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Self-assembled monolayers of *n*-hexanethiol and 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol on polycrystalline nickel substrates†

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It is shown in this work that *n*-hexanethiol and 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol form stable monolayers on electrochemically reduced polycrystalline nickel substrates, but not on the oxidised ones. Both thiols, when directly adsorbed on the nickel surfaces without electrochemical pretreatment, show significant proportions of oxidised sulfur species (sulfinates and sulfonates) in their XPS spectra. In contrast, the electrochemical pretreatment leads to monolayers exhibiting S 2p levels essentially characteristic of sulfur atoms bound to metallic sites and corroborating the good chemical stability and resistance to electrochemical oxidation of such monolayers.

Introduction

Conducting polymers such as polythiophene are often synthesised by electrochemical oxidative coupling of the heterocyclic moieties of the monomers. Direct electropolymerisation at a metal anode is of special interest from the point of view of surface coatings with organic films. First, the conductivity of the growing layer allows an easy control of the film thickness, which is in contrast to similar processes where intrinsically insulating polymers are electrochemically deposited. In that respect, the method has many features in common with galvanotechniques, the main difference being in the electrode bias. Second, possible applications are many and promising: they range from protective layers to electronic devices.[1]

In most cases, electrodeposition of conducting polymers (aniline, pyrrole, *etc.*) is carried out on inert electrodes and results in the precipitation of the growing polymer to form, upon the electrode surface, an insoluble layer, mechanically attached, but easily peeled off. To circumvent the problems raised by such weakly bound coatings, a two-step procedure has been proposed by which self-assembled monolayers (SAM) of selected thiols, *e.g. n*-alkanethiol, phenyl- and pyrrolyl-alkanethiols, are formed on the metal substrate and then suitable monomers are electrodeposited on the modified electrodes.[2–5] The approach exploits the affinity of the thiol group, —SH, for noble (Au, Pt)[6] as well as several oxidisable (Cu, Fe, Ni, *etc.*)[2,7–11] metals. For instance, very good adhesion is observed for the films electrodeposited on the phenyl- and pyrrolyl-alkanethiol monolayers, but not on the alkanethiols. In 1993, Kowalik *et al.* reported a one-step oxidative polymerisation directly from a solution of 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]propanethiol (**TPT-C$_3$SH**) on Pt and Au electrodes to produce films exhibiting remarkable stability and toughness.[12] Common to both approaches is the fact that adherence properties of the electrodeposited films are observed for alkanethiol chains terminated with reactive groups such as phenyl, pyrrolyl and 2,5-di(2′-thienyl)pyrrol-1-yl (**TPT**). In the one-step procedure, thin films of **TPT-C$_3$SH** on platinum could not be detached when in their electrochemically compensated state, but could be removed in their doped state.[12] In the two-step approach, films are adherent to the substrate in both the electrochemically compensated and doped states.[2] We suspect that, in the one-step process, **TPT-C$_3$SH** undergoes ready electropolymerisation and that adhesion results from the binding with the metallic substrate of the available alkylthiol pendant groups of the electrodeposited polymer in the interfacial region. In the approach where the electrode is chemically modified with phenyl- or pyrrolyl-alkanethiols, the thiol strongly binds to the metallic substrate and attractive interactions, possibly including covalent bonds, are established between the phenyl or pyrrolyl groups at the first stages of the polymer film growth, hence the resulting adhesion.

Our main goal is to construct compact and organised monolayers on oxidisable metals that can sustain the electrodeposition of conductive polymers and yield electroactive films with good morphological, adherence and electronic properties. A difficulty with the otherwise attractive approach proposed by Kowalik *et al.* is the need to graft alkanethiol chains on the polymerisable monomers. This can have adverse consequences such as complexity and cost of the synthesis of the monomers,[13] diminished conductivity[12,14] and quality in the morphological and electronic properties of the polymer films. In the two-step approach, the choice of the monomer is in principle independent of the nature of the SAM. However, the electrochemical properties of the modified electrode should allow electrodeposition without oxidation of the metal substrate and promote strong (ideally covalent) attractive interactions between the organic monolayer and the electrodeposited polymer. Accordingly, it is reasonable to assume that, the lower the oxidation potential of the end groups at the monolayer surface, the better the chances to promote electrodeposition of conductive polymers. In that respect, **TPT-C$_3$SH**, with a reported oxidation potential of $+0.89$ V *vs.* Ag/Ag$^+$ measured[12] by cyclic voltammetry in acetonitrile solution using EtN$_4$BF$_4$ (0.1 M) is certainly a good candidate. The corresponding value for pyrrole in the same conditions would be $+0.91$ V (adapted from ref. 15). By its structure, analogous to **TPT-C$_6$SH** shown in Fig. 1, **TPT-C$_3$SH** also provides two possible sites, α and β, for the oxidative coupling to take place.

In this contribution we study the formation and properties of *n*-hexanethiol and **TPT-C$_6$SH** monolayers (Fig. 1) adsorbed on polycrystalline nickel substrates, either oxidised (Ni-ox) or electrochemically reduced (Ni-red). Both *n*-hexanethiol (**C$_6$SH**)

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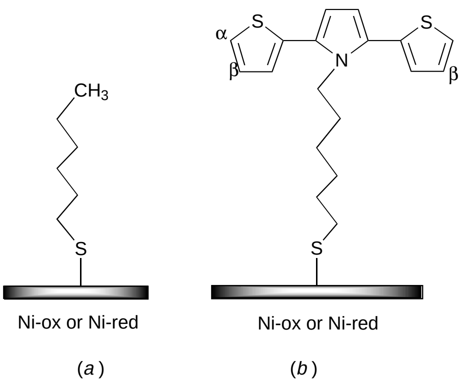


Fig. 1 Schematic description of (*a*) *n*-hexanethiol (**C$_6$SH**) and (*b*) 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol (**TPT-C$_6$SH**) molecules on the polycrystalline surfaces, Ni-ox or Ni-red

and **TPT-C$_6$SH** include the same alkanethiol chain, $-(CH_2)_6-SH$; hence the properties of their chemisorbed monolayers are reported comparatively to identify and account for possible influences of the bulky **TPT** group.

