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Synthesis of new hydroxylated mono and bis-tetrathiafulvalenes: Electrochemical behaviour, X-ray analysis and conductivity

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Series of unsymetrical and judiciously functionnalized tetrathiafulvalenes (TTFs) are elaborated by the protection-deprotection of thiolates or selenolates strategy. We have connected the physical properties of the corresponding materials to the interactions born out of the presence of selenium atoms on one side or both sides of the TTF core. The electrochemical values of the new donors are presented. Radical cation salts (RCS) and charge transfer complexes (CTC) were prepared in order to study, in particular, their electrical conductivity.

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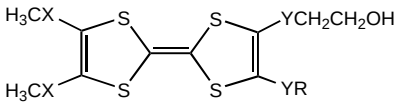
Keywords: Tetrathiafulvalene, Selenium, Cyclic voltammetry, Organic materials, Conductivity

1. Introduction

The most organic materials have Peierls distortion [1] Increasing their dimension by modifying the TTF core stabilize their metallic state leading to superconductivity at low temperature [2]. Therefore, functional TTF derivatives have received much attention [3]. In this context, the design of TTF- based donor molecules bearing substituents capable of effective intermolecular hydrogen-bonding is an emerging area [4,5] Hydrogen-bonding has been observed in a lot of conducting and superconducting salts of TTF derivatives [6] More recently, donor.....donor hydrogen-bonding interactions have been revealed by X-ray analysis of a number of TTF systems [7,8] In this paper we present the synthetis of mono and dihydroxylated TTF derivatives prepared from a chalcogenate protection-deprotection strategy (scheme 1) [9,10]



X, Y=S, Se; R=CH_3, $(CH_2)_2OH$

Scheme 1

2. Experimental

NMR spectra were recorded on a Brucker AC 200 instrument. FAB mass spectra were recorded on a JOEL JMS-DX 300 spectrometer. Melting points were mesured on a Buchi apparatus. Cyclic voltammetry measurements were carried out on a PAR-273 potentiostat/galvanostat.

4,5-bis(2'-cyanoethylseleno)-6,7-dimethylselenoTTF (DCES-DMSTTF) 3a, 4,5-bis(2'-cyanoethylthio)-6,7-dimethylselenoTTF (DCET-DMSTTF) 3b and 4,5-bis(2'-cyanoethylthio)-6,7-dimethylthioTTF (DCET-DMTTTF) 3c. 4,5-dimethyl thio-1,3-dithiole-2-thione 1a (0.24 g, 1.08 mmol) or 4,5-dimethylseleno-1,3-dithiole-2-thione 1b (0.34 g, 1.08 mmol) and 4,5- bis-(2'-cyanoethylthio) -1,3-dithiole-2-one 2a (0.31 g, 1.08 mmol) or 4,5- bis-(2'-cyanoethylseleno) -1,3-dithiole-2-one 2b (0.41 g, 1.08 mmol) were suspended in freshly distilled triethylphosphite (10 ml) under nitrogen and heated with stiring at 100°C for 90 mn. Then, the mixture was cooled to 0°C and the precipitate filtered. The product was washed with cold MeOH (3 x 10 ml), dried in *vacuo* and chromatographed (silica gel, CH_2Cl_2).

Compound **3a**: Orange powder (85%), mp=100°C, ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 6H, $SeCH_3$), 2.86 (t, 4H, *J*=7.0Hz, CH_2CN), 3.08 (t, 4H, *J* =7.0Hz, CH_2Se), ^{13}C NMR ($CDCl_3$): δ 9.92 ($SeCH_3$), 19.40 (CH_2CN), 23.55 (CH_2Se), 118.2 (CN), MS (Fab+) *m/z* 654 (M^+), Found C 25.72, H 2.24 $C_{14}H_{14}N_2S_4Se_4$ requires C 25.68, H 2.14

