UNIVERSITÀ DEGLI STUDI DI TRIESTE

DSCF Dipartimento di Scienze Chimiche e Farmaceutiche

CORSO DI LAUREA MAGISTRALE in CHIMICA

MATERIALI ORGANICI

Prof. Lucia Pasquato

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6 CFU

Anno Accademico 2026/2027

CONTENTS

- introduction to molecular and supramolecular organic material
  - supramolecular chemistry
  - weak interactions
- self-assembled monolayers in 2-D and in 3-D
  - functionalization of the surface
  - Cycloaddition reactions
  - Click Chemistry
  - Methatesis reactions
  - control of the monolayer morphology
  - applications
- organic semiconductors
  - definition, examples
- fullerenes, carbon nanotubes, graphene, other carbon (nano)materials
  - properties, preparation, functionalization and applications
- Metal Organic Frameworks and Covalent Organic Frameworks

TEACHING MATERIALS

1. files of the teachers, slides on Moodle

2. scientific papers from literature

3. registerd lectures

Books related to the course

March, Advanced Organic Chemistry – available for students in the library

F. A. Carey, R. J. Sundberg Advanced Organic Chemistry Part B – in the library

suggested literature

SCHEDULE

Classes: 4 hours per week

Tuesday 11:15 – 13:00 room A7
Wednesday 9:15 – 11:00 room A6

Building C11

The lectures of October 20, 21 and 27 will be delivered by professor Francesco Stellacci, EPFL

students may contact the teacher by
e-mail: lpasquato@units.it asking for a meeting

ASSESSMENT OF THE KNOWLEDGE/EXAM

1. The assesment of the knowledge will be based on an **oral examination**
To this aim a scientific papers, from the literature will be assigned to the student on a specific topic selected by the student among those of the programme. (please contact the professor at least 15 days before the exam for the assignement of the paper).

2. The presentation, 15 minutes, must contain: the title of the paper and the complete reference, a short introduction, the claim of the paper, a critical description of the results and the conclusion.
Personal comments are appreciated.

3. The assesment will continued with some questions on the publication presented and completed with questions on 3 different arguments of the programme.

MATERIALI ORGANICI

Principali pregi

- possibilità di design strutturale infinita
- versatilità della struttura e della sintesi: custom-tailoring
- modulazioni delle caratteristiche strutturali ed elettroniche: molecular engineering
- proprietà e prestazioni interessanti
- diverse morfologie: cristalli amorfi, polveri, film,...
- compatibilità con le attuali tecnologie di manipolazione dei materiali
- produzione su grossa scala, basso costo

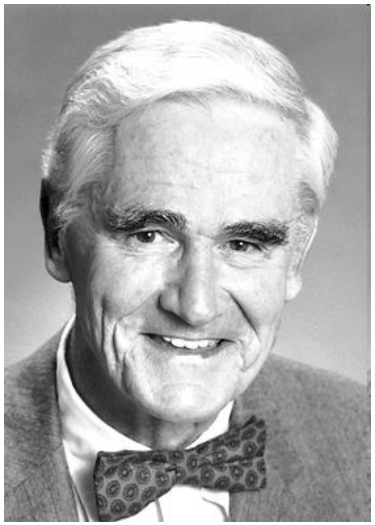
Principali limiti

- stabilità chimica, termica e fotochimica
- solubilità e compatibilità
- resistenza meccanica

Materiali supramolecolari organici

molecular self-assembly: organizzazione di molecole che si basa su ***interazioni deboli***, legami ionici, ad idrogeno, non-covalenti e metallo-legante.
Porta ad ottenere sistemi con strutture e proprietà che non sono presenti nei singoli componenti.

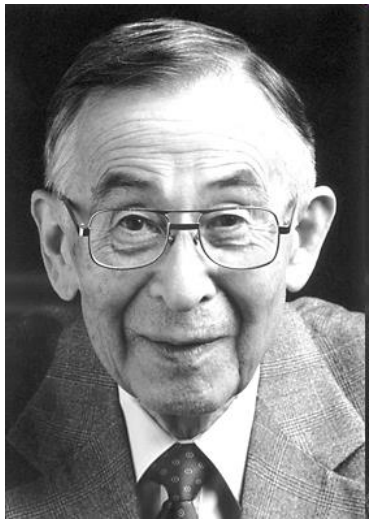
Questa è la **chimica supramolecolare** sviluppata da:
Donald J. Cram,
Jean-Marie Lehn,
and Charles J. Pedersen
che per questo sono stati insigniti del Premio Nobel per la Chimica nel 1987.



Donald J. Cram



Jean-Marie Lehn



Charles J. Pedersen

molecular machines

The Nobel Prize in Chemistry 2016



Jean-Pierre Sauvage



Sir J. Fraser Stoddart



Bernard L. Feringa

"for the design and synthesis of molecular machines".

self-assembly and self-organization

We define self-assembly as the process via which molecules come together to produce a supramolecular object.
This process may occur in solution, including water, or in solid state.

When this event provides to form an order, functional and dynamic structure or pattern without external control the process is called self-organization.

Nanomaterials - What is nano?

nano deriva dal greco *νανο*

Nanoscience refers to the science and manipulation of chemical and biological structures with dimensions in the range from 1-100 nanometers.

Nanoscience building blocks may consist of anywhere from a few hundred atoms to millions of atoms. On this scale, new properties (electrical, mechanical, optical, chemical, and biological) that are fundamentally different from bulk or molecular properties can emerge.

Nanoscience is about creating new chemical and biological nanostructures, uncovering and understanding their novel properties, and ultimately about learning how to organize these new nanostructures into larger and more complex functional structures and devices.

Nanoscience is a new way of thinking about building up complex materials and devices by exquisite control of the functionality of matter and its assembly at the nanometer-length scale.

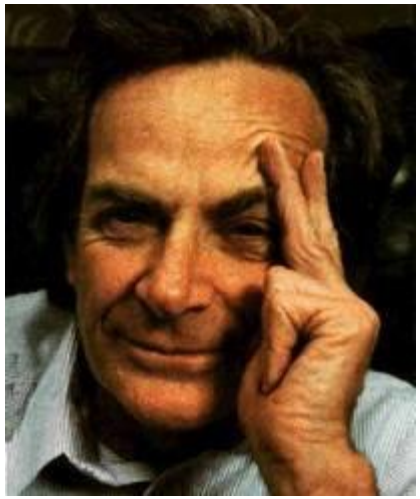
Nanoscience inherently bridges disciplinary boundaries. The "nano" length scale requires the involvement of chemical concepts at the atomic and molecular level.

NANOMATERIALS

definition

size In the scientific community, it is commonly used to designate structures at least 1 nm but less (often much less) than 1μm. However, semantics apart, there is another requirement that is commonly accepted for inclusion in the "nanoclub"; **the structure should be artificially made**. Note that the word 'structure' is deliberately used: macromolecules, for example, can justifiably be considered to be nanomaterials, yet they are not usually so classified.

- "what is so special about nanomaterials"?



In December of **1959**, the eminent physicist **Richard Feynman** (1965 Physics Nobel Prize) described the future in a groundbreaking talk entitled "**Plenty of Room at the Bottom** " about the physical possibilities for "making, manipulating, visualizing and controlling things on a small scale," and imaging that in decades to come, it might be possible to arrange atoms " the way we want."

"*Why cannot we write the entire 24 volumes of the Encyclopaedia Brittanica on the head of a pin? "*
"*..... and there is no question that there is enough room on the head of a pin to put all of the Encyclopaedia Brittanica.*"

NANOMATERIALS

- What properties or behavior can nanomaterials exhibit that they would not do if they were not so small?

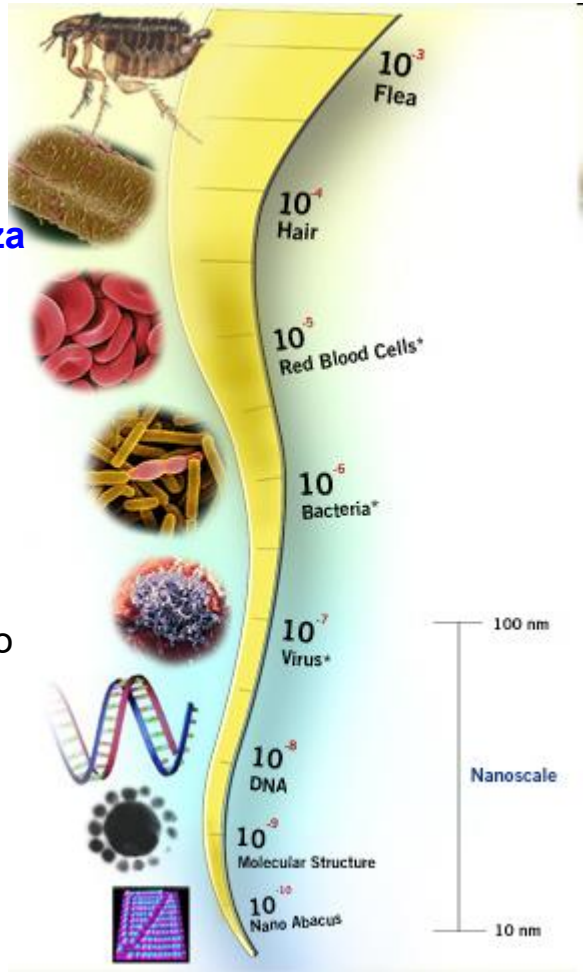
Table 1. Different size-related phenomena. The length scales are a rough estimation of the size below which the phenomenon can be observed (for the last three phenomenon, typical values of the sizes—screening lengths and ballistic transport in particular—can vary over orders of magnitude).

Phenomenon	Typical length scale
Size quantization	tens of nanometers
Crystal phase	tens of nanometers
Doping/defects	tens of nanometers
Single-charge effects	ca. 50 nm (at room temperature)
Charge depletion (screening length)	ca. 100 nm
Scattering/interference of light	hundreds of nanometers
Ballistic electron transport	hundreds of nanometers

Nanoscale

Nanoscale objects have at least one dimension (height, length, depth) that measures between 1 and 999 nanometers (1-999 nm).

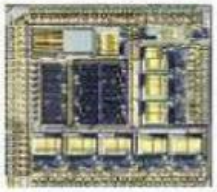
unità di misura	*abbreviazione*	*descrizione*
metro	**m**	**unità base SI della lunghezza**
centimetro	cm	$1x10^{-2}$ m (0.01 m)
millimetro	mm	$1x10^{-3}$ m (0.001 m)
micrometro	μm	$1x10^{-6}$ m
nanometro	nm	$1x10^{-9}$ m la billionesima parte di 1 metro o 10 Å

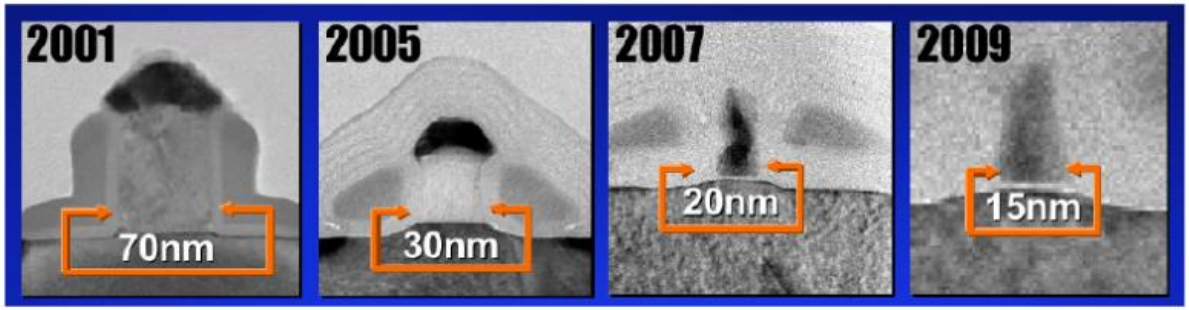


Why Nano?

