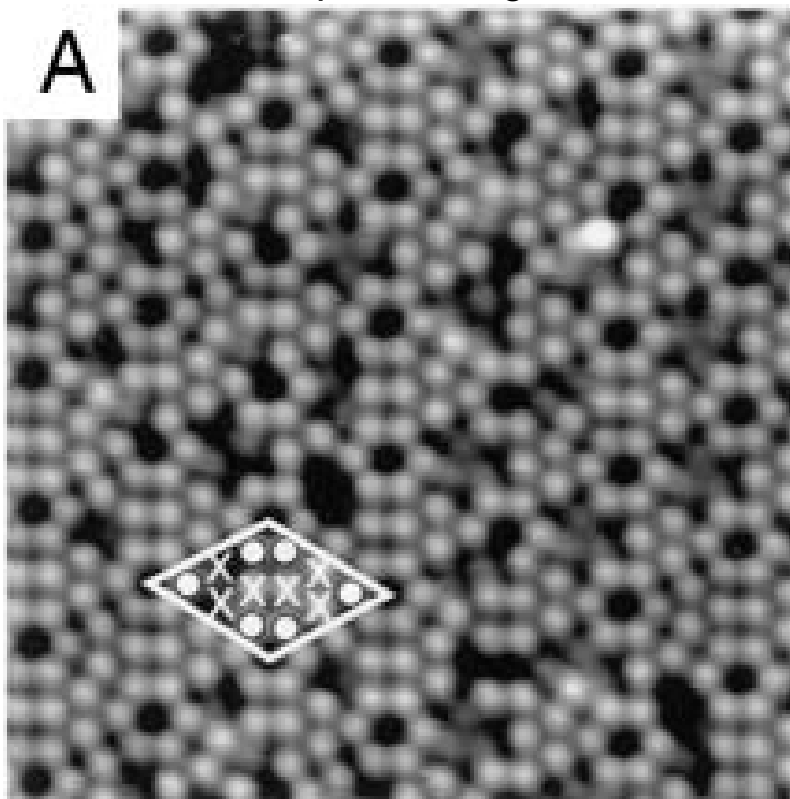
STM image recorded at 120 K of benzene adsorbed on Si(111)-7×7 at a coverage of ~0.2 monolayer. The **white** protrusions are **silicon** adatoms; **darkened** adatom sites have **benzene** molecules chemisorbed. The white diamond shape marks a single 7×7 unit cell. In the absence of benzene, each unit cell would exhibit 12 adatoms: the six center adatoms marked with X's, and the six corner adatoms marked with white circles.

STM image of benzene on Si(111)-7×7 at 78 K at a coverage of ~0.5 monolayer. The precursors appear as protrusions positioned over the center adatoms.

Vsample = +1.5 V, current = 0.1 nA, 140 × 140 Å.

Tuning adsorption property with temperature

- Chemisorption at 120 K --- Benzene molecules are seen as darkened sites, consistent with a chemisorbed state.

- Physisorption at 78 K --- Strikingly different images result when the experiment is carried out with a surface maintained at 78 K. Adsorbed benzene molecules now appear as prominent protrusions.

- Because this state is only observed at low temperature, it is identified as the physisorbed state indicated in thermal desorption measurements. ***Although observation of a physisorbed state is not in itself remarkable, this particular physisorbed state is remarkable in that the molecules exist spatially over a site where relatively strong chemical adsorption can (and <u>in time will</u>) occur***.

- By changing only the substrate temperature, a different adsorbed molecular state has been prepared. This state is an intrinsic precursor to chemisorption.

Decay of the precursor state at 95 K
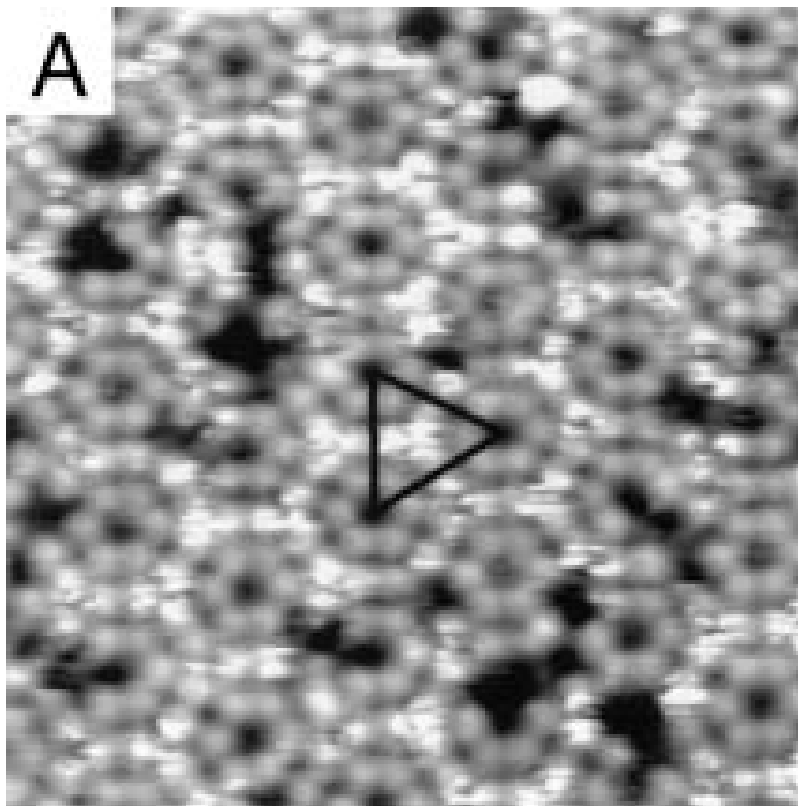
Immediately after preparing the precursor state using the tip electric field.
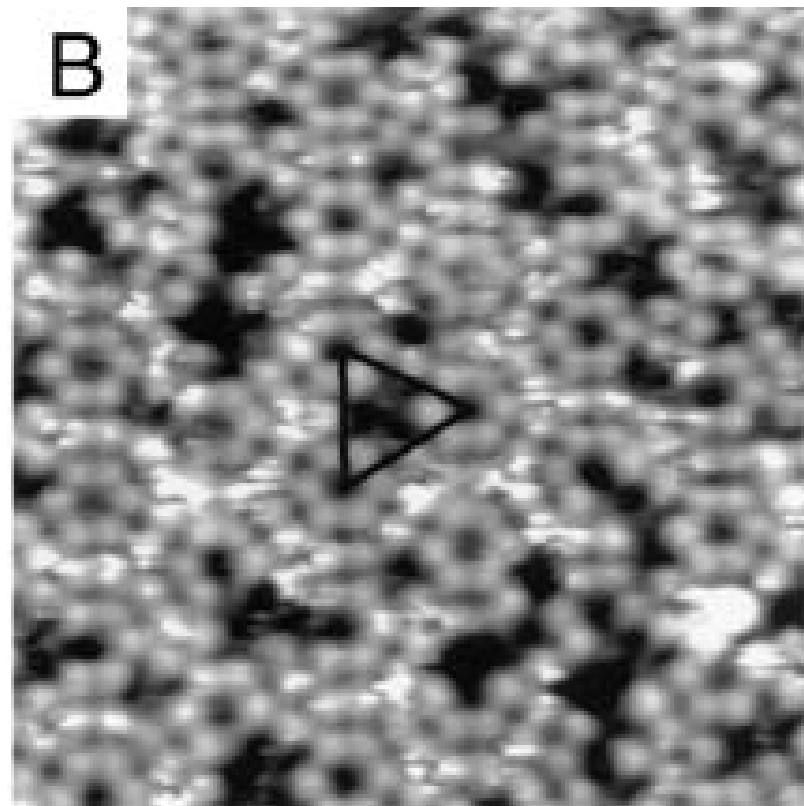
After 7 min, a reduction in the number of precursor molecules is observed.

The triangular region marks one area where precursor decay to the chemisorbed state has occurred. Careful inspection reveals numerous other examples.
Vsample = +1.5 V, current = 0.1 nA, 140 × 140 Å.

Decay of the precursor state at 95 K

- To better study the kinetics of precursor decay, an electric field effect was used to prepare the precursor state at will.
- The electric field in the immediate vicinity of the STM tip can be used to place molecules in the precursor state by **dislodging** chemisorbed molecules.
- Scanning conditions may be set either for **imaging**, with virtually no disruption of the molecule-surface complex, or for **dislodging** of the chemisorbed molecules within the vicinity of the tip (typically -3 V sample bias, 0.1 nA).
- Chemisorbed benzene molecules can be dislodged at *any of the temperatures* studied. From room temperature down to ~150 K, molecules disrupted in this way cannot be observed as they move laterally or desorb from the surface. However, below ~100 K, the benzene molecules are trapped long enough to be visible with the STM.
- Precursor molecules were prepared using the above method, at a substrate temperature of 95 K. Through a time sequence of images, the kinetics of the decay to the precursor state have been monitored.
- The first image in the sequence is shown in the left of the figure.
- The image recorded ~7 min later (right of the figure) reveals that some benzene molecules have converted back to the dark-appearing chemisorbed state.

Statistics of Decay of the precursor state at 95 K
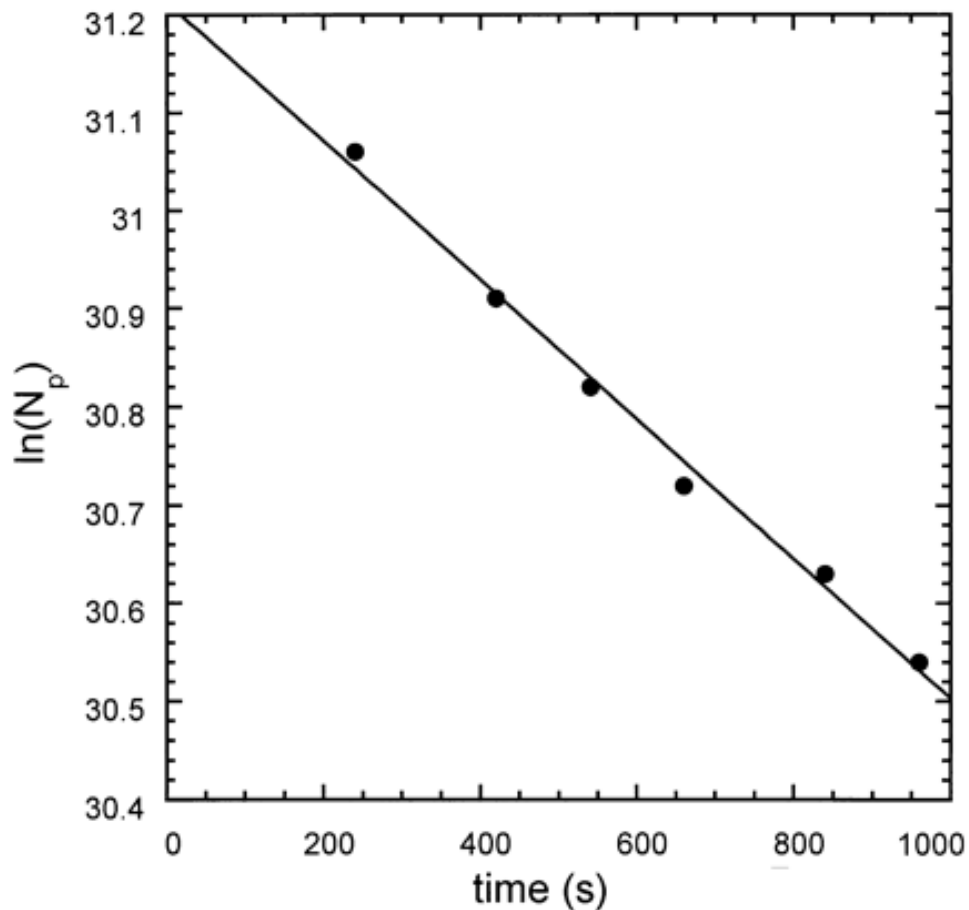
Plot showing the decrease in the number of benzene molecules in the precursor state with time. N_p is the number of precursor molecules per square centimeter. Analysis of the data yields $E_b = 0.30 \pm 0.03$ eV.

Statistics of Decay of the precursor state at 95 K

- The rate of change in the number of precursor molecules can be expressed as

$$dN_p/dt = -\upsilon N_p \exp(-E_b/kT_s),$$

  where N_p is the coverage of precursor molecules, υ is the preexponential, T_s is the substrate temperature, and E_b is the barrier to chemisorption from the precursor state.

- From the measured change in precursor coverage with time from successive images at 95 K and assuming a preexponential of 10^{13} s-1, an activation barrier of $E_b = 0.30 \pm 0.03$ eV can be deduced.

Self-directed growth of molecular nanostructures on silicon

- Advances in techniques for the nanoscale manipulation of matter are important for miniaturization of molecule-based devices with new or advanced functions.

- A particularly promising approach involves the construction of hybrid organic-molecule/silicon devices.

