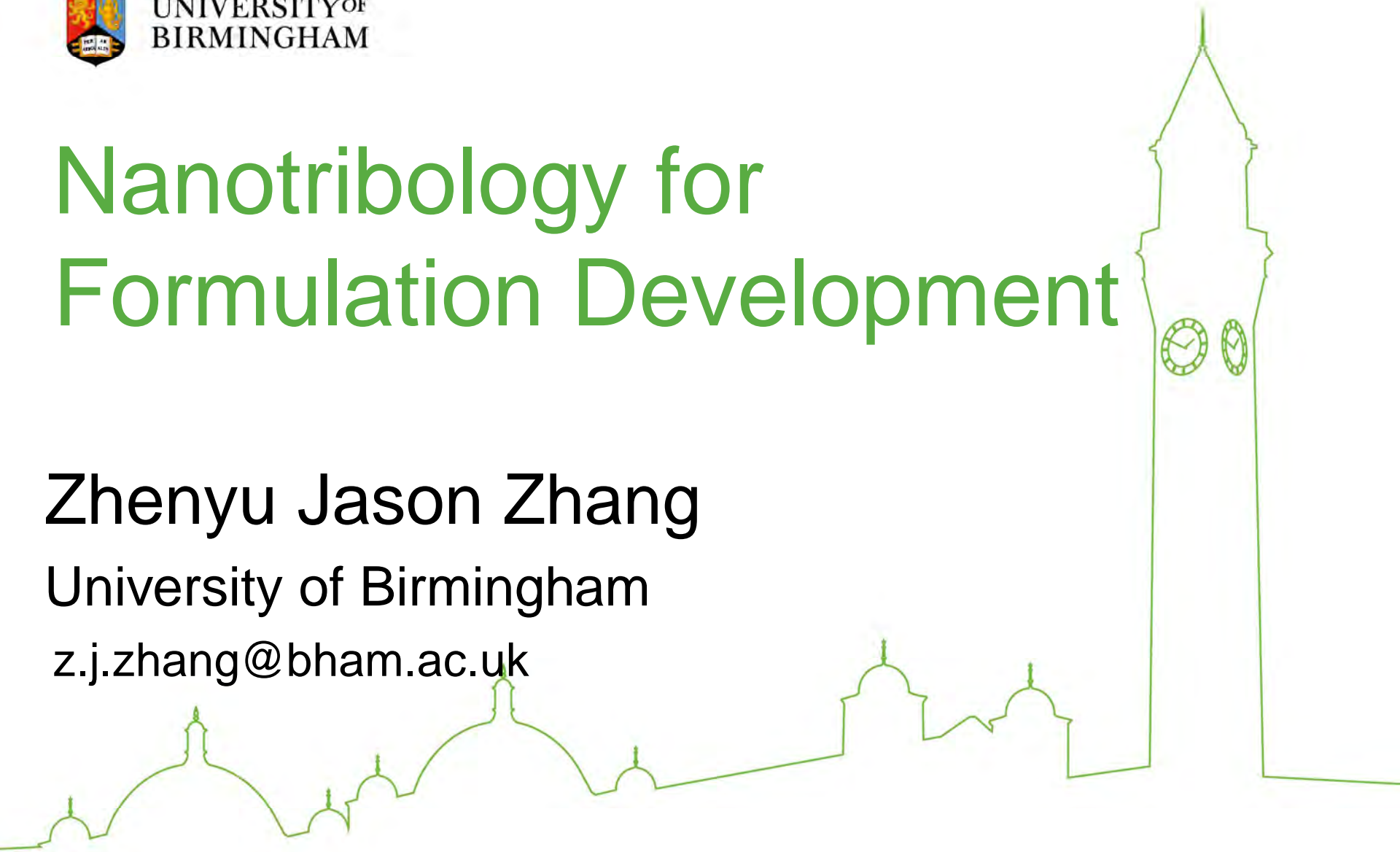# Nanotribology for Formulation Development

Zhenyu Jason Zhang

University of Birmingham

z.j.zhang@bham.ac.uk
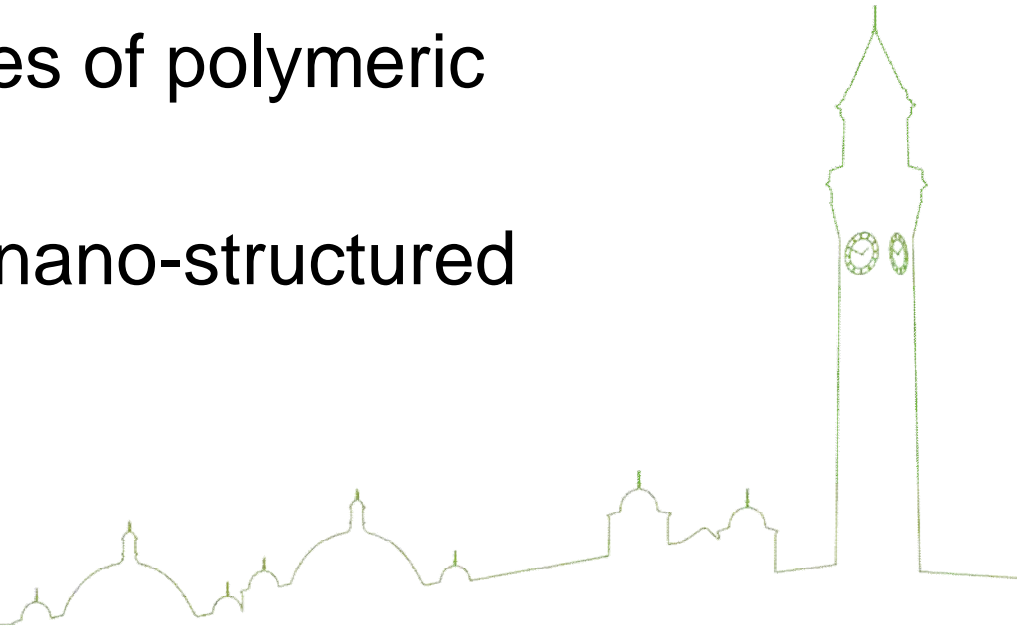
UNIVERSITY OF BIRMINGHAM

Outline

- Nanotribology
  - Scanning Probe Microscopy
- Case studies
  - Performance of laundry products
  - Lubrication properties of polymeric coating
  - Characterisation of nano-structured objects

Why am I interested in

Soft matter at surface/interface

- Surface functionalization / coating
- Colloidal stabilization
- Lubrication
- Detergents
- Fouling/Cleaning
  - Biomaterials
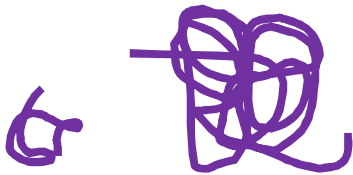 - Drug delivery
  - Cell mechanics
  - etc.

| Concept | → | Synthesis | → | Characterisation | → |

Interfacia
l
propertie
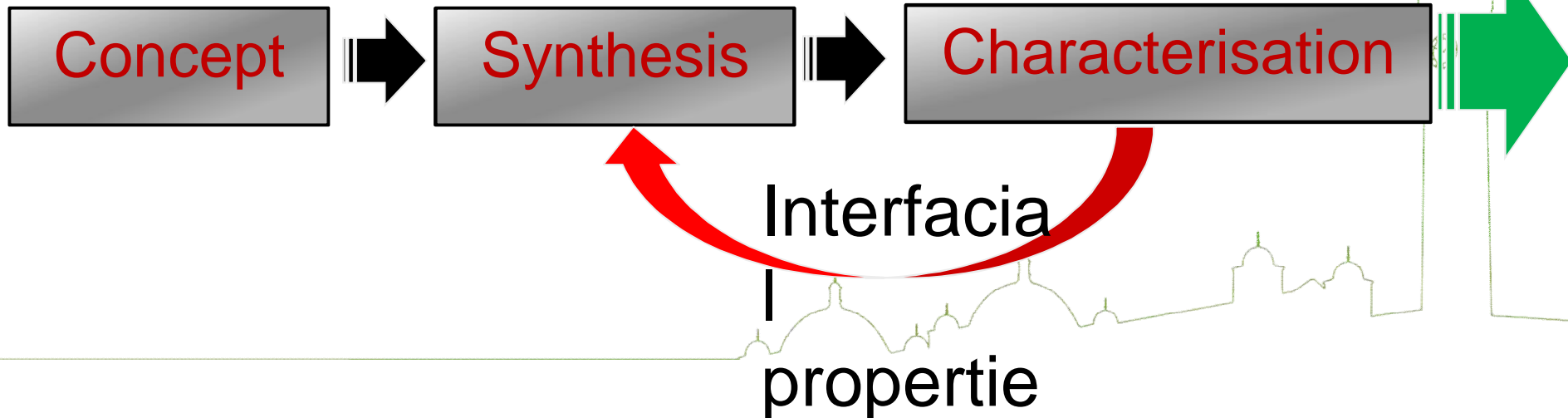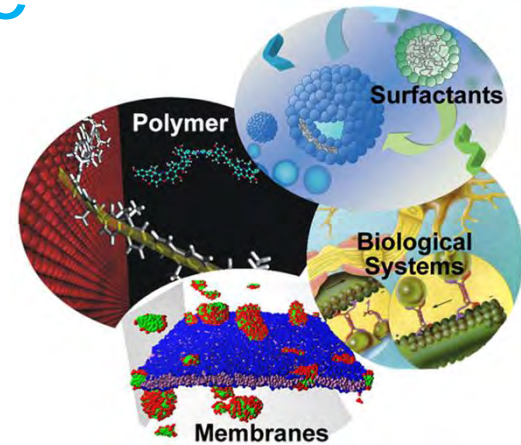
The fundamentals
Soft matter *vs* surface

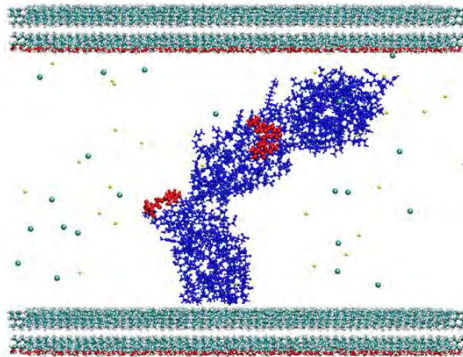| Prior	In contact	Film formation

Prior
- Stability in bulk solution
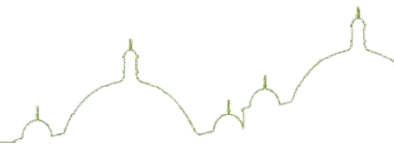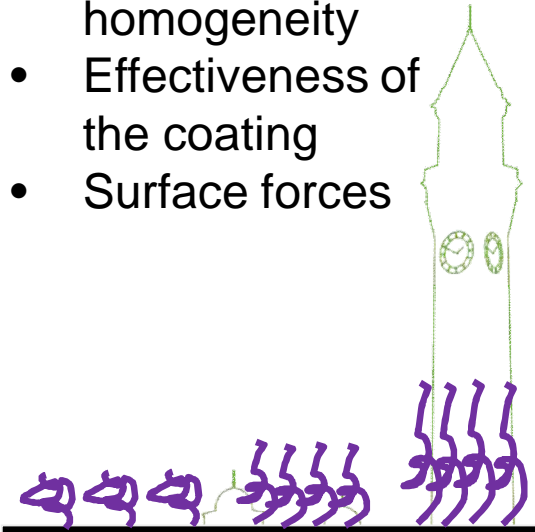- Diffusion rate
- Substrate characteristics

In contact
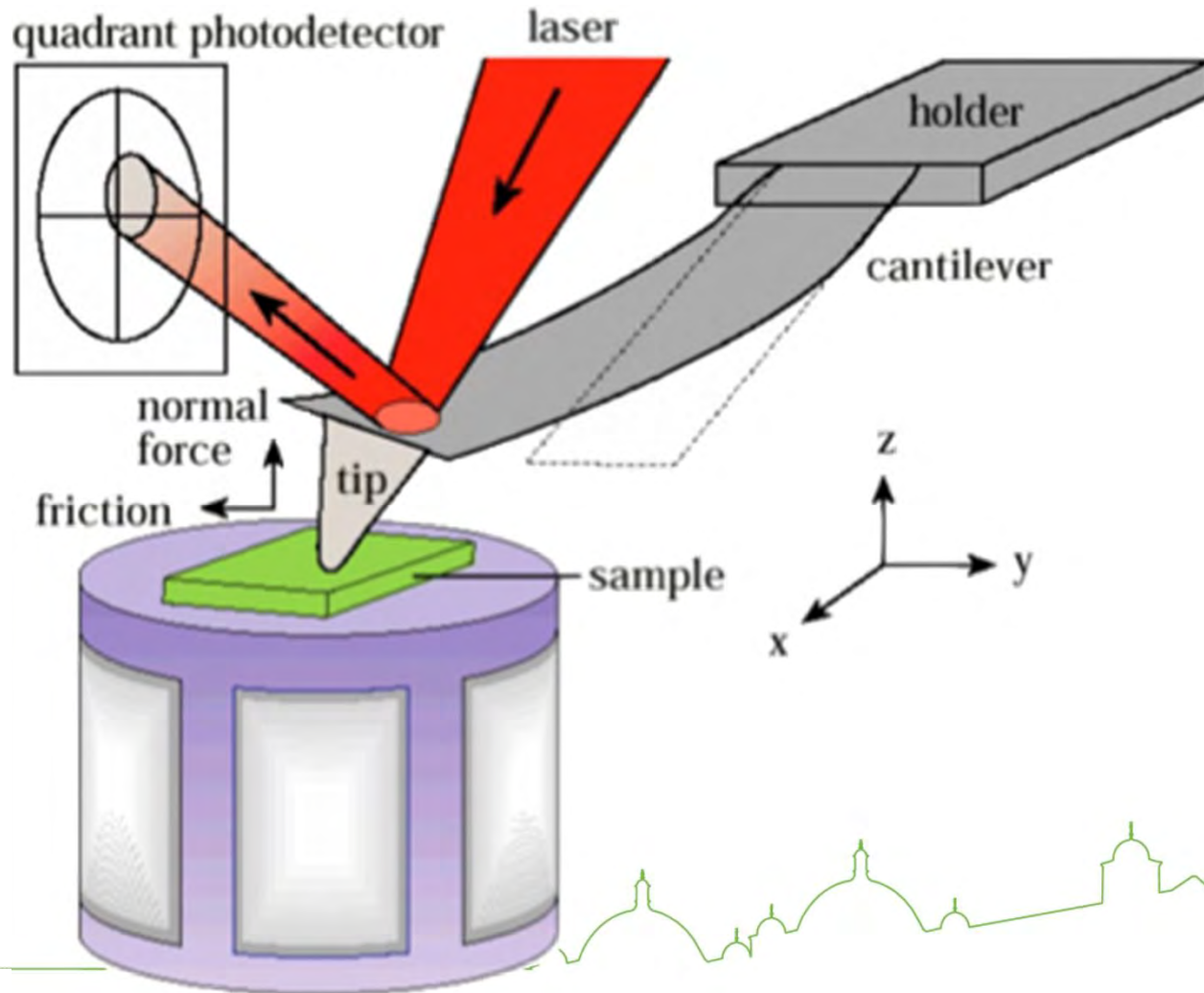- Adsorption/desorption
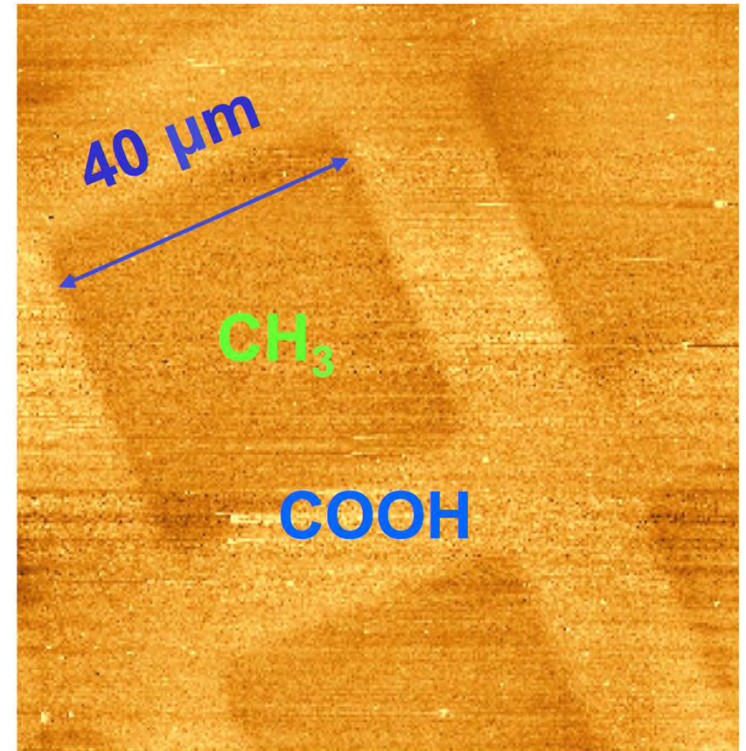- Binding energy
- Molecular interaction

Film formation
- Conformation
- Response to external stimuli
- Surface distribution / homogeneity
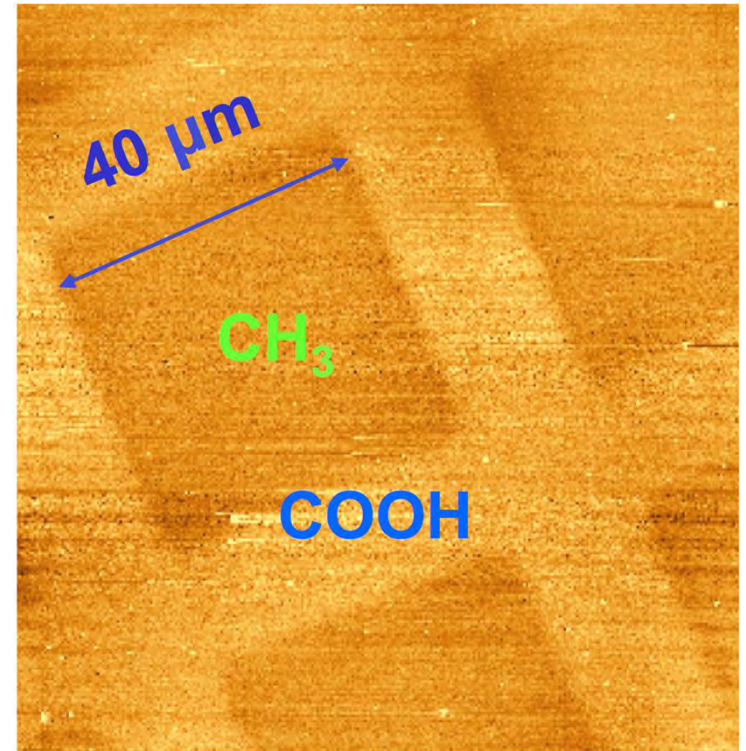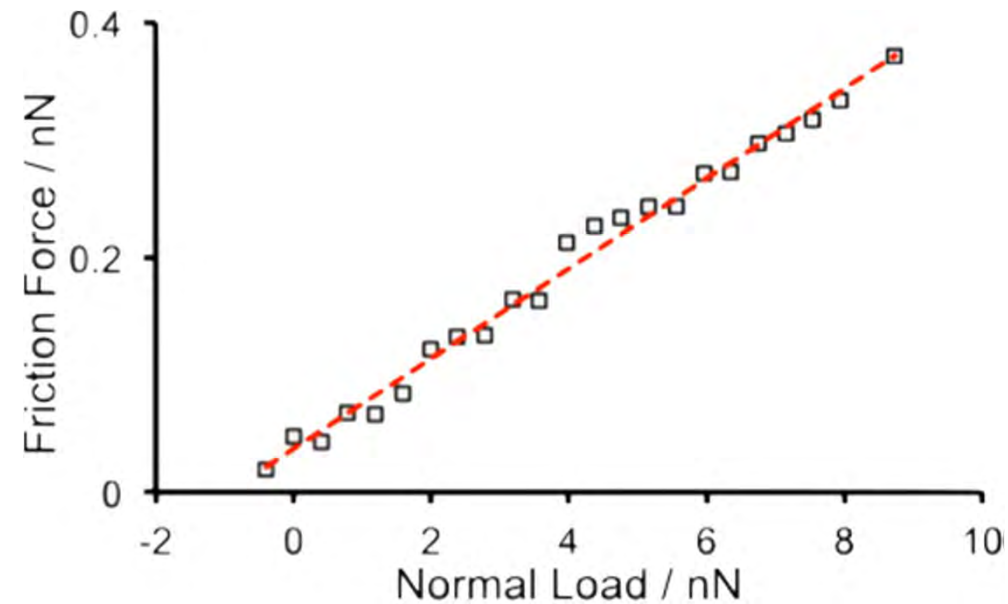- Effectiveness of the coating
- Surface forces

