Functions of self-assembled soft material designed through **Materials Nanoarchitectonics**

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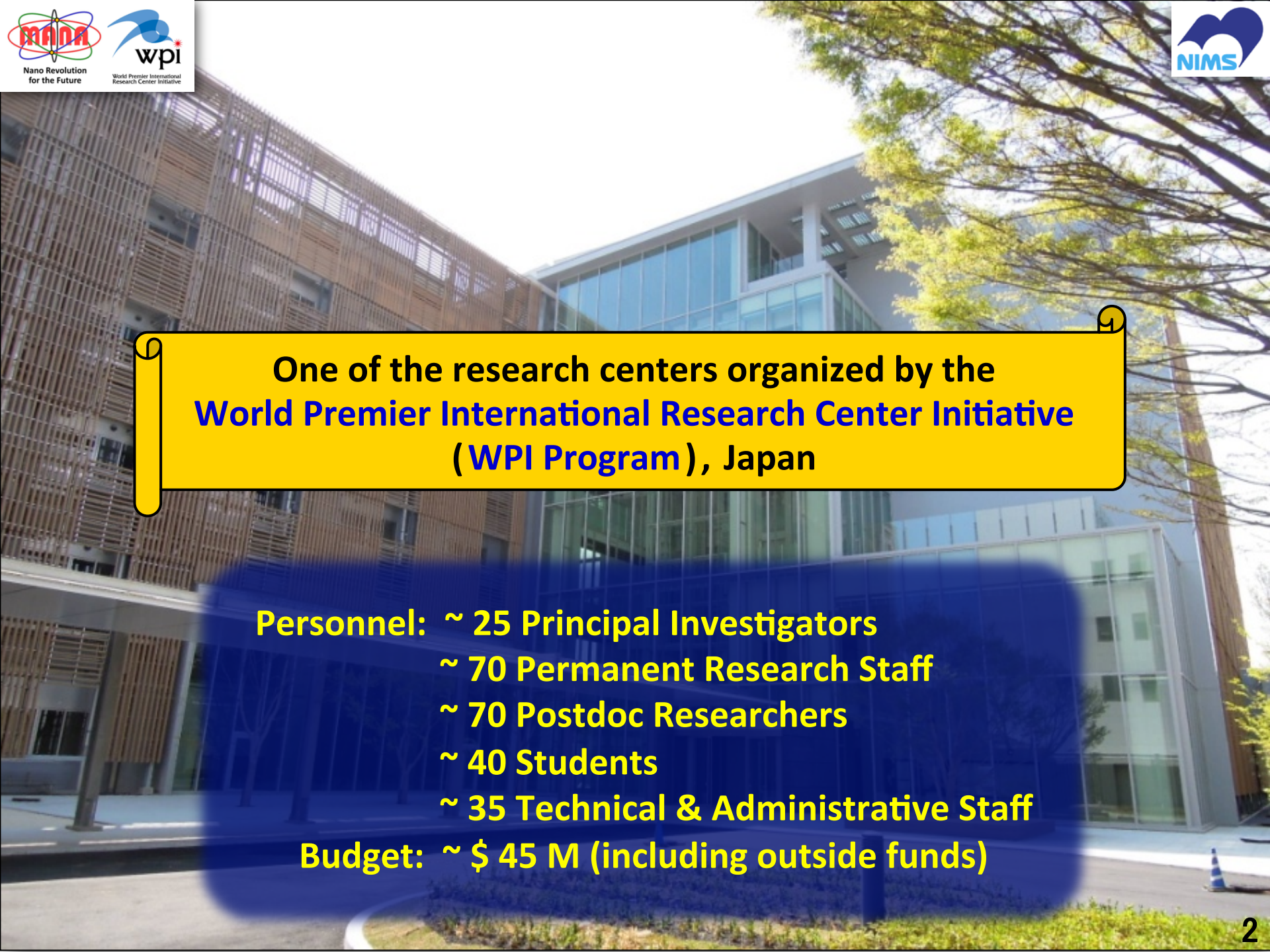
University of Helsinki Finland

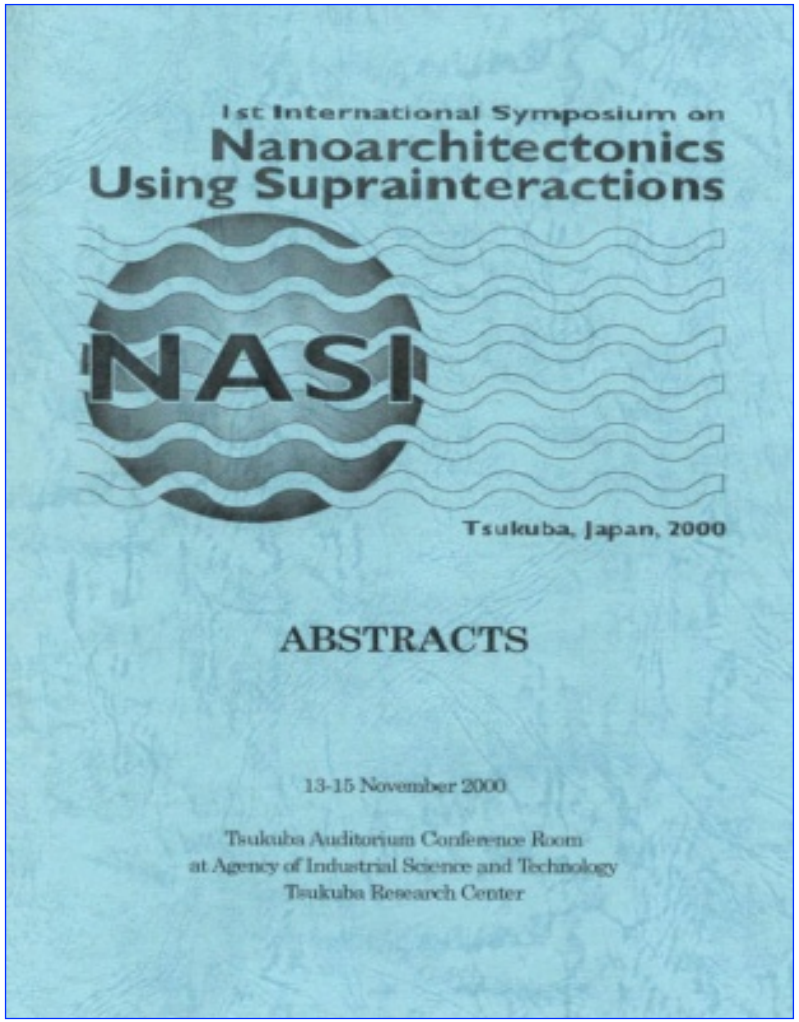


One of the research centers organized by the
World Premier International Research Center Initiative
(WPI Program), Japan

Personnel: ~ 25 Principal Investigators
~ 70 Permanent Research Staff
~ 70 Postdoc Researchers
~ 40 Students
~ 35 Technical & Administrative Staff

Budget: ~ $ 45 M (including outside funds)

The word "Nanoarchitectonics" was used for the first time in the name of a symposium held in 2000:



ORGANIZING COMMITTEE

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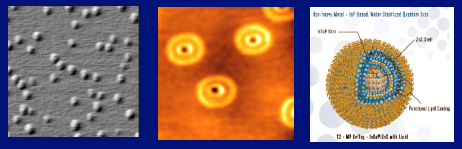
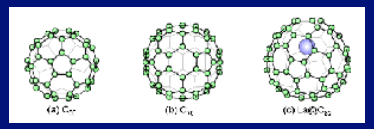
Max Lagally
Matthias Scheffler
Junzo Tanaka
Masaru Tsukada
Mark Welland
Stanley Williams
Kazuhiro Yoshihara

From nanofunctionality ····

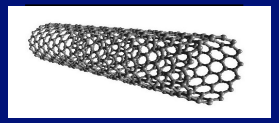
Quantum dots



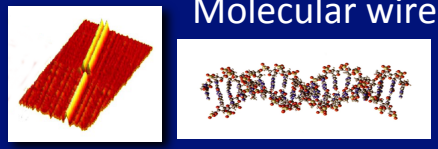
Fullerenes



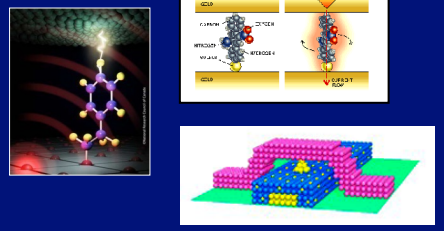
Nanotubes



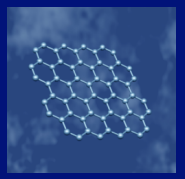
Molecular wires



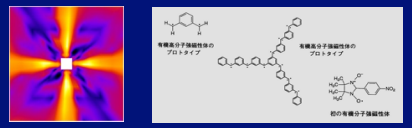
Molecular & atomic devices



Graphene



Functional molecules

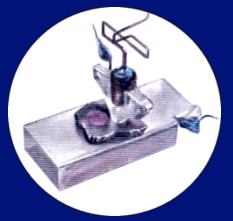


NANOTECHNOLOGY

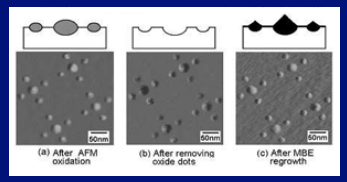
CRUCIAL DIFFERENCE vs.

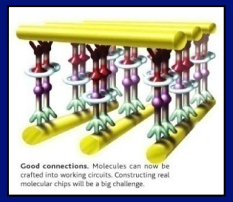
MICROTECHNOLOGY

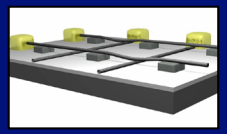
First Transistor

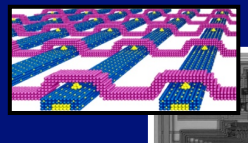


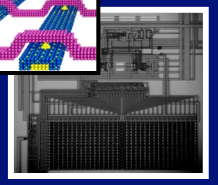
···· to nanosystem functionality

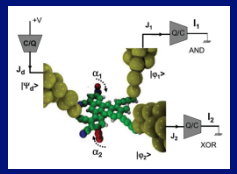


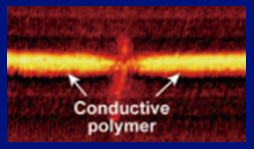


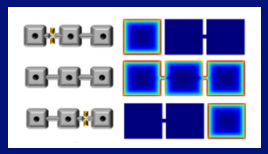


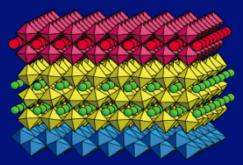












Integrated systems

Modern IC

Why nanoarchitectonics ?

1) How can one construct ***reliable nanosystems*** using ***unreliable*** *nanostructures* (the building blocks) connected ***unreliably***. *(consequence of nanosize);*

2) The main players are not the building blocks *per-se*, but the ***mutual interactions*** among the blocks;

3) Unexplored functions emerge from the network of a huge number of interacting nanoparts.

Materials Nanoarchitectonics:

a research approach conducive to innovation in nanotechnology using:

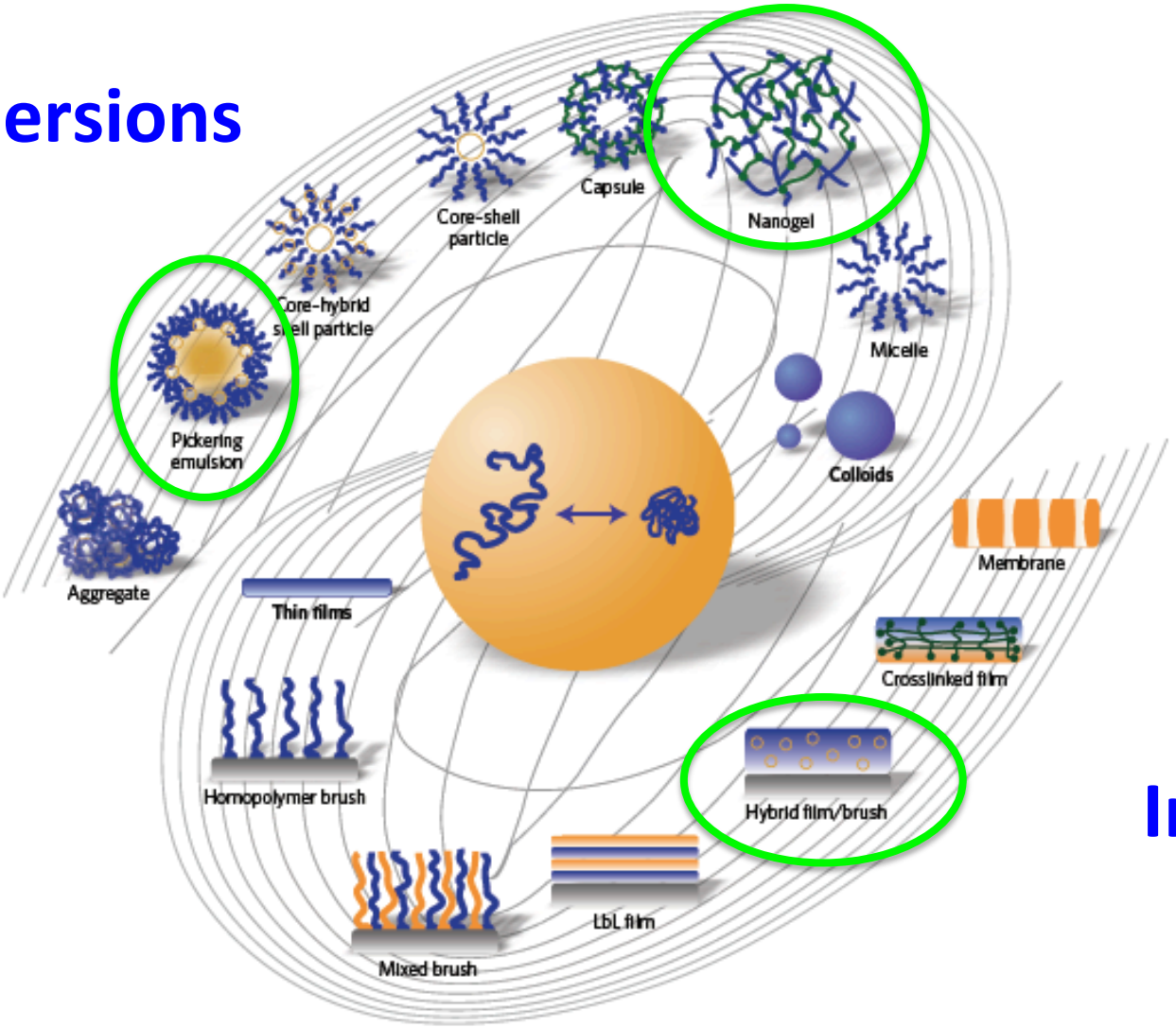
1. Controlled *self-organization*
2. Chemical *nano-manipulation*
3. *Field*-induced materials control
4. *Manipulation* of atoms or molecules
5. *Theoretical* modeling and design

