A variety of intermolecular interactions in tetracyanotetrafluoroquinodimethane ($TCNQF_4$) charge transfer salts of fluorinated tetrathiafulvalenes

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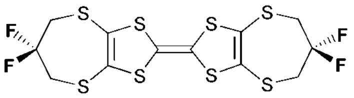
The preparation and crystal structures of the 1 : 1 $TCNQF_4$ (tetracyanotetrafluoroquinodimethane) salts of two unsymmetrically substituted, fluorinated tetrathiafulvalenes, (2,2-difluorotrimethylenedithio)(ethylenedithio)tetrathiafulvalene (**2**) and (2,2-difluorotrimethylenedithio)tetrathiafulvalene (**3**) are described. A strong LUMO···LUMO overlap interaction leads to diamagnetic $(TCNQF_4)_2^{2-}$ dimers in both salts. In ($\mathbf{2}$)($TCNQF_4$)$\cdot$(Cl_2HCCH_2Cl), the $\mathbf{2}^{\bullet+}$ radical cations also dimerise, giving rise to a layered, pseudo κ-type phase with alternating $(\mathbf{2})_2^{2+}$ and $(TCNQF_4)_2^{2-}$ and diamagnetic behaviour. On the other hand, in ($\mathbf{3}$)($TCNQF_4$) the cationic dimers adopt a weaker overlap and exhibit a magnetic singlet–triplet behaviour. The salt is also characterised by a complete fluorine segregation, the CF_2 groups of **3** facing the fluorine atoms of the $TCNQF_4$ moieties. In both salts the relative orientation of the cationic and anionic dimers is controlled by C–H···(N,F) hydrogen bonds (HB), demonstrating the activated HB donor character of the hydrogen atoms of the tetrathiafulvalenes upon oxidation together with the enhanced HB acceptor character of the nitrile groups of the $TCNQF_4^{\bullet-}$ radical anions.

Introduction

In organic conductors based on oxidised tetrathiafulvalenes the overlap interactions between open-shell molecules add to the S···S van der Waals interactions, already present in the neutral state, to stabilise the formation of dimers, trimers, and extended solid state arrangements, stacks or slabs.[1] Specific functional groups have been introduced on the TTF core in order to compete with those interactions, such as alcohols,[2] amides[3,4] or phosphonates[5] (for hydrogen bonding)[6] or halides[7] (for X···X[8] or X···N interactions,[9] X = halide). Among those intermolecular interactions which control the self-assembly of molecular entities in the solid state, fluorine–fluorine interactions play a unique role precisely because they are very weak if not negligible.[8a] This behaviour originates in the low polarisability of the fluorine atom (comparable to that of hydrogen) combined with its larger size, whose influence (as inverse sixth power) dominates the interaction energy and leads to vanishing attractive interatomic dispersion forces. We wanted to take advantage of the segregation effects of those exclusion interactions, essentially observed in fluorinated fluid phases, as a structure-orienting tool in the control of the solid state architectures of fluorinated molecules and we recently described the synthesis and the solid state structures of the fluorinated tetrathiafulvalenes **1**–**3**,[10] whose layered structures in the neutral, unoxidised state revealed a strong segregation of the CF_2 groups on the outer ends of those slabs and the formation of compact fluorinated bilayers, further stabilised by C–H···F interactions.

Attempts to form charge-transfer salts of **1** with TCNQ or tetracyanotetrafluoroquinodimethane ($TCNQF_4$) were however unsuccessful because of its somewhat high oxidation potential (0.79 V *vs.* SCE (saturated calomel electrode) in THF), due to the limited but sizeable electron-withdrawing effect of the two CF_2 groups. On the other hand, the unsymmetrically substituted molecules **2** and **3** oxidise at lower potentials, 0.59 and 0.48 V *vs.* SCE in CH_3CN respectively, values which compare favourably with the reduction potential of $TCNQF_4$ (0.53 V *vs.* SCE in CH_3CN). Accordingly, the $TCNQF_4$ oxidation of these two donor molecules was attempted and afforded 1 : 1 salts whose structures and properties are analysed in this paper. The presence of both aliphatic (in **2** and **3**) and aromatic (in $TCNQF_4$) fluorine atoms in the salts offers novel possibilities for exploring the structural and electronic consequences of the fluorine segregation and the C–H···F hydrogen bonds identified in the neutral compounds **1**–**3**.[10]



