A Convenient Synthesis of Novel 20-, 23-, and 26-Membered Macrocyclic Oxathiadibenzo- and Oxathiadinaphthalenocrown Ethers, Part 1

Muhammad Ashram

Chemistry Department, College of Science, Mutah University, Mutah, Al-Karak, Jordan

Reprint requests to Dr. Muhammad Ashram. E-mail: ashram_1961@yahoo.com

Z. Naturforsch. **60b,** 891 – 900 (2005); received March 7, 2005

A series of novel oxathiadibenzo- and oxathiadinaphthalenocrown ethers **1 – 18** have been successfully synthesized in good yield and in a simple way. They were characterized by NMR, mass spectroscopy and elemental analysis.

Key words: Fullerenes, Macromolecules, Crown Ethers, Oxathiacrown Ethers

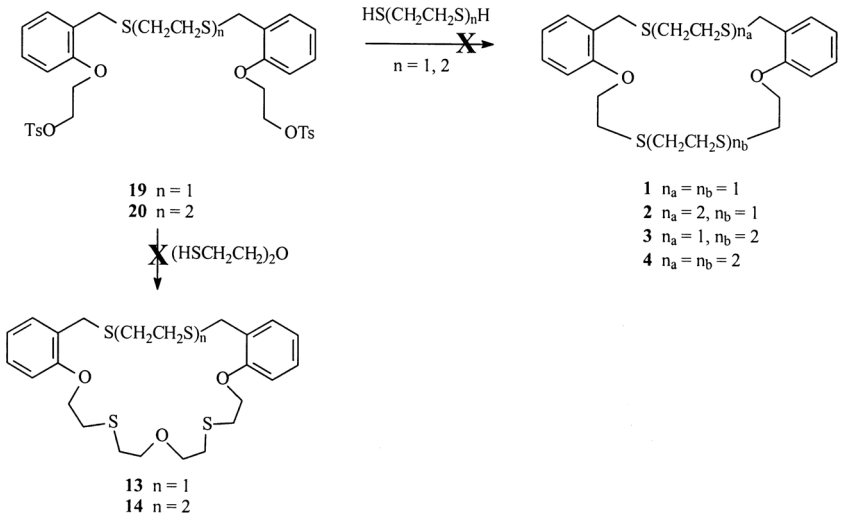
Introduction

Fullerenes appeared as third generation of carbon clusters after graphite and diamond [1]. Several methods have been developed and applied for the separation of specific size and/or isomers of fullerenes from mixtures [2].

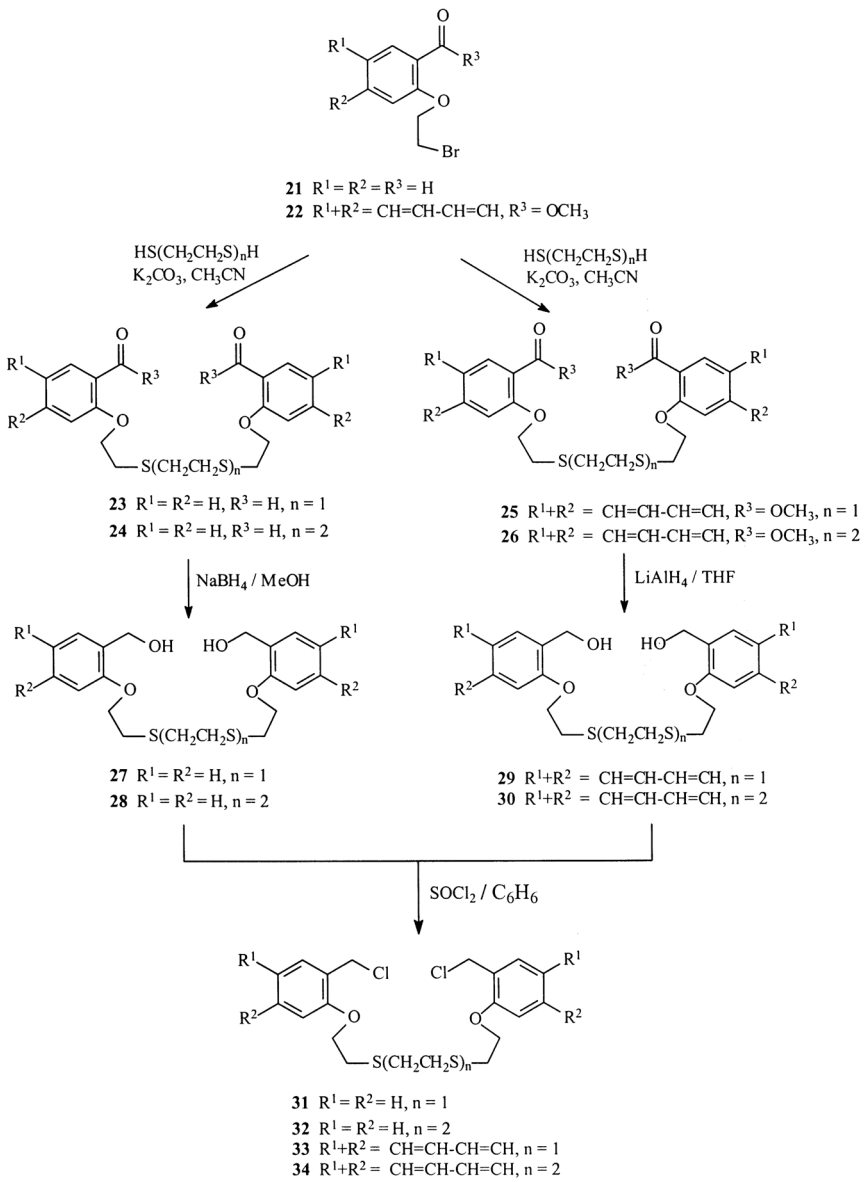
The supramolecular (*i. e.*, non-covalent or ionic) complexation of fullerenes with a variety of macromolecule hosts is a subject of extensive ongoing interest [3 – 15]. It has been shown that dibenzo-24-crown-8 forms an inclusion complex with C_{60} in preference to C_{70} [16] while azacrown ethers form a complex with C_{70} in preference to C_{60} [17].

As part of our ongoing research towards developing and designing new supramolecules [5, 18, 19] that might be capable to include fullerenes, we undertook a program to synthesize new series of large ring size and deep cavity of crown ethers namely oxathiadibenzocrown ethers (**1 – 4**, **9**, **10**, **13**, **14**, **17**) and oxathiadinaphthalenocrown ethers (**5 – 8**, **11**, **12**, **15**, **16**, **18**) in order to evaluate, in future studies, their potential as suitable new supramolecular hosts for fullerenes.

It has been shown that molecules of large ring size, deep cavity and presence of multiple π-π van der Waals interactions between the electron-rich aromatic ring(s) and the electron-poor fullerenes are of interest in host-guest fullerene chemistry [4]. Therefore, we believe that the above crowns and in particular the ones that contain naphthalene units, could be attractive candidates as receptors for C_{60} or / and C_{70}.



Scheme 1.

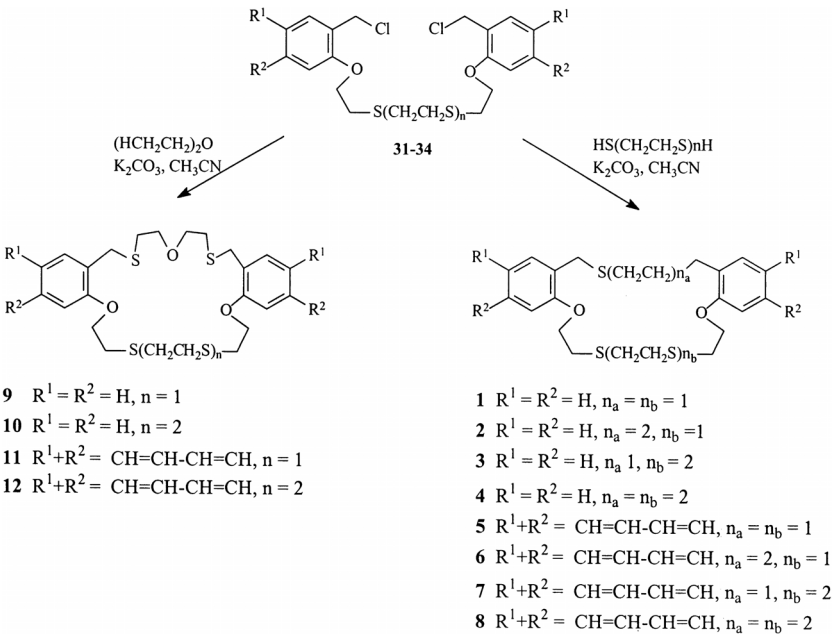


Scheme 2.

