

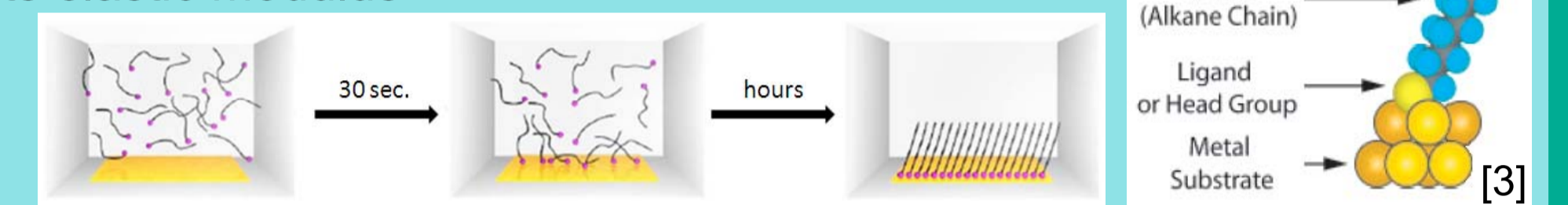
Introduction

Biofouling

- undesired growth of marine organisms on submerged structures and devices
- ubiquitously occurring phenomenon in tidal zones worldwide [1]
- world fleet fuel consume is additional 300 million tonnes higher as a result of fouling [2]
- to prevent these effects caused by biofouling, suitable non-toxic coatings for the marine environment are required
- our approach is to use well defined model surfaces to investigate influences of surface chemistry and morphology to develop design rules for non-fouling coatings

Self-assembled monolayers

- Self-assembled monolayers (SAMs) on gold provide access to highly controlled surface chemistries
- SAMs allow to fine tune physicochemical surface properties
- SAMs are a highly versatile tool to create defined thin organic films
- allow to change the surface chemistry without affecting the morphology or its elastic modulus

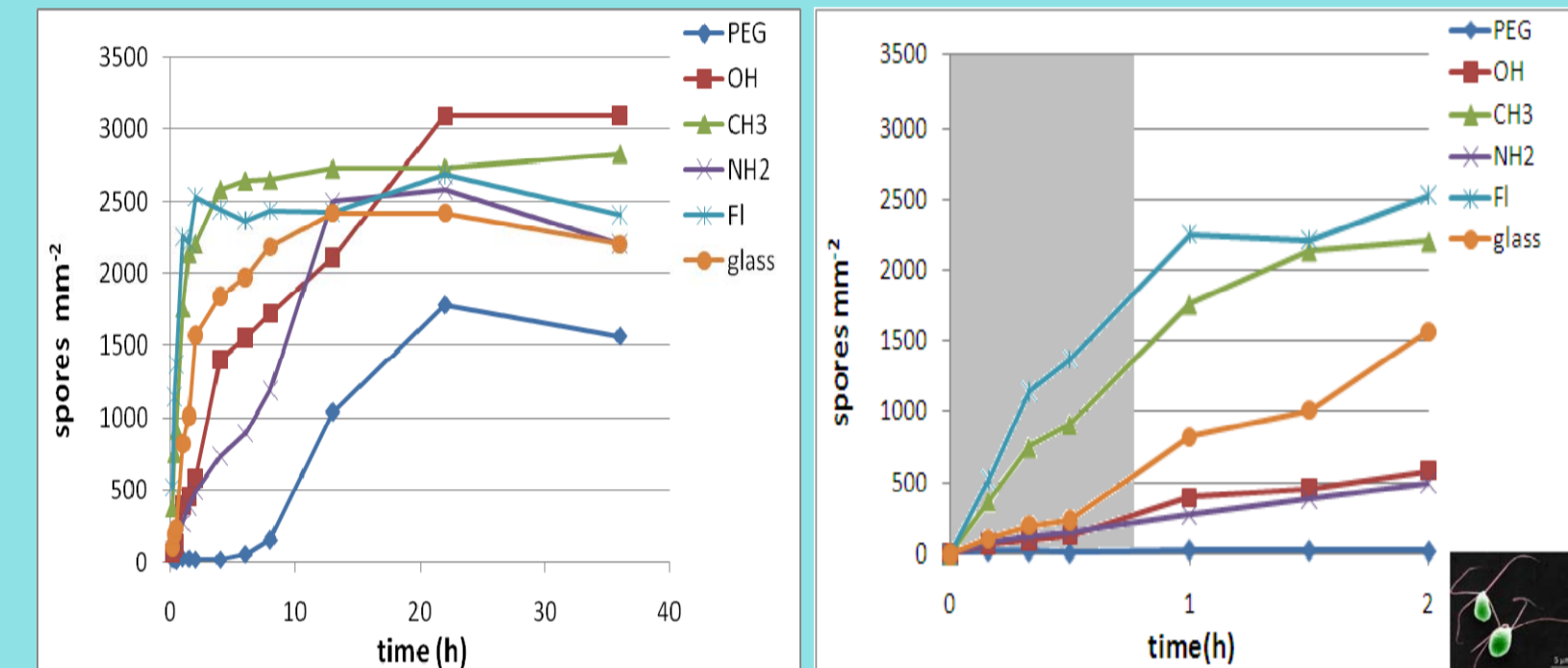


Kinetic experiments

Motivation

- surface chemistry and surface wettability strongly influence the rate of settlement of *Ulva* zoospores
- Ista et al. showed different rates of spore settlement on different SAMs in assays of 60 min duration [4]