- But challenges remain—both in the formation of nanostructures that will constitute the active parts of future devices, and in the construction of commensurately small connecting wires.

- Atom-by-atom crafting of structures with scanning tunnelling microscopes, although essential to fundamental advances, is too slow for any practical fabrication process;

- self-assembly approaches may permit rapid fabrication, but lack the ability to control growth location and shape. Furthermore, molecular diffusion on silicon is greatly inhibited, thereby presenting a problem for self-assembly techniques.

- Here, a combined techniques involving STM and self-directed assembly, where STM helps the positioning the self-growth.
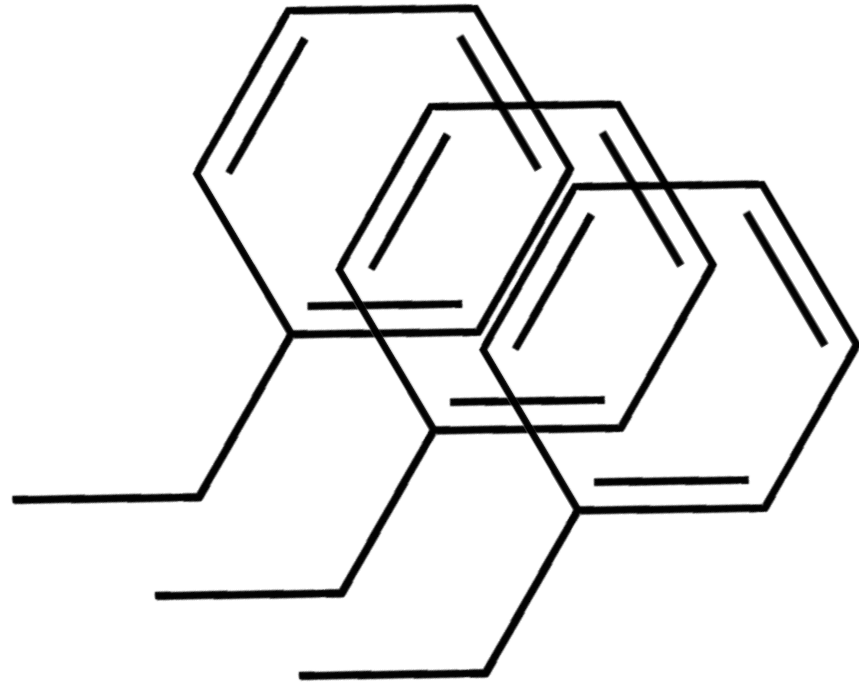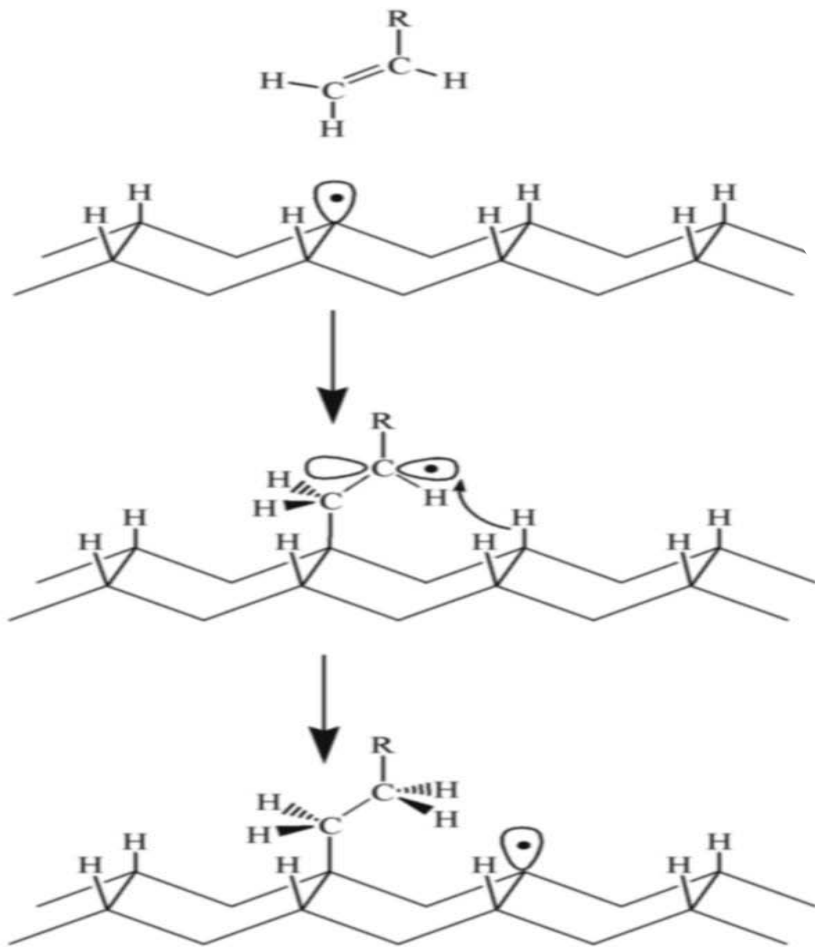
Proposed chain reaction mechanism for self-directed growth of molecular nanostructures on silicon.

# Self-growth initiated by a [2+2] cycloaddition

- On a clean Si(100) surface, an alkene reacts with the dangling bonds of a Si dimer to form two Si–C bonds, in a process analogous to a [2+2] cycloaddition.

- An alkene to react with only one Si dangling bond on an otherwise hydrogen-terminated surface. Initially, the C–C -bond opens to form one Si–C bond and one C radical, as shown schematically in the figure.

- If subsequently a hydrogen atom is abstracted from a neighbouring surface site to satisfy the radical, a new Si dangling bond—and the possibility for a chain reaction—is created.

- Such a mechanism has been suggested to account for alkene reactions with H-terminated Si(111) under liquid-phase reaction conditions.

- On H-terminated Si(111), which presents a <u>hexagonal</u> array of sites, the chain reaction is expected to lead to irregular islands of adsorbed molecules.

- On the anisotropic Si(100) surface, a directional preference associated with the H-abstraction step may be expected, directing the growth of <u>one-dimensional lines</u>.
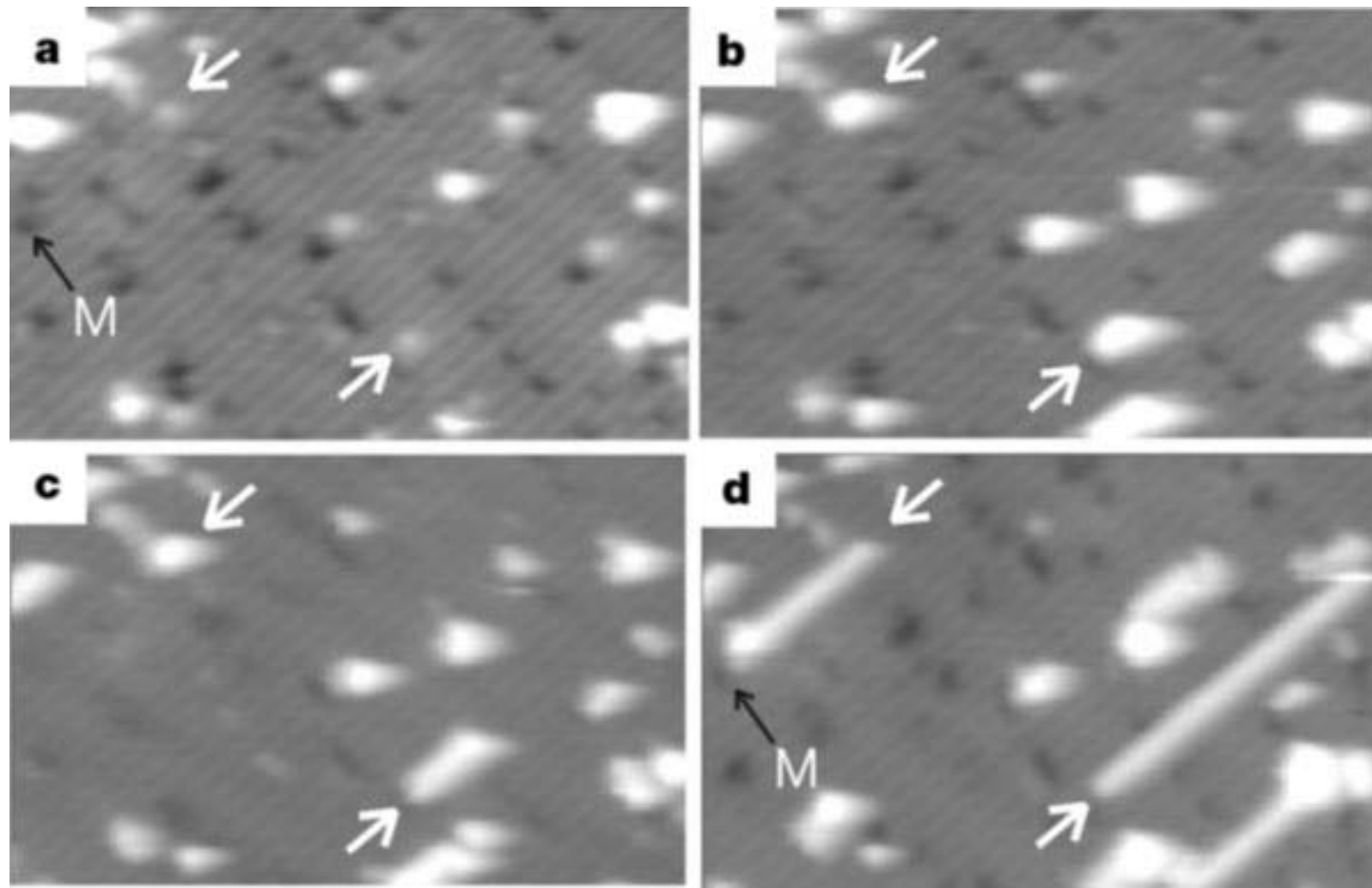
a) Single Si dangling bonds were created with the tip of STM.

b-d) Growth of styrene lines on a H-terminated Si(100) surface with a dilute concentration of single Si dangling bonds.

Structure of styrene lines: *atomic control of molecular assembly!*
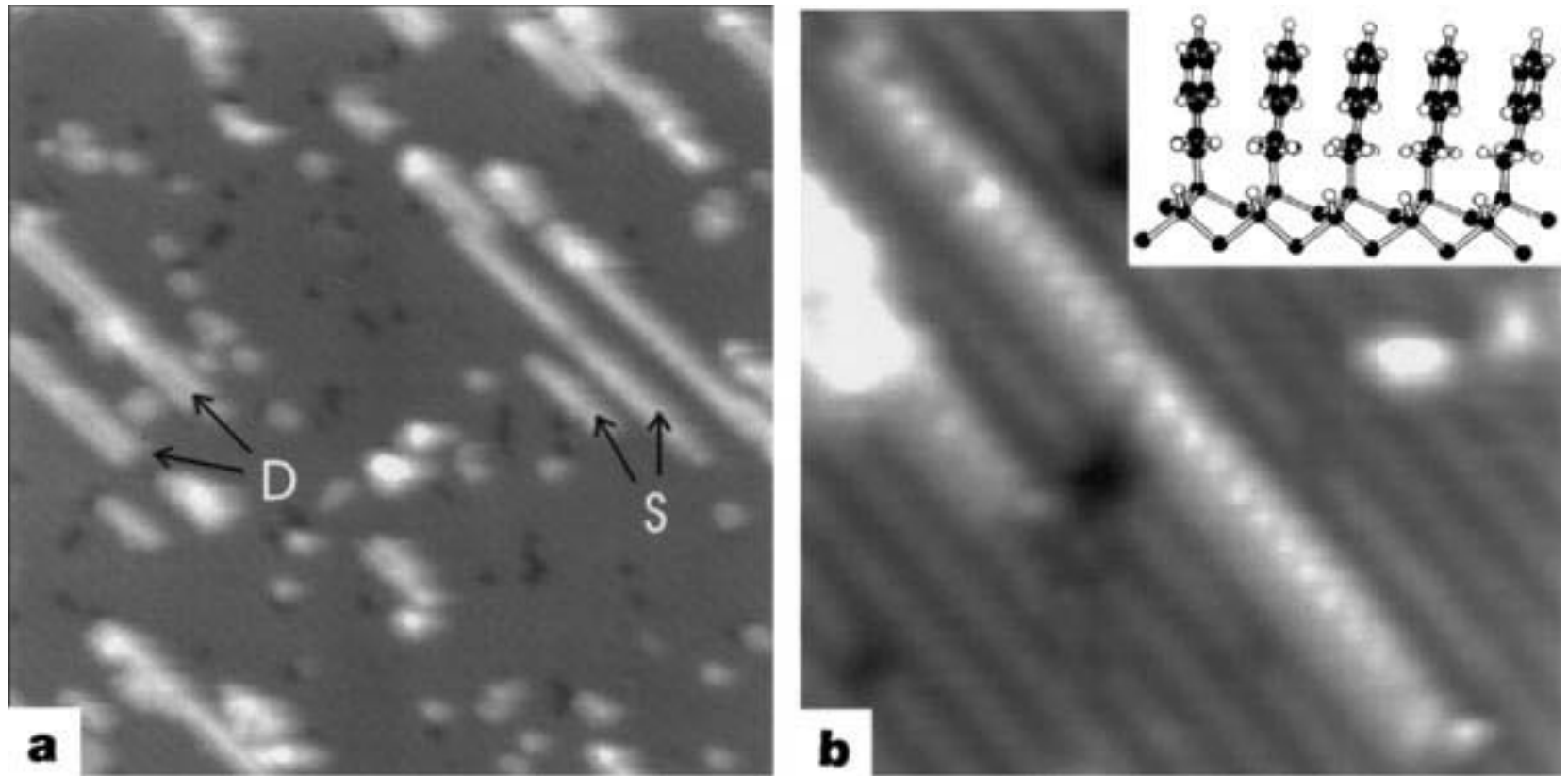
Part II:
Molecular Self-assembly: *significance and implications*

- Self-assembling: under appropriate conditions (temperature, solvent, pH, concentration, etc.), highly organized/ordered structures (1D, 2D, 3D) are formed spontaneously from individually molecules.

