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# One- or two-dimensional fluorine segregation in amphiphilic perfluorinated tetrathiafulvalenes

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## Abstract

A perfluorinated tetrathiafulvalene (TTF) derivative **1**, that is a bis(vinylenedithio)TTF substituted with  $-(CF_2)_3-$  chains on both ends, is prepared from the reaction of  $Na_2dmit$  ( $dmit$ : 1,3-dithiole-2-thione-4,5-dithiolate) with 1,2-dichlorohexafluorocyclopentene, oxymercuration of the obtained dithiolethione to the corresponding dithiolone and phosphite coupling. An unsymmetrical TTF **2** fused with only one hexafluorocyclopenta[1,2-b]1,4-dithiine moiety is also described together with the X-ray crystal structures and electrochemical properties of **1** and **2**. The amphiphilic character provided by the rigid  $-(CF_2)_3-$  moieties in **1** and **2** leads to a strong segregation of the aliphatic fluorinated moieties in the solid state, affording fluorinated columns or bilayer structural motifs. **To cite this article:** O. Jeannin, M. Fourmigué, C. R. Chimie 9 (2006).

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## Résumé

Un tétrathiafulvalène perfluoré **1** dérivé du bis(vinylènedithio)tétrathiafulvalène par substitution avec des fragments  $-(CF_2)_3-$  est préparé par réaction de  $Na_2dmit$  ( $dmit$ : 1,3-dithiole-2-thione-4,5-dithiolate) avec le 1,2-dichlorohexafluorocyclopentène, oxymercuration de la dithiolethione ainsi obtenue en dithiolone correspondante et couplage en présence de phosphite. Le dérivé dissymétrique **2** portant un seul groupement hexafluorocyclopenta[1,2-b]1,4-dithiine est également décrit, ainsi que les structures cristallines et propriétés électrochimiques de **1** et **2**. Le caractère amphiphile apporté par les groupements  $-(CF_2)_3-$  dans **1** et **2** conduit, à l'état solide, à une forte ségrégation des fragments aliphatiques perfluorés et à l'apparition de structures colonnaires ou en bicouches fluorées. **Pour citer cet article :** O. Jeannin, M. Fourmigué, C. R. Chimie 9 (2006).

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**Keywords:** Crystal engineering; Fluorine; Layered compounds; Tetrathiafulvalene

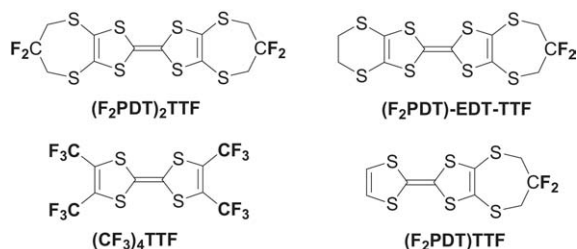
**Mots clés :** Ingénierie cristalline ; Fluor ; Composés lamellaires ; Tétrathiafulvalène

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## 1. Introduction

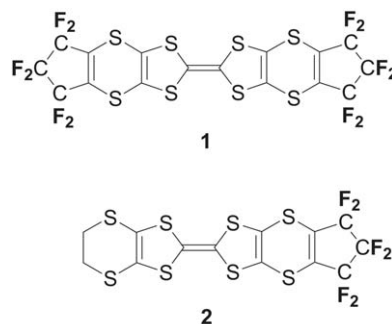
The control of solid state architectures of molecular organic solids through directional, strong intermolecular interactions such as hydrogen [1] or halogen [2] bonds forms the basis of supramolecular solid state chemistry [3], a very successful approach which has allowed a very fine control of supramolecular solid state architectures. On the other hand, in soft matter chemistry, amphiphilic molecules with a strong incompatibility between the different parts give rise to a variety of mesophase morphologies based on the segregation of hydrophilic vs. hydrophobic but also rigid vs. flexible fragments [4]. We wanted to take advantage of segregation effects of fluoroaliphatic groups, well known in soft-matter chemistry, in the realm of crystalline molecular materials as a tool to obtain controlled solid state organizations. For example, semifluorinated tetrathiafulvalenes (TTF) have been prepared for Langmuir–Blodgett films formation [5], while incorporation of highly fluorinated anions such as  $(CF_3)_3CF(CH_2)_2-SO_3^-$  in TTF salts also stabilized the formation of layered materials [6,7]. The very strong contrast offered by fluoroaliphatics in polymer science, biochemistry and soft matter chemistry let us infer that a limited number of  $CF_3$  or  $CF_2$  groups, rather than long  $C_{nF_{2n+1}}$  perfluoroalkyl chains, adequately positioned on the rigid core, could be sufficient to provide a segregation and formation of layered crystalline structures, also desirable in the structures of the neutral TTF-like donor molecules if one is interested in the design of crystalline thin films for transistor devices [8,9]. In that respect, we already described a series of TTF molecules [10,11] substituted with 2,2'-difluoropropylene-1,3-dithio groups such as  $(F_2PDT)_2TTF$ ,  $(F_2PDT)EDT-TTF$  or  $(F_2PDT)TTF$  where an effective segregation of the  $CF_2$  moieties led to the formation of layered structures with fluorinated bilayers. However, the presence of methylenic  $CH_2$  groups, activated by the neighboring S and  $CF_2$  moieties, did not allow to completely eliminate the possibility that these layers were also stabilized by additional  $C-H\cdots F$  hydrogen bonds.



