Synthesis and Properties of Higher-Order Tetrathiafulvalene Oligomers up to the Dodecamer

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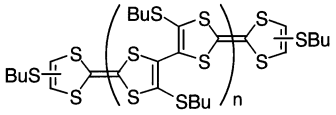
A series of TTF oligomers, the monomer (**1**), the dimer (**2**), the trimer (**3**), the tetramer (**4**), the hexamer (**5**), the octamer (**6**), the decamer (**7**), and the dodecamer (**8**) has been synthesized as novel electrooptical materials. Their structures were well characterized by MS and NMR spectroscopy. GPC measurements indicated that they have extended structures, with the increasing number of TTF units, but comprised various isomeric mixtures due to the *E*/*Z* conformations. A cyclic voltammetric study revealed that these oligomers are highly multiple redox systems, and, in particular, the highest dodecamer demonstrates a reversible, less-structured redox wave involving twenty-four electron oxidation steps. The spin-coated film of the dodecamer exhibits electrochromism of yellow, yellowish green, and blue colors, due to the neutral, radical cationic, and dicationic states of the TTF units, respectively.

Introduction

Recently, well-defined nanoscale oligomeric compounds have attracted much attention in terms of the development of advanced electronic materials.[1] Most of them are based on the extension of π-conjugated rings, such as paraphenylene, thienylene, thienylene-ethynylene, and porphyrin. Tetrathiafulvalene (TTF) and its derivatives are well-known as the best electron donor components for organic conductors,[2] and extension of these compounds to dimers,[3−10] trimers,[4,6−8,10] and tetramers[4,10] has also been studied.[11] However, such extended TTFs are not necessarily such good electron donors as the monomers. Considering the ready oxidation ability of TTF, we thought that TTF oligomers might be useful from the viewpoint of highly multiple redox systems for electrooptical materials rather than good electron donors. We would now like to report the synthesis and properties of a series of TTF oligomers, the monomer (**1**), the dimer (**2**), the trimer (**3**), the tetramer (**4**), the hexamer (**5**), the octamer (**6**), the decamer (**7**), and the dodecamer (**8**) (Figure 1).



1, n = 0, **2**, n = 1; **3**, n = 2; **4**, n = 3; **5**, n = 5; **6**, n = 7; **7**, n =9; **8**, n = 11

Figure 1. Molecular structures of higher-order tetrathiafulvalene oligomers

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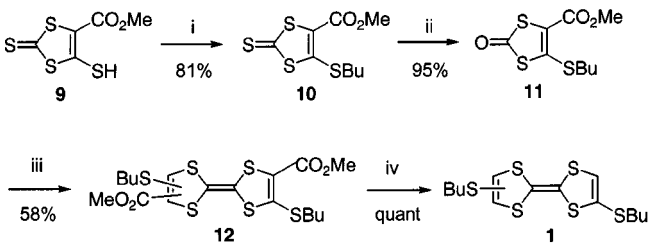
Results and Discussion

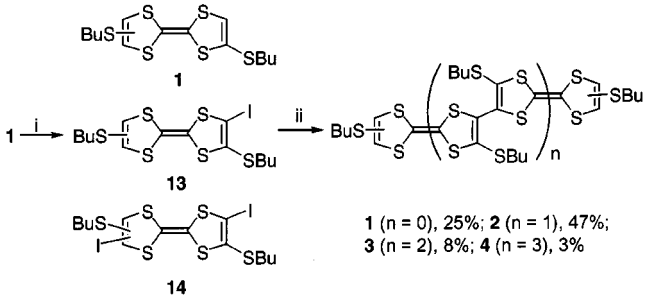
Simple oligomerization of TTF itself results in poor solubility, even at the dimeric step, which hardly leads to the development of the higher oligomers. In order to avoid such a solubility problem, we used 2,6(7)-bis(butylthio)TTF (**1**) as a fundamental unit, where the butylthio groups are very helpful not only in the tractability of higher-order TTF oligomers, due to their enhanced solubilities, but also in the ready separation of the oligomeric homologues by size-exclusion liquid chromatography. According to Scheme 1, compound **1** was obtained in good yield by a reaction sequence which involves initial butylation of methyl 5-mercapto-2-thioxo-1,3-dithiole-4-carboxylate (**9**)[12] to **10**, the subsequent conversion into the ketone **11**, triethyl phosphite-induced coupling to the TTF derivative **12**, and finally lithium bromide-induced decarboxylation to **1**. In the NMR spectrum of **1**, the appearance of two signals for the TTF protons, for the methylene protons adjacent to the sulfur atoms of the butylthio groups, and for the outer TTF olefinic carbons indicates that they comprise a 1:1 mixture of the *E* and *Z* isomers, which are readily interconvertible, as usually seen for such unsymmetrically substituted TTF derivatives.[13]



