



Nitroxyl Radical Self-Assembled Monolayers on Gold: Versatile Electroactive Centers system in both Aqueous and Organic Media

Olivier Alévêque, Fawzia Seladji, Christelle Gautier, Marylène Dias, Tony Breton, Eric Levillain

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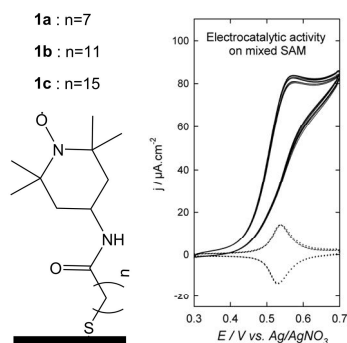
Entry for the Table of Contents

Layout 1:

Electrochemistry

O. Alévêque, F. Seladji, C. Gautier, M. Dias, T. Breton* and E. Levillain* __ Page – Page

Nitroxyl radical self-assembled monolayers (SAMs) on gold: versatile electroactive centers system in both aqueous and organic media.



Nitroxyl radical self-assembled monolayers (SAMs) on gold afford a noteworthy electrochemical stability in both aqueous and organic media. The control of the redox center accessibility using mixed SAMs is illustrated by the electrocatalytic activities towards benzyl-alcohol oxidation in CH₂Cl₂ and H₂O.

Nitroxyl radical self-assembled monolayers on gold: versatile electroactive centers in both aqueous and organic media.

O. Alévêque, F. Seladji, C. Gautier, M. Dias, T. Breton* and E. Levillain*

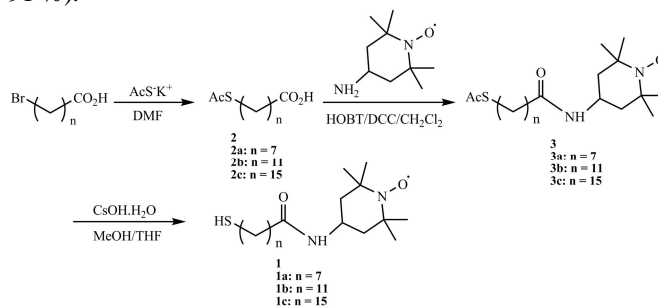
Dedicated to Professor E. Laviron

Since the pioneering work by Nuzzo and Allara in 1983,^[1] self-assembled monolayers (SAMs) of alkanethiols have gained much attention in the interfacial electrochemistry and other research fields.^[2,3] During the last decade,^[4,5] increasing attention has been dedicated to the design and elaboration of redox-responsive SAMs. Employing redox SAM-modified electrodes for catalysis, recognition and sensing have resulted in some elegant examples that incorporate sophisticated receptors on the electrode surfaces.^[5] However, to the best of our knowledge, no redox-responsive SAM was designed to be active and stable in both aqueous (on wide range of pH) and organic media.

TEMPO (2,2,6,6-Tetramethylpiperidine-1-oxyl) and its derivatives (under their oxoammonium form) have been extensively studied in the search for organic synthesis as a redox mediator, mostly, for the oxidation of primary alcohols.^[6,7,8] The electrochemical oxidation of TEMPO is known to be a stable and reversible one-electron process in both aqueous^[9,10,11] and non-aqueous electrolytes.^[12,13] Despite the wide electrochemical applications of nitroxyl radical, rare works have been devoted to design and elaborate of redox-responsive TEMPO SAMs.^[14,15,16] In 1997, Fuchigami *et al.*^[14] have reported the first preparation of stable self-assembled TEMPO-modified electrodes in acetonitrile: the electrochemical stability was only reached with highly diluted mixed SAMs of nitroxyl radical derivative and hexadecanethiol. In 1999, Kashiwagi *et al.*^[15] have reported electrocatalysis attempts of amines with a mixed SAM of chiral nitroxyl radical derivative and hexadecanethiol: as mentioned by authors, results could be applied to the determination of optical purity of chiral amines. After a ten-years pause, Finklea *et al.*^[15] have worked on Au-S(CH₂)₁₀C(O)N(H)-TEMPO SAM to the first

estimation of the standard rate constant and the reorganization energies of TEMPO/TEMPO⁺ in 1 M H₂SO₄.

Herein, we raised the challenge of a design of redox-responsive TEMPO SAMs to be active, stable and providing electrocatalytic activities in both aqueous and non-aqueous solvents. To reach this goal, we synthesized the three nitroxyl radical derivatives **1a**, **1b** and **1c** shown in Scheme 1. The synthesis of **1a**, **1b** and **1c** were carried out as outlined in Scheme 1. ω -thioacetyl carboxylic acids with different carbon chains length **2a-c** were synthesized from the corresponding ω -bromocarboxylic acids by nucleophilic displacement with potassium thioacetate in DMF.^[17] 4-aminoTEMPO was coupled to ω -thioacetyl carboxylic acids **2a-c** via the active ester method, using dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBT) in methylene chloride (CH₂Cl₂), to give the TEMPO derivatives **3a-c** in good yields (77 to 84 %). The thioacetates **3a-c** were subsequently deprotected to thiols **1a-c**, under basic conditions, using CsOH.H₂O in a mixture of THF and MeOH (yields: 50 to 91 %).



