Galo Soler Illia

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CONICET - CNEA – Buenos Aires - ARGENTINA

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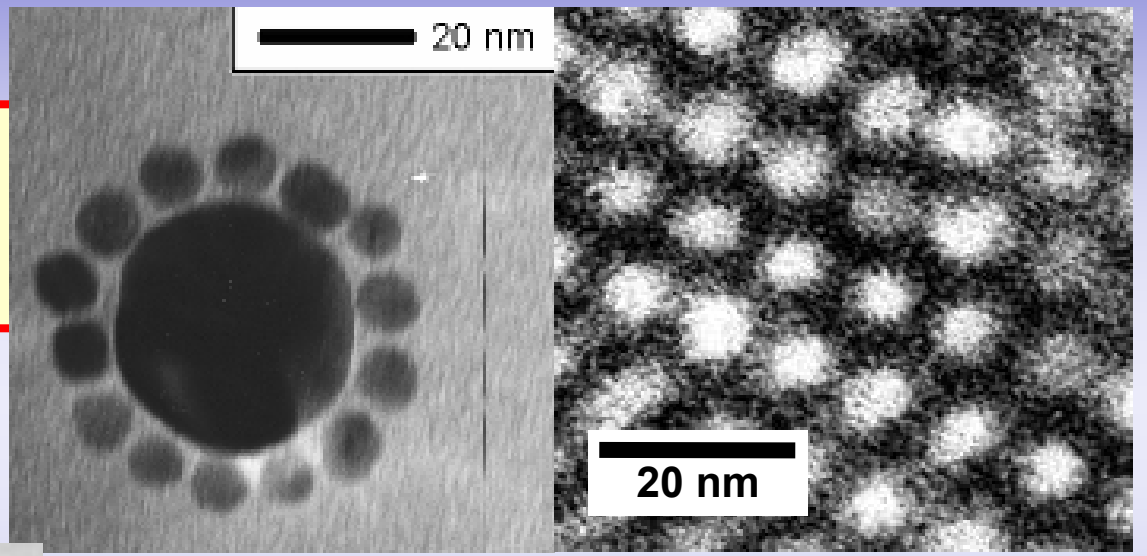
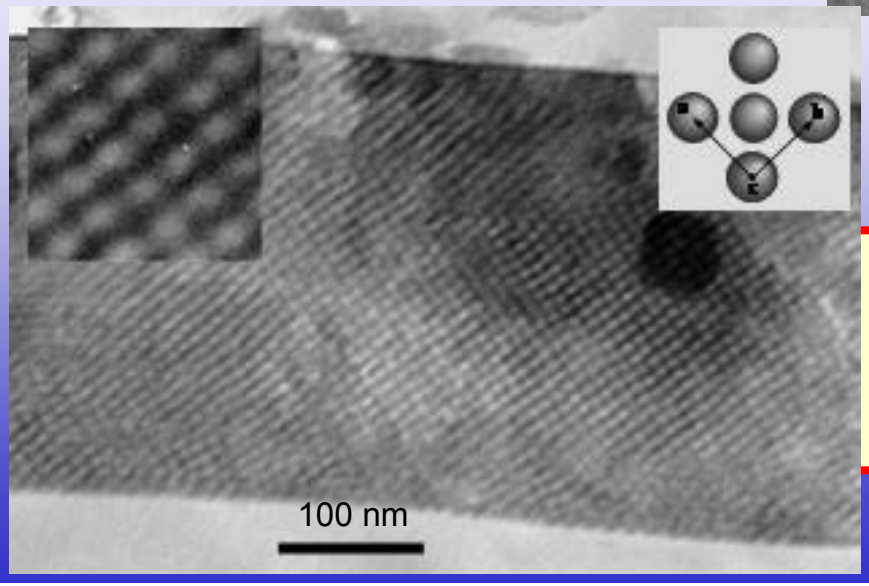
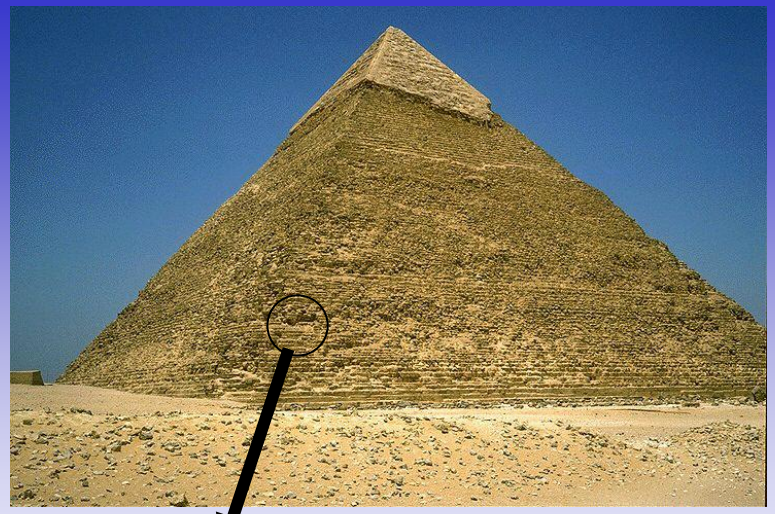
Chemical synthesis of organized matter

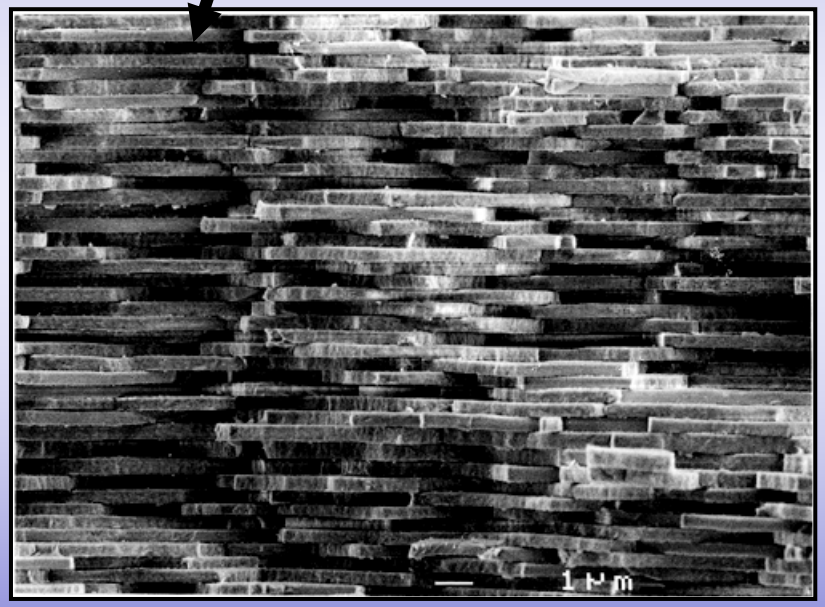




Mesoporous Thin Films

Building multifunctional nanocavity arrays





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I - Chemical synthesis of organized matter

Outline

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- A construction toolbox for NanoBuilding Blocks (NBB)
- NBB organized in Mesoscopic Scale
- Templating techniques
- Mesoporous materials
- Integrative synthesis towards multiscale and multifunction

Chemical Synthesis of Complex Materials

"From serendipity to design"

Towards complex materials

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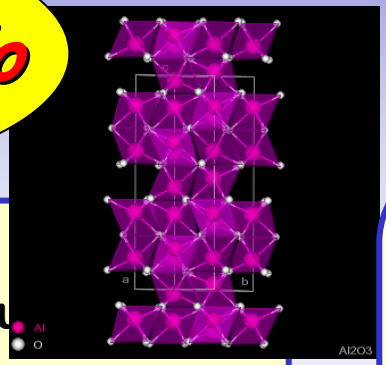
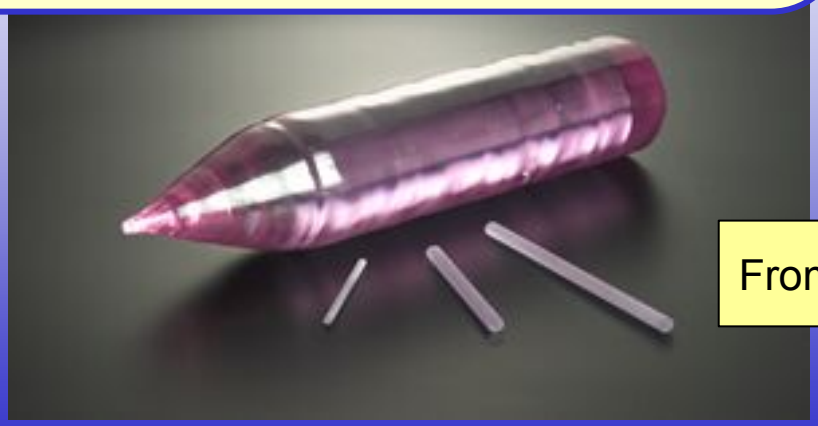
What we can do



- "Simple" Materials
- Controlled Crystal Structu
- Mostly monofunctional
- Composition-determined properties

- Bulk properties are determinant



What we should be able to do

- Multiscale patterned Materials
- Controlled structure, ***texture***, ***position***
- Multifunctional
- Composition AND synergy-defined properties
- Interface betw
  determinant

From ***SIMPLE*** to ***COMPLEX***

Biomaterials are a source of inspiration

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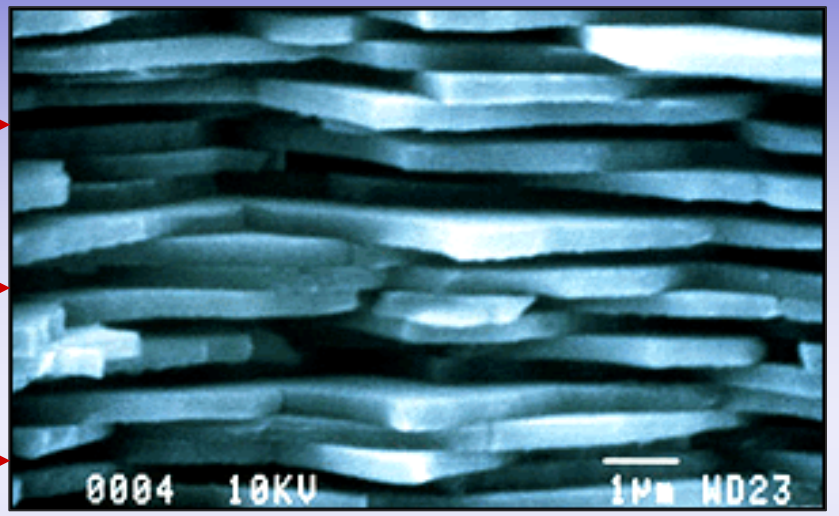
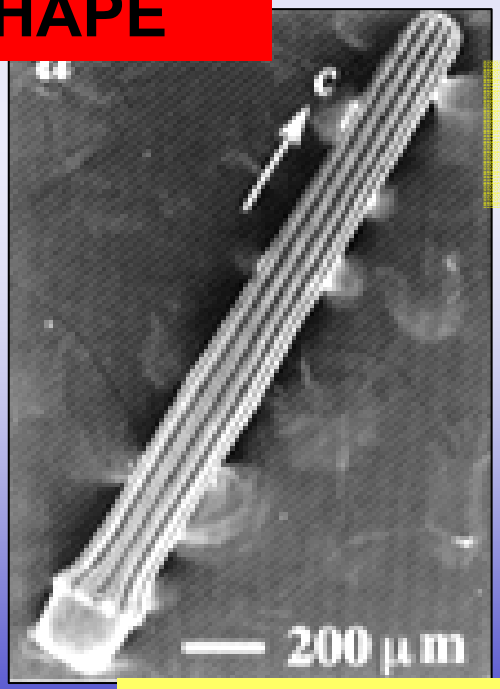
ARCHITECTURE

"bricks and mortar"
hybrid nanocomposites



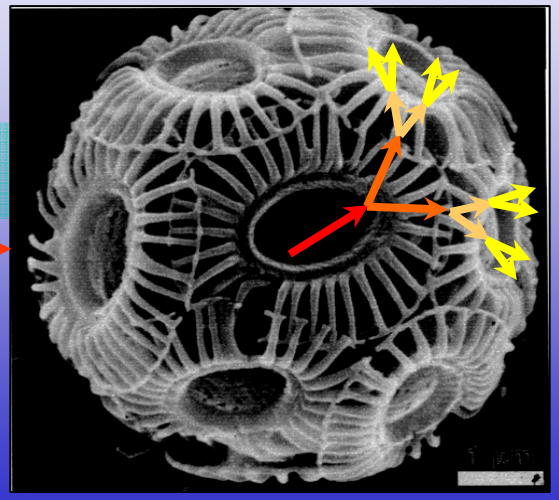
SHAPE



Order and Position in Space

ASSEMBLY

Hierarchy



structure ↔ function
compartmentalization

Example: Nacre

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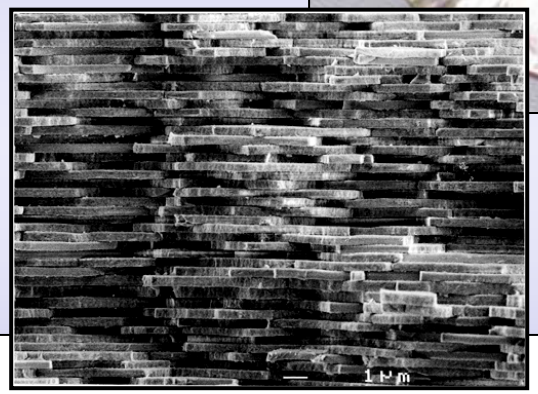
Inorganic phase = $CaCO_3$ platelets

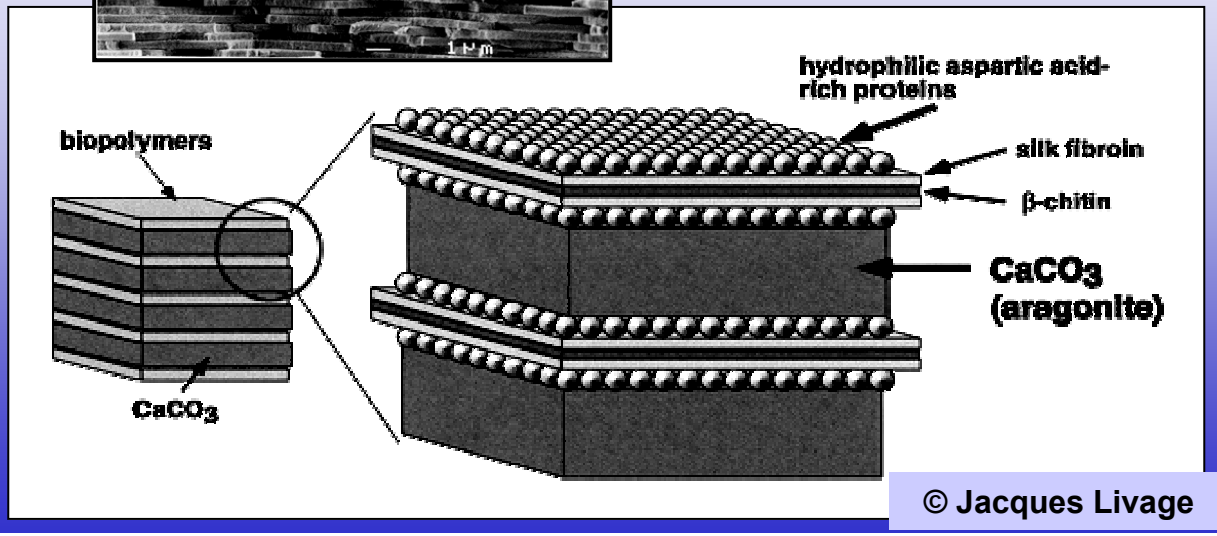
+ Organic layer ≈ 30 nm (protein layers)

Glue + positioning



Organization of BB in space

Composite structure
Improves mech properties (composite 3000 times harder than $CaCO_3$ single crystals!)
Bulletproof vests



The Build-and-Assemble Paradigm

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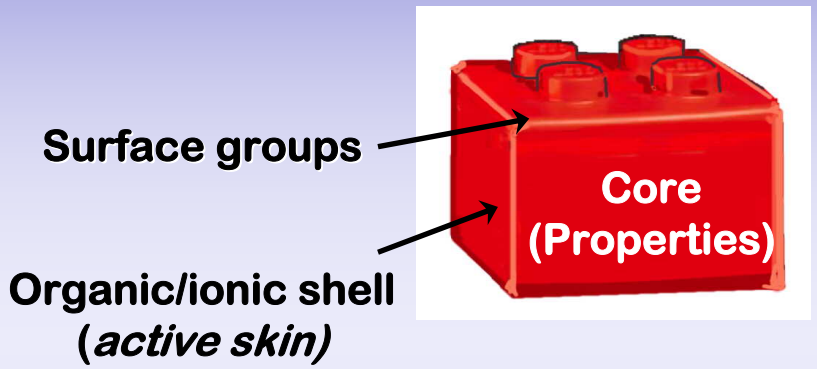
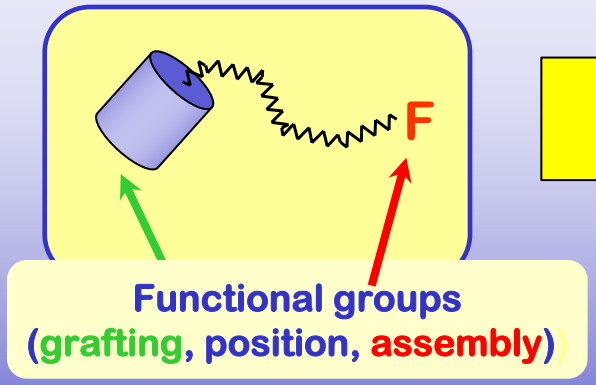
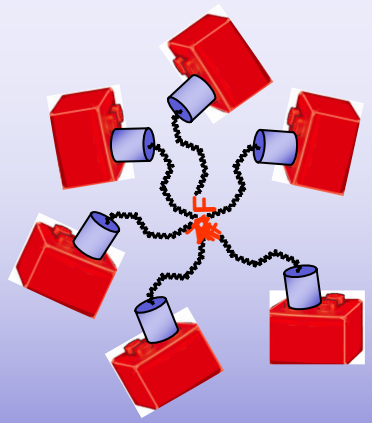
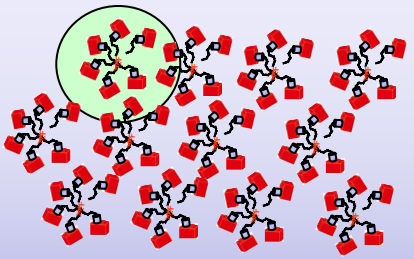
- **Primary Nanobuilding Blocks (NBB)**
- **Use complementary properties**
- **Assembly in space at various levels**









Building Blocks

Assembled Object

Array

The Nanosized Realm

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Finely Divided Matter

1-100 nm

Enhanced Properties

(Size)

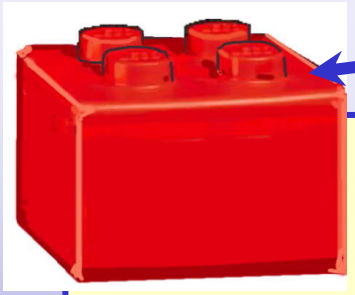
- ***Surface***
- ***Electronic***
- Optical
- Magnetic

Control of

- Morphology
- Structure
- Size

Core (properties)

Organic/ionic shell
(*protective skin*)



High Surface + Functional groups

Nanometric Brick

- Properties in the ***CORE***
- ***SHELL: Interactions***
  Protection + Functions

Conserve Properties of Inorganic + ORDER in SPACE

We need to invent…

- …methods to build "solid" nanometric building blocks ***(inorganic NBB)*** with targeted properties in an easy and reproducible way

- …methods to develop intelligent molecules (***organic NBB***) able to ***order*** the inorganic NBB ***in space***

- …ways to ***integrate*** both kinds of components in a complex material, with new properties derived from the ***SYNERGY*** of the inorganic and organic **NBB**

A Chemist's view: «bottom-up» construction of inorganic NBB

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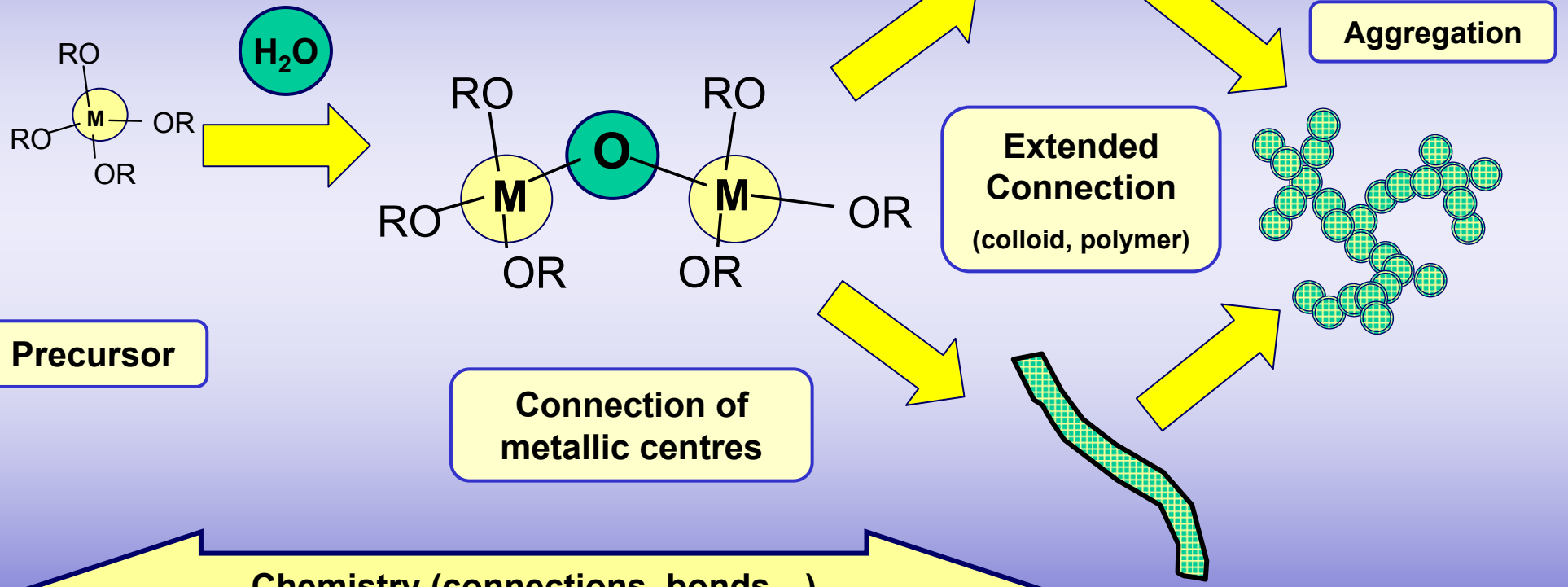

Chemistry (connections, bonds…)
CONNECTIVITY/ Building Blocks

Phys. Chem. (Interactions)
Morphology/ *OBJECT*

Sol-Gel : Controlled Formation of a *metal-oxo* network

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Low Temperature "soft process"

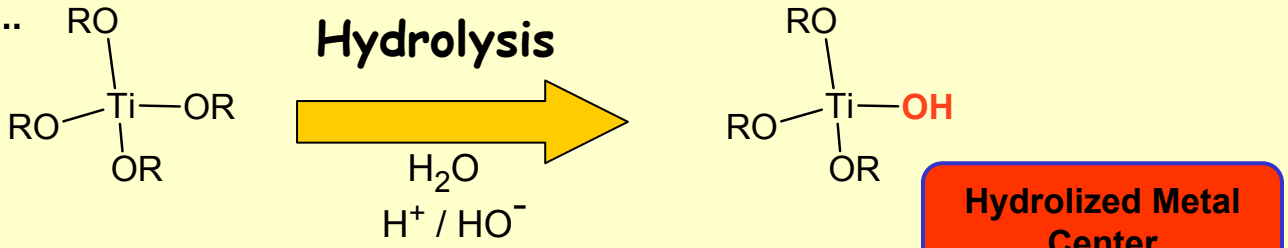
Water is a reagent (controlled amounts)

Inorganic Precursors

$M(X)_4$

M = Si, Ti, Sn,...

X = OR, Cl,...



C. J. Brinker, G.W. Scherer *Sol-Gel Science.* **1990,** Academic Press

Sol-Gel synthesis in a nutshell

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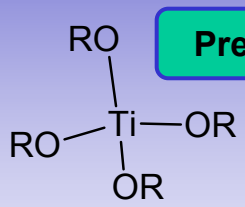
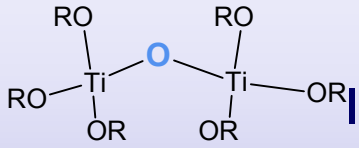


Precursor

Sol-gel Process

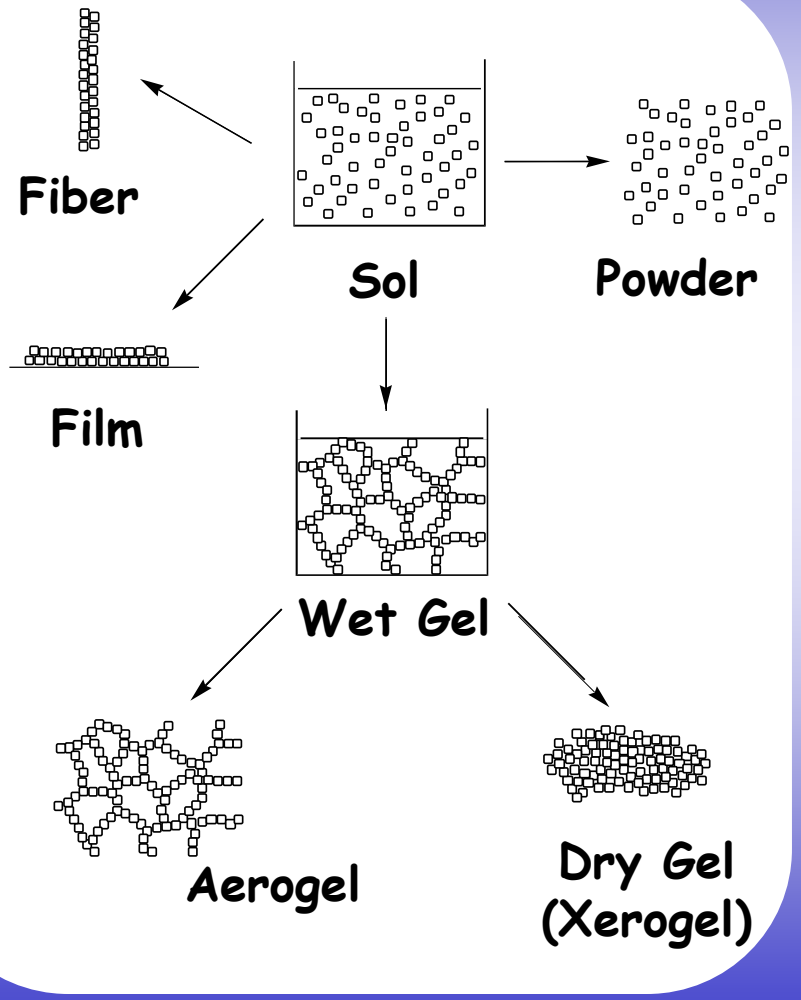
Hydrolysis

Condensation



Dimer…

Oligomers



Materials features controlled by solution chemistry

Low T, integration of organic or biological groups

Controlling polymer size, shape and philicity

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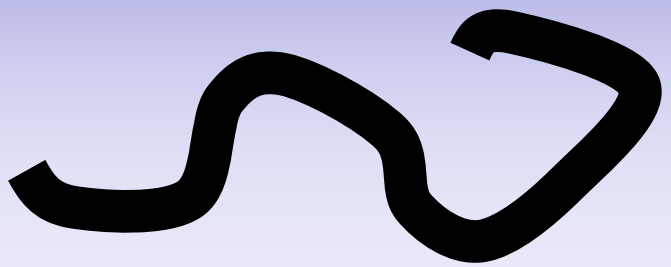
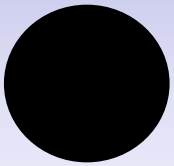
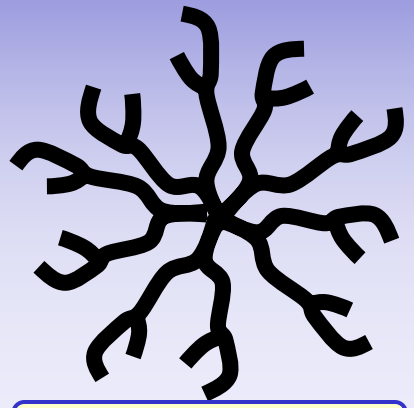


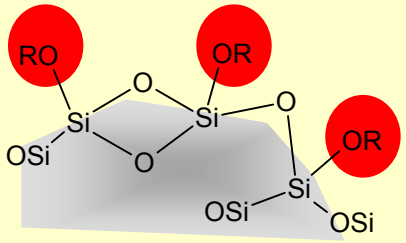
Linear polymers



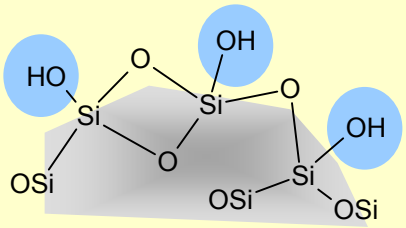
Amorphous or crystalline nanoparticles



fractal polymers

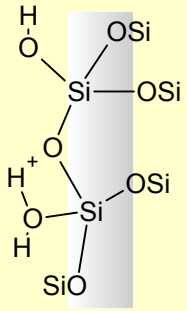


hydrophobic

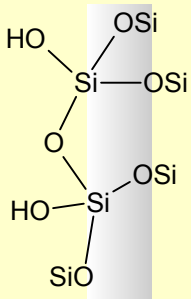


hydrophilic

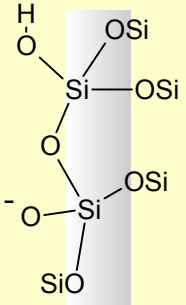
Controlling surface philicity (hydrolysis)



pH < iep



iep



pH > iep

Controlling surface charge (pH)

Hybrid Materials

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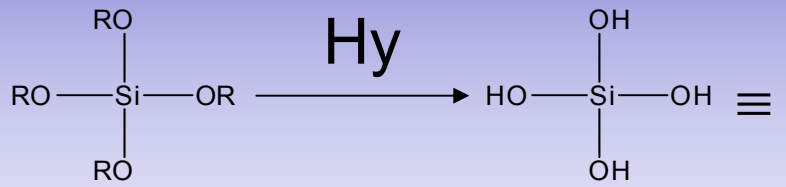
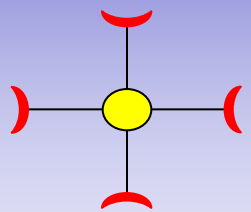
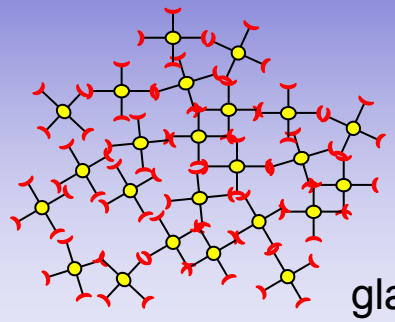


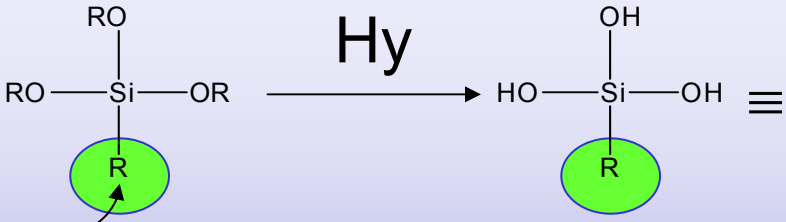


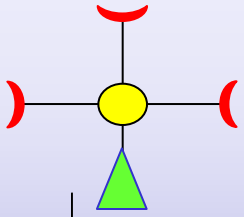
Cond



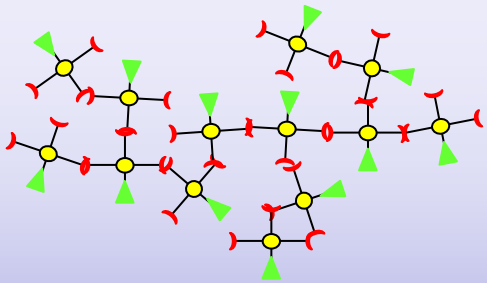
glass

Purely inorganic precursor
Inorganic M-oxo network





Cond

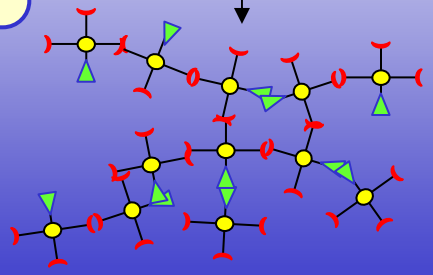


Function
Organic or biological residue

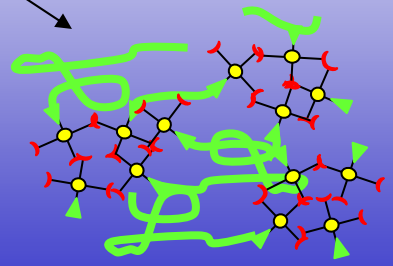
Polifunctional precursor

Hybrid Network

Polym



CoPo



Processing leads to applications: Nanoparticles, Gels, Thin Films…

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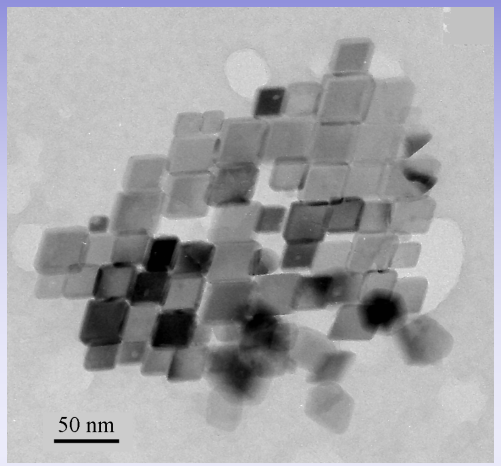
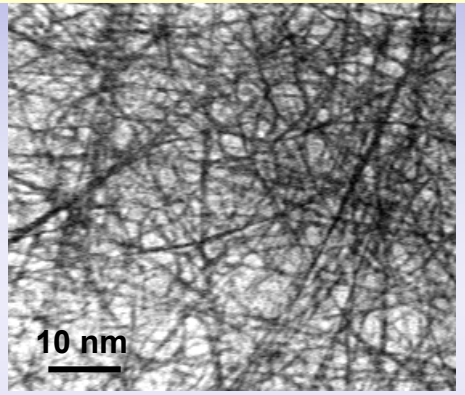


n-Hematite (Jolivet *et al.*)

Fibrous V_2O_5 gels (Livage)



Coatings (Minami - Schottner)

Hybrid Gels SiO_2/dye
(Chaput)

Prague Cathedral,
E. Bescher, UCLA

How to make a Nano-object (bonsai techniques…)

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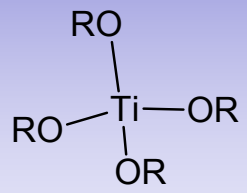
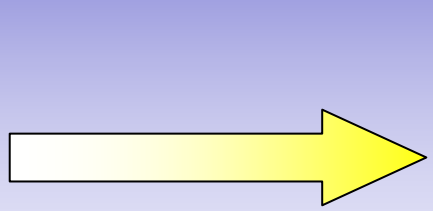
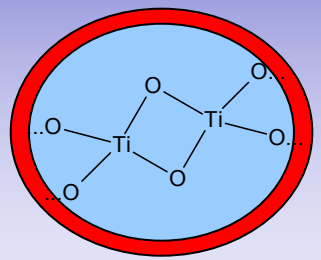
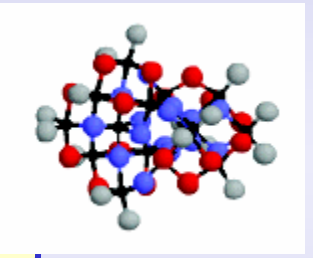


+ H_2O Conector + X-X Growth Controller



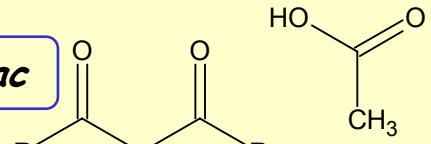


Cluster= molecule ~1 nm



$Ti_{16}O_{16}(OEt)_{32}$

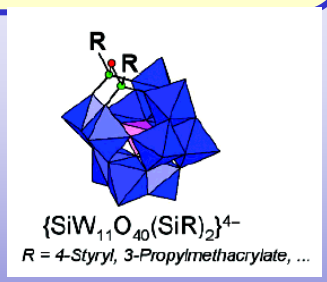
acac



AcOH

Control nucleation and growth

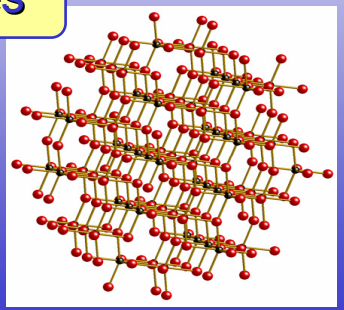
- Control Connections between M centers
- **Capping**: Protection + Functions



$\{SiW_{11}O_{40}(SiR)_2\}^{4-}$

R = 4-Styryl, 3-Propylmethacrylate, ...

