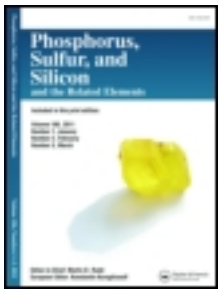

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS AND CHARACTERIZATION OF NITROGEN AND SULFUR CONTAINING 1,4-NAPHTHOQUINONES

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SYNTHESIS AND CHARACTERIZATION OF NITROGEN AND SULFUR CONTAINING 1,4-NAPHTHOQUINONES

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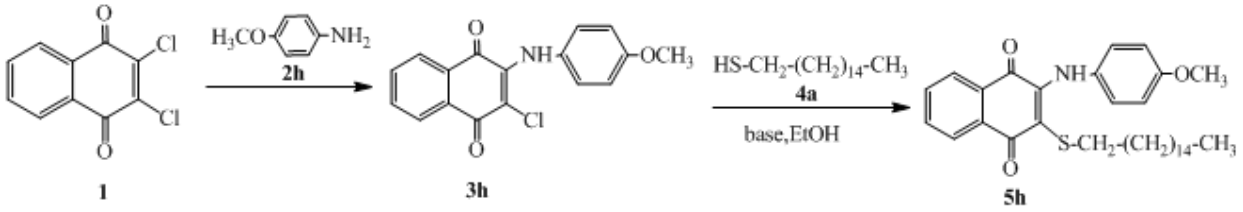
Abstract New *N*,*S*-disubstituted naphthoquinones were synthesized by reactions of *S*- and *N*-nucleophiles with 2,3-dichloro-1,4-naphthoquinone. 2-(Hexadecylthio)-3-(phenylamino)-naphthalene-1,4-dione **5a** was synthesized by reaction of 2-chloro-3-(phenylamino)-naphthalene-1,4-dione **3a** with hexadecanethiol **4a**. The structures of the new synthesized naphthoquinone derivatives were determined by micro analyses and spectroscopic methods (FT-IR, ^{1}H NMR, ^{13}C NMR, MS and UV/Vis.). Photo- and electrochemical properties of selected compounds were investigated by using fluorescence spectroscopy and the cyclovoltammetry method.



Key Words *N*,*S*-Disubstituted naphthoquinones; spectroscopic properties; fluorescence spectroscopy; cyclovoltammetry

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INTRODUCTION

It has been reported that some *N*-, *S*- and *N*,*S*-subsituted[1-4] 1,4-naphthoquinones were synthesized from 2,3-dichloro-1,4-naphthoquinone. 1,4-Naphthoquinone derivatives in general, and those possessing an amino group in particular, have stimulated enormous interest due to their biological activities, including antiproliferative, antiallergic, antifungal, antibacterial, antitumoral properties e.t.c.[3,5-9] However, the value of quinones is not restricted to biological activity. Quinoidal compounds are also used as dyes, photo-conductors and magnetic materials.[10-13]

Primary and secondary aliphatic amines, cyclic amines and anilines substituted with electron-donating groups, are quite reactive and afford high yields of the corresponding aminoquinones. Treatment of 2,3-dichloro-1,4-naphthoquinone with amines affords mono amino derivatives. Both halogen atoms can be replaced by using nitrogen containing heterocycles.[14]

Naphthoquinone pigments typically exhibit variable colors, and are widely used in the cosmetic industry for the production of cosmetic dyes. Naphthoquinone dyes possess the advantages of having strong, stable coloring properties.[15,16] There is an US patent about manufacturing of some organomercapto-substituted quinones which can be used as oil-soluble fungicidal sprays for plants.[17]

Fluorescence is an important photochemical property of quinones for the use as organic materials.[2,18-20] There are, however, few reports on fluorescence studies of *N*-, and *S*-substituted-1,4-naphthoquinones. The fluorescence excitation and emission maxima of *N*- and *N*,*S*-substituted-1,4-naphthoquinones in trichloromethane, methanol or aqueous solutions at room temperature have been reported.[21-25]

A plethora of quinones is known, the electrochemistry of which has been widely studied.[18,26] There are some reports on electrochemical studies of *N*-, *S*-, and *O*-substituted naphthoquinones.[4,21,23] As the bioreduction of quinones is influenced by their redox properties, the understanding of how structural features of the quinones are related to these properties is an important step to comprehend their mechanism of action and predict modifications to improve their biological activity.[27]

We have earlier reported the synthesis of new sulfur containing 1,4-naphthoquinones.[23-45,28-29] The goal of the presented work is to continue the study on this subject by synthesizing nitrogen and sulfur containing hetero-1,4-naphthoquinones and characterization of their structures by using microanalysis, FT-IR, ^{1}H NMR, ^{13}C NMR, mass, and UV/Vis spectroscopy. Photo- and electrochemical properties of selected compounds were investigated by using fluorescence spectroscopy and the cyclovoltammetry method.

RESULTS AND DISCUSSION

Syntheses

In the course of our work, we prepared the amino and thio derivatives of 1,4-naphthoquinone. The precursors, 2-alkylamino-3-chloro-naphthoquinones **3a-i** and 2-chloro-3-

alkylsulfanyl-1,4-naphthoquinone **7a-b** required for the synthesis of **5a-i**, **6a-i** and **11a-f**, have been synthesized according to Scheme 1. The reaction of 2,3-dichloro-1,4-naphthoquinone 1 with alkanethiols **4a-b** afforded mixtures of 2-chloro-3-alkylsulfanyl-1,4-naphthoquinones (53–55%) **7a**,**b**, 2,3-bis-alkylsulfanyl-1,4-naphthoquinones (21–26%) **8a**,**b** and 2-ethoxy-3-alkylsulfanyl-1,4-naphthoquinones (10–12%) **9a**,**b**. This reaction involves nucleophilic displacement of chloride ions in 2,3-dichloro-1,4-naphthoquinone **1** with sulfur nucleophile (1:1) resulting in the formation of **7a**,**b**, **8a**,**b**. Nucleophilic displacement of chloride in 2,3-dichloro-1,4-naphthoquinone **1** with ethoxide from the solvent, instead of the sulfur nucleophile resulted exclusively in the formation of 2-ethoxy-3-alkylsulfanyl-1,4-naphthoquinones **9a**,**b** as shown in Scheme 1. In the meantime, 2-chloro-3-(hexadecylthio)naphthalene-1,4-dione **7a** was newly synthesized as precursor in this study. The reactions of 2,3-dichloro-1,4-naphthoquinone **1** with aromatic amines **2a-i** resulted in the formation of 2-arylamino-3-halo-1,4-naphthoquinones **3a-i** as main products.

<Scheme 1>

Firstly, we studied the reactions of 2,3-dichloro-1,4-naphthoquinone **1** with different aryl amines **2a-i** and alkanethiols **4a**,**b** in the presence or absence of a base and synthesized with previously reported 2-arylamino-3-halo-1,4-naphthoquinones **3a-i** and 2-chloro-3-alkylsulfanyl-1,4-naphthoquinones **7a**,**b** utilized precursors.[28-32]. Aryl amines with enhanced nucleophilicity replaced only one chlorine substituent upon reaction with 2,3-dichloro-1,4-naphthoquinone **1**, due to electronic enrichment of the quinone system. To achieve the substitution of the second

chlorine atom, an electron-withdrawing effect must be imposed on the quinone ring[33] or a catalyst must be used.[34]

The second synthetic step towards the desired novel products **5a-i**, **6a-i** and **11a-f** was achieved with good yields by reaction of alkanethiols **4a,b** with 2-arylamino-3-halo-1,4-naphthoquinones **3a-i** and primary alkyl amines **10a-c** with 2-chloro-3-alkylsulfanyl-1,4-naphthoquinones **7a**,**b**. The reaction conditions for the synthesis of 2,3-disubstituted 1,4-naphthoquinones are reported in Table 1. Both aromatic amines and aliphatic thiols smoothly substituted one chlorine atom of **1**, producing the mono-substituted derivatives **3** and **7**, but aromatic amines react with **1** to yield **3a-i** with higher yields (70–95%) compared to aliphatic thiols which result in the formation **7a**,**b** (53–55%).

<Table 1>

FT-IR and NMR Spectra

All products were identified by FT-IR, ^{1}H NMR, ^{13}C NMR, MS, and UV/Vis spectroscopic data. The IR spectra of **5a-i, 6a-i** and **11a-f** exhibit typical strong quinone carbonyl absorption between 1628 and 1669 cm^{-1}. The NH stretching vibration appeared between 3288 and 3322 cm^{-1}. The ^{1}H NMR spectra of **5a-i** and **6a-i** appeared as double-doublets and triplet of triplets between at δ_H 7.96–8.10 (2H) and 7.52–7.68 (2H) which could be distinguished. These were attributed to naphthalene protons, as expected from such non-symmetric systems and the NH proton was observed as triplet at 6.64–6.56 ppm for **5c**, **6c** and the other derivatives of **5** and **6** as singlet at between 7.52 and 7.91 ppm. Two different carbonyl signals appear at around 180 ppm in the ^{13}C NMR spectra of **11a-f** as expected and the structures of **5g-i** were also confirmed by

^{13}C NMR APT spectra in the present study. The protons of SCH_2 have close values of the chemical shift as triplet at around 2.50 ppm. In the ^{1}H NMR spectra of **11c** and **11f**, the vinylic protons are observed as multiplets at 5.26–5.28.

Absorption and Fluorescence Spectroscopy

The absorption spectra of compounds **5a-i**, **6a-i** and **11a-f** were measured in the nonpolar solvent petroleum ether and in the more polar solvent trichloromethane. The molar absorption coefficients were determined in the solvents and the data are presented in Table 2.

<Table 2>

In the absorption spectra of the 2,3-bis-donor-substituted 1,4-naphthoquinones **5a-i** and **6a-i**, the π-π* character of the longest wavelength band was indicated by its intensity and its displacement to longer wavelengths in the polar solvent trichloromethane. In view of the sensitivity of this band towards the electron-donating strength of the donor atom, it is reasonable to assume that the transition involves electron-density transfer from the donor group to the quinone system, as in the similarly substituted benzoquinones and anthraquinones.[35]

The electronic absorption spectra of **5a-i** and **6a-i** showed the expected benzene and naphthoquinone bands in the UV region at around 232–243 nm (λ_1) and at 281–289 nm (λ_2). In addition, another lower energy band appeared in the visible region centered between 485–539 nm (λ_3) in trichloromethane. **5h**, **6h** and **5i**, **6i** having an electron-donor substituent (OCH_3) were observed at the longest wavelength. The absorption spectra of **5a**, **5c**, **5h**, **5i** and **11a-c** in trichloromethane solution are shown in Fig.1 and Fig.2. Furthermore, the synthesized dyes of aliphatic derivatives **11a-f** show the characteristic long wavelength thio-substituted quinone π-π*

broad transition at 478–492 nm in trichloromethane. As illustrated in the Table 2, in the absorption spectra of the compounds **5a-i**, **6a-i** and **11a-f** considerable differences depending on the substituent in the naphtoquinone fragment were observed. The anilino-derivatives (**5a-i**, **6a-i)** absorb at longer wavelengths than the aliphatic derivatives (**11a-f)**.

<Figure 1>

<Figure 2>

In general, the light fastness properties of phenylaminonaphthalene derivatives always showed better photochemical stability than their alkylamino counterparts. Derivatives of **5a-i** and **6a-i** approached commercial acceptability in this respect (on polyester substrates).[11,35]

It is known that 2-donor- and 2,3-bis-donor-substituted 1,4-naphthoquinones evidently can provide almost the full spectral range of colors[35] shown in Table 1. Both mass spectra and elemental analyses confirm the molecular formula of the products **5a-i**, **6a-i** and **11a-f**.

