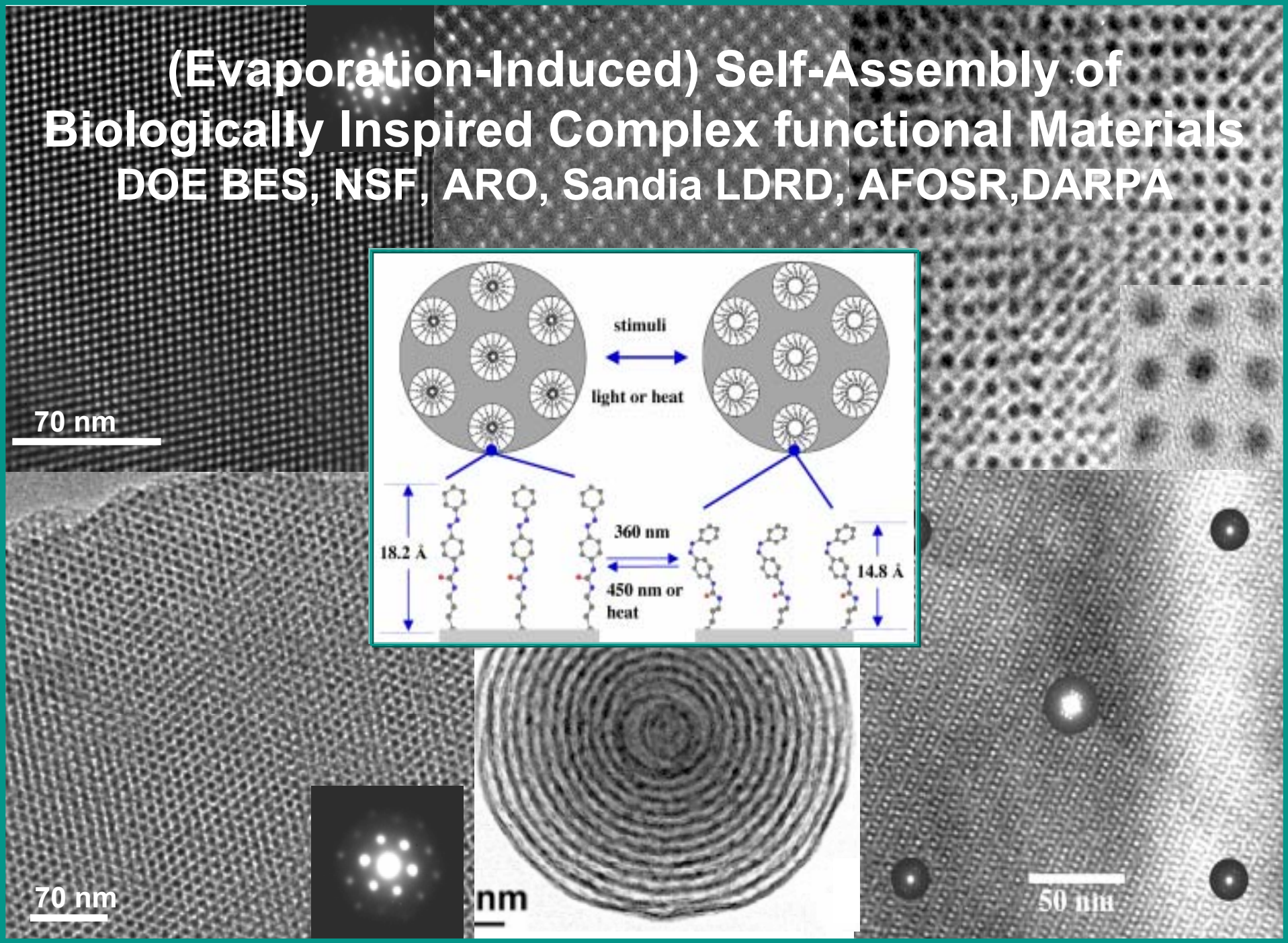
(Evaporation-Induced) Self-Assembly of Biologically Inspired Complex functional Materials

DOE BES, NSF, ARO, Sandia LDRD, AFOSR,DARPA

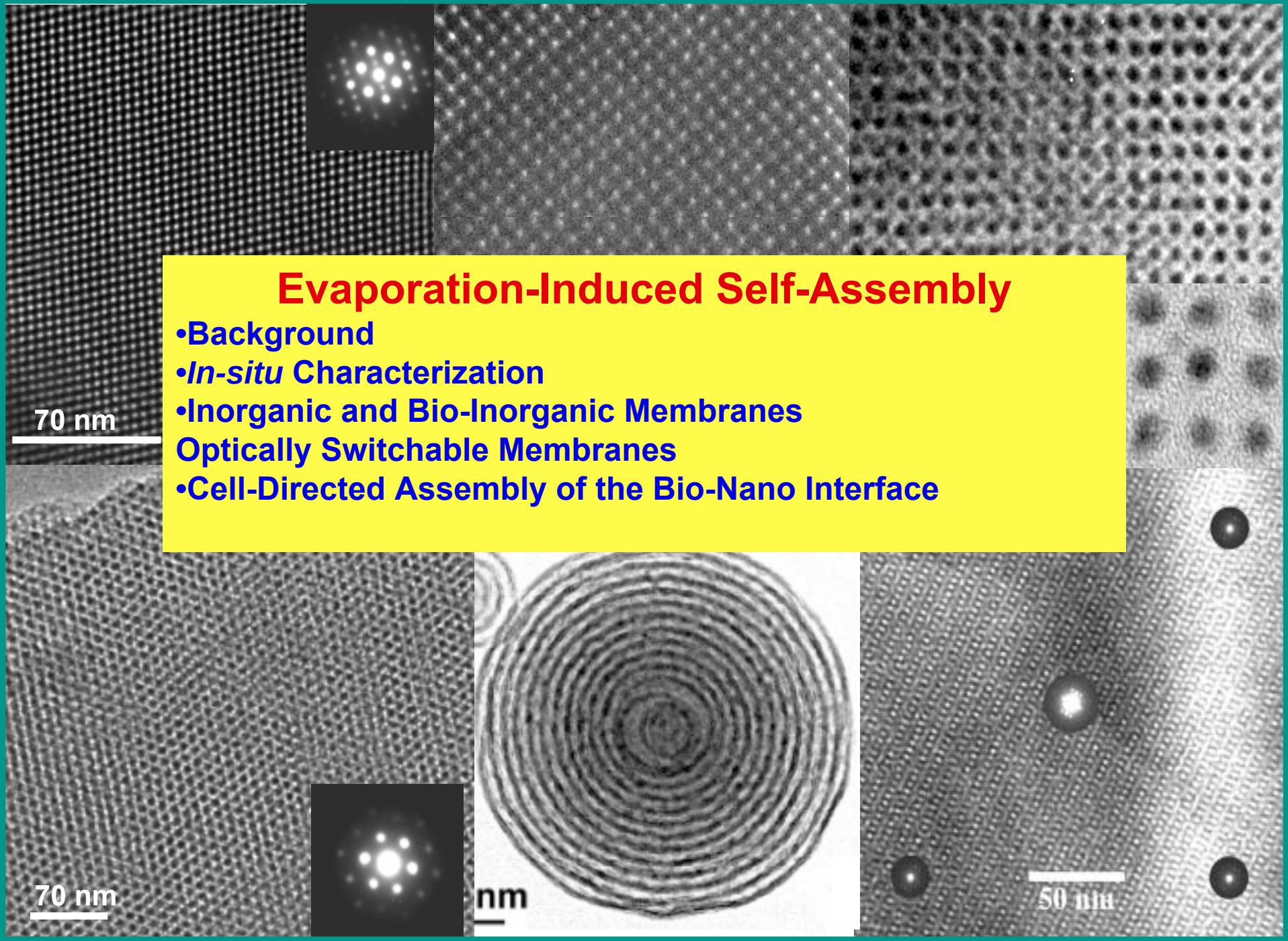


Evaporation-Induced Self-Assembly

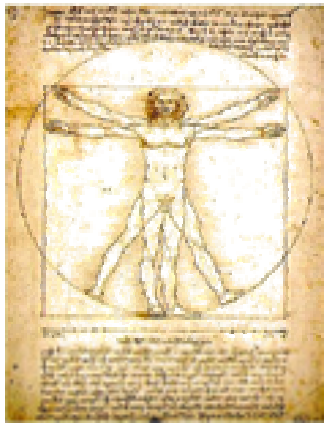
- Background
- *In-situ* Characterization
- Inorganic and Bio-Inorganic Membranes

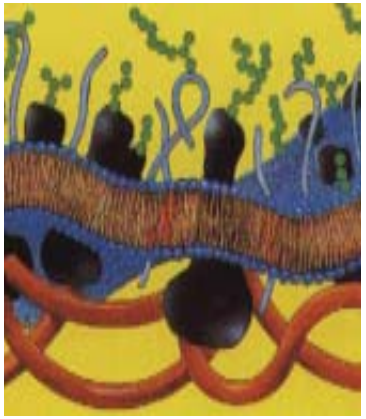
Optically Switchable Membranes

- Cell-Directed Assembly of the Bio-Nano Interface



Biological materials and systems exhibit complex functionality, are composed of nano-scale components and have evolved to work.





Nature combines hard and soft materials often in hierarchial architectures to get synergestic, optimized properties and combinations of properties →useful functionality.

Goals:

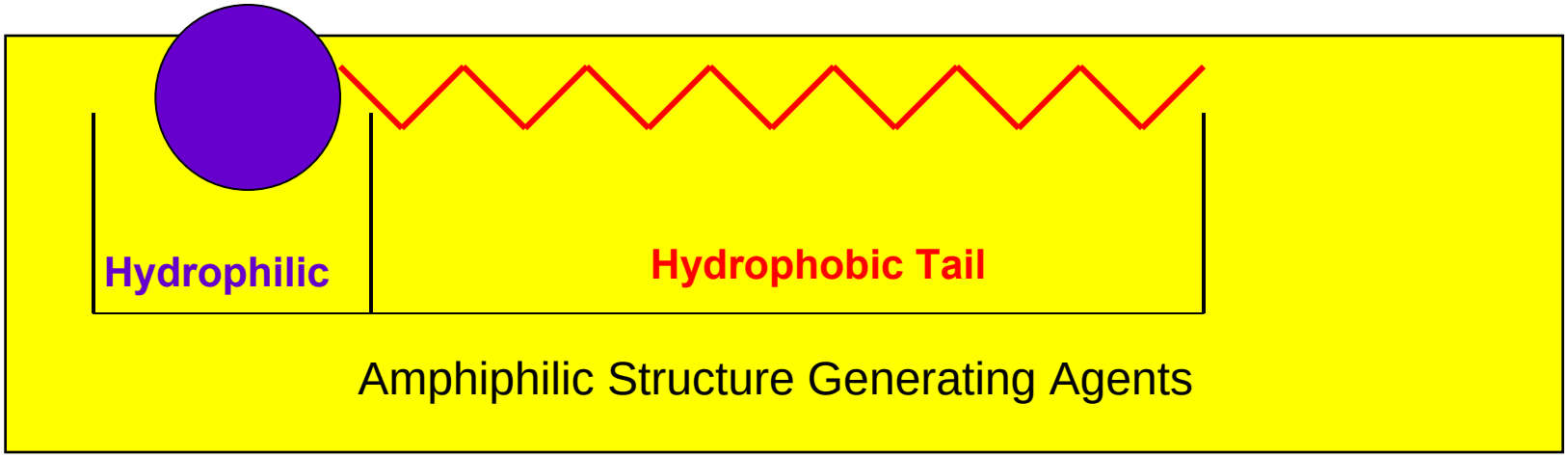
- Emulate proven biological designs
- Develop new properties by nanostructuring
- Impart responsive life-qualities to robust engineering materials
- Integrate on meso and macroscales →FILMS

CHALLENGE: How to controllably organize multiple (hard/soft) materials on multiple length scales

Approach: Use surfactant self-assembly to direct the organization of inorganic and organic precursors

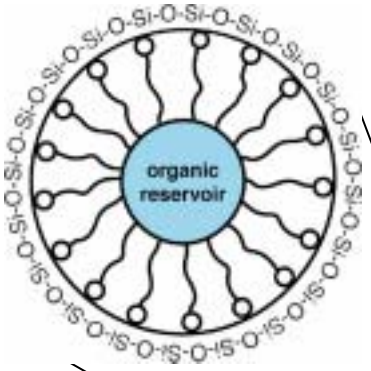
Self-Assembly **- Spontaneous organization via non-covalent interactions - electrostatics, van der Waals, hydrogen bonding, π-π, etc.**

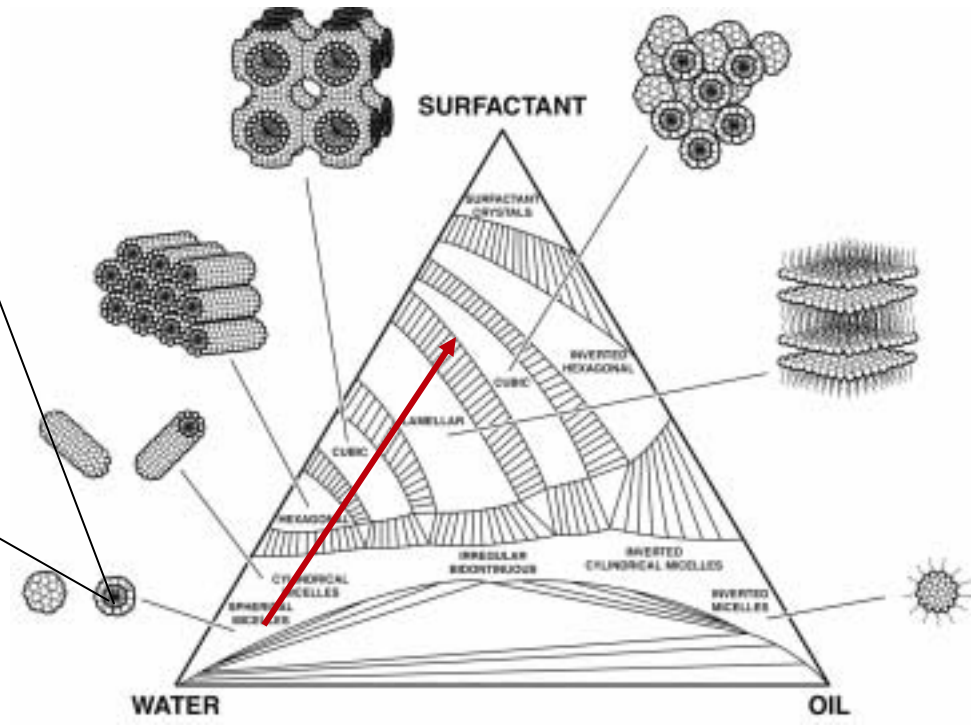
Employ amphiphilic molecules pre-programmed to self-assemble



Cationic Surfactant	$CH_3(CH_2)_nN^+(CH_3)_3BR$
Anionic Surfactants	$CH_3(CH_2)_nSO_3^-Na^+$
Non-ionic Surfactants	$CH_3(CH_2)_n(CH_2CH_2O)_n\text{-}OH$
Block Copolymers	$HO\text{-}(CH_2CH_2O)_n\text{-}(CH_2C(CH_3)HO)_m\text{-}(CH_2CH_2O)_nH$

Generic Detergent Phase Diagram





Micelles act as nanocontainers

Silicic Acid+ other hydrophilic precursors

Ethanol Co-Solvent

Monomers, PhotoInitiators, Hydrophobic Precursors

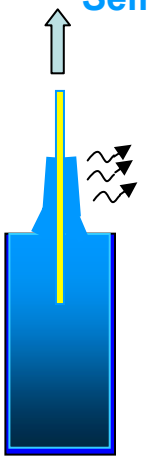
Davis and Scriven

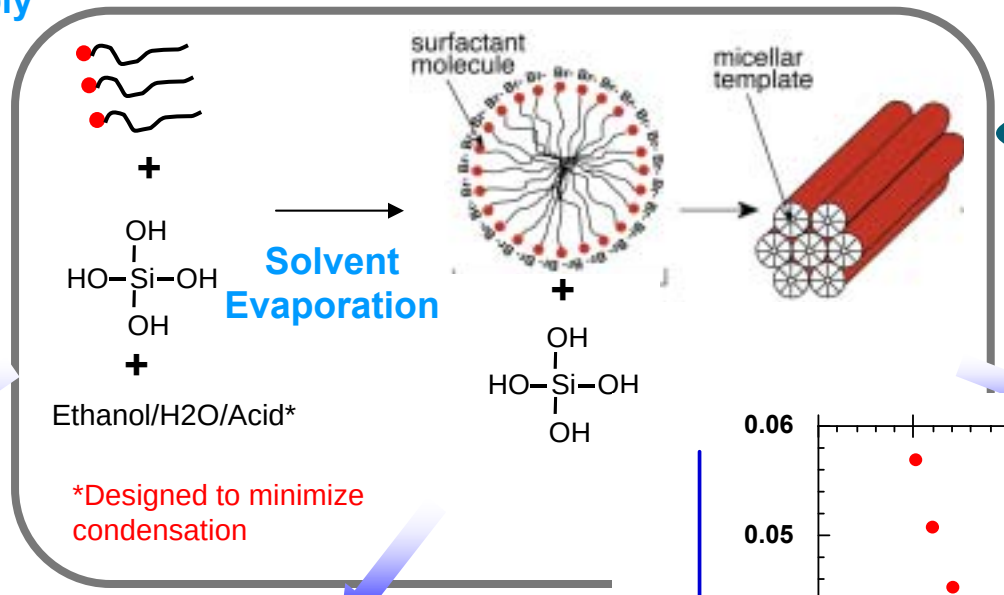
Near Equilibrium - Reversible

Sol-Gel Chemistry + Surfactant Self-Assembly + Evaporation

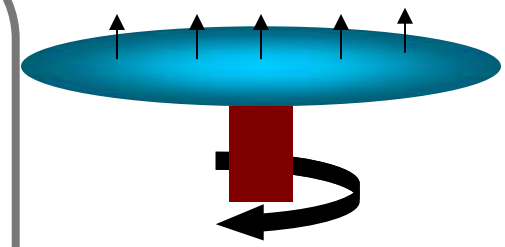
Kresge, C.T. et al., Nature, 359, 710-712, 1992
Ogawa, M., J. Am. Chem. Soc. 1996

