PERKIN 2

Electron acceptors of the fluorene series. Part 13.[1] 9-(5-Nitrofuran-2-ylidene)- and 9-(5-nitro-2-thienylidene)-2,4,5,7-tetranitrofluorenes: novel π-extended electron acceptors. Synthesis, cyclic voltammetry and X-ray crystal structures for the acceptor and its 4,5-dimethyltetrathiafulvalene complex, and a theoretical study †

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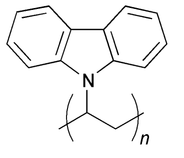
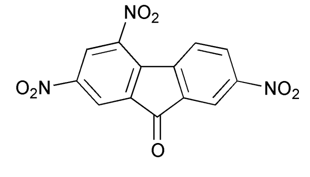
Two novel polynitrofluorene acceptors π-extended with 5-nitrofuran and 5-nitrothiophene moieties (**2** and **3**), have been synthesised. Cyclic voltammetry experiments show single electron reduction peaks at *ca.* −0.66–0.67 V (*vs.* Fc/Fc^+); however, this process (probably due to substantial changes in geometry of reduced species) is electrochemically irreversible and re-oxidation of the derived radical anions is observed at +0.05 and −0.04 V, for **2** and **3**, respectively. Electronic absorption spectroscopy confirms charge transfer complexation of the studied acceptor with 4,5-dimethyltetrathiafulvalene (Me_2TTF) in solution. The X-ray crystal structure of the 1 : 1 charge transfer complex (CTC) of acceptor **2** with Me_2TTF shows mixed A · · · D · · · A · · · D stacking, and its comparison with the structure of the acceptor itself indicates a neutral ground state of this CTC. Theoretical HF/6-31G(d) calculations for the acceptor **2** and its radical anion and dianion states are in agreement with this conclusion. Intramolecular hydrogen bonding in **2** between the oxygen of the furan ring and C(8)-H hydrogen of the fluorene moiety is observed in both solution (^1H NMR) and solid state (X-ray) and also supported by theoretical calculations

Introduction

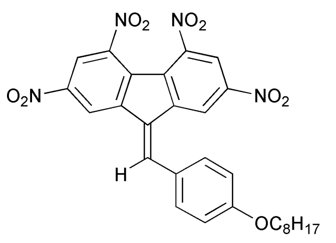
Polynitrofluorene derivatives are widely known electron acceptors which readily form charge transfer complexes (CTCs) with electron donors. Since the introduction of the CTC of poly-*N*-vinylcarbazole (PVK) and 2,4,7-trinitrofluoren-9-one (TNF) in the IBM Copier 1 series in 1970,[2] electron acceptors of the fluorene series have attracted tremendous interest as excellent sensitisers of the photoconductivity of carbazole-containing and related polymeric semiconductors[3,4] and a wide range of fluorene derivatives with electron withdrawing substituents on the benzene rings have been reported.[1c,4,5] A number of 9-arylidenepolynitrofluorenes have been obtained by condensation of the corresponding polynitrofluorenes with benzaldehydes.[6–8] In the case of electron donating substituents in the benzylidene fragment, the HOMO is located on the benzylidene moiety and the LUMO is located on the fluorene moiety, resulting in intramolecular charge transfer (ICT) in these compounds.[7] Among them the acceptor **1** has been shown to be an efficient sensitiser for PVK and related polymers, especially in its ICT region (500–550 nm).[8] Both semiconductive (A : D = 1 : 1 composition) and metallic type (A : D = 1 : 2 composition) of electrical conductivity were recently reported for some CTC of several fluorene acceptors with bis(ethylenedioxy)tetrathiafulvalene (in compressed pellets),[9] although to date all known X-ray structures of different stoichiometries for fluorene acceptors with electron donors of tetrathiafulvalene family are of mixed stacks.[1c,5,10]



PVK



TNF



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Herein we describe two novel π-extended fluorene acceptors **2** and **3** in which the 9-arylidene fragment is also electron deficient thus allowing extended delocalisation of the LUMO over two moieties linked by a methine bridge. The five-membered heteroaromatic rings in **2** and **3** are designed to have smaller steric requirements than a six-membered phenyl ring, thus allowing extended planarity with the fluorene moiety. Moreover, in the case of acceptor **2** possible hydrogen bonding between the oxygen of the furan ring and the hydrogen at position 1 of the fluorene ring should also stabilise a planar structure of the molecule. We report the synthesis and electrochemistry of these acceptors, the X-ray structures for **2** and its

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† This paper is dedicated to the memory of Professor Lennart E. Eberson

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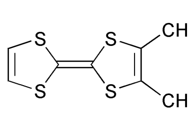
CTC with 4,5-dimethyltetrathiafulvalene (Me_2TTF) and a comparison of these data with *ab initio* HF/6-31G(d) calculated structures.

