Alkane-tetrathiol induced formation of remarkably stable self-assembled monolayer and polymer films containing electroactive tetrathiafulvalene moieties on metal electrodes

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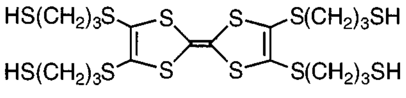
Remarkably stable self-assembled monolayer and polymer films composed of a new tetrathiafulvalenyl-tetrathiol have been formed on metal electrodes: this is a new class of surface modification by self-assembly and electrochemical polymerization using the same alkane-tetrathiol.

Self-assembled monolayer and polymer films on metal surfaces are the focus of intense investigation, because these films constitute an important strategy in the surface modification of electrodes.[1–4] The majority of self-assembled organosulfur monolayers studied consist of adsorbates which contain an alkyl chain with a surface-active sulfur group, such as alkane-*monothiols* and *n*-alkyl disulfides, however, such surface modification using alkane-*polythiols* has received much less attention. Meanwhile, the modification of electrodes with electroactive polymer films has been performed from the electrochemical polymerization of pyrrole and thiophene-based monomers which are the most commonly used materials.[4] We have now found that a new class of surface-modification reagent, tetrathiafulvalenyl alkane-tetrathiol **1**, gives remarkably stable self-assembled monolayers on a gold (Au) electrode and polymer films on a glassy carbon (GC) electrode. To our knowledge, this is the first example for the surface modification of metallic electrodes with the same adsorbate molecule by the self-assembly method and electropolymerization using the same starting material.



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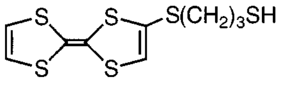

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The immersion of a clean polycrystalline gold electrode in a solution of the new tetrathiol **1**[5] (1.0 mM in CH_2Cl_2, 40 °C, 24 h) resulted in the formation of a monolayer of tetrathiol **1**, which chemisorbed on the gold surface *via* thiolate–Au bonds. After extensive rinsing of the modified electrode, the voltammetric response in CH_2Cl_2 clearly exhibited anodic and cathodic waves characteristic of the reversible two-electron oxidation of the immobilized tetrathiafulvalene (TTF)-groups [Fig. 1(a)]. The potential ($E_{1/2}$) for the oxidation process was +0.35 and +0.66 V (*vs.* Ag/0.1 M $AgNO_3$). The potential difference between the anodic and cathodic peaks was 20 mV at v = 100 mV s^{-1}, and the peak current increased linearly with the scan rate. These two voltammetric features unequivocally indicate the surface-confined nature of the electroactive TTF groups. The surface coverage (Γ) of **1** on the Au electrode was found to be 1.6×10^{-10} mol cm^{-2}.

Tetrathiol-monolayer modified Au electrode allowed to stand at 0 V in CH_2Cl_2 or MeCN showed no diminution of the anodic peak current response over more than several weeks, showing that the molecular film is not readily stripped by non-aqueous solvents. The electrochemical stability of the monolayer of **1** on an Au electrode in CH_2Cl_2 was investigated by continuously cycling the potential. After 10 scans between −0.05 and +0.95 V, only 5% of the electroactivity is lost [Fig. 1(b)]. This finding indicates that the monolayer of tetrathiol **1** is stable in non-aqueous solvents.[6] Interestingly, the monolayer of the *tetrathiol* **1** was remarkably stable compared to the monolayer of the *monothiol* **2** on an Au electrode as evidenced from the repeated electrochemical cycling of those monolayers.

Normally, alkane-monothiols can not be polymerized by repeated anodic oxidations and none of the polymer film from monothiol **2** was formed upon repeated cyclic scanning of the potential.[7] However, tetrathiol **1** on repeated electrochemical oxidation showed intriguing results. The first scan of the cyclic voltammogram of tetrathiol **1** in CH_2Cl_2 + 0.1 M NBu_4PF_6 at a glassy carbon electrode exhibited the regular reversible waves corresponding to the TTF–$TTF^{\cdot+}$–TTF^{2+} system at $E_{1/2}$ = +0.34 and +0.67 V [Fig. 2(a)]. These two waves are followed by an irreversible oxidation peak at +0.90 V (E_p) which seems to correspond to oxidation of thiol groups. Surprisingly, repeated

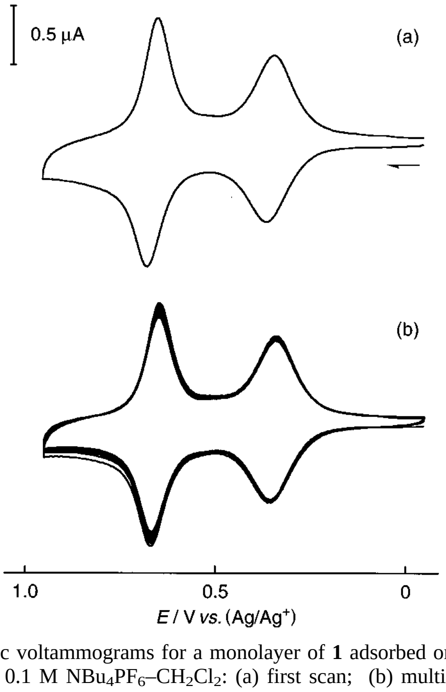

Fig. 1 Cyclic voltammograms for a monolayer of **1** adsorbed onto an Au electrode in 0.1 M NBu_4PF_6–CH_2Cl_2: (a) first scan; (b) multiple scans. Scan rate 100 mV s^{-1}.