Like other common oxidisable metals (Fe, Cu, *etc.*), Ni is an interesting substrate for technological applications. For instance, Ni can be used as the final coating in separable electrical contacts on which growth on the metal of poorly conducting layers (oxides, contaminants) due to environmental conditions has up to now limited its use to most common applications. We have recently shown that excellent tribological behaviour can be obtained when electrochemically reduced polycrystalline Ni substrates are modified with *n*-dodecanethiol molecules.[16]

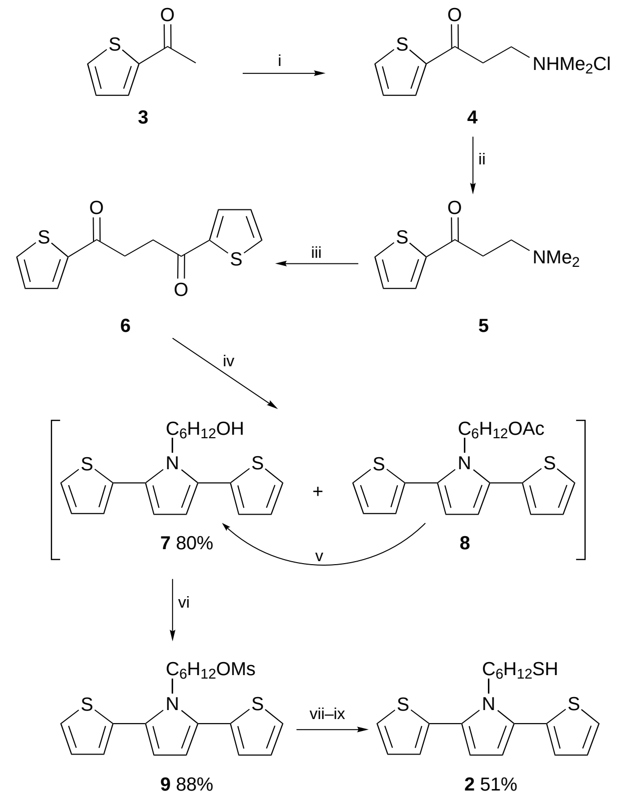
TPT-C$_6$SH differs from **TPT-C$_3$SH**[12] by the presence of three additional methylenes in the alkanethiol pendant chain. This slight difference in the structural feature has been selected as a compromise between expected improved molecular organisation in the monolayer, known to be promoted by longer alkyl chains,[17] and the possibility for future electrodeposition of conductive polymers to proceed. Furthermore, there are clues that electrodeposition of conductive polymer films on organised monolayers leads to chains with longer conjugation pathways.[18] Finally, the delamination rate of coatings is determined not by the thickness of the coating, but by the bonds that prevail at the interface as well as the packing and the molecular organisation in the monolayer,[9] hence the use of a C$_6$ alkyl chain in the present study.

Experimental

6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol 2 (TPT-C$_6$SH) (Scheme 1)

Synthesis of 2-acetylthiophene 3. A solution of tin tetrachloride (5.22 g, 20 mmol) and freshly distilled acetyl chloride (1.57 g, 20 mmol) in 10 ml of dry dichloromethane was added dropwise at room temp over 0.5 h to a dichloromethane (10 ml) solution of thiophene (1.68 g, 20 mmol) under argon atmosphere. The mixture was stirred for an additional 30 min. Water (20 ml) and diethyl ether (100 ml) were added, the organic phase was washed once more with water and aqueous hydrogen carbonate, dried over MgSO$_4$ and evaporated. The essentially pure crude product (2.42 g, 96% yield) was used without purification. ν/cm^{-1} (liq. film): 3089, 3001, 2922, 1662, 1517, 1414, 1355, 1273, 725. δ_H (CDCl$_3$) 2.55 (s, 3H), 7.12 (m, 1H), 7.67 (m, 2H).

Synthesis of compounds 4, 5 and 6. These compounds were prepared according to literature procedures:[19] **4**, mp 179–180 °C, 72% yield; **6**, off-white solid, mp 129–131 °C, 71% yield, δ_H (CDCl$_3$): 3.4 (s, 4H), 7.14 (m, 2H), 7.64 (m, 2H), 7.81 (m, 2H).



Scheme 1 *Reagents and conditions*: i, (CH$_2$O)$_n$, Me$_2$NH HCl, EtOH, conc. HCl, reflux, 40 h; ii, aq. NH$_4$OH; iii, thiophene-2-carbaldehyde, NaCN, DMF, room temp.; iv, H$_2$NC$_6$H$_{12}$OH, C$_6$H$_6$, AcOH, reflux, 50 h; v, EtOH, aq. NaOH, reflux, 4 h; vi, MsCl, DMAP, pyridine, CH$_2$Cl$_2$; vii, thiourea, reflux; viii, NaOH, reflux; ix, HCl

