1,4-Naphthoquinone Disulfides and Methyl Sulfides: Self-Assembled Monolayers on Gold Substrates

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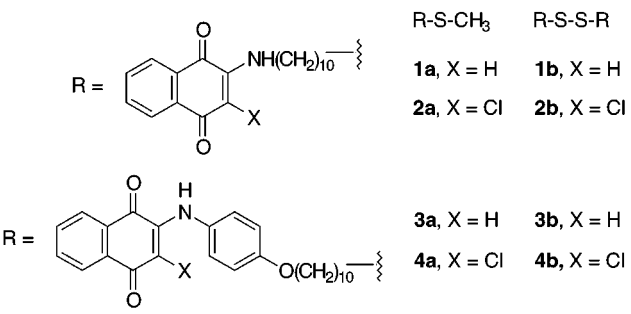
The preparation and electrochemistry of self-assembled monolayers (SAMs) of organic disulfides on gold were first described in the publications of Nuzzo[1] and Taniguchi[2] about 15 years ago. Since then, many reports have appeared concerning the modification of gold surfaces with dialkyl disulfides[3] and other organosulfur compounds, including dialkyl sulfides.[4,5]

Our laboratory has been active in the synthesis of a variety of redox-active disulfides for a number of years. These have incorporated electron-acceptor moieties, such as 1,4-naphthoquinones and TCNQs, (tetracyanoquinodimethanes) electron-donating moieties, such as pyrenes and ferrocenes, or both donors and acceptors in the same molecule. More recently, methyl sulfides of 1,4-naphthoquinones were also prepared here, and we then became aware that although many examples of disulfide and dialkyl sulfide SAMs have been reported in the literature, the direct comparison of the two sulfur classes with identical terminal groups was not studied until recently.[6]

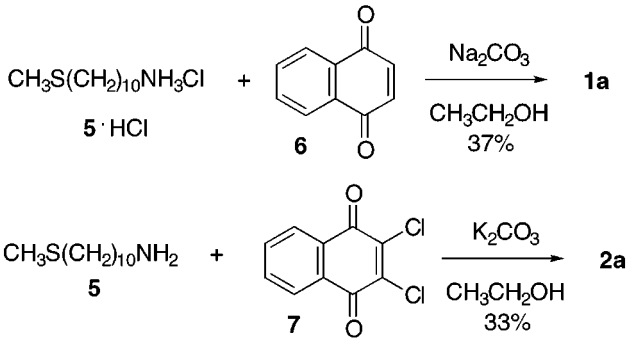
It is generally recognized that the structure and interfacial properties of disulfide-modified surfaces were effectively indistinguishable from those of surfaces modified with thiols with the same terminal alkyl groups. However, the nature of the dialkyl sulfide-to-gold adsorption process is not at all conclusive. Some studies conclude that the S−C bonds of dialkyl sulfides cleave before formation of a gold thiolate,[7,8] whereas others report evidence that there is no S−C bond cleavage during the adsorption process.[6,9] The results of the present work indicate that disulfides and methyl sulfides with identical redox moieties (1,4-naphthoquinones) produce SAMs on gold that have quite different electrochemical properties. However, one cause of these differences may be due to the differences in the way the monolayers pack.

In general, the methyl sulfides of electron acceptors were easier to synthesize compared with the preparations of disulfides. The former would be the preferred organosulfur derivatives for SAMs on gold if they showed any clear advantages in their stability or electrochemistry.

Scheme 1. Naphthoquinone Methyl Sulfides and Disulfides Prepared in This Work



Scheme 2. Preparation of Naphthoquinone Methyl Sulfides 1a and 2a



Four pairs of 2-alkylamino- and 2-alkoxyarylamino-1,4-naphthoquinone disulfides and methyl sulfides (**1**−**4**, Scheme 1) were prepared by various synthetic routes. All eight were new compounds and were completely purified and characterized. These were the methyl sulfides and disulfides of 2-decylamino-1,4-naphthoquinone (**1**), 3-chloro-2-decylamino-1,4-naphthoquinone (**2**), 2-(4-decoxyphenyl)amino-1,4-naphthoquinone (**3**), and 3-chloro-2-(4-decoxyphenyl)amino-1,4-naphthoquinone (**4**).

Two routes were used to prepare the methyl sulfides. 10-(Methylthio)decanamine[10,11] (**5**) was the required intermediate in the syntheses of products **1a** and **2a**. Treatment of the hydrochloride of **5** with 1,4-naphthoquinone (**6**) afforded a 37% yield of **1a**, while product **2a** resulted from a monosubstitution reaction of **5** with 2,3-dichloro-1,4-naphthoquinone (**7**, 33%, Scheme 2).

The decoxyphenylaminonaphthoquinone methyl sulfides, **3a** and **4a**, were both prepared by a route that started with *p*-nitrophenol (Scheme 3). Products **2a** and **4a** were completely characterized except that the resonances of the amine hydrogens were not observed in the NMR spectra.