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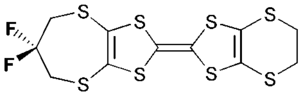

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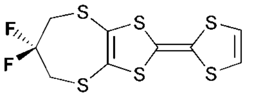

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Results and discussion

Structural organisation

Both 1 : 1 salts were obtained by slow diffusion. ($\mathbf{2}$)($TCNQF_4$)$\cdot$($ClCH_2CHCl_2$) crystallises in the triclinic system, space group $P\bar{1}$ with both donor, acceptor and 1,1,2-trichloroethane (TCE) molecules in general positions in the

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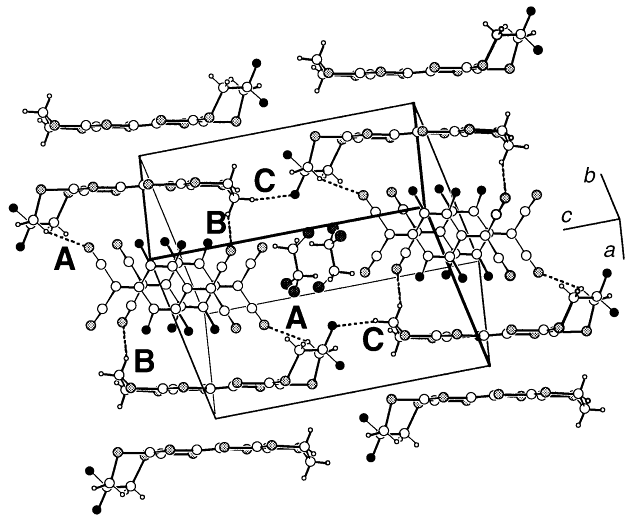


Fig. 1 A view of the unit cell in $(\mathbf{2})(TCNQF_4)\cdot$TCE. Note the alternating dicationic and dianionic dimers linked in the (*a*,*b*) plane through the A and B C–H···N hydrogen bonds. The CF_2 groups and TCE molecules segregate into layers at $c = \frac{1}{2}$, with one single C–H···F hydrogen bond (denoted C) identified at this interface.

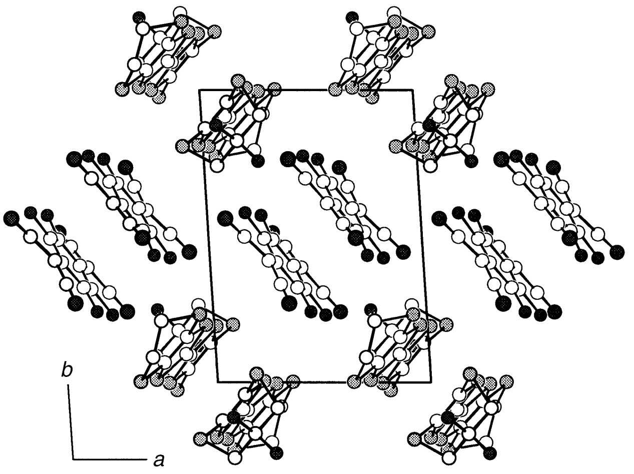
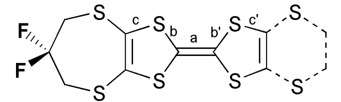


Fig. 2 A projection view of $(\mathbf{2})(TCNQF_4)\cdot$TCE along *c* showing the pseudo κ-type arrangement. TCE molecules have been excluded for clarity.

