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2-Methyl-1,4-naphthoquinones containing 3-[*N*-(ω-mercaptoalkyl)alkanamide] chains: synthesis, self-assembling, and electrochemical properties

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ABSTRACT

2-Methyl-1,4-naphthoquinone derivatives containing 3-[*N*-(ω-mercaptoalkyl)alkanamide] chains were synthesized from ω-bromoalkylamine salts of 2-methyl-3-carboxyalkyl-1,4-naphthoquinones in the presence of *N,N′*-dicyclohexylcarbodiimide at ambient temperature, and then transformed into the corresponding mercapto derivatives. Their self-assembling and electrochemical properties on gold were studied. The influence of an intrachain amide group on the structure and electron transfer properties of self-assembled monolayers were evaluated by comparison with analogous ester and alkyl chain-containing 2-methyl-1,4-naphthoquinones.

2-Methyl-1,4-naphthoquinone derivatives (vitamins of the K-group) are of physiological importance due to their ability to transport both electrons and protons across biological membranes. By selecting suitable molecular structures and using an electrochemical approach to study the electron transport phenomena, it is possible to obtain important information on the efficiency of biological long-range electron transfer through the medium separating two redox sites. Model molecular systems to study these processes can be two-dimensional self-assembled monolayers (SAMs)[1] functionalized with a 2-methyl-1,4-naphthoquinone (2-MeNQ) group. Published studies on naphthoquinone-based SAMs involve molecules in which the quinone ring has substituents other than a methyl group, and/or where the alkylthiol linker is attached to the naphthoquinone moiety through the nitrogen atom.[2] Recently, we synthesized and studied the structural and electrochemical characteristics of SAMs using Au modified with 2-MeNQ derivatives containing 3-(ω-mercaptoalkyl)[3] or 3-(ω-mercaptoalkylalkanoate)[4] linkers. These new SAMs demonstrate high stability in electrochemical polarization experiments, but exhibit slow electron transfer and are relatively disordered.[3]

One of the approaches to decrease distortions in monolayer packing and/or change electron transfer efficiency in electroactive SAMs is based on the introduction of internal functionalities ('bridges') in the linker. The most important bridge in biological systems is an amide group, which is able to form hydrogen bonds inside the SAM.[5] However, investigations of SAMs with attached redox groups (ferrocenyl or pentaamine(pyridine)ruthenium) containing an amide bridge in the linker are scarce.[6]

Among the most relevant methods to form SAMs containing an amide bond in the linker are the covalent attachment of carboxylic acids to SAMs functionalized with ω-aminoalkylthiols, or the attachment of 1-alkylamines to SAMs functionalized with ω-carboxyalkylthiols in a solution containing a water-soluble derivative of carbodiimide as coupling reagent.[7] However, the SAMs formed using these approaches are not well suited for structural studies, as the reactions performed are usually incomplete, the analysis of reaction products is difficult, and the SAMs formed are composed of nonidentical molecules. Therefore, it is preferable to prepare SAMs from pure compounds, either individual or mixed with the desirable diluents in the appropriate compositions.

We pursued a convenient method for the synthesis of 2-methyl-1,4-naphthoquinones containing 3-*N*-[(ω-mercaptoalkyl)alkanamide] groups of different alkyl chain length and location of the amide bond. The reaction sequence for the synthesis of the target compounds was developed analogously to that for the above-mentioned 3-(ω-mercaptoalkylalkanoates)[4] using the amidation reaction instead of esterification. The most common method for amide bond formation is the reaction between a carboxylic acid and an amine via conversion of the carboxy group to a more reactive functional group, for example, acyl chloride and *N*-acylbenzotriazole, or via in situ activation of the carboxy group using coupling agents such as *N,N′*-dicyclohexylcarbodiimide (DCC).[8] However, certain functional groups are incompatible with the presence of a free amine group or conversion of a carboxylic acid to a more reactive functional group is impossible, and acylation by heating the components leads to undesirable side reactions.

