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The First Discotic Liquid Crystal with a Tetrathiafulvalene Central Core

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Abstract: The synthesis and characterization of tetrasubstituted tetrathiafulvalenes **7 a-b** and **18 a-b**, which bear promesogenic units such as 4-decyloxybenzoyl and 3,4,5-tris(decyloxy)benzoyl groups, are described. Such units are linked to the TTF core through spacers of different lengths. Compound **18b** exhibits a metastable discotic mesophase and constitutes the first example of a discotic liquid crystal with a tetrathiafulvalene central core. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The chemistry of tetrathiafulvalene (TTF) and its derivatives[1] has been at the forefront of research in the field of organic conductors for the last twenty five years.[2] Since the physical properties displayed by these materials depend on the intermolecular architecture, it is not surprising that a great deal of effort has been devoted to the preparation of suitably organized supramolecular entities, such as single crystals or soft molecular materials. To this end, electrocrystallization and deposition of Langmuir-Blodgett films[2d,3] constitute the most widely used techniques.

An alternative approach, which is much less used in the case of TTF derivatives, is based on the preparation of mesogenic compounds. Indeed, very few liquid crystalline tetrathiafulvalenes have been described[4] and most of those that have are calamitic. On the other hand, a discotic liquid crystalline phtalocyanine bearing a peripheral TTF unit has recently been reported.[4f] This case is especially relevant, since appropriately substituted disc-like molecules form columnar structures that resemble the segregated stacking of 1D organic conductors. Nevertheless, discotic liquid crystals in which the TTF moiety constitutes the central core of the required disc-shaped molecules have not yet been described. This is surprising since some other electroactive building blocks, such as 4,4'-bi(chalcogenopyranylidenes)[5] and bis(dithiolene) complexes,[6] have given rise to columnar mesophases.

In the work described here we focus on the synthesis of tetrasubstituted tetrathiafulvalenes in which the electroactive core is surrounded by four or twelve flexible alkoxy chains. These flexible chains originate from 4-decyloxybenzoic acid and 3,4,5-tris(decyloxy)benzoic acid, respectively, both of which have been widely used in the preparation of lamellar and discotic liquid crystals. These side groups have been attached to the TTF core through spacers of different lengths, namely -$S(CH_2)_6$- and -CH_2-. The former spacer was chosen because it has, in previous studies carried out in our laboratories, given rise to TTF-containing liquid crystals.[4g,4h] The much shorter methylene spacer seemed interesting to us in order to ascertain the importance of the rigidity of the central core in this series of compounds.

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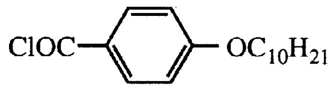
In addition to the preparation of mono- and disubstituted tetrathiafulvalenes **3** and **5**, we report the synthesis and electrochemical characterization of tetrasubstituted derivatives **7 a-b** and **18 a-b**. A study of the mesomorphic properties of these derivatives reveals that **18b** is the first discotic liquid crystal with a TTF-containing central core.

RESULTS AND DISCUSSION

Synthesis

Esterification reactions of hydroxy-TTF derivatives are usually carried out using acid chlorides. Monoalcohols have been used most often,[7] but there are a few reports on esterification reactions of dihydroxy-TTF derivatives[7c,7g,8] and tetrahydroxy-compounds.[8,9]

As previously indicated, our initial targets were compounds **7 a-b**. Nevertheless, before attempting their synthesis we decided to explore the reactivity of acid chloride **2** (prepared from commercially available acid **12a**) towards simple alcohols, namely **1**[7d] and **4**.[10] Since the corresponding esters, (**3**) and (**5**), were easily prepared (Scheme 1), the reaction of **2** with tetraalcohol **6**[4g] was attempted.



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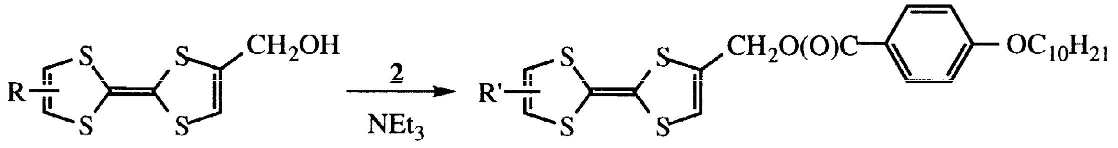
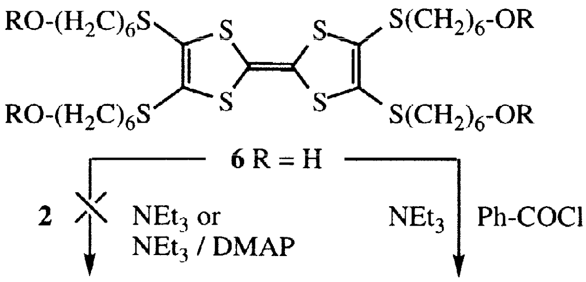


1 R = H
4 R = HOCH$_2$-

3 R' = H
5 R' = p-C$_{10}$H$_{21}$O-C$_6$H$_4$-COO-CH$_2$-

Scheme 1

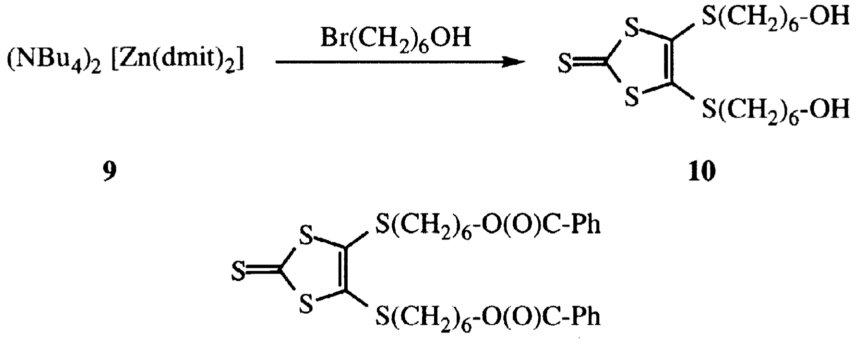
To our surprise, tetraester **7a** could not be obtained, even under a variety of reaction conditions (NEt$_3$ or NEt$_3$/DMAP either in CH$_2$Cl$_2$ or DMF) (Scheme 2). Only the corresponding monoester could be identified (^{1}H-NMR spectroscopy and MS) when triethylamine in refluxing CH$_2$Cl$_2$ was used. In all other cases, a mixture of starting materials and decomposition products was obtained. Nevertheless, the feasibility of the tetraesterification of alcohol **6** was demonstrated by the synthesis of compound **8** in 46% yield. Thus, it was thought that the failure in the preparation of **7a** could be attributed to steric factors (each newly introduced acyl group could render the subsequent acylation steps more difficult).



7a R = p-C$_{10}$H$_{21}$O-C$_6$H$_4$-CO **8** R = Ph-CO

Scheme 2

In order to alleviate this problem, thione **10**, bearing two alkyl chains, was synthesized (Scheme 3) since reaction of this compound with **2** was expected to proceed more easily than that of **6**. Nevertheless, the desired diester (**14a**) could only be isolated in low yield (using either NEt_3 or DMAP[11]) and after a tedious purification process. On the other hand, dibenzoate **11** was prepared in 90% yield, thus confirming the role played by steric factors in these acylation reactions.



