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# Synthesis and Structural Characterization of a Bis-arborol−Tetrathiafulvalene Gel: Toward a Self-Assembling "Molecular" Wire

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A gel-forming compound, 4,4′-bis[[*N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)ethyl]-7,7-diamidoheptyl]thio]-5,5′-dimethyltetrathiafulvalene (**1**) has been prepared, with the aim of manufacturing a self-assembling "molecular" wire. The gel has been characterized structurally by optical and atomic force microscopy. These investigations revealed stringlike superstructures with lengths of the order of microns and diameters ranging from about 30 to several hundred nanometers. Absorption spectroscopy of **1**, both in the neutral and in the oxidized state, indicates that the tetrathiafulvalene units form stacks through which conduction could take place.

## Introduction

One of the interesting fields in organic materials chemistry is the preparation of "molecular" scale electronic and optical components, such as rectifiers, switches, and wires.[1−3] These ultra small scale components have potential use in future generation computers and sensors. This strategy is complementary to the miniaturization efforts in the more conventional inorganic semiconductor research.

This article describes an attempt to manufacture a prototype "molecular" wire by utilizing self-assembly principles.

"Molecular" wires are in this context defined as molecular size conduits of electrons/holes with stringlike structure. Conduction along such a structure depends in part on the mobility of the carriers, i.e., the overlap of orbitals and the availability of a certain number of unfilled states, in a periodic array.

Several candidates for "molecular" wires have been suggested: conjugated polyenes like the naturally occuring carotenes and synthetic analogs[4] or aromatic and heteroaromatic polymers (e.g., poly(thiophene)). Conduction occurs through the conjugated $\pi$-electron system, and unfilled states are created by photoexitation or by oxidation/reduction reactions. Another strategy has been to utilize the ability of specially designed molecules to form stacks. Alkyl-substituted phthalocyanine complexes, forming liquid crystals, have thus been proposed as a form of "molecular" wire and have been shown to be semiconducting.[5]

The molecular requirements of self-assembling structures have been studied extensively during the last decade.[2,3] Of special interest to us was the work of Newkome et al., who prepared the so-called bis-arborols that readily form gels in water consisting of stringlike assemblies.[6,7] Arborols are branched polyalcohols resembling a tree. Bis-arborols are bidirectional molecules with a lipophilic central chain (or trunk), substituted on the ends with polyalcohol groups (the branches and the root) (see Figure 1). On gelation in water these bis-arborols form strings of helical structures with a lipophilic interior and the hydrophilic spheres of polyalcohols on the exterior. Newkome et al. prepared a bis-arborol with an alkyne function in the central part of the molecule and proposed to polymerize this into a conjugated polyalkene with hydrophilic side chains. The hydrophilic polyalcohols would then form an electrically insulating layer around the conductive polyalkene thus forming a true "molecular" wire.

Conductivity is, however, not dependent on covalent bonding, as shown by the highly electrically conductive tetrathiafulvalene (TTF) and tetraselenafulvalene salts. In these crystalline compounds the partially oxidized heteroaromatic systems overlap to form stacks with high electron mobility along the stacking axis.[8,9]

It seemed natural to combine our past experiences with these "organic" metals with the self-assembling properties of the bis-arborols and synthesize the bis-arborol−tetrathiafulvalene **1** (see Figure 1). If the gel-forming properties were retained, such a compound might self-assemble into strings of "molecular" wires, with the TTF moieties forming an internally conductive stack isolated by the arborol groups (see Figure 2). The TTF moieties are easily oxidized to the cation radical stage,

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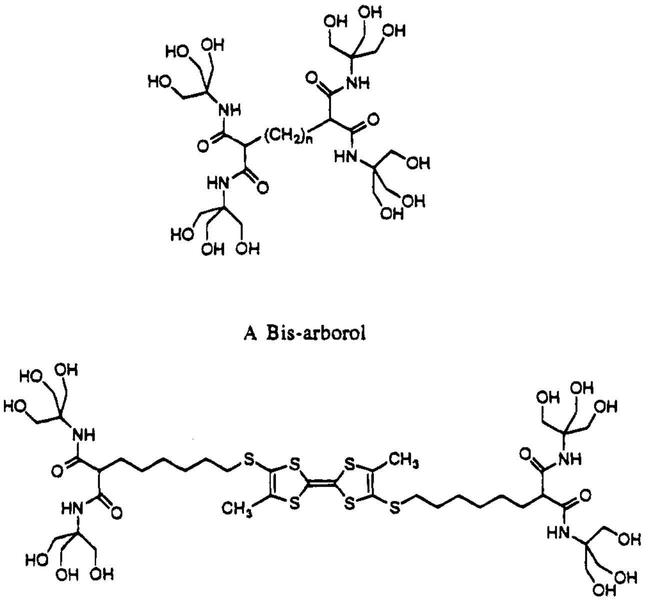

