

Self-Assemblies Bridging the Length Scales for Biomimetic and Functional Materials

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**Centre of Excellence in
Molecular Engineering of Biosynthetic Hybrid Material
Research**

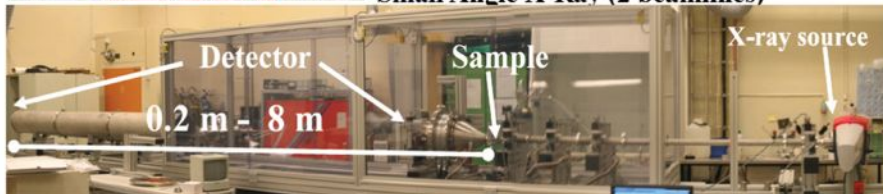
Hierarchical self-assemblies and biomimetics



Nanomicroscopy Center and Nanopoli



Small Angle X-Ray (2 beamlines)

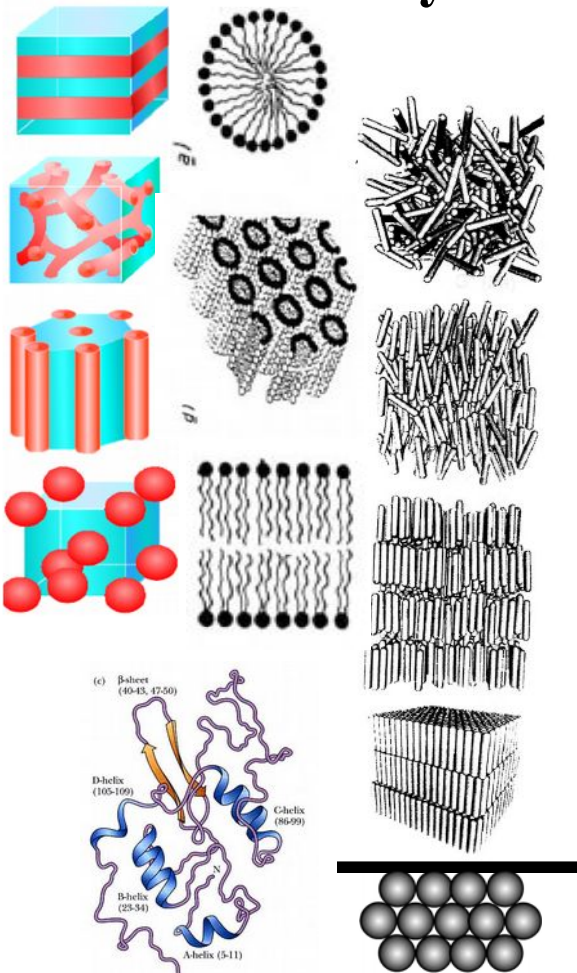


Liq-He cryo-TEM JEOL 3200FSC



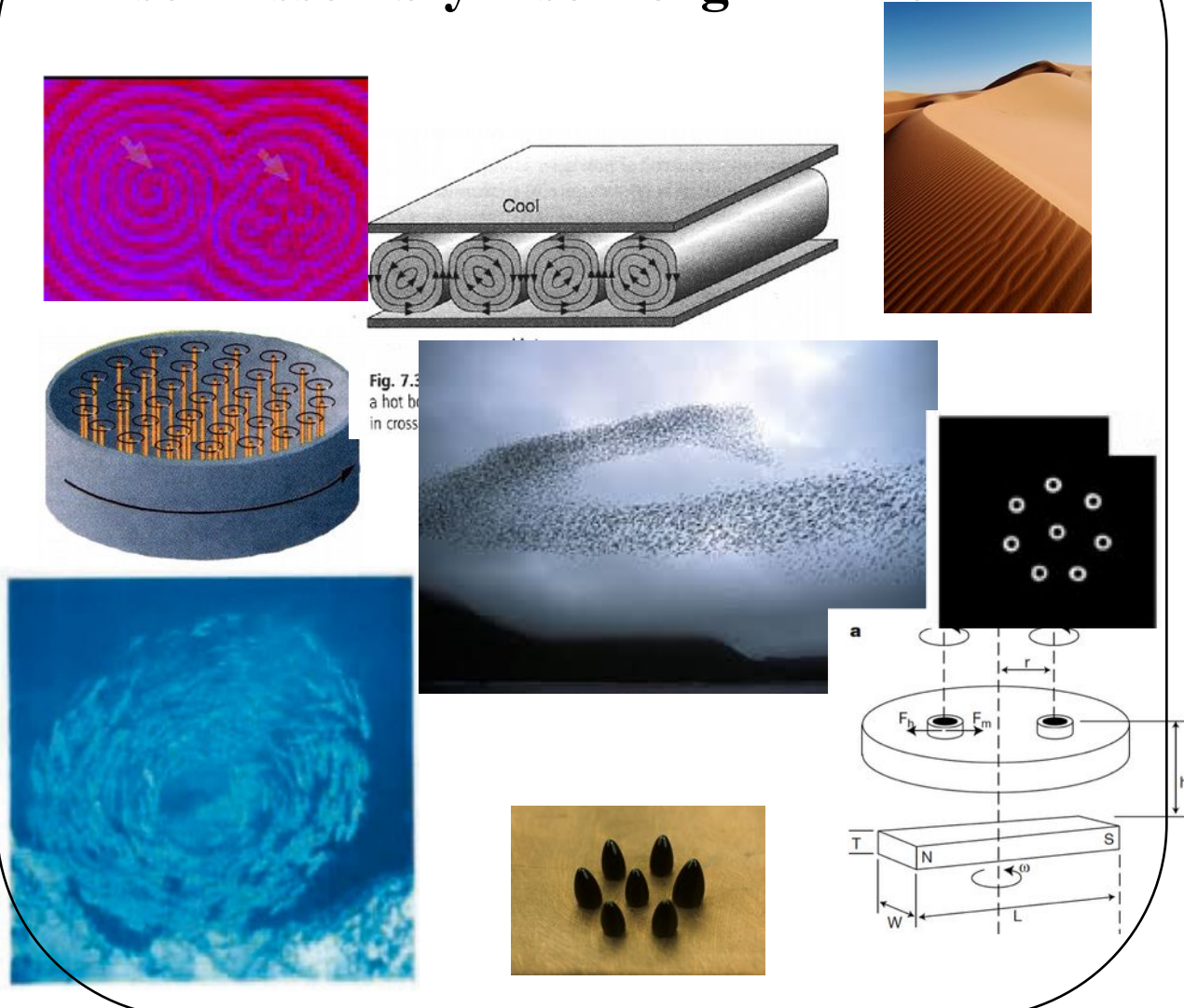
Ruokolainen

Equilibrium self-assembly



Local structures vs **monodomain** structures
 Primary-secondary-tertiary etc structures

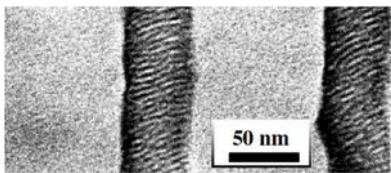
Dissipative out-of-equilibrium self-assembly = self-organization



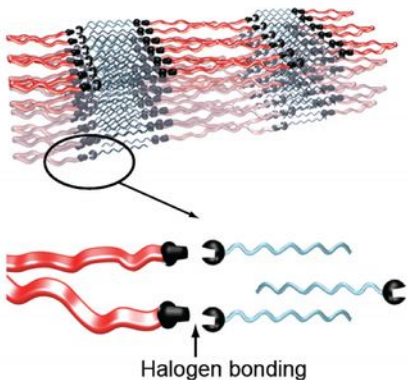
Grzybowski, Stone, Whitesides, *Nature* 405 1033 2000
 Whitesides, Grzybowski, *Science* 295, 2418 2002
 Timonen, Latikka, Leibler, Ras, Ikkala, *Science* 341, 253 2013

Supramolecular (hierarchical) self-assembly of polymers

Hydrogen bond



Halogen bond



Science 1998

Science 2002

Nature Mat. 2004

Angew Chem 2010

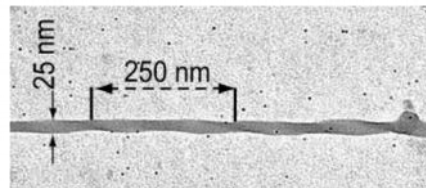
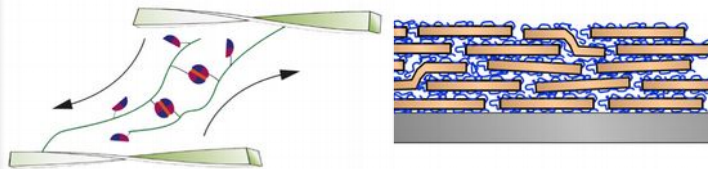
Nature Comm 2014

Nat Comm 2016

Chemistry 2017

Biomimetic materials

Sacrificial bonds Nacre mimics



Amyloids

Angew Chem 2010

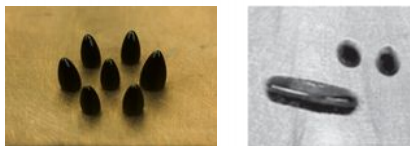
Nano Lett 2010

Angew Chem 2014

Nature Comm 2015

Adv Funct Mat 2017

Dynamic **dissipative** self-assemblies



Science 2013

Nature Comm 2013

Functional nanocelluloses



Photocatalytic
Semiconducting
Conducting

Transparent

Sensing

Magnetic

Superhydrophobic

Oil repulsive

Oil spill absorbing

Fibers

Soft Matter 2008

Nature Nano 2010

ACS Nano 2011

Adv Funct Mat 2011

Adv Mat 2013

Adv Funct Mat 2015

Centre of Excellence in Molecular Engineering of Biosynthetic Hybrid Materials Research

Self-Assembled Materials Aalto, Applied Physics

Prof. Olli Ikkala, director



Protein Genetic Engineering for Materials Aalto, Biotechnology and Chemical tech.

Prof. Markus Linder,
vice-director

**Biological concepts for the
next generation biomimetic materials science**

Biological Production and Synthetic Biology VTT Industrial Biotechnology

Prof. Merja
Penttilä



Plant Cells for Materials Aalto, Forest Products Technology

Prof. Orlando Rojas



Equilibrium self-assemblies **bridging the length scales**

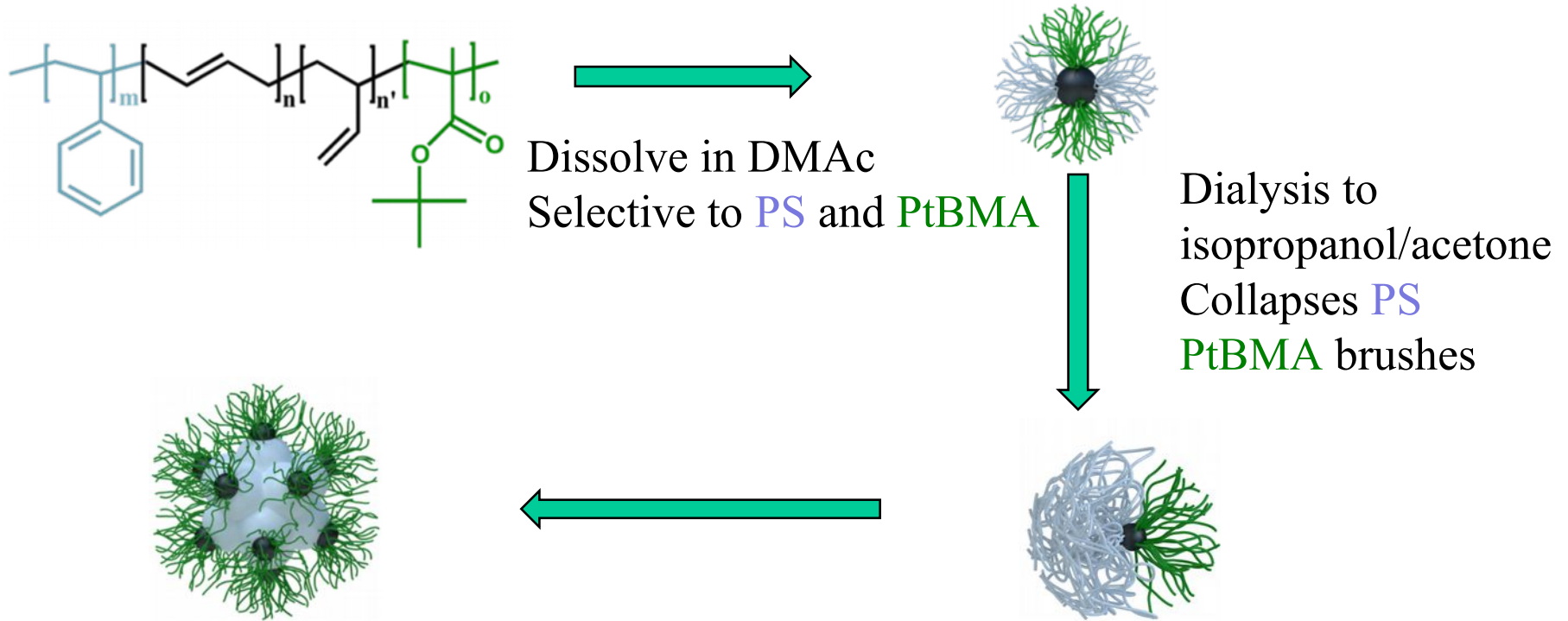
Single type of structural unit forming sequences of higher order structures