Nanoparticles



MO_2, γ -Fe_2O_3, Fe_3O_4, CdS, metals
2-50 nm

G. Cao, *Nanostructures and Nanomaterials*
ICP, 2004
Works by Matijevic, Pileni, Bawendi, Alivisatos, Murray, Jolivet,…

Surface Functionalization

NBB with modified features

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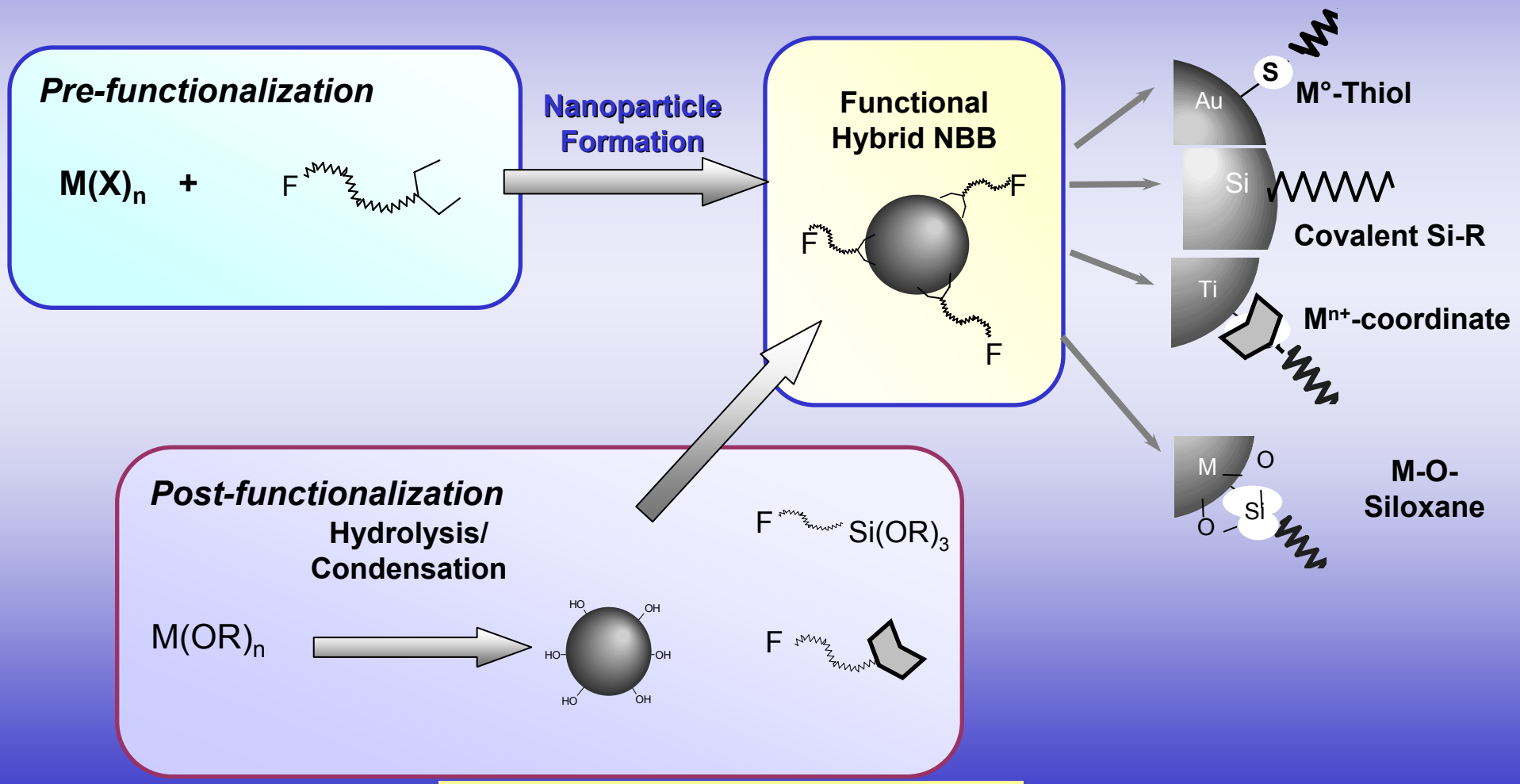
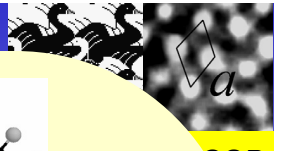


C. Sanchez et al., *Chem.Mater.* **2001,** *13*, 3061



R'-M-$(OR)_x$

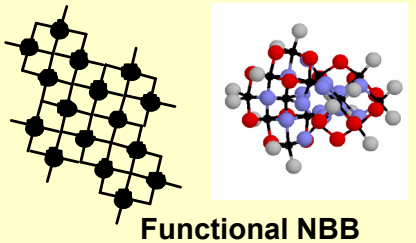
Organo-Functional Metal Alkoxide

+

$M(OR)_n$

Metal Alkoxide

Controlled H_2O



Functional NBB Metal-oxo clusters or Nanoparticles

Organic Modifiers

Templates
Connectors
Structure directing agents

H_2O

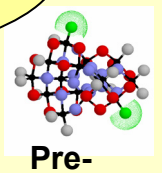
R' moiety may be reactive

Conventional SOL-GEL Route

SELF ASSEMBLY

Assembly of Nanobuilding Blocks (*ANBB*)

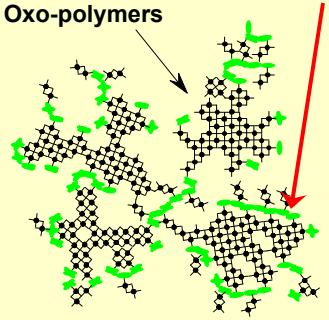
Organic Connectors

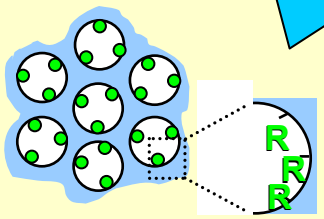


Pre-functionalised nanobricks

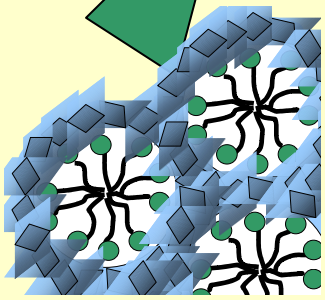
Organic components

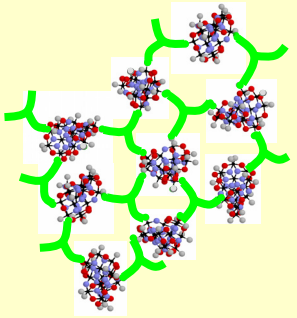
Oxo-polymers





Periodic Functional Porosity





Mesostructured NBB-based hybrids

Organised Nano-Matter: How?

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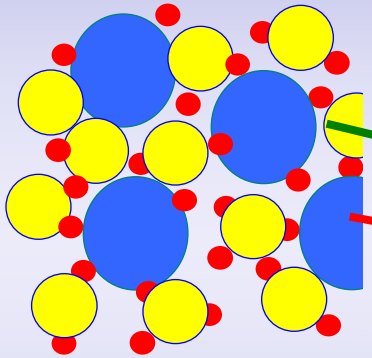
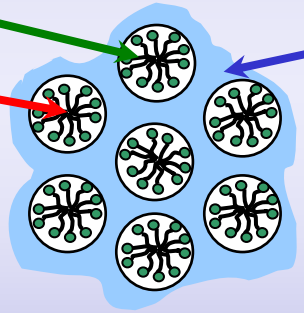
By Coupling *Sol-Gel* and *Self Assembly*

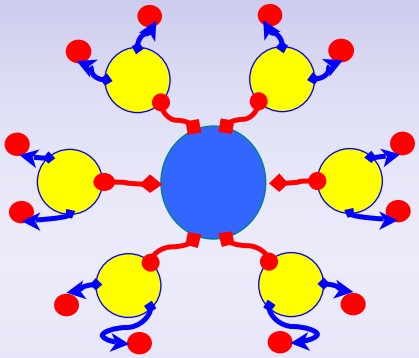
Non-covalent links
(Classical Self-Assembly)



A Combination of both



Covalent links



- ➢Colloidal Interactions
- ➢van der Waals and H-bonding
- ↑Spontaneous Organisation
- ↑Multiscale possibility
- ↓Lack of Directionality
- ↓Packing ⇒ Surface Loss

- ➢Covalent Connection
- ➢Complexation
- ↑Directionality
- ↑Simplicity
- ↑Specificity
- ↑Hierarchical Materials
- ↓Poisoning

Interactions between charged colloidal objects

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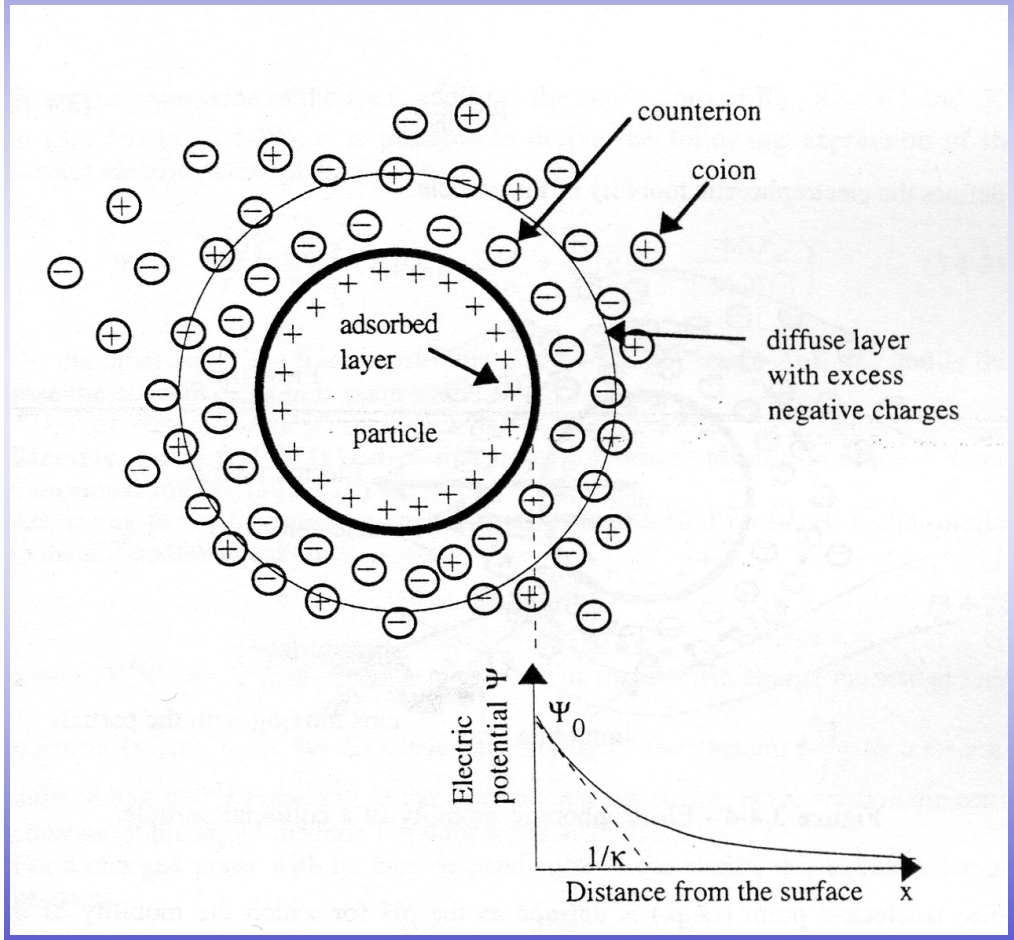

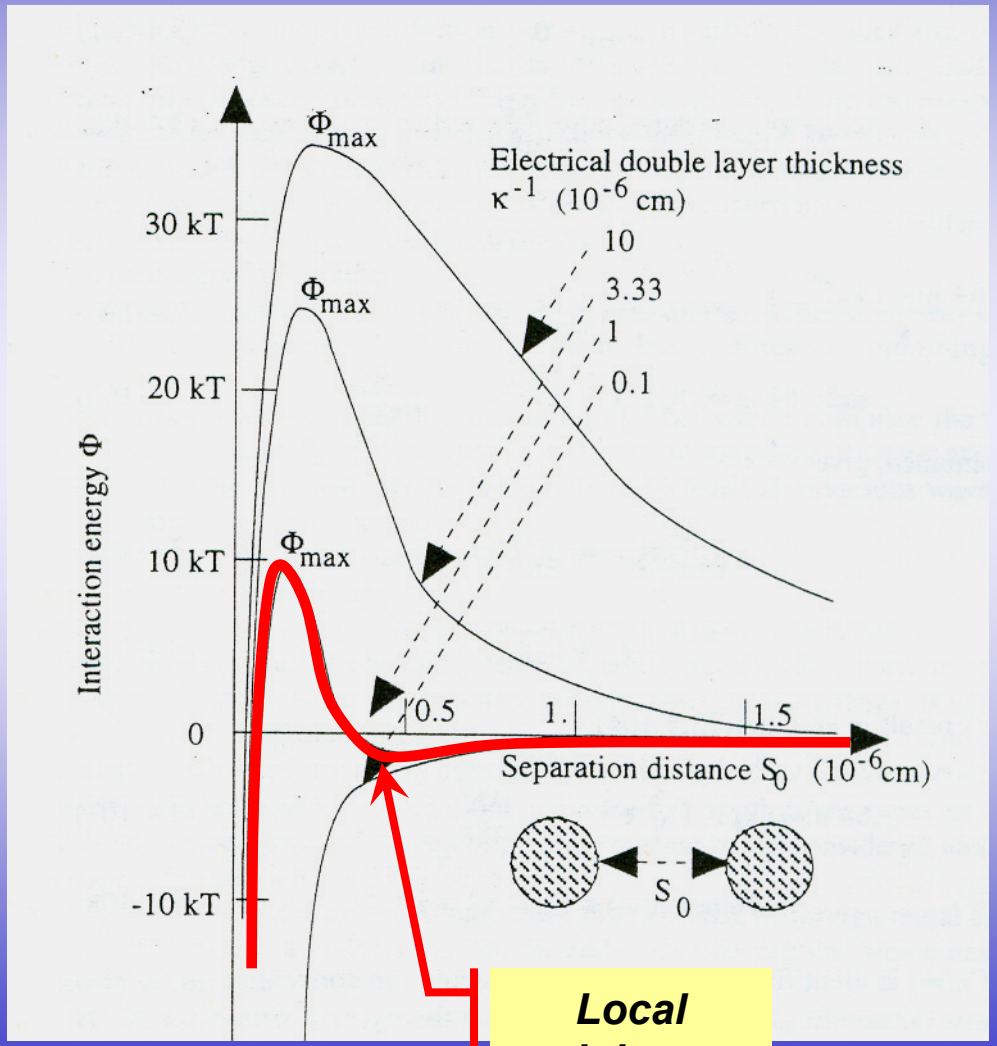

Using weak forces to Order
(C. Murray-IBM)

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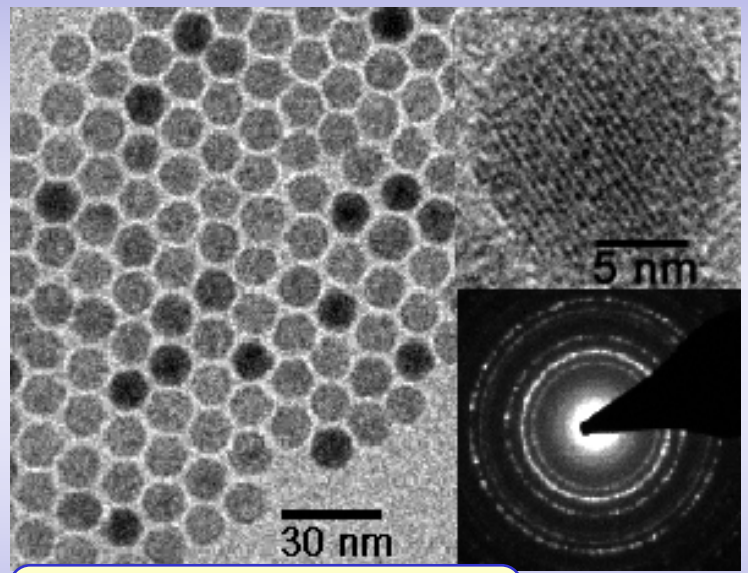
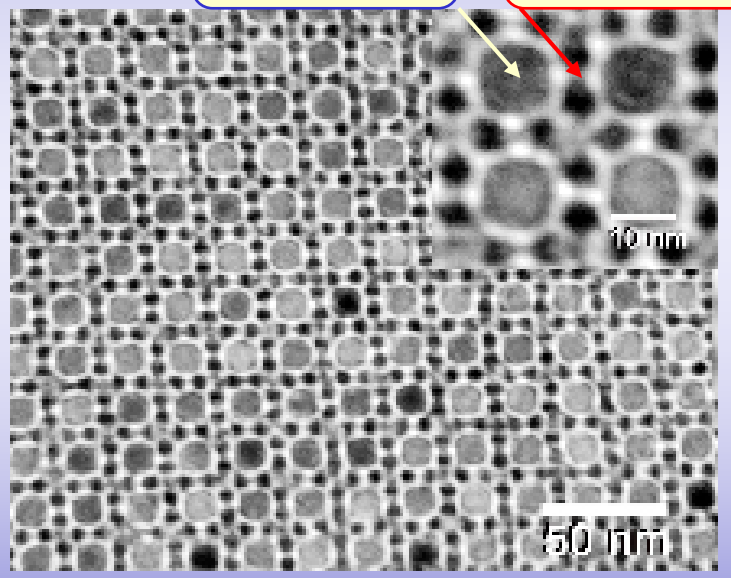


γ-Fe_2O_3
10 nm magnets !!!



Perfectly monodisperse nanoparticles
Colloidal Forces to order
INTEGRATION and SPACE DISTRIBUTION of NP
Robust arrangements ??

Organizing and Attaching functional NBB

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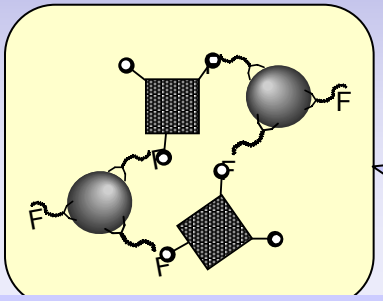
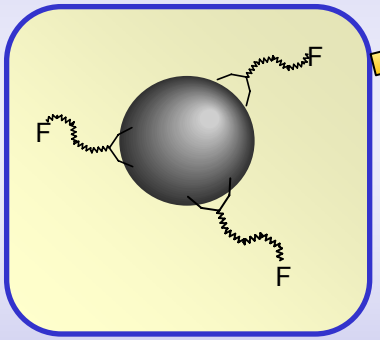
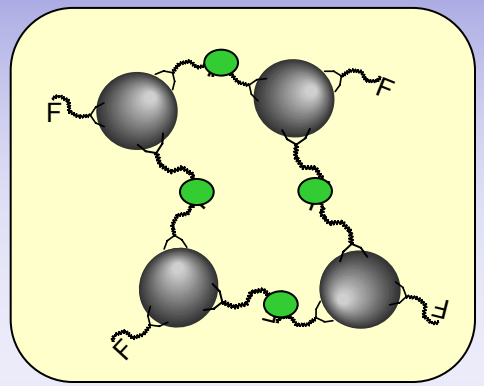


S. Mann *et al*. *Adv. Mater.* **2000**, *12*, 147.

Recognition

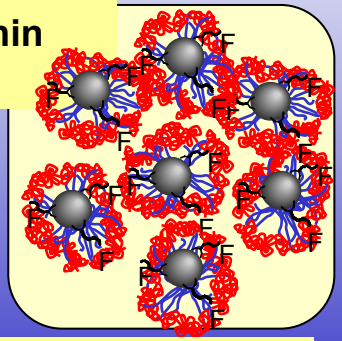
Polymerization





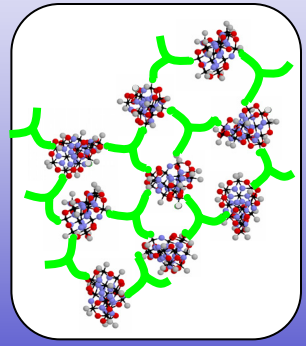
Trimmel et al. *Chem. Mater.* **2000**, *12*, 602.

Particles within micelles



S. Förster; M. Antonietti, *Adv. Mater.* **1999**

Organic Connectors



Soler-Illia et al., *Angew Chem. Int Ed*, **2000**

Ready-to-assemble NBB

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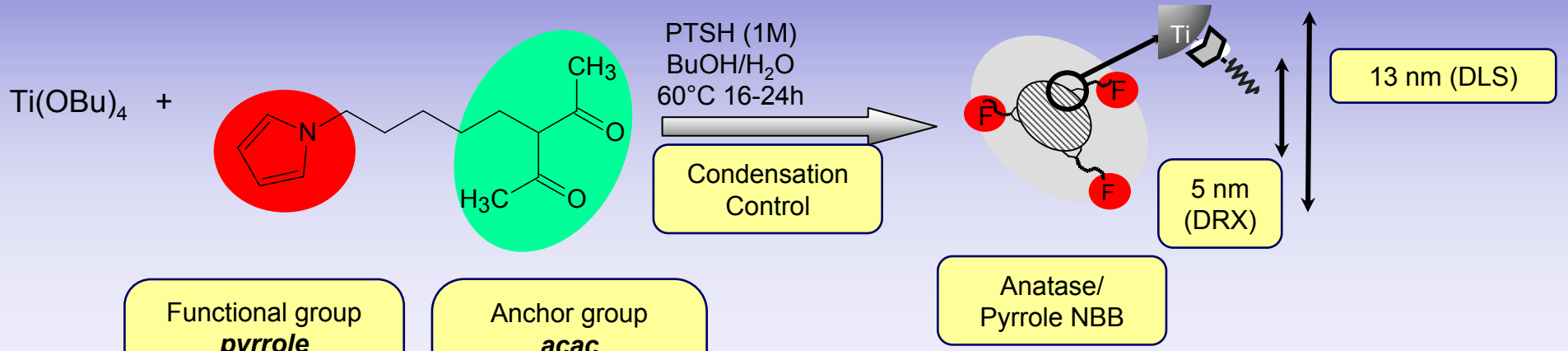
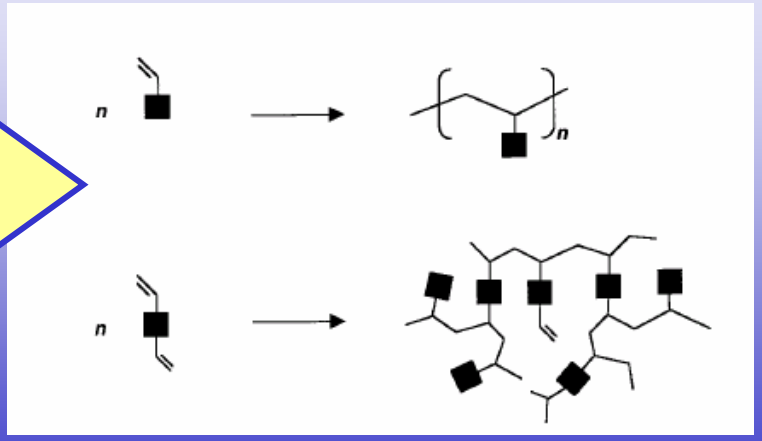
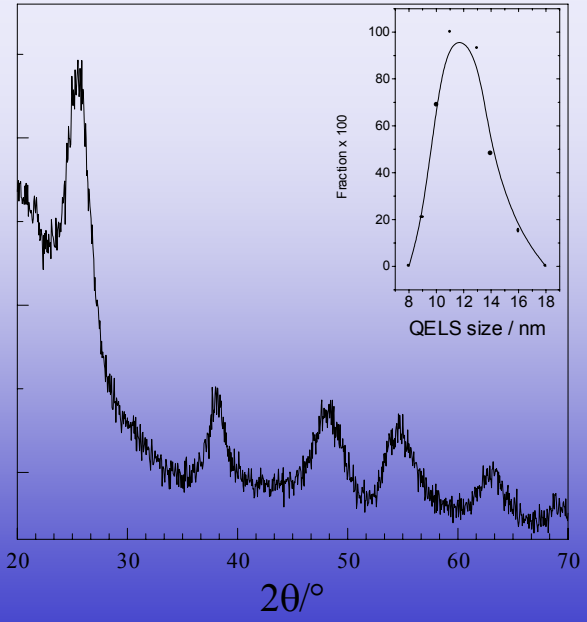


Functional group
pyrrole
•Polymerizable
•Conductor

Anchor group
acac
•Fixes function
•Controls condensation

Nanocrystalline Particles with polymerizable ends





Roux et al., *Adv. Mater.* **2003,** *13*, 3061

NM Semiconductor / Conductive Polymer Nanocomposites

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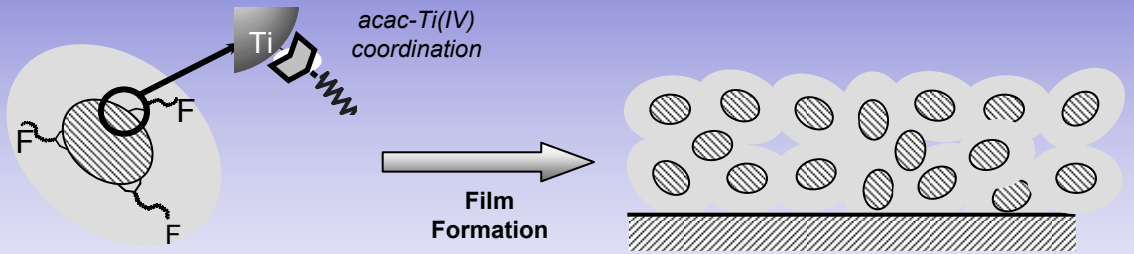
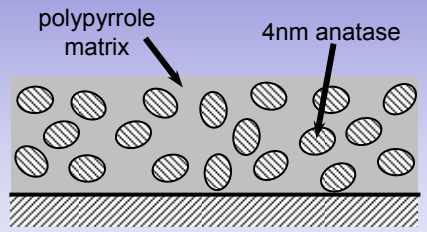
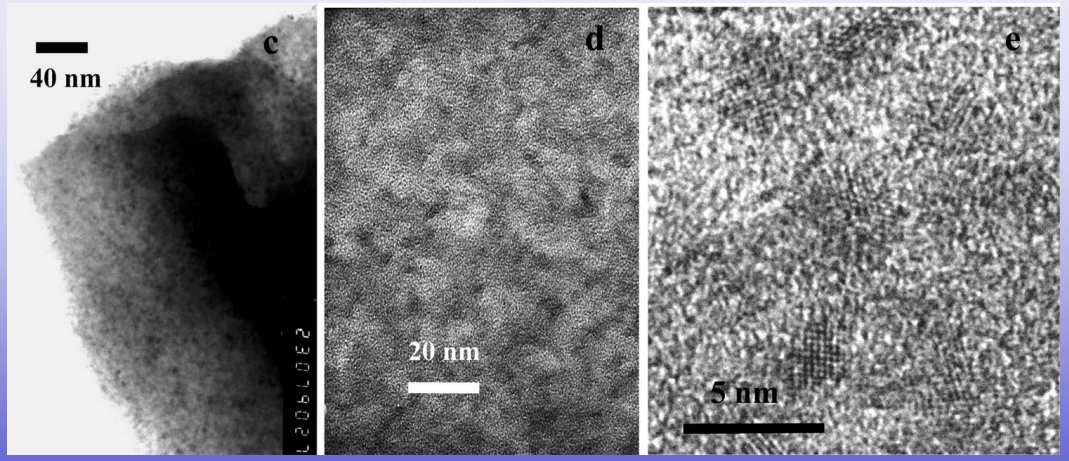


Anatase/
Pyrrole NBB

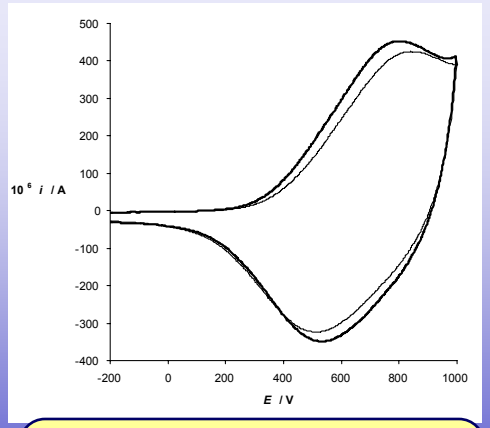
Chemical or
electrochemical
polymerization



Nanocomposite
Continuous Film



Roux et al., *Adv. Mater.* **2003,** *13*, 3061



Semiconductor photoactive NP embedded in a conducting polymer

Recognition between functional nano-Au (Mirkin)

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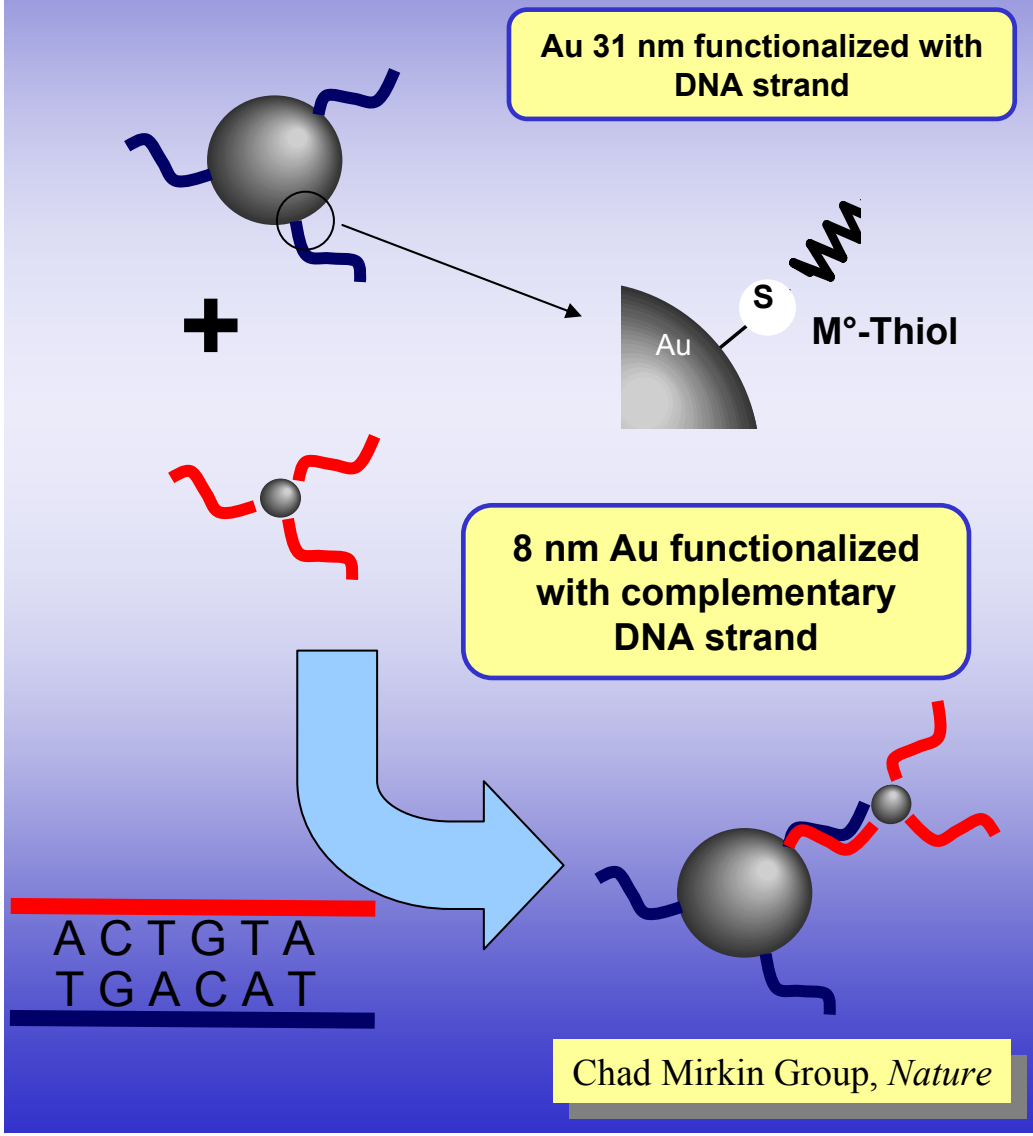


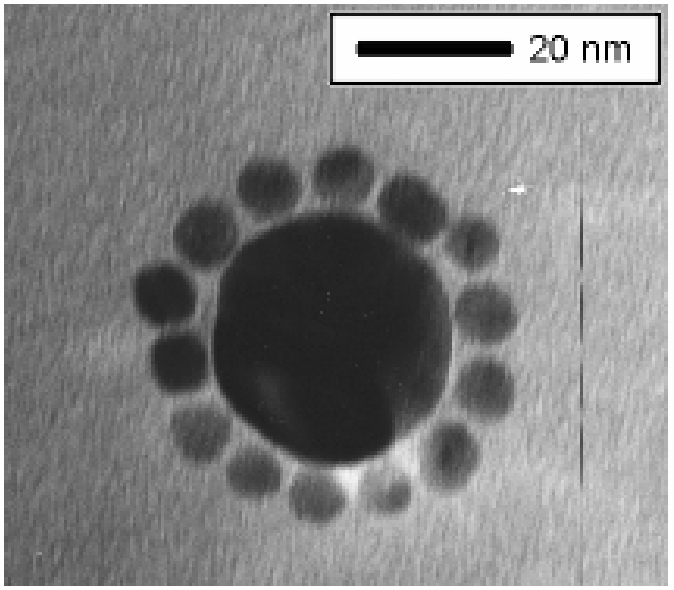
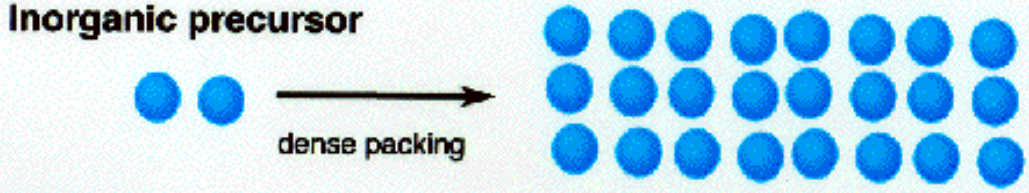


Figure 2. TEM image of a nanoparticle "satellite structure" generated from DNA-linked 8 and 31 nm diameter Au nanoparticles.

