Observations of Photo-Switching in Tethered Spiropyrans Using the Interfacial Force Microscope

S. T. Picraux, R. Rosario, A. A. Garcia, M. Hayes, and D. Gust,
and B. C. Bunker, B. I. Kim, and J. E. Houston, Sandia National Laboratories

Reversible switching of interfacial properties is being investigated for applications in microfluidic systems including analytical chemistry, chemical processing, biothreat detection, and biomedical devices. For biological applications, the use of light offers unique opportunities, as light fluxes are easy to control temporally and are less likely to perturb delicate biological structures than most other stimuli. Recently, we have demonstrated that tethered films of spiropyran molecules (Fig. 1) respond to optical stimulation resulting in significant changes in water contact angle. Here, we report on the use of a scanning probe system to investigate interactions between the spiropyran and model surfaces to further elucidate the changes in surface chemistry induced by light.

The primary interest in tethered spiropyrans is for photo-switching of surface chemistry. Our previous studies for spiropyran monolayers indicate that water contact angles can be switched between approximately 60^o and 75^o corresponding to the open and closed ring states, respectively. We tether the photochromic spiropyran to a glass surface to investigate the extent to which such switching can be used to modify surface chemistry. The tethering is accomplished by reacting the carboxylic acid end group of this functionalized spiropyran with a self-assembled monolayer containing (3-aminopropyl)triethoxysilane (ATES) to form a covalent amide linkage that is diluted with a base monolayer consisting of tert-butyldiphenylchlorosilane (TBDS).

To obtain more detailed information regarding the switching of interface states, we quantitatively measure the interaction force between tethered spiropyran and functionalized silica using the interfacial force microscope (IFM). The IFM instrument was developed at Sandia and this capability has recently been set up in CSSER. The self-balancing force-feedback sensor of the IFM enables the quantitative mapping of the entire force-distance profile as a tip approaches a substrate surface without the mechanical instabilities that limit other interaction force measurements. Thus IFM measurements enable the direct nanoscale characterization of the changes in surface chemistry that accompany the photo-activated opening and closing of rings in tethered spiropyran monolayers (see Fig. 2). Normal force measurements conducted in electrolyte solutions show that double-layer forces can be doubled by exposing spiropyran monolayers to ultraviolet light and reversibly reset with exposure to visible light. Contact potential measurements show that the switching is associated with dipole moment changes that accompany ring opening and closing events. These results demonstrate the potential of the IFM to probe at the nanoscale the optical switching of molecular surface states.

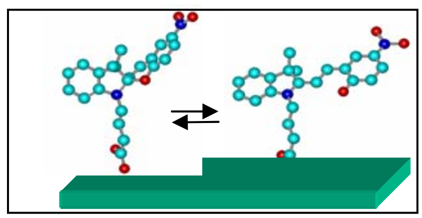

Fig. 1 Schematic of tethered spiropyran in the closed (left) and open (right) state.

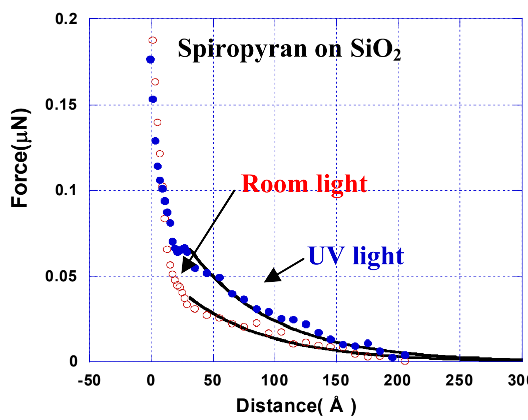

Fig. 2 IFM force profiles for spiropyran surface monolayers on silica after UV and visible light exposure (approach with a silica tip in the liquid formamide with 2mM KCl).