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## Synthesis and Spectroscopic Properties of *S*-, *O*-Substituted Naphthoquinone Dyes

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## SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF S-,O-SUBSTITUTED NAPHTHOQUINONE DYES

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*New S-,O-substituted naphthoquinone compounds (3a, 4b, 6, 7c, 9d, 10, 12, 13c, 14d, 15) were synthesized via vinilic substitution. 2,3-Dichloro-1,4-naphthoquinone gave 3a and 4b with 4,4'-thiobisbenzenethiol, respectively. Compounds 6 and 7c were obtained from the reaction of 2,3-dichloro-1,4-naphthoquinone with cyclohexylmercaptane. The compounds 9d and 10 were prepared from the reaction of 2,3-dichloro-1,4-naphthoquinone with 6-mercapto-1-hexanol. Compounds 12, 13c, 14d, and 15 were synthesized from the reaction of 2,3-dichloro-1,4-naphthoquinone with 1,6-hexanedithiol. Their structures were characterized by micro analysis, FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, UV-Vis, and fluorescence spectroscopy.*

**Keywords** Fluorescence spectroscopy; heterocyclic compounds; 1,4-naphthoquinone; spectroscopic method; synthesis; thioethers

## INTRODUCTION

Quinonic compounds are of great importance to understand different processes that are related to biology. Macrocyclic thioethers could be useful for treatment of heavy-metal poisoning as potential of heavy-metal receptors.<sup>1</sup> Quinone-containing thio-crown ethers represent a coupled system in which two mechanisms mutually influence each other, and which might add to our understanding of the analogous biologically active compounds.

Naphthoquinones have been used to treat burns, cuts, and a variety of skin diseases worldwide.<sup>2</sup> Sulfur-containing naphthoquinones have been the subject of much interest for a number of years due to anti-inflammatory,<sup>3</sup> antibacterial,<sup>4</sup> antifungal,<sup>5</sup> and antiviral<sup>6</sup> biological activities. It is also well known that quinone-bearing macrocycles have great potential as antibiotics and antitumor agents.<sup>7</sup>

Naphthoquinone pigments typically demonstrate variable colors as a result of changes in pH; hence, they are widely used in the chemical industry for the production of dyes, medicines, food, etc. Naphthoquinone derivatives are yellow, orange, and purple-red pigments, with UV absorptions at 214, 275, and 520 nm, respectively.<sup>8</sup> Cosmetics such as lipstick, rouge, and face powder made with naphthoquinone dyes possess the advantages of having strong, stable coloring properties as well as certain antiphlogistic, antibacterial, and antiviral properties.<sup>9</sup> Some thioquinone dye molecules are employed as organic nonlinear

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optical (NLO) materials,<sup>10</sup> organic photoconductors (OPC), and emitters for electroluminescence (EL).<sup>11</sup>

In recent years, several *S*-,*O*-substituted naphthoquinone compounds have been synthesized.<sup>11</sup> *S*-,*S*-substituted naphthoquinone compounds have been prepared by the reactions of 2,3-dichloro-1,4-naphthoquinone with alkyl chain mercaptan, cycloalkyl mercaptan, aryl mercaptan, etc.<sup>12,13</sup> The aim of this study was the synthesis and characterization of new *S*-,*O*-substituted naphthoquinone compounds.

## RESULTS AND DISCUSSION

The reaction of 2,3-dichloro-1,4-naphthoquinone with 4,4'-thiobisbenzenethiol in ethanol in the presence of Na<sub>2</sub>CO<sub>3</sub> gave **3a** and **4b**, respectively. Compounds **6** and **7c** were obtained from the reaction of 2,3-dichloro-1,4-naphthoquinone with cyclohexylmercaptan in ethanol. Mono(thio)substituted naphthoquinone **9d** and bis(thio)substituted naphthoquinone **10** compounds were obtained from the reaction of 2,3-dichloro-1,4-naphthoquinone with 6-mercapto-1-hexanol. The reaction of 2,3-dichloro-1,4-naphthoquinone with 1,6-hexanedithiol gave thioether compounds **12**, **13c**, **14d**, and **15** in ethanol. It was shown that interesting heterocyclic compounds **12** and **15** could be obtained from the reaction of long alkyl chain dithiol **11** with 2,3-dichloro-1,4-naphthoquinone. Isolation and identification proved that a cyclization reaction had taken place, yielding the compound **12** (Scheme 1).

The ESI mass spectrum of the compound **12** displayed a molecular ion peak at  $m/z$  (%) 305 (100) [M]<sup>+</sup>. The <sup>13</sup>C NMR spectra of compound **12** gave a single carbonyl signal at 179.0 ppm (C=O). Compound **13c** was a *S*-,*O*-substituted naphthoquinone compound. While compound **13c** was formed, two chloro atoms were replaced with ethoxy groups, which acted as a nucleophilic compound. On the contrary, these two chloro atoms were not substituted in the compound **14d**. The <sup>13</sup>C NMR spectra of compound **14d** gave two carbonyl signals at 174.0 and 178.9 ppm (C=O), while compound **15** showed a carbonyl signal at 177.8 ppm (C=O) (Figure 1).