On the other hand, the X-ray crystal structure of tetrakis(trifluoromethyl)TTF,  $(CF_3)_4TTF$  [12], exhibits a

one-dimensional pseudo-columnar arrangement with the outer surface of each stack is essentially covered with fluorine atoms. These examples demonstrate that the introduction of  $CF_3$  or  $CF_2$  moieties on the rigid TTF core can induce a molecular contrast strong enough to force a micro segregation of the fluorinated and aromatic moieties, but does not allow anticipating the formation of either layered or columnar structures.

We therefore decided to prepare the novel fluorinated TTF molecule **1**, based on the bis(vinylene-dithio)TTF (BVDT-TTF) capped here with two hexafluorotrimethylene  $-(CF_2)_3-$  chains, and lacking any activated hydrogen atoms which could interfere with the fluorine segregation effects in the formation of the supramolecular solid-state organization. We describe here the synthesis of **1** and the analogous, unsymmetrical TTF **2**, their electrochemical properties and the X-ray crystal structures of **1** and **2** together with those of intermediate perfluorinated 1,3-dithiole-2-thione and 1,3-dithiole-2-one derivatives.



## 2. Experimental

### 2.1. Synthesis

#### 2.1.1. General

Nuclear magnetic resonance spectra were recorded at 500.04 MHz for  $^1H$ , 470.28 MHz for  $^{19}F$  and 125.75 MHz for  $^{13}C$ . Mass spectrometry was performed in the MALDI-TOF or high-resolution modes as indicated. 1,2-Dichlorohexafluorocyclopentene was obtained from Aldrich.

#### 2.1.2. Synthesis of 6,7-dihydro-5H-hexafluorocyclopenta[b]-1,3-dithiole[4,5-e] [1,4] dithiin-2-thione **3**

4,5-Bis(benzoylthio)-2-thioxo-1,3-dithiole (7.4 g, 21.6 mmol) was added to a freshly prepared solution of sodium (1 g, 43.5 mmol) in freshly distilled MeOH (25 ml). After stirring for 20 min, the disodium salt was precipitated by addition of  $Et_2O$ , filtered and dissolved

in freshly distilled  $\text{CH}_3\text{CN}$  (100 ml). 1,2-Dichlorohexafluorocyclopentene (3.2 ml, 21.3 mmol) was added to this solution and the reaction stirred overnight. The solvents were evaporated and the solid residue washed with water ( $2 \times 250$  ml). The aqueous fraction is extracted with dichloromethane and the combined organic extracts are dried over  $\text{MgSO}_4$  and evaporated. The residue is chromatographed on silica gel with pentane elution to give **3** as yellow needles (5.04 g, 63%). Suitable crystals for X-ray studies are obtained by recrystallization in pentane. M.p.  $100^\circ\text{C}$ .  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $-110.97$  (t, 4F,  $^3J_{\text{FF}} = 1$  Hz);  $-127.25$  (quint., 2F,  $^3J_{\text{FF}} = 1$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $109.3$ – $115.41$  (m,  $\text{CF}_2\text{--CF}_2\text{--CF}_2$ );  $122.02$  (s,  $\text{S}_2\text{C}=\text{CS}_2$ );  $138.39$  (t of m.,  $\text{CF}_2\text{SC}=\text{CSCF}_2$ );  $209.94$  (s,  $\text{C}=\text{S}$ ). EI. HRMS: Calcd: 369.85078; Found: 369.8473. Anal. Calcd. for  $\text{C}_8\text{F}_6\text{S}_5$ , C: 25.94; Found, C: 25.48.

#### 2.1.3. Synthesis of 6,7-dihydro-5H-hexafluorocyclopenta[b]-1,3-dithiolo[4,5-e] [1,4] dithiin-2-one **4**

$\text{Hg}(\text{OAc})_2$  (3.61 g, 11.33 mmol) was added to a solution of **3** (2.1 g, 5.67 mmol) in a 3:1 chloroform/acetic acid mixture (200 ml). After 1-h stirring, the resulting suspension was filtered on celite<sup>®</sup> and washed with  $\text{CHCl}_3$  (250 ml). The filtrate was washed with a saturated solution of  $\text{NaHCO}_3$  ( $3 \times 200$  ml), with water ( $2 \times 300$  ml) and dried over  $\text{MgSO}_4$ . After evaporation, the crude product is chromatographed on silica gel with pentane/dichloromethane elution (1:1) to give **4** as a pale yellow powder (1.16 g, 58%). Suitable crystals for X-ray studies were obtained by recrystallization from pentane. M.p.  $84^\circ\text{C}$ .  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $-110.23$  (s, 4F),  $-127.25$  (s, 2F).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $109.7$ – $115.19$  (m,  $\text{CF}_2\text{--CF}_2\text{--CF}_2$ );  $113.81$  (s,  $\text{S}_2\text{C}=\text{CS}_2$ );  $137.97$  (t of multiplet,  $\text{CF}_2\text{SC}=\text{CSCF}_2$ );  $188.95$  (s,  $\text{C}=\text{O}$ ). EI. HRMS: Calcd: 353.87362; Found: 353.8764. Anal. Calcd. for  $\text{C}_8\text{F}_6\text{OS}_4$ , C: 27.12; Found, C: 26.86.

