ICN2 Institut Català de Nanociència i Nanotecnologia

P2N PHONONIC & PHOTONIC NANOSTRUCTURES

Large-area ordered nanostructures by directed self-assembly

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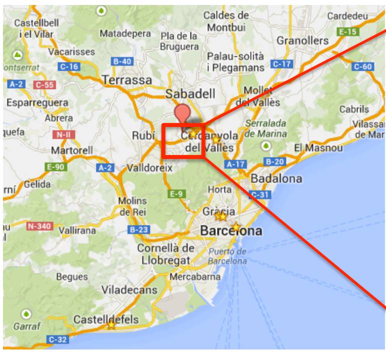
Summer School of Nanofabrication – Nanolito Network
Jaca, Spain, 15th July



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http://www.icn.cat/

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Large-area ordered nanostructures by directed self-assembly

Outline

- General introduction to self-assembled systems
- **Molecular self-assembly** (SA) systems
  - Molecular and biomolecular SA
  - Large area Molecular SA case study: self-assembly monolayers
- **Nano to Micro** SA systems
- **Micro to Mili** SA systems
  - Large area SA case study: Block copolymers
- Conclusions

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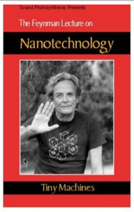
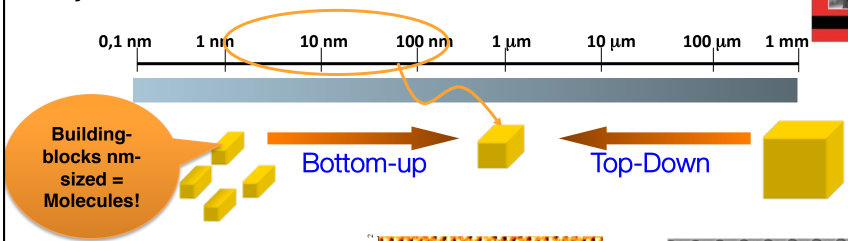
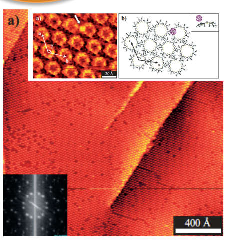
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

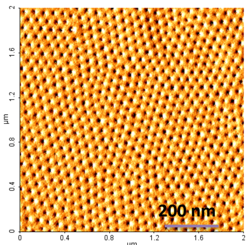
The kick-off of nanotechnology

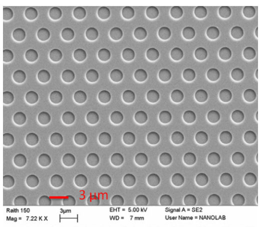


Richard P. Feynman made the first suggestion of <u>nanotechnology</u> in his notorious speech '*Theres plenty of room at the bottom*', in early 1960s.









E. Mena-Osteritz, Adv. Mater. 2006, 18, 447–451 T. Kehoe et al., 2011 MRS Fall Meeting

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Need for functional systems of all sizes

Technological imperatives:

Electronics
- Processors and memory

Biomedicine
- Bioanalysis

National security
- Sensors, materials

10 mm	**Non-equilibrium systems** •complexity •the cell
1 mm	
100 µm	**Microtechnology** •microelectronics •communications
10 µm	•emerging technologies: MEMS, µfluidics, µTAS, µoptics
1 µm	**Nanoscience / Nanotechnology** •new phenomena •new materials
100 nm	
10 nm	**Molecular Chemistry** •materials •sensors •bioanalysis
1 nm	

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Examples of methods for making functional systems

Top - down ⇩

1 mm – 10 µm	robotic fabrication and assembly; pick-and-place, monolithic microfabrication, surface patterning, laser micromachining, multiphoton polymerization, deterministic assembly
1 µm – 10 nm	photo- and soft lithography, e-beam, STM writing
1 nm	organic, molecular synthesis

⇧ **Bottom - up**

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Making functional systems:
Why do we need a new method?

Evolution:
When old methods are "no good":
cost, range of materials, precision,…

Revolution:
When there are no old methods:
new size or type of components,
new phenomena, …

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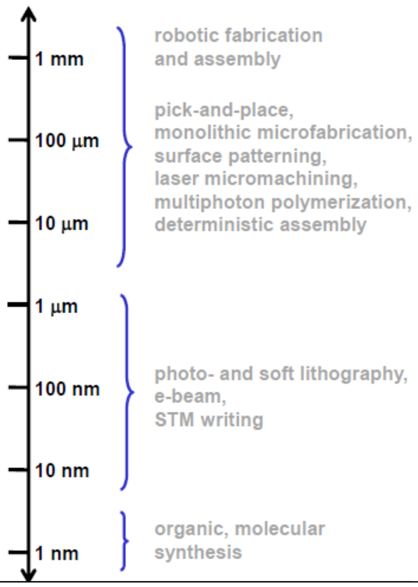
Using self-assembly to make functional systems:

Top - down

•To connect top-down and bottom-up

•To stand alone

Bottom - up



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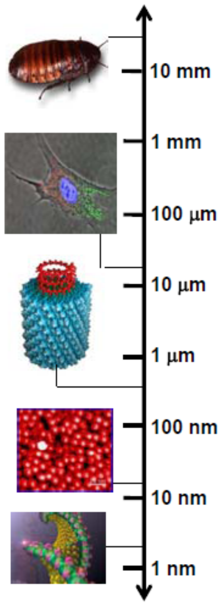
Why self-assembly?



1. Functional, self-assembled systems are ubiquitous in biology

- 3D structure
- Information storage and processing
- Efficient use of energy
- Self-healing
- Self-replicating
- Material properties
- Signal transduction
- Molecular recognition

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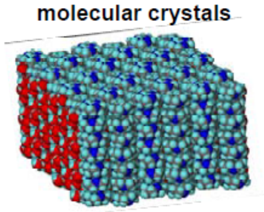
Why self-assembly?

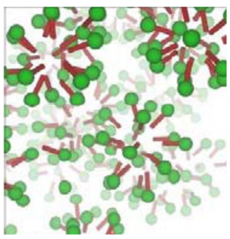
2. Self-assembly is ubiquitous in chemistry

molecular crystals

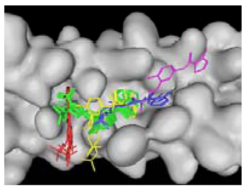


non-molecular crystals

organized amphiphiles



molecular recognition



protein folding

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Self-assembly:
The spontaneous generation of order in systems of pre-existing components

This definition implies:

Information for self-assembly is encoded in the components
(*e.g.*, shape, topology, sequence, surface properties)

Less ordered → higher order (*e.g.*, form, function)

Σ components ≠ result (*e.g.*, new property)

Reversible, adjustable interactions

This definition excludes:

"Order, reversibility": no precipitation, ripening, coagulation processes

"Pre-existing components": no pattern formation in continuous medium

Characteristics of self-assembled systems:
1. Components

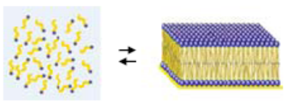
Size

All sizes, all numbers, all matter
Separate or connected

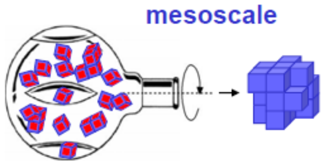
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Characteristics of self-assembled systems: 2. Motion

Molecular



Non-molecular, mesoscale



Molecular		Non-molecular, mesoscale
kT	Temperature/agitation	effectively 0 °K; external
few layers	Wall Effects	few layers

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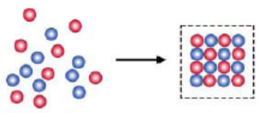
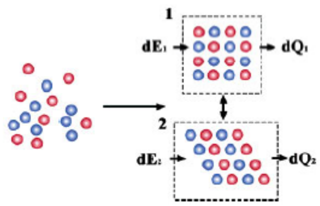
Characteristics of self-assembled systems: 3. Structures formed

Static



Dynamic



Result:
Equilibrium structures, at global or local energy minima

Result:
Non-equilibrium, energy dissipating structures, maintained in a steady state by constant supply of energy

NB: The classification is based on the final structure, not on the self-assembly processes!

J. Phys. Chem. B 110 (2006) 2482

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Characteristics of self-assembled systems: 4. Interactions

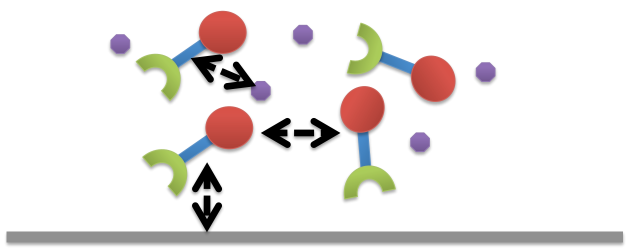
- Recognition motifs
- Van der Waals
- Hydrogen bonding
- Electrostatic
- Capillary
- Surface tension

↔

- **Molecule-Molecule**
- **Molecule-Interface**
- **Molecule-Media**
- **Rheology**

↔

- Thermodynamic rule
  $\Delta G_{SA} = \Delta H_{SA} - T\Delta S_{SA}$
- Kinetic rule
  k = A e^((-Ea)/(RT))



Boundary conditions that affect the SA → Directed SA!

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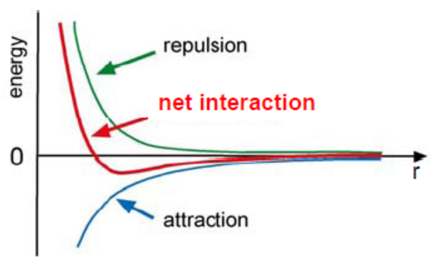
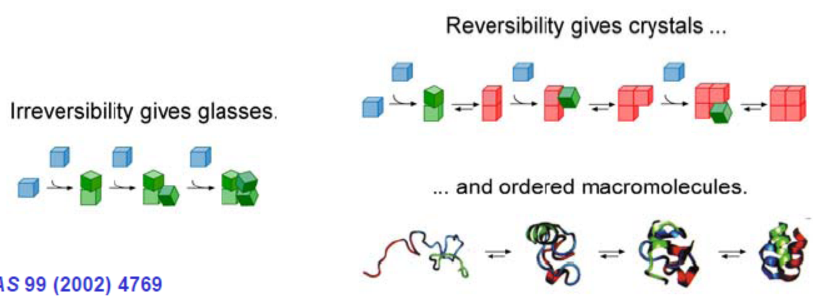
Characteristics of self-assembled systems: 4. Interactions





PNAS 99 (2002) 4769

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Minimal thermodynamic potential

for T, P, N = *const*,

SA when G = H – TS = min
G: Gibbs free energy

spontaneous process:
$\Delta G = \Delta H - T\Delta S < 0$

for T, V, N = *const*,

SA when F = U – TS = min
F: Helmholtz free energy

spontaneous process:
$\Delta F = \Delta U - T\Delta S < 0$

Static SA can be driven by:

- enthalpic/energetic effects: ΔH or $\Delta U < 0$ when $\Delta S \approx 0$
- entropic effects: $\Delta S > 0$ when ΔH or $\Delta U \approx 0$
- combination of both

Soft Matter 5 (2009) 1110

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Interactions for molecular self-assembly

weak (~0.5-20 kJ/mol); comparable to thermal energies (~2.5 kJ/mol)
unlike kinetically-stable covalent bonds (~80-1000 kJ/mol)