Nanotribology

Nanotribology

Surface analysis

Nanotribology

Quantitative friction measurement
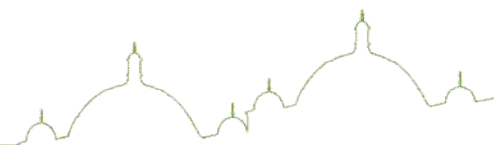
Surface analysis

SPM - a versatile toolbox

Objects

- Single molecule
- Monolayer
- Polymeric coating
- Colloidal particle

Environment

- Controlled ambient
- Aqueous solution
- Organic liquid
- Controlled temperature
- Polymer solution

- In-situ measurement in various environment
  - Observe and manipulate molecular machinery
- No complex sample preparation
  - No need for fixation or staining
- Time-lapse imaging with nanometre resolution
  - Directly observe biological specimens
- Molecular/colloidal interactions
  - Pico-newton sensitivity
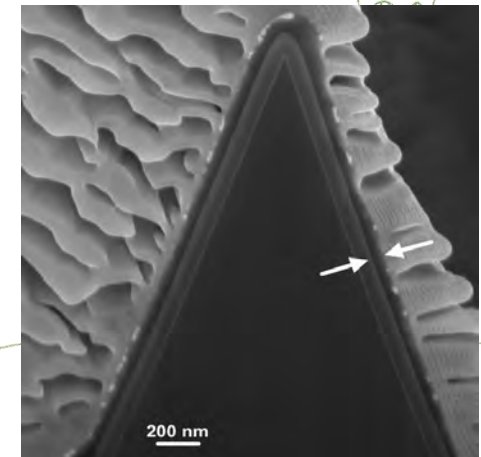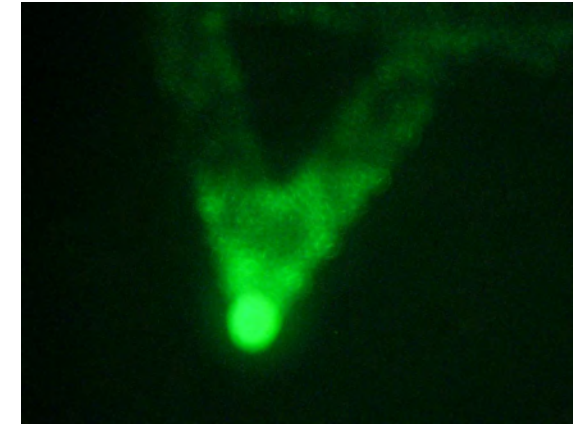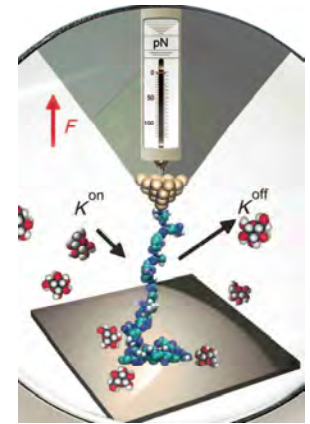
200 nm

Performance of laundry product Surface analysis

- Deposition/residue of laundry products on cotton fibres
- ToF-SIMS
- Resolution of ~200 nm (one pixel in the images)
- Distribution of surfactants on treated fibre
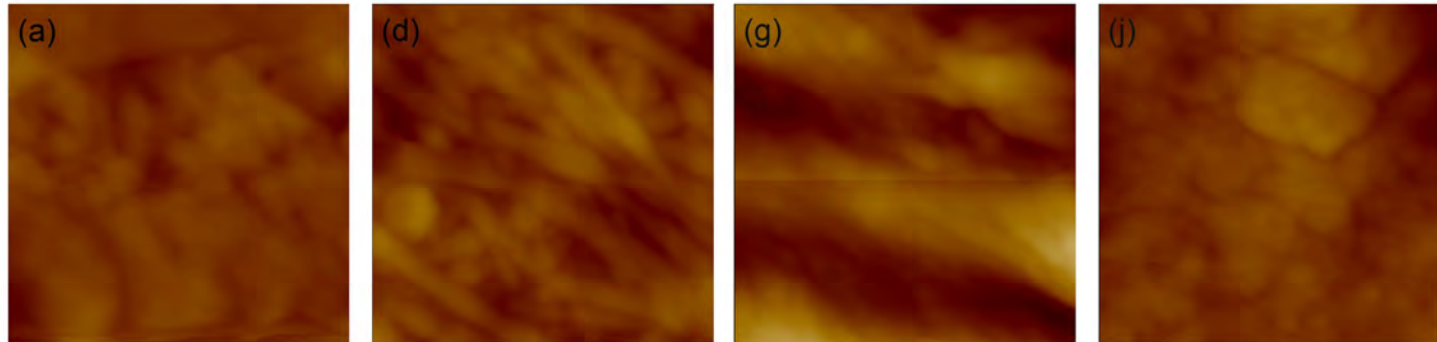- High vacuum
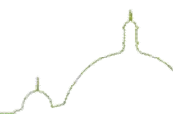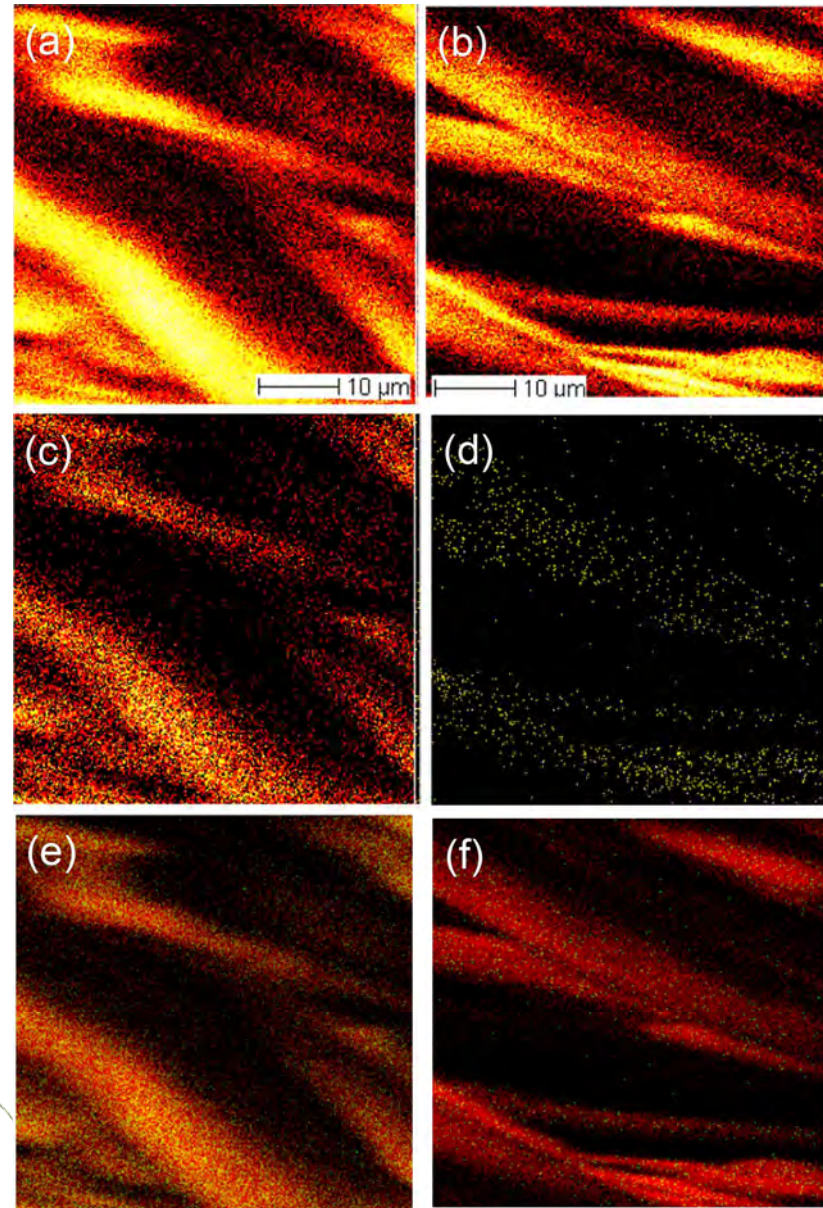
Surface topography
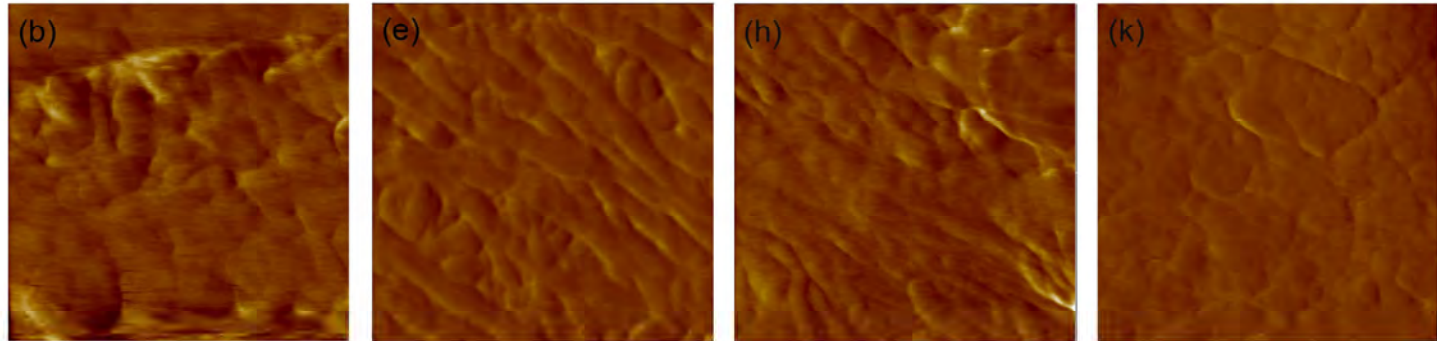
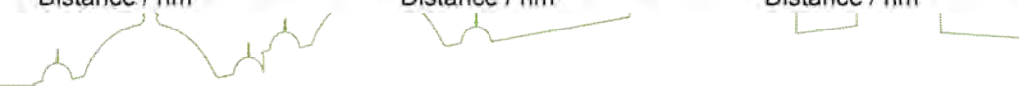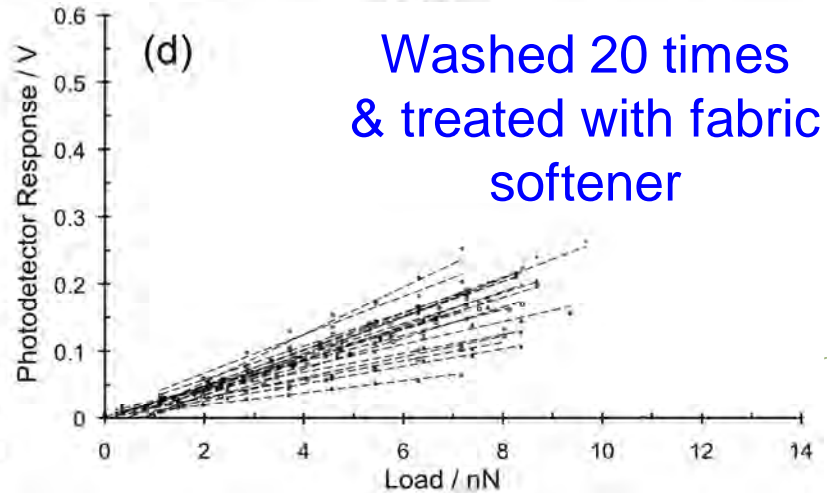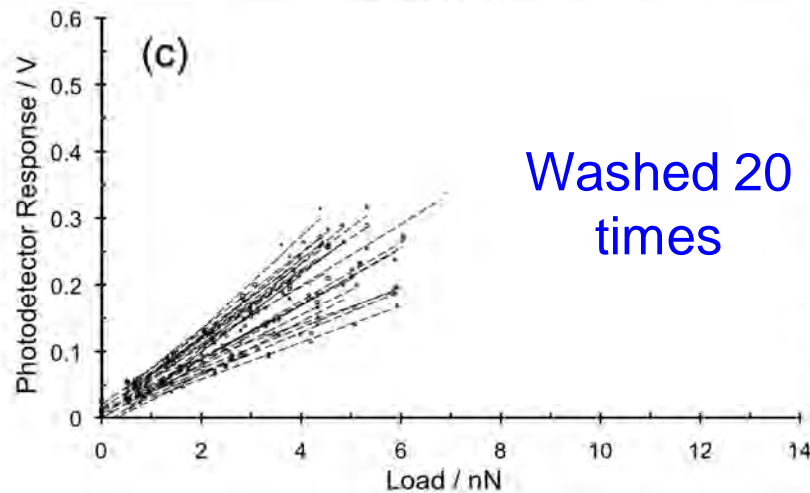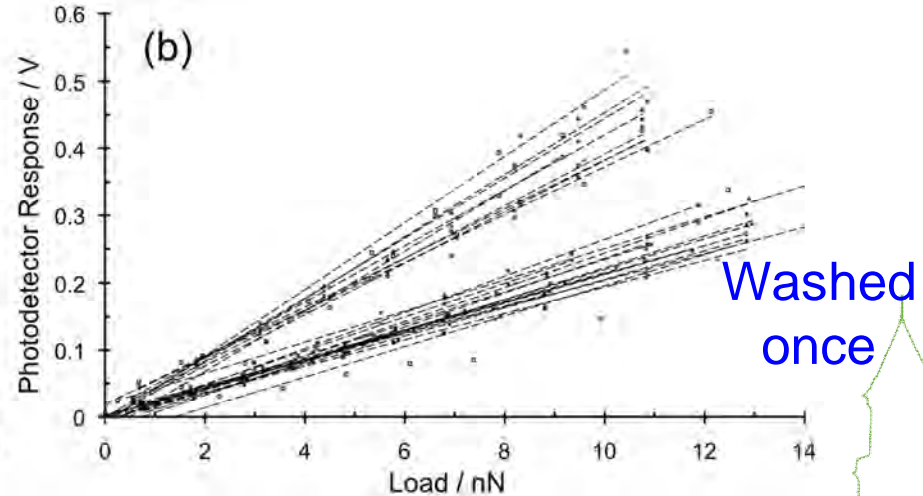| Data channel	New cotton	Washed once	Washed 20 times	Washed 20 times & treated with fabric softener
Height	(a)	(d)	(g)	(j)
Friction	(b)	(e)	(h)	(k)
Section	(c)	(f)	(i)	(l)
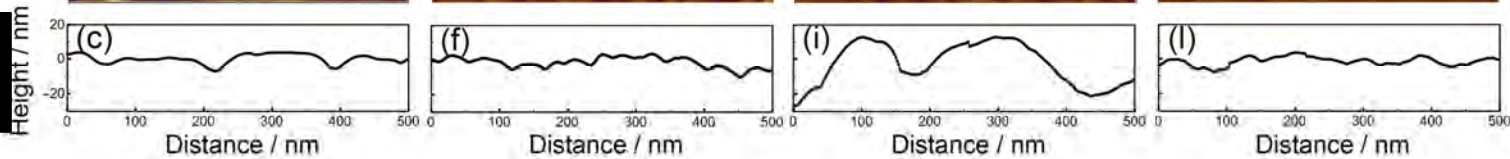
Frictional-load relationship

$$F = mL$$

Note: the greater the slop, the higher coefficient of friction

New cotton

Washed once

Washed 20 times

Washed 20 times & treated with fabric softener
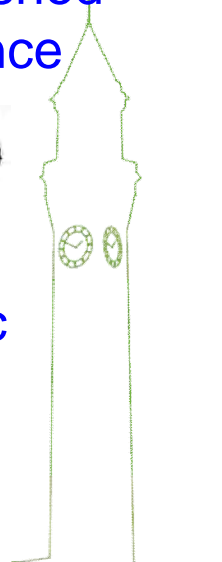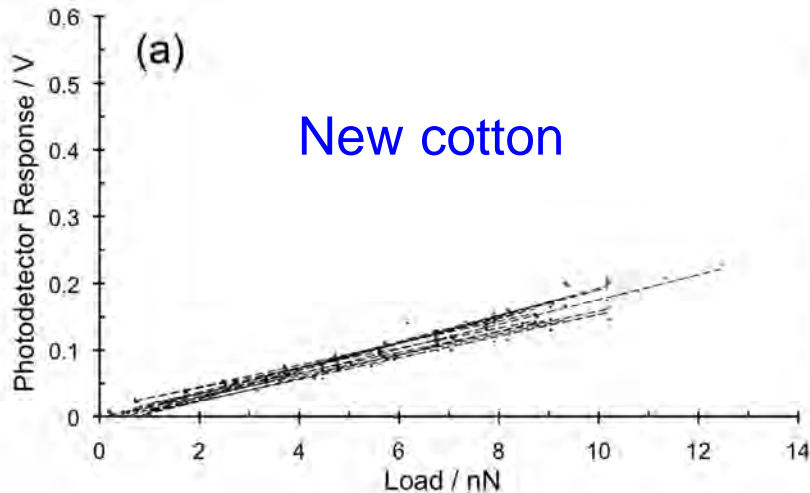
Summary 1