Results and Discussion

The first synthetic approach investigated towards thiacrown ethers **1–4**, **13** and **14** is outlined in Scheme 1.

The ditosylates **19** and **20** were envisioned as being suitable precursors to condense with ethane 1,2-dithiol, bis(2-mercaptoethyl)sulfide or bis(2-mercaptoethyl)ether. However all attempts to synthesize the above crown ethers *via* this route failed, affording only resinous products. Fortunately, an alternative route for synthesizing the macrocycles was successful as shown in Schemes 2, 3 and 4. As shown in Scheme 2, reaction of two equivalents of aldehyde **21** or ester **22** with one equivalent of ethane1,2-dithiol or bis(2-mercaptoethyl)sulfide in presence of anhydrous potassium carbonate in refluxing anhydrous acetonitrile for 24 h afforded the compounds **23–26** in quantitative yield. Reduction of dialdehydes **23** or **24** with $NaBH_4$ in methanol and diesters **25** or **26** with $LiAlH_4$ in tetrahydrofuran followed by chlorination with freshly distilled thionyl chloride in dry benzene at room tem-



Scheme 3.

perature produced dichlorides **31 – 34** as key precursors in very good yield. The syntheses of crown ethers **1 – 8** and **9 – 12** were accomplished by reaction of dichlorides **31 – 34** with corresponding aliphatic thiols (Scheme 3). Several attempts of final cyclization of precursors **31** or **32** with an appropriate thiol in presence of potassium hydroxide and ethanol/benzene mixture failed to give the expected macrocycles **1**, **2**, **3** or **4**. However, replacement of the ethanol/benzene solvent mixture by acetonitrile in presence of potassium carbonate at reflux temperature afforded the desired macrocycles **1 – 12** in very good yield. The synthetic procedure for crown ethers **13 – 18** is the same as for crowns **1 – 12** except the use of dichlorides **39** and **40** as key precursors (Scheme 4).

Experimental Section

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 200 MHz and 50 MHz NMR spectrometers, respectively. Unless otherwise noted, samples were dissolved in $CDCl_3$ using TMS as internal standard. All reagents were of analytical grade and used without further purification. Chromatographic separations were carried out on thin layer chromatography (TLC) using silica gel GF254 (Fluka) or column chromatography using silica gel columns (60 – 120 mesh, CDH). All reactions were carried out under dry nitrogen. Ditosylates **19** and **20** and *o*-(2-bromoethoxy)benzaldehyde **21** were prepared according to the literature procedures [20].

General procedure for the synthesis of dialdehydes **23**, **24** *and* **35**

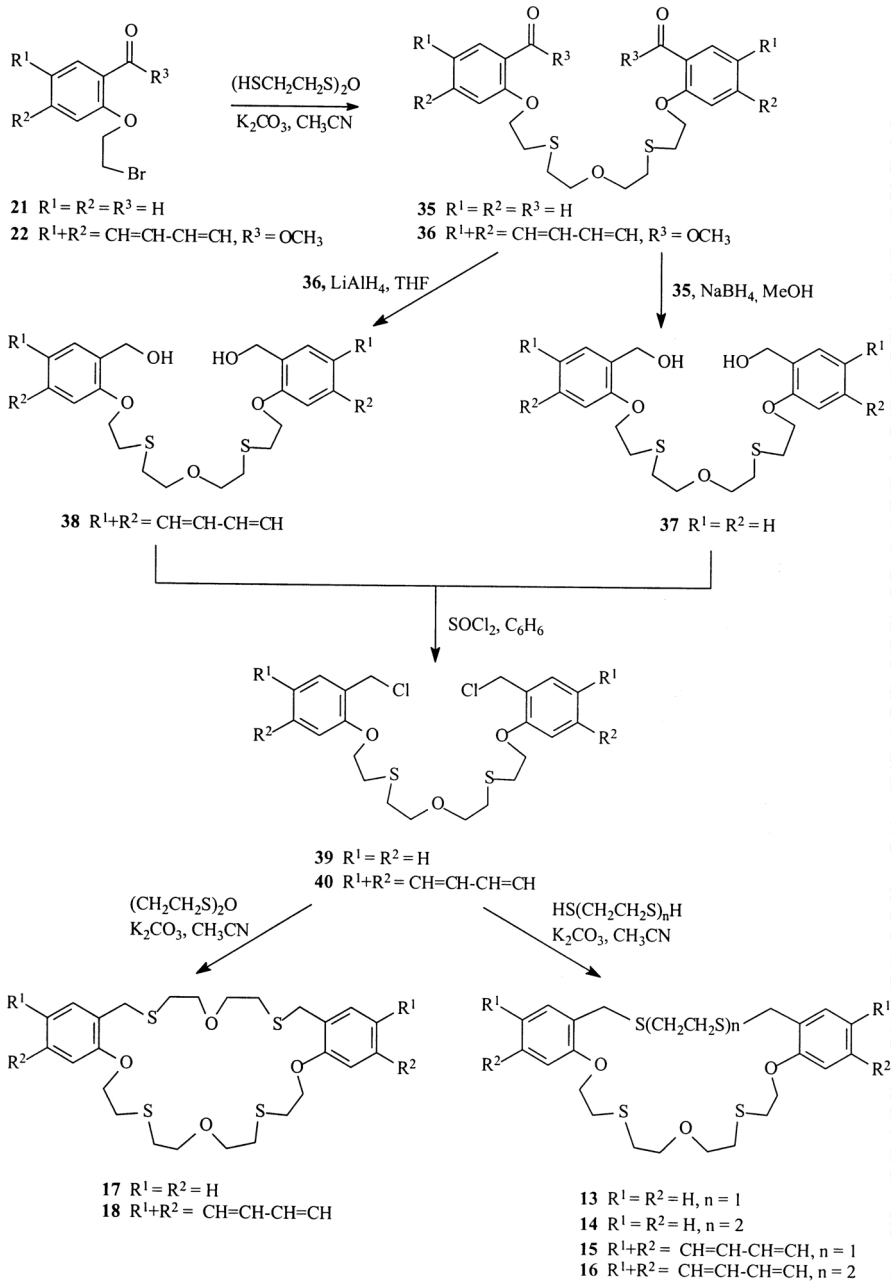
In a 100 ml one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, *o*-(2-bromoethoxy)benzaldehyde **21** (2.0 g, 8.7 mmol), dithiol (4.35 mmol) and anhydrous K_2CO_3 (1.81 g, 13.1 mmol) were mixed with anhydrous CH_3CN (50 ml). The mixture was refluxed for 24 h and then allowed to cool to room temperature. The mixture was filtered and the solid was washed with $CHCl_3$. The combined filtrate was evaporated to dryness to obtain the desired dialdehydes in nearly quantitative yield.

1,14-Diformyl-1,2;13,14-dibenzo-3,12-dioxa-6,9-dithiatetradeca-1,13-diene (**23***)*

Pale yellow solid. Yield 1.65 g (97%). An analytical sample was purified by TLC using ethyl acetate/hexane (2:3) as eluent. – M. p. 93 – 94 °C. – ^{1}H NMR: $\delta = 2.90$ (s, 4 H, SCH_2CH_2S), 3.02 (t, $J = 6$ Hz, 4 H, SCH_2CH_2O), 4.22 (t, $J = 6$ Hz, 4 H, SCH_2CH_2O), 6.90 – 7.06 (m, 4 H), 7.52 (t, $J = 3$ Hz, 2 H), 7.80 (d, $J = 4$ Hz, 2 H), 10.48 (s, 2 H, CHO). – ^{13}C NMR: $\delta = 30.1$, 33.0, 68.6, 113.0, 121.4, 125.0, 128.8, 135.6, 160.6, 189.5 (C=O). – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{20}H_{22}S_2O_4$: 391.1; found 391.2 (25%).