Interaction	Range	Scaling relations
Screened Ionic (*attractive/repulsive*)	1 nm–1μm	$U \propto \pm e^{\kappa r}/r$ where $\kappa^{-1} = (2e^2c_s/k_BT\varepsilon_0\varepsilon)^{-1/2}$ is the screening length (k_BT, thermal energy; $\varepsilon_0\varepsilon$, dielectric permittivity of solvent; e, fundamental charge; c_s, salt concentration)
van der Waals (*attractive*)[a]	1 nm–10 nm	$U \propto -1/r^6$ (London dispersion energy). The strength is ≈10 kJ mol^{-1} for two alkane molecules (*e.g.*, CH_4, C_6H_6 or C_6H_{12}) in water
Dipole dipole (*attractive/repulsive*)	0.1 nm–1 nm	$U \propto -1/r^3$ (fixed) and $U \propto -1/r^6$ (rotating, Keesom energy). The strength is ≈10 kJ mol^{-1} for two dipoles of strength 1D separated by 0.2 nm
Hydrogen-bond (*attractive*)	0.1 nm–1 nm	$U \propto -1/r^2$ (roughly). The strength of most hydrogen-bonds is between 10 and 40 kJ mol^{-1}
Aromatic (π–π) (*attractive*)	0.1 nm–1 nm	Arise from overlapping of p-orbitals in π-conjugated systems. Magnitude scales with the number of π-electrons Typically the length scale of interaction is ≈3.4 Å

Soft Matter 5 (2009) 1110
Science 254 (1991) 1312

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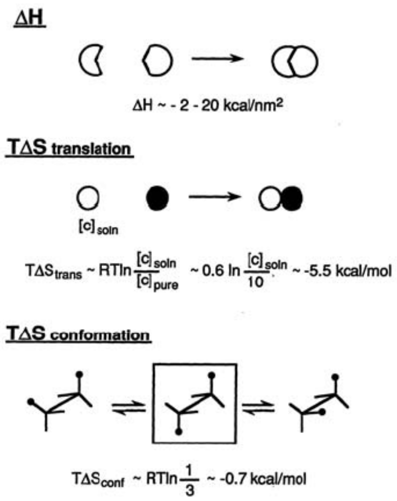
Particularities of molecular self-assembly



$\Delta G = \Delta H - T\Delta S < 0$

Lessons from biology:

- Multiple, weak interactions
- Often, 3D recognition surfaces
- Modular process / "convergent"
- Small number of types of molecules
- Positive cooperativity
- Water!

⇒ **make big contact surfaces**
to maximize enthalpic return

⇒ **use rigid molecules**
to minimize entropic losses

Science 254 (1991) 1312

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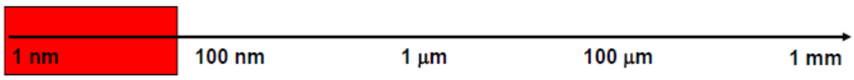
Molecular self-assembled systems



Opportunities for self-assembly:

Understand biological self-assembled systems
- Protein-ligand interactions
- Rational drug design
- Protein folding

Make things that cannot be made by covalent synthesis:
- Big molecules
- Materials (structured, self-healing)
- Nano-structures
- Patterned surfaces

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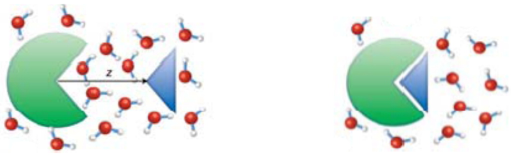
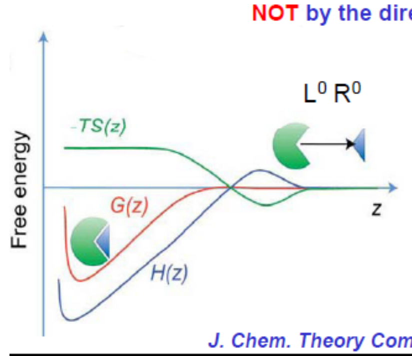
Understanding biomolecular self-assembly
Contribution of water to ligand-receptor binding



The free energy of the process is dominated by the water contributions, NOT by the direct L-R interactions!

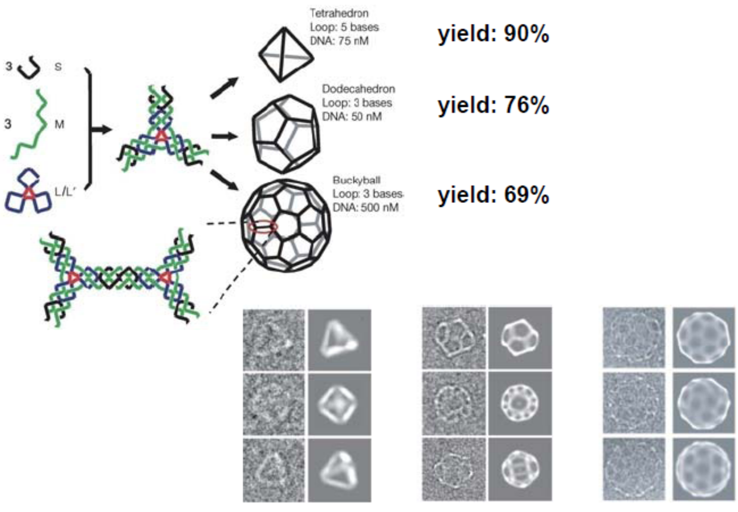


- $L^{+/-} R^{-/+} < L^0 R^0$
- $L^+ R^- \neq L^- R^+$
- hydrophobic binding is driven by ΔH!

H gain: from H_2O release from binding pocket and increased H_2O- H_2O bonds
S loss: from elimination of solvent fluctuations in the binding pocket

J. Chem. Theory Comput. 6 (2010) 2866 *JACS* 132 (2010) 12091

Self-assembly of DNA



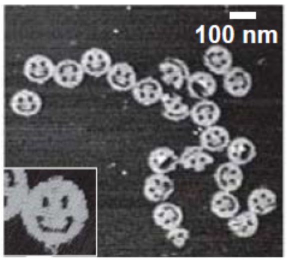
yield: 90%

yield: 76%

yield: 69%

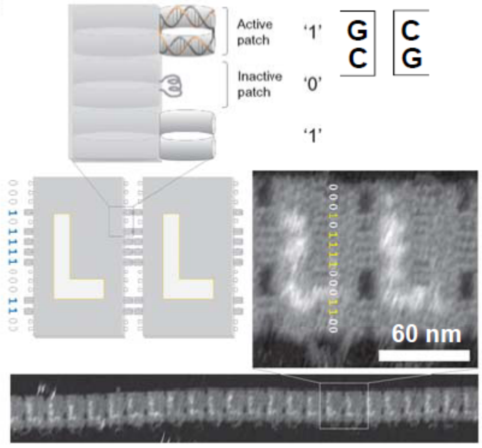
Nature 452 (2008) 198

DNA nano-origami: a breadboard for molecular components



Mechanism:
Single-step assembly of single-stranded scaffold and short oligonucleotide "staple strands".

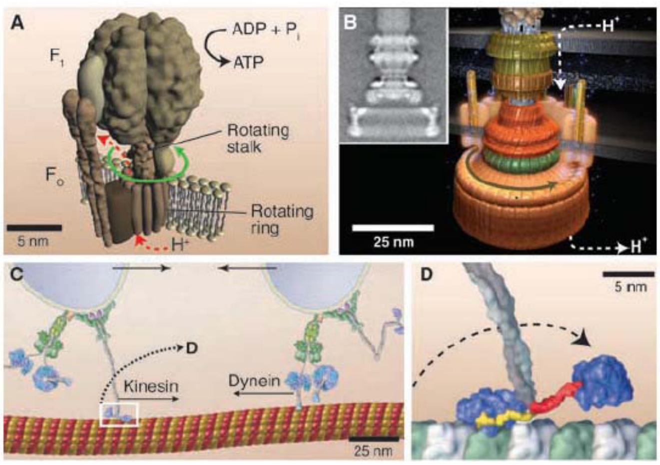
Nature 440 (2006) 297



Mechanism:
stacking of GC/CG base-pairs (-2.17 kcal/mol)

Nature Chem. 3 (2011) 620

Self-assembled little machines out of molecules: possible, but we're not there yet



Science 317 (2007) 333

Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Rational drug design based on polyvalency

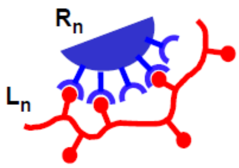
Multivalent adhesion in pathogenesis:
- virus-cell association
- toxins (anthrax, ricin, cholera)
- bacteria
- inflammation
- metastasis

$\Delta G_3 = 3^*\Delta G_1$, and $\Delta G = -RT \ln K$
$\Rightarrow K_3 = K_1^3$

$K_3 = 4 \times 10^{-17}$ M *Science* 280 (1998) 708

General case

$\Delta G_n = \Delta H_n - T\Delta S_n$



1) $\Delta H_n \approx n^*\Delta H_1$ ↑ or ↓ (depending on strain)

2) ΔS = rotational + translational + conformational + water

* if $\Delta S_{conf} = 0$ (no loss of degrees of freedom)
entropic enhancement:
$|\Delta S_{rot,\ transl.\ n}| \sim |\Delta S_{rot,\ transl.\ 1}| < n * |\Delta S_{rot,\ transl.\ 1}|$

* if $\Delta S_{conf} \neq 0$
neutral, enhancement ↑, or interference ↓

Angew. Chem. 37 (1998) 2754

3) steric shielding of R (adhesion inhibition)

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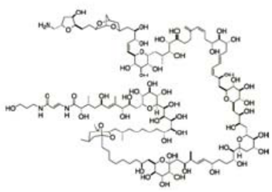
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Self-assembly for synthesis
Complex molecules and structures from simple components

Covalent synthesis: very good for making 100-3000 D



palytoxin
MW 2680.13

No simple strategy to make 10^4-10^6 kD (3-20 nm big)

Self-assembly:

- **Simple components: by covalent chemistry (organic, organometallic)**
- **Molecules are formed under TD equilibrium, *i.e.*, can correct errors in the synthesis**
- **Reversibility, entropy**

Science 295 (2002) 2403

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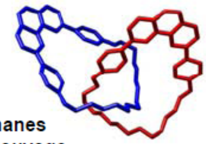
Self-assembly for tough synthetic targets

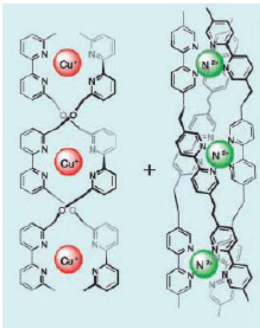
Molecular shuttles and switches

Rotaxanes
F. Stoddart



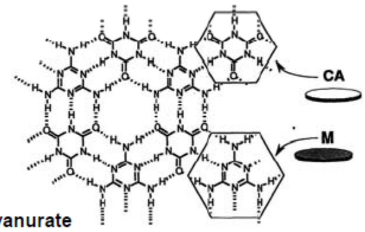
Catenanes
J.P. Sauvage

Chirality



J.-M. Lehn

Biosynthesis, drug design



Melamine cyanurate
G.M. Whitesides

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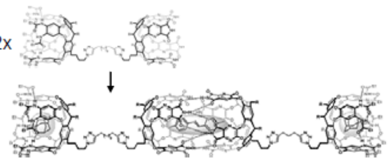
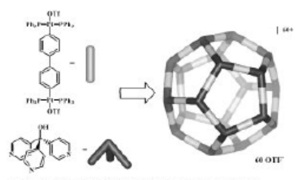
Host-guest chemistry

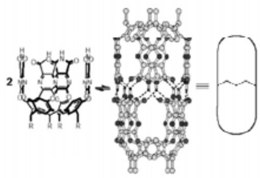
- molecular vessels (for catalysis, sensing)
- stabilization of reaction intermediates
- induction of stereoisomerism



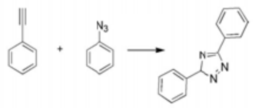
J. Rebek, Jr.