#### 2.1.4. Synthesis of TTF **1**

Dithiolone **4** (0.27 g, 0.76 mmol) was heated at  $100^\circ\text{C}$  in (*n*-BuO)<sub>3</sub>P (8 ml) for 30 min. After cooling, the orange precipitate was filtered and recrystallized in THF to yield **1** as orange crystals (0.14 g, 54%). Single crystals suitable for X-ray diffraction studies were obtained from a second recrystallization in THF. The very low solubility of the compound did not allow its NMR characterization. M.p.  $260^\circ\text{C}$ . MALDI-TOF MS: Calcd. 675.75, Found: 675.75. Anal. Calc for ( $\text{C}_{16}\text{F}_{12}\text{S}_8$ ): C: 28.40; Found: 27.88.

#### 2.1.5. Synthesis of TTF **2**

In  $\text{P}(\text{OEt})_3$ : The dithiolone **4** (0.2 g, 0.78 mmol) and 4,5-ethylenedithio-2-thioxo-1,3-dithiole **5** (0.17 g, 0.78 mmol) were heated at  $110^\circ\text{C}$  for 1 h in  $\text{P}(\text{OEt})_3$  (8 ml). TLC ( $\text{SiO}_2$  3:1 pentane/ $\text{CH}_2\text{Cl}_2$ ) of the reaction mixture shows the presence of at least seven compounds. Chromatography on silicagel (eluent 3:1 pentane/ $\text{CH}_2\text{Cl}_2$ ) afforded the expected dissymmetrical derivative **2** in small quantities (20 mg, 6.7%) together with some symmetrical BEDT-TTF. The product slowly crystallized in the eluent giving only a few orange plates suitable for X-ray diffraction studies.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.31 (s,  $\text{CH}_2$ ),  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-111.21$  (s, 4F),  $-127.37$  (s, 2F); MALDI-TOF MS Calcd. 529.80, Found: 529.69.

In  $\text{P}(\text{OMe})_3$ : The dithiolone **4** (0.66 g, 1.86 mmol) and 4,5-ethylenedithio-2-thioxo-1,3-dithiole **5** (0.40 g, 1.86 mmol) were heated to reflux in  $\text{P}(\text{OMe})_3$  (15 ml) for 1.5 h. Precipitation of an orange product occurred after 30 min and then rapidly dissolved giving a dark red solution. The mixture was concentrated and chromatographed on silica gel (eluent:  $\text{CH}_2\text{Cl}_2$ ). The first fraction was essentially a mixture of tetrakis (methylthio)TTF **7** and the unsymmetrical fluorinated TTF **6**. A second chromatography on silica gel with pentane elution removed some non-polar impurities while elution with a 1:1 pentane/ $\text{CH}_2\text{Cl}_2$  mixture yielded impure tetramethylthio-TTF **7** followed by a small amount of **6**, obtained as red plates after solvent removal. Data for **6**: M.p.  $154^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.43 (s, Me).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $-111.21$  (t, 4F,  $^3J_{\text{FF}} = 4.6$  Hz);  $-127$ , 33 (quint., 2F,  $^3J_{\text{FF}} = 4.6$  Hz). MALDI-TOF MS: Calcd: 531.81; Found: 531.61.

#### 2.2. Electrochemistry

Cyclic voltammetry experiments were performed in  $\text{CH}_2\text{Cl}_2$  solutions containing *n*-Bu<sub>4</sub>NPF<sub>6</sub> 0.05 M as electrolyte at a scan rate of  $100\text{ mV s}^{-1}$  with Pt working and counter electrode and  $\text{Ag}^+/\text{Ag}$  reference electrode. Ferrocene was used as internal reference.

