

## Lecture 11: AFM imaging of self-assembled nanostructures

- About self-assembly: free vs. templated self-assembly;
- DNA template self-assembly:
  - 1-dimensional DNA strands (2 papers);
  - 2-dimensional DNA grids.
- Self-assembly of polymers: *popular materials suited for large area processing, with applications in various electronic and optoelectronic devices.*

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## Self-assembly: *do the job by themselves*

- **Self-assembly:** a spontaneous, thermodynamically driven process that leads to formation of organized structure from the building-blocks, which can be molecules, atoms, or any appropriate species.
  - Self-assembly can be one-, two- or three-dimensional, forming nanoparticles, nanowires/nanorods, or cross-linked uniform structure.
  - Self-assembly is popular in Nature, and has been employed extensively in new materials design and development, along with the nanotechnology advances.
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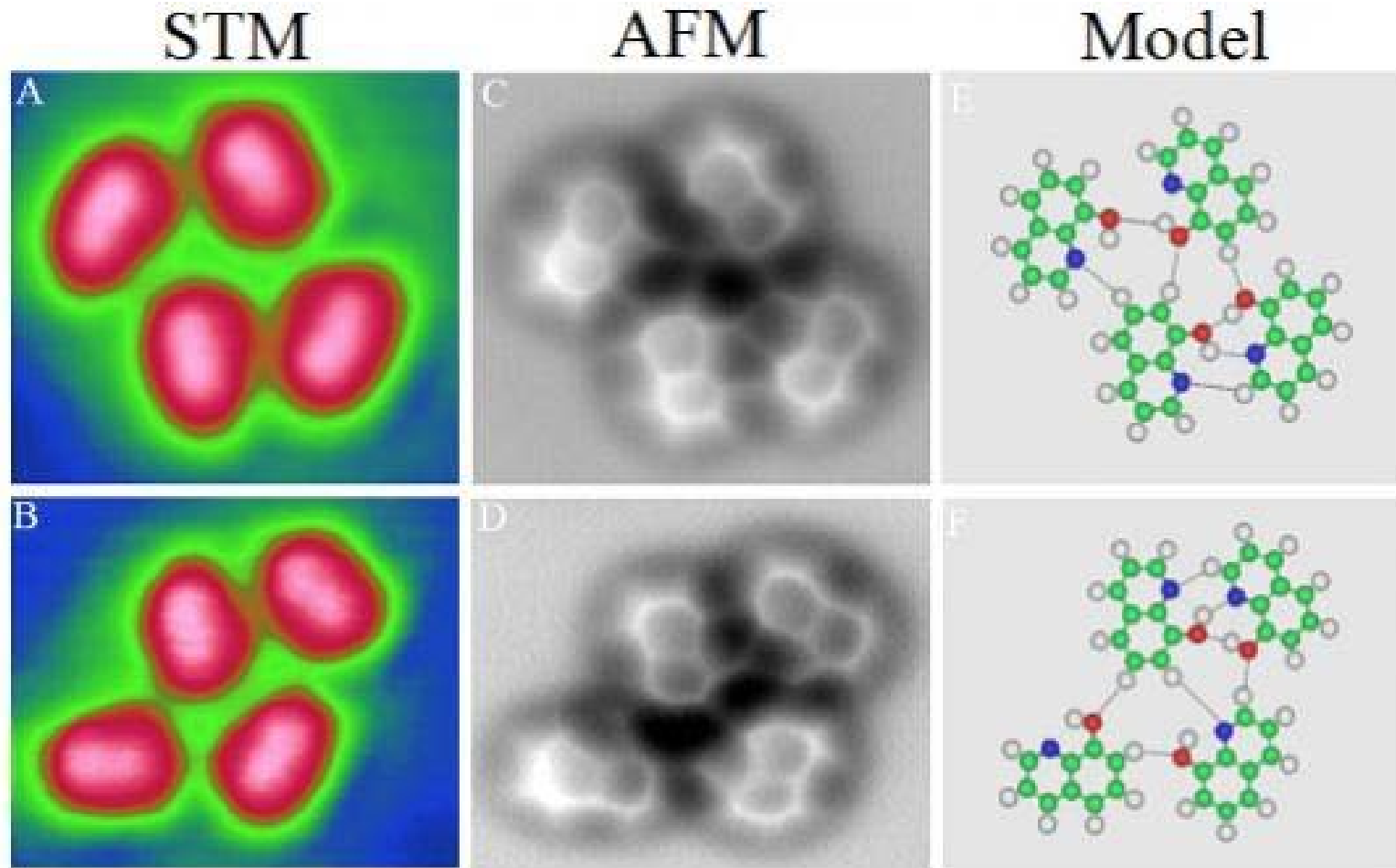
## Self-assembly driven by various intermolecular interactions:

- $\pi$ - $\pi$  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.

One or more of these interaction result in highly organized structure (packing) of molecules.

All these interactions are **non-covalent bonding**, i.e., somehow reversible. For example, the assembled materials can be dissociated back to individual molecules by dispersion in solvents.

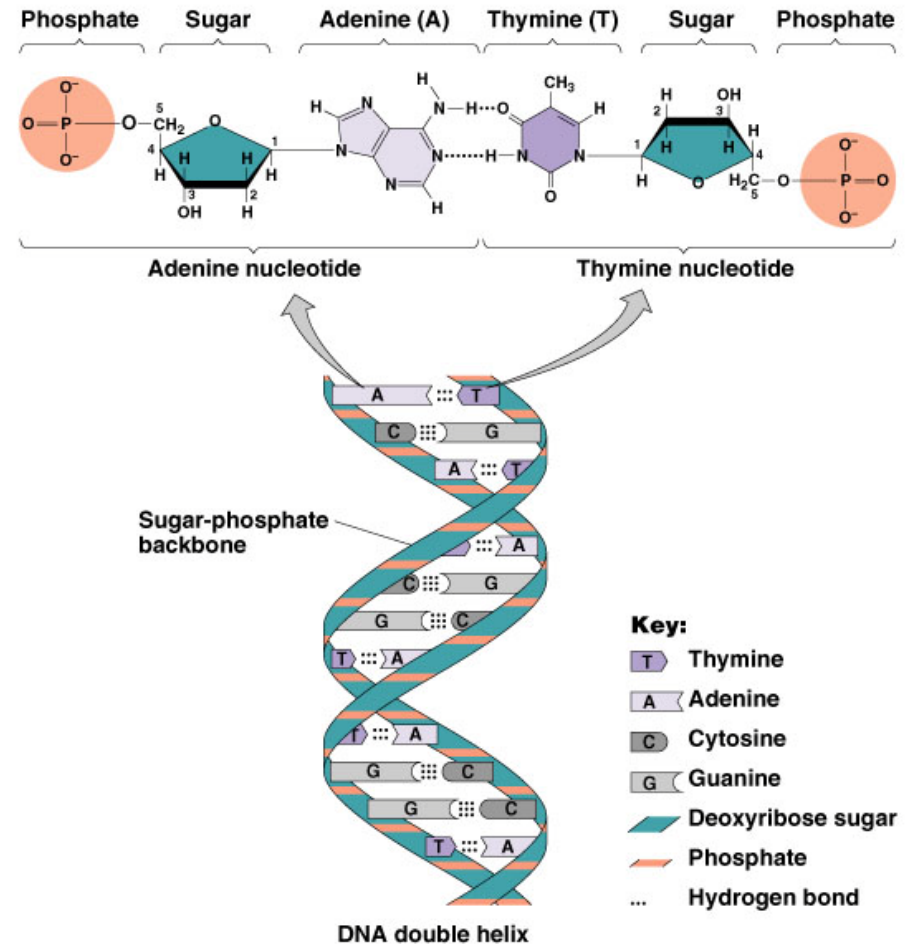
# Hydrogen Bonds Visualized by AFM Imaging



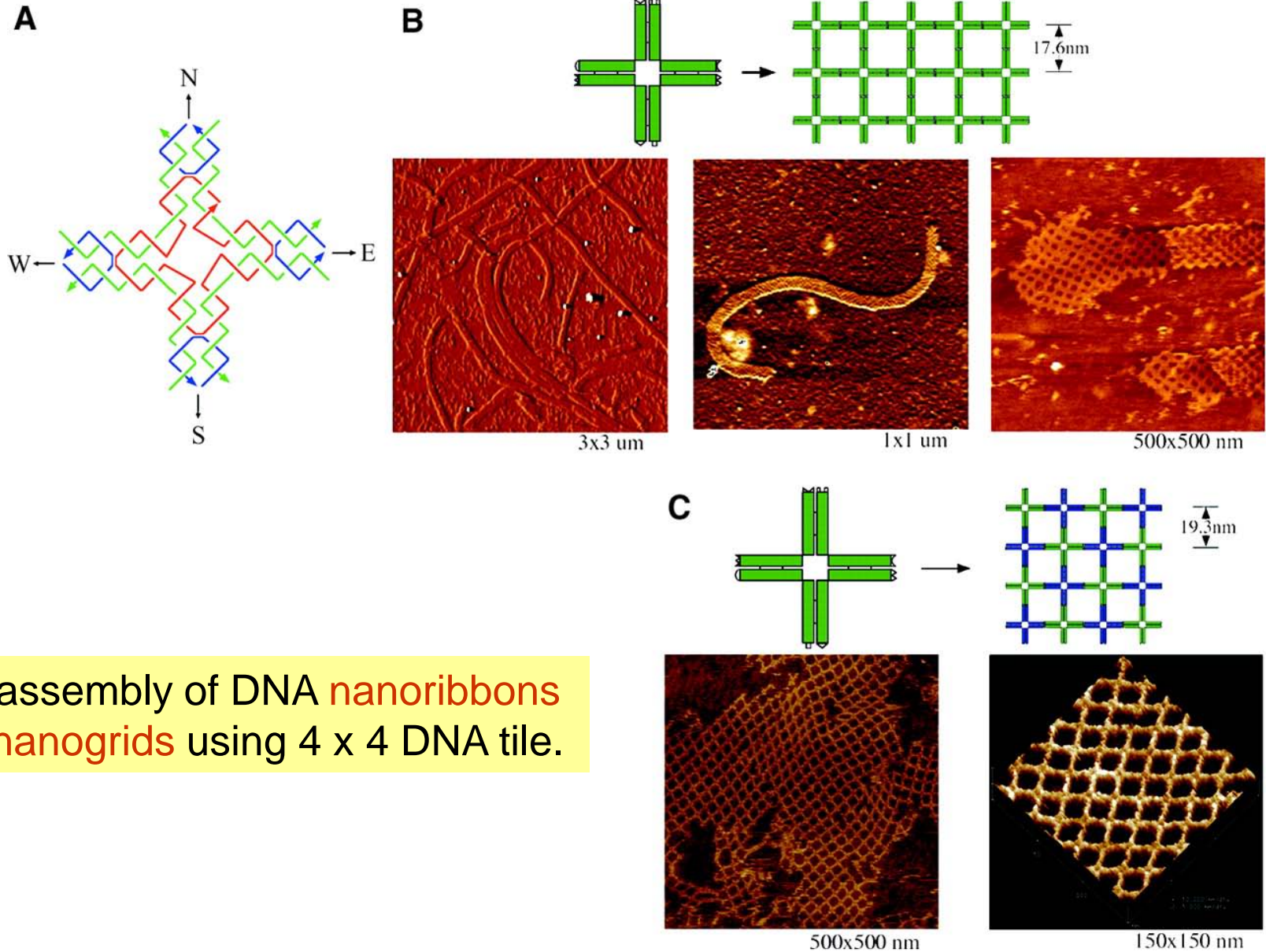
# DNA

--- an Perfect Self-assembler by Nature

- Extremely high selectivity;
- Strong binding via H-bonds;
- Highly flexible for modification;
- Good physicochemical stability;
- Good mechanical rigidity.

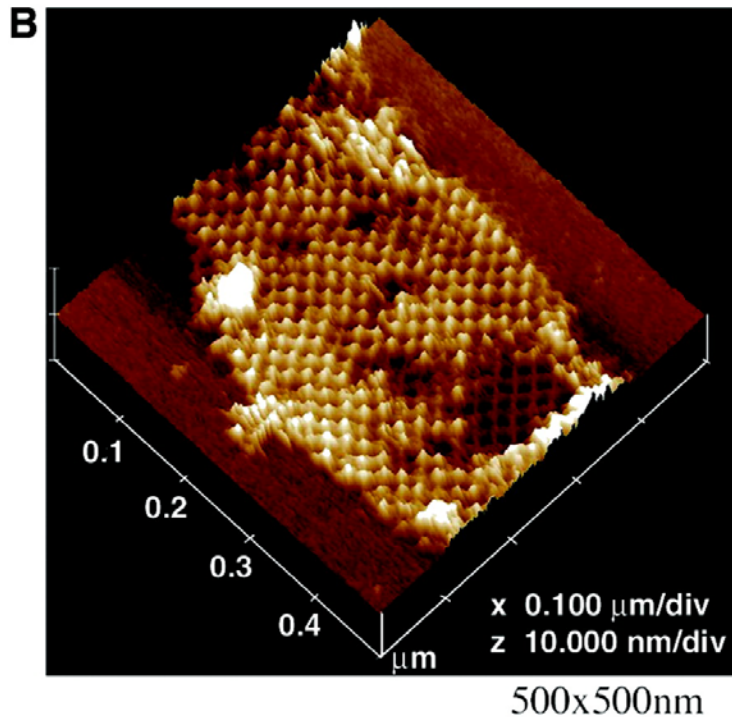
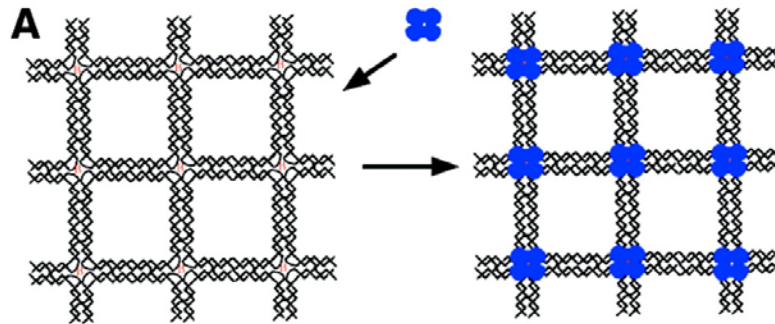


## 2D Self-Assembly of DNA



Self-assembly of DNA nanoribbons and nanogrids using 4 x 4 DNA tile.

## DNA templated assembly of proteins



Question:

*can we measure or image well such structures using electronic microscope or STM?*

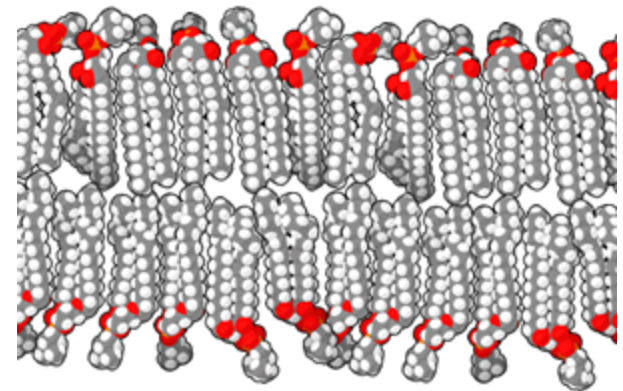
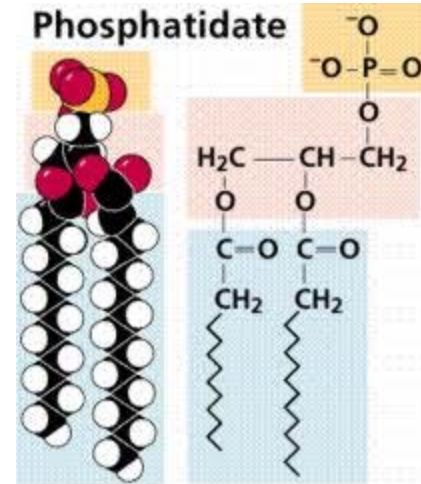
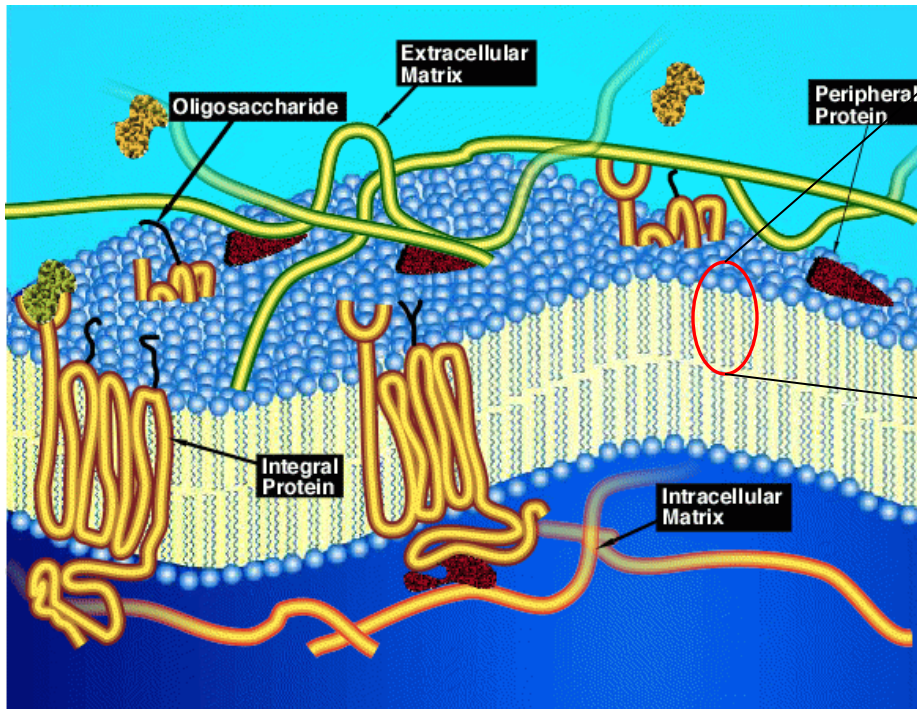
*Neither DNA or Proteins are conductive materials.*

Self-assembly of protein arrays templated by 4 x 4 DNA nanogrids.

