Umpolung of the 5-Alkyl-2-dimethylamino-1,3-dithiolium-4-thiolate Mesoion and Its Application in the Synthesis of Some New Tetrathiafulvalenes

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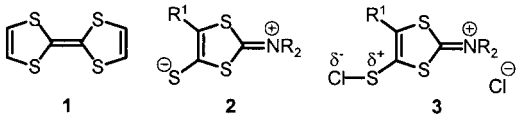
Keywords: Umpolung / Mesoion / 1,3-Dithiolium ion / Tetrathiafulvalene / Cyclic voltammetry

The 5-alkyl-2-dimethylamino-1,3-dithiolium-4-thiolate mesoion could be umpoled with sulfuryl chloride to yield a dicationic electrophile **3** that reacted with various electron-rich aromatic substrates to yield arylthio-substituted 1,3-dithiolium salts **13**–**25**. Two of these compounds have been transformed to the corresponding symmetrical tetrathiafulvalenes **43** and **44**, and their cyclovoltammetric behaviour recorded.

Introduction

Tetrathiafulvalenes (TTFs) (**1**) have received a lot of interest during the last two decades due to their ability to act as π-donors in charge-transfer salts and cation radical salts, which show metallic and even superconducting behaviour.[1] Their synthesis has been reviewed.[2] One of the strategies used to construct the TTF skeleton has been to utilize the readily available 5-alkyl-2-dialkylamino-1,3-dithiolium-4-thiolate mesoion (**2**), as first described by Robert et al.,[3] and later by other groups.[4] These mesoions have also been used as starting materials for making dithiadiazafulvalenes,[5] as well as 1,4-dithiafulvenes[6] and other extended π-systems.[7]

There are, however, no previous examples of attempts to transform mesoions of type **2** to electrophiles with the generic structure **3** by umpolung of the thiolate anion.



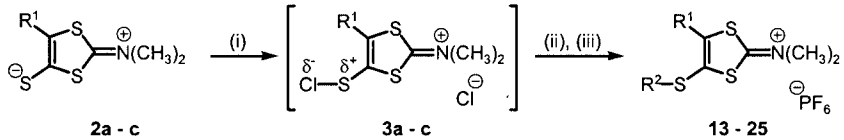
1 **2** **3**

We speculated that structures of type **3** would react with electron-rich nucleophiles, thereby providing a new way to synthesize TTFs substituted with a variety of electron-rich structures. Furthermore, since the alkyl group in the 5-position can be easily varied, and also be replaced by aromatic systems (e.g. naphthalene), it should be possible to construct donor structures containing several different assembled π-systems.

We would herein like to report our results from the reactions of electrophilic agents of type **3** with a number of electron-rich aromatics, together with elaboration to the corresponding symmetrical TTFs. The electrochemical properties of these TTFs are also presented.

Results and Discussion

The reaction sequence we used is illustrated in Scheme 1. The 5-alkyl-2-dimethylamino-1,3-dithiolium-4-thiolate mesoions **2a**−**c** could be conveniently umpoled with sulfuryl chloride in dichloromethane at room temperature. The resulting intermediates **3a**−**c**[8] were treated with the nucleophile in situ. The progress of the reaction could be moni-



2a - c **3a - c** **13 - 25**

Scheme 1. Reagents and conditions: (i) SO_2Cl_2, CH_2Cl_2, room temp.; (ii) Substrate: R^2; (iii) KPF_6, H_2O, room temp.

tored by TLC, and was usually complete overnight, yielding the chloride salt. These products were dissolved in water and precipitated with KPF_6 to give the corresponding hexafluorophosphonium salts **13**−**25** (Table 1). This reprecipitation led to pure, crystalline salts, which were stable at ambient temperature and atmosphere.

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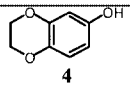
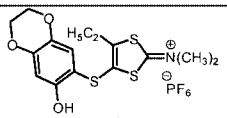
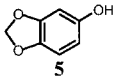
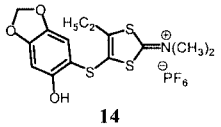
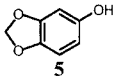
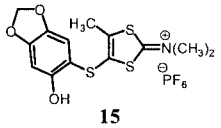
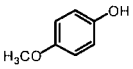
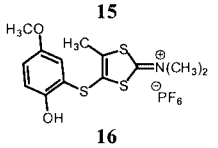
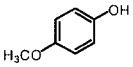
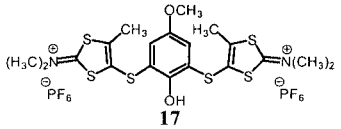
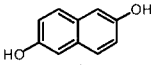
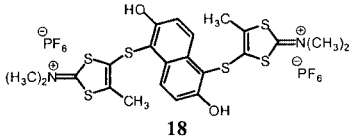
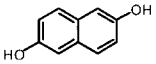
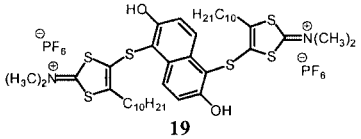
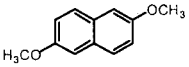
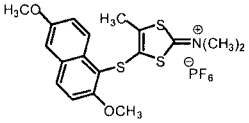
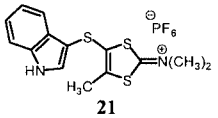
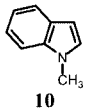
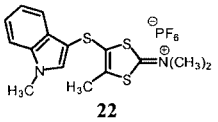
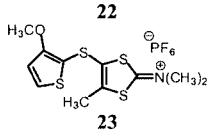
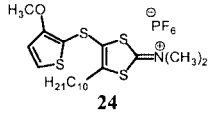
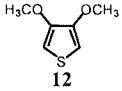
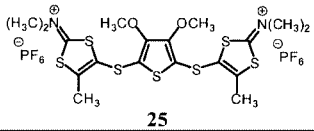
Table 1. In situ electrophilic aromatic substitution with an umpoled mesoion[a]

Mesoion	R^1	R^2	Product	Yield[b] (%)
2a	C_2H_5	 **4**	 **13**	78
2a	C_2H_5	 **5**	 **14**	88
2b	CH_3	 **5**	 **15**	75
2b	CH_3	 **6**	 **16**	64
2b	CH_3	 **6**	 **17**	26[c]
2b	CH_3	 **7**	 **18**	74
2c	$C_{10}H_{21}$	 **7**	 **19**	63
2b	CH_3	 **8**	 **20**	75
2b	CH_3	 **9**	 **21**	74
2b	CH_3	 **10**	 **22**	76
2b	CH_3	 **11**	 **23**	77
2c	$C_{10}H_{21}$	 **11**	 **24**	70
2b	CH_3	 **12**	 **25**	68

[a] Reagents and conditions: (i) SO_2Cl_2, CH_2Cl_2, room temp.; (ii) substrate: R^2; (iii) KPF_6, H_2O, room temp. [b] Yield of isolated pure product based on substrate R^2. [c] Product not analytically pure.