In the ESI mass spectrum of the compound **14d**, the respective molecular ion peak was observed at  $m/z$  (%) 531 (100) [M]<sup>+</sup>. The cleavage of the chloro ion from compound **14d** of the molecular ion gave a fragment at  $m/z$  (%) 493 (100), which was the base peak.

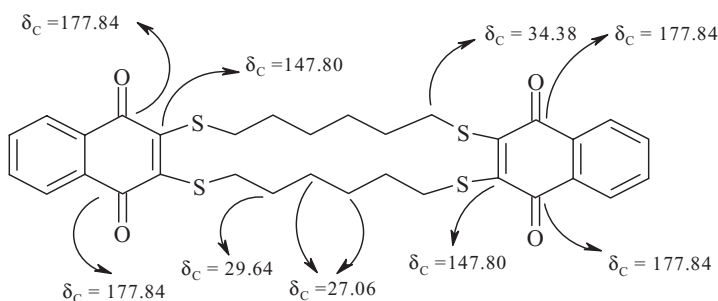
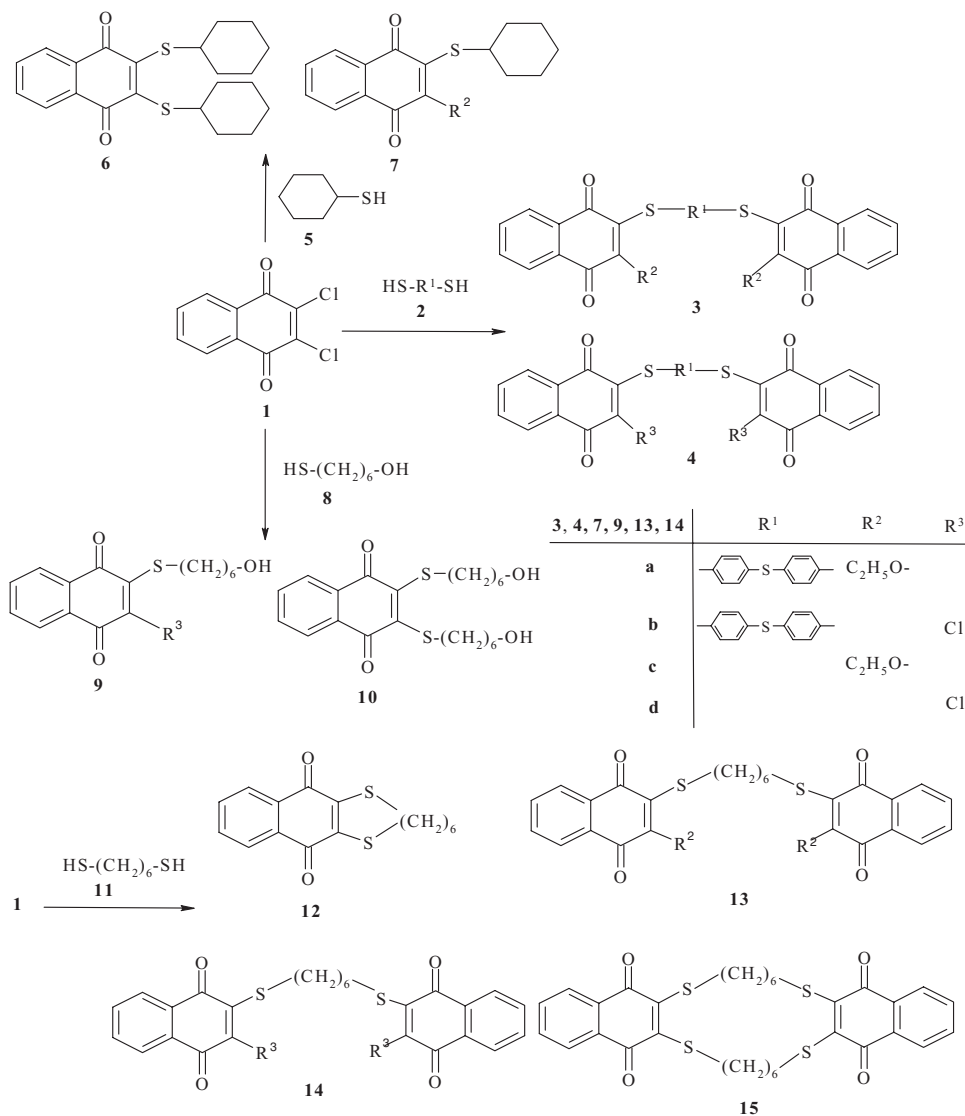


Figure 1 Distinctive  $\delta_C$  values of compound **15**.