Much of the motivating force and technology for nanotechnology came from integrated circuit industry







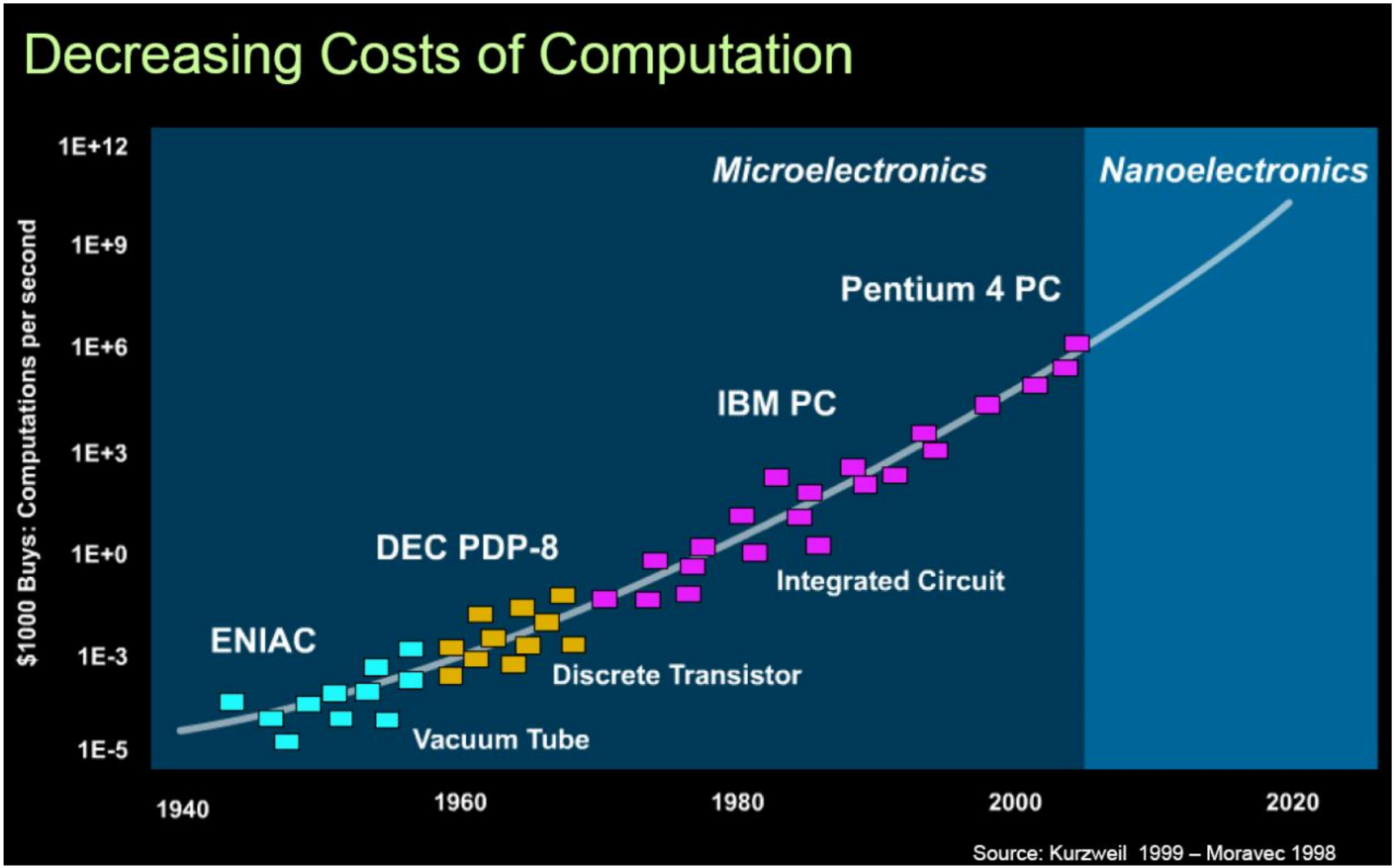
Intel's transistors

As with the fabrication of integrated circuits, nanotechnology is based on building structures and systems at very small sizes

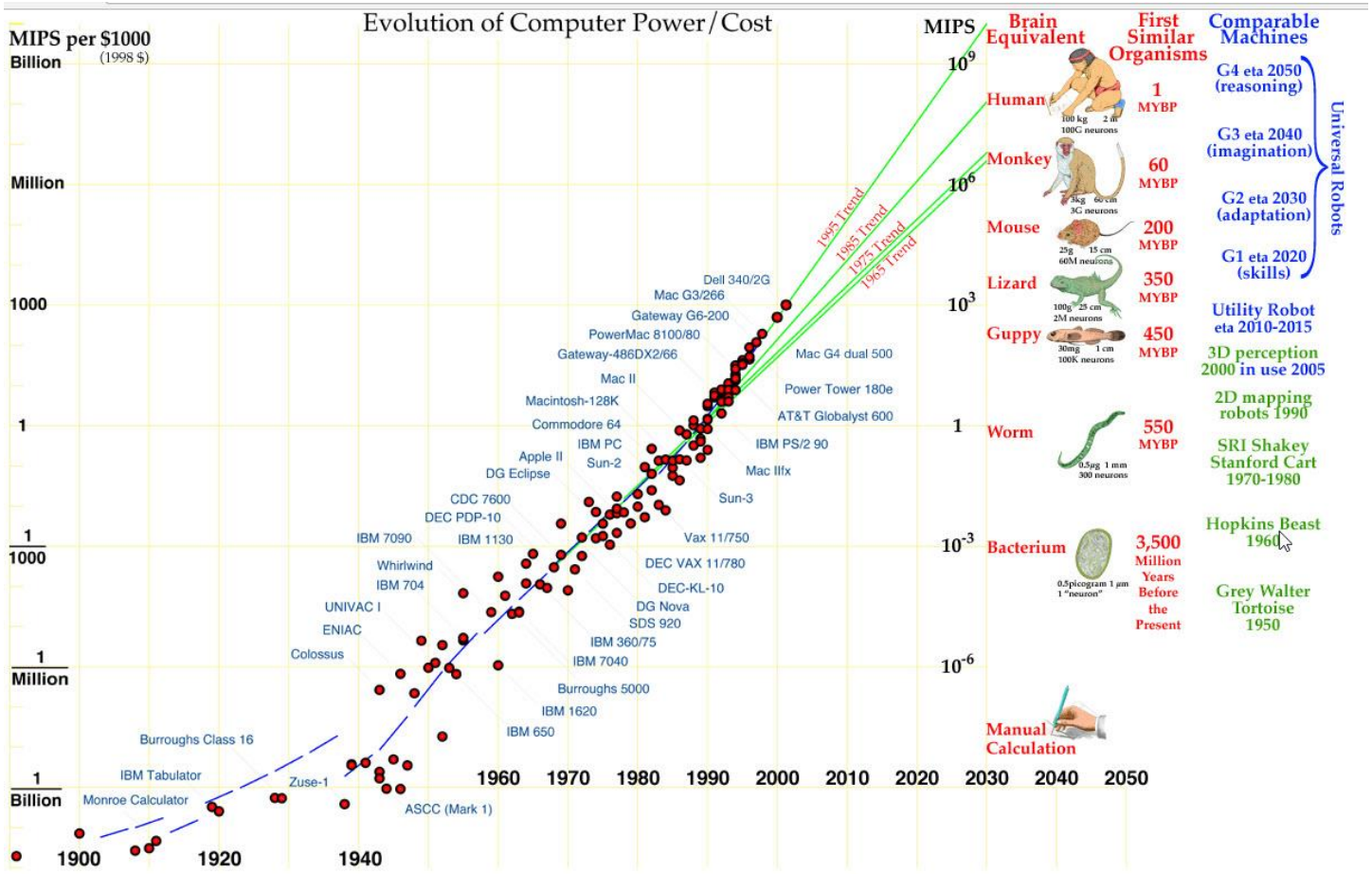
- to enhance performance and produce new properties and applications

- for many types of systems (mechanical, biological, chemical, optical) in addition to electronic

Why Nano?

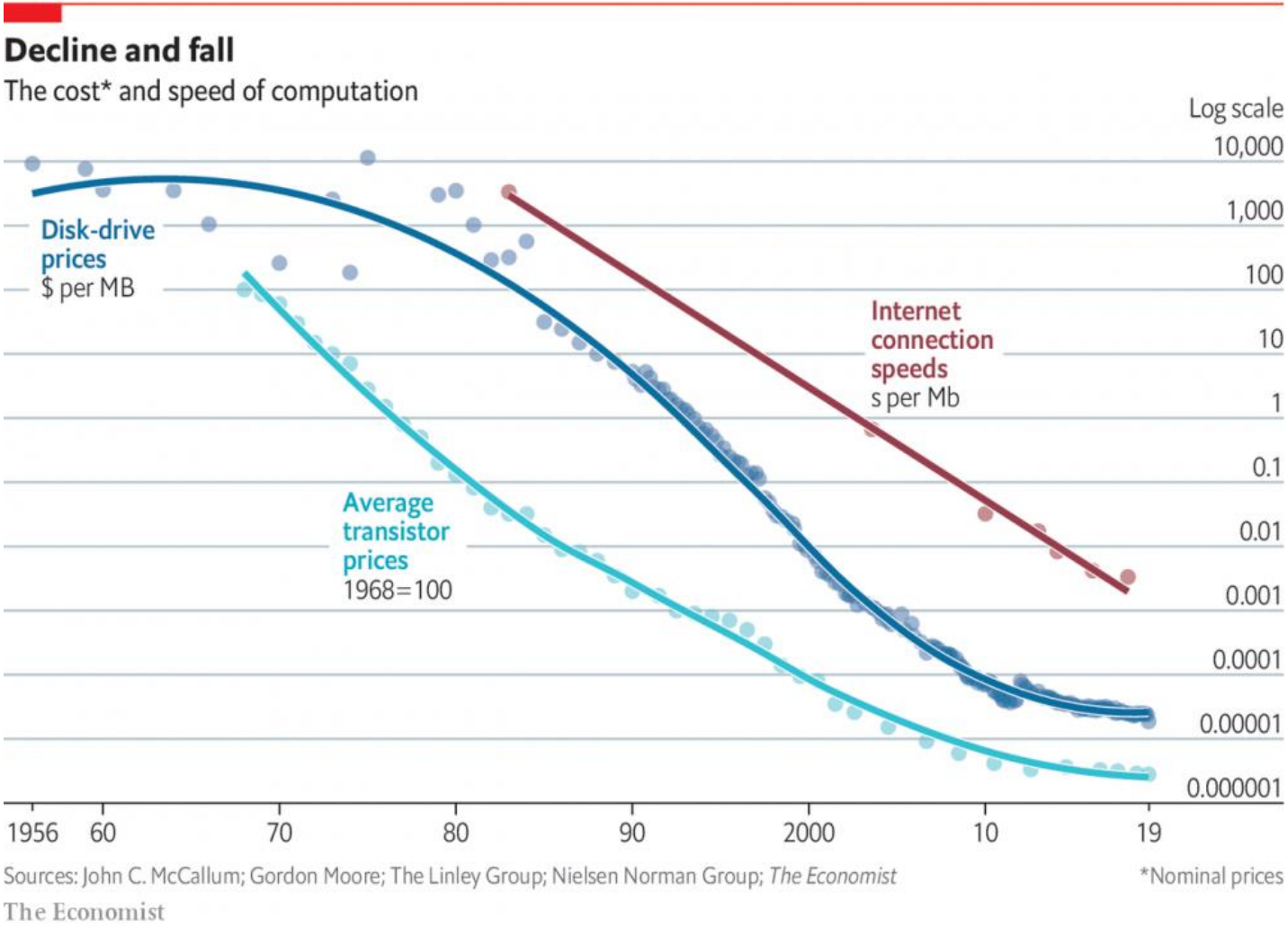

Decreasing Costs of Computation
$1000 Buys: Computations per second
1E+12
1E+9
1E+6
1E+3
1E+0
1E-3
1E-5
Microelectronics
Nanoelectronics
Pentium 4 PC
IBM PC
DEC PDP-8
Integrated Circuit
ENIAC
Discrete Transistor
Vacuum Tube
1940
1960
1980
2000
2020
Source: Kurzweil 1999 – Moravec 1998

