



**UNIVERSITÀ
DEGLI STUDI
DI TRIESTE**

**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 2021/2022

CONTENTS

- introduction to molecular and supramolecular organic material
 - supramolecular chemistry
 - weak interactions
- organic semiconductors
 - definition, examples
- 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
- fullerenes, carbon nanotubes, graphene, other carbon (nano)materials
 - properties, preparation, functionalization and applications

TEACHING MATERIALS

1. files of the teachers slides on Moodle
2. scientific papers from literature
3. registered 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](#)

T. J. J. Müller, U. H. F. Bunz, Functional Organic Materials –
[in the teacher office](#)

SCHEDULE

classes: 4 hours per week

Monday	10.15 – 11.00
Thursday	12.15 – 13.00
Wednesday	10.15 – 11.00
Friday	10.15 – 11.00

students can contact the teachers by
e-mail: lpasquato@units.it or prato@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 presented

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 Power Point (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 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.

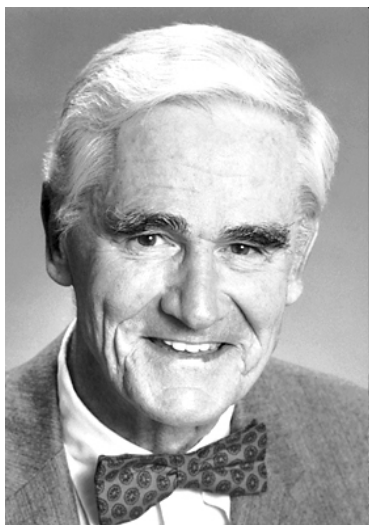
Questa è la **chimica supramolecolare** sviluppata da:

Donald J. Cram,

Jean-Marie Lehn,

and Charles J. Pedersen

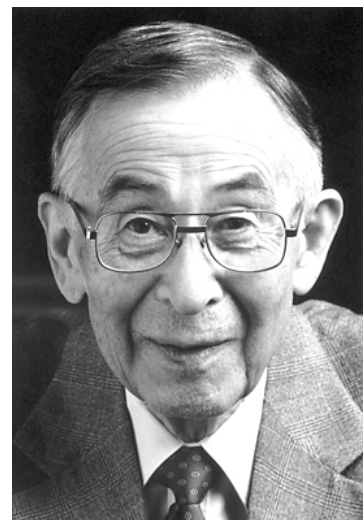
che per questo sono stati insigniti del Premio Nobel per la Chimica nel 1987.



Donald J. Cram



Jean-Marie Lehn



Charles J. Pedersen

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".

materials self-assembly

materials self-assembly: is related to that part of chemistry beyond molecular assembly. In this case the forces driving self-assembly are capillary interactions, colloids formation, elastic interactions, electric field gradient, magnetic fields, etc. The system evolve towards a lower energy material with a higher structural stability.

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.

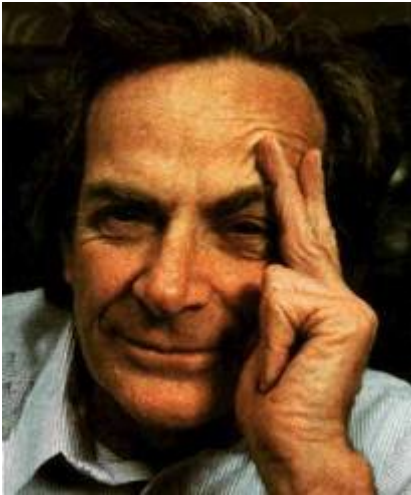
NANOMATERIALS

definition

size In the scientific community, it is commonly used to designate structures at least 1 nm but less (often much less) than 1 μm . 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 Britannica 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 Britannica.”

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).

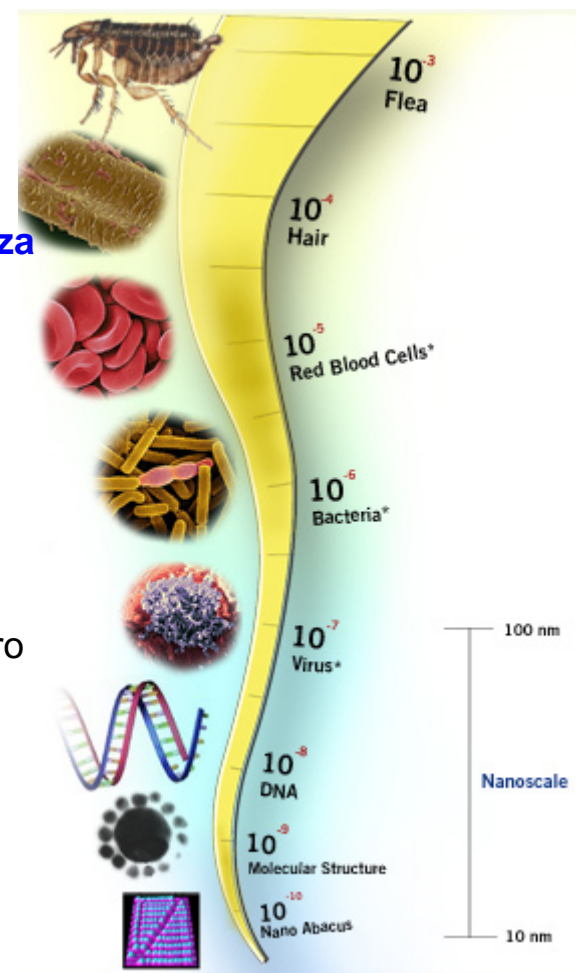
Phenomenon	Typical length scale
Size quantization	tens of nanometers
Crystal phase	tens of nanometers
Doping/ defects	tens of nanometers
Single-charge effects	ca. 50 nm (at room temperature)
Charge depletion (screening length)	ca. 100 nm
Scattering/ interference of light	hundreds of nanometers
Ballistic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

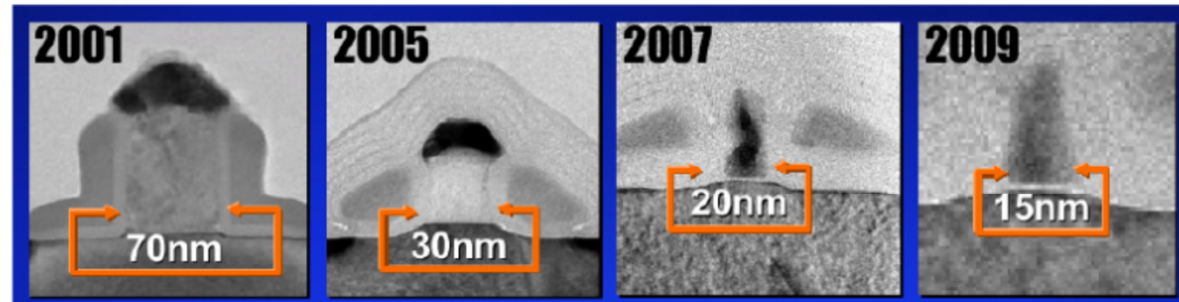
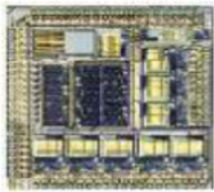
unità di misura abbreviazione descrizione

metro	m	unità base SI della lunghezza
centimetro	cm	1×10^{-2} m (0.01 m)
millimetro	mm	1×10^{-3} m (0.001 m)
micrometro	μm	1×10^{-6} m
nanometro	nm	1×10^{-9} m la billionesima parte di 1 metro o 10 \AA



Why Nano?