Scheme 1

The respective molecular ion peak was observed at  $m/z$  (%) 609 (100) for compound **15** in the mode of ESI.

2,5-Diethoxy- and 2,6-diethoxybenzoquinone compounds have been prepared previously in the presence of an aliphatic base such as ethanol.<sup>6</sup> In this study, *S*-, *O*-substituted-1,4-naphthoquinone compounds **3a**, **7c**, and **13c** have been obtained from the reactions of 2,3-dichloro-1,4-naphthoquinone with thiol in ethanol, which have been formed as side products. Ethanol acted as a *O*-nucleophilic compound in these reactions.

<sup>13</sup>C NMR spectra of compound **6** gave a carbonyl signal at 178.2 ppm (C=O). Compound **7c** showed two carbonyl signals at 178.1 and 178.7 ppm (C=O). The <sup>1</sup>H NMR spectra of the compound **7c** in CDCl<sub>3</sub> displayed distinct signals with appropriate

**Table I** Fluorescence data of the compounds **3a**, **4b**, **6**, **7c**, **9d**, **10**, **12**, **13c**, **14d**, and **15**

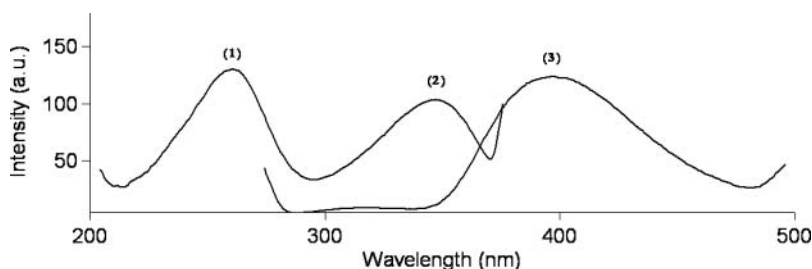
Compound	Solvent	$\lambda_{\text{max}}(\text{ex})$ (nm)	$\lambda_{\text{max}}(\text{em})$ (nm)
<b>3a</b>	CHCl <sub>3</sub> /MeOH (1:1)	245, 334	412
<b>4b</b>	CHCl <sub>3</sub> /MeOH (1:1)	259, 342	407
<b>6</b>	CHCl <sub>3</sub>	261, 345	395
<b>7c</b>	CHCl <sub>3</sub>	266, 307, 358	405
<b>9d</b>	CHCl <sub>3</sub> /MeOH (1:1)	261, 347	397
<b>10</b>	CHCl <sub>3</sub> /MeOH (1:1)	253, 341	414
<b>12</b>	CHCl <sub>3</sub> /MeOH (1:1)	257	406
<b>13c</b>	CHCl <sub>3</sub> /MeOH (1:1)	260	407
<b>14d</b>	CHCl <sub>3</sub> /MeOH (1:1)	251	309, 377
<b>15</b>	CHCl <sub>3</sub> /MeOH (1:1)	265, 345	425

multiples. The triplet ( $J = 7.32$  Hz) accounting for three protons centered at 1.22 ppm was assigned to the protons of the methyl group. The multiplet in the region of 1.41–1.54 ppm, accounting for 10 protons, was assigned to the methylene protons. The two methylene protons of (-O-CH<sub>2</sub>) grouping resonated as a quartet centered at 4.75 ppm. The aromatic region corresponds to four protons at 7.70 (t,  $J = 7.81$  Hz), 7.75 (t,  $J = 5.37$  Hz), 8.07 (dd,  $J = 6.83$  and  $J = 7.39$  Hz), and 8.13 ppm (dd,  $J = 6.83$  and  $J = 7.39$  Hz).

Fluorescence is an important property of quinone compounds for the use of organic materials.<sup>14,15</sup> The new naphthoquinone compounds **3a**, **4b**, **6**, **7c**, **9d**, **10**, **12**, **13c**, **14d**, and **15** showed the fluorescence property. The fluorescence excitation and emission maxima of the synthesized compounds in CHCl<sub>3</sub> or CHCl<sub>3</sub>/MeOH solution are summarized in Table I. Figure 2 shows the excitation (1, 2) and the emission (3) spectra of **9d** in CHCl<sub>3</sub>/MeOH. The first and second bands at 261, 347 nm were assigned to the excited bands, and the third band at 397 nm was the emission band at room temperature.

## CONCLUSION

The obtained new products were stable naphthoquinone dyes. These compounds may attract attention as organic dyes because of their high solubility in various organic solvents such as chloroform, dichloromethane, etc. and their red color in the solid state. The structures of products were determined by microanalysis and spectroscopic data such as FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and UV/Vis. All these new compounds gave spectroscopic data in accordance with the proposed structures.

