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Wetting of Photoswitchable Substrates and Polymer Brushes and Their Investigation with Vibrational Sum-Frequency Generation

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Smart surfaces that can change their wetting behavior on demand are interesting for applications such as self-cleaning surfaces or tunable lenses. We report on the use of vibrational sum-frequency generation (SFG) to study the molecular structure of photoswitchable surfaces as well as polymer brushes that do show structural adaptation. Results from SFG report on the molecular scale changes and are useful to explain wetting dynamics on macroscopic length scales. In case of polymer brushes, we have addressed the influence of the wetting liquid and the gas phase on the molecular structure of the terminal part of the polymer brush, while for butyl-AAP-C_{18}-PA monolayers we show that E to Z photo switching can trigger a contact angle change by ~10° and that the dynamic changes in contact angle are partially synchronized to the molecular structure changes. For that we have synthesized arylazopyrazole phosphonic acids (butyl-AAP-$_{18}$-PA) and deposited a monolayer of these molecules on aluminum oxides. The molecular changes were studied by time-resolved vibrational SFG spectroscopy, which provided information on the structural transitions within the AAP monolayer as well as their kinetics. Analysis of SFG spectra has allowed us to determine the characteristic switching times of the monolayer upon irradiation with UV and green light. Further, we demonstrate that interaction of water can stabilizes the Z configuration to a large extend. We propose that the exposed polar azo groups of the Z isomer in the AAP monolayer interact strongly with water at the solid-liquid but also at the solid-gas interface, which can stabilize the Z state and hinder the AAP monolayer to switch back into the E state when it is fully immersed in H_2O. Having established the characteristic times for switching on the molecular scale, we have modelled the dynamic contact angle and demonstrate, for the system in our study, that the wetting dynamics are mostly synchronized to the changes on the molecular level.

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