- Ability to examine meso-scale objects
- In both ambient and liquid environment
- Surface properties of porous material
- High spatial resolution
- Effective approach in evaluating surface-deposited soft matter quantitatively
- Consistency over different length scales
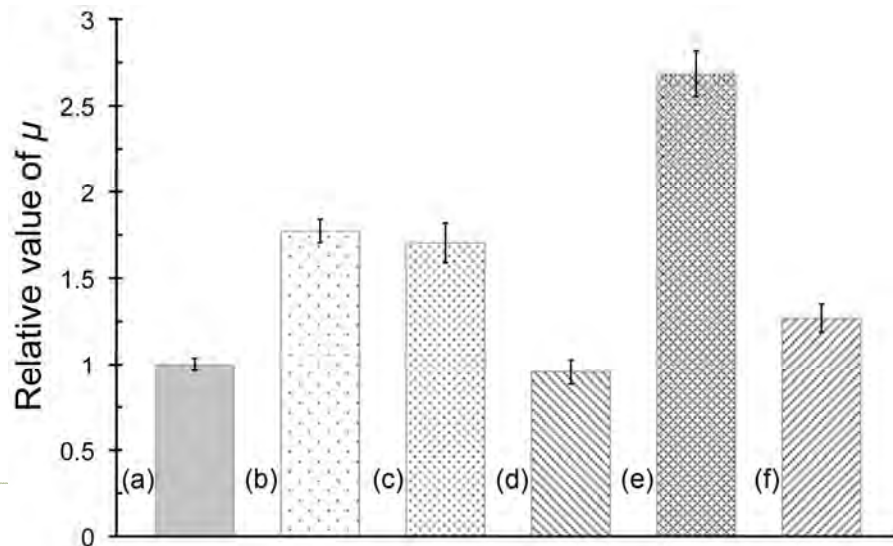
(a) New cotton
(b) Clean cotton
(c) Washed once
(d) Washed once & treated with conditioner
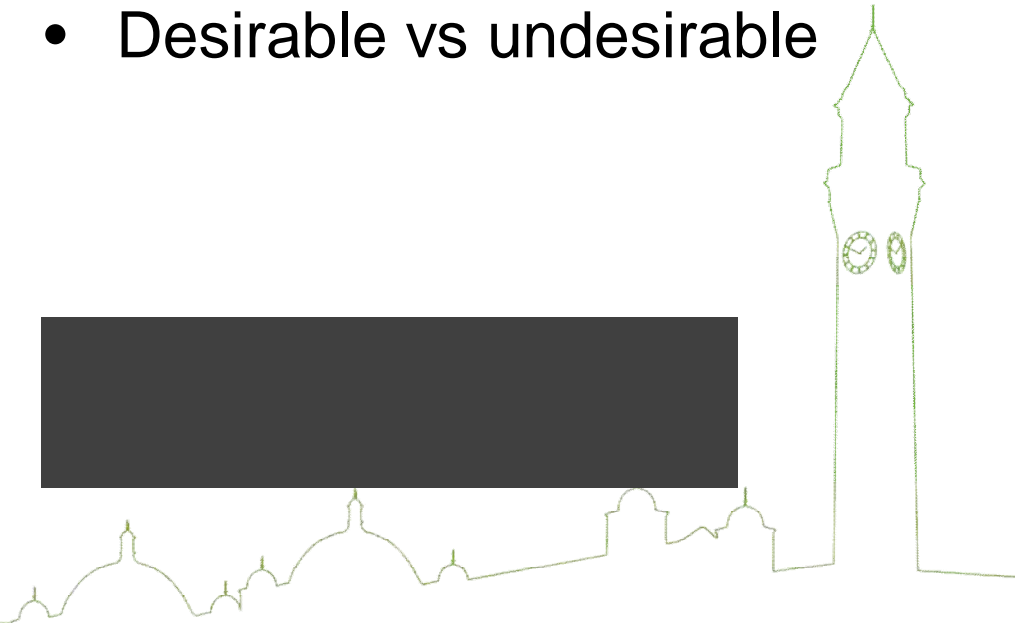(e) Washed 20 times
(f) Washed 20 times & treated with conditioner
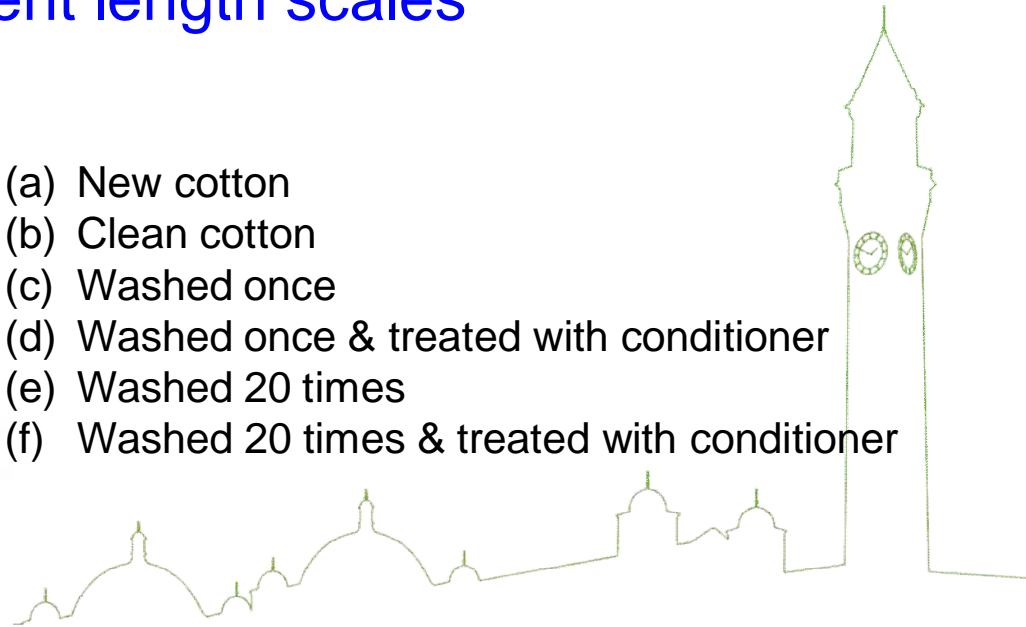
Molecular sweeping

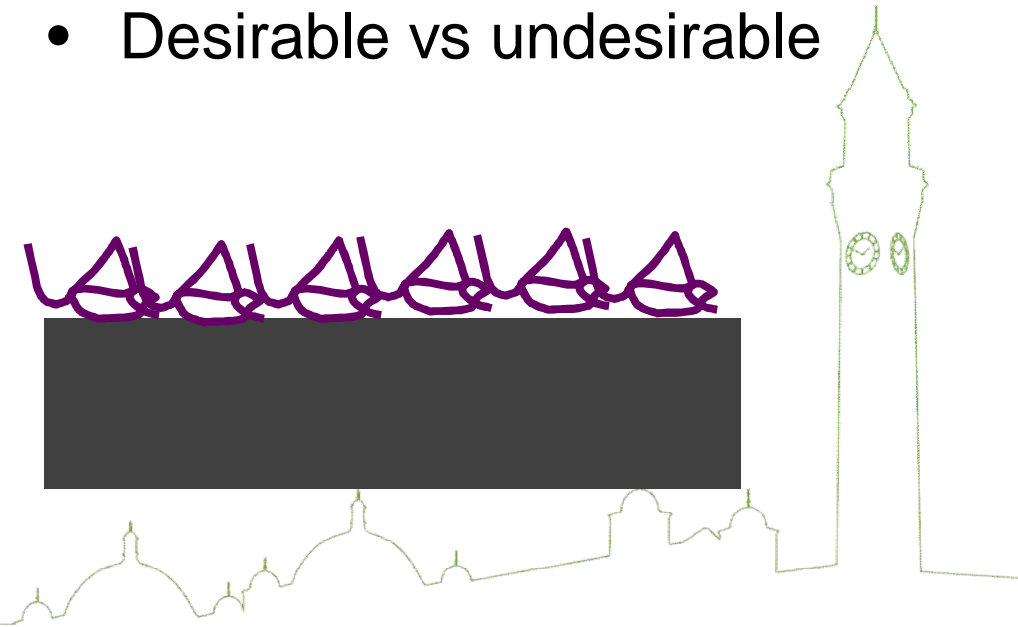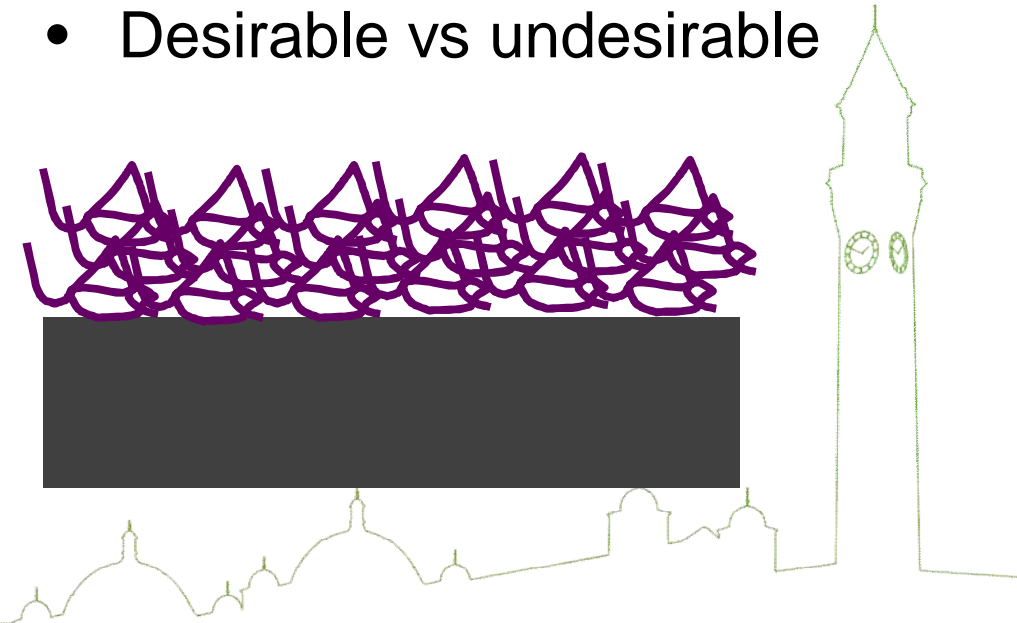## Surface fouling

- Desirable vs undesirable

Molecular sweeping

Surface fouling

- Desirable vs undesirable

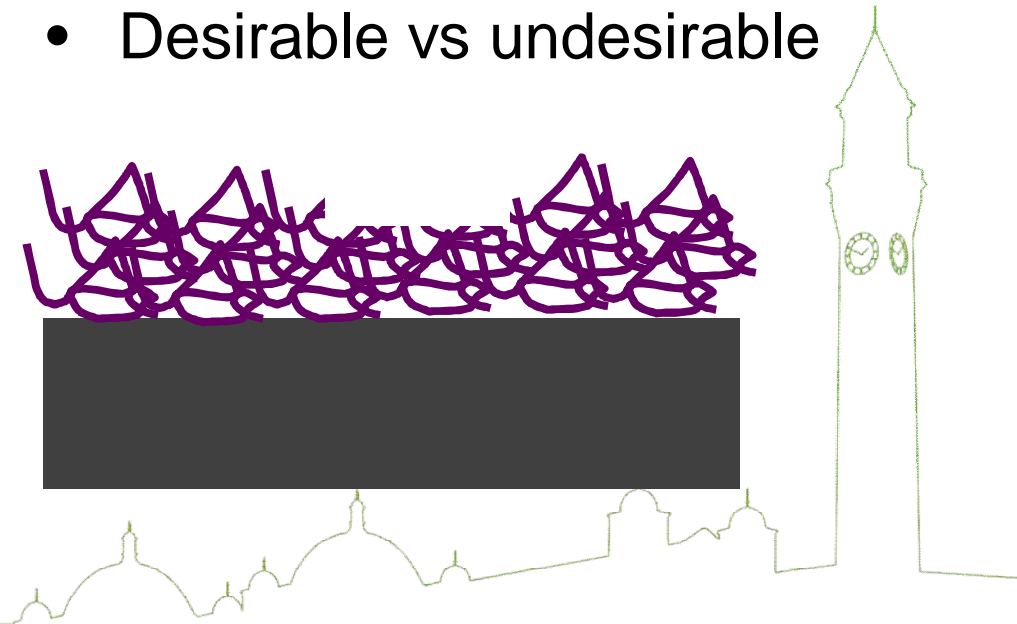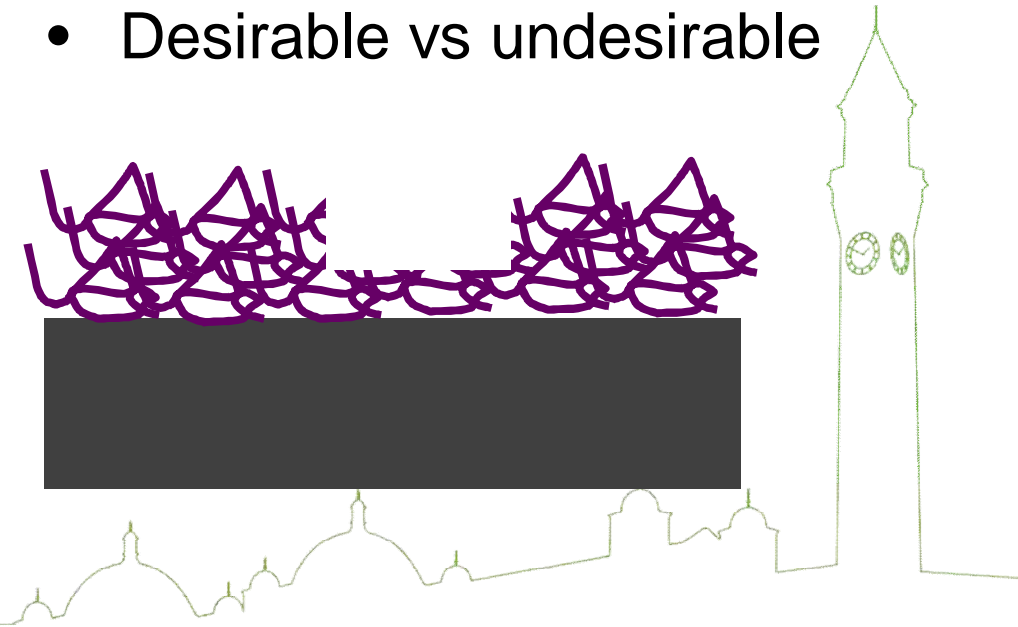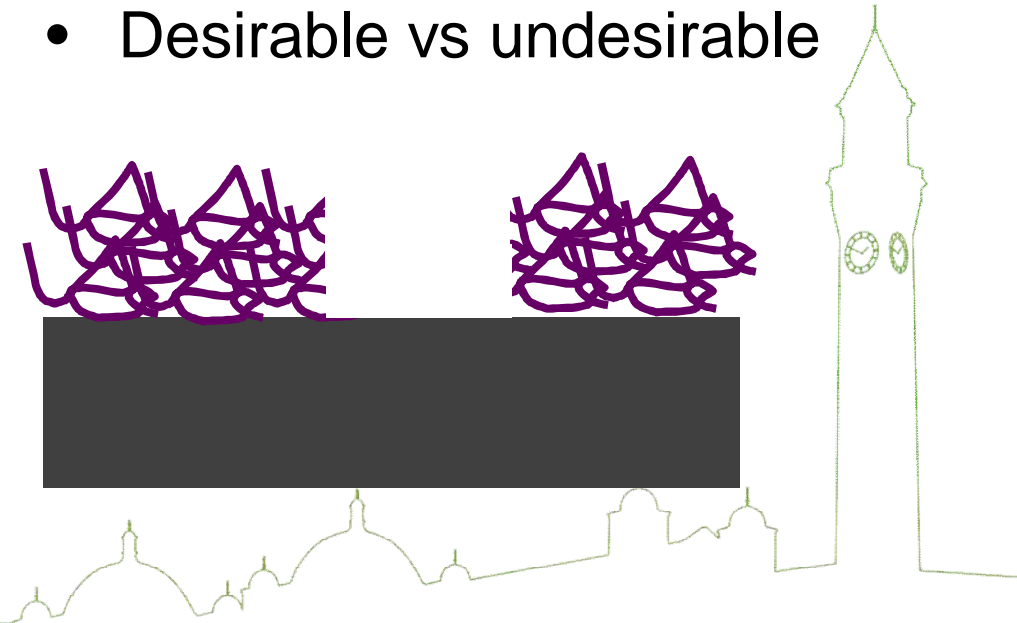# Molecular sweeping

Surface fouling
- Desirable vs undesirable

Molecular sweeping

Surface fouling
- Desirable vs undesirable

Molecular sweeping

Surface fouling
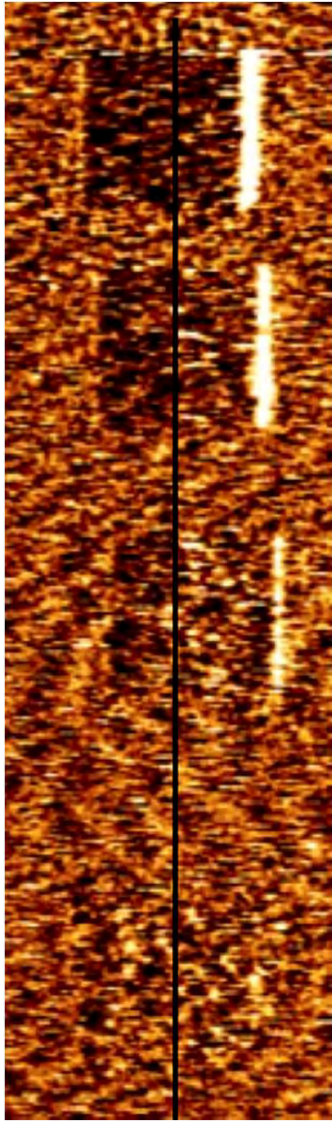- Desirable vs undesirable