*1,17-Diformyl-1,2;16,17-dibenzo-3,15-dioxa-6,9,12-trithiaheptadeca-1,16-diene (***24***)*

Pale yellow solid. Yield 1.88 g (95%). An analytical sample was purified by TLC using ethyl acetate/hexane (2:3) as



Scheme 4.

eluent. – M. p. 71 – 72 °C. – ^{1}H NMR: $\delta = 2.82$ (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.04 (t, $J = 6$ Hz, 4 H, SCH_2CH_2O), 4.28 (t, $J = 6$ Hz, 4 H, SCH_2CH_2O), 6.92 – 7.10 (m, 4 H), 7.55 (t, $J = 4$ Hz, 2 H), 7.84 (d, $J = 4$ Hz, 2 H), 10.50 (s, 2 H, CHO). – ^{13}C NMR: $\delta = 30.0$, 32.4, 32.6, 68.2, 112.5, 121.1, 125.2, 128.5, 135.4, 160.1, 189.4 (C=O). – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{22}H_{26}S_3O_4$: 451.1; found 451.2 (65%).

*1,17-Diformyl-1,2;16,17-dibenzo-3,9,15-trioxa-6,12-dithiaheptadeca-1,16-diene (***35***)*

The crude product was purified by column chromatography using ethyl acetate/hexane (2:3) as eluent to give a pale yellow oil. Yield 1.87 g (98%). – ^{1}H NMR: $\delta = 2.79$ (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.02 (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.68 (t, $J = 4$ Hz,

4 H, O*CH*$_2$CH$_2$SCH$_2$CH$_2$OAr), 4.20 (t, J = 4 Hz, 4 H, OCH$_2$CH$_2$SCH$_2$*CH*$_2$OAr), 6.92 – 7.05 (m, 4 H), 7.50 (t, J = 4 Hz, 2 H), 7.83 (d, J = 4 Hz, 2 H), 10.48 (s, 2 H, CHO). – ^{13}C NMR: δ = 31.0, 32.1, 69.1, 71.0, 112.6, 121.0, 124.5, 128.5, 136.1, 160.6, 189.6 (C=O). – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{22}H_{26}S_2O_5$: 435.1; found 435.1 (80%).

General procedure for the synthesis of diols **27**, **28** *and* **37**

To a solution of dialdehyde (4.44 mmol) in THF (50 ml) at room temperature was added $NaBH_4$ (0.68 g, 17.8 mmol). After 10 min the reaction was quenched by adding 5 ml of cold water followed by aqueous 5% HCl until the solution becomes acidic to pH paper. The mixture was extracted with diethyl ether (50 ml). The organic layer was dried over anhydrous $MgSO_4$ and then evaporated to afford the diols in high yield.

*1,16-Dihydroxy-2,3;14,15-dibenzo-4,13-dioxa-7,10-dithiahexadeca-2,14-diene (***27***)*

Pale yellow semi-solid. Yield 1.76 g (98%). – ^{1}H NMR: δ = 2.84 (s, 4 H, SCH$_2$CH$_2$S), 2.89 (s, 2 H, OH), 2.98 (t, J = 4 Hz, 4 H, S*CH*$_2$CH$_2$O), 4.21 (t, J = 4 Hz, 4 H, SCH$_2$*CH*$_2$O), 4.69 (s, 4 H, Ar*CH*$_2$), 6.82 (d, J = 4 Hz, 2 H), 6.92 (t, J = 4 Hz, 2 H), 7.25 (m, 4 H). – ^{13}C NMR: δ = 31.9, 32.2, 62.2, 67.0, 111.3, 121.2, 128.9, 129.0, 130.0, 156.8. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{20}H_{26}S_2O_4$: 395.13; found 377.1 (M$^+$-OH, 100%).

*1,19-Dihydroxy-2,3;17,18-dibenzo-4,16-dioxa-7,10,13-trithianonadeca-2,17-diene (***28***)*

The crude product was washed with benzene to give a colorless solid. Yield 1.8 g (94%). – M. p. 75 – 76.5 °C. – ^{1}H NMR: δ = 2.81 (br, 8 H, SCH$_2$CH$_2$SCH$_2$CH$_2$S), 2.98 (t, J = 4 Hz, 4 H, S*CH*$_2$CH$_2$O), 4.21 (t, J = 4 Hz, 4 H, SCH$_2$*CH*$_2$O), 4.69 (s, 4 H, Ar-*CH*$_2$), 6.88 (d, J = 4 Hz, 2 H), 6.97 (t, J = 4 Hz, 2 H), 7.18 – 7.33 (br, 4 H). – ^{13}C NMR: δ = 31.5, 32.1, 32.2, 61.9, 66.5, 111.1, 121.0, 128.4, 128.5, 129.0, 156.1. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{22}H_{30}S_3O_4$: 455.13; found 437.2 (M$^+$-OH, 100%).

*1,19-Dihydroxy-2,3;17,18-dibenzo-4,10,16-trioxa-7,13-dithianonadeca-2,17-diene (***37***)*

Colorless oil. Yield 1.9 g (97%). – ^{1}H NMR: δ = 2.78 (t, J = 6 Hz, 4 H, OCH$_2$*CH*$_2$SCH$_2$CH$_2$OAr), 3.0 (t, J = 6 Hz, 4 H, OCH$_2$CH$_2$S*CH*$_2$CH$_2$OAr), 3.66 (t, J = 6 Hz, 4 H, O*CH*$_2$CH$_2$SCH$_2$CH$_2$OAr), 4.21 (t, J = 6 Hz, 4 H, OCH$_2$CH$_2$SCH$_2$*CH*$_2$OAr), 4.69 (s, 4 H, Ar*CH*$_2$), 6.85 (d, J = 4 Hz, 2 H), 6.95 (t, J = 4 Hz, 2 H), 7.19 – 7.31 (m, 4 H). – ^{13}C NMR: δ = 31.9, 32.0, 62.1, 67.0, 71.0, 111.0, 120.8, 128.6, 129.0, 129.5, 156.4. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{22}H_{30}S_2O_5$: 439.15; found 421.2 (M$^+$-OH, 100%).

*Synthesis of methyl 3-(2-bromoethoxy)-2-naphthoate (***22***)*

In a 250 ml one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, methyl 3-hydroxy-2-naphthoate (10.1 g, 0.05 mol), 1,2-dibromoethane (93.1 g, 0.5 mol) and anhydrous K_2CO_3 (13.8 g, 0.1 mol) were mixed with anhydrous CH_3CN (500 ml). The mixture was refluxed for 2 days and then cooled to room temperature, filtered and the solid was washed with CH_3CN. The filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:4) as eluent to give **22** as a pale yellow oil 12.8 g (83%). – ^{1}H NMR: δ = 3.75 (t, J = 6 Hz, 2 H, OCH$_2$*CH*$_2$Br), 3.99 (s, 3 H, OCH$_3$), 4.46 (t, J = 6 Hz, 2 H, O*CH*$_2$CH$_2$Br), 7.20 (s, 1 H), 7.41 (t, J = 4 Hz, 1 H), 7.52 (t, J = 4 Hz, 1 H), 7.71 (d, J = 4 Hz, 1 H), 7.82 (d, J = 4 Hz, 1 H), 8.32 (s, 1 H). – ^{13}C NMR: δ = 28.6, 52.2, 69.0, 109.0, 122.1, 125.0, 127.5, 127.9, 128.0, 128.8, 133.0, 135.9, 154.0, 166.6 (C=O). – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{14}H_{13}BrO_3$: 309.0; found 309.0 (M$^+$, 100%).

General procedure for the synthesis of diesters **25**, **26** *and* **36**

In a 250 ml one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, methyl 3-(2-bromoethoxy)-2-naphthoate **22** (3.1 g, 10.0 mmol), dithiol [HS(CH$_2$CH$_2$S)$_n$H, n = 1, 2, or (HSCH$_2$CH$_2$)$_2$O] (5.0 mmol) and anhydrous K_2CO_3 (10.0 mmol) were mixed with anhydrous CH_3CN (150 ml). The mixture was refluxed for 24 h and then allowed to cool to room temperature. The mixture was filtered and the solid was washed with CH_3CN. The combined filtrate was evaporated to dryness to obtain the desired diesters in nearly quantitative yield.