**Figure 2** The excitation (1, 2) and emission (3) bands of **9d** in CHCl<sub>3</sub>/MeOH at rt.

## EXPERIMENTAL

Melting points were measured on a Buchi B-540 melting point apparatus. Elemental analyses were performed on a Thermo Finnigan Flash EA 1112 Elemental analyser. Infrared spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FT-IR spectrometer. UV spectra in chloroform solution were recorded on a Perkin Elmer Lambda 35 UV/Vis spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Unity Inova operating at 500 MHz. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer according to ESI probe. Fluorescence spectra were run on a Varian Cary Eclipse Fluorescence Spectrophotometer. Excitation and emission spectra were measured for  $10^{-4}$  M solutions for all compounds in  $\text{CHCl}_3$  and  $\text{MeOH/CHCl}_3$  (1:1) at rt. Excitation and emission slit widths were set at 5 or 10 nm. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size 63–200  $\mu\text{m}$ ) TLC plates, silica 60F<sub>254</sub> (Merck, Darmstadt), and detection with ultraviolet light (254 nm). All chemicals were reagent grade and were used without further purification. Moisture was excluded from the glass apparatus using  $\text{CaCl}_2$  drying tubes.

### General Procedure for the Synthesis of S-,O-Substituted Naphthoquinone Compounds (3a, 4b, 6, 7c, 9d, 10, 12, 13c, 14d, 15)

Sodium carbonate was dissolved in ethanol (20 mL), and equimolar amounts of 2,3-dichloro-1,4-naphthoquinone and thiols were added slowly. Without heating, the mixture was stirred for 24 h. The color 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, washed with water ( $4 \times 30$  mL), and dried with  $\text{Na}_2\text{SO}_4$ . After the solvent was evaporated, the residue was purified by column chromatography on silica gel.

#### 4,4'-Thiobisbenzylsulfanyl[2,2':e]-diethoxy[3,3']-bis(1,4-naphthoquinone) (3a)

Compound **3a** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 4,4'-thiobisbenzenethiol **2** (1.2 g, 4.4 mmol) according to the above general procedure.

Red oil, yield: 0.4 g (14%).  $R_f$ : 0.75 ( $\text{CHCl}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3059 (Ar-H), 2920, 2851 (C-H), 1669 (C=O), 1591 (C=C). UV-vis [ $\text{CHCl}_3$ ,  $\lambda(\log \epsilon)$ ]: 204(3.4), 242(3.9), 343(3.0), 465(3.2) nm.  $^1\text{H}$  NMR (499.74 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.32 (t,  $J$  = 6.83 Hz, 6H,  $\text{CH}_3$ ), 4.21 (q, 4H, O- $\text{CH}_2$ ), 6.81–7.15 (m, 8H,  $\text{H}_{\text{arom}}$ ), 7.25 (t,  $J$  = 5.32 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 7.31 (t,  $J$  = 5.84 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 7.75 (dd,  $J$  = 5.85 Hz,  $J$  = 5.86 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 8.05 ppm (dd,  $J$  = 5.86 Hz,  $J$  = 5.86 Hz, 2H,  $\text{H}_{\text{naph}}$ ).  $^{13}\text{C}$  NMR (125.66 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 13.0 ( $\text{CH}_3$ ), 30.8 (O- $\text{CH}_2$ ), 126.4, 127.7, 129.0, 129.3 ( $\text{CH}_{\text{arom}}$ ), 130.3, 133.1 ( $\text{C}_{\text{arom}}$ ), 161.8 (=C-S), 170.2 (=C-O), 190.2, 208.0 ppm (C=O). MS [+ESI]:  $m/z$  651 [ $\text{M}]^+$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{26}\text{O}_6\text{S}_3$  (M, 650.79): C, 66.44; H, 4.02; S, 14.78. Found: C, 66.60; H, 4.14; S, 14.09.

#### 4,4'-Thiobisbenzylsulfanyl[2,2':e]-dichloro[3,3']-bis(1,4-naphthoquinone) (4b)

Compound **4b** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 4,4'-thiobisbenzenethiol **2** (1.2 g, 4.4 mmol) according to the general procedure above.