#### 2.3. X-ray crystallography

Crystals were mounted on top of a thin glass fiber. Data were collected on a Stoe Imaging Plate Diffraction System (IPDS) or a Enraf-Nonius Kappa CCD with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The crystal data are summarized in Table 1. Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) by full-matrix

Table 1  
Crystallographic data

Compound	<b>4</b>	<b>3</b>	<b>2</b>	<b>1</b>
Formula	C <sub>8</sub> F <sub>6</sub> OS <sub>4</sub>	C <sub>8</sub> F <sub>6</sub> S <sub>5</sub>	C <sub>13</sub> H <sub>4</sub> F <sub>6</sub> S <sub>8</sub>	C <sub>16</sub> F <sub>12</sub> S <sub>8</sub>
Fw	354.32	370.38	530.64	676.64
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	6.9286(13)	4.8012(3)	6.7950(7)	6.9433(7)
<i>b</i> (Å)	8.3690(18)	16.1384(13)	9.4646(10)	11.5381(13)
<i>c</i> (Å)	10.171(2)	17.280(2)	15.8552(18)	27.453(3)
$\alpha$ (°)	91.44(3)	109.917(8)	96.055(13)	93.093(13)
$\beta$ (°)	97.74(3)	95.726(7)	102.053(13)	90.361(12)
$\gamma$ (°)	101.79(2)	91.305(7)	110.209(12)	93.860(13)
<i>V</i> (Å <sup>3</sup> )	571.2(2)	1250.2(2)	918.12(17)	2191.0(4)
<i>Z</i>	2	4	2	4
<i>d</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	2.060	1.968	1.919	2.052
Diffractometer	Stoe-IPDS	Siemens CCD	Stoe-IPDS	Stoe-IPDS
Temperature (K)	293(2)	293(2)	293(2)	293(2)
$\mu$ (mm <sup>-1</sup> )	0.897	0.979	1.028	0.923
$\theta$ -Range (°)	2.49–26.11	2.99–27.50	2.34–25.82	1.88–25.90
Measured reflections	5604	17 155	8953	21 422
Independent reflections	2086	5691	3289	7926
<i>R</i> <sub>int</sub>	0.0572	0.1413	0.0493	0.0395
<i>I</i> > 2 $\sigma$ ( <i>I</i> ) reflections	1718	2423	2261	5794
Abs. corr.	Multi-scan	Multi-scan	Multi-scan	Multi-scan
<i>T</i> <sub>max</sub> , <i>T</i> <sub>min</sub>	0.5352, 0.6870	0.7243, 1.0554	0.7163, 0.8006	0.7185, 0.7783
Refined par.	173	343	280	649
<i>R</i> ( <i>F</i> ), <i>I</i> > 2 $\sigma$ ( <i>I</i> )	0.0353	0.050	0.0346	0.0402
<i>wR</i> ( <i>F</i> <sup>2</sup> ), all	0.0928	0.1059	0.0883	0.1129
$\Delta\rho$ (e Å <sup>-3</sup> )	+0.30, -0.29	+0.33, -0.34	+0.29, -0.29	+1.02, -0.45

least-squares methods. Absorption corrections were applied for all structures. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined. The cif files have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (CCDC 293155–293158 for **3**, **4**, **2** and **1**, respectively) and can be obtained by contacting the CCDC (quoting the article details and the corresponding SUP numbers).

### 3. Results and discussion

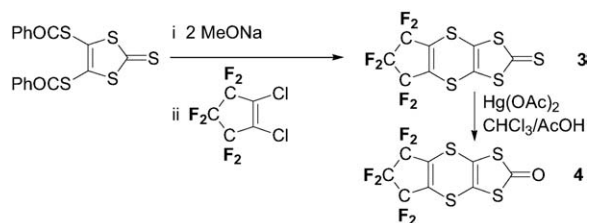
#### 3.1. Syntheses

The preparation of TTFs **1** and **2** is based on cross coupling reactions in phosphite medium of the corresponding perfluorinated dithiolone **4**. Reaction of 1,2-dichlorohexafluorocyclopentene with various thiolates (K<sub>2</sub>S [13], NaSAr) [14] is known to afford the corresponding thioethers in good yields. Accordingly (Scheme 1), we performed the reaction of bis(benzoylthio)-2-thioxo-1,3-dithiole with NaOMe to generate the dmit<sup>2-</sup> nucleophile which was further reacted with

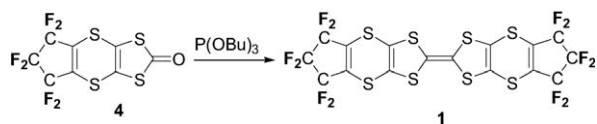
1,2-dichlorohexafluorocyclopentene in CH<sub>3</sub>CN to afford **3** in 63% yield. Oxymercuration with Hg(OAc)<sub>2</sub> in CHCl<sub>3</sub>/AcOH afforded the corresponding 1,3-dithiolone **4** in 58% yield.

The corresponding symmetrical perfluorinated TTF **1** was then obtained from **4** by a coupling reaction in tributylphosphite at 100 °C (Scheme 2), as a poorly soluble orange powder. The reaction time should be controlled carefully as the TTF **1**, which precipitates after 30 min, rapidly redissolves in P(OBu)<sub>3</sub> irreversibly to other products if reaction is not stopped at this stage. This surprising observation has been attributed to a rapid decomposition with elimination of the five-membered perfluorinated ring (see below).