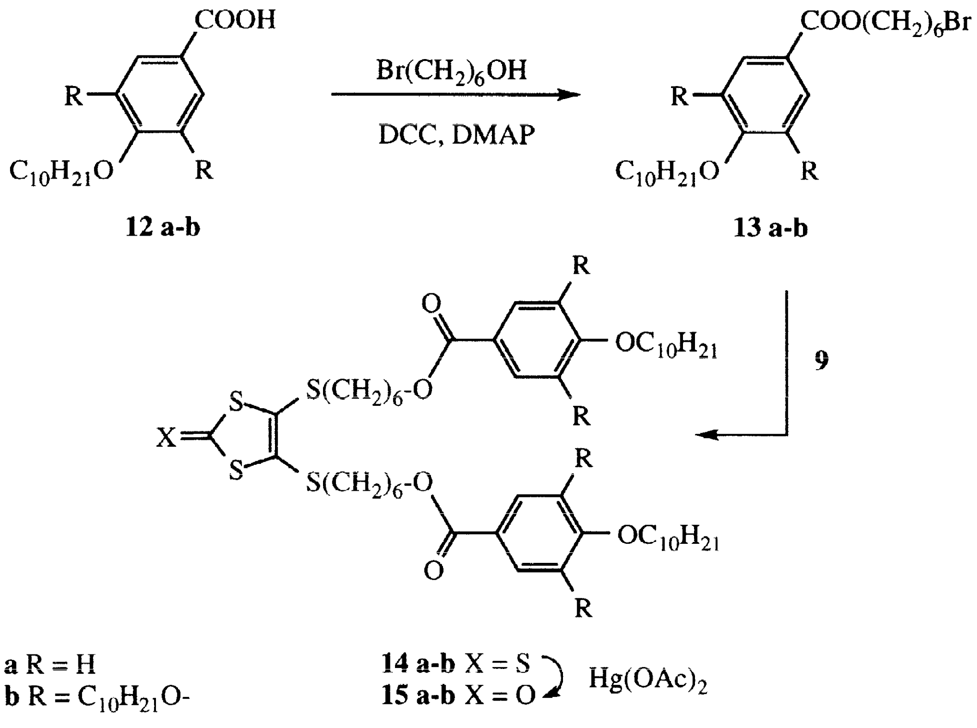
9

10

11

Scheme 3

At this point a more efficient route to thione **14a** was sought. We reasoned that steric hindrance would be less severe in the reaction of **9** with an appropriate alkylating reagent, such as **13a**, than in the previously studied esterification reactions. Thus, bromide **13a** was prepared using the Steglich-Hassner procedure,[12] and its reaction with **9** occurred smoothly to give **14a** in 95% yield (Scheme 4). In a similar way, **13b** (prepared from commercially available methyl gallate *via* **12b**) yielded thione **14b** (90% yield).

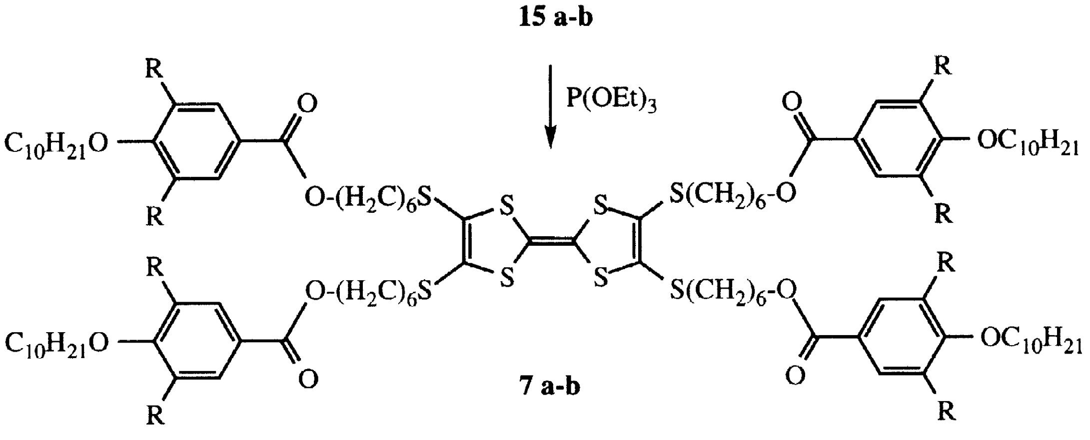


a R = H
b R = $C_{10}H_{21}O$-

14 a-b X = S
15 a-b X = O

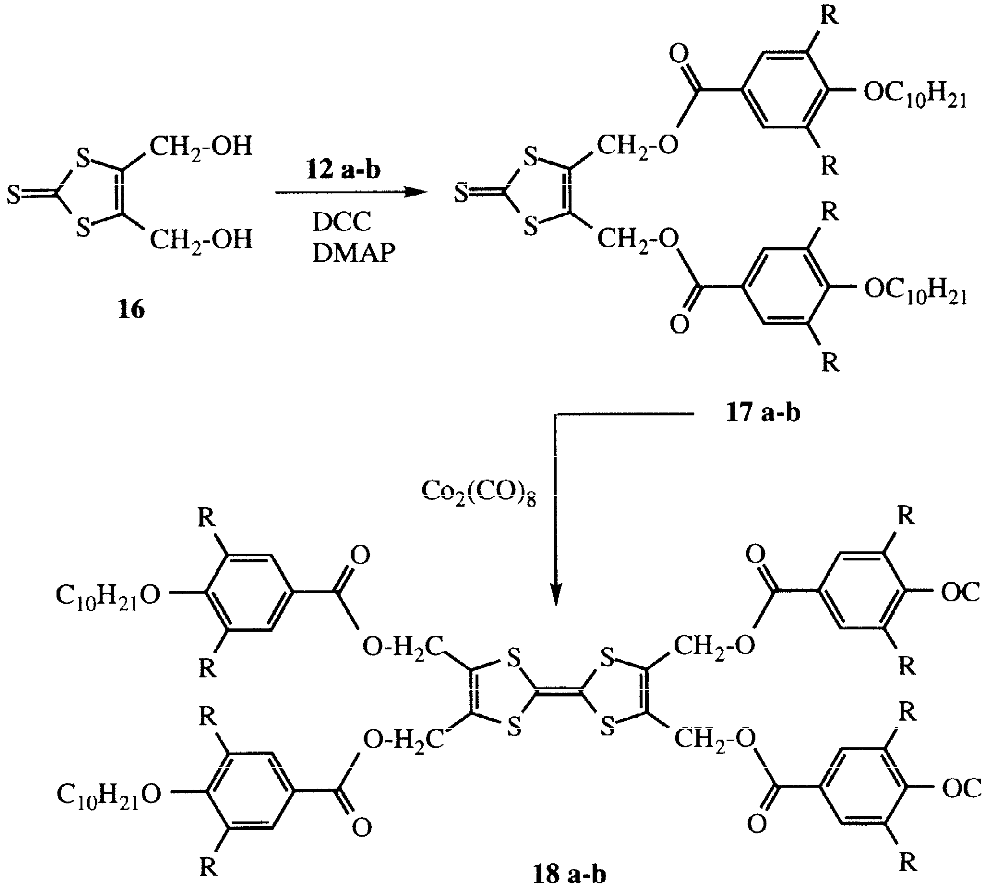
Scheme 4

Treatment of these thiones with mercury (II) acetate afforded the corresponding 1,3-dithiol-2-ones **15 a-b** in high yield (90%), and phosphite-mediated coupling of the latter compounds eventually yielded the desired tetrathiafulvalenes **7a** and **7b**, respectively (Scheme 5).



a R = H; **b** R = $C_{10}H_{21}O$-

Scheme 5



a R = H; **b** R = $C_{10}H_{21}O$-

Scheme 6

The reaction was monitored by IR and ^{13}C-NMR spectroscopy (disappearance of the characteristic features of the dithiolone group: band at *ca.* 1670 cm^{-1} and signal at *ca.* $\delta = 190$, respectively). Mass spectrometry of the resulting compounds confirmed the structure of **7 a-b** unambiguously.