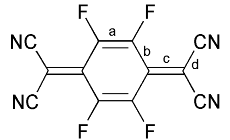
unit cell (Fig. 1). By comparison with the structures of the neutral molecules[10,11] and various $TCNQF_4$ salts,[12,13] the bond length evolutions within **2** (Table 1) and the $TCNQF_4$ (Table 2) moieties indicate a full charge transfer, *i.e.* a formulation $(\mathbf{2}^{\cdot+})\cdot(TCNQF_4^{\cdot-})\cdot$TCE. This is also confirmed by the nitrile stretching frequency (Table 2). In the solid, both cation and anion are associated into inversion-centred dicationic or dianionic dimers with almost eclipsed overlaps and very short plane-to-plane distances, 3.315(2) Å in $(\mathbf{2})_2^{2+}$, 3.216(2) Å in $(TCNQF_4)_2^{2-}$ bimolecular entities. As shown in Fig. 2, those dimers arrange orthogonally to each other into pseudo κ-type[14] layers with the CF_2 fragments and TCE solvent molecules located at the interface between those layers (Fig. 1). Besides the HOMO···HOMO and LUMO···LUMO overlap interactions within each homodimer (see below), other weaker intermolecular interactions are also identified in the structure which might contribute to its overall stability. Three C–H···X (X = N or F) hydrogen bonds are indeed observed, denoted A, B and C in Fig. 1; their structural characteristics are collected in Table 3. Such hydrogen bonds based on C–H donor groups rather than OH or NH ones, albeit weaker, have been shown to play a crucial role in the organic and organometallic solid state.[15] The A and B C–H···N hydrogen bonds involve the hydrogen atoms of both the CH_2CH_2 and $CH_2CF_2CH_2$ groups of $\mathbf{2}^{\cdot+}$, and the nitrogen atom of the $TCNQF_4^{\cdot-}$ radical anion. These interactions are short and directional. As observed in the cation radical salts of tetrathiafulvalenyl amides,[3] in TTF·TCNQ[16] or in the TTF·chloranil complex,[17] the oxidation of **2** to $\mathbf{2}^{\cdot+}$ and concomitant reduction of $TCNQF_4$ to $TCNQF_4^{\cdot-}$ activate both the hydrogen atoms of the $\mathbf{2}^{\cdot+}$ cation as hydrogen bond donors and the nitrogen atoms of the $TCNQF_4^{\cdot-}$ anion as hydrogen bond acceptors for entering into $C\text{–}H^{\delta+}\cdots{}^{\delta-}N$ hydrogen bonds. Furthermore, the ethylenic bridge in $\mathbf{2}^{\cdot+}$ exhibits no positional disorder, while such disorder is often observed in BEDT-TTF salts.[1] The principal mean square atomic displacements of the thermal ellipsoids of the two carbon atoms are indeed normal and comparable to those of the 2,2-difluorotrimethylene bridge, a further indication of the stabilising

Table 1 Intramolecular distances (Å) within the TTF cores of **2** and **3** in the neutral donor molecules and in the two salts



	Neutral **2**	$\mathbf{2}^{\cdot+}$	Neutral **3**	$\mathbf{3}^{\cdot+}$
a	1.339(5)	1.372(8)	1.332(4)	1.386(4)
b	1.754(4)	1.722(6)	1.758(3)	1.715(4)
b′	1.750(4)	1.722(6)	1.755(3)	1.707(4)
c	1.748(5)	1.726(6)	1.746(8)	1.742(6)
c′	1.760(3)	1.741(6)	1.736(4)	1.700(4)
Ref.	10	This work	10	This work

Table 2 Intramolecular distances (Å) within the $TCNQF_4$ molecules in the two salts and reference compounds together with IR stretching frequencies (cm^{-1}) of the nitrile groups



	$TCNQF_4^0$	In $\mathbf{2}^{\cdot+}$ salt	In $\mathbf{3}^{\cdot+}$ salt	$TCNQF_4^{\cdot-\,a}$	$TCNQF_4^{2-\,b}$
a	1.335	1.345(8)	1.356(4)	1.36	1.373
b	1.439	1.420(8)	1.407(8)	1.42	1.398
c	1.373	1.400(8)	1.413(8)	1.42	1.457
d	1.440	1.432(8)	1.416(8)	1.435	1.403
C=N	1.142	1.142(8)	1.140(4)	1.14	1.154
ν_{CN}	2215, 2230	2175, 2191	2175, 2192	2179, 2195	2133, 2167
Ref.	11	This work	This work	12	13

[a] In $[FeCp^*_2][TCNQF_4]$. [b] In $[FeCp^*_2]_2[TCNQF_4]$.