**Figure 1.** Molecular structures of a bis-arborol-type molecule and **1**.

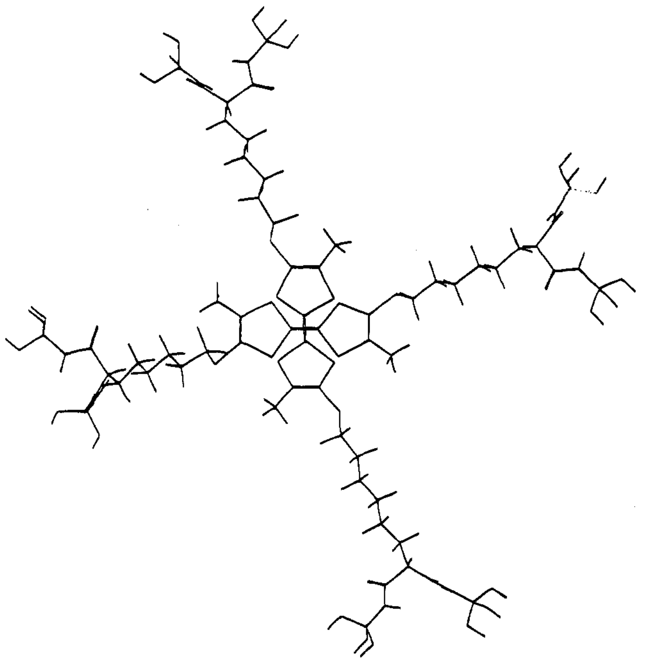

**Figure 2.** Molecular modeling of **1**, as a stack of molecules.

so addition of small aliquots of iodine to the gel could create the necessary unfilled states required for conduction.

## Results

**Synthesis of the Bis-arborol–Tetrathiafulvalene.** Previous experience with the synthesis of *S*-alkyl-substituted tetrathiafulvalenes[10] via mesoionic 2-(dimethylamino)-5-methyl-1,3-dithiolium 4-thiolate (**2**) enabled us to formulate the procedure outlined in Scheme 1. Mesoion **2** was S-alkylated with the bromo diester **3**, prepared by a standard malonic ester synthesis,[11] yielding the 4-*S*-alkyl-1,3-dithiolium salt **4**. Reduction of this salt with sodium borohydride[12] produced the 2-(dimethylamino)-2*H*-1,3-dithiole **5**. Compound **5** was deaminated by reaction with cold sulfuric acid followed by metathesis of the resulting 1,3-dithiolium salt into the hexafluorophosphate salt **6**. Alternatively, **5** was converted into the 2-ethoxy-2*H*-1,3-dithiole **7** by treatment with hydrochloric acid in ethanol. The bis[[(7,7-bis(ethoxycarbonyl)heptyl]thio]-substituted tetrathiafulvalene **8** was then prepared by either dimerizing compound **6** with triethylamine in acetonitrile[13] or by reacting **7** with trichloroacetic acid in hot toluene.[14] High-resolution $^{13}$C NMR showed a doubling of two of the carbon atoms in the TTF moiety indicating that **8** is a mixture of cis and trans isomers around the central double bond in the molecule.

Finally, amidation of the ester groups with Tris base (Tris(hydroxymethyl)aminomethane), according to the procedure developed by Newkome et al.,[7] gave the desired bis-arborol–tetrathiafulvalene **1**.

**Preparation and Characterization of the Bis-arborol–TTF Gel.** Compound **1** could be dissolved, up to several percent, in hot solvent mixtures of 25% (v/v) ethanol/water or dimethylformamide/water. On cooling, these solutions became opaque with the formation of a stiff gel, as described in the Experimental Section.

To describe in more detail the formation of the gel, the temperature dependent $^{1}$H NMR spectrum was recorded for a 2% solution of **1** in a mixture of dimethylformamide-$d_6$ and $D_2O$ (3:1). The spectra were recorded from 323 to 363 K in steps of 10° to follow the changes when the gel dissolved. The spectrum displayed the expected number of lines, but at ambient temperature they were all broadened. This behavior is commonly found in gelating systems where the highly ordered domains are invisible in NMR due to low mobility. At higher temperature the lines became progressively sharper and their intensity increased, leveling off above 343 K. To assess the fraction of molecules present as free in solution the signal intensities were normalized using the asymptotic intensity at high temperature. The percentage of mobile molecules at 323 K is 30% of the limiting value found at high temperature. A pronounced hysteresis is seen in the formation of aggregates. A similar observation was made on solutions in the alcohol–water mixture.

