Trimethyltetrathiafulvalene Bearing an *N*-Methylpyridinium Substituent: Synthesis, Crystal Structures, and Charge Transfer Properties

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The synthesis of 4,4′,5-trimethyl-5′-(4-pyridyl)tetrathiafulvalene (**3**), has been accomplished by reaction of the stannylated precursor **2** with 4-bromopyridine. Alkylation of **3** affords the *N*-methylpyridinium salt **4** which displays intramolecular charge transfer properties in solution as deduced from UV/Vis spectra, cyclic voltammetric data, and semiempirical quantum mechanical calculations. The X-ray crystal structures of neutral molecule **3**, the salt ($\mathbf{4}^+$)I$^-$ and the charge transfer salt $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$ are reported. The positive charge in ($\mathbf{4}^+$)I$^-$ and $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$ is predominantly confined on the pyridinium ring. The structure of $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$ comprises segregated stacks of cations and TCNQ radical anions, with the anions overlapping in the usual ring-over-bond fashion. This salt is a semiconductor ($\sigma_{rt} = 10^{-2}$ S cm^{-1}).

Introduction

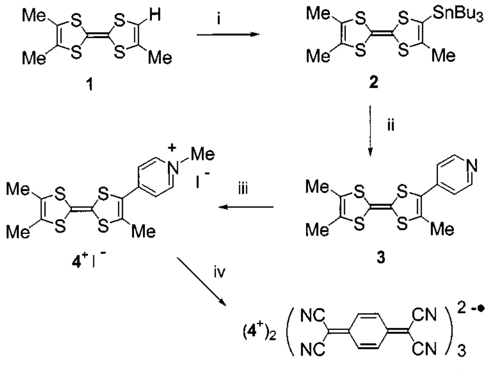
New tetrathiafulvalene (TTF) derivatives continue to be extensively studied as π-electron donors for the preparation of intermolecular charge-transfer complexes and radical ion salts which possess unusual electronic properties, notably high electrical conductivity in the solid state.[1] The study of *intra*molecular charge-transfer (ICT) in TTF-based compounds is also a topic of considerable current interest, and several TTF−spacer−A diads (A = electron acceptor moiety) have been reported recently.[2] Typical acceptor groups in this context are quinones,[3] 9,9,10,10-tetracyanoanthraquinodimethane,[4] C_{60},[5] pyridinium,[6] or bipyridinium cations,[7] and the extent of ICT has been studied as a function of the steric and electronic properties of the donor and acceptor moieties and the spacer unit.

The aim of the present work was to explore the consequence of both intramolecular and intermolecular charge transfer on the structural and electronic properties of a conjugated TTF−acceptor system. To this end we have studied the synthesis and properties of the new TTF−A diad molecule ($\mathbf{4}^+$)I$^-$. To facilitate ICT we used trimethyl-TTF as the donor moiety,[8] directly attached to the very strongly electron-accepting *N*-methylpyridinium cation.[9] We describe the crystal structures of the precursor compound **3**, salt ($\mathbf{4}^+$)I$^-$ and a charge-transfer salt formed between $\mathbf{4}^+$ and TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) of stoichiometry $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$.

Results and Discussion

Synthesis

Lithiation of trimethyl-TTF (**1**)[8] followed by reaction with tributylstannyl chloride[10] gave the stannylated derivative **2** (90% yield) which reacted with 4-bromopyridine to afford compound **3** as orange crystals in 63% yield (Scheme 1). *N*-Methylation to produce the pyridinium salt ($\mathbf{4}^+$)I$^-$ was achieved by reaction with an excess of methyl iodide. The charge-transfer salt $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$ was obtained by slow cooling of equimolar quantities of ($\mathbf{4}^+$)I$^-$ and TCNQ in acetonitrile/methanol.