Evolution of computer power



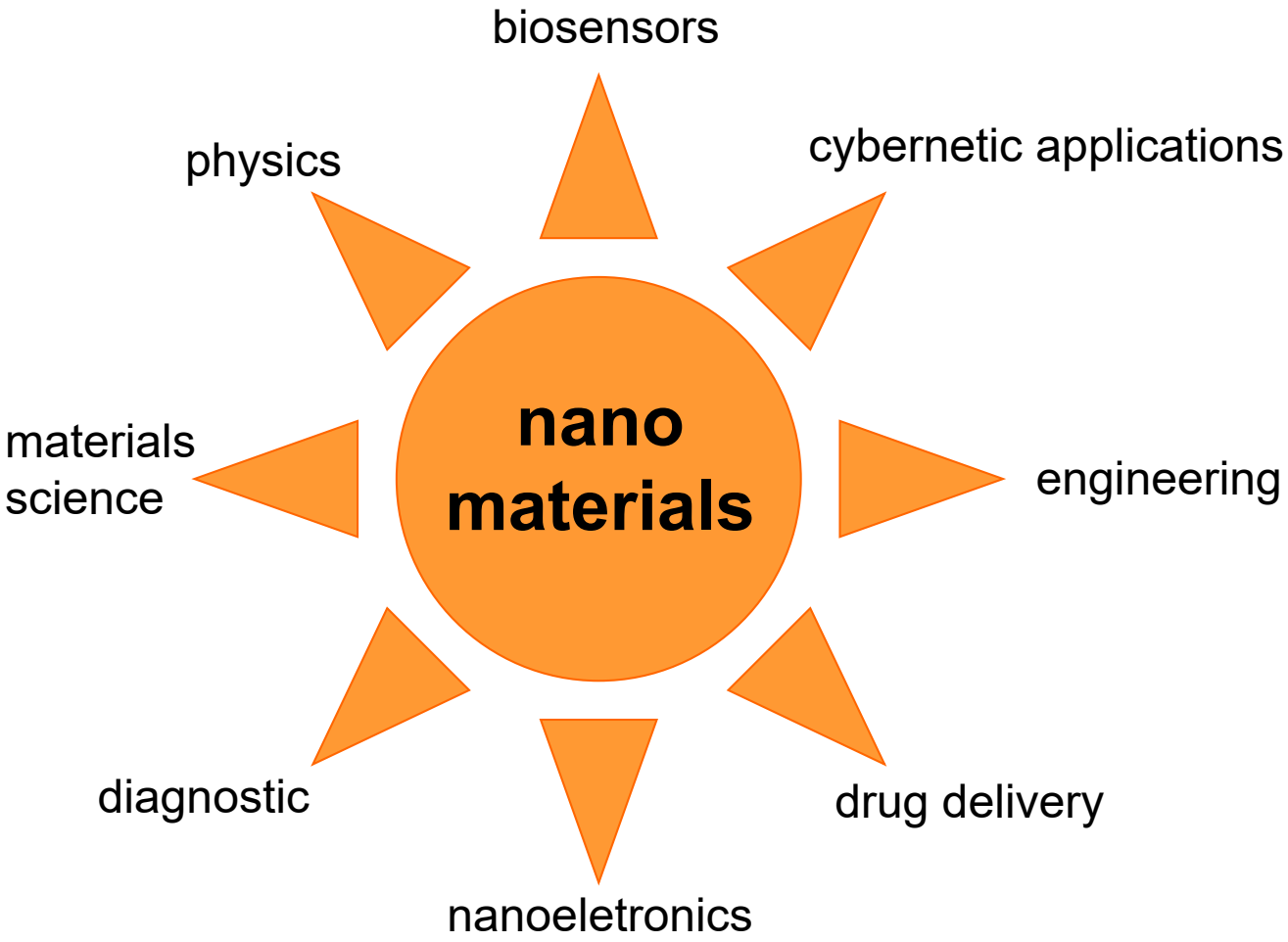
Cielotech Online – WordPress.com

MIPS: millions of instructions per second



The Economist: The price of computation today is roughly one hundred-millionth what it was in the 1970s, when the first microprocessors became commercially available (see chart). According to figures collected by John McCallum, a computer scientist, a megabyte of data storage in 1956 would have cost around $9,200 ($85,000 in today's prices). It now costs just $0.00002.

design, creation and characterization of nanostructures and nanostructured materials



Nanotechnology

Nanotechnology is …

…research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 –100 nm …

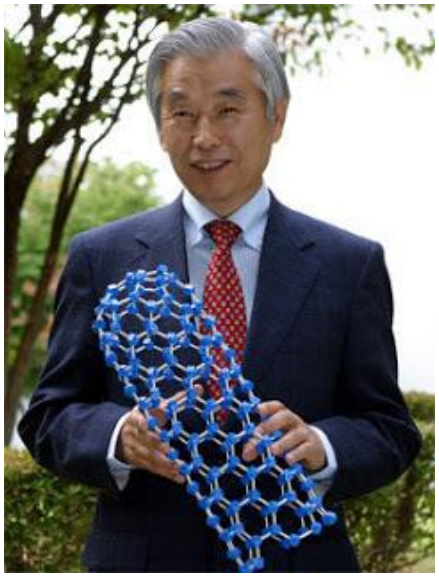
National Science Foundation

National Nanotechnology Initiative, which defined nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers.

Nanotechnology encompasses the understanding of the fundamental physics, chemistry, biology and technology of nanometre-scale objects.

How it Started

In **1974** Professor **Norio Taniguchi,** of the Tokyo Science University, introduced the term "**nanotechnology"** to describe a process exhibiting characteristic control on the order of a nanometer: "Nano-technology' mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule."



Prof. Kim Eric Drexler (MIT) is also a pioniering of Nanotechnology. He used the term "nanotechnology" in his 1986 book *Engines of Creation: The Coming Era of Nanotechnology.*

Nanochemistry:

the whole chemical processes that enable to build nanomaterials from simple building blocks and the study of the chemical properties and reactivity of the nanomaterial.

Organic Materials

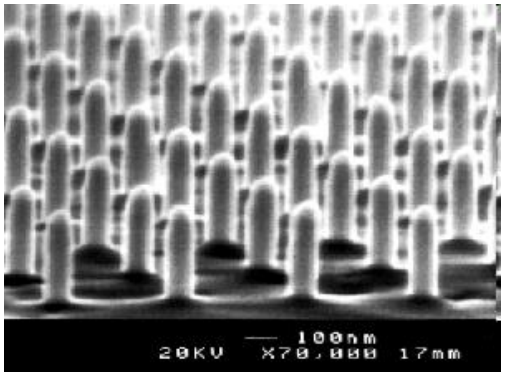
synthetic approaches

top-down approach: make a smaller object from a larger one
This approach enable to reach materials in the size 10-100 nm.









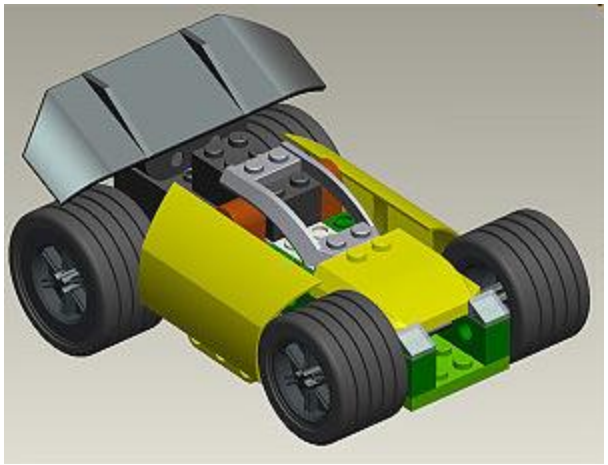
many devices are obtained with this approach with a fine control of the miniaturization processes.

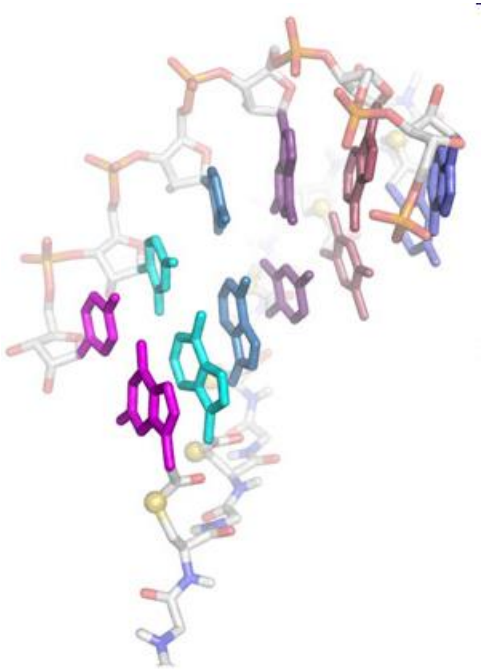
Organic Materials

synthetic approaches

approach **bottom up**: to build from the bottom: use of
"building blocks", to be assembled or self-assembled
in order to obtain the new material.







