An Efficient Method for Synthesizing Substituted Naphtho-1,3-dithiole-2-thiones from Tetrachlorotetrathionaphthalene and Sodium Trithiocarbonate

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Two types of naphtho-fused 1,3-dithiole-2-thiones (**2a–f** and **4a–d**) were obtained by the reaction of 3,4,7,8-tetrachloronaphtho[1,8-*cd*:5,6-*c′d′*]bis(1,2-dithiole) (**1**) and sodium trithiocarbonate. The dechalcogenization of the thiones, using mercury acetate, leads to the corresponding naphtho-1,3-dithiol-2-ones (**3a–d** and **5a–d**). The structures of **3a** and **4a** were confirmed by X-ray investigation. The tetrathiafulvalenes (TTFs) **6** and **7** were synthesized from **2d** and **3c** by coupling of the starting compounds with the help of triethyl phosphite. Using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) the TTFs were converted into semiconducting charge-transfer complexes.

1,3-Dithiole-2-thiones are starting compounds for the synthesis of tetrathiafulvalenes (TTFs)[1] and also, by cleavage of the 1,3-dithiole-2-thione ring, for those of the dithiolene complexes[2]. Charge-transfer complexes (CT complexes), of TTFs, as well as dithiolene complexes, exhibit interesting solid-state properties, e.g. high electrical conductivity[1][3].

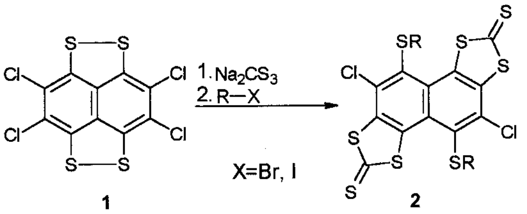
Heteroatoms at peripheral sites of the donor molecules, and the extended π-system of molecules such as tetrathiafulvalenes, increase both the inter-stack and the intra-stack interactions in the corresponding solid CT and dithiolene complexes[4]. The increased dimensionality of the interactions stabilizes the solid with respect to the Peierls transition[5], and enables the synthesis of organic superconductors.

In this paper we describe new naphtho-fused 1,3-dithioles and 1,2-dithioles, as well as 1,3-TTFs with an extended π-system based on the naphtho-fused starting compounds.

The treatment (in a one-pot synthesis) of 3,4,7,8-tetrachloronaphtho[1,8-*cd*:5,4-*c′d′*]bis(1,2-dithiole) (**1**) (tetrachlorotetrathionaphthalene) with an excess of sodium trithiocarbonate in DMF, and alkylation of the intermediate formed, leads to the new 4,9-dichloro-5,10-dialkylthionaphtho[1,2-*d*:5,6-*d′*]bis(1,3-dithiole-2-thiones) **2**, with high yields (ca. 70%) (see Scheme 1).

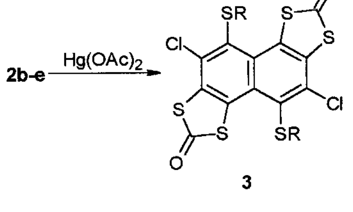
Compound **1** is easily available by heating octachloronaphthalene and sulfur[6]. The yellow reaction products **2** show the characteristic IR absorption of 1,3-dithiole-2-thiones (ca. 1060 cm^{-1}). The ^{1}H-NMR and the ^{13}C-NMR spectra are also in accordance with the proposed structure. By desulfurization of **2**, using mercury(II) acetate in boiling 1,2-dichlorobenzene (*o*-DCB), the 1,3-dithiol-2-ones **3** were obtained (see Scheme 2).