P. Stang



cycloaddition
without resorcinarene dimer: years
with : days



Review: Chem. Rev. 105 (2005) 1445

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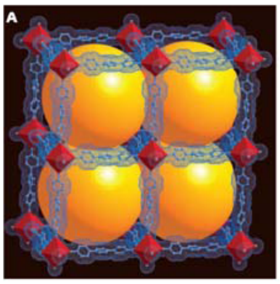
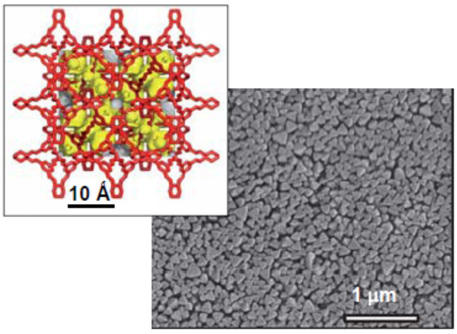
Self-assembled materials
Crystal engineering
for separation, storage, catalysis

Octahedral Zn and
organic bis-carboxylates



!!!
density: 0.21 g/cm^3
free volume: 91.1 %

Predictable assembly
of porous organic crystals



Review: Science 295 (2002) 2410

Nature 474 (2011) 367

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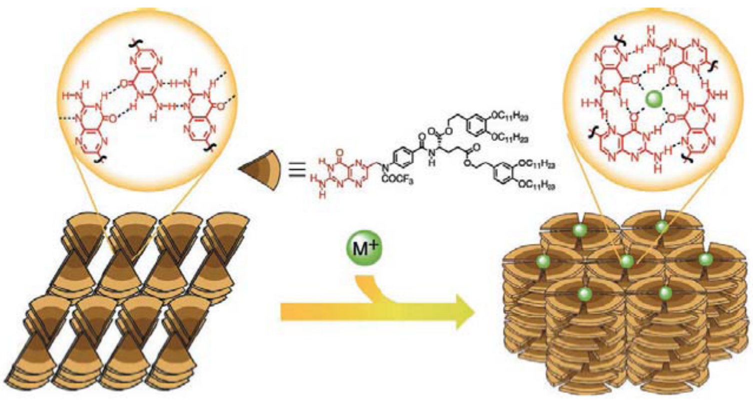
Phase-segregated liquid crystals



**Smectic to hexagonal columnar phase change:
potential readout for sensor applications.**

Science 295 (2002) 2414

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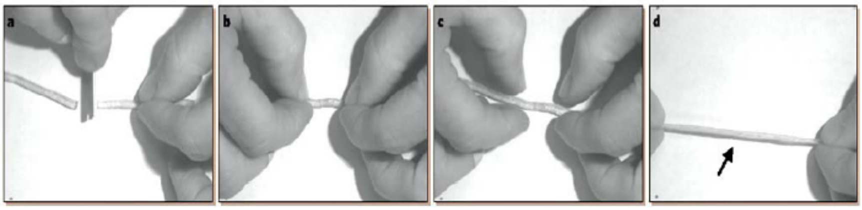
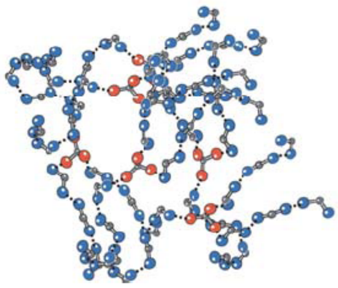
Self-healing materials



partial cross-linking through H-bonds
=> elastic, not crystalline material

healing: 15 min contact at RT



Nature 451 (2008) 977

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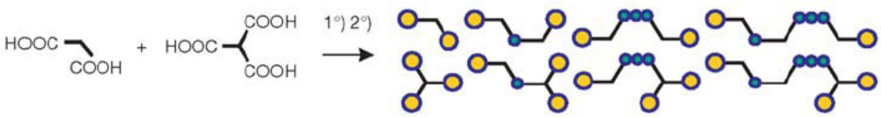
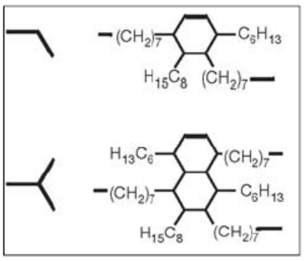
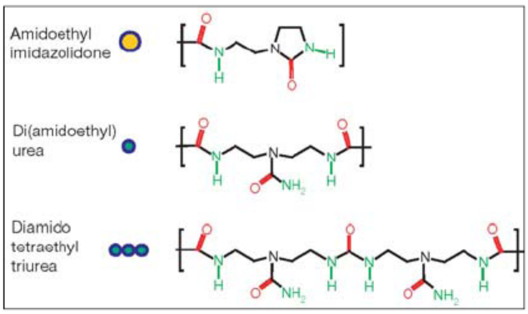


1) diethylene triamine
2) urea





plasticizer:
11% dodecane
Tg: 8 °C

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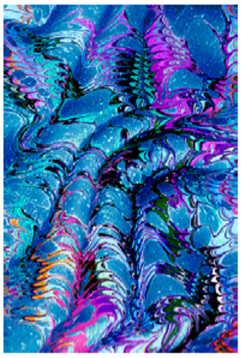
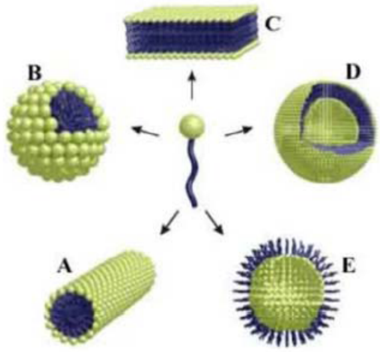
Making nanostructures and patterned surfaces
Self-assembly of amphiphiles



Sumi nagashi
ca. 900 AD



Review: http://www.physmathcentral.com/1757-5036/2/3

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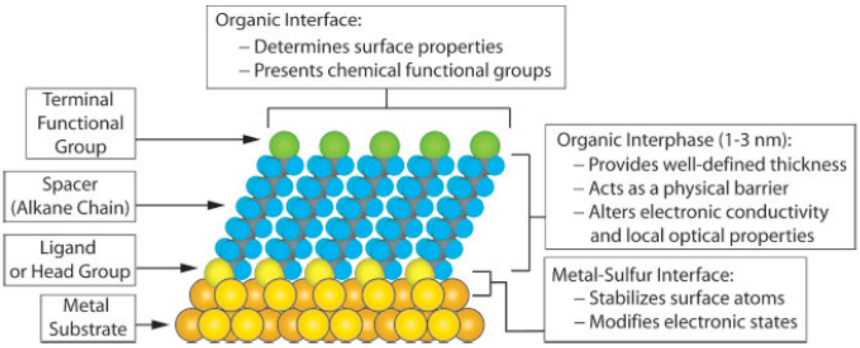
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Self-assembled monolayers (SAMs): design of macroscopic surfaces with nanoscale control of surface properties



A must-read: Chem. Rev. 105 (2005) 1103

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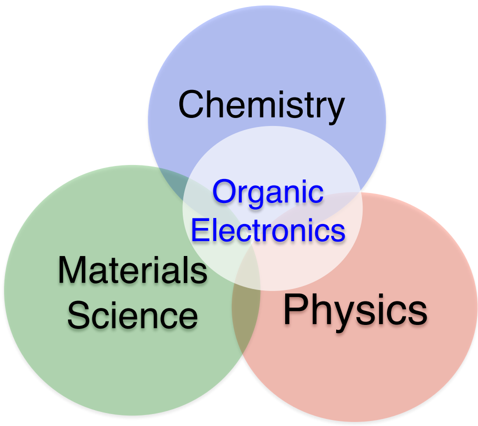
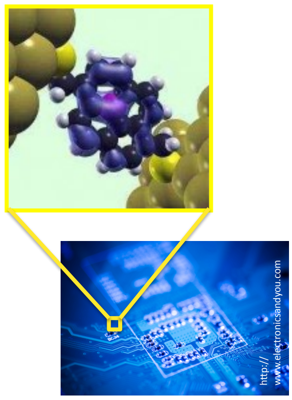
Case study: Self-assembly for organic and molecular electronics

Is the field dedicated to the *study and application of organic molecules building blocks* for the fabrication of electronic components.





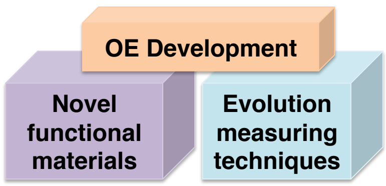
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

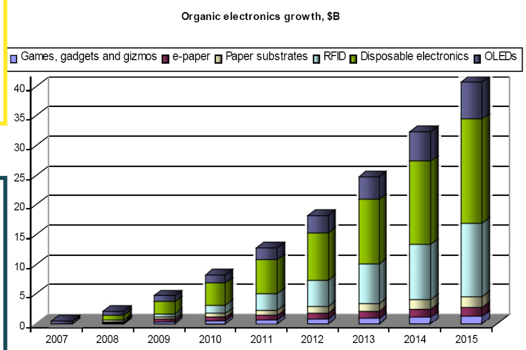
Advantages of OE:

- ✓Miniaturization
- ✓Soft fabrication techniques
- ✓More environmental friendly
- ✓More cost effective
- ✓Less power consumption

Current challenges in OE:

- ❑Functional molecules
- ❑Electron transfer yield
- ❑Large-area devices
- ❑Reproducibility



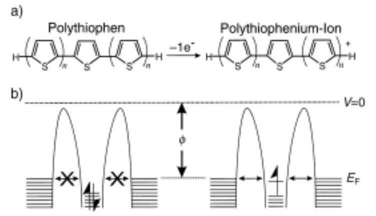


Worldwide Organic Electronics Market September 2009 press release

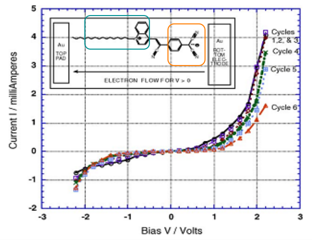
Molecular devices

In the last years, many examples of molecular systems have been published behaving as wires, diodes or switches.

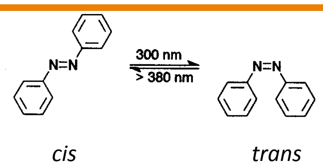
Wires



Rectifiers



Switches



Carrol, Gorman, *Angew. Chem. Int. Ed.*, 41 (2002), 4378-4400
R. M. Metzger, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 284–285 (2006), pp. 2–10
M. Irie, *Chem. Rev.*, 100 (2000), 1685-1716

Molecular-level switch

A molecule having two stable and fully reversible states exhibiting a different secondary property.

