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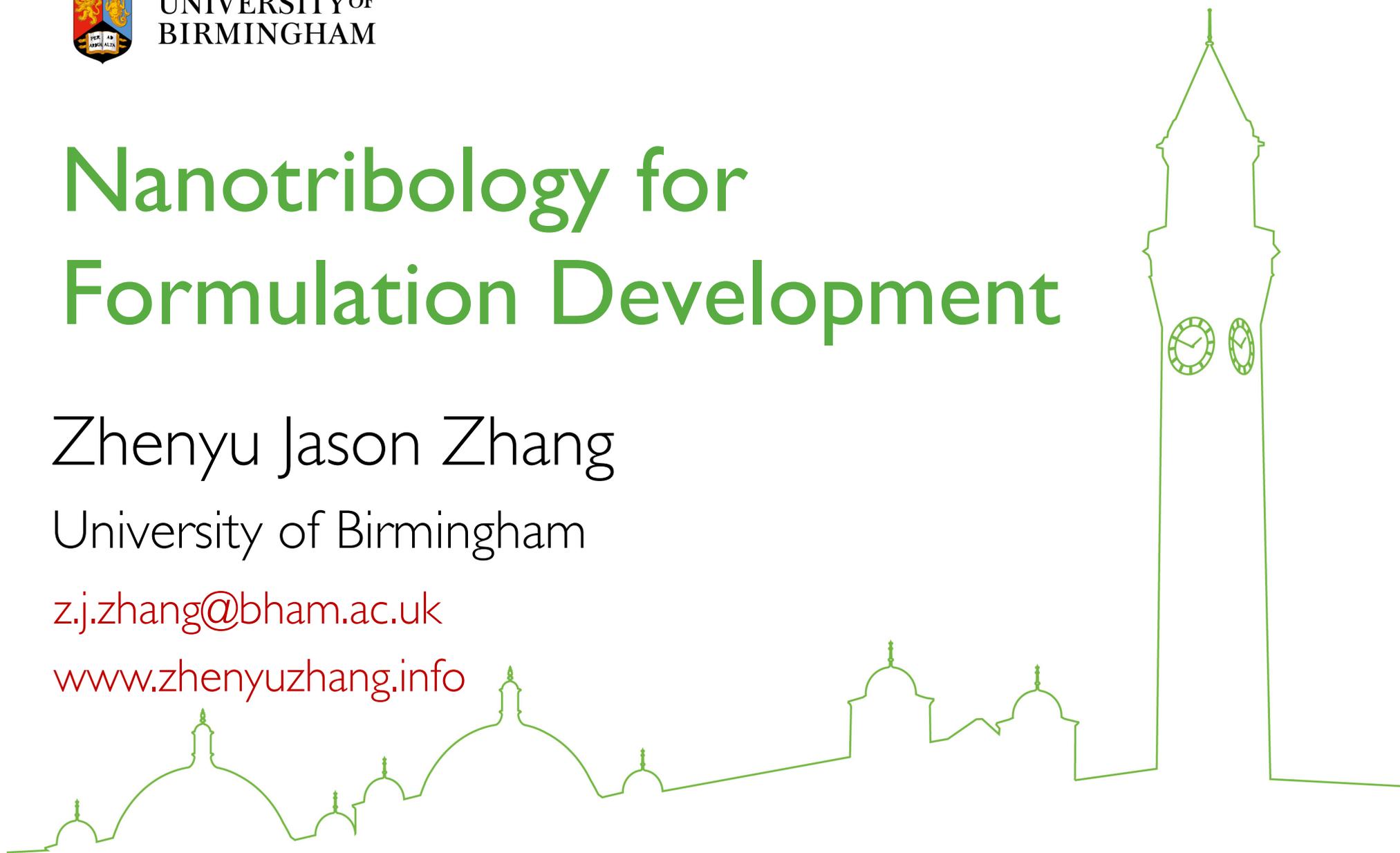
Nanotribology for Formulation Development

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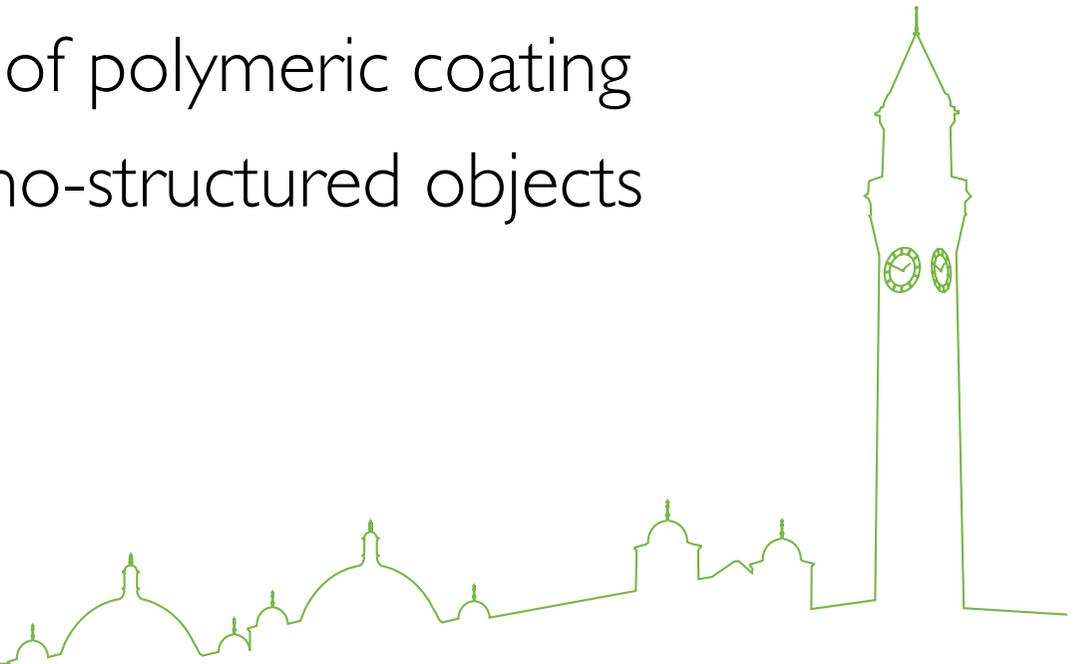
www.zhenyuzhang.info



RSC Symposium at Chemspec Europe 2018

Outline

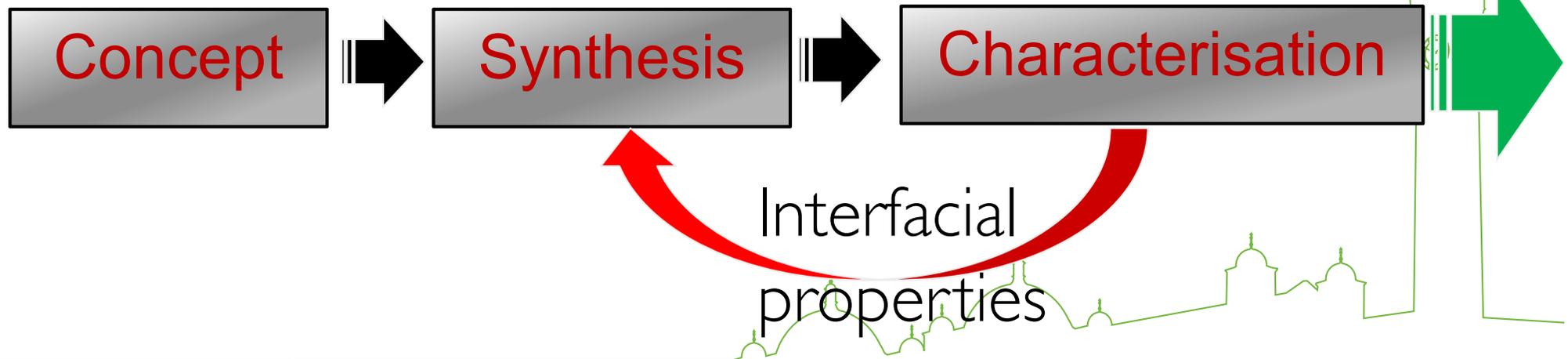
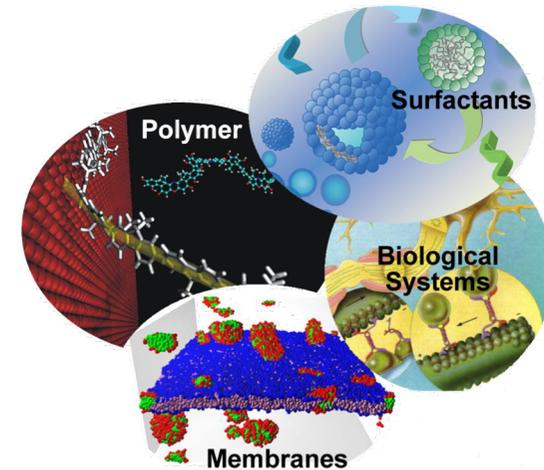
- Nanotribology
 - Scanning Probe Microscopy
- Case studies
 - Performance of laundry products
 - Lubrication properties of polymeric coating
 - Characterisation of nano-structured objects



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.