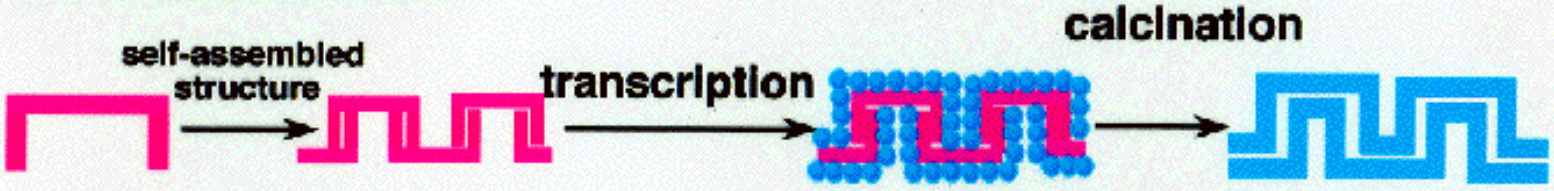
Plasmon band shifts **when Au NP connect**
DIAGNOSTICS

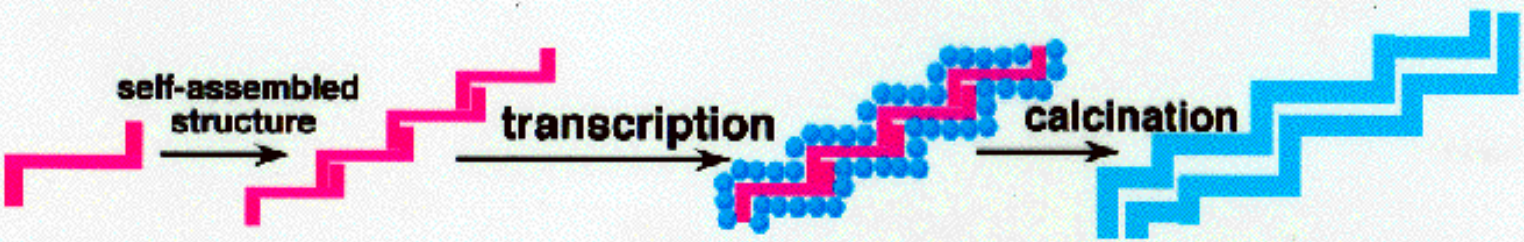
Complex Solids: Transcription of position information

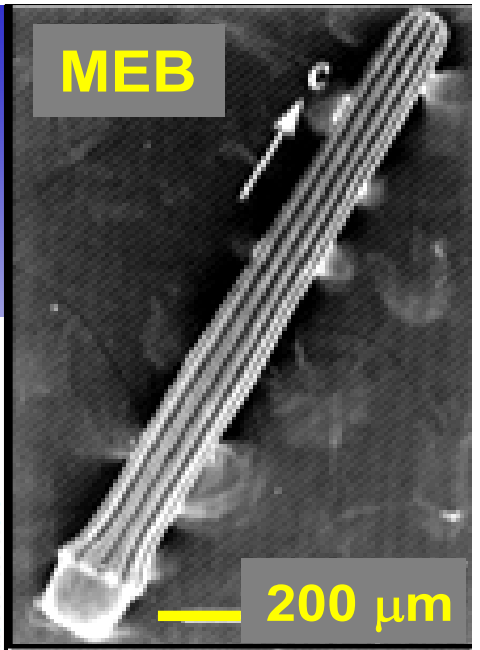
Inorganic material = "globular"

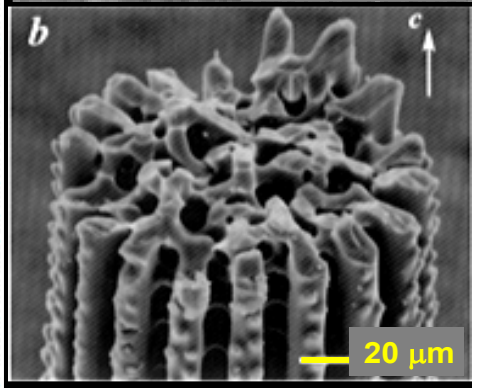


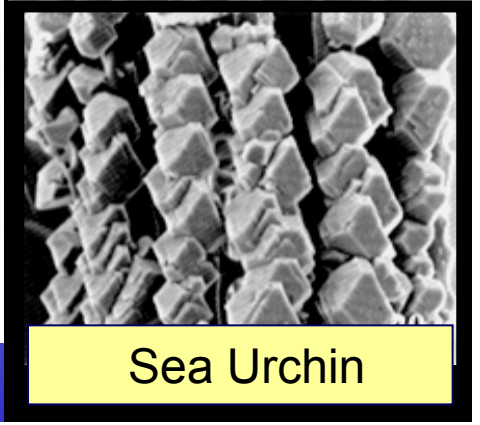
Organic material = "shape"











Sea Urchin

The templating concept in zeolites
Transcription of shape

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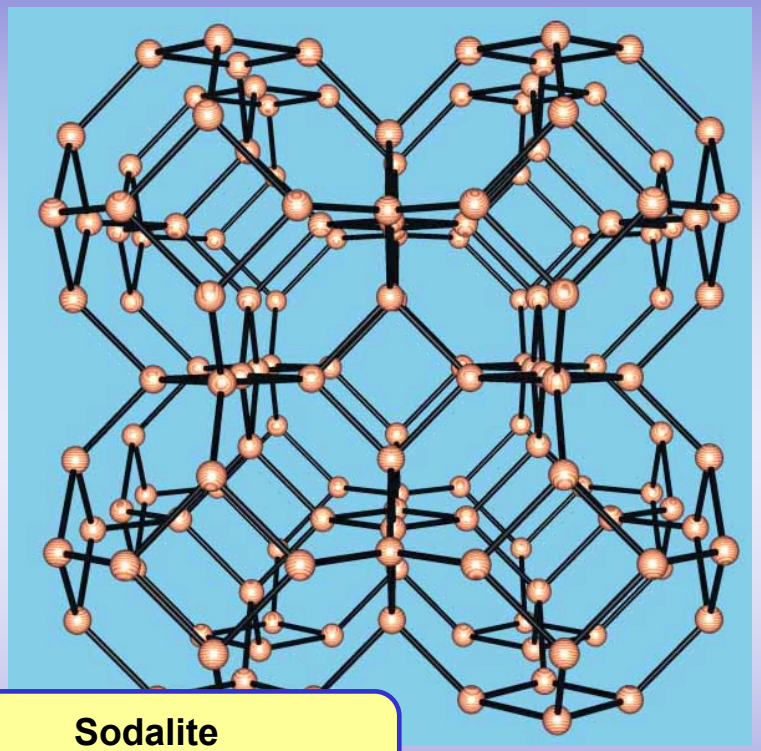
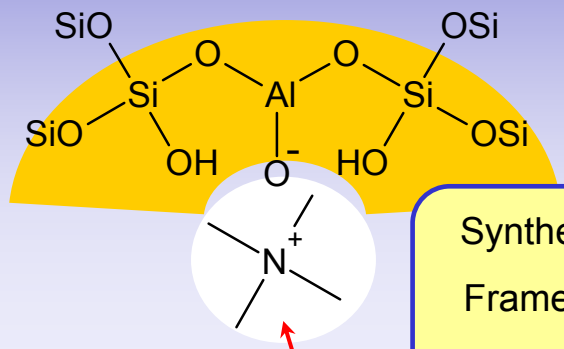


Sodalite

$Na_8[(AlO_2)_6(SiO_2)_6]Cl_2$

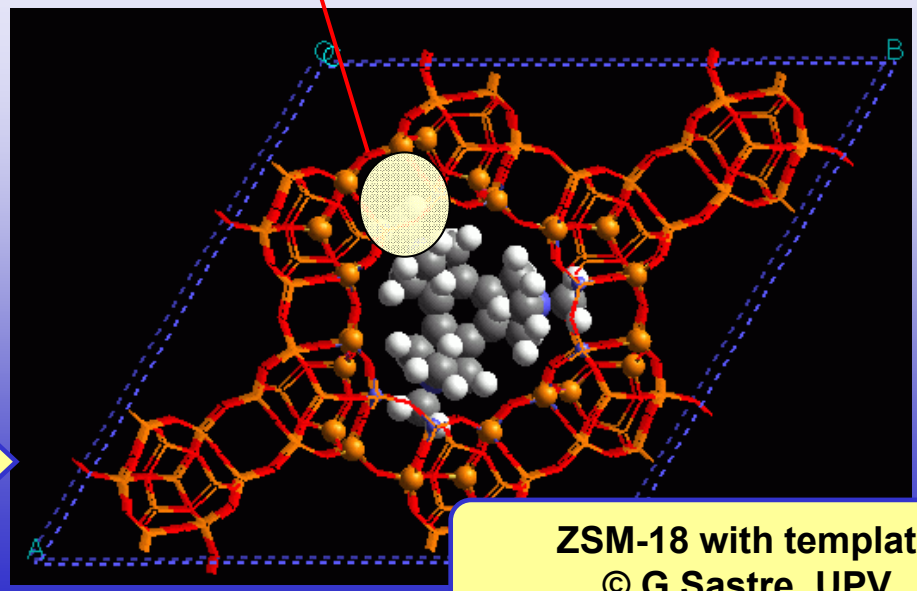


Synthesis in alkaline conditions

Framework negatively charged

Template positively charged

We can use molecules as ***pore templates***



ZSM-18 with template
© G Sastre, UPV

Formation of the SIL-1 zeolite

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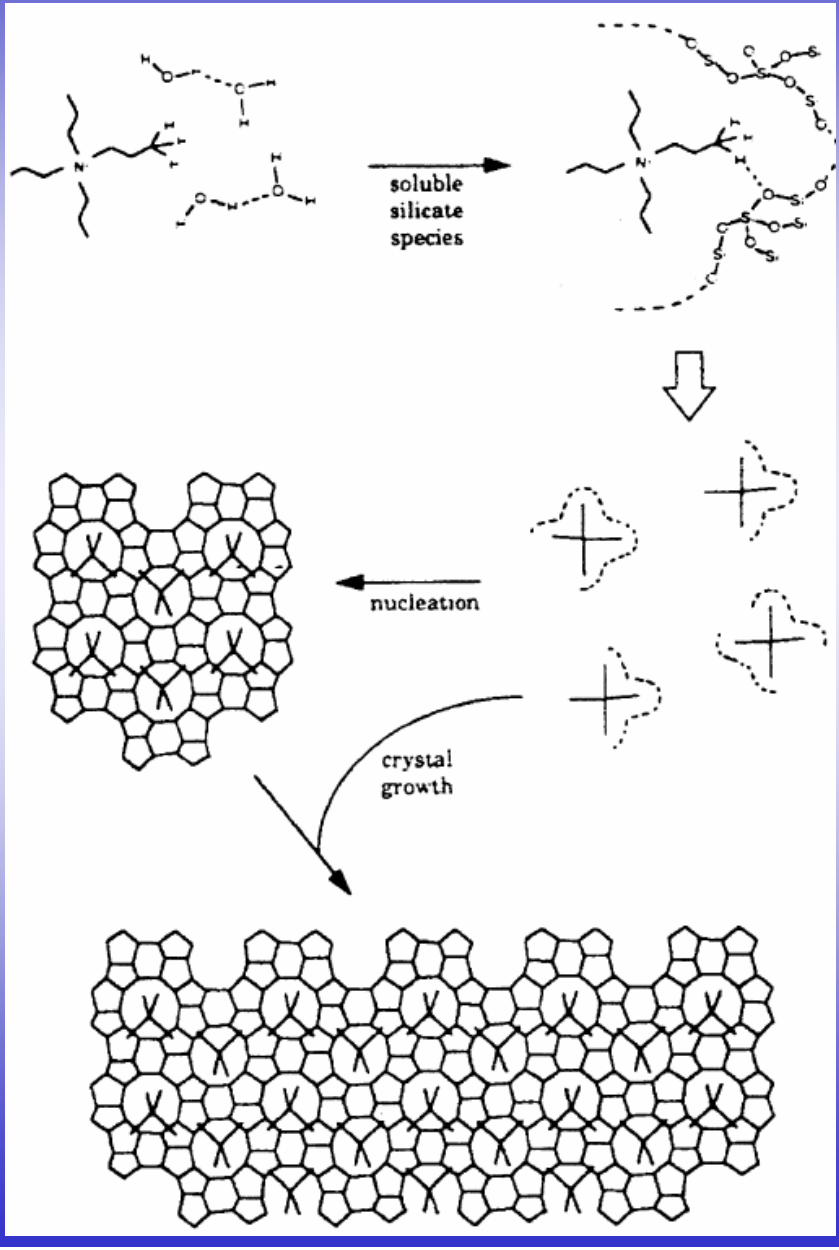

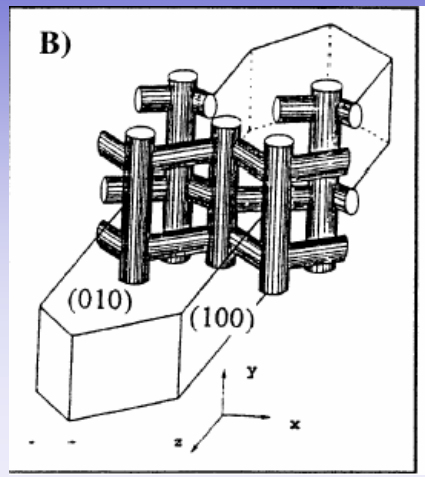

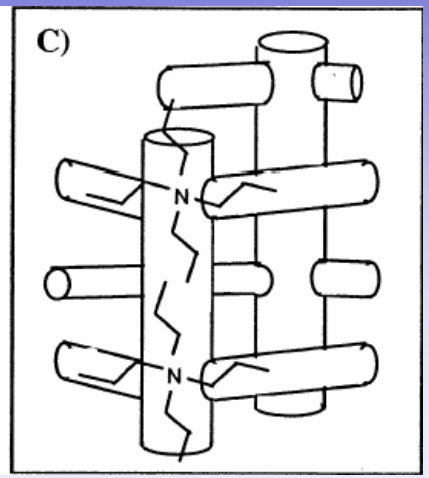

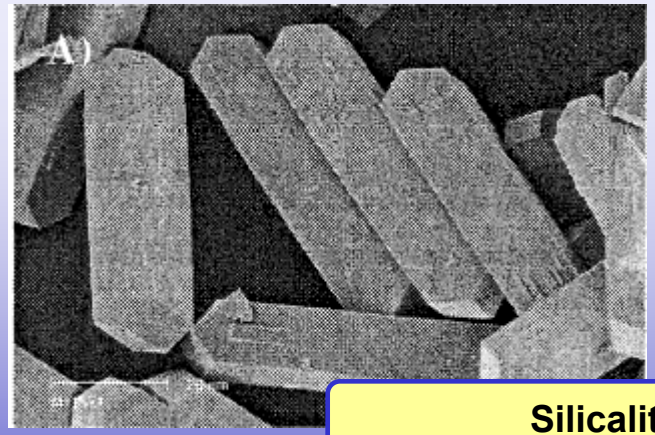

Silicalite-1

Limits of templating ?

Porous Materials: scales of porosity

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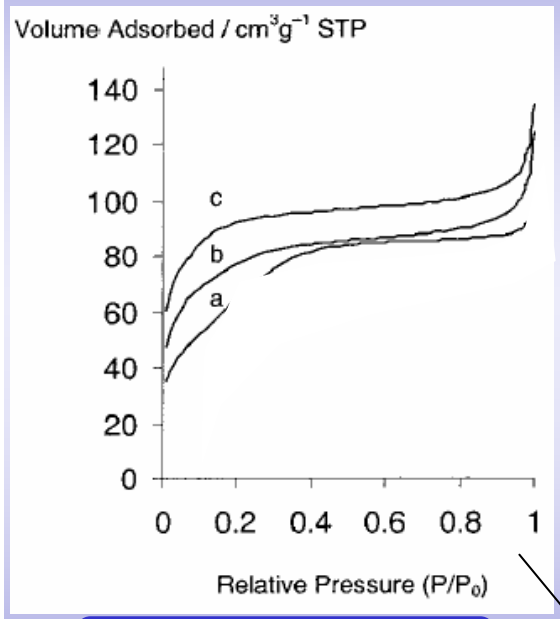
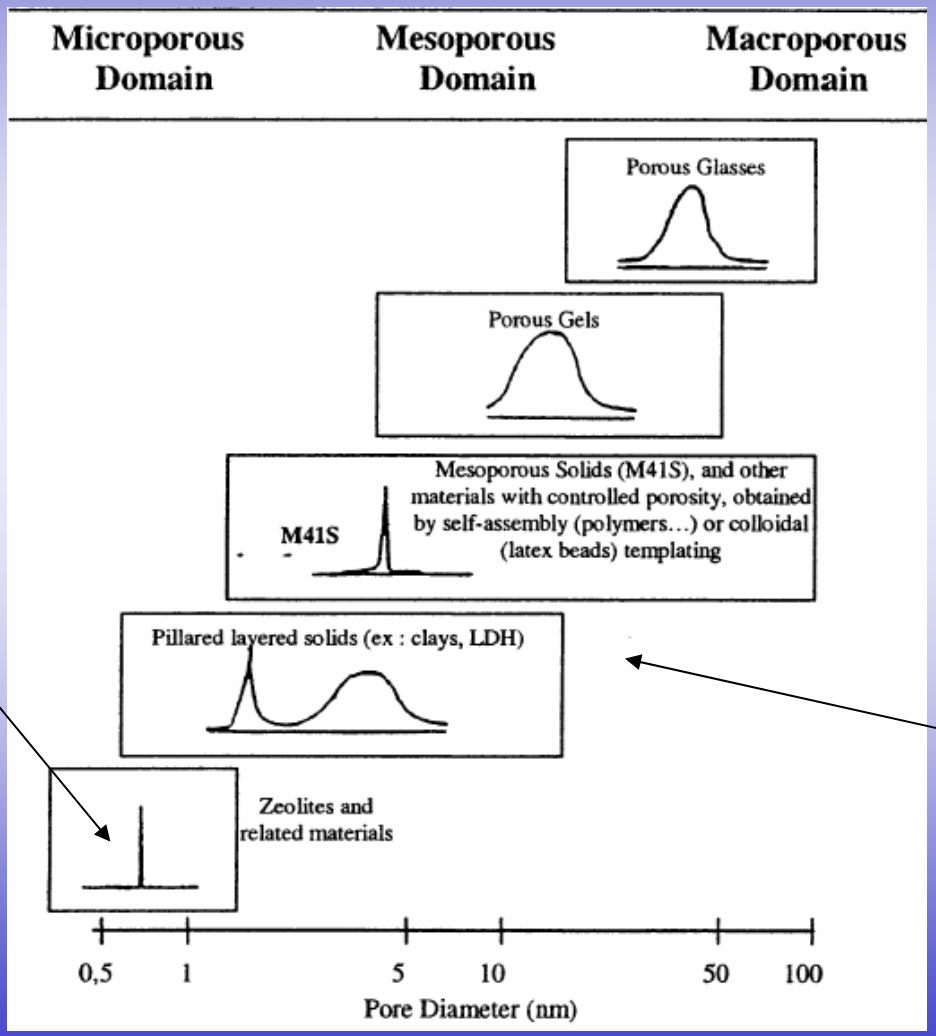
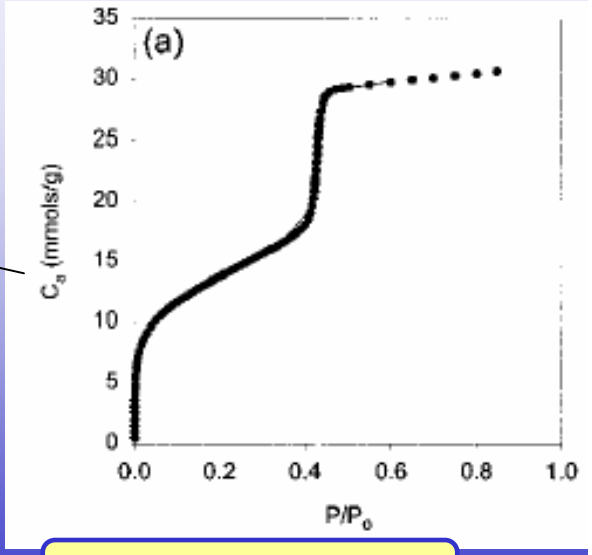


microporous





mesoporous

Self-Assembly using surfactants

Precise Supramolecular fingers

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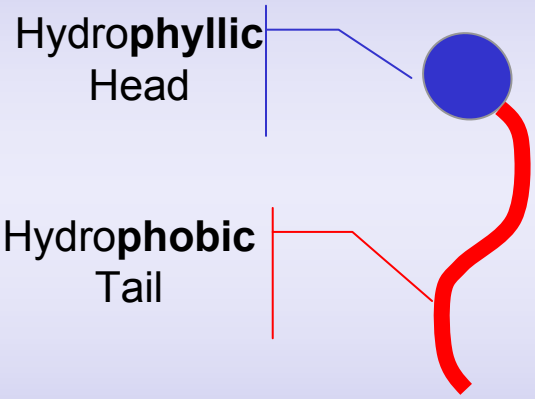
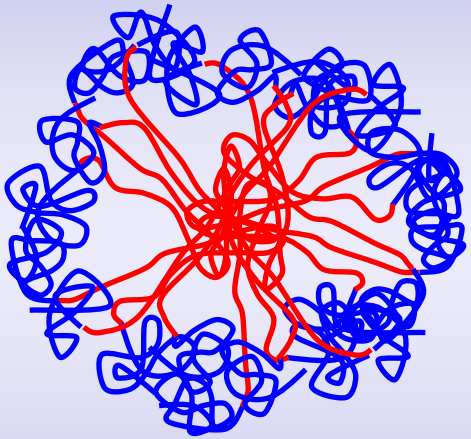
Surfactant

Asymmetric Molecule

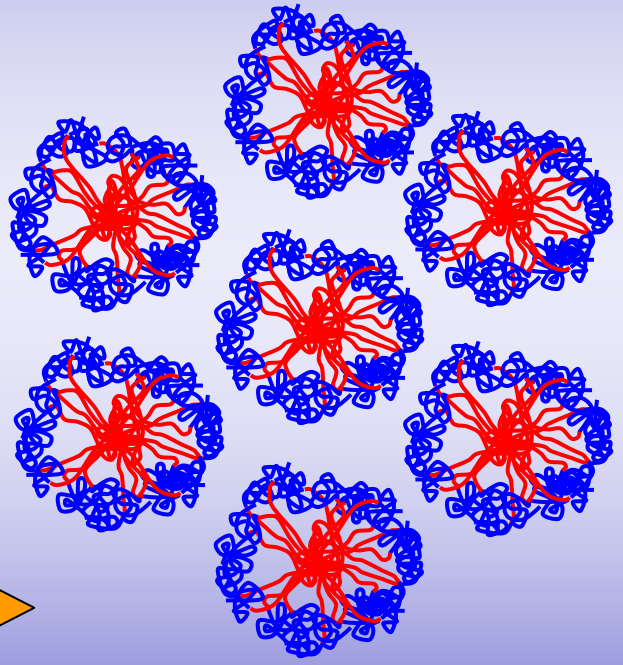


Micelle (NanoObject)



Lyotropic assembly

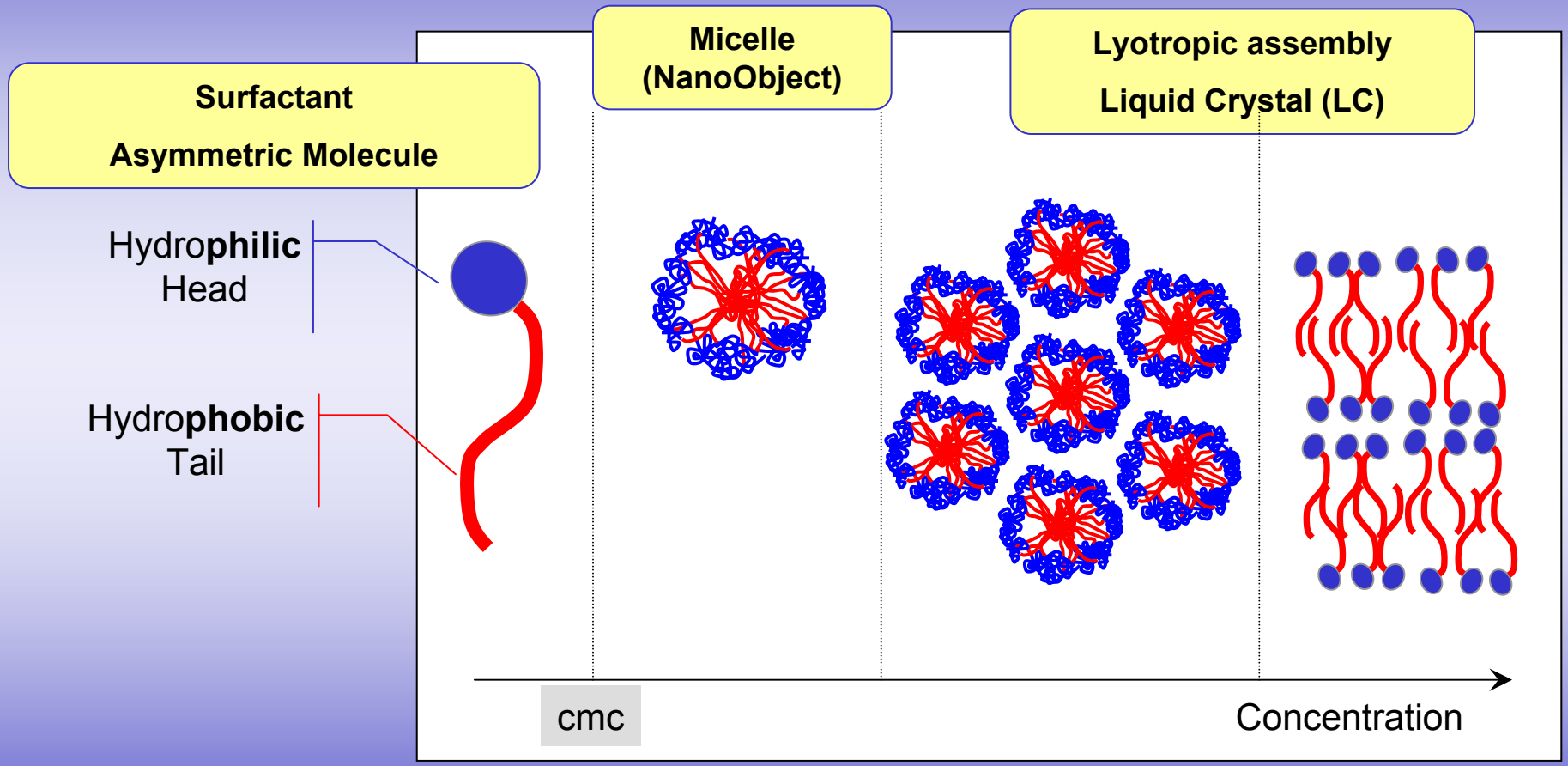
Liquid Crystal (LC)



Concentration

- Spontaneous Organization of asymmetric molecules
- Thermodynamic Control of Weak Interactions

Using Self-Assembly to create Supramolecular NBB



- Spontaneous Organization of asymmetric molecules
- Thermodynamic Control of Weak Interactions

Understanding micelle shape

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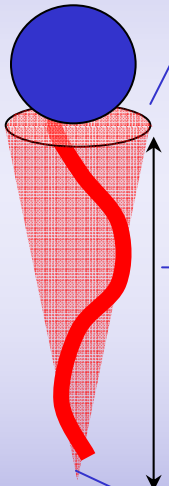
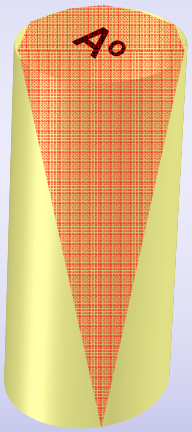


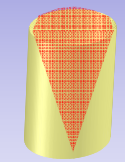
Area of the headgroup (A^0)

Length of the tail (l)

Volume of the tail (V)

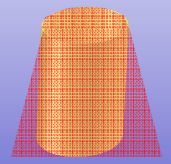


$$g = \frac{V}{A^0 l}$$



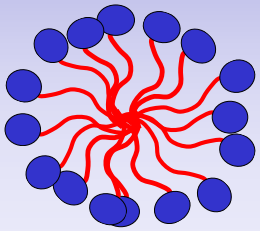
$g << 1$

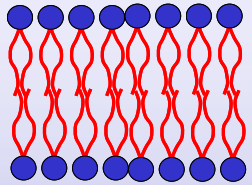
$g = 1$



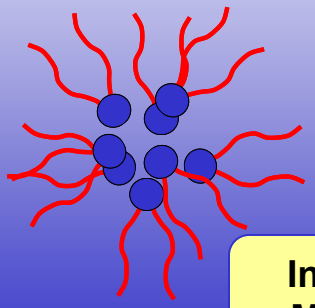
$g >> 1$

Micelle





Bilayer



Inverse Micelle

J. Israelachvili, *Intermolecular and Surface Forces, AP, 1992*

From micelles to Lyotropic Gels

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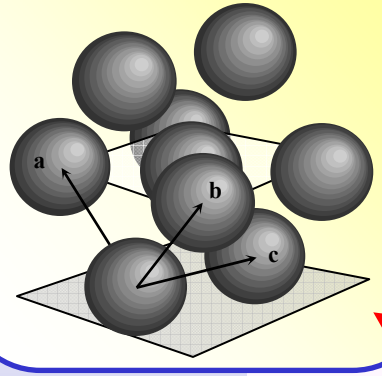
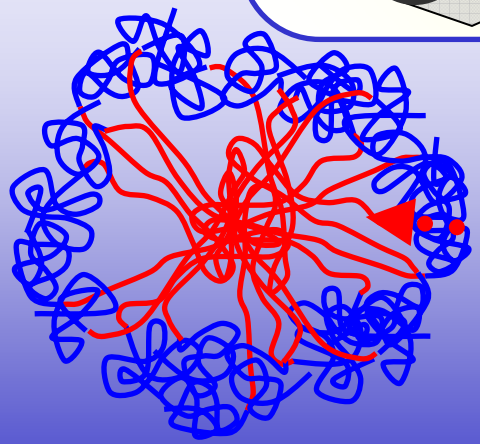
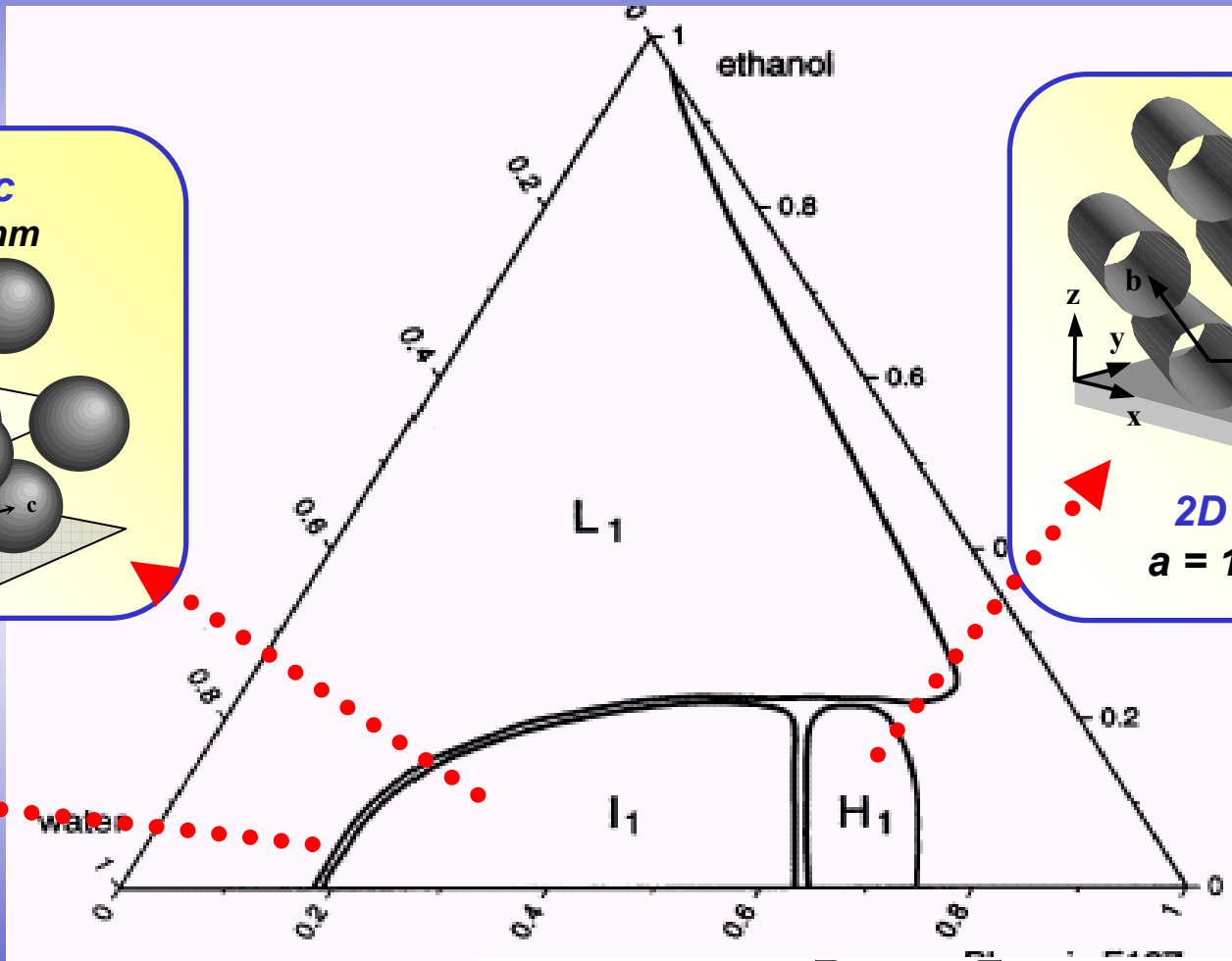
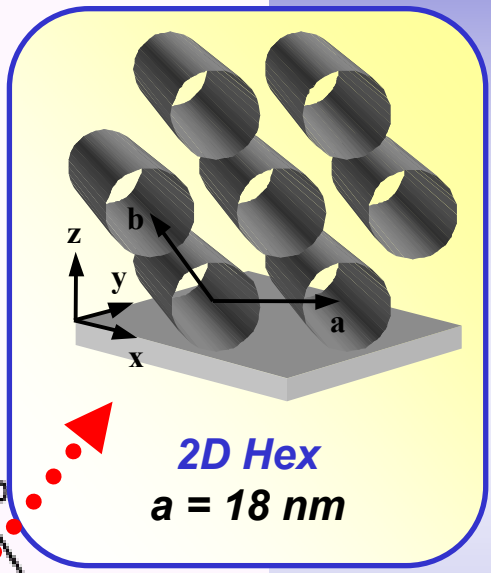
Cubic
a = 19 nm

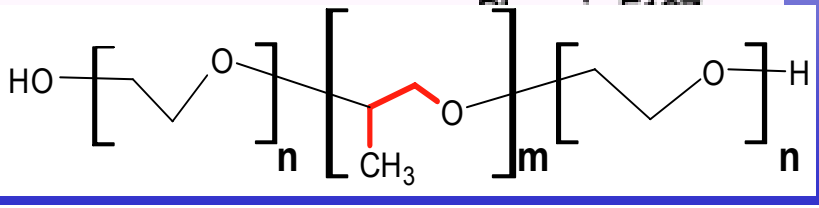








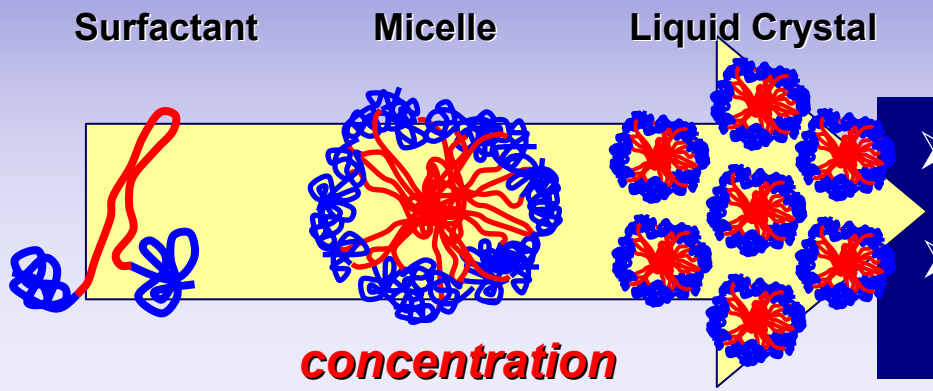
2D Hex
a = 18 nm



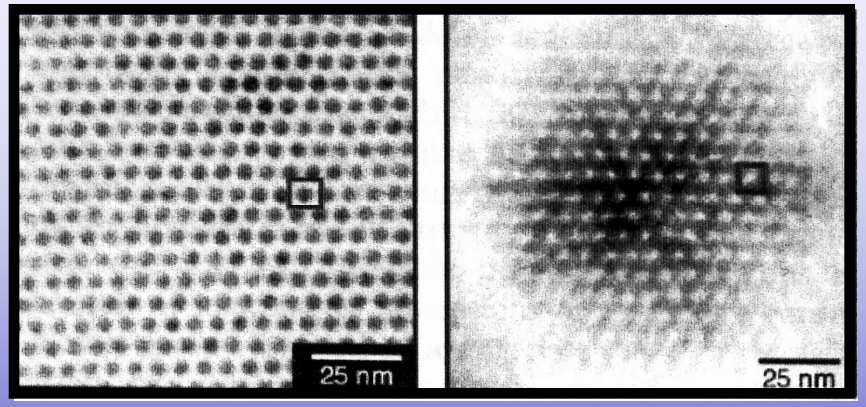
P. Alexandridis, ***AMPHIPHILIC BLOCK COPOLYMERS***
Self-Assembly and Applications, Elsevier, 2000