Scheme 1. Synthesis of nitroxyl radical derivatives **1a**, **1b** and **1c**.

Cyclic voltammograms (CVs)^[18] of **3a**, **3b** or **3c** exhibit a reversible one-electron process in CH₂Cl₂ and CH₃CN, close to 0.56 V and 0.41 V (vs. Ag/AgNO₃ in 0.1 M Bu₄NPF₆) respectively.

The kinetics for the formation of SAMs, prepared on Au substrate^[19] from 1 mM solution of **1a**, **1b** or **1c** in CH₂Cl₂ or CH₃CN, were followed by using quartz crystal microbalance (QCM) measurements. By employing, the Langmuir adsorption isotherm model,^[20] it is possible to establish that deposition kinetics are chain length (n) dependent: k_s increase with n and are smaller than 0.1 s⁻¹ (Figure SI-1).^[3] A maximum coverage, close to ~4.5x10⁻¹⁰ mol.cm⁻² in both solvents, is reached within a few minutes ($\tau_{99\%} < 3$ min for **1a**).

In non-aqueous solvents (*i.e.* DCM or CH₃CN; Bu₄NPF₆ 0.1M), the electrochemical properties of SAM prepared from **1a**, **1b** or **1c** were very similar to those reported above for **3a**, **3b** or **3c** in solution (*vide supra*), but

[*] Dr. O. Alévêque, Dr. C. Gautier, Dr. M. Dias, Dr. T. Breton and Dr. E. Levillain
Laboratoire CIMA - Université d'Angers - CNRS
2 boulevard Lavoisier 49045, Angers cedex (France)
E-mail: tony.breton@univ-angers.fr and eric.levillain@univ-angers.fr
Dr. F. Seladji
Laboratoire de chimie et d'électrochimie des complexes organométalliques.
Université des Sciences et de la technologie Mohammed Boudiaf
BP 1505 – El'M'naouer ORAN (Algérie)

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the shape of voltammetric waves and the linear dependency between peak intensities and scan rates were characteristic of surface-confined redox species (Figure 1). CVs parameters are quasi chain-length (n) independent (Table 1) and surface coverages, deduced by integration of the voltammetric signal, are in agreement with QCM experiments in both solvents. Interestingly, shapes of voltammetric waves are solvent and supporting electrolyte dependent: sharp (FWHM ~ 36 mV) in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ and broad (FWHM ~ 117 mV) in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ (Figure 1 and Table 1).

Table 1. CV parameters of SAMs prepared from 1b.

Medium	at 0.1 V.s ⁻¹	CH ₂ Cl ₂	MeCN	H ₂ O
0.1 M Bu ₄ NPF ₆	Γ (mol.cm ⁻²)	4.7x10 ⁻¹⁰	4.5x10 ⁻¹⁰	
	FWHM (mV)	36	117	—
	E _p (V)	0.52 ^a	0.49 ^a	
0.1 M NaClO ₄	Γ (mol.cm ⁻²)		4.6x10 ⁻¹⁰	5.0x10 ⁻¹⁰
	FWHM (mV)	—	87	96
	E _p (V)		0.43 ^a	0.71 ^b

[a] vs. Ag/AgNO₃ (0.01M), [b] vs. Ag/AgCl/KCl_{sat}

These reproducible opposite values of full width at half maximum (FWHM) deviate from the expected value ($\sim 89/n$ mV at 293 K) of an "ideal system", based on a Langmuir isotherm (*i.e.* all adsorption sites are equivalents and there are no interactions between immobilized electroactive centers). The interfacial electron transfer process and the interaction between the immobilized functional moieties have been widely studied to clarify the "non ideality" of experimental data^[21,22,23,24,25,26,27,28,29,30] but it still remains an open-ended question.

