Academia Romana

SELF – ASSEMBLING

a step in the development of complex organized matter

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41A, Aleea Grigore Ghica Voda, 700487 Iasi

Dynamic Nano Systems: Concepts and Application

Bucuresti, September 23-24, 2010

TOPICS

- ***Concepts, definitions***
- ***Self-assembling systems***

  Chemistry laboratory

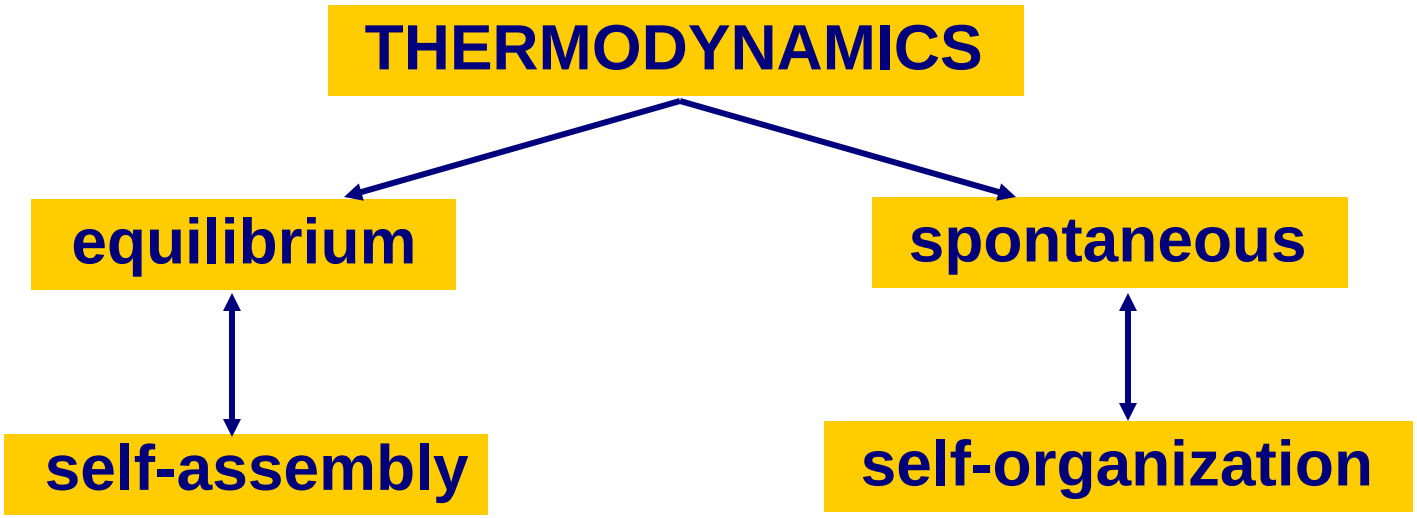
  Drug loaded nanoparticles
  (Poly)rotaxanes
  LB films of modified cyclodextrins

  Nature

- ***Perspectives***

CONCEPTS

Halley and Winkler, *Complexity, 2008*



- ❒ Collective interactions
- ❒ Nondissipative, equilibrium order
- ❒ Thermodynamically controlled
- ❒ Stable at equilibrium, no need for energy input

- ❒ Collective, nonlinear interactions
- ❒ Dissipative, nonequilibrium order
- ❒ Interplay between intrinsic/ extrinsic factors
- ❒ Decay upon removal of the energy source

WHAT CHEMISTS KNOW TO DO ?

« Petru Poni » Institute of Macromolecular Chemistry

Dynamic Nano Systems: Concepts and Application
Bucuresti, September 23-24, 2010

Drug loaded nanoparticles

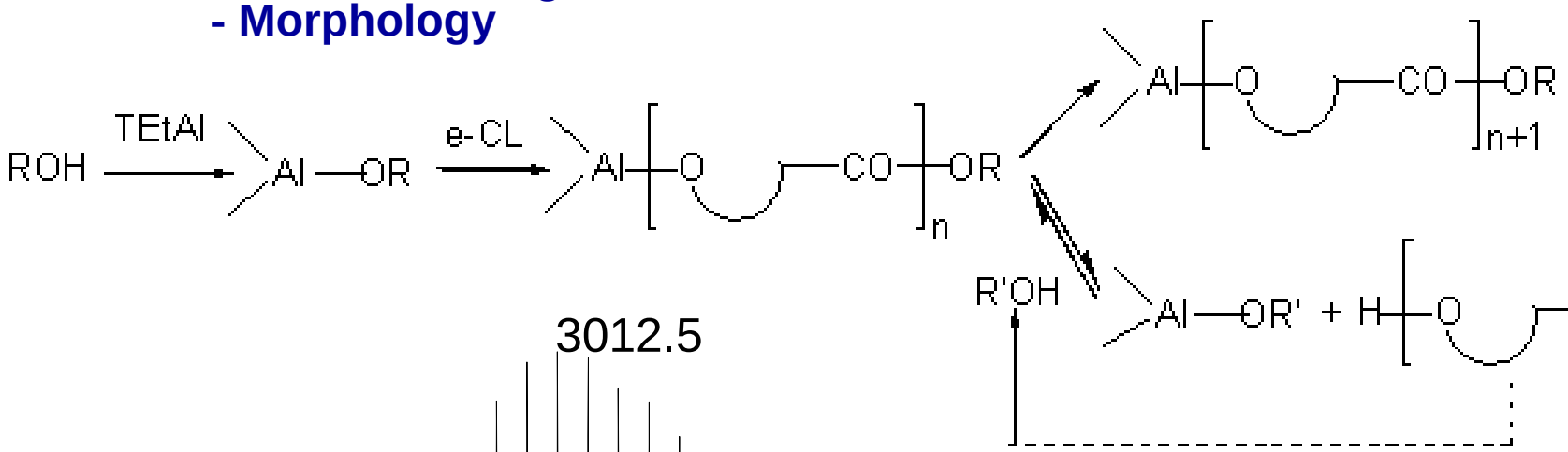
- Controlled structures of poly(siloxane – caprolactone) copolymers
- Controlled morphology (reduced crystallinity of polycaprolactone rich domain)
- (co)nanoprecipitation ⟹ drug loaded nanoparticles
- Nanoparticle functionalization ⟹ application

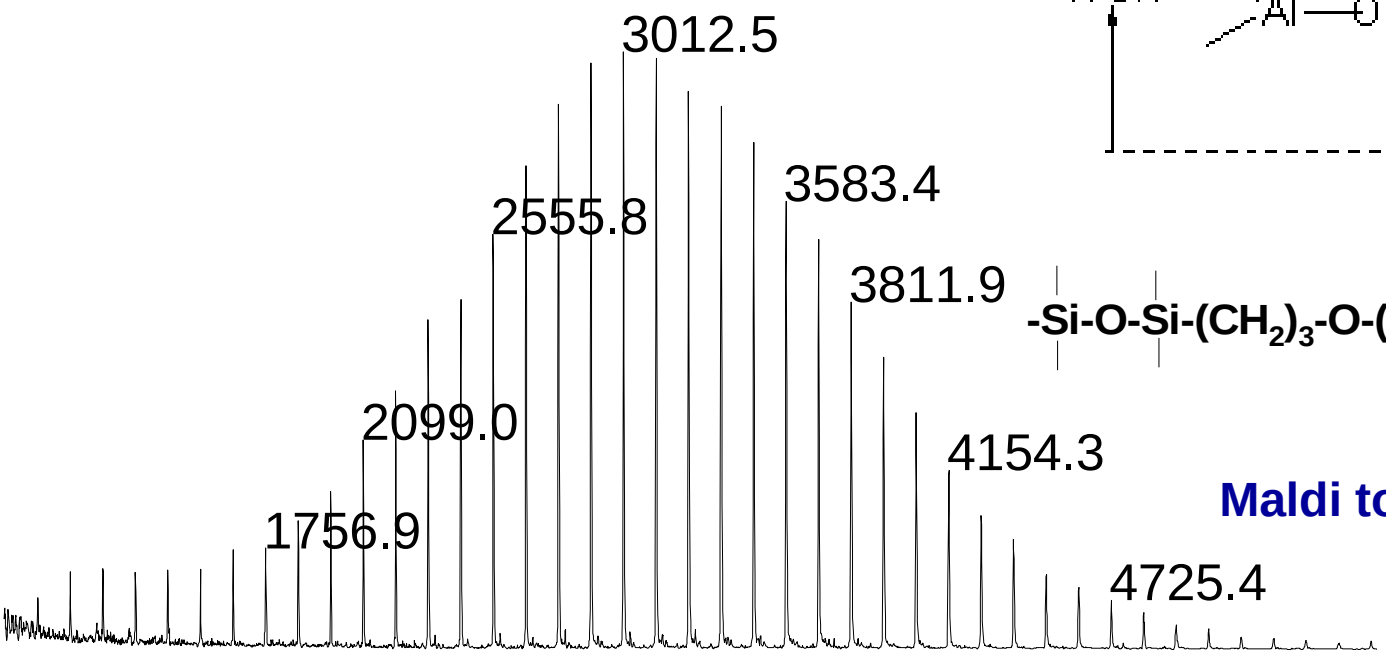
C. Iojoiu *et al.*,
J. Polym. Sci.: Part A: Polym. Chem. **42**(3), 689-700 (2004)
C. Racles, *Macromol. Chem. Phys.* **206**, 1757-1768 (2005)