According to the described procedure, three mesoions **2a**−**c** with different alkyl chain-lengths, were treated with a variety of aromatic substrates (Table 1).

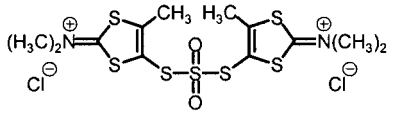
As shown in Table 1, the electrophilic intermediate **3** adds to electron-rich phenols such as dihydrobenzo[1,4]dioxin-6-ol (**4**), sesamol (**5**) and *p*-methoxyphenol (**6**), yielding the products **13**−**17**. With *p*-methoxyphenol (**6**), synthesis of both mono- and disubstituted products (**16** and **17**) could be achieved, depending on the amount of electrophile used. However, total conversion into compound **17** could not be accomplished, since the reaction stopped at the monosubstituted product **16**. Even with prolonged reaction times, elevated temperatures and an increased amount of electrophile, the reaction could not be driven to completion. Unfortunately, we were not able to separate the products in order to attain analytically pure **17**.

The electrophile **3** reacted with 2,6-dihydroxynaphthalene (**7**) and 2,6-dimethoxynaphthalene (**8**), yielding in the former case the 1,5-disubstituted products **18** and **19**, whereas in the latter case, only the monosubstituted product **20** was produced. We also tried substitution with 1,5-dihydroxynaphthalene, but this only resulted in oxidation of the starting material.

Heteroaromatic systems such as indole and electron-rich thiophenes were also tried. Indole (**9**) and *N*-methylindole (**10**) were substituted in the 3-position to give **21** and **22**. Whereas 3-methoxythiophene (**11**) also yielded the monosubstituted products **23** and **24**, 3,4-dimethoxythiophene (**12**) gave the disubstituted product **25**. In the cases where an additional quantity of electrophile was needed to increase the conversion of starting material, the electrophile seemed to form a stable compound with sulfuryl chloride, rather than with the substrate. ^{1}H NMR spectroscopy and MS (EI) confirmed the structure of this product as the dimer **26**.[9] This problem could not be overcome by use of an inert atmosphere, prolonged reaction time or elevated temperatures. Addition of the substrate before the sulfuryl chloride resulted (in some cases) in chlorination of the substrate prior to umpolung of the mesoion **2**.

Once prepared, the 4-arylthio-2-(dialkylimino)-1,3-dithiolium salts could then be used in the synthesis of TTFs, according to the procedure outlined in Scheme 2.

The salts **13**−**16** and **18**−**25** were reduced to the corresponding amino compounds **27**−**38** with sodium borohydride (Table 2). The products **27**−**38** were obtained in almost quantitative yield, either as oils or crystalline compounds. The oily products were not stable at ambient temperature and were best used as soon as possible. The crystalline compounds were somewhat more stable.[10]



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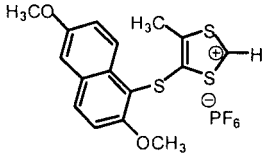
Deamination of the amino compounds was carried out by use of hexafluorophosphoric acid,[11] giving the four dithiolium salts **39**−**42** in moderate yield (60−70%).



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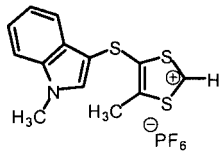

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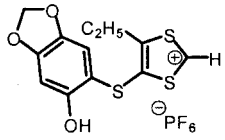

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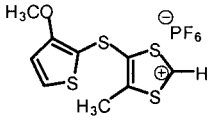
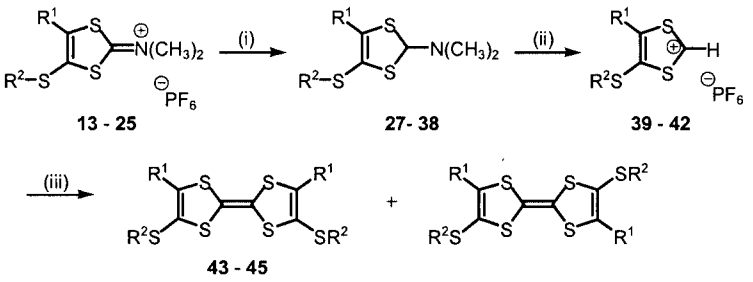


42

From these salts, we could isolate the corresponding tetrathiafulvalenes **43**, **44** and **45** after treatment with triethylamine. We were able to characterize **43** and **44** fully, but unfortunately TTF **45** could only be identified by MS (EI), because decomposition during column chromatography prevented it being obtained in analytical purity. TTF **43** was obtained in 35% yield after purification, whereas TTF **44** resulted only in 16% yield. We could not detect any TTF from the reaction of **41** with triethylamine.[12]

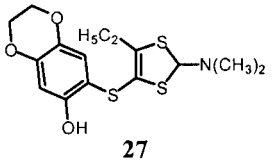
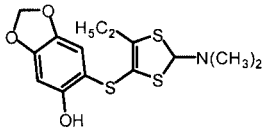
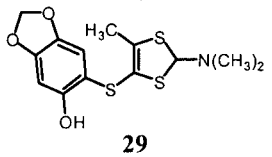
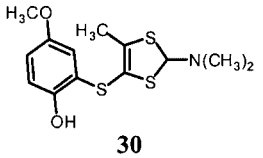
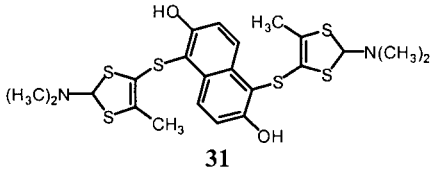
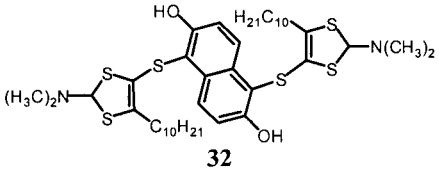
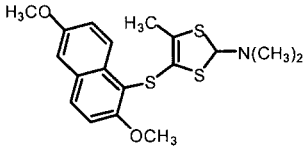
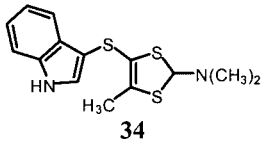
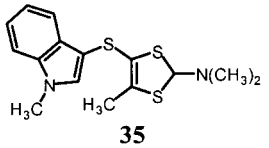
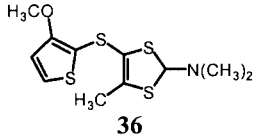
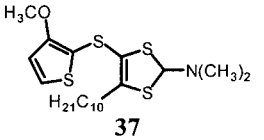
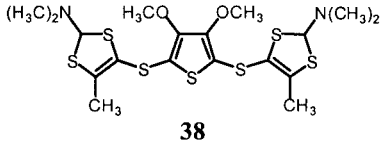
The electrochemical behaviour of the TTFs **43** and **44** was investigated by cyclic voltammetry (CV) in dichloromethane; the results are shown in Figures 1 and 2.

