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Synthesis and self-assembling properties on gold of 2-methyl-1,4-naphthoquinone derivatives containing ω-mercaptoalkylalkanoate groups

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Abstract—The synthesis of a series of 2-methyl-1,4-naphthoquinone (2-MeNQ) derivatives containing surface active ω-mercaptoalkylalkanoate groups with 5–12 atoms in the side-chains is reported. The compounds form stable self-assembled monolayers (SAMs) on gold. The complete reduction of the terminal 2-MeNQ group in the SAMs was confirmed by in situ Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS). The basic electrochemical properties of the monolayers were determined by cyclic voltammetry (CV).

Derivatives of 2-methyl-1,4-naphthoquinone (2-MeNQ), mena- and phylloquinones (lipid-soluble vitamins K), are known to play important roles in biological systems including electron transport in photosynthesis and the build up of a proton gradient across the biomembrane. To gain a better insight into the redox functioning of natural 2-MeNQ derivatives, it is very important to explore the electrochemical properties of such molecules under conditions close to those prevailing in the lipid bilayer. To this end, among various possible models of the biomembrane, self-assembled monolayers (SAMs) of two-dimensional order on an electrode surface, are particularly attractive.[1] Additionally, the naphthoquinone (NQ)-terminated SAMs are in themselves of particular interest because of the possibility of constructing chemically modified electrodes with pH-dependent electrocatalytic properties. Self-assembling compounds, as a rule, are surface-active ω-mercaptoalkanes or corresponding dialkyldisulfides that also may contain different terminal redox-active groups. Benzoquinone-terminated SAMs are the most widely studied among the quinone derivatives.[2] Their redox and structural properties were elucidated by vibrational spectroscopic,[2a] electrochemical[2b,c] and electrogravimetrical methods.[2d] The importance of mutual interactions between the redox active groups in determining the SAM's electrochemical properties was demonstrated by the analysis of the effect of coating solution concentration on the voltammetric characteristics.[2c] An increase in electrochemical reversibility was detected for a series of planar-shaped anthraquinone derivatives as the result of dilution of the monolayer with 1-alkanethiols.[3] Complicated electrochemical behaviour is expected for the biologically relevant quinones possessing a bulky aromatic 2-MeNQ group because of π–π stacking interactions and distortions in the monolayer packing induced by the large cross-sectional area of the terminal group.

As far as we know, the investigations of NQ-containing SAMs are few in number. Thus, Mukae et al.[4] anchored 2,3-dichloro-NQ through the SAMs of ω-aminoalkanethiols of varied chain length ($m = 2$, 5 and 8, where m is the number of CH_2 groups) on a Au electrode, and studied their redox behaviour by voltammetry. Panetta et al.[5] formed SAMs from 2-decylamino- and 3-chloro-2-decylamino-NQ disulfides and methyl sulfides. The self-assembling properties of dialkyl disulfides containing 2-chloro-3-alkylamino-NQ group with different lengths of spacer were studied by Ohtsuka et al.[6] SAM-forming compounds containing 3-chloro-2-alkylamino- or 3-chloro-2-alkylthio-NQ groups were also used.[7] It should be emphasized that, on the one hand, the NQ

