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Surface-Bound Norbornylogous Bridges as Molecular Rulers for Investigating Interfacial Electrochemistry and as Single Molecule Switches

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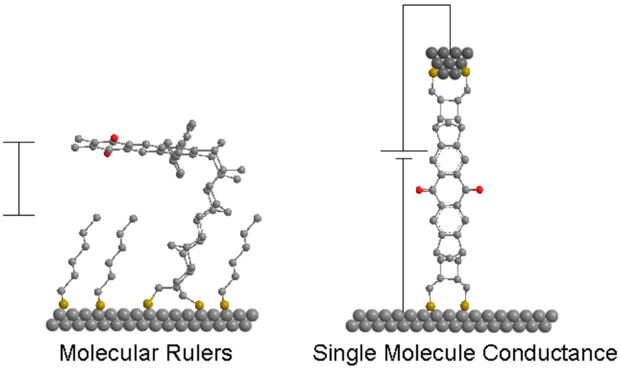

Electron transfer (ET) reactions through molecules attached to surfaces, whether they are through single molecules or ensembles, are the subject of much research in molecular electronics, bioelectronics, and electrochemistry. Therefore, understanding the factors that govern ET is of high importance. The availability of rigid hydrocarbon molecular scaffolds possessing well-defined configurations and lengths that can be systematically varied is crucial to the development of such devices.

In this Account, we demonstrate how suitably functionalized norbornylogous (NB) systems can provide important insights into interfacial ET processes and electrical conduction through single molecules. To this end, we created NB bridges with *vic-trans*-bismethylenethiol groups at one end so they can assemble on gold electrodes and redox species at the distal ends. With these in hand, we then formed mixed self-assembled monolayers (SAMs) containing a small proportion of the NB bridges diluted with alkanethiols. As such, the NB bridges served as molecular rulers for probing the environment above the surface defined by the diluent species. Using this construct, we were able to measure the interfacial potential distribution above the diluent surface, and track how variation in the ionic distribution in the electrical double layer impacts ET kinetics.

Using the same construct, but with a redox molecule that remains neutral in both oxidized and reduced states, we could explore the impact of the chemical environment near a surface on ET processes. These results are important, because with conventional surface constructs, ET occurs across this interfacial region. Such knowledge is therefore relevant to the design of molecular systems at surfaces involving ET.

With a second family of molecules, we investigated aspects of single-molecule electrical conduction using NB bridges bearing *vic-trans*-bismethylenethiol groups at both ends of the bridge. This gave us insights into distance-dependent electron transport through single molecules and introduced a method of boosting the conductance of saturated molecules by incorporating aromatic moieties in their backbone. These partially conjugated NB molecules represent a new class of molecular wires with far greater stability than conventional completely conjugated molecular wires. Of particular note was our demonstration of a single molecule switch, using a NB bridge containing an embedded anthraquinone redox group, the switching mechanism being via electrochemically controlled quantum interference.

1. Introduction

Electron transfer (ET) reactions through organic molecules bound to surfaces are the basis of many envisaged devices such as molecular switches, photovoltaic devices, and sensors.[1,2] Hence electrode–*organic layer*–redox species and electrode–*organic layer*–electrode constructs have attracted intense interest.[2] The presence of a surface at which ET is occurring provides an extra complication compared

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with solution phase intramolecular ET between covalently linked donor and acceptor groups. For example, electrical and chemical gradients that exist in the region between the electrode and the electrolyte can have a profound influence on the ET process. Successful engineering of systems for various applications requires understanding all the processes at the interface. With the discovery of self-assembled monolayers (SAM) on metal surfaces in the 1980s, enormous progress has been made in achieving such an understanding. The most heavily studied systems of this type comprise alkanethiols self-assembled on gold surfaces.[3] The key to using these monolayers for ET studies is the ability to prepare mixed SAMs; containing an inert alkylthiol diluent, in which the redox-active species constitute only a small portion of the monolayer. In this way, well-defined distance relationships between the redox center and the electrode surface can be achieved through packing of the flexible alkylthiolate chains in their all-*trans* conformations. However, the interpretation of the experimental results is complicated by the effects of electrical and chemical gradients at the SAM–solvent interface, which are produced both by the chemical nature of the diluent terminus and by the electric potential of the metal electrode. The investigation of such effects requires the small proportion of redox-active species to be projected above the diluent layer at well-defined distances. The conformational flexibility of the alkanethiol systems precludes their use in such studies because of the ambiguity related to the position of the redox-active group relative to the interface.

The solution to conformational ambiguity is to use rigid hydrocarbon bridges that are incapable of undergoing internal rotation about C–C single bonds. In this respect, the oligonorborane–bicyclo[2.2.0]hexane bridges, referred to as norbornylogous (NB) bridges (Figure 1), are an excellent choice for SAM construction, having played a key role in the elucidation of the superexchange mechanism in solution phase intramolecular ET processes.[4,5] NB molecules have several unique features that have made them attractive for such studies: (1) The bridge is inherently rigid, meaning the terminal donor and acceptors are held in a fixed, well-defined orientation and distance from each other (Figure 1). (2) The nature of the bridge allows systematic variation of its length and configuration. (3) A wide range of groups can be attached to the termini of the bridge. The application of NB bridges to the study of intramolecular ET has been reviewed in an earlier Account.[5]

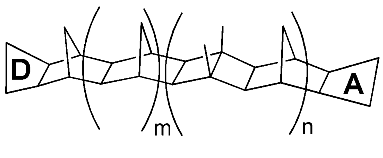

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FIGURE 1. Schematic of a norbornylogous bridge. "A" stands for electron acceptor, and "D" stands for electron donor.