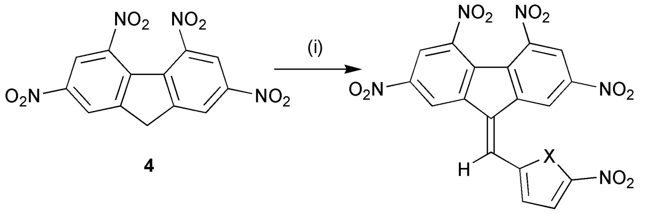


Me_2TTF

Results and discussion

Synthesis and ^{1}H NMR spectra

2,4,5,7-Tetranitrofluorene **4**[7,11,12] is a strong CH-acid[7] and reacts readily with aldehydes,[1a,6–8] ketones,[13] amides,[14] and dithiolium salts.[1b,15] The reaction of **4** with 5-nitro-2-furaldehyde or 5-nitrothiophene-2-carbaldehyde in *N*,*N*-dimethylformamide (DMF) at room temperature gave compounds **2** and **3**, respectively, which precipitated from the mixture (Scheme 1). From acetonitrile or dioxane they crystallised with a solvent molecule, and the solvate **3**·CH_3CN is rather stable and does not lose the solvent even at heating for 48 h at 130 °C/0.1 mbar. In all the solvents studied ($CDCl_3$, CD_3CN, acetone-d_6, DMSO-d_6) both compounds show fine resolution of the signals from the aromatic protons‡ confirming the structures of compounds **2** and **3**. This fine structure is retained unchanged upon heating the samples to 75 °C in CD_3CN, thus confirming that the rotation barrier about the exocyclic C(9)=C(α) double bond is much higher than that in fluorene acceptors with ICT, *e.g.* 9-aminomethylenepolynitrofluorenes[16] or 9-dithiolylidenepolynitrofluorenes,[15d] where fast rotation is observed on the NMR time scale. Proton *H*-8 in **3** is observed at its expected position (9.47 pm in DMSO-d_6) whereas for compound **2** it undergoes a down-field shift of *ca.* 0.6–0.8 ppm (*e.g.* 10.15 ppm in CD_3CN, 10.29 ppm in $CDCl_3$) which can be attributed to intramolecular hydrogen bond formation between C(8)-H of the fluorene ring and the oxygen of the furan ring (see also the crystallographic section).



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2, X = O
3, X = S

Scheme 1 (i) 5-Nitrothiophene-2-carbaldehyde or 5-nitro-2-furaldehyde, DMF, 10–24 h, 20 °C.

Electrochemistry

The electrochemical behaviour of compounds **2** and **3** was studied by cyclic voltammetry (CV) in CH_3CN solution at room temperature,§ using Bu_4NPF_6 (0.10 M) as supporting electrolyte. The CV of thiophene derivative **3** (Fig. 1b) shows the first reduction (presumably single-electron) at $E_{1pc} = -0.67$ V (at 100 mV s^{-1}) which, however, is electrochemically irreversible: switching the sweep direction shows the re-oxidation peak at −0.04 V, *i.e.* the difference in anodic and cathodic peaks $\Delta E_1 = E_{1pa} - E_{1pc} = 0.63$ V (which is much higher than 0.059 V required for a reversible single-electron process). This indicates that substantial changes occur in the structure of the resulting reduced species (see *e.g.* ref. 17). Similar electrochemical irreversibility of radical anion formation in fluorene derivatives was previously observed by us for 2,7-dicyano-4,5-dinitrofluoren-9-one oxime[5] and 9-ferroceneylidene-polynitrofluorenes.[1a]¶ The electron affinity of this reduced species is much lower than expected for the radical anion of **3** (compared to 2,4,5,7-tetranitrofluorenone, see below): the second quasi-reversible reduction wave is observed at a much more cathodic potential ($E_{2pc} = -1.36$ V; $E_{2pa} = -1.23$ V). Equal current values suggest the same number of electrons participating in both reduction processes, indirectly confirming that they are both single-electron reductions.