- Significance of studying self-assembly: help understanding the fundamental processes in nature and then improve the manmade devices which in many cases are mimicking the natural systems, like photosynthesis → solar energy utilization (e.g., light conversion to fuels) beyond photovoltaics; emitting insects (fire fly) → LED.

- Direction of self-assembly: controlled by template (like substrate crystal lattice, DNA for 1D, edge-transfer lithography for 1D).

- Dimensionality (or orientation) of self-assembly (0D, 1D, 2D, 3D): controlled by 1). Non-covalent molecular interactions (e.g., H-bonding, hydrophobic interaction, metal coordination), which in turn are dictated by molecular structures (side chains, backbones, etc.); 2). substrate morphology or crystal lattice to lead to surface directed assembly (e.g., DNA template, soft stamping lithography); 3). fabrication processing (e.g., order of deposition in subliming methods, annealing temperature and time, laser).

- Typical examples of self-assembly in nature: cell membrane (bilipid layer, draw on board), DNA (slide), leaf structure (slide), photosynthetic system (slide).

Vast majority of the real-world materials composes of molecules, not neutral atoms.

Molecular assembly → organization → functions.

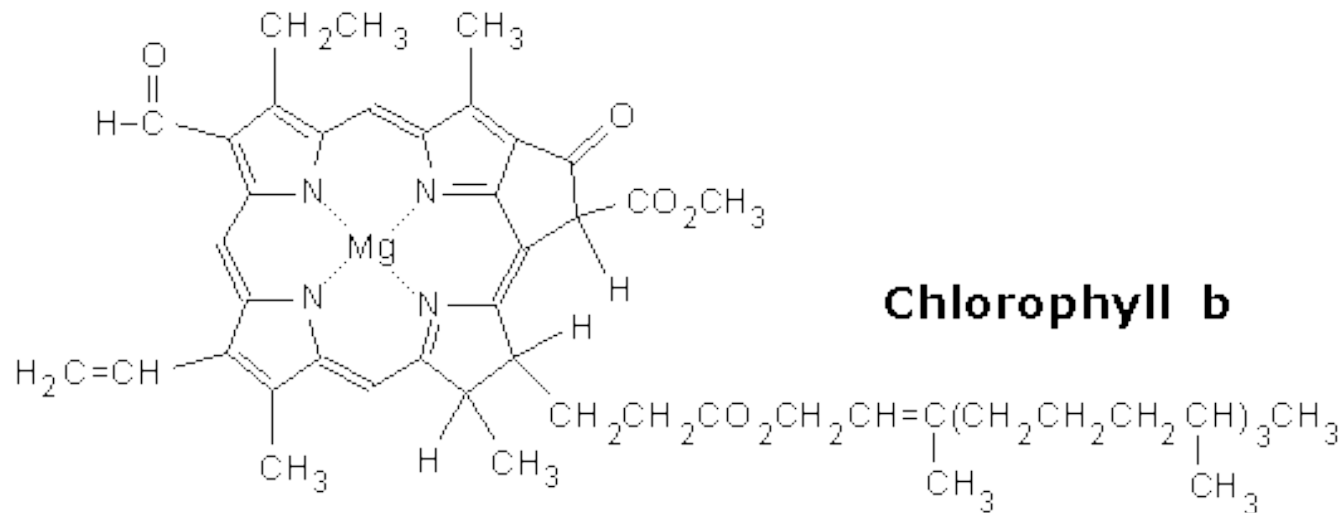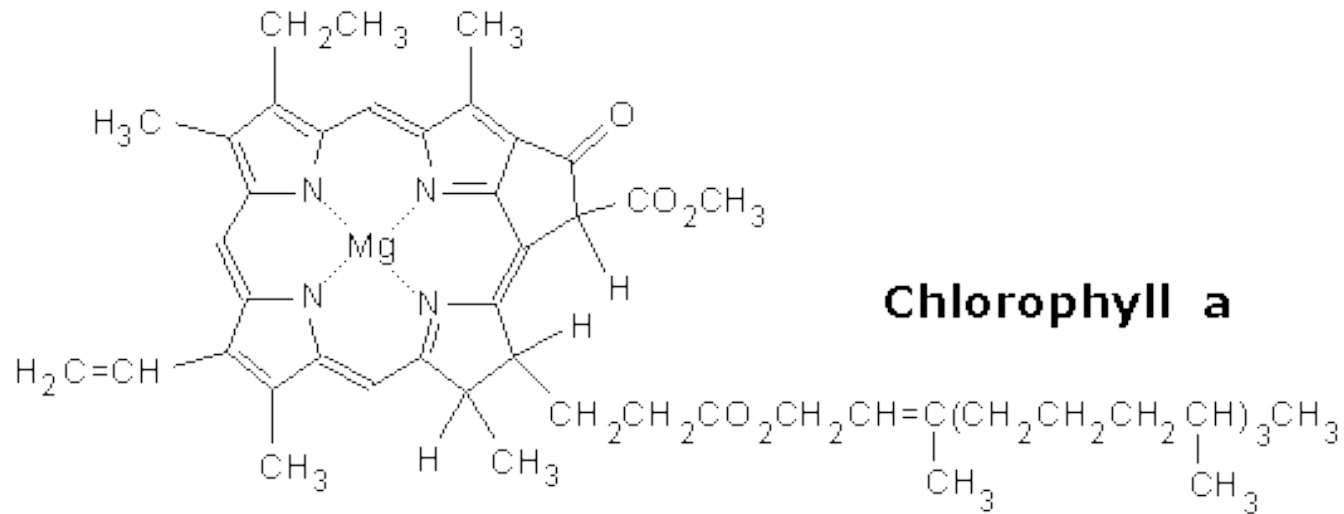# Growth of green plant: *self-assembly driven by photosynthesis …*

Growing amazingly fast under light and water …

Photosynthesis Center: *perfect intermolecular alignment for highly efficient conversion of absorbed light into charges and chemicals*
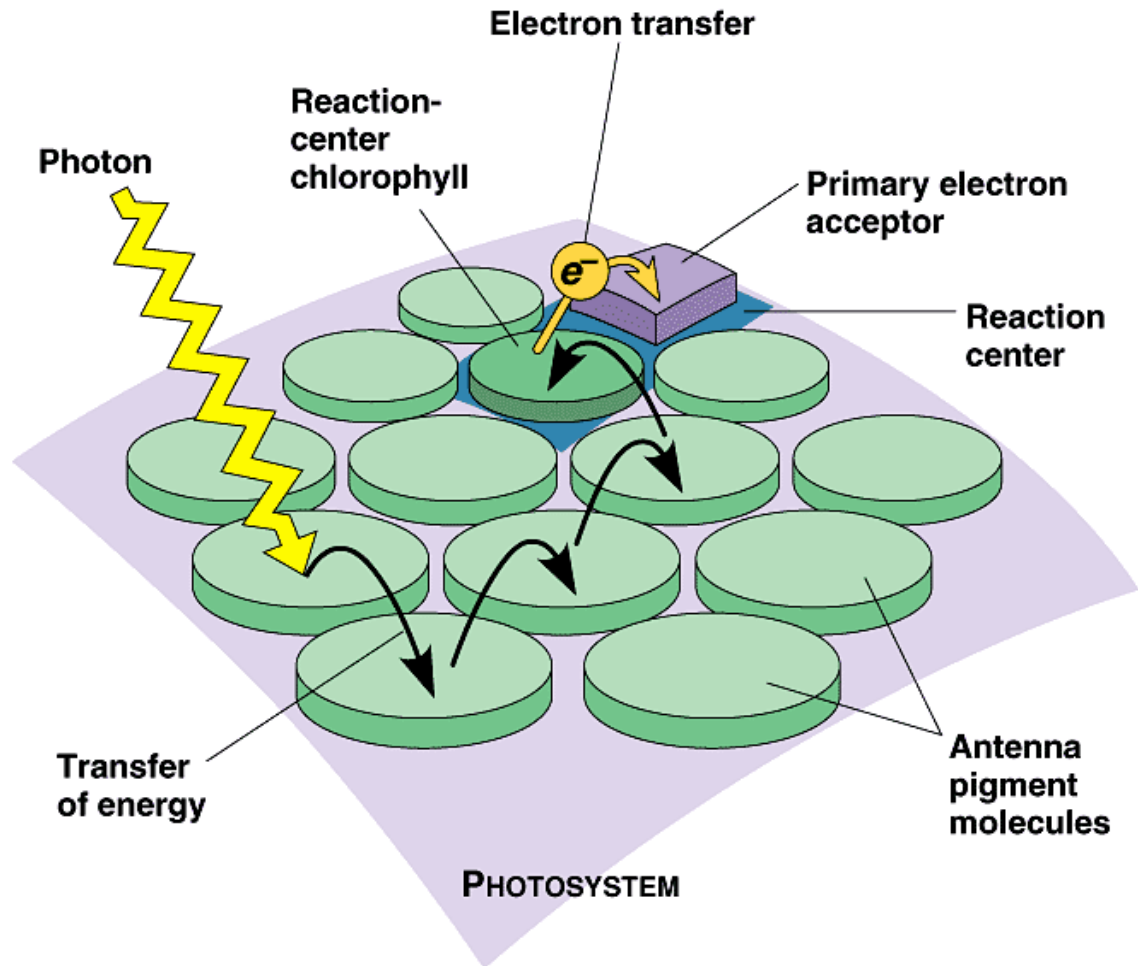
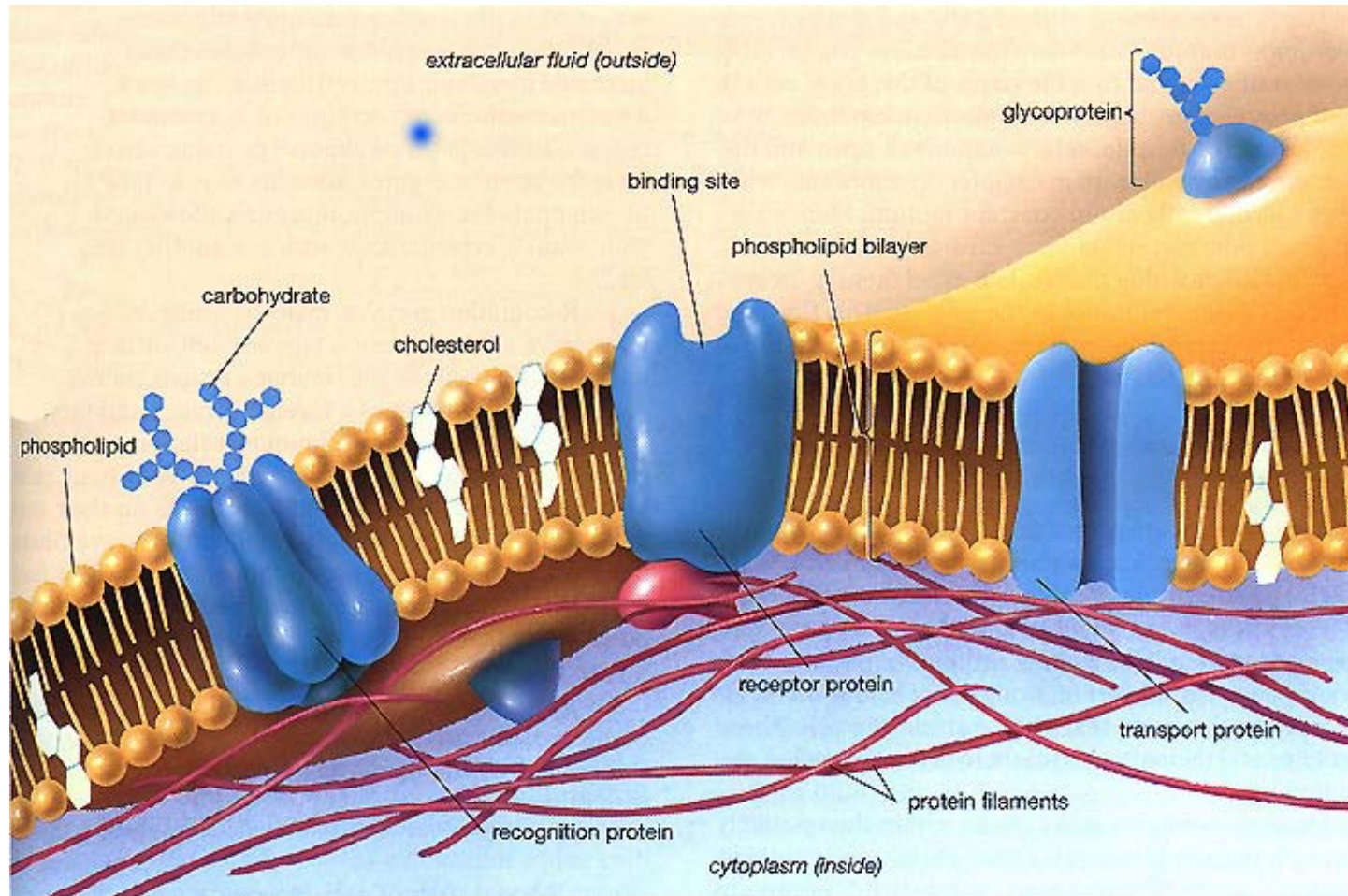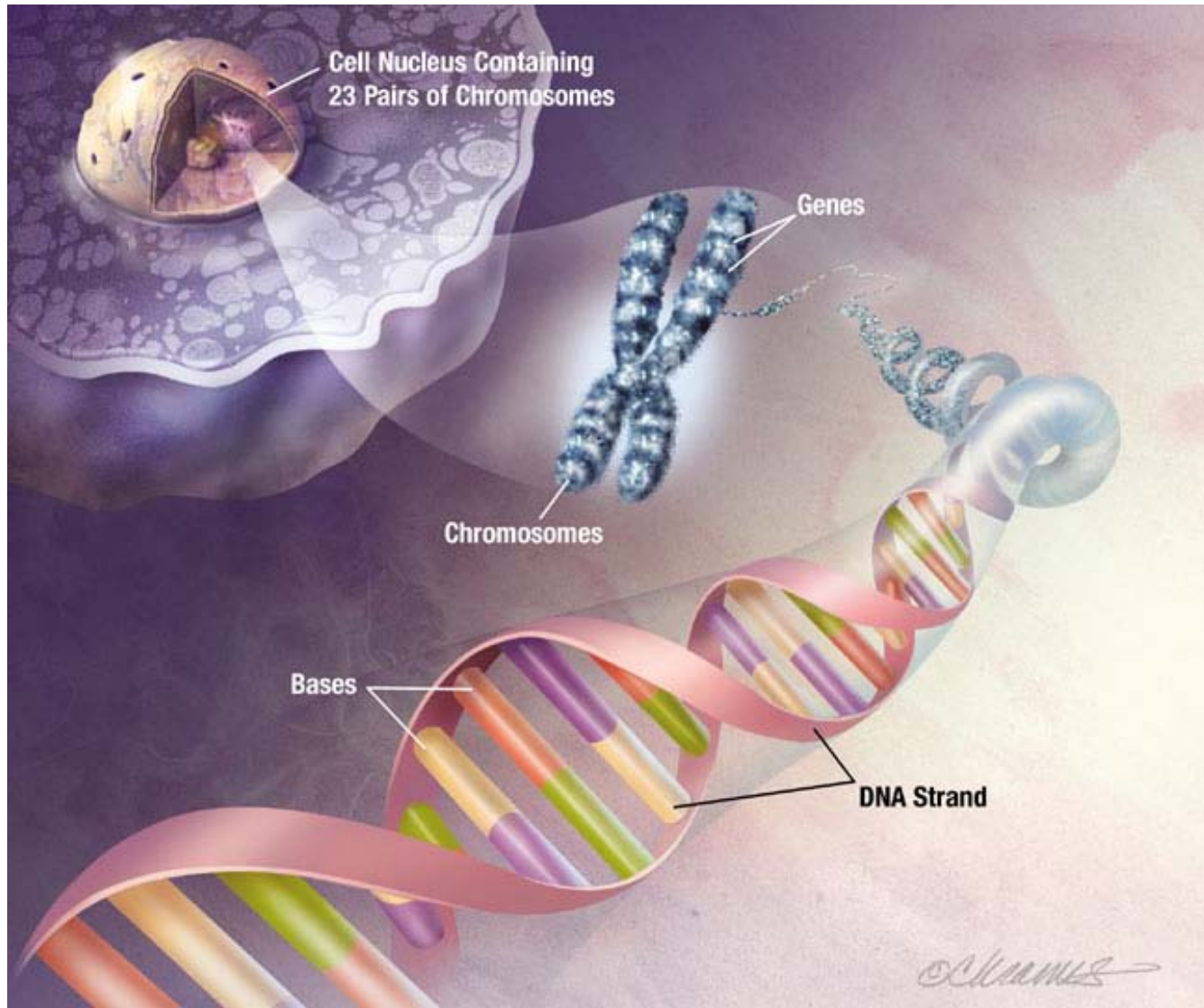**Two chromophores involved in photosynthesis for absorbing sun light**