In response to the conformational ambiguity of alkyl chains, we have developed a SAM system comprising *vic-trans*-bismethylenethiolate-terminated NB bridges with a redox-active group attached to the other terminus (Figure 2). This system provides an experimental approach to systematically probe the interfacial region above a SAM and its influence on electrochemical reactions.

We are also studying electron transport through single NB-based molecules capped at each end with *vic-trans*-bismethylenethiolate groups that can form well-defined nanojunctions between two gold electrodes (Figure 3). These devices provide valuable insights into the distance-dependent conductivity, conductivity boosting, and conductivity switching within single molecules.

2. Molecular Design

The first series of NB-based systems, which gave proof of principle that NB bridges may form useful SAMs, is illustrated

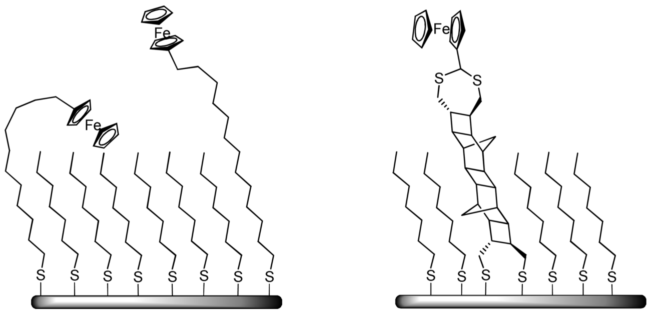

FIGURE 2. A schematic outlining the difference between the ambiguous location of redox-active moieties in flexible molecules compared with rigid NB bridges.

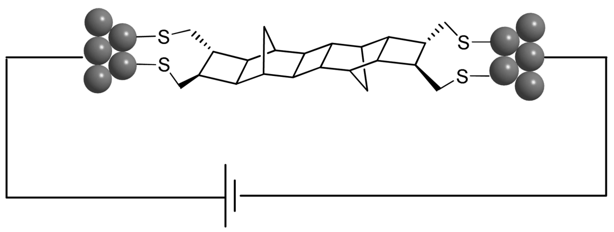

FIGURE 3. Schematic of an NB bridge forming a single-molecule circuit.

in Figure 4a.[6,7] The molecules incorporate a *vic-trans*-bismethylenethiol group, the purpose of which was to provide two-point attachment to the electrode surface, thereby both conferring strong SAM–electrode stability toward dissociation and restricting orientational degrees of freedom of the NB molecules. The results demonstrated that NB molecules form very stable and robust SAMs. An added bonus was the finding that the *vic-trans*-bismethylenethiol group is substantially more resistant to electrochemically induced reductive desorption compared with monothiol groups commonly used in SAM forming molecules.[6,7] Other research groups have also shown increased stability of dithiol contacts over monothiol contacts such as dithiazepane[8] and dithiocarbamate[9] contacts. Equally important was the finding that electrochemically initiated ET between the electrode and the dimethoxynaphthalene group was very fast ($>10^3$ s^{-1}), even through the 15 σ bond NB bridge in **2**, once again, testifying to the remarkable efficacy of the NB bridge to mediate ET by through-bond (superexchange) mechanism.[6]

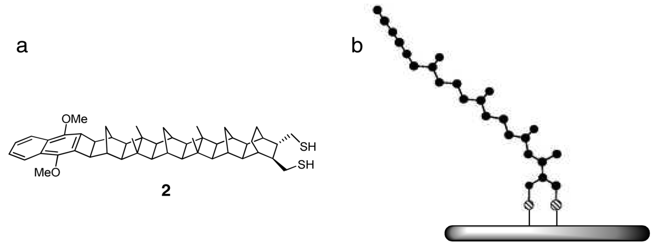

FIGURE 4. (a) Structure of NB bridge **2** with a *vic-trans*-bismethylenethiol group at one terminus and a dimethoxynaphthalene redox group at the other terminus. (b) A schematic outlining the B3LYP/6-31G(d) optimized geometry of bridge **2** on the surface.

The NB bridges used for intramolecular solution phase ET studies, and in the SAM mentioned above, were constructed from fusing alternating norbornane and bicyclo[2.2.0]hexane units, as illustrated in Figures 1 and 4. This mode of concatenation results in the NB bridge displaying marked curvature for bridges longer than 12 σ bonds. This is seen in molecule **2** (Figure 4) and molecule **3** (Figure 5a,b), with bridge lengths of 15 and 20 σ bonds, respectively.[10] While this curvature poses no problems when investigating intramolecular ET processes, it is essential to minimize it when constructing SAMs using NB bridges because it can lead to unpredictable SAM packing and structure. For example, X-ray photoelectron spectroscopy revealed that the 20-bond tetrathiol **3** adopts two orientations on a gold surface: an upright orientation, in which only one dithiol group bonds to gold, and a hairpin orientation, in which, by dint of the curved bridge, both dithiol groups bond to gold (Figure 5b).[10] The problem of bridge curvature was overcome by incorporating a single *anti*-norbornadiene-dimer unit into the bridge. As shown in Figure 5d, the two sub-bridges extending from the *anti*-norbornadiene-dimer unit slightly curve in opposite directions, resulting in zero average curvature for the entire bridge.[11]

