Cholestano-Fused Electron Donors and Acceptors

Michael P. Cava,* Jesper Lau, Klaus B. Simonsen

Department of Chemistry, University of Alabama, Box 870336, Tuscaloosa, Alabama 35487-00336

Jan Becher

Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense, Denmark

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The synthesis of the cholestano-fused tetrathiafulvalene (TTF) **3** and cyanoethyl- protected cholestano TTF **4** is described. Compound **4** was deprotected under basic conditions and then treated with 2-bromoethanol or 1,2-dibromoethane to give the corresponding cholestano (hydroxyethyl)thio TTF **18** and the cholestano ethylenedithio TTF **19**, respectively. The synthesis of the electron acceptors, cholestanonaphthoquinone **20** and the corresponding dicyanonaphthoquinodiimine **5** is likewise reported.

Introduction

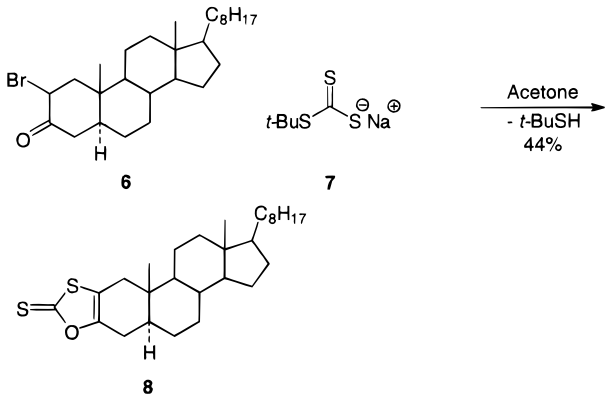
The cholestano moiety is a good candidate for incorporation into compounds with the potential of forming Langmuir−Blodgett (LB) films. It provides a rigid, chiral, and lipophilic backbone, and if combined with the right correctly situated polar substituent, it should afford molecules very likely to form LB films. Indeed, Naito and co-workers have reported cholestanyl-substituted (TTF) **1**[1] as well as cholestanyl-substituted tetracyanoquinodimethane derivative **2**,[2] both of which show the desired LB film forming properties. The redox active units in both derivatives were attached to the cholestane nucleus *via* a single bond, allowing free rotation between the steroid portion and the redox active unit. Another approach was initiated some years ago by our group, with the preparation of the TTF cholestanone derivative **3**.[3] In this approach the redox active unit is directly fused to the steroid moiety, allowing little conformational freedom. This conformational restriction is likely to facilitate film formation since the backbone is already in the correct conformation for molecular assembling.

Here we report the synthesis and characterization of **3** and cyanoethyl-protected cholestano TTF **4**. The latter can be deprotected under basic conditions, giving a bisthiolate that can be alkylated with a variety of electrophiles to give cholestano TTFs with a desirable functionality. We show that the bisthiolate smoothly reacts with 2-bromoethanol or 1,2-dibromoethane to give the corresponding cholestano (hydroxyethyl)thio TTF **18** and cholestano ethylenedithio TTF **19**, respectively. The synthesis of the electron acceptors cholestanonaphthoquinone **20** and the corresponding dicyanonaphthoquinodiimine **5** is likewise reported.

Results and Discussion

Numerous synthetic routes are available for the preparation of 1,3-dithiole-2-thiones.[4] For the preparation of dithioles fused directly to cyclic systems such as cyclohexane and cyclopentane, the acid-catalyzed ring closure of α-keto *tert*-butyl trithiocarbonates reported by Haley et al. seems to be the obvious choice.[5] The α-keto *tert*-butyl trithiocarbonates are generally prepared from 2-bromo ketones; hence by employing the readily prepared 2-bromocholestanone,[6,7] 1,3-dithioles fused onto the steroid skeletons A ring should be available.

Scheme 1



The reaction of 2-bromocholestanone **6** with sodium *tert*-butyl trithiocarbonate **7**[5] did not give the expected product, instead the 1,3-oxathiole-2-thione **8** was isolated as pale yellow crystals (Scheme 1). The enolate of the intermediate α-oxotrithiocarbonate apparently attacks the thiocarbonyl of the trithiocarbonate followed by elimination of *tert*-butyl mercaptan affording the 1,3-oxathiole-2-thione **8**.

Because of this unpredicted result, alternative ring closures of α-keto dithiocarbamates and xanthates[8] were investigated. First the iminocholestanone **10** was synthesized by reacting 2-bromocholestanone **6** with piperidinium *N*,*N*-pentamethylenedithiocarbamate **9** in acetone to give white plates of **10** after recrystallization (Scheme 2). Compound **10** tends to form a gel in a variety of solvents but crystallized overnight from a mixture of ethyl acetate and ethanol.

The acid-mediated ring closure of **10** was carried out by stirring in concentrated sulfuric acid for 4 h. The