The cyclic voltammograms indicated the presence of two reversible one-electron transfer processes, corresponding to the successive formation of the cation radical (E^1) and di-



Scheme 2. Reagents and conditions: (i) $NaBH_4$, EtOH, room temp.; (ii) HPF_6, H_2SO_4, 0 °C; (iii) Et_3N, CH_3CN, N_2, room temp.

Table 2. Synthesis of compounds **27**−**38** from reduction[a] of the 2-(dialkylimino)-4-arylthio-1,3-dithiolium salts **13**−**16** and **18**−**25**

Product	Yield (%)	Product	Yield (%)
 **27**	93	 **28**	98
 **29**	95	 **30**	quant.
 **31**	79	 **32**	99
 **33**	94	 **34**	88
 **35**	98	 **36**	95
 **37**	93	 **38**	89

[a] Reagents and conditions: $NaBH_4$, EtOH, room temp.

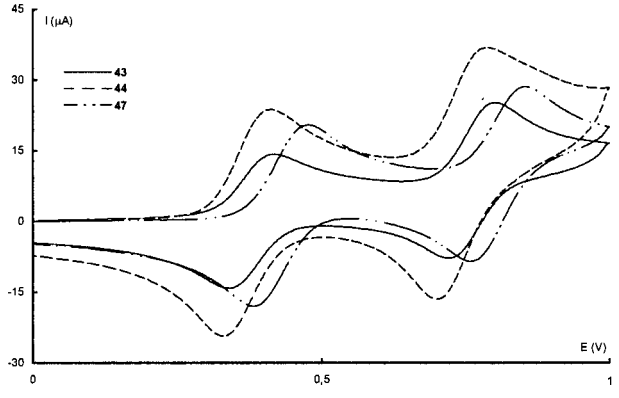
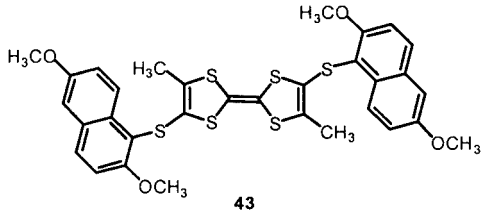
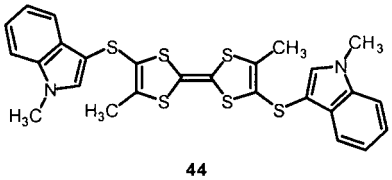
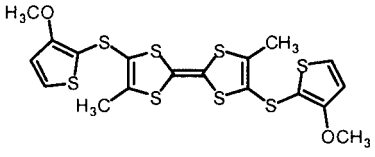


Figure 1. Cyclic voltammograms of TTFs **43**, **44** and **47** (0.1 M in CH_2Cl_2), 1 mM $(n\text{Bu})_4NClO_4$, scan rate 500 mV s^{-1}, E vs. SCE

cation (E^2), as expected for TTFs. The compounds also showed a third irreversible oxidation potential (Figure 1), possibly due to additional oxidation of the aromatic substituents. The first and second reduction waves of indole-TTF **44** were severely perturbed by the third oxidation, whereas the reductions of naphthalene-TTF **43** were less affected, as can be seen in Figure 2.


43


44


45

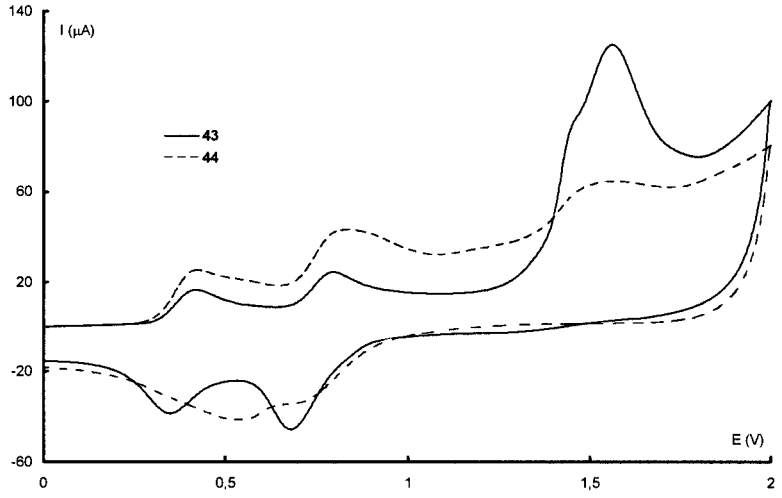
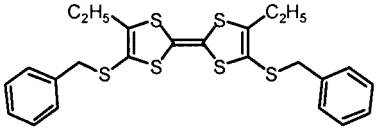


Figure 2. Cyclic voltammograms of TTFs **43** and **44** (0.1 M in CH_2Cl_2), 1 mM $(nBu)_4NClO_4$, scan rate 500 mV s^{-1}, *E vs.* SCE

We expected that the sulfur bridge between the TTFs and the aromatic substituents would not completely disrupt the conjugation within the molecule, but allow electronic "cross-talk" between the π-systems within the molecules, thereby lowering the oxidation potential. However, we cannot detect such an inductive behaviour in the potentials measured (which are quite normal), but the potentials are a little lower than for the corresponding bis(benzylthio)-substituted TTF **47** (see Figure 1), as shown in Table 3.