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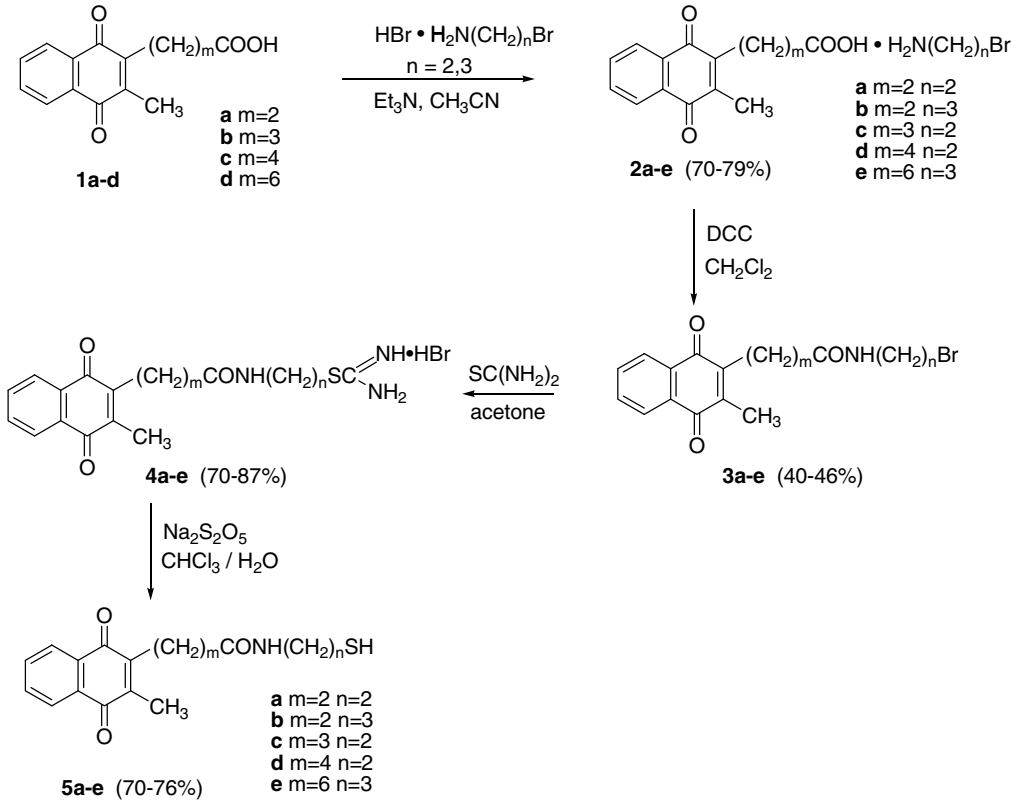
In this work, the free base of the ω-halogeno-alkylamines is unstable due to condensation with itself and conversion to an imine. Only a few methods are reported in the literature for the preparation of *N*-halogenoalkyl substituted amides. One example involves reaction under Schotten–Baumann conditions using a halogenoalkyl amine hydrohalogenide and acyl chloride in the presence of a base.[9] Another method involves the synthesis of amides from ω-halogenoalkylamine hydrohalogenides and acyl chlorides at high temperature. The poor reactivity of the protonated amine group requires lengthy reflux in toluene for reaction.[10] Both methods could not be applied in this work due to the sensitivity of the 2-methyl-3-carboxyalkyl-1,4-naphthoquinones to transformation into acyl halides. Acylation of unstable amines through stable salts under mild conditions is described in patents.[11] In one case,[11a] prior to acylation, the amine salt of 1-hydroxybenzotriazole (HOBt) or 3-hydroxy-4-oxo-3,4-dihydro-1,2,3-benzotriazine (HOOBt) was prepared. The salts could be acylated directly with carboxylic acids or their activated esters in the presence of DCC in aprotic solvents. The disadvantage of this method is the difficulty in removing HOBt or HOOBt from the reaction. In another case,[11b] amide bond formation (without conversion of the amine salt to an amine base prior to the coupling) was achieved by applying insoluble inorganic bases, for example, $Ca(OH)_2$. One further possibility for stabilization of unstable amine components prior to the coupling could involve formation of salts between the reacting components. Such salts of various solubilities can be formed in amidation reactions when the carboxylic acid and amine are introduced simultaneously, and salt formation does not hinder coupling with DCC in a suitable solvent.[12]