Organised Nano-Matter by Coupling *Sol-Gel* and *Self Assembly*

GSI-ICMR/UCSB
August 2005

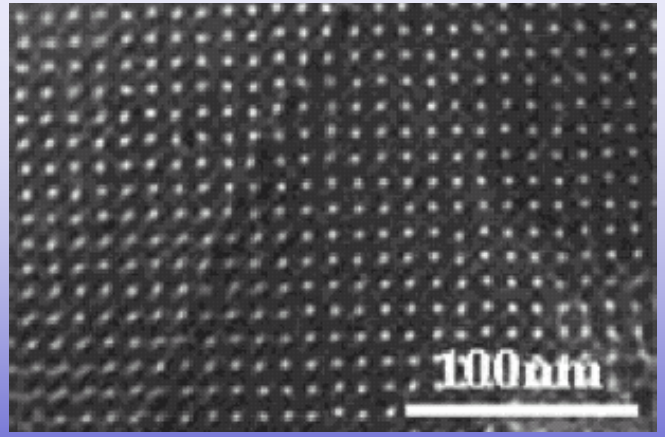


- Sol-Gel: Soft Synthesis methods (low T)
- Self-Assembly: Controlled Organization at the *mesoscale* (2-50 nm)



Organised B-Blocks

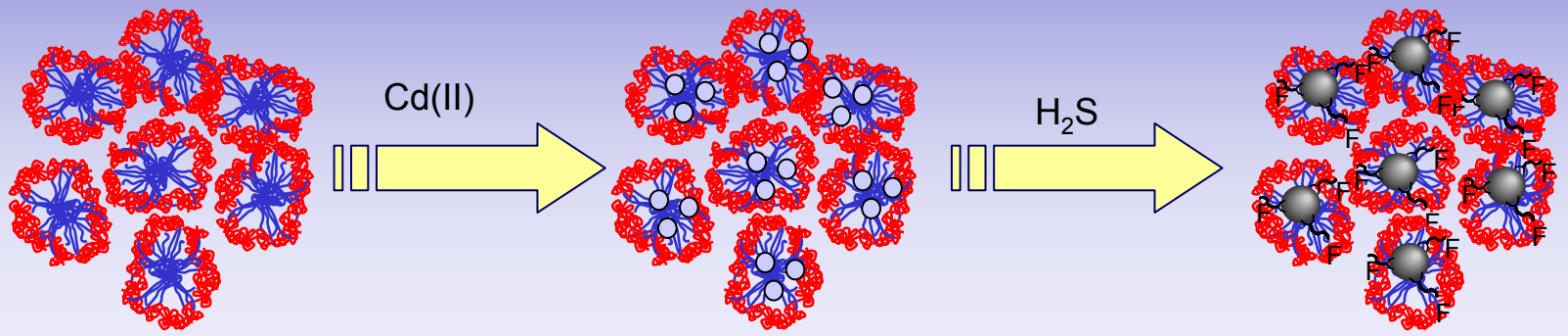
Organised CdS Stupp et al., *Science*, **1997**



Organised Voids

Mesoporous Silica
Beck et al., *Nature*, **1992**

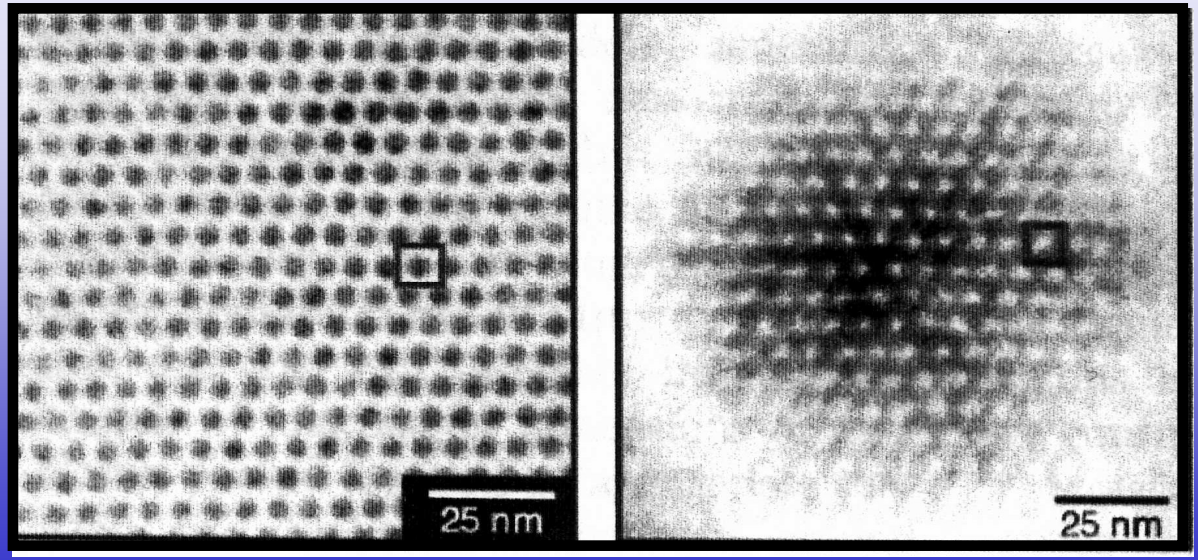
NBB Synthesis + Inverse micelles = Organized Nanoparticles



***nano*CdS Arrays (semiconductor)**

- **Controlled Space Distribution**
- **Multifuncional Materials**

(size + distance + function…)



Braun et al., *JACS*, **1999**, *121*, 7302
Stupp and Braun., *Science*, **1999**, *277*, 1242

Mesoporous Oxides

Using supramolecular templating

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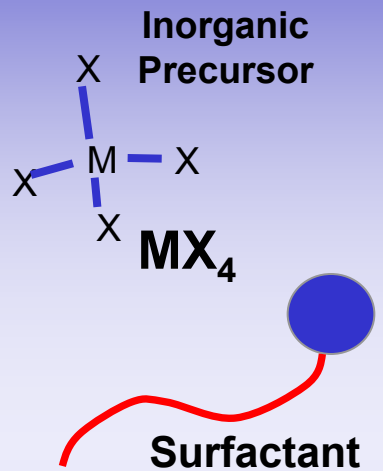
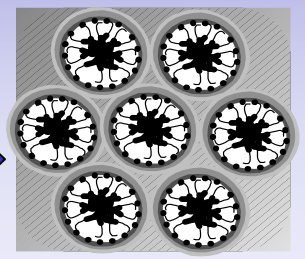
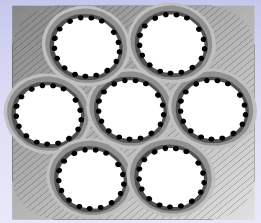


Sol-Gel + Self-Assembly



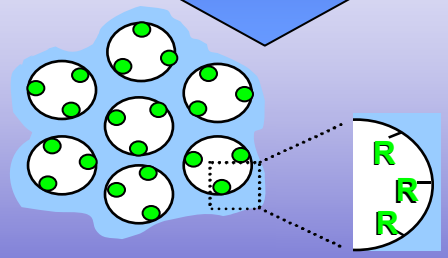
Mesostructured Precursor
"Fossile LC"

Elimination of the Template



Mesoporous Oxide

Functionalization



Multifunctional Material

- Micelles or LLC as templates (Supratemplates)
- Periodic Porous Network, Robust Systems
- High Surface (200-1000m^2/g)
- Ordered Monodisperse Pores, 2-50 nm
- Accessibility

Soler-Illia *et al.*, *Chem. Rev.*, **2002**

MCM-41: typical example of "supramolecular templating"

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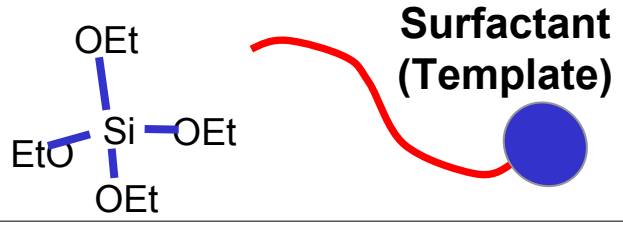
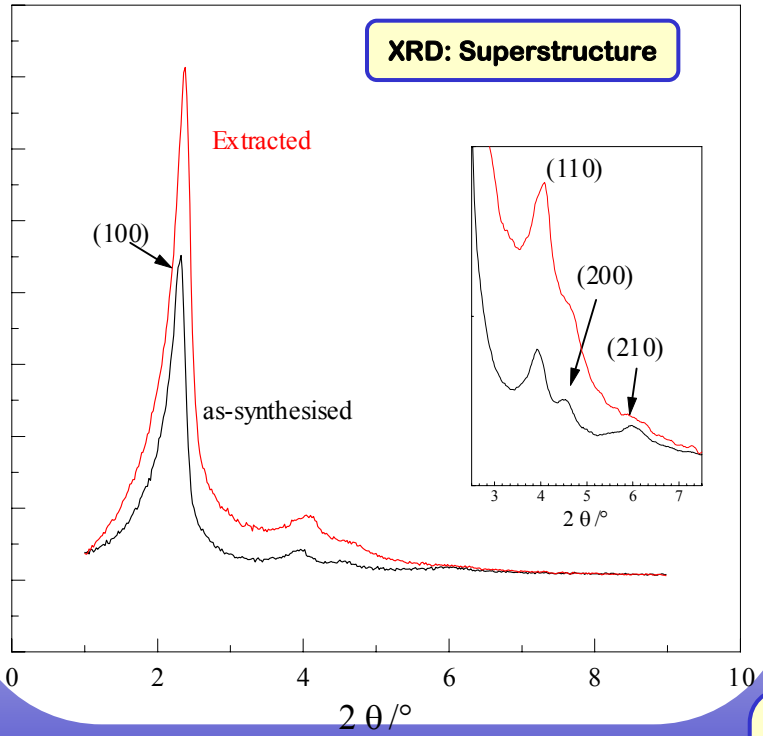
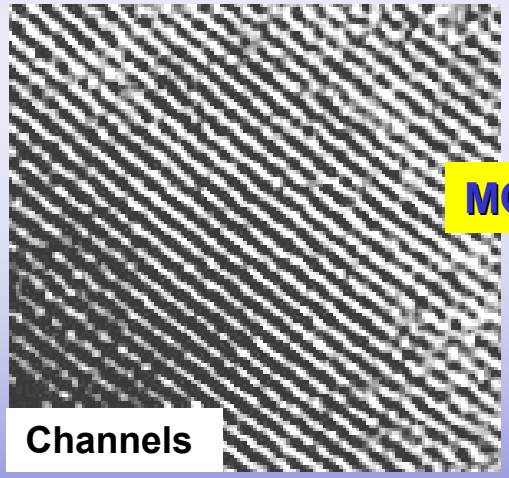


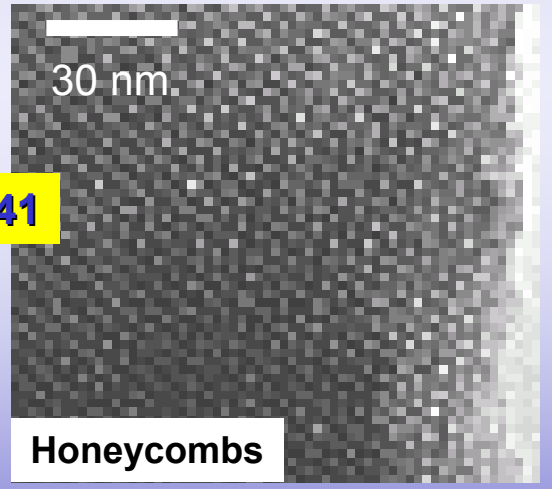


Mesoporous Silica MCM 41

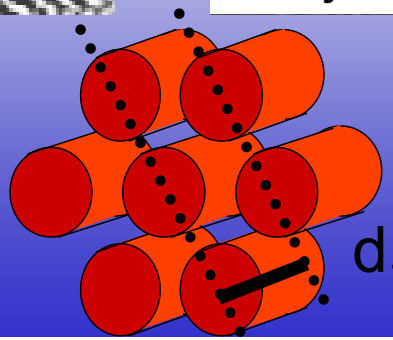
Chiola et al. US Pat 1971
Yanagisawa et al. *Bull. Ch. Soc. Jpn*. 1990
Beck et al., *Nature*, 1992



MCM 41



XRD and TEM: periodicity in the 30-50 Å scale



2D Hexagonal Mesostructure

Porosity and formation mechanism

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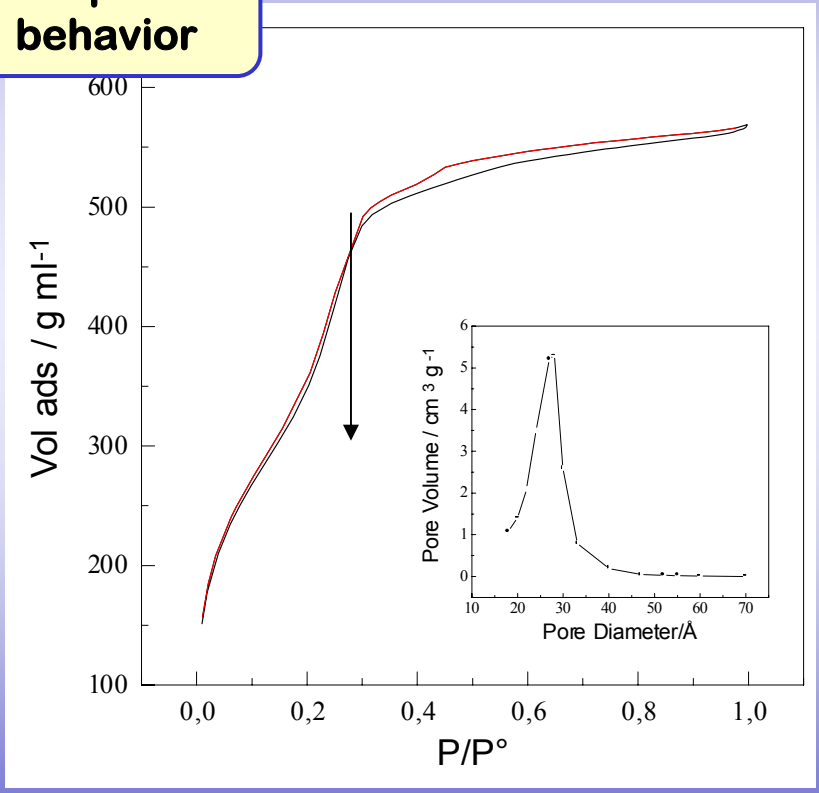
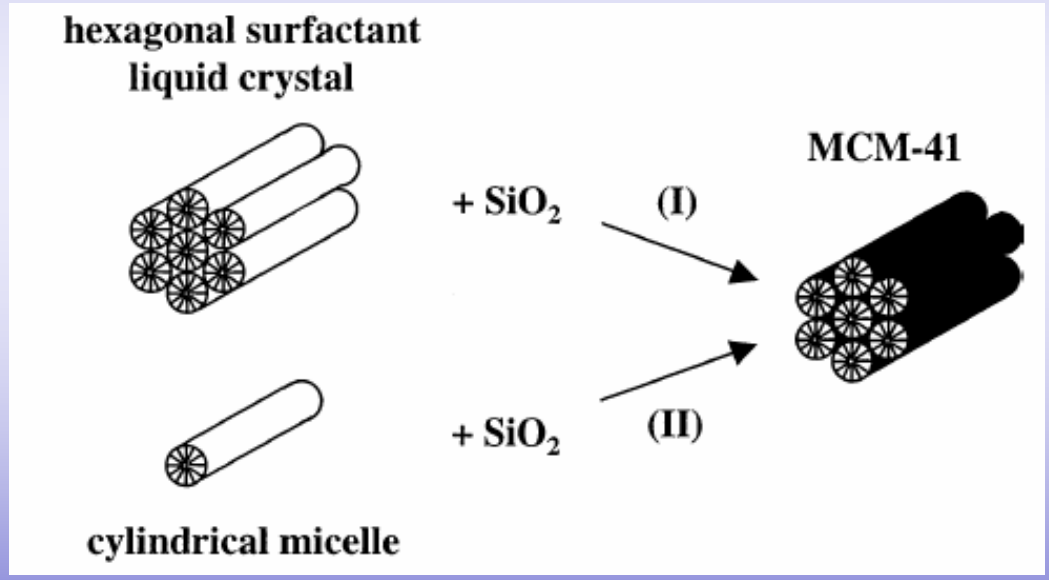
Mesoporous behavior





Synthesis Paths for Mesostructures

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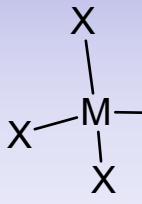
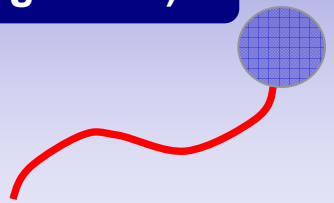
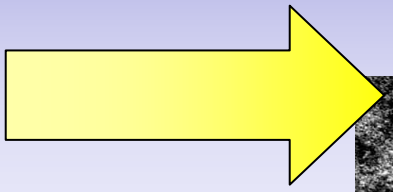
➢ **Precipitation (Kresge 1992)**

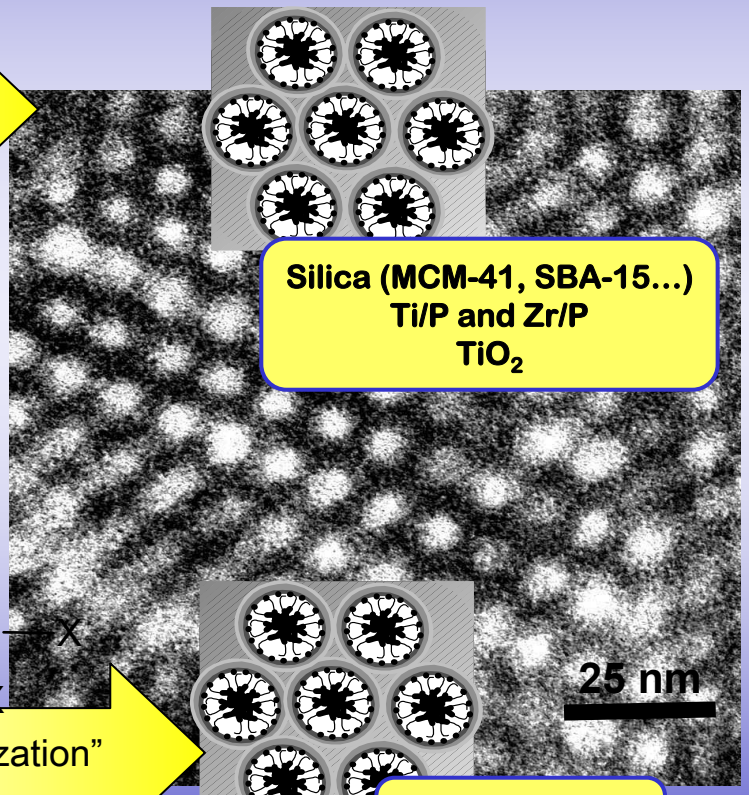


MX_4
(X=OR, Cl…)



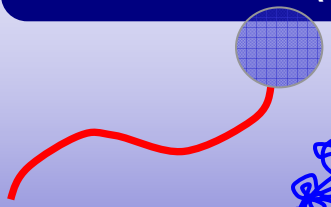
Template
(Surfactant)



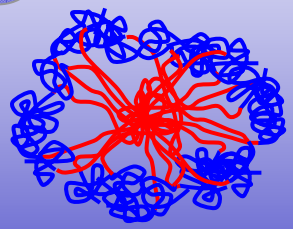


Silica (MCM-41, SBA-15…)
Ti/P and Zr/P
TiO_2

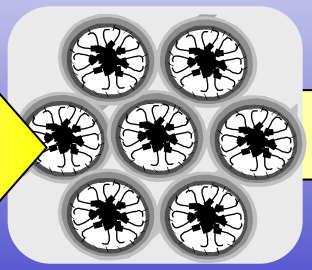
➢ **True *Liquid Crystal Templating***
(Attard 1995)

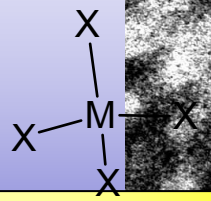


Template

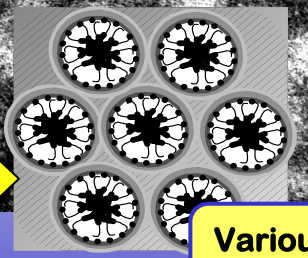


Micelle→LC





"fossilization"



25 nm

Various Oxides
and metals

Ionic, non-ionic and polymeric templates

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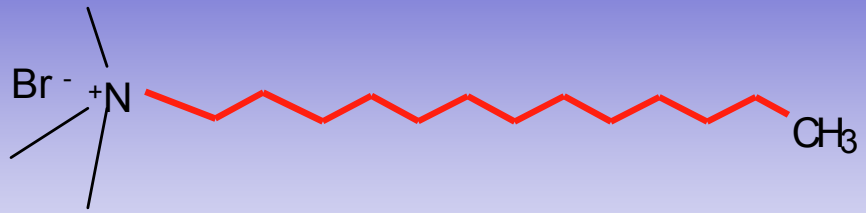
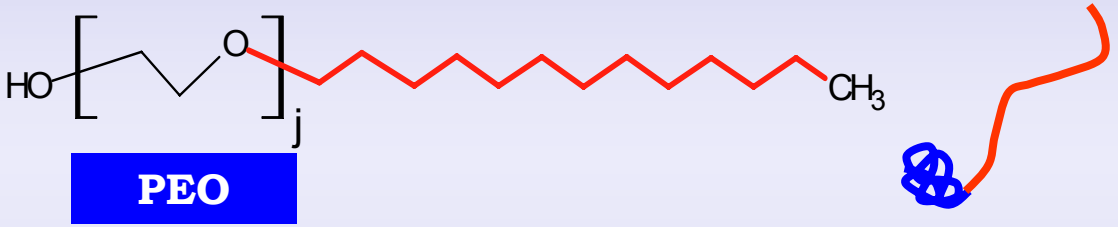
CTAB: $C_{16}NMe_3^+ Br^-$

30-40Å



Diblocks alkyl-PEO

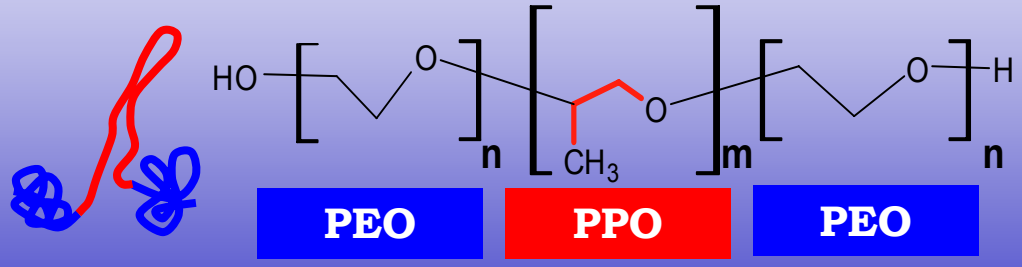
60-80Å



PEO

Triblock Copolymers

100-180Å



PEO **PPO** **PEO**

- *Choice of surfactant class interactions (HLB, template/inorg)*
- *g factor ⇒ structure director*
- *Size*

Soler-Illia *et al.*, *Current Opin. Colloids Surf. Sci.*, **2003**

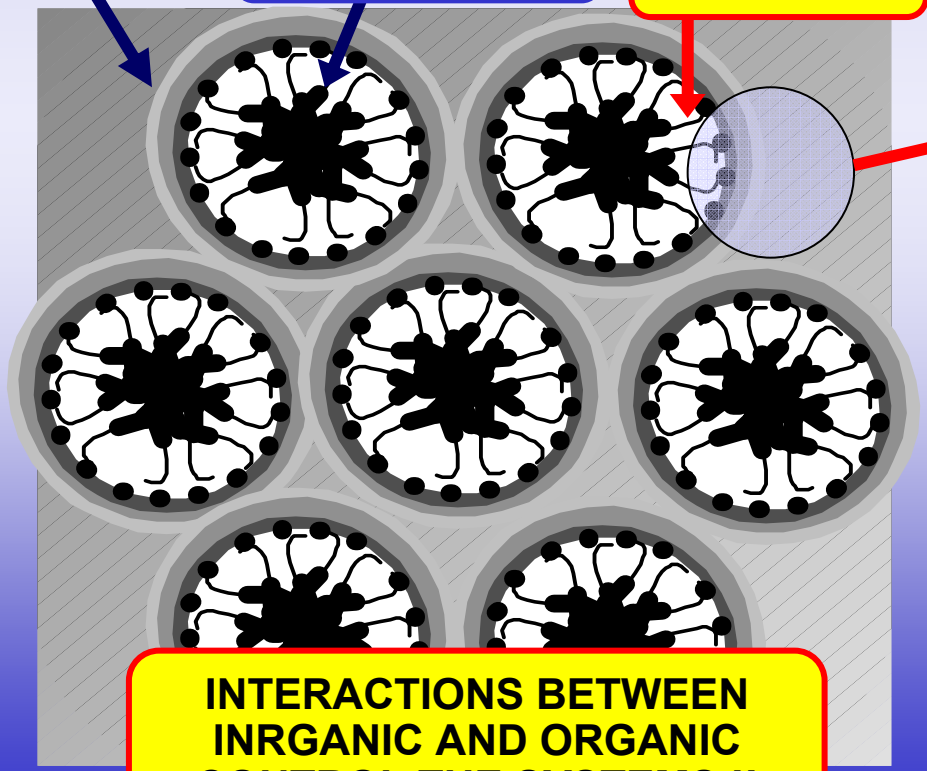
Forces Towards Order

$$\Delta G_{form} = \Delta G_{Inorg} + \Delta G_{templ} + \Delta G_{interf} + \Delta G_{solv}$$

Inorganic Matrix

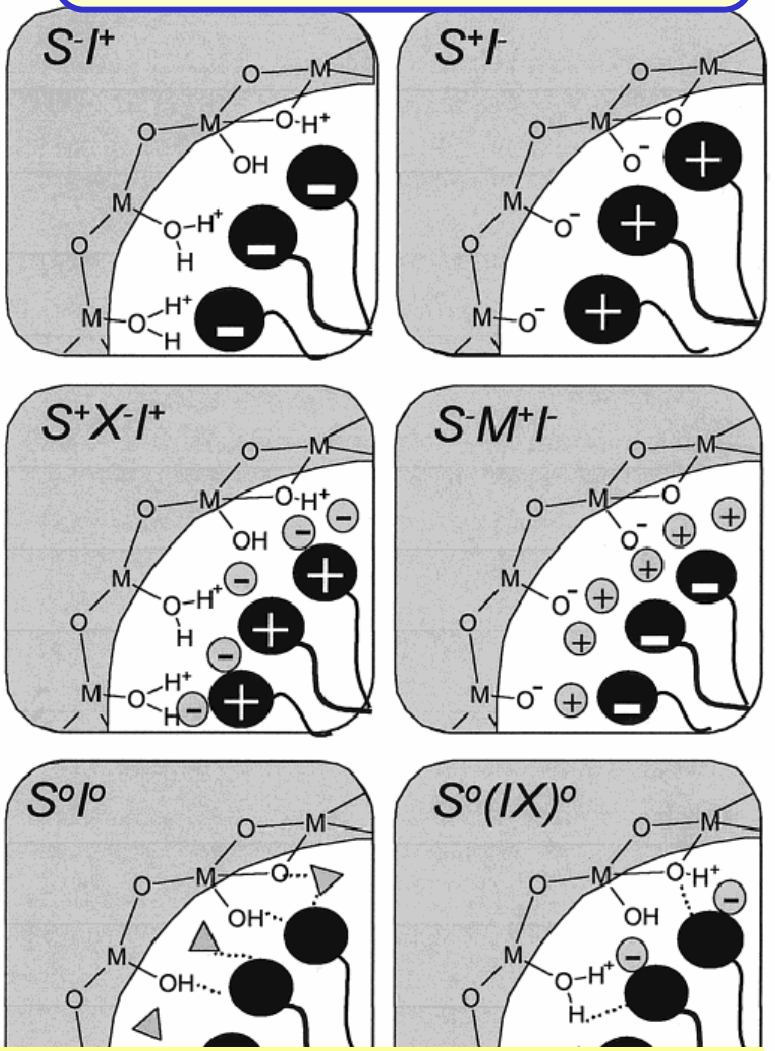
Self-assembly of template

Hybrid Interface



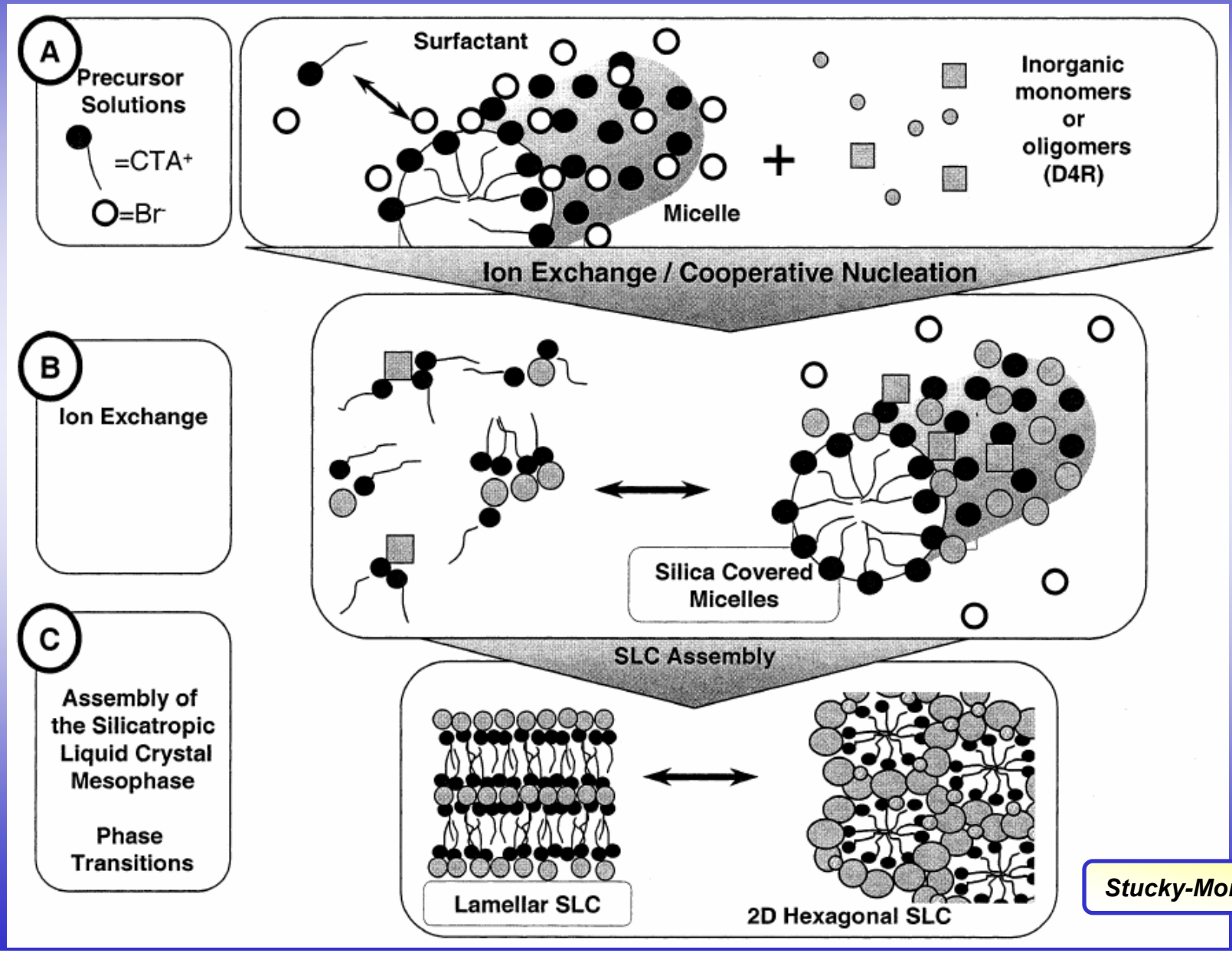
INTERACTIONS BETWEEN INRGANIC AND ORGANIC CONTROL THE SYSTEMS !!