http://www.nims.go.jp/mana/about/ourgoal/nanoarchitectonics.html

Self-assembly of soft matter and

Materials Nanoarchitectonics

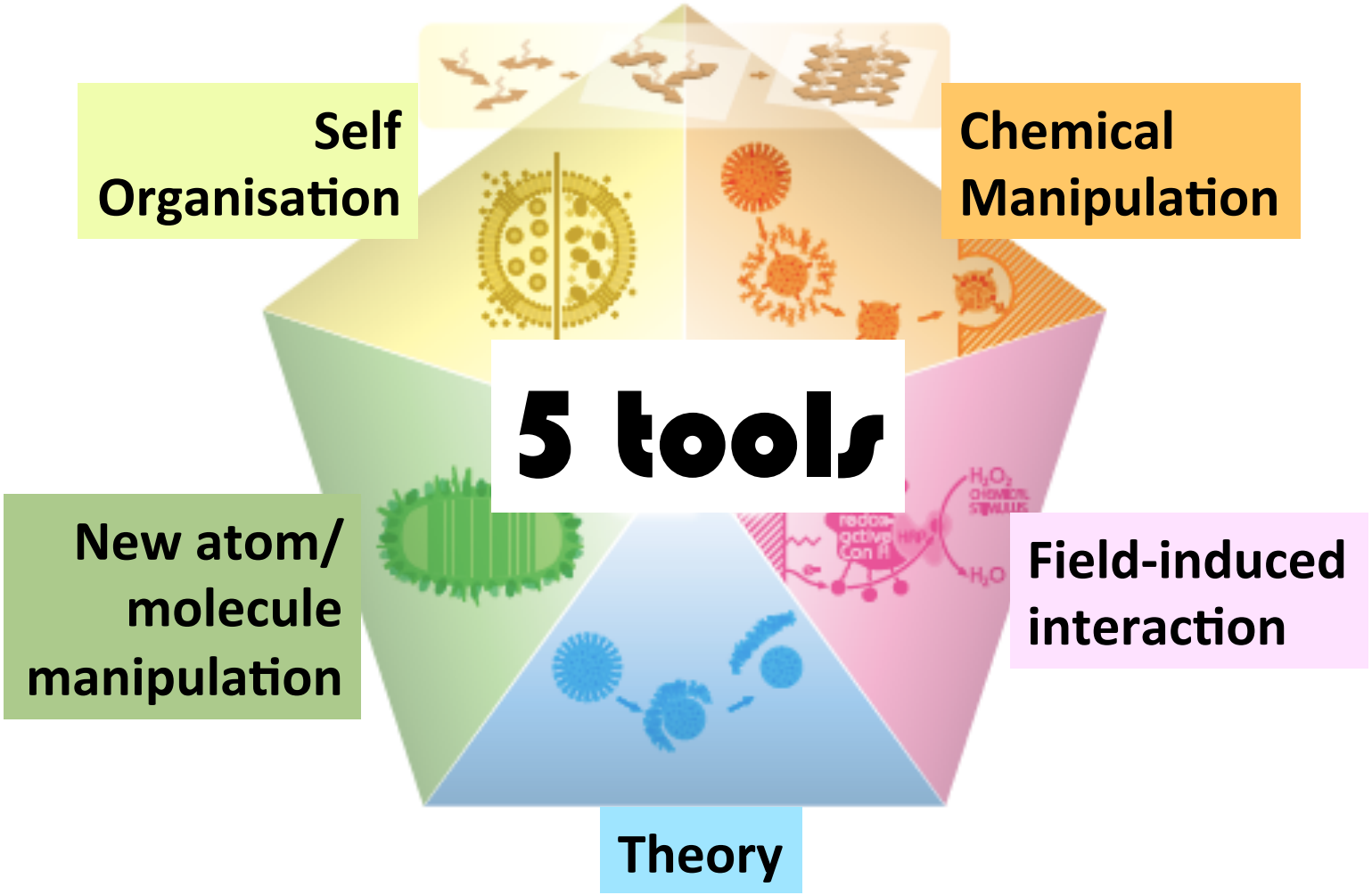
Dispersions



Interfaces

From: *Nature Materials*, 2010, 9 (2) 101-113.

Materials Nanoarchitectonics



Kujawa and Winnik, *Langmuir*, 2013, 29, 7354-7561.

Chemical manipulation

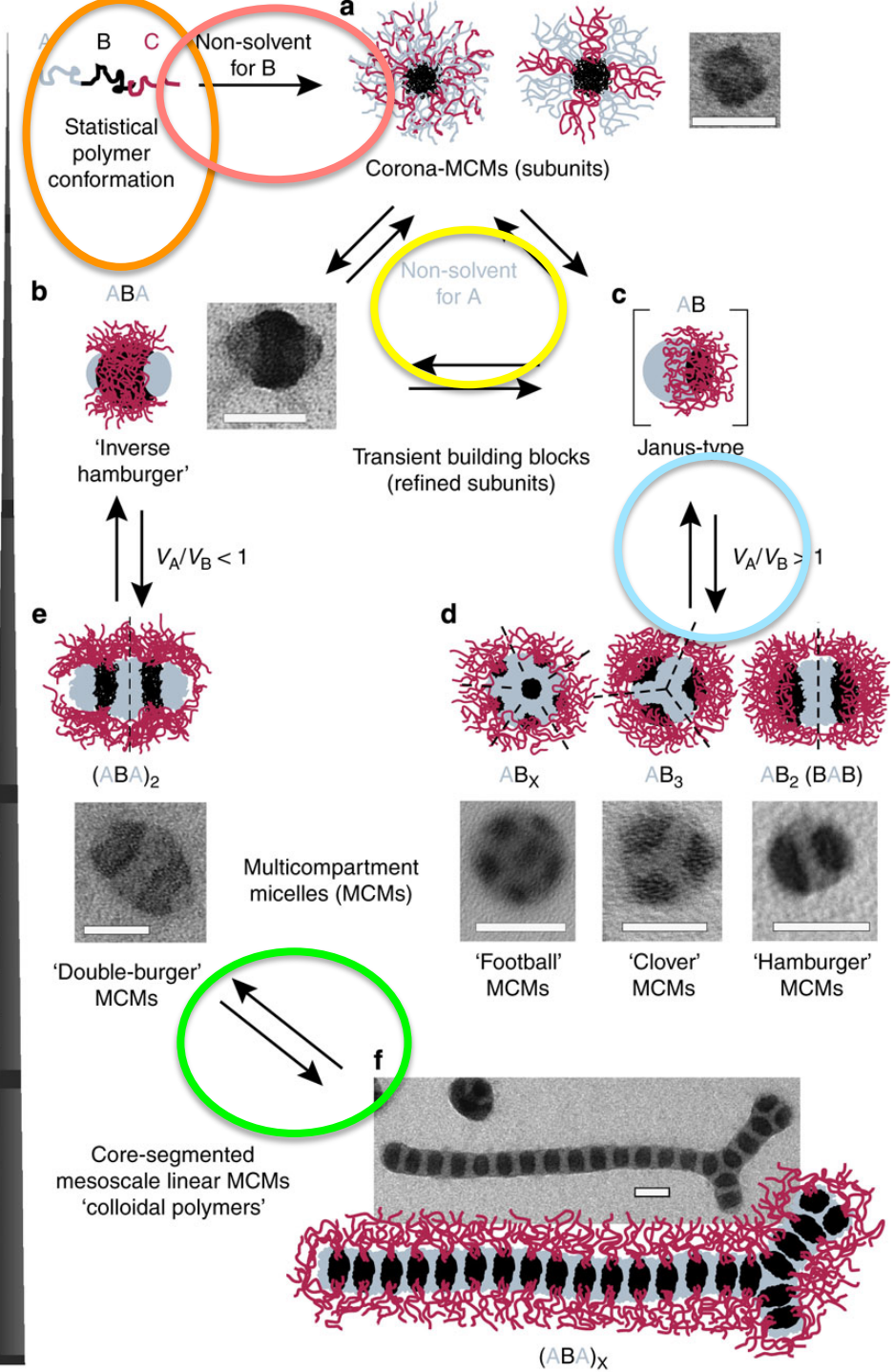
(controlled free-radical polymerization)

Field-induced interaction

(change of solvent quality)

Molecular manipulation

(pH switch leading to superstructures)



Self Organization

(2-step solvent exchange)

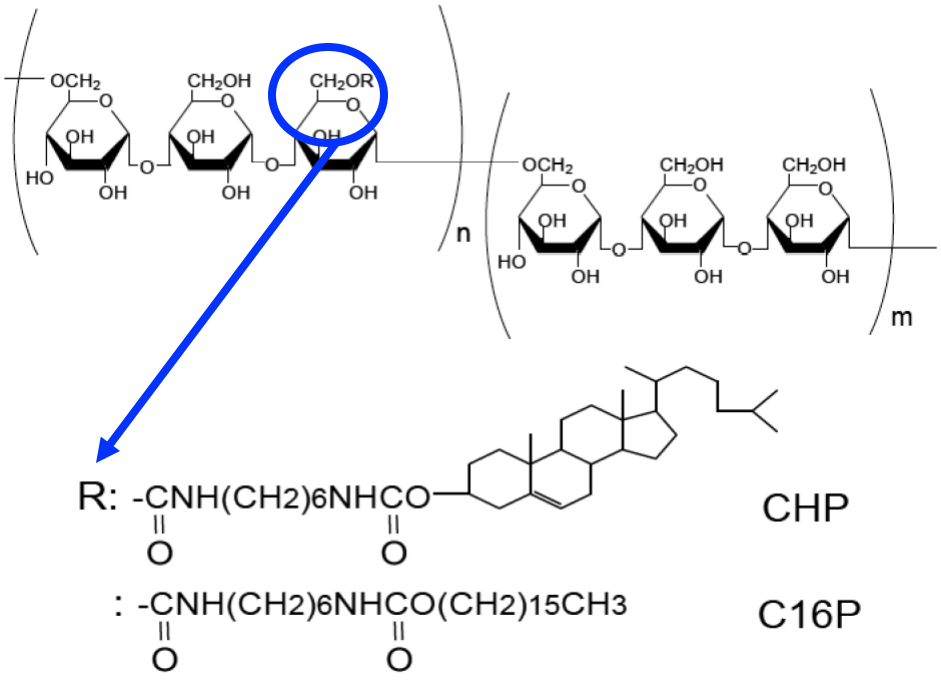
Theory

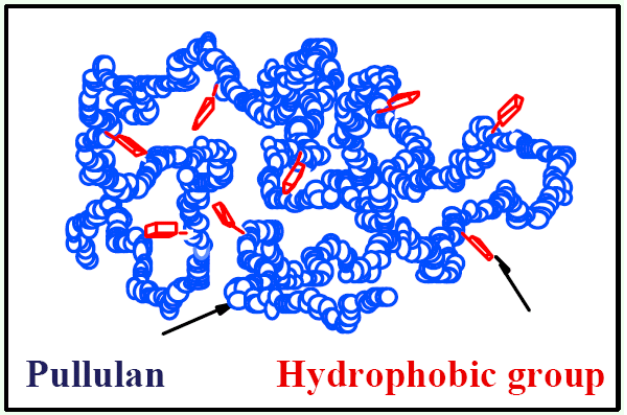
(subunit organization)