Table 3 Hydrogen bond geometrical features (distances in Å, angles in °) in (**2**)(TCNQF$_4$)·TCE and (**3**)(TCNQF$_4$)

Compound	Interaction		
(**2**)(TCNQF$_4$)·TCE	H···N	C···N	C–H···N
A: C$_6$H$_{6A}$···N2^i	2.501	3.411(7)	156.2
B: C$_{10}$H$_{10A}$···N4^i	2.675	3.624(7)	134.8
	H···F	C···F	C–H···F
C: C$_{10}$H$_{10B}$···F1^{ii}	2.552	3.419(8)	148.9
(**3**)(TCNQF$_4$)	H···N	C···N	C–H···N
D: C$_3$H$_3$···N1^{iii}	2.467	3.361(8)	161.2
E: C$_4$H$_4$···N3^{iv}	2.525	3.213(7)	131.0

i: $1-x, -1-y, -z$; ii: $x, y, -1+z$; iii: $x, 1+y, z$; iv: $2-x, 1-y, 1-z$.

role of the hydrogen bonds.[18] One single C–H···F interaction (C) is also identified at the interface between the pseudo κ-type slabs (Fig. 2); its geometrical characteristics (Table 3) compare very well with those observed in the neutral **1**–**3** molecules[10] as well as in fluoroaromatics.[19] The layered nature of this salt is further confirmed by the plate-like shape of the crystals: the largest faces are [001] and [00$\bar{1}$], confirming that the weakest interactions indeed occur at the fluorinated interface including the TCE solvent molecules at $z = \frac{1}{2}$.

The 1 : 1 salt with **3** exhibits a fully different structure characterised by a one dimensional stacking of the TCNQF$_4^{\cdot-}$ anions. (**3**)(TCNQF$_4$) crystallises in the monoclinic system, space group $P2/c$. Both cation and anion are located in general positions in the unit cell (Fig. 3). Bond lengths within the donor (Table 1) and TCNQF$_4$ moieties (Table 2) indicate a full charge transfer and justify the (**3**$^{\cdot+}$)(TCNQF$_4^{\cdot-}$) formulation. In the solid state the TCNQF$_4^{\cdot-}$ radical anions arrange into inversion-centred face-to-face dimers with a short interplanar distance [3.188(1) Å] and a nearly eclipsed geometry, characteristic of dianionic (TCNQF$_4^{\cdot-}$)$_2$ dimers. These dimers stack along the [010] direction to afford a strongly alternated chain, with an inter-dimer plane-to-plane distance of 3.306(2) Å (Fig. 4). The oxidised donor molecules organise in between the dimerised TCNQF$_4^{\cdot-}$ columns into dimers related by the twofold axis with an interplanar distance of 3.63 Å. This microscopic one-dimensional description of the structure is also confirmed by the needle-like shape of the crystals whose long axis is indeed the TCNQF$_4$ stacking [010] direction. Besides the HOMO···HOMO and LUMO···LUMO overlap interactions (see below), weaker intermolecular interactions can also be identified. The first notable feature is the complete fluorine segregation, with the CF$_2$ groups of the **3**$^{\cdot+}$ radical cations pointing towards the fluorine atoms of TCNQF$_4^{\cdot-}$ (Fig. 3). This segregation does not result from a specific attractive interaction between the fluorine atoms[8a] but from a segregation of the other more polarisable atoms (C, H, S) which experience stronger van der Waals interactions when they develop contacts with each other rather than with fluorine atoms. This effect was clearly observed for example in the neutral donor molecules **1**–**3** which adopt layered structures with fluorous bilayers[10] or in the neutral tetrakis(trifluoromethyl)tetrathiafulvalene,[20] (CF$_3$)$_4$TTF, which organises into columns whose surface is fully covered by the CF$_3$ groups. Furthermore, two C–H···N hydrogen bonds are identified (noted D and E in Fig. 5), whose geometrical characteristics are reported in Table 3. Note that they involve the C$_{sp^2}$–H hydrogen atom of the unsubstituted dithiole ring of **3** rather than the sp^3 CH$_2$ substituents, confirming that the carbon hybridisation plays a crucial role in the donor strength of a given group.[15] As discussed above, we also expect that the positive charge of the **3**$^{\cdot+}$ cation increases the donor strength of the C$_{sp^2}$–H groups to a larger extent than the C$_{sp^3}$H$_2$ groups of the 2,2-difluorotrimethylene bridge.