Scheme 1. Synthesis of compounds **3**, ($\mathbf{4}^+$)I$^-$, and $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\bullet}$: (i) LDA, THF, −78 °C, then $\mathrm{Bu_3SnCl}$, −78 to 20 °C; (ii) 4-bromopyridine hydrochloride, $\mathrm{NaHCO_3}$, PhMe, $\mathrm{Pd(PPh_3)_4}$, reflux; (iii) MeI, acetone, reflux; (iv) TCNQ, MeCN/MeOH, reflux

UV/Vis Spectra and Redox Properties

A freshly-prepared solution of the salt ($\mathbf{4}^+$)I$^-$ shows a broad absorption band in acetonitrile at λ_{max} = 573 nm. This band is red-shifted by ca. 70 nm in iodobenzene and can be attributed to an ICT transition since its intensity does not depend on concentration. Solvatochromic behavi-

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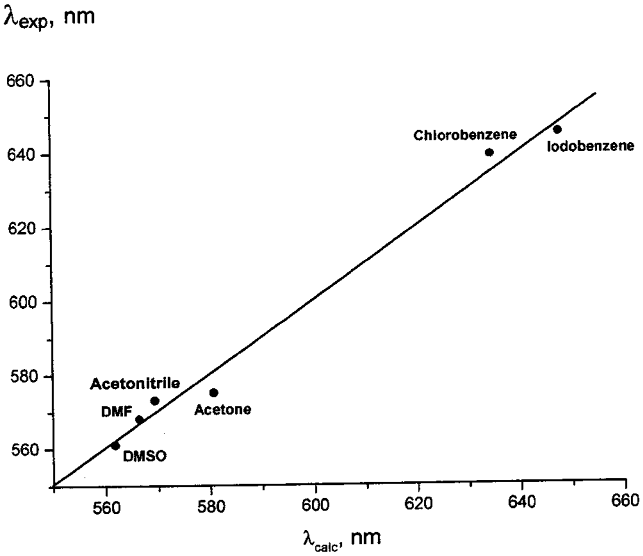

Figure 1. Solvatochromism in compound ($\mathbf{4}^+$)I^-; experimental and calculated data in various solvents as shown:

$$\nu = \nu_{vac} - A*\left(\frac{n^2-1}{n^2+2}\right) - B*\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)$$

A, B < 0, correlation coefficient (λ_{exp}, λ_{calc}) = 0.994

our of ($\mathbf{4}^+$)I^- was studied in more detail (Figure 1) and an excellent correlation with the theoretical prediction[11] was found. The observed solvatochromism is negative (i.e. a red shift with decreasing solvent polarity) and the dipole moment should be larger in the ground state than in the excited state. This conclusion is fully supported by semiempirical quantum mechanical calculations (AM1, Hyperchem, version 5.0). Thus, the calculated ground-state dipole moment is 14.6 D, whereas the excited-state dipole moment is only 2.8 D. The same ICT transition and solvatochromic behaviour was observed for the corresponding hexafluorophosphate salt ($\mathbf{4}^+$)PF_6^-.

Solutions of ($\mathbf{4}^+$)I^- are stable in the absence of light, but irradiation with unfiltered visible light under an inert atmosphere leads to a gradual disappearance of the ICT band with isosbestic points clearly seen at 370 and 450 nm in DMSO (Figure 2). The same behaviour was observed in acetonitrile and dichloromethane solutions. The disappearance of the ICT band was accompanied by the emergence of an EPR signal (g = 2.009) which became weak and broad within a few minutes. This signal is assigned to the decomposition products of an initially formed TTF$^{+\cdot}$−Py$^{\cdot}$ species. These data are similar to that observed recently in a TTF−thioindigo conjugate.[12]