Can be challenging to achieve and understand

Examples



Example: ABC triblock terpolymer self-assemblies

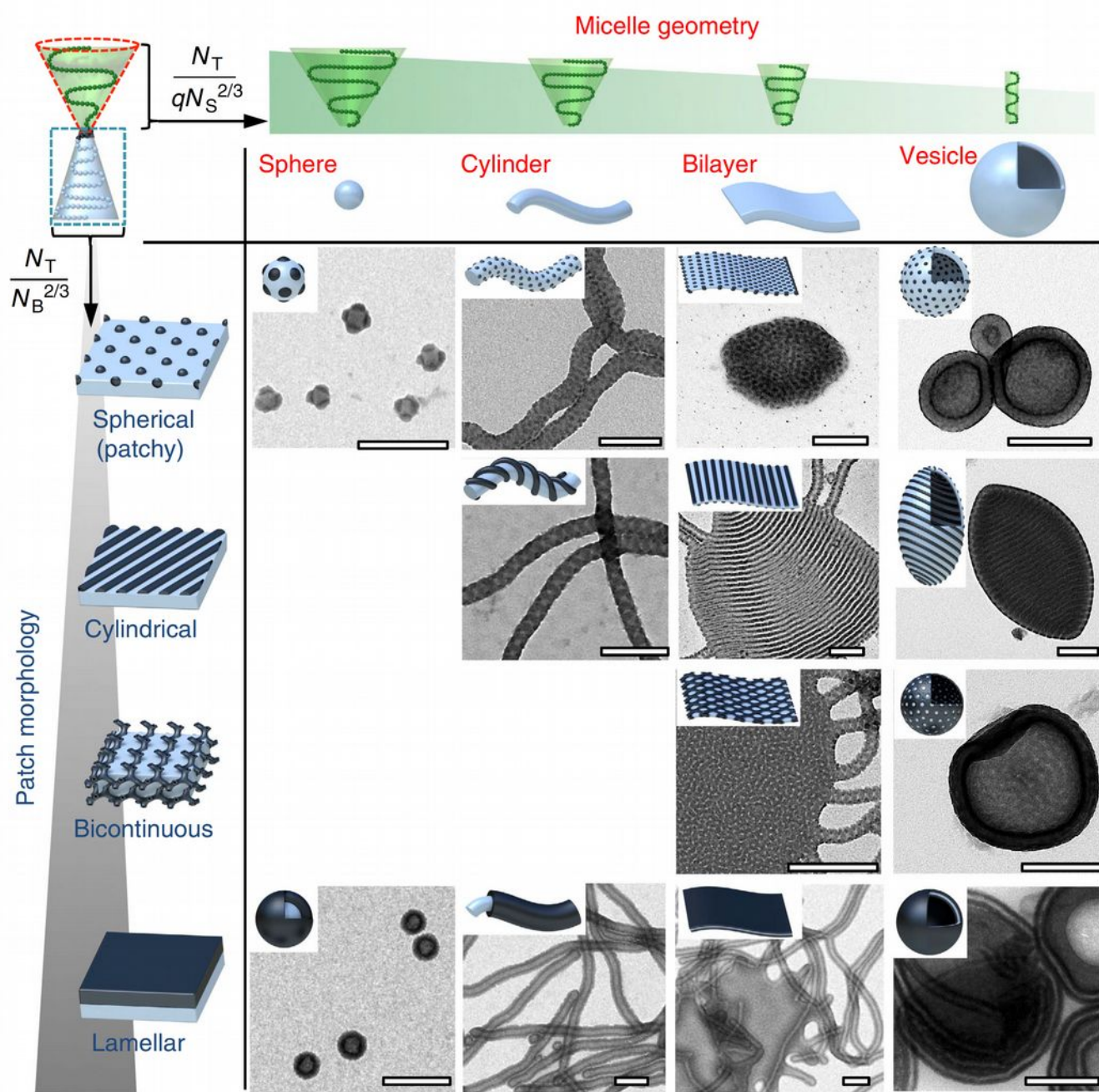
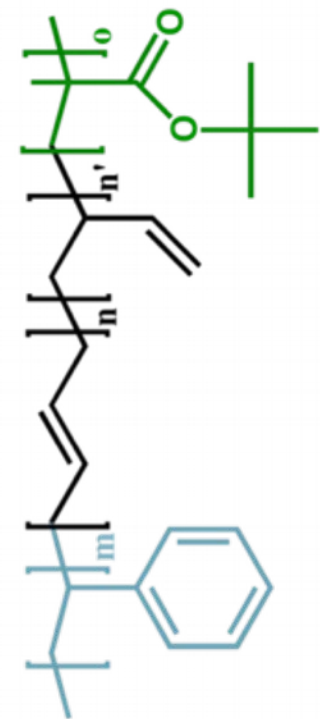


Well-defined patchy colloids

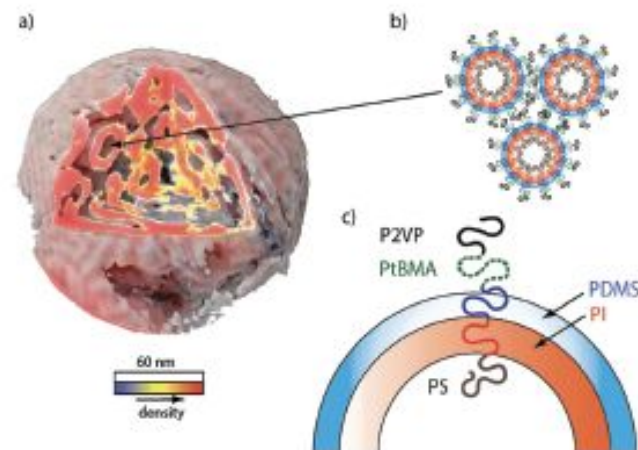
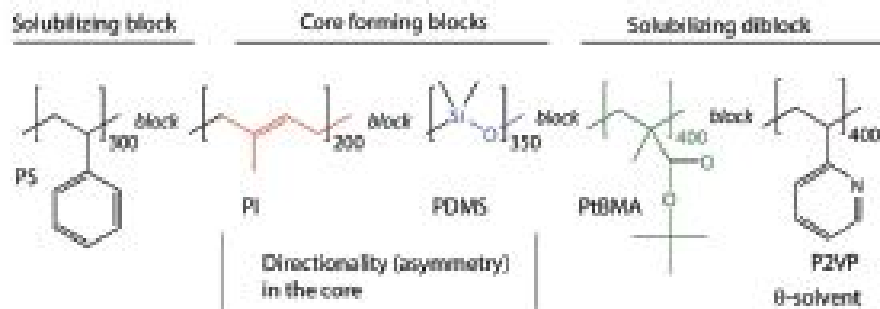
Gröschel, Walther, Löblich, Schacher,
Schmalz,
Müller, *Nature* 2013, **503**, 247



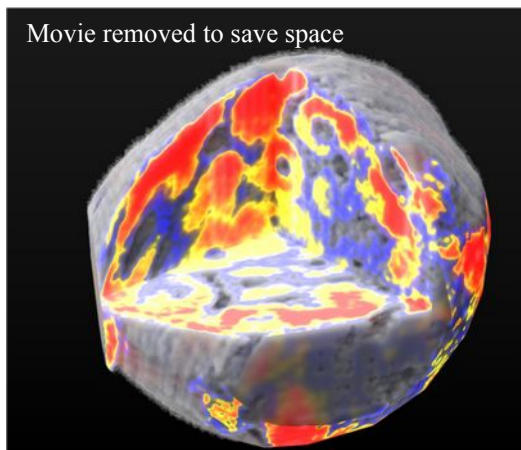
Generalized



Uncommon hierarchies, illustrating generic challenges to characterize future complex self-assemblies



Movie removed to save space



Haataja, Houbenov, Aseyev, Fragouli, Iatrou, Sougrat, Hadjichristidis, Ikkala
Chem. Comm. 2018, **54**, 1085

- **Early concepts for directed/templated self-assembly**
 - **(Block co)polymer templated oligomers**
 - *Nat Comm 2014, Chem 2017*
- **Colloid templated polymers**
 - **Nacre and nacre-mimetics by self-assembly**
 - *Adv Funct Mater 2016, Adv Sci 2017*
 - **Nanocellulose templated block copolymers**
 - *ACS Macro Letters 2016*
- **Metal nanocluster self-assembly**
 - **2D self-assembly**
 - **Virus-capsid like self-assembly of**
 - *Angew Chem 2016, 2017*
- **Nanocellulose as a transparent films or strong light scatterer**
 - *Adv Funct Mater 2015, Adv Mater 2018*
- **Block copolymeric photonic crystal as structural color**
 - **”Superstretched” block copolymers**
 - *Nat Mater 2004, ACS Nano 2018*

Sequential directed/templated self-assemblies

- Hierarchical equilibrium self-assemblies

- Colloidal self-assembly for length scales > 100 nm



Template/direct

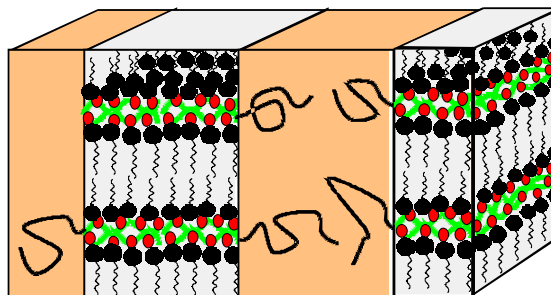
- Polymers and macromolecules self-assembly for 10 nm 100 nm



Template/direct

- Small molecular self-assembly for < 10 nm
- By supramolecular/supracolloidal construction principles

These early works inspired for **sequentially templated self-assemblies**

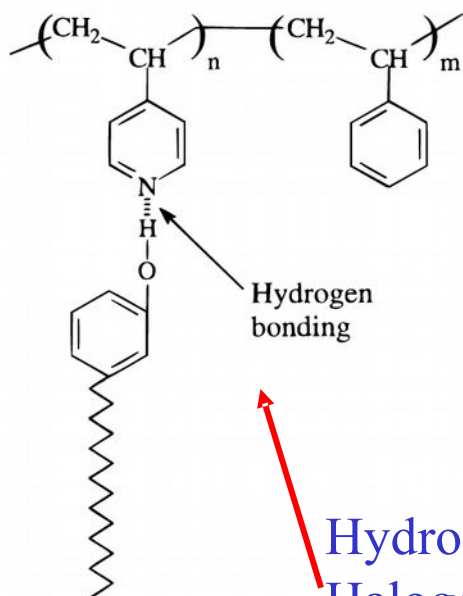


Switchable
and
tunable
photonic
crystals

Science, 280, 557, 1998

Science, 295 2407, 2002

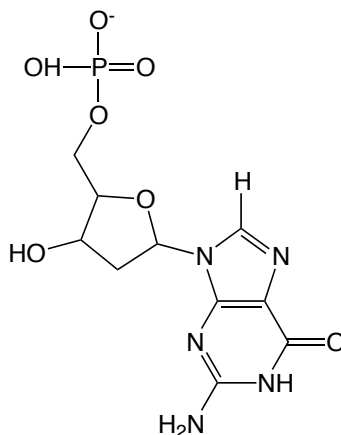
Nature Materials, 3, 872, 2004



Hydrogen bond
Halogen bond
Coordination bond
Ionic bond

Diblock copolymer
Triblock copolymer
Block copolypeptide

Surfactant
Liquid crystal mesogen
Supramolecular motif

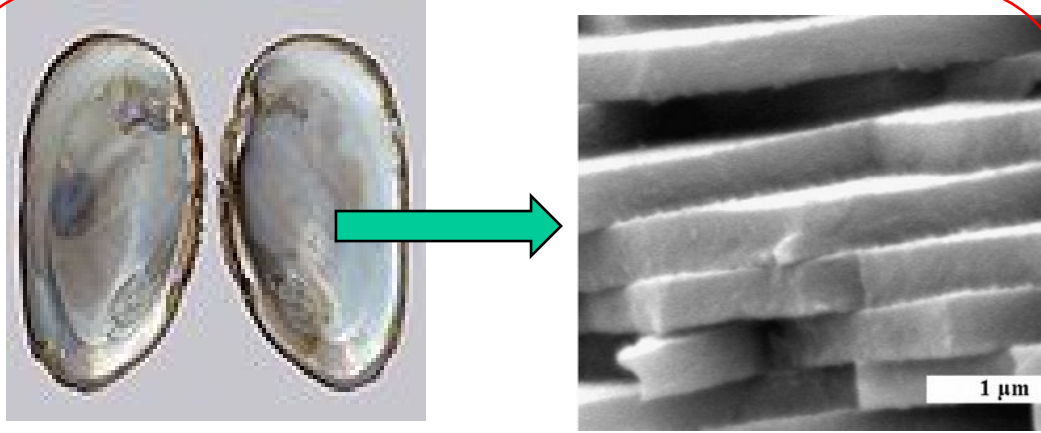


Optical properties
Electrical properties
Porosity
Templating nanoparticles

- **Early concepts for directed/templated self-assembly**
 - **(Block co)polymer templated oligomers**
 - *Nat Comm 2014, Chem 2017*
- **Colloid templated polymers**
 - **Nacre and nacre-mimetics by self-assembly**
 - *Adv Funct Mater 2016, Adv Sci 2017*
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 - **”Superstretched” block copolymers**
 - *Nat Mater 2004, ACS Nano 2018*

Pearl of nacre as a model for nanocomposite materials with all properties excellent

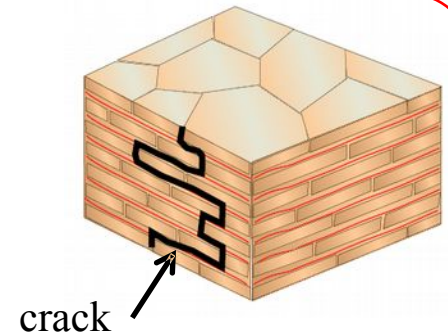
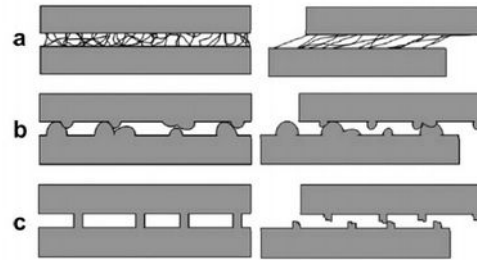
- Stiff
 - Modulus 40-70 GPa
 - vs Aluminium alloy
- Strong
 - Strength 80-130 MPa
 - vs cast iron
- Extremely tough, as wet
- Lightweight 2.8 g/cm³
- But expensive



- Aragonite (CaCO₃) plates (**95 vol% = high**)
 - Thickness 0.5 μm, width 20-30 μm
- Polymer glue in between
 - Thin layers (only!)

Why

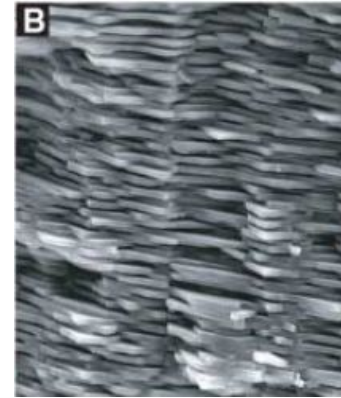
- Thin reinforcing platelets reinforce
- Several energy dissipation mechanisms in deformation



Mimicking nacre

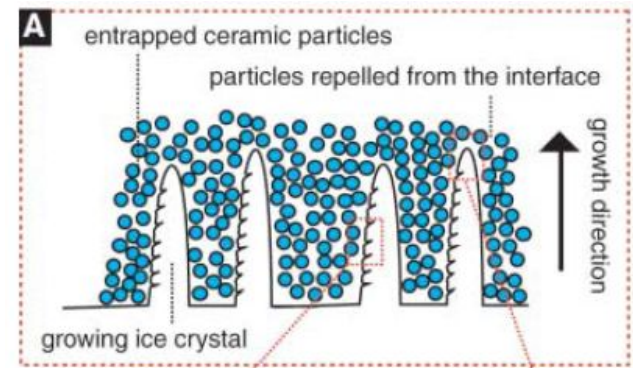
- Sequential depositions of inorganic platelets and polymers
 - e.g. layer-by-layer deposition
 - Sequential spin coatings

Kotov et al, *Nature Mat.* 2003 2 413
Kotov et al, *Science* 2007 318 80
Stuart et al, *Science* 2008 319 1069
Stuart et al, *Science* 2012 335 199



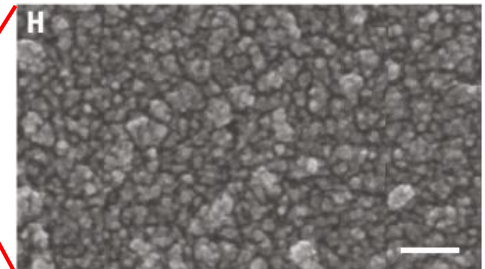
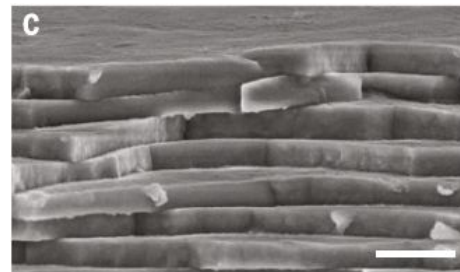
- Ice templating
 - Control freezing of water containing ceramic particles

Deville et al *Science* 2006 311 515
Ritchie et al, *Science* 2008 322 1516



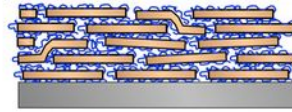
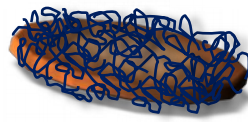
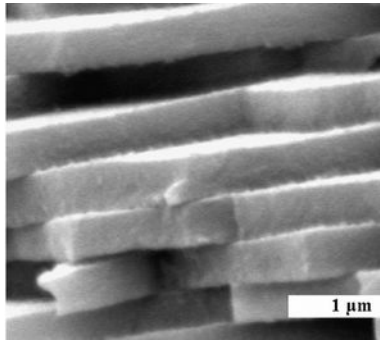
- Mimicking biomineralization