Scheme 1. Reagents and conditions: i) NaOMe, MeOH, THF, reflux, 1 h, then BuBr, reflux, 12 h; ii) $Hg(OAc)_2$, $CHCl_3$/AcOH, room temp., 12 h; iii) $P(OEt)_3$, toluene, reflux, 12 h; iv) $LiBr{\cdot}H_2O$, DMA, 140−150 °C, 0.5 h

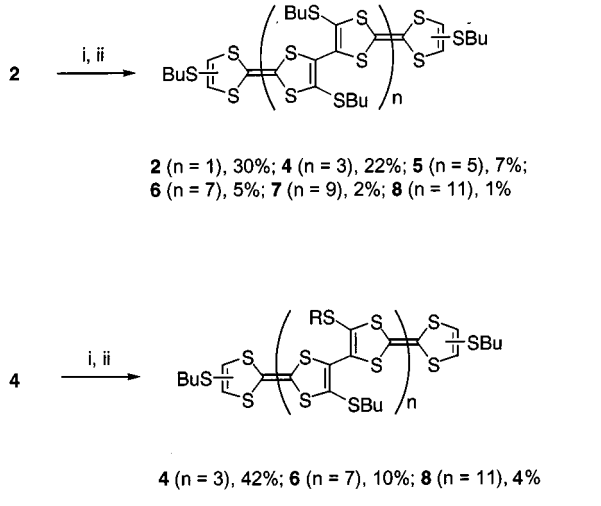
  1434−193X/01/0815−2983 $ 17.50+.50/0

Lithiation of **1** with 1.2 equiv. of LDA in THF at −78 °C, followed by iodination with 1,2-diiodoethane gave a mixture of the unchanged **1**, the mono-iodo derivative **13**, and the di-iodo derivative **14** in a product ratio of 0.35:0.5:0.15 (Scheme 2). When the mixture was subjected to an Ullmann-type coupling with excess copper(I) thiophene-2-carboxylate,[9,14] a random oligomerization reaction smoothly occurred to give a mixture of the dimer **2** (47%), the trimer **3** (8%), and the tetramer **4** (3%), together with recovered **1** (25%). These compounds were readily separated by size-exclusion liquid chromatography. The ^{13}C NMR spectra of these compounds also showed multiple signals due to the coexistence of the *E*/*Z* structural isomers, although the ^{1}H NMR spectra were not so complicated.



Scheme 2. Reagents and conditions: i) 1.2 equiv. LDA, THF, −78 °C, 0.5 h, then ICH_2CH_2I, room temp., overnight; ii) 4 equiv. copper(I) thiophene-2-carboxylate, NMP, room temp., 1 h

A similar oligomerization reaction using the dimer **2** gave a mixture of the tetramer **4** (22%), the hexamer **5** (7%), the octamer **6** (5%), the decamer **7** (2%), and the dodecamer **8** (1%) (Scheme 3). Furthermore, improved yields of the octamer **6** (10%) and the dodecamer **8** (4%) were accomplished by a similar reaction with the tetramer **4**, although higher homologues were not obtained.



Scheme 3. Reagents and conditions: i) 1.2 equiv. LDA, THF, −78 °C, 0.5 h, then ICH_2CH_2I, room temp., overnight; ii) 4 equiv. copper(I) thiophene-2-carboxylate, NMP, room temp., 1 h

All the obtained TTF oligomers are dark-orange oils, which become viscous with the chain extension. The higher order homologues can form environmentally stable films by spin coating (vide infra). The structures of the oligomers were characterized by MS and NMR measurements and elemental analyses. In particular, MALDI-TOF MS spectroscopy was very effective in the identification of the oligomers up to the octamer. However, the molecular ion peaks of the higher homologues could not be detected because of ready fragmentation into small oligomeric units. As shown in Figure 2, there is a good linear relationship between the actual molecular weights and the analytical GPLC molecular weights of the TTF oligomers, clearly supporting the steady elongation of the molecular chain in the oligomeric series. In a detailed comparison, the closeness between the actual molecular weights and analytical GPLC molecular weights using polystyrene standards suggests that the effective volumes of the oligomers resemble those of randomly shaped polystyrenes. In addition, the GPC peaks show broadening relative to the usual single component peaks. These observations can be ascribed to an isomeric mixture of the TTF oligomers due to the *E* and *Z* configurations.

