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Electrochemical control of surface properties using a quinone-functionalized monolayer: effects of donor–acceptor complexes†

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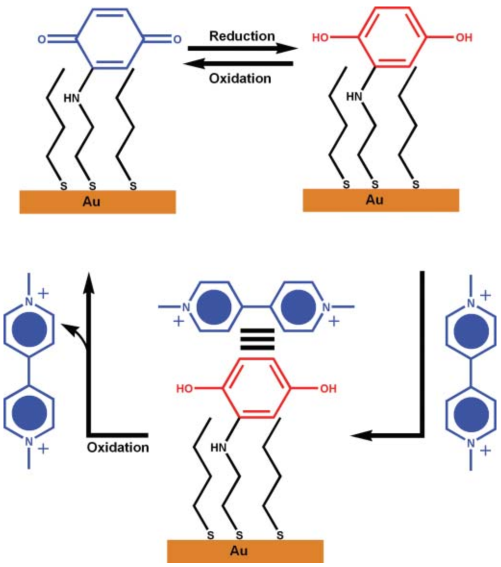
A benzoquinone monolayer-functionalized electrode reveals electrochemically or chemically controlled wettability; the hydrophobicity of the hydroquinone-modified surface is enhanced by the presence of a donor–acceptor complex with *N*,*N*′-dimethyl-4,4′-bipyridinium as the π-electron acceptor.

Surfaces whose hydrophobicity/hydrophilicity change[1] in response to stimuli have attracted substantial interest for the development of self-cleaning[2] surfaces and microfluidics.[3] Electrical control of wettability has been accomplished[4,5] previously using long-chain alkane monolayers with charged head groups at the liquid–monolayer interface. Control of hydrophobicity/hydrophilicity was also attained by electrochemical control using either redox-active head groups whose response[6] to applied potential changes the wettability of the surface or electrochemically induced shuttling[7] of mechanically interlocked molecular machines. Alternative electrochemical approaches to reversibly control surface behaviour involve the reduction[8] of Ag^+ or Hg^{2+} ions into metallic nanoclusters or the redox controlled changes in surface wettability in hemoglobin–Fe_3O_4 nanocomposites.[9] Photochemical switching of hydrophobicity/hydrophilicity has been demonstrated[10] with photoisomerisable monolayers or by using photo-induced charge transfer to form ionic films. Herein we report the control of surface hydrophobicity/hydrophilicity using an alkane monolayer with terminal 1,4-quinone head groups. We describe their preparation, characterisation using electrochemical methods, the switching of hydrophilic/hydrophobic properties in response to chemical and electrochemical stimuli and the effect of electrochemically controlled, surface-associated donor–acceptor complexes. We also describe the electroswitchable force interactions between a bipyridinium (π-electron acceptor)-modified AFM tip and the quinone-modified surface.

A self-assembled monolayer (SAM) with terminal 1,4-benzoquinone functionalities (Scheme 1) was prepared following[11] literature protocols and characterised by electrochemical methods. Modification of a cystamine-coated surface with quinones proceeds *via* a Michael addition to provide a redox-active, surface-bound species whose structures can be reversibly switched between the benzoquinone and the hydroquinone forms. The donor–acceptor complex with *N*,*N*′-dimethyl-4,4′-bipyridinium that is generated can be switched off following oxidation of the hydroquinone to the benzoquinone. Successful modification of the surface was demonstrated using cyclic voltammetry in aqueous phosphate buffer (10 mM PB, pH 7.0, 0.1 M $NaClO_4$, Au/graphite/SCE) in which a single peak corresponding to the 2-electron reduction of the benzoquinone was easily resolved (Fig. 1). A linear plot of current *vs.* scan rate (Fig. 1 inset) confirmed that the quinones were surface confined, and the density of the quinones on the surface was found to be 1.1×10^{-11} mol cm^{-2}. Previous studies of SAMs on gold formed *via* gold–thiol linkages have demonstrated that the additional adsorption of linear alkanethiols into the functionalized monolayer improves[12] the monolayer packing. So the surfaces were immersed in a 1 mM 1-butanethiol solution for 30 min, and we observed a decrease in the density of the surface-bound quinones (7.9×10^{-12} mol cm^{-2}). This finding is most likely the result of partial displacement of the quinones by the 1-butanethiols during formation of the mixed monolayer.[13]