Table 3. Electrochemical data for TTFs **43**, **44** and **47** (0.1 M in CH_2Cl_2), [1 mM $(nBu)_4NClO_4$, scan rate 500 mV s^{-1}, *E* vs. SCE]

	E^1 (V)	E^2 (V)	$\Delta E = E^2 - E^1$ (V)
43	0.38	0.76	0.39
44	0.37	0.75	0.38
47	0.43	0.81	0.38

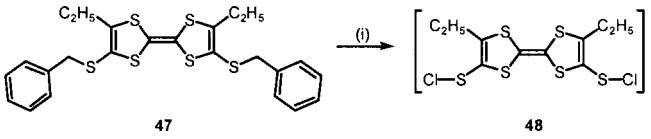


47

Whether the electrochemical behaviour of indole-TTF **44** reflects a less stable tricationic species, a more effective cross-talk of the same state, or is a consequence of the visible precipitation on the anode, remains undecided.

The first attempts at electrocrystallization of **43** were performed in the presence of four different counterions $(nBu)_4NClO_4$, $(nBu)_4NBF_4$, $(nBu)_4NPF_6$, and $(nBu)_4NAsF_6$. So far, however, we have only obtained polycrystalline material.

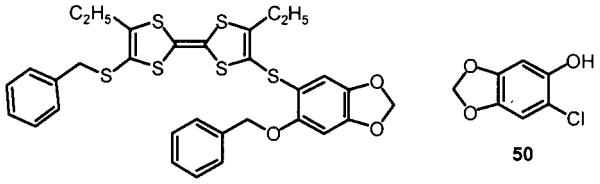
An alternative and more reliable way to achieve the synthesis of arylthio-substituted TTFs could be to prepare the TTF bis(sulfenyl chloride) **48** in situ by the debenzylation of the bis(benzylthio)-substituted TTF **47** with sulfuryl chloride (Scheme 3). Compound **47** could then be treated with various electron-rich aromatic compounds.



47 **48**

Scheme 3. Attempted synthesis of a dicationic electrophile. Reagents and conditions: (i) SO_2Cl_2, CH_2Cl_2, room temp.

Preliminary results from reactions of **47** with sesamol (**9**) as substrate gave a number of products, of which we could identify compound **49** (by NMR spectroscopy and MS), as well as the chlorinated by-product **50**. The result is similar when two or four equivalents of sulfuryl chloride are used. We could not detect any non-benzylated **49** in the reaction mixtures, which led us to the hypothesis that the benzylation of the hydroxy function is occurring at the same time as the electrophilic attack of the sulfur. Further investigations of this reaction will be performed and reported in due course.



49 **50**

Conclusions

We have demonstrated that the 5-alkyl-2-dimethylamino-1,3-dithiolium-4-thiolate mesoion **2** can be umpoled to the electrophile **3**, and utilized in reactions with various electron-rich aromatics. Three of the resulting dithiolium salts

13−**25** have been transformed to the corresponding symmetrical tetrathiafulvalenes in three steps. Further applications of these electron-rich donor molecules are now being investigated.

Experimental Section

General Remarks: All operations (except where indicated) were performed under ambient conditions, without any special care taken for the exclusion of air or moisture. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AM 400 (400 MHz) or Bruker DMX 500 (500 MHz) spectrometer. Mass spectra were recorded with a Finnigan SSQ 7000 (electron impact) or a Bruker Reflex III (MALDI-TOF) MS instrument. Elemental analyses were performed by Analytische Laboratorien GmbH, Germany. THF was freshly distilled from sodium benzophenone ketyl. Mesoions **2a**, **2b** and **2c** and compound **47** were prepared in accordance to previous reported procedures.[4b] All other commercial reagents and solvents were used as received. Cyclic voltammetry was carried out at ambient temperature in dichloromethane at 500 mV·s^{-1} with tetrabutylammonium perchlorate (0.1 M) as the electrolyte and a SCE reference electrode. The half-wave potential for the ferrocene/ferrocenium couple was found to be 0.49 V in our system. Electrocrystallization was carried out in a U-shaped electrocrystallization cell. The donor (20 mg) was put in the anode compartment and separated from the cathode compartment by a porous glass frit. Dry dichloromethane (40 mL) was added, together with the electrolyte (0.1 M), and the compartments were degassed with nitrogen. The experiments were carried out at ambient temperature, with a platinum wire anode of about 1 cm^2. Currents used were 1.0 μA·cm^{-2} at the beginning of each experiment and increased to 4 μA·cm^{-2} over a period of 15 days.

General Procedure for the Formation of 4-Arylthio-2-(dialkylimino)-1,3-dithiolium Hexafluorophosphates 13−25 from the Reaction of a Nucleophilic Substrate with the in situ Generated Electrophile

Preparation of 13: Mesoion **2a** (10 mmol) was dissolved in CH_2Cl_2 (80 mL) in a round-bottomed flask, which was flushed with N_2. SO_2Cl_2 (1.35 g, 10 mmol) was added dropwise, to give a light yellow solution. Substrate **4** (10 mmol) was dissolved in CH_2Cl_2 (40 mL) and added to the mixture; the reaction was monitored by TLC analysis. When the reaction was complete, the solvent was evaporated, yielding the chloride salt, which was then dissolved in H_2O (100 mL). A solution of KPF_6 (5 g) in H_2O (100 mL) was added to the solution; a yellow precipitate formed immediately. The precipitate was filtered off, washed with H_2O and then dissolved in CH_2Cl_2. This solution was dried with $MgSO_4$, and the solvent was removed under reduced pressure, yielding **13**. Yield: 78% (3.10 g); apricot crystals. M.p. 165.3−167.0 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.22 (t, *J* = 7.5 Hz, 3 H), 3.01 (q, *J* = 7.5 Hz, 2 H), 3.42 (s, 3 H), 3.45 (s, 3 H), 4.14−4.17 (m, 2 H), 4.20−4.23 (m, 2 H), 6.45 (s, 1 H), 6.90 (s, 1 H), 10.11 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.7, 23.1, 46.7, 47.1, 63.6, 64.5, 104.3, 107.9, 121.1, 124.7, 136.7, 144.8, 145.7, 151.7, 184.0 ppm. $C_{15}H_{18}F_6NO_3PS_3$: calcd. C 35.93, H 3.62; found C 35.65, H 3.62.

Compounds **14**−**25** were prepared in the above manner.