Nature Comm. 2012, 3, 710

Nanogels: Self-organization

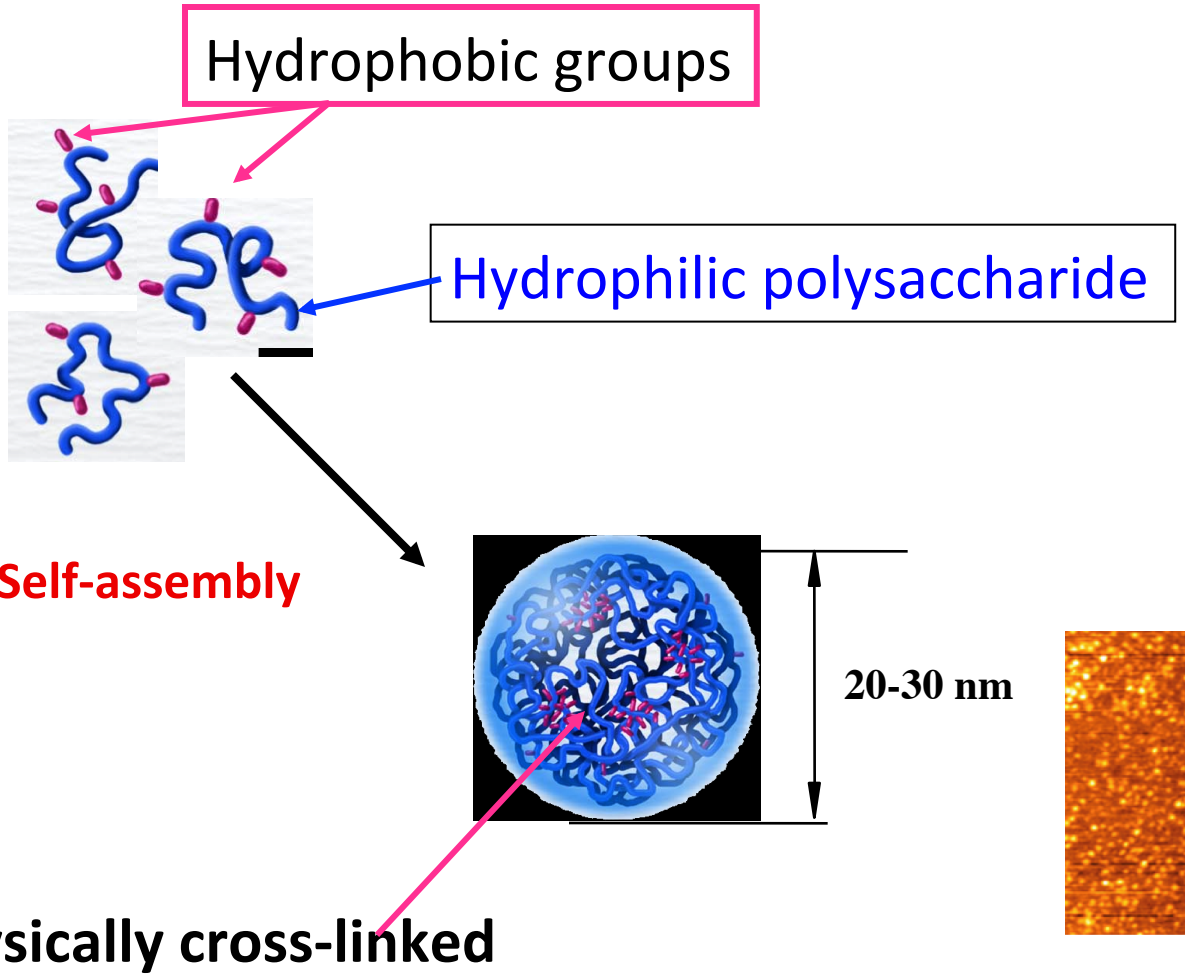
Physically cross-linked nanogels formed by self-assembly in water of hydrophobically modified polysaccharides





K. Akiyoshi et al (Kyoto University)

Nanogels: Self-organization

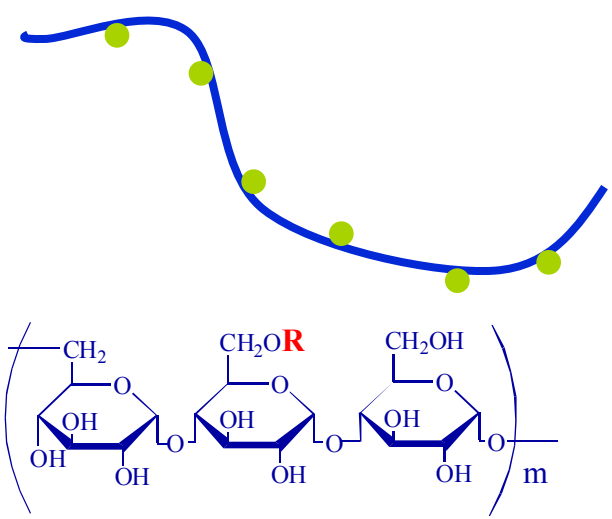


Physically cross-linked hydrophobic nanodomains

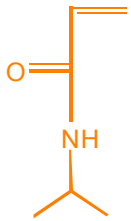
K. Akiyoshi

Macromolecules **26,** 3062**(1993)**, *Macromolecules* **30,** 857**(1997)**
Langmuir, **18,** 3780 **(2002)**, *Biomaterials*, **25,** 2911**(2004)**

Field-induced formation of a *hydrophobic nanodomains* can yield nanogels (reversibly)

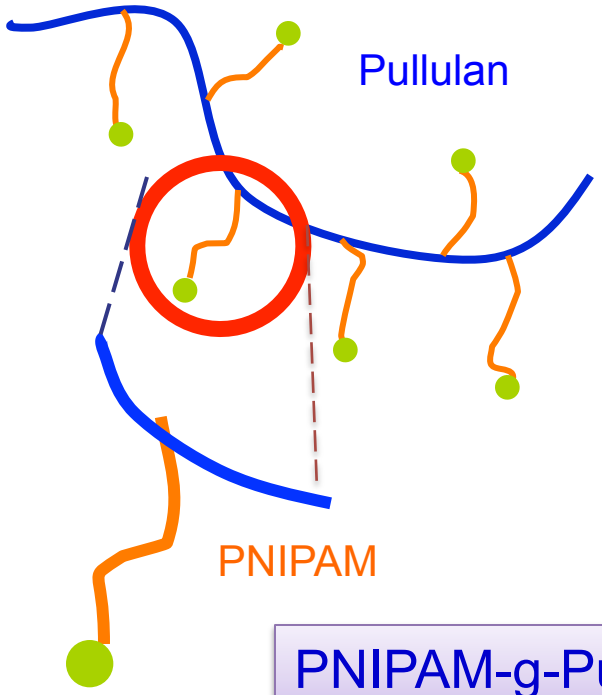


RAFT polymerization



H_2O

NIPAM



PNIPAM-g-Pul

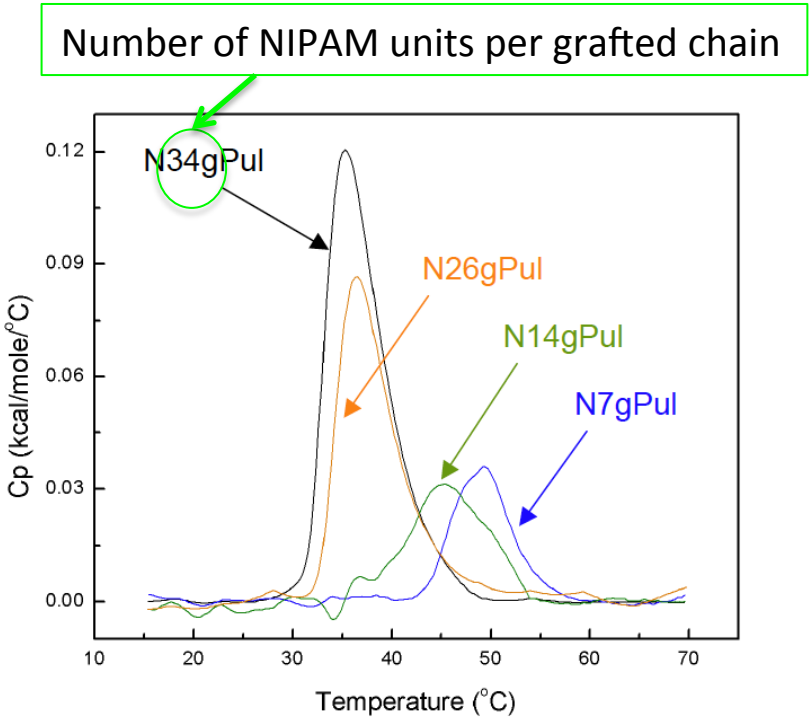
PulSTS:

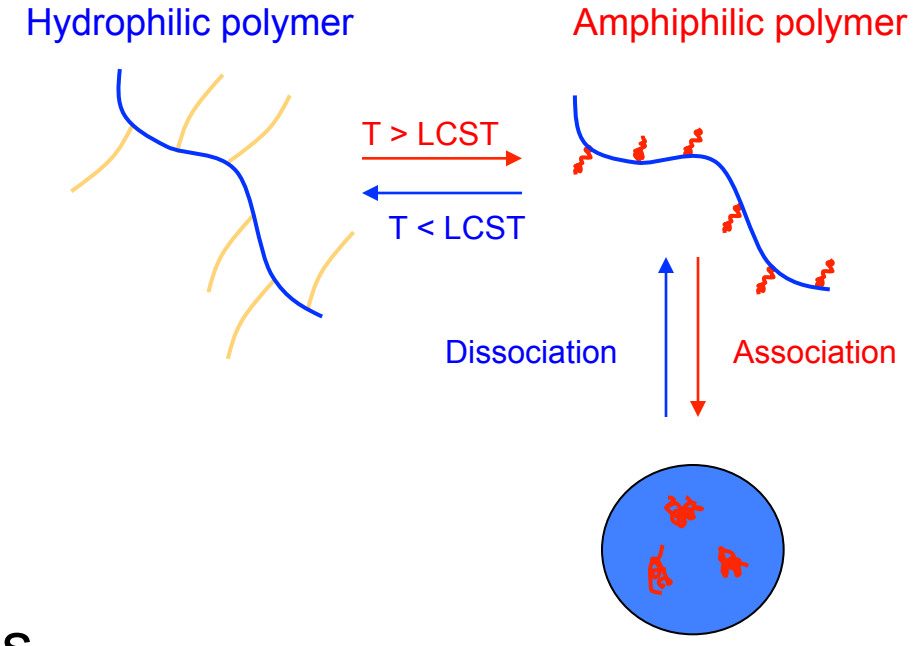
macro-chain transfer agent

End functional group

1. Aminolysis
2. Possible reaction

Lightly-grafted PNIPAM-g-pullulan forms nanogels in **hot water**,
… *even in the absence of cholesteryl group !*



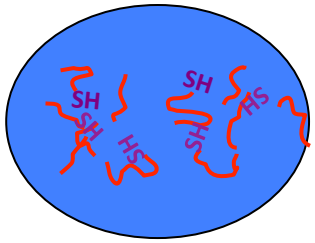


Differential calorimetry scans of PNIPAM-g-pullulan

Morimoto et al , Macromolecules, 2008, 41, 5985

Field-induced materials control

+ Controlled self-organization



Crosslinking via oxidation

Reducing agent

Dual crosslinked nanogel

Heat-induced Association

Δ

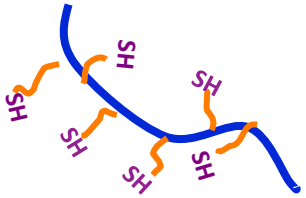
−Δ

Shrinking

Δ

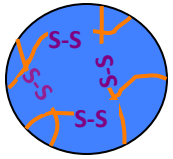
−Δ

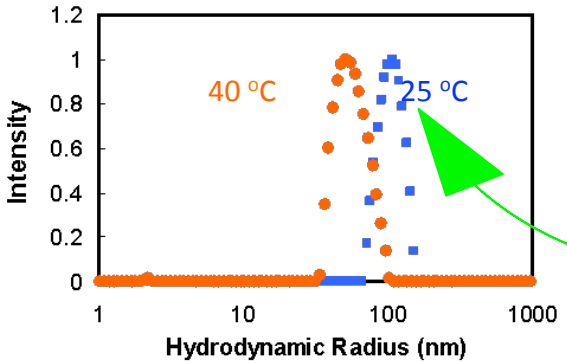
Swelling



Reducing agent

X





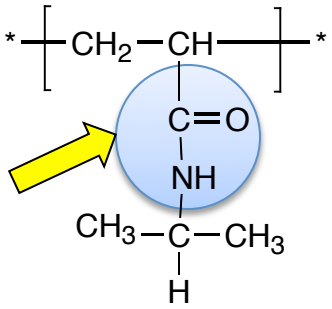
Oxidative crosslinking does not occur in cold water

Multi-responsive nanogels

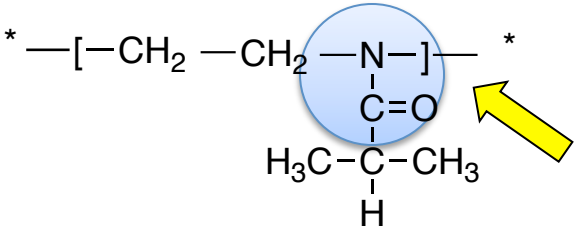
Morimoto et al. Soft Matter 2009 5, 1597-1600

Towards composite nanogels….

