7 Self-Assembled Monolayers of Donor–(σ-Bridge)–Acceptor Units on a Gold Electrode

7.1 Introduction

The study of organic monolayers, multilayers and self-assembled monolayers (SAMs) that incorporate redox-active units is pursued by many research groups since they are of interest for the development of integrated molecular electronic circuits and devices. For instance, it has been reported that mono- and multilayers of zwitterionic electron donor–(σ-bridge)–acceptor (D–σ–A) units placed between two metal electrodes can rectify an electrical current. It has been claimed that SAMs of π-conjugated molecules between two gold electrodes can function as field-effect transistors. SAMs on gold incorporating integrated artificial photosynthetic assemblies were found to generate a photocurrent. SAMs with redox-active porphyrin or ferrocene moieties can function as an electronically addressable memory and can display negative differential resistance, a property required for resonant tunnelling diodes.

The above mentioned examples concern mono- and multilayers consisting of organic compounds only. Recently, interest has grown to involve metal and semiconductor nanoparticles and clusters in the self-assembly process. The resulting composites offer great opportunities for the development of novel electronic devices such as single electron transistors. Recently, a switch based on a gold nanoparticle separated from a gold surface by a redox-active monolayer controlling the gold-to-gold electron transport was reported. Three-dimensional systems incorporating SAM-covered metal nanoparticles on a metal surface have been proposed as platforms for antenna molecules in light harvesting devices.

Here we report on the synthesis and monolayer formation of two redox-active adsorbates, DA11S1 and DA11S10 (Figure 7.1) that consist of an electron donor–(σ-bridge)–acceptor (D–σ–A) moiety which bears two dialkyl sulfide chains. The (D–σ–A) moiety consists of an N,N-dialkylanilino donor which is connected via a four-σ-bond bridge to a 1,1-di(alkoxycarbonyl)vinyl-type acceptor. The monolayer formation of the two model compounds A11S1 and A11S10 is reported as well.

The dialkyl sulfide functionalities in DA11S1 and DA11S10 serve to induce monolayer formation of the adsorbate on a gold surface. Dialkyl sulfides are known to adsorb
by physisorption.\textsuperscript{275–278} Although dialkyl sulfides do not give monolayers as dense as found for alkanethiols,\textsuperscript{280} the presence of two sulfide groups per adsorbate molecule is expected to lead to good quality monolayers. This is corroborated by the fine quality of monolayers prepared from adsorbates with four dialkyl sulfide adsorption functionalities.\textsuperscript{281, 282} From the same studies it was also inferred that the area occupied by the dialkyl sulfide supporting structure should match that of the supported structure or be slightly larger. For DA11S1 the surface within the van der Waals boundary of the cross section of two alkyl chains is approximately equal to that of the cross section of the D–σ–A unit. For DA11S10 two additional alkyl chains form part of the supporting structure and hence the area of the supporting structure is larger than that of the supported D–σ–A unit.

Although DA11S1 and DA11S10 have been designed to attach to gold with the sulfide moieties, the \textit{N},\textit{N}-dimethylaniline functionality may have affinity for gold as well. This is because amines such as aniline\textsuperscript{283, 284} are known to adsorb to a gold surface. Thus, if DA11S1 and DA11S10 form well-ordered monolayers with the sulfide groups attached to the gold surface, the \textit{N},\textit{N}-dimethylaniline functionalities may be used for the subsequent attachment of metal or semiconductor particles. In this way a system is created in which a layer of asymmetric redox-active units is held between two conducting layers.

The D–σ–A moiety present in DA11S1 and DA11S10 has been shown to produce a charge-separated state $D^+−\sigma−A^−$ upon photoexcitation.\textsuperscript{248} Hence, if these molecules form well ordered monolayers on a Au(111) surface, the excited state processes such as electron and hole transport between SAM and gold can be investigated.