One of the primary goals of this study is to exploit the electrochemical conversion of 1,4-benzoquinone to 1,4-hydroquinone to cause reversible changes in surface energy of the SAM. Initially, in the benzoquinone state, the surface should exhibit hydrophobic properties and thus reveal a large contact angle with water. Upon reduction to the hydroquinone, the contact angle should decrease because the presence of the OH groups increases



Scheme 1 Electrochemical or chemical switching of the hydrophilic/hydrophobic properties of a monolayer functionalized Au surface in the absence and the presence of the bipyridinium π-acceptor.

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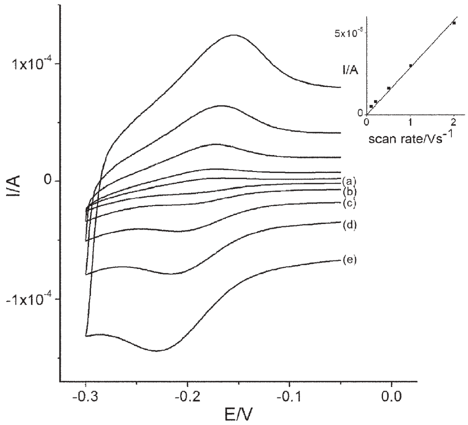

Fig. 1 Cyclic voltammograms[a] of the benzoquinone monolayer-functionalized electrode at different scan rates. Scan rates are (a) 100 mV s^{-1}, (b) 200 mV s^{-1}, (c) 500 mV s^{-1}, (d) 1000 mV s^{-1}, (e) 2000 mV s^{-1}. Inset: Plot of the current *vs.* scan rate. [a]Data recorded in 10 mM phosphate buffer, pH 7.0, 0.1 M $NaClO_4$, reference electrode: SCE.

Table 1 Contact angles[a] of phosphate buffer droplets on the quinone/butanethiol mixed monolayer in response to chemical and electrochemical switching

Switching method	Oxidized/°	Reduced/°	Viologen/°
Electrochemical	66 ± 3	48 ± 6	36 ± 4
Chemical	63 ± 1	52 ± 2	45 ± 3
1-Butanethiol[b]	74 ± 10	76 ± 2	79 ± 1

[a] Contact angles are reported as the oxidized 1,4-benzoquinone (Oxidized), the 1,4-hydroquinone (Reduced), and the 1,4-hydroquinone in the presence of 50 mM methyl viologen (Viologen). [b] Surface modified with 1-butanethiol without quinone.