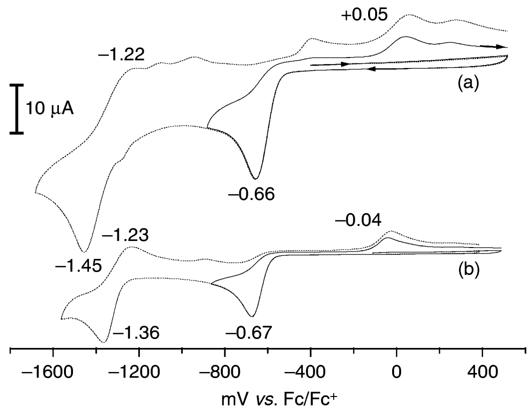

Fig. 1 Cyclic voltammograms of compounds **2** and **3** in acetonitrile at room temperature, 0.1 M Bu_4N PF_6: (a) compound **2**, scan rate 100 mV s^{-1}; (b) compound **3**, scan rate 300 mV s^{-1}.

Similar behaviour is observed for furan derivative **2**, although the CVs are more complicated by following chemical reactions and are more sensitive to the experimental conditions (scan rate, concentration, *etc.*), which is due to the lower stability of the furan system as compared to the thiophene analogue. Nevertheless, at 300 mV s^{-1} compound **2** shows two single-electron reduction peaks at $E_{1pc} = -0.66$ V and $E_{2pc} = -1.45$ V (Fig. 1a) which is close to the values for compound **3**. Switching the sweep direction after the first reduction results in a re-oxidation process at a much more anodic potential ($E_{1pa} = 0.05$ V). However, when the sweep direction is switched after the second reduction, several additional poorly defined re-oxidation processes are observed, together with the unchanged E_{2pa} peak.

In summary, compounds **2** and **3** are reasonably strong electron acceptors, very similar to 2,4,5,7-tetranitrofluoren-9-one ($E_{1red}^{1/2} = -0.57$ V, $E_{1pc} = -0.60$ V; $E_{2red}^{1/2} = -0.83$ V, $E_{2pc} = -0.86$ V; $E_{3red}^{1/2} = -1.74$ V, $E_{3pc} = -1.80$ V *vs.* Fc/Fc$^+$; 100 mV s^{-1}; MeCN; 0.1 M Bu_4NPF_6).

Complexation with Me_2TTF in solution and in solid state

Compounds **2** and **3** are able to form CTCs with π-electron donors in solution which is manifested by the appearance of new long-wavelength absorption bands (CT bands) in their electronic absorption spectra. Fig. 2 shows the broad CT band in the near-infrared region with $\lambda_{max}^{ICT} = 795$ nm which appears on mixing acceptor **2** with Me_2TTF in benzonitrile.

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‡ Some strong electron acceptors of the fluorene series (especially in polar solvents) show substantial broadening of the aromatic protons in the fluorene ring due to a paramagnetic effect (formation of radical anions through interaction with electron donor species) [refs. 1*c*,5], with more pronounced broadening of the protons in positions 3 and 6.

§ CV experiments were also performed at −25 °C and at 20 °C in thin-layer conditions at slow scan rates (2–20 mV s^{-1}) in CH_3CN, CH_2Cl_2 and THF, but in these conditions the electrochemical behaviour is complicated by adsorption phenomena.

¶ A possible explanation could be a dimerisation of the radical anion (in which the spin is expected to be localised on the α-C atom) to form a new sigma bond C(α)–C′(α). Detailed studies of the processes which occur during electrochemical reduction of these type of compounds are underway.

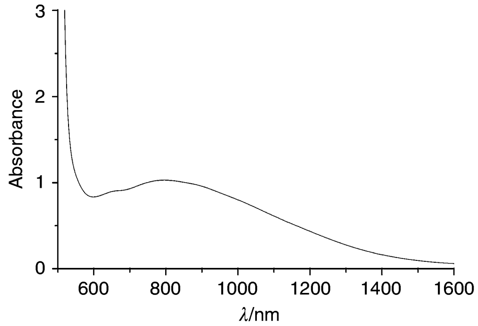


Fig. 2 Electronic absorption spectra of CTC between acceptor **2** (0.10 M) and Me_2TTF (0.10 M) in benzonitrile, 25 °C; l = 1 mm.