\textsuperscript{4}See, however, ref. 279, where evidence for chemisorption is reported.
7.2 Results and Discussion

7.2.1 Synthesis

The compounds DA11S1 and DA11S10 were synthesized as follows. 11-(Methylsulfanyl)undecan-1-ol (1) was prepared from sodium methanethiolate and 11-bromo-undecanol according to Wada et al. 285 11-(Decylsulfanyl)undecan-1-ol (2) was prepared by a radical addition of decane-1-thiol to 10-undecen-1-ol using 9-BBN as radical initiator. 286 Both 1 and 2 were esterified with malonoyl dichloride to form malonic ester derivatives A11S1 and A11S10, respectively. These compounds were then condensed with 4-[4-(dimethylamino)phenyl]cyclohexanone 248 (3) using TiCl4 and pyridine in THF 219 (Figure 7.2) to give DA11S1 and DA11S10, respectively.

\[
\begin{align*}
\text{DA11S1} & \quad \text{DA11S10} \\
R = -(\text{CH}_2)_n-\text{S-CH}_3 & \quad R = -(\text{CH}_2)_n-\text{S-(CH}_2)_m-\text{CH}_3
\end{align*}
\]

Figure 7.2. Syntheses of DA11S1 and DA11S10.

7.2.2 Monolayer Formation on a Au(111) Surface

Self-assembled monolayers on a Au(111) surface were prepared from 1 to 5 mM solutions of DA11S1, DA11S10, A11S1 and A11S10 in ethanol. The gold surface was immersed in the solution for 2 days at a temperature of 60 °C. In all cases a reduction of the surface wettability was observed when sprinkling water over the surface. This indicates that a substantial degree of coverage of the surface had taken place. Although contact angles were not determined, it was observed that the surfaces covered with D–σ–A containing SAMs on one hand and with SAMs of A11S1 and A11S10 on the other hand had distinctly different wettabilities.

To test the quality of the deposited layers, the covered gold substrates were used as the working electrode in a cyclic voltammetry (CV) set-up with [Fe(CN)6]3−/4− in aqueous solution as the redox couple. In this way the ability of the monolayer to block the current between the gold electrode and the redox couple can be determined. The cyclic voltammograms are depicted in Figure 7.3. For comparison, the response of the redox couple with a bare gold surface is also depicted. The cyclic voltammograms of the SAM covered Au surfaces were reproducible upon repeated cycling.
Figure 7.3. Cyclic voltammograms of the aqueous $[\text{Fe(CN)}_6]^{3-/4-}$ couple measured with a DA11S1-covered Au electrode (A), a DA11S10-covered Au electrode (B) and a A11S10-covered Au electrode (C) (—). For comparison, in each panel the response measured with a bare Au electrode is given as well (— — —). In each case the second scan recorded is depicted.

It is evident that for the DA11S10 and DA11S1 covered Au surfaces a decreased current is observed when compared to bare gold. For DA11S1-Au the maximum current is about 5 % of that for bare Au, for DA11S10-Au it is 20 % and for A11S10-Au it is about 60 %. Moreover, the peak-to-peak distance has increased in the order A11S10 < DA11S10 < DA11S1. Thus, the most efficient blocking of the current is observed for DA11S1-Au, followed by DA11S10-Au and A11S10-Au. This nicely reflects the more favourable ratio of cross sections for supporting and supported structure of DA11S1 as compared to DA11S10. On the basis of the CV curves the presence of pinholes in the monolayers of DA11S1-Au and DA11S10-Au can be excluded since only a very small current is observed on the positions where for bare Au the peak potentials of the $\text{Fe(CN)}_6^{3-/4-}$ couple are present. Nevertheless, the electrochemical responses of DA11S1-Au and DA11S10-Au are different. Relatively sharp drops in the current are observed in the cyclic voltammogram of DA11S1-Au at $-0.29$ and $0.66$ V versus SCE. These values are centred around the $E_{1/2}$ value of the $\text{Fe(CN)}_6^{3-/4-}$ couple of 0.19
V versus SCE and can therefore still be associated with that couple. No indication is found for the oxidation of the \(N,N\)-dimethylanilino group at potentials up to 0.8 V versus SCE, while it is known that 4-cyclohexyl-\(N,N\)-dimethylaniline has an oxidation potential of 0.63 V versus SCE in acetonitrile.\(^{248}\) Although these values cannot be compared directly, the absence of an oxidation current for \(\text{DA11S1-Au}\) suggests that the \(N,N\)-dimethylanilino group is not directly attached to the gold.