Dip-coating
Spatially resolves
Self-assembly



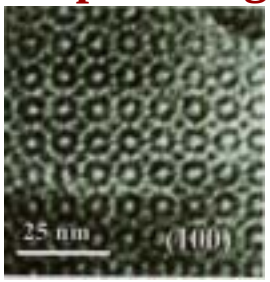


Solvent Evaporation



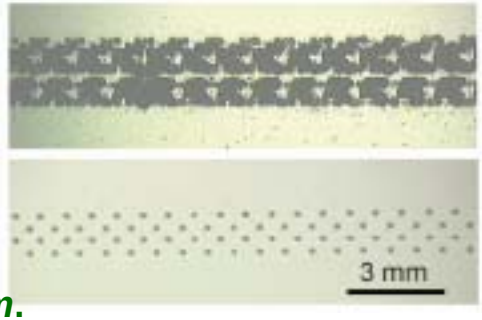
Spin-Coating

Dip-coating

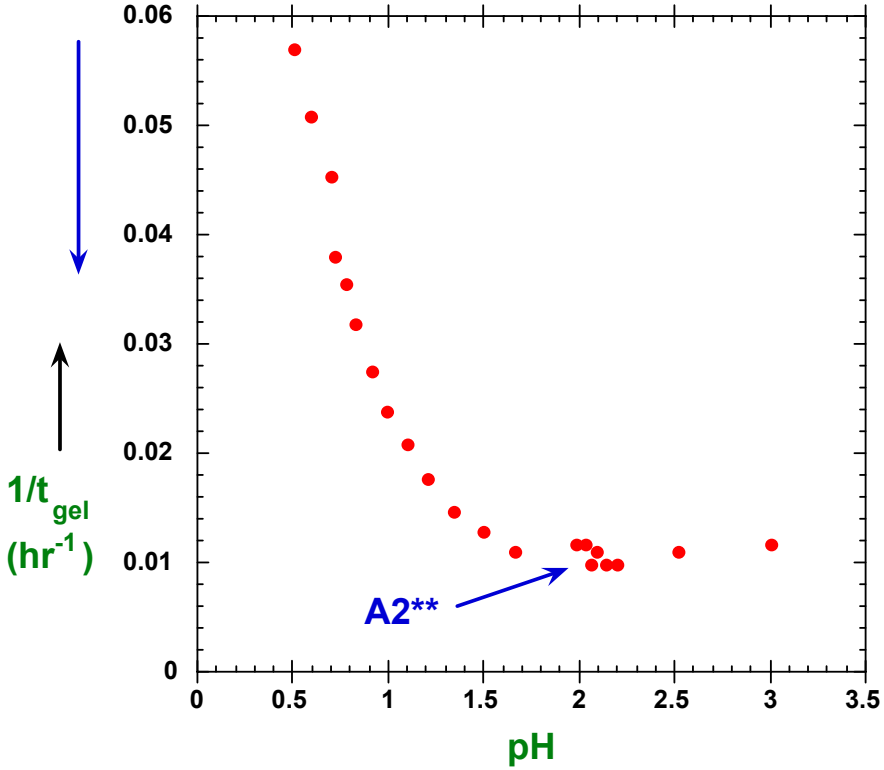


Lu *et al.*, Nature 1997

Ink-jet Printing



Fan *et al.*, Nature, 2000

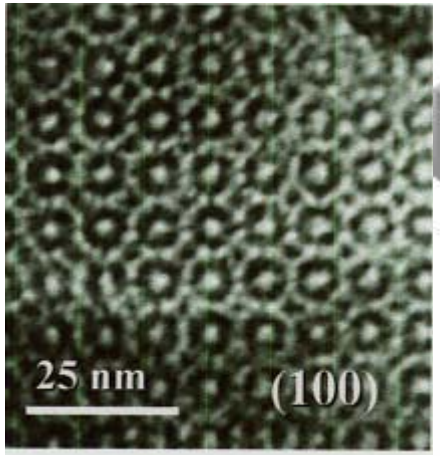


In Situ Characterization

Grosso *et al. Chem. Comm.*
Chem. Mater., J. Mater. Chem.
Doshi *et al. J.Am.Chem.Soc.*
J. Phys. Chem. B
Gibaud *et al. J. Phys. Chem. B*

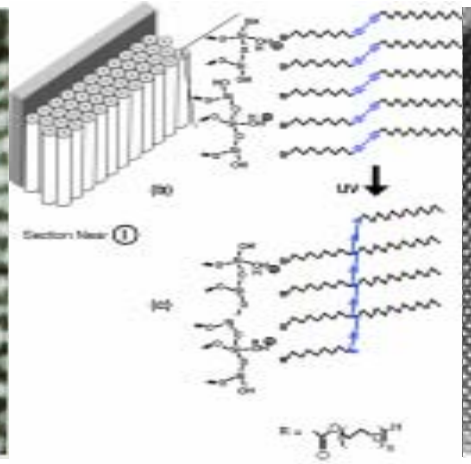
Self-Assembly + Sol-Gel Processing + Evaporation

Membrane

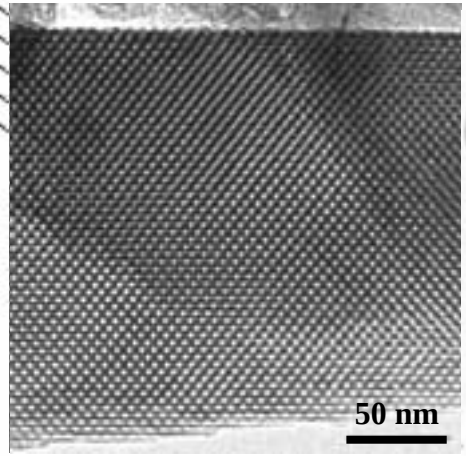


Lu et al., Nature 1997, 2001

Sensor

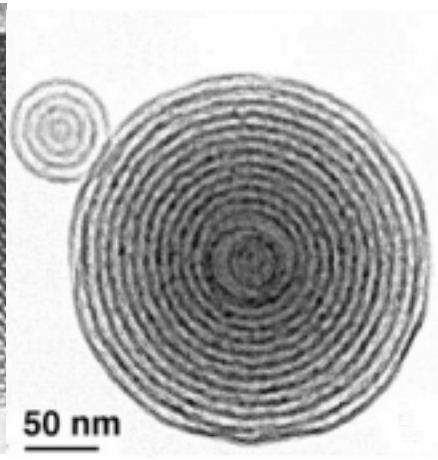


low k



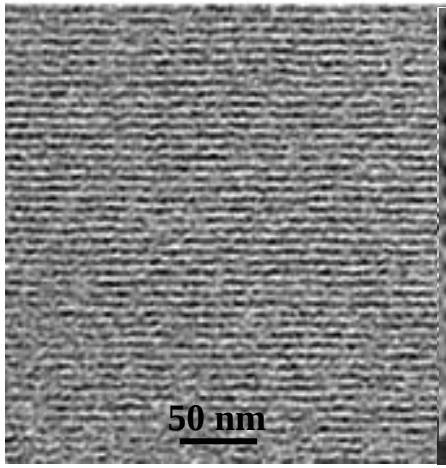
Brinker et al., Adv. Mater. 1999

Controlled release



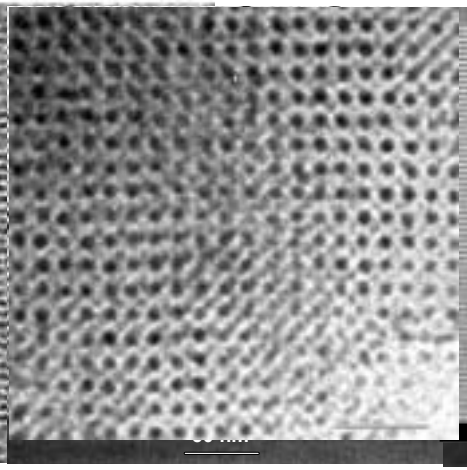
Lu, et al., Nature 1999

Sea-Shell-Like



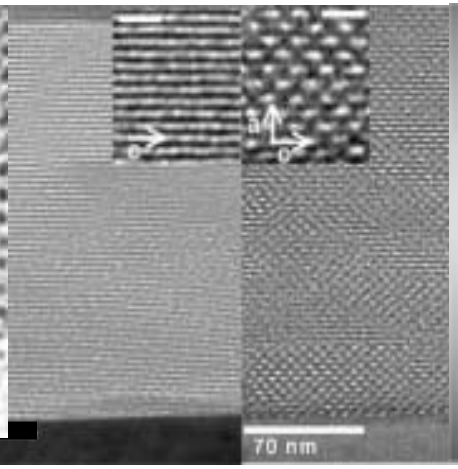
Sellinger et al., Nature 1998

3D Nanocrystalline Solid



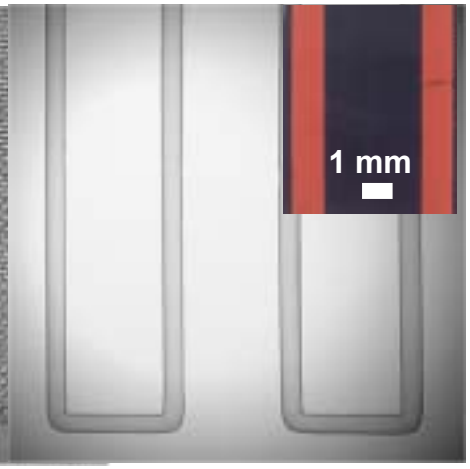
Fan et al., Science, 2004

Phase Transition



Doshi et al., Science 2000

Patterns

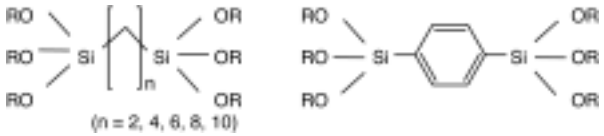


Fan et al., Nature 2000

Pore Chemistry

$(RO)_3Si\ OH$

$(RO)_3Si\text{-}R'\text{-}Si(OR)_3$



$(CH_3O)_3SiCH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$ (TFTS)

$(CH_3O)_3SiCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ (OTS)

$(CH_3O)_3SiCH_2CH_2CH_2CH_2CH_2C\ H_2CH{=}CH_2$

$(CH_3O)_3SiC_6H_5$ (PTS)

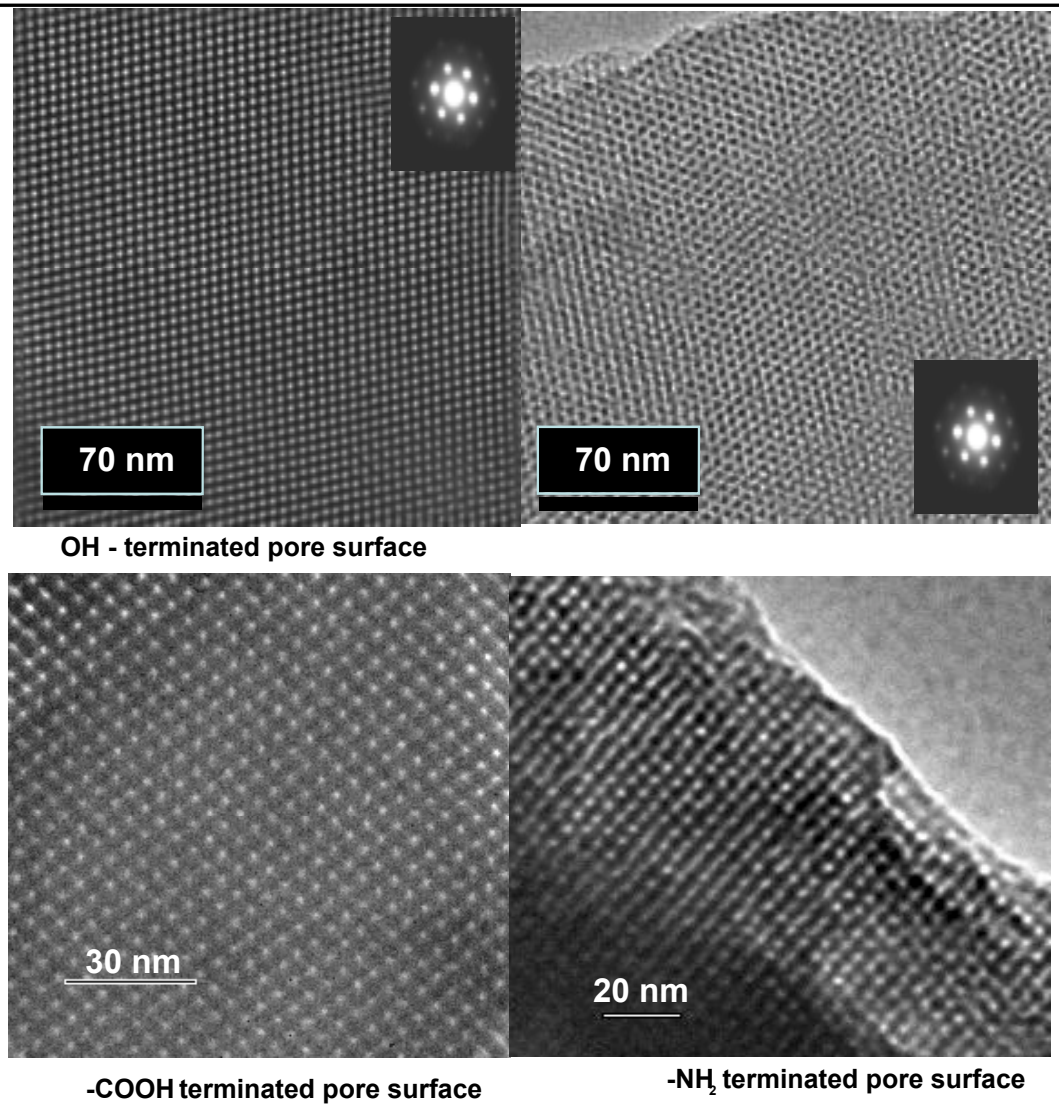
$(CH_3O)_3SiCH_2CH_2CH_2SH$ (MPS)

$(CH_3O)_3SiCH_2CH_2CH_2NH_2$ (APS)

Post-Self-Assembly Derivatization with Organic Monolayers
Liu , J. et al., ***J. Phys. Chem.***, 104, 8328-2339, 2000

Fan, H. et al., ***Nature***, 405, 56-60, 2000
Lu, Y. *et al*., ***J. Am. Chem. Soc***., 122, 5258-5261, 2000.

In order to emulate natural ion channels, we developed approaches to vary pore size, charge sign, and density



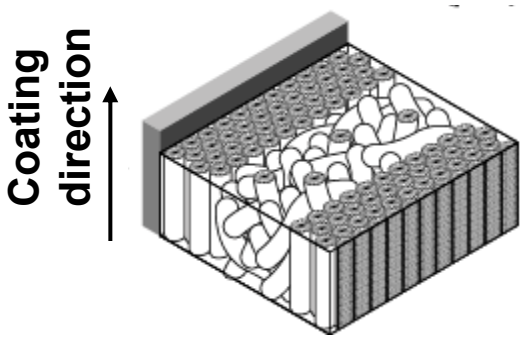
OH - terminated pore surface

-COOH terminated pore surface

-NH_2 terminated pore surface

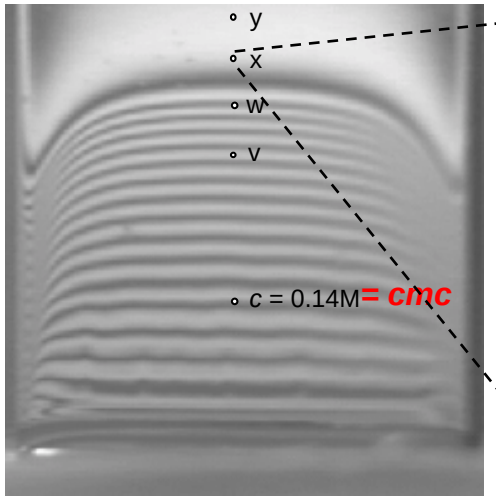
Liu et al, *Chem. Comm*. 2003

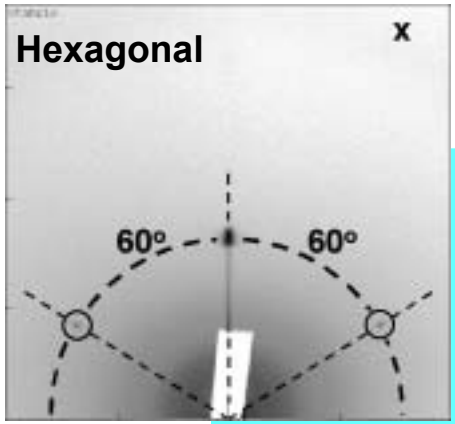
In situ Characterization of Self-Assembly

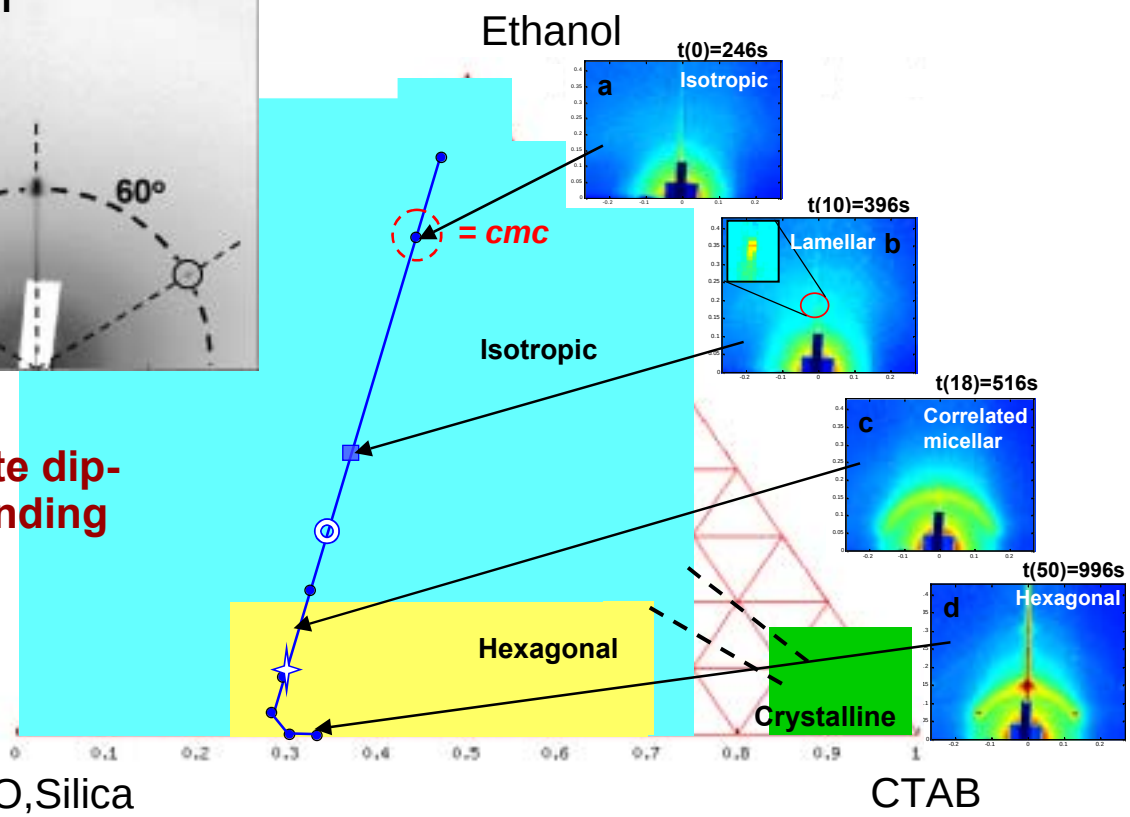


GISAXS patterns (a-d below) obtained using the liquid spectrometer at X22B, NSLS, Brookhaven National Laboratory (left) mapped onto the bulk CTAB/ethanol/water phase diagram