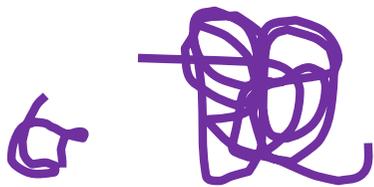


The fundamentals

Soft matter vs surface

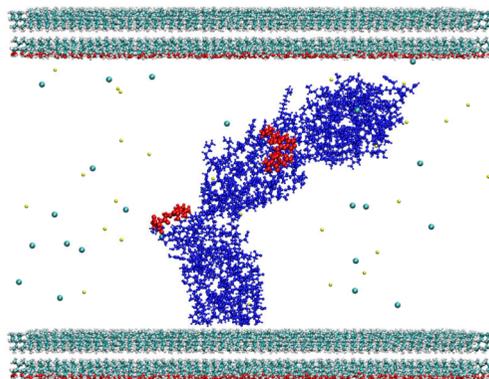
Prior

- Stability in bulk solution
- Diffusion rate
- Substrate characteristics



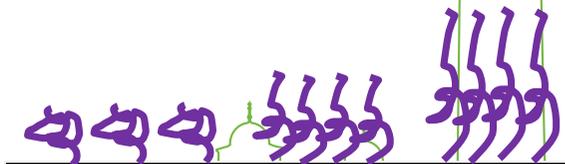
In contact

- Adsorption/desorption
- Binding energy
- Molecular interaction

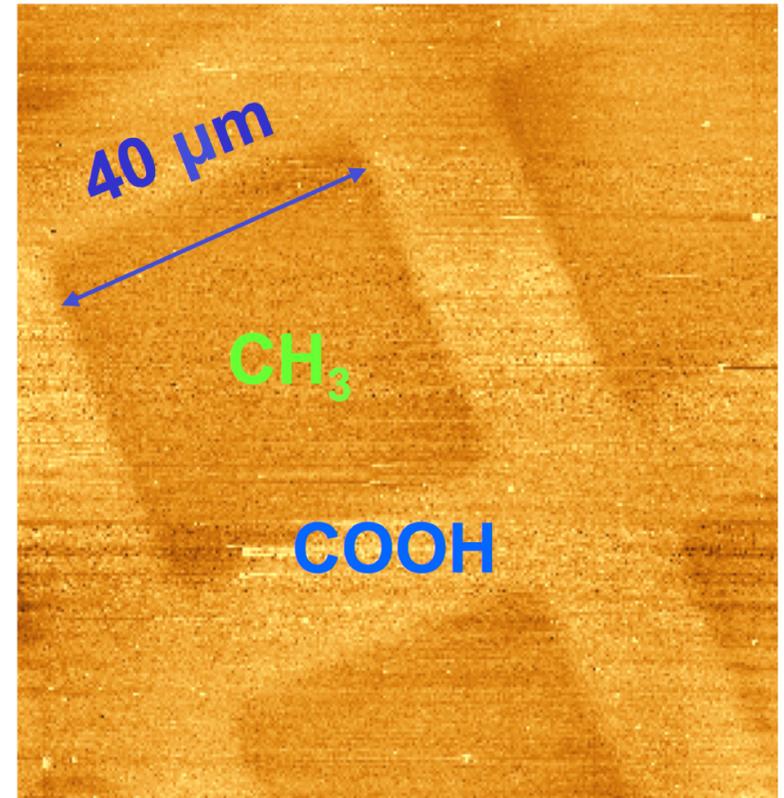
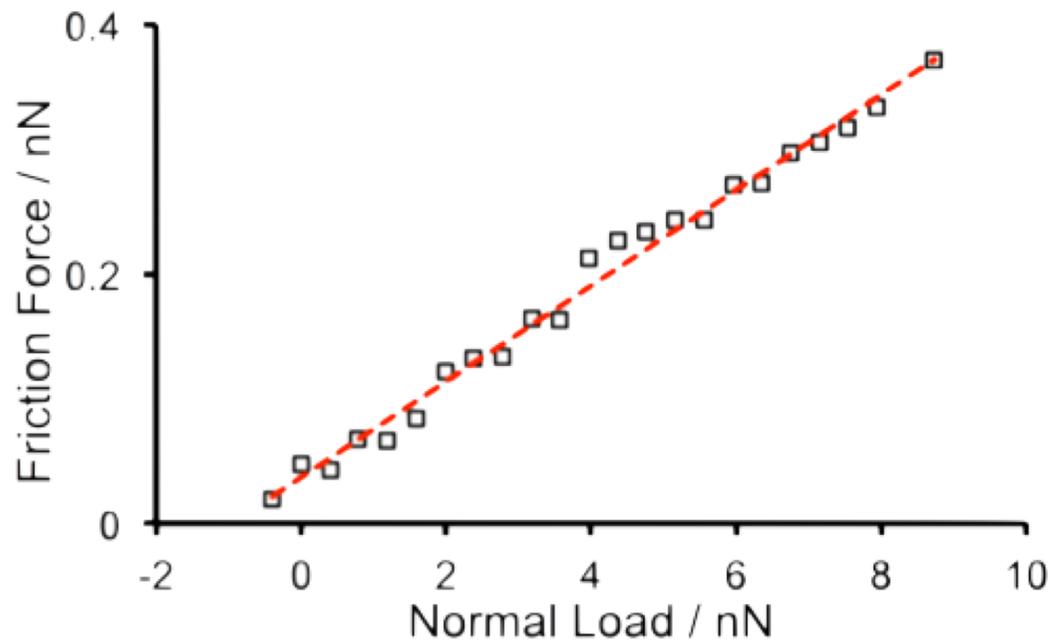


Film formation

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



Nanotribology



Quantitative
friction
measurement

Surface analysis

SPM - a versatile toolbox

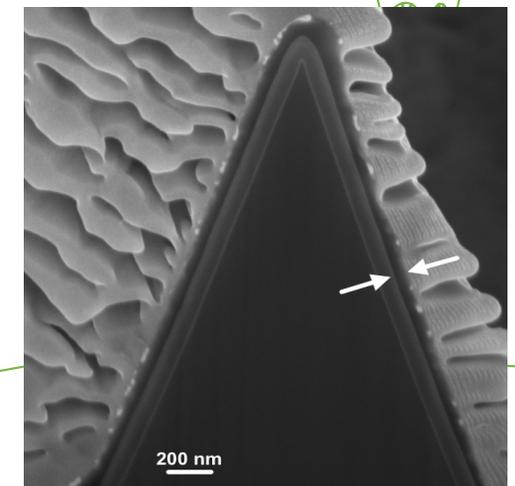
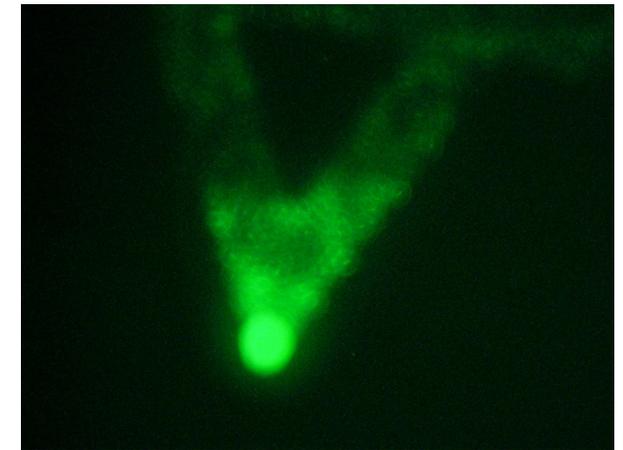
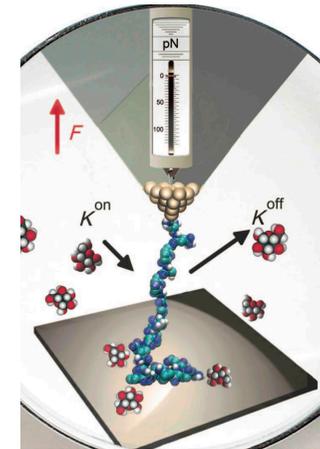
Objects

- Single molecule
- Monolayer
- Polymeric coating
- Colloidal particle

Environment

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

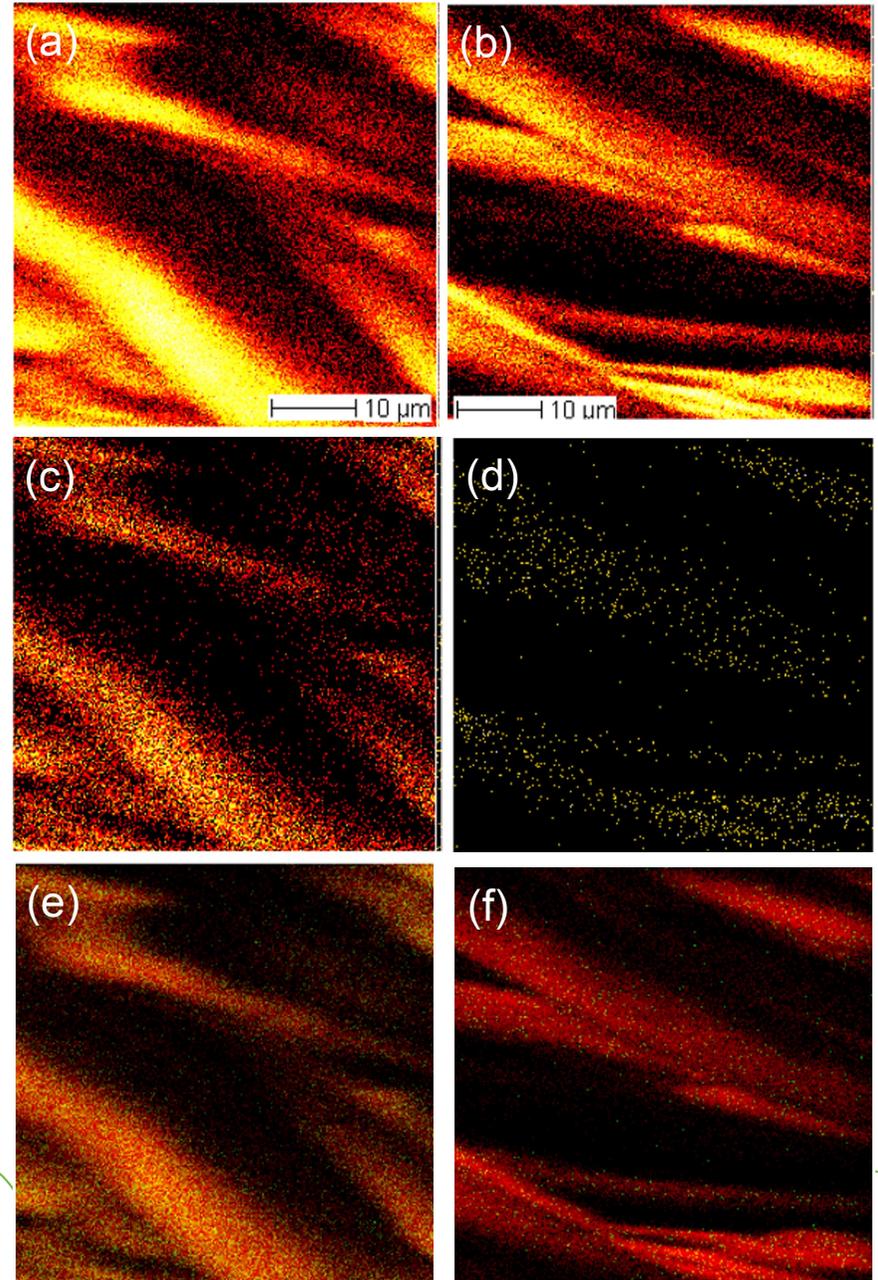
- In-situ measurement in various environment
 - Observe and manipulate molecular machinery
- No complex sample preparation
 - No need for fixation or staining
- Time-lapse imaging with nanometre resolution
 - Directly observe biological specimens
- Molecular/colloidal interactions
 - Pico-newton sensitivity



