

## Switchable Monolayers for Microfluidic Systems

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**Motivation**—Interfacial water plays a key role in mediating the performance of microsystems ranging from fluidic devices to sensors to micromachines. The structure and properties of water can be changed dramatically near surfaces. Particularly as system dimensions enter the sub-micron regime (e.g., in small channels, pores, or spacings between micromachine components), the anomalous behavior of water can lead to system behavior that is dramatically different from that predicted on the basis of the properties of bulk water. We have been using a scanning probe instrument called the interfacial force microscope (IFM) to detect the presence of interfacial water and to probe interactions between materials that are mediated by the presence of water at length scales from microns to atomic dimensions. Recently, we have been using the IFM to probe changes in interactions that can be achieved using programmable self-assembled monolayers (SAMS).

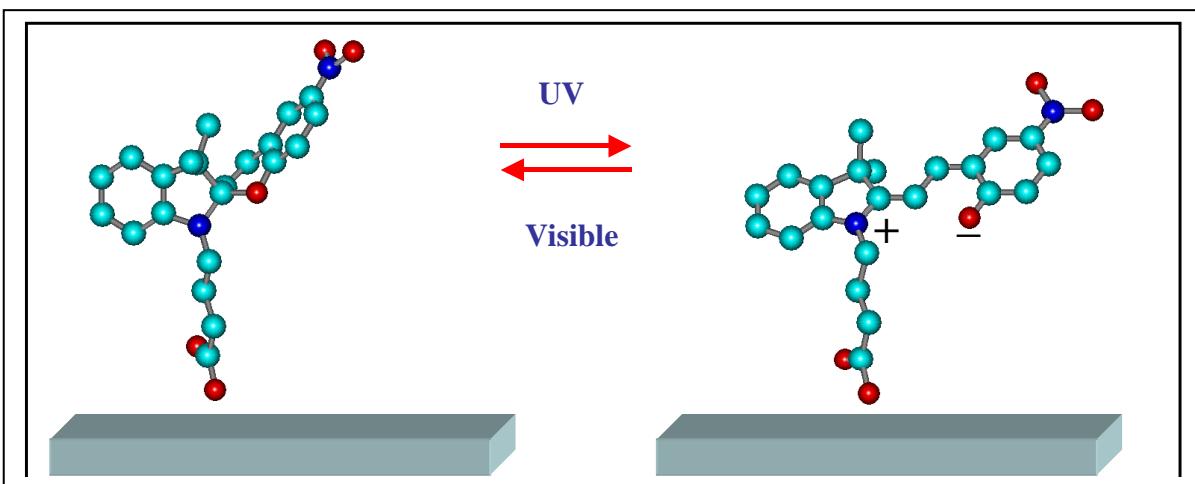
**Accomplishment**—Interactions between water and substrates are normally controlled by the number and spacing of specific functional groups that terminate the surface. We have been investigating methods of switching the behavior of surface functional groups using signals that can be generated “on-chip”, including heat, light, and electric fields. All systems investigated to date involve the incorporation of active molecules into self-assembled monolayers. Configuration changes within the active molecules promote changes in the adjacent solution, allowing us to manipulate interactions including repulsive and attractive hydration forces, double layer forces, hydrophobic/hydrophilic character, and capillary forces. The switching of interfacial interactions has been monitored using the interfacial force microscope, which enables us to obtain force-distance profiles between a

functionalized substrate and a scanning probe tip as a function of separation distances typically ranging from 100 nm down to less than 1 nm. An example of a switchable surface is provided by the changes in surface chemistry that accompany the photoactivated opening and closing of rings in tethered spirocyclic monolayers (Fig. 1). Contact potential measurement performed in the IFM show that exposure of native spirocyclic to UV light opens an aromatic ring to produce an open isomer containing charged groups. This light-induced ring opening can be reversed with visible light, regenerating an aromatic, hydrophobic surface. Normal force measurements performed in the IFM (Fig. 2) show that the creation of charged sites via ring opening generates significant electrical double layer forces when the monolayer is immersed in water. These double layer forces can be switched on and off by exposing the surface to UV and visible light, respectively.

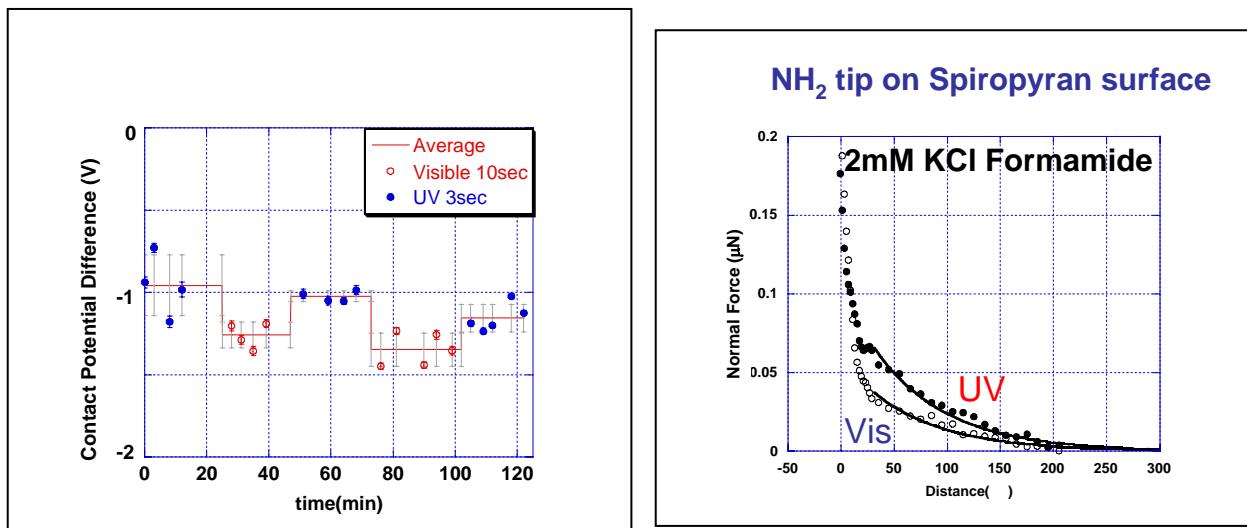
**Significance**—The IFM results demonstrate that it is possible to program interactions between surfaces immersed in water using heat, light, or electric fields. Such surfaces can be used to perform a wide range of functions in microfluidic devices, including pumping and control of fluid flows, reversible switching of adsorption and desorption of solution species, and controlling surface chemistries for switchable separations and sensor devices. For example, we have demonstrated that a thermally-switchable polymer film (PNIPAM) can be used as a reversible trap for proteins. Development of such devices requires a fundamental understanding of how materials interact with each other in water at sub-micron length scales. The interfacial force microscope provides a unique tool for measuring such interactions and probing interaction mechanisms.

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**Figure 1.** Representations of the spirobifluorene molecule in its native state (left) and after exposure to UV light (right).



**Figure 2.** Interfacial force microscope results on switchable spirobifluorene films. Left – Changes in contact potential induced by sequential exposures to UV and visible light showing reversible creation and elimination of charged surface states due to ring opening and closing, respectively. Right – Force-distance profiles showing the UV-activated enhancement of electrical double repulsion that accompanies the formation of charged sites due to ring opening in tethered spirobifluorene monolayers.