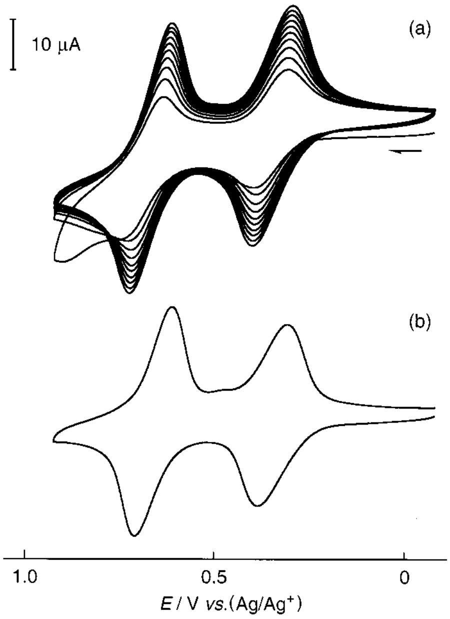

Fig. 2 (a) Oxidative electropolymerization of **1** (1 mM) by repeated potential scans on a GC electrode in 0.1 M NBu_4PF_6–CH_2Cl_2; scan rate 100 mV s^{-1}. (b) Cyclic voltammogram of a poly-TTF modified GC electrode in 0.1 M NBu_4PF_6–CH_2Cl_2; scan rate 100 mV s^{-1}.

scans over the −0.08 to +0.92 V range led to the growth of a polymer film on the electrode.[8] Evidence for this is given by the continuous increase in the peak intensity of the TTF–TTF$^{\cdot+}$–TTF^{2+} system. After 10 scans, the electrode was rinsed copiously with solvent and dipped into fresh CH_2Cl_2 solution. The cyclic voltammogram of the polymer–TTF modified electrode (Γ = 1.0 × 10^{-9} mol cm^{-2} after 10 cycles) is shown in Fig. 2(b).[9] The cyclic voltammogram of the polymer modified GC electrode displayed only two redox peaks corresponding to the TTF–TTF$^{\cdot+}$–TTF^{2+} system at $E_{1/2}$ = +0.34 and +0.66 V. This contrasts with the electropolymerization of pyrrole-substituted electroactive compounds which showed oxidation waves of both the pyrrole and the electroactive groups in the cyclic voltammogram. Many scans of the poly-TTF modified electrode can be performed without any change of the voltammetric wave. Thus, poly-TTF is readily formed as stable films on a GC electrode surface. This is a new type of controlled polymerization using alkane-polythiols.[10]

In summary, a monolayer of a new TTF-derivatized tetrathiol **1** on a gold electrode is more stable than that of monothiol **2** under electrochemical recycling. Tetrathiol **1** can be easily electropolymerized at moderate potential into highly stable poly-TTF films. Thus, alkane-tetrathiol **1** provides both remarkably stable monolayers and multilayers containing electroactive TTF moieties. Further work is currently in progress in this and related areas.

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Notes and references

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5 **1**: FTIR 2554 cm^{-1} (SH); ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 4H, *J* 8.1 Hz, SH), 1.94 (q, 8H, *J* 6.8 Hz, CH_2), 2.69 (dt, 8H, *J* 8.1, 6.8 Hz, CH_2SH), 2.96 (t, 8H, *J* 6.8 Hz, SCH_2); ^{13}C NMR ($CDCl_3$) δ 23.0, 33.3, 34.5, 110.5, 127.9. Exact mass: calc. for $C_{18}H_{28}S_{12}$: 627.8840. Found: 627.8856. **2**: FTIR 2557 cm^{-1} (SH); ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 1H, *J* 8.0 Hz, SH), 1.93 (q, 2H, *J* 7.0 Hz, CH_2), 2.65 (dt, 2H, *J* 8.0, 7.0 Hz, CH_2SH), 2.87 (t, 2H, *J* 7.0 Hz, SCH_2), 6.32 (s, 2H, C=CH), 6.37 (s, 1H, C=CH); ^{13}C NMR ($CDCl_3$) δ 22.9, 33.2, 34.0, 109.4, 112.9, 118.9, 119.0, 122.9, 126.6. MS, *m/z* 310 (M$^+$). The synthesis of **1**, **2** and related compounds will be reported elsewhere.

6 Most electrochemical studies of self-assembled monolayers carried out to date have used aqueous media. The properties of self-assembled monolayers in organic solvents have been discussed: K. A. Groat and S. E. Creager, *Langmuir,* 1993, **9**, 3668 and references therein.

7 The tetramethylsulfide of **1** did not polymerize upon repeated electrochemical oxidation. This result indicates that the tetrathiol needs to form polymer films for this to occur.

8 The polymerization may proceed *via* the formation of disulfide linkages upon oxidation of the thiol groups of **1**. Mechanistic studies for the electropolymerization of tetrathiol **1** are in progress.

9 The surface coverage of the polymer films on the electrode can be controlled by cycling times.

10 Although there have been numerous investigations into the electropolymerization of pyrrole- and thiophene-based monomers, the mechanism for the deposition of these films on electrode surfaces is not well defined.[4]

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