Cyclic voltammetric (CV) data confirm the electron-withdrawing effect of the conjugated pyridinium cation. Compound **3** displays two, reversible, one-electron oxidation waves in acetonitrile solution at $E_1^{1/2}$ = 0.31 and $E_2^{1/2}$ = 0.70 V (vs. Ag/AgCl) which are typical of a trimethyl-TTF derivative (cf. **1**: 0.29 and 0.69 V).[8] The corresponding oxidation waves for ($\mathbf{4}^+$)PF_6^- were positively shifted by ca. 100 mV to $E_1^{1/2}$ = 0.40 and $E_2^{1/2}$ = 0.81 V. (The waves for the iodide salt were broadened and ill-defined, possibly due to accompanying oxidation of the iodide anion, as suggested previously.)[6c] A similar positive shift has been reported recently by Cassoux et al. for the conjugated TTF−π−A system 4-(tetrathiafulvalen-4-ylethenyl)pyridinium,[6c] whereas nonconjugated (noninteracting) TTF−σ-pyridinium salts do not show this shift.[6b] Strong solvation effects, as discussed previously,[6b] make the electrochemical reduction potentials of the pyridinium moiety an inappropriate measure of ICT. In spite of the observed positive shift of the oxidation potential, we suggest that the HOMO of TTF does not contribute significantly to the conjugation in $\mathbf{4}^+$. Indeed, the LUMO of $\mathbf{4}^+$ involves primarily the pyridinium moiety, the C−S and external double bond of TTF. The calculated LUMO energy is −5.07 eV, which means that the pyridinium unit retains its strong electron accepting properties (cf. −5.33 eV for a nonconjugated analogue).[6b]

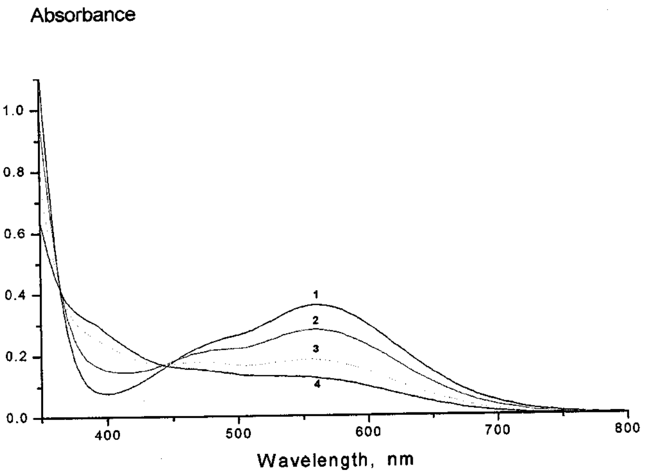

Figure 2. Absorption spectra of ($\mathbf{4}^+$)I^- in DMSO: 1) freshly-prepared; 2), 3), and 4) after 2, 5, and 9 min irradiation with visible light under argon

A comparison of the geometrical features of optimized structures (AM1) for **1**, **3**, and $\mathbf{4}^+$ is instructive. The length of the central double bond of the TTF moiety varies between 1.351 (**1**), 1.352 (**3**), and 1.356 A ($\mathbf{4}^+$). The dihedral angle between the TTF and pyridine moieties decreases from 42.6° to 18.2° and the bond linking these moieties becomes shorter, from 1.449 to 1.421 A, upon methylation. Correspondingly, the adjacent peripheral TTF double bond is longer by 0.022 A and the single C−S bond is shorter by 0.040 A in $\mathbf{4}^+$ compared to **3**. The differences in other bond lengths in **1**, **3**, and $\mathbf{4}^+$ are very small. These results are in good agreement with the experimentally found X-ray geometries (see below).

Crystals of the charge transfer salt ($\mathbf{4}^+$)$_2$(TCNQ$_3$)$^{2-\cdot}$ are semiconducting, σ_{rt} = 10^{-2} Scm^{-1} (four-probe measurement). This value is typical of a mixed-valence TCNQ salt with a nonuniform TCNQ stack.[13]

X-ray Crystal Structures

The structures of **3**, ($\mathbf{4}^+$)I^- and the charge transfer salt ($\mathbf{4}^+$)$_2$(TCNQ$_3$)$^{2-\cdot}$ were determined by single-crystal X-ray