*1,14-Di-(methoxycarbonyl)-1,2;13,14-dinaphthaleno-3,12-dioxa-6,9-dithiatetradeca-1,13-diene (***25***)*

The crude product was washed with diethyl ether to give a pale yellow solid. Yield 2.7 g (98%). – M. p. 108 – 109.5 °C. – ^{1}H NMR: δ = 2.99 (s, 4 H, SCH$_2$CH$_2$S), 3.06 (t, J = 5 Hz, 4 H, S*CH*$_2$CH$_2$OAr), 3.92 (s, 6 H, OCH$_3$), 4.31 (t, J = 5 Hz, 4 H, SCH$_2$*CH*$_2$OAr), 7.20 (s, 2 H), 7.39 (t, J = 4 Hz, 2 H), 7.51 (t, J = 4 Hz, 2 H), 7.70 (d, J = 4 Hz, 2 H), 7.81 (d, J = 5 Hz, 2 H), 8.30 (s, 2 H). – ^{13}C NMR: δ = 31.0, 32.0, 52.5, 69.1, 108.4, 121.6, 124.9, 127.5, 127.7, 128.5, 128.6, 133.0, 136.0, 154.9, 166.5. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{30}H_{30}S_2O_6$: 551.15; found 349 (M$^+$-$C_{12}H_9O_3$, 21%).

*1,17-Di-(methoxycarbonyl)-1,2;16,17-dinaphthaleno-3,15-dioxa-6,9,12-trithiaheptadeca-1,16-diene (***26***)*

The crude product was purified by column chromatogtaphy using ethyl acetate/hexane (3:7) as eluent to give a colorless solid. Yield 2.51 g (81%). – M. p. 80 – 81 °C. – ^{1}H NMR: δ = 2.88 (br, 8 H, SCH$_2$CH$_2$SCH$_2$CH$_2$S), 3.05 (t, J = 4 Hz,

4 H, SCH_2CH$_2$OAr), 3.93 (s, 6 H, OCH$_3$) 4.30 (t, $J = 5$ Hz, 4 H, SCH$_2$$CH_2$OAr), 7.18 (s, 2 H), 7.37 (t, $J = 5$ Hz, 2 H), 7.50 (t, $J = 5$ Hz, 2 H), 7.57 (d, $J = 5$ Hz, 2 H), 7.80 (d, $J = 6$ Hz, 2 H), 8.30 (s, 2 H). – ^{13}C NMR: $\delta = 30.9$, 32.1, 32.3, 52.2, 68.8, 108.0, 121.5, 124.6, 126.2, 127.5, 127.9, 128.0, 132.5, 136.0, 154.5, 166.5 (C=O). – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{32}H_{34}S_3O_6$: 611.15; found 409.1 (M$^+$-$C_{12}H_9O_3$,100%).

*1,17-Di-(methoxycarbonyl)-1,2;16,17-dinaphthaleno-3,9,15-trioxa-6,12-dithiaheptadeca-1,16-diene (***36***)*

Golden oil. Yield 2.88 g (98%). – ^{1}H NMR: $\delta = 2.87$ (t, $J = 4$ Hz, 4 H, OCH$_2$$CH_2SCH_2CH_2$OAr), 3.04 (t, $J = 3$ Hz, 4 H, OCH$_2$CH$_2$SCH_2CH$_2$OAr), 3.70 (t, $J = 4$ Hz, 4 H, OCH_2CH$_2$SCH$_2$CH$_2$OAr), 3.95 (s, 6 H, OCH$_3$), 4.30 (t, $J = 4$ Hz, 4 H, OCH$_2$CH$_2$SCH$_2$$CH_2$OAr), 7.20 (s, 2 H), 7.39 (t, $J = 3$ Hz, 2 H), 7.54 (t, $J = 3$ Hz, 2 H), 7.71 (d, $J = 4$ Hz, 2 H), 7.80 (d, $J = 4$ Hz, 2 H), 8.29 (s, 2 H). – ^{13}C NMR: $\delta = 31.5$, 32.1, 52.1, 69.0, 71.0, 108.0, 122.0, 124.9, 126.6, 127.8, 128.2, 128.5, 132.8, 135.9, 154.3, 166.8 (C=O). – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{32}H_{34}S_2O_7$: 595.17; found 393.1 (M$^+$-$C_{12}H_9O_3$, 100%).

General procedure for the synthesis of diols **29**, **30** *and* **38**

To a suspension of LiAlH$_4$ (0.34 g, 8.9 mmol) in anhydrous THF (100 ml) was added a solution of diester (4.45 mmol) in anhydrous THF (50 ml) at room temperature. The reaction mixture was stirred for 5 – 10 min and then was quenched by adding the mixture into wet diethyl ether (250 ml) at 0 °C. The mixture was then acidified with aqueous 5% HCl. The organic layer was separated and the aqueous layer was extracted with diethyl ether (100 ml). The combined organic layers were dried over anhydrous MgSO$_4$ and evaporated to give the product.

*1,16-Dihydroxy-2,3;14,15-dinaphthaleno-4,13-dioxa-7,10-dithiahexadeca-2,14-diene (***29***)*

Pale yellow solid. Yield 2.0 g (91%). – M. p. 139 – 140 °C. – ^{1}H NMR [D$_6$]-acetone: $\delta = 2.99$ (s, 4 H, SCH$_2$CH$_2$S), 3.11 (t, $J = 3$ Hz, 4 H, SCH_2CH$_2$OAr), 4.20 (t, $J = 2$ Hz, 2 H, OH), 4.34 (t, $J = 4$ Hz, 4 H, SCH$_2$$CH_2$OAr), 4.58 (d, $J = 2$ Hz, 4 H, ArCH_2), 7.29 (s, 2 H), 7.30 – 7.48 (m, 6 H), 7.80 (t, $J = 3$ Hz, 2 H), 7.92 (s, 2 H). – ^{13}C NMR [D$_6$]-acetone: $\delta = 33.6$, 31.6, 60.1, 68.9, 106.5, 124.5, 125.0, 126.6, 127.5, 128.4, 128.8, 132.4, 133.1, 155.0. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{28}H_{30}S_2O_4$: 495.16; found 477.2 (M$^+$- OH, 100%).

*1,19-Dihydroxy-2,3;17,18-dinaphthaleno-4,16-dioxa-7,10,13-trithianonadeca-2,17-diene (***30***)*

Colorless solid. Yield 2.4 g (98%). – M. p. 142 – 143 °C. – ^{1}H NMR [D$_6$]-DMSO: $\delta = 2.60$ (br, 8 H, SCH$_2$CH$_2$SCH$_2$CH$_2$S), 2.71 (t, $J = 3$ Hz, 4 H, SCH_2CH$_2$OAr), 4.05 (t, $J = 3$ Hz, 4 H, SCH$_2$$CH_2$OAr), 4.41 (d, $J = 2$ Hz, 4 H, ArCH_2), 5.02 (br, 2 H, OH), 7.08 (s, 2 H), 7.10 – 7.22 (m, 4 H), 7.53 – 7.61 (m, 4 H), 7.65 (s, 2 H). – ^{13}C NMR [D$_6$]-DMSO: $\delta = 31.0$, 32.5, 32.6, 58.9, 68.2, 106.2, 124.1, 125.6, 126.0, 126.9, 128.0, 128.9, 132.7, 133.5, 154.4. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{30}H_{34}S_3O_4$: 555.16; found 537.1 (M$^+$- OH, 100%).

