Adsorption and desorption of water on protein-repelling self-assembled monolayers

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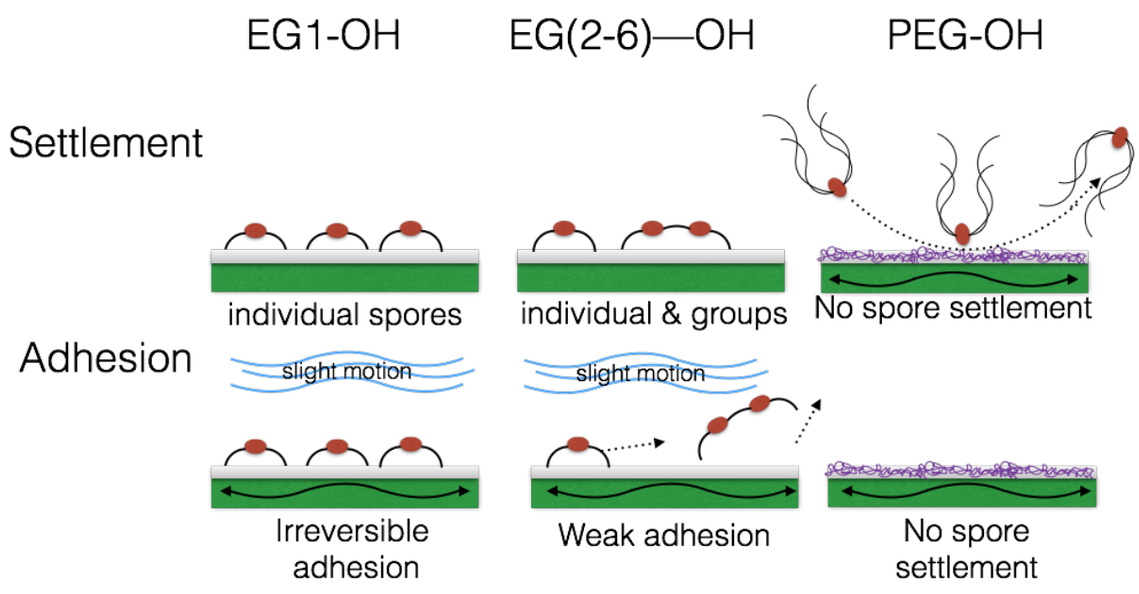
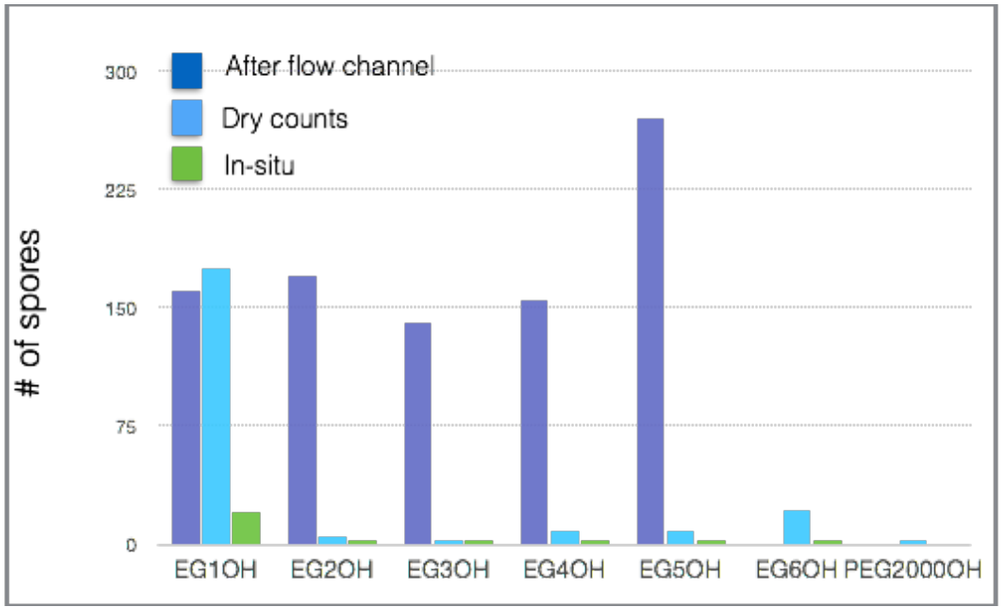
Protein repelling

- Proteins adhere strongly to almost all materials, which may result in their denaturing.
- There are only few materials which interact weakly with proteins – so called protein-repelling materials.
- The most efficient ones are oligo/poly(ethylene glycols).
- They exhibit protein-repelling properties at sufficient density and amount of material.



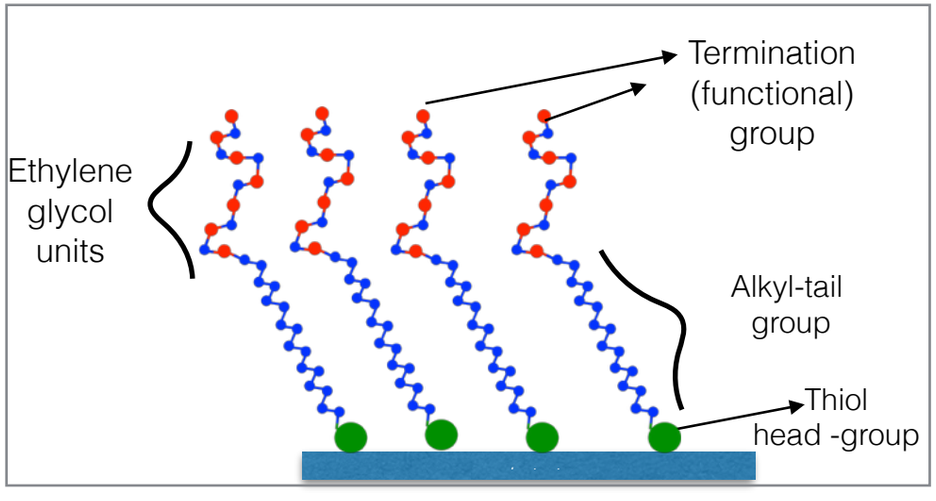


Rosenhahn A. et al, Phys Chem Chem Phys, 2010, 12, 4275

SAM	contact Angle	SAM thickness/A° (XPS)	SAM thickness/A° (Ellipsometry)	Thickness of adsorbed fibrinogen /A° (ellipsometry)
EG1OH	(28±4)°	13±3	17±2	19±2
EG2OH	(33±4)°	15±3	18±2	5±2
EG3OH	(31±4)°	16±3	18±2	0±2
EG4OH	(33±4)°	18±3	22±2	0±2
EG5OH	(34±4)°	21±3	23±2	0±2
EG6OH	(33±4)°	24±3	25±2	0±2

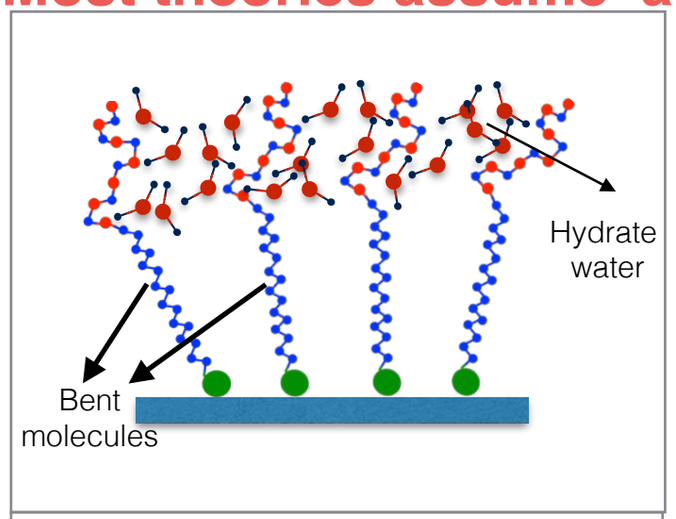
Motivation

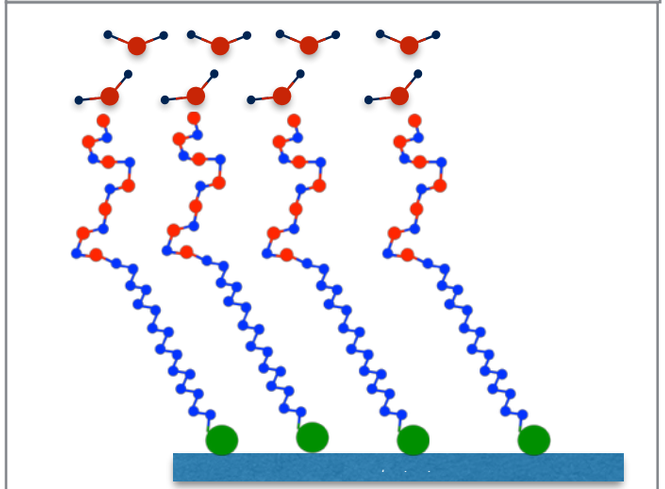
To get a better understanding of the mechanism behind the inertness of oligo(ethylene glycol), with respect to biofouling and protein adsorption.