Cölfen, Yu et al, *Science* 2016, 354, 107

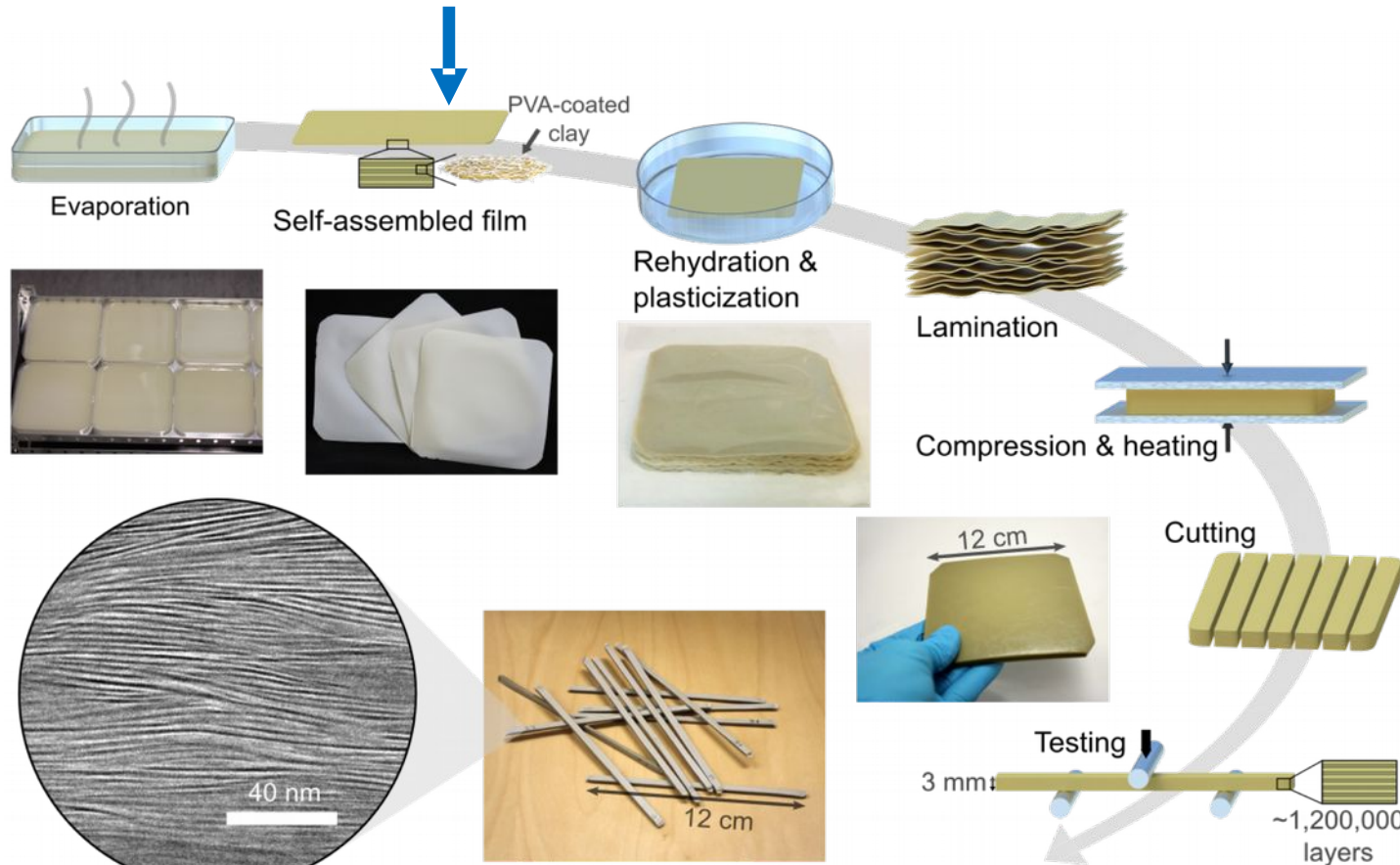


Biomimetic nanocomposites: strong and tough

Nacre



Clay + polyvinyl alcohol



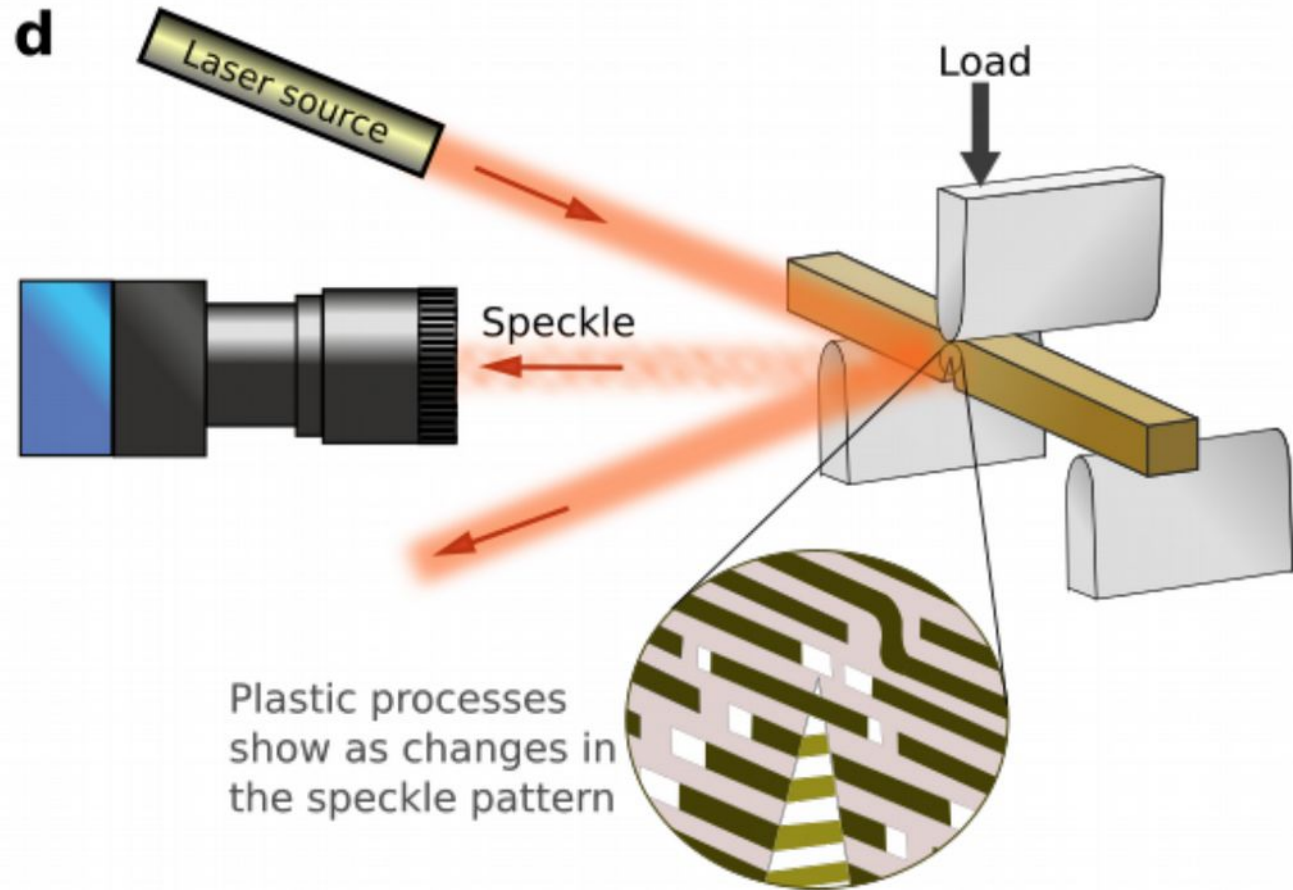
$$K_{IC} = 4-10 \text{ MPa m}^{1/2}$$

$$K_{IC} = 3.4 \text{ MPa m}^{1/2}$$

Morits, Sorvari, Verho, Liljeström, Kostianen, Gröschel, Ikkala, *Adv Funct Mater*, 27, 1605378, 2017

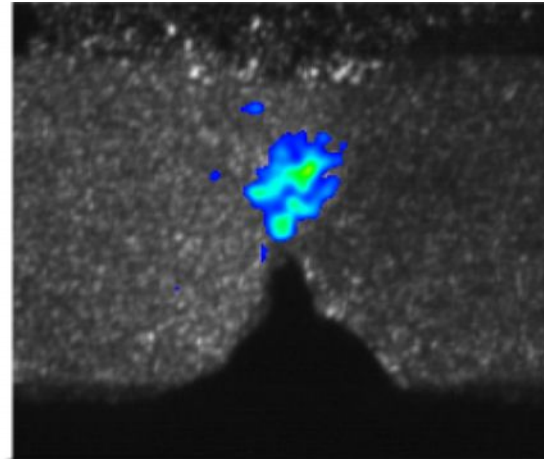
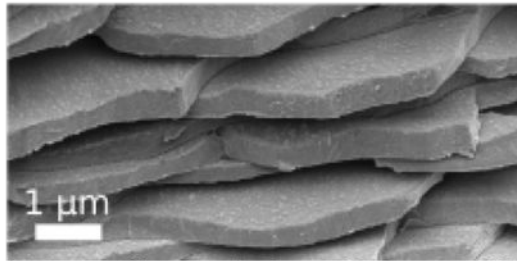
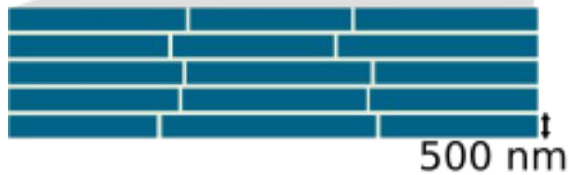


Imaging **pre-fracture dissipative** processes of the biological and biomimetic nanocomposites by laser speckle imaging



Imaging **pre-fracture dissipative** processes of the biological and biomimetic nanocomposites by laser speckle imaging

Red abalone

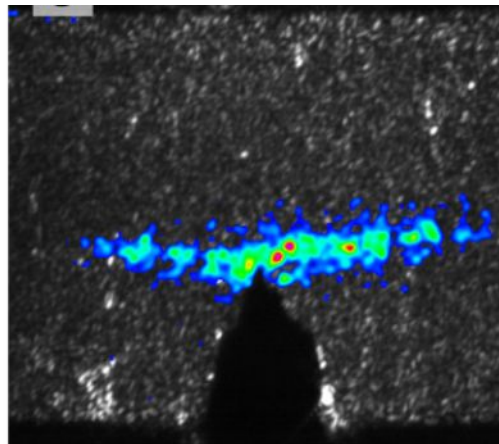
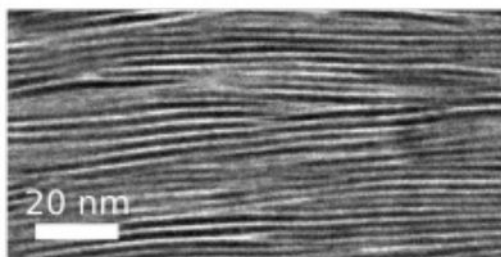
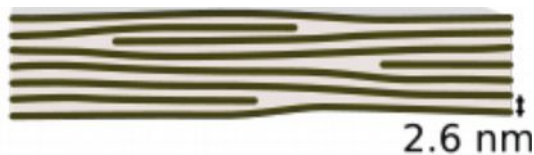


Movies removed to save space

Process zone = 0.17 mm

$$K_{Ic} = 4 - 10 \text{ MPa m}^{1/2}$$

Self-assembled clay-polymer nanocomposite (Morits, *Adv Funct Mat* 2017)



Process zone = 0.06 mm

$$K_{Ic} = 3 - 4 \text{ MPa m}^{1/2}$$

Verho, Karppinen, Gröschel, Ikkala, *Adv Sci*, 2017 1700635

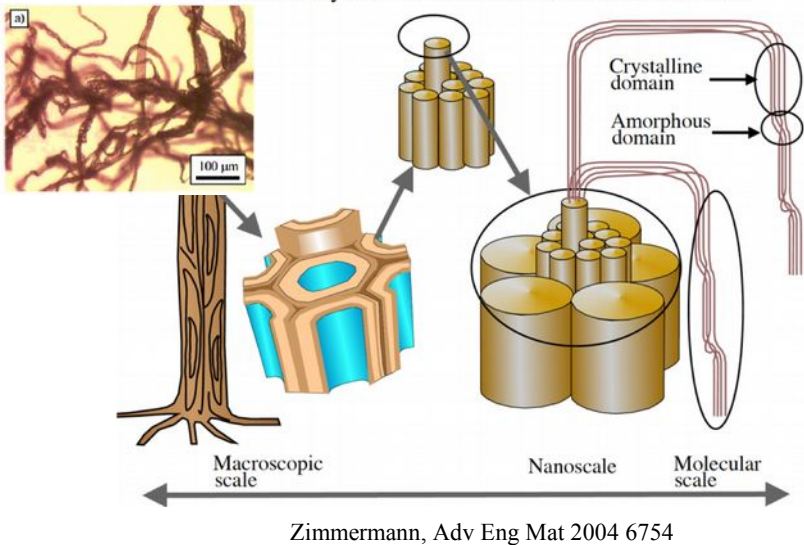
Nanocellulose brushes

New structured colloids

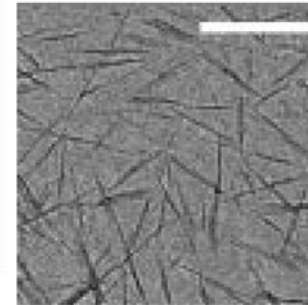
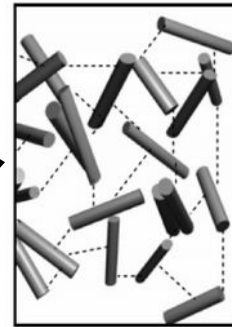
Interface tailoring

Types of (native) nanocelluloses

Wood hierarchy as a source for native cellulose nanofibrils

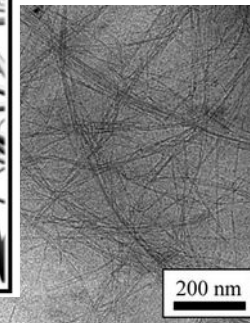
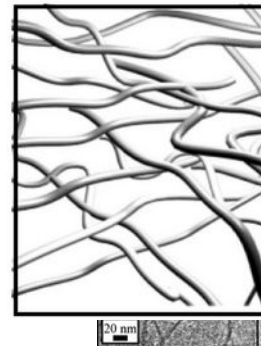


Cellulose nanocrystals (CNC)



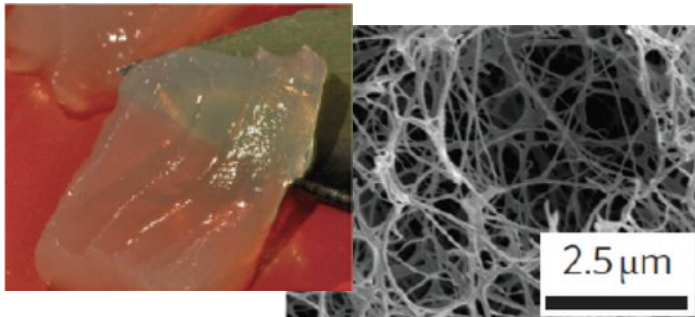
Ordered structures

Cellulose nanofibrils (CNF)