The fluorescence excitation and emission maxima of compounds **3a**,**b**, **3g**, **5a,b**, **5e-g**, **6b-d**, **6h-i**, and **11c-e** in trichloromethane solution are summarized in Table 3. The spectrum was composed of two excitation bands and two emission bands comparable to those of the similar compounds.[21-25]

<Table 3>

Electrochemical Study

Cyclovoltammetry measurements of **5g**, **6b**, **6h**, **11c** and **11d** were performed in aprotic medium (DMF) to explore the substituent effects on their redox potentials. The voltammetric data of these compounds i. e. cathodic peak potentials (E_{pc}) and anodic peak potentials (E_{pa})

versus a glassy carbon electrode (GCE), half-wave potentials ($E_{1/2}$), the difference between the first oxidation and reduction processes (E_p) and cathodic *vs*. anodic peak current ratio (i_{pc}/i_{pa}) are shown in Table 4. Experiments using a glassy carbon electrode were performed in order to investigate the electro-oxidizable groups and to complete the information in the presence of proton sources. Additional oxidation waves were discernible.

<Table 4>

2,3-Dichloro-1,4-naphthoquinone **1** was used as standard. Compound **1** showed behaviors typical of quinones in aprotic medium.[23,36] Two reversible one-electron waves are observed for **1**. The first reversible reduction wave is due to the formation of a semiquinone anion radical Q^- [$Q + e^- \rightleftharpoons Q^-$ (reversible)]. In the case of more negative reduction processes, the reduction of the semiquinone anion radical Q^- to the dianion Q^{2-} [$Q^- + e^- \rightleftharpoons Q^{2-}$ (quasi-reversible)] possibly was partially controlled by the electronic transference and by diffusion.[37] The reversibility of this redox couple ($I_{pc} \approx I_{pa}$) suggests that the dianion was also stable in the time scale of the voltammetric experiments. The ratio i_{pc}/i_{pa} was near 1 for compounds **6h** and **11d**. Two reduction waves were observed for **5g**, **6h**, **11c** and **11d** at a scan rate of 0.1 Vs^{-1} (see Table 4). The redox behavior of compound **6b** was different. Three reduction waves were observed for **6b**. The cyclovoltamogram of compound **6b** in DMF is given in Fig. 3.

<Figure 3>

EXPERIMENTAL

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). The precursors **3a-i**, **7b** and by-products **8a**,**b** and **9a**,**b** were synthesized from 1,4-naphthoquinone **1** and aromatic amines or alkyl thiols according to the procedures reported in the literatures and confirmed by melting points, elemental analyses, FT-IR spectroscopy by comparison with published data.[28-32]

Methods

Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 elemental analyzer. IR (cm^{-1}) spectra were recorded in KBr pellets or Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometer. NMR spectra ($CDCl_3$) were recorded on a Varian UNITY INOVA instrument operating at 499.74 MHz for ^1H and at 125.66 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 and petroleum ether solution were recorded on Perkin Elmer Lambda 35 UV/vis Spectro. 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 $CHCl_3$ at room temperature. Excitation and emission slit widths were set at 5 nm.

Cyclovoltammetry Measurements

Cyclovoltammetry measurements were performed at room temperature in an airtight three-electrode cell by using a glassy carbon electrode (GCE) with a 0.071 cm^2 surface area as the

working electrode, a platinum wire served as the counter electrode and a Ag/AgCl (in a saturated KCl solution) reference electrode. The cell was driven with a computer controlled system of a Gamry Reference 600 Model potentiostat/galvanostat. The solutions were deoxygenated by bubbling nitrogen through them for approximately 5 min. The surface of the working electrode was polished with de-agglomerated alumina (a particle size of 0.05 micron) before each run. The electrochemical reaction vessel was charged with 10 mL of a DMF solution of **5g**, **6b**, **6h**, **11c** and **11d** (1×10^{-4} M) and tetrabutylammonium perchlorate (0.1 M) as the electrolyte. Measurements were made over a potential range between 0.5V and −2.0V for **6h**, **11d**, 0.0V and −1.5V for **5g**, **11c**, 1.0 and −2.0V for **6b** with a scan rate of 0.1V s^{-1}. Voltammetric parameters for all compounds are summarized in Table 4.

General Procedure for the Preparation of Hetero-1,4-naphthoquinones

Equimolar amounts of 2,3-dichloro-1,4-naphthoquinone **1** or monosubstituted naphthoquinone derivatives **3**, **7** and *N*- or *S*-nucleophilic compounds **2a-i**, **4a-b**, **10a-c** in abs. EtOH (50 mL) were stirred at different temperatures using base, where required (Table 1). The color of the solution quickly changed and the extent of the reaction was monitored by TLC. $CHCl_3$ (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 resulting solution was concentrated in vacuo and the residue was subjected to column chromatography on silica gel using suitable solvents (Table 1).

Scheme 1 represents the reaction of 2,3-dichloro-1,4-naphthoquinone **1** with aromatic amines, aliphatic amines and aliphatic thiols, yielding the desired novel 2-arylamino-3-

alkylsulfanyl-1,4-naphthoquinones **5** and **6,** and 2-alkylamino-3-alkylsulfanyl-1,4-naphthoquinones derivatives of **11**, respectively. The composition and properties of the corresponding products are summarized in Table 1.

Experimental and spectroscopic data of compounds **5a**–**5i** and **6a**–**6i** are compiled in the "SUPPLENTAL MAERIALS" file

2-(Hexadecylthio)-3-(phenylamino)naphthalene-1,4-dione (5a): Compound **5a** was synthesized from 0.20g (0.704 mmol) 2-chloro-3-(phenylamino)naphthalene-1,4-dione **3a** and 0.182g (0.704 mmol) hexadecanethiol **4a** using triethylamine as base according to the general procedure. IR: 3310 (NH), 3052 ($CH_{arom.}$), 2914, 2849 ($CH_{aliph.}$), 1665, 1634 (C=O), 1591, 1555 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.07–1.30, 1.51–1.59 (m, 28H, C***H***$_2$), 2.49–2.52 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.94–6.95 (d, 2H, J = 7.32 Hz, C***H***$_{arom}$), 7.05–7.08 (t, 1H, J = 7.32 Hz, C***H***$_{arom}$), 7.23–7.26 (t, 2H, J = 7.31 Hz, C***H***$_{arom}$), 7.59 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.66 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.73 (bs, 1H, N***H***), 7.99 (d, 1H, J = 7.56 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.1 (***C***H$_3$), 21.6, 28.0, 28.6, 29.2, 31.0 (***C***H$_2$), 33.1 (S***C***H$_2$), 117.4, 121.4, 127.4 (***C***H$_{arom}$), 123.5 (S***C***$_{napht}$), 129.6 (NH***C***$_{napht}$), 125.6, 125.8, 131.6, 132.5 (***C***H$_{napht}$), 133.4, 137.5 (***C***$_{napht}$), 144.0 (NH***C***), 179.4, 180.0 (***C***=O). MS (+ESI): *m/z* = 506 $[M]^+$, $C_{32}H_{43}NO_2S$ (505.75). Calcd.: C 75.99; H 8.57; N 2.77; S 6.34. Found: C 75.02; H 8.61; N 2.59; S 6.12.

2-(Octadecylthio)-3-(phenylamino)naphthalene-1,4-dione (6a): Compound **6a** was synthesized from 0.15g (0.528 mmol) 2-chloro-3-(phenylamino)naphthalene-1,4-dione **3a** and 0.15g (0.528 mmol) octadecanethiol **4b** using triethylamine as base according to the general

procedure. IR: 3309 (NH), 3052 ($CH_{arom.}$), 2913, 2849 ($CH_{aliph.}$), 1665, 1634 (C=O), 1591, 1554 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.08–1.36, 1.50–1.61 (m, 32H, C$\boldsymbol{H}_2$), 2.49–2.52 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 6.94–6.95 (d, 2H, J = 7.81 Hz, C$\boldsymbol{H}_{arom}$), 7.06–7.09 (t, 1H, J = 7.32 Hz, C$\boldsymbol{H}_{arom}$), 7.23–7.27 (t, 2H, J = 6.83 Hz, C$\boldsymbol{H}_{arom}$), 7.56 (t, 1H, J = 7.64 Hz, C$\boldsymbol{H}_{napht}$), 7.66 (t, 1H, J = 7.64 Hz, C$\boldsymbol{H}_{napht}$), 7.73 (bs, 1H, N$\boldsymbol{H}$), 7.99 (d, 1H, J = 7.33 Hz, C$\boldsymbol{H}_{napht}$), 8.08 (d, 1H, J = 7.33 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 14.2 ($\boldsymbol{C}H_3$), 21.6, 27.6, 28.6, 29.4, 31.0 ($\boldsymbol{C}H_2$), 33.2 (S$\boldsymbol{C}H_2$), 117.4, 121.4, 127.4 ($\boldsymbol{C}H_{arom}$), 123.5 (S$\boldsymbol{C}_{napht}$), 129.7 (NH$\boldsymbol{C}_{napht}$), 125.6, 125.8, 131.7, 132.5 ($\boldsymbol{C}H_{napht}$), 133.4, 137.5 ($\boldsymbol{C}_{napht}$), 144.0 (NH$\boldsymbol{C}$), 179.4, 180.0 ($\boldsymbol{C}$=O). MS (+ESI): *m/z* = 534$[M]^+$, $C_{34}H_{47}NO_2S$ (533.81). Calcd.: C 76.50; H 8.87; N 2.62; S 6.01. Found: C 76.45; H 9.73; N 2.55; S 6.33.

2-Chloro-3-(hexadecylthio)naphthalene-1,4-dione (7a): Compound **7a** was synthesized from 1.00g (4.404 mmol) 2,3-dichloro-1,4-naphthoquinone **1** and 1.138g (4.404 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 2915, 2848 ($CH_{aliph.}$), 1671 (C=O), 1590, 1523 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.13–1.42, 1.49–1.62 (m, 28H, C$\boldsymbol{H}_2$), 3.30–3.33 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 7.63–7.68 (m, 2H, C$\boldsymbol{H}_{napht}$), 7.99–8.07 (m, 2H, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 13.1 ($\boldsymbol{C}H_3$), 21.6, 27.6, 28.5, 29.4, 30.9 ($\boldsymbol{C}H_2$), 33.3 (S$\boldsymbol{C}H_2$), 138.7 (S$\boldsymbol{C}_{napht}$), 148.4 (Cl$\boldsymbol{C}_{napht}$), 126.2, 126.3, 130.3, 131.6, ($\boldsymbol{C}H_{napht}$), 132.7, 133.1 ($\boldsymbol{C}_{napht}$), 174.0, 178.8 ($\boldsymbol{C}$=O). MS (+ESI): *m/z* = 450 $[M+H]^+$, $C_{26}H_{37}ClO_2S$ (449.09). Cald.: C, 69.54; H, 8.30; S, 7.14. Found: C, 69.78; H, 8.45; S, 6.85.