Scheme 1



	R
2a	$-CH_3$
2b	$-C_2H_5$
2c	$-C_4H_9$
2d	i-C_5H_{11}
2e	-Bz
2f	$-C_{12}H_{25}$

Scheme 2

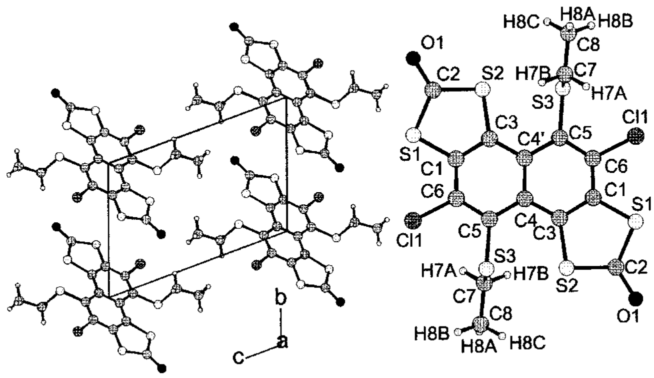


	R
3a	$-C_2H_5$
3b	$-C_4H_9$
3c	i-C_5H_{11}
3d	-Bz

These carbonyl compounds **3** are more soluble than the corresponding thiocarbonyl derivatives **2** and, therefore, single crystals suitable for X-ray analysis were obtained by diffusion of methanol into a solution of **3a** in *o*-DCB. The compound crystallizes as yellow needles in the triclinic space group *P*1 with one molecule (Z = 1) in the unit cell. The molecules form stacks along the *b* axis with an interplanar distance of 837.4 pm (see Figure 1).

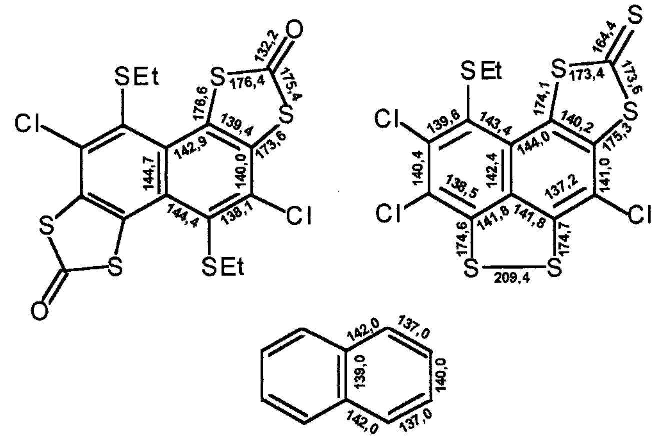
1434–193X/98/0808–1577 $ 17.50+.50/0

Figure 1. Section of the crystal lattice and crystal structure of **3a**



The shortest intermolecular $S_1{-}S_1'$ distance (365.2 pm) is close to the sum of the van der Waals radii of two sulfur atoms ($2v_S^{vdW}$ = 2 × 185 pm = 370 pm). Moreover, relatively short intermolecular distances (ca. 260 pm), were found between the oxygen atoms and the hydrogen atoms H7B′. The molecule has an inversion centre and is planar (with the exception of both ethyl groups). The sum of the angles of all centers is 360°. The bond lengths and angles of the C−SEt and C−Cl substituents are in the usual range. Some bonds of the naphthalene system are elongated. In particular the C4−C4′ bond exhibits an elongation of about 6 pm compared to that of unsubstituted naphthalene (see Scheme 3).

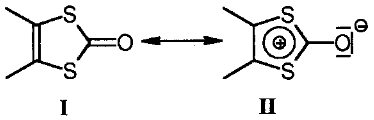
Scheme 3



Typical C−O bond lengths of 1,3-dithiol-2-ones are in the range of 117.8[7] to 122.7[8] pm. In **3a** a value of 132.2 pm was found for the C−O bond. This value is between that of a C−O double bond (120 pm) and a C−O single bond (143 pm). The measured bond length in **3a** can be explained by a mixture of the two resonance structures **I** and **II**[9] (see Scheme 4).

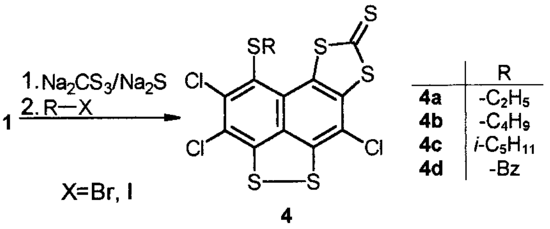
The 1,3-dithiole ring stabilizes the positive charge by the formation of an aromatic 6π-system and therefore enables the elongation of the C=O bond. The conjugation of the electron-rich 10π-system of naphthalene with the heterocycle also stabilizes the mesoionic form **II**.