Networks
Percolation

Bacterial cellulose



Klemm, Kramer, Moritz, Lindström, Ankerfors, Gray, Dorris, *Angew. Chem. Int. Ed.* 2011, **50**, 5438

Kontturi, Laaksonen, Linder, Nonappa, Gröschel, Rojas, Ikkala, *Adv Mat* 2018 1703779

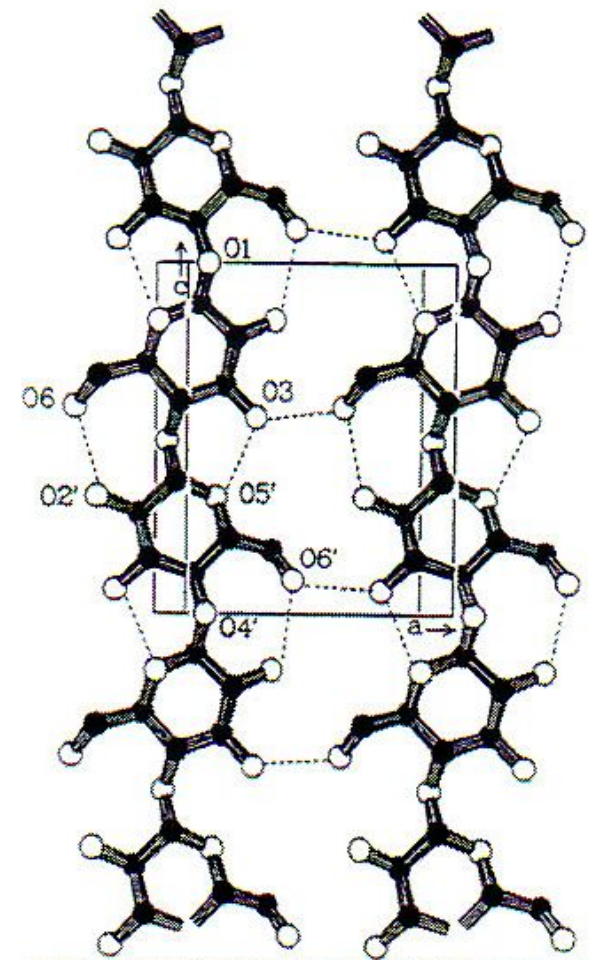
Berglund, Burgert *Adv Mater* 2018 1704285

Native nanocelluloses:

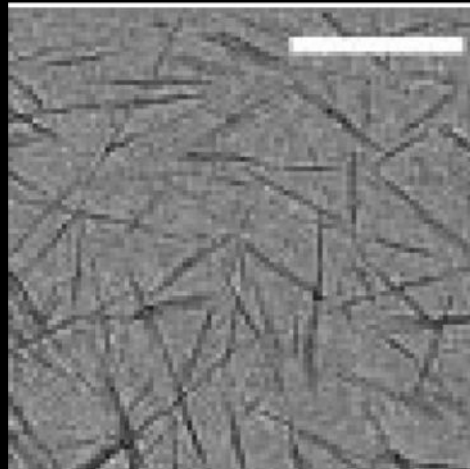
- Native cellulose I crystal modification
 - Parallel hydrogen bonded chains
- Modulus up to ca. 130-150 GPa
 - Iwamoto, Kai, Isogai, Iwata,
Biomacromolecules 2009 10 2571
- Strength in the 2-6 GPa range
 - Saito, Kuramae, Wohlert, Berglund, Isogai,
Biomacromolecules 2013, 14, 248
- Very good mechanical properties !

Platform for chemical modification

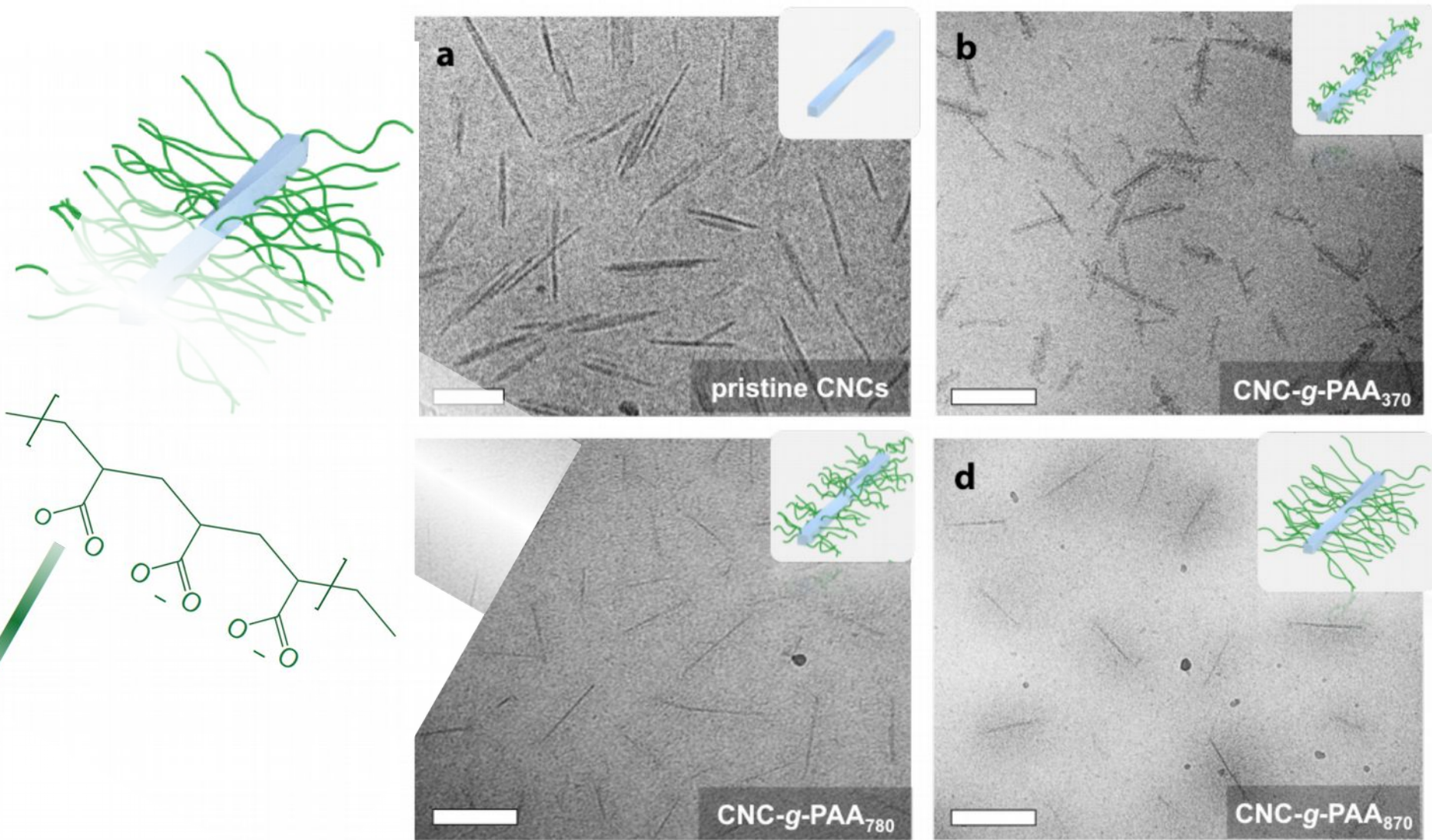
Cellulose I crystal



Nanocellulose directs block copolymer self-assembly



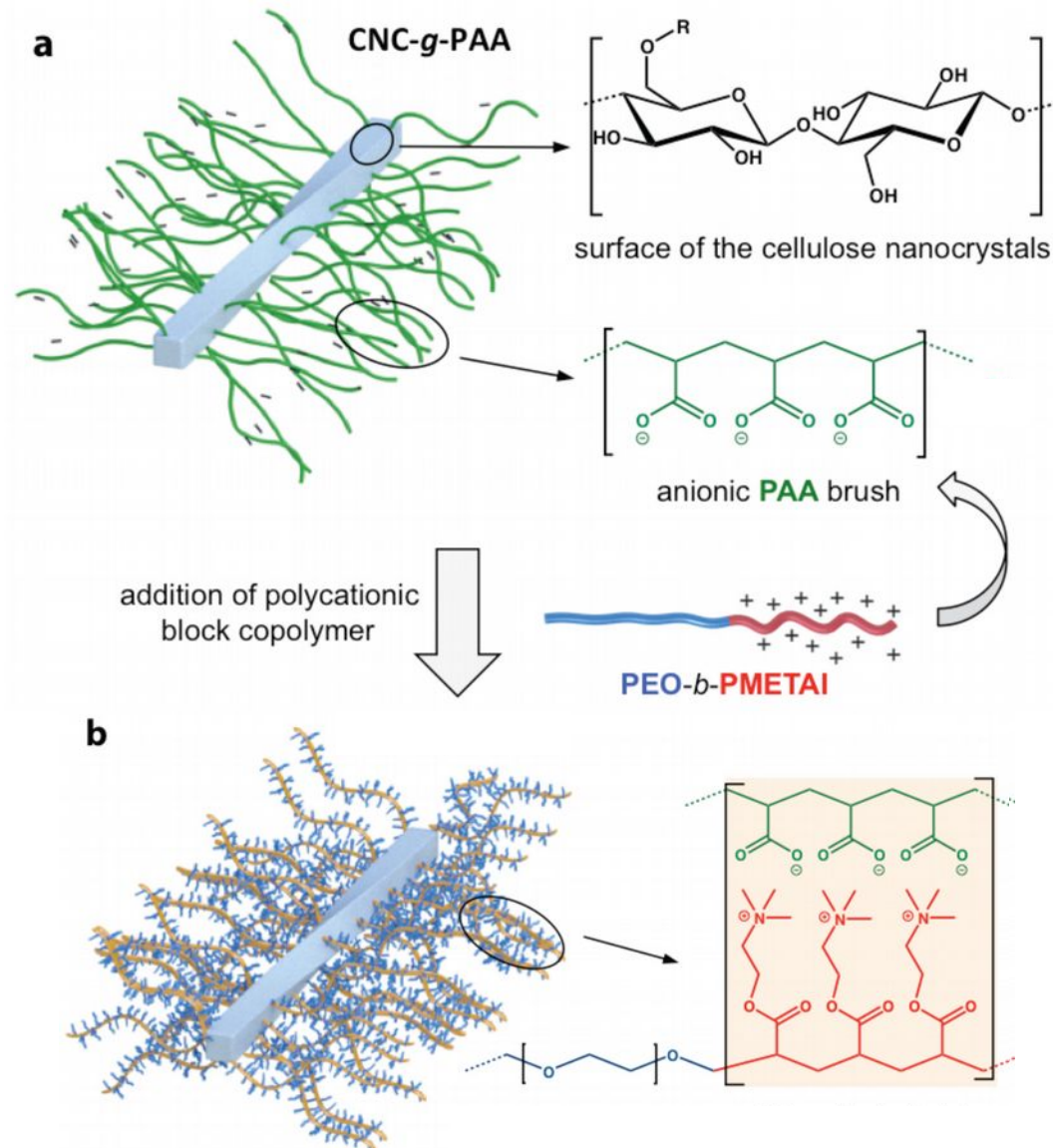
Polyacrylic acid brushes on cellulose nanocrystals



Majoinen, Walther, McKee, Kontturi, Aseyev, Malho, Ruokolainen, Ikkala, *Biomacromolecules*, **12**, 2997, 2011

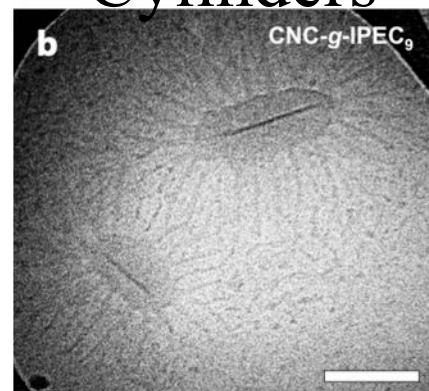
Malho, Morits, **Löblich**, Nonappa, Majoinen, Schacher, Ikkala, **Gröschel**, *ACS Macro Lett* 2016 **5** 185.

Double hydrophilic diblock copolymer ionically complexed to anionic brush decorated cellulose nanocrystals

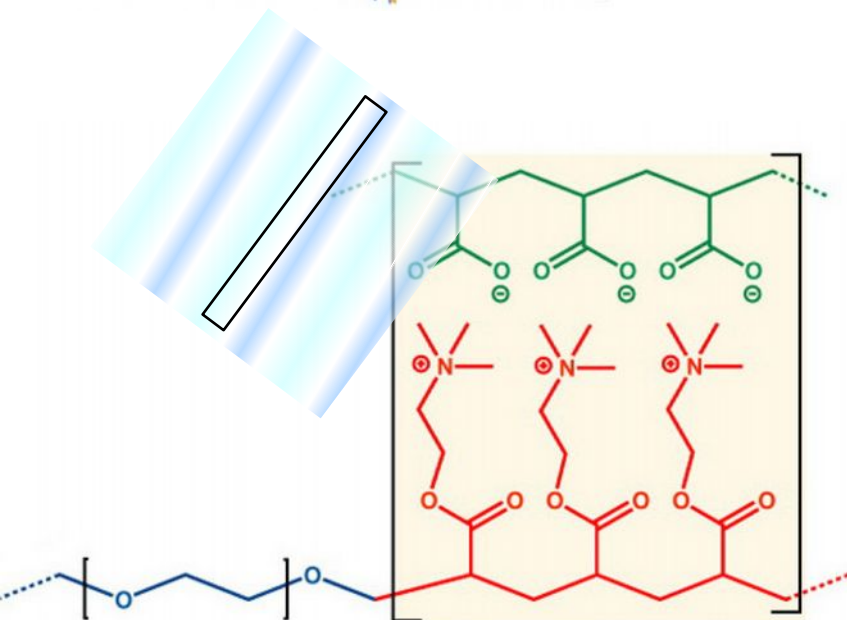
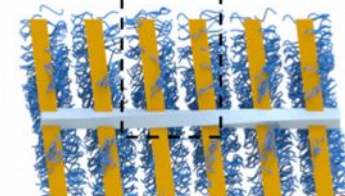
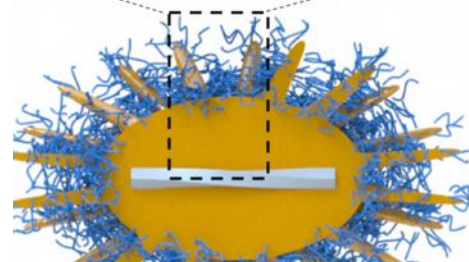
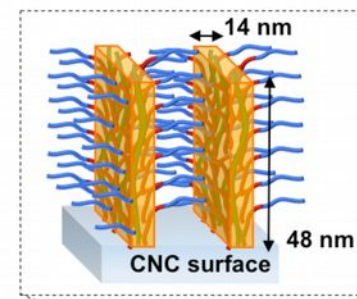
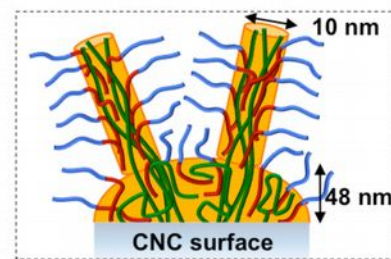
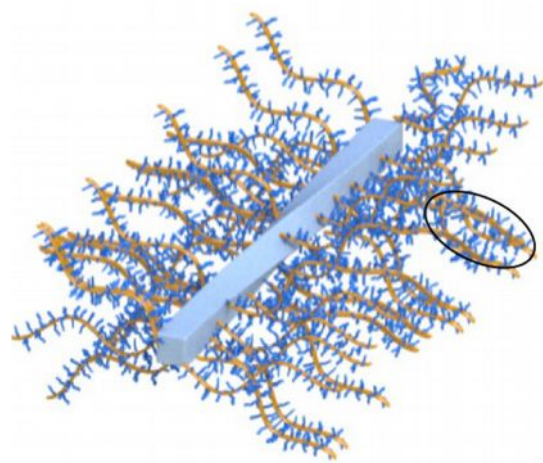
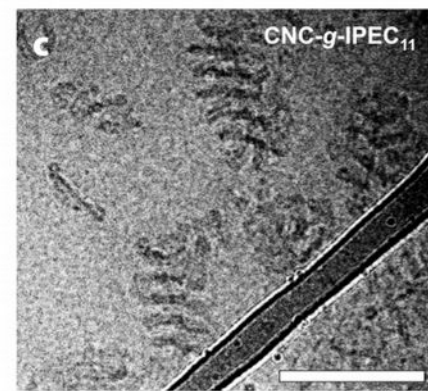