*1,19-Dihydroxy-2,3;17,18-dinaphthaleno-4,10,16-trioxa-7,13-dithianonadeca-2,17-diene (***38***)*

Colorless solid. Yield 2.18 g (91%). – M. p. 103 – 104 °C. – ^{1}H NMR [D$_6$]-DMSO: $\delta = 2.89$ (t, $J = 4$ Hz, 4 H, OCH$_2$$CH_2SCH_2CH_2$OAr), 3.10 (t, $J = 4$ Hz, 4 H, OCH$_2$CH$_2$SCH_2CH$_2$OAr), 3.71 (t, $J = 4$ Hz, 4 H, OCH_2CH$_2$SCH$_2$CH$_2$OAr), 4.35 (t, $J = 3$ Hz, 4 H, OCH$_2$CH$_2$SCH$_2$$CH_2$OAr), 4.76 (d, $J = 2$ Hz, 4 H, ArCH_2), 5.34 (t, $J = 2$ Hz, 2 H, OH), 7.39 (s, 2 H), 7.41 – 7.56 (m, 4 H), 7.85 – 7.92 (m, 4 H), 7.96 (s, 2 H). – ^{13}C NMR [D$_6$]-DMSO: $\delta = 31.3$, 31.8, 59.0, 68.6, 70.1, 106.5, 124.5, 126.0, 126.7, 127.1, 128.0, 129.0, 132.9, 133.8, 154.8. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{30}H_{34}S_2O_5$: 539.18; found 521.2 (M$^+$- OH, 100%).

General procedure for the synthesis of dichlorides **31** – **34** *and* **39** – **40**

To a solution of diol (1.08 mmol) in anhydrous benzene (150 ml) was added freshly distilled SOCl$_2$ (0.24 ml, 3.2 mmol). The reaction mixture was stirred at room temperature for 0.5 – 1.5 h and then was quenched by adding 20 ml of cold water. The organic layer was washed with water until the aqueous layer was neutral to pH paper. The organic layer was dried over anhydrous MgSO$_4$ and evaporated to give the product.

*1,16-Dichloro-2,3;14,15-dibenzo-4,13-dioxa-7,10-dithiahexadeca-2,14-diene (***31***)*

Colorless solid. Yield 0.38 g (81%). – M. p. 91 – 92 °C. – ^{1}H NMR: $\delta = 2.89$ (s, 4 H, SCH$_2$CH$_2$S), 3.00 (t, $J = 3$ Hz, 4 H, SCH_2CH$_2$OAr), 4.20 (t, $J = 4$ Hz, 4 H, SCH$_2$$CH_2$OAr), 4.66 (s, 4 H, Ar$CH_2$), 6.85 – 7.00 (m, 6 H), 7.35 (t, $J = 3$ Hz, 2 H). – ^{13}C NMR: $\delta = 31.5$, 33.1, 41.5, 68.5, 112.1, 121.1, 126.0, 130.5, 131.0, 156.0. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{20}H_{24}S_2O_2Cl_2$: 431.06; found 395.1 (M$^+$-Cl, 100%).

*1,19-Dichloro-2,3;17,18-dibenzo-4,16-dioxa-7,10,13-trithianonadeca-2,17-diene (***32***)*

The crude product was washed with diethyl ether to give a pale yellow solid. Yield 0.39 g (74%). – M. p. 54 – 55 °C. – ^{1}H NMR: $\delta = 2.81$ (br, 8H, SCH$_2$CH$_2$SCH$_2$CH$_2$S), 2.98 (t, $J = 3$ Hz, 4 H, SCH_2CH$_2$OAr), 4.20 (t, $J = 3$ Hz, 4 H,

SCH_2CH_2OAr), 4.65 (s, 4 H, $ArCH_2$), 6.86 – 7.10 (m, 4 H), 7.28 – 7.40 (m, 4 H). – ^{13}C NMR: $\delta = 31.7$, 32.4, 33.0, 42.0, 68.5, 112.0, 121.2, 126.1, 130.0, 130.6, 157.0. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{22}H_{28}S_3O_2Cl_2$: 491.06; found 455.1 (M^+-Cl, 100%).

*1,16-Dichloro-2,3;14,15-dinaphthaleno-4,13-dioxa-7,10-dithiahexadeca-2,14-diene (**33**)*

Pale yellow solid. Yield 0.43 g (75%). – M. p. 104 – 105 °C. – ^1H NMR: $\delta = 2.99$ (s, 4 H, SCH_2CH_2S), 3.08 (t, $J = 3$ Hz, 4 H, SCH_2CH_2OAr), 4.34 (t, $J = 3$ Hz, 4 H, SCH_2CH_2OAr), 4.79 (s, 4 H, $ArCH_2$), 7.14 (s, 2 H), 7.30 – 7.50 (m, 4 H), 7.66 – 7.78 (m, 4 H), 7.82 (s, 2 H). – ^{13}C NMR: $\delta = 31.1$, 32.9, 42.1, 68.6, 105.8, 124.1, 126.5, 127.0, 128.0, 130.1, 131.0, 132.7, 133.3, 154.9. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{28}H_{28}S_2O_2Cl_2$: 531.1; found 495.0 (M^+- Cl, 100%).

*1,19-Dichloro-2,3;17,18-dinaphthaleno-4,16-dioxa-7,10,13-trithianonadeca-2,17-diene (**34**)*

Pale yellow solid. Yield 0.46 g (73%). – M. p. 94 – 95 °C. – ^1H NMR [D_6]-DMSO: $\delta = 2.62$ (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 2.80 (t, $J = 3$ Hz, 4 H, SCH_2CH_2OAr), 4.08 (t, $J = 3$ Hz, 4 H, SCH_2CH_2OAr), 4.61 (s, 4 H, $ArCH_2$), 7.18 (s, 2 H), 7.08 – 7.28 (m, 4 H), 7.55 – 7.62 (m, 4 H), 7.74 (s, 2 H). – ^{13}C NMR [D_6]-DMSO: $\delta = 31.0$, 32.2, 32.6, 42.9, 68.9, 107.5, 124.9, 127.1, 127.5, 127.8, 128.2, 128.6, 130.9, 134.8, 154.2. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{30}H_{32}S_3O_2Cl_2$: 591.1; found 556.1 (M^+- Cl, 46%).

*1,19-Dichloro-2,3;17,18-dibenzo-4,10,16-trioxa-7,13-dithianonadeca-2,17-diene (**39**)*

The crude product was purified by column chromatography using ethyl acetate/hexane (1:4) to give a colorless oil. Yield 0.36 g (71%). – ^1H NMR: $\delta = 2.84$ (t, $J = 3$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.00 (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.70 (t, $J = 3$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 4.21 (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 4.75 (s, 4 H, $ArCH_2$), 6.89 (d, $J = 3$ Hz, 2 H), 6.96 (t, $J = 3$ Hz, 2 H), 7.29 (d, $J = 2$ Hz, 2 H) 7.37 (t, $J = 2$ Hz, 2 H). – ^{13}C NMR: $\delta = 31.0$, 31.5, 41.2, 68.0, 70.1, 111.5, 120.1, 129.5, 130.0, 156.4. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{22}H_{28}S_2O_3Cl_2$: 476.09; found 476.1 (M^+, 80%).

*1,19-Dichloro-2,3;17,18-dinaphthaleno-4,10,16-trioxa-7,13-dithianonadeca-2,17-diene (**40**)*

Colorless solid. Yield 0.42 g (67%). – M. p. 61 – 62 °C. – ^1H NMR [D_6]-DMSO: $\delta = 2.85$ (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.02 (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.62 (t, $J = 4$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 4.35 (t, $J = 3$ Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 4.88 (s, 4 H, $ArCH_2$), 7.40 (s, 2 H), 7.33 – 7.51 (m, 4 H), 7.79 – 7.87 (m, 4 H), 7.96 (s, 2 H). – ^{13}C NMR [D_6]-DMSO: $\delta = 31.2$, 31.9, 42.7, 68.8, 71.0, 107.8, 124.8, 127.0, 127.4, 127.8, 128.2, 128.4, 131.0, 135.0, 154.5. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{30}H_{32}S_2O_3Cl_2$: 575.12; found 538.2 (M^+- Cl, 100%).