Synthesis of alcohol 7. Diketone **6** (2.5 g, 10 mmol), 6-aminohexan-1-ol (1.2 g, 10.5 mmol) and acetic acid (12 ml) were refluxed in 25 ml of benzene for 50 h. At this point the reaction had reached only 50% conversion. On cooling the mixture to room temp., the unreacted diketone crystallised out and was recovered by filtration. The solution was concentrated by evaporation, the residue taken up with diethyl ether, washed successively with aqueous sodium hydrogen carbonate, then with water, dried over MgSO$_4$ and evaporated. The crude product (1.91 g) thus obtained contained the desired alcohol **7** and its acetate. For hydrolysis of the latter, the mixture was dissolved in ethanol (20 ml) containing 1 g of NaOH and 2 ml of water and refluxed for 4 h. Conventional work-up of this reaction mixture followed by column chromatographic purification (SiO$_2$, eluent pentane–diethyl ether, 50:50 v/v) led to 1.33 g of pure **7** (80% yield based on consumed **6**). Analysis for C$_{18}$H$_{21}$NOS$_2$, calc. C: 65.21, H: 6.39; found C: 64.24, H: 6.26%. ν/cm^{-1} (liq. film): 3356, 3102, 3071, 2931, 2857, 1461, 1404, 1052, 843, 767, 730, 697. δ_H (CDCl$_3$): 1.18 (m, 4H), 1.40 (m, 2H), 1.50 (bs, 1H), 1.58 (m, 2H), 3.52 (t, J 7 Hz, 2H), 4.17 (m, 2H), 6.33 (s, 2H), 7.05 (m, 2H), 7.32 (m, 2H). δ_C (CDCl$_3$): 24.9, 26.0, 30.9, 32.3, 44.9, 62.4, 110.7, 125.1, 125.8, 127.2, 128.4, 135.

Synthesis of mesylate 9. The alcohol **7** (1.324 g, 4 mmol), methanesulfonyl (mesyl) chloride (0.58 g, 5 mmol), 4-dimethylaminopyridine (DMAP, 0.61 g, 5 mmol) and pyridine (1.28 g, 16 mmol) were dissolved in 15 ml of dry dichloromethane at 0 °C and stirred for 6 h at room temp. The mixture was then acidified with 10% HCl, extracted with diethyl ether, and the ethereal layer washed with water, dried and evaporated to give 1.77 g of crude product. Purification by column chromatography (SiO_2, eluent pentane–diethyl ether, 50:50 v/v) led to 1.43 g (88% yield) of **9**. δ_H ($CDCl_3$) 1.1–1.25 (m 4H), 1.5–1.63 (m, 4H), 2.93 (s, 3H), 4.05–4.20 (m, 4H), 6.32 (s, 2H), 7.05 (m, 4H), 7.31 (m, 2H).

Synthesis of thiol 2 (TPT-C$_6$SH). The mesylate **9** (1.43 g, 3.5 mmol) and thiourea (0.38 g, 5 mmol) were refluxed in 10 ml of degassed ethanol under argon for 16 h (disappearance of **9**). Concentrated aqueous sodium hydroxide (5 ml) was added and the mixture refluxed for another 10 h. After cooling to room temp., the mixture was acidified with 10% HCl, extracted with diethyl ether and the ethereal layer washed with water, dried and evaporated. Column chromatographic purification of the crude product (SiO_2, eluent pentane–diethyl ether, 9:1 v/v) led to 0.63 g (51% yield) of thiol **2** (**TPT-C$_6$SH**) as a yellow–green fluorescing viscous liquid which solidified on standing. Analysis for $C_{18}H_{21}NS_3$: calc. C: 62.20, H: 6.09, found: C: 62.09, H: 5.96%. ν/cm^{-1} (liq. film): 3101, 3069, 2929, 2854, 2565, 1461, 1402, 843, 766, 695. δ_H ($CDCl_3$) 1.10–1.32 (m, 5H), 1.42–1.60 (m, 4H), 2.42 (q, J 7 Hz, 2H), 4.17 (t, J 7 Hz), 2H), 6.35 (s, 2H), 7.06 (m, 4H), 7.32 (m, 2H). δ_C ($CDCl_3$) 24.3, 25.6, 27.5, 30.8, 33.5, 44.8, 110.7, 125.2, 127.2, 128.2, 134.

Chemical modification of polycrystalline nickel surfaces with C$_6$SH and TPT-C$_6$SH

Chemicals. *n*-Hexanethiol (Acros, 98%, 21527–0050), $HClO_4$ p.a. (Acros, 22. 331. 21), acetone (Aldrich, 99.9%, HPLC grade 27, 072-5), H_2O, ultrapure water (18 MΩ cm), absolute ethanol p.a. (Merck, 1.000983.2500), NaOH Suprapur (Merck, 017 C762966) were used without additional purification.

Metal substrates and monolayer preparation. Disk-shaped metal substrates (thickness 6 mm) were cut from polycrystalline Ni rods (Ø = 6.35 mm, Aldrich, 99.99%, 26,707-4) and mechanically polished using various grit diamond pastes down to 1 μm. Before use for monolayer adsorption, these substrates were rinsed with copious amounts of acetone. Two types of metallic substrates differing in their surface chemical state were compared. The first type (Ni-ox) consists of nickel surfaces mirror polished, cleaned as indicated above and used directly for the monolayer adsorption. The second type (Ni-red) concerns nickel surfaces, polished, cleaned and electrochemically reduced prior to thiol adsorption. The electrochemical pretreatment consists of a 20 min reduction in an aqueous solution of $HClO_4$ (1 M) of the nickel substrates at −0.7 V *vs.* a saturated calomel electrode (SCE).

The monolayers were formed by immersion of the nickel substrates in 1×10^{-3} M solutions of **C$_6$SH** or **TPT-C$_6$SH** in hexane for 12 h. The samples were then quenched with hexane and ultrasonically cleaned for 15 min in hexane to remove the excess of thiol molecules physisorbed on the monolayer surfaces. The samples were finally dried under an argon flow and used immediately for characterisation.