Siloxane-caprolactone copolymers

Controlled coordinating anionic polymerization

- **Molecular weight**
- **Morphology**



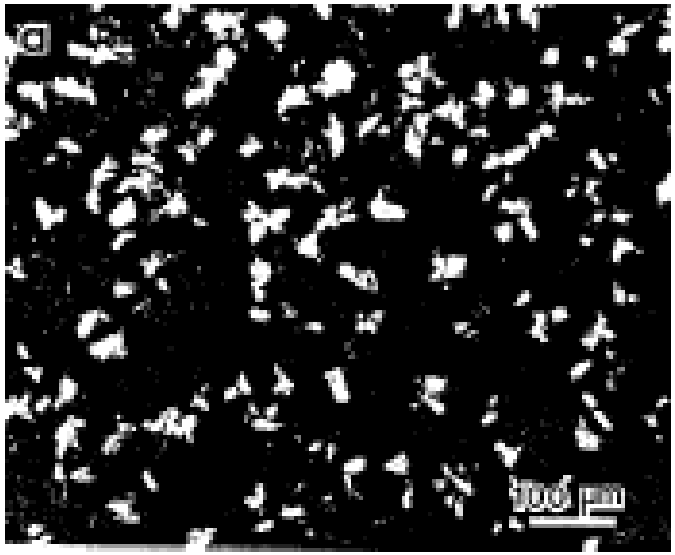


-Si-O-Si-$(CH_2)_3$-O-$(CH_2)_3$-OH + caprolactone

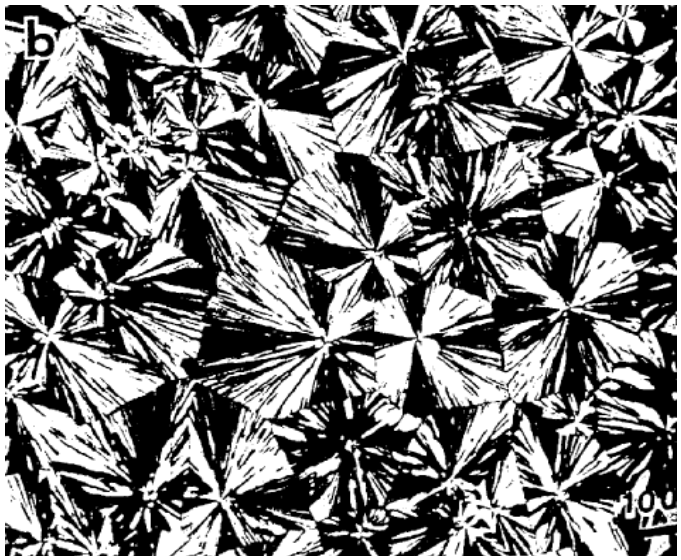
Maldi tof spectra

C. Iojoiu *et al., J. Polym. Sci.: Part A: Polym. Chem.* **42**(3), 689-700 (2004)

Copolymer morphology (polarized optical micrographs)



CL_{2000}-SiO_{1000}-CL_{2000}



CL_{6000}-SiO_{1000}-CL_{6000}

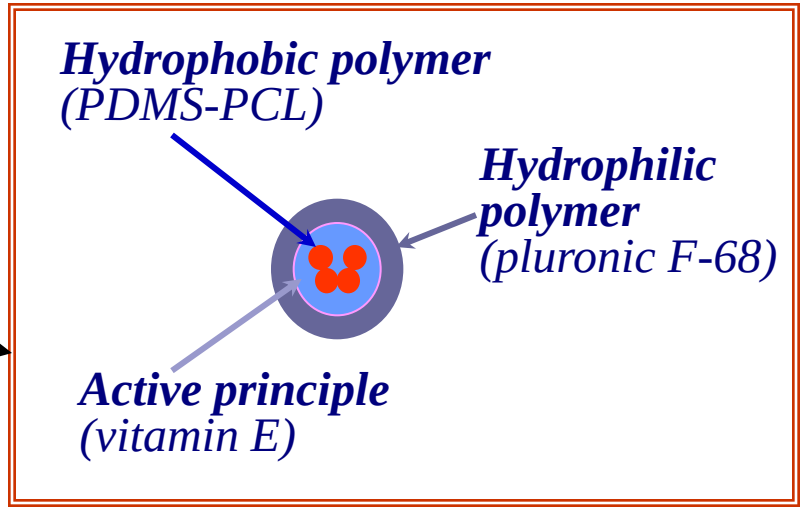
Nanoprecipitation

Organic solution
0.2 g PDMS-PCL
1 g vitamin E
20 ml acetone

Aqueous Solution
0.4 g pluronic F-68
40 ml water

1. Precipitation
2. Evaporation of solvent

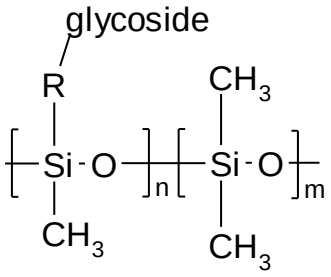
Nanoparticle Suspension
Stable
Dimensions: around 200 nm

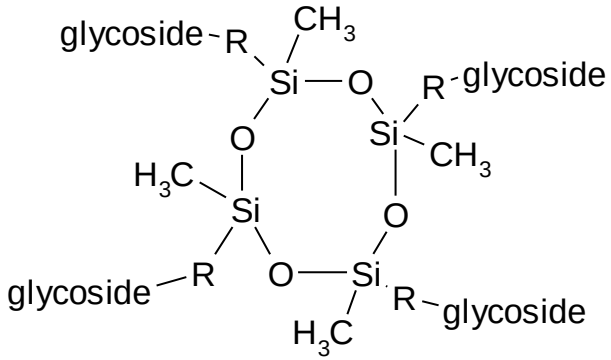


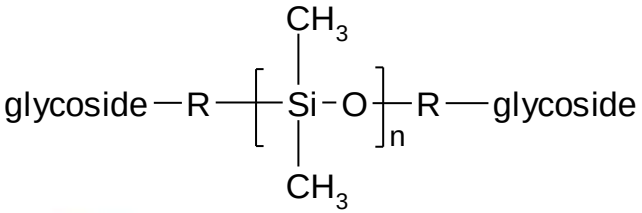
Pluronic F-68 = PEO/PPO/PEO 76/30/76

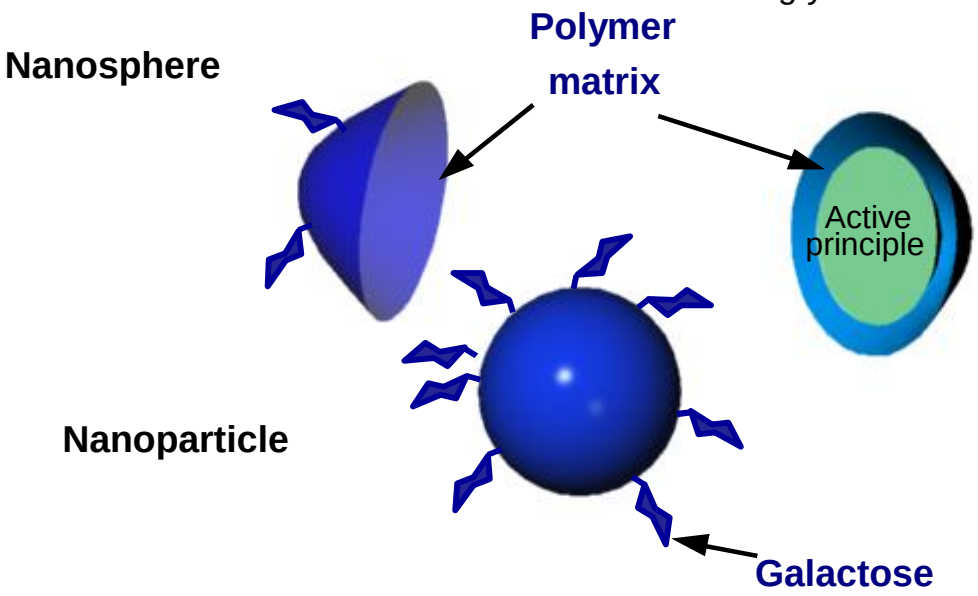
Application

- ***Controlled release***
- ***Catalysis***









C. Racles,
Macromol. Chem. Phys. **206**, 1757-1768 (2005)

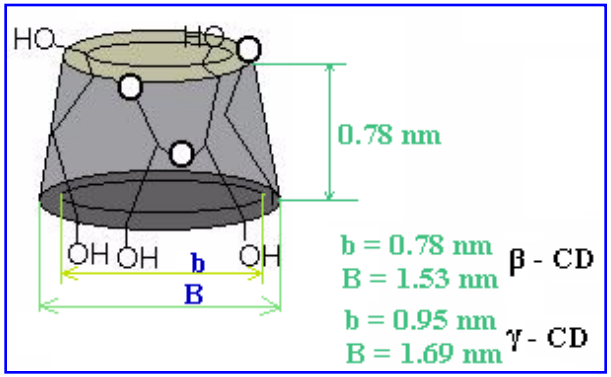
(Poly)rotaxanes

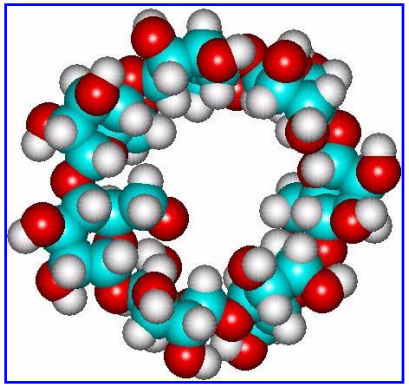
typical example of non-covalent association of non-identical molecules

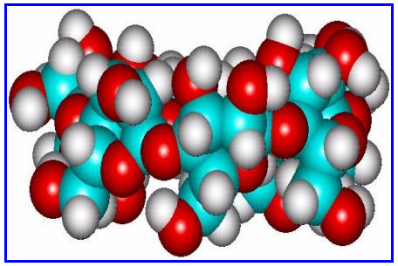
macrocycle + organic/inorganic compound/polymer

- **Polysiloxanes / cyclodextrins**
- **Fullerene C60 / carboxyester modified cyclodextrin**

