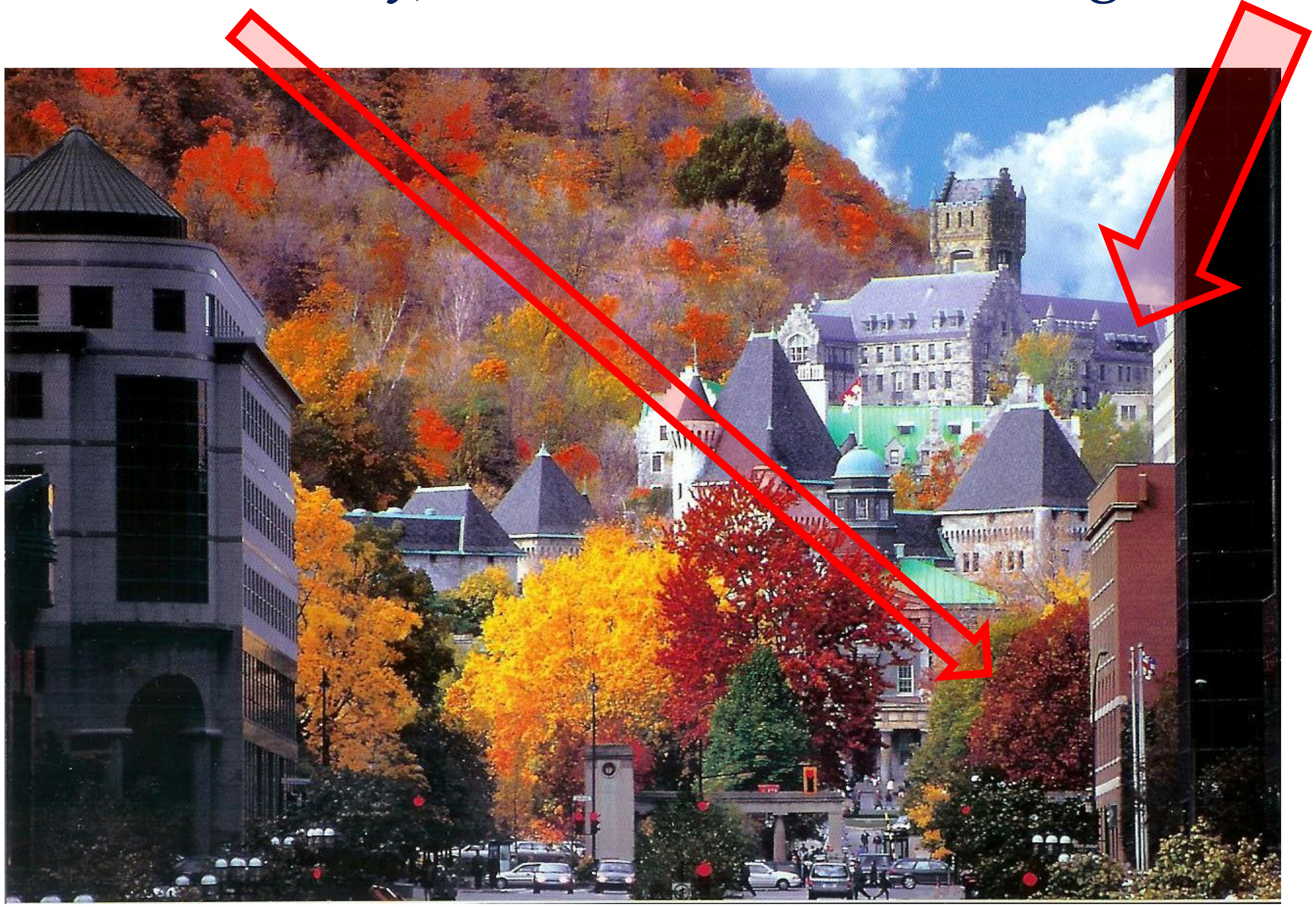
Bio-Inspired soft, squishy, materials for Neuro-Engineering at the Brain-Machine Interface.

Christopher Barrett, O. Mermut, T. Kennedy, E. Musk, A. MacDonald.
c/o McGill U. Chemistry, and the Montreal Neurological Institute



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c/o McGill U. Chemistry, and the Montreal Neurological Institute

C. J. Barrett, Art MacDonald, and students,

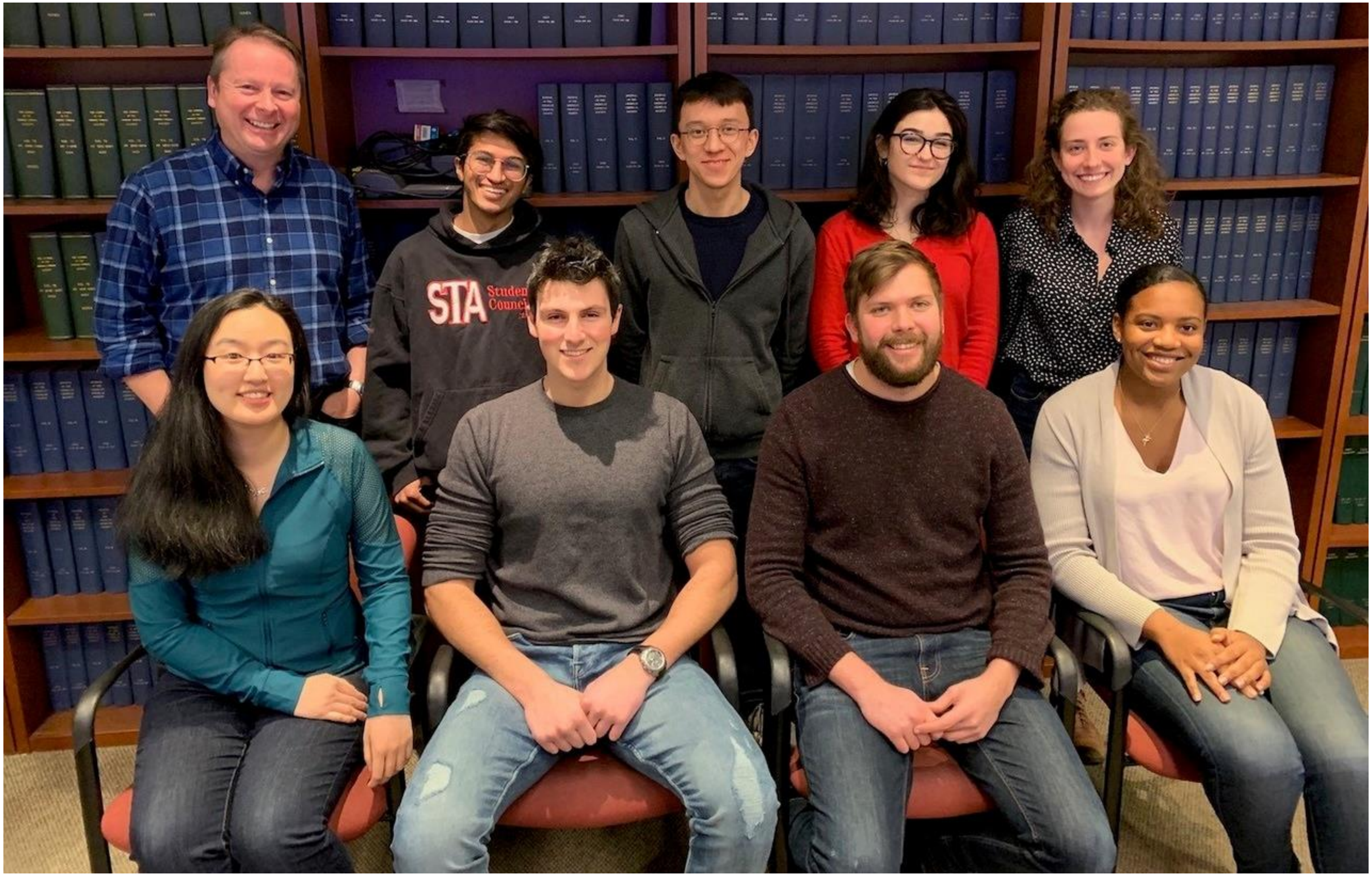
Queen's U. Physics, CINS, Sudbury Neutrino Observatory (1993 – 2014)

Elon Musk, Max Hodak and 6 other founders,

NeuraLink Corporation, Berkeley /San Fran (Fulbright 2016 –)

Also: MIT, Tokyo Tech, Chalk River Nuclear Labs, Grenoble, NIST, Los Alamos, Lawrence Berkeley National Labs, York U. (2021-)

Merci York. & the terrific McGill U. Students who did all the work :

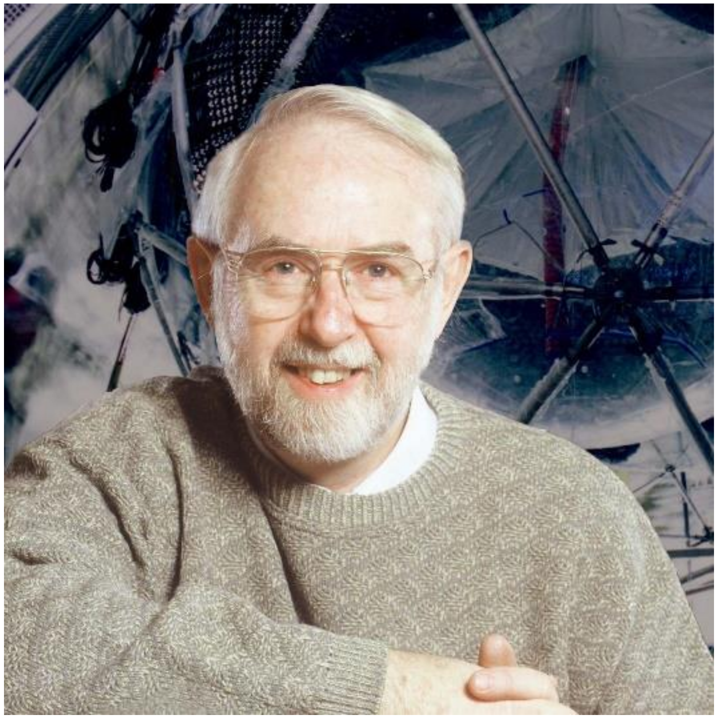


Dr. Igor Elkin, Anais Robert, Mikel Landry, Maria Gorenflo,
Monica Lin, Dr. Issei Otsuka, Dean Noutsios, Victoria Chang,
Tristan Borchers, Kayrel Edwards, Mikhail Kim, Shayne Gracious.

JSPS Visiting Sabbatical Professor, Tokyo Tech 2017

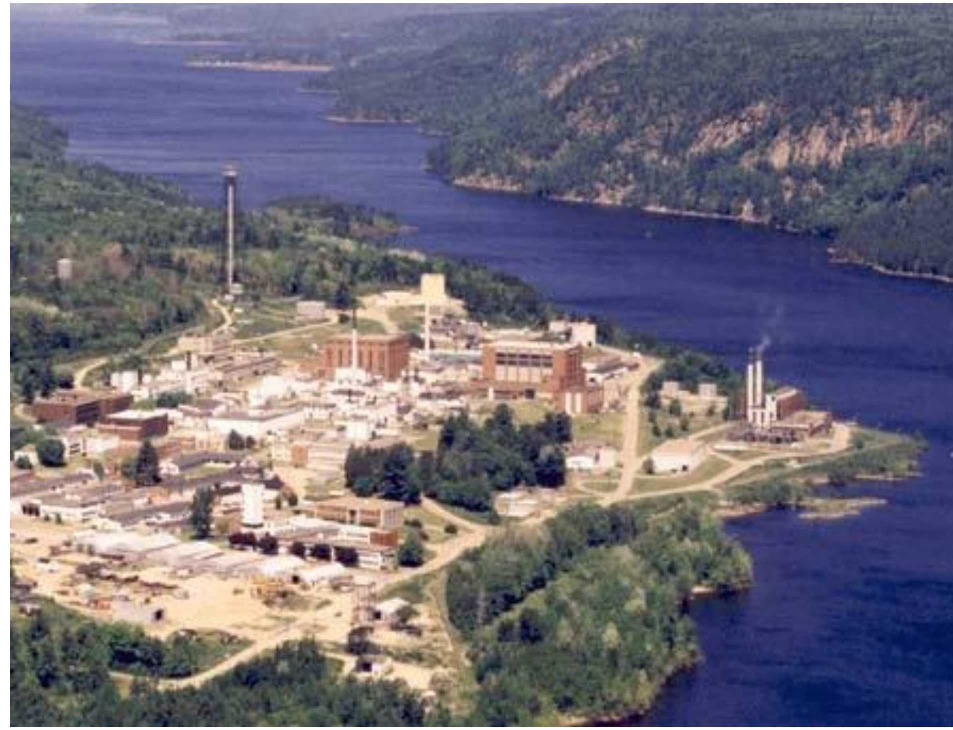
Atsushi Shishido, Tokyo Tech Materials Engineering, Liquid Crystals, Robotics, Flex Display Engineering.

The SNO project (Sudbury Neutrino Observatory), and Canada's Chalk River Nuclear Laboratories, and CINS:



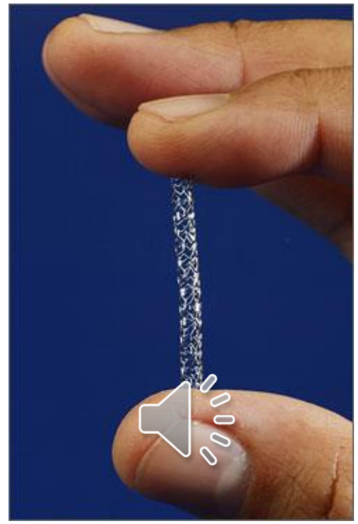
Prof. Art MacDonald, Queen's. SNO Director, Nobel Prize in Physics 2015 for SNO Team.

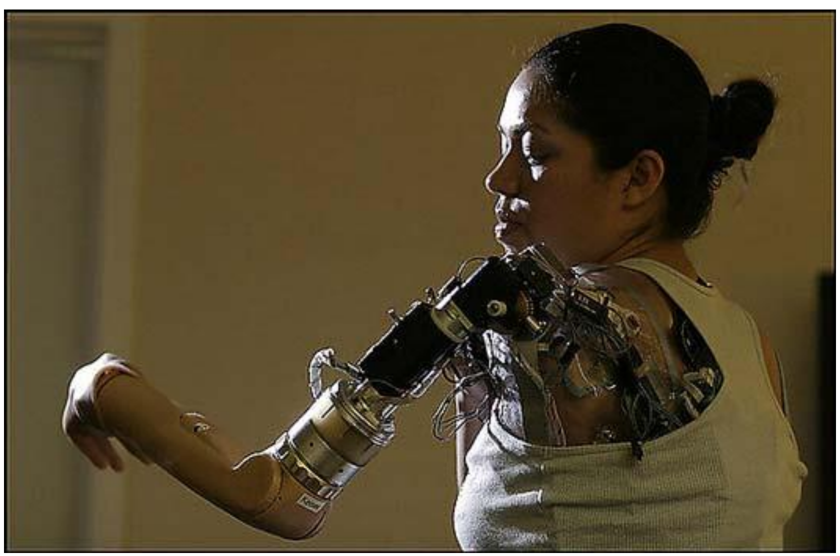
(incl. students C. Barrett, E. Musk…)

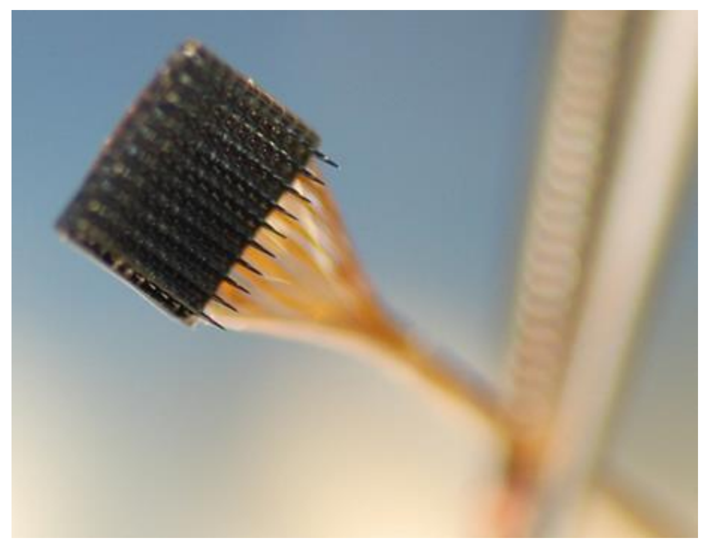


Neutron Beam Research Centre: new $8M beamline in 2009 for soft, wet, biomaterials, coatings.

The end goal and big dream ?
to Engineer the Human-Machine Interface…

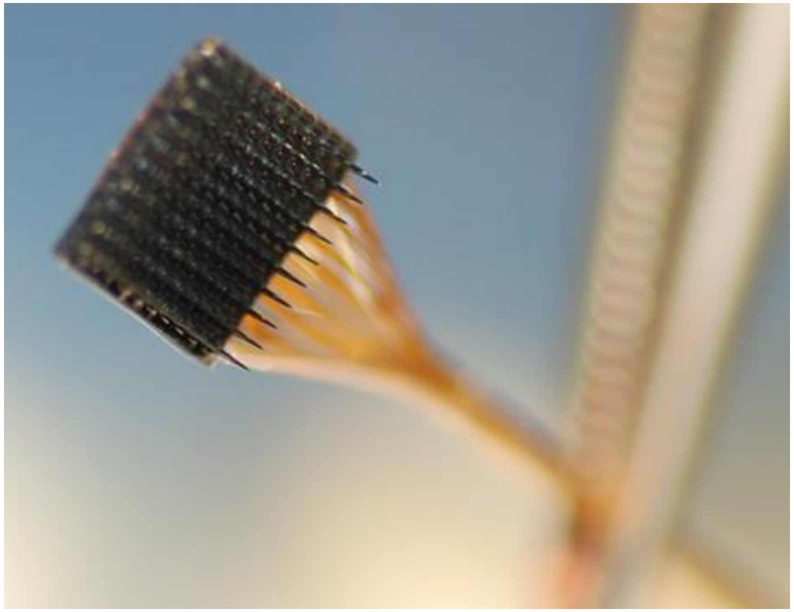






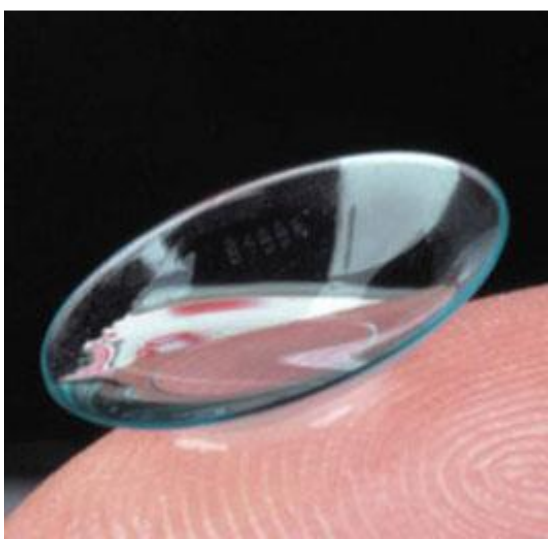
Self-Assembly of soft wet polymer nano-layers: towards engineering bio-compatible surfaces

The GOAL is to coat surfaces of implants, so that they don’t suffer rejection–hips, artificial organs, valves, stents drain pipes, artificial limb ends, grafts, tissue scaffolds…



Self-Assembly of soft wet polymer nanolayers: towards engineering bio-compatible surfaces

The GOAL is to coat surfaces of implants, so that they don't suffer rejection–hips, artificial organs, valves, stents drain pipes, artificial limb ends, grafts, tissue scaffolds… dentistry, plates, pins, contact lenses, sutures, stitches…



John Donoghue Lab's 'BrainGate 2' Brown U., 2015.

Paralyzed woman controls tablet with her thoughts

CLAIRE BROWNELL

A California woman with a chip implanted in her brain has successfully browsed the web using a tablet powered by her thoughts, bringing scientists one step closer to helping people who are completely paralyzed engage with the outside world.

The woman, known as clinical trial participant T6, has Amyotrophic Lateral Sclerosis, which is otherwise known as ALS or Lou Gehrig's disease. She can talk, manipulate objects and get around in a wheelchair, but the terminal disease will eventually render her completely paralyzed.

T6 volunteered to let scientists implant a microchip in her brain as part of a clinical trial called BrainGate 2, hoping to help them figure out how to help paralyzed people communicate by programming computers to read their minds. At the annual Society for Neuroscience Conference in Chicago on Oct. 21, Stanford post-doctoral researcher Paul Nuyujukian gave a presentation announcing T6 had successfully operated a tablet using the technology.

What's more, scientists were able to replicate the results in a second participant on the east coast, Nuyujukian said in an interview. But Nuyujukian approaches the topic with a scientist's caution, noting the technology is still being tested for safety and it's too early to say for sure whether it will have useful medical applications.

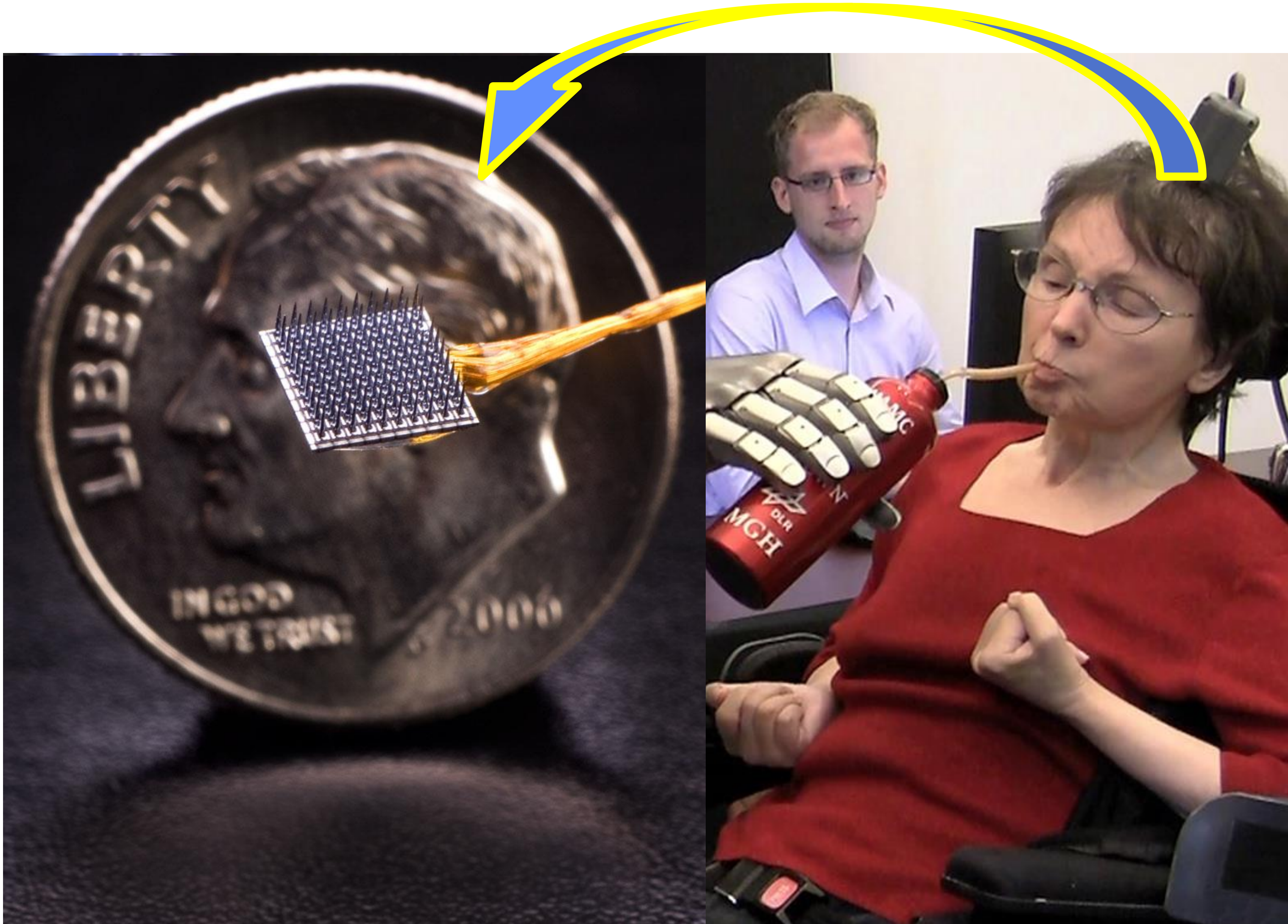
"This is still very much a research study," he said. "There's no implication of clinical benefit."

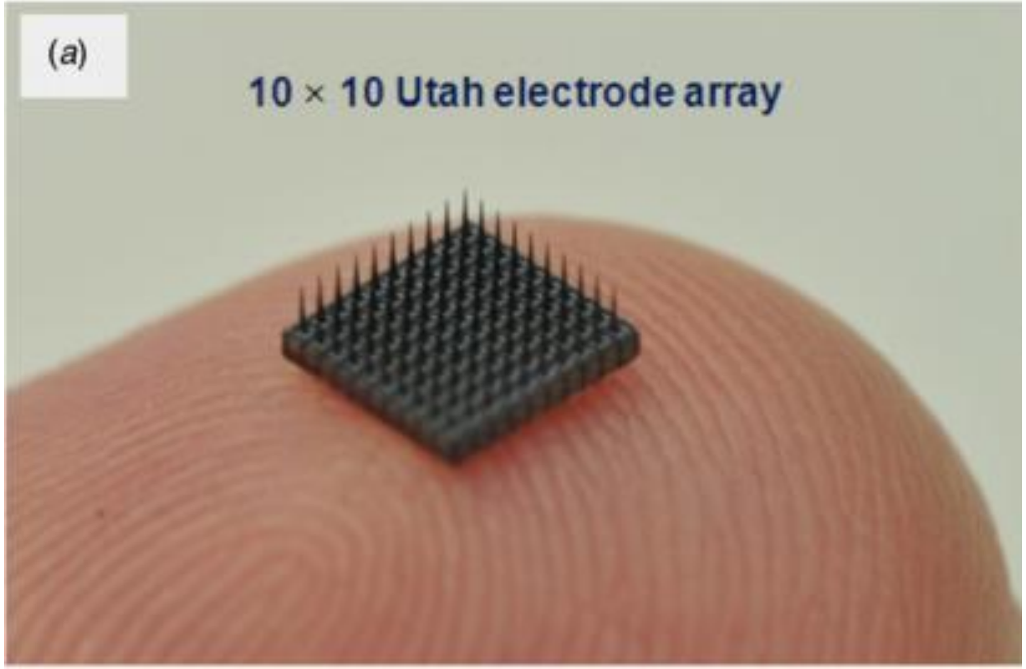
A less cautious person might be forgiven for being a little more excited. Scientists have plugged a woman's head into a mind-reading computer that helped her browse the web for gardening advice. "Implication of clinical benefit" or not, that's huge. If future trials prove successful, the same technology could also allow paralyzed people to control robot arms and other prostheses with their thoughts.

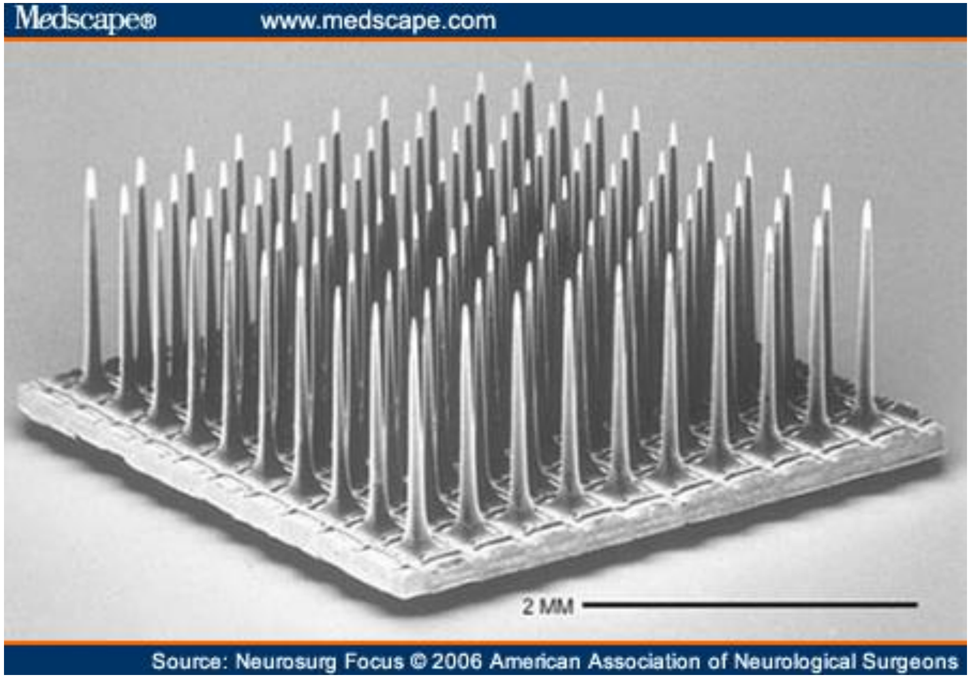
The cable sticking out of this woman's head is attached to an implant in her brain that allows a computer to interpret her thoughts.

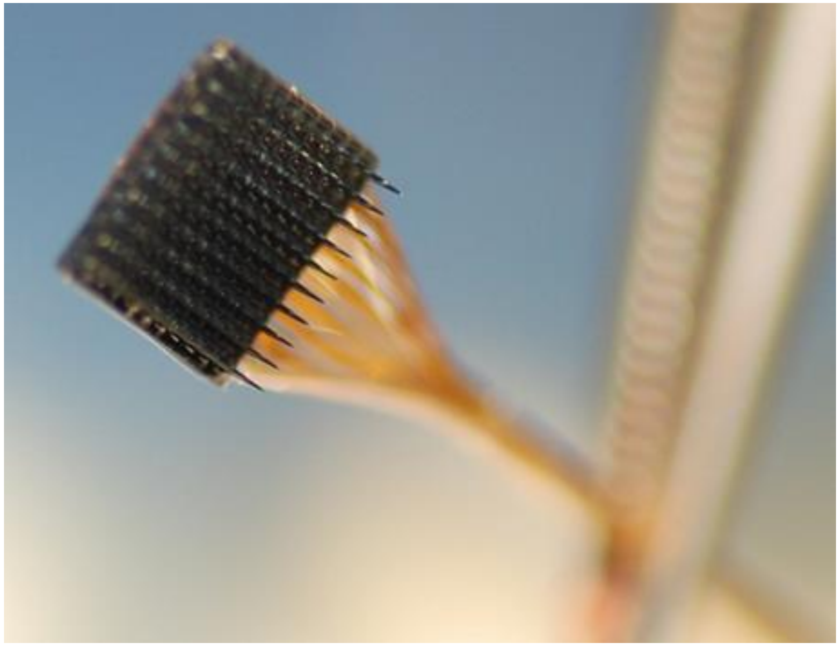
Before the tablet trial, BrainGate 2 scientists had developed a custom piece of software with a virtual keyboard, allowing participants to move a cur-

John Donoghue Lab's 'BrainGate' Brown U., 2015.

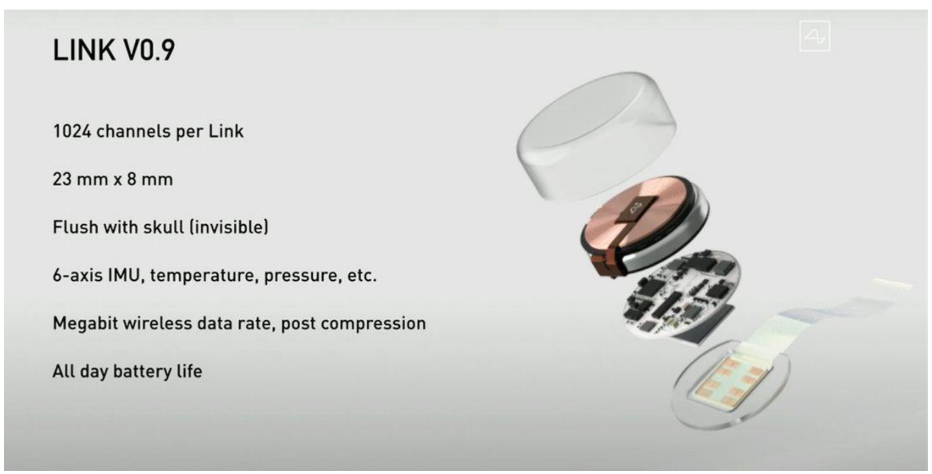



(a)
10 × 10 Utah electrode array


Medscape®
www.medscape.com
2 MM
Source: Neurosurg Focus © 2006 American Association of Neurological Surgeons



‘NeuraLink Corporation, 2015- (E. Musk, $150M)



‘NeuraLink Corporation’, San Francisco, CA

Developing implantable Brain Machine Interfaces ($150M+)

Founded 2015, E. Musk. M. Hodak.

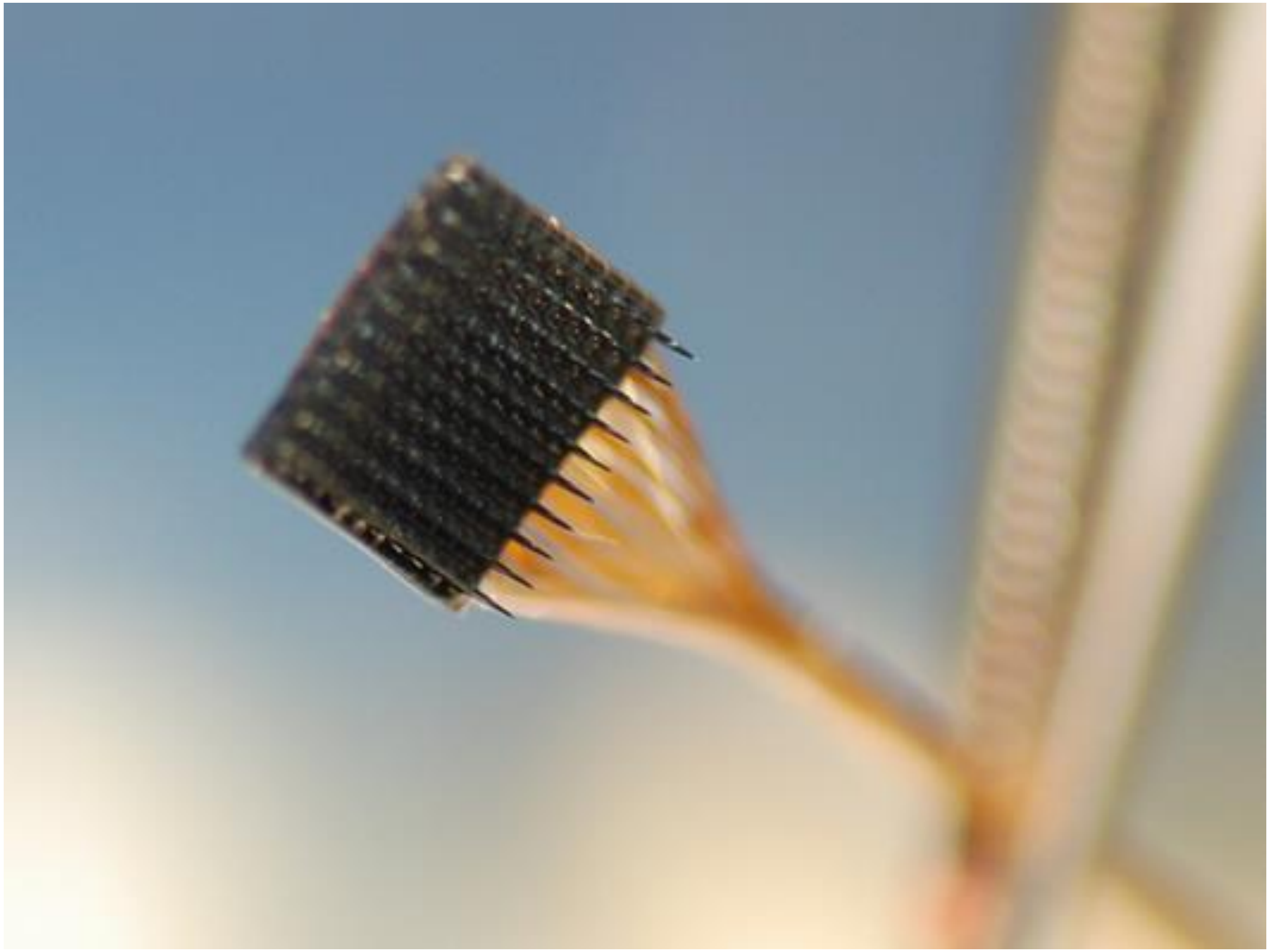
1,536 channel recording,
expandable to 3072 electrodes.

W-Ru Robot surgeon can implant
192 electrodes /min., many cm deep
40 micron diameter, ‘hair bundle’

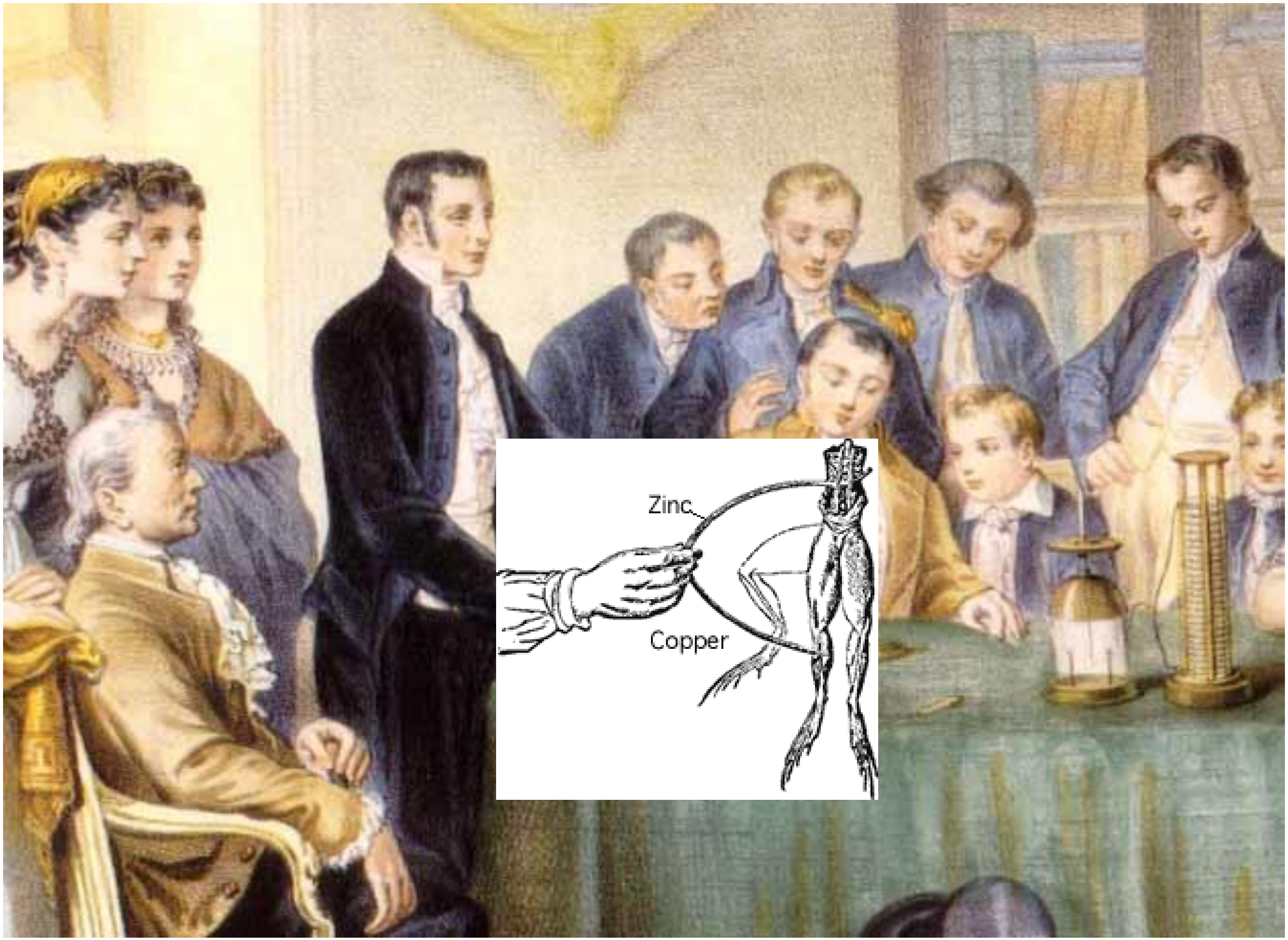
In July 2020, Neuralink obtained
FDA breakthrough device
designation, to allow human testing.

bio-compatibility now key challenge

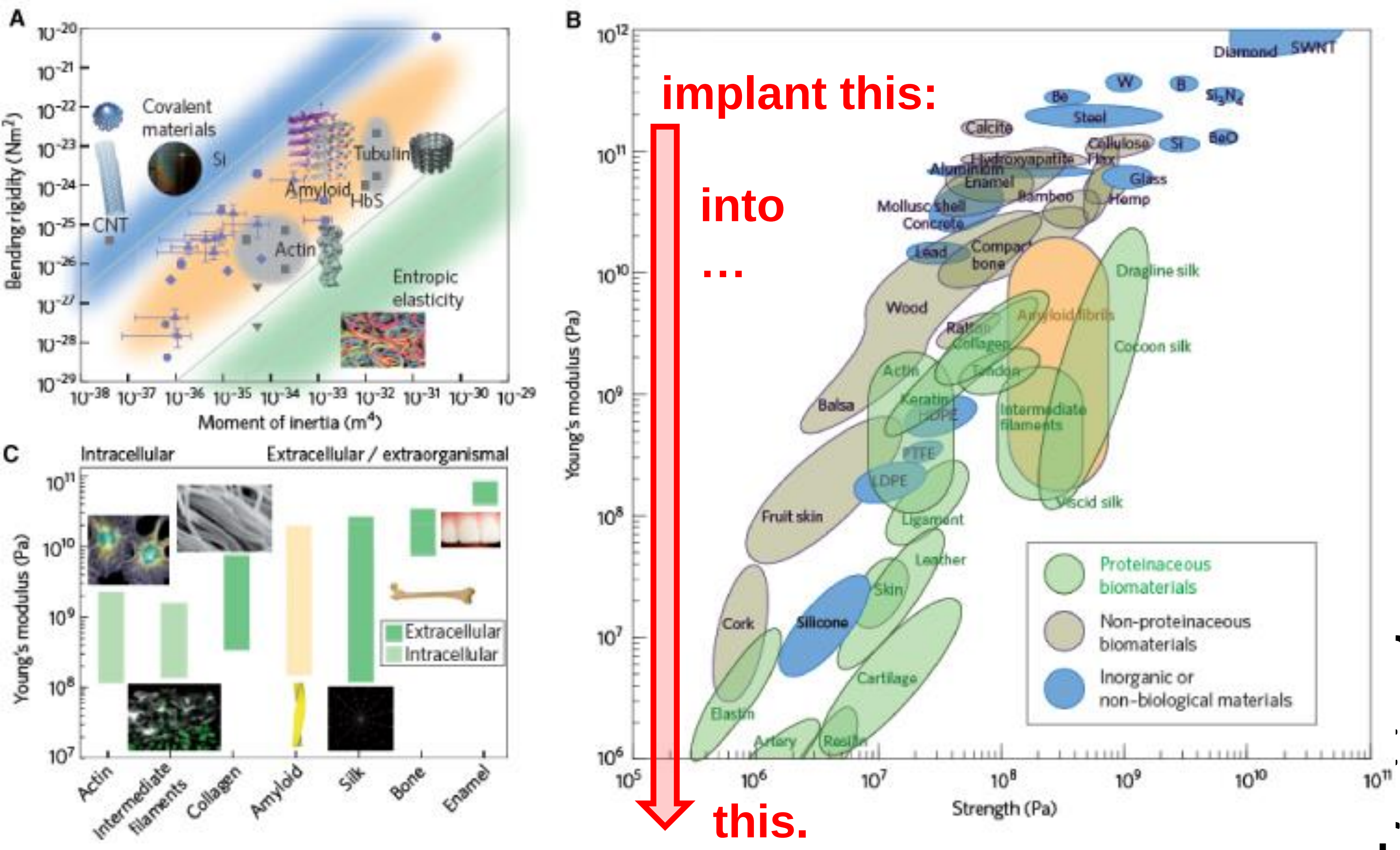
‘Cutting Edge’ in ‘99 ...

