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Tetraformyltetrathiafulvalene (TFTTF) and Acetals, Precursors of Polyfunctionalized TTFs.

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Abstract : A short synthesis of 1,3-dithiol-2-thiones bearing two aldehyde functionalities, free and/or masked as diethylacetals is described. They are shown to be convenient precursors for synthesizing di- and tetraformyl-TTF. When submitted to four-fold nucleophilic attacks, the latter readily affords new substituted derivatives such as the bis-(pyridazino)-TTF 8, the tetrakis-(hydroxymethyl)-TTF 9 and the tetravinylic-TTF 10 whose π-donor ability has been characterized.

The discovery of the conducting properties of the charge transfer and cation radical salts of tetrathiafulvalene (TTF) has prompted numerous chemical modifications of this heterocycle in order to tailor the transport properties of the related organic metals.[1] Thus, for example, the tetramethyl derivative of the seleno analog (TMTSF) is the molecular constituent of the first organic superconductor,[2] while the bis-ethylenedithio derivative of TTF (BEDT-TTF) is the basic unit of a series of salts which, so far, achieved the highest superconducting transition temperatures for organic molecular solids.[3]

Despite several attempts of rationalization,[4] it is still very difficult to predict what is the requisite chemical structure of a π-donor to act as a precursor of organic conductor or superconductor: therefore, improvements of the physical properties (conductivity, magnetism...) in such materials still require systematic explorations which implies, at first, the design and synthesis of new π-donors. In that respect, any new contribution in the field of TTF chemistry appears to be useful and of current interest.[5]

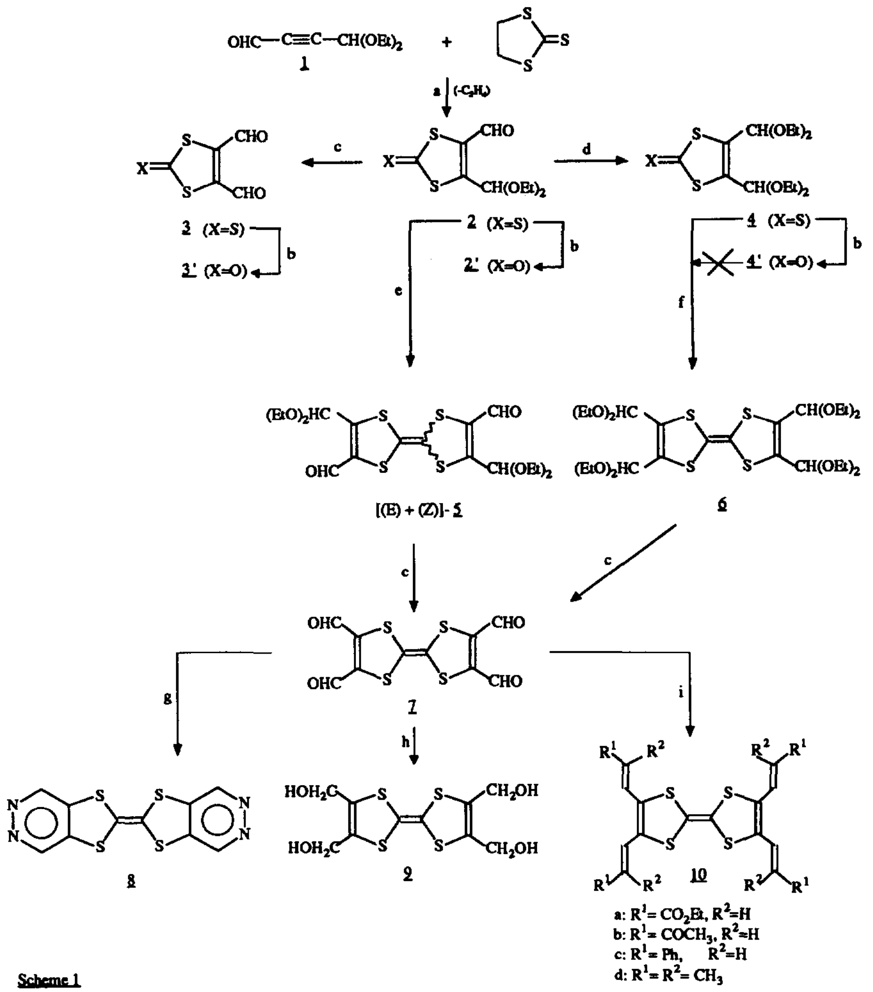
We reported earlier the synthesis and subsequent uses of tetraformyl-TTF (TFTTF) 7 and the corresponding diacetals 5,[6] as well as their extension to the Se series.[7] Because of their highly reactive aldehyde functional groups, such derivatives have been shown to act as good precursors of polyfunctionalized TTFs (or TSFs), and more recently, of giant and sulfur-rich TTFs held to be prone to drive novel structural organizations in the corresponding salts.[8] Therefore, we have decided to report on these useful starting materials of TTF derivatives.