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

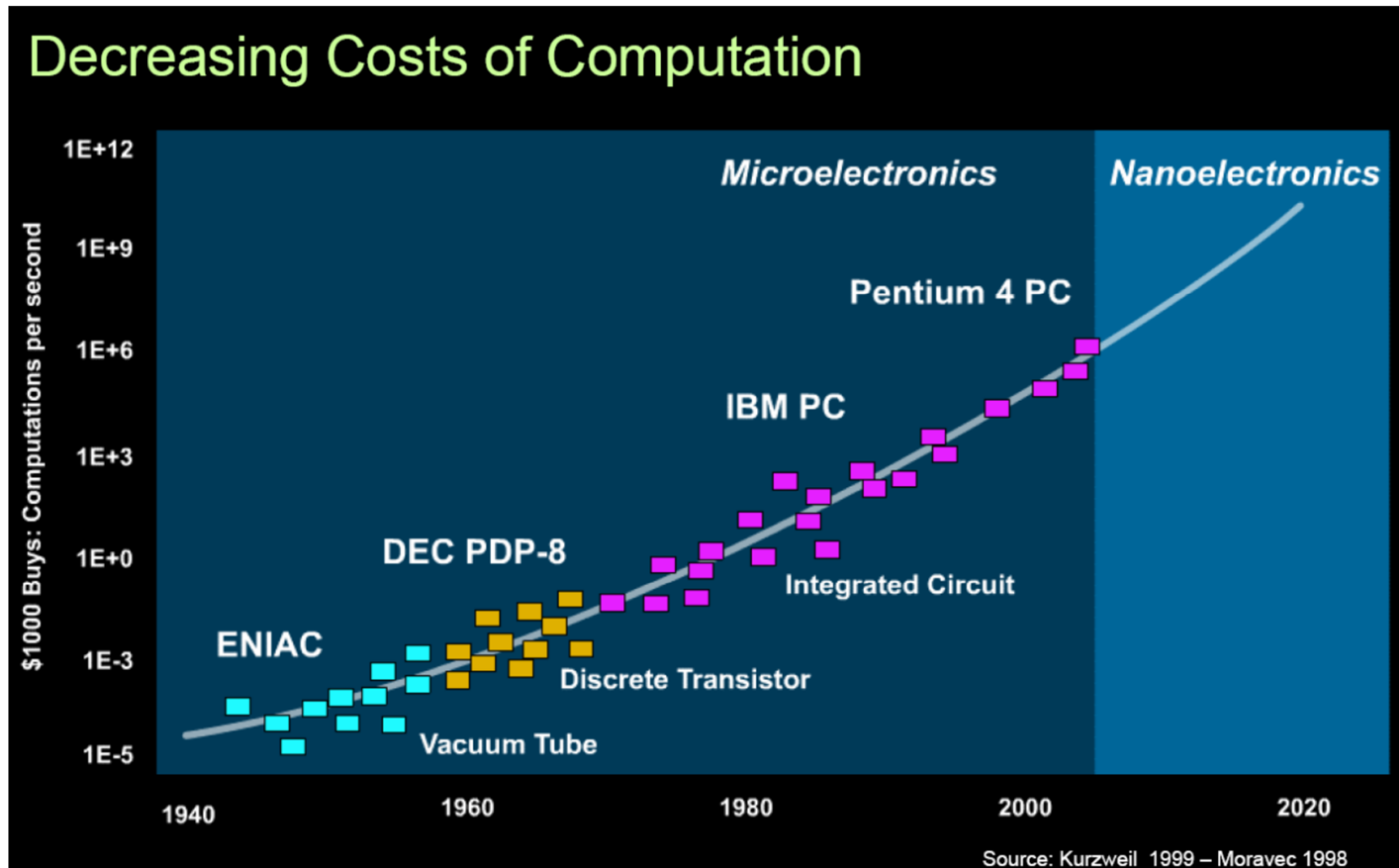


Intel's transistors

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

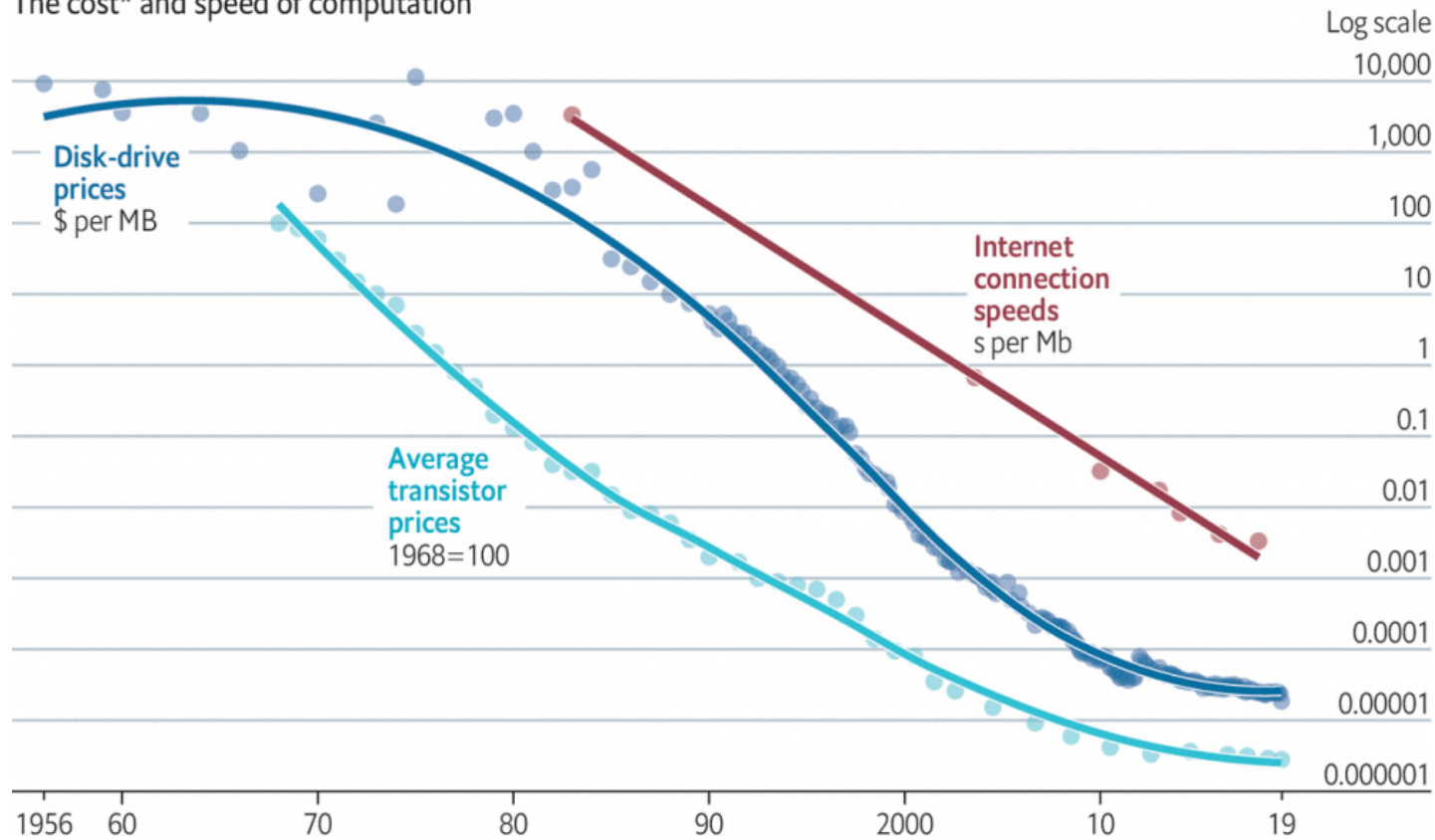
- to enhance performance and produce new properties and applications
- for many types of systems (mechanical, biological, chemical, optical) in addition to electronic

Why Nano?



Decline and fall

The cost* and speed of computation

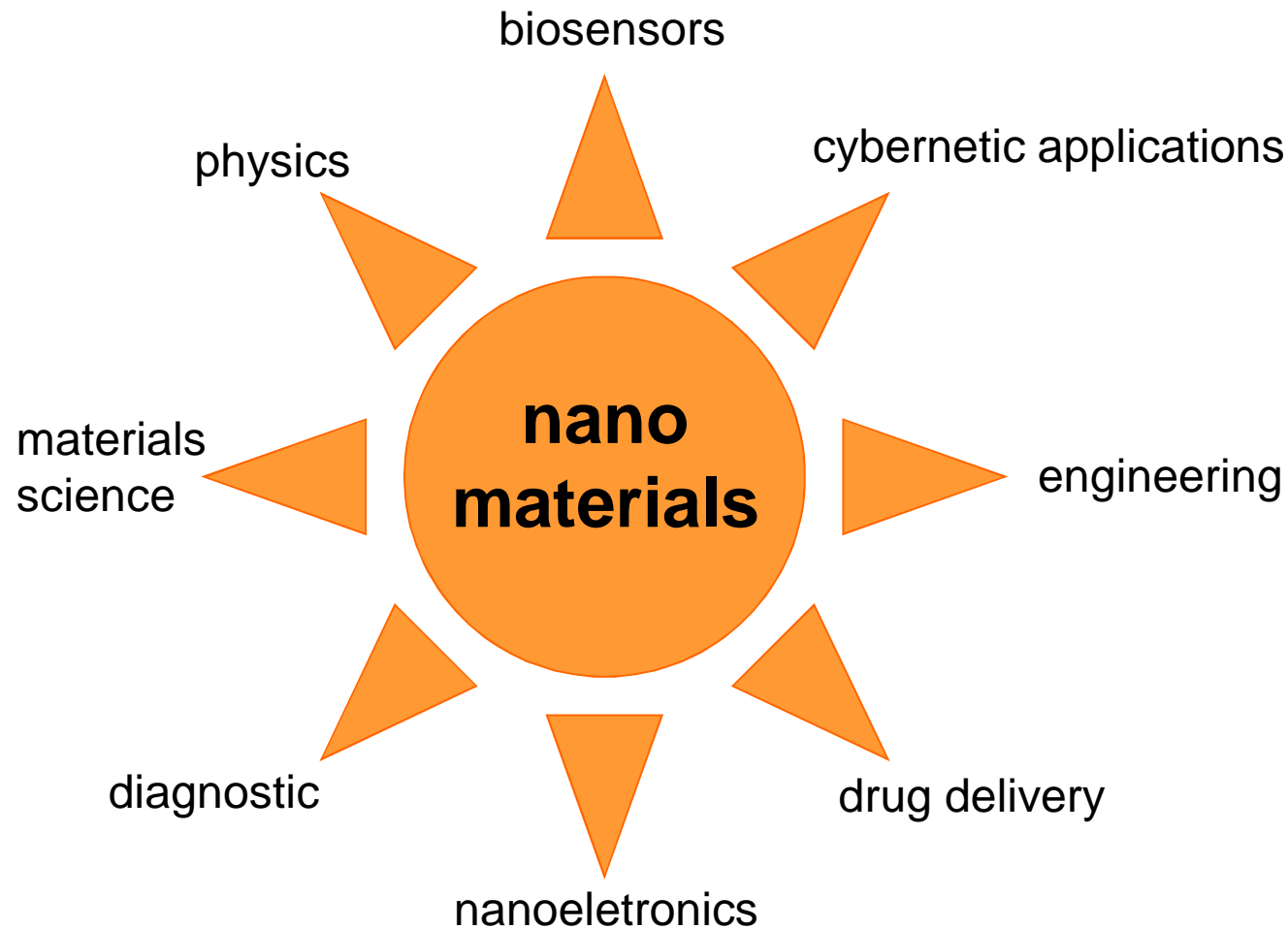


Sources: John C. McCallum; Gordon Moore; The Linley Group; Nielsen Norman Group; *The Economist*

*Nominal prices

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

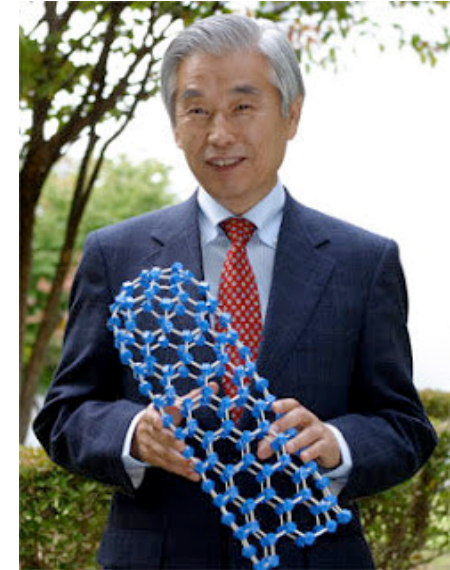
National Nanotechnology Initiative, which defined nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers.