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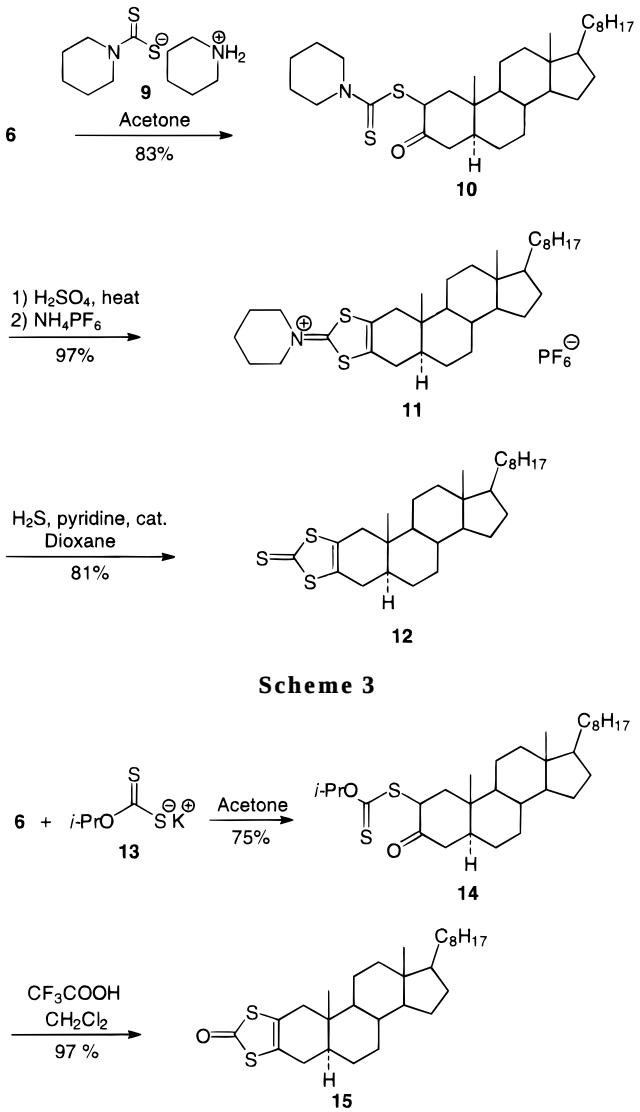
(1) Naito, K.; Miura, A.; Azuma, M. *J. Am. Chem. Soc.* **1991**, *113*, 6386.
(2) Naito, K.; Miura, A.; Azuma, M. *Langmuir* **1991**, *7*, 627.
(3) Metzger, R. M.; Schumaker, R. R.; Cava, M. P.; Laidlaw, R. K.; Panetta, C. A.; Torres, E. *Langmuir* **1988**, *4*, 298.
(4) (a) Schukat, G.; Richter, A. M.; Fanghänel, E. *Sulfur Rep.* **1987**, *7*, 155−240; (b) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1993**, *14*, 245−390; (c) Schukat, G.; Fanghänel, E. *Sulfur Rep.* **1996**, *18*, 1−294
(5) Haley, N. F.; Fichtner, M. W. *J. Org. Chem.* **1980**, *45*, 175.
(6) Fieser, L. F.; Dominguez, X. A. *J. Am. Chem. Soc.* **1953**, *75*, 1704.
(7) Nace, H. R.; Iacona, R. N. *J. Org. Chem.* **1967**, *29*, 3498.
(8) Bhattacharya, A. K.; Hortmann, A. G. *J. Org. Chem.* **1974**, *39*, 95.

S0022-3263(97)00777-9 CCC: $14.00

Scheme 2



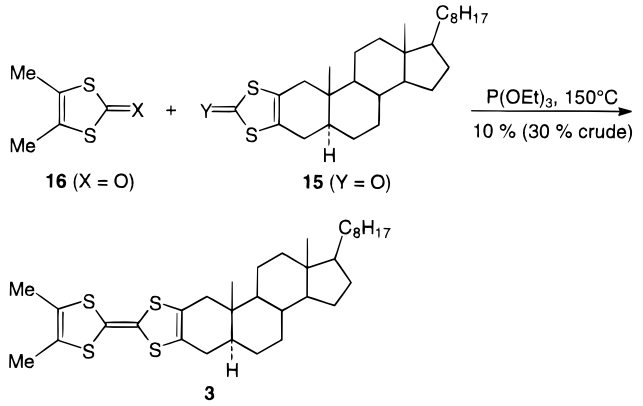
Scheme 3

mixture was poured onto ice and water, resulting in a gum/gel. This sparingly soluble hydrogen sulfate salt was heated and water was added until a clear gel was obtained. Addition of a saturated aqueous solution of ammonium hexafluorophosphate caused the precipitation of **11** as a white solid. Treatment of the iminium salt **11** with hydrogen sulfide in 1,4-dioxane in the presence of a catalytic amount of pyridine gave 80% of the trithiocarbonate **12** after recrystallization (Scheme 2).

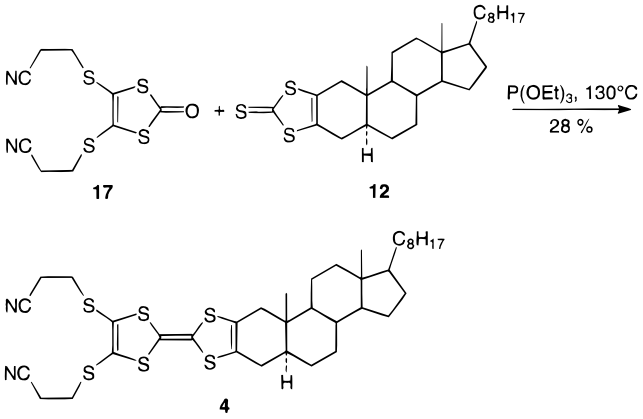
In order to synthesize the 2,3-cholestano TTF **3**, 2-bromocholestanone **6** was treated with potassium *O*-isopropyl xanthate[9] **13** in acetone to give the corresponding cholestanyl xanthate **14** in 75% yield after recrystallization in 2-propanol (Scheme 3). Acid-mediated ring closure of **14** in concd sulfuric acid[10] failed, whereas treatment with trifluoroacetic acid in methylene chloride afforded the dithiocarbonate **15** in almost quantitative yield. Recrystallization from ethyl acetate and methanol afforded large colorless crystals.

