Dipartimento di Scienze Chimiche
e Farmaceutiche

CORSO DI LAUREA MAGISTRALE in CHIMICA

CURRICULUM “SISTEMI NANOSTRUTTURATI E SUPRAMOLECOLARI"

MATERIALI ORGANICI

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www.dsch.units.it/pasquato

6 CFU

Anno Accademico 2018/2019

CONTENUTI DEL CORSO

- introduzione ai materiali molecolari e supramolecolari organici
  - chimica supramolecolare
  - interazioni deboli
- monostrati organici in 2-D e in 3-D
  - funzionalizzazione della superficie
  - reazioni di Cicloaddizione
  - Click Chemistry
  - reazioni di Metatesi
  - controllo della morfologia del monostrato
  - applicazioni
- fullereni, nanotubi di carbonio e grafene
  - proprietà, sintesi, applicazioni
- dendrimeri
- materiali organici conduttori e semiconduttori
  - definizioni, esempi
- OLED (organic light emitting devices)
  - elettroluminescenza

MATERIALE DIDATTICO

1. files di diapositive del docente su MOODLE

2. alcuni articoli di letteratura su MOODLE

per accedere usare la password: LUCIALM1

LIBRI da consultare

March, Advanced Organic Chemistry – si trova in biblioteca

F. A. Carey, R. J. Sundberg Advanced Organic Chemistry Part B – si trova in biblioteca

T. J. J. Müller, U. H. F. Bunz, Functional Organic Materials – presso lo studio del docente

ORARIO

Lezioni: 4 ore la settimana

lunedì	10.15 – 11.00
martedì	12.15 – 13.00
mercoledì	9.15 – 10.00
venerdì	10.15 – 11.00

RICEVIMENTO STUDENTI: **su appuntamento,**
e-mail: lpasquato@units.it

MODALITÀ svolgimento della VERIFICA

1. Per la verifica vi sarà assegnato un lavoro scientifico su un argomento trattato a lezione e di vostro interesse.

2. lo studente dovrà leggere e comprendere il lavoro eventualmente con l'ausilio del supporting information o di altri lavori citati, e preparare una presentazione PowerPoint (o analogo) che dovrà durare non più di 15 minuti (max 15 diapositive).
Dovrà contenere il titolo del lavoro, la rivista, anno, volume, pagine della pubblicazione. Una breve introduzione, il claim del lavoro, una descrizione critica dei risultati e le conclusioni.

3. La verifica è orale e inizierà con la presentazione che offrirà spunti per la successiva discussione. L'esame orale continuerà con domande centrate su altri due argomenti trattati a lezione.

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

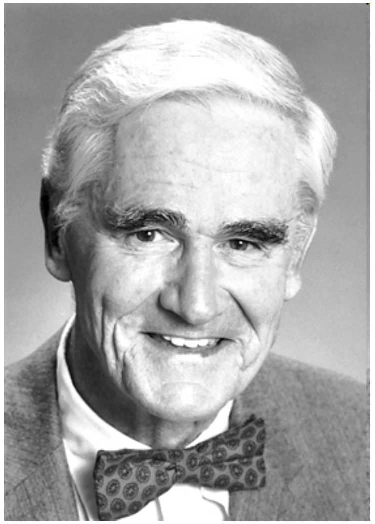
Principali limiti

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

Materiali supramolecolari organici

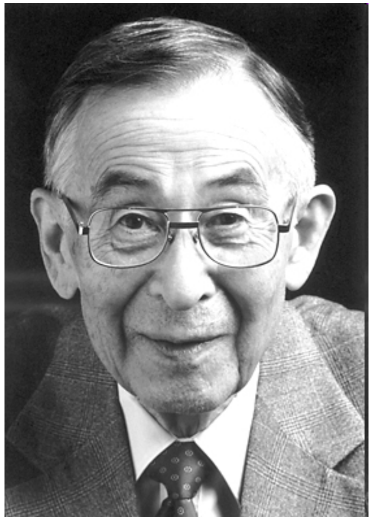
molecular self-assembly: organizzazione di molecole che si basa su ***interazioni deboli***,
legami ionici, ad idrogeno, non-covalenti e metallo-legante.
Porta ad ottenere sistemi con strutture e proprietà che non sono presenti nei singoli componenti.

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

materials self-assembly: riguarda quella parte della chimica che va oltre il molecular assembly. Le forze responsabili comprendono quella capillare, colloidale, elastica, elettrica, magnetica e di taglio.
Il sistema procede verso uno stato di minore energia e maggiore stabilità strutturale.

Nanomaterials - What is nano?

nano deriva dal greco *$\nu\alpha\nu o$*

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.

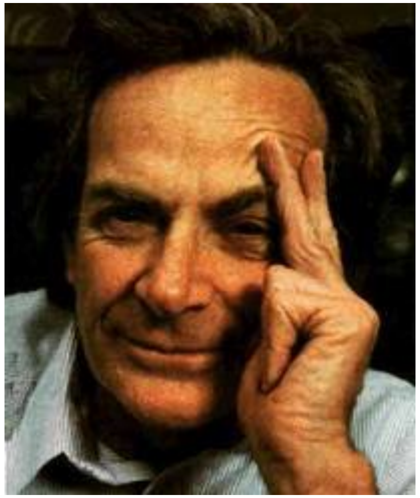
NANOMATERIALS

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”?

Nano — The Interdisciplinary Science



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?

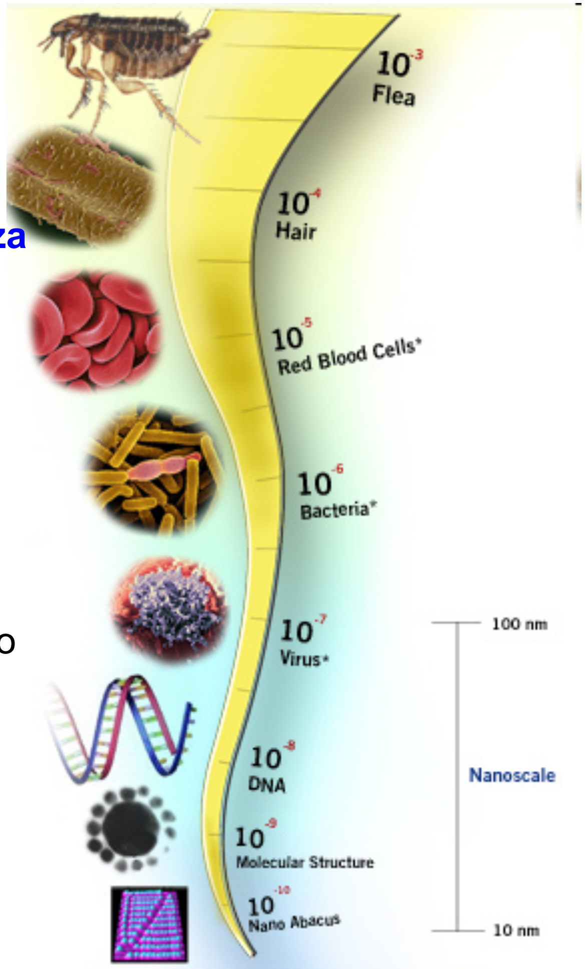
Table 1. Different size-related phenomena. The length scales are a rough estimation of the size below which the phenomenon can be observed (for the last three phenomenon, typical values of the sizes—screening lengths and ballistic transport in particular—can vary over orders of magnitude).

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

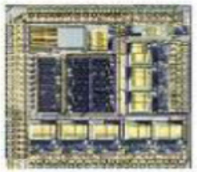
Nanoscale objects have at least one dimension (height, length, depth) that measures between 1 and 999 nanometers (1-999 nm).

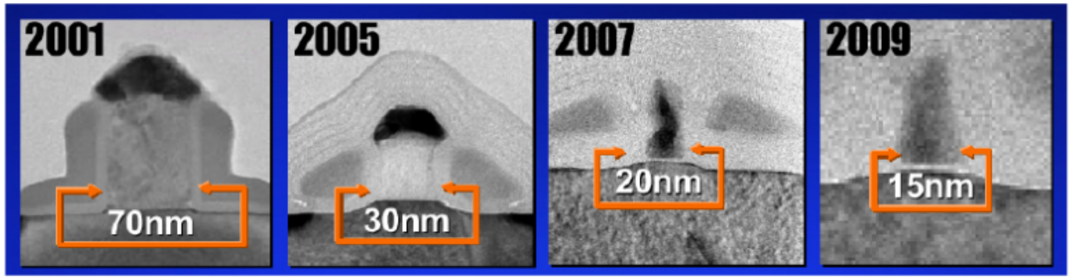
unità di misura	*abbreviazione*	*descrizione*
metro	**m**	**unità base SI della lunghezza**
centimetro	cm	$1x10^{-2}$ m (0.01 m)
millimetro	mm	$1x10^{-3}$ m (0.001 m)
micrometro	μm	$1x10^{-6}$ m
nanometro	nm	$1x10^{-9}$ m la billionesima parte di 1 metro o 10 Å



Why Nano?