For the synthesis of the title compounds, and based on the above considerations, we selected the latter method for stabilization of ω-bromoalkylamines during amide bond formation using DCC as the coupling agent. The starting 2-methyl-3-carboxyalkyl-1,4-naphthoquinones **1a**–**d** (Scheme 1) were obtained by free-radical alkylation of 2-methyl-1,4-naphthoquinone with the appropriate dicarboxylic acids using the method of Jacobsen and Torssell[13] adopted by us previously.[4] Next, these compounds were converted to their ω-bromoalkylamine salts **2a**–**e** by the addition of triethylamine to a CH_3CN solution containing an equimolar amount of ω-bromoalkylamine hydrobromide and 2-methyl-3-carboxyalkyl-1,4-naphthoquinones **1a**–**d.** Shortly after the addition a fine yellow precipitate formed in good yield, and the salts were isolated by filtration and used in the next step without further purification. The condensation reaction between salts **2a–e** leading to amide bond formation was successfully performed using DCC as coupling reagent at ambient temperature. Salts **2a–e** were dissolved in methylene chloride, then treated with a CH_2Cl_2 solution of DCC (30% excess) for 48 h at ambient temperature. The *N*-(ω-bromoalkyl)alkanamides **3a–e** obtained were isolated by standard methods. Next, they were transformed into isothiouronium salts **4a–e,** and, after decomposition in a water/chloroform heterogeneous phase containing $Na_2S_2O_5$,[4] the target 2-MeNQ derivatives **5a–e** with a terminal mercapto group were obtained.

The structures and electrochemical properties of the SAMs formed from derivatives **5a-e** on an Au electrode were studied by Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS) and cyclic voltammetry (CV). Procedures for electrode pretreatment and modification with SAM-forming compounds have been described in detail in previous papers.[2e,3,4] Electrochemical and spectral measurements were performed in 0.1 M $HClO_4$ solution. All potentials are given versus a saturated sodium calomel electrode (SSCE). SAM formation was probed using FT-SERS, and by comparing the Raman spectra of bulk compounds with the SERS spectra of SAMs formed on a roughened Au electrode. The main differences observed between the Raman spectrum of bulk **5c** (Fig. 1, curve 1) and the SERS spectrum of the Au electrode



Scheme 1.

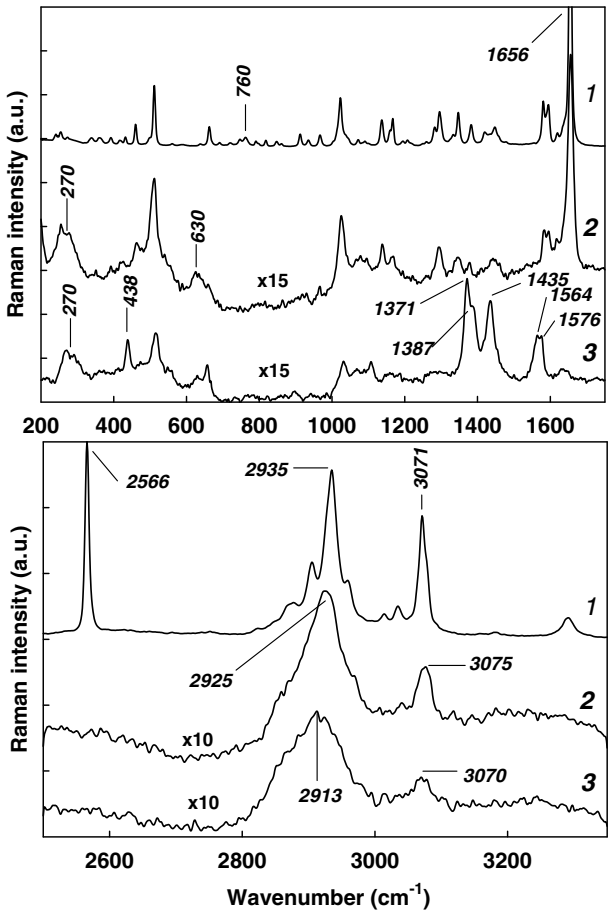


Figure 1. FT-Raman and FT-SERS spectra of compound **5c**: FT-Raman spectrum of solid compound (1); FT-SERS of self-assembled **5c** on the Au electrode in 0.1 M $HClO_4$ at a potential of 605 (2); and −595 mV versus SSCE (3). Laser power (1064 nm) is: 1–200 mW, 2 and 3–300 mW.