Bistable systems

Stimuli

ON: Chemical, Electric, Optical, Magnetic

OFF: Chemical*, Electric*, Optical*, Magnetic*

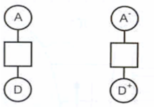
Read-out mechanisms

Switches: ON/OFF ⇔ Memory devices: 1/0

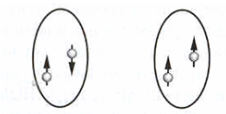
A molecular-level switch should be:
1. Controllable
2. Reversible
3. Readable at molecular scale

Bistability mechanisms in molecular switches

Redox

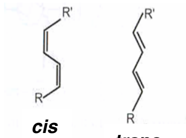


Magnetic spin orientation



Electronic excitation

Conformational

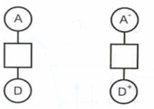


cis ***trans***

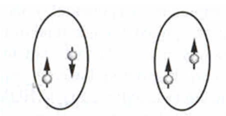
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Bistability mechanisms in molecular switches

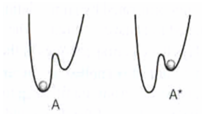
Redox



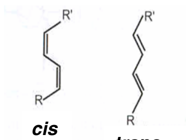
Magnetic spin orientation



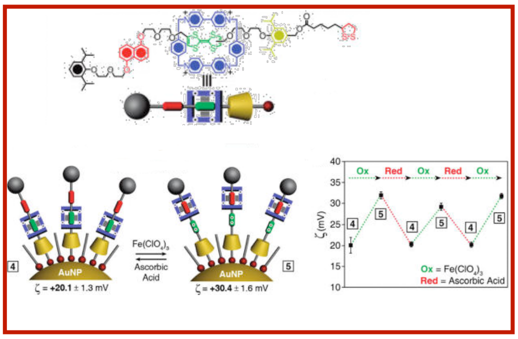
Electronic excitation

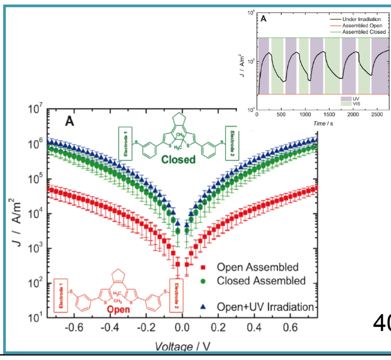


Conformational



cis ***trans***

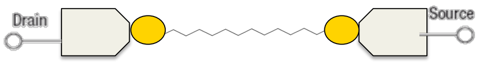




Approaches to use molecules for molecular devices

Molecules can be used as a single component:

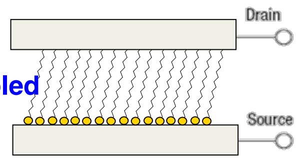
A single-molecule junction or wire



Or as a group of molecules:

A large-area molecular junction

Self-assembled monolayers



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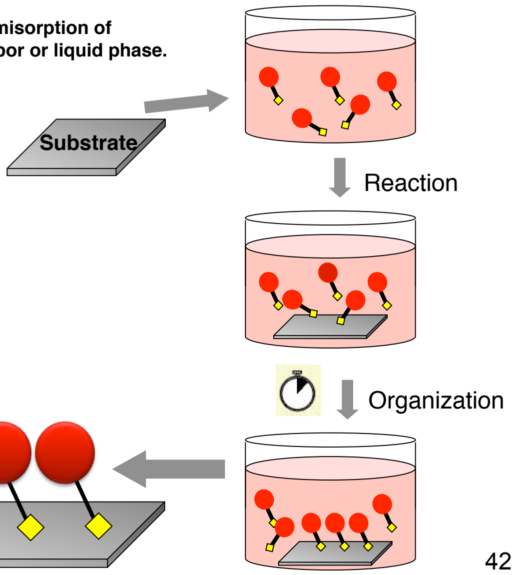
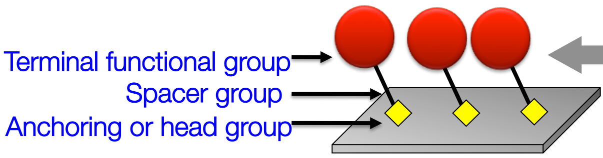
Towards devices: Self-Assembled Monolayers

SAMs are a ordered layer formed by the chemisorption of hydrophilic groups onto a substrate from vapor or liquid phase.

Important advantages

- ✓**High stability layers**
- ✓**Single molecule property**
- ✓**Versatile**
- ✓**Patternable**
- ✓**Low cost**
- ✓**Fixed physical location**





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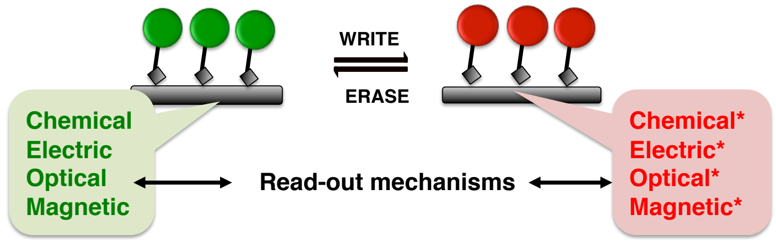
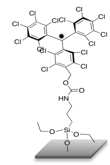
Stimuli responsive systems
for Smart Surfaces

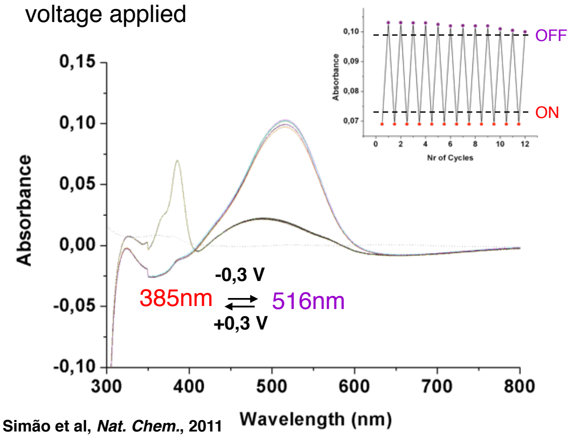


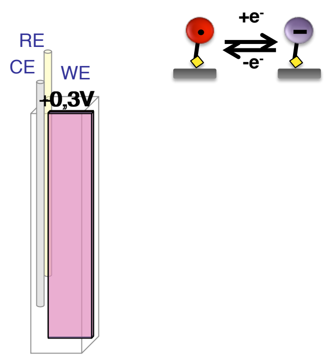
SAMs Optical absorbance

Consecutive absorbance spectra while applying consecutive ON/OFF voltage cycles

S4 absorbance spectra shows the radical or anion band depending on the voltage applied





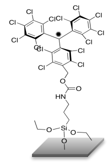


0,02M Bu_4NPF_6 in CH_3CN

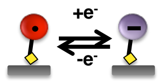
Simão et al, *Nat. Chem.*, 2011

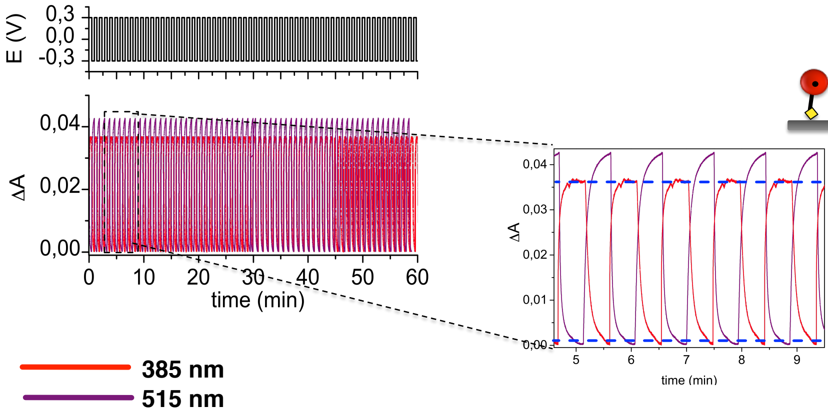
High reversibility

Full recovery of ON/OFF ratios after hundreds of cycles



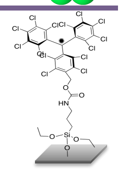
S4





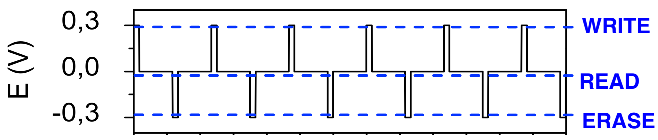
Simão et al, *Nat. Chem.*, 2011

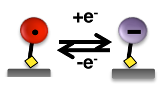
Optical absorbance as output of S4 molecular switch



S4

Removing WRITE or ERASE voltage = READ at 0V

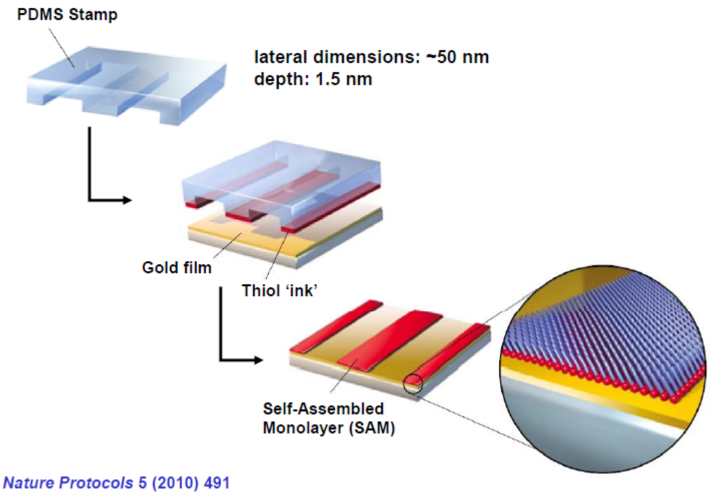




Non-volatile memory applications

Simão et al, *Nat. Chem.*, 2011

Microcontact printing of SAMs



Nature Protocols 5 (2010) 491

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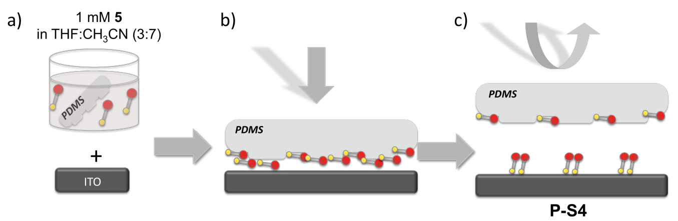
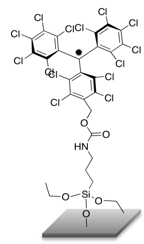
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Patterning SAMs by μcontact-printing





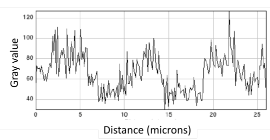
S4

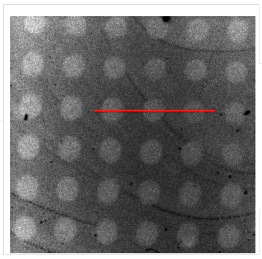
Applications in memory devices and circuitry printing

Fluorescence image of patterned S4 as 5 μm dots

λ_{exc} = 380nm

λ_{em}= 500 nm (DAPI filter)





