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Synthesis and Spectral Properties of Novel Thionaphtoquinone Dyes

Cigdem Sayil* **and Cemil Ibis**

Istanbul University, Faculty of Engineering, Department of Chemistry, 34320 Avcılar-Istanbul, Turkey
**E-mail: sayil@istanbul.edu.tr*
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2,3-Dichloro-1,4-naphtoquinone **1** compound was reacted with octadecanethiol **2** in two different mole ratio. Compound **3** was obtained from the reaction of **1** and **2** in 1:2 mole/mole ratio. Compounds **7** and **8** were obtained from reaction of **1** and **2** in 1:1 mole/mole ratio and known compound **9** was synthesized as by-product in this reaction. Novel compounds **5a-e** were obtained from reaction of **1** and related thiols **4a-e**. Known compounds **6c** and **6e** were synthesized as by-product in this reaction. The structures of the compounds were characterized by elemental analysis, UV-vis, FTIR, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopies.

Key Words: 1,4-Naphtoquinone, Disubstituethionaphtoquinone dyes, Michael reaction, Spectroscopic method

Introduction

Quinones, substituted quinones, bis-quinones were synthesized during the last century and their properties extensively studied.[1-5] Their unique ability to attract electrons made them a desirable target in the fast growing fields of moleculer electronics and organic semiconductors.[6] Moreover, different ainon radicals of more complex quinonic compounds exhibit intense absorbtion in the visible or near-infrared (NIR) region. Such a property is of importance in the fields of communication devices,[7] optical storage[8] and organic nonlinear optical (NLO) materials.[9] Our recent work was on the synthesis of symmetrical and non-symmetrical thioquinonyl derivatives.[4,5]

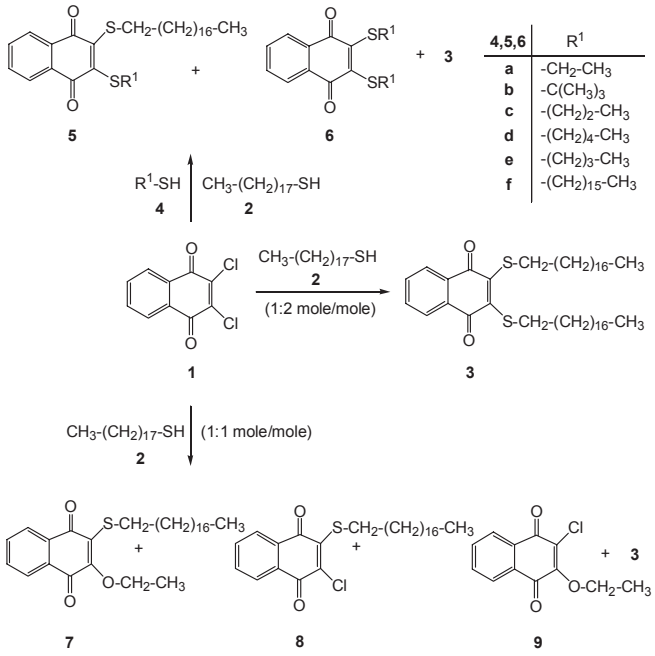
This paper describes the synthesis of new members of a series of alkylmercapto-1,4-naphthoquinones by a Michael-Type addition reaction and their spectral properties.

Results and Discussion

In this study we designed a synthesis of symmetrical and non-symmetrical naphtoquinonyl derivatives through which the quinone can be bridged *via* a thiolate moiety (Scheme 1).