Results and discussion

1- *Synthesis and structure of aldehyde-functionalized TTFs*

Our straightforward synthetic strategy of the target molecule 7, depicted in Scheme 1, involves in the key steps (e and f) the dimerization-desulfurization of 1,3-dithiol-2-thione derivatives bearing the aldehyde functionalities, possibly masked as an acetal.

The first step lies in the cycloaddition of an electrophilic alkyne onto ethylenetrithiocarbonate with ethylene evolution.[9] When starting from acetylenedicarbaldehyde (ADCA)[10,11] under neutral conditions (in refluxing dichloromethane or toluene), the formation of the expected dialdehyde 3 never occurs. On the contrary, although less electrophilic than ADCA, but much more thermally stable, the mono-diEt-acetal 1 [10,11] affords 2 by refluxing in xylene; the latter is isolated (60%) by recrystallization after the excess of ethylenetrithiocarbonate has been discarded by a prior sublimation of the crude product. Finally, when starting from the less electrophilic tetra-Et-diacetal of ADCA, no reaction occurs so that 4 cannot be prepared in this way .



Scheme 1

(a) Xylene, reflux; (b) $Hg(OAc)_2$, AcOH, $CHCl_3$; (c) HCO_2H, CH_2Cl_2; (d) $HC(OEt)_3$, EtOH, PTSA; (e) $Co_2(CO)_8$, toluene, reflux; (f) $P(OMe)_3$, 80°C; (g) N_2H_4, DMF; (h) $NaBH_4$, THF-MeOH; (i) $Ph_3P{=}CR^1R^2$.

Since 1,3-dithiol-2-thiones are usually convenient intermediates for the synthesis of TTFs, we have converted the aldehyde-acetal 2 into the free dialdehyde 3 as well as into the corresponding diacetal 4. The deketalization of 2 into 3 was cleanly performed (86% yield) by formolysis in dichloromethane. The acetalization of 2 into 4 (94% yield) proceeded under the usual conditions with triethylorthoformate-ethanol and *p*-toluenesulfonic acid (PTSA) as the catalyst. Also, the C=S (2) to C=O conversion (2', 94% yield) was accomplished by treatment with mercuric acetate in chloroform and acetic acid.[12] Note that no acetic acidolysis of the acetal group occurs under those conditions. Similarly, 3 and 4 were quantitavely converted into the corresponding C=O derivatives 3' and 4'.

The usual desulfurizing coupling by phosphines or phosphites[13] failed to give the corresponding TTF framework in the cases of 2 and 2'. This was successfully achieved using dicobaltoctacarbonyl instead.[14] Hence, a mixture of essentially equal amounts of the (Z) and (E) isomers of 5 was obtained in high yield (70%, based on 2).The latter were separated, at first by selective solubilisation of the (Z)-isomer in diethylether, then by chromatography on a SiO_2 column (CH_2Cl_2-pentane 9 :1). Note that no acid-mediated (Z)-(E) isomerization is observed, since slightly acidic chloroformic solutions are stable in contrast to solutions of TTFs substituted by electron donating groups.[15]

Assuming the (E)-isomer to present a better conjugation, their respective configuration was first established as follows, on the basis of the differences of the UV-vis. spectra : *i)* (E)-5, mp 172°C, λ_{max} 526 nm, $\varepsilon = 4800$ (CH_2Cl_2), and *ii)* (Z)-5 mp 130-2°C, λ_{max} 504 nm, $\varepsilon = 4250$ (CH_2Cl_2).