Molecular sweeping

Surface fouling
- Desirable vs undesirable

Molecular sweeping

Surface fouling
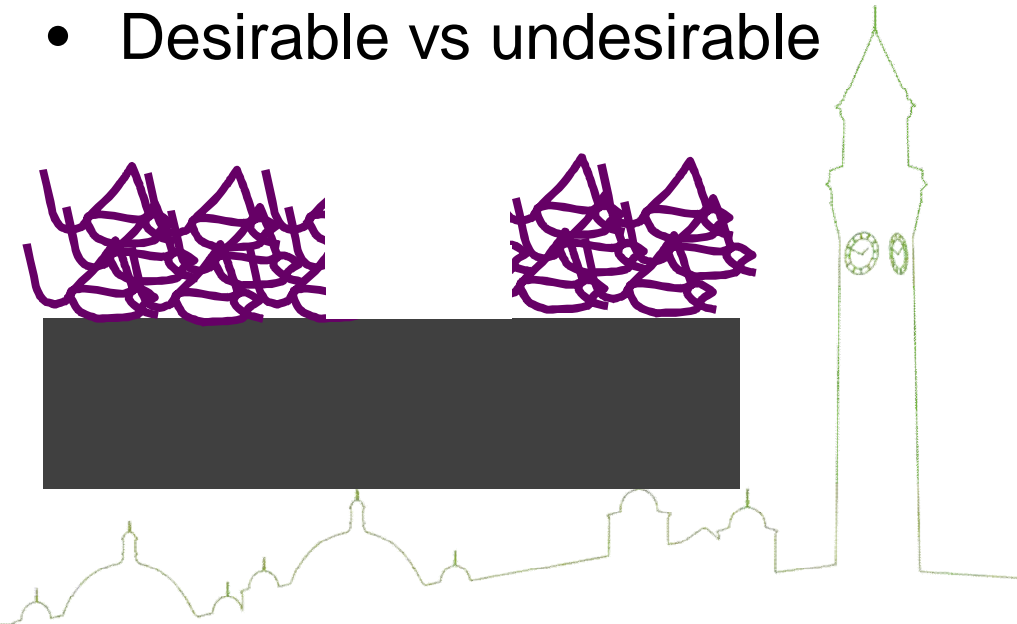- Desirable vs undesirable
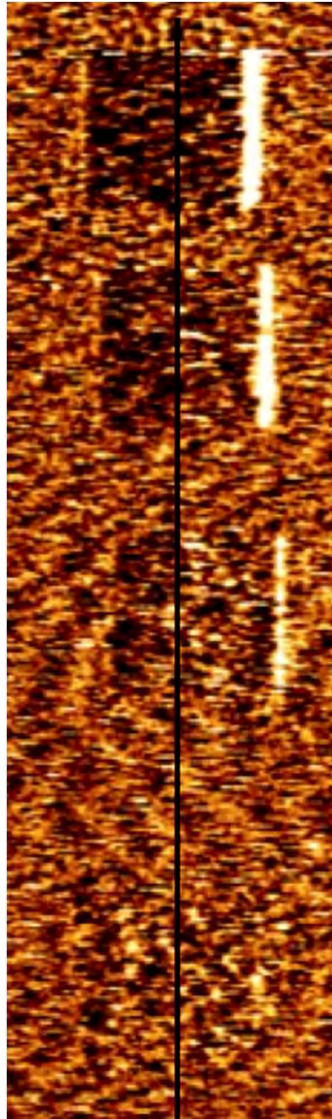
Molecular sweeping

5 nN

Surface fouling
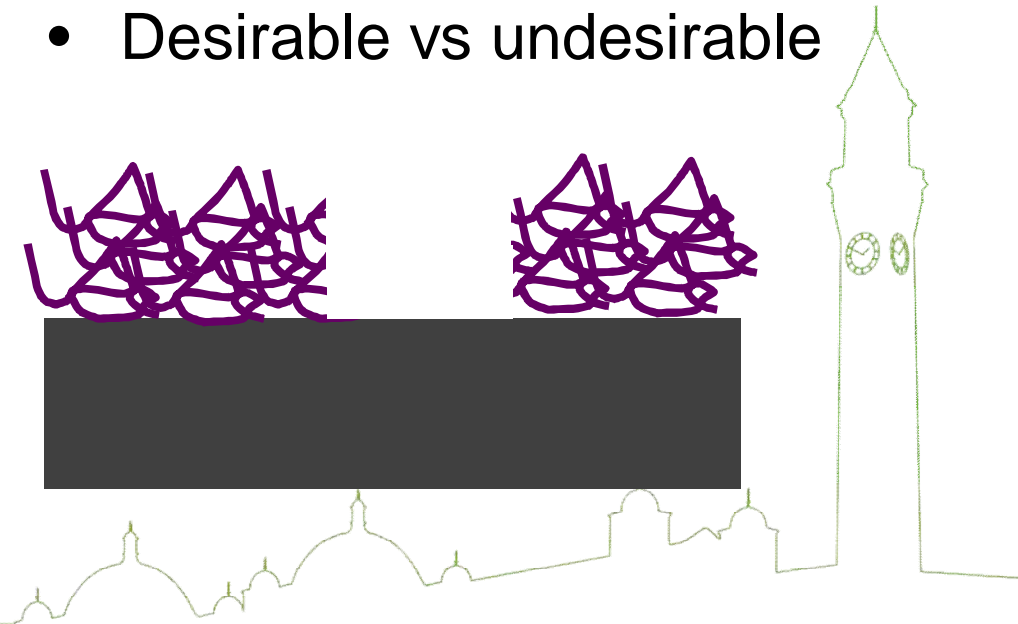- Desirable vs undesirable

Molecular sweeping

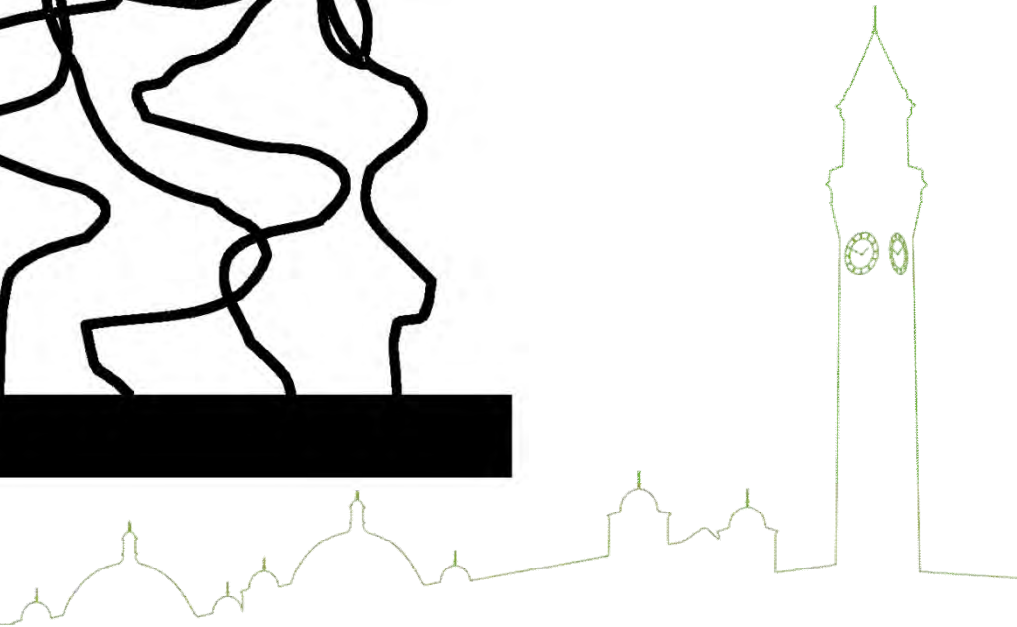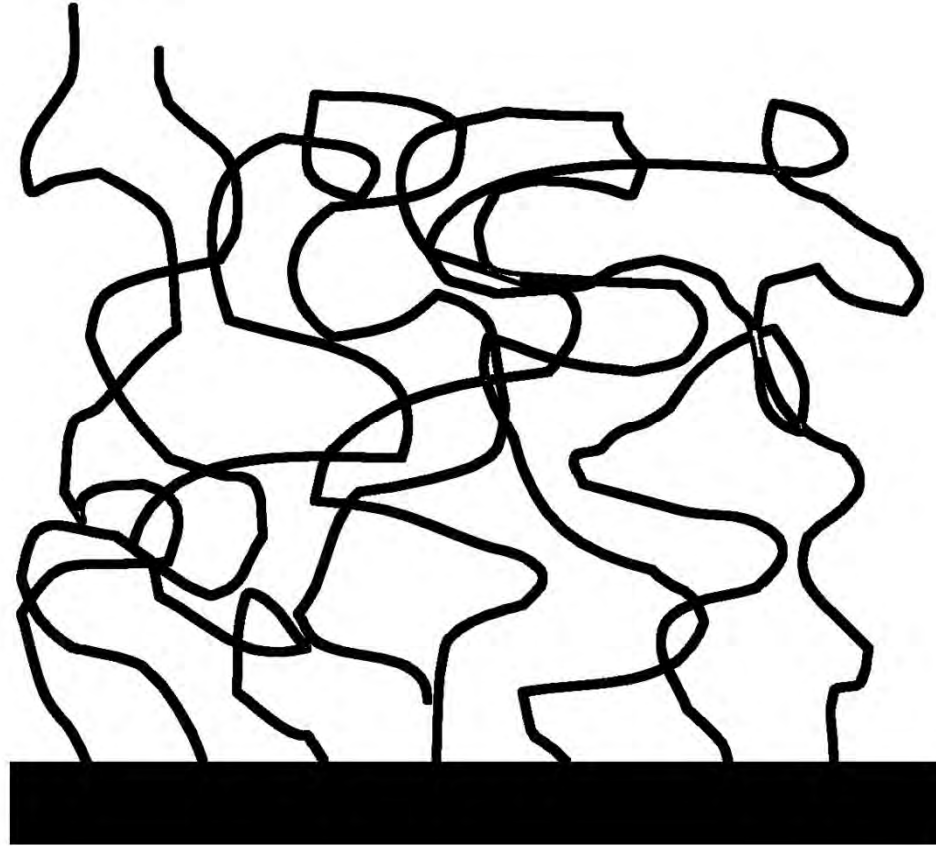20 nN

15 nN
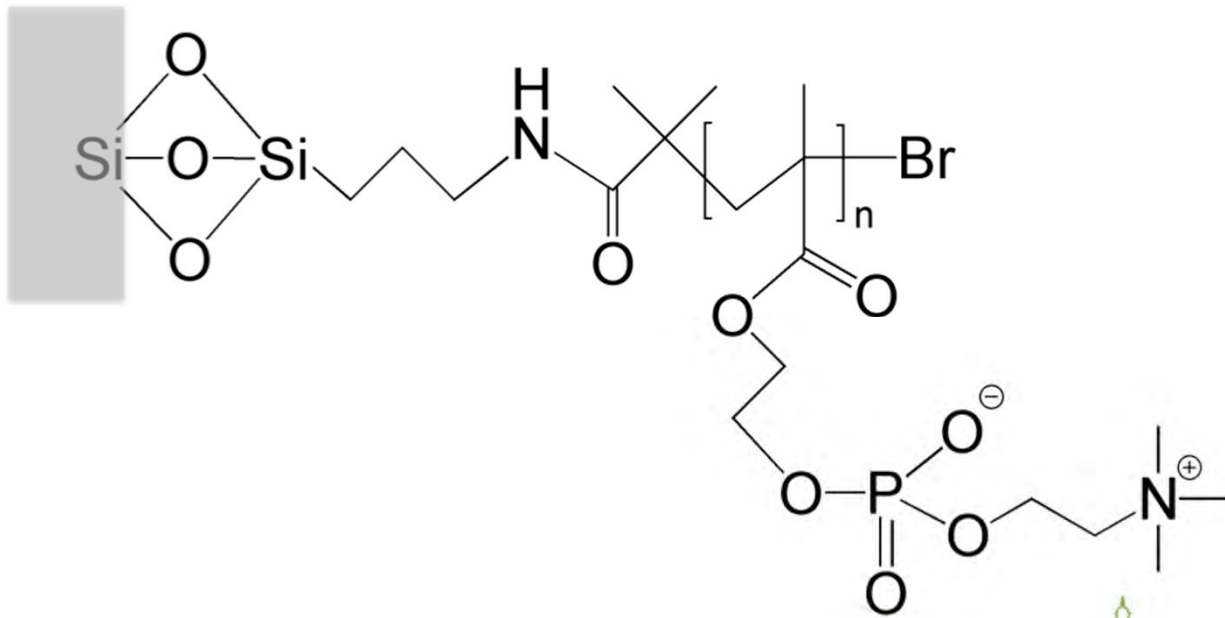
10 nN

5 nN

Surface fouling
- Desirable vs undesirable

Polymeric coating

Polymeric coating

Poly(2-(methacryloyloxy)ethyl phosphorylcholine)

μ=0.0004 (7.5 MPa)

Moro T. et al., *Nat. Mater.*, 2004, 3, 829
Chen M. et al., *Science*, 2009, 323, 1698
Hunter D. et al., *BMJ*, 2006, 332, 639

Polymeric coating

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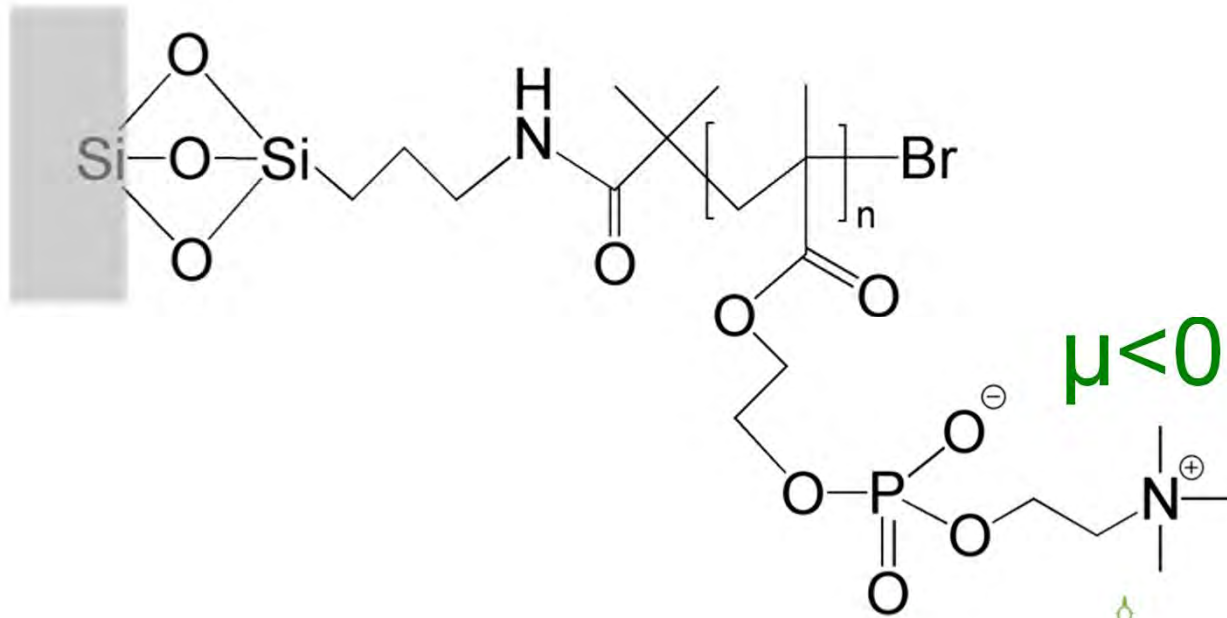
Image courtesy of Hunter D.

μ<0.002 (5 MPa)

Moro T. et al., *Nat. Mater.*, 2004, 3, 829
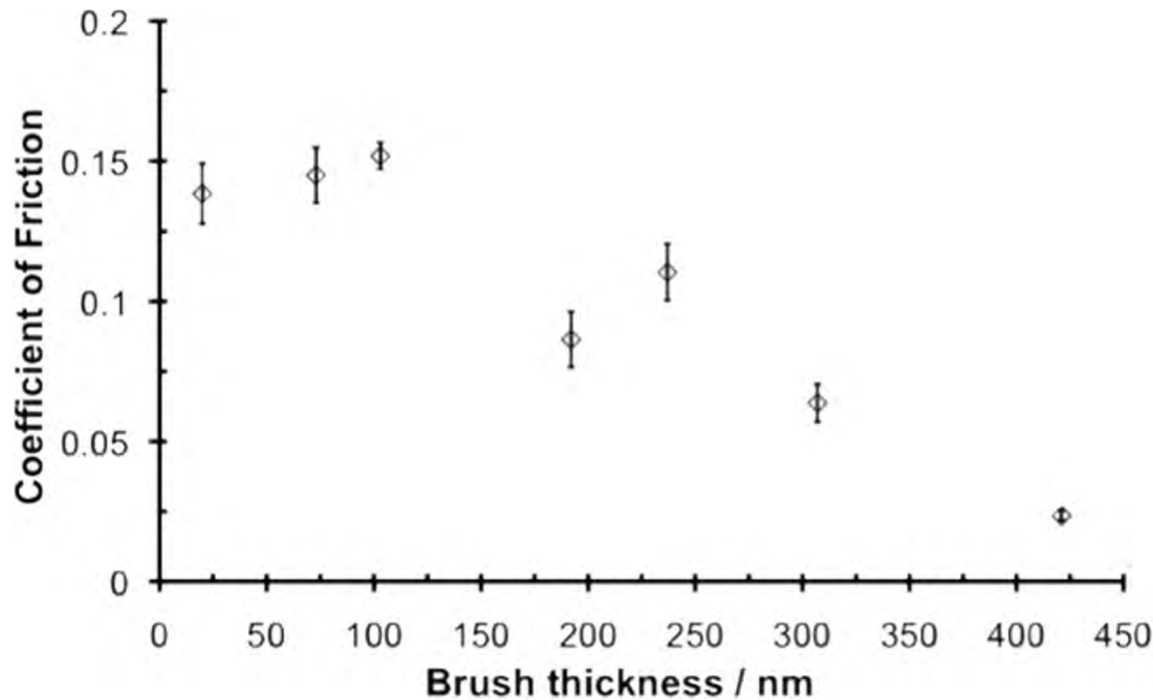Chen M. et al., *Science*, 2009, 323, 1698
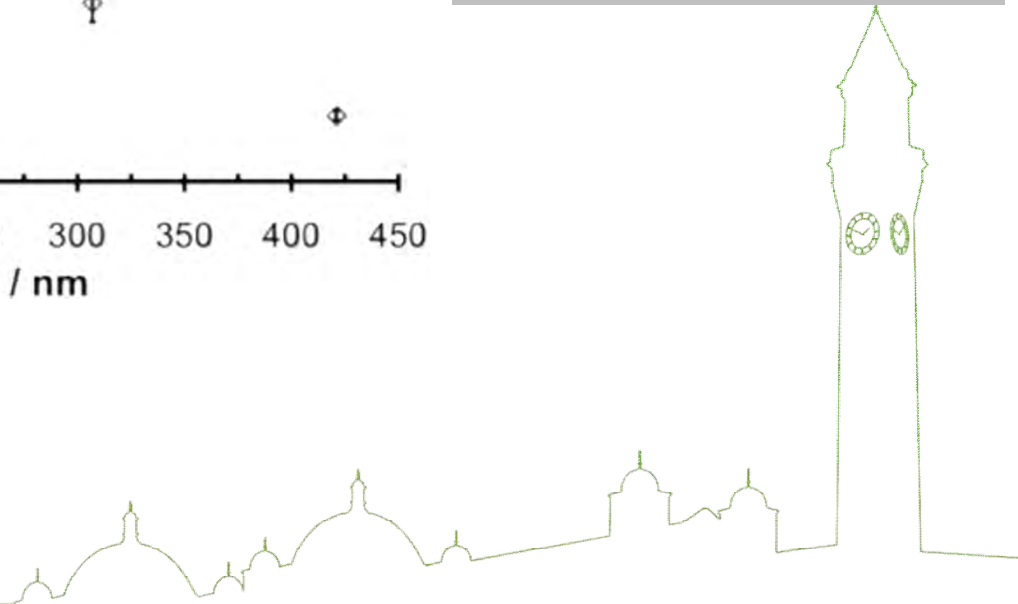Hunter D. et al., *BMJ*, 2006, 332, 639