the hydrophilicity of the surface (Fig. 2). Additionally, hydroquinone is a strong π-electron donor,[14] and we hoped to exploit this property to increase contact angle changes by reacting the surface with the hydrophilic π-electron acceptor, methyl viologen. We expected that the dication, *N*,*N*′-dimethyl-4,4′-bipyridinium, would associate to the hydroquinone surface, as a result of donor–acceptor interactions, thereby increasing the hydrophilicity as a consequence of the presence of charges on the surface. Changes in the contact angle of the benzoquinone–butanethiol SAMs were measured in response to both chemical and electrochemical oxidative/reductive switching and are summarized in Table 1. The freshly prepared quinone surface had a contact angle with aqueous buffer (10 mM PB, pH 7.0, 0.1 M $NaClO_4$) of 66° ± 3 (Fig. 2a). Upon application of a potential of −0.55 V (Au/Ag/Pt) using a silver wire as a reference, the contact angle was lowered to 48° ± 6. Interestingly, upon returning the potential to 0 V, a contact angle of 54° ± 4, rather than the initial value of 66° ± 3, was observed. However, upon applying a positive potential of +0.2 V, the contact angle returned to a value of 64° ± 7 that remained constant even as the potential was returned to 0 V. This phenomenon occurs because the tail end of the oxidation peak occurs at a potential greater than 0 V when the Ag wire quasi-reference electrode is used, and as a result, the surface is only partially oxidized until an over-potential of +0.2 V is applied. These experiments were repeated with methyl viologen (50 mM) added to the buffer solution. While the initial contact angle of 64° ± 2 is nearly identical to the initial value measured in the absence of viologen, the contact angle of 36° ± 4 was measured at −0.55 V (Fig. 2b), and this reflects the effect of having a strongly ionic surface. This lower contact angle is the result of association of the π-electron acceptor viologen units to the π-electron rich hydroquinone units on the surface to form a donor–acceptor complex with ionic head groups. Upon oxidation of the surface with a potential of +0.2 V, a contact angle of 58° ± 2 was obtained. This value, lower than the initial value, is a reflection of the increased oxidation potential of the quinone that occurs in the presence of the π-electron poor viologen,[15] thereby resulting in some hydroquinone remaining on the surface. The relatively large standard deviations in the contact angle measurements taken under electrochemical potential can be attributed to the slight distortions in the droplet that occur upon the introduction of the electrode wires. Switching of the surface wettability in response to chemical oxidation/reduction was also observed (Fig. 2c). Upon reduction of the quinone-modified surface with a 10 mM solution of ascorbic acid, the contact angle of the surface decreased from 63° ± 1 to 52° ± 2, and in the presence of methyl viologen, the contact angle further decreased to 45° ± 3 (Fig. 2d). Oxidation of the surface with a 10 mM solution of $KMnO_4$ resulted in a contact angle of 64° ± 1 that was independent of the presence of methyl viologen. The lower contact angle observed for electrochemical reduction of the surface in the presence of methyl viologen when compared to chemical reduction is caused by electrostatic attraction between the surface and the dication, which results in a lower relative contact angle. Control experiments that involved application of electrochemical potential on a 1-butanethiol monolayer resulted in minute changes in contact angle (Table 1), indicating that the effects of ion double-layer charging on surface wettability are negligible.

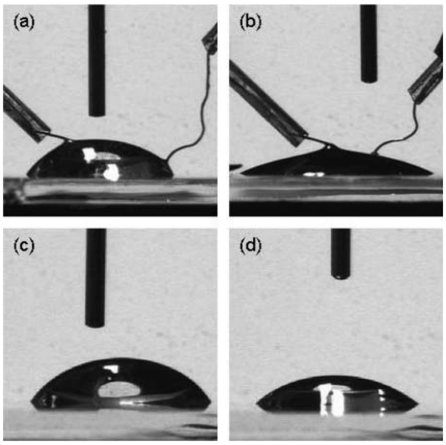

Fig. 2 Contact angle images on the switchable surfaces. (a) Droplet on quinone surface, 0 V applied potential, 50 mM methyl viologen. (b) Droplet on quinone surface, −0.55 V applied potential, 50 mM methyl viologen. (c) Droplet on quinone surface, 50 mM methyl viologen. (d) Droplet on quinone surface, after ascorbic acid reduction, 50 mM methyl viologen.

Finally, we confirmed that the surface was indeed switching between the π-acceptor benzoquinone and the π-donor hydroquinone with chemical force microscopy (CFM). CFM is a technique that is widely used to measure force interactions between two surfaces and has been used to quantitatively determine forces