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

Nanotechnology

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.

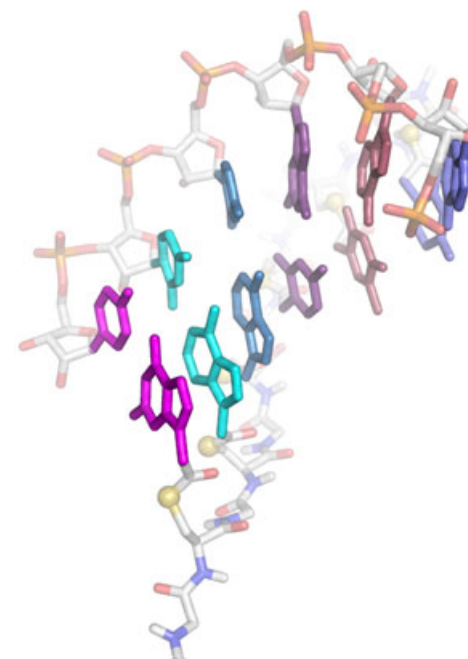
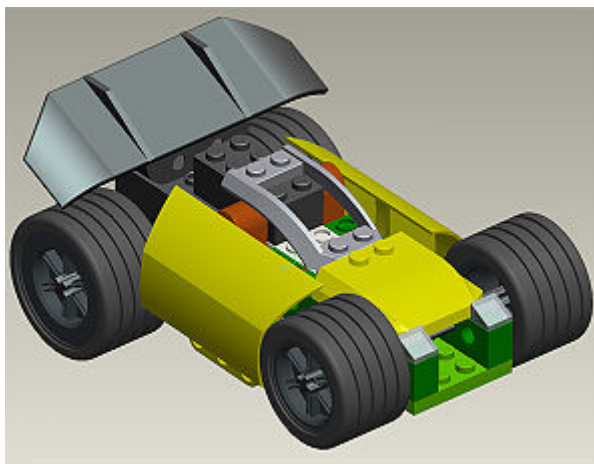


many devices are obtained with this approach with a fine control of the miniaturization processes.

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

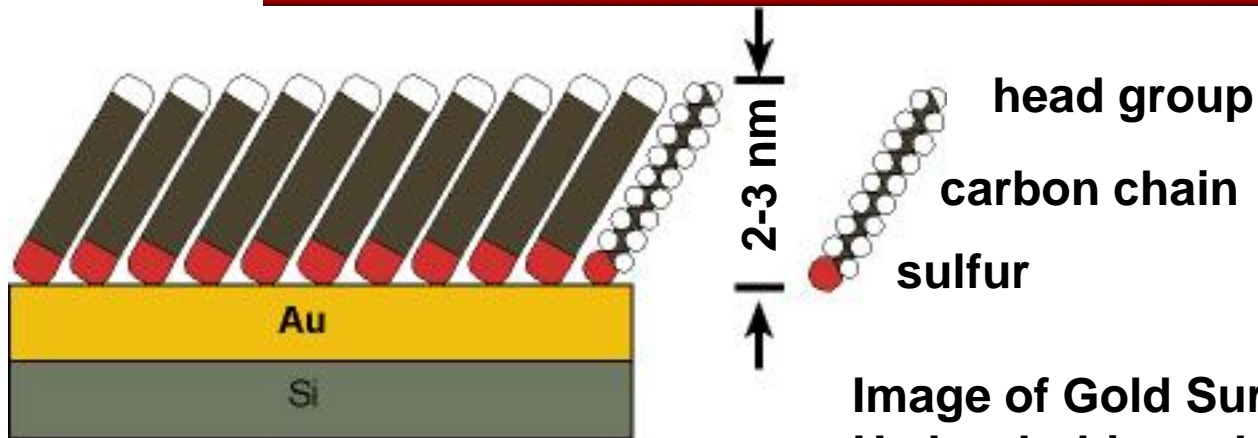
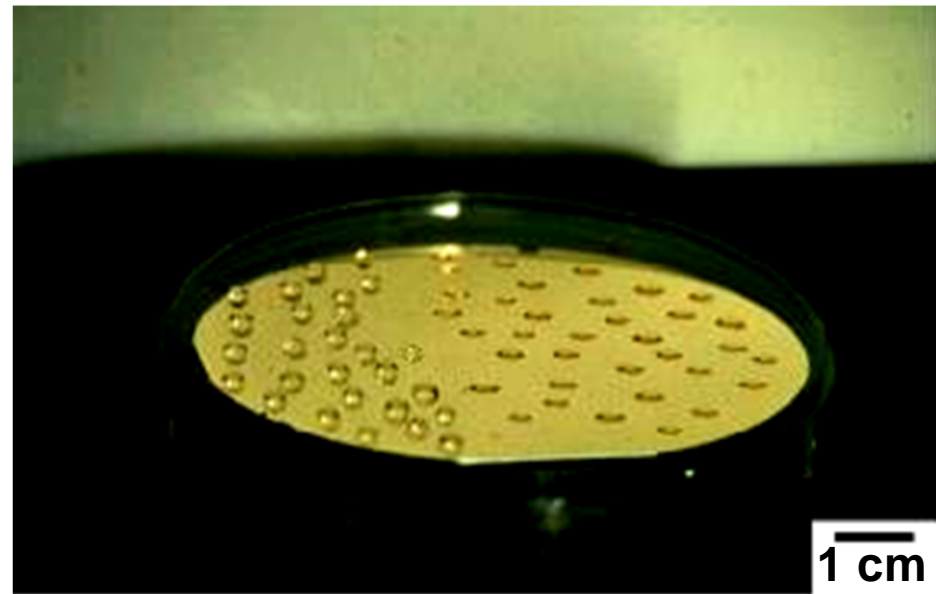
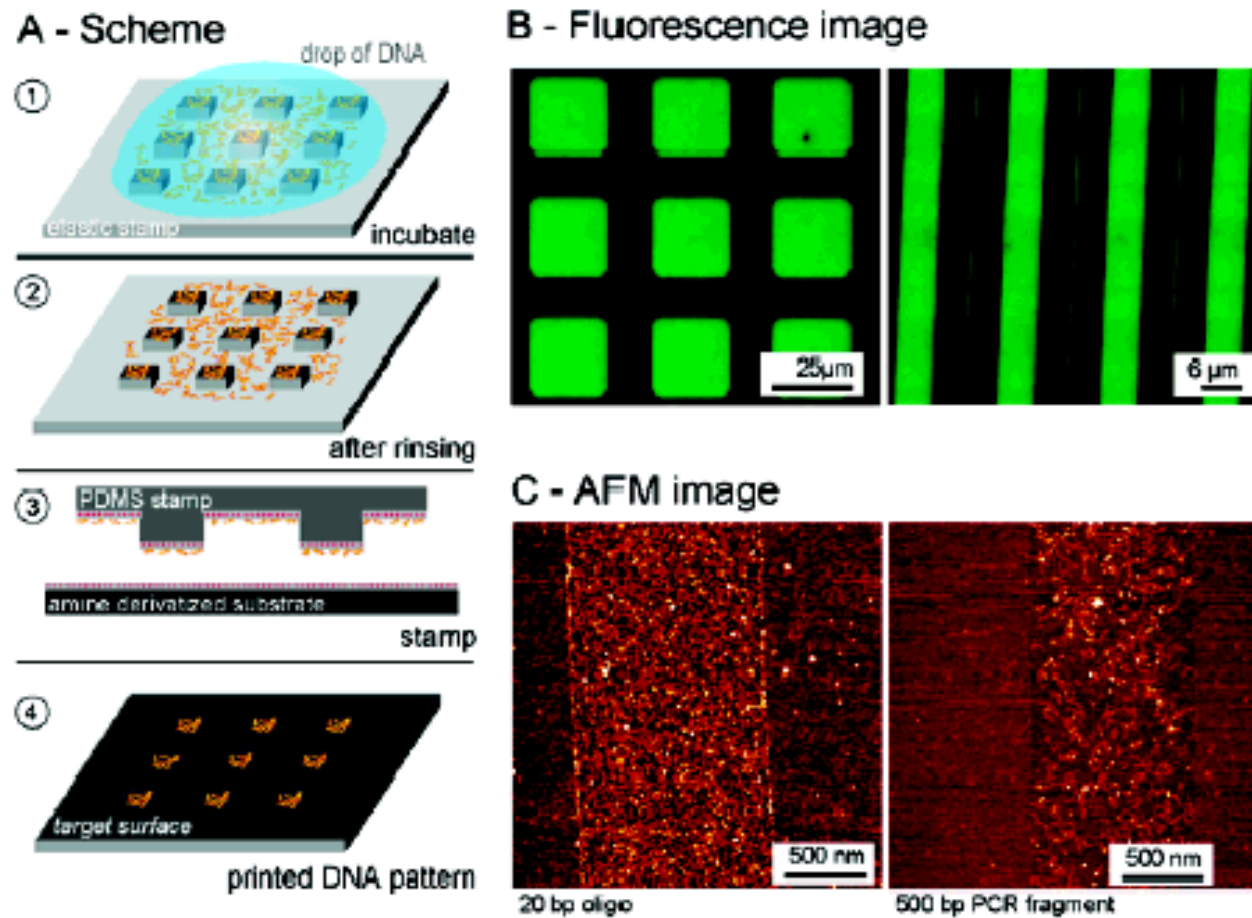