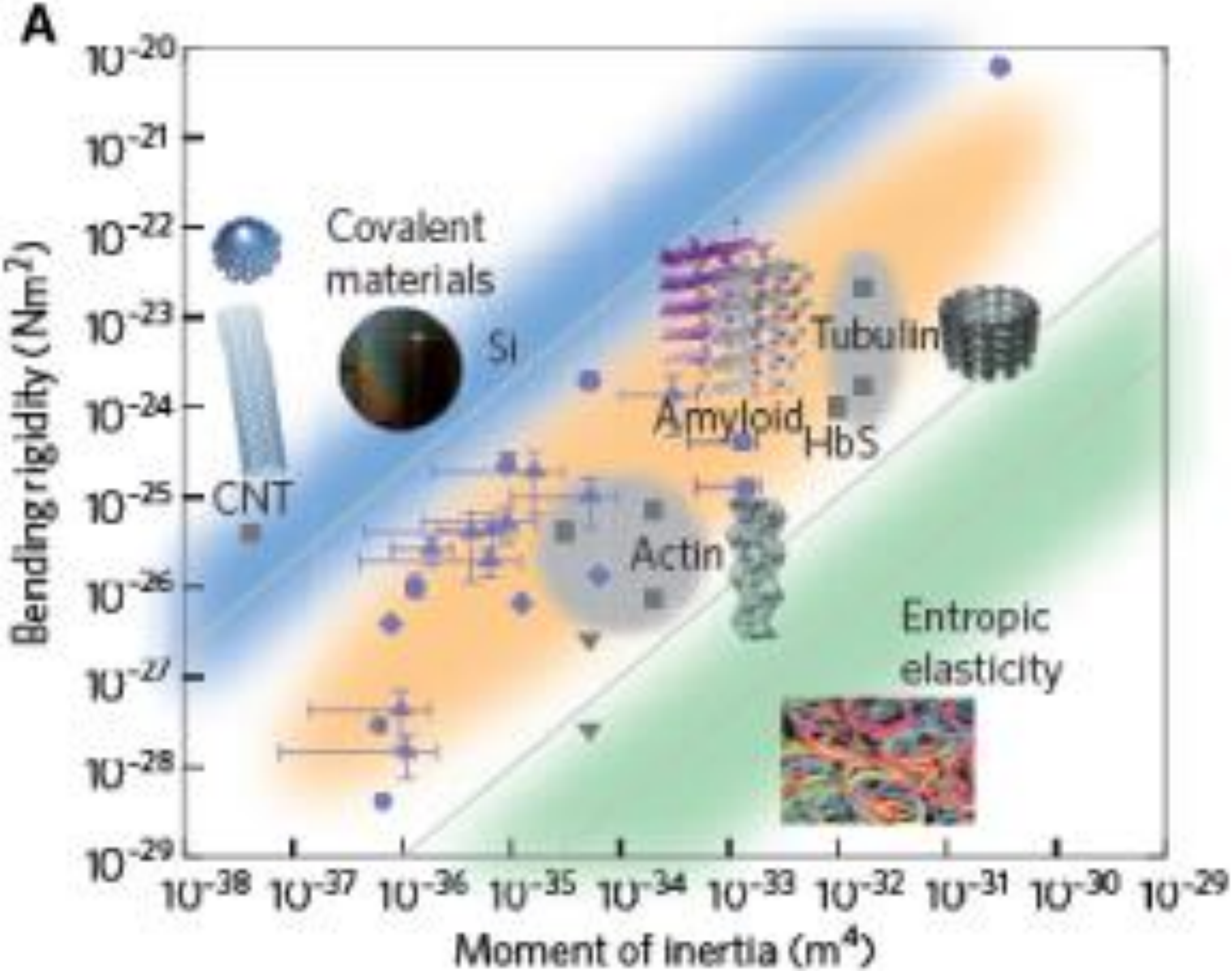


‘Cutting Edge’ in ‘99 ... in 1799 : Volta, Galvani



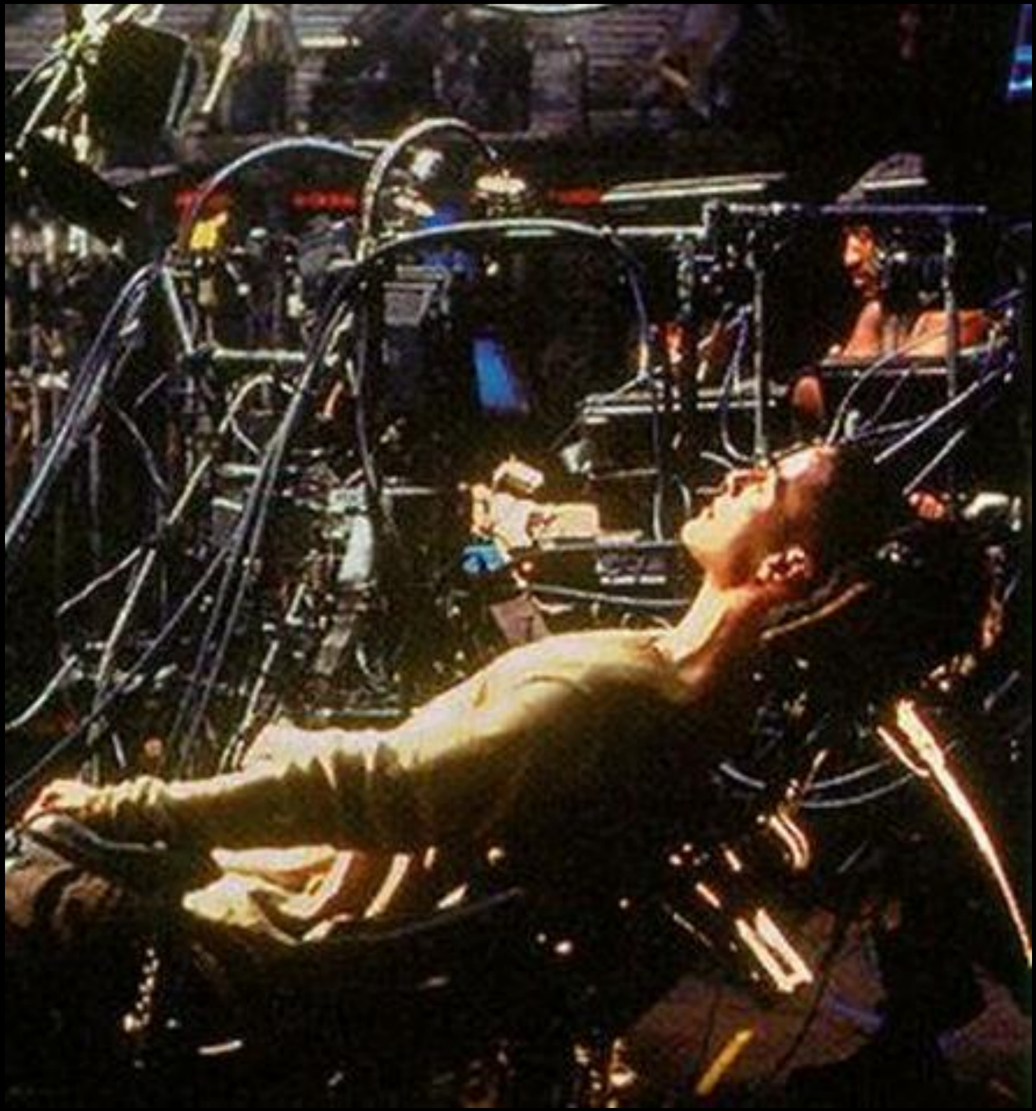
Implant materials can be too dry, hydrophobic, and too hard/stiff by a factor of >1 million...





A
Bending rigidity (Nm²)
10⁻²⁰
10⁻²¹
10⁻²²
10⁻²³
10⁻²⁴
10⁻²⁵
10⁻²⁶
10⁻²⁷
10⁻²⁸
10⁻²⁹
Covalent materials
Si
CNT
Tubulin
Amyloid
HbS
Actin
Entropic elasticity
10⁻³⁸
10⁻³⁷
10⁻³⁶
10⁻³⁵
10⁻³⁴
10⁻³³
10⁻³²
10⁻³¹
10⁻³⁰
10⁻²⁹
Moment of inertia (m⁴)

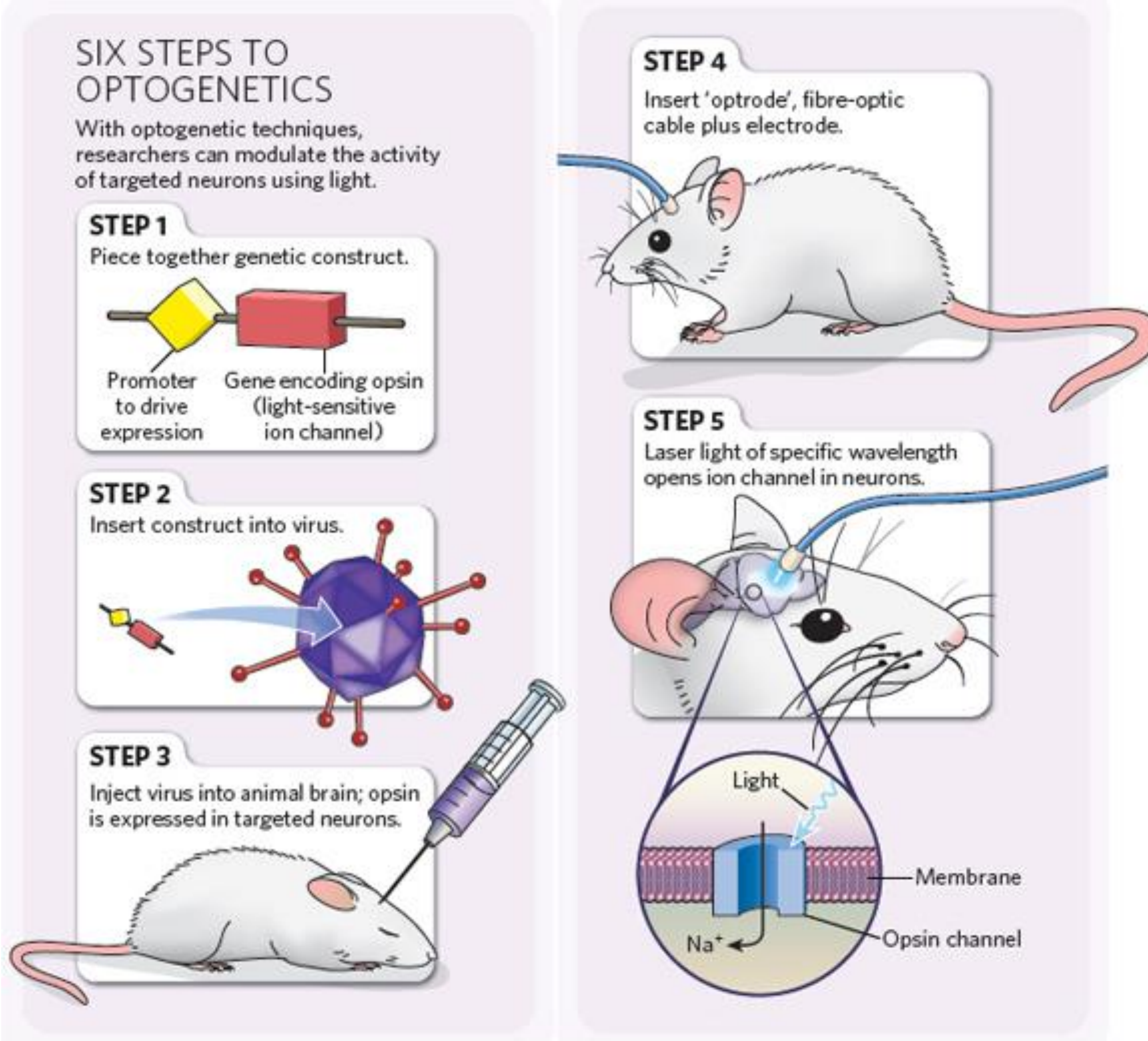
an improved class of Brain-Machine interface:
with LIGHT and not electrodes; SOFT materials.



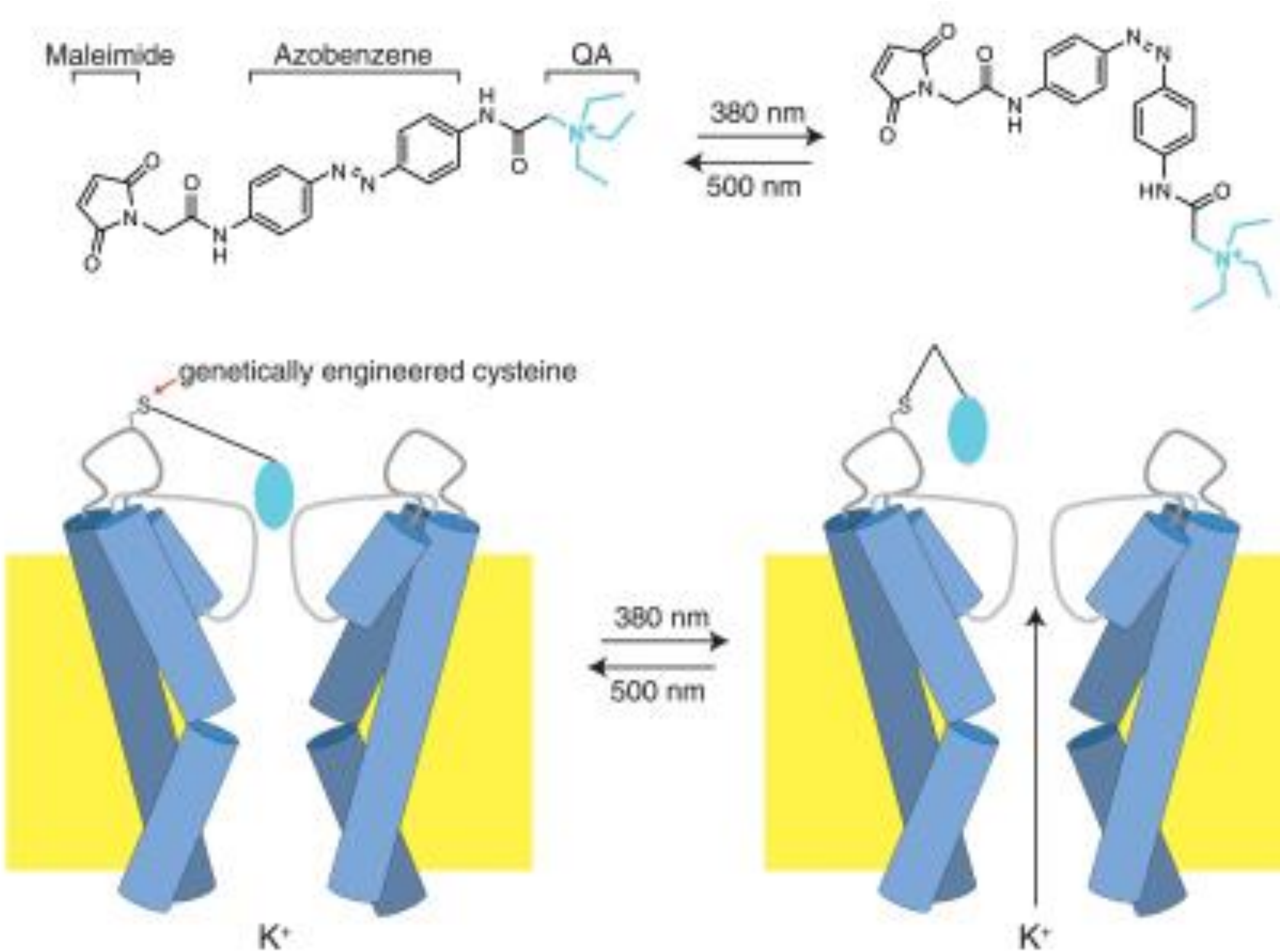
an improved class of Brain-Machine interface:

with LIGHT and not electrodes; soft materials.

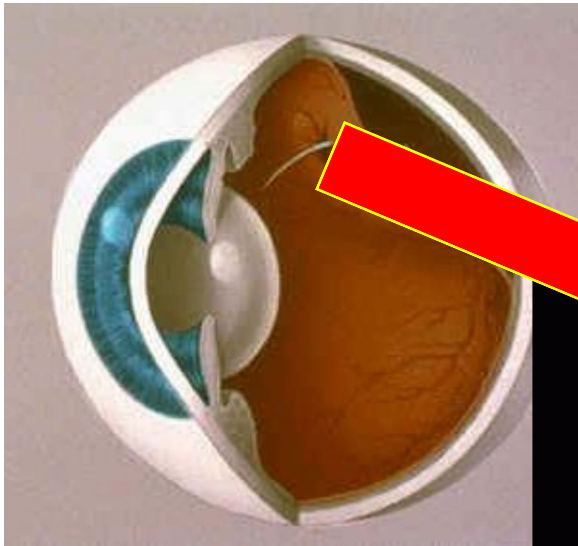
(Opto-Genetics demonstrates input possible)

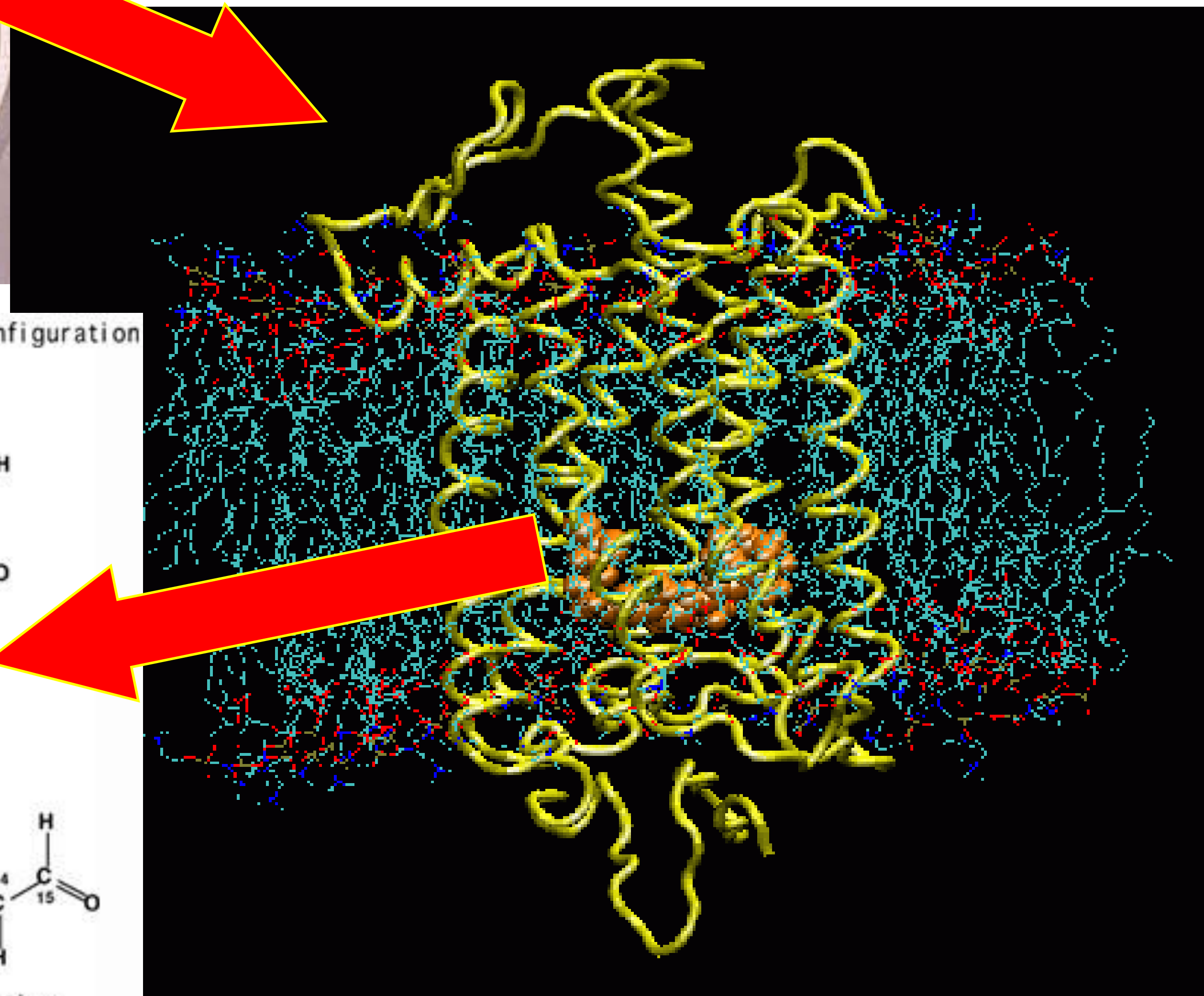

SIX STEPS TO OPTOGENETICS
With optogenetic techniques, researchers can modulate the activity of targeted neurons using light.
STEP 1
Piece together genetic construct.
Promoter to drive expression
Gene encoding opsin (light-sensitive ion channel)
STEP 2
Insert construct into virus.
STEP 3
Inject virus into animal brain; opsin is expressed in targeted neurons.
STEP 4
Insert 'optrode', fibre-optic cable plus electrode.
STEP 5
Laser light of specific wavelength opens ion channel in neurons.
Light
Membrane
Opsin channel
Na+

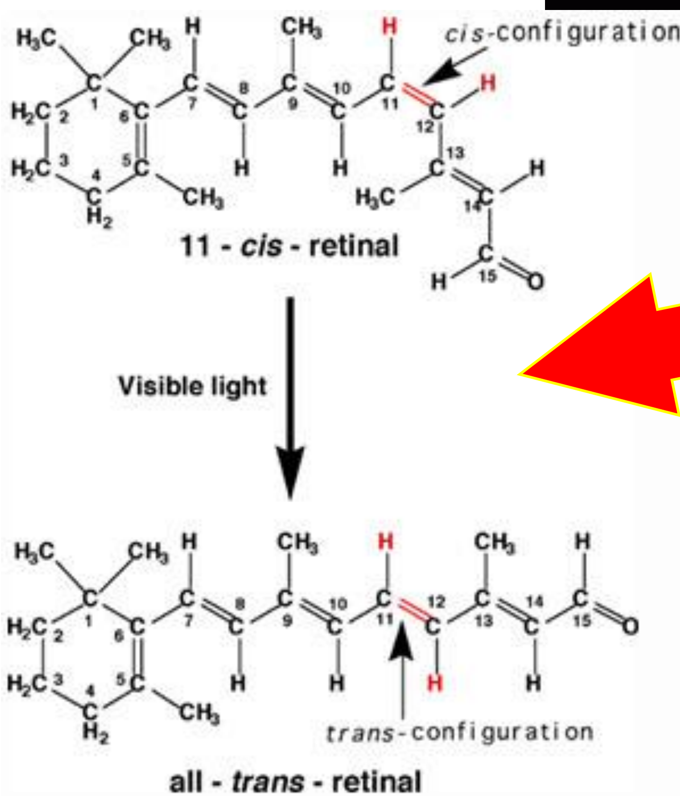
The present ? ‘azo’ modification for 1-way communication (Isachoff, Trauner, UC Berkeley)

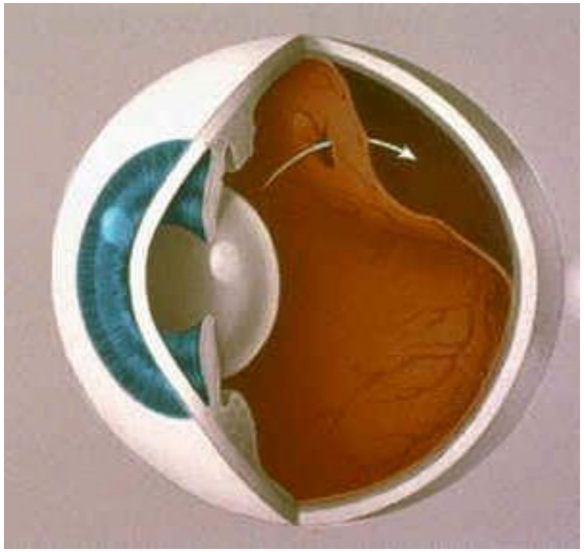


Three inspiring lessons from retinal:
1) Photo-Physics only, 2) Amplification,
3) a natural Opto-Bio interface.



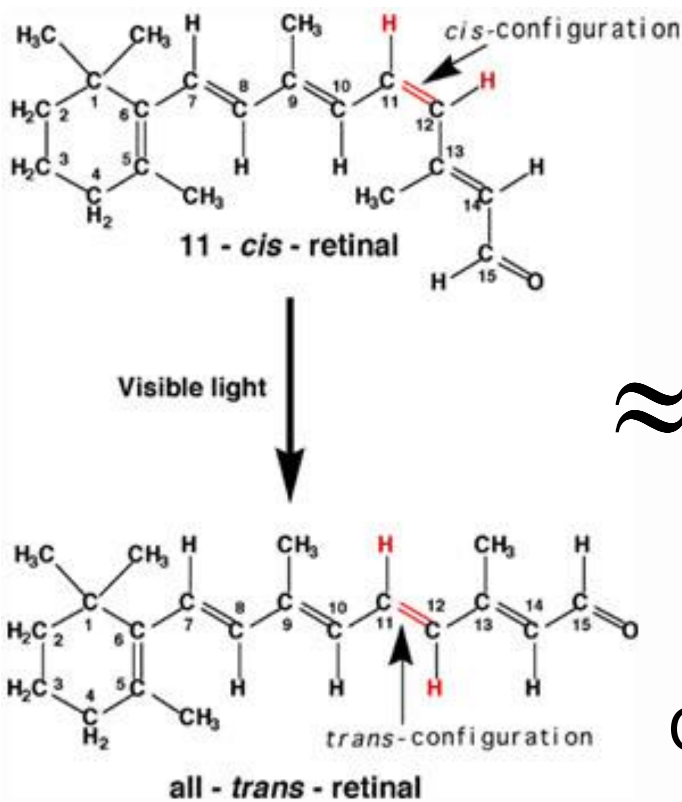




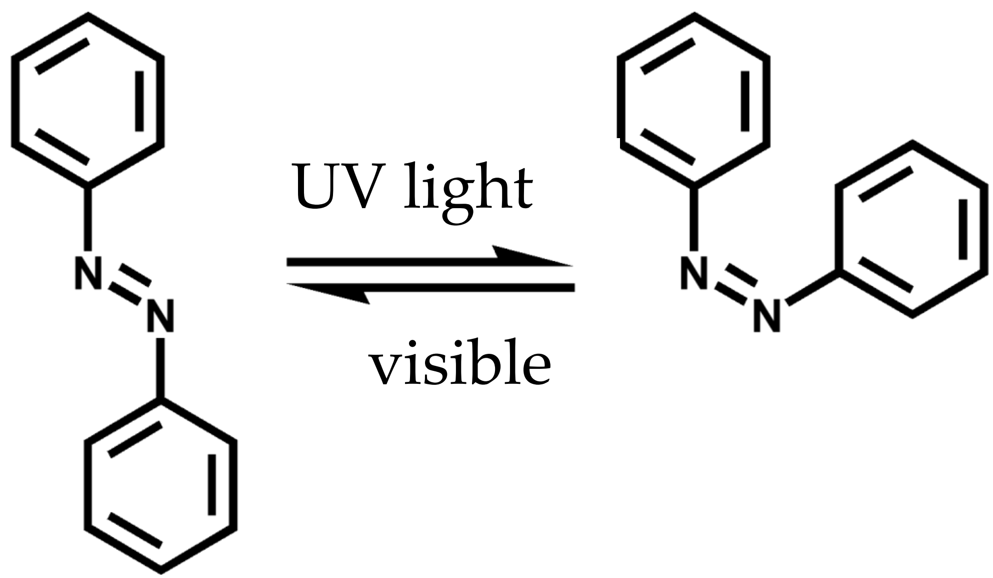


A simple mimic of retinal in rhodopsin is azobenzene embedded in a self-assembled polyelectrolyte structure.

Three inspiring lessons from retinal:
1) Photo-Physics only, 2) Amplification,
3) a natural Opto-Bio interface.



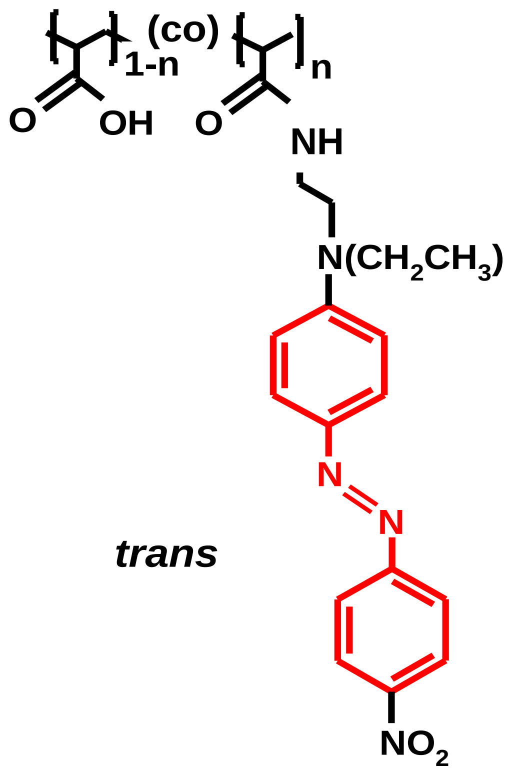
≈

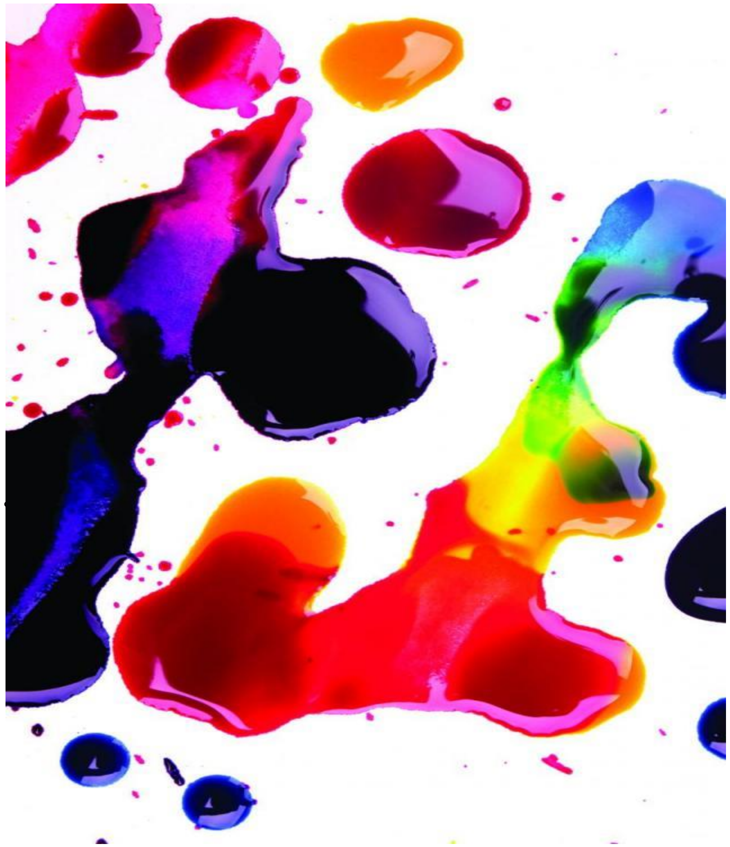


Goal: to sense, and signal, using light.

Azobenzene parents a large family of dyes & photo-materials:

(*crystals, polymers, liquid crystals, particles, surface layers…*)



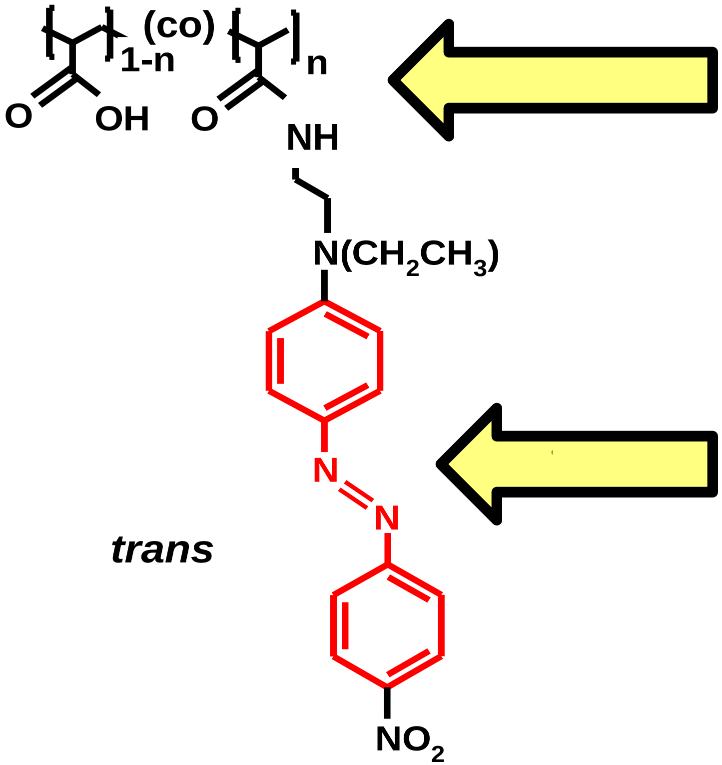


AZO DYES studied for 200 years now, large growing field…

(most dyes world-wide, pH indicators, a rainbow of colors)

Cis-Trans

Azobenzene parents a large family of polymeric photo-materials:



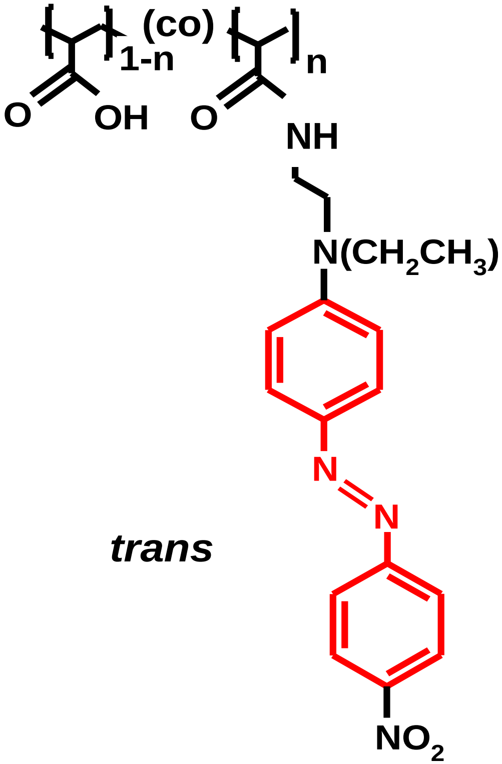
Polyelectrolyte backbones: soft, wet, bio-compatible

Azo dyes: photo-reversible (for lots of other effects)

AZO DYES studied for 200 years now, large growing field…

(most dyes world-wide, pH indicators, a rainbow of colors)

Cis-Trans



Azo dye TIMELINE:

1832- first paper, preparation

later **1800s**- clothing dyes

early **1900s**- pH paper, indicators

from **1920s**- food colourings

1960s- fibers ‘move’ in sunlight

1970s- orientation, LC displays

1980s- reversible optical storage

1990s- photonics, nano-patterning

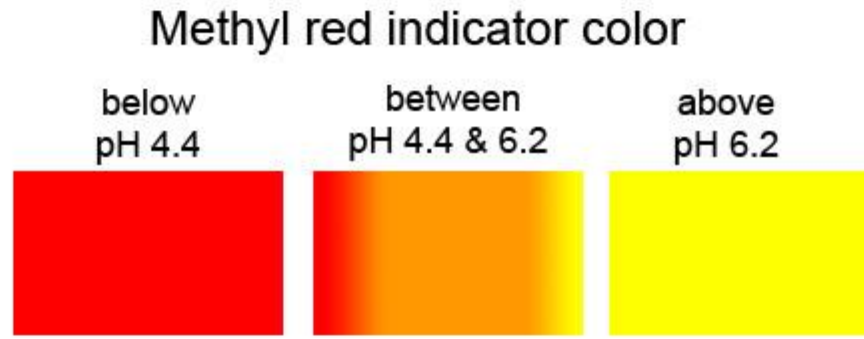
2000s- photo-mechanics, softening

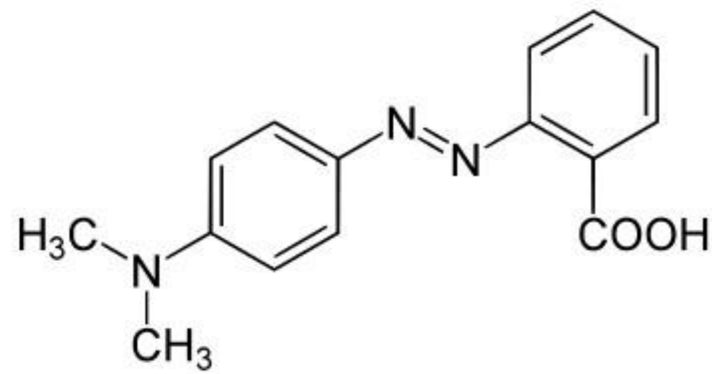
2010s + - surface-switching, bio-control

Cis-Trans

And sensitive functional groups can lead to color changes:

E. coli ?:



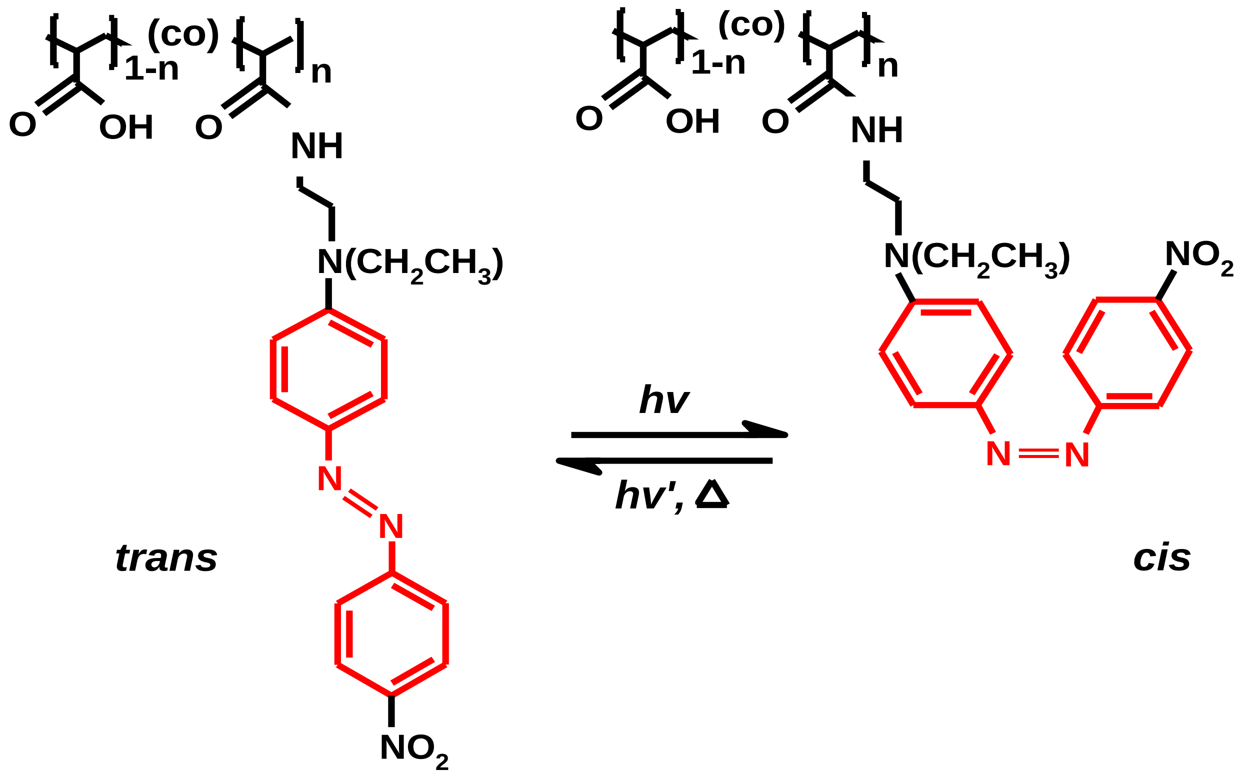


azo dyes studied for 200 years now, large growing field…

(most dyes world-wide, pH indicators, a rainbow of colors)

Cis-Trans

Polymers containing azobenzene chromophore sidegroups:



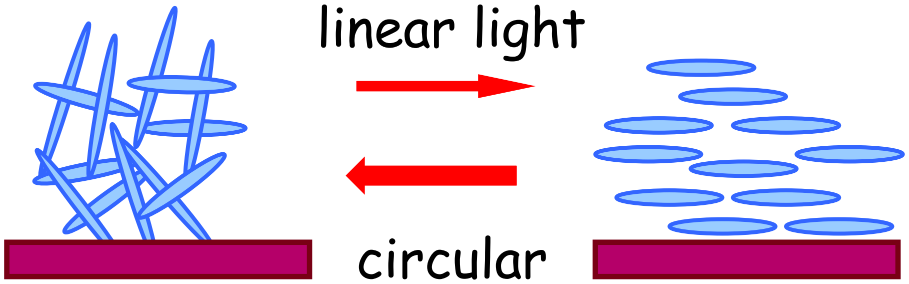
azo dyes can be photo-switched between *TRANS* and *CIS*

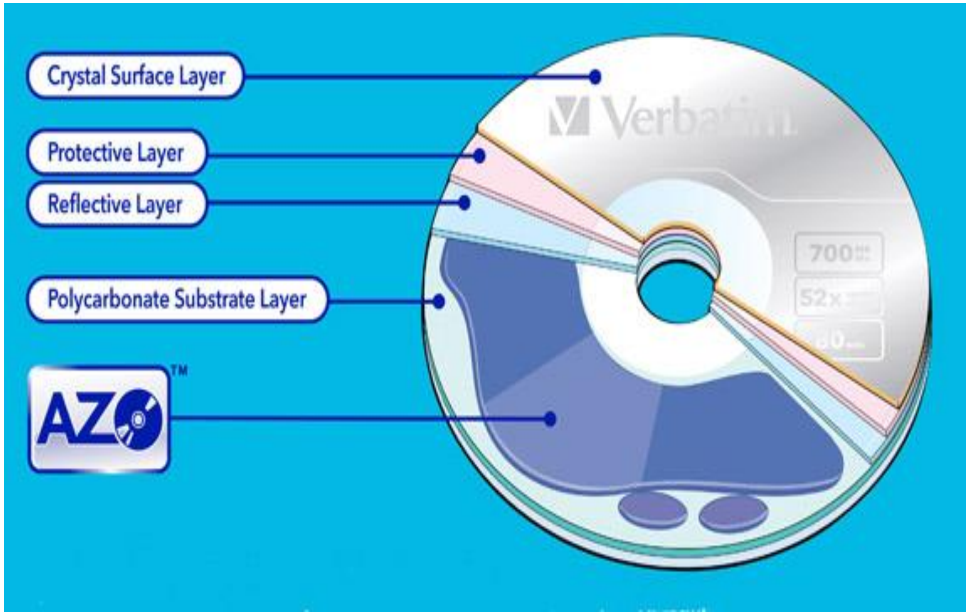
(fast, visible, reversible, robust, tunable, distinct, efficient…)

SO: Azo 'stuff': orients, triggers, softens, pushes, & wiggles…

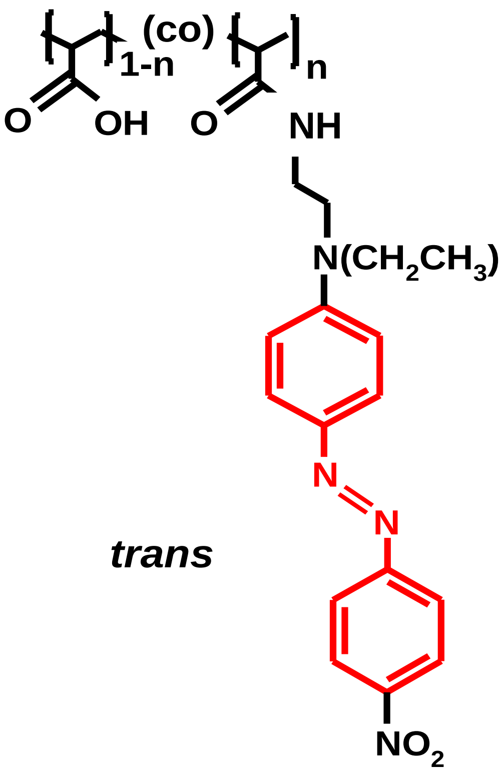
much interest in 1990s: high density reversible optical storage

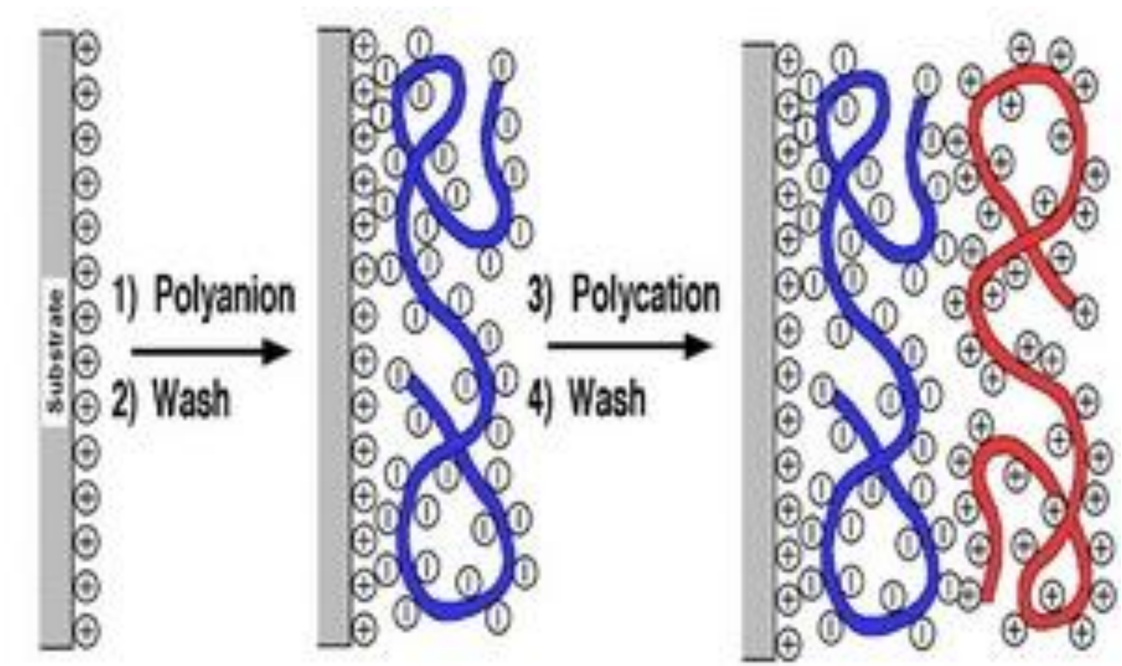
Used for Verbatim 'super-azo' RW optical storage disks.
5 nsec write time and *in principle,* 10 nm^2 resolution bits.