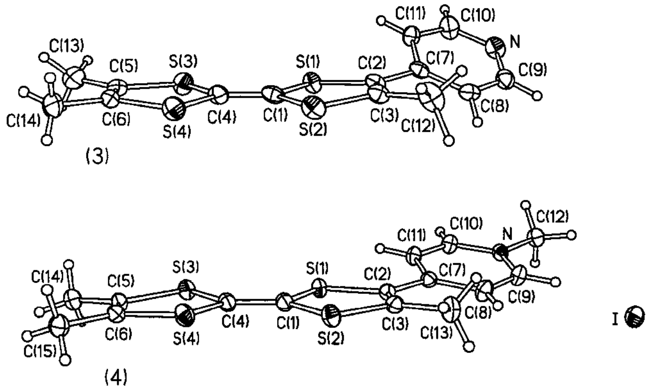

Figure 3. Molecular structures of **3** and (**4**$^+$)I$^-$, showing 50% thermal ellipsoids

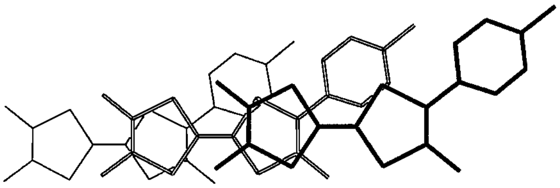

Figure 4. Overlap of cations (**4**$^+$) in a stack in the structure of (**4**$^+$)I$^-$

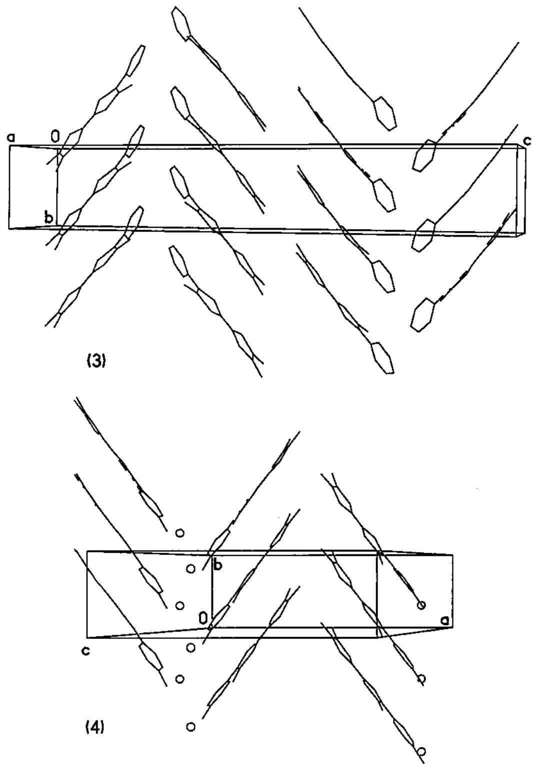

Figure 5. Crystal packing of **3** and (**4**$^+$)I$^-$

diffraction. In the neutral molecule of **3** (Figure 3) the TTF moiety is folded along the S(1)···S(2) and S(3)···S(4) vectors by 13.0° and 2.8° in a boat fashion. In the cation of (**4**$^+$)I$^-$ the folding is only 2.9° and 2.8°, respectively (Figure 3). Both structures contain similar stair-like stacks of translationally equivalent molecules (cations) with a longitudinal slip between adjacent species (Figure 4) and a uniform interplanar separation, which is reduced from 3.78 A in **3** to 3.42 A in (**4**$^+$)I$^-$ (as measured between mean TTF planes). However, the stacks are combined in a different way (Figure 5).

The structure of (**4**$^+$)$_2$(TCNQ$_3$)$^{2-\cdot}$ contains segregated stacks of cations and TCNQ radical anions (Figure 6 and Figure 7). Its asymmetric unit (= half the formula unit) comprises one donor and one TCNQ (A) in general positions and a half of another TCNQ (B), which is located at a crystallographic inversion centre. The bond lengths in the TCNQ moieties correspond[14] to charges of −0.6 (A) and −0.7 (B), consistent with the cation's charge of +1. The anions in the stack (···AABAAB···) overlap in a usual ring-over-bond manner. Anion B is strictly planar, while the cyano groups of A are tilted into the A−A gap (away from B). The interplanar separations (calculated ignoring the above-mentioned CN groups) alternate between 3.25 (A−A) and 3.08 A (A−B), making a strongly dimerised stack. In the cationic stack, the adjacent cations are antiparallel [while in **3** and (**4**$^+$)I$^-$ they are parallel], the interplanar separations alternating between 3.45 and 3.57 A.

