

## The impact of intramolecular $\pi$ -coupling and steric flexibility on the ordering of organic films at solid/liquid-interfaces

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### ABSTRACT

In the present work the effect of the intramolecular steric flexibility on the structural self-assembly of organic cations and their redox activity at a chloride precovered Cu(100) electrode is investigated. In particular the adsorption of 1,1'-dibenzyl-4,4'-(propane-1,3-diyl)dipyridinium (C3-DBDP) is studied by means of cyclic voltametry (CV), in situ scanning tunneling microscopy (EC-STM) and ex situ X-ray photoelectron spectroscopy (XPS) and the experimental results are compared to previously published findings on related bipyridinium ("viologen") molecules. The CV measurements reveal a loss of the redox activity of the more flexible C3-DBDP<sup>2+</sup> compared to dibenzylviologen (DBV<sup>2+</sup>), as the first electron reduction step of C3-DBDP<sup>2+</sup> does not appear within the potential window of the Cu(100), but is shifted below the hydrogen evolution regime. This reduced redox activity is the result of the lifting of the extended  $\pi$ -system of the bipyridinium core by introducing the propyl chain between the two pyridinium rings. In agreement with this result, XP spectra prove that the C3-DBDP<sup>2+</sup> cations retain their initial dicationic charge within the entire potential window in solution but also upon adsorption on the Cl-c(2x2)/Cu(100) substrate, where they are found to form an inter-linked stripe phase. The building blocks of each stripe are attributed to one pyridinium-benzyl moiety, which represents half of one C3-DBDP<sup>2+</sup> molecule. The resulting consecutive arrangement of half C3-DBDP<sup>2+</sup> molecules along one stripe is stabilized by electrostatic attraction between the positively charged pyridinium rings and the negatively charged  $\pi$ -system of the benzyl rings.

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### 1. Introduction

A promising route towards molecular sized functional units relies on the deposition and self-assembly of molecular building blocks on single crystal surfaces, i.e. the so-called "bottom-up" approach, in the case of thermally unstable organic molecules preferably at ambient conditions from solution. In order to exploit and fully control the self-assembly of building blocks at solid/liquid interfaces a fundamental understanding of the driving forces of the underlying processes is mandatory.

The structure formation process of molecules at solid/liquid interfaces is a complex interplay between adsorbate-substrate and intermolecular adsorbate-adsorbate interactions, as well as possible solvent effects. The role of the solvent in the structure formation process is not within the focus of the present study but cannot generally be ruled out [1]. The substrate imposes – mostly periodic – boundary conditions for the molecular adsorption, which influence the adsorption and ordering of ions and molecules at surfaces. Electrochemical systems

allow the variation of the charge state of the solid/liquid interface (by varying the working potential), which, in addition, may strengthen or weaken the adsorbate-substrate interaction [2–4]. Moreover the structure formation of the molecular adlayers is governed by interactions between the building blocks themselves. Changes of the electrochemical conditions may lead to the oxidation or reduction of the molecular building blocks in the interfacial regime, which directly affects their electronic state and thereby, of course, all their interactions.

Under electrochemical conditions the total intermolecular interactions of organic molecules are thus a superposition of hydrogen bridge bonds and van der Waals like interactions between molecular groups as well as electrostatic interactions depending on the molecular redox state.

#### 1.1. Viologens as molecular building block

The properties of viologens (1,1'-disubstituted-4,4'-bipyridinium), such as their redox activity [5,6] or nature of their intermolecular interactions, are easy to modify by exchanging their substituents. This makes them potent model systems to study the impact of the molecular

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structure and redox state on the structural self-assembly of molecules at solid/liquid interfaces. A variety of viologen derivatives, among others dibenzyl- (DBV) and diheptyl- (DHV) viologen, have been studied at chloride precovered Cu(100) surfaces [1,7,8], which revealed the impact of the intermolecular attraction between the viologen substituents in the structure formation of viologen monolayers. These substituents stabilize the viologen monolayers by first increasing the intermolecular attraction and second sterically minimizing the intermolecular electrostatic repulsion between the cationic bipyridinium cores. The intermolecular repulsive contribution of the cationic bipyridinium core is counteracted in the structure formation process by the electrostatic attraction of the cationic core to the underlying anionic chloride substrate. This electrostatic “anchoring” of the bipyridinium unit even persists when the viologen dication  $V^{2+}$  is reduced to its monocation radical state  $V^{+•}$  and is assumed to be the origin of the highly substrate related structure of both, dicationic and monocationic radical viologen adlayers [1,7,8].

### 1.2. C3-DBDP as molecular building block

One may ask the question: “Does the electrostatic anchoring of the bipyridinium unit persists when the bipyridinium core is split up into two monocationic cores by e.g. introducing a flexible saturated chain of  $sp^3$ -hybridized carbon atoms”? This question can be addressed in a more general way by investigating the impact of the intramolecular steric flexibility in the structure formation process at solid/liquid interfaces. Therefore the steric flexibility of the well studied Dibenzylviologen (DBV) [3,7,9] was increased here by introducing a propane-1,3-diyl chain between the 4,4'-connection of the bipyridinium core and splitting it up into two single pyridinium rings, as shown in Fig. 1. The resulting molecule 1,1'-dibenzyl-4,4'-(propane-1,3-diyl)dipyridinium is no longer part of the viologen family and is abbreviated as C3-DBDP (Fig. 1).