Cyclodextrin macrocycles

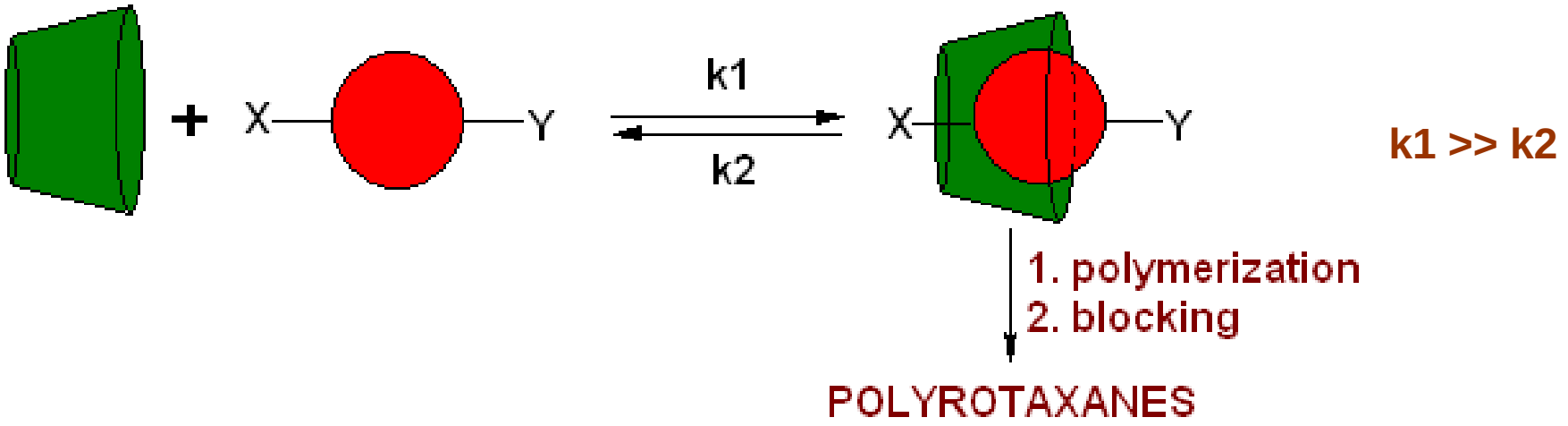






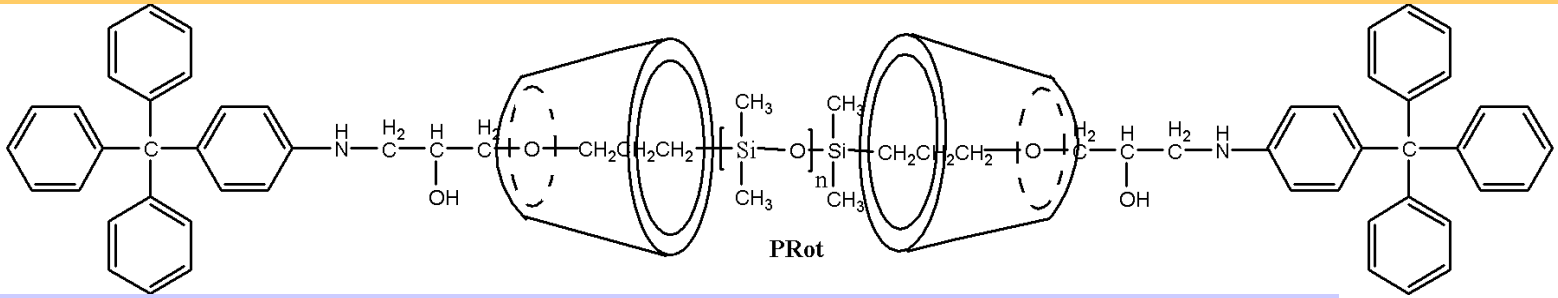
Preparation

- **Polymerization of inclusion complexes**



- **Inclusion of pre-synthesized polymers**

Epoxy-terminated polydimethylsiloxane/cyclodextrin polyrotaxanes

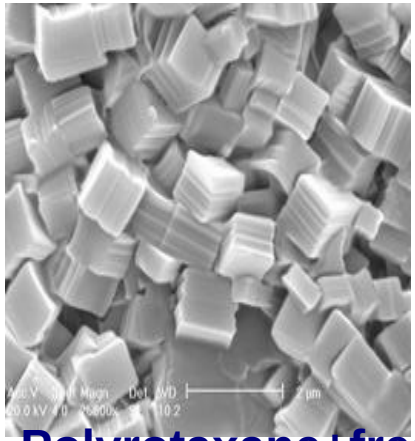


Polydimethylsiloxane (E-PDMS): **Mn = 1000, 2000, 3000**

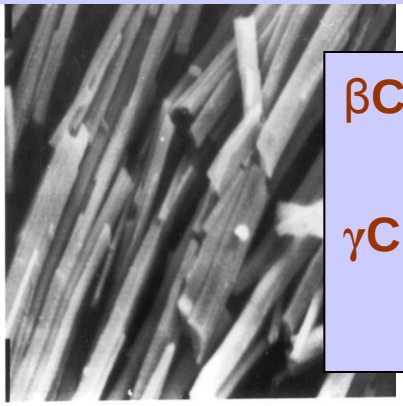
Cyclodextrins: **βCD or γCD**

Polyrotaxanes: **crystallinity and morphology depending on**

- **PDMS molecular weight**
- **CD dimension and content**



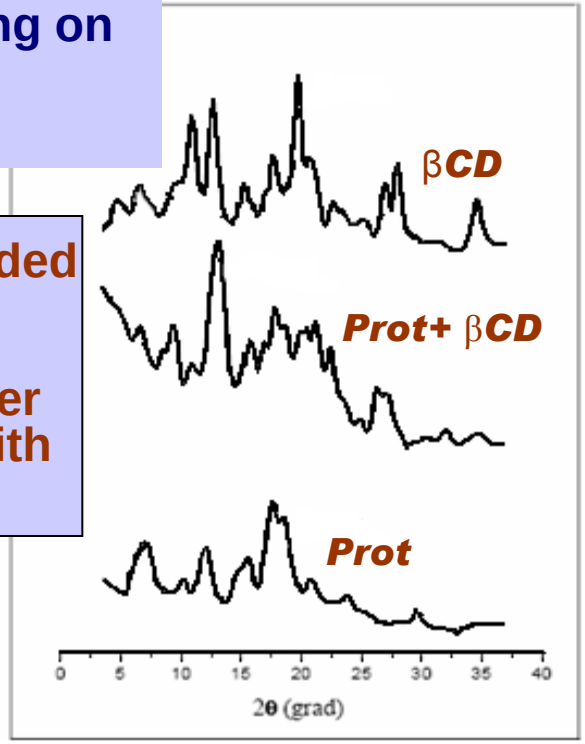
Polyrotaxane+free βCD



Polyrotaxane

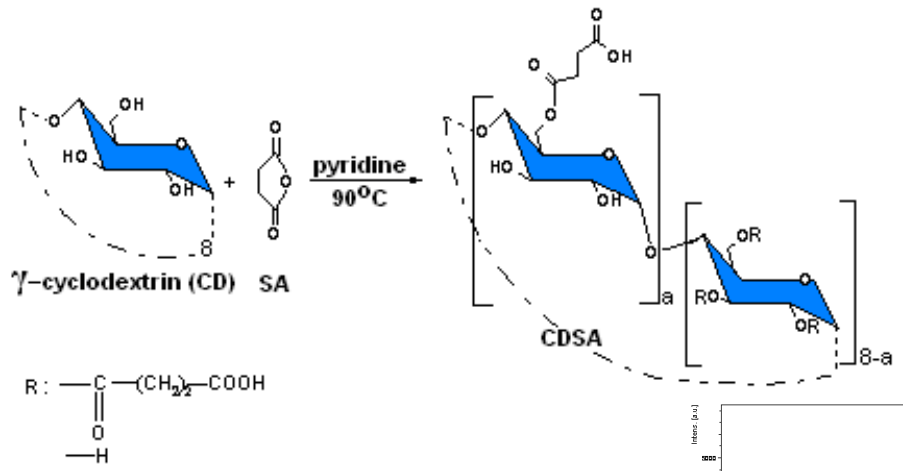
βCD: 2 molecules threaded on each organic chain end

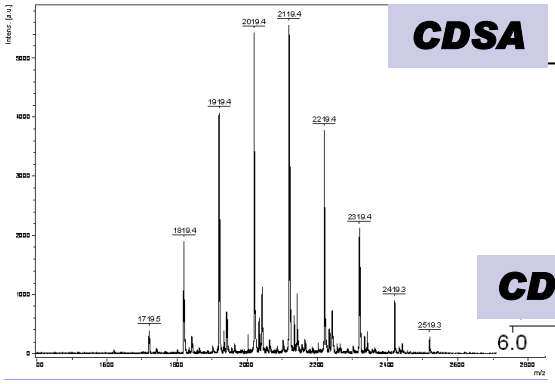
γCD: the content/polymer chain increases with chain length

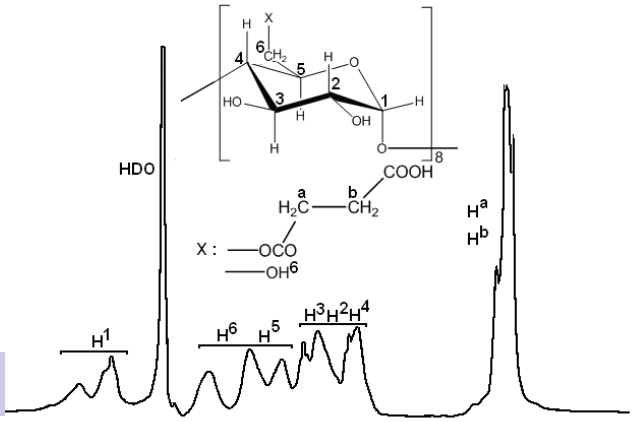


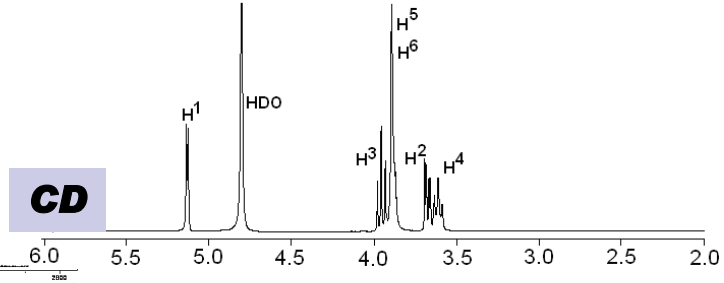
Marangoci *et al.*
High Perform. Polym. **20,** 251 (2008)
J. Incl. Phenom. Macrocycl. Chem. **63**, 355 (2009)