The bis-arborol–TTF molecules may have a cis or trans configuration around the central double bond in the TTF moiety. Molecular modeling shows that the cis conformer may form a helical structure similar to the alkane–bis-arborols, while the trans conformers can only form more restricted stacked structures due to steric interactions. Calculations performed on a dimer of two trans conformers showed that the planes of the TTF moieties were parallel to each other with a distance of 0.37 nm and that one molecule was rotated 90° relative to the other. Repetition of the dimer motif would give a stack of molecules with a diameter of approximately 3.5 nm (see Figure 2).

Phase contrast optical microscopy of an air-dried sample of the bis-arborol–TTF gel clearly revealed thin stringlike aggregates, with a length in the order of tens of microns (see Figure 3). These structures are also

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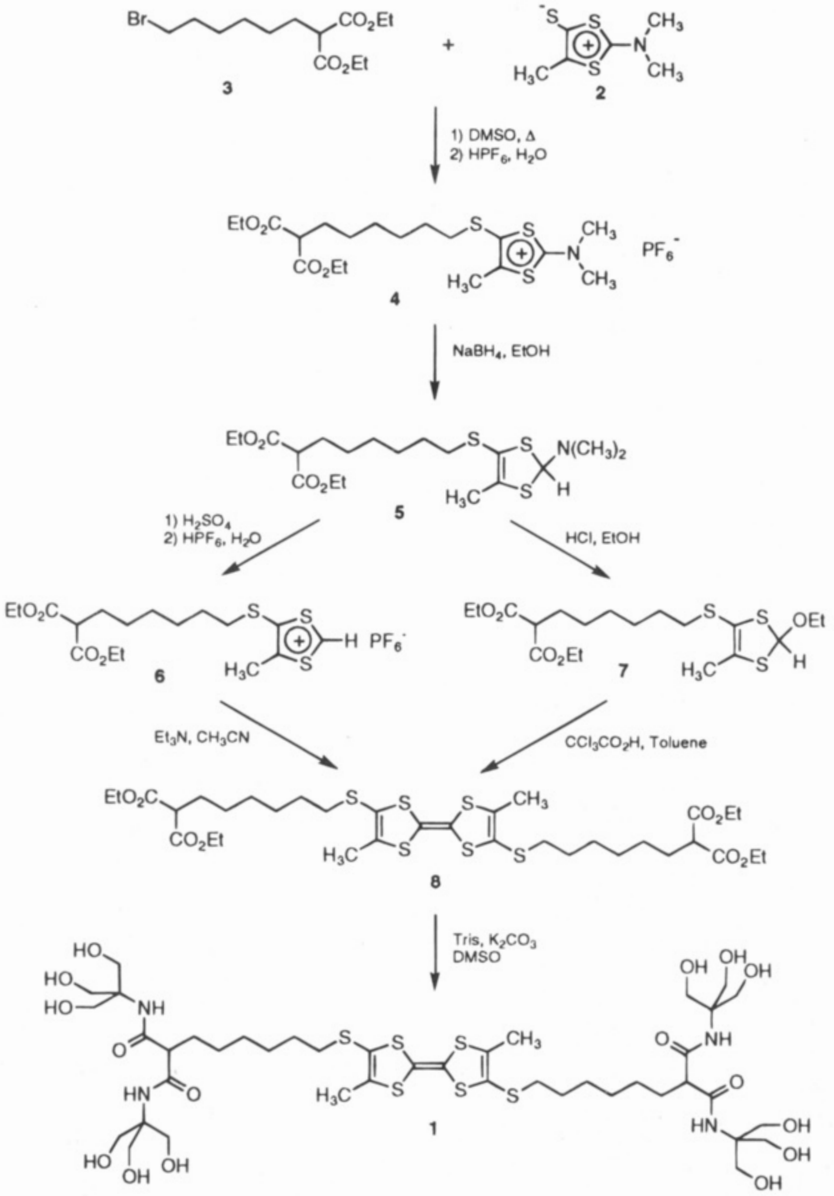
**Scheme 1. Synthesis of Bis-arborol–Tetrathiafulvalene 1**



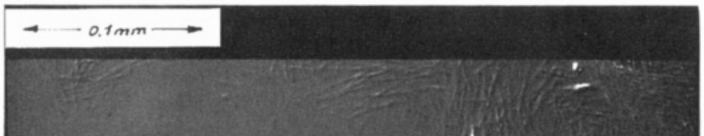


Figure 3. Phase contrast microscopy of **1** as dried gel on silicon.

visible when viewed with crossed polarizing filters, indicating an internally ordered arrangement.