Self-assemblies on CNC surfaces

Cylinders

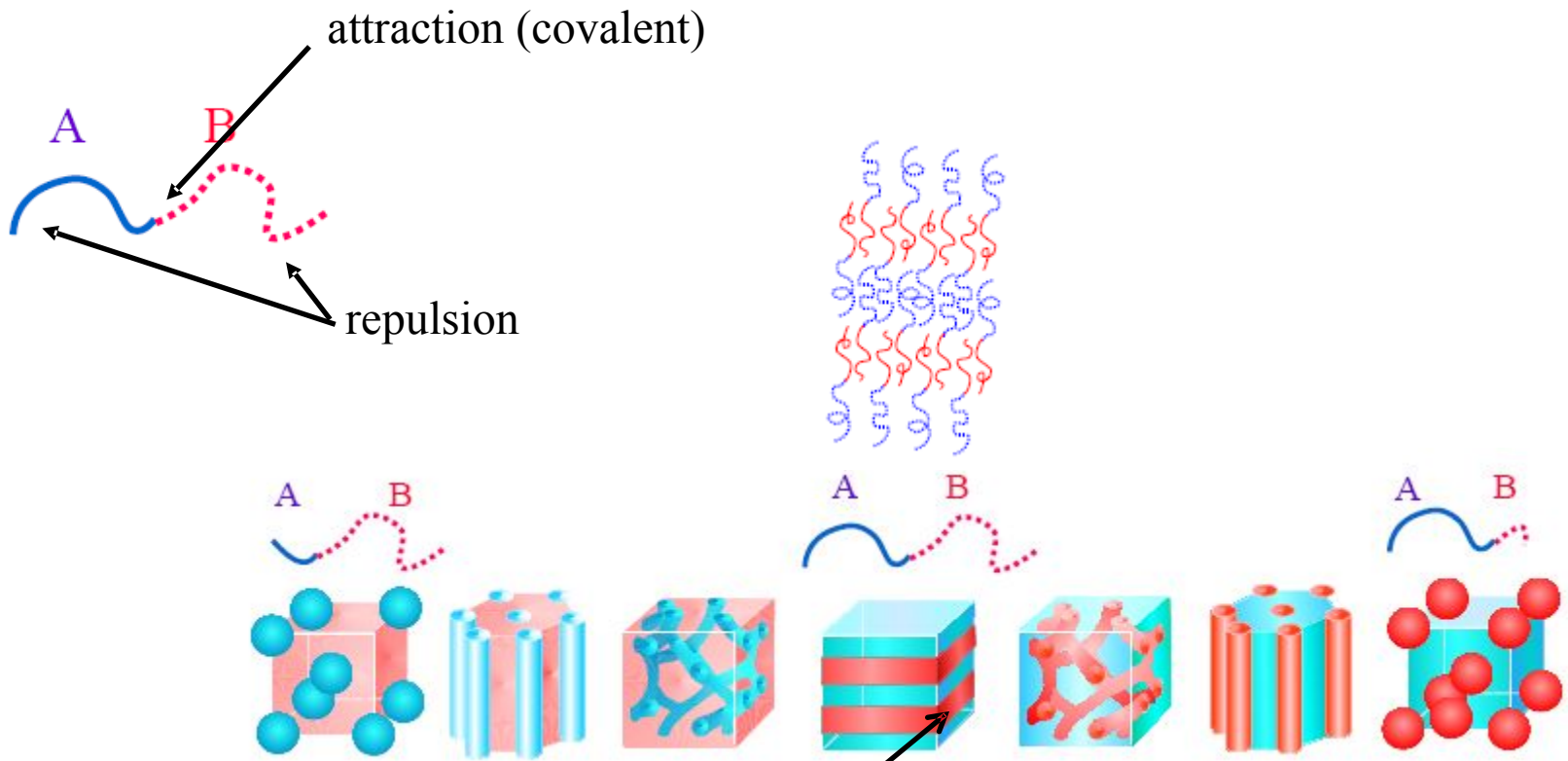


Lamellae



Increase block copolymer volume fraction

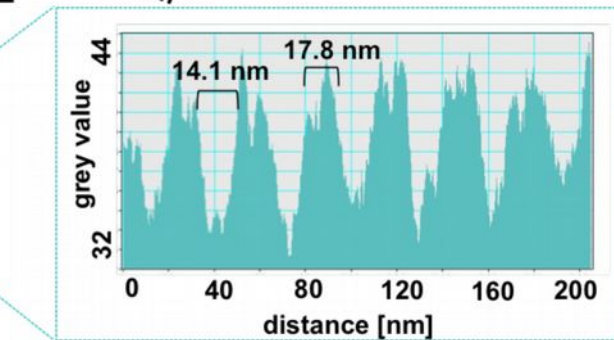
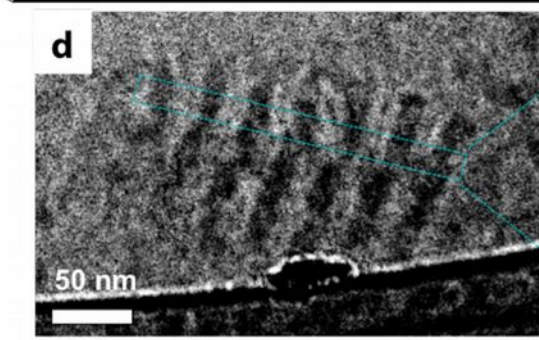
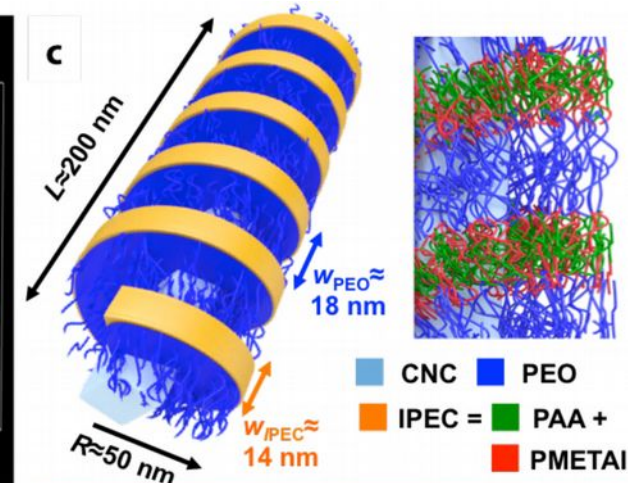
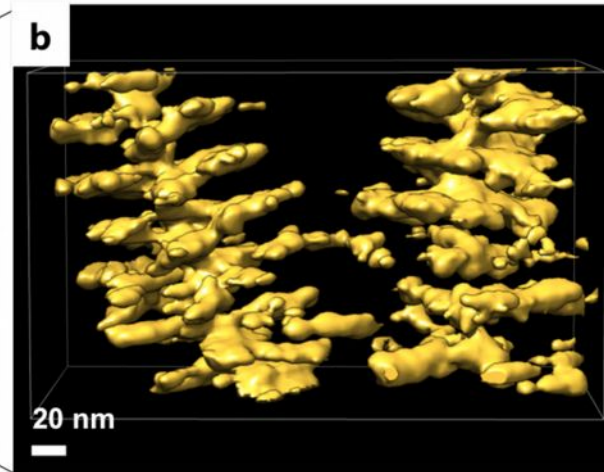
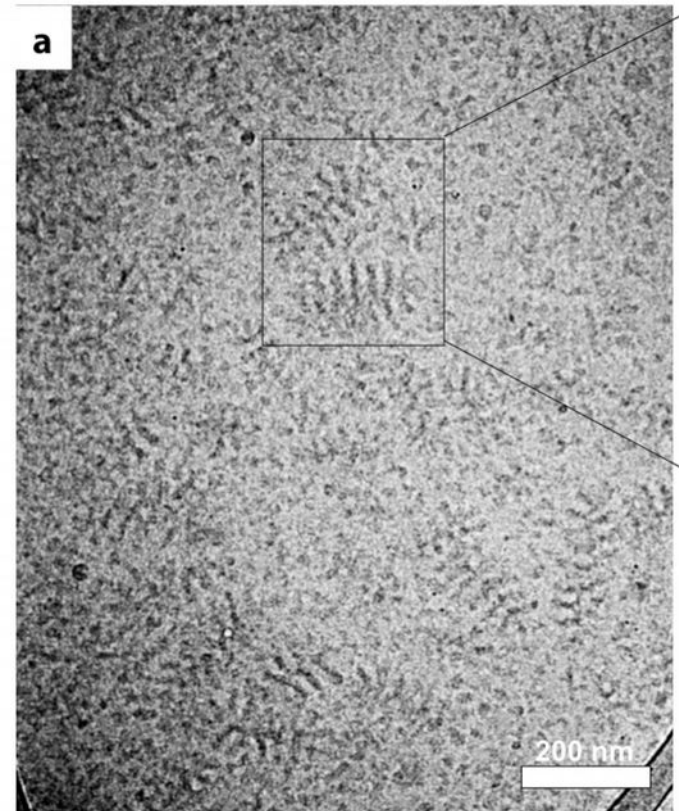
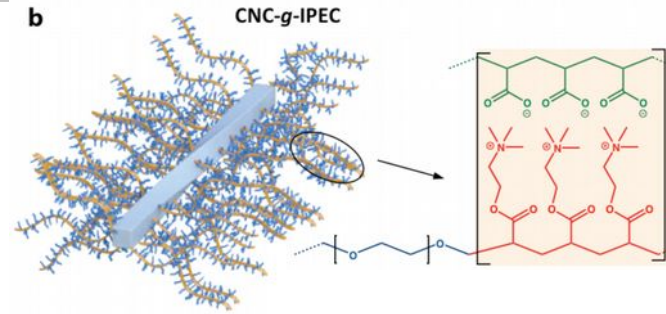
Self-assembly diblock copolymers due to competing interactions



- The structures controlled by the relative weight fractions of the blocks

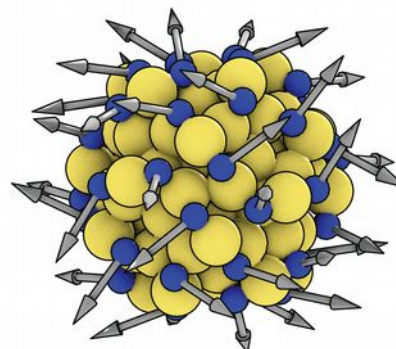
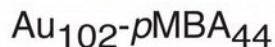
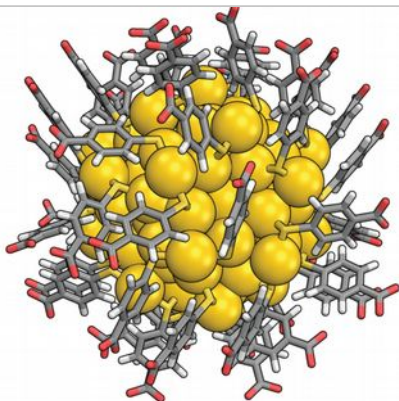
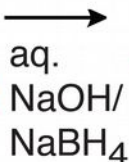
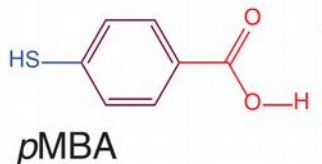
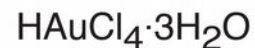
Interfaces

Helical colloids upon templating block copolymer on cellulose nanocrystals

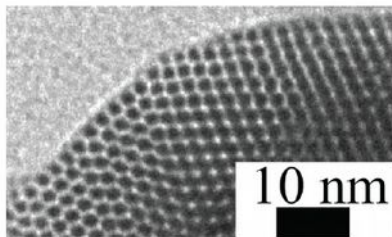
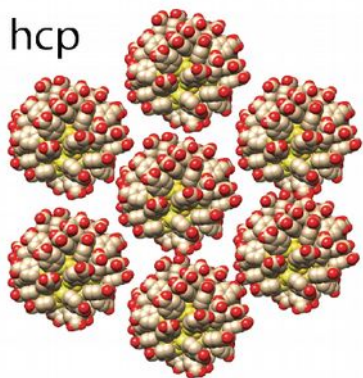


- **Early concepts for directed/templated self-assembly**
 - **(Block co)polymer templated oligomers**
 - *Nat Comm 2014, Chem 2017*
- **Colloid templated polymers**
 - **Nacre and nacre-mimetics by self-assembly**
 - *Adv Funct Mater 2016, Adv Sci 2017*
 - **Nanocellulose templated block copolymers**
 - *ACS Macro Letters 2016*
- **Metal nanocluster self-assembly**
 - **2D self-assembly**
 - **Virus-capsid like self-assembly of**
 - *Angew Chem 2016, 2017*
- **Nanocellulose as a transparent films or strong light scatterer**
 - *Adv Funct Mater 2015, Adv Mater 2018*
- **Block copolymeric photonic crystal as structural color**
 - **”Superstretched” block copolymers**
 - *Nat Mater 2004, ACS Nano 2018*