*General procedure for the synthesis of the crown ethers **1** – **18***

Macrocycles **1** – **18** were synthesized under high dilution employing in modified form cyclization procedure of Buter and Kellogg [21]. In a 250 ml three-necked flsask equipped with a magnetic stirrer bar and a reflux condenser and a gas line to maintain a nitrogen atmosphere, anhydrous K_2CO_3 (0.54 g, 3.9 mmol) was suspended in anhydrous CH_3CN (150 ml). To this well-stirred solution at reflux temperature was added a solution containing dithiol [$HS(CH_2CH_2S)_nH$, $n = 1$, 2 or $(HSCH_2CH_2)_2O$] (1.3 mmol) and dichloride **31** – **34**, **39**, **40** (1.3 mmol) in anhydrous CH_3CN (50 ml or 3 ml of DMF + 47 ml of CH_3CN in the case of dichloride **33**, **34** and **40**) was added drop wise over a period of 10 – 12 h. The reaction mixture was further refluxed with stirring for another 12 h. The reaction mixture was filtered and the filtrate was evaporated. The residue was dissolved in $CHCl_3$ (100 ml) and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated. The purification was carried out as indicated by the entries below for the separate compounds.

*2,3;10,11-Dibenzo-1,12-dioxa-5,8,15,18-tetrathiacycloeicosane-2,10-diene (**1**)*

The crude product was purified by column chromatography using ethyl acetate/hexane (1.5:8.5) as eluent to give **1** as a colorless solid. Yield 0.31 g (53%). – M. p. 78 – 79 °C. – ^1H NMR: $\delta = 2.77$ (s, 4 H, SCH_2CH_2S), 2.98 (s, 4 H, SCH_2CH_2S), 3.10 (t, $J = 3$ Hz, 4 H, SCH_2CH_2O), 3.80 (s, 4 H, $ArCH_2$), 4.21 (t, $J = 3$ Hz, 4 H, SCH_2CH_2O), 6.85 (d, $J = 4$ Hz, 2 H), 6.95 (t, $J = 3$ Hz, 2 H), 7.18 – 7.30 (m, 4 H). – ^{13}C NMR: $\delta = 30.6$, 31.5, 32.0, 33.2, 69.0, 112.0, 121.6, 127.2, 128.6, 130.6, 156.4. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{22}H_{28}S_4O_2$: 453.09; found 453.2 (100%). – Analysis for $C_{22}H_{28}S_4O_2$: calcd. C 58.37, H 6.23, S 28.33; found C 58.29, H 6.20, S 28.39.

*2,3;13,14-Dibenzo-1,15-dioxa-5,8,11,18,21-pentathiacyclotricosane-2,13-diene (**2**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **2** as a colorless solid. Yield 0.26 g (39%). – M. p. 105 – 106 °C. – ^1H NMR:

δ = 2.67 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 2.94 (s, 4 H, SCH_2CH_2S), 3.05 (t, J = 4 Hz, 4 H, SCH_2CH_2O), 3.82 (s, 4 H, $ArCH_2$), 4.20 (t, J = 4 Hz, 4 H, SCH_2CH_2O), 6.86 (d, J = 3 Hz, 2 H), 6.95 (t, J = 3 Hz, 2 H), 7.16 – 7.32 (m, 4 H). – ^{13}C NMR: δ = 30.0, 32.0, 32.1, 33.2, 33.4, 68.3, 111.6, 121.5, 127.0, 128.3, 131.0, 156.1. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{24}H_{32}S_5O_2$: 513.1; found 513.2 (100%). – Analysis for $C_{24}H_{32}S_5O_2$: calcd. C 56.21, H 6.29, S 31.26; found C 56.11, H 6.21, S 31.19.

*2,3;10,11-Dibenzo-1,12-dioxa-5,8,15,18,21-pentathiacyclotricosane-2,10-diene (**3**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **3** as a colorless solid. Yield 0.29 g (44%). – M. p. 85 – 86 °C. – ^1H NMR: δ = 2.75 (s, 4 H, SCH_2CH_2S), 2.92 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.00 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.79 (s, 4 H, $ArCH_2$), 4.19 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 6.88 (d, J = 3 Hz, 2 H), 6.94 (t, J = 3 Hz, 2 H), 7.18 – 7.28 (m, 4 H). – ^{13}C NMR: δ = 30.5, 31.5, 31.8, 32.9, 33.2, 69.0, 112.0, 121.3, 127.8, 129.0, 131.0, 156.5. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{24}H_{32}S_5O_2$: 513.1; found 513.2 (100%). – Analysis for $C_{24}H_{32}S_5O_2$: calcd. C 56.21, H 6.29, S 31.26; found: C 56.27, H 6.35, S 31.32.

*2,3;13,14-Dibenzo-1,15-dioxa-5,8,11,18,21,24-hexathiacyclohexacosane-2,13-diene (**4**)*

The crude product was washed with diethyl ether to give **4** as a pale yellow solid. Yield 0.29 g (39%). – M. p. 103 – 104.5 °C. – ^1H NMR: δ = 2.69 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 2.88 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.00 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.79 (s, 4 H, $ArCH_2$), 4.20 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 6.83 (d, J = 2 Hz, 2 H), 6.94 (t, J = 3 Hz, 2 H), 7.15 – 7.30 (m, 4 H). – ^{13}C NMR: δ = 30.1, 31.4, 32.0, 32.2, 32.6, 33.0, 68.8, 112.0, 121.3, 127.5, 128.5, 130.6, 157.0. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{26}H_{36}S_6O_2$: 573.1; found 573.2 (100%). – Analysis for $C_{26}H_{36}S_6O_2$: calcd. C 54.51, H 6.33, S 33.57; found C 54.41, H 6.26, S 33.48.

*2,3;10,11-Dinaphthaleno-1,12-dioxa-5,8,15,18-tetrathiacycloeicosane-2,10-diene (**5**)*

The crude product was washed with diethyl ether to give **5** as a pale yellow solid. Yield 0.34 g (48%). – M. p. 135 – 136 °C. – ^1H NMR: δ = 2.85 (s, 4 H, SCH_2CH_2S), 3.05 (s, 4 H, SCH_2CH_2S), 3.08 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.96 (s, 4 H, $ArCH_2$), 4.35 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 7.10 (s, 2 H), 7.30 – 7.45 (m, 4 H), 7.60 – 7.72 (m, 4 H), 7.74 (s, 2 H). – ^{13}C NMR: δ = 31.5, 31.8, 32.8, 33.5, 69.0, 106.9, 124.2, 126.5, 126.8, 127.8, 128.7, 129.0, 129.9, 133.9, 155.0. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{30}H_{32}S_4O_2$: 553.13; found 553.0 (100%). – Analysis for $C_{30}H_{32}S_4O_2$: calcd. C 65.18, H 5.83, S 23.20; found C 65.11, H 5.76, S 23.10.

*2,3;13,14-Dinaphthaleno-1,15-dioxa-5,8,11,18,21-pentathiacyclotricosane-2,13-diene (**6**)*

The crude product was washed with benzene to give **6** as a pale brown solid. Yield 0.48 g (61%). – M. p. 145 – 146 °C. – ^1H NMR: δ = 2.75 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.00 (s, 4 H, SCH_2CH_2S), 3.11 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.94 (s, 4 H, $ArCH_2$), 4.31 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 7.13 (s, 2 H), 7.31 – 7.48 (m, 4 H), 7.68 – 7.74 (m, 4 H), 7.78 (s, 2 H). – ^{13}C NMR: δ = 30.2, 31.3, 32.0, 32.2, 33.5, 68.5, 106.3, 124.1, 125.2, 125.4, 127.3, 128.6, 128.8, 129.6, 133.8, 154.6. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{32}H_{36}S_5O_2$: 613.13, found 613.2 (100%). – Analysis for $C_{32}H_{36}S_5O_2$: calcd. C 62.71, H 6.09, S 26.15; found C 62.80, H 5.88, S 26.21.

*2,3;10,11-Dinaphthaleno-1,12-dioxa-5,8,15,18,21-pentathiacyclotricosane-2,10-diene (**7**)*

The crude product was purified by column chromatography using $CHCl_3$ as eluent to give **7** as a colorless solid. Yield 0.49 g (63%). – M. p. 136 – 138 °C. – ^1H NMR: δ = 2.79 (s, 4 H, SCH_2CH_2S), 2.92 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.02 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.90 (s, 4 H, $ArCH_2$), 4.29 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 7.08 (s, 2 H), 7.18 – 7.45 (m, 4 H), 7.61 – 7.71 (m, 6 H). – ^{13}C NMR: δ = 31.0, 31.4, 32.0, 32.9, 33.1, 68.8, 106.8, 124.0, 126.2, 126.6, 127.5, 128.8, 129.0, 129.2, 134.0, 154.8. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{32}H_{36}S_5O_2$: 613.13; found 613.0 (100%). – Analysis for $C_{32}H_{36}S_5O_2$: calcd. C 62.71, H 5.92, S 26.15; found C 62.67, H 5.81, S 26.09.