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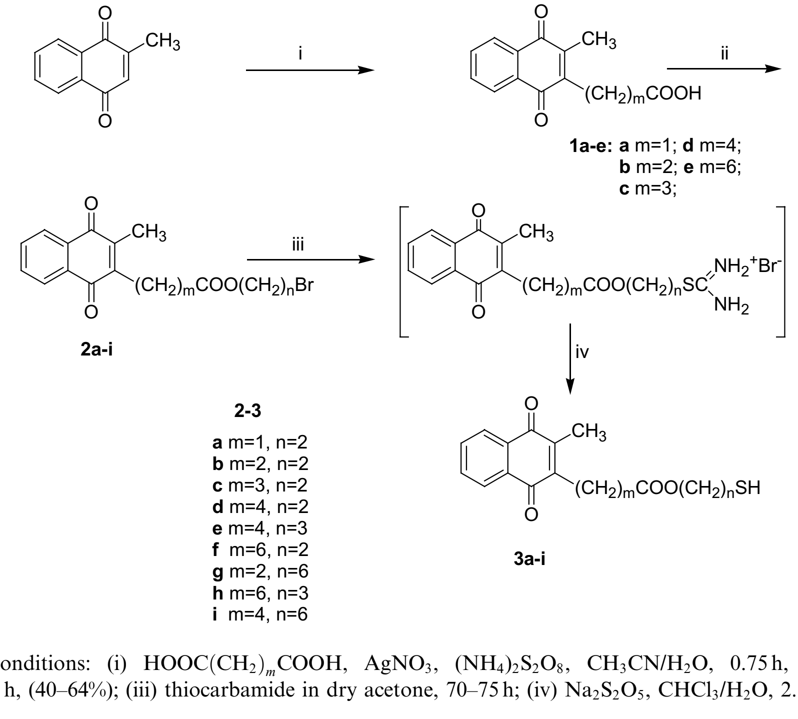
ring in all of these compounds has additional substituents strongly affecting the redox characteristics, and on the other hand, the alkyl chain serves as a spacer between the mercapto (disulfide) and terminal NQ groups. At this point, mention may be made of our earlier studies,[8] in which very stable SAMs were obtained by the introduction of an ester group in the alkyl side-chain of ferrocene.

With the above in mind, our objective was to synthesize SAM-forming NQ derivatives bearing the same redox-active moiety as vitamins K, and also containing the ester bridge in thiol-functionalized alkyl chains of different lengths. We present here the synthesis of 2-MeNQ derivatives containing ω-mercaptoalkylalkanoate groups at C-3 of NQ, and a preliminary study of their interfacial properties on gold. To the best of our knowledge, there is no report in the literature regarding SAMs containing terminal 2-MeNQ.

The strategy used to obtain the title derivatives of 2-MeNQ was based on a direct functionalization of the quinone ring via radical substitution reactions using dicarboxylic acids. The synthetic steps are shown in Scheme 1. It should be mentioned that the synthesis of 1,4-NQs containing an aliphatic carboxylic acid as a substituent to the quinone ring presents a synthetic problem, and only a few reports on this topic are available in the literature.[9–11] Thus, the 2-MeNQ-containing carboxylic acids with *m* equal to 4 and 5 were obtained by the reaction of NQ with appropriate diacylperoxides followed by the hydrolysis of the ester group.[11] This method is not convenient because diacylperoxides are commercially unavailable and the procedure also involves an additional hydrolysis step. The more attractive free-radical alkylation of 1,4-NQs using dicarboxylic acids (Jacobsen and Torssell[9]) was applied to the synthesis of the 2-MeNQ containing carboxylic acid with $m = 8$.[10] However, short dicarboxylic acids did not give the desired derivatives due to side reactions that involved radical recombination or cyclization to, for example, butyrolactone, etc., and led to mixtures.[9] We successfully developed the reaction conditions for 1,4-MeNQ acids **1a**–**e**, including those with a short carboxylic acid chain ($m = 1$–3). In contrast to the above mentioned report,[9] we used a slight excess of dicarboxylic acid, and increased the quantities of $AgNO_3$ (2-fold) and ammonium persulfate (1.6-fold) in the reaction mixture. A carefully controlled rate of persulfate addition and the optimal ratio of CH_3CN/H_2O have to be selected in order to avoid precipitate formation and enable a satisfactory yield of the product to be achieved. Derivatives **1a**–**e** were isolated from the reaction mixture by transforming them into salts with potassium carbonate, and extracting the side-products with methylene chloride.[12] The following step of the synthesis was the esterification of acids **1a**–**e** with ω-bromoalkanols to give the corresponding esters **2a**–**i**.[13] Finally, ω-mercapto derivatives **3a**–**i** were obtained via isothiouronium salts by using the modified procedure[14] developed by us previously.[8a] The structures of the synthesized compounds were confirmed by spectral and elemental analyses.