Synthesis of naphtoquinonyl derivatives were carried out similarly to the method described.[10] The ^{1}H-NMR spectra ($CDCl_3$) of the symmetrical molecules **3**, **6c** and **6e** exhibits double-doublets of AA'BB' spin systems characteristic of two different *para* disubstituted aromatic compounds. The four naphthoquinone protons show chemical shifts at δ_H 7.58-7.67(2H) and 7.95-8.04(2H) as double-doublets of AA'BB' system. The hydrogen atoms of the methylene group (S-*C*H$_2$) adjacent to the sulfur atom were shifted to a lower field and display as triplet at δ_H 3.17-3.28. In the ^{13}C-NMR APT spectra ($CDCl_3$) of the symmetrical molecules **3**, **6c** and **6e**, only one C signal of two C=O groups appeared at δ_c 178-179 and only two C signals of four quaternary naphthoquinone carbons resonated at δ_c 146-148 and 132.3-133.2 and two C signals of four vinylic naphthoquinone carbons appeared at δ_c 132.3 and 125. Compound **6c** and **6e** were known compounds earlier but their spectroscopic properties weren't investigated in detail.

The ^{1}H-NMR spectra ($CDCl_3$) of the nonsymmetrical molecules **5a-f**, **7**, **8** and **9** similar shifts and splitting patterns at aromatic region. The four naphthoquinone protons show chemical shifts at δ_H 7.64-7.75(2H) and 8.04-8.14(2H) as double-doublets of AA'BB' system. The hydrogen atoms of the methylene group (S-*C*H$_2$) adjacent to the sulfur atom were shifted to a lower field and display as triplet at δ_H 3.17-3.28. In addition, In the ^{1}H-NMR spectra of **7** and **9**, the hydrogen atoms of the methylene group (O-C*H*$_2$) adjacent to the oxygen atom were shifted a quartet at δ_H 4.46 and 4.63. In the ^{13}C-NMR APT spectra ($CDCl_3$) of the nonsymmetrical molecules **5a-f**, **7**, **8** and **9** not similar to symmetric molecules. The nonsymmetrical molecules exhibit two C signal of two C=O groups appeared at δ_c 178.8-181.4 and four C signals of four quaternary naphthoquinone carbons resonated at δ_c 131-156 and and four C signals of four vinylic



Scheme 1

naphthoquinone carbons appeared at δ_c 125-132. Compound **9** was known compounds earlier but their spectroscopic properties weren't investigated in detail.

In this study, we investegated solvent effect of synthesized dyes on the theirs absorption spectra by use of solvatochromism method. The absorption spectra of compounds **3**, **5**, **6a-e** and **7b** were measured in the nonpolar solvent 1,4-dioxane and in the polar solvents $CHCl_3$ and CH_2Cl_2. The molar absorption coefficients were determined in the solvents and the data are presented in Table 1. As seen that, in the absorption spectra of the compound **5**, **7**, **8** and **9** were observed considerable differences depending on the substituent in the naphtoquinone fragment. Compounds **5** and **7** having electron-donor groups (RS and EtO) were absorbed at the longest wavelength, λ_{max} = 473 and 461 nm in the $CHCl_3$. Compounds **8** and **9** having electron-acceptor substituent (Cl) were absorbed at the shortest wavelength λ_{max} = 440 and 335 nm. in the CH_2Cl_2 (Fig. 1).[11] The synthesized dyes (**3**, **5a**,**b-f**, **6e**, **8**) show the characteristic long wavelength thio-substituted quinonoid π-π* broad transition at 432 ~ 471 nm.

Experimental

Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba 1106 Elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FTIR-8101 spectrometry. NMR spectra were recorded on a Varian^{UNITY} INOVA instrument operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS spectrometer according to ESI probe. UV spectra in chloroform, dichloromethane and 1,4-dioxan solution were recorded on UV/vis Spectrometer TU-1901.