Well-defined model **OEG-terminated** surfaces by using molecular self assembly were used.

Most theories assume a key role of water adsorption properties related to protein repelling.



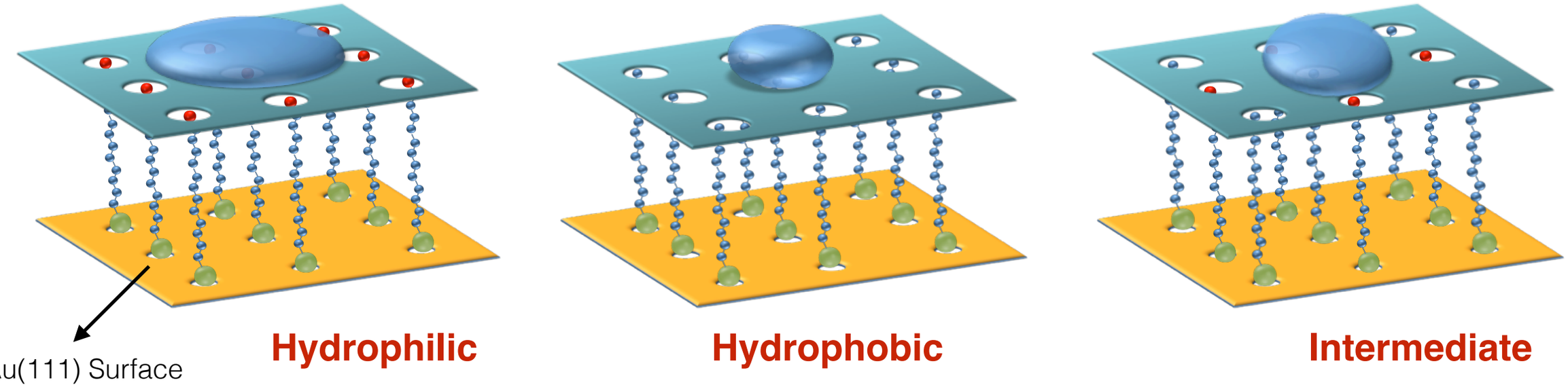


Focus on:

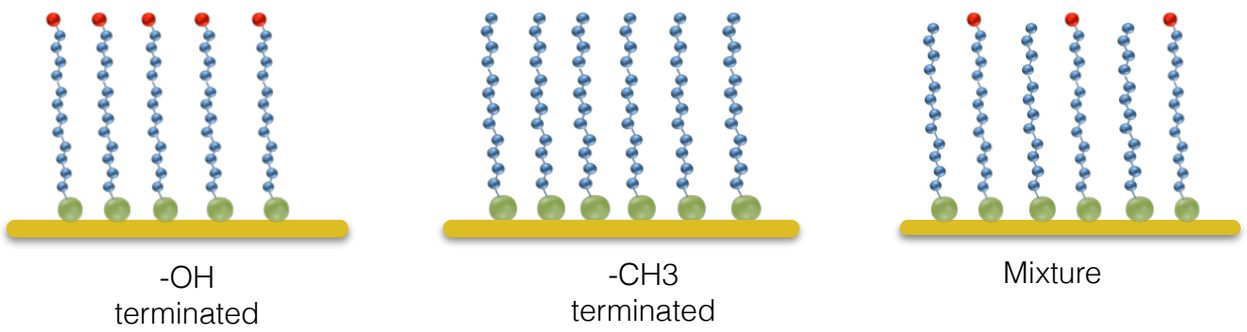
- Kinetics and thermodynamics of water adsorption and desorption.
- Monitoring the transfer from hydration to wetting regime.
- The bonding character of hydration phase.
- The structure and morphology of the interfacial phase.

Model System

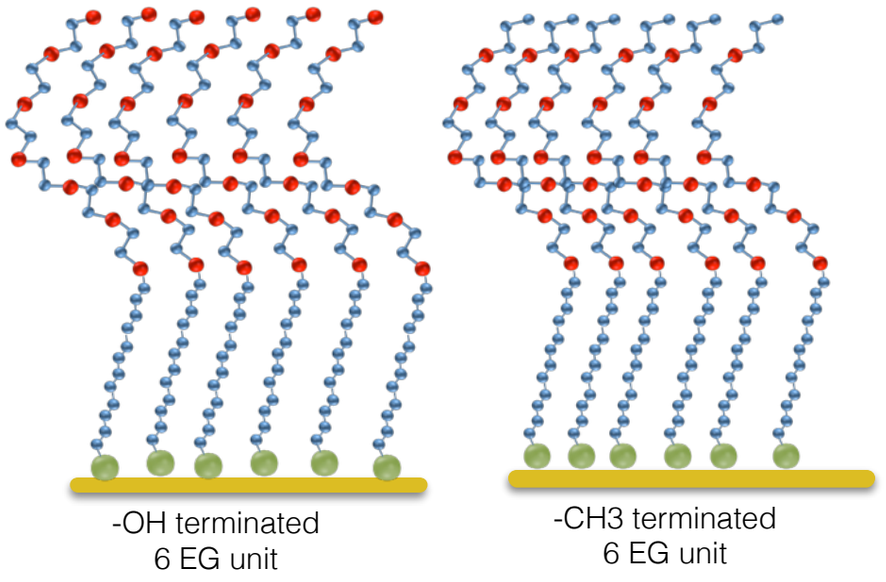
Termination group & change in wetting character



Macroscopic wetting is a factor determines the bio-inertness up to a point



-OH and/or -CH3 terminated
Alkane thiols with 12 or 16 Carbon tail



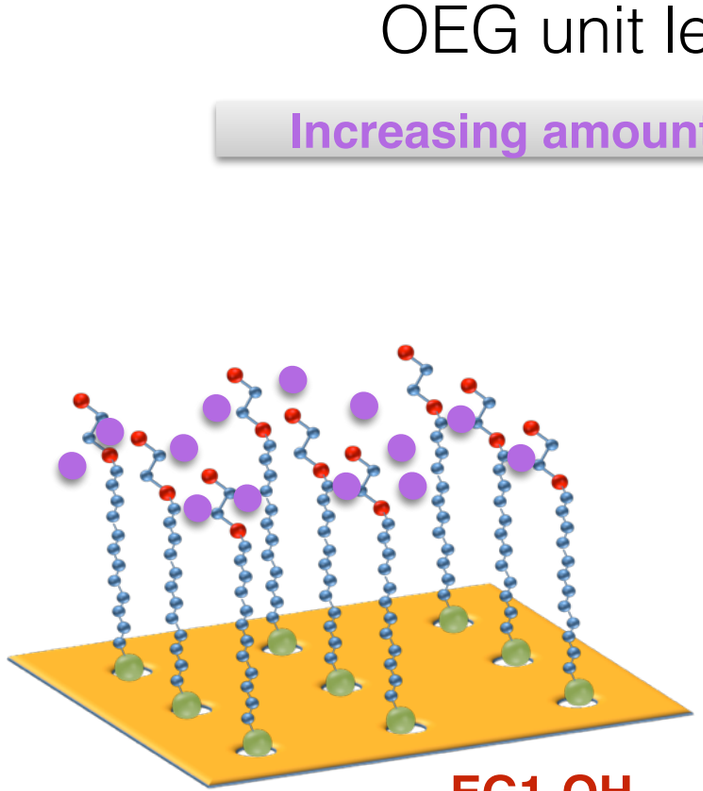
-OH and -CH3 terminated Alkane thiols with 6EG units having 12 carbon tail

