Unusually rapid heterogeneous electron transfer through a saturated bridge 18 bonds in length†

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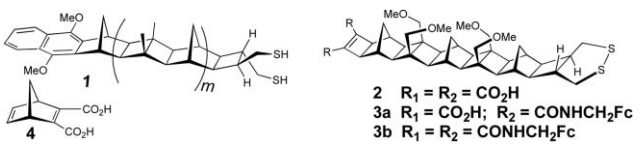
Ferrocene modified self-assembled monolayers of a novel saturated norbornylogous bridge, 21.3 Å long, demonstrated unusually rapid rates of heterogeneous electron transfer, three orders of magnitude faster than the equivalent length alkanethiol.

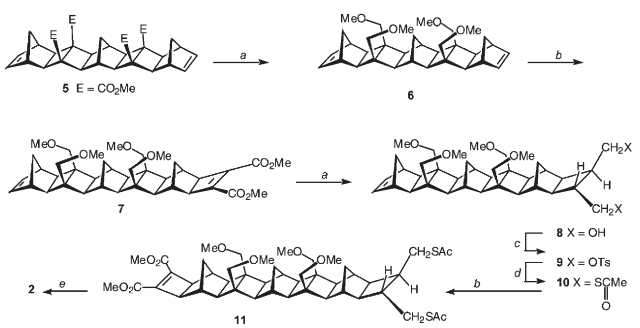
Heterogeneous electron transfer (ET) processes taking place through self-assembled monolayers (SAMs) attached to an electrode are being intensely studied, both from a fundamental, mechanistic, point of view and from the recognition that SAM-modified electrodes have a broad range of important uses.[1] The majority of SAM-modified electrodes studied to date possess a common design feature, namely the SAM comprises a bridge, one end of which is attached to the electrode surface by some functionality, *e.g.* thiol, and the other end is attached to a redox-active group. In many applications two requirements of SAM design should be met. These are: (1) The bridge should be sufficiently long to prevent close proximity between the electrode surface and redox-active centre, thereby minimizing undesirable interactions between the two sites. This requires the bridge to be at least 15 Å in length, particularly if unwanted electrode quenching of electronically excited states of redox-active centres are a possibility. (2) The electron transfer between electrode and bridge must be efficient in order to provide effective response times.

Unsaturated, fully conjugated, bridges, such as oligo-*p*-phenylenevinylene bridges,[2] oligo-*p*-phenyleneethynylene bridges[3] and single-wall nanotubes (SWNTs),[4,5] have the important advantages of being structurally rigid and possessing good distance dependence characteristics of ET rates but suffer from the disadvantage of being susceptible to oxidative degradation under certain conditions. In addition, it is currently not possible to prepare SWNTs possessing uniform, well-defined lengths. Saturated hydrocarbon bridges are also being actively investigated, partly because of their ease of synthesis but also because of their increased inertness to chemical degradation, compared to their unsaturated analogues. The most common type of bridge in this category is the redox-capped *n*-alkylthiol system. These systems offer only fair response times for reasonably long alkyl bridges comprising 12 or more bonds (ET rates through these bridges ~1 s).[6] Furthermore, these bridges are conformationally flexible which makes the use of alkyl bridge-containing SAMs problematic when constructing junctions involving adventitious stress, such as with conducting probe AFM.[7]

Several years ago, we described a new approach to the construction of SAMs possessing saturated hydrocarbon bridges, namely the norbornylogous bridge (NB) system **1**.[8,9] This type of bridge offers a number of important advantages over the single alkyl chain bridge: (1) complete structural rigidity; (2) improved SAM stability by covalent attachment of the SAM to the electrode through *two* sulfur atoms. Based on a large number of studies of homogeneous ET through NBs,[10] we expect these bridges to be much faster (superexchange) mediators of ET than single chain alkyl bridges—the NB bridge has two main ET pathways connecting the electrode and the redox-active group, compared to only one for the alkyl bridge. This communication presents the design of a more versatile bridge, **2**, which is simpler to synthesize than **1**. Kinetic evidence which confirms that heterogeneous ET through a SAM, comprising the 18-bond bridge **2**, is *three orders of magnitude faster* than that through an alkanethiol of comparable length.



The synthesis of **2**, full details of which are given in the supporting information,† is summarized in Scheme 1. Conversion of the known diene **5**[11] to the *trans*-dithioacetate **11** followed known procedures.[8,12] Deacylation of **11** with catalytic amounts of NaOMe in methanol, followed by addition of HCl resulted in the formation of **2**. That the disulfide was formed, rather than the dithiol, is probably due to the presence of traces of oxygen during



Scheme 1 Reagents: *a* $LiAlH_4$, THF; NaH, MeI, DMF. *b* DMAD, $RuH_2CO(PPh_3)_3$, refluxing benzene. *c* TsBr, pyridine. *d* KSCOMe, DMSO. *e* NaOMe, MeOH; H_3O^+.

† Electronic supplementary information (ESI) available: synthesis and characterisation of compounds used in this work. See http://www.rsc.org/suppdata/cc/b4/b413612h/

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the base-catalyzed deacylation reaction and has precedent.[11] The disulfide character of compound **2** was supported by the presence of a parent ion at *m*/*z* 735.338 in the electrospray negative ion FTICR mass spectrum.