14: Yield: 88% (9.60 g); white crystals. M.p. 168.8−169.8 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.22 (t, *J* = 7.5 Hz, 3 H), 3.01 (q, *J* = 7.5 Hz, 2 H), 3.41 (s, 3 H), 3.45 (s, 3 H), 5.99 (s, 2 H), 6.56 (s, 1 H), 7.00 (s, 1 H), 10.35 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.7, 23.1, 46.7, 47.1, 98.0, 101.7, 106.2, 112.4, 125.2, 140.5, 144.2, 150.0, 153.5, 184.0 ppm. $C_{14}H_{16}F_6NO_3PS_3$: calcd. C 34.50, H 3.31; found C 34.47, H 3.36.

15: Yield: 75% (6.80 g); pink crystals. M.p. 187.7−188.4 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.54 (s, 3 H), 3.41 (s, 3 H), 3.44 (s, 3 H), 5.99 (s, 2 H), 6.56 (s, 1 H), 6.99 (s, 1 H), 10.31 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.2, 46.6, 47.0, 98.0, 106.3, 112.4, 125.7, 137.9, 140.5, 149.9, 153.3, 183.9 ppm. $C_{13}H_{14}F_6NO_3PS_3$: calcd. C 32.98, H 2.98; found C 32.90, H 3.02.

16: Yield: 64% (0.67 g); beige crystals. M.p. 139.5−141.3 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.54 (s, 3 H), 3.44 (s, 3 H), 3.47 (s, 3 H), 3.67 (s, 3 H), 6.77 (d, *J* = 2.5 Hz, 1 H), 6.85 (d, *J* = 2.5 Hz, 1 H), 6.86 (d, *J* = 0.8 Hz, 1 H), 10.00 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.3, 46.6, 47.0, 55.5, 115.5, 116.2, 116.5, 118.1, 123.0, 141.0, 149.9, 152.5, 183.9 ppm. $C_{13}H_{16}F_6NO_2PS_3$: calcd. C 33.99, H 3.51; found C 33.74, H 3.40.

17: Yield: 26% (0.945 g); yellow crystals. The product was not analytically pure and could not be separated from the monosubstituted *p*-methoxyphenol **16**. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.55 (s, 6 H), 3.46 (s, 6 H), 3.49 (s, 6 H), 3.70 (s, 3 H), 6.73 (2 H) ppm.

18: Yield: 74% (0.65 g); beige crystals. M.p. 238.0−240.0 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.65 (s, 6 H), 3.29 (s, 6 H), 3.39 (s, 6 H), 7.44 (d, *J* = 9.3 Hz, 2 H), 8.44 (d, *J* = 9.3 Hz, 2 H), 11.00 (s, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.4, 46.6, 46.9, 108.8, 120.1, 125.6, 128.4, 130.0, 136.1, 156.3, 183.8 ppm. $C_{22}H_{24}F_{12}N_2O_2P_2S_6$: calcd. C 31.81, H 2.91; found C 31.52, H 3.06.

19: Yield: 63% (0.59 g); brown crystals. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.86 (t, *J* = 7.3 Hz, 6 H), 1.20−1.30 (m, 28 H), 1.50−1.57 (m, 4 H), 3.07 (t, *J* = 7.5 Hz, 4 H), 3.30 (s, 6 H), 3.40 (s, 6 H), 7.42 (d, *J* = 9.1 Hz, 2 H), 8.43 (d, *J* = 9.1 Hz, 2 H), 11.02 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 29.0, 29.1, 29.2, 29.4, 29.5, 30.2, 31.7, 31.8, 46.5, 46.9, 109.1, 117.1, 120.5, 127.1, 130.3, 139.9, 155.9, 185.2 ppm. $C_{40}H_{60}F_{12}N_2O_2P_2S_6$: calcd. C 44.35, H 5.58; found C 44.50, H 5.76.

20: Yield: 75% (3.91 g); pale yellow crystals. M.p. 218.9−220.8 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.64 (s, 3 H), 3.30 (s, 3 H), 3.38 (s, 3 H), 3.87 (s, 3 H), 4.00 (s, 3 H), 7.36 (dd, *J* = 9.3 Hz, 2.5 Hz, 1 H), 7.42 (d, *J* = 2.5 Hz, 1 H), 7.55 (d, *J* = 9.1 Hz, 1 H), 8.07 (d, *J* = 9.1 Hz, 1 H), 8.32 (d, *J* = 9.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.3, 46.6, 46.9, 55.3, 56.7, 107.1, 110.6, 114.3, 121.0, 125.1, 125.3, 129.6, 130.1, 132.1, 136.8, 156.0, 157.1, 183.6 ppm. $C_{18}H_{20}F_6NO_2PS_3$: calcd. C 41.30, H 3.85; found C 41.09, H 3.87.

21: Yield: 74% (0.40 g); pale yellow crystals. M.p. 165.8−166.7 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.63 (s, 3 H), 3.30 (s, 3 H), 3.38 (s, 3 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 7.23 (t, *J* = 7.8 Hz, 1 H) 7.50 (d, *J* = 7.8 Hz, 1 H), 7.59 (d, *J* = 7.8 Hz, 1 H), 7.94 (d, *J* = 3.0 Hz, 1 H), 11.88 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.0, 46.6, 47.0, 98.9, 112.6, 117.7, 120.8, 122.7, 127.8, 128.6, 132.9, 133.3, 136.3, 183.3 ppm. $C_{14}H_{15}F_6N_2PS_3$: calcd. C 37.16, H 3.34; found C 36.78, H 3.42.

22: Yield: 76% (1.77 g); pale yellow crystals. M.p. 159.5−161.4 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.63 (s, 3 H), 3.31 (s, 3 H), 3.37 (s, 3 H), 3.85 (s, 3 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 7.30 (t, *J* = 8.3 Hz, 1 H) 7.57 (d, *J* = 8.3 Hz, 1 H), 7.60 (d, *J* = 7.8 Hz, 1 H), 7.95 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.1, 33.0, 46.6, 47.0, 97.7, 111.0, 118.0, 121.1, 122.7, 128.2, 133.8, 136.4, 137.0, 183.3 ppm.

23: Yield: 77% (5.56 g); brown oil. M.p. 158.5−160.5 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.56 (s, 3 H), 3.42 (s, 3 H), 3.43 (s, 3 H), 3.92 (s, 3 H), 7.16 (d, *J* = 5.8 Hz, 1 H), 7.83 (d, *J* = 5.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.1, 46.7, 47.1, 59.1, 102.0, 117.0, 126.2, 131.8, 137.4, 161.5, 183.5 ppm. $C_{11}H_{14}F_6NOPS_4$: calcd. C 29.39, H 3.14; found C 29.29, H 3.17.