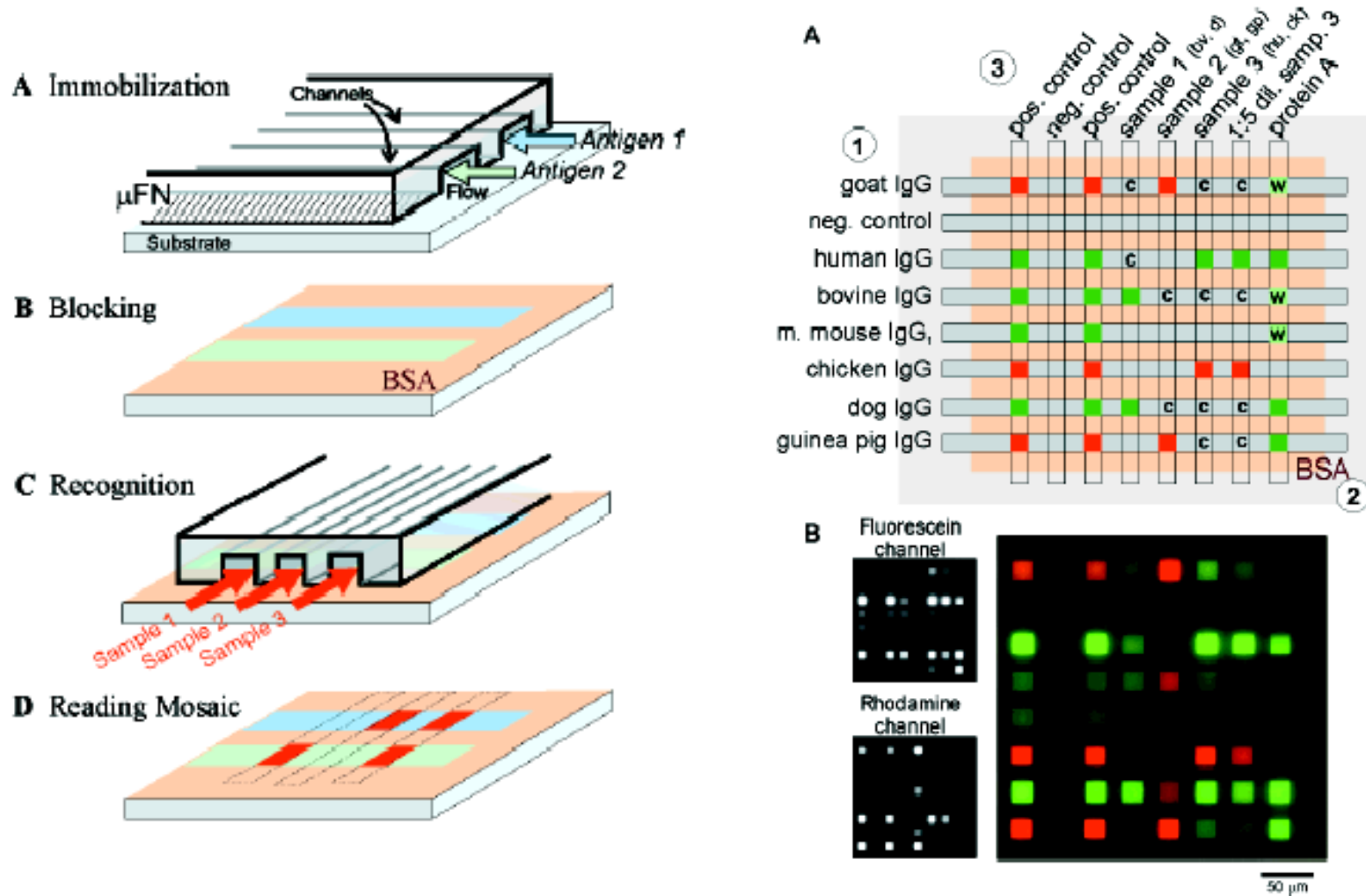
Image of Gold Surface Patterned with Hydrophobic and Hydrophilic SAMs



Microcontact Printing DNA

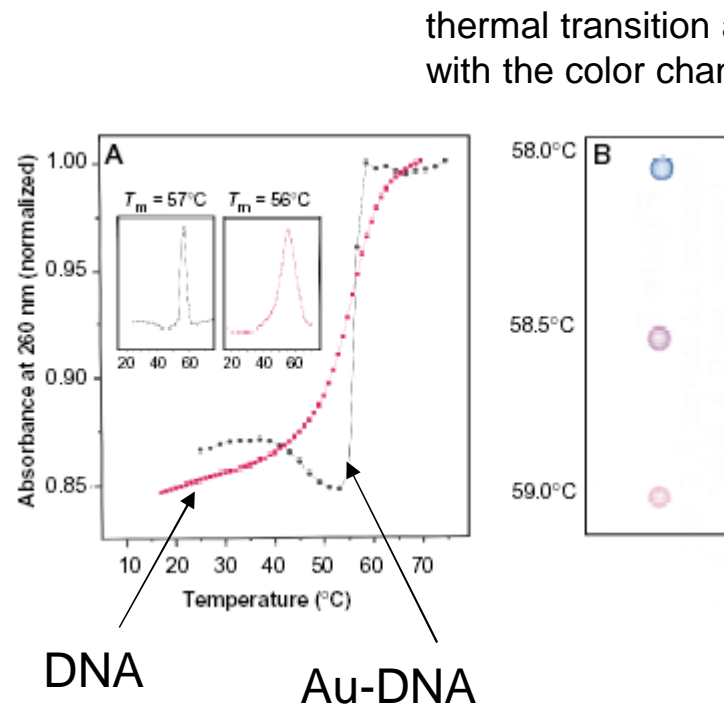


Immunoassays



Nanoparticle-based Sensors

selective colorimetric detection system for polynucleotides



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- μ l thin-walled Eppendorf tube by addition of 1 μ l of a 6.6 μ M oligonucleotide target to a mixture containing 50 μ l of each probe (0.06 μ M 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- μ l aliquots were removed at the indicated temperatures and spotted on a C₁₈ 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

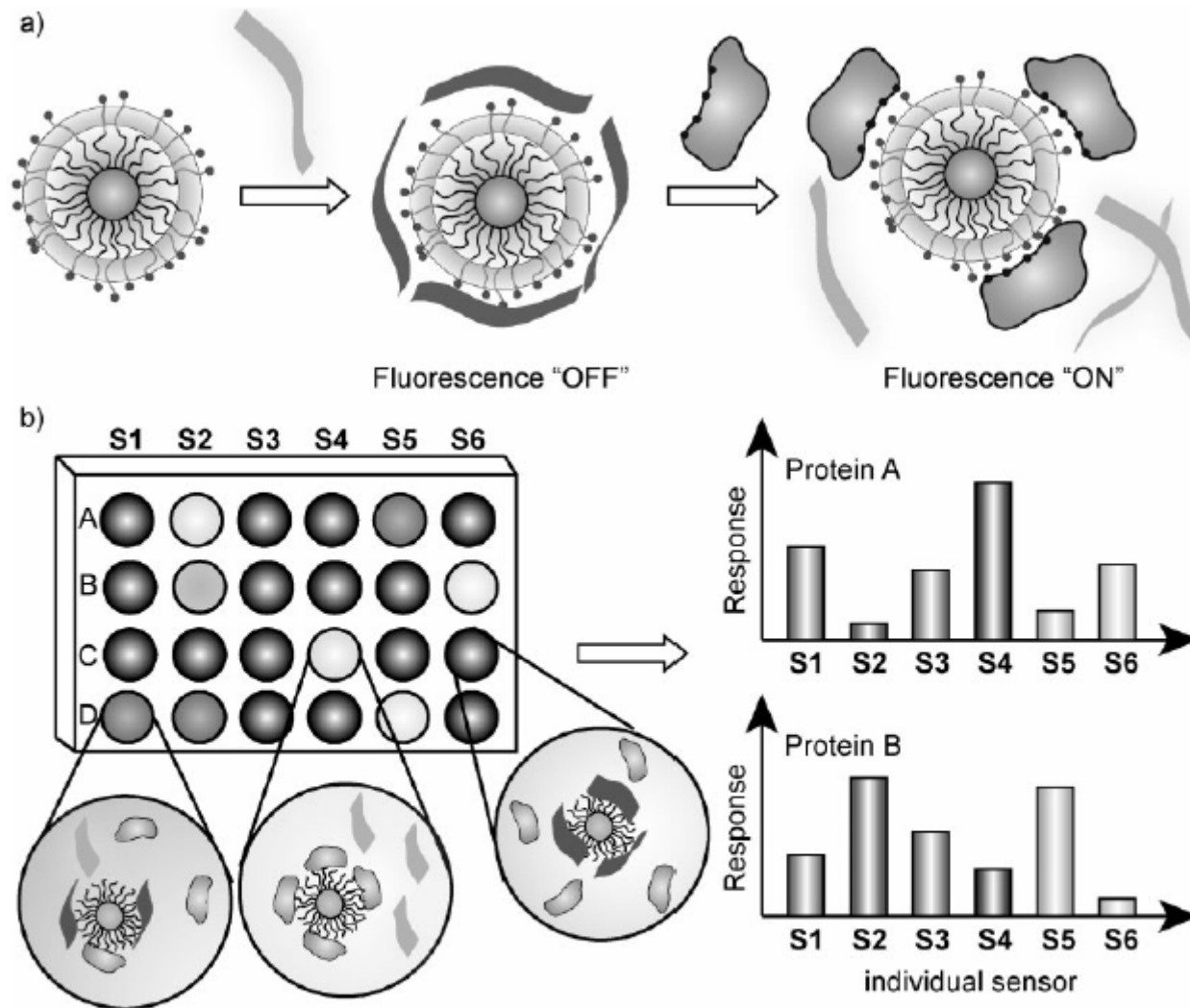


Figure 8. Schematic drawing of a “chemical nose” sensor array based on nanoparticle and fluorescence assay. a) The competitive binding between protein and quenched polymer leads to the fluorescence light-up. b) The combination of an array of sensors generates fingerprint response patterns for individual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