Once the synthesis of compounds **7 a-b** was successfully completed, we turned our attention to derivatives **18 a-b**. Since we were not confident about the tetraesterification of the sparingly soluble tetrakis(hydroxymethyl)tetrathiafulvalene,[9,13] a different synthetic route was chosen, starting from the readily available diol **16**[9] (Scheme 6). Thus, treatment of **16** with acids **12 a-b** afforded diesters **17 a-b**, respectively, in good yields. The absence of sulfur atoms directly linked to the 4- and 5- positions of the 1,3-dithiole ring in these compounds prevented their successful phosphite-mediated self-coupling. However, the use of $Co_2(CO)_8$[14] allowed the preparation of the desired tetrathiafulvalenes **18 a-b**.

Cyclic Voltammetry

The solution redox properties of some of the newly prepared tetrasubstituted TTF derivatives have been studied by cyclic voltammetry in dichloromethane solution. The data are collected in Table 1.

Table 1. Cyclic Voltammetric Data [a]

Compound	E_1^{ox}	E_2^{ox}
7a	0.59	0.94
7b	0.59	1.05
18a	0.61	1.14
18b	0.80	1.33

[a] In volts. 0.1 M TBA PF_6 / CH_2Cl_2 *vs.* SCE, scan rate 100 mV s^{-1}.Working and counter electrodes: Pt.

All of the compounds studied show two, separate, reversible or quasi-reversible, one-electron oxidation waves. For the sake of comparison, the anodic peak potentials of TTF ($E_1^{ox} = 0.38$ V; $E_2^{ox} = 0.91$ V) and ester **3** ($E_1^{ox} = 0.47$ V; $E_2^{ox} = 0.97$ V) have been measured under the same conditions. As expected,[1c] alkylthio substituted derivatives **7 a-b** show higher peak potentials than TTF itself. In addition, the waves of the more heavily substituted derivative **7b** are broadened in comparison to those of **7a** (see below).

The redox properties of compounds **18** warrant further comment. The marked increase in half-wave potentials caused by the introduction of $-CH_2-O(O)C-R$ onto the periphery of the TTF core has already been noted.[7e,9] This trend is confirmed in the present case since (a) the peak potentials of **3** agree very well with the reported values for tetrathiafulvalenylmethyl benzoate [7e] and (b) the presence of four ester groups in compounds **18** markedly raises the E^{ox} values. Nevertheless, the E^{ox} values of compound **18b** are unusually high, and the corresponding waves are broader than those of **18a**. A possible explanation for this behaviour lies in the increased number of chains around the TTF core, which could render the electron-transfer processes more difficult. A MM+ conformational search[15] carried out on **18b** (Figure 1) lends support to this assumption. In fact, similar phenomena (noticeable modifications of peak potential values, decrease in reversibility) have been noted in the case of porphyrins with an increasing degree of substitution around the electroactive core.[16]

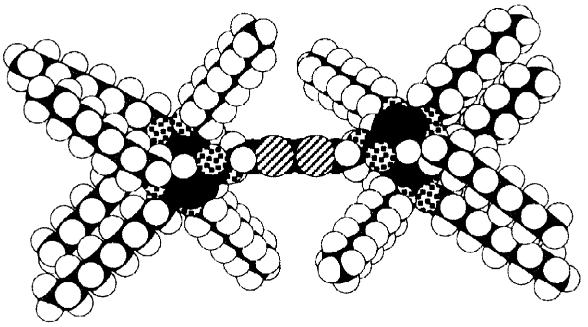


Figure 1. MM+ minimized structure of compound **18b**

Mesogenic Behaviour

Tetrathiafulvalenes **7** and **18** could, in principle, show mesomorphic properties. Derivatives **7b** and **18b**, both of which contain twelve alkoxy chains, seemed to be better candidates to form discotic liquid crystalline phases than their less-substituted analogues **7a** and **18a**. However, it should be remembered that some compounds with only four flexible chains are columnar mesogens[17] and, in addition, derivatives **7a** and **18a** have the potential to show lamellar mesophases.[18] Moreover, compounds **3** and **5** were also studied since they are potential candidates to be calamitic liquid crystals.

Unfortunately, neither **3** nor **5** showed mesomorphic properties, although the combined optical microscopy and DSC study of compound **5** revealed the existence of two melting points (100°C and 105°C), which can be assigned to the corresponding (*Z*) and (*E*) isomers.

As far as the newly prepared tetrasubstituted tetrathiafulvalenes are concerned, only **18b** showed mesogenic behaviour (at this point it should be remembered that tetrakis(heptanoyloxymethyl)tetrathiafulvalene[9] and several tetrakis(4-alkoxyphenyl)tetrathiafulvalenes[4b] are also non-mesogenic).

Optical Microscopy and DSC Study. The mesomorphic behaviour of **18b** was investigated by means of polarizing optical microscopy and differential scanning calorimetry (DSC). When first heated on the heating stage of the microscope, the sample melted from the solid to a fluid state that exhibited a blurred, fur-like texture when observed between crossed polarizers (Figure 2). Immediately, upon further heating, this phase transformed into an isotropic liquid. In the cooling process, the fluid birefringent phase appeared at 71°C. The fur-like texture characteristic of this phase was preserved down to room temperature, although the fluidity of the phase decreased on cooling, and probably froze at a certain temperature.

The observations by microscopy suggest a liquid crystal nature for this phase. On the basis of the disc-like shape of the molecule the mesophase is probably of the columnar type, and its structure might well be rectangular as the observed texture is not characteristic of a hexagonal columnar mesophase (hexagonal and rectangular are the two most common symmetries in columnar liquid crystals).

According to observations by microscopy, the DSC thermograms of **18b**, carried out at a scanning rate of 10°C/min (experiment 1) (Figure 3) correspond to a typical mesogen which melts into a mesophase, **M**, which turns into an isotropic liquid beyond the clearing temperature (scan A). The enthalpy of the transition **M**→**I** is very high (28.8 kJ/mol), indicating a high degree of order within this mesophase. This supports the possibility of a rectangular columnar structure, as this enthalpy value is too high for a hexagonal columnar mesophase.

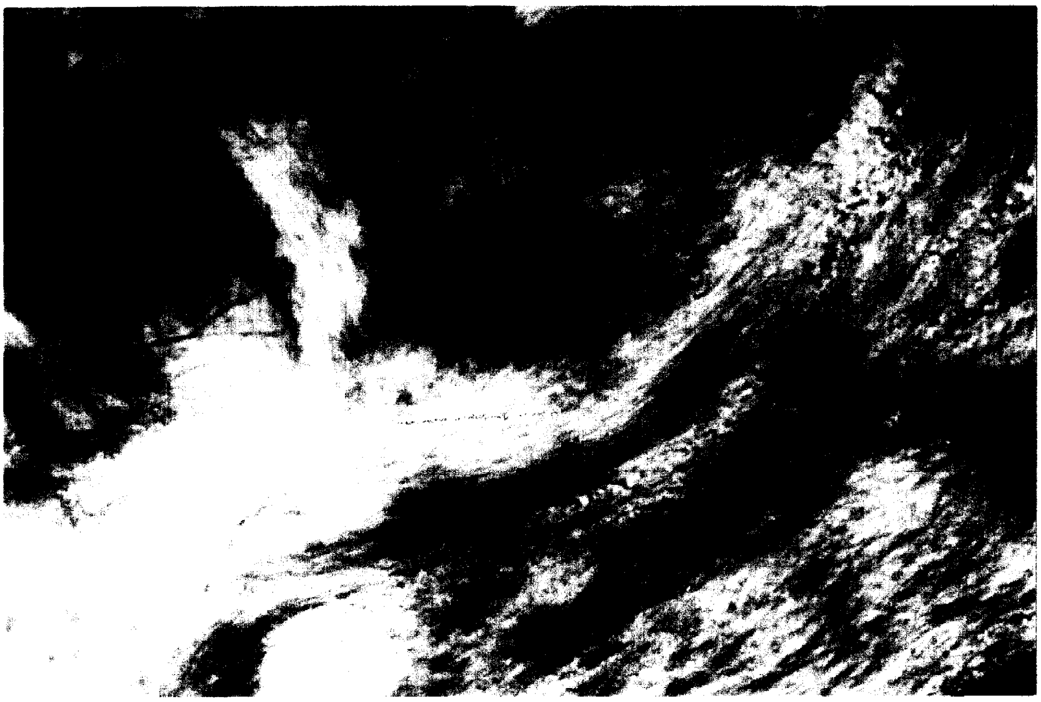


Figure 2. Photomicrograph of the optical texture of the mesophase of compound **18b** at 75°C

