Low Oxidation Potential Tetrathiafulvalene Analogues Based on 3,4-Dialkoxythiophene π-Conjugating Spacers

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Tetrathiafulvalene analogues involving dihexyloxythiophene (**1**), ethylenedioxythiophene (**2**), and bis(3,4-dihexyloxy-2-thienyl)ethylene (**3**) as conjugating spacer and diversely substituted at the 1,3-dithiole ring (R) have been synthesized. Electronic absorption spectra show the expected decrease of HOMO−LUMO gap when increasing the electron-releasing power of R or the length of the conjugating spacer. Cyclic voltammetry (CV) shows that whereas compounds **1** and **2** are reversibly oxidized into their cation radical and dication through two one-electron steps, for compounds **3** the dication is formed directly via a two-electron transfer. Comparison of the data for compounds **2** and **3** with those of their respective analogues based on thiophene and dithienylethylene shows that introduction of the electron-donating alkoxy groups at the 3 and 4 positions of the thiophene ring produces a 150−200 mV negative shift of the first redox potential ($E°_1$). On the other hand, CV data for compounds **1** and **2** reveal several unusual features such as $E°_1 \approx 0.10$ V/SCE ranking among the lowest known to date and a Coulombic repulsion between positive charges in the dication larger than for the analogue π-donors based on unsubstituted thiophene. These results are interpreted by a major reorganization of the electronic distribution in the donor molecule due to alkoxy groups: the highest electron density moving from the 1,3-dithiole moiety toward the central thiophene ring.

Introduction

Linearly extended tetrathiafulvalene (TTF) analogues built by insertion of a π-conjugating spacer between two 1,4-dithiafulvenyl groups have been subject to intensive studies over the past few years.[1] Interest in these systems was initially motivated by the increased dimensionality and hence improved charge transport properties expected for the corresponding cation radical salts in the general frame of the chemistry of extended TTF analogues.[2] However, more recent work has shown that these hybrid π-conjugated systems are also potentially interesting as small gap organic semiconductors[3] or as building blocks for push−pull or push−push chromophores for second- or third-order nonlinear optics.[4] While the first examples of such π-conjugated systems were built around olefinic[5] or simple heterocyclic systems such as furan, thiophene, or pyrrole,[6] extended TTF analogues involving oligomers of the thiophene,[7] thienylenevinylene,[8] or furylenevinylene[9] series have been recently described. With the lengthening of the spacer group, these compounds appear more and more as end-capped conjugated oligomers in which the HOMO energy level is raised by the electron-releasing effect of the end 1,4-dithiafulvenyl groups (DTF). As shown by many of the above examples, such compounds in which the intrinsic properties of the conjugating spacer are somewhat exalted represent interesting models for analyzing the relative efficiency of various structures of π-conjugating spacers as electron relay.

While a major trend involves the lengthening of a π-conjugating spacer of known structure such as polyenes[10] or polythienylenevinylenes,[8,11] we have recently shown that rigidification of a simple dithienylethylene spacer produces significant changes in the electrochemical behavior of the derived TTF analogues due to a reorganization of the electronic distribution in both the neutral and oxidized state.[12] As a further step we report here the synthesis of new series of TTF analogues built

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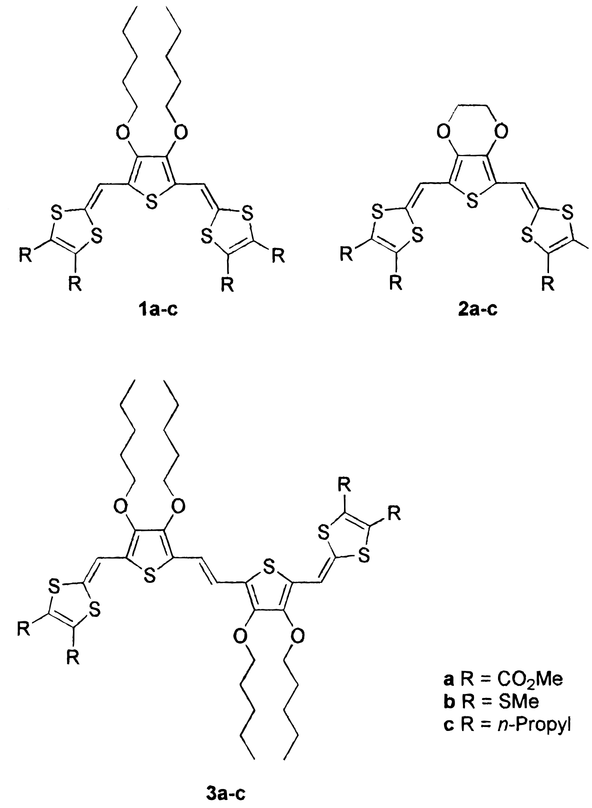
Chart 1