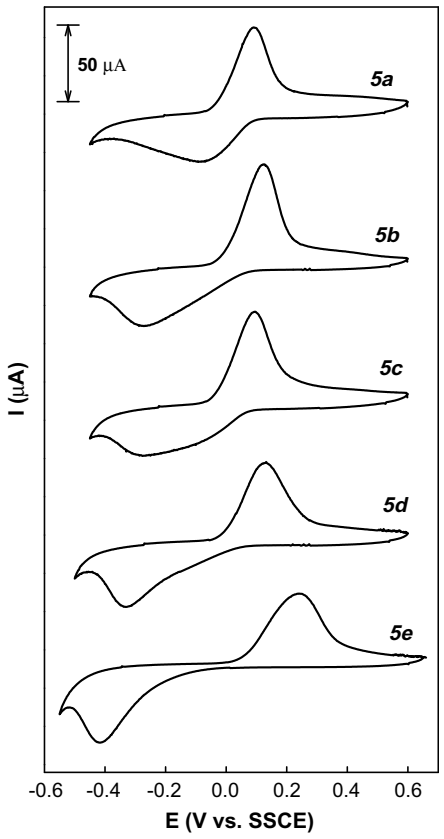


Figure 2. Cyclic voltammograms of smooth Au electrode modified with compounds **5a–e.** Measurements performed in anaerobic 0.1 M $HClO_4$ at 25 °C. Potential scan rate is 100 mV/s.

modified with **5c** at an electrode potential of 605 mV (Fig. 1, curve 2) are as follows: (a) the prominent S–H stretching band at 2566 cm^{-1} disappears, indicating cleavage of the S–H bond upon formation of the SAM; (b) the new band at 270 cm^{-1} is characteristic of Au–S stretching vibrations[2e,3,4,14] and infers chemisorption of **5c** onto the surface via the S atom; (c) the C–S stretching vibrations of the *trans*-conformers of solid **5c** observed at 760 cm^{-1} were transformed into a new band at 630 cm^{-1}, which are characteristic of *gauche*-conformers in the adsorbed state,[15] indicating a change of conformation of the alkyl chain near the surface. The frequencies and relative intensities of the other bands belonging to the naphthoquinone ring are similar in the solid and adsorbed states, implying that this moiety is not strongly perturbed upon SAM formation. When the potential of the Au electrode is switched to negative values (−595 mV vs. SSCE), the SERS spectrum of adsorbed **5c** (Fig. 1, curve 3) changes radically: (a) the very intense stretching vibration band of the C=O group of 2-MeNQ observed at 1656 cm^{-1} completely disappears[16]; (b) new bands at 438, 1371–1387, 1435 and ca. 1564–1576 cm^{-1} characteristic of a substituted naphthalene ring occur.[17] These data provide direct evidence that, at negative potential, 2-MeNQ is reduced to 2-methyl-1,4-dihydroxynaphthalene.

The cyclic voltammograms (CVs) of Au electrodes modified by compounds **5a**–**e** exhibit characteristic reduction and oxidation waves (Fig. 2) with anodic and cathodic peak-currents linearly dependent on the potential sweep rate (Supplementary data, Fig. S1). The CVs remain stable during long-term cycling implying high stability of the SAMs. For instance, the surface concentration calculated from the CV of compound **5c** during 6 h potential sweeping between 700 and −500 mV (100 mV/s scan rate) in 0.1 M $HClO_4$ solution decreases by less than 10% without any notable changes in the FT-SERS spectrum.

The main electrochemical redox conversion parameters calculated from the CV curves are summarized in Table 1. The estimated surface concentration (Γ), determined by integration of the anodic peak-current at 100 mV/s and assuming two-electron reduction of the 2-MeNQ group in the SAM, practically does not depend on the linker length and is close to the value calculated for vertically orientated 2-MeNQ groups ($\Gamma = 3.4 \times 10^{-10}$ mol/cm^2).[4] Thus, the SAMs formed from compounds **5a–e** exhibit surface coverage amounting to more than 85% of the monolayer. Cathodic (E_p^c) and anodic (E_p^a) peak-potentials depend on the total number of atoms in the linker. Increasing the linker length moves the formal redox potential, $E^{o'} = (E_p^c + E_p^a)/2$, to negative values similar to observations in the case of related compounds.[3,4,18] Furthermore, the peak-to-peak separation, ΔE_p, increases almost linearly with an increase in the number of atoms in the linker with values ranging from 219 to 652 mV being characteristic of irreversible electrochemistry. Thus, the modified Au electrodes demonstrate slow electron transfer kinetics. The apparent heterogeneous electron transfer rate constants, k_{app}, established by the method of Laviron[19] from linear dependencies (E_p^a) and (E_p^c) versus ln(E scan rate) in the range 10 and 750 mV/s, decrease with increased linker length. The amount of electrons transferred per molecule, n, determined from the same dependence, for compounds **5a**, **5b**, and **5c** is close to 2, but it is somewhat lower for compounds with a longer linker. Taken together, these electrochemical data support the fact that the studied SAMs are sufficiently compact and ordered.