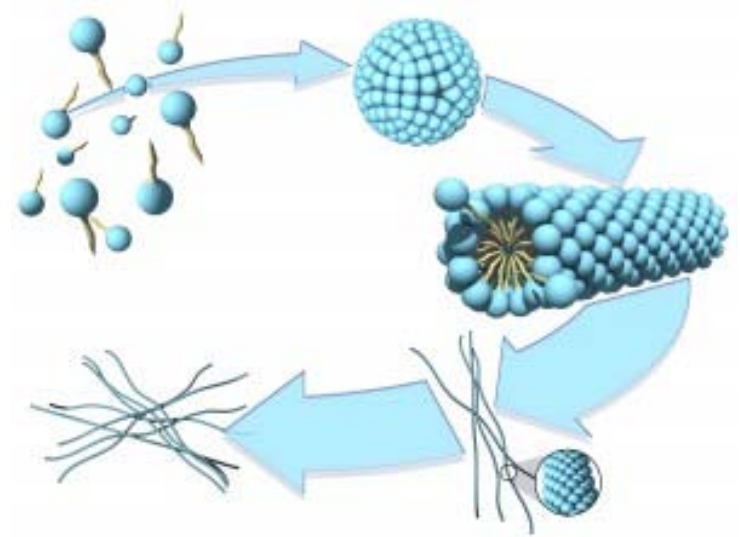
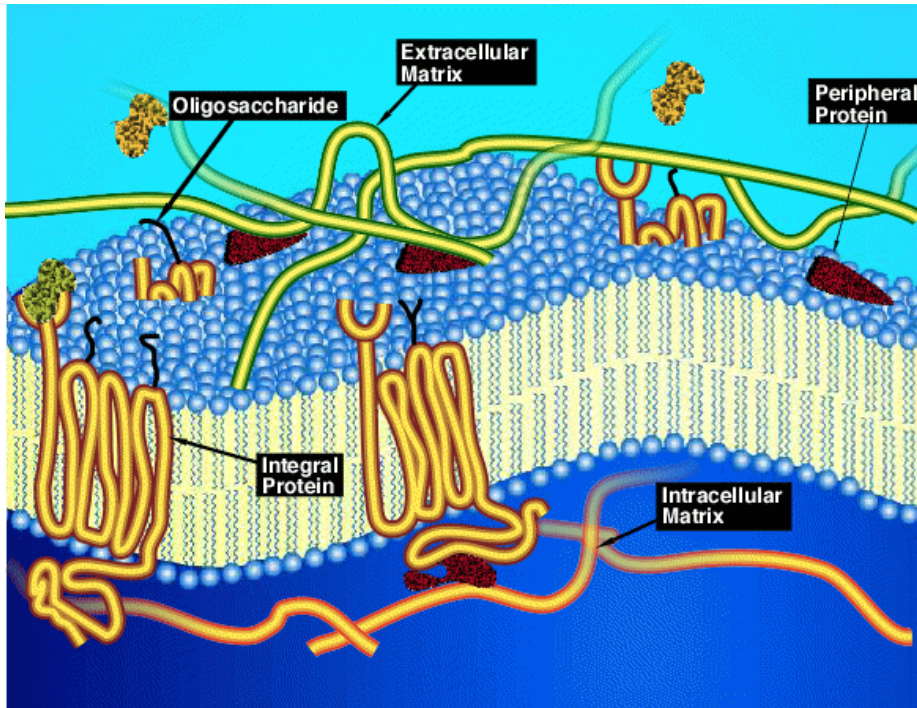
More details of DNA self-assembly  
will be given in Lecture 14.



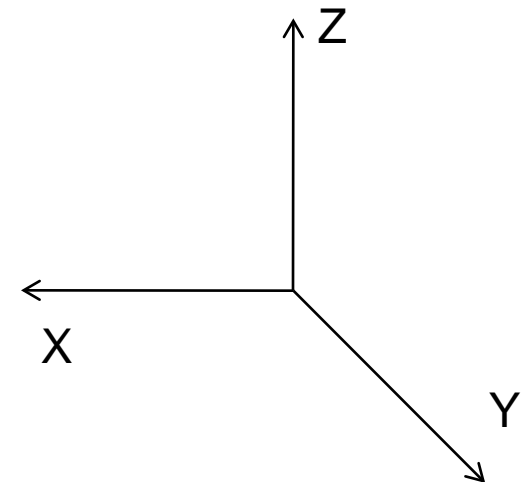
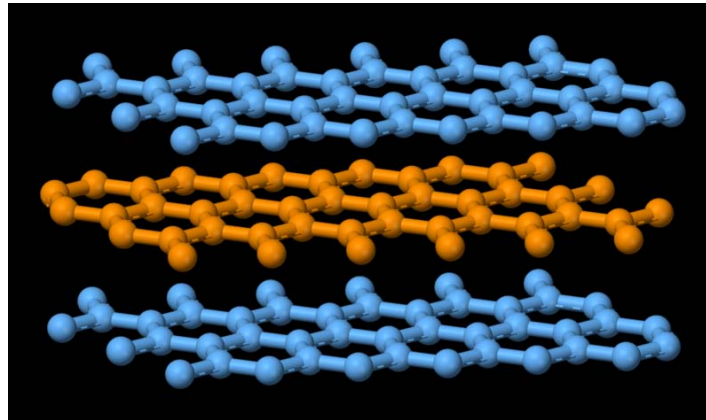
# Self-assembly via hydrophobic interaction: *cell membrane*



**Self-assembly via hydrophobic interaction:** *from the two-dimensional assembly of cell membrane to one-dimensional assembly to form nanorods*

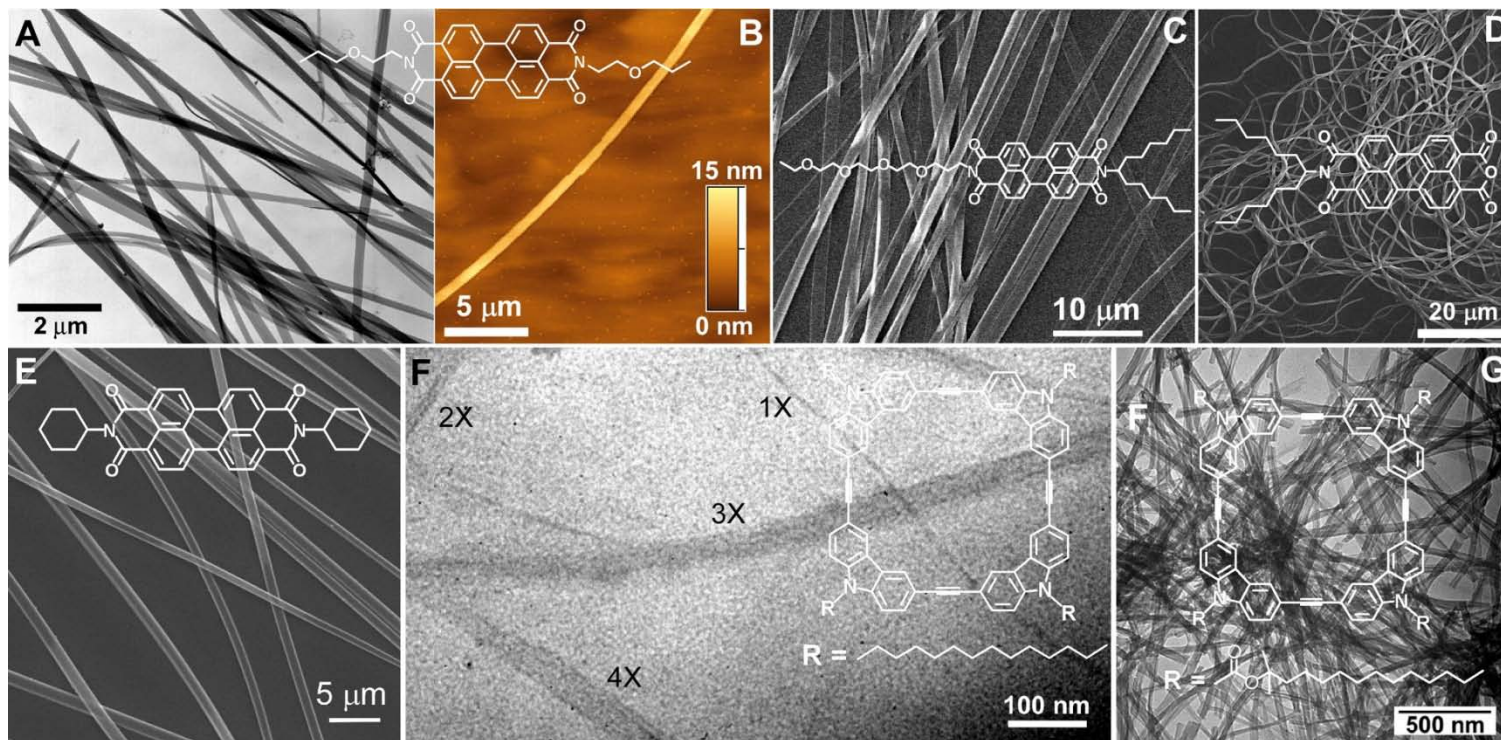
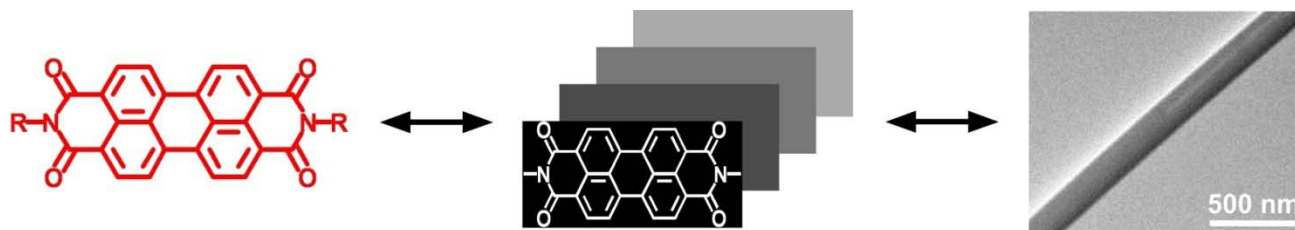


# Graphite: *layer-by-layer stacks of $\pi$ -electron sheets (the graphenes)*

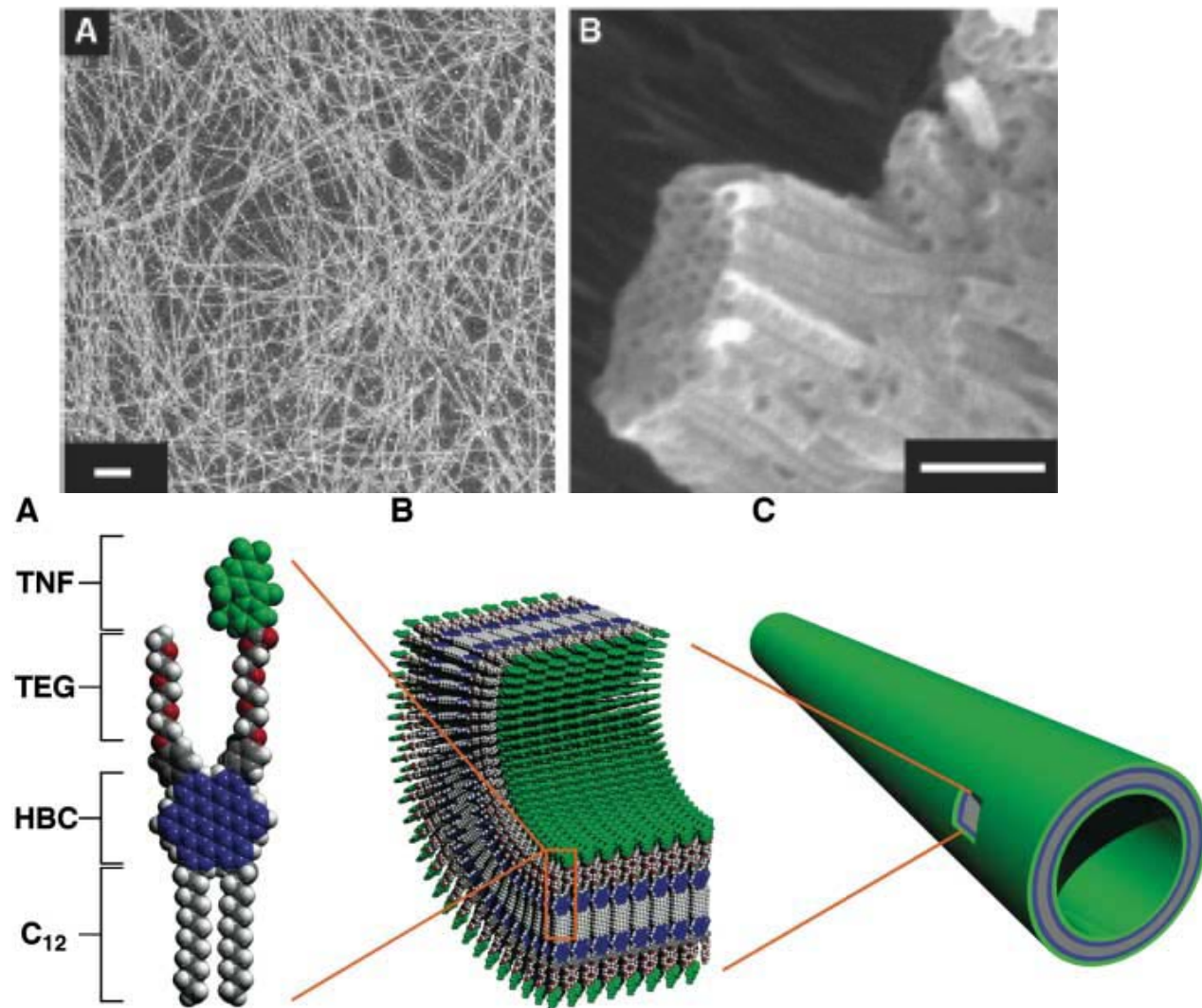
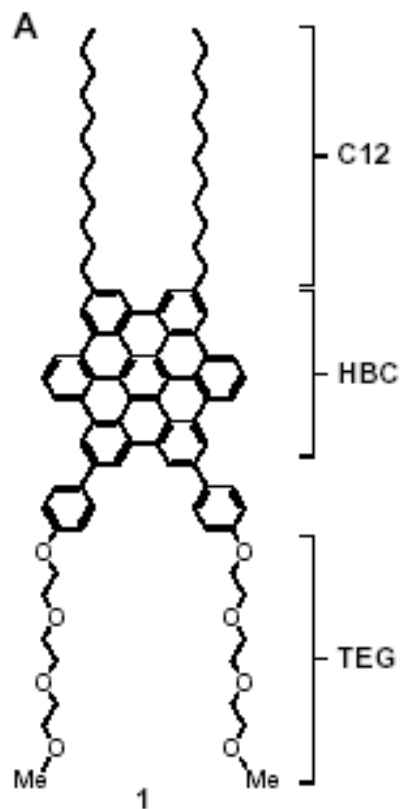


Tuning the materials growth as dominated by the  $\pi$ - $\pi$  stacking  $\rightarrow$  formation of nanowires.