Compound **3b**: Orange powder (67%), mp=113°C, ^{1}H NMR ($CDCl_3$): δ 2.35 (s, 6H, $SeCH_3$), 2.73 (t, 4H, *J* =7.03Hz, CH_2CN), 3.08 (t, 4H, *J* =7.1Hz, CH_2Se); ^{13}C NMR ($CDCl_3$): δ 9.90 ($SeCH_3$), 18.93 (CH_2CN), 31.29 (CH_2S), 118.2 (CN), MS (Fab+) m/z 560 (M^+), Found C 30.05, H 2.84 $C_{14}H_{14}N_2S_6Se_2$ requires C 30.00, H 2.50

Compound **3c**: Orange oil (81%), ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 6H, SCH_3), 2.70 (t, 4H, *J* =7.0Hz, CH_2CN), 3.02 (t, 4H, *J* =7.0Hz, CH_2S); ^{13}C NMR ($CDCl_3$): δ 19.20 (SCH_3), 18.74 (CH_2CN), 31.21 (CH_2S), 118.2 (CN), MS (Fab+) m/z 466 (M^+), Found C 35.98, H 2.96$C_{14}H_{14}N_2S_8$ requires C 36.05, H 3.00

4,5-bis(2'-hydroxyethylseleno)-6,7-dimethylselenoTTF (DHES-DMSTTF) 4a, 4,5-bis(2'-hydroxyethylthio)-6,7-dimethylselenoTTF (DHET-DMSTTF) 4b and 4,5-bis(2'-hydroxyethylthio)-6,7-dimethylthioTTF (DHET-DMTTTF) 4c. To a solution of compound **3a** (0.3 g, 0.45 mmol), **3b** (0.25 g, 0.45 mmol) or **3c** (0.21 g, 0.45 mmol), in 7 mL of anhydrous ethanol we add, slowly and under nitrogene, 1.5 mL (0.81 mmol) of sodium ethanolate solution 1M freshely prepared. After stiring 15 min, 3-chloroethanol (0.19 mL) was added to the mixture. After 16 h, CH_2Cl_2 was added to the solution which was washed with water, dried on $MgSO_4$ and finally evaporated in *vacuo*. The obtained oil was chromatographed (silica gel, carbone disulfide as eluant) and washed with ether**.**

Compound **4a**: Orange needles (42%), mp=100-104°C, ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 6H, $SeCH_3$), 2.72 (s, 2H, OH), 3.07 (t, 4H, *J* =5.59Hz, CH_2Se), 3.82 (t, 4H, *J* =5.26Hz, CH_2OH); ^{13}C NMR ($CDCl_3$): δ 9.98 ($SeCH_3$), 23.50 (CH_2Se), 59.98 (CH_2O), MS (Fab+) m/z 636 (M^+), Found C 22.54, H 2.50 $C_{12}H_{16}O_2S_4Se_4$ requires C 22.64, H 2.51

Compound **4b**: Orange powder (45%), mp=98°C, ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6H, $SeCH_3$), 2.91 (s, 2H, OH), 3.00 (t, 4H, *J* =5.38Hz, CH_2S), 3.75 (t, 4H, *J* =5.26Hz, CH_2OH), ^{13}C NMR ($CDCl_3$): δ 9.99 ($SeCH_3$), 39.35 (CH_2S), 59.9 (CH_2O), MS (Fab+) m/z 542 (M^+), Found C 26.75, H 3.00 $C_{12}H_{16}O_2S_6Se_2$ requires C 26.56, H 2.95

Compound **4c**: Orange needles (47%), mp=110-112°C, ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 2H, OH), 2.48 (s, 6H, SCH_3), 3.02 (t, 4H, *J* =5.38Hz, CH_2S), 3.78 (t, 4H, *J* =5.26Hz, CH_2OH); ^{13}C NMR ($CDCl_3$): δ 19.20 ($SeCH_3$), 39.40 (CH_2S), 59.95 (CH_2O), MS (Fab+) m/z 448 (M^+), Found C 32.25, H 3.43 $C_{12}H_{16}O_2S_8$:requires C 32.14, H 3.57

4-(2'-cyanoethylthio)-5-methylthio-6,7-dimethylselenoTTF (CETMT-DMSTTF) 5b and 4-(2'-cyanoethylthio)-5-methylthio-6,7-dimethylthioTTF (CETMT-DMTTTF) 5c. To a solution of compound **3b** (0.45 g, 0.8 mmol) or **3c** (0.37 g, 0.8 mmol) in 9 mL of anhydrous DMF we add, slowly and under nitrogene, cesium hydroxide (0.19 g, 1.13 mmol) in 1 mL of anhydrous methanol. During this addition, the coloration of the solution become dark. After stiring 15 min, iodomethane (0.67 mL) was added to the mixture. After 2 h, CH_2Cl_2 was added to the solution which was washed with water, dried on $MgSO_4$ and finally evaporated in *vaccu*. The obtained oil was chromatographed (silica gel, CH_2Cl_2/Hexane (2 :1.5)).