2-(Hexadecylthio)-3-(hexylamino)naphthalene-1,4-dione (11a): Compound **11a** was synthesized from 0.10g (0.222 mmol) 2-chloro-3-(hexadecylthio)naphthalene-1,4-dione **7a**

and 0.022g (0.222 mmol) hexylamine **10a** using Na_2CO_3 as base according to the general procedure. IR: 3292 (NH), 3050 ($CH_{arom.}$), 2918, 2849 ($CH_{aliph.}$), 1670, 1625 (C=O), 1590, 1551 (C=C). ^{1}H NMR: 0.79–0.85 (t, 6H, *J* = 6.83 Hz, C***H***$_3$), 1.12–1.37, 1.57–1.63 (m, 28H, C***H***$_2$), 1.12–1.37, 1.46–1.53 (m, 8H, C***H***$_{2(hexyl)}$), 2.71–2.74 (t, 2H, *J*= 7.32 Hz, SC***H***$_2$), 3.81–3.84 (t, 2H, *J* = 7.32 Hz, NHC***H***$_2$), 7.53 (bs, 1H, N***H***), 7.52 (t, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 7.63 (t, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 7.93 (d, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.32 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.2, 14.3 (***C***H$_3$), 22.8, 22.9, 26.7, 29.1, 29.5, 29.6, 29.8, 29.9, 30.1, 30.9, 31.7, 32.1, 33.9 (***C***H$_2$), 46.4 (S***C***H$_2$), 128.4 (S***C***$_{napht}$), 134.1 (NH***C***$_{napht}$), 126.6, 126.8, 132.1, 134.8 (***C***H$_{napht}$), 130.9, 136.6 (***C***$_{napht}$), 181.7, 181.8 (***C***=O). MS (+ESI): *m/z* = 514 $[M]^+$, $C_{32}H_{51}NO_2S$ (513.83). Calcd.: C, 74.80; H, 10.00; N, 2.73; S, 6.24. Found: C, 75.46; H, 10.54; N, 2.89; S, 6.02.

2-[(2-Morpholinoethyl)amino]-3-(octadecylthio)naphthalene-1,4-dione (11b): Compound **11b** was synthesized from 0.10g (0.209 mmol) 2-chloro-3-(octadecylthio)naphthalene-1,4-dione **7b** and 0.027 mL (0.209 mmol) 4-(2-aminoethyl)-morpholine **10b** using Na_2CO_3 as base according to the general procedure. IR: 3201 (NH), 3049 ($CH_{arom.}$), 2917, 2848 ($CH_{aliph.}$), 1678, 1624 (C=O), 1588, 1538 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.12–1.31, 1.44–1.53 (m, 32H, C***H***$_2$), 2,44–2.45 (t, 4H, *J* = 4.39 Hz, C***H***$_{2morpholine}$), 2.57–2.59 (t, 2H, *J* = 5.86 Hz, C***H***$_2$N), 2.72–2.75 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.66–3.68 (t, 4H, *J* = 4.88 Hz, C***H***$_{2morpholine}$), 3.90–3.93 (q, 2H, *J* = 5.37 Hz, NHC***H***$_2$), 7.20–7.22 (t, 1H, *J* = 5.86 Hz, N***H***), 7.50 (t, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 7.64 (t, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 7.93 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H$_3$), 21.6, 27.8, 28.4, 29.0, 31.0 (***C***H$_2$) 33.9 (S***C***H$_2$), 41.0, 56.1 (***C***H$_{2morph.aliph.}$), 52.1, 66.1 (***C***H$_{2morph.cyclo}$), 129.8 (S***C***$_{napht}$), 133.4 (NH***C***$_{napht}$), 125.3, 125.5 (***C***H$_{napht}$), 130.9, 132.8 (***C***$_{napht}$), 180.6, 180.8

(***C***=O). MS (+ESI): *m/z* = 571 $[M]^+$, $C_{34}H_{54}N_2O_3S$ (570.87). Cald.: C, 71.53; H, 9.53; N, 4.91; S, 5.62 Found: C, 71.58; H, 9.89; N, 4.97; S, 5.32.

(*E*)-2-(Hexadecylthio)-3-(octadec-9-en-1-ylamino)naphthalene-1,4-dione (11c): Compound **11c** was synthesized from 0.10g (0.222 mmol) 2-chloro-3-(hexadecylthio)naphthalene-1,4-dione **7a** with 0.059g (0.222 mmol) octadec-9-enylamine **10c** using Na_2CO_3 as base according to the general procedure. IR: 3290 (NH), 3050 ($CH_{arom.}$), 2920, 2849 ($CH_{aliph.}$), 1671, 1645 (C=O), 1591, 1552 (C=C). ^{1}H NMR: 0.79–0.82 (t, 6H, *J* = 6.83 Hz, C***H***$_3$), 1.12–1.35, 1.47–1.53, 1.90–1.92 (m, 28H, C***H***$_2$), 1.12–1.35, 1.57–1.62 (m, 24H, C***H***$_{2(oleyl)}$), 1.90–1.96 (m, 4H, *J* = 7.32 Hz, C***H***$_2$–CH=CH–C***H***$_2$), 2.71–2.74 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.80–3.83 (t, 2H, *J* = 7.32 Hz, NHC***H***$_2$), 5.26–5.27 (m, 2H, C***H***=C***H***), 5.31 (bs, 1H, N***H***), 7.52 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.63 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.94 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.2, 14.3 (***C***H$_3$), 22.8, 27.0, 27.4, 28.8, 29.1, 30.1 32.1, 32.8, 35.3, 39.5 (***C***H$_2$), 46.4 (S***C***H$_2$),126.4 (S***C***$_{napht}$), 134.2 (NH***C***$_{napht}$), 126.6, 126.8, 130.0, 130.2 (***C***H$_{napht}$), 130.2, 132.2 (***C***$_{napht}$), 134.8 (C***H***$_{oleyl}$), 181.6, 181.7 (***C***=O). MS (+ESI): *m/z* = 681 $[M+H]^+$, $C_{44}H_{73}NO_2S$ (680.14). Calcd.: C, 77.70; H, 10.82; N, 2.06; S, 4.71. Found: C, 77.18; H, 11.42; N, 2.11; S, 4.66.

2-(Hexylamino)-3-(octadecylthio)naphthalene-1,4-dione (11d): Compound **11d** was synthesized from 0.10g (0.209 mmol) 2-chloro-3-(octadecylthio)naphthalene-1,4-dione **7b** and 0.021g (0.209 mmol) hexylamine **10a** using Na_2CO_3 as base according to the general procedure. IR: 3293 (NH), 3051($CH_{arom.}$), 2917, 2848 ($CH_{aliph.}$), 1670, 1625 (C=O), 1590, 1551 (C=C). ^{1}H NMR: 0.80–0.85 (t, 6H, *J* = 6.83 Hz, C***H***$_3$), 1.15–1.37, 1.57–1.63 (m, 32H, C***H***$_2$), 1.15–1.37, 1.46–1.53 (m, 8H, C***H***$_{2(hexyl)}$), 2.71–2.74 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.81–3.84 (t, 2H,

J = 7.32 Hz, NHC***H***$_2$), 7.53 (bs, 1H, N***H***), 7.52 (t, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 7.63 (t, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 7.93 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.2, 14,3 (***C***H$_3$), 22.8, 22.9, 26.7, 29.1, 29.5, 29.6, 29.8, 29.9, 30.1, 30.9, 31.7, 32.1, 35.3 (***C***H$_2$),46.4 (S***C***H$_2$), 128.2 (S***C***$_{napht}$), 134.2 (NH***C***$_{napht}$), 126.6, 126.8, 132.1, 134.8 (***C***H$_{napht}$), 130.9, 136.6 (***C***$_{napht}$), 181.7, 181.8 (***C***=O). MS (+ESI): *m/z* = 542 [M]$^+$, $C_{34}H_{55}NO_2S$ (541.89). Calcd.: C, 75.36; H, 10.23; N, 2.58; S, 5.92. Found: C, 76.02; H, 10.69; N, 2.87; S, 5.76.

2-(Hexadecylthio)-3-[(2-morpholinoethyl)amino]naphthalene-1,4-dione (11e): Compound **11e** was synthesized from 0.10g (0.222 mmol) 2-chloro-3-(hexadecylthio)naphthalene-1,4-dione **7a** and 0.028 mL (0.222 mmol) 4-(2-aminoethyl)-morpholine **10b** using Na_2CO_3 as base according to the general procedure. IR: 3280 (NH), 3050 (CH$_{arom.}$), 2921–2851 (CH$_{aliph.}$), 1672–1629 (C=O), 1556 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.15–1.31, 1.44–1.54 (m, 28H, C***H***$_2$), 2,44–2.46 (t, 4H, *J* = 4.39 Hz, C***H***$_{2morpholine}$), 2.57–2.59 (t, 2H, *J* = 5.86 Hz, C***H***$_2$N), 2.72–2.75 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.67–3.69 (t, 4H, *J* = 4.88 Hz, C***H***$_{2morpholine}$), 3.90–3.93 (q, 2H, *J* = 5.37 Hz, NHC***H***$_2$), 7.20–7.23 (t, 1H, *J* = 5.86 Hz, N***H***), 7.51 (t, 1H, *J* = 6.83 Hz, C***H***$_{napht}$), 7.64 (t, 1H, *J* = 6.83 Hz, C***H***$_{napht}$), 7.93 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H$_3$), 21.6, 27.8, 28.5, 29.0, 31.0 (***C***H$_2$) 33.9 (S***C***H$_2$), 41.0, 56.1 (***C***H$_{2morph.aliph.}$), 52.1, 66.1 (***C***H$_{2morph.cyclo}$), 128.8 (S***C***$_{napht}$), 133.4 (NH***C***$_{napht}$), 125.2, 125.5 (***C***H$_{napht}$), 130.9, 132.8 (***C***$_{napht}$), 180.6, 180.8 (***C***=O). MS (+ESI): *m/z* = 543 [M+H]$^+$, $C_{32}H_{50}N_2O_3S$ (542.35). Calcd.: C, 70.81; H, 9.28; N, 5.16; S, 5.91. Found: C, 70.88; H, 9.76; N, 5.24; S, 5.57.

(*E*)-2-(Octadec-9-en-1-ylamino)-3-(octadecylthio)naphthalene-1,4-dione (11f): Compound **11f** was synthesized from 0.10g (0.209 mmol) 2-chloro-3-(octadecylthio)naphthalene-1,4-dione **7b** and 0.056g (0.209 mmol) octadec-9-enylamine **10c** using Na_2CO_3 as base according to the general procedure. IR: 3291 (NH), 3052 ($CH_{arom.}$), 2921, 2849 ($CH_{aliph.}$), 1671, 1629 (C=O), 1590, 1552 (C=C). ^{1}H NMR: 0.78–0.82 (t, 6H, *J* = 6.83 Hz, C***H***$_3$), 1.12–1.35, 1.47–1.53, 1.89–1.92 (m, 32H, C***H***$_2$), 1.12–1.35, 1.56–1.63 (m, 24H, C***H***$_{2(oleyl)}$), 1.90–1.96 (m, 4H, C***H***$_2$–CH=CH–C***H***$_2$), 2.71–2.74 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.81–3.83 (t, 2H, *J* = 7.32 Hz, NHC***H***$_2$), 5.26–5.28 (m, 2H, C***H***=C***H***), 5.31 (bs, 1H, N***H***), 7.52 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.62 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.93 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$), 8.06 (d, 1H, *J* = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.2, 14.3 (***C***H$_3$), 22.9, 24.9, 27.0, 27.4, 27.5, 29.1, 30.9, 32.1, 32.8, 35.3 (***C***H$_2$), 46.4 (S***C***H$_2$), 126.6 (S***C***$_{napht}$), 134.2 (NH***C***$_{napht}$), 126.6, 126.9, 130.2, 130.9 (***C***H$_{napht}$), 131.2, 134.1 (***C***$_{napht}$), 134.8 (C***H***$_{oleyl}$), 180.6, 181.7 (***C***=O). MS (+ESI): *m/z* = 709 [M+H]$^+$, $C_{46}H_{77}NO_2S$ (708.20). Calcd.: C, 78.02; H, 10.96; N, 1.98; S, 4.53. Found: C, 78.23; H, 10.75; N, 2.02; S, 4.66.

CONCLUSION

We have designed and synthesized new *N*,*S*-disubstituted naphthoquinones and completely characterized them by CHN analyses, FT-IR, Mass, ^{1}H NMR, ^{13}C NMR and UV/Vis spectroscopy. Photo- and electrochemical properties of selected compounds were investigated by using fluorescence spectroscopy and the cyclovoltammetry method. 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.