Results



Time depending settlement process on surfaces over a time of 36 h;

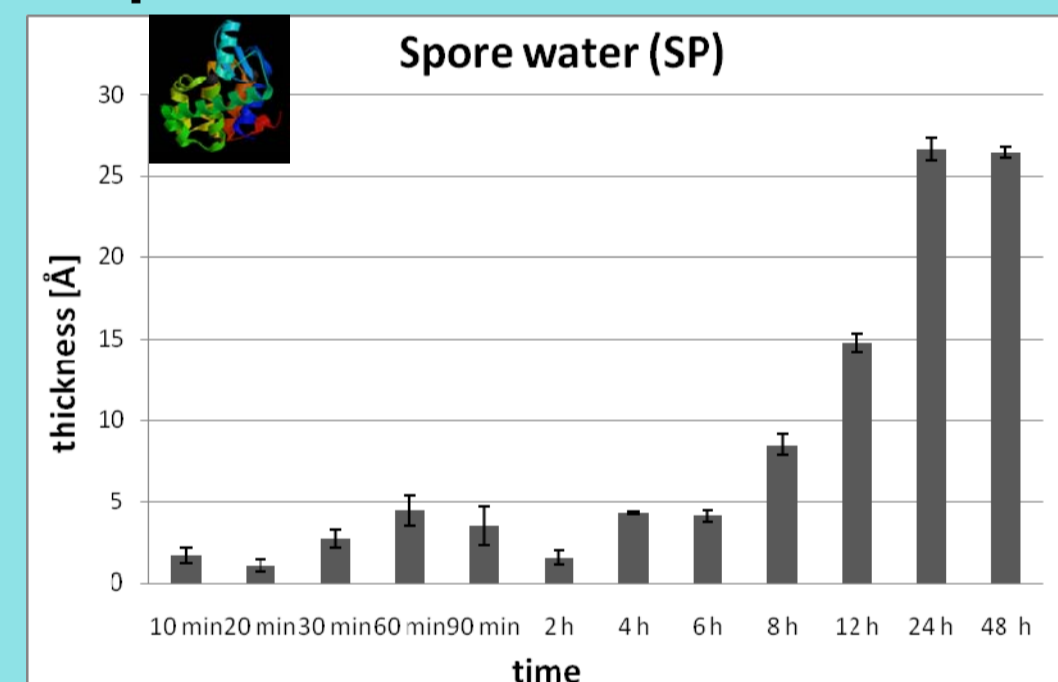
- whole experimental duration of 36 h
- detailed view at first 2 h of the experiments, grey area: Duration of a spore settlement assay of UoB

- PEG 2000-OH surface is resistant against spore settlement for about 10 hours before PEG 2000-OH degradation changes the surface properties
- SAMs have different affinity towards macromolecules
- settlement could be a combined effect of surface chemistry and the formation of a conditioning layer

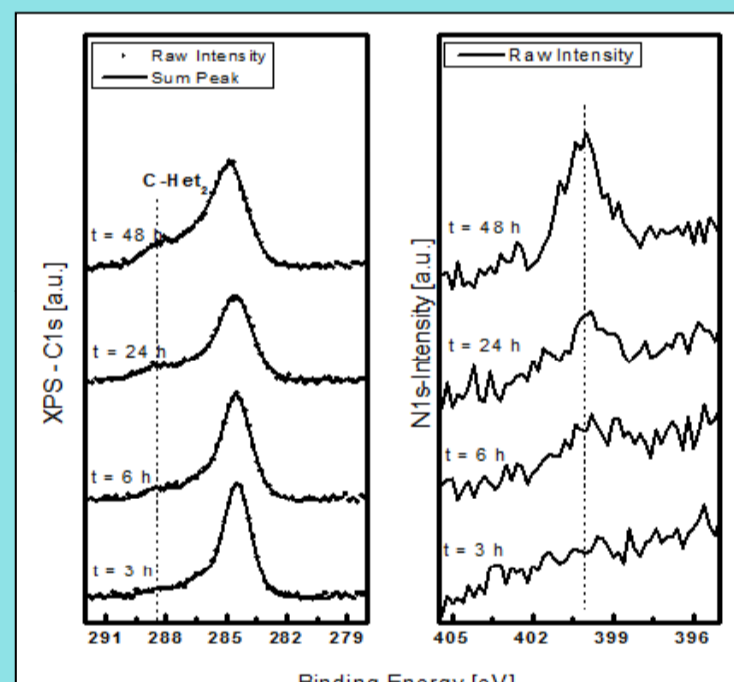
Conditioning film experiments

- C12 (dodecanthiolate SAM) is the reference surface
- Kinetic experiments with spore water and Tropic Marine (commercial ASW)