# Lubrication of polymer brushes

Optimum thickness, solvent, ionic strength, pH?
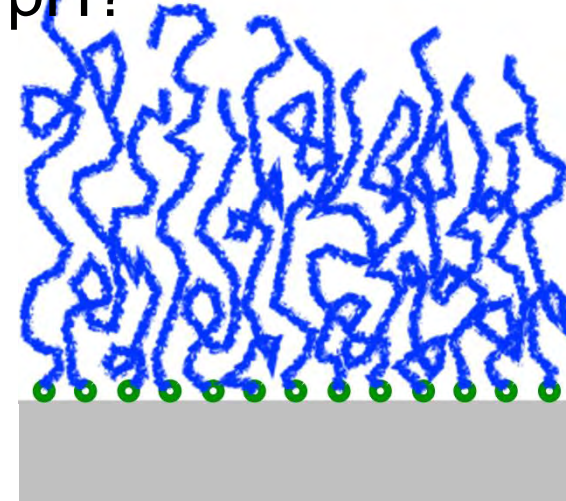
Zhang et al. *Langmuir*, **2011**
Busuttil et al. *Faraday Discuss.*, **2012**
Zhang et al. *Langmuir*, **2013**
Raftari et al. *Soft Matter*, **2014**
Raftari et al. *Macromolecules,* **2015**
Zhang et al. *Langmuir*, **2016**
Zhang et al. *Langmuir*, **2017**
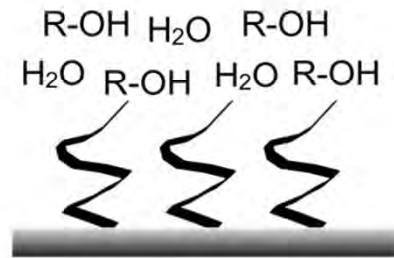Raftari et al. Trib. Lett. accepted

Response to stimuli

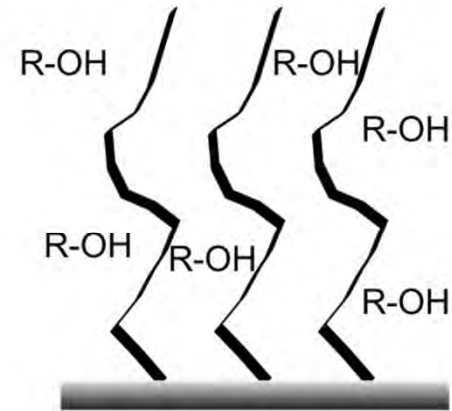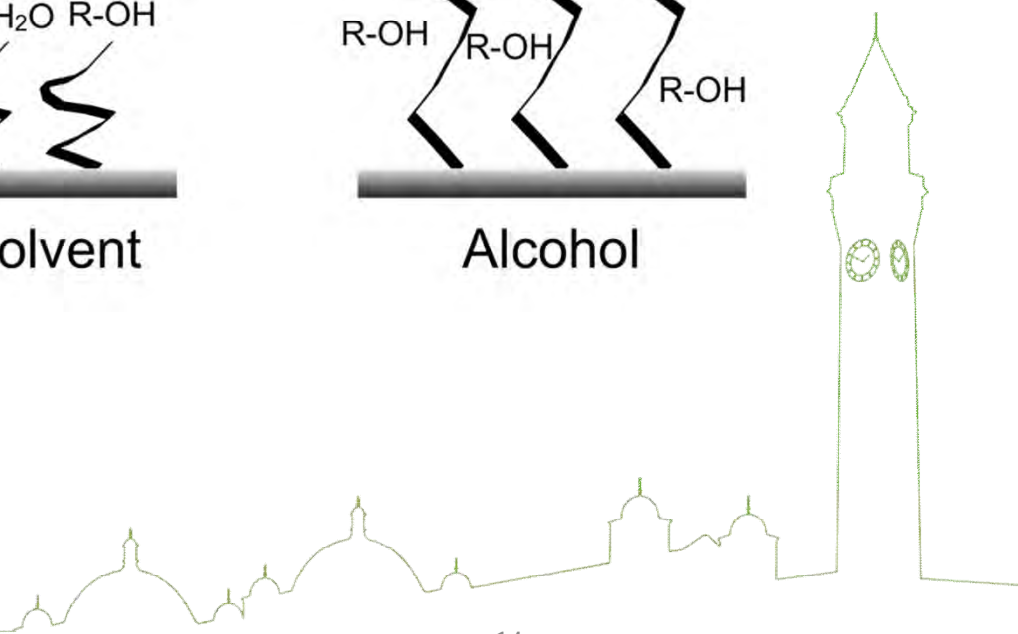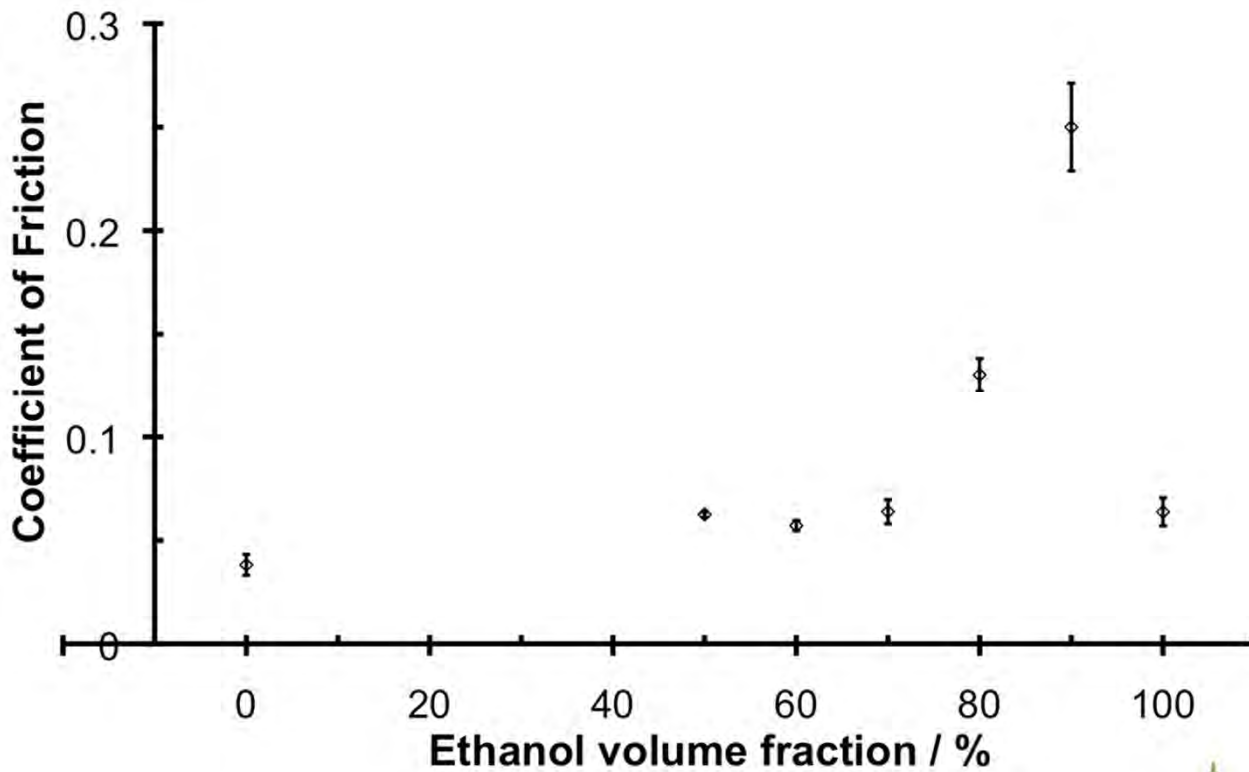○ Brush collapsed at 90/10 volume ratio
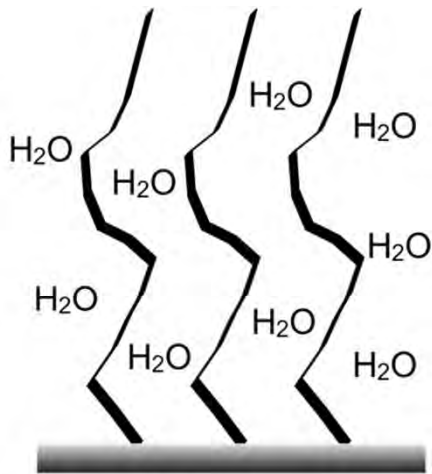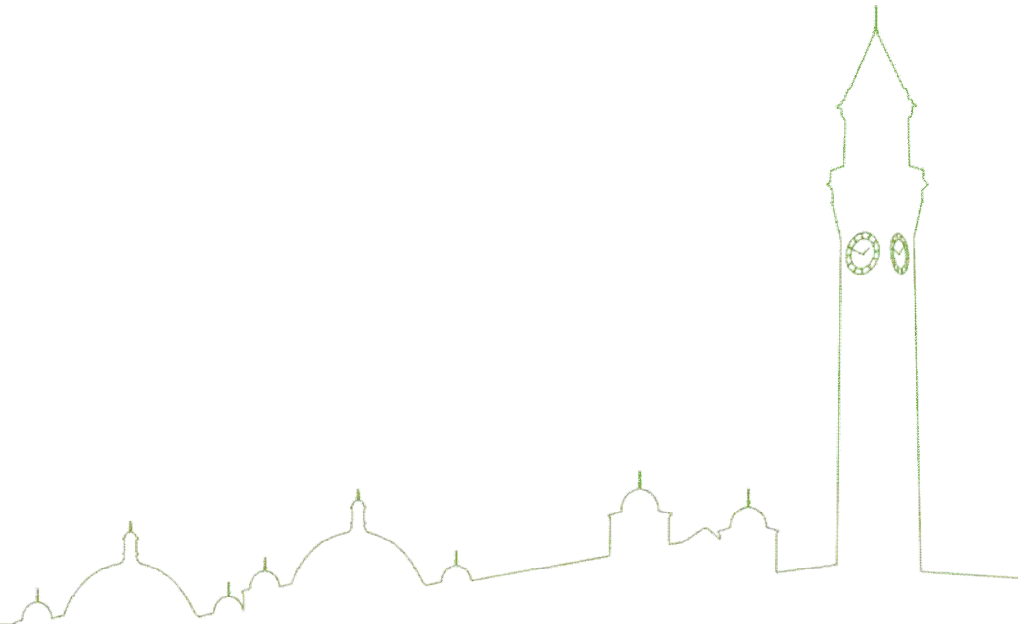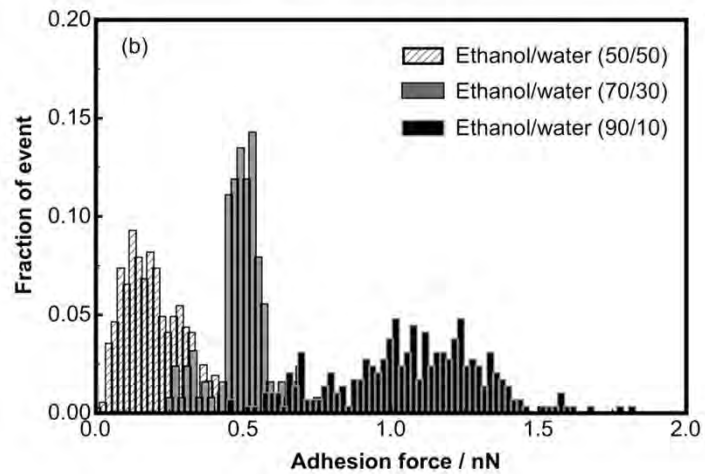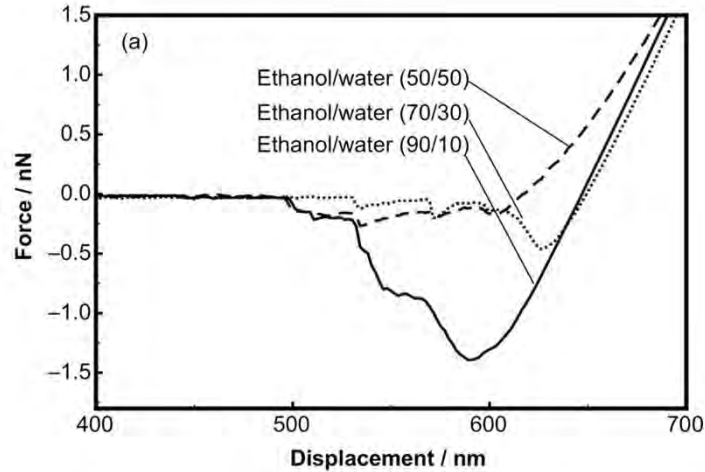

Water

Mixed solvent

Alcohol

Response to stimuli

○ Brush collapsed at 90/10 volume ratio

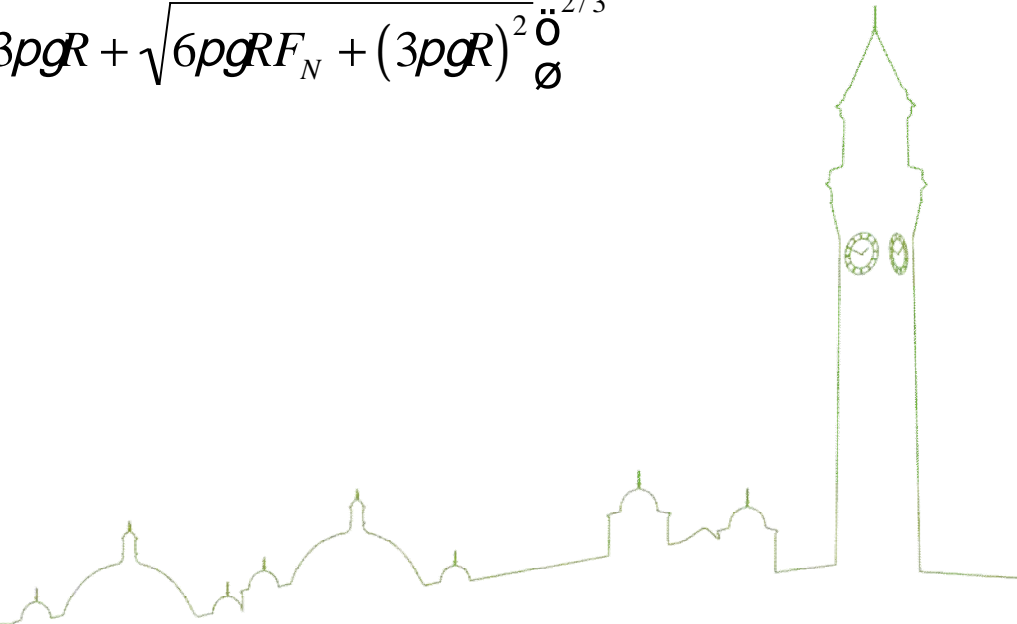# Response to stimuli

○ Brush collapsed at 90/10 volume ratio

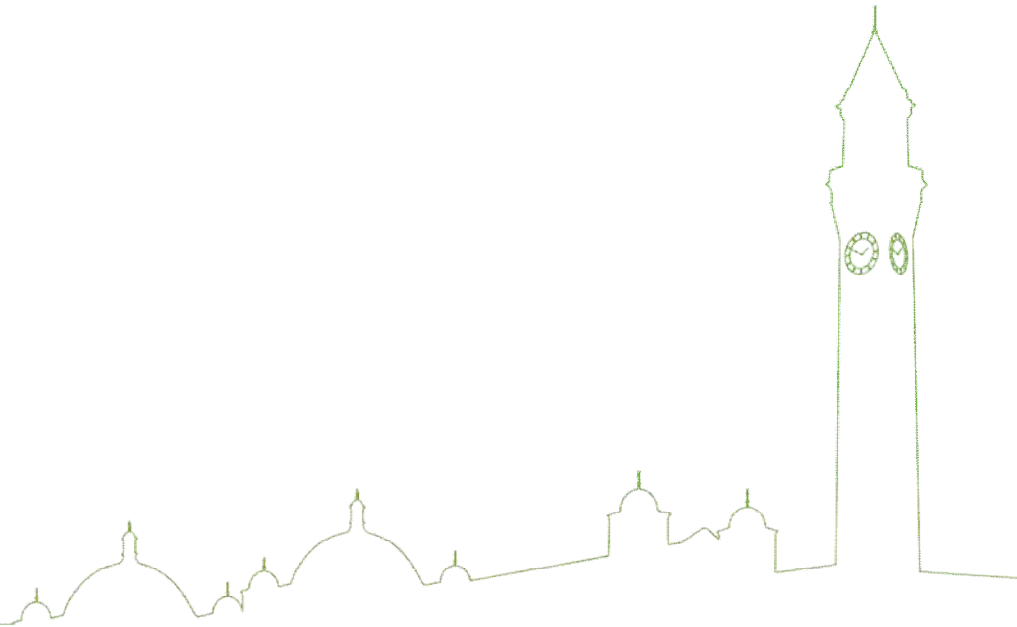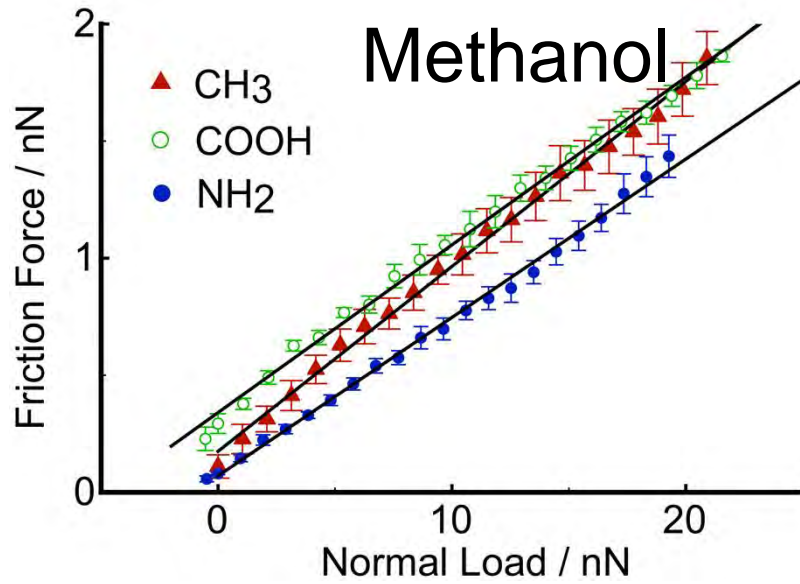# Single asperity contact mechanics

Amontons' law

$$F_F = mF_N$$

DMT

$$A = p \left(\frac{R}{K} \right)^{2/3} \left(F_N + 4 p g R \right)^{2/3}$$

JKR

$$A = p \left(\frac{R}{K} \right)^{2/3} \left(F_N + 3 p g R + \sqrt{6 p g R F_N + \left(3 p g R \right)^2} \right)^{2/3}$$