Simão et al, *Nat. Chem.*, 2011

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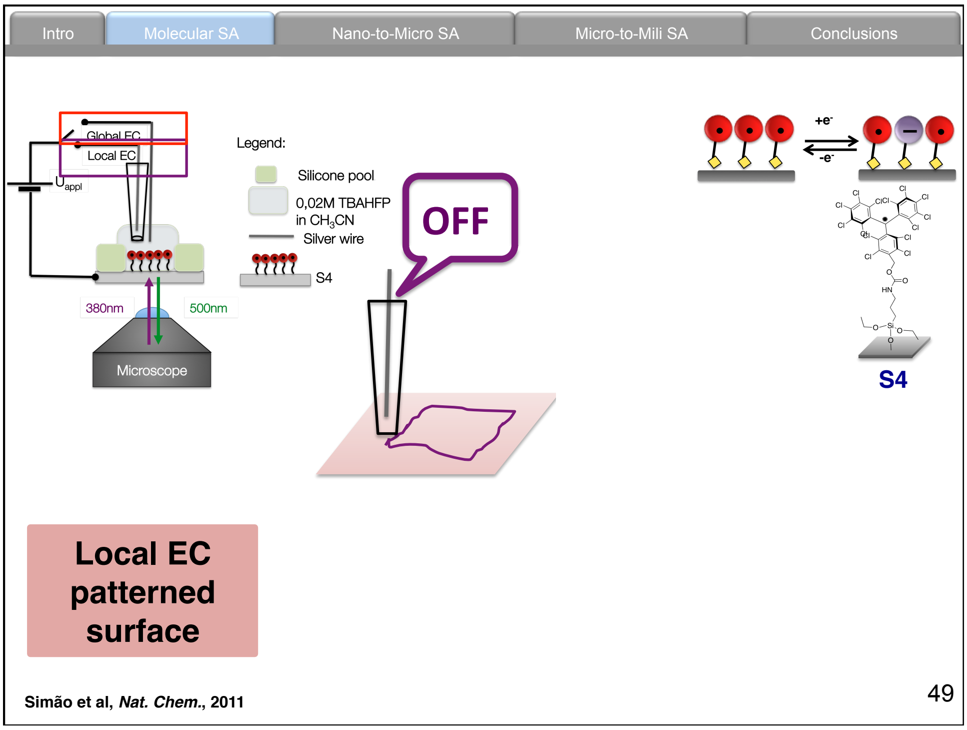
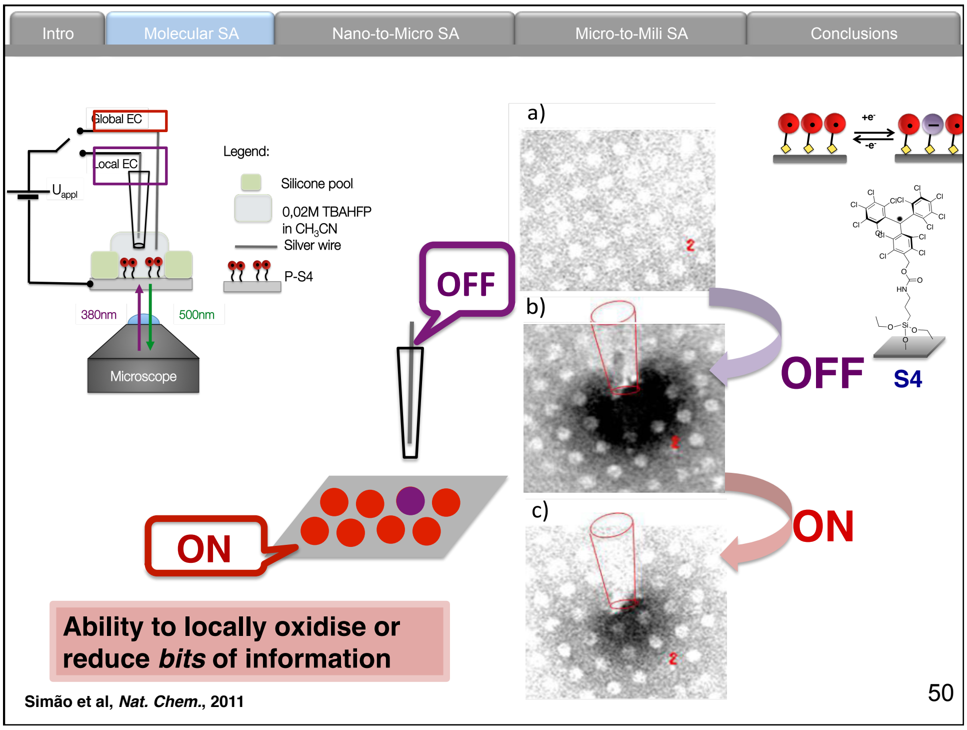

Intro
Molecular SA
Nano-to-Micro SA
Micro-to-Mili SA
Conclusions
Global EC
Local EC
Uappl
Legend:
Silicone pool
0,02M TBAHFP in CH3CN
Silver wire
S4
380nm
500nm
Microscope
OFF
+e-
-e-
S4
Local EC patterned surface
Simão et al, Nat. Chem., 2011
49


Intro
Molecular SA
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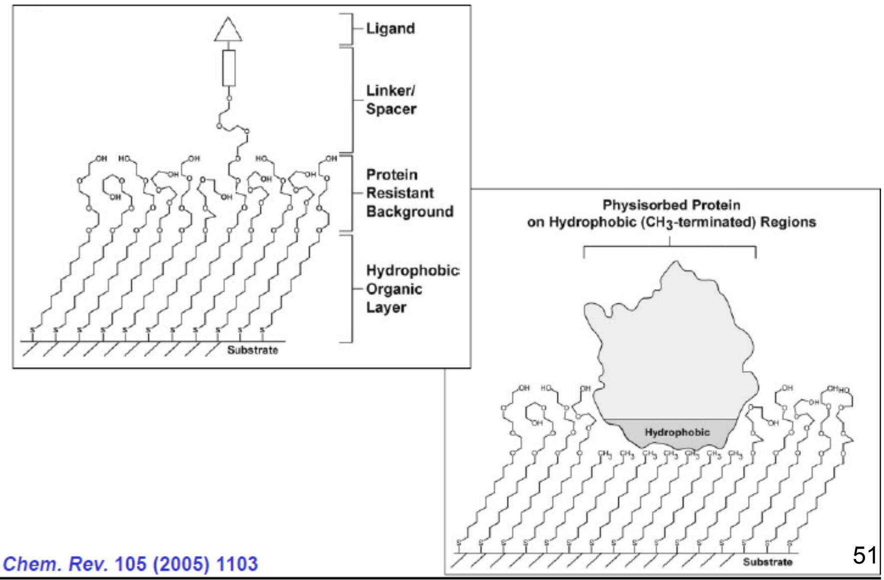
Micro-to-Mili SA
Conclusions
Global EC
Local EC
Uappl
Legend:
Silicone pool
0,02M TBAHFP in CH3CN
Silver wire
P-S4
380nm
500nm
Microscope
OFF
ON
a)
b)
c)
OFF
ON
S4
Ability to locally oxidise or reduce bits of information
Simão et al, Nat. Chem., 2011
50

Designer surfaces using SAMs



Chem. Rev. 105 (2005) 1103

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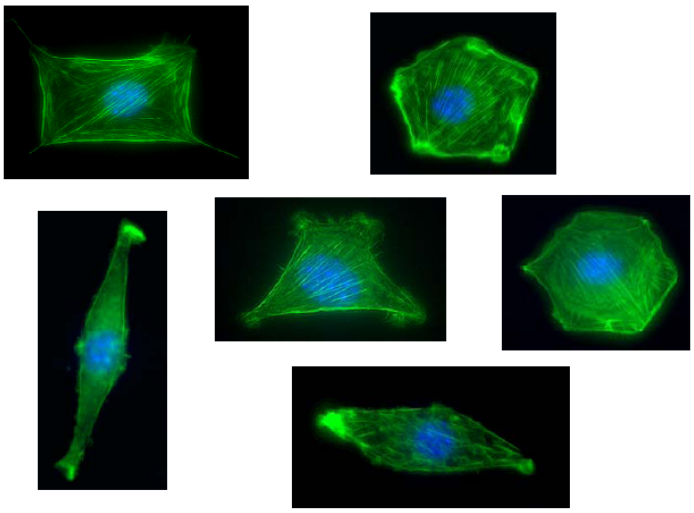
Cell-based assays: cell shape, size, and function



Science 264 (1994) 696

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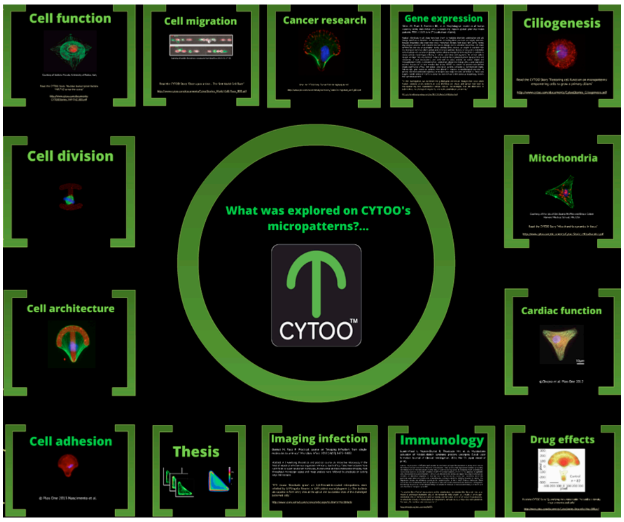
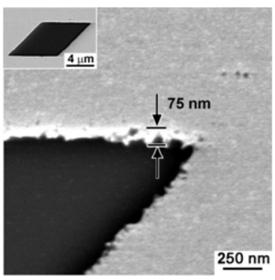
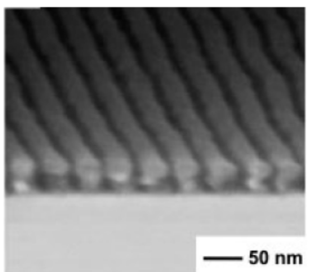
- Cytoo is a startup of self-assembly monolayers substrates for molecular and bio assays



SAMs as tools for nano- and microfabrication





etch resists:
SAM with n >16
Pd on Si/SiO_2

epitaxial self-assembly of domains:
PS-*b*-PMMA on patterned
SAM template.

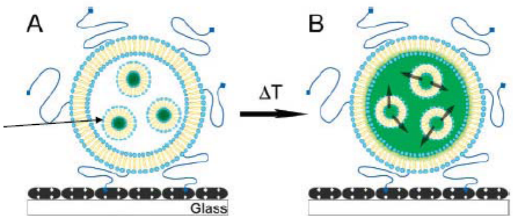
J. Am. Chem. Soc. 124 (2002) 1576

Nature 424 (2003) 411

Self-assembly of nano-reactors from amphiphiles: Towards artificial cells

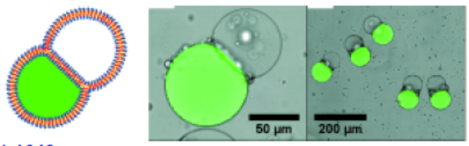
lipids

SUV:
d=20 nm
$V=10^{-21}$ L!



J. Am. Chem. Soc. 126 (2004) 8594

diblock co-polymers



Angew. Chem. 50 (2011) 1648

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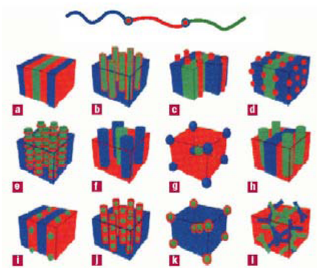
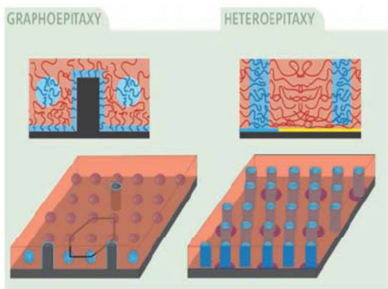
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Self-assembly of block co-polymers



aspect ratios: ≥ 50:1!

biggest issue: long-range order



PS-*b*-PMMA, PS-*b*-PDMS
resulting pitch: 20-40 nm; d: 20 nm
over 3 mm !

Nature Mater. 4 (2005) 277

Science 321 (2008) 936, 939

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SUMMARY
Functional systems by molecular self-assembly

Biggest success:

1. Materials for
   - Biomedicine/biomaterials
   - IT/photonics
2. Patterned surfaces
   - Tools for biology
   - Tools for nanofab

Opportunities:

Targets that require synthesis
Crystal engineering
Rational drug design
Understanding the biophysics of water
Protein folding
"Things that can't be done"
(hydrophobic interactions in water vs. widely used H-bonding in organic solvents)
Intelligent machines

Issues:

1. Limited functionality
2. No flexibility in the design of components

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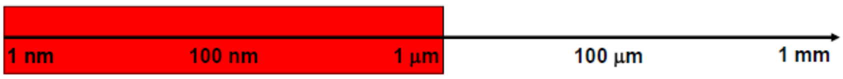
Non-molecular self-assembled systems: *nano- to micro-*



"It's function and cost that count, not size!"