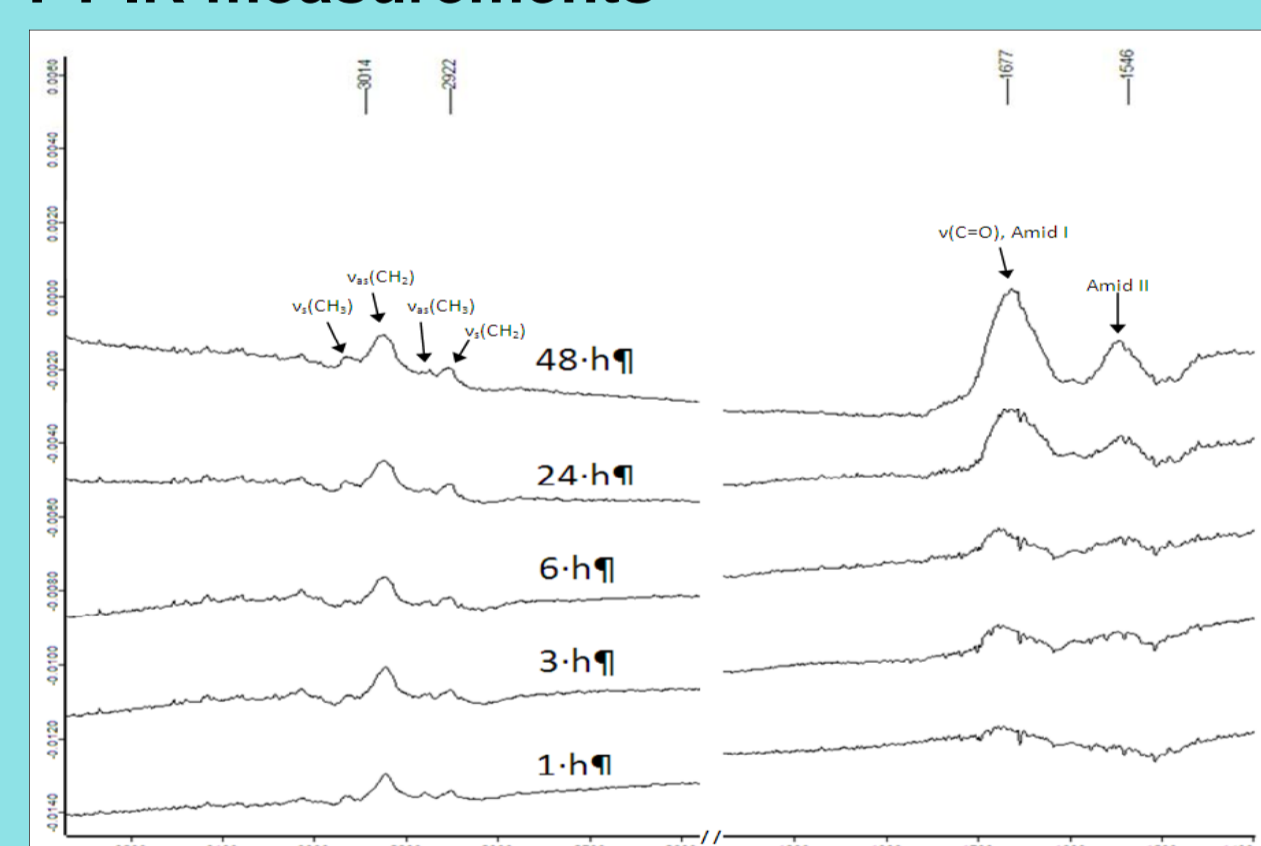
Ellipsometric Data



XPS measurements



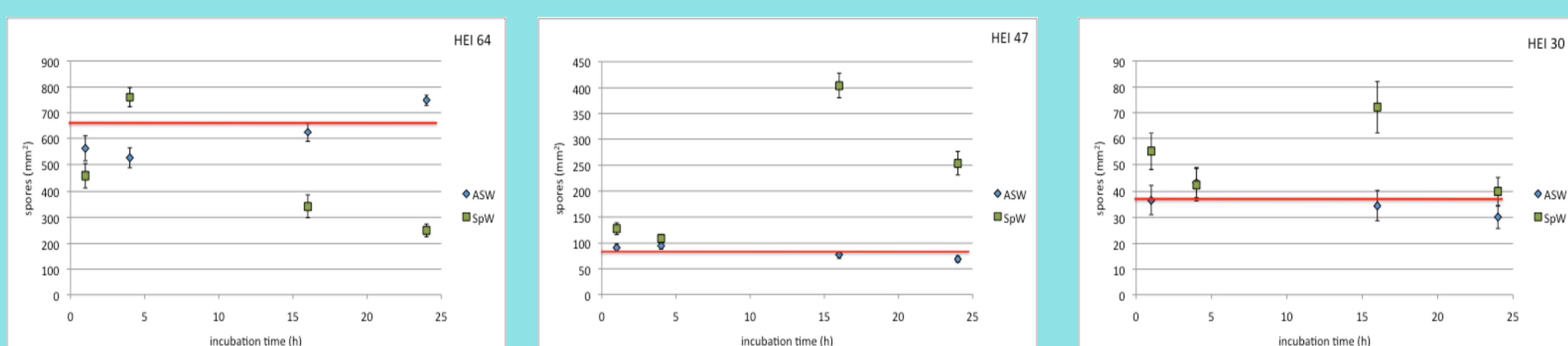
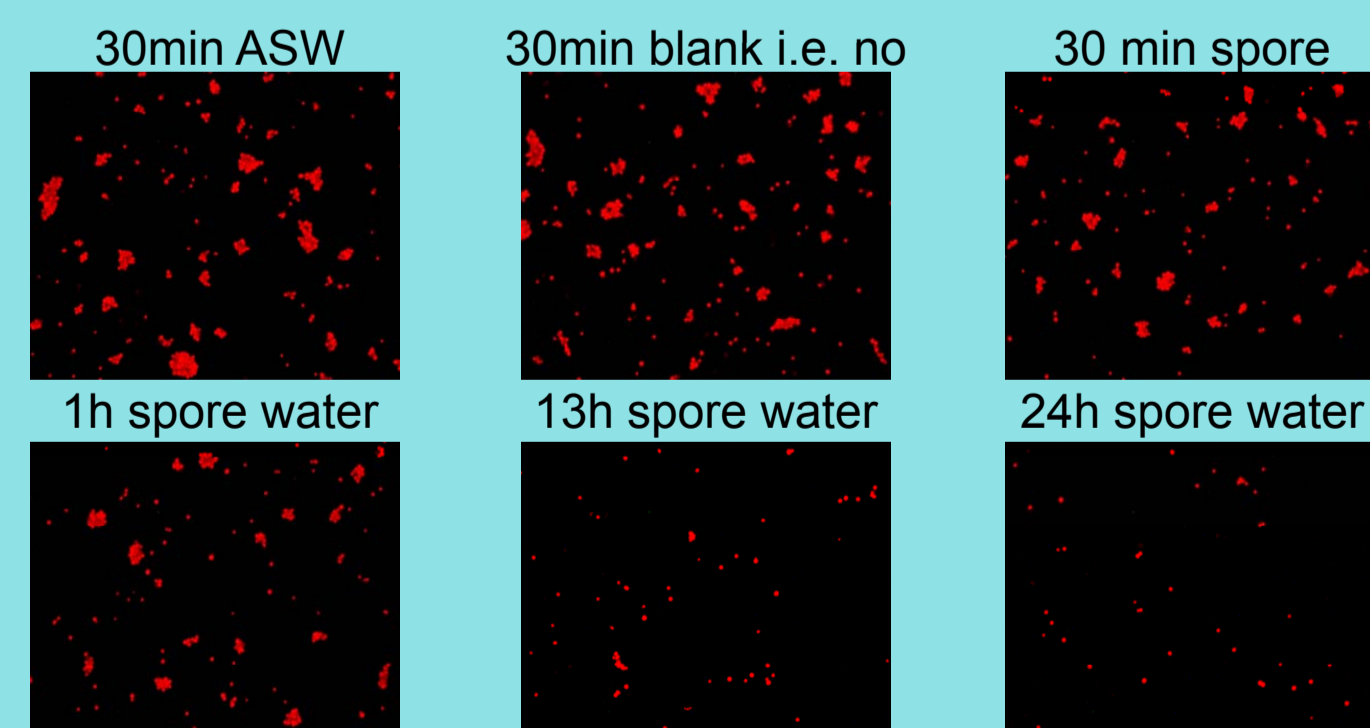
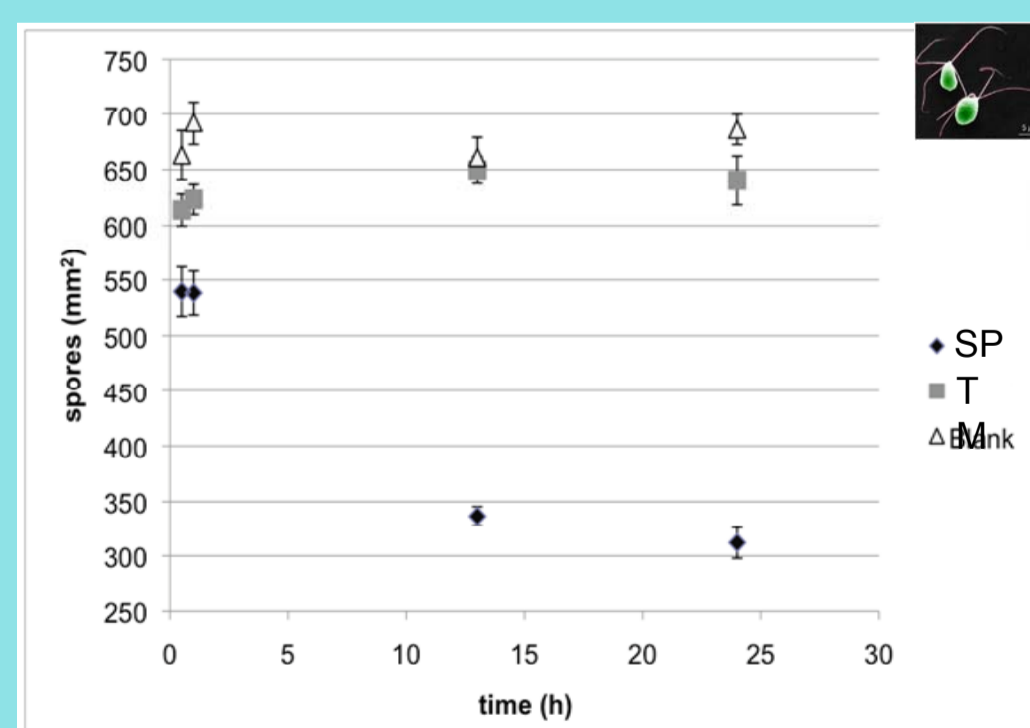
FT-IR measurements



→conditioning film is built up over time by macromolecules released from adult plants or swimming spores

Influence of conditioning film on settlement of alga *Ulva linza*

- normal assay with C12 surfaces incubated for different times in SP, TM and without incubation