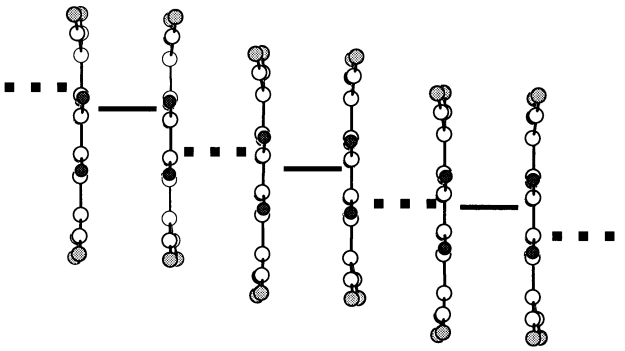


Fig. 4 Detail of the dimerised TCNQF$_4$ chains in (**3**)(TCNQF$_4$). The full line indicates the eclipsed strong interaction, the dashed line the weaker inter-dimer interaction (see text).

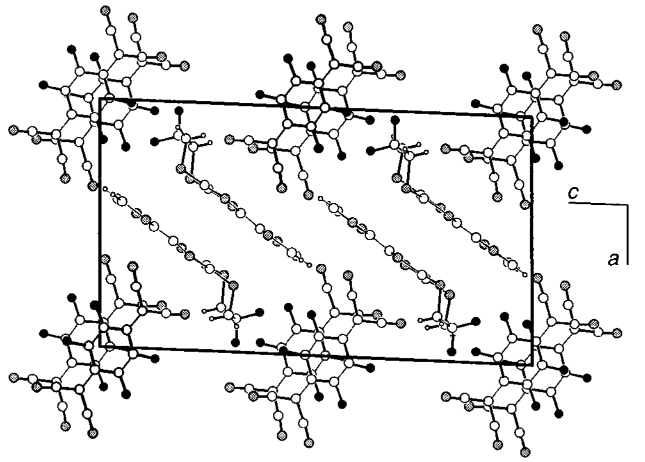


Fig. 3 A projection of the unit cell of (**3**)(TCNQF$_4$). Note the segregation of the fluorine atoms (dark) with the CF$_2$ groups facing the fluorine atoms of the TCNQF$_4$ molecules.

In conclusion the overall structure of both salts is dominated by the formation of homomolecular face-to-face dimers stabilised by the overlap of the open-shell molecules. Their relative arrangement is controlled by weaker intermolecular interactions and particularly here the fluorine segregation and the C–H···N hydrogen bonds with the nitrile groups of TCNQF$_4^{\cdot-}$. Such C–H···N are particularly favourable in these salts given the polarisation of both ions.

Magnetic properties

In the two salts the 1 : 1 stoichiometry rules out the possibility of metallic conductivity, but their magnetic behaviour will reflect the strength of the overlap interactions within the dimers. While (**2**)(TCNQF$_4$)·(TCE) is essentially diamagnetic, in (**3**)(TCNQF$_4$) a susceptibility increase (Fig. 6) at higher temperatures indicates a thermally activated behaviour which can

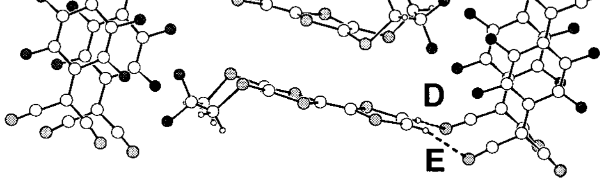


Fig. 5 Detail of the C–H···F hydrogen bonds (denoted D and E) in (**3**)(TCNQF$_4$).