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Supplemental Materials

Characterization Data for Compounds 5 and 6

2-(Hexadecylthio)-3-(phenylamino)naphthalene-1,4-dione (5a): Compound **5a** was synthesized from 0.20g (0.704 mmol) 2-chloro-3-(phenylamino)naphthalene-1,4-dione **3a** and 0.182g (0.704 mmol) hexadecanethiol **4a** using triethylamine as base according to the general procedure. IR: 3310 (NH), 3052 ($CH_{arom.}$), 2914, 2849 ($CH_{aliph.}$), 1665, 1634 (C=O), 1591, 1555 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.07–1.30, 1.51–1.59 (m, 28H, C***H***$_2$), 2.49–2.52 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.94–6.95 (d, 2H, J = 7.32 Hz, C***H***$_{arom}$), 7.05–7.08 (t, 1H, J = 7.32 Hz, C***H***$_{arom}$), 7.23–7.26 (t, 2H, J = 7.31 Hz, C***H***$_{arom}$), 7.59 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.66 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.73 (bs, 1H, N***H***), 7.99 (d, 1H, J = 7.56 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.1 (***C***H$_3$), 21.6, 28.0, 28.6, 29.2, 31.0 (***C***H$_2$), 33.1 (S***C***H$_2$), 117.4, 121.4, 127.4 (***C***H$_{arom}$), 123.5 (S***C***$_{napht}$), 129.6 (NH***C***$_{napht}$), 125.6, 125.8, 131.6, 132.5 (***C***H$_{napht}$), 133.4, 137.5 (***C***$_{napht}$), 144.0 (NH***C***), 179.4, 180.0 (***C***=O). MS (+ESI): *m/z* = 506 [M]$^+$, $C_{32}H_{43}NO_2S$ (505.75). Calcd.: C 75.99; H 8.57; N 2.77; S 6.34. Found: C 75.02; H 8.61; N 2.59; S 6.12.

2-[(4-Fluorophenyl)amino]-3-(hexadecylthio)naphthalene-1,4-dione (5b): Compound **5b** was synthesized from 0.20g (0.662 mmol) 2-chloro-3-[(4-fluorophenyl)amino]naphthalene-1,4-dione **3b** and 0.171g (0.662 mmol) hexadecanethiol **4a** using triethyl amine as base according to the general procedure. IR: 3296 (NH), 3051 ($CH_{arom.}$), 2915, 2849 ($CH_{aliph.}$), 1665,

1631 (C=O), 1556 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.09–1.33, 1.49–1.57 (m, 28H, C$\boldsymbol{H}_2$), 2.50–2.53 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 7.65 (bs, 1H, N$\boldsymbol{H}$), 6.91–6.94 (m, 2H, C$\boldsymbol{H}_{arom}$), 6.95–6.97 (m, 2H, Hz, C$\boldsymbol{H}_{arom}$), 7.57 (t, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$), 7.67 (t, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$), 7.98 (d, 1H, J = 7.08 Hz, C$\boldsymbol{H}_{napht}$), 8.08 (d, 1H, J = 7.08 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 13.0 ($\boldsymbol{C}$H$_3$), 21.7, 27.6, 28.3, 28.7, 30.9 ($\boldsymbol{C}$H$_2$), 33.0 (S$\boldsymbol{C}$H$_2$), 114.1, 123.6 ($\boldsymbol{C}$H$_{arom}$), 116.7 (S$\boldsymbol{C}_{napht}$), 129.5 (NH$\boldsymbol{C}_{napht}$), 125.6, 125.8, 131.7, 132.5, ($\boldsymbol{C}$H$_{napht}$), 133.5, 133.6 ($\boldsymbol{C}_{napht}$), 144.4 (NH$\boldsymbol{C}$), 157.9–159.8 (d, F$\boldsymbol{C}_{arom}$), 179.3, 179.9 ($\boldsymbol{C}$=O). MS (+ESI): m/z = 524 [M]$^+$, $C_{32}H_{42}FNO_2S$ (523.74). Calcd.: C 73.38; H 8.08; N 2.67; S 6.12. Found: C 73.66; H 8.08; N 2.68; S 6.18.

2-[(4-Fluorobenzyl)amino]-3-(hexadecylthio)naphthalene-1,4-dione (5c): Compound **5c** was synthesized from 0.20g (0.633 mmol) 2-(4-fluorobenzylamino)-3-chloronaphthalene-1,4-dione **3c** and 0.163g (0.633 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 3306 (NH), 3052 (CH$_{arom.}$), 2913, 2849 (CH$_{aliph.}$), 1669 (C=O), 1551–1503 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, J = 6.84 Hz, C$\boldsymbol{H}_3$), 1.10–1.26, 1.40–1.52 (m, 28H, C$\boldsymbol{H}_2$), 2.67–2.70 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 5.01–5.02 (d, 2H, J = 5.85 Hz, NHC$\boldsymbol{H}_2$), 6.96–7.00 (m, 2H, C$\boldsymbol{H}_{arom}$), 7.18–7.23 (m, 2H, Hz, C$\boldsymbol{H}_{arom}$), 6.55 (t, 1H, J = 5.87 Hz, N$\boldsymbol{H}$), 7.51 (t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.65 (t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.93 (d, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$), 8.06 (d, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 13.0 ($\boldsymbol{C}$H$_3$), 21.6, 27.6, 28.3, 28.7, 30.9 ($\boldsymbol{C}$H$_2$), 34.1 (S$\boldsymbol{C}$H$_2$), 48.1 (NH$\boldsymbol{C}$H$_2$), 114.7, 128.2 ($\boldsymbol{C}$H$_{arom}$), 129.3 (S$\boldsymbol{C}_{napht}$), 133.7 (NH$\boldsymbol{C}_{napht}$), 125.4, 125.6, 131.1, 131.2 ($\boldsymbol{C}$H$_{napht}$), 132.7, 133.0 ($\boldsymbol{C}_{napht}$), 133.2 ($\boldsymbol{C}_{arom}$), 160.3–162.3 (d, F$\boldsymbol{C}_{arom}$), 179.3, 179.9 ($\boldsymbol{C}$=O). MS (+ESI): m/z = 538 [M]$^+$, $C_{33}H_{44}FNO_2S$ (537.77). Calcd.: C 73.70; H 8.25; N 2.60; S 5.96. Found: C 74.52; H 8.43; N 2.68; S 5.74.

2-(Hexadecylthio)-3-(naphthalen-2-ylamino)naphthalene-1,4-dione (5d): Compound **5d** was synthesized from 0.20g (0.599 mmol) 2-chloro-3-(naphthalen-3-ylamino)naphthalene-1,4-dione **3d** and 0.155g (0.599 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 3288 (NH), 3052 ($CH_{arom.}$), 2916, 2849 ($CH_{aliph.}$), 1661, 1628 (C=O), 1588 (C=C). ^{1}H NMR: 0.79–0.81 (t, 3H, J = 6.84 Hz, C***H***$_3$), 1.02–1.26, 1.49–1.55 (m, 28H, C***H***$_2$), 2.44–2.47 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 7.14–7.18 (m, 2H, C***H***$_{naphthyl}$), 7.26 (bs, 1H, C***H***$_{naphthyl}$), 7.32–7.41 (m, 2H, C***H***$_{naphthyl}$), 7.69–7.73 (m, 2H, C***H***$_{naphthyl}$), 7.57–7.68 (m, 2H, C***H***$_{napht}$), 7.91 (bs, 1H, N***H***), 8.01 (d, 1H, J = 7.08 Hz, C***H***$_{napht}$), 8.10 (d, 1H, J = 7.08 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H$_3$), 21.6, 27.5, 28.3, 28.7, 30.9 (***C***H$_2$), 32.7 (S***C***H$_2$), 117.9, 121.0, 125.6, 126.5, 127.2, 129.6 (***C***H$_{naphthyl}$), 131.7, 134.5 (***C***$_{naphthyl}$), 121.0 (S***C***$_{napht}$), 126.0 (NH***C***$_{napht}$), 126.7, 127.2, 132.1 (***C***H$_{napht}$), 132.6, 134.5 (***C***$_{napht}$), 143.5 (NH***C***), 179.5, 180.1 (***C***=O). MS (+ESI): *m/z* = 556 $[M+H]^+$, $C_{36}H_{45}NO_2S$ (556.58). Calcd.: C 77.79; H 8.16; N 2.52; S 5.77. Found: C 77.65; H 8.75; N 2.49 S 5.10.

2-(Hexadecylthio)-3-(*o*-tolylamino)naphthalene-1,4-dione (5e): Compound **5e** was synthesized from 0.10g (0.335 mmol) 2-(*o*-tolylamino)-3-chloronaphthalene-1,4-dione **3e** and 0.086g (0.335 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 3304 (NH), 3050 ($CH_{arom.}$), 2916, 2849 ($CH_{aliph.}$), 1664, 1633 (C=O), 1587, 1552 (C=C). ^{1}H NMR: 0.80–0.83 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.09–1.35, 1.46–1.54 (m, 28H, C***H***$_2$), 2.26 (s, 3H, C***H***$_{3arom}$), 2.51–2.54 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.83–6.85 (d, 1H, J = 7.81 Hz, C***H***$_{arom}$), 7.04–7.12 (m, 2H, C***H***$_{arom}$), 7.13–7.16 (d, 1H, J = 6.83 Hz, C***H***$_{arom}$), 7.52 (bs, 1H, N***H***), 7.56 (t, 1H, J = 7.57 Hz, C***H***$_{napht}$), 7.67 (t, 1H, J = 7.57 Hz, C***H***$_{napht}$), 7.98 (d, 1H, J = 7.81 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H$_3$), 17.3 (***C***H$_{3arom}$), 22.7, 28.3, 28.6, 29.3,

31.9 (***C***H_2), 33.7 (S***C***H_2), 115.4, 124.9, 129.3, 129.8, (***C***H_{arom}), 123.1 (S***C***$_{napht}$), 124.6 (NH***C***$_{napht}$), 125.5, 125.8, 130.8,132.6 (***C***H_{napht}), 131.5 (***C***$_{arom}$), 133.4, 136.6 (***C***$_{napht}$), 145.6 (NH***C***), 179.4, 179.7 (***C***=O). MS (+ESI): *m/z* = 520 $[M]^+$, $C_{33}H_{45}NO_2S$ (519.78). Calcd.: C 76.25; H 8.73; N 2.69; S 6.17. Found: C 76.49; H 9.68; N 2.60; S 6.02.

2-(Hexadecylthio)-3-(*m*-tolylamino)naphthalene-1,4-dione (5f): Compound **5f** was synthesized from 0.10g (0.335 mmol) 2-(*m*-tolylamino)-3-chloronaphthalene-1,4-dione **3f** and 0.086g (0.335 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 3305 (NH), 3053 ($CH_{arom.}$), 2916, 2849 ($CH_{aliph.}$), 1656, 1645 (C=O), 1587, 1546 (C=C). ^{1}H NMR: 0.80–0.82 (t, 3H, *J* = 6.34 Hz, C***H***$_3$), 1.09–1.32, 1.44–1.51 (m, 28H, C***H***$_2$), 2.28 (bs, 3H, C***H***$_{3arom}$), 2.51–2.54 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 6.75 (bs, 1H, C***H***$_{arom}$), 6.75–6.77 (d, 1H, *J* = 6.35 Hz, C***H***$_{arom}$), 6.88–6.90 (d, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 7.12–7.15 (t, 1H, *J* = 7.81 Hz, C***H***$_{arom}$), 7.56 (t, 1H, *J* = 7.08 Hz, C***H***$_{napht}$), 7.67 (t, 1H, *J* = 7.08 Hz, C***H***$_{napht}$), 7.72 (bs, 1H, N***H***), 8.00 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 8.08 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H_3), 20.4 (***C***H_{3arom}), 21.6, 27.6, 28.3, 28.7, 31.0 (***C***H_2), 32.7 (S***C***H_2), 117.1, 118.5, 122.0, 127.2 (***C***H_{arom}), 118.5 (S***C***$_{napht}$), 124.4 (NH***C***$_{napht}$), 125.5, 125.8, 131.6, 132.6 (***C***H_{napht}), 133.4 (***C***$_{arom}$), 129.7, 137.4 (***C***$_{napht}$), 144.1 (NH***C***), 179.4, 180.0 (***C***=O). MS (+ESI): *m/z* = 521 $[M+H]^+$, $C_{33}H_{45}NO_2S$ (519.78). Calcd.: C 76.25; H 8.73; N 2.69; S 6.17. Found: C 76.11; H 9.31; N 2.91; S 6.40.