Compound **5b**: Orange solid (91%), mp=108°C, ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6H, $SeCH_3$), 2.46 (s, 3H, SCH_3), 2.69 (t, 2H, *J* =7.24Hz, CH_2CN), 3.01 (t, 2H, *J* =7.13Hz, CH_2S); ^{13}C NMR ($CDCl_3$): δ 9.90 ($SeCH_3$), 19.20 (SCH_3), 18.74 (CH_2CN), 31.21 (CH_2S), 118.2 (CN), MS (Fab+) m/z 521 (M^+), Found C 27.54, H 2.46 $C_{12}H_{13}NS_6Se_2$ requires C 27.63, H 2.49

Compound **5c**: Red powder (82%), mp=104°C, ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 6H, SCH_3), 2.46 (s, 3H, SCH_3), 2.69 (t, 2H, *J* =6.9Hz, CH_2CN), 3.02 (t, 2H, *J* =7.03Hz, CH_2S); ^{13}C NMR ($CDCl_3$): δ 19.20 (SCH_3), 18.75 (CH_2CN), 31.20 (CH_2S), 118.2 (CN), MS (Fab+) m/z 427 (M^+), Found C 33.82, H 2.98 $C_{12}H_{13}NS_8$ requires C 33.72, H 3.04

4-(2'-hydroxyethylthio)-5-methylthio-6,7-dimethylselenoTTF (HETMT-DMSTTF) 6b and 4-(2'-hydroxyethylthio)-5-methylthio-6,7-dimethylthioTTF (HETMT-DMTTTF) 6c. To a solution of compound 5**b** (0.2 g, 0.38 mmol) or **5c** (0.16 g, 0.38 mmol), in 7 mL of anhydrous ethanol we add, slowly and under nitrogene, 0.92 mL (0.91 mmol) of sodium ethanolate solution 1M freshely prepared. After stiring 15 min, 3-chloroethanol (0.26 mL) was added to the mixture. After 16 h, CH_2Cl_2 was added to the solution which was washed with water, dried on $MgSO_4$ and finally evaporated in *vacuo*. The obtained oil was chromatographed (silica gel, CH_2Cl_2).

Compound **6b**: Orange solid (90%), mp=61°C, ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 6H, $SeCH_3$), 2.46 (s, 1H, OH), 2.51 (s, 3H, SCH_3), 2.98 (t, 2H, *J* =5.57Hz, CH_2S), 3.78 (m, 2H, CH_2O); ^{13}C NMR ($CDCl_3$): δ 9.90 ($SeCH_3$), 19.20 (SCH_3), 39.08 (CH_2S), 59.99 (CH_2O), MS (Fab+) m/z 512 (M^+), Found C 25.65, H 2.70 $C_{11}H_{14}OS_6Se_2$ requires C 25.78, H 2.73

Compound **6c**: Orange solid (70%), mp=92-95°C, ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 6H, SCH_3), 2.43 (s, 3H, SCH_3), 2.46 (s, 1H, OH), 2.91 (t, 2H, *J* =5.59Hz, CH_2S), 3.70 (t, 2H, *J* =5.60Hz, CH_2O); ^{13}C NMR ($CDCl_3$): δ 19.30 (SCH_3), 39.14 (CH_2S), 60.06 (CH_2O), MS (Fab+) m/z 418 (M^+), Found C 31.41, H 3.28 $C_{11}H_{14}OS_8$ requires C 31.57, H 3.34