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

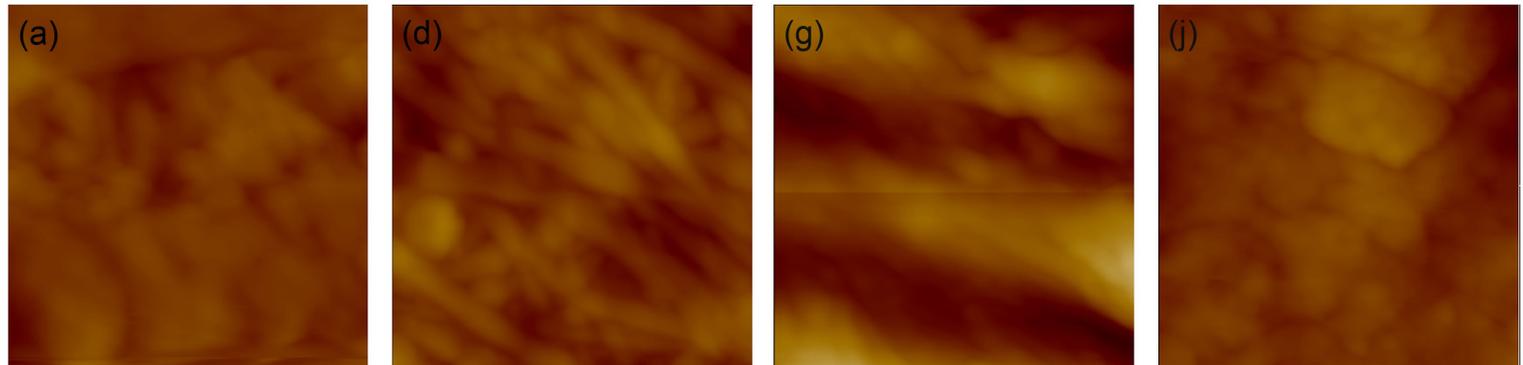
New cotton

Washed once

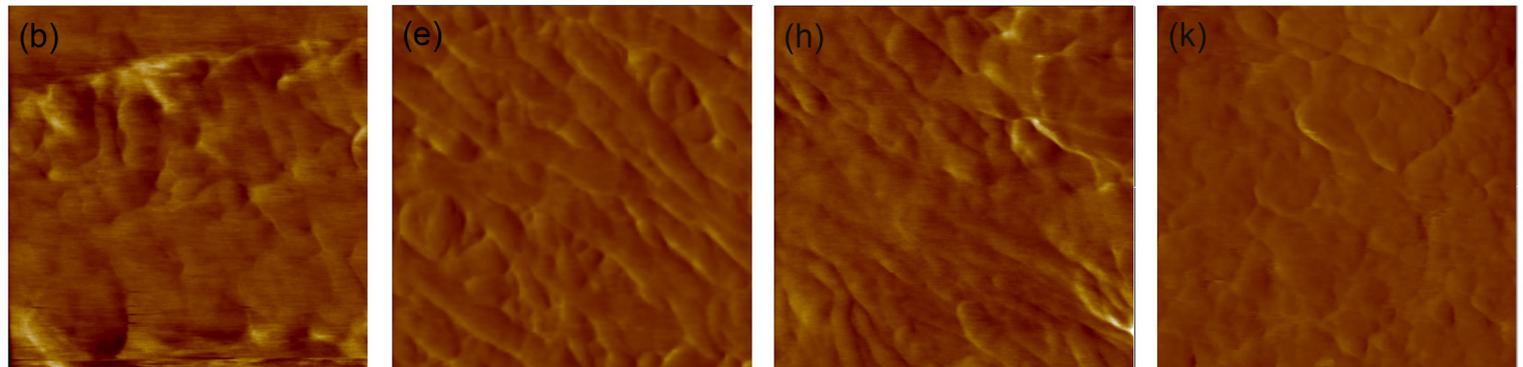
Washed 20 times

Washed 20 times & treated with fabric softener

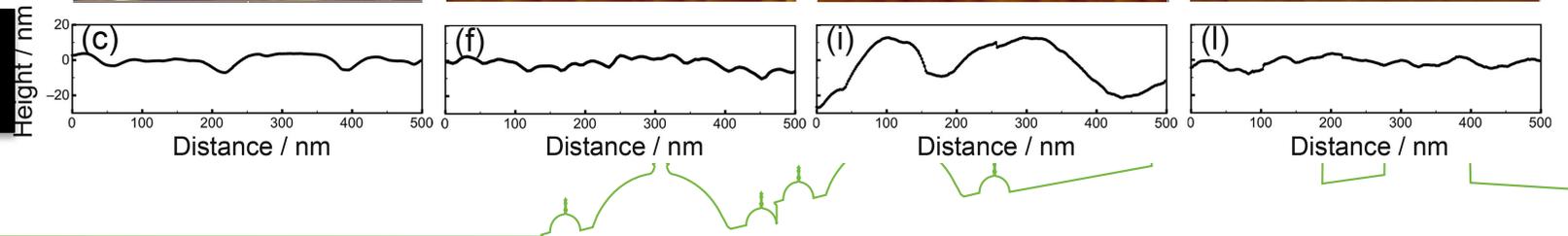
Height



Friction



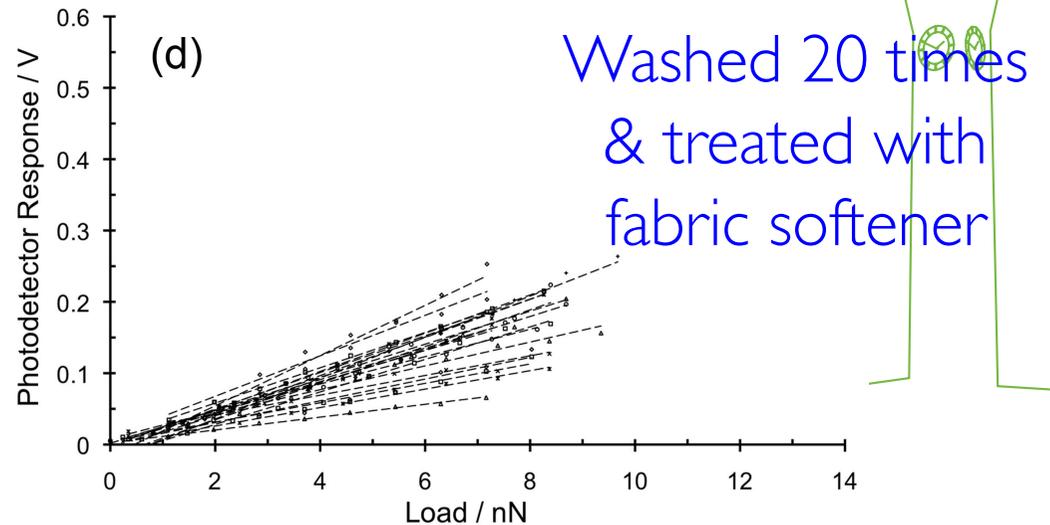
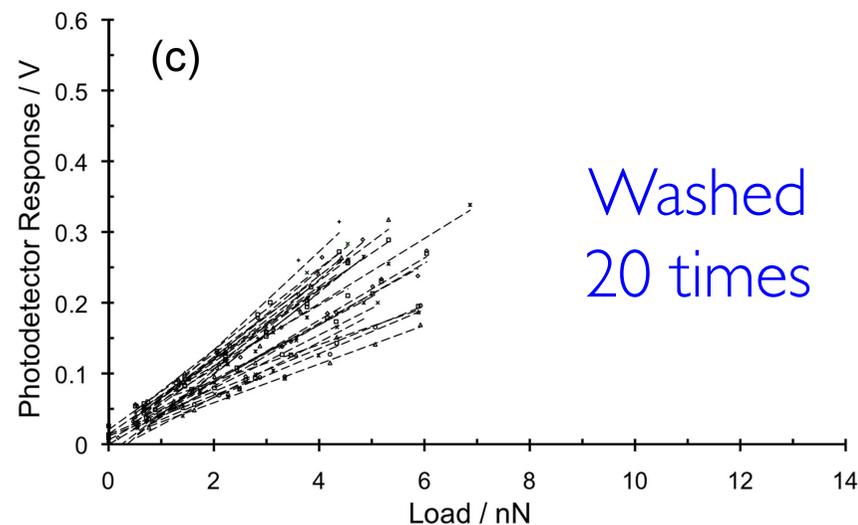
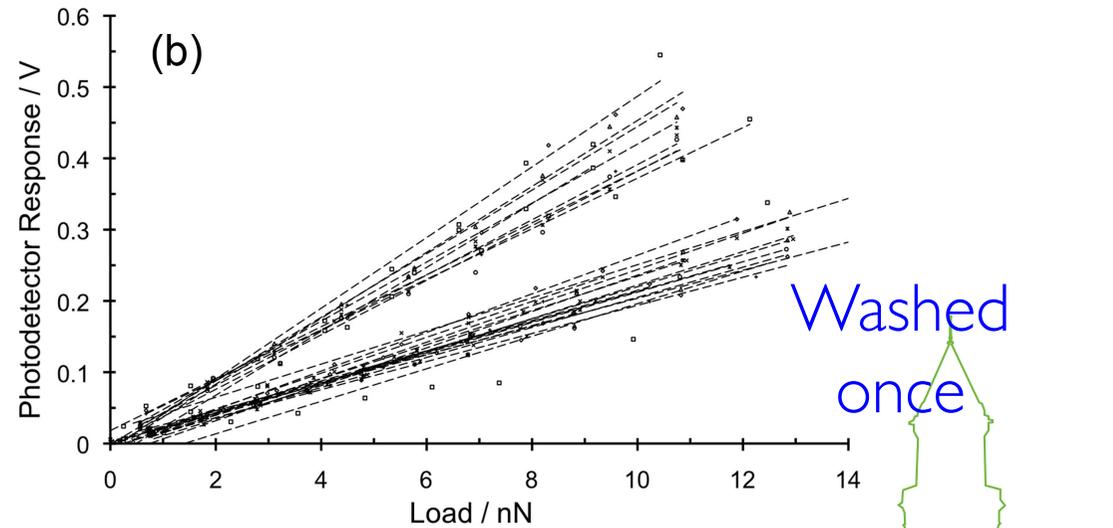
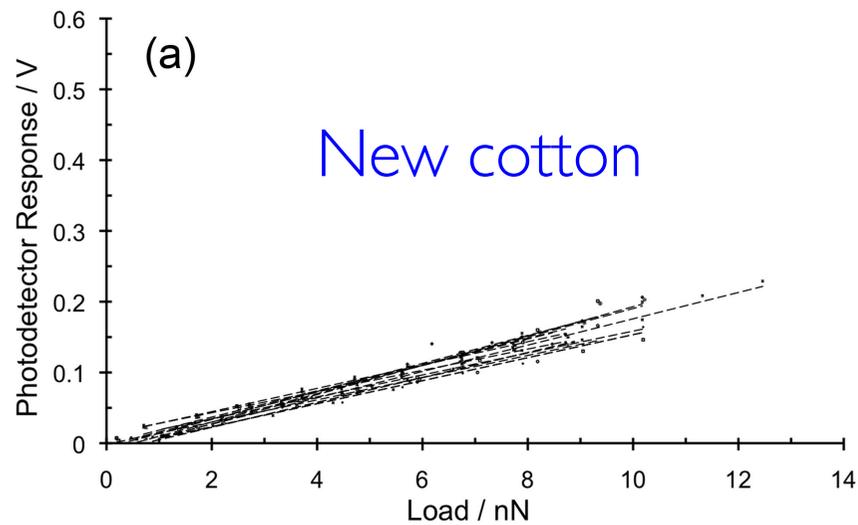
Section



Frictional-load relationship