Temperature-driven conversion of amorphous to semi-crystalline nanogels



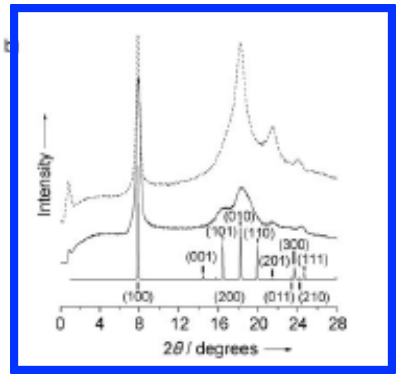
Isomeric monomer units



PIPOZ

Poly(2-isopropyl-2-oxazoline)

Cloud point ~ 32 °C
Reversible phase transition



XRD pattern of powder recovered after heating PIPOZ in water at 70°C

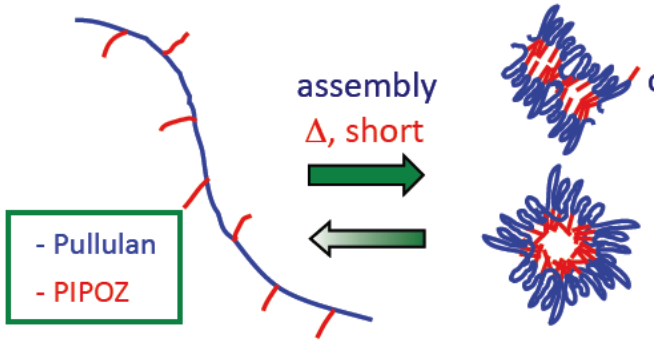
Cloud point in water ~ 36 °C……
but …

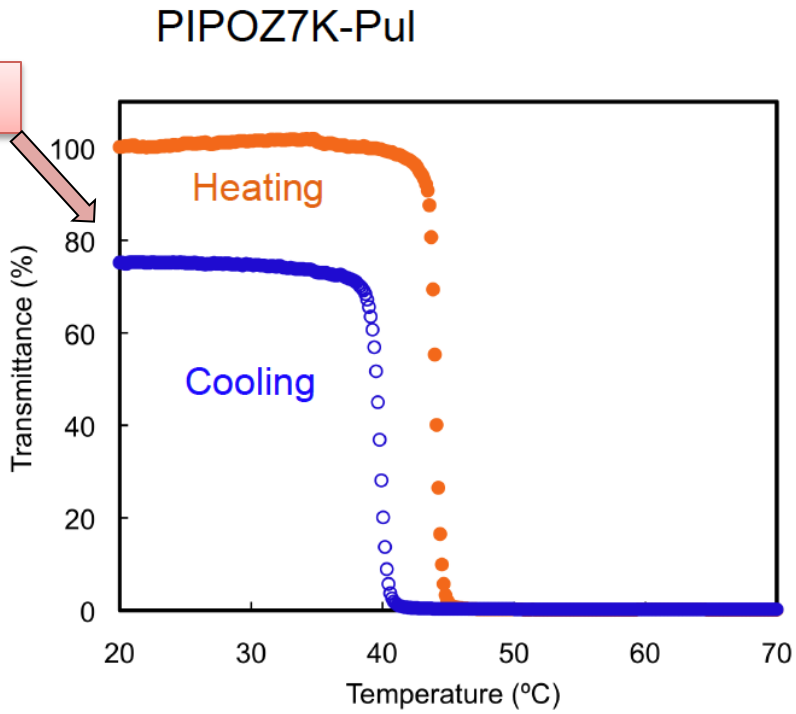
prolonged heating triggers
irreversible crystallization from water

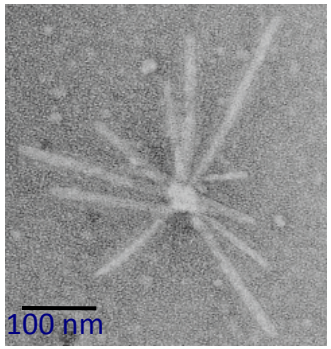
From: A. Levent Demirel et al, Angew Chem 2008, 46, 8622

A look on the transmittance as a function of temperature for a solution of pullulan-PIPOZ in water

Incomplete transmittance recovery upon cooling







PIPOZ Crystallization ???

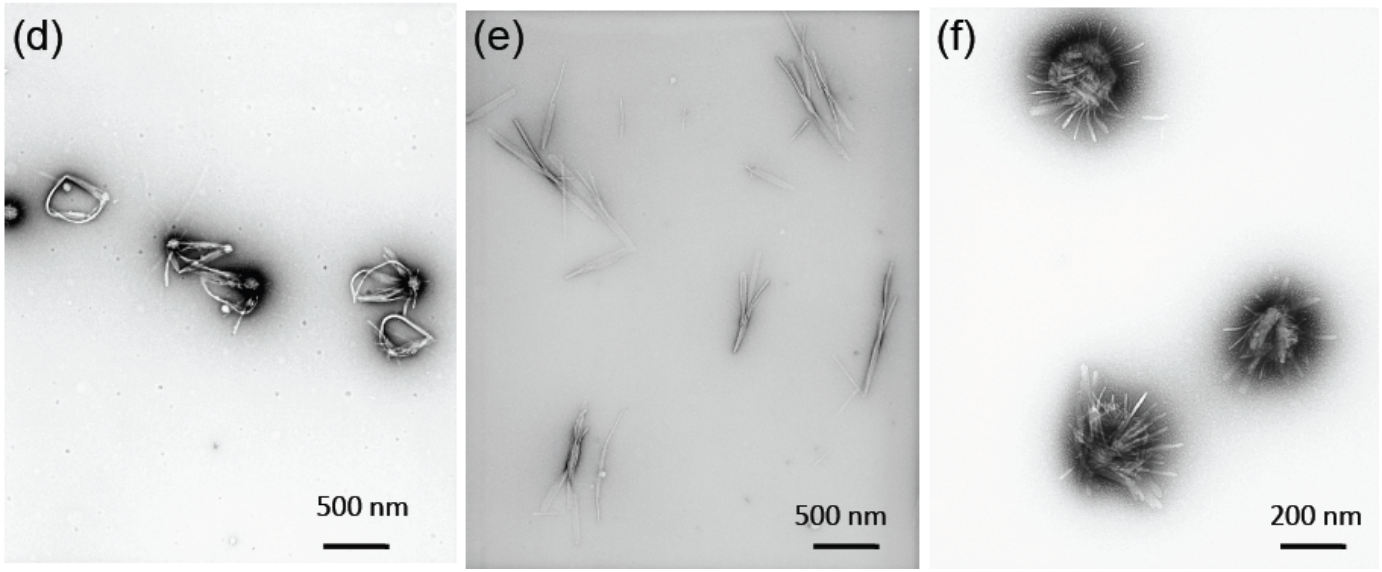
10 min, 70 ºC

The morphology is affected by the conditions of the heat treatment

60 °C, 1hr

70 °C, 3 hr
stirring, 1 M NaCl

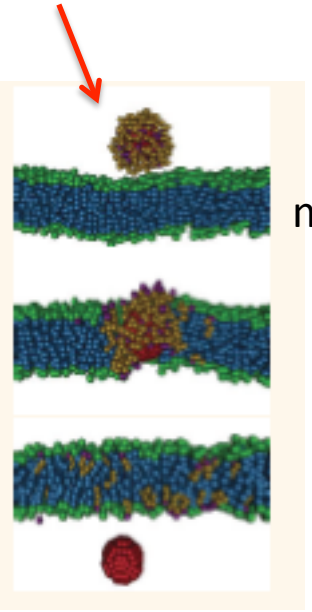
70 °C, 3 hr



+ Theoretical modeling and design

Nanoparticle Translocation through membranes

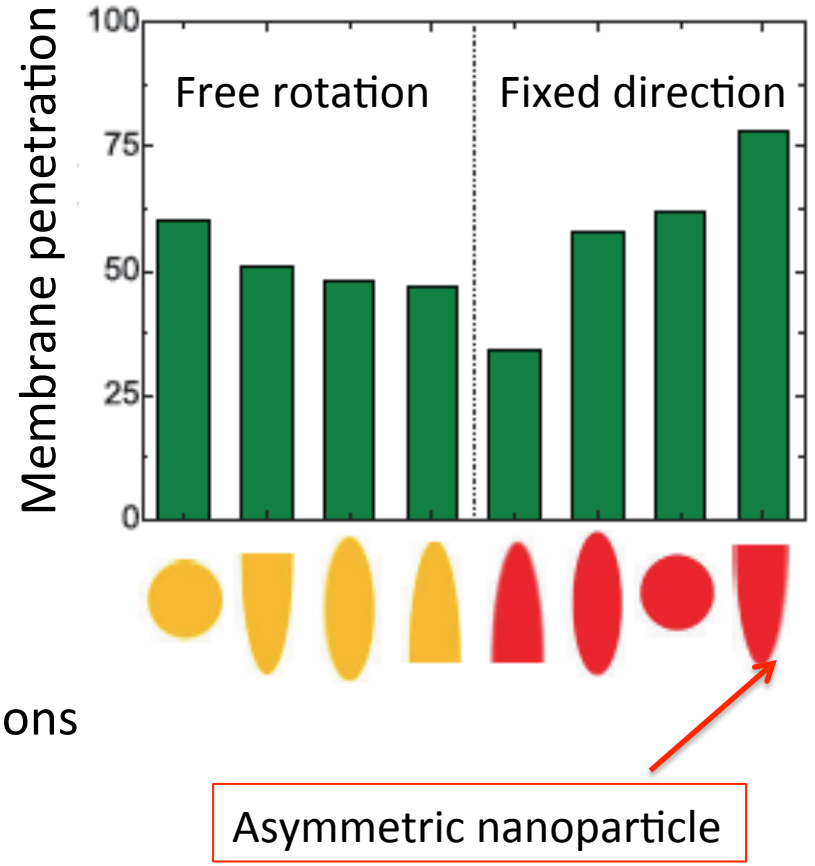
Particle decorated with dynamic bonds



Cell membrane

Dissipative particle dynamic simulations (coarse grain simulation)

Shape of the nanoparticle



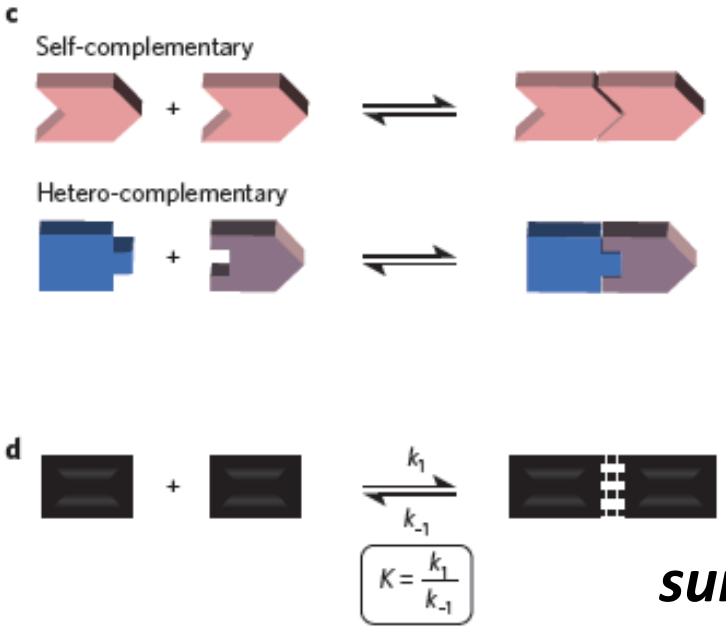
Ding et al. ACS Nano, 2012, 2, 1230

Controlled self-organization

+ *field*-induced materials control

+ *New manipulations* of atoms and molecules

"dynamic bonds"



Nature Materials 2011, 10, 14

Novel nanoparticle design ?

Dynamic particle/ligand bond

Specific change in shape or surface chemistry only on the targeted site

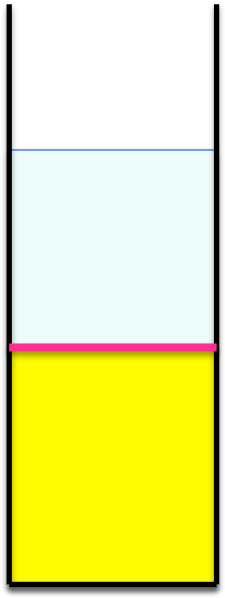
ellipse elongation to enhance penetration in the cell membrane ??

field induced materials control

Interfacial forces (II)

Chemical manipulation

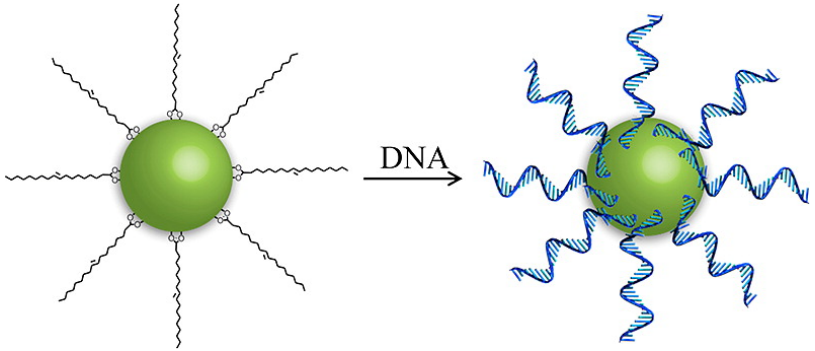
mild, one-step method to prepare functional hydrophilic particles



water + DNA

interface:
locus of ligand exchange

chloroform
+ oleic acid coated NP



Hydrophobic Hydrophilic

Lanthanide-based up-conversion NPs
useful for bio imaging, therapeutics

Le-Le Li et al. *J. Am. Chem. Soc.* **2013,** 135, 2411-2414.

