Polyaminoquinone self-assembled films on electrodes: synthesis of all-organic molecular wires by solution phase epitaxy

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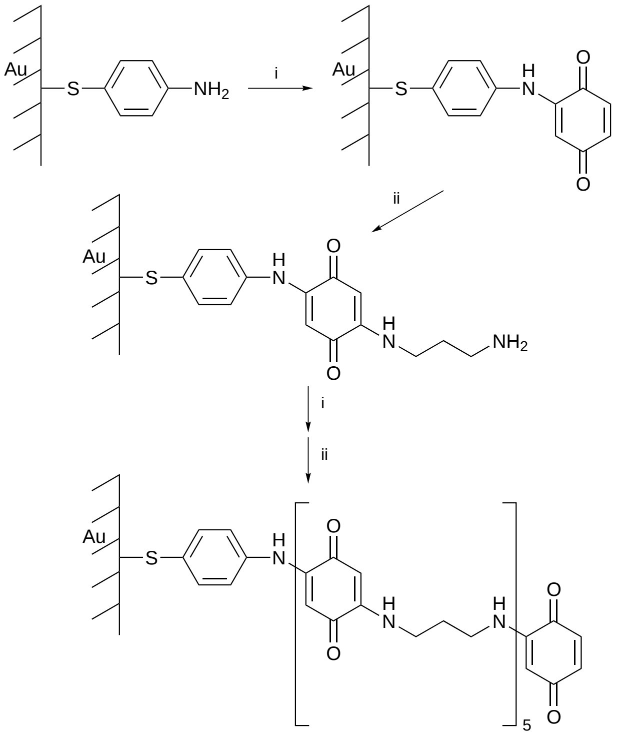
Redox active molecular wires consisting of successive benzoquinone and diamino moieties are formed on a gold surface using repetitive self-assembly and solution epitaxy.

Quinones constitute an interesting group of electroactive compounds which take part in several biologically important oxidation–reduction processes. The electrochemistry of quinones has been extensively studied and their complex redox mechanisms considered in detail.[1a,2] The reactivity of quinones towards nitrogen addition is also well known.[1b] The reaction of 1,4-benzoquinone with an amine is kinetically facile and proceeds, in the presence of an oxidant, *via* successive addition of amines predominantly at the 2,5-positions. Nitrogen addition lowers the redox potential of quinone and, therefore, unreacted benzoquinone can serve as an oxidant in the process. Several aliphatic diaminoquinones have been prepared and their spectral and electrochemical properties studied.[3,4]

Berlin and co-workers have employed 1,4-amino addition, using aromatic diamines, to prepare aminoquinone polymers.[1c] These polymers are obtained as dark powders, which are insoluble in most solvents, rendering their purification and study difficult. They were, however, found to possess semiconducting properties, which makes them interesting candidates for molecular wires and other devices in molecular electronics.[5] In order to avoid problems in the synthesis and purification of aminoquinone oligomers we have utilised repetitive self-assembly onto a solid substrate in order to grow aminoquinone molecular wires by solution epitaxy. The process involves successive immobilisation of quinones and diamines on a suitable primed electrode surface (Scheme 1), as originally suggested by Katz and Schmidt.[6] We have chosen *p*-mercaptoaniline for surface priming because it has been shown to form well ordered monolayers on Au(111).[7]

The sequential formation of polyaminoquinone on the surface of a polycrystalline gold electrode was followed by cyclic voltammetry (Fig. 1).† The gold electrode primed with the monolayer of *p*-mercaptoaniline exhibits no electroactivity in the potential range studied. After the immobilisation of the



Scheme 1 *Reagents and conditions*: i, benzoquinone (0.5 M), MeCN–phosphate buffer (pH 7.2) (1 : 1), 3 h; ii, 1,3-diaminopropane in EtOH (30% v/v), 40 min

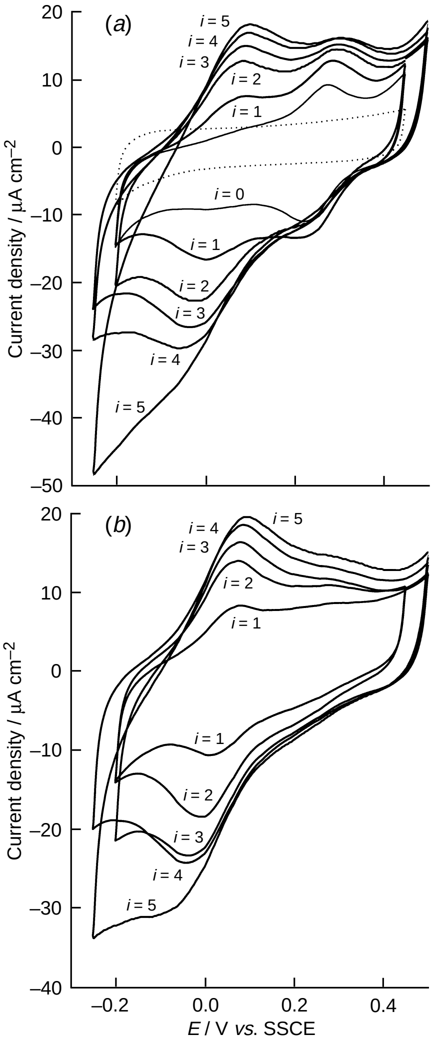


Fig. 1 Cyclic voltammograms of (*a*) quinone terminated Au–SPhNH–(Q–A)$_i$–Q, and (*b*) amino terminated Au–SPhNH–(Q–A)$_i$ electrodes in 0.5 M $HClO_4$ at 100 mV s^{-1}. Dotted curve is Au–SPhNH$_2$ electrode.