Note in addition that only (Z)-5 was able to afford macrocyclic derivatives as a result of its [2+2] cyclocondensation with diamino compounds such as ortho-phenylenediamine[16] or phosphodihydrazides.[17]

Finally, these assignments were fully supported by the crystal structure determination of (E)-5 by X-ray diffraction (Figure 1).[18] Suitable single-crystals of (E)-5 were obtained by slow hexane vapor diffusion onto a saturated $CHCl_3$ solution. The CHO groups and one branch of each acetal moiety ($C_5O_3C_8C_9$ or $C_{5'}O_{3'}C_{8'}C_{9'}$) lie in the TTF plane. Therefore, and since the angle at C_5 is smaller (sp^3 carbon, 105.8(3)°) than the one at C_4 (sp^2 atom, 123.4(3)°), a short non-bonded C-S...O contact occurs with an intermolecular S_2...O_3 distance of 2.692(3)Å (sum of S...O Van der Waals radii, 3.32 Å) and a C_1-S_2...O_3 angle of 154.2(1)°, strikingly similar to those reported recently[19] for such interactions. The resulting attracting character of these sulfur-oxygen close contacts might control the conformation of the molecule in the solid state.

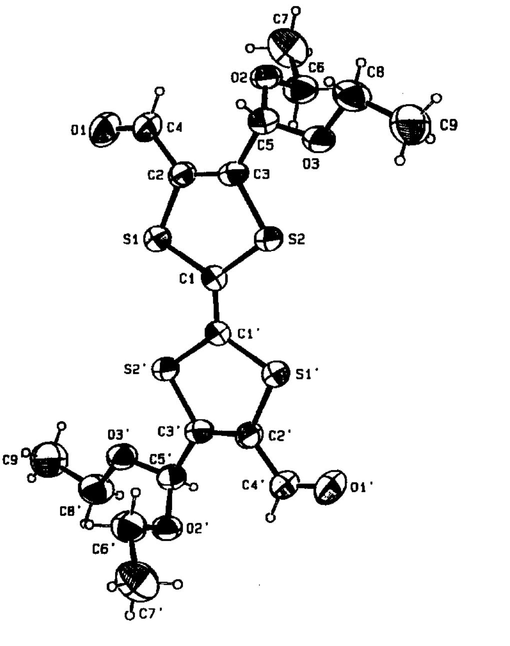


Figure 1. Molecular structure of (E)-5 in the crystal; ellipsoids at the 50% probability level.

While the phosphine or phosphite-mediated couplings of 2 do not proceed, it is found however that this one takes place readily after appropriate masking of the aldehyde functionality. Thus, the thione-diacetal 4 affords the tetraacetal 6 in 42% yield upon heating with trimethyl phosphite.

Note that no self-coupling of the oxygenated analogue 4' occurs by reaction with phosphites or phosphines.

Finally, TFTTF 7 is readily obtained by formolysis of the acetal functions of 5 ((Z)-5 and/or (E)-5) or 6, the best yields (95%) being achieved in dichloromethane.

2 - *Examples of tetrafunctionalizations of TTF from 7*

As shown in Scheme 1, tetrafunctionalized TTFs are readily reached *via* four-fold nucleophilic attacks of the four aldehydic functional groups of 7.

Reacting 7 with hydrazine hydrate in N,N-dimethylformamide (DMF) affords the bispyridazino-TTF 8 (80% yield). Note that a painful former synthesis of 8 was reported earlier.[20]

Likewise, the tetrakis-(hydroxymethyl)-TTF 9 is easily obtained (80% yield) by a simple $NaBH_4$ reduction (THF-MeOH solvent) of 7 . It is of interest to note that this synthesis of 9 avoids the puzzling reduction problems [21, 22] encountered with CO_2R, CO_2H and COCl derivatives of TTF, and improves another recent preparation.[23] It should also be noted that the availability of hydroxy groups at the outskirts of 9 makes it an attractive precursor of novel structural organizations for conducting salts. Indeed, such functionalities are expected to enhance intermolecular patterns of interactions of higher dimensionality, most notably by promoting (donor)-OH...anions hydrogen-bonded networks.[24,25]

A four-fold Wittig olefination allows the preparation of tetravinylic TTFs such as 10d, starting from TFTTF 7. Preliminary attempts to direct four-fold Wittig olefination of 7 were conducted on stabilized P-ylids such as $Ph_3P{=}CH{-}CO_2Et$ and $Ph_3P{=}CH{-}CO{-}CH_3$ in CH_2Cl_2; as the reaction proceeds, one observes the intermediate products of mono-, di- and tri- olefination which finally convert into the expected essentially all-trans derivatives 10a and 10b in good yields.

