

Quantitative Evaluation of Perfluorinated Alkylthiol Molecular Order on Gold Surfaces

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Self-assembled monolayers (SAMs) of perfluoroalkylthiols [$\text{CF}_3(\text{CF}_2)_x\text{CH}_2\text{CH}_2\text{SH}$ ($x=3, 5, 7, \text{ and } 9$)] on gold were examined by X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS), and static time of flight secondary ion mass spectrometry (ToF-SIMS) methods. The perfluoroalkylthiols were synthesized by a new approach based on hydride reduction for transforming commercially available perfluoroalkyl iodides to corresponding perfluoroalkylthiols. This drastically improved the yields of these products over former routes based on hydrolysis from the common thiolacetyl perfluoroalkyl intermediate. Angle-dependent XPS analysis revealed that $\text{CF}_3(\text{CF}_2)_x\text{CH}_2\text{CH}_2\text{SH}$ ($x= 5, 7, \text{ and } 9$; F6, F8 and F10 respectively) SAMs on gold exhibited significant enrichment of the terminal CF_3 groups at the outer monolayer surface with sulfur chemistry consistent with bound thiolates located at the monolayer-gold interface. XPS of the $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{SH}$ (F4) monolayer revealed a thin film with a significant (>50%) amount of hydrocarbon contamination consistent with poorly organized monolayers while the longest thiol (F10) showed XPS signals attributed to substantial ordering and anisotropy. ToF-SIMS spectra from all four SAMs contained molecular ions that were representative of the particular perfluorinated thiol used to prepare the monolayer. NEXAFS methods were used to determine degrees of ordering and average tilt for molecules comprising monolayers. The SAMs prepared from the longest (F10) thiols exhibited the highest degree of ordering with the molecular axis nearly perpendicular to the gold surface. The degree of ordering decreased significantly with decreasing length of the fluorocarbon tail.