Self-assembly driven by  $\pi$ - $\pi$  cofacial interaction: *nanowires, nanobelts, etc.*



# Combining $\pi$ - $\pi$ stacking and hydrophobic interaction leads to formation of more sophisticated nanostructures



**A movie clip showing the free molecular self-assembly in solutions that combines the  $\pi$ - $\pi$  stacking and hydrophobic interdigitation interaction**

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# Self-assembly: free molecules vs. template directed

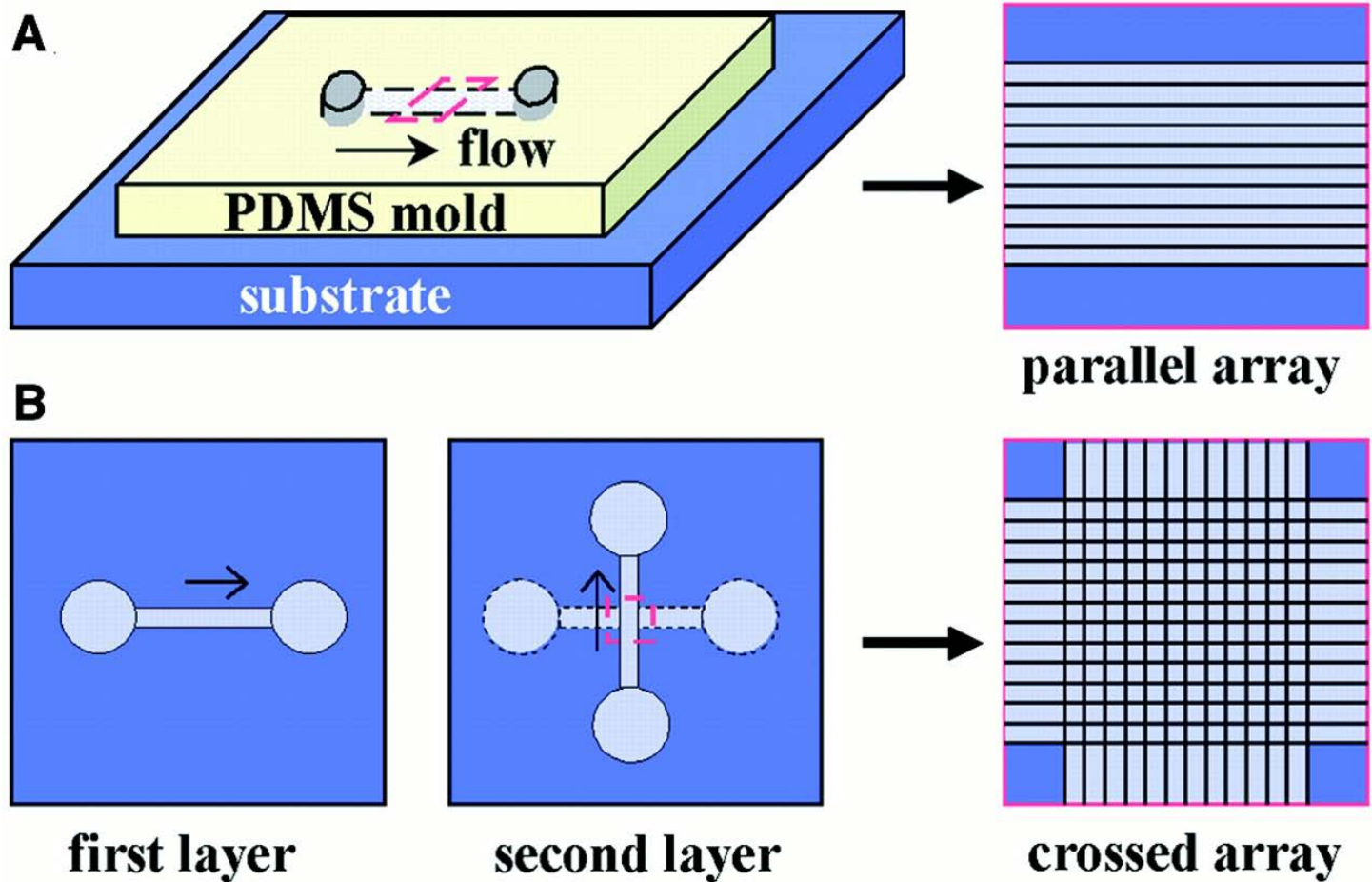
- Free self-assembling:
    - ✓ Depends on various conditions, temperature, solvent, pH, concentration, etc.);
    - ✓ Form highly organized/ordered structures in different dimensions, 1D, 2D, 3D.
  
  - Directed self-assembly:
    - ✓ Controlled and enhanced by template structure and properties;
    - ✓ 1D template: DNA, edge-transfer lithography;
    - ✓ 2D template: crystalline surface, like gold for thiol monolayer.
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# DNA template assembly: demanded by molecular electronic

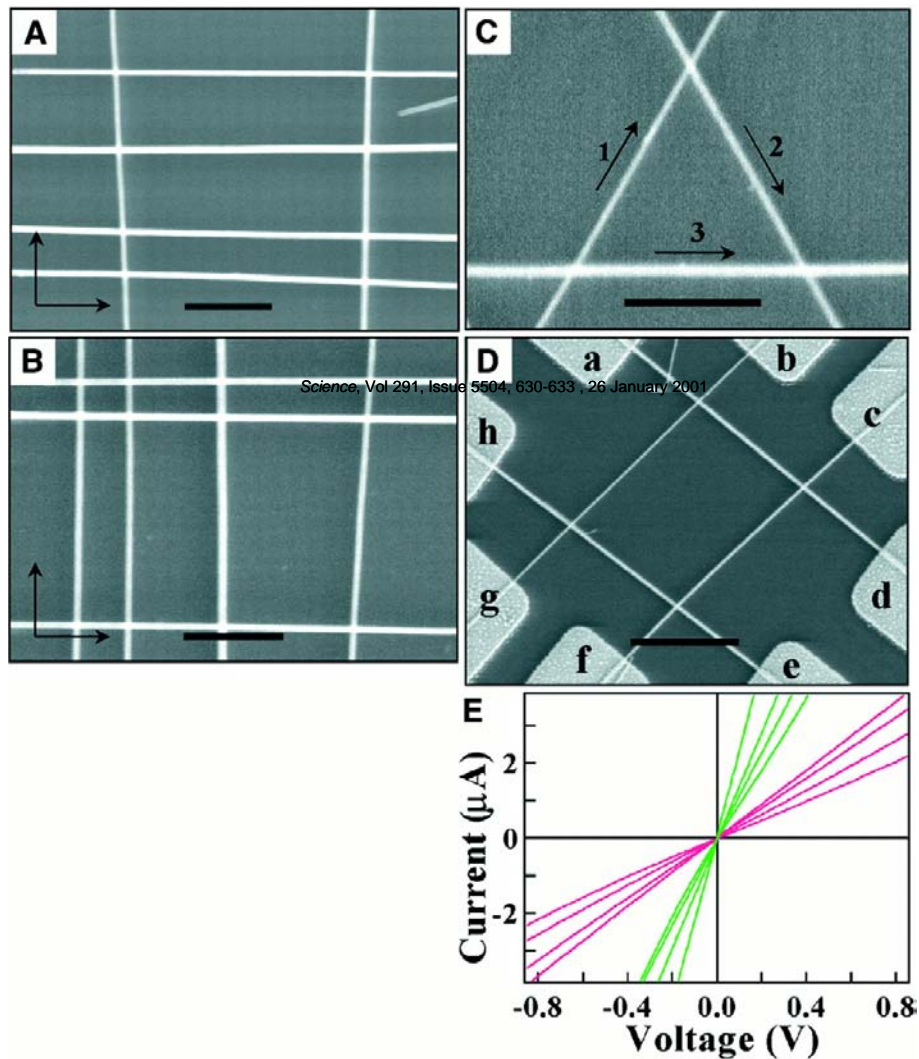
- A challenge in molecular electronics --- *develop novel tools or concepts capable of assembling **large number** of individual devices (molecules) into large-scale functional circuits.*
- One successful attempt --- fluid flowing to make crossed structure of nanowires (as shown in next two slides); but not as sufficient as needed for large area processing (especially for assembly of molecules).
- A more promising approach should be based on molecular self-recognition and self-assembly.
- DNA again appears to be the most attractive choice: *Here are the approaches to metallic nanowire fabrication by two different groups.*



# Assembling large area circuits: *fluidic channel structures for flow assembly*



# Layer-by-layer assembly and transport measurements of crossed NW arrays



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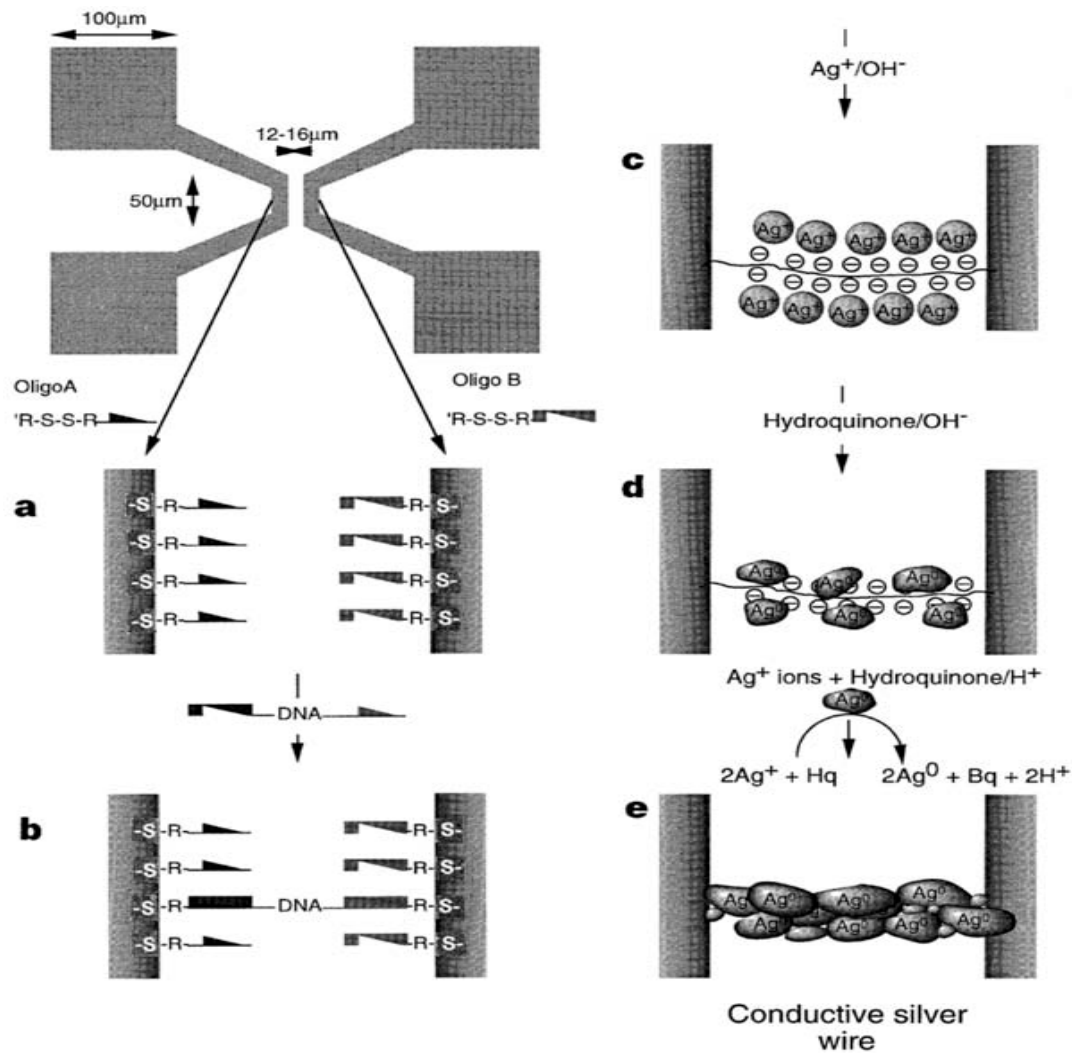
# DNA-templated assembly and electrode attachment of a conducting silver wire

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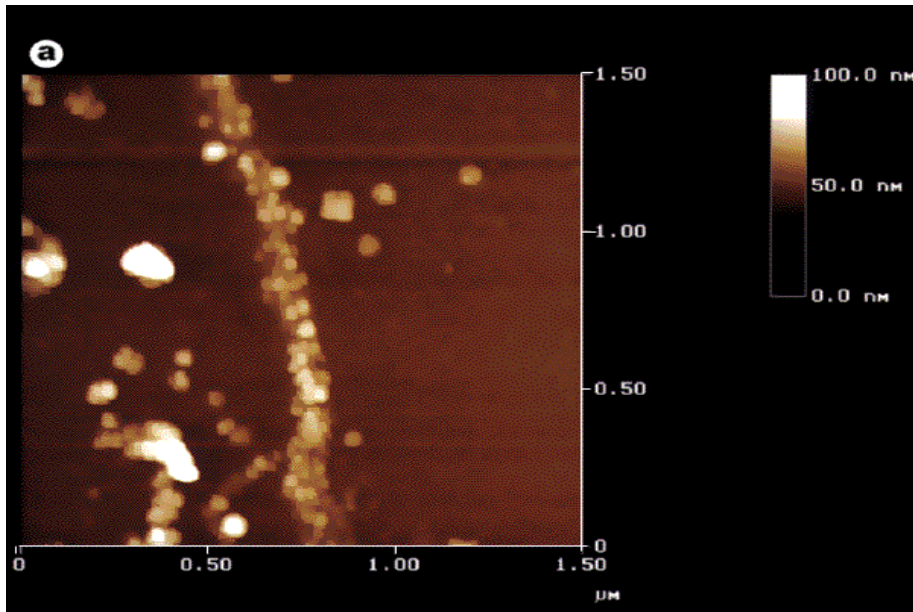


## Construction of a silver wire connecting two gold electrodes.

- Oligonucleotides with two different sequences attached to the electrodes.
- $\lambda$ -DNA bridge connecting the two electrodes.
- Silver-ion-loaded DNA bridge.
- Metallic silver aggregates bound to the DNA skeleton.
- Fully developed silver wire.

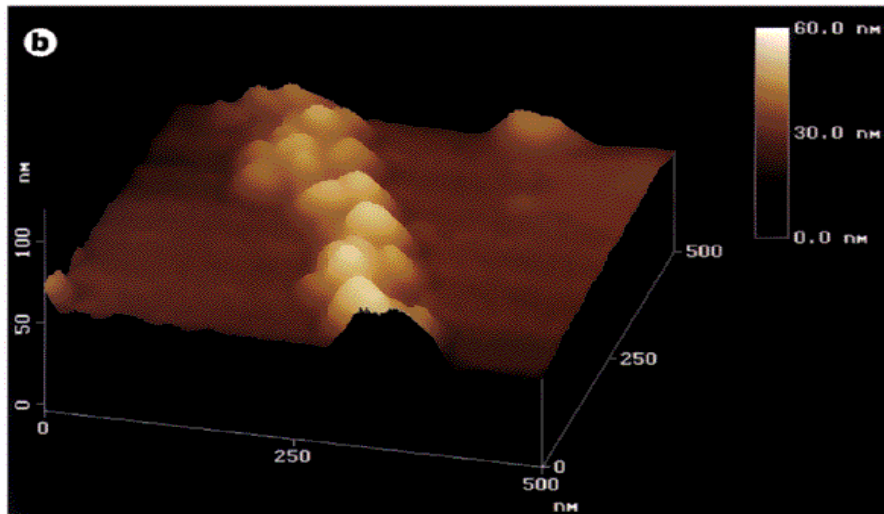
$\lambda$ -DNA comes from a virus called Phage Lambda. This virus is harmless to man and therefore makes an excellent source of DNA.

The top left image shows the electrode pattern ( $0.5 \times 0.5 \text{ mm}$ ) used in the experiments. The two  $50 \mu\text{m}$  long, parallel electrodes are connected to four ( $100 \times 100 \mu\text{m}$ ) bonding pads.



**AFM images of a silver wire connecting two gold electrodes 12  $\mu\text{m}$  apart.**

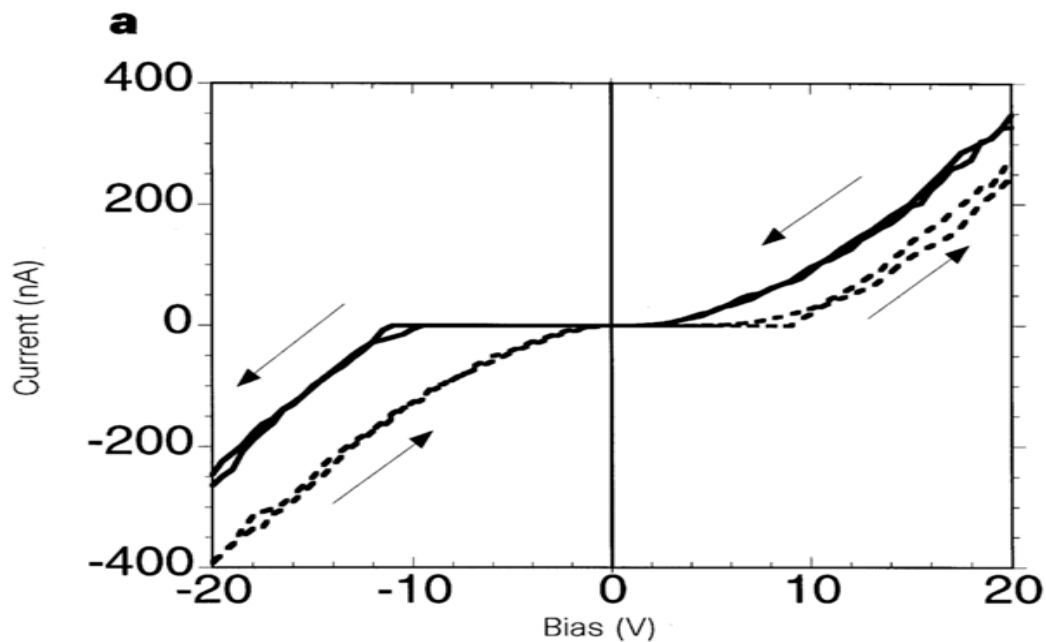
a, 1.5x1.5  $\mu\text{m}$ ;



b, 0.5x0.5  $\mu\text{m}$  field sizes.