The structure and electrochemical properties of the SAMs formed by derivatives **3a**–**i** on gold were probed by cyclic voltammetry (CV) and near-infrared (NIR) Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS). For the electrochemical experiments, the SAMs were formed by soaking a pre-treated polycrystalline gold electrode in a 0.1 mM solution of compound **3** in ethanol for 20 h. The surface pre-treatment was accomplished by polishing with 0.05 μm alumina



Scheme 1. Reagents and conditions: (i) $HOOC(CH_2)_mCOOH$, $AgNO_3$, $(NH_4)_2S_2O_8$, CH_3CN/H_2O, 0.75 h, (6–30%); (ii) $Br(CH_2)_nOH$, p-$CH_3C_6H_4SO_3H$, benzene, 6 h, (40–64%); (iii) thiocarbamide in dry acetone, 70–75 h; (iv) $Na_2S_2O_5$, $CHCl_3/H_2O$, 2.5 h, (38–55%).

slurry, rinsing with water and ethanol, cleaning for 5 min in an ultrasonic bath (water/ethanol, 1:1 v/v), and electrochemical cleaning in 0.1 M H_2SO_4 within the potential (E) range 0.4–1.6 V (vs sodium saturated calomel electrode, SSCE) for 25 min at a E scan rate of 0.1 V/s. Measurements were performed in a 0.1 M $HClO_4$ solution purged with Ar at 25 °C. All potentials are given versus SSCE. The real surface area of the bare gold electrode was determined by measuring the area of the gold oxide reduction peak in 1.0 M H_2SO_4.[15] The typical CV of the 2-MeNQ-terminated SAM exhibits well-defined redox waves (Fig. 1). The parameters derived from the CV curves are summarized in Table 1. Assuming the two-electron electrochemical conversion of terminal NQ, the estimated surface concentration (Γ) of the redox-active 2-MeNQ groups in the monolayer was found to be only slightly dependent on the spacer length, and are about 1.5 times lower than the expected value of 3.4×10^{-10} mol/cm^2 for the close-packed assembly, considering that one vertically orientated 2-MeNQ group occupies ca. 0.49 nm^2 (estimated using the MOPAC[16] program). This result indicates that the monolayer is sufficiently compact even for the shortest side-chain (five atoms) compound **3a**. The formal redox potential, $E^{0\prime} = (E_p^c + E_p^a)/2$, where E_p^c and E_p^a are, respectively, cathodic and anodic peak-potentials, shifts to the negative region with a slope of ca. 15 mV per chain atom as the overall number of side-chain atoms ($m + n + 2$) increases (Fig. 2a). At the same E scan rate, the separation between E_p^c and E_p^a (ΔE_p) increases with increasing ($m + n$), indicating a decrease of electrochemical reversibility, and a slowing of the redox process. It should be noted that, with the increase of spacer length, E_p^a shifts towards the positive values much more slowly than E_p^c shift towards negative values implying that the oxidation process at the SAM's head-group is more favourable than its reduction. Such a phenomenon was detected earlier for the hydroquinone-terminated