Nanoparticles for new therapeutic strategies

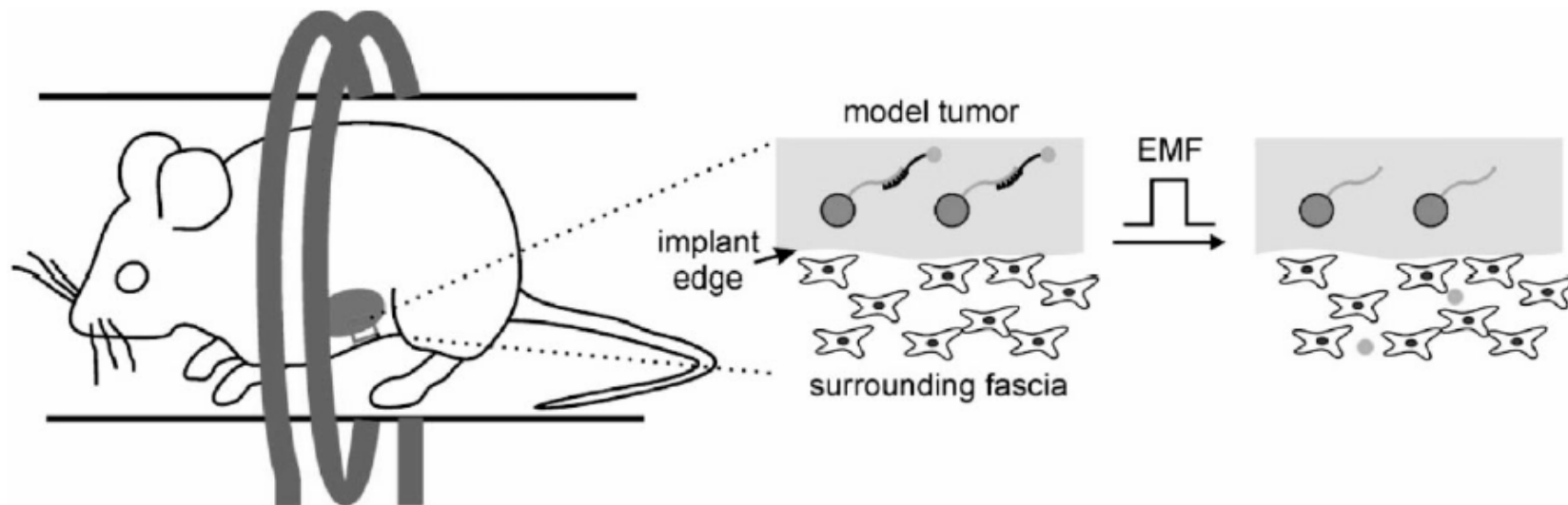
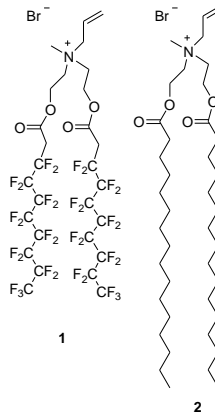


Figure 12. Controlled release of payloads using oligonucleotide-modified iron oxide nanoparticles for drug delivery at a remote location. Adapted with permission from [105].

polymers/block copolymers

A 3D diagram of a lipid bilayer. The outer surface is composed of blue spheres representing hydrophilic heads. The inner core consists of yellow wavy lines representing hydrophobic tails. The structure is shown in a cross-section, revealing the internal arrangement of the molecules.



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.

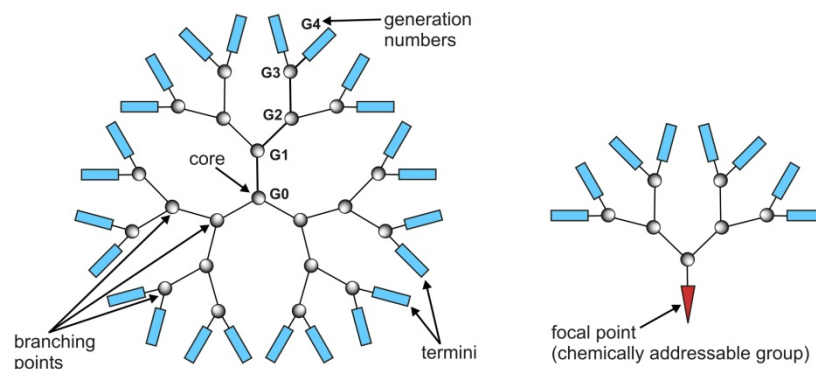
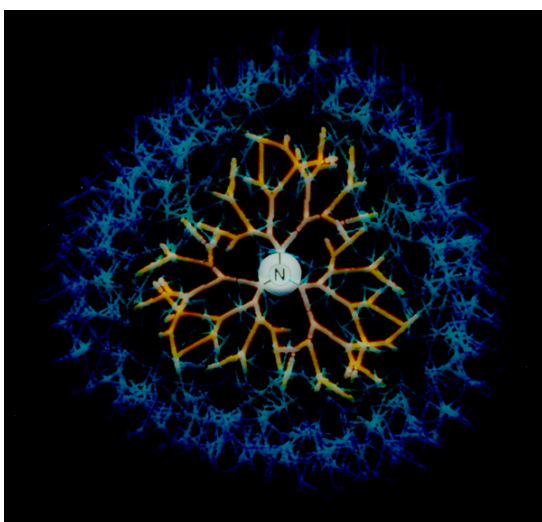
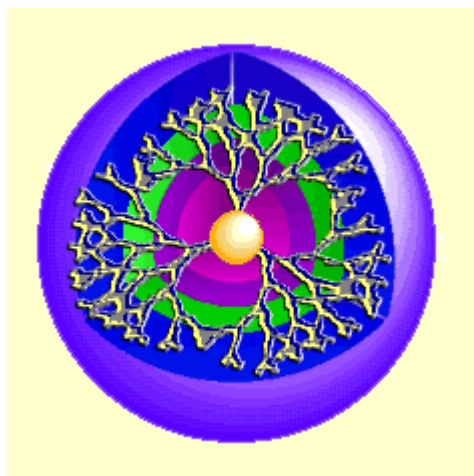
Liposomes are often composed of phosphatidylcholine-enriched phospholipids and may also contain mixed lipid chains with surfactant properties such as egg phosphatidylethanolamine

30

DENDRIMERS

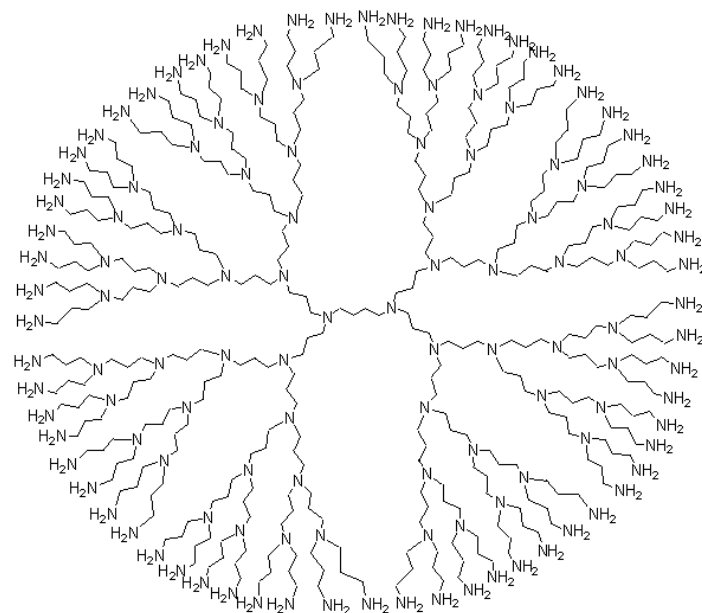
Dendrimers are repetitively branched molecules. The name comes from the Greek word δένδρον (**dendron**), which translates to "tree".