Note the **granular** morphology of the conductive wire.

Such grain boundary results in low conductivity, compared to the crystalline silver.

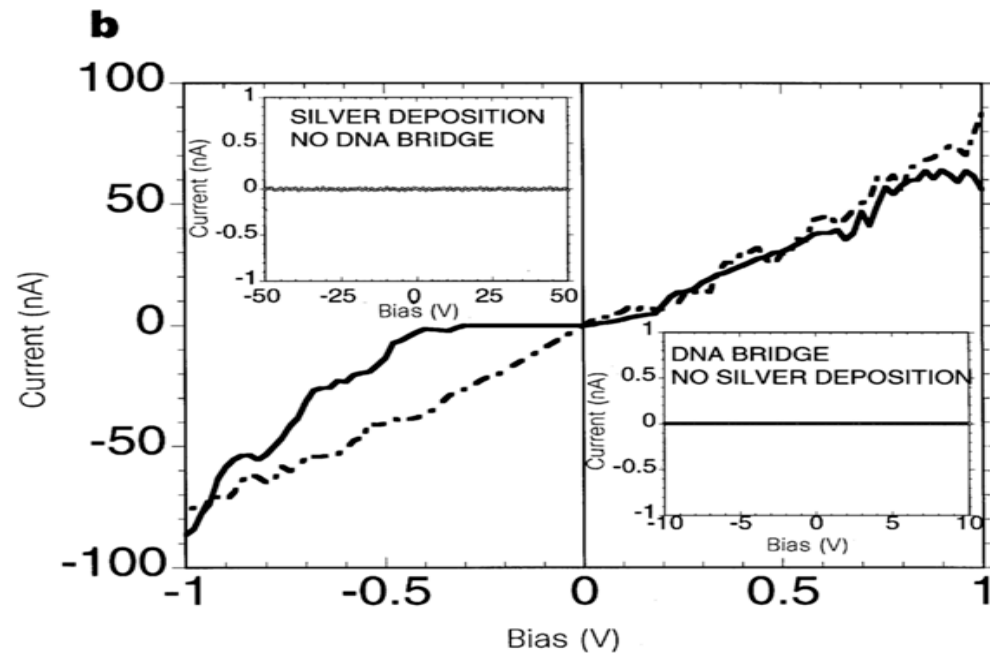


## $I$ - $V$ curves of the nanowire.

a, Two terminal  $I$ - $V$  curves of the silver wire.

Arrows indicate voltage **scan direction**. The two curves in each direction present repeated measurements thus demonstrating the stability of a given wire. Note the **different asymmetry** pertaining to the two scan directions.

b,  $I$ - $V$  curves of a different silver wire in which the silver growth was more **extensive** than in a.



**Extensive growth** resulted in a **narrower** current plateau (solid curve), on the order of 0.5 V, and a lower differential resistance (7 M $\Omega$  versus 30 M $\Omega$  in a).

By applying 50 V, the plateau has been permanently eliminated to give an **ohmic behaviour** (dashed-dotted line), over the whole measurement range.

*A DNA bridge with no silver deposition, and silver deposition without a DNA bridge, are insulating.*

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# Summary

- The silver wire obtained is quite **thick**;
- Silver **grain size** is hard to control;
- Presence of excess reducing reagent or other ionic species results in poor grain contact between the silver particles, thus results in **low conductivity**.
- The **contact** to the two bulk electrodes is hard to control --- poor **reproducibility** of the fabrication.
  
- *All these pitfalls require more elaborate fabrication techniques.*

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# Sequence-Specific Molecular Lithography on Single DNA Molecules

Kinneret Keren,<sup>1</sup> Michael Krueger,<sup>1</sup> Rachel Gilad,<sup>1</sup> Gdalyahu Ben-Yoseph,<sup>1, 2</sup> Uri Sivan,<sup>1, 2</sup> Erez Braun<sup>1, 2\*</sup>

<sup>1</sup> Department of Physics,

<sup>2</sup> Solid State Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel.

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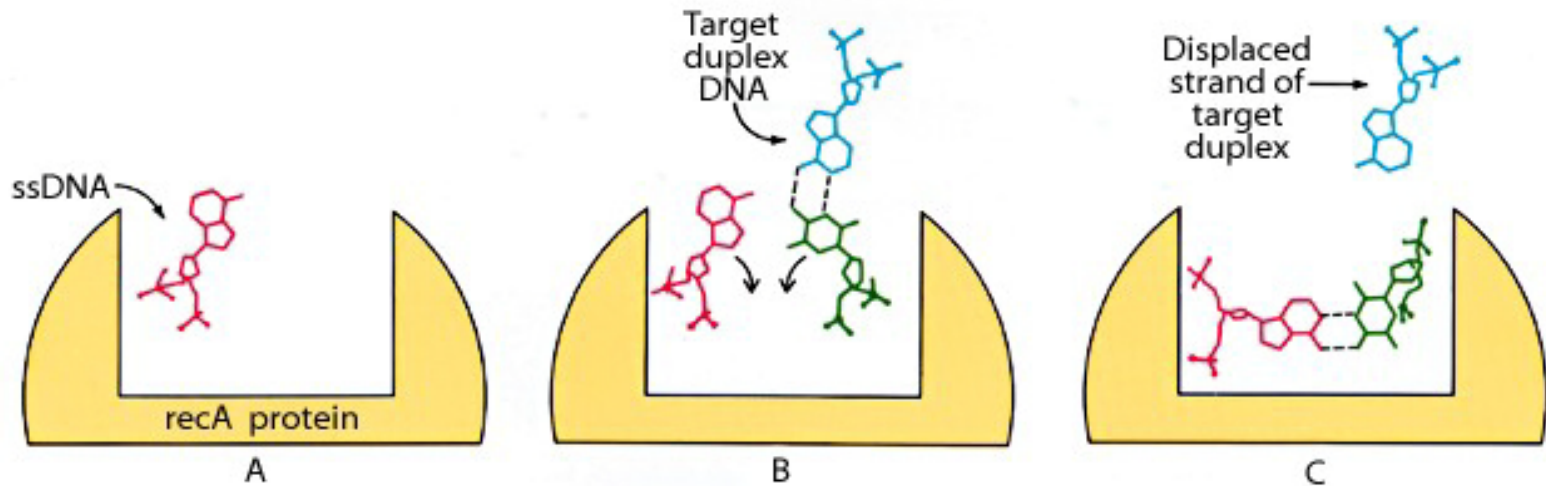
## RecA protein

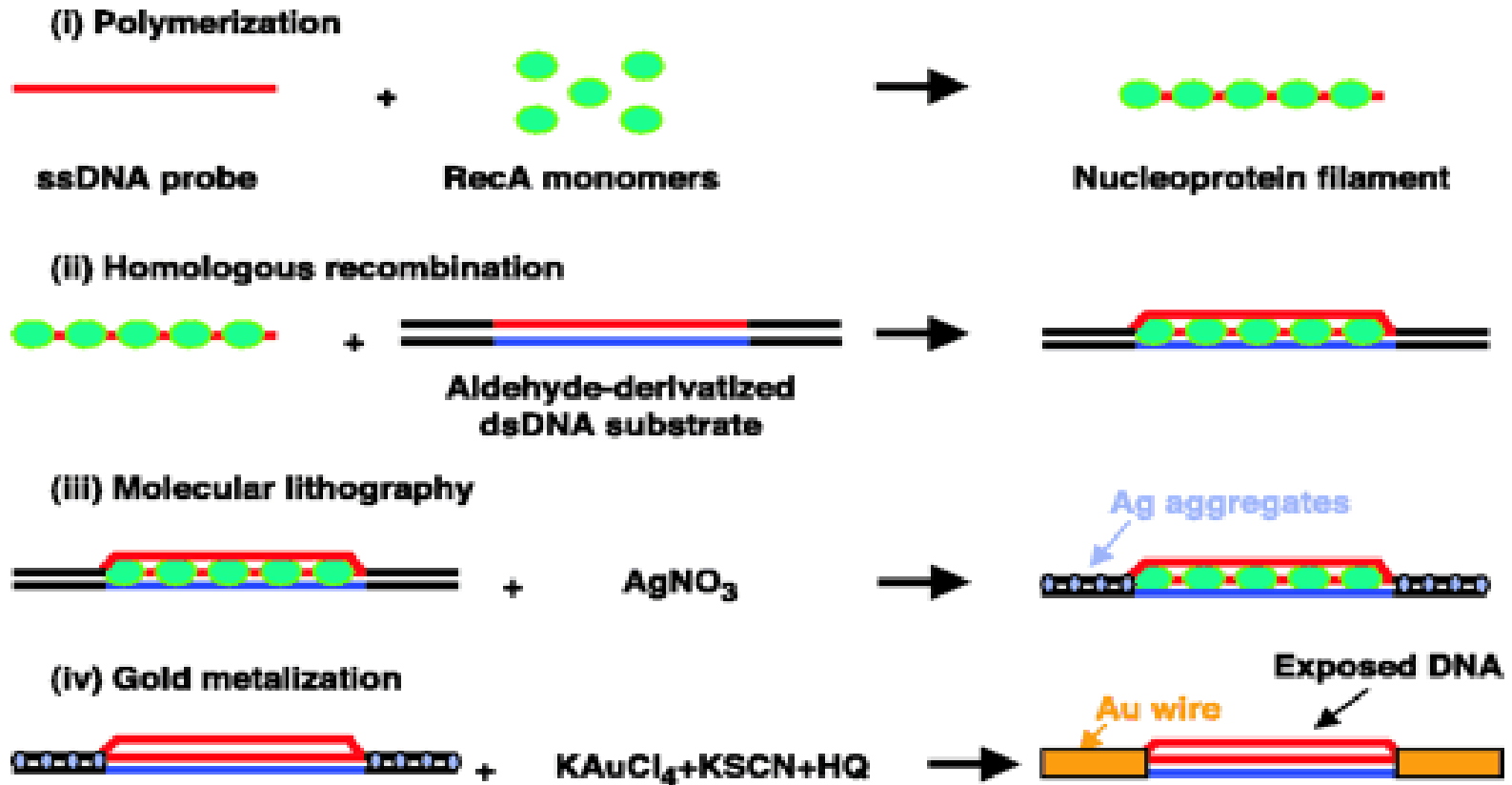
- A multifunctional protein, 352 amino-acid, 38 kDa;
- It has strand-exchange, ATPase and co-protease activities all packed into the compact structure.
- RecA protein binds cooperatively to a ssDNA molecule with each monomer of RecA binding to a span of **4-6 nucleotides**.



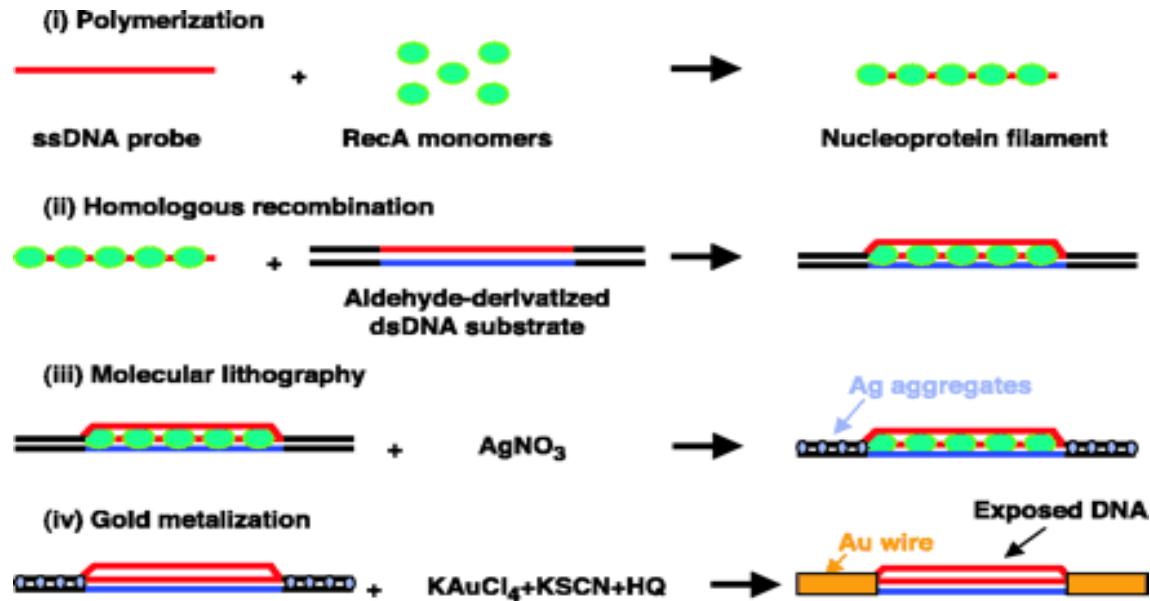
RecA protein promotes **strand exchange** between DNA molecules as long as the following conditions apply:

- One of the two DNA strands must have a **binding region** for RecA.
- The two molecules must share a region of **homologous** (i.e. nearly identical) DNA sequence - a minimum of 50 bp is required.





Schematics of the homologous recombination reaction and molecular lithography.



## The process of homologous recombination reaction and molecular lithography.

(i), RecA monomers polymerize on a ssDNA probe molecule to form a nucleoprotein filament.

*Here, the ssDNA is a 2027-base strand.*

(ii), the nucleoprotein filament binds to an **aldehyde**-derivatized dsDNA substrate molecule at a homologous sequence.

*The aldehyde acts as a reducing agent for the formation of silver cluster. The aldehyde derivatization left the DNA intact and biologically active. Localized reduction results in small silver particles and very low background metallization (see the following SEM image).*

*Here, the substrate is a 48,502–base pair double-strands derivatized by aldehyde.*

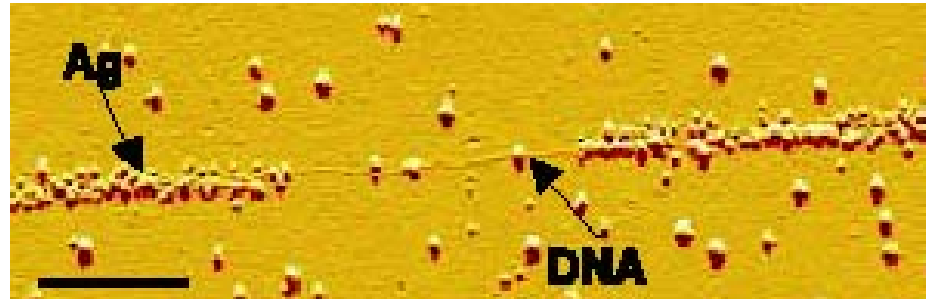
(iii), incubation in AgNO<sub>3</sub> solution results in the formation of Ag aggregates along the substrate molecule at regions unprotected by RecA.

(iv), the Ag aggregates serve as catalysts for specific gold deposition, converting the unprotected regions to conductive gold wires. HQ, hydroquinone.

AFM is specifically powerful for imaging these small, non-conducting structures.