NB bridge modified electrodes were prepared by incubating polycrystalline gold surfaces, cleaned and characterised as described previously,[13] in a solution of 1 mM NB and 1-undecanethiol in a molar ratio of 1 : 20 and total concentration in DMF for 30 min. After being washed with copious amounts of Milli-Q water and dried under a stream of argon, the electrode was incubated in 1 mM undecanethiol solution in ethanol overnight. The SAM modified electrode was rinsed in ethanol and water before being activated in an aqueous solution of 40 mM 1-ethyl-3(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) and 10 mM *N*-hydroxysuccinimide (NHS) for 1 h. After activation, the electrode was rinsed in water and incubated in 5mM ferrocene methylamine solution in HEPES buffer pH 7.3 for 24 h. Rates of electron transfer were measured using cyclic voltammetry measured at a number of scan rates between 1 mV s^{-1} and 200 V s^{-1} and the method of Laviron.[14]

Cyclic voltammograms (CVs) of NB modified electrodes after attachment of ferrocene, at a variety of scan rates, are shown in Fig. 1. The CVs show strong redox peaks despite the redox centre being more than 20 Å from the electrode surface. The peak current was linear with scan rate, indicative of a surface bound species, and the transfer coefficient, α, was 0.5 for both the cathodic and anodic process. The standard electrode potential ($E^{\circ\prime}$) was 287 mV with a E_{FWHM} of 147 mV. Both the greater than ideal FWHM (ideally 90.6/*n* mV, where *n* is the number of electrons transferred) and a non-zero peak separation (ΔE_p) (ideally $\Delta E_p = 0$ at slow scan rates but in common with aliphatic alkanethiols[15] this is not observed) have been attributed to a redox species being in a range of environments with a range of $E^{\circ\prime}$.[9,16] We have noted previously[15] that fabricating redox active SAMs by assembling the SAM and then attaching the redox molecule, although compatible with the stepwise fabrication of molecular scale devices, results in broader FWHM than observed with electrodes where a redox active alkanethiol was attached directly to the electrode. With **2**, the presence of two carboxylic acid moieties on the end presents the possibility of there being either one or two ferrocenes attached to the NB. To explore this possibility a model bridge compound **4** was reacted with ferrocene methylamine in aqueous solution as

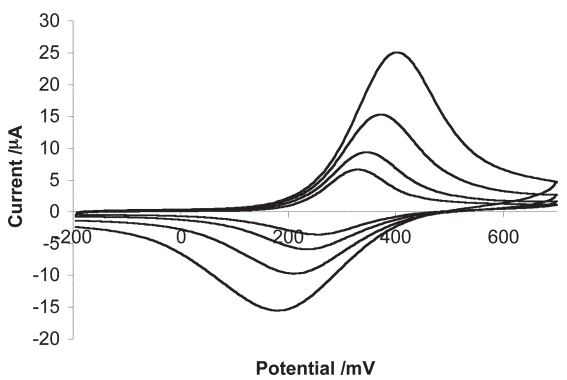

Fig. 1 Cyclic voltammograms of ferrocene methylamine attached to a self-assembled monolayer of **2** at scan rates of 1, 2, 4 and 8 V s^{-1} (from inner to outer).

described above to ascertain whether the coupling of two ferrocenes is possible. The separation of components from this reaction mixture showed that some disubstituted **4** was produced, as confirmed by NMR spectroscopy, and therefore it was plausible that two ferrocene units could be attached to bridge molecules self-assembled onto the electrode surface. However, the charged passed during either the oxidation or reduction of the ferrocene corresponds to a surface coverage of 2.5×10^{-11} mol cm^{-2}. With this surface coverage, assuming a homogeneous distribution, there is approximately 6.6 nm^2 per ferrocene which suggests there is no association between ferrocene molecules and that **3a** would be the dominant species rather than **3b** on the electrode surface.

The apparent rate constant of electron transfer (k_{app}) calculated from the variation in peak separation of the anodic and cathodic peaks with scan rate was 21 s^{-1}. This rate is almost three orders of magnitude greater than the k_{app} of 0.022 s^{-1} for ferrocene attached to a SAM of mercaptohexadecanoic acid.

The rate of electron transfer through the NB is significantly faster than through the mercaptohexanoic acid despite both systems being composed of entirely sp^3 saturated carbon–carbon bonds. The greater rate of electron transfer of the NBs has been shown in solution studies[17] to be due to the strict adherence to the all *trans* configuration of the rigid bridge molecules.[18] The rapid rate of electron transfer is accompanied by the versatility of having a monolayer system that can project out above the plane of a mixed self-assembled monolayer of a shorter alkanethiol due to the rigidity of the NB and greater monolayer stability because of the two thiolate feet. We will exploit the rapid rate of ET and the ability of rigid molecules to project above the plane of the diluent layer to plug these molecules into the redox active centre of the enzyme glucose oxidase with a view to making efficient bioelectronic devices. The stability of the NB bridges is also an advantage over the conjugated molecular wires, although these molecular wires do possess considerably faster rates of electron transfer. For oligophenyleneethynylene bridges[3] and oligophenylenevinylene bridges[2] of similar length the rate constants of electron transfer are 5×10^5 s^{-1} and 3.6×10^6 s^{-1} (rates too fast to measure by cyclic voltammetry). The far greater rate constants for the conjugated systems are clearly advantageous at this stage despite the poorer stability (although it should be noted that with the NB the ferrocene is attached to the ends of the bridge by a 4 carbon flexible chain, whilst in the two conjugated systems the ferrocene is connected directly at the end of the conjugated wire. This difference should account for the more than one order of magnitude greater rate of ET). The far greater rate of ET with the conjugated bridges is attributed to greater electronic coupling between the electrode and the ferrocene.

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