Variety of Hybrid Interfaces + Inorganic Frameworks = Complex Organized Materials



Huo *et al.* (Stucky), *Chem. Mater.*, **1994**

Cooperative Mechanism



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August 2005

Stucky-Monnier-Chmelka

Large pore mesostructures: the SBA series

GSI-ICMR/UCSB
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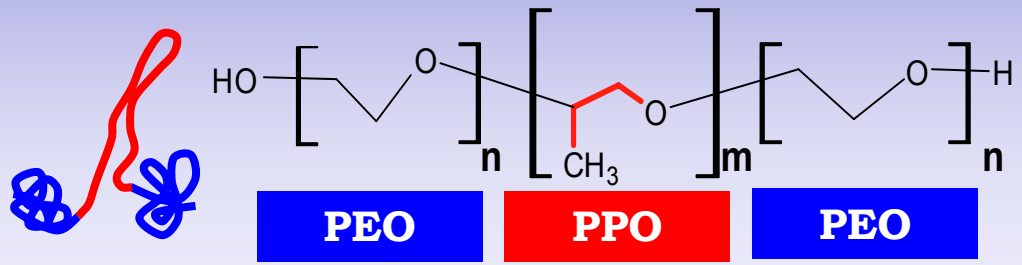
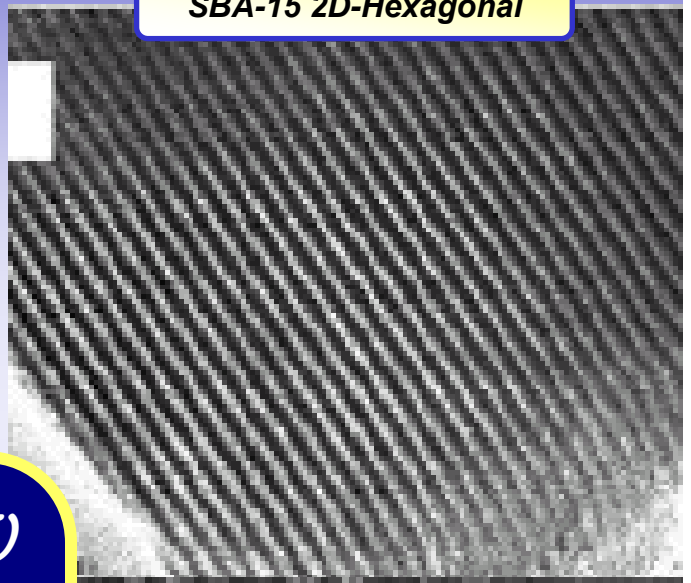
Polymer templates

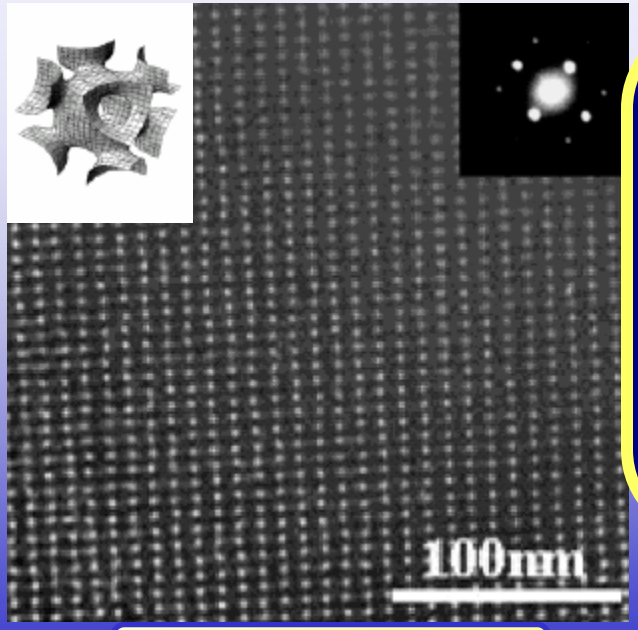
100-180Å



PEO **PPO** **PEO**

SBA-15 2D-Hexagonal

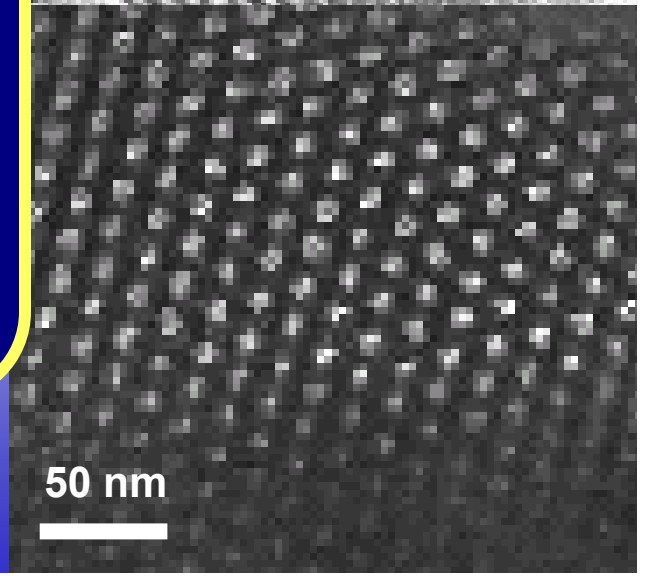




SBA-16 3D-Cubic

- *Robust walls (5 nm vs 1.5)*
- *Hydrothermal stability (catalysis!!)*
- *Larger pores*
- *Polymers are tailorable*

Stucky and Wiesner groups



Non-ionic surfactants: interactions and entanglement

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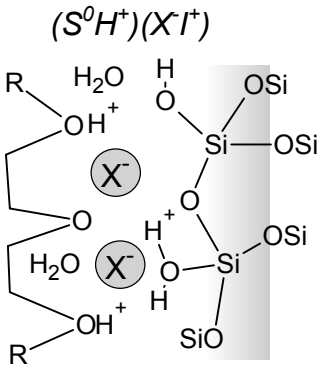
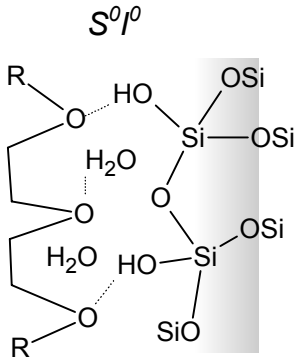
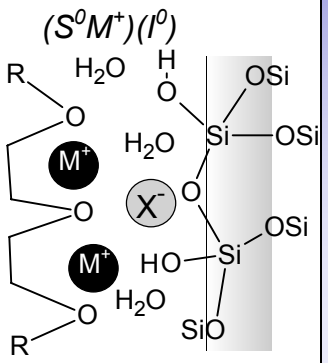
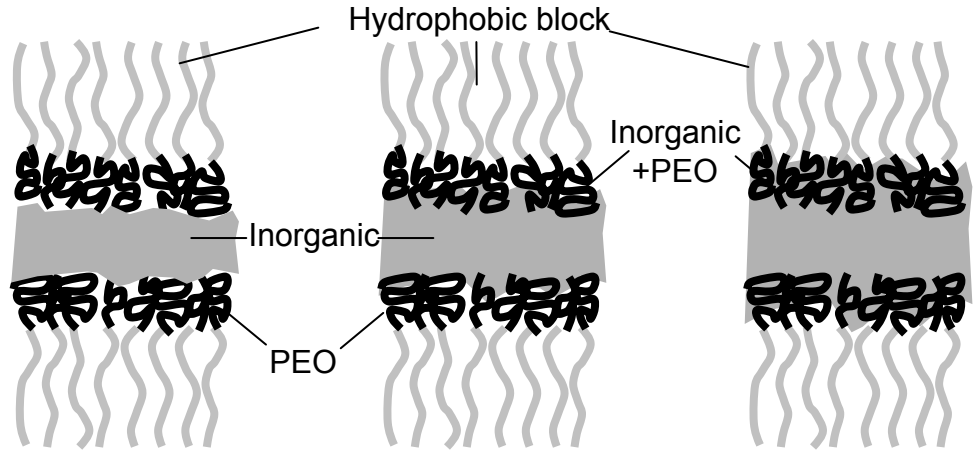
August 2005

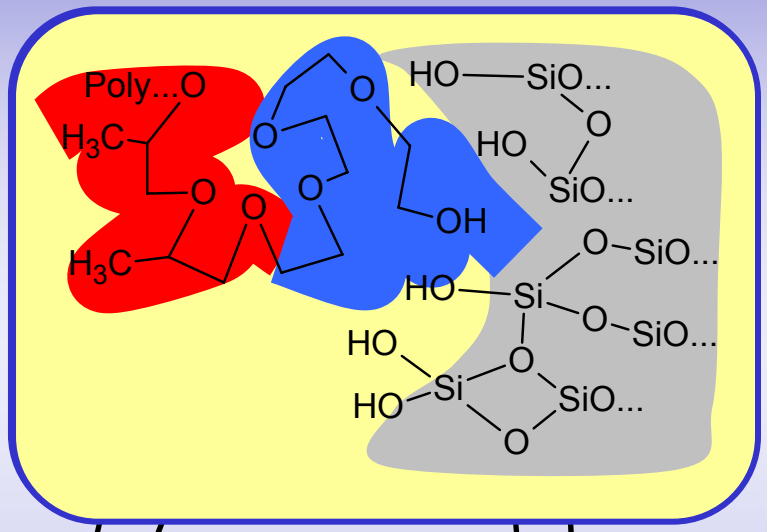








Soler-Illia *et al.*, *Current Opin. Colloids Surf. Sci.*, **2003**



Mobile protons
« liquid »

No correlation with ^{29}Si

Non-Mobile protons
« solid »

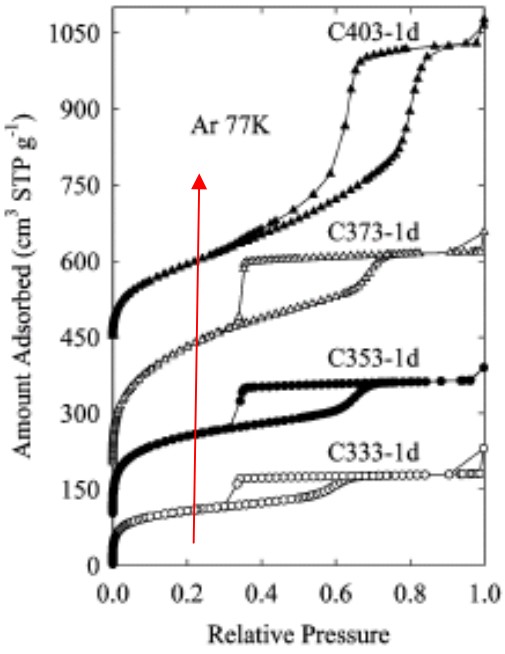
Correlated with ^{29}Si

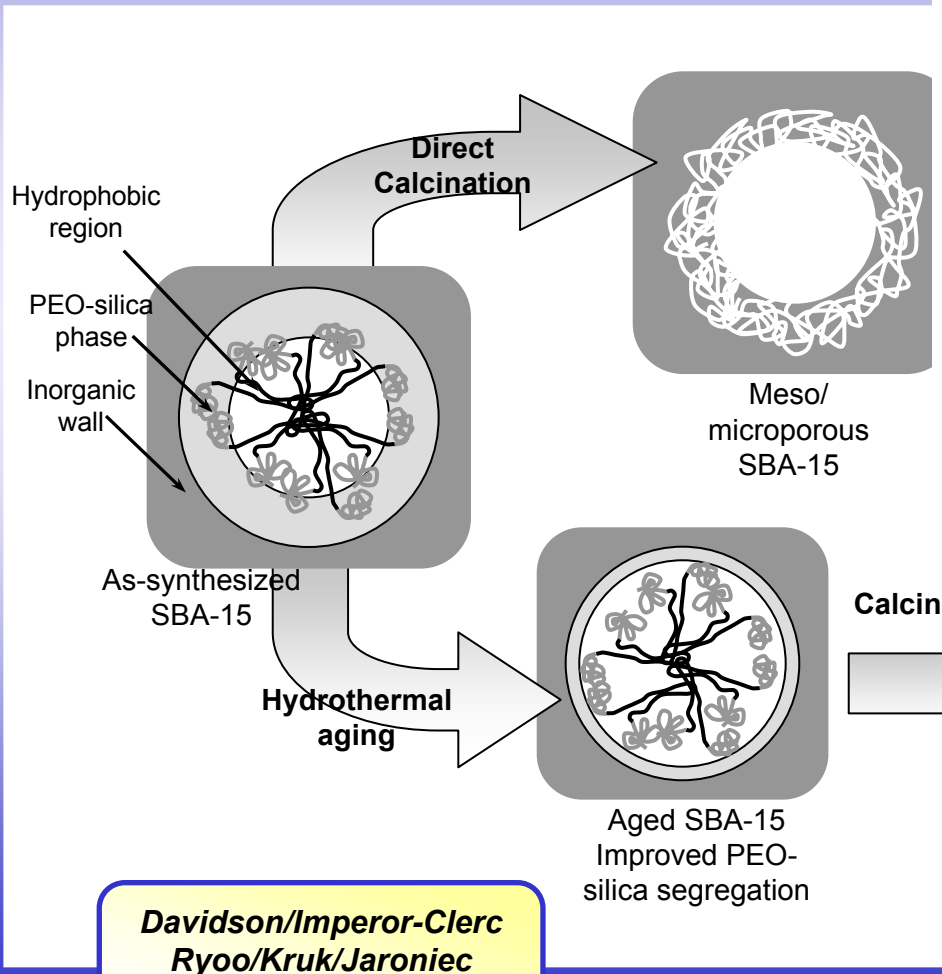
MAS NMR: polymer chains penetrate the inorganic framework

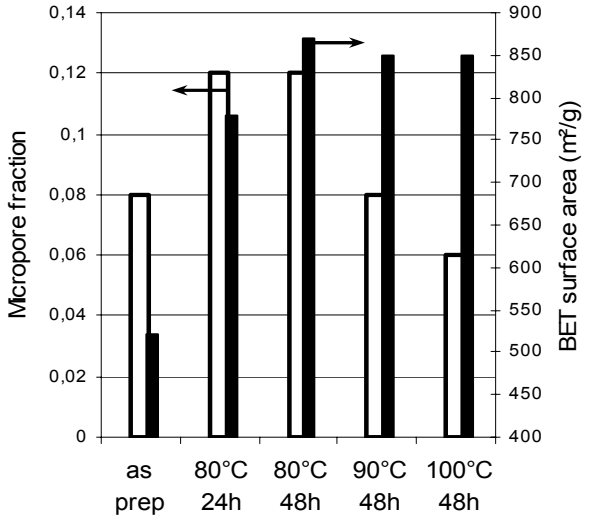
Melosh/Chmelka et al.
Macromolecules 1999

Control of micro and mesoporosity by hydrothermal treatment

GSI-ICMR/UCSB
August 2005







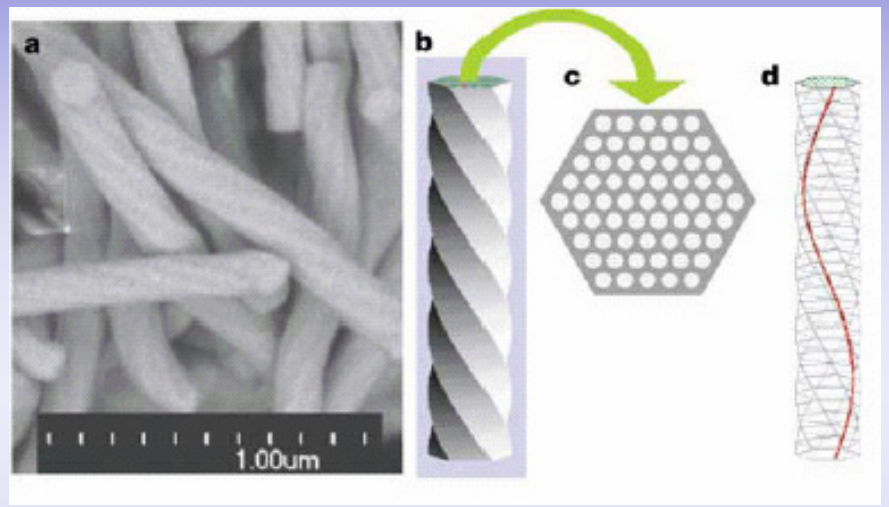
The micropore fraction decreases with treatment

The surface area is optimised

Pore accessibility is better

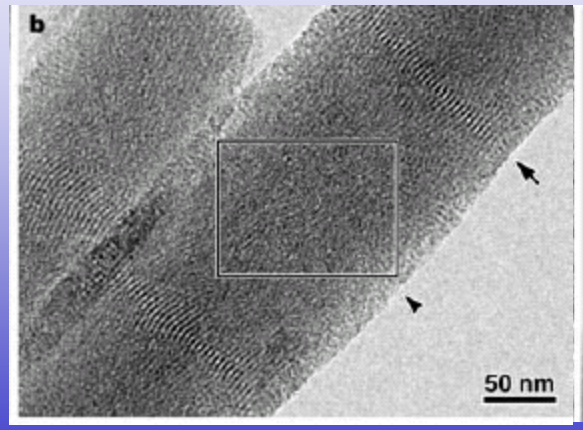
Davidson/Imperor-Clerc
Ryoo/Kruk/Jaroniec
Stucky/Chmelka

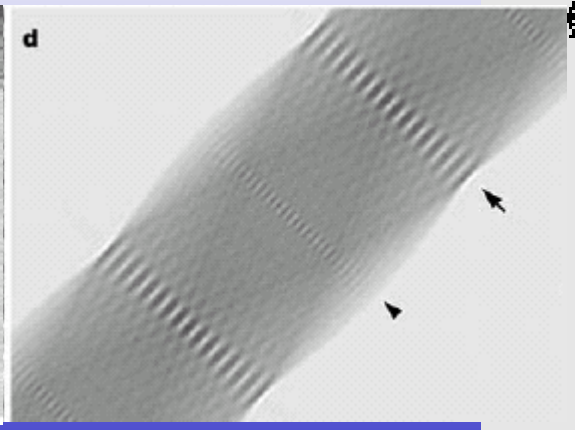
Effects of a Chiral Surfactant

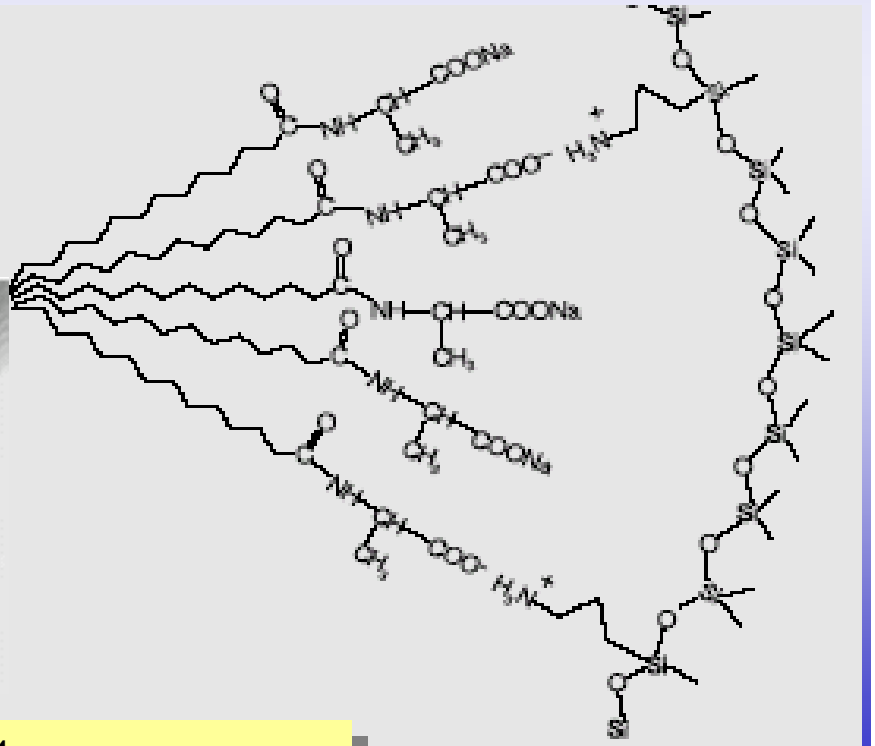


Using a chiral surfactant (glycine amide) results in ordered channels

…with a twist!

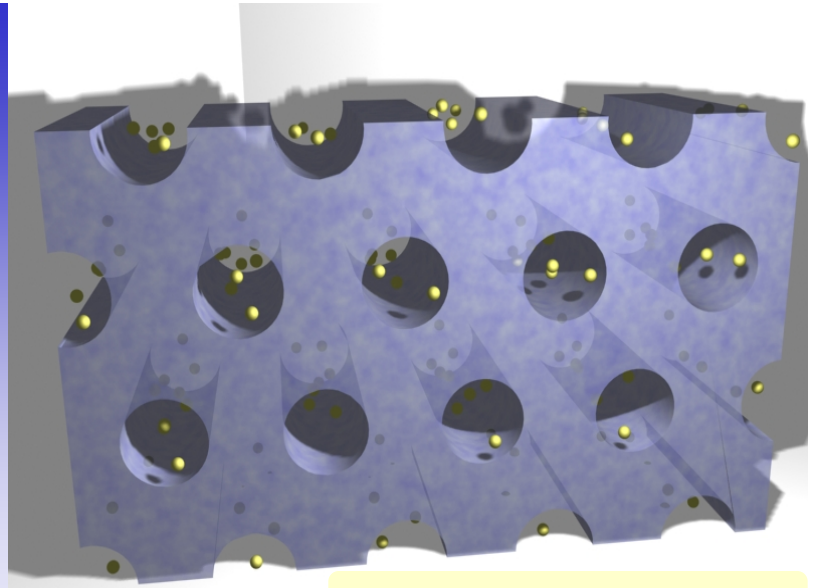






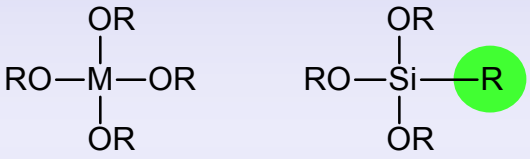
Che *et al.*, *Nature.*, **2004**

Hybrid Organosilica
Putting Functions into pores



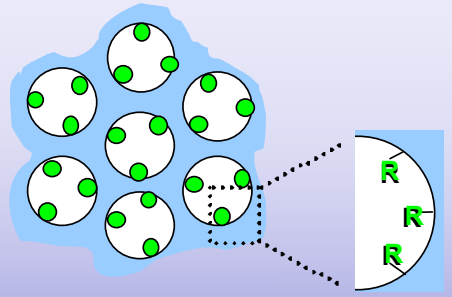
© P. Falcaro and P. Innocenzi

One Pot

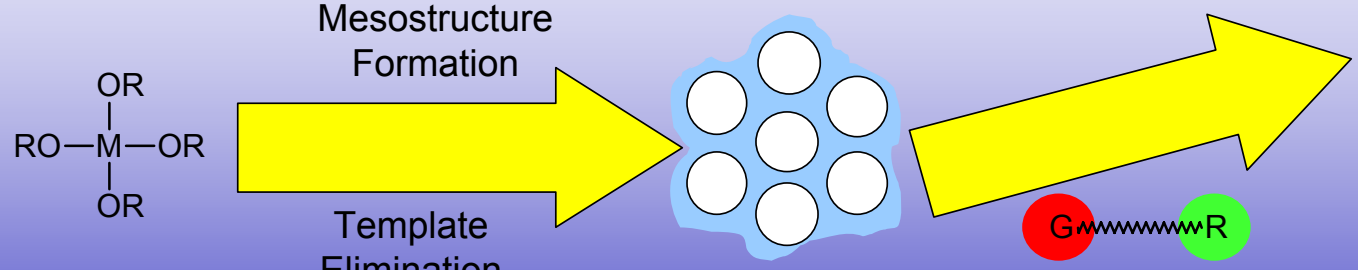


Mesostructure Formation

Template Elimination



Post-grafting



Reviews:
Shi et al. *J. Mater. Chem.* **2004**; Kickelbick *Angew. Chem.* **2004**

A special case: crystalline organic walls!

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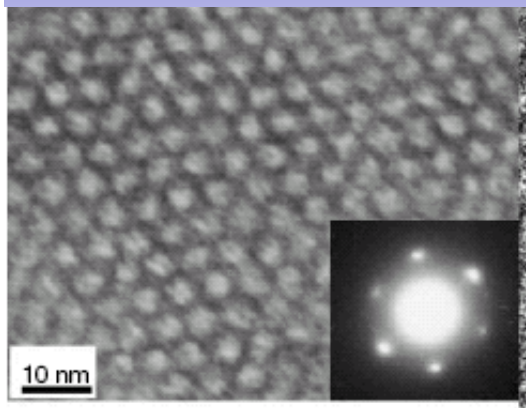

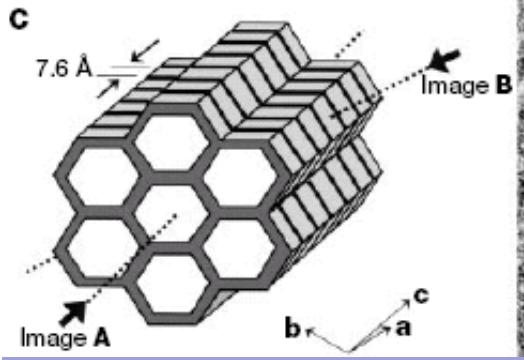

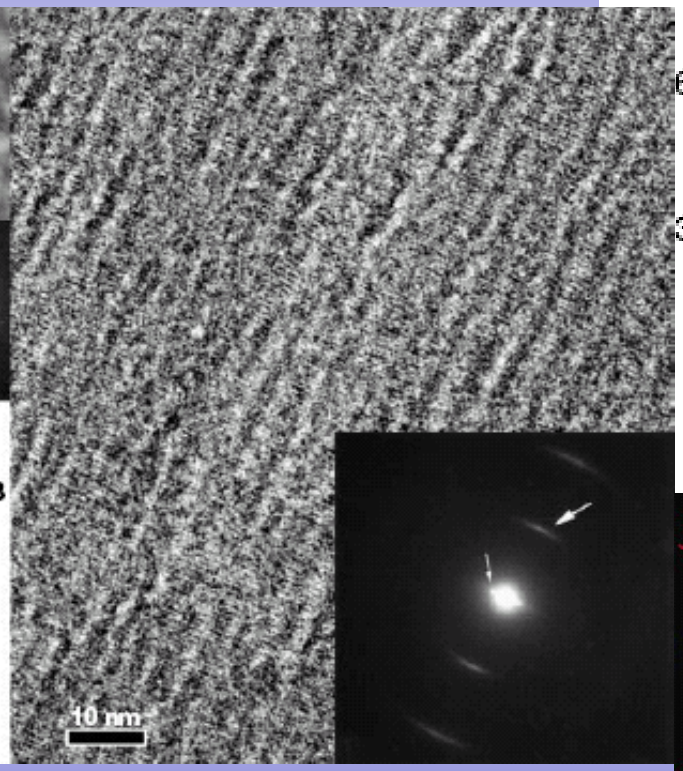

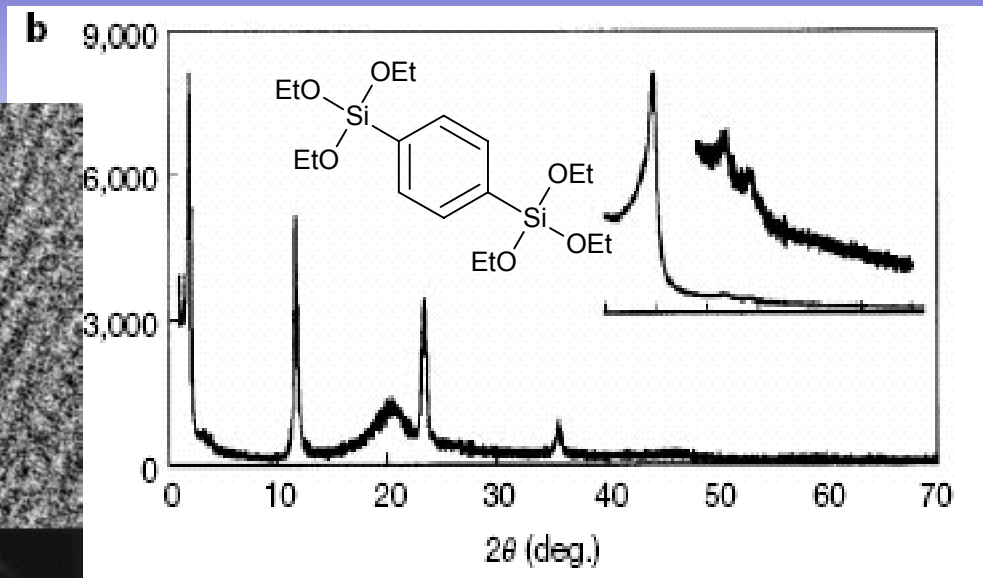

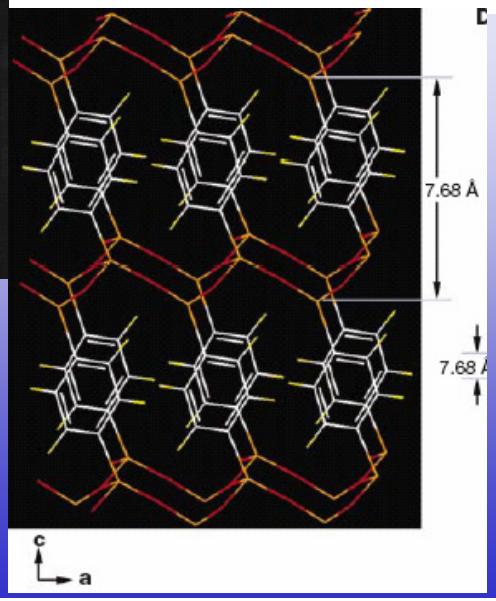

Using a bridging precursor results in 2D Hexagonal channels

…with ordered phenyl residues !

Inagaki et al.
Nature **2002**

Synthesis of non-silica oxides

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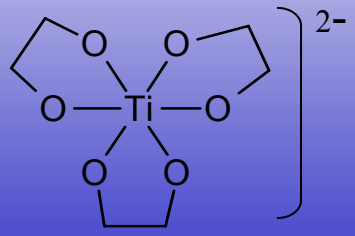
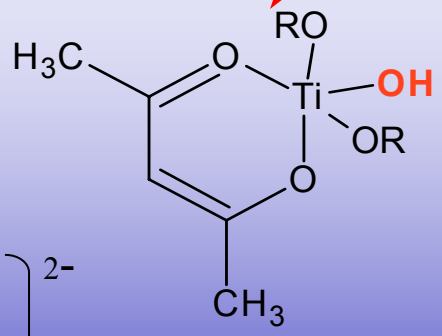
Hinder Condensation

Control Water	Modified Precursors
Nonaqueous Media (Stucky/Ozin)	**Complexation (Ying/Amoros/On)**

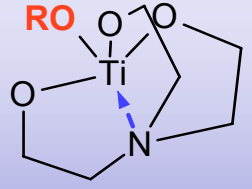
$TiCl_4$ / EtOH
Atmospheric H_2O
EISA

1 - Ti(O-*i* Pr)$_4$ / Etgli / NaOH
2 - H_2O

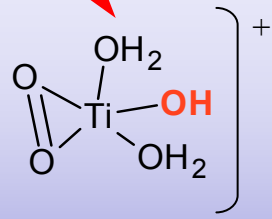




acacH



TEA



Peroxide

Ligand-Assisted Templating (Ying)

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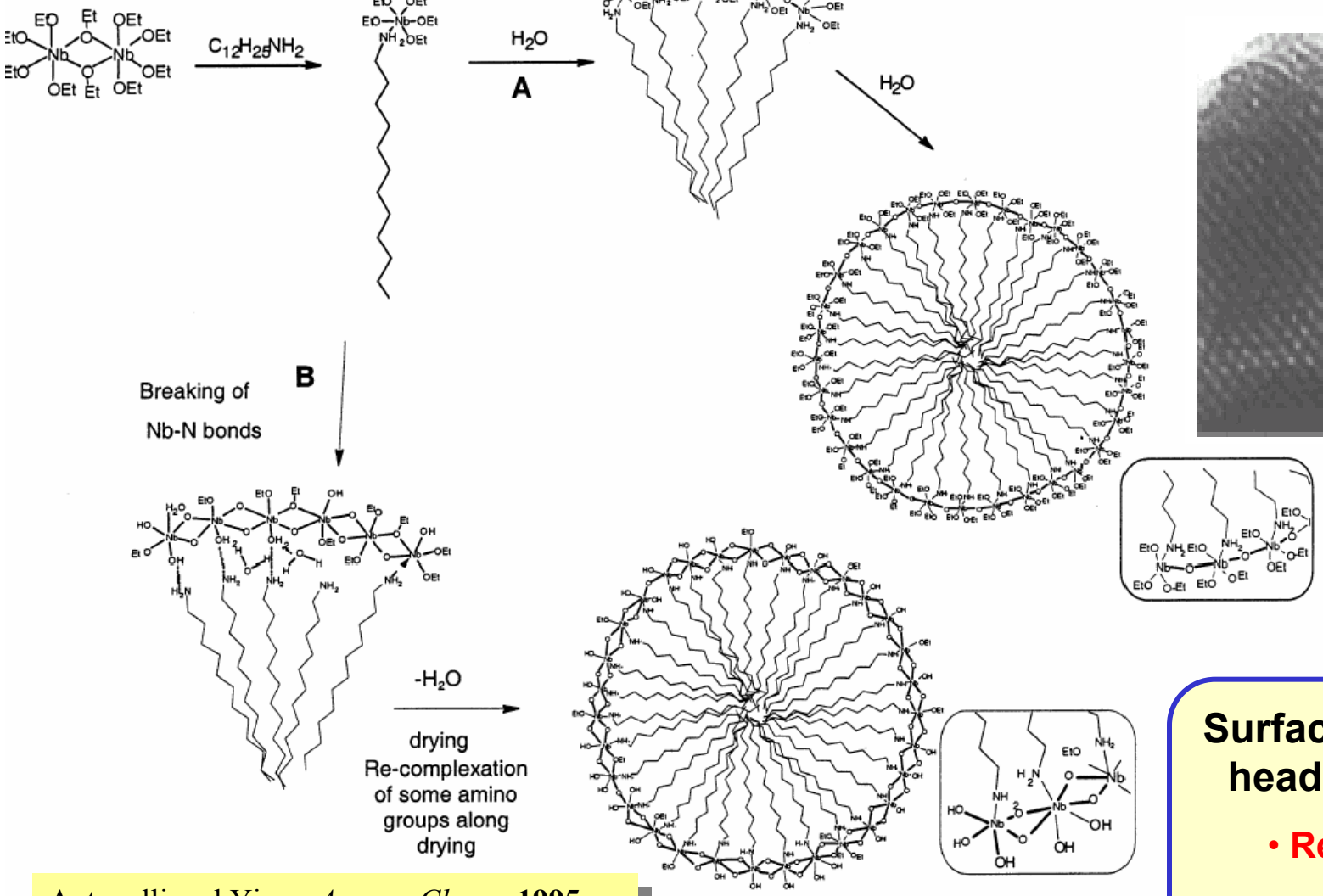

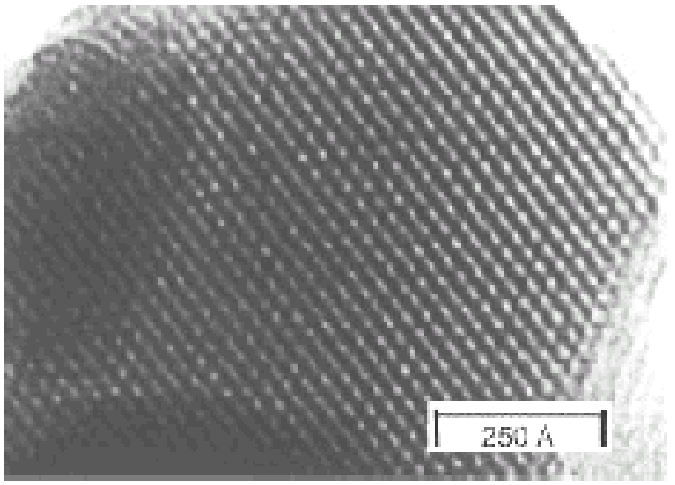

Antonelli and Ying., *Angew. Chem.*, **1995**

Surfactant with complexing head (amino, phosphate)

- **Retards condensation**
- **Creates a "pre-structure"**

Evaporation-Induced Self Assembly

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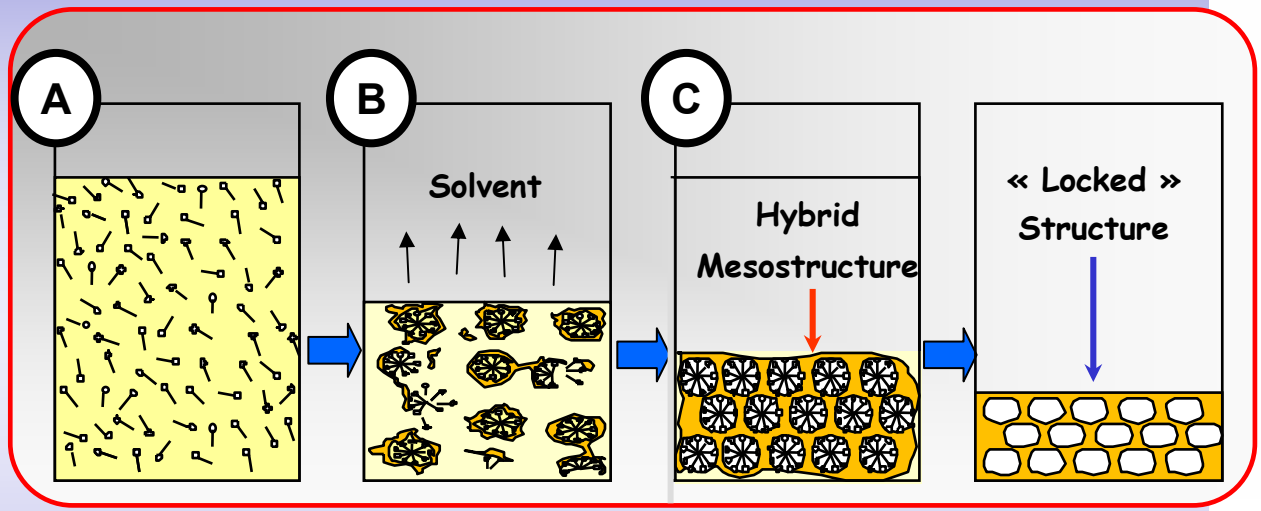
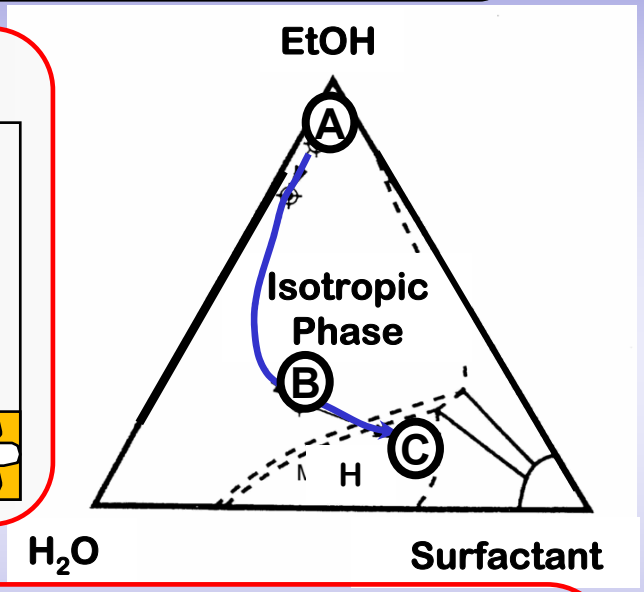
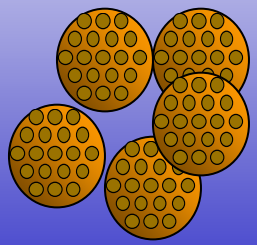
Templated Phase upon Drying
Creation of a Hybrid Liquid Crystal

« Locking » of a Robust Phase upon processing

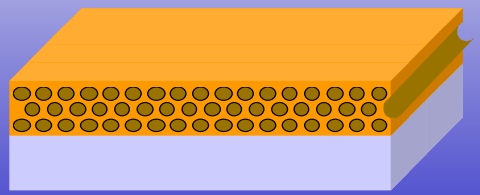




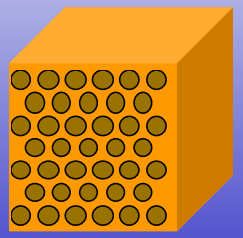
Particles (aerosol)