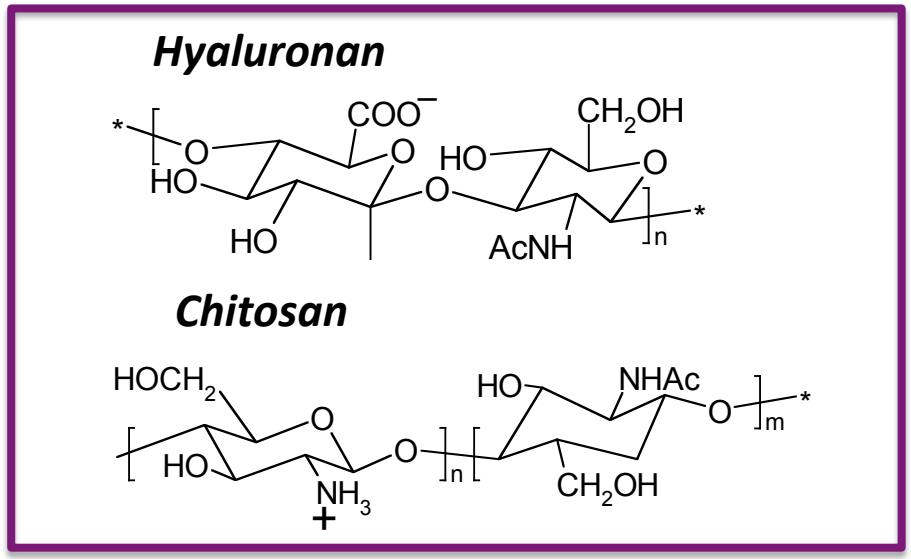
Hetero-complementarity

Boron nitride Nanotubes (BNNT)

D. Golberg
MANA, NIMS

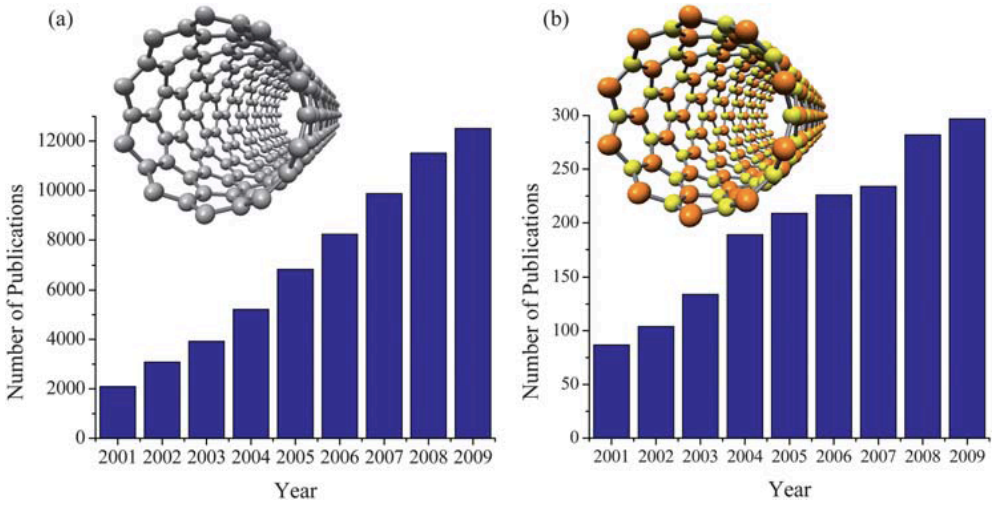
Biopolymers

F. M. Winnik



see: Adv. Mater., 2007, 19, 2413–2432.
ACS Nano, 2010, 4, 2979–2993.

Boron nitride Nanotubes
Vs
Carbon Nanotubes



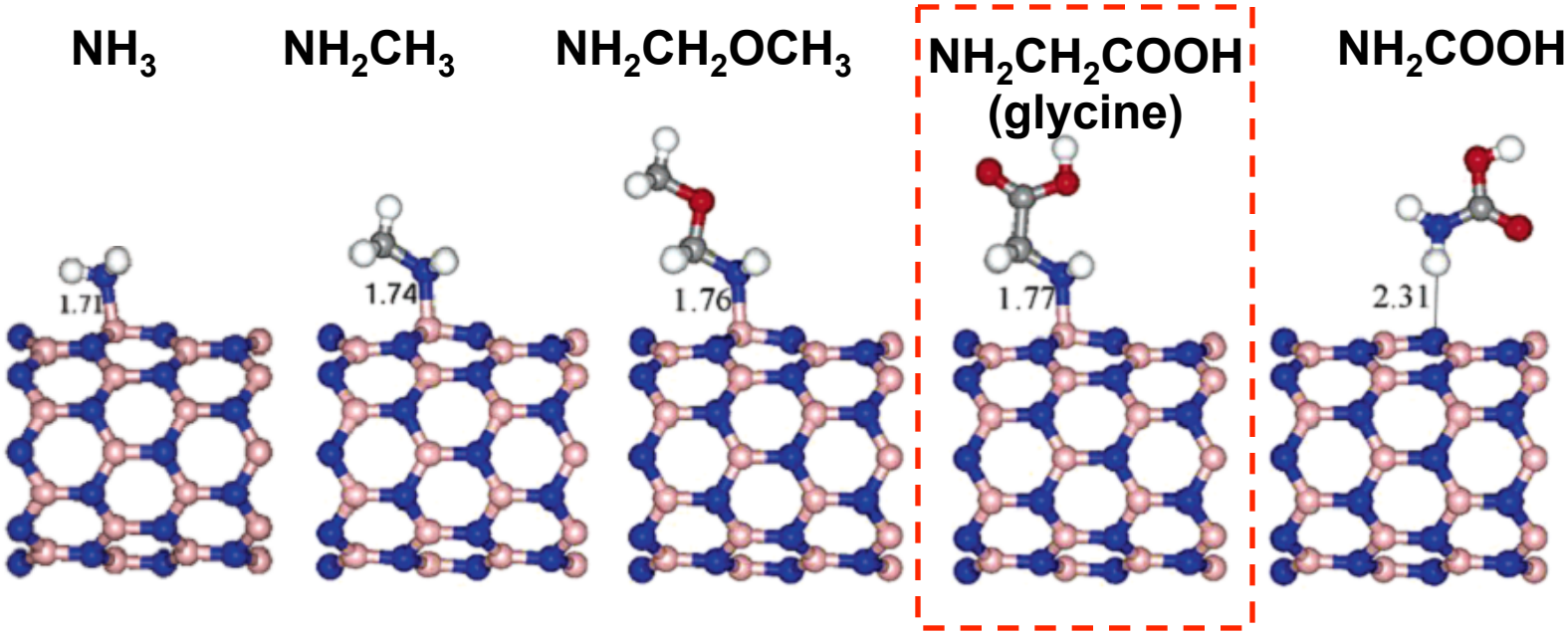
Citations: 12,000 vs 250

Property	Carbon NT	Boron nitride NT
Color	Black	White
Electrical	Semi metallic, conducting	Wide band gap
Young Modulus	~ 1.25 TPa	~ 1.18 TPa
Chemical stability	Stable to 500 C	Stable to 1000 C
Optical properties	Near IR	Deep UV

Nanoscale, 2010, 2, 2028

Chemisorption of amines on BN nanotubes

Energy of formation of B---N bond



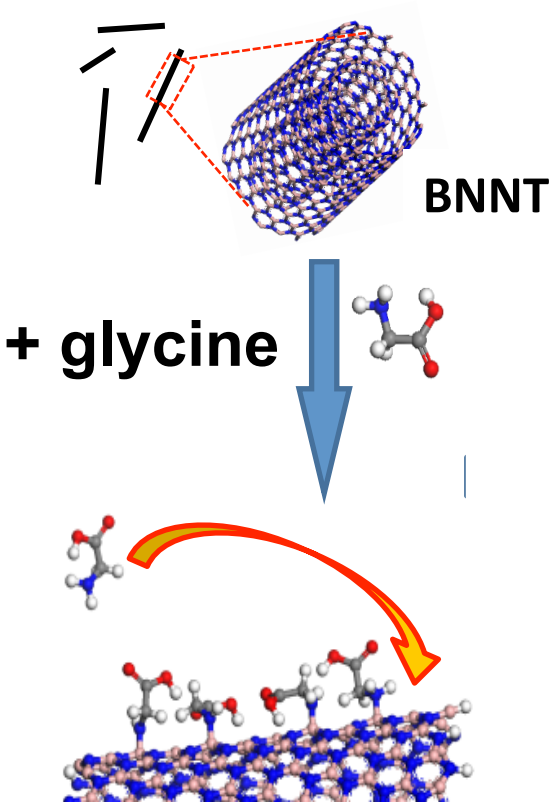
	NH_3	NH_2CH_3	$NH_2CH_2OCH_3$	NH_2CH_2COOH (glycine)	NH_2COOH
E_{ads} (exo)	0.45 eV	0.45 eV	0.29 eV	0.34 eV	0.16 eV

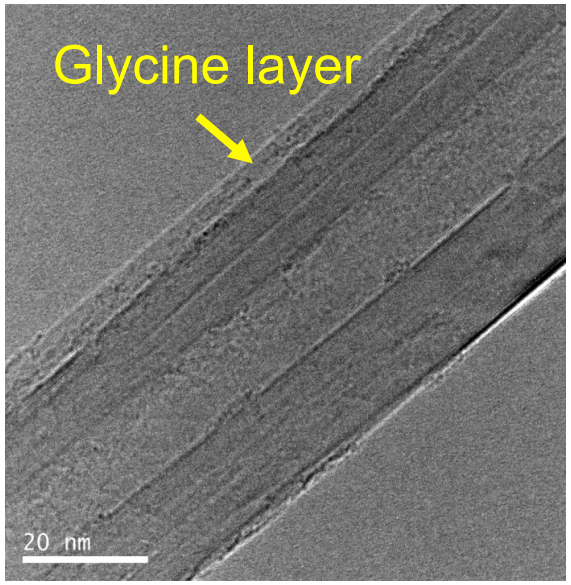
theoretical calculations...

Density Functional Calculations (minimum energy)

Wu et al. *JACS* 128, **2006**, 12001

To Practice…..



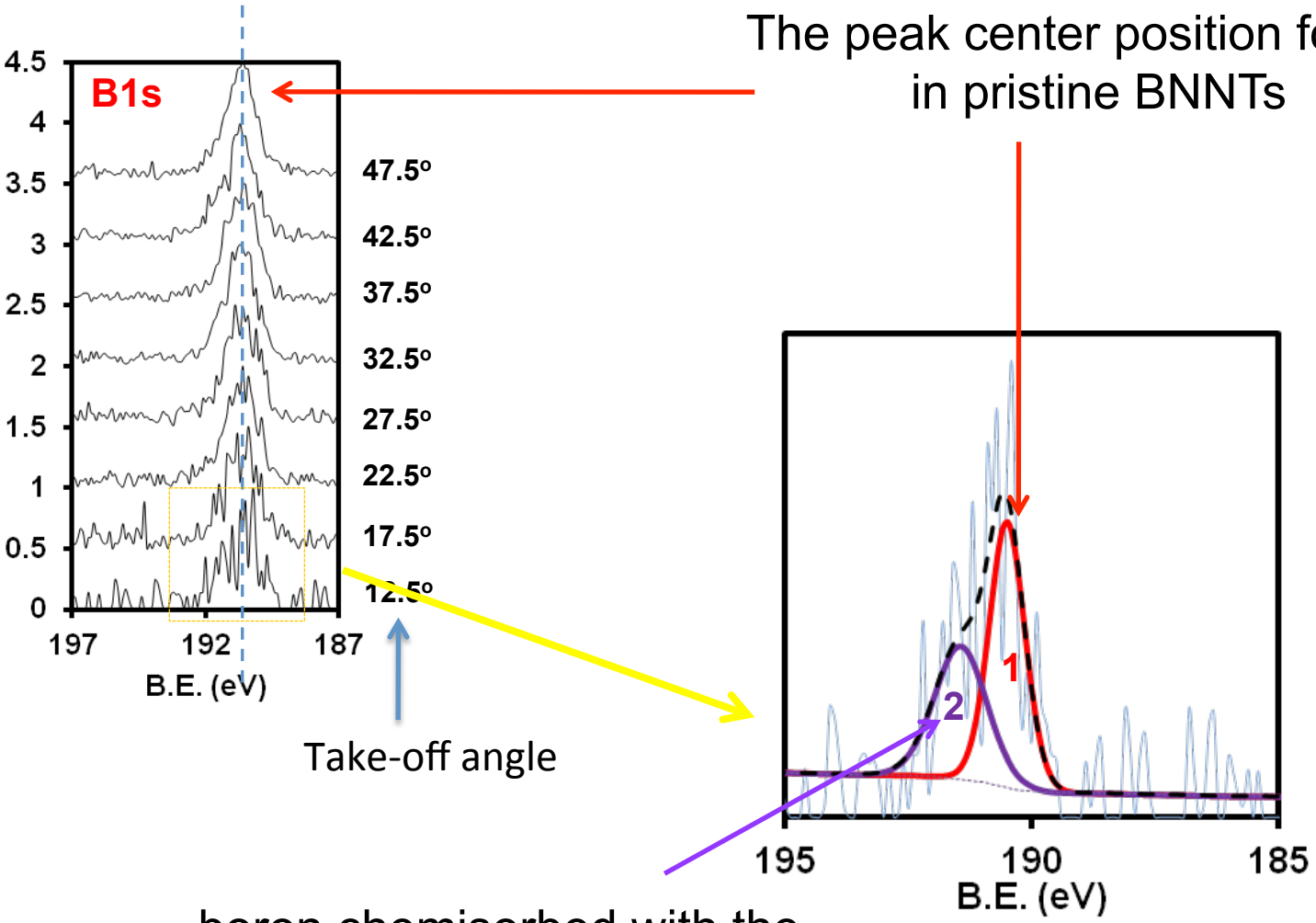


High resolution TEM

30 min sonication in ethanol/glycine

“De-bundling” of BN nanotubes

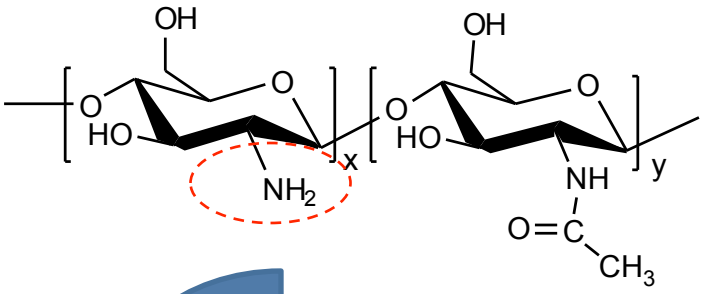
Angle Resolved -XPS



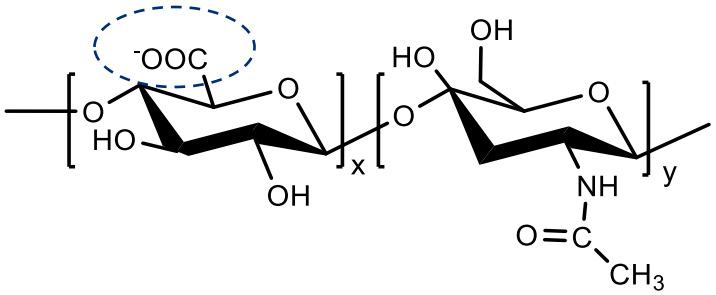
Y-T. R.Lau et al., J. Phys. Chem. C (2013) doi.org/10.1021/jp4073729