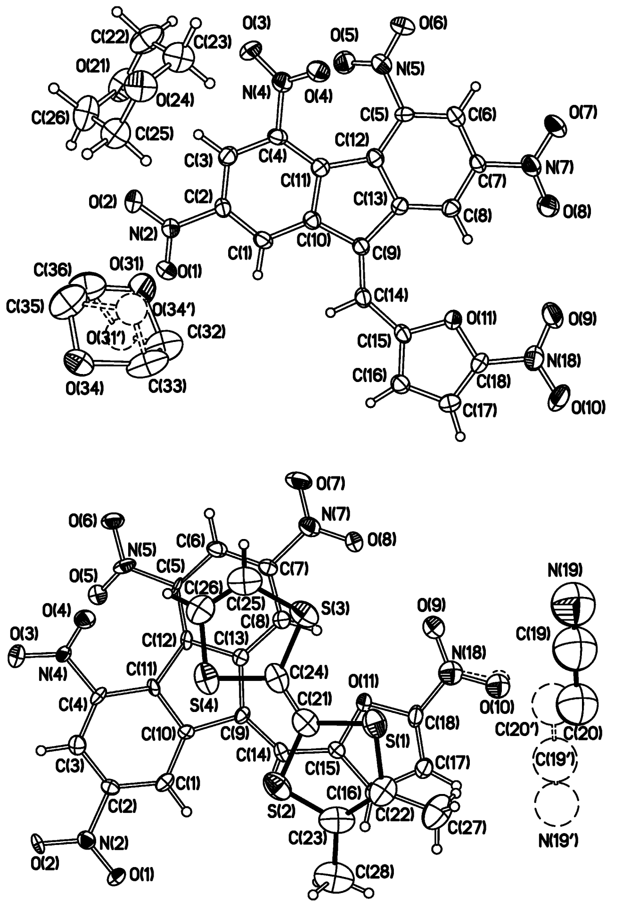


Fig. 3 Molecular structures of $2{\cdot}2C_4H_8O_2$ (**2a**), top, and $2{\cdot}Me_2TTF{\cdot}\frac{1}{2}MeCN$ (**2b**), bottom, showing 50% thermal ellipsoids.

Table 1 X-Ray crystal data and experimental details

Compound	**2a**	**2b**
Formula	$C_{18}H_7N_5O_{11}{\cdot}\ 2C_4H_8O_2$	$C_{18}H_7N_5O_{11}{\cdot}$ $C_8H_8S_4{\cdot}\frac{1}{2}C_2H_3N$
Formula weight	645.49	722.20
T/K	150	120
Symmetry	Monoclinic	Monoclinic
Space group	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)
a/Å	15.588(5)	16.872(3)
b/Å	8.667(3)	7.755(1)
c/Å	21.798(4)	23.201(6)
β/°	109.43(2)	103.99(1)
V/Å^3	2777(1)	2946(1)
Z	4	4
μ/cm^{-1}	1.12	0.40
λ/Å	1.54184	0.71073
Refls collected	3426	10116
Max. 2θ/°	100	50
Unique refls	2770	3668
R_{int}	0.022	0.087
Refls $F^2 > 2\sigma(F^2)$	2236	2120
$R[F^2 > 2\sigma(F^2)]$	0.037	0.082
$wR(F^2)$, all data	0.097	0.212

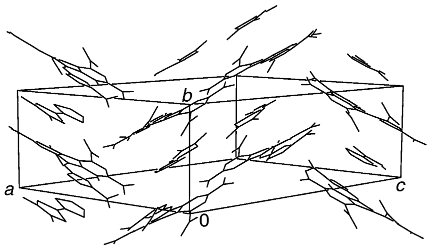


Fig. 4 Crystal packing in **2b**.

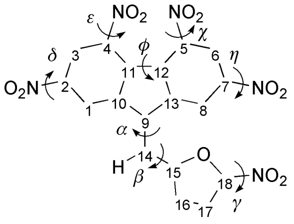
To study in more detail this complexation in the solid state we grew crystals of acceptor **2** and its complex with Me_2TTF. Crystallisation of **2** from dioxane yielded crystallosolvate $2{\cdot}2C_4H_8O_2$ (**2a**), and co-crystallisation of **2** and Me_2TTF from acetonitrile gave the complex $2{\cdot}Me_2TTF{\cdot}\frac{1}{2}MeCN$ (**2b**), which were characterised by single-crystal X-ray diffraction (Fig. 3, Table 1). The crystal packing of **2a** and **2b** (Fig. 4) is remarkably similar, and is reflected in the similarity of their unit cell parameters (see Table 1). Both structures contain "stacks" of parallel molecules **2** (related by the b translation) with large interplanar separations (8.3 Å in **2a**, 7.0 Å in **2b**). The stacks related by screw axes, form a flattened herringbone motif with dihedral angles of *ca.* 50° (**2a**) or 30° (**2b**) between T-contacting molecules. The gap between parallel molecules **2** is filled in **2a** by two dioxane molecules (one of them disordered), whose long axes are directed normally to the molecular planes of **2**. In **2b** such a gap is occupied by a nearly-planar Me_2TTF molecule, which is approximately parallel to **2**. Thus structure **2b** contains infinite mixed donor–acceptor stacks; the acetonitrile molecule of crystallisation lies in an inter-stack cavity near an inversion centre and is disordered between two positions, related by this centre.