Single asperity contact mechanics

Methanol

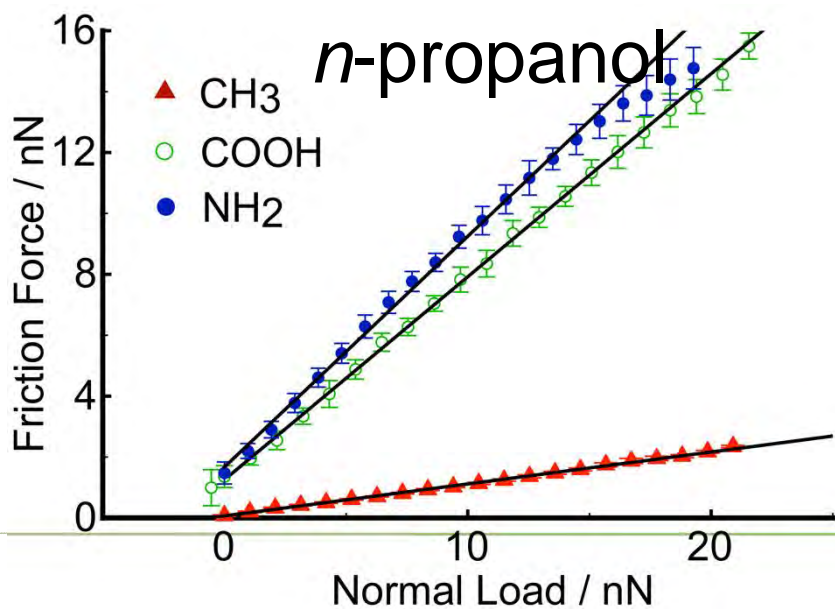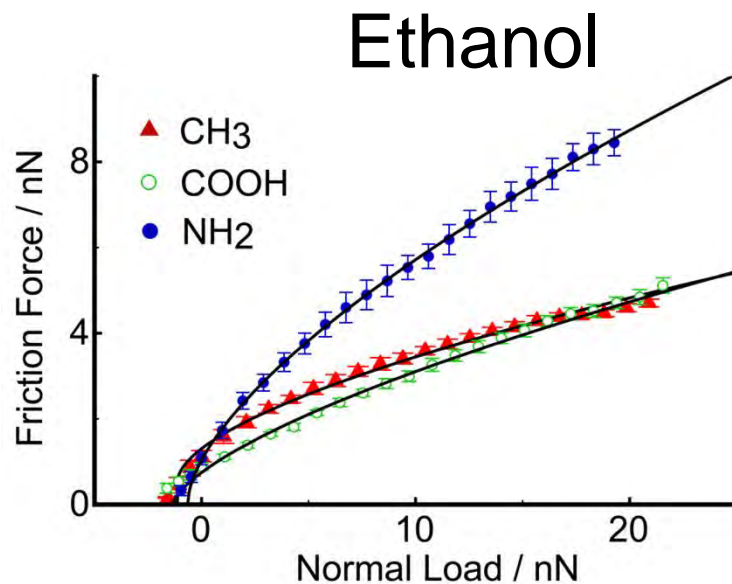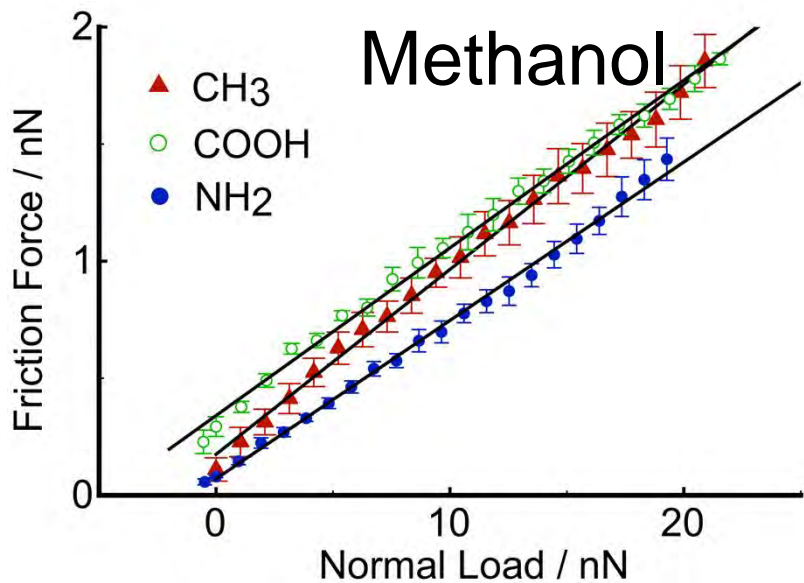Plot of Friction Force / nN versus Normal Load / nN with data series: CH3 (red triangles), COOH (green open circles), NH2 (blue filled circles).
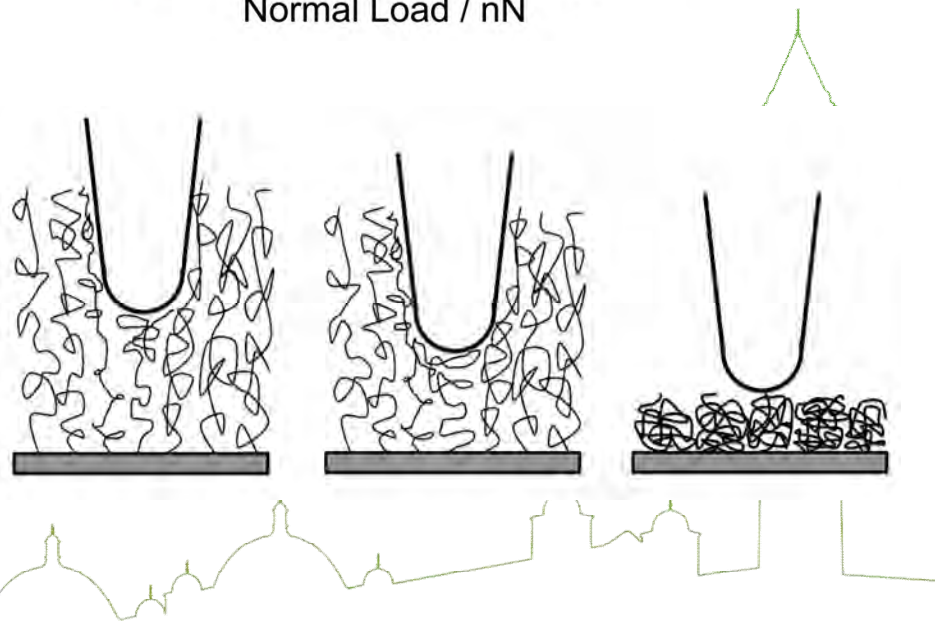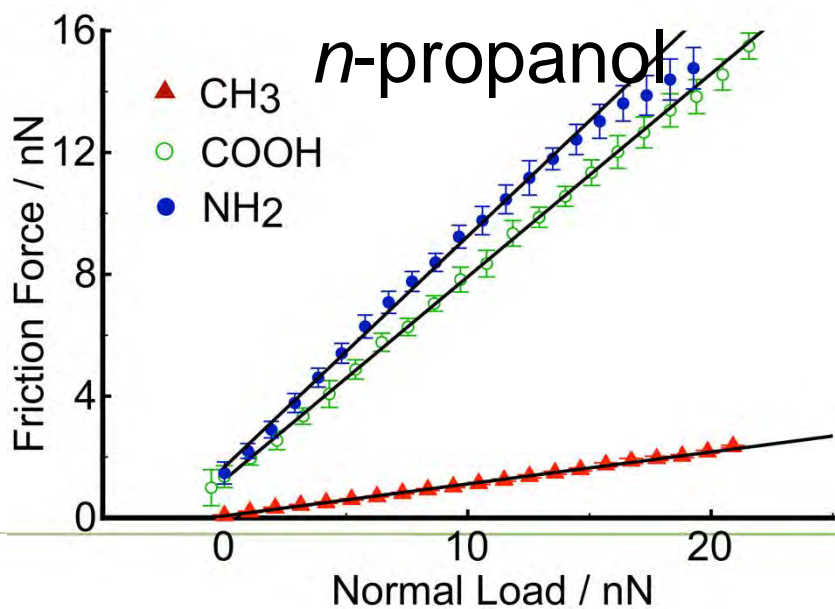
Single asperity contact mechanics

Single asperity contact mechanics

Methanol

Ethanol

n-propanol

Single asperity contact mechanics
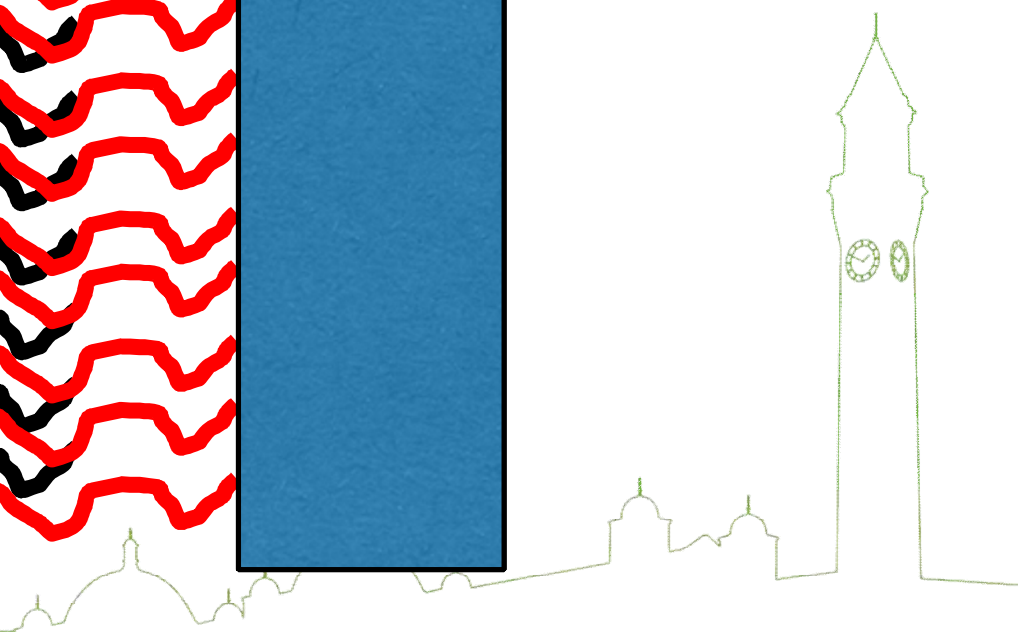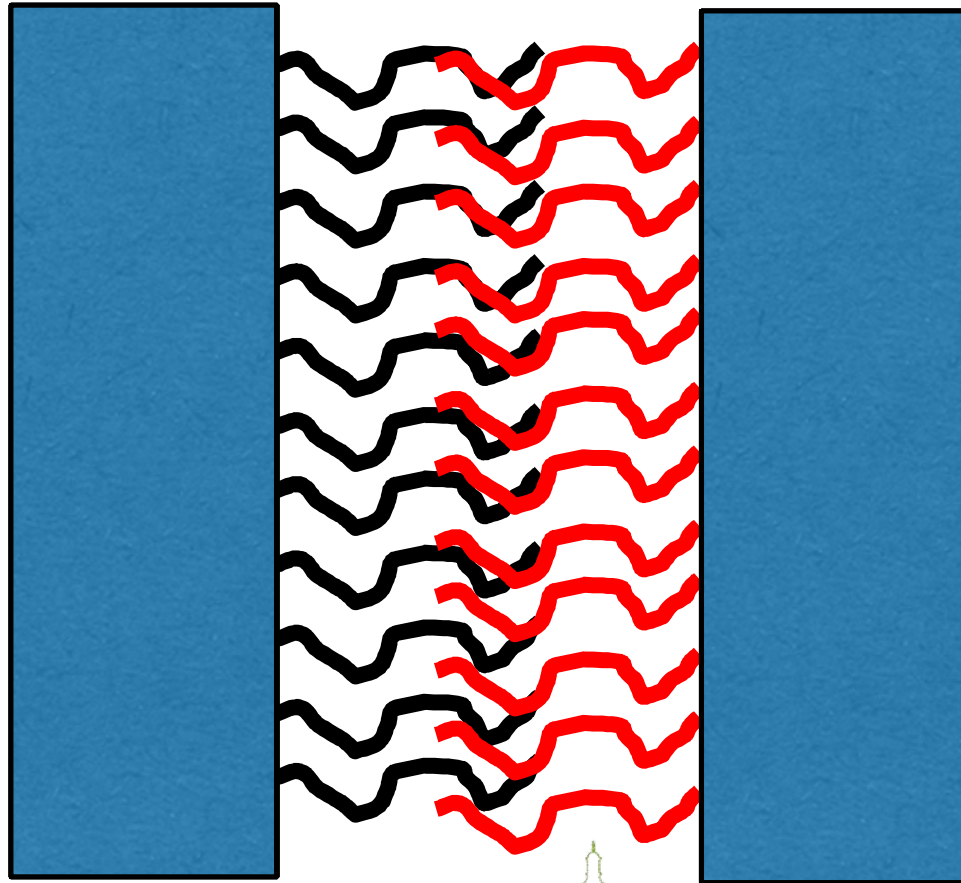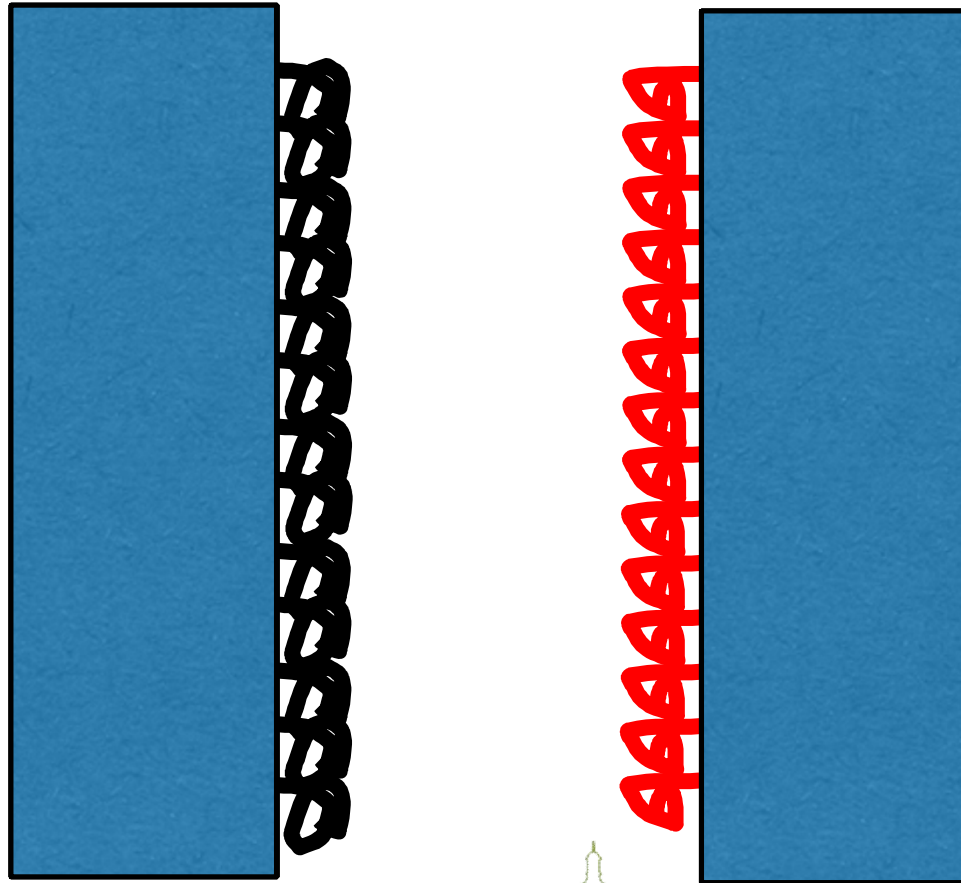

Methanol

Ethanol

n-propanol
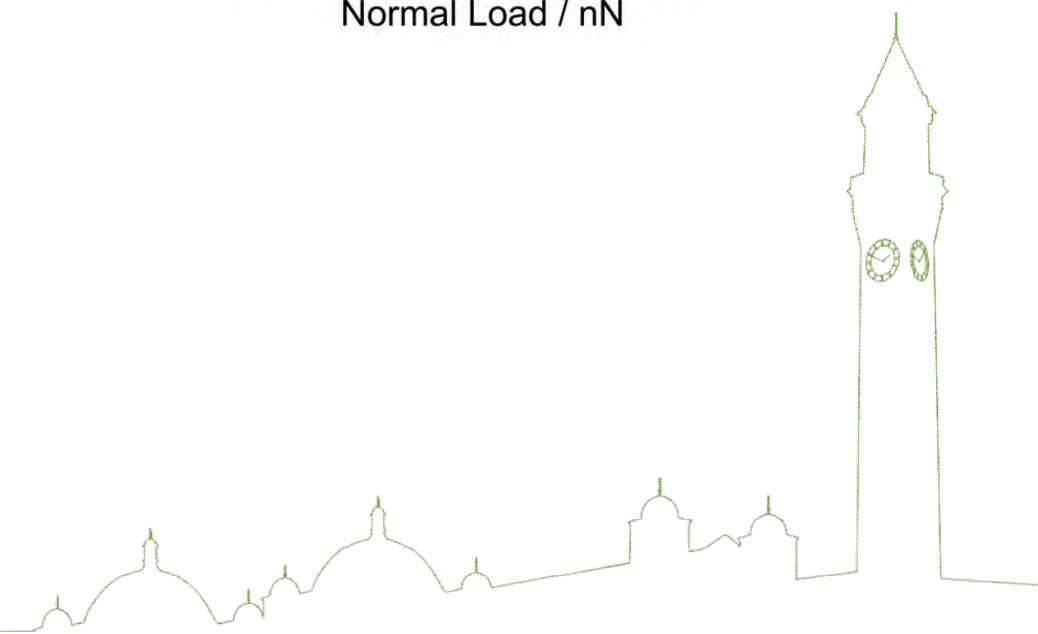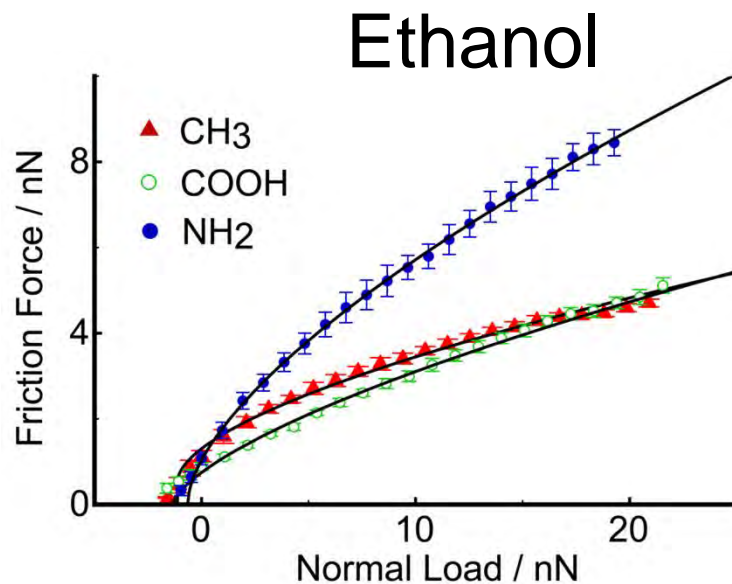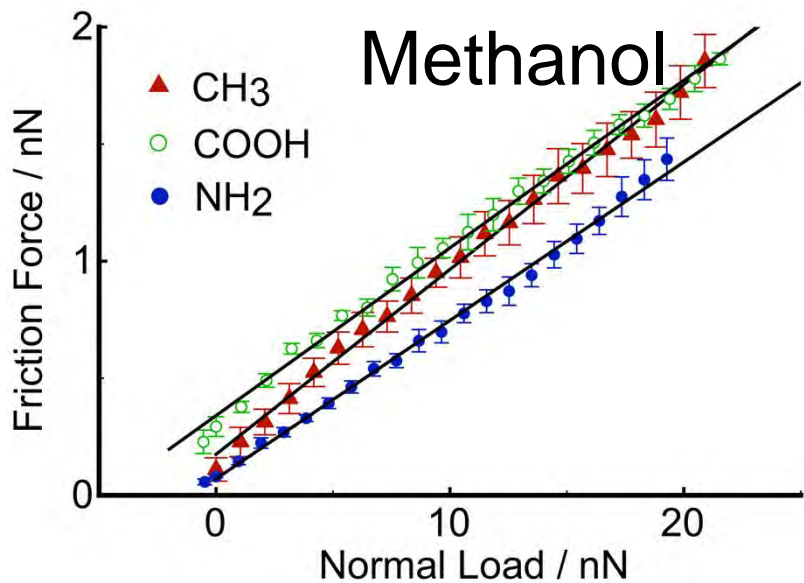
Summary 2