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



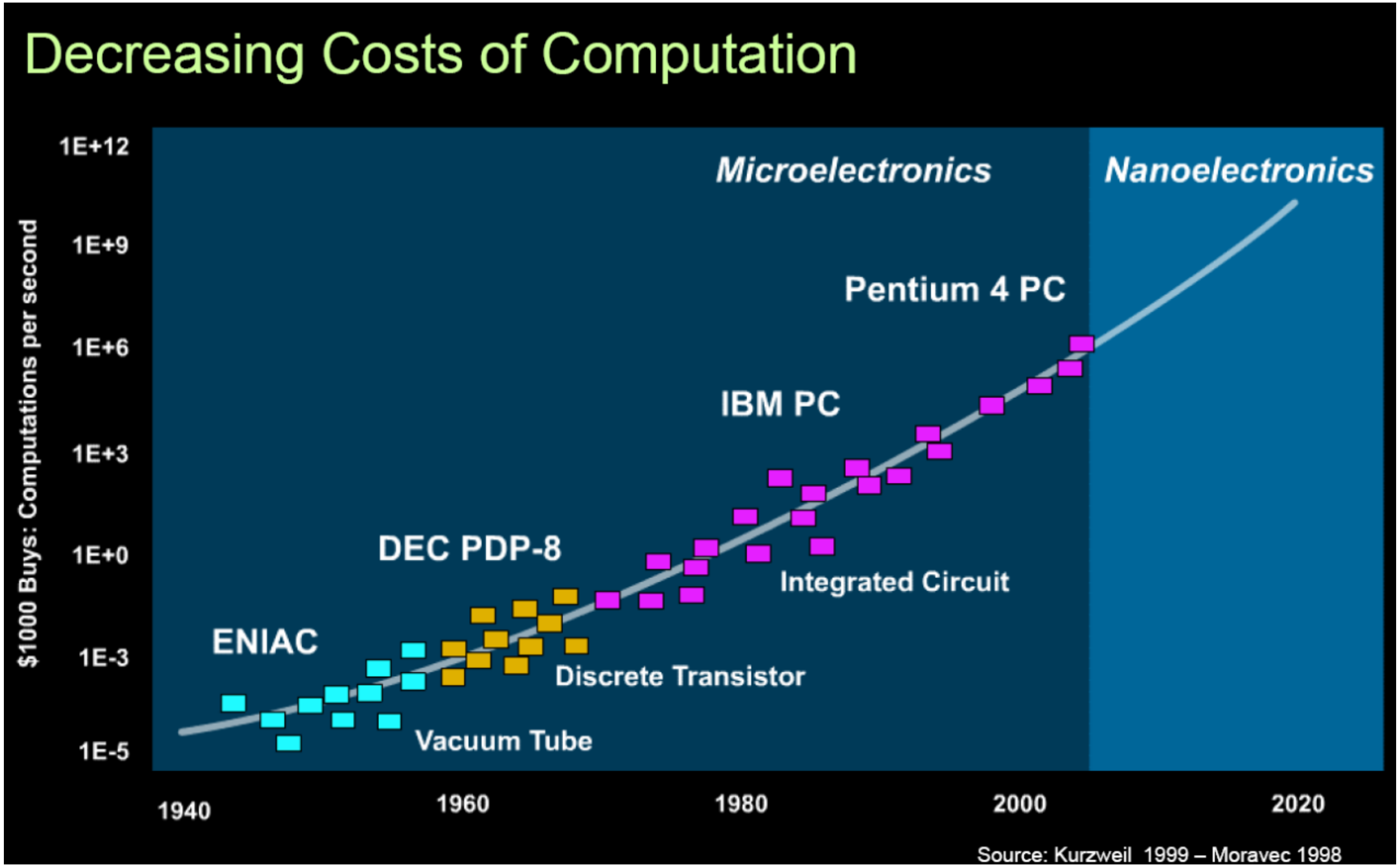


Intel's transistors

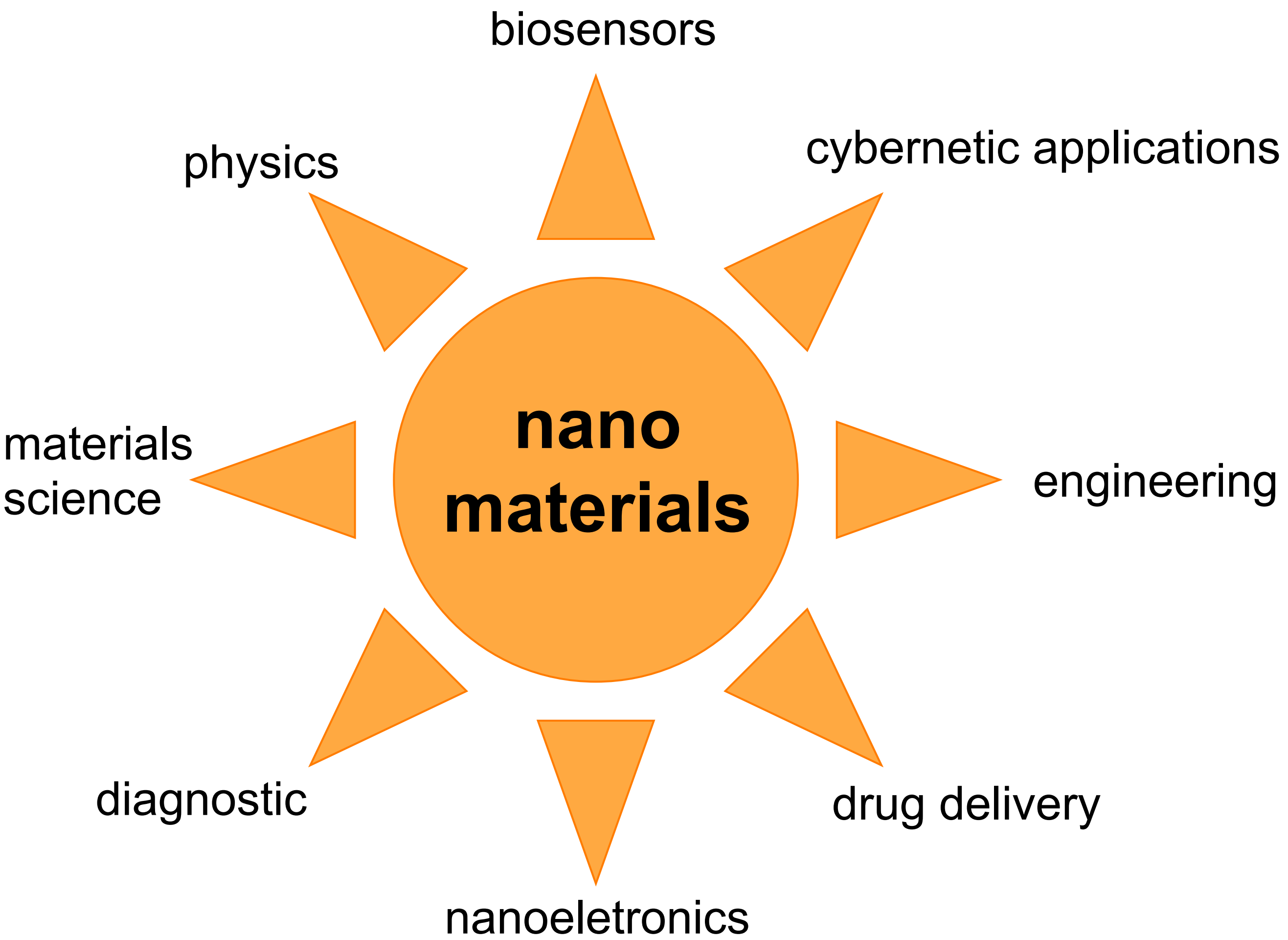
As with the fabrication of integrated circuits, nanotechnology is based on building structures and systems at very small sizes

- to enhance performance and produce new properties and applications

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


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

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

Le nanotecnologie operano in un ambito d'investigazione **multidisciplinare**, coinvolgendo molteplici settori di ricerca, tra cui:

chimica,
scienza dei materiali,
fisica (sia applicata che di base),
ingegneria meccanica,
ingegneria chimica ed elettronica.
biologia molecolare

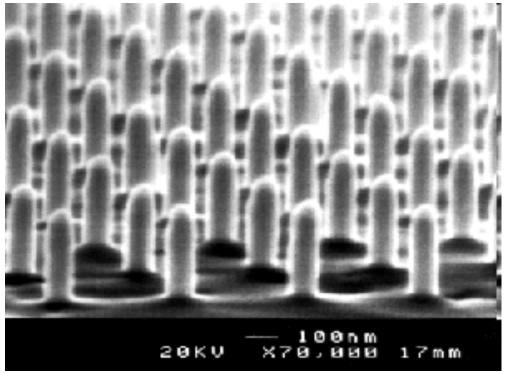
Nanochimica:

l'insieme dei processi chimici che consentono di fabbricare nanomateriali a partire da semplici mattoni, "building blocks" e lo studio delle proprietà chimiche e della reattività dei nanomateriali.

Materiali organici

metodi di sintesi e fabbricazione di nanomateriali

approccio **top-down**: ricavare un oggetto più piccolo da uno più grande. Questa tecnica comporta la riduzione delle dimensioni di un materiale fino a 10-100 nm.



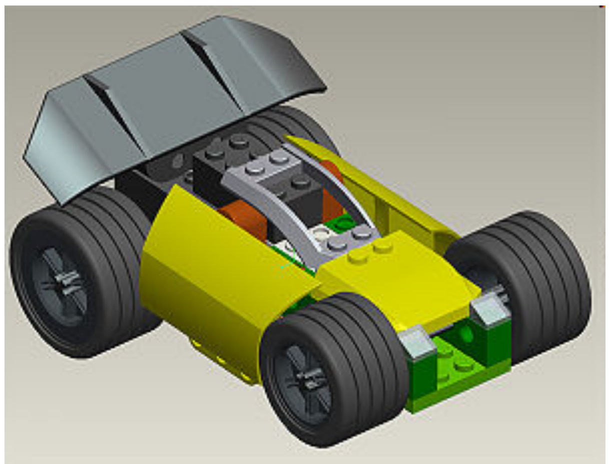
i dispositivi sono fabbricati da materiali macroscopici
attraverso un attento controllo dei processi di miniaturizzazione a livello atomico.