Selected biopolymers

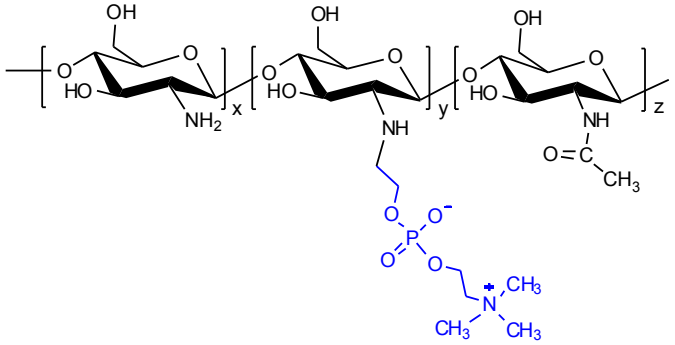
Polycation (chitosan, CH)



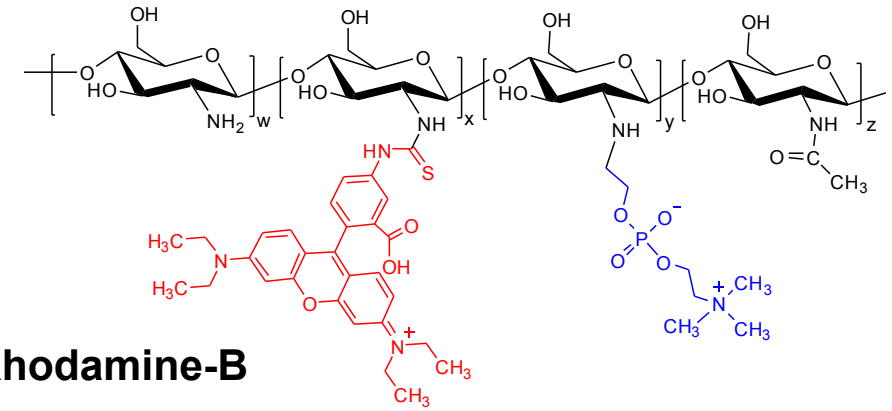
Polyanion (hyaluronan, HA)



Polyzwitterion (phosphorylcholine-modified CH, CHPC)

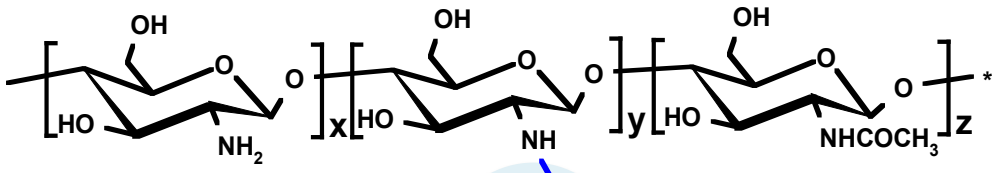


Labeled with a dye (RhCHPC)

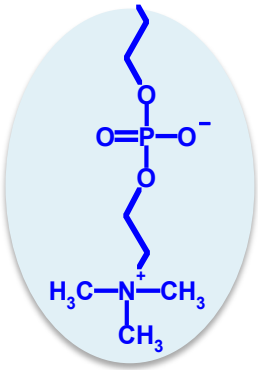


Rhodamine-B

Phosphorylcholine-modified Chitosan (CH-PC)



chitosan

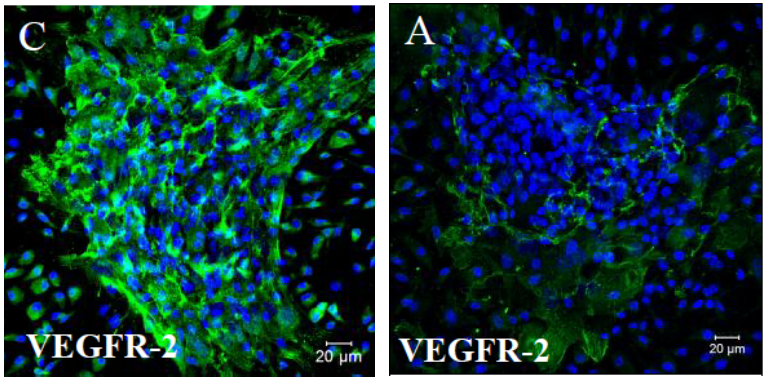


phosphorylcholine

- Soluble under physiological conditions
- non-fouling

M.J. Tiera et al., Biomacromolecules, 2006, 7, 3151-3156.
P. Kujawa et al., Biomacromolecules, 2007, 8, 3169-3176.
S. Mansouri et al., Biomacromolecules, 2011, 12, 585-592.

CH-PC **Fibronectin**

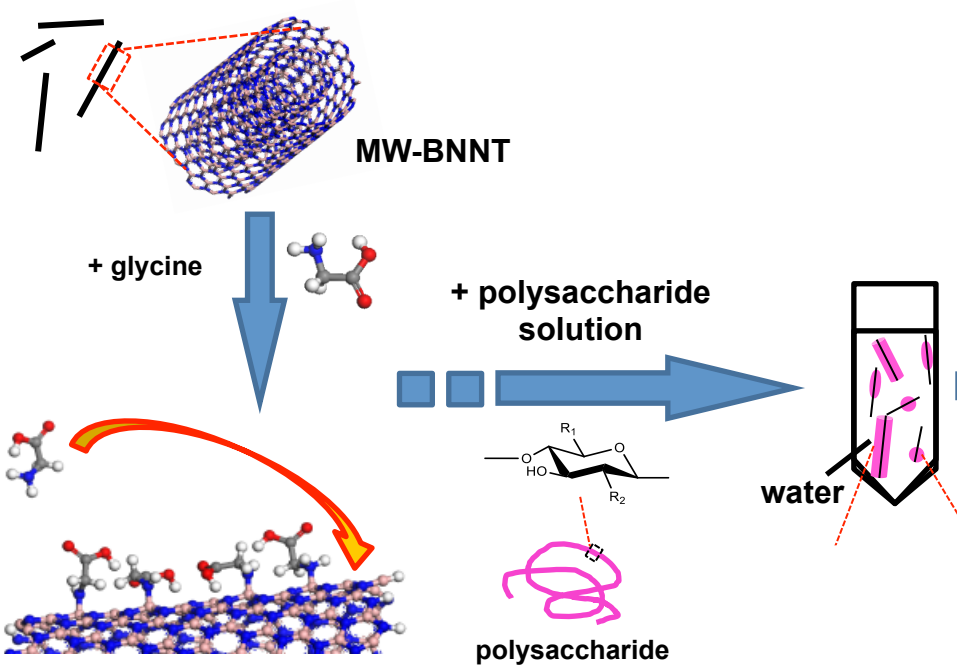


Expression of endothelial cells markers:
VEGFR-2+ (green)

CH-PC forms a compatible matrix for progenitor cells (EPC), allowing amplification and improvement in EPC survival compared to fibronectin.

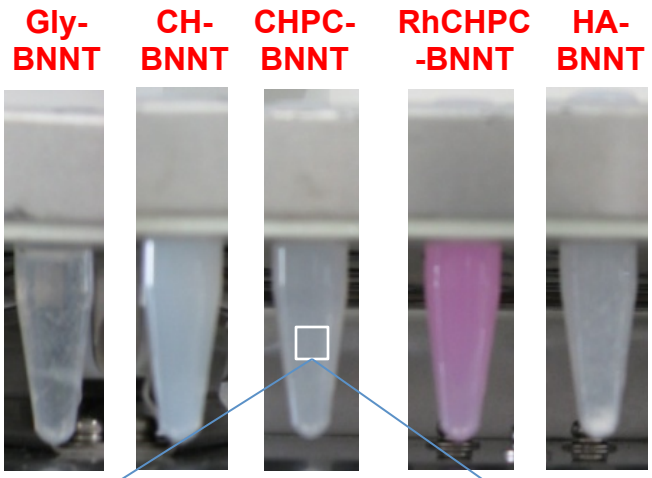
K. Tardif et al., Biomaterials, 2011, 32, 5046-5055.

First attempts….



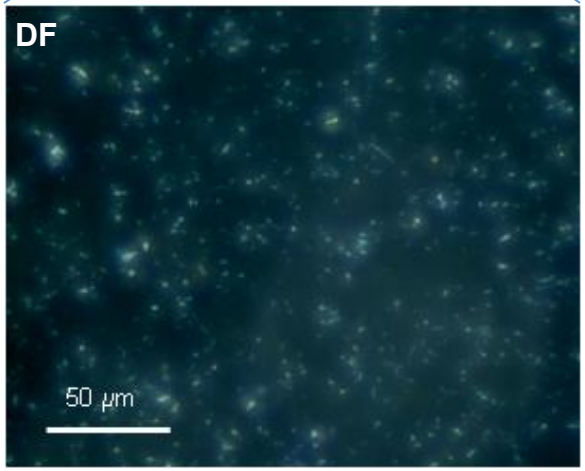
Gly-BNNT added to a polysaccharide solution in water
mild sonication for 30 min

The role of glycine and the dispersion stability of polymer-coated BNNTs

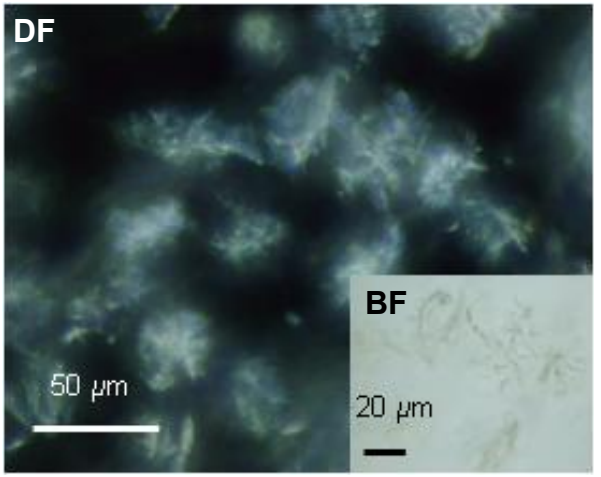


The stability of dispersions after overnight shaking

Aggregation/Bundling



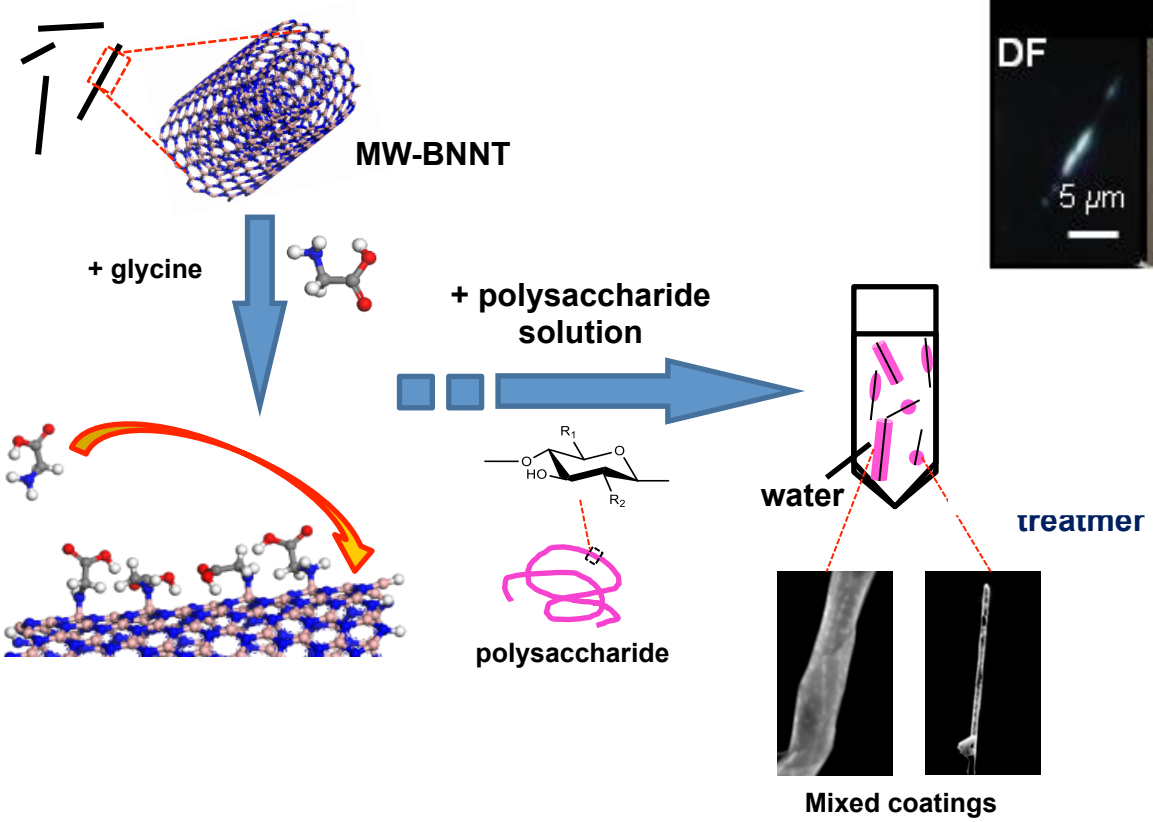
V.S.



