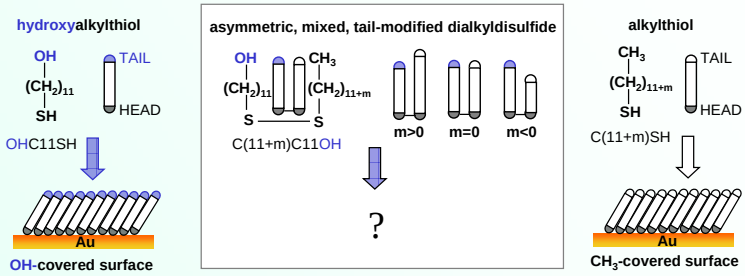
Self- assembled monolayers of asymmetric, mixed, tail-modified dialkyldisulfides on gold: Effect of chain difference

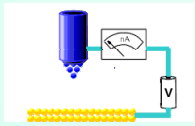
Susana Moreno Flores[1], Rüdiger Berger[1], Hans-Jürgen Butt[1], Chandrasekhar Vavilala[2], Michael Schmittel[2]

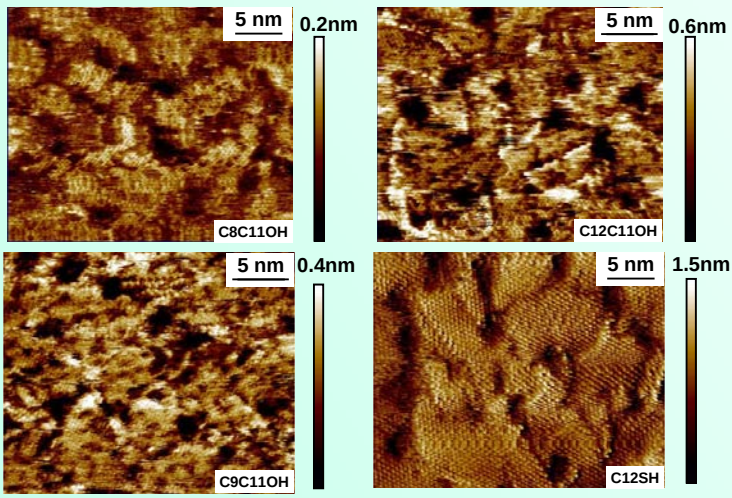
1 Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany
2 University of Siegen, Organische Chemie Abteilung, Adolf-Reichwein Str. 2, 57068 Siegen, Germany

We have synthesized and studied the surface properties of self-assembled monolayers (SAMs) of asymmetric, mixed, tail-modified dialkyldisulfides on gold. The chemical structure of the molecules we have chosen for our study is **CH_3-$(CH_2)_{11+m}$-S-S-$(CH_2)_{11}$-OH** with m=0,-3,-4. These molecules self-assemble on gold like the standard alkylthiols but they adsorb in thiolate pairs where the CH_3-terminated and OH- terminated chains are forced to be close to each other. This induces chemical heterogeneity at a nanometer scale within the surface, while the surface composition of functional groups is expected to be 1:1. Both facts make SAMs of this type of disulfides specially interesting for tailoring surface properties. We will show that it is possible to modify surface properties such as wetting and adhesion by slightly changing the chain difference **m**.

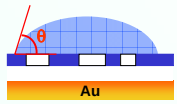


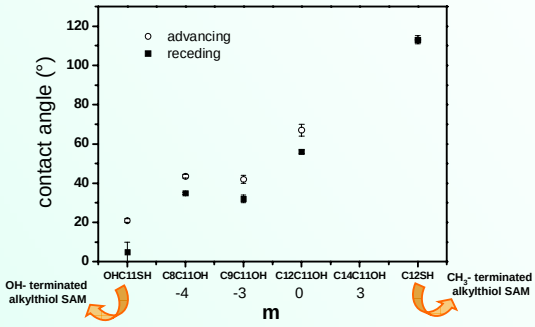
STM: Topology of the surfaces



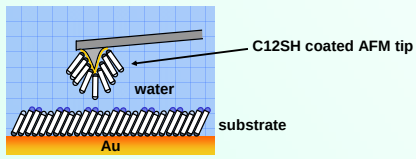


Contact angles: wettability in water

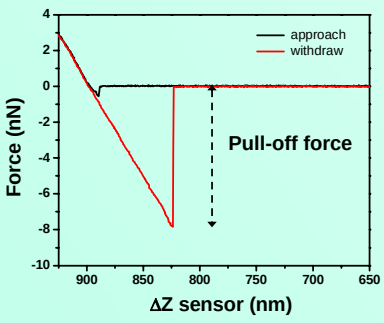




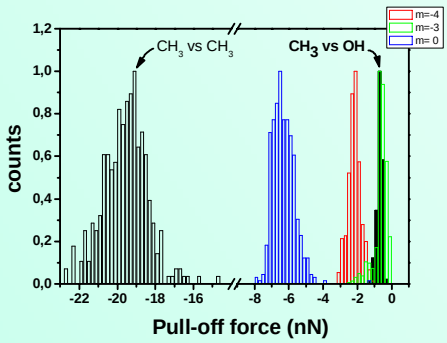
Wetting is sensitive to the outermost functional groups, which define the plane of the solid-liquid interface.



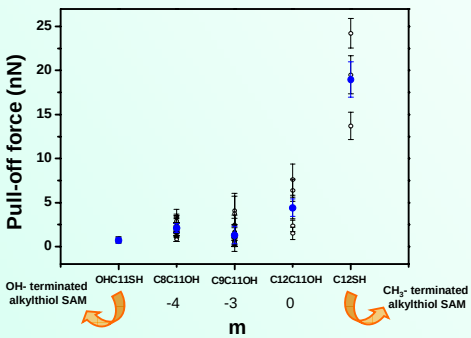
Chemical Force Microscopy (CFM): dialkyldisulfide SAM vs a hydrophobic tip



Tip and substrate are approached and withdrawn at a certain speed (~500nm/s). Maximum applied loads ranged 0.5-3nN.The force necessary to separate both surfaces once they are in contact is the so-called **Pull-off force**.
This magnitude is computed for each withdrawing curve.



Histograms of pull-off forces are obtained from the analysis of at least 200 curves for each tip-substrate.



Histogram peak positions and widths for different set of experiments. The adhesion properties seem to correlate with the parameter **m.** The slight increase of adhesion at m=-4 may show hindering of the hydroxyl-groups due to the enhanced mobility of the longer chains.

Outlook

- Asymmetric, mixed, tail-modified dialkyldisulfides with **longer** methyl-terminated chains (**m>0**) will complete the picture of how **m** can alter the surface properties of SAMs
- A molecular model that accounts for the experimental observations is being developed

Acknowledgements

- Uwe Rietzler, Gunnar Glasser, Gabi Hermann, Gunnar Kircher (MPI-P)
- Marco Möller (Universität Mainz)
- Max Planck Gesellschaft for financial support

Contact

Dr.Susana Moreno Flores
E-mail : **moreno@mpip-mainz.mpg.de**
Tel.: 00 49 (0) 6131 379 469
Fax: 00 49 (0) 6131 379 100