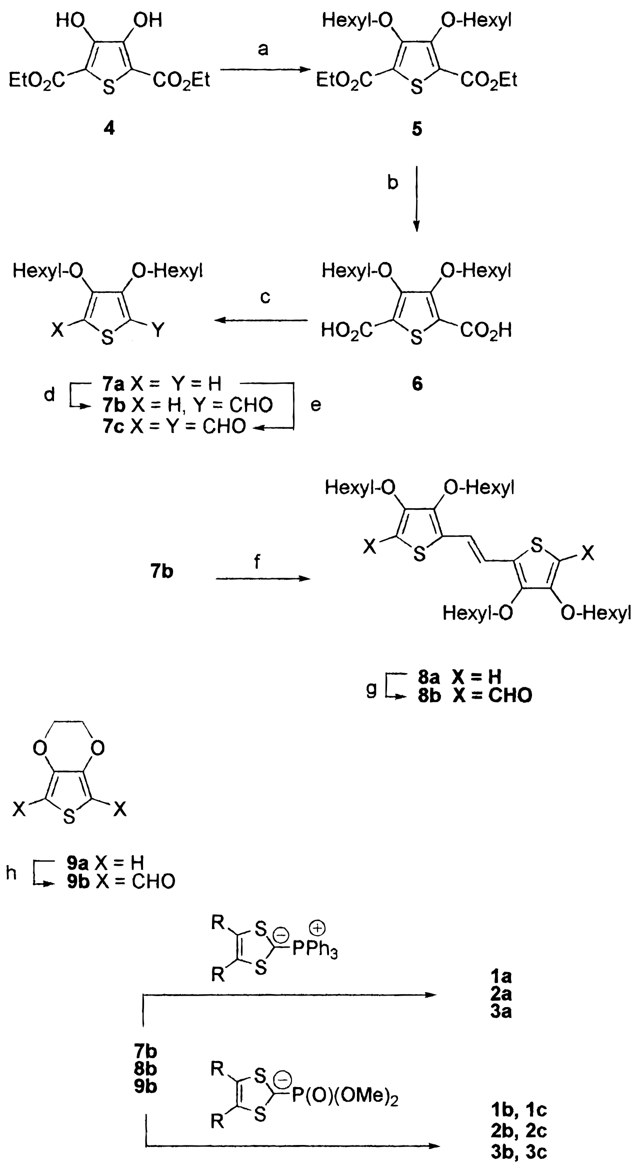
around π-conjugating spacers bearing dialkoxy electron-releasing substituents such as 3,4-dihexyloxythiophene (**1a**−**c**), 3,4-ethylenedioxythiophene (**2a**−**c**), and bis(3,4-dihexyloxy-2-thienyl)ethylene (**3a**−**c**) (Chart 1). Characterization of the structure and electronic properties of these compounds by X-ray diffraction, UV−vis spectroscopy, and cyclic voltammetry shows that the introduction of alkoxy groups on the thiophenic spacer leads to new π-donors with original electronic properties.

Results and Discussion

The synthesis of the new compounds is depicted in Scheme 1.

3,4-Dihydroxythiophene (**4**) prepared by the Hinsberg method[13] was reacted with 1-bromohexane in the presence of K_2CO_3 to give 2,5-dicarboethoxy-3,4-dihexyloxythiophene (**5**) in 82% yield. Saponification of **5** with NaOH and acidification afforded 2,5-dicarboxy-3,4-dihexyloxythiophene (**6**) in 78% yield. 3,4-Dihexyloxythiophene (**7a**) was then obtained in 78% yield by decarboxylation of **6** in the presence of Cu_2O. Vilsmeier formylation of **7a** afforded the monoaldehyde **7b** in 92% yield, while dialdehyde **7c** was prepared in 58% yield by reaction of DMF on the dilithiated derivative of **7a**. McMurry dimerization[14] of monoaldehyde **7b** gave (*E*)-1,2-bis[2-(3,4-dihexyloxythienyl)]ethylene (**8a**) in 72% yield. This compound was then converted into the corresponding dicarbaldehyde (**8b**) by dilithiation and reaction with DMF (yield 66%). 3,4-Ethylenedioxy-2,5-thiophenedicarbaldehyde (**9b**) was prepared from 3,4-ethylenedioxythiophene (**9a**) (Bayer) by reaction of DMF on the dilithiated derivative obtained using an excess of *t*-BuOK and *n*-BuLi.

Scheme 1[a]



[a] (a) $C_6H_{13}Br$, K_2CO_3, (b) NaOH, H_2O, EtOH, (c) Cu_2O, Δ, (d) $POCl_3$/DMF, CH_2Cl_2, (e) *n*-BuLi/DMF, TMEDA/hexane, (f) $TiCl_4$/Zn/pyridine/THF (g) *n*-BuLi, (h) *n*-BuLi, *t*-BuOK/LiBr, DMF/THF.

All target donor molecules **1**−**3a**−**c** have been synthesized by double Wittig (**a**) or Wittig−Horner (**b**,**c**) olefination of the appropriate dicarbaldehyde using the already described procedures and reagents.[6−9,15]

Monocrystals of **2a** have been obtained by slow evaporation of a $CHCl_3$ solution. The X-ray structure was determined from two independent molecules of donor and one molecule of solvent. As shown by the side view in Figure 1, the π-conjugated system in the molecule adopts a planar conformation. For each molecule, the distance between the sulfur atom of thiophene and those of the 1,4-dithiafulvenyl groups (3.074 and 3.122 Å) are intermediate between twice the van der Waals radius of sulfur (3.70 Å) and a covalent S−S bond (2.04 Å). These short distances are characteristic of the strong 1−5 S- - -S