Azobenzene is incorporated as a water-soluble polyelectrolyte





Which can then be self-assembled as a Multilayer Bio-Film

(push-pull azos for visible light response, top layer only, at 1% or less)

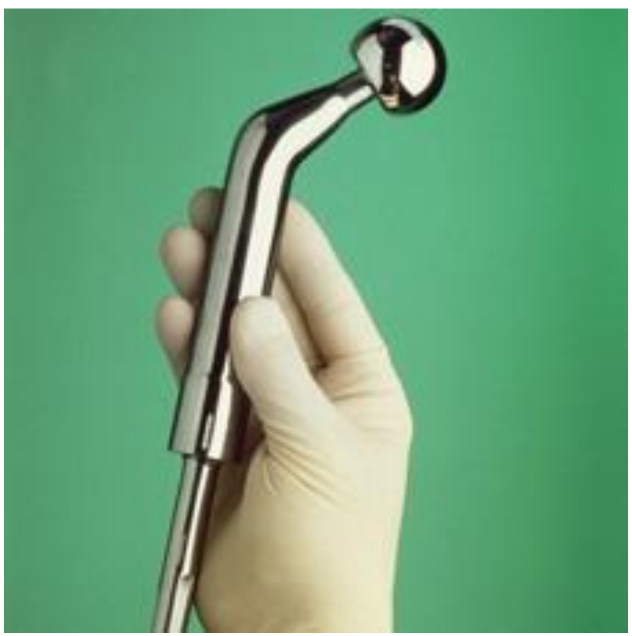
Cis-Trans

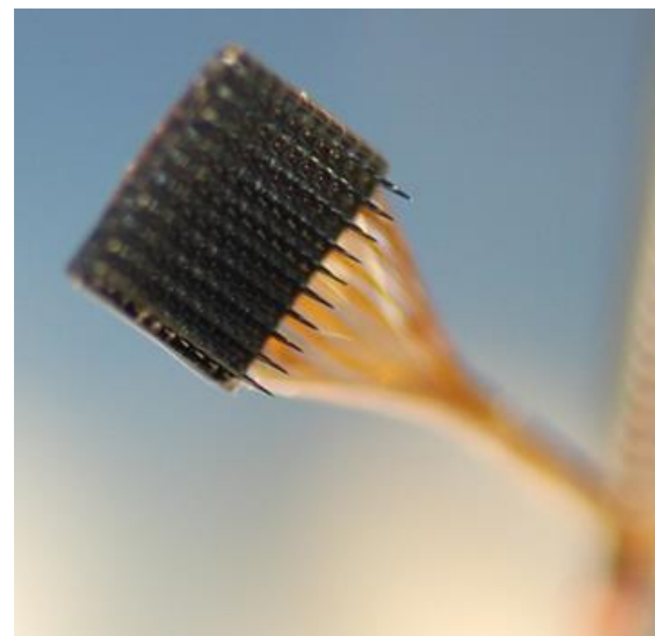
The GOAL is to coat surfaces of hard implants, to minimize rejection– hips, stents, contact lenses, and **neural probes**.

Layer-by Layer coatings as “Bio – Camouflage“

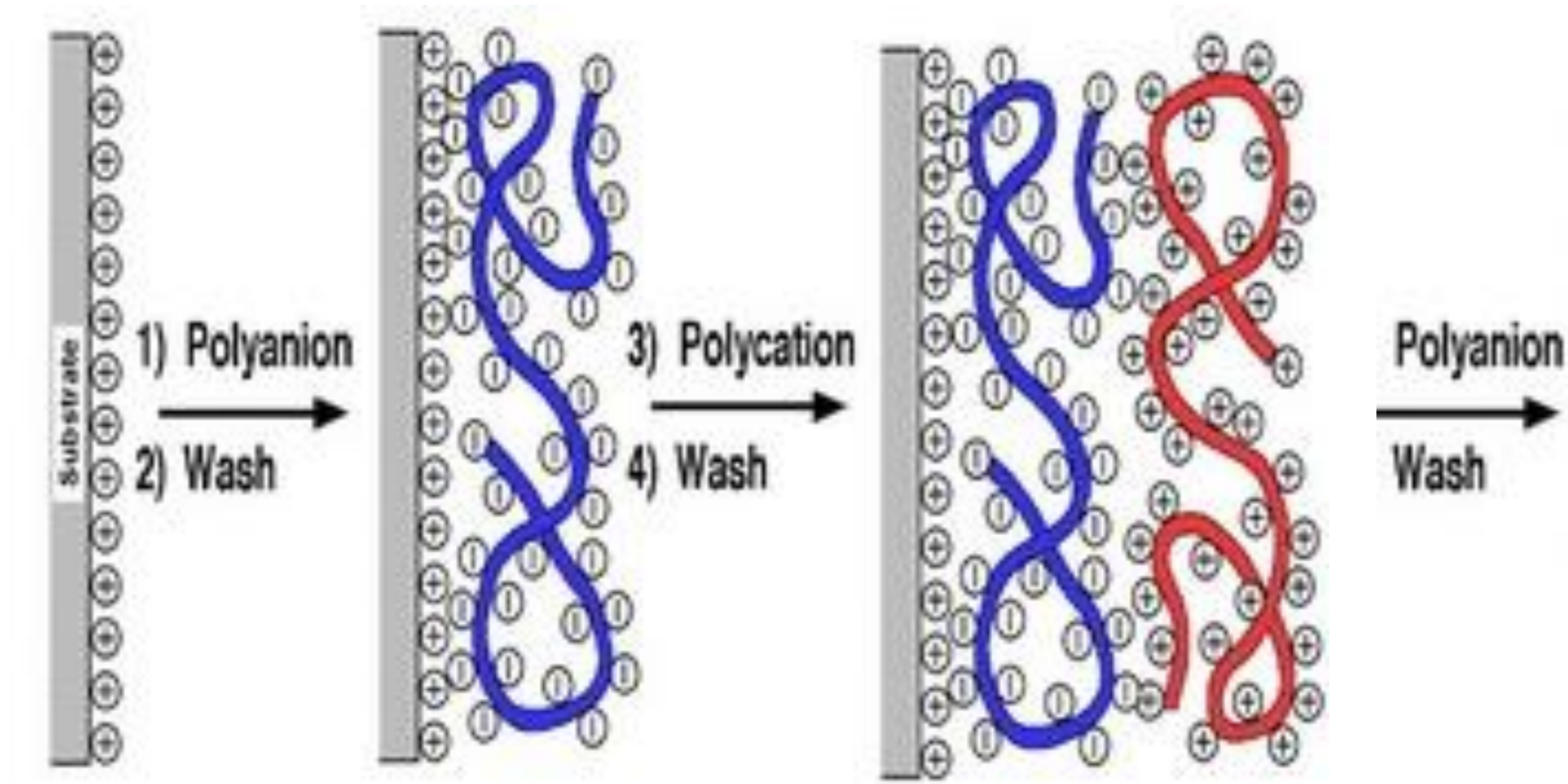
(with Tim Kennedy, Montreal Neurological Institute)

a mis-match in: Chemistry, Charge, **Water Content**, and **Stiffness**





Soft, Wet, robust bio-films can be built up on hard surfaces:



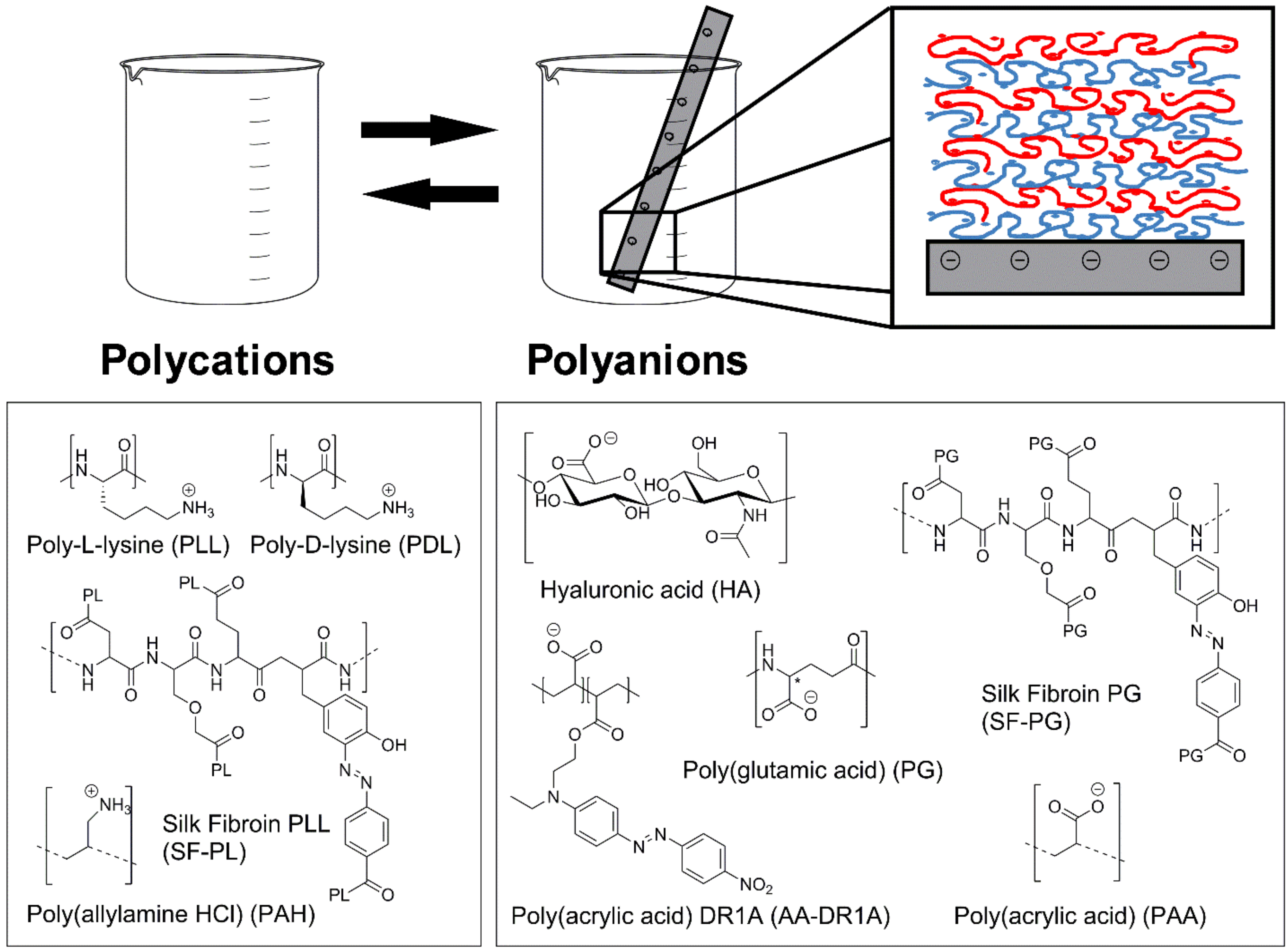
Self-Assembled Multi-Layers from water, become fixed, stable

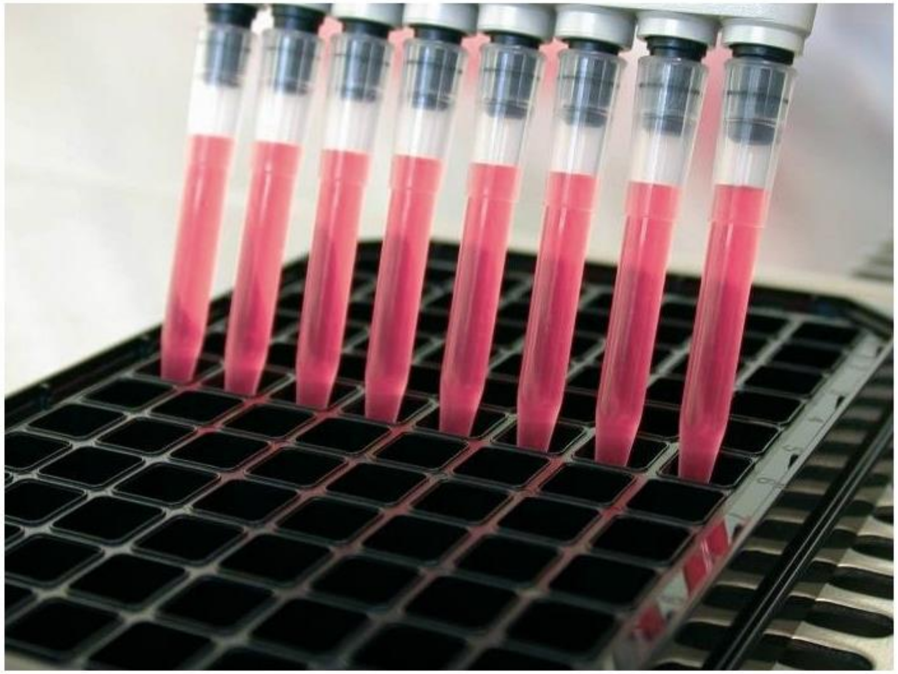
WEAK acid, base groups control charge, ‘loops’, properties,

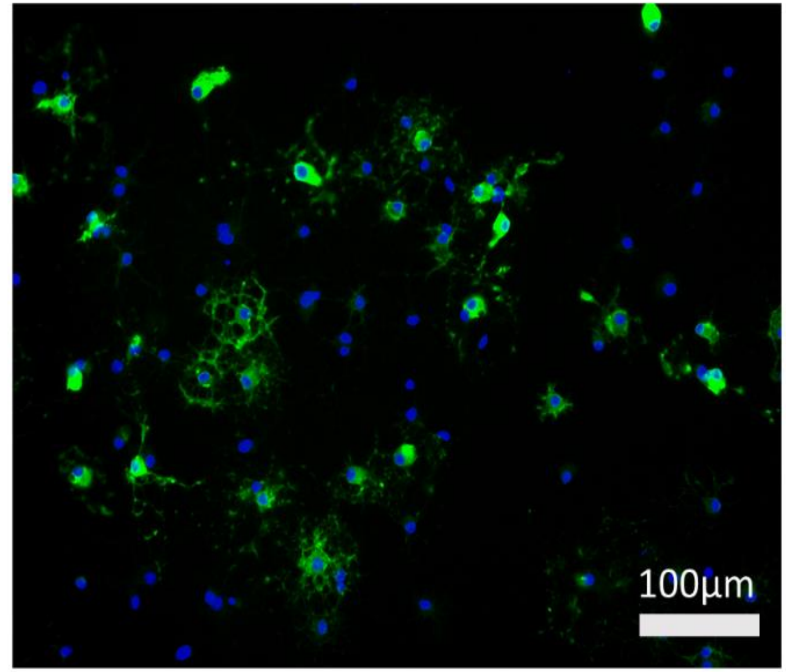
for many polymer combos, pH, [ion], tested *in vitro* by cells.

(measured via ellipsometry, AFM, NMR, zetaP, neutrons…)

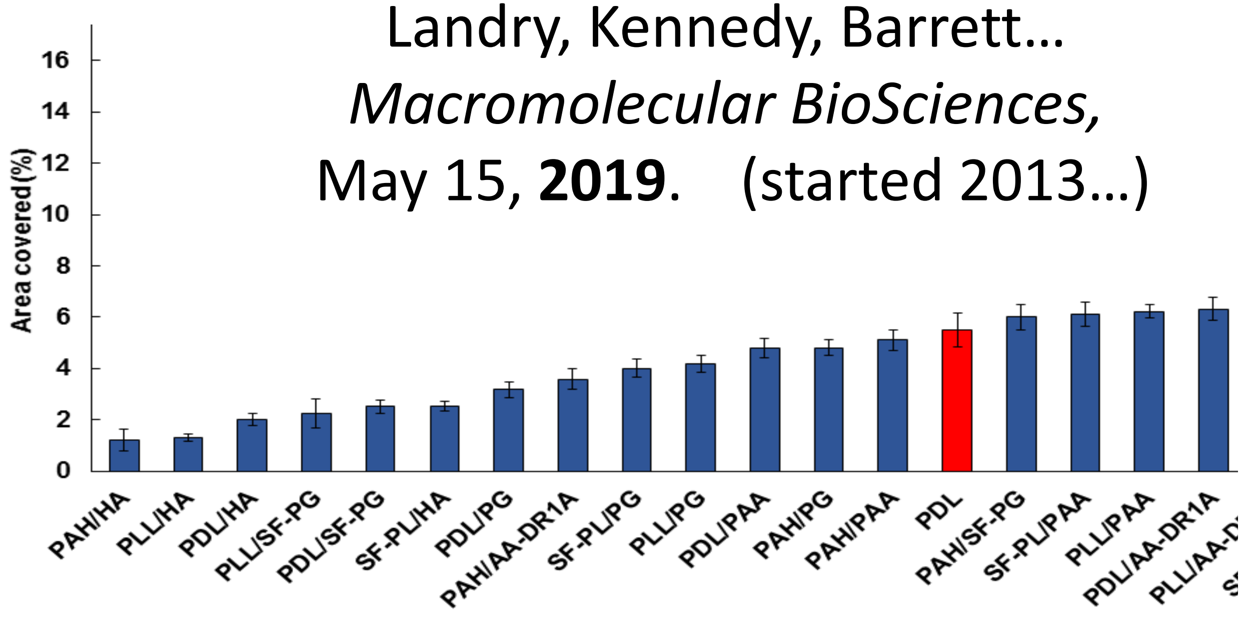
Cis-Trans


Polycations
Polyanions
Poly-L-lysine (PLL)
Poly-D-lysine (PDL)
Silk Fibroin PLL
(SF-PL)
Poly(allylamine HCl) (PAH)
Hyaluronic acid (HA)
Silk Fibroin PG
(SF-PG)
Poly(glutamic acid) (PG)
Poly(acrylic acid) DR1A (AA-DR1A)
Poly(acrylic acid) (PAA)



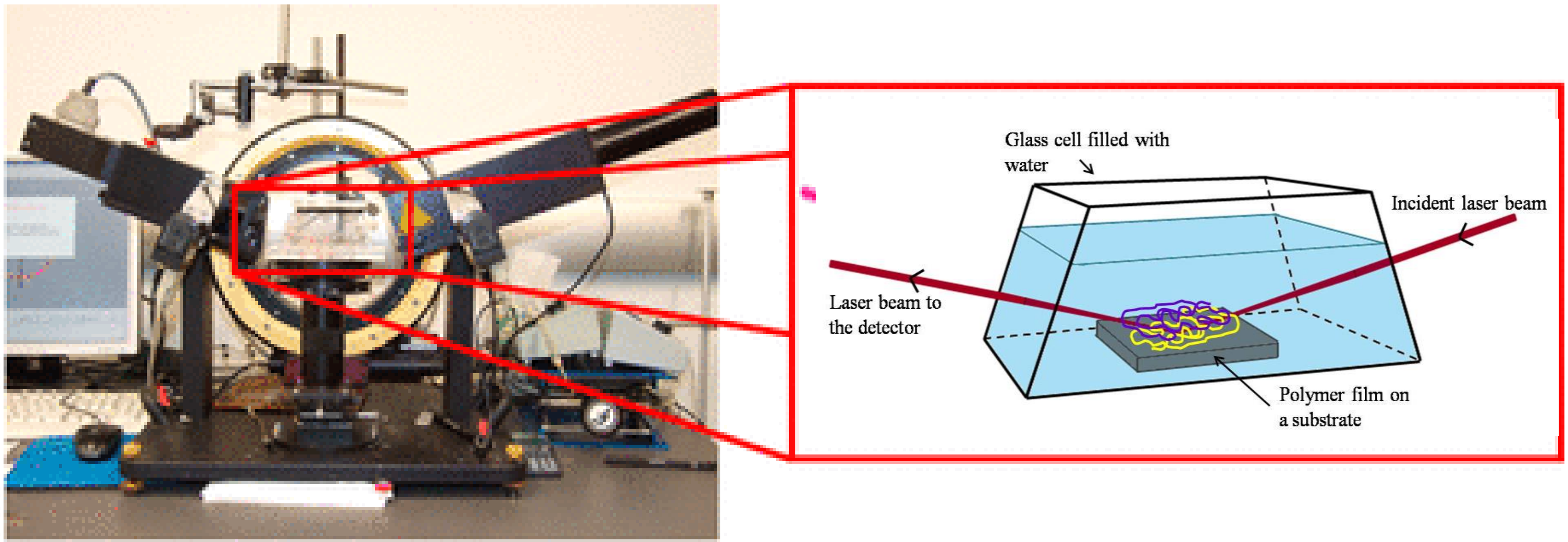


Landry, Kennedy, Barrett…
Macromolecular BioSciences,
May 15, **2019**. (started 2013…)

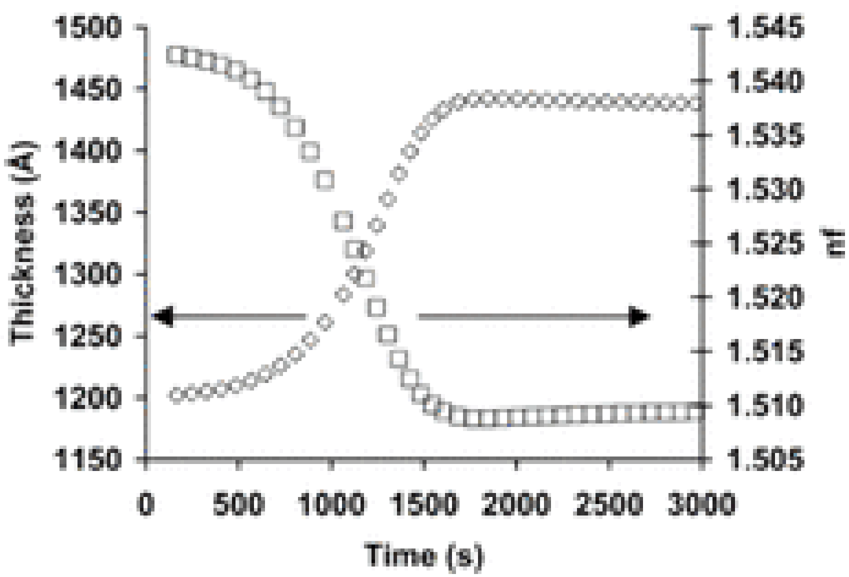


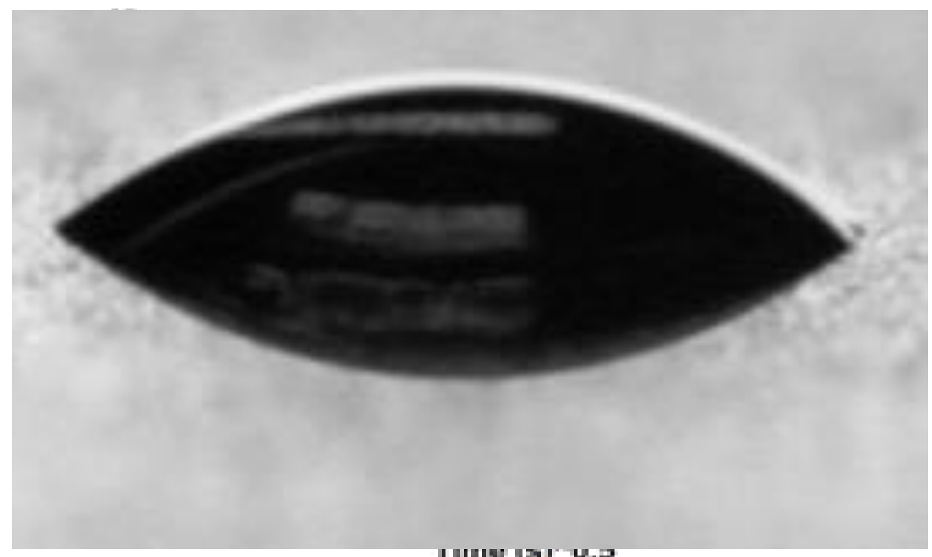
Water content, surface E of wet multilayers

A

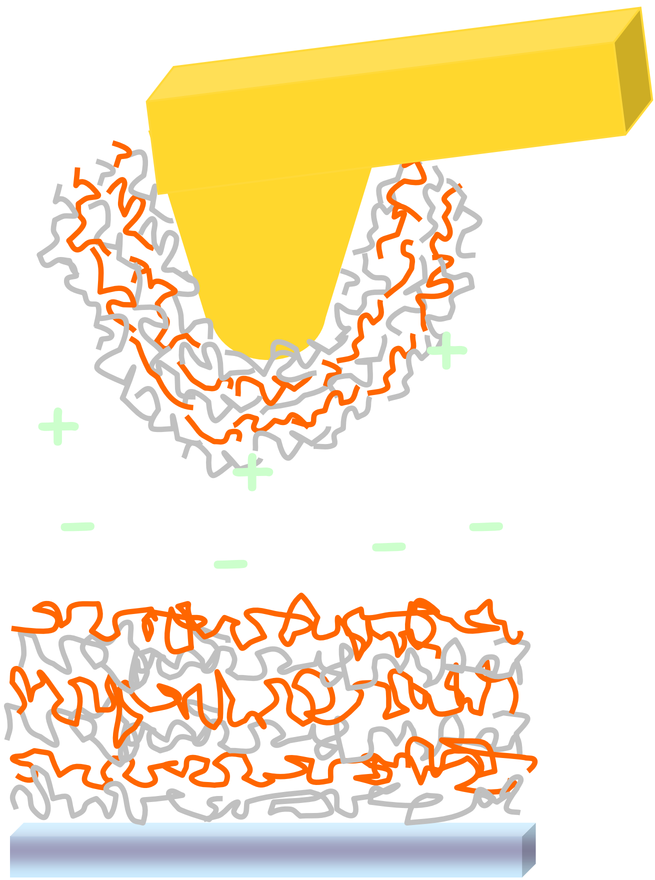


B



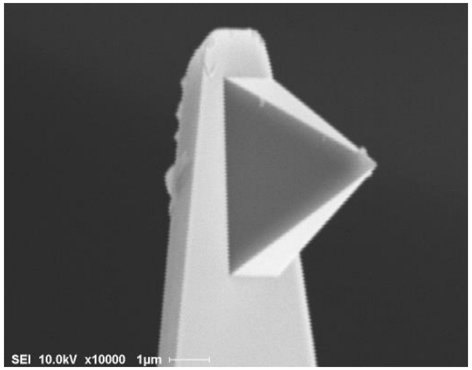


Measuring Modulus, Adhesion in Multilayer Films with AFM :

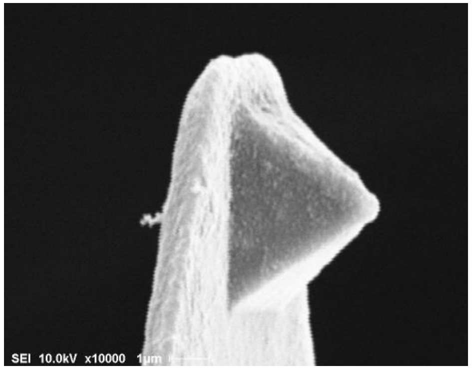


30- multilayer coated tip indented into 30 multilayers

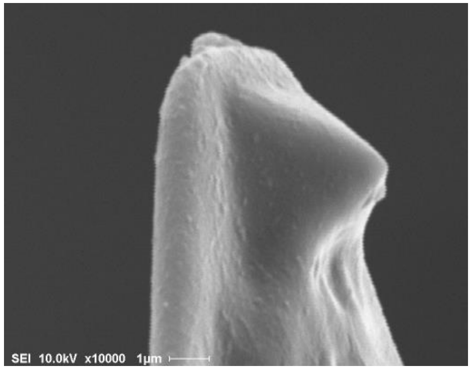
Bare Silicon Nitride AFM tip



tip coated with thin layers pH 5



tip coated with thick layers pH 9

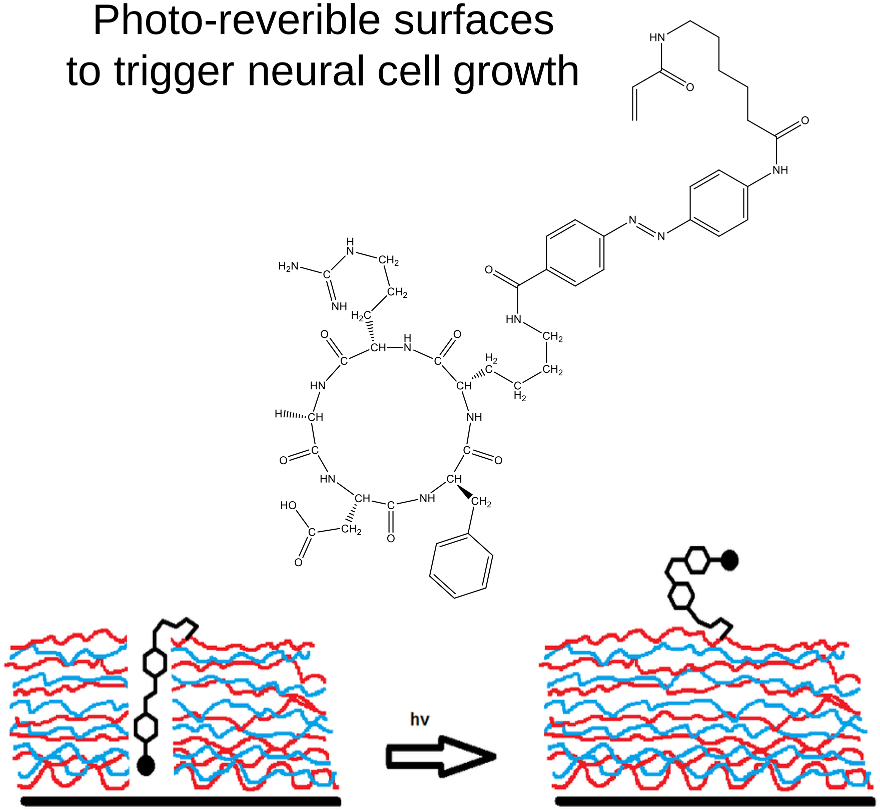


recent group work with azobenzenes as bio-interface layers:

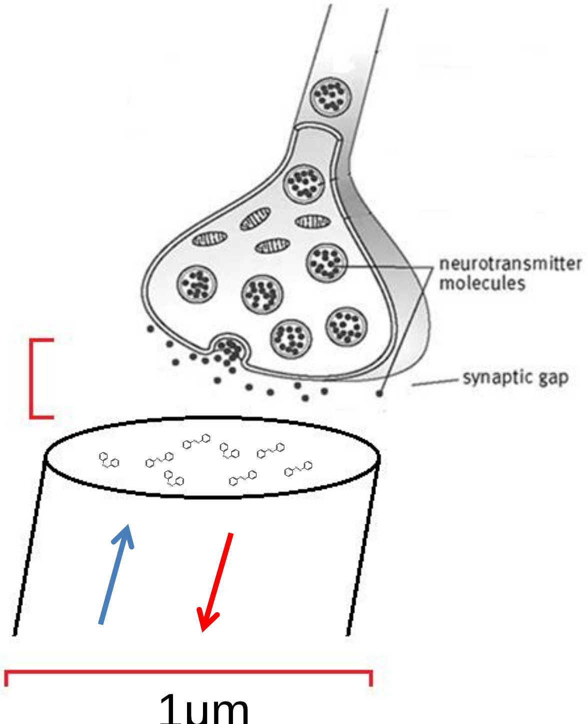
Dr. Alexis Goulet-Hanssens (then w/ S. Hecht, Humboldt U. Berlin)

Dr. Thomas Singleton (then w/ D. Leigh, U. Manchester)

Photo-reverible surfaces to trigger neural cell growth



All-optical sensor interfaces with neural cells



recent group work with azobenzenes as bio-interface layers:

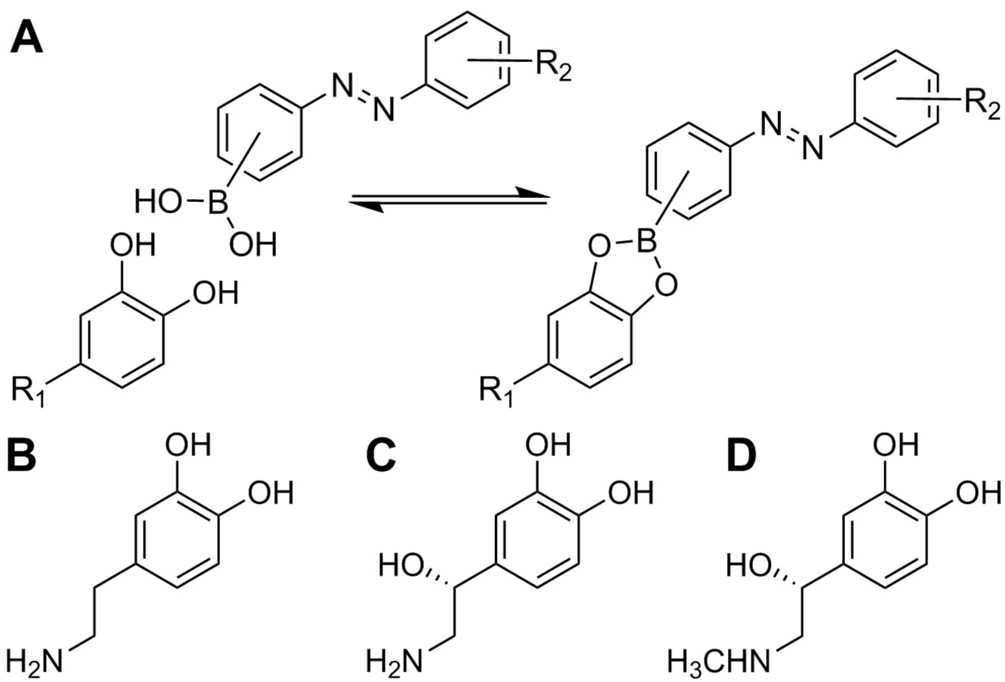
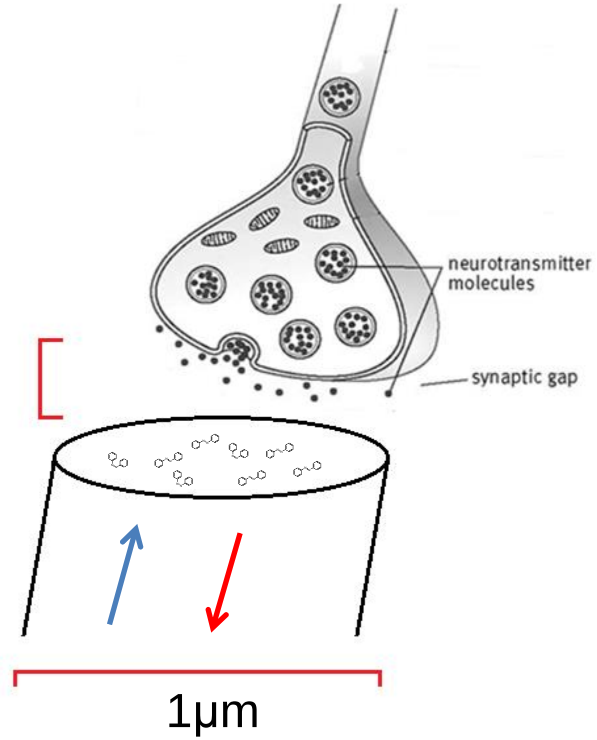


Figure 1 A) Reversible binding between catecholates and boronic-acid functionalised azobenzene derivatives. B–D)

The three main aminocatecholate neurotransmitters:
B) dopamine mediates signals within the frontal cortex of the brain, while **C) norepinephrine** and **D) epinephrine** also act as hormones used to convey signals from the sympathetic nervous system to various organs.

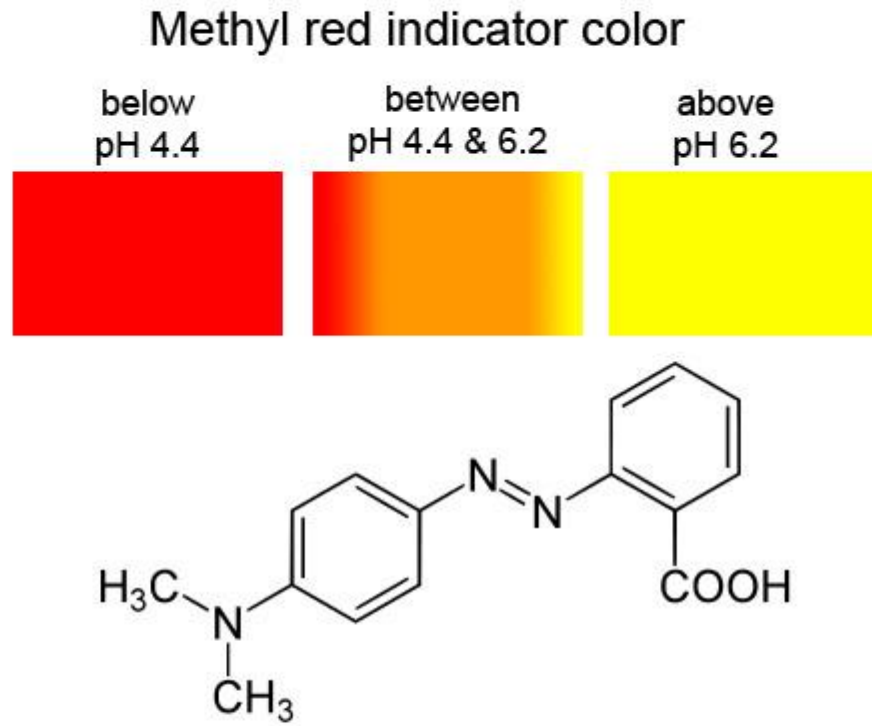
Dr. Thomas Singleton (then w/ D. Leigh, U. Manchester)

All-optical sensors for 2-way interfaces with neural cells



And sensitive functional groups can lead to colour changes:

E. coli ?:

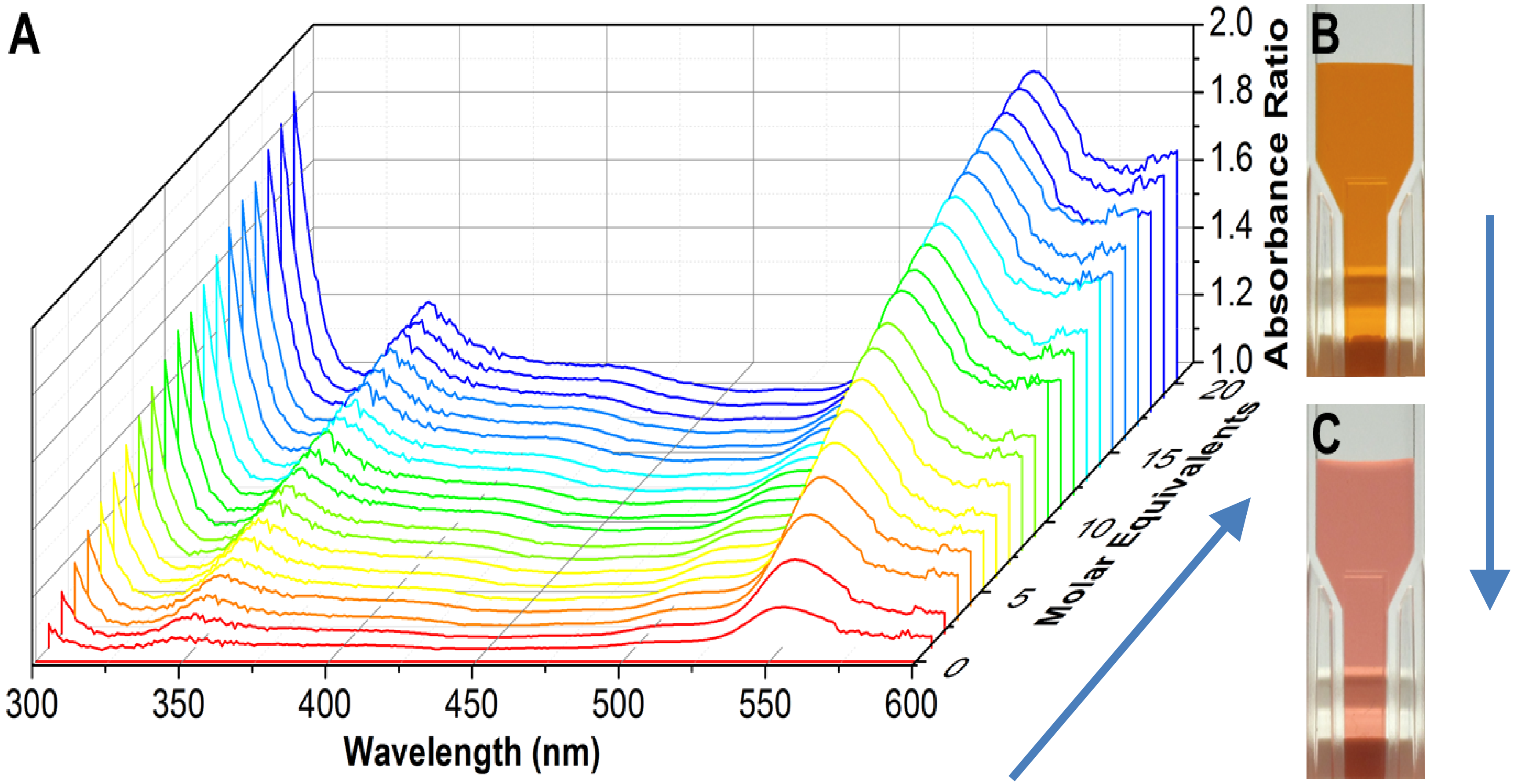


azo dyes studied for 200 years now, large growing field…

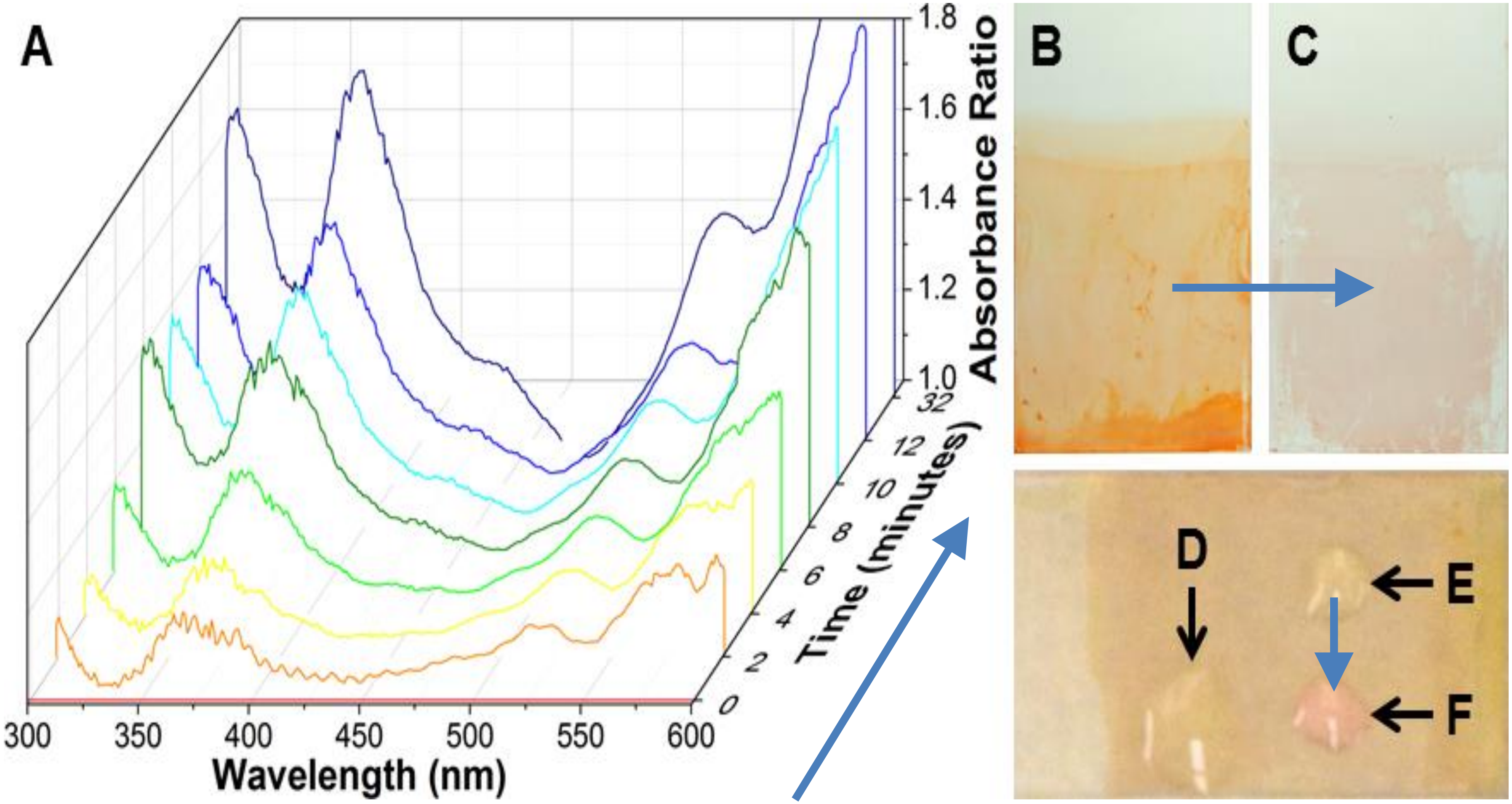
(most dyes world-wide, pH indicators, a rainbow of colors)

Cis-Trans

an azobenzene as a dopamine-sensing bio-interface dye:

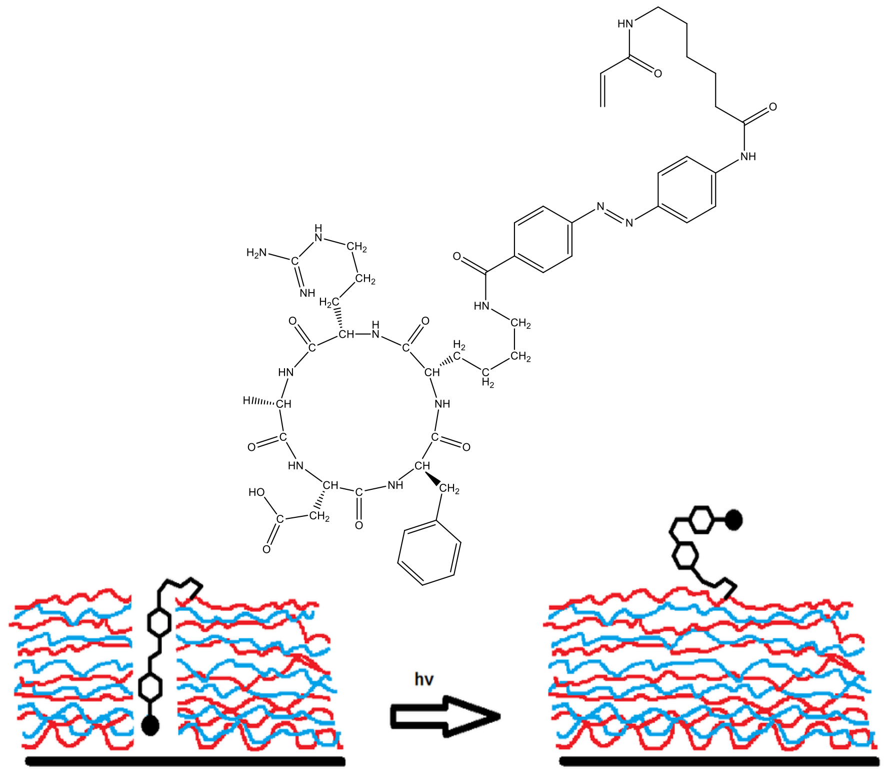


an azobenzene as a dopamine-sensing bio-interface layer:



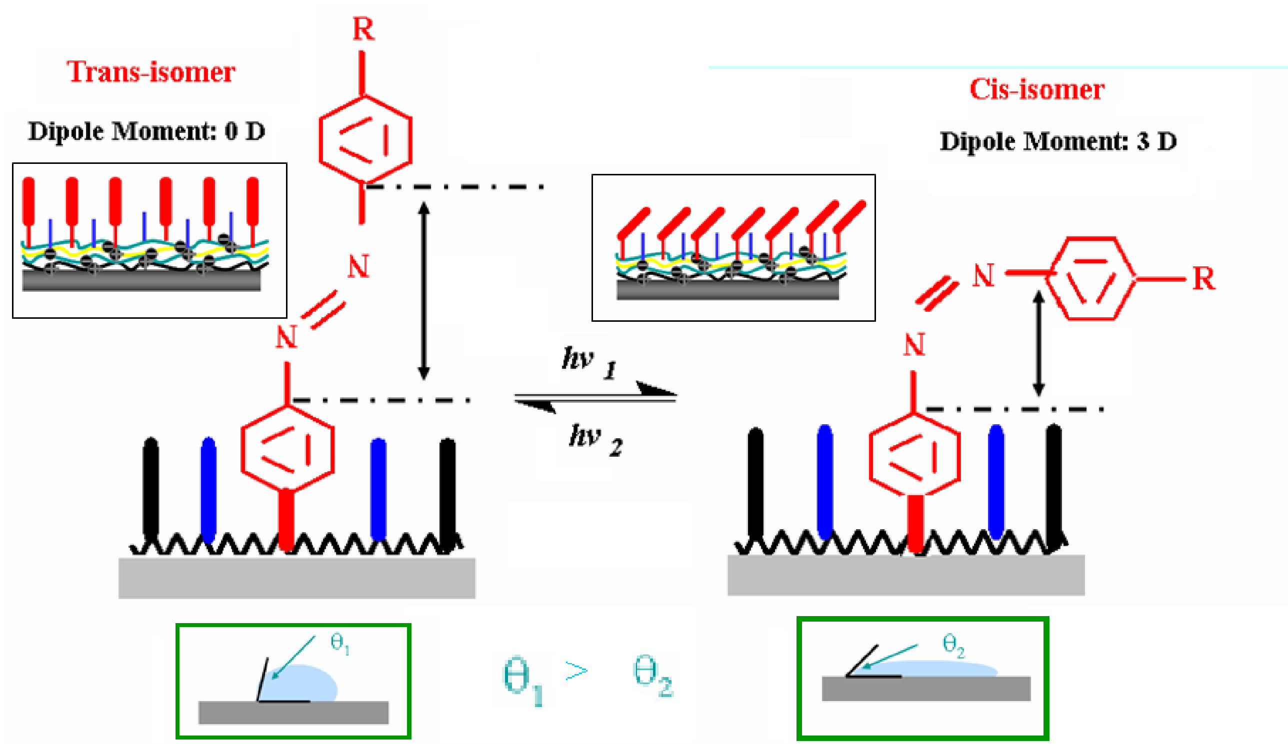
More recent work is with azobenzenes as bio-interface **triggers**, when incorporated <1% in Polyelectrolytes, in a Multilayer:

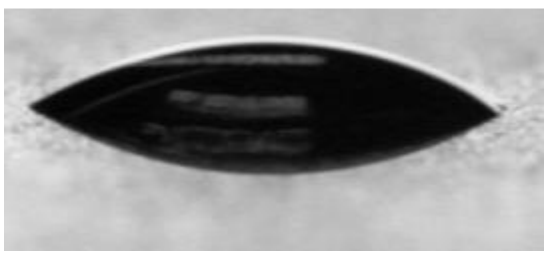
Dr. Alexis Goulet-Hanssens
(then w/ Stefan Hecht)
Photoreverible surfaces
to regulate cell adhesion

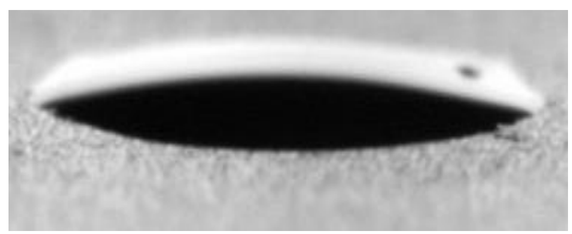


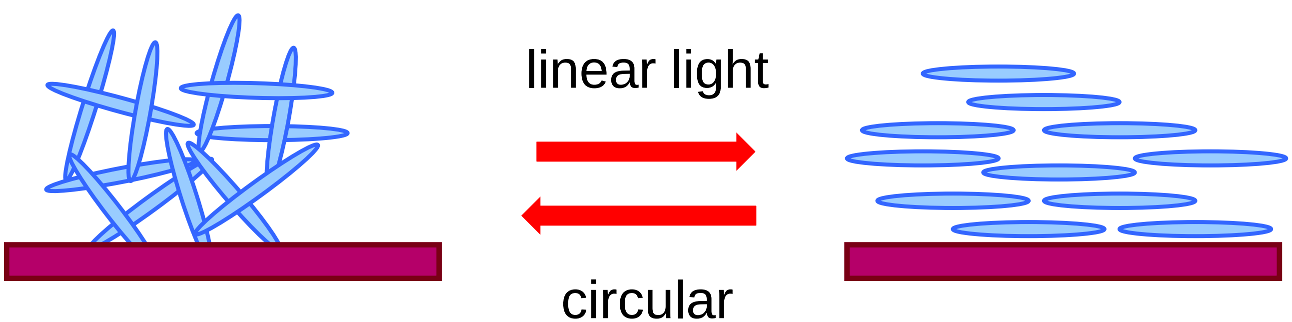
"Photo-Control of Biological Systems with Azobenzene Polymers"

Alexis Goulet-Hanssens, Christopher Barrett, *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 3058.