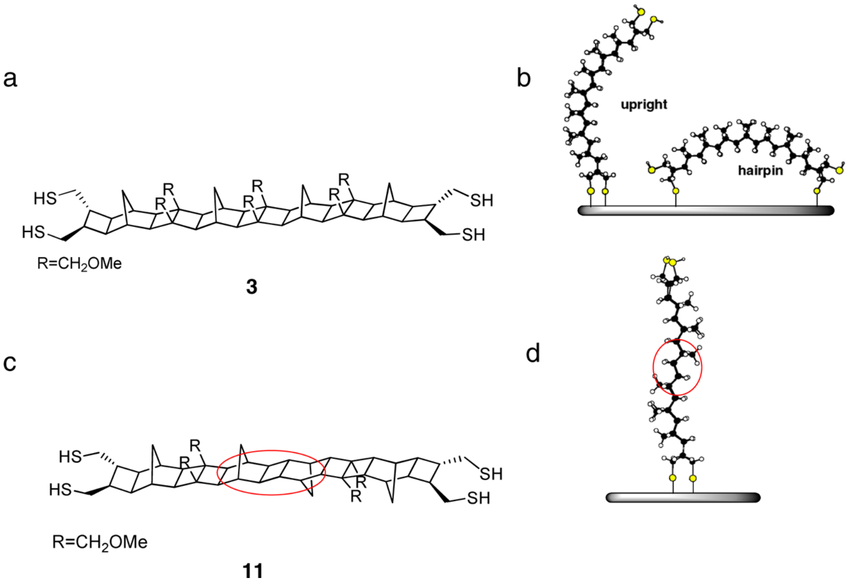

FIGURE 5. (a) A representative curved NB bridge. (b) A schematic of the hairpin and straight orientation of bridge **3** on the surface. (c) A representative straight NB bridge; circled in red is the *anti*–*anti*-bisnorbornene dimer unit. (d) A schematic outlining the straight orientation of bridge **11** on the surface. The structures of the molecules in panels b and d are B3LYP/6-31G(d) optimized structures.

3. Probing the Electrical Double Layer above a SAM

Characteristic features of processes occurring at an electrified interface are the presence of electrical and chemical gradients, which have effects on ET kinetics and on the redox potential. Creager and co-workers have extensively investigated, in a series of excellent studies, how the microenvironments in the interfacial region affect the kinetics and the thermodynamics of ET based on systems comprising ferrocene-terminated alkanethiol diluted with alkanethiol diluents.[12−14] Despite the presence of a certain degree of control over the environment that such systems provided, the flexible alkane chains tethering the redox moiety to the electrode may cause the redox moiety to nestle into the terminal groups of the diluent[12] and therefore complicate the distinguishing of electrical double layer effects from solvation effects. Creager and co-workers pointed out that microscopic characterization and accurate interfacial structures are necessary for better understanding of the interplay between the interfacial microenvironment and long-range interfacial electron transfer.[12] Further, the flexibility of the molecules employed precluded the probing of solution effects just above the interface defined by the SAM.

We extended the work of Creager and co-workers and others by measuring the potential drop across a well-defined interface by incorporating NB molecules **4** and **5** (Figure 6) in matrices of SAMs formed on atomically flat Au(111) surfaces such that a well-defined environment above the diluent could be achieved. NB−diluent mixed monolayers were constructed so that the center of the ferrocene moiety (plane of electron transfer) is situated at different distances from the distal surface of the SAM. Hence, the NB molecule used was kept the same and the length of the diluent was changed (Figure 7), and both redox potential and electron transfer kinetics were measured.[15]

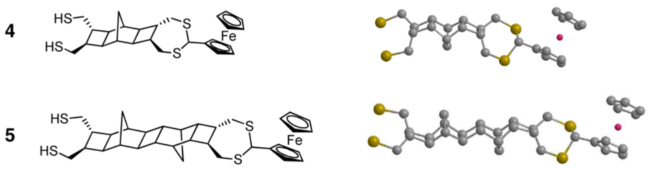

FIGURE 6. Structures of the molecules **4** and **5** along with their B3LYP/6-31G(d) optimized structures.