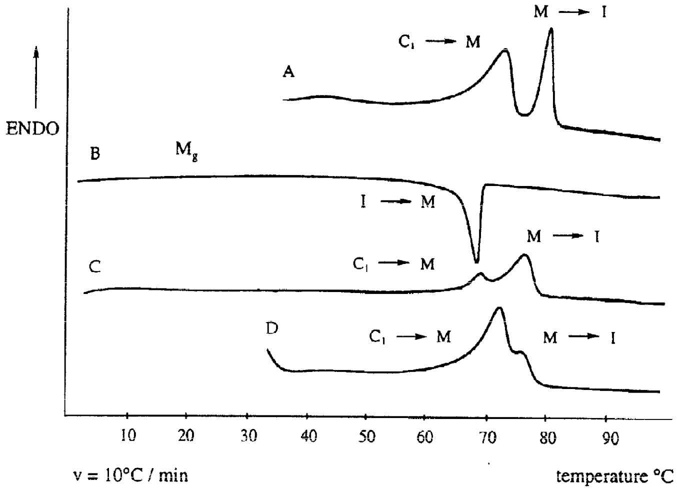


Figure 3. DSC of compound **18b** at 10°C/min

No crystallization peak is observed in the cooling process (scan B) down to 0°C. Freezing of the mesophase into a glass, $\mathbf{M}_\mathbf{g}$, was confirmed by optical observation, although the glass transition is not visible in the DSC scan. However, partial crystallization of the material must occur, since subsequent heating of the $\mathbf{M}_\mathbf{g}$ phase (scan C) gives rise to a small DSC peak at the temperature of the previously observed transition ($\mathbf{C_1 \rightarrow M}$). A second heating scan, carried out after maintaining the glass at room temperature for 72 h, (scan D) shows a larger $\mathbf{C_1 \rightarrow M}$ transition peak. This indicates a strong increase in the degree of crystallization, and this was also observed by X-ray diffraction (see below).

In order to establish whether this crystallization process could be affected by the cooling rate as well as with time, a second DSC experiment was carried at a scanning rate of 2°C/min (Figure 4). After obtaining the $\mathbf{M}_\mathbf{g}$ phase, further heating (scan G) did not give rise to the $\mathbf{C_1 \rightarrow M}$ transition peak. This peak only appeared in a subsequent heating run performed on the sample after it had been kept at room temperature for 24 h (scan H). These results confirm the idea that crystallization mainly occurs with time. In this second experiment it is worth mentioning that a slow heating rate favours the appearance of a second crystalline form, $\mathbf{C_2}$, evidenced by an extra peak in all the heating scans (E, G, H). Moreover, $\mathbf{C_2}$ must have a more organized structure than $\mathbf{C_1}$ given the exothermic character of the transition $\mathbf{C_1 \rightarrow C_2}$. Transformation of this crystalline form into the mesophase occurs simultaneously with the clearing process, and hence only an endothermic peak with an associated enthalpy of 109.3 kJ/mol appears in the heating scans.

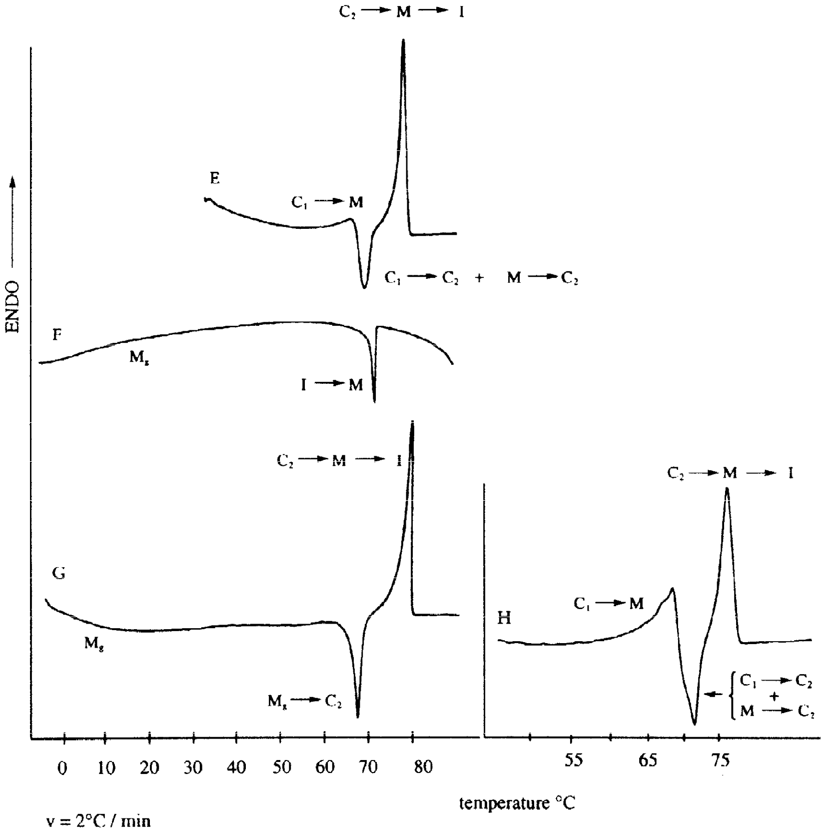


Figure 4. DSC of compound **18b** at 2°C/min

X-ray Diffraction Study. Compound **18b** was also studied by X-ray diffraction in order to gain an insight into the structures of its liquid crystal and crystalline phases. The experiments were performed both on powder samples and aligned samples.

First of all, we attempted to study the mesophase in its frozen state by heating a virgin sample of **18b** up to a temperature above the clearing point and then cooling the sample down quickly to room temperature.

However, all attempts to obtain diffraction patterns of the glassy mesophase were unsuccessful as, unfortunately, during the X-ray experiments (that need several hours of exposure to the X rays) the sample partially crystallized in all cases. Thus, the patterns obtained from powder as well as from oriented samples correspond to mixtures of the frozen mesophase and the crystalline solid ($\mathbf{M_g}$ and $\mathbf{C_1}$ phases, respectively). This conclusion is consistent with the DSC results, which indicated that the $\mathbf{C_1}$ phase forms slowly from the mesophase over the course of time. The different X-ray experiments yielded different patterns depending on the $\mathbf{C_1/M}$ ratio, and this ratio is highly time-dependent. This problem, together with the low number of reflections, precluded a precise determination of the structure of the **M** phase. However, it is reasonable to suggest that the molecules adopt a stacked structure, because a maximum is observed that is reinforced in the alignment direction in the oriented patterns. Bragg's law gives a distance of 4.7 Å for this maximum. This spacing seems reasonable for the distance between stacked molecules within the columns. Furthermore, the fact that the **M** phase is easily aligned supports its liquid crystal nature (aligned samples were obtained by scratching the inner wall of the glass capillary, containing the sample, with a small metal or glass rod along the direction of the capillary axis at a temperature slightly below the clearing point). In the direction perpendicular to the alignment direction a strong reflection is observed at small angles corresponding to a spacing of 31 Å. On the assumption that the molecules stack into columns and the molecular planes are roughly contained in the plane perpendicular to the column axes, it is reasonable to assign this spacing to the distance between neighbouring molecules in the aforementioned plane.