2-(Hexadecylthio)-3-(p-tolylamino)naphthalene-1,4-dione (5g): Compound **5g** was synthesized from 0.20g (0.67 mmol) 2-chloro-3-(*p*-tolylamino)naphthalene-1,4-dione **3g**, 0.172g (0.67 mmol) hexadecanethiol **4a** and K_2CO_3 as base according to the general procedure. IR: 3322 (NH), 3051 ($CH_{arom.}$), 2915, 2849 ($CH_{aliph.}$), 1659, 1637 (C=O), 1591, 1547 (C=C). ^{1}H NMR:

0.81–0.83 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.08–1.36, 1.54 (m, 28H, C***H***$_2$), 2.27 (s, 3H, C***H***$_{3arom}$), 2.50–2.54 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.84–6.85 (d, 2H, J = 8.3 Hz, C***H***$_{arom}$), 7.03–7.05 (d, 2H, J = 8.3 Hz, C***H***$_{arom}$), 7.56 (t, 1H, J = 8.46 Hz, C***H***$_{napht}$), 7.65 (t, 1H, J = 8.05 Hz, C***H***$_{napht}$), 7.71 (bs, 1H, N***H***), 8.00 (d, 1H, J = 7.32 Hz, C***H***$_{napht}$), 8.07 (d, 1H, J = 7.32 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.1 (***C***H$_3$), 20.0 (***C***H$_{3arom}$), 21.6, 27.6, 28.3, 28.7, 30.9 (***C***H$_2$), 32.9 (S***C***H$_2$), 121.6, 125.6, 125.8, 128.0 (***C***H$_{arom}$), 116.3 (S***C***$_{napht}$), 129.7 (NH***C***$_{napht}$), 131.6, 133.4, 133.5 (***C***H$_{napht}$), 135.0 (***C***$_{arom}$), 129.7, 133.5 (***C***$_{napht}$), 144.5 (NH***C***), 179.8, 179.9 (***C***=O). MS (+ESI): *m/z* = 521 [M+H]$^+$, $C_{33}H_{45}NO_2S$ (519.78). Calcd.: C 76.25; H 8.73; N 2.69; S 6.17. Found: C 76.57; H 8.39; N 2.66; S 6.48.

2-(Hexadecylthio)-3-[(4-methoxyphenyl)amino]naphthalene-1,4-dione (5h): Compound **5h** was synthesized from 0.20g (0.64 mmol) 2-(4-methoxyphenylamino)-3-chloronaphthalene-1,4-dione **3h** and 0.165g (0.64 mmol) hexadecanethiol **4a** using K_2CO_3 as base according to the general procedure. IR: 3291 (NH), 3051 (CH$_{arom.}$), 2916, 2848 (CH$_{aliph.}$), 1665, 1629 (C=O), 1589, 1512 (C=C), ^{1}H NMR: 0.80–0.81 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.10–1.31, 1.55 (m, 28H, C***H***$_2$), 2.50-2.53 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 3.75 (bs, 3H, OC***H***$_{3\ arom}$), 6.80 (d, 2H, J = 7.81 Hz, C***H***$_{arom}$), 6.94 (d, 2H, J = 8.79 Hz, C***H***$_{arom}$), 7.55 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.64 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.66 (bs, 1H, N***H***), 7.97 (d, 1H, J = 7.32 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 7.32 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.3 (***C***H$_3$), 20.4 (O***C***H$_{3arom}$), 29.7, 29.8, 29.9, 32.1 (***C***H$_2$), 34.3 (S***C***H$_2$), 126.8, 127.0, 124.8, 113.9 (***C***H$_{arom}$), 116.3 (S***C***$_{napht}$), 124.8 (NH***C***$_{napht}$), 132.7, 134.7 (***C***H$_{napht}$), 131.9, 130.9 (***C***$_{arom}$), 133.9, 146.3 (***C***$_{napht}$), 157.3 (NH***C***), 180.8, 181.0 (***C***=O). MS (+ESI): *m/z* = 537 [M+H]$^+$, $C_{33}H_{45}NO_3S$ (535.80). Calcd.: C 73.98; H 8.47; N 2.61; S 5.98. Found: C 74.55; H 8.15; N 2.59; S 5.71.

2-[(3,5-Dimethoxyphenyl)amino]-3-(hexadecylthio)naphthalene-1,4-dione (5i): Compound **5i** was synthesized from 0.20 g (0.582 mmol) 2-(3,5-dimethoxyphenylamino)-3-chloronaphthalene-1,4-dione **3i** and 0.150g (0.582 mmol) hexadecanethiol **4a** using Na_2CO_3 as base according to the general procedure. IR: 3316 (NH), 3051 ($CH_{arom.}$), 2915, 2848 ($CH_{aliph.}$), 1664, 1632 (C=O), 1593, 1553 (C=C). ^{1}H NMR: 0.79–0.81 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.09–1.31, 1.55 (m, 28H, C***H***$_2$), 2.42–2.45 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.73 (bs, 3H, OC***H***$_{3\ arom}$), 3.75 (bs, 3H, OC***H***$_{3arom}$), 6.38 (d, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 6.40 (bs, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 6.83 (d, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 7.54 (t, 1H, *J* = 7.56 Hz, C***H***$_{arom}$), 7.64 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.66 (bs, 1H, N***H***), 7.96 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.3 (***C***H$_3$), 22.9 (O***C***H$_{3arom}$), 28.9, 29.6, 29.8, 29.9, 32.1 (***C***H$_2$), 34.0 (S***C***H$_2$), 103.3, 99.0(***C***H$_{arom}$), 121.0 (S***C***$_{napht}$), 134.0 (NH***C***$_{napht}$), 124.9, 126.6, 132.5, 134.5 (***C***H$_{napht}$), 131.0, 114.8 (***C***$_{arom}$), 146.8, 153.7 (***C***$_{napht}$), 158.5 (NH***C***), 180.8, 180.9 (***C***=O). MS (+ESI): *m/z* = 567 $[M+H]^+$, $C_{34}H_{47}NO_4S$ (565.82). Calcd.: C 72.17; H 8.77; N 2.48; S 5.67. Found: C 72.04; H 8.22; N 2.33; S 5.00.

2-(Octadecylthio)-3-(phenylamino)naphthalene-1,4-dione (6a): Compound **6a** was synthesized from 0.15g (0.528 mmol) 2-chloro-3-(phenylamino)naphthalene-1,4-dione **3a** and 0.15g (0.528 mmol) octadecanethiol **4b** using triethylamine as base according to the general procedure. IR: 3309 (NH), 3052 ($CH_{arom.}$), 2913, 2849 ($CH_{aliph.}$), 1665, 1634 (C=O), 1591, 1554 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.08–1.36, 1.50–1.61 (m, 32H, C***H***$_2$), 2.49–2.52 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 6.94–6.95 (d, 2H, *J* = 7.81 Hz, C***H***$_{arom}$), 7.06–7.09 (t, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 7.23–7.27 (t, 2H, *J* = 6.83 Hz, C***H***$_{arom}$), 7.56 (t, 1H, *J* = 7.64 Hz, C***H***$_{napht}$), 7.66 (t, 1H, *J* = 7.64 Hz, C***H***$_{napht}$), 7.73 (bs, 1H, N***H***), 7.99 (d, 1H, *J* = 7.33 Hz, C***H***$_{napht}$), 8.08 (d,

1H, J = 7.33 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 14.2 (***C***H$_3$), 21.6, 27.6, 28.6, 29.4, 31.0 (***C***H$_2$), 33.2 (S***C***H$_2$), 117.4, 121.4, 127.4 (***C***H$_{arom}$), 123.5 (S***C***$_{napht}$), 129.7 (NH***C***$_{napht}$), 125.6, 125.8, 131.7, 132.5 (***C***H$_{napht}$), 133.4, 137.5 (***C***$_{napht}$), 144.0 (NH***C***), 179.4, 180.0 (***C***=O). MS (+ESI): *m/z* = 534[M]$^+$, $C_{34}H_{47}NO_2S$ (533.81). Calcd.: C 76.50; H 8.87; N 2.62; S 6.01. Found: C 76.45; H 9.73; N 2.55; S 6.33.

2-[(4-Fluorophenyl)amino]-3-(octadecylthio)naphthalene-1,4-dione (6b): Compound **6b** was synthesized from 0.10 g (0.331 mmol) 2-chloro-3-((4-fluorophenyl)amino)naphthalene-1,4-dione **3b** and 0.095 g (0.331 mmol) octadecanethiol **4b** using triethylamine as base according to the general procedure. IR: 3296 (NH), 3051 (CH$_{arom.}$), 2914, 2849 (CH$_{aliph.}$), 1664, 1631 (C=O), 1589, 1541 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.09–1.32, 1.50–1.57 (m, 32H, C$\boldsymbol{H}_2$), 2.50–2.53 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 7.67 (bs, 1H, N***H***), 6.91–6.94 (m, 2H, C$\boldsymbol{H}_{arom}$), 6.95–6.97 (m, 2H, Hz, C$\boldsymbol{H}_{arom}$), 7.56 (t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.67 (t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.98 (d, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$), 8.07 (d, 1H, J = 7.56 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 14.3 (***C***H$_3$), 22.9, 28.8, 29.5, 30.0, 32.1 (***C***H$_2$), 34.2(S***C***H$_2$), 115.4, 124.6 (***C***H$_{arom}$), 117.9 (S***C***$_{napht}$), 130.8 (NH***C***$_{napht}$), 126.8, 127.1, 132.9, 133.7 (***C***H$_{napht}$), 134.7, 134.8(***C***$_{napht}$), 145.6 (NH***C***), 159.1–161.1 (d, F***C***$_{arom}$), 180.5, 181.1 (***C***=O). MS (+ESI): *m/z* = 552[M]$^+$, $C_{34}H_{46}FNO_2S$ (551.32). Calcd.: C 74.01; H 8.40; N 2.54; S 5.81. Found: C 74.38; H 9.02; N 2.74; S 5.70.