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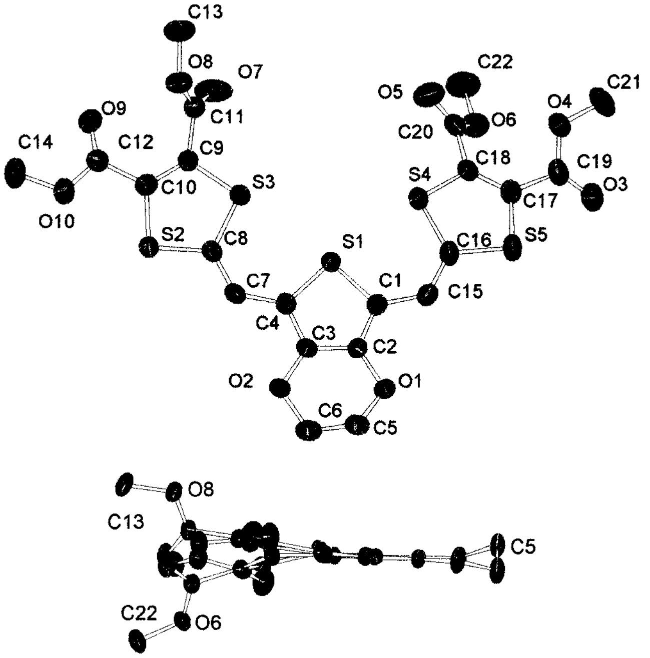

Figure 1. ORTEP view of compound **2a**.

Table 1. UV−Vis Spectroscopic Data for Compounds 1−3a−c in Methylene Chloride

compd	λ_{max} (nm)	λ_{0-0} (nm)	log ϵ_{max}	ΔE (eV)
1a	421	446	4.68	2.77
1b	440	465	4.73	2.66
1c	442	471	4.68	2.62
2a	427	449	4.43	2.75
2b	446	474	4.44	2.61
2c	446	476	4.43	2.60
3a	484	511	4.64	2.42
3b	492	528	4.67	2.34
3c	505	537	4.61	2.30

intramolecular interactions that contribute to stabilize the δ-*syn* conformation of both for the neutral and oxidized states of TTF analogues containing thiophene or furan spacers.[7b,9a,12,16]

Table 1 lists the main UV−vis spectral data for compounds **1**−**3a**−**c** in CH_2Cl_2. As for previous series of extended TTF analogues, the various substituents (R) attached at the DTF moiety have been selected in order to analyze the effects of substitution on the electronic properties of the π-conjugated system.[6−9]

For each type of spacer, the absorption maximum (λ_{max}) shifts bathochromically when the electron-releasing effect of R increases, i.e., in the order CO_2Me, SMe, and *n*-propyl, as already observed for other series of TTF analogues.[6−9] Comparison of the values of the HOMO−LUMO energy gap (ΔE) on the basis of the maximum of the transition of lowest energy (λ_{0-0}) shows that the effect of R is roughly independent of the structure of the spacer. Thus, substitution of the CO_2Me group by the *n*-propyl one produces in every case a 0.12−0.15 eV decrease of ΔE, changes which are comparable to those observed for other donors with spacers of different structure.[6−9]

Comparison of the UV−vis spectra of compounds **2** shows that in addition to the above-discussed red shifts of the absorption bands, the relative intensity of the low energy absorption band increases with electron-donating effect of R, i.e., in the order R = CO_2Me, SMe, *n*-propyl (Figure 2).

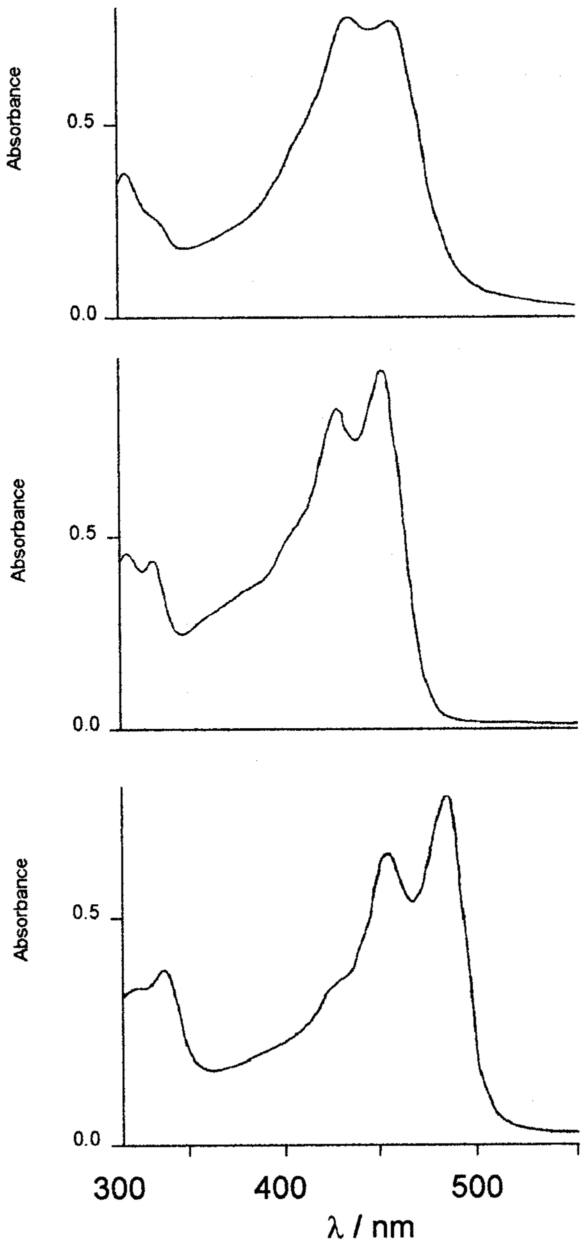

Figure 2. Electronic absorption spectra recorded in methylene chloride: (top) **2a**, (middle) **2b**, (bottom) **2c**.