24: Yield: 70% (1.56 g); brown oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.86 (m, 3 H), 1.21−1.38 (m, 14 H), 1.58−1.65 (m, 2 H), 3.00 (t, *J* = 7.3 Hz, 2 H), 3.42 (s, 3 H), 3.44 (s, 3 H), 3.92 (s, 3 H), 7.17 (d, *J* = 5.8 Hz, 1 H), 7.84 (d, *J* = 5.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 13.9, 22.1, 28.2, 28.5, 28.6, 28.8, 28.9, 29.1, 29.7, 31.2, 46.8, 47.1, 59.0, 101.7, 117.0, 126.2, 132.0, 142.1, 161.6, 183.6 ppm.

25: Yield: 68% (1.39 g); white crystals. M.p. 160.7−162.5 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.59 (s, 6 H), 3.45 (s, 6 H), 3.46 (s, 6 H), 3.98 (s, 6 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 15.5, 46.9, 47.3, 61.3, 115.1, 123.2, 141.0, 152.4, 183.4 ppm. $C_{18}H_{24}F_{12}N_2O_2P_2S_7$: calcd. C 26.53, H 2.97; found C 26.50, H 3.00.

Reduction of the Hexafluorophosphate Salts 13−16 and 18−25 to the Corresponding Amino Products 27−38

Preparation of 27: 13 (8.2 mmol) was dissolved in 99% EtOH (80 mL). $NaBH_4$ (40.8 mmol) was added over a period of 5 minutes. After stirring at room temp for 1 h, 10% aqueous NH_4Cl and Et_2O (or CH_2Cl_2) were added and the layers separated. The organic phase was washed with H_2O, dried with $MgSO_4$, filtered and the solvents evaporated to dryness, yielding **27**. This product was used without further purification in the deamination reaction. Yield: 93% (1.89 g); brown oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.08 (t, *J* = 7.5 Hz, 3 H), 2.14 (s, 6 H), 2.47−2.52 (m, 1 H), 2.66 (quint, *J* = 7.5 Hz, 1 H), 4.11−4.13 (m, 2 H), 4.16−4.18 (m, 2 H), 6.28 (s, 1 H), 6.34 (s, 1 H), 6.58 (s, 1 H), 9.55 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.7, 23.6, 37.7, 63.7, 64.3, 76.7, 103.8, 111.9, 112.6, 117.7, 136.4, 140.7, 143.0, 149.6 ppm. MS (MALDI-TOF): *m*/*z* = 356.50 [M$^+$].

Compounds **28**−**38** were prepared in the above manner.

28: Yield: 98% (1.17 g); wine-red oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.09 (t, *J* = 7.3 Hz, 3 H), 2.12 (s, 6 H), 2.45−2.55 (m, 1 H), 2.65−2.74 (quint, *J* = 7.3 Hz, 1 H), 5.92 (s, 2 H), 6.24 (s, 1 H), 6.48 (s, 1 H), 6.65 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 14.6, 14.7, 23.5, 37.6, 76.6, 97.7, 97.8, 101.1, 110.0, 113.3, 139.8, 140.1, 147.6, 151.1 ppm. MS (MALDI-TOF): *m*/*z* = 342.47 [M$^+$].

29: Yield: 95% (1.10 g) wine-red oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.11 (s, 6 H), 2.14 (s, 3 H), 5.92 (s, 2 H), 6.23 (s, 1 H), 6.47 (s, 1 H), 6.64 (s, 1 H), 9.70 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.3, 37.7, 76.6, 76.7, 97.7, 101.1, 110.0, 114.1, 133.3, 140.1, 147.5, 151.1 ppm. MS (MALDI-TOF): *m*/*z* = 329.18 [M$^+$].

30: Yield: Quantitative (0.28 g); orange oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.14 (s, 6 H), 2.26 (s, 3 H), 3.74 (s, 3 H), 5.88 (s, 1 H), 6.83 (dd, *J* = 8.8 Hz, 1 H, 2.8 Hz), 6.88 (d, *J* = 8.8 Hz, 1 H), 6.97 (d, *J* = 2.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.5, 18.4, 38.1, 55.9, 58.5, 114.0, 116.0, 117.6, 118.6, 118.7, 132.9, 150.3, 153.3 ppm. MS (EI): *m*/*z* (%) = 315.2 (2) [M$^+$], 270.1 (100).

31: Yield: 79% (0.78 g); orange crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 6 H), 1.92 (s, 6 H), 2.36 (s, 3 H), 2.37 (s, 3 H), 5.75 (s, 1 H), 5.76 (s, 1 H), 6.87 (br. s, 2 H), 7.30 (d, *J* = 9.1 Hz, 1 H), 7.31 (d, *J* = 9.1 Hz, 1 H), 8.28 (d, *J* = 9.1 Hz, 1 H), 8.29 (d, *J* = 9.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 37.9, 77.8, 110.8, 114.5, 118.0, 128.9, 129.7, 130.6, 154.8 ppm. MS (MALDI-TOF): *m*/*z* = 541.66 [M$^+$].

32: Yield: 99% (0.28 g); brown oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.81−0.89 (m, 6 H), 1.23−1.34 (m, 28 H), 1.41−1.53 (m, 8 H), 1.87 (s, 12 H), 6.03 (s, 2 H), 7.21 (d, *J* = 9.1 Hz, 2 H), 8.24 (d, *J* = 9.1 Hz, 1 H), 8.25 (d, *J* = 9.1 Hz, 1 H),10.04 (br. s, 2 H) ppm. MS (MALDI-TOF): *m*/*z* = 792.27 [M$^+$ −2H].

33: Yield: 94% (2.48 g); orange crystals. M.p. 96.5−97.9 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.85 (s, 6 H), 2.29 (s, 3 H), 3.86 (s, 3 H), 3.89 (s, 3 H), 6.02 (s, 1 H), 7.26 (dd, *J* = 9.3 Hz, 2.8 Hz, 1 H), 7.33 (d, *J* = 2.8 Hz, 1 H), 7.43 (d, *J* = 9.1 Hz, 1 H), 7.94 (d, *J* = 9.1 Hz, 1 H), 8.32 (d, *J* = 9.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.3, 37.2, 55.2, 56.3, 76.5, 106.6 113.3 113.9, 115.2, 119.9, 126.0, 129.7, 129.8, 130.4, 130.5, 155.6, 156.8 ppm. MS (EI): *m*/*z* (%) = 379.2 (20) [M$^+$].