Starting from the fairly stabilized $Ph_3P{=}CHPh$, 10c (73% yield) is similarly produced. From the unstabilized P-ylid $Ph_3P{=}CH_2$, the required reaction does proceed, but tetravinyl-TTF (10 with $R^1{=}R^2{=}H$) cannot be isolated because of its high propensity to polymerize; fortunately, this is not the case for 10d, readily isolated (60% yield) after 7 is reacted with $Ph_3P{=}CMe_2$.[26]

Such Wittig olefinations of TFTTF were undertaken because the corresponding tetravinylic TTFs are assumed to be suitable to reach highly conducting materials since, when compared to TTF itself, one should expect that *i)* a better π-donor ability might result from the accumulation of the four conjugated electron-rich ethylenic linkages, *ii)* a larger spatial extension is prone to a better charge delocalization, resulting in the decreasing of the on-site Coulombic repulsion in the ionized states.

3- *π-donor ability*

The oxidation potential values Epa_1 and Epa_2 (Table 1) determined by cyclic voltammetry are found to be solvent dependent, a typical feature of the TTF series.[27] As expected, the most anodic potentials are found for the highly electrophilic tetraaldehyde 7, the less anodic one is for the tetraacetal 6 and the intermediate values for the (Z)- and (E)-isomers of 5.

Among the conversion products of TFTTF, the bis-pyridazino derivative 8 presents one irreversible oxidation only at a highly anodic potential. On the contrary, the tetraalcohol 9 appears to be a suitable precursor of conducting cation-radical salts because of its two reversible redox systems (Epa_1-Epc_1 = Epa_2-Epc_2 = 0.06V) and a π-donor ability comparable to TTF.

Table 1: Oxidation peak potentials (in Volts vs SCE) as determined by cyclic voltammetry: Pt electrode, 20°C, under nitrogen, $Bu^n_4NClO_4$ 0.1 $mol.l^{-1}$, scan rate 0.2 $V.s^{-1}$.

Compound	Epa_1	Epa_2	Solvent	Reversibility
5	0.78	0.98	DMF	b
	0.95	1.30	Ph-Cl	a
	0.84	1.24	1,1,2-TCE	a
6	0.62	1.05	Ph-Cl	a
7	1.04	1.15	DMF	c
	1.20	1.48	Ph-Cl	b
	1.00	1.30	CH_3CN	c
8	1.05		DMF	c
9	0.39	0.65	DMF	a
10a	0.86	1.14	CH_3CN	a
10b	0.78	0.95	CH_3CN	a
10c	0.42	0.67	CH_3CN	a
10d	0,33	0,65	CH_3CN	a

a: Reversible redox systems; b: Poorly reversible redox systems; c: Irreversible redox systems.

Thus, when microelectrolyses were achieved in DMF at a potential close to Epa_1, dark green turbidity was observed in the vicinity of the anode, in agreement with the formation of soluble cation radical salts. Further experiments will be necessary in order to determine the required solvent and supporting electrolyte (i.e the anion) to give good quality single crystals by electrocrystallization.

The values for 10 are strongly dependent on the R^1 and R^2 substituents: more anodic for 10a-c with electron withdrawing groups (R^1 = Ph , COMe and CO_2Et), and less anodic in the case of 10d having two releasing groups ($R^1 = R^2$ = Me).The latter is as good a π-donor as TTF itself when one considers the reversibility and the potential values of the two redox systems (to be compared to 0.38 V and 0.74 V for TTF). Therefore, we can assume this compound to be convenient precursor of conducting salts.

Thus 10d reacts instantaneously with tetracyanoquinodimethane (TCNQ) in methylene chloride to give a dark blue polycrystalline semiconductor $(10d)_1(TCNQ)_2$, with a r.t. conductivity of 0.5 $S.cm^{-1}$ (measured on a compressed pellet by the four probe technique); unfortunately, all attempts to get single crystals of this charge transfer salt were unsuccessful. Besides, good quality, albeit insulating, single crystals of $(10d).(PF_6)$ have been grown by anodic oxidation of 10d in THF, with Bu^n_4 PF_6 as the supporting electrolyte.[28]

Conclusion

This paper described the efficient preparation of powerful synthetic intermediates in TTF chemistry with free or masked aldehyde functionalities, including the 4,5-diformyl-1,3-dithiol-2-thiones 2-4 and their oxygenated analogous -2-ones 2'- 4', as well as the tetraformyl-TTFs 5-7.