This enhancement of the resolution of the vibronic fine structure suggests a parallel increase of the rigidity of the molecule. In fact, it has been shown that the strength of the 1−5 intramolecular interactions depends on the electronic effect of R.[16] The fact that this effect is less apparent in the spectra of compounds **3** (not shown) could be related to the larger degree of freedom of the molecule allowed by the central double bond. Further comparison of the data for compounds **1**−**3** shows, as expected, that for compounds of series **3** the extension of the conjugating spacer produces a bathochromic shift of the absorption bands and a ca. 0.30 eV decrease of ΔE.

Cyclic Voltammetry. Table 2 lists the main cyclic voltammetric (CV) data for compounds **1**−**3** in CH_2Cl_2. The CVs of compounds **1** and **2** exhibit two reversible one-

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Table 2. Cyclic Voltammetric Data for Compounds 1–3a–c (ca. 5 × 10^{-4} M in 0.10 M Bu_4NPF_6–CH_2Cl_2)[a]

compd	E°_1 (V)	E°_2 (V)	E°_3	$E^\circ_2 - E^\circ_1$
1a	0.55	0.79		0.23
1b	0.34	0.51		0.17
1c	0.12	0.35		0.23
10a[b]	0.65	0.84		0.19
10b[b]	0.46	0.62		0.16
2a	0.49	0.78		0.29
2b	0.30	0.51		0.21
2c	0.08	0.35		0.27
3a	0.49		1.58	
3b	0.31		1.30	
3c	0.18		1.40	

[a] Pt electrodes, ref SCE, scan rate 100 mV s^{-1}. [b] From ref 8a.

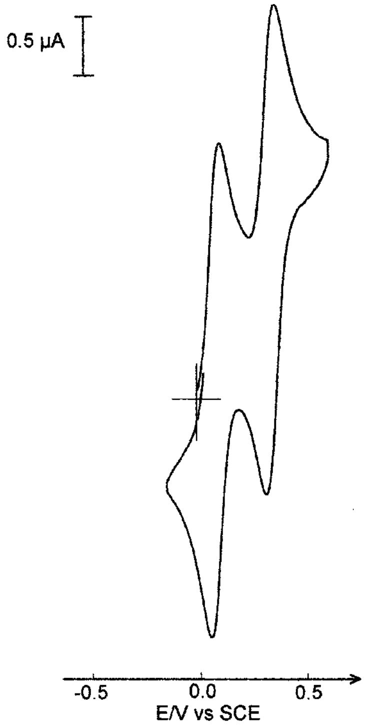

Figure 3. Cyclic voltammogram of compound **1c** ca. 5 × 10^{-4} M in 0.10 M Bu_4NPF_6/CH_2Cl_2. Pt electrodes, ref SCE, $v = 50$ mV s^{-1}.

electron oxidation steps which correspond to the successive generation of the cation radical and dication (Figure 3).

For compounds of series **1** and **2** the two redox potentials E°_1 and E°_2 undergo a 0.40–0.45 V negative shift when increasing the electron-donating effect of R, as observed for other series of extended TTFs.[7–9,12] For compounds **3** E°_1 decreases according to the same sequence; however, the smaller negative shifts observed when changing R in this case could be related to the fact that the first oxidation step corresponds to the direct formation of the dication through a two-electron transfer. Furthermore, a third redox system corresponding to the formation of the trication radical is observed in this case (Figure 4).

While the electrochemical properties of compounds **3** are qualitatively similar to those of other series of extended TTF analogues, those of compounds **1** and **2** present some unusual and interesting features. Thus, the combined effects of the alkoxy substituent at the 3,4-positions of the thiophene ring and of the *n*-propyl chains on the DTF moieties allow the **1c** and **2c** E°_1 values to reach 0.10 V, which is among the lowest redox potentials ever reported for TTF analogues.[2b] In fact under the same conditions TTF shows E°_1 and E°_2 values of 0.40 and 0.80 V vs SCE. Furthermore, it is worth noting that until now such low redox potentials have been reached at the price of a considerable spatial extension of the analogue TTF molecule.[17]

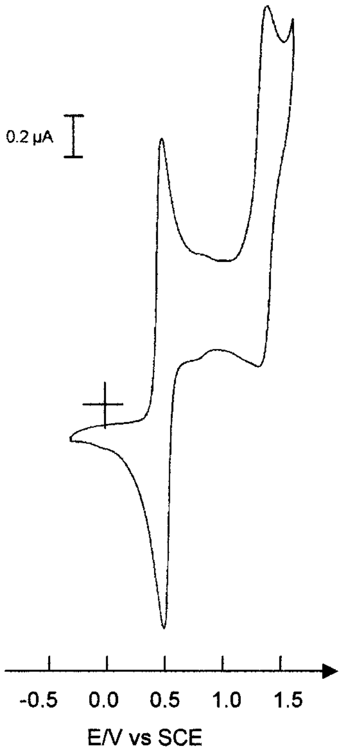

Figure 4. Cyclic voltammogram of compound **3a** ca. 5 × 10^{-4} M in 0.10 M Bu_4NPF_6/CH_2Cl_2. Pt electrodes, ref SCE, $v = 50$ mV s^{-1}.