We also attempted to investigate the structure of the $\mathbf{C_1}$ phase by studying the X-ray diffraction patterns of a virgin sample of **18b**. However, the photographs obtained contain only a low number of reflections, some of which are of weak intensity. This prevented the interpretation of the patterns and the assignment of the unit cell. It can be concluded that this phase, although crystalline, is very disorganized.

Finally, we investigated the structure of the $\mathbf{C_2}$ phase, which is more organized that the virgin solid according to DSC (see above). The $\mathbf{C_2}$ phase is obtained after prolonged heating at 65.7°C. X-ray photographs were registered from powder as well as from aligned samples both at high and room temperature. Given the high number of reflections observed, the experiments were carried out at two different sample-to-film distances, in order to explore both the small-angle region and the large-angle region of the patterns. A first examination of the photographs clearly indicates the existence of a crystalline three-dimensional order, because the oriented patterns show a number of maxima out of the meridian and equator. In the meridian direction (alignment direction) a strong maximum is observed that corresponds to a distance of 4.76 Å. In the equatorial plane a set of reflections is observed that can be assigned to a rectangular lattice. Taking into account the orthogonal character of the pattern (the *00l* direction is perpendicular to the *hk0* plane), it is concluded that the $\mathbf{C_2}$ crystalline phase has an orthorhombic cell with lattice constants $a = 59.5$ Å, $b = 28.2$ Å, $c = 4.76$ Å. The fact that one of the axes of the unit cell (the c axis) is significantly shorter than the other two axes indicates the existence of a columnar structure in which the molecules stack up along the *c* axis and the molecular planes lie approximately in the *ab* plane. It is interesting to note that the *c* parameter (4.76 Å) is in fair agreement with the stacking parameter proposed for the glassy mesophase (4.7 Å).

From the volume V (in cm^3) of the unit cell, the density of this structure can be estimated using the following equation: $\rho = (M/N)/(V/Z)$, where M is the molar mass (g), N the Avogadro number and Z the number of molecules per unit cell. Taking into account that the volume of an orthorhombic cell is $V = a\,b\,c \cdot 10^{-24}$ cm^3 it is deduced that Z is 2, from which a reasonable density value of 1.086 g cm^{-3} is calculated.

The results drawn from the three experimental techniques used to study the liquid crystal behaviour of **18b** (polarizing optical microscopy, DSC and X-ray diffraction) are consistent with the existence of a metastable columnar mesophase obtained by cooling the isotropic liquid. Based on the texture and the enthalpy of the mesophase-to-isotropic liquid transition , a rectangular structure can be proposed for this mesophase, and thus it can be denoted Col_r.This assignment is consistent with the orthorhombic symmetry of the $\mathbf{C_2}$ phase, which contains a rectangular packing of columns. Indeed, in columnar liquid crystals the crystal-to-mesophase transition involves either preservation or an increase in the symmetry.[17a,19] This excludes an oblique (monoclinic) packing of columns in the mesophase of this compound, as this would mean a change to a lower symmetry. A hexagonal packing is also discarded on the basis of the optical textures and the transition enthalpy (see above).

CONCLUSION

In conclusion, we have succeeded in obtaining columnar mesomorphism in a system based on a TTF-containing central core. Although mesomorphism has been found in only one compound, this represents a promising result that opens new possibilities. In particular, from the results of this work it can be deduced that both the number of peripheral chains and the structure of the central core play a crucial role in the occurrence of mesomorphism. Thus, the fact that **18a** is not mesogenic can be accounted for by the low number (four) of peripheral chains in this compound, whereas **18b** (with twelve chains) does show liquid crystal properties. The effect of increasing the number of peripheral chains in promoting columnar mesomorphism has previously been observed in other series of discotic liquid crystals.[20] This observation has been attributed to the fact that a high number of long aliphatic chains allows their adequate arrangement in the periphery of the disc and the effective filling of the space around the central core.

It is interesting to note the absence of mesomorphism in **7b** in spite of the presence of twelve decyloxy groups in this compound. In contrast to **18b**, compund **7b** contains a flexible hexamethylene spacer between the central TTF unit and the benzene rings, and this leads to a central core that is too small as it consists only of the TTF moiety. In this case the benzene rings are far enough removed from the core that they can be considered as part of the flexible periphery of the molecule. This small core upsets the sensitive balance between the inner rigid part and the outer flexible part of the molecule needed for the existence of columnar mesomorphism. On the other hand, in **18b** the connecting unit between the central TTF and the benzene rings is much shorter, its mobility is more restricted, and as a consequence the benzoate groups can be considered to be part of the central core. Thus, the molecules of **18b** possess the characteristics of a disc-like mesogenic molecule.

Acknowledgements. We are indebted to DGICYT (Project PB94-0577) for financial support.

EXPERIMENTAL

General. All new compounds gave satisfactory microanalyses. Melting points were measured on a Büchi 510 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Varian Unity-300 or a Bruker ARX-300 spectrometer. IR spectra (Nujol mulls) were recorded using a Perkin-Elmer FTIR 1600 spectrophotometer. Mass spectra were obtained on a VG Autospec mass spectrometer: 3-NBA and 2-NPOE were used as LSIMS matrixes; the *m/z* value of the most intense peaks in the isotopic distribution is reported. Cyclic voltammograms were measured using an EG&G PARC model 273 potentiostat. The optical textures of the mesophases were studied with an Olympus BH-Z polarizing microscope equipped with a hot stage and a LINKAM THMS 600 controller. The transition temperatures were determined by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument. The apparatus was calibrated with indium (156 °C; 28.4 J g^{-1}) as a standard. X-ray diffraction experiments were carried out using a Pinhole camera (Anton-Paar) operating with a Ni-filtered Cu-$K\alpha$ beam. The samples were held in Lindemann glass capillaries (0.7 mm diameter) and the patterns were recorded on photographic film.

4-Decyloxybenzoyl chloride (2). A mixture of 4-decyloxybenzoic acid (**12a**) (556 mg, 2 mmol), thionyl chloride (1.46 mL, 20 mmol) and DMF (5 drops) was refluxed for 4-6 h (until he acid had completely dissolved) under N_2. Excess thionyl chloride was then removed under vacuum. In order to ensure complete removal of unreacted thionyl chloride, toluene was added and then removed on a rotary evaporator. This process was repeated twice. The resulting yellow oil was used without further purification (yield 90%). IR ν (cm^{-1}): 1769, 1739. MS(EI): *m/z* = 296 (M$^{+\cdot}$, 10%), 261 (100), 121 (70).

4-(4-(Decyloxy)benzoyloxymethyl)tetrathiafulvalene (3). A solution of **2** (533 mg, 1.8 mmol) in the minimum amount of CH_2Cl_2 was added to a solution of hydroxymethyltetrathiafulvalene (**1**) (210 mg, 0.9 mmol) in CH_2Cl_2 (20 mL), at 0°C under a N_2 atmosphere. NEt_3 (0.44 mL, 3.15 mmol) was then added dropwise. The mixture was stirred at room temperature for 4 h and the solvent removed under vacuum.The crude product was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1 v/v)) followed by recrystallization from EtOH to give compound **3** as a yellow solid (309 mg, 70%); mp 92-93°C . IR ν (cm^{-1}): 1714, 1603, 1250. ^{1}H-NMR ($CDCl_3$) δ: 7.98 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.38 (s, 1H), 6.30 (s, 2H), 5.01 (s, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 1.81-1.77 (m, 2H), 1.50-1.20 (m, 14H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 165.71, 163.35, 131.87, 131.51, 121.45, 119.08, 118.99, 118.88, 114.20, 68.27, 61.02, 31.88, 29.54, 29.35, 29.30, 29.08, 25.97, 22.67, 14.01. MS(EI): *m/z* = 494 (M$^{+\cdot}$, 100%), 217 (20), 146 (15), 121 (25). HR-MS: 494.1078, calculated for $C_{24}H_{30}O_3S_4$: 494.1078. Anal. Found: C, 58.39; H, 6.21. Calcd. for $C_{24}H_{30}O_3S_4$: C, 58.27; H, 6.11.