The disulfides of the 2-decylamino-1,4-naphthoquinones, **1b** and **2b**, were both prepared from di(10-aminodecyl) disulfide dihydrochloride (**13**) (Scheme 4).[12]

The disulfides of the 2-(4-decoxyphenyl)amino-1,4-naphthoquinones, **3b** and **4b**, were synthesized using 10-

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(11) Walker, J. *J. Chem. Soc.* **1950**, 193.
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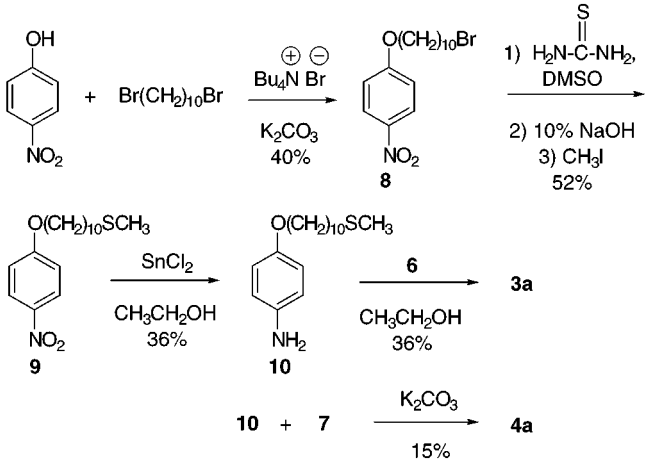
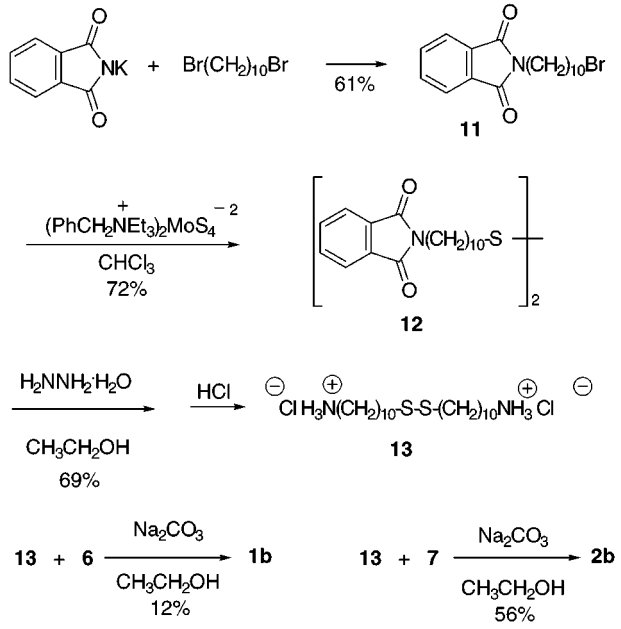
Scheme 3. Preparation of Naphthoquinone Methyl Sulfides 3a and 4a



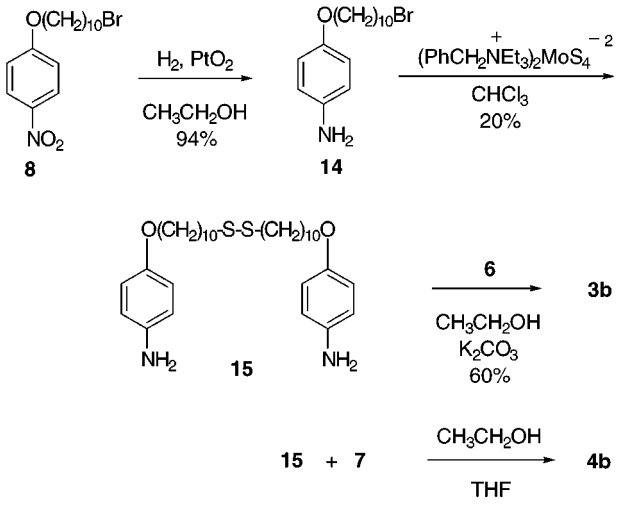
Scheme 4. Preparation of Naphthoquinone Disulfides 1b and 2b



(4-nitrophenoxy)decyl bromide[13] (**8**) as the starting material and the previously unknown **15** as an intermediate (Scheme 5).