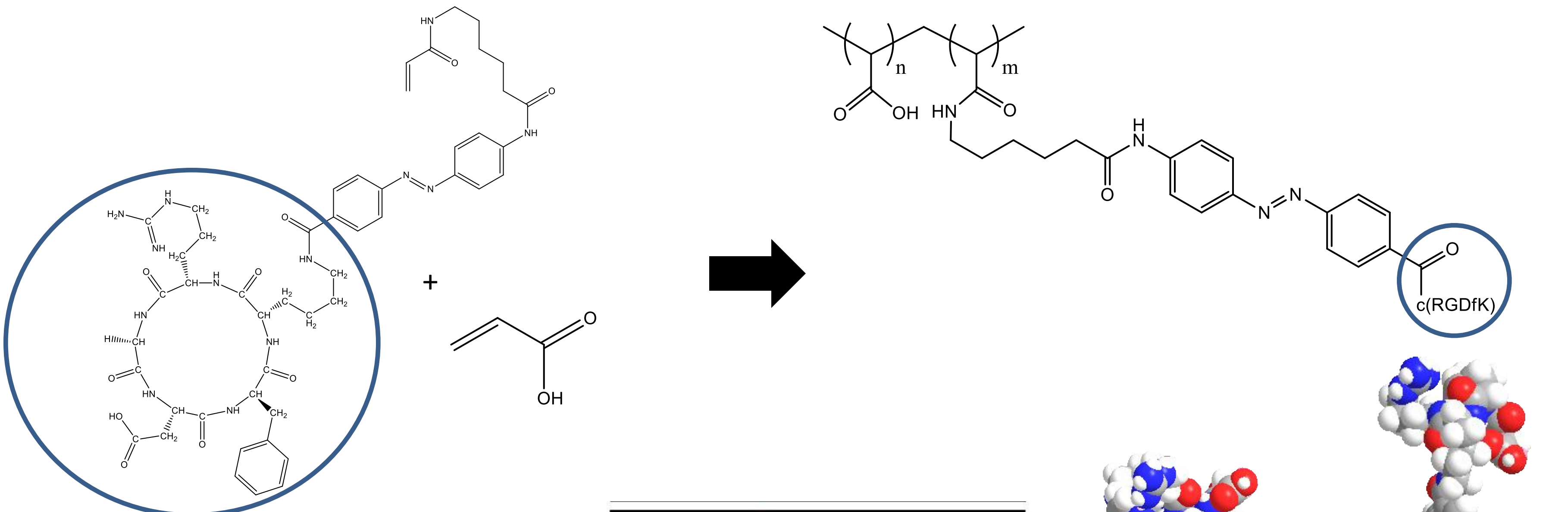


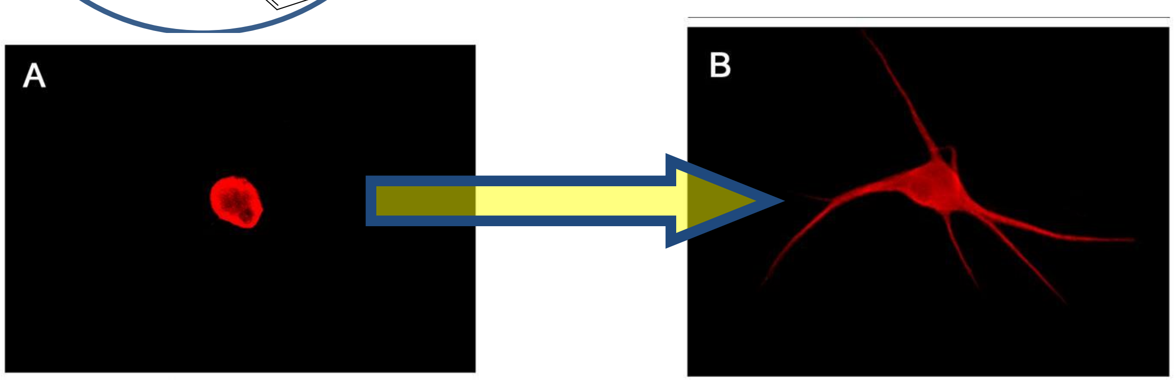
A SINGLE LAYER is enough to SWITCH the surface energy (contact angle) reversibly with light

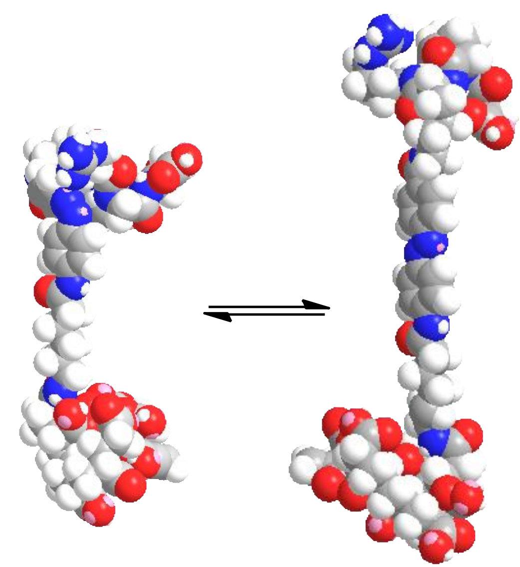
Polymer headgroup	Contact angle
R = $-SO_3H$	30 deg.
R = $-COOH$	38 deg.
R = $-OC_2H_5$	40 deg.
R = $-C_8H_{17}$	48 deg.
R = $-C_8F_{17}$	62 deg.

Light-Switchable Bio-surfaces *BioMacromolecules* **2012**

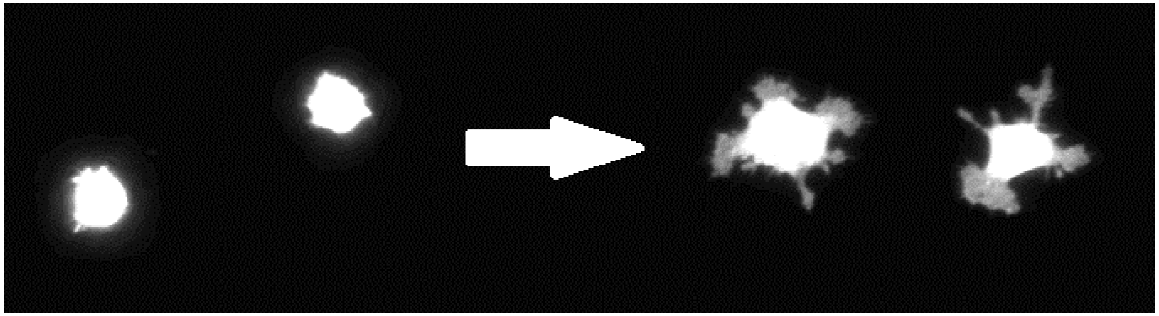
We desiged opto-switchable bio-surfaces with an azo RGD peptide (1%) to trigger cell growth/function



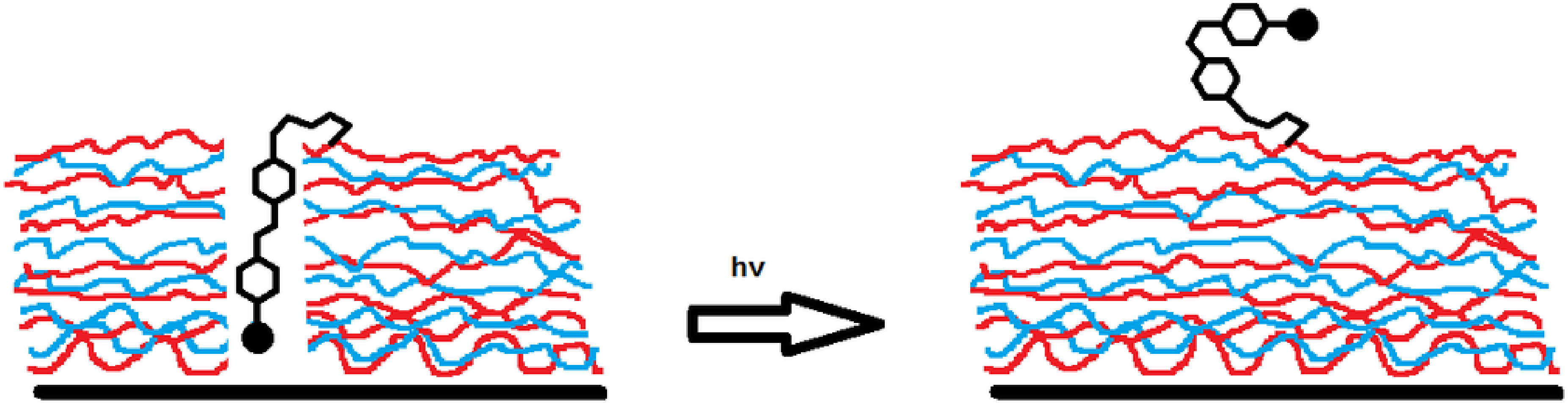


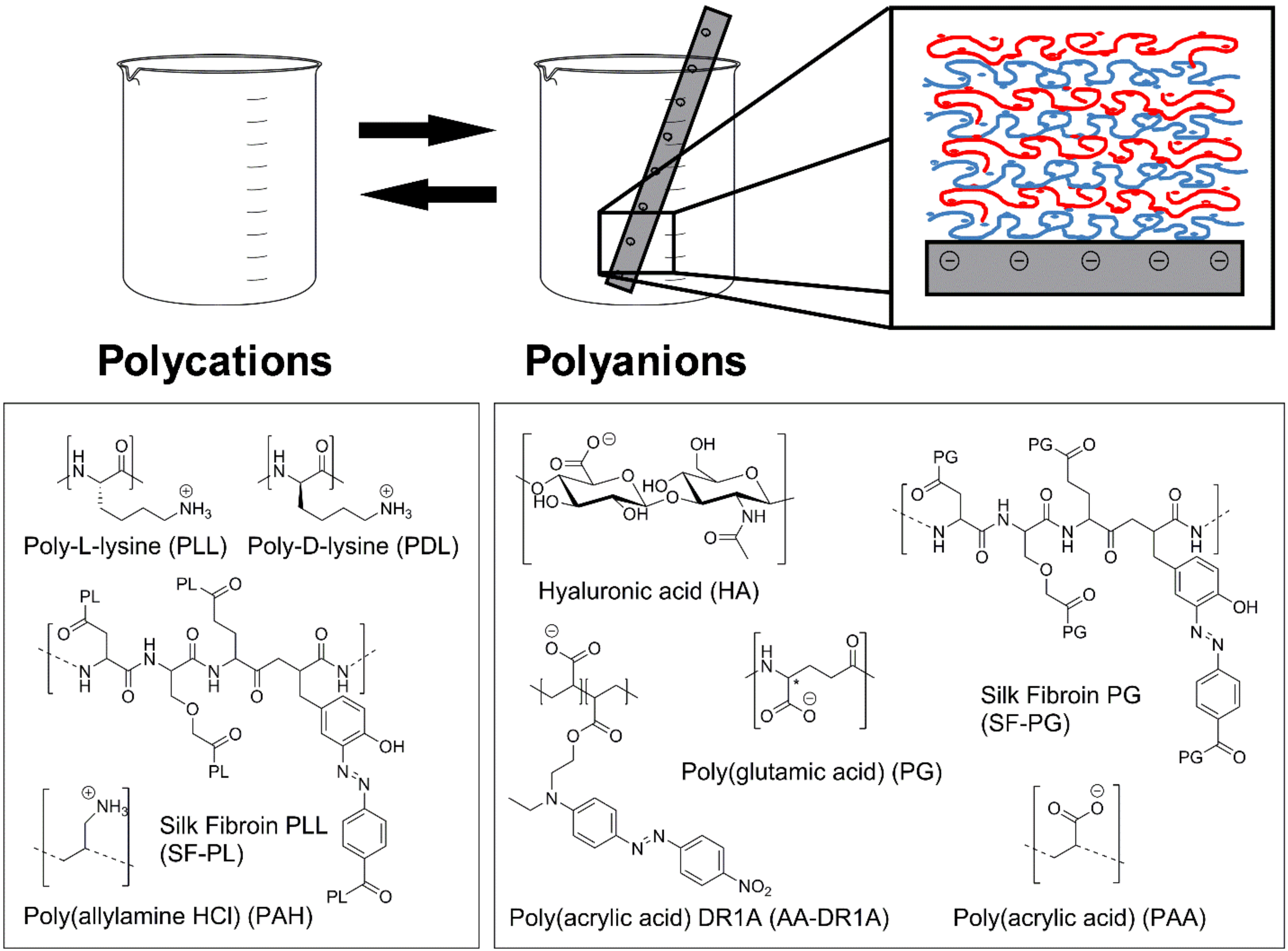


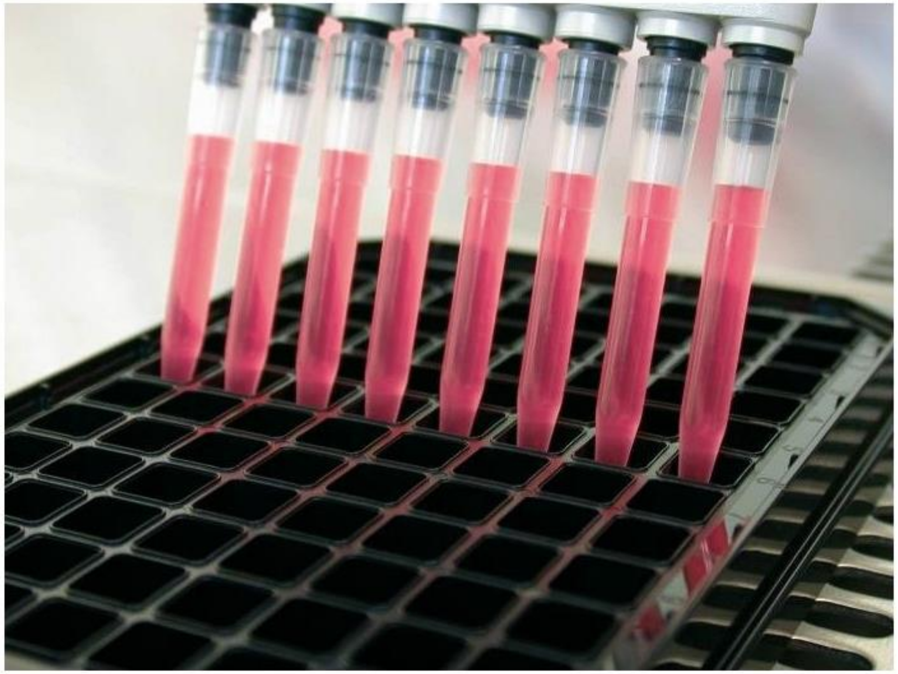
We could induce a significant (>40%) increase in cell size with light.
(Goulet-Hanssens, Barrett: *Biomacromolecules* '**12**, *J Poly Chem* '**13**)

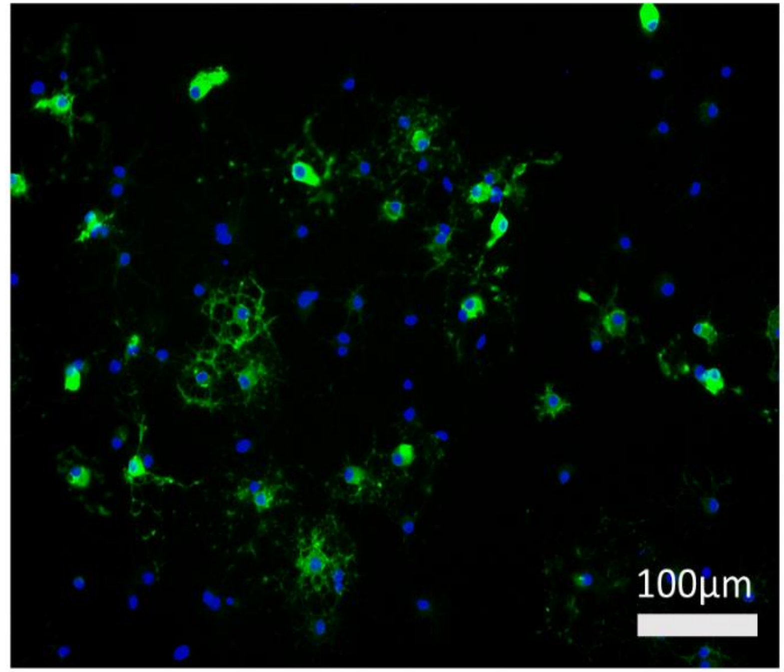


But HOW does it really work? We'd need to measure the photo-orientation underwater…

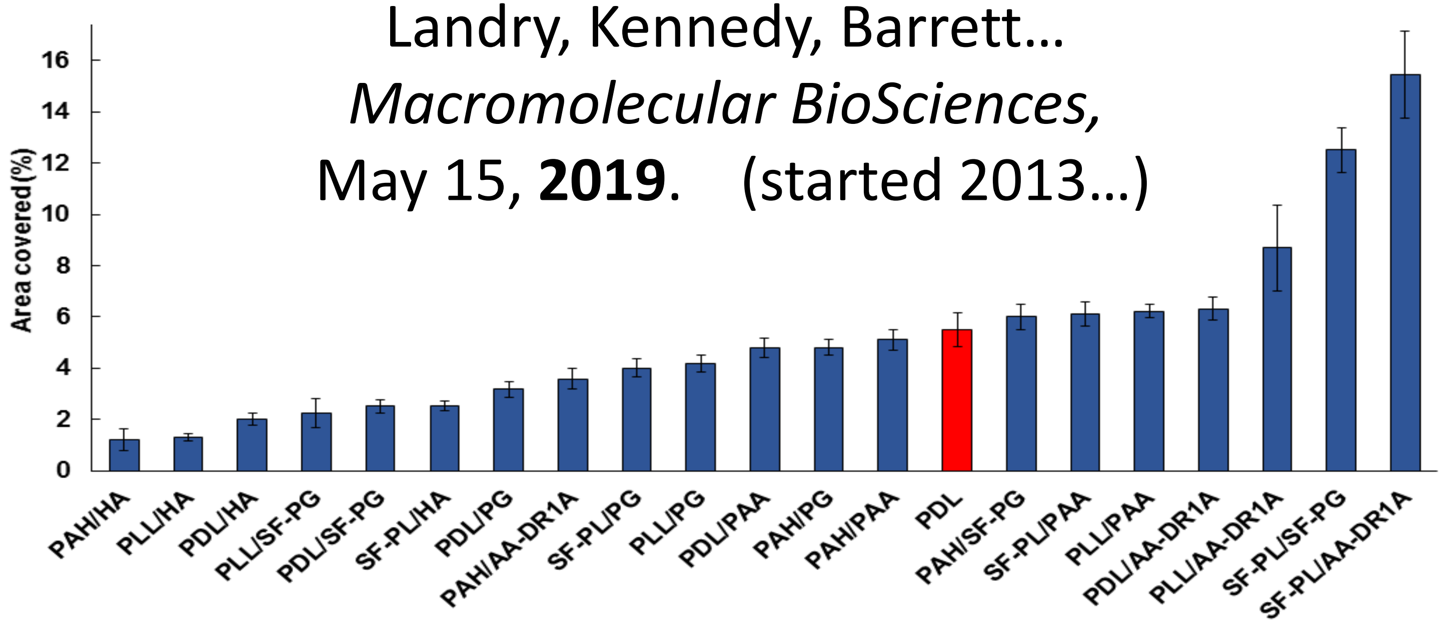



Polycations
Polyanions
Poly-L-lysine (PLL)
Poly-D-lysine (PDL)
Silk Fibroin PLL
(SF-PL)
Poly(allylamine HCl) (PAH)
Hyaluronic acid (HA)
Silk Fibroin PG
(SF-PG)
Poly(glutamic acid) (PG)
Poly(acrylic acid) DR1A (AA-DR1A)
Poly(acrylic acid) (PAA)





Landry, Kennedy, Barrett…
Macromolecular BioSciences,
May 15, **2019**. (started 2013…)



ADVANCED OPTICAL MATERIALS

Progress Report

Photoreversible Soft Azo Dye Materials: Toward Optical Control of Bio-Interfaces

Victoria Y. Chang, Chiara Fedele, Arri Priimagi, Atsushi Shishido, Christopher J. Barrett

First published: 29 May 2019 | https://doi.org/10.1002/adom.201900091

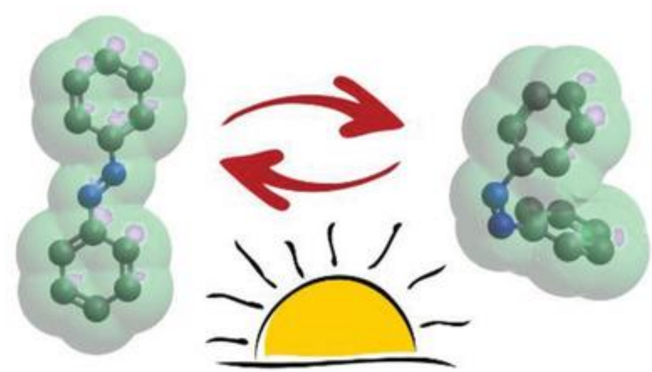
Read the full text >

PDF TOOLS SHARE

Early View

Online Version of Record before inclusion in an issue

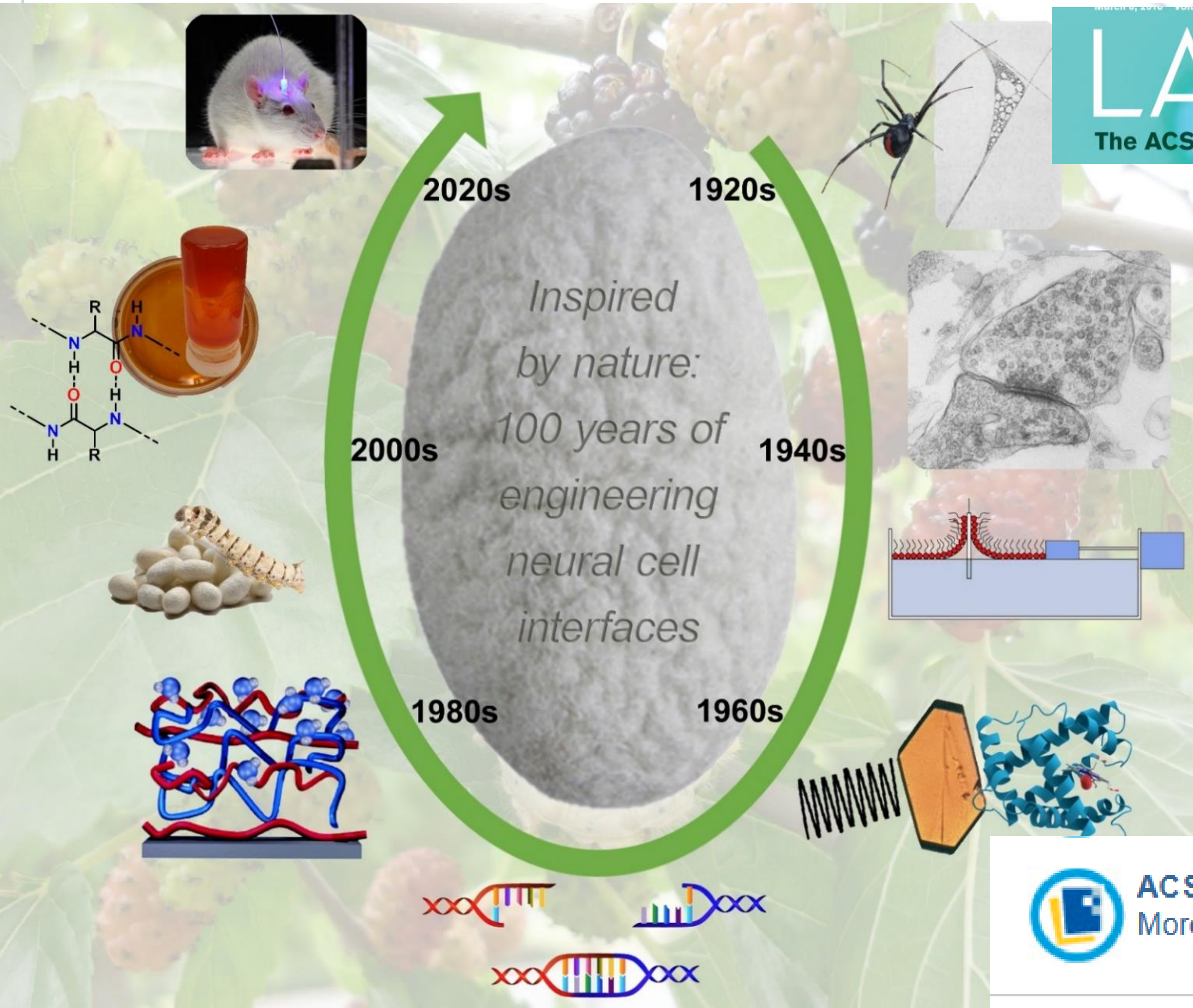
1900091



INVITED FEATURE ARTICLE

Layers and Multilayers of Self-Assembled Polymers: Tunable Engineered Extracellular Matrix Coatings for Neural Cell Growth

Michael J. Landry, Frédéric-Guillaume Rollet, Timothy E. Kennedy, and Christopher J. Barrett



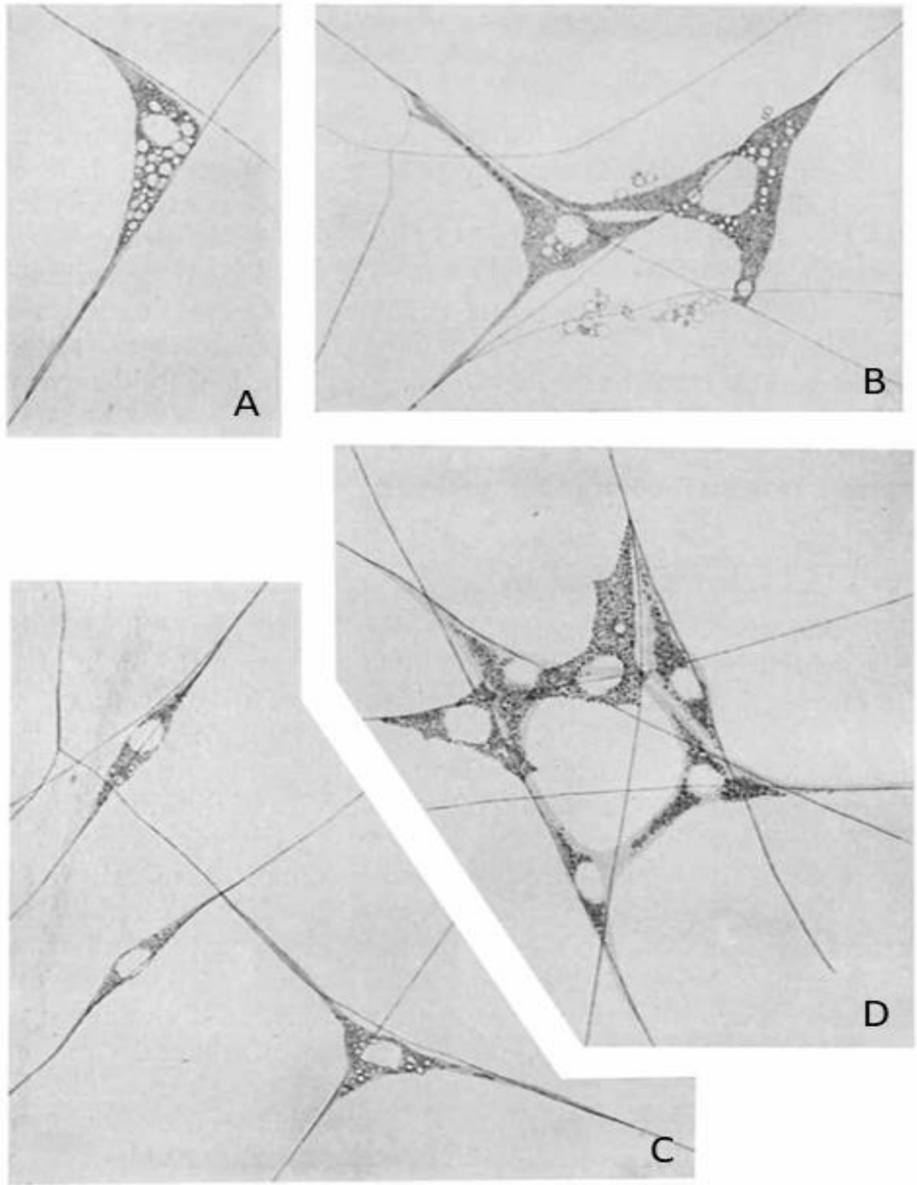
LANGMUIR
The ACS journal of fundamental interface science

July 31, 2018
Volume 34, Issue 30
Pages 8709-9096

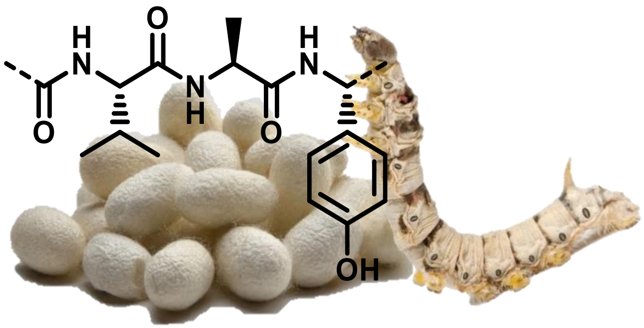
About the Cover:

Cover image by Michael J. Landry, Christopher J. Barrett.

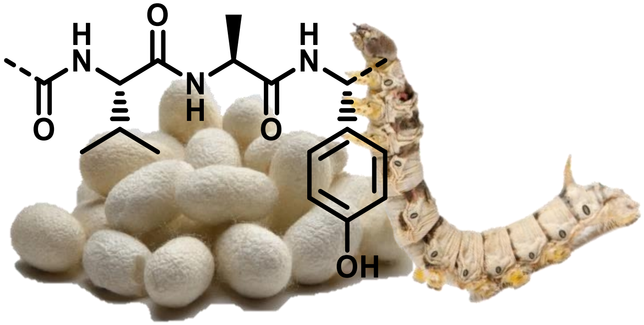
Neural cells on artificial surfaces, Harrison 1914



Rare Silks from Asia as bio-materials

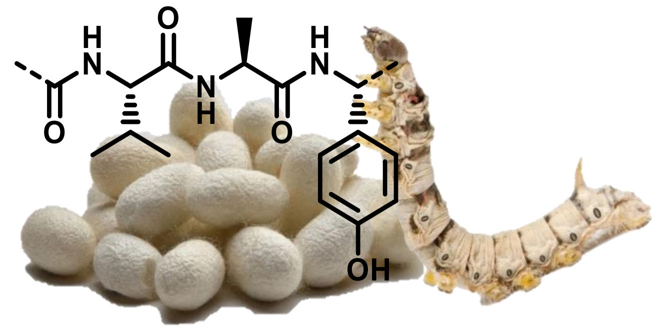


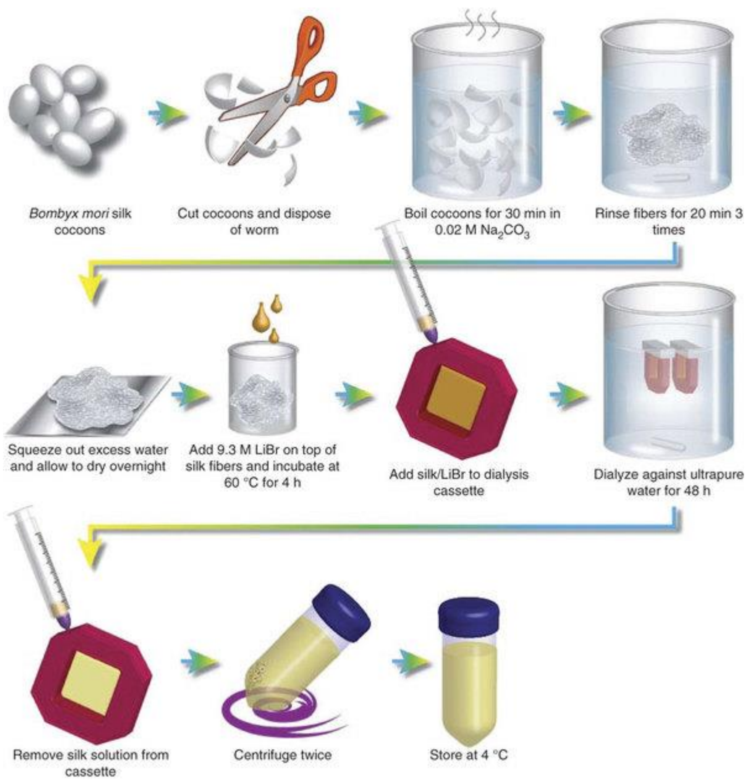
Home-grown McGill silk as a bio-material



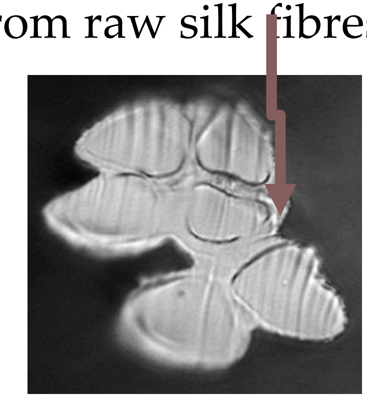
Bombyx mori (Victoria Chang), eating *Morus alba* (from McGill Arboretum), July 2018

light-triggered azo silk as a bio-material

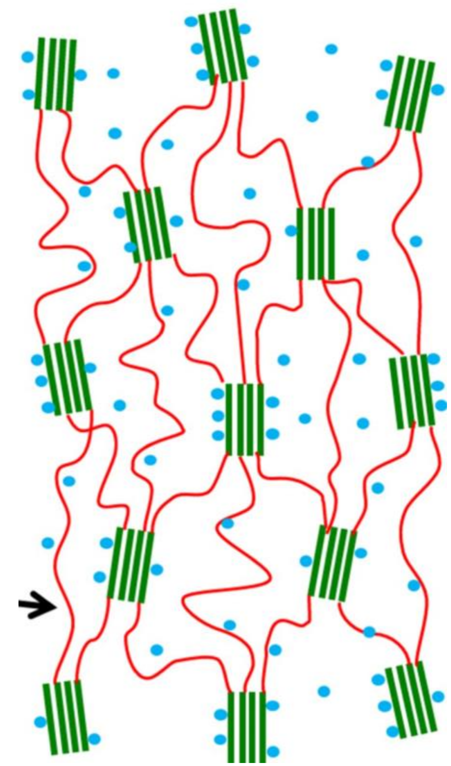




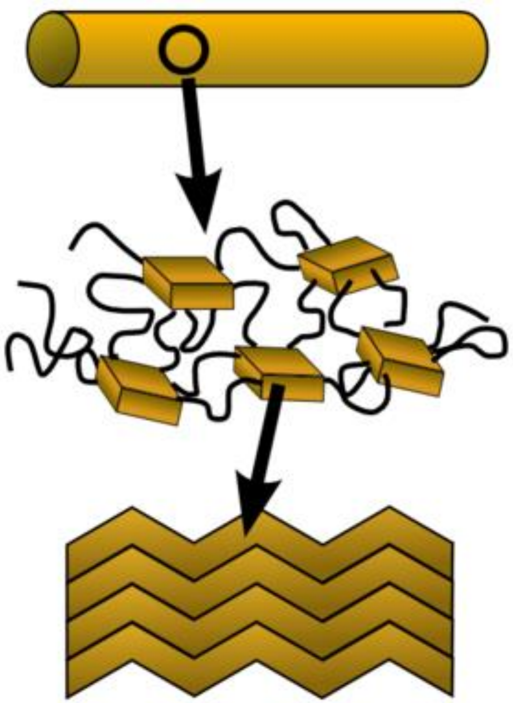
Boiling removes sericin from raw silk fibres

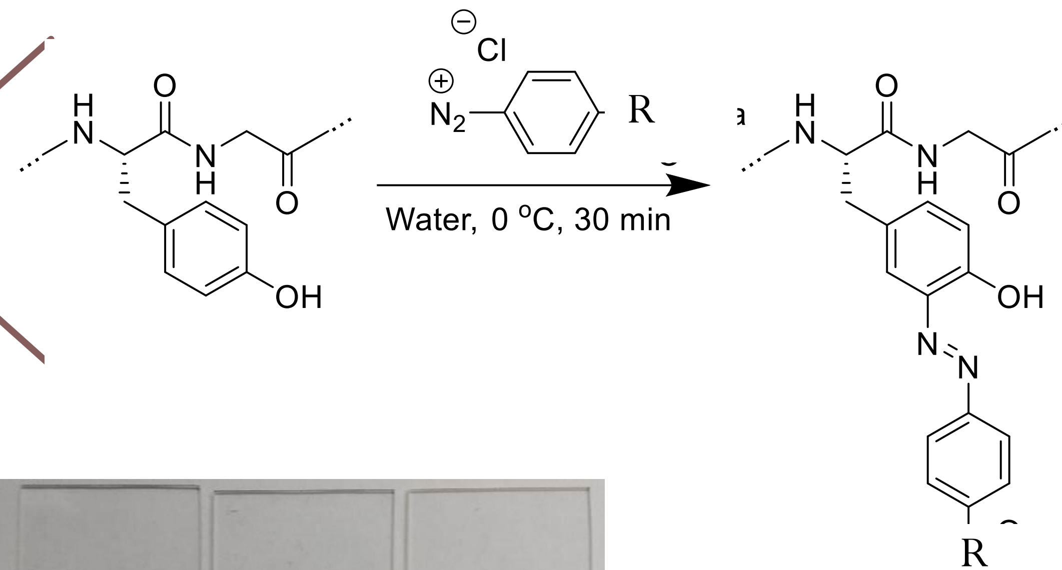


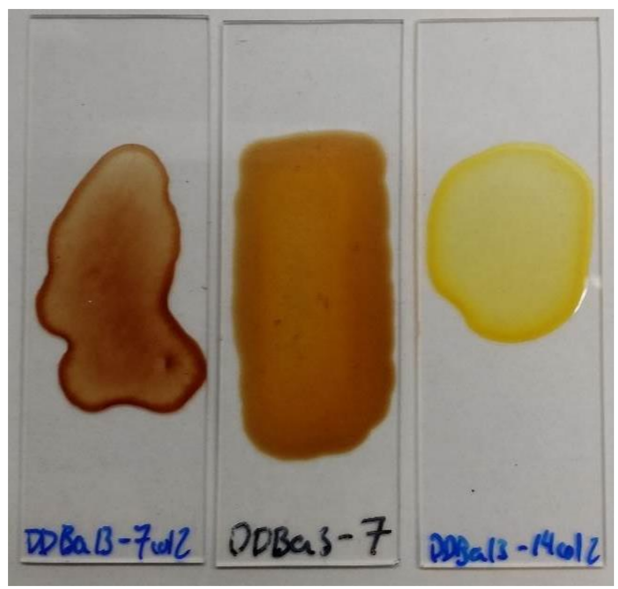
LiBr breaks up β-sheet clusters and dissolves the protein.