Red oil, yield: 0.9 g (32%).  $R_f$ : 0.50 ( $\text{CHCl}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3068 (Ar-H), 2922, 2851 (C-H), 1664 (C=O), 1589 (C=C). UV-vis [ $\text{CHCl}_3$ ,  $\lambda(\log \epsilon)$ ]: 204(3.5), 257(4.0), 344(3.1), 460(3.3) nm.  $^1\text{H}$  NMR (499.74 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.01–7.45 (m, 8H,  $\text{H}_{\text{arom}}$ ), 7.62 (t,  $J$  = 5.37 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 7.71 (t,  $J$  = 5.84 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 7.93 (dd,  $J$  = 7.33 Hz,  $J$  = 7.32 Hz, 2H,  $\text{H}_{\text{naph}}$ ), 8.15 ppm (dd,  $J$  = 6.84 Hz,  $J$  = 6.83 Hz, 2H,  $\text{H}_{\text{naph}}$ ).  $^{13}\text{C}$  NMR (125.66 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 126.3, 130.5, 130.7, 133.0 ( $\text{CH}_{\text{arom}}$ ), 131.6, 131.6, 134.3 ( $\text{C}_{\text{arom}}$ ), 140.3 (=C–S), 147.0 (=C–Cl), 177.7, 179.1 ppm (C=O). MS [+ESI]:  $m/z$  563  $[\text{M}-2\text{Cl}]^+$ . Anal. Calcd for  $\text{C}_{32}\text{H}_{16}\text{O}_4\text{S}_3\text{Cl}_2$  (M, 631.58): C, 60.85; H, 2.55; S, 15.23. Found: C, 60.60; H, 2.14; S, 15.09.

### 2,3-Bis(cyclohexylsulfanyl)-1,4-naphthoquinone (6)

Compound **6** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with cyclohexylmercaptan **5** (0.51 g, 4.4 mmol) according to the general procedure above.

Red solid, yield: 0.9 g (53%). M.p. 57–58°C.  $R_f$ : 0.75 ( $\text{CHCl}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3062 (Ar-H), 2926, 2851 (C-H), 1659 (C=O), 1592 (C=C). UV-vis [ $\text{CHCl}_3$ ,  $\lambda(\log \epsilon)$ ]: 239(3.8), 278(3.7), 345(3.0), 469(3.5) nm.  $^1\text{H}$  NMR (499.74 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.21–2.23 (m, 20H,  $\text{CH}_2$ ), 3.91–4.05 (m, 2H, S–CH<), 7.65 (dd,  $J$  = 5.37 Hz,  $J$  = 5.86 Hz, 2H,  $\text{H}_{\text{arom}}$ ), 8.12 ppm (dd,  $J$  = 5.86 Hz,  $J$  = 5.85 Hz, 2H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (125.66 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 24.5, 24.9, 33.0 ( $\text{CH}_2$ ), 46.0 (CH), 125.9, 132.3 ( $\text{CH}_{\text{arom}}$ ), 132.0 ( $\text{C}_{\text{arom}}$ ), 147.7 (=C–S), 178.2 ppm (C=O). MS [+ESI]:  $m/z$  386  $[\text{M}]^+$ , 303  $[\text{M}-(\text{C}_6\text{H}_{11})]^+$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{S}_2$  (M, 386.57): C, 68.35; H, 6.78; S, 16.58. Found: C, 68.45; H, 7.13; S, 16.61.

### 2-(1-Cyclohexylsulfanyl)-3-(1-ethoxy)-1,4-naphthoquinone (7c)

Compound **7c** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with cyclohexylmercaptan **5** (0.51 g, 4.4 mmol) according to the general procedure above.

Dark red oil, yield: 0.4 g (28%).  $R_f$ : 0.50 ( $\text{CHCl}_3$ ). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3069 (Ar-H), 2983, 2936 (C-H), 1676, 1660 (C=O), 1592, 1563 (C=C). UV-vis [ $\text{CHCl}_3$ ,  $\lambda(\log \epsilon)$ ]: 239(2.8), 273(3.8), 340(3.8), 468(3.2) nm.  $^1\text{H}$  NMR (499.74 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.22 (t,  $J$  = 7.32 Hz, 3H,  $\text{CH}_3$ ), 1.41–1.54 (m, 10H,  $\text{CH}_2$ ), 4.40–4.52 (m, 1H, S–CH<), 4.75 (q, 2H, O– $\text{CH}_2$ ), 7.70 (t,  $J$  = 7.81 Hz, 1H,  $\text{H}_{\text{arom}}$ ), 7.75 (t,  $J$  = 5.37 Hz, 1H,  $\text{H}_{\text{arom}}$ ), 8.07 (dd,  $J$  = 6.83 Hz,  $J$  = 7.39 Hz, 1H,  $\text{H}_{\text{arom}}$ ), 8.13 ppm (dd,  $J$  = 6.83 Hz,  $J$  = 7.39 Hz, 1H,  $\text{H}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (125.66 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.9 ( $\text{CH}_3$ ), 24.6, 25.0, 32.9 ( $\text{CH}_2$ ), 43.9 (CH), 69.6 (O– $\text{CH}_2$ ), 125.8, 125.9, 132.4, 132.5 ( $\text{CH}_{\text{arom}}$ ), 129.8, 132.8 ( $\text{C}_{\text{arom}}$ ), 132.2 (=C–S), 155.6 (=C–O), 178.1, 178.7 ppm (C=O). MS [+ESI]:  $m/z$  317  $[\text{M}]^+$ , 234  $[\text{M}-(\text{C}_6\text{H}_{11})]^+$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{O}_3\text{S}_1$  (M, 316.42): C, 68.32; H, 6.37; S, 10.13. Found: C, 68.37; H, 6.94; S, 10.34.