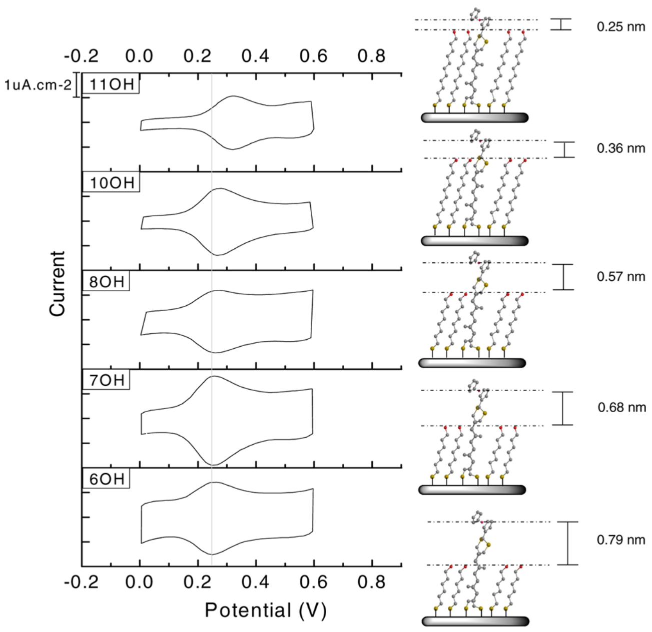

FIGURE 7. Cyclic voltammetry (CV) of the SAMs formed from compound **4** mixed with 11-mercaptoundecanol (**4**-11OH), **4** mixed with 10-mercaptodecanol (**4**-10OH), **4** mixed with 8-mercaptooctanol (**4**-8OH), **4** mixed with 7-mercaptoheptanol (**4**-7OH), and **4** mixed with 6-mercaptohexanol (**4**-6OH). Schematic drawings of the corresponding SAMs are shown.

The measurements exhibited a shift in the apparent formal potential to more negative values with an increase in the ferrocene−diluent distance, which agrees with the interfacial potential distribution model theoretical described by Smith and White[16] and Fawcett.[17] In the theory of interfacial potential distribution, Smith and White predicted that the formal potential typically measured in redox-active SAMs inherently contains an electrostatic potential term ($\phi_{\mathrm{PET}} - \phi_{\mathrm{SOL}}$) due to surface charge at the electrode−electrolyte interface. The terms ϕ_{PET} and ϕ_{SOL} represent the potential at the plane of electron transfer and at the bulk solution, respectively. Therefore, what is actually measured is not the formal potential but an "apparent formal potential".[16] Hence, when the ferrocene center becomes further away from the distal end of the SAM, ϕ_{PET} approaches ϕ_{SOL} and hence the apparent formal potential, $E° + (\phi_{\mathrm{PET}} - \phi_{\mathrm{SOL}})$ approaches $E°$. A steep drop in potential from the distal surface of the diluent was observed followed by a smaller potential drop, which are attributed to the potential drop in the Stern and the diffuse layers, respectively (Figure 8).[15]

The impact of the nonuniform ionic distribution in the electrical double layer was also evident from our measurements of ET rate constants, which were found to decrease with increasing ferrocene−diluent surface distance.[16] Since the ferrocene redox reaction occurs at potentials positive of the point of zero charge of the modified surface,[18] the perchlorate anions will be in excess near the surface of the diluent compared with bulk solution. Because ET kinetics

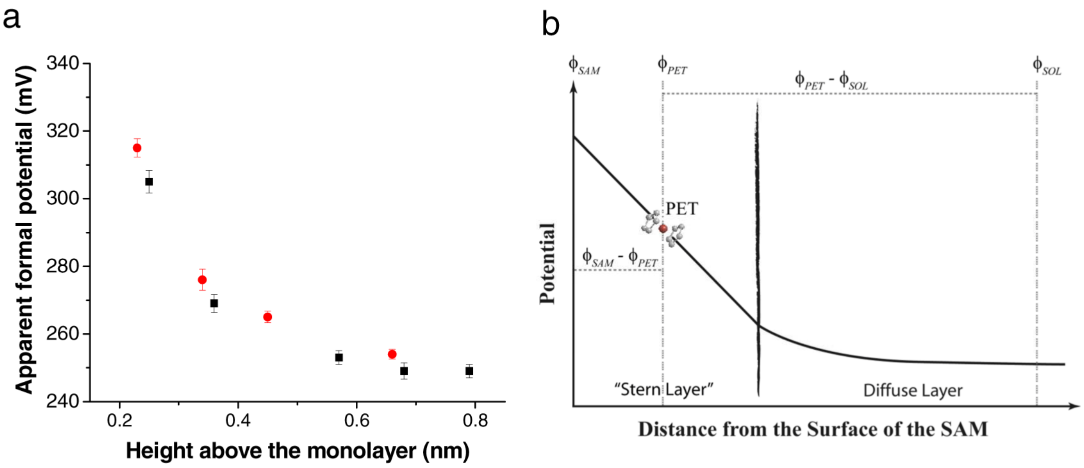

FIGURE 8. (a) An overlay of the plots of the apparent formal potential vs the distance between the ferrocene moiety of compounds **4** (red circles) and **5** (black squares) and the distal surface of the diluent and (b) schematic describing the potential drop across the electrical double layer. ϕ_{SAM}, ϕ_{PET}, and ϕ_{SOL} are the potentials of the SAM (surface of the diluent), the plane of electron transfer, and the bulk solution, respectively.

of ferrocene redox reactions are known to be highly dependent on ion pairing,[19,20] the decreasing concentration of the perchlorate counterions as the ferrocene is moved through the Stern and diffuse layers explains the corresponding decrease in ET rate as the ferrocene moves away from the diluent surface.

Our methodology described above provides a tool for measuring interfacial potential distribution above a SAM surface, which is not possible with conventional flexible alkane chains and provides a strategy to systematically tune the redox properties of ferrocene moieties, which have widespread use in biosensors and other devices such as molecular memory.[21] We, and others, have exploited that sensitivity in the development of an electrochemical immunobiosensors[22] where a biological event at the interface changes the ionic environment around the ferrocene moiety and consequently alters the electrochemical signal.

