

On the Apparent Fluorescence Recovery Due to  
Electrosorption.

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Characterization of the potential dependent adsorption/desorption of an insoluble surfactant adsorbed onto Au(111) using fluorescence microscopy is described. The adsorbed organic monolayer was composed of 3mol% of a carbocyanine dye added to octadecanol to allow imaging. Potential of the electrochemical interface controls the distance separating a previously adsorbed organic layer and the metal electrode by way of a unique adsorption/desorption process. Controlling the distance separating the fluorophore from the metal surface resulted in fluorescence around the desorption potential. The character of the desorbed layer was determined using image analysis techniques. During these experiments, extended time at the desorption potential resulted in quick decay in fluorescence intensity. Readsorption of the organic layer resulted in a close to total recovery in the measured fluorescence intensity when the monolayer was re-desorbed. This process was found to be due to two parallel reactions: irreversible photodecomposition and formation of non-fluorescent dye-aggregates. Readsorption onto the metal electrode results in destruction of the aggregate and a recovery in fluorescence intensity of nearly 85%. This process was modeled and rate constants for both processes determined. The dependence of the aggregation rate constant on the number of adsorption/desorption cycles revealed that the organic layer, when desorbed, is close enough to the electrode surface so that a significant amount of the desorbed surfactant remains quenched. We believe that the aggregated complex reverts to the monomer form due to electrosorption, illustrating the electrochemical control over radiative characteristics of the carbocyanine dye.