Opportunities for self-assembly:

Large numbers of components
- High-density technologies (*e.g.*, memory)
- New optics (photonic bandgap materials)

New materials
- Ultrahigh surface area
- Low defects

Hierarchical structures: bottom-up and top-down

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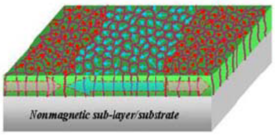
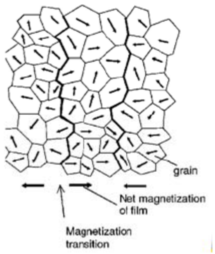
Nano-structured materials for magnetic storage

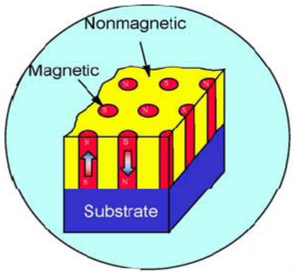
Longitudinal magnetic storage:
grain size and thermal stability





schemes: M. Dumoulin, T. Veres;
***J. Appl. Phys.* 76 (1994) 6673**

Alternatives:
Perpendicular recording
and/or
One grain per bit



Fabrication in a controllable process at low cost ?!?!?!

***IBM J. Res. Develop.* *44* (2000) 311**

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Structured materials for optics

Photonic crystals, "the semiconductors of light"

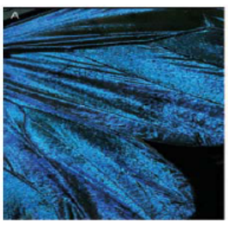
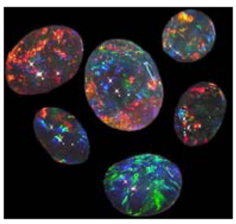
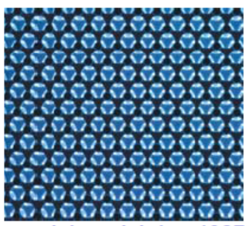


Image: F. Frankel





Yablonovich and John, 1987

Confine, control, and manipulate photons in 3D:
by the long-range order in the material

***Sci. Amer.* Dec (2001) 47** ***NPG Asia Mater.* 3 (2011) 25**

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Photonic crystals:
Periodic electromagnetic media

Bandgap: prohibited electromagnetic propagation throughout a specific frequency band

Bandgap depends on:
-crystalline lattice
-symmetry of the lattice points
-contrast in ε

Long-distance optical fiber communications: 1.5 μm

For UV or Vis:
100-300/400-800 nm in all 3D, registration ≤10 nm

Fabrication of big amounts in a controllable process at low cost ?!?!?!

http://ab-initio.mit.edu/photons/tutorial/

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Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

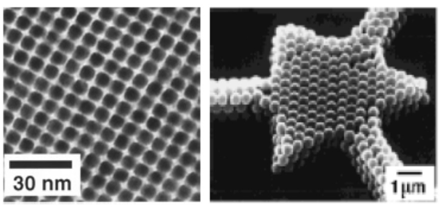
Why self-assembly:
To bridge the gap between synthesis and fabrication

r (nm)	C atoms (sphere)
1,000	7×10^{11}
100	7×10^{8}
10	7×10^{5}
1	7×10^{2}
0.1	0.7

Fabrication “Top-Down”

Synthesis “Bottom-Up”

ordered 2D and 3D arrays of nano-micro-sized objects



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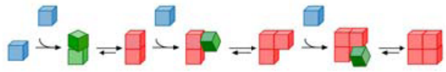
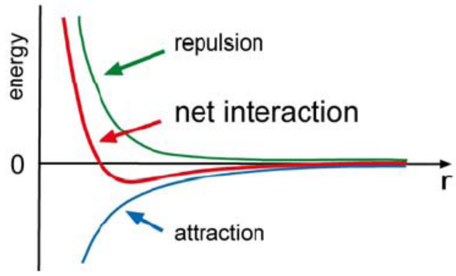
Particularities of mesoscale SA (nm–μm)



Motion/Temperature — **"0 K", non-Boltzmann distribution often steady state and not equilibrium**

Agitation — **External, non-uniform spatially**

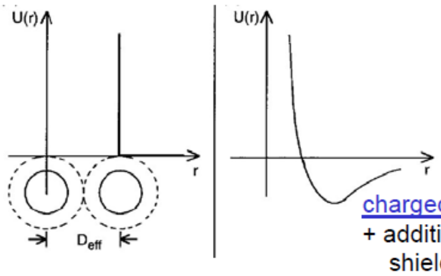
Electrostatic
Hydrophobic
van der Waals
Hydrodynamic
Magnetic
Capillary
Fluid Shear
Gravitational
Centrifugal
Osmotic
Light



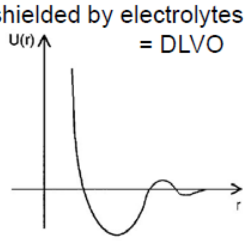
63

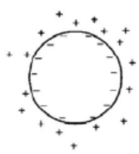
Interactions between colloidal particles in solution

uncharged (hard) spheres:
short-range steric repulsion
+ long-range (100 nm) VdW attraction



charged (soft) spheres:
+ additional long-range Coulombic repulsion shielded by electrolytes
= DLVO





Adv. Mater. **12 (2000) 693**

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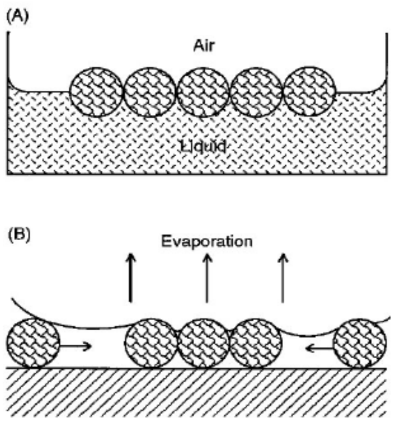
Self-assembly of 2D arrays of colloids



surface-modified particles attraction by induced dipoles at an asymmetric interface

slow solvent evaporation

major limitation: small arrays
(< 10,000 particles/single domain)

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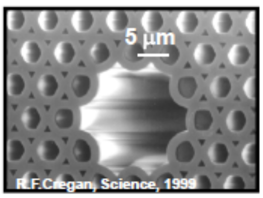
Non-molecular (mesoscale) self-assembled systems: *micro*- to *milli*-

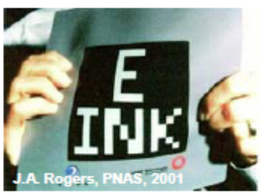
1 nm | 100 nm | 1 μm | 100 μm | 1 mm

"It's function and cost that count, not size!"

Micrometers



Millimeters



Why that big: application-specific needs
simple models for smaller sizes

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Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Possible and optimal design: 2D *vs.* 3D

~ 40 M Transistors — 10^5 M nerve cells

Density	n^2 components	n^3 components
Speed	long interconnects lead to low speed	shorter interconnects lead to higher speed
Architecture	weakly connected networks	strongly connected networks

???
Fabrication
Defects
Cooling

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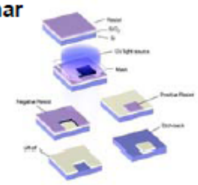
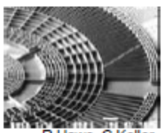
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Micromanufacturing technologies: How to make and position small things?

Photolithography:
massively parallel
But: planar



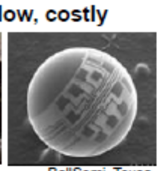
Wafer-to-wafer:
10-4000 μm,
yield > 99%, precision ± 0.1 μm
But: not for numerous parts; planar



R.Howe, C.Keller

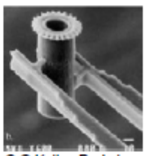
Monolithic microfabrication
and surface patterning
in 3D:
But: serial, slow, costly

C.G.Keller, Berkeley



BallSemi, Texas

Micro-gripper arrays:
massively parallel
But: not < 100 μm



C.G.Keller, Berkeley

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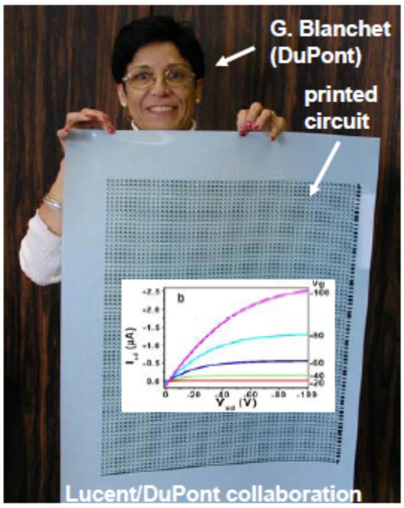
Problems / opportunities in microelectronics and microfabrication

- Registration and assembly of many components
- Formation of micro-/nano- 3D structures
- New materials: structured, composite
- New structures: self-healing and defect-free
- Strategies for lowering costs
- Differentiation/development (sensors smaller than the cell)

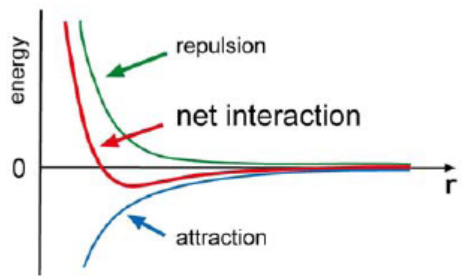
Macroelectronics: distributed active systems that cover large areas

Smart artificial skins,
Wearable electronics,
Large-area radars, antennas,
Flexible displays,
Electronic paper,
X-ray imagers,
Solar cell arrays,
Structural health monitoring,
etc.



Proc. IEEE 93 (2005):
Special issue on
Flexible electronics technology

Particularities of mesoscale SA (μm–mm)



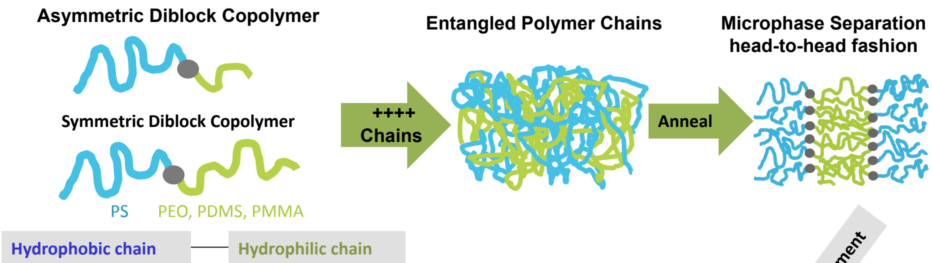
Interactions:
Electrostatic
Hydrophobic
van der Waals
Hydrodynamic
Magnetic
Capillary
Fluid Shear
Gravitational
Centrifugal
Osmotic
Light

Motion/Temperature
"0 K", non-Boltzmann distribution
often steady state and not equilibrium

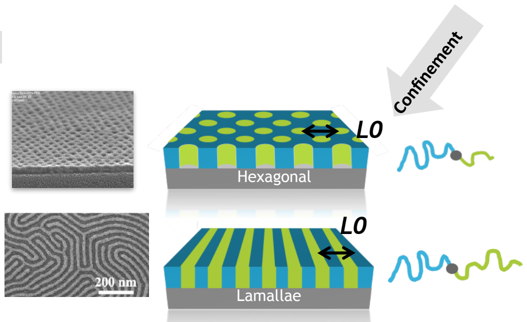
Agitation
External, spatially non-uniform

Capillary interactions:
- controlled strength
- mathematically modeled
- act in 2D and in 3D
- can impart function