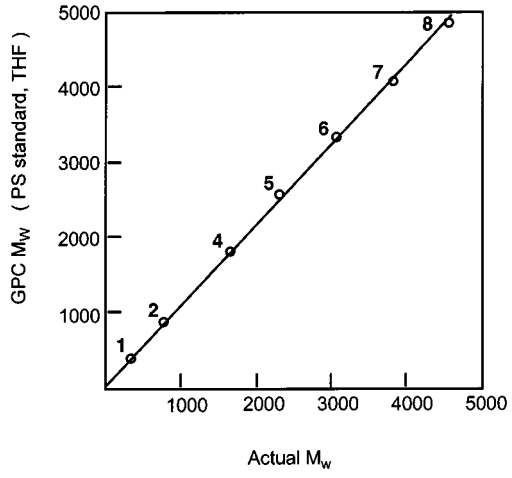


Figure 2. Relationship of molecular weights determined by GPLC in THF using polystyrene standards versus the actual molecular weights of a series of TTF oligomers

Figure 3 shows the cyclic voltammogram of the bis(butylthio)TTF **1** in the sweep from 0.0 to +1.4 V, with two reversible oxidation waves at $E_{1/2}$ = +0.50 and +0.84 V vs. Ag/AgCl in benzonitrile, corresponding to the successive formation of the radical cation and dication species. The voltammogram of the dimer **2** shows two similar oxidation waves, but with splitting for the first wave and broadening for the second wave, which can be ascribed to coulombic interactions between the two linked TTF units. Furthermore, those of the higher TTF oligomers are characterized by ill-defined broad redox waves due to the superposition of multiple oxidation processes. It can be estimated from the peak area that the broad redox processes involve four-electron oxidation for **2**, eight-electron oxidation for **4**,

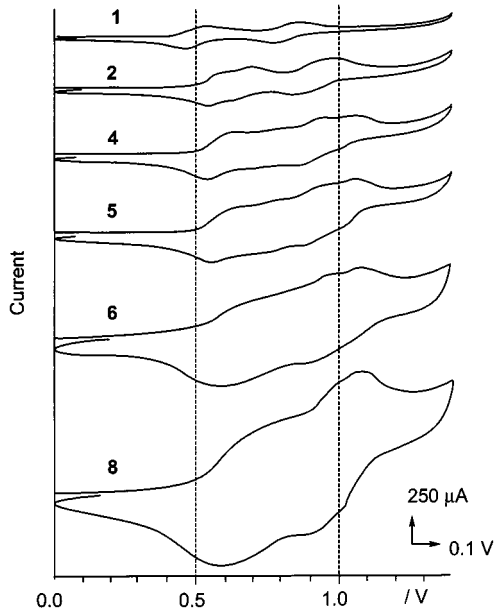


Figure 3. Cyclic voltammograms of TTF oligomers (5×10^{-4} M, vs. Ag/AgCl in benzonitrile containing 10^{-1} M Bu_4NClO_4 at 25 °C)

twelve-electron oxidation for **5**, sixteen-electron oxidation for **6**, and twenty-four-electron oxidation for **8**.

The electronic absorption spectrum of the TTF monomer **1** (Figure 4) exhibits π−π* transition bands at 306, 321, and 380 nm, and the longer wavelength shoulder band is red-shifted to 405 nm due to conjugation for the dimer **2**. However, there are no longer distinct shifts with further extension, even though the intensity still increases with increasing TTF units. This means that there is a very limited length for effective conjugation in the oligomeric TTF chain.