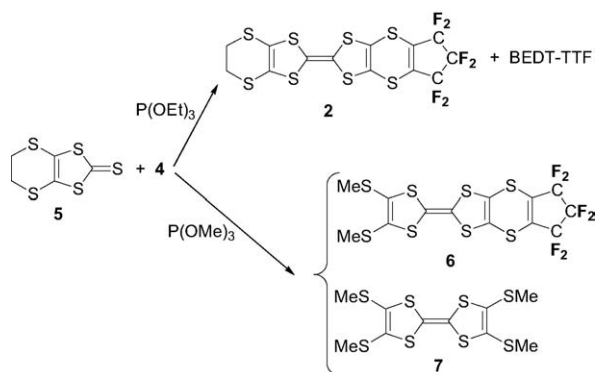
Attempts to prepare the unsymmetrical TTF **2** were performed in triethyl or trimethylphosphite in the presence of 1 eq. of 4,5-ethylenedithio-2-thioxo-1,3-dithiole (**5**) (Scheme 3). A limited amount of **2** was obtained in P(OEt)<sub>3</sub>, separated from some BEDT–TTF as symmetrical coupling product of **5**. On the other hand, reaction performed in P(OMe)<sub>3</sub> afforded a complex mixture where, to our surprise, TTFs **6** and **7**, bearing –SMe substituents, were isolated in low yields. The presence of **6** and **7** can only be understood from the decomposi-



Scheme 1.



Scheme 2.



Scheme 3.

tion of some symmetrical TTF **1** that was formed during the reaction of **4** on itself, followed by alkylation with  $\text{P(OMe)}_3$ . It demonstrates that the hexafluorocyclopentene ring is easily removed from **1** in the conditions of phosphite coupling. This process is most probably at the origin of (i) the rapid decomposition of **1** mentioned above and, (ii) the low yield obtained in the formation of **2**.

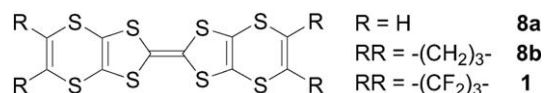
Nevertheless and despite the low yields obtained from those reactions, TTFs **1** and **2** could be characterized electrochemically and structurally, as described below.

### 3.2. Electrochemical properties

Cyclic voltammetry experiments were performed in  $\text{CH}_2\text{Cl}_2$  to determine the evolution of the redox potentials, particularly by comparison with non-fluorinated analogs such as **8a** [15] or **8b** [16] (Table 2). Despite the low solubility of the symmetrical derivative **1**, a cyclic voltammogram was obtained in  $\text{CH}_2\text{Cl}_2$

Table 2

Cyclic voltammetry data for **1–3** and reference compounds (in V vs. SCE). Values in parenthesis and italics are experimental values determined vs.  $\text{Fc}^+/\text{Fc}$



Compound	$E_{\text{ox}}^1$	$E_{\text{ox}}^2$	Solvent	References
<b>1</b>	0.85 (0.45)	1.09 (0.59, irr)	$\text{CH}_2\text{Cl}_2$	This work
<b>8a</b>	0.68	0.94	PhCN	[15]
<b>8b</b>	0.76	1.02	PhCN	[16]
<b>2</b>	0.64 (0.24)	1.08 (0.58)	$\text{CH}_2\text{Cl}_2$	This work
<b>6</b>	0.61 (0.21)	0.92 (0.52)	$\text{CH}_2\text{Cl}_2$	This work

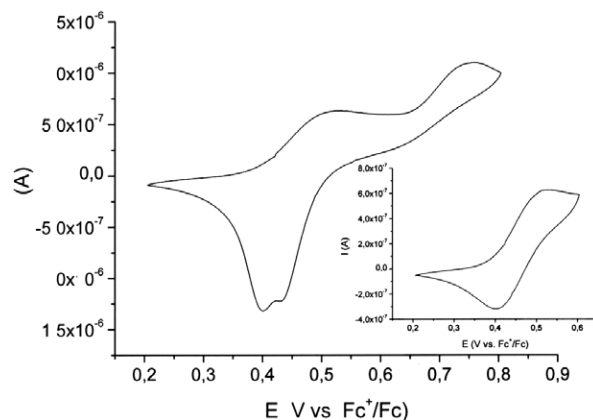


Fig. 1. Cyclic voltammogram of **1** (in V vs.  $\text{Fc}^+/\text{Fc}$ ). Scan limited to the first oxidation wave.

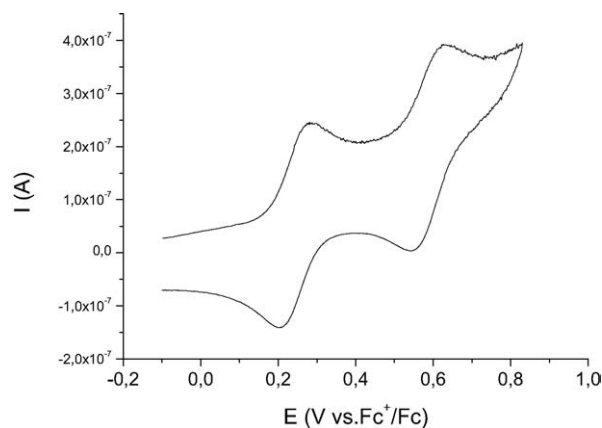


Fig. 2. Cyclic voltammogram of **2** (in V vs.  $\text{Fc}^+/\text{Fc}$ ).