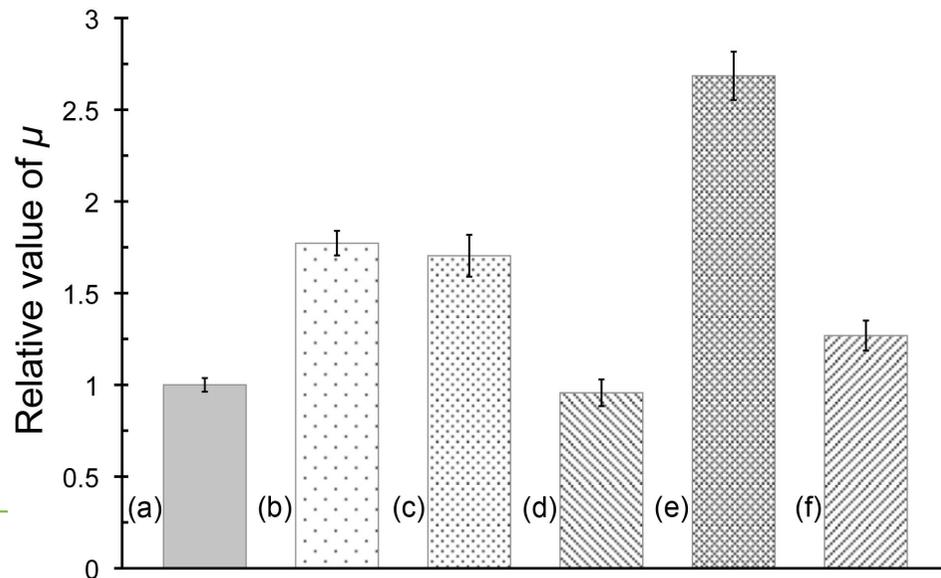
$$F = \mu \cdot L$$

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

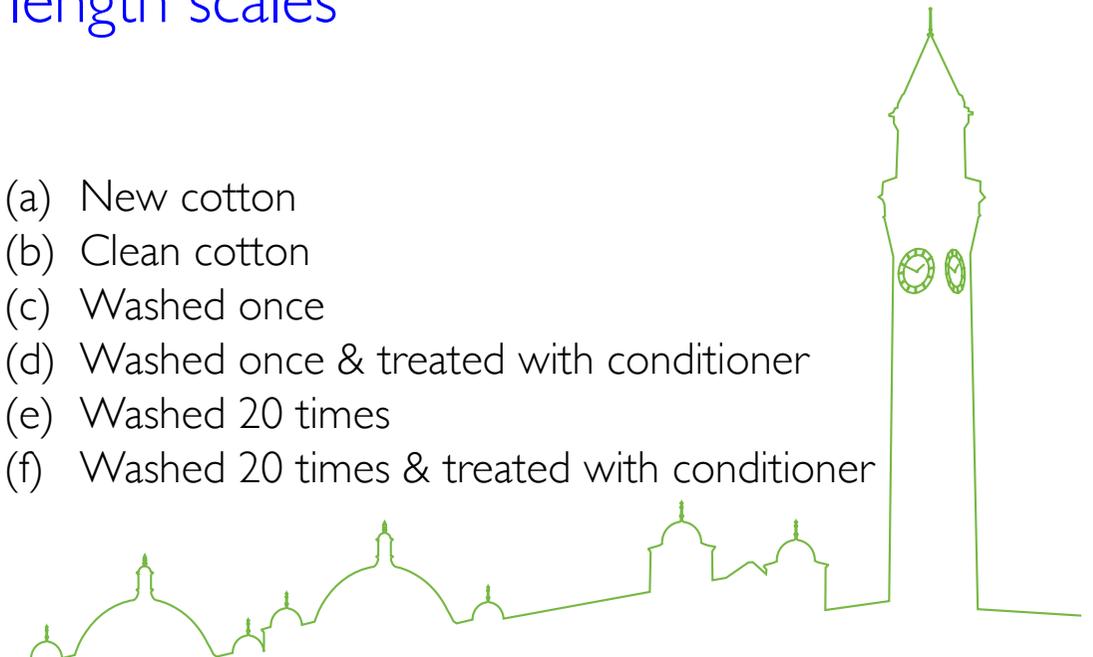


Summary I

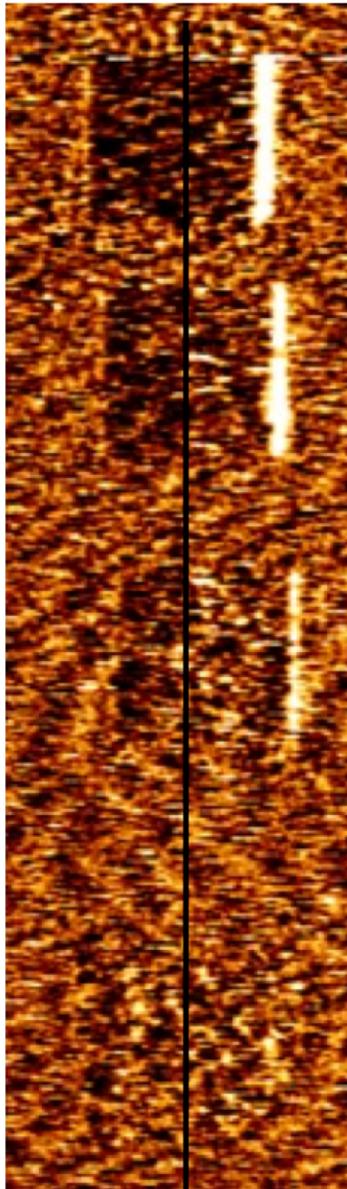
- Ability to examine meso-scale objects
- In both ambient and liquid environment
- Surface properties of porous material
- High spatial resolution
- Effective approach in evaluating surface-deposited soft matter quantitatively
- Consistency over different length scales