Table 1
The main electrochemical parameters (± standard deviation) of the SAMs, obtained from compounds **5a–e** on Au measured in 0.1 M $HClO_4$ at 25 °C

m, *n*	E_p^c (mV) versus SSCE	E_p^a (mV) versus SSCE	$E^{o'}$ (mV) versus SSCE	ΔE_p (mV)	$-\lg(k_{app}, s^{-1})$	*n*	$\Gamma^* 10^{10}$ (mol/cm^2)
2, 2 (**5a**)	−128 ± 39	91 ± 2	−19 ± 19	219 ± 39	1.34 ± 0.10	2.1 ± 0.2	2.9 ± 0.2
2, 3 (**5b**)	−269 ± 6	124 ± 4	−73 ± 5	394 ± 4	2.84 ± 0.31	2.0 ± 0.2	2.8 ± 0.3
3, 2 (**5c**)	−277 ± 29	97 ± 16	−90 ± 7	373 ± 45	2.48 ± 0.10	2.0 ± 0.2	2.9 ± 0.6
4, 2 (**5d**)	−332 ± 6	125 ± 11	−104 ± 4	458 ± 17	2.67 ± 0.19	1.7 ± 0.1	3.1 ± 0.6
6, 3 (**5e**)	−416 ± 5	236 ± 5	−90 ± 12	652 ± 9	3.24 ± 0.11	1.6 ± 0.1	2.9 ± 0.6

In order to determine the impact of the intrachain amide group on the electrochemical and structural parameters of the SAMs, the $E^{o'}$ and k_{app} values were compared with the corresponding data for previously studied compounds containing an ester group[4] or an unfunctionalized hydrocarbon linker[3] (Table 2). The $E^{o'}$ values of amides **5a** and **5b** and the corresponding esters with $m = 1$ or 2 are shifted positively[4] in comparison with hydrocarbons of the same length.[3] This effect could be explained by the inductive action of these polar groups to the redox center. The difference in $E^{o'}$ disappears when $m + n + 2 \geqslant 7$. As concerns k_{app}, this parameter for amides **5a–e** is much higher than for the corresponding esters, but almost approaches the value for compounds with hydrocarbon linkers.

In an attempt to explain the observed differences in the electron transfer rate of the above-mentioned compounds, containing the different intrachain bridges, we studied the structure of the monolayers in more detail by comparing the FT-SERS spectra of amides **5a** and **5d** with the spectra of appropriate ester analogues. To this end, we used the CH_2 stretching region, which is known to be sensitive to the lateral interaction between *n*-alkyl chains.[20] The data obtained (Fig. 3) show that, in the SAM spectra, the wavenumbers of the asymmetric CH_2 stretching band ($\nu_{asym}(CH_2)$; in the vicinity of 2900 cm^{-1}) of the oxidized amides **5a** and **5d** are 5–7 cm^{-1} lower than those of the corresponding alkanoates, 2-Me-3-[$(CH_2)_2$-$COO(CH_2)_2$SH]-1,4-NQ or 2-Me-3-[$(CH_2)_4COO(CH_2)_2$SH]-1,4-NQ, whereas the values are 9–10 cm^{-1} lower for the reduced substrates (Table 3). This implies that SAMs containing amide linkages have a higher degree of order than those of alkanoates. Again, the estimated surface concentrations Γ of the amides **5a–e** are about 20% higher than those of the ester analogues,[4] which confirms the increased packing density of amides. Therefore, it is assumed that compounds **5a-e**, containing an intrachain amide group, form a hydrogen bond network between the neighboring linkers. The impact of hydrogen bonding on the electron transfer rate has been shown previously in the case of electroactive monolayers containing intrachain amide groups and ferrocenylamide[6a] or ferrocenyl head groups.[6c] Notably, our data are in accordance with the findings of Seo et al.[7c] where the packing of monolayers from 11-ferrocenecarbonyloxy- and 11-ferrocenecarbonylamino-1-undecylthiols are compared. Tillman et al.[21] also pointed out the unfavorable influence of ester groups on chain packing in SAMs.