(Fig. 1), exhibiting a first pseudo-reversible oxidation wave, followed by a second irreversible process.

On the other hand, the more soluble unsymmetrical derivatives **2** and **6** exhibit the two prototypical reversible waves of TTF derivatives (Fig. 2). As seen in

Table 2, the perfluorination of **8a** to **1** induces an anodic shift of the first oxidation potential ( $\Delta = +190$  mV), albeit this shift remains limited, when one compares for example the first oxidation potentials of TTF and the perfluorinated (F<sub>3</sub>C)<sub>4</sub>TTF [17] which oxidize at 0.33 and 1.05 V ( $\Delta = +720$  mV), respectively. This is a likely consequence of the larger distance to the redox core, furthermore through a folded dithiine ring.

### 3.3. Molecular and solid-state structures

Crystals of the dithiocarbonate **4** have been obtained from pentane. It crystallizes in the triclinic system, space group  $P\bar{1}$ , with one molecule in general position in the unit cell (Fig. 3). While the five-membered dithiole ring is essentially planar, the central six-membered dithiine ring is strongly folded along the S—S hinge by  $40.41(0.12)^\circ$ , a recurrent feature for this formally antiaromatic  $8e^-$  ring system. In the solid state, molecules associate pair wise through S...S van der Waals interactions between the planar dithiole fragments while the outer C<sub>3</sub>F<sub>6</sub> fragments segregate, giving rise to fluorinated layers parallel to the (*a*, *b*) plane, alternating with sulfur-rich layers along *c*.

The corresponding trithiocarbonate **3** also crystallizes in the triclinic system, space group  $P\bar{1}$  with now two crystallographically independent molecules A and B in the unit cell, which differ by the folding of the dithiine ( $49.14(0.12)^\circ$  and  $48.40(0.12)^\circ$ , respectively) and the hexafluorocyclopentene rings ( $19.65(10.36)^\circ$  and  $25.67(0.22)^\circ$ , respectively), both molecules adopting a chair conformation. Each of them forms homostacks AAA and BBB by translations along *a* (Fig. 4) Those columns associate in the (*bc*) plane by orienting their fluorinated face toward the fluorinated face of neighboring columns, affording again a striking segregated layered structure.

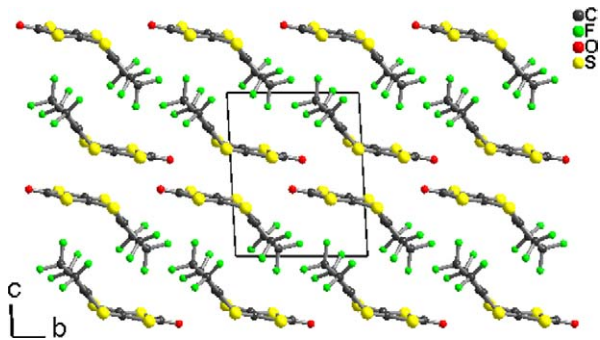


Fig. 3. Solid-state organization in **4**, showing the segregation of the fluorinated moieties.

The symmetrical TTF derivative **1** crystallizes in the triclinic system, space group  $P\bar{1}$  with two crystallographically independent molecules in the unit cell. Both molecules deviate strongly from planarity (Fig. 5), not only because of the dithiine rings as observed above in **3** and **4** but also because of the dithiole rings which experience a strong folding along the S—S hinge with angles as large as  $28.90(0.26)^\circ$ . Such folding distortions of the TTF core are not unusual and allow here for a mutual adaptation of both boat-like molecules in an almost eclipsed conformation with the shortest intermolecular S...S contacts ( $3.82$  Å) exceeding the sum of the van der Waals radii.

In the solid state, these dyadic moieties with large perfluorinated ends stack side-by-side along *a* and organize into a chessboard-like pattern in the (*bc*) plane (Fig. 6), delineating two different kinds of fluorinated zones alternating along the *c* direction, one of them giving rise to fluorinated bilayers parallel to the (*ab*) plane, the other limited to columns running along *a*. This original structural arrangement for neutral TTF

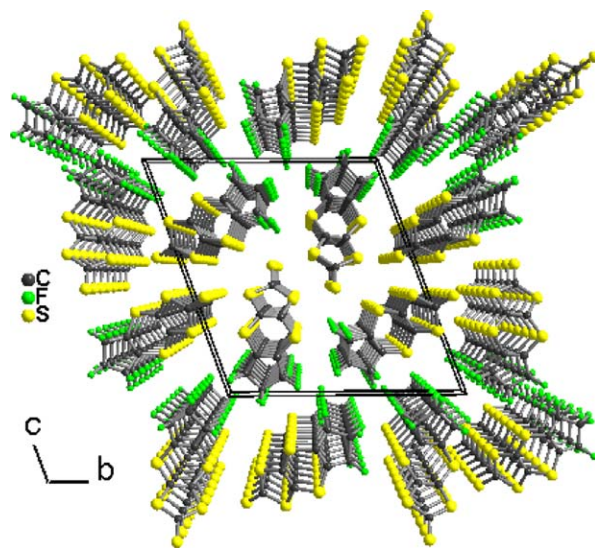


Fig. 4. Unit-cell projection view along *a* of the trithiocarbonate **3**.