2D-Self-Assembled Monolayers

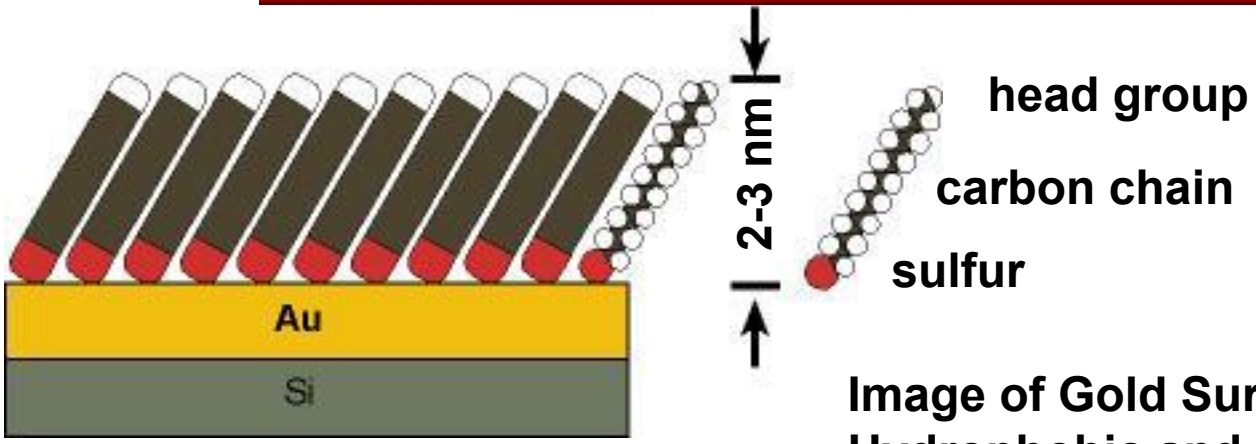
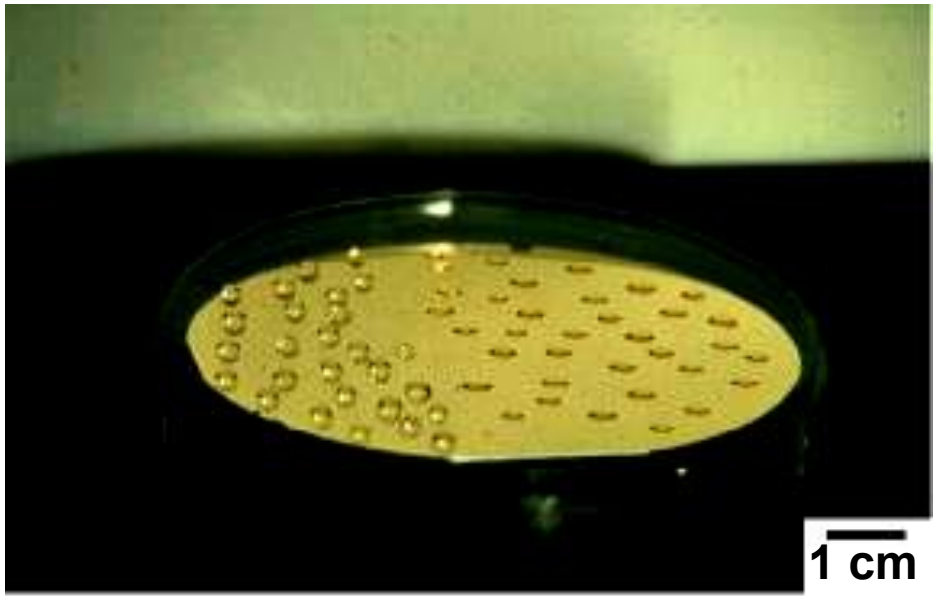
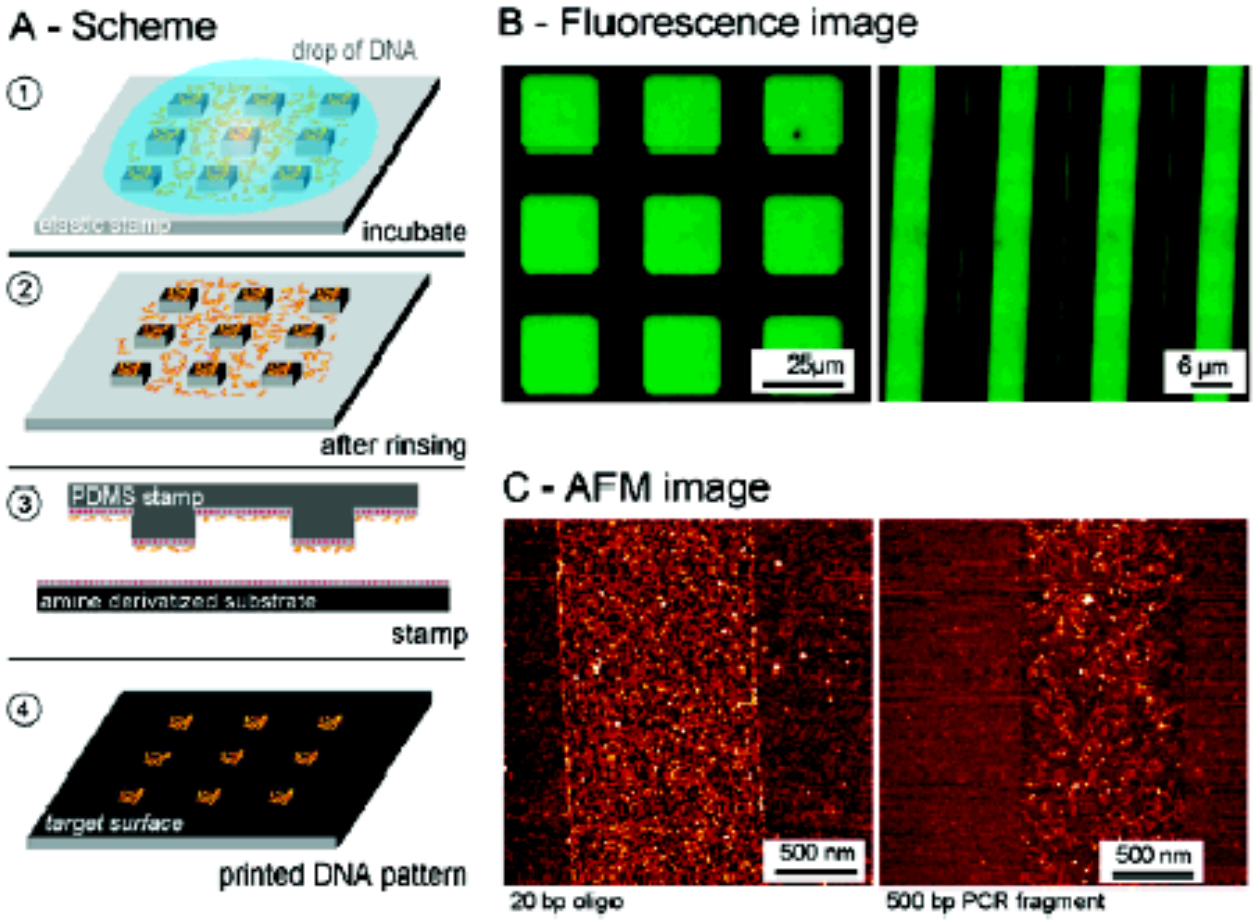


Image of Gold Surface Patterned with Hydrophobic and Hydrophilic SAMs

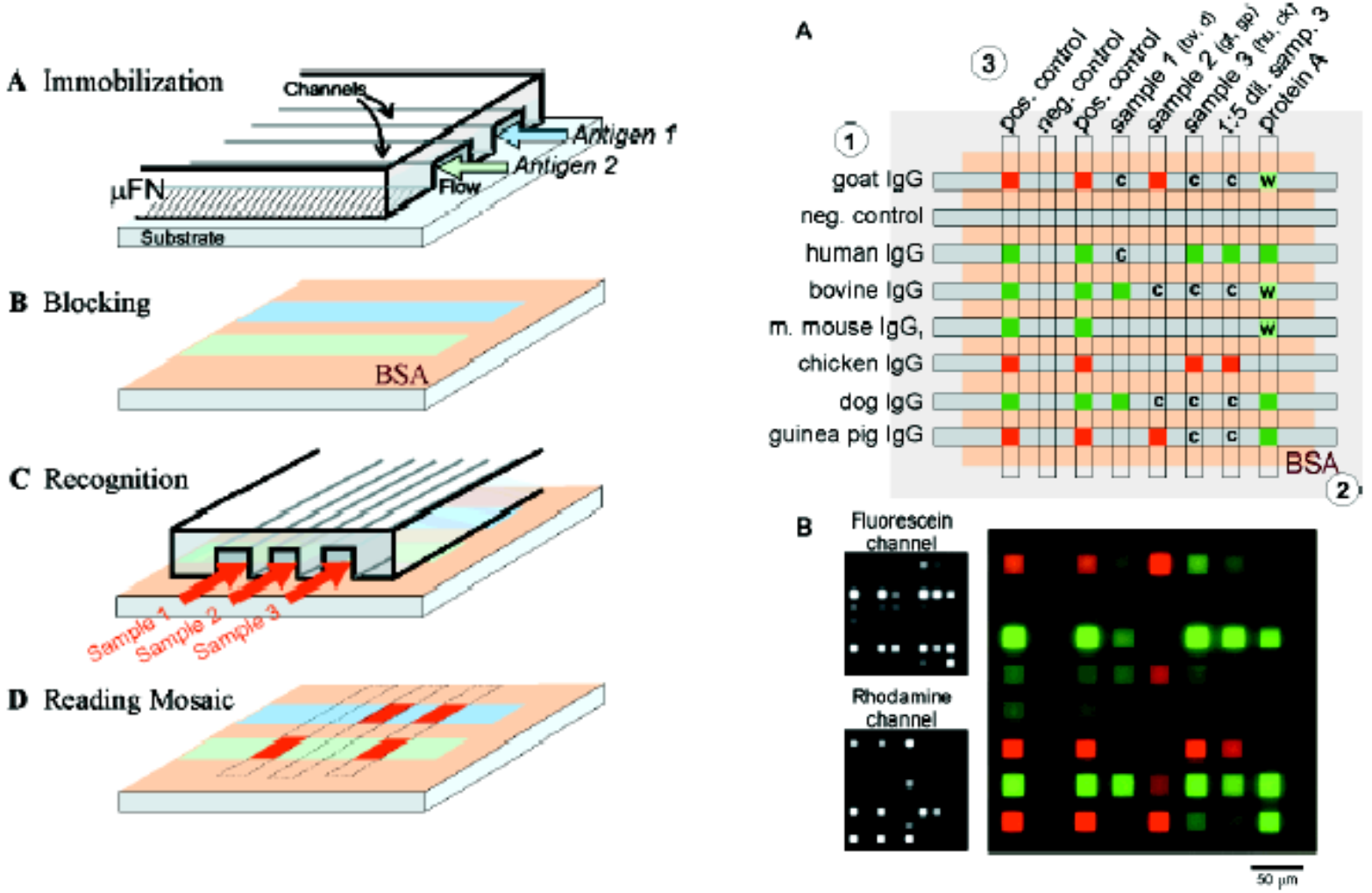


Microcontact Printing DNA



S.A. Lange, V. Benes, D.P. Kern, J.K.H. Horber, A. Bernard, *Anal. Chem.* **2004**, 76, 1641.

Immunoassays

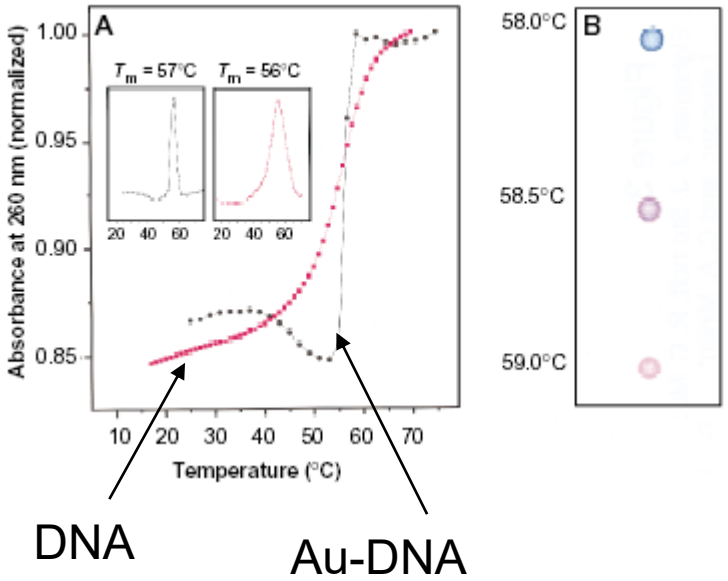


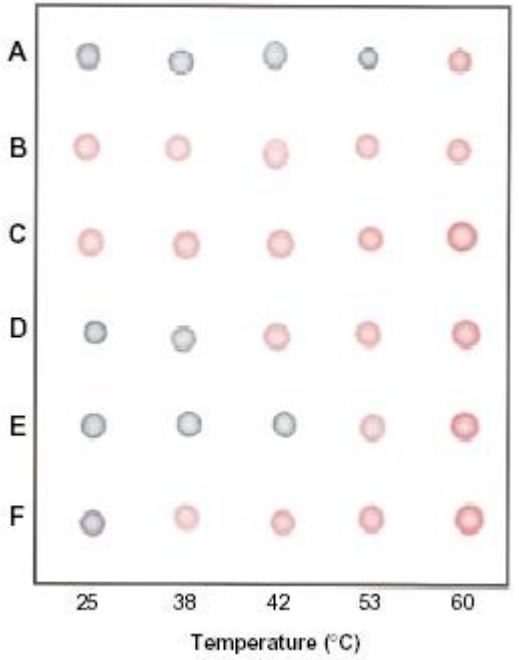
A. Bernard, B. Michel, E. Delamarche, *Anal. Chem.* **2001**, 73, 8.

Nanoparticle-based Sensors

selective colorimetric detection system for polynucleotides

thermal transition associated with the color change





Selective polynucleotide detection for the target probes : (**A**) complementary target; (**B**) no target; (**C**) complementary to one probe; (**D**) a 6-bp deletion; (**E**) a 1-bp mismatch; and (**F**) a 2-bp mismatch. Nanoparticle aggregates were prepared in a 600-μl thin-walled Eppendorf tube by addition of 1 μl of a 6.6μM oligonucleotide target to a mixture containing 50 μl of each probe (0.06 μM final target concentration). The mixture was frozen (5 min) in a bath of dry ice and isopropyl alcohol and allowed to warm to room temperature. Samples were then transferred to a temperature controlled water bath, and 3-μl aliquots were removed at the indicated temperatures and spotted on a C_{18} reverse phase plate.

Elganian, R.; Storhoff, J.J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. *Science* **1997**, *277*, 1078-1081.

