

# Study of Potential-Driven Phase Transition of Redox-Active Organic Molecules at Electrified Solid/Liquid Interface

Department of Science and Technology, Graduate School of Engineering,  
Nagasaki University

Tomohiro Higashi

A number of adlayers of organic molecules undergo potential-driven phase transitions at electrified solid/liquid interfaces. A deeper understanding of the phase transition mechanisms and molecular-level phase structures leads us to the development of devices that achieve drastic, sharp, and chemically reversible response to the potential change at electrified interface.

Viologens are among the most extensively studied redox-active organic molecules, which form their adlayers on the surfaces of several electrodes. The adlayer of heptyl viologen (HV), a typical dialkyl viologen possessing long alkyl chains, exhibits a spike-like voltammetric peak pair at less negative potential than the redox potential of solution phase HV. It has been concluded that the spike

response originates from the first-order faradaic phase transition between a gas-like adlayer of dication form of viologen ( $HV^{2+}$ ) and a two-dimensional (2D) condensed monolayer of radical cation form of viologen ( $HV^{•+}$ ) as shown in Figure 1. The key of the occurrence of the first-order phase transition is a synergy of strong intermolecular interactions, namely  $\pi$ - $\pi$  stacking between  $HV^{•+}$  neighbors as well as chain-chain interactions.

The phase transitions of viologen adlayers are governed by the type and strength of attractive intermolecular interactions in the condensed phase. The substitution of aromatic groups for alkyl chains should enable us to examine the effect of  $\pi$ - $\pi$  interaction between viologens and with HOPG surface upon the transition.

This thesis is devoted to comprehensive discussions on molecular-level adlayer structures and the effects of  $\pi$ - $\pi$  interaction and anions upon the 2D phase transition of viologens. For this purpose, I have used the viologens possessing aromatic rings, dibenzyl viologen (dBV) and diphenyl viologen (dPhV). Phase transition mechanisms and phase structures of the adlayers

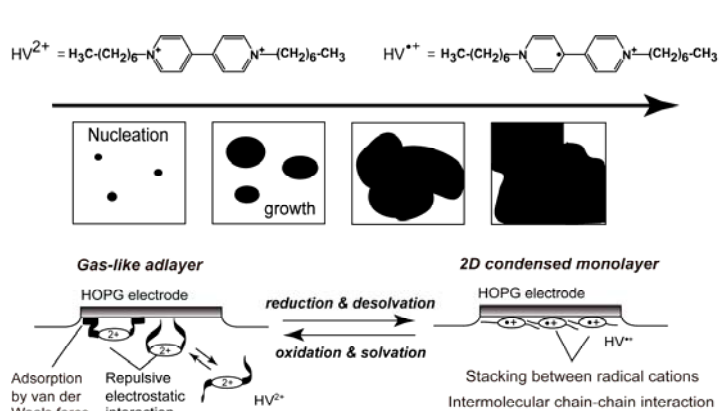


Figure 1. Schematic depiction of the first-order faradaic phase transition of heptyl viologen (HV) on an HOPG electrode surface.

have been investigated on HOPG and Au(111) electrodes using the results of voltammetric, electroreflectance (ER) spectroscopic and electrochemical scanning tunneling microscopic (EC-STM) measurements. The effects of the coexistent anions upon the 2D phase transitions have been highlighted through in-depth analyses of mesophase formation at the HOPG electrode surface and coadsorption of the coexistent anions at the Au(111) electrode surface.

This thesis consists of eight Chapters.

Introduction to this doctoral dissertation research is given in Chapter 1.

Chapter 2 is a review on the potential-driven phase transition of adlayers at solid/liquid interfaces. The review includes the underpotential deposition of metal ions, non-faradaic phase transition of organic molecules, and faradaic phase transition of viologens at several metal electrode surfaces.

Chapter 3 contains experimental methods including synthesis of viologens, electrochemical measurements, and electroreflectance (ER) spectroscopic measurements. The concise outline of the theory necessary for understanding the experiments and for the discussions of the results is added.

In Chapter 4, I focused on the phase transition at an HOPG electrode in dBV + KCl aqueous solution. dBV exhibited a single-step faradaic phase transition to form a 2D condensed monolayer of  $\text{dBV}^{++}$  as revealed by ER and EC-STM measurements. I found that the face-to-face  $\pi$ - $\pi$  stacking interactions with  $\text{dBV}^{++}$  neighbors, both between bipyridinium moieties and between benzene rings, cause the formation of a 2D condensed monolayer.

In Chapter 5, I described the anion dependent phase transition process at an HOPG electrode in dBV aqueous solution. In KBr solutions of  $[\text{Br}^-] > 180 \text{ mM}$ , the phase transition emerged as two-step processes. The first-step (at less negative potential) was ascribed to a formation of a mesophase of  $\text{dBV}^{++} \text{Br}^-$ . The second-step transition was ascribed to a phase transition between  $\text{dBV}^{++} \text{Br}^-$  mesophase and a 2D condensed phase of  $\text{dBV}^{++}$ .

Chapter 6 shows that  $\text{dPhV}^{2+}$  took a strongly adsorbed state on an HOPG surface, unlike  $\text{dBV}^{2+}$ . The phase change of dPhV was not of the first-order. Strong  $\pi$ - $\pi$  interaction of  $\text{dPhV}^{2+}$  with HOPG surface hampered its sharp phase transition.

In Chapter 7, I described the phase transition mechanism at a Au(111) electrode in dPhV aqueous solution. dPhV exhibited two-step transition; one was a non-faradaic order-disorder phase transition from an ordered coadsorption layer of  $\text{dPhV}^{2+}$  and  $\text{Cl}^-$  to a gas-like adlayer of  $\text{dPhV}^{2+}$ , and the other was a faradaic phase transition from gas-like adlayer of  $\text{dPhV}^{2+}$  to a 2D condensed monolayer of  $\text{dPhV}^{++}$ .

In Chapter 8, I described a summary of the significance of the results and the achievement of this project from the perspective of the dynamic molecular self-assembly. The future scope was also summarized.