first quinone the peaks due to the oxidation and reduction of amino substituted quinone appear at +0.26 V *vs.* sodium saturated calomel electrode (SSCE). The redox potential shifts 58 mV decade^{-1} to the cathodic direction in the pH range from 0 to 8, showing the ($2H^+$, $2e^-$) nature of the reaction. The surface density of aminoquinone was calculated from the charge under the oxidation wave. Using the real surface area of the electrode, determined by oxidation of the bare gold electrode in 0.5 M H_2SO_4 up to the Burshtein minimum, a surface density of 1.75×10^{-11} mol cm^{-2} was obtained.[8] This is somewhat lower than reported for naphthoquinone or benzoquinone monolayer electrodes with aliphatic amino thiol primer.[6,9] The width of the voltammetric peak is 86 mV, which is much larger than the theoretically expected value of 90.6/*n* mV.

Fig. 1(*a*) and (*b*) shows the voltammograms of the successively formed quinone and amino terminated surfaces, respectively. Qualitatively the trend is very clear. The peaks due to monoaminoquinone in the Au–SPhNH–Q electrode (Q = benzoquinone) disappear after treating the electrode with 1,3-diaminopropane (A). Instead, a pair of peaks appears at 0.045 V *vs.* SSCE indicating the formation of a Au–SPhNH–Q–A electrode. A small residual peak can be seen at +0.26 V, which shows that the conversion is not complete, and the charge under this peak corresponds to *ca.* 12% of the total charge. After further reaction with benzoquinone the peak originating from monoaminoquinone reappears. It disappears after treatment with 1,3-diaminopropane with a concomitant increase in the peak attributable to diaminoquinone. These observations indicate the formation of Au–SPhNH–Q–A–Q and Au–SPhNH–Q–A–Q–A surfaces, respectively. It is noteworthy that the amount of the residual monoaminoquinone does not increase in the last step. The same process can be repeated with the same observed voltammetric behaviour, so that the final curves in Fig. 1(*a*) and (*b*) correspond to Au–SPhNH–$(Q–A)_5$–Q and Au–SPhNH–$(Q–A)_5$ electrode surfaces, respectively.

The quantitative determination of the charges under the waves in the cyclic voltammograms is complicated due to the large width of the waves. We chose to fit the data to the sum of two reversible surface waves, with separate linear baselines.[10]

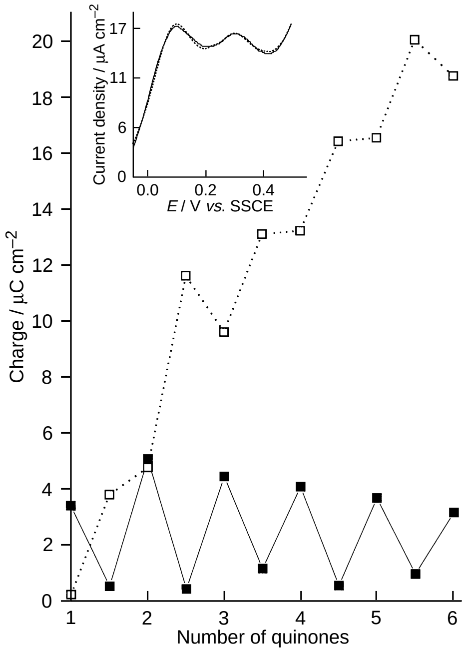


Fig. 2 Charges calculated from oxidation peaks in Fig. 1; monoaminoquinone (■) and diaminoquinone (□). Inset shows the fit (dashed line) to the curve with *i* = 4 in Fig. 1(*a*) (solid line).

The results of such analysis are shown in Fig. 2, where the half-integer values on the *x*-axis refer to amino terminated surfaces. The inset shows an example of fitting results and demonstrates the reasonably good success of the simple model used. The charge due to the monoaminoquinone oscillates between *ca.* zero and 4 µC cm^{-2}, with very little damping. On the other hand, the charge due to diaminoquinones increases upon amine addition but stays more or less constant during the addition of quinone to the chain. This kind of behaviour is exactly what is expected for the sequential formation of polyaminoquinone chains on the electrode surface. Other charge integration procedures used all produced qualitatively the same result, *i.e.* a saw-tooth curve for the monoaminoquinone and a staircase curve for the diaminoquinone.

We have demonstrated the feasibility of building long aminoquinone chains on a solid substrate by repetitive self-assembly. The approach is very flexible and using only commercially available quinones and diamines it is possible to create, with minimal synthetic work, a large variety of structures with different properties. Preliminary results show that Au–SPhNH–$(Q–A)_5$–Q electrode retains *ca.* 70% of its total electroactivity after 40 days when stored in water under ambient atmosphere. The data in Fig. 2 show that the conversion efficiency is not markedly decreased with increasing number of quinone units. This implies that the reactivity of the chains, as a function of length, is not a limiting factor for attainable aminoquinone chain lengths. On the other hand, peak separations and widths increase with increasing chain length. These effects can be attributed to non-equal positions of the quinones within the chain and to the intra-chain interactions between the quinone redox centres. A detailed study of the structure, electrochemical and spectroelectrochemical properties of mono- and poly-aminoquinone modified electrodes, with aliphatic and aromatic diamines, is underway in our laboratory and will be reported in forthcoming papers.

Footnotes

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† The Au rod was cleaned in hot piranha solution for 2 min (**WARNING!** Piranha solution reacts violently with organic material and should be treated with extreme care), rinsed with water (18 MΩ, Millipore) and immersed in 20 mM ethanol solution of bis(4-aminophenyl) disulfide (Aldrich) overnight.

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