The cross coupling was carried out by heating the dithiocarbonate **15** to 150 °C for 6 h in freshly distilled triethyl phosphite with a 2-fold excess of 4,5-dimethyl-

Scheme 4



Scheme 5



1,3-dithiol-2-one **16**[11] (Scheme 4). After cooling and addition of methanol, a pale orange precipitate was filtered off. The crude product (30% yield) was contaminated with only a trace of tetramethyltetrathiafulvalene. Column chromatography in basic alumina afforded the pure product **3** in only 10% yield.

In order to try to improve the procedure, cross couplings by systematic variation of X and Y were attempted (X = S or O, Y = S or O, Scheme 4). However, all combinations but X = O and Y = O gave only trace amounts of the desired product.

The synthesis of unsymmetric tetrathiafulvalenes has previously been carried out by cross coupling of two different 1,3-dithioles-2-thiones,[12] but lately it has been shown that the cross coupling of an equimolar amount of a 1,3-dithiole-2-thione and a 1,3-dithiol-2-one in neat triethyl phosphite gave much higher yields.[13]

Cross coupling in neat freshly distilled triethyl phosphite using 1 equiv of **12** and 2 equiv of the bis-protected 4,5-bis[(2-cyanoethyl)thio]-1,3-dithiolone **17**[14] afforded, after column chromatography, the cyanoethyl-protected 2,3-cholestano TTF **4** in moderate yield (Scheme 5). Compound **4** is an orange glass and attempts to recrystalize it failed, due to its tendency to form gels in a variety of solvents. Cross couplings by systematic variation of the thiocarbonyl and carbonyl functionalities were attempted. However, all combinations but the one

(9) (a) Berger, J. *Acta Chem. Scand.* **1952**, *6*, 1564; (b) Berger, J.; Uldall, I. *Acta Chem. Scand.* **1964**, *18*, 1353.

(10) Guziea, J. M.; Russo, J. M.; Torres, F. F.; Long, G. C.; Tellez, M. R. *J. Chem. Soc. Perkin Trans.* **1989**, 1068.

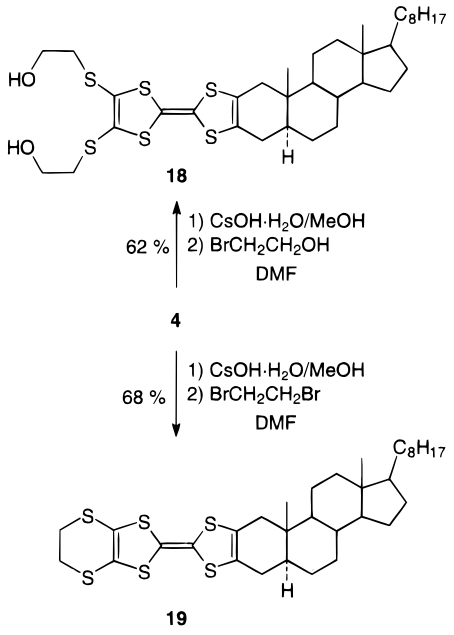
(11) Rae, I. D. *Int. J. Sulfur Chem.* **1973**, *3*, 273; *C. A.* **1973**, *79*, 137013.

(12) Spencer, K.; Cava, M. P.; Garito, A. F. *J. Chem. Soc., Chem. Commun.* **1976**, 966.

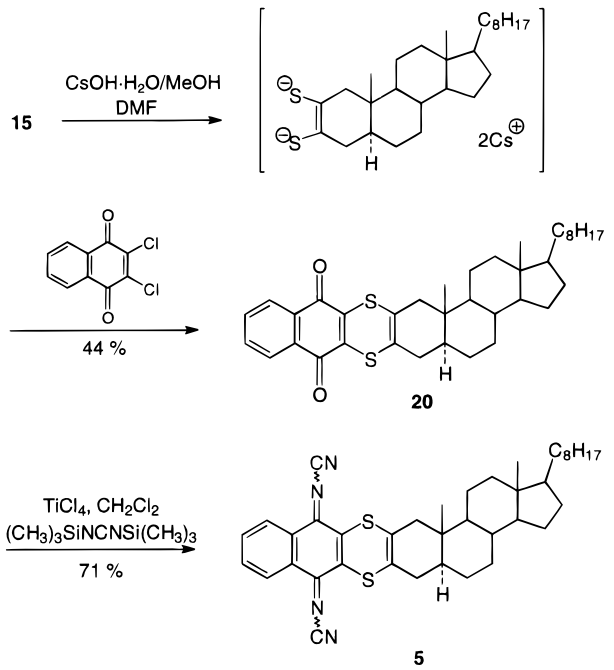
(13) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407.

(14) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. H.; Becher, J. *Synthesis* **1994**, 809.

Scheme 6



Scheme 7



depicted in Scheme 5 gave only a trace amount of the desired product.

The protected cholestano TTF **4** is an excellent precursor for the preparation of a variety of functionalized cholestanotetrathiafulvalenes. The deprotection of the cyanoethylated TTF **4** proceeded easily in *N*,*N*-dimethylformamide by treatment with cesium hydroxide in methanol.[13,14] The intermediate bis-thiolate was reacted with either 2-bromoethanol to give the corresponding bis[(2-hydroxyethyl)thio] TTF **18** in 62% yield or with 1,2-dibromoethane to give the ethylenedithio derivative **19** in 68% yield, as outlined in Scheme 6.

After having prepared a number of electron donors fused to a cholestano moiety, the challenge now was to find a synthetic route to a complementary electron acceptor with the same steroid backbone. It is well-known that trithiocarbonates and dithiocarbonates react with nucleophiles like methoxide to give ring opening of the dithiol moiety.[15] Since dithiocarbonates are more prone to ring opening than trithiocarbonates, we decided to utilize **15**. Hence **15**, in a well-degassed *N*,*N*-dimethylformamide solution, was treated with excess cesium hydroxide in methanol to afford the intermediate bis-thiolate. Addition of 2,3-dichloro-1,4-naphthoquinone gave the deep blue 2,3-cholestanonaphthoquinone **20** in 44% yield after column chromatography (Scheme 7).

