Engineering (mostly) Supramolecular Nanosystems at Surfaces

Control of Matter at the Nanoscale

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Outline

• principles of supramolecular engineering

• semantic excursion on « self-processes »
  → origins of terminology & notions on its interpretation

• self-organized growth at surfaces
  → nanoscale constructions atom by atom
  → patterns and quantum dots by strain relief
  → 2-dim synthesis of H-bonded architectures
  → design of low-dim metallosupramolecular systems
Supramolecular Engineering
From Molecules to Functional Materials
Meaning of Supramolecular Chemistry


Development and Use of Molecules with Structure-Specific Interactions of High Selectivity

Chemistry « beyond the molecule »
- inspired by animate systems
- rationalize molecular recognition
- control noncovalent interactions
  → hydrogen and coordination bonds
- self-assembly
- supramolecular engineering
- supramolecular functional materials
- supramolecular technology
The Molecule of Life: DNA

- base pairs in DNA with complementary groups for hydrogen bonding
  ⇒ molecular recognition, stabilization of double helix

Noncovalent Interactions are Ubiquitous in Biology
Principles of Hydrogen Bonding

$\text{H}_2\text{O}$

$\text{XH} \cdots \text{A}$

(proton)  (proton)

donor acceptor

$\text{X} : \text{electronegative atom}$

$\text{e.g., O, N, S, P, Se, C}$

$\text{A} : \text{lone electron pair of}$

$\text{electronegative atom or}$

$\pi$ orbital

$\text{H} \cdots \text{A distance : } \sim 1.2 \text{ – } 3 \, \text{Å}$

• Hydrogen bonds feature

  - directionality
  - selectivity
  - versatility

$E \sim 0.2 \text{ eV}$

water dimer : OH bonds polar

$\rightarrow$ OH dipoles point to filled $p$ orbitals

Water Clusters

bond motif in solid

small ring clusters for max. H-bonding

five isomers for hexamer, close in energy (cage lowest)

• barely controllable molecular arrangements

Cf.: http://www.sbu.ac.uk/water/
Supramolecular Engineering

molecular linkage by coupling of functional carboxyl groups


1-dim linear chains

3-dim architecture

2-dim honeycomb sheet
Synthons & Tectons

- Synthon
- Tecton

Chain motif using linear linkers

Honeycomb network from complementary tectons (melamine – cyanuric acid)

Information contained in molecules
→ supramolecular organization

Energetics and Need of Cooperativity

- Assemblies based on single H-bonds have low stability.

- Typical energy range: $E \sim 0.2 - 0.4$ eV

- Strong: $E > 0.5$ eV

- Weak: $E < 0.2$ eV

- Cooperative H-bonding in artificial systems

- Multiple links!

- Assemblies based on single H-bonds have low stability

DNA

Cooperative H-bonding in artificial systems


Supramolecular Self-Assembly

9 components, 36 hydrogen bonds

designed molecules \(\rightarrow\) self-assembly \(\rightarrow\) highly organized systems

molecular recognition

\(\Rightarrow\) functional materials for supramolecular technology

Univ. Twente, MESA+
Group D.N. Reinhoudt

Designing H-bonded Nanotubes

cyclic peptide of amino acids $\rightarrow$ self-assembled organic nanotube

insertion of biomimetic assembly in bacterial membrane increases transmembrane mobility

$\Rightarrow$ potential selective antibacterial agent
Supramolecular Polymers

Supramolecular Polymers are polymeric assemblies with reversible bonding, often referred to as ‘molecular velcro’.

The self-complementary ureidopyrimidinone derivative leads to quadruple H-bonding, resulting in tunable polymeric materials.

- Self-healing polymer networks
- Easy production of copolymers
- Thermoplastic elastomers


Metal Coordination in Biology

**Operating unit:**
5-coordinate Fe site

**Fe-heme complex**

**Breathing:**
Capture & release of $O_2$
**Coordination Compounds**

- Square planar
- Tetrahedral
- Octahedral

Central metal ion binds to several ligands (e⁻ pair donors)

**Stereoisomers**

- *cis*-\([\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\)
- *trans*-\([\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\)

- Anticancer drug (cisplatin)
- No therapeutic use
Bonding Types and Ligands

**Bonding Type**

**unidentate**

Typical bond strength ~ 0.5 – 1 eV → robust architectures

- **pyridine ligands**
  - ![Pyridine ligand](image)

- **carboxylate**
  - ![Carboxylate](image)

**bidentate**

- **porphyrin ligand**
  - ![Porphyrin ligand](image)

- **terpyridine**
  - ![Terpyridine](image)

- **ortho-phenanthroline**
  - ![Ortho-phenanthroline](image)
Metallosupramolecular Chemistry