Numerous synthetic opportunities are offered by their highly reactive aldehyde groups, examples of which were presented to illustrate the great variety of tetrafunctionalized TTFs (including good π-donors) which can be prepared from various nucleophilic reagents.

Acknowledgements

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Experimental section

High resolution mass spectra and ^1H and ^{13}C n.m.r. spectra were recorded by Drs P. Guénot and S. Sinbandhit (Centre de Mesures Physiques de l'Ouest, Rennes) who are thanked. The chemical shifts are expressed in p.p.m. towards tetramethylsilane as internal reference, and the coupling constants in Hz. Absorption wave numbers in IR are expressed in cm^{-1}. Elemental analyses have been run by the CNRS (Centre d'Analyses, Vernaison).

* 4,5-disubstituted-1,3-dithiol-2-thiones 2-4

- Aldehyde-acetal 2

A soln of 10.39 g (67mmol) of 1 and 8.30 g (61 mmol) of ethylenetrithiocarbonate in 50 ml of xylene is refluxed 6 hrs under nitrogen. After evaporation *in vacuo*, tars are removed by SiO_2 filtration (toluene) and the crude oil thus collected is submitted to a sublimation (oil bath 100°C, pressure 0.1 torr, cooling finger at -30°C) to remove the starting sulfur material. The residual unsublimated oil is recrystallized from hexane-CH_2Cl_2 and yields 9.56 g (60%) of 2 as thin yellow needles.

mp 42-43°C; IR (CCl_4) 1672; ^1H NMR (CCl_4) 1.28 (t, ^3J=7, 6H, CH_3), 3.72 (q, ^3J=7, 4H, CH_2), 5.87 (s, 1H, CH acetal), 9.86 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) 14.95 (CH_3), 62.18 (CH_2), 96.47 (CH), 141,48 (=C-CHO), 158,77 (=C-CH), 179,43 (CHO), 209,80 (C=S); $C_9H_{12}O_3S_3$, M^+ Calcd 263.994855, Found 263.995; Anal Calcd: C, 40.89; H, 4.57; O, 18.15; S, 36.39. Found: C, 40.78; H, 4.77; O,18.38; S, 36.33.

- Dialdehyde 3

A soln of 3.0 g (11.4 mmol) of 2 in 50 ml of CH_2Cl_2 is treated by 200 ml of formic acid (99%). After 1 h, the soln is diluted with 200 ml of water, and extracted with 5 x 100 ml of CH_2Cl_2. The organic layer is washed with aq. $NaHCO_3$ (0.3N), water and then dried over $CaCl_2$. After evaporation the crude orange powder is recrystallized in ethyl acetate to furnish 3 as big brownish spangles (1.86g, 86%).

mp 124-25.5°C; IR ($CHCl_3$) 1672; ^1H NMR (DMSO-d_6) 10.37 (s, CHO); ^{13}C NMR (acetone-d_6) 153.74 (=C-CHO), 181.23 (CHO), 206.12 (C=S); $C_5H_2S_3O_2$, M^+ Calcd 189.921696, Found 189.9215; Anal Calcd: C, 34.47; H 1.16. Found: C, 34.21; H, 1.19.

- Diacetal 4

A soln of 5g (18.9 mmol) of 2 in 100 ml of absolute ethanol is added dropwise to a soln containing 3.1g (20.8 mmol) of triethylorthoformate and 300 mg of PTSA in 20 ml of absolute ethanol. The reaction mixture is then refluxed for 2 hrs. After cooling, the solution is diluted with CH_2Cl_2 and washed with

Na_2CO_3 (1N), twice with water and then dried over $CaCl_2$. The solid obtained after evaporation is recrystallized in hexane to give 4 as yellow needles (5.99g, 94%).
mp 51,5-52,5°C; IR (CCl_4) 1133-1059; ^1H NMR (CCl_4) 1.24 (t, ^3J=7, 12H, CH_3), 3.67 (q, ^3J=7, 8H, CH_2), 5.62 (s, 2H, CH acetal); ^{13}C NMR ($CDCl_3$) 14.98 (CH_3), 62.07 (CH_2), 96.35 (CH), 142.24 (=C-CH), 212.95 (C=S); $C_{13}H_{22}O_4S_3$, M^+ Calcd 338.06802, Found 338.0671; Anal Calcd: C, 46.13; H, 6.55; O,18.91; S, 28.42. Found: C, 45.75; H, 6.60; O, 19.35; S, 28.20.