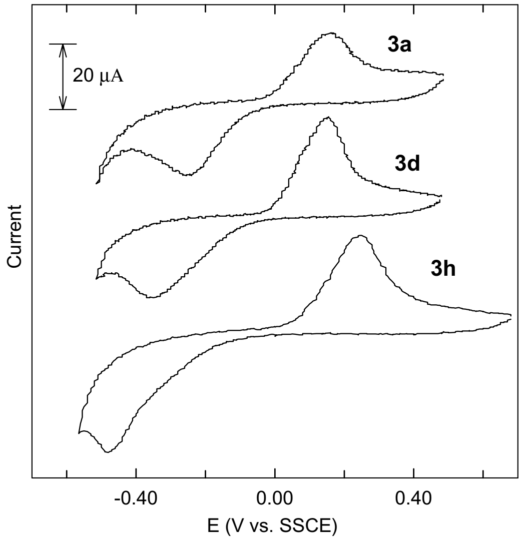


Figure 1. Cyclic voltammograms of the gold electrode modified by compounds **3a**, **3d** and **3h**. Measurements performed in anaerobic 0.1 M $HClO_4$ solution at 25 °C. Potential scan rate 0.1 V/s.

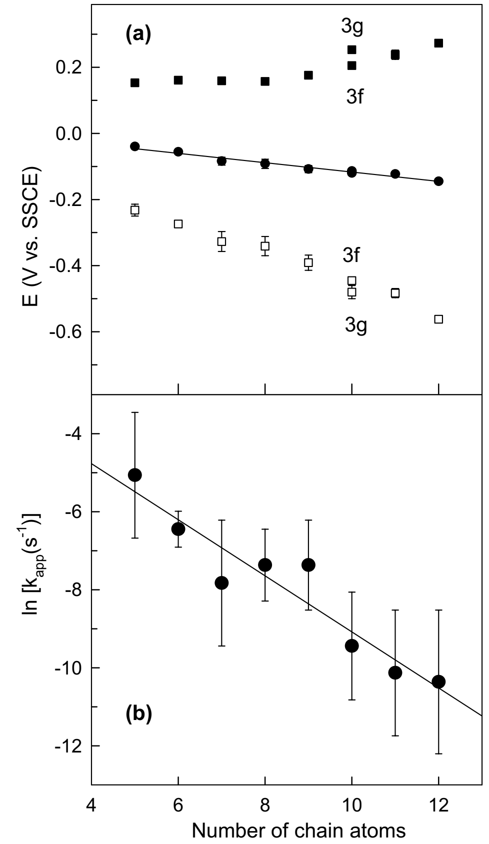


Figure 2. Dependence of (a) potentials [(■) E_p^a, (□) E_p^c, (●) $E^{0\prime}$] and (b) ln[k_{app}(s^{-1})] on the number of side-chain atoms ($m + n + 2$) in 2-MeNQ$(CH_2)_m$COO$(CH_2)_n$SH SAMs on gold. Parameters determined in anaerobic 0.1 M $HClO_4$ solution at 25 °C with an E scan rate of 0.1 V/s.

Table 1. Electrochemical parameters (mean ± S.E.) of the SAMs formed by compounds **3** (in anaerobic 0.1 M $HClO_4$ at an E scan rate of 0.1 V/s, 25 °C).

Compound	Γ (10^{-10}, mol/cm^2)	$E^{0\prime}$ (mV vs SSCE)	$-\ln[k_{app}(s^{-1})]$	αn	$(1-\alpha)n$
3a	2.0 ± 0.5	−40 ± 7	4.6 ± 1.1	0.73 ± 0.21	1.16 ± 0.20
3b	2.1 ± 0.3	−56 ± 4	6.4 ± 0.5	0.78 ± 0.06	1.19 ± 0.25
3c	2.3 ± 0.3	−84 ± 12	7.8 ± 1.6	0.94 ± 0.46	1.12 ± 0.10
3d	2.4 ± 0.3	−92 ± 14	7.4 ± 0.9	0.80 ± 0.20	1.21 ± 0.17
3e	2.3 ± 0.2	−108 ± 11	7.4 ± 1.1	0.65 ± 0.07	1.22 ± 0.26
3f	2.3 ± 0.1	−120 ± 3	9.4 ± 1.4	0.72 ± 0.11	1.36 ± 0.24
3g	2.5 ± 0.3	−114 ± 7	12.2 ± 2.3	0.92 ± 0.12	1.06 ± 0.13
3h	2.6 ± 0.2	−123 ± 4	10.4 ± 2.5	0.70 ± 0.16	1.17 ± 0.14
3i	2.3 ± 0.3	−145 ± 6	10.4 ± 1.4	0.61 ± 0.12	0.89 ± 0.09