In order to increase the its electron-accepting abilities, we decided to convert the quinone **20** to the corresponding *N*,*N*′-dicyanonaphthoquinonediimine.[16] A solution of quinone **20** in dry methylene chloride was treated with titanium tetrachloride, whereupon the color changed from deep blue to deep green. After stirring for a few minutes, bis(trimethylsilyl)carbodiimide was added dropwise. The workup for the product **5** is crucial since it is very prone to hydrolysis as well as reduction. Hence the methylene chloride solution of the reaction mixture was washed three times with ice cold brine. After drying, the solution was flash filtered through a short plug of silica. The silica gel was washed well with methylene chloride until no more color was eluted. It is very important that the compound remain in contact with the silica gel for the shortest possible time, since it is partly hydrolyzed even in the time it takes to run a TLC plate. The highly colored (blue/purple) products from the hydrolysis run in front of the *N*,*N*′-dicyanonaphthoquinonediimine on the TLC plate. After appropriate workup, the yield of pure **5** is 71%.

Table 1. Cyclic Voltammetry Results (vs SCE)[a]

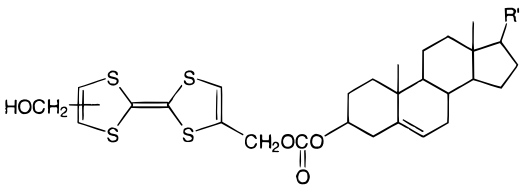
compd	$E_{1/2}^{ox\ 1/V}$	$E_{1/2}^{ox\ 2/V}$	$E_{1/2}^{red\ 1/V}$	$E_{1/2}^{red\ 2/V}$
3	0.23	0.77		
4	0.49	0.94		
18	0.40	0.80		
19	0.38	0.85		
20			−0.62	−1.35
5			−0.11	−0.44
naphthoquinone[b,17]			−0.38	−1.06
N,*N*′-dicyanonaphthoquinonediimine[b,17]			0.34	−0.20

[a] All measurement were carried out in methylene chloride at 100 mV/s. [b] These values were converted to SCE from Ag/AgCl by adding a factor of 150 mV.

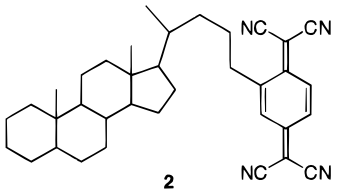
The redox behaviors of the new 2,3-cholestano-fused donors (**3**, **4**, **18**, and **19**) and acceptors (**5** and **20**) were investigated by cyclic voltammetry (Table 1). All compounds exhibit two reversible one-electron redox couples. In the series of the new cholestano TTFs (**3**, **4**, **18**, and **19**), compound **3** is the strongest donor, with the first half-wave potential at 0.23 and 0.77 V. This is in accordance with the fact that alkylthio groups are electron-withdrawing, whereas methyl groups are electron releasing. Cyclic voltammetry of **20** revealed a two-electron acceptor with half-wave potentials $E^1 = -0.62$ V and $E^2 = -1.35$ V. This is a slightly poorer acceptor than naphthoquinone ($E^1 = -0.38$ V and $E^2 = -1.06$ V) because of the influence of the two sulfur substituents. Interestingly, sulfur substitution makes a donor less electron donating as well as an acceptor less electron accepting. As expected, the potential of dicyanoquinonediimine **5** is approximately 0.5 V lower relative to **20**. Compound **5** is a strong two-electron acceptor, with half-wave potentials at $E^1 = -0.11$ V and $E^2 = -0.44$ V.

(15) Vance, C. T.; Bereman, R. D.; Bordner, J.; Hartfield, W. E.; Helms, J. H. *Inorg. Chem.* **1985**, *24*, 2905.
(16) Aumuller, A.; Hunig, S. *Liebigs Ann. Chem.* **1986**, 142.

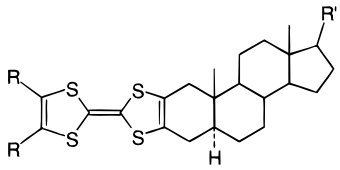
Chart 1



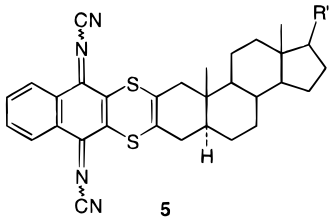
1



2

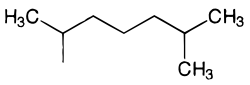


3 R = CH_3
4 R = SCH_2CH_2CN



5

R' = C_8H_{17} =



However, the parent system, *N,N′*-dicyanonaphtoquinonediimine, is a much stronger acceptor, with a first half -wave potential at 0.34 V.

In conclusion, we have established a convenient route to a number of different electroactive cholestano derivatives using common intermediates for the preparation of both electron donors as well as electron acceptors. All the steps to the cholestano dithio- or trithiocarbonates can conveniently be performed on a large scale without purification by column chromatography, since the highly crystalline intermediates are easily recrystallized. The preparation and investigation of LB films of these are now being performed and the results will be published elsewhere.

Experimental Section

Cyclic voltammograms were carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAHFP) in distilled methylene chloride. The measurements were performed in a single-compartment cell with a disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode.