Films or **Fibers** (*dip* or *spin coating, extrusion*)



Xerogels by controlled evaporation



C.J. Brinker *et al.*, *Adv. Mater.*, **1999**

Oriented SiO_2 Mesostructured Gels

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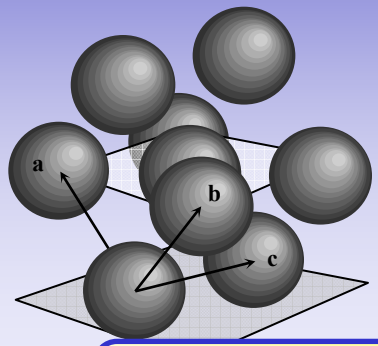
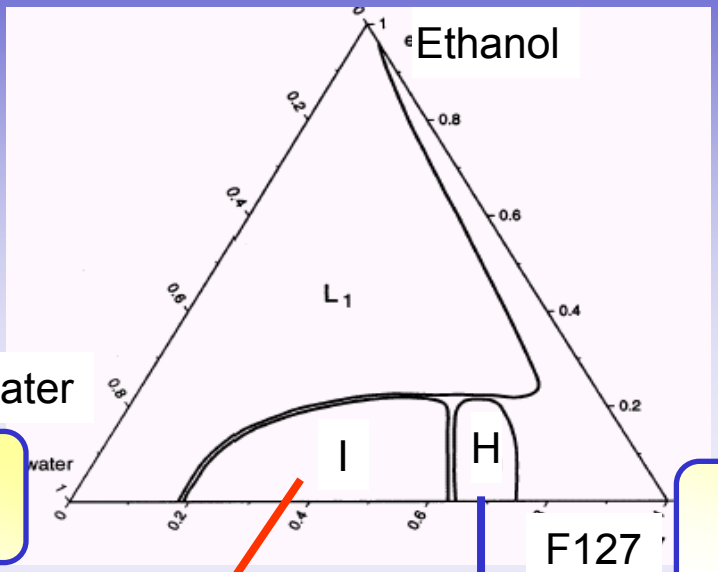
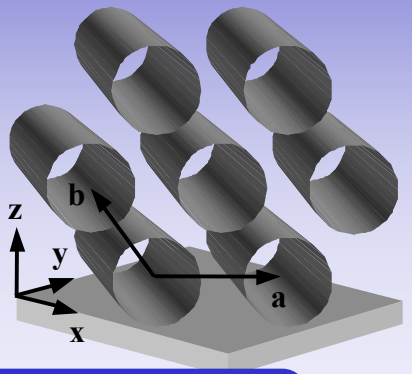
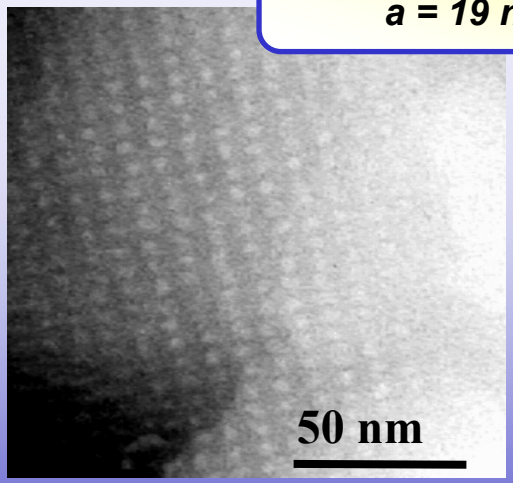


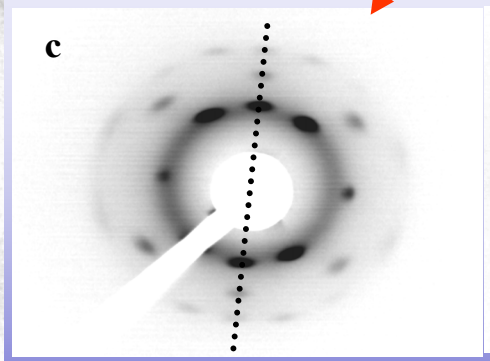
Cubic
***a* = 19 nm**

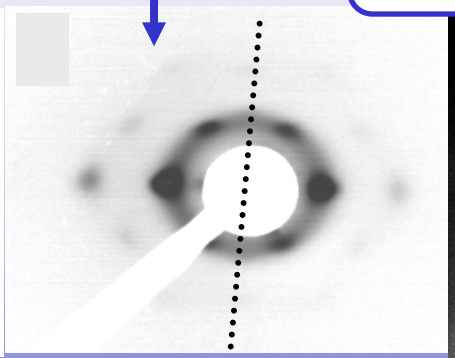


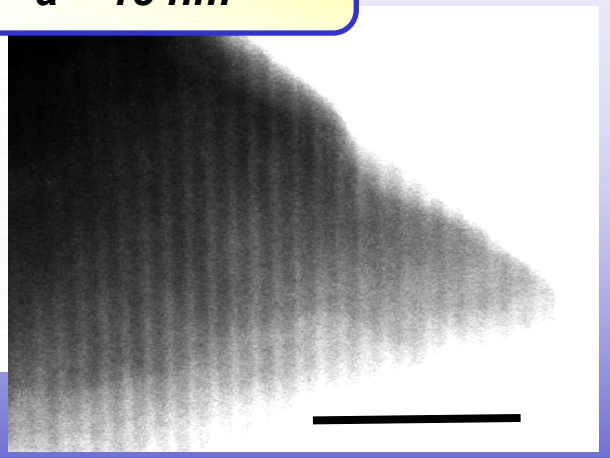


2D Hex
***a* = 18 nm**



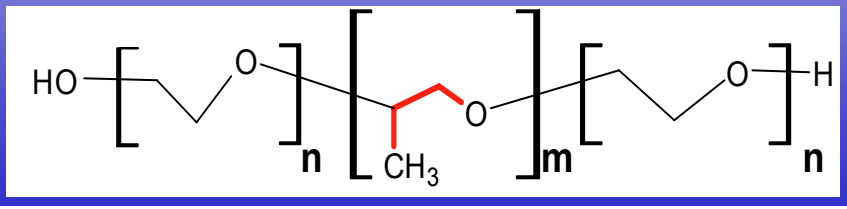






Melosh et al. *Macromolecules*, 1999

Soler-Illia et al. *Chem. Commun, 2002, 2298*



The SBA secret recipe

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August 2005

EISA

- ✓ M(IV) precursors
- ✓ Nonionic Surfactants as templates
- ✓Nonaqueous media
- ✓ DRY CONDITIONS
- ✓ Wide range of compositions possible (potentially)

Generalized syntheses of large-pore mesoporous metal oxides with semicrystalline frameworks

Peidong Yang*, Dongyuan Zhao*†, David I. Margolese*, Bradley F. Chmelka†‡ & Galen D. Stucky*†

* *Department of Chemistry and Materials,* † *Materials Research Laboratory,* ‡ *Department of Chemical Engineering, University of California, Santa Barbara, California 93106, USA*

sation rates as demonstrated for TiO_2 (ref. 11). We have adopted a procedure that can regulate the hydrolysis/condensation and self-assembly processes simultaneously. We anticipate that with this method, the syntheses of other mesoscopically ordered inorganic compounds (including sulphides[16]) should also be possible.

Important!! To control the hydrolysis/condensation And To compatibilze species at the interface (to be continued)

Mesoporous Thin Films

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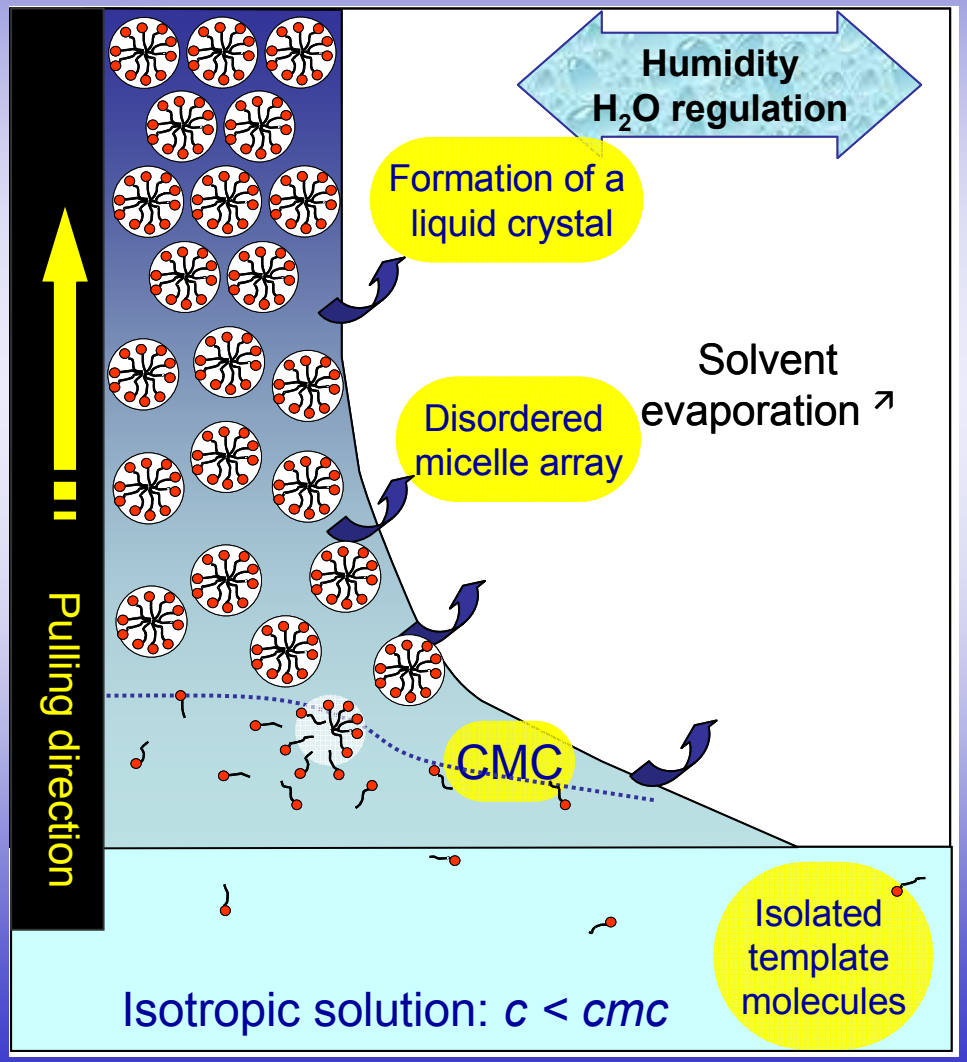
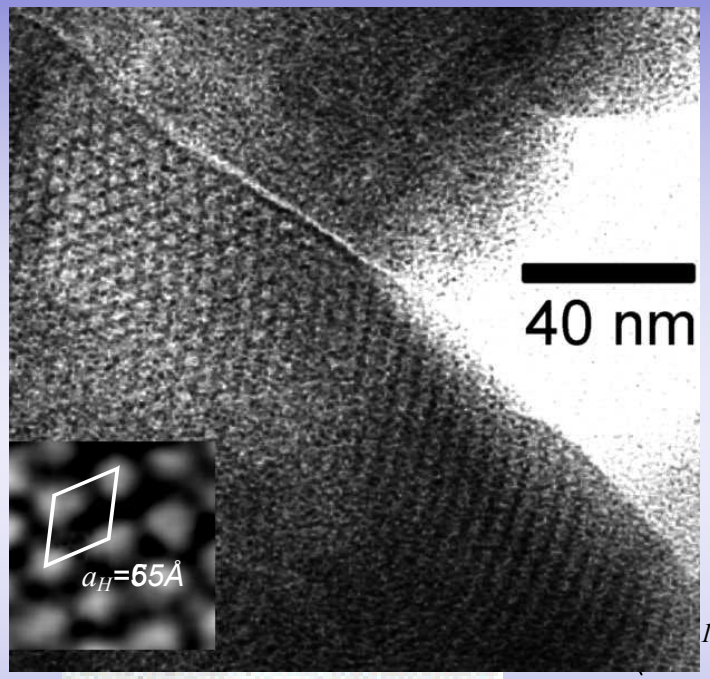
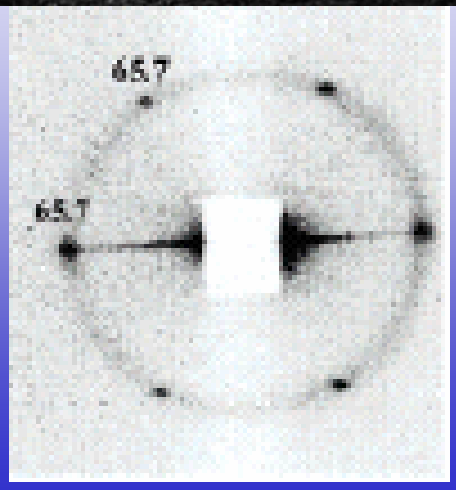
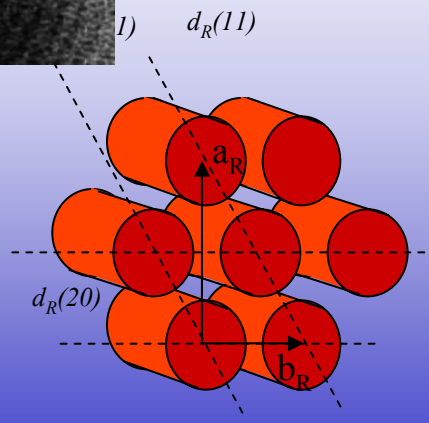




(2D Hex)





2D-hexagonal

Multifunctional Porous Materials

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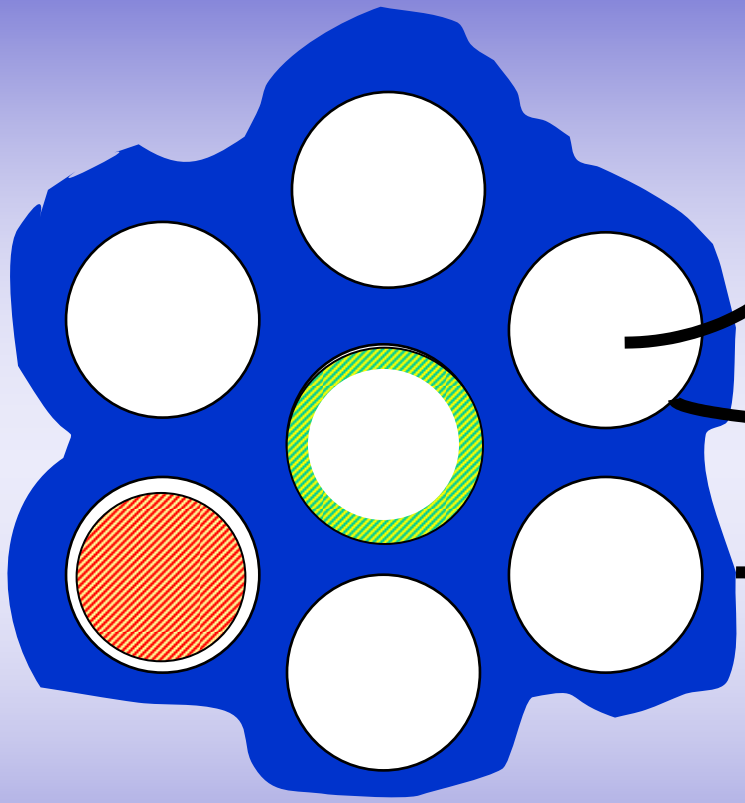
August 2005



Pore System
- Symmetry
- Size
- Shape
- Accessibility
- Inclusions

Pore Surface (Skin)
- Surface features (acidity,…)
- Organic Modifiers

Inorganic Framework (Bones)
- Crystallinity
- Bulk properties (n,)
- Wall Thickness
- Wall Nature (porosity, composition)

- *Changing the Skeleton (TM or Mixed Oxides)*
- *Changing the Pore Skin (Functions)*
- *Including Nanospecies within pores*

Key Aspects of MesoStructure Formation

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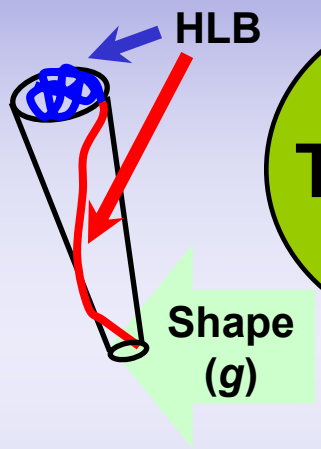


Template

Inorganic

Chemical Features

Hydrolysis
Condensation
Complexation
Charge

Interactions
(Hybrid Interface)

Tuning of

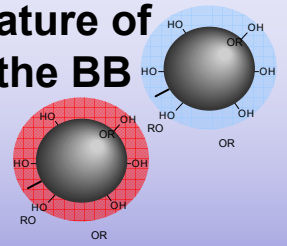
- ✓ Micellization
- ✓ Condensation
- ✓ Nanosegregation

Self-Assembly

Sol-Gel

Phase Diagram

Nature of the BB



Solvent

Polarity

Specific Interactions
Complexation

Lessons for success

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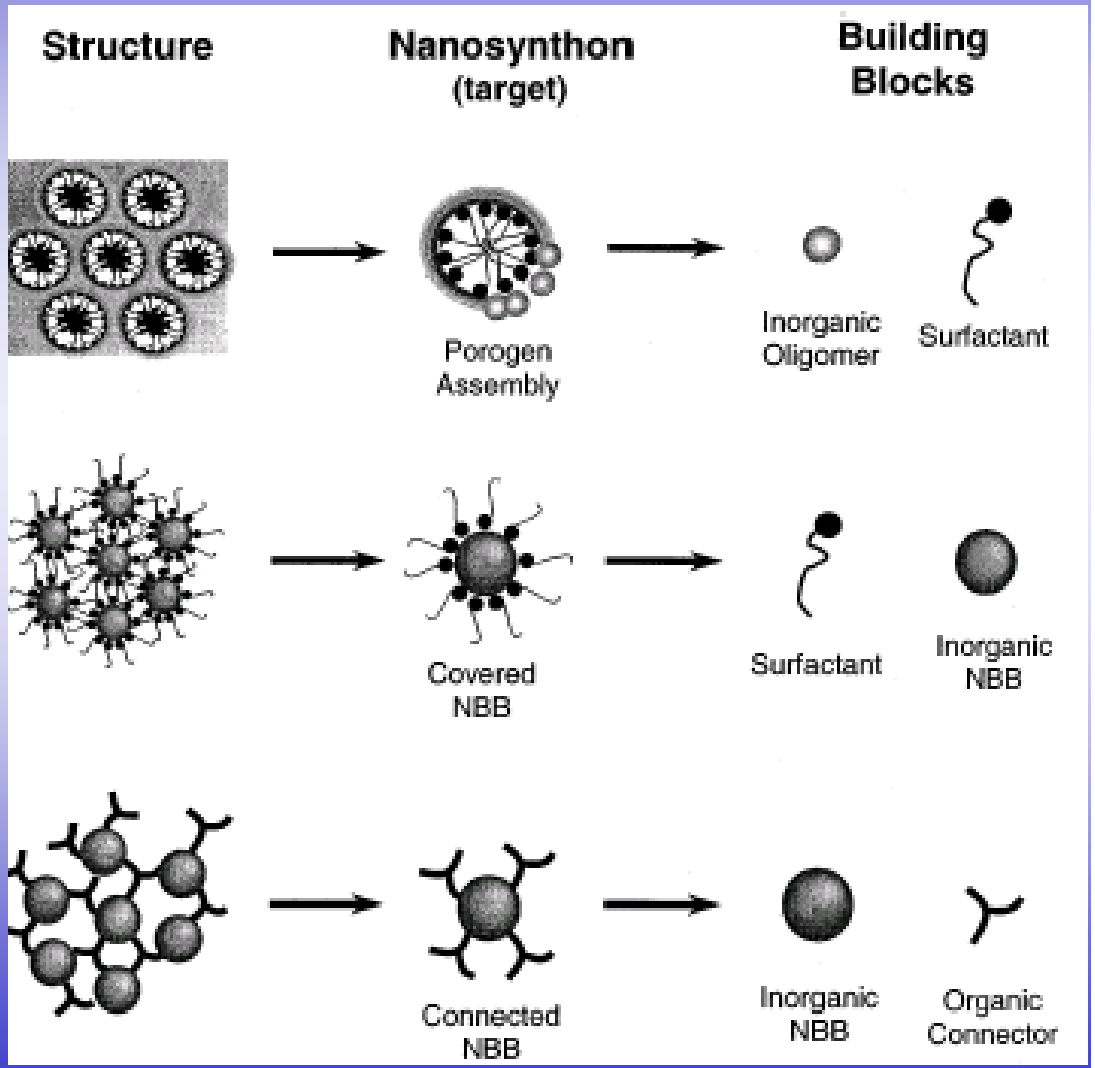
- Know your Building Blocks
- Combine them Wisely
- Take Kinetics into account
- Design your material



Soler-Illia *et al.*, *Chem. Rev.*, **2002**

Colloidal crystal templates

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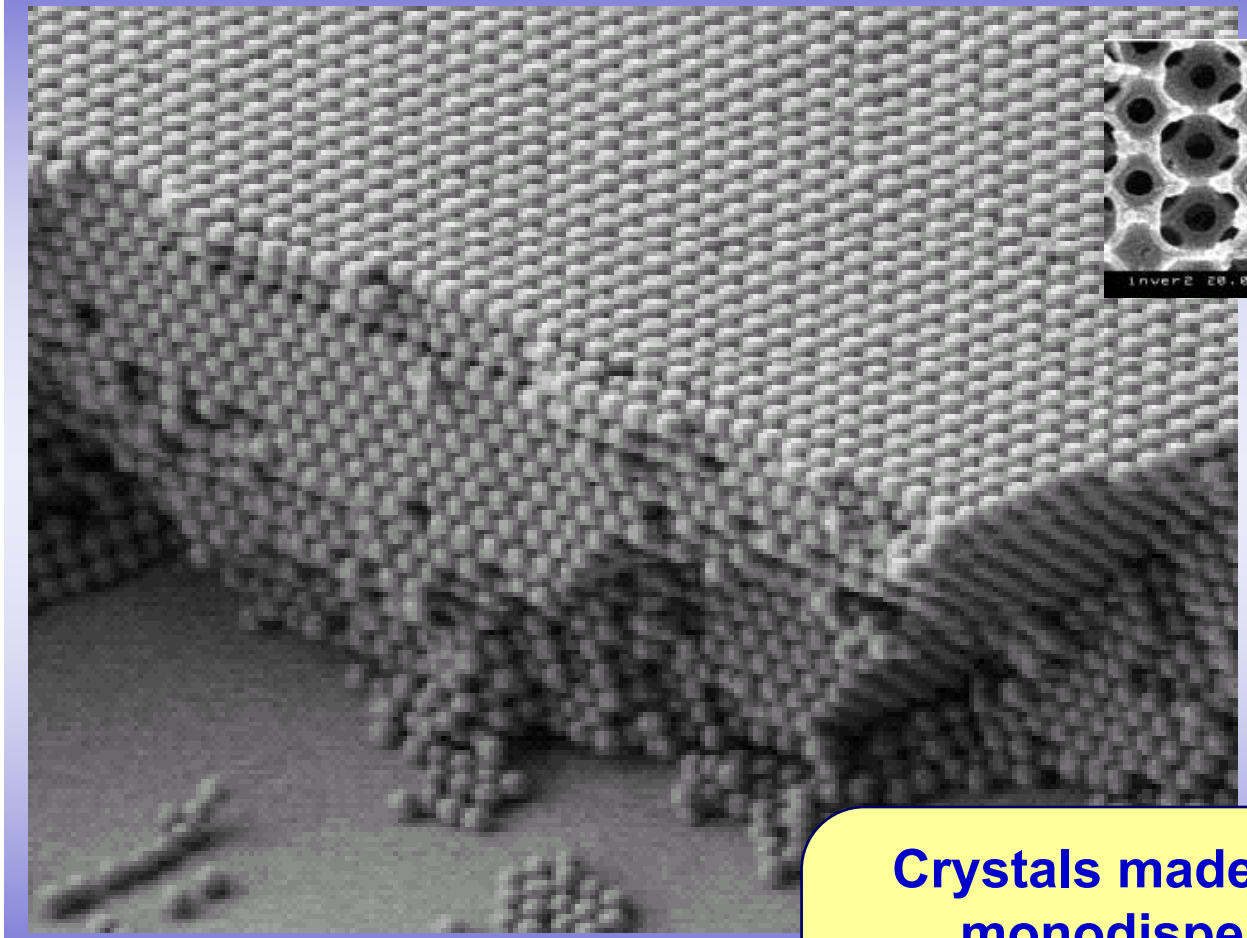

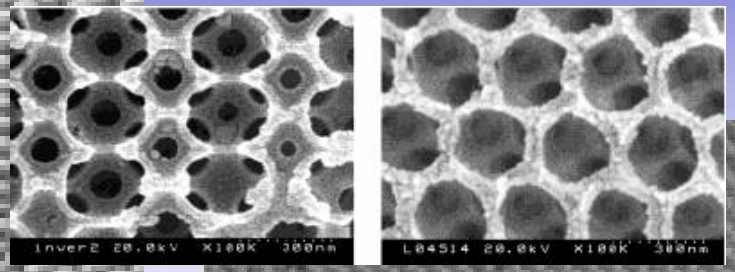

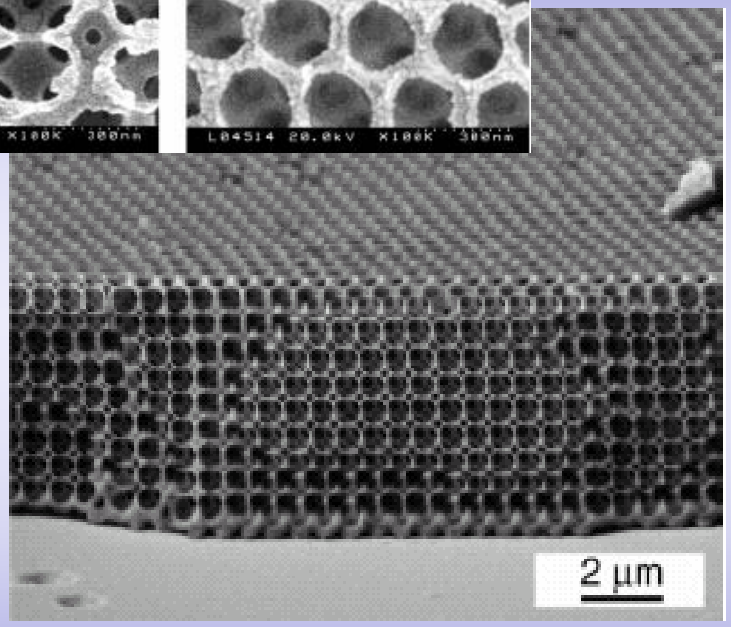

Crystals made up of ***cubic arrangements*** of monodisperse SiO_2 or latex nanoparticles

Optical properties: Photonic Band Gap

Can be filled by a ceramic precursor

⇒ Ordered Macropores

D.J. Norris, *Adv. Mater*, 2004 (Review)

"Know your Building blocks and use them"

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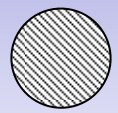
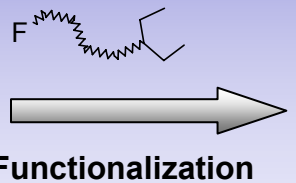
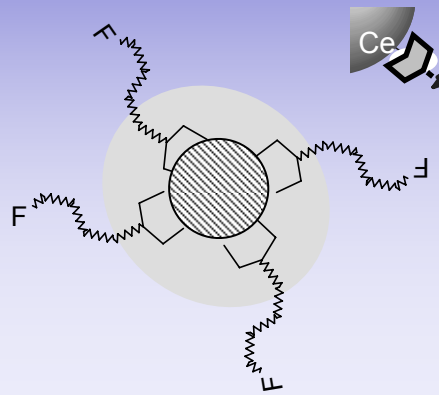
August 2005

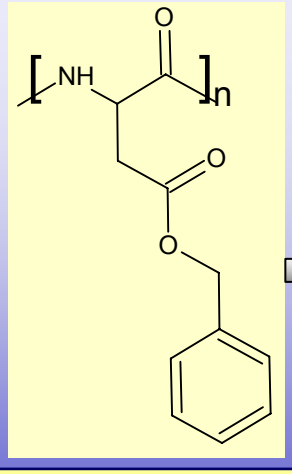
Nano-CeO_2
Stabilized
colloid



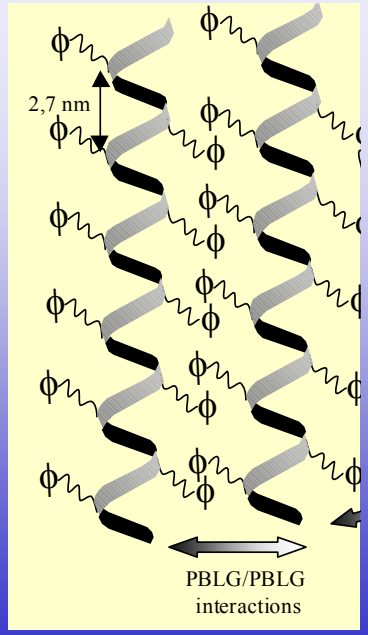




Functional
Nano-CeO_2
F=
Alkyl
Phenyl
…



solvent



PBLG coils
in an α-helix

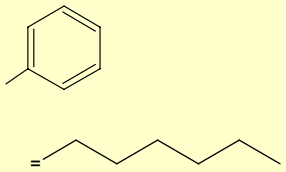
Organic BB
Poly-benzyl-L-glutamate
PBLG

Using nanoceria building blocks and biomimetic polymers to control morphology

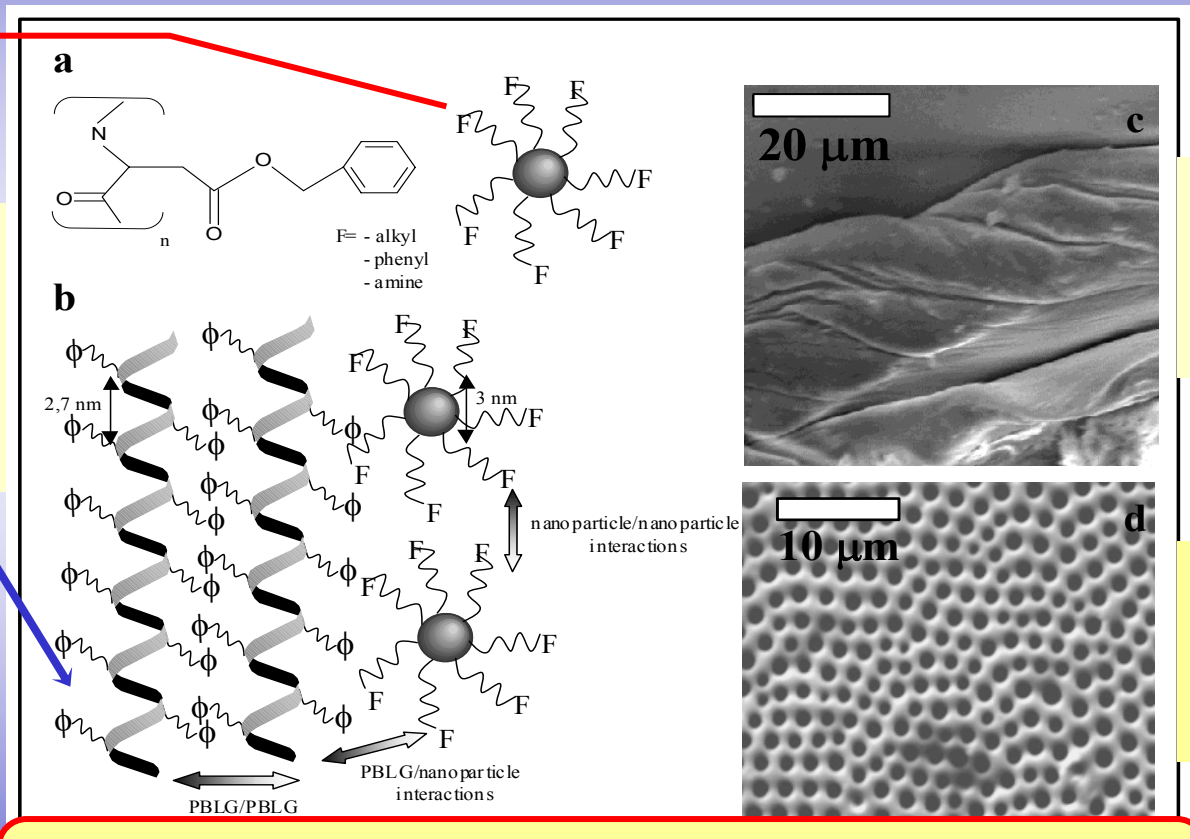
CSI-ICMR/UCSB
2005

Functional Nanoparticle
Nanoceria 2-5 nm

Functions



Modified Polypeptide



Template folding dominates

Coils and corkscrews

Template-NB dominates

Array of Micronic holes

Set of POLYMERS + NANOPARTICLES + MODIFIERS=

TOOLBOX TO CONTROL MORPHOLOGY

Bouchara *et al.*, *Chem. Commun.*, **2002**, *J. Mater. Chem.*, **2004**

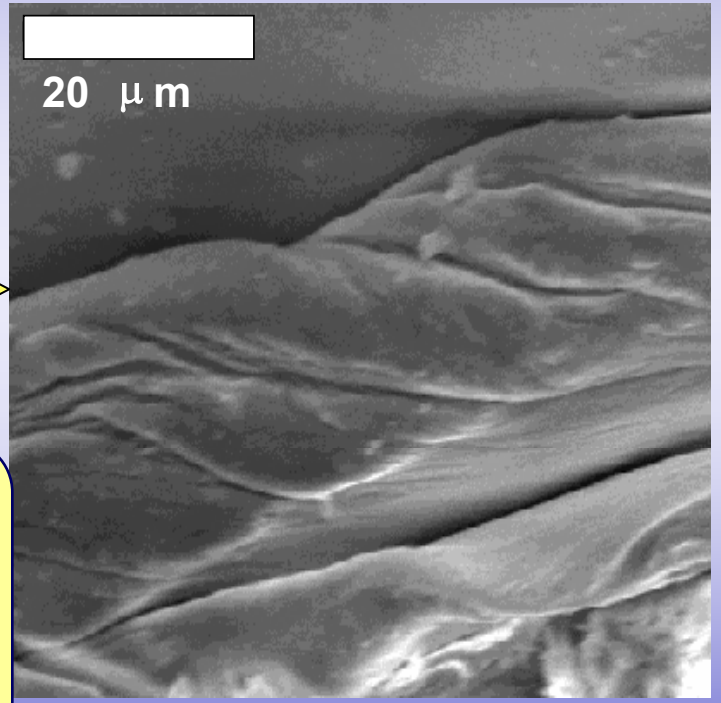
Controlled Interactions from morphology control …

Functional Nanoparticle
Nanoceria 2-5 nm

Modified Polypeptide

PBLG

Low NBB/PBLG
Polymer/polymer interactions dominate
NBB « decorates » PBLG
Twisted CeO_2 fibers