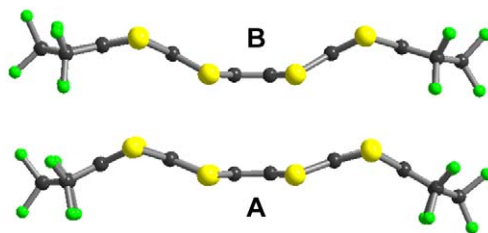


Fig. 5. The two crystallographically independent molecules (A and B) in **1**.

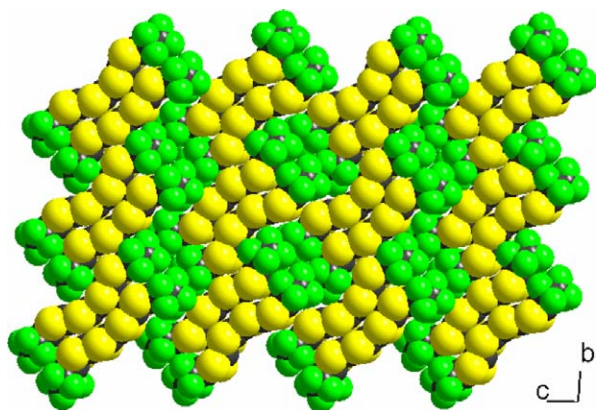


Fig. 6. Solid-state arrangement in the symmetrical TTF **1**.

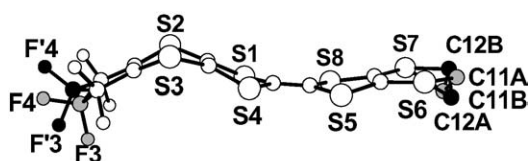


Fig. 7. View of **2** with the disordered difluoromethylene (left) and ethylene (right) moieties.

derivatives further illustrates the strong tendency of fluorinated aliphatic moieties to segregate in the solid state, without need for long  $C_nF_{2n+1}$  chains, usually used for this purpose [5,18].

This effect is also observed in the unsymmetrically substituted TTF **2**, characterized by two different ends, a  $-(CF_2)_3-$  fluorinated one and a  $-(CH_2)_2$  hydrogenated one. It crystallizes in the triclinic system, space group  $P\bar{1}$  with one molecule in general position in the unit cell. Both ends of the molecule are affected by disorder with (i) the ethylenic moiety found in two orientations (in black or gray in Fig. 7), with one carbon atom above and one below the molecular plane and (ii) the five-membered perfluorinated ring found in two conformations (in black or gray in Fig. 7). As observed in **1**, not only the dithiine ring exhibits a strong folding along the S(2)—S(3) hinge (by  $43.9(1)^\circ$ ) but also the two dithiole rings with folding angles of  $24.2(2)^\circ$  along S(1)—S(4) and  $17.9(2)^\circ$  along S(5)—S(8).

In the solid state, the molecules associate two by two to form slabs parallel to the  $(ab)$  plane, with again a strong segregation of the fluorinated moieties, despite the limited number of fluorine atoms when compared with the symmetrical molecule **1**. In that respect, the structure of **2** is reminiscent of that described for  $(F_2PDT)_2TTF$  [10], where a similar layered structure was observed, with stacks of TTF moieties most probably stabilized by  $S\cdots S$  van der Waals interactions to

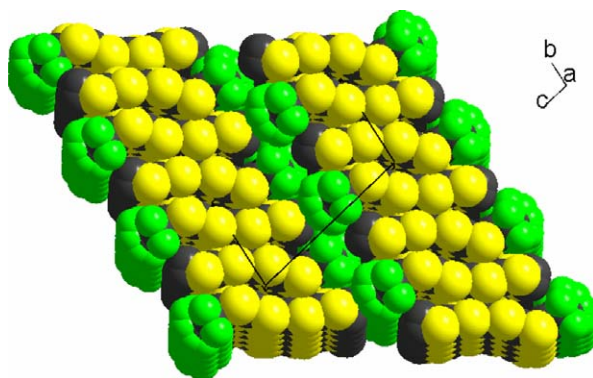


Fig. 8. Solid-state arrangement of **2**, showing the efficient fluorine segregation.

form slabs, separated from each other by the fluorous bilayer structure. The strong disorder described above, which affects both ends of the molecule, can be interpreted as a lack of structure-directing  $C-H\cdots F$  hydrogen bonds, contrariwise to the situation observed in  $(F_2PDT)_2TTF$  [10]. Note that this type of layered structures has proven very desirable for their use in field effect transistor (FET) devices [8,9] and the structure of **2** provides an attractive candidate for this application (Fig. 8).