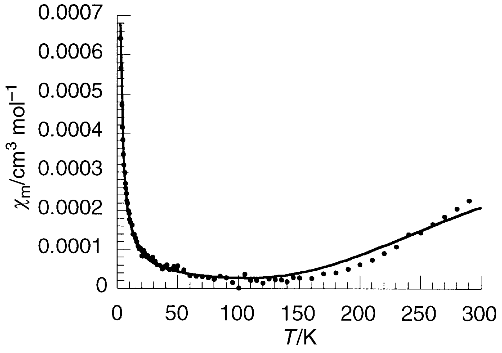


Fig. 6 Temperature dependence of the magnetic susceptibility of (**3**)(TCNQF$_4$). The solid line is a fit by the Bleaney–Bowers equation for singlet–triplet behaviour, together with a Curie tail at low temperature (see text).

be fitted with a singlet–triplet contribution, $|J|/k = 950$ K, together with a Curie tail at low temperature (0.06% $S = 1/2$ magnetic defects per mol). A rationale for the different behaviours in the two salts is to be found in the various overlap interactions experienced within each homomolecular dimer. In (**2**)(TCNQF$_4$)·(TCE), the calculated LUMO···LUMO overlap interaction[21] $\beta_{\mathrm{LUMO\cdots LUMO}}$ within the (TCNQF$_4$)$_2{}^{2-}$ dimers amounts to 1.0 eV, a large value which reflects the short plane-to-plane distance and the eclipsed overlap. As a consequence this dimer is magnetically silent for $T < 300$ K. The same conclusion holds for the dicationic (**2**)$_2{}^{2+}$ dimers identified in Fig. 1; the intra dimer $\beta_{\mathrm{HOMO\cdots HOMO}}$ interaction amounts to 0.83 eV together with a weaker overlap between dimers β_{inter} of 0.2 eV. As the $J_{\mathrm{intra}}:J_{\mathrm{inter}}$ ratio is $(\beta_{\mathrm{intra}}/\beta_{\mathrm{inter}})^2 = 17$, the magnetic behaviour of the donor sublattice is dominated by the strong intra dimer antiferromagnetic interaction, hence the diamagnetic behaviour of the (**2**)$_2{}^{2+}$ dimers and of the whole salt.

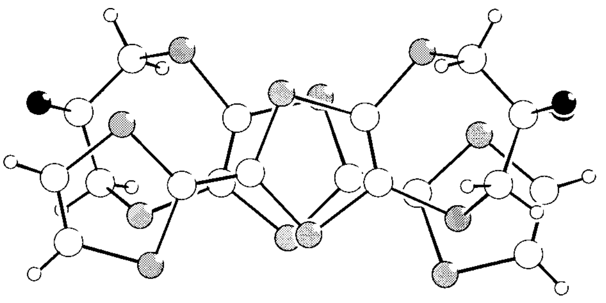


Fig. 7 Detail of the peculiar overlap between **3**$^{\cdot+}$ radical cations in (**3**)(TCNQF$_4$).

Table 4 Crystallographic data

	(**2**)(TCNQF$_4$)·TCE	(**3**)(TCNQF$_4$)
Formula	$C_{25}H_{11}Cl_3F_6N_4S_8$	$C_{21}H_6F_6N_4S_6$
Formula mass	844.21	620.66
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$
a/Å	8.5798(17)	13.7985(15)
b/Å	11.544(2)	7.0222(5)
c/Å	15.944(3)	23.996(2)
α/°	93.28(3)	—
β/°	101.93(3)	92.546(12)
γ/°	92.84(3)	—
V/Å^3	1539.5(5)	2322.8(4)
Z	2	4
μ/mm^{-1}	0.906	0.659
Data collected	15 027	18 315
Independent data (R_{int})	5527(0.061)	4448(0.1008)
Observed data [$I > 2\sigma(I)$]	2550	3055
Param. refined	408	334
$R(F)$	0.0567	0.0449
$wR(F^2)$	0.1523	0.1146

