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Tetrathiafulvalenyl-acetylacetonate complexes of difluoroboron

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ABSTRACT

A series of tetrathiafulvalene (TTF) derivatives functionalized by one or two β-diketonatoboron difluoride groups were synthesized through the addition of borontrifluoride to TTF substituted by one or two acetylacetone functions. The influence of the β-diketonatoboron difluoride moiety on the redox properties of the TTF has been investigated by cyclic voltammetry.

1. Introduction

For more than three decades, tetrathiafulvalene (TTF) and its derivatives have focused a lot of attention as precursors of molecular conductors.[1] As these observed properties are the results of interacting TTF radical ion species, numerous functionalization of this electroactive TTF framework has been realized with the aim of generating increased interactions.[1] Within this frame, a very active and recent research area trends towards the elaboration of TTF functionalized by coordination function due to strong potentialities of this type of electroactive ligand.[2] Accordingly, we recently investigated the synthesis of acetylacetone substituted TTF either connected through a sulfur atom to the donor core[3] or directly linked to the TTF moiety.[4] These acetylacetone TTF derivatives have shown their efficiency for the generation of β-diketonate ions, which form stable chelate complexes with various transition metal derivatives such as Zn, Ni, Mn and Cu.[2–4,5,6,7] Moreover, TTF substituted by a thioacetylacetone substituent can also be transformed into another electroactive pyrazole ligand, which forms stable complexes with Re.[8] In continuation of our studies on acetylacetonate TTF, we investigated the chelating ability of this ligand towards difluoroboron moiety. This work was motivated by the fact that β-diketonate complexes of boron difluorides are known as potential electron-transporting materials[9] and to the best of our knowledge no association of the TTF electroactive core with this type of complex has been reported so far. Moreover, it has been observed also that C–H···F hydrogen bonding between two neighbouring molecules plays an important role in the self assemblies of such complexes.[10] Herein, we report the synthesis of a series of β-diketonatoboron difluoride TTF together with the electrochemical investigations carried out on these derivatives to study the influence of the BF_2 moiety on the donating ability of the TTF core. In addition, the structural properties of a β-diketonate BF_2 complex are presented.

2. Results and discussion

In order to synthesize substituted TTF two main strategies are often followed. The first one consists in preparing the functionalized precursors and then to form the TTF skeleton essentially by self-coupling of these precursors while the second approach requires the formation of the TTF core and then the functionalization.[11] Therefore, in order to prepare the TTF functionalized by a β-diketonate complex of difluoroboron, we investigated first the synthesis of the corresponding moiety, the dithiole-2-thione, as this type of derivative is known to be excellent precursor of TTF.[11] For that purpose, we used the dithiole-2-thione **1**[12] bearing a cyanoethylthio-protected group as starting material (Scheme 1). The cyanoethyl group can be easily removed in the presence of $CsOH·H_2O$[13] and the free thiolate can be further alkylated with 3-chloropentane-2,4-dione to give in good yield the dithiole **2**. The corresponding difluoroboron complex **3** was prepared by adding an excess of borontrifluoride diethyletherate ($BF_3·OEt_2$) to a solution of dithiole **2** in dichloromethane. According to the same synthetic strategy, we also prepared the corresponding dithiol-2-ones **4**–**6**, thanks to the conversion of the dithiole-2-thione **1** into the corresponding dithiole-2-one **4** by treating **1** with $Hg(OAc)_2$ in the presence of CH_3CO_2H (Scheme 1).

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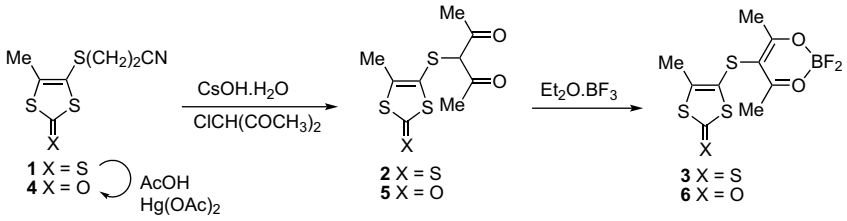


Scheme 1.

