

Formation and characterization of self-assembled monolayers of 2'-fluoro-4,4'-di(phenylethynyl)-1-benzenethiolate on gold

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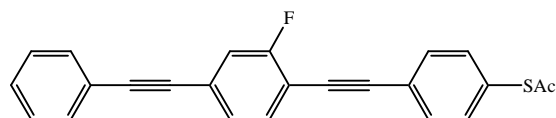
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Attachment of organic molecules to gold electrodes is of increasing importance for applications in molecular electronics. Self-assembled monolayers (SAMs) of phenylene ethylene oligomers have become the target of considerable research as they exhibit interesting electrical properties on gold electrodes. Conjugated phenylene ethylene molecules containing mono nitro-substitution and both nitro- and amino-substituents on the central phenyl ring have been previously shown to exhibit negative differential resistance (increased resistance with increasing driving voltage) and bistable conductance states (memory), while self-assembled monolayers formed from unfunctionalized molecules act as molecular rectifiers.¹⁻³ We have begun to explore the chemistry of fluorine substituents to test the universality of the electrical behavior of the substituted oligomers. The structure and chemical reactivity of gold-alkanethiol based SAMs is well understood, in part due to the robust nature of the self-assembly process. Self-assembly of the fully conjugated phenylene ethylene molecules is complicated by side-reactions and varies considerably with experimental conditions. However, fundamental knowledge of the SAM chemical and physical properties is essential to understanding the electrical properties of conjugated SAMs and charge transport mechanisms therein. Moreover, in order to make the metal/molecule/metal device structures, typically used in molecular electronics, a high-quality, well-understood monolayer is imperative.

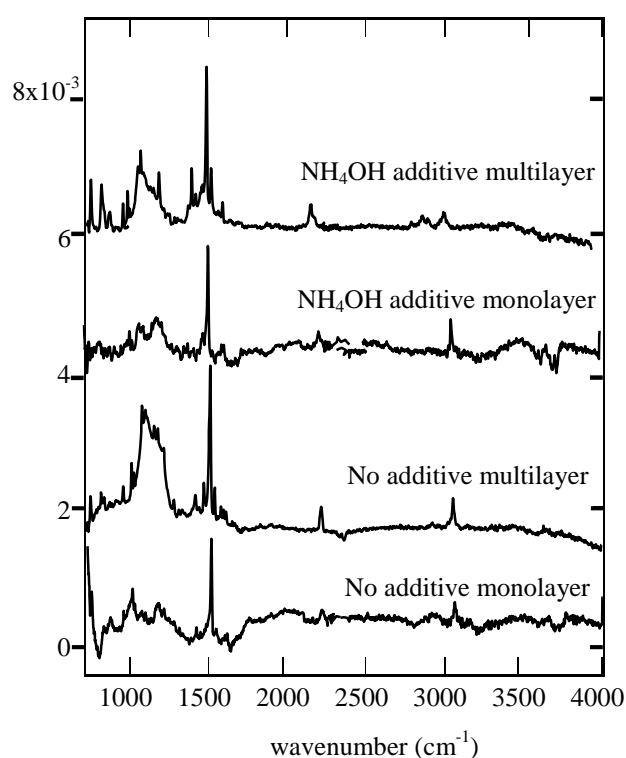
Monolayers of 2'-fluoro-4,4'-di(phenylethynyl)-1-benzenethiolate were self-assembled on evaporated gold films. The chemical properties of the monolayer were studied by using variable angle spectroscopic ellipsometry, reflection infrared spectroscopy, and contact angle measurements. The film morphology was characterized with scanning probe microscopy. A comparison of different chemical routes of cleaving the acetate protection group was explored in order to minimize sulfur oxidation and other side reactions while preparing a dense monolayer. The properties of the organic monolayers were highly dependent on the environment in which these films were prepared and stored. The duration of gold immersion in the molecular solution was examined to understand the mechanisms of film formation and reduce contributions from side-reactions. The optimal conditions necessary to form high-quality SAMs and the physical and chemical properties of the gold-organic monolayer of the fluorine substituted phenylene ethylene oligomer will be presented.

References:

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2'-fluoro-4,4'-di(phenylethynyl)-1-benzenethiolate (F-wire)



Reflection Absorption Infrared Spectroscopy of F-wire SAM on an evaporated gold film. SAM formation was facilitated by base-catalyzed (NH₄OH) deprotection of the acetate protecting group and no deprotection additive.