4,4'(5')-Bis(4-(decyloxy)benzoyloxymethyl)tetrathiafulvalene (5). This was prepared in an analogous way to **3**, using 4,4'(5')-bis(hydroxymethyl)tetrathiafulvalene (**4**) (132 mg, 0.5 mmol), **2** (440 mg, 1.5 mmol) and NEt_3 (0.28 mL, 2 mmol). Column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (1:1

v/v)) followed by recrystallization from EtOH (twice) gave compound **5** as a yellow solid (157 mg, 40%); mp 100-105°C . IR ν (cm^{-1}): 1708, 1288, 1250. ^1H-NMR ($CDCl_3$) δ: 7.98 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.00 (s, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 1.85-1.76 (m, 2H), 1.50-1.20 (m, 14H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 165.69, 163.33, 131.85, 121.39, 114.17, 68.24, 31.86, 29.52, 29.33, 29.28, 29.06, 25.95, 22.65, 14.09. LSIMS: *m/z* = 784 ($M^{+\cdot}$). Anal. Found: C, 64.39; H, 7.38. Calcd. for $C_{42}H_{56}O_6S_4$: C, 64.25; H, 7.19.

Tetrakis(6-(benzoyloxy)hexylthio)tetrathiafulvalene (8). A solution of tetraalcohol **6** (73.2 mg, 0.1 mmol) and NEt_3 (0.08 mL) in CH_2Cl_2 (20 mL) was added dropwise to a solution of benzoyl chloride (0.07 mL, 0.6 mmol) in CH_2Cl_2 (10 mL), at 0°C and under a N_2 atmosphere. The mixture was stirred at room temperature for 14 h. and the solvent was removed under vacuum.The crude product was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2) to afford **8** as an orange oil (53 mg, 46%). IR ν (cm^{-1}): 1715, 1273. ^1H-NMR ($CDCl_3$) δ: 8.04-8.00 (m, 2H), 7.56-7.49 (m, 1H), 7.44-7.37 (m, 2H), 4.28 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 1.78-1.63 (m, 4H), 1.45 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 166.54, 132.78, 130.36, 129.46, 128.28, 127.60, 64.78, 36.05, 29.50, 28.54, 28.05, 25.52. LSIMS: *m/z* = 1148 ($M^{+\cdot}$).

4,5-Bis(6-hydroxyhexylthio)-1,3-dithiole-2-thione (10). 6-bromo-1-hexanol (1.05 mL, 8 mmol) was added to a solution of compound **9** (0.941 g, 1 mmol) in acetone (30 mL), and the mixture was refluxed under a N_2 atmosphere for 2.5 h. The reaction mixture was allowed to cool to room temperature, the solvent was evaporated under vacuum and the crude product was purified by column chromatography (silica gel 70-230 mesh, EtAcO/hexane (2:1 v/v)), giving **10** as a very viscous orange oil (716 mg, 90%). IR ν (cm^{-1}): 3335, 1067. ^1H-NMR ($CDCl_3$) δ: 3.64 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.63 (s, 1H, ex. D_2O), 1.69-1.54 (m, 4H), 1.45-1.30 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 211.41, 136.35, 62.90, 36.62, 32.22, 29.55, 28.17, 25.22. MS(EI): *m/z* = 398 ($M^{+\cdot}$, 55%), 198 (30), 83 (50).

4,5-Bis(6-(benzoyloxy)hexylthio)-1,3-dithiole-2-thione (11). NEt_3 (0.33 mL, 2.4 mmol) and benzoyl chloride (0.2 mL, 1.8 mmol) were successively added to a solution of compound **10** (240 mg, 0.6 mmol) in CH_2Cl_2 (15 mL), at 0°C under a N_2 atmosphere. The mixture was stirred at room temperature for 14 h and the solvent was removed under vacuum.The crude product was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (2:1 v/v)) to afford **11** as an orange oil (327 mg, 90%). IR ν (cm^{-1}): 1715, 1272, 1067. ^1H-NMR ($CDCl_3$) δ: 8.03-8.00 (m, 2H), 7.55-7.48 (m, 1H), 7.43-7.39 (m, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 1.77-1.62 (m, 4H), 1.47-1.40 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 211.15, 166.48, 136.14, 132.78, 130.24, 129.40, 128.25, 64.64, 36.49, 29.39, 28.47, 28.01, 25.46. MS(EI): *m/z* = 606 ($M^{+\cdot}$, 35%), 105 (100), 77 (25).

3,4,5-Tris(decyloxy)benzoic acid (12b). Anhydrous K_2CO_3 (26.33 g, 0.19 mol) and 1-bromodecane (12.7 mL, 0.06 mol) were successively added to a solution of methyl gallate (3.69 g, 0.02 mol) in anhydrous DMF (150 mL). The mixture was heated at 120°C under a N_2 atmosphere for 20 h. The reaction mixture was allowed to cool to room temperature, water (200 mL) was added and the mixture was extracted three times with hexane/EtOAc (4:1 v/v). The organic layer was washed with water (4 x 400 mL), dried ($MgSO_4$) and evaporated under vacuum to give methyl 3,4,5-tris(decyloxy)benzoate as a brown oil (10.42 g, 85%), which was used in the next step without further purification.

To the methyl ester obtained above was added a solution of KOH (15.35 g, 0.27 mol) in EtOH (300 mL), and the mixture was refluxed until the starting material disappeared (*ca.* 4 h). The mixture was allowed to cool to room temperature, most of the solvent was evaporated under vacuum and water (200 mL) was added. The mixture was cooled to 0°C and concentrated aqueous hydrochloric acid (80 mL) was added dropwise (exothermic reaction!). Precipitation was observed, but on addition of Et_2O (100 mL) the solid dissolved. The mixture was extracted with Et_2O (3 x 300 mL) and the organic layer was washed with water (4 x 300 mL), dried (Na_2SO_4) and the solvent evaporated under vacuum. The resulting brown oil was purified by column chromatography (silica gel 70-230 mesh, hexane/EtOAc (4:1 v/v)), followed by recrystallization from EtOH. Pure compound **12b** was obtained as an off-white solid (4.72 g, 40%); mp 54°C . IR ν (cm^{-1}): 1682, 1586, 1120. ^1H-NMR ($CDCl_3$) δ: 10.6 (br s, 1H), 7.31 (s, 2H), 4.05-3.98 (m, 6H), 1.83-1.76 (m, 6H), 1.47-1.26 (m, 42H), 0.86 (t, J = 6.6 Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 172.12, 152.79, 143.08, 123.68, 108.48, 73.50, 69.12, 31.89, 30.29, 29.70, 29.61, 29.56, 29.37, 29.33, 29.24, 26.05, 22.66, 14.07. LSIMS: *m/z* = 635 $(M+2Na-H)^+$, 613 $(M+Na)^+$, 591 $(M+H)^+$.

ω-Bromohexyl benzoates 13 a-b. General Procedure. DCC (618 mg, 3 mmol) was added to a solution of the corresponding substituted benzoic acid (**12a** or **12b**) (2 mmol) in CH_2Cl_2 (20 mL; 40 mL in the case of **12b**), at 0°C under a N_2 atmosphere. After stirring for 10 min, a solution of 6-bromo-1-hexanol (0.40 mL, 3 mmol) and DMAP (195 mg, 1.6 mmol) in CH_2Cl_2 (10 mL) was added. The mixture was stirred at room temperature for 15 h and the precipitated dicyclohexylurea was filtered off and washed repeatedly with CH_2Cl_2. The combined organic layer was washed with aqueous 1N HCl (2 x 100 mL), then with water (2 x 100 mL), dried (Na_2SO_4) and the solvent evaporated under vacuum. The crude product was purified by column chromatography (silica gel 70-230 mesh, hexane/Et_2O (1:1 v/v) for **13a** and hexane/Et_2O (6:1 v/v) for **13b**).