Positive charge on a TTF moiety is usually revealed by a lengthening of the central C=C bond and shortening of the adjacent C−S bonds.[15] Both effects were observed in (**4**$^+$)I$^-$ and (**4**$^+$)$_2$(TCNQ$_3$)$^{2-\cdot}$ compared to **3**, only on the limits of the experimental precision (see Table 1) and may

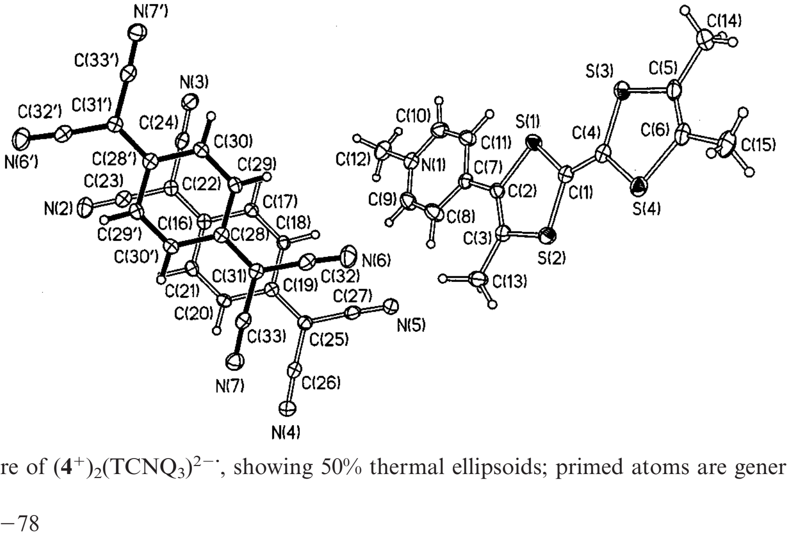

Figure 6. Molecular structure of (**4**$^+$)$_2$(TCNQ$_3$)$^{2-\cdot}$, showing 50% thermal ellipsoids; primed atoms are generated by an inversion centre

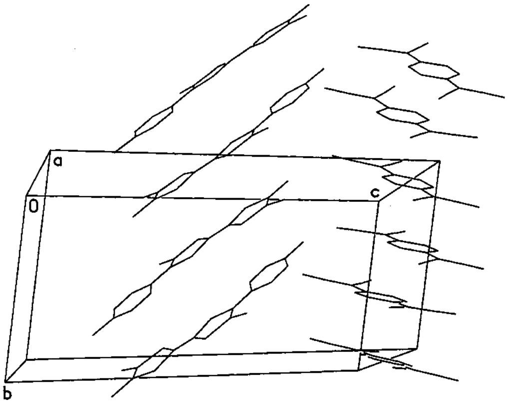

Figure 7. Crystal packing of $(\mathbf{4}^{+})_2(\mathrm{TCNQ}_3)^{2-\cdot}$

Table 1. Selected bond lengths [Å]

	3	$(\mathbf{4}^{+})\mathrm{I}^{-}$	$(\mathbf{4}^{+})_2(\mathrm{TCNQ}_3)^{2-\cdot}$
C1−S1	1.763(3)	1.756(3)	1.756(2)
C1−S2	1.765(3)	1.759(3)	1.756(2)
C4−S3	1.763(3)	1.755(3)	1.754(2)
C4−S4	1.760(3)	1.763(3)	1.762(2)
S1−C2	1.773(3)	1.782(3)	1.777(2)
S2−C3	1.753(3)	1.748(3)	1.746(2)
S3−C5	1.764(4)	1.766(3)	1.765(2)
S4−C6	1.763(4)	1.767(3)	1.773(2)
C1−C4	1.333(5)	1.349(4)	1.347(3)

indicate, at most, a 0.1−0.15 *e* charge.[15] Thus the cation's charge is basically confined to the pyridinium ring. However, the torsion angle between this ring and the TTF is reduced from 34° in **3** to 15° in $(\mathbf{4}^{+})\mathrm{I}^{-}$ and 5° in $(\mathbf{4}^{+})_2(\mathrm{TCNQ}_3)^{2-\cdot}$.