Monolayer characterisation

X-Ray photoelectron spectroscopy (XPS) is mainly used here to control the elemental composition of the monolayer and identify the oxidation states of the nickel and sulfur atoms located at the top layers. The spectra were recorded with an SSX-100 spectrometer using monochromatised Al-Kα radiation (1486.6 eV). All reported spectra, except the one shown in Fig. 6(*a*) (9 weeks), were recorded using identical conditions. The samples were analysed at 35° take off angle, which corresponds to a sampled thickness of approximately 4 nm.

Fig. 2(*a*) and (*b*) show the XPS spectra of the Ni 2p and O 1s regions of a representative Ni-ox surface. From published literature on nickel hydroxide, β-$Ni(OH)_2$ and $Ni(OH)_2$ slightly hydrated,[20] it is known that the Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ lines are located around 855.8 and 873.4 eV, respectively.

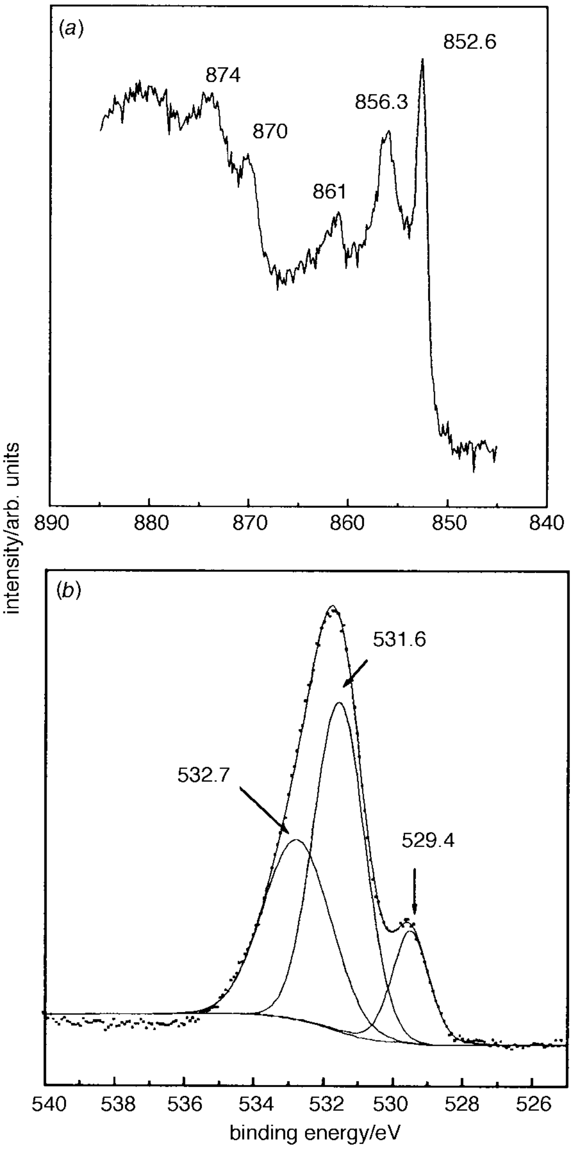


Fig. 2 XPS spectra of the (*a*) Ni 2p and (*b*) O 1s core levels of a bare Ni-ox polycrystalline surface

Associated with $Ni(OH)_2$ a shake-up structure around 861.4 eV also occurs. The Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ lines characteristic of metallic nickel are found at 852.7 and 870.0 eV, respectively.[20] The shape of the spectrum and the line positions in Fig. 2(*a*) point to a Ni-ox surface composed of a mixture of metallic and oxidised nickel, $Ni(OH)_2$, atoms. Three features are also noted in the O 1s line; they arise at 529.4, 531.6 and 532.7 eV. They nicely correspond to values reported for slightly hydrated $Ni(OH)_2$[20] where three components are also found; they are assigned to ionic oxygen (529.0 eV), $Ni(OH)_2$ and C with O (530.5 eV), and finally H_2O and O with C (531.8 eV), respectively.[9,20] The exposure time to the atmosphere necessary to transfer the Ni-red surfaces from the electrochemical cell to the spectrometer and mount the samples in the analysis chamber is too long (~30 min) to maintain the surface nickel atoms in their reduced state, hence the corresponding XPS spectra resemble those of Ni-ox substrates and are not shown in this paper.

In the case of the modified nickel surfaces with the thiol molecules, the Ni 2p, O 1s and S 2p core levels were calibrated by reference to the recorded C 1s peak characteristic of the alkyl moiety of the compounds and conventionally set at 284.5 eV, which is a commonly used procedure for organic films.[9,21] In the case of the hexanethiol chain, the C 1s line mainly consists of carbon atoms linked to hydrogen atoms and emerges as a well-defined and intense structure. With a calibration performed with respect to that intense structure, the energy at which the S $2p_{3/2}$ signal arises for the free thiols, disulfides, thiolates, sulfinates and sulfonates is equal to 163.3, 163.3, 161.8, 165.5 and 168.0 eV, respectively.[9] In the case of **TPT-C$_6$SH**, the sulfur atoms from the two thiophenes contribute to the S 2p region; the S $2p_{3/2}$ component for thiophene is located at 164.3 eV.[20] The S 2p line is naturally a doublet structure, (S $2p_{3/2}$) and (S $2p_{1/2}$), where the spacing between the components is equal to 1.13 eV and the theoretical intensity ratio (S $2p_{3/2}$)/(S $2p_{1/2}$) is equal to 2/1. Deconvolution of the S 2p lines has been carried out assuming a doublet structure and the theoretical intensity ratio 2/1 between the two components.

Electrochemical characterisation of nickel with and without monolayers was carried out in a conventional three-electrode cell. A calomel electrode saturated with KCl was used as reference electrode, a platinum grid as counter-electrode and the nickel disks as working electrodes. The cell was connected to a TACUSSEL PJT 24 potentiostat/galvanostat linked to an IMT1 interface. Characterisation was performed in a 0.1 M NaOH aqueous solution (deoxygenated by argon bubbling for 30 min prior to measurements) with a potential scan ranging from -0.3 to $+0.6$ V at 10 mV s^{-1}. Voltammograms were digitally recorded using the VOLTMASTER program.