The electrochemistry of gold electrodes modified with each of the eight methyl sulfides and disulfides was compared according to four parameters: the surface coverage (Γ, in mol/cm^2); the formal potential ($E^{o\prime}$, in volts) estimated from the average of the reduction and oxidation peak potentials; the peak separation (ΔE_p, in millivolts); and the peak-width at half-maximum (ΔE_{fwhm}, in millivolts). The peak separation is inversely related to the electron-transfer rate, and the peak-width at half-maximum is a measure of the lateral interactions between molecules in SAMs (at 298 K, ΔE_{fwhm} should be 90.3/n mV, where n is the number of electrons involved in the redox reaction). The best coverages were observed mainly for the disulfide derivatives, especially those with the aliphatic side chains (**1b** and **2b**) (Table 1). The same disulfides had lower oxidation potentials and were 23−9

Scheme 5. Preparation of Naphthoquinone Disulfides 3b and 4b



mV easier to oxidize than the corresponding methyl sulfides, **1a** and **2a**. Both disulfides and methyl sulfides with aliphatic spacers and chlorine substitution (**2a** and **2b**) had lower electron-transfer rates and substantial repulsive interactions between adjacent redox centers compared with the deschloro products, **1a** and **1b**. Note that the voltammograms of SAMs modified with naphthoquinones **3** and **4** each showed both oxidation and reduction reactions. The former was thought to be the result of the donor properties of the phenylamino moiety.[14] Indeed, a similar wave was observed in the CV of 4-[(10-methylthio)decoxy]aniline. These results are summarized in Table 1. All data in this table were collected after repetitive scanning. When cycling, coverage dropped fast at the very beginning and gradually slowed and tended to be stable. SAMs of the methyl sulfides stabilized after 15−20 cycles, and the decreasing rate of surface coverage was less than 10%. SAMs of the disulfides stabilized after 5−10 cycles, and the decreasing rate of surface coverage was less than 5%. The cyclic voltammograms of gold substrates modified with products **1a** and **1b** (Figure 1) and **2a** and **2b** (Figure 2) have been included in this paper.

Experimental Section

Electrochemistry. Acetonitrile (Fisher Optima grade) was distilled from CaH_2 under nitrogen, passed through activated alumina, and stored in a tightly capped bottle over 4 Å molecular sieves until needed. Absolute ethanol was used as received from McCormick Distilling Co., Inc. Tetra-*n*-butylammonium hexafluorophosphate (TBAHFP) was synthesized and purified according to standard procedures. Standard glass microscope slides (Fisher Cat. No.12-549) served as gold substrates; they were cleaned by ultra sonication in successive baths of piranha solution (1:3 by volume 30% H_2O_2/concentrated H_2SO_4), distilled water, and 2-propanol (Fisher Optima grade). The oven-dried microscope slides were coated with 50 Å of chromium followed by 1500 Å of gold by thermal evaporation at a base pressure of 7×10^{-7} Torr by using an Edwards Auto 306 vacuum coater equipped with a Sycon model STM-100/MF thin film monitor. After coating was complete, the vacuum chamber was back-filled with high-purity nitrogen gas. The gold films prepared by this method were found by X-ray diffraction analysis to exhibit strong Au {111} crystal-

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Table 1. Electrochemical Results for Gold Electrodes Modified with Each of the Eight Methyl Sulfides and Disulfides[a]

SAM modified with naphthoquinone	$\Gamma \times 10^{10}$ (mol/cm^2)[b]	$E^{o\prime}$ (V)[c]	ΔE_p (mV)	ΔE_{fwhm} (mV)
1a	0.88 ± 0.07	0.089 ± 0.004	27 ± 3	98 ± 4
1b	2.9 ± 0.3	0.066 ± 0.001	67 ± 4	164 ± 5
2a	1.3 ± 0.1	0.094 ± 0.007	290 ± 30	210 ± 16
2b	2.2 ± 0.2	0.085 ± 0.006	275 ± 7	196 ± 10
3a (donor portion)	0.195 ± 0.00	0.687 ± 0.001	50 ± 4	75 ± 4
3a (acceptor portion)	0.27 ± 0.03	−0.055 ± 0.003	26 ± 2	77 ± 2
3b (donor portion)[d]	0.10 ± 0.01	0.647 ± 0.005	168 ± 9	128 ± 6
3b (acceptor portion)[d]	0.47 ± 0.3	−0.004 ± 0.003	103 ± 5	249 ± 12
3b (acceptor portion)	1.9 ± 0.1	−0.022 ± 0.007	65 ± 4	138 ± 6
4a (donor portion)	1.0 ± 0.1	0.479 ± 0.006	200 ± 14	210 ± 13
4a (acceptor portion)	0.17 ± 0.03	0.071 ± 0.008	43 ± 8	71 ± 5
4b (donor portion)	0.23	0.490	248	136
4b (acceptor portion)	0.15	0.058	72	82
4-$H_2NC_6H_4O(CH_2)_{10}SCH_3$	1.35 ±0.03	0.463 ±0.004	54 ±5	130 ±7

[a] All measurements were collected at the same scan rate (100 mV/s) after 24 h unless otherwise noted. The +/− indicates the 95% confidence limit. [b] Both acceptor and donor reactions involve two electrons and two protons. [c] Versus SCE. [d] Measured after 10 min.