Model System

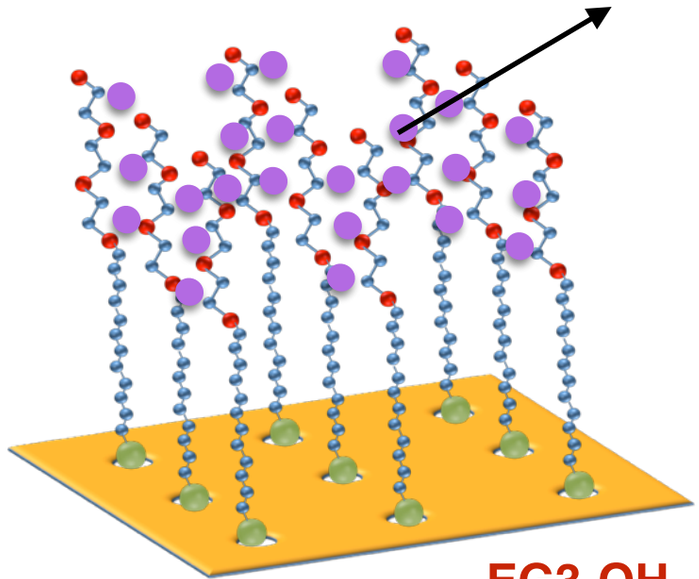
OEG unit length & Change in hydration character

Increasing amount of hydrate water

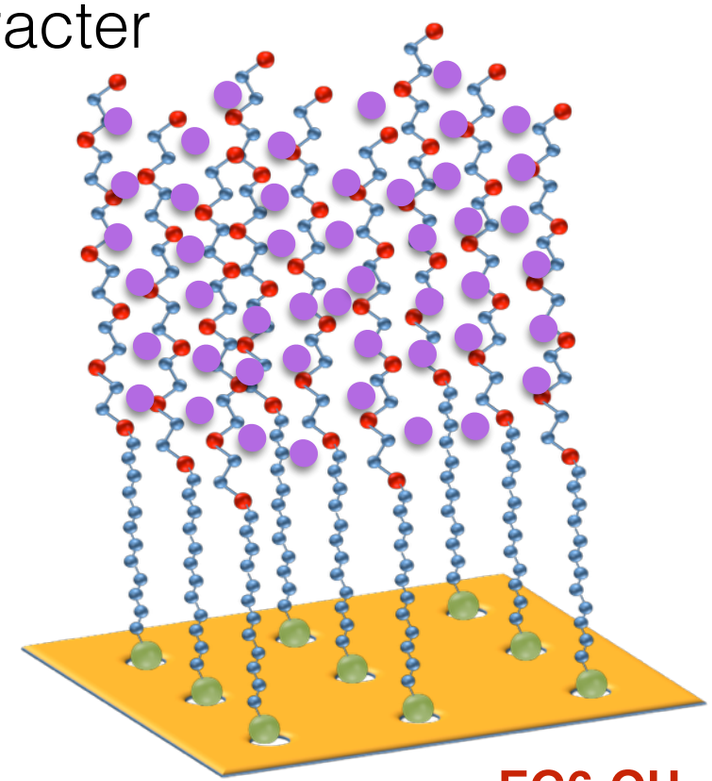
Hydrate Water



EG1-OH

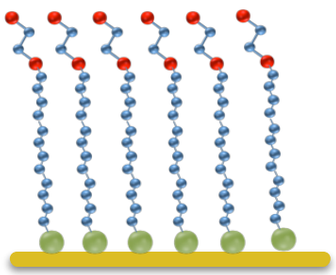


EG3-OH

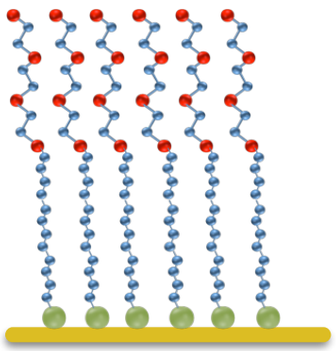


EG6-OH

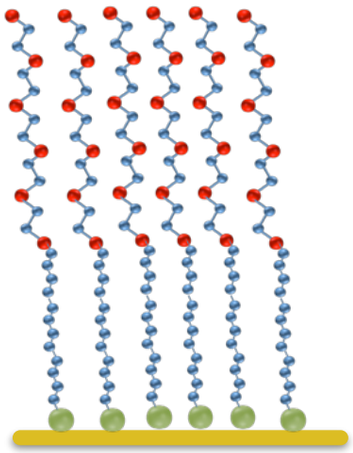
The key factor for the bio-inertness is presumably the extent of hydration



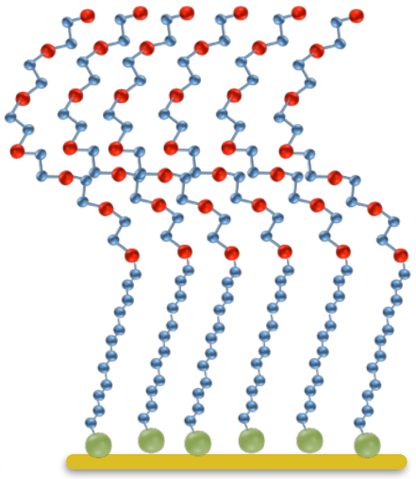
-OH terminated 1 EG unit



-OH terminated 3 EG unit



-OH terminated 5 EG unit



-OH terminated 6 EG unit

-OH terminatedAlkane thiols with different number of EG units having 12 carbon tail

Analysis Techniques

Basic Characterisation

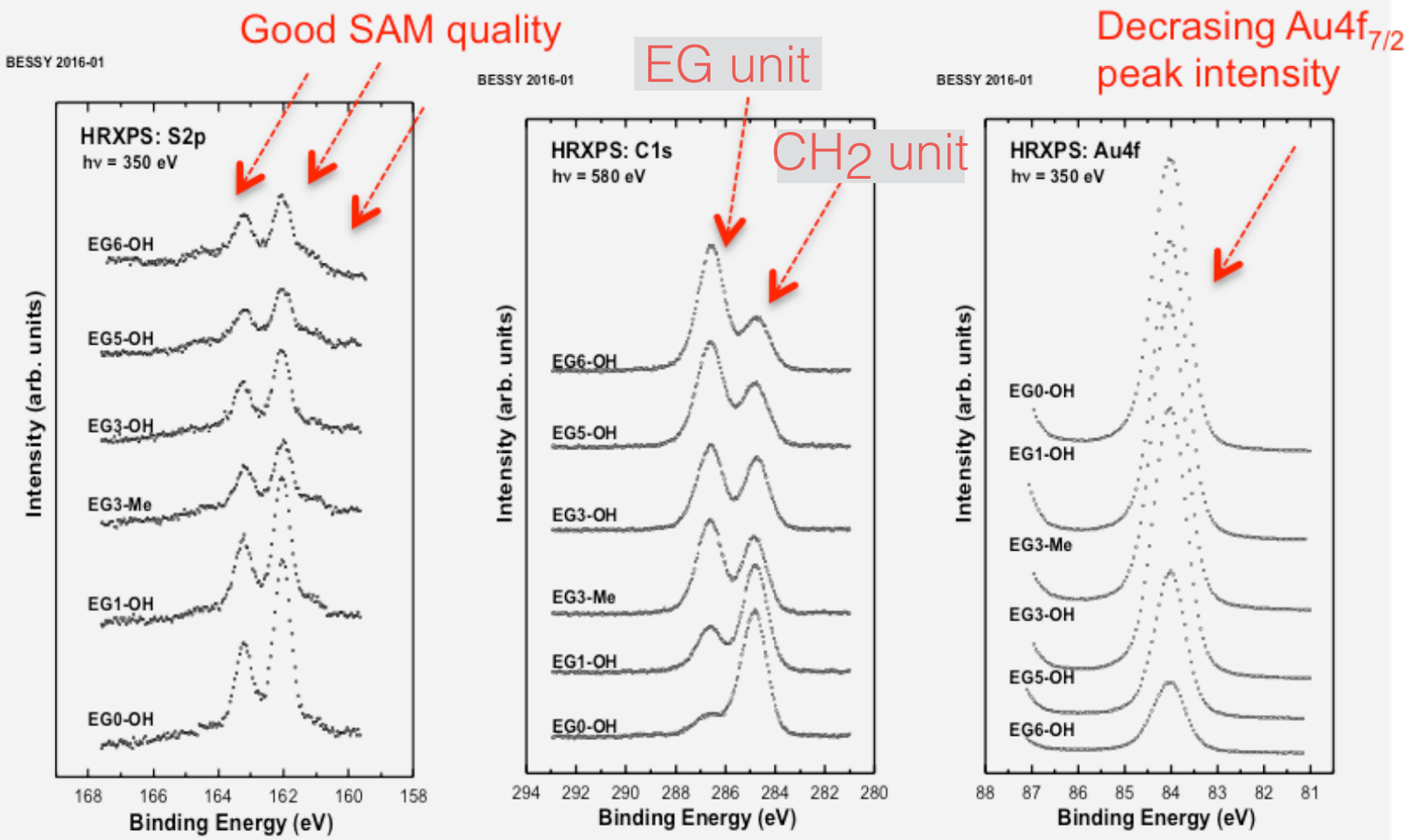
- **Contact Angle Goniometry**
  Wetting properties
- **Ellipsometry**
  Film thickness
- **X-ray photoelectron spectroscopy**
  Identity, purity and packing density
- **X-ray absorption spectroscopy**
  Structure, composition, morphology and bonding character