Scheme 4



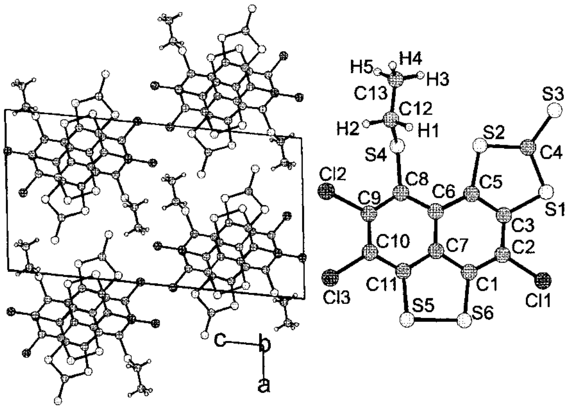
By the reaction of equimolar amounts of **1** and sodium trithiocarbonate only traces of the mono-substitution product **4** could be isolated. The yield of **4** is increased to 80% by the addition of anhydrous sodium sulfide to the reaction mixture (see Scheme 5).

Scheme 5



The compounds of type **4** are more soluble than those of type **2**. Single crystals suitable for X-ray investigations were obtained by recrystallization of **4a** from DMF. The compound crystallizes in dark red needles in the monoclinic space group $P2_1/n$. The unit cell includes 4 molecules (Z = 4, see Figure 2).

Figure 2. Section of the crystal lattice crystal structure of **4a**



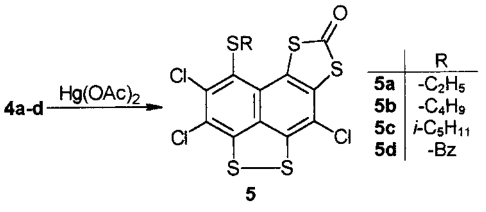
Some of the intermolecular S···S′ distances are close to the van der Waals radii. The shortest intermolecular S···S′ distance was found between the S3···S6′ atoms. This distance of 322.8 pm is about 15% less than the sum of the van der Waals radii of two sulfur centers (370 pm). The reason for this very short distance may be an intermolecular Lewis acid/base interaction. The thiocarbonyl centers are sulfur lone-pair donors and the sulfur atoms of the 1,2-dithiole rings are acceptors[10].

The bond lengths and angles in **4a** are comparable to those in **3a**. With the exception of the S−Et group the molecule is planar.

Compound **4a** exhibits the trend of elongation of the bonds in the naphthalene ring, similar to **3a**, but the C6−C7 bond is only 3.4 pm longer than in the unsubstituted naphthalene (Scheme 3). The bond lengths and angles of the five-membered 1,2-dithiole ring are similar to those in the tetrathiotetracene[11]. The C−S bond lengths of the 1,3-dithiole ring correspond to values described for other 1,3-dithiole-2-thiones[8].

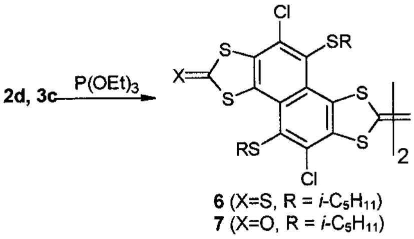
The thiocarbonyl group of **4** can be converted with the help of mercury acetate into the carbonyl group, yielding the 1,3-dithiol-2-ones **5a−d** (see Scheme 6).

Scheme 6



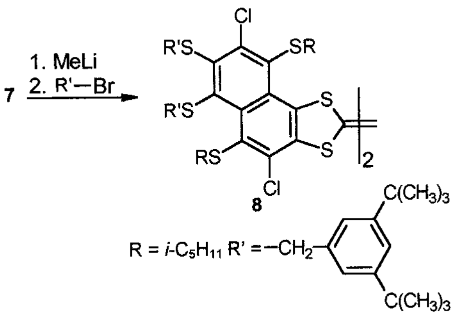
Dechalcogenization of **2d** and **3c**, using triethyl phosphite leads to the TTFs **6** and **7** (see Scheme 7).

Scheme 7



TTF **8** was synthesized by cleavage of the 1,3-dithiol-2-one ring in **7** with methyllithium and alkylation of the intermediate tetrathiolate by 3,5-di-*tert*-butylbenzyl bromide (see Scheme 8). In this way a TTF with improved solubility was available for cyclic voltammetry measurements.

Scheme 8



The cyclic voltammogram of **8** shows the two reversible oxidation steps at 0.54 V and 0.84 V, as expected for TTFs. The values are lower than those of substituted dibenzo-TTFs[1][12], indicating the easier oxidation of the extended π-system in **8**, and correspond to the values for the known naphtho-TTFs[13]. The TTFs form black CT complexes with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The conductivity of pressed pellets is in the range $3.7 \cdot 10^{-5} - 1.0 \cdot 10^{-4}$ Scm^{-1}, typical for semiconductor behavior. Table 1 summarizes the data for the three CT complexes.