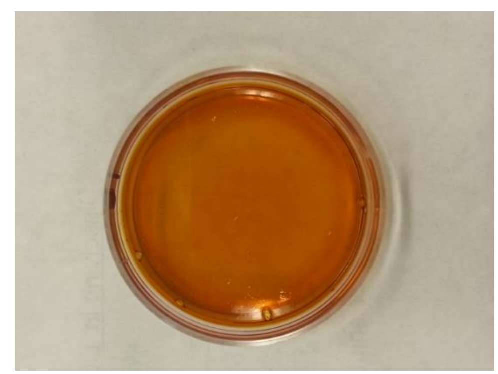


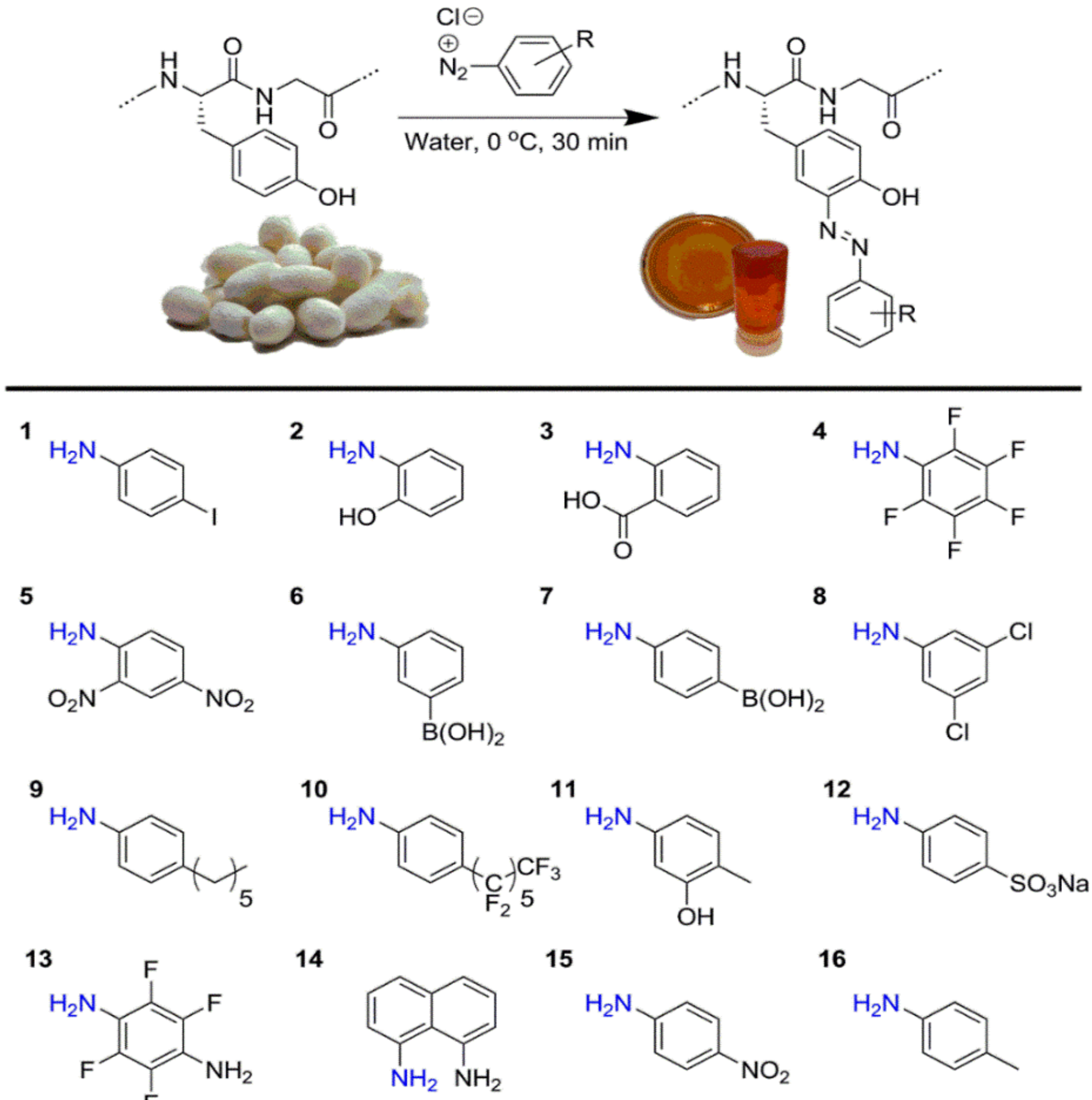
Modifying silk with azobenzene, < 1%



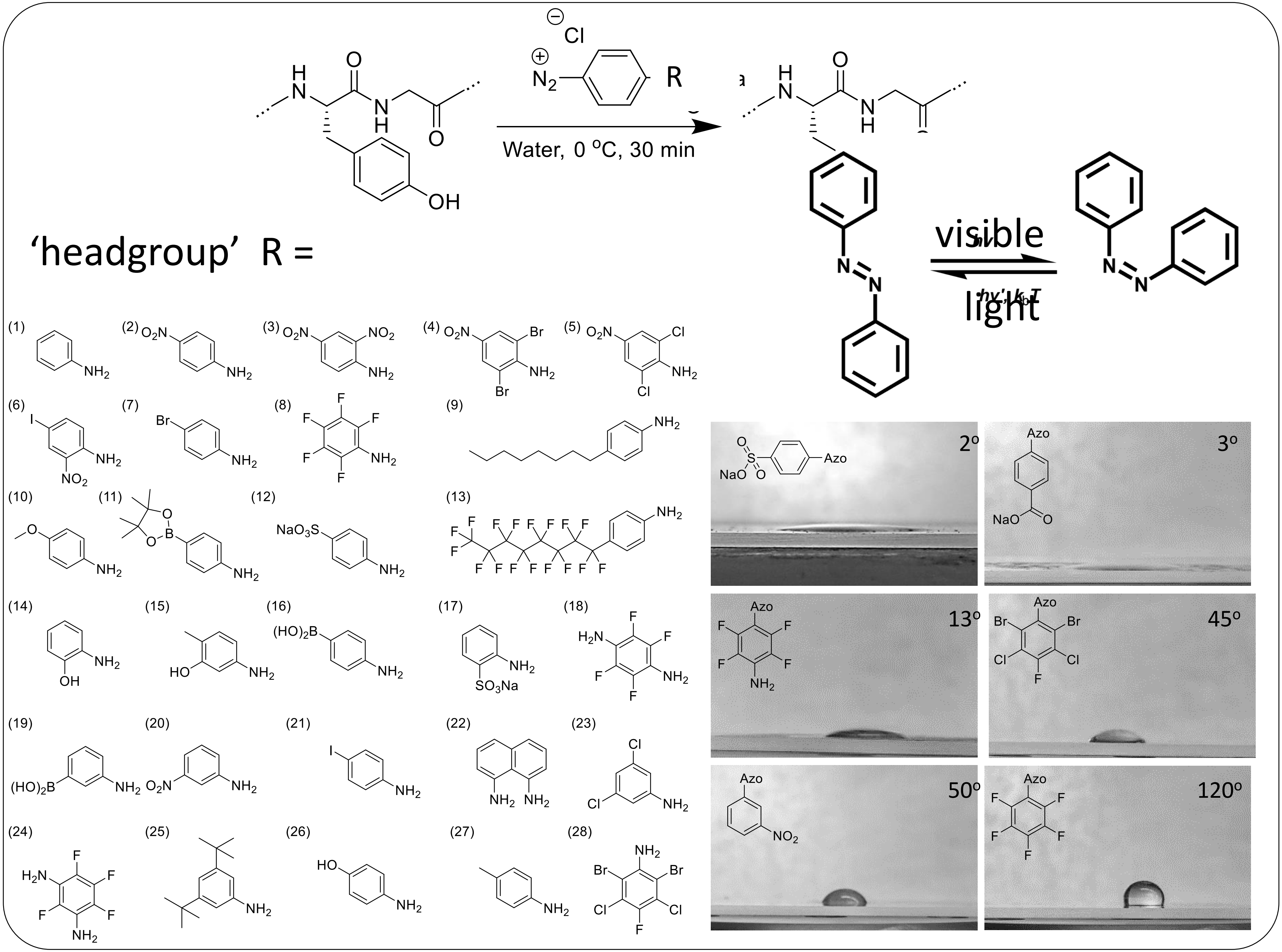






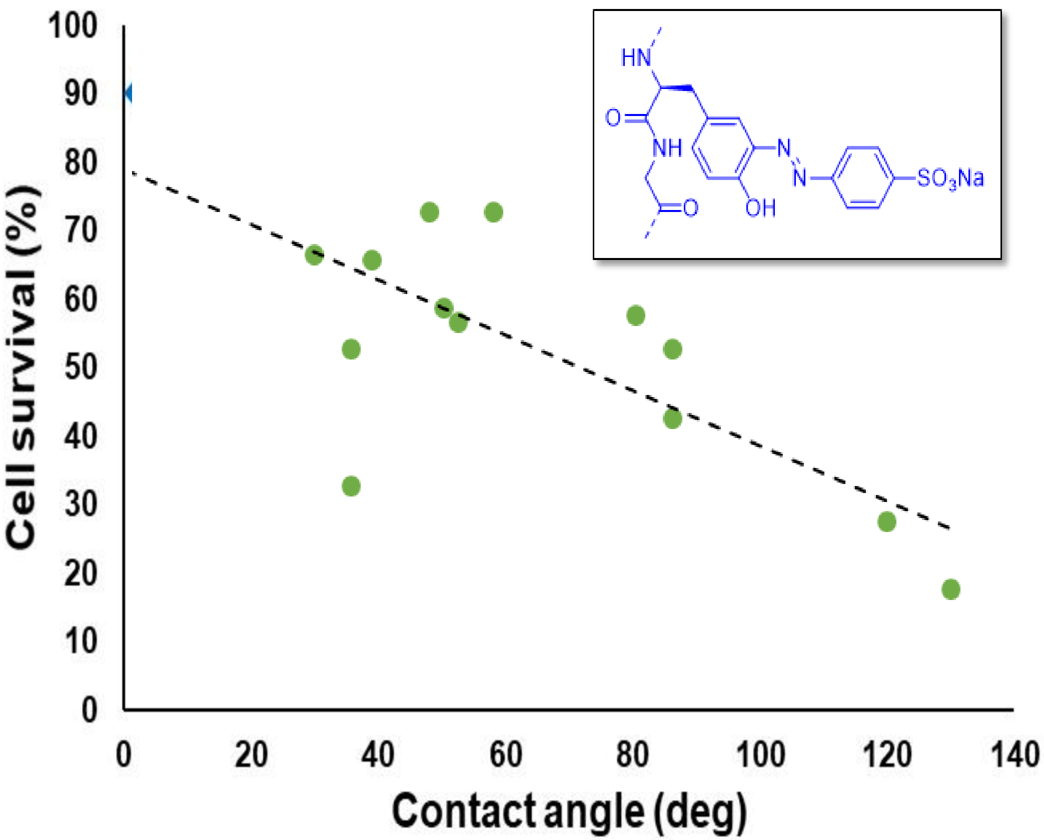


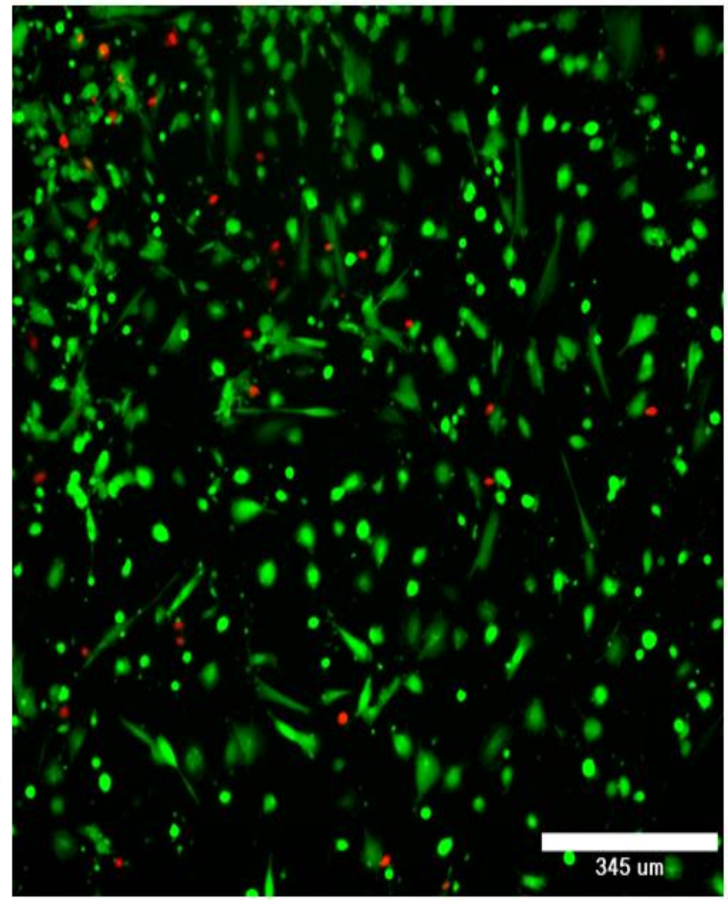
Cl⊖
⊕
N2
R
H
N
O
N
H
O
Water, 0 °C, 30 min
OH
N
N
R
1
H2N
I
2
H2N
HO
3
H2N
HO
O
4
F
H2N
F
F
F
F
5
H2N
O2N
NO2
6
H2N
B(OH)2
7
H2N
B(OH)2
8
H2N
Cl
Cl
9
H2N
5
10
H2N
CF3
C
F2
5
11
H2N
OH
12
H2N
SO3Na
13
F
H2N
F
F
NH2
F
14
NH2
NH2
15
H2N
NO2
16
H2N



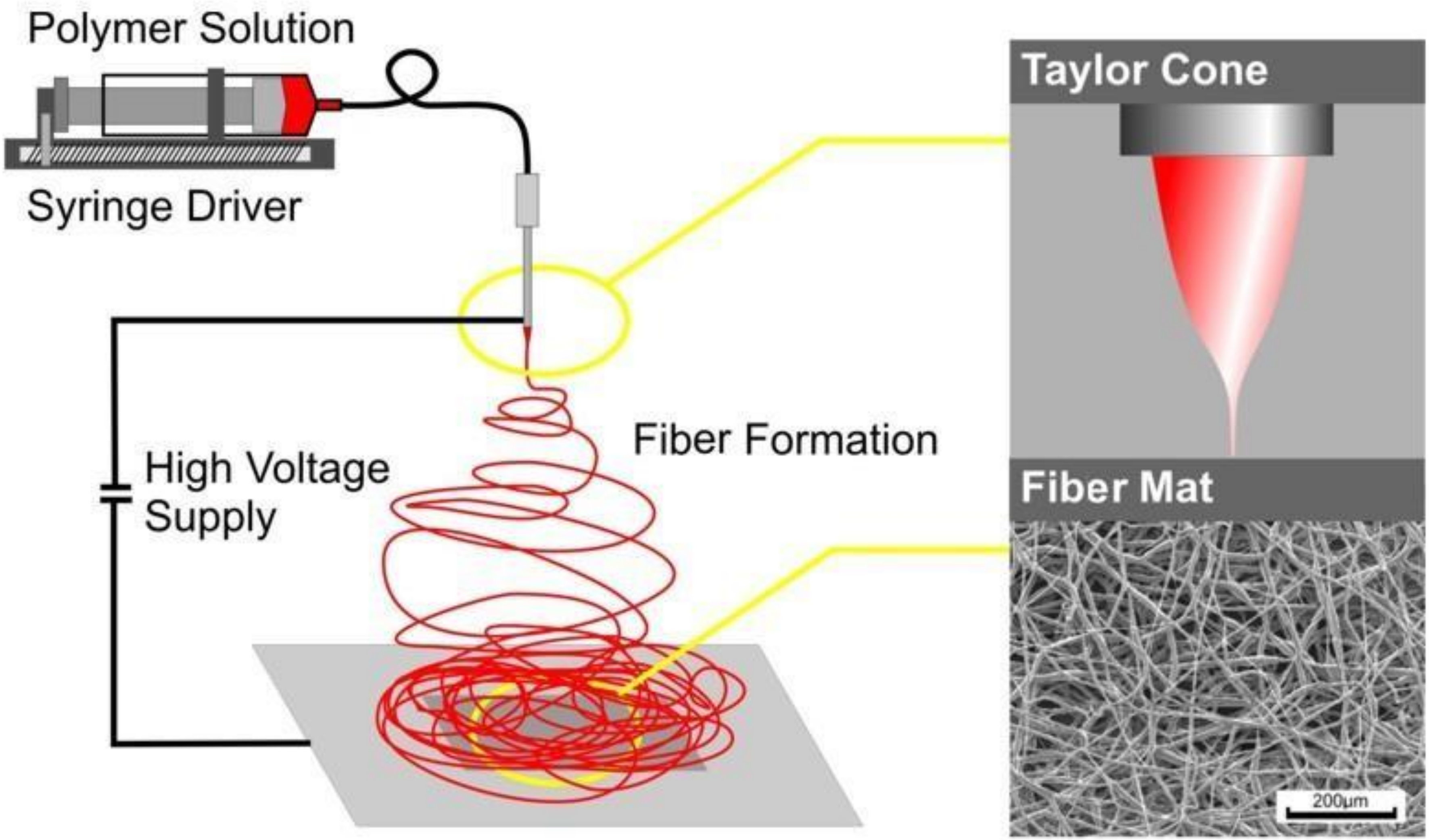
Water, 0 °C, 30 min
visible
light
'headgroup' R =
(1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18) (19) (20) (21) (22) (23) (24) (25) (26) (27) (28)
2°
3°
13°
45°
50°
120°

Modulus of photo-softened regions

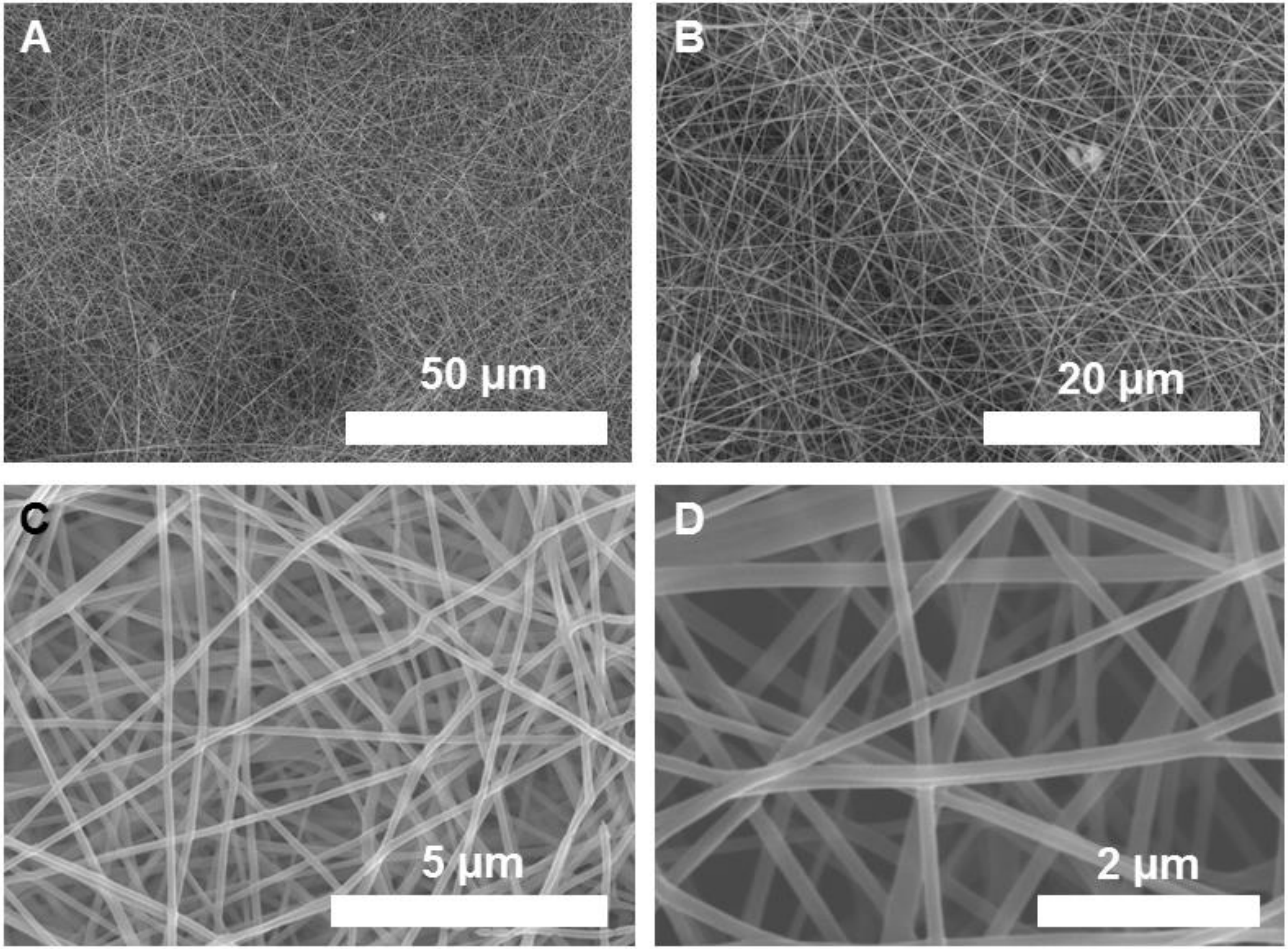




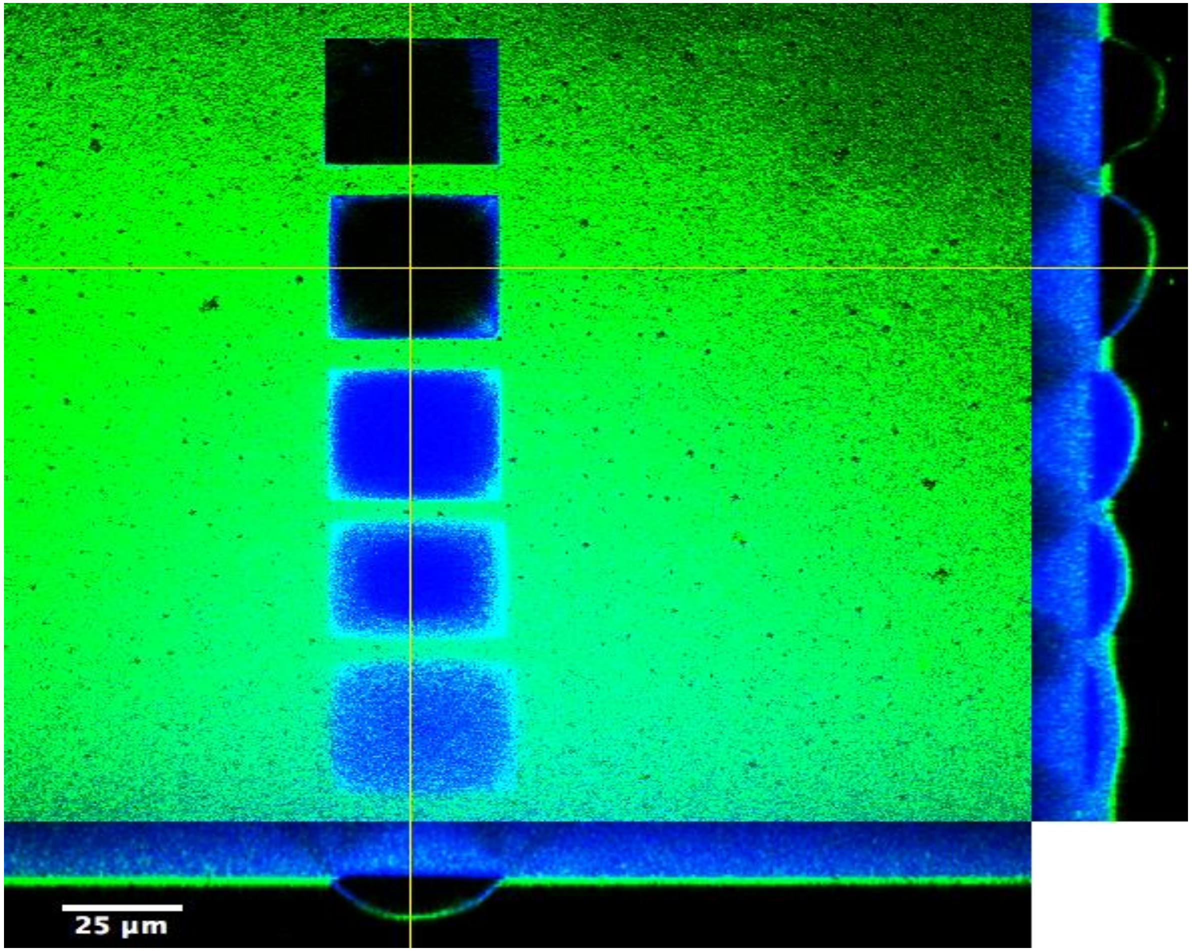
Electrospinning azosilk into fibre mat materials:



Electrospinning azosilk into fibre mat materials:

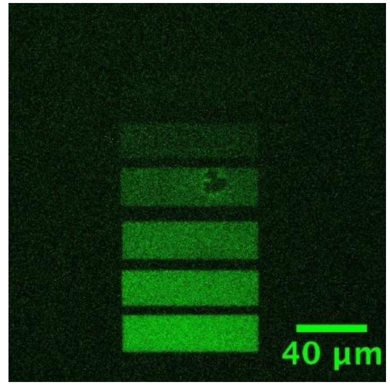


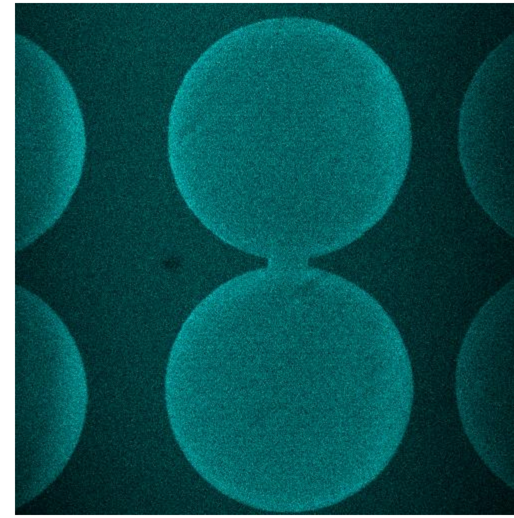
creating Light-induced ‘solubility’ as the azo disrupts the beta sheets and the silk ‘springs open’ to water



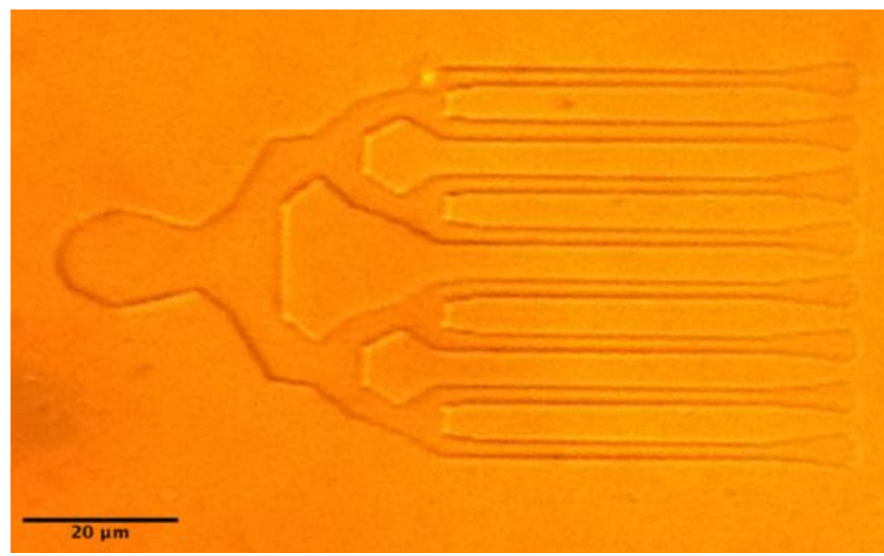
“Photo-Induced Structural Modification of Azo-Silk Gels”
M. Landry, M. Cronin-Golomb, D. Kaplan, C. J. Barrett, *Soft Matter* **2017**.

2-photon Laser patterning for 3D 'writing'

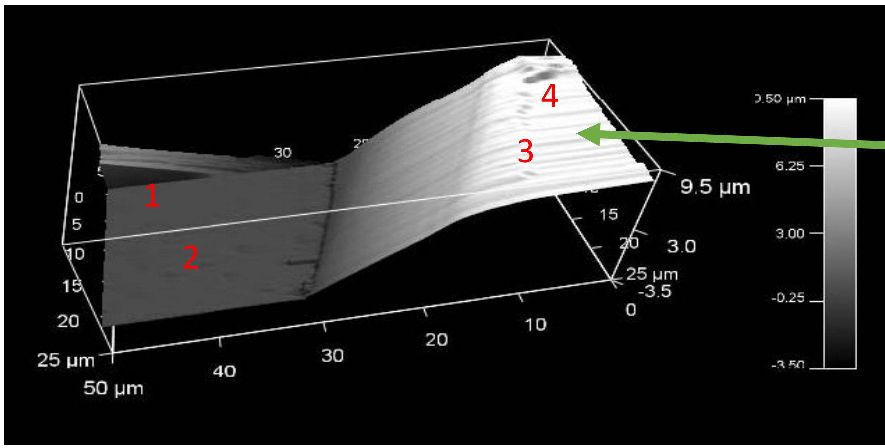




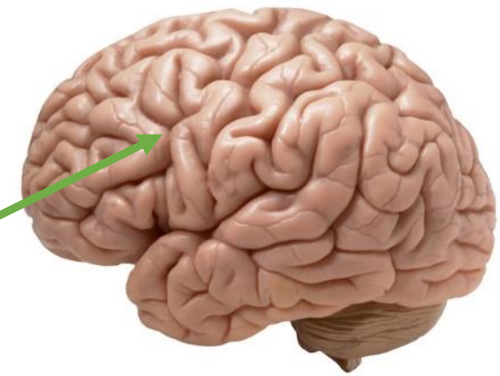
Writing at different depths in a 200 µM azosilk gel



Modulus of photo-softened regions



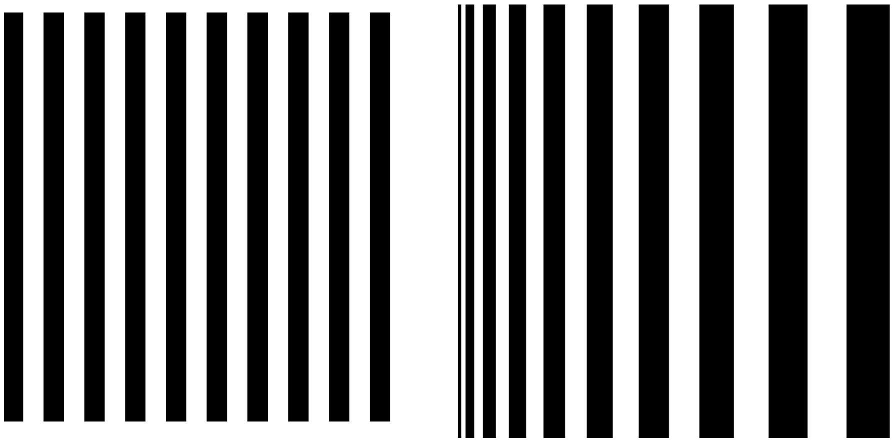
Brain modulus is 0.6-10 kPa



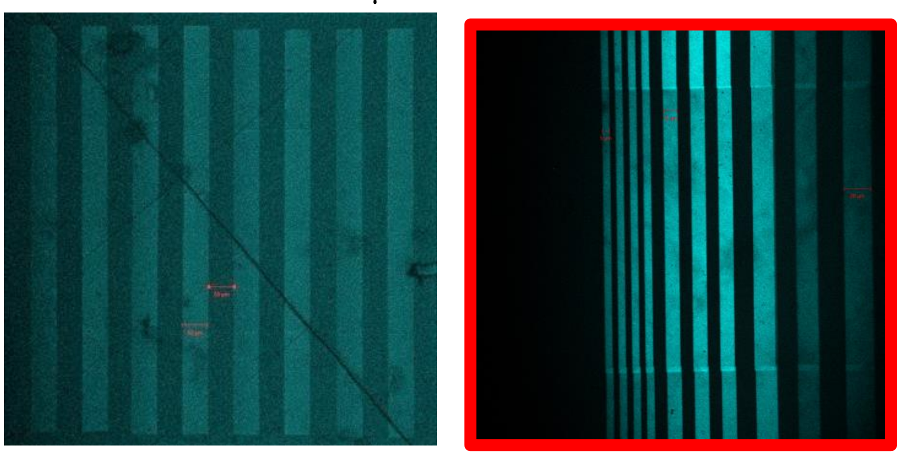
underwater AFM image of micro-bubbles using iDrive AFM tips to measure modulus and image features.

Spot	Elastic modulus (E_s)	Reduced modulus (E_c)
1 (Dark)	11 kPa	14 kPa
2 (Dark)	12 kPa	16 kPa
3 (Light)	0.65 kPa	0.9 kPa
4 (Light)	0.60 kPa	0.8 kPa

Patterning Optosilk Films



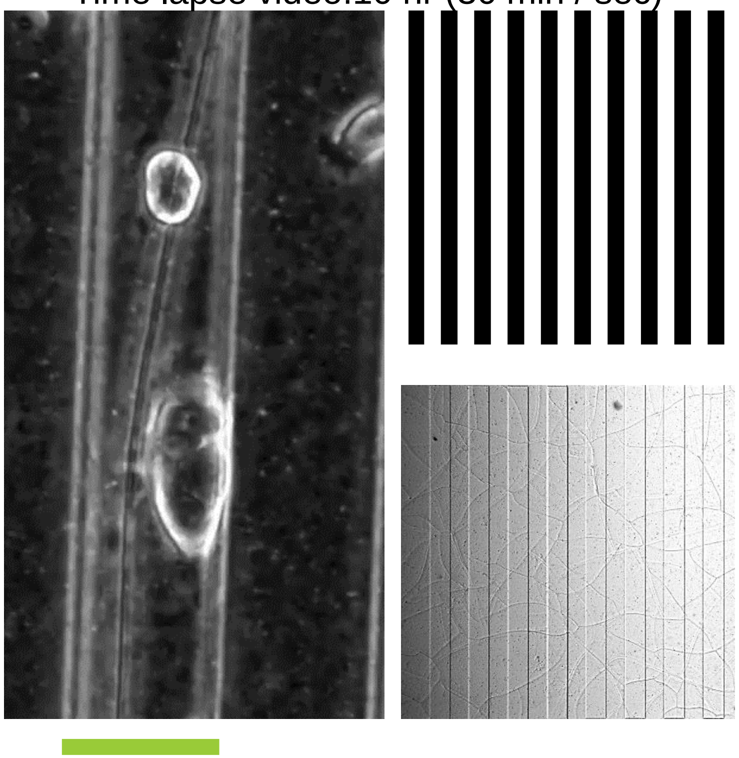
50 μm lines



- Multiphoton excitation – biocompatible 800nm
- Induces photo-isomerization of the azobenzene moiety, disrupting beta sheets and forming fluorescent raised regions (“bubbles”)
- Height of raised patterned bubbles can be controlled by irradiating at different depths from the surface
- Raised patterned bubbles are softer than unpatterned opto-silk
- We use a MATLAB script to generate regions of interest for precise patterning

Cell Guidance on Opto-Silk Films

nMUMG cells on 50 μm wide raised lines
Time lapse video:10 hr (30 min / sec)

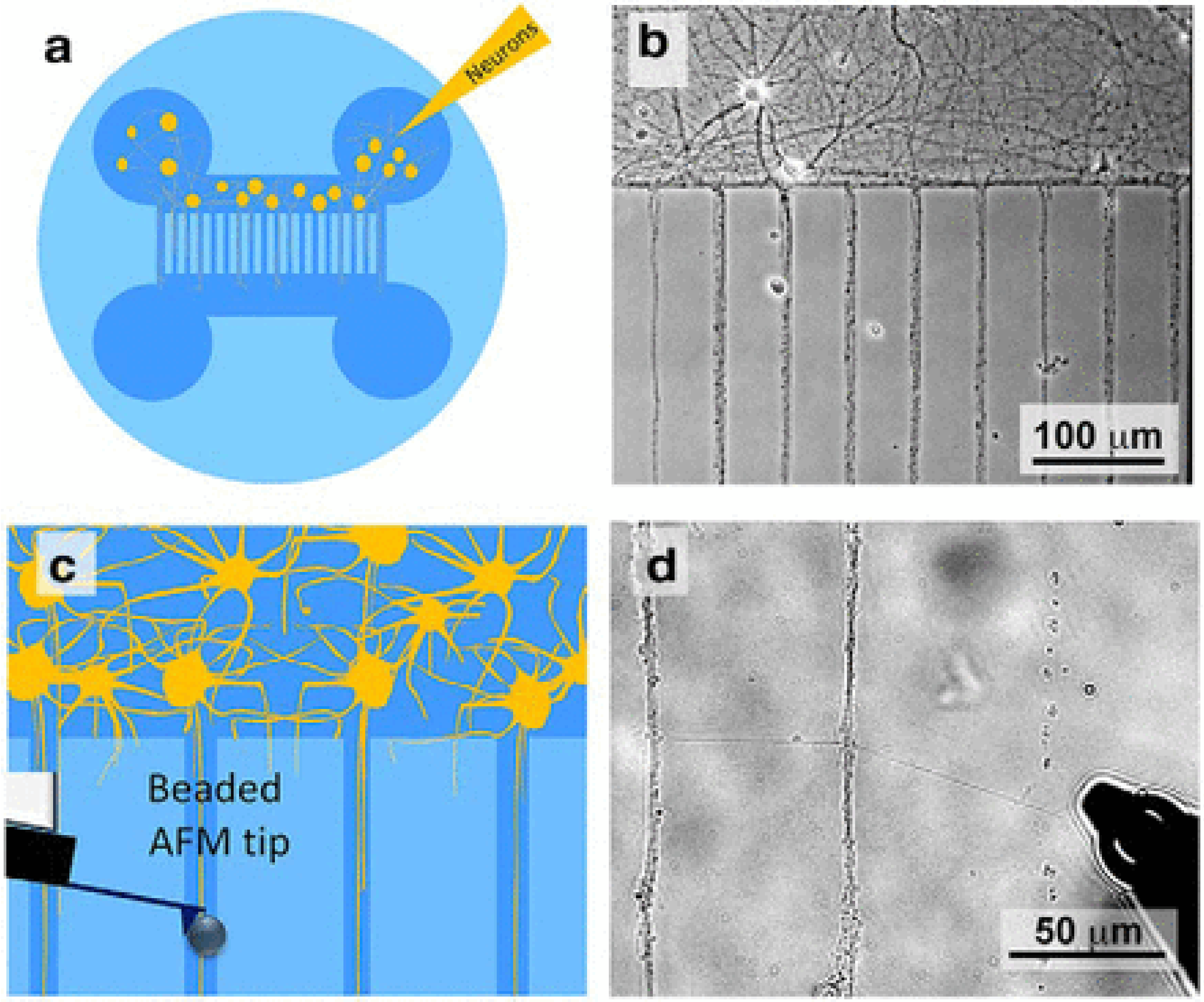


50 μm

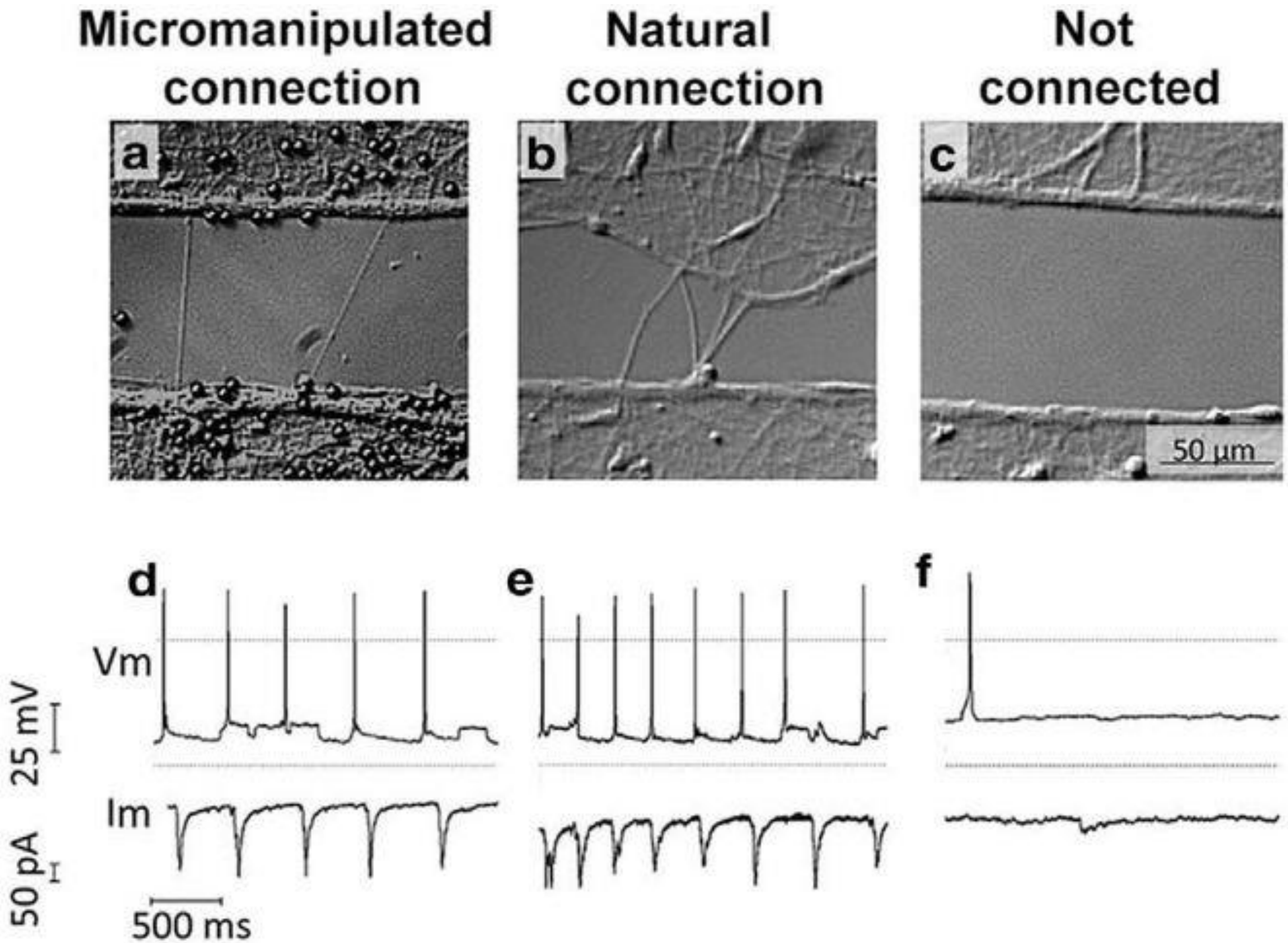
- We use a MATLAB script for generating regions of interest for precise patterning
- Patterns were designed for guidance of cells along grooves or raised region
- A range of patterned surfaces were made to study cell interaction
- Initial work shows cells responding to opto-silk surface

"Rapid Mechanically Controlled Rewiring of Neuronal Circuits"

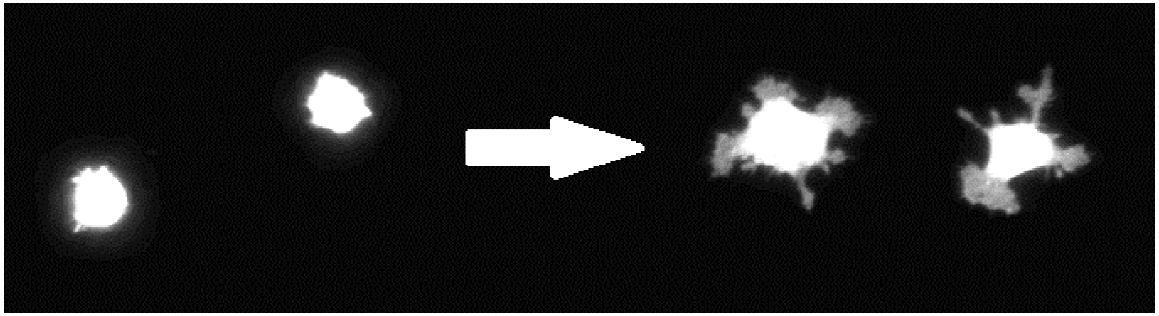
Journal of Neuroscience **2016**, *36,* 979



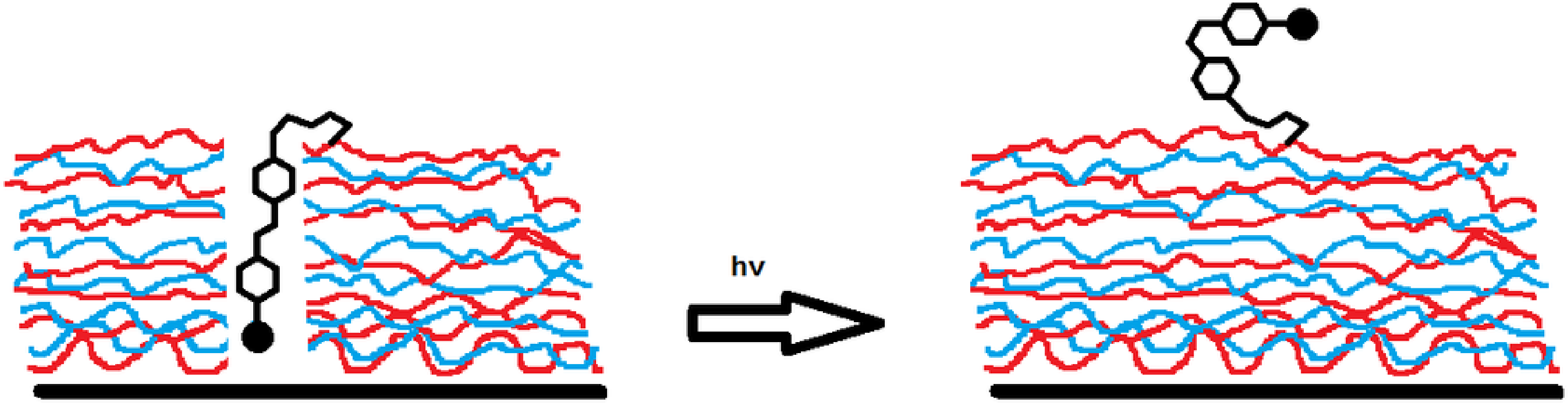
“Rapid Mechanically Controlled Rewiring of Neuronal Circuits”
Journal of Neuroscience **2016**, *36,* 979. (cb- slide 139 now?)