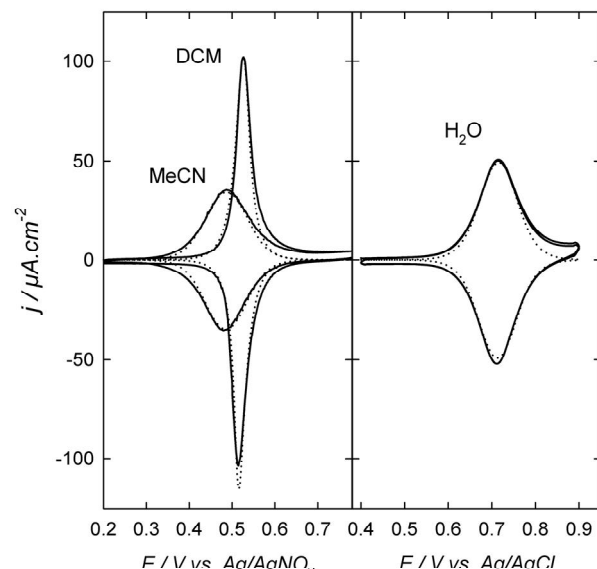


Figure 1. (Solid line): (left): CVs of SAM prepared from **1b** in 0.1 M Bu₄NPF₆/CH₂Cl₂ and in Bu₄NPF₆/CH₃CN; (right): CVs of SAM prepared from **1b** in HClO₄/NaClO₄/H₂O; It is noteworthy that CVs are superimposable upon one another from pH=2 to pH=6.6. (Dashed line): CVs calculated from theoretical models based on a Frumkin type isotherm).^[31] All CVs were performed at 0.1 V.s⁻¹.

However, from a Frumkin type isotherm (*i.e.* all adsorption sites are equivalents and there are interactions between immobilized electroactive centers), Laviron³¹ developed in the seventies a lateral interaction model to account for the sharpness or broadening and shifts of apparent formal potentials of experimental CVs. Based on diagnostic criteria reviewed in reference 31e, strong attractive interactions between immobilized oxidized centers lead to a sharp shape

(*i.e.* in CH_2Cl_2) and, medium or weak repulsive interactions to a broad shape (*i.e.* in CH_3CN) (Figure 1 and see below Figure 2). Taken in concert, these results suggest that the local ionic environment (coulombic repulsion and solvation) of charged redox centers plays a significant role in the electrochemical behaviour of the electroactive SAMs.

In aqueous media, a drastic preparation^[32] of SAMs is required to reach a stable and reproducible redox activity (Figure SI-2). As in solution,^[12,13] apparent redox potentials (E_{app} (at pH=7) ~ 0.71 V vs. Ag/AgCl/KCl_{sat}) and shape of SAMs prepared from **1a**, **1b** and **1c** are not pH dependent (Figure 1). Between pH=0 and pH=10.5, voltammetric waves (Figure SI-3) are quasi chain-length (n) independent and close to an "ideal system" (*i.e.* based on a Langmuir isotherm). Surface coverages, deduced by integration of the voltammetric signal, are comparable to the ones assessed in non aqueous solvents (Tableau 1). Beyond pH=10.5, the electrochemical behaviour of SAMs is unstable due to the proximity of the water oxidation.

Because the structure of monolayer limits the accessibility of the interfacial reactive sites,^[31] the control of the structure-electroactivity relationship is decisive for enhancing interfacial reactions. An approach to improve the problems arising from intermolecular interactions is to dilute the electroactive species in the monolayer by mixing alkanethiols.³³ Indeed, electrochemical behaviours of mixed SAMs, prepared from **1a**, **1b** or **1c**:alkanethiol mixtures,^[34] fit with the interaction model developed by Laviron: the full width at half maximum and the apparent redox potential are linearly dependent on the surface coverage (Figure SI-4), and the simulations are in qualitative (*i.e.* shape) and quantitative (*i.e.* intensities) agreement with CVs of mixed SAMs (Figure 2). The excellent and rare^[35] agreement observed between theory and experiments provides evidence of a random distribution of electroactive centers on gold.

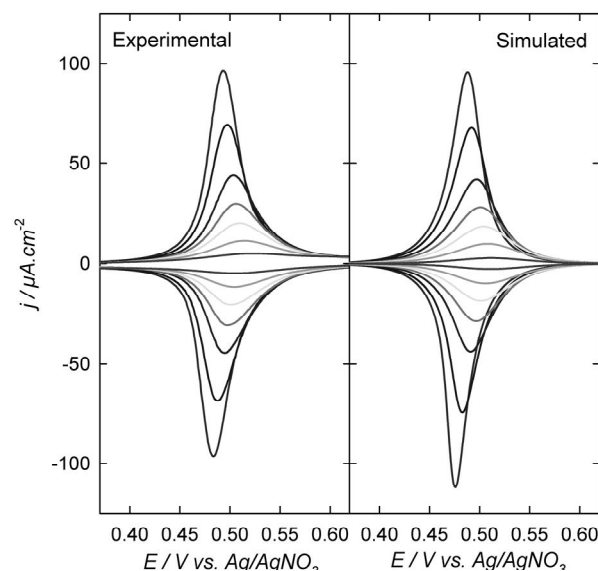


Figure 2. (Left): CVs of SAM prepared from different **1c**:decanethiol ratios, leading to 4.6, 3.8, 2.9, 2.1, 1.5 and 0.9 10^{-10} mol.cm $^{-2}$; (Right): CVs calculated from theoretical models based on a Frumkin type isotherm. In addition to the usual electrochemical parameters, calculations were performed with $r_0 = 1.0$ (corresponding to a strong interaction between oxidized centers) and only one variable changes at a time, the surface coverage ($\theta = 1.00, 0.74, 0.62, 0.52$ and 0.38).^[31] All CVs were performed in 0.1 M Bu $_4$ NPF $_6$ /CH $_2$ Cl $_2$ at 0.1 V.s $^{-1}$.