Doshi et al. *J.Phys. Chem. B-J.Am. Chem. Soc.* 2003



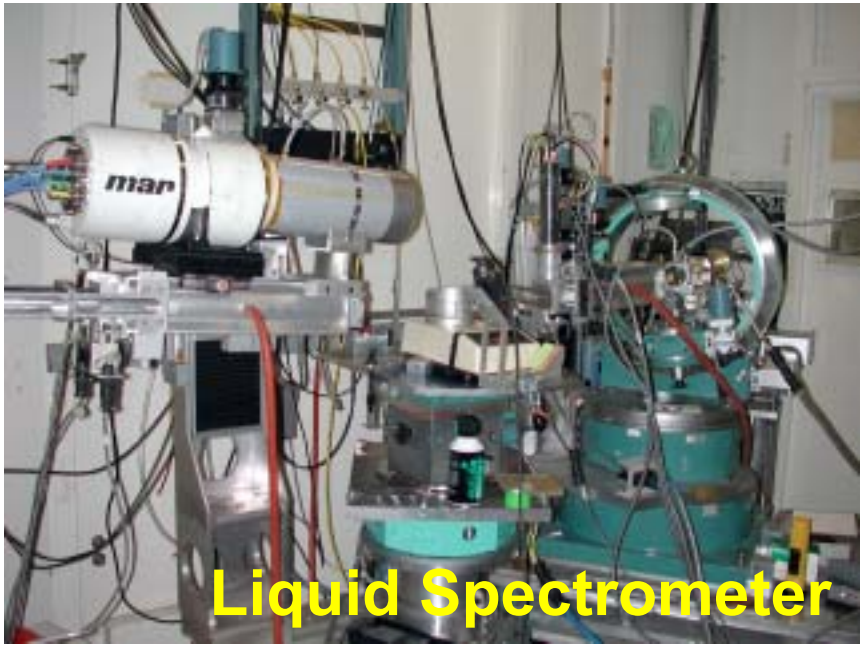


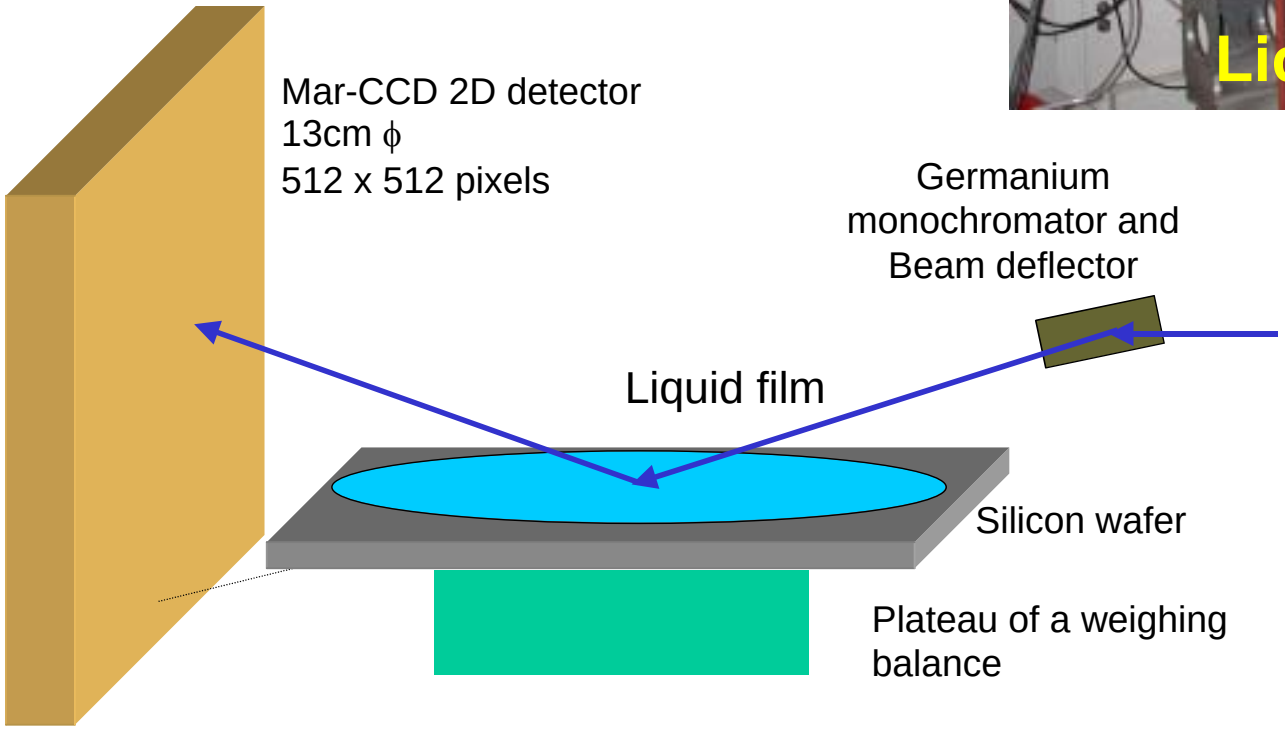


Optical interferograph of a steady state dip-coating profile (left) and the corresponding GISAXS pattern obtained *in-situ* for a hexagonal mesophase that forms via an interfacially mediated transformation of a correlated micellar intermediate (see schematic above)

In-situ Grazing Incidence X-ray Scattering (GISAXS) Studies of Evaporation Induced Self-Assembly

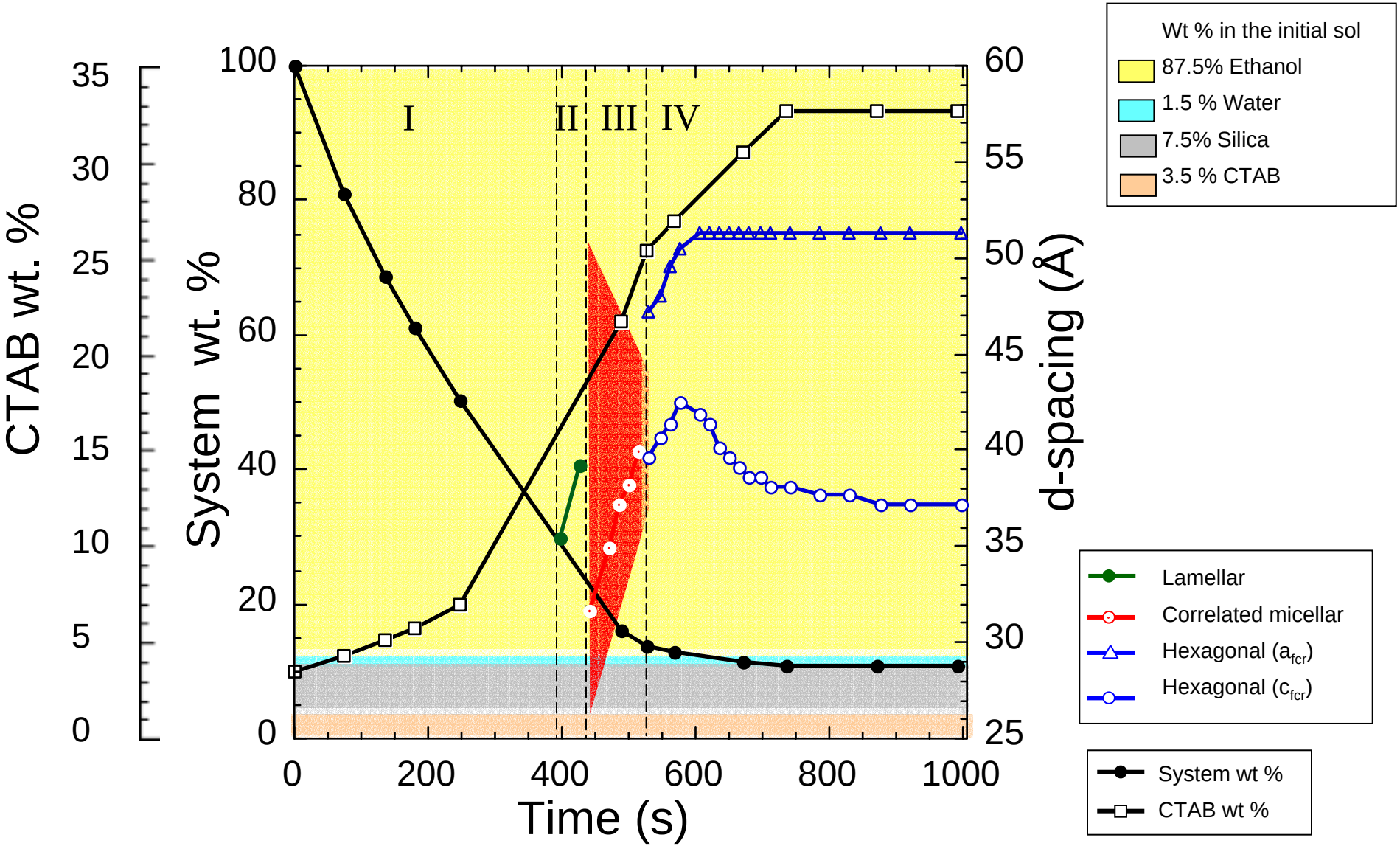
X22B, NSLS, Brookhaven National Laboratory.





Combine *in-situ* GISAXS with gravimetric analysis during controlled evaporation

Evolution of Weight and Structure during EISA



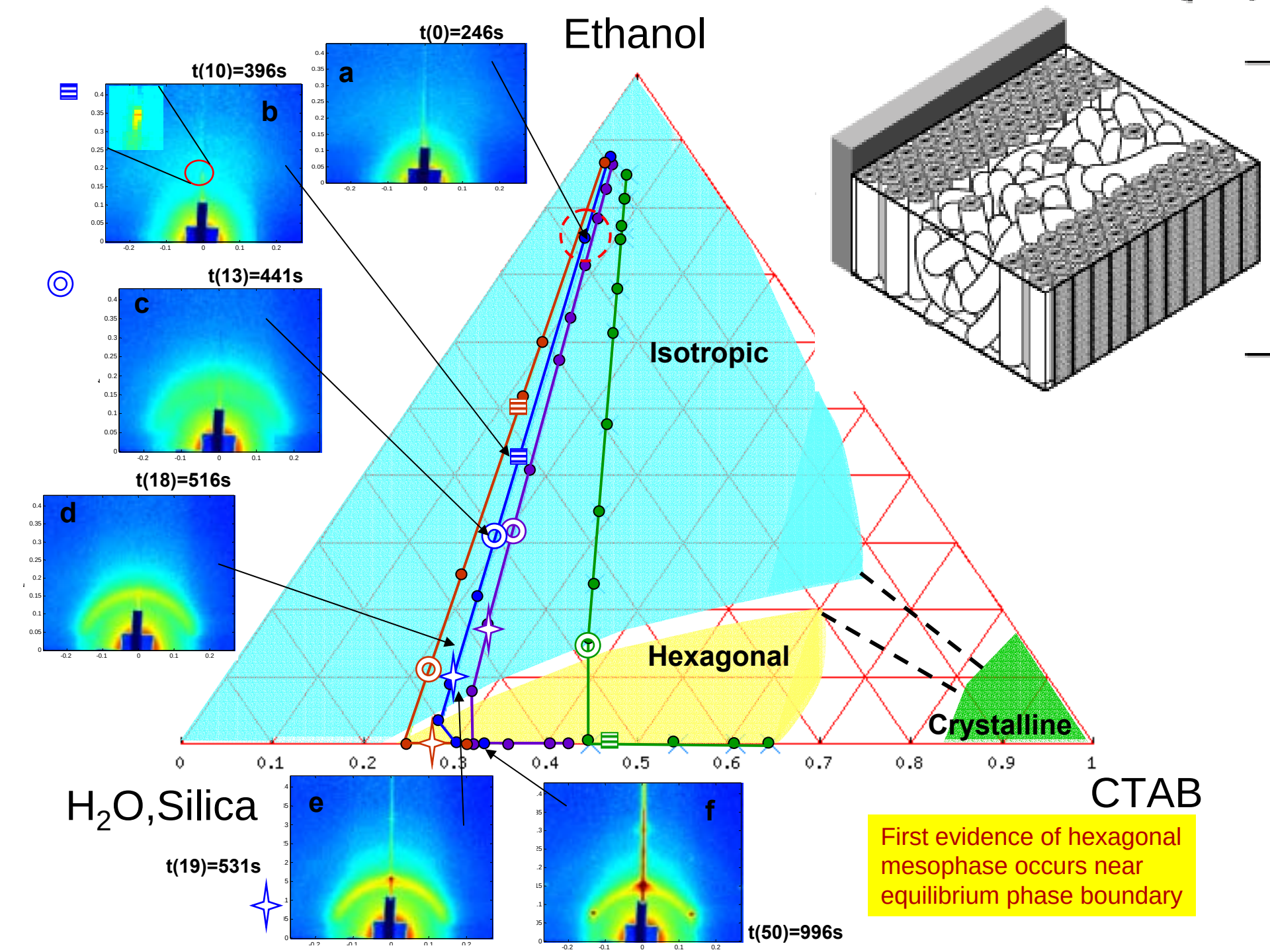
CTAB/Si=0.12

Doshi et al. *J. Am. Chem. Soc.* 2003

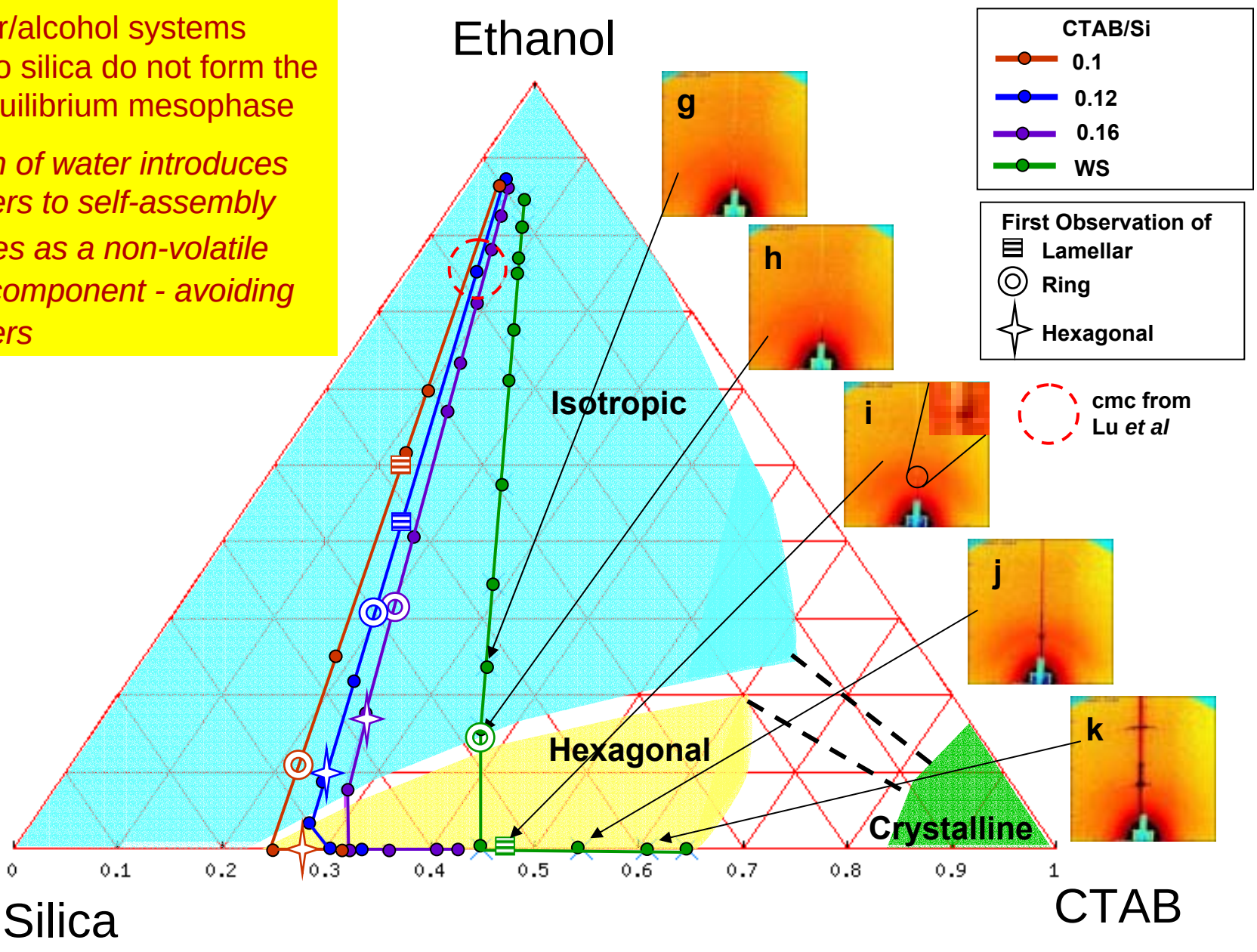
Evaporation Induced Self-Assembly

Directed by Mother Nature

QuickTime™ and a Microsoft Video 1 decompressor are needed to see this picture.