(2,3-Cholestano)-1,3-oxathiole-2-thione (8). To a suspension of 2α-bromocholestan-3-one (**6**) (0.80 g, 1.7 mmol) in acetone (50 mL) was added a solution of sodium *tert*-butyl trithiocarbonate dihydrate (**7**)[5] (0.42 g, 1.9 mmol) in acetone (30 mL) and the reaction mixture was stirred overnight and concentrated. The resulting oil was redissolved in CH_2Cl_2 (100 mL), washed with H_2O (2 × 100 mL) and aqueous NaCl (2 × 100 mL), and dried (Na_2SO_4). Chromatography (silica gel, CH_2Cl_2/hexanes 1:2, R_f = 0.7) gave 0.35 g (44%) of **8** as white crystals: mp 148−149 °C; ^{1}H-NMR ($CDCl_3$) δ 2.49 (dd, *J* = 15.2 and 5.0 Hz, 1H), 2.45 (d, *J* = 15.0 Hz, 1H), 2.22 (m, 1H), 2.2 (m, 1H), 2.10 (d, *J* = 15.0 Hz, 1H), 2.00 (dd, *J* = 12.6 and 3.2 Hz, 1H), 1.7−0.95 (m, 24H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.85 (2 d, *J* = 6.8 Hz, 6H), 0.82 (s, 3H), 0.67 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 203.99, 150.52, 116.94, 56.19, 56.12, 53.29, 42.38, 41.69, 39.68, 39.47, 37.04, 36.53, 36.11, 35.72, 35.44, 31.32, 28.34, 28.14, 27.96, 27.92, 24.16, 23.79, 22.77, 22.52, 21.25, 18.65, 11.93, 11.75; MS (EI) *m*/*z* 460 (M^+, 21). Anal. Calcd for $C_{28}H_{44}OS_2$: C, 72.94; H, 9.63; S, 13.92. Found: C, 72.88; H, 9.69; S, 13.88.

2α-(*N,N*-Pentamethylenedithiocarbamato)-cholestan-3-one (10). To a solution of 2α-bromocholestan-3-one (**6**) (3.00 g, 6.4 mmol) in acetone (150 mL) was added piperidinium *N,N*-pentamethylenedithiocarbamate (**9**)[17] (1.70 g, 6.9 mmol) and the reaction mixture was stirred for 6 h at rt. The solvent was removed *in vacuo* and the crude product was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (2 × 100 mL) and aqueous NaCl (2 × 100 mL) and dried (Na_2SO_4). The solvent was removed to give **10** as a pale yellow powder. Recrystallization from EtOAc/EtOH gave 2.9 g (83%) of **10** as white needles/plates: mp 154−155 °C; ^{1}H-NMR ($CDCl_3$) δ 5.25 (dd, *J* = 6.0 and 13.4 Hz, 1H), 4,24 (br s, 2H), 3.93 (br s, 2H), 2.6−2.5 (m, 2H), 2.27 (dd, *J* = 3.6 and 14.1 Hz, 1H), 1.96 (br dt, 1H), 1.8 (m, 1H), 1.69 (br s, 6H), 1.65-1.22 (m, 15H), 1.22 (s, 3H), 1.20−0.95 (m, 9H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.85 (2d, *J* = 6.5 Hz, 6H), 0.67 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 205.83, 193.82, 59.44, 56.21, 56.17, 53.81, 53.52, 51.82, 48.06, 47.59, 45.03, 42.58, 39.76, 39.47, 37.86, 36.11, 35.71, 35.10, 31.64, 28.59, 28.17, 27.96, 26.01, 25.31, 24.22, 24.18, 23.77, 22.77, 22.51, 21.59, 18.64, 12.06; MS (EI) *m*/*z* 460 (M^+, 21). Anal. Calcd for $C_{33}H_{55}NOS_2$: C, 72.60; H, 10.15; N, 2.57; S, 11.75. Found: C, 72.66; H, 10.10; N, 2.65; S, 11.83.

2-(*N,N*-Pentamethyleneimino)(2,3-cholestano)-1,3-dithiolium Hexafluorophosphate 11. Compound **10** (1.32 g, 2.4 mmol) was dissolved slowly in ice-cold concd sulfuric acid (1.5 mL) over a period of 1 h and stirred for 4 hours. The reaction mixture was then triturated twice with ice water (2 mL) and the resulting paste was poured onto ice water (50 mL), which gave a gel/paste; addition of more water (total volume of 175 mL) and heating on a steam bath gave a thick clear gel. Addition of a saturated aqueous solution of ammonium hexafluorophosphate caused a rapid precipitation of **11** as a white powder; yield 1.38 g (97%). Recrystallization from $CHCl_3$/hexane gave **11** as soft white needles: mp 143−145 °C (dec); ^{1}H-NMR ($CDCl_3$) δ 3.80 (t, 1H, *J* = 5.6 Hz, 4H), 2.6−2.5 (m, 2H), 2.35−2.2 (m, 2H), 1.87 (m, 6H), 1.8−0.9 (m, 24H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.85 (2 d, *J* = 6.8 Hz, 6H), 0.82 (s, 3H), 0.65 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 185.72, 130.38, 129.26, 56.82, 56.12, 56.03, 53.02, 42.32, 41.51, 39.54, 39.44, 39.26, 36.45, 36.08, 35.70, 35.35, 31.13, 29.76, 28.03, 27.95, 24.90, 24.12, 23.77, 22.77, 22.51, 21.49, 21.03, 18.63, 11.91, 11.70. Anal. Calcd for $C_{33}H_{54}F_6NOPS_2 \cdot {}^1/_2H_2O$: C, 58.04; H, 8.11; N, 2.05; S, 9.39. Found: C, 57.87; H, 7.96; N, 2.01; S, 9.39.