This outlook is established by electrocatalytic activities of SAMs towards benzyl-alcohol oxidation in CH_2Cl_2 and in H_2O (pH=10). First, SAMs prepared from **1a**, **1b** or **1c** are stable under electrocatalytic conditions because catalytic currents are persistent under repetitive potential scans in aqueous and non aqueous media (Figure 3 and Figure SI-5). Second, mixed SAMs (up to a limiting **1a**, **1b** or **1c**:alkanethiol ratio) increase absolute catalytic current in spite of few immobilized electroactive centers (e.g. despite five-fold lower electroactive sites, the catalytic current is 50 % higher on mixed SAMs compared to unmixed ones) and improved the stability of electrocatalytic process (Figure 3). These results also provide support for the claim^[36] that electroactive centers are random distributed on gold. As expected,^[37] oxidations of benzyl-alcohol led to benzaldehyde.

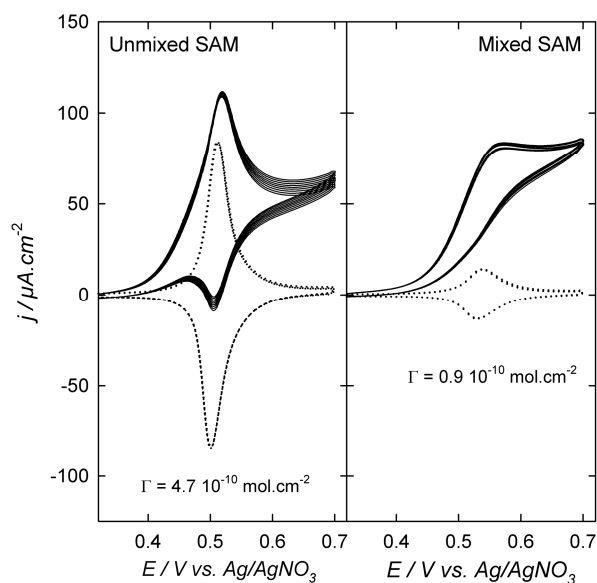


Figure 3. (Dashed line): CVs of SAMs prepared from **1c** (left) and from **1c**:dodecanethiol (right) in absence of benzyl-alcohol; (Solid line): CVs of SAMs prepared from **1c** (left) and from **1c**:dodecanethiol (right) in presence of 10 mM benzyl-alcohol. On unmixed SAM in presence of benzyl-alcohol, the persistence of a reversible oxidation wave shows that many redox centers are not active. All CVs were performed with 80 mM of 2,6-lutidine in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at 0.1 V.s^{-1} under 20 repetitive cycles.

In summary, nitroxyl radical SAMs present a noteworthy electrochemical stability in both aqueous (from pH=0 to pH=10.5) and organic media. The control of the surface coverage associated with the catalytic properties of oxoammonium cation provide a clear and convincing illustration of potentialities of nitroxyl radical SAMs. Further work is aimed at developing mixed SAMs designed to a redox-responsive material.

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- [32] To reach a stable and reproducible redox activity in aqueous media, SAMs, elaborated from CH_2Cl_2 , must be immersed in pure CH_3CN and then in pure H_2O .
- [33] a) C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Majsce, *J. Am.Chem. Soc.* **1990**, 112, 4301-4306. b) C.E.D. Chidsey, *Science* **1991**, 251, 919-922.
- [34] Mixed SAMs were prepared from a mixture TEMPO derivative/Alkanethiol solution. This procedure led to stable and reproducible SAMs.
- [35] Rare because, as mentioned by G. M. Whitesides (Ref. 3), "There are not enough experimental data to establish detailed structure-reactivity relationships for interfacial reactions on SAMs, especially on mixed SAMs".
- [36] To the best of our knowledge, SEM or AFM microscopies are not suitable to confirm this conclusion because subnanometer spatial resolution is required to characterize the organization of mixed SAMs.
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Supporting Information

Contents

EXPERIMENTAL SECTION -----	S2
CHARACTERIZATION BY ELECTROCHEMISTRY -----	S6
Figure SI-1 — QCM experiments	S6
Figure SI-2 — Electrochemical test of stability <i>vs.</i> solvent	S6
Figure SI-3 — CVs at pH = 2 <i>vs.</i> scan rate	S7
Figure SI-4 — FWHM and E_{app} <i>vs.</i> surface coverage	S7
Figure SI-5 — Electrocatalytic activity in H ₂ O	S8
REFERENCES -----	S9



EXPERIMENTAL SECTION

Materials. All reagents were purchased from commercial suppliers (Sigma-Aldrich or Acros Organics) and were used without further purification. ω -Thioacetyl carboxylic acids **2a-c** were prepared according to literature procedures.^[S1] Alkanethiols were used as received.