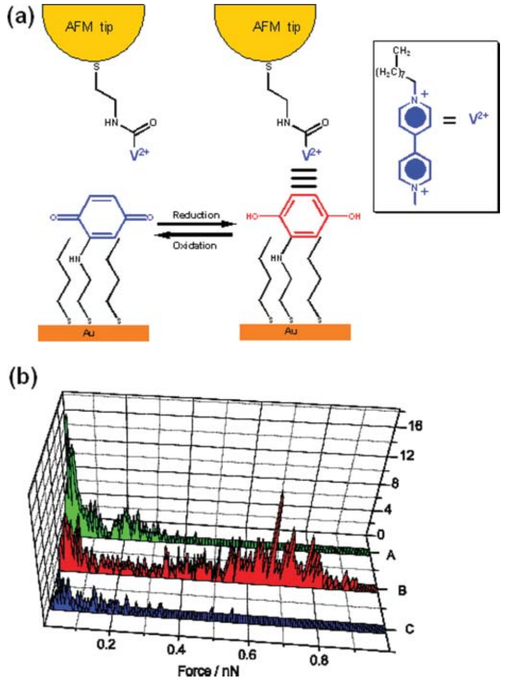

Fig. 3 (a) Schematic illustration of the chemical force microscopy (CFM) measurements between a viologen-modified AFM tip and a quinone-modified gold surface. (b) Histograms of forces measured after over 300 pulling experiments between the quinone-modified surface and a *N*,*N*′-dimethyl-4,4′-bipyridinium-functionalized AFM tip (**A**) after preparation of the surface, (**B**) following reduction with ascorbic acid, and (**C**) following oxidation with $KMnO_4$.

of supramolecular complexes formed by hydrogen bonding, hydrophilic–hydrophobic, and π-donor–acceptor interactions with single-molecule sensitivity.[16] It has been demonstrated that a viologen-coated AFM tip will interact with a surface coated with a monolayer of hydroquinone donors, but upon oxidation to the benzoquinone form, the forces disappear.[17] In the present experiment, a SAM of the bipyridinium π-electron acceptor was anchored to a gold-coated AFM tip by following literature protocols.[17] The tip was brought into contact with the surface, and forces were measured upon retraction of the tip in both the oxidized and reduced state (Fig. 3a). The forces determined from 300 such pulling events were combined into histograms (Fig. 3b) to obtain the average force of each pulling event. Initially, a force of 0.143 ± 0.010 nN per pull was observed between the tip and the surface. Reducing the surface with ascorbic acid (10 mM) for 20 min resulted in significantly stronger forces (0.655 ± 0.011 nN) in each pulling experiment. We attribute the strong forces observed following reduction of the surface to the formation of a donor–acceptor complex between the π-electron accepting bipyridinium units and the π-electron donating hydroquinone components associated with the surface.[17] After oxidation with $KMnO_4$ (10 mM) for 20 min, forces well below the initial value were measured (0.056 ± 0.004 nN).[18] Oxidizing the hydroquinone surface to benzoquinones prohibits the formation of the donor–acceptor complex, thereby explaining the absence of strong pull-off events.[19] The small but significant initial force measured prior to chemical reduction is most likely the result of a small amount of hydroquinone present on the initial surface. This observation is consistent with electrochemical contact angle measurements in which the observed initial contact angle was lower than the angle determined following electrochemical oxidation.

In conclusion, we have demonstrated the preparation of a quinone-terminated monolayer whose surface wettability changes in response to both electrochemical and chemical stimuli. Upon reduction of the benzoquinone to its hydroquinone analogue, contact angle changes of up to 18° were observed, and a further 12° reduction in the contact angle, for a total change of 30°, was induced by introducing methyl viologen to the water droplet. The methyl viologen-induced enhanced wettability of the surface originates from the association of the dicationic π-electron acceptor to the hydroquinone terminated monolayer as a result of π-donor–acceptor interactions. Finally, we demonstrated that attractive forces between a bipyridinium-modified AFM tip and the quinone-modified surface could be switched on and off in response to the oxidation state of the quinone. We foresee that such "smart" surfaces have applications in microfluidics, biosensing and self-cleaning surfaces.

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18 For representative force curves see ESI†.
19 Based on a force of 0.655 nN per pull, an average density of 7.9×10^{-12} mol cm^{-2} and 60 nm diameter AFM tips, we calculate a force of 4.5 pN per viologen–hydroquinone complex based on previously established methods.[17] This value is slightly higher than the values of 1.7 pN and 2.1 pN obtained for tyramine- and dopamine-coated surfaces respectively[17].