(2,3-Cholestano)-1,3-dithiole-2-thione (12). Com-

(17) Aumuller, A.; Hunig, S. *Liebigs Ann. Chem.* **1986**, 165.
(18) Takamizawa, A.; Hirai, K. *Chem. Pharm. Bull.***1969**, *17*, 1924.

pound **11** (1.31 g, 1.9 mmol) was dissolved in 1,4-dioxane (60 mL) and pyridine (10 drops, catalytic amount) and H_2S was passed through the stirred solution at room temperature. The pale yellow solution turned darker yellow after 30 min, indicating the formation of the thione. After 4 h, the reaction mixture was degassed with nitrogen (to remove excess of H_2S) and concentrated *in vacuo*. If this reaction is carried out on a larger scale, the excess H_2S should be trapped by an alkaline scrubber solution. The crude product was dissolved in CH_2Cl_2 (100 mL), washed with H_2O (3 × 100 mL) and aqueous $NaHCO_3$ (2 × 100 mL), dried (Na_2SO_4), and concentrated to a yellow powder. Recrystallization from $CHCl_3$/EtOH gave **12** as yellow crystals; yield 0.75 g (81%); mp 143−144 °C; ^{1}H-NMR ($CDCl_3$) δ 2.5−2.4 (m, 2H), 2.2−2.1 (m, 2H), 1.8−0.9 (m, 24H), 0.92 (d, J = 6.7 Hz, 3H), 0.86 (m, 9H), 0.67 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 212.48, 137.00, 135.85, 56.19, 53.26, 42.38, 41.76, 39.67, 39.48, 39.22, 36.28, 36.12, 35.73, 35.45, 31.32, 29.78, 28.15, 27.97, 24.16, 23.80, 22.78, 22.53, 21.08, 18.67, 11.94, 11.78; MS (EI) m/z 476 (M^+, 100). Anal. Calcd for $C_{28}H_{44}S_3$: C, 70.53; H, 9.30; S, 20.17. Found: C, 70.37; H, 9.24; S, 20.10.

2α-(*O*-Isopropyldithiocarbonato)cholestan-3-one (14). Potassium isopropyl xanthate **13**[9] (1.67 g, 9.57 mmol) was added to a stirred suspension of 2-bromocholestan-3-one (**6**) (3.72 g, 7.97 mmol) in dry acetone (100 mL). The reaction mixture was stirred for 1 h before the solvent was evaporated. The residue was divided between diethyl ether (100 mL) and water (50 mL). The ether phase was washed with water (2 × 50 mL), dried ($CaCl_2$), and evaporated. Recrystallization from 2-propanol yielded 3.10 g (75%) of **14** as small needles: mp 81−83 °C; ^{1}H-NMR ($CDCl_3$) δ 5.73 (heptet, J = 6.2 Hz, 1 H), 4.69 (dd, J = 13.4 and 6.0 Hz, 1 H), 2.6−0.7 (m, 44 H) with the following distinct signals: 1.38 (2d, J = 6.2 Hz, 6 H), 1.18 (s, 3 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.86 (2d, J = 6.7 Hz, 6 H), 0.68 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 212.74, 204.53, 78.11, 57.20, 56.18, 56.11, 53.69, 47.78, 46.60, 44.78, 42.57, 39.72, 39.46, 37.59, 36.09, 35.72, 35.11, 31.57, 28.57, 28.16, 27.96, 24.17, 23.77, 22.77, 22.52, 21.51, 21.29, 21.25, 18.62, 12.05, 12.00; MS (EI) m/z 520 (M^+, 1). Anal. Calcd for $C_{31}H_{52}O_2S_2$: C, 71.48; H, 10.06; S, 12.31. Found: C, 71.54; H, 10.15; S, 12.20.

(2,3-Cholestano)-1,3-dithiole-2-one (15). Trifluoroacetic acid (50 mL) was added to a stirred solution of 2α-(*O*-isopropyldithiocarbonato)cholestane-3-one (**14**) (2.43 g, 4.67 mmol) in methylene chloride (100 mL). After stirring for 3 h the solution was washed with brine (3 × 100 mL), dried (Na_2SO_4), and evaporated to yield 2.10 g (97%) pure by NMR and TLC. Recrystallization from EtOAc−MeOH gave 1.57 g (73%) of **15** as large colorless crystals: mp 134−135 °C; ^{1}H-NMR ($CDCl_3$) δ 2.40−0.70 (m, 41 H) with the following distinct signals: 0.91 (d, J = 6.5 Hz, 3H), 0.88 (s, 3 H), 0.86 (2d, J = 6.7 Hz, 6H), 0.67 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 192.82, 124.97, 124.03, 56.19, 53.34, 42.36, 42.22, 39.69, 39.47, 36.65, 36.11, 35.73, 35.40, 31.35, 30.25, 29.68, 28.16, 27.97, 24.13, 23.80, 22.78, 22.53, 21.04, 18.66, 11.93, 11.80; MS (EI) m/z 460 (M^+, 100). Anal. Calcd for $C_{28}H_{44}OS_2$: C, 72.99; H, 9.62; S, 13.92. Found: C, 73.01; H, 9.73; S, 13.98.

(2,3-Cholestano)dimethyltetrathiafulvalene (3). (2,3-Cholestano)-1,3-dithiol-2-one (**15**) (230 mg, 0.5 mmol) and 4,5-dimethyl-1,3-dithiol-2-one (**16**)[11] (146 mg, 1.0 mmol) were heated under N_2 to 150 °C in freshly distilled triethyl phosphite (5 mL) for 6 h. After cooling to room temperature MeOH (15 mL) was added, whereupon the yellow-orange product was filtered off (crude yield 86 mg, 30%). (Only a trace amount of the tetramethyl tetrathiafulvalene is present in the otherwise pure product). Column chromatography (basic alumina, hexane−CH_2Cl_2 4:1) gave 30 mg (10%) of the pure product: mp 224 °C (dec); ^{1}H-NMR ($CDCl_3$) δ 2.05−0.70 (m, ∼47 H) with the following distinct signals: 0.90 (d, J = 6.4 Hz, 3H), 0.86 (2d, J = 6.6 Hz, 6 H), 0.80 (s, 3 H), 0.66 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 139.79, 56.22, 53.39, 46.80, 42.42, 42.05, 39.77, 39.50, 36.35, 36.15, 35.77, 35.50, 31.46, 29.69, 28.33, 28.19, 28.00, 24.21, 23.83, 22.80, 22.55, 21.06, 18.67, 11.95, 11.78; MS (EI) m/z 574 (M^+, 82), 149 (100); CV (CH_2Cl_2) $E_{1/2}^1$ = 0.23, $E_{1/2}^2$ = 0.77 V. Anal. Calcd for $C_{33}H_{50}S_4$: C, 68.93; H, 8.77; S, 22.30. Found: C, 69.19; H, 8.74; S, 22.04.