- Performance of the polymeric coating
- Response to external stimuli, e.g. pH, salt concentration, presence of other surfactants
- Polymer-surface interaction – not restricted by the size of the objects
- Polymer film formation kinetics
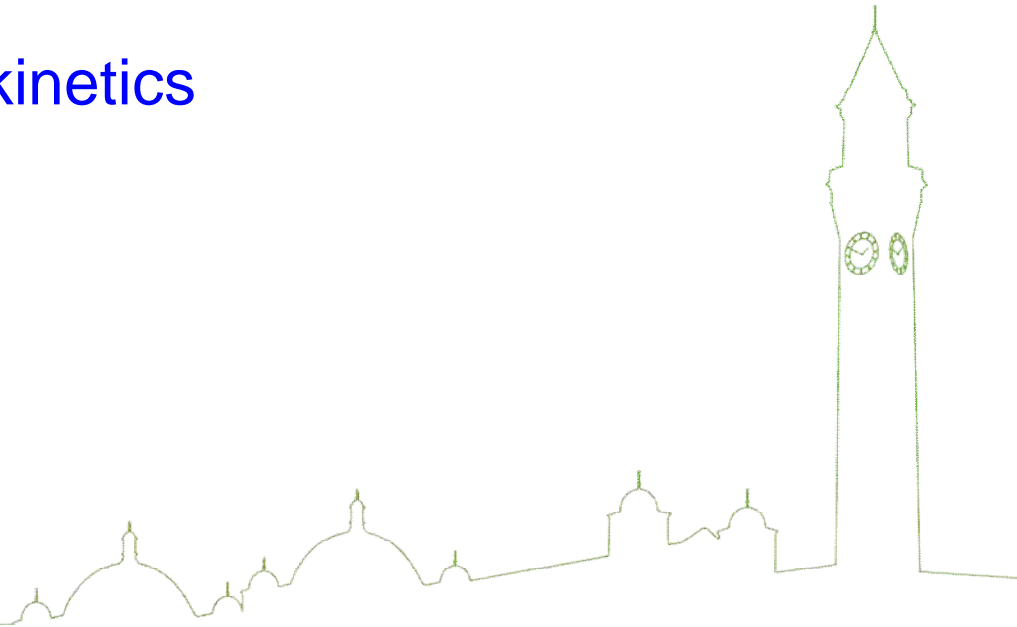
Molecular fabrication

Molecular fabrication

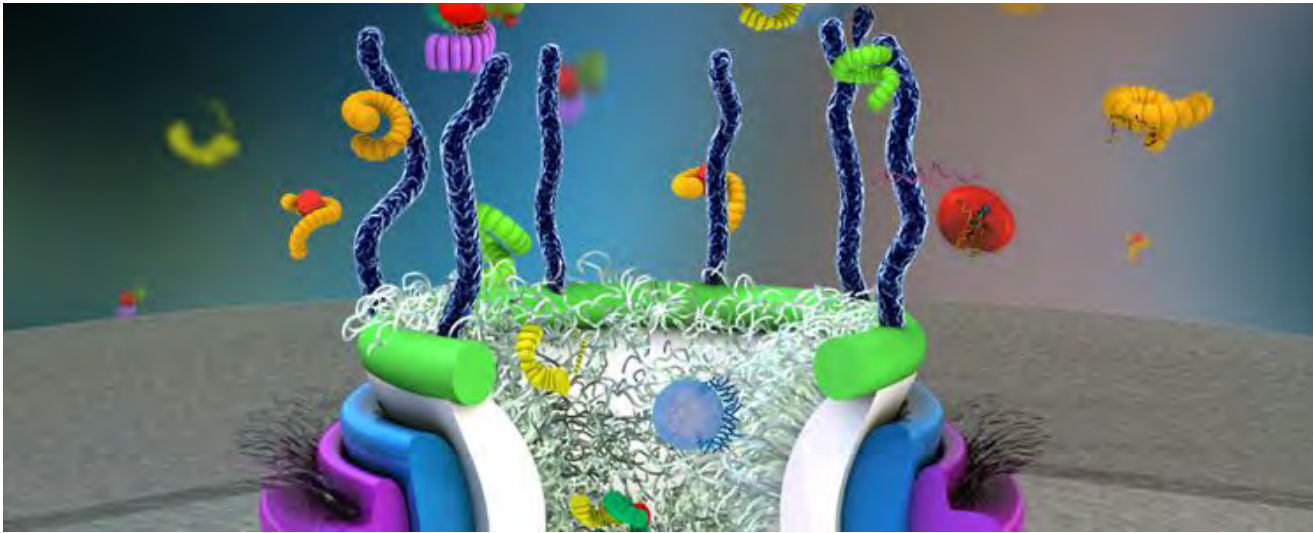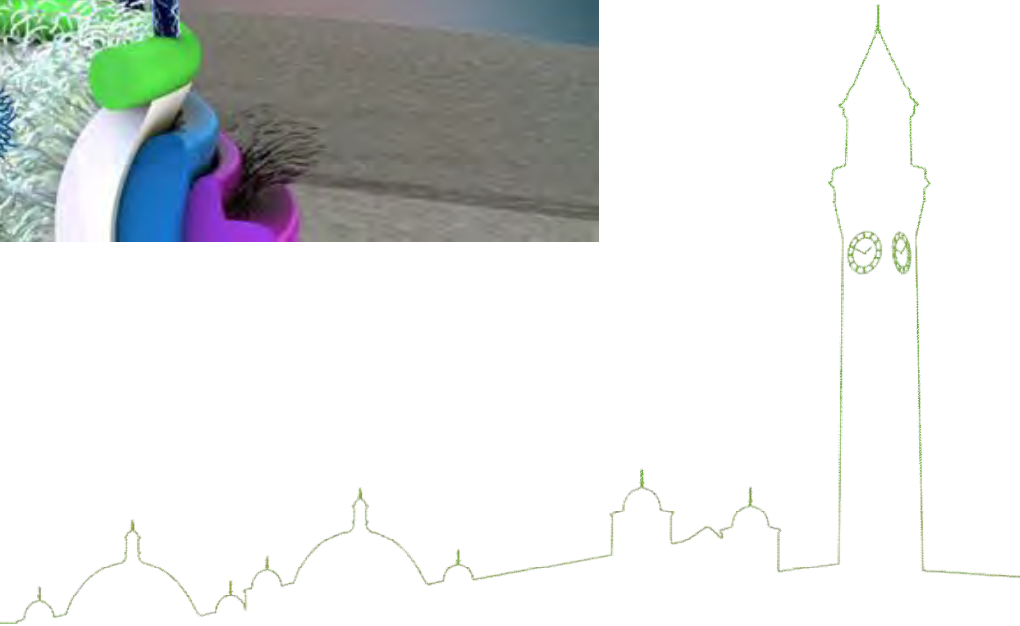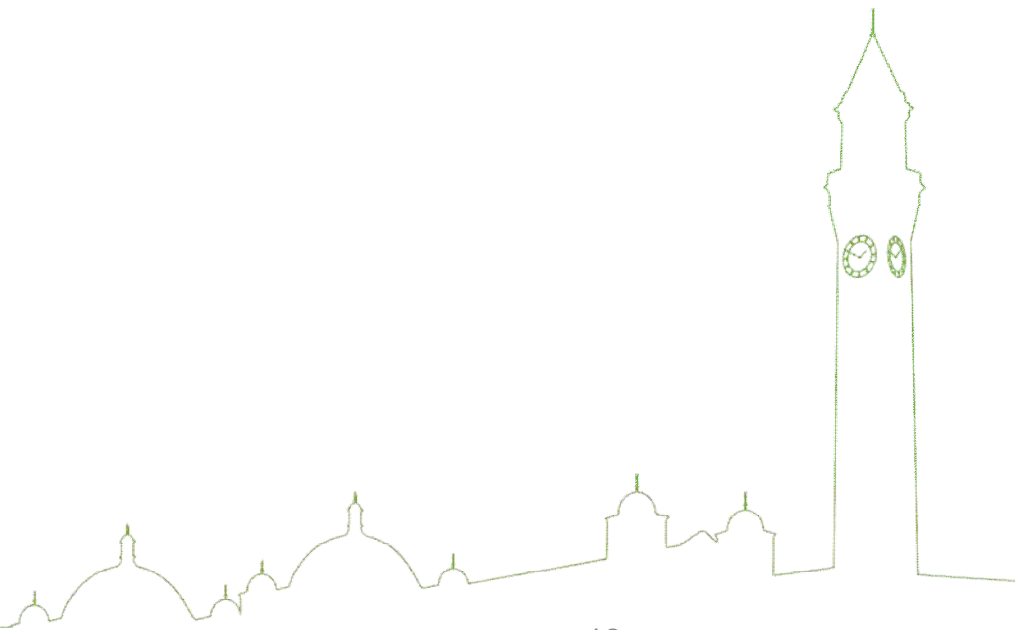# Molecular fabrication
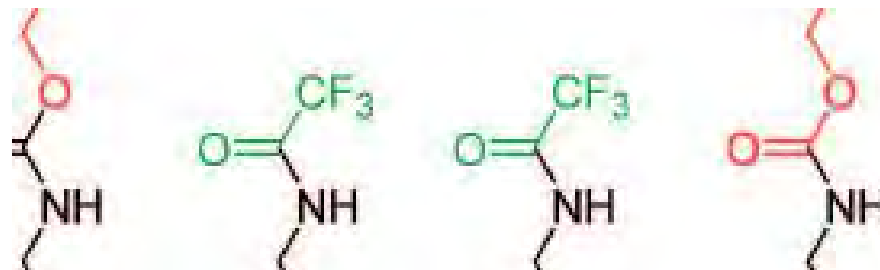
Nuclear Pore Complex

Image courtesy: Mofrad's lab, UC Berkeley

Constructing molecular objects

Constructing molecular objects

Top-down

- Photolithography: Scanning Near-field Optical Microscopy (SNOM
- 2-nitrophenylpropyloxycarbonyl (NPPOC)

SNOM

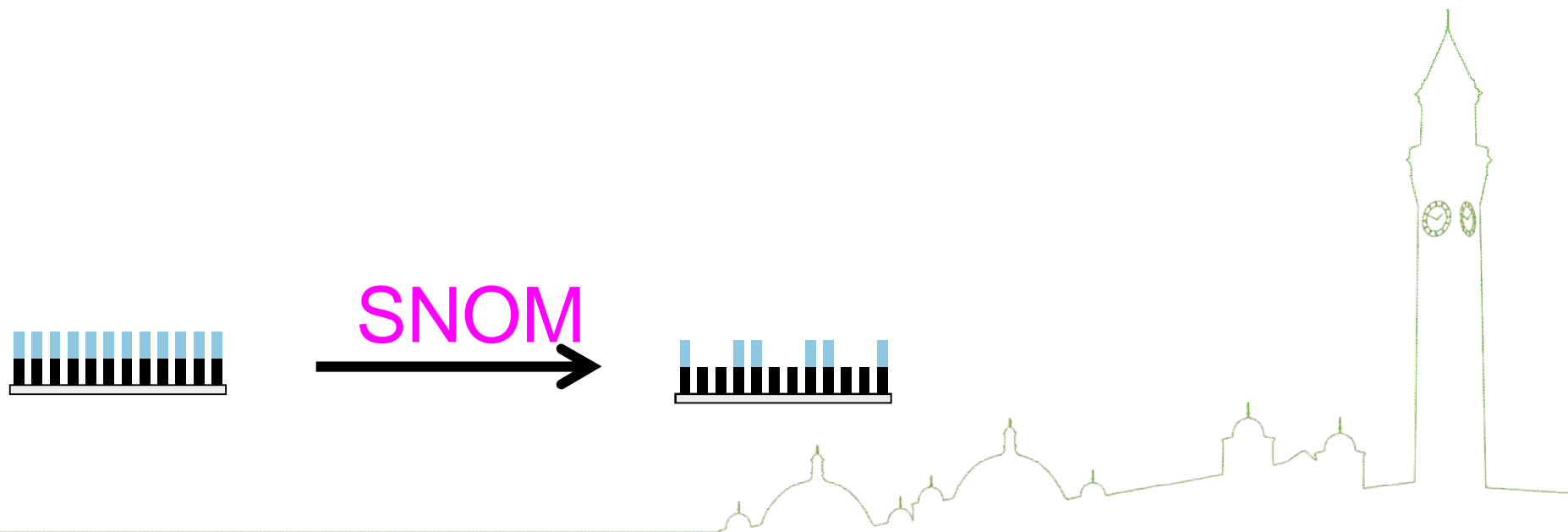S A A Ahmad et al., J. Am. Chem. Soc., 2009, 131, 1513
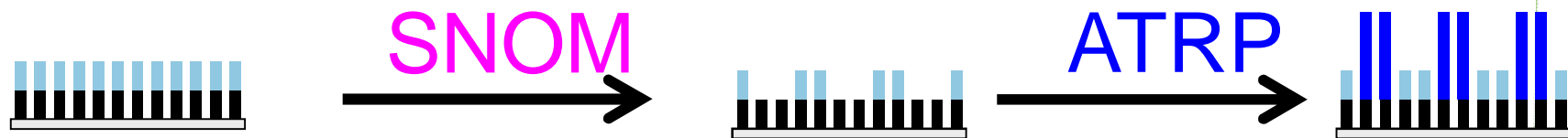
Constructing molecular objects

Top-down
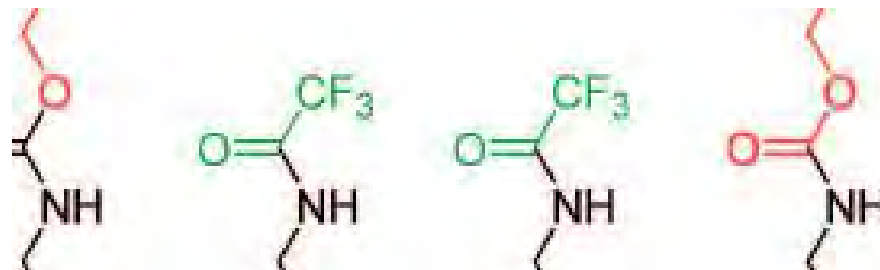
- Photolithography: Scanning Near-field Optical Microscopy (SNOM
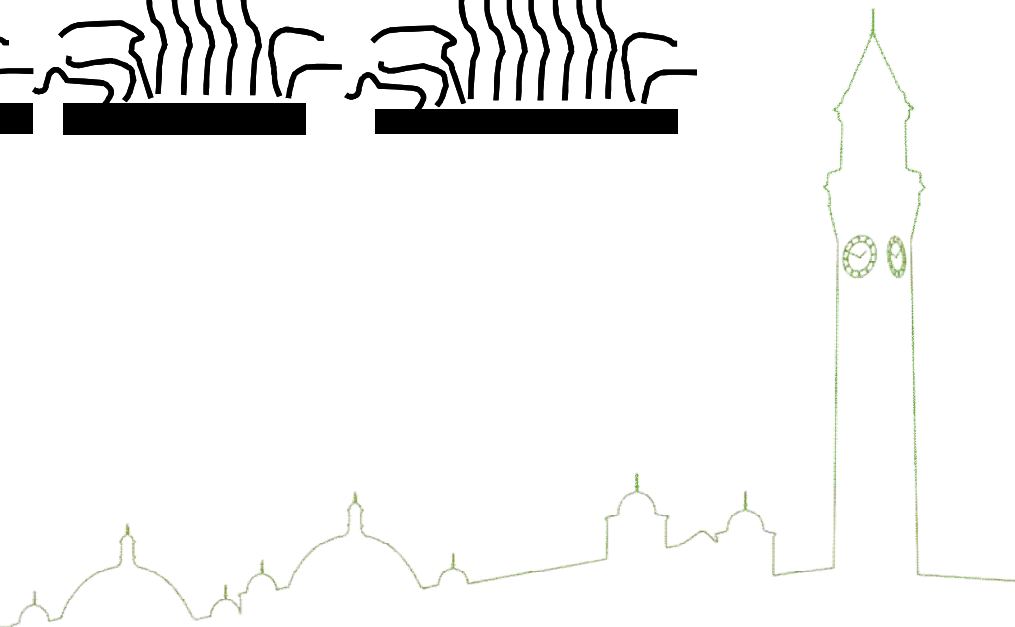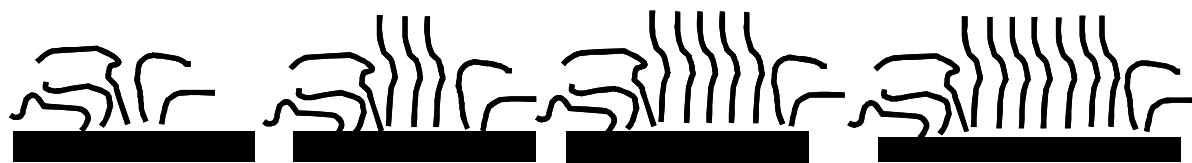- 2-nitrophenylpropyloxycarbonyl (NPPOC)

Bottom-up

- Atomic Transfer Radical Polymerization
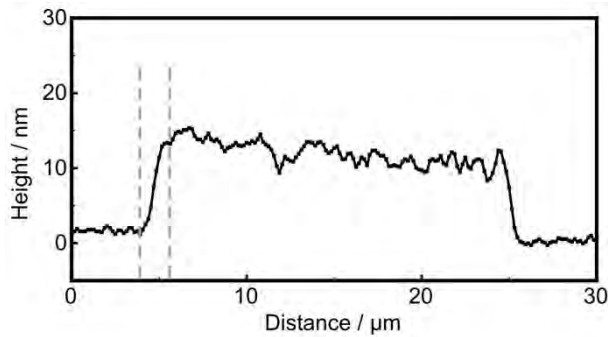- Poly(methacryloyloxy)ethyl phosphorylcholine) (PMPC)