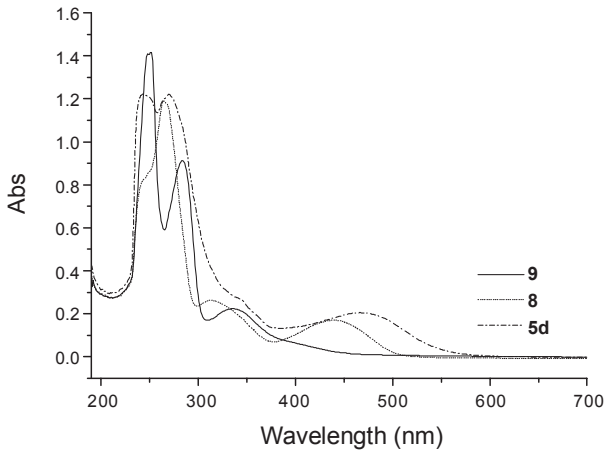


Figure 1. The absorbtion spectra of **5d**, **8** and **9** in CH_2Cl_2 solution.

All chemicals and solvents were obtained commercially and used without purification. Products were isolated by column chromatography on SiO_2 (Fluka Kieselgel 60, particle size 63 ~ 200 μm). TLC plates: silica $60F_{254}$ (Merck, Darmstadt), detection with ultraviolet light (254 nm).

Preparations.

General procedure for preparation of thiosubstituted naphthoquinones:[10] Sodium carbonate was dissolved in ethanol and equimolar amounts of 2,3-dichloro-1,4-naphtoquinone (**1**) and thiols were added slowly. Without heating, the mixture was stirred for 24 hr. The colour of the solution quickly changed and the extent of the reaction was monitored by TLC. Chloroform (30 mL) was added to the reaction mixture. The organic layer was separated and washed with water (4 × 30 mL), and dried with Na_2SO_4. The mixture was concentrated in vacuo, and the residue was extracted with dichloromethane using a Soxhlet extractor. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

Synthesis.

Synthesis of 2,3-bis(octaadecylthio)-1,4-naphthoquinone (3): Compound **3** was synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (2.72 g, 8.8 mmol) in 1:2(*m/m*) ratio according to this general procedure.

The yield was 2.9 g. (93.0%), pink coloured solid, mp 84 ~ 86 °C (from CCl_4). R_f (CCl_4) = 0.36. Found (%): C, 74.92; H, 10.67; S, 8.45. $C_{46}H_{78}O_2S_2$. Calculated (%): C, 75.97; H, 10.81; S 8.81. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 468 (3.43), 274 (4.27), 241 (4.34). IR (KBr): υ/cm^{-1}: 2850, 2919 (C-H); 1656 (C=O); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.88 (t, 6H, *J* = 7.08 Hz., C***H***$_3$); 1.20-1.66 (m, 64H, SCH$_2$C***H***$_2$); 3.26 (t, 4H, *J* = 7.56 Hz., SC***H***$_2$); 7.67 (AA'BB' system, dd, 2H, *J* = 8.79 Hz., C$\underline{H}_{napht}$); 8.04 (A A'BB' system, dd, 2H, *J* = 9.27 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.0 (-***C***H$_3$); 21.60, 27.50, 27.70, 28.10, 28.20, 28.30, 28.50,

Table 1. UV-visible absorption data for compounds **3**, **5a**,**b-f**, **6e**, **7**, **8** and **9**

	λ_{max} in nm (log ε)		
	1,4-Dioxane	$CHCl_3$	CH_2Cl_2
3	461(3.38) 274(4.14) 243(4.09)	468(3.43) 274(4.27) 241(4.34)	464(3.75) 274(4.47) 240(4.46)
5a	467(3.76) 282(4.44) 243(4.40)	471(3.52) 274(4.26) 241(4.31)	467(3.74) 278(4.42) 242(4.42)
5c	466(4.14) 281(4.80) 245(4.77)	469(3.51) 273(4.28) 241(4.32)	464(3.76) 270(4.34) 245(4.37)
5d	465(3.74) 272(4.51) 243(4.48)	473(3.52) 274(4.29) 241(4.34)	467(3.70) 270(4.47) 244(4.47)
5e	467(3.65) 280(4.35) 243(4.32)	470(3.56) 274(4.29) 241(4.32)	467(3.59) 270(4.28) 245(4.30)
5f	467(3.62) 273(4.37) 242(4.33)	471(3.53) 273(4.29) 241(4.31)	467(3.55) 270(4.22) 248(4.23)
6e	464(3.74) 279(4.44) 243(4.40)	469(3.37) 274(4.35) 242(4.38)	467(3.60) 278(4.28) 244(4.26)
7	458(3.52) 276(4.33) 243(4.323	464(3.47) 275(4.37) 241(4.37)	460(3.86) 276(4.63) 246(4.55)
8	432(3.71) 265(4.59) 192(4.02)	433(3.18) 260(4.46) 237(3.80)	440(3.87) 313(4.06) 265(4.71)
9	281(4.27) 251(4.47)		335(3.85) 284(4.46) 252(4.65)

