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Potential-controlled molecular machinery of bipyridinium monolayer-functionalized surfaces: an electrochemical and contact angle analysis†

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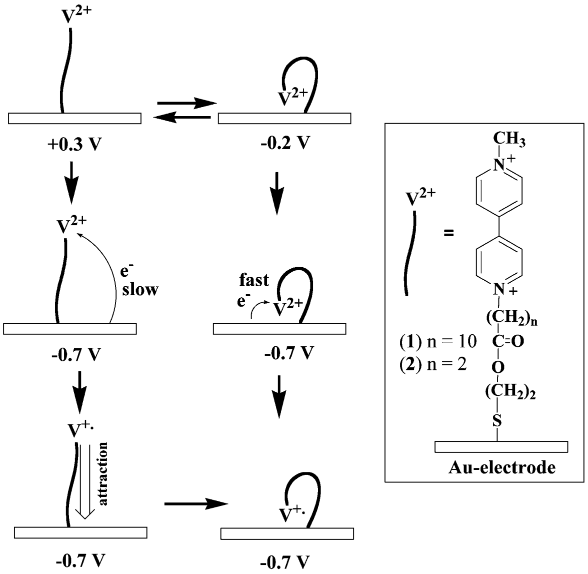
A non-dense long-chain tethered bipyridinium monolayer linked to an electrode support is reversibly retracted and attracted from and to the electrode respectively by the applied potential. The "molecular machinery" functions of the monolayer are probed by chronoamperometry and contact angle measurements.

Molecular machinery functionalities attract substantial recent research efforts directed to the development of nanometer size information storage and processing systems.[1–4] Different molecular machinery functions such as rotors, "brakes" "ratchets" or "tweezers"[5–7] were synthetically fabricated. Various external input signals such as photonic,[8,9] electrical[10–12] or pH[13] were used to trigger molecular mechanical transformations in solutions or on surfaces. While the mechanical translocation of molecular components in solution can be probed by different spectroscopic methods, the identification of mechanical changes on surfaces is of higher complexity. Chronoamperometry, probing the electron transfer rates to redox labels, was used to follow signal-triggered structural changes on surfaces.[14] Very recently, contact angle measurements and sum-frequency generation (SFG) spectroscopy were used to follow potential-induced structural changes in a monolayer-assembly associated with an electrode.[15] Here we report on the potential-controlled bending of a bipyridinium-functionalized monolayer associated with an electrode. We characterize the mechanical functions of a "molecular arm" by electrochemical and contact angle measurements.

The bipyridinium monolayer was assembled by the covalent linkage of *N*-methyl-*N*′-carboxydecyl-4,4′-bipyridinium[16] (**1**) to a mercaptoethanol monolayer associated with a Au-electrode, Scheme 1.† Coulometric assay of the reduction (or oxidation) of the bipyridinium units cyclic voltammogram ($E° = -0.55$ V *vs.* SCE) indicates that their surface coverage corresponds to 4.2×10^{-11} mol cm^{-2}. The surface-projected area of a perpendicularly oriented bipyridinium group was estimated[17] to be 45 ± 2 Å^2, suggesting that the observed coverage is *ca.* 11% of a densely packed monolayer. This low coverage was purposely designed to allow flexibility of the monolayer components and the potential-induced bending or stretching of the monolayer constituents. The preparation of this surface coverage is controlled by the time interval of the coupling reaction and it can be followed by cyclic voltammetry experiments.