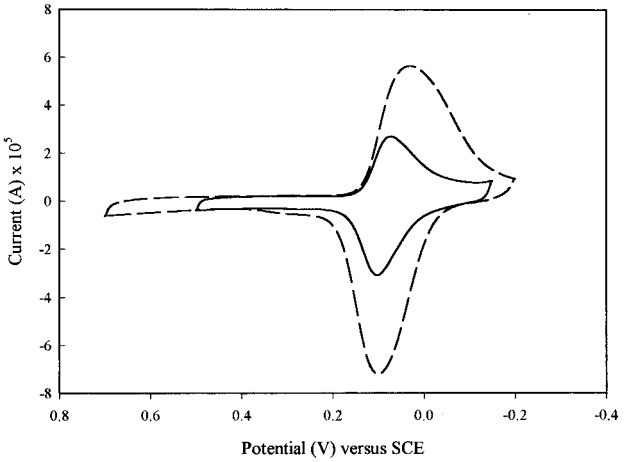

Figure 1. Cyclic voltammograms of the SAMs of 2-*N*-(10-methylthio)decylamino-1,4-naphthoquinone, **1a** (—), and Di[*N*-(1,4-naphthoquinon-2-yl)-10-aminodecyl] disulfide,**1b** (- - -).

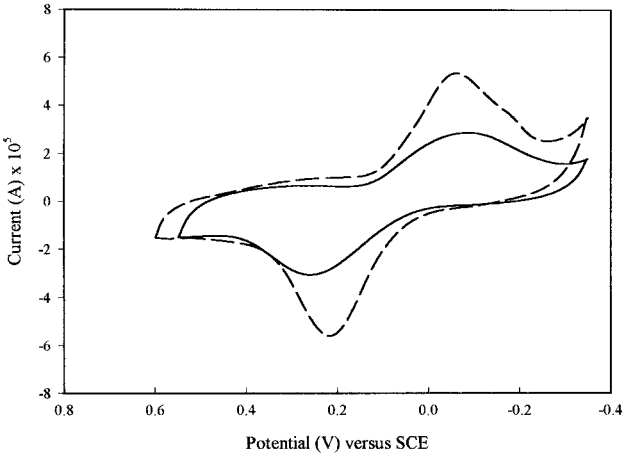

Figure 2. Cyclic voltammograms of the SAMs of 3-chloro-2-*N*-(10-methylthio)decylamino-1,4-naphthoquinone, **2a** (—), and di[*N*-(3-chloro-1,4-naphthoquinon-2-yl)-10-aminodecyl] disulfide, **2b** (- - -).

lographic texture.[15] The gold electrodes were taken directly from the vacuum coater and immersed in solutions containing **1**−**4**. Films were prepared by immersion of the substrates in 0.5−1.0 mM solutions of the methyl sulfides and disulfides in methylene chloride or tetrahydrofuran for 24 h. Cyclic voltammetric measurements were made in a three-electrode cell with an EG&G Princeton Applied Research Corp. (PARC) model 283 potentiostat/galvanostat employing PARC model 270 electrochemistry analysis software running on an IBM-compatible 386 computer. For studies with self-assembled monolayers, the gold-coated substrates served as the working electrodes. They were clamped to an O-ring joint attached to the side of the cell. The O-ring provided a liquid-tight seal and defined the area of the working electrode, which was ca. 1.54 cm^2. The reference electrode for all experiments was an EG&G saturated calomel electrode (SCE) separated from the working electrode compartment by means of a Luggin capillary. All potentials mentioned in this paper were measured with respect to this reference electrode. The counter electrode was a platinum wire spiral. The electrolyte solutions used for aqueous experiments were 1.0 M aqueous $HClO_4$ and a pH = 7.2 phosphate buffer solution (Aldrich Chemical Co.). The solutions in the electrochemical cells were deaerated with high-purity N_2 before each experiment, and an atmosphere of N_2 was maintained over the solution in the cell during measurements. Electronic resistance compensation was employed during all experiments. The equilibrium surface coverage, Γ, reported for each monolayer was estimated from the charge under the appropriate voltammetric oxidation or reduction wave after subtraction of the residual current.

Synthetic Chemistry. The following general techniques were followed unless otherwise stated. All reactions sensitive to air and moisture were carried out in flame-dried apparatus, under a dry nitrogen atmosphere using either magnetic or mechanical stirring. All melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a FT-IR spectrometer using KBr pellets or thin liquid films. ^{1}H (300 MHz) and ^{13}C NMR spectra were determined on a spectrometer using $CDCl_3$, DMSO-d_6, or D_2O with tetramethylsilane (Me_4Si) as the internal standard. Column chromatography was carried out by gravity or low pressure using 230−400 mesh E. Merck silica gel (9385). Thin-layer chromatography was performed on Analtech Silica Gel HLF Uniplates (10 × 20 cm, #47521) with a fluorescence indicator. TLC spots were visualized either by exposure to iodine vapors or by irradiation with UV light. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Atlantic Microlab, Inc., Norcross, GA.