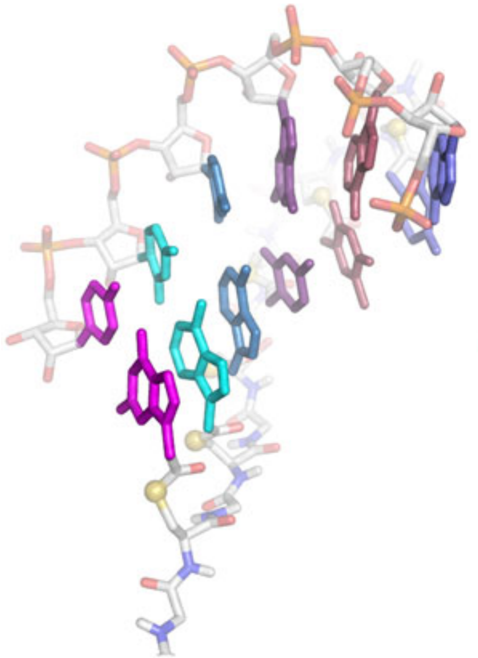
Materiali organici

metodi di sintesi e fabbricazione di nanomateriali

approccio **bottom up**: costruire dal basso usando elementi unitari, "building blocks", per formare oggetti di dimensioni maggiori.

Il prodotto finale si ottiene assemblando progressivamente gli elementi costitutivi – atomi, ioni, molecole, nanoparticelle – per formare congegni, dispositivi, macchine a livello molecolare.





2D-Self-Assembled Monolayers

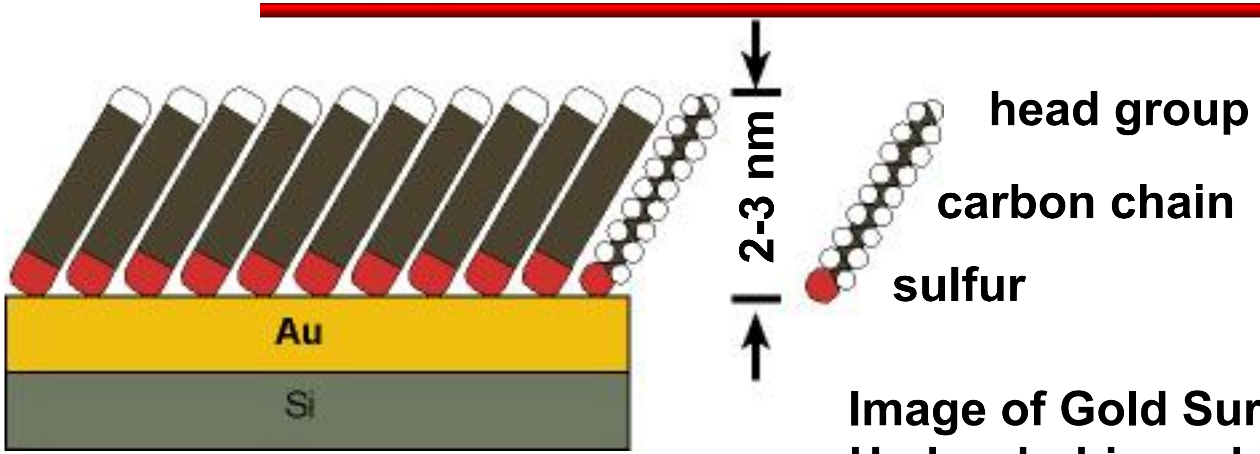
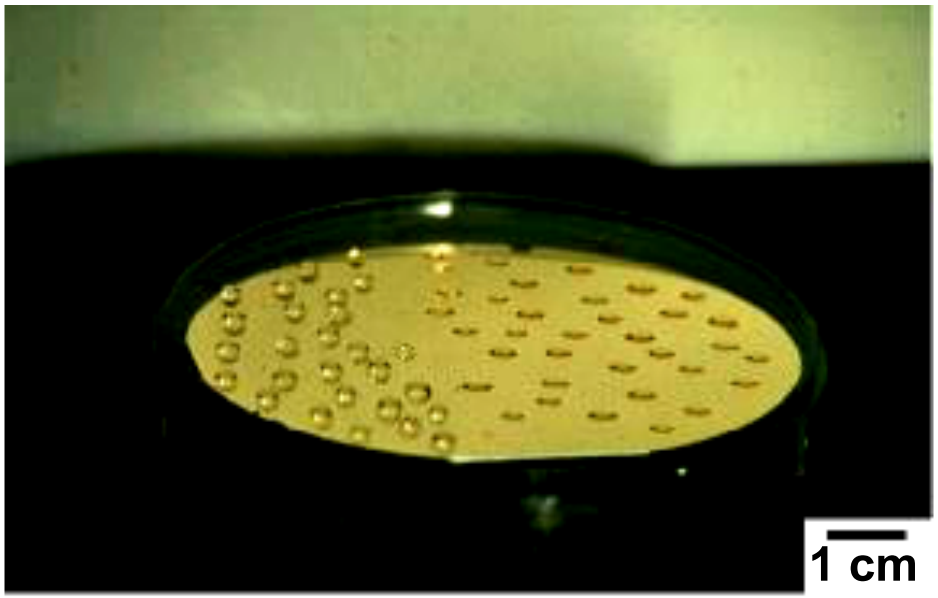
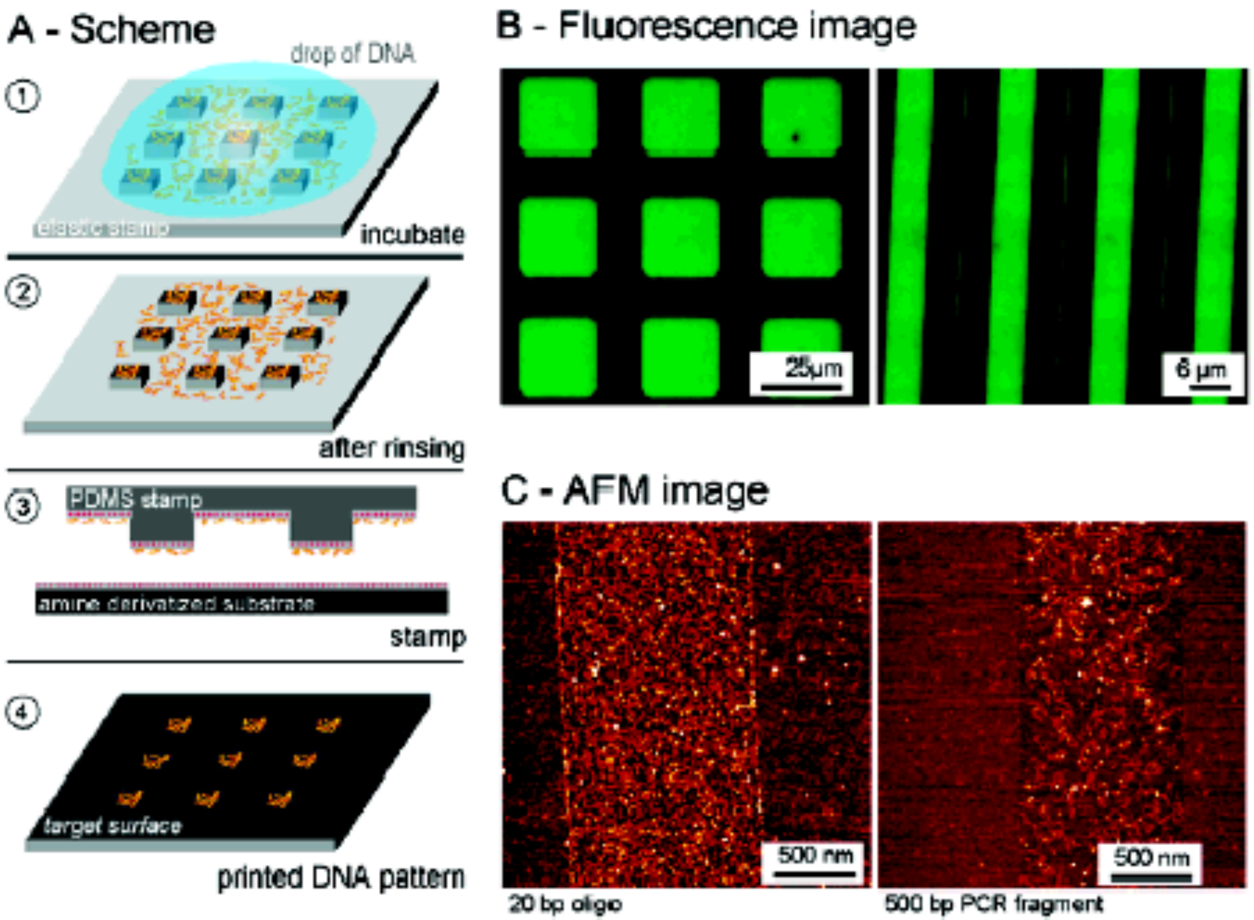