Nanoparticle-based Sensors

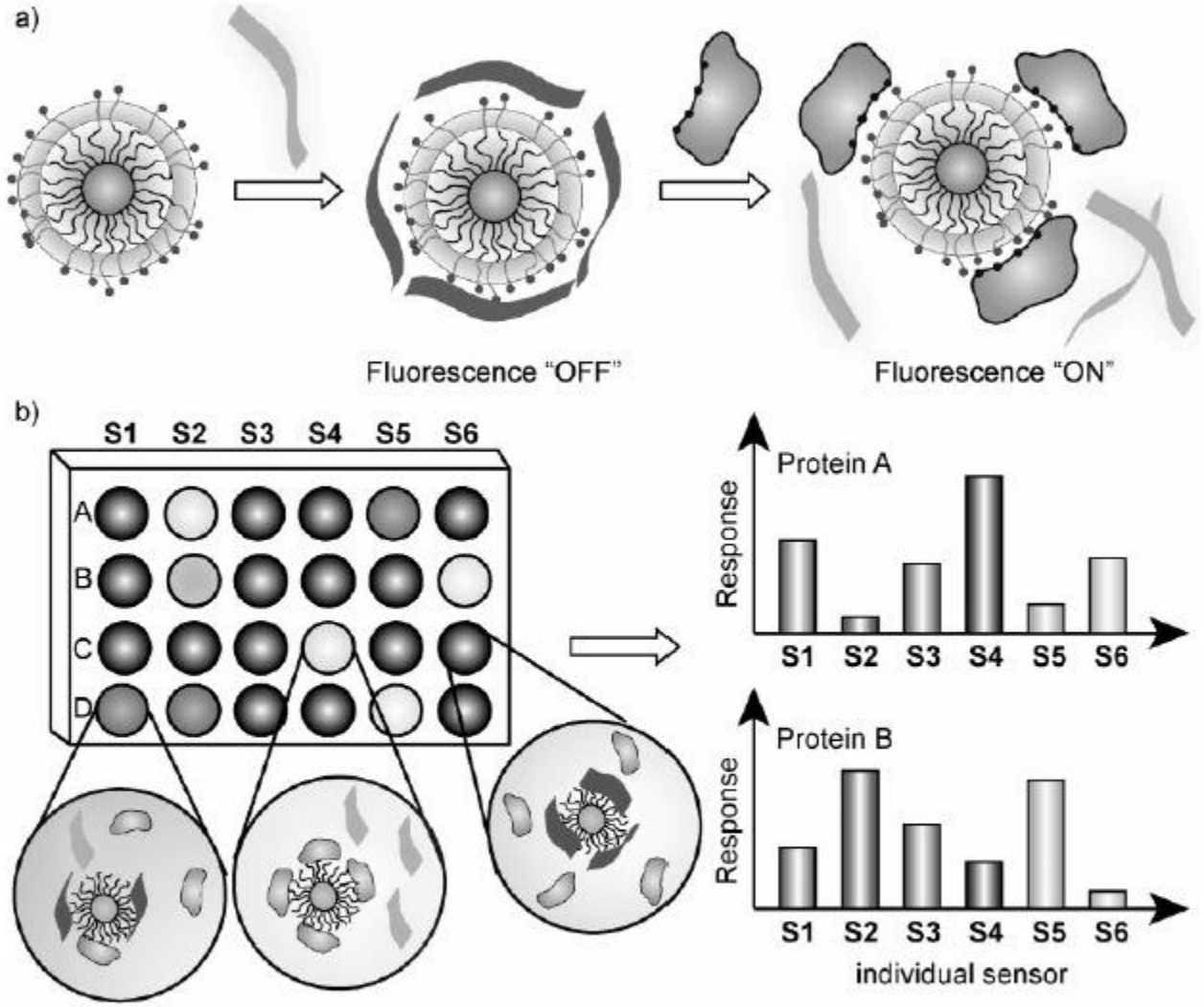


Figure 8. Schematic drawing of a "chemical nose" sensor array based on nanoparticle and fluorescence assay. a) The competitive binding between protein and quenched polymer leads to the fluorescence light-up. b) The combination of an array of sensors generates fingerprint response patterns for individual proteins.

Nanoparticles for new therapeutic strategies

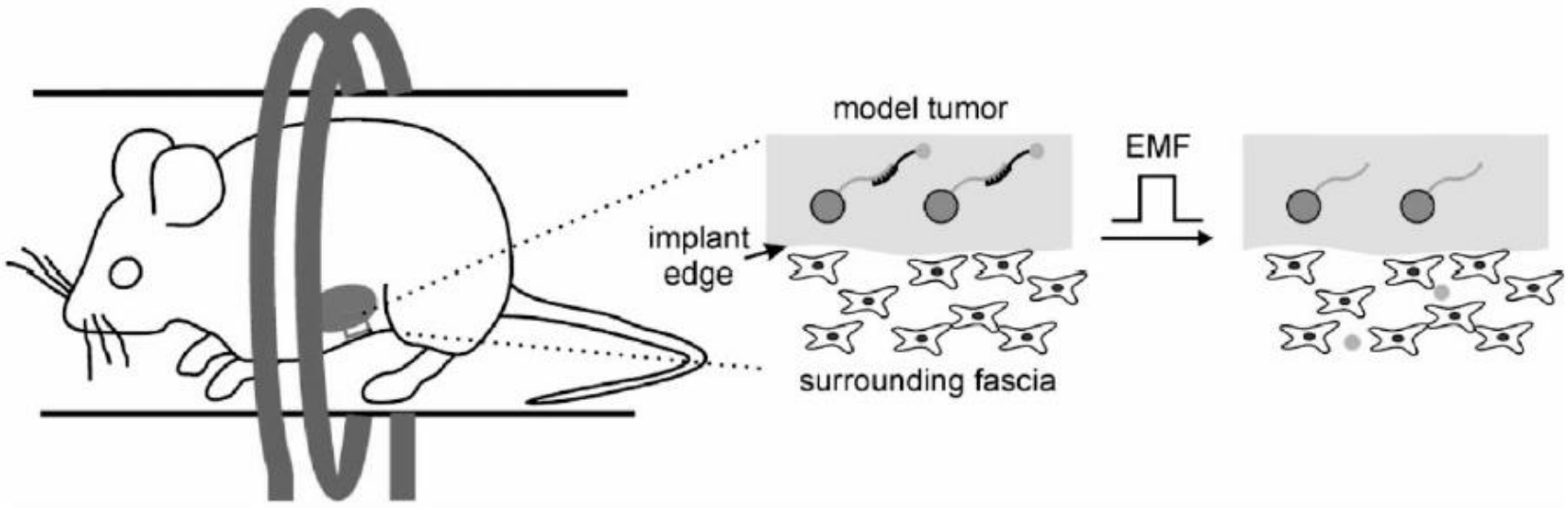
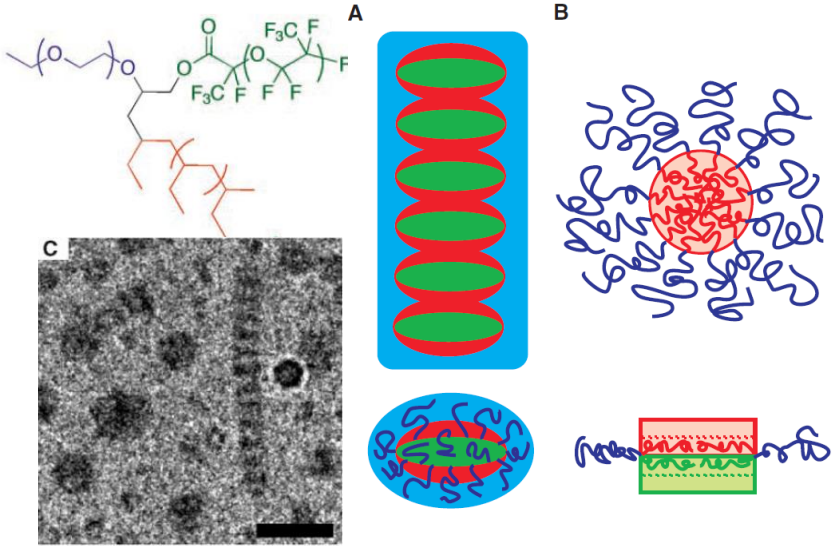


Figure 12. Controlled release of payloads using oligonucleotide-modified iron oxide nanoparticles for drug delivery at a remote location. Adapted with permission from [105].

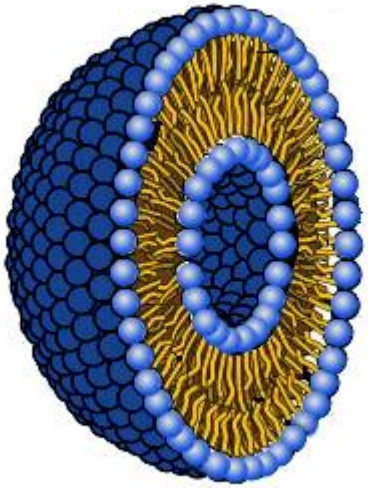
SOFT MATERIALS

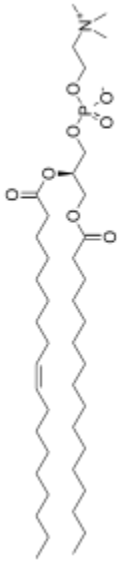
polymers/block copolymers

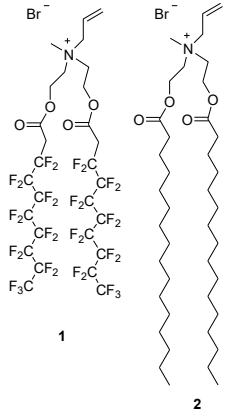
block terpolymer



T. P. Lodge et al. *Science* **2004**, *306*, 98







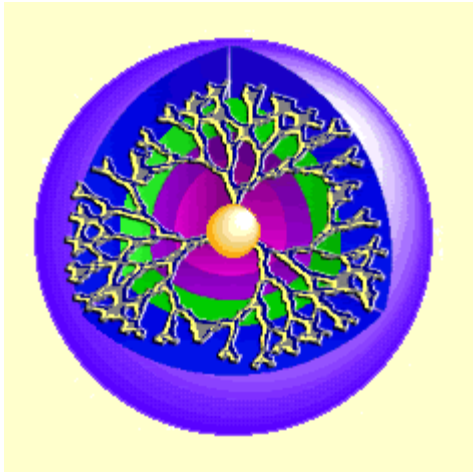
liposomes

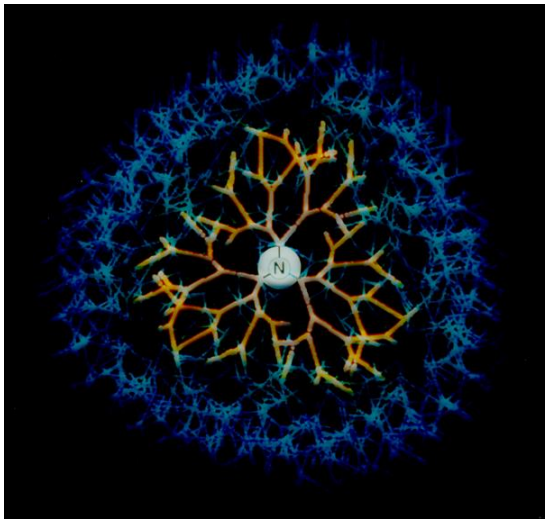
A **liposome** is an artificially-prepared vesicle composed of a lipid bilayer.
The liposome can be used as a vehicle for administration of nutrients and pharmaceutical drugs.
Liposomes are often composed of phosphatidylcholine-enriched phospholipids and may also contain mixed lipid chains with surfactant properties such as egg phosphatidylethanolamine

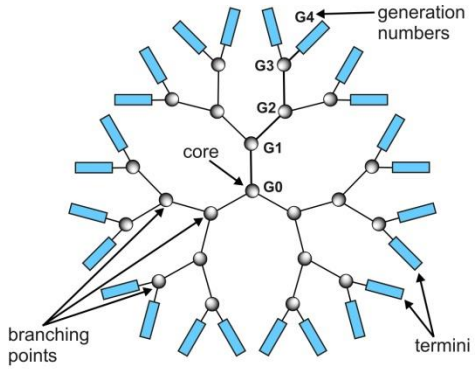
DENDRIMERS

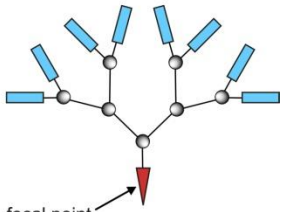
Dendrimers are repetitively branched molecules. The name comes from the Greek word δένδρον (**dendron**), which translates to "tree".