Table 1. Composition and electrical conductivity of the TTF/DDQ CT complexes

Compound	Composition TTF/DDQ	Electrical conductivity [Scm^{-1}]
6/DDQ	1:1.3	$3.7 \cdot 10^{-5}$
7/DDQ	1:0.5	$6.5 \cdot 10^{-5}$
8/DDQ	1:0.8	$1.0 \cdot 10^{-4}$

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Experimental Section

General: IR: Philips PU 9426 FTIR spectrometer as KBr (Fluka Chemical Co.) pellets. − NMR: Varian Gemini 200, solvent $CDCl_3$. − Cyclic voltammetry: Autolab PGSTAT 20, solvent CH_2Cl_2, supporting electrolyte NBu_4PF_6, reference: Ferrocene/SCE. − Electrical conductivity: Pressed pellet (p = 18 kg/cm^2), room temp.

3,4,7,8-Tetrachloronaphtho[1,8-cd:5,4-c′d′]bis(1,2-dithiole) (**1**): Synthesized as described in the literature[6].

5,10-Dialkylthio-4,9-dichloronaphtho[1,2-d:5,6-d′]bis(1,3-dithiole-2-thiones) **2a−f**: All steps of the reaction of **1** and sodium trithiocarbonate were carried out in argon. A mixture of 1 g (2.5 mmol) of **1** and 1.58 g (10 mmol) of sodium trithiocarbonate in 40 ml of DMF was stirred at room temp. for 20 h. With the addition of 25 mmol of the alkyl halide and stirring for 5 h an air-stabile yellow product resulted. The precipitate was filtered off, washed with water, methanol, and ether, dried under vacuum, and recrystallized from *o*-DCB (or 1,2-DCE in the case of **2f**).

2a: Yield 0.8 g (63%), m.p. 325−327°C. − IR (C=S): $\tilde{\nu}$ = 1060 cm^{-1}. − $C_{12}H_6Cl_2S_8$ (501.59): calcd. C 33.52, H 1.21, Cl 14.14, S 51.13; found C 33.52, H 1.64, Cl 13.60, S 50.34.

2b: Yield 0.82 g (62%), m.p. 319°C. − IR (C=S): $\tilde{\nu}$ = 1064 cm^{-1}. − $C_{14}H_{10}Cl_2S_8$ (529.64): calcd. C 36.28, H 1.90, Cl 13.39, S 48.43; found C 35.96, H 1.89, Cl 13.76, S 48.17.

2c: Yield 0.82 g (62%), m.p. 319°C. − IR (C=S): $\tilde{\nu}$ = 1064 cm^{-1}. − $C_{20}H_{18}Cl_2S_8$ (585.74): calcd. C 41.01, H 3.10, Cl 12.11, S 43.79; found C 40.96, H 3.29, Cl 12.16, S 43.17.

2d: Yield 1.19 g (78%), m.p. 297°C. − IR (C=S): $\tilde{\nu}$ = 1064 cm^{-1}. − $C_{22}H_{22}Cl_2S_8$ (613.80): calcd. C 43.07, H 3.61, Cl 11.58, S 41.76; found C 43.40, H 4.22, Cl 11.26, S 41.52. − ^1H NMR: δ = 2.829 (t, −S−CH$_2$−, 2 H), 1.554 (m, −C−CH−C−, 1 H), 1.225 (m, C−CH$_2$−C, 2 H), 0.880 (d, −CH$_3$, 6 H). − ^{13}C NMR: δ = 136.475, 135.676, 133.064, 131.533, 128.910, 37.369, 29.700, 27.635, 22.232.

2e: Yield 1.01 g (61%), m.p. 273°C. − IR (C=S): $\tilde{\nu}$ = 1065 cm^{-1}. − $C_{26}H_{14}Cl_2S_8$ (653.78): calcd. C 47.77, H 2.16, Cl 10.85, S 39.23; found C 47.96, H 1.67, Cl 10.49, S 38.81.