2-[(4-Fluorobenzyl)amino]-3-(octadecylthio)naphthalene-1,4-dione (6c): Compound **6c** was synthesized from 0.10g (0.316 mmol) 2-(4-fluorobenzylamino)-3-chloronaphthalene-1,4-dione **3c** and 0.09g (0.316 mmol) octadecanethiol **4b** using Na_2CO_3 as base according to the general procedure. IR: 3308 (NH), 3053(CH$_{arom.}$), 2912, 2849 (CH$_{aliph.}$), 1669 (C=O), 1591,

1551(C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.10–1.26, 1.40–1.51 (m, 32H, C$\boldsymbol{H}_2$), 2.67–2.69 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 5.01–5.02 (d, 2H, J = 5.86 Hz, NHC$\boldsymbol{H}_2$), 6.96–7.00 (m, 2H, C$\boldsymbol{H}_{arom}$), 7.19–7.24 (m, 2H, Hz, C$\boldsymbol{H}_{arom}$), 6.55 (t, 1H, J = 5.86 Hz, N$\boldsymbol{H}$), 7.52(t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.65 (t, 1H, J = 7.57 Hz, C$\boldsymbol{H}_{napht}$), 7.94 (d, 1H, J = 7.49 Hz, C$\boldsymbol{H}_{napht}$), 8.07 (d, 1H, J = 7.49 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 14.3 ($\boldsymbol{C}$H$_3$), 22.9, 29.1, 29.8, 30.1, 32.1 ($\boldsymbol{C}$H$_2$), 35.4(S$\boldsymbol{C}$H$_2$), 49.4(NH$\boldsymbol{C}$H$_2$), 115.9, 129.4 ($\boldsymbol{C}$H$_{arom}$), 131.0 (S$\boldsymbol{C}_{napht}$), 134.8 (NH$\boldsymbol{C}_{napht}$), 126.7, 126.9, 132.1, 132.4 ($\boldsymbol{C}$H$_{napht}$), 133.1, 133.9 ($\boldsymbol{C}_{napht}$), 134.3 ($\boldsymbol{C}_{arom}$), 160.3–162.3 (d, F$\boldsymbol{C}_{arom}$), 180.4, 181.5 ($\boldsymbol{C}$=O). MS (+ESI): m/z = 566[M]$^+$, $C_{35}H_{48}FNO_2S$ (565.82). Calcd.: C 74.29; H 8.55; N 2.48; S 5.67. Found: C 74.37; H 9.27; N 2.69; S 5.45.

2-(Naphthalen-2-ylamino)-3-(octadecylthio)naphthalene-1,4-dione (6d): Compound **6d** was synthesized from 0.10g (0.299 mmol) 2-chloro-3-(naphthalen-3-ylamino)naphthalene-1,4-dione **3d** and 0.085g (0.299 mmol) octadecanethiol **4b** using Na_2CO_3 as base according to the general procedure. IR: 3289 (NH), 3053 (CH$_{arom.}$), 2914, 2848 (CH$_{aliph.}$), 1666, 1628 (C=O), 1589, 1541 (C=C). ^{1}H NMR: 0.79–0.82 (t, 3H, J = 6.83 Hz, C$\boldsymbol{H}_3$), 1.02–1.25, 1.49–1.54 (m, 32H, C$\boldsymbol{H}_2$), 2.44–2.47 (t, 2H, J = 7.32 Hz, SC$\boldsymbol{H}_2$), 7.14–7.16 (m, 2H, C$\boldsymbol{H}_{naphthyl}$), 7.27(bs, 1H, C$\boldsymbol{H}_{naphthyl}$), 7.32–7.41 (m, 2H, C$\boldsymbol{H}$ $_{naphthyl}$), 7.69–7.73 (m, 2H, C$\boldsymbol{H}_{naphthyl}$), 7.57–7.68 (m, 2H, C$\boldsymbol{H}_{napht}$), 7.91 (bs, 1H, N$\boldsymbol{H}$), 8.01 (d, 1H, J = 7.08 Hz, C$\boldsymbol{H}_{napht}$), 8.10 (d, 1H, J = 7.08 Hz, C$\boldsymbol{H}_{napht}$). ^{13}C NMR: 13.1 ($\boldsymbol{C}$H$_3$), 21.6, 28.0, 28.6, 29.2, 30.9 ($\boldsymbol{C}$H$_2$), 32.7 (S$\boldsymbol{C}$H$_2$), 117.8, 121.0, 125.7, 126.5, 127.2, 129.6 ($\boldsymbol{C}$H$_{naphthyl}$), 131.7, 134.5 ($\boldsymbol{C}_{naphthyl}$), 121.0 (S$\boldsymbol{C}_{napht}$), 126.0 (NH$\boldsymbol{C}_{napht}$), 126.7, 127.2, 132.1 ($\boldsymbol{C}H_{napht}$), 132.6, 134.5 ($\boldsymbol{C}_{napht}$), 143.5 (NH$\boldsymbol{C}$), 179.5, 180.1 ($\boldsymbol{C}$=O). MS (+ESI): m/z = 585 [M]$^+$, $C_{38}H_{49}NO_2S$ (583.87). Calcd.: C 78.17; H 8.46; N 2.40; S 5.49. Found: C 78.27; H 9.32; N 2.46 S 5.25.

2-(Octadecylthio)-3-(*o*-tolylamino)naphthalene-1,4-dione (6e): Compound **6e** was synthesized from 0.10g (0.335 mmol) 2-(*o*-tolylamino)-3-chloronaphthalene-1,4-dione **3e** and 0.096g (0.335 mmol) octadecanethiol **4b** using Na_2CO_3 as base according to the general procedure. IR: 3305 (NH), 3050 ($CH_{arom.}$), 2915, 2849 ($CH_{aliphatic}$), 1665, 1633 (C=O), 1587, 1553 (C=C). ^{1}H NMR: 0.80–0.83 (t, 3H, J = 6.34 Hz, C***H***$_3$), 1.09–1.35, 1.45–1.53 (m, 32H, C***H***$_2$), 2.26 (s, 3H, C***H***$_{3arom}$), 2.51–2.54 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.84–6.85 (d, 1H, J = 7.81 Hz, C***H***$_{arom}$), 7.04–7.12 (m, 2H, C***H***$_{arom}$), 7.14–7.16 (d, 1H, J = 7.32 Hz, C***H***$_{arom}$), 7.52 (bs, 1H, N***H***), 7.55 (t, 1H, J = 7.57 Hz, C***H***$_{napht}$), 7.67 (t, 1H, J = 7.57 Hz, C***H***$_{napht}$), 7.98 (d, 1H, J = 7.81 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 7.81 Hz, C***H***$_{napht}$). ^{13}C NMR: 13.0 (***C***H$_3$), 17.3 (***C***H$_{3arom}$), 21.6, 28.1, 28.6, 29.2, 31.0 (***C***H$_2$), 32.9 (S***C***H$_2$), 115.4, 124.9, 129.3, 129.8 (***C***H$_{arom}$), 123.1 (S***C***$_{napht}$), 124.6 (NH***C***$_{napht}$), 125.5, 125.8, 130.8,132.6 (***C***H$_{napht}$), 131.5 (***C***$_{arom}$), 133.4, 136.6 (***C***$_{napht}$), 145.6 (NH***C***), 179.4, 179.7 (***C***=O). MS (+ESI): *m/z* = 547 $[M]^+$, $C_{35}H_{49}NO_2S$ (547.83). Calcd.: C 76.73; H 9.02; N 2.56; S 5.85. Found: C 77.79; H 9.12; N 2.75; S 5.73.

2-(Octadecylthio)-3-(*m*-tolylamino)naphthalene-1,4-dione (6f): Compound **6f** was synthesized from 0.10g (0.335 mmol) 2-(*m*-tolylamino)-3-chloronaphthalene-1,4-dione **3f** and 0.096g (0.335 mmol) octadecanethiol **4b** using Na_2CO_3 as base according to the general procedure. IR: 3295 (NH), 3049 ($CH_{arom.}$), 2913, 2850 ($CH_{aliph.}$), 1665, 1630 (C=O), 1587, 1560 (C=C). ^{1}H NMR: 0.80–0.82 (t, 3H, J = 6.83 Hz, C***H***$_3$), 1.08–1.32, 1.45–1.53 (m, 32H, C***H***$_2$), 2.28 (bs, 3H, C***H***$_{3arom}$), 2.50–2.53 (t, 2H, J = 7.32 Hz, SC***H***$_2$), 6.75 (bs, 1H, C***H***$_{arom}$), 6.75–6.76 (d, 1H, J = 6.35 Hz, C***H***$_{arom}$), 6.88–6.90 (d, 1H, J = 7.81 Hz, C***H***$_{arom}$), 7.12–7.15 (t, 1H, J = 7.57 Hz, C***H***$_{arom}$), 7.56 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.67 (t, 1H, J = 7.56 Hz, C***H***$_{napht}$), 7.71 (bs, 1H, N***H***), 7.99 (d, 1H, J = 8.78 Hz, C***H***$_{napht}$), 8.08 (d, 1H, J = 8.78 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.3 (***C***H$_3$),

21.6 (***C***H_{3arom}), 22.9, 28.8, 29.4, 29.9, 32.1 (***C***H_2), 34.0 (S***C***H_2), 118.3, 119.7, 123.2, 128.5 (***C***H_{arom}), 119.7 (S***C***$_{napht}$), 125.6 (NH***C***$_{napht}$), 126.8, 127.0, 132.8, 133.8 (***C***H_{napht}), 134.6 (***C***$_{arom}$), 130.9, 138.6 (***C***$_{napht}$), 145.3 (NH***C***), 180.7, 181.2 (***C***=O). MS (+ESI): *m/z* = 549 $[M+H]^+$, $C_{35}H_{49}NO_2S$ (547.83). Calcd.: C 76.73; H 9.02; N 2.56; S 5.85. Found: C 76.66; H 8.84; N 2.49; S 5.89.

2-(Octadecylthio)-3-(*p*-tolylamino)naphthalene-1,4-dione (6g): Compound **6g** was synthesized from 0.15g (0.50 mmol) 2-chloro-3-(*p*-tolylamino)naphthalene-1,4-dione **3g** and 0.143g (0.50 mmol) octadecanethiol **4b** using K_2CO_3 as base according to the general procedure. IR: 3325 (NH), 3052 ($CH_{arom.}$), 2916, 2849 ($CH_{aliph.}$), 1658, 1636 (C=O), 1591, 1547 (C=C). ^{1}H NMR: 0.80–0.84 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.08–1.36, 1.53 (m, 32H, C***H***$_2$), 2.27 (s, 3H, C***H***$_{3arom}$), 2.50–2.53(t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 6.84–6.86 (d, 2H, *J* = 8.3 Hz, C***H***$_{arom}$), 7.04–7.05 (d, 2H, *J* = 8.3 Hz, C***H***$_{arom}$), 7.56 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.65 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.71 (bs, 1H, N***H***), 7.99 (d, 1H, *J* = 7.32 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.32 Hz, C***H***$_{napht}$). ^{13}C NMR: 14.3 (***C***H_3), 21.2 (***C***H_{3arom}), 22.9, 28.7, 29.3, 29.6, 29.8, 29.9,32.1 (***C***H_2), 34.1 (S***C***H_2), 122.9, 126.8, 127.0 (***C***H_{arom}), 117.5 (S***C***$_{napht}$), 134.7 (NH***C***$_{napht}$), 129.3, 132.8, 134.8 (***C***H_{napht}), 136.3 (***C***$_{arom}$), 131.0, 133.8 (***C***$_{napht}$), 145.8 (NH***C***), 181.1, 181.2 (***C***=O). MS (+ESI): *m/z* = 549 $[M+H]^+$, $C_{35}H_{49}NO_2S$ (547.83). Calcd.: C 76.73; H 9.02; N 2.56; S 5.85. Found: C 76.15; H 9.40; N 2.41; S 5.75.