We could induce a significant (>40%) increase in cell size with light.
(Goulet-Hanssens, Barrett: *Biomacromolecules* '**12**, *J Poly Chem* '**13**)

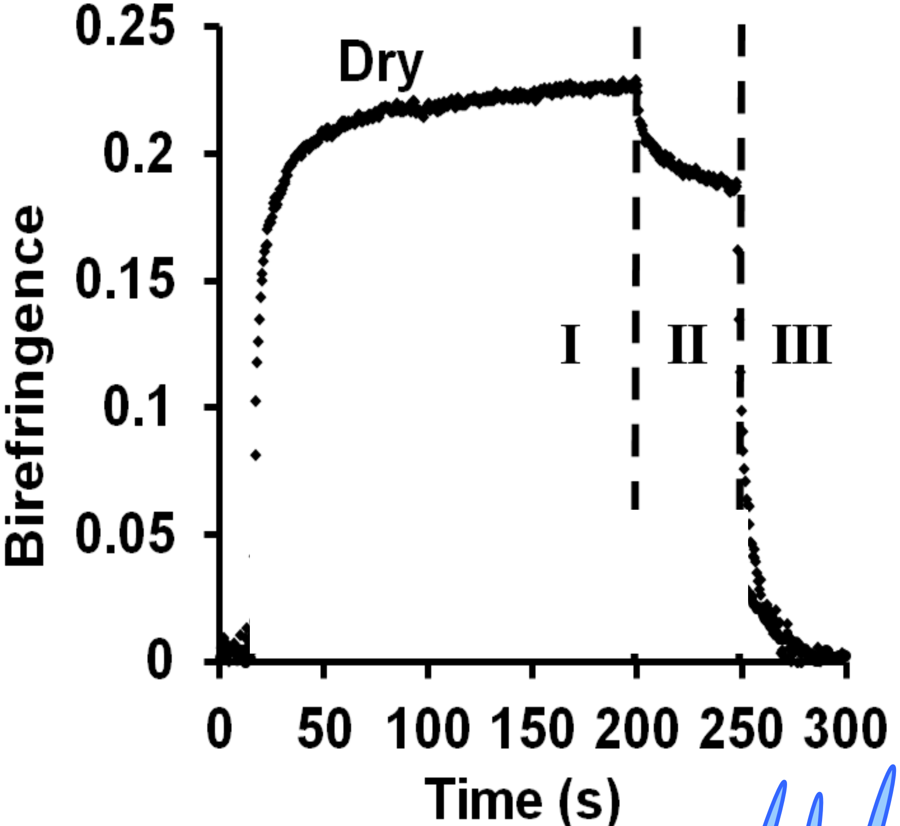


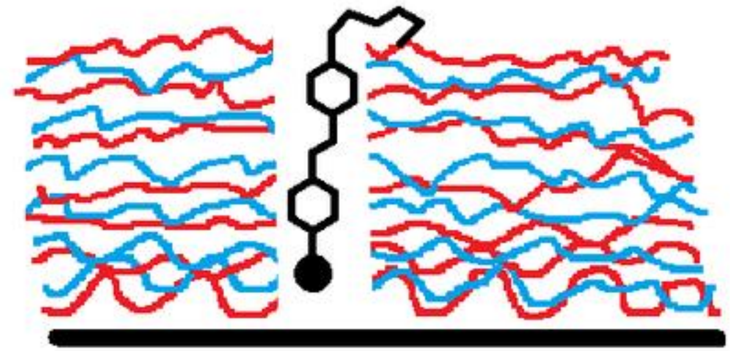
But HOW does it really work? We need to measure the photo-orientation underwater…

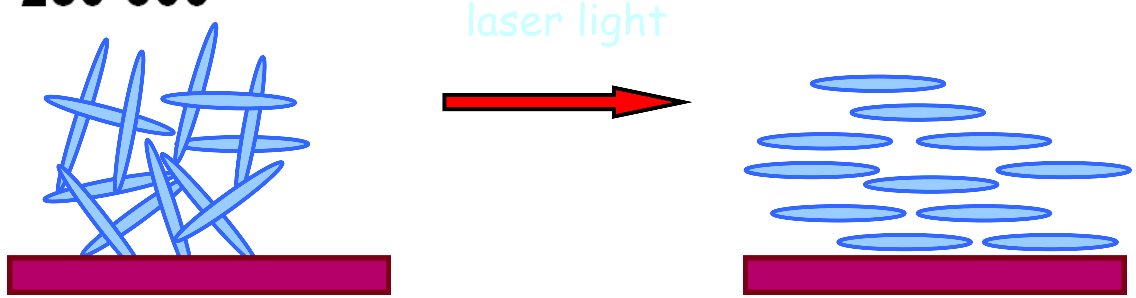


Molecular orientation is probed via birefringence a ‘linear pump’ – relax – ‘circular erase’ cycle

(Sailer, Barrett: *Physical Chemistry Chemical Physics* **2013**)

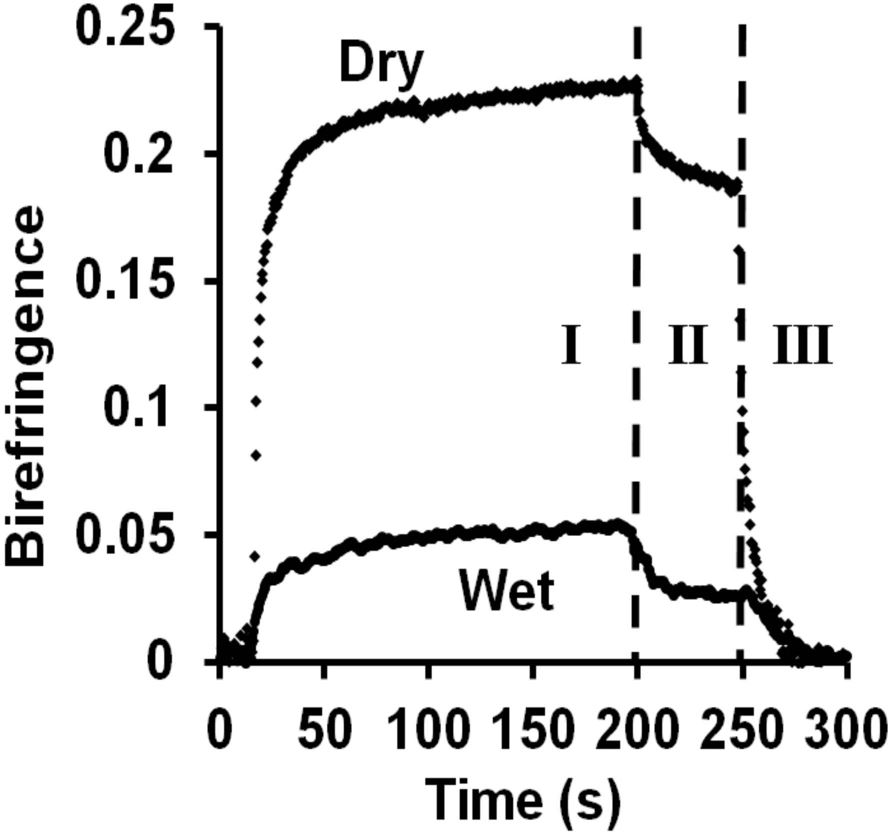


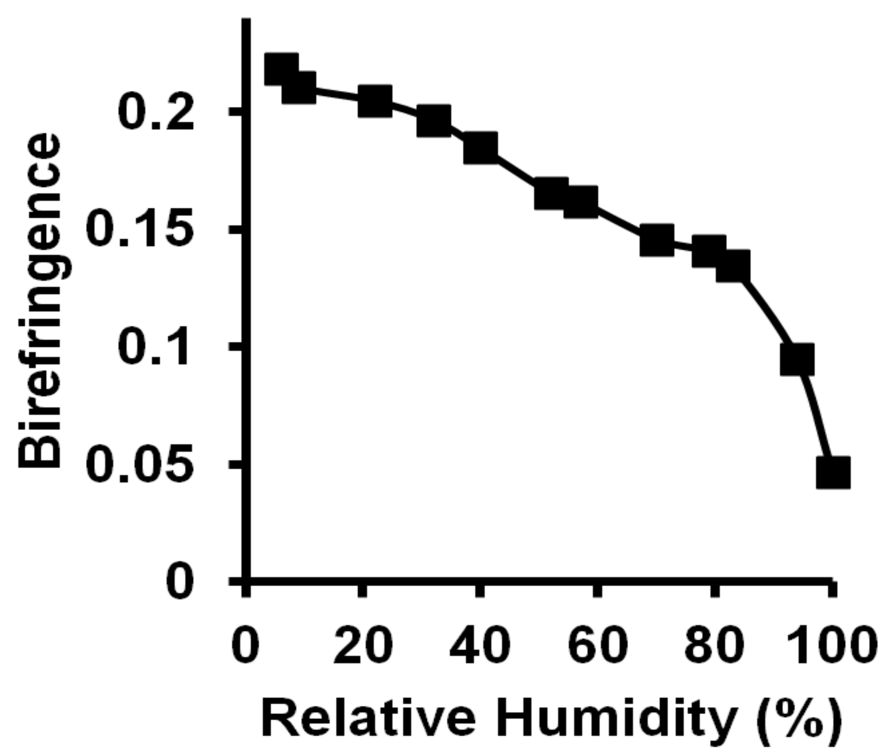




Molecular orientation is probed via birefringence

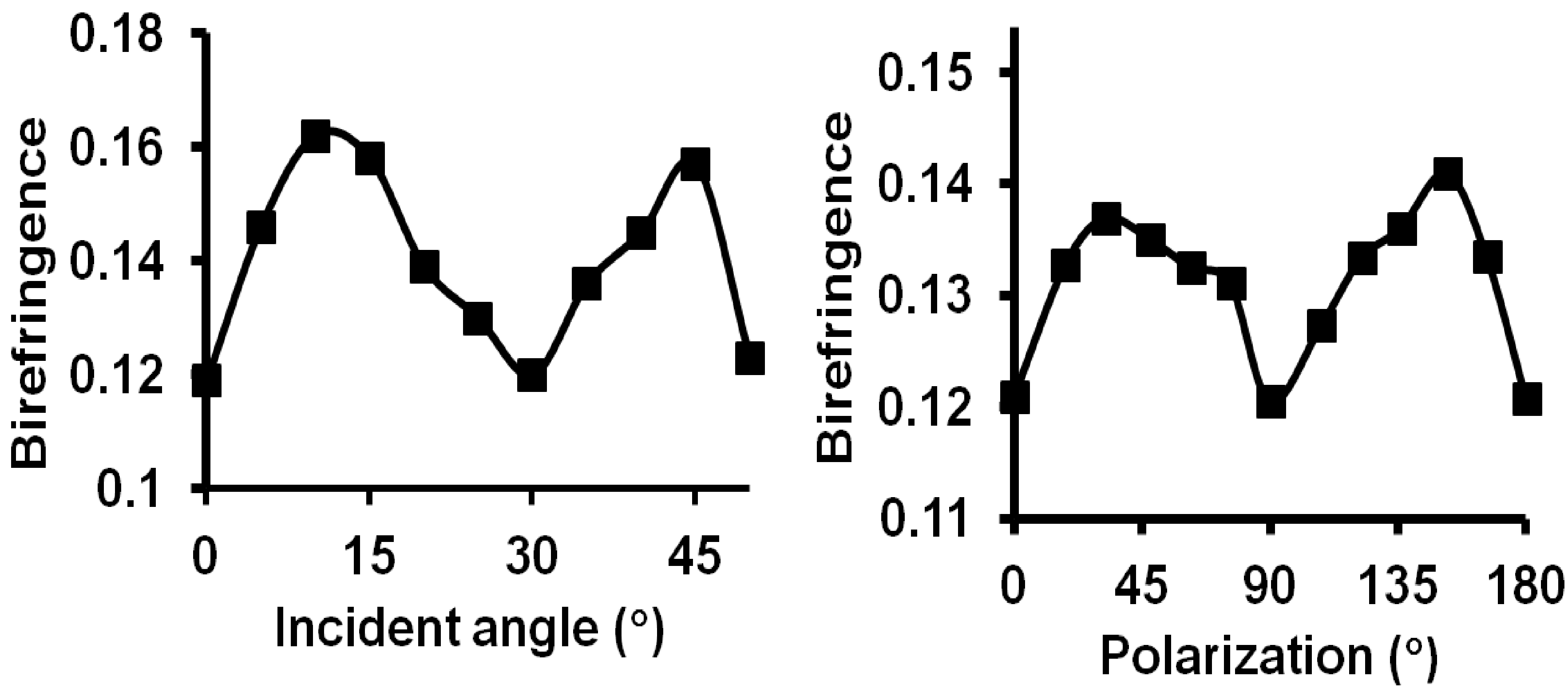
a ‘linear pump’ – relax – ‘circular erase’ cycle as we slowly transition from dry to wet.

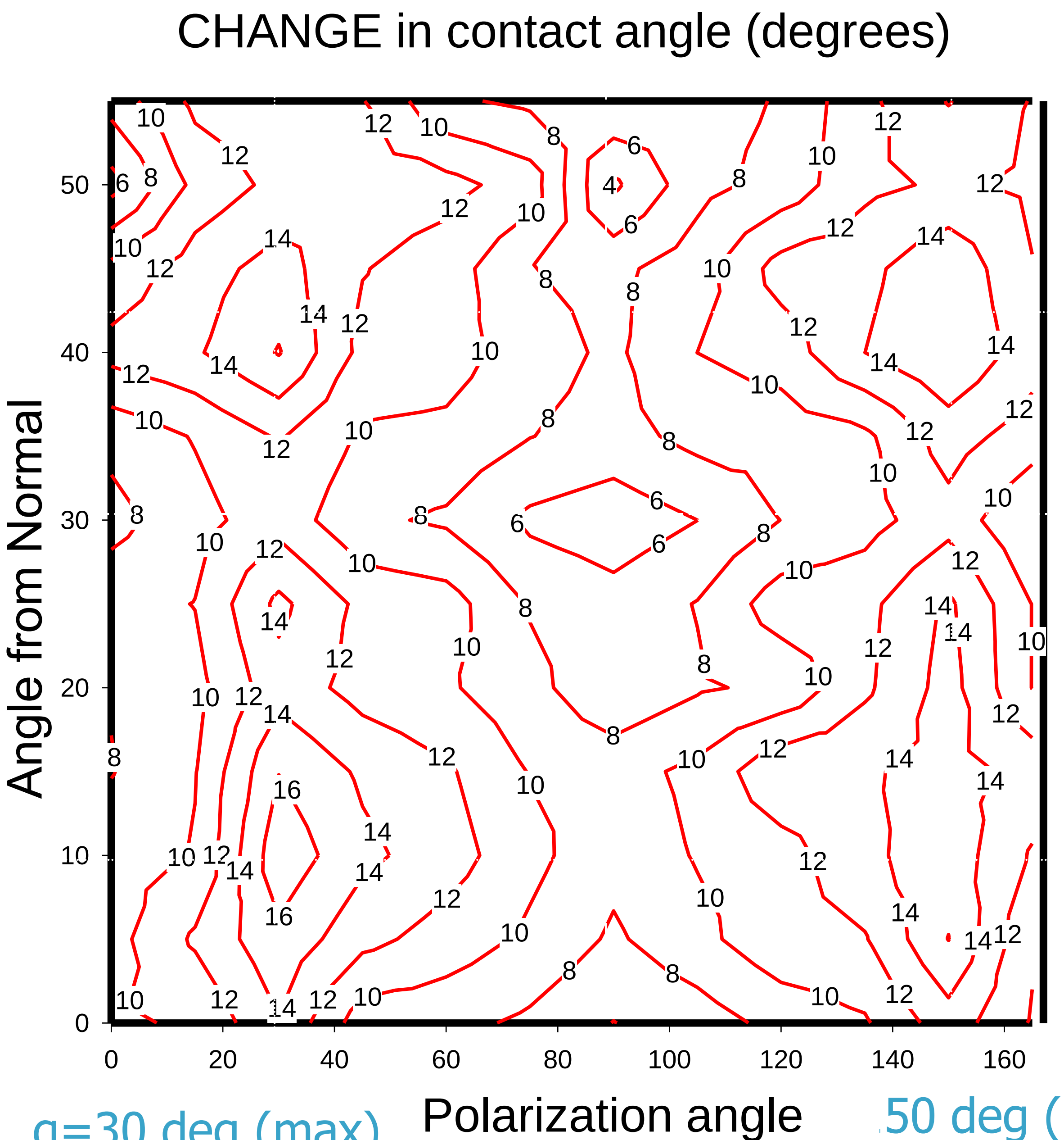




Molecular orientation is probed via birefringence

and: a constant observation is a strong, ubiquitous dependence on both the geometry, polarization:





we observe a strong dependence on the ANGLE of irradiation, and the POLARIZATION

Φ=40-45 deg (max)

Φ=30 deg (min)

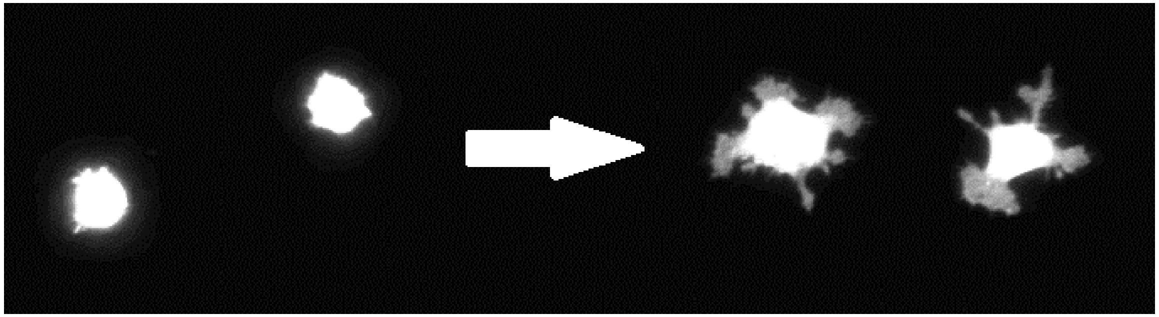
Φ=5-10 deg (max)

α=30 deg (max)

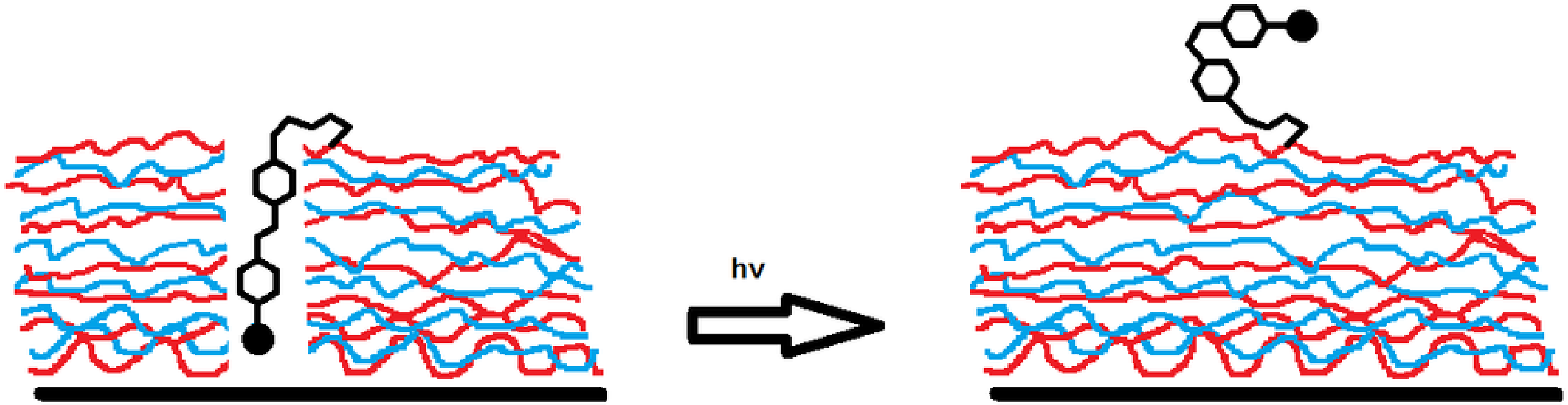
50 deg (max)

α=90 (min)

Results and Mechanism?



So, this in effect is a significant (>40%) increase in size on irradiation. If conditions are chosen not too phylic, not too phobic, but transition.

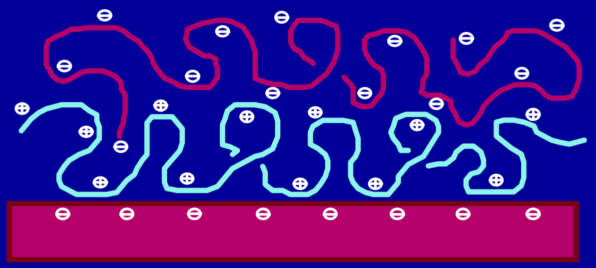


Although mechanism is not fully understood yet, different surface conditions may trigger different adhesion pathways in the cells.

Now the 'sticky' experimental question:

The biocompatible properties of these self-assembled layers depend STRONGLY on the film morphology:.

a) SWELLING, b) ELASTICITY, and c) CHARGE



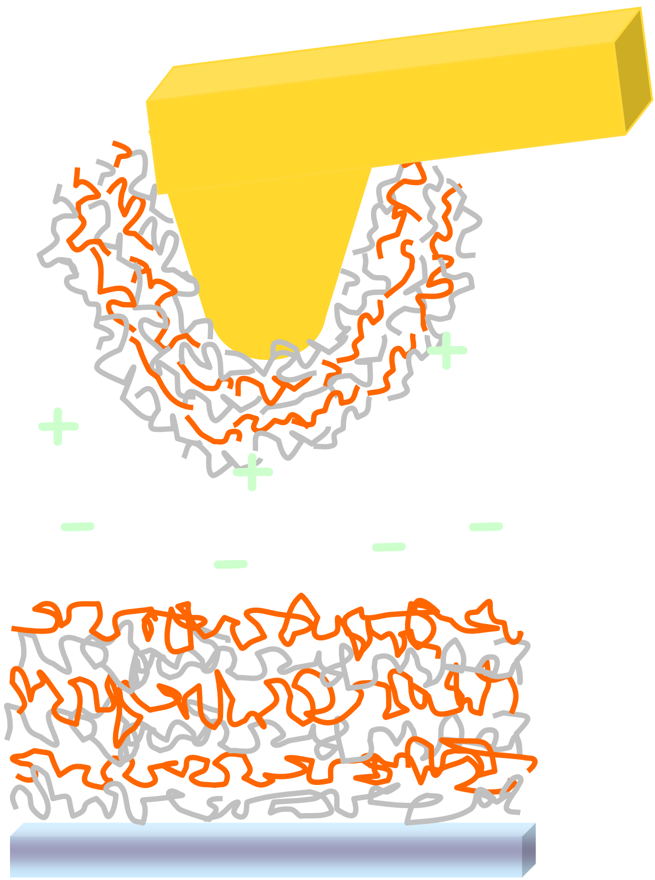
So,

What IS this *in situ*

Layer conformation ?

b) ELASTICITY.

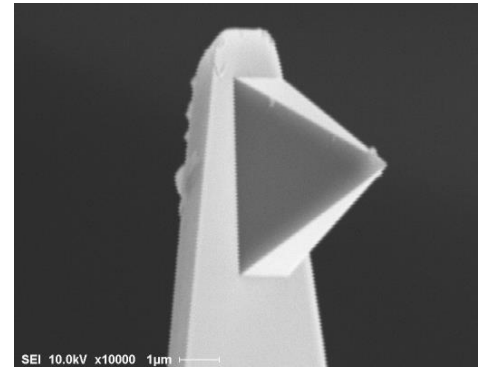
Measuring Modulus, Adhesion in Multilayer Films with AFM :



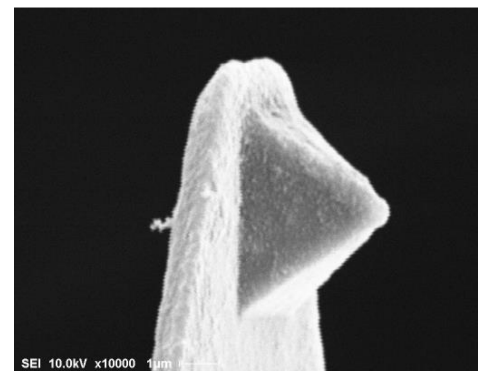
30- multilayer coated tip

indented into 30 multilayers

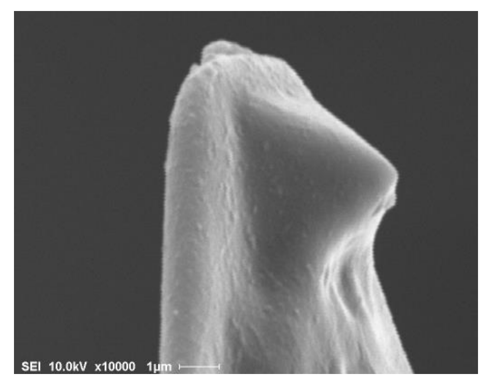
Bare Silicon Nitride
AFM tip



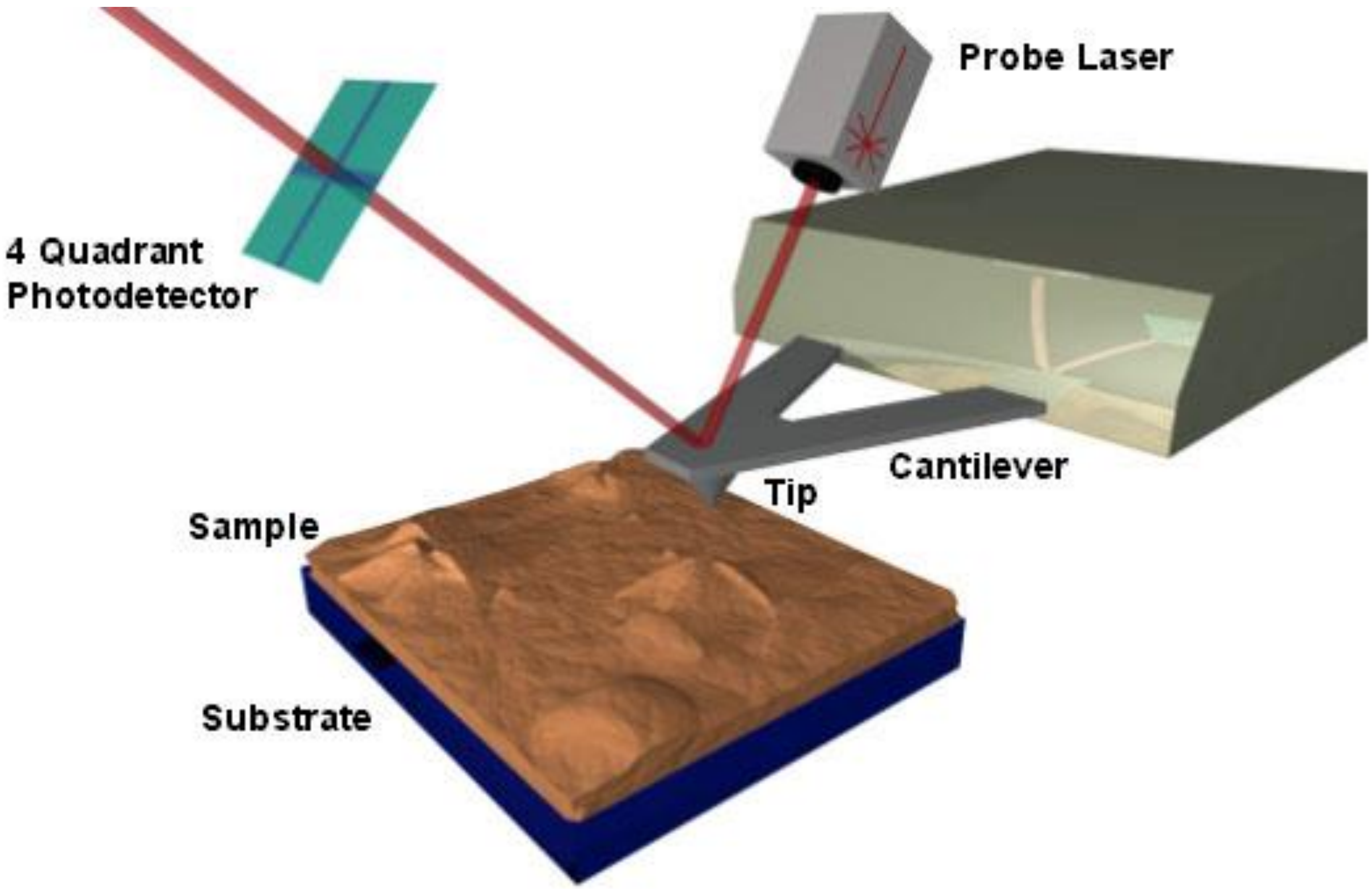
tip coated with thin
layers pH 5



tip coated with
thick layers pH 9



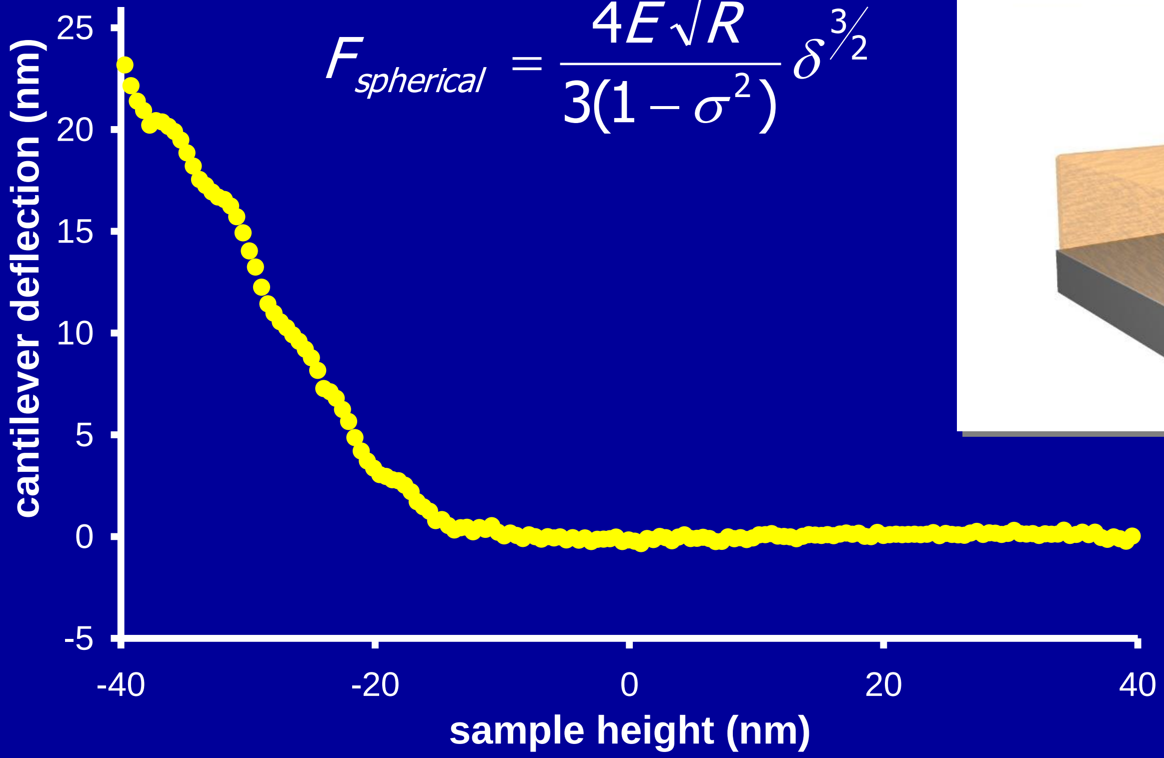
Measuring Modulus, Adhesion in Multilayer Films with AFM, an Atomic Force Microscope, to 'feel a surface' in Nano Newtons

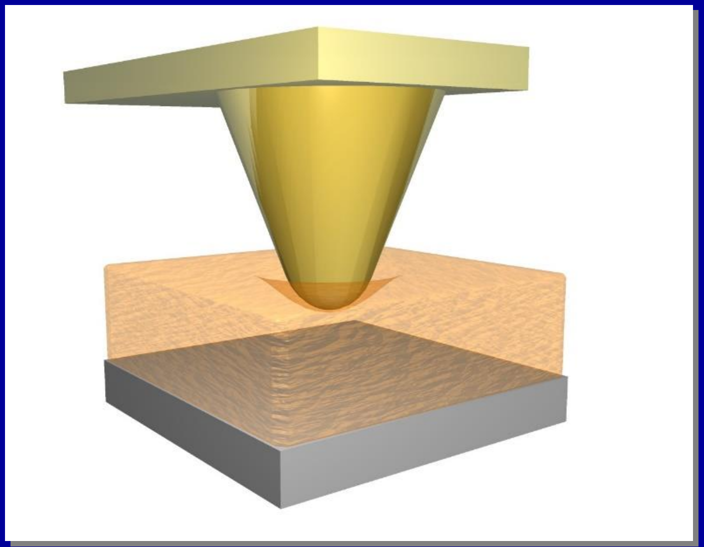


Force-Distance Curves obtained by AFM (O. Mermut)

Elastic Deformation of a sphere touching a flat surface under load (k = 0.12 N/m)

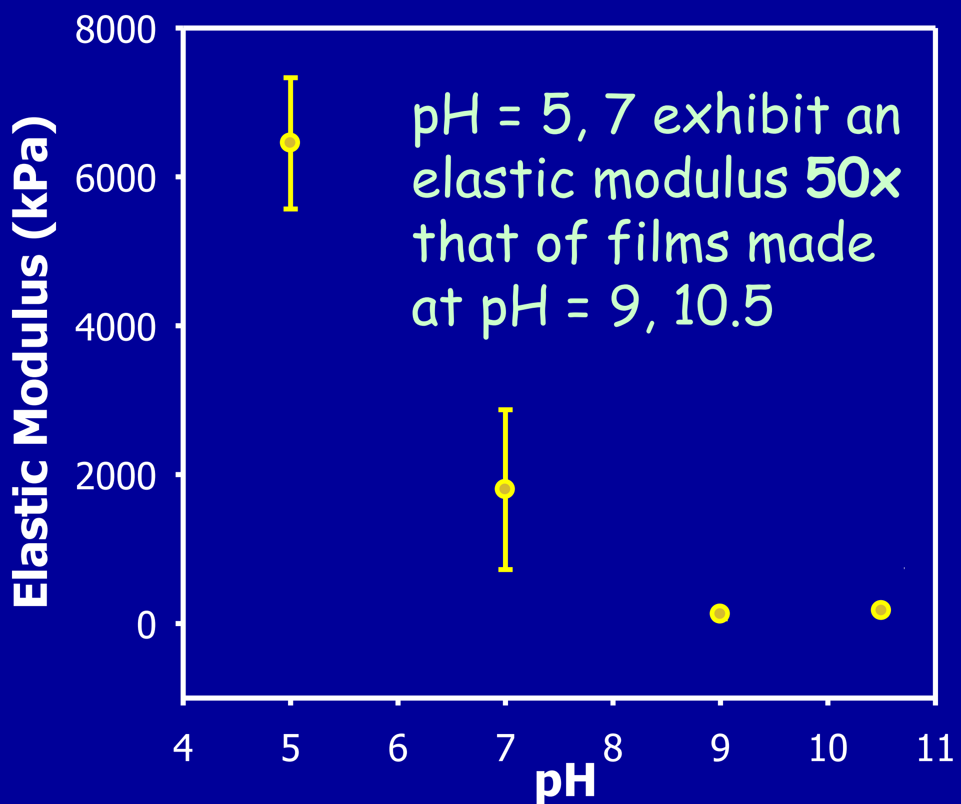
$$F_{spherical} = \frac{4E\sqrt{R}}{3(1-\sigma^2)}\delta^{3/2}$$



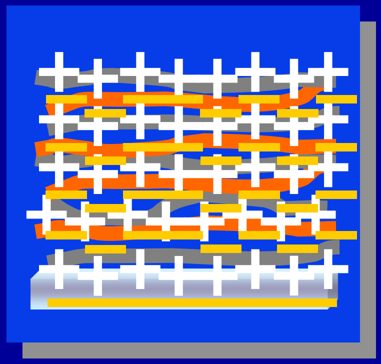


We measure δ. Knowing R (tip radius) and σ (poisson ratio ~ 0.5) we can solve for the Young's Modulus (E), which is related to 'crosslink' density

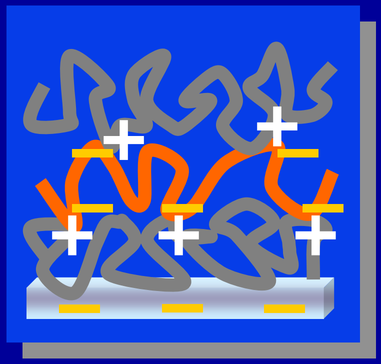
Relative Elasticity of PAH/P-Azo films



assembly
pH = 5, 7

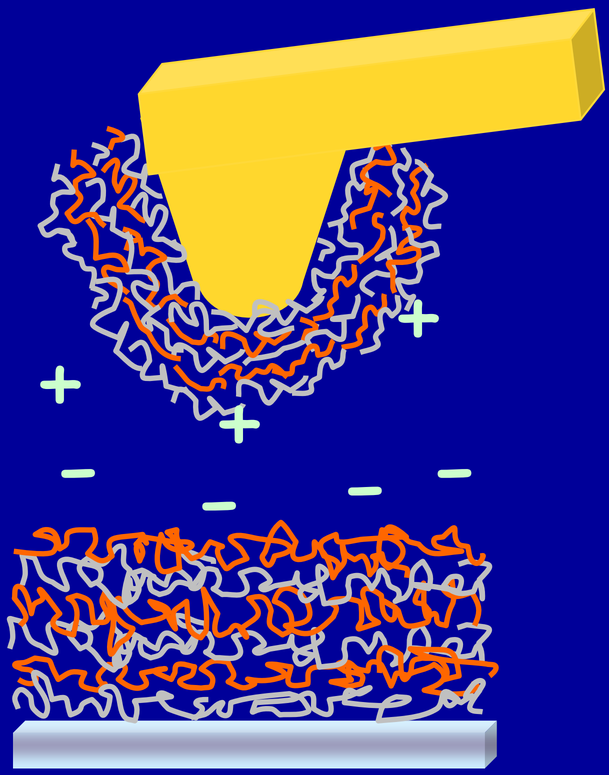


assembly
pH = 9, 10



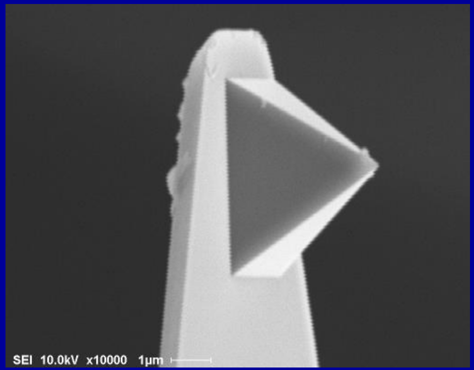
Sample pH	Elastic Modulus, E (kPa)	Crosslink Density [ρ/M_c] in mol/m^3	% Relative Crosslink Density	Relative Loop Length
5	6500 ± 900	870	100	1
7	1800 ± 1100	240	28	4
9	120 ± 60	17	2	50
10.5	170 ± 40	23	3	33

Measuring Adhesion in Multilayer Films

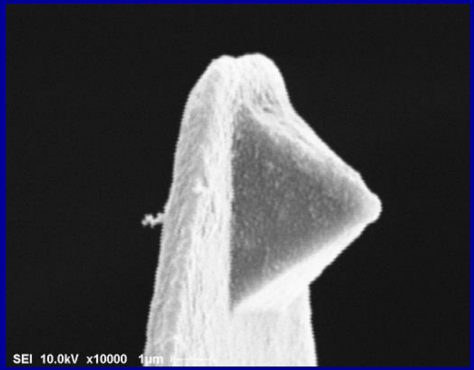


- PAH/P-Azo coated tip indented into PAH/P-Azo layers on glass (400nm)

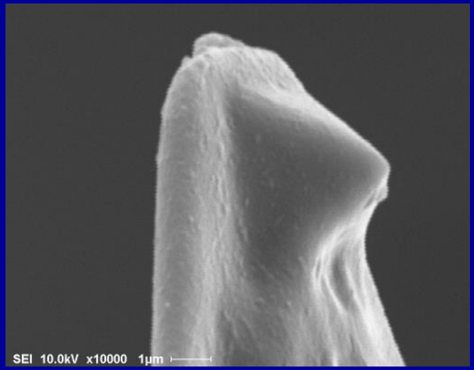
Bare Silicon Nitride AFM tip



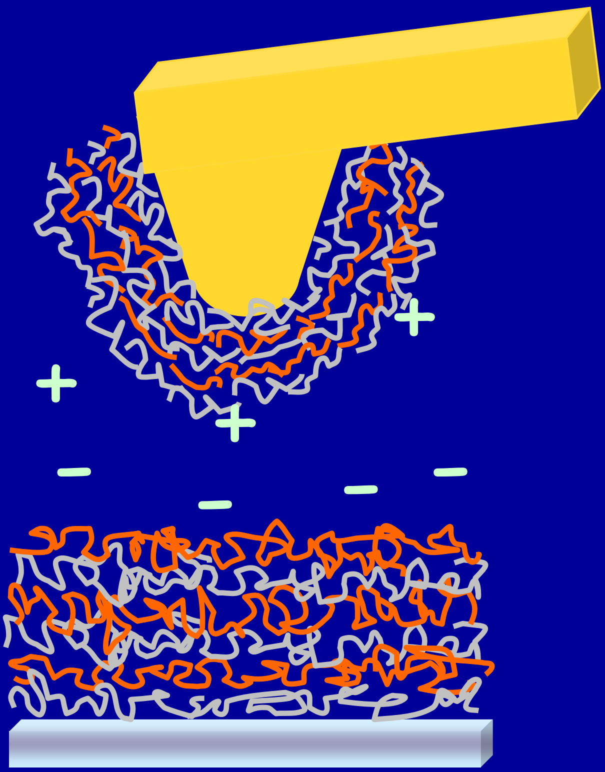
tip coated with thin layers pH 5

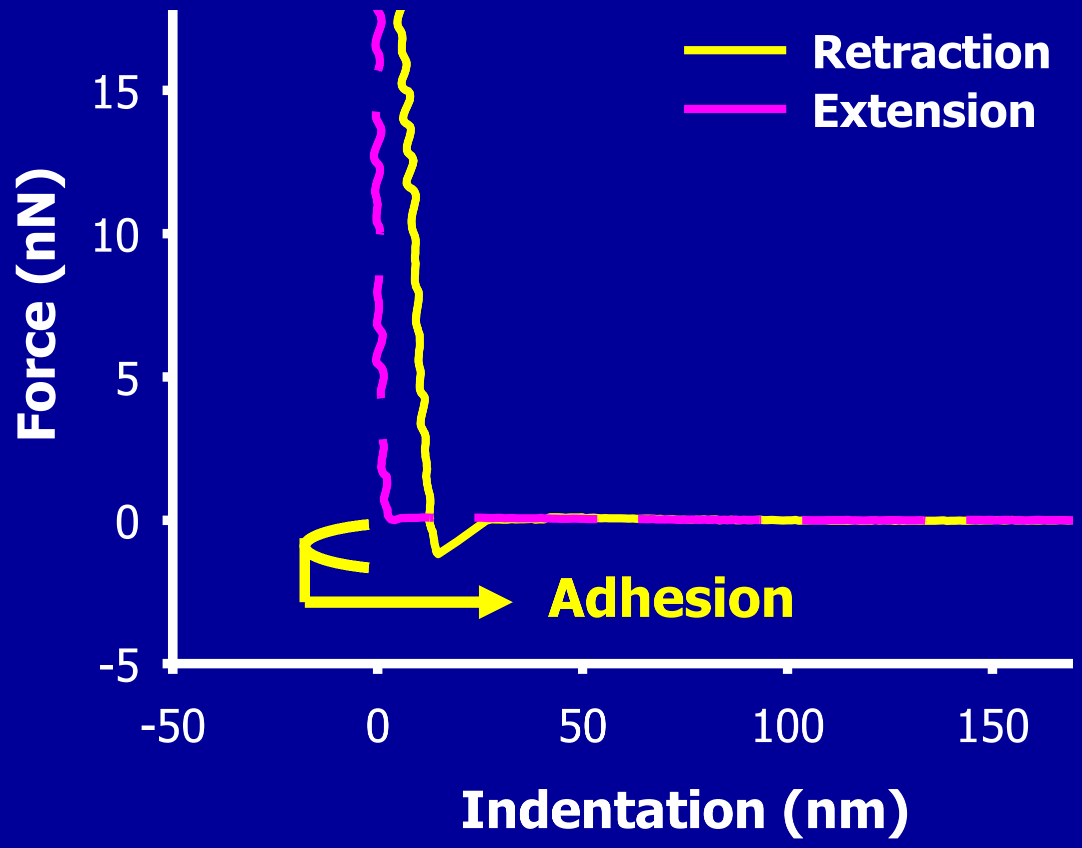


tip coated with thick layers pH 9



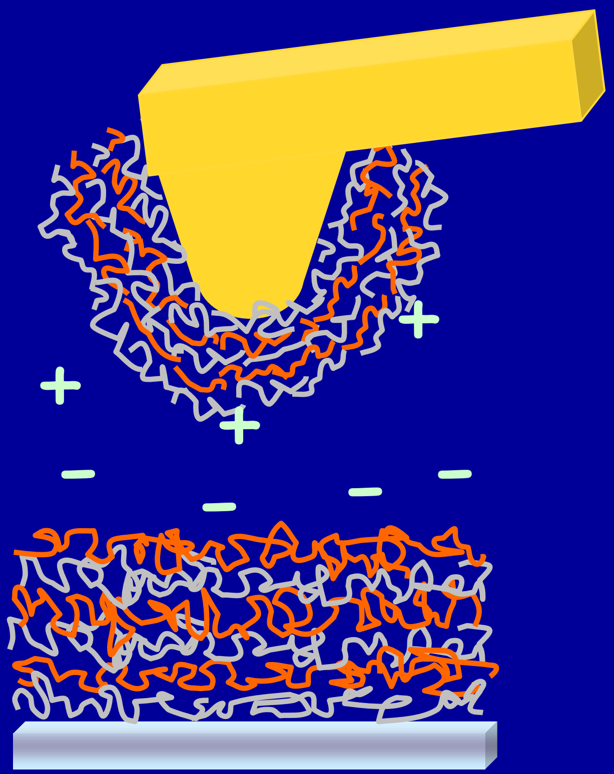
Measuring Adhesion in Multilayer Films



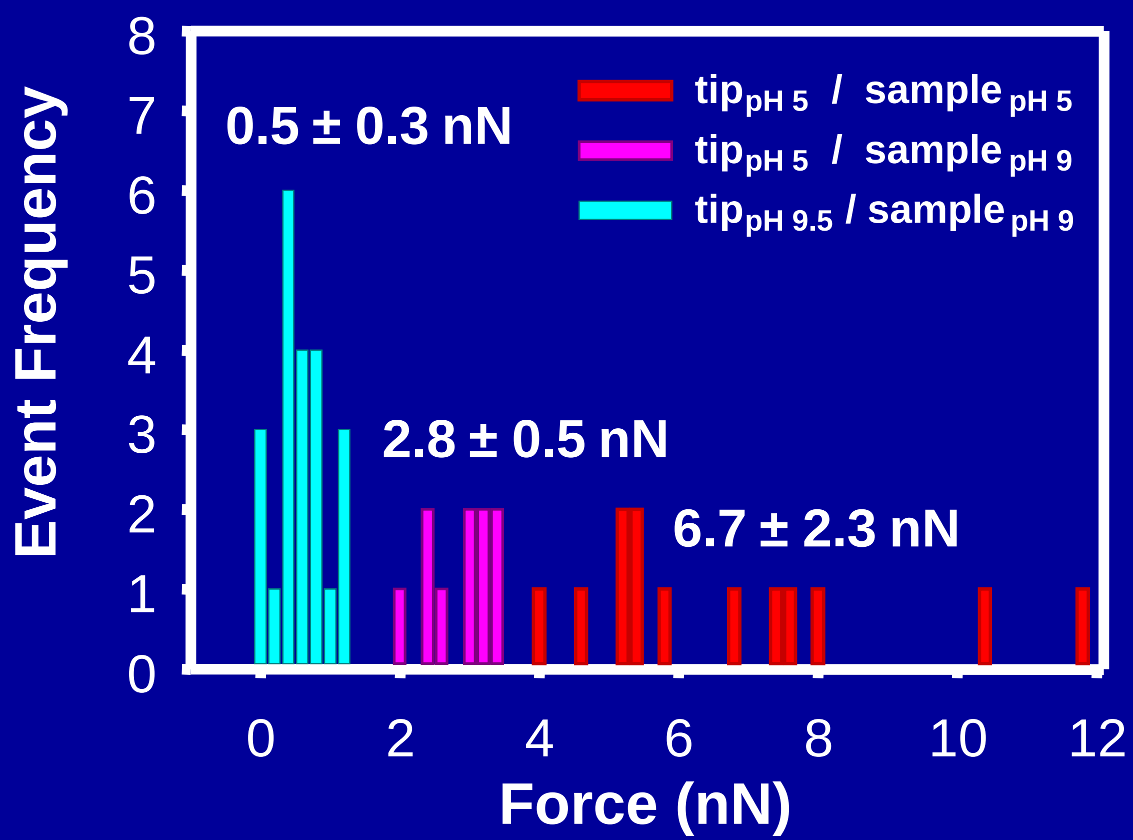


• PAH/P-Azo coated tip indented into PAH/P-Azo layers on glass (400nm)

Measuring Adhesion in Multilayer Films



- PAH/P-Azo coated tip indented into PAH/P-Azo layers on glass (400nm)



So,

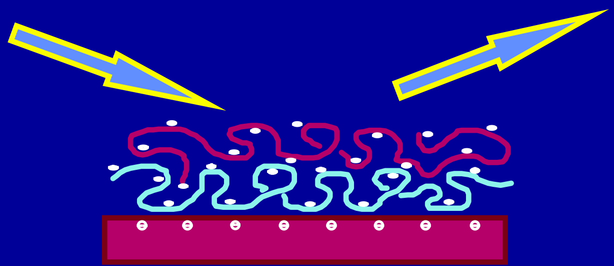
What IS this *in situ*

Layer conformation ?