ω-Bromohexyl 4-decyloxybenzoate (13a). White solid (664 mg, 75%); mp 38-39°C. IR ν (cm^{-1}): 1712, 1605, 1272, 1251. ^1H-NMR ($CDCl_3$) δ: 7.97 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.95-1.72 (m, 6H), 1.60-1.25 (m, 18H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 166.39, 162.88, 131.45, 122.49, 113.99, 68.15, 64.41, 33.66, 32.59, 31.84, 29.50, 29.49, 29.31, 29.26, 29.06, 28.58, 27.81, 25.93, 25.26, 22.63, 14.07. MS(EI): *m/z* = 440 ($M^{+\cdot}$, 15%).

ω-Bromohexyl 3,4,5-tris(decyloxy)benzoate (13b). Oil (1.26 g, 84%). IR ν (cm^{-1}): 1715, 1586, 1214. ^1H-NMR ($CDCl_3$) δ: 7.20 (s, 2H), 4.24 (t, *J* = 6.6 Hz, 2H), 3.98-3.94 (m, 6H), 3.33 (t, *J* = 6.8 Hz, 2H), 1.82-1.68 (m, 10H), 1.44-1.23 (m, 46H), 0.83 (t, *J* = 6.6 Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 166.25, 152.77, 142.38, 124.89, 107.96, 73.35, 69.08, 64.67, 33.27, 32.57, 31.90, 30.32, 29.71, 29.62, 29.57, 29.38, 28.58, 27.75, 26.07, 25.20, 22.66, 14.04. MS(EI): *m/z* = 752 ($M^{+\cdot}$, 55%).

4,5-Disubstituted-1,3-dithiole-2-thiones 14 a-b. General Procedure. A solution of the appropriate bromide (**13a** or **13b**, 1 mmol) in acetone (10-12 mL) was added to a solution of compound **9** (188 mg, 0.2 mmol) in acetone (25 mL), and the mixture was refluxed under a N_2 atmosphere for 48 h. After cooling to room temperature, the solvent was evaporated under vacuum and the crude product was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (2:1 v/v) for **14a**, hexane/Et_2O (6:1 v/v) for **14b**).

4,5-Bis[6-(4-decyloxybenzoyloxy)hexylthio]-1,3-dithiole-2-thione (14a). Yellow solid (349 mg, 95%); mp 47-49°C. IR ν (cm^{-1}): 1712, 1605, 1067. ^1H-NMR ($CDCl_3$) δ: 7.96 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 2H), 3.99 (t, *J* = 6.6Hz, 2H), 2.87 (t, *J* = 7.3 Hz, 2H), 1.81-1.66 (m, 6H), 1.50-1.30 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 166.35, 162.89, 136.19, 131.44, 122.43, 113.99, 68.15, 64.32, 36.54, 31.82, 29.48, 29.44, 29.30, 29.24, 29.05, 28.58, 28.07, 25.92, 25.52, 22.61, 14.05. LSIMS: *m/z* = 918 ($M^{+\cdot}$). Anal. Found: C, 64.29; H, 8.30. Calcd. for $C_{49}H_{74}O_6S_5$: C, 64.01; H, 8.11.

4,5-Bis[6-(3,4,5-tris(decyloxy)benzoyloxy)hexylthio]-1,3-dithiole-2-thione (14b). Orange oil (555 mg, 90%). IR ν (cm^{-1}): 1710, 1612, 1075. ^{1}H-NMR ($CDCl_3$) δ: 7.22 (s, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.99 (t, *J* = 6.5Hz, 6H), 2.85 (t, *J* = 7.2Hz, 2H), 1.81-1.65 (m, 10H), 1.45-1.18 (m, 46H), 0.86 (t, *J* = 6.6Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 211.09, 166.41, 152.77, 142.36, 136.13, 124.85, 107.96, 73.46, 69.15, 64.71, 36.55, 31.89, 30.30, 29.62, 29.56, 29.38, 29.33, 28.59, 28.09, 26.07, 25.50, 22.66. LSIMS: *m/z* = 1544 ($M^{+\cdot}$).

4,5-Bis[6-(4-decyloxybenzoyloxy)hexylthio]-1,3-dithiol-2-one (15a). Mercury (II) acetate (1.04 g, 3.25 mmol) was added to a solution of **14a** (600 mg, 0.65 mmol) in a mixture of $CHCl_3$ (30 mL) and AcOH (15 mL). After stirring at room temperature for 1.5 h, the white precipitate was filtered off through a celite pad and washed with CH_2Cl_2 (3 x 20 mL). The filtrate was washed with water (3 x 100 mL), aqueous $NaHCO_3$ (3 x 100 mL) and again with water (3 x 100 mL). The organic layer was dried (Na_2SO_4), and the solvent evaporated under vacuum to afford crude product **15a**, which was purified by column chromatography (silica gel 70-230 mesh, Et_2O/hexane (1:1 v/v)), giving a pale yellow oil (527 mg, 90%). IR ν (cm^{-1}): 1712, 1670. ^{1}H-NMR ($CDCl_3$) δ: 7.94 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.96 (t, *J* = 6.5Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 1.79-1.63 (m, 6H), 1.46-1.24 (m, 18H), 0.85 (t, *J* = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 189.87, 166.33, 162.86, 131.42, 127.09, 122.42, 113.96, 68.12, 64.34, 36.45, 31.82, 29.49, 29.41, 29.30, 29.25, 29.04, 28.57, 28.07, 26.84, 25.91, 25.53, 22.61, 14.06. LSIMS: *m/z* = 902 ($M^{+\cdot}$).

4,5-Bis[6-(3,4,5-tris(decyloxy)benzoyloxy)hexylthio]-1,3-dithiol-2-one (15b). This was prepared analogously to **15a**, using **14b** (555 mg, 0.36 mmol) and mercury (II) acetate (574 mg, 1.8 mmol). After column chromatography (silica gel 70-230 mesh, Et_2O/hexane (1:5 v/v)), pure **15b** was isolated as a pale yellow oil (490 mg, 90%). IR ν (cm^{-1}): 1715, 1674. ^{1}H-NMR ($CDCl_3$) δ: 7.21 (s, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 3.98 (t, *J* = 6.4 Hz, 6H), 2.81 (t, *J* = 7.2 Hz, 2H), 1.81-1.66 (m, 10H), 1.45-1.25 (m, 46H), 0.85 (t, *J* = 6.6Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 189.50, 166.36, 152.78, 142.42, 127.11, 124.87, 108.02, 73.43, 69.16, 64.70, 36.47, 31.89, 30.34, 29.69, 29.61, 29.44, 29.38, 29.33, 28.60, 28.08, 26.08, 25.49, 22.66, 14.07. LSIMS: *m/z* = 1528 ($M^{+\cdot}$).

