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Molecular Kinetics and Dynamic Wetting of Self-Assembled Monolayers with Arylazopyrazole Photoswitches on Oxide Surfaces

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In this presentation we report on self-assembled monolayers (SAMs) with photo-switchable arylazopyrazole (AAP) silanes [1] on SiO₂ surfaces as well as AAP phosphonic acids [2] on α -Al₂O₃ which exhibit fluorinated and aliphatic terminal groups, respectively. By switching the AAP moieties in the SAM from their E to their Z state, the molecules are driven from a linear to a bend configuration which exposes the more hydrophilic azo group. This causes changes in surface wettability and a change in static contact angle of about 10°. We have now analysed the molecular kinetics of the photoswitchable SAMs in detail using both vibrational sum-frequency generation (SFG) and dynamic contact angle measurements. For that, we have systematically changed the surface coverage of the AAP photoswitches by changing either the deposition time of the fluorinated AAP or by adjusting the Langmuir-Blodgett transfer of the AAP phosphonic acids to the aluminium oxide substrates. Previously, we have shown that the drop and substrate dynamics are coupled and that using an analytical model one can determined the molecular kinetics of the AAP during dynamic wetting [2]. In fact, the kinetics of the wetted monolayer are surprisingly slow, which we have now addressed on a molecular level by using surfaces of different coverage. This has allowed us to discuss the role of packing density of the SAMs on the dynamic wetting of the monolayer.

[1] N. Arndt, F. Schlüter, M. Böckmann, T. Adolphs, H. F. Arlinghaus, N. L. Doltsinis, and B. J. Ravoo, Langmuir 38, 735-742 (2022)

[2] H. Honnigfort, L. Topp, N. García Rey, A. Heuer, B. Braunschweig, Dynamic Wetting of Photo-Responsive Arylazopyrazole Monolayers is Controlled by the Molecular Kinetics of the Monolayer, J. Am. Chem. Soc. 144, 4026-4038 (2022)

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Sitzung Einordnung: Short Talks