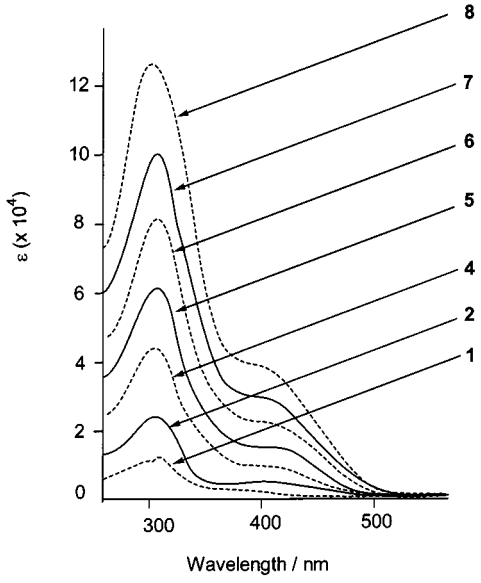


Figure 4. Electronic absorption spectra of TTF oligomers in dichloromethane

The oxidized species of the TTF oligomers show new absorption peaks in the near-infrared region. As Figure 5 demonstrates spectral changes for the dodecamer **8**, controlled oxidation of **8** by addition of different amounts of $FeCl_3$ induced the appearance of two new peaks at 463 and 796 nm in the visible region, which increase up to twelve-electron oxidation, evidently meaning that the new peaks originate from the radical cationic species on each TTF unit; the two peaks correspond to SOMO−LUMO and HOMO−SOMO transitions. Further oxidation up to twenty-four electrons resulted in the decrease of the two peaks and the appearance of a new peak at 704 nm, corresponding to the formation of the dicationic species on each TTF unit. From the change of the absorption spectra at the different oxidation stages, one may thus expect electrochromism for the TTF oligomeric system: when a film of **8** spin-coated on an ITO glass was voltammetrically oxidized in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate, it was yellow in the region of +0 and +0.5 V, turned yellowish green in the region of +0.5 and +1.0 V, and blue in the region of +1.0 and +1.5 V.

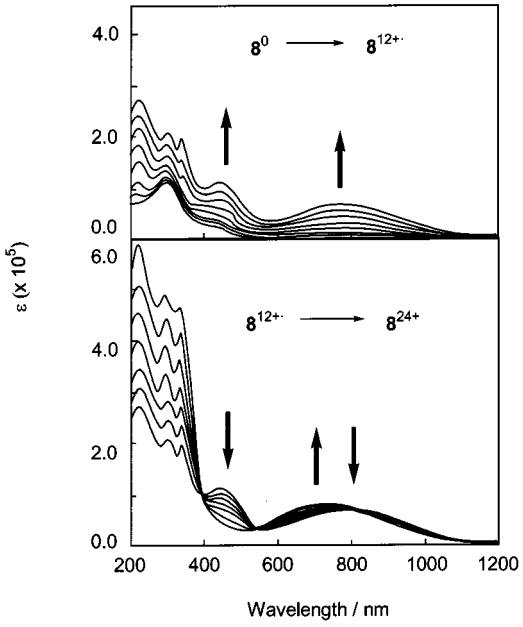


Figure 5. Absorption spectral change of the TTF dodecamer (**8**) in dichloromethane at different oxidation states

Conclusion

In summary, we have succeeded in the synthesis of a series of higher-order TTF oligomers up to the dodecamer. It turned out that these oligomers are highly multiple redox systems that serve as electrooptical materials. In fact, the spin-coated film of the dodecamer shows very pronounced electrochromism involving three reversible changes of color depending on the applied potentials.

Experimental Section

General Remarks: Melting points are uncorrected. All chemicals and solvents were of reagent grade, and all reactions were carried out under a nitrogen atmosphere. NMR spectra were recorded on a JEOL JNM-LA 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in deuterochloroform, with tetramethylsilane as an internal standard. The slash marks in the chemical shifts indicate paired signals due to *E*/*Z* isomers. MS spectra were measured with a Shimadzu QP-2000 (EI) or a Shimadzu KOMPACT-MALDI PROBE (MALDI-TOF) using a dithranol matrix. IR spectra were measured with a Shimadzu FTIR-8100A. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Cyclic voltammetry was carried out on a Hokuto Denko HA-301 potentiostat equipped with a Hokuto Denko HB-104 function generator.