28.60, 28.65, 28.67, 28.69, 29.46, 30.92, 33.98, 38.30 (-***C***H_2-); 132.0, 125.0 (C$\underline{H}_{napht.}$); 146.0, 132.3 (C$\underline{}_{napht.}$); 178.0 (***C***=O). Found: *m*/*z* 727.5 [M^+]. $C_{46}H_{78}O_2S_2$. Calculate: M = 727.2.

Synthesis of 2-(octadecylthio)-3-(ethylthio)-1,4-naphthoquinone (5a): Compound **5a** was synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and ethanethiol **4a** (0.27 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 1.0 g. (45.0%), deep bordeaux coloured solid, mp 83 ~ 84 °C (from CCl_4). R_f (CCl_4) = 0.31. Found (%): C, 71.79; H, 8.78; S, 12.83. $C_{30}H_{46}O_2S_2$. Calculated (%): C, 71.66; H, 9.22; S 12.75. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 471 (3.52), 274 (4.26), 241 (4.31). IR (KBr): υ/cm^{-1}: 2850, 2917, 2950 (C-H); 1653 (C=O); 1589 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.89 (t, 6H, *J* = 6.84 Hz., C***H***$_3$); 1.24-1.66 (m, 32H, SCH_2C***H***$_2$); 3.30 (t, 4H, *J* = 7.56 Hz., SC***H***$_2$); 7.68 (AA'BB' system, dd, 2H, *J* = 8.78 Hz., C$\underline{H}_{napht}$); 8.04 (AA'BB' system, dd, 2H, *J* = 9.27 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.0, 15.26 (-***C***H_3); 22.86, 24.08, 28.91, 29.32, 29.54, 29.67, 29.76, 29.83, 29.85, 29.89, 30.67, 32.12, 35.20, 37.11 (-***C***H_2-); 127.0, 127.02, 133.58 (C$\underline{H}_{napht.}$); 133.30, 133.51, 147.93, 148.24 (C$\underline{}_{napht.}$); 179.14, 179.17 (***C***=O). Found: *m*/*z* 503.24 [M^+]. $C_{20}H_{46}O_2S_2$. Calculated: M= 502.82.

Synthesis of 2-(octadecylthio)-3-(*t*-butylthio)-1,4-naphthoquinone (5b): Compound **5b** was synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and *t*-butanethiol **4b** (0.4 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 1.2 g. (51.2%), red coloured solid, mp 58 ~ 59 °C (from CCl_4). R_f (CCl_4) = 0.31. Found (%): C, 72.02; H, 9.49. $C_{32}H_{50}O_2S_2$. Calculated (%): C, 72.40; H, 9.49. IR (KBr): υ/cm^{-1}: 2848, 2922, 2954 (C-H); 1666 (C=O); 1591 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.88 (t, 12H, *J* = 6.83 Hz., C***H***$_3$); 1.21-1.66 (m, 32H, SCH_2C***H***$_2$); 3.30 (t, 2H, *J* = 7.56 Hz., SC***H***$_2$); 7.67-7.73 (m, 2H, C$\underline{H}_{napht}$); 8.04-8.11 (m, 2H, C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 14.29, 16.11, 22.87, 32.13 (-***C***H_3); 28.93, 28.99, 29.02, 29.53, 29.55, 29.67, 29.90, 30.46, 30.76, 31.65, 32.63, 33.33, 35.36, 52.69 (-***C***H_2-); 70.1 (-S-***C***-); 133.58, 133.69, 133.74, 134.0 (C$\underline{H}_{napht.}$); 132.82, 133.33, 141.08, 161.78 (C$\underline{}_{napht.}$); 179.11, 181.14 (***C***=O). Found: *m*/*z* 530.95 [M^+]. $C_{32}H_{50}O_2S_2$. Calculated : M = 530.88.

