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Preparation and Characterization of a Self-assembled Monolayer of 3-(3-thienyl)benzonitrile on Gold

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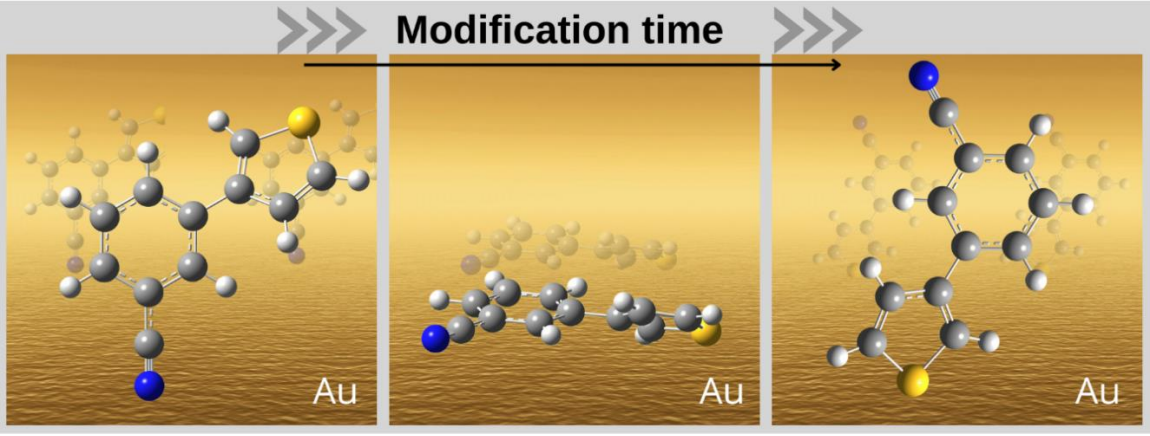
Self-assembled monolayers (SAMs) are molecular aggregates that are formed through the spontaneous adsorption of molecules on a solid substrate. Essentially, one part of the molecule has a strong affinity to the substrate whereas the other part has minimal or no affinity. The chemisorption of sulfur compounds on gold has been frequently studied due to the high chemical stability of gold and the covalent Au-S interaction thus leading to the formation of high-ordered SAMs with particular chemical and/or electrochemical properties. In this study, we have prepared and assessed the SAM of 3-(3-thienyl)benzonitrile (3-TBN) on gold surfaces. Firstly, the non-adsorbed 3-TBN compound was evaluated using nuclear magnetic resonance (NMR), infrared, Raman, and UV-Vis spectroscopies. Furthermore, quantum computational calculations based on density functional theory (DFT) were performed to aid in the assignment of the electronic and vibrational transitions. Real-time monitoring of the 3-TBN SAM formation on gold was performed by surface plasmon resonance (SPR) technique that is sensitive to refractive index variations at or near the interface. Accordingly, the SPR angle change ($\Delta\theta$) due to the adsorption of 3-TNB was converted into mass allowing the calculation of surface coverage (Γ). Reductive desorption charge (QRD) and potential (ERD), obtained from linear voltammogram, was also used to calculate Γ and indirectly assess the strength of the Au-S interaction, respectively. The results of surface enhanced Raman spectroscopy (SERS) acquired at different modification times suggest that the adsorbed molecules undergo a gradual self-reorganization on the surface until they reach a particular orientation, as depicted in the figure bellow.



Illustrative representation of the formation of the SAM of 3-TBN on a gold surface

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