Both molecules, DBV and C3-DBDP, consist of two pyridinium-benzyl moieties arranged symmetrically to the center of the molecule. The positive charge of both,  $DBV^{2+}$  and  $C3-DBDP^{2+}$ , is situated within the molecular pyridinium rings and is delocalized over each aromatic pyridinium  $\pi$ -system.

Reducing  $DBV^{2+}$  to its monocationic radical state ( $DBV^{+•}$ ) results in the delocalization of the remaining positive charge and radical state over both directly neighboring pyridinium  $\pi$ -systems. This is proven by XPS spectra [1], which reveal that both pyridinium rings are in the same redox state. Therefore the redox state of  $DBV^{+•}$  cannot be understood as the neighboring of one cationic and one reduced neutral pyridinium ring as this would lead to two distinguishable N1s signals of similar intensity.

The delocalization of the cationic charge and the radical state of  $DBV^{+•}$  over the whole bipyridinium core is only possible when the

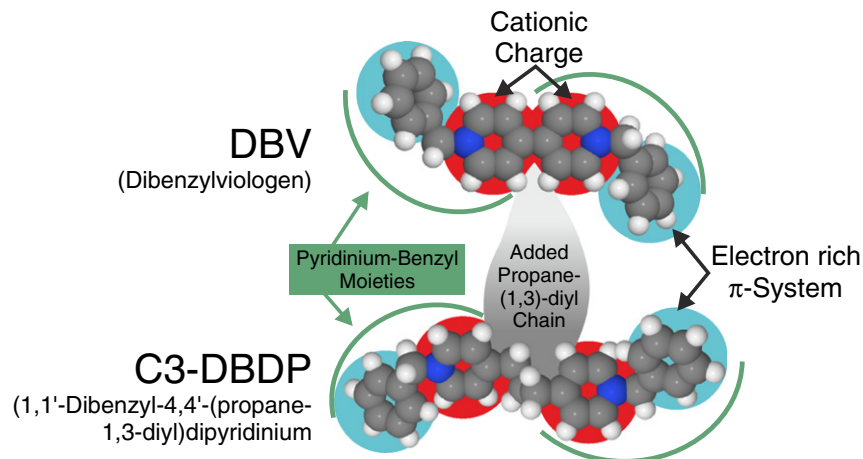
two single pyridinium  $\pi$ -systems are coupled. This  $\pi$ -system coupling is impossible to occur in C3-DBDP, as the introduced propane-1,3-diyl chain between the pyridinium rings consists fully of  $sp^3$ -hybridized carbon atoms. The propane-1,3-diyl chain therefore leads to the fragmentation of the DBV bipyridinium  $\pi$ -system into two isolated pyridinium  $\pi$ -systems, which modifies the molecular orbital structure of C3-DBDP and prevents the stabilization of possible cationic radical and neutral redox states. This leads to a reduced redox activity of  $C3-DBDP^{2+}$  compared to  $DBV^{2+}$ , as will be proven later.

The added propane-1,3-diyl chain increases, on the other hand, the steric flexibility of C3-DBDP compared to DBV, due to intramolecular rotations around all C–C single bonds between the saturated (tetrahedral) C-atoms. These extra degrees of rotational freedom permit C3-DBDP to arrange within a greater conformational space on the Cl/Cu(100) surface, i.e. to maximize the intermolecular adsorbate–adsorbate and adsorbate–substrate attractions as well as to minimize the electrostatic repulsion between the cationic pyridinium rings in the adlayer formation process.

In order to investigate the electrochemistry, and in particular the redox activity, of the  $C3-DBDP^{2+}$  at the Cl/Cu(100) electrode cyclic voltammetry (CV) is employed. Further, the chemical and redox state of the interface layer was studied by ex situ XPS. As third method in situ ElectroChemical Scanning Tunneling Microscopy (EC-STM) is utilized in order to image and study the actual structure formation of C3-DBDP on the Cl/Cu(100) electrode surface.

## 2. Experimental section

All scanning tunneling microscopy (STM) results presented in this work were obtained with a home-built Bonn-type electrochemical scanning tunneling microscope (EC-STM) presented in details elsewhere [10,11], and analyzed with WSxM software by Nanotec [12]. The X-ray photoelectron spectroscopy (XPS) experiments were performed either in a home-built in-house XPS chamber [13] or at the SoLiAs station [14] at the synchrotron radiation facility BESSY II. Both experimental setups allow a contamination-free transfer of the sample from the electrochemical preparation cell (under Ar atmosphere) to the XPS analysis chamber; either the U-49/2-PGM-2 beamline at BESSY (Helmholtz-Centre, Berlin) which provides a photons from 86 eV to 1890 eV with an energy resolution of 10000 (minimum flux  $3 \times 10^{12}$  photons/s) or a non-monochromatized Mg/Al-twin-anode (XPS system in Bonn) were used as X-ray sources. The photoelectrons were collected by a SPECS Phoibos 150 MCD-9 analyzer (SoLiAs) or a SPECS EA 10 analyzer (XPS-system, Bonn). In both cases the binding energies are referred to the Fermi level.



**Fig. 1.** Model of the investigated molecules DBV and C3-DBDP. The inserted propyl chain (C3) between the central pyridinium rings increases the intramolecular flexibility and leads to the fragmentation of the inner bipyridinium  $\pi$ -system of DBV into two isolated pyridinium  $\pi$ -systems of C3-DBDP.

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