### 2-(6-Sulfanyl-1-hexanol)-3-chloro-1,4-naphthoquinone (9d)

Compound **9d** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 6-mercapto-1-hexanol **8** (0.59 g, 4.4 mmol) according to the general procedure above.

Red oil, yield: 0.4 g (28%).  $R_f$ : 0.67 ( $3\text{CH}_2\text{Cl}_2$ :1EtAc). IR (KBr pellet,  $\text{cm}^{-1}$ ): 3401 (OH), 3065 (Ar-H), 2930, 2856 (C-H), 1661 (C=O), 1592, 1570 (C=C), 707 (C–Cl). UV-vis [ $\text{CHCl}_3$ ,  $\lambda(\log \epsilon)$ ]: 235(3.3), 247(3.2), 253(3.4), 281(3.5), 334(3.2), 470(3.0) nm.  $^1\text{H}$  NMR (499.74 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.22–1.41 (m, 4H,  $\text{CH}_2$ ), 1.52 (m, 2H, S– $\text{CH}_2$ – $\text{CH}_2$ ),

1.74 (m, 2H, CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.32 (t,  $J = 6.83$  Hz, 2H, S-CH<sub>2</sub>), 3.65 (t,  $J = 7.33$  Hz, 2H, CH<sub>2</sub>-OH), 4.42 (s, 1H, OH), 7.80 (t,  $J = 7.32$  Hz, 1H, H<sub>arom</sub>), 7.92 (t,  $J = 7.32$  Hz, 1H, H<sub>arom</sub>), 8.05 (dd,  $J = 7.81$  Hz,  $J = 7.32$  Hz, 1H, H<sub>arom</sub>), 8.10 ppm (dd,  $J = 6.83$  Hz,  $J = 7.39$  Hz, 1H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta = 28.2, 28.4$  (CH<sub>2</sub>), 30.3 (S-CH<sub>2</sub>-CH<sub>2</sub>), 32.5 (CH<sub>2</sub>-CH<sub>2</sub>-OH), 34.8 (S-CH<sub>2</sub>), 62.8 (CH<sub>2</sub>-OH), 126.8, 126.9, 133.4, 134.2 (CH<sub>arom</sub>), 130.8, 131.2 (C<sub>arom</sub>), 147.8 (=C-S), 156.7 (=C-Cl), 178.6, 179.8 ppm (C=O). MS[+ESI]:  $m/z$  325 [M]<sup>+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>S<sub>1</sub>Cl<sub>1</sub> (M, 324.82): C, 59.16; H, 5.27; S, 9.87. Found: C, 59.40; H, 5.38; S, 9.28.

### 2,3-Bis(6-sulfanyl-1-hexanol)-1,4-naphthoquinone (10)

Compound **10** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 6-mercapto-1-hexanol **8** (0.59 g, 4.4 mmol) according to the general procedure above.

Red solid, yield: 1.1 g (59%). Mp 70.1–70.5 °C.  $R_f$ : 0.30 (3CH<sub>2</sub>Cl<sub>2</sub>:1EtAc). IR (KBr pellet, cm<sup>-1</sup>): 3382 (OH), 3071 (Ar-H), 2932, 2858 (C-H), 1660 (C=O), 1591, 1545 (C=C). UV-vis[CHCl<sub>3</sub>,  $\lambda(\log \epsilon)$ ]: 235(3.2), 240(3.3), 276(3.7), 336(3.1), 459(3.0) nm. <sup>1</sup>H NMR (499.74 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 1.21$ – $1.42$  (m, 8H, CH<sub>2</sub>), 1.53 (m, 4H, S-CH<sub>2</sub>-CH<sub>2</sub>), 1.62 (m, 4H, CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.25 (t,  $J = 6.83$  Hz, 4H, S-CH<sub>2</sub>), 3.46 (t,  $J = 7.33$  Hz, 4H, CH<sub>2</sub>-OH), 4.32 (s, 2H, OH), 7.80 (dd,  $J = 7.32$  Hz,  $J = 6.83$  Hz, 2H, H<sub>arom</sub>), 7.95 ppm (dd,  $J = 7.80$  Hz,  $J = 6.84$  Hz, 2H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta = 24.2, 24.3$  (CH<sub>2</sub>), 27.4 (S-CH<sub>2</sub>-CH<sub>2</sub>), 29.3 (CH<sub>2</sub>-CH<sub>2</sub>-OH), 33.8 (S-CH<sub>2</sub>), 61.7 (CH<sub>2</sub>-OH), 125.8, 132.4 (CH<sub>arom</sub>), 132.0 (C<sub>arom</sub>), 146.8 (=C-S), 178.0 ppm (C=O). MS[-ESI]:  $m/z$  404 [M-OH]<sup>+</sup>. Anal. Calcd for C<sub>22</sub>H<sub>30</sub>O<sub>4</sub>S<sub>2</sub> (M, 422.61): C, 62.52; H, 7.15; S, 15.17. Found: C, 62.55; H, 7.09; S, 15.32.