Ethanol
t(0)=246s
a
t(10)=396s
b
t(13)=441s
c
t(18)=516s
d
Isotropic
Hexagonal
Crystalline
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
H2O,Silica
CTAB
t(19)=531s
e
f
t(50)=996s
First evidence of hexagonal mesophase occurs near equilibrium phase boundary

- CTAB/water/alcohol systems prepared w/o silica do not form the expected/equilibrium mesophase
- *Evaporation of water introduces kinetic barriers to self-assembly*
- *Water serves as a non-volatile hydrophilic component - avoiding kinetic barriers*

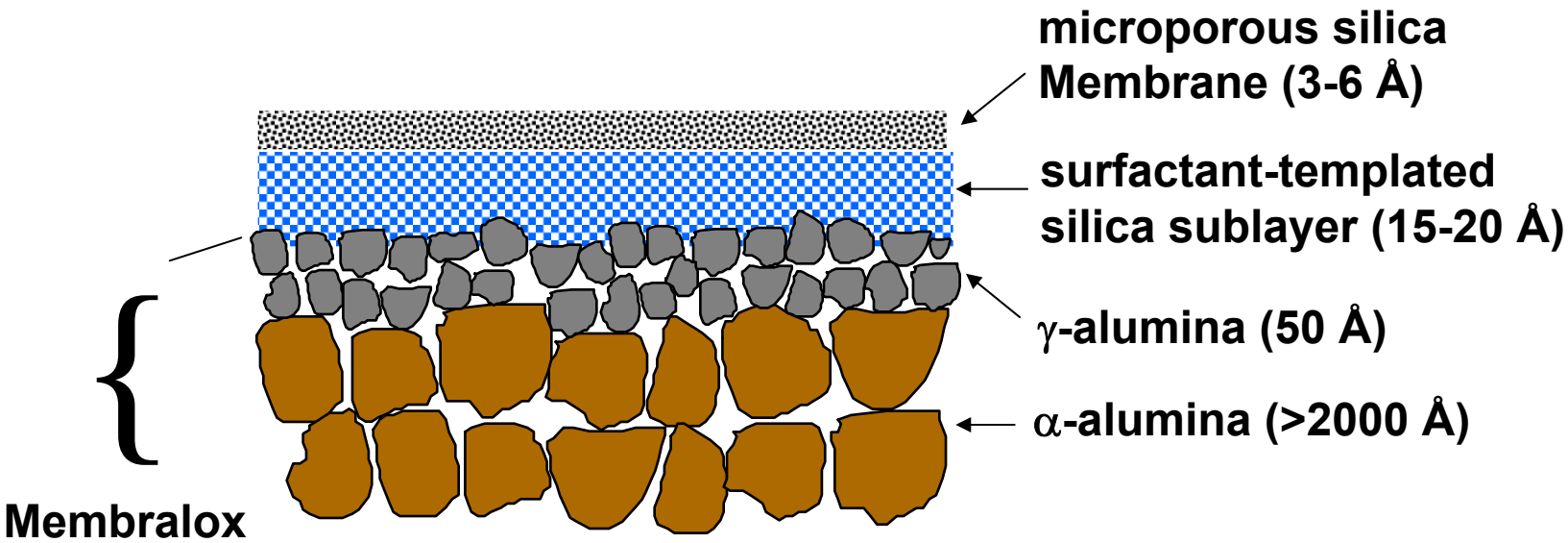


Lamellar to Hexagonal Transition

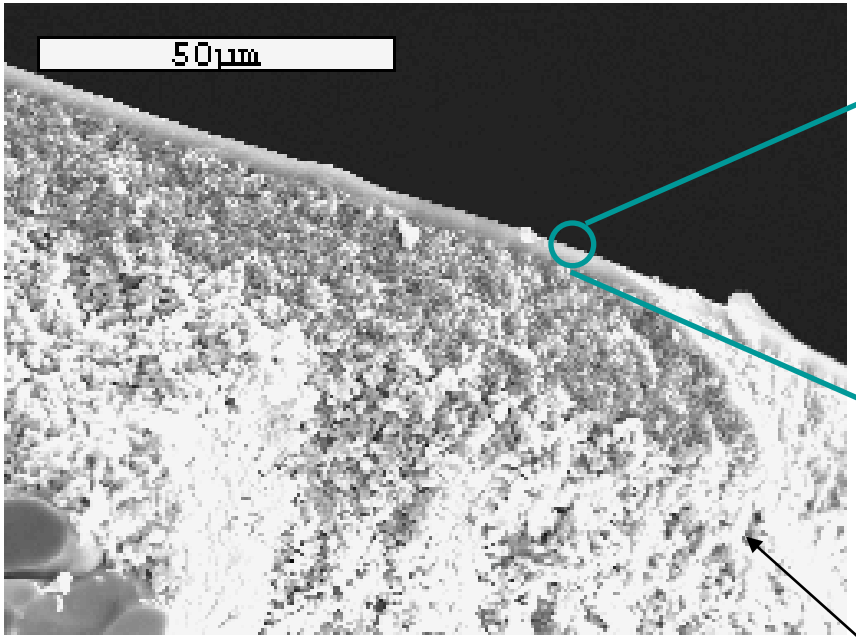
QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
QuickTime™ and a YUV420 codec decompressor are needed to see this picture.
QuickTime™ and a
decompressor
are needed to see this picture.

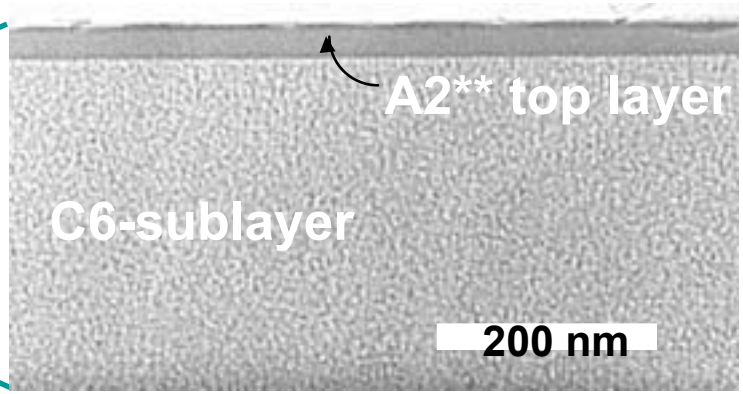
LAMELLAE BUCKLE, FORM CYLINDERS DIRECTLY

Overview of Membrane Microstructure



Electron Micrographs of tubular Silica Membrane





TEM cross-section of dual-layer membrane

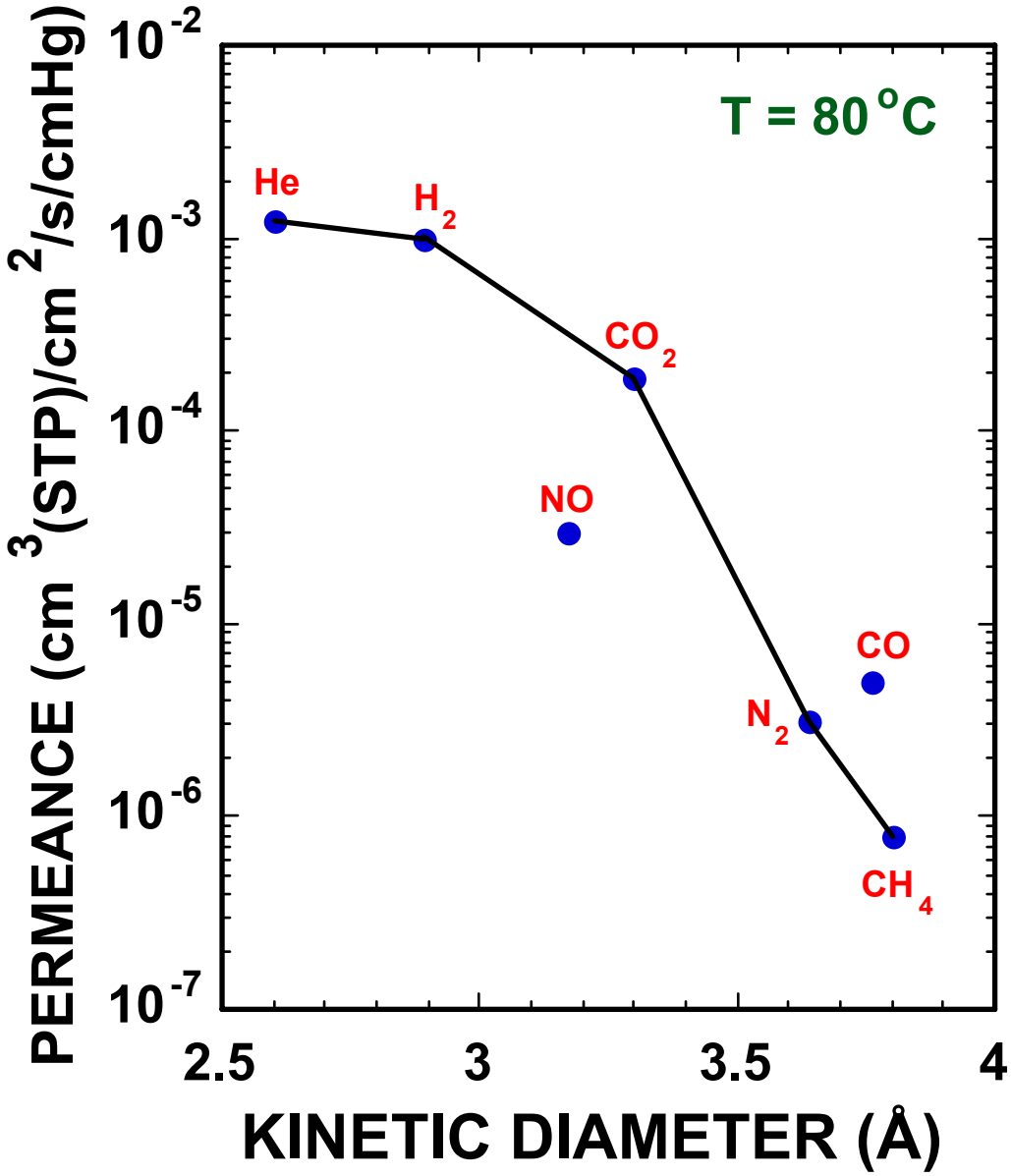
SEM cross-section of ceramic support

α-Al_2O_3 support w/ γ-Al_2O_3 top-layer

The University of New Mexico

Molecular Sieving Property of solvent-templated Silica Membrane

Membrane with extended calcination at 450°C



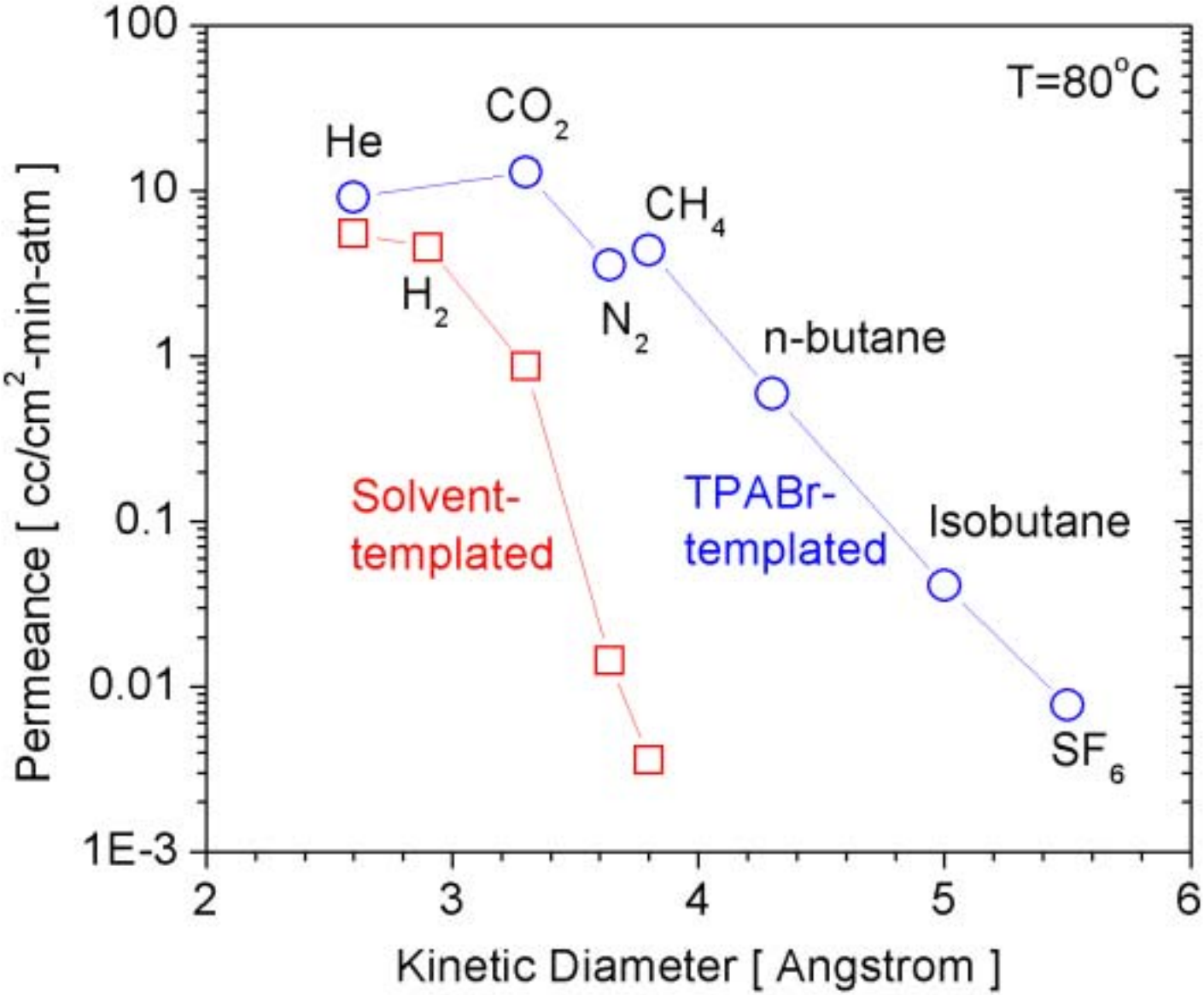
Ratio of Pure Gas Permeances

He/CH_4	1530
H_2/CH_4	1265
H_2/CO_2	5.3
H_2/CO	199
H_2/N_2	316
CO_2/N_2	60
CO_2/CH_4	240
N_2/CH_4	4.0
NO/N_2	9.3

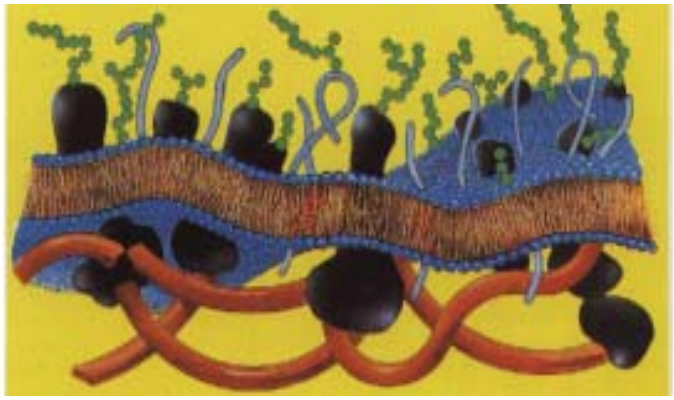
The University of New Mexico

Solvent-templated vs. TPABr-templated Silica Membrane

Tsai et al. and Xomeritakis et al. *J. Membr. Sci.*



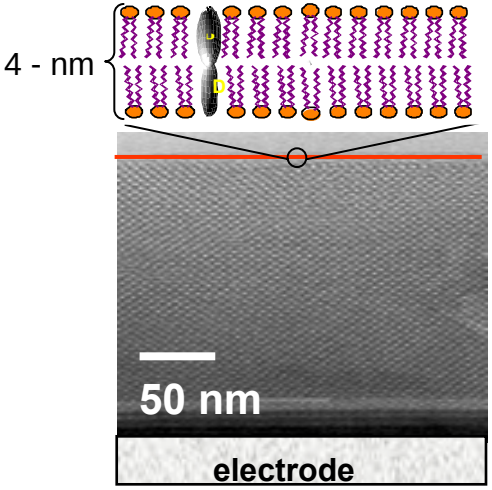
The Nano-Bio Interface: A New Platform for Ion Channel-Based Devices



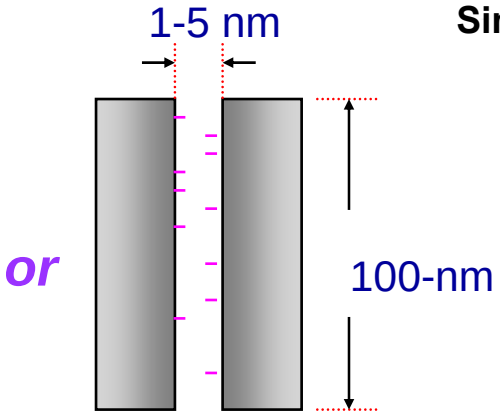
Approach:

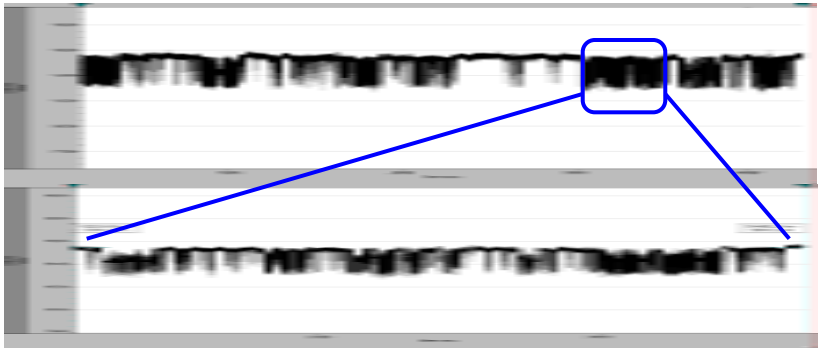
Use self-assembled nanoporous thin films to create integrated fluidic platforms for membrane-based ion channel devices and/or robust totally synthetic ion channel sensors.

Single channel recordings of natural ion channel.



Ion channels supported on nanoporous silica.





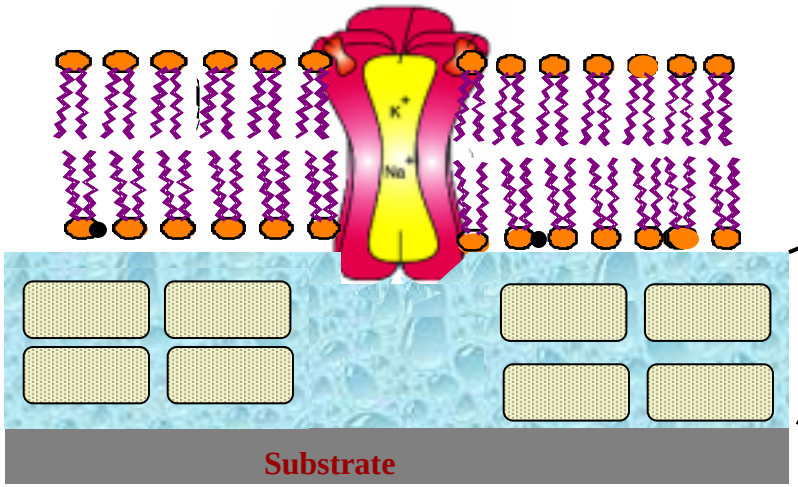
Single channel current recordings in a synthetic silica channel.

Liu and Brinker, unpublished

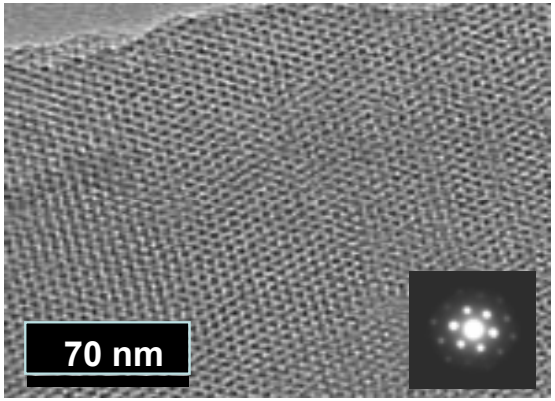
Small pores create permanently water-filled pores to maintain bilayer fluidity and to serve as ion / reagent reservoir. Individual nanopores exhibit ion-channel-like behavior of interest for a new class of stochastic ion channel sensors.