34: Yield: 88% (0.20 g); orange oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.91 (s, 6 H), 2.27 (s, 3 H), 6.05 (s, 1 H), 7.09 (t, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1 H) 7.42 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 7.8 Hz, 1 H), 7.62 (d, *J* = 2.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.3, 30.7, 37.4, 76.3, 101.8, 112.1, 117.8, 118.3, 119.8, 121.9, 128.1, 128.5, 131.2, 136.1 ppm. MS (MALDI-TOF): *m*/*z* = 307.10 [M$^+$ − H].

35: Yield: 98% (0.70 g); dark orange crystals. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.92 (s, 6 H), 2.27 (s, 3 H), 3.80 (s, 3 H), 6.06 (s, 1 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 7.22 (t, *J* = 8.3 Hz, 1 H) 7.48 (d, *J* = 8.3 Hz, 1 H), 7.55 (d, *J* = 7.8 Hz, 1 H), 7.65 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.2, 32.7, 37.4, 76.4, 100.7, 110.4, 117.6, 118.5, 120.0, 122.0, 128.3, 128.8, 134.9, 136.7 ppm. MS (EI): *m*/*z* (%) = 322.2 (15) [M$^+$]. $C_{15}H_{18}N_2S_3$: calcd. C 55.86, H 5.63; found C 55.51, H 5.55.

36: Yield: 95% (1.45 g); red oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.01 (s, 6 H), 2.20 (s, 3 H), 3.83 (s, 3 H), 6.13 (s, 1 H), 7.03 (d, *J* = 5.8 Hz, 1 H), 7.63 (d, *J* = 5.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 15.2, 37.3, 58.6, 58.7, 76.8, 105.9, 116.1, 116.6, 129.3, 131.5, 159.9 ppm. MS (EI): *m*/*z* (%) = 305.1 (45) [M$^+$].

37: Yield: 93% (1.02 g); dark orange oil. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.85 (m, 3 H), 1.21−1.31 (m, 14 H), 1.45−1.54 (m, 2 H), 2.51−2.57 (m, 1 H), 2.67−2.76 (m, 1 H), 3.82 (s, 3 H), 6.16 (s, 1 H), 7.03 (d, *J* = 5.8 Hz, 1 H), 7.63 (d, *J* = 5.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 13.9, 22.1, 28.5, 28.6, 28.7, 28.8, 28.9, 29.4, 29.7, 31.2, 37.4, 58.6, 76.7, 105.8, 115.9, 116.6, 129.2, 136.5, 159.9 ppm. MS (MALDI-TOF): *m*/*z* = 430.62 [M$^+$]. $C_{20}H_{33}NOS_4$: calcd. C 55.64, H 7.70; found C 55.82, H 7.84.

38: Yield: 89% (0.73 g); dark orange oil. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.19 (s, 12 H), 2.24 (s, 6 H), 3.97 (s, 6 H), (s, 2 H) ppm. ^{13}C NMR (124 MHz, [D$_6$]DMSO): δ = 15.6 (2 C), 38.2 (4 C), 61.0 (2 C), 99.6 (2 C), 115.0 (2 C), 117.2 (2 C), 133.7 (2 C), 151.0 (2C) ppm. MS (MALDI-TOF): *m*/*z* = 525.63 [M$^+$].

Deamination of 28, 33, 35 and 36 with HPF_6 to Give the Dithiolium Salts 39−42

Preparation of 39: 33 (1.9 mmol) was added in portions to ice-cold concd. H_2SO_4 (15 mL) The mixture was stirred in an ice bath for 30 minutes and then poured onto 100 mL crushed ice containing

60% aqueous HPF_6 (1 mL). The orange precipitate formed was filtered and washed with cold H_2O. The product was dissolved in Et_2O (or CH_2Cl_2) and dried with $MgSO_4$, filtered and concentrated to yield **39**, which was used immediately in the TTF-forming reaction. Yield: 60% (0.29 g); orange crystals. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.89 (s, 3 H), 3.93 (s, 3 H), 4.03 (s, 3 H), 7.18 (d, *J* = 2.5 Hz, 1 H), 7.31 (dd, *J* = 9.1, 2.5 Hz, 1 H), 7.36 (d, *J* = 9.1 Hz, 1 H) 7.99 (d, *J* = 9.1 Hz, 1 H), 8.26 (d, *J* = 9.1 Hz, 1 H), 10.76 (s, 1 H ppm.

Compounds **40**−**42** were prepared in the above manner.

40 (from 35): Yield: 71% (0.30 g); brown crystals.

41 (from 28): Yield: 89% (1.35 g); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.55 (t, *J* = 7.6 Hz, 3 H), 3.19 (q, *J* = 7.6 Hz, 2 H), 6.03 (s, 2 H), 6.69 (s, 1 H), 6.93 (s, 1 H), 10.72 (s, 1 H) ppm.

42 (from 36): Yield: 70% (0.48 g); dark purple crystals.

Preparation of TTF 43: 39 (1.1 mmol) was dissolved (or suspended) in dry CH_3CN (10 mL) and the mixture purged with N_2. Et_3N (1.1 equiv.) was added dropwise, resulting in the formation of a precipitate and the clearance of the solution. After approx 1 h the precipitate was filtered, washed with CH_3CN and dried, yielding crude **43** (268 mg, 75%) as orange crystals. After purification by chromatography on a silica gel column (CH_2Cl_2) and recrystallization from CH_2Cl_2/heptane, pure **43** was obtained. Yield: 35% (125 mg); pale orange crystals. M.p. > 210 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 6 H), 3.86 (s, 6 H), 3.92 (s, 6 H), 7.28 (dd, *J* = 9.3, 2.8 Hz, 2 H), 7.37 (d, *J* = 2.8 Hz, 2 H), 7.47 (d, *J* = 9.1 Hz, 2 H) 7.98 (d, *J* = 9.1 Hz, 2 H), 8.23 (d, *J* = 9.3 Hz, 2 H) ppm. MS (EI): *m*/*z* (%) = 668.17 (100) [M^+]. $C_{32}H_{28}O_4S_6$: calcd. C 57.45, H 4.22; found C 56.98, H 4.30.