The currents recorded for \(\text{DA11S10-Au}\) are larger than for \(\text{DA11S1-Au}\) but seem to reach their largest values at larger overpotentials than for \(\text{DA11S1-Au}\). If the larger currents originated from shallow defects they would be expected to occur at a smaller overpotential. The origin of the difference between the \(\text{DA11S1-Au}\) and \(\text{DA11S10-Au}\) responses therefore remains unclear. An influence of the redox-active moieties incorporated in the monolayers may be involved, but the currents are not of sufficient magnitude to be conclusive. Experiments with \(D-\sigma-A\) compounds with shorter alkyl chains between the acceptor and the sulfide are expected to clarify this point.

### 7.2.3 Deposition of Au Nanoparticles

In order to get more information pertaining to how the gold adsorbates are attached to the surface, the covered Au substrates were immersed in an aqueous dispersion of 16 nm \(\varnothing\) Au nanoparticles for approximately 4 hrs at room temperature. Subsequently, the surface was examined using tapping mode AFM. It was observed that the \(\text{DA11S10-Au}\) and \(\text{DA11S1-Au}\) surfaces were covered to a large degree with the Au particles (see Figure 7.4). As the Au particles on \(\text{DA11S10-Au}\) did not move across the surface with the AFM tip, they are chemically bound to the surface.\(^{287}\) A surface of \(\text{A11S10-Au}\) did not give a satisfactory coverage with Au particles. Parts of the surface were covered by Au particles that were clustered in lumps, while other parts were completely uncovered. The lumps moved across the substrate surface with the AFM-tip, indicating that they are only physically bound to the surface.

The binding of significant quantities of Au particles to the \(\text{DA11S10-Au}\) and \(\text{DA11S1-Au}\) surfaces confirms that a good coverage of the surface with \(\text{DA11S10}\) and \(\text{DA11S1}\) has been obtained, since our experience is that particles normally, instead of homogeneously spreading over the bare Au surface, tend to cluster in the grain boundaries.\(^{287}\) The fact that Au particles do not bind well to the \(\text{A11S10-Au}\) surface indicates that the sulfide groups of \(\text{A11S10}\) remain attached to the flat Au surface; once a layer has been formed they are not available for subsequent binding of Au particles under the applied conditions. If it is assumed that the \(N,N\)-dimethylanilino groups in the SAMs do not attach to the Au(111) surface and are pendant in solution, as is indicated by CV for \(\text{DA11S1-Au}\) and to a lesser extent for \(\text{DA11S10}\), the coverage of the SAMs of \(\text{DA11S1}\) and \(\text{DA11S10}\) must be explained by binding of Au particles to these \(N,N\)-dimethylanilino groups. It thus seems that the order in which the Au surfaces (flat and
nanoparticle) are offered to the substrate may be used to introduce directionality in the formed nanocomposite. This can be of great interest to the design of organic-inorganic systems in general. If, in contrast, the \( N,N \)-dimethylanilino moieties effectively compete with the sulfide moieties in the initial SAM formation process, a binding of Au particles may result as well and the previous conclusion would be invalid. Nevertheless, a Au\(|\text{DA–A}|\text{Au} \) system is formed.

### 7.3 Conclusions and Outlook

It has been shown that DA11S1 and DA11S10 form self-assembled monolayers on a Au(111) surface, most probably via preferential adsorption of the sulfide groups to the Au(111) surface. The SAM of DA11S1 is more densely packed than that of DA11S10, presumably due to a better match of the cross section of the supporting alkyl tails with that of the supported D–B–A moiety in the first compound. A dense layer of gold nanoparticles (16 nm diameter) could be deposited on both SAMs. These particles are likely to be attached via the \( N,N \)-dialkylaniline donors of the D–B–A moieties. As was stated in §7.2.2, experiments with D–σ–A adsorbates with shorter polymethylene chains between the acceptor and the sulfide are expected to provide insights into the different CV responses for DA11S1 and DA11S10. We have already prepared a compound with two \(-\text{CH}_2\text{CH}_2\text{S}–\text{CH}_3\) groups attached to the acceptor and are investigating this compound at the time of writing.
The SAMs of DA11S1 and DA11S10 are believed to be good starting points for investigations into the behaviour of excited molecules at a SAM/metal interface. Although it has been shown that a photocurrent can be generated from SAMs on gold,\textsuperscript{85, 87} it is also known that a metal surface is capable of quenching the excited state of a molecule by means of energy transfer.\textsuperscript{288, 289} Recent studies on SAMs of \(\omega\)-fluorophore-functionalized alkanethiols on a gold surface and on gold nanoparticles have indicated that quenching of the excited state by the metal decreases with increasing chain length of the alkanethiol spacer\textsuperscript{261, 262, 290, 291} Questions remain with regard to which extent monolayer properties and fluorophore concentrations will influence the results (see for example ref. 291). Interestingly, as expected for an energy transfer mechanism,\textsuperscript{291} it has been found that excited state quenching on SAM covered nanometre sized gold particles can be significantly less efficient than on a flat gold surface.\textsuperscript{87, 292, 293}