Chlorophyll a

Chlorophyll b

Fire fly
--- as high as 88% efficient production of light.

Copyright 2003 D. L. Pietryka

Photo: James Sternburg

Cell Membranes

DNA, Chromosomes, and Genes: The Body's Amazing Control Center

Coast redwood: *the highest tree, 115.55 m (379.1 ft),*

The Structure of a Leaf

PLASTIDS
The colors in leaves are contained in tiny structures within the cells called plastids. Plastids with green chlorophyll are called chloroplasts, those with yellow and orange colors are called chromoplasts.

Leaf surfaces are coated with a WAXY CUTICLE to prevent water loss.

The EPIDERMIS is a layer of specialized flattened cells which appear on all plant surfaces.

PALISADE PARENCHYMA cells are rich in chloroplasts and are a primary site of photosynthesis in the leaf.

The SPONGY MESOPHYLL cells are also photosynthetic, and the large spaces between the cells allow diffusion of carbon dioxide.

STOMA
Openings in the leaf called stomata are controlled by doors called guard cells. Stomata permit the exchange of moisture and carbon dioxide between the leaf and atmosphere.

XYLEM and PHLOEM
Xylem transports water and minerals from roots while phloem moves the products of photosynthesis throughout the tree.

Molecular interactions in Self-assembly:

☐ $\pi-\pi$ stacking: between aromatic molecules, particularly for the large platelet shape, like in photosynthetic system, the porphyrin.

• Hydrogen bonding: between molecules or the side chains, like DNA.

• Hydrophobic interaction: between long alkyl chains, like bilipids.

• Metal-coordination: highly selective and strong.

• Template assembling on surface: thiols on gold following the gold lattice.

These might be somehow beyond the scope of this lecture, but helpful for understanding the crucial role of STM in studying the intermolecular interaction in self-assembling.