Results and Discussion

This section is organised in two main parts. In the first one we focus our attention on the XPS characteristics of the **C$_6$SH** and **TPT-C$_6$SH** monolayers freshly formed on both Ni-ox and Ni-red surfaces. The second part concerns the stability of such monolayers under ambient conditions for periods of 9 weeks and response to cyclic voltammetry in a rather aggressive medium.

XPS characteristics of the monolayers

Fig. 3 shows the Ni 2p, O 1s and S 2p core level regions of the monolayers of **C$_6$SH** chemisorbed on Ni-ox and Ni-red substrates recorded 30 min after the dipping step. Significant differences are observed between the Ni-ox and Ni-red samples.

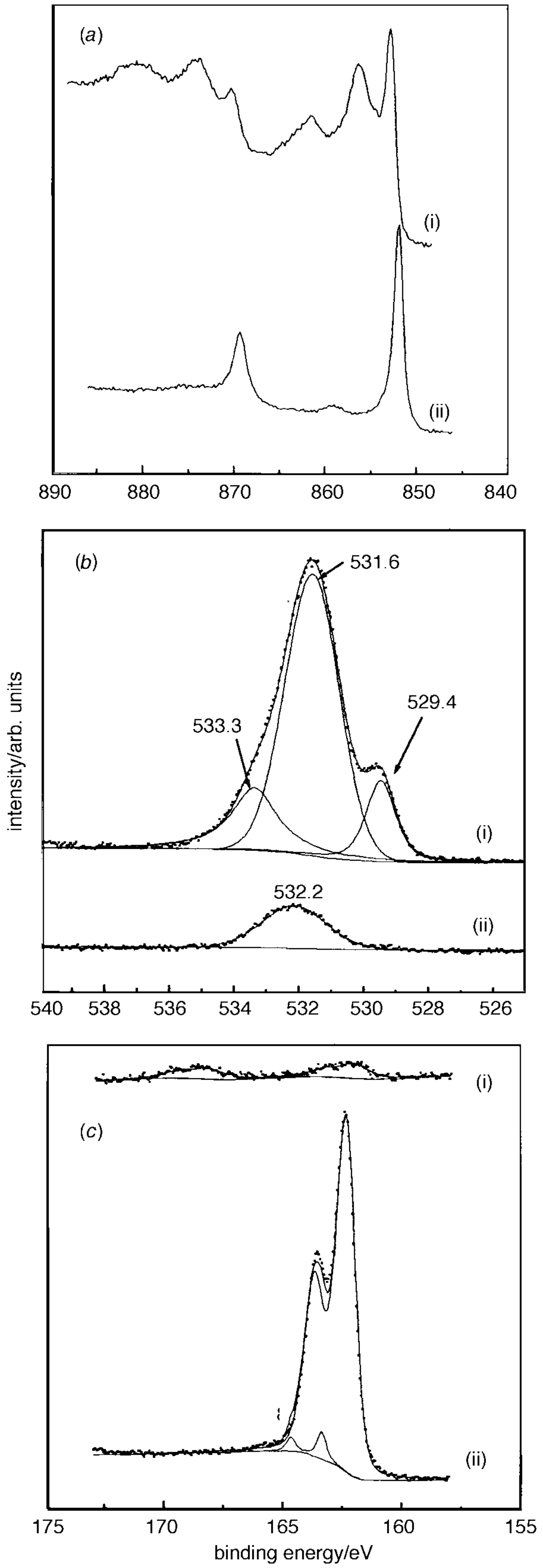


Fig. 3 XPS spectra of the (*a*) Ni 2p, (*b*) O 1s and (*c*) S 2p core levels of (i) Ni-ox and (ii) Ni-red polycrystalline surfaces modified with *n*-hexanethiol (**C$_6$SH**)

As in the case of the reference Ni-ox surface [Fig. 2(*a*)], the Ni 2p spectrum of the modified Ni-ox substrate [Fig. 3(*a*)] exhibits the spectral features of both oxidised, Ni(OH)$_2$, and metallic nickel atoms with comparable intensities. The situation is totally different in the case of the **C$_6$SH** monolayer adsorbed on a Ni-red substrate for which only the characteristic features of metallic nickel are detected in the Ni 2p spectrum [Fig. 3(*a*)]. This means that reduction in the electrochemical cell immediately followed by immersion in the **C$_6$SH** solution keeps the nickel atoms under the monolayer in their metallic state. This is corroborated by the spectroscopic characteristics of the O 1s [Fig. 3(*b*)] and S 2p [Fig. 3(*c*)] lines. In the case of **C$_6$SH** on Ni-ox, the intense O 1s line exhibits the three peaks already observed for the reference Ni-ox surface [Fig. 2(*b*)]. The presence of these lines at 529.4, 531.6 and 533.3 eV indicates the presence of Ni(OH)$_2$, H$_2$O and possibly oxygen containing carbon contaminants in amounts comparable to what was observed on the Ni-ox reference substrate [Fig. 2(*b*)]. This is in contrast to the Ni-red case [Fig. 3(*b*)] for which a low intensity O 1s line appears as a single peak centred at 532.2 eV, which is more typical of oxygen in the form of hydroxy ($-$OH).[9,20] In the wide scan spectra, not reported here but very similar to those reported in figure 1 of ref. 4 for *n*-dodecanethiol, the O 1s peak intensity was also substantially lower for Ni-red than Ni-ox surfaces. Very instructive is the inspection of the S 2p spectra shown in Fig. 3(*c*) for **C$_6$SH** monolayers on Ni-ox and Ni-red. In the case of Ni-ox, the S 2p line is composed of two large features of very low intensity: one centred around 162.9 eV and the other around 169.3 eV. The first one corresponds to the doublet structure (S $2p_{3/2}$) at 161.8 and (S $2p_{1/2}$) at 163.0 eV as observed in the case of thiols chemisorbed on gold substrates in the form of thiolates.