Univ. Louis Pasteur, Strasbourg, Group J.-M. Lehn

chiral double helicate

(2×2) Fe nanoarray

building blocks → metal-ligand interactions → polynuclear complex

⇒ molecular engineering of advanced materials
- frameworks, sensors, photosensitizers, molecular magnets
Tailored Metal-Organic Coordination Frameworks

\[ \text{Zn}_4(O)O_{12}C_6 \] ditopic carboxylate linkers

⇒ tuning of homogenous periodic pores
cavity range : 3.8 – 28.8 Å

octahedral Zn-O-C cluster
van der Waals cavity
TPDC linker

methane uptake in MOF6

Hybrid Systems for Sensing Devices

bifunctional anchor

Porphyrin

Detection of low-concentration NO in physiological solutions

Unfunctionalized GaAs

Molecular controlled semiconductor resistor

Nanoelectronics with Coordination Compounds


single-atom transistor

conducting supramolecular films
Supramolecular Dyes in Solar Cells

TiO$_2$ nanocrystalline film

N3 dye
Ru-complex as sensitizer

COO$^-$

TiO$_2$ (anatase)

charge transfer at functionalized semiconductor surface

Key Messages from Introductory Lesson

- **Supramolecular Chemistry**
  Development and use of molecules with structure specific noncovalent interactions, notably H-bonding & coordination bonds

- **Molecular Recognition**
  Controls the selective linkage between two molecules, or a molecule and a metal atom

- **Self-Assembly**
  Spontaneous association of complementary units to an integral whole, stabilized by noncovalent bonds

- **Supramolecular Engineering**
  Art of construction for highly organized molecular architectures

- **Supramolecular Materials**
  Meet function and performance criteria using supramolecular engineering and appropriate self-assembly strategies

- **Supramolecular Technology**
  Use of supramolecular materials & processes for specific needs and device concepts
What are Self-Processes ??!? 

- self-organization
- self-assembly
- self-organized growth
- self-replication, self-correction, …

- widespread confusion about meaning & significance
- very popular hype & buzz words in ‘nano‘-community
- limitlessly elastic term … overused to the point of cliché

[G. Whitesides on self-assembly, Science 2002]
Self-Organization

- term in use since ~ 1898

- organization of oneself or itself; specifically: the act or process of forming or joining a labor union

- no entry in scientific sense

Oxford English Dictionary - no entry
Self-Organization: Publication Trends


1947: Principles of the Self-Organizing Dynamic System
W. Ross Ashby, Journal of General Psychology, volume 37, pages 125-128

1953: SELF-ORGANIZATION AS A FACTOR IN THE PERFORMANCE OF SELECTED COGNITIVE TASKS

1971: SELFORGANIZATION OF MATTER AND EVOLUTION OF BIOLOGICAL MACROMOLECULES
EIGEN M, NATURWISSENSCHAFTEN 58 (10): 465–times cited 1087

1977: Self-organization in non-equilibrium systems: From dissipative structure formation to order through fluctuations

1978: Synergetics - An Introduction. Nonequilibrium Phase Transition and Self-Organization in Physics, Chemistry, and Biology
Haken, H. (Springer, Berlin)

1990: PERSPECTIVES IN SUPRAMOLECULAR CHEMISTRY - FROM MOLECULAR RECOGNITION TOWARDS MOLECULAR INFORMATION-PROCESSING AND SELF-ORGANIZATION
LEHN JM, ANGEWANDTE CHEMIE - INT. ED. 29 (11): 1304-1319 NOV 1990 – times cited 1411
Systems Associated with Self-Organization

- Belousov-Zhabotinsky reaction
- Sand dune shaped by wind
- Collective movement of social beings

- Pattern formation in inanimate & biological systems
- Emergence of order
- Dynamic features
Self-Organization: Definitions & Use

Self-organization is a process in which a pattern at the global level of a system emerges solely from numerous interactions among the lower level components of the system. [Deneubourg 1977]

- **physics** - order phenomena in non-equilibrium thermodynamics → fluid dynamics, lasers … galaxy formation
  - (spontaneous symmetry breaking, crystallization, …)
- **chemistry** - oscillating chemical reactions, reaction-diffusion systems
  - synonyme for self-assembly
- **biology** - origin of life
  - lipid bilayer membranes
  - morphogenesis
  - homeostasis (self-regulation of cells, organisms)
  - social behavior (fish swarms, insects, flocks, …)
- **mathematics, social sciences, cybernetics, geosciences, economy, …**
The Self-Assembly Paradigm

- term in use since ~ 1960s

Oxford English Dictionary

1. Subsequent assembly of something bought in the form of a kit; usu. *attrib.*, denoting items (e.g. furniture) sold in this form.

   → 1966 in G. N. Leech Eng. in Advertising (1966) xv. 137

   ... *the luxury of a Built-in Bedroom at a price you can really afford*

   *With Dovetail Self-assembly Units*

   → “*Self-assembly means not having to pay the cost of someone in a factory doing it for you*”

   (www.ikea.co.uk - in rubrique FAQ)

2. The spontaneous formation of a sub-cellular particle from its components, e.g. that of a ribosome or of a virus in a medium containing the appropriate RNA and proteins.