Methyl 5-(Butylsulfonyl)-1,3-dithiole-2-thioxo-4-carboxylate (10): Methyl 5-mercapto-2-thioxo-1,3-dithiole-4-carboxylate (**9**)[12] (27 g, 120 mmol) was added to a solution of sodium methoxide generated in situ from sodium (2.9 g, 130 mmol) and methanol (100 mL) in THF (500 mL), and the mixture was refluxed for 1 h. Butyl bromide (14 mL, 130 mmol) was then added, and the mixture was refluxed for 12 h. After concentration in vacuo, the residue was treated with water (200 mL) and extracted with dichloromethane (3 × 200 mL). After drying over $MgSO_4$ and concentration in vacuo, the residual solid was purified by column chromatography on silica gel with dichloromethane as eluent, followed by recrystallization from chloroform/hexane (1:10) to give yellow needles of **10** (27 g, 81% yield). M.p.: 38−39 °C. − ^{1}H NMR: δ = 0.96 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.48 (sext., ^3J = 7.6 Hz, 2 H, CH_2), 1.74 (quin., ^3J = 7.6 Hz, 2 H, CH_2), 3.00 (t, ^3J = 7.6 Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3). − ^{13}C NMR: δ = 13.4, 21.8, 31.1, 35.2, 52.8, 120.8, 154.0, 158.9, 208.0. − IR (KBr): ṽ = 1707 (C=O), 1073 cm^{-1} (C=S). − MS (EI): *m*/*z* = 280 [M$^+$]. − $C_9H_{12}O_2S_4$ (280.43): calcd. C 38.55, H 4.31; found C 38.48, H 4.28.

Methyl 5-(Butylsulfonyl)-2-oxo-1,3-dithiole-4-carboxylate (11): Mercury(II) acetate (80 g, 250 mmol) was added to a solution of **10** (27 g, 97 mmol), chloroform (500 mL), and acetic acid (100 mL), and the mixture was stirred at room temp. for 12 h and then filtered through celite. After this time the filtrate was concentrated in vacuo, the residue was treated with sat. aq. sodium hydrogen carbonate (600 mL), and extracted with chloroform (3 × 300 mL). After drying over $MgSO_4$ and concentration in vacuo, the residual solid was purified by column chromatography on silica gel with dichloromethane as eluent, followed by recrystallization from chloroform/hexane (1:10) to give colorless needles of **11** (24 g, 95% yield). M.p.: 59−60 °C. − ^{1}H NMR: δ = 0.95 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.47 (sext., ^3J = 7.6 Hz, 2 H, CH_2), 1.72 (quin., ^3J = 7.6 Hz, 2 H, CH_2), 2.98 (t, ^3J = 7.6 Hz, 2 H, CH_2), 3.85 (s, 3 H, CH_3). − ^{13}C NMR: δ = 13.5, 21.8, 31.2, 35.5, 52.7, 111.6, 145.8, 160.3, 187.8. − IR (KBr): ṽ = 1705 (C=O), 1659 cm^{-1} (C=O). − MS (EI): *m*/*z* = 264 [M$^+$]. − $C_9H_{12}O_3S_3$ (264.37): calcd. C 40.89, H 4.57; found C 40.82, H 4.56.

2,6(7)-Bis(butylthio)-3,7(6)-bis(carbomethoxy)tetrathiafulvalene (12): A mixture of **11** (24 g, 91 mmol), triethyl phosphite (20 mL), and toluene (150 mL) was refluxed for 12 h, and concentrated in vacuo. The residue was treated with hexane (100 mL) to precipitate a red solid, which was collected by filtration and recrystallized from chloroform/hexane (1:10) to give red needles of **12** (13 g, 58% yield). M.p.: 121−122 °C. − ^{1}H NMR: δ = 0.952/0.955 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.471/1.479 (sext., ^3J = 7.3 Hz, 4 H, CH_2), 1.704/1.708 (quin., ^3J = 7.3 Hz, 4 H, CH_2), 3.037/3.031 (t, ^3J = 7.3, 4 H, CH_2), 3.801/3.796 (s, 6 H, CH_3). − ^{13}C NMR: δ = 13.5, 14.2, 21.8, 31.44/31.50, 35.17/35.21, 52.3, 109.31/109.36, 113.2/114.0, 147.0/147.8, 160.34/160.35. − IR (KBr): ṽ = 1698 (C=O) cm^{-1}. − MS (EI): *m*/*z* = 496 [M$^+$]. − $C_{18}H_{24}O_4S_6$ (496.75): C 43.52, H 4.87; found C 43.52, H 4.87.