* 4,5-disubstituted-1,3-dithiol-2-ones 2'- 4'

A soln of 4.88g of mercuric acetate in 40 ml of glacial acetic acid is added to the thione 2 - 4 (6 mmol) in 30 ml of $CHCl_3$. The reaction mixture is stirred for 30 min, and the white precipitate discarded by centrifugation. The soln is washed with water, sodium hydrogenocarbonate (1N) and water, dried over $CaCl_2$ and finally evaporated.

-2' (94 % yield) pale yellow crystals from ligroin
mp 33-34°C; IR ($CHCl_3$) 1664, 1130-1058; ^1H NMR (CCl_4) 1.28 (t, ^3J=7, 6H, CH_3), 3.68 (q, ^3J=7, 4H, CH_2), 5.88 (s, 1H, CH acetal), 10.00 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) 14.95 (CH_3), 62.15 (CH_2), 96.79 (CH), 133.60 (=C-CHO), 151.14 (=C-CH), 180.82 (CHO), 187.81 (S_2C=O); $C_9H_{12}O_4S_2$, $M^{+\cdot}$ Calcd 248.01770, Found 248.0179; Anal Calcd: C, 43.53; H, 4.87; O, 25.77; S, 25.83. Found: C, 43.64; H, 4.92; O, 25.64; S, 25.24.

-3' (90% yield) pale yellow crystals from chloroform
mp 142-44°C; IR ($CDCl_3$) 1670; ^1H NMR ($CDCl_3$) 10.37 (s, CHO); $C_5H_2O_3S_2$, M^+ Calcd 173.94454, Found 173.9441; Anal Calcd: C, 34.47; H, 1.16. Found: C, 34.21; H, 1.19.

-4' (99% yield) white crystals from pentane
mp 26-29°C; IR (CCl_4) 1649; 1125-1058; ^1H NMR ($CDCl_3$) 1.21 (t, ^3J=7, 12H, CH_3), 3.63 (q, 3J=7, 8H, CH_2), 5.60 (s, 2H, CH acetal).

* Tetraformyl TTF and acetals

- Dialdehyde diacetal TTF E-(5) and (Z)- 5

A soln of 1.82 g (5.32 mmol) of $Co_2(CO)_8$ in 15 ml of toluene is slowly added under nitrogen to 2.0 g (7.58 mmol) of 2 in 5 ml of toluene. The temperature is raised to 40°C for 0.5 hr and then to 120°C for 1.5 hr. After cooling, the reaction mixture is filtered through a short silicagel column and eluted with CH_2Cl_2 to remove the black pyrophoric insoluble material. Essentially equal amounts of (E)-5 and (Z)-5 are collected by evaporation of the solvent (1.23g, 70%). These two isomers could be cleanly separated by a two steps procedure. The mixture is repeatedily diluted in small amounts of Et_2O and then filtrated on SiO_2 column (methylene chloride-pentane, 9:1 (V/V)). Crystals of (E)-5 available for X-Ray analysis have been obtained by slow diffusion of hexane vapours into a chloroformic solution of (E)-5.

- (E)-5, purple crystals
mp 172°C; IR (CH_2Cl_2) 1653, 1128-1056; ^1H NMR ($CDCl_3$) 1.25 (t, ^3J=7, 12H, CH_3), 3.75 (q, ^3J=7, 8H, CH_2), 5.83 (s, 2H, CH acetal), 10.05 (s, 2H, CHO); ^{13}C NMR ($CDCl_3$) 14.90 (CH_3), 61.85 (CH_2), 96.58 (CH acetal), 108.66 (=CS_2), 135.40 (=C-CHO), 155.00 (=C-CH), 180.09 (CHO); UV (CH_2Cl_2) λmax 526 nm(4800); $C_{18}H_{24}O_6S_4$, $M^{+\cdot}$ Calcd 464.045566, Found 464.0414; Anal Calcd: C, 46.53; H, 5.21; O, 20.66. Found: C, 46.74; H, 5.09; O, 20.04.