An efficient solar cell made of discotic molecules

hexabenzocoronene

p-channel

n-channel

e⁻

h⁺

nano-coaxial cable

ITO Glass

Metal Coating

R = visible chromophore

Nanotube & Core
p-surrounding-n
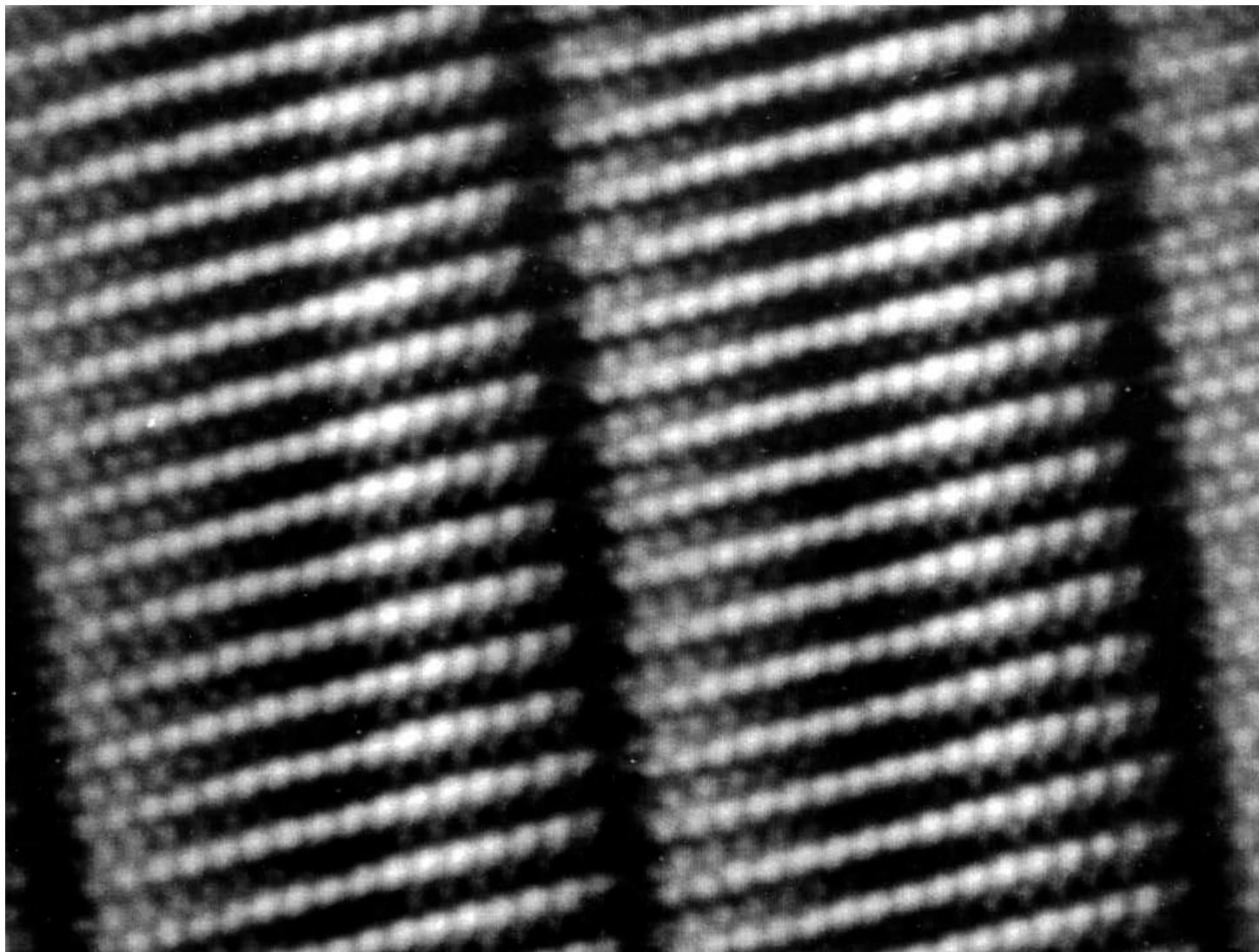
R =

Hub & Spoke
n-surrounding-p
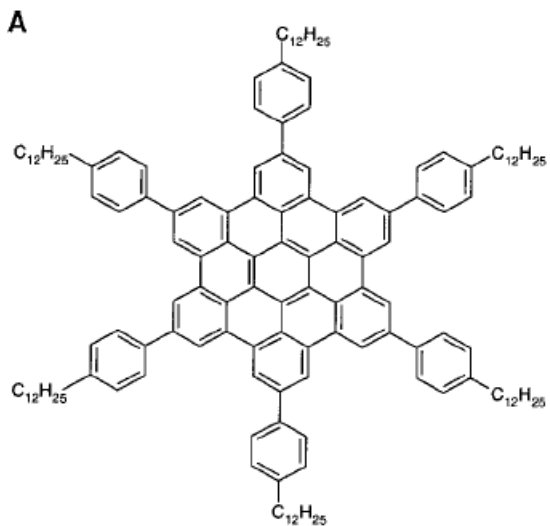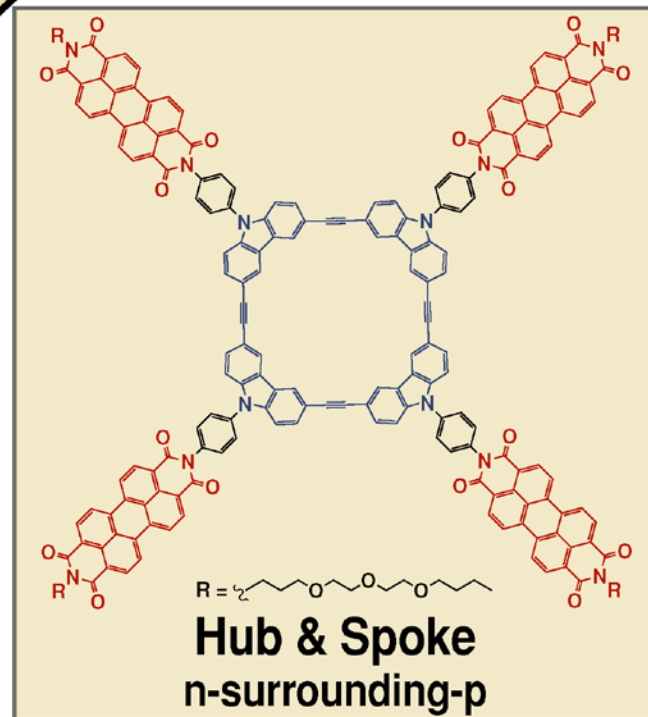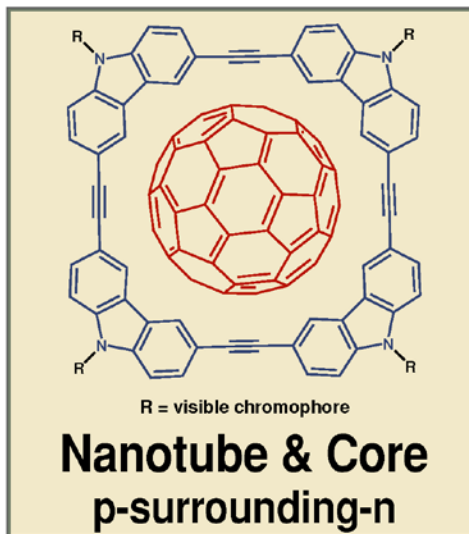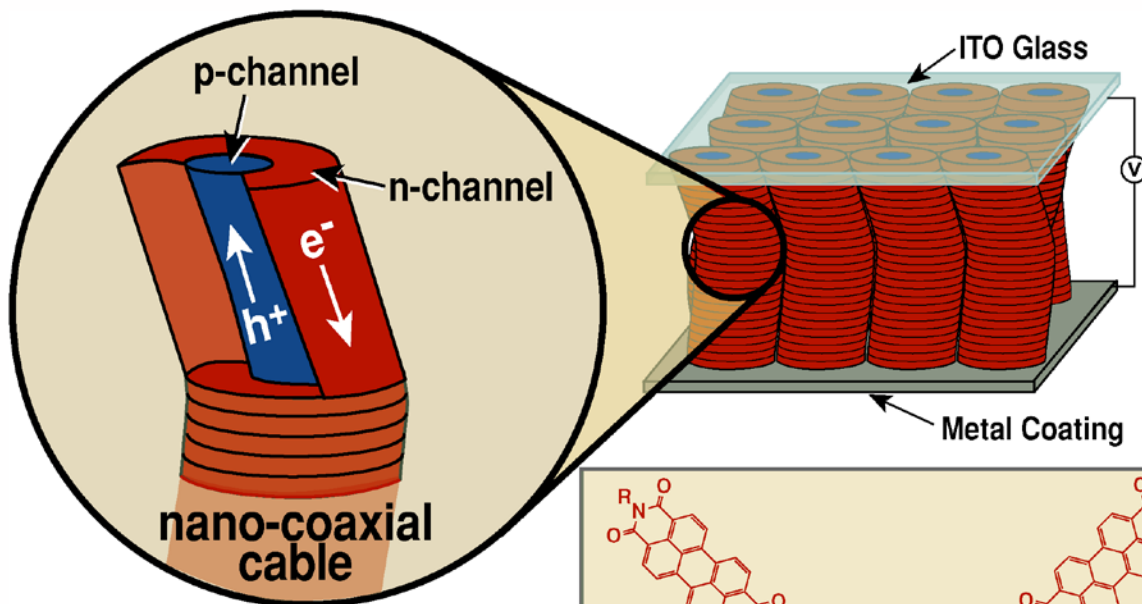
Nanotubes formed from LCD discotic molecules
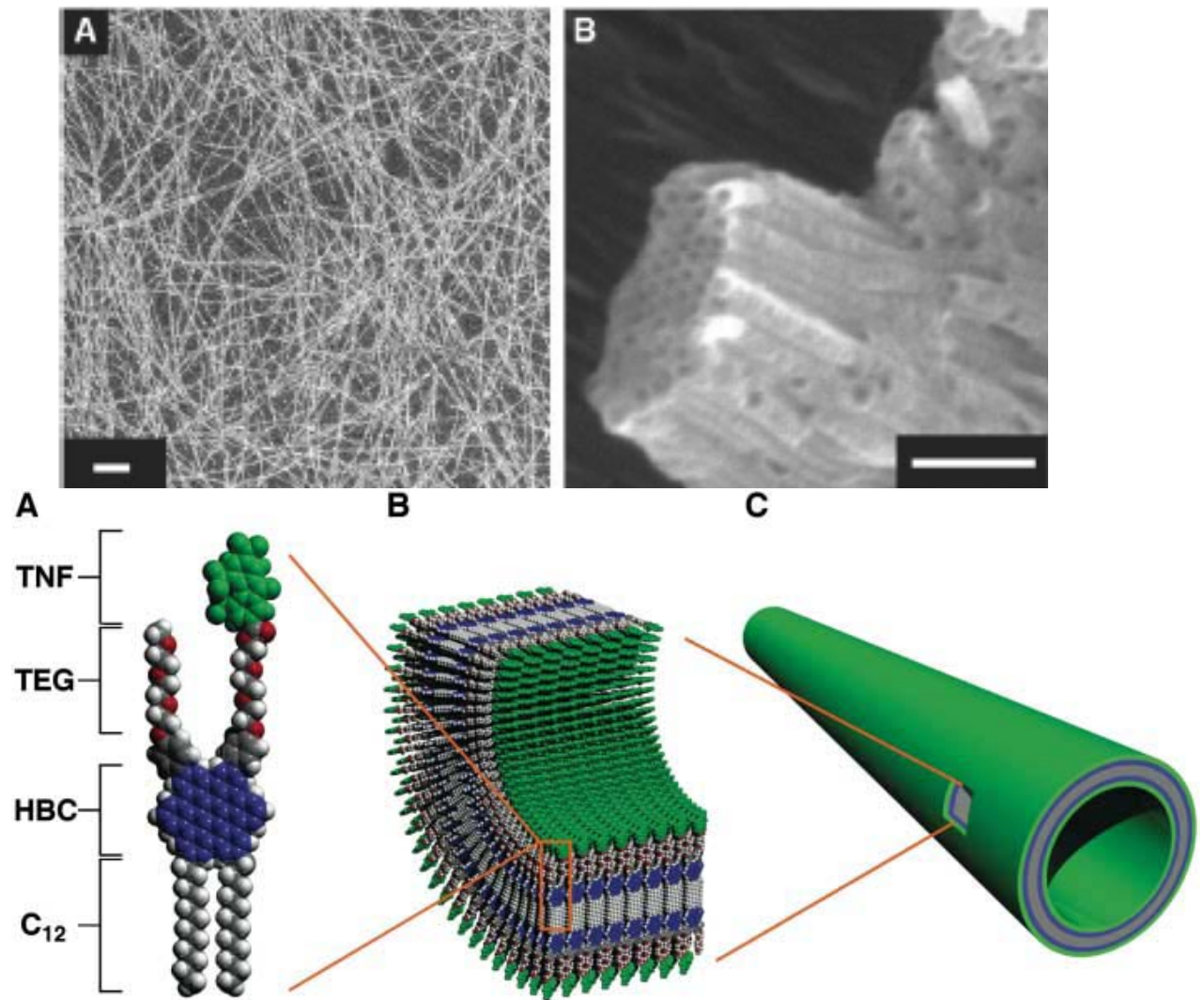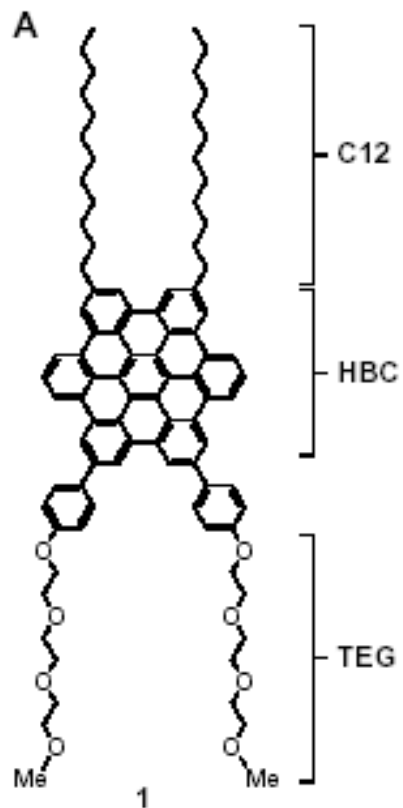
Nanoribbon self-assembly enhanced by H-bonding
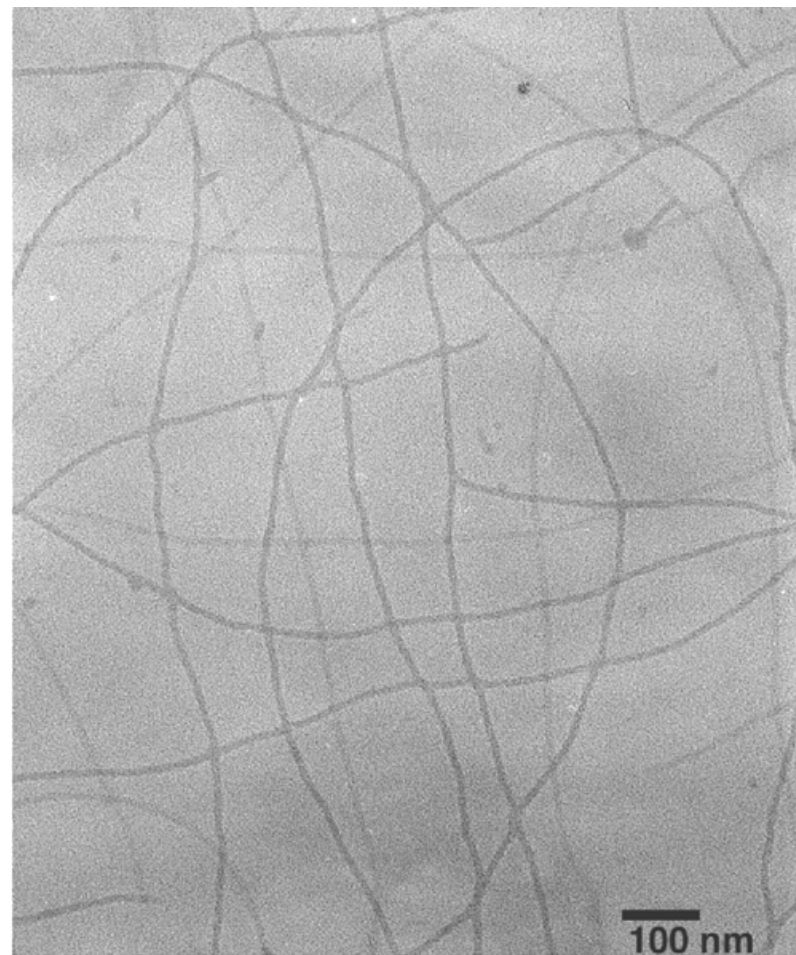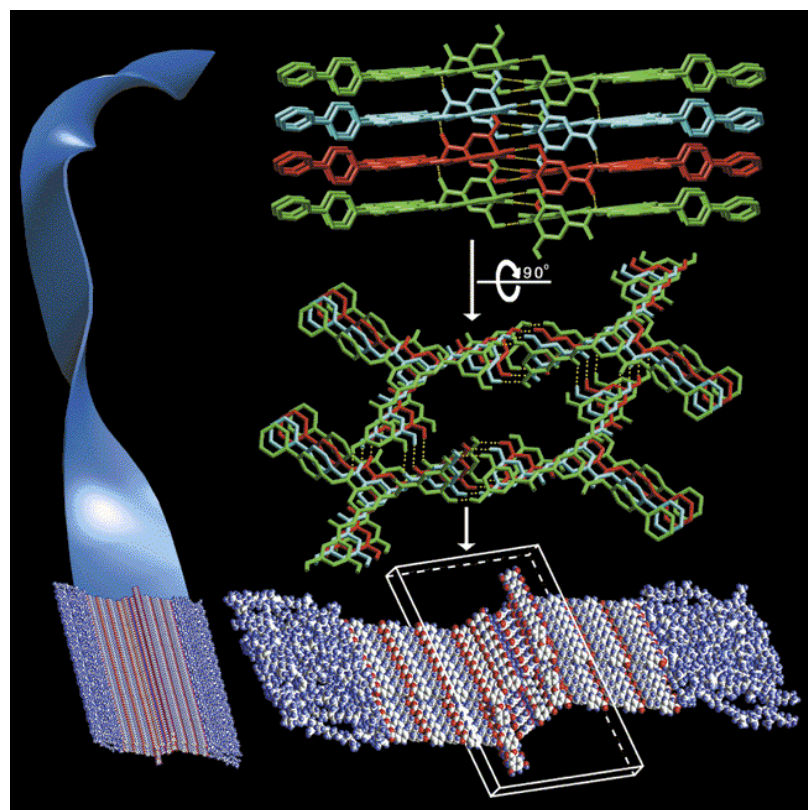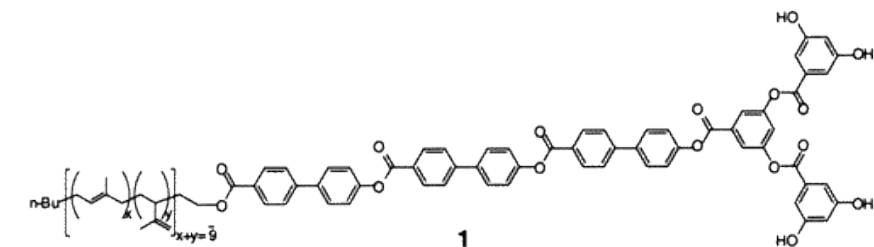
Sam Stupp et al. *J. Am. Chem. Soc.,* **123** (17), 4105-4106, 2001.
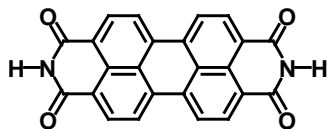
STM Image of n-C32H66 absorbed on graphite (McGonigal)