2-*N*-(10-Methylthio)decylamino-1,4-naphthoquinone (1a). A mixture of 0.35 g (1.5 mmol) of 10-(methylthio)decylammonium chloride (**5**·HCl)[10,11] and 96 mg (0.77 mmol) of Na_2CO_3·H_2O in 95% ethanol was refluxed for 15 min and cooled to room temperature. 1,4-Naphthoquinone (0.23 g, 1.46 mmol) was added with stirring, and the mixture was refluxed for 5 h. After the solvent was removed, the crude orange solid was placed on a silica gel column and eluted with hexane/acetone (9:1). The product was recrystallized from ethanol to give 0.19 g (37%) of **1a** as an orange solid: mp 94.5−96.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, 1H), 8.04 (d, 1H), 7.72 (m, 1H), 7.61 (m, 1H), 5.89 (bs, 1H, exchangeable), 5.73 (s, 1H), 3.18 (q, 2H), 2.50 (t, 2H), 2.10

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(s, 3H), 1.67 (m, 4H), 1.50−1.29 (m, 12H); IR (KBr) 3342, 2917, 2848, 1676, 1600, 1567, 1512, 1507, 1460, 1114, 720 cm^{-1}. Anal. Calcd for $C_{21}H_{29}NO_2S$: C, 70.16; H, 8.13; N, 3.90; S, 8.92. Found: C, 70.10; H, 8.10; N, 3.83; S, 8.84.

3-Chloro-2-*N*-(10-methylthio)decylamino-1,4-naphthoquinone (2a). 10-(Methylthio)decanamine (**5**)[10,11] (0.25 g, 1.23 mmol), 0.28 g (1.23 mmol) of 2,3-dichloro-1,4-naphthoquinone, and 0.34 g (2.46 mmol) of K_2CO_3 were mixed in 10 mL of 95% ethanol, and the resultant mixture was refluxed for 10 h. After the solvent was removed, the crude red solid was adsorbed on 0.5 g of Celite, and this was placed on a column containing 10 g of silica gel and eluted with hexane/EtOAc (1:1). The product was recrystallized from hexane to afford 0.16 g (33%) of a red solid: mp 118−120 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.17 (d, 1H), 8.02 (d, 1H), 7.72 (dd, 1H), 7.61 (dd, 1H), 3.83 (q, 2H), 2.49 (t, 2H), 2.10 (s, 3H), 1.74−1.51 (m, 4H), 1.48−1.13 (br, 12H); IR (KBr) 3284, 2921, 2850, 1675, 1599, 1569, 1509, 1331, 1295, 1129 cm^{-1}. Anal. Calcd for $C_{21}H_{28}ClNO_2S$: C, 64.02; H, 7.16; N, 3.56; S, 8.14. Found: C, 63.93; H, 7.02; N, 3.54; S, 8.04.

10-(4-Nitrophenoxy)decyl Methyl Sulfide (9). 10-(4-Nitrophenoxy)decyl bromide[13] (**8**) (11.1 g, 31 mmol), 2.6 g (34 mmol) of thiourea, and 100 mL of DMSO were stirred and warmed until a solution was obtained, and stirring was continued for 16 h. A 10% solution of NaOH (300 mL) was added, and the mixture was stirred in an ice bath for 30 min. Methyl iodide (8.8 g, 62 mmol) was slowly added, and the resultant mixture was stirred for 6 h. A sticky yellow solid was collected and washed with water. It was crystallized from 2-propanol to afford 5.2 g (52%) of **9**: mp 58.0−59.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (d, 2H), 6.94 (d, 2H), 4.05 (t, 2H), 2.50 (t, 2H), 2.10 (s, 3H), 1.82 (m, 2H), 1.62 (m, 2H), 1.49−1.30 (m, 12H); IR (KBr) 2979, 2848, 1595, 1516, 1337, 1258, 1173, 1108, 843 cm^{-1}.

10-(4-Aminophenoxy)decyl Methyl Sulfide (10). Compound **9** (4.6 g, 0.014 mol) and 12.6 g (56 mmol) of $SnCl_2 \cdot 2H_2O$ were added to 50 mL of dry EtOAc, and the mixture was refluxed for 16 h. EtOAc (50 mL) was added, and the result was washed with several small portions of a 5% solution of EDTA·disodium salt dihydrate in order to remove ionic tin. The EtOAc solvent was removed to give a yellow residue. It was recrystallized from hexane to afford 1.5 g (36%) of **10**: mp 68−70 °C; ^{1}H NMR ($CDCl_3$) δ 6.75 (d, 2H), 6.65 (d, 2H), 3.87 (t, 2H), 2.50 (t, 2H), 2.10 (s, 3H), 1.73 (m, 2H), 1.57 (m, 2H), 1.50−1.25 (m, 12H); IR (KBr) 3317, 2918, 2851, 1517, 1250, 1108, 843 cm^{-1}.