Atomically precise nanoparticles: Template-free 2-dimensional self-assembly

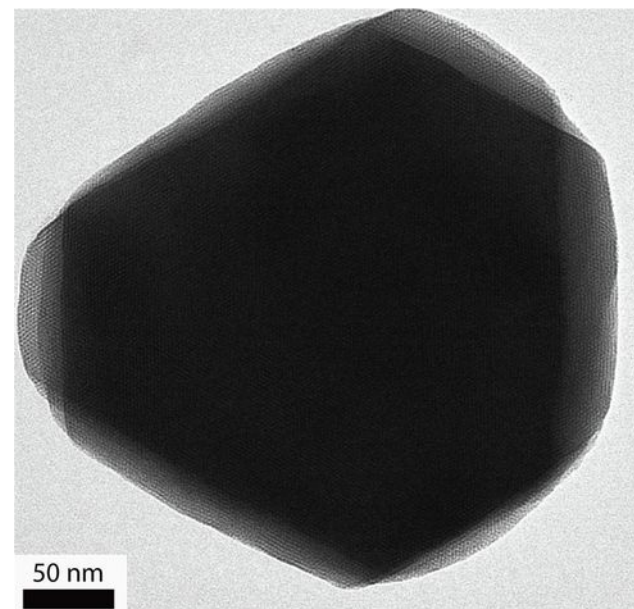


hcp

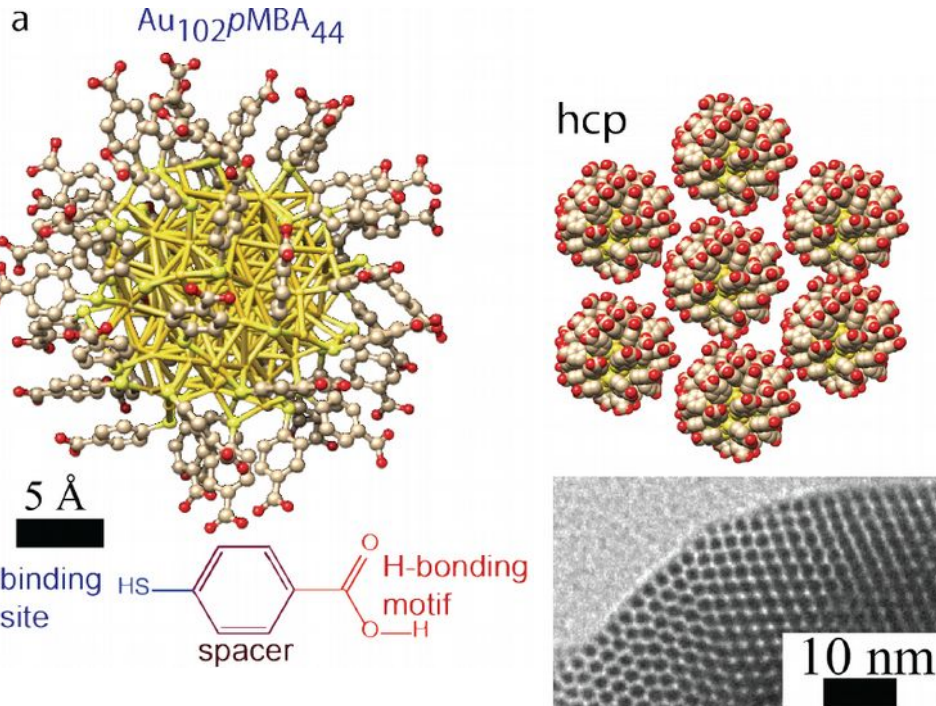


- Water/NaOH
 - Dispersed
 - Acids partly salt
- Dialyze against methanol
 - Trigger hydrogen bonds

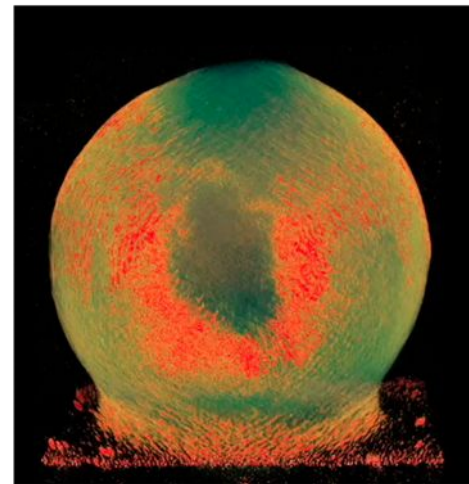
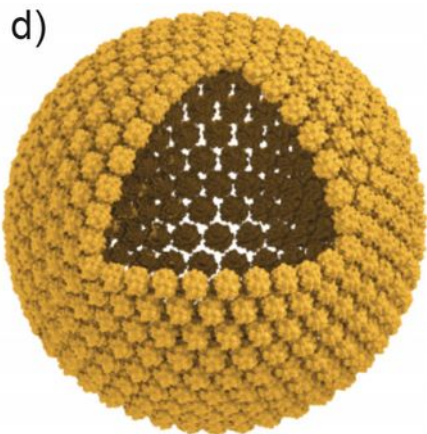
“Hexosome-like”



Gold colloidal capsids

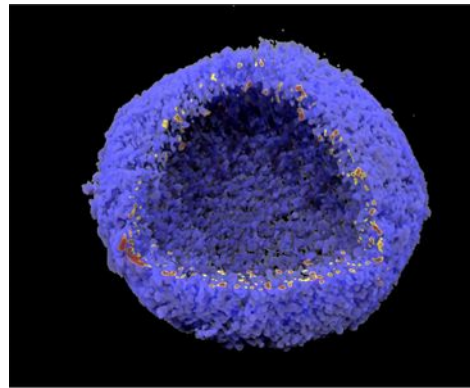
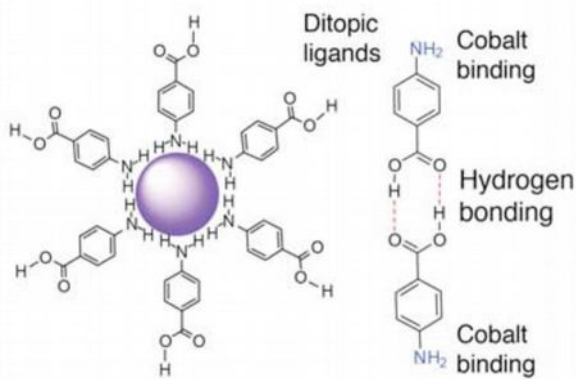


- Water/NaOH
 - Dispersed
 - Acids partly salt
- Rapid transfer to methanol
 - Trigger hydrogen bonds
 - Defects: bending

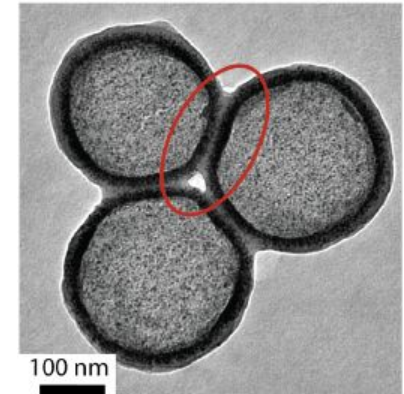


Movie removed to save space

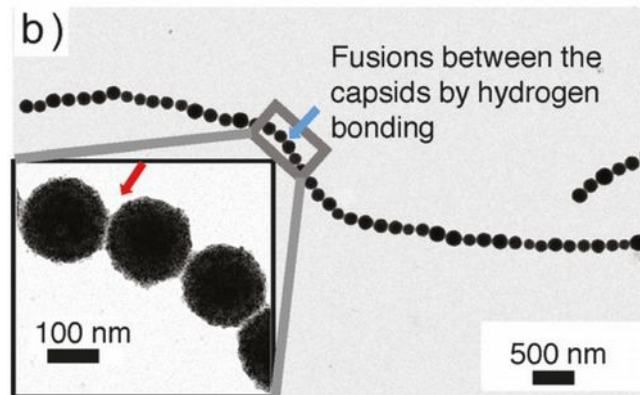
Cobalt-capsids



Movie removed to save space



Superparamagnetic, directing with magnetic fields



Nonappa, Haataja, Timonen, Malola, Engelhardt, Houbenov, Lahtinen, Häkkinen, Ikkala, *Angew. Chem Int Ed.* 2017, 56, 6473

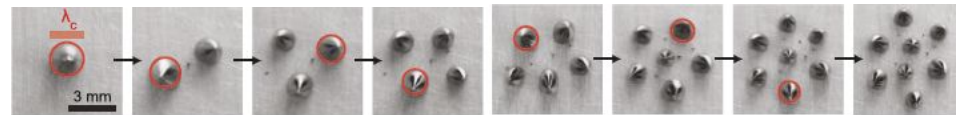
Nonappa, Ikkala, *Adv Funct Mater*, 2017, in press

Dissipative nanoparticle-driven self-assembly

Out-of-equilibrium

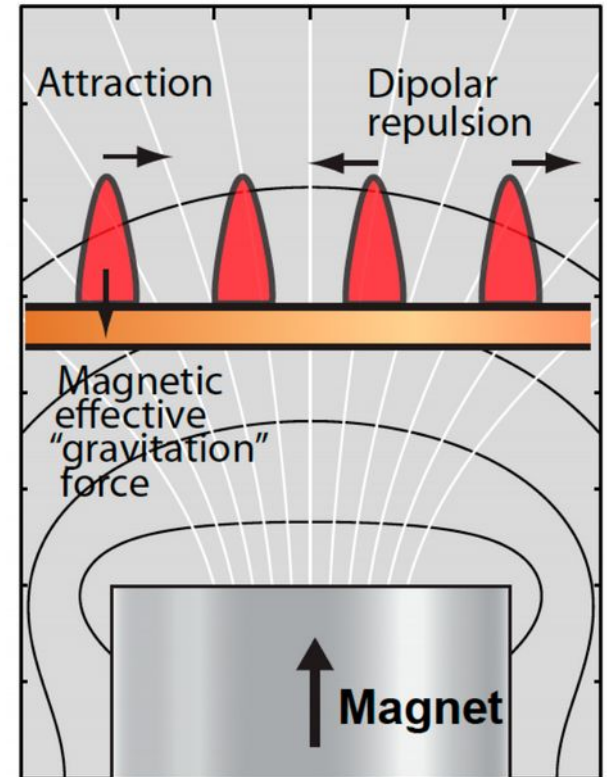
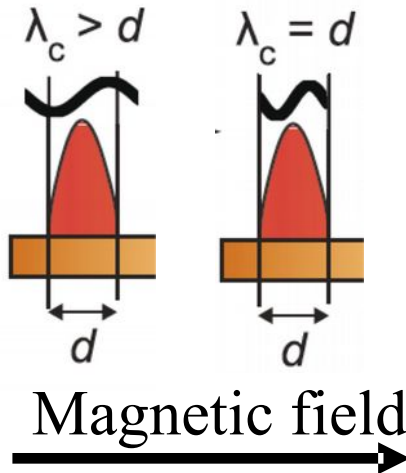
Self-assembly of ferrofluid droplets on superhydrophobic surfaces

Increasing magnetic field and curvature



Movie removed to save space

Fluctuation driven droplet splitting



Self-assembly

- Competing attraction and repulsion between the droplets

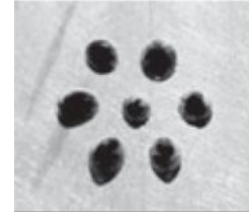
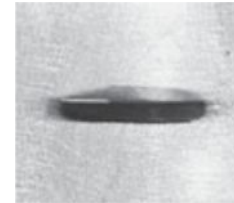
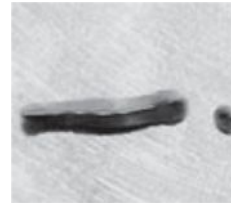
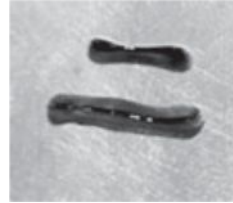
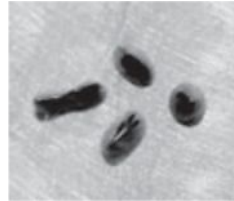
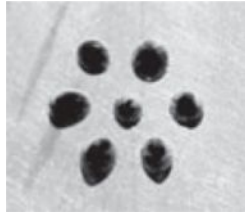
Dissipative self-assembly by feeding AC magnetic fields

Static H

Oscillating magnetic field

Static H

$H = \text{fixed}$



Movie removed to save space

Different dissipative self-assembled patterns depending on AC H -field frequency and amplitude

There can be reversibility between equilibrium self-assembly and dissipative self-assembly

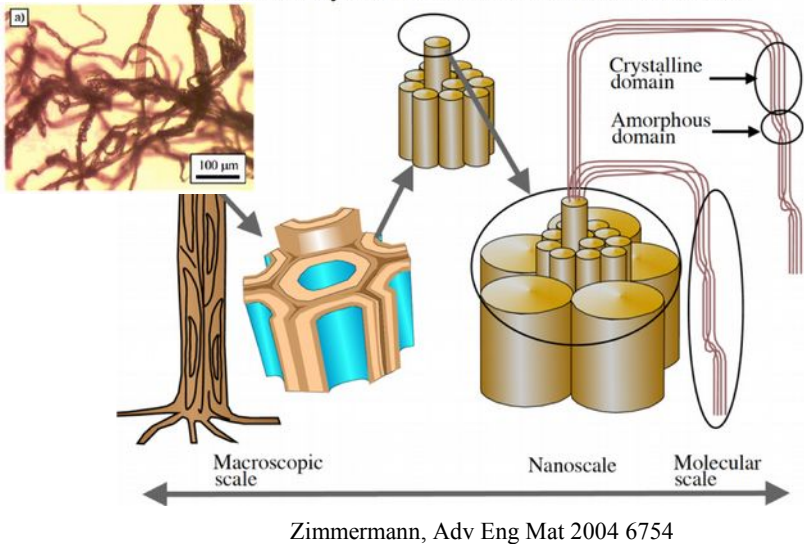
Complexity

Timonen, Latikka, Leibler, Ras, Ikkala, *Science* 341, 253 2013

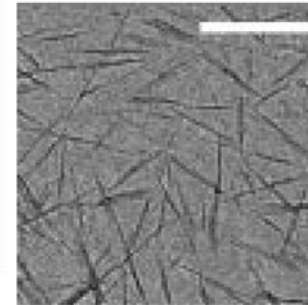
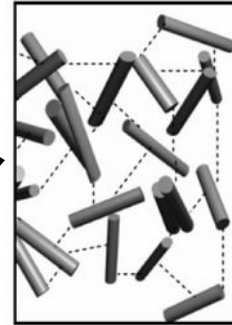
Spinning (functional) nanocellulose fibers

Types of (native) nanocelluloses

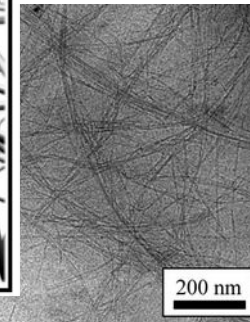
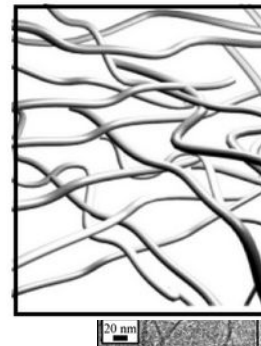
Wood hierarchy as a source for native cellulose nanofibrils



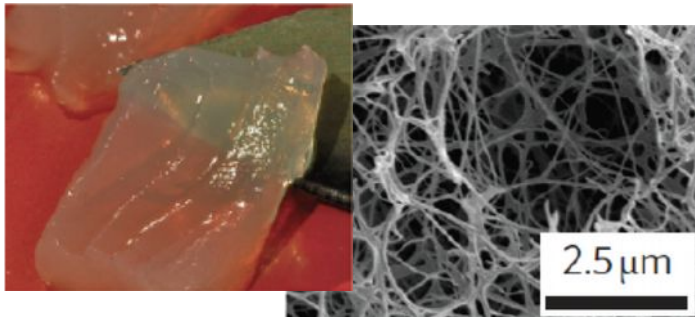
Cellulose nanocrystals (CNC)



Cellulose nanofibrils (CNF)