### 7.4 Experimental

**General.** All reactions were carried out in an atmosphere of dry nitrogen unless stated otherwise. Commercially available reagents were used without further purification. Toluene, THF and diethyl ether were distilled from Na/benzophenone prior to use. Acetonitrile was distilled from CaH\(_2\). Pyridine, DMF and CCl\(_4\) were stored on 3 Å molecular sieves. Column chromatography was performed using silica gel 60 (230–400 mesh ASTM). Thin layer chromatography was performed on Merck silica gel 60 F\(_{254}\). Spots were made visible with iodine vapour and/or UV light. Melting points were determined on a home made melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300.13 MHz for \(^1\)H NMR and at 75.47 MHz for \(^13\)C NMR. Samples were dissolved in deuterated chloroform unless stated otherwise. Chemical shifts (in ppm) are given relative to internal TMS (0.00 ppm) in the case of \(^1\)H NMR and relative to external TMS in the case of \(^13\)C NMR. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 5000 operating with 2 cm\(^{-1}\) resolution. Solids were measured in KBr pellets, while liquid materials were measured as a thin film between NaCl plates. Peak maxima are given in cm\(^{-1}\), while intensities are designated as s (strong), m (medium) or w (weak).

**Synthesis.** The synthesis of ketone 3 is given elsewhere.\textsuperscript{248}

**11-(Methylsulfanyl)undecan-1-ol (1).** This compound was prepared according to Wada et al.\textsuperscript{285} from sodium methanethiolate and 11-bromoundecanol in DMF on a 38 mmol scale yielding 1 as a white solid in quantitative yield (mp 36–38 °C, lit. 33–35 °C [ref. 285]). \(^1\)H NMR \(\delta\) 1.28–1.40 (m, 14H), 1.54–1.66 (m, 4H), 2.09 (s, 3H), 2.14 (s, 1H), 2.48 (t, \(J = 7.3\) Hz, 2H), 3.61 (t, \(J = 6.6\) Hz, 2H). \(^13\)C NMR \(\delta\) 15.4, 25.6, 28.7, 29.1 (2x), 29.3, 29.4 (2x), 29.5, 32.7, 34.2, 62.8. FT-IR \(\tilde{v}_{\text{max}}\) 3423, 3364 (OH, br, m); 2922 (s); 2848 (s); 1468 (s); 1355, 1347 (m).

**11-(Decylsulfanyl)undecan-1-ol (2).** To a solution of 10-undecen-1-ol (4.44 g, 26.1 mmol) and decane-1-thiol (11.91 g, 68.3 mmol) in THF (350 mL), cooled to −5 °C was added 9-BBN (3 mL, 0.5 M in THF). The mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in CH\(_2\)Cl\(_2\) (150 mL) and washed with a dilute NH\(_4\)Cl solution (59 mg mL\(^{-1}\), 2 × 100 mL). The solvent was removed under
reduced pressure. Excess decane-1-thiol was distilled off by means of a Kugelrohr distillation at 80 °C (0.005 Torr). At 140 °C (0.005 Torr) the product was collected. It was recrystallized from EtOH (80 mL) yielding as a white solid (6.88 g, 77%) of mp 54–56 °C. 1HN M R δ 0.86–0.90 (m, 3H), 1.27–1.36 (m, 28 H), 1.49–1.62 (m, 6 H + OH), 2.47–2.52 (m, 4H), 3.60–3.66 (m, 2H). 13CN M R δ 14.0, 22.6, 25.7, 28.9 (2x), 29.2 (2x), 29.3, 29.4, 29.5 (5x), 29.7 (2x), 31.8, 32.2 (2x), 32.8, 62.9. FT-IR νmax 3334, 3241 (br, OH); 2922, 2850 (s); 1472, 1463 (s); 1065 (s); 734, 719 (m).