they are monodisperse and usually highly symmetric compounds

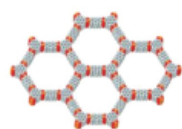


DENDRIMER

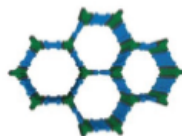
DENDRON



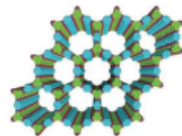
Covalent Organic Frameworks



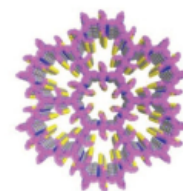
COF-10^{a)}



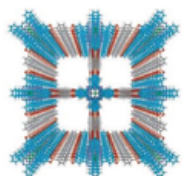
HHTP-DPB COF^{b)}



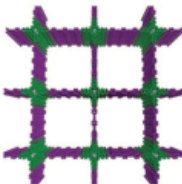
TP-COF^{c)}



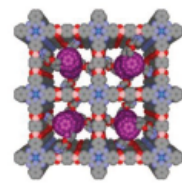
COF-S-SH^{d)}



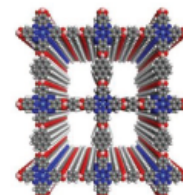
NiPc COF^{e)}



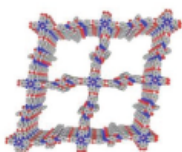
ZnPc-PPE COF^{f)}



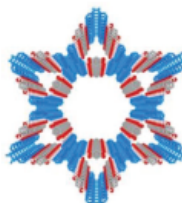
[C₆₀]-ZnPc-COF^{g)}



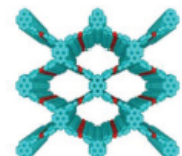
MC-COF-NiPc-E₁E₇^{h)}



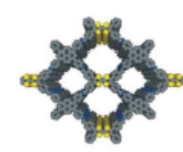
CuPc-FPBA-DETHzⁱ⁾



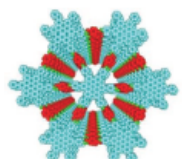
TPE-Ph COF^{j)}



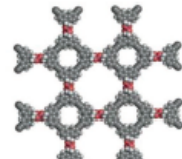
Py-Azine COF^{k)}



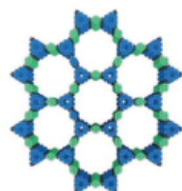
TTF-Py-COF^{l)}



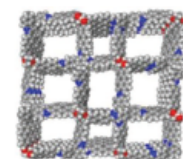
HBC-COF^{m)}



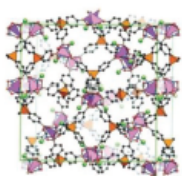
ICOF-2ⁿ⁾



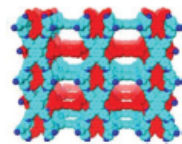
Star-COF-2^{o)}



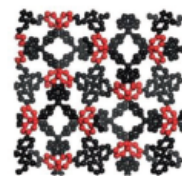
CCOF-2^{p)}



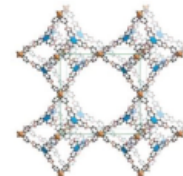
COF-202^{q)}



3D-Py-COF^{r)}



COF-102^{s)}



COF-108^{t)}

organic materials

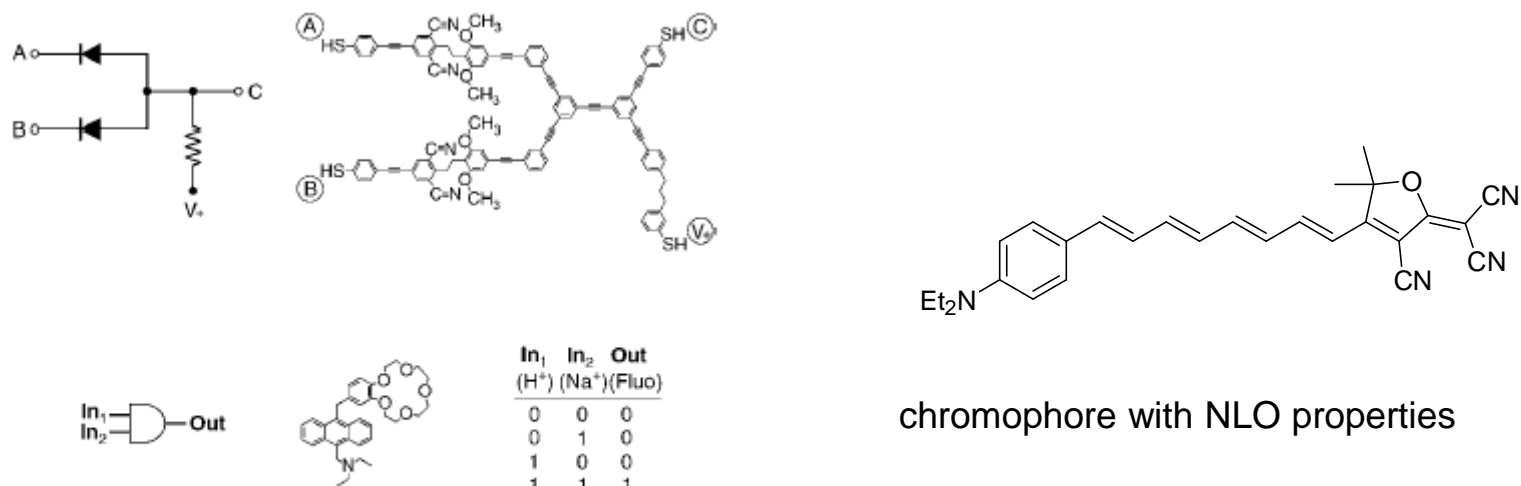
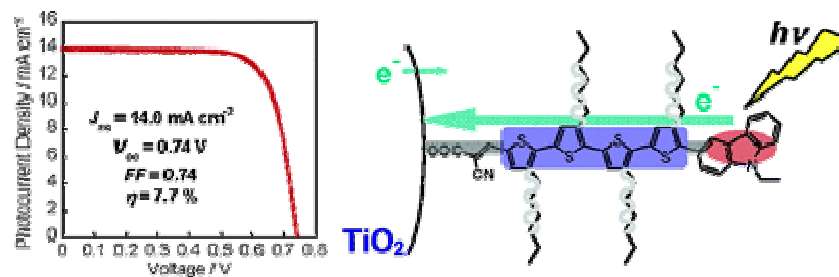


Figure 5. Top: molecular implementation of a diode-diode AND logic gate.^[35] Bottom: a molecule that performs in solution according to AND logic.^[37a]

Alkyl-Functionalized Organic Dyes for Efficient Molecular Photovoltaics

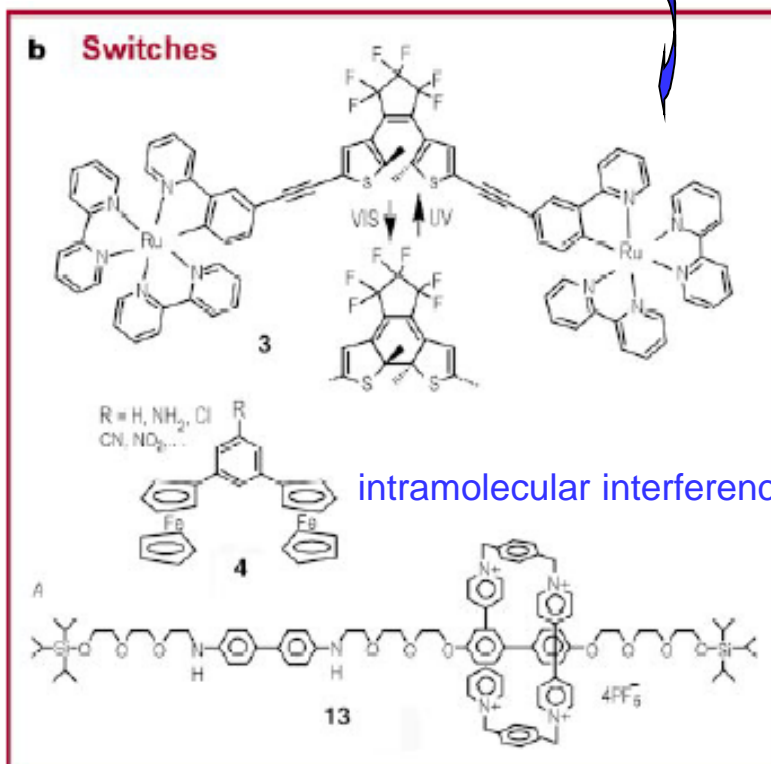
Nagatotoshi Koumura, Zhong-Sheng Wang, Shogo Mori, Masanori Miyashita, Eiji Suzuki, and Kohjiro Hara

Web Release Date: 18-Oct-2006; (Communication) DOI: [10.1021/ja0645640](https://doi.org/10.1021/ja0645640)