Tetrakis[6-(4-decyloxybenzoyloxy)hexylthio]tetrathiafulvalene (7a). A solution of **15a** (528 mg, 0.585 mmol) in freshly distilled triethyl phosphite (10 mL) was heated at 120-130°C under a N_2 atmosphere for 3 h. After cooling to room temperature, excess $P(OEt)_3$ was distilled off under vacuum, and the resulting oil was purified by column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane (2:1 v/v)), followed by recrystallization from EtOAc/pentane. **7a** was obtained as an orange solid (218 mg, 42%); mp 69°C. IR ν (cm^{-1}): 1713, 1606. ^{1}H-NMR ($CDCl_3$) δ: 7.95 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.96 (t, *J* = 6.6Hz, 2H), 2.79 (t, *J* = 7.2 Hz, 2H), 1.82-1.52 (m, 6H), 1.45-1.25 (m, 18H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 166.38, 162.87, 131.46, 127.68, 122.49, 113.99, 109.95, 68.15, 64.46, 36.52, 31.84, 29.51, 29.32, 29.26, 29.07, 28.62, 28.08, 25.94, 25.55, 22.63, 14.07. LSIMS: *m/z* = 1773 ($M^{+\cdot}$). Anal. Found: C, 66.09; H, 8.22. Calcd. for $C_{98}H_{148}O_{12}S_8$: C, 66.32; H, 8.41.

Tetrakis[6-(3,4,5-tris(decyloxy)benzoyloxy)hexylthio]tetrathiafulvalene (7b). This was prepared analogously to **7a**, starting from **15b** (494 mg, 0.324 mmol). Column chromatography (silica gel 70-230 mesh, Et_2O/hexane (1:6 v/v)) afforded **7b** as an orange solid (147 mg, 30%); mp 36°C. IR ν (cm^{-1}): 1712, 1587. ^1H-NMR ($CDCl_3$) δ: 7.22 (s, 2H), 4.26 (t, J = 6.7 Hz, 2H), 3.99 (t, J = 6.4 Hz, 6H), 2.80 (t, J = 8.1 Hz, 2H), 1.81-1.62 (m, 10H), 1.45-1.25 (m, 46H), 0.86 (t, J = 6.6Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 166.43, 152.81, 142.42, 127.72, 124.93, 109.90, 108.03, 73.48, 69.19, 64.83, 36.09, 31.91, 30.32, 29.64, 29.58, 29.40, 29.38, 28.65, 28.10, 26.10, 25.51, 22.67, 14.09. LSIMS: m/z = 3024 ($M^{+\cdot}$), 1512 (M^{2+}). Anal. Found: C, 70.39; H, 10.48. Calcd. for $C_{178}H_{308}O_{20}S_8$: C, 70.68; H, 10.26.

4,5-Disubstituted-1,3-dithiole-2-thiones 17 a-b. General Procedure. DCC (360 mg, 1.75 mmol) was added to a solution of the appropriate benzoic acid (**12a** or **12b**, 1.25 mmol) in CH_2Cl_2 (20 mL), at 0°C under a N_2 atmosphere. After stirring for 10 min, a suspension of compound **16** (97 mg, 0.5 mmol) and DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added. The mixture was stirred at room temperature for 3-4 h (monitored by TLC) and the precipitated dicyclohexylurea was filtered off and washed repeatedly with CH_2Cl_2. The combined organic layer was washed with aqueous 1N HCl (3 x 100 mL), then with water (2 x 100 mL), dried ($CaCl_2$) and the solvent evaporated under vacuum. The desired products were obtained after column chromatography (silica gel 70-230 mesh, hexane/Et_2O(3:1 v/v) for **17a**, hexane/Et_2O(4:1 v/v) for **17b**).

4,5-Bis(4-decyloxybenzoyloxymethyl)-1,3-dithiole-2-thione (17a). Yellow solid (260 mg, 73%); mp 60°C. IR ν (cm^{-1}): 1717, 1073. ^1H-NMR ($CDCl_3$) δ: 7.97 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.33 (s, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.87-1.75 (m, 2H), 1.50-1.28 (m, 14H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 210.48, 164.95, 163.14, 138.49, 131.46, 120.21, 113.80, 67.81, 62.91, 31.38, 29.02, 28.84, 28.79, 28.55, 25.45, 22.16, 13.60. LSIMS: m/z = 715 [$(M+H)^+$]. Anal. Found: C, 65.68; H, 7.80. Calcd. for $C_{39}H_{54}O_6S_3$: C, 65.51; H, 7.61.

4,5-Bis[3,4,5-tris(decyloxy)benzoyloxymethyl]-1,3-dithiole-2-thione (17b). Yellow solid (395 mg, 73%); mp 53-55°C. IR ν (cm^{-1}): 1706, 1068. ^1H-NMR ($CDCl_3$) δ: 7.23 (s, 2H), 5.35 (s, 2H), 4.00 (t, J = 6.8 Hz, 6H), 1.85-1.72 (m, 6H), 1.50-1.22 (m, 42H), 0.89 (t, J = 6.6 Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 210.29, 165.17, 152.49, 142.68, 138.46, 122.52, 107.69, 73.07, 68.75, 31.41, 29.82, 29.22, 29.13, 28.92, 28.85, 25.58, 22.19, 13.63. LSIMS: m/z = 1339 ($M^{+\cdot}$). Anal. Found: C, 70.52; H, 10.28. Calcd. for $C_{79}H_{134}O_{10}S_3$: C, 70.81; H, 10.08.

Tetrakis(4-decyloxybenzoyloxymethyl)tetrathiafulvalene (18a). A solution of $Co_2(CO)_8$ (192 mg, 0.56 mmol) in toluene (10 mL) was added dropwise and under a N_2 atmosphere to a stirred solution of **17a** (571 mg, 0.8 mmol) in the minimum amount of toluene. The mixture was refluxed for 3-3.5 h (TLC monitoring) and then cooled to room temperature. The black pyrophoric residue formed was removed by filtration through silicagel, and then washed with toluene and CH_2Cl_2. The solvent from the filtrate was evaporated under vacuum and the residue purified by repeated column chromatography (silica gel 70-230 mesh, first with CH_2Cl_2/hexane(3:1 v/v), and then with toluene/EtOAc(60:1 v/v)) to give **18a** as a pale orange solid (136 mg, 25%); mp 125°C. IR ν (cm^{-1}): 1715, 1595, 1120. ^1H-NMR ($CDCl_3$) δ: 7.97 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 5.15 (s, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.83-1.75 (m, 2H), 1.49-1.28 (m, 14H), 0.89 (t, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ: 166.11, 163.80, 132.37, 130.34, 121.74, 114.61, 109.04, 68.69, 58.86, 32.32, 29.99, 29.80, 29.74, 29.53, 26.39, 23.11, 14.55. LSIMS: *m/z* = 1366 [$(M+H)^+$]. Anal. Found: C, 68.40; H, 7.78. Calcd. for $C_{78}H_{108}O_{12}S_4$: C, 68.59; H, 7.97.

Tetrakis[3,4,5-tris(decyloxy)benzoyloxymethyl]tetrathiafulvalene (18b). This was prepared analogously to **18a**, using **17b** (803 mg, 0.6 mmol) and $Co_2(CO)_8$ (144 mg, 0.42 mmol). Column chromatography (silica gel 70-230 mesh, CH_2Cl_2/hexane(2:1 v/v)) afforded **18b** as a pale orange solid (118 mg, 15%); mp 75°C. IR ν (cm^{-1}): 1721, 1590, 1121. ^{1}H-NMR ($CDCl_3$) δ: 7.23 (s, 2H), 5.17 (s, 2H), 3.99 (t, *J* = 6.3 Hz, 6H), 1.83-1.75 (m, 6H), 1.47-1.27 (m, 42H), 0.88 (t, *J* = 6.5 Hz, 9H). ^{13}C-NMR ($CDCl_3$) δ: 165.83, 152.87, 142.84, 130.01, 123.53, 108.12, 73.50, 69.16, 31.90, 29.71, 29.62, 29.57, 29.40, 29.34, 26.09, 22.66, 14.09. LSIMS: *m/z* = 2614 ($M^{+\cdot}$). Anal. Found: C, 72.70; H, 10.08. Calcd. for $C_{158}H_{268}O_{20}S_4$: C, 72.54; H, 10.33.

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