2f: Yield 0.98 g (50%), m.p. 241−243°C. − IR (C=S): $\tilde{\nu}$ = 1067 cm^{-1}. − $C_{36}H_{50}Cl_2S_8$ (810.18): calcd. C 53.37, H 6.22, Cl 8.75, S 31.66; found C 53.32, H 6.52, Cl 9.08, S 31.43.

5,10-Dialkylthio-4,9-dichloronaphtho[1,2-d:5,6-d′]bis(1,3-dithiol-2-ones) **3**: A mixture of 1 mmol of 1,3-dithiole-2-thione **3** and 1.27

g (4 mmol) of $Hg(OAc)_2$ in 25 ml of 1,2-dichlorobenzene was refluxed for 2 h. After addition of 500 mg of $Na_2S \cdot 9\ H_2O$ the HgS formed was filtered off from the hot solution. 100 ml of methanol was added to the cold solution. The precipitate was filtered off and washed with methanol, ether, dried under vacuum, and recrystallized from DMF.

3a: Yield 0.38 g (75%), m.p. 282°C. − IR (C=O): $\tilde{\nu}$ = 1651 cm^{-1}. − $C_{16}H_{10}Cl_2O_2S_6$ (497.52): calcd. C 38.62, H 2.03, Cl 14.25, S 43.49; found C 38.88, H 1.65, Cl 13.72, S 42.61.

3b: Yield 0.42 g (77%), m.p. 212°C. − IR (C=O): $\tilde{\nu}$ = 1650 cm^{-1}. − $C_{20}H_{18}Cl_2O_2S_6$ (553.62): calcd. C 43.39, H 3.28, Cl 12.81, S 34.75; found C 43.23, H 3.59, Cl 13.10, S 34.21.

3c: Yield 0.41 g (71%), m.p. 183−184°C. − IR (C=O): $\tilde{\nu}$ = 1653 cm^{-1}. − $C_{22}H_{22}Cl_2O_2S_6$ (581.68): calcd. C 45.43, H 3.81, Cl 12.19, S 33.07; found C 45.33, H 3.77, Cl 12.78, S 32.76.

3d: Yield 0.42 g (68%), m.p. 160−162°C. − IR (C=O): $\tilde{\nu}$ = 1654 cm^{-1}. − $C_{26}H_{14}Cl_2O_2S_6$ (621.66): calcd. C 50.23, H 2.27, Cl 11.41, S 30.94; found C 49.78, H 2.14, Cl 10.87, S 31.20.

5H-7-Alkylthio-3,8,9-trichloro-1,3-dithiolo[4,5-d]naphtho-[3,4,5-a,j]-1,2-dithiole-5-thiones **4a−d**: Compounds **4a−d** were synthesized as were **2a−f**, using 1 g (2.5 mmol) of **1** and 400 mg (2.5 mmol) of sodium trithiocarbonate and 400 mg (5 mmol) of Na_2S in 40 ml of DMF. The products **4a−d** were recrystallized from DMF.

4a: Yield 0.98 g (85%), m.p. 283°C. − IR (C=S): $\tilde{\nu}$ = 1066 cm^{-1}. − $C_{13}H_5Cl_3S_6$ (459.90): calcd. C 33.95, H 1.09, Cl 23.13, S 41.83; found C 34.08, H 1.21, Cl 22.98, S 41.67.

4b: Yield 0.91 g (75%), m.p. 238°C. − IR (C=S): $\tilde{\nu}$ = 1062 cm^{-1}. − $C_{15}H_9Cl_3S_6$ (487.95): calcd. C 36.92, H 1.86, Cl 21.80, S 39.42; found C 36.68, H 1.94, Cl 21.72, S 38.97.

4c: Yield 0.78 g (62%), m.p. 223−225°C. − IR (C=S): $\tilde{\nu}$ = 1064 cm^{-1}. − $C_{16}H_{11}Cl_3S_6$ (501.98): calcd. C 38.28, H 2.21, Cl 21.19, S 38.32; found C 37.52, H 2.27, Cl 21.94, S 37.83.

4d: Yield 0.93 g (71%), m.p. 186°C. − IR (C=S): $\tilde{\nu}$ = 1065 cm^{-1}. − $C_{18}H_7Cl_3S_6$ (521.97): calcd. C 41.42, H 1.35, Cl 20.38, S 36.85; found C 41.21, H 1.72, Cl 20.42, S 36.82.