2-[(4-Methoxyphenyl)amino]-3-(octadecylthio)naphthalene-1,4-dione (6h): Compound **6h** was synthesized from 0.20g (0.637 mmol) 2-(4-methoxyphenylamino)-3-chloronaphthalene-1,4-dione **3h** and 0.183g (0.637 mmol) octadecanethiol **4b** using K_2CO_3 as base according to the

general procedure. IR: 3293 (NH), 3053 ($CH_{arom.}$), 2915, 2847 ($CH_{aliph.}$), 1665, 1629 (C=O), 1589, 1512 (C=C), ^{1}H NMR: 0.80–0.81 (t, 3H, *J* = 6.83 Hz, C***H***$_3$), 1.09–1.32, 1.52 (m, 32H, C***H***$_2$), 2.50–2.52 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.78 (bs, 3H, OC***H***$_{3\ arom}$), 6.80 (d, 2H, *J* = 8.79 Hz, C***H***$_{arom}$), 6.93 (d, 2H, *J* = 7.81 Hz, C***H***$_{arom}$), 7.54 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.64 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.65 (bs, 1H, N***H***), 7.98 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 4.7 (***C***H$_3$), 14.3 (O***C***H$_{3arom}$), 29.7, 29.8, 29.9, 32.1 (***C***H$_2$), 34.3 (S***C***H$_2$), 126.8, 127.0, 124.8, 113.9 (***C***H$_{arom}$), 116.3 (S***C***$_{napht}$), 131.9 (NH***C***$_{napht}$), 132.7, 134.7 (***C***H$_{napht}$) ,130.9 (***C***$_{arom}$), 133.9, 146.2 (***C***$_{napht}$), 157.3 (NH***C***), 180.8, 181.0 (***C***=O). MS (+ESI): *m/z* = 565 $[M+H]^+$, $C_{35}H_{49}NO_3S$ (563.85). Calcd.: C 74.56; H 8.76; N 2.28; S 5.69. Found: C 75.12; H 8.43; N 2.55; S 5.75.

2-[(3,5-Dimethoxyphenyl)amino]-3-(octadecylthio)naphthalene-1,4-dione (6i): Compound **6i** was synthesized from 0.20g (0.582 mmol) 2-(3,5-dimethoxyphenylamino)-3-chloronaphthalene-1,4-dione **3i** and 0.167g (0.582 mmol) octadecanethiol **4b** using Na_2CO_3 as base according to the general procedure. IR: 3316 (NH), 3051 ($CH_{arom.}$), 2915, 2848 ($CH_{aliph.}$), 1664, 1632 (C=O), 1593, 1553 (C=C). ^{1}H NMR: 0.79–0.83 (t, 3H, *J* = 6.83 Hz,C***H***$_3$), 1.09–1.32, 1.56 (m, 32H, C***H***$_2$), 2.42–2.45 (t, 2H, *J* = 7.32 Hz, SC***H***$_2$), 3.73 (bs, 3H, OC***H***$_{3arom}$), 3.75 (bs, 3H, OC***H***$_{3arom}$), 6.37 (d, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 6.41 (bs, 1H, *J* = 7.32 Hz, C***H***$_{arom}$),6.82 (d, 1H, *J* = 7.32 Hz, C***H***$_{arom}$), 7.55 (t, 1H, *J* = 7.56 Hz, C***H***$_{arom}$), 7.64 (t, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 7.66 (bs, 1H, N***H***), 7.96 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$), 8.07 (d, 1H, *J* = 7.56 Hz, C***H***$_{napht}$). ^{13}C NMR: 4.7 (***C***H$_3$), 14.3 (OCH$_{3arom}$), 28.9, 29.6, 29.8, 29.9, 32.1 (***C***H$_2$), 34.0 (S***C***H$_2$), 103.3, 99.0 (***C***H$_{arom}$), 121.0 (S***C***$_{napht}$), 134.0 (NH***C***$_{napht}$), 124.9, 126.6, 132.5, 134.5 (***C***H$_{napht}$), 131.0, 114.8 (***C***$_{arom}$), 146.8,

153.7 ($\boldsymbol{C}_{napht}$), 158.5 (NH***C***), 180.8, 181.0 (***C***=O). MS (+ESI): *m/z* = 595 $[M+H]^+$, $C_{36}H_{51}NO_4S$ (593.88). Calcd.: C 72.81; H 8.66; N 2.36; S 5.40. Found: C 72.31; H 9.02; N 2.09; S 5.50.

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Table 1. Summarized reaction conditions for the preparation of **5a-i**, **6a-i**, **7a** and **11a-f**

Compd.	Base	R.time/min	R.Temp./°C	Yield/%	m.p./°C	Color[b]	Solvent[c]
5a	Et_3N	20	RT[a]	96	69-70	Dark blue	PET/$CHCl_3$ (2:1)
5b	Et_3N	25	40	93	79-80	Red	PET/$CHCl_3$ (2:1)
5c	Na_2CO_3	25	40	91	81-82	Red	PET/$CHCl_3$ (2:1)
5d	Na_2CO_3	40	60	85	71-72	Red	PET/$CHCl_3$ (2:1)
5e	Na_2CO_3	20	RT[a]	91	79-80	Dark blue	PET/$CHCl_3$ (2:1)
5f	Na_2CO_3	20	RT[a]	92	68-69	Dark red	PET/$CHCl_3$ (2:1)
5g	K_2CO_3	15	40	75	76-77	Red	PET/$CHCl_3$ (3:1)
5h	K_2CO_3	25	60	70	58-59	Dark blue	PET/$CHCl_3$ (3:1)
5i	Na_2CO_3	45	70	72	71-72	Dark blue	PET/$CHCl_3$ (2.5:1)
6a	Et_3N	20	RT[a]	96	75-76	Dark blue	PET/$CHCl_3$ (2:1)
6b	Et_3N	25	40	93	86-87	Red	PET/$CHCl_3$ (2:1)
6c	Na_2CO_3	25	40	91	86-87	Red	PET/$CHCl_3$ (2:1)
6d	Na_2CO_3	40	60	85	73-74	Red	PET/$CHCl_3$ (2:1)
6e	Na_2CO_3	20	RT[a]	91	79-80	Dark blue	PET/$CHCl_3$ (2:1)
6f	Na_2CO_3	20	RT[a]	92	74-75	Dark red	PET/$CHCl_3$ (2:1)
6g	K_2CO_3	15	40	75	69-71	Red	PET/$CHCl_3$ (3:1)
6h	K_2CO_3	15	60	70	77-78	Dark blue	PET/$CHCl_3$ (3:1)
6i	Na_2CO_3	45	70	72	73-74	Dark blue	PET/$CHCl_3$ (2.5:1)

7a	Na_2CO_3	45	40	55	91-93	Yellow	PET/$CHCl_3$ (5:2)
11a	Na_2CO_3	30	RT[a]	87	64-65	Orange	PET/$CHCl_3$ (2.5:1)
11b	Na_2CO_3	60	80	78	64-65	Dark red	$CHCl_3$
11c	Na_2CO_3	60	80	83	60-61	Red	PET/$CHCl_3$ (2.5:1)
11d	Na_2CO_3	30	RT[a]	84	66-67	Orange	PET/$CHCl_3$ (2.5:1)
11e	Na_2CO_3	60	70	81	58-59	Dark red	$CHCl_3$
11f	Na_2CO_3	60	90	80	63-64	Red	PET/$CHCl_3$ (2.5:1)

[a] RT = Room temperature; [b] Solid state; [c] for column chromatography.

Table 2. UV-visible absorption data for **5a-i**, **6a-i** and **11a-f**

Compd.	**λmax in nm (log ε)**	
	$CHCl_3$	**PET**
5a	518(3.42) 284(4.27) 241(4.05)	513(3.37) 294(4.19)
5b	512(3.89) 286(3.80) 234(3.63)	507(3.13) 292(3.95)
5c	485(3.05) 282(3.89) 234(3.72)	484(2.86) 286(3.60)
5d	526(3.42) 289(4.30) 240(4.27)	519(4.40) 295(5.25)
5e	513(2.67) 282(3.55) 241(3.36)	515(3.59) 296(4.38)
5f	520(3.18) 285(4.02) 241(3.82)	515(3.23) 292(3.95)
5g	517(3.31) 288(4.33) 241(4.45)	512(3.39) 293(4.19)
5h	529(3.40) 282(4.26) 240(4.10)	520(3.12) 285(3.90)

5i	539(2.97) 289(3.81) 241(3.60)	532(3.18) 293(3.93)
6a	515(3.54) 283(4.40) 243(4.19)	512(3.03) 293(3.87)
6b	512(3.08) 287(3.92) 241(3.75)	509(2.88) 292(3.71)
6c	487(3.83) 283(4.66) 232(4.40)	483(2.66) 284(3.54)
6d	528(3.10) 289(3.98) 240(4.00)	520(2.52) 287(3.42)
6e	514(3.24) 283(4.11) 239(3.93)	512(2.83) 291(3.66)
6f	524(3.24) 284(4.09) 241(3.85)	516(3.09) 289(3.91)
6g	513(2.78) 281(3.64) 242(3.40)	504(2.46) 290(3.26)
6h	531(3.88) 282(4.74) 241(4.55)	526(2.82) 288(3.65)
6i	538(2.81) 288(3.65) 241(3.47)	529(3.11) 287(3.92)
11a	490(3.49) 284(4.29) 232(4.07)	490(3.39) 286(4.12)
11b	478(3.34) 282(4.17) 232(3.94)	490(3.14) 289(3.84)
11c	491(3.44) 284(4.25) 233(4.04)	489(3.34) 286(4.08)
11d	492(3.37) 284(4.17) 234(3.99)	490(2.89) 284(3.66)
11e	478(3.09) 282(3.93) 234(3.74)	489(3.94) 285(4.67)
11f	492(3.13) 283(3.94) 236(3.77)	490(3.60) 286(4.34)

Table 3. Fluorescence data in $CHCl_3$ of **3a-b**, **3g**, **5a-b**, **5e-g**, **6b-d**, **6h-i**, **11c-e**.

Compd.	**λmax (ex.) in nm**	**λmax (em.) in nm**
3a	261, 313	521, 623
3b	248, 382	494, 763

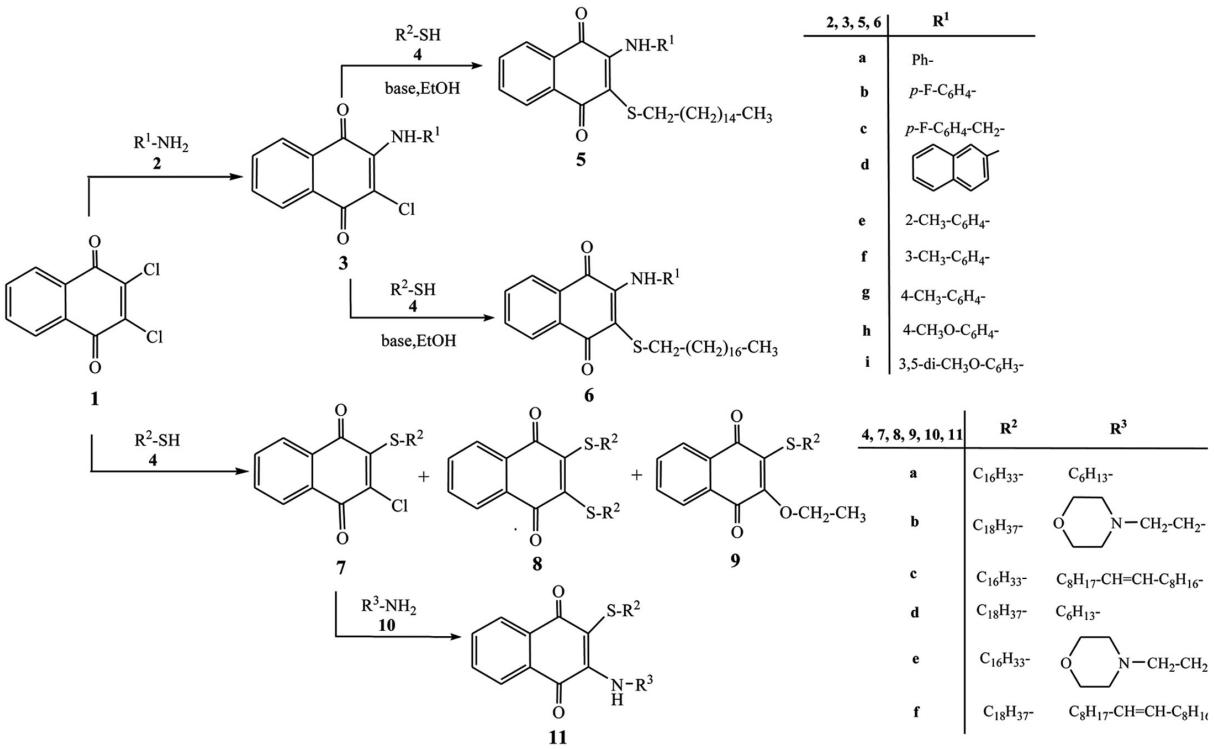
3g	253, 312	506, 622
5a	255, 395	506, 789
5b	252, 386	500, 771
5e	254, 405	507, 809
5f	253, 385	506, 769
5g	261, 319	521, 638
6b	254, 382	507, 763
6c	260, 391	522, 782
6d	256, 261	508, 521
6h	276, 349	548, 697
6i	254, 382	506, 762
11c	254, 353	505, 703
11d	253, 373	506, 746
11e	254, 381	508, 762

Table 4. Voltammetric parameters of **1**, **5g**, **6b**, **6h**, **11c,d** in DMF/TBAP 0.1 M, v = 0.1 V s^{-1}.