General Methods. All reactions were carried out under an inert N₂ or Ar atmosphere. THF was distilled from sodium-benzophenone immediately prior to use. MeOH was distilled from Mg and I₂ immediately prior to use. Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F₂₅₄ 0.2 mm thickness precoated TLC plates, which were inspected by UV-light prior to development with iodine vapor. Column chromatography was performed using Acros Organics Kieselgel 60 (0.040–0.060 mm, 230–240 mesh ASTM). ¹H NMR spectra were recorded at room temperature on a Bruker Advance DRX 500 MHz and ¹³C NMR spectra were recorded at 125.75 MHz on a Bruker Advance DRX. Chemical shifts are quoted on the δ scale and coupling constants (*J*) are expressed in Hertz (Hz). Samples for ¹H NMR spectroscopic studies were prepared using solvents purchased from C.E Saclay Euriso-Top. All spectra were referenced using the residual solvent peak. Exact mass measurements were performed using a JMS-700 (JEOL Ltd, Akishima, Tokyo, Japan) double focusing reversed geometry mass spectrometer. FAB was used as ionisation method in positive ion mode with mNBA as matrix. The sample was introduced into the ion source of the mass spectrometer and irradiated with a xenon gun at 5 keV energy and an emission current of 10.6 mA. The source pressure was kept at 2×10^{-5} Torr at room source temperature. A 7-kV acceleration voltage was applied and nominal resolution was 10000 (10 % valley definition). The elemental composition of ions was checked by high resolution measurements using an electric-field scan with a mixture of PEGs as internal standard with nominal molecular weights centered around 600.

Compound 3a

To a stirred solution of 8-(acetylthio)octanoic acid **2a** (230 mg, 1.06 mmol) in CH₂Cl₂ (20 mL) at 0°C were added 4-aminoTEMPO (270 mg, 1.58 mmol) in CH₂Cl₂ (5 mL), 1-hydroxybenzotriazole (HOBT) (210 mg, 1.58 mmol) and finally dicyclohexylcarbodiimide (330 mg, 1.58 mmol). The reaction mixture was allowed to attain room temperature and stirred under N₂ for 24 h. The precipitate of dicyclohexylurea was eliminated by filtration. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel,

eluent CH₂Cl₂/MeOH 96:4) giving **3a** as an orange oil (300 mg, 77 %); ¹H NMR (500 MHz, CDCl₃): δ 1.08-1.45 (2 m, 4H + 12H), 1.45-1.75 (m, 8H), 1.94 (m, 2H), 2.16 (bs, 2H), 2.34 (s, CH₃CO), 2.87 (t, CH₂S, *J* = 6.8 Hz), 3.50 (bs, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 24.8, 25.4, 25.6, 25.8, 25.9, 28.7, 29.0, 29.3, 29.6, 31.2, 34.5, 35.0, 40.3, 49.2, 172.6, 196.3. FAB-MS: calcd for C₁₉H₃₅N₂O₃S^{•+}, 371.2368; found: 371.2357.

Compound **1a**

A solution of **3a** (150 mg, 0.40 mmol) in anhydrous THF (30 mL) was deoxygenated with N₂ for 1 h before a solution of CsOH•H₂O (203 mg, 1.21 mmol, 3 eq.) in anhydrous MeOH (5mL), which was deoxygenated for 1 h with N₂, was added dropwise *via* a syringe. The reaction mixture was stirred 4h30, whereafter the solvent was evaporated in *vacuo* and the resulting orange residue was dissolved in CH₂Cl₂ (50 mL), washed with H₂O (3 × 30 mL) and dried (MgSO₄). Evaporation of the solvent gave an orange oil identified to **1a** (120 mg, 91 %); ¹H NMR (500 MHz, CDCl₃): δ 1.05-1.55 (m, 17H), 1.60-1.80 (m, 8H), 1.98 (bs, 2H), 2.22 (bs, 2H, CH₂CO), 2.72 (bs, 2H, CH₂S), 3.56 (bs, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 21.5, 21.9, 22.1, 22.2, 24.6, 25.4, 25.6, 25.9, 30.6, 35.4, 36.7, 45.3, 168.7; FAB-MS: calcd for C₁₇H₃₃N₂O₂S^{•+}, 329.2263; found: 329.2275.