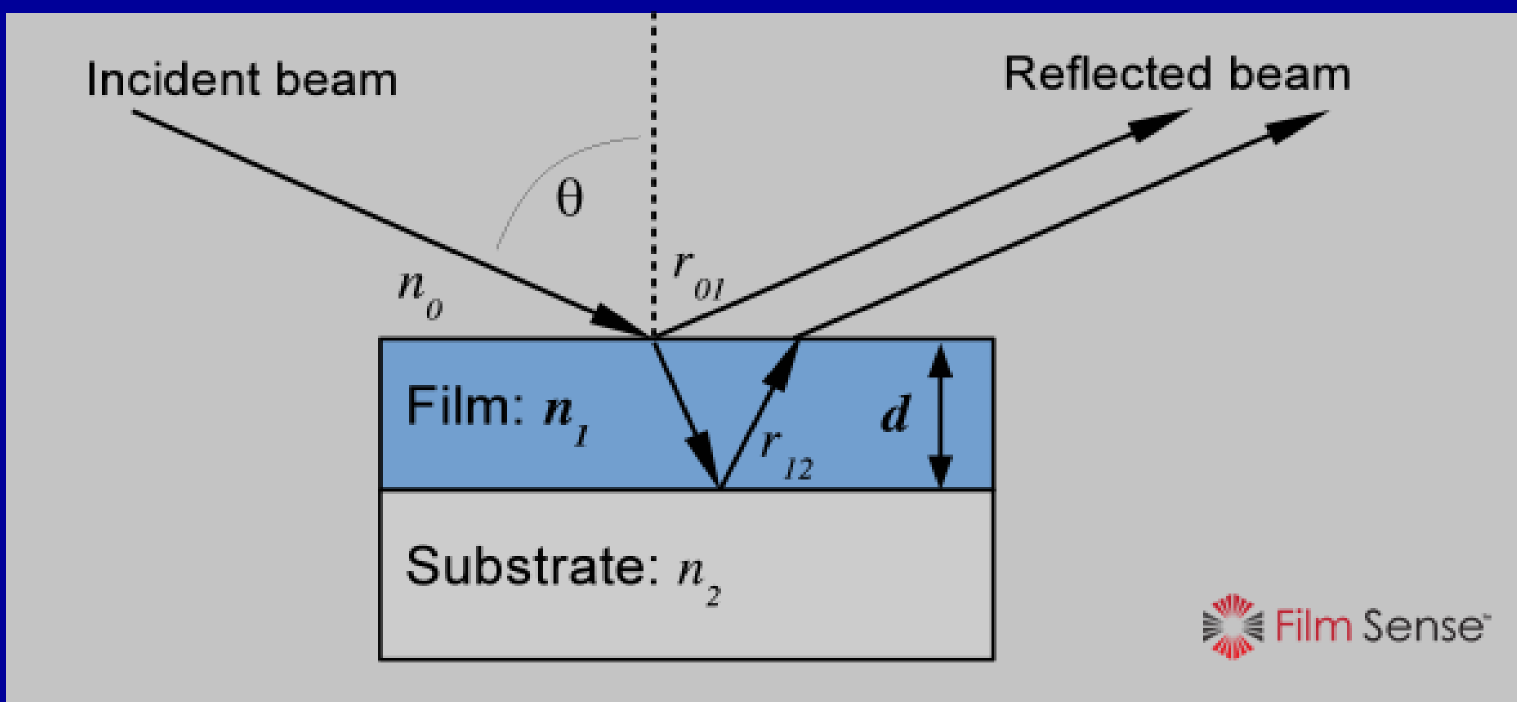
a) SWELLING.

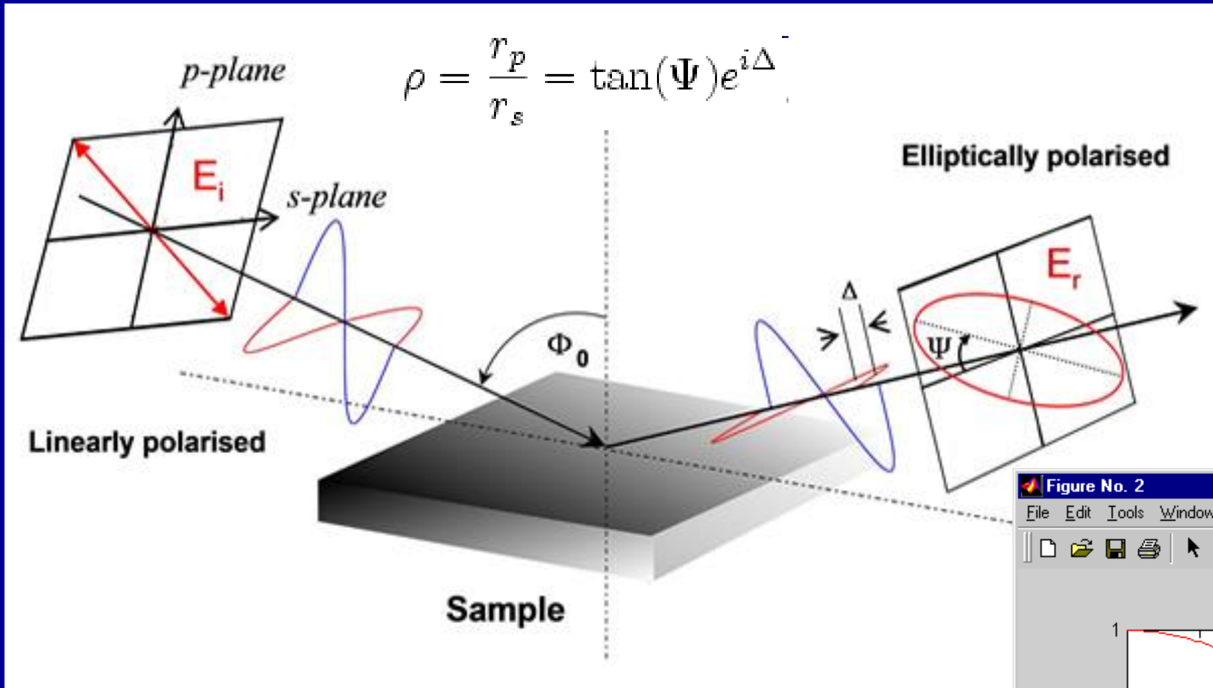
How WET ?   The Water Content…

Using *in situ* ellipsometry to measure layer thickness :



dry sample




$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$
p-plane
s-plane
E_i
Elliptically polarised
E_r
Δ
Ψ
Φ_0
Linearly polarised
Sample

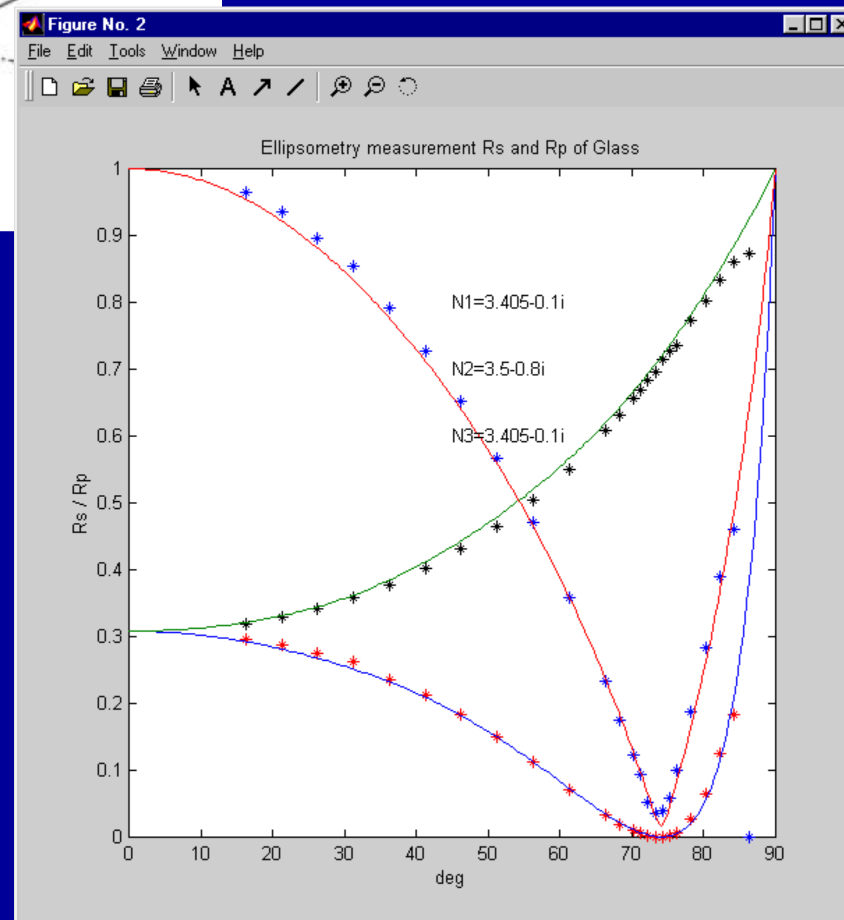
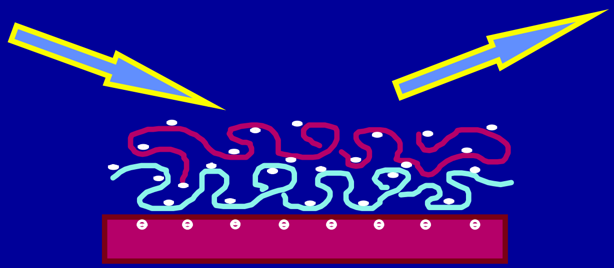
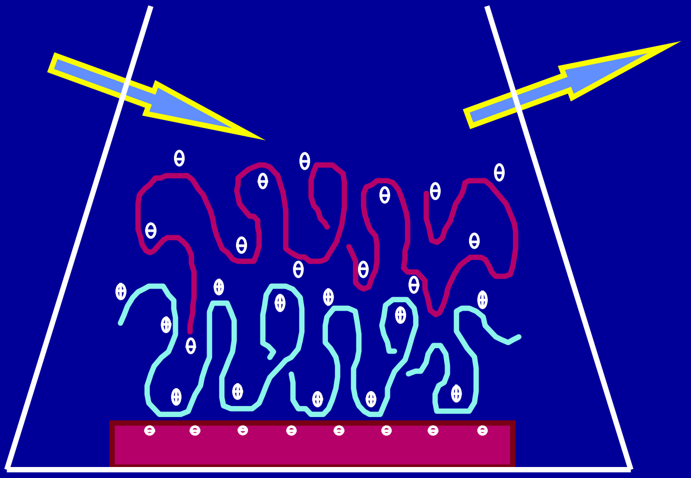


Figure No. 2
File Edit Tools Window Help
Ellipsometry measurement Rs and Rp of Glass
N1=3.405-0.1i
N2=3.5-0.8i
N3=3.405-0.1i
Rs / Rp
deg
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
0 10 20 30 40 50 60 70 80 90

Using *in situ* ellipsometry to measure layer thickness :



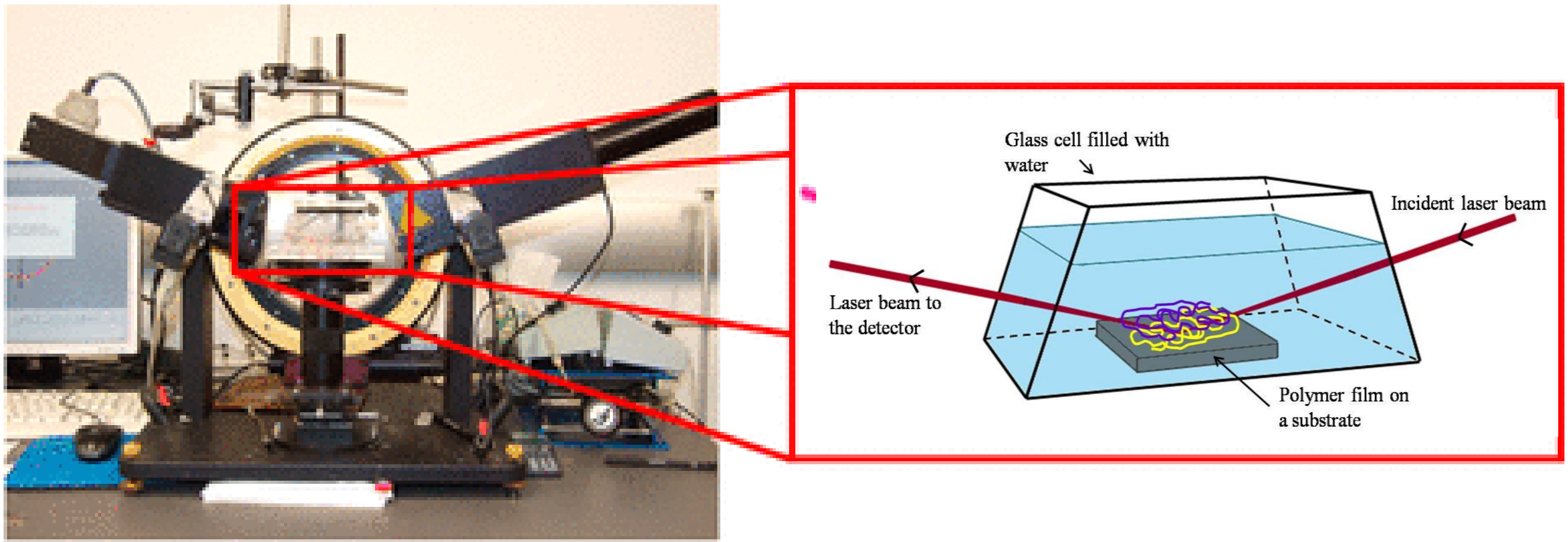
dry sample



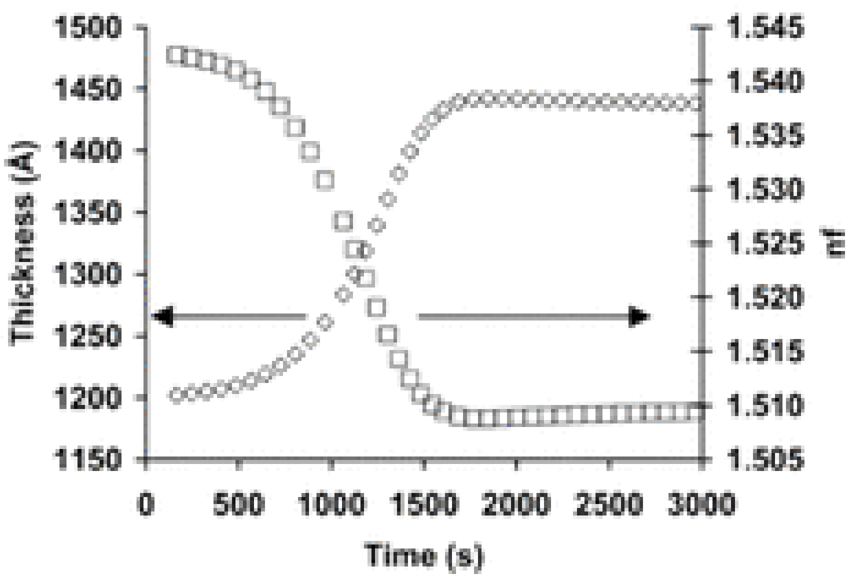
sample in liquid cell

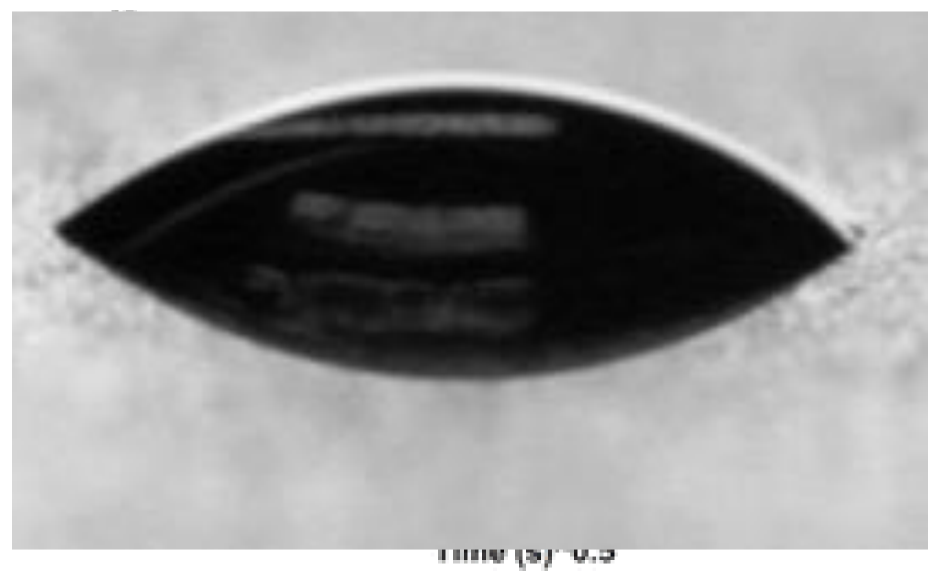
Water content, surface E of wet multilayers

A

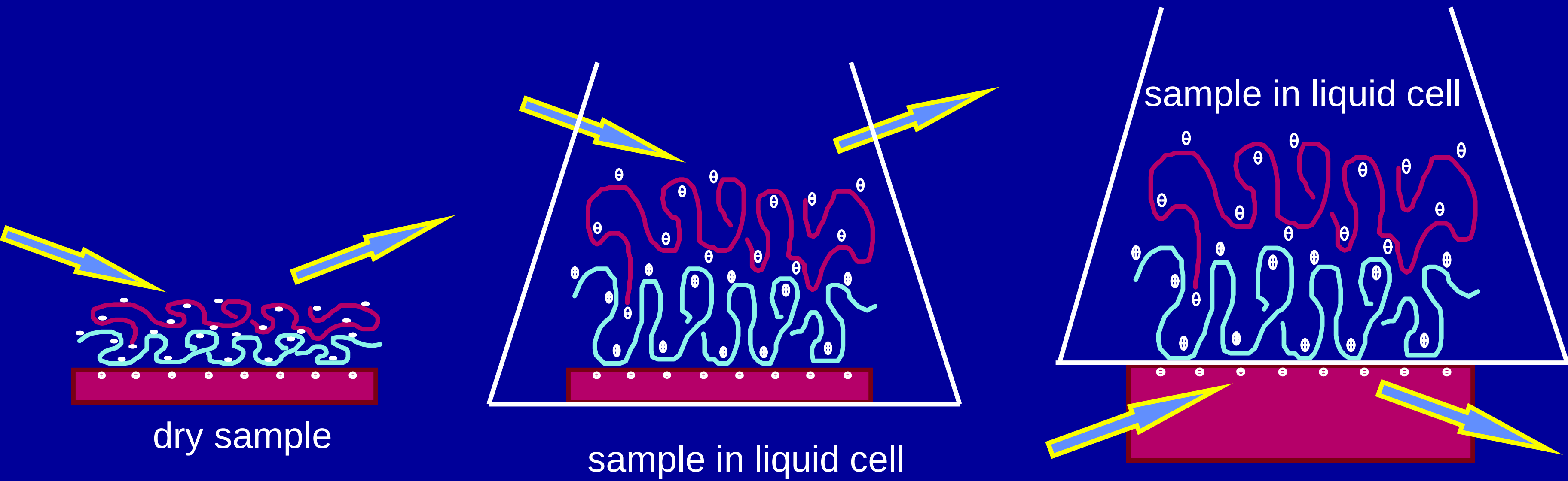


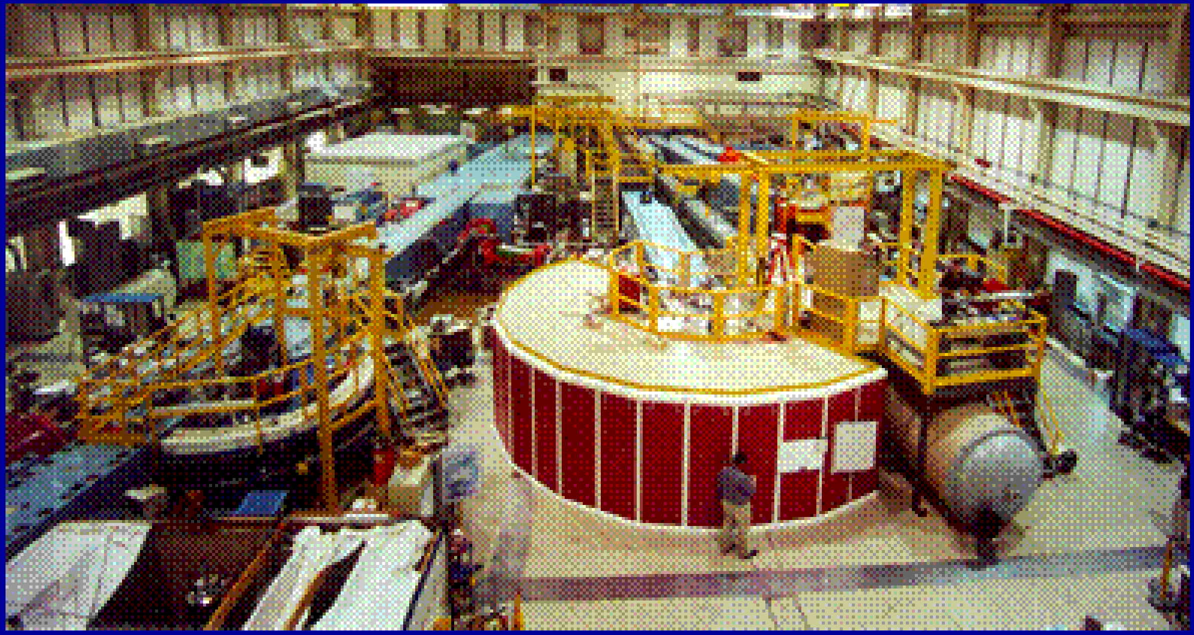
B





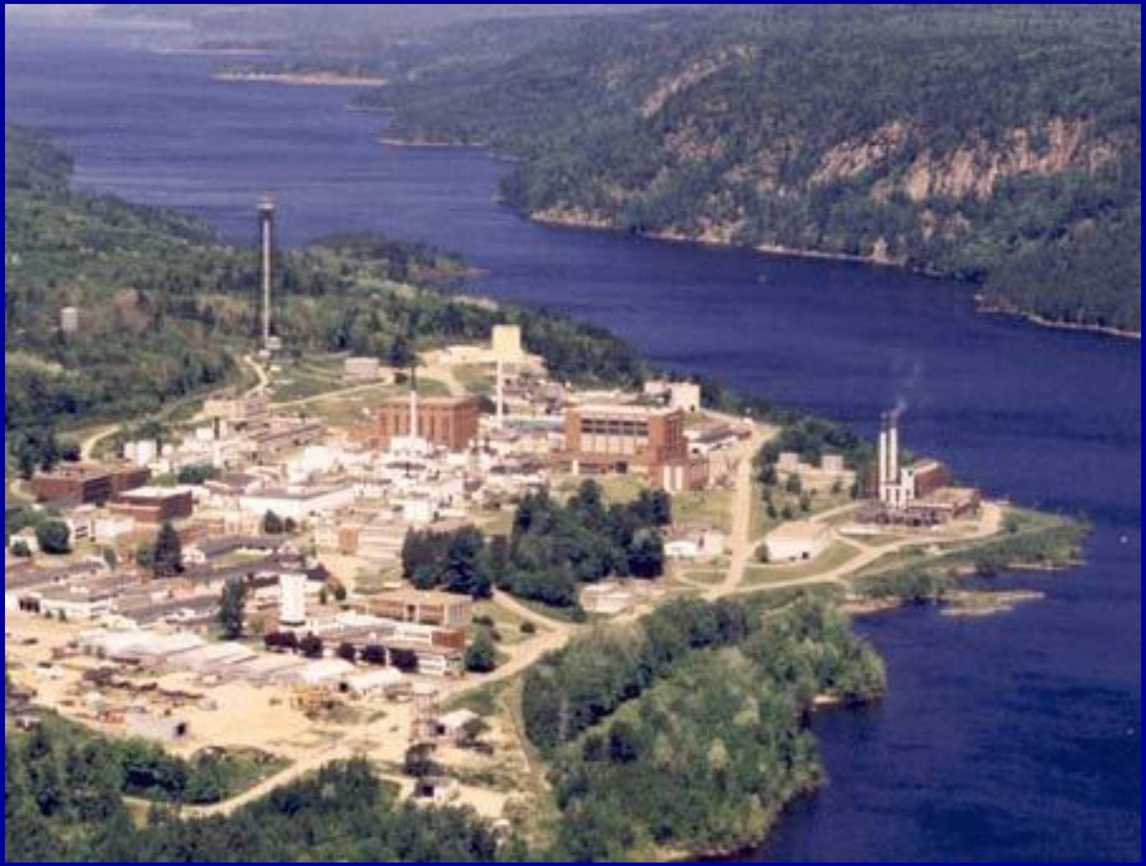
Ellipsometry can only measure *average* density however, but, we can use variable angle neutron reflectivity :

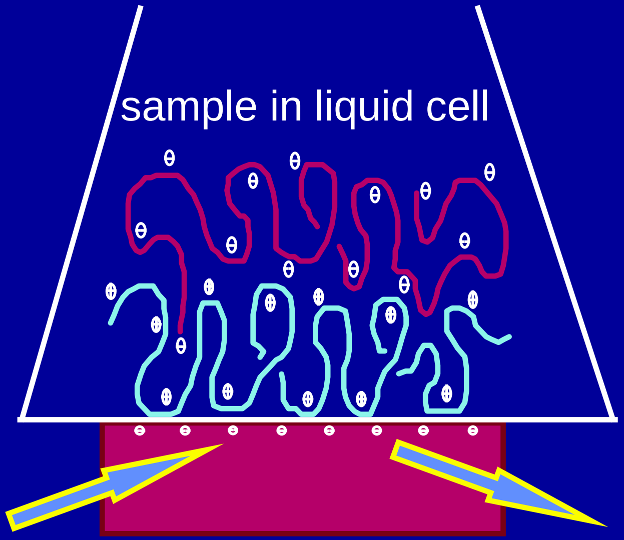




thermal neutrons wavelength 2.4Å. Measure reflected intensity as incident angle is increased.

Ellipsometry can only measure *average* density however, but, we can use variable angle neutron reflectivity :

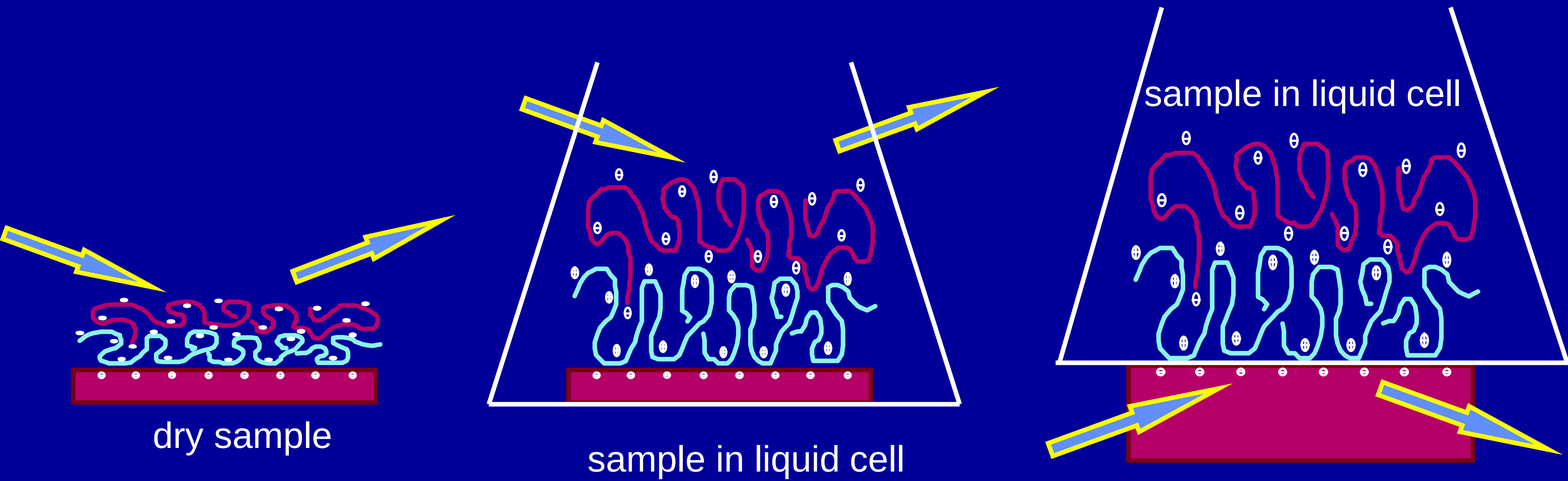




thermal neutrons wavelength 2.4Å. Measure reflected intensity as incident angle is increased.

Canadian Neutron Beam Centre, Chalk River, Canada. new $10M line '09

Ellipsometry can only measure *average* density however, but, we can use variable angle neutron reflectivity :



"Variable temperature, 0-100% humidity, and liquid neutron reflectometry sample cell for biomimetic materials."

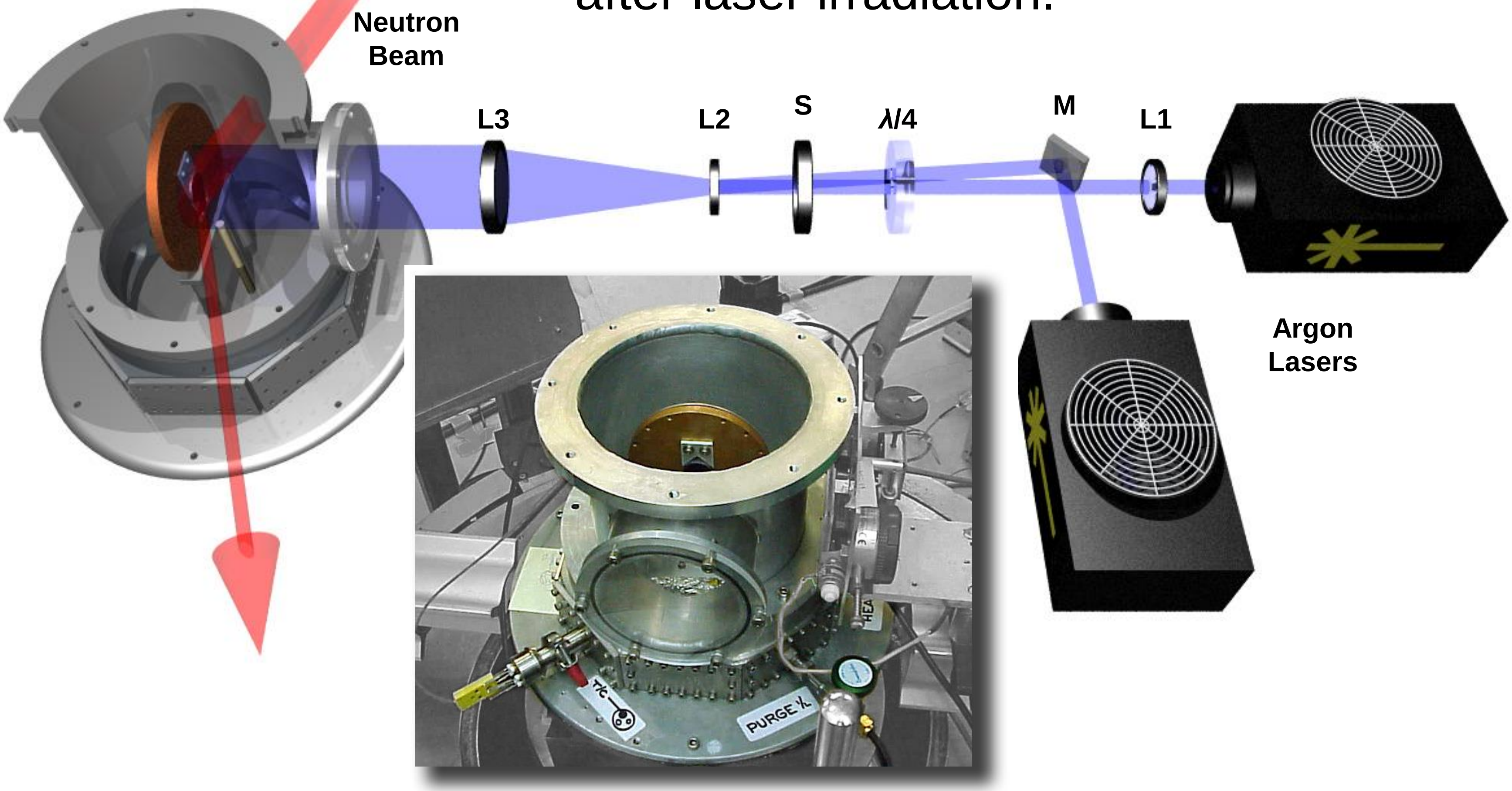
Review of Scientific Instruments **2015**

Harroun, Fritzsche, Watson, Yager, Tanchak, Barrett, and Katsaras.

Now use neutrons wavelength 2.37Å. To be able to measure the water and ion distribution

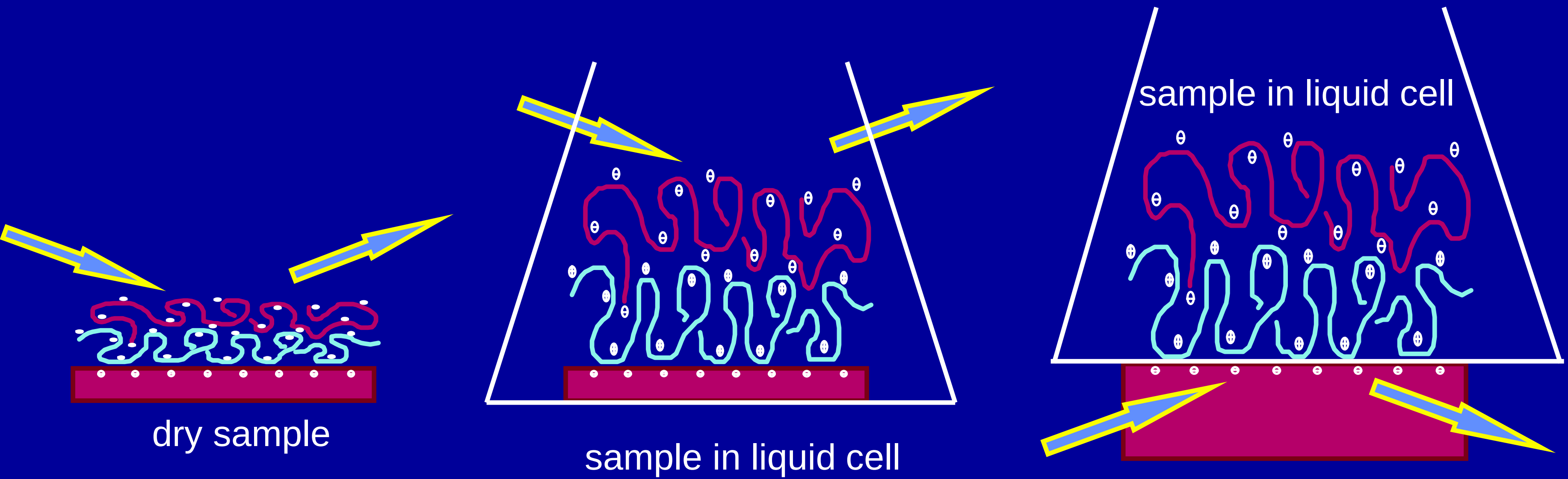
Neutron Reflectivity

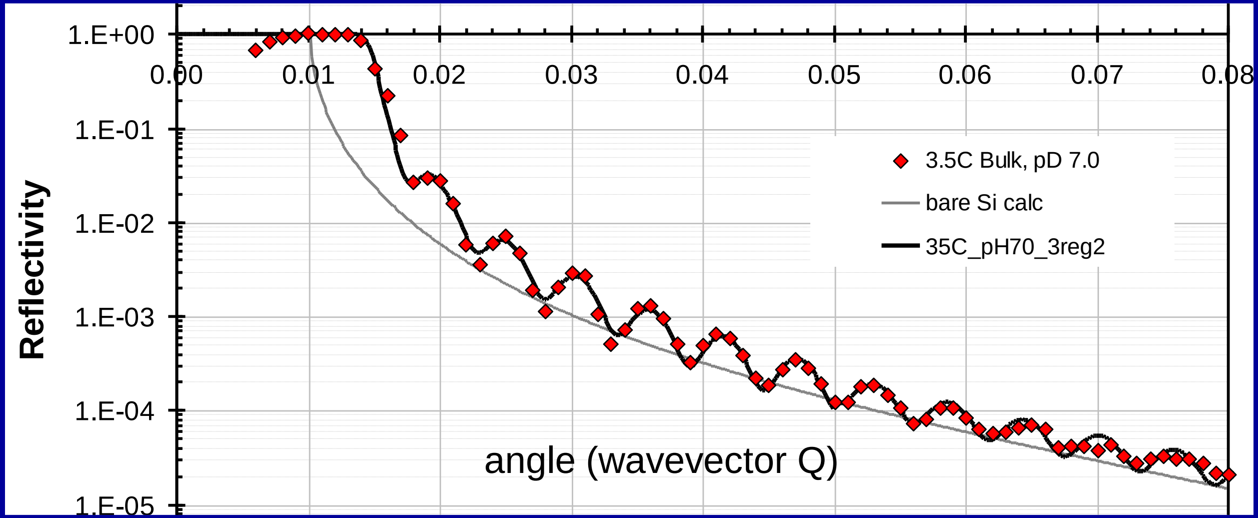
•Neutron reflectivity was measured before, during, and after laser irradiation.



Yager, Tanchak, Barrett, Watson, Fritzsche: PATENT, *Review of Scientific Instruments*

Ellipsometry can only measure *average* density however, but, we can use variable angle neutron reflectivity :

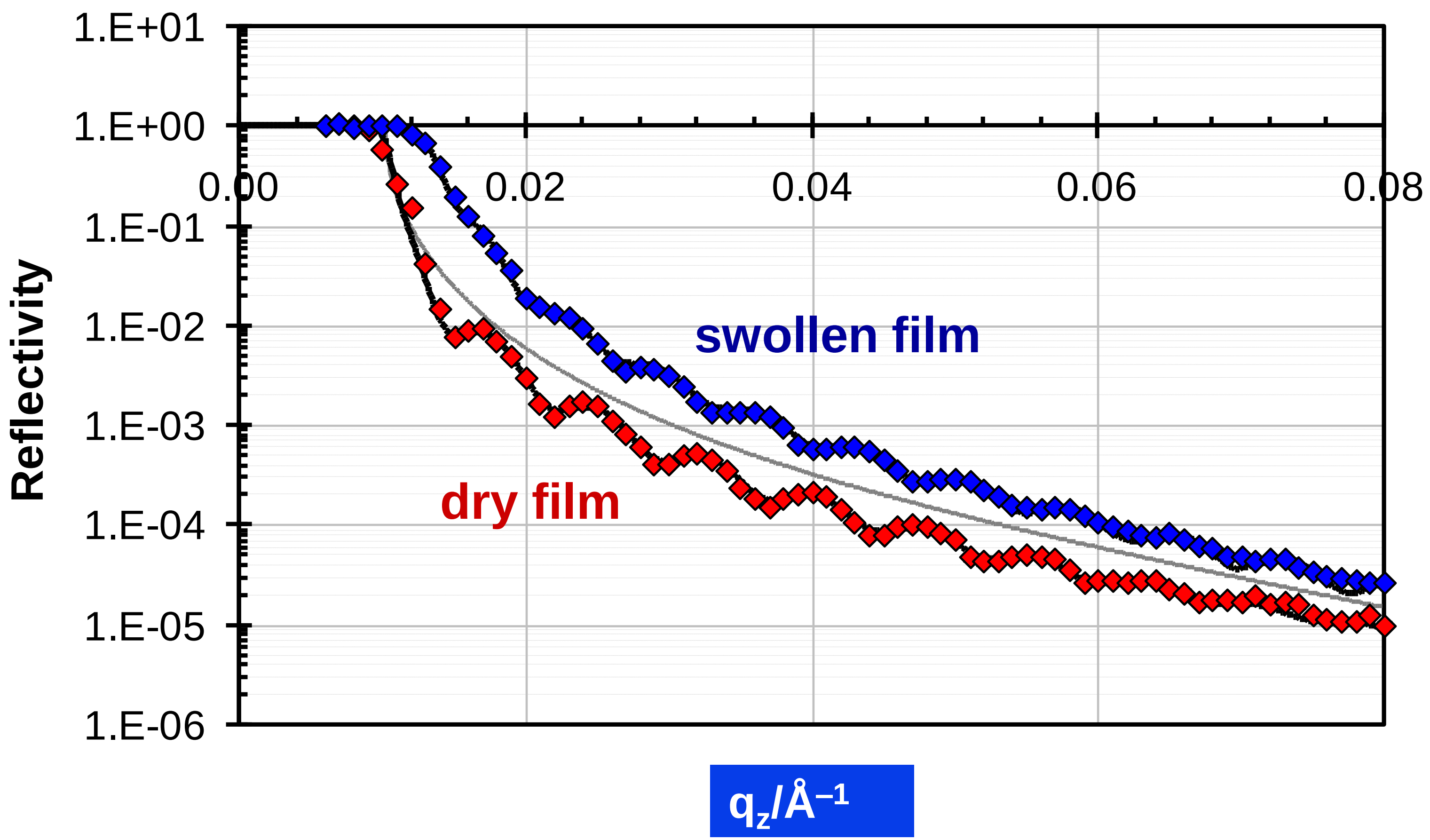


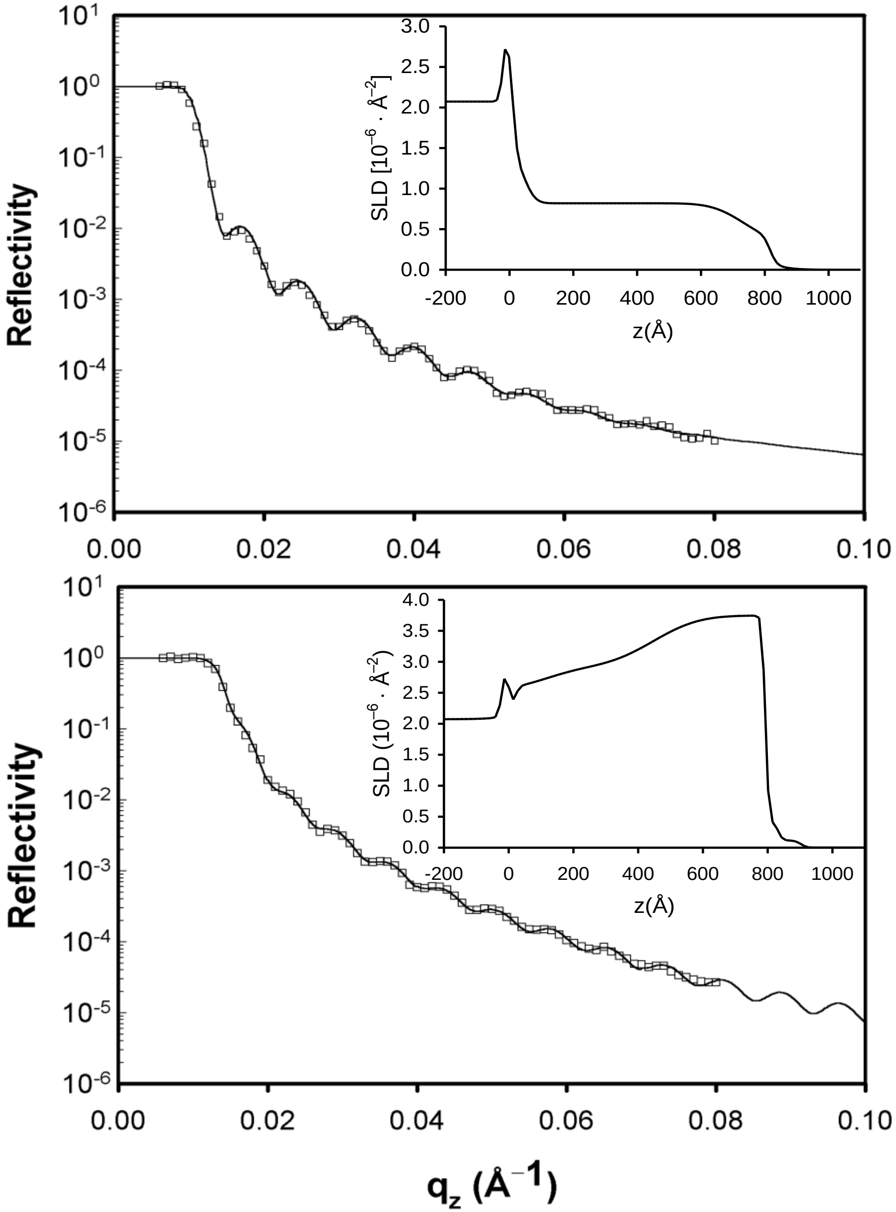


Now use neutrons wavelength 2.4Å. Measure reflected intensity as incident angle is increased.