$CH_3(CH_2)_{30}CH_3$
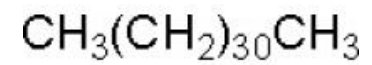
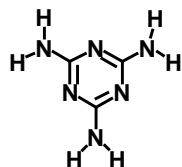# Controlling molecular deposition and layer structure with supramolecular surface assemblies

JAMES A. THEOBALD[1], NEIL S. OXTOBY[2], MICHAEL A. PHILLIPS[1], NEIL R. CHAMPNESS[2] & PETER H. BETON[1]
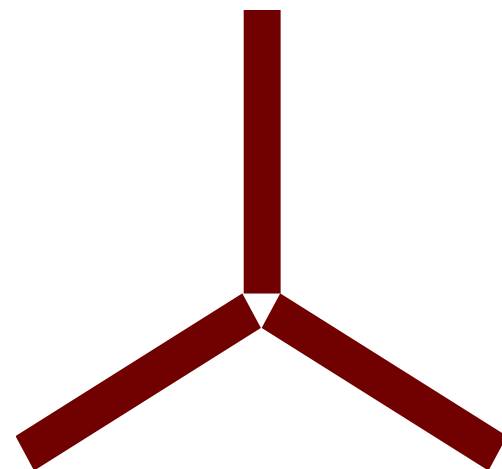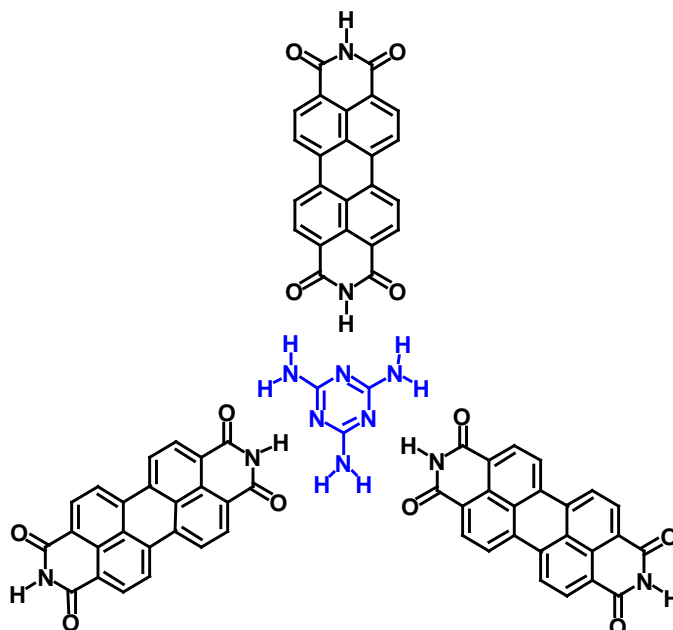
[1] School of Physics and Astronomy,
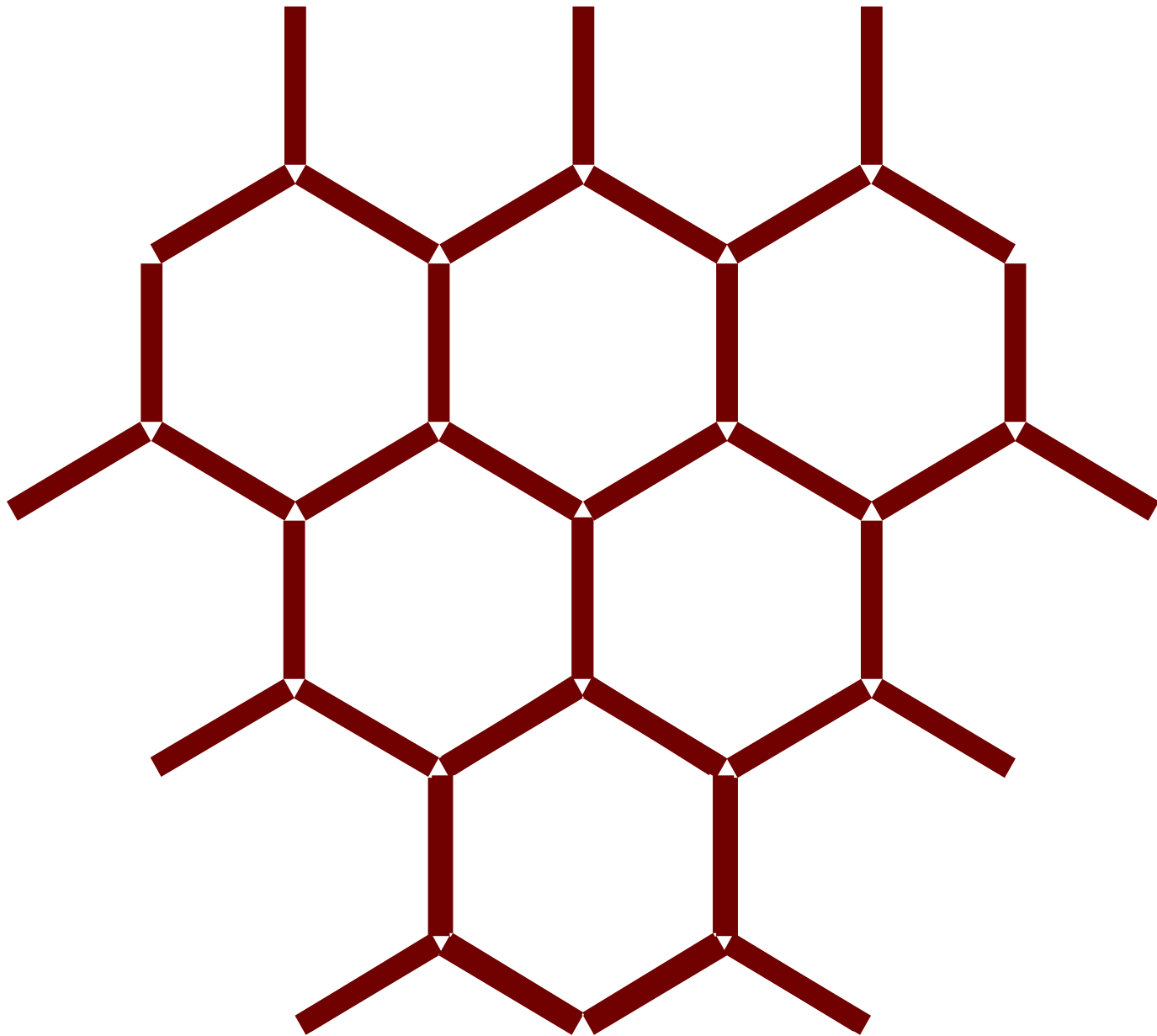[2] School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK
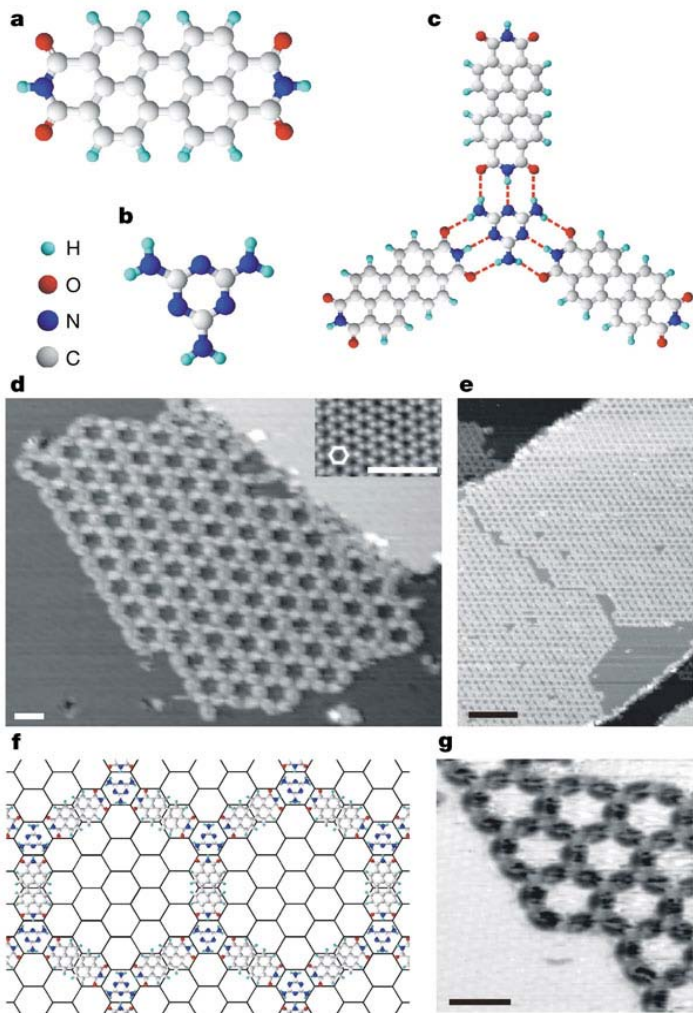
PTCDI

Melamine

Molecular Lego → 2D assembly

- An open honeycomb network was formed when perylene tetra-carboxylic di-imide (PTCDI) is co-adsorbed with melamine (1,3,5-triazine-2,4,6-triamine) on a silver-terminated silicon surface.

- Melamine, which has a three-fold symmetry, forms the vertices of the network while the straight edges correspond to PTCDI.

- The network is stabilized by melamine–PTCDI hydrogen bonding.

- Melamine and PTCDI were chosen for this application because they are expected to exhibit much stronger hetero- as opposed to homo-molecular hydrogen bonding. The compatibility of molecular geometries results in <u>three</u> hydrogen bonds per melamine–PTCDI pair, as compared with just <u>two</u> for a PTCDI or melamine pair --- *leading to high selectivity/favorability for the desired dimensional structure --- a smart molecular design!*

- A combined approach: using hydrogen bonding to guide the assembly of two types of molecules into a two-dimensional open honeycomb network, which then controls and templates new surface phases formed by subsequently deposited fullerene (C60) molecules.

- The open network acts as a two-dimensional array of large pores of sufficient capacity to accommodate several large guest molecules, with the network itself also serving as a template for the formation of a fullerene layer.

Self-assembly of a PTCDI–melamine supramolecular network

Chemical structure of PTCDI (a) and melamine (b).

Schematic diagram of a PTCDI–melamine junction (c).

d, STM image of a PTCDI–melamine network. <u>Inset, high-resolution view of the Ag/Si(111) substrate surface.</u> the vertices and centres of hexagons correspond, respectively, to the bright (Ag trimers) and dark (Si trimers) topographic features in the STM image (surface lattice constant, $a0 = 6.65$ Å). Scale bars, 3 nm.

e, STM image of large-area network, with domains extending across terraces on the Ag/Si(111) surface. Scale bar, 20 nm.

sample voltage -2 V, tunnel current 0.1 nA.

f, Schematic diagram showing the registry of the network with the surface.

g, Inverted contrast image (- 2 V, 0.1 nA) of the network. Scale bar, 3 nm.