SAMs, and was explained by the differences in the solvation of the two redox forms.[2b,c] Interestingly, the position of the ester group influences ΔE_p and the apparent heterogeneous electron-transfer rate constant (k_{app}), but does not affect $E^{0\prime}$ (see data for **3f** and **3g** in Table 1 and Fig. 2a). The electrochemical transfer coefficients times the expected number of transferred electrons n, αn and $(1-\alpha)n$, respectively, associated with the reduction and oxidation processes, and also the k_{app} values for the overall two-electron reaction were determined (Table 1) by Laviron's method[17] from the dependencies E_p versus $\ln(E$ scan rate). In most cases, the sum $[\alpha n + (1-\alpha)n]$ is close to 2, except for the longest chain compound **3i**. For this monolayer, the sum is 1.5. Compared to α, the anodic transfer coefficients tend to be higher. This effect might be associated with slightly different solvent reorganization energy for the oxidized and reduced centres. The general decrease of k_{app} with increasing distance between the electrode and the redox moiety indicates that the electron transfer rate is controlled by the length of the spacer, as expected for the compact and ordered SAM.[1] The exponential decrease of k_{app} with increasing number of chain atoms between sulfur and 2-MeNQ is demonstrated in Figure 2b. From the slope of the plot $\ln(k_{app})$ versus distance (number of chain atoms) the exponential decay factor for tunneling through the SAM (β) can be obtained, assuming that the free and reorganization energies are comparable for all the studied SAMs.[2c] The calculated value $\beta = 0.89 \pm 0.16$ per chain atom for the 2-MeNQ SAMs agrees fairly well with β estimated previously for compact hydroquinone- (1.04 ± 0.06)[2c] or pentaamine(pyridine)ruthenium-terminated (1.06 ± 0.04)[18] SAMs. A much lower β value (0.42) was reported for the 2,3-dichloro-NQ monolayers anchored to the gold surface through the SAMs of aminoalkanethiols.[4] However, such low β values might be determined by the defects and disorder of the monolayer.[2c]

Further, the FT-SERS technique was applied with the aim of determining some structural features of new SAMs, and also the particular characteristics of their redox conversions. For the FT-SERS measurements, the pre-treated gold electrode was roughened by E cycling (0.3 V/s) in 0.1 M KCl between −0.3 and 1.35 V for 10 min, rinsed with water and ethanol, and soaked in 0.1 mM solution of compound **3** for about 20 h. Figure 3 compares the bulk FT-Raman spectrum of solid **3e** and the FT-SERS spectra of SAM formed by this compound on gold. Two spectral features unambiguously demonstrate that formation of the SAM proceeds through the bonding of the sulfur atom with gold. The intense S–H stretching vibrational band at 2569 cm^{-1} observed in the spectrum of bulk **3e** (Fig. 3a) disappears upon formation of the monolayer (Fig. 3b and c). Consequently, a new broad low-frequency mode at 279–285 cm^{-1} appears in the SERS spectra. This band was previously attributed to the stretching vibrational mode ν(Au–S),[19] directly indicating formation of the Au–S moiety due to the self-assembly of compound **3** on the surface. The intense peak in the vicinity of 1654 cm^{-1} (Fig. 3a) was assigned predominantly to the symmetric stretching vibration of the C=O groups of the NQ ring.[20] The frequency of this vibration is sensitive to the interaction of C=O with environmental molecules.[20] As can be seen from Figure 3b, the formation of the SAM does not noticeably affect the position of the C=O band, implying that the group does not interact directly with the surface. The FT-SERS spectrum of **3e** provides direct evidence of the complete reduction of the NQ moiety as E is swept to −0.5 V. The intense ν(C=O) peak disappears and three strong bands characteristic of naphthalene ring vibrations emerge at 1372, 1434 and 1566 cm^{-1}.[21] These features indicate that the 2-MeNQ-terminal group converts to a 2-methyl-1,4-dihydroxynaphthalene moiety due to the reduction process. The FT-SERS method was also used for the evaluation of stability and integrity of new SAMs after a particular time of electrode polarization. Thus, it was found that the integrated intensity of the ν(C=O) band at 1655 cm^{-1} changes only by ca. 1% during 6 h of polarization (3 h at −0.6 and 3 h at 0.5 V). The relative intensities and frequencies of other bands also remained practically unchanged after polarization experiments. These facts demonstrate the exceptional stability of the new SAMs.