We then turned to atomic force microscopy (AFM) in the hope of obtaining further insight to the internal structure of the gel. Again string- or bandlike structures are clearly visible (Figure 4 with a diameter in the order of ca. 100 nm. AFM has the added advantage that hight profiles can be obtained, showing that the structures all have the same thickness of about 60 nm, regardless of their diameter. The transverse dimensions of the fibers are 1 order of magnitude greater than one would expect from the modeling of simple stacked strings. We therefore interpret the observed structures as probable higher aggregates. This type of behavior was also seen for some of the alkane–bis-arborols studied by Newkome et al.[6,7]

Transmission electron microscopy was also used to characterize the gel, but gave almost identical information as AFM, and is therefore not included.

**Absorption Spectroscopy.** HPLC analysis of **1** reveals two peaks in a 1:0.6 ratio (Figure 5A). The UV–vis spectra of the peaks are identical and resemble spectra of alkylthio-substituted TTF molecules; i.e., the spectrum is dominated by excitations located in the TTF moiety (Figure 5B). A plausible explanation for the presence of two peaks with identical spectra is the

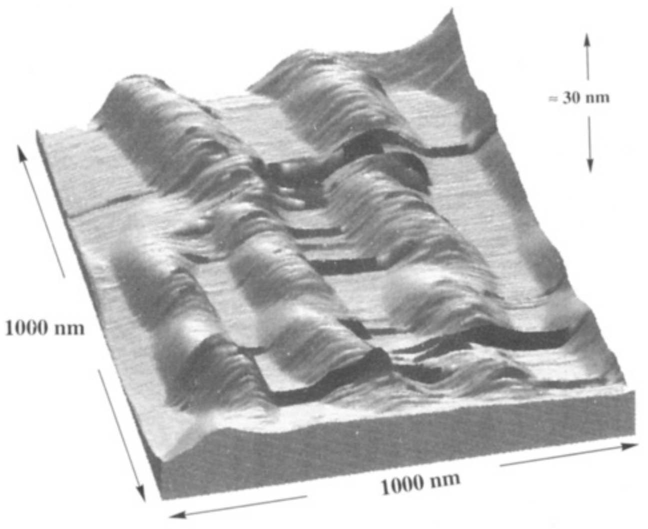


**Figure 4.** Atomic force microscopy of **1** as dried gel on silicon.

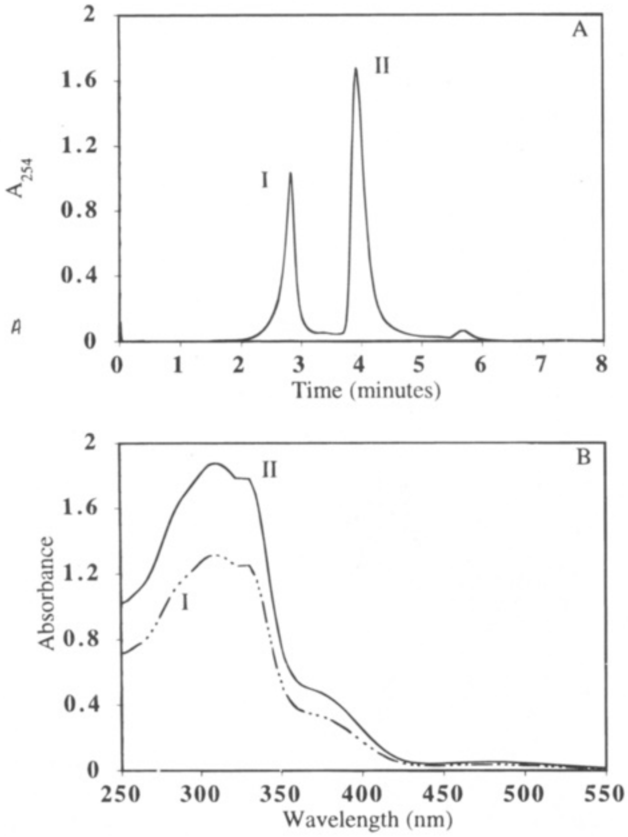


**Figure 5.** (A) HPLC trace of **1**. The two peaks are due to cis and trans isomers around the central double bond. (B) UV–vis spectrum of the two isomers of **1**.

presence of cis and trans isomers of **1** (see discussion in the Experimental Section).