The Me_2TTF molecule in **2b** is folded by 9° along the S(1)···S(2) vector and by 2° along the S(3)···S(4) vector and twisted by 3° around the central C(21)=C(24) bond (Fig. 3). The bond lengths are essentially the same as in the pure Me_2TTF,[18] indicating very little or no charge transfer in **2b**. The bond lengths in the acceptor molecules are also equal in **2a** and **2b** within experimental error, and the conformations of these molecules are similar. As in other tetranitrofluorene systems,[1c,5,16] steric repulsion between the 4- and 5-nitro groups causes them to tilt to opposite sides of the aromatic plane; adjacent carbon atoms follow the tilt and produce a warped conformation of the fluorene moiety. The puckering in **2a** is somewhat stronger than in **2b**: the average deviation of the 13 fluorene carbon atoms from their mean plane is 0.08 Å (**2a**) and 0.10 Å (**2b**), and the maximum deviation is 0.17 and 0.22 Å, respectively. On the other hand, in **2a** the (planar) furan moiety is slightly tilted out of the mean fluorene plane by the twists of *ca.* 6° around both the double C(9)=C(14) and the single C(14)–C(15) bond, whereas in **2b** the tilting is negligible.

Notwithstanding these distortions, the overall conformation of **2** in both structures is sufficiently planar for extended π-conjugation. Thus, the C(9)=C(14) bond (1.359(4) Å in **2a**, 1.36(1) Å in **2b**) is longer, and the C(14)–C(15) bond is shorter (1.419(4) Å in **2a**, 1.400(9) Å in **2b**) than the corresponding exocyclic C=C and C–C bonds in eight structurally characterised (5-nitrofuran-2-yl)propene derivatives,[19] averaging 1.332(7) and 1.440(5) Å, respectively, indicating a significant π-conjugation between the fluorene and furan systems of **2a**.

In both structures, there is a short intramolecular contact between the furan O(11) and the fluorene C(8)H hydrogen atoms: H···O distance 2.11 Å (**2a**) and 2.07 Å (**2b**) and the

Table 2 Selected bond lengths and dihedral angles in **2a** and its complex (**2b**) from X-ray data, and HF/6-31G(d) calculated values for **2**, $\mathbf{2}^{\bullet -}$ and $\mathbf{2}^{2-}$



		X-Ray		Theoretical calculations		
		2a	**2b**	**2**[a]	$\mathbf{2}^{\bullet -}$[b]	$\mathbf{2}^{2-}$[a]
	E_{total}/hartree (E_h)	—	—	−1780.76334	−1780.83018	−1780.78979
	E_{LUMO}/eV	—	—	−0.86	2.78	5.55
	E_{HOMO}/eV	—	—	−9.39	−0.17[c]−5.93	−0.24
	Dipole moment/D			8.91	8.24	8.11
Bond lengths/Å						
	C9–C10	1.471(4)	1.481(9)	1.482	1.471	1.420
	C9–C13	1.476(4)	1.467(10)	1.482	1.466	1.407
	C10–C11	1.411(4)	1.401(9)	1.396	1.432	1.458
	C12–C13	1.428(4)	1.433(10)	1.405	1.439	1.461
	C11–C12	1.471(4)	1.462(9)	1.483	1.415	1.379
	C9–C14	1.359(4)	1.361(10)	1.337	1.356	1.451
	C14–C15	1.419(4)	1.400(9)	1.448	1.435	1.353
	C15–C16	1.368(4)	1.378(10)	1.355	1.369	1.446
	C16–C17	1.400(4)	1.422(10)	1.427	1.415	1.353
	C17–C18	1.347(4)	1.336(11)	1.339	1.345	1.400
	C18–N	1.424(4)	1.46(2)[d]	1.426	1.409	1.327
	C15–O	1.379(3)	1.394(8)	1.342	1.340	1.349
	C18–O	1.347(3)	1.351(8)	1.331	1.340	1.381
	C2–N	1.471(4)	1.483(9)	1.459	1.429	1.422
	C4–N	1.464(4)	1.470(9)	1.458	1.446	1.453
	C5–N	1.467(4)	1.484(9)	1.457	1.445	1.452
	C7–N	1.465(4)	1.480(10)	1.459	1.435	1.432
	C(8)H · · · O(furan)	2.11	2.07	2.16	2.21	2.45
Dihedral angles/°						
	α	6.0	1.6	2.3	7.7	32.2
	β	5.8	1.4	9.8	10.3	1.5
	γ	5.2	18.1, 1.9[d]	1.8	1.6	1.5
	δ	11.1	2.7	1.3	1.9	1.6
	ε	41.1	28.3	32.5	26.5	30.2
	φ	8.2	11.1	11.3	8.6	5.4
	χ	45.6	31.5	29.7	23.9	27.8
	η	8.5	9.4	12.6	5.5	6.4

[a] RHF/6-31G(d)//RHF/6-31G(d). [b] ROHF/6-31G(d)//ROHF/6-31G(d). [c] E_{SOMO}/eV. [d] Two positions of the nitro group.