- (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



20 nN

15 nN

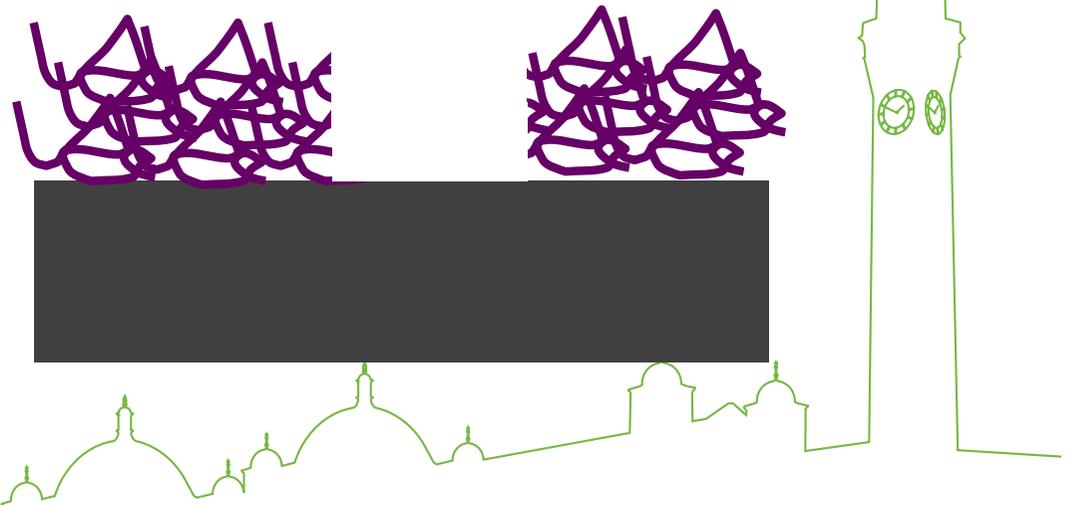
10 nN

5 nN



Surface fouling

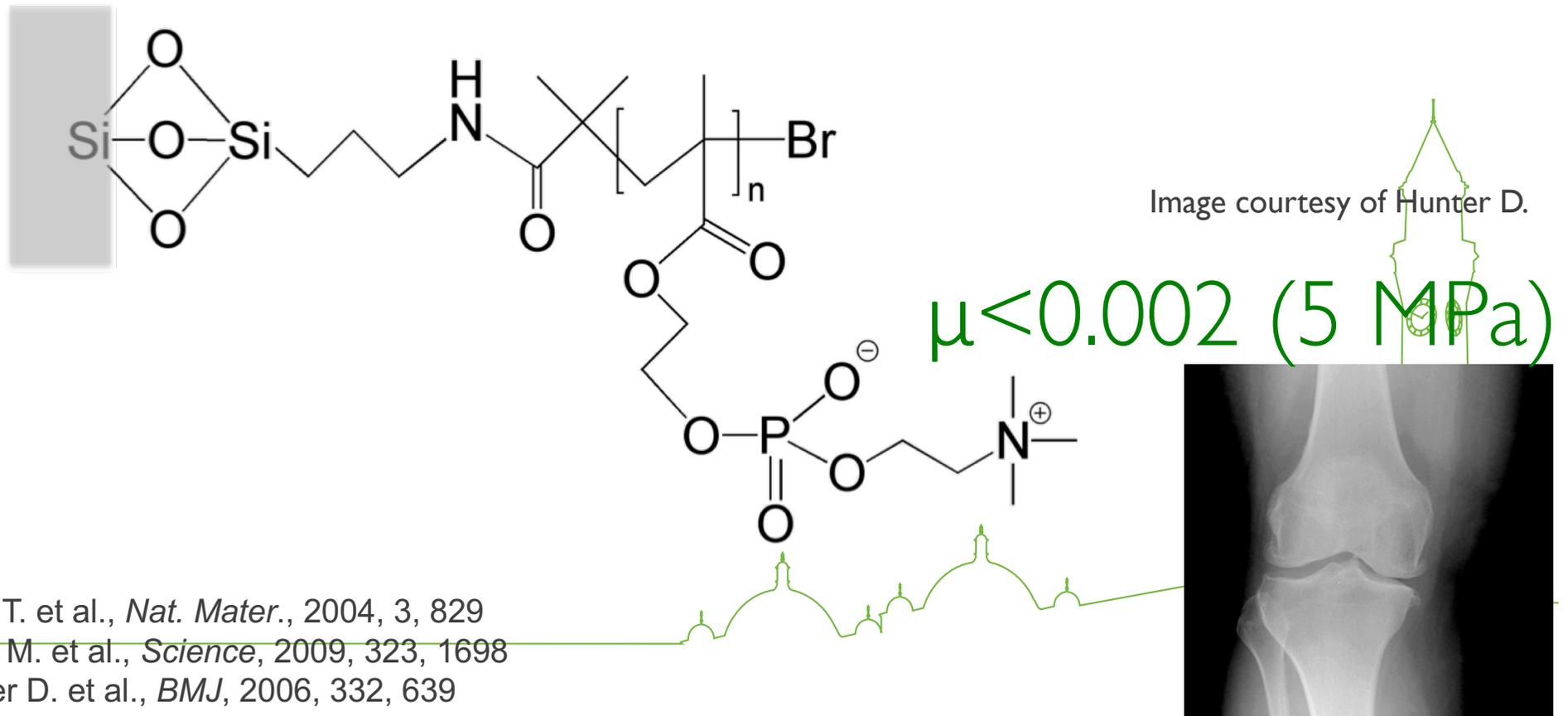
- Desirable vs undesirable



Polymeric coating

Poly(2-(methacryloyloxy)ethyl phosphorylcholine)

$\mu=0.0004$ (7.5 MPa)



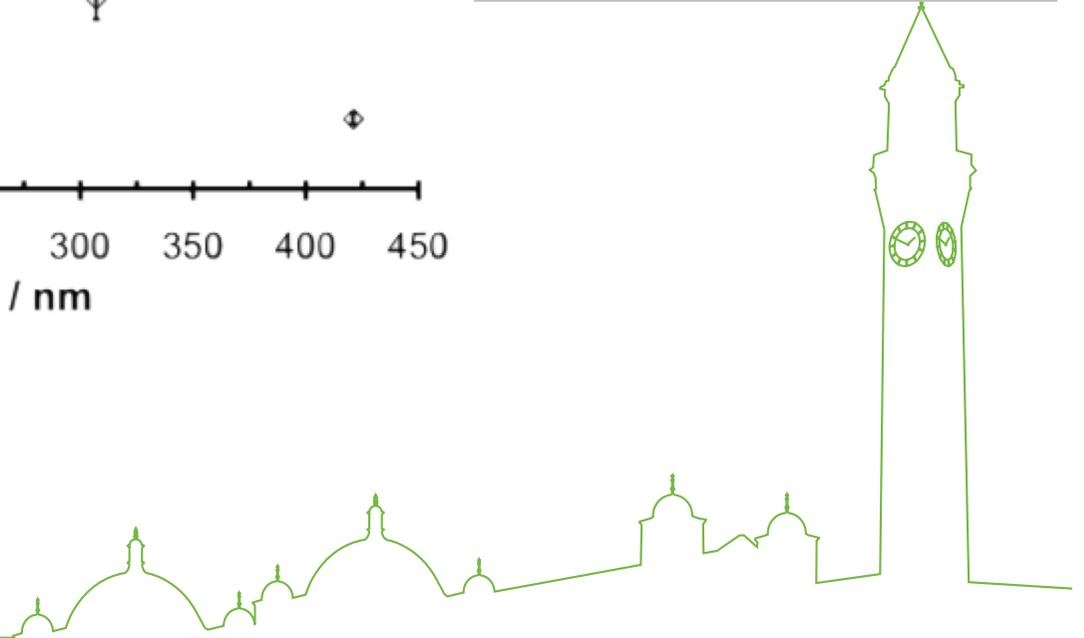
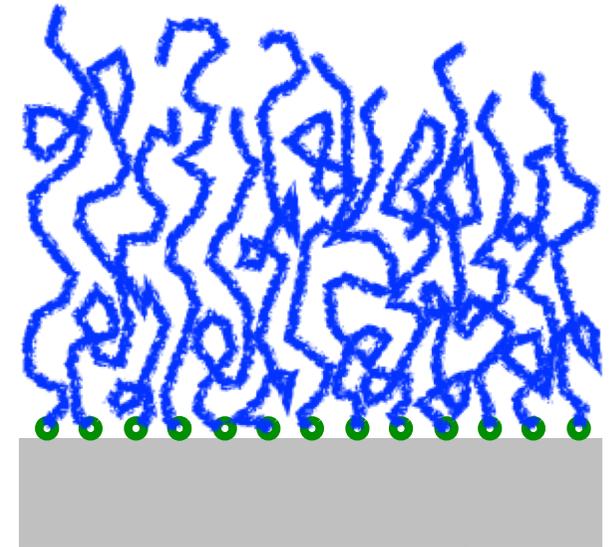
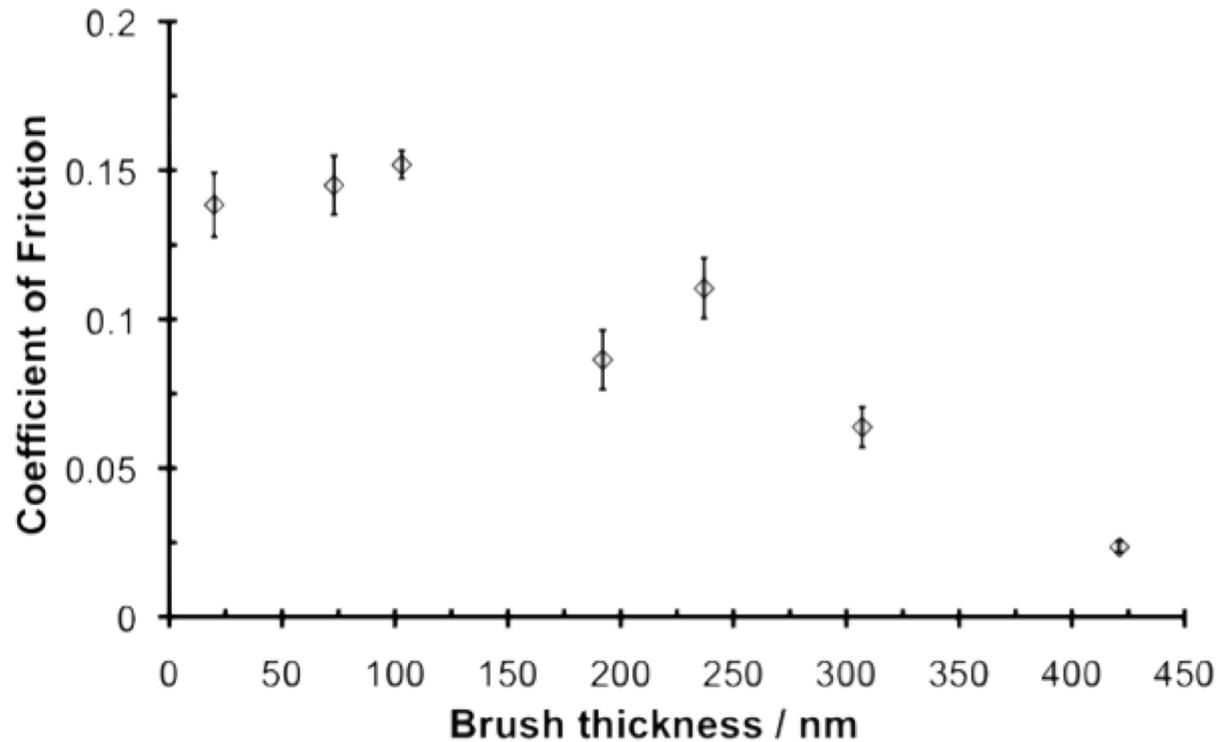
Moro T. et al., *Nat. Mater.*, 2004, 3, 829