(2,3-Cholestano)bis[(2-cyanoethyl)thio]tetrathiafulvalene 4. (2,3-Cholestano)-1,3-dithiole-2-thione (**12**) (330 mg, 0.69 mmol) and 4,5-[(2-cyanoethyl)thio]-1,3-dithiol-2-one (**17**)[14] (200 mg, 0.69 mmol) were heated in freshly distilled triethyl phosphite (5 mL) under nitrogen to 130 °C for 30 min, and another portion of 4,5-[(2-cyanoethyl)thio]-1,3-dithiol-2-one (200 mg, 0.69 mmol) was then added. The reaction mixture was stirred for another 4 h at 130 °C. After cooling to room temperature MeOH (25 mL) was added. The precipitate was filtered off and washed with MeOH (4 × 50 mL). Column chromatography (silica gel, CH_2Cl_2) afforded 140 mg (28%) of **4** as a red glass: ^{1}H-NMR ($CDCl_3$) δ 3.08 (t, J = 7.1 Hz, 4 H), 2.73 (t, J = 7.2 Hz, 4H), 2.30 - 0.70 (m, ˜ 41 H) with the following distinct signals: 0.90 (d, J = 6.5 Hz, 3 H), 0.87 (2d, J = 6.6 Hz, 6 H), 0.81 (s, 3 H), 0.66 (s, 3 H); ^{13}C-NMR δ 128.04, 125.47, 124.22, 117.45, 56.21, 53.40, 42.41, 42.02, 39.90, 39.74, 39.49, 36.38, 36.13, 35.75, 35.58, 31.56, 31.43, 31.22, 30.42, 28.28, 28.16, 27.99, 24.19, 23.81, 22.79, 22.63, 22.54, 21.07, 18.83, 18.66, 14.10, 11.95, 11.80; MS (EI) m/z 716 (M^+, 2); HRMS: found 716.2458, calcd 716.2455; CV (CH_2Cl_2): $E_{1/2}^1$ = 0.49 V, $E_{1/2}^2$ = 0.94 V. Anal. Calcd for $C_{37}H_{52}N_2S_6$: C, 61.96; H, 7.31; N, 3.91. Found: C, 62.16; H, 7.41; N, 3.70.

(2,3-Cholestano)bis[(2-hydroxyethyl)thio]tetrathiafulvalene 18. $CsOH·H_2O$ (105 mg, 0.63 mmol) in MeOH (1 mL) was added dropwise to a degassed solution of cholestanobis[(2-cyanoethyl)thio]tetrathiafulvalene **4** (150 mg, 0.21 mmol) in DMF (10 mL) under nitrogen. The reaction mixture was stirred 30 min before 2-bromoethanol (78 mg, 0.63 mmol) was added. After stirring for another 90 min the solvent was removed *in vacuo*. Column chromatography (silica gel, CH_2Cl_2−EtOAc, 10:1) afforded 90 mg (62%) of a pale yellow crystalline compound: mp 177−178 °C; ^{1}H-NMR ($CDCl_3$) δ 3.74 (t, J = 5.3 Hz, 4 H), 3.00 (t, J = 5.4 Hz, 4 H), 2.90 (br s, ∼2 H), 2.25−0.70 (m, ∼41 H) with following distinct signals: 0.90 (d, J = 6.4 Hz, 3 H), 0.86 (2d, J = 6.6 Hz, 6 H), 0.82 (s, 3 H), 0.66 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 128.21, 125.42, 124.18, 59.85, 56.23, 53.40, 42.42, 42.04, 39.93, 39.76, 39.50, 39.28, 36.38, 36.15, 35.76, 35.49, 31.45, 30.45, 28.30, 28.18, 28.00, 24.20, 23.82, 22.80, 22.55, 21.08, 18.68, 12.53, 11.96, 11.81; PDMS m/z 698.2; CV (CH_2Cl_2) $E_{1/2}^1$ = 0.40, $E_{1/2}^2$ = 0.80 V. Anal. Calcd for $C_{35}H_{54}O_2S_6$: C, 60.12; H, 7.78; S, 27.51. Found: C, 59.93; H, 7.68; S, 27.40.