Single crystals of the difluoroboron complex **3** were obtained, suitable for X-ray structure analysis. The ORTEP diagram of **3** is shown in Figure 1 and selected bond lengths and distances are listed in figure caption. As seen in Figure 1, the dithiole ring is planar while the dioxaborine cycle is not planar. Indeed the dioxaborine cycle exhibits a boat conformation with a plane formed by C(12)–O(15)–O(14)–C(10) and the cycle is puckered along the O14···O15 vector and the C(12)···C(10) one with angles of about 33° and 11°, respectively. Therefore this distorted structure strongly differs either from the one observed for diphenyl,[14] dipyrrole[15] or disymetrically[16] substituted derivative where the dioxaborine cycles are planar or from the quasi planar structure observed for the difluoroborondimethylacetonate.[17] Within this cycle in **3** the carbonyl bond lengths are of similar value as well as the C–C bond lengths. These C–O and C–C bond distances are of comparable value with those observed in the thioacetylacetone moiety of the TTFSacacH **7b** where the H atom is shared symmetrically with the O atoms with a complete π-delocalization (C–O: 1.284(4), 1.299(5) and C–C: 1.410(5), 1.406(5)).[3b] Moreover this dithiole **3**, in the solid state, forms supramolecular network due to weak intermolecular C–H···F–B interactions between C(13)–H···F(17) 2.799(2) Å and C(5)–H···F(17) 2.728(1) Å, which are shown in Figure 2.[18]

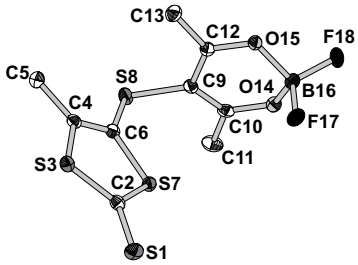


Figure 1. ORTEP diagram of dithiole **3**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 50% probability. Selected bond lengths (Å): C(9)–C(10) 1.407(3), C(9)–C(12) 1.401(3), C(10)–O(14) 1.294(2), C(12)–O(15) 1.291(2), O(14)–B(16) 1.495(2), O(15)–B(16) 1.502(2), B(16)–F(17) 1.373(2), B(16)–F(18) 1.363(2).

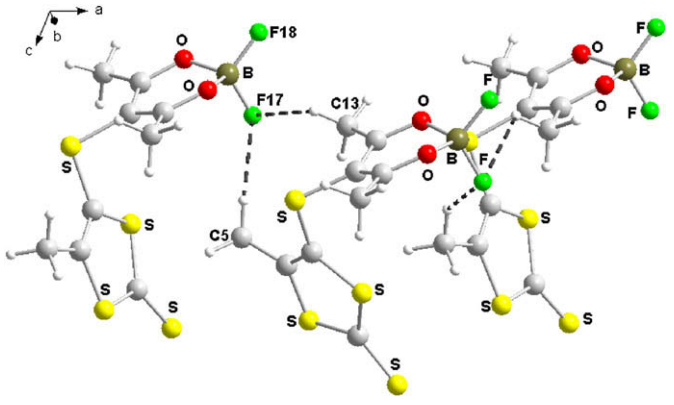
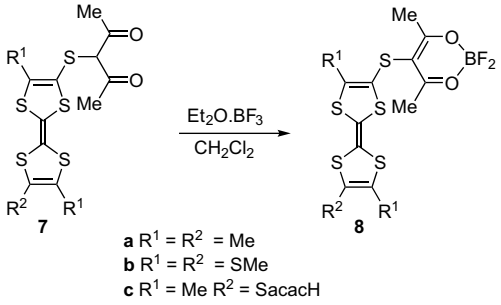


Figure 2. View of the weak intermolecular C–H···F–B interactions.