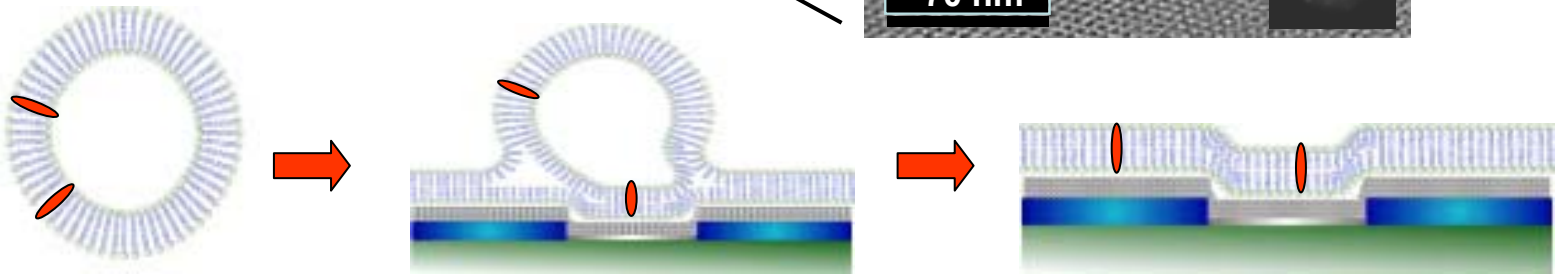
Bilayer Formation on Buffer-Filled Mesoporous Support Provides Bio-Functionality, Robustness, and High Ω

Our approach: **Lipid membrane is deposited on top of an ordered porous silica support which serves as an ionic reservoir and enhances film stability and robustness.**



Mesoporous silica support



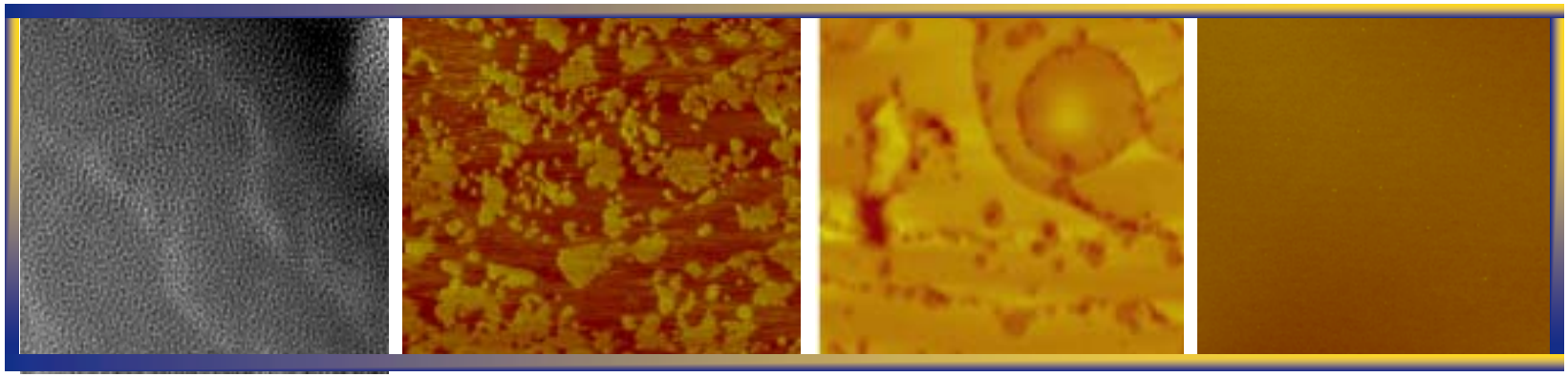


Vesicles fuse to sol-gel film

4-nm thick lipid bilayer on sol-gel film

Bilayer preparation by vesicle fusion above Tc of phospholipids (process sped up in presence of meso-porous support)

Bilayer Formation on Mesoporous Support Via Vesicle Fusion Monitored by In Situ AFM

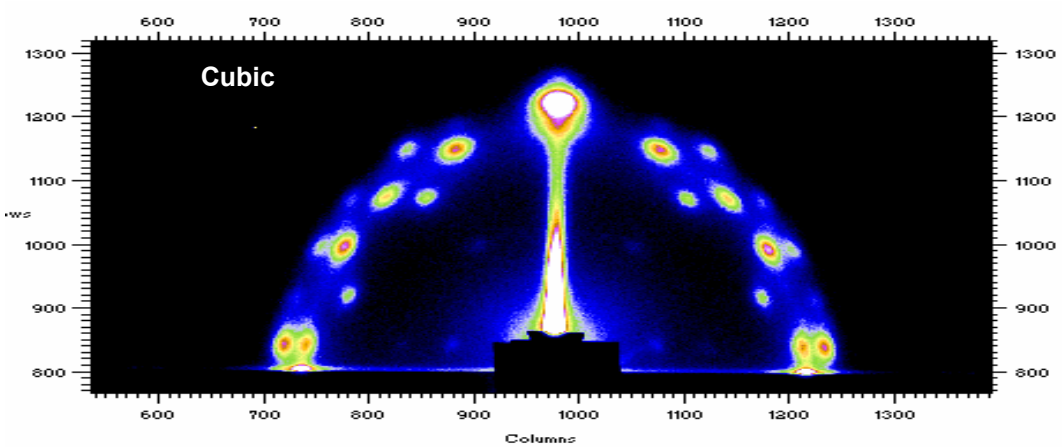


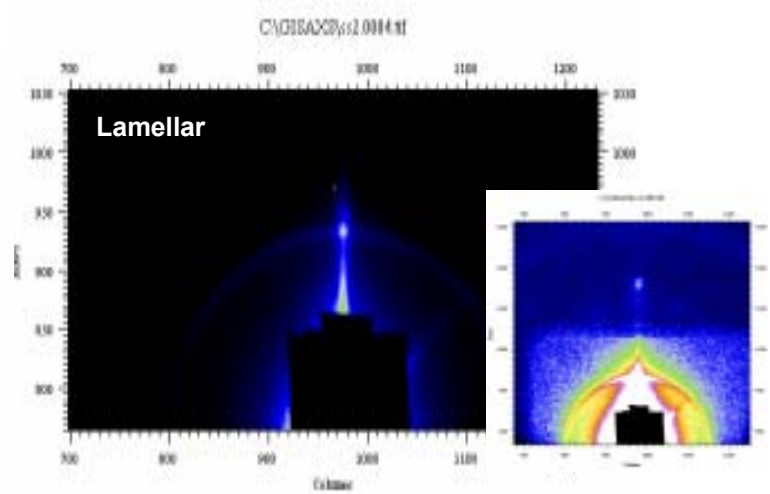
Mesoporous silica support used as a platform for bilayer formation

After 12 minutes of incubation

After 32 minutes

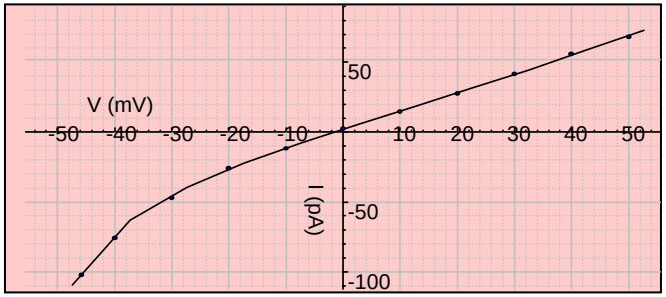
After 45 minutes, bilayer self-healed and imperfections disappeared





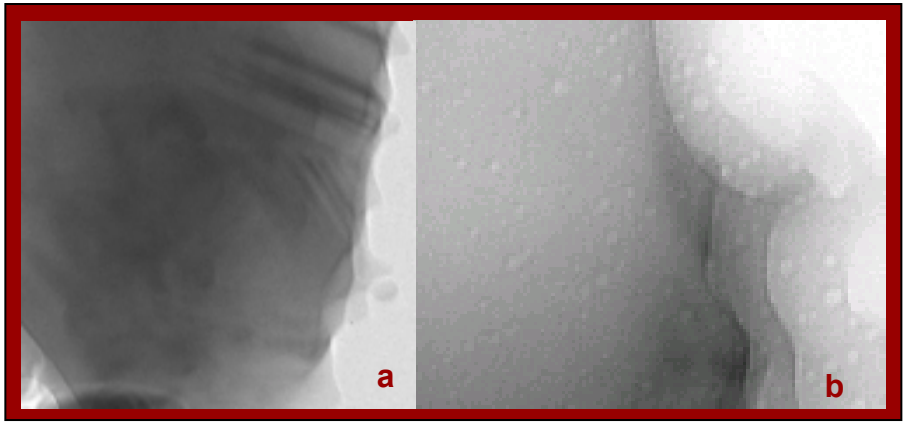
GISAXS of a) mesoporous silica support showing highly ordered cubic mesophase and b) DPPC bilayer formed on mesoporous silica support

In Situ Imaging of Ion Channel Formation

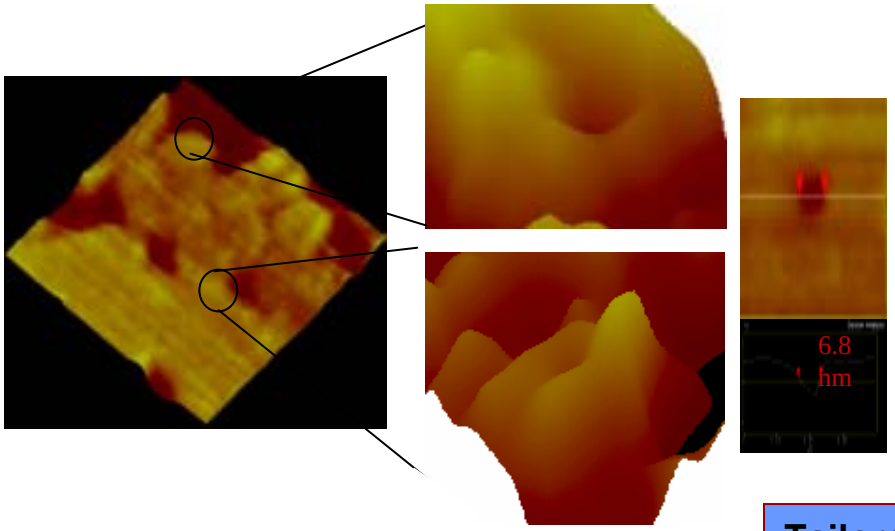


I-V curve showing bilayer with ~giga ohm resistivity

Applied mV	Lipid w/ AmB
0	0
1000	180 pA
2000	365 pA
4000	790 pA

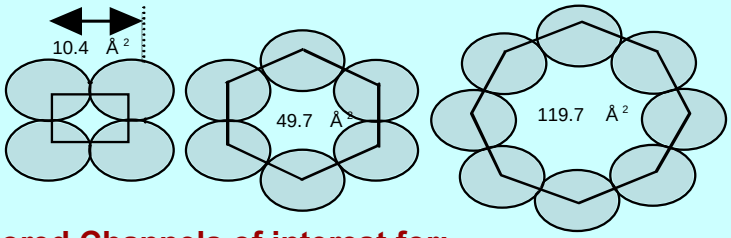


Cryo-TEM of a) phopholipid bilayer, b)phospholipid bilayer containing ion channel on mesoporous silica film supported on Cu grid.



AFM of AmB incorporated in lipid bilayer showing channel formation

We are evaluating how underlying mesoporous support influences AmB channel dimension



Tailored Channels of interest for:

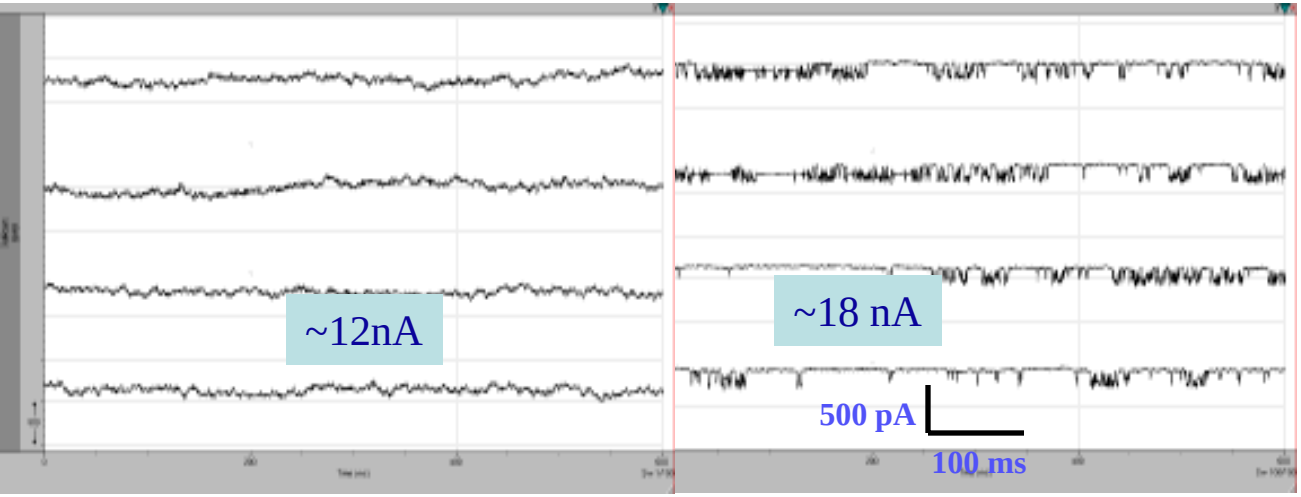
DNA sequencing (hours opposed to days needed in electrophoresis based techniques), Proteomics, Stochastic sensing etc.

Tailored channels with custom designed surface properties capable of molecular recognition have tremendous potential.

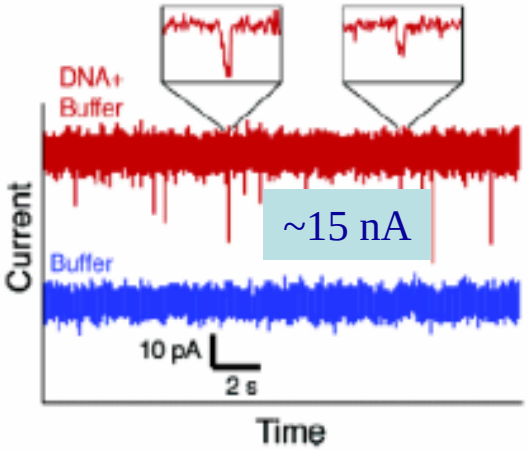
CTAB templated mesoporous silica membrane

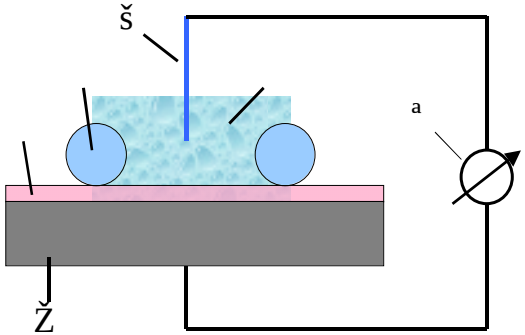
Collaboration with Vitaly Vodyanoy -- Auburn University

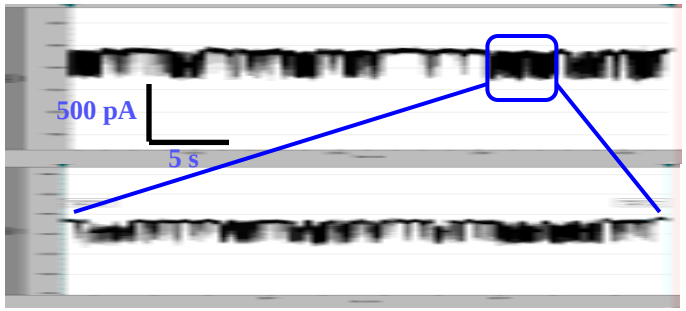
0.1 M KCl **0.1M TPAC + 0.1 M KCl**

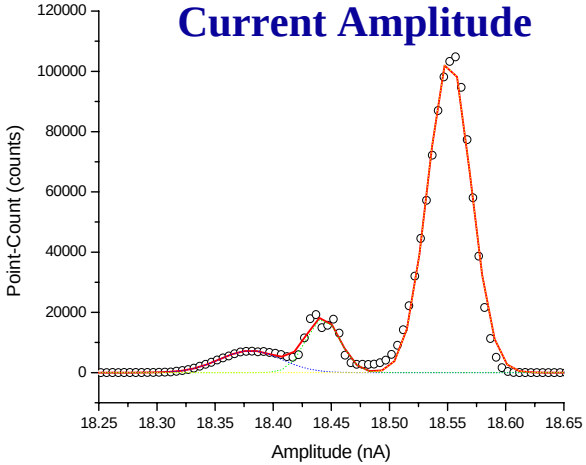


Nanopore embedded in PDMS for DNA detection (Saleh et al. Nanoletters, 2003)









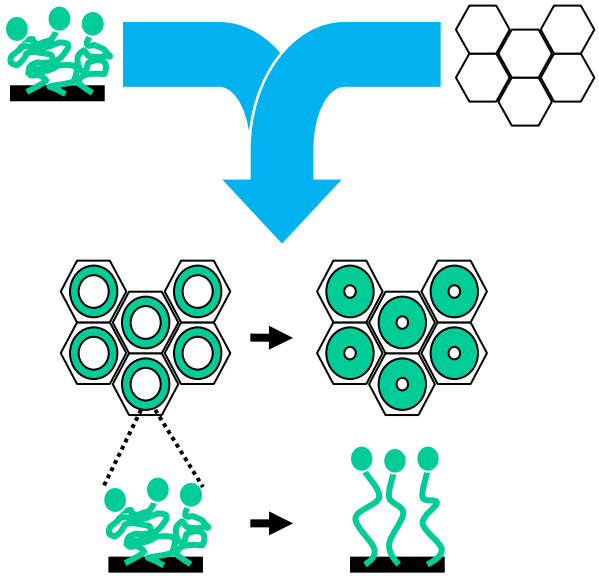
Ž -Substrate, -Mesoporous membrane, -O-ring, š -Electrode, -Ionic solution, a - Voltage clamp.