- The network is prepared under ultra-high vacuum (UHV) conditions (base pressure ,5x10^{-11} torr).
- PTCDI and melamine were placed in effusion cells and sublimed (by heating to ~360 ^{o}C and ~100 ^{o}C, respectively) onto a Ag/Si(111).
- The first step in the formation of the network is deposition of 0.1–0.3 monolayers (ML) of PTCDI onto a surface, on which the molecules can diffuse freely and then form close packed islands and short chains similar to those reported in previous studies.
- Melamine is then deposited while the sample is annealed at ~100 ^{o}C.
- The positions of the two molecules may be clearly discerned, with melamine and PTCDI forming respectively the <u>vertices and edges</u> of the network, which is stabilized by the hydrogen bonding illustrated in the figure.
- Annealing provides sufficient thermal energy for molecules to detach from PTCDI islands and diffuse across the surface. These PTCDI molecules interact with melamine to nucleate the hexagonal network, which then grows through further capture of diffusing molecules.
- If deposition of PTCDI is continued or restarted during formation of the network, the pores become 'filled' with other PTCDI molecules, presumably by their direct impinging on the pore area.
- Therefore, the open network may only be formed from PTCDI molecules released from pre-formed islands and thus constrained to two dimensional diffusion on the surface.
- The stepwise introduction of the two components is thus vital for the synthesis of the PTCDI–melamine network.

a

b
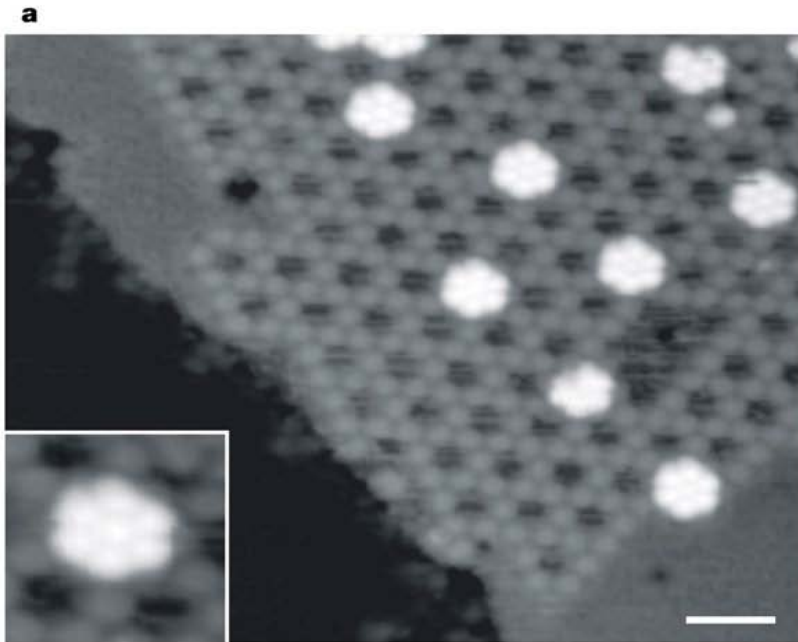
a, STM image (- 2 V, 0.1 nA) of C_{60} heptamers on a PTCDI–melamine network. Inset, high-resolution view showing an individual cluster. Scale bar, 5 nm.
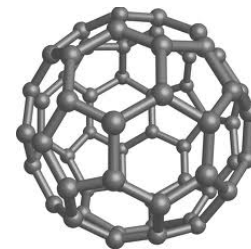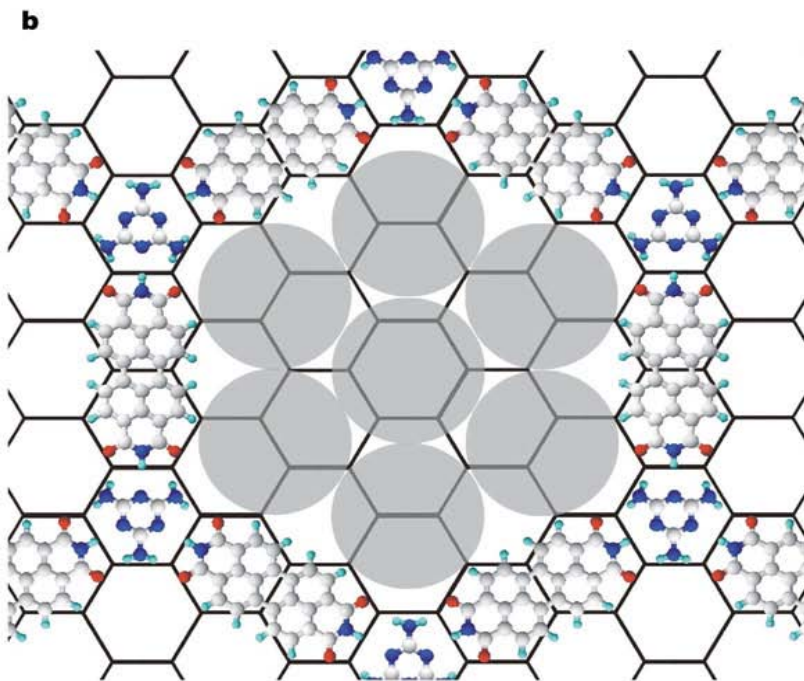
C_{60} : fullerene, often nicked "buckyball".

b, Schematic diagram of a C_{60} heptamer.

- The incorporation of linear PTCDI edge molecules into a bimolecular assembly yields pores that are much larger than the constituent building blocks of the network and thus capable of serving as traps, or vessels, for the co-location of several large molecules.
- The fraction of pores containing adsorbed molecules and stabilized heptameric clusters increases with increasing C60 coverage.
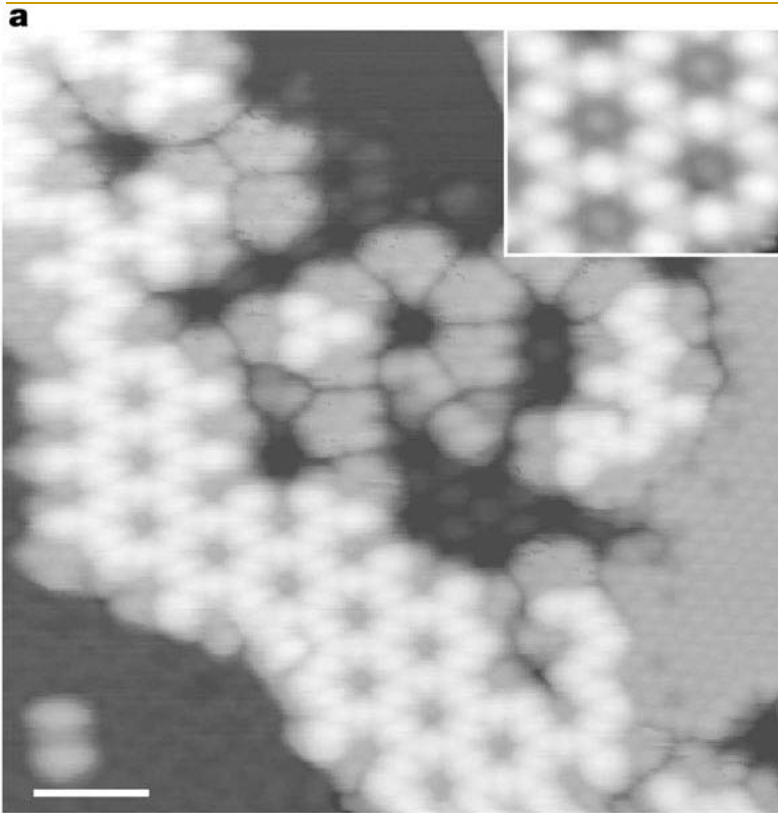
Images of the C60 honeycomb network formed by over-layering on the molecule framework.

a, Image showing the PTCDI–melamine lattice, C_{60} heptamers and the raised C_{60} honeycomb network (- 2 V, 0.1 nA). Scale bar, 5 nm. Inset, high-resolution view showing the C_{60} honeycomb network.

b, Schematic diagram showing the registry of the raised C_{60} network with the surface.

- The hexagonal network of C_{60} molecules, marked A and B, sit directly above the melamine and PTCDI, respectively.

- These molecules are raised with respect to the heptamers by 2.1 and 2.8 Å, respectively.

- The elevation of molecules A and B results in an increase in their separation from molecules at the heptamer edge (marked C) to 10.3 Å.
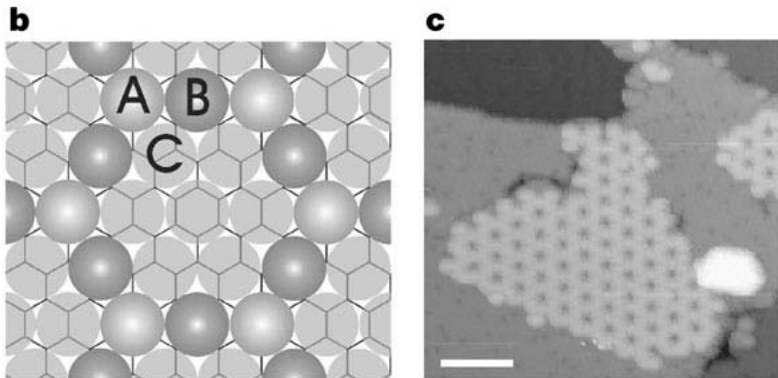
c, Low defect termination of a PTCDI–melamine lattice with C_{60} (- 2 V, 0.1 nA). Scale bar, 10 nm.

Understanding and tuning the epitaxy of large aromatic adsorbates by molecular design

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Why Epitaxy of surface assembly is crucial?

- Organic **epitaxy** — the growth of molecular films with a commensurate structural relationship to their crystalline substrates.

- Epitaxy relies on successful recognition of preferred epitaxial sites.

- Interface properties of organic materials with various (metallic and insulating) substrates must be tailored carefully, if the rich functionality of organic molecules is to be exploited in devices such as light-emitting diodes or field-effect transistors.

- In many cases, this calls for well-ordered interfaces. For some large conjugated (discotic) molecules ('molecular platelets') this works surprisingly well, even if the substrate exhibits no template structure into which the molecules can lock.

- Here, an explanation for site recognition in non-templated organic epitaxy, and thus resolve a long-standing puzzle.

- This form of site recognition relies on the existence of a local molecular reaction centre in the extended-electron system of the molecule.

- Its activity can be controlled by appropriate side groups and in a certain regime, may also be probed by molecularly sensitized STM.
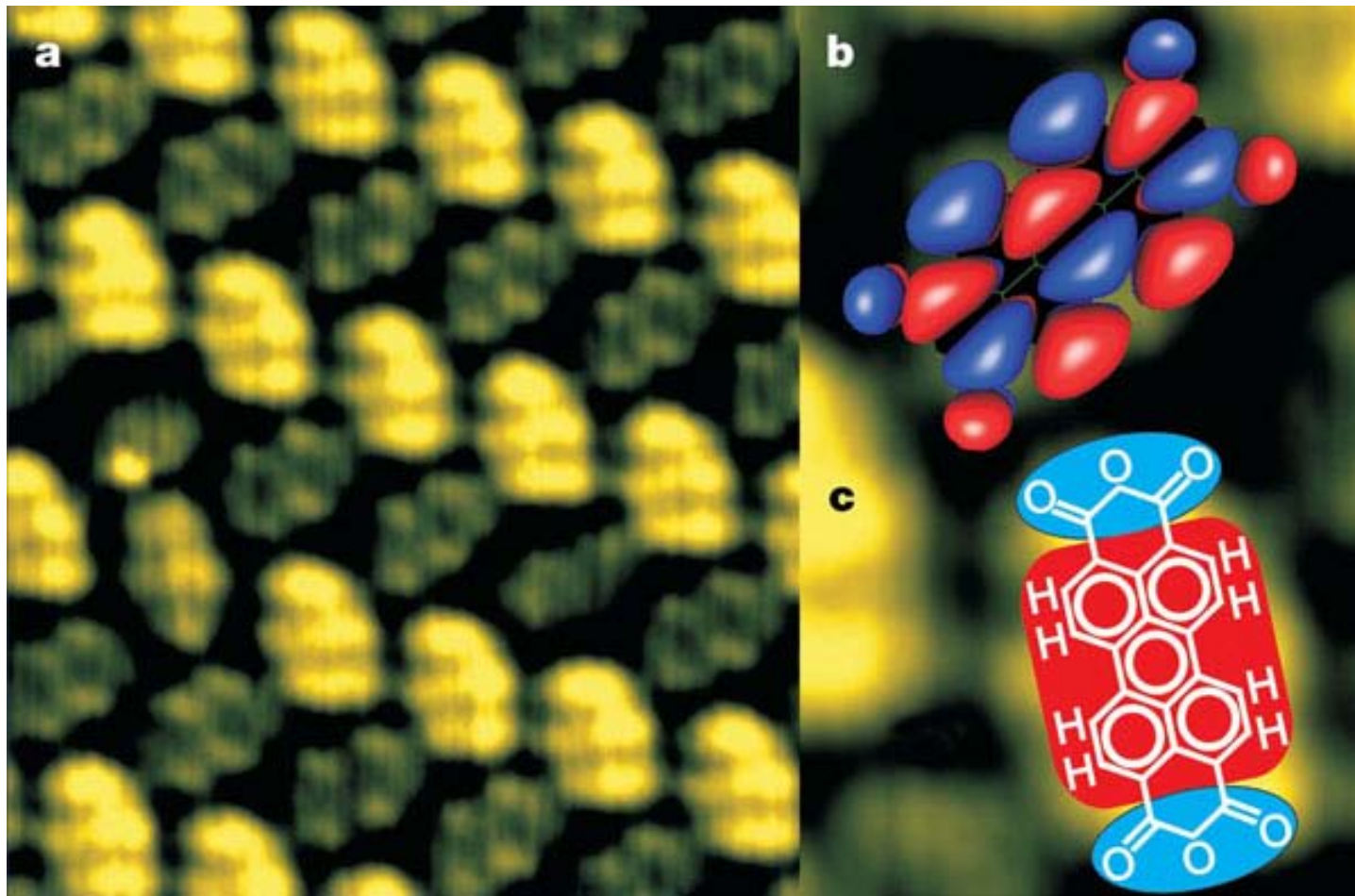
a, STM image of PTCDA 'herringbone' layer on Ag(111), image area 7X7 nm^2 (tunnelling parameters: I_T = 0.46 nA, U_S = -2.3 V).

b, Calculated probability density of the LUMO of PTCDA.

c, Chemical structure of PTCDA, with schematic indication of intramolecular charge distribution (red shows positive, and blue shows negative, partial charges).