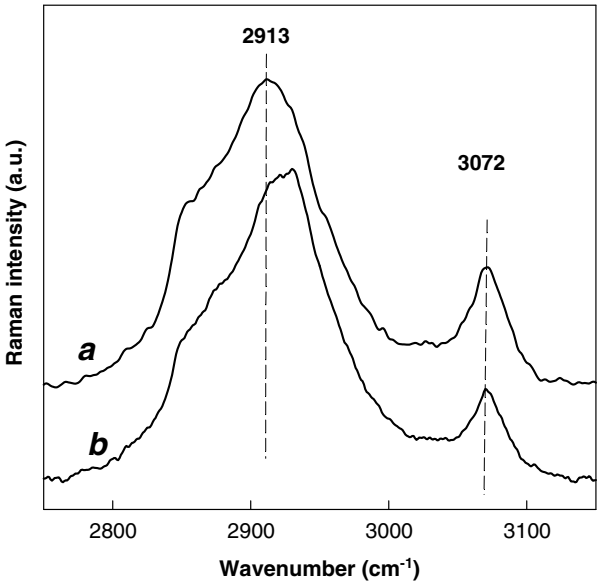


Figure 3. FT-SERS spectra of compound **5a** (a) and 2-Me-3-[$(CH_2)_2COO(CH_2)_2$ SH]-1,4-NQ (b) self-assembled on Au electrodes in 0.1 M $DClO_4$ (D_2O) at a potential of −595 mV versus SSCE. Laser power (1064 nm) is 300 mW.

Table 3
Comparison of the Raman peak frequencies (in cm^{-1}) of asymmetric CH_2 (in the vicinity of 2900 cm^{-1}) and aromatic C–H stretching vibrations in SAMs formed from the oxidized (Ox-form) and reduced (Red-form) of 2-methyl-3-[$(CH_2)_m$-CONH-$(CH_2)_n$SH]-1,4-naphthoquinones and 2-methyl-3-[$(CH_2)_m$-COO-$(CH_2)_n$SH]-1,4-naphthoquinones measured in 0.1 M $DClO_4$ (D_2O)

m, *n*	X = –CONH–		X = –COO–	
	Ox-form	Red-form	Ox-form	Red-form
2, 2	2922 (2924)[a]	2913 (2917)	2929 (2927)	2923 (2921)
	3038 (3035)	—	3036 (3038)	—
	3075 (3074)	3072 (3073)	3075 (3076)	3071 (3070)
4, 2	2924	2915	2929	2924
	3037	—	3036	—
	3075	3072	3074	3071

[a] Data in parentheses obtained from the SERS spectra measured in 0.1 M $HClO_4$ (H_2O).

Table 2
Comparison of the formal redox potentials ($E^{o'}$, mV vs SSCE) and heterogeneous electron transfer rate constants (k_{app}, s^{-1}) of SAMs (± standard deviation) obtained of 2-methyl-3-[$(CH_2)_m$-X-$(CH_2)_n$SH]-1,4-naphthoquinones on Au measured in 0.1 M $HClO_4$ at 25 °C

m, *n*	X = –CONH–		X = –COO–[4]		X = –CH_2CH_2–[3]	
	$E^{o'}$	$-\lg(k_{app})$	$E^{o'}$	$-\lg(k_{app})$	$E^{o'}$	$-\lg(k_{app})$
1, 2	—	—	−40 ± 7	2.0 ± 0.5	−79 ± 4	1.92 ± 0.11
2, 2	−19 ± 19	1.3 ± 0.1	−56 ± 4	2.8 ± 0.2	—	—
2, 3	−73 ± 5	2.8 ± 0.3	—	—	−92 ± 4	2.8 ± 0.22
3, 2	−90 ± 7	2.5 ± 0.1	−84 ± 12	3.4 ± 0.7	−92 ± 4	2.8 ± 0.22
4, 2	−104 ± 4	2.7 ± 0.2	−92 ± 14	3.2 ± 0.4	—	—
4, 3	—	—	−108 ± 11	3.2 ± 0.5	−107 ± 5	3.28 ± 0.18
6, 3	−90 ± 12	3.24 ± 0.11	−123 ± 4	4.5 ± 1.1	—	—

In conclusion, we have synthesized 2-methyl-1,4-naphthoquinone derivatives containing 3-[*N*-(ω-mercaptoalkyl)alkanamide] chains that form stable self-assembled monolayers on gold. It has been found that replacement of the ester group in the hydrocarbon linker results in increased surface coverage and an apparent heterogeneous electron transfer rate constant. Structural studies of the monolayers by FT-SERS indicated increases in interchain interactions and ordering within the monolayer.

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Supplementary data

Supplementary data (experimental procedures and characterization of the synthesized compounds by ^{1}H NMR and FT-IR spectra, descriptions of the Au electrode preparation, procedures for FT-Raman spectra measurements and additional electrochemical data) associated with this article can be found in the online version, at doi:10.1016/j.tetlet.2008.08.039.

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