Image of Gold Surface Patterned with Hydrophobic and Hydrophilic SAMs

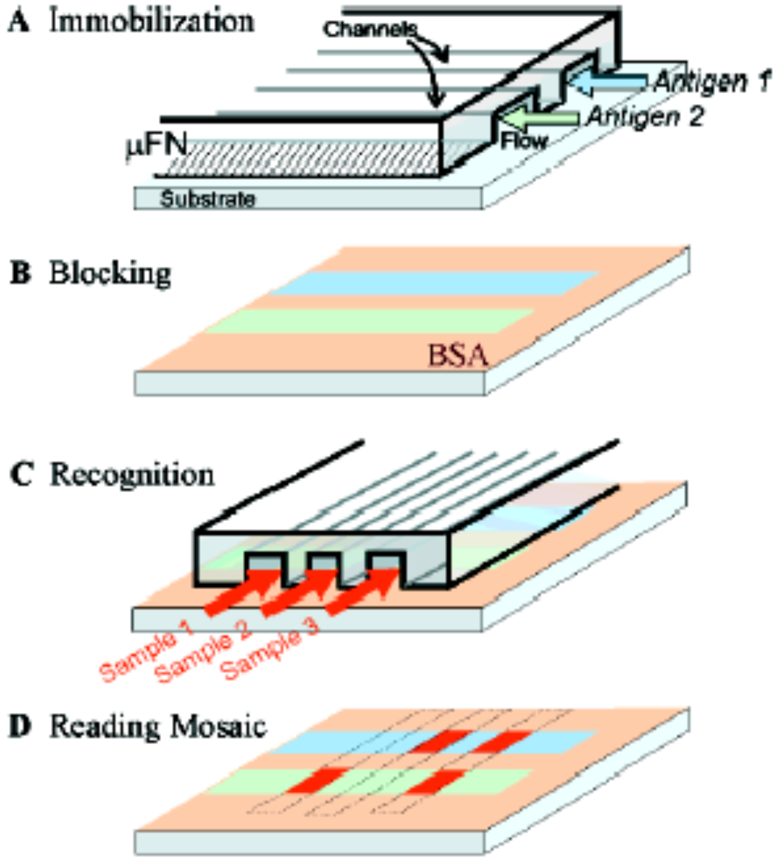


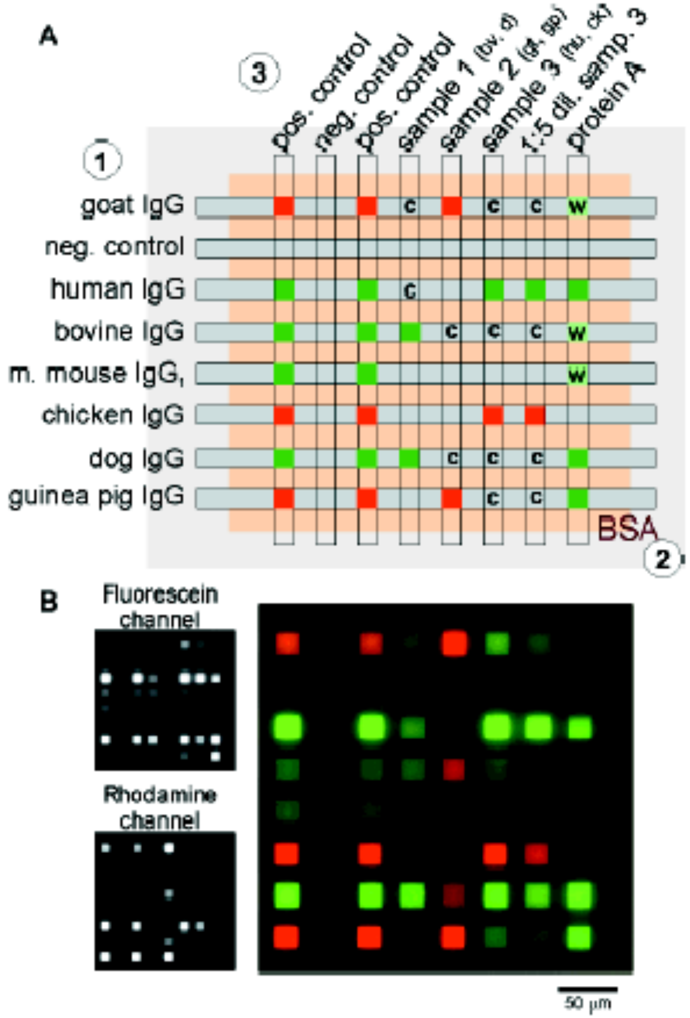
Microcontact Printing DNA



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

Immunoassays

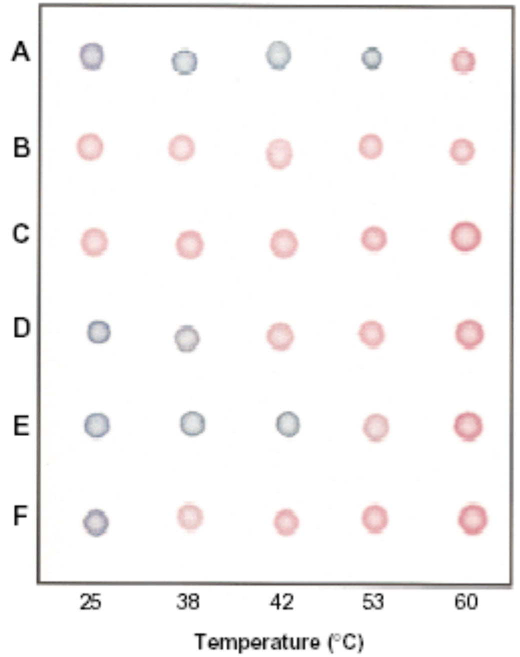




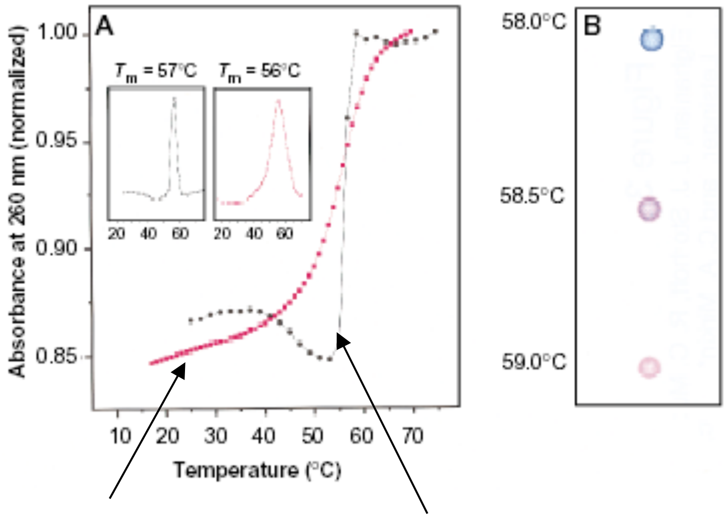
A. Bernard, B. Michel, E. Delamarche, *Anal. Chem.* **2001**, 73, 8.

Nanoparticle-based Sensors

selective colorimetric detection system for polynucleotides



thermal transition associated
with the color change



DNA

Au-DNA

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

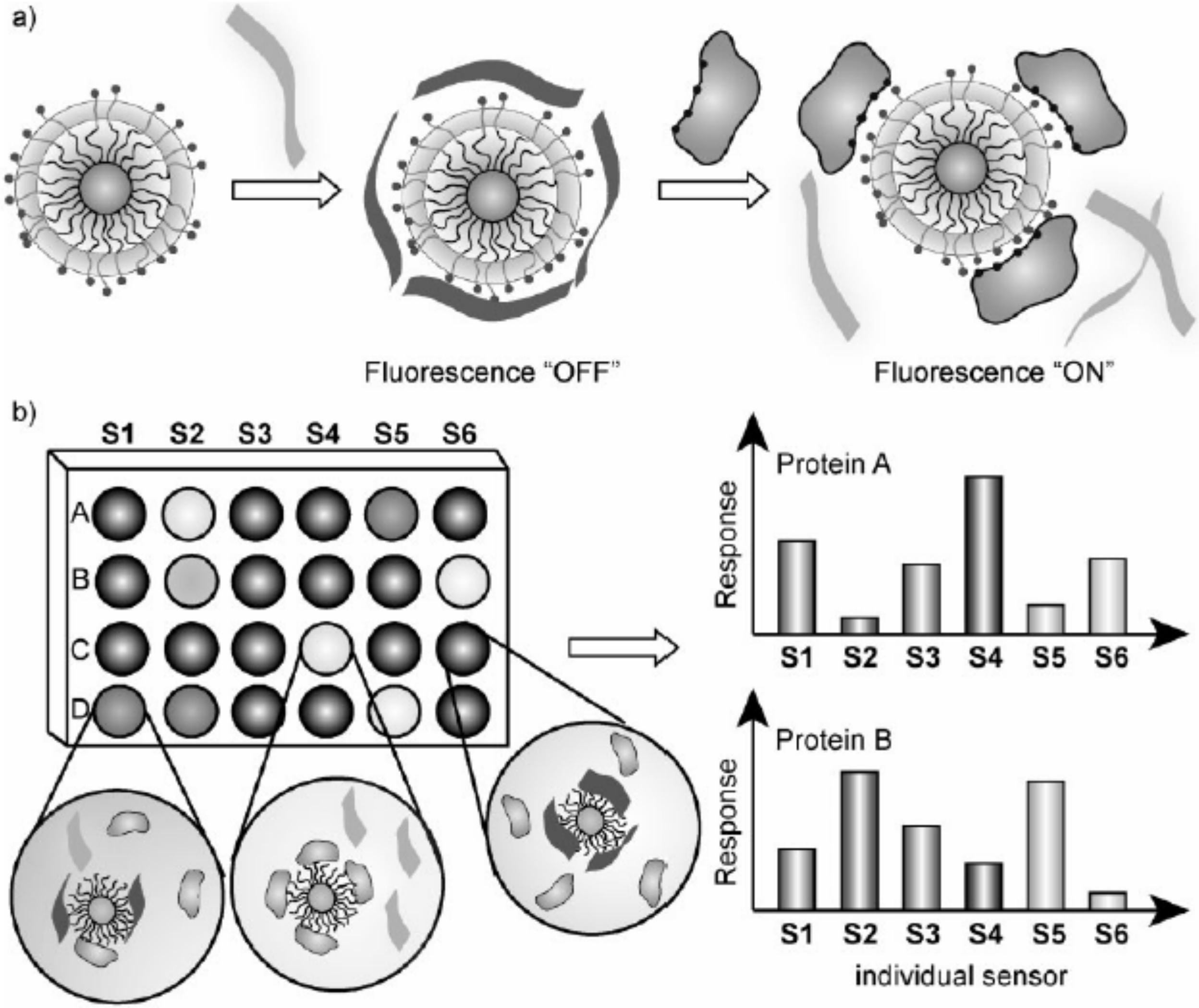


Figure 8. Schematic drawing of a "chemical nose" sensor array based on nanoparticle and fluorescence assay. a) The competitive binding between protein and quenched polymer leads to the fluorescence light-up. b) The combination of an array of sensors generates fingerprint response patterns for individual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