### 2,3,4,5,6,7-Hexahydronaphtho[2,3-e][1,8]dithionine-9,14-dione (12)

Compound **12** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 1,6-hexanedithiol **11** (0.66 g, 4.4 mmol) according to the general procedure above.

Red solid, yield: 0.4 g (30%). Mp 138–139 °C.  $R_f$ : 0.75 (CHCl<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3065 (Ar-H), 2922, 2852 (C-H), 1667, 1653 (C=O), 1590 (C=C). UV-vis[CHCl<sub>3</sub>,  $\lambda(\log \epsilon)$ ]: 229(3.1), 239(3.2), 268(3.5), 343(3.1), 469(3.4) nm. <sup>1</sup>H NMR (499.74 MHz, CDCl<sub>3</sub>):  $\delta = 1.31$ – $1.52$  (m, 4H, CH<sub>2</sub>), 1.73 (m, 4H, CH<sub>2</sub>), 3.25 (t,  $J = 6.34$  Hz, 4H, S-CH<sub>2</sub>), 7.51 (dd,  $J = 7.32$  Hz,  $J = 6.84$  Hz, 2H, H<sub>arom</sub>), 8.05 ppm (dd,  $J = 5.86$  Hz,  $J = 8.78$  Hz, 2H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta = 23.7$  (CH<sub>2</sub>), 24.0 (S-CH<sub>2</sub>-CH<sub>2</sub>), 33.0 (S-CH<sub>2</sub>), 126.2, 132.7 (CH<sub>arom</sub>), 131.6 (C<sub>arom</sub>), 149.1 (=C-S), 179.0 ppm (C=O). MS [+ESI]:  $m/z$  305 [M]<sup>+</sup>, 271 [M-S]<sup>+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>S<sub>2</sub> (M, 304.43): C, 63.12; H, 5.29; S, 21.06. Found: C, 62.98; H, 5.20; S, 21.43.

### 7,8,9,10,11,12-Hexahydrodinaphtho[2,2'-e]-diethoxy[3,3']-[1,8]dithionine-5,14,19,20-tetrone (13c)

Compound **13c** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 1,6-hexanedithiol **11** (0.66 g, 4.4 mmol) according to the general procedure above.

Dark red oil, yield: 0.4 g (16%).  $R_f$ : 0.30 (CHCl<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3071 (Ar-H), 2918, 2849 (C-H), 1658 (C=O), 1589 (C=C). UV-vis[CHCl<sub>3</sub>,  $\lambda(\log \epsilon)$ ]: 224(3.2), 232(3.3), 239(3.4), 266(3.5), 444(3.5) nm. <sup>1</sup>H NMR (499.74 MHz, CDCl<sub>3</sub>):  $\delta = 1.12$  (t,  $J = 7.32$  Hz, 3H, CH<sub>3</sub>), 1.21– $1.54$  (m, 4H, CH<sub>2</sub>), 1.62– $1.75$  (m, 4H, S-CH<sub>2</sub>-CH<sub>2</sub>), 3.24 (t,  $J =$



7.32 Hz, 4H, S-CH<sub>2</sub>), 3.42 (t,  $J$  = 7.32 Hz, O-CH<sub>2</sub>), 7.60 (t,  $J$  = 5.86 Hz, 2H, H<sub>arom</sub>), 7.65 (t,  $J$  = 6.83 Hz, 2H, H<sub>arom</sub>), 7.96 (dd,  $J$  = 8.29 Hz,  $J$  = 8.79 Hz, 2H, H<sub>arom</sub>), 8.05 ppm (dd,  $J$  = 7.80 Hz,  $J$  = 6.84 Hz, 2H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.0 (CH<sub>3</sub>), 27.1 (CH<sub>2</sub>), 28.6 (S-CH<sub>2</sub>-CH<sub>2</sub>), 33.7 (S-CH<sub>2</sub>), 68.3 (O-CH<sub>2</sub>), 126.3, 132.4 (CH<sub>arom</sub>), 131.9 (C<sub>arom</sub>), 148.1 (=C-S), 174.0 (=C-O), 177.9, 178.8 ppm (C=O). MS [+ESI]:  $m/z$  550 [M]<sup>+</sup>. Anal. Calcd for C<sub>30</sub>H<sub>30</sub>O<sub>6</sub>S<sub>2</sub> (M, 550.69): C, 65.43; H, 5.49; S, 11.64. Found: C, 65.09; H, 5.19; S, 11.24.