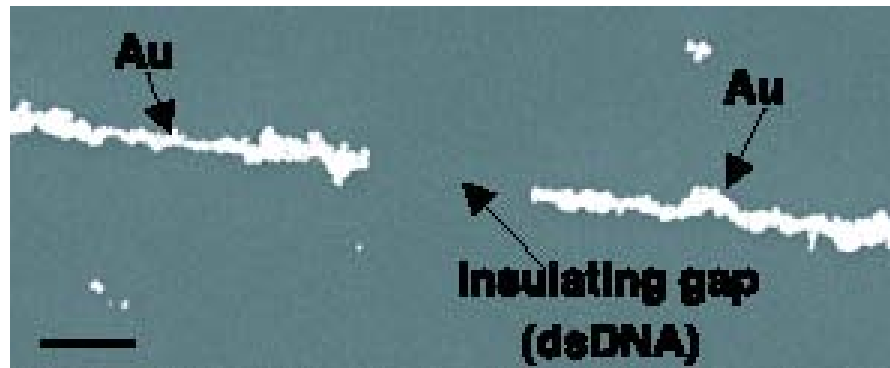
**AFM** image of a 2027-base RecA nucleoprotein filament bound to an aldehyde-derivatized DNA substrate molecule. Scale bar 0.5  $\mu\text{m}$



AFM image of the sample after Ag deposition. DNA is exposed at the gap between the Ag-loaded sections. Scale bar 0.5  $\mu\text{m}$



AFM image of the sample after gold metallization. Inset, close-up image of the gap. The height of the metallized sections is  $\sim 50$  nm. Scale bar  $0.5 \mu\text{m}$



SEM image of the wire after gold metallization. Scale bar 0.5  $\mu\text{m}$

*The very low background metallization in the SEM images compared with the AFM ones indicates that most of the [background](#) in the AFM image is [insulating](#).*

*In other words, AFM imaging reveals more detailed composition and morphology information.*



# Self-organized nanostructure of polymer materials ---

One of the major applications of AFM imaging

Polymers, particularly conducting polymers, have drawn huge amount of interest in materials science and engineering, as they prove useful for various optoelectronic applications, such as,

- Thin Film Transistors (TFT) and other photonic switches/sensors --- photon driven switch.
- Light-emitting diodes (LED) --- *transforming electricity to light.*
- Photovoltaic devices (solar cells) --- *transforming light to electricity.*



## Conducting polymers The Nobel Prize in Chemistry 2000



Alan J. Heeger



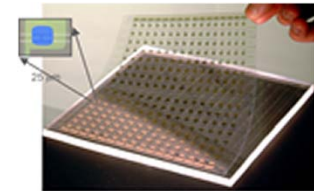
Alan G.  
MacDiarmid



Hideki  
Shirakawa

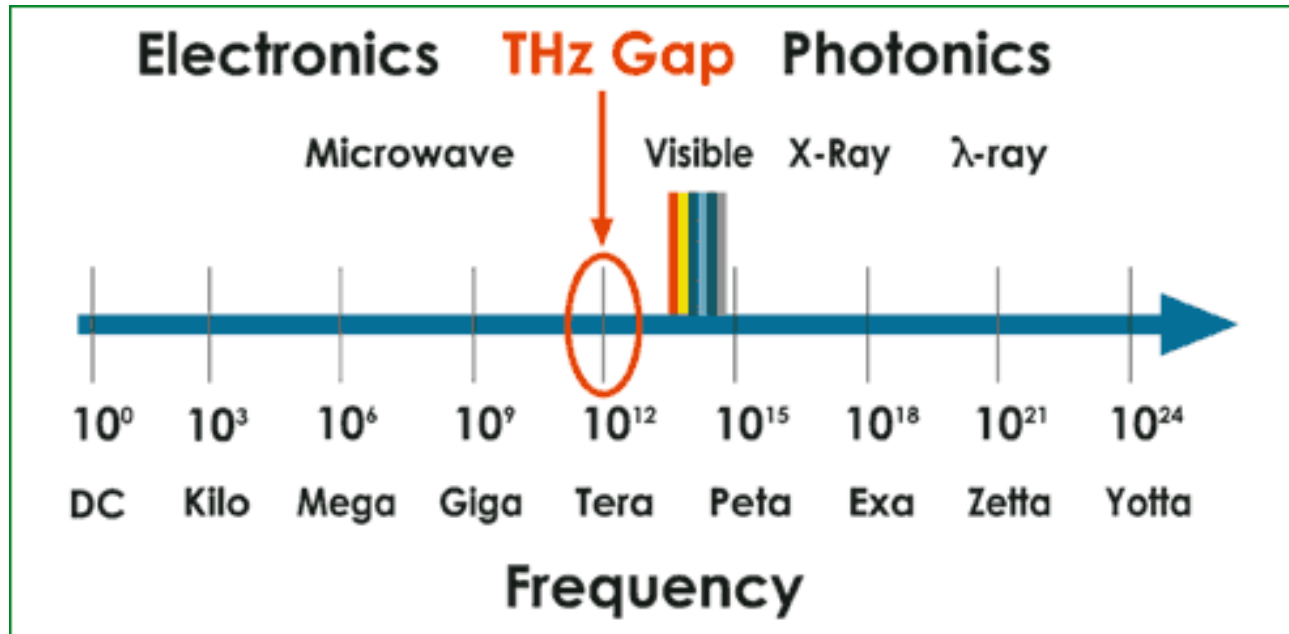
### Advantages for applications in optoelectronics:

- Large area processing.
- Compatible with flexible plastic substrate.
- In-expensive.



A rubber stamped plastic circuit  
and an electronic paper display.

# Photonics: *a promise for high-speed*



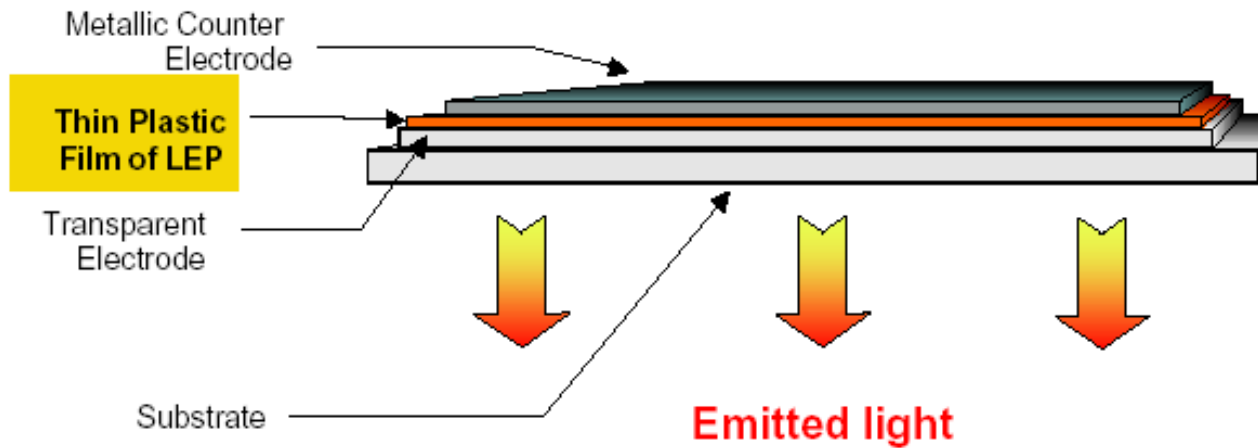
# Light-emitting diode (LED) devices:



- Mechanism: electrical excitation → electron-hole recombination → light emission.
- Different channel materials:
  - PLED --- Polymer Light-Emitting Diode;
  - OLED --- Organic Light- Emitting Diode.
- The displays emit high-intensity light with just a few applied volts.
- The emitting color --- precisely controlled by altering the composition of the material.
- Full-color displays --- using arrays of RGB (Red, Green, Blue) on a display screen.
- Two main challenges --- poor efficiency and short lifetime.

# Schematic structure of a LED

## Light Emitting Polymer Device



# Light-emitting diode (LED) devices: *next generation of lighting and display*

## Organic (plastic) LEDs

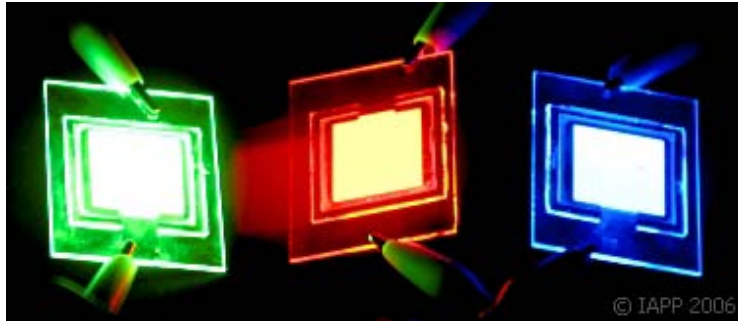
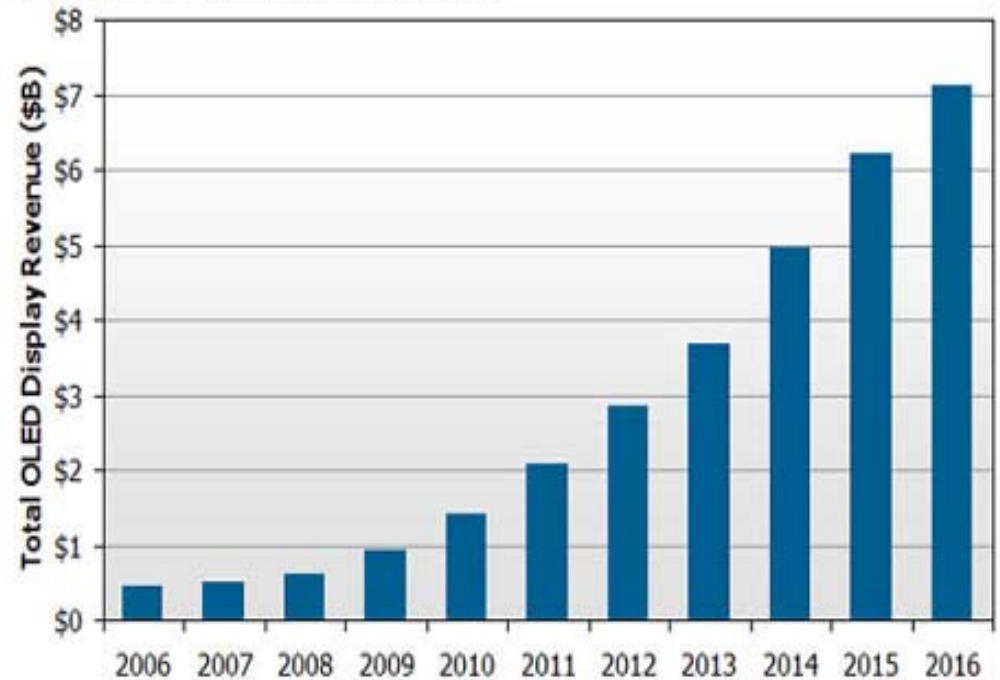


Figure 1: OLED Display Revenue Forecast



Source: DisplaySearch Q2'09 Quarterly OLED Shipment and Forecast Report

# **OLED TV:** *never cool like this*



**Thin:** millimeter

**Flat:** full view angle

**Bright:** 1,000,000:1

and ...

**Flexible, foldable !**



**Why organic (plastic)?**

**Cheap: \$\$\$**

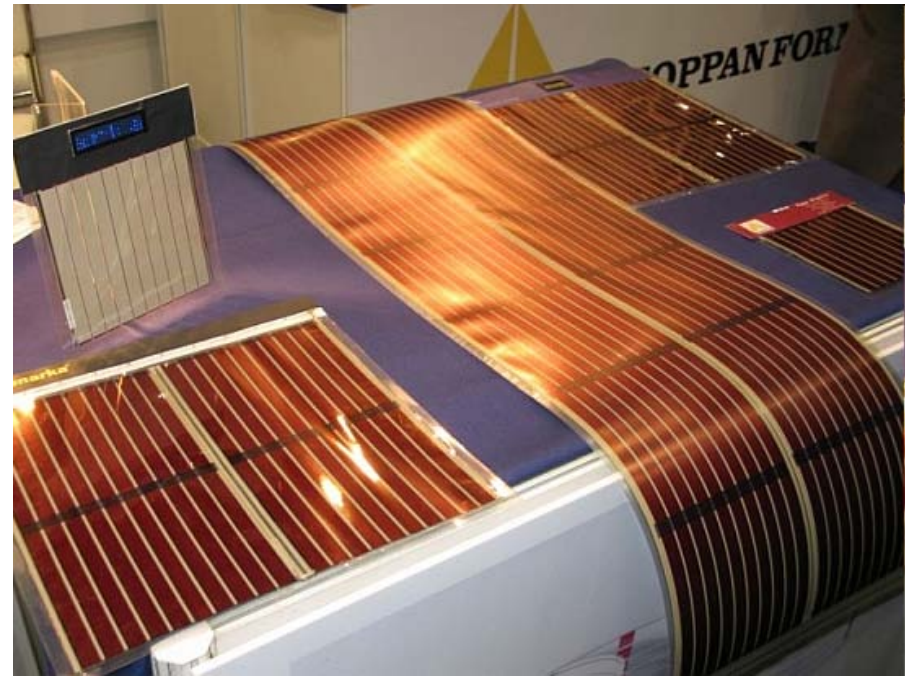
**Flexible: in shape**

**Coatable: like paint**

## Breaking Through

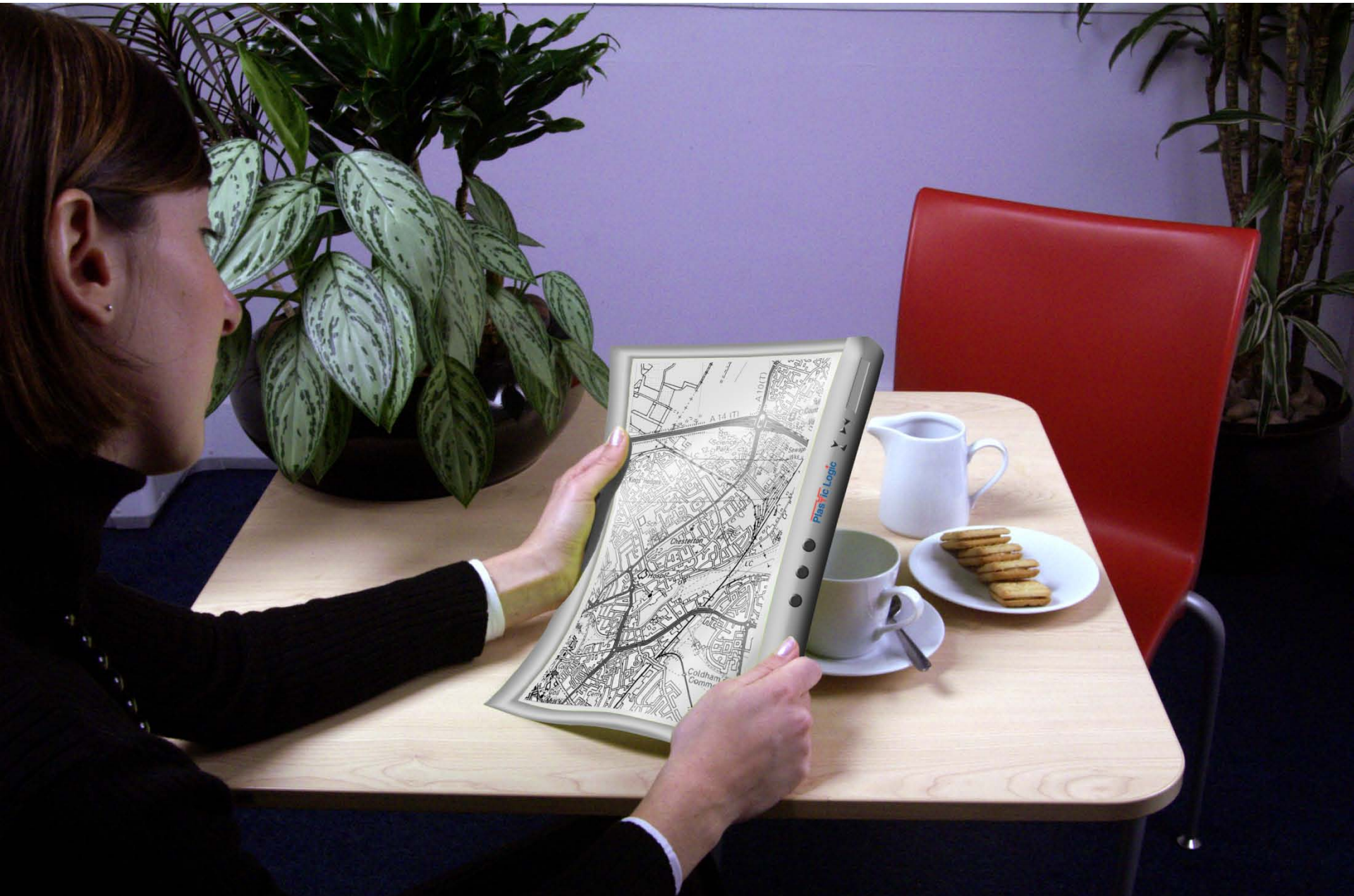
Printable electronics is attracting growing interest and is gearing up for commercial applications

[Alexander H. Tullo](#)





# **E-book:** *fold it as you like*



## **Recent news about flexible/bendable OLED display:**

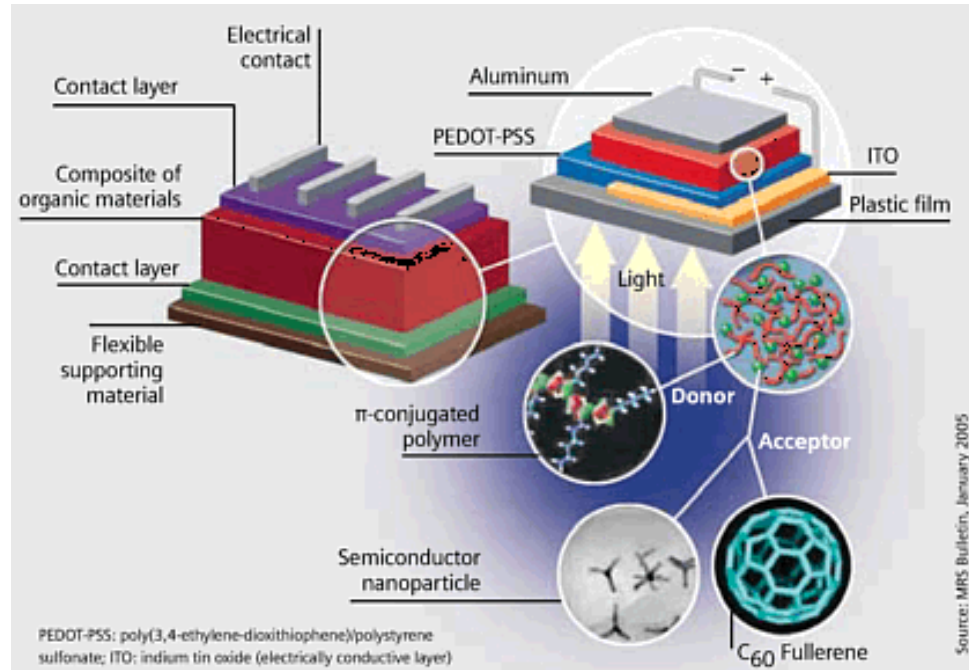
Samsung Flexible Display at CES 2013,

<http://www.youtube.com/watch?v=N3E7fUynrZU>

Engineers develop a stretchable, foldable transparent electronic display,

<http://phys.org/news/2013-09-stretchable-foldable-transparent-electronic-video.html>

# Polymer/organic solar cells: *where nanostructural organization of materials is crucial for charge transport*



Organic, Paint-on Technique will eventually dominate the solar cell market

- **Cheap**, \$0.25-0.30 per kWh, compared to silicon based solar cells, ~ **\$6** per kWh.
- **Ease of large-area** processing and large-scale manufacturing.
- **Flexible, adaptable** to various substrate: *e.g., coated on roof to power buildings and houses, coated on vehicles, clothes or other items as portable power supply.*
- **More options** for improving the efficiency, currently 3-6%, ideally 10% or above.