Nanoparticles for new therapeutic strategies

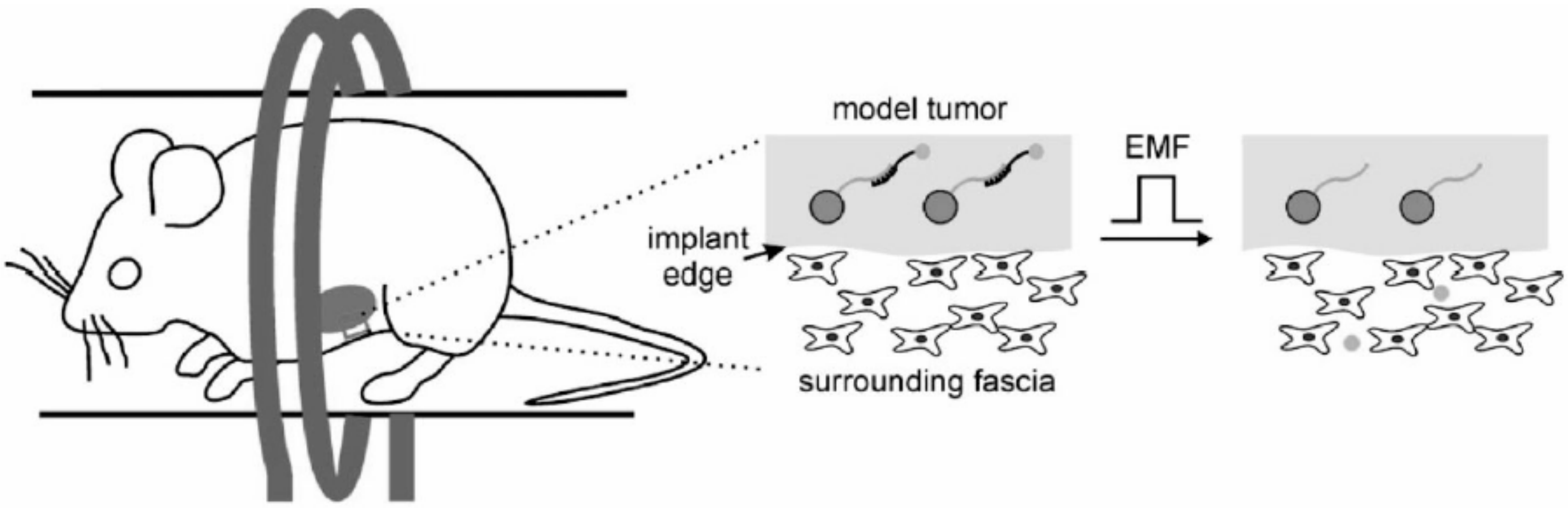
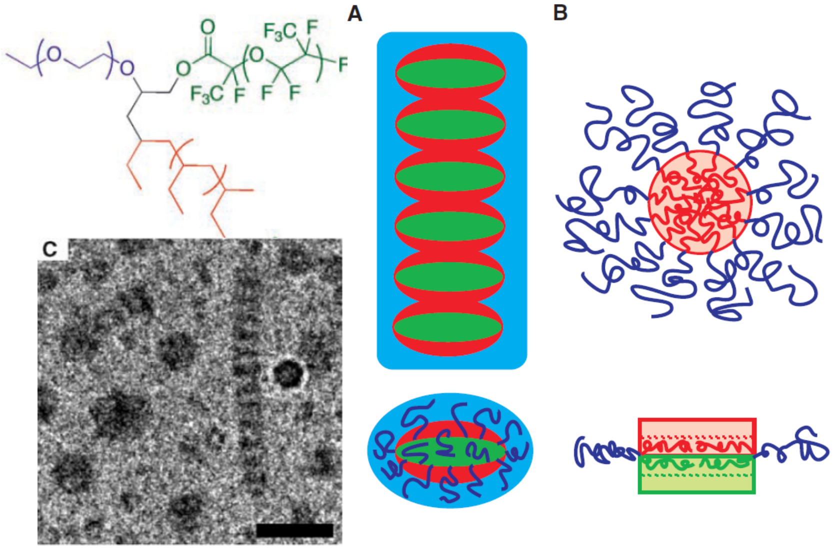


Figure 12. Controlled release of payloads using oligonucleotide-modified iron oxide nanoparticles for drug delivery at a remote location. Adapted with permission from [105].

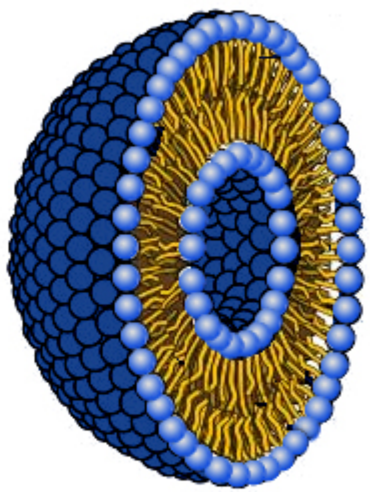
SOFT MATERIALS

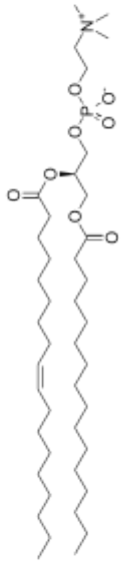
polymers/block copolymers

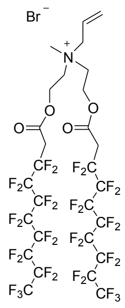
block terpolymer



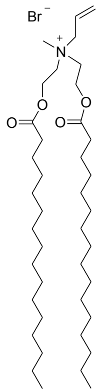
T. P. Lodge et al. *Science* **2004**, *306*, 98







1



2

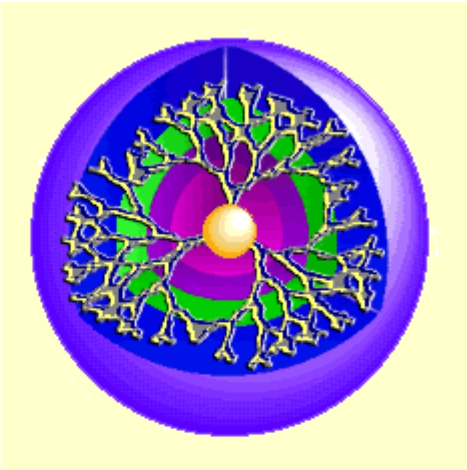
liposomes

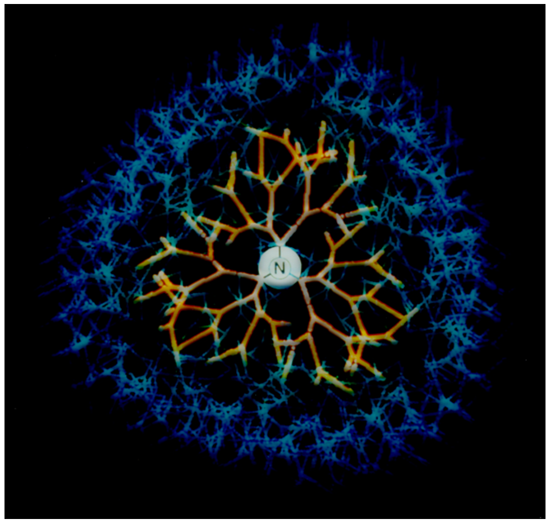
A **liposome** is an artificially-prepared vesicle composed of a lipid bilayer.
The liposome can be used as a vehicle for administration of nutrients and pharmaceutical drugs.
Liposomes are often composed of phosphatidylcholine-enriched phospholipids and may also contain mixed lipid chains with surfactant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

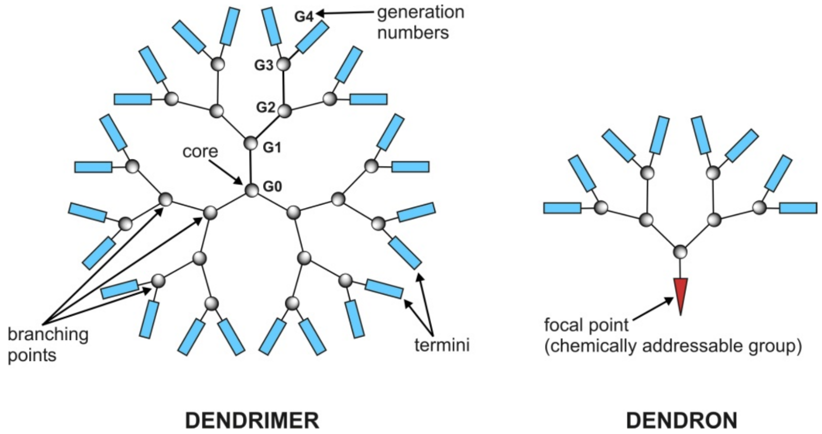
DENDRIMERS

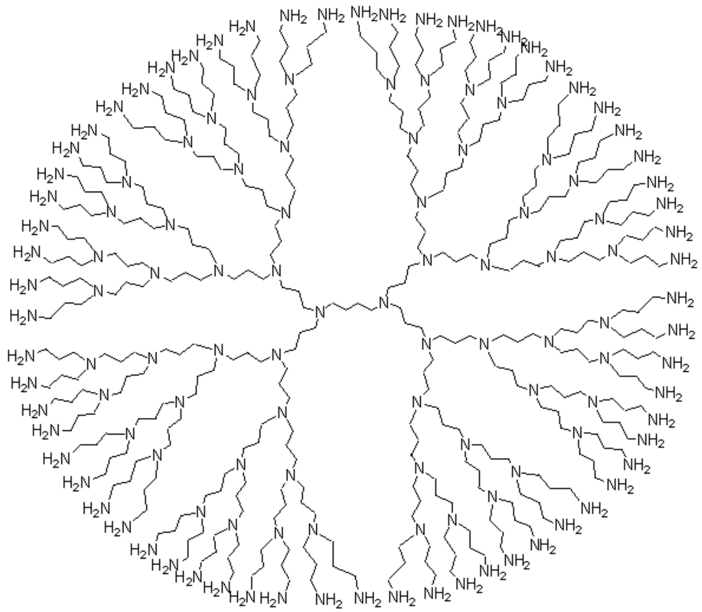
Dendrimers are repetitively branched molecules. The name comes from the Greek word δένδρον (**dendron**), which translates to "tree".