### 7,8,9,10,11,12-Hexahydrodinaphtho[2,2':e]-dichloro[3,3']**[1,8]** dithionine-5,14,19,20-tetrone (**14d**)

Compound **14d** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 1,6-hexanedithiol **11** (0.66 g, 4.4 mmol) according to the general procedure above.

Red oil, yield: 0.3 g (13%).  $R_f$ : 0.60 (CHCl<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3076 (Ar-H), 2924, 2853 (C-H), 1671, 1658 (C=O), 1589 (C=C), 705 (C-Cl). UV-vis[CHCl<sub>3</sub>,  $\lambda$ (log $\epsilon$ )]: 229(3.1), 239(3.2), 267(3.5), 315(3.1), 446(3.3) nm. <sup>1</sup>H NMR (499.74 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.21–1.55 (m, 4H, CH<sub>2</sub>), 1.64–1.75 (m, 4H, S-CH<sub>2</sub>-CH<sub>2</sub>), 3.31 (t,  $J$  = 7.81 Hz, 4H, S-CH<sub>2</sub>), 7.65 (t,  $J$  = 5.37 Hz, 2H, H<sub>arom</sub>), 7.70 (t,  $J$  = 6.83 Hz, 2H, H<sub>arom</sub>), 8.00 (dd,  $J$  = 8.78 Hz,  $J$  = 8.30 Hz, 2H, H<sub>arom</sub>), 8.06 ppm (dd,  $J$  = 7.81 Hz,  $J$  = 7.32 Hz, 2H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta$  = 27.0 (CH<sub>2</sub>), 29.1 (S-CH<sub>2</sub>-CH<sub>2</sub>), 33.0 (S-CH<sub>2</sub>), 126.2, 126.3, 132.8, 133.1 (CH<sub>arom</sub>), 130.2, 131.6 (C<sub>arom</sub>), 139.0 (=C-S), 148.1 (=C-Cl), 174.0, 178.9 ppm (C=O). MS [+ESI]:  $m/z$  531 [M]<sup>+</sup>, 493 [M-Cl]<sup>+</sup>. Anal. Calcd for C<sub>26</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>Cl<sub>2</sub> (M, 531.48): C, 58.75; H, 3.79; S, 12.06. Found: C, 58.59; H, 3.49; S, 12.24.

### 7,8,9,10,11,12,21,22,23,24,25,26-Dodecahydrodinaphtho[2,3-e:2',3'-n] [1,8,11,18]tetrathiacyclotetracosine-5,14,19,28-tetrone (**15**)

Compound **15** was synthesized from the reaction of **1** (1.0 g, 4.4 mmol) with 1,6-hexanedithiol **11** (0.66 g, 4.4 mmol) according to the general procedure above.

Red solid, yield: 0.7 g (26%). Mp 176–177 °C.  $R_f$ : 0.50 (CHCl<sub>3</sub>). IR (KBr pellet, cm<sup>-1</sup>): 3065 (Ar-H), 2922, 2851 (C-H), 1660 (C=O), 1590 (C=C). UV-vis[CHCl<sub>3</sub>,  $\lambda$ (log $\epsilon$ )]: 225(3.0), 232(3.1), 241(3.5), 456(3.6) nm. <sup>1</sup>H NMR (499.74 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.21–1.40 (m, 8H, CH<sub>2</sub>), 1.49–1.65 (m, 8H, S-CH<sub>2</sub>-CH<sub>2</sub>), 3.22 (t,  $J$  = 7.32 Hz, 8H, S-CH<sub>2</sub>), 7.63 (dd,  $J$  = 5.85 Hz,  $J$  = 5.85 Hz, 4H, H<sub>arom</sub>), 7.97 ppm (dd,  $J$  = 5.37 Hz,  $J$  = 5.86 Hz, 4H, H<sub>arom</sub>). <sup>13</sup>C NMR (125.66 MHz, CDCl<sub>3</sub>):  $\delta$  = 27.0 (CH<sub>2</sub>), 29.6 (S-CH<sub>2</sub>-CH<sub>2</sub>), 34.3 (S-CH<sub>2</sub>), 132.0 (C<sub>arom</sub>), 125.9, 132.5 (CH<sub>arom</sub>), 147.8 (=C-S), 177.8 ppm (C=O). MS [+ESI]:  $m/z$  609 [M]<sup>+</sup>. Anal. Calcd for C<sub>32</sub>H<sub>32</sub>O<sub>4</sub>S<sub>4</sub> (M, 608.87): C, 63.12; H, 5.29; S, 21.06. Found: C, 63.40; H, 5.48; S, 21.28.

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