Potential: +160 mV, 0.1M KCl, Pore size: 1.8nm, Axopatch 200B

Hierarchical 3-D Organization Provides New Function

molecular systems

- smart response
- self-repairing
- poor stability
- difficult to manufacture



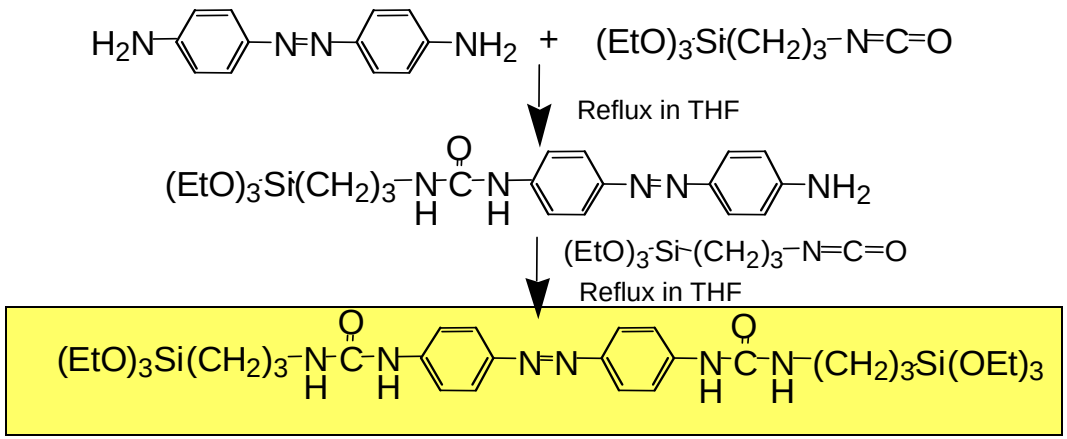
inorganic hosts

- robust, stable
- manufacturable
- limited dynamic response
- static properties

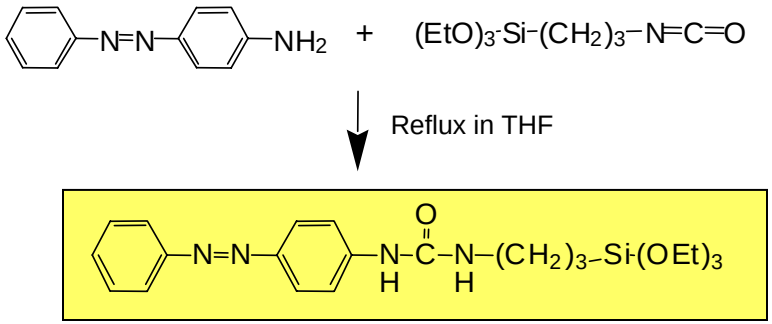
molecular nanocomposites

A new class of synergistic materials in which 3D positioning of Responsive molecules on inorganic framework creates qualitatively new function and imparts mechanical and thermal robustness

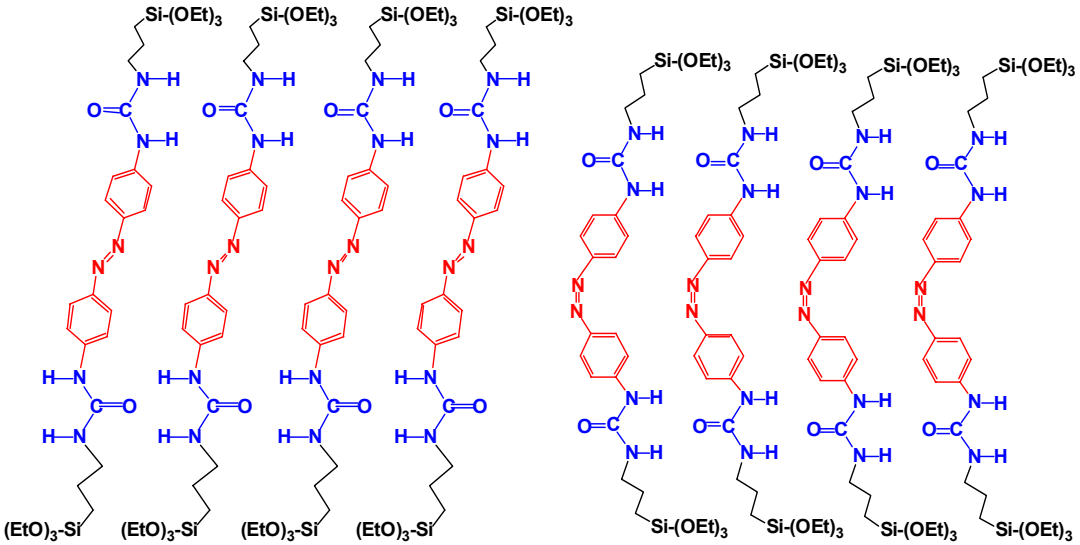
We synthesized several new optically-switchable silanes to achieve opto-mechanical actuation on the nanoscale.



Bridged azobenzene (BAB)



Pendant azobenzene (PAB)



Optically-directed self-assembly of layered nanostructures

J. Am. Chem. Soc., 2002

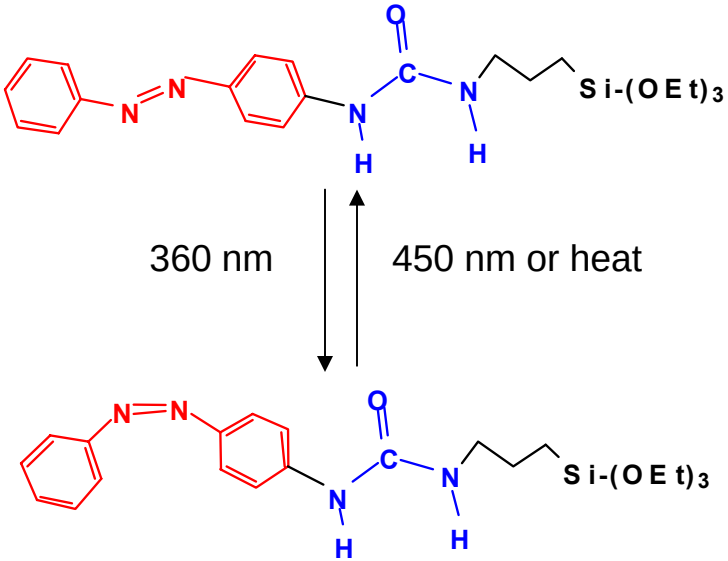
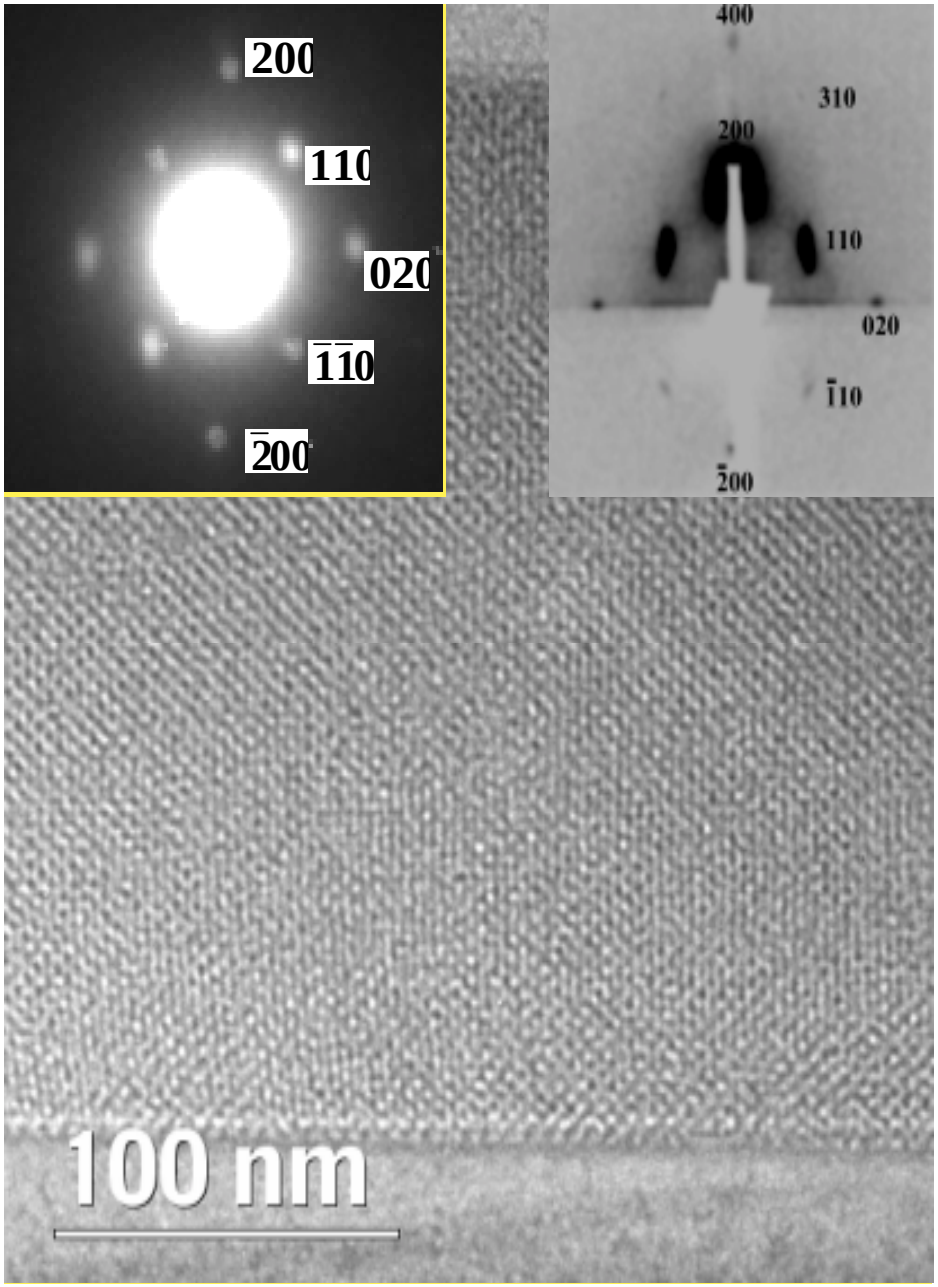


Photo-isomerization of PAB

Angew Chemie, 2003

Mesostructure

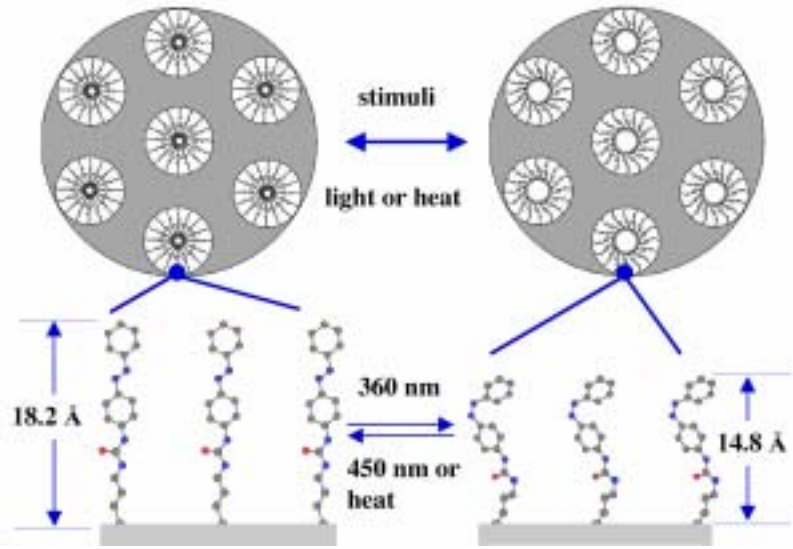
TEM cross–sectional image, electron diffraction, and 2D GISAXS data of Brij56 templated photoresponsive films indicate a BCC cubic mesostructure (Space Group *Im3m*) with a unit cell dimension *a* = 5.7 nm (d_{200} = 2.85 nm). The 2D GISAXS data indicates that the (100) plane of the *bcc* mesostructure is oriented parallel to the silicon substrate.

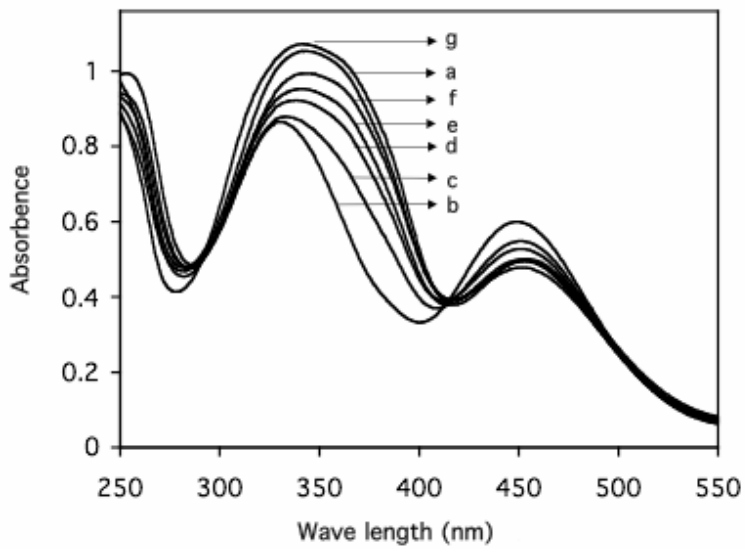


Liu *et al. Nano Lett.* 2004

Optically Switchable Nanocomposite

Only upon surfactant removal do we realize photoisomerization, enabling optical switching of pore size - Surfactant required to create isomerization volume





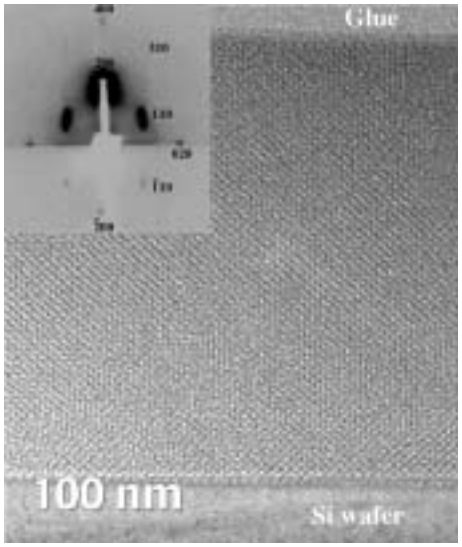
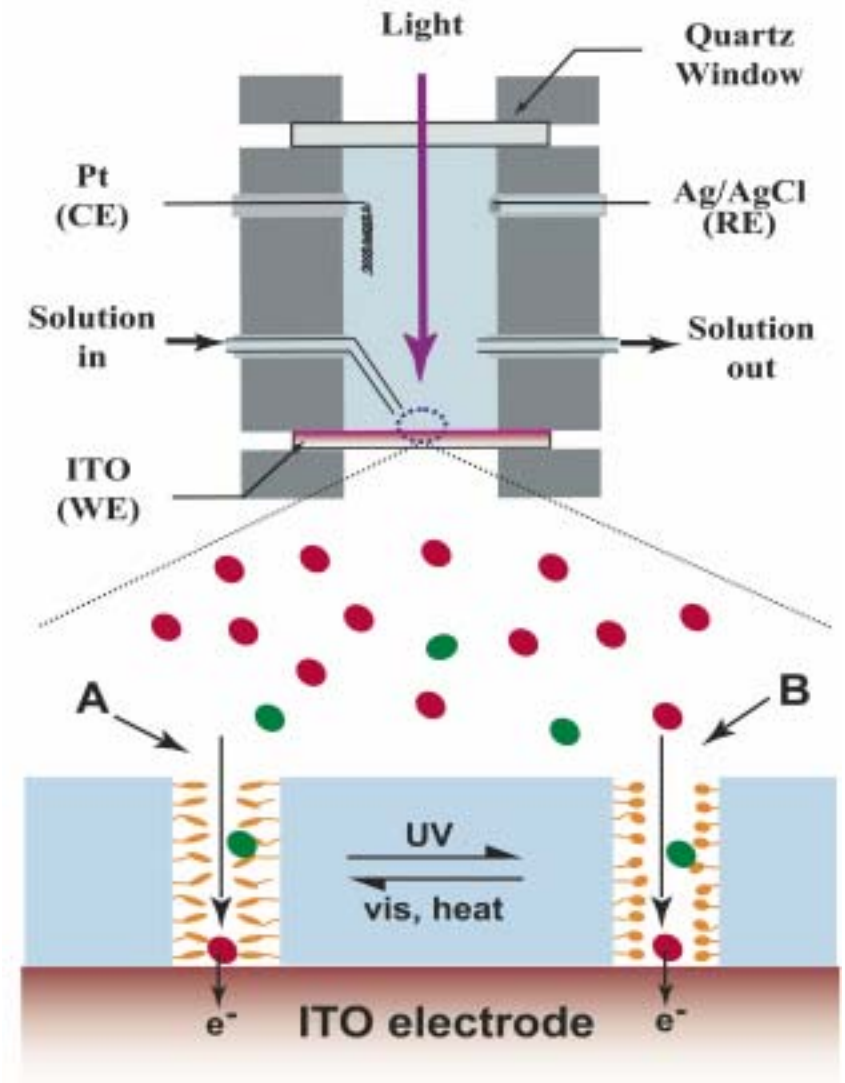
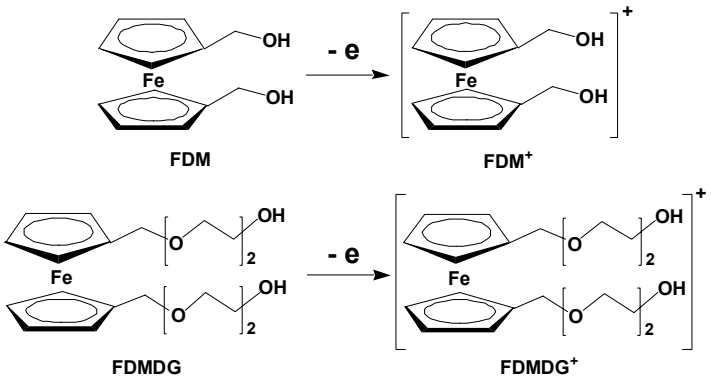
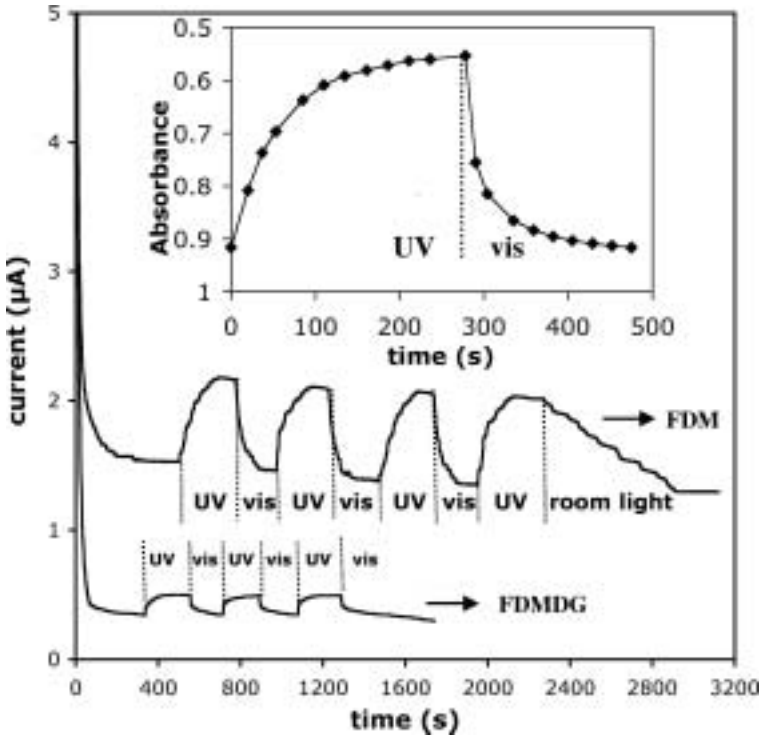


Photo and thermal isomerization of azobenzene ligands in the nanocomposite films prepared with Brij56 template. a) As-prepared; b) after UV irradiation of sample (a) for 30 minutes; c, d, e, f) after room light exposure of sample (b) for 3, 15, 35, and 60 minutes, respectively; g) after heating sample (b) to 100˚C for 5 minutes.

Photoregulated mass transport through photoresponsive azobenzene-modified nanocomposite membranes





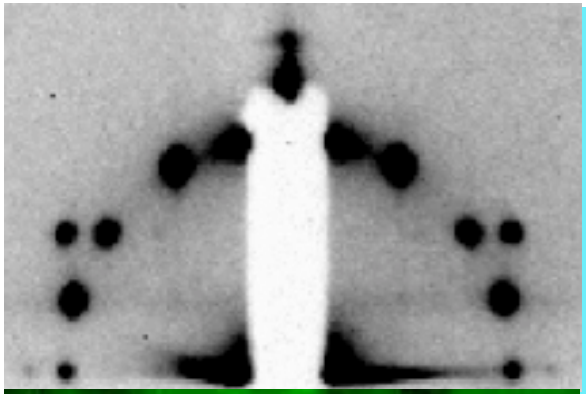


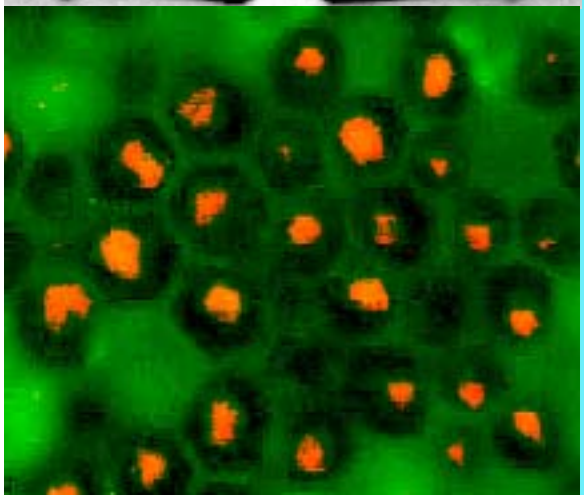
Optically switchable conformation (*trans* or *cis*) of azobenzene ligands controls the effective pore size, and, correspondingly, transport behavior on the nanoscale. Liu et al. Nano Lett. 2004

QuickTime™ and a
YUV420 codec decompressor
are needed to see this picture.