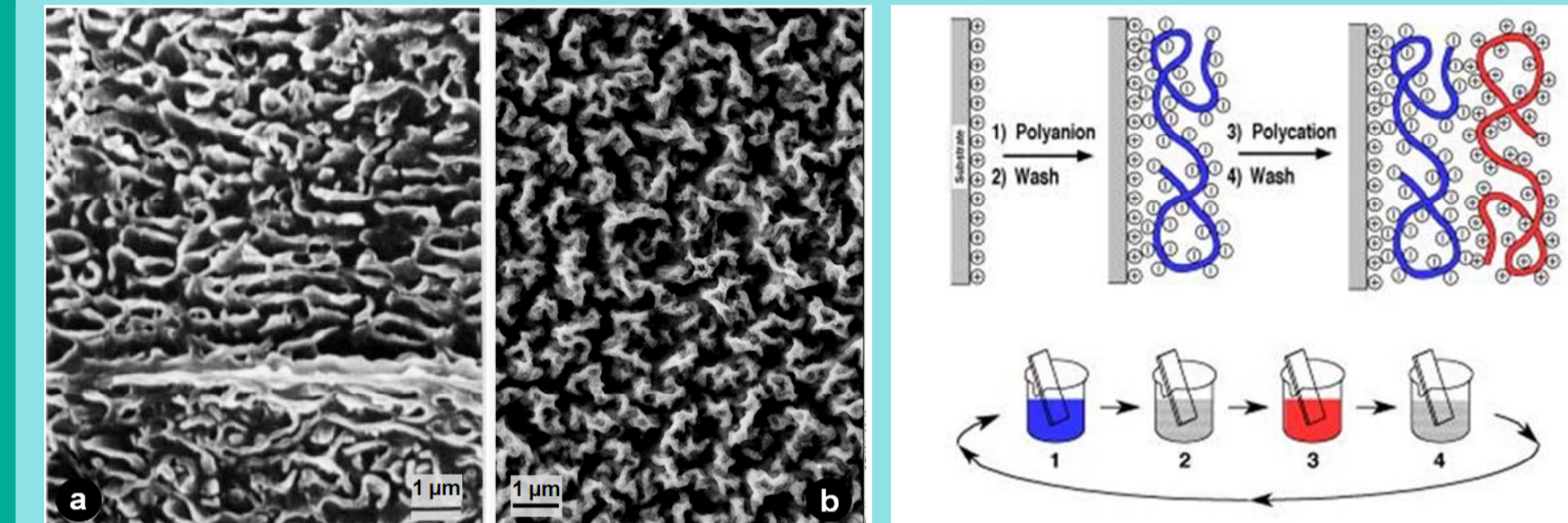


- data above show that pre-incubation with 'spore water' leads to a change in subsequent spore settlement
- the adsorbed dissolved organic carbon (DOC) molecules deter or promote spores settlement
- distribution of settled spores changes from gregarious (clumped) to single spores and small groups with exposure to the conditioning solution

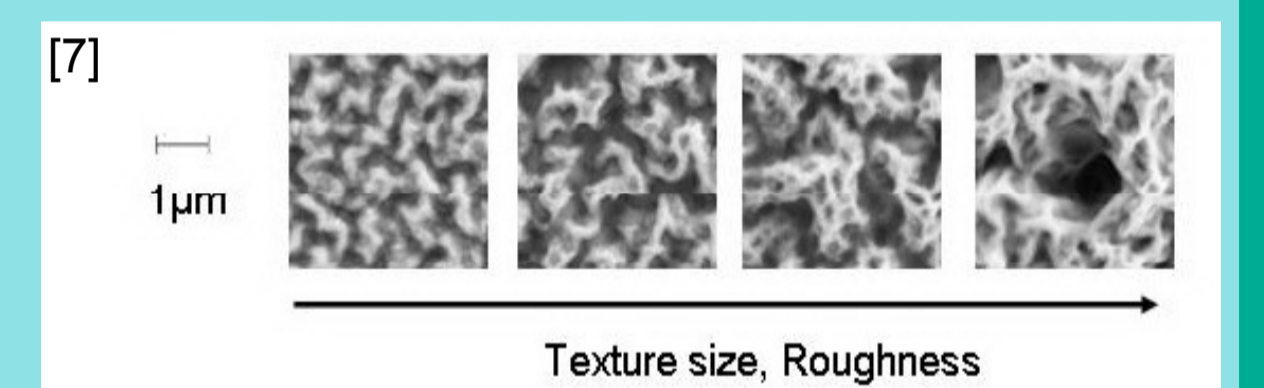
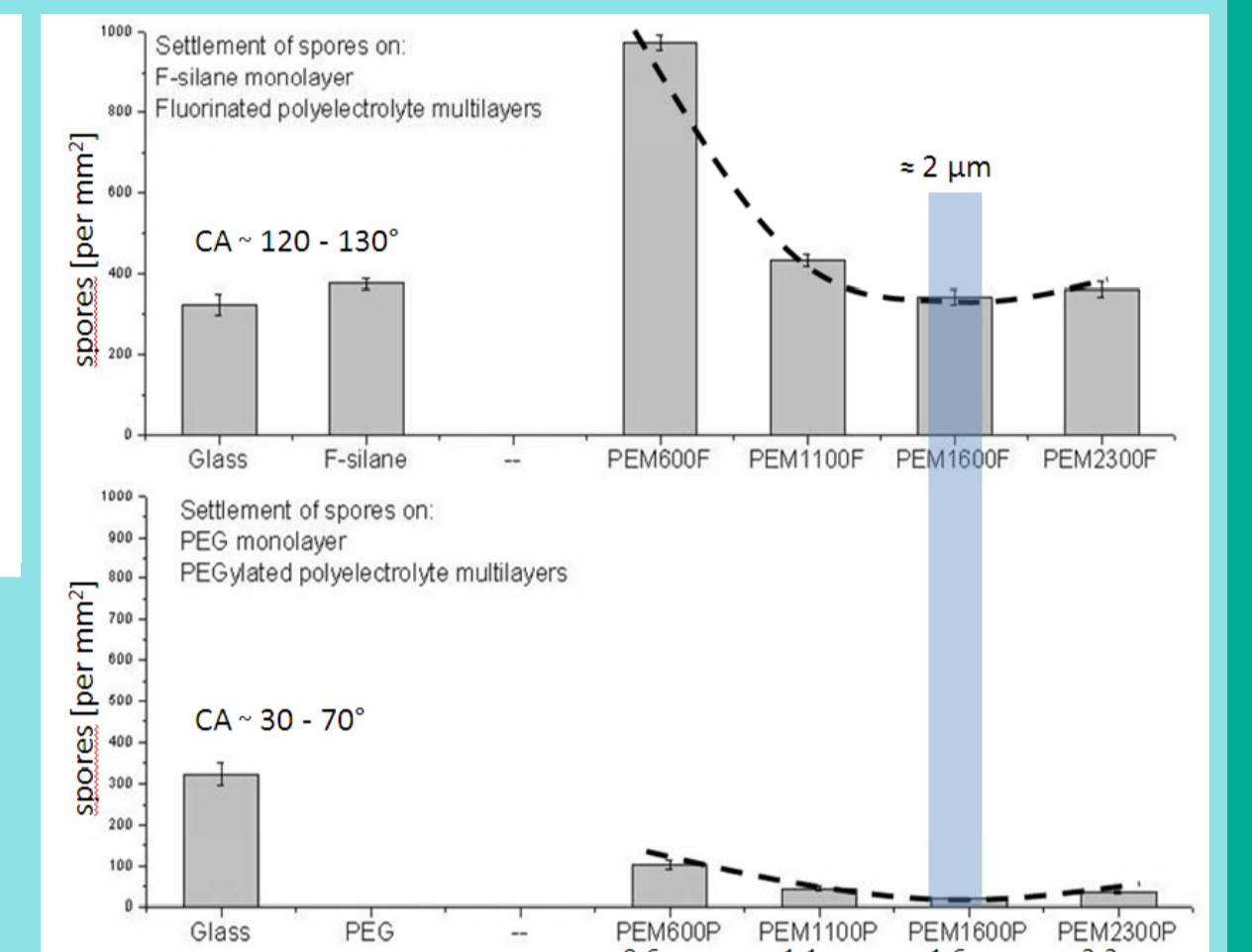
Bioinspired micro- and nanostructures