Synthesis of 2-(octadecylthio)-3-(propylthio)-1,4-naphthoquinone (5c) and 2,3-bis (propylthio)-1,4-naphthoquinone (6c): Compound **5c** and **6c** were synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and propanethiol **4c** (0.33 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 0.5 g. (21.4%), pink coloured solid, mp 71 ~ 72 °C (from CCl_4). R_f (CCl_4) = 0.50. Found (%): C, 71.17; H, 9.50. $C_{31}H_{48}O_2S_2$. Calculated (%): C, 72.04; H, 9.36. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 469 (3.51), 273 (4.28), 241 (4.32). IR (KBr): υ/cm^{-1}: 2850, 2917, 2950 (C-H); 1655 (C=O); 1589 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.86 (t, 6H, *J* = 6.84 Hz., C***H***$_3$); 1.21-1.65 (m, 34H, SCH_2C***H***$_2$); 3.27 (t, 4H, *J* = 6.84 Hz., SC***H***$_2$); 7.66 (AA'BB' system, dd, 2H, *J* = 9.28 Hz., C$\underline{H}_{napht}$); 8.04 (AA'BB' system, dd, 2H, *J* = 8.78 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.53, 14.26 (-***C***H_3); 22.87, 24.08,28.91, 29.54, 29.67, 29.76, 29.83, 29.85, 29.89, 30.67, 32.12, 35.20, 37.11 (-***C***H_2-); 127.0, 127.15, 133.45 (C$\underline{H}_{napht.}$); 133.30, 133.51, 147.91, 148.24 (C$\underline{}_{napht.}$); 179.15, 179.17 (***C***=O). Found: *m*/*z* 517.22 [M^+]. $C_{31}H_{48}O_2S_2$. Calculate: M = 516.85.

The yield was 0.4 g. (27.5%), red coloured solid, mp 54 ~ 55 °C (lit.[2] 56 °C); R_f (CCl_4) = 0.26. Found (%): C, 63.20; H, 6.54. $C_{31}H_{48}O_2S_2$. Calculated (%): C, 62.71; H, 5.92. IR (KBr): υ/cm^{-1}: 2857, 2927, 2958 (C-H); 1658 (C=O); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.78-0.96 (t, 6H, *J* = 6.84 Hz., C***H***$_3$); 1.15-1.62 (m, 44H, SCH_2C***H***$_2$); 3.17 (t, 4H, *J* = 7.32 Hz., SC***H***$_2$); 7.59 (AA'BB' system, dd, 2H, *J* = 8.78 Hz., C$\underline{H}_{napht}$); 7.94 (AA'BB' system, dd, 2H, *J* = 9.27 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 14.29 (-***C***H_3); 33.30, 37.10 (-***C***H_2-); 126.76, 133.56 (C$\underline{H}_{napht.}$); 133.25, 148.05 (C$\underline{}_{napht.}$); 179.13 (***C***=O). Found: *m*/*z* 306.96 [M^+]. $C_{16}H_{18}O_2S_2$. Calculate: M = 306.45.