*2,3;13,14-Dinaphthaleno-1,15-dioxa-5,8,11,18,21,24-hexathiacyclohexacosane-2,13-diene (**8**)*

The crude product was washed with benzene to give **8** as a colorless solid. Yield 0.56 g (64%). – M. p. 156 – 158 °C. – ^1H NMR: δ = 2.74 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 2.91 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.08 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 3.92 (s, 4 H, $ArCH_2$), 4.30 (t, J = 3 Hz, 4 H, SCH_2CH_2O), 7.11 (s, 2 H), 7.32 – 7.48 (m, 4 H), 7.63 – 7.75 (m, 6 H). – ^{13}C NMR: δ = 30.8, 31.4, 32.1, 32.2, 32.5, 33.1, 68.8, 106.8, 124.0, 126.2, 126.4, 127.6, 128.5, 128.7, 129.6, 133.7, 154.2. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{34}H_{40}S_6O_2$: 673.13, found 673.0 (100%). – Analysis for $C_{34}H_{40}S_6O_2$: calcd. C 60.68, H 5.99, S 28.58; found C 60.77, H 6.11, S 28.45.

*2,3;13,14-Dibenzo-1,8,15-trioxa-5,11,18,21-tetrathiacyclotricosane-2,13-diene (**9**)*

The crude product was washed with benzene to give **9** as a colorless solid. Yield 0.30 g (47%). – M. p.

83–84 °C. – ^{1}H NMR: δ = 2.70 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 2.98 (s, 4 H, SCH_2CH_2S), 3.05 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.64 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.81 (s, 4 H, $ArCH_2$), 4.20 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OA$), 6.86 (d, J = 4 Hz, 2 H), 6.92 (t, J = 4 Hz, 2 H), 7.14–7.30 (m, 4 H). – ^{13}C NMR: δ = 30.5, 31.2, 31.5, 33.4, 68.6, 70.6, 112.1, 121.3, 127.6, 128.8, 130.9, 156.2. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{24}H_{32}S_4O_3$: 497.12, found 497.2 (100%). – Analysis for $C_{24}H_{32}S_4O_3$: calcd. C 58.03, H 6.49, S 25.82; found C 58.12, H 6.40, S 25.91.

*2,3;13,14-Dibenzo-1,8,15-trioxa-5,11,18,21,24-pentathiacyclohexacosane-2,13-diene (**10**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **10** as a pale yellow solid. Yield 0.48 g (66%). – M. p. 72–73 °C. – ^{1}H NMR: δ = 2.70 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 2.90 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.09 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.62 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.82 (s, 4 H, $ArCH_2$), 4.22 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 6.85 (d, J = 3 Hz, 2 H), 6.92 (t, J = 3 Hz, 2 H), 7.12–7.28 (m, 4 H). – ^{13}C NMR: δ = 31.0, 31.2, 31.8, 32.5, 33.0, 68.9, 70.5, 112.0, 121.0, 127.5, 128.1, 130.5, 157.0. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{26}H_{36}S_5O_3$: 557.13; found 557.2 (100%). – Analysis for $C_{26}H_{36}S_5O_3$: calcd. C 56.08, H 6.52, S 28.79; found C 56.20, H 6.61, S 28.91.

*2,3;13,14-Dinaphthaleno-1,8,15-trioxa-5,11,18,21-tetrathiacyclotricosane-2,13-diene (**11**)*

The crude product was washed with diethyl ether to give **11** as pale yellow solid. Yield 0.43 g (55%). – M. p. 152–153.5 °C. – ^{1}H NMR: δ = 2.75 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.00 (s, 4 H, SCH_2CH_2S), 3.11 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.64 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.96 (s, 4 H, $ArCH_2$), 4.30 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 7.10 (s, 2 H), 7.46–7.52 (m, 4 H), 7.68 (br, 4 H), 7.70 (s, 2 H). – ^{13}C NMR: δ = 30.9, 31.2, 32.6, 33.0, 68.5, 70.5 107.0, 123.8, 126.1, 126.3, 127.2, 128.6, 128.7, 128.9, 133.7, 154.6. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{32}H_{36}S_4O_3$: 597.15; found 597.2 (100%). – Analysis for $C_{32}H_{36}S_4O_3$: calcd. C 64.39, H 6.08, S 21.49; found C 64.31, H 6.17, S 21.61.

*2,3;13,14-Dinaphthaleno-1,8,15-trioxa-5,11,18,21,24-pentathiacyclohexacosane-2,13-diene (**12**)*

The crude product was washed with diethyl ether to give **12** as a colorless solid. Yield 0.61 g (72%). – M. p. 98–99.5 °C. – ^{1}H NMR: δ = 2.75 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 2.91 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 3.08 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.68 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.99 (s, 4 H, $ArCH_2$), 4.31 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 7.12 (s, 2 H), 7.29–7.48 (m, 4 H), 7.70 (br, 4 H), 7.72 (s, 2 H). – ^{13}C NMR: δ = 31.0, 31.2, 32.8, 33.0, 68.9, 70.8, 106.9, 124.0, 126.2, 126.5, 127.6, 128.9, 129.3, 154.3. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{34}H_{40}S_5O_3$: 657.16; found 657.2 (100%). Analysis for $C_{34}H_{40}S_5O_3$: calcd. C 62.16, H 6.14, S 24.40; found C 62.28, H 6.17, S 24.51.

*2,3;10,11-Dibenzo-1,12,18-trioxa-5,8,15,21-tetrathiacyclotricosane-2,10-diene (**13**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **13** as pale yellow solid. Yield 0.25 g (38%). – M. p. 74–75 °C. – ^{1}H NMR: δ = 2.71 (s, 4 H, SCH_2CH_2S), 2.88 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.02 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.75 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.78 (s, 4 H, $ArCH_2$), 4.18 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 6.82 (d, J = 4 Hz, 2 H), 6.91 (t, J = 4 Hz, 2 H), 7.12–7.25 (m, 4 H). – ^{13}C NMR: δ = 30.0, 31.4, 31.6, 31.9, 68.8, 71.5, 112.0, 121.0, 127.4, 128.5, 131.0, 156.2. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{24}H_{32}S_4O_3$: 497.12; found 497.2 (100%). – Analysis for $C_{24}H_{32}S_4O_3$: calcd. C 58.03, H 6.49, S 25.82; found C 58.15, H 6.56, S 25.93.

*2,3;13,14-Dibenzo-1,15,21-trioxa-5,8,11,18,24-pentathiacyclohexacosane-2,13-diene (**14**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **14** as pale yellow solid. Yield 0.27 g (37%). – M. p. 68–69 °C. – ^{1}H NMR: δ = 2.64 (br, 8 H, $SCH_2CH_2SCH_2CH_2S$), 2.85 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.20 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.71 (t, J = 4 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.81 (s, 4 H, $ArCH_2$), 4.16 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 6.82 (d, J = 2 Hz, 2 H), 6.92 (t, J = 2 Hz, 2 H), 7.12–7.29 (m, 4H). – ^{13}C NMR: δ = 30.0, 31.9, 32.0, 32.2, 32.3, 68.1, 71.2, 111.8, 121.2, 127.5, 128.6, 130.9, 156.0. – +APCI MS: *m/z* $[M+1]^+$ calcd. for $C_{26}H_{36}S_5O_3$: 557.13; found 557.2 (100%). – Analysis for $C_{26}H_{36}S_5O_3$: calcd. C 56.08, H 6.52, S 28.79; found C 56.15, H 6.59, S 28.87.