Bis[11-(methylsulfanyl)undecyl] malonate (A11S1). To a stirred solution of malonoyl dichloride (2.59 g, 18.4 mmol) in diethyl ether (20 mL) was dropwise added a solution of triethyl amine (3.82 g, 37.8 mmol) and 1 (8.17 g, 37.4 mmol) in diethyl ether (80 mL) while keeping the temperature between and 0 °C. Subsequently, the reaction mixture was stirred for three days at room temperature. The mixture was washed with a 0.05 M HCl solution (100 mL) and the water layer was extracted with diethyl ether (75 mL). The combined organic layers were extracted with water (2 x 50 mL). The combined water layers were washed with diethyl ether (2 x 50 mL) and the combined organic layers were washed with saturated NH₄Cl solution (80 mL) and dried on MgSO₄. After filtration the solvent was removed under reduced pressure leaving a brown solid. Remaining 1 was distilled off by means of a Kugelrohr distillation at 83 °C (0.005 Torr). The product was found to decompose at higher temperature. It was purified by two crystallizations from MeOH (50 mL) yielding an off-white solid (7.58 g, 82%; mp 33–34 °C). 1HN M R δ 1.28 (m, 28H), 1.54–1.66 (m, 8H), 2.09 (s, 6H), 2.46–2.51 (m, 4H), 3.36 (s, 2H), 4.11–4.16 (m, 4H). 13CN M R δ 15.5, 25.7, 28.4, 28.7, 29.1, 29.2, 29.4, 34.2, 41.6, 65.6, 166.6. FT-IR νmax 2917 (s); 2849 (s); 1750, 1717 (s); 1183 (s).

Bis[11-(decylsulfanyl)undecyl] malonate (A11S10). This compound was prepared as described for A11S1 using 1.40 g (9.94 mmol) of malonoyl dichloride in 30 mL of diethyl ether and 6.64 g (19.3 mmol) of 2 in 190 mL of diethyl ether. A light brown solid was obtained as the crude product. Remaining 2 and other volatiles were removed at the Kugelrohr at 110 °C (0.005 Torr). Since it was found that the product decomposes at higher temperature, it was not distilled. Yield: 7.58 g (82%; mp 59–61 °C). 1HN M R δ 0.86–0.90 (m, 6H), 1.27–1.39 (m, 56H), 1.52–1.66 (m, 12H), 2.47–2.52 (m, 8H), 3.36 (s, 2H), 4.11–4.15 (m, 4H). 13CN M R δ 14.0, 22.6, 25.8, 28.4, 28.9, 29.2, 29.3, 29.5, 29.7, 31.9, 32.2, 41.6, 65.6, 166.6.

Bis[11-(methylsulfanyl)undecyl]{4-[4-(dimethylamino)phenyl]cyclohexylidene} malonate (DA11S1). A solution of TiCl₄ (3.48 g, 18.2 mmol) of dry CCl₄ (15 mL) was slowly added to THF (50 mL), while maintaining the temperature below 0 °C. To this mixture was added a solution of malonic ester derivative A11S1 (4.61 g, 9.13 mmol) and ketone 3 (2.98 g, 13.7 mmol) in THF (40 mL). Subsequently, a solution of pyridine (2.89 g, 36.5 mmol) in THF (15 mL) was slowly added while maintaining the temperature just below 0 °C. The resulting reaction mixture was stirred for 3 days at room temperature. A sample was worked-up and analysed with NMR. It was found that A11S1 was still present in large excess. Thus, a solution of TiCl₄ (2.61 g, 13.8 mmol) in CCl₄ (10 mL), ketone 3 (2.23 g, 10.3 mmol) in THF (20 mL) and pyridine (2.17 g, 27.4 mmol) in THF (15 mL) were added in this order, while maintaining the temperature just below 0 °C. After another 3 days stirring at room temperature, the mixture was poured into water (100 mL) and extracted with CHCl₃ (3 x 75 mL). The combined organic layers were washed with a saturated Na₂CO₃ solution (100 mL), dried on MgSO₄ and filtered. Removal of the solvent under reduced pressure yielded a white solid which was subjected to
column chromatography (hexane–ethyl acetate, 10 : 1 v/v). The product was crystallized from EtOH twice to yield DA11S1 as a white solid (1.13 g, 18%, mp 43–44 °C). 1H NMR δ 1.27–1.34 (m, 28H), 1.54–1.72 (m, 10H), 2.09 (s, 6H) superposed on 2.04–2.21 (2 × m, 4H), 2.46–2.51 (m, 4H), 2.68–2.76 (m, 1H), 2.91 (s, 6H), 3.18–3.22 (m, 2H), 4.14–4.19 (m, 4H), 6.68–6.71 (m, 2H), 7.06–7.09 (m, 2H). 13C NMR δ 15.5, 25.9, 28.5, 28.8, 29.2, 29.5, 32.3, 34.3, 35.2, 40.7, 42.8, 65.0, 112.8, 122.3, 127.3, 133.6, 149.2, 160.2, 165.8. FT-IR νmax 2916 (s); 2850 (s); 1733, 1722 (s); 1614, 1522, 1469 (m); 1059 (s); 720 (m).