Bacterial cellulose



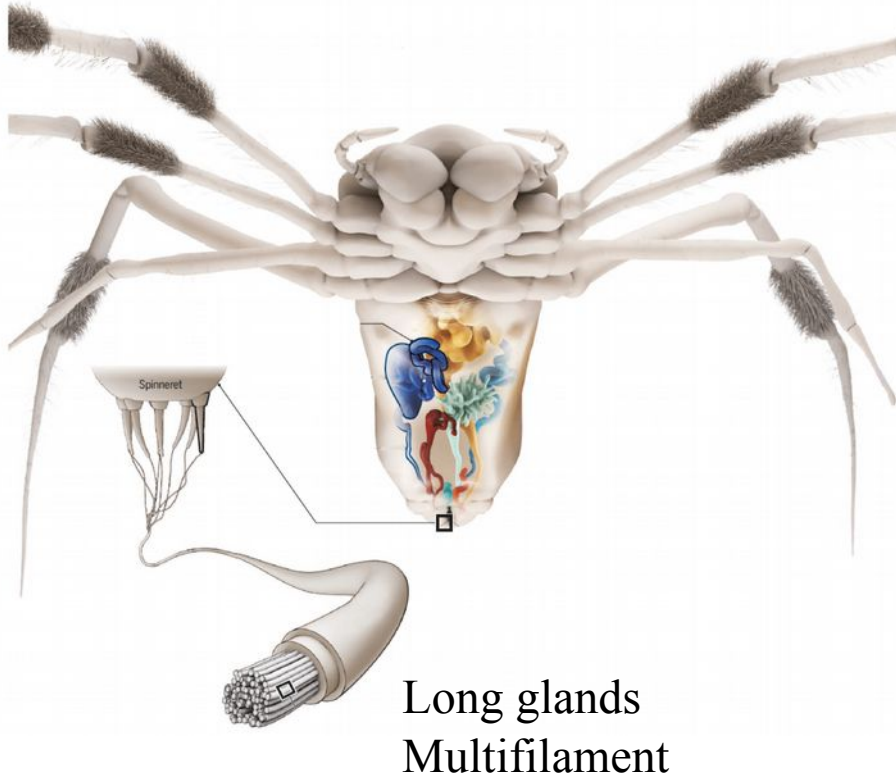
Klemm, Kramer, Moritz, Lindström, Ankerfors, Gray, Dorris, *Angew. Chem. Int. Ed.* 2011, **50**, 5438

Kontturi, Laaksonen, Linder, Nonappa, Gröschel, Rojas, Ikkala, *Adv Mat* 2018 1703779

Berglund, Burgert *Adv Mater* 2018 1704285

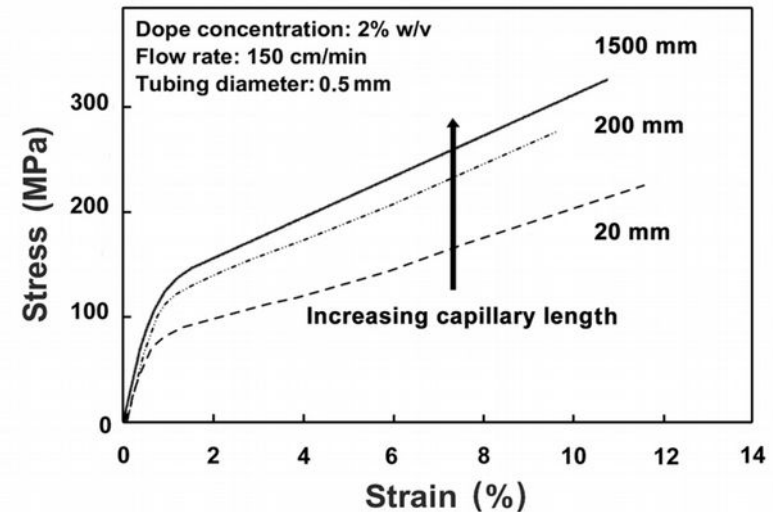
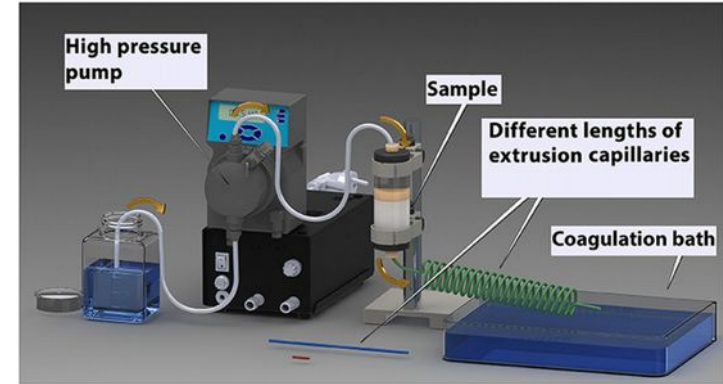
Cellulose nanofiber spinning to coagulation path

Silk spinning



Altounian, Pennisi, Service,
Science 2017 **358**, 292

Nanocellulose spinning

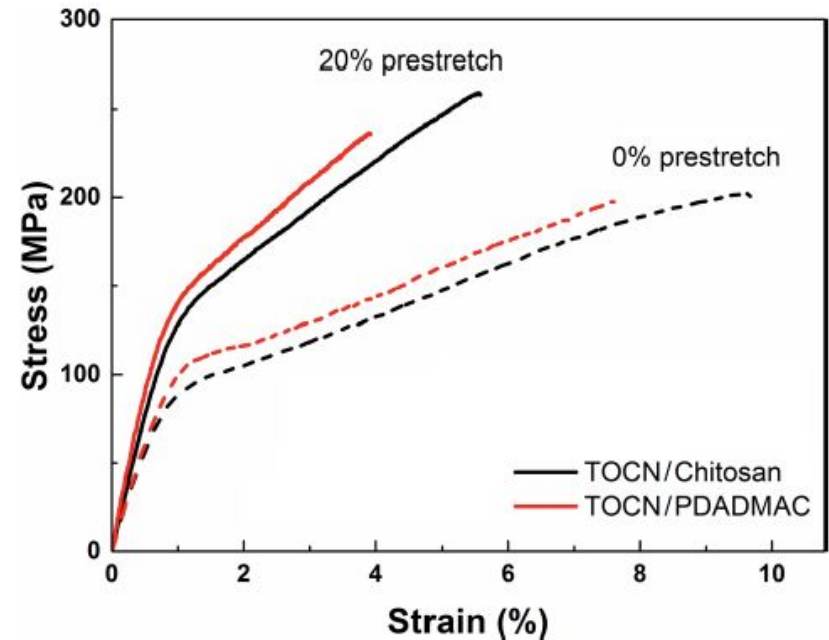
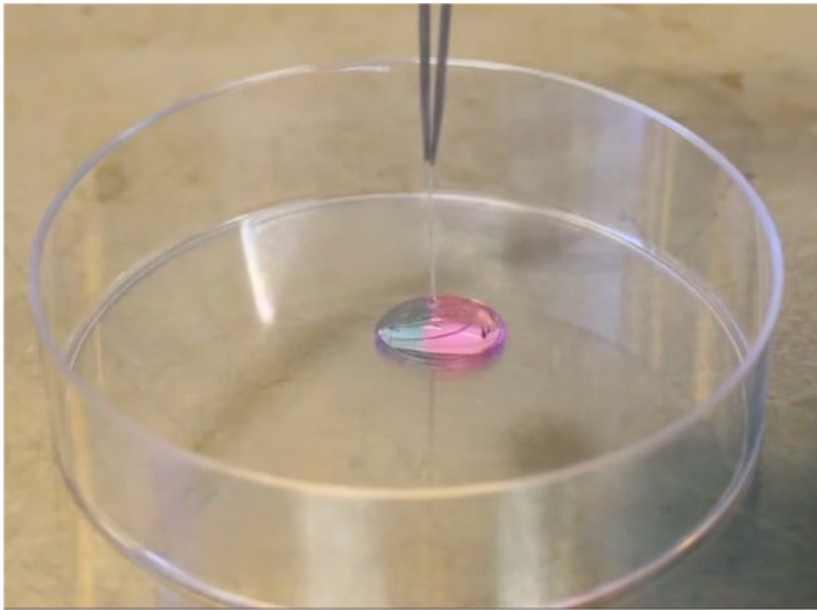


Walther, Timonen, Díez, Laukkanen, Ikkala,
Adv. Mat., 2011 **23**, 2924

Mohammadi, Toivonen, Ikkala,
Wagermaier, Linder, *Sci Rep* 2017 **7**, 11860

Interfacial Polyelectrolyte Complex Spinning

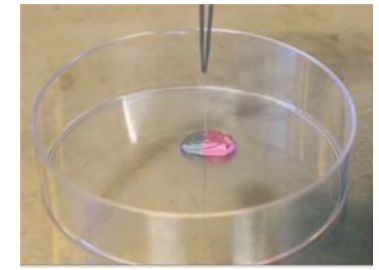
- TEMPO-CNF
- Poly(diallyldimethylammonium chloride) (PDADMAC) or chitosan
- Interfacial fiber drawing



Toivonen, Kurki-Suonio, Wagermaier, Hynninen, Hietala, Ikkala, *Biomacromolecules*, 2017 **18** 1293

Grande, Trovatti, Carvalho, Gandini *J. Mater. Chem. A*, 2017, **5**, 13098

Interfacial Polyelectrolyte Complex Spinning



- Tuning the fiber diameter

- TEMPO-CNF
- Chitosan

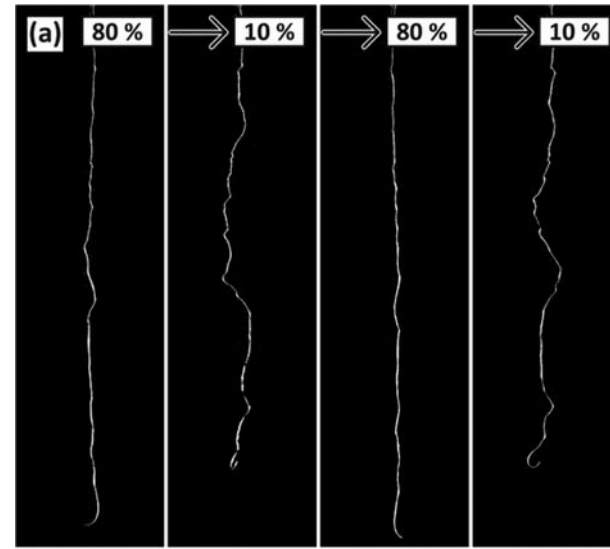
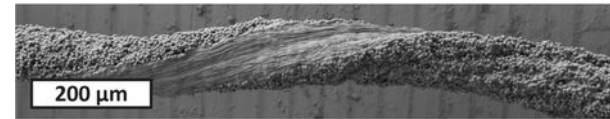
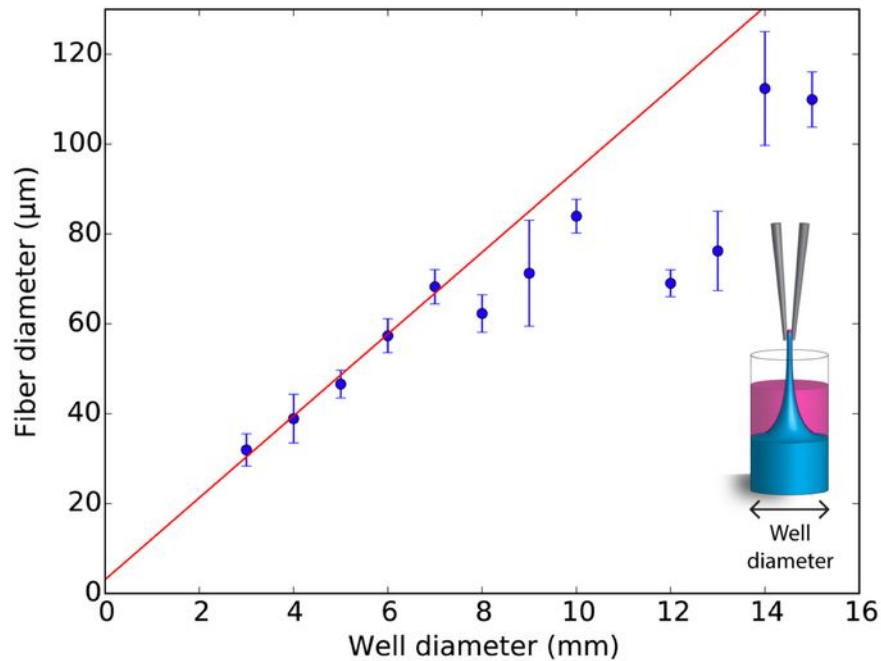
- Bilayer fibers undergo responsive crimping

Fiber 1

- TEMPO-CNF
- Chitosan

Fiber 2

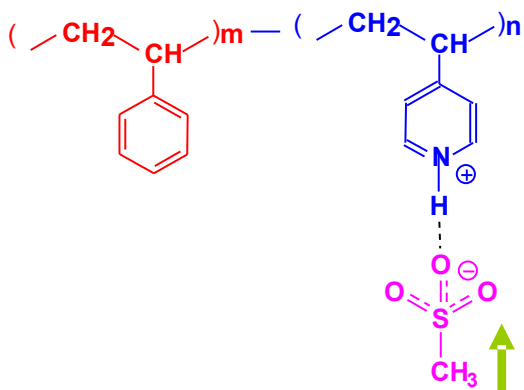
- Polystyrene sulfonate (labelled with microparticles)
- Chitosan



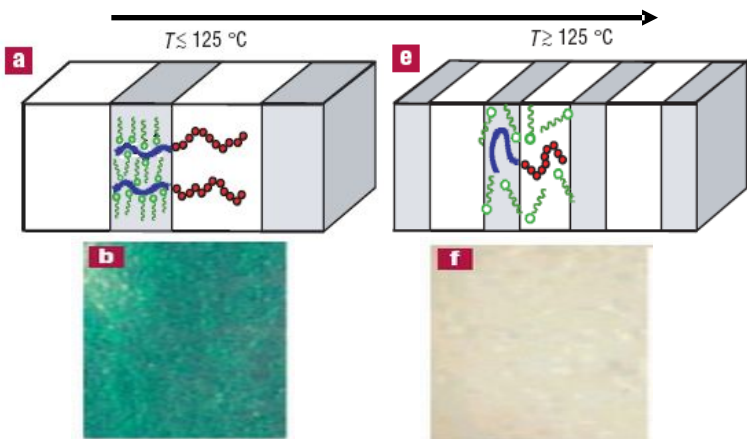
Towards
multi-
filament
compartmental
fibers

- **Early concepts for directed/templated self-assembly**
 - **(Block co)polymer templated oligomers**
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- **Colloid templated polymers**
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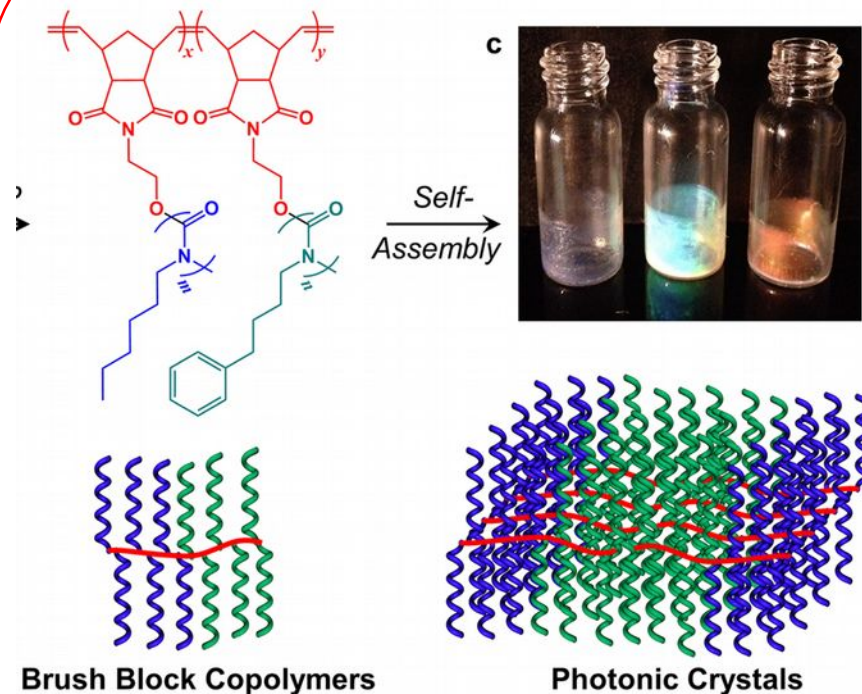
Comb-shape polymers lead to stretching of the chain and high periodicity using short polymers for photonic bandgaps