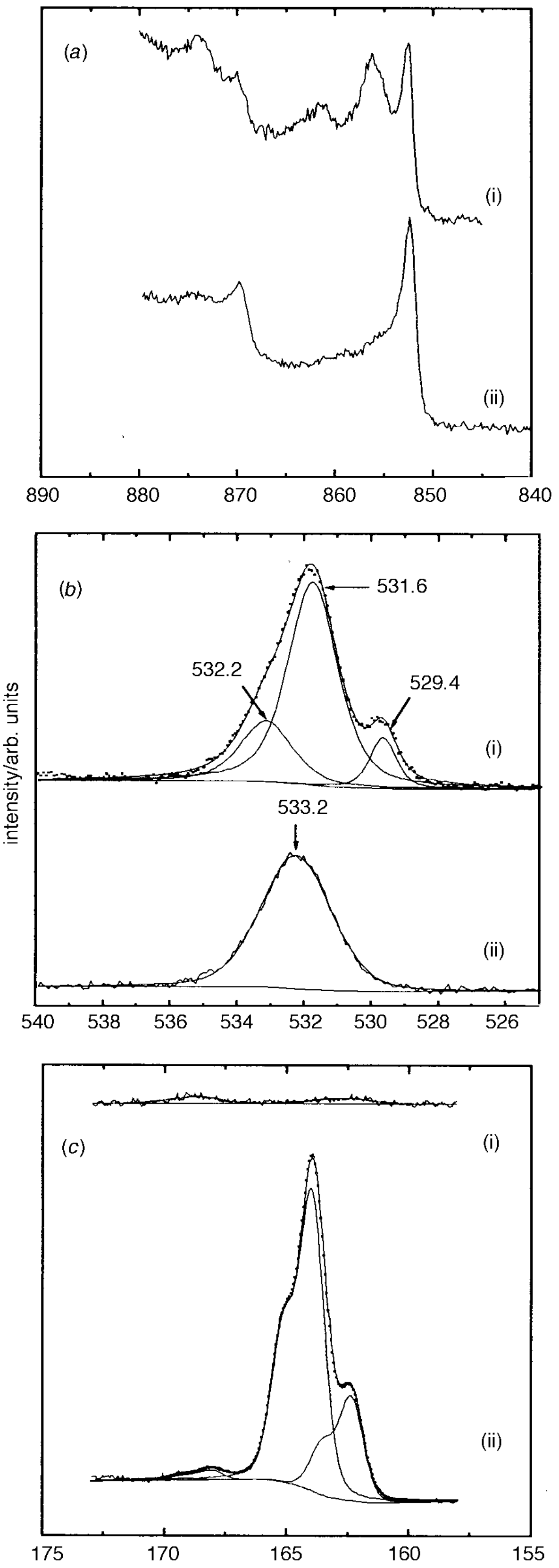


Fig. 4 XPS spectra of the (*a*) Ni 2p, (*b*) O 1s and (*c*) S 2p core levels of (i) Ni-ox and (ii) Ni-red polycrystalline surfaces modified with 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol (**TPT-C$_6$SH**)

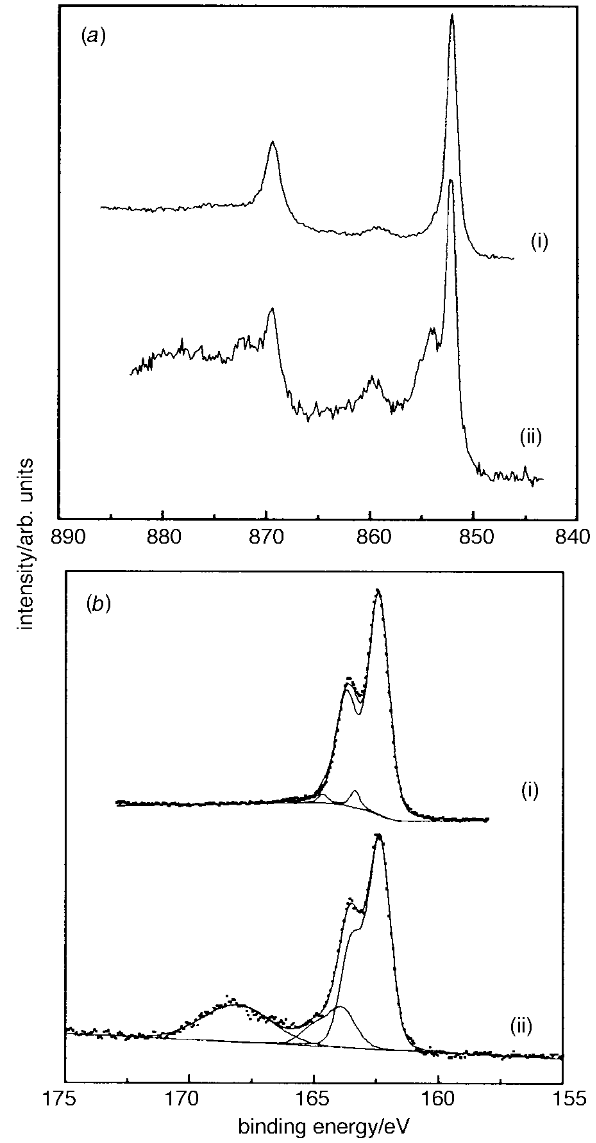


Fig. 5 XPS spectra of the (*a*) Ni 2p and (*b*) S 2p core levels of Ni-red polycrystalline surfaces modified with *n*-hexanethiol (**C$_6$SH**), (i) fresh and (ii) after 9 weeks of exposure to atmospheric oxygen