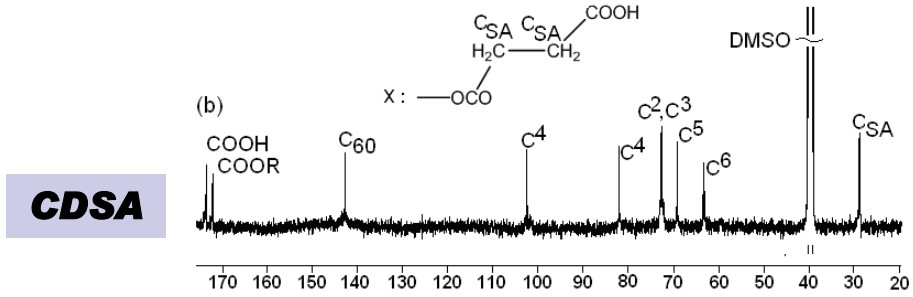
C60 / carboxyester modified γCD







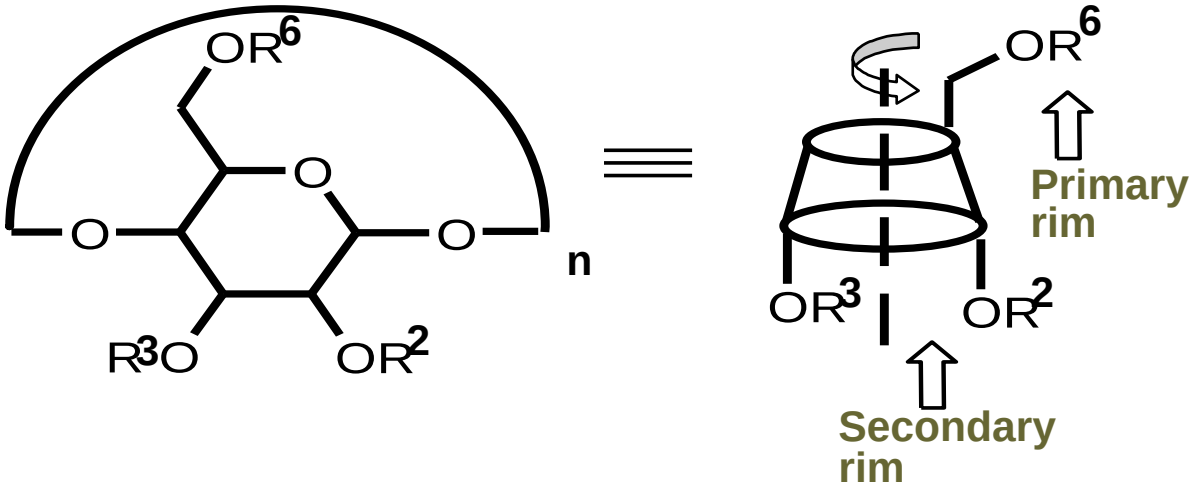




A. Fifere *et al.*
J. Incl. Phenom. Macrocycl. Chem. **64**, 83 (2009)

LB films

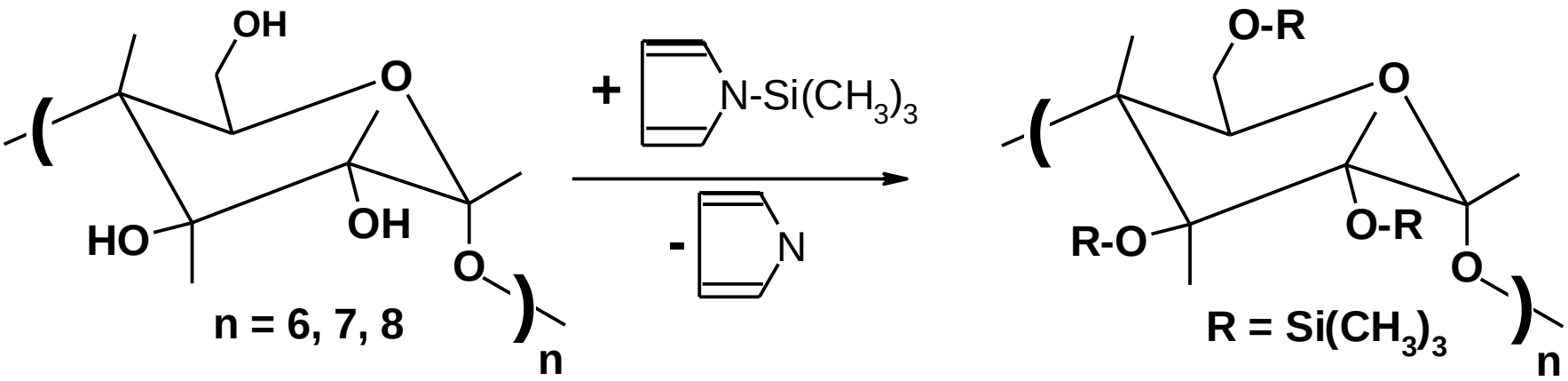
n	Modification
6	$R_2=R_3=R_6=Si(CH_3)_3$
7	$R_2=R_3=R_6=Si(CH_3)_3$
8	$R_2=R_3=R_6=Si(CH_3)_3$
7	$R_2=R_3=Si(CH_3)_3$; $R_6=SH$



- To synthesize well defined modified cyclodextrins with an appropriate hydrophobic-hydrophylic balance
- To demonstrate their LB film forming ability
- To check for possible application of LB films

Persilylated cyclodextrins (CD-Si$_{3xn}$)

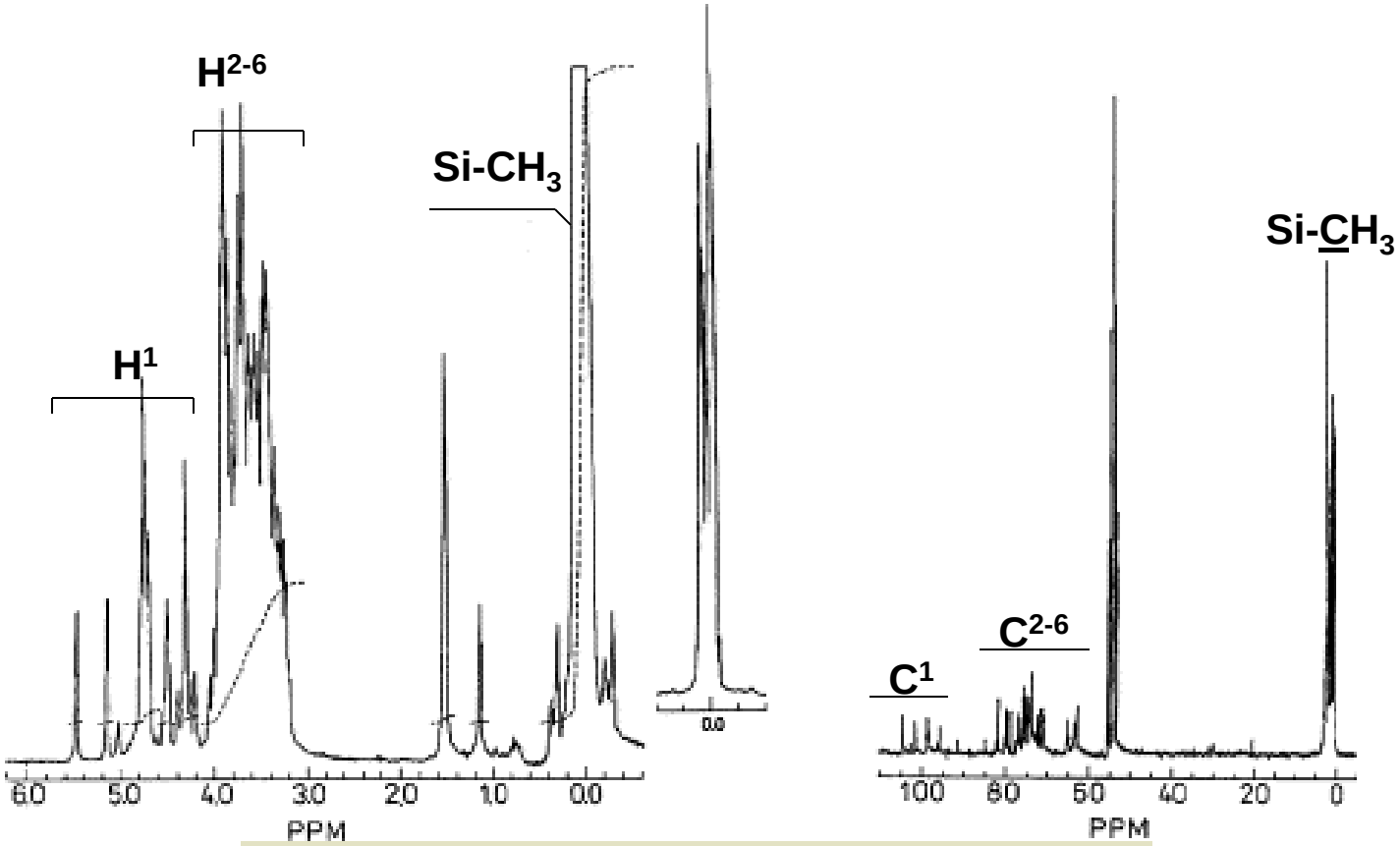
Preparation



Room temperature
DMF/chloroform solvent mixture
100 % yield

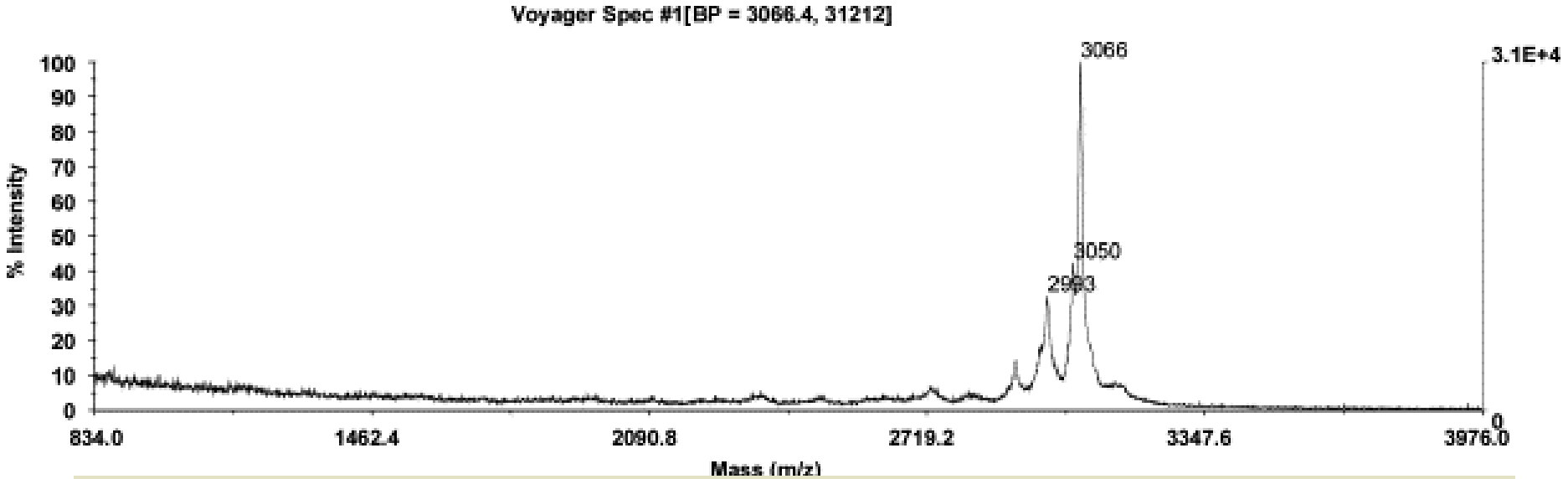
V. Harabagiu *et al., Carbohydrate Polymers* **56**, 301 (2004)

Structural characterisation



^{1}H- and ^{13}C-NMR spectra of α-CD-Si$_{3x6}$

MALDI-TOF mass spectrum of γ-CD-Si_{24}



obtained with 2-nitrophenyloctyl ether as matrix (5·10−3 M in THF) (reflected mode)