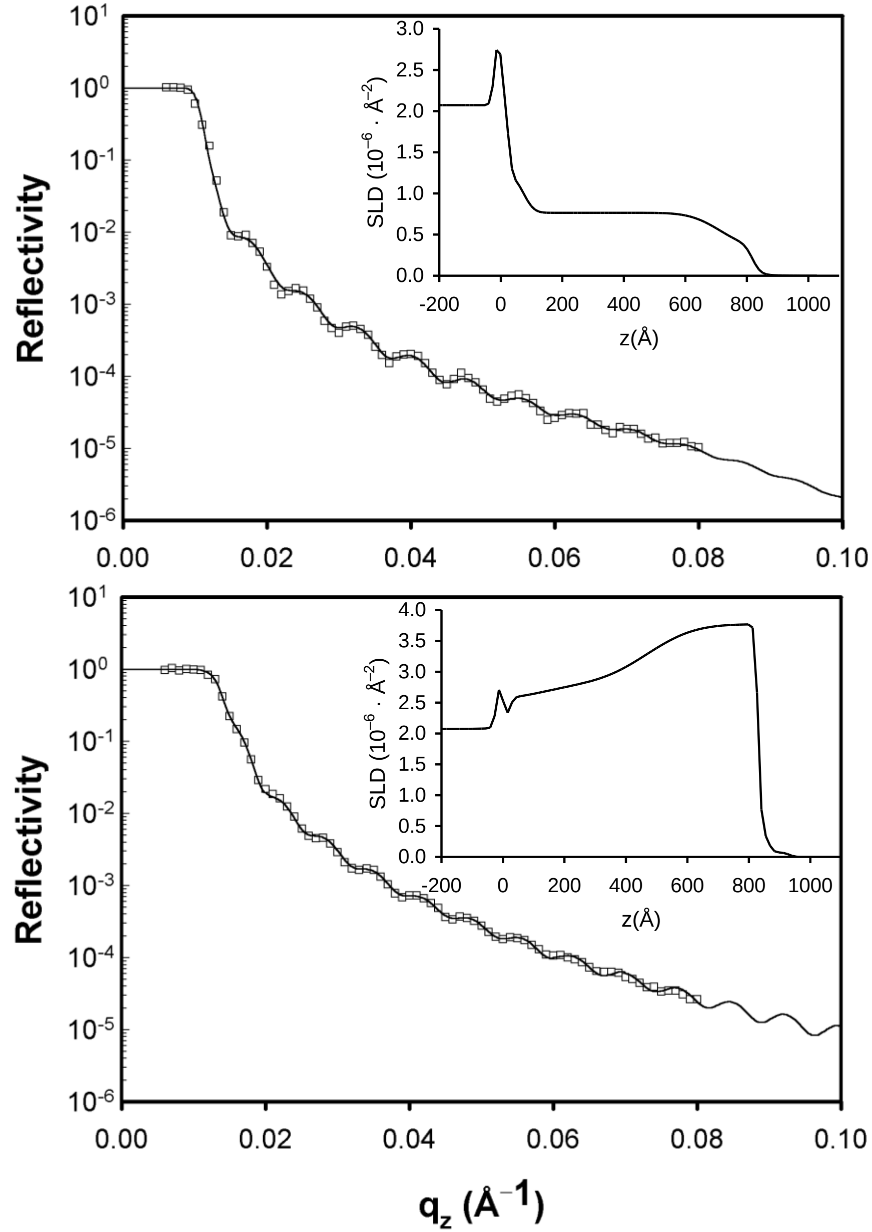
We can now observe a gradient polymer swelling profile (after fitting):

Humidity-Swollen Multilayer





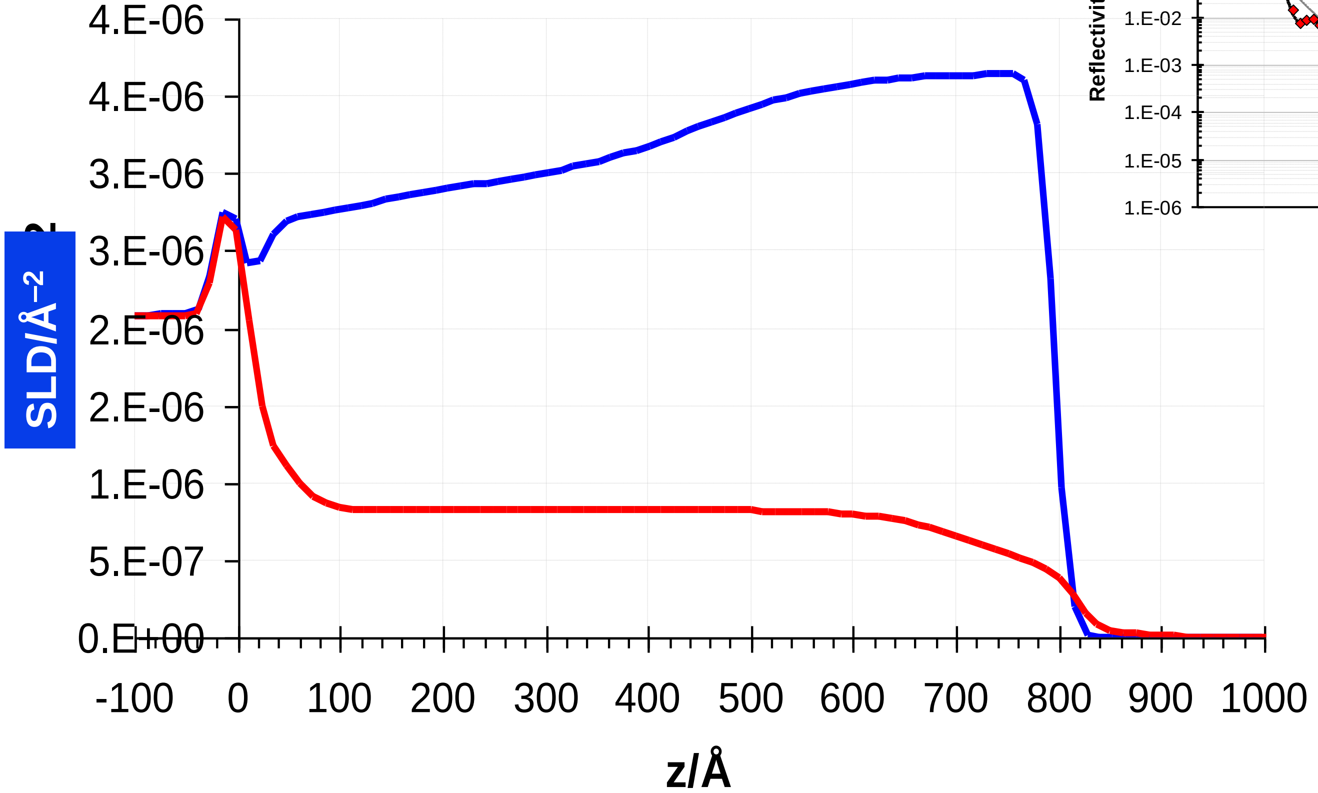
Dry (top), 10% RH D_2O (bottom)

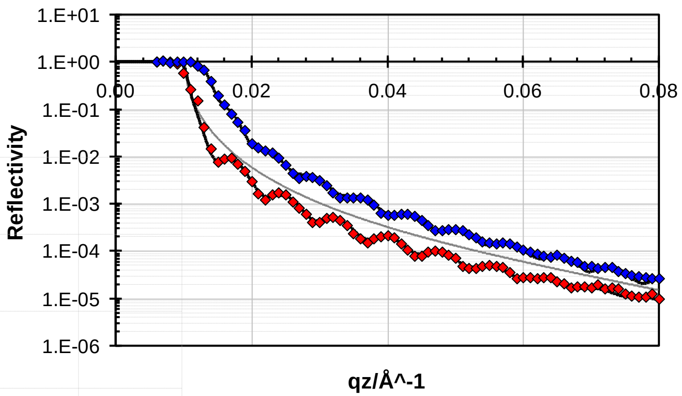


10% RH mix (top), 40% RH D_2O

Humidity-Swollen Multilayer

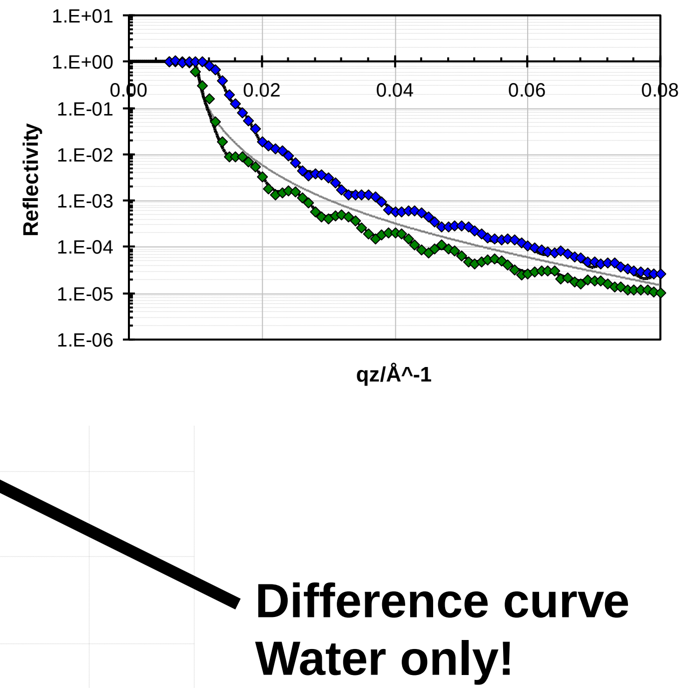
- decrease in film roughness
- Water contribution is greater on top

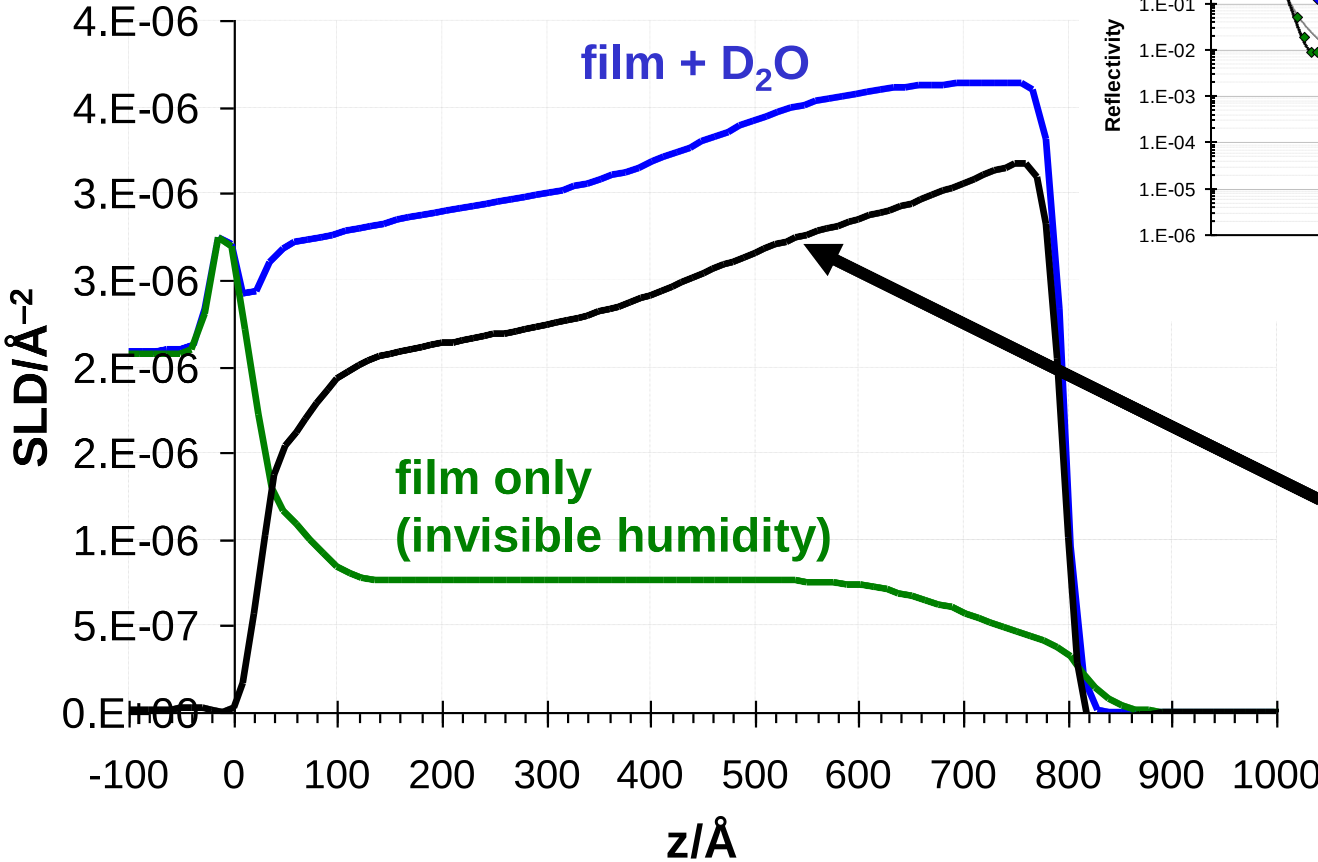




"Invisible" Humidity

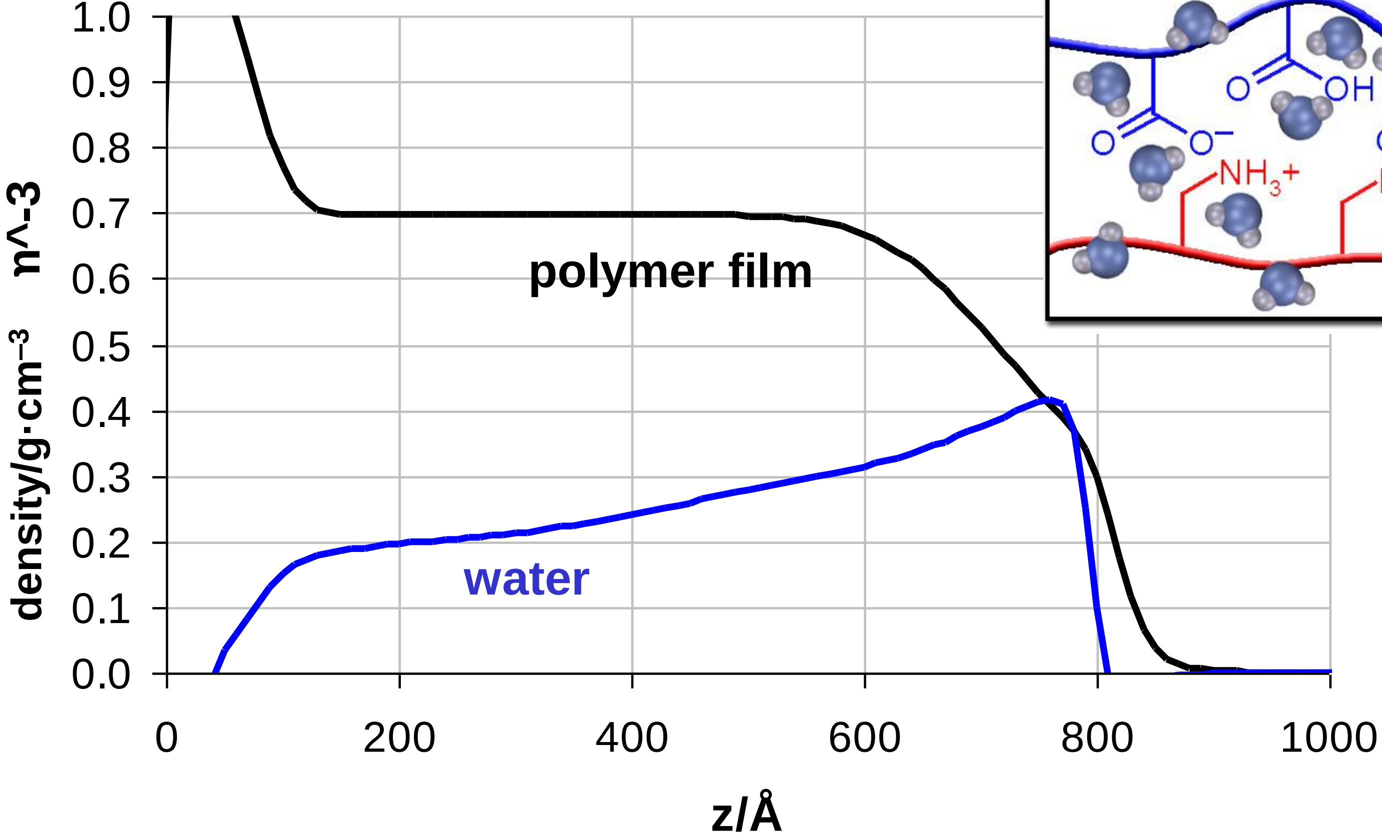
- A mix of 92:8 $H_2O:D_2O$ has SLD = 0.00 ("invisible"), allowing deconvolution of film and water SLD
- Water localized to surface

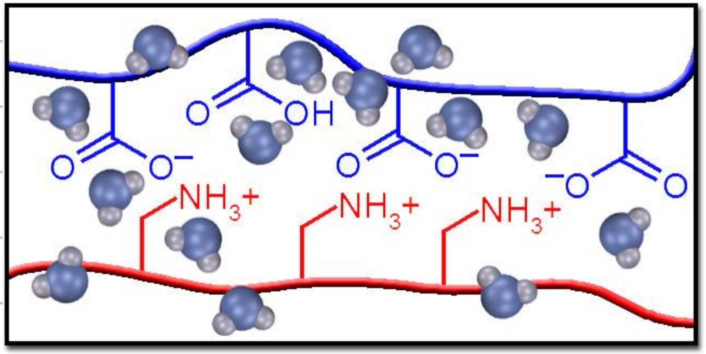




Density Distribution

- By assuming a stoichiometry densities is calculated
- Water localized to surface





~1000 Å³

Tanchak, Yager, Fritzsche, Harroun, Katsaras, Barrett *Langmuir* **2010**

So,

What IS this *in situ*

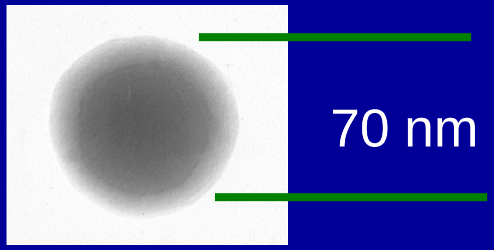
Layer conformation ?

c) CHARGE.

(We're going to layer onto nanoparticles, which we can then stuff inside the spinner of a solid state NMR)

We can try to measure the ionic *surface* charge :

by layering onto Si nanoparticles

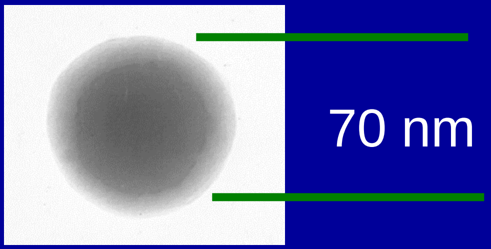


with repeated washing, drying

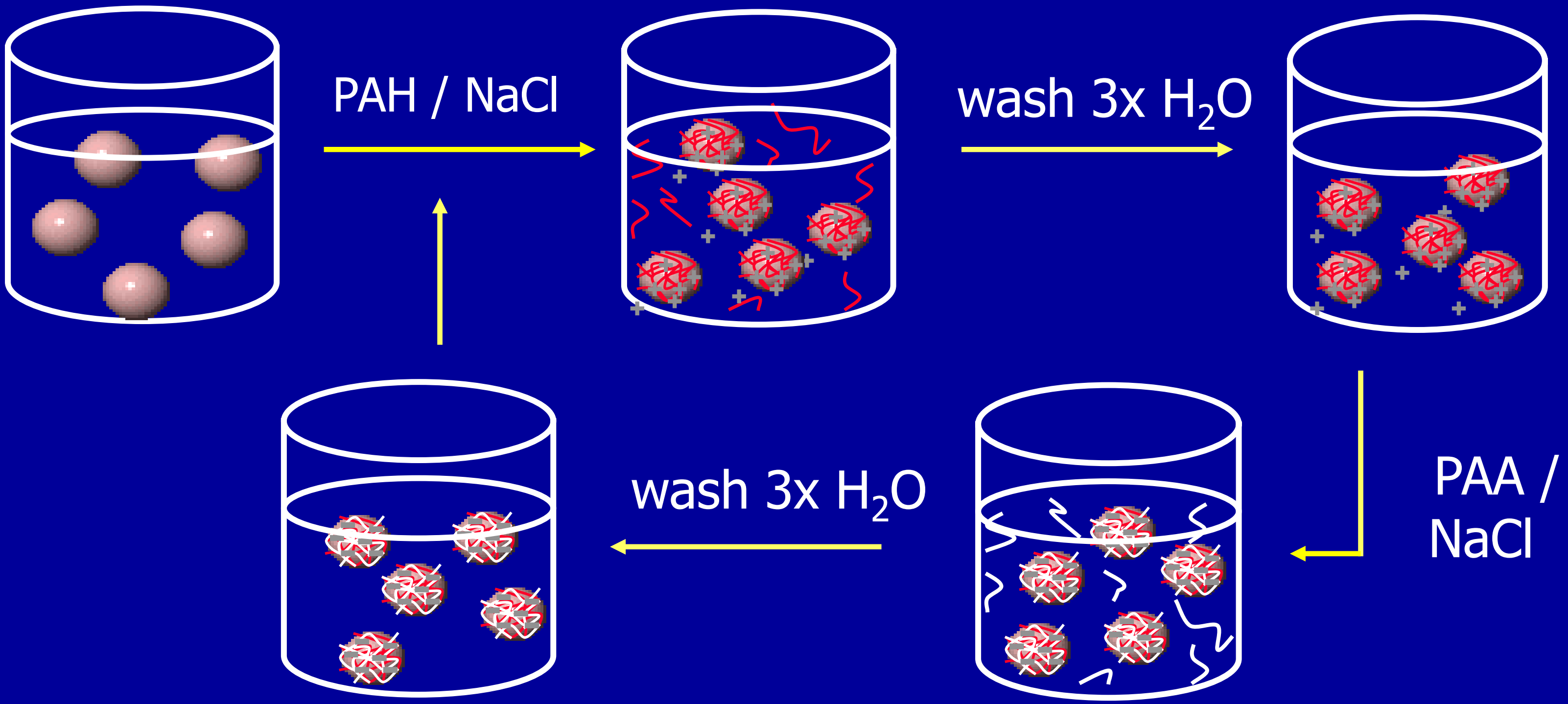
surfacechar

We can try to measure the ionic *surface* charge :

by layering onto Si nanoparticles



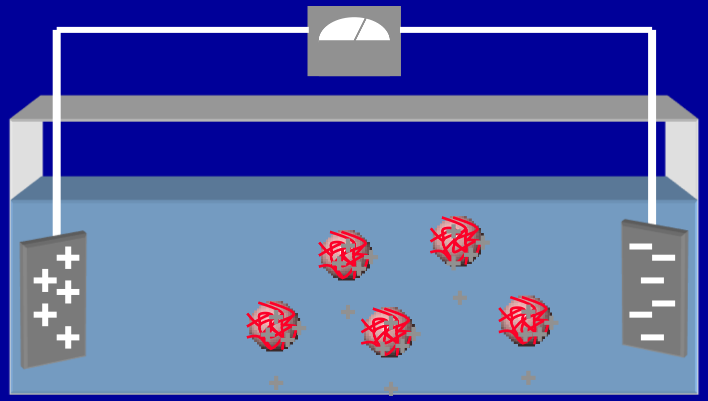
with repeated washing, drying



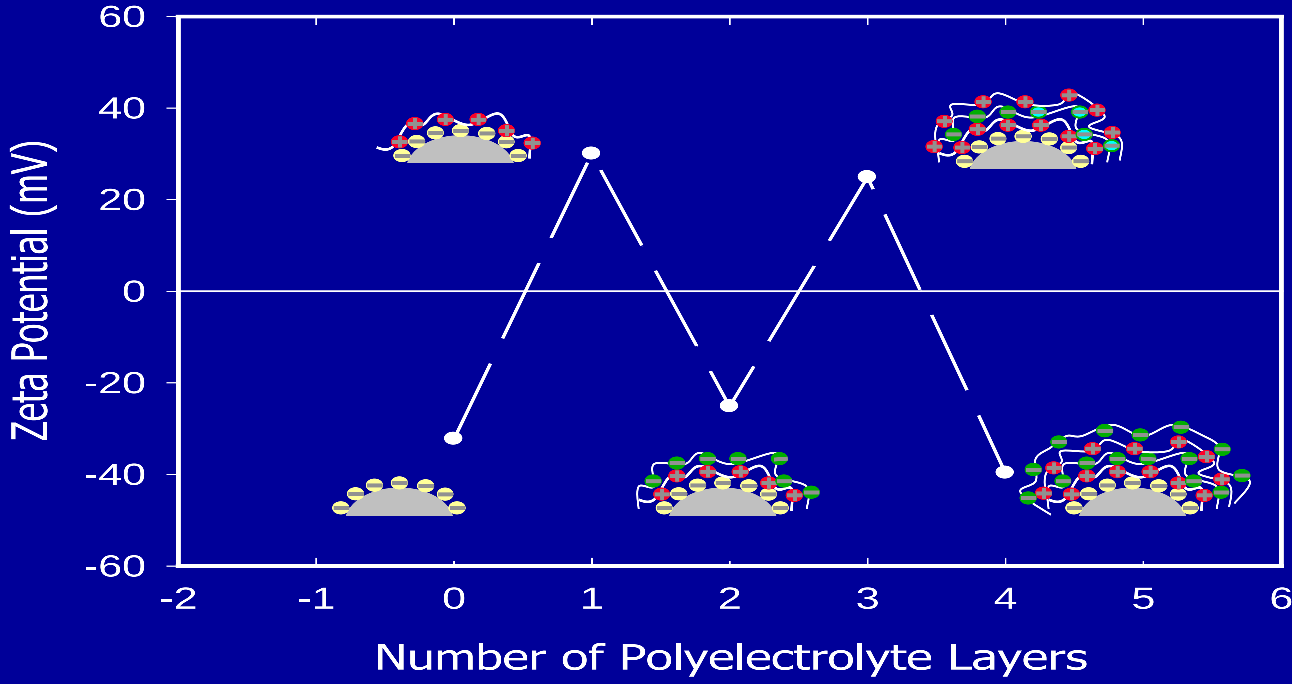
Rashida Smith, Linda Reven, C. J. Barrett, McGill

with the coated colloid between electrodes the electrophoretic mobility

$$\zeta = \frac{\upsilon\eta}{\varepsilon}$$

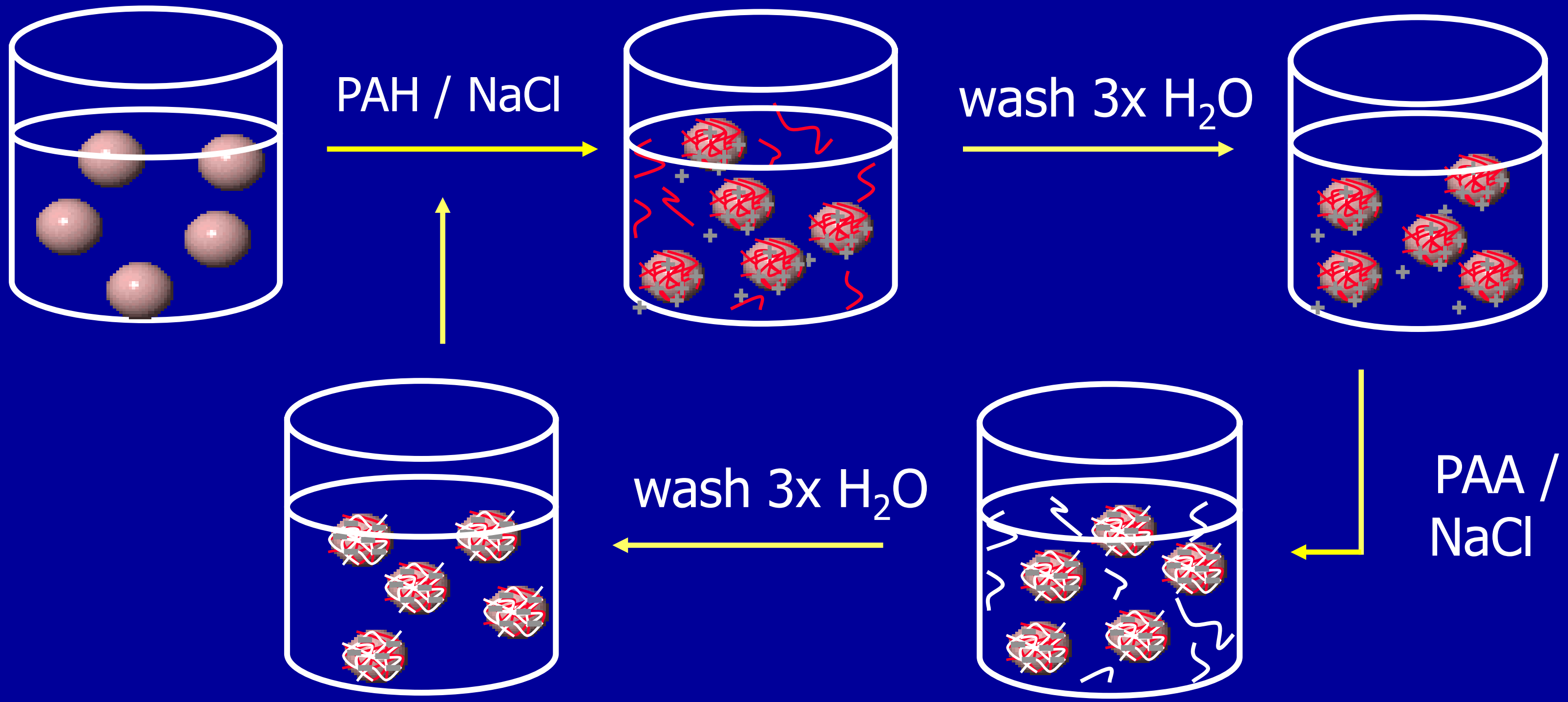


is proportional to the zeta potential of the charged colloid



A 2nd interesting, and un-planned SPINOFF application is to control Nd oxide nanoparticle stability,

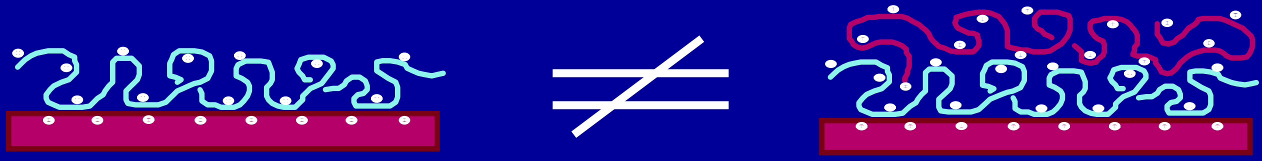
on a larger scale than microlitres: (SNO Project)



S
N

Challenges for the Study of Polyelectrolyte Multilayers:

1) New *theoretical approaches* are required :



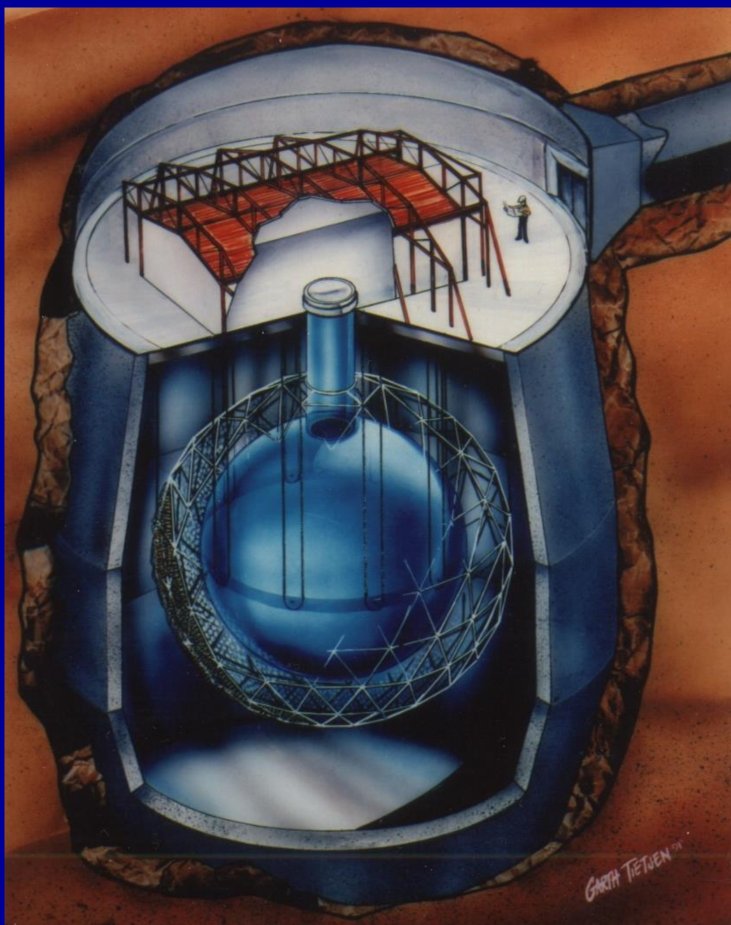
adsorption is irreversible, layer properties not necess. same as bulk:

Just published, from York U. (BioPhysics, and Mathematics) :

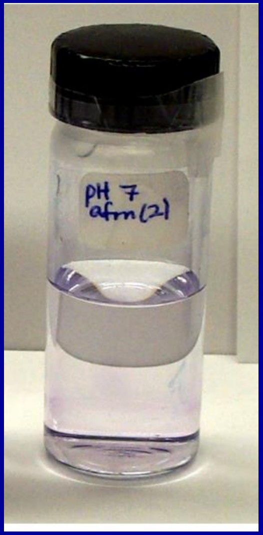
"Theory and experiment of chain length effects on the adsorption of polyelectrolytes onto spherical particles: the long and the short of it"

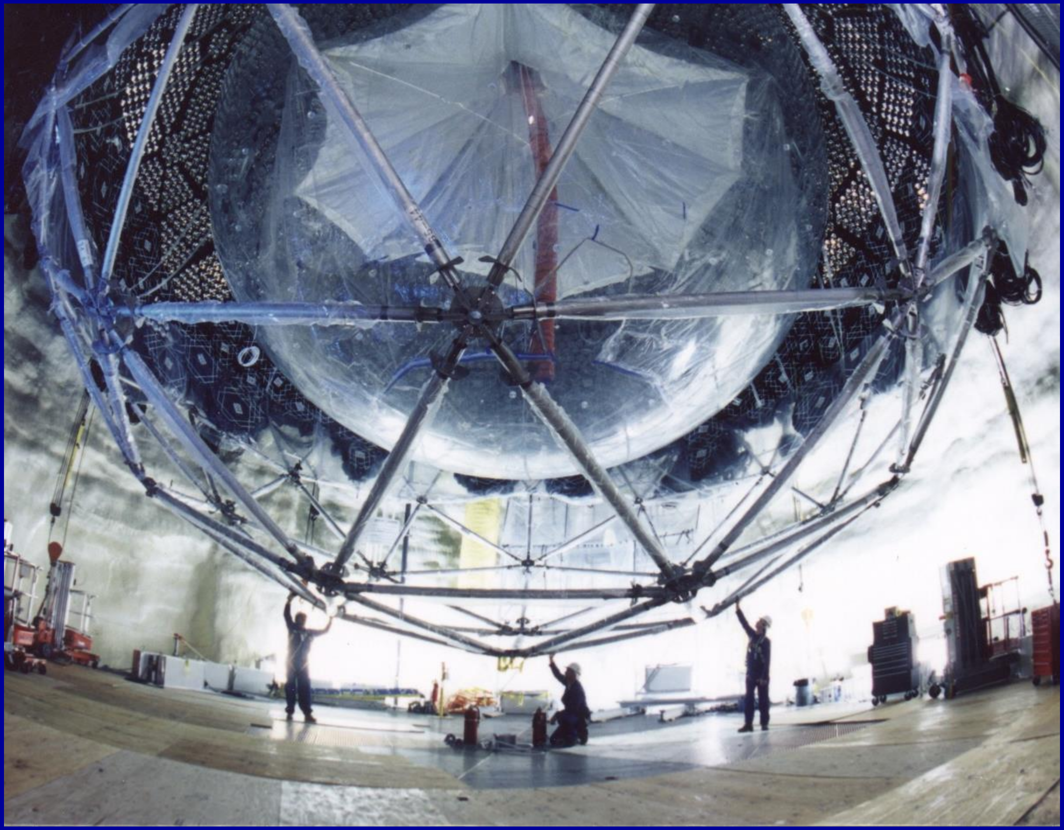
Royal Society of Chemistry's 'PCCP' Journal, 2021
Sperydon Koumarianos, Rohith Kaiyum, Prof. Christopher J. Barrett, Prof. Neal Madras, and Prof. Ozzy Mermut*

The SNO project (Sudbury Neutrino Observatory) required perfect transparency from all scintillator materials used, for 10,000 PMTs to detect a single photon



The SNO project (Sudbury Neutrino Observatory) poses an interesting opportunity to control 3nm Nd oxide nanoparticle stability, on a larger scale than microlitres:





Nd oxide nanoparticles in trimethyl benzene at 1% by mass (*l*), coated with PSS of MW 4k (*r*), stable and transparent, spaced ~15nm apart.

Dorris, Barrett, MacDonald, 2011 patent, publication in ACS-AMI

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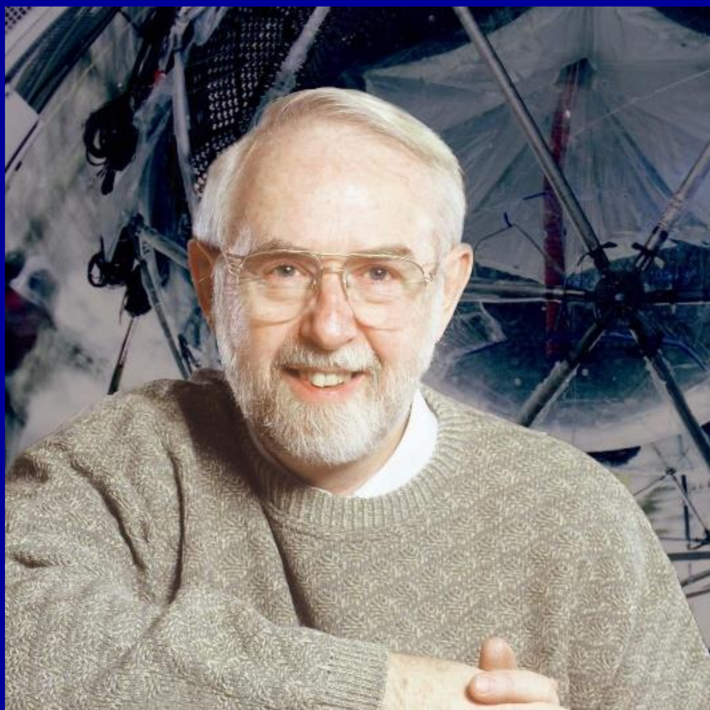
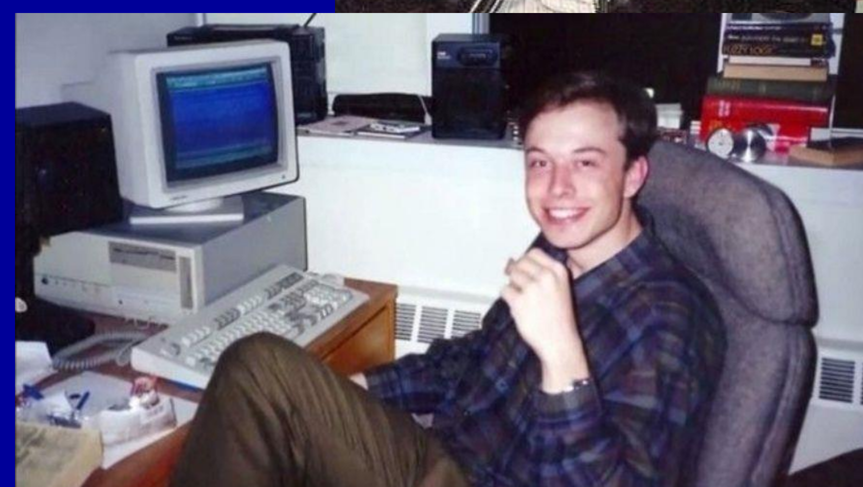




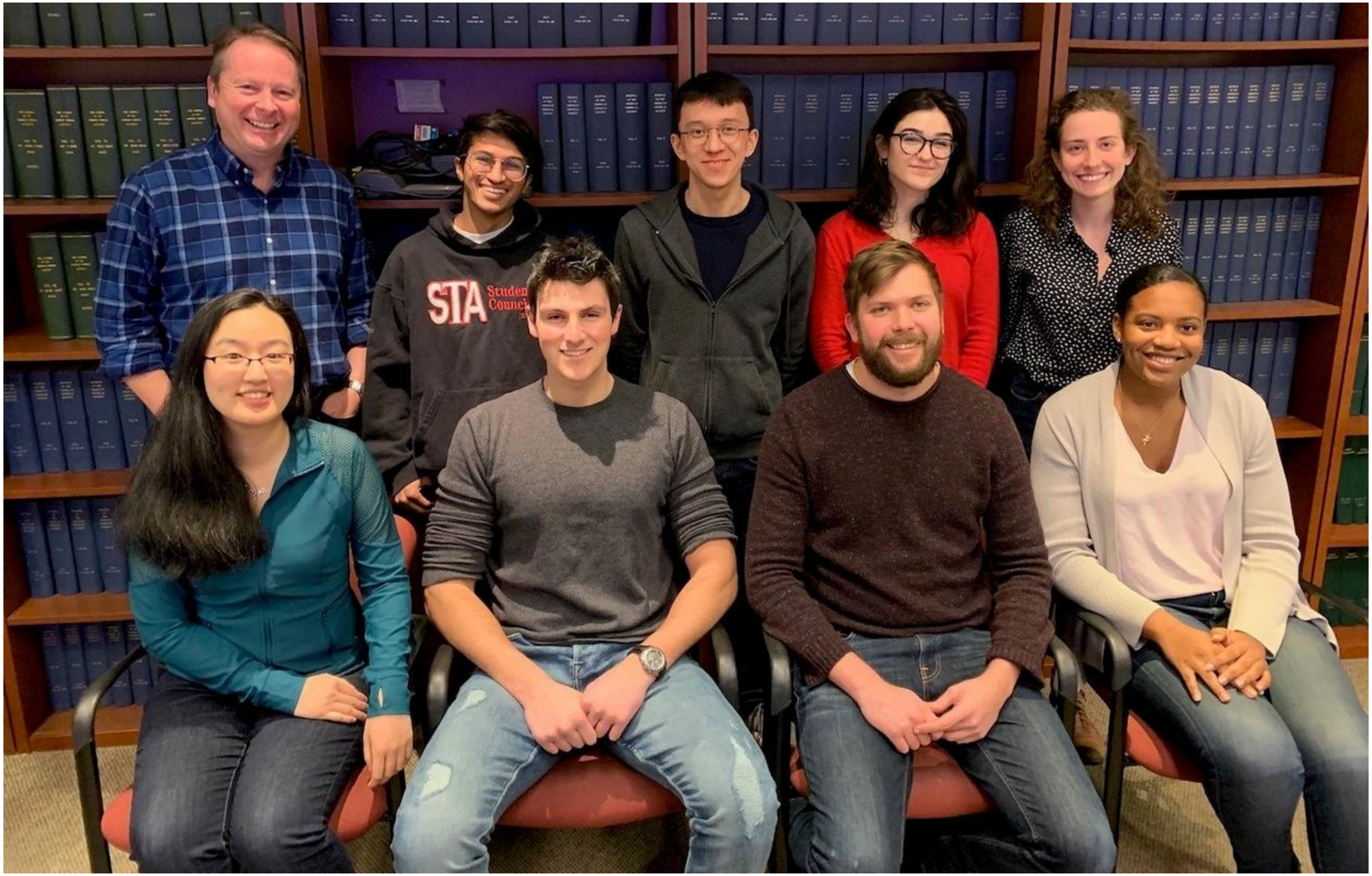
Prof. Art MacDonald, Queen's.
SNO Director, Nobel Prize in Physics 2015 for SNO Team.

(incl. students C. Barrett, E. Musk...)

JSPS Visiting Sabbatical Professor, Tokyo Tech 2017

Atsushi Shishido, Tokyo Tech Materials Engineering, Liquid Crystals, Robotics, Flex Display Engineering.

Merci.   & the terrific McGill U. Students who did all the work :



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