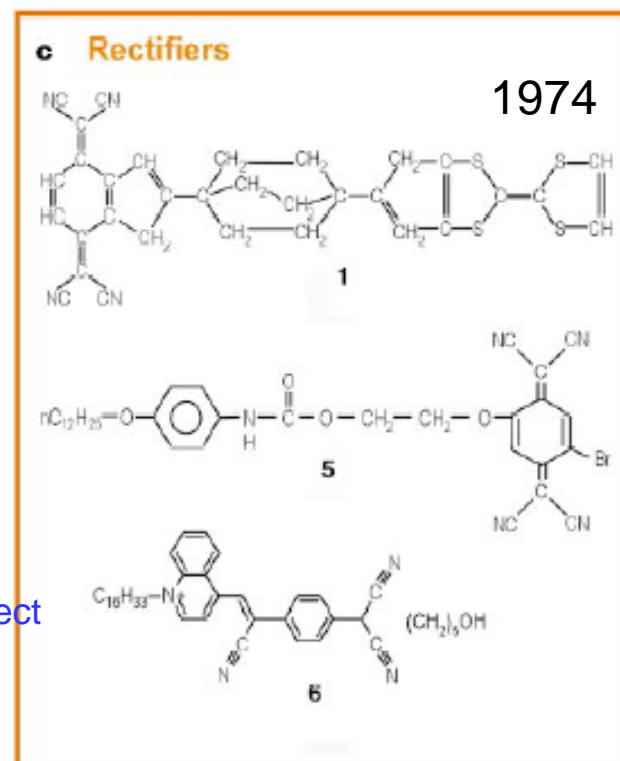


organic materials

intramolecular light-induced
conformation changes



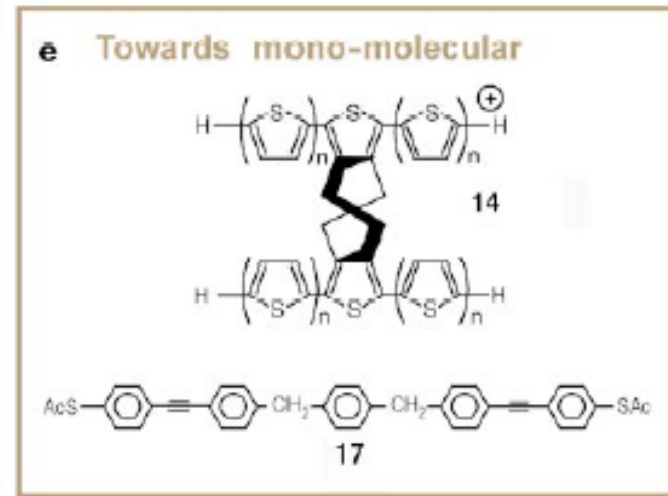
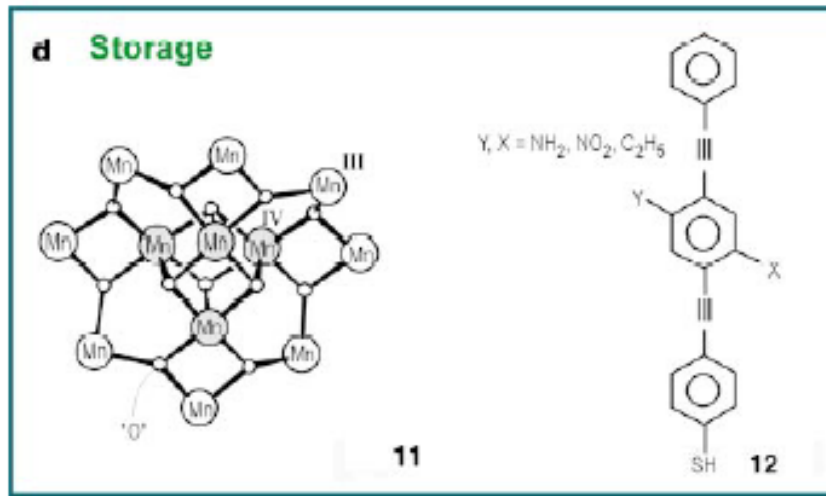
molecular electronic switches



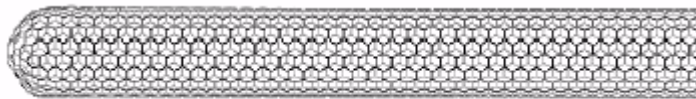
molecular rectifiers

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

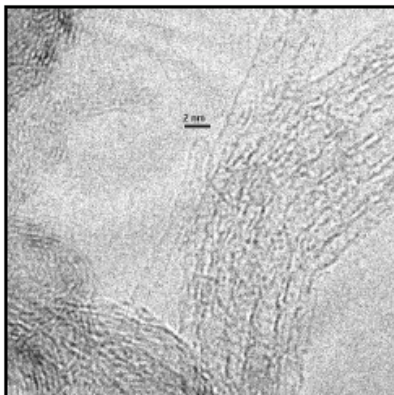
organic materials



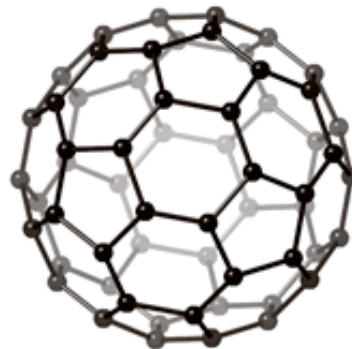
14: intramolecular transistor
17: intramolecular quantic tran



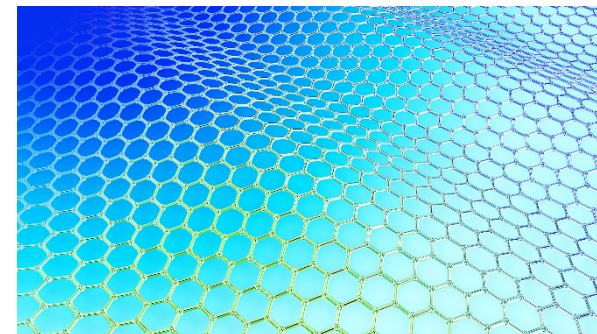
SWCNT
MWCNT



FULLERENES



GRPHFENE



A Molecular Elevator

Jovica D. Badjic¹, Vincenzo Balzani,²

Alberto Credi,^{2*}

Serena Silvi,² J. Fraser Stoddart^{1*}

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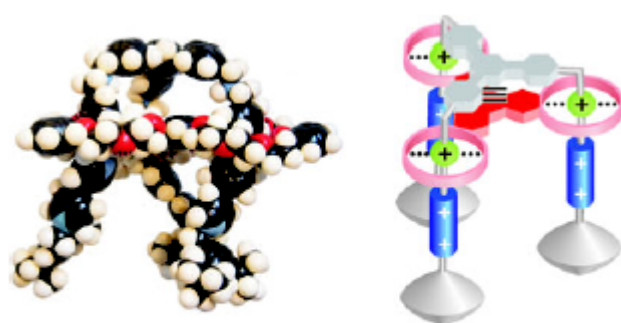
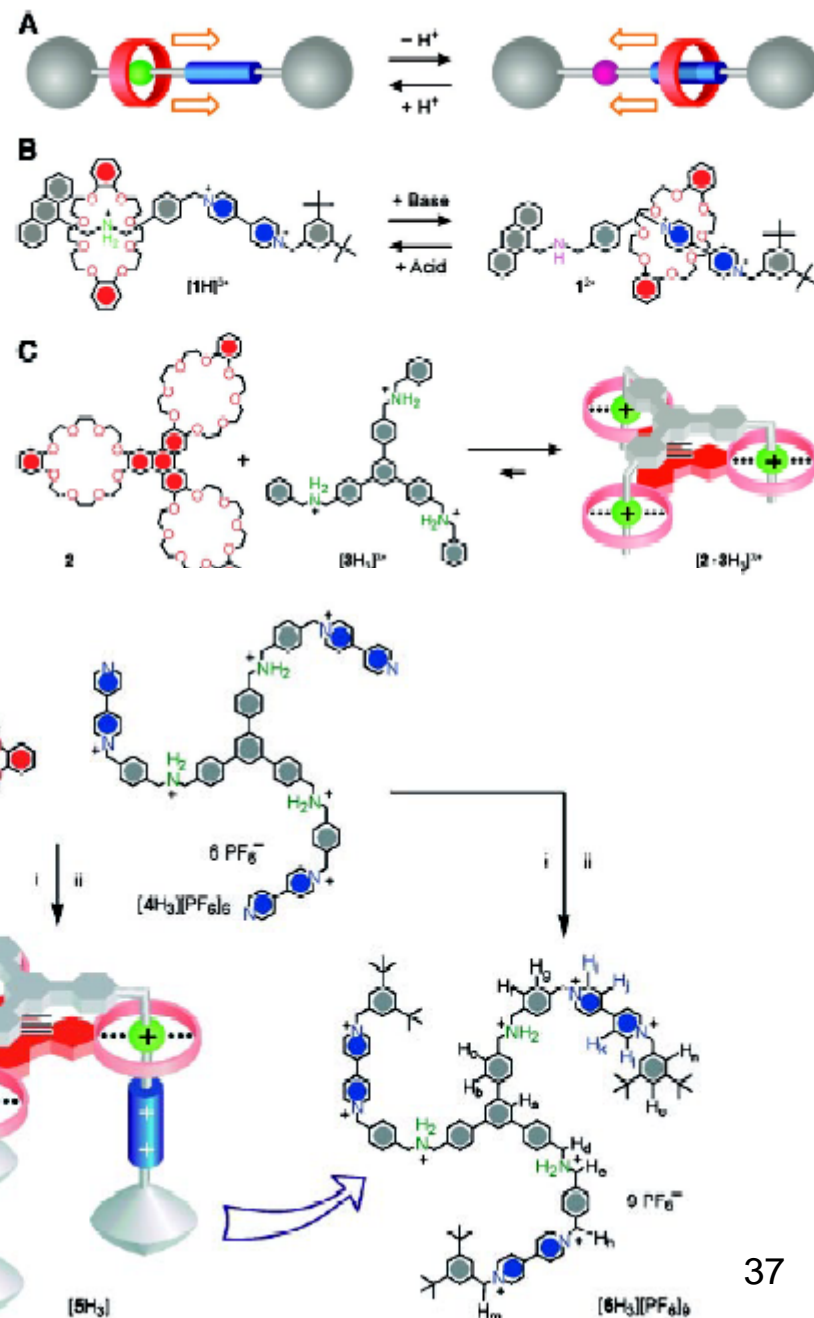


Figure 4. A molecular elevator: the red platform moves up and down upon the addition of acid and base, respectively.^[14]



organic materials

Light-driven monodirectional molecular rotor

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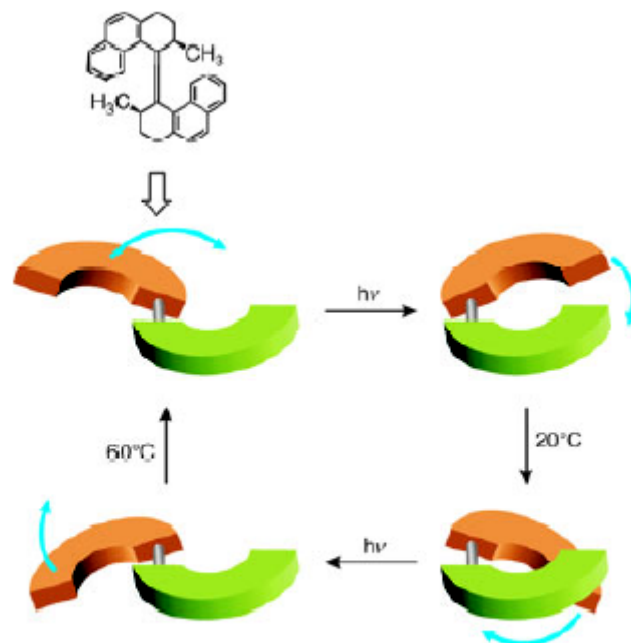