Chen M. et al., *Science*, 2009, 323, 1698

Hunter D. et al., *BMJ*, 2006, 332, 639

Lubrication of polymer brushes

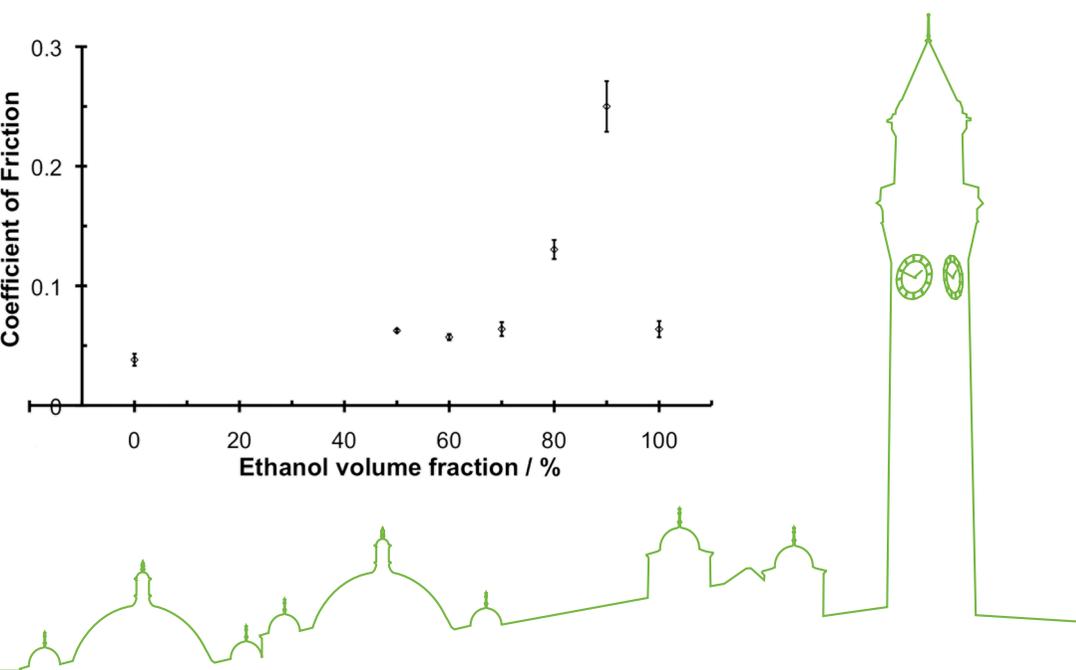
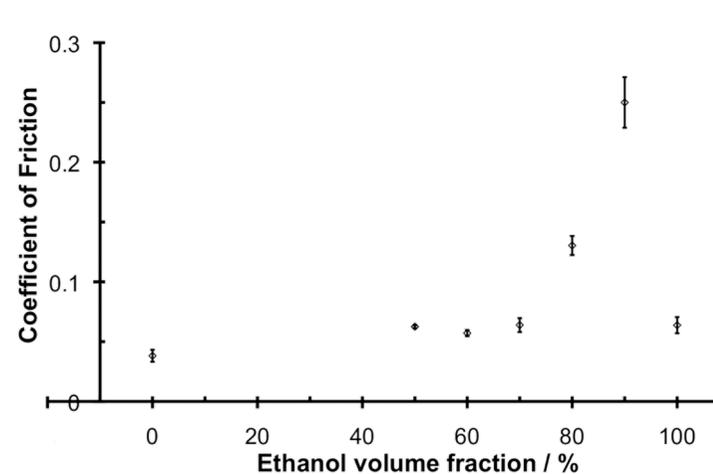
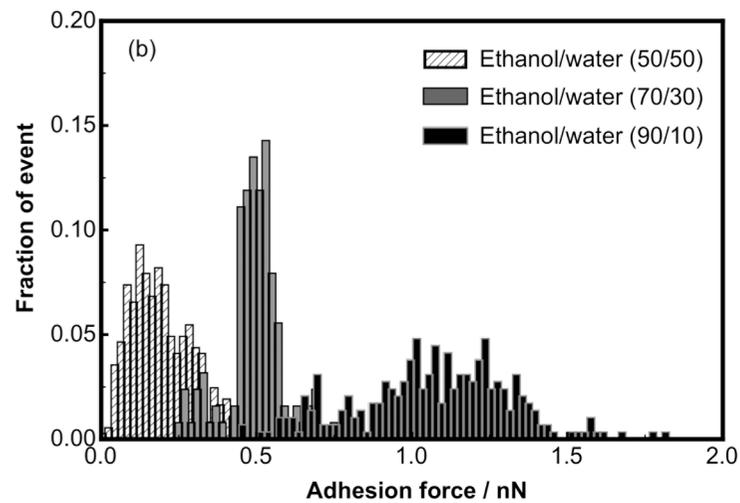
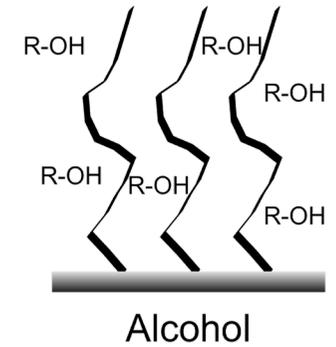
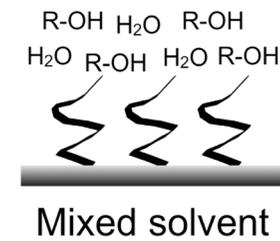
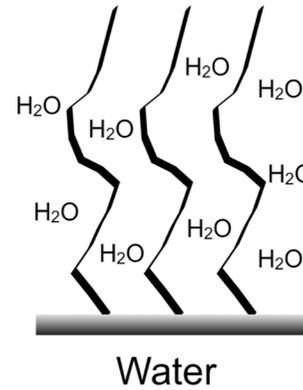
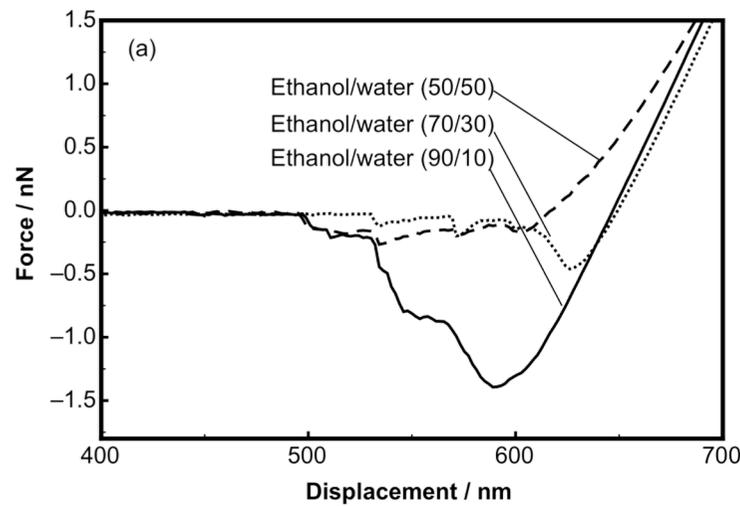
Optimum thickness, solvent, ionic strength, pH?