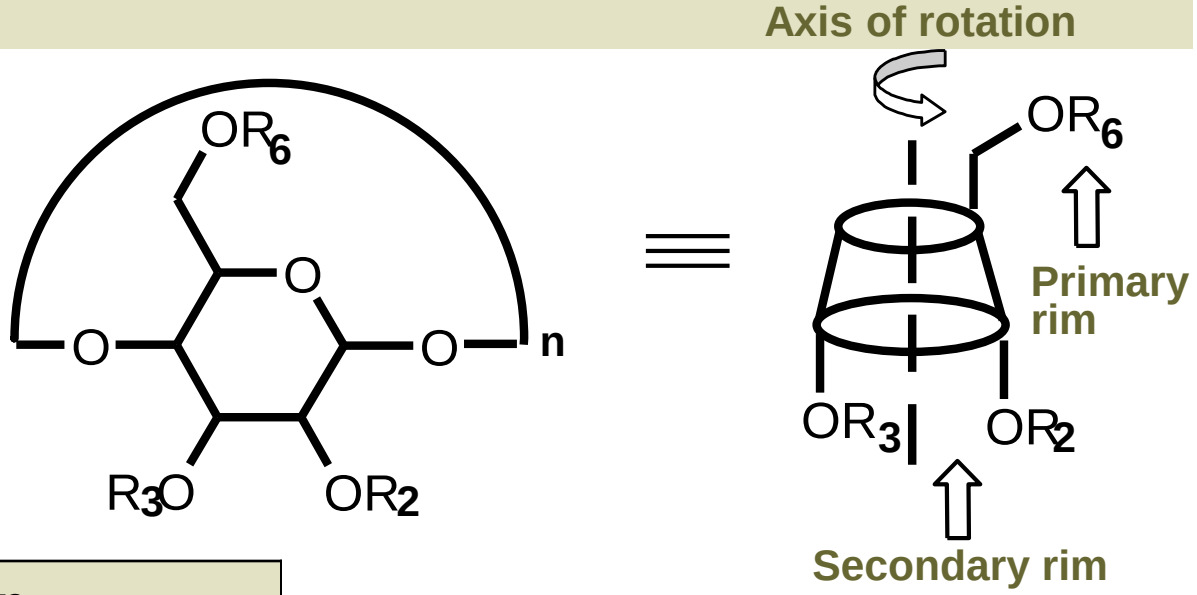
m/z = 3066: γ-CD-Si_{24} + K^+

m/z = 3050: γ-CD-Si_{24} + Na^+

m/z = 2993: γ-CD-Si_{24} – $Si(CH_3)_3$ + K^+

LB films

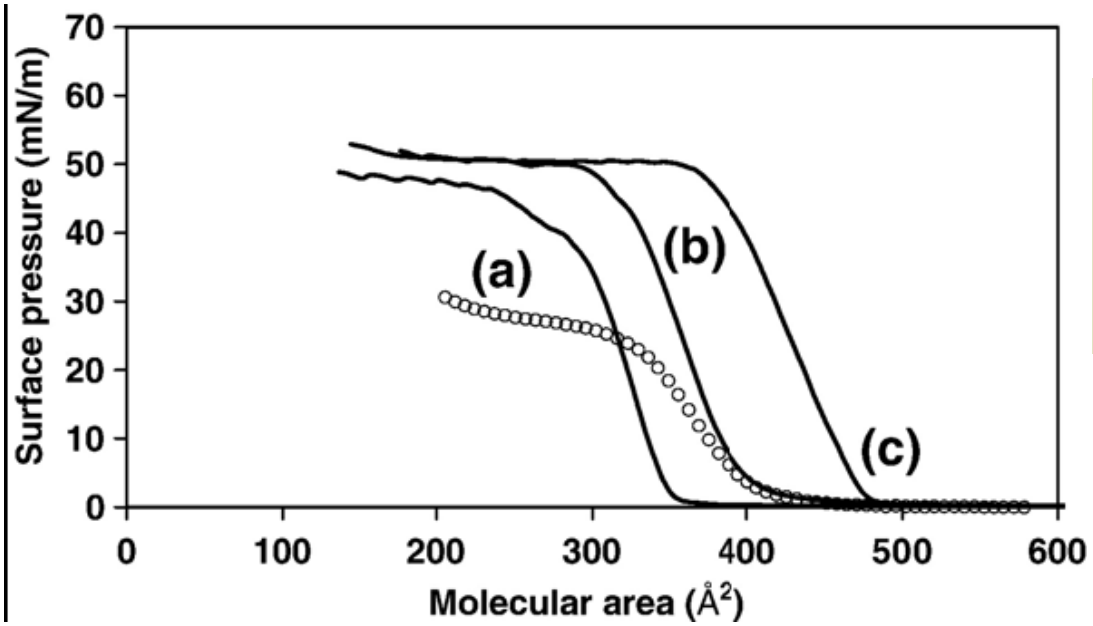
Structure of modified cyclodextrins



n	Modification
6	$R_2=R_3=R_6=Si(CH_3)_3$
7	$R_2=R_3=R_6=Si(CH_3)_3$
8	$R_2=R_3=R_6=Si(CH_3)_3$
7	$R_2=R_3=Si(CH_3)_3$; $R_6=SH$

O. Fichet *et al.*, *Thin Solid Films* (2008)

Pressure surface isotherms

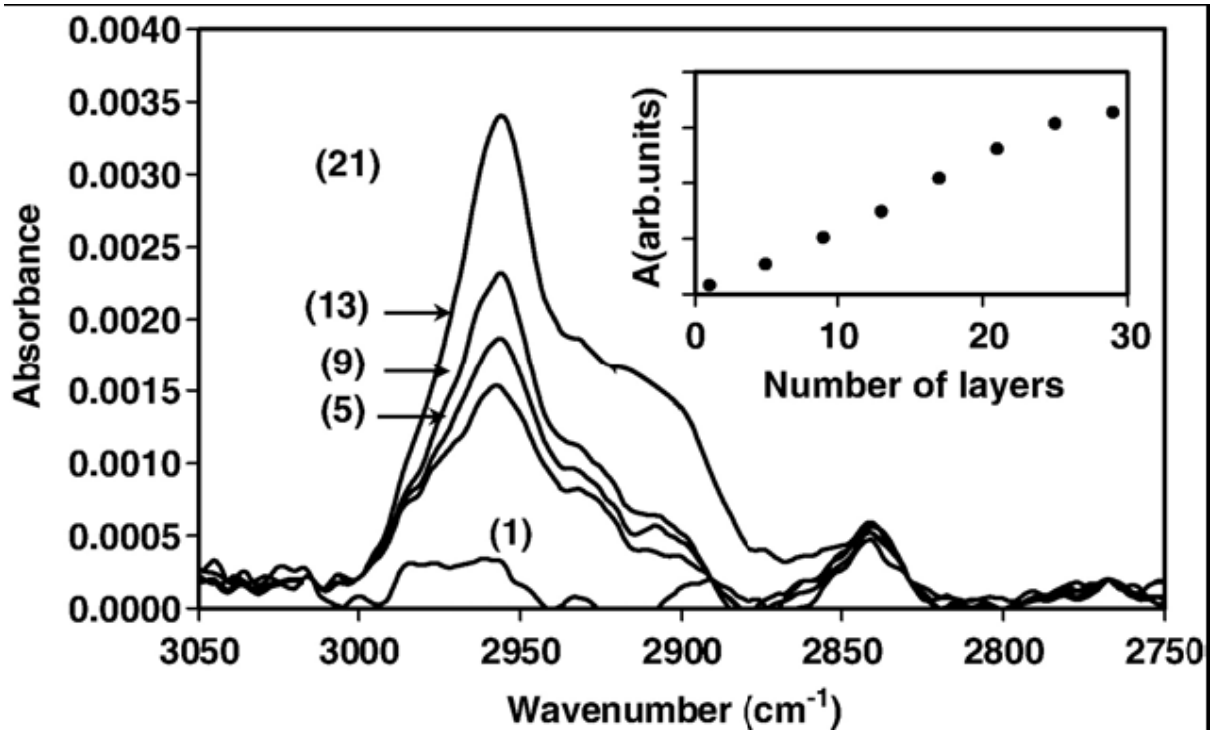


recorded on a water subphase temperature 20 °C; compression rate, 20 Å² molecule⁻¹ min⁻¹

(a) αCD-Si3x6	(b) βCD-Si3x7	(c) γCD-Si3x8	(○) βCD-7S-14Si
A_0 346	400	470	412
A_{COLL} 208	295	356	330

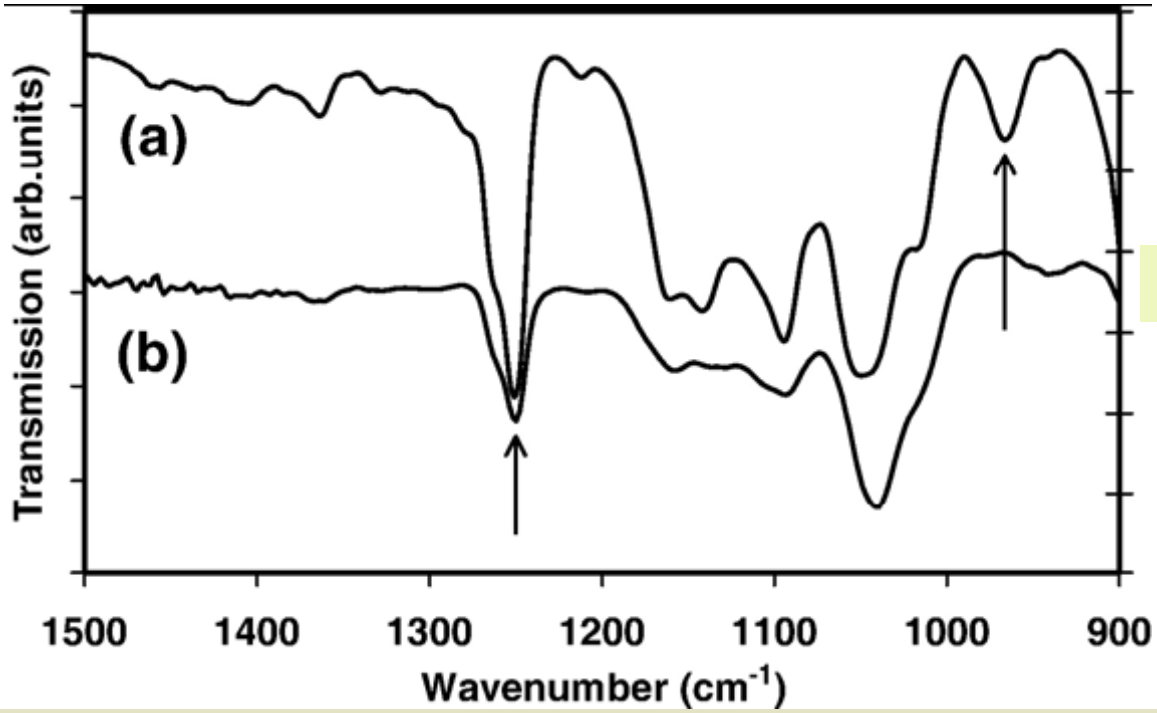
	A_0	A_{COLL}	π_{COLL}
pC8-βCD	455	428	12
6SiMe$_2$tBu-βCD	380	278	47