they are monodisperse and usually higly symmetric compounds

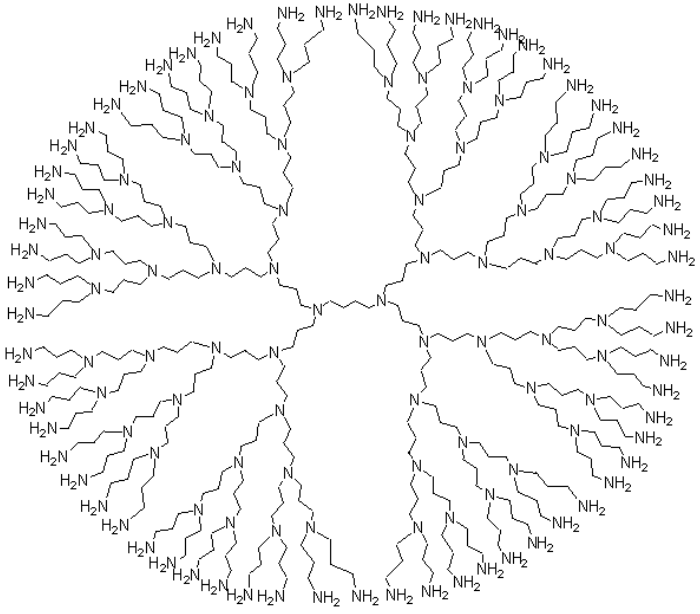




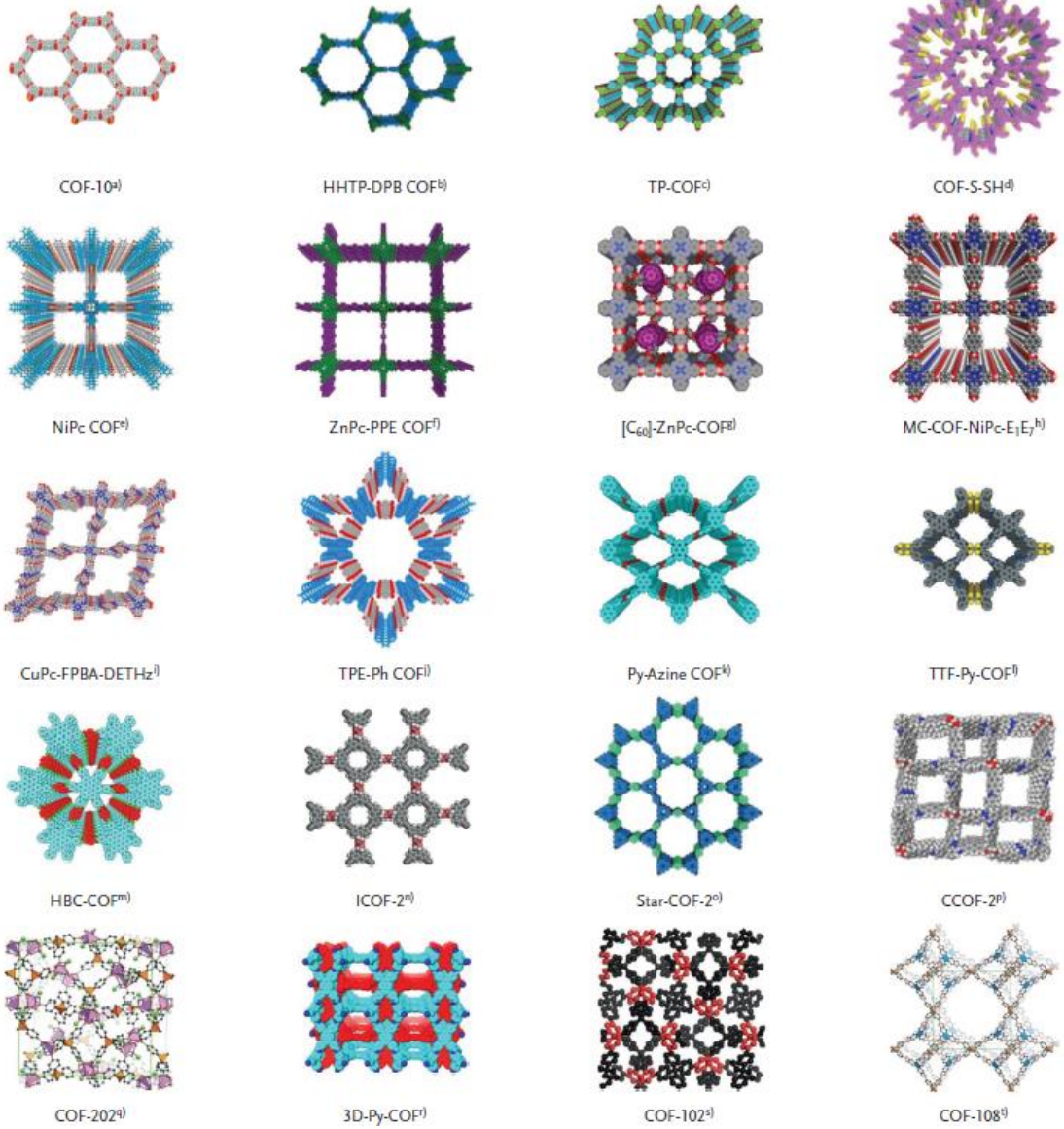




DENDRIMER **DENDRON**



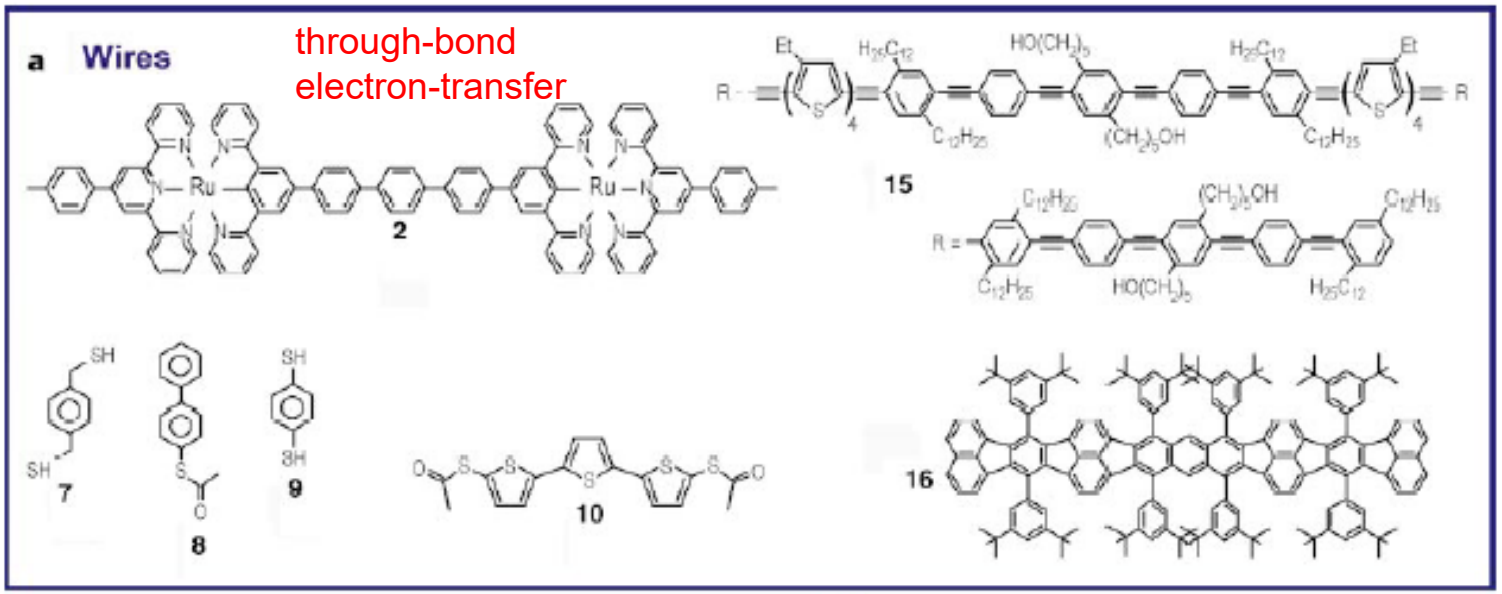
Covalent Organic Frameworks



Adv. Funct. Mater. **2018**, *28*, 1705553

organic materials

some examples:



electron wires

organic materials

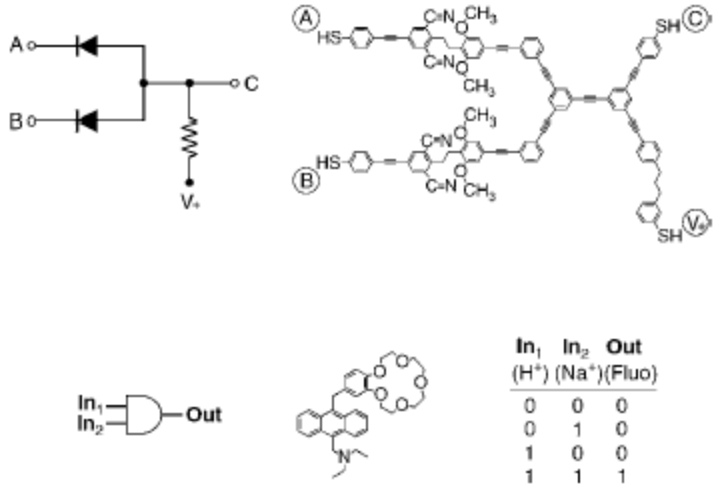
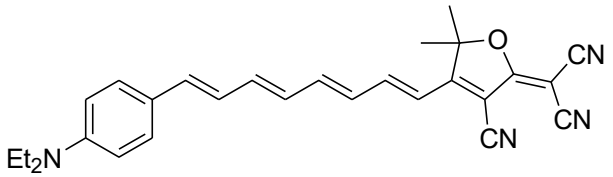


Figure 5. Top: molecular implementation of a diode–diode AND logic gate.[35] Bottom: a molecule that performs in solution according to AND logic.[37a]

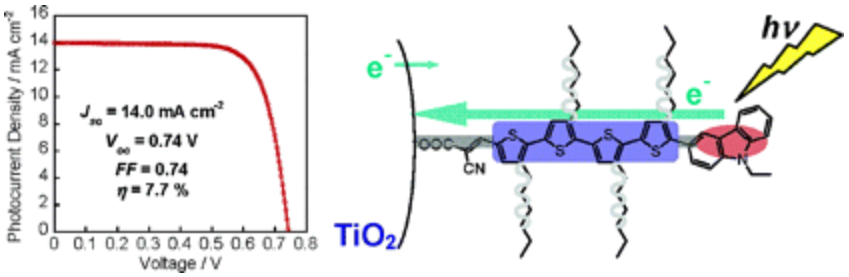


chromophore with NLO properties

Alkyl-Functionalized Organic Dyes for Efficient Molecular Photovoltaics

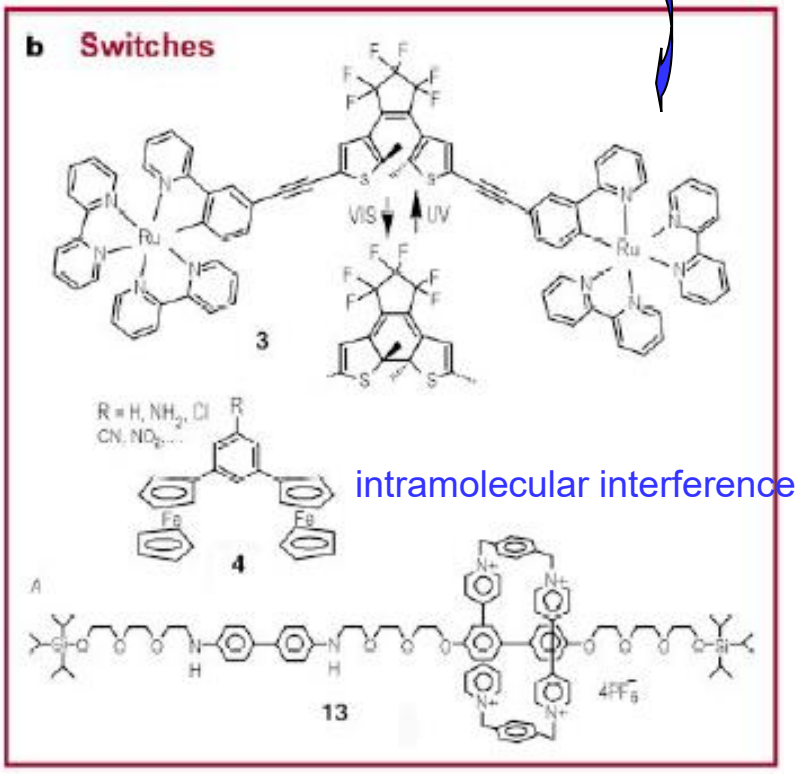
Nagatotoshi Koumura, Zhong-Sheng Wang, Shogo Mori, Masanori Miyashita, Eiji Suzuki, and Kohjiro Hara