5H-7-Alkylthio-3,8,9-trichloro-1,3-dithiolo[4,5-d]naphtho-[3,4,5-a,j]-1,2-dithiol-5-ones **5a−d**: The desulfurization of **4a−d** was carried out as described for **3**, using 1 mmol of **4** and 0.63 g (2 mmol) of $Hg(OAc)_2$ in 25 ml of *o*-DCB. The products **5a−d** were recrystallized from 1,2-DCE.

5a: Yield 0.39 g (87%), m.p. 242°C. − IR (C=O): $\tilde{\nu}$ = 1648 cm^{-1}. − $C_{13}H_5Cl_3OS_5$ (443.84): calcd. C 35.18, H 1.13, Cl 23.96, S 36.12; found C 35.22, H 1.42, Cl 24.07, S 35.99.

5b: Yield 0.35 g (75%), m.p. 208°C. − IR (C=O): $\tilde{\nu}$ = 1647 cm^{-1}. − $C_{15}H_9Cl_3OS_5$ (471.89): calcd. C 38.18, H 1.92, Cl 22.54, S 33.97; found C 38.31, H 2.11, Cl 22.49, S 33.76.

5c: Yield 0.36 g (75%), m.p. 175−176°C. − IR (C=O): $\tilde{\nu}$ = 1648 cm^{-1}. − $C_{16}H_{11}Cl_3OS_5$ (485.92): calcd. C 39.55, H 2.27, Cl 21.94, S 32.96; found C 40.02, H 2.77, Cl 21.67, S 32.26.

5d: Yield 0.38 g (75%), m.p. 157°C. − IR (C=O): $\tilde{\nu}$ = 1650 cm^{-1}. − $C_{18}H_7Cl_3OS_5$ (505.91): calcd. C 42.73, H 1.39, Cl 21.02, S 31.68; found C 42.57, H 1.62, Cl 21.33, S 31.09.

4,9-Dichloro-2-(4,9-dichloro-5,10-diisopentylthio-7-thioxo-1,3-dithiolo[4',5':5,6]naphtho[1,2-d]-1,3-dithiol-2-ylidene)-5,10-diisopentylthio-1,3-dithiolo[4',5':5,6]naphtho[1,2-d]-1,3-dithiole-7-thione (**6**), *4,9-Dichloro-2-(4,9-dichloro-5,10-diisopentylthio-7-oxo-1,3-dithiolo[4',5':5,6]naphtho[1,2-d]-1,3-dithiol-2-ylidene)-5,10-diisopentylthio-1,3-dithiolo[4',5':5,6]naphtho[1,2-d]-1,3-dithiole-7-one* (**7**): A mixture of 570 mg (1 mmol) of **2d** [or 540 mg (1 mmol) of **3c**], 20 ml of *o*-DCB and 1.1 ml of triethyl phosphite was refluxed for 2 h. After this time, the precipitate was filtered off from the hot solution, washed with *o*-DCB, ether, and dried under vacuum.

6: Yield 0.39 g (68%), m.p. > 360°C. − IR (C=S): $\tilde{\nu}$ = 1068 cm^{-1}. − $C_{44}H_{44}Cl_4S_{14}$ (1163.48): calcd. C 45.42, H 3.81, Cl 12.19, S 38.58; found C 44.96, H 3.86, Cl 12.22, S 37.82.

7: Yield 0.45 g (80%), m.p. > 360°C. − IR (C=S): $\tilde{\nu}$ = 1653 cm^{-1}. − $C_{44}H_{44}Cl_4O_2S_{12}$ (1131.36): calcd. C 46.72, H 3.90, Cl 12.56, S 33.98; found C 46.73, H 4.29, Cl 12.54, S 33.27.

4,8,4',8'-Tetrachloro-6,7,6',7'-tetrakis(3,5-di-tert-butylbenzylthio)-5,9,5',9'-tetraisopentylthio-1,3-binaphtho[1,2-d]dithiol-2-ylidene (**8**): Under inert gas 260 mg (0.23 mmol) of **7** was suspended in 20 ml of dry THF at −60°C. A solution of methyllithium (2.5 ml of a 1.6 M solution in ether, 4 mmol) was added. The mixture was slowly warmed up. After stirring for 2 h at room temp., 5 ml of methanol was added dropwise, followed by the addition of a solution of 205 mg (1 mmol) of 2,4-di-*tert*-butylbenzyl bromide in 10 ml of methanol. The mixture was stirred for 10 h. After this time, the precipitated solid was filtered off, washed with water, methanol and ether.