One day, power your house by painting solar cells



One day, power yourself using solar cell paints ...



# **Solar cell powered windows:**

*Hong Kong Science Park*



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## breakthrough papers of interests: *conducting polymer devices*

- Field-effect transistor (FET):

G. H. Gelinck, T. C. T. Geuns, D. M. **de Leeuw**, *Appl. Phys. Lett.* 2000, **77**, 1487.

- Integrated circuits:

A. **Dodabalapur**, Z. Bao, A. Makhija, J. G. Laquindanum, V. R. Raju, Y. Feng, H. E. Katz, **J. Rogers**, *Appl. Phys. Lett.* 1998, **73**, p. 142.

- Light-emitting diode (LED):

J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, **R. H. Friend**, P. L. Burns, **A. R. Holmes**, *Nature* 1990, **347**, 539.

- Active matrix display:

H. Sirringhaus, N. Tessler, **R. H. Friend**, *Science* 1998, **280**, 1741.

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# Nanoscopic structures of polymer materials

- Performance of polymer opto-electronic devices depends on exciton (electron-hole pair) diffusion, exciton dissociation at p-n junctions, charge carrier mobility, which in turn are all determined by the intermolecular interaction --- self-assembled nanostuctures.
  - Highly ordered polymer phase enhances the conductivity --- by orders of magnitude.
  - *Measurement of nanostructure → microscopes*
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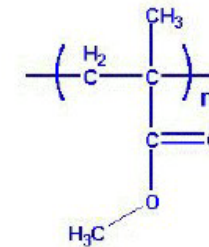
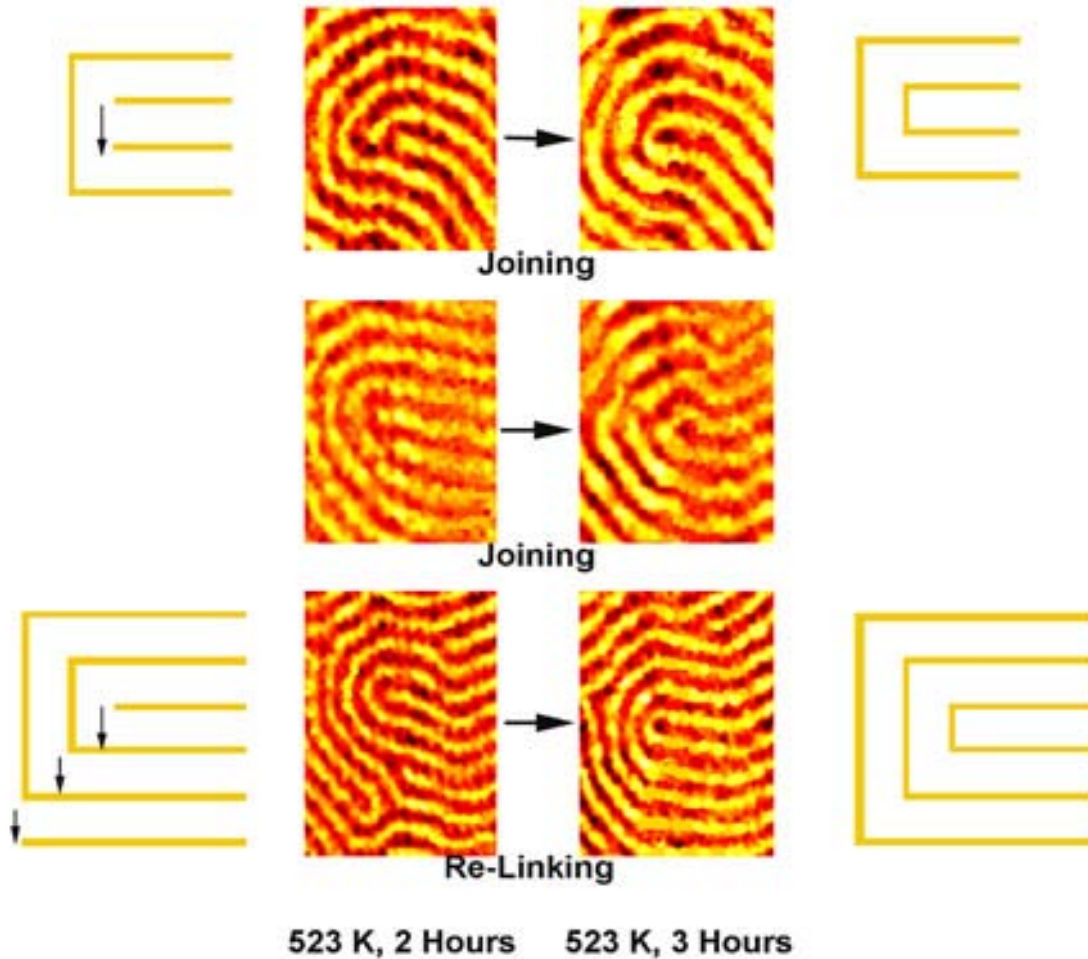
## Uniqueness of AFM imaging for polymers

- Polymer sample (like a film) may be too thick for TEM, or not conducting enough for SEM measurement;
  - The substrate (like glass or other plastic) is usually too thick for TEM to transmit electrons.
  - Coating or stain treatment (required by EM) destroys or distorts the self-assembled structures;
  - AFM does not require conductivity;
  - AFM offers *in situ* monitoring of structure change (*next two slides*);
  - AFM offers multimode scanning for different materials: tapping, FMM, LFM, **phase**.
-

# Polymer blend of PS-b-PMMA

Example #1:

In-situ imaging of nanostructure formation



Poly(methyl methacrylate)

Example #2:

**Tuning the Electrical **Conductivity** and **Self-Assembly** of Regioregular **Polythiophene** by Block Copolymerization: **Nanowire** Morphologies in New Di- and Triblock Copolymers**

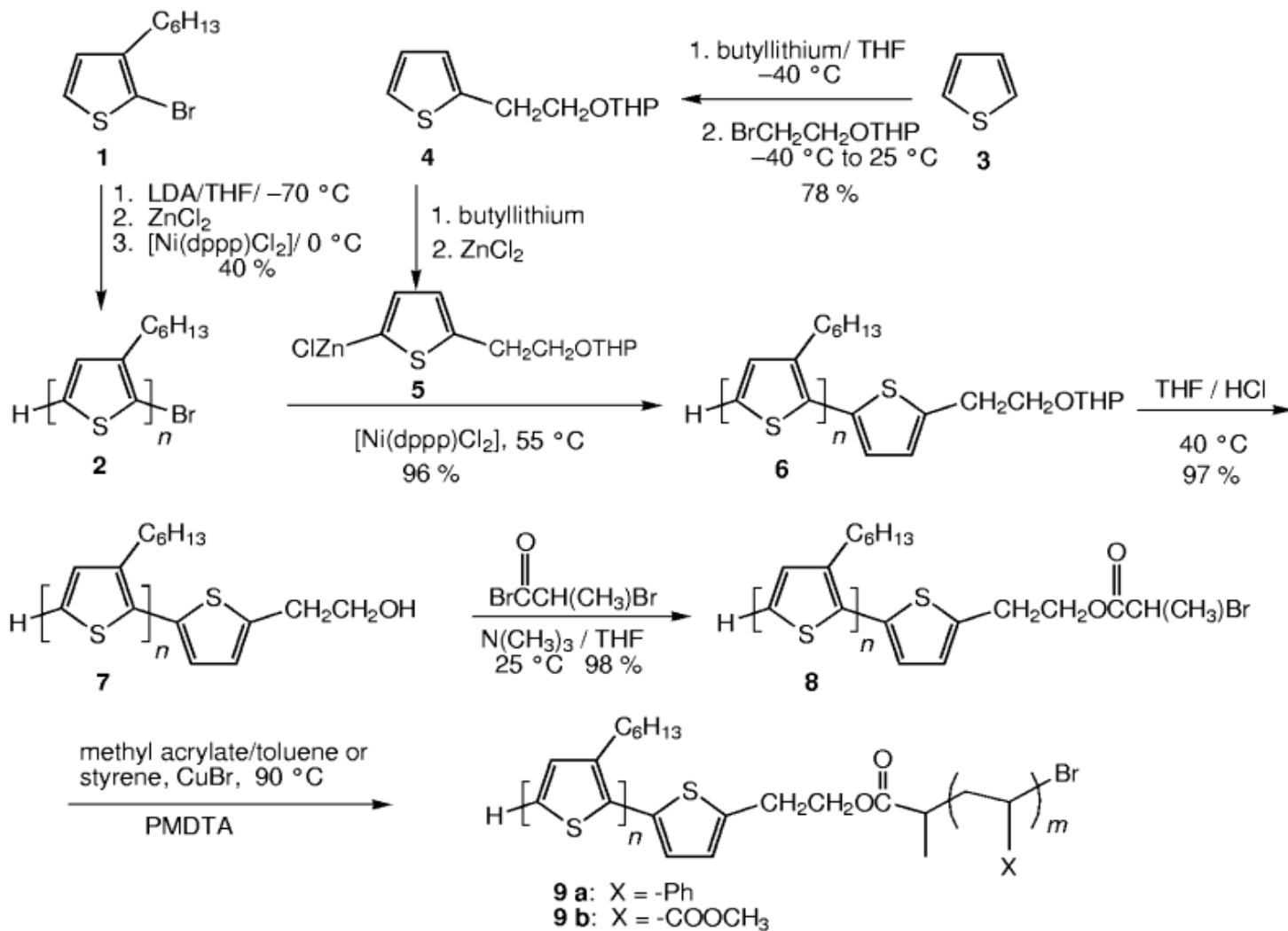
Jinsong Liu, Elena Sheina, Tomasz Kowalewski, Richard D. McCullough,

*Carnegie Mellon University, Department of Chemistry*

## Rationale

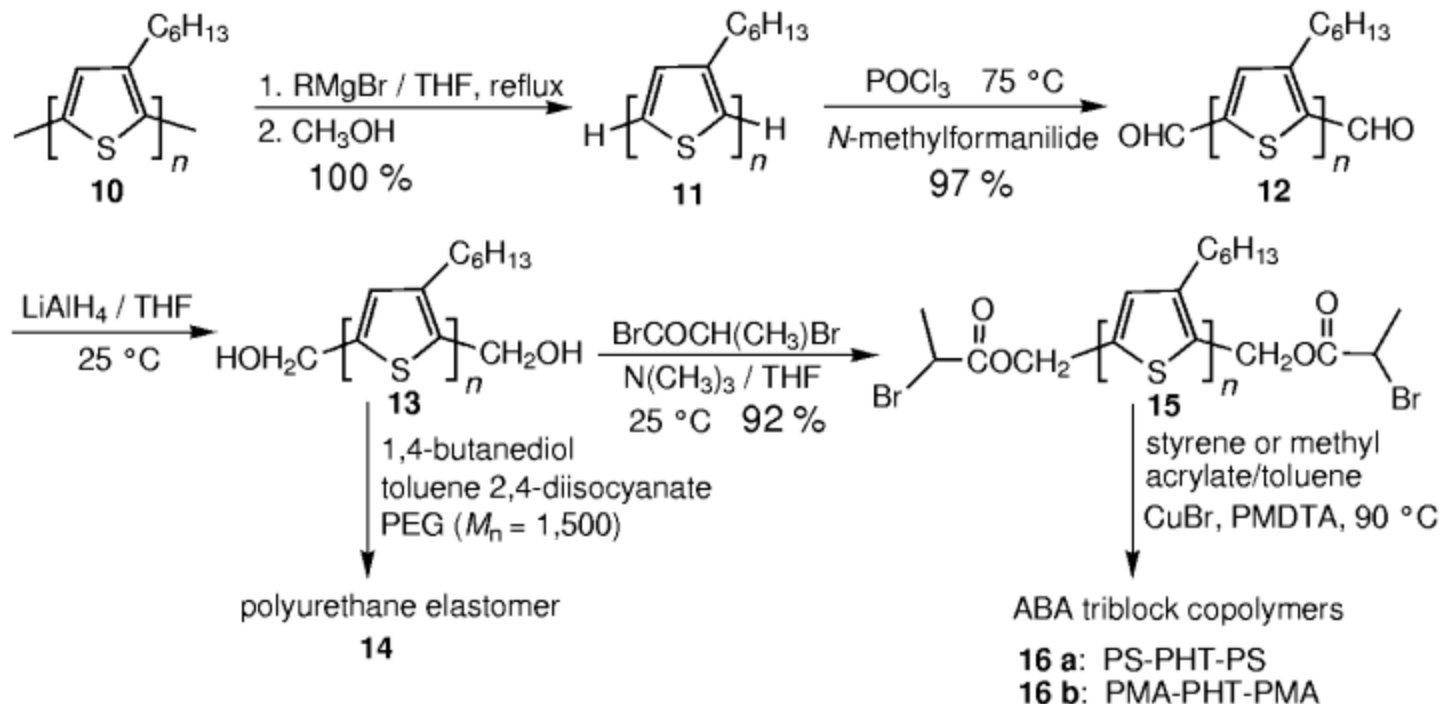
- Polythiophenes, a conjugated polymer, self-assemble into well-defined superstructures.
- Formation of ordered supermolecular structures in these **regioregular** materials correlates strongly with their excellent electrical conductivities, i.e.  $10^2 - 10^3 \text{ S cm}^{-1}$  vs. a few  $\text{S cm}^{-1}$  for **regiorandom** polymers.
- However, **regioregular** polythiophenes still have **poor mechanical and processing** properties relative to typical flexible polymers.
- One approach to solving this problem is to synthesize block copolymers that contain conducting polymer or oligomer units.
- Block copolymers self-assemble into a number of nanoscale morphologies, such as **lamellar, spherical, cylindrical, and vesicular structures**, leading to the possibility to design and fabricate new components for optoelectronic nanodevices.

# Synthesis of diblock polymers



LDA=lithium diisopropylamine, dppp =propane-1,3-diylbis(diphenylphosphane), THP=tetrahydropyran.

## Synthesis of triblock polymers

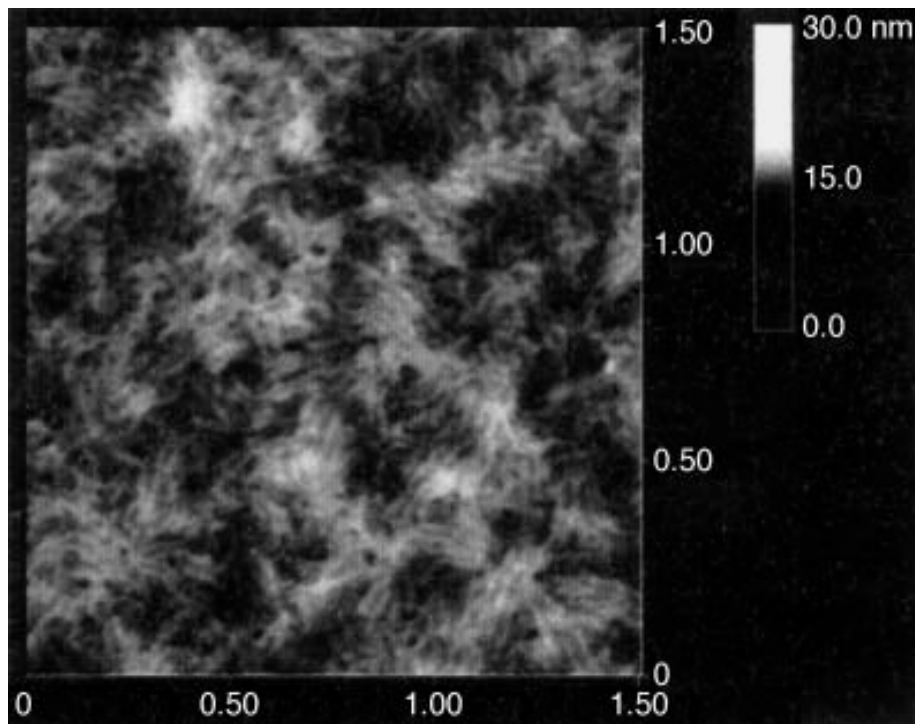


PEG=polyethyleneglycol, PMDTA=*N,N,N,N,N*-pentamethyldiethylenetriamine.