- motivated by patterns found on the skin of dolphins [5]

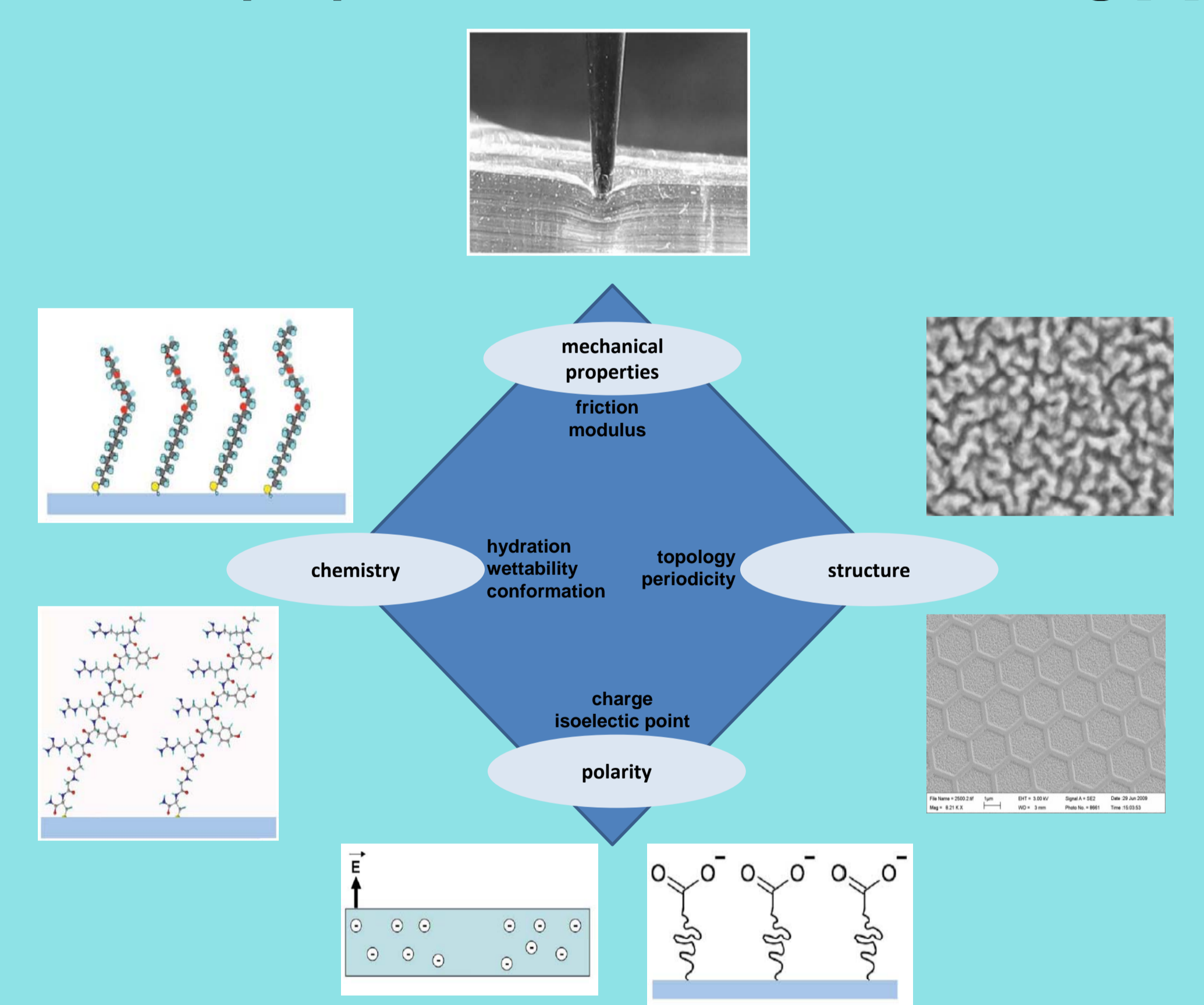
dolphin skin Polyelectrolyte coating



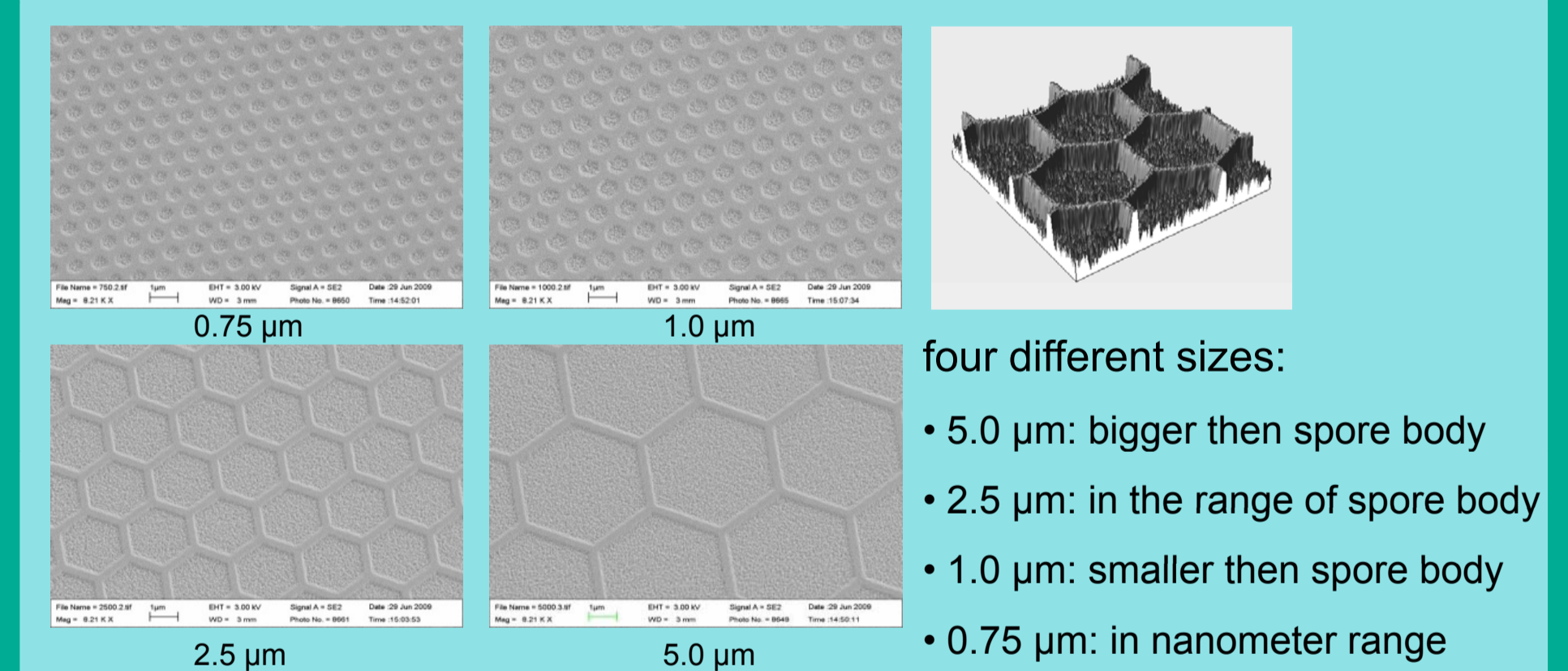
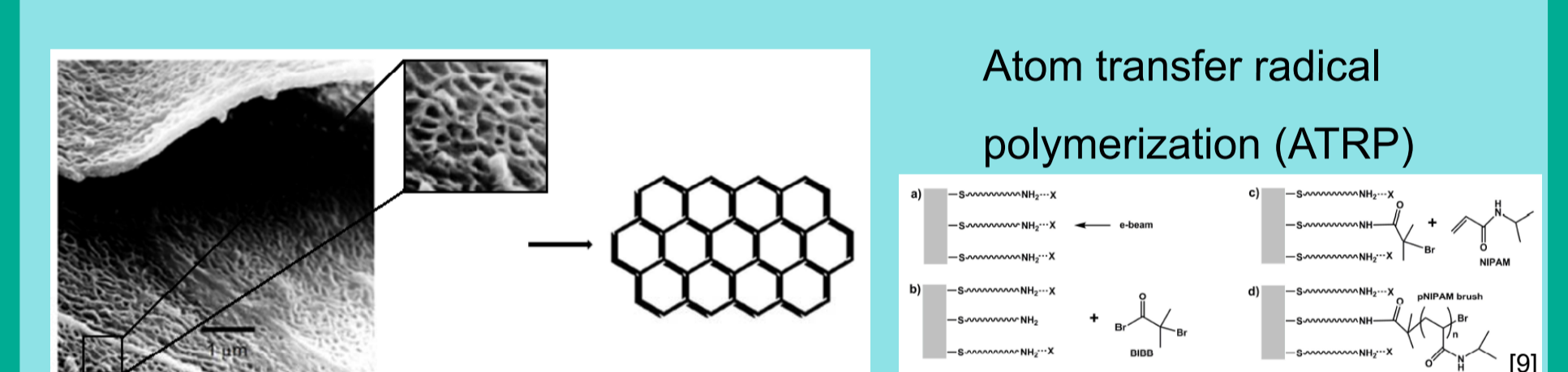
- Polyelectrolyte self assembly used to prepare bioinspired, tuneable surface topographies
- Ulva* spores show reduced settlement density on structures smaller than spore body size (~30-50% of its diameter)
- chemical modification enhances or reduces roughness response but influence of roughness is preserved