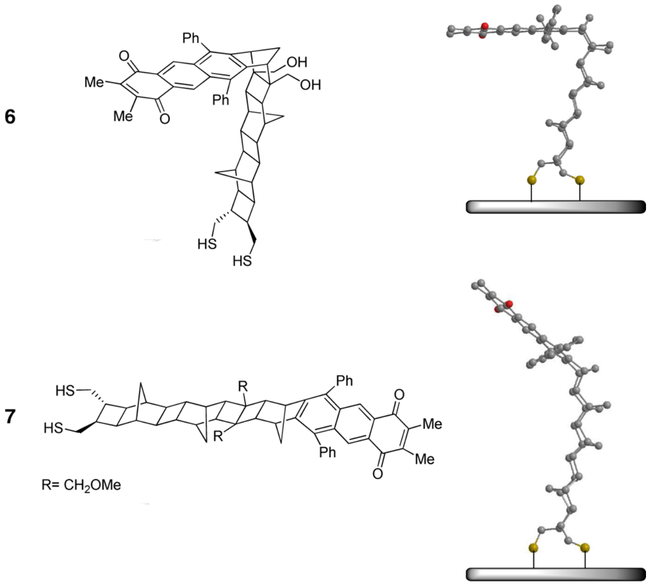

FIGURE 9. Structures of the molecules **6** and **7** along with their orientation on the gold surface as determined by *in situ* electrochemical IR spectroscopy and sum frequency generation spectroscopy.[23,24] The quinone ring in molecule **6** is oriented close to the surface parallel while that of molecule **7** is oriented ca. 45° from the surface parallel.[23,24]

4. Probing the Chemical Environment above a SAM

Having demonstrated, using the ferrocene system, that ET kinetics are markedly affected by the electrical double layer near the SAM surface, we then investigated how ET kinetics are influenced by the chemical environment above the diluent surface. Such studies required the synthesis of NB-based anthraquinone molecules, **6** and **7** (Figure 9).[23,24] We chose to employ the anthraquinone (AQ) redox probes for two reasons. First, in aqueous electrolytes both molecules of the anthraquinone/hydroanthraquinone (AQ/H_2AQ) redox couple are chargeless, meaning that the electrochemistry of this couple, unlike that of the ferrocene/ferricinium couple, is insensitive to the distribution of counterions at the SAM/electrolyte interface. Second, the AQ redox reaction is strongly influenced by hydrogen bonding between AQ and protic solvents,[25] and therefore AQ moieties are ideal probes for electrochemically sensing H-bonding interactions with the solvent above the surface of the diluent. The different molecule shapes, L-shape in the case of **6** and straight in the case of **7**, were chosen so that in mixed SAMs they would have quite different AQ−diluent orientations. In mixed SAMs constructed from **6**, the AQ redox species should be nearly parallel to the diluent surface, whereas in mixed SAMs made from **7**, the AQ moiety is closer to the surface normal (Figure 9). The different orientations mean with **7**, water can easily access the quinone portion of the molecule and hence easily hydrogen bond to the carbonyls. In contrast, with **6** the carbonyls are less accessible to water but can hydrogen bond with the diluent in the SAM. That **6** and **7** did adopt these orientations in mixed SAMs was confirmed by *in situ* electrochemical IR spectroscopy and sum frequency generation spectroscopy (SFG).[23,24]

Since the AQ redox reaction is pH dependent, as are both the apparent formal potential ($E^{\circ\prime}$) and ET rate constant (k_{et}), buffered solutions were used to keep the pH at the interfacial region constant, and therefore, the variations in $E^{\circ\prime}$ and k_{et} as a function of the position of the AQ moiety relative to the SAM can be strictly correlated with the chemical environment across the interface. Electrochemical studies were conducted on mixed SAMs constructed from **6** and **7**, using diluents of different lengths bearing different end groups (OH and CH_3). Results showed that at a given pH, $E^{\circ\prime}$ and k_{et} are dramatically influenced by the AQ carbonyl groups being within 0.21 nm from the diluent surface. At such a location, changing the diluent from CH_3 terminated to OH terminated produces a positive shift in $E^{\circ\prime}$ and an increase in the value of k_{et}. If the AQ carbonyl groups are positioned further from the diluent surface, greater than 0.21 nm, a similar trend in the shifts in $E^{\circ\prime}$ and k_{et} are observed but typically the magnitude of the change is larger when the diluent is CH_3 terminated. These surface effects are not attributed to electrical double layer effects. This is because the pH dependence of the anthraquinone electrochemistry allows the effects to be investigated at both positive and negative of the point-of-zero-charge (pzc) of the SAM. If the phenomena being observed was due to electrostatics, then the direction of the shift in $E^{\circ\prime}$ would be opposite depending on whether the $E^{\circ\prime}$ was positive or negative of the pzc.