Multilayered LB films – chemical structure



FTIR spectra films in the range 3100–2750 cm^{-1} of 1 to 21 layered LB films
Inserted picture: 2956 cm^{-1} absorbance of pTMS-βCD-Si_{3x7}
measured as a function of the number of LB layers

LB films – chemical structure



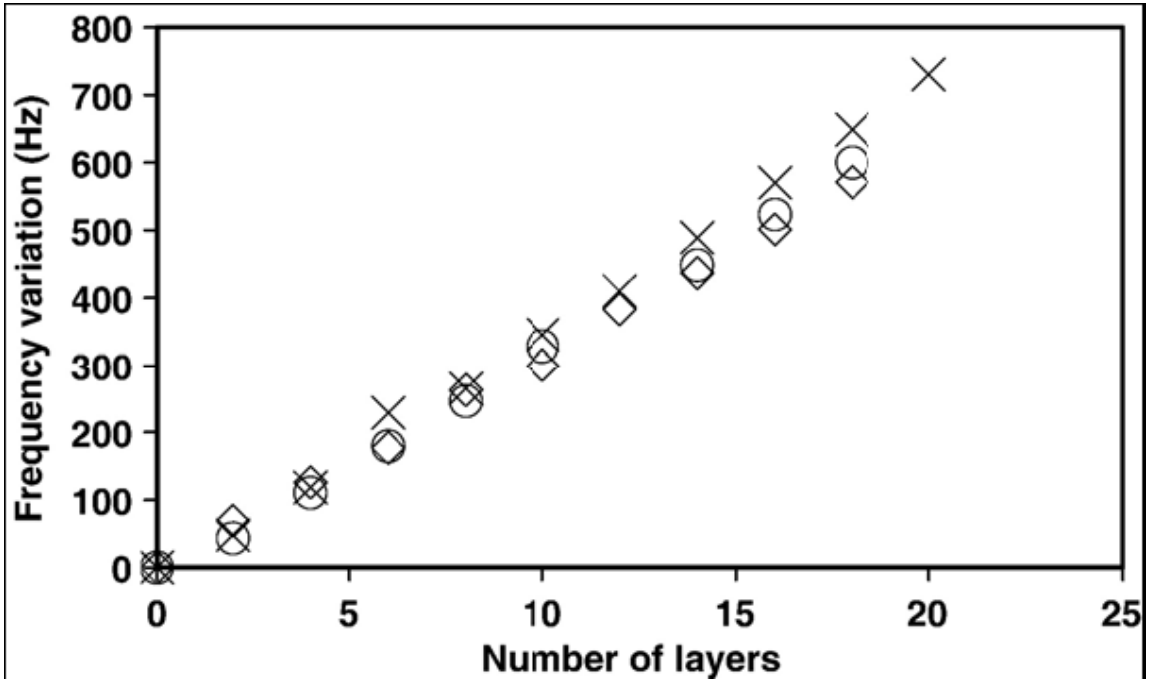
HYDROLYSIS

$CD\text{-}nSi(CH_3)_3$

$- m(CH_3)_3SiOH$ $+ H_2O$

$CD\text{-}(n\text{-}m)Si(CH_3)_3(OH)_m$

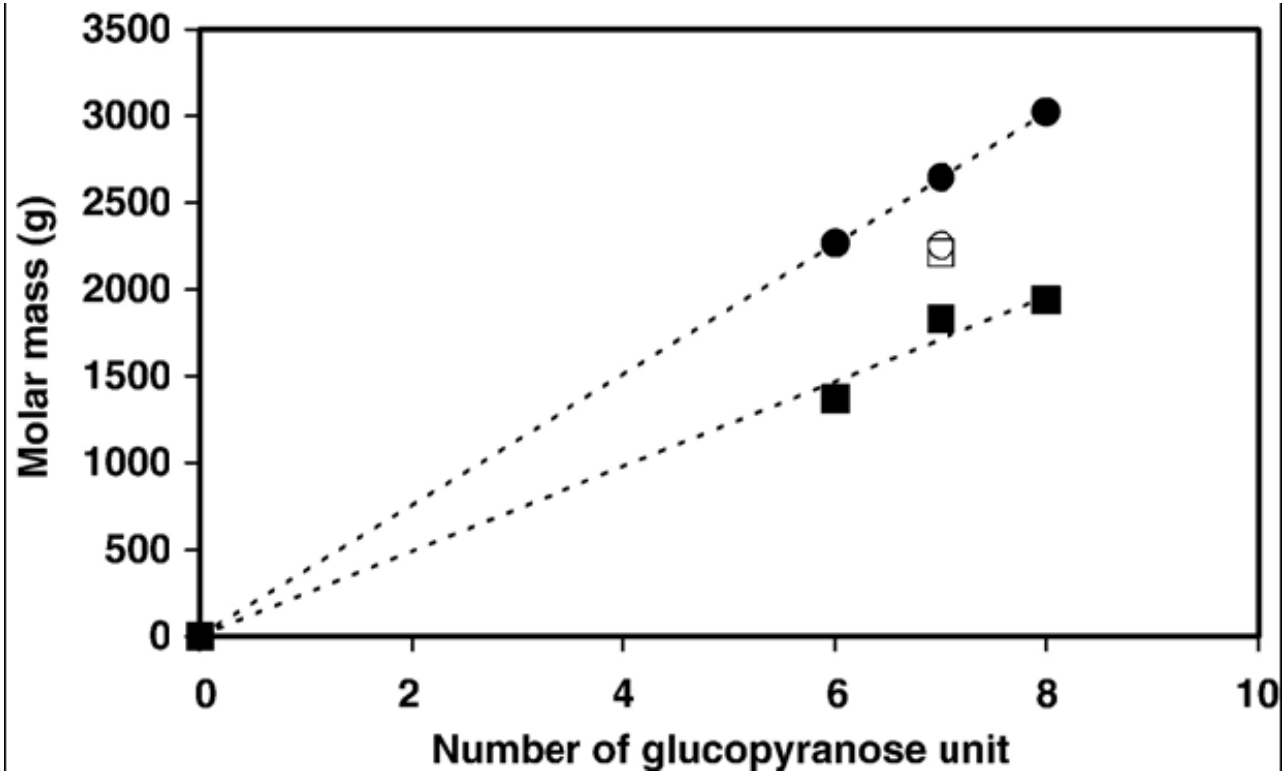
Infrared spectra (10 scans) of
(a) βCD-Si_{3x7} powder *(KBr pellet—resolution: 1 cm^{-1})*
(b) 21 layers of pTMS-βCD LB film *(CaF2—resolution: 4 cm^{-1})*



(◊) αCD-Si_{3x6}
(×) βCD-Si_{3x7}
(○) γCD-Si_{3x8}

Frequency change of the quartz crystal microbalance as a function of the number of deposited layers at 30 $mN.m^{-1}$

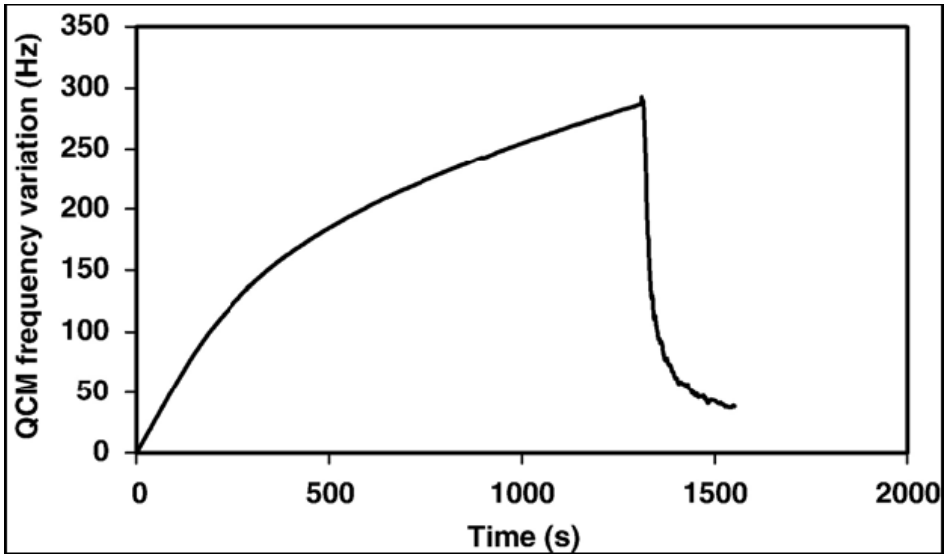
Molar masses versus D-glucopyranose unit number



(•) theoretical and
(▪) measured values
of the different
CD-Si_{3xn}
(○) theoretical and
(□) measured values
of βCD-6S-14Si

APPLICATION of modified CDs LB films

Arrays for non polar gas sensors

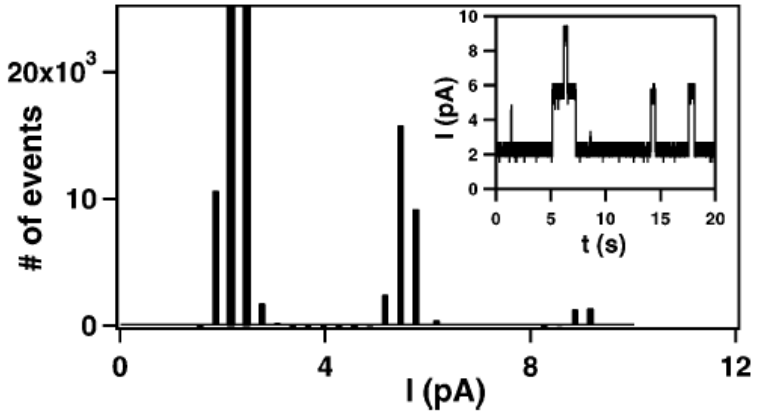


Benzene vapors up-take

* *LB films (20 layers) of βCD-Si3x7 exposed to benzene vapours*
* *at t = 1200 s, LB films were removed in air*

O. Fichet *et al., Thin Solid Films* (2008)

CD-7S-14Si ionic channels in lipid membranes



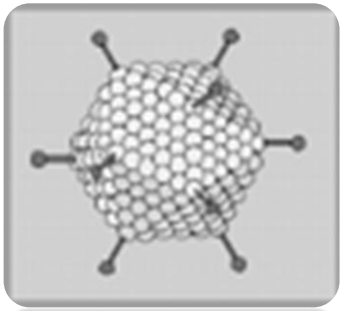
Asolectin + CD-7S-14Si
ΔV = 150 mV

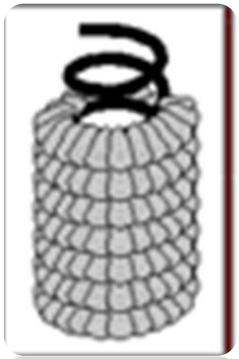
L. Bacri *et al., Langmuir* **21**, 5842 (2005)

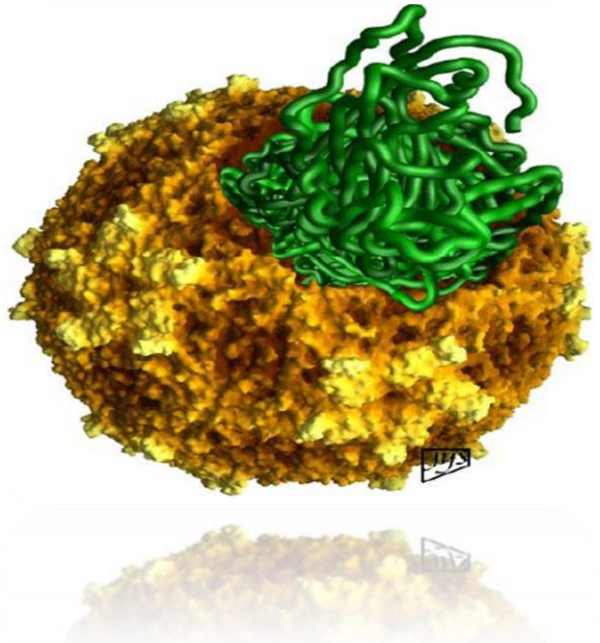
WHAT NATURE KNOWS TO DO ?