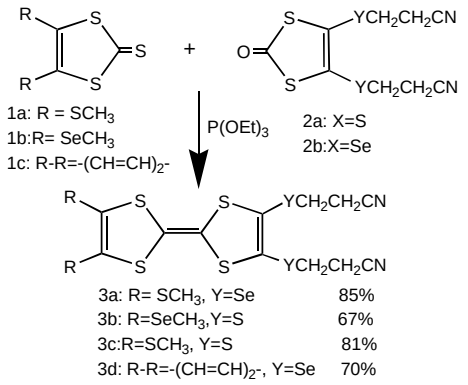
1,4-bis[3-(2-cyanoethylthio)-6,7-dimethyldiseleno TTF-2-methylthio] benzene 7b. To a solution of 4,5- bis-(2'-cyanoethylthio)-6,7-dimethylselenoTTF (DCET-DMSTTF) 3b (0.4 g, 0.71 mmol) in DMF was added, under nitrogen, a solution of $CsOH.H_2O$ (0.13 g, 0.75 mmol) in 1 mL of MeOH. During this addition, the mixture become dark green. After 15 min, we add 0.1 g of 1,4-dibromomethylbenzene. The stiring was maintained for 2 h at room temperature and then CH_2Cl_2 was added. The organic layer was washed with water, dried on $MgSO_4$ and evaporated in vacuo. The obtained oil was finally chromatographed on silica gel using the mixture CH_2Cl_2/Hexane (2 :1,5) as eluant to leads 0.29 g (75%) of the product 7b as an orange solid, mp=185°C, ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 12H, $SeCH_3$), 2.77 (t, 4H, *J*=7,2 Hz, CH_2CN), 2.93 (t, 4H, *J*=7,2 Hz, CH_2S), 4.04 (s, 4H, CH_2C_{ar}), 7.26 (s, 4H, H_{ar}), ^{13}C NMR ($CDCl_3$): δ 9.98 ($SeCH_3$), 18.94 (CH_2CN), 31.40 (CH_2S), 33.70 ($\underline{C}H_2C_{ar}$), 129.70 (C_{ar}), MS (Fab+) m/z 1116 (M^+), Found C 32.40, H 2.72 $C_{30}H_{28}N_2S_{12}Se_4$ requires C 32.25, H 2.50

1,4-bis[3-(2-hydroxyethylthio)-6,7-dimethyl diselenoTTF-2-methylthio] benzene 8b. This compound was prepared by adaptation of the same procedure described for the compounds **4a-c**. We obtain an orange solid (70%), mp=182°C, ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 12H, $SeCH_3$), 2.83 (t, 4H, *J* =5.60Hz, CH_2S), 2.90 (s, 2H, OH), 3.76 (t, 4H, *J* =5.60Hz, CH_2O), 4,02 (s, 4H, CH_2C_{ar}), ^{13}C NMR ($CDCl_3$): δ 9,98 ($SeCH_3$); 33,65 ($\underline{C}H_2C_{ar}$); 39,40 (CH_2S); 59,96 (CH_2O), 129,60 (C_{ar}), MS (Fab+) m/z 1098 (M^+).

3. Results and discussion

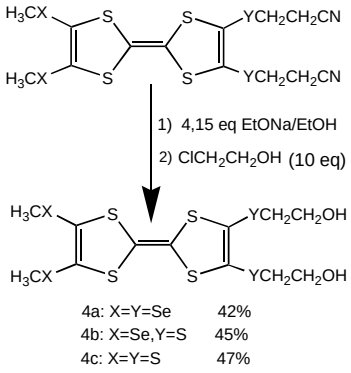
As shown in the scheme 2, the intermediates **3a-c** were prepared via the phosphite-mediated cross coupling of chalcogenones **1a, 1b** or **1c** and **2a** or **2b** leading to a

mixture from which the desired species must be separated easealy in good yield.