- Zhang et al. *Langmuir*, **2011**
- Busuttill 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

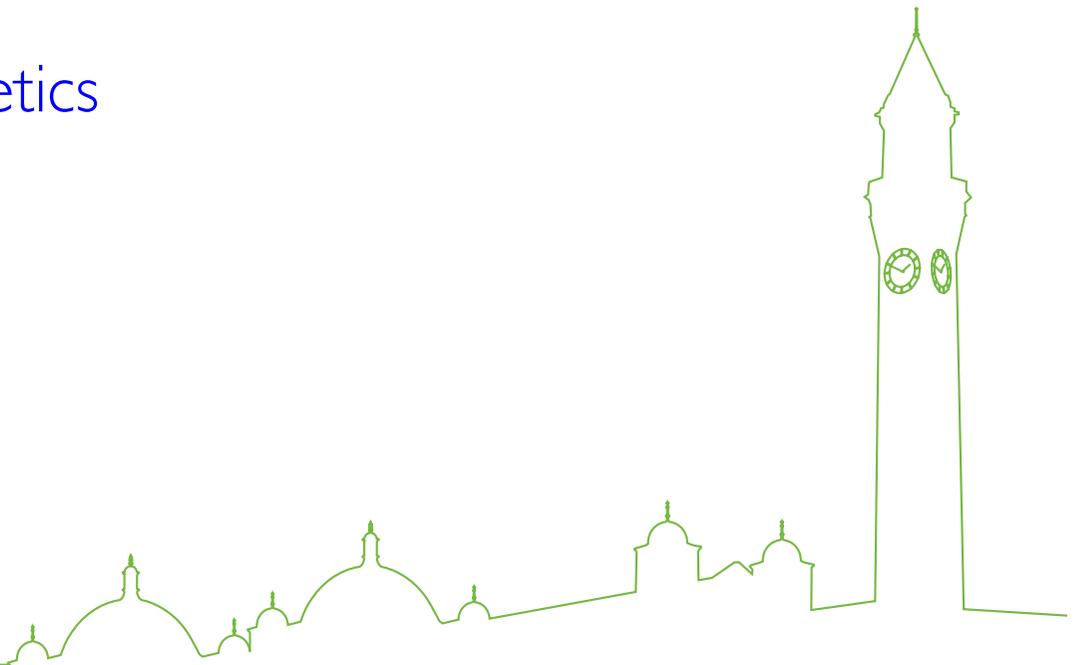
Response to stimuli

- Brush collapsed at 90/10 volume ratio

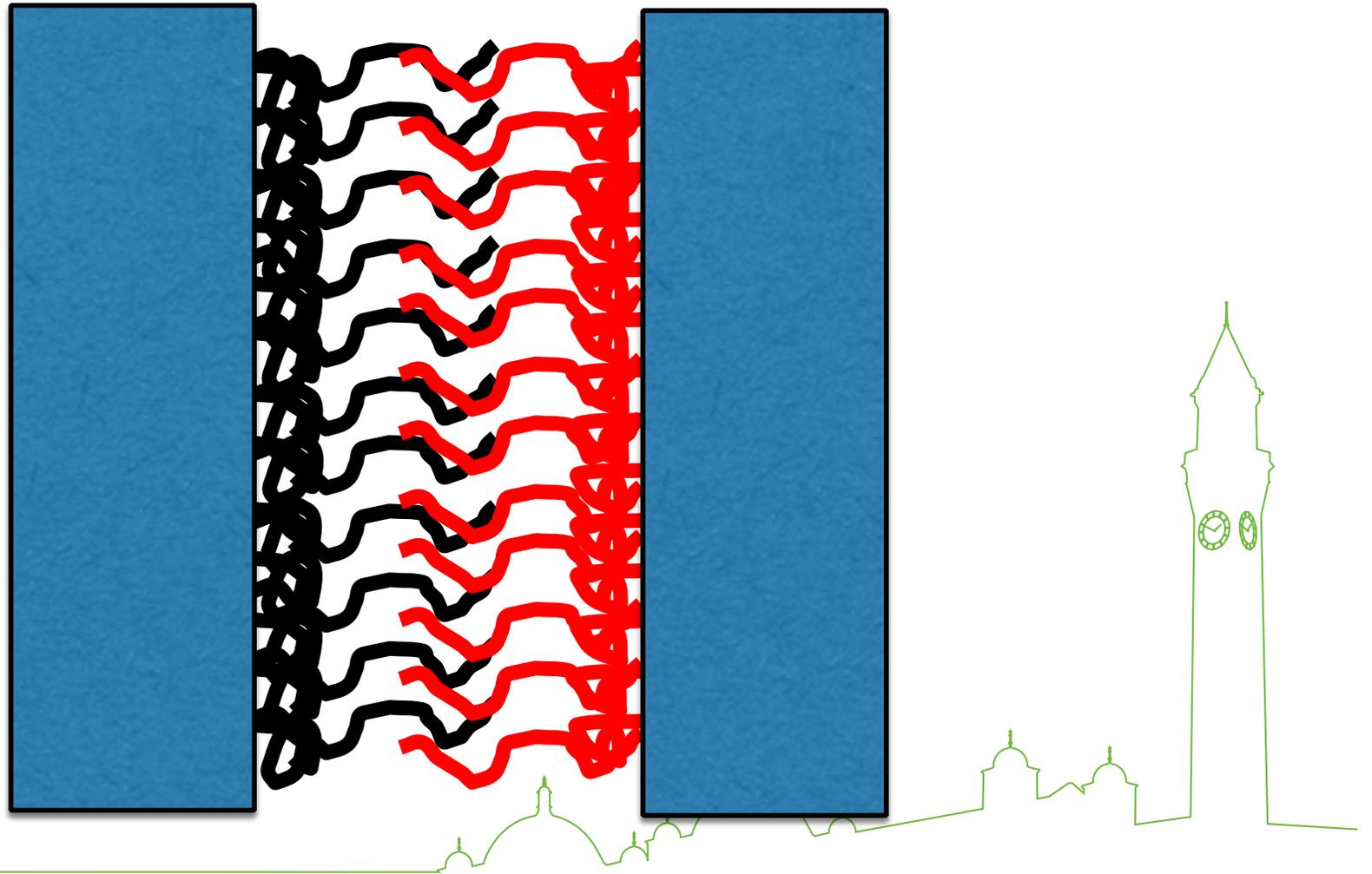


Summary 2

- 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

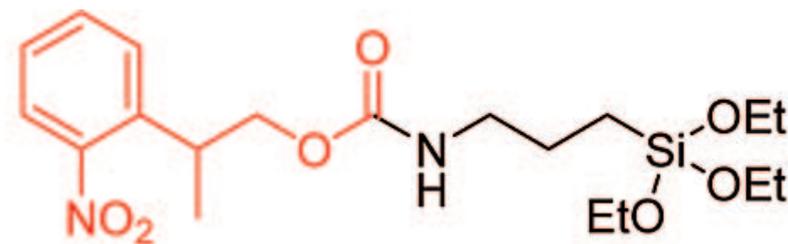


Molecular fabrication



Constructing molecular objects

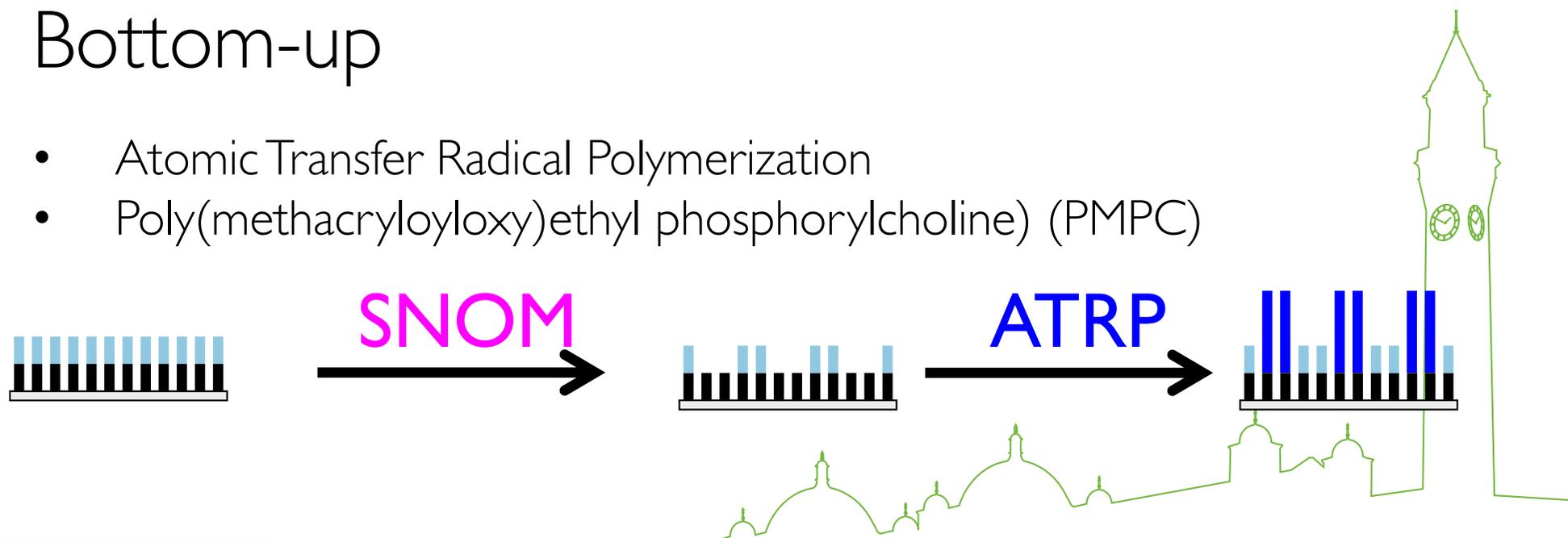
Top-down



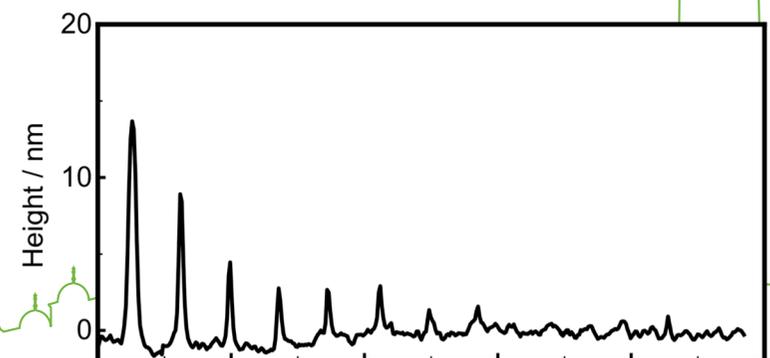
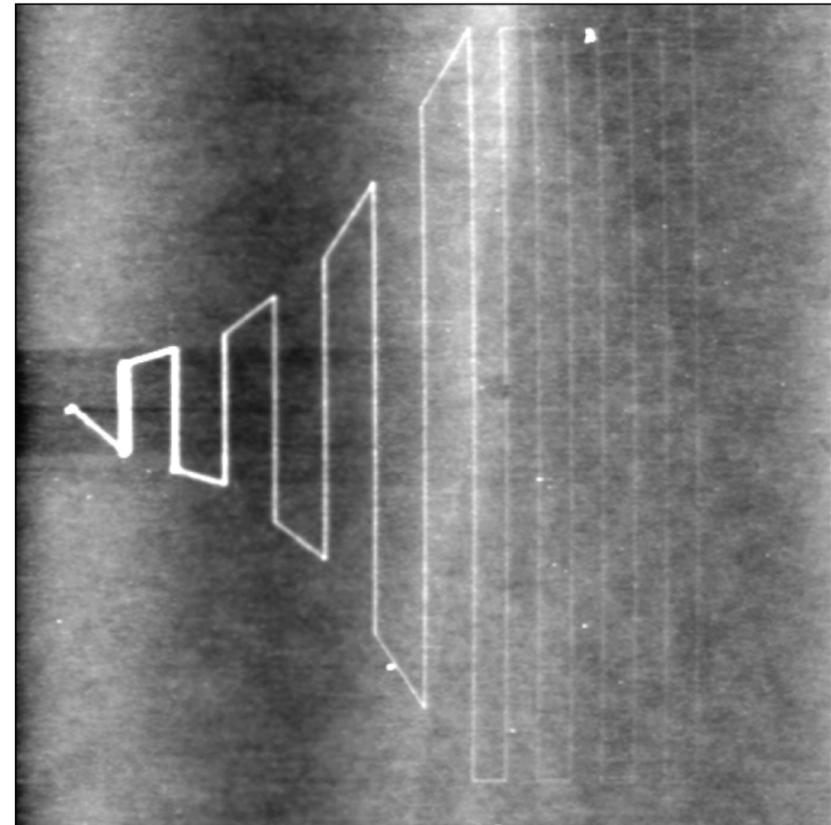
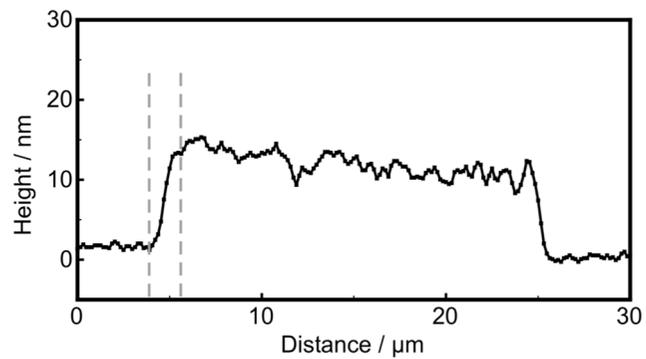