We proposed that the shift to more positive $E^{\circ\prime}$ and greater values of k_{et} was related to H-bonding interactions with water becoming more favorable. H-bonding interactions were clearly demonstrated in the same systems using the SFG spectroscopic technique.[19] That is, the AQ carbonyl groups can form H-bonds with OH groups of the diluent and with water at the interface.[23,24] Our findings of positive shifts in $E^{\circ\prime}$ values and increasing ET rate constants when the AQ carbonyl groups are progressively situated further from the SAM surface are consistent with those recently demonstrated for quinone species in organic solvents upon the addition of water.[25] We speculate that the impact of the CH_3 terminated diluent, relative to the OH diluent, is far greater on the $E^{\circ\prime}$ and k_{et} because close to the diluent surface there is a "water depletion layer" as recently revealed by X-ray and neutron reflectometry studies.[26] In this "water depletion layer" the ability for water to H-bond to the AQ carbonyl groups is diminished to a greater extent than with a −OH diluent where there is no such depletion layer. The results also demonstrate that it was the position of the quinone moieties relative to the surface that was crucial. That is when SAMs formed from molecule **7** were compared with those formed from molecule **6** using the same diluent, the former showed higher values of k_{et} and more positive $E^{\circ\prime}$. This is a consequence of the straighter geometry of molecule **7** positioning the carbonyl groups of the AQ moiety away from the distal surface of the diluent, unlike molecule **6** where the carbonyl groups are closer to the distal surface of the diluent.

Combined, the two families of redox-active NB bridges (ferrocene and anthraquinone) provide a wide picture about the electrical and compositional characteristics of SAM−electrolyte interfaces. The ferrocene family probes the electrical gradients above an electrode−SAM surface while the anthraquinone species probe chemical gradients such as H-bonding effects and the "water depletion layer" above a SAM. From a more applied perspective, NB molecules can be used to detect changes in the chemical and charge composition at the interface, enabling miniaturized chemical and biosensors. The results also highlight the types of redox species that should be employed at surfaces, depending on the phenomenon one wishes to probe. For example, in our biosensing studies we rely on the change in counterion accessibility to redox species, and hence, ferrocene is the molecule of choice. However, for specific analytes that are hydrophobic, quinone based redox probes are preferable since they are more sensitive to hydrophobic environments.

5. Single Molecule Circuitry Using NB Molecules

The concept of molecular electronics has sparked intense interest in the miniaturization of electrical circuitry down to single molecules, which can be designed to have properties that resemble traditional electronic components such as wires, transistors, or rectifiers.[27,28] Further, using molecules as the component in circuits can introduce novel stimuli to control the charge transport because single molecules operate in a size regime where quantum effects are important, unlike the classical physics that governs electron transport in conventional electronics.

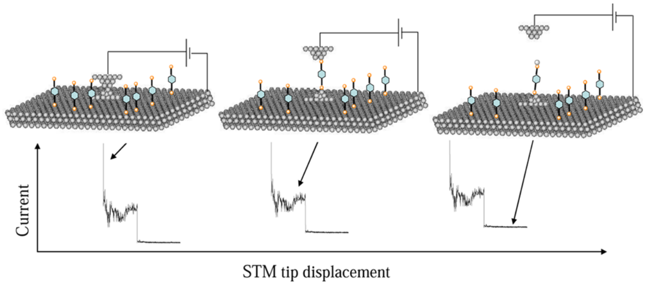

FIGURE 10. Schematic representation of an STM-break junction experiment.

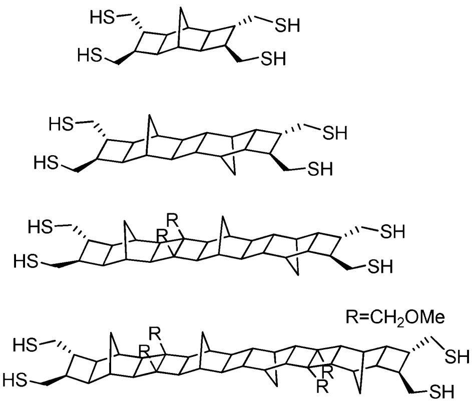

FIGURE 11. Structure of the saturated NB molecules of different lengths. Compound **8** possesses 8 σ bonds, **9** possesses 11 σ bonds, **10** possesses 15 σ bonds, and **11** possesses 19 σ bonds.

The highly attractive concept of integrating individual molecules into electronic devices was pushed forward by the development of the scanning tunneling microscope (STM) break-junction technique by Tao and co-workers,[29] in which thousands of molecular junctions can be formed in few hours thus producing a statistical analysis of the single-molecule conductance. The method is based on forcing a gold STM tip in and out of contact with a gold substrate functionalized with thiolated molecules (Figure 10). During the contact process, adsorbed molecules can bridge between the tip and the surface electrodes via thiol linkers at both ends of the molecules. As one of the electrodes is pulled away (typically the STM tip), plateaus appear in the current vs distance profile, which are attributed to single-molecule events.[29] Grouping the values of the conductance plateaus into histograms gives the most frequently observed conductance for the single-molecule electrical contact.[29]

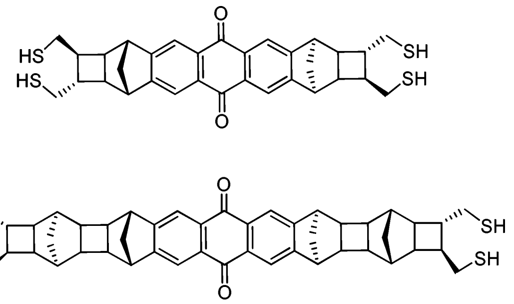

FIGURE 12. Structures of partially conjugated NB molecules. Compound **12** possesses five bonds on each side and an AQ moiety in the center. Compound **13** possesses eight bonds on each side and an AQ moiety in the center.