## Experimental procedure:

- Thin and ultrathin films of block copolymers containing PHT (>50%) were prepared by casting from toluene followed by free evaporation of a solvent.
- Well-defined nanowires were formed through self-assembly.
- Size of the nanowire, 30-40 nm, corresponds to a fully extended HT-PHT block.
- Lengths of nanowire were on the order of  $\mu\text{m}$ .

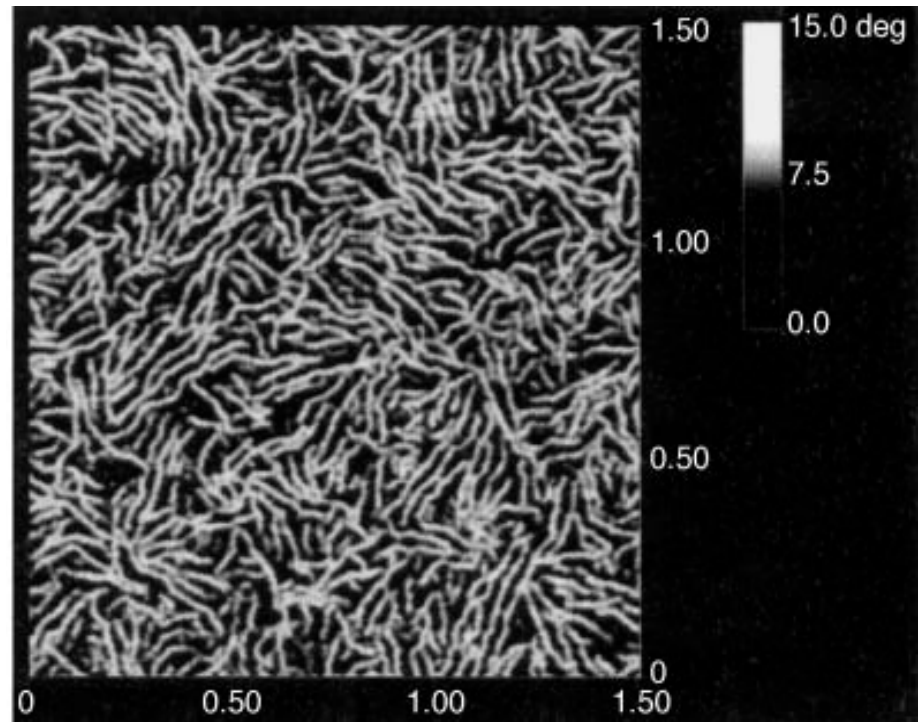
# Nanowires of poly(3-hexylthiophene)-b-poly(styrene) copolymers: PHT-PS



solvent-cast from toluene and visualized with **tapping-mode** AFM.



# Nanowires of poly(3-hexylthiophene)-b-poly(styrene) copolymers: PHT-PS

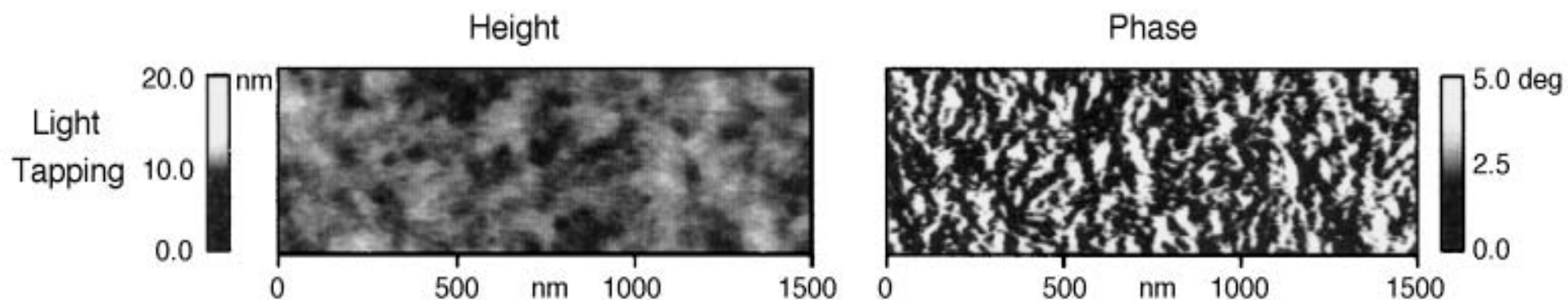


solvent-cast from toluene and visualized with **phase-mode** AFM.

## Experimental procedure:

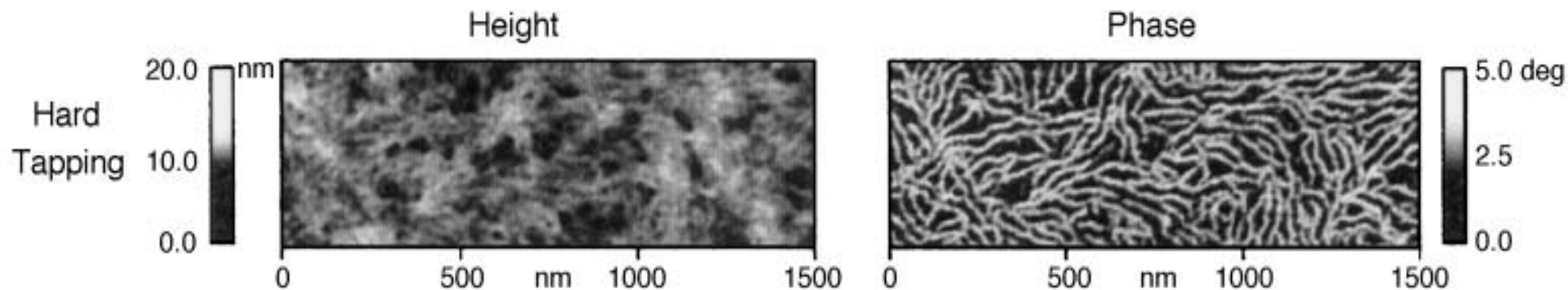
- Film of a di-block polymer, weight percentage of **PHT 37 %**, was cast from a  $0.5 \text{ mg mL}^{-1}$  solution in toluene.
- Nanowires of PS-PHT have a core-shell architecture, with the minority component (**PHT**) constituting the **core**.
- The samples were then imaged using the **variable-tapping force** tapping-mode AFM.
- Under **light tapping** conditions (**a few nN**), the tip-sample force is not high enough to **penetrate** through the outer sheath of the nanowires.
- Since the PS segments in the sheath can **mix** with the chains from **adjacent aggregates**, the **boundaries** between nanowires are **not well resolved**.
- Under hard tapping conditions (**tens to hundreds nN**), the **probe-sample force** is high enough to deform the outer sheath and **sense** the presence of a **rigid core**.

## Effect of tapping strength on AFM imaging



Under **light tapping** conditions, only the outer, partially overlapping shells of aggregates are visualized and the nanowire morphology is not apparent.

## Effect of tapping strength on AFM imaging



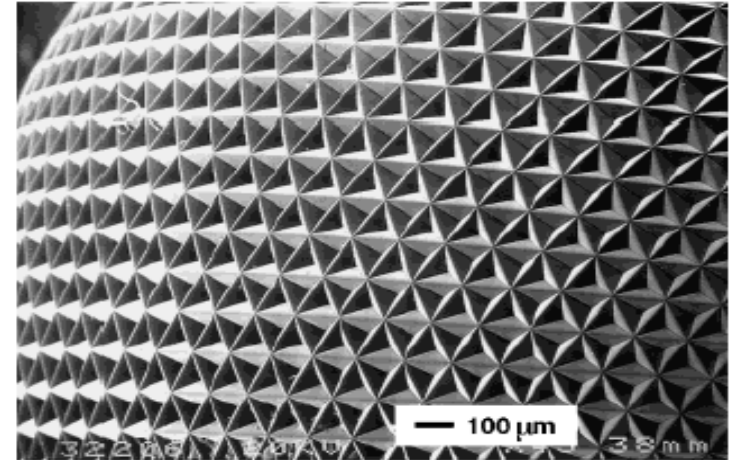
Under **hard tapping** conditions, the probe interacts with the outer shells with sufficient force to sense the presence of rigid poly(3-alkylthiophene) cores.

Example #3:

Soft Lithography:

*using a patterned elastomer as the mask, stamp, or mold.*

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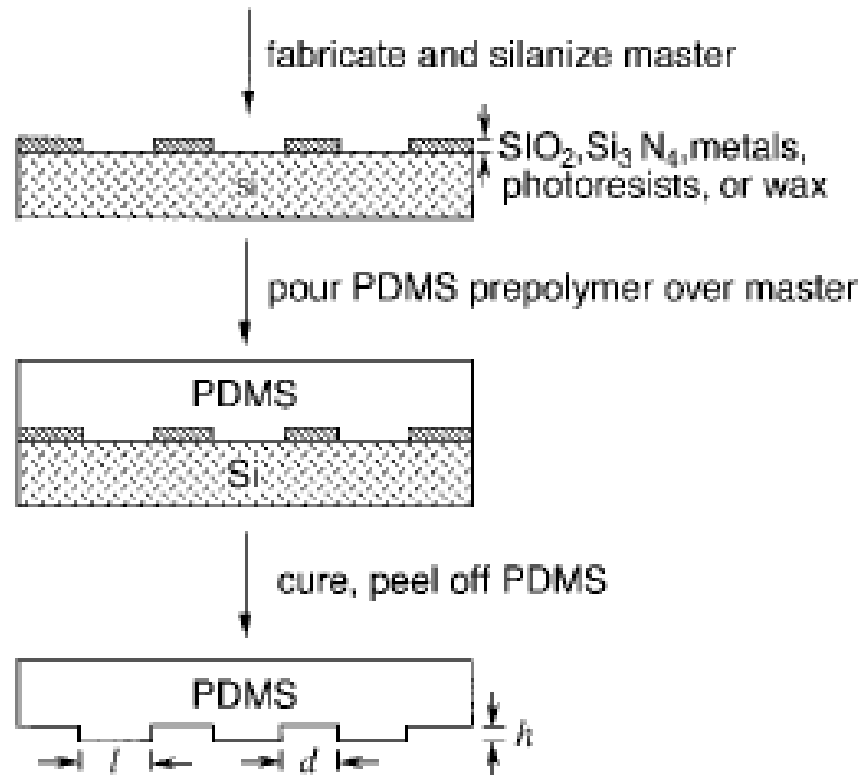
**The central point here: to understand how AFM imaging is uniquely powerful of these R & D.**

Table 1. The recent past, present, and future of semiconductor technology.<sup>[10c, 12]</sup>

Year	Lithographic method	Resolution [nm] <sup>[a]</sup>	Bits (DRAM) <sup>[b]</sup>
	<i>Photolithography (<math>\lambda</math>[nm])</i>		
1992	UV (436), g line of Hg lamp	500	16 M
1995	UV (365), i line of Hg lamp	350	64 M
1998	DUV (248), KrF excimer laser	250	256 M
2001	DUV (193), ArF excimer laser	180	1 G
2004	DUV (157), F <sub>2</sub> excimer laser	120	4 G
2007	DUV (126), dimer discharge from an argon laser	100	16 G
2010	<i>Advanced lithography</i> extreme UV (EUV, 13 nm) soft X-ray (6–40 nm) focused ion beam (FIB) electron-beam writing proximal-probe methods	< 100 <sup>[c]</sup>	> 16 G

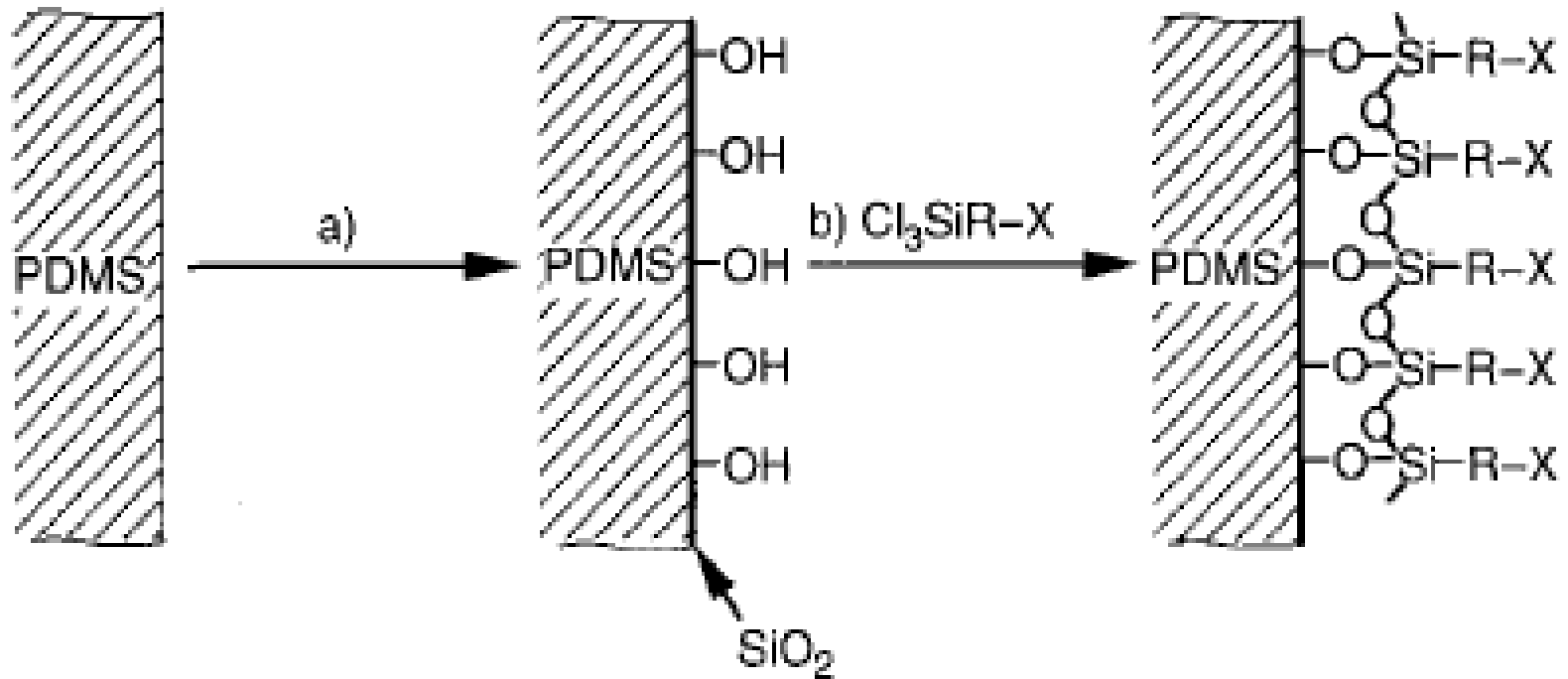
[a] The size of the smallest feature that can be manufactured. [b] The size of the dynamic random access memory (DRAM). [c] These techniques are still in early stages of development, and the smallest features that they can produce economically have not yet been defined.

## The procedure for making PDMS replicas from a master



Each master can be used to fabricate more than 50 PDMS replicas.  
 $h$ ,  $d$ , and  $l$  are  $0.2 \pm 20$ ,  $0.5 \pm 200$ , and  $0.5 \pm 200$  mm, respectively.

## modification of the PDMS surface



a) Treatment with an  $\text{O}_2$  plasma; b) reaction with silyl chloride vapor.  
Different terminal groups  $\text{X}$  of the SAMs give different interfacial properties.