2-{*N*-4-[(10-Methylthio)decoxy]phenylamino}-1,4-naphthoquinone (3a). A mixture of 3.5 g (12 mmol) of **10**, 1.9 g (12 mmol) of 1,4-naphthoquinone (**6**), and 50 mL of 95% ethanol was refluxed for 22 h. After cooling, a purple precipitate formed and was collected by filtration, and the residue was washed with water and ethanol. The crude product was chromatographed on silica gel and eluted with hexane/EtOAc (8.9:1.1). It was recrystallized from CH_2Cl_2/EtOH (3:7) to give 2.0 g (36%) of **3a** as a purple solid: mp 111−112 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (m, 2H), 7.75−7.65 (m, 2H), 7.43 (s, 1H, exchangeable), 7.19 (d, 2H), 6.94 (d, 2H), 6.23 (s, 1H), 3.97 (t, 2H), 2.50 (t, 2H), 2.10 (s, 3H), 1.78 (m,2H), 1.57 (m, 2H), 1.50−1.33 (m, 12H); IR (KBr) 3279, 2915, 2847, 1671, 1595, 1565, 1512, 1345, 1238, 931 cm^{-1}. Anal. Calcd for $C_{27}H_{33}NO_3S$: C, 71.81; H, 7.37; N, 3.10; S, 7.10. Found: C, 71.70; H, 7.42; N, 3.07; S, 7.01.

2-Chloro-3-{*N*-4-[(10-methylthio)decoxy]phenylamino}-1,4-naphthoquinone (4a). A mixture of 2.8 g (9.6 mmol) of **10**, 2.2 g (9.6 mmol) of 2,3-dichloro-1,4-naphthoquinone (**7**), 1.38 g (10 mmol) of K_2CO_3, and 50 mL of 95% ethanol was refluxed for 16 h. The solution changed from yellow to dark red, and a dark brown precipitate separated. The latter was collected and washed with 5 mL portions of acetone and hot water until it was neutral. The mother liquor was extracted two times with 50 mL portions of $CHCI_3$. After removal of the organic solvent, 0.71 g (15%) of a purple solid was isolated. Recrystallization once from hexane/ethyl acetate (8:2) and twice from hexane gave 0.17 g (3%) of a pure product: mp 118−120 °C (dec); ^{1}H NMR ($CDCl_3$) δ 8.20 (d, lH), 8.17 (d, lH), 7.77 (m, lH), 7.75 (m, lH), 7.05 (d, 2H), 6.87 (d, 2H), 3.96 (t, 2H), 2.49 (t, 2H), 2.10 (s, 3H), 1.76 (m, 2H), 1.57 (m, 2H), 1.37−1.25 (br, 12H); IR (KBr) 3243, 2923, 2844, 1677, 1633, 1606, 1562, 1495, 1464, 1287, 1234, 1140, 826 cm^{-1}. Anal. Calcd for $C_{27}H_{32}ClNO_3S$: C, 66.72; H, 6.64; N, 2.88; S, 6.60. Found: C, 66.54; H, 6.84; N, 2.74; S, 6.74.

Di(10-phthalimidodecyl) Disulfide (12). Benzyltriethylammonium tetrathiomolybdate[16] (7.3 g, 12 mmol) was slurried in 40 mL of dry $CHCl_3$. *N*-(10-Bromodecyl)phthalimide[12] (**11**) (4.0 g, 11 mmol) was added. The resulting mixture was stirred vigorously at room temperature overnight. The volume was reduced by approximately one-third, and the dark concentrate was triturated several times with ether. The combined ether layers were dried with anhydrous $MgSO_4$. Evaporation of the solvent yielded a colored oil which crystallized from hexane to afford 2.5 g (72%) of **12** as a white solid: mp 58−60 °C (lit.[12] mp 49 °C); ^{1}H NMR ($CDCl_3$) δ 7.85 (m, 4H), 7.75 (m, 4H), 3.65 (t, 4H) 2.65 (t, 4H), 1.70 (m, 8H), 1.35−1.25 (m, 24H); IR (KBr) 2923, 2841, 1769, 1712, 1461, 1394, 1359, 1184, 1051, 717 cm^{-1}.