C–H · · · O angle 136° (**2a**) and 134° (**2b**) for the idealised hydrogen positions (C–H 1.08 Å). In **2b**, the nitro group at C(18) is disordered, the N(18) and O(10) atoms occupying two sets of positions with equal probability.

Theoretical calculations

Quantum mechanical calculations of the geometries and electronic structures for compound **2**, its radical anion $\mathbf{2}^{\bullet -}$ and dianion $\mathbf{2}^{2-}$ performed at the Hartree–Fock (HF) level of theory [RHF/6-31G(d)//RHF/6-31G(d) for **2** and $\mathbf{2}^{2-}$, and ROHF/6-31G(d)//ROHF/6-31G(d) for $\mathbf{2}^{\bullet -}$] show good agreement with experimental data.

Geometry optimisation for compound **2** results in a structure with only minor rotation around the C9=C14 bond ($\alpha = 2.3°$, Table 2) which is close to the values from X-ray data for **2a** (6.0°). Consequently C(8)H · · · O(furan) distance in **2** (2.16 Å) is only slightly longer than this distance found in X-ray experiment (2.11 Å, Table 2). On reduction ($\mathbf{2} \longrightarrow \mathbf{2}^{\bullet -} \longrightarrow \mathbf{2}^{2-}$) the C9–C14 bond order is decreased (the bond length is increased: 1.337 ⟶ 1.356 ⟶ 1.451 Å) and the α dihedral angle is increased (2.3 ⟶ 7.7 ⟶ 32.2°) leading to substantial increasing in C(8)H · · · O(furan) distance (2.16 ⟶ 2.21 ⟶ 2.45 Å, Table 2). More pronounced changes in bond lengths upon the first reduction ($\mathbf{2} \longrightarrow \mathbf{2}^{\bullet -}$) are observed for C10–C11, C12–C13 and C11–C12 bonds ($\Delta = +0.038$, $+0.034$ and -0.068 Å, respectively). In the X-ray experiments, the transition from the acceptor (**2a**) to its complex (**2b**) results in only minor changes in these bond lengths ($\Delta = -0.010$, $+0.005$ and -0.009 Å, respectively) (Table 2). These results are in agreement with a neutral state of the complex **2b** with only minor charge transfer from Me_2TTF to acceptor **2** in the ground state.

Due to the presence of electron withdrawing nitro groups in both fluorene and furan moieties the HOMO and LUMO orbitals are notably delocalised over the whole molecule with no significant ICT in the ground state (in contrast to **1**[8]), so the calculated dipole moments are of moderate values and practically unchanged with the transformation $\mathbf{2} \longrightarrow \mathbf{2}^{\bullet -} \longrightarrow \mathbf{2}^{2-}$ (8.91 ⟶ 8.24 ⟶ 8.11 D, Table 2). Analysis of the charge distribution in **2** shows neglegible summative charges on both fluorene (+0.01) and nitrofurylidene (−0.01) moieties (separated at the C9=C14 bond). A similar situation is observed for the dianion $\mathbf{2}^{2-}$: the sum of Mulliken's charges are −1.10 and −0.90 at the fluorene and nitrofurylidene moieties, respectively. For the open-shell system $\mathbf{2}^{\bullet -}$ an asymmetry in both charge and spin density distribution between the moieties is observed, in accordance with differences in the sizes of their π-systems: the sum of the charges are −0.70 and −0.30, and the spin densities are 0.86 and 0.14 at the fluorene and nitrofurylidene moieties, respectively.