A relative shortening of the S(2)−C(3) and lengthening of the S(1)−C(2) bonds in all three structures is similar to that observed earlier in carbamoyl, thiocarbamoyl, and ester derivatives of TTF and results from the electron-withdrawing effect of these substituents.[16] As expected, this difference is larger (0.03 A) in the structures containing the cations $\mathbf{4}^{+}$, which possess the strongly electron-withdrawing *N*-methylpyridinium group, than for neutral pyridine system **3** (0.02 A).

Conclusion

This work describes a new D−π−A system comprising directly linked strong electron-donating and -accepting trimethyl-TTF and pyridinium moieties, respectively. Intramolecular charge transfer in solution is manifested in the absorption spectra and cyclic voltammetric data, and in the solid state by X-ray crystallographic analysis of $(\mathbf{4}^{+})\mathrm{I}^{-}$ and $(\mathbf{4}^{+})_2(\mathrm{TCNQ}_3)^{2-\cdot}$. Only a few TTF−spacer−A compounds have been structurally characterized and the latter complex is particularly interesting as it is a rare example of a TTF system which displays both intra- and inter-molecular charge-transfer properties. It is interesting that in the reaction of $(\mathbf{4}^{+})\mathrm{I}^{-}$ with TCNQ the TTF moiety plays little (or no) part in the redox reaction; rather, it is the iodide ion which reduces TCNQ. This study should stimulate further work on specifically functionalized TTF derivatives as components of charge-transfer materials with interesting optoelectronic properties.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were obtained with Oxford 200, Varian Unity 300, and Varian VXR 400S spectrometers operating at 199.992 (^{1}H) and 50.293 (^{13}C), 299.908 (^{1}H) and 75.420 (^{13}C), and 400.0 (^{1}H) and 100.6 (^{13}C) MHz, respectively. − Mass spectra were recorded with a Micromass Autospec spectrometer operating at 70 eV. − Elemental analyses were obtained with an Exeter Analytical Inc. CE-440 Elemental Analyzer. − Melting points were obtained with a Philip Harris melting point apparatus and are uncorrected. − All reagents were of commercial quality; solvents were dried using standard procedures. − All reactions were performed under argon in pre-dried glassware. − Cyclic voltammetric data were measured with *iR* compensation using a BAS 50 electrochemical analyser. The experiments were carried out with 5 mL of a ca. 10^{-4} M solution of the compound in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte, at scan rate 100 mV s^{-1}. The electrodes were platinum wire and data are reported versus Ag/AgCl.

4,4′,5-Trimethyl-5′-(tributylstannyl)tetrathiafulvalene (2): To a stirred solution of **1** (1.0 g, 4 mmol) in dry THF (100 mL) at −78 °C under argon was added lithium diisopropylamide (1.5 M in cyclohexane, 3.0 mL, 4.4 mmol) and stirring continued for 1.5 h. Tributylstannyl chloride (1.15 mL, 4.4 mmol) was added, the mixture stirred for a further 1 h at −78 °C and then allowed to warm to room temperature for about 12 h. The solvent was evaporated, water was added (100 mL) and the mixture extracted with dichloromethane (3 × 75 mL). The combined organic extracts were washed with water (2 × 75 mL), dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the residue (silica) eluting with hexane/dichloromethane (1:4, v/v) afforded compound **2** as an orange oil (1.95 g, 90%). − MS (EI); *m/z* (%): 534 [M$^+$] (100). − ^{1}H NMR ($CDCl_3$): δ = 2.04 (3 H, s), 1.92 (6 H, s), 1.53 (6 H, m), 1.34 (6 H, m), 1.09 (6 H, t, *J* 8.4), 0.93 (9 H, t, *J* 7.5). − ^{13}C NMR ($CDCl_3$): δ = 133.8, 128.2, 127.8, 126.3, 125.5, 122.8, 115.1, 105.0, 28.8, 27.2, 18.3, 13.7, 13.6, 13.5, 11.2. − $C_{21}H_{36}S_4Sn$ (535.5): calcd. C 47.1, H 6.8; found C 46.9, H 7.0.