they are monodisperse and usually higly symmetric compounds



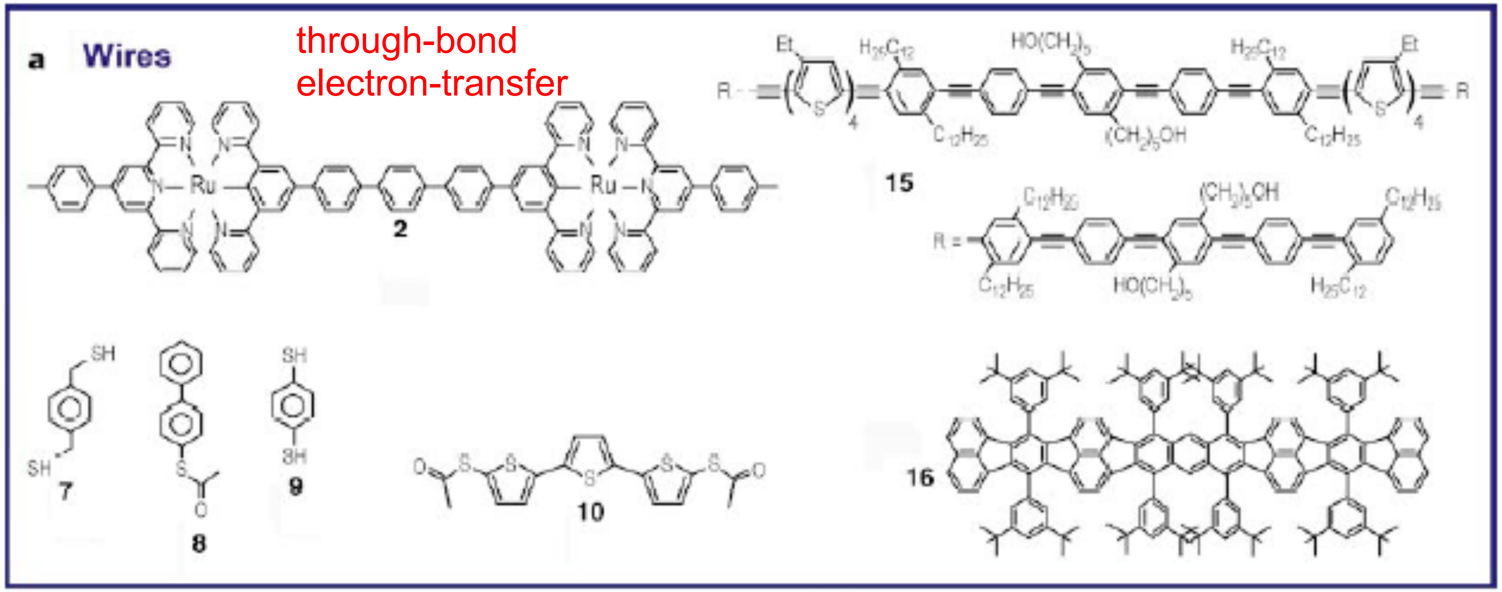






Perchè parlare di **materiali organici**?

ecco alcuni esempi:



fili conduttori

materiali organici

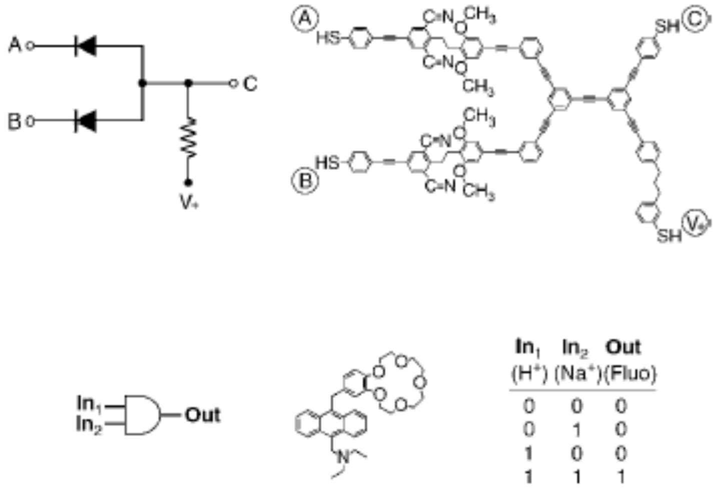
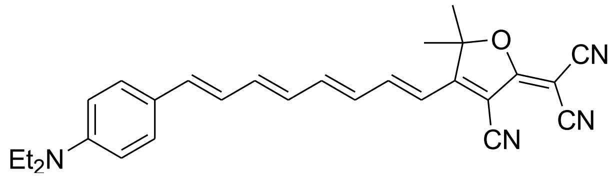
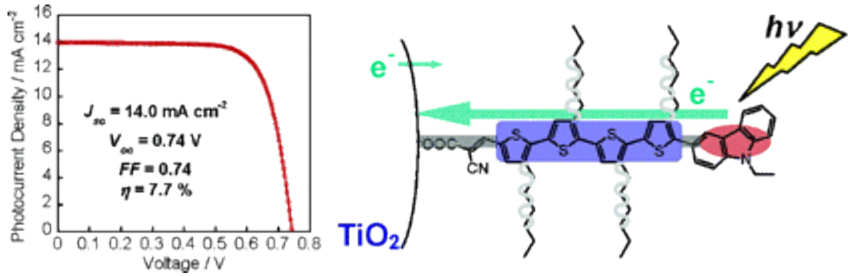


Figure 5. Top: molecular implementation of a diode–diode AND logic gate.[35] Bottom: a molecule that performs in solution according to AND logic.[37a]