Fig. 1, curve (a), shows the contact angle changes† as a result of the potential-induced bending/stretching of the monolayer and upon electron transfer in the monolayer assembly (the error in the experimental contact angles is estimated to be ±0.5°). At step (1) the applied potential is 0.3 V (*vs.* SCE), and the electrode is positively charged (potential of zero-charge of the electrode E_{pzc} is *ca.* 0.15 V). The positively charged head groups of the monolayer are electrostatically repelled from the electrode surface and the spacers are stretched with the hydrophilic bipyridinium units facing the exterior of the monolayer. This yields a hydrophilic interface with a contact angle of 69.5°. Biasing the potential of the electrode to −0.2 V does not yield any electron transfer, yet a significant change in the contact angle to 73.5° is observed, Fig. 1, curve (a), step (2). This is consistent with the fact that the positively charged bipyridinium groups are attracted to the negatively charged electrode surface. This mechanical attraction of the bipyridinium units leads to the bending of the long chain and its exposure to the solution, resulting in the formation of a less hydrophilic interface revealing a higher contact angle value, Scheme 1. Control experiments reveal that the application of the



Scheme 1 Potential-induced molecular motion and redox-transformation of a bipyridinium monolayer associated with an electrode surface.

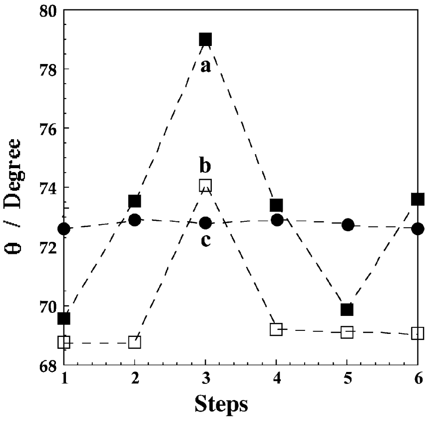


Fig. 1 Change in the contact angles of an aqueous droplet containing 0.1 M phosphate buffer solution, pH 7.0, on an electrode surface modified with: (a) the (**1**)-monolayer, (b) the (**2**)-monolayer, and (c) the mercaptoethanol monolayer upon application of biasing potentials: (1) 0.3 V, (2) −0.2 V, (3) −0.7 V, (4) −0.2 V, (5) 0.3 V, (6) −0.2 V.

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† Electronic supplementary information (ESI) available: experimental details on the electrode modification, electrochemical and contact angle measurements. See http://www.rsc.org/suppdata/cc/b3/b303845a/

different potentials on the mercaptoethanol monolayer-functionalized electrode that lacks the bipyridinium units does not alter significantly the contact angle values, Fig. 1, curve (c), indicating that those potential changes have a minute effect on the respective contact angles. Biasing the potential on the electrode at −0.7 V results in the reduction of the bipyridinium units to the radical-cation state and the attraction of the radical-cation head groups to the negatively charged surface (*vide infra*). Formation of the radical-cation and bending of the chain increase the hydrophobicity of the interface, resulting in the increase of the contact angle to 79°. Reoxidation of the radical-cation to the dication, while bending the monolayer constituents ($E = -0.2$ V), yields the original contact angle, *ca.* 73°, and stretching of the positively charged head group ($E = 0.3$ V), yields an interface of enhanced hydrophilicity, *ca.* 69°, Fig. 1, curve (a), steps (4) and (5), respectively.

In a reference system, a short chain tethered bipyridinium monolayer was assembled on a Au electrode by the coupling of *N*-methyl-*N′*-carboxyethyl-4,4′-bipyridinium[8] (**2**) to the mercaptoethanol monolayer, Scheme 1. The surface coverage of the bipyridinium units is 4.6×10^{-11} mol cm^{-2} (12% of a densely packed monolayer). In this system, the potential-induced bending of the short chain-tethered bipyridinium monolayer should not expose a hydrophobic interface on the surface, and thus, no significant changes in the contact angles at the different bending/stretching potentials are expected. On the other hand, reduction of the bipyridinium units is still expected to enhance the hydrophobicity of the interface and to change the contact angle. Fig. 1, curve (b), shows that these predictions are, indeed experimentally observed. The contact angles at 0.3 V and at −0.2 V, where the monolayer is in the bipyridinium state are almost the same, *ca.* 69°, steps (1) and (2), respectively. Reduction of the monolayer to the bipyridinium radical-cation, $E = -0.7$ V, yields a less hydrophilic interface, contact angle 74°, and reoxidation of the monolayer to the bipyridinium constituents regenerates the hydrophilic interface, contact angle *ca.* 69°, steps (3) and (4), respectively. It should be noted that as the surface coverage of (**1**) increases its potential-induced bending is perturbed and at a surface coverage of *ca.* 60% of the densely packed monolayer the bending can not be detected.