(2,3-Cholestano)(ethylenedithio)tetrathiafulvalene 19. $CsOH·H_2O$ (105 mg, 0.63 mmol) in MeOH (0.5 mL) was added dropwise to a degassed solution of cholestanobis[(2-cyanoethyl)thio]tetrathiafulvalene **4** (150 mg, 0.21 mmol) in DMF (10 mL) under nitrogen, where-

upon a purple solid precipitated. The mixture was stirred for 30 min before 1,2-dibromoethane (0.1 mL, excess) was added. The reaction mixture was stirred for 40 min before MeOH (5 mL) was added. The orange precipitate was filtered off, washed with water (10 mL) and MeOH (10 mL), and dried *in vacuo* to yield 90 mg (68%). It can be recrystallized from $CHCl_3$−MeOH: mp 248 °C (dec, loses color over a wide range); ^{1}H-NMR ($CDCl_3$) δ 3.28 (s, 4 H), 2.25−0.70 (m, ∼44 H) with following distinct signals: 0.90 (d, J = 6.5 Hz, 3 H), 0.86 (2d, J = 6.6 Hz, 6 H), 0.79 (s, 3 H), 0.66 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 125.34, 124.11, 117.87, 114.03, 103.26, 56.22, 53.38, 42.42, 42.03, 39.90, 39.76, 39.50, 36.36, 36.15, 35.77, 35.49, 31.45, 30.43, 30.23, 28.31, 28.18, 28.00, 24.21, 23.83, 22.80, 22.55, 21.07, 18.67, 11.96, 11.77; MS (EI) m/z 636 (M, 5), 476 (10), 169 (100); CV (CH_2Cl_2) $E_{1/2}^1$ = 0.38, $E_{1/2}^2$ = 0.85 V. Anal. Calcd for $C_{33}H_{48}S_6$: C, 62.21; H, 7.59; S, 30.19. Found: C, 62.22; H, 7.59; S, 30.20.

(2,3-Cholestano)-1,4-dithiaanthraquinone 20. $CsOH·H_2O$ (262 mg, 1.56 mmol) in MeOH (1 mL) was added dropwise, under nitrogen, to a suspension of (2,3-cholestano)-1,3-dithiol-2-one (**15**) (300 mg, 0.65 mmol) in degassed DMF. After stirring for 1.5 h, 2,3-dichloro-1,4-naphthoquinone (148 mg, 0.65 mmol) in DMF (5 mL) was added dropwise over 15 min. The dark reaction mixture was stirred for 1 h before it was poured into 150 mL of brine. The purple precipitate was filtered off and washed with water (25 mL) and EtOH (3 × 25 mL). Column chromatography (silica gel, hexane−CH_2Cl_2 2:1) afforded 170 mg (44%) of a purple compound. Recrystallization from toluene−hexane gave dark blue needles: mp 213.5−214.5 °C; ^{1}H-NMR ($CDCl_3$) δ 8.10 (d, J = 5.6 Hz, 1 H), 8.09 (d, J = 5.6 Hz, 1 H), 7.72 (d, J = 5.8 Hz, 1 H), 7.71 (d, J = 5.7 Hz, 1 H), 2.20−0.70 (m, ∼41 H) with the following distinct signals: 0.90 (d, J = 6.5 Hz, 3 H), 0.86 (2d, J = 6.7 Hz, 6 H), 0.78 (s, 3 H), 0.65 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 177.91, 143.37, 133.93, 131.83, 127.05, 124.65, 123.68, 56.21, 53.38, 45.92, 42.42, 42.13, 39.75, 39.51, 36.15, 36.05, 35.99, 35.77, 35.39, 31.39, 28.16, 28.00, 27.86, 24.18, 23.81, 22.80, 22.55, 21.06, 18.67, 11.94, 11.87; PDMS m/z 588.2; CV (CH_2Cl_2): $E_{1/2}^1$ = −0.62, $E_{1/2}^2$ = −1.35 V; UV-Vis (CH_2Cl_2): λ_{max} = 581, 277, 231, 212 cm^{-1}. Anal. Calcd for $C_{37}H_{48}O_2S_2$: C, 75.46; H, 8.22; S, 10.89. Found: C, 75.21; H, 8.33; S, 11.02.

(2,3-Cholestano)dicyano-1,4-dithianthraquinonediimine (5). To cholestanoanthraquinone **20** (157 mg, 0.267 mmol) in dry CH_2Cl_2 (20 mL), under nitrogen, was added a solution of $TiCl_4$ (1.34 mL of a 1.0 M solution in CH_2Cl_2, 1.34 mmol), whereupon the color changed from blue to green. After 5 min bis(trimethylsilyl)carbodiimide (1.34 mmol, 248 mg) was added dropwise. The reaction mixture was stirred for 75 min before it was partitioned between 100 mL of CH_2Cl_2 and 100 mL of ice/brine. The organic phase was washed with 3 × 100 mL, ice cold brine and dried with Na_2SO_4. After drying, the solution was flash filtered through a 1.5 cm layer of silica gel. The silica was washed with CH_2Cl_2 until the eluent was clear. After evaporation, the black solid was triturated with hexane (5 mL) to give 120 mg (71%) of pure **5** as a black powder, which recrystallized from EtOAc to give a microcrystalline product: mp 160−162 °C; ^{1}H-NMR ($CDCl_3$) δ 8.88 (br s, 2 H), 7.83 (d, J = 5.9 Hz, 1 H), 7.82 (d, J = 5.8 Hz, 1 H), 2.30−0.60 (m, ∼44 H) with the following distinct signals: 0.90 (d, J = 6.4 Hz, 3 H), 0.86 (2d, J = 6.6 Hz, 6 H), 0.77 (s, 3 H), 0.65 (s, 3 H); ^{13}C-NMR ($CDCl_3$) δ 134.62, 127.55, 112.80, 56.18, 53.36, 46.04, 42.41, 42.21, 39.68, 39.49, 36.22, 36.13, 35.75, 35.39, 31.34, 28.15, 27.99, 27.84, 24.18, 23.80, 22.80, 22.54, 21.10, 18.67, 11.94; CV (CH_2Cl_2): $E_{1/2}^1$ = −0.11, $E_{1/2}^2$ = −0.44 V; UV−vis (CH_2Cl_2): λ_{max} = 668, 346, 330, 218 cm^{-1}. Anal. Calcd for $C_{39}H_{48}N_4S_2$: C, 73.54; H, 6.60; N, 8.80. Found: C, 73.56; H, 7.63; N, 8.73.

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