376f Loosely Packed, Hydroxyl Terminated Sams on Gold

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While self-assembled monolayers (SAMs) are ubiquitous for the preparation of dense, two-dimensional sheets of surface functionality, loosely packed, fluid-like monolayers could offer advantages in interfacial recognition, biological adsorption, and the creation of dynamic surfaces. We report the development of loosely-packed, hydroxyl-terminated SAMs on gold by adsorption of bis (11,11'-dithioundecyl) perfluoroheptanoate and base-mediated cleavage of the fluorocarbon terminal group. As shown through infrared spectroscopy, contact angle goniometry, ellipsometry and electrical impedance spectroscopy (EIS), the partially fluorinated SAM yields a densely packed film in which the fluorocarbon groups govern the packing. Upon cleavage of the fluorocarbon group, the hydroxyl-terminated alkyl chains cant from the surface normal and are in a fluid like state. The resulting monolayer packing uniquely alters the wettability of the film by exposing methylene functionality in addition to the hydroxyl functionality yielding an intermediate surface energy (θa(H20) ~64˚). In comparison with densely packed hydroxyl-terminated monolayers of identical chain length, these films exhibit a reduced thickness (by 2 Å), 41% higher capacitance, and a 3-fold reduced charge transfer resistance. Analogous studies on bis (6,6'-dithiohexyl) perfluoroheptanoate and bis (11,11'-dithioundecanoic) perflouroheptanoic anhydride were performed to evaluate the impact of alkyl chain length and terminal group functionality.