In order to study the effect of oxidation with iodine, two experiments were carried out. First the spectra of the non-gel-forming ester **8** in 25% ethanol were recorded (Figure 6a). Addition of iodine caused the appearance of a new peak at $\lambda = 678$ nm, which is typical of the oxidized TTF monomers.[15] Secondly, iodine was added to the gel of **1** suspended in 25% ethanol, resulting in two new peaks at $\lambda = 673$ nm, presumably due to oxidized monomers (as for **8**), and $\lambda = 874$ nm (Figure 6b). This latter peak is typical for TTF dimers or oligomers, and it is observed in solutions of TTF cation radicals at low temperature and in stacks of TTF salts in the crystalline state.[15] The presence of this peak in the spectrum of **1** at ambient temperature shows that dimers or higher oligomers are formed in the gel. These results therefore strongly suggest a stacklike arrangement of the TTF moieties. The same spectral features were observed when a sample of the dried gel, on quartz, was exposed to iodine vapor (Figure 6c).

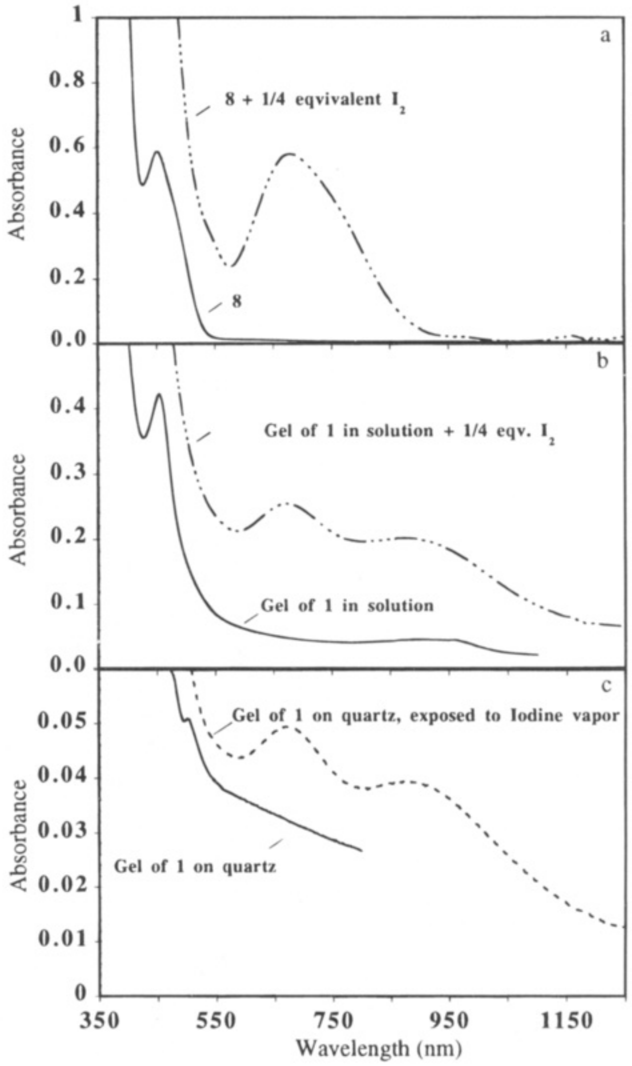


**Figure 6.** UV–vis–NIR spectra of the neutral and oxidized forms of (a) **8** in solution. (b) **1** in solution (25% ethanol), and (c) **1** as dried gel on quartz.

**Cyclic Voltammetry.** Cyclic voltammetry was carried out to ensure that the redox potentials of the TTF moiety of **1** were not altered significantly by the arborol substituents. The first and second oxidation potentials were measured to be 460 and 780 mV, relative to a saturated calomel electrode in acetonitrile. These potentials are very similar to those of a model compound: 4,4′-dimethyl-5,5′-bis(methylthio)tetrathiafulvalene (455 and 760 mV).

## Conclusion

It has been possible to prepare a bis-arborol–TTF derivative **1** which forms a gel, consisting of strong- or

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bandlike structures with a length of tens of microns and diameters in the 30−100 nm range. Clearly these are larger aggregates of smaller filaments, which we have not yet been able to visualize individually. UV−vis spectroscopy indicates that the TTF moieties form stack-like arrangements. It is therefore plausible that the observed structures are in fact larger superstructures of single strings with a molecular diameter of about 3.5 nm.