All the attempts to realize the TTF skeleton through the phosphite coupling of the dithiole-2-thione **2** and **3** were unsuccessful as well as with the dithiol-2-ones **5** and **6**. Therefore, we choose the second approach to form the TTF β-diketonate difluoroboron complexes, which consists in chelating the difluoroboron in the last synthetic step. First, we realized the acetylacetone functionalized TTF **7a–c**[3] and then we added an excess of $BF_3{\cdot}OEt_2$ to a CH_2Cl_2 solution of these TTF **7a–c** under inert atmosphere (Scheme 2). TTF **8c**, as TTF **7c**, was obtained as a mixture of two isomers, cis and trans, which could not be separated upon chromatography.

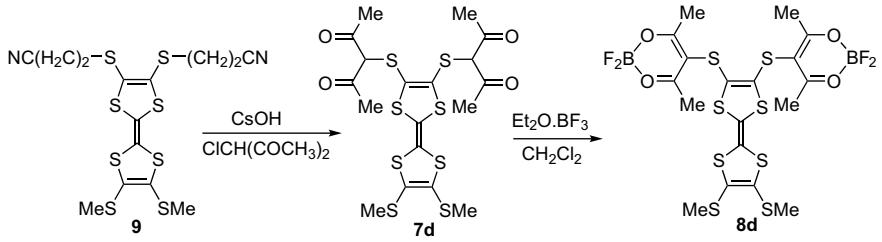


Scheme 2.

We also prepared the bis substituted TTF **7d**, where the two SacacH groups are located on the same dithiole ring, using bis-(cyanoethylthio)-bis(methylthio)TTF **9**[19] as precursor (Scheme 3). The two thiolate groups can be easily recovered by treating TTF **9** with 2 equiv of $CsOH{\cdot}H_2O$ and then further alkylated with 3-chloropentane-2,4-dione to give TTF **7d**. Addition of an excess of borontrifluoride diethyletherate ($BF_3{\cdot}OEt_2$) to a solution of TTF **7d** in dichloromethane affords TTF **8d**. The target molecules **8a–d** are obtained as air stable derivatives after purification by column chromatography on silica gel.

The influence of the difluoroboron moiety on the electron donating ability of these TTFs **8a–d** was analyzed by cyclic voltammetry. They all exhibit two reversible monoelectronic oxidation waves, a typical redox behaviour for TTF. The oxidation potentials are collected in Table 1 together with the oxidation potentials of the TTF precursors **7a–d**. As seen in Table 1, when passing from the acetylacetone substituent in TTFs **7a–d** to the diketonate difluoroboron complex in TTF **8a–d** the oxidation potentials are shifted towards more positive potentials indicating the electron withdrawing effect of the dioxaborine cycle on the TTF core. Also, in all the cases the potential difference between the second and the first oxidation potential is decreased. It is worth noting that on cathodic scan no reduction process was observed as in the case *tert*-butyl borondifluoridediketonate[18] or with bis(dioxaborine)fluorene derivatives.[20]

We also investigated the synthesis of vinylogous TTF (TTFV) substituted by two thioacetylacetone groups. This was realized starting from TTFV **10** substituted by two cyanoethylthio-protected thiolate groups (Scheme 4).[12] Treatment of **10** with $CsOH{\cdot}H_2O$

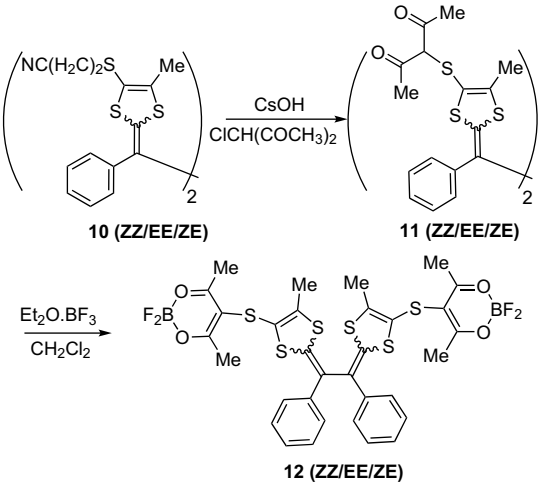


Scheme 3.