#### 4. Concluding remarks

Novel, highly fluorinated TTF derivatives have been prepared by an original method, however limited by the high thermal instability of the hexafluorocyclopentene ring when linked to 1,2-dithiolate moieties. While the low solubility of the symmetrical perfluorinated TTF **1** precluded any possible electrocrystallization experiments [19], the lower oxidation potential and higher solubility of **2** and **6** provides new opportunities for growing single crystals of mixed valence conducting materials. Those experiments are currently in progress, particularly in the presence of organic fluorinated anions [6,7].

#### 5. Supplementary information available

Crystallographic data of **1–4** as cif files. They can also be obtained from the Cambridge Crystallographic Data Center, 12 Union road, Cambridge CB2 IEZ, UK (fax: +44 1223 33 6033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)) as supplementary publication on quoting the depository number, No. CCDC 293155–293158 for **3**, **4**, **2** and **1**, respectively.

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## References

- [1] G.A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer Verlag, Berlin & Heidelberg, 1991.
- [2] (a) J.P.M. Lommerse, A.J. Stone, R. Taylor, F.H. Allen, *J. Am. Chem. Soc.* 118 (1996) 3108; (b) P. Metrangolo, G. Resnati, *Chem. Eur. J.* 7 (2001) 2511; (c) R. S. Walsh, C.W. Padgett, P. Metrangolo, G. Resnati, T.W. Hanks, W.T. Pennington, *Cryst. Growth Des.* 1 (2001) 165.
- [3] (a) G.R. Desiraju, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2311; (b) G.R. Desiraju, in: *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; (c) J.L. Atwood, J.-M. Lehn, J.E.D. Davies, D.D. MacNicol, F. Vogtle, *Comprehensive Supramolecular Chemistry: 11-Volume Set*, Pergamon Press, 1996.
- [4] C. Tschierske, *J. Mater. Chem.* 11 (2001) 2647.
- [5] C. Mingotaud, B. Agricole, T. Nozdryn, J. Cousseau, A. Gorgues, P. Delhaes, *Thin Solid Films* 300 (1997) 228.
- [6] U. Geiser, J.A. Schlueter, A. Kini, H.H. Wang, B.H. Ward, J. Mohtasham, G.L. Gard, *Synth. Met.* 133–134 (2003) 401.
- [7] U. Geiser, J.A. Schlueter, *Chem. Rev.* 104 (2004) 5203.
- [8] (a) M. Mas-Torrent, M. Durkut, P. Hadley, X. Ribas, C. Rovira, *J. Am. Chem. Soc.* 126 (2004) 984; (b) S. T. Bromley, M. Mas-Torrent, P. Hadley, C. Rovira, *J. Am. Chem. Soc.* 126 (2004) 6544.
- [9] J.-I. Naraso, S. Nishida, J. Ando, K. Yamaguchi, H. Itaka, H. Koinuma, S. Tada, Y. Tokito, Yamashita, *J. Am. Chem. Soc.* 127 (2005) 10142.
- [10] O.J. Dautel, M. Fourmigué, *J. Org. Chem.* 65 (2000) 6479.
- [11] O.J. Dautel, M. Fourmigué, E. Canadell, *Chem. Eur. J.* 7 (2001) 2635.
- [12] S. Mono, H. Pritzkow, W. Sundermeyer, *Chem. Ber.* 126 (1993) 2111.
- [13] C.G. Krespan, D.C. England, *J. Org. Chem.* 33 (1968) 1850.
- [14] M. Matsui, M. Tsuge, K. Funabiki, K. Shibata, H. Muramatsu, K. Hirota, M. Hosoda, K. Tai, H. Shiozaki, M. Kim, K. Nakatsu, *J. Fluorine Chem.* 97 (1999) 207.
- [15] T. Nogami, K. Inoue, T. Nakamura, S.-I. Iwasaka, H. Nakano, H. Mikawa, *Synth. Metals* 19 (1987) 539.
- [16] V. Khodorkovsky, A. Edzifna, O. Neilands, *J. Mol. Electronics* 5 (1989) 33.
- [17] H. Müller, A. Lerf, H.P. Fritz, *Liebigs Ann. Chem.* (1991) 395.
- [18] (a) A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Siringhaus, T.J. Marks, R.H. Friends, *Angew. Chem. Int. Ed.* 39 (2000) 4547; (b) A. Facchetti, M. Mushrush, H.E. Katz, T.J. Marks, *Adv. Mater.* 15 (2003) 33; (c) A. Facchetti, J. Letizia, M.-H. Yoon, M. Mushrush, H.E. Katz, T.J. Marks, *Chem. Mater.* 16 (2004) 4715; (d) A. Facchetti, M. Mushrush, M.-H. Yoon, G.R. Hutchison, M.A. Ratner, T.J. Marks, *J. Am. Chem. Soc.* 126 (2004) 13859.
- [19] P. Batail, K. Boubekeur, M. Fourmigué, J.-C.P. Gabriel, *Chem. Mater.* 10 (1998) 3005.