By the method described above it has been possible to study electron transport through many molecular systems. In addition to the role of chemical composition of the bridge in determining the conductance of the junctions, geometrical factors such as contact separation, conformation distribution, molecular/electrode contact geometry and molecular tilt angle in the junction have been found to significantly influence the measurements and can complicate the interpretation of the results.[30−32] In response to such complications, NB bridges owing to their rigidity and unambiguous orientation on surfaces make them suitable candidates for forming well-defined junctions.

NB molecules **8**−**11** (Figure 11)[11] were designed to measure single molecule conductance as a function of the molecular length. The conductance was found to decrease exponentially with decay constant, β, of ca. 1 bond^{-1} via superexchange-mediated charge transport. These observations are in agreement with those obtained for saturated alkyl chains in gold−SAM−gold junctions via conducting atomic force microscopy.[33]

Another attractive feature of NB bridges is their chemical stability. Stability is one of the key shortcomings of many highly conjugated molecular wires, but their conductance is much higher and much less distance-dependent than NB bridges.[34] Hence we sought to combine the best of both classes of molecules by designing NB molecules in which an AQ moiety was introduced into the center of an NB bridge.[35,36] The purpose of the AQ group was to provide low-lying virtual states that facilitate superexchange-mediated electron transport, thereby resulting in higher conductance compared with purely saturated NB bridges. This expectation was confirmed experimentally. For example, the conductance of the AQ-embedded **13** (Figure 12) was found to be $(1.7 \pm 1.0) \times 10^{-5}$ G_0, a value comparable to that $(3.5 \pm 1.2) \times 10^{-5}$ G_0 obtained for "pure" NB molecule **9**, despite **13** being 11 bonds longer than **9**. The enhanced conductance of these partially conjugated molecules is promising for the design of rigid molecules of extensive length without compromising their chemical stability.

It transpired in the course of this work that our AQ-based molecule **13** could serve as a single molecule switch, the switching mechanism arising from electronically controlled quantum interference (Figure 12).[35] The quantum interference referred to here relates to the fact that AQ is a cross-conjugated molecule, whereas its reduced form, H_2AQ, is a linearly conjugated molecule (Figure 13).

It has been pointed out that conductivity in cross-conjugated molecules should be weaker than that in linearly conjugated molecules because of the presence of destructive interference in the former type of conjugation.[37] Consequently, single molecule conductivity through the AQ molecule **13** should be lower than that through the reduced H_2AQ form. Another interesting property of the AQ redox reaction is its pH dependence and therefore the switching between the AQ and the H_2AQ can be controlled via the pH of the electrolyte. We have tested these predictions by electrochemically gating molecule **13** using single-molecule STM break junction measurements, which revealed that the switching between the AQ and the H_2AQ forms in molecule **13** leads to an increase in conductance by an order of magnitude (Figure 14).[35,36] This magnitude, which is due to differential quantum interference effects operating in AQ and H_2AQ, is smaller than that predicted from simple theoretical calculations but is similar to that experimentally found from self-assembled monolayers.[38]

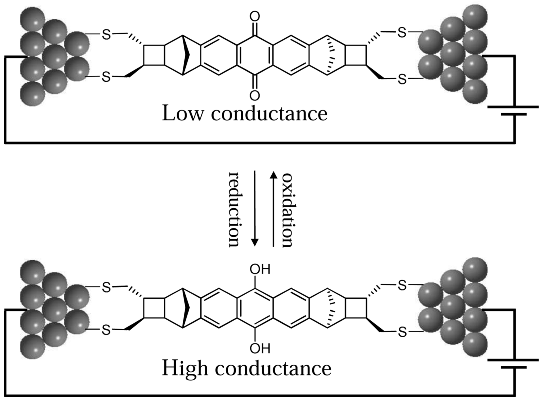

FIGURE 13. Schematic showing the switching from the cross-conjugated AQ moiety in molecule **13** to the linear conjugated H_2AQ.

Interestingly, the electrochemical gate potential at which switching between the low-conducting AQ form and the higher conducting H_2AQ in **13** was altered using electrolytes of different pH.[35] This last point gives more degrees of freedom to control the charge transport across molecules toward pH-gated single molecule transistors. The maximum