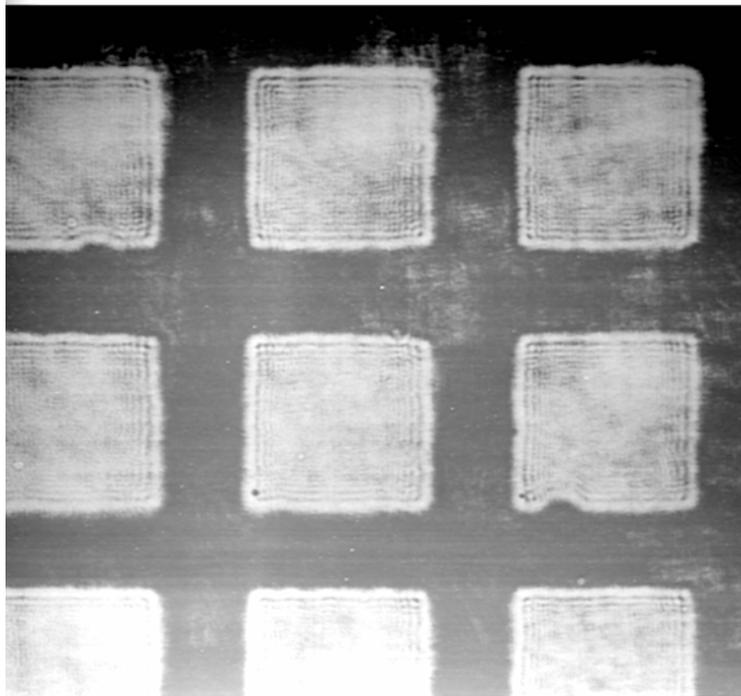
- Photolithography: Scanning Near-field Optical Microscopy (SNOM)
- 2-nitrophenylpropoxycarbonyl (NPPOC)

Bottom-up

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



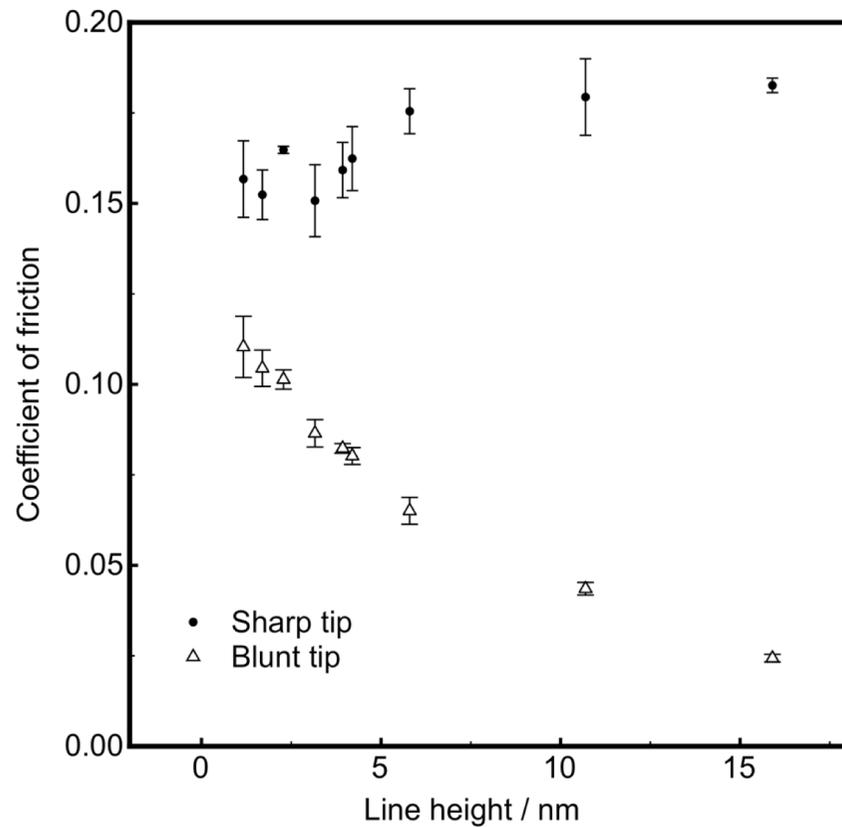
Nanoscopic objects



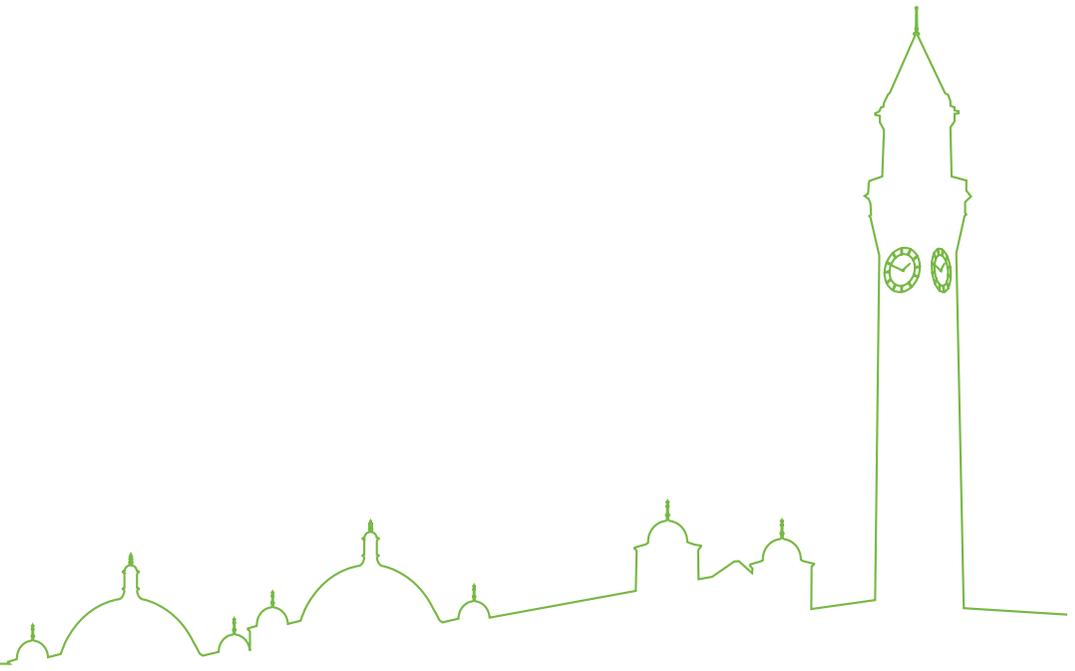
Zhang et al. *Langmuir*, 2016

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

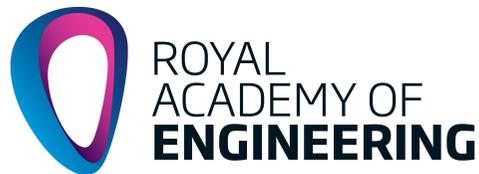


Acknowledgement

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)

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Thank you!