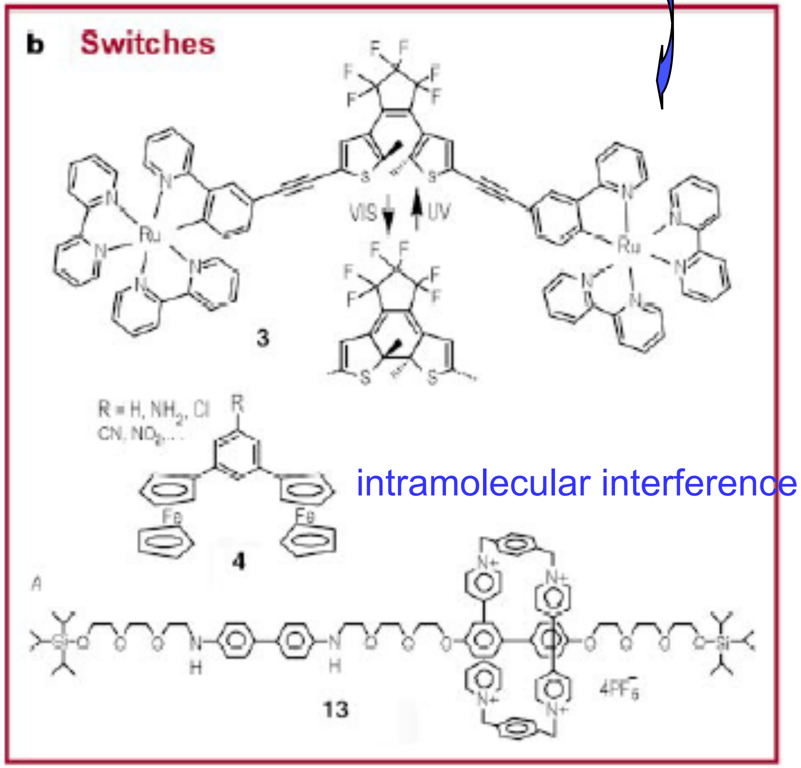
cromoforo con proprietà NLO

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



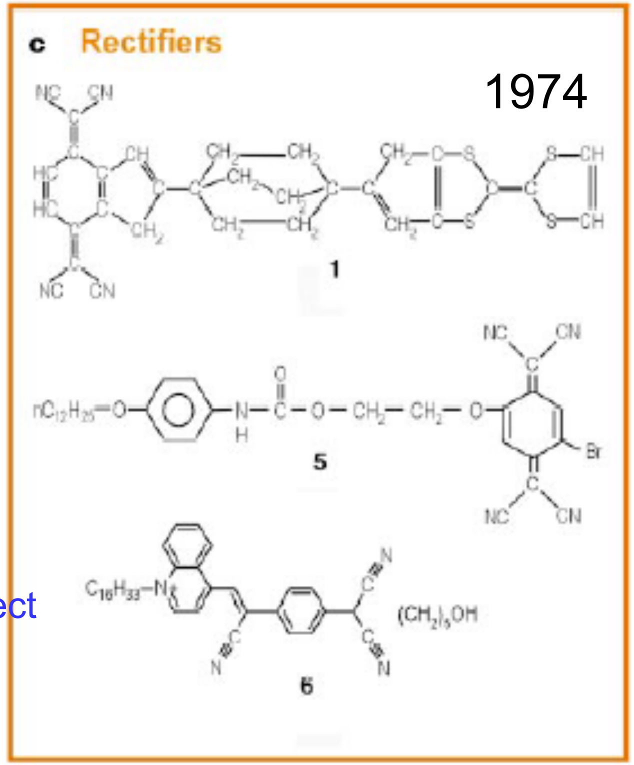
materiali organici

intramolecular light-induced conformation changes



intramolecular interference effect

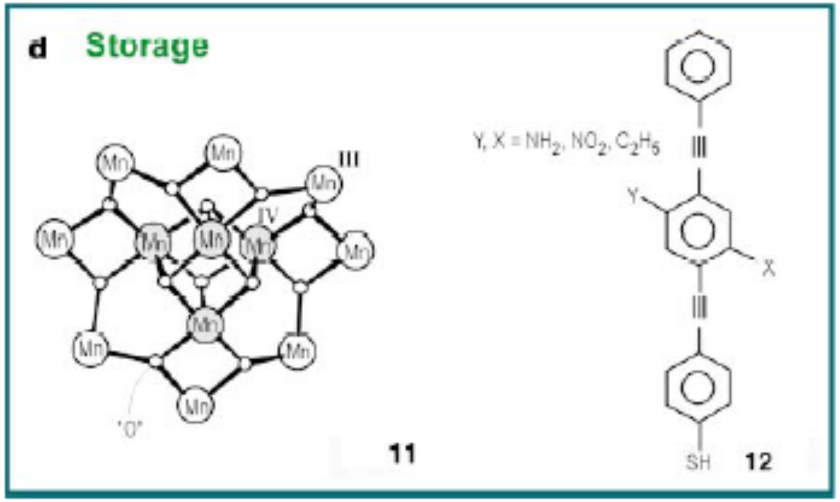
interruttori molecolari elettronici

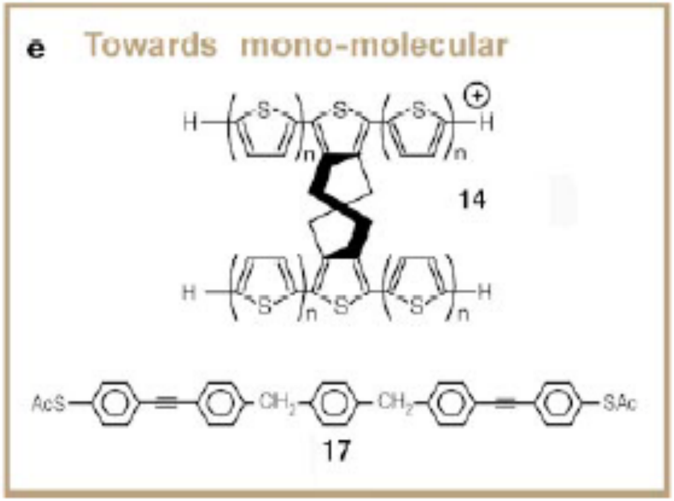


raddrizzatori molecolari

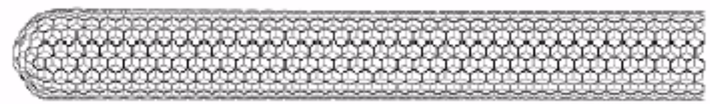
donor-spacer-acceptor (d-s-a)

materiali organici

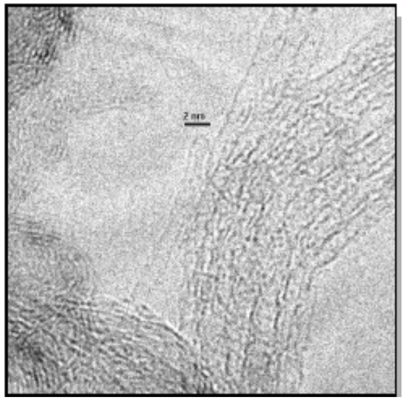




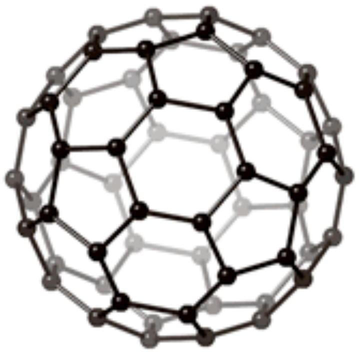
14: transistore intramolecolare
17: componente quantico intramolecolare



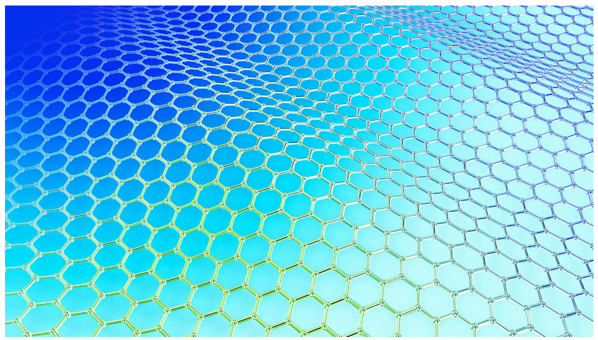
SWCNT
MWCNT



FULLERENI



GRAFENE



macchine molecolari

The Nobel Prize in Chemistry 2016

Jean-Pierre Sauvage

Sir J. Fraser Stoddart

Bernard L. Feringa

"for the design and synthesis of molecular machines".

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

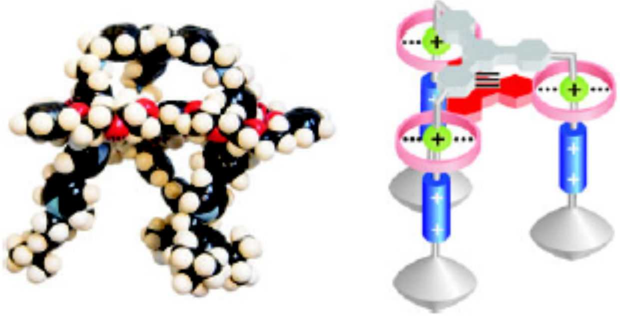
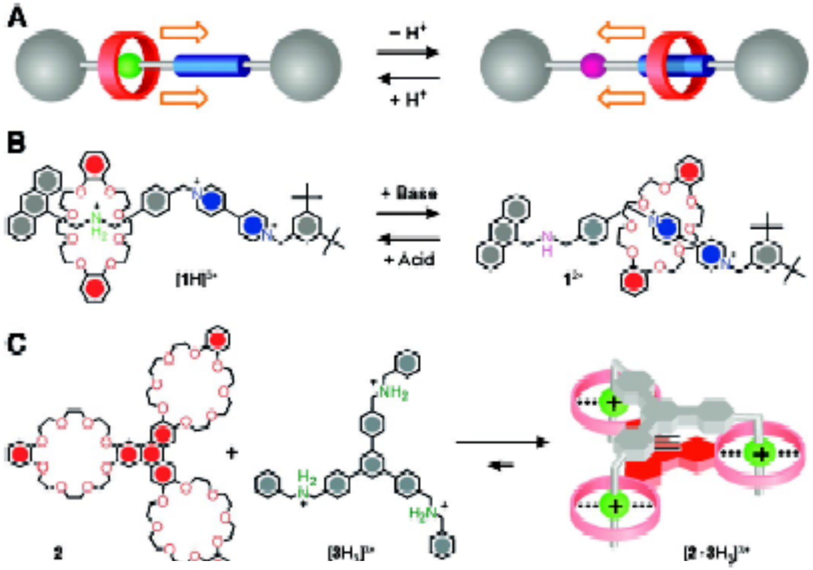
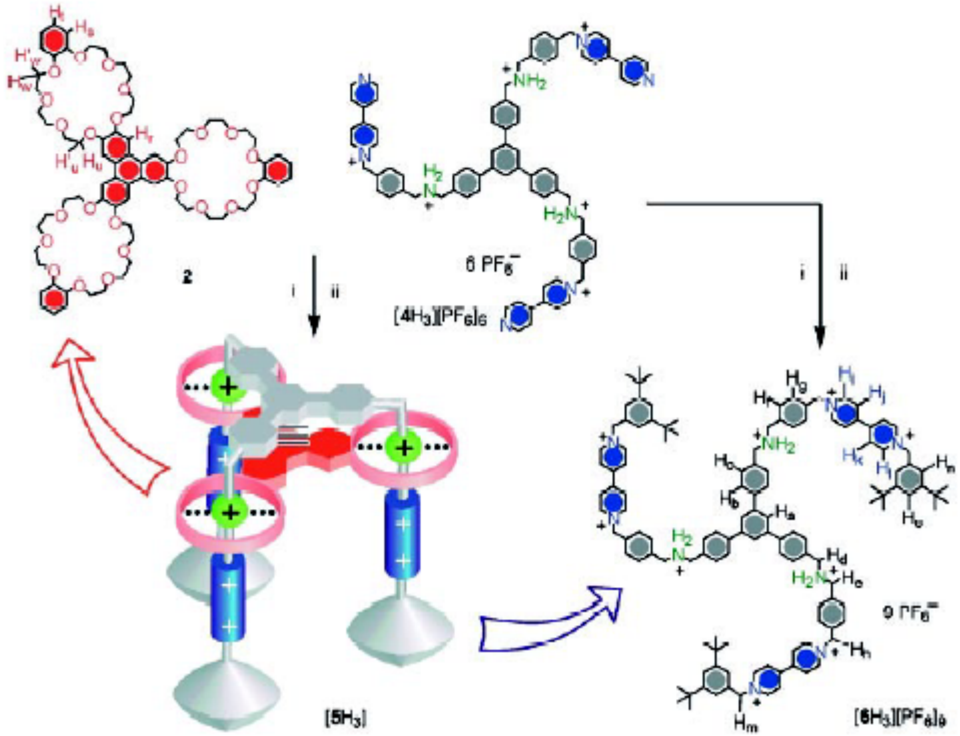


Figure 4. A molecular elevator: the red platform moves up and down upon the addition of acid and base, respectively.[14]





Light-driven monodirectional molecular rotor

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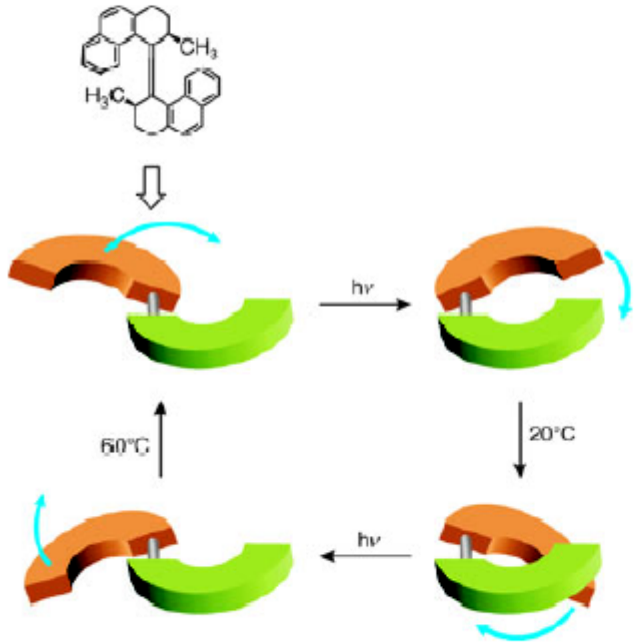