- (Z)-5, salmon red powder
mp 130-32°C; IR (CH_2Cl_2) 1653, 1129-1056; ^1H NMR ($CDCl_3$) sim. to 5-(E); ^{13}C NMR ($CDCl_3$) 14.98 (CH_3), 61.92 (CH_2), 96.63 (CH acetal), 108.62 (=CS_2), 135.89 (=C-CHO), 155.50 (=C-CH), 179.96 (CHO); UV (CH_2Cl_2) λmax 504 nm(4250); $C_{18}H_{24}O_6S_4$, $M^{+\cdot}$ Calcd. 464.045566, Tr. 464.0414.

- Tetraacetal TTF 6

A stirred soln of 400 mg (1.18 mmol) of 4 in 15 ml of freshly distilled trimethyphosphite is heated at 80°C for 3 hrs. After evaporation *in vacuo*, the crude solid is purified by SiO_2 column chromatography (CH_2Cl_2-pentane, 3:1 (V/V) then CH_2Cl_2). The orange powder obtained by evaporation is recrystallized in hexane to furnish 6 as thin orange needles (150 mg, 42%).
mp 136.5-37.5°C; IR (CCl_4) 1130-1000; ^1H NMR (CCl_4) 1.20 (t, ^3J=7, 24H, CH_3), 3.63 (q, ^3J=7, 16H, CH_2), 5.47 (s broad, 4H, CH acetal); ^{13}C NMR ($CDCl_3$) 15.05 (CH_3), 61.72 (CH_2), 96.72 (CH acetal), 107.95 (=CS_2), 132.96 (=C-CH);

$C_{26}H_{44}O_8S_4$, $M^{+\cdot}$ Calcd. 612.19189, Found 612.1903; Anal Calcd: C, 50.95; H, 7.24; O, 20.88; S, 20.93. Found: C, 51.17; H, 7.50; O, 20.00; S, 20.53.

- Tetraformyl TTF 7

A CH_2Cl_2 soln (15 ml) of [(E) + (Z)]-5 (520 mg, 1.12 mmol) is treated by 35 ml of pure formic acid; the initial purple colour of the solution rapidly turns deep blue. The reaction mixture is partially evaporated *in vacuo*, and the blue spangles thus produced are collected by filtration, and repeatedly washed with a CH_2Cl_2-Et_2O, 1:4 (V/V) mixture (336 mg, 95%).

mp 280°C (decomp.); IR (nujol) 1660; ^1H NMR (DMSO-d_6) 10.75 (s,CHO); ^{13}C NMR (DMSO-d_6) 108.00 (=CS_2), 148.89 (=C-CHO), 181.60 (CHO); $C_{10}H_4O_4S_4$, $M^{+\cdot}$ Calcd. 315.899246, Found 315.8992; Anal Calcd: C, 37.96; H, 1.27. Found: C, 38.08; H, 1.61.

* Tetrafunctionalized TTFs 8-10

- Bis-pyridazino-TTF 8

A soln of 7 (75 mg, 0.24 mmol) in 20 ml of DMF is treated by a 0.1 M soln of N_2H_4, H_2O in DMF until the initial blue color has turned red (5.5 ml). The reaction mixture is concentrated *in vacuo*, and the crude solution is stored overnight at -20°C. Yellow needles of 8 are then collected by filtration, and washed with Et_2O (58 mg, 80%).

mp 300°C (decomp.); IR (nujol) 1660; ^1H NMR (DMSO-d_6) 9.78 (s, CH); $C_{10}H_4N_4S_4$, $M^{+\cdot}$ Calcd 307.931884, Found 307.9316.