Comparison of the CV data for compounds **1** and **2** with those of the parent donors based on unsubstituted thiophene (**10**) shows that although compounds **1** and **2** have lower E°_1 and E°_2 values, they exhibit potential differences $E^\circ_2 - E^\circ_1$ slightly larger than those for compounds **10**, thus indicating a larger Coulombic repulsion between positive charges in the dication. Since the extent of the π-conjugated system is similar for compounds **1**, **2**, and **10**, this larger Coulombic repulsion suggests that the distances between the maximum density of positive charges in the dicationic state are smaller in compounds **1** and **2** than in compound **10**.

Previous theoretical works on extended TTF analogues have shown that the end DTF groups bear the highest HOMO coefficients in the ground state and the highest density of positive charge in the cationic state.[5,12] These conclusions have been confirmed by recent X-ray data.[16c] However, a recent study of extended TTFs based on dithienylethylene (DTE) spacers has demonstrated that the covalent bridging the DTE spacer produces a negative shift of E°_1 associated with an increase of Coulombic repulsion. Theoretical calculations have shown that for bridged compounds the highest HOMO coefficients in the ground state and the highest density of positive charges

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in the dication are homogeneously delocalized over the whole molecule, in sharp contrast with the unbridged compounds.[12]

The similarity of the electrochemical behavior of these bridged compounds with that of the new donors **1** and **2** suggests that substitution of thiophene by dialkoxy groups produces a major reorganization of the electronic distribution of the molecule; the highest densities of positive charges in the dication which are essentially localized on the DTF groups in compounds **10**,[16c] move toward the middle of the molecule, thus leading to an increased Coulombic repulsion.

Preliminary attempts to electrocrystallize cation radical salts of compounds **1b** and **2b** have remained unsuccessful, and further experiments are in progress. However, to gain some information on the electrical properties of these compounds, the four-probe conductivity of a compacted pellet of compound **1a** has been measured after iodine doping, giving a value of 5×10^{-3} S cm^{-1}.

Conclusion

TTF analogues built around π-conjugating spacers based on 3,4-dialkoxythiophenes have been synthesized. The electron-releasing effect of the dialkoxy groups contribute to strongly enhancing the π-donor properties of the system, allowing for oxidation potentials lower than 0.10 V, which are among the lowest reported so far for TTF-based π-electron donors. On the other hand, the increase of the Coulombic repulsion in the dication suggests that the dialkoxy groups induce a major reorganization of the electronic distribution in the molecule. While a detailed understanding of this unusual behavior requires further experimental and theoretical work, these results show that TTF analogues with strong π-donor ability can be reached at the cost of a limited spatial extension of the molecule.

Experimental Section

X-ray Structural Analysis. Crystal Data for 2a. The structure of $C_{45}S_{10}O_{20}Cl_3H_{37}$ (M_w = 1324.78) is triclinic P-1, Z = 2, a = 12.921(3) Å, b = 15.164(3) Å, c = 15.767(3) Å, α = 109.82(2)°, β = 97.41(2)°, γ = 101.13(3)°, V = 2788(1) Å^3, calculated density 1.58 g cm^{-3}.

A single crystal of the title compound was selected by optical examination, and X-ray diffraction data were collected at 293 K on an Enraf Nonius MACH3 four-circle diffractometer. The crystal cell was obtained from a set of 25 reflections randomly found in the 10−16° θ range; 9676 reflections were collected by the ω scan technique in the 2−25° θ range ($\lambda_{\mathrm{Mo\ K\alpha}}$ = 0.71069, h 0,15; k −18,18; l −18,18)). A total of 5913 independent reflections (R = 0.018) with $I/\sigma(I) > 3$ were available for structure refinement. A starting set of non-hydrogen atomic coordinates was obtained from the direct methods (SIR). Two independent $C_{22}S_5O_{10}H_{18}$ molecules were found in the structure, as a consequence of one well-ordered $CHCl_3$ solvent molecule. Refinement of structure did not allow for location of hydrogen atoms which were then fixed at 0.95 Å from carbon atoms (Hydro program). Finally, refinement of all non-H atomic coordinates and anisotropic thermal factors led to R = 0.052, R_w = 0.075 (use of F magnitude, 703 parameters for 5913 reflections). All calculations were performed using the MolEN package.