Figure 2. Structural formula and schematic representation of a molecular motor, based on the photoisomerization of an alkene-type compound containing chiral centers, that exhibits light-induced unidirectional rotation.[11]

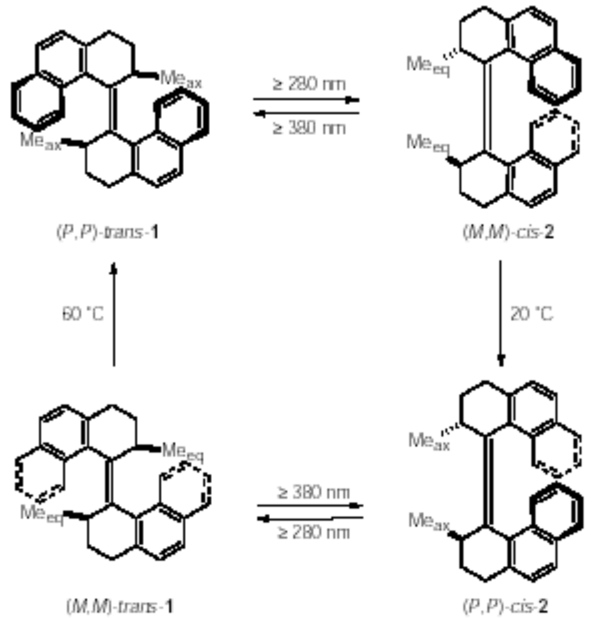


Figure 1 Photochemical and thermal isomerization processes of (*P,P*)-*trans*-**1**. UV irradiation with high pressure Hg-lamp, Pyrex filter, $\lambda \geq 280$ nm or Xe-lamp, Toshiba L-3g glass filter, $\lambda \geq 380$ nm. First order kinetics were observed for the thermal processes and temperature 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.

materiali organici

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

STRUMENTAZIONE

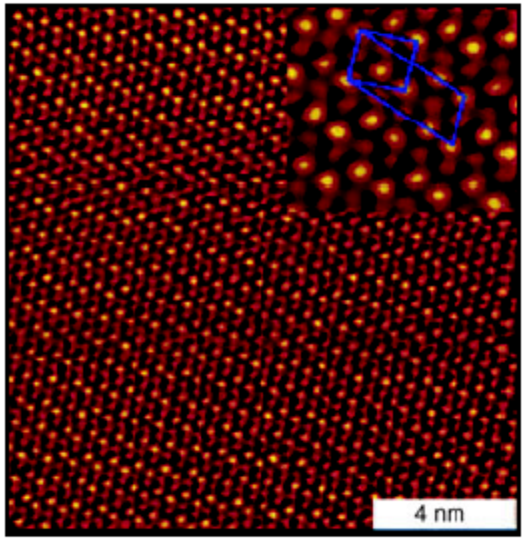


Figure 5. Scanning tunneling microscope image of a self-assembled monolayer (SAM) of decanethiol on gold.[83] The scanning probe microscopes make it possible to view nanostructures in molecular detail, and have revolutionized surface science. SAMs represent a class of material in which properties such 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.

ISPIRAZIONE DALLA NATURA

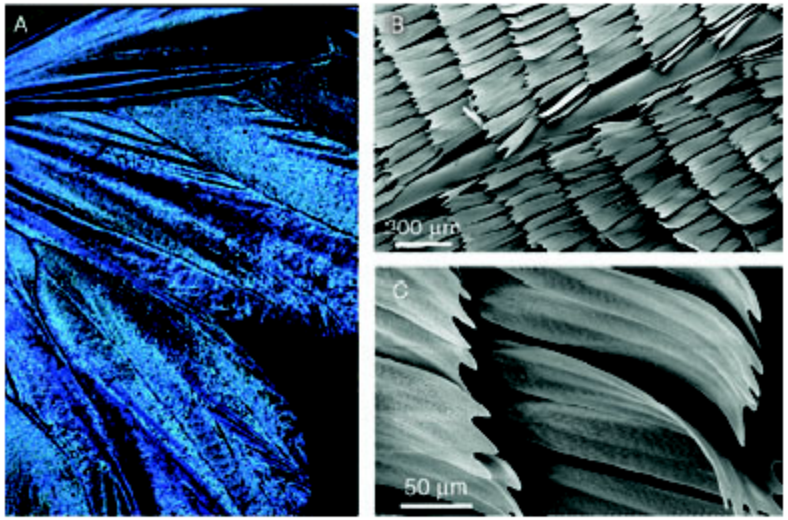


Figure 6. Photograph (A) and SEM images (B,C) of the wing of the *morpho* butterfly (images by Felice Frankel). The brilliant blue reflection from the wing of this butterfly is due to the operation of a remarkable, optically sophisticated photonic bandgap structure, which not only is wavelength selective, 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.

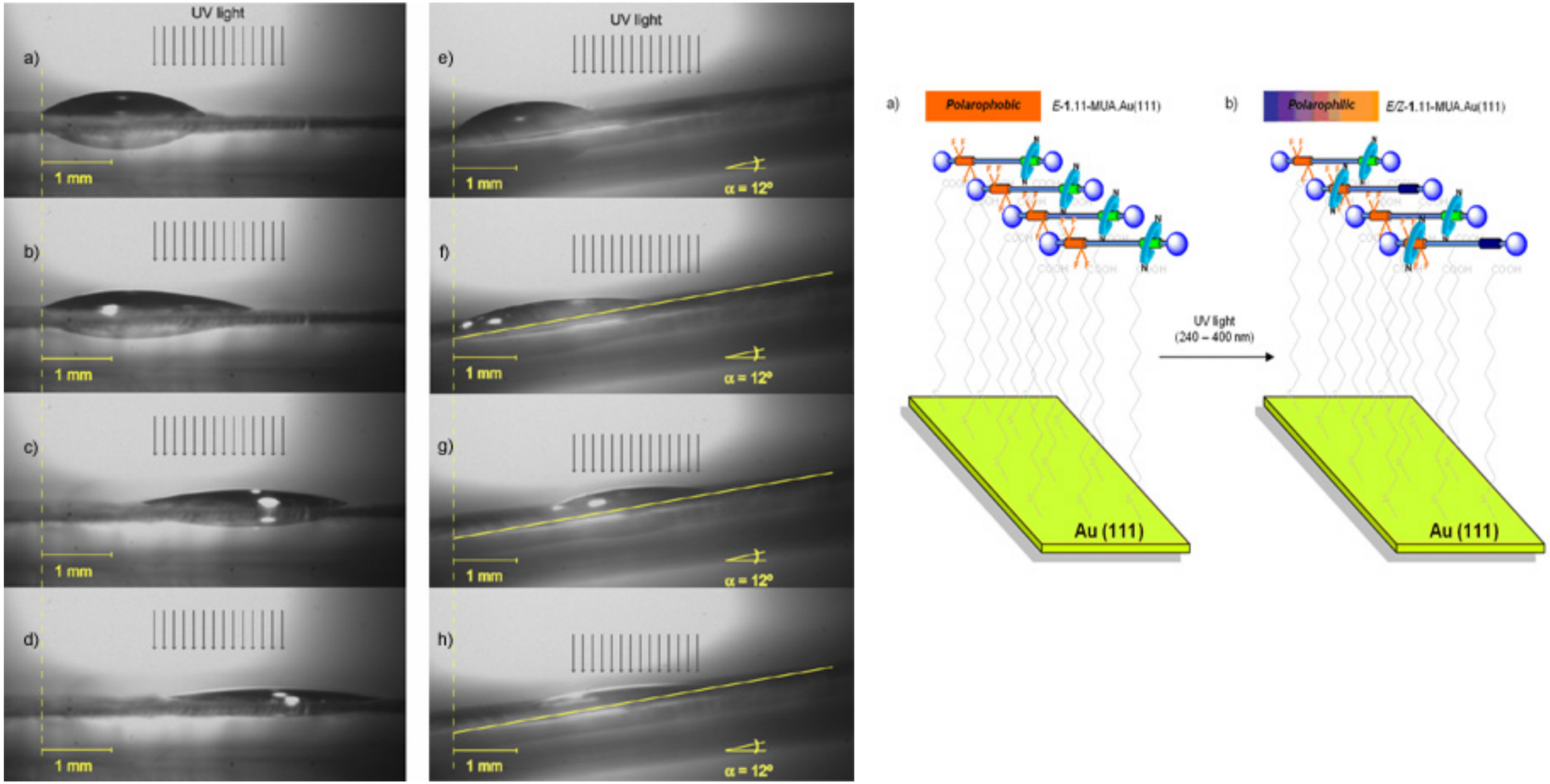
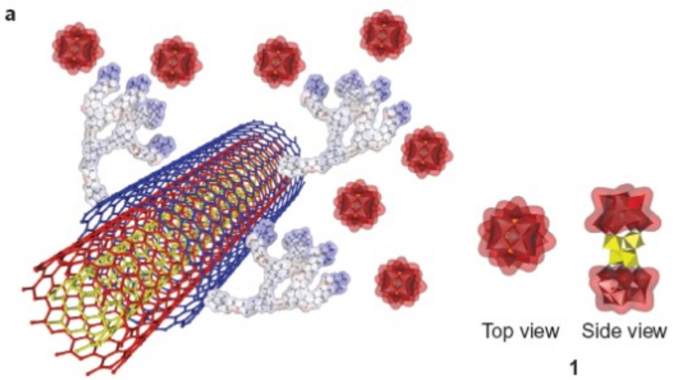


Figure 2. Light-driven directional transport of a 1.25 µl diiodomethane drop across the surface of monolayer of molecular machines, both flat (a)-(d) and up a twelve degree incline (e)-(h). This extrapolation across 6 orders of magnitude in length scales from mechanical motion at the molecular level 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