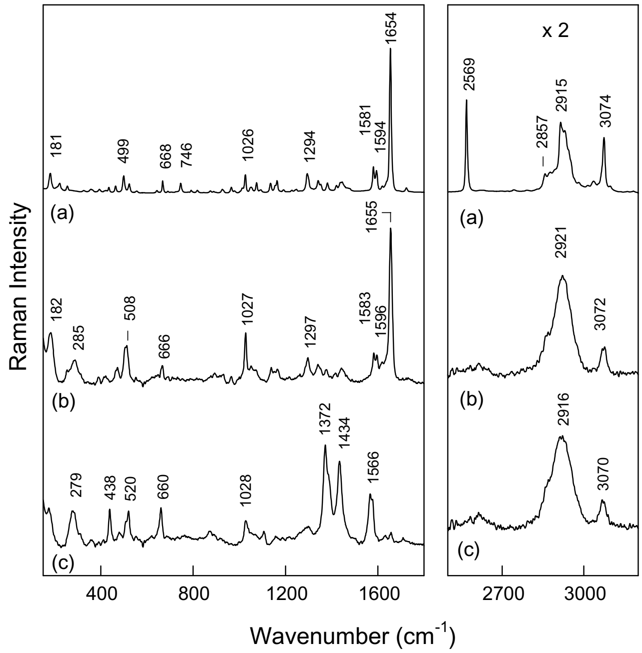


Figure 3. Comparison of (a) the FT-Raman spectrum of solid compound **3e** and (b, c) the FT-SERS spectra of SAM formed by **3e** on gold at (b) 0.6 and (c) −0.5 V versus SSCE. The excitation wavelength is 1064 nm. Laser power at the sample is 200 mW for (a) and 300 mW for (b, c).

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12. General procedure for the radical alkylation of 2-MeNQ. To the boiling solution of 2-MeNQ (2 g, 11.6 mmol), the appropriate dicarboxylic acid ($n = 1$–4 or 6, 11.9 mmol) and silver nitrate (0.5 g, 3 mmol) in a mixture of acetonitrile/water (50:20 mL for $n = 1$–4, and 60:10 mL for $n = 6$) an aqueous solution of ammonium persulfate (4.6 g, 20.2 mmol, 20 mL) was added dropwise over 45 min. The reaction mixture was cooled to room temperature, and 100 mL of water was added. The mixture was extracted with methylene chloride, and the organic phase was washed with water. Then the organic phase was extracted with an aqueous solution of potassium carbonate (1.5 g in 100 mL). The separated aqueous phase was washed with methylene chloride (2×) and acidified with diluted (1:5) hydrochloric acid (aq.) to pH 4 at 5–10 °C. The resulting precipitated product was filtered off, washed with water and recrystallized to yield yellow crystals.