Compound **3b**

To a stirred solution of 12-(acetylthio)dodecanoic acid **2b** (230 mg, 0.84 mmol) in CH₂Cl₂ (20 mL) at 0°C were added 4-aminoTEMPO (220 mg, 1.58 mmol) in CH₂Cl₂ (5 mL), 1-hydroxybenzotriazole (HOBT) (170 mg, 1.26 mmol) and finally dicyclohexylcarbodiimide (260 mg, 1.26 mmol). The reaction mixture was allowed to attain room temperature and stirred under N₂ for 24 h. The precipitate of dicyclohexylurea was eliminated by filtration. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH 96:4) giving **3b** as an orange oil (300 mg, 84 %); ¹H NMR (500 MHz, CDCl₃): δ 1.05-1.50 (m, 24H), 1.55-1.80 (m, 8H), 1.96 (m, 2H), 2.19 (bs, 2H), 2.36 (s, CH₃CO), 2.89 (t, CH₂S, *J* = 7 Hz), 3.55 (bs, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 23.1, 26.0, 26.3, 26.4, 26.5, 26.6, 26.7, 26.8, 28.1, 37.3, 51.9, 169.8, 193.4. FAB-MS: calcd for C₂₃H₄₃N₂O₃S^{•+}, 427.2994; found: 427.2997.

Compound **1b**

A solution of **3b** (400 mg, 0.94 mmol) in anhydrous THF (30 mL) was deoxygenated with N₂ for 1 h before a solution of CsOH•H₂O (470 mg, 2.80 mmol, 3 eq.) in anhydrous MeOH (5mL), which was deoxygenated for 1 h with N₂, was added dropwise *via* a syringe. The reaction mixture was stirred 4h30, whereafter the solvent was evaporated in *vacuo* and the resulting orange residue was dissolved in CH₂Cl₂ (50 mL), washed with H₂O (3 × 30 mL) and dried (MgSO₄). Evaporation of the solvent gave an orange oil which was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH 98:2) yielding **1b** as an orange oil (180 mg, 50 %); ¹H NMR (500 MHz, CDCl₃): δ 1.20-1.80 (m, 35H), 2.18 (bs, 2H, CH₂CO), 2.70 (t, 2H, CH₂S, *J* = 6 Hz), 3.67 (bs, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 24.2, 24.8, 24.9, 27.7, 28.1, 28.2, 28.3, 28.4, 28.5, 28.6, 28.7, 30.0, 33.2, 34.7, 38.4, 171.7, , one signal is missing or overlapping; FAB-MS: calcd for C₂₁H₄₁N₂O₂S^{•+}, 385.2889; found: 385.2899.

Compound **3c**

To a stirred solution of 16-(acetylthio)hexadecanoic acid **2c** (230 mg, 0.70 mmol) in CH₂Cl₂ (20 mL) at 0°C were added 4-aminoTEMPO (180 mg, 1.05 mmol) in CH₂Cl₂ (5 mL), 1-hydroxybenzotriazole (HOBT) (140 mg, 1.05 mmol) and finally dicyclohexylcarbodiimide (220 mg, 1.05 mmol). The reaction mixture was allowed to attain room temperature and stirred under N₂ for 24 h. The precipitate of dicyclohexylurea was eliminated by filtration. The solvent was evaporated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH 96:4) giving **3c** as an orange oil (280 mg, 83 %); ¹H NMR (500 MHz, CDCl₃): δ 1.20-1.50 (m, 32H), 1.55-1.85 (m, 8H), 1.97 (m, 2H), 2.22 (bs, 2H, CH₂CO), 2.38 (s, CH₃CO), 2.92 (t, CH₂S, *J* = 7 Hz), 3.25 (bs, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 21.6, 22.0, 22.3, 22.5, 22.7, 25.7, 25.9, 26.1, 26.2, 26.3, 26.35, 26.4, 26.46, 26.5, 27.8, 31.1, 31.8, 37.0, 52.6, 169.5, 193.0. FAB-MS: calcd for C₂₇H₅₁N₂O₃S^{•+}, 483.3620; found: 483.3636.

Compound **1c**

A solution of **3c** (163 mg, 0.34 mmol) in anhydrous THF (30 mL) was deoxygenated with N₂ for 1 h before a solution of CsOH•H₂O (170 mg, 1.01 mmol, 3 eq.) in anhydrous MeOH (5mL), which was deoxygenated for 1 h with N₂, was added dropwise *via* a syringe. The reaction mixture was stirred 4h, whereafter the solvent was evaporated in *vacuo* and the resulting orange residue was

dissolved in CH₂Cl₂ (50 mL), washed with H₂O (3 × 30 mL) and dried (MgSO₄). Evaporation of the solvent gave an orange oil which was purified by column chromatography (silica gel, eluent CH₂Cl₂/MeOH 90:10) yielding **1c** as an orange oil (100 mg, 67 %); ¹H NMR (500 MHz, CDCl₃): δ 1.10-1.50 (m, 33H), 1.60-1.80 (m, 8H), 2.01 (bs, 2H), 2.24 (bs, 2H, CH₂CO), 2.74 (t, 2H, CH₂S, *J* = 6.5 Hz), 3.41 (s, 1H); ¹³C NMR (125.75 MHz, CDCl₃): δ 23.2, 23.7, 23.9, 26.6, 27.2, 27.3, 27.35, 27.5, 27.57, 27.6, 27.7, 27.8, 28.0, 29.0, 29.1, 32.2, 37.3, 38.2, 47.2, 52.3, 170.7; FAB-MS: calcd for C₂₅H₄₉N₂O₂S^{•+}, 441.3515; found: 441.3500.