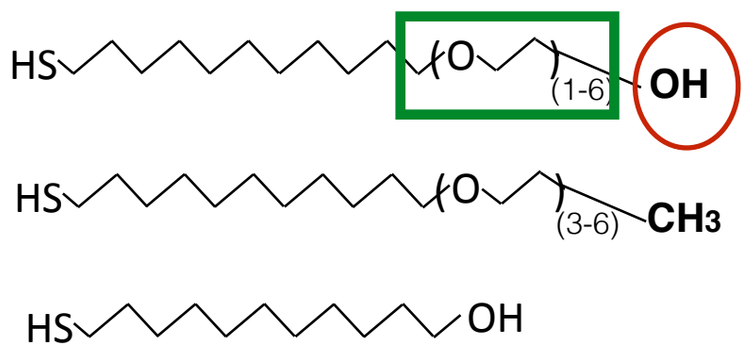
Kinetic Experiments

- **Temperature programmed desorption**
  Water desorption kinetics
- **X-ray photoelectron spectroscopy**
  Water desorption kinetics

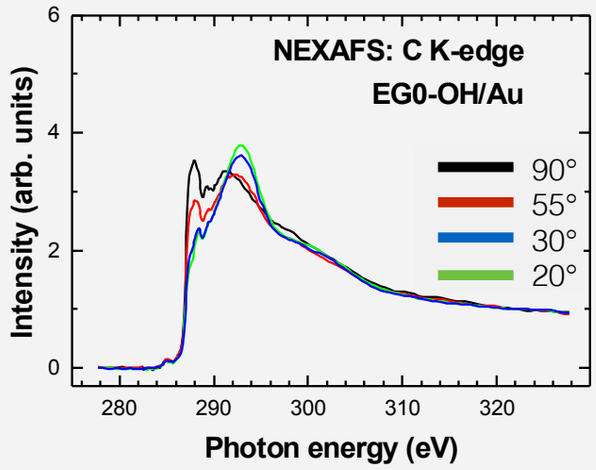
HRXPS & NEXAFS Characterization: $C_{11}(EG)_n$ series