44: This was prepared (from **40**) in the same manner as for **43**. The crude product (68 mg, 36%) was collected as red crystals. After purification by chromatography on a silica gel column (CH_2Cl_2) followed by recrystallization from CH_2Cl_2/heptane, pure **44** (11 mg) was obtained. Yield: 16% (31 mg); pale orange crystals. M.p. 142.3−144.2 °C. An additional 20 mg of product was obtained from chromatography of the mother liquor. A mixture of *cis* and *trans* isomers were obtained, which were not separable by chromatography. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.20/2.24 (s, 6 H), 3.81/3.79 (s, 6 H), 7.13−7.17 (m, 2 H), 7.22−7.27 (m, 2 H), 7.49−7.53 (m, 4 H), 7.72/7.70 (s, 2 H) ppm. MS (EI): *m*/*z* (%) = 554.16 (100) [M^+]. $C_{26}H_{22}N_2S_6$: calcd. C 56.28, H 4.00; found C 56.10, H 4.14.

45: This was prepared (from **42**) in the same manner as for **43**. MS (EI): *m*/*z* (%) = 520.15 (100) [M^+]. The product could not be obtained analytically pure due to decomposition during purification by column chromatography.

Preparation of TTF 47 from Mesoion 2a: The mesoion **2a** (0.1 mol) was refluxed in acetone (500 mL) with benzyl bromide (0.1 mol) until the yellow colour faded. After cooling to room temperature, the bromide salt precipitated. This was filtered and washed with acetone and Et_2O (to remove traces of starting material), to yield **47**. Yield: 96% (36 g); white crystals. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (t, *J* = 7.6 Hz, 3 H), 2.24 (q, *J* = 7.6 Hz, 2 H), 3.52 (s, 3 H), 3.55 (s, 3 H), 3.80 (s, 2 H), 7.02−7.09 (m, 3 H), 7.10−7.15 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.9, 41.3, 47.6, 47.9, 123.6, 127.5, 128.5, 128.6, 135.1, 149.0, 184.6 ppm. MS (EI): *m*/*z* (%) = 296.1 (100) [M^+]. $C_{14}H_{18}BrNS_3$: calcd. C 44.67, H 4.82; found C 44.64, H 4.87.

The bromide salt **47** (61 mmol) was dissolved in EtOH (150 mL), and the flask put in an ice bath. $NaBH_4$ (305 mmol) was added in portions over 1 h, and the mixture stirred for a further 30 minutes before it was quenched with 10% aqueous NH_4Cl. This mixture was extracted with CH_2Cl_2 and the organic phase washed with water and dried with $MgSO_4$. Evaporation gave the amino compound as an oil. Yield: 77% (14.02 g); brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.55 Hz, 3 H), 2.18 (s, 6 H), 2.16−2.25 (m, 1 H), 2.38−2.48 (m, 1 H), 3.87 (q, *J* = 12.2 Hz, 2 H), 5.92 (s, 1 H), 7.16−7.29 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 23.7, 40.2 (2 C), 77.2, 114.0, 127.1, 128.3 (2 C), 128.9 (2 C), 137.8, 140.5.

The amino compound (46 mmol) was added to ice-cooled concd. H_2SO_4 (150 mL) over 15 minutes. The resulting mixture was stirred for another 40 minutes before it was slowly added to a slurry of crushed ice (500 mL) and HPF_6 (30 mL). The precipitate that formed was filtered and washed with cold H_2O, dissolved in CH_2Cl_2 and reprecipitated with 1 volume of Et_2O. After filtration and washing with Et_2O, the dithiolium salt was dried in a desiccator overnight. Yield: 87% (15.94 g); orange crystals. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.6 Hz, 3 H), δ = 3.09 (q, *J* = 7.6 Hz, 2 H), 4.23 (s, 2 H), 7.22−7.25 (m, 2 H), 7.33−7.37 (m, 3 H), 10.97 (s, 1 H) ppm.

The dithiolium salt (39 mmol) was dissolved in 200 mL CH_3CN; the flask was then sealed and purged with N_2. Et_3N (46 mmol) was added dropwise; an orange precipitate formed. The mixture was stirred for 10 minutes, and then the precipitate was filtered, washed with CH_3CN and EtOH and dried to give TTF **47**. Yield: 89% (8.67 g); orange crystals. R_f (hexane/CH_2Cl_2) = 0.23. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.73−0.79 (m, 6 H), 2.15−2.23 (m, 4 H), 3.96−3.99 (m, 4 H), 7.23−7.36 (m, 10 H) ppm. MS (MALDI-TOF): *m*/*z* (%) = 504.03 (100) [M^+]. $C_{24}H_{24}S_6$: calcd. C 57.10, H 4.79; found C 57.02, H 4.83.

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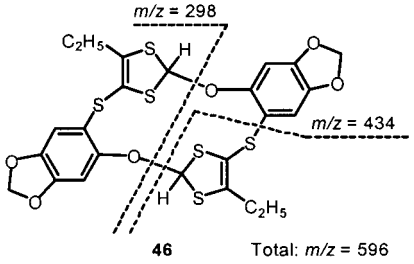
[8] The actual electrophile could have a structure different from **3**, although we believe this is less probable. In this redox reaction we believe that sulfuryl chloride is converted to the chlorides and sulfur dioxide, which is lost by evaporation during the reaction.

[9] Analysis of compound **26**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 6 H), 3.52 (s, 3 H), 3.53 (s, 3 H) ppm. MS (EI): *m*/*z* (%) = 445.72 (20) [M^+], 242.06 (100).

[10] Confirmed by ^{1}H NMR analysis.

[11] We found that the use of counterion PF_6^- is superior to BF_4^- for the deamination reaction.

[12] The reaction of **41** with triethylamine yielded a mixture of products according to the NMR spectrum, which could not be separated by chromatography. Direct inlet MS (EI) shows predominant peaks at *m*/*z* (%) = 298 (100), 181 (85), 434 (35) and 254 (40) for both the crude material and the products arising from chromatography. There is a small signal (1%) at *m*/*z* = 596 that corresponds to the corresponding TTF M^+ ion. However, if one assumes that a mixture of oligomeric products and a dimer **46** has been formed, the signal at *m*/*z* = 596 would be the molecular ion of the dimer, that at *m*/*z* = 434 would be a sesamol-1,3-dithiol-sesamol fragment and the mother ion (*m*/*z* = 298) would be a sesamol-1,3-dithiol fragment. This could explain the behaviour apparent from the chromatography, NMR spectra and mass spectra.



46 Total: *m*/*z* = 596

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