CHARACTERIZATION BY ELECTROCHEMISTRY

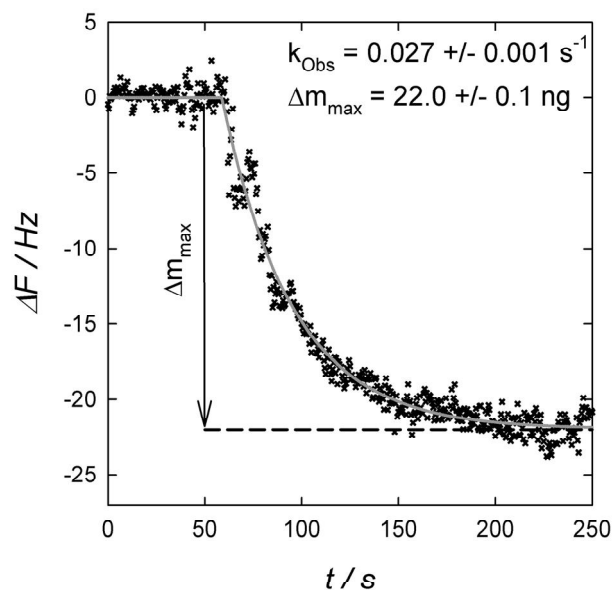


Figure SI-1. Frequency variations as a function of time of the gold coated quartz crystal during the addition of a 1 mM CH_2Cl_2 solution of **1a** into the QCM cell. The data points have been fitted according to the Langmuir adsorption isotherm model.^[S2]

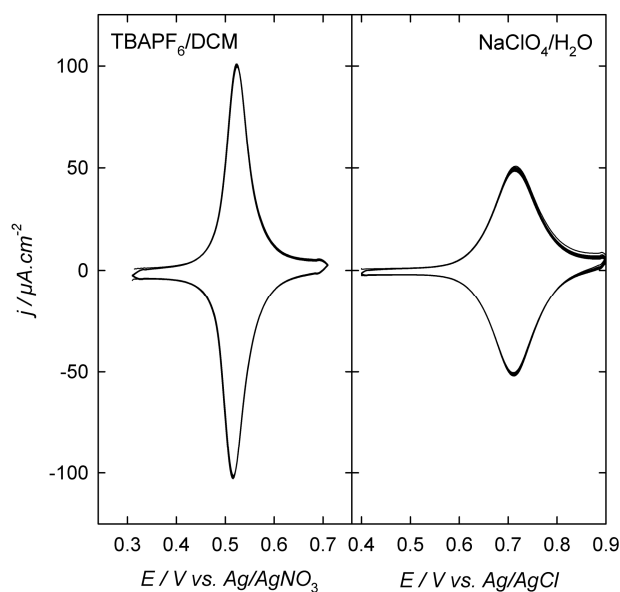


Figure SI-2: (left): CVs of SAM prepared from **1b** in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$; (right): CVs of SAM prepared from **1b** in 0.1 M $\text{NaClO}_4/\text{H}_2\text{O}$ (pH~7). Nitroxyl radical SAMs were stable: no decay of current was observed after 20 repetitive cycles at 0.1 V.s^{-1} .

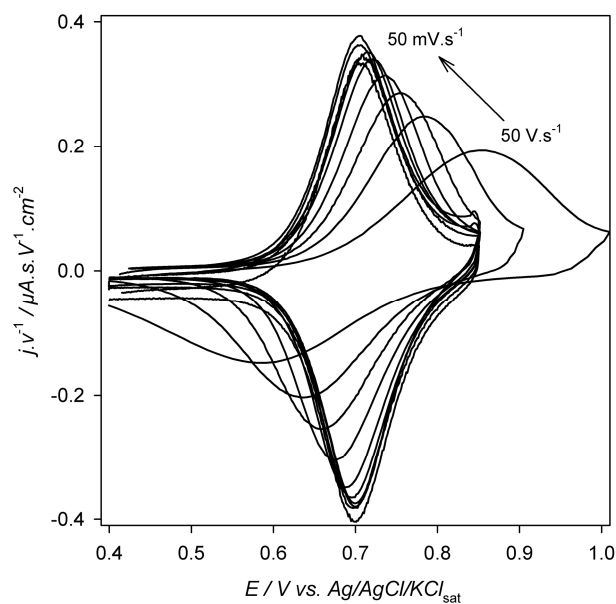


Figure SI-3: CVs of SAM prepared from **1c** vs. scan rate in $\text{HClO}_4/\text{H}_2\text{O}$ ($\text{pH}=2$). The current has been normalized to scan rate (0.05 to 50 V.s^{-1}).