Synthesis of 2-(octadecylthio)-3-(penthylthio)-1,4-naphthoquinone (5d): Compound **5d** was synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and pentanethiol **4d (**0.46 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 0.7 g. (27.9%), pink coloured solid, mp 65 ~ 66 °C (from CCl_4). R_f (CCl_4) = 0.64. Found (%): C, 72.81; H, 9.04. $C_{33}H_{52}O_2S_2$. Calculated (%): C, 72.79; H, 8.17. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 473 (3.52), 274 (4.29), 241 (4.34). IR (KBr): υ/cm^{-1}: 2850, 2917, 2950 (C-H); 1657 (C=O); 1592 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.86-0.90 (m, 6H, C***H***$_3$); 1.24-1.67 (m, 38H, SCH_2C***H***$_2$); 3.28 (t, 4H, *J* = 7.56 Hz., SC***H***$_2$); 7.68 (AA'BB' system, dd, 2H, *J* = 8.79 Hz., C$\underline{H}_{napht}$); 8.04 (AA'BB' system, dd, 2H, *J* = 9.27 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 14.07, 14.26 (-***C***H_3); 22.40, 22.87, 29.67, 29.76, 29.83, 29.84, 29.85, 29.86, 29.89, 30.35, 30.68, 31.10, 32.12, 35.16, 35.20 (-***C***H_2-); 127.01, 133.53 (C$\underline{H}_{napht.}$); 133.32, 148.08, 148.11 (C$\underline{}_{napht.}$); 179.21 (***C***=O). Found: *m*/*z* 545.25 [M^+]. $C_{33}H_{52}O_2S_2$. Calculate: M = 544.50.

Synthesis of 2-(octadecylthio)-*n*-butylthio)-1,4-naphthoquinone (5e) and 2,3-bis (*n*-butylthio)-1,4-naphthoquinone (6e): Compound **5e** and **6e** were synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and *n*-butanethiol **4e (**0.40 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 1.0 g. (43.0%), pink coloured solid, mp 73 ~ 74 °C (from CCl_4). R_f[CCl_4/CH_2CI_2 (1:1)] = 0.73. Found (%): C, 72.93; H, 9.73; S, 11.24. $C_{32}H_{50}O_2S_2$. Calculated (%): C, 72.40; H, 9.49; S, 12.07. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 470 (3.56), 274 (4.29), 241 (4.32). IR (KBr): υ/cm^{-1}: 2850, 2917, 2950 (C-H); 1655 (C=O); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.86-0.93 (m, 6H, C***H***$_3$); 1.21-1.65 (m, 36H, SCH_2C***H***$_2$); 3.27 (m, 4H, SC***H***$_2$); 7.68 (AA'BB' system, dd, 2H, *J* = 9.27 Hz., C$\underline{H}_{napht}$); 8.04 (AA'BB' system, dd, 2H, *J* = 9.28 Hz.,C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.77, 14.24 (-***C***H_3); 22.07, 22.86, 28.92, 29.32, 29.53, 29.83, 29.67, 29.75, 29.84, 29.85, 29.88, 29.89, 30.68, 32.11, 32.74, 34.88, 35.20 (-***C***H_2-); 127.0, 133.43 (C$\underline{H}_{napht.}$); 133.33, 133.52, 148.08, 148.14 (C$\underline{}_{napht.}$); 179.20 (***C***=O). Found: *m*/*z* 531.25 [M^+]. $C_{32}H_{50}O_2S_2$. Calculate: M = 530.88.

The yield was 0.3 g. (22.0%), red coloured solid, mp 37 °C (lit.[2] 37 °C); R_f [CCl_4/CH_2CI_2 (1:1)] = 0.50. Found (%): C, 65.46; H, 6.97. $C_{18}H_{22}O_2S_2$. Calculated (%): C, 64.63; H, 6.62.

UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 469 (3.37), 274 (4.35), 242 (4.38). IR (KBr): υ/cm^{-1}: 2857, 2927, 2958 (C-H); 1658 (C=O); 1589 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.86-0.93 (m, 6H, C***H***$_3$); 1.42-1.65 (m, 8H, SCH$_2$C***H***$_2$); 3.28 (t, 4H, J = 7.32 Hz, SC***H***$_2$); 7.66 (AA'BB' system, dd, 2H, J = 8.78 Hz., C$\underline{H}_{napht}$); 8.03 (AA'BB' system, dd, 2H, J = 9.27 Hz.,C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.80 (-***C***H$_3$); 33.30, 34.86 (-***C***H$_2$-); 126.74, 133.53 (C$\underline{H}_{napht.}$); 133.25, 148.02 ($\underline{C}_{napht.}$); 179.12 (***C***=O). Found: *m*/*z* 335.02 [M$^+$]. $C_{18}H_{22}O_2S_2$. Calculate: M = 334.50.

Synthesis of 2-(octadecylthio)-3-(hexadecylthio)-1,4-naphthoquinone (5f): Compound **5f** was synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol **2** (1.26 g, 4.4 mmol) and hexadecanethiol **4f** (1.14 g, 4.4 mmol) according to this general procedure. In this reaction compound **3** was obtained as by-product.

The yield was 1.7 g. (56.5%), orange coloured solid, mp 59 ~ 60 ^{o}C (from CCl_4). R_f (CCl_4) = 0.36. Found (%): C, 75.62; H, 10.33; S, 8.62. $C_{44}H_{74}O_2S_2$. Calculated (%): C, 75.58; H, 10.66; S, 9.17. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 471 (3.53), 273 (4.29), 241 (4.31). IR (KBr): υ/cm^{-1}: 2848, 2915 (C-H); 1666 (C=O); 1589 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.88 (t, 6H, J = 6.84 Hz, C***H***$_3$); 1.24-1.66 (m, 60H, SCH$_2$C***H***$_2$); 3.26 (t, 4H, J = 7.56 Hz., SC***H***$_2$); 7.67 (AA'BB' system, dd, 2H, J = 8.79 Hz., C$\underline{H}_{napht}$); 8.04 (AA'BB' system, dd, 2H, J = 8.79 Hz., C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 14.30 (-***C***H$_3$); 22.91, 28.96, 29.36, 29.58, 29.72, 29.81, 29.88, 29.88, 29.89, 29.92, 30,70, 32.15, 35.21 (-***C***H$_2$-); 127.0, 133.0 (C$\underline{H}_{napht.}$); 133.50, 148.0 ($\underline{C}_{napht.}$); 179.20 (***C***=O). Found: *m*/*z* 699.42 [M$^+$]. $C_{44}H_{74}O_2S_2$. Calculate: M = 699.21.

Synthesis of 2-(octadecylthio)-3-(etoxy)-1,4-naphthoquinone (7), 2-(octadecylthio)-3-(choloro)-1,4-naphthoquinone (8) and 2-(choloro)-3-(etoxy)-1,4-naphthoquinone (9): Compound **7**, **8** and **9** were synthesized from reaction of **1** (1 g, 4.4 mmol) with octadecanethiol (1.26 g, 4.4 mmol) in 1:1 (*m*/*m*) ratio according to this general procedure. In this reaction compound **3** was obtained as by-product.