Synthesis. 2,5-Dicarboethoxy-3,4-dihydroxythiophene (**4**) was prepared according to the Hinsberg method.[13]

2,5-Dicarboethoxy-3,4-dihexyloxythiophene (5). A mixture of 15 g of compound **4**, 16 g (2 equiv) of K_2CO_3, and 178 mL (22 equiv) of 1-bromohexane is heated at 110−120 °C for 30 h. After cooling to room temperature the solution is washed with water and the organic phase is dried over $MgSO_4$. Evaporation of the excess of 1-bromohexane leaves 20.15 g (82%) of crude product which can be directly used for the next step: ^{1}H NMR ($CDCl_3$) δ ppm 4.30 (m, 4H), 4.14 (t, 4H), 2.00−1.53 (m, 8H), 0.8 (t, 6H); ^{13}C NMR ($CDCl_3$) 148.2, 112.1, 71.47, 33.5, 25.4, 14.2.

2,5-Dicarboxy-3,4-dihexyloxythiophene (6). A mixture of compound **5** (76.2 g, 0.178 mol), 145 mL of 10% NaOH, and 120 mL of ethanol is refluxed for 2 h. After cooling to room temperature water is added and hydrochloric acid (25%) is added until precipitation occurs. The product is dried by filtration to give 51.4 g (78%) of a white compound: ^{1}H NMR ($CDCl_3$) δ ppm 13.0 (s, 2H), 4.1 (t, 4H), 2.0−1.5 (m, 8H), 0.8 (t, 6H); ^{13}C NMR (CDCl3) 148.2, 112.2, 71.5, 33.5, 25.4, 14.

3,4-Dihexyloxythiophene (7a). A mixture of 30 g of compound **6** and 1 g of Cu_2O is introduced in a round-bottom flak equipped with a distillation apparatus. The mixture is heated gently until ca. 2 L of CO_2 is recovered and then distilled under reduced pressure to give 17.86 g (78%) of the title compound: Eb$_{(0.19\ \mathrm{mbar})}$: 154 °C; ^{1}H NMR δ (ppm, $CDCl_3$) 6.16 (s, 2H), 4.00 (t, 4H), 1.98−1.4 (m, 16H), 0.96 (t, 6H); ^{13}C NMR 147.46, 96.69, 70.47, 31.51, 28.92, 25.58, 22.53, 13.97; MS (EI) 284 ($M^{+\bullet}$, 100%). Anal. (Calcd) C 67.56 (67.60), H 9.86 (9.92), S 11.11 (11.27).

3,4-Dihexyloxythiophene-2-carbaldehyde (7b). A mixture of 8 g (28.2 mmol) of compound **7a** and 4.47 mL of DMF (56.4 mmol) in 100 mL of dichloroethane is cooled to 0 °C, $POCl_3$ (4.31 mL, 45 mmol) is slowly added, and the solution is refluxed for 2 h. After cooling to room temperature 250 mL of 1 M aqueous sodium acetate is introduced and the mixture is stirred for 30 min and extracted with methylene chloride. The organic phase is washed with water and dried ($MgSO_4$). Evaporation of the solvent and column chromatography (silica gel, 1:1 CH_2Cl_2/petroleum ether) gave 8.1 g (92%) of a yellow oil: ^{1}H NMR ($CDCl_3$) 10.0 (s, 1H), 7.11 (s, 1H), 4.25−3.96 (2t, 4H), 1.96−0.7 (m, 22H); ^{13}C NMR 182.0, 147.5, 98.2, 70.5, 31.5, 29.1, 25.7, 22.6, 14.0; MS (EI) 312 (M^+ 100%).

3,4-Dihexyloxythiophene-2,5-dicarbaldehyde (7c). To a solution of 5.5 g (19 mmol) of compound **7a** and 3.85 mL (20 mmol) of TMEDA in 10 mL of hexane is added 15.88 mL of *n*-BuLi (1.6 M in hexanes) under an inert atmosphere, and the mixture is refluxed for 30 min. After cooling to room temperature THF (30 mL) is added, the mixture is cooled to −40 °C, and 2.47 mL (32 mmol) of DMF is added dropwise. The solution is allowed to warm to room temperature, poured into 300 mL of 0.5 M aqueous HCl, and stirred vigorously for 15 min. After neutralization with 0.5 M $NaHCO_3$, the aqueous phase is extracted with diethyl ether, the organic phase is washed with water and dried ($MgSO_4$), and the solvent is evaporated. Column chromatography (silica gel, CH_2Cl_2/petroleum ether 2:3) gave 3.8 g (58%) of the target compound as an orange oil: ^{1}H NMR ($CDCl_3$) 10.2 (s, 1H), 4.25−3.96 (2t, 4H), 1.97−0.7 (m, 22H); ^{13}C NMR 182.0, 147.6, 97.2, 71.5, 31.5, 25.7, 22.6, 14.0; MS (EI) 340 (M^+ 100%).