   → 1969 Jrnl. Molecular Biol. XL. 412 :

   *We feel that the general principle of self-assembly revealed in the present in vitro system also operates in vivo.*

   → ... *Thus all the information necessary to assemble the particle must be contained in its components, that is, the (tobacco mosaic) virus “self assembles”.*

   *(A. Klug, Nobel lecture 1982)*
The Archetype of a Self-Assembled System

Tobacco Mosaic Virus
(Length : 300 nm, Diameter : 18 nm)

- helix stabilized by hydrogen bonds
  - ca. 2130 identical protein units (à 158 amino acids)
  - central RNA strand (6390 base pairs)
- mixing of separated components under appropriate conditions *in vitro*

⇒ self-assembly of active virus from inactive subunits

Complementary units spontaneously assemble to an integral whole, stabilized by many noncovalent interactions

Self-Assembly: Publication Trends


1967: STUDIES ON SELF-ASSEMBLY OF PHAGE T2 HEAD
POGLAZOV BF, KESYANZH.VV, KOSOUROV GI; BIOCHEMISTRY-MOSCOW 32: 588 – times cited 0

1976: THEORY OF SELF-ASSEMBLY OF HYDROCARBON AMPHIPHILES INTO MICELLES AND BILAYERS
ISRAELACHVILI JN, MITCHELL DJ, NINHAM BW

1986: BEYOND SELF-ASSEMBLY - FROM MICROTUBULES TO MORPHOGENESIS
KIRSCHNER M, MITCHISON T; CELL 45 (3): 329-342 MAY 9 – times cited 616

1991: MOLECULAR SELF-ASSEMBLY AND NANOQUIMISTRY - A CHEMICAL STRATEGY FOR THE SYNTHESIS OF NANOSTRUCTURES
WHITESIDES GM, MATHIAS JP, SETO CT; SCIENCE 254 (5036): 1312-1319 NOV 29 – times cited 1063

1996: Self-assembly in natural and unnatural systems
Philp D, Stoddart JF; ANGEWANDTE CHEMIE-INT. ED. 35 (11): 1155-1196 JUN 1 – times cited 266
Snowflakes & Galaxies

- autonomous ordering in accumulation of matter
Self-Organized Growth of Quantum Dots

molecular beam epitaxy chamber

Ge pyramids on Si(100)

Self-organized growth in strained structures

→ simple and efficient way to build regular semiconductor nanoarchitectures

Appl. Phys. Lett. 64, 196 (1994); 74, 994 (1999)
Self-Organized Growth : Publication Trends

- in use since ~ 1990s

→ ISI-WOS search : 315 records, some plant science, mostly semiconductor quantum dot & nanoscience community; starting 1991

1991 : FEEDBACK INDUCTION - A POSSIBLE EXPLANATION FOR SELF-ORGANIZED GROWTH OF X(2) GRATING IN SILICA FIBERS
ZHENG XH, CARROLL JE, OPTICAL AND QUANTUM ELECTRONICS 23 : 29-33– times cited : 0

1992 : PHYLLOTAXIS AS A PHYSICAL SELF-ORGANIZED GROWTH PROCESS
S Douady & Y Couder, Phys. Rev. Lett. 68, 2098

1994 : SELF-ORGANIZED GROWTH OF REGULAR NANOMETER-SCALE InAs DOTS ON GaAs
MOISON JM, HOUZAY F, BARTHE F, et al. APPLIED PHYSICS LETTERS 64 (2): 196-198
– times cited : 660

1998 : SELF-ORGANIZED GROWTH OF NANOSTRUCTURE ARRAYS ON STRAIN RELIEF PATTERNS
H BRUNE, M GIOVANNINI, K BROMANN & K KERN, Nature 394 : 451
Thermodynamic vs. Kinetic Control


Crystallization pathways
[$\Delta G$ : free energy of activation]

- spatial & temporal evolution of system controls final architecture
  → analogous principles in biomineralization
self-assembly
  - spontaneous formation of a textured product with
definite shape integrating clearly identifiable components
  - proceeds near equilibrium in closed systems
  - ensembles of identical products can be obtained or even replicated

self-organized growth
  - order phenomena controlled by (mesoscale) force fields or kinetic
limitations arising in processes mediating accumulation of matter
  - corresponding products are uniform to a certain extent but a priori not
identical at the atomic or molecular scale

self-organization (substantial)
  - spatiotemporal order phenomena in open systems far from equilibrium
(kinetically unlimited continuous substance and energy exchange with environment)
  - autonomous coding or superior spatial organization of matter beyond
self-assembly or self-organized growth
(→ evolution, morphogenesis, …)