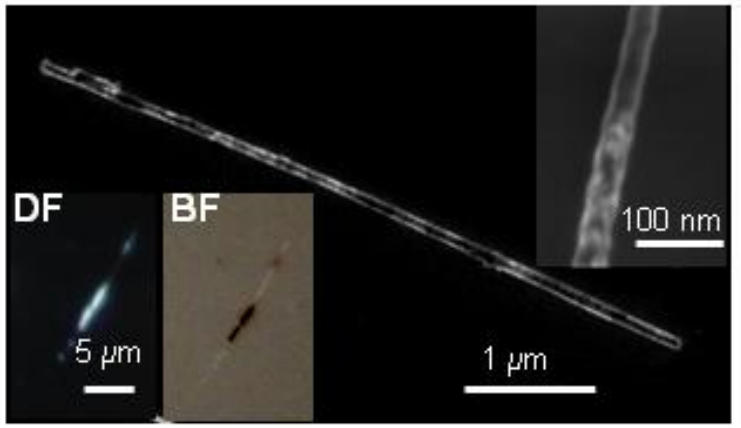
CH-PC onto **BNNT-Gly**

CH-PC onto BNNT
No Glycine

First attempts….



Poorly-coated example



Optical microscope
DF: dark field
BF: bright field

Gly-BNNT added to a polysaccharide solution in water, mild sonication for 30 min

field induced materials control

Liquid-liquid interfacial treatment

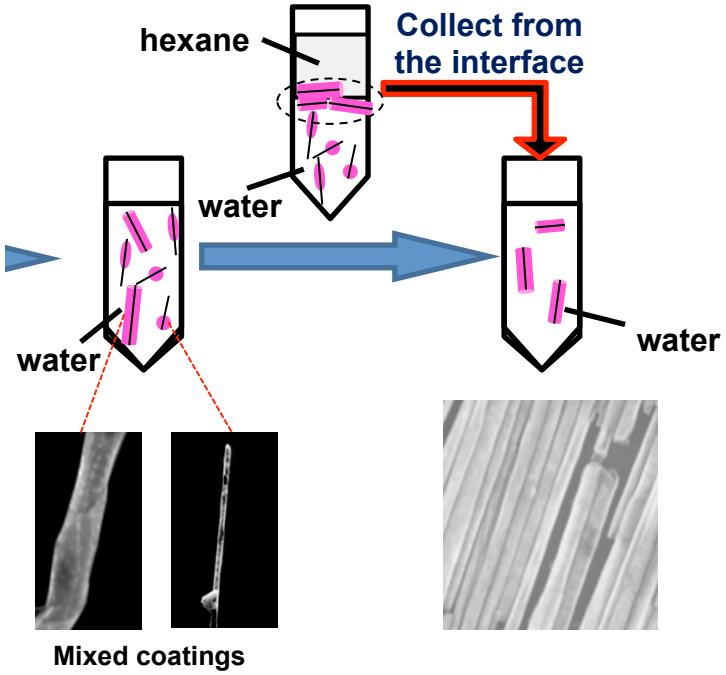
1. Add hexane on top of the polymer-BNNT aqueous dispersion;

2. Sonicate for 5 min

3. Keep still for 30 min

4. Collect the interfacial layer

5. Dry the film

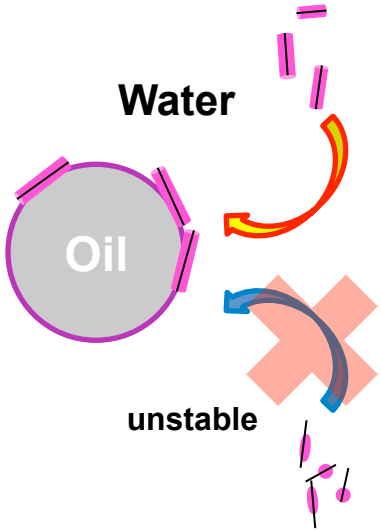


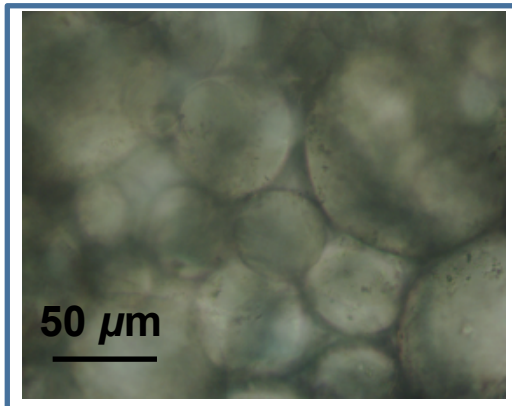
All BNNTs are uniformly-coated after the interfacial treatment

Y-T. R.Lau et al., J. Phys. Chem. C (2013) doi.org/10.1021/jp4073729

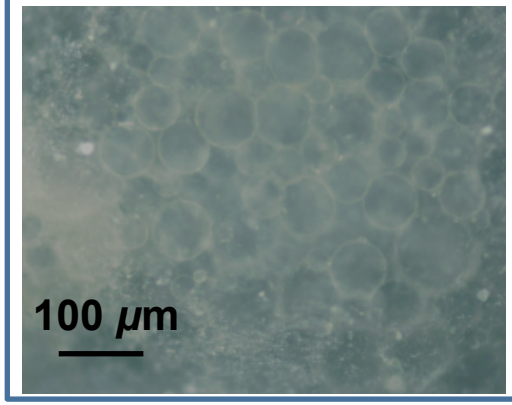
Mechanism of the oil-water interfacial treatment

Polymer-coated BNNT (Pickering agent)

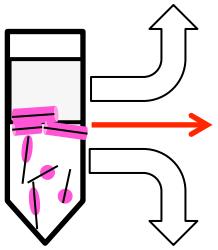




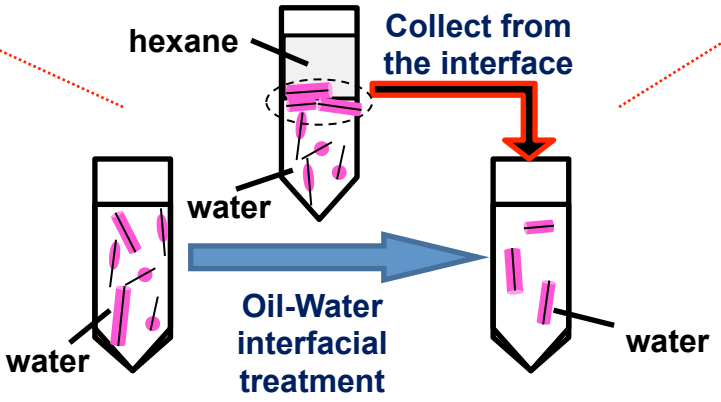
BF



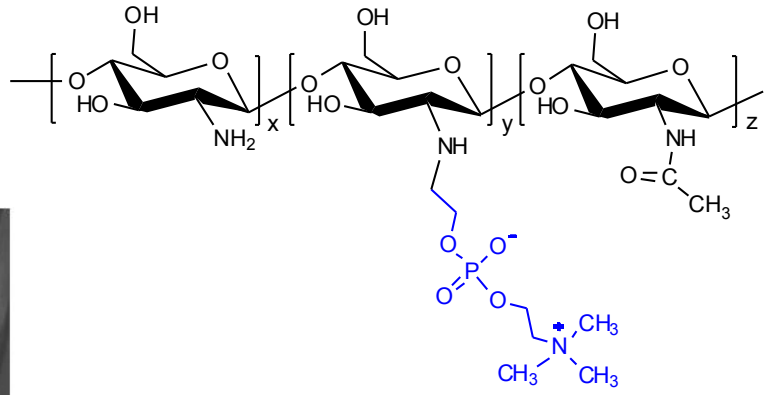
DF

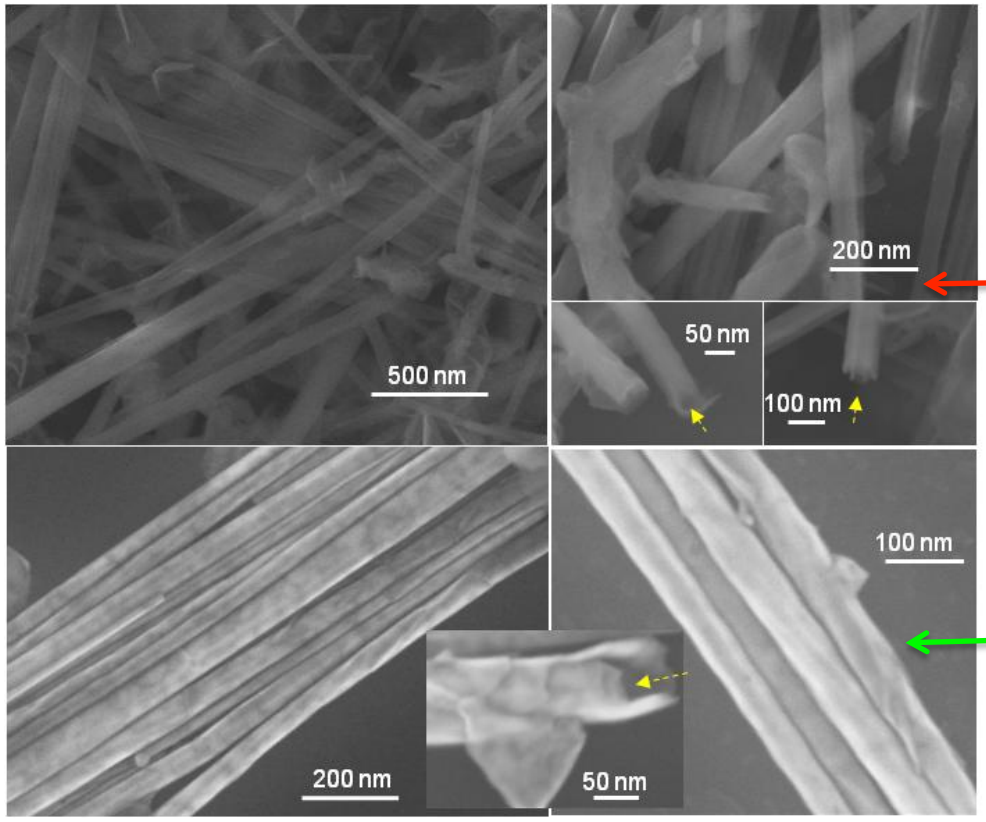


Surface tension of pristine BNNT ~ 20-30 mN/m ≈ hexane (18.4 mN/m). But water is ~72 mN/m!