## Schematic illustration of procedures for $\mu$ CP of hexadecanethiol (HDT) on a gold surface:

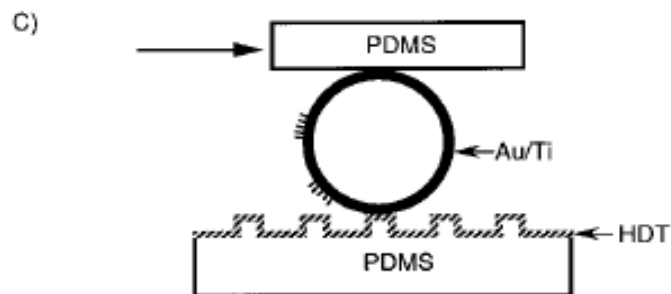
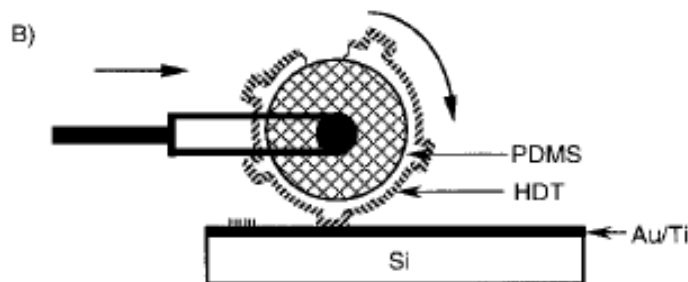
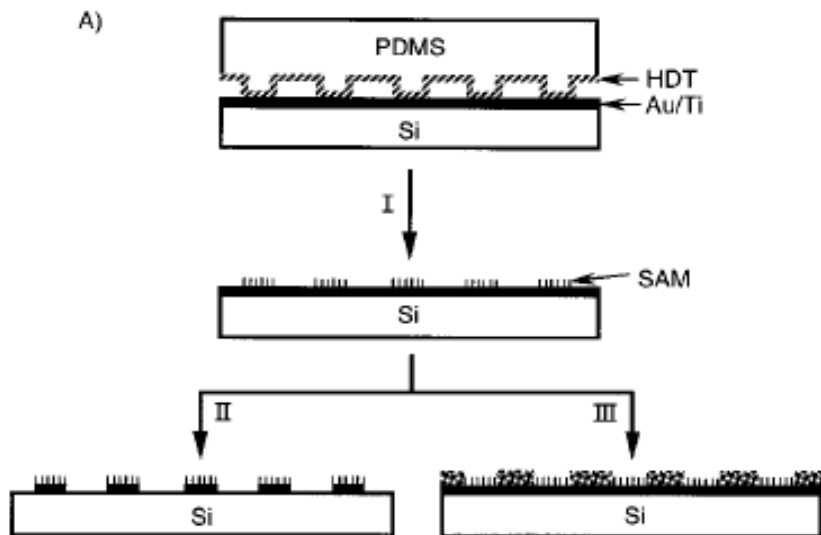
A) printing on a planar surface with a **planar stamp**:

I: printing of the SAM,  
II: etching,  
III: deposition;

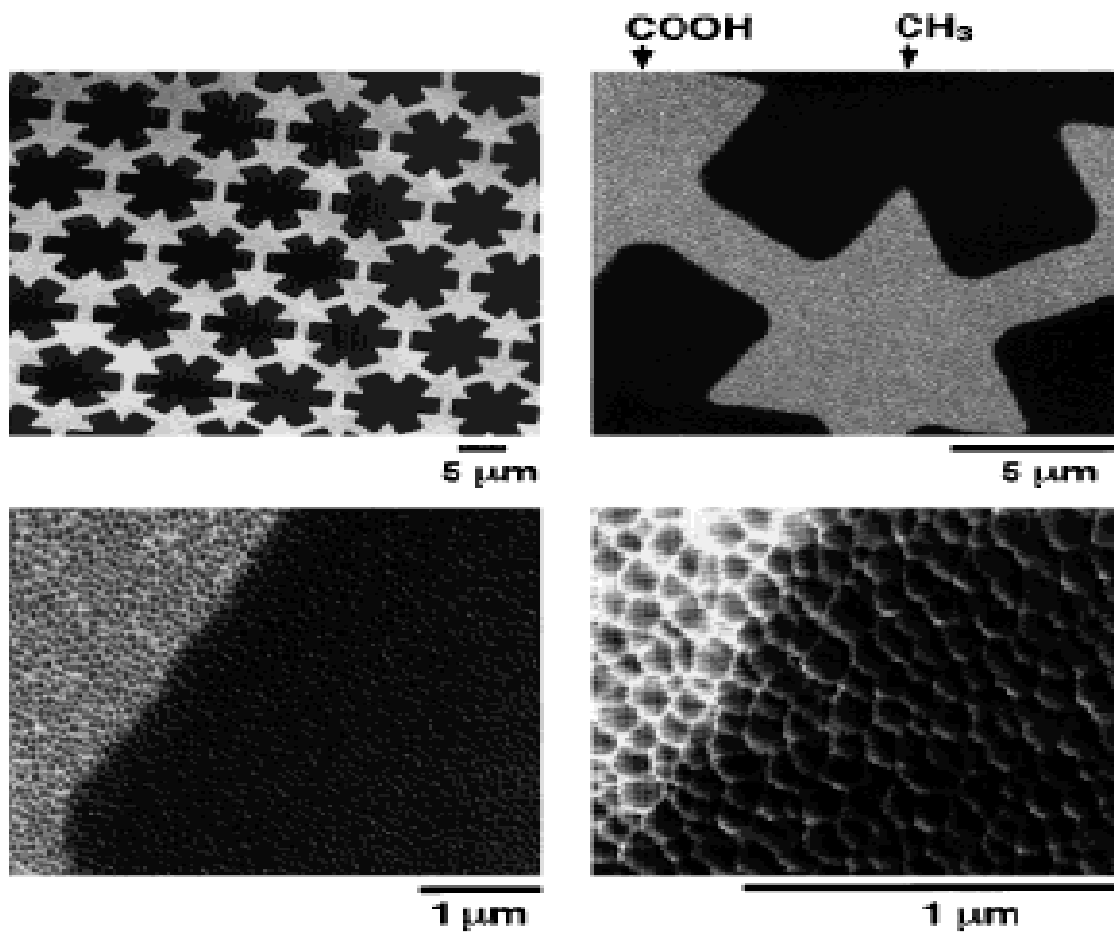
B) large-area printing on a planar surface with a **rolling stamp**;

C) printing on a **nonplanar surface** with a **planar stamp**.

*After the “ink” (ca. 2 mM HDT in ethanol) was applied to the PDMS stamp with a cotton swab, the stamp was dried in a stream of  $N_2$  (ca. 1 min) and then brought into contact with gold surface.*



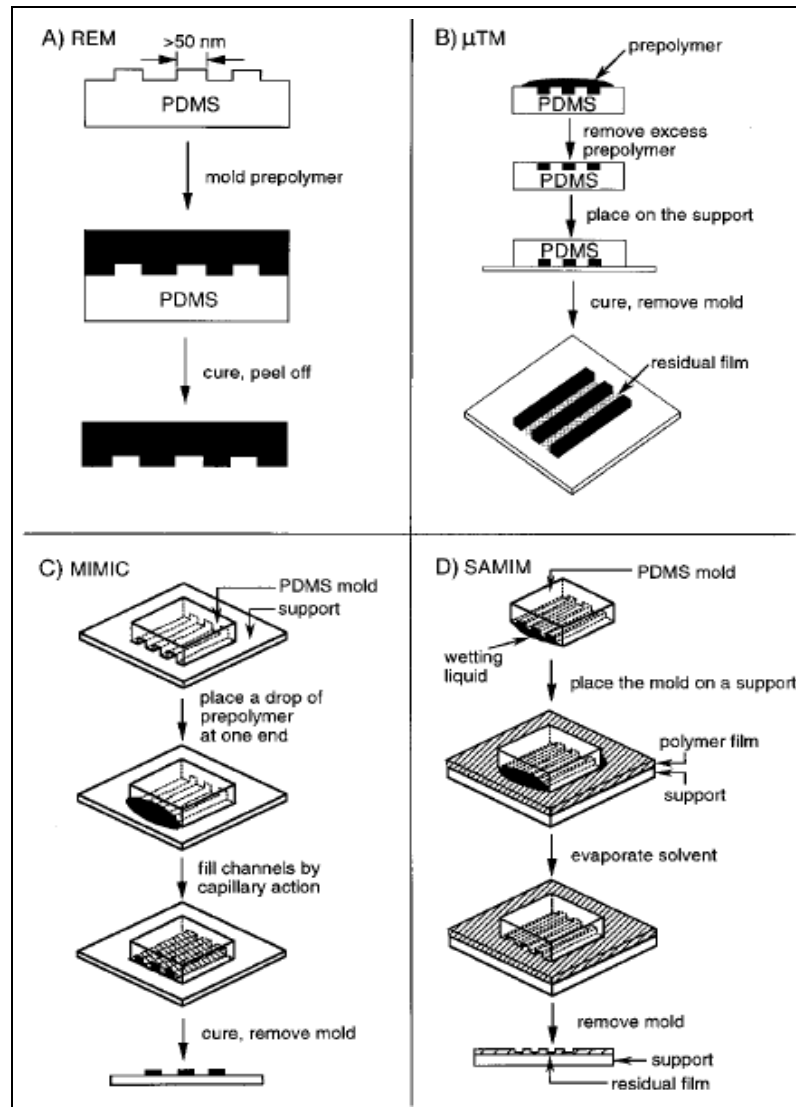
## LFM images of a gold surface patterned with SAMs



The surface was printed in HDT; the remaining regions were then derivatized with HS(CH<sub>2</sub>)<sub>15</sub>COOH by immersing the patterned sample in a solution containing the second thiol. Relatively high frictional forces in the regions covered with a COOH terminated SAM (light), and relatively low frictional forces in the regions covered with a CH<sub>3</sub> terminated SAM (dark).

# Different molding methods for surface patterning

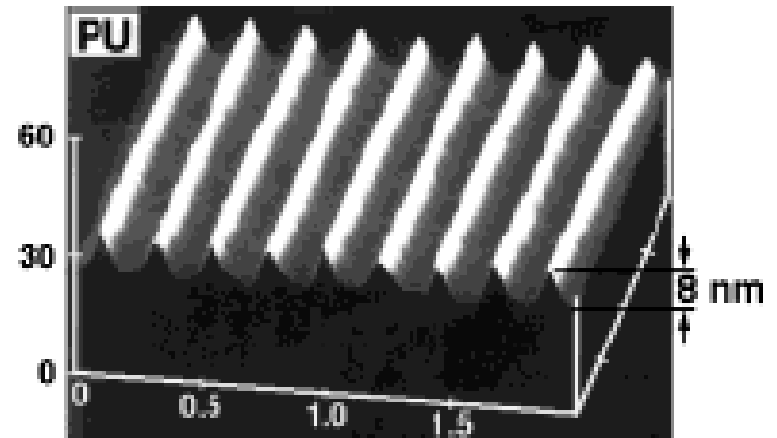
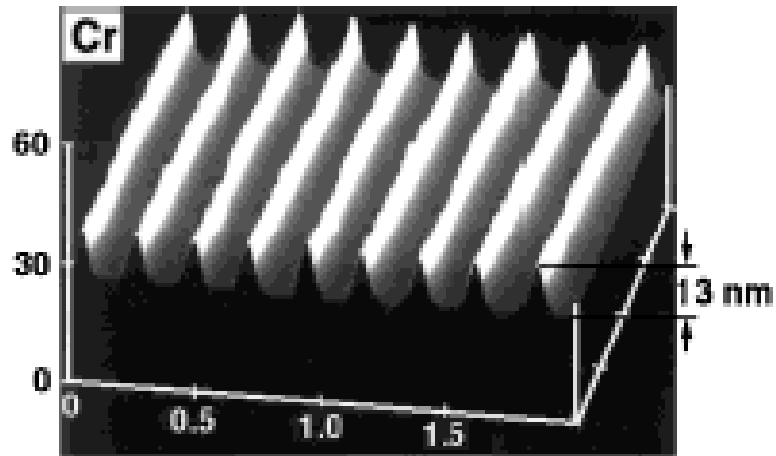
Replica  
molding,



Microtransfer  
molding

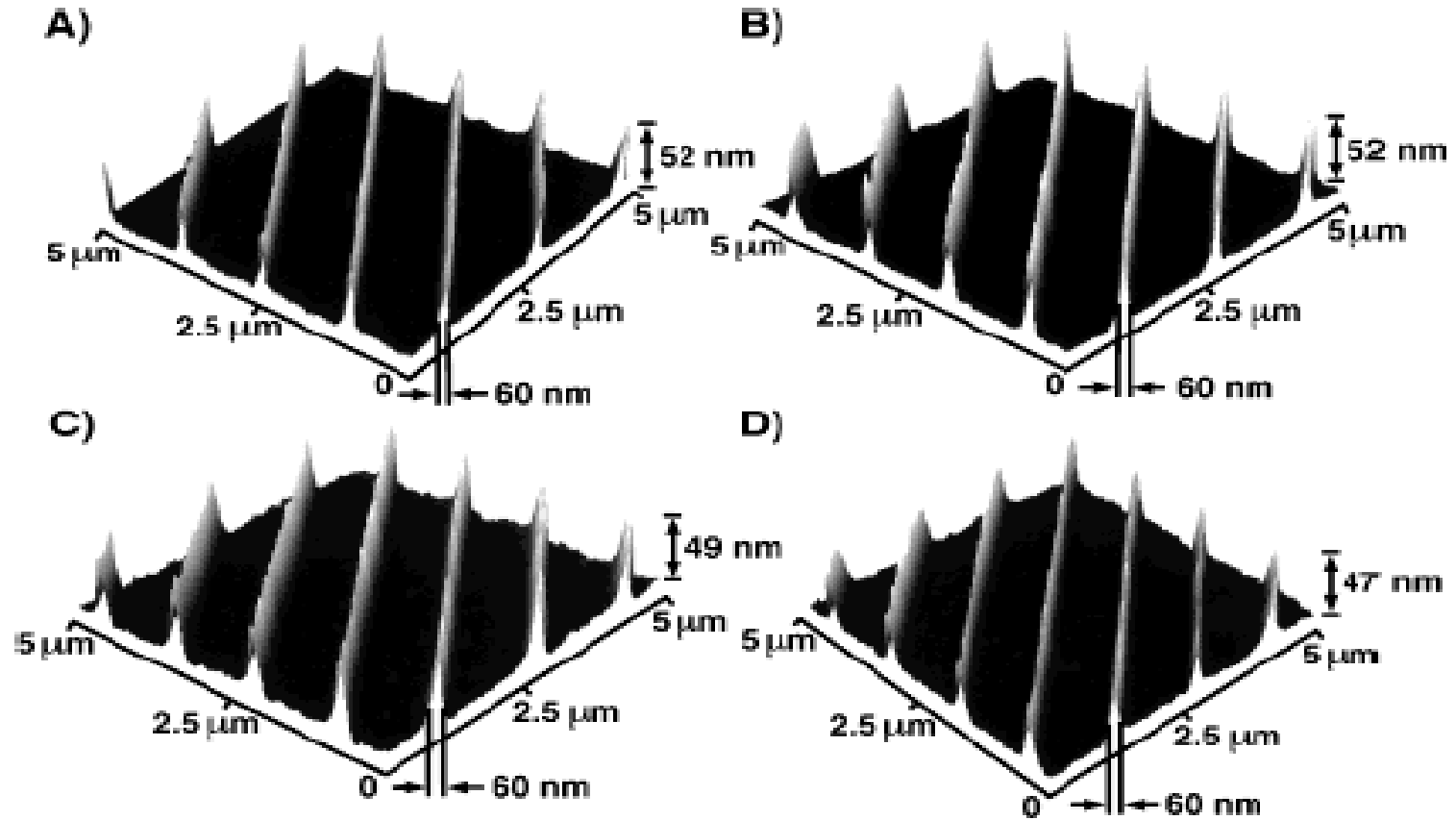
Micromolding  
in capillaries

Solvent assisted  
micromolding



**Left:** AFM images of chromium structures on a master;

**Right:** a PU (polyurethane) replica prepared from a PDMS mold cast from the master.



Top: AFM images of gold structures on a master

**A)**, before it was used to cast PDMS molds; **B)**, after being used to cast seven PDMS molds.

Bottom: AFM images of PU replicas produced from *different PDMS* molds cast from this master.

# Advantages of soft lithography.

- Convenient, inexpensive, accessible to chemists, biologists, and material scientists.
- Basis in self-assembly tends to minimize certain types of defects.
- Many soft lithographic processes are additive and minimize waste of materials.
- Readily adapted to rapid prototyping for feature sizes  $>20\ \mu\text{m}$ .
- Isotropic mechanical deformation of PDMS mold or stamp provides routes to complex patterns.
- No diffraction limit; features as small as 30 nm have been fabricated.
- Nonplanar surfaces (lenses, optical fibers, and capillaries) can be used as substrates.
- Generation and replication of three-dimensional topologies or structures are possible.
- Optical transparency of the mask allows through-mask registration and processing.
- Good control over surface chemistry, very useful for interfacial engineering.
- A broad range of materials can be used: functional polymers, sol-gel materials, colloidal materials, suspensions, solutions of salts, and precursors to carbon materials, glasses, and ceramics.
- Applicable to manufacturing: production of indistinguishable copies at low cost.
- Applicable in patterning large areas.

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## Disadvantages of soft lithography.

- Patterns in the stamp or mold may distort due to the deformation (peeling, sagging, swelling, and shrinking) of the elastomer used.
- Difficulty in achieving accurate registration with elastomers ( $<1\ \mu\text{m}$ ).
- Compatibility with current integrated-circuit processes and materials must be demonstrated.
- Defect levels higher than for photolithography.
- $\mu\text{CP}$  works well with only a limited range of surfaces; MIMIC is slow;
- leave a thin film of polymer over the surface.

*MIMIC: micromolding in capillaries; REM: replica molding;  $\mu\text{TM}$ : microtransfer molding; SAMIM: solvent-assisted micromolding.*

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