## Experimental Section

**General.** HPLC analyses were performed using a Beckman System-Gold with diode array detector, reversed phase column (Beckman ultrasphere ODS 5 $\mu$m) and using 45% THF in water as eluent. UV−vis spectra were recorded on a Perkin-Elmer Lambda 9 spectrograph. Gel suspensions were studied in 1 mm cuvettes. Phase contrast microscopy was performed using a Nikon microscope equipped with Nomarsky optics. Atomic force microscopy was performed using a Rasterscope 3000 AFM (Danish Micro Engineering A/S).

**2-(Dimethylamino)-4-[[7,7-bis(ethoxycarbonyl)heptyl]-thio]-5-methyl-1,3-dithiolium Hexafluorophosphate (4).** 2-(Dimethylamino)-5-methyl-1,3-dithiolium 4-thiolate[10] (**2**) (7.7 g, 40 mmol) and bromo diester **3**[11] (13.0 g, 40 mmol) were mixed in DMSO (50 mL) and heated to 160 °C for 2 min and then left to cool to ambient temperature. After 1 h the reaction mixture was poured into a mixture of hexafluorophosphoric acid (30 mL, 60%) in ice−water (200 mL) and stirred vigorously for a few minutes. The product was then extracted twice with methylene chloride (75 and 25 mL). The combined organic phase was washed with dilute hydrochloride acid (50 mL) and evaporated under vacuum to a reddish oil. Most of the colored byproducts were removed by dissolving the oil in hot ethanol (100 mL, 96%), treating it with activated carbon at reflux and filtering hot. The now slightly red solution was stirred while cooling in an ice−methanol bath to precipitate the product as white or slightly red crystals.

Yield: 19.01 g, 92.2%. Mp: 59−60 °C. $^1$H NMR (DMSO-$d_6$) $\delta$: 1.18 (t, 6H, $J$ = 7 Hz), 1.2−2 (broad multiplets, 10H), 2.48 (s, 3H), 2.92 (t, 2H, $J$ = 5 Hz), 3.48 (s+t, 6H + 1H), 4.10 (q, 4H, $J$ = 7 Hz) ppm. $^{13}$C NMR (DMSO-$d_6$) $\delta$: 13.86, 15.16, 26.28, 27.26, 27.98, 28.69, 36.56, 46.58, 47.04, 51.07, 60.83, 124.65, 140.27, 169.02, 183.86 ppm. Anal. Calcd for $C_{19}H_{32}NF_6PO_4S_3$: C, 39.37; H, 5.56; N, 2.42. Found: C, 39.34; H, 5.45; N, 2.35.

**2-(Dimethylamino)-4-[[7,7-bis(ethoxycarbonyl)heptyl]-thio]-5-methyl-2*H*-1,3-dithiole (5).** Hexafluorophosphate **4** (19 g, 37 mmol) was dissolved in ethanol (200 mL, 99%) by gentle heating after cooling in an ice bath. Sodium borohydride (2 g, 53 mmol) was added in small portions, under stirring for a few minutes. Some gas evolution occurred, and the temperature was allowed to rise to 10 °C. The ice bath was removed, and the reaction mixture was stirred vigorously at ambient temperature for 1 h. The mixture was diluted with petroleum ether (100 mL) and diethyl ether (100 mL) and carefully hydrolyzed with water (200 mL). The phases were separated, and the water phase was extracted with a mixture of petroleum ether (50 mL) and diethyl ether (50 mL), the combined organic phase was dried over $MgSO_4$, and the solvents evaporated in vacuum.

Yield: 13.8 g, 86% yellowish oil used without further purification in the preparation of compounds **6** and **7**. $^1$H NMR (CDCl$_3$) $\delta$: 1.19 (t, 6H, $J$ = 7 Hz), 1.2−1.8 (b, 10H), 2.11 (s, 3H), 2.26 (s, 6H), 2.72 (m, 2H), 3.30 (t, 1H, $J$ = 5 Hz), 4.2 (q, 4H, $J$ = 7 Hz) ppm. $^{13}$C NMR (CDCl, $\delta$: 14.11, 15.41, 27.18, 28.29, 28.61, 28.81, 29.72, 35.77, 38.24, 52.02, 61.26, 115.89, 131.69, 169.47 ppm.