    Selected data for new compounds: **1a** (mp 210–213 °C, DMF/MeOH (1:5 v/v); 6%) ^{1}H NMR (80 MHz, DMF-d_6) δ (ppm): 2.20 (s, 3H, CH_3), 3.77 (s, 2H, CH_2), 7.7–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1702 (carboxylic C=O), 1666 (quinone C=O); **1d** (mp 108–110 °C, MeOH; 30%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.2–1.9 (m, 4H, 2CH_2), 2.18 (s, 3H, CH_3), 2.3–2.8 (m, 4H, CH_2 CO, NQ–CH_2), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1702 (carboxylic C=O), 1660 (quinone C=O); **1e** (mp 78–79 °C, Et_2O; 15%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.3–1.9 (m, 8H, 4CH_2), 2.18 (s, 3H, CH_3), 2.2–2.8 (m, 4H, CH_2CO, NQ–CH_2), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1719 (carboxylic C=O), 1659 (quinone C=O).
13. General procedure for the synthesis of **2a**–**i**. A mixture of 2-MeNQ-carboxylic acid **1a**–**e** (1.0 mmol), ω-bromoalkanol (1.0 mmol) and *p*-toluenesulfonic acid (1.0 mmol) in benzene (30 mL) was refluxed for 6 h in a flask filled with a Dean–Stark head under Ar. After this time, the reaction mixture was washed with water, the organic phase was dried over $MgSO_4$ and after evaporation under reduced pressure the residue was purified by column chromatography on silica gel (eluent-CH_2Cl_2).
14. General procedure for the synthesis of **3a**–**i**. ω-Bromoester **2a**–**h** (1.0 mmol) and thiocarbamide (4.0 mmol) in dry acetone (30 mL) were refluxed for about 70 h under Ar. The solvent was evaporated in vacuo and the crude isothiouronium salt was poured into a mixture of $CHCl_3$ (40 mL) and water (20 mL). After addition of solid $Na_2S_2O_5$ (2 mmol), the reaction mixture was vigorously stirred and refluxed for 2.5 h under Ar. The organic phase was washed with water (2×), dried over $MgSO_4$ and after evaporation in vacuo, the residue was purified by column chromatography on silica gel (eluent-CH_2Cl_2). Crystallization of the residue from hexane yielded yellow crystals. Selected data for new compounds: **3a** (mp 75–76 °C, 42%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.49 (t, 1H, SH, $J = 8.3$ Hz), 2.22 (s, 3H, CH_3), 2.5–3.0 (m, 2H, CH_2S), 3.75 (s, 2H, NQ–CH_2), 4.25 (t, 2H, OCH_2, $J = 6.2$ Hz), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1722 (ester C=O), 1663 (quinone C=O), 2570 (S–H); **3d** (mp 48–50 °C, 49%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.48 (t, 1H, SH, $J = 8.3$ Hz), 1.3–2.1 (m, 4H, 2CH_2), 2.20 (s, 3H, CH_3), 2.3–3.0 (m, 6H, CH_2S, CH_2CO, NQ–CH_2), 4.20 (t, 2H, OCH_2, $J = 6.2$ Hz), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1731 (ester C=O), 1656 (quinone C=O), 2562 (S–H); **3e** (mp 50–51 °C, 51%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.2–2.1 (m, 5H, 2CH_2, SH), 2.20 (s, 3H, CH_3), 2.3–2.8 (m, 8H, CH_2S, CH_2, CH_2CO, NQ–CH_2), 4.20 (t, 2H, OCH_2, $J = 6.2$ Hz), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1723 (ester C=O), 1659 (quinone C=O), 2568 (S–H); **3h** (mp 35–37 °C, 41%) ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm): 1.1–2.0 (m, 11H, 5CH_2, SH), 2.20 (s, 3H, CH_3), 2.0–2.8 (m, 6H, CH_2S, CH_2CO, NQCH_2), 4.19 (t, 2H, OCH_2, $J = 6.2$ Hz), 7.5–8.2 (m, 4H, C_6H_4); IR (KBr cm^{-1}): 1732 (ester C=O), 1659 (quinone C=O), 2572 (S–H).

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