(*E*)-1,2-Bis[2-(3,4-dihexyloxythienyl)]ethylene (8a). $TiCl_4$ (5.27 mL, 46 mmol) and 6.3 g of Zn (96 mmol) are added portionwise to 100 mL of dry THF at 0 °C under an inert atmosphere, and the mixture is refluxed for 30 min. After cooling to 0 °C, a solution consisting of 7.49 g (24 mmol) of aldehyde **7b** and 5 mL of pyridine in 20 mL of THF is slowly added. The mixture is refluxed for 2 h and allowed to cool to room temperature. After addition of ice and 100 mL of CH_2Cl_2, the mixture is stirred for 15 min and filtrated over hyflosupercel. The solution is washed with dilute HCl and then with water to neutrality and dried over Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2/petroleum ether 1:1) and recrystallization in methanol give 5.37 g (76%) of the target compound: mp 86 °C; ^{1}H NMR ($CDCl_3$) 6.96 (s, 2H), 5.99 (s, 2H), 4.05 (t, 4H), 3.94 (t, 4H), 1.78−1.30 (m, 32H), 0.93−0.90 (m, 12H); ^{13}C NMR ($CDCl_3$) 150.4, 143.95, 125.08, 116.86, 93.92, 69.88, 31.62, 31.47, 29.99, 29.07, 25.74, 22.63, 14.04; MS (EI) 592 (M^+ 100%). Anal. (Calcd) C 68.25 (68.87), H 9.52 (9.52), O 10.98 (10.79), S 10.86 (10.81).

(*E*)-1,2-Bis(5-formyl-3,4-dihexyloxy-2-thienyl)ethylene (8b). Compound **8a** (1.7 g, 2.86 mmol) is dissolved in 25 mL of dry ether, and the solution is cooled to 0 °C. After dropwise addition of 4.47 mL (7.15 mmol) of *n*-BuLi (1.6 M in hexanes), the solution is stirred for 15 min and DMF (0.7 mL 13.4 mmol) is added. The mixture is allowed to warm to room temperature, aqueous NH_4Cl is added, and the solution is extracted with ether. The organic phase is dried (Na_2SO_4), and the solvent is evaporated to leave a brown solid. Recrystallization in methanol gives 1.22 g (66%) of an orange powder: mp 81 °C; ^1H NMR ($CDCl_3$) 9.98 (s, 2H), 7.19 (s, 2H), 4.31 (t, 4H), 4.00 (t, 4H), 1.85−1.24 (m, 32H), 0.91 (t, 12H); ^{13}C NMR ($CDCl_3$) 180.87, 156.66, 147.32, 135.11, 122.68, 119.84, 31.54, 31.44, 29.91, 25.58, 22.59, 14.00; IR (KBr) 1667 ($C=O$); MS (EI) 648 (M^+, 100%).

3,4-Ethylenedioxy-2,5-thiophenedicarbaldehyde (9b). Under an inert atmosphere ethylenedioxythiophene (1.4 g 10 mmol) and *t*-BuOK (3.36 g 30 mmol) are added to in 30 mL of dry THF under stirring. The mixture is cooled to −90 °C, and 12 mL (30 mmol) of *n*-BuLi (1.6 M in hexanes) is added dropwise. The mixture is stirred for 30 min, LiBr (2.61 g, 30 mmol) is slowly added, and the solution is stirred for another 30 min before the slow addition of 50 mL of DMF. The mixture is allowed to warm to room temperature, hydrolyzed with 3 N aqueous HCl, and extracted with CH_2Cl_2. The organic phase is washed with 1 M $NaHCO_3$ and water and dried over Na_2SO_4. After solvent removal the crude solid is chromatographed (silica gel, CH_2Cl_2/petroleum ether 3:2) to give 50 mg of starting compound, 0.4 g of monoaldehyde, and 0.4 g (26%) of the desired dialdehyde: mp 155 °C; ^1H NMR ($CDCl_3$) 10.2 (s, 2H), 4.31 (t, 4H); ^{13}C NMR 180.87, 142.10, 110.25, 67; MS (EI) 316 (M^+ 100%).

2,5-Bis[4,5-bis(methoxycarbonyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-dihexyloxythiophene 1a: yield 90%, dark red solid; mp 89 °C; ^1H NMR ($CDCl_3$) 6.64 (s, 2H), 3.96 (t, 4H), 3.88−3.85 (2s, 12H), 1.91−1.15 (m, 16H) 0.8 (t, 6H); ^{13}C NMR 160.07, 159.98, 144.74, 130.88, 126.17, 122.52, 105.98, 74.05, 53.37, 31.53, 29.85, 29.66, 25.57, 22.59, 14.00; UV−vis (λ_{max} nm, log ϵ) 421, 4.68; MS (EI) 744 (M^+, 100%); HRMS calcd for $C_{32}H_{40}O_{10}S_5$ 744.1225, found 744.1225.

2,5-Bis[4,5-bis(methylsulfanyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-dihexyloxythiophene 1b: yield 84%; ^1H NMR ($CDCl_3$) 6.69 (s, 2H), 3.97 (t, 4H), 2.58−2.26 (m, 12H), 1.80−0.77 (m, 22H); ^{13}C NMR 144.16, 128.32, 127.48, 122.62, 105.61, 3.56, 29.91, 22.60, 19.23, 14.03; UV−vis (λ_{max} nm, log ϵ) 440, 4.73; MS (EI) 696 (M^+, 100%); HRMS calcd for $C_{28}H_{40}O_2S_9$ 696.0531, found 696.0531.

2,5-Bis[4,5-bis(*n*-propyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-dihexyloxythiophene 1c: yield 87%; ^1H NMR ($CDCl_3$) 6.66 (s, 2H), 3.97 (t, 4H), 2.58−2.43 (m, 8H), 1.69−1.5 (m, 8H), 1.8−1.2 (m, 16H), 1.12−0.78 (t, 18H); ^{13}C NMR 143.18, 129.44, 128.06, 122.76, 102.69, 46.17, 31.58, 29.94, 25.63, 23.09, 22.60, 14.01; UV−vis (λ_{max} nm, log ϵ) 442, 4.68; MS (EI) 680 (M^+, 100%); HRMS calcd for $C_{36}H_{56}O_2S_5$ 680.2894, found 680.2894.