On the other hand, in (**3**)(TCNQF$_4$), the interactions within the dimerised TCNQF$_4$ chains are also strong ($\beta_{\mathrm{intra}} = 1.09$ eV, $\beta_{\mathrm{inter}} = 0.18$ eV) and the anionic sublattice most probably does not contribute to the susceptibility. On the other hand, the overlap interaction $\beta_{\mathrm{HOMO\cdots HOMO}}$ between **3**$^{\cdot+}$ cations amounts to 0.43 eV only, and is at the origin of the singlet–triplet contribution observed in (**3**)(TCNQF$_4$). This weaker $\beta_{\mathrm{HOMO\cdots HOMO}}$ value originates from the larger plane-to-plane distance (3.63 Å with **3** *vs.* 3.31 Å with **2**) and a very unusual overlap (Fig. 7) which does not favour an optimised overlap interaction between HOMOs whose strong coefficients are essentially localised on the central C_2S_6 core. These results also demonstrate that the crystal packing and the variety of weaker intermolecular interactions identified above (C–H···N, C–H···F hydrogen bonds, fluorine segregation, ...) are able to compete with the otherwise strongly favoured overlap interaction of the open shell molecules since they destabilise the classical bond-over-ring or eclipsed overlaps usually observed in TTF salts. In that respect, the confrontation of those donor molecules with other counter anions, of different size, shape and charge, is expected to offer a rich solid state chemistry. In particular, electrocrystallisation experiments with smaller anions such as $ICl_2{}^-$ or much larger ones such as $Mo_6Cl_{14}{}^{2-}$ are underway with the hope that the smaller anions might allow for stronger fluorine segregation effects.

Experimental

Synthesis

2 and **3** were prepared as previously described.[10] Both salts were obtained by slow diffusion in U-shape tubes of solutions of both donor and acceptor in the same solvent (10 mg in 1 mL), separated from each other by 1 mL of a less polar and heavier solvent. The couple CH_3CN–CH_2Cl_2 was used with **2**, CH_2Cl_2–$CHCl_2CH_2Cl$ (TCE) with **3**. (**2**)(TCNQF$_4$)·(TCE). Calc. (found) for $C_{25}H_{11}Cl_3F_6N_4S_8$: C, 35.75 (36.82); H, 1.31 (1.16); N, 6.64 (7.19); S, 30.38 (35.68)%. Note that the analysis reflects a TCE loss. IR (KBr): 2175, 2191 cm^{-1} (CN). (**3**)(TCNQF$_4$). Calc. (found) for $C_{21}H_6F_6N_4S_6$: C, 40.64 (40.62); H, 0.97 (1.06); N, 9.03 (8.99); S, 31.00 (30.79)%. IR (KBr): 2175, 2192 cm^{-1} (CN).

X-Ray crystallography

Table 4 summarises the data collection conditions and refinement results. Data were collected on a Stoe-IPDS diffractometer with Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 293(2) K. The structures were solved by direct methods and all atoms (except hydrogen atoms) refined anisotropically by full matrix least squares on F^2 using the SHELXL suite of programs.[22] Hydrogen atoms were placed at calculated positions (C_{sp^2}–H 0.93, C_{sp^3}–H 0.97 Å), included in structure factor calculations but not refined (riding model). Numerical absorption corrections based on crystal faces were applied for both structures.

CCDC reference numbers 156226 and 156227. See http://www.rsc.org/suppdata/nj/b0/b010099o/ for crystallographic data in CIF or other electronic format.

Magnetic measurements

Magnetic susceptibility data were collected on a Quantum Design MPMS5 SQUID magnetometer at 10000 G with polycrystalline samples of (**2**)(TCNQF$_4$)·TCE (11.07 mg) and

(**3**)(TCNQF$_4$) (13.46 mg). They were corrected for molecular diamagnetism and sample holder contributions.

Acknowledgements

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