Di(10-aminodecyl) Disulfide Dihydrochloride (13). Compound **12** (2.7 g, 4.2 mmol) was added to 30 mL of ethanol in a 50 mL round-bottom flask. The mixture was warmed, and 64% aqueous hydrazine hydrate (0.43 g, 8.4 mmol) was added dropwise with stirring. Warming was continued until a homogeneous solution was obtained, which was stirred overnight. A gelatinous suspension was formed. Approximately 1 mL of concentrated HCI was added to adjust the pH to 1. A copious white precipitate was formed, and the mixture was refluxed for 0.5 h. After cooling to room temperature, the phthalimide hydrazide was removed by filtration. The filtrate was then evaporated to give a white solid that was dissolved in a mixture of 20 mL of ethanol and 20 mL of water. The mixture was made basic with 10% NaOH and extracted with ether (30 mL × 4). The ether layer was dried with anhydrous $MgSO_4$, and the volume was reduced in half. Dry HCI gas was bubbled through the ether solution, and a white precipitate separated, which was collected and washed with ether. After drying, 1.03 g (55%) of **13** was collected (Dirscherl and Weingarten prepared this product in 49% yield, and it melted at 180 °C)[12]: ^{1}H NMR (D_2O) δ 2.50 (t, 4H), 2.35 (t, 4H), 1.23 (m, 8H), 1.1−0.85 (m, 24H); IR (KBr) 2909−2857 (broad),1604, 1513, 1461,1130, 1001, 721 cm^{-1}.

Di[*N*-(1,4-naphthoquinon-2-yl)-10-aminodecyl] Disulfide (1b). A mixture of 200 mg (0.44 mmol) of **13**, 124 mg (0.96 mmol) of $Na_2CO_3 \cdot H_2O$, and 3.0 mL of 95% ethanol was heated to the reflux temperature and then allowed to cool to room temperature. A solution of 142 mg (0.90 mmol) of 1,4-naphthoquinone (**6**) in 3.0 mL of ethanol was added, and the stirred mixture was refluxed for 1 h and then allowed to stir at ambient temperature for 4 days. The brick-red mixture was diluted with about 10 mL of CH_2Cl_2 and filtered to separate 198 mg of mostly inorganic solids. The filtrate was concentrated under reduced pressure to afford 236 mg of a dark, tarry residue, which was chromatographed on silica gel using CH_2Cl_2/EtOAc (94:6). A middle faction containing **1b** (36 mg, 12%) was isolated. It was recrystallized from EtOAc: mp 99−101 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (d, 2H), 8.08 (d, 2H), 7.75 (dd, 2H), 7.62 (dd, 2H), 5.91 (bs, 2H), 5.72 (s, 2H), 3.17 (m, 4H), 2.67 (t, 4H), 1.37−1.68 (m, 32H); IR (KBr) 3344, 2993, 2850, 1675, 1600, 1570, 1520 cm^{-1}. Anal. Calcd for $(C_{40}H_{52}N_2O_4S_2)_2 \cdot H_2O$: C, 68.83; H, 7.65; N, 4.01. Found: C, 69.09; H, 7.50; N, 3.95.

Di[*N*-(3-chloro-1,4-naphthoquinon-2-yl)-10-aminodecyl] Disulfide (2b). A mixture of **13** (0.48 g, 11 mmol), $Na_2CO_3 \cdot H_2O$ (0.28 g, 23 mmol), and 95% ethanol (45 mL) was refluxed for 15 min and cooled to room temperature. 2,3-Dichloro-1,4-naphthoquinone (**7**, 0.49 g, 22 mmol) was added, and the mixture was refluxed and stirred for 14 h. The precipitate was collected by filtration and washed with water and cold ethanol. Purification by column chromatography (hexane/EtOAc, 80:20) on silica gel gave **4** as a red powder weighing 0.47 g (56%). Recrystallization from $CHCl_3$/ethanol (6:4) gave an analytical sample: mp 91.5−92.5 °C; ^{1}H NMR ($CDCI_3$) δ 8.14 (d, 2H),8.02 (d, 2H), 7.72 (m, 2H), 7.62 (m, 2H), 6.15 (bs, 2H, exchangeable), 3.85 (q, 4H), 2.67 (t, 4H), 1.70−1.60 (m, 8H) 1.55−1.20 (m, 24H); IR (KBr) 3273, 2922, 2844, 1676, 1598, 1572, 1507, 1442, 1332, 1293, 1130, 715 cm^{-1}. Anal. Calcd for $C_{40}H_{50}Cl_2N_2O_4S_2$: C, 63.39; H, 6.65; N, 3.70; S, 8.46. Found: C, 63.30; H, 6.86; N, 3.66; S, 8.35.

10-(4-Aminophenoxy)decyl Bromide (14). 10-(4-Nitrophenoxy)decyl bromide[13] (**8**) (8.8 g, 25 mmol) was added to a

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hydrogenation bottle containing 200 mL of 95% ethanol. The bottle was warmed gently until the solid dissolved, and 0.3 g of PtO_2 was added. The mixture was placed in a Parr hydrogenation apparatus and was treated with 50 psi of hydrogen at room temperature until no more hydrogen was taken up (about 2 h). The reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from ethanol to yield 7.0 g (94.3%) of **14**: mp 66−68 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 6.74 (d, 2H), 6.66 (d, 2H), 3.88 (t, 2H), 3.40 (t, 2H), 2.92 (broad s, 2H, exchangeable) 1.77−1.89 (m, 4H), 1.23−1.41 (m, 12H); IR (KBr) 3331 (broad), 2917, 2850, 1517, 1465, 1246, 1039, 828, 649 cm^{-1}.