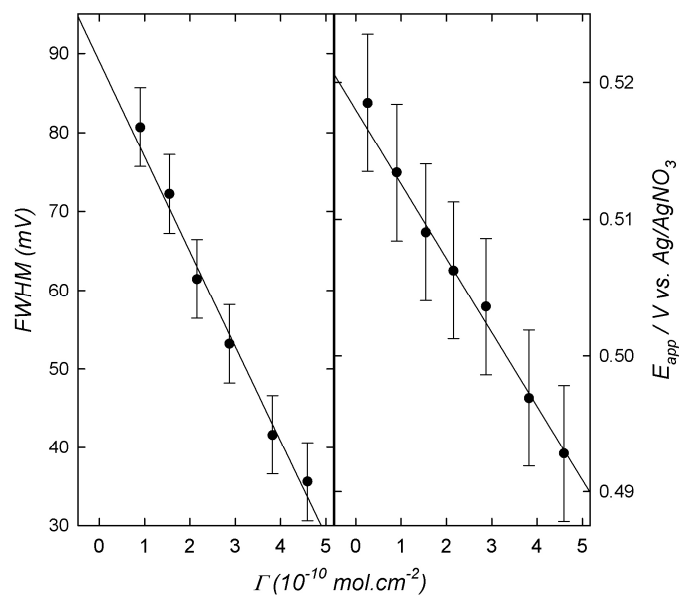


Figure SI-4: (left): Full width at half maximum (FWHM) as a function of the surface coverage; (right): Apparent redox potential (E_{app}) as a function of the surface coverage. Mixed SAMs were prepared from different **1c**:decanethiol ratios, leading to 4.6, 3.8, 2.9, 2.1, 1.5 and $0.9 \times 10^{-10} \text{ mol.cm}^{-2}$.

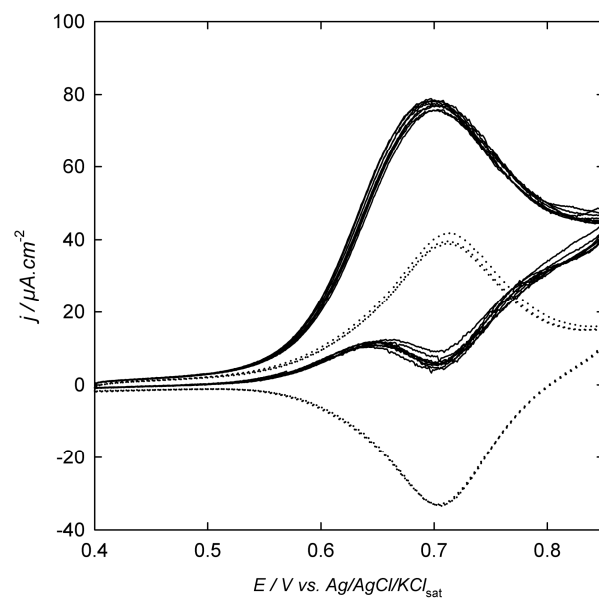


Figure SI-5: (Dashed line): CVs of SAMs prepared from **1c** in absence of benzyl-alcohol; (Solid line): CVs of SAMs prepared from **1c** in presence of 10 mM benzyl-alcohol. All CVs were performed in 0.1 M $\text{NaClO}_4/\text{NaOH}/\text{H}_2\text{O}$ (pH=10) at $0.1 \text{ V}\cdot\text{s}^{-1}$ under 20 repetitive cycles.

REFERENCES

- [S1] S. Svedhem, C.-A. Hollander, J. Shi, P. Konradsson, B. Liedberg, S. C. T. Svensson, *J. Org. Chem.* **2001**, 66, 4494-4503
- [S2] a) D. S. Karpovich, G. J. Blanchard, *Langmuir*, **1994**, 10, 3315-3322; b) It is possible to extract the deposition rate constant (k_{obs}) from the following integrated equation:

$$\theta(t) = K' [1 - \exp(-k_{\text{obs}}t)] \quad \text{where} \quad \begin{cases} k_{\text{obs}} = k_a C + k_d \\ K' = \frac{C}{C + \frac{k_d}{k_a}} \end{cases}$$

θ is the fraction of surface covered, $(1-\theta)$ represents the available sites for adsorption and C is the analytical concentration. The values of both k_a and k_d corresponding to adsorption/desorption rate constants enable the kinetic parameters to be calculated. The values of K' and k_{obs} are obtained by fitting the experimental data to the equation.