4,4′,5-Trimethyl-5′-(4-pyridyl)tetrathiafulvalene (3): To a solution of 4-bromopyridine hydrochloride (200 mg, 1.03 mmol) in toluene (20 mL) was added sodium hydrogen carbonate (1 M, aqueous) until carbon dioxide evolution ceased. The mixture was washed with water (3 × 25 mL). The organic phase was dried ($MgSO_4$) and the mixture concentrated to ca. 5 mL. This solution was added to a solution of compound **2** (500 mg, 0.93 mmol) in dry toluene (25 mL) and the mixture degassed with argon. Tetrakis(triphenylphosphane)palladium(0) (54 mg, 5 mol-%) was added and the mixture stirred at reflux for 24 h. After evaporation of the solvent, the residue was chromatographed (silica) eluting with ethyl acetate to afford compound **3** as an orange solid (190 mg, 63%), m.p. 123 °C (from acetonitrile). − MS (EI); *m/z* (%): 323 [M$^+$] (100). − ^{1}H NMR ($CDCl_3$): δ = 8.62 (2 H, dd, J_1 = 4.3, J_2 = 1.8), 7.25 (2 H, dd, J_1 = 4.3, J_2 = 1.8), 2.10 (3 H, s), 1.90 (6 H, s) − ^{13}C NMR ($CDCl_3$): δ = 150.0, 140.2, 131.9, 131.7, 128.4, 128.2, 122.8, 110.3, 104.8, 15.1, 13.6. − $C_{14}H_{13}NS_4$ (323.5): calcd. C 52.0, H 4.1, N

Table 2. Crystal data and experimental details

Compound	**3**	$(\mathbf{4}^+)\mathrm{I}^-$	$(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\cdot}$
Empirical formula	$C_{14}H_{13}NS_4$	$C_{15}H_{16}NS_4{}^+I^-$	$(C_{15}H_{16}NS_4)_2(C_{12}H_4N_4)_3$
Molecular mass	323.49	465.43	1289.63
T [K]	153	123	123
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	7.2065(5)	19.471(3)	8.135(1)
b [Å]	5.9169(4)	5.877(1)	9.705(1)
c [Å]	35.263(2)	17.141(2)	19.995(1)
α [°]	90	90	94.98(1)
β [°]	94.010(3)	116.05(1)	92.18(1)
γ [°]	90	90	108.03(1)
V [Å^3]	1499.9(2)	1762.2(5)	1491.9(3)
Z	4	4	1
D_x [g cm^{-3}]	1.433	1.754	1.435
μ(Mo-K_α) [mm^{-1}]	0.62	2.28	0.36
Crystal size [mm]	0.55×0.14×0.03	0.7×0.35×0.04	0.50×0.13×0.05
Max. 2θ [°]	50	58	58
Reflections collected	7632	8600	18658
Unique reflections	2563	4130	7780
R_{int} before/after abs. corr.	0.097/0.085	0.112/0.039	0.042/0.038
Transmission max/min	0.9844/0.7969	0.9106/0.2521	0.9838/0.8482
Reflections with $F^2 > 2\sigma(F^2)$	2117	3979	5430
Refined parameters	224	219	485
R [$F^2 > 2\sigma(F^2)$]	0.045	0.023	0.039
wR (F^2), all data	0.094	0.057	0.113
Residual max/min $\Delta\rho$ [e Å^{-3}]	0.32/−0.33	1.18/−0.55	0.41/−0.32

4.3; found C 52.1, H 4.0, N 4.2. − A crystal suitable for X-ray analysis was grown from acetonitrile.