Web Release Date: 18-Oct-2006; **(Communication)** DOI: 10.1021/ja0645640



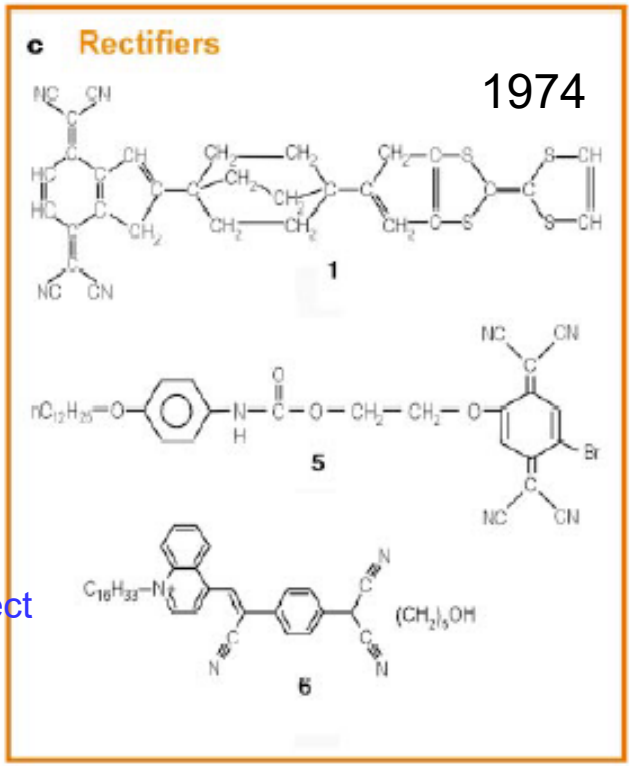
organic materials

intramolecular light-induced conformation changes



intramolecular interference effect

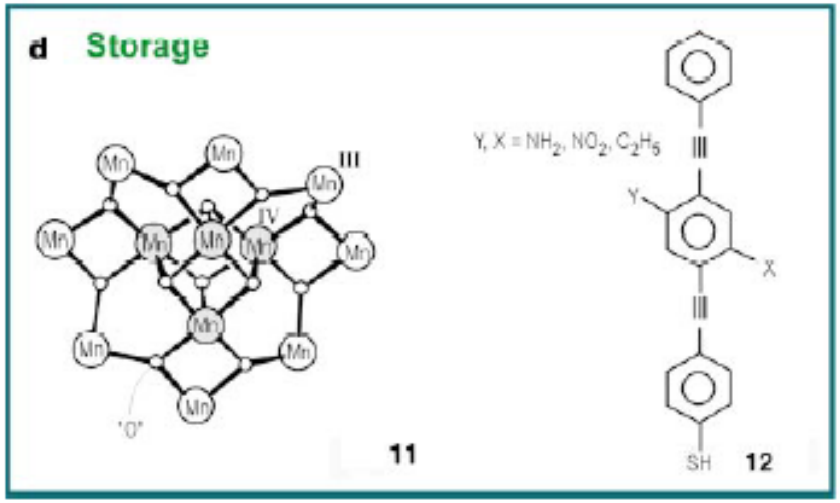
molecular electronic switches

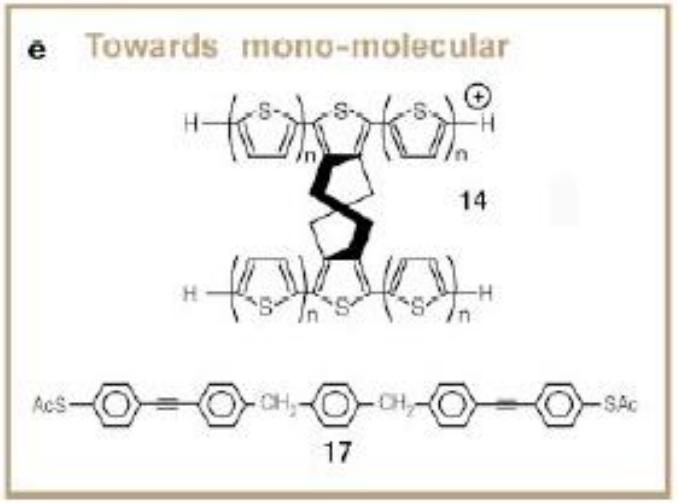


molecular rectifiers

donor-spacer-acceptor (d-s-a)

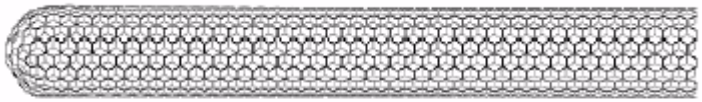
organic materials

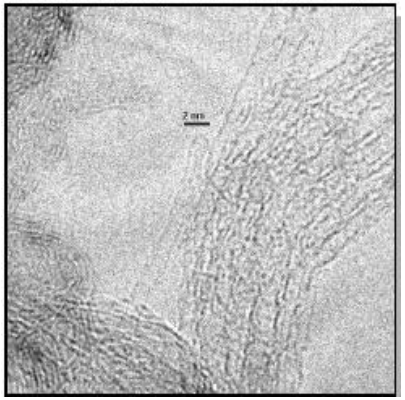




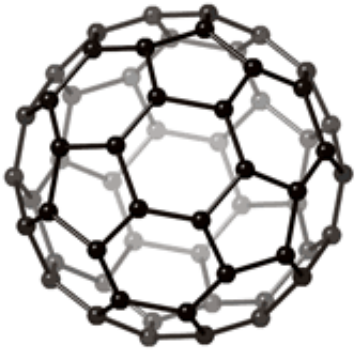
SWCNT
MWCNT

14: intramolecular transistor
17: intramolecular quantic tran

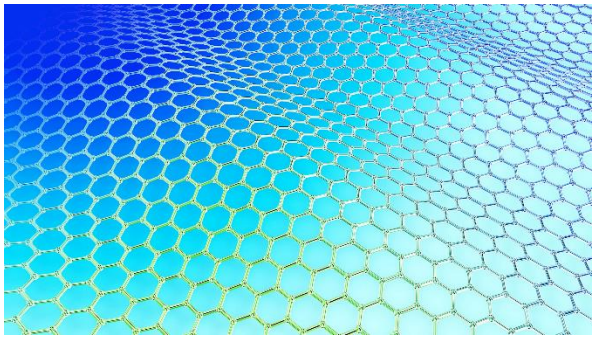




FULLERENES



GRPHFENE



A Molecular Elevator

Jovica D. Badjic´,1 Vincenzo Balzani,2
Alberto Credi,2*
Serena Silvi,2 J. Fraser Stoddart1*

SCIENCE VOL 303 19 MARCH 2004

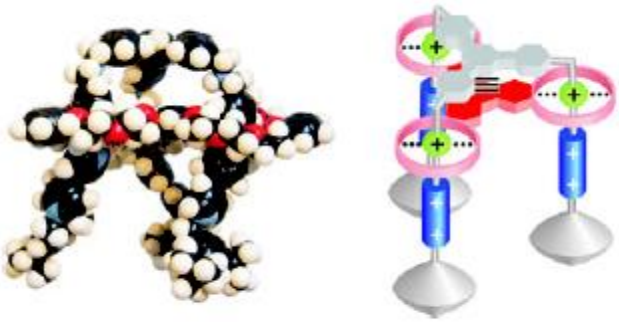
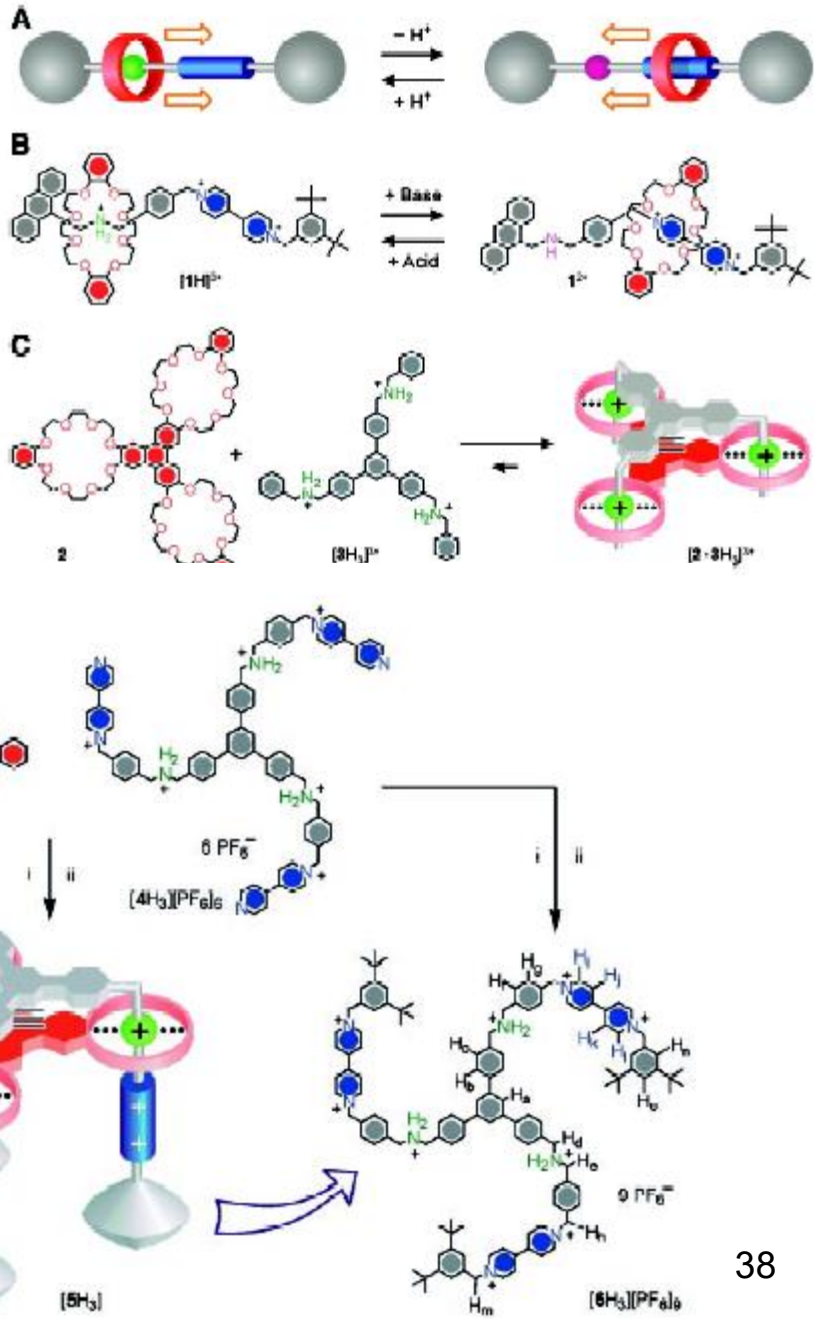