Temperature

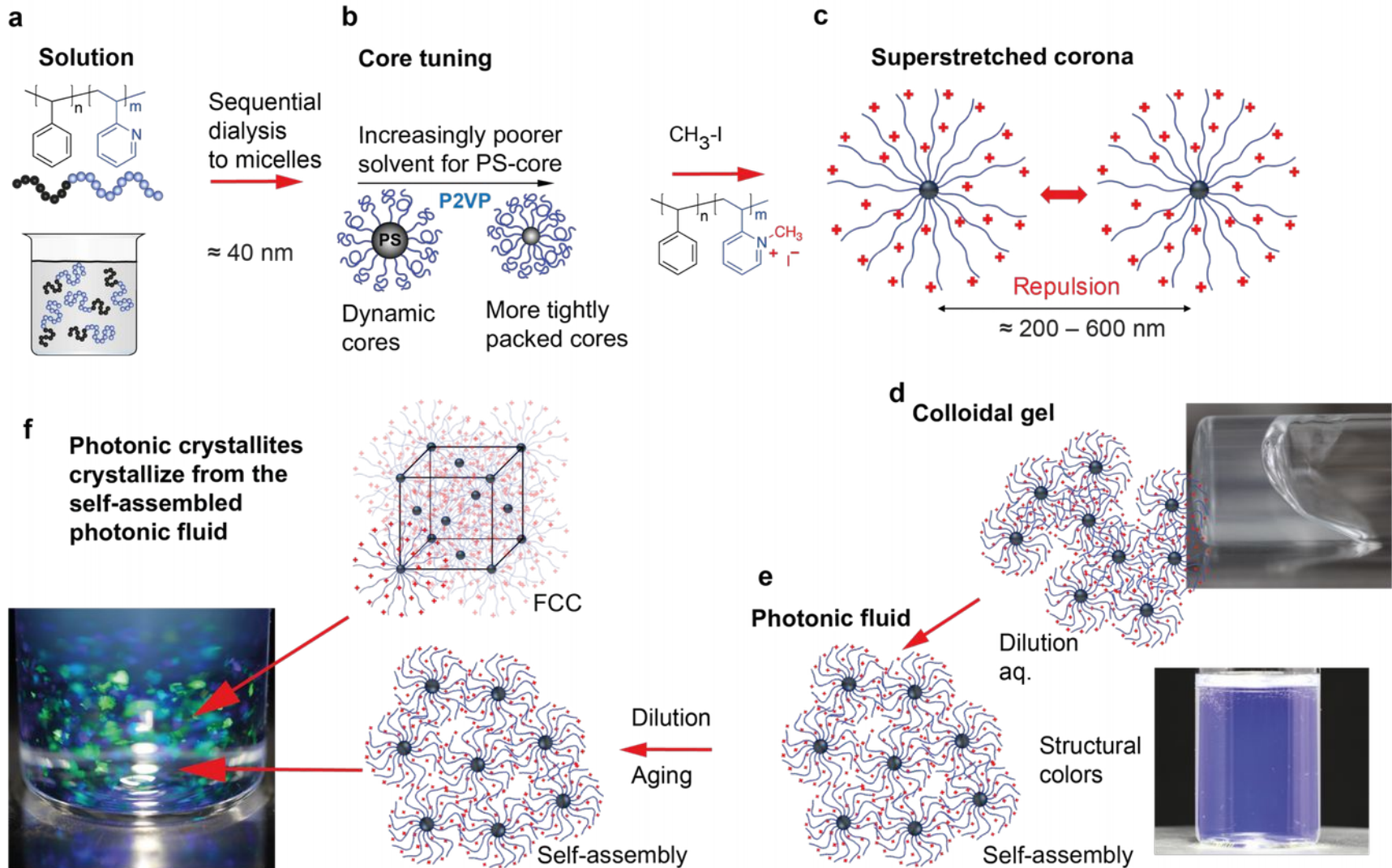


Valkama, Kosonen, Ruokolainen,
Haatainen, Torkkeli, Serimaa, ten
Brinke, Ikkala,
Nature Materials, **3**, 872 (2004)



Miyake, Weitekamp, Piunova, Grubbs,
JACS. 2012, **134**, 14249

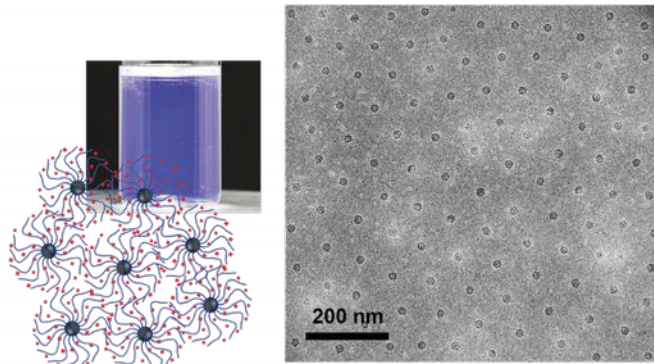
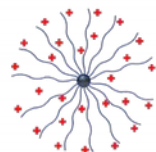
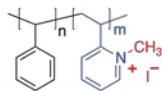
Photonic fluids and photonic crystals at extreme dilution



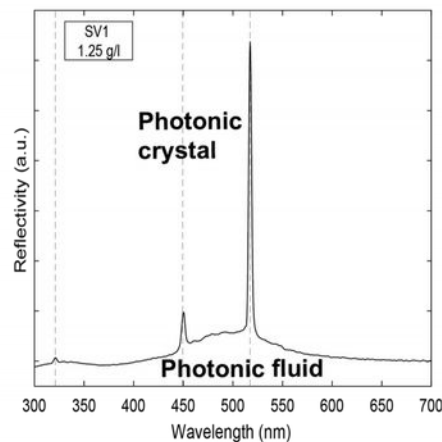
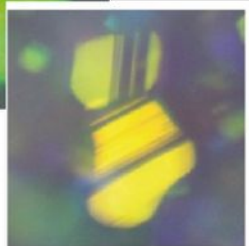
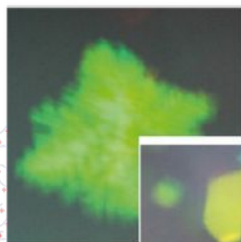
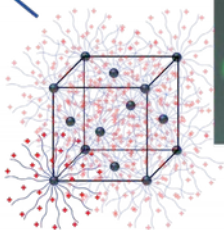
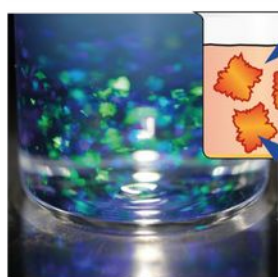
Poutanen, Guidetti, Gröschel, Borisov, Vignolini, Ikkala, Gröschel,
ACS Nano, **12** 3149, 2018

Photonic fluids and photonic crystals at extreme dilution

Photonic fluid background

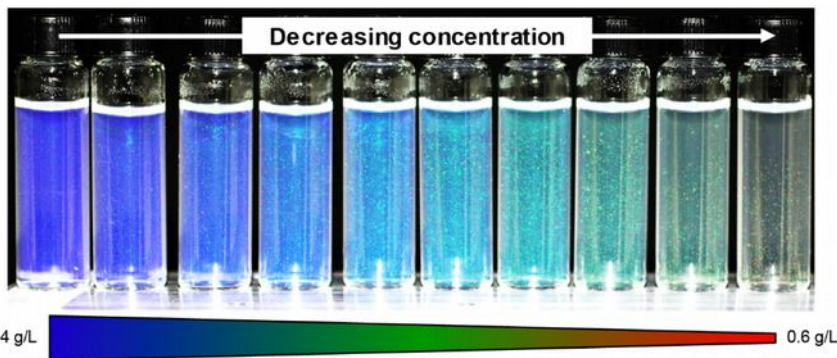


Photonic crystals grow from the photonic fluid



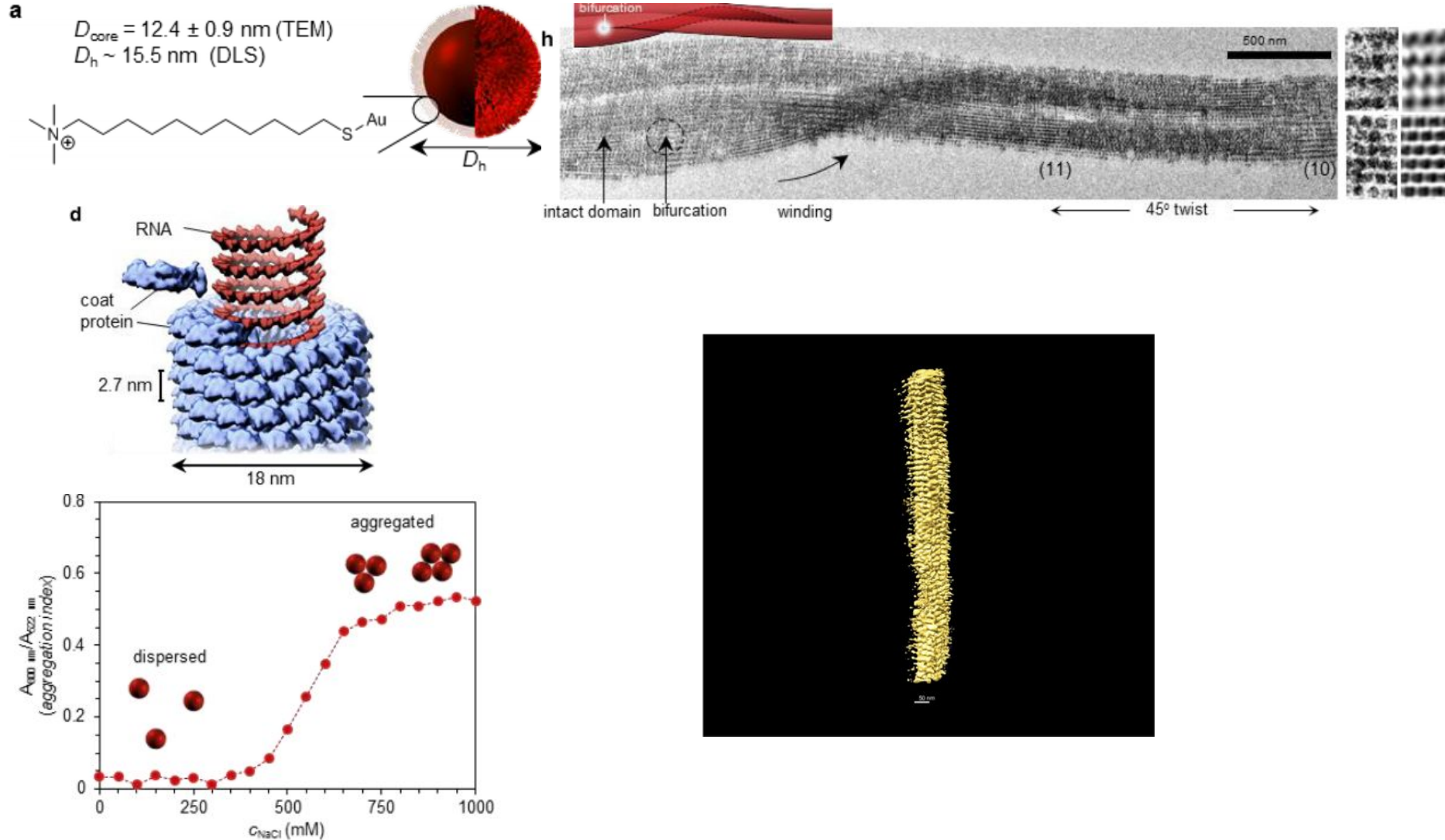
Even twinning observed

Tuning of the colors by concentration



Poutanen, Guidetti, Gröschel, Borisov, Vignolini, Ikkala, Gröschel, ACS Nano, **12** 3149, 2018

Superlattice wires by cationic Au nanoparticles on tobacco mosaic virus



Liljeström, Ora, Hassinen, Rekola, Nonappa, Heilala, Joensuu, Ras, Törmä, Ikkala, Kostianen, *Nat. Comm.*, 2017

Funding acknowledgement

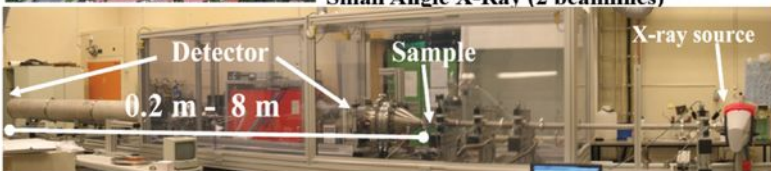
ERC Advanced Grant
Center of Excellency
(Ikkala, Laine, Linder, Penttilä)
Finnish Center for Nanocellulose
Technologies, UPM, Academy of
Finland, TEKES
Sustaincomp/EU NMP
Designcell/Woodwisdom



Nanomicroscopy Center and Nanopoli



Small Angle X-Ray (2 beamlines)



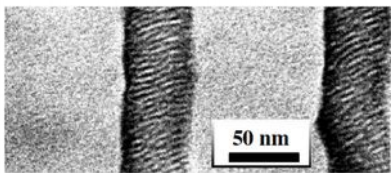
Liq-He cryo-TEM JEOL 3200FSC



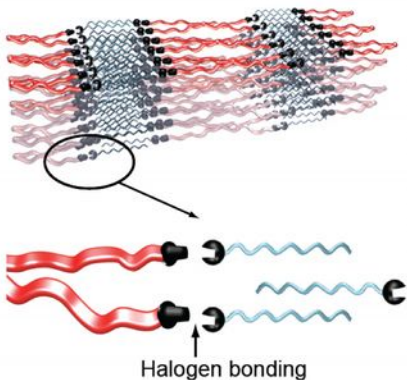
Ruokolainen

Supramolecular (hierarchical) self-assembly of polymers

Hydrogen bond



Halogen bond



Science 1998

Science 2002

Nature Mat. 2004

Angew Chem 2010

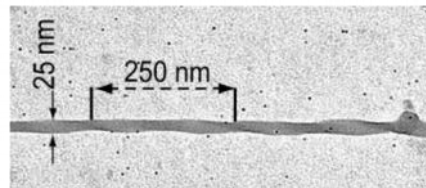
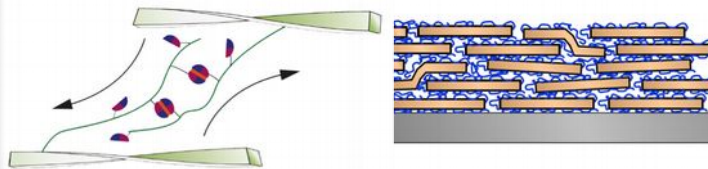
Nature Comm 2014

Nat Comm 2016

Chemistry 2017

Biomimetic materials

Sacrificial bonds Nacre mimics



Amyloids

Angew Chem 2010

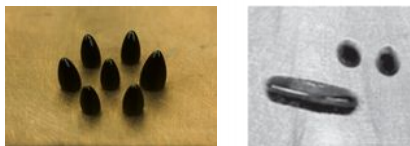
Nano Lett 2010

Angew Chem 2014

Nature Comm 2015

Adv Funct Mat 2017

Dynamic **dissipative** self-assemblies



Science 2013

Nature Comm 2013

Functional nanocelluloses



Photocatalytic
Semiconducting
Conducting

Transparent

Sensing

Magnetic

Superhydrophobic

Oil repulsive

Oil spill absorbing

Fibers

Soft Matter 2008

Nature Nano 2010

ACS Nano 2011

Adv Funct Mat 2011

Adv Mat 2013

Adv Funct Mat 2015