The doublet structure is not very apparent because of the low intensity and poor quality of the spectrum in that region, which also indicates very low chemisorption on the substrate. The group centred at 169.3 eV suggests that the amount of oxidised sulfur species (sulfinates and sulfonates) is comparable to that of the thiolates and disulfides. A different situation prevails for the monolayer adsorbed on the Ni-red surface. First, the group at 169.3 eV characteristic of the oxidised sulfur species is not detected, which correlates well with the already mentioned low intensity of the O 1s line. The XPS data point to the fact that the electrochemical treatment, as in the case of *n*-dodecanethiol,[4] has reduced the amount of nickel oxides to the point that the oxidised species cannot be detected. The S 2p doublet is also closer to the expected theoretical ratio 2/1; the small deviation is likely due to small amounts of disulfides as suggested by the deconvolution in the figure.

A similar analysis can be carried out on the Ni 2p, O 1s and S 2p core level regions of the **TPT-C$_6$SH** chemisorbed monolayers on Ni-ox and Ni-red substrates shown in Fig. 4. A comparison between Fig. 3 and 4 reveals a close similarity in the XPS features. The only differences to be noted are in the shape of the S 2p levels due to the thiophene sulfur contribution, on the one hand, and the presence of traces of oxidised species in the **TPT-C$_6$SH** monolayer on Ni-red (Fig. 4), on the other hand.

XPS analysis of the freshly prepared monolayers of **C$_6$SH** and **TPT-C$_6$SH** on Ni-ox and Ni-red point to similar properties and suggest that the **TPT** terminal group in **TPT-C$_6$SH** does not interfere with a proper chemisorption of the molecule. The low S 2p line intensities of Ni-ox substrates modified with either **C_6SH** or **TPT-C_6SH** indicate very low amounts of chemisorbed species present on these substrates.

Stability of the monolayer

Since the modified Ni-ox substrates are of poor quality, in this part we assess only the stability of the monolayers on the sole Ni-red surfaces. The first test is on the barrier properties of the monolayer against atmospheric oxygen permeation. If oxygen reaches the metal surface, oxidation of the metal occurs, which in turn leads to oxidation of the sulfur species bound to the substrate. The second test is on the electrochemical stability and blocking efficiency of the modified electrode.

Resistance to atmospheric oxygen permeation. In Fig. 5 and 6 are shown the Ni 2p and S 2p levels of **C_6SH** and **TPT-C_6SH** monolayers, respectively, recorded 30 min (fresh) and 9 weeks after preparation. The shape of the O 1s line being essentially the same for both samples after 30 min and 9 weeks, the corresponding spectra have been omitted. Both the Ni 2p and S 2p spectra indicate that the **C_6SH** monolayers act as better barriers to atmospheric oxygen than **TPT-C_6SH**. First, the increase in the intensity of the $Ni(OH)_2$ features in the Ni 2p spectra is more pronounced at comparable exposures to the atmosphere for **TPT-C_6SH** [Fig. 6(*a*)] than **C_6SH** [Fig. 5(*a*)]. With the S 2p spectra [Fig. 5(*b*) and 6(*b*)] it is possible to see a qualitative difference in the modification of the chemical state of the sulfur atoms bound to the surface. After 9 weeks the amount of oxidised sulfur species (sulfinates and sulfonates) increases in both **C_6SH** and **TPT-C_6SH** monolayers. However, a larger proportion of thiolates remains in the case of **C_6SH**, while they have practically disappeared from the S 2p spectrum of the **TPT-C_6SH** monolayer (9 weeks). This different behaviour suggests that **TPT-C_6SH** molecules form less densely packed monolayers than **C_6SH**. It is interesting to note the increase in disulfide species with increasing oxidation. This suggests that oxidation gradually evolves from the thiolates to the highly oxidised species (sulfinates and sulfonates) *via* the formation of disulfides. At present, however, this is only a conjecture based on the present observations which corroborate similar trends noted in the case of the Ni surfaces.[11]

Electrochemical stability. Here we report preliminary tests on the blocking efficiency of the **C_6SH** and **TPT-C_6SH** monolayers chemisorbed on Ni-red. The results are shown in Fig. 7(*a*)