- Tetrakis-(hydroxymethyl)-TTF 9

Sodium borohydride (38 mg) is added portionwise into a stirred suspension of TFTTF 7 (158 mg, 0.5 mmol) in a mixture THF-MeOH 2:1 (V/V) at room temperature. After 2 hrs, the solvent is evaporated *in vacuo* and the residual solid is triturated in a hot water-MeOH 1:1 (V/V) soln. The tetraalcohol 9 is obtained after filtration and subsequent washings with MeOH and Et_2O, as an orange powder (130 mg, 80%).

mp 220°C (decomp.); IR (nujol) 3200; ^1H NMR (DMSO-d_6) 4.04 (d, ^3J = 5.5, CH_2), 5.28 (t, ^3J = 5.5, OH); ^{13}C NMR (DMSO-d_6) 56.54 (CH_2), 107.03 (=CS_2), 131.66(=C-CH_2OH); $C_{10}H_{12}O_4S_4$, $M^{+\cdot}$ Calcd 323.96184, Found 323.9622; Anal Calcd : C, 37.02; H, 3.73; O, 19.72 Found : C, 36.91; H, 3.81; O, 20.40.

- Tetraolefinated TTFs 10 a-b, from 7 and stabilized ylids

A soln of 126 mg (0.4 mmol) of TFTTF 7 in 100 ml of CH_2Cl_2 is treated at rt with the appropriate P-ylid (4.4 eq.). After 2 hrs stirring, the solvent is evaporated and the residual solid filtrated and washed with ethanol.

- 10a (92% yield) violet powder from CH_2Cl_2-hexane

mp 250°C; IR ($CDCl_3$) 1712; ^1H NMR ($CDCl_3$) 1.35 (t, ^3J = 7.5, CH_3), 4.33 (q, ^3J = 7.5, CH_2), 6.01 (d, ^3J= 15.5, CH) 7.79 (d, ^3J= 15.5, CH); $C_{26}H_{28}O_8S_4$, $M^{+\cdot}$ Calcd 596.066692, Found 596.0669.

- 10b (91% yield) dark blue powder from CH_2Cl_2

mp > 260° C; $C_{22}H_{20}O_4S_4$, M^+ Calcd 476.024439, Found 476.0238.

- Tetra-(styrenyl)-TTF 10c

A 0.6 N soln (5 ml) of $(Me_3Si)_2NLi$ in THF, is added under nitrogen to a stirred soln of 1.56 g (4 mmol) of Ph_3PCH_2Ph,Cl in 20 ml of THF. After 1 hr, 158 mg (0.5mmol) of solid TFTTF is added. The solvent is evaporated and the crude solid is filtrated off and rinsed with Et_2O to finally afford 222 mg of a violet powder (73%). An analytical sample gives rise to violet needles by recrystallisation in THF.

mp 152-4°C; ^1H NMR (HMPT) 6.65 (d, ^3J = 16, CH); 7.20 (d, ^3J = 16, CH), 7.43 (m, arom ^1H); $C_{38}H_{24}S_4$, $(M\text{-}4H)^+$ Calcd 608.076081, Found 608.0728.

- Tetrakis (2'-methyl-1'-propenyl)-TTF 10d

A soln of 2.16g (5mmol) of $Ph_3P\text{-}CH(CH_3)_2$, I in 15 ml of THF at 0°C under nitrogen, is treated by 6.7 ml of a 0.6 N soln of $(Me_3Si)_2NLi$ in THF. The temperature of the bath is raised to 40°C for 30 min and then cooled to 0°C. The TFTTF 7 (158 mg) is then introduced in the dry state. After the reaction mixture is allowed to warm up to r.t., the solvent is evaporated and the crude solid is purified by SiO_2 column chromatography (pentane-Et_2O 8:2 (V/V)); 10d is isolated as orange needles after recrystallisation from Et_2O-EtOH (126 mg, 60%).

mp 114-5°C; ^1H NMR ($CDCl_3$) 1.83 (s, CH_3), 5.72 (m,CH); $C_{22}H_{28}S_4$, $M^{+\cdot}$ Calcd 420.107379, Found 420.1067.

- Charge transfer salt $(\underline{10}d)_1(TCNQ)_2$

A dark blue polycrystalline powder is obtained by mixing saturated CH_2Cl_2 solutions of $\underline{10}$d and TCNQ. The complex obtained is then filtrated and then recrystallized from THF (85% yield).

mp 180-85°C; Anal Cald for ($\underline{10}$d) $(TCNQ)_2$, $C_{46}H_{36}N_8S_4$: C, 66.64; H, 4.38; N,13.52; S, 15.47. Found: C, 66.47; H, 4.31; N,13.58; S, 15.34.

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bond distances and angles, observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW. Any request should be accompanied by the full litterature citation for this communication.

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