HRXPS

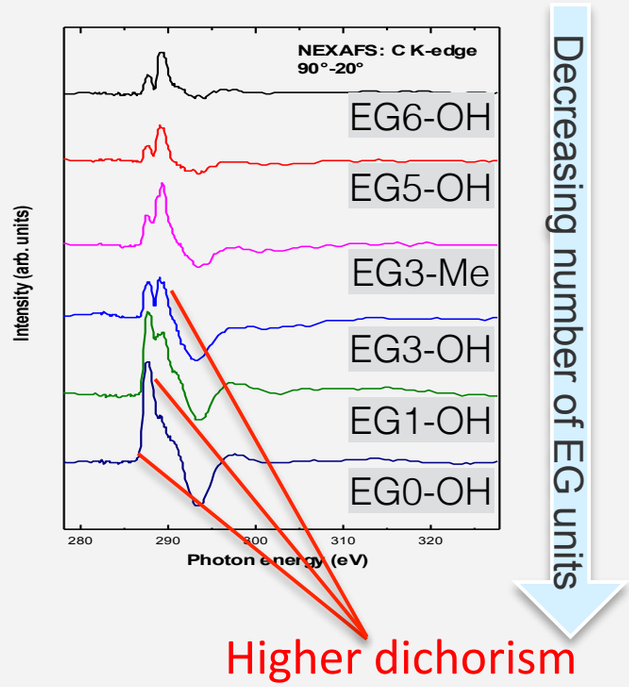




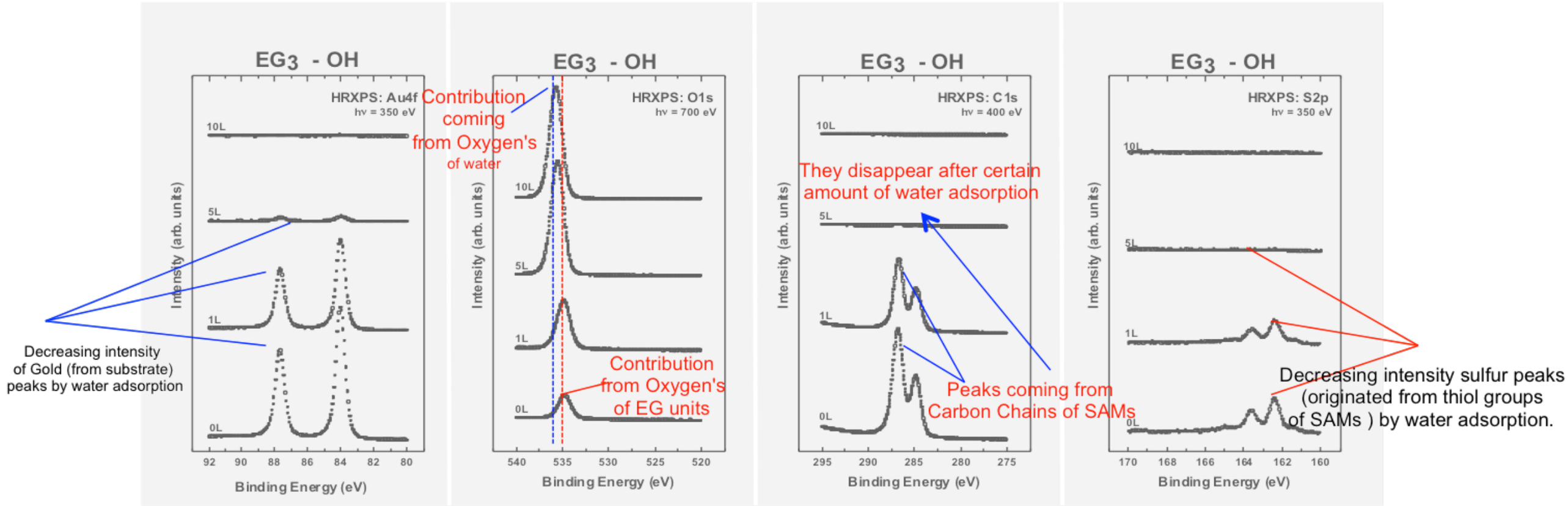
NEXAFS spectra

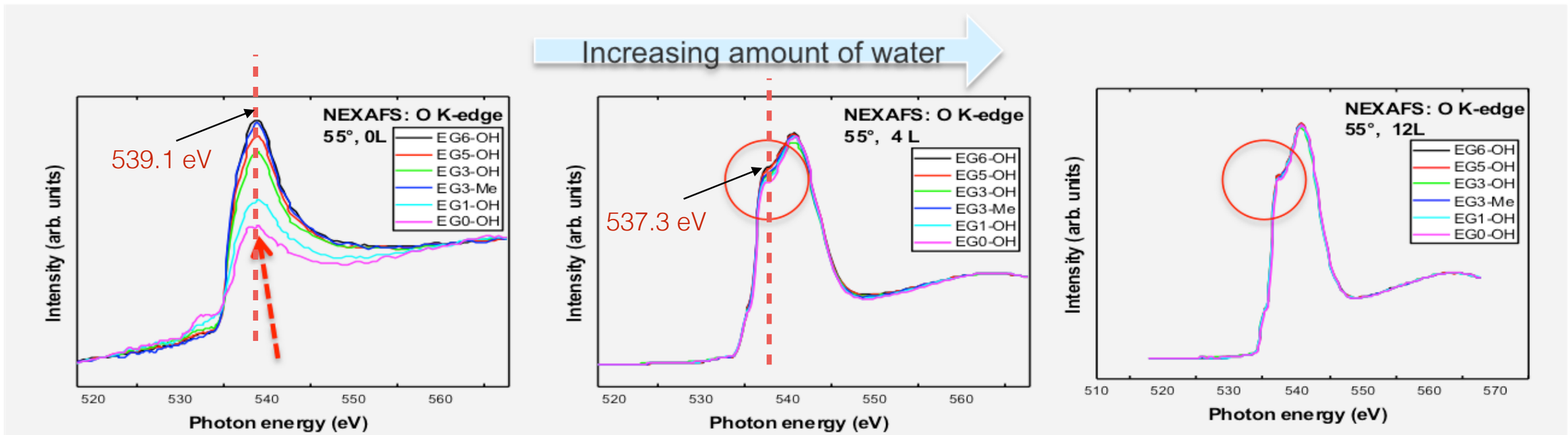


NEXAFS difference spectra



Monitoring of Water Adsorption by HRXPS and NEXAFS



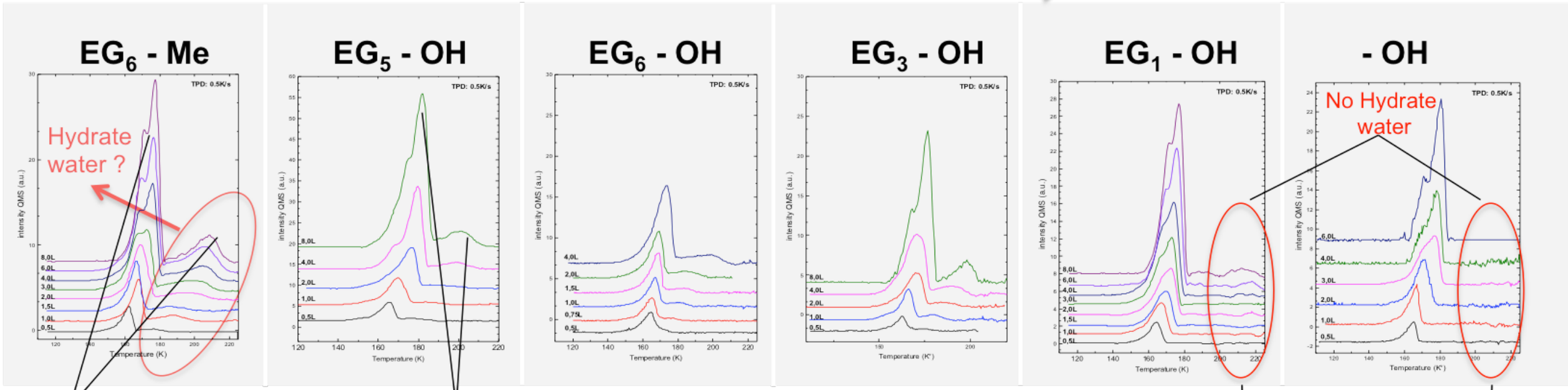


Can be speculated that transition between amorphous ice to crystalline ice is observable