SEM observation CH-PC-BNNT



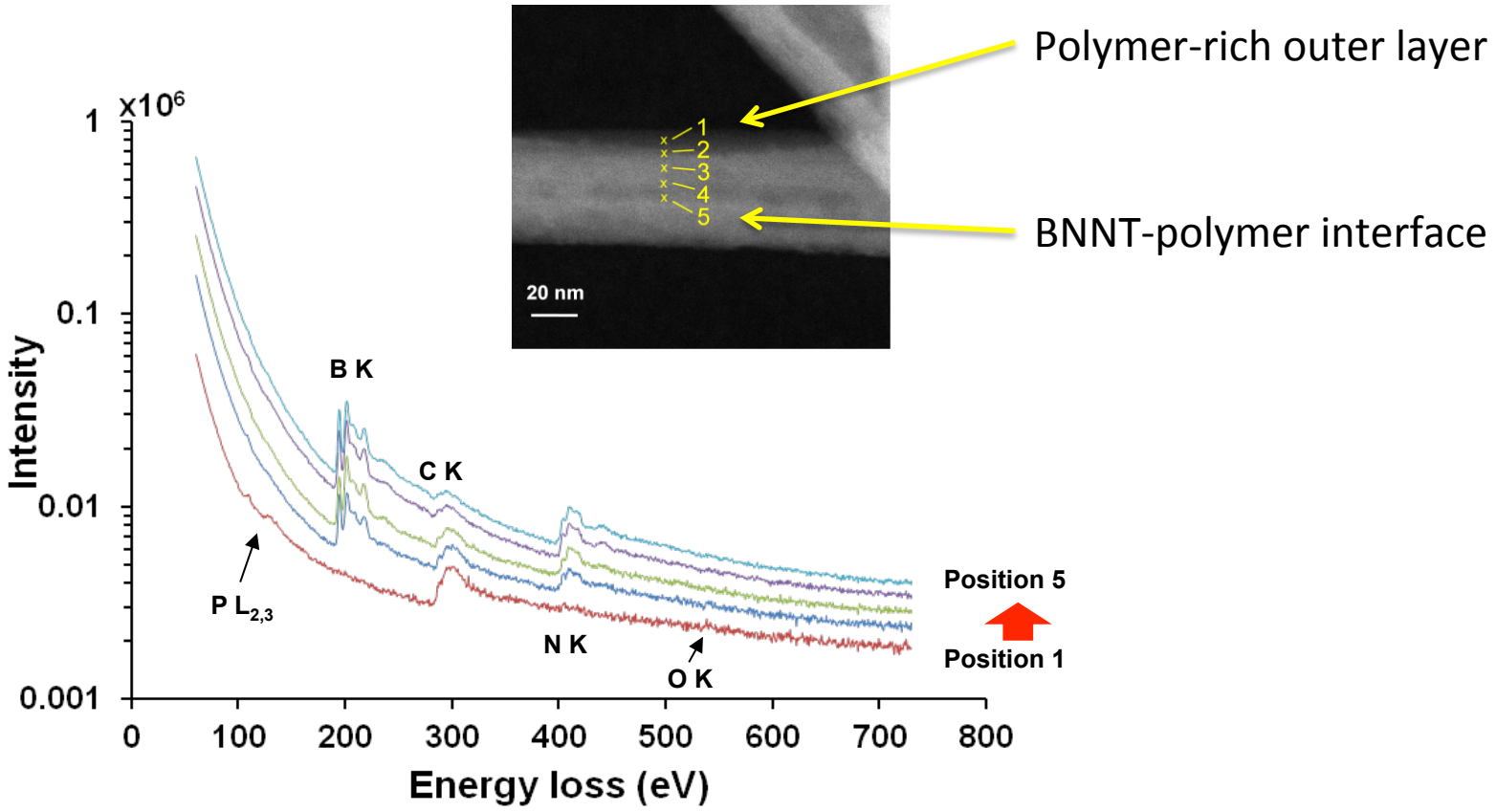


As collected from the interface

Resuspended in water

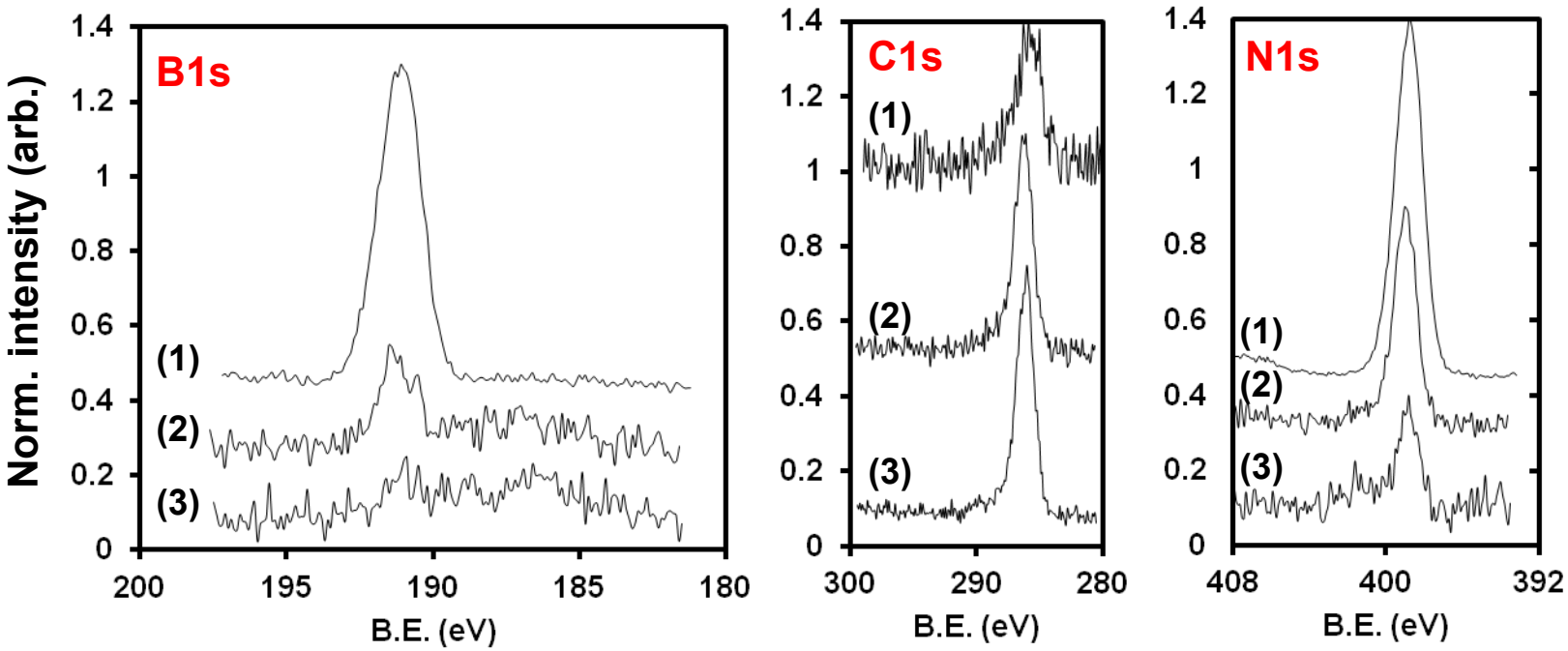
(dried prior to SEM imaging)

EELS line profiling of the exterior polymer (CH-PC) coating on the BNNTs



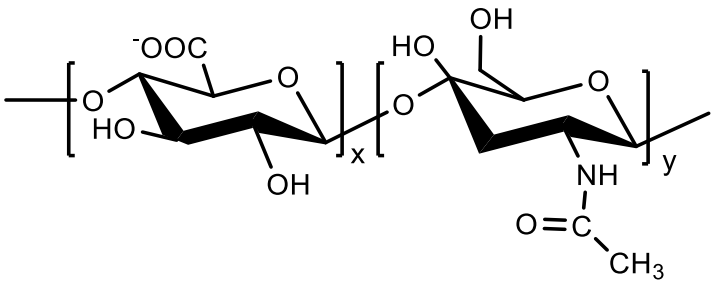
Y-T. R.Lau et al., J. Phys. Chem. C (2013) doi.org/10.1021/jp4073729

XPS confirmation of the exterior polymer coating with full coverage on BNNTs

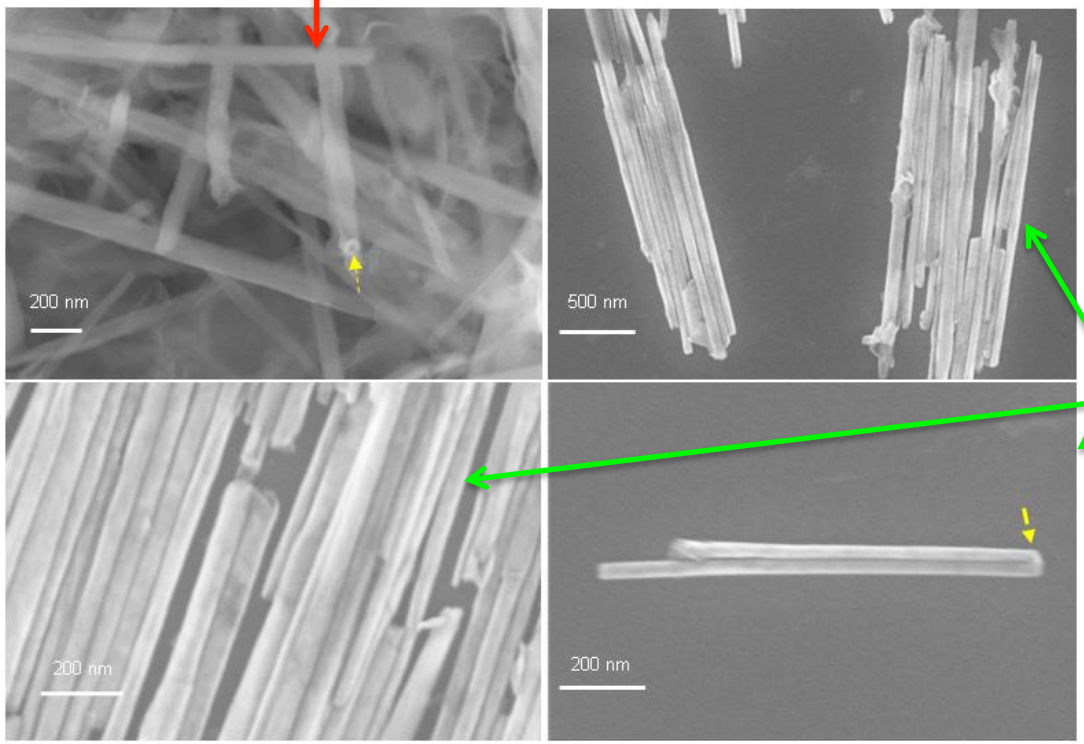


(1) Pristine BNNTs
(2) Crude CH-PC-BNNTs (before oil-water interfacial treatment)
(3) Purified CH-PC-BNNTs (after oil-water interfacial treatment)

SEM observation HA-BNNT



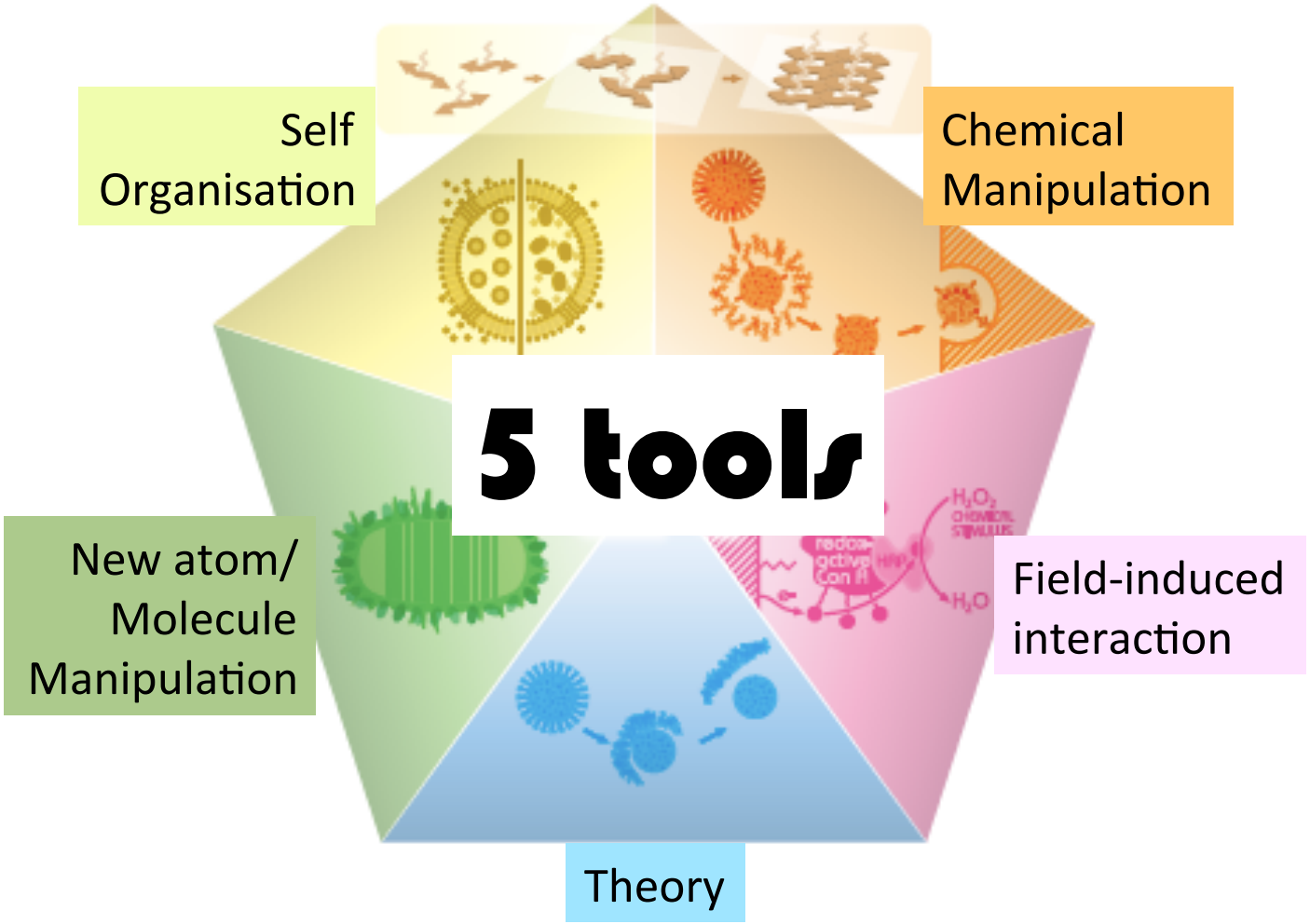
As collected from the interface



Hyaluronic acid (Polyanion)

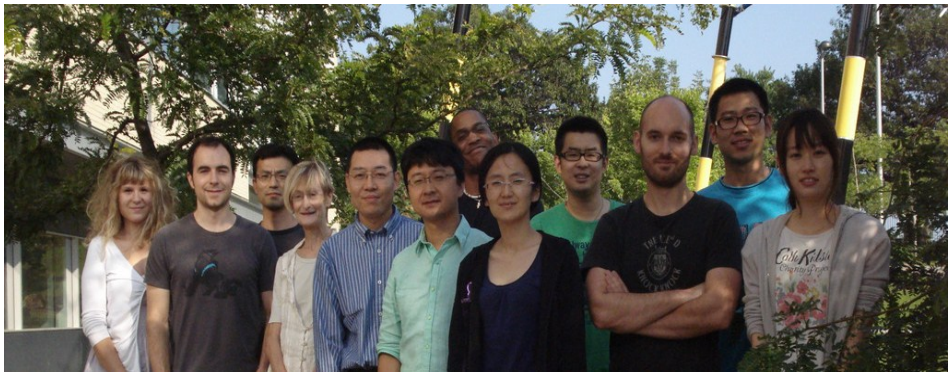
Resuspended in water

Materials Nanoarchitectonics



Acknowledgements

in Montreal, Canada

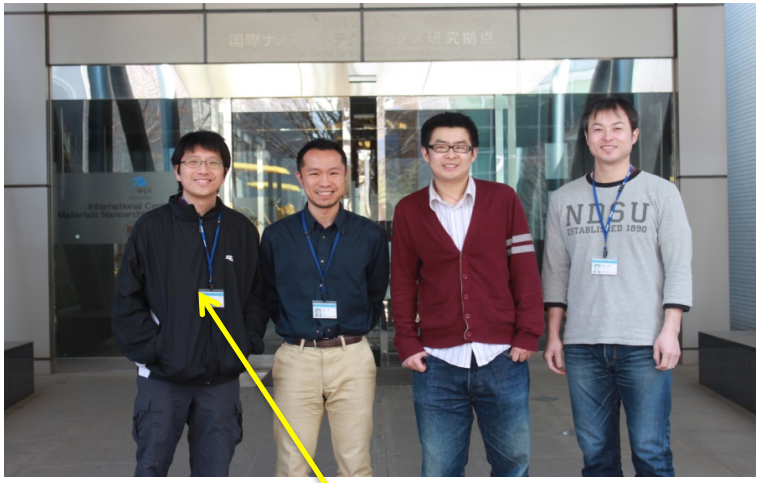


Université de Montréal

Natural Sciences and Engineering Research Council of Canada

Conseil de recherches en sciences naturelles et en génie du Canada

in Tsukuba, Japan



Y-T. R. Lau

MANA

wpi

NIMS National Institute for Materials Science