SNOM

ATRP

S A A Ahmad et al., J. Am. Chem. Soc., 2009, 131, 1513

Constructing molecular objects

How do they behave?
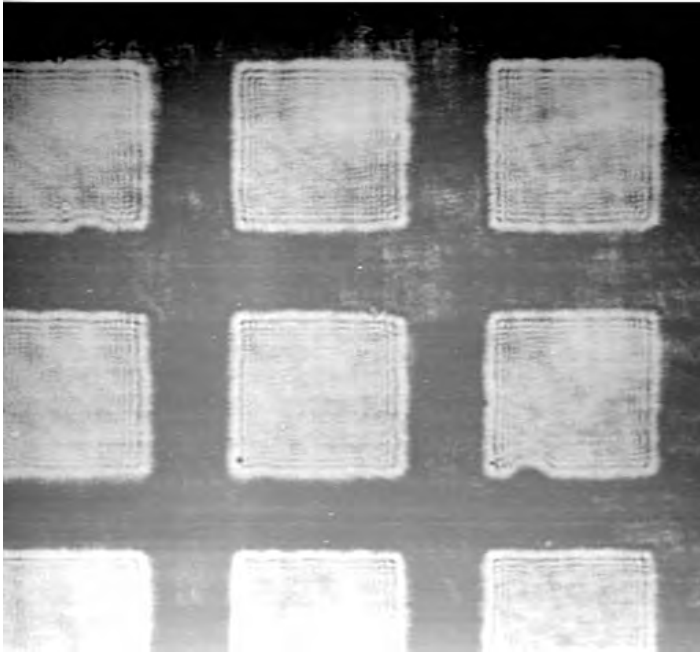
S A A Ahmad et al., J. Am. Chem. Soc., 2009, 131, 1513

Nanoscopic objects

Zhang et al. *Langmuir*, **2016**
Zhang et al. *Langmuir*, **2017**

Nanoscopic objects

Zhang et al. *Langmuir*, **2016**
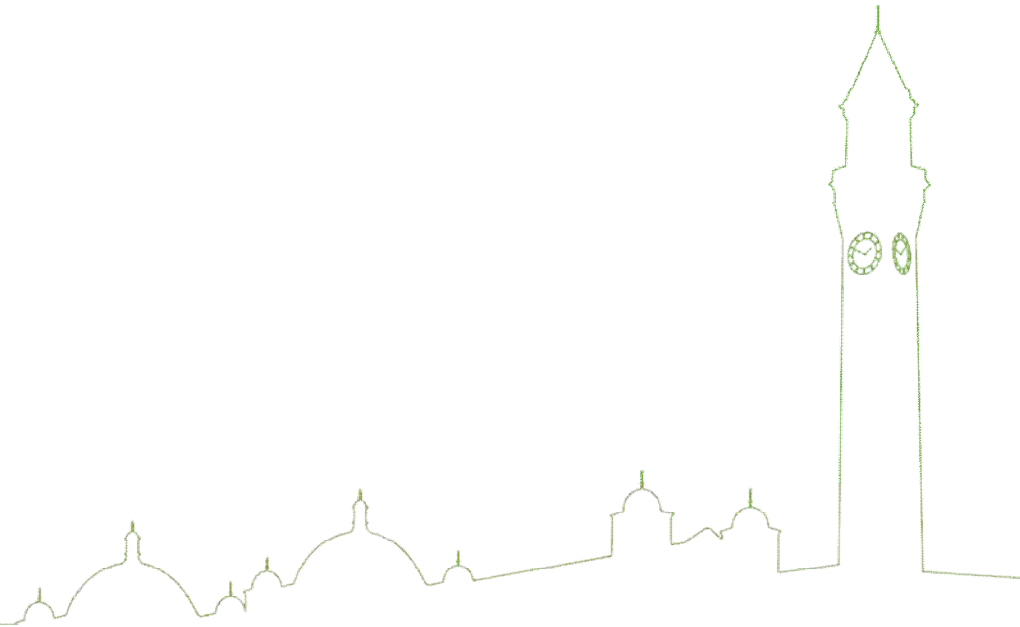Zhang et al. *Langmuir*, **2017**
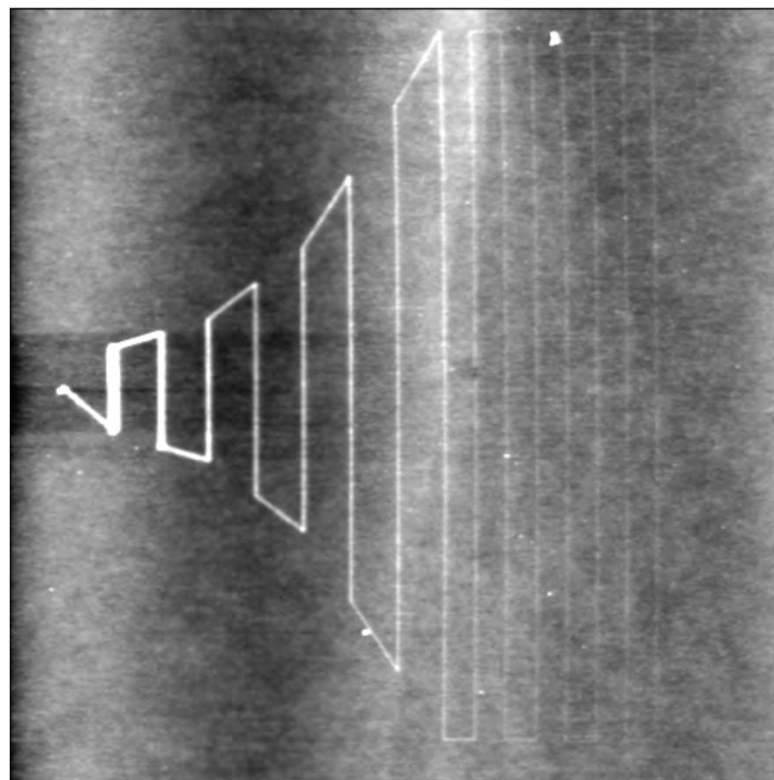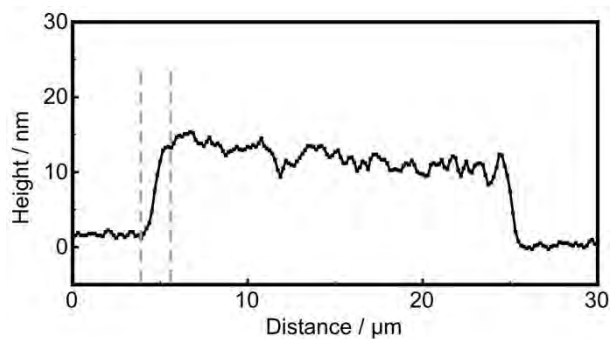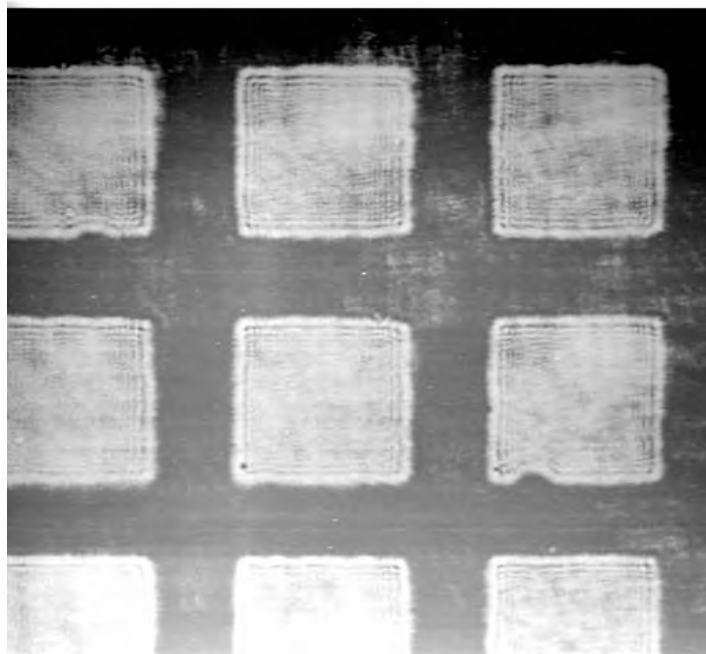
Nanoscopic objects

Zhang et al. *Langmuir*, **2016**
Zhang et al. *Langmuir*, **2017**

Nanoscopic objects

- Combination of imaging and mechanical test
- Assessing molecular arrangements

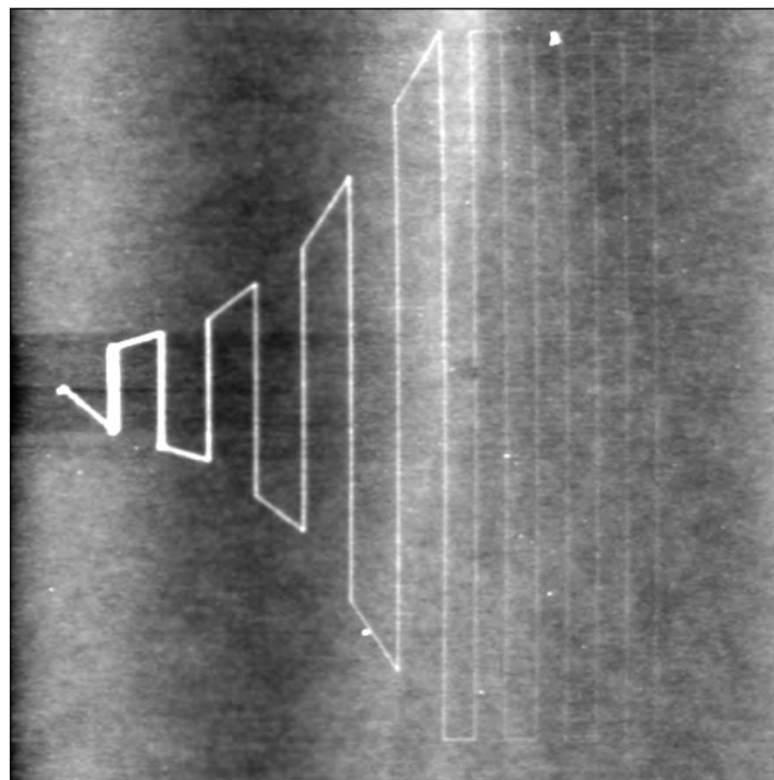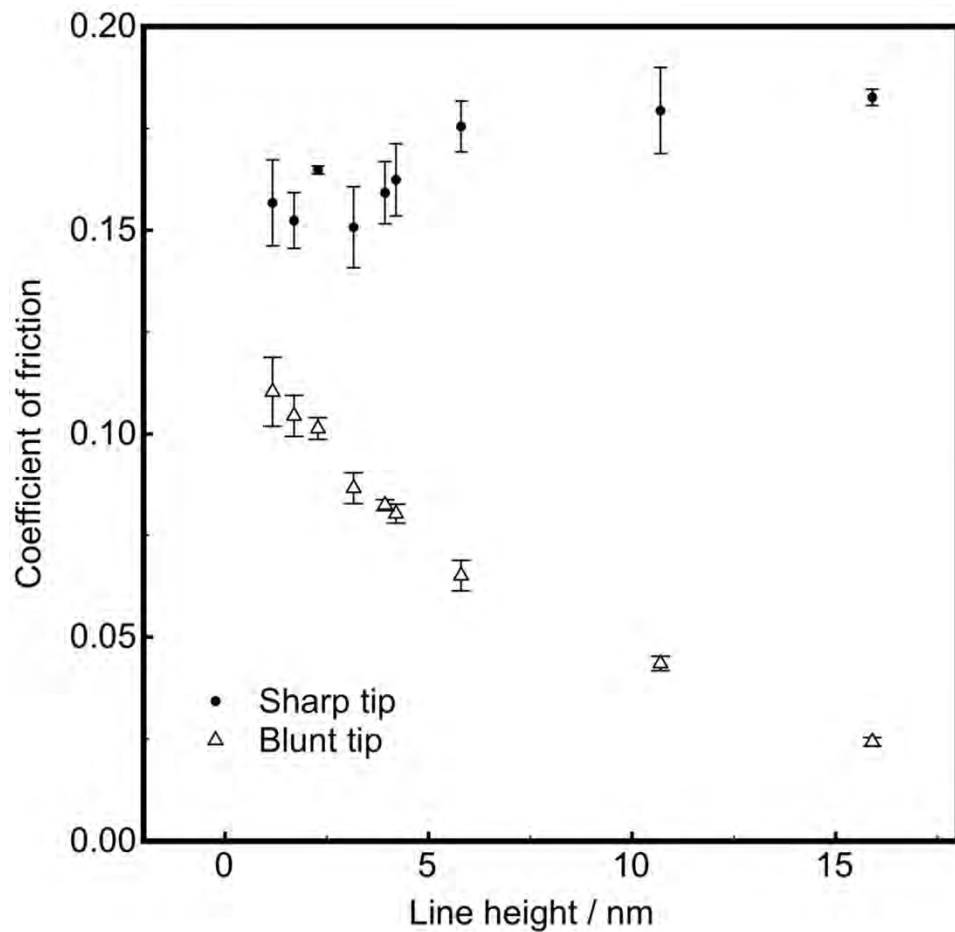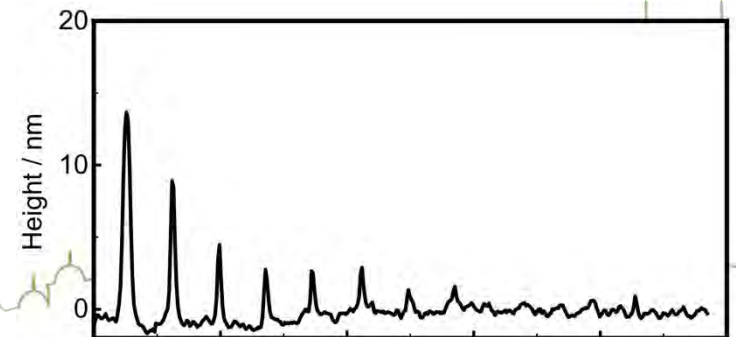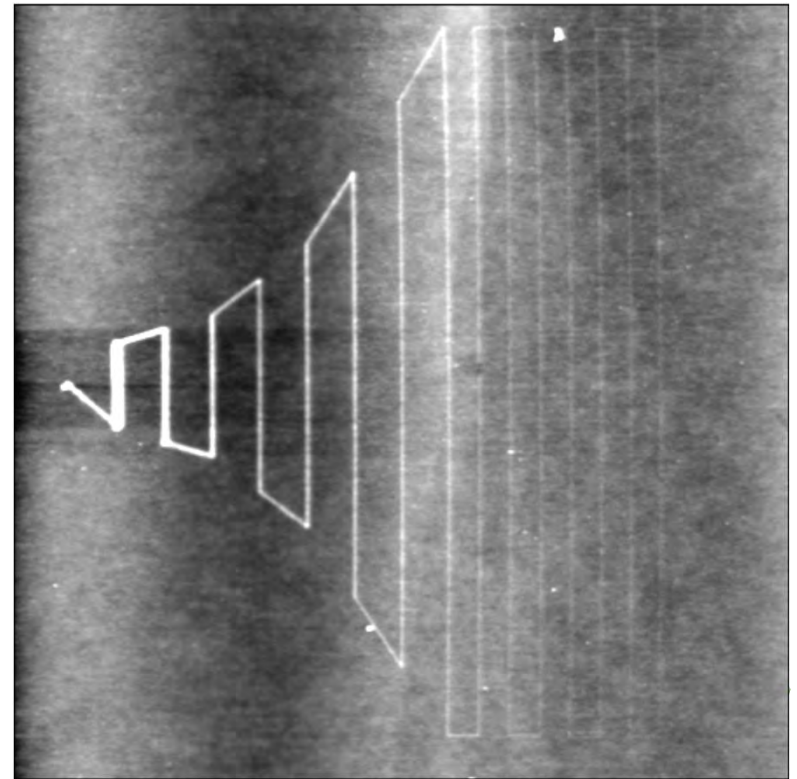Zhang et al. *Langmuir*, **2016**
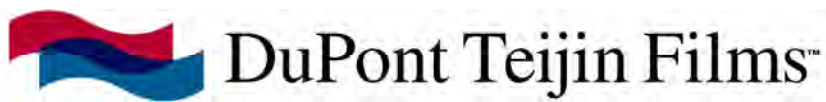Zhang et al. *Langmuir*, **2017**

Summary

- High spatial resolution
- Well correlated quantitative properties across length scales
- Effective evaluation of surface deposition
- Optimisation of surface coating
- Indicator for interfacial configuration
- Combination of imaging and mechanical test
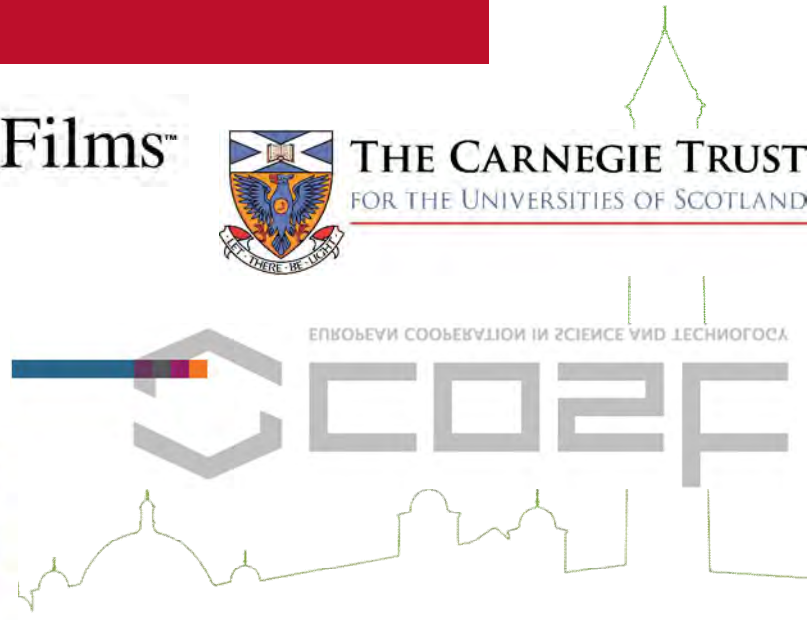- Assessing molecular arrangements

Acknowledgement

Graham Leggett (Sheffield)
Mark Geoghegan (Sheffield)
Steve Armes (Sheffield)
Andrew Morse (Sheffield)
Mark Moxey (Sheffield)
Abdullah Alswieleh (Sheffield)
Andrew Lewis (Biocomp.)
Chris Boardman (Unilever)
Peter Doyle (Unilever)
Maxim Fedorov (Strath)
James Anderson (Aber)
Wael Abdallah (SDCR)
Bastian Sauber (SDCR)
Ian McRobbie (Innospec)
Nick Dixon (Innospec)
Kieran Looney (DTF)
Karl Rakos (DTF)
Carlos Amador (P&G)
Anju Brooker (P&G)

Thank you!