Case study: Large area nanofabrication with Block Copolymers



$$\chi = V_m(\delta_A - \delta_B)^2/RT$$



R_g is the chain radius of gyration
$\mathbf{R_g^2 = N_a^2/6}$

L_0 is the period between features in a bulk annealed BCP
$\mathbf{L_0 = 4.05R_g}$

Thin film morphology

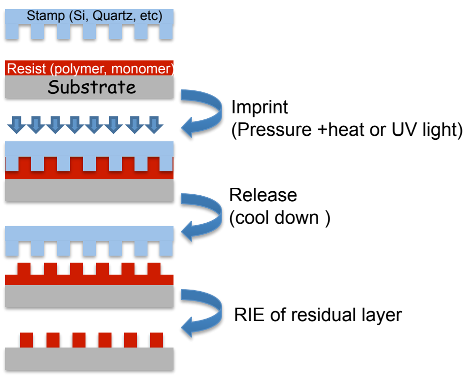
X. Man et al., *Macromolecules* 2011, 44, 2206–2211

Lithography techniques for Nanofabrication

Techniques	Resolution	Process	Limitation
Immersion	Approx 30 nm	Parallel	High cost, Precision
Extreme-UV	10 -14 nm	Parallel	interlayer interference, resist issues
X-ray interference (XIL)	<10 nm	Parallel	Synchrotron, complexity
Scanning Beam Lithography	10 nm	Serial	Slow rate, precision
NIL	**10 nm**	**Parallel**	**Template patterning/wear**
BCP Self-Assembly	**5 nm**	**Parallel**	**Long range order**
Soft Lithography	2 nm	Parallel	Distortion
Scanning Probe Lithography	1 nm	Serial	Slow rate

Top-down

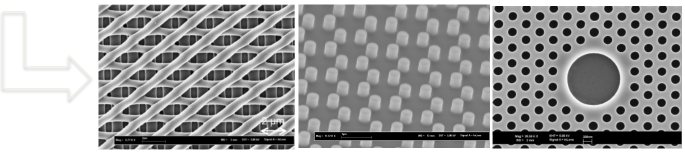
Bottom-up



NIL

Advantages
- Resolution
- Soft materials compatible
- Fast (sec/cycle)
- Low cost ($0.2M vs $25M)
- Simple
- Flexible (UV, heat)

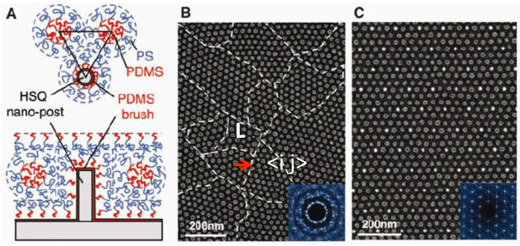
Complex patterns **Functional devices**



Semiconductors; Optics; Bio; Organic electronics; Sensors

N.Kehagias, *Nanotechnology* 18 (2007)
V.Reboud, *Jpn. J. Appl. Phys.*, 47 (2008)

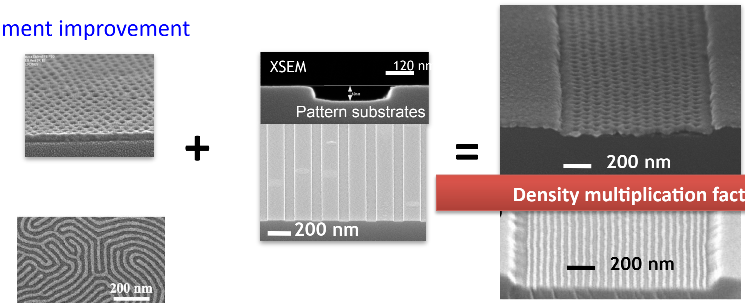
✓Order improvement



PS-PDMS microphase segregation (A) in flat substrates (B) and with templates (C)

Bita et al, *Science* 321, 939 (2008)

✓Alignment improvement



Aligned nanodots (PS-PEO)

Density multiplication factor

nanowires (PS-PDMS)

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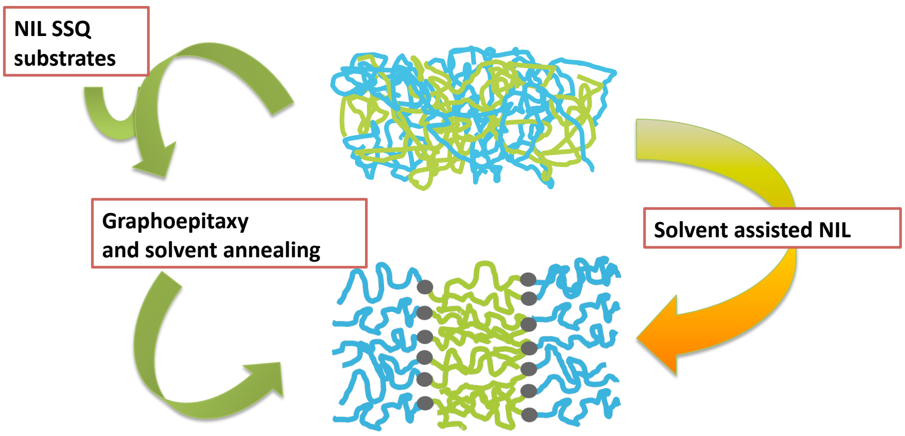
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Combination of top-down and bottom-up methodologies:

A. Two step process

B. One step process



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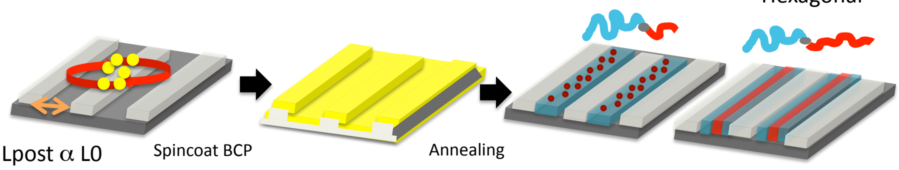
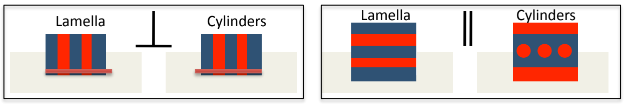
A: Two step process by graphoepitaxy



Lpost α L0

L_{post}/L_0 **range between 1.65 to 4.6**

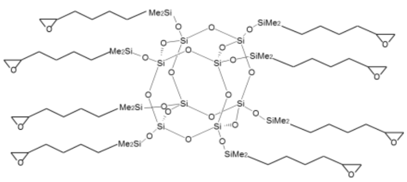
Self-assembled BCPs configurations



Si | BCP film | Annealed BCP film: Block 2 cylinders in a Block 1 matrix | Surface treatment

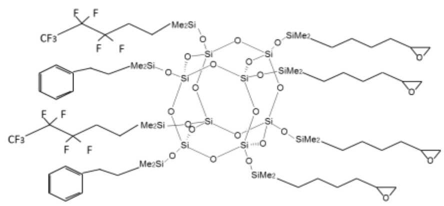
Polyhedral Oligomeric Silsesquioxanes (POSS or SSQs)

- **-Silicon based cage-polymer**
- **-UV curable**
- **-Facile and industry compatible processing**
- **-Tunable surface free energy by synthesis**



Surface free energy 30.9 mN/m

8E-POSS



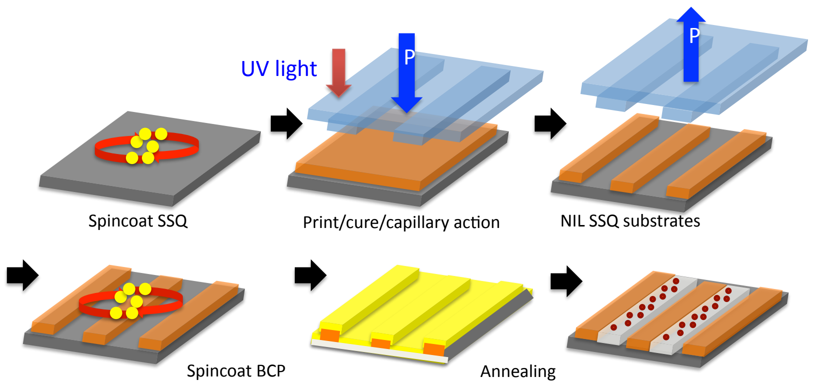
Surface free energy 23 mN/m
6EF2-POSS

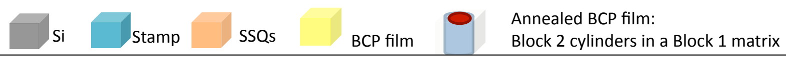
Tailored designed SSQs with desired SFE andinterfatial groups

Si | Stamp | SSQs | BCP film | Annealed BCP film: Block 2 cylinders in a Block 1 matrix

Polyhedral Oligomeric Silsesquioxanes (POSS or SSQs)

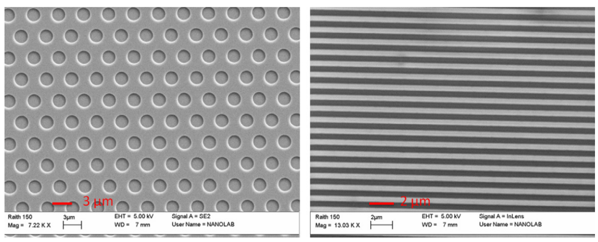
-fabrication methodology





2D circular features and lines replicated in SSQs

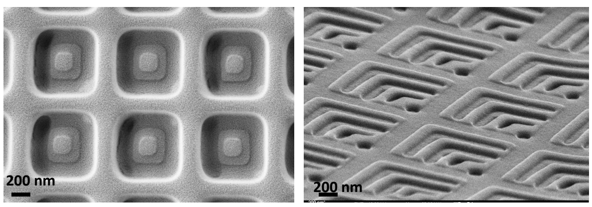
✓High resolution
✓Large area



N. Kehagias et al., Microelectronic Engineering 88 (8)1997-1999

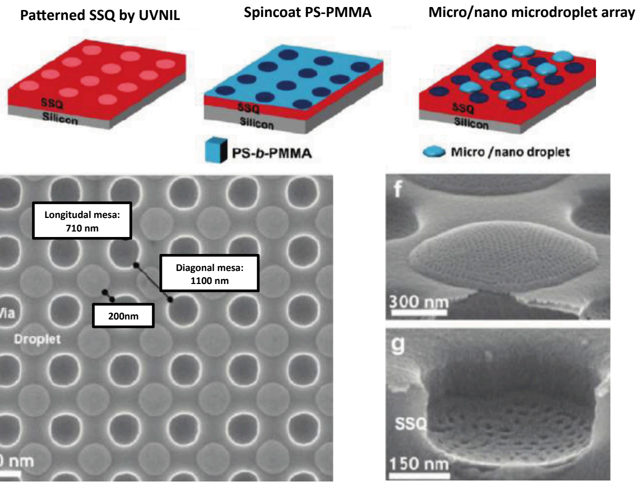
3D features

***Sub-100 nm three dimensional diffractive optical elements fabricated* by *UV light* assisted roll-to-roll NIL**



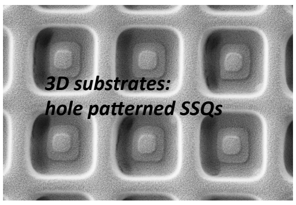
N. Kehagias et al., EIPBN 2012, 29 May-01 June 2012

DSA of PS-b-PMMA in SSQ patterned substrates



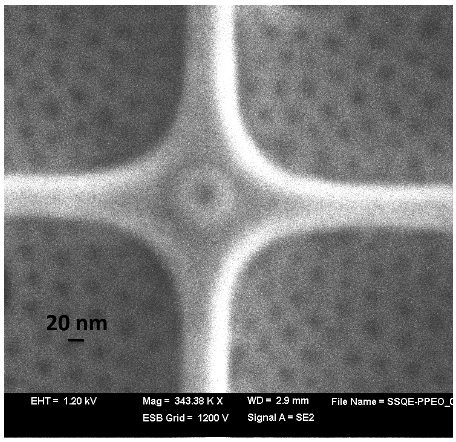
R.A. Farrell et al, *ACS Nano, 5 (2011) 1073.*

The BCP film was inside and on top of the nanoimprinted features, where the last formed dewetted nanodroplets due to the SSQ SFE.