U of Illinois
Tajkhorshid et al. (2002)

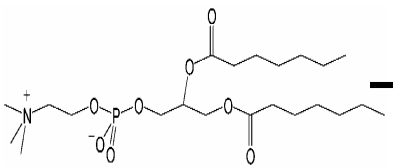
Part 3

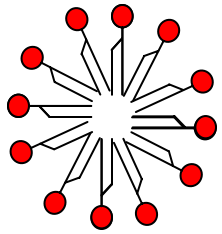


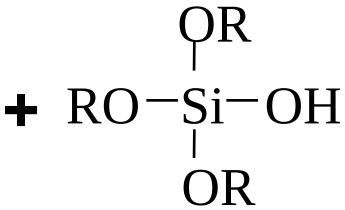


- Biocompatible Self-Assembly
- Cell Immobilization in Nanostructured Hosts→(Living) Particle Nanocomposite
- Cell-Directed Self-Assembly

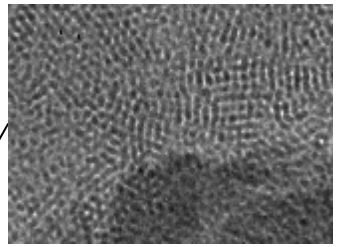
Immobilization of Genetically Engineered Cells



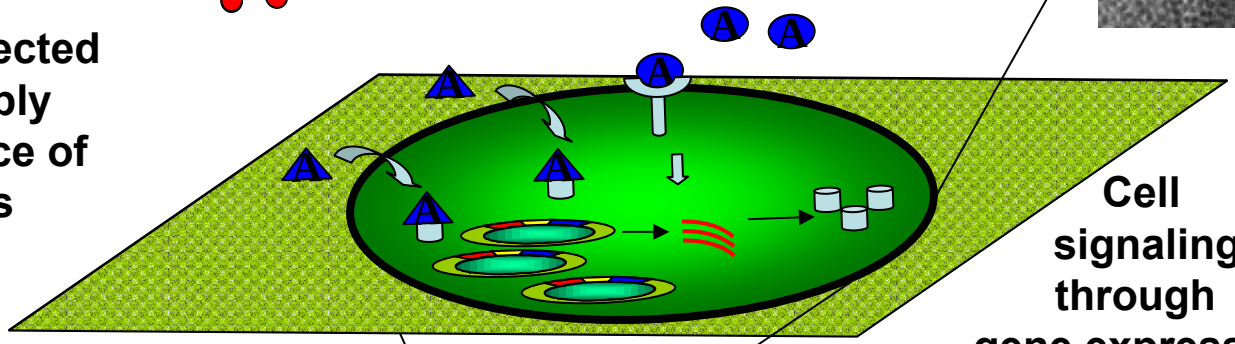




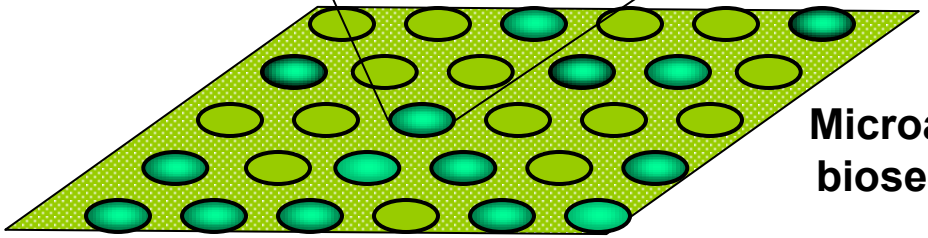
S. cerevisiae



Surfactant-directed self-assembly in the presence of living cells



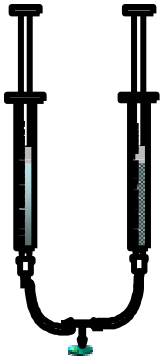
Cell signaling through gene expression



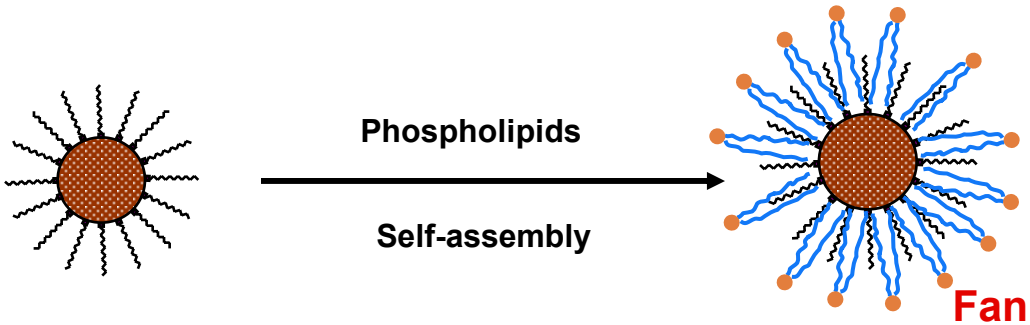
Microarray biosensor

Viable cells retain functionality through biocompatible self-assembly

Biocompatible patterning and cell localization



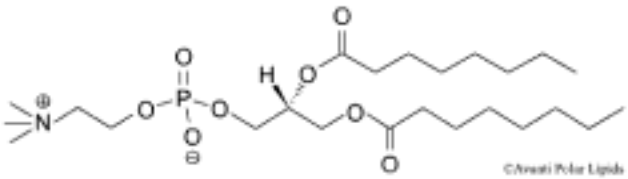
Phospholipid Encapsulated Gold Nanocrystals



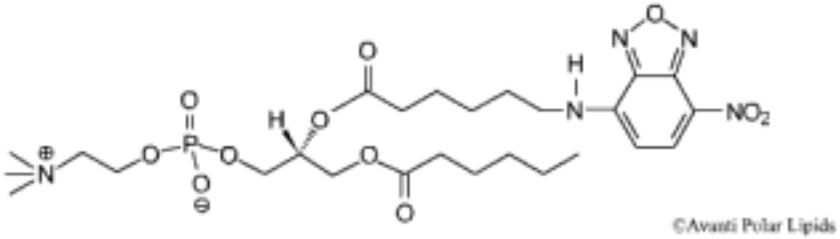
Fan *et al. Science, 2004*

Functional lipids and surfactants and connectors:

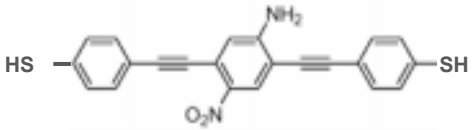
1,2-Dioctanoyl-*sn*-Glycero-3-Phosphocholine



1-Hexanoyl-2-[6-[(7-nitro-2-1,3-benzoxadiazol-4-yl) amino]hexanoyl]-*sn*-Glycero-3-Phosphocholine

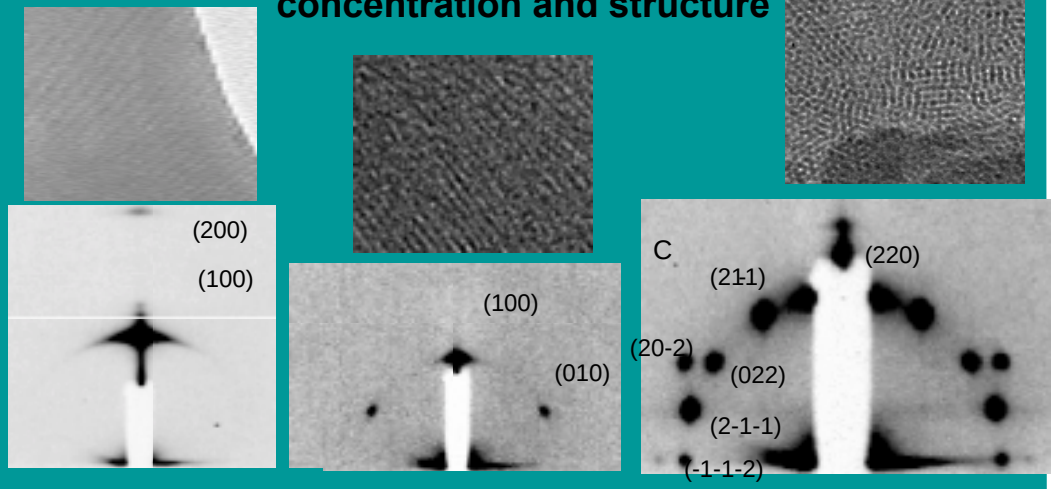


HS-R-SH, R= alkane, conjugated units, conducting units etc.



Living Cells Direct Assembly of Silica Nanostructure Through Phospholipid Interface

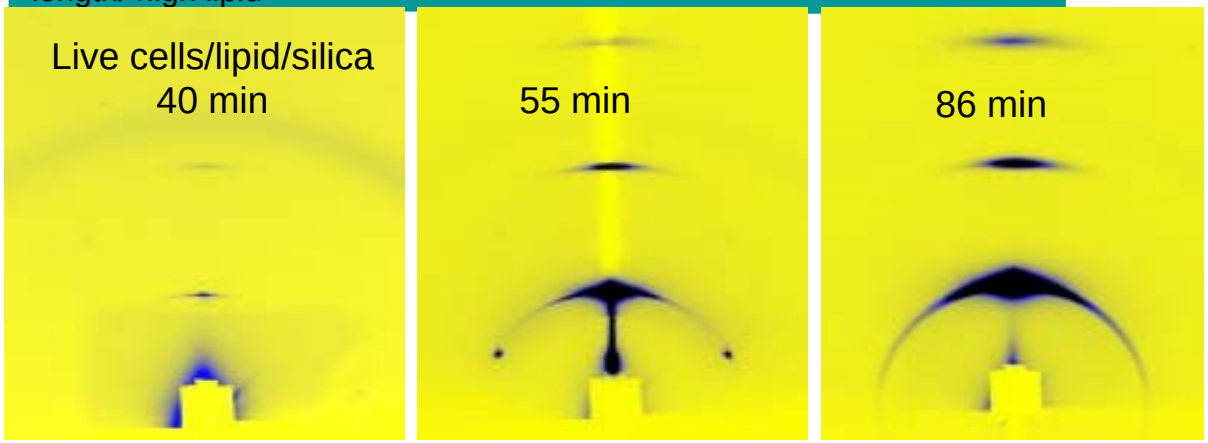
Silica mesophase depends on lipid concentration and structure



C10, high C6, C8 Lamellar- long tail length/ high lipid

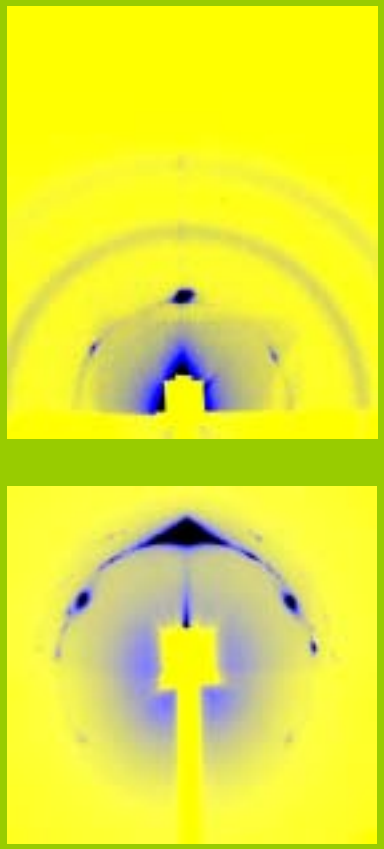
low C6, C8Hexagonal-short tail length/ low lipid

Cubic phase (Im3m or Pm3n) of GMO (glycero-monooleate).

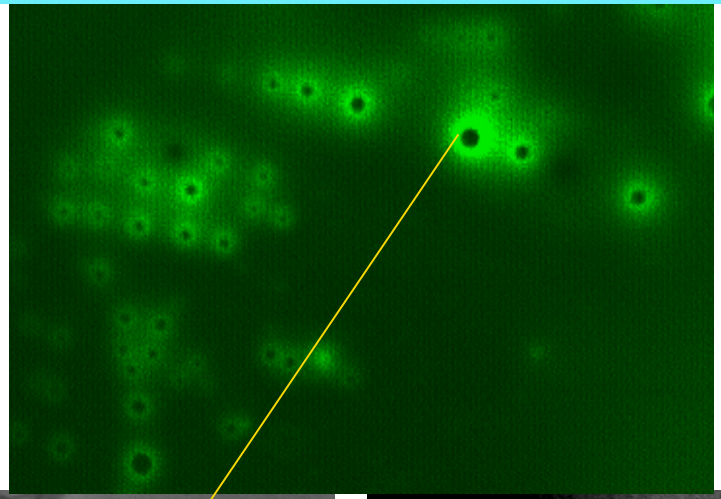


Live cells direct silica self-assembly-hexagonal to lamellar phase transition

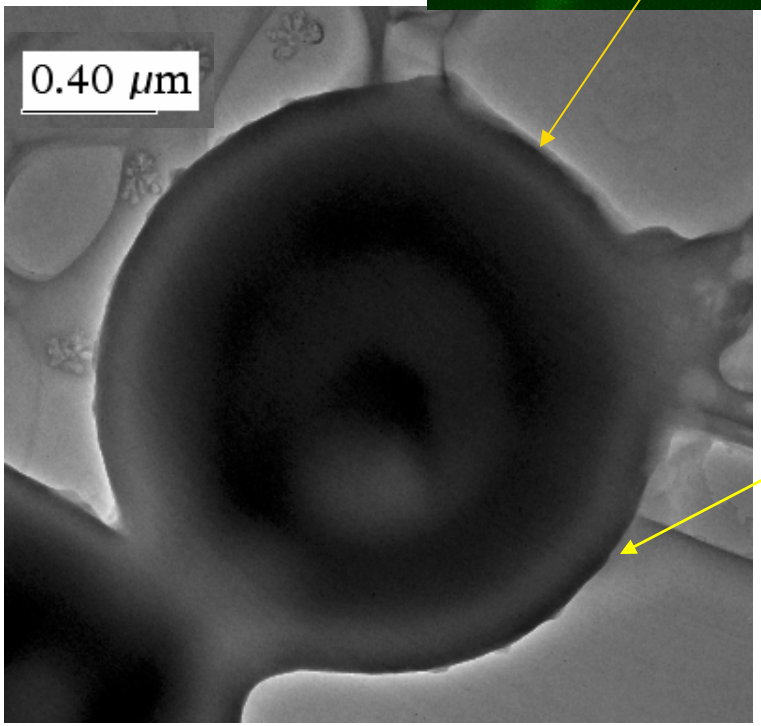
Surrogate cells do not affect silica self-assembly

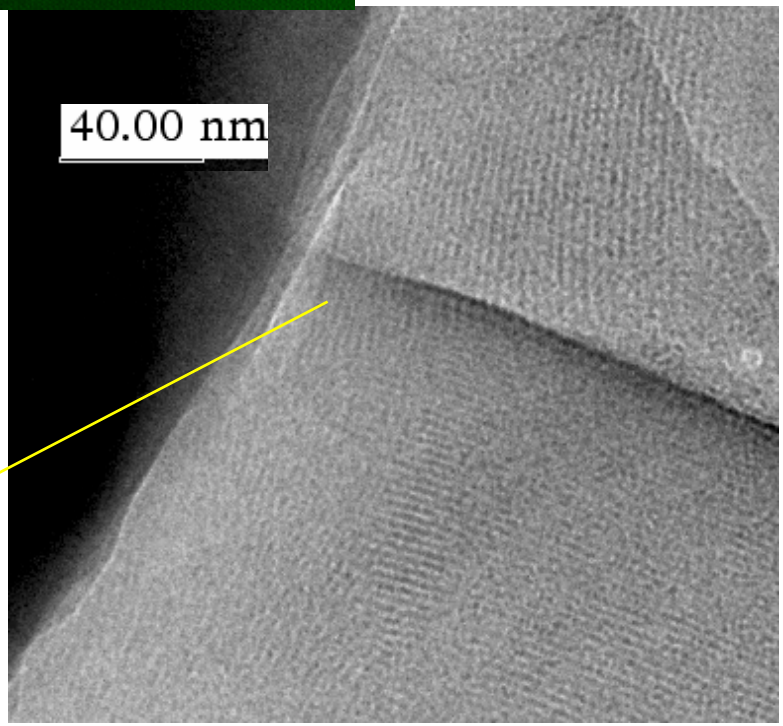


Cells Co-Opt Self-Assembly - creating a phospholipid reservoir at the bio/nano interface that largely excludes silicic acid