Water Desorption Analysis by TPD

Decreasing number of EG units

Decreasing amount of hydrate water

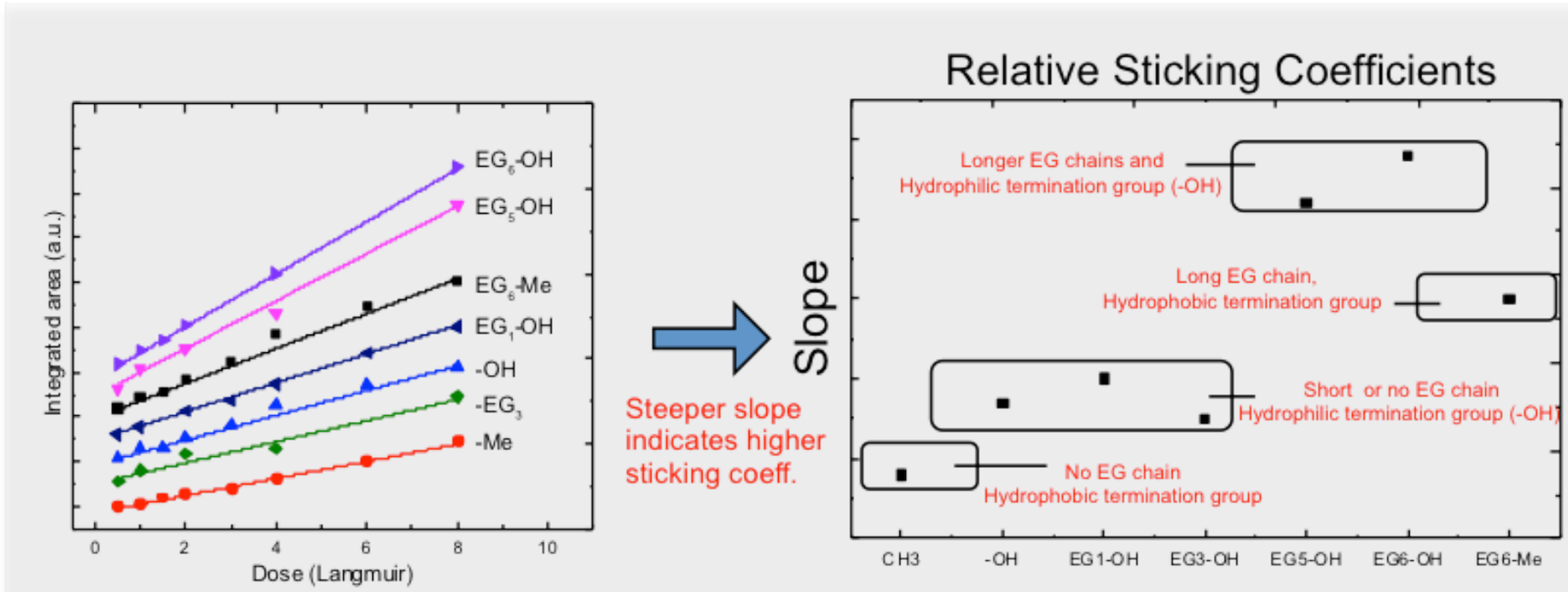


Higher ratio of hydrate water

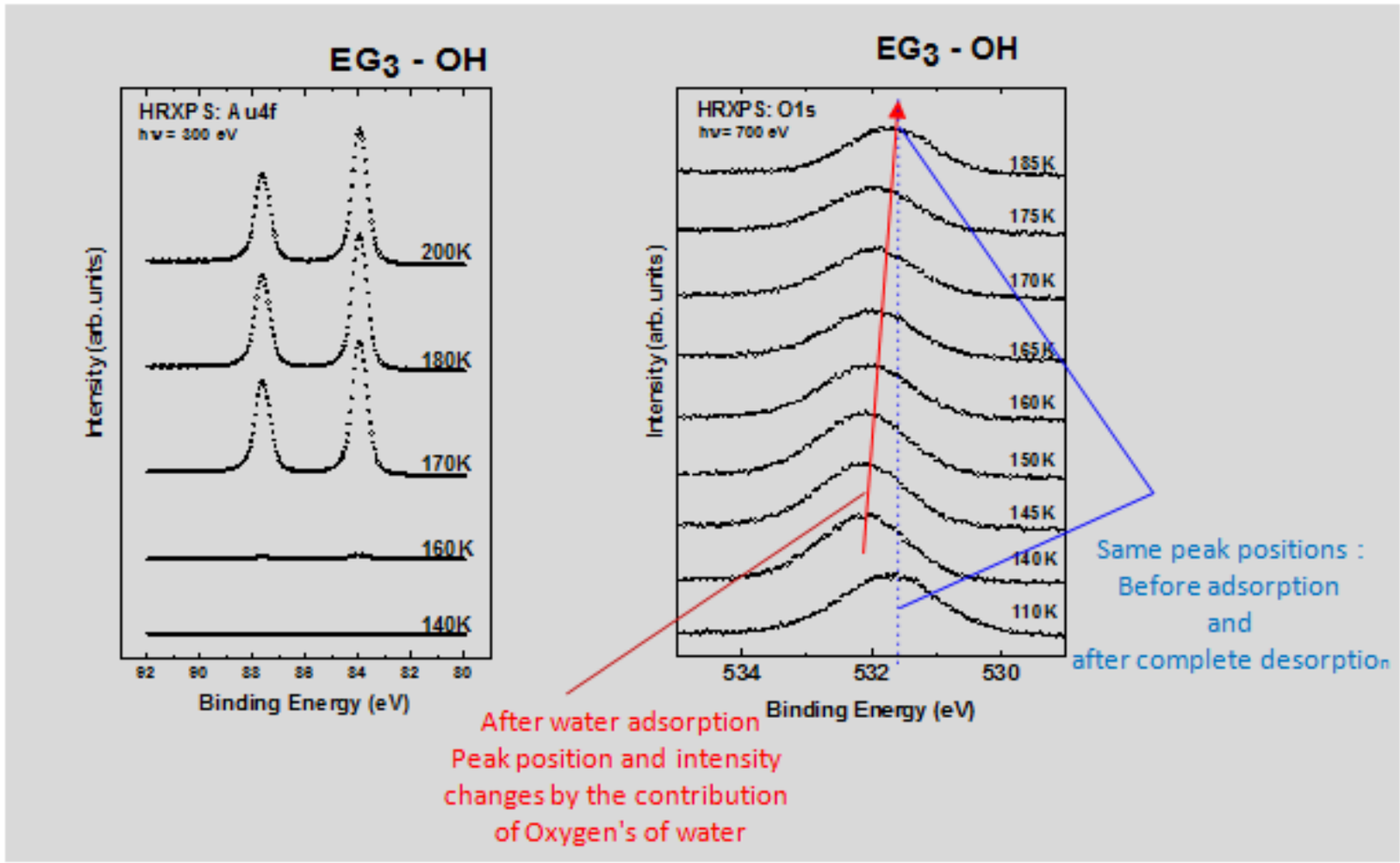
Lower ratio of hydrate water

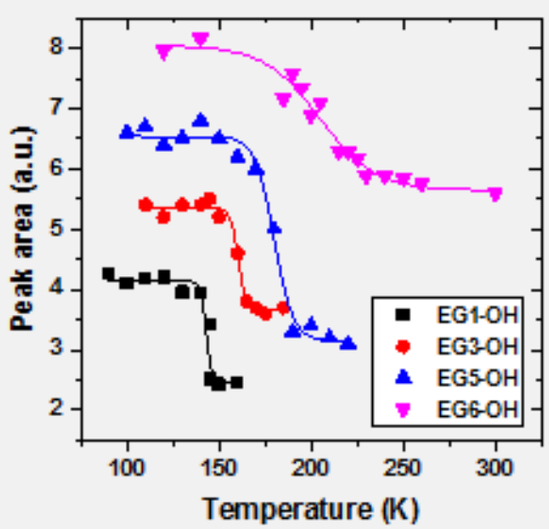
Reason: Termination group

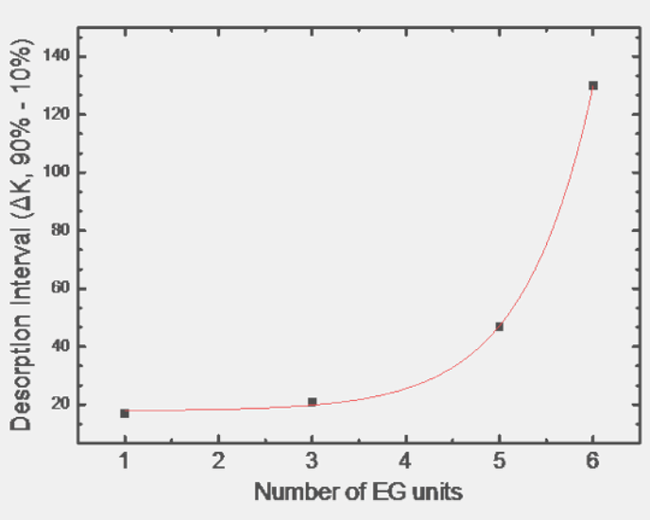
Reason: No or Short EG chain
No place for embedding water molecules



Monitoring Water Desorption by HRXPS







- By increasing amount of EG units desorption temperature moves to higher values.
- Desorption interval gets broader.

Summary

- Series of model OEG-terminated surfaces were prepared.
- Basic characterisations were done.
- The impact of the EG- unit length on hydration was monitored.
- The transition from hydration from wetting regime was observed.
- The kinetics of the water desorption was studied by TPD.

Thanks to:

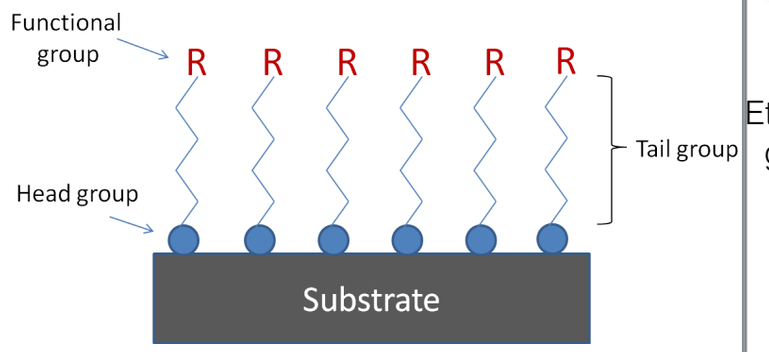
DFG Deutsche Forschungsgemeinschaft

HZB Helmholtz Zentrum Berlin

Thank you for your attention …

Introduction & Keywords

1)



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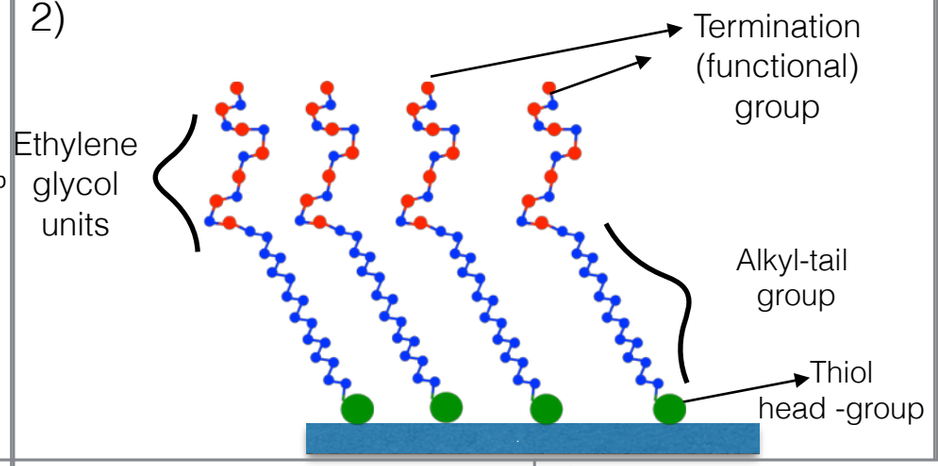