- The case of 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA on Ag(111) is one of the most prominent examples of organic epitaxy.

- If PTCDA is deposited onto Ag(111) substrates by physical vapour deposition under ultrahigh vacuum, it forms almost perfectly ordered commensurate overlayers.

- The figure shows a STM image of such an epitaxial monolayer, exhibiting the characteristic 'herringbone' pattern known from the bulk crystal structure of PTCDA.

- This arrangement results from the minimization of electrostatic interaction energy originating in the quadrupolar field associated with the molecule --- kind of electron transfer interaction between molecule and surface.

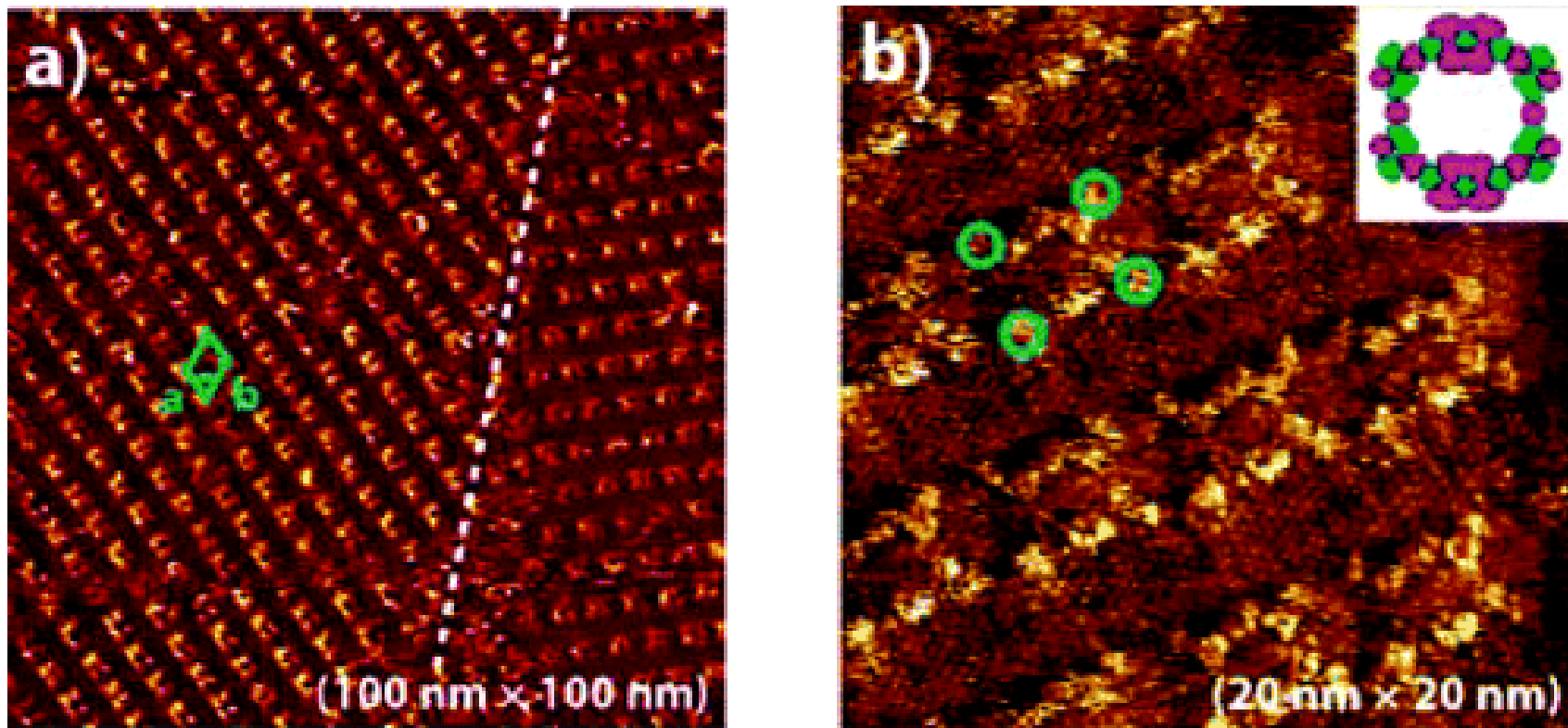- The similar inaction was found for perylene, the backbone molecule of PTCDA

2D Supramolecular Structures of a Shape-Persistent Macrocycle and Co-deposition with Fullerene on HOPG
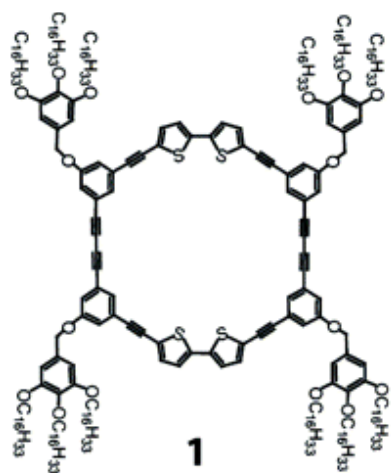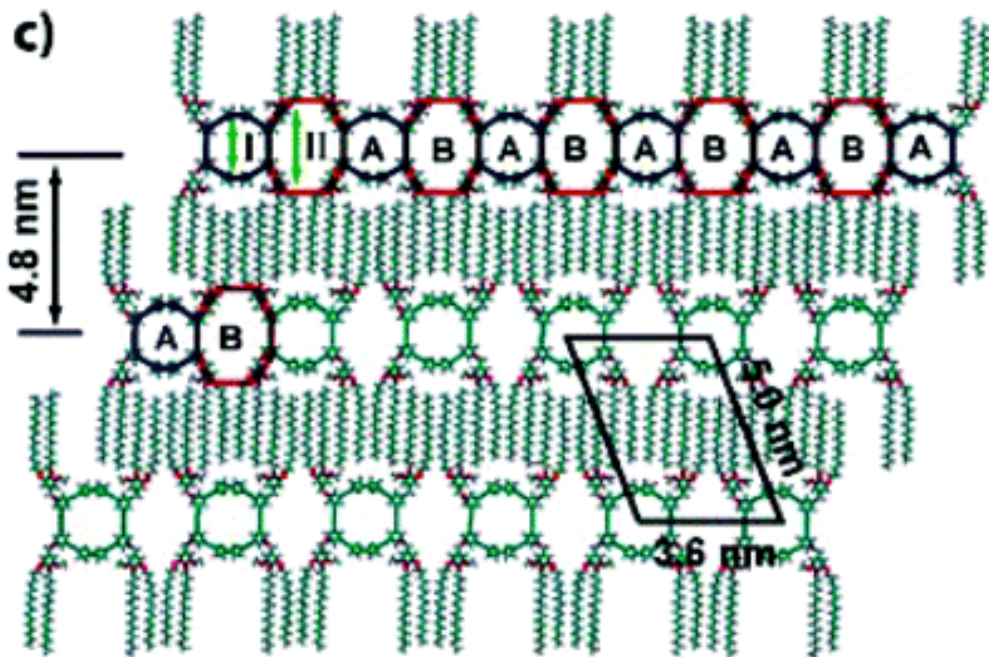
# 2D Supramolecular Structures of a Shape-Persistent Macrocycle and Co-deposition with Fullerene on HOPG

(a) Typical large-scale STM image. Vbias $= 0.35$ V; It $= 0.6$ nA. An oblique unit cell is indicated in green.

(b) (b) Higher resolution STM image. Vbias $= 0.41$ V; It $= 0.5$ nA. The four extraannular groups are indicated with green circles. The inset is the HOMO of the cyclic backbone of **1**.

Directed deposition of C60 on the supra-molecular layer
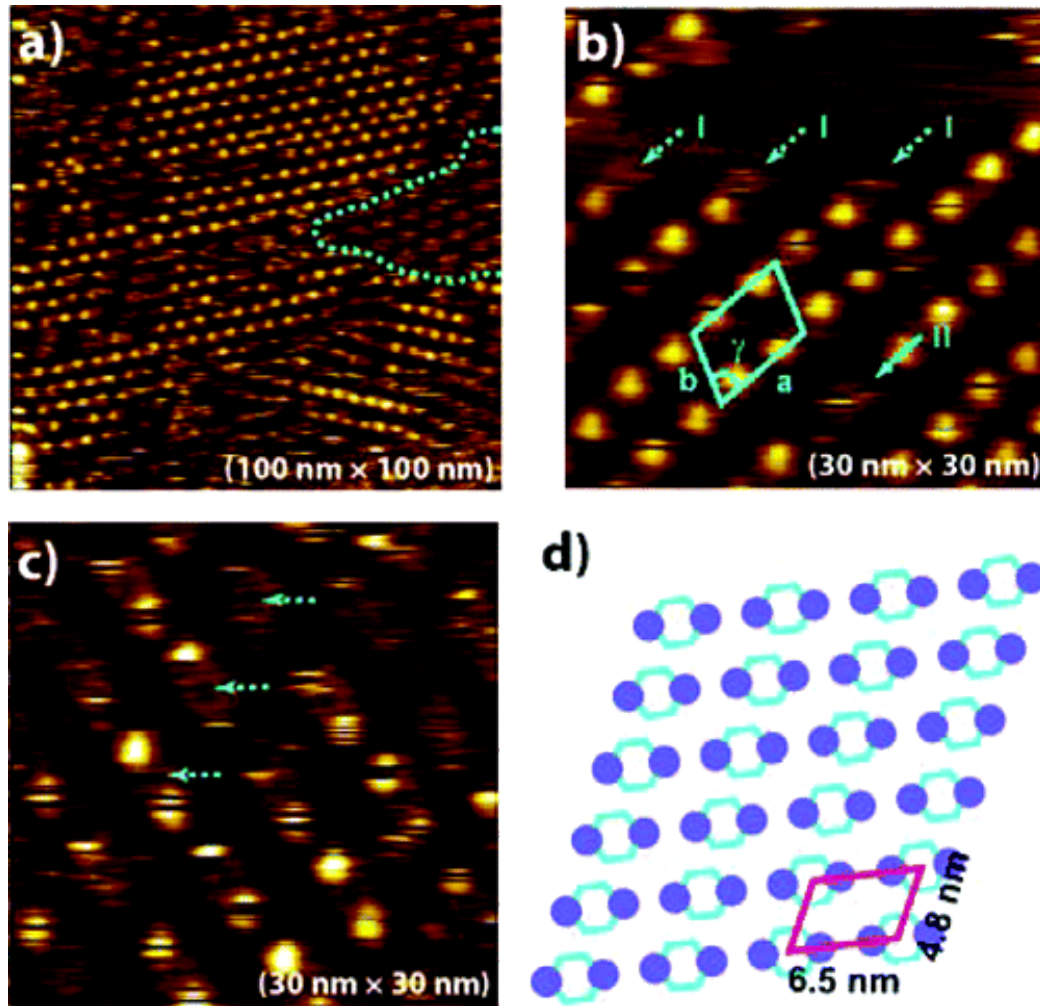
a) Typical large-scale STM image. V bias $= 0.8$ V; I t $= 0.3$ nA.

b, c) Higher resolution STM image, revealing the adsorption site of C60 on the macrocycle. V bias $= 1.0$ V; I t 0.3 nA. Arrows I and II indicate individual macrocycles.

d) Proposed structural model.