(7): The yield was 0.2 g. (7.2%), red coloured solid, mp 61 ~ 62 ^{o}C (from CCl_4). R_f (CCl_4) = 0.28. Found (%): C, 73.61; H, 9.56; S, 5.94. $C_{30}H_{46}O_3S$. Calculated (%): C, 74.02; H, 9.50; S, 6.58. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 464 (3.47), 275 (4.37), 241 (4.37). IR (KBr): υ/cm^{-1}: 2920, 2952 (C-H); 1661 (C=O); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.88 (t, 6H, J = 7.08 Hz, C***H***$_3$); 1.21-1.65 (m, 32H, SCH$_2$C***H***$_2$); 3.17 (t, 4H, J = 7.56 Hz., SC***H***$_2$); 4.46 (q, 2H, J = 7.32 Hz, OC***H***$_2$); 7.67-8.05 (m, 4H, CH$_{napht}$). ^{13}C NMR ($CDCl_3$), δ 13.09, 14.89 (-***C***H$_3$); 27.72, 28.44, 29.57, 28.63, 28.66, 28.68, 28.69, 29.21, 29.24, 29.33, 30.43, 30.92, 32.10 (-***C***H$_2$-); 68.88 (O***C***H$_2$-); 125.36, 125.58, 130.52, 132.52 (C$\underline{H}_{napht.}$); 131.47, 132.47, 133.93, 156.76 ($\underline{C}_{napht.}$); 177.79, 181.7 (***C***=O). Found: *m*/*z* 487.28 [M$^+$]. $C_{30}H_{46}O_3S$. Calculate: M = 486.76.

(8): The yield was 0.9 g. (42.0%), yellow coloured solid, mp 90 ~ 92 ^{o}C (from $CHCl_3$). R_f ($CHCl_3$) = 0.77. Found (%): C, 71.39; H, 8.03; S, 7.60. $C_{28}H_{41}O_2SCl$. Calculated (%): C, 70.48; H, 8.66; S, 6.72. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 433 (3.18), 260 (4.46), 237 (3.80). IR (KBr): υ/cm^{-1}: 2849, 2917, 2953 (C-H); 1672 (C=O); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ 0.89 (t, 3H, J = 6.83 Hz, C***H***$_3$); 1.25-1.69 (m, 32H, SCH$_2$C***H***$_2$); 3.37 (t, 4H, J = 7.56 Hz., SC***H***$_2$); 7.70-7.75 (m, 2H, C$\underline{H}_{napht}$); 8.07-8.14 (m, 2H, C$\underline{H}_{napht}$). ^{13}C NMR ($CDCl_3$), δ 14.28 (-***C***H$_3$); 22.88, 28.85, 29.29, 29.55, 29.64, 29.75, 29.83, 29.86, 29.89, 30,67, 32.13, 34.57 (-***C***H$_2$-); 127.40, 127.49, 133.93, 134.26 (C$\underline{H}_{napht.}$); 131.56, 131.90, 133.99, 149.67 ($\underline{C}_{napht.}$); 175.25, 180.10 (***C***=O). Found: *m*/*z* 477.18 [M$^+$]. $C_{28}H_{41}O_2SCl$. Calculate: M = 477.15.

(9): The yield was 0.2 g. (14.4%), yellow coloured solid, mp 94 ~ 96 ^{o}C (lit.[1] 97 ~ 98 ^{o}C). R_f (CCl_4) = 0.33. Found (%): C, 61.45; H, 4.30. $C_{12}H_9O_3Cl$. Calculated (%): C, 60.95; H, 3.83. UV/vis ($CHCl_3$), λ_{max}/nm (lg ε_{max}): 335 (3.85), 284 (4.46), 252 (4.65). IR (KBr): υ/cm^{-1}: 2937, 2985, 3086 (C-H); 1677 (C=O); 1591 (C=C). ^{1}H NMR ($CDCl_3$), δ 1.47 (t, 6H, J = 7.32 Hz, C***H***$_3$); 4.63 (q, 2H, J = 7.32 Hz, OC***H***$_2$); 7.70-8.14 (m, 4H, CH$_{napht}$). ^{13}C NMR ($CDCl_3$), δ 16.19 (-$\underline{C}$H$_3$); 70.89 (-O-***C***H$_2$-); 127.04, 127.13, 131.06, 131.37 (C$\underline{H}_{napht.}$); 129.47, 131.06, 131.27, 156.83 ($\underline{C}_{napht.}$); 178.81, 179.75 (***C***=O). Found: *m*/*z* 236.87 [M$^+$]. $C_{12}H_9O_3Cl$. Calculate: M = 236.65.

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