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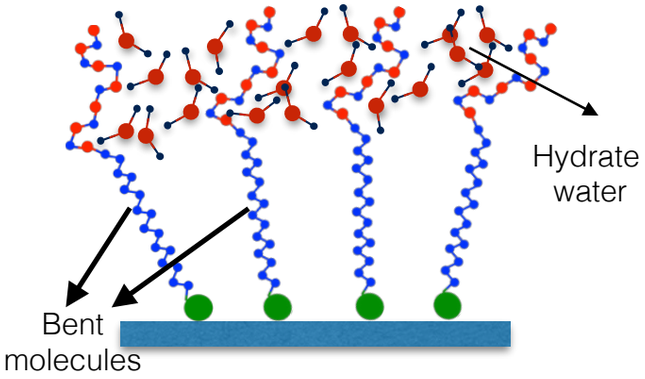

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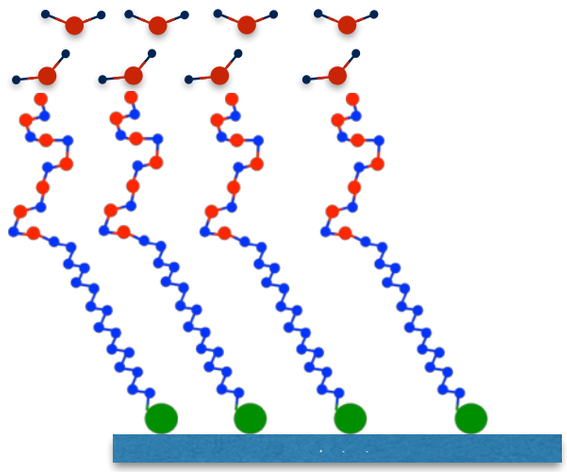

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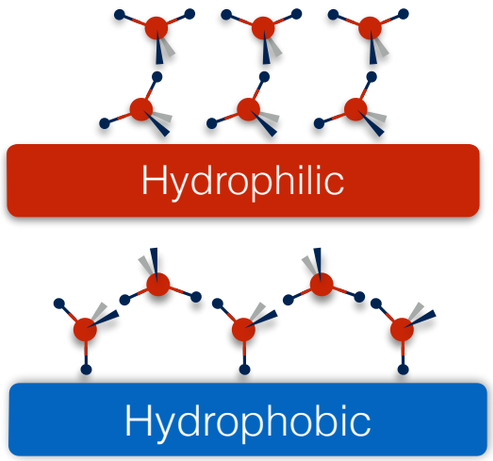

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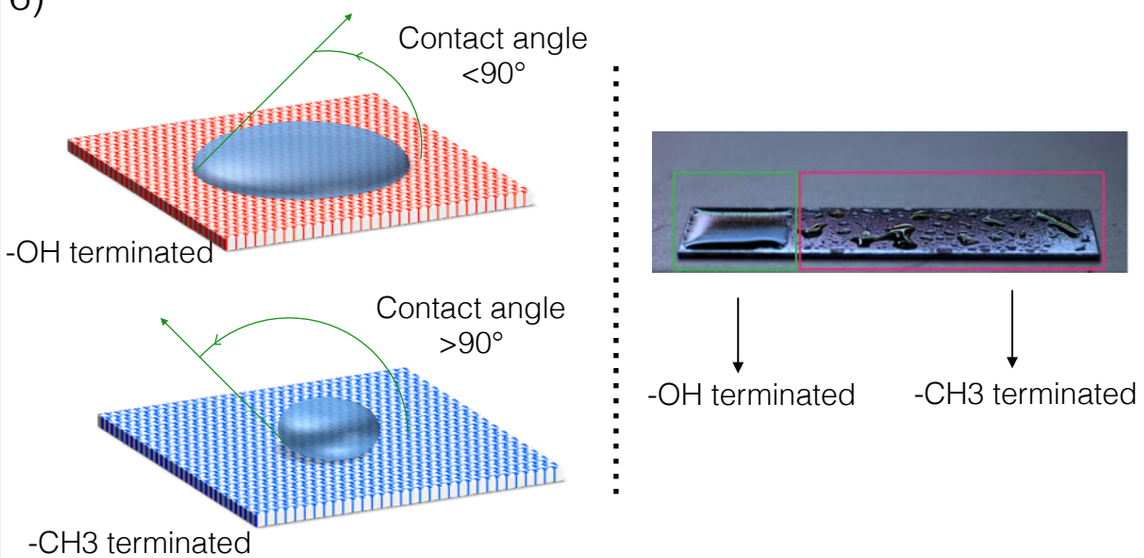

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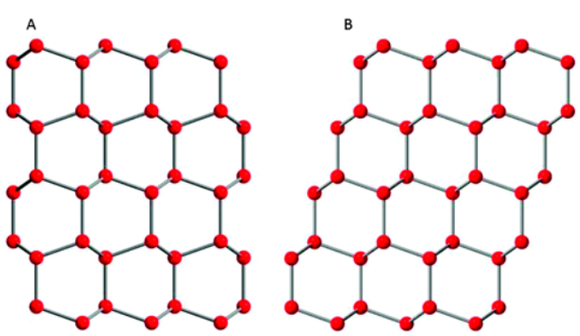

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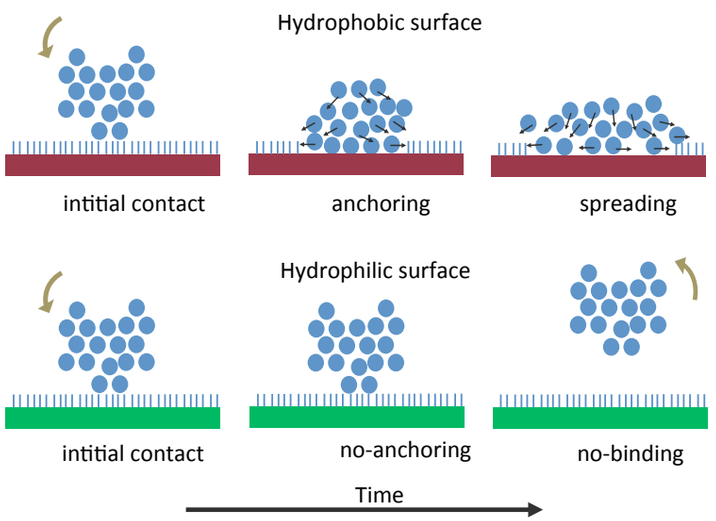