Figure 4. A molecular elevator: the red platform moves up and down upon the addition of acid and base, respectively.[1a]



organic materials

Light-driven monodirectional molecular rotor

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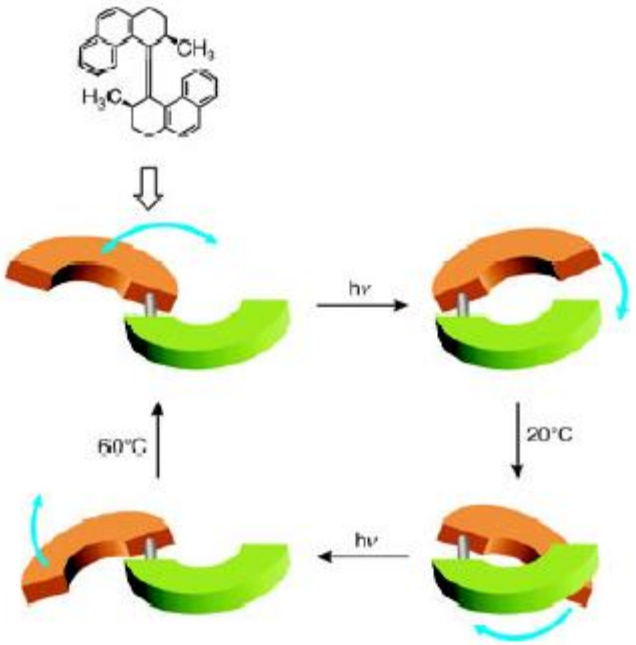


Figure 2. Structural formula and schematic representation of a molecular motor, based on the photoisomerization of an alkene-type compound containing chiral centers, that exhibits light-induced unidirectional rotation.[11]

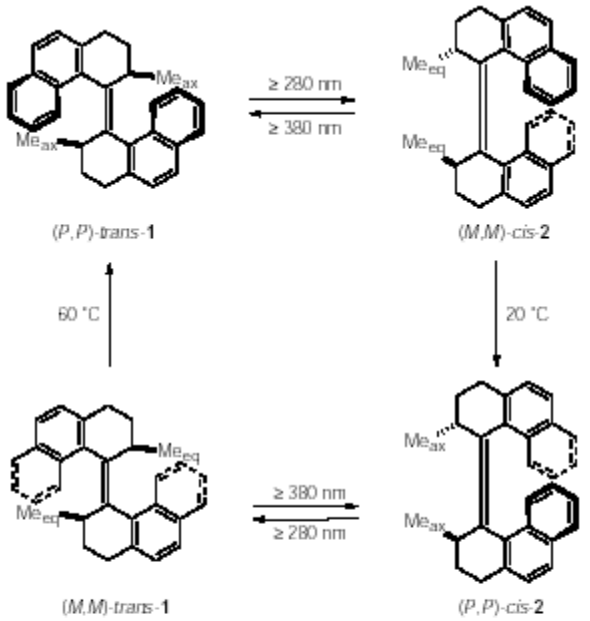


Figure 1 Photochemical and thermal isomerization processes of (*P,P*)-*trans*-**1**. UV irradiation with high pressure Hg-lamp, Pyrex filter, $\lambda \geq 280$ nm or Xe-lamp, Toshiba L-3g glass filter, $\lambda \geq 380$ nm. First order kinetics were observed for the thermal processes and temperature dependent ^{1}H NMR and CD studies in the range 50.0–81.1 °C gave Ea = 26.4 kcal mol^{-1} for the (*M,M*)-*trans*-**1** to (*P,P*)-*trans*-**1** interconversion. It should be noted that no racemization takes place during any of the photochemical or thermal steps as was proven by chiral HPLC analysis of the isomers obtained after the individual steps.

organic materials







Mobile phones can be charged in a remote location where there is no access to electricity.

INSTRUMENTS

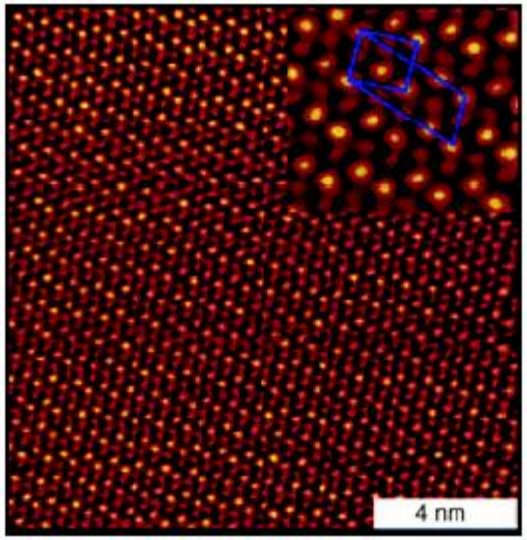


Figure 5. Scanning tunneling microscope image of a self-assembled monolayer (SAM) of decanethiol on gold.[83] The scanning probe microscopes make it possible to view nanostructures in molecular detail, and have revolutionized surface science. SAMs represent a class of material in which properties such as wetting and biocompatibility can be engineered at the molecular level; many other examples of materials engineered at the nanoscale are now emerging from nanoscience.

INSPIRATION FROM NATURE

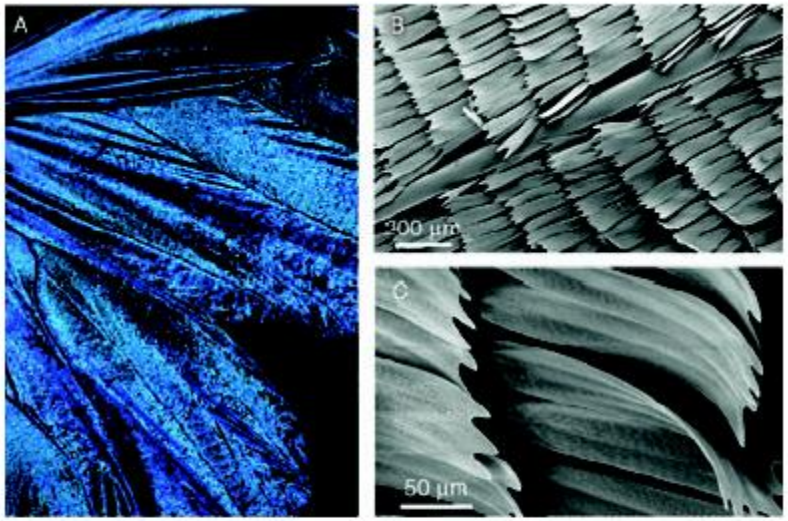


Figure 6. Photograph (A) and SEM images (B,C) of the wing of the *morpho* butterfly (images by Felice Frankel). The brilliant blue reflection from the wing of this butterfly is due to the operation of a remarkable, optically sophisticated photonic bandgap structure, which not only is wavelength selective, but also reflects over a broad range of angles of incidence and observation. Biology presents examples of functional nanostructures of a wide range of types, and has much to teach nanoscience and nanotechnology.

molecular machines

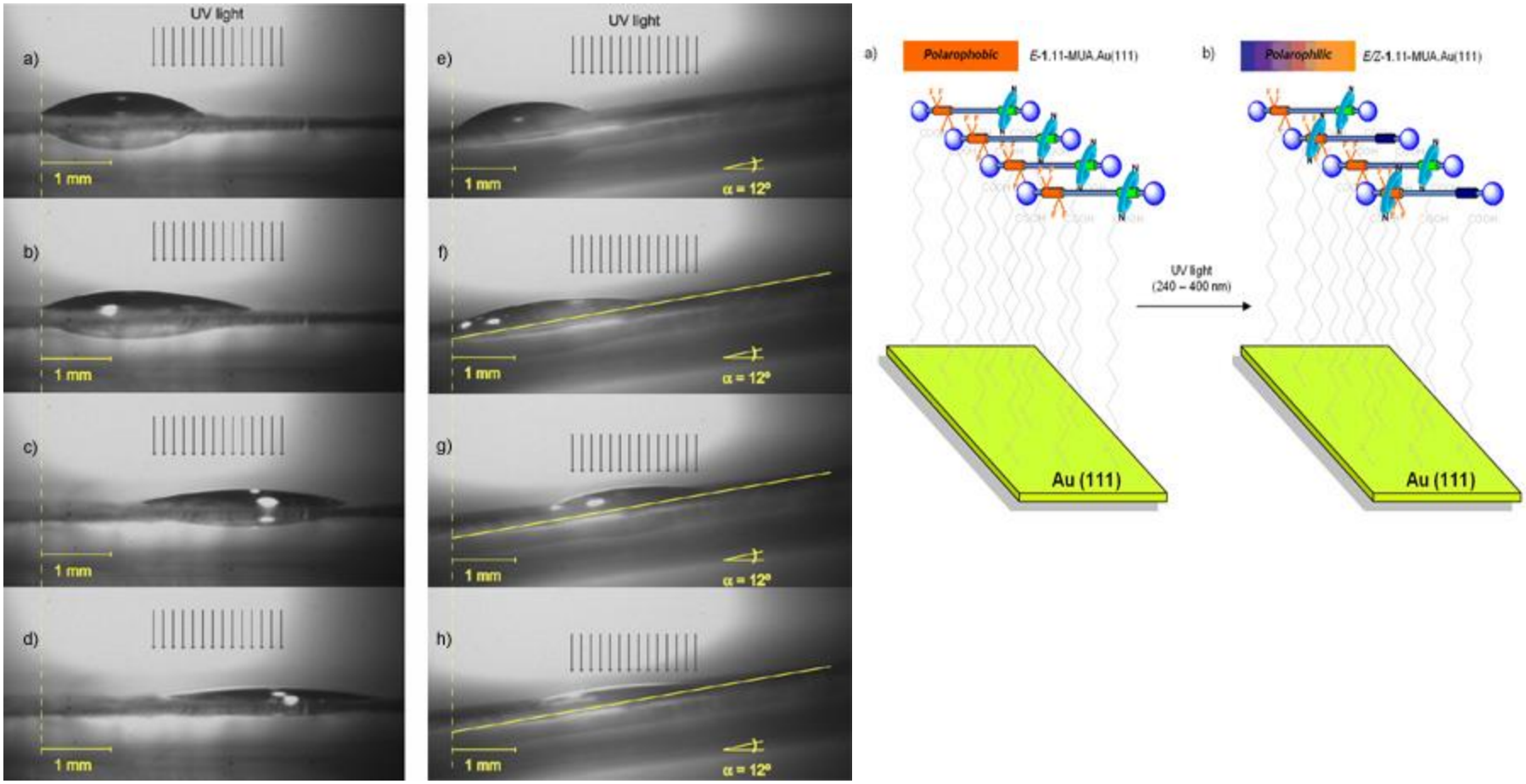
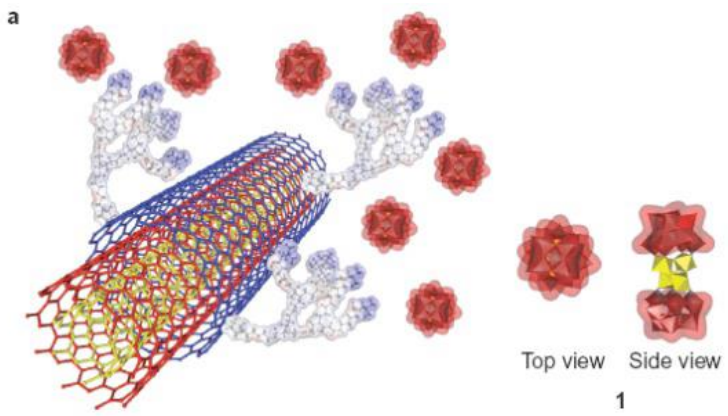


Figure 2. Light-driven directional transport of a 1.25 µl diiodomethane drop across the surface of monolayer of molecular machines, both flat (a)-(d) and up a twelve degree incline (e)-(h). This extrapolation across 6 orders of magnitude in length scales from mechanical motion at the molecular level to macroscopic transport is truly remarkable - the equivalent of millimetre motion of components in a machine working to raise an object to over twice the height of the CN Tower, the world's tallest building. The work done by the monolayer of molecular machines is stored as potential energy.

Efficient **water oxidation** at carbon nanotube–polyoxometalate electrocatalytic interfaces



Organization of Inorganic Nanomaterials via **Programmable DNA** Self-Assembly and Peptide Molecular Recognition