Conclusions

The attachment of electron deficient 5-nitrofurylidene or 5-nitrothienylidene moieties to tetranitrofluorene results in the π-extended electron acceptors **2** and **3**. Their reduction in CV experiments, which occurs at −0.66 and −0.67 V (*vs.* Fc/Fc$^+$), respectively, indicates they are reasonably strong electron acceptors, similar to 2,4,5,7-tetranitrofluoren-9-one. This is an electrochemically irreversible process and the re-oxidation process is observed at +0.05 and −0.04 V, for **2** and **3**, respectively. The single crystal X-ray structures of the acceptor (**2a**) and its CTC with Me$_2$TTF (**2b**) shows insignificant changes in bond lengths indicating a neutral ground state of this complex. Crystal packing in **2b** shows mixed A···D···A···D stacks characteristic for semiconductive CTC. Theoretical HF/6-31G(d) calculations for acceptor **2** and its radical anion and dianion states are in agreement with this conclusion. ^{1}H NMR and X-ray data, as well as theoretical calculations prove intramolecular hydrogen bonding in **2** between the oxygen of the furan ring and C(8)-H hydrogen of the fluorene moiety. Further studies on π-extended polynitrofluorene acceptors are in progress.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 instrument, operating at 299.91 MHz. Chemical shifts, given in ppm, are relative to tetramethylsilane (Me$_4$Si) as internal standard. All *J* values are in Hz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. UV–VIS–NIR spectra were recorded on a Varian Cary 5E in acetonitrile solution for acceptors and in benzonitrile for CTC **2**·Me$_2$TTF.

9-(5-Nitrofuran-2-ylidene)-2,4,5,7-tetranitrofluorene (2)

Fluorene **4**[11] (5.35 g, 15.5 mmol) was suspended in DMF (25 cm^3) at ambient temperature and 5-nitro-2-furaldehyde (2.50 g, 17.7 mmol) was added with stirring. The mixture became dark green, the solid dissolved and in 5–10 min precipitation was observed. The mixture was stirred at room temperature for 10 h, then the solid was filtered, washed with DMF (4 × 7 cm^3), propan-2-ol and dried *in vacuo* affording compound **2** (5.85 g, 81%). The product was recrystallised from acetonitrile (*ca.* 500 cm^3) yielding the product as solvate **2**·CH$_3$CN (5.19 g, 66%) as light yellow-brownish needles, mp 280 °C (decomp.). Acetonitrile can be removed by drying at 130–140 °C *in vacuo*, by recrystallisation from another solvent or by re-precipitation of a solution in an appropriate solvent into water or ethanol. **2**·CH$_3$CN: δ_H (300 MHz; CDCl$_3$) 2.01 (3 H, s, MeCN), 7.36 (1 H, d, ^3J 3.8, furan), 7.61 (1 H, d, ^3J 3.8, furan), 7.78 (1 H, s, C=C-*H*), 8.93 (1 H, d, ^4J 1.8, *H*-1), 9.02 (2 H, d, ^4J 1.9, *H*-3,6), 10.29 (1 H, d, ^4J 1.8, *H*-8).

MS (CI, NH$_4^+$): *m*/*z* (%) = 487 (M$^+$ + 18, 100), 457 (36), 453 (42), 442 (36), 133 (42). λ_{max} (CH$_3$CN)/nm (ε/M^{-1} cm^{-1}) 415 (45600), 331 (46600), 288 (45500), 255 (47900) (Found: C, 46.12; H, 1.65; N, 15.20. C$_{18}$H$_7$N$_5$O$_{11}$ requires C, 46.07; H, 1.50; N, 14.92%). Recrystallisation from dioxane afforded **2a** (*i.e.* **2**·2C$_4$H$_0$O$_2$).

9-(5-Nitro-2-thienylidene)-2,4,5,7-tetranitrofluorene (3)

Fluorene **4** (3.00 g, 8.7 mmol) was suspended in DMF (15 cm^3) at ambient temperature and 5-nitrothiophene-2-carbaldehyde (1.40 g, 8.90 mmol) was added with stirring. The mixture became dark green and the solid dissolved. The mixture was stirred at room temperature for 24 h, the solid was filtered off, washed with DMF (2 × 5 cm^3), propan-2-ol and dried *in vacuo* affording compound **3** (2.42 g, 58%). The product was recrystallised from acetonitrile (100 cm^3) yielding brown crystals of solvate **3**·CH$_3$CN (1.97 g, 43%), mp 160 °C (−MeCN, decomp.). δ_H (300 MHz; DMSO-*d*$_6$) 7.95 (1 H, br.d, ^3J 4.0, thiophene), 8.33 (1 H, d, ^3J 4.4, thiophene), 8.80 (1 H, d, ^4J 1.9, *H*-Ar), 8.83 (1 H, d, ^4J 1.9, *H*-Ar), 8.93 (1 H, br s, C=C-*H*), 9.22 (1 H, d, ^4J 1.9, *H*-Ar), 9.47 (1 H, d, ^4J 1.9, *H*-Ar). MS (CI, NH$_4^+$): *m*/*z* (%) = 503 (M$^+$ + 18, 100), 473 (90), 469 (68), 458 (32), 157 (61), 128 (37), 112 (67), 100 (58). λ_{max} (CH$_3$CN)/nm (ε/M^{-1} cm^{-1}) 455sh (21000), 433 (22400), 405 (21500), 375 (22000), 290 sh (26700), 261 (32700) (Found: C, 45.57; H, 1.81; N, 15.71; S, 6.31. C$_{20}$H$_{10}$N$_6$O$_{10}$S [C$_{18}$H$_7$N$_5$O$_{10}$S·CH$_3$CN] requires C, 45.63; H, 1.91; N, 15.97; S, 6.09%).