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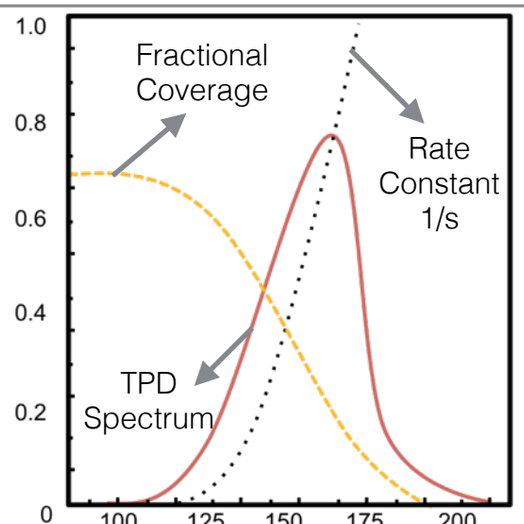
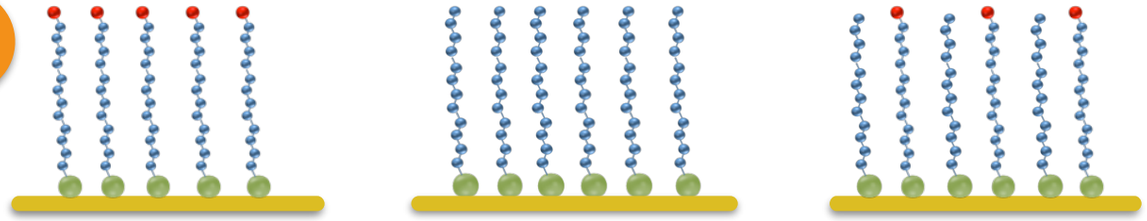


$$r(t) = -\frac{d\sigma}{dt} = v_n \sigma^n * e^{-E_{act}/RT}$$

Model System

1



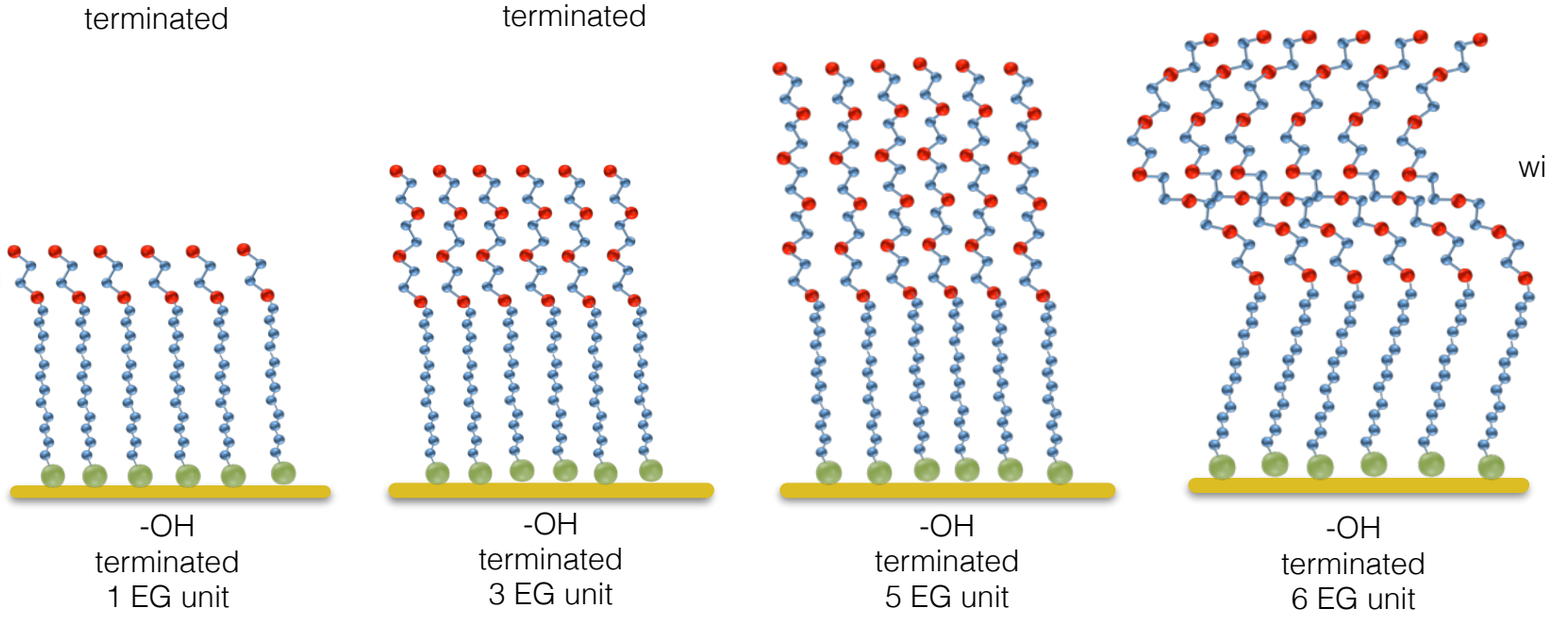
-OH terminated

-CH3 terminated

Mixture

-OH and/or -CH3 terminated
Alkane thiols with 12 or 16 Carbon tail

2



-OH terminated 1 EG unit

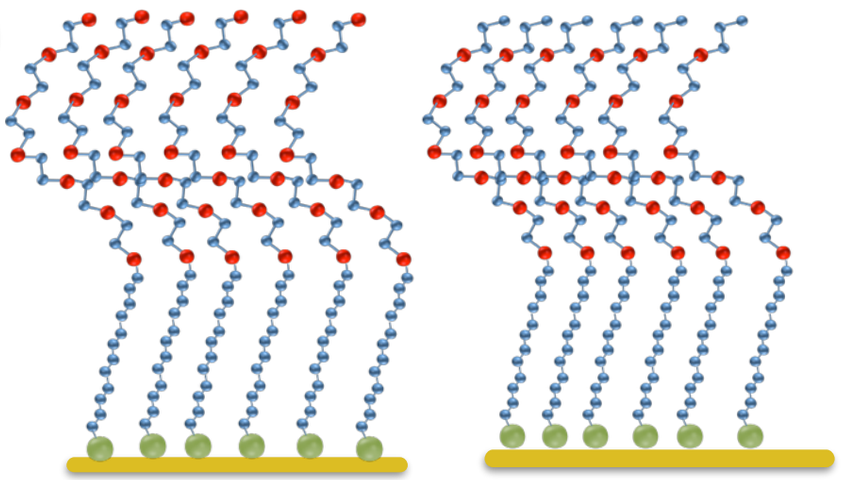
-OH terminated 3 EG unit

-OH terminated 5 EG unit

-OH terminated 6 EG unit

-OH terminatedAlkane thiols with different number of EG units having 12 carbon tail

3

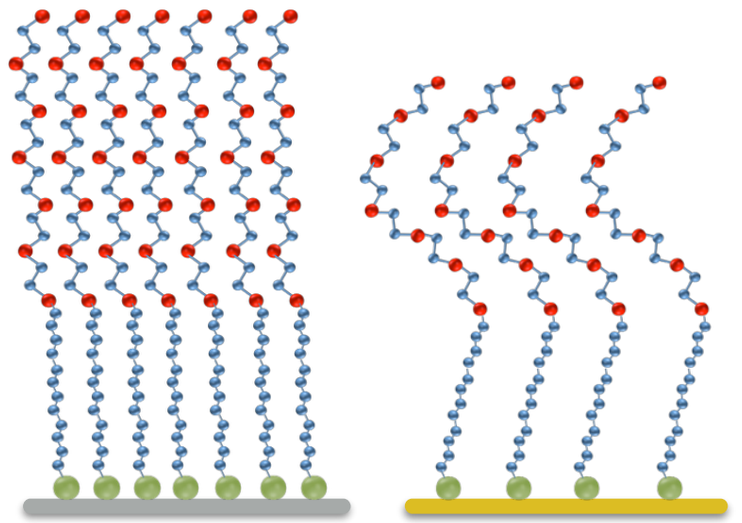


-OH terminated 6 EG unit

-CH3 terminated 6 EG unit

-OH and -CH3 terminated Alkane thiols with 6EG units having 12 carbon tail

4

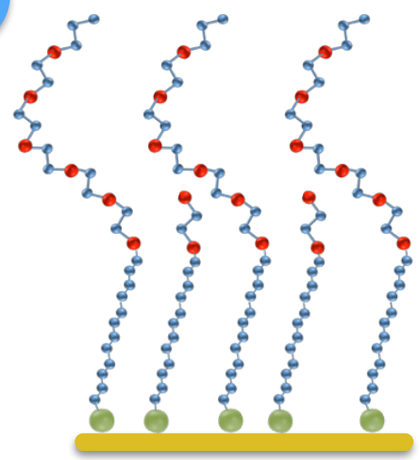


-OH terminated ,6 EG unit, Zigzag conformation

-OH terminated, 6 EG unit, Helix conformation

-OH terminated Alkane thiols with 6 EG units having 12 carbon tail on Au(111) and Ag (111)

5



Various combinations:
UV/e-beam irridation or dilution