Figure 2. Structural formula and schematic representation of a molecular motor, based on the photoisomerization of an alkene-type compound containing chiral centers, that exhibits light-induced unidirectional rotation.^[11]

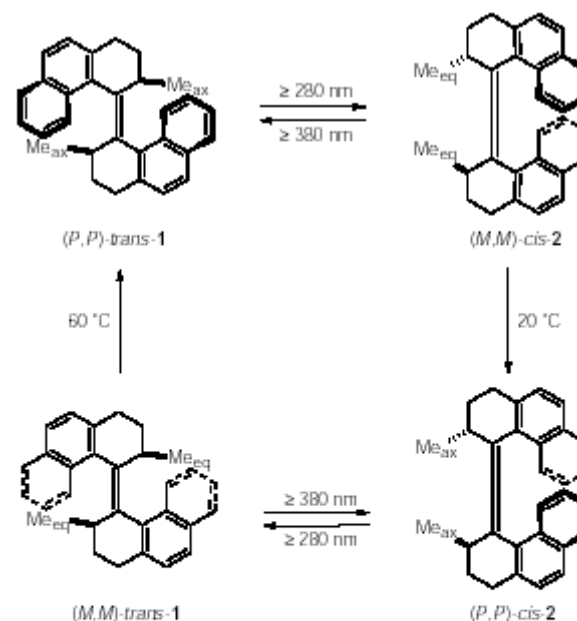


Figure 1 Photochemical and thermal isomerization processes of *(P,P)*-trans-1. UV irradiation with high pressure Hg-lamp, Pyrex filter, $\lambda \geq 280$ nm or Xe-lamp, Toshiba L-3g glass filter, $\lambda \geq 380$ nm. First order kinetics were observed for the thermal processes and temperature dependent ^1H NMR and CD studies in the range 50.0–81.1 °C gave $E_a = 26.4 \text{ kcal mol}^{-1}$ 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

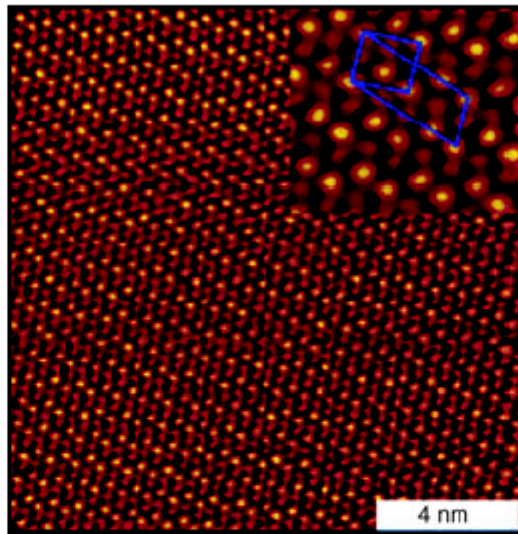


Figure 5. Scanning tunneling microscope image of a self-assembled monolayer (SAM) of decanethiol on gold.^[83] The scanning probe microscopes make it possible to view nanostructures in molecular detail, and have revolutionized surface science. SAMs represent a class of material in which properties such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

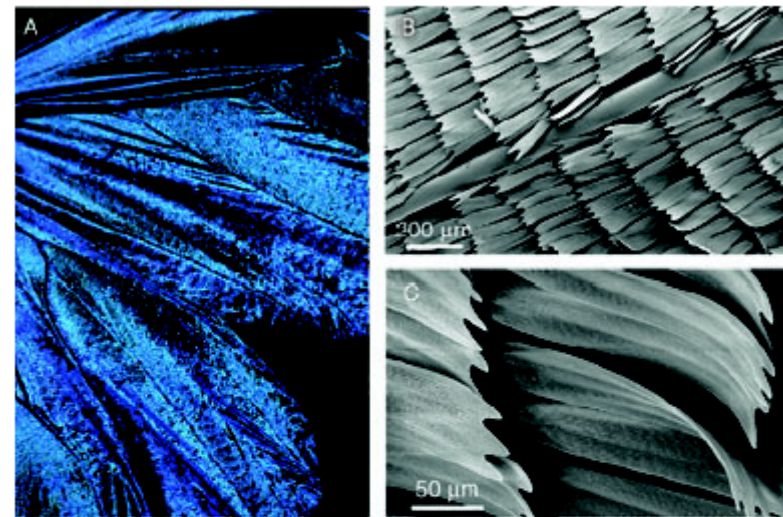


Figure 6. Photograph (A) and SEM images (B,C) of the wing of the *morpho* butterfly (images by Felice Frankel). The brilliant blue reflection from the wing of this butterfly is due to the operation of a remarkable, optically sophisticated photonic bandgap structure, which not only is wavelength selective,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

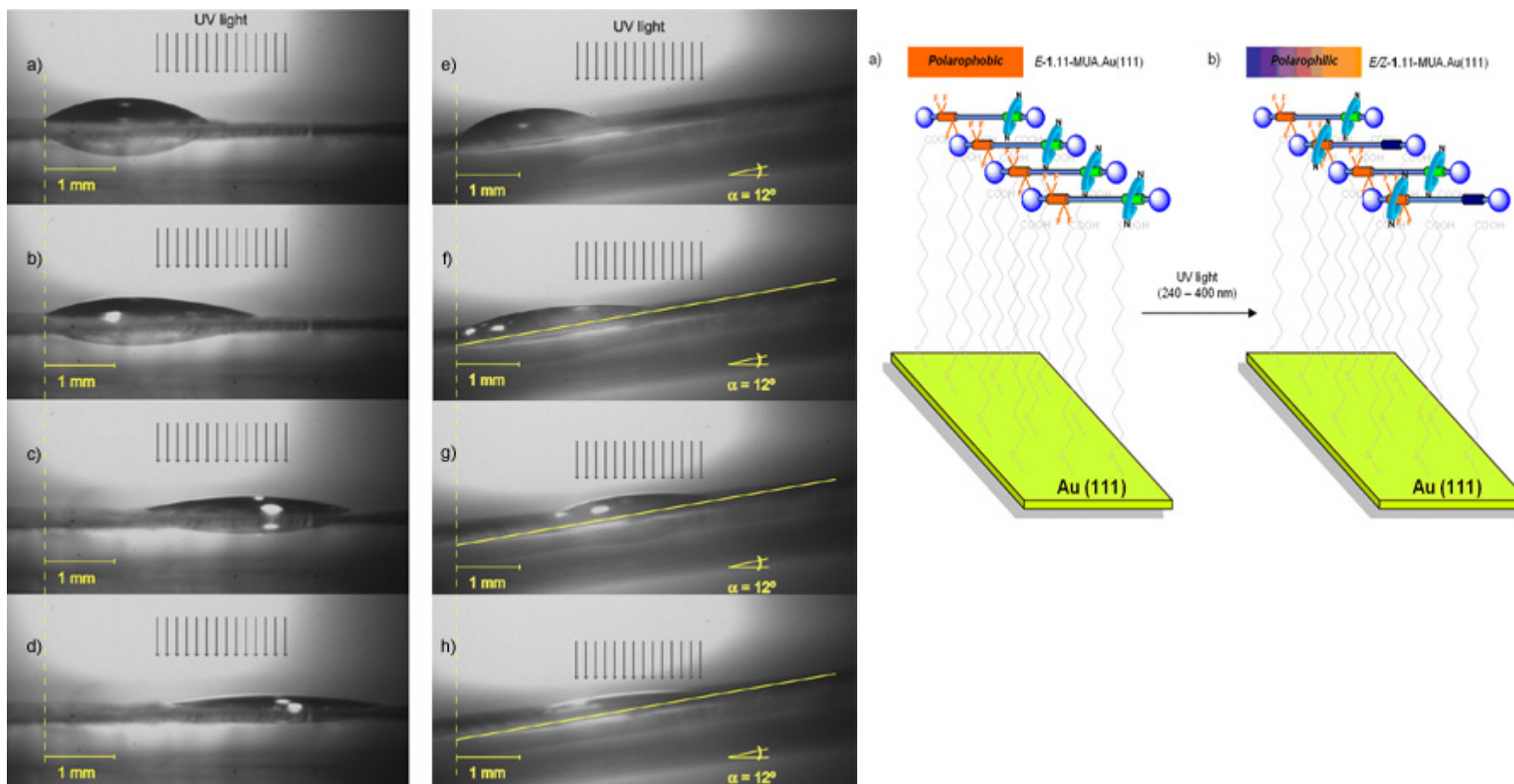
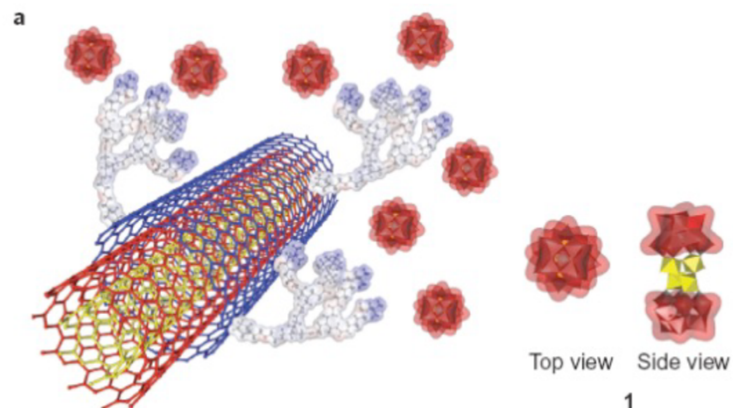


Figure 2. Light-driven directional transport of a 1.25 μl diiodomethane drop across the surface of monolayer of molecular machines, both flat (a)-(d) and up a twelve degree incline (e)-(h). This extrapolation across 6 orders of magnitude in length scales from mechanical motion at the molecular level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