***N*-Methyl-4-(4,4′,5-trimethyltetrathiafulvalen-5′-yl)pyridinium Iodide and Hexafluorophosphate Salts (4):** To a stirred solution of compound **3** (75 mg, 0.23 mmol) in dry acetone (5 mL) was added methyl iodide (1 mL, excess) and the mixture refluxed for 4 h. During this time, the solution darkened considerably and a precipitate formed. After cooling, the solid was collected by filtration, and washed sequentially with cold acetone (5 mL) and then with diethyl ether (30 mL). The salt $(\mathbf{4}^+)\mathrm{I}^-$ was obtained as a dark blue solid (95 mg, 88%), m.p. > 250 °C (from methanol). − ^{1}H NMR ([D$_6$]DMSO): δ = 8.93 (2 H, d, J = 6.8), 8.09 (2 H, d, J = 6.8), 4.30 (3 H, s), 2.28 (3 H, s), 1.98 (6 H, s). − $C_{15}H_{16}INS_4$ (465.5): calcd. C 38.7, H 3.5, N, 3.0; found C 38.4, H 3.4, N 2.9. − A crystal suitable for X-ray analysis was grown from methanol. The corresponding hexafluorophosphate salt $(\mathbf{4}^+)\mathrm{PF}_6{}^-$ was prepared as a black solid by cooling a hot aqueous solution of $(\mathbf{4}^+)\mathrm{I}^-$ and potassium hexafluorophosphate. − $C_{15}H_{16}F_6NPS_4$ (438.5): calcd. C 37.3, H 3.3, N 2.9; found C 37.4, H 3.5, N 2.8.

***N*-Methyl-4-(4,4′,5-trimethyltetrathiafulvalen-5′-yl)pyridinium Tetracyanoquinodimethanide Salt [$(\mathbf{4}^+)_2(\mathbf{TCNQ}_3)^{2-\cdot}$]:** A solution of salt $(\mathbf{4}^+)\mathrm{I}^-$ (40 mg, 0.086 mmol) in warm dry methanol (3 mL) was added to a solution of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (17.5 mg, 0.086 mmol) in warm dry acetonitrile (10 mL) and the mixture heated at reflux for 5 min. After cooling and partial evaporation of the solvent, the solid which formed was collected by filtration and washed sequentially with cold acetonitrile (2 mL) and diethyl ether (10 mL). Compound $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\cdot}$ was obtained as a blue-black solid (25 mg, 68%) containing a crystal suitable for X-ray analysis. − $C_{66}H_{44}N_{14}S_8$ (i.e. 2:3 stoichiometry): calcd. C 61.5, H 3.4, N, 15.2; found C 61.2, H 3.3, N 15.3.

X-ray Diffraction Experiments: Bruker SMART 1 K CCD area detector, graphite-monochromated Mo-K_α radiation (λ =0.71073 Å), Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. 4 sets of ω (0.3°) scans, each set at different φ and 2θ angles, nominally covered over a hemisphere of reciprocal space. Absorption corrections by numerical integration based on face-indexing were applied. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXL97 programs (G. M. Sheldrick, University of Göttingen, **1997**). The crystal of $(\mathbf{4}^+)\mathrm{I}^-$ was a merohedral twin; twinning law $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = -\mathbf{c}$ [component contributions 0.6415 and 0.3585(7)] gives an orthorhombic pseudo-cell of a = 34.984, b = 5.877, c = 17.141 Å. Crystal data and experimental parameters are summarised in Table 2; full structural information in CIF format (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142182, -142183, and -142184 for **3**, $(\mathbf{4}^+)\mathrm{I}^-$, and $(\mathbf{4}^+)_2(\mathrm{TCNQ}_3)^{2-\cdot}$, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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