Bis[11-(decylsulfanyl)undecyl]{4-[4-(dimethylamino)phenyl]cyclohexylimidene} malonate (DA11S10). This compound was prepared as described for DA11S1. The following amounts were used: a solution of TiCl4 (2.87 g, 15.1 mmol) and dry CCl4 (15 mL) in THF (50 mL), a solution of malonic ester derivative A11S10 (5.71 g, 7.54 mmol) and ketone 3 (2.46 g, 11.3 mmol) in THF (60 mL) and a solution of pyridine (2.39 g, 30.2 mmol) in THF (15 mL). The work-up of a sample after three days showed that A11S10 was still present in large excess and the following amounts were added as described for DA11S1: a solution of TiCl4 (2.33 g, 12.3 mmol) in CCl4 (15 mL), ketone 3 (1.99 g, 9.16 mmol) in THF (20 mL) and pyridine (1.93 g, 10.2 mmol) in THF (15 mL). A white solid was obtained which was subjected to column chromatography (hexane–ethyl acetate, 20 : 1 v/v). This yielded DA11S10 as a white solid (0.20 g, 3%). 1H NMR δ 0.86–0.90 (m, 6H), 1.27–1.36 (m, 56H), 1.52–1.72 (m, 14H), 2.04–2.19 (m, 4H), 2.47–2.52 (m, 8H), 2.67–2.77 (m, 1H), 2.91 (s, 6H), 3.18–3.22 (m, 2H), 4.14–4.19 (m, 4H), 6.68–6.71 (m, 2H), 7.06–7.09 (m, 2H). FT-IR νmax 2916 (s); 2850 (s); 1733, 1722 (s); 1614, 1521, 1469 (s); 1059 (s); 720 (m).

Substrate and SAM preparation and measurements. The Au(111) surfaces were prepared by consecutive vacuum deposition of Cr (2 nm) and Au (200 nm) on borosilicate glass. The surface was flame annealed in a H2 flame. This gives a clean Au(111) surface which is atomically flat over large areas. Monolayer formation was carried out by placing the Au surface in a 1 (DA11S1) to 5 (DA11S10, A11S10) mM substrate solution in EtOH for approximately 2 days. This was conducted in an oven at 60 °C to ensure complete dissolution of DA11S10 and A11S10 in EtOH.

The 16 nm Ø gold particles were prepared via citrate reduction of a HAuCl4 solution according to the method of Frens.294 The final particle size was determined from the position of the plasmon absorption band maximum (λmax = 520 nm) and by AFM. For AFM a Digital Instruments NanoScope IIIA was used and the images were recorded in tapping mode.

Cyclic voltammetry (CV) measurements were performed with an EG&G Potentiostat/Galvanostat Model 273A in aqueous solution using a 3 electrode set-up with a Pt counter electrode and a saturated calomel reference electrode (water: R > 16 MΩ cm−1). The working electrode had a surface area of 0.273 cm². A solution of 5 mM K3[Fe(CN)6] and 5 mM K4[Fe(CN)6] was used as the redox couple. The scan rate was 50 mV s−1.