

Redox Actuation of Microcantilevers Functionalized with Ferrocenyldodecanethiolate Self-Assembled Monolayer: Effect of the Surface Composition and Molecular Clustering.

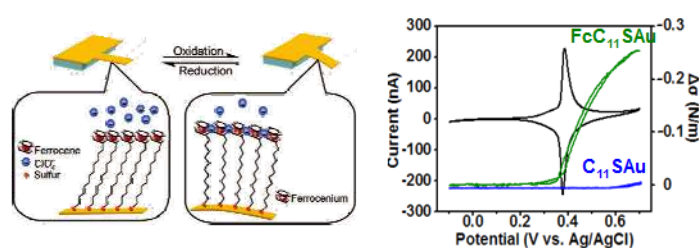
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The detection and quantification of trace levels of (bio-)molecules in a complex matrix constitute an important challenge in (bio-)analytical chemistry. Advances in microfabrication and surface functionalisation chemistry are providing the sensitivity to overcome this challenge. Microcantilevers are highly flexible devices capable of transducing very small physical changes induced by (bio-)chemical reactions into a mechanical motion. Briefly, microcantilever sensors work as follows: the microcantilever is modified with a reactive self-assembled monolayer (SAM). Binding of the analyte to the reactive groups in the monolayer induces intermolecular forces that result in a differential surface stress change and a vertical deflection or bending of the cantilever. The magnitude of the deflection, typically on the nanometer to micron scale, depends on the analyte concentration. Detection limits as low as ppt ( $10^{-12}$  level) have been reported.<sup>[4]</sup> These are potentially good candidates for the label-free in-situ detection of biomolecules and biomolecular interactions.<sup>[1-3]</sup>

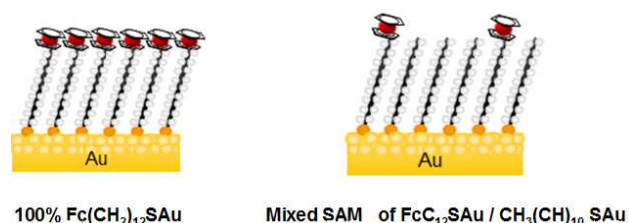
The major problem with microcantilever sensors is the variability of the reported surface stress results. The main reason for this irreproducibility is that the mechanisms responsible for the microcantilever deflection are poorly understood. To gain a better understanding, we have focused on investigating the origin of the surface stress changes that arise during the electrochemical oxidation of ferrocenyldodecanethiolate-modified microcantilevers (Figure 1).<sup>[5]</sup> In our earlier work, the cantilever bending was found to result from collective in-plane molecular interactions within the SAM and not from individual interfacial binding events.<sup>[2]</sup>



**Figure 1.** (Left) Scheme of the redox-induced deflection of a ferrocenyldodecanethiolate functionalized microcantilever. (Right) Example of cyclic voltammograms and deflection curves for Au-coated microcantilevers functionalized with an electroactive ferrocene-terminated SAM (FcC<sub>11</sub>SAu) and an inert alkanethiolate SAM (C<sub>11</sub>SAu). Adapted from ref. [5]

We have extended this previous study of ferrocenyldodecanethiolate-modified cantilevers to investigate the effects of ferrocene coverage and dispersion in mixed SAMs on the amplitude of the

microcantilever deflection signal. Sensors surfaces are functionalized with pure or mixed SAMs. Steric constraints exist between the end groups in pure SAMs that can affect molecular recognition. The introduction of an inert diluent minimizes steric crowding of the reactive groups. However, the nanoclustering of reactive groups can still occur in mixed binary SAMs. Nanometer-scale phase separation is a largely ignored phenomenon, even though it can affect the magnitude of the bending response.



**Figure 2:** Scheme of a pure ferrocenyldodecanethiolate SAM on gold (left) and a SAM of ferrocenyldodecanethiolates dispersed in an electrochemically inert alkanethiolate matrix.

This poster presents the results obtained for binary SAMs containing different surface concentrations and phase states (i.e., aggregated vs. isolated) of ferrocene (Figure 2). We correlate the molar fraction of the clustered ferrocenyldodecanethiolates to the measured microcantilever deflection. The consequences of our findings for employing SAM-functionalized cantilever microdevices for quantification purposes are discussed.

## References

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