Bouchara *et al.*, *Chem. Commun.*, **2002**, *J. Mater. Chem.*, **2004**

…to phase segregation

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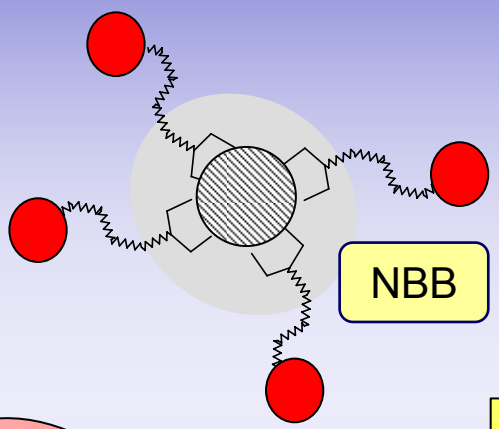
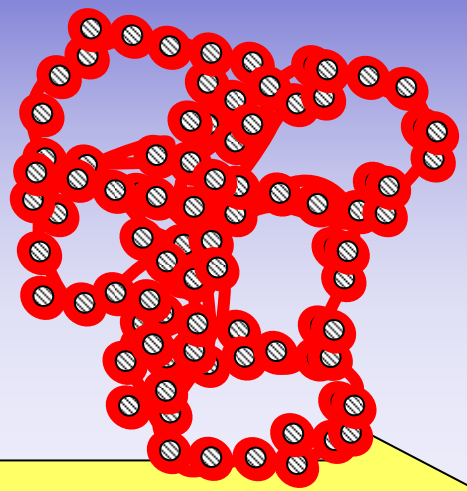
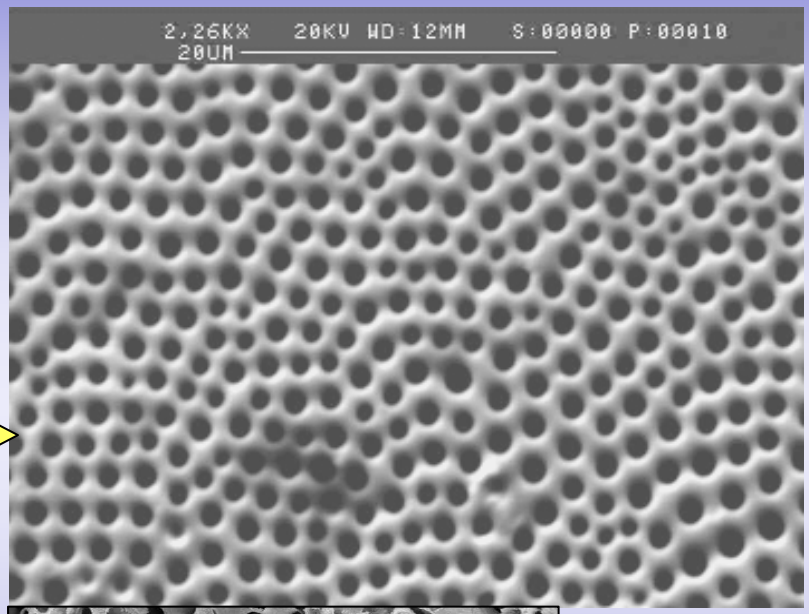
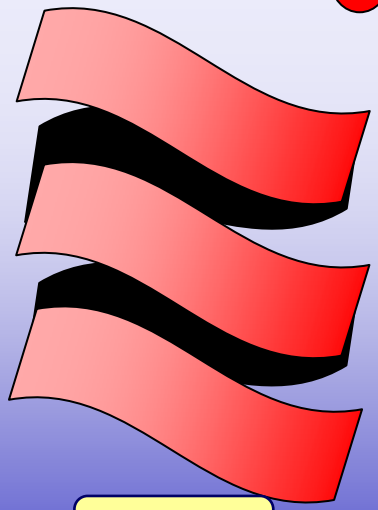
August 2005



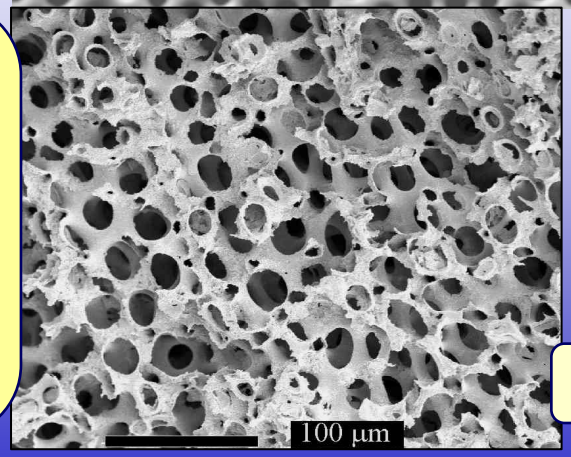






High NBB/PBLG ratio
NBB/polymer interactions dominate and disrupt coiling

Solvent drops segregate **Macroporous CeO_2** by spinodal phase separation



Sea urchin

Controlled Phase Segregation and complexation NBB go Macrotextured

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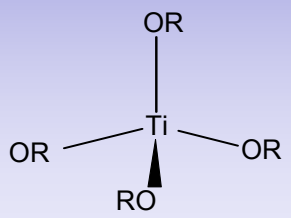
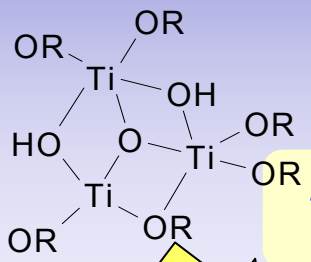
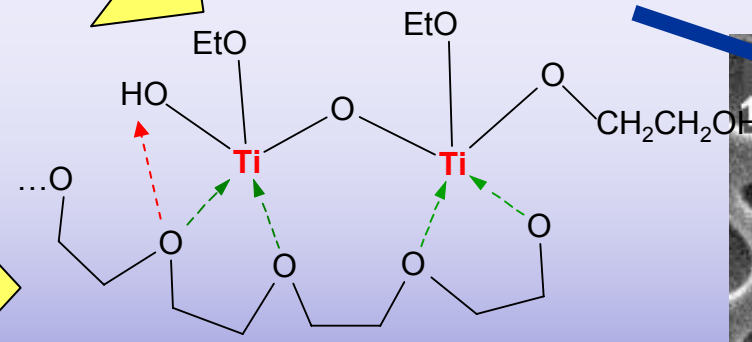


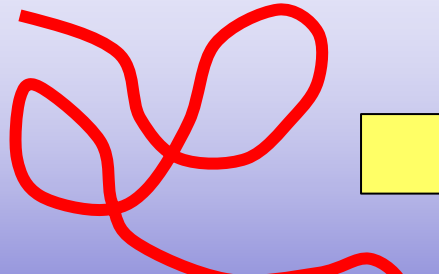
h < 1



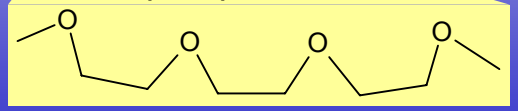
hydrophobic Ti-oxo clusters

- ***Macroporous Oxides***
- ***Micron scale compatible with biospecies (enzymes, membranes, antibodies, cells)***

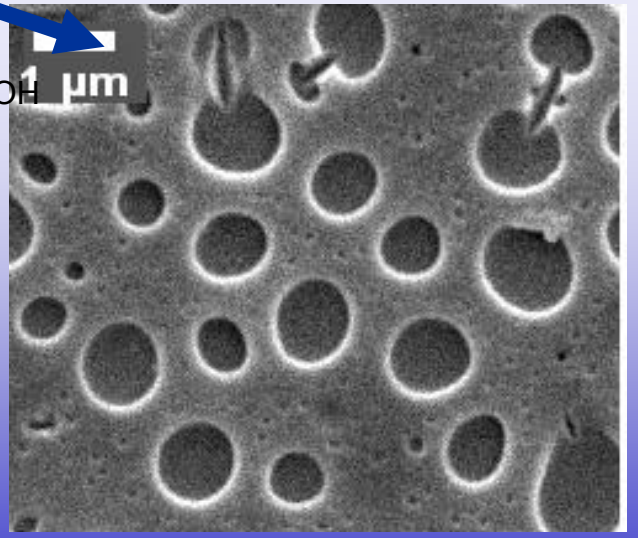




Poly ethylene glycol
(PEG)

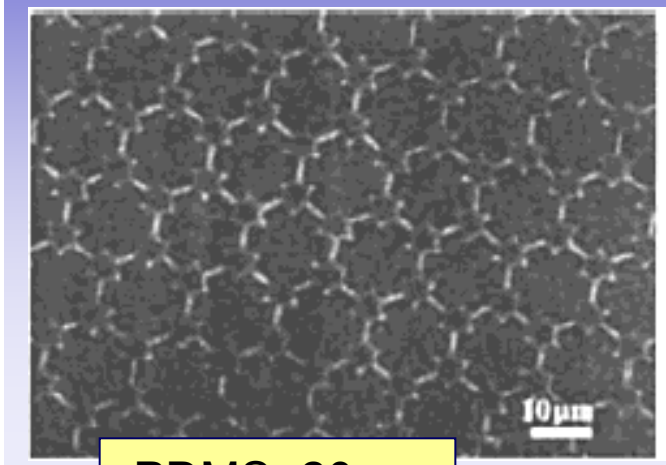


- ***Clusters associate with PEG***
- ***Solvent phase segregates (spinodal)***

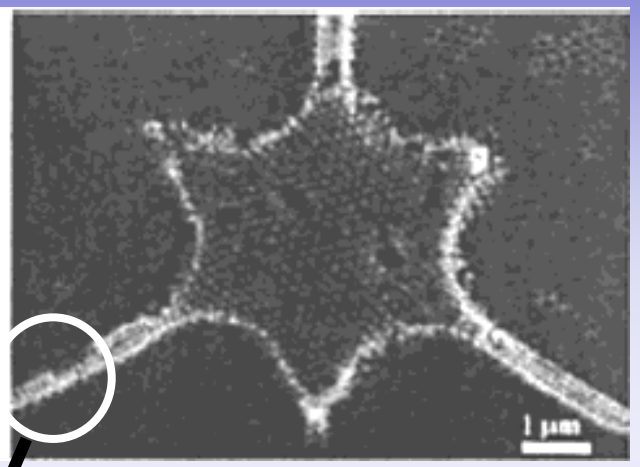


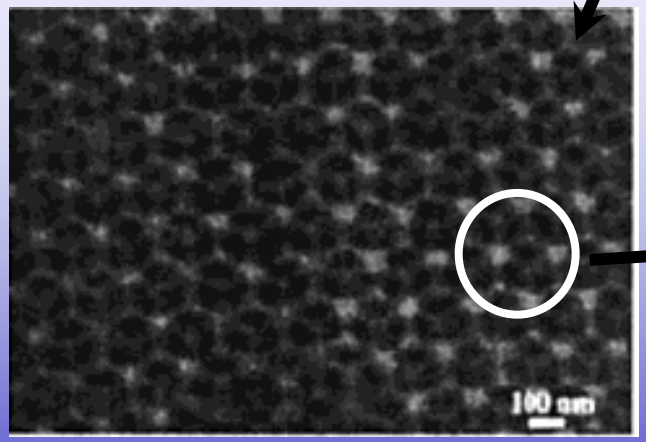
Fuertes and Soler-Illia, work in progress
Nakanishi., *J. Porous Mater.*, **1999**

Hierarchical systems
Order at different scales

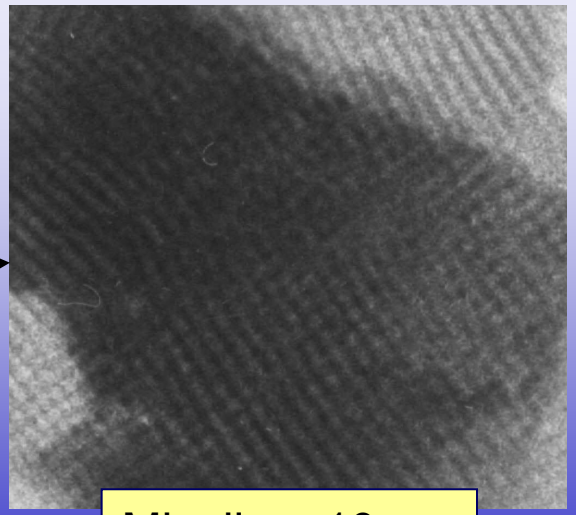


PDMS~20µm



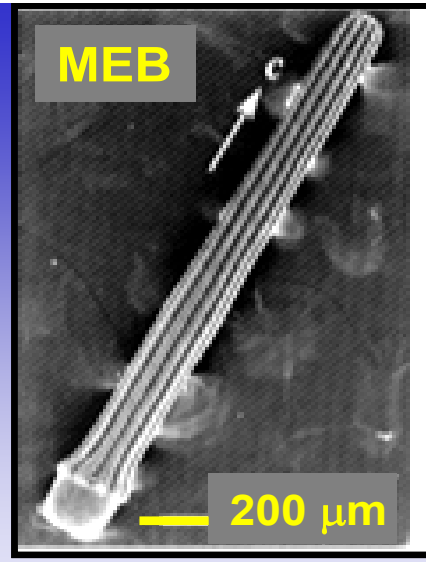


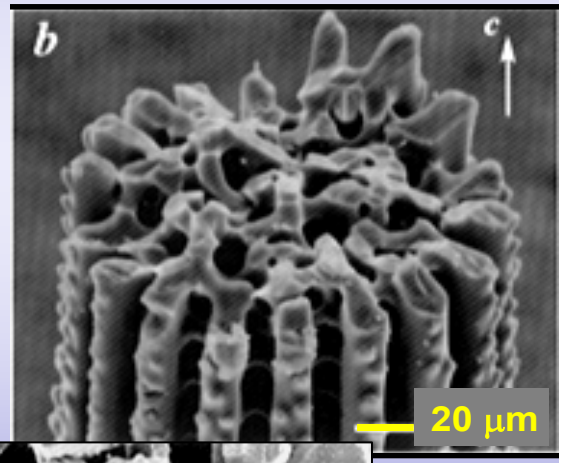
Colloidal Latex ~200nm

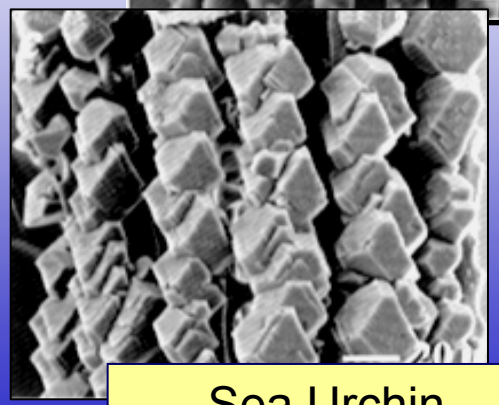


Micelles~10 nm

Stucky/Chmelka/Whitesides







Sea Urchin

Pathways towards Organized Matter

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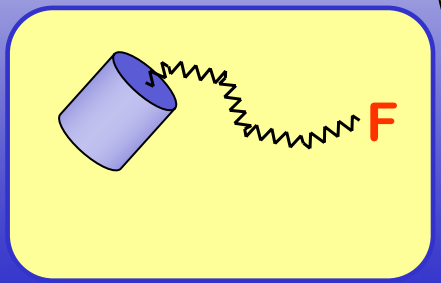
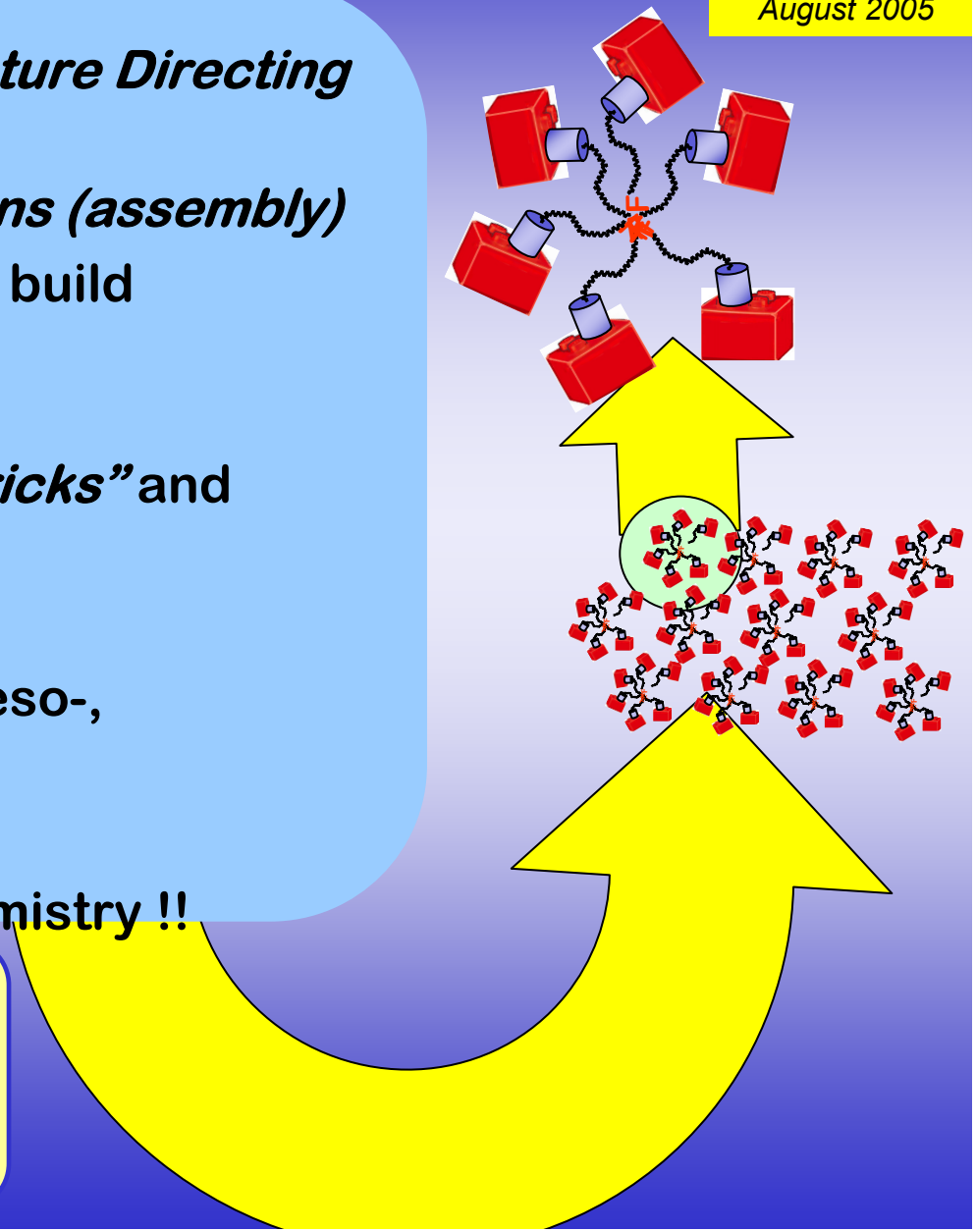
- *Generate Building blocks* and *Structure Directing agents (templates)*
- Control on *chemistry* and *interactions (assembly)*
- *Integrate Templating techniques* to build *Hierarchical Materials*

- Room for Synthesis of *Inorganic "bricks"* and *Organic "tweezers"* NBB

- Understanding Structure (nano-, meso-, macroscales)
- Understanding Interactions
- Understanding Mechanisms ⇔ Chemistry !!





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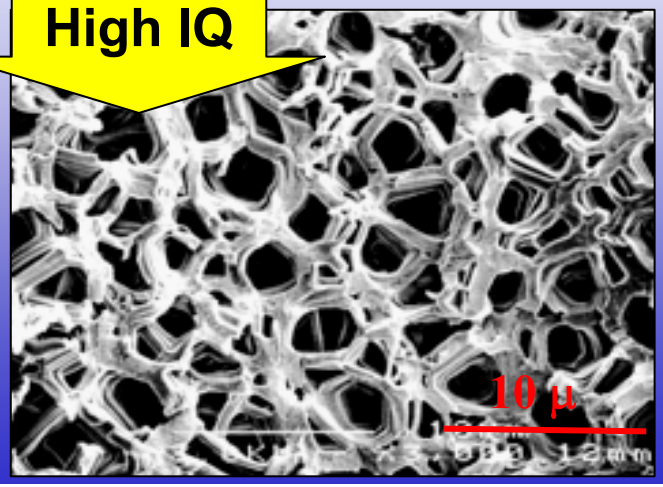
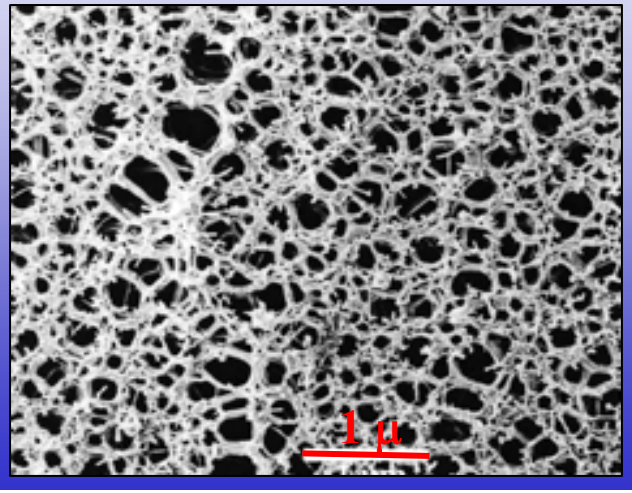
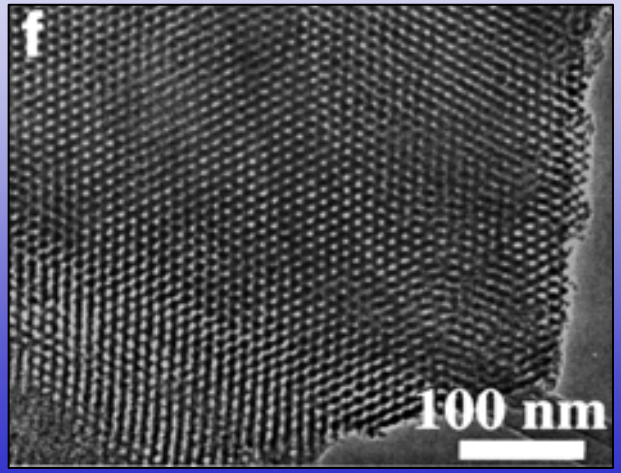
Low IQ

High IQ

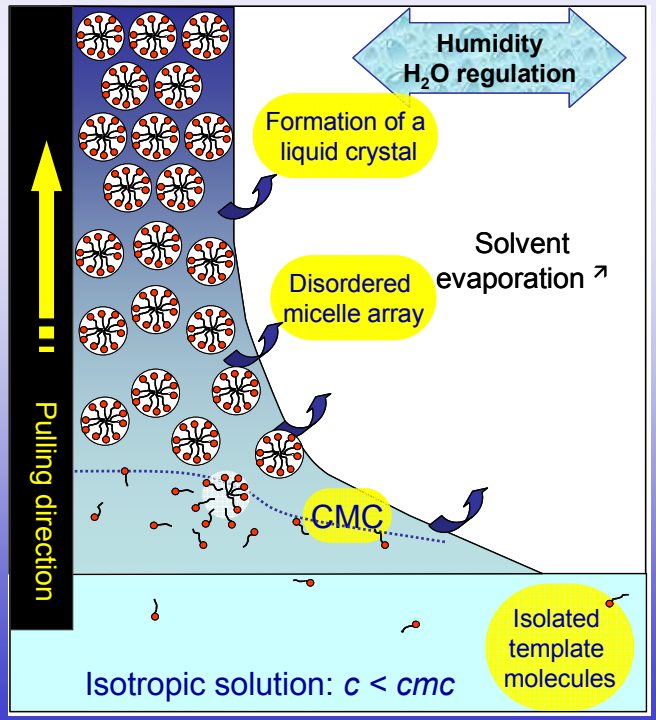


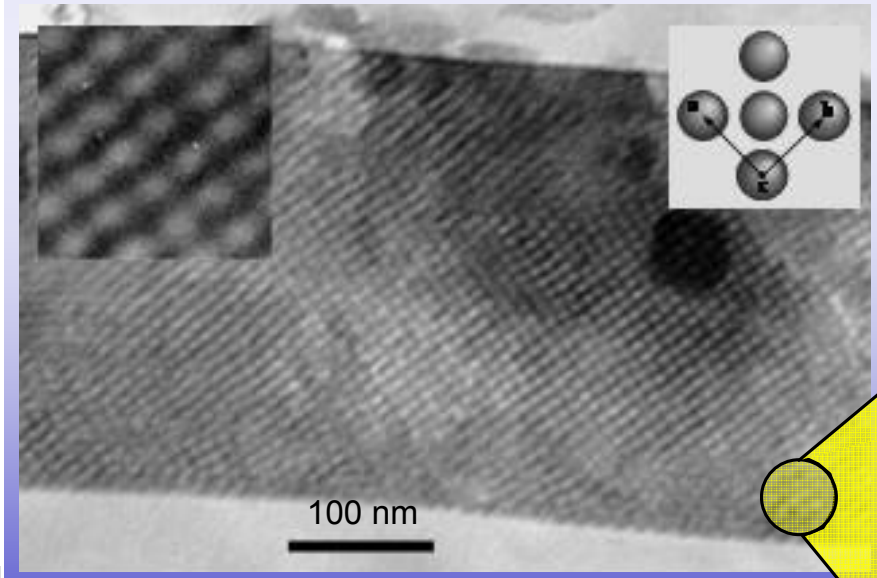


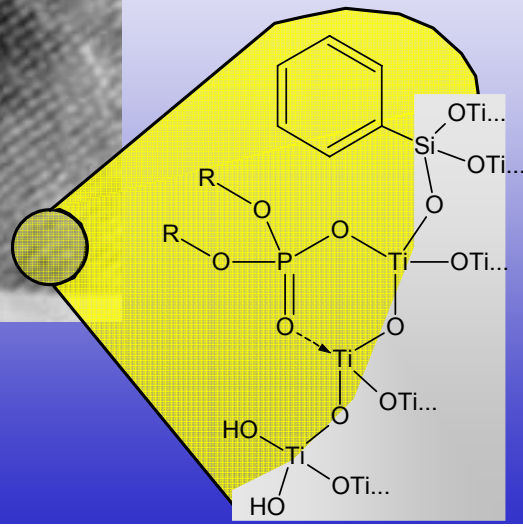


Coming Next…

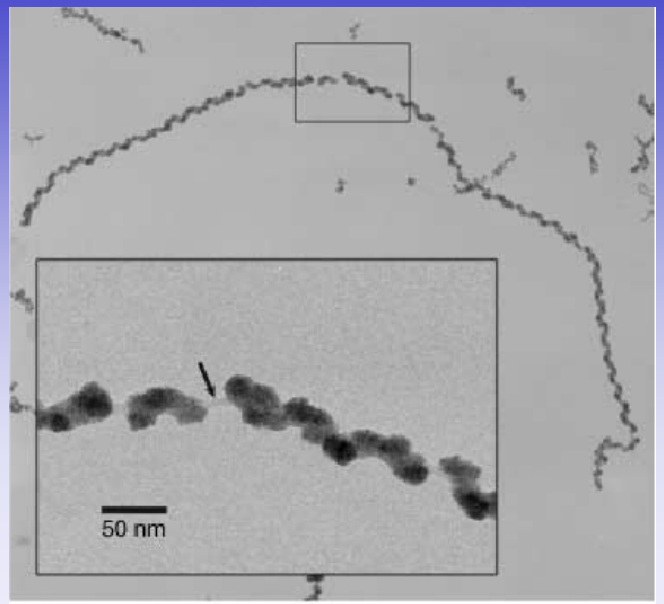
➢Mesoporous Thin Films

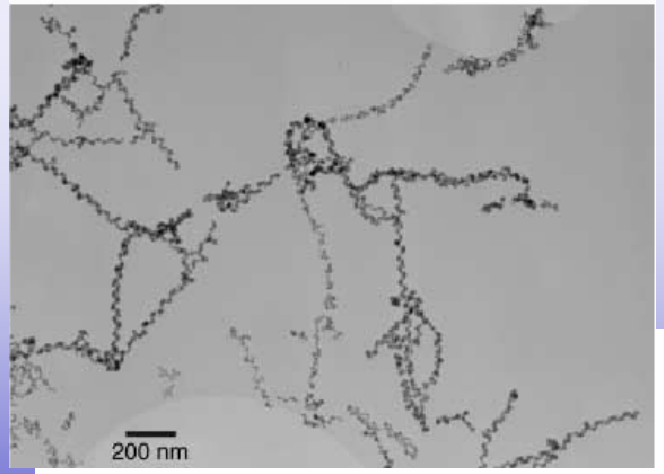


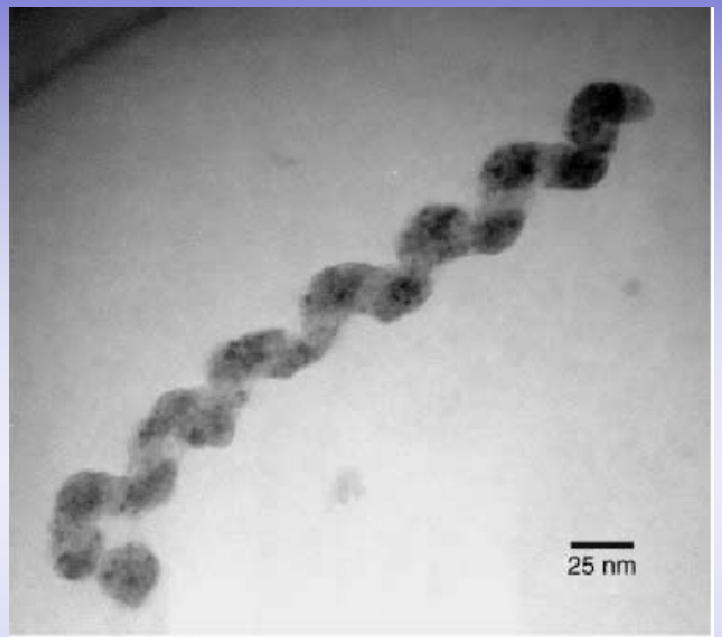




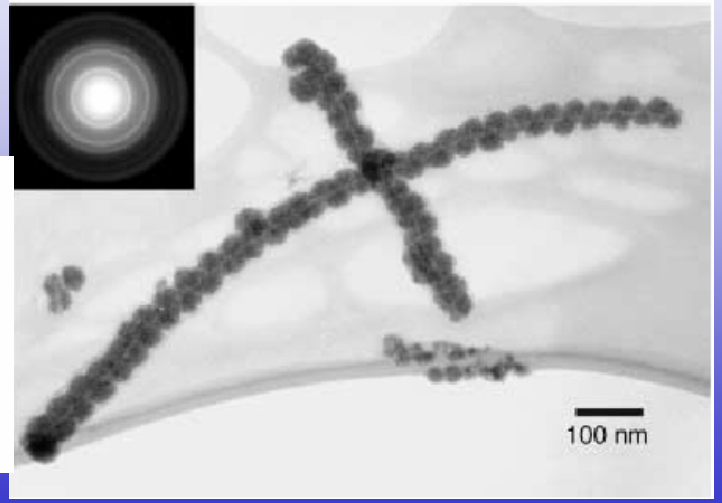
Using Complex molecules to direct Assembly…

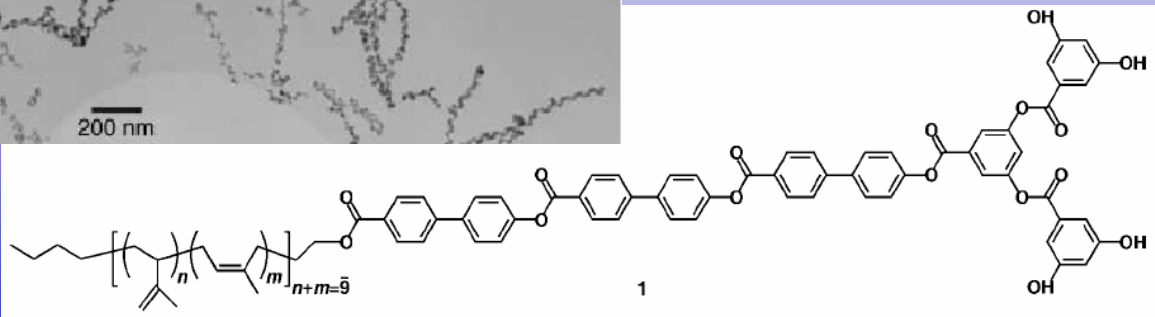






Sone et al., *Angew. Chem*, **2002**





1

...Double helix patterned silica

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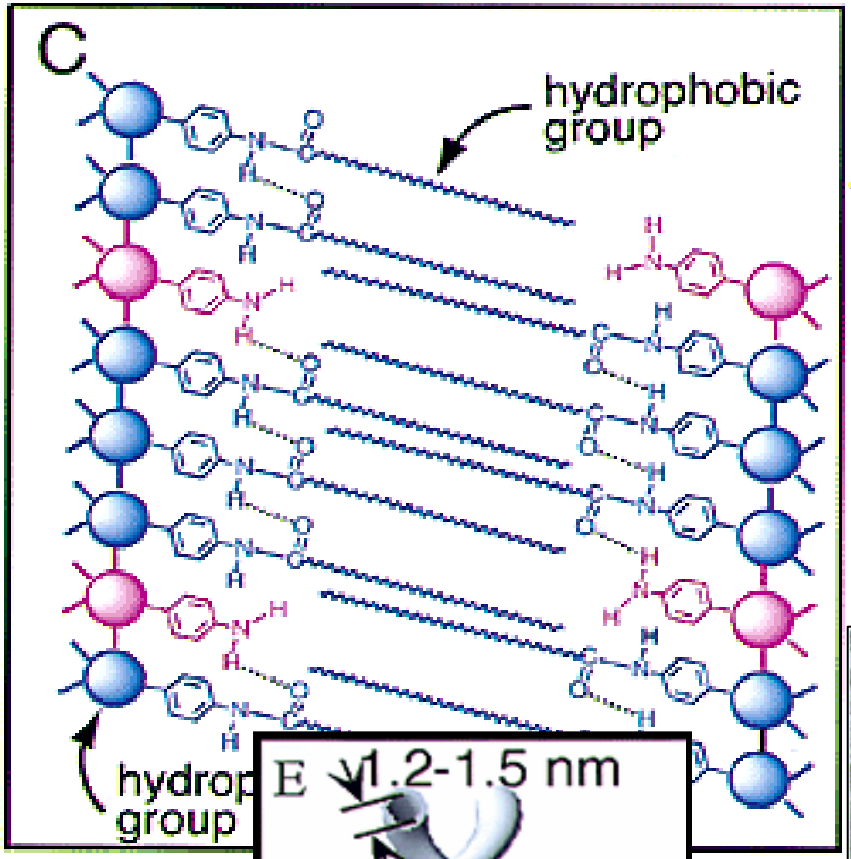
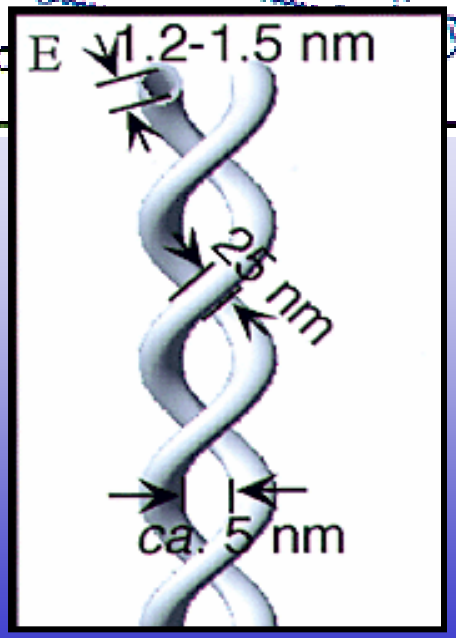
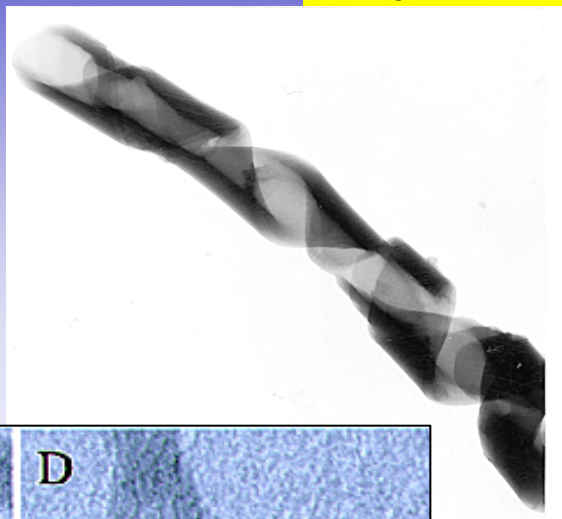
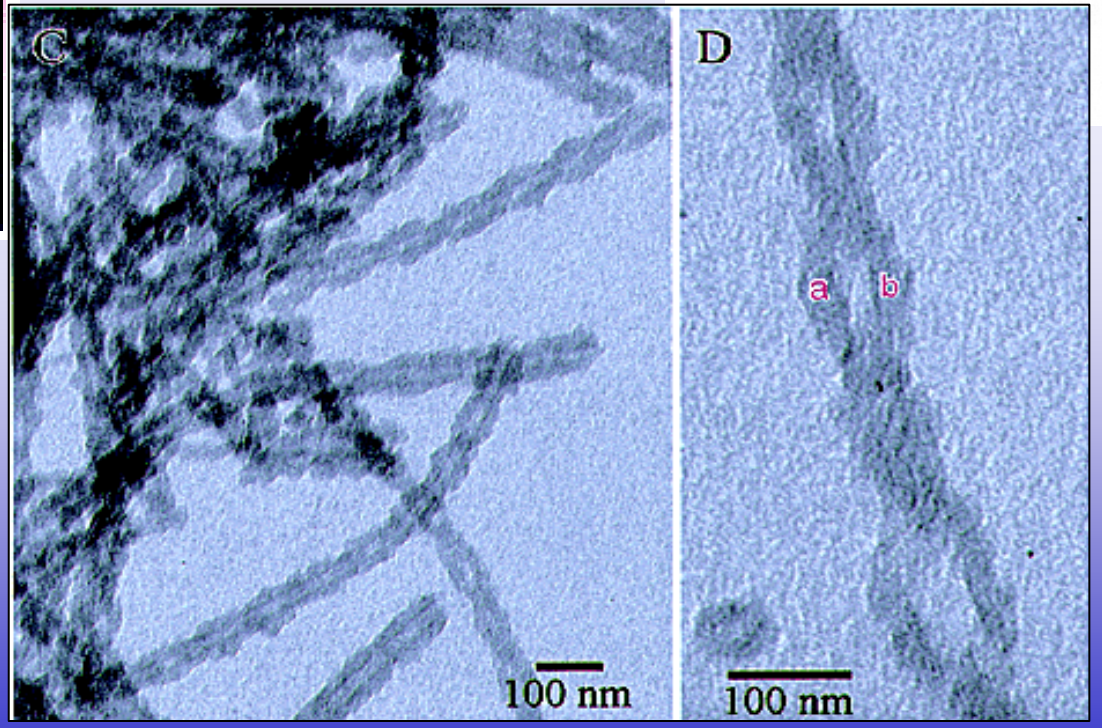
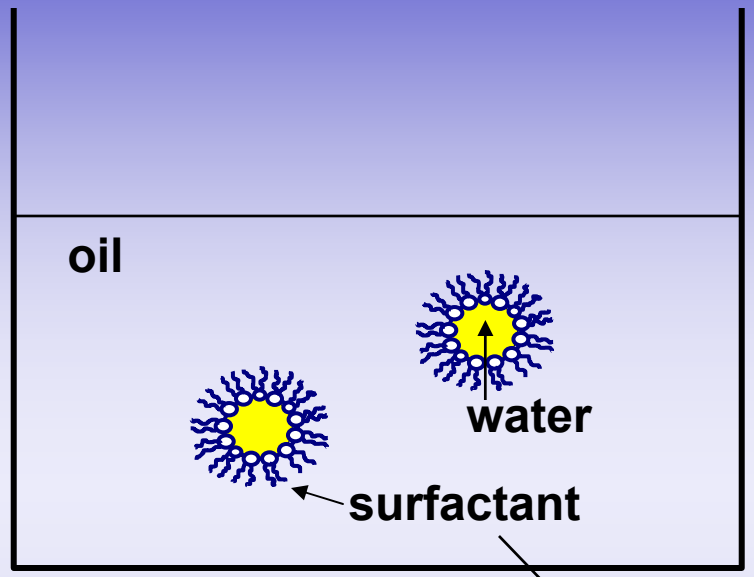