2,6(7)-Bis(butylthio)tetrathiafulvalene (1): A mixture of **12** (8.7 g, 17.5 mmol) and lithium bromide monohydrate (9.1 g, 88 mmol) in *N*,*N*-dimethylacetamide (DMA, 150 mL) was heated and stirred at 140−150 °C for 0.5 h, quickly cooled in a water bath, and then poured into water (300 mL). After stirring for 10 min., the product was extracted with dichloromethane (3 × 100 mL). After drying over $MgSO_4$ and evaporation of the solvents, the residue was purified by column chromatography on silica gel with dichloromethane as eluent to give a dark orange oil of **1** (6.7 g, quant.): ^{1}H NMR δ = 0.92 (t, ^3J = 7.3 Hz, 6 H, CH_3), 1.41 (sext., ^3J = 7.3 Hz, 4 H, CH_2), 1.60 (quin., ^3J = 7.3 Hz, 4 H, CH_2), 2.742/2.745 (t, ^3J = 7.3 Hz, 4 H, CH_2), 6.317/6.318 (s, 2 H, CH). − ^{13}C NMR δ = 13.5, 21.5, 31.4, 35.6, 111.9, 121.45/121.57, 127.29/127.35. − MS (MALDI-TOF): *m*/*z* = 380.79 (calcd. for M$^+$, 379.99). − $C_{14}H_{20}S_6$ (380.67): calcd. C 44.17, H 5.30; found C 44.11, H 5.31.

TTF Oligomers: LDA (1.0 M, 11 mL, 11 mmol) was added at −78 °C to a solution of the monomer **1** (3.4 g, 8.8 mmol) in dry THF (50 mL), and the mixture was stirred at the same temperature for 0.5 h. After this time 1,2-diiodoethane (3.1 g, 11 mmol) was added, the mixture was gradually warmed to room temp. and stirred overnight. Water (200 mL) was then added, and the product was extracted with dichloromethane (3 × 100 mL). After drying over $MgSO_4$ and concentration in vacuo, the residue was chromatographed on silica gel with dichloromethane to give a red oil consisting of a mixture of **1**, **13**, and **14** (0.35:0.5:0.15 by ^{1}H NMR spectroscopy). This oil was treated with copper(I) thiophene-2-carboxylate[14] (8.5 g, 44 mmol) in 1-methyl-2-pyrrolidinone (NMP, 50 mL) at room temp. for 1 h. The mixture was then filtered through celite, the filtrate was treated with water (200 mL) and extracted with dichloromethane (3 × 200 mL). After drying over $MgSO_4$ and evaporation of the solvent, the residue was purified by column chromatography on silica gel with dichloromethane, followed by preparative gel-permeation liquid chromatography (JAIGEL 3H/4H) with chloroform as eluent to give dark orange oils of the tetramer **4** (92 mg, 3% yield), the trimer **3** (267 mg, 8% yield), the dimer **2** (1.6 g, 47% yield), and the monomer **1** (836 mg, 25% recovery) eluted in that order.

A similar reaction starting with the dimer **2** (600 mg) produced an oligomeric mixture of the dimer **2** (184 mg, 30% recovery), the tetramer **4** (133 mg, 22% yield), the hexamer **5** (42 mg, 7% yield), the octamer **6** (23 mg, 5% yield), the decamer **7** (12 mg, 2% yield), and the dodecamer **8** (6 mg, 1% yield), which were also separated by preparative gel-permeation liquid chromatography.

When a similar reaction with the tetramer **4** (400 mg) was carried out, the octamer **6** (40 mg, 10% yield) and the dodecamer **8** (15 mg, 4% yield) were obtained together with recovered **4** (170 mg). The hexamer and the higher homologues are very viscous oils and only sparingly soluble, thus preventing the measurement of ^{13}C NMR spectra.

The Dimer (2): ^{1}H NMR: δ = 0.91 (t, ^3J = 7.3 Hz, 6 H, CH_3), 0.92 (t, ^3J = 7.3 Hz, 6 H, CH_3),. 1.41 (sext., ^3J = 7.3 Hz, 4 H, CH_2), 1.43 (sext., ^3J = 7.3 Hz, 4 H, CH_2), 1.59 (quin., ^3J = 7.3 Hz, 4 H, CH_2), 1.61 (quin., ^3J = 7.3 Hz, 4 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.80 (t, ^3J = 7.3 Hz, 4 H, CH_2), 6.331/6.333 (s, 2 H, CH). − ^{13}C NMR: δ = 13.40, 13.41, 21.26, 21.32, 31.2, 31.4, 35.4, 35.89/35.93, 108.0, 113.90/113.94, 121.3/121.6, 124.04/124.06,

124.14/124.16, 127.3/127.6, 130.25/130.30. − MS (MALDI-TOF): *m/z* = 757.82 (calcd. for M^+, 757.96). − $C_{28}H_{38}S_{12}$ (759.34): calcd. C 44.29, H 5.04; found C 44.04, H 5.05.