Table 1
Oxidation potentials of the TTFs **7a–d** and TTFs **8a–d**, *E* in V versus SCE, Pt working electrode with 0.1 M *n*-Bu_4NPF_6 scanning rate100 mV s^{-1}

compound	E^1	E^2	ΔE
7a	0.33	0.78	450
8a	0.42	0.86	440
7b	0.52	0.83	310
8b	0.58	0.88	300
7c	0.48	0.87	390
8c	0.57	0.91	340
7d	0.55	0.85	300
8d	0.64	0.91	270
11	0.32	0.45	130
12	0.47	0.55	80

allowed the deprotection of the two thiolate functions, which are further alkylated with 3-chloropentane-2,4-dione. According to this strategy, **11** was obtained in 80% yield as a mixture of three isomers (*ZZ*/*EE*/*ZE*), which are observed on ^{1}H NMR spectra but could not be separated by column chromatography. Addition of an excess of $BF_3\cdot OEt_2$ to a solution of **11** in CH_2Cl_2 allowed us to isolate TTFV **12** also as a mixture of three isomers. The analysis of these two TTFV **11**–**12** by cyclic voltammetry shows that they exhibit two close reversible monoelectronic oxidation waves (Table 1). The electron withdrawing effect of the dioxaborine ring can be observed here by a positive shift of the oxidation potentials and also by the decrease of the oxidation potential difference between the first and the second oxidation potentials (Table 1). A significant decrease of the ΔE and a stronger enhancement of E^1 between TTFV **11** and **12** are observed compared to the other TTF derivatives (Table 1). This redox behaviour has its origin in the fact that, for all TTFV, molecular movements are concerted with electron transfer, which induces a compression of potentials especially when increasing the withdrawing strength of the substituent.[21]



Scheme 4.

It is worth mentioning that β-diketonatoboron difluoride complexes are known to exhibit interesting spectroscopic features, such as high molar absorptivity and fluorescence intensities.[22] However, it should be pointed out that only the boron difluoride complexes with aromatic structure, like dibenzoyl(methano)boron difluoride, exhibited such characteristics while the complex of acetylacetonate gave no fluorescence.[22] Nevertheless, being aware that structural parameters might modify such emissive properties, we investigated the various β-diketonatoboron difluoride TTFs, the oxidized TTFs (**8a–c**)(PF_6), generated by the addition of 1 equiv of $NOPF_6$ to a solution of TTF **8a–c** and dithiole derivatives prepared but none of them shows fluorescence when excited at the wavelength of the absorption maximum.

3. Conclusion

In summary, we prepared a series of β-diketonatoboron difluoride dithioles and TTF derivatives by adding in the last synthetic step the Lewis acid reagent. Even if none of this compound exhibits fluorescence properties, we demonstrated the feasibility of this approach in order to reach β-diketonatoboron difluoride TTF derivatives. Future investigations will be devoted to the synthesis of TTF substituted by aromatic β-diketonatoboron difluorides in order to observe fluorescence properties, which could be modulated by the redox state of the TTF.

4. Experimental section

4.1. General

^{1}H NMR, ^{13}C NMR and ^{11}B spectra were recorded on a Bruker Avance 300 III spectrometer with tetramethylsilane as internal reference. Chemical shifts are reported in parts per million. Mass spectra and elemental analysis results were performed by the Centre de Mesures Physiques de l'Ouest, Rennes. Melting points were measured using a Kofler hot stage apparatus and are uncorrected. Cyclic voltammetry was carried out on a 10^{-3} M solution of the compounds in dichloromethane, containing 0.1 M *n*-Bu4NPF6 as supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} on a platinum disk electrode (A=1 mm^2). The potentials were measured versus Saturated Calomel Electrode.