Virusii

- bio-nano-coloizi
- prezinta, in general, doua forme:
  - icosaedrica
  - helicoidala

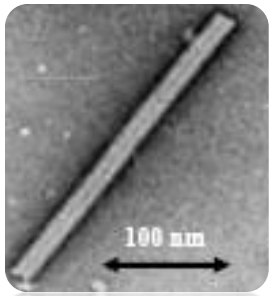


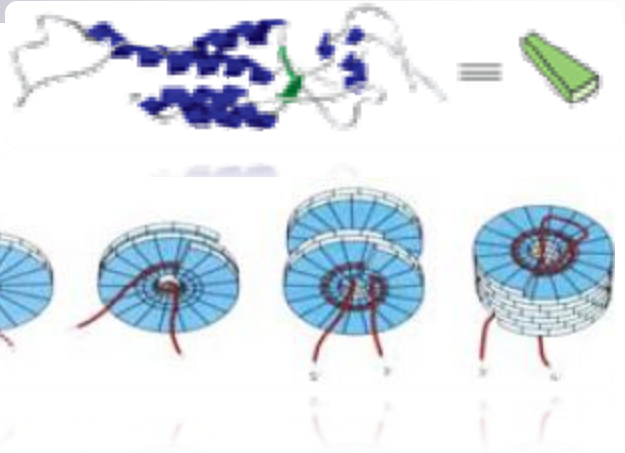




Scheletul unui burete de mare

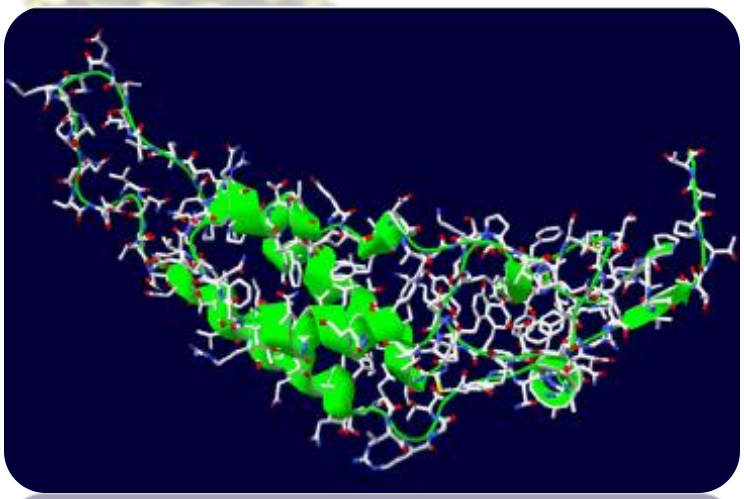
Virusul mozaicul tutunului (TMV)

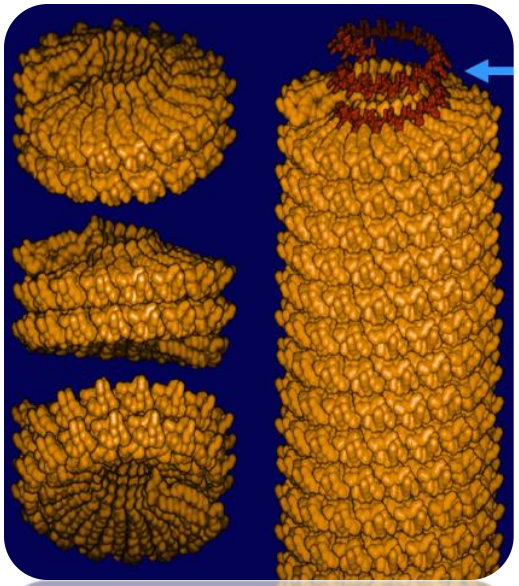




2,130 unitati, Mw 40,000,000

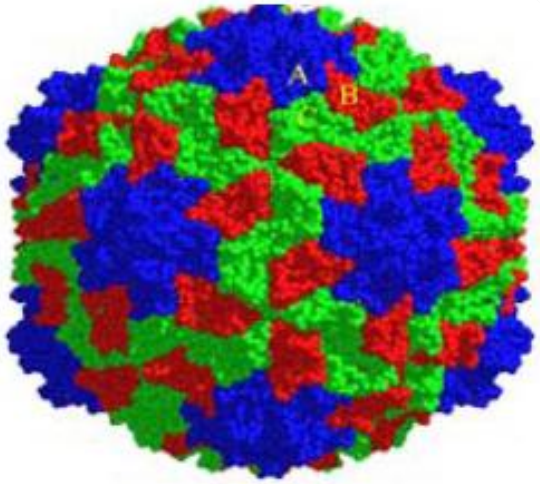
A. Klug, *Angew. Chem. Int. Ed. Engl.* 1983, *22*, 565



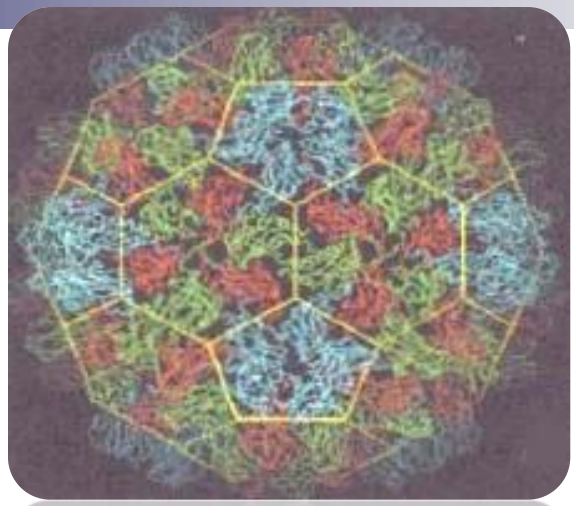


ARN

Lungime ~ 300 nm
Intindere ~ 18 nm
Agregate liotrope de tipul baghetelor

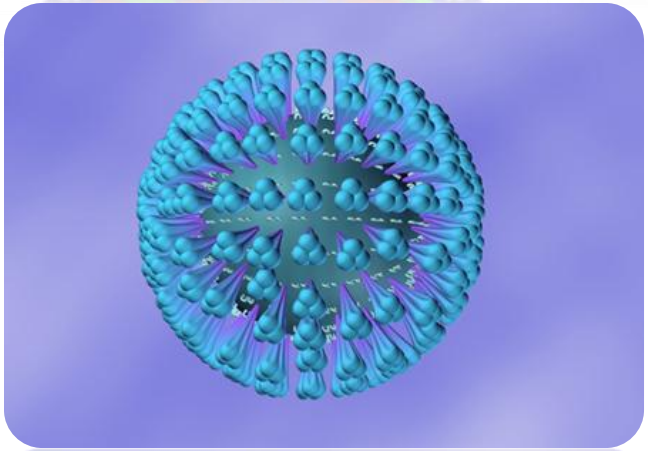


Rice Yellow Mottle Virus



Stuctura icosaedrica
180 subunitati identice (20kD)
Diametru 30 nm
Cavitate interna 18 nm

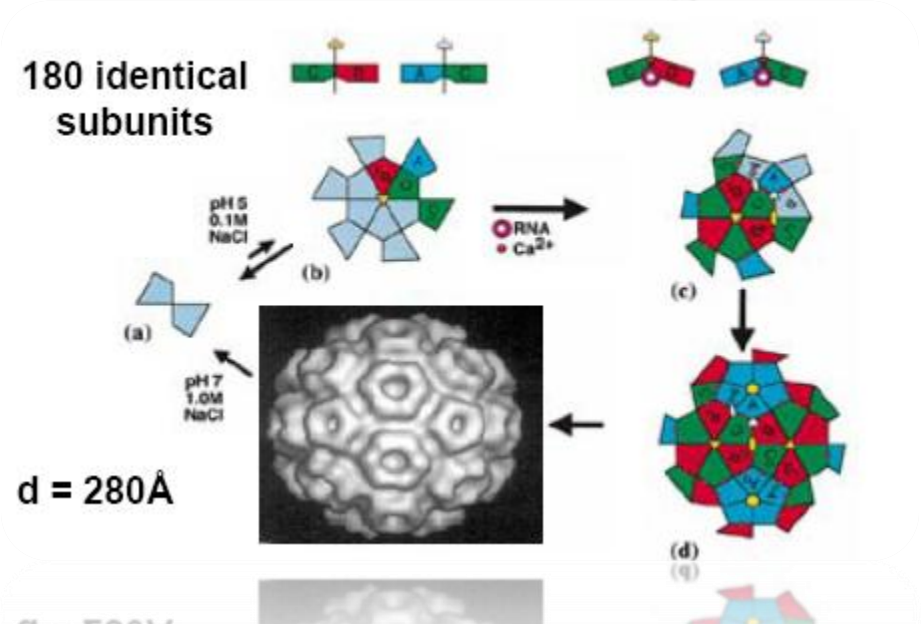
Cowpea Chlorotic Mottle Virus (CCMV)



Virus SARS (sindrom respirator sever acut)

Redrawn from Johnson and Speir, J. Mol. Biol. 269, 665.

Platforma de asamblare pentru CCMV



? ? ? ! ! !

evolution from divided to condensed and to organized, living and thinking matter

increase in complexity through self-organization

- ***Ontogenetic questions:*** how the matter became complex (thinking organisms) starting from elementary particles?
- ***Epigenetic questions:*** what other complex matter does exists or is to be created?