The Trimer (3): ^{1}H NMR: δ = 0.92 (t, ^3J = 7.3 Hz, 18 H, CH_3), 1.41 (sext., ^3J = 7.3 Hz, 12 H, CH_2), 1.60 (quin., ^3J = 7.3 Hz, 12 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 8 H, CH_2), 6.33 (s, 2 H, CH). − ^{13}C NMR: δ = 13.6, 21.5, 21.6, 31.5, 31.7, 35.7, 36.2, 108.0, 110.01/110.06, 114.04/114.08, 121.4, 121.6/121.7, 124.0, 124.1, 124.3, 127.39/127.42, 127.6, 130.2, 130.48/130.51. − MS (MALDI-TOF): *m/z* = 1135.81 (calcd. for M^+, 1135.93). − $C_{42}H_{56}S_{18}$ (1138.00): calcd. C 44.33, H 4.96; found C 44.39, H 4.86.

The Tetramer (4): ^{1}H NMR: δ = 0.93 (t, ^3J = 7.3 Hz, 24 H, CH_3), 1.42 (sext., ^3J = 7.3 Hz, 16 H, CH_2), 1.61 (quin., ^3J = 7.3 Hz, 16 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 12 H, CH_2), 6.34 (s, 2 H, CH). − ^{13}C NMR: δ = 13.6, 21.5, 21.6, 31.6, 31.7, 35.7, 36.3, 107.8, 109.81/109.82, 110.0, 110.5, 113.9, 113.99, 114.03, 121.2, 121.5, 123.7, 123.82, 123.84, 123.87, 123.91, 123.94, 124.0, 124.14, 124.16, 124.2, 127.3, 127.5, 130.08/130.11, 130.25, 130.35/130.36, 130.5. − MS (MALDI-TOF): *m/z* = 1516.48 (calcd. for M^+, 1515.91). − $C_{56}H_{74}S_{24}$ (1516.65): calcd. C 44.35, H 4.92; found C 44.15, H 4.93.

The Hexamer (5): ^{1}H NMR: δ = 0.93 (t, ^3J = 7.3 Hz, 36 H, CH_3), 1.42 (sex, ^3J = 7.3 Hz, 24 H, CH_2), 1.61 (quin., ^3J = 7.3 Hz, 24 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 20 H, CH_2), 6.34 (s, 2 H, CH). − MS (MALDI-TOF): *m/z* = 2273.85 (calcd. for M^+, 2273.86). − $C_{84}H_{110}S_{36}$ (2273.97): calcd. C 44.37, H 4.88; found C 44.33, H 4.88.

The Octamer (6): ^{1}H NMR: δ = 0.93 (t, ^3J = 7.3 Hz, 48 H, CH_3), 1.42 (sext, ^3J = 7.3 Hz, 28 H, CH_2), 1.61 (quin, ^3J = 7.3 Hz, 28 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 24 H, CH_2), 6.34 (s, 2 H, CH). − MS (MALDI-TOF): *m/z* = 3030.38 (calcd. for M^+, 3029.98). − $C_{112}H_{146}S_{48}$ (3031.29): calcd. C 44.38, H 4.85; found C 44.62, H 4.82.

The Decamer (7): ^{1}H NMR: δ = 0.93 (t, ^3J = 7.3 Hz, 60 H, CH_3), 1.42 (sext., ^3J = 7.3 Hz, 40 H, CH_2), 1.61 (quin., ^3J = 7.3 Hz, 40 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 36 H, CH_2), 6.34 (s, 2 H, CH). − $C_{140}H_{182}S_{60}$ (3788.61): calcd. C 44.38, H 4.84; found C 44.48, H 4.86.

The Dodecamer (8): ^{1}H NMR: δ = 0.93 (t, ^3J = 7.3 Hz, 72 H, CH_3), 1.42 (sext., ^3J = 7.3 Hz, 48 H, CH_2), 1.61 (quin., ^3J = 7.3 Hz, 48 H, CH_2), 2.75 (t, ^3J = 7.3 Hz, 4 H, CH_2), 2.81 (t, ^3J = 7.3 Hz, 44 H, CH_2), 6.34 (s, 2 H, CH). − $C_{168}H_{218}S_{72}$ (4545.9): calcd. C 44.39, H 4.83; found C 44.38, H 4.74.

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