Complex 2·Me$_2$TTF·$\frac{1}{2}$MeCN

Acceptor **2** (10.4 mg) was dissolved in hot acetonitrile (2 cm^3) and Me$_2$TTF[20] (5.2 mg) was added. The mixture was filtered and left to cool slowly. Black crystals of **2**·Me$_2$TTF·$\frac{1}{2}$MeCN, suitable for single crystal X-ray analysis, were formed.

Electrochemical measurements

Cyclic voltammetry experiments were performed on a BAS CV50W electrochemical analyser with *iR* compensation. Platinum wire, platinum disk (Ø 1.6 mm) and Ag/Ag$^+$ were used as counter, working, and reference electrodes, respectively. CV experiments were performed in dry CH$_3$CN, CH$_2$Cl$_2$ and THF with Bu$_4$N$^+$PF$_6^-$ as supporting electrolyte (0.10 M in CH$_3$CN, 0.20 M in CH$_2$Cl$_2$ and in THF) under Ar flow; concentrations of acceptors were *ca.* 10^{-3} M^{-1}. The scan rate was varied from 2 (in a case of thin-layer CV) to 5000 mV s^{-1}. All potentials were referenced to Fc/Fc$^+$ couple as the internal reference, which showed a potential of +0.08 V *vs.* Ag/Ag$^+$ (+0.45 V *vs.* Ag/AgCl) in our conditions (in CH$_3$CN).

X-Ray Crystallography

The X-ray diffraction experiment for **2a** was carried out on a Rigaku AFC6S 4-circle diffractometer (graphite-monochromated Cu-Kα radiation, 2*θ*/*ω* scan mode), for **2b** on a SMART 3-circle diffractometer with a 1K CCD area detector (graphite-monochromated Mo-Kα radiation; a hemisphere of reciprocal space was covered by a combination of 4 sets of *ω* scans, each set at different *φ* and/or 2*θ* angles). Crystals were cooled using a Cryostream (Oxford Cryosystems) open-flow N$_2$ gas cryostat. For **2a**, absorption correction was performed by *ψ*-scans (transmission factors 0.85 to 1). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[21] Crystals of **2b** grow as non-merohedral twins. During the indexing procedure, we found two orientation matrices (corresponding to the same unit cell parameters), one of which described 75% and the other 25% of the observed reflections. Comparison of the matrices, using TWROT program (Bruker AXS, Madison, WI, USA, 1997), showed that the twin components are related by a 180° rotation around the [5 0 −2] axis in the direct space, or [1 0 −1] axis in the reciprocal space. Hence when $|h + l| = 5n$, an *h*, *k*, *l* reflection of one component overlaps with the $0.4h - 0.6l$, k, $-1.4h - 0.4l$ reflection of the other. The usual least squares refinement of the structure converged at $R = 0.118$ with the typical signs of twinning: $K = \langle F_o^2\rangle / \langle F_c^2\rangle$ for the weakest reflections ($F/F_{max} < 0.008$) was *ca.* 20 times higher than the average, all the most disagreeable reflections had $|h + l| = 5n$ and $|F_o| \gg |F_c|$. In the final refinement, all 770 reflections with $|h + l| = 5n$ (n = 1 to 5) were excluded from the data, whereupon R decreased to 0.082 and the variations of K halved. However, the reflections of the two components overlapped imperfectly, and their intensities could not be satisfactorily integrated together. For this reason, an attempt to refine the contributions of the twin components by the usual

SHELXL-97 technique for non-merohedral twins[22] was unsuccessful. ||

Computational Procedure

The *ab initio* computations were carried out with the Gaussian94[23] package of programs using the Hartree–Fock (HF) level of theory with Pople's 6-31G split valence basis set supplemented by *d*-polarisation functions on heavy atoms. The spin restricted HF method (RHF) was employed for **2** and $\mathbf{2}^{2-}$ [RHF/6-31G(d)//RHF/6-31G(d)], whereas the open spin-restricted (ROHF) method was employed for $\mathbf{2}^{\bullet -}$ [ROHF/6-31G(d)//ROHF/6-31G(d)]. Berni algorithm was used for geometry optimisations in all the cases. No constrains of bonds/angles/dihedral angles were applied in the calculations and all the atoms were free to optimise.

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