**4-[[7,7-Bis(ethoxycarbonyl)heptyl]thio]-5-methyl-1,3-dithiolium Hexafluorophosphate (6).** Compound **5** (13.5 g, 31 mmol) was added dropwise to ice cold sulfuric acid (98%, 100 mL) while the temperature was kept below 10 °C. After 10 min of stirring, the reaction mixture was poured into a mixture of ice (500 mL) and hexafluorophosphoric acid (60%, 25 mL) under vigorous stirring. The product separates as a semicrystalline mass, which was taken up in methylene chloride (100 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated under vacuum.

Yield: 16.7 g (quantitative) of a dark oil that was used without further purification in the preparation of **8**. $^1$H NMR (DMSO-$d_6$) $\delta$: 1.18 (t, 6H, $J$ = 7 Hz), 1.2−1.8 (b, 8H), 1.94 (s, 3H), 2.69 (b, 2H), 3.3 (t, 1H), 3.41 (t, 2H), 4.01 (q, 4H, $J$ = 7 Hz), 10.5 (s, 1H) ppm. $^{13}$C NMR (DMSO-$d_6$) $\delta$: 13.8, 14.9, 26.3, 27.5, 28.0, 28.8, 29.3, 34.7, 51.1, 60.7, 116.3, 133.2, 168.9 ppm.

**2-Ethoxy-4-[[7,7-bis(ethoxycarbonyl)heptyl]thio]-5-methyl-2*H*-1,3-dithiole (7).** Compound **5** (8.6 g, 17 mmol) was dissolved in ethanol (150 mL, 96%) and added to concentrated hydrochloric acid (10 mL) while being stirred and then left at an ambient temperature for 30 min. Petroleum ether (75 mL), diethyl ether (75 mL), and water (100 mL) were added to the reaction mixture and the phases separated. The organic phase was dried over $MgSO_4$, filtered, and evaporated in vacuum to give a yellowish oil.

Yield: 5.32 g, 73.0%. $^1$H NMR (CDCl, $\delta$: 1.16 (t, 3H, $J$ = 7 Hz), 1.22 ppm (t, 6H, $J$ = 7 Hz), 1.2−1.4 (broad multiplets, 6H), 1.53 (pentet, 2H, 7Hz), 1.83 (m, 2H), 2.11 (s, 3H), 2.66 (m, 2H), 3.26 (t, 1H, $J$ = 7 Hz), 4.15 (double quartet, 4 + 2 H, $J$ = 7 Hz), 6.42 (2, 1H) ppm. $^{13}$C NMR (CDCl$_3$) $\delta$: 13.89, 14.52, 15.17, 26.97, 27.99, 28.40, 28.59, 29.34, 35.63, 51.76, 59.18, 61.04, 86.12, 115.69, 131.17, 169.21 ppm.

**4,4′-Bis[[7,7-bis(ethoxycarbonyl)heptyl]thio]-5,5′-dimethyltetrathiafulvalene (8). From Compound 7.** Compound **7** (5.3 g, 12 mmol) was dissolved in toluene (25 mL) and added dropwise to a solution of trichloroacetic acid (2 g) in toluene (200 mL) at reflux and under argon over 10 min. Reflux was continued for 1 h. The reaction mixture turned dark red-orange. The reaction mixture was cooled to an ambient temperature and washed with sodium dithionite (5 g) in water (200 mL). The phases were separated, and the deep orange-red toluene solution was adsorbed on silica (50 g). First, some byproducts were eluted with toluene, and then the product was eluted with 5% ethyl acetate in toluene (500 mL). The solvents were removed in vacuum to obtain an orange-red oil, which crystallized on standing. It was recrystallized from ethanol several times by heating gently and then precipitating the solid at −18 °C.

Yield: 3.13 g, 66.8%. Mp: 55−7 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.13 (t, 12H, $J$ = 7 Hz), 1.26−1.3 (broad multiplets, 12H), 1.45 (pentet, 4H, $J$ = 7 Hz), 1.74 (m, 4H), 1.98 (s, 6H), 2.55 (double triplet, 4H), 3.17 (t, 2H, $J$ = 7 Hz), 4.05, (double quartet, 8H, $J$ = 7 Hz) ppm. $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$: 13.64, 14.85, 26.64, 27.61, 28.09, 28.27, 29.01, 35.43, 51.38, 60.66, 107.53, (118.93, 119.06), (134.01), 134.18), 168.79 ppm. Anal. Calcd for $C_{34}H_{52}O_8S_6$: C, 52.28; H, 6.71; S, 24.63. Found: C, 52.13; H, 6.75; S, 24.35.