8: Yield 0.31 g (71%), m.p. 264−267°C. − IR ($-CH_3$): $\tilde{\nu}$ = 2954 cm^{-1}. − $C_{102}H_{136}Cl_4S_{12}$ (1888.73): calcd. C 64.80, H 7.20, Cl 7.50, S 20.83; found C 64.41, H 7.29, Cl 7.23, S 20.72.

TTF/DDQ Complexes: A solution of 0.2 g (2 mmol) of DDQ in 10 ml of $CHCl_3$ was added to a suspension of 0.5 mmol of the corresponding TTF in 10 ml of $CHCl_3$. After stirring for 10 h, the black solid was filtered off, washed with $CHCl_3$ and dried under vacuum. The yields were nearly quantitative.

6·(DDQ)$_{1.33}$: M.p. ca. 200°C (decomp.). − IR (C≡N): $\tilde{\nu}$ = 2210 cm^{-1}. − $C_{54.66}H_{44}Cl_{6.66}N_{2.66}O_{2.66}S_{14}$ (1466.16): calcd. C 44.78, H 3.02, Cl 16.12, N 2.55, S 30.61; found C 44.59, H 3.17, Cl 16.49, N 2.79, S 30.12.

7·(DDQ)$_{0.5}$: M.p. ca. 200°C (decomp.) . − IR (C≡N): $\tilde{\nu}$ = 2217 cm^{-1}. − $C_{48}H_{44}Cl_5NO_3S_{12}$ (1244.86): calcd. C 46.31, H 3.56, Cl 14.24, N 1.12, S 30,09; found C 46.66, H 3.86, Cl 13.75, N 1.09, S 29.24.

8·(DDQ)$_{0.8}$: M.p. ca. 200°C (decomp.). − IR (C≡N): $\tilde{\nu}$ = 2209 cm^{-1}. − $C_{108.4}H_{136}Cl_{5.6}N_{1.6}O_{1.6}S_{12}$ (2070.34): calcd. C 62.88, H 6.62, N 1.08, S 18.58; found C 62.46, H 6.86, N 1.13, S 18.63.

Crystal-Structure Determination: The crystal-structure determinations were performed with a Stoe IPDS diffractometer mated with a graphite monochromator at room temp. Final lattice parameters were obtained from least-squares refinements using 5000 reflections. The structures were solved by direct methods using the SHELXS-86 program[14]. The full-matrix least-square structure refinements were performed with the SHELXL-93 program[15]. All non-H atoms were refined anisotropically.

Crystal Data of Compound **3a**[16]: $C_{16}H_{10}Cl_2O_2S_6$, triclinic, $P1$, a = 536.5(4), b = 857.4(6), c = 1182.9(7) pm, α = 107.11(5), β = 96.50(5), γ = 106.04(5)°, V = 488.5(6)·10^6 pm^3, Z = 1, $\rho_{calcd.}$ = 1.69 g/cm^3, μ = 0.98 mm^{-1}, 2θ = 3.68−50.0°, 1716 independent reflections with 1544 $F_o > 4\ \sigma(F_o)$, 119 parameters, R_{int} = 0.0262, R_1 [$F_o > 4\sigma(F_o)$] = 0.0440, wR_2 (all data) = 0.1269, largest diff. peak: 0.620·10^{-6} e/pm^3.

Crystal Data of Compound **4a**[16]: $C_{13}H_5Cl_3S_6$, monoclinic, $P2_1/n$, a = 1124.2(2), b = 700.5(2), c = 2100.4(4) pm, β = 96.82(2)°,

$V = 1642.5(5)\cdot 10^6$ pm^3, $Z = 4$, $\rho_{calcd.} = 1.86$ g/cm^3, $\mu = 1.31$ mm^{-1}, $2\theta = 6.14-56.18°$, 3927 independent reflections with 2678 $F_o > 4\sigma(F_o)$, 199 parameters, $R_{int} = 0.0702$, R_1 $[F_o > 4\sigma(F_o)] = 0.0370$, wR_2 (all data) = 0.0851, largest diff. peak: $0.559\cdot 10^{-6}$ e/pm^3.

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[16] Crystallographic data for the structures reported in this paper have been deposited with the Cambride Crystallographic Data Centre as supplementary publication no. CCDC-101394. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat.): + 44(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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