PS-b-PEO 42k-11k
8E-SSQ
15h anneal in toluene vapors

50 nm droplet → cylinders
→ nanoring 50 nm ||



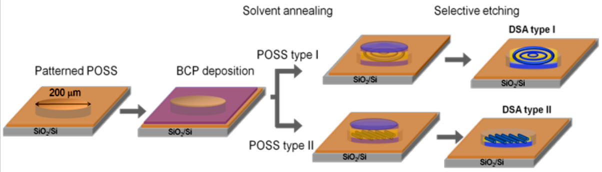
Ongoing work

C. Simao et al, in preparation..

SSQs with residual layer

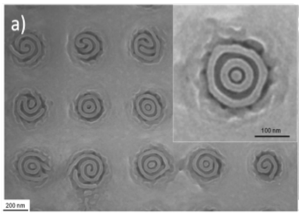
Table 1. Nanoimprinted POSS substrates SFE.

SSQ derivative	Contact angle (deg)	SFE (mN/m)
C6-SSQ	72	42
8E-SSQ	84	30

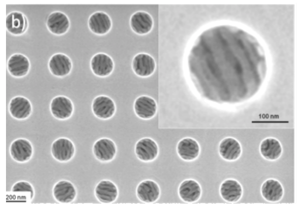


Orientation is dependent on the substrate interfatial surface SFE and terminal groups of the film

PDMS nanorings (pore size 25 nm)



PDMS toroidal structures (pore size 25 nm)



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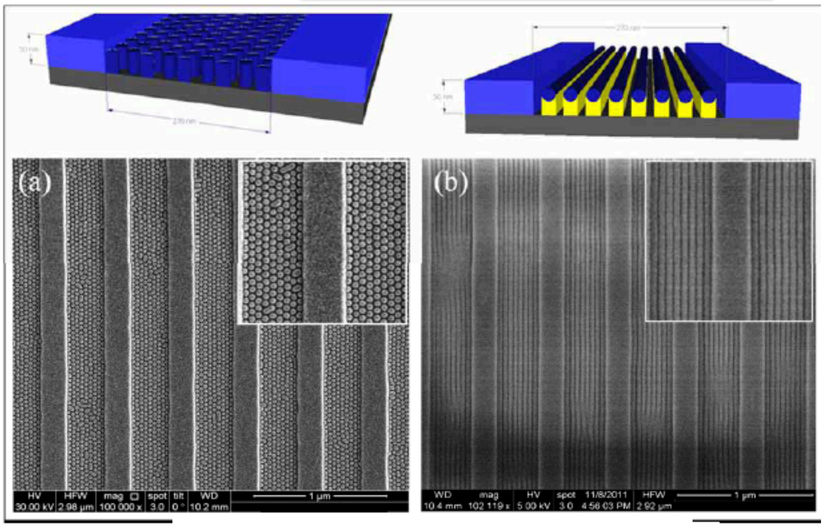
C. Simao et al, *J. Photopolymer Sci. & Technol.*, 2012

PS-PDMS in SSQ-C6 (A) and in Glycidyl-SSQ (B)

Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

SSQs without residual layer

Improved long range order



PS-PDMS 31k-14k, 15 h toluene anealing

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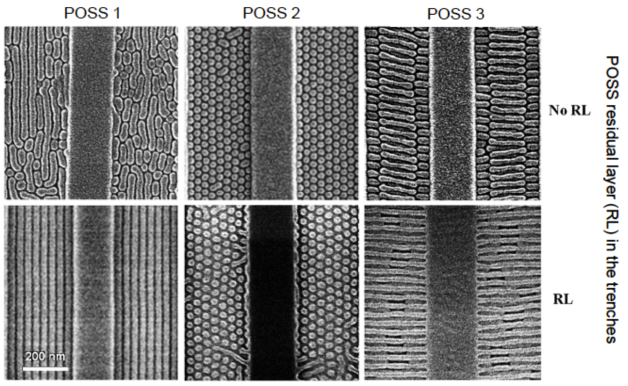
Tuning SSQ terminal groups and surface free energy → Control of alignment and orientation in a predictable way

PS-b-PDMS graphoepitaxy: substrate chemistry

Library of processes

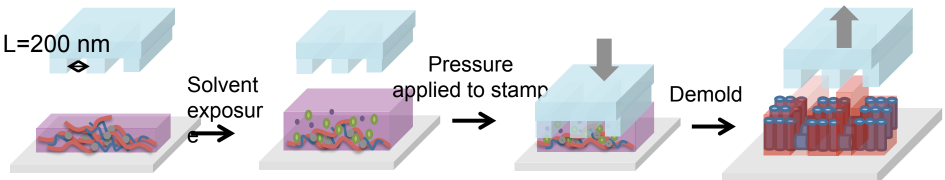


Solvent annealing in Toluene

M. Zelsmann et al, Nano Letters, submitted.

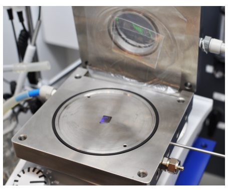
Approach B: One-step process NIL+BCP DSA

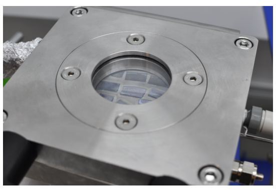
Solvent vapors assisted nanoimprint lithography (SAIL)



Legend
Toluene   Water   PEO block   PS block

Orientation of the features dependent on the groove height

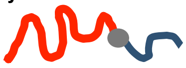




SAIL chamber:
Transparent window for *in situ* optical characterization

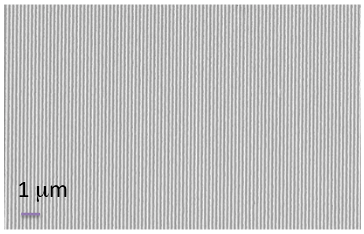
C. Simão et al, 2013, submitted.

Asymmetric Diblock Copolymer

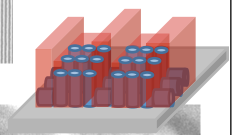


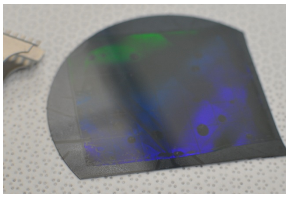
PS-PEO 42k-11k
Hexagonal phase 35 nm pitch

Field emission SEM

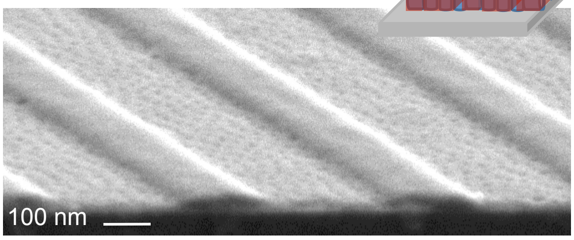


- 4" wafer imprint
- High resolution
- No dewetting





Large area ordered nanodot hexagonal arrays



→Only one step process and overall time decreased from 3 hours to 35 minutes

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What can self-assembly offer to microfabrication:

1. Organization of small and numerous components into ordered 2D and 3D structures in a parallel process
   Compatible with variety of materials, flat and curved surfaces
   Electric/electronic and optical functionality
   Can eliminate process incompatibilities (e.g., CMOS & III IV tech.)

2. Parallel, fast process
   Current best *pick-and-place*: ~26,000 pph, 300 μm
   Alien Technologies: 2,000,000 pph, 10-100 μm
   cut the price of RFID tags form 0.5 $ to 0.2 $

3. High accuracy of registration
   MEMS micro-mirrors, 150-400 μm: ±0.2 μm, 0.3°
   out-of-plane rotation: ≤0.1°

4. Low defect rates and high yields
   Correction mechanisms: assemble only working devices
   misaligned components are unstable
   multiple assembly steps

MRS Bull. 30 (2005) 736

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Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

SUMMARY
Functional systems by non-molecular (*μm to mm*) self-assembly

Opportunities:

1. Plausible engineering strategy
   - Microfabrication
   - Micro- and macro- electronics
2. A new route to functional 3D structures
   - Templating
   - Molecule-mimetic and biomimetic strategies
3. Versatile and simple models

Issues: operational, not intrinsic

1. Fabrication of 3D and functional components
2. Design of patterns for recognition and binding

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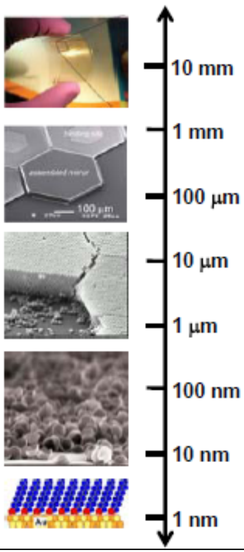
Intro | Molecular SA | Nano-to-Micro SA | Micro-to-Mili SA | Conclusions

Using self-assembly to make functional systems:
- **bridge top-down and bottom-up**
- **stand alone**



- Low cost
- Simple processes
- Fewer defects
- New route to 3D structures
- Reconfigurable and conformal structures
- Assembly in inaccessible spaces

- New, non-molecular materials
  - Self-healing and reject defects
  - Ultra-high surface areas
  - Optical properties
  - High density
- Bio-medicine, delivery, manipulation
- New technology based on nano-sized components

- Big molecules
- Nano-structures
- New molecular materials
- Patterned surfaces

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Main problems (cont'd)

Tradeoffs between size, complexity, and functionality of components

Topology/topography of "recognition" in self-assembly

Generation of asymmetry: "proteins" rather than "crystals"

Theoretical basis:
- Molecular self-assembly: solvent, entropy
- Analogue of thermodynamics/statistical mechanics for nano / micro
- Range of structures that can be formed
- Perfection of the structures, nature of defects
- Prediction of yield by shape, size of components, and conditions of assembly
- Dynamic self-assembly

Design
- fail-safe or adaptive (redundant); flow of materials or information

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Self-assembly: opportunities

New tools

New science
New materials
New technology

New devices

1 nm — 100 nm — 1 μm — 100 μm

Mesoscale structured materials
- **magnetic assemblies**
- **structured colloids**
- **catalysts**

Composites
- **high- and low-*k* dielectrics**
- **mechanical reinforcement**
- **new electronic properties**

Photonics
- **sub-λ optics**
- **fluidic optics**
- **PBG materials**

Electronics
- **3D *vs.* 2D**
- **biomimetics**
- **molecular electronics**
- **flexible electronics**
- **macroelectronics**

Dynamic self-assembly
- **complexity**
- **the cell**

The far future
- **Nano-IC**
- **Bio/IT interface**
- **Quantum computation**
- **Mechanical genomic surgery**
- **Synthetic complexity**
- **… ??**

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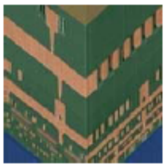

Integration / Synergy

- Size boundaries: **"It's function and cost that count, not size!"**
- Disciplines: physics, chemistry, biology, materials science, engineering
- Divisions: applied, fundamental, and exploratory R&D

Cross-talk and collaboration

Strategies, concepts ⟷ Synthesis, fabrication ⟷ Characterization ⟷ Applications

Any doubts?

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