4.2. Synthesis

*4.2.1. 3-[(5-Methyl-2-thioxo-1,3-dithiol-4-yl)thio]pentane-2,4-dione (**2**)*

To a solution of cyanoethylthiodithiole-2-thione **1** (230 mg, 1 mmol) in 10 mL of DMF was added under argon a solution of $CsOH\cdot H_2O$ (180 mg, 1.1 mmol) in 3 mL of MeOH. The mixture was allowed to stir for 2 h at rt after which 3-chloropentane-2,4-dione (0.125 mL, 1.1 mmol) was added. The reaction mixture was stirred for 5 h and then the solvents were evaporated. The residue was extracted with CH_2Cl_2 and washed 2×20 mL with water. The organic layer was dried over $MgSO_4$ and evaporated. Chromatography

over silica gel using CH_2Cl_2 as eluent afforded **2** as a brown powder, yield 60%, mp=115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (s, 3H, CH_3), 2.43 (s, 6H, CH_3), 17.16 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 24.7, 102.7, 131.8, 135.8, 197.4, 210.4; HRMS calcd for $C_9H_{10}O_2S_4$: 277.95637, found: 277.95637.

*4.2.2. Difluoroboron dimethyldiketonate dithiole (**3**)*

An excess of $BF_3{\cdot}OEt_2$ (0.8 mL, 10 mmol) was added to a solution of dithiole **2** (116 mg, 0.5 mmol) in 5 mL of dry and degassed CH_2Cl_2 under inert atmosphere. The reaction mixture was stirred at rt for 3 h. The organic phase was washed with water 2×20 mL and dried over $MgSO_4$. The dithiole **3** was obtained as a yellow powder after column chromatography using CH_2Cl_2 as eluent in 66% yield, mp=148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 2.66 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 24.7, 105.2, 127.0, 140.0, 197.1(t, J^3_{CF}=1.5 Hz), 209.2; ^{11}B NMR (96 MHz, $CDCl_3$) δ −0.61; UV–vis (CH_2Cl_2) λ=379 nm (ε=11,860 L mol^{-1} cm^{-1}), 287 (ε=9700 L mol^{-1} cm^{-1}), 237 (ε=6830 L mol^{-1} cm^{-1}); HRMS calcd for $C_9H_9O_2F_2BS_4$: 325.9546, found: 325.9562.

*4.2.3. 3-[(5-Methyl-2-oxo-1,3-dithiol-4-yl)thio]propanenitrile (**4**)*

To a solution of dithiole-2-thione **1** (2.24 g, 9.6 mmol) in 10 mL of $CHCl_3$ was added 4 mL of CH_3CO_2H and $Hg(OAc)_2$ (8 g, 25 mmol). The reaction mixture was stirred for 2 h at rt and then filtered on short Celite column, which was washed with 30 mL of $CHCl_3$. The organic phase was washed 2×30 mL with water, then with a saturated solution of $NaHCO_3$ (30 mL) and with 30 mL of water. The organic phase was dried over $MgSO_4$ and then the solvent was removed under reduced pressure. The residue was chromatographed over silica gel using Et_2O/pretoleum ether as eluent (50/50). The dithiole-2-one was obtained as a yellow oil in 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H, CH_3), 2.70 (t, 2H, CH_2), 2.99 (t, 2H, CH_2); ^{13}C NMR (75 MHz, CD_3Cl) δ 15.8, 18.5, 31.6, 116.0, 117.4, 138.5, 189.7. Anal. Calcd for $C_7H_7NOS_3$: C, 38.69; H, 3.25; N. 6.44. Found: C, 38.82; H, 3.24; N. 6.45.

*4.2.4. 3-[(5-Methyl-2-oxo-1,3-dithiol-4-yl)thio]pentane-2,4-dione (**5**)*

Similar procedure as the one described above for the synthesis of dithiole **2** using dithiole **4** (1.43 g, 6.6 mmol) as starting material, $CsOH{\cdot}H_2O$ (1.2 g, 7.2 mmol) and 3-chloro-2,4-pentanedione (7.2 mmol, 0.82 mL). The dithiole **5** was obtained in 53% yield as a light pink powder, mp=74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H, CH_3), 2.42 (s, 6H, CH_3), 17.1 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 24.7, 102.9, 121.7, 126.2, 189.7, 197.4. Anal. Calcd for $C_9H_{10}O_3S_3$: C, 41.20; H, 3.84. Found: C, 41.28; H, 3.89.