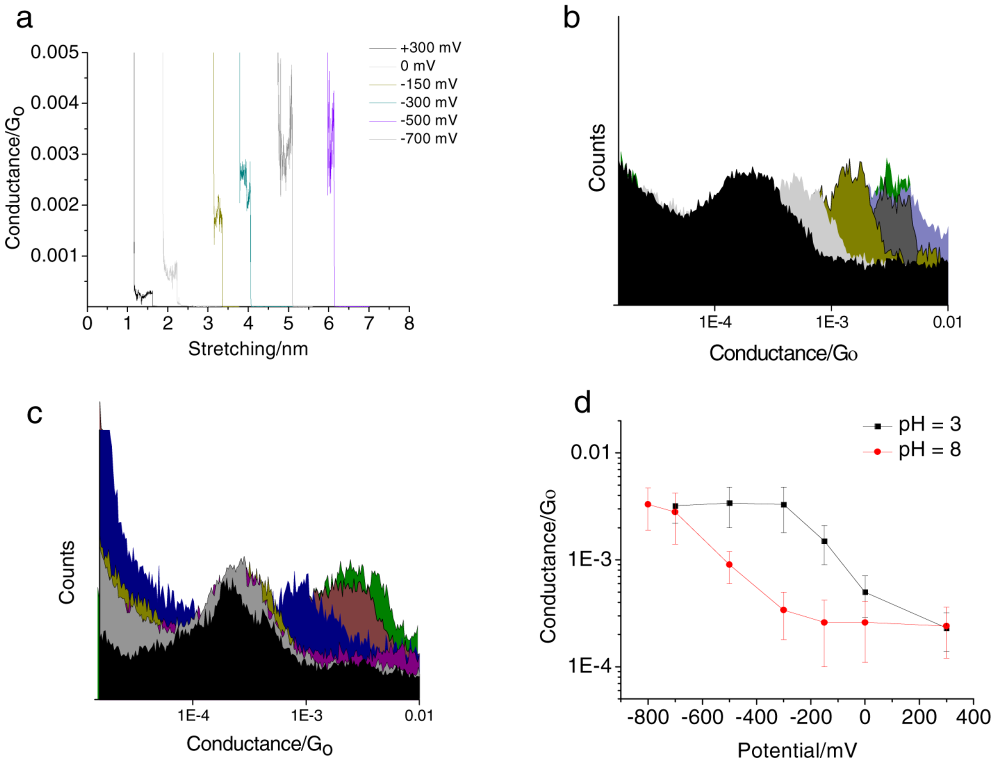

FIGURE 14. (a) Representative current traces of molecule **13** at different gate potentials at pH 3. (b) Conductance histograms of molecule **13** at different gate potentials at pH 3. (c) Conductance histograms of molecule **13** at different gate potentials at pH 8. (d) Evolution of conductance as a function of the gate potentials at pH 3 (black line) and pH 8 (red line).

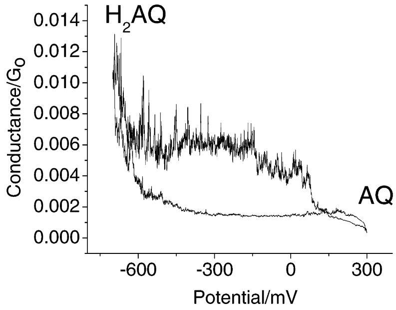

FIGURE 15. Conductance–gate voltage sweep conducted on molecule **13**.

increase in conductance was observed at a gate potential more cathodic than the half wave potential of the redox reaction, a potential window at which there is a greater possibility of the anthraquinone molecules being in their reduced (higher conductance) hydroanthraquinone form. Further, we were able to record the conductance of a single molecule of **13** while sweeping the gate potential. This experiment could be envisioned as monitoring dynamically the effect of cyclic voltammetry on a single molecule (Figure 15). The order of magnitude increase in conductance obtained from sweeping the potential (dynamic approach) of a single molecule is consistent with those obtained from measuring the conductance at several fixed potentials (static approach).[36]

Apart from the fundamental insights that NB systems provided, their ability to promote and control charge transport over long distances is promising for other single molecule-based switches. For example, the strategy adopted to control the current in the electrochemically responsive AQ-based NB molecule can be extended to incorporate other molecular entities into the NB frame whose conjugation and therefore conductance can be altered by exotic stimuli such as light (photochromic moieties)[39] or chemical stimuli (metal-ion recognition moieties).

6. Concluding Remarks

We have used terminally functionalized NB bridges of variable but well-defined structures to gain fundamental insights into several important aspects of interfacial ET, ranging from probing the electrode–electrolyte interface to controlling electrical conduction through single molecules. We show in sections 3 and 4 how controlling the structures of SAMs can tune the kinetics and thermodynamics of interfacial electron transfer, which aims to contribute to the development of a molecular understanding of the electrical double layer and molecular interactions at the interfacial region. This knowledge offers strategies to modify the interfacial properties of surfaces for molecular recognition. In section 5, we used NB bridges to form single-molecule circuits, which offered advantages over the library of molecules currently being used in single molecule circuitry owing to their length-persistent structures, stable contacts to the electrodes, and efficient electron transport properties. These unique properties enabled us to build a single molecule transistor-like switch based on incorporating an anthraquinone redox moiety in a NB bridge, which can alternate between a high-conducting and a low-conducting state.

To date, our efforts and other contributions from other research groups have largely focused on molecular systems formed on metal electrodes, usually gold. However, interesting physics appears when the electrode or the two electrode leads (in case of molecular junctions) are replaced with semiconductors including negative differential resistance and rectification. The dominance of silicon in the semiconducting industry suggests the need to develop hybrid electronics where single molecules or molecular films are integrated with conventional silicon technology. A highly stable and well-defined geometry of molecules on the semiconducting surfaces is a necessary precondition for measurements of charge transport through molecule–semiconductor junctions. In response to such requirements, NB based molecules were recently shown to form very stable contacts to Si(100) surfaces owing to controlled multiple Si–C covalent bonds per molecule.[40] Using different dopants in the semiconducting materials along with highly stable and well-defined molecular films would modify the band structure and the charge transport properties of the junctions. Semiconductors can also introduce mechanisms for interesting molecular vibrational dynamics, along with approaches for optical control.[41] With these thoughts in mind, we leave the reader with what we have concluded that rigid and highly stable molecular components will become the backbone of molecular electronic devices.

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FOOTNOTES

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