Further support that the contact angle measurements follow the potential-induced mechanical motion of the “molecular arm” is obtained from chronoamperometric experiments. It was demonstrated[18] that the electron transfer rate constant to or from a redox label associated to the electrode in a monolayer configuration is controlled by the chain length (distance) bridging the redox label to the electrode ($i = k_{et}Q\exp(-k_{et}t)$; where i is a transient current density, k_{et} is the electron transfer rate constant and Q is the surface coverage of the redox label).[18] The interfacial electron transfer rate constants for the different monolayer configurations were determined by applying a reduction potential step and analyzing the resulting current transients.[18] Fig. 2, curves (a) and (b), shows the chronoamperometric transients observed upon the application of a reductive potential step on the (**2**)-functionalized electrode biased at 0.3 V and −0.2 V, respectively. In these experiments the biased electrodes are stepped to −0.7 V, resulting in the reduction of the bipyridinium units to the radical-cation. The current transients consist of a monoexponential rapid electron transfer rate corresponding to the reduction of the bipyridinium units.[19] The interfacial electron transfer rate constants to the bipyridinium units biased at 0.3 V and −0.2 V are identical and correspond to $k_{et} = 140$ s^{-1}, indicating that the position of the bipyridinium units is almost identical relative to the electrode support at these two applied potentials. These results are consistent with the contact angle measurements. Fig. 2, curve (c), shows the current transient observed upon the application of the potential step on the electrode modified with the long chain-tethered bipyridinium monolayer (**1**) biased at −0.2 V. In this system, the positively charged head groups are attracted by the electrode, the “molecular arms” are in the bent configuration, and the close proximity of the bipyridinium units to the electrode results in a rapid interfacial electron transfer, $k_{et} = 250$ s^{-1}. In Fig. 2, curve (d), the potential step is applied on the long chain-tethered bipyridinium monolayer (**1**) biased at 0.3 V. In this configuration, the “molecular arms” are in the stretched configuration, and the bipyridinium units are repelled from the electrode and separated by the long chains from the surface. This results in a slow interfacial electron transfer that corresponds to $k_{et} = 13$ s^{-1}. This result implies that the relocation of the bipyridinium units is much slower than the electron transfer process. That is, the potential-induced stretching or bending of the long chain-tethered bipyridinium constituents result in interfacial electron transfer rate constants that differ by a factor of *ca.* 20.

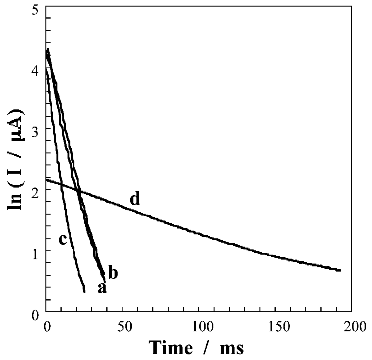

Fig. 2 Chronoamperometric transients measured upon application of the potential steps: (a) from −0.2 V to −0.7 V on the (**2**)-functionalized electrode, (b) from 0.3 V to −0.7 V on the (**2**)-functionalized electrode, (c) from −0.2 V to −0.7 V on the (**1**)-functionalized electrode, (d) 0.3 V to −0.7 V on the (**1**)-functionalized electrode. Background electrolyte: 0.1 M phosphate buffer, pH = 7.0, under Ar; a Au-electrode area, ca. 0.24 cm^2.

In conclusion, chronoamperometry and contact angle measurements enabled us to follow the potential-induced mechanical motion of a “molecular arm” associated with an electrode in a monolayer configuration.

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