*4.2.5. Difluoroboron dimethyldiketonate dithiole-2-one (**6**)*

Similar procedure as the one described above for the synthesis of dithiole **3** using dithiole **5** (1.26 g, 1 mmol) as starting material. The dithiole **6** was obtained in 43% yield as a white powder, mp=146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 2.66 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.3, 24.6, 105.4, 117.9, 130.5, 188.4, 197.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ 0.06. Anal. Calcd for $C_9H_9O_3F_2BS_3$: C, 34.85; H, 2.92; S, 31.01. Found: C, 35.07; H, 2.85; S, 31.51.

*4.2.6. Synthesis of TTF(acacH) (**7d**)*

To a solution of biscyanoethylthio bis(methylthio)-TTF (460 mg, 1 mmol) in 8 mL of DMF was slowly added under argon a solution of $CsOH{\cdot}H_2O$ (370 mg, 2.2 mmol) in 3 mL of MeOH. The mixture was allowed to stir for 5 h at rt after which 3-chloro-2,4-pentanedione (0.25 mL, 2.2 mmol) was added. The reaction mixture was stirred for 3 h at rt and the solvents were removed in vacuo. The resulting oil was extracted with CH_2Cl_2, the organic phase was washed with water 3×20 mL, dried over $MgSO_4$ and chromatographed over silica using CH_2Cl_2/PE (2/1) as eluent to afford TTF **7d** (620 mg, 68%) as a dark-red powder. Mp=142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 6H, CH_3), 2.49 (s, 12H, CH_3), 17.23(s, 2H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 24.9, 102.4, 108.6, 111.6, 122.7, 127.5, 197.4; IR ν C=O=1556, 1417 cm^{-1}.

*4.2.7. General procedure for the synthesis of TTF(acacBF$_2$) (**8**)*

To a solution of TTF(acacH) **7** (0.5 mmol) in dried and degassed CH_2Cl_2 (15 mL), under inert atmosphere, was added $BF_3{\cdot}OEt_2$ (10 mmol) and the resulting solution was stirred at rt for 3 h. The organic phase was washed with water 2×20 mL and dried over $MgSO_4$. The solvent was removed and the residue was purified by silica gel column chromatography using Et_2O as eluent. Al the TTF β-diketonate complexes of difluoroboron were obtained as red powders.

$Me_3TTFS(acacBF_2)$ (**8a**): yield 90%, mp=200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 6H, CH_3), 2.19 (s, 3H, CH_3), 2.65 (s, 6H, CH_3); ^{11}B NMR (96 MHz; $CDCl_3$) δ −0.56; HRMS calcd for $C_{14}H_{15}O_2F_2BS_5$: 423.97368, found: 423.9730. Anal. Calcd for $C_{14}H_{15}O_2F_2BS_5$: C, 39.62; H, 3.56; S, 37.78. Found: C, 39.48; H, 3.60; S, 38.16.

$(MeS)_3TTFSacacBF_2$ (**8b**): yield 56%, mp=154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.67 (s, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 19.4, 24.9, 105.4, 108.1, 113.6, 125.1, 126.7, 126.8, 128.1, 196.9; ^{11}B NMR (96 MHz, $CDCl_3$) δ −0.55; UV–vis (CH_2Cl_2) λ=283 nm (ε=21,650 L mol^{-1} cm^{-1}); HRMS calcd for $C_{14}H_{15}O_2F_2BS_8$: 519.8898, found: 519.8936. Anal. Calcd for $C_{14}H_{15}O_2F_2BS_8$: C, 32.30; H, 2.90 Found: C, 31.94; H, 2.79.