ABIOTIC SYNTHESIS OF ORGANIC COMPOUNDS

"cold theory"

SYNTHESE ABIOTIQUE DES PORPHIRINES: C.I. Simionescu *et al.*, 1977

BIOGENESE: C.I. Simionescu *et al.*, 1978

simple inorganic compounds = primordial reducing atmosphere

H_2 CH_4 ?
CO NH_3 ?
CO_2
H_2O

?

highly energetic chemistry

organic compounds

adsorption on the frozen surface of primary ocean
(prevention of the destructive action of high energy sources)

- ***with O_2***:
  no amino acids
  no life possible
- ***no O_2***:
  no ozone
  no life possible

slow thaw of frozen ocean
formation of "primordial soup"

organic compounds
inorganic salts

diverse and more complex compounds

?

- ***dilution***: Hull, *Nature*, 1960
- ***incompatibility***: amino acids and sugars destroy each other

lifeless coarcevates

COMPLEX ORGANIZED MATTER – evolution to life

other mysteries

Building proteins and nucleic acids
other necessary components of life: lipids, carbohydrates etc.

↕ ?

- ***some components are not available in appropriate state***
  ex.: phosphoric acid required for DNA reacts with Ca^{2+} - insoluble salt
- ***polymerisation***
  through what mechanism the amino acids were transformed into proteins?
- ***sequences***
  F. Hoyle (astronomer): *"the probability of life evolving anywhere in the universe is likely a tornado sweeping through a junkyard and assembling a Boeing 747"*
- ***optical isomers***
  how the optical isomers were produced?

Building biological systems from biological components

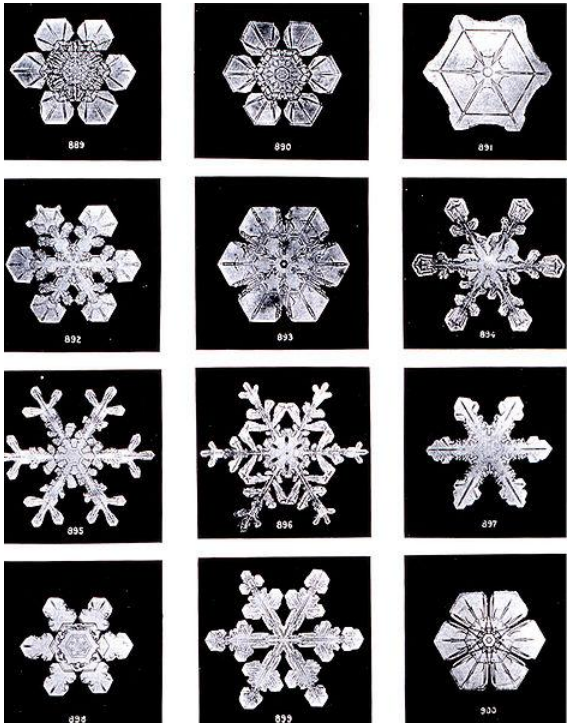
↕ ?

- ***mechanism of the controlled building of the systems (how a biological system could arise) ?***

WATER

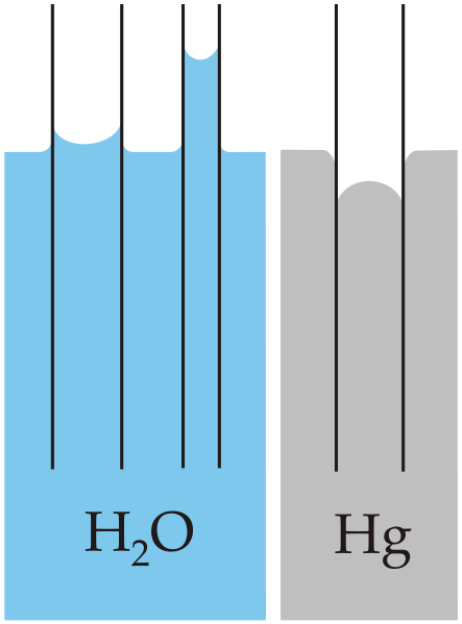
PROPERTIES

- ***self-assembling (crystallization)***
- ***dipolar molecule***
- ***hydrogen bonding***



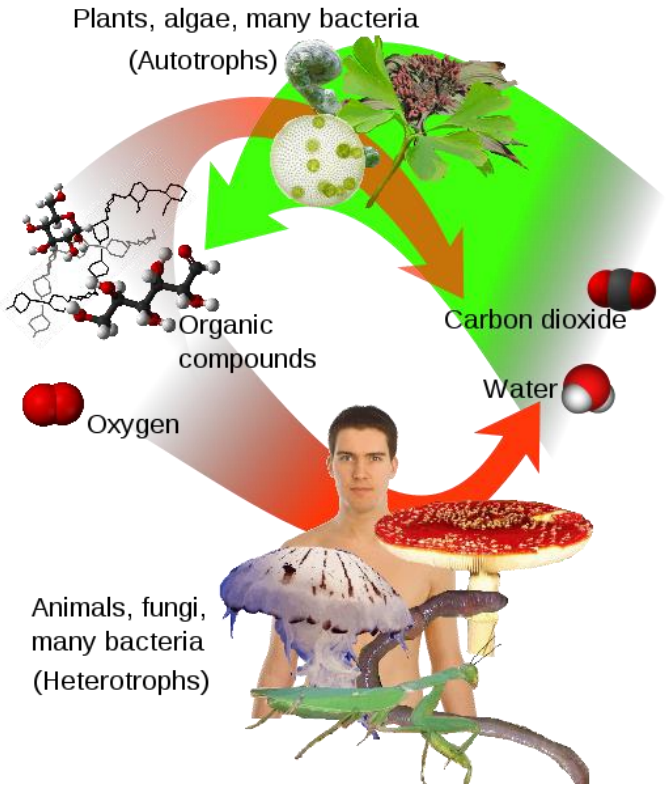
snowflakes

- ***capillary action***



WATER AND LIFE

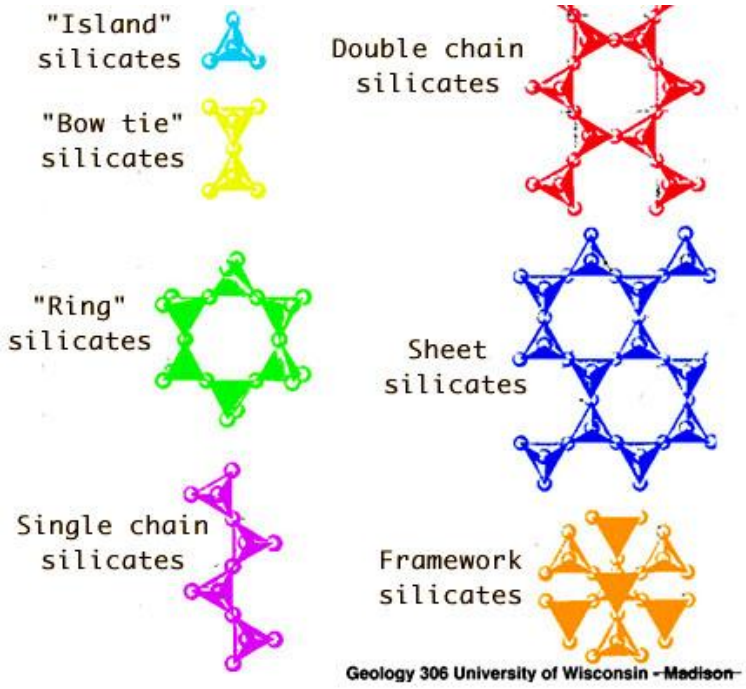
- ***solvent for vital organic and inorganic compounds***
- ***metabolism component***
- ***photosynthesis and respiration***



SILICATES $(Si\text{-}O)_m\ (O^{-}Metal^{+})_n$

PROPERTIES

- large diversity
- crystallized or amorphous

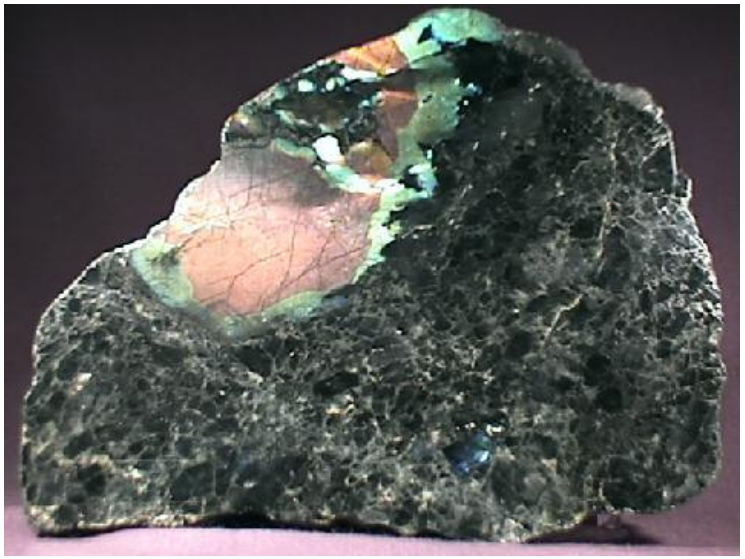


SILICATES AND LIFE IN THE PRIMARY AGE OF EARTH

- were they one of the promoters in the synthesis of organic molecules?

- did they represent the template for the structuring (ordering) of organic molecules?

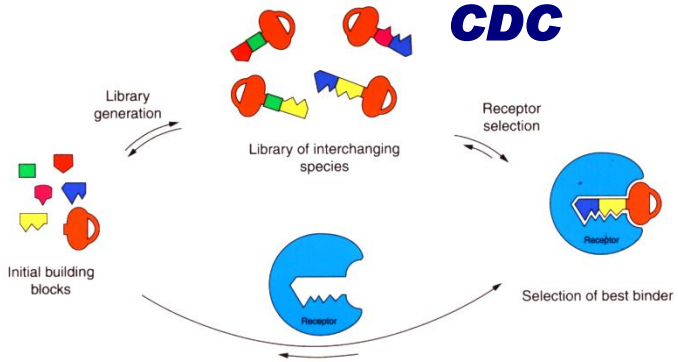
N. Oita, CICATROL, '80



WHERE CHEMISTS ARE?

combinatorial dynamic chemistry (CDC)

CDC



→ **adaptive and evolutive chemistry**

SUPRAMOLECULAR CHEMISTRY – SCOPE AND PERSPECTIVES
MOLECULES – SUPERMOLECULES – MOLECULAR DEVICES
Nobel lecture, December 8, 1987

JEAN-MARIE LEHN
Institut Le Bel, Université Louis Pasteur, Strasbourg
and Collège de France, Paris

Conclusions

Chemists are able to investigate the past, to create the present and to provide links to the future

There is still a long way for human intelligence to mach NATURE abilities