10-(4-Aminophenoxy)decyl Disulfide (15). A solution of 1.0 g (2.8 mmol) of 10-(4-aminophenoxy)decyl bromide (**14**) in 10 mL of dry $CHCl_3$ was prepared. This was added during a period of 10 min to a stirred solution of 2.0 g (3.3 mmol) of benzyltriethylammonium tetrathiomolybdate[16] in 15 mL of dry $CHCl_3$. One hour later, the mixture turned black, and it was stirred for an additional 20 h at room temperature. The solvent was removed under reduced pressure, and the resultant sticky residue was extracted first with ether (3 × 30 mL) and then with THF (3 × 20 mL). Evaporation of the extracts left a pale orange residue that was recrystallized from ether/$CHCl_3$ to give 1.78 g (71%) of **15**: mp 87−88 °C; ^{1}H NMR ($CDCl_3$) δ 6.72 (d, 4H), 6.65 (d, 4H), 3.87 (t, 4H), 3.44 (bs, 4H), 2.68 (t, 4H), 1.67 (m, 8H), 1.30 (m, 24H); IR (KBr) 3380, 3311, 2919, 2850, 1512, 1246, 830, 765, cm^{-1}. Anal. Calcd for $C_{32}H_{52}N_2O_2S_2 \cdot H_2O$: C, 66.39; H, 9.40; N, 4.84; S, 11.08. Found: C, 66.79; H, 9.44; N, 4.76; S, 11.54.

Di{10-[*N*-(1,4-naphthoquinon-2-yl)-4-aminophenoxy]decyl} Disulfide (3b). A mixture of 136 mg (0.24 mmol) of **15**, 100 mg (0.63 mmol) of 1,4-naphthoquinone (**6**), and 15 mL of 95% ethanol was stirred and heated at the reflux temperature for 6 h and then at room temperature for 16 h. Anhydrous THF (5 mL) was added to increase the solubilities of the reactants, and the 6 h of reflux and 16 h of stirring at room temperature were repeated. The solvents were removed, and the residue was chromatographed ($CHCl_3$/EtOAc, 95:5) on a silica gel column. Fractions which contained the red product were combined and evaporated, and the residue was recrystallized from $CHCl_3$/EtOH to afford 29 mg of **3b** (14%), a red solid that melted at 127−128 °C: ^{1}H NMR ($CDCl_3$) δ 8.10 (d, 4H), 7.80 (dd, 2H), 7.60 (dd, 2H), 7.45 (s, 2H), 7.20 (d, 4H), 6.95 (d, 4H), 6.25 (s, 2H), 3.95 (t, 4H), 2.70 (t, 4H), 1.75 (m, 8H), 1.40 (m, 24H); IR (KBr) 3252, 2900, 2840, 1677, 1590, 1563, 1510, 1237, 822, 722, cm^{-1}. Anal. Calcd for $C_{52}H_{60}N_2O_6S_2$: C, 71.55; H, 6.88; N, 3.21. Found: C, 71.18; H, 6.91; N, 3.22.

Di{10-[*N*-(3-chloro-1,4-naphthoquinon-2-yl)-4-aminophenoxy]decyl} Disulfide (4b). A mixture of 10-(4-aminophenoxy)-decyl disulfide (**15**, 141 mg, 0.25 mmol) and 2,3-dichloro-1,4-naphthoquinone (**7**, 114 mg, 0.50 mmol) was added to 20 mL of 95% ethanol in a round-bottom flask. Then, $NaCO_3 \cdot H_2O$ (62 mg, 0.50 mmol) was added, and the mixture was heated at 65 °C for 6 h. The reaction mixture was cooled to room temperature; the red solid that was formed was filtered and washed with cold water and then ethanol. This solid was air-dried and chromatographed on silica gel with CH_2Cl_2 and then with CH_2Cl_2/EtOAc, 1:4. The first purple faction was collected, the solvent was removed, and the residue was recrystallized from DMSO to afford 160 mg (60%) of **4b**: mp 123−124 °C; ^{1}H NMR (DMSO-d_6) δ 9.24 (s, 2H, exchangeable), 8.02 (d, 4H), 7.83 (m, 4H), 7.06 (d, 4H), 6.85 (d, 4H), 3.94 (t, 4H), 2.68 (t, 4H), 1.70 (t, 4H), 1.61 (t, 4H), 1.27−1.20 (m, 24H); IR (KBr) 3330, 2919, 2851, 1684, 1671, 1576, 1512, 1397, 1240, 1138, 826, 716 cm^{-1}. Anal. Calcd for $C_{52}H_{58}Cl_2N_2O_6S_2$: C, 66.30; H, 6.20; Cl, 7.53; N, 2.97. Found: C, 66.05; H, 6.25; Cl, 7.75; N, 2.93.

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