*2,3;10,11-Dinaphthaleno-1,12,18-trioxa-5,8,15,21-tetrathiacyclotricosane-2,10-diene (**15**)*

The crude product was washed with benzene to give **15** as a pale yellow solid. Yield 0.53 g (68%). – M. p. 115–116 °C. – ^{1}H NMR: δ = 2.78 (s, 4 H, SCH_2CH_2S), 2.90 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.10 (t, J = 3 Hz, 4 H, $OCH_2CH_2SCH_2CH_2OAr$), 3.79 (t, J = 3 Hz, 4 H,

OCH_2CH$_2$SCH$_2$CH$_2$OAr), 3.91 (s, 4 H, ArCH_2), 4.30 (t, J = 4 Hz, 4 H, OCH$_2$CH$_2$SCH$_2$$CH_2$OAr), 7.08 (s, 2 H), 7.28 – 7.45 (m, 4 H), 7.62 – 7.75 (br, 6 H). – ^{13}C NMR: δ = 31.0, 31.2, 32.0, 68.9, 71.4 106.6, 124.0, 126.0, 126.3, 127.5, 128.9, 129.0, 129.8, 133.9, 154.4. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{32}H_{36}S_4O_3$: 597.15; found 597.1 (100%). – Analysis for $C_{32}H_{36}S_4O_3$: calcd. C 64.39, H 5.99, S 21.49; found C 64.46, H 6.01, S 21.57.

*2,3;13,14-Dinaphthaleno-1,15,21-trioxa-5,8,11,18,24-pentathiacyclohexacosane-2,13-diene (**16**)*

The crude product was washed with benzene to give **16** as a colorless solid. Yield 0.37 g (43%). – M. p. 133 – 135 °C. – ^{1}H NMR: δ = 2.69 (br, 8 H, SCH$_2$CH$_2$SCH$_2$CH$_2$S), 2.89 (t, J = 3 Hz, 4 H, OCH$_2$$CH_2SCH_2CH_2$OAr), 3.09 (t, J = 3 Hz, 4 H, OCH$_2$CH$_2$SCH_2CH$_2$OAr), 3.72 (t, J = 3 Hz, 4 H, OCH_2CH$_2$SCH$_2$CH$_2$OAr), 3.90 (s, 4 H, ArCH_2), 4.29 (t, J = 3 Hz, 4 H, OCH$_2$CH$_2$SCH$_2$$CH_2$OAr), 7.10 (s, 2 H), 7.28 – 7.42 (m, 4 H), 7.69 (br, 6 H). – ^{13}C NMR: δ = 30.8, 31.8, 32.1, 68.1, 71.4, 106.5, 124.0, 126.5, 126.6, 127.5, 128.8, 128.9, 129.7, 133.9, 154.5. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{34}H_{40}S_5O_3$: 657.16; found 657.2 (100%). – Analysis for $C_{34}H_{40}S_5O_3$: calcd. C 62.16, H 6.14, S 24.40; found C 62.11, H 6.09, S 24.48.

*2,3;13,14-Dibenzo-1,8,15,21-tetraoxa-5,11,18,24-tetrathiacyclohexacosane-2,13-diene (**17**)*

The crude product was purified by TLC using ethyl acetate/hexane (1:4) as eluent to give **17** as pale yellow solid. Yield 0.27 g (38%). – M. p. 54 – 55 °C. – ^{1}H NMR: δ = 2.69 (t, J = 3 Hz, 4 H), 2.90 (t, J = 3 Hz, 4 H), 3.01 (t, J = 3 Hz, 4 H), 3.61 (t, J = 3 Hz, 4 H), 3.72 (t, J = 4 Hz, 4 H), 3.81 (s, 4 H, ArCH_2), 4.18 (t, J = 3 Hz, 4 H), 6.81 (d, J = 2 Hz, 2 H), 6.90 (t, J = 2 Hz, 2 H), 7.18 (d, J = 2 Hz, 2 H), 7.23 (t, J = 2 Hz, 2 H). – ^{13}C NMR: δ = 31.2, 32.0, 32.9, 33.0, 69.9, 71.5, 72.3, 113.0, 122.4, 128.8, 129.5, 130.6, 157.7. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{26}H_{36}S_4O_4$: 541.13; found 541.2 (100%). – Analysis for $C_{26}H_{36}S_4O_4$: calcd. C 57.74, H 6.71, S 23.71; found C 57.65, H 6.66, S 23.63.

*2,3;13,14-dinaphthaleno-1,8,15,21-tetraoxa-5,11,18,24-tetrathiacyclohexacosane-2,13-diene (**18**)*

The crude product was washed with diethyl ether to give **18** as a pale yellow solid. Yield 0.63 g (76%). – M. p. 79 – 80 °C. – ^{1}H NMR: δ = 2.72 (t, J = 3 Hz, 4 H), 2.90 (t, J = 3 Hz, 4 H), 3.09 (t, J = 3 Hz, 4 H), 3.60 (t, J = 3 Hz, 4 H), 3.75 (t, J = 4 Hz, 4 H), 3.94 (s, 4 H, ArCH_2), 4.29 (t, J = 3 Hz, 4 H), 7.09 (s, 2 H), 7.25 – 7.42 (m, 4 H), 7.66 (br, 6 H). – ^{13}C NMR: δ = 31.0, 31.1, 31.3, 32.0, 68.8, 70.9, 71.2, 116.9, 124.0, 126.1, 126.5, 127.5, 128.6, 128.8, 129.5, 133.8, 154.9. – +APCI MS: *m/z* [M+1]$^+$ calcd. for $C_{34}H_{40}S_4O_4$: 641.18; found 641.2 (100%). – Analysis for $C_{34}H_{40}S_4O_4$: calcd. C 63.72, H 6.29, S 20.01; found C 63.80, H 6.23, S 20.11.

Acknowledgement

I thank Ms. Linda Winsor at Memorial University of Newfoundland, Canada for recording the mass spectra reported herein.

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. Huffman, Nature **347**, 354 (1990).
[2] E. C. Constable, Angew. Chem. Int. Ed. Engl. **33**, 2269 (1994).
[3] T. Braun, Fullerene Sci. Technol. **5**, 615 (1997).
[4] S. Shinkai, A. Ikeda, Pure Appl. Chem. **71**, 275 (1999).
[5] S. Mizyed, P. E. Georghiou, M. Ashram, J. Chem. Soc., Perkin Trans 2, 277 (2002).
[6] J. L. Atwood, G. A. Koutsantonis, C. L. Ratson, Nature **368**, 229 (1994).
[7] T. Suzuki, K. Nakashima, S. Shinkai, Chem. Lett. 699 (1994).
[8] T. Andersson, G. Westman, G. Stenhagen, M. Sundahi, O. Wennerstorm, Tetrahedron Lett. **36**, 597 (1995).
[9] M. J. Hardie, P. D. Godfrey, L. C. Ratson, Chem. Eur. J. **5**, 1828 (1999).
[10] J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto, K. Yamaguchi, Angew. Chem. Int. Ed. **40**, 1858 (2001).
[11] M. Numata, A. Ikeda, C. Fukuhara, S. Shinkai, Tetrahedron Lett. **40**, 6945 (1999).
[12] O. Ermer, C. Robke, J. Am. Chem. Soc. **115**, 10077 (1993).
[13] A. Ikeda, H. Hudzu, M. Yoshimura, S. Shinkai, Tetrahedron **56**, 1825 (2000).
[14] N. Komatsu, Org. Biomol. Chem. 204 (2003).
[15] M. Dudič, P. Lhoták, I. Stibor, H. Petřičková, K. Lang, New J. Chem. **28**, 85 (2004).
[16] A. Saha, S. K. Nayak, S. Chottopadhyay, A. K. Mukherjee, J. Phys. Chem. B **107**, 11889 (2003).
[17] K. Datta, M. Banetjee, A. K. Mukherjee, J. Phys. Chem. B **108**, 16100 (2004).
[18] P. E. Georghiou, M. Ashram, H. J. Clase, N. J. Bridson, J. Org. Chem. **63**, 1819 (1998).
[19] M. Ashram, S. Mizyed, P. E. Georghiou, J. Org. Chem. **66**, 1473 (2001).
[20] M. Ashram, J. Chem. Soc., Perkin Trans 2 1662 (2002).
[21] J. Buter, R. M. Kellogg, J. Org. Chem. **46**, 4481 (1981).