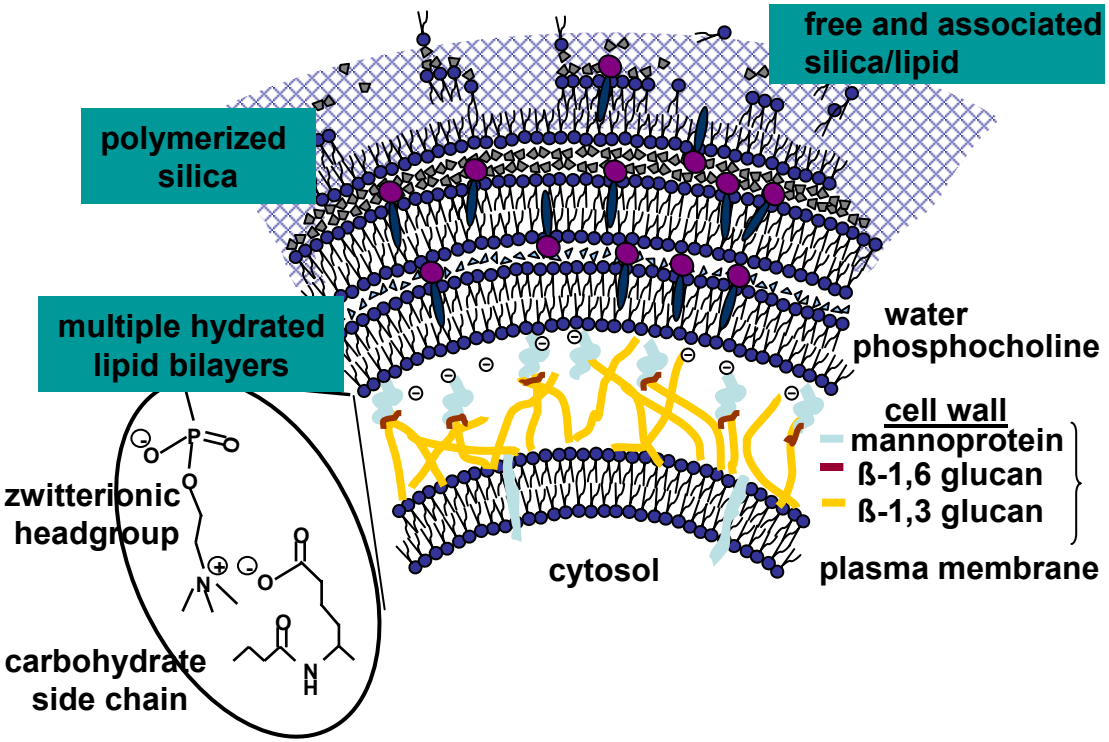


1% optically labeled lipid

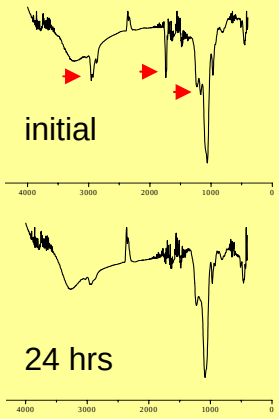


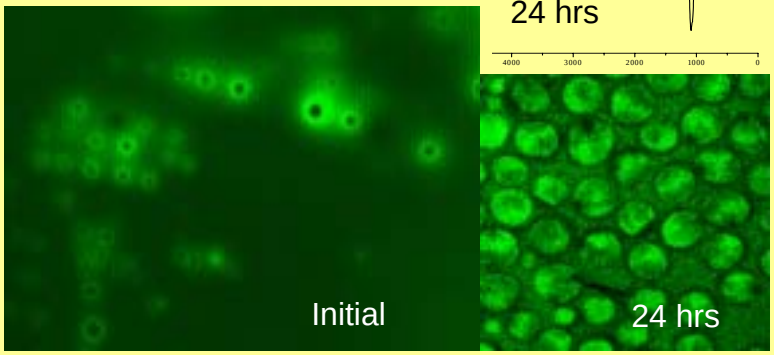


Living Cells Direct Assembly of Novel Phospholipid / Silica Interface

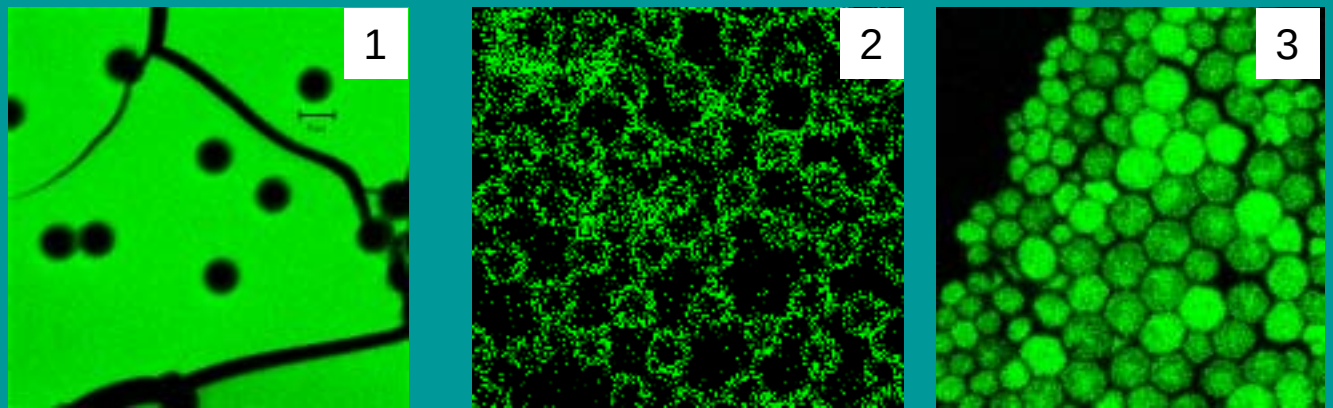


Phospholipid concentrates around cell. Gradual uptake over 24 hrs corresponds to ester cleavage





Models show living cell necessary for phospholipid organization



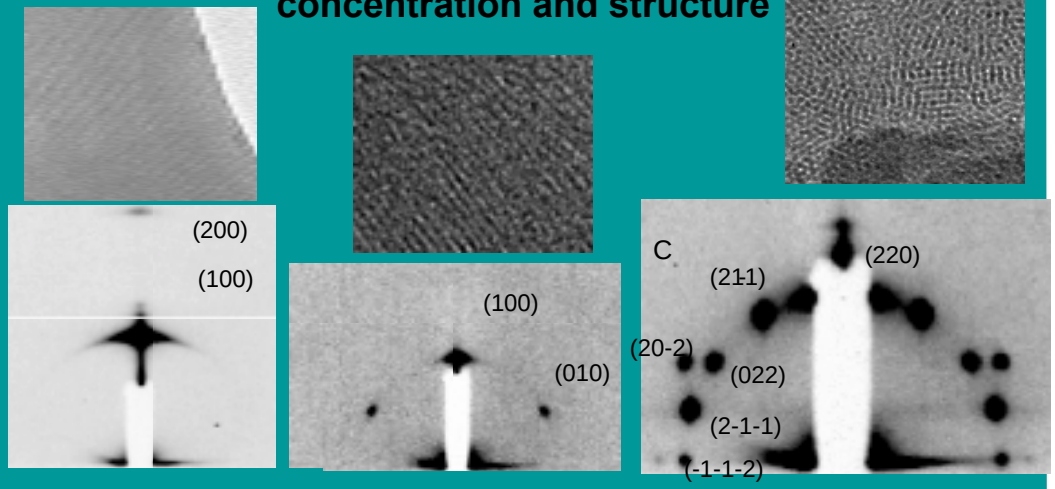
1.Latex beads show no lipid aggregation

2. Negatively charged latex beads(cell wall model) concentrate lipid

3. Dead cells (compromised membrane) show lipid uptake

Living Cells Direct Assembly of Silica Nanostructure Through Phospholipid Interface

Silica mesophase depends on lipid concentration and structure



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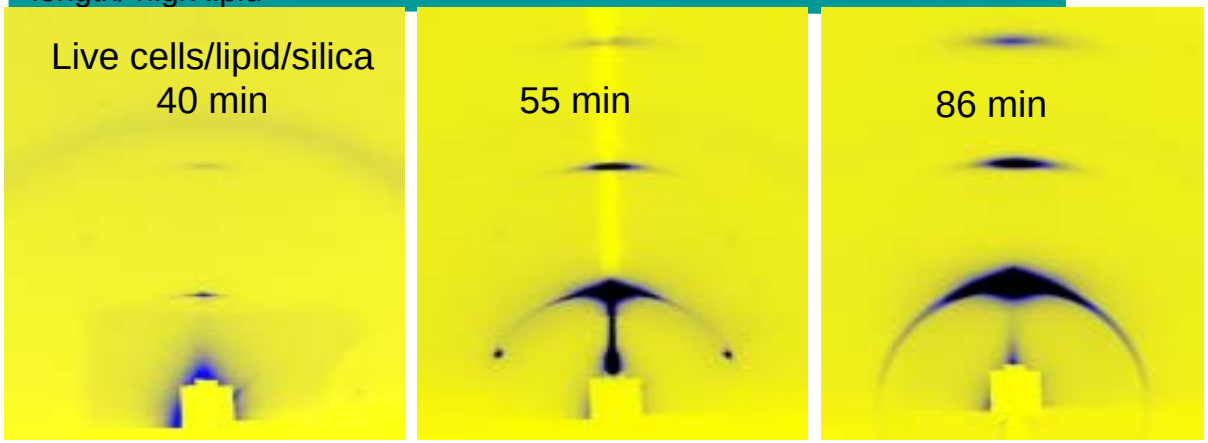

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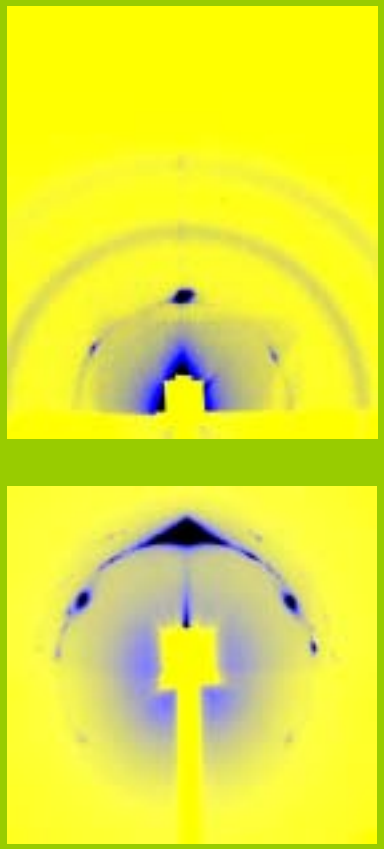
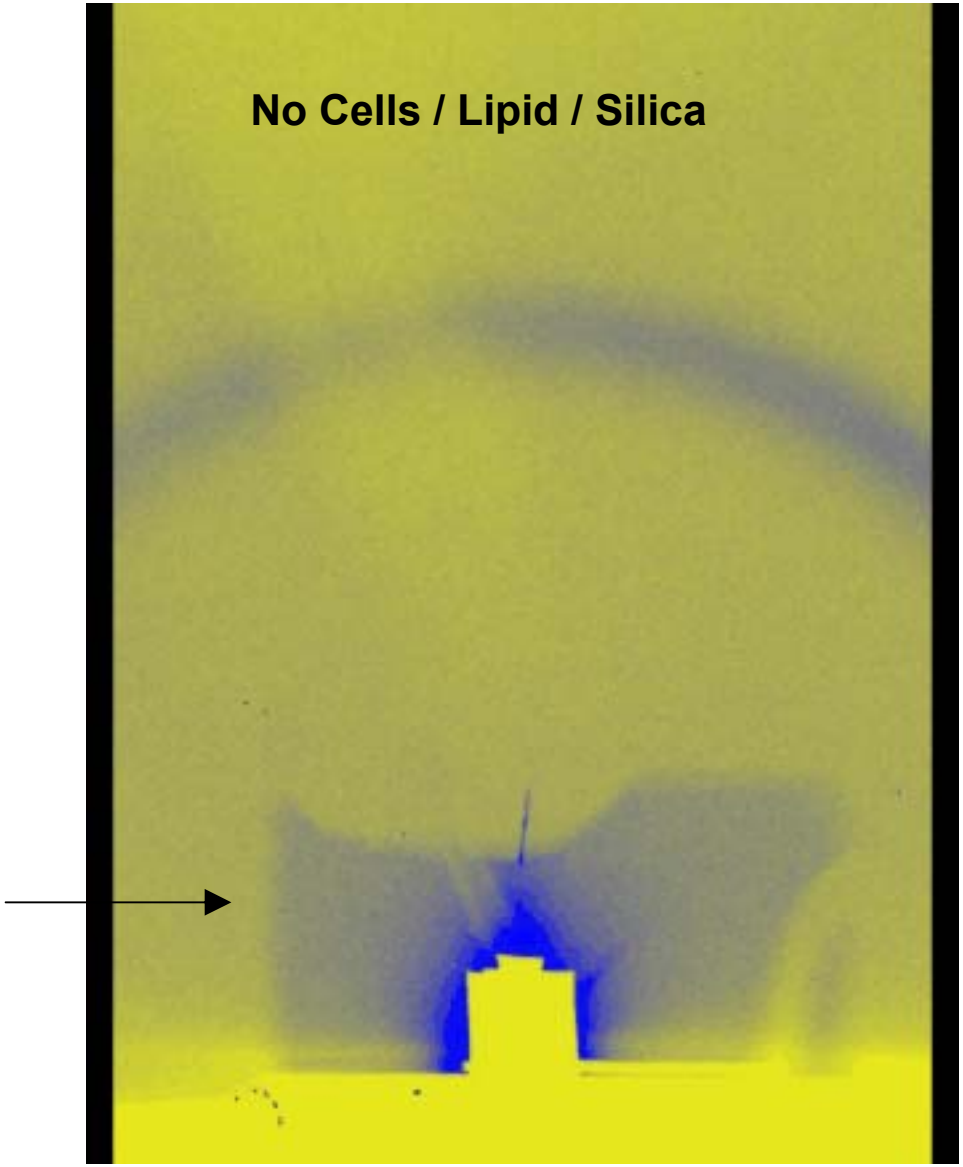
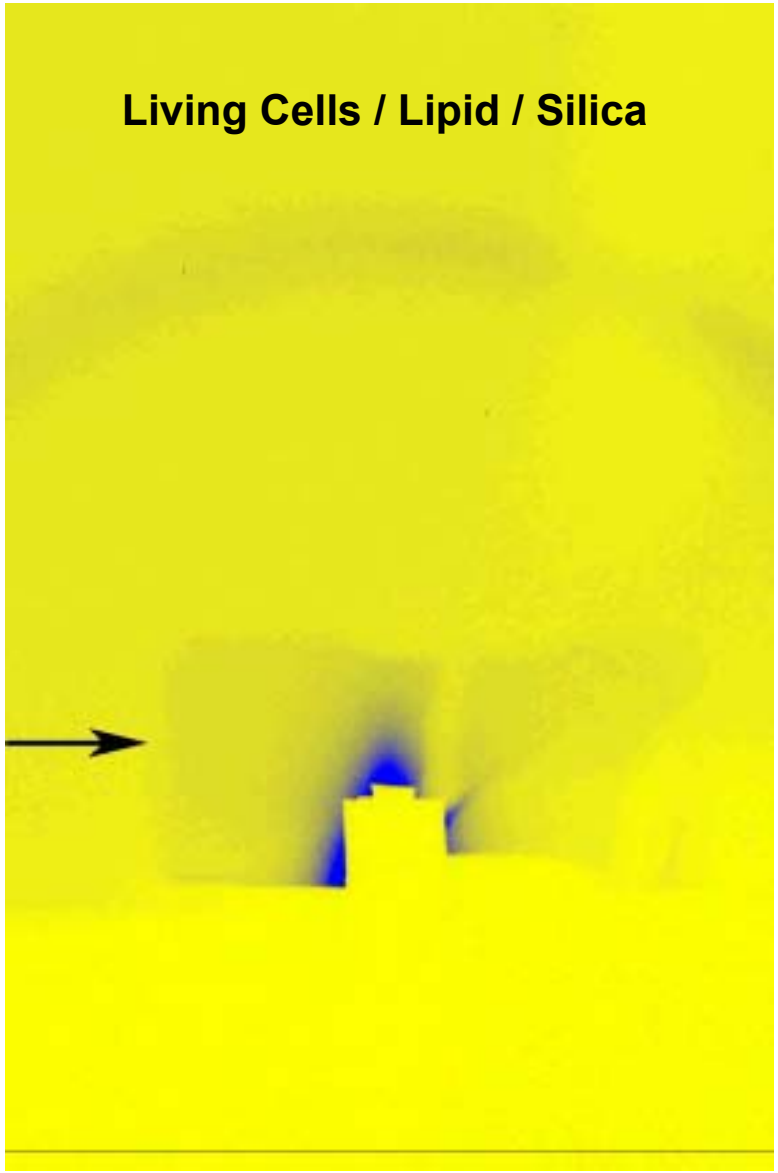


In Situ Grazing Incident X-Ray Scattering

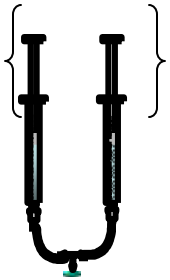




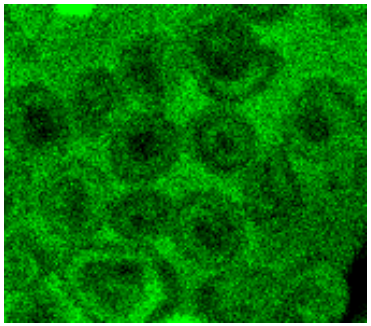
Living Cells Direct Assembly of Nanocrystals / Proteins Through Phospholipid Interface

Nanocrystals without added lipid

Silica precursors



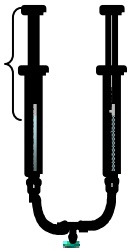
Cells,gold nano-crystals with NBD label



Cells collapse, labeled crystals dispersed through sol

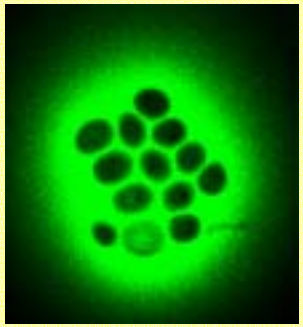
Nanocrystals in silica with added lipid

Silica precursors

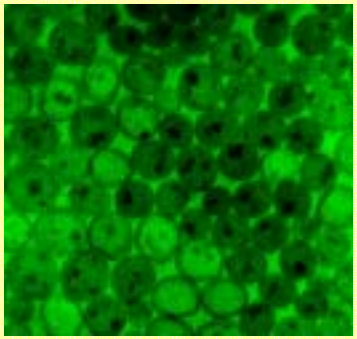


Cells,gold nano-crystals with NBD label lipid template

6 hrs ← → 24 hrs

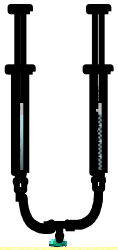


Cells viable, labeled crystals aggregate around sol

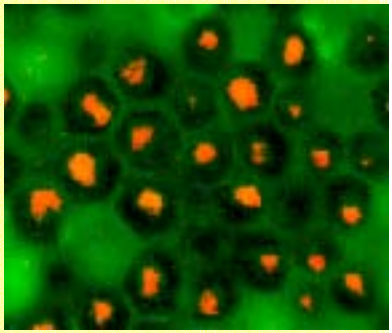


Nanocrystals at cell wall. High intracellular density and fluorescence indicate intracellular nanocrystals and lipid

Semiconductor nanocrystals in silica with added labeled lipid



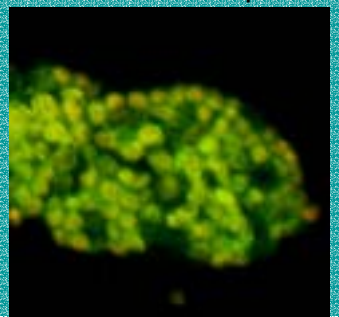
Cells,CdSe nano-crystals, labeled lipid template



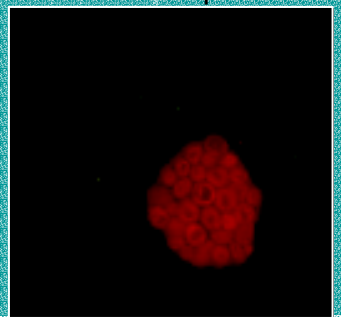
Red emission from nanocrystals in cells. Green labeled lipid concentrates around cell, may also be present in cell

Phospholipids required for cell viability

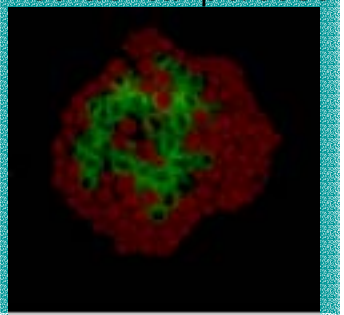
Cells/silica/no lipid



Cells/silica/lipid/Gold



Cells/silica lipid/CdSe



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