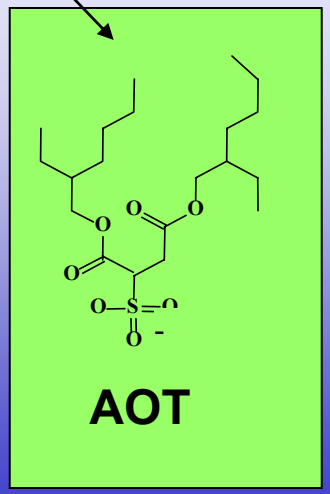
Nanoparticle synthesis in water - in - oil microemulsions
(S. Mann & coworkers)

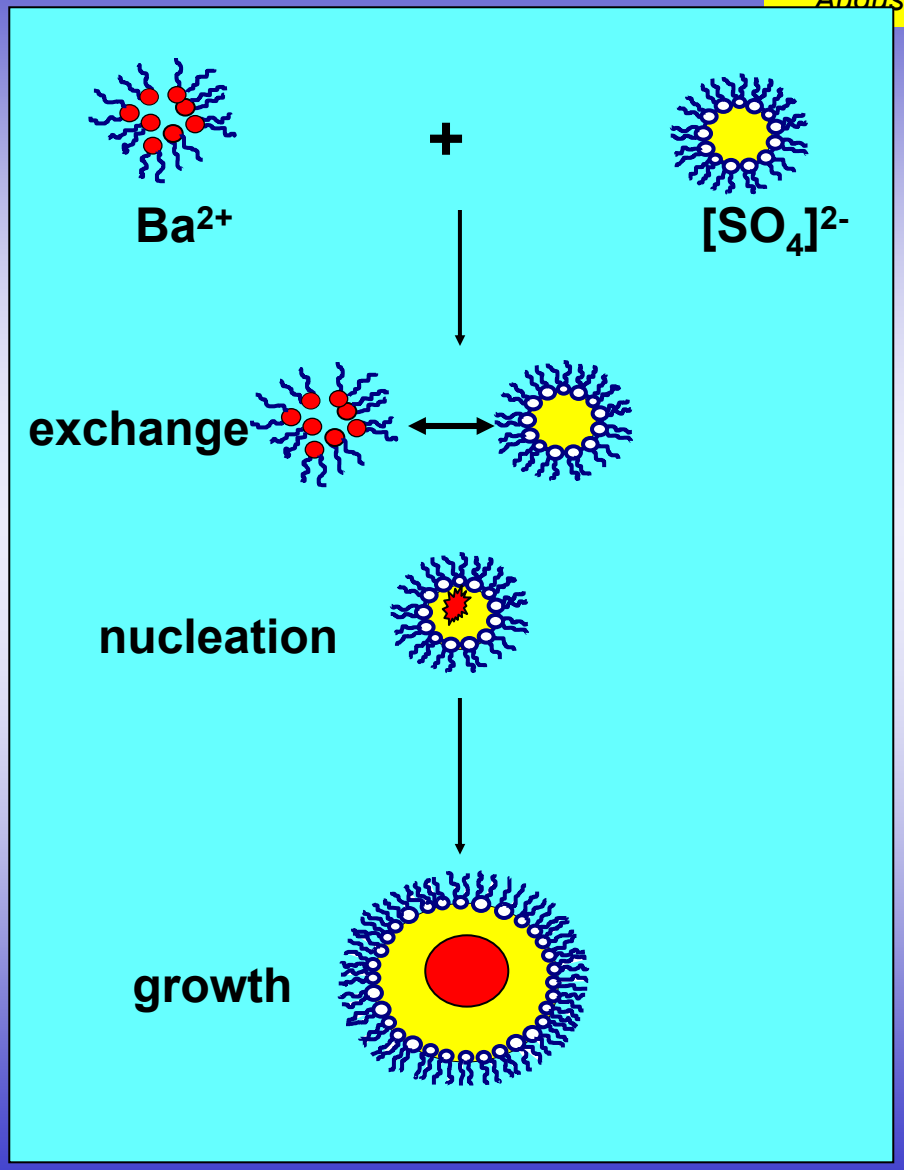


$Ba(AOT)_2$
reverse micelle
$w < 1$; R = 1 nm; N = 20

+

Na_2CrO_4 or Na_2SO_4
microemulsion droplet
w = 10; R = 2.2 nm
100 mM = 3 ions





Controlling the building blocks

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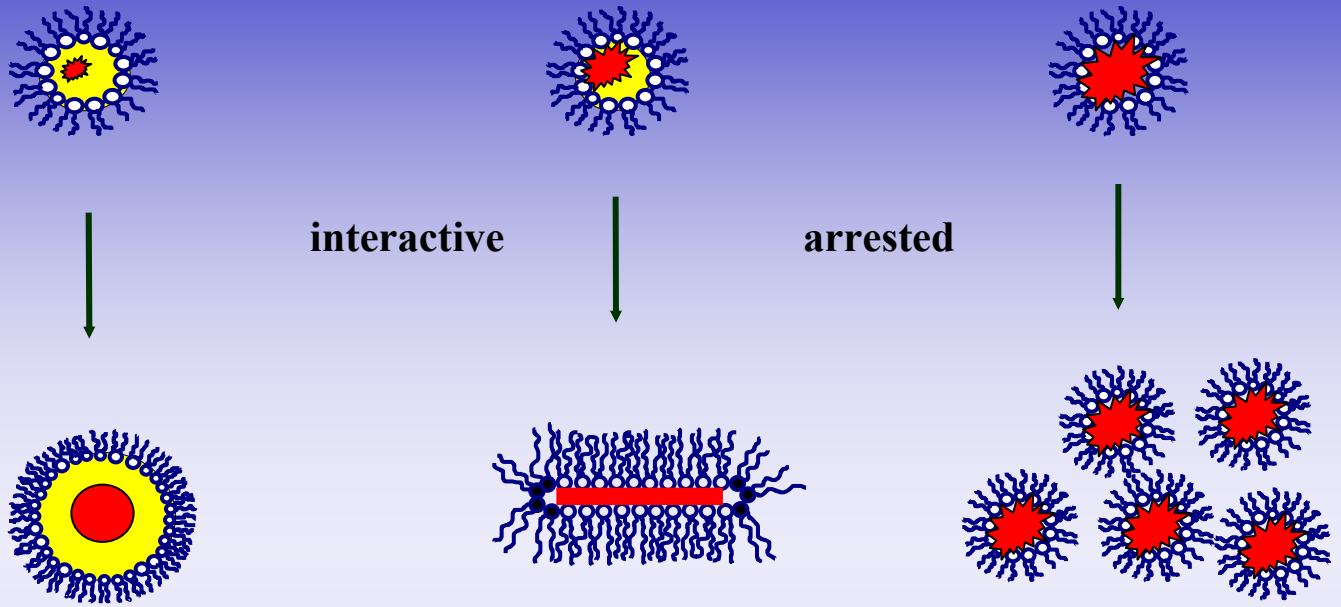
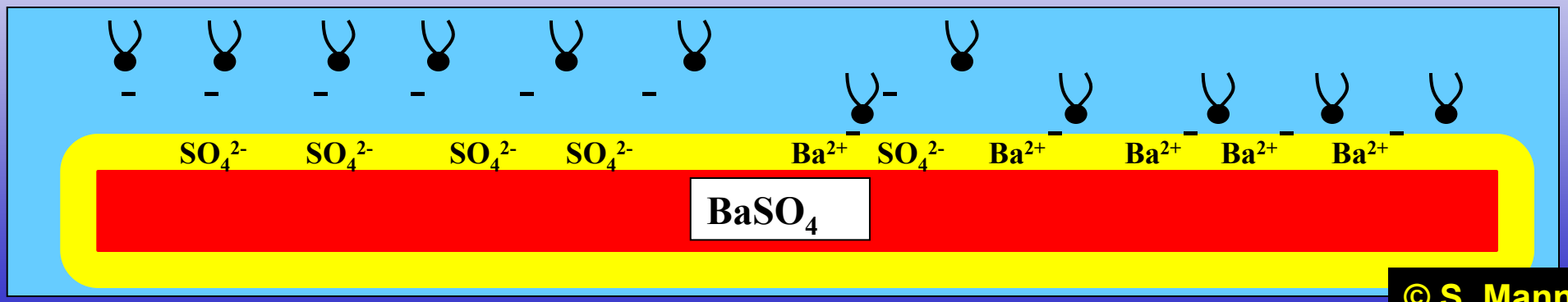


$[Ba^{2+}] : [SO_4^{2-}]$ molar ratio

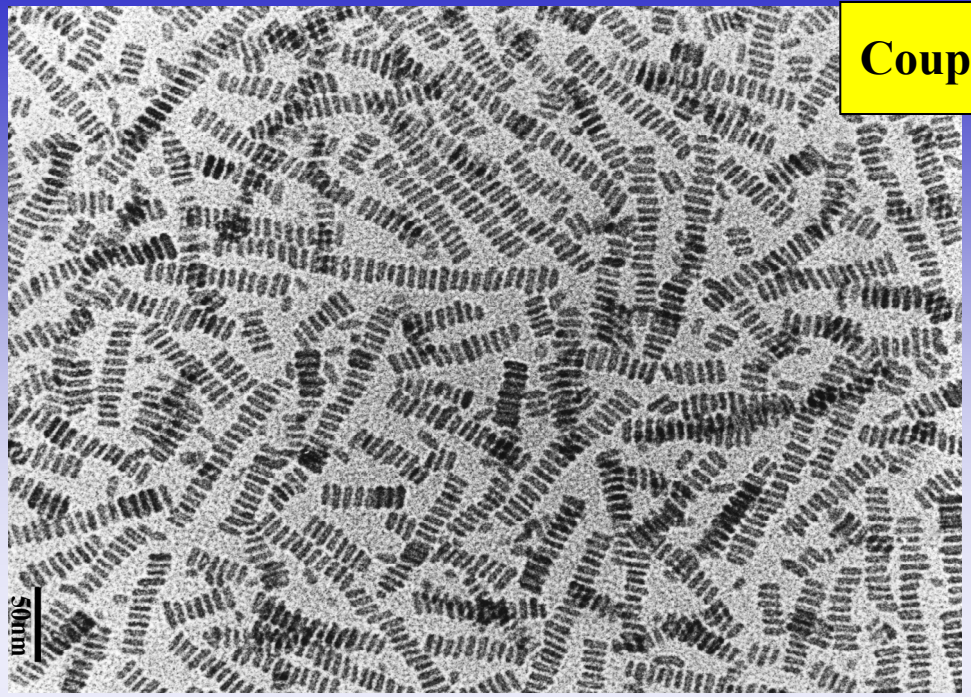
1 : 5 weak

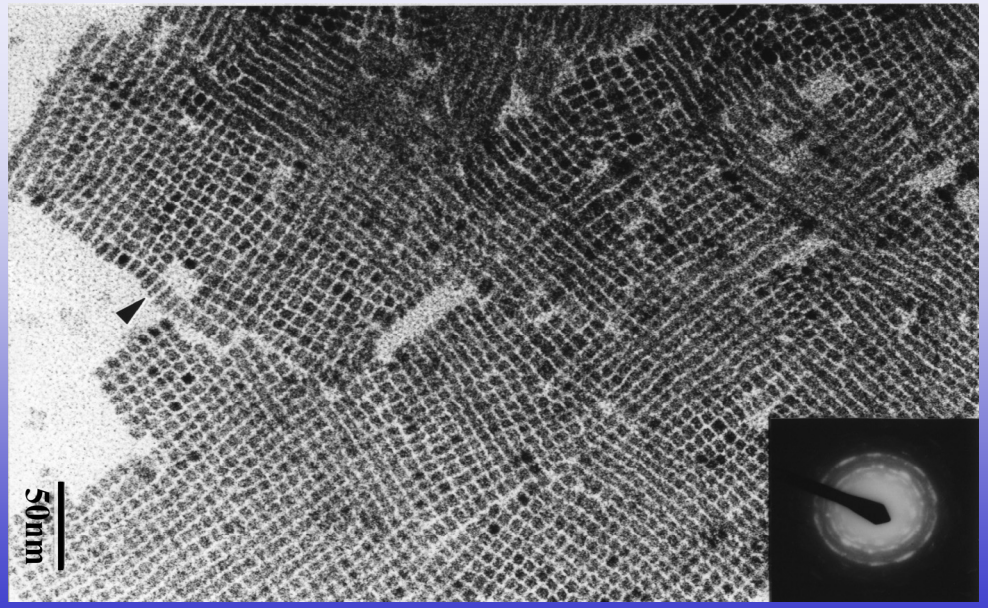
1 : 1 intermediate

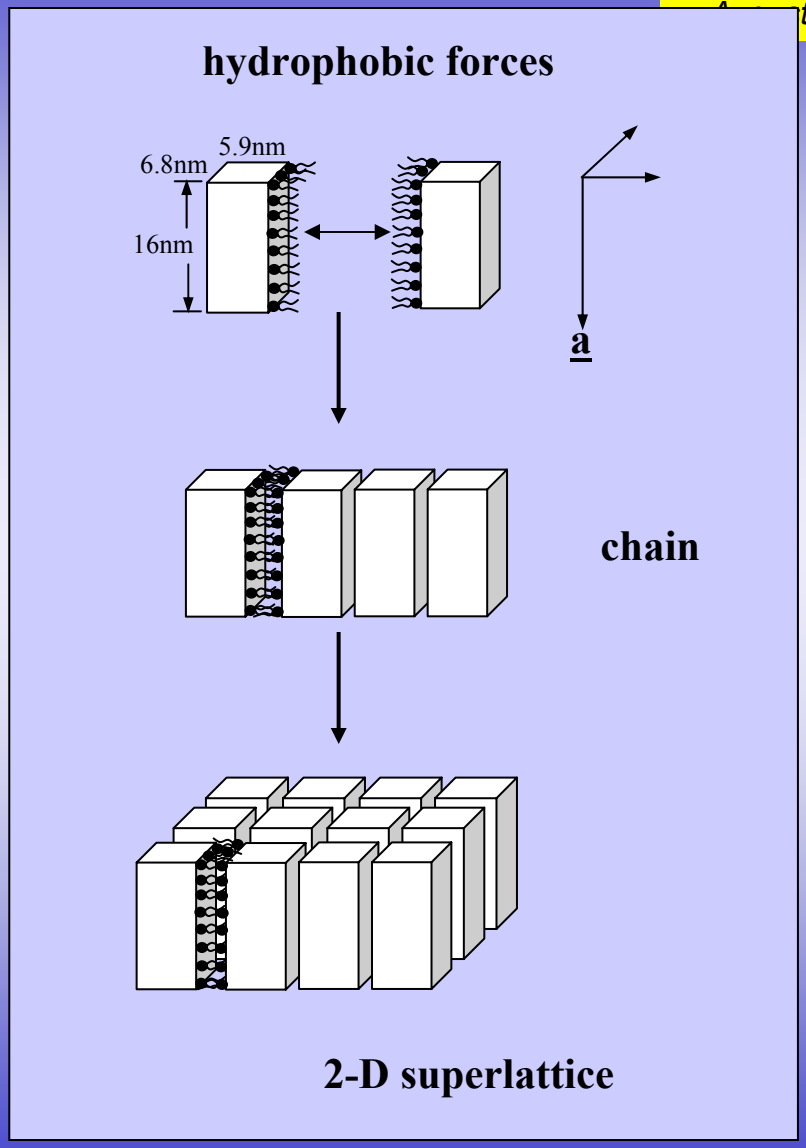
5 : 1 strong



Coupled synthesis and self-assembly







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"LEGOchemistry" with clusters $[Ti_{16}O_{16}(OEt)_{32}]$

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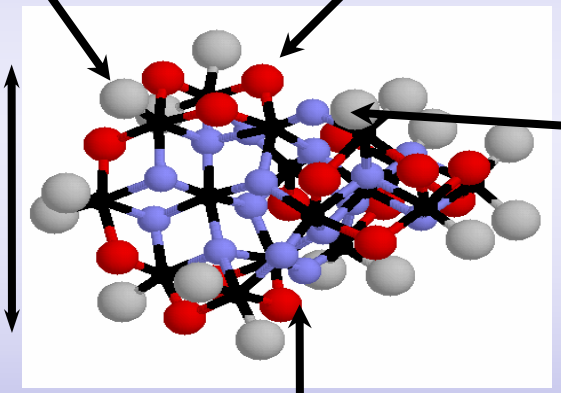
- Easy made
- Robust core
- Well characterised
- Model Brick

Terminal -OEt groups

Bridging -OEt groups

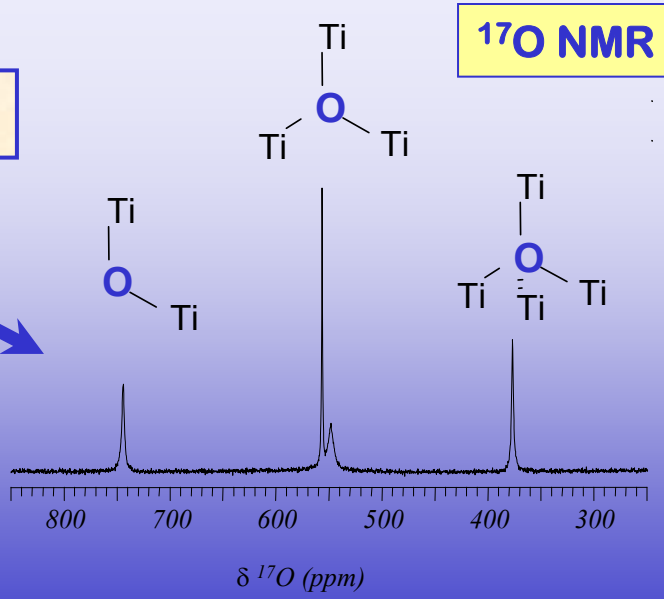


Core
Oxo bridges
^{17}O NMR

Integrity

All Ti(IV) are hexacoordinated

^{17}O NMR



Soler-Illia, Scolan, Sanchez, *New J. Chem.* **2001**
Rozes, Sanchez, *JACS.* **2005**

Ti_{16} + dendrimers

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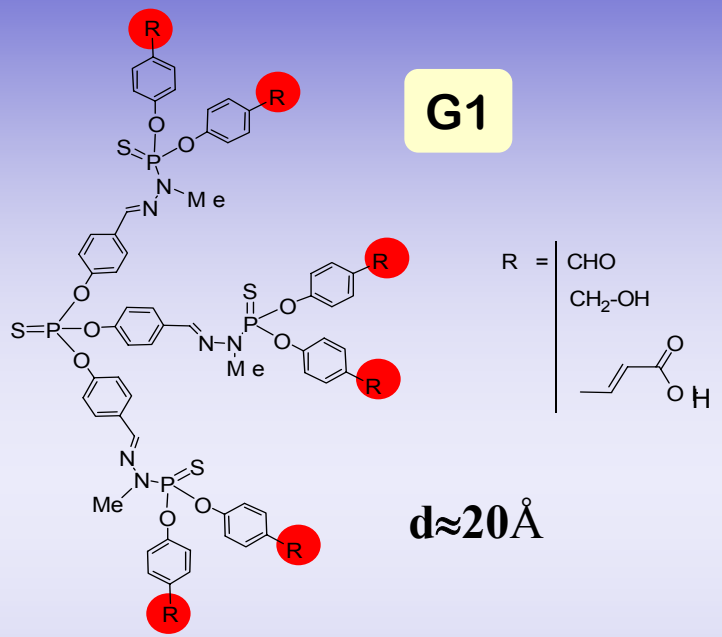
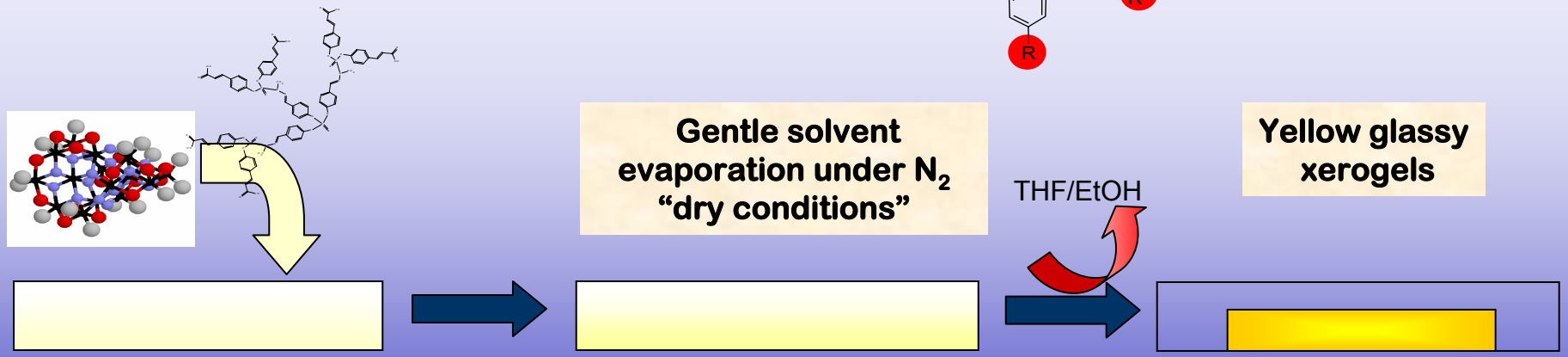
- G1 and G5 Dendrimers
- Controlled size and functions
- Controlled connectivity and symmetry





Soler-Illia et al., *Angew. Chem.* **2000,** *39*, 4249

Local Structure of the Cluster/Dendrimer Hybrid

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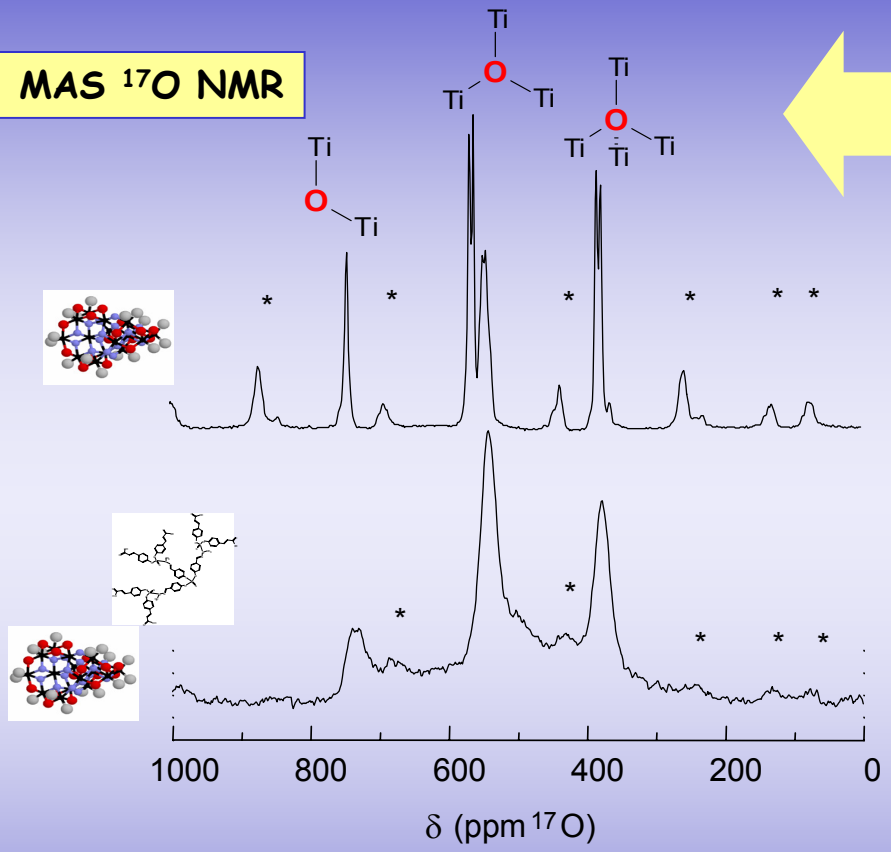
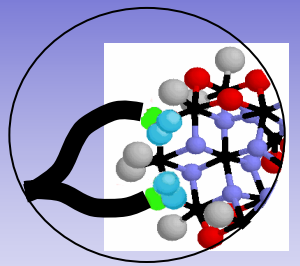
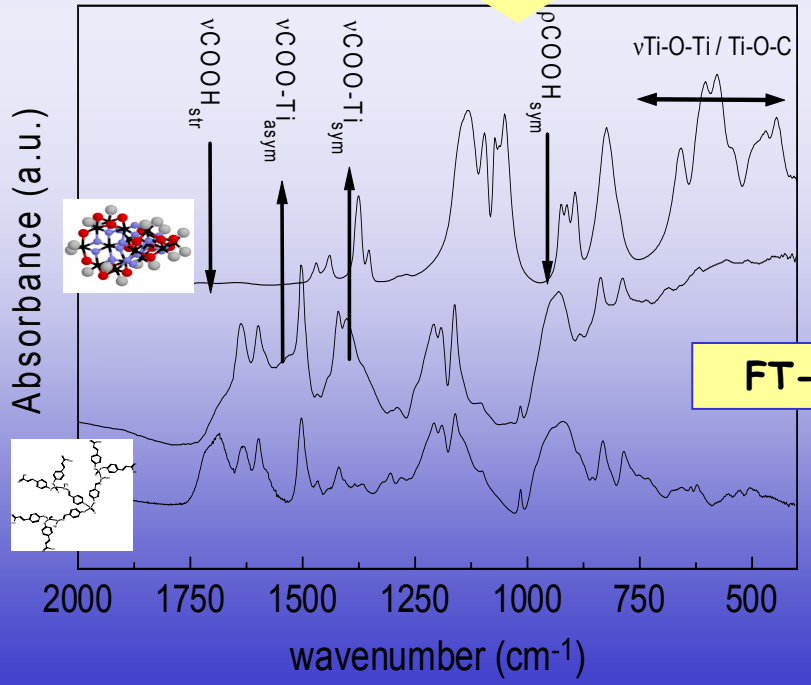
MAS ^{17}O NMR



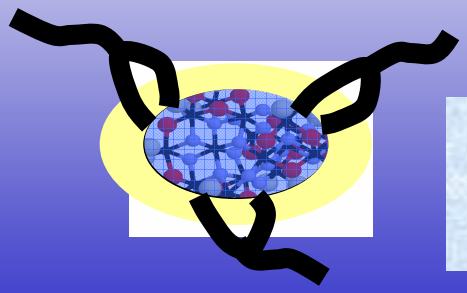
- The Ti-oxo core is conserved
- Substitution limited to hybrid interface



$\Delta\nu$=140 cm^{-1}
bidentate bridge



FT-IR



Clusters connected to the dendrimer

Mesostructured Cluster Arrays

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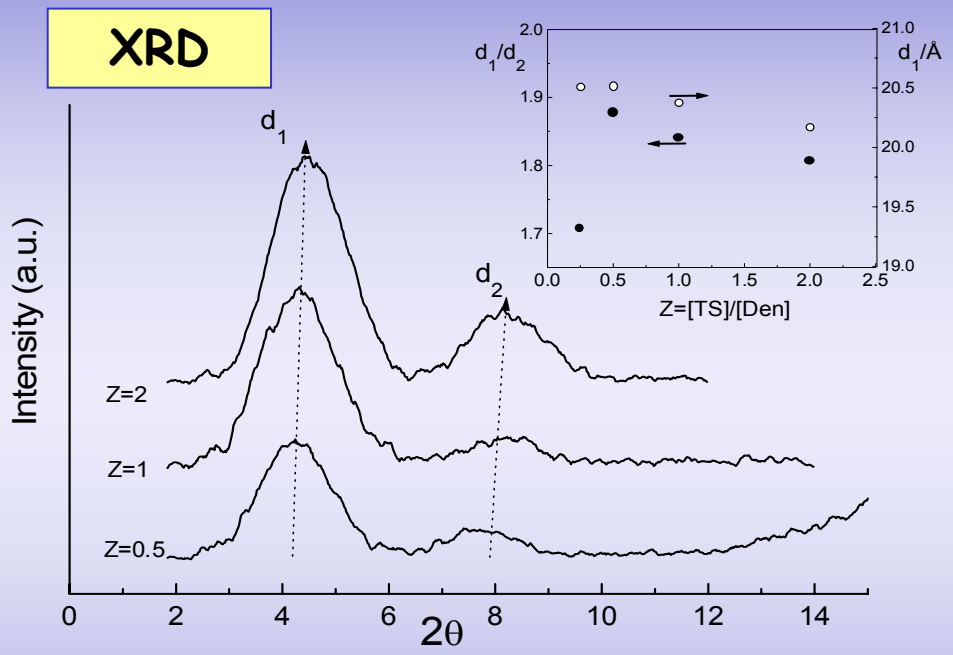
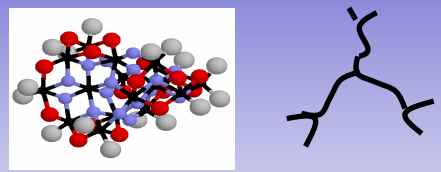
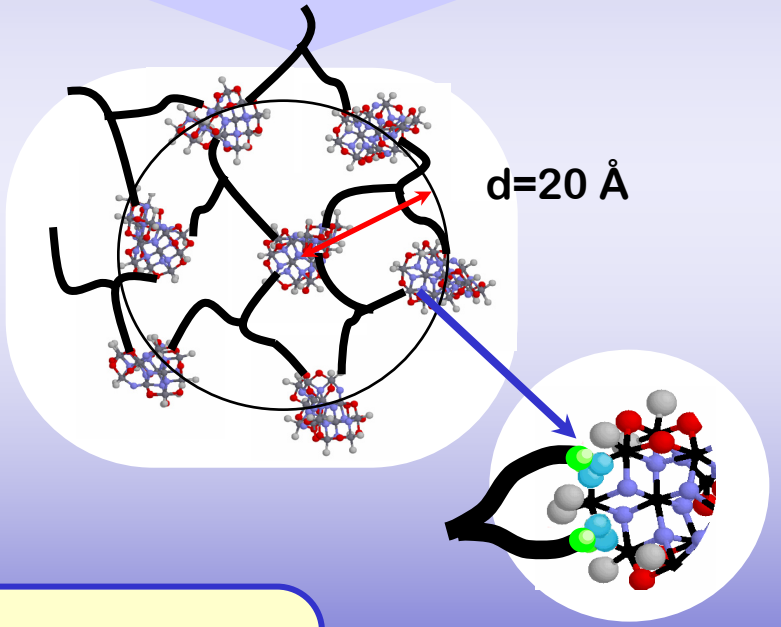




Mesostructured Hybrid



- **Diffraction at low angles is compatible with periodicity**
- **2 nm distance between dense objects (clusters) scales like the folded polymer**

Mesostructured Cluster Arrays

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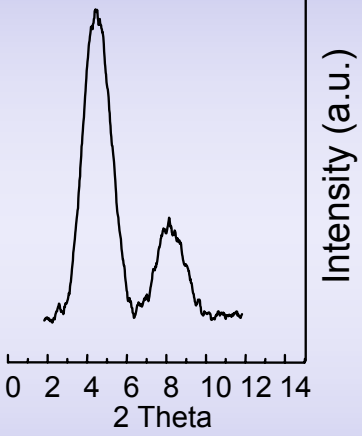
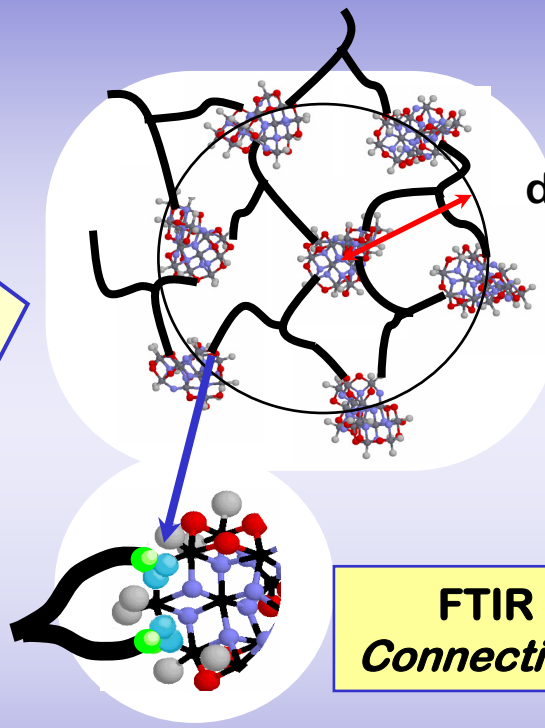
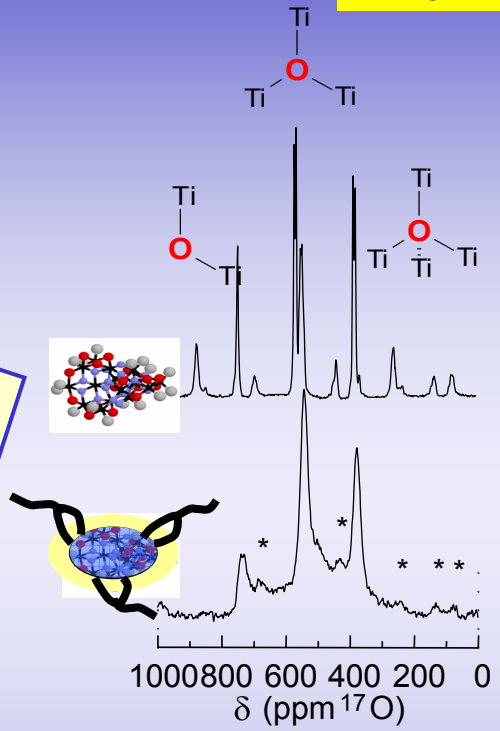
XRD
Mesostructure





FTIR
Connectivity



^{17}O MAS NMR
Integrity of the brick

- **Simple chemistry - complementary quick reactions**
- **Symmetry of the polymer → local order (6-7 nm)**
- **Interface reactions + viscous media = core protection**
- **Adaptable to clusters with magnetic or optical properties**