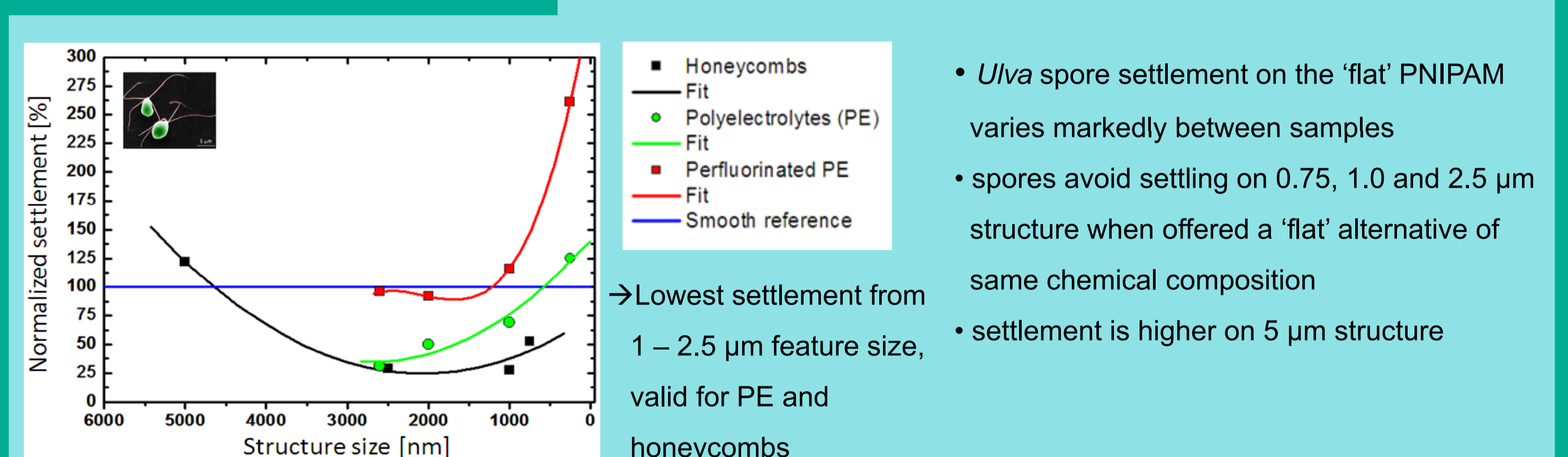
Surface properties relevant for biofouling [8]



E-beam activated lithography (EBAL)



Comparison polyelectrolyte with pNIPAM structures



Conclusions

- surfaces condition within 24h if spore water (SP) is used
- surfaces conditioning is happening at longer timescale than typical *Ulva* assays
- conditioning film influences spore settlement
- spores avoid surface structures which are approximately half of their own size
- convoluted effect between chemistry and structure has been disentangled

Acknowledgment

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Literature

- M.E. Callow, J.A. Callow, J.D. Pickett-Heaps, R. Wetherbee, *J. Phycol.*, **1997**, 33, 938.
- J. J. Corbett, H. W. Koehler, *Journal of Geophysical Research*, **2003**, 108, (D20), 4650.
- J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.*, **2005**, 105, 1103-1169.
- M. E. Callow, J. A. Callow, L. K. Ista, S. E. Coleman, A. C. Nolasco, G. P. Lopez, *Appl. Environ. Microbiol.*, **2000**, 66, (8), 3249-3254.
- C. Baum, W. Meyer, R. Stelzer, L.-G. Fleischer, D. Siebers, *Marine Biology*, **2002**, 140, 635-657.
- X. Cao, M. E. Pettitt, F. Wode, M. P. Arpa Sancel, J. Fu, J. Ji, M. E. Callow, J. A. Callow, A. Rosenhahn, M. Grunze, *Adv. Funct. Mater.*, **2010**, 20, 1984.
- A. Rosenhahn, T. Ederth, M. E. Pettitt, *Biointerfaces*, **2008**, 3, (1), IR1-IR5.
- S. Schilp, N. Ballav, M. Zharnikov, *Angew. Chem. Int. Ed.*, **2008**, 47, 6786-6789.