$(Me)_2TTF(SacacBF_2)_2$ (**8c**): yield 39%, mp=246 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 6H, CH_3), 2.64 (s, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 24.7, 109.3, 115.1, 127.1, 131.9, 133.5, 196.7; ^{11}B NMR (96 MHz, $CDCl_3$) δ −0.57; UV–vis (CH_2Cl_2) λ=320 nm (ε=16,070 L mol^{-1} cm^{-1}), 292 (ε=25,300 L mol^{-1} cm^{-1}); HRMS calcd for $C_{18}H_{18}O_4F_4B_2S_6$: 587.9651, found: 587.9639.

$(MeS)_2TTF(SacacBF_2)_2$ (**8d**): yield 30%, mp=196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 6H, CH_3), 2.72 (s, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 24.9, 104.4, 122.7, 127.4, 127.6, 133.5, 197.0; ^{11}B NMR (96 MHz, $CDCl_3$) δ −0.55; UV–vis (CH_2Cl_2) λ=291 nm (ε=28,550 L mol^{-1} cm^{-1}); HRMS calcd for $C_{18}H_{18}O_4F_4B_2S_8$: 651.9093, found: 651.9080.

*4.2.8. Synthesis of TTFV(SacacH)$_2$ (**11**)*

To a solution of TTFV **10** (650 mg, 1.1 mmol) in 25 mL of DMF was added under argon a solution of $CsOH{\cdot}H_2O$ (1.5 g, 8.8 mmol) in 3 mL of MeOH. The mixture was allowed to stir for 3 h at rt after which 3-chloropentane-2,4-dione (0.51 mL, 4.4 mmol) was added. The reaction mixture was stirred for 3 h and then the solvents were evaporated. The residue was extracted with CH_2Cl_2 and washed 2×20 mL with water. The organic layer was dried over $MgSO_4$ and evaporated. Chromatography over silica gel using CH_2Cl_2/ethylacetate (4/1) as eluent afforded **11** as a yellow powder, yield 80%, mp=80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.10 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 7.20–7.44 (m, 10H, Ar), 17.1 (m, 2H, OH); HRMS calcd for $C_{32}H_{30}O_4S_6$: 670.0468, found: 670.0521. Anal. Calcd for $C_{32}H_{30}O_4S_6$: C, 57.28; H, 4.51; S, 28.67. Found: C, 56.52; H, 4.58; S, 28.67.

*4.2.9. Synthesis of TTFV(SacacBF$_2$)$_2$ (**12**)*

Similar procedure as the one described above for the synthesis of TTF **8**. TTFV **12** was obtained as a brown powder in 34% yield; mp=65 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 6H, CH_3), 2.66 (s, 12H, CH_3), 7.15–7.35 (m, 10H, Ar), 17.1 (m, 2H, OH); ^{11}B NMR (96 MHz; CD_3Cl) δ −0.58. Anal. Calcd for $C_{32}H_{28}B_2F_4O_4S_6$: C, 50.13; H, 3.68. Found: C, 49.75; H, 3.55.

4.3. Molecular structure

Single-crystal diffraction data were collected on APEXII, Bruker-AXS diffractometer (Centre de diffractométrie X, Université de

Rennes, France). Crystal data and structure refinement parameters for compound **3** ($C_9H_9BF_2O_2S_4$): M=326.21, Mo Kα radiation (λ=0.71073 Å), T=100(2) K; monoclinic $P21/a$, a=10.4729(14), b=10.0048(12), c=13.6070(17) Å, β=109.196(6)°, V=1346.5(3) Å^3, Z=4, d=1.609 g cm^{-3}, μ=0.716 mm^{-1}. The structure was solved by direct methods using the SIR97 program,[23] and then refined with full-matrix least-square methods based on F^2 (SHELX97)[24] with the aid of the WINGX program.[25] All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were finally included in their calculated positions, with starting position extracted from maxima in difference electron density maps (HFIX 137). A final refinement on F^2 with 3040 unique intensities and 166 parameters converged at $\omega R(F^2)$=0.0765 ($R(F)$=0.032) for 2897 observed reflections with $I>2\sigma(I)$. The X-ray crystallographic data for **3** have been deposited, as supplementary publication number CCDC 725800 at the Cambridge Crystallographic Data. Copies of the data can be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk.

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