2,5-Bis[4,5-bis(methoxycarbonyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-ethylenedioxythiophene 2a: yield 40%, dark red solid; mp 162 °C; ^1H NMR ($CDCl_3$) 6.59 (s, 2H), 4.22 (s, 4H), 3.88−3.85 (2s, 12H); ^{13}C NMR 159.0, 136.4, 131.2, 130.79, 105.20, 64.82, 53.37; UV−vis (λ_{max} nm, log ϵ) 427, 4.43; MS (EI) 602 (M^+, 100%); HRMS calcd for $C_{22}H_{18}O_{10}S_5$ 601.9503 found 601.9513.

2,5-Bis[4,5-bis(methylsulfanyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-ethylenedioxythiophene 2b: red oil, yield 27%; ^1H NMR ($CDCl_3$) 6.61 (s, 2H), 4.21 (s, 4H), 246−243 (2s, 12H); ^{13}C NMR 136.26, 128.32, 125.18, 104.85, 64.82, 19.24, 18.95; UV−vis (λ_{max} nm, log ϵ) 446, 4.44; MS (EI) 554 (M^+, 100%); HRMS calcd for $C_{18}H_{18}O_2S_9$ 553.8793, found 553.8773.

2,5-Bis[4,5-bis(*n*-propyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-3,4-ethylenedioxythiophene 2c: red oil, yield 50%; ^1H NMR ($CDCl_3$ 6.60 (s, 2H), 4.2 (s, 4H), 2.56−2.25 (m, 8H), 1.69−1.50 (m, 8H), 0.98−0.75 (m, 12H); ^{13}C NMR 135.28, 127.94, 127.33, 101.85, 64.81, 31.93, 31.79, 30.56, 23.57, 22.20, 15.24, 14.63, 13.79, 13.60, 13.52; UV−vis (λ_{max} nm, log ϵ) 446, 4.43; MS (EI) 538 (M^+, 100%); HRMS calcd for $C_{26}H_{34}O_2S_5$ 538.1162, found 538.1152.

1,2-Bis{5-[4,5-bis(methoxycarbonyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-2-(3,4-dihexyloxy)thienyl}ethene 3a: yield 41%, red solid; mp 105 °C; ^1H NMR ($CDCl_3$) 6.99−6.98 (2s, 2H), 6.62 (s, 2H), 4.08 (q, 8H), 3.88−3.87 (2s, 12H), 1.70 (m, 16H), 1.05 (2s, 12H); ^{13}C NMR 160.18, 159.72, 146.97, 145.11, 132.10, 130.13, 126.37, 125.28, 115.93, 106.09, 53.45, 53.02, 31.59, 29.92, 25.63, 25.60, 22.62, 14.03; UV−vis (λ_{max} nm, log ϵ) 484, 4.64; (MS EI) 1052 (M^+, 100%); HRMS calcd for $C_{50}H_{68}O_{12}S_6$ 1052.3035, found 1052.3065.

1,2-Bis{5-[4,5-bis(methylsulfanyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-2-(3,4-dihexyloxy)thienyl}ethene 3b: red oil, yield 33%; ^1H NMR ($CDCl_3$) 6.96 (s, 2H), 6.69 (s, 2H), 4.11−3.93 (m, 8H), 2.70−2.11(m, 12H), 1.97−0.85 (m, 44H); ^{13}C NMR 146.88, 144.46, 128.45, 127.99, 125.56, 124.64, 122.01, 115.64, 105.52, 74.00, 54.76, 54.65, 42.81, 40.47, 31.62, 29.92, 25.64, 19.23, 14.09, 14.04; UV−vis (λ_{max} nm, log ϵ) 492, 4.67; MS (EI) 1004 (M^+, 100%); HRMS calcd for $C_{46}H_{68}O_4S_{10}$ 1004.2324, found 1004.2333.

1,2-Bis{5-[4,5-bis(*n*-propyl)-2*H*-1,3-dithiol-2-ylidenemethyl]-2-(3,4-dihexyloxy)-thienyl}ethene 3c: red oil, yield 67%; ^1H NMR ($CDCl_3$) 6.96 (s, 2H), 6.69 (s, 2H), 4.15−3.95 (m, 8H), 2.58−2.43 (m, 8H), 1.69−1.5 (m,8H), 1.8−1.2 (m, 32H), 1.10−0.75 (m, 24H); ^{13}C NMR 146.69, 143.52, 131.34, 128.42, 127.55, 123.52, 123.17, 115.29, 102.49, 73.89, 31.62, 31.60, 30.7, 29.9, 25.65, 23.15, 23.0, 22.6, 22.5, 14.05, 14.02; UV−vis (λ_{max} nm, log ϵ) 505, 4.61; MS (EI) 989 (M^+, 100%); HRMS calcd for $C_{54}H_{84}O_4S_6$ 988.4693, found 988.4673.

Supporting Information Available: Tables giving positional and thermal parameters and bond distances for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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