Compound	$-(E_{pc})^a$	$-(E_{pa})^a$	$-(E_{1/2})^a$	$(\Delta E_p)^b$	$(i_{pc}/i_{pa})^c$
1	0.287 [d], 1.074 [d]	0.189 [d], 0.973 [d]	0.238, 1.023	0.097, 0.099	0.992, 2.034
5g	0.537 [d], 1.152	0.459 [d] –	0.498 –	0.078 –	1.484 –
6b [e]	0.523 [d], 1.114	0.454 [d] –	0.489 –	0.069 –	1.709 –
6h	0.566 [d], 1.153	0.477 [d] –	0.522 –	0.089 –	1.276 –
11c	0.668 [d], 1.201	0.465 [d] –	0.567 –	0.203 –	2.196 –
11d	0.659 [d], 1.171	0.576 [d] –	0.618 –	0.083 –	0.937 –

[a] Peak potential (V *vs.* Ag/AgCl) at room temperature as determined by cyclovoltammetry at a GC electrode and given without *i*R drop correction, $E_{1/2}$ [approximated by $(E_{pa} + E_{pc})/2$] in V *vs.* Ag/AgCl; supporting electrolyte tetrabutylammonium perchlorate (0.1 M) in DMF, scan rate 0.1 V s^{-1} concentration of compounds 10^{-4} M. [b] $(E_{pa} - E_{pc})$ in V. [c] Cathodic *vs*. anodic peak current ratio. [d] Reversible wave. [e] an additional cathodic peak is observed at –0.003 V.

Scheme 1



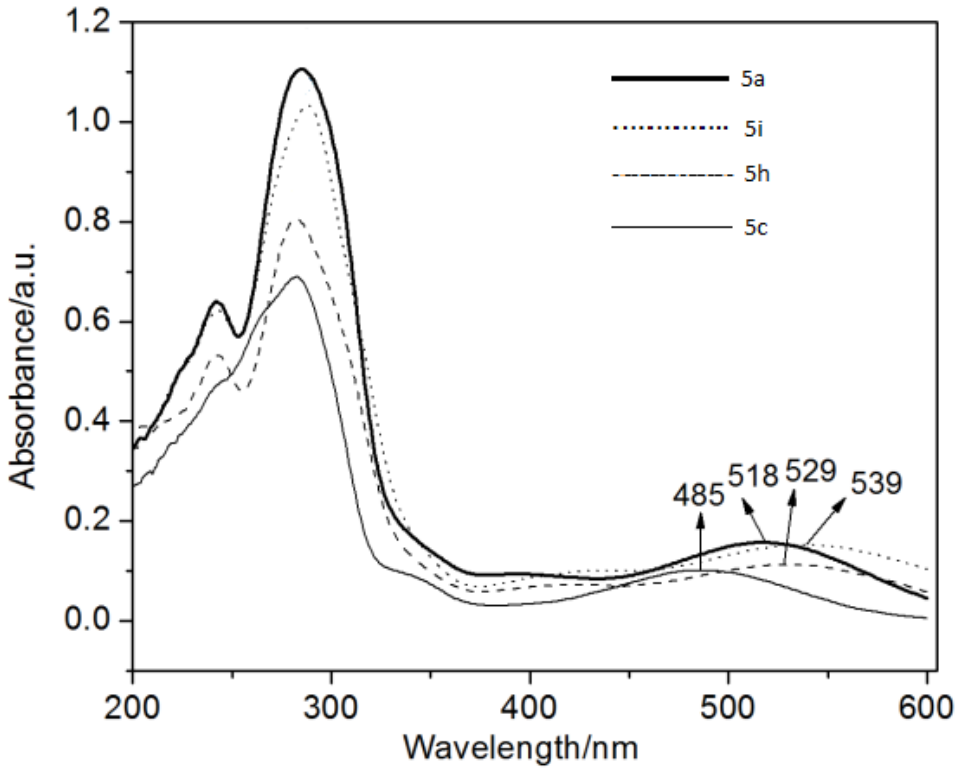


Figure 1. Absorption spectra of **5a**, **5c**, **5h** and **5i** in $CHCl_3$.

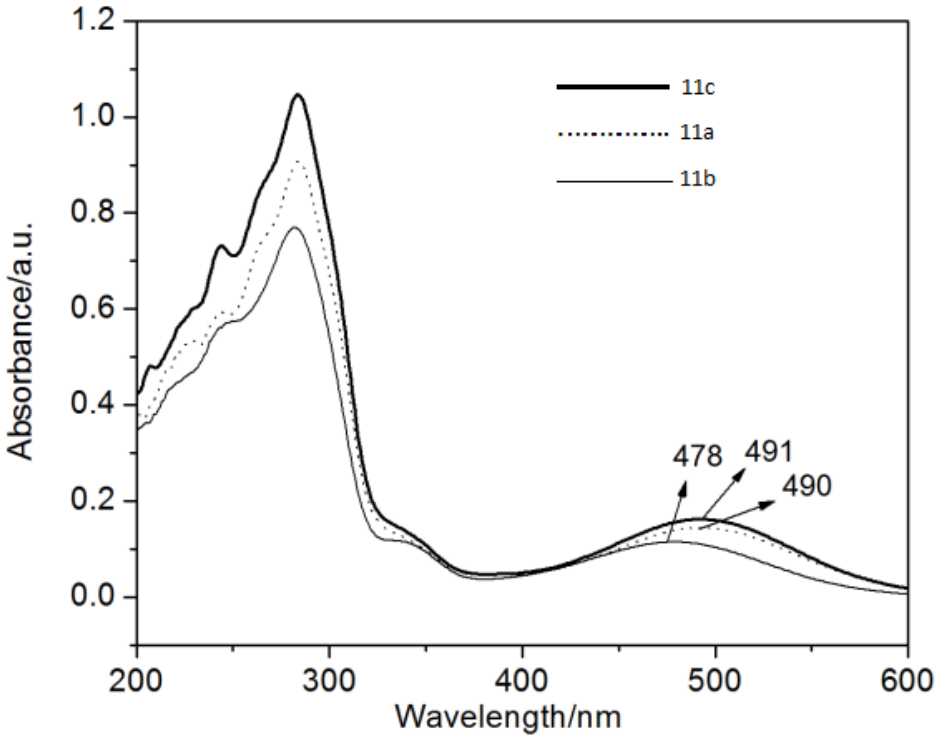


Figure 2. Absorption spectra of **11a-c** in $CHCl_3$.

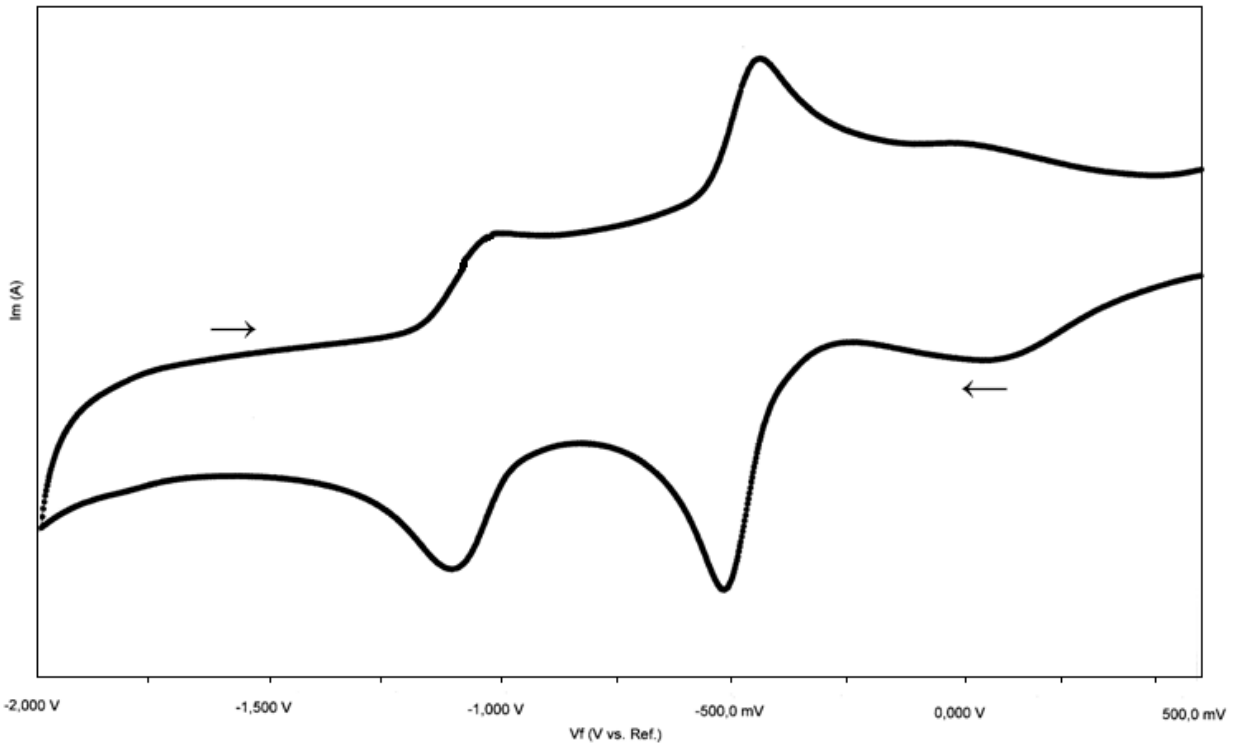


Figure 3. Cyclic voltamogram of **6b** in DMF obtained by using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte at a scan rate of v = 0.1 V s^{-1}.

FIGURE CAPTIONS

Figure 1. Absorption spectra of **5a**, **5c**, **5h**, and 5**i** in $CHCl_3$.

Figure 2. Absorption spectra of **11a-c** in $CHCl_3$.

Figure 3. Cyclovoltamogram of **6b** in DMF obtained with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte at a scan rate of v = 0.1 V s^{-1}.

TABLE CAPTIONS

Table 1. Summarized reaction conditions for the preparation of **5a-i**, **6a-i**, **7a** and **11a-f**.

Table 2. UV-Visible absorption data for **5a-i**, **6a-i** and **11a-f**.

Table 3. Fluorescence data in $CHCl_3$ of **3a-b**, **3g**, **5a-b**, **5e-g**, **6b-d**, **6h-i**, **11c-e**.

Table 4. Voltammetric parameters of **1**, **5g**, **6b**, **6h**, **11c,d** in DMF/TBAP 0.1 M, v = 0.1 V s^{-1}.