**4,4′-Bis[[7,7-bis(ethoxycarbonyl)heptyl]thio]-5,5′-dimethyltetrathiafulvalene (8). From Compound 6.** Compound **6** (16.7 g, 31 mmol) was dissolved in acetonitrile (100 mL) and the solution flushed with argon. Triethylamine (10 mL, 72 mmol) was added in about 10 min with ice cooling. After another 15 min the dark greenish reaction mixture was diluted with water (200 mL) and extracted with diethyl ether (100 mL). The organic phase was washed with water, dried over $MgSO_4$, and filtered through silica gel to retain some darkly colored byproducts. The solvent was evaporated under vacuum, leaving an orange oil that solidified overnight.

Yield: 9.61 g, 79.4%. Identical by NMR to the compound obtained from compound **7**.

**4,4′-Bis[[*N*,*N*′-bis[2-hydroxy-1,1-bis(hydroxymethyl)-ethyl]-7,7-diamidoheptyl]thio]-5,5′-dimethyltetrathiafulvalene (Bis-arborol−Tetrathiafulvalene) (1).** Tetraester **8** (4.00 g, 5.12 mmol), Tris(hydroxymethyl)aminomethane (Tris) (4.25 g, 6 equiv) and potassium carbonate (4.2 g, 6 equiv) were mixed in dry DMSO (50 mL) and stirred for 48 h at ambient temperature. The DMSO was then distilled off under vacuum (0.05 mmHg), and the residue was triturated with hot water (50 mL) and methanol (50 mL). The cooled suspension was centrifugated at 3000 rpm for 15 min to precipitate the product. The supernatant was decanted, and the solid was resuspended in pure water (50 mL) and centrifugated. The precipitate was suspended in ethanol (100 mL), filtered off, and washed, first with ethanol (100 mL) and then with diethyl ether (200 mL). The orange solid was dried overnight in vacuum. HPLC on a reversed-phase column with THF/water as eluent showed two products in the ratio 64:36, with a purity greater than 95%. Their UV–vis spectra were almost identical (see Figure 6B), indicating that they both contained the same TTF chromophore, presumably being the cis and trans isomers around the central double bond. In order to confirm this assignment the most abundant component was isolated from several HPLC runs and added to a trace of hydrochloric acid, a process that will isomerize TTF's. It was then reanalyzed by HPLC, now showing the two original peaks. High-resolution NMR is consistent with this explanation. The $^{13}$C NMR signals corresponding to two of the TTF carbon atoms are doubled. No effort was made to separate larger quantities of the isomers, since subsequent oxidation with iodine would isomerize them anyway. A correct microanalysis was impossible to obtain, probably due to inclusion of small amounts of water and salts.

Yield: 4.03 g, 72.8%. Mp: 145–150 °C (dec with the evolution of a gas). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 1.2–1.35 (b, 8H), 1.35–1.45 (b, 4H), 1.58 (p, 4H, $J = 6$ Hz), 1.70 (b, 4H), 2.19 (s, 6H), 2.81 (p, 4H, $J = 6$ Hz), 3.4 (b, NH + OH), 3.60 (s, 24H). $^{13}$C NMR (DMSO-$d_6$) $\delta$: 15.14, 26.62, 27.61, 28.39, 29.05, 30.00, 35.41, 53.44, 60.67, 107.48, (118.65, 118.77), (134.99, 135.04), 170.94 ppm. IR (KBr) 3315 (OH), 2926, 2853 ($CH_2$OH), 1651, 1629 (amide I and II), 1593, 1524, 1283, 1126, 1058, 1030 (COH), 669. Plasma desorption MS in the presence of trifluoroacetic acid: 1081.4 (M$^+$), 1177.8 (M$^+$ + TFA).

**Preparation of the Bis-arborol–TTF Gel for Microscopy and NMR Studies.** A 2% (w/v) solution of **1** in hot 25% (v/v) ethanol/water was prepared and filtered through a micron filter to exclude dust particles. When this solution was cooled below 60 °C it became opaque with the formation of a stiff gel. Viscosity measurements indicated a gelation temperature in the interval of 60–70 °C. Some hysteresis was observed when cycling over the transition temperature.

For the microscopy studies the gel was diluted 10 times with the mixed solvent. A sample for optical microscopy was obtained by smearing a few drops over a glass slide and air drying for a few minutes. AFM samples were prepared by smearing a drop of the diluted gel over a slide of amorphous silica or mica and air drying for 30 min.

For temperature dependent NMR studies, a 2% solution of **1** in 25% (v/v) dimethylformamide-$d_6$/$D_2O$ was prepared. It was heated to 100 °C to obtain a clear solution and then cooled to an ambient temperature for 1 h, to allow complete gelation, and then used for measurements.

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