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

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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, CDCl$_3$): $\delta$ 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 C$_{10}$H$_{35}$N$_2$O$_3$S$^*$, 371.2368; found: 371.2357.

**Compound 1a**

A solution of 3a (150 mg, 0.40 mmol) in anhydrous THF (30 mL) was deoxygenated with N$_2$ for 1 h before a solution of CsOH•H$_2$O (203 mg, 1.21 mmol, 3 eq.) in anhydrous MeOH (5 mL), which was deoxygenated for 1 h with N$_2$, was added dropwise via a syringe. The reaction mixture was stirred 4 h 30, whereafter the solvent was evaporated in *vacuo* and the resulting orange residue was dissolved in CH$_2$Cl$_2$ (50 mL), washed with H$_2$O (3 × 30 mL) and dried (MgSO$_4$). Evaporation of the solvent gave an orange oil identified to 1a (120 mg, 91 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.05-1.55 (m, 17H), 1.60-1.80 (m, 8H), 1.98 (bs, 2H), 2.19 (bs, 2H, CH$_2$CO), 2.72 (bs, 2H, CH$_2$S), 3.56 (bs, 1H); $^{13}$C NMR (125.75 MHz, CDCl$_3$): $\delta$ 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 C$_{17}$H$_{33}$N$_2$O$_2$S$^*$, 329.2263; found: 329.2275.

**Compound 3b**

To a stirred solution of 12-(acetylthio)dodecanoic acid 2b (230 mg, 0.84 mmol) in CH$_2$Cl$_2$ (20 mL) at 0°C were added 4-aminoTEMPO (220 mg, 1.58 mmol) in CH$_2$Cl$_2$ (5 mL), 1-hydroxybenzotriazole (HOBT) (170 mg, 1.26 mmol) and finally dicyclohexyl carbodiimide (260 mg, 1.26 mmol). The reaction mixture was allowed to attain room temperature and stirred under N$_2$ 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 CH$_2$Cl$_2$/MeOH 96:4) giving 3b as an orange oil (300 mg, 84 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.05-1.50 (m, 24H), 1.55-1.80 (m, 8H), 1.96 (m, 2H), 2.19 (bs, 2H), 2.36 (s, CH$_3$CO), 2.89 (t, CH$_2$S, $J = 7$ Hz), 3.55 (bs, 1H); $^{13}$C NMR (125.75 MHz, CDCl$_3$): $\delta$ 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 C$_{23}$H$_{43}$N$_2$O$_3$S$^*$, 427.2994; found: 427.2997.

**Compound 1b**

A solution of 3b (400 mg, 0.94 mmol) in anhydrous THF (30 mL) was deoxygenated with N$_2$ for 1 h before a solution of CsOH•H$_2$O (470 mg, 2.80 mmol, 3 eq.) in anhydrous MeOH (5 mL), which was deoxygenated for 1 h with N$_2$, was added dropwise *via* a syringe. The reaction mixture was stirred 4 h 30, whereafter the solvent was evaporated in *vacuo* and the resulting orange residue was dissolved in CH$_2$Cl$_2$
(50 mL), washed with H$_2$O (3 x 30 mL) and dried (MgSO$_4$). Evaporation of the solvent gave an orange oil which was purified by column chromatography (silica gel, eluent CH$_2$Cl$_2$/MeOH 98:2) yielding 1b as an orange oil (180 mg, 50 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.20-1.80 (m, 35H), 2.18 (bs, 2H, CH$_2$CO), 2.70 (t, 2H, CH$_3$S, $J = 6$ Hz), 3.67 (bs, 1H); $^{13}$C NMR (125.75 MHz, CDCl$_3$): $\delta$ 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 C$_{21}$H$_{41}$N$_2$O$_2$S$,^+$, 385.2889; found: 385.2899.

**Compound 3c**

To a stirred solution of 16-(acetylthio)hexadecanoic acid 2c (230 mg, 0.70 mmol) in CH$_2$Cl$_2$ (20 mL) at 0°C were added 4-aminoTEMPO (180 mg, 1.05 mmol) in CH$_2$Cl$_2$ (5 mL), 1-hydroxybenzotriazole (HOBT) (140 mg, 1.05 mmol) and finally dicyclohexyl carbodiimide (220 mg, 1.05 mmol). The reaction mixture was allowed to attain room temperature and stirred under N$_2$ 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 CH$_2$Cl$_2$/MeOH 96:4) giving 3c as an orange oil (280 mg, 83 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.20-1.50 (m, 32H), 1.55-1.85 (m, 8H), 1.97 (m, 2H), 2.22 (bs, 2H, CH$_2$CO), 2.38 (s, CH$_3$CO), 2.92 (t, CH$_2$S, $J = 7$ Hz), 3.25 (bs, 1H); $^{13}$C NMR (125.75 MHz, CDCl$_3$): $\delta$ 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 C$_{27}$H$_{51}$N$_2$O$_3$S$,^+$, 483.3620; found: 483.3636.

**Compound 1c**

A solution of 3c (163 mg, 0.34 mmol) in anhydrous THF (30 mL) was deoxygenated with N$_2$ for 1 h before a solution of CsOH•H$_2$O (170 mg, 1.01 mmol, 3 eq.) in anhydrous MeOH (5mL), which was deoxygenated for 1 h with N$_2$, 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 CH$_2$Cl$_2$ (50 mL), washed with H$_2$O (3 x 30 mL) and dried (MgSO$_4$). Evaporation of the solvent gave an orange oil which was purified by column chromatography (silica gel, eluent CH$_2$Cl$_2$/MeOH 90:10) yielding 1c as an orange oil (100 mg, 67 %); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.10-1.50 (m, 33H), 1.60-1.80 (m, 8H), 2.01 (bs, 2H), 2.24 (bs, 2H, CH$_2$CO), 2.74 (t, 2H, CH$_2$S, $J = 6.5$ Hz), 3.41 (s, 1H); $^{13}$C NMR (125.75 MHz, CDCl$_3$): $\delta$ 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, 28.9, 29.0, 29.1, 32.2, 37.3, 38.2, 47.2, 52.3, 170.7; FAB-MS: calcd for C$_{25}$H$_{49}$N$_2$O$_2$S$,^+$, 441.3515; found: 441.3500.
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Figure SI-1. Frequency variations as a function of time of the gold coated quartz crystal during the addition of a 1 mM CH$_2$Cl$_2$ solution of 1a into the QCM cell. The data points have been fitted according to the Langmuir adsorption isotherm model.$^{[82]}$

Figure SI-2: (left): CVs of SAM prepared from 1b in 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$; (right): CVs of SAM prepared from 1b in 0.1 M NaClO$_4$/H$_2$O (pH~7). Nitroxy 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 HClO₄/H₂O (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 10⁻¹⁰ 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 NaClO₄/NaOH/H₂O (pH=10) at 0.1 V.s⁻¹ under 20 repetitive cycles.
REFERENCES


[S2] a) D. S. Karpovich, G. J. Blanchard, *Langmuir*, **1994**, *10*, 3315-3322; b) It is possible to extract the deposition rate constant ($k_{ob}$) from the following integrated equation:

\[ \theta(t) = K \left[ 1 - \exp\left(-k_{ob}t\right) \right] \]

where

\[
\begin{align*}
    k_{ob} &= k_a C + k_d \\
    K' &= \frac{C}{C + \frac{k_d}{k_a}}
\end{align*}
\]

$\theta$ 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 $k_{ob}$ are obtained by fitting the experimental data to the equation.