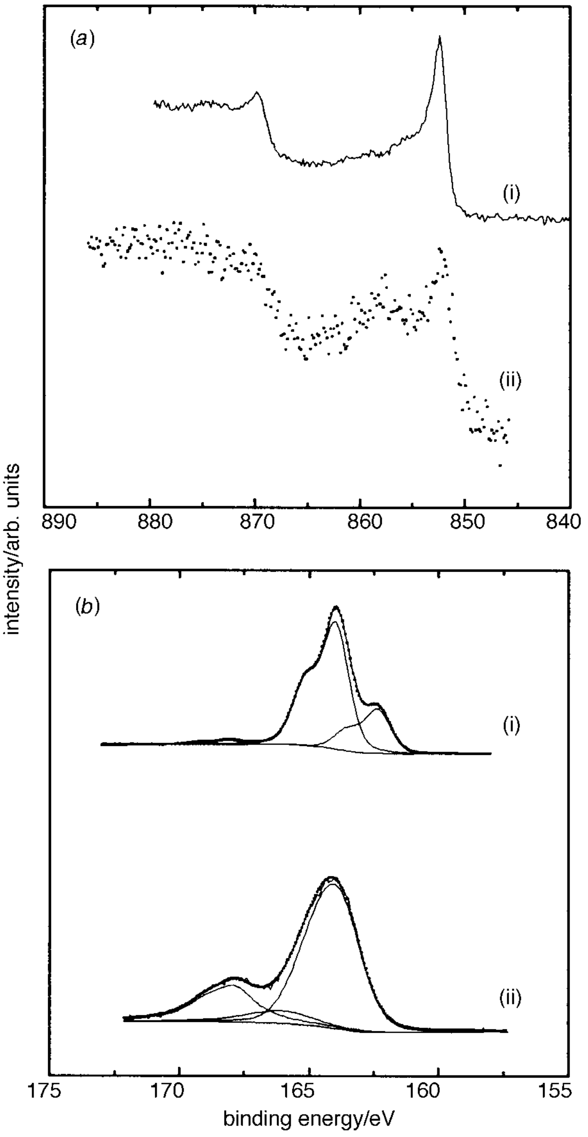


Fig. 6 XPS spectra of the (*a*) Ni 2p and (*b*) S 2p core levels of Ni-red polycrystalline surfaces modified with 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol (**TPT-C_6SH**) (i) fresh and (ii) after 9 weeks of exposure atmospheric oxygen

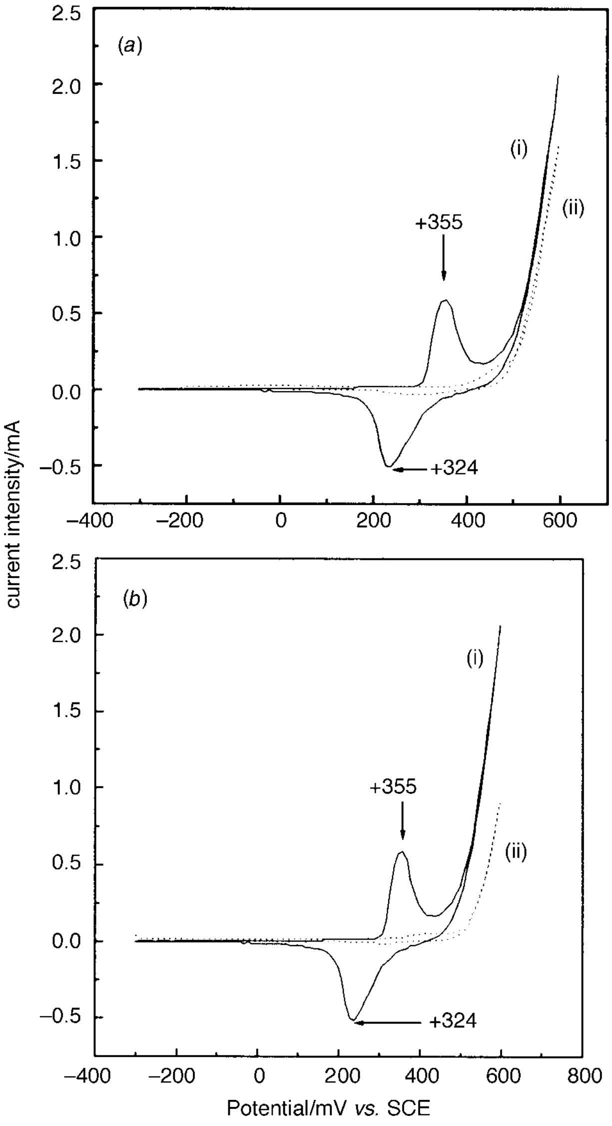


Fig. 7 Cyclic voltammogram of (i) polycrystalline nickel and (ii) Ni-red substrates modified with (*a*) *n*-hexanethiol (**C_6SH**) and (*b*) 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]hexanethiol (**TPT-C_6SH**) (0.1 M NaOH, argon bubbling)

and (*b*), respectively. For comparison, the cyclic voltammogram of a clean nickel substrate (solid line) is superimposed on those of the modified substrates (dotted lines). During the anodic potential sweep, the clean polycrystalline nickel electrode shows a peak at 0.355 V assigned to the oxidation of the metal and the formation of a passive nickel oxide layer. The high current rise starting at +0.52 V is due to oxygen evolution, while the cathodic peak at +0.234 V corresponds to the reduction of the oxide layer. Fig. 7(*a*) shows the voltammogram (dotted line) corresponding to a Ni-red substrate modified with **C_6SH**. By comparison with the clean nickel surface, the modified electrode exhibits a substantial decrease in its electrochemical activity. A similar conclusion holds in the case of a **TPT-C_6SH** monolayer chemisorbed on a Ni-red substrate [Fig. 7(*b*)]. This is in line with the previous observations on the stability of the monolayer to ambient atmosphere. It constitutes additional evidence that the freshly formed organic layer is firmly and densely chemisorbed on the surface to the point that water and electrolytic species are prevented from reaching the metal thiol interface.

The cyclic voltammetry studies which were carried out on freshly prepared monolayers do not reveal substantial differences in the electrochemical behaviour of **C_6SH** and **TPT-C_6SH** as was observed in the XPS spectra of samples exposed to atmospheric oxygen for 9 weeks. In the future, it would be interesting to carry out detailed electrochemical characterisations on such layers.

Conclusion

This study show that *n*-hexanethiol, **C_6SH**, and 6-[2′,5′-di(2″-thienyl)pyrrol-1′-yl]-hexanethiol, **TPT-C_6SH**, do chemisorb on reduced polycrystalline nickel, a technologically important metal, and form stable self-assembled layers, much like *n*-dodecanethiol.[11]

Preliminary results indicate that electropolymerisation of 2,5-di(2′-thienyl)-*N*-methylpyrrole on the **TPT-C_6SH** monolayers on polycrystalline Ni-red substrates leads to strongly adherent films.[22] More systematic studies of the chemisorption parameters (time, concentration, solvents, nature of the metal), stability of the monolayers and electrodeposition of conductive polymers will be necessary to elaborate adherent electroactive films on oxidisable metals with good morphological, adherence and electronic properties.

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