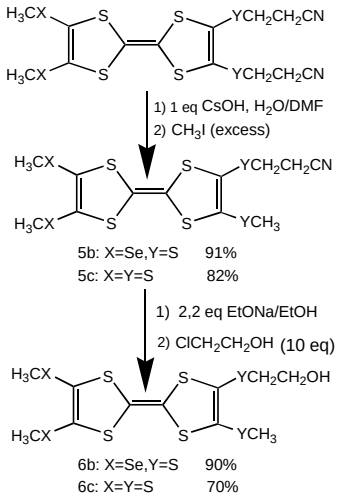
Scheme 2

The 4,5-bis(2'-hydroxyethylseleno) -6,7-dimethylseleno TTF (DHES-DMSTTF) **4a**, 4,5-bis(2'-hydroxyethylthio)-6,7-dimethylselenoTTF (DHET-DMSTTF) **4b**, 4,5-bis(2'-hydroxyethylthio)-6,7-dimethylthioTTF (DHET-DMTTTF) **4c**, have been obtained by thiolate or selenolate deprotection of the corresponding molecules **3a-c** with sodium ethoxide in ethanol followed by the treatment with 2-chloroethanol in 42%, 45% and 47% yield respectively (scheme 3). The same products were obtained from the compound 3d[11].



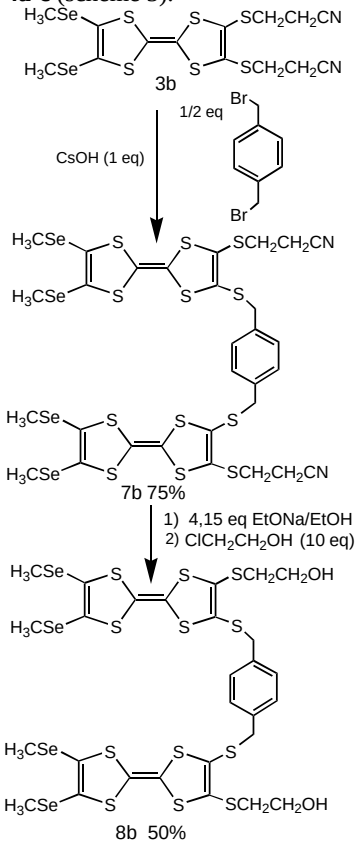
Scheme 3

Similarly, the 4-(2'-hydroxyethylthio)-5-methylthio-6,7-dimethylselenoTTF (HETMT-DMSTTF) **6b** and 4-(2'-hydroxyethylthio)-5-methylthio-6,7-dimethylthio TTF (HETMT - DMTTTF) **6c** have been prepared from the compounds **5b** and **5c** by the thiolate or selenolate deprotection – alkylation described bellow in 90 and 70% yield respectively. Derivatives **5b** and **5c** have been synthesized by the mono – deprotection of compounds **3b** and **3c** by cesium hydroxide monohydrate, followed by their methylation with iodomethane in 91 and 82% yield respectively (scheme 4).



Scheme 4

Bi-TTF **7b** has been synthezised from the TTF **3b** by his monodeprotection with cesium hydroxide monohydrate and then his alkylation with 0,5 equivalent of 1,4-bis(bromomethyl)benzene. Bi-TTF **8b** has been obtained with a similar procedure as used for the compounds **4a-c** (scheme 5).



Scheme 5

The redox potentials of all the new donors and BEDT-TTF [bis (ethylenedithio) tetrathiafulvalene], taken as reference, were determined by cyclic voltammetry (CV).

Table 1. Oxidation potentials (mV) of all the new donors.

Donor	Eox_1	Eox_2	ΔEox	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
3a	698	1056	358	656	1018	362
3b	714	1078	364	675	1040	365
3c	716	1064	348	690	1026	336
4a	620	952	332	580	918	338
4b	632	950	318	593	914	321
4c	666	966	300	628	927	299
5b	662	1024	362	624	987	363
5c	684	1020	336	646	982	336
6b	632	968	336	594	930	336
6c	666	982	316	627	942	317
7b	682	1036	354	644	989	345
8b	686	1040	345	646	994	348
BEDT-TTF	550	965	415	590	1000	410

Measurements were performed on platinum electrodes *versus* SCE at room temperature in CH_2Cl_2 containing nBu_4NPF_6 (0,1 M) as supporting electrolyte. The results were reported in Table 1.

The half-wave potentials of these donors show that the presence of alcohol –OH functions and selenium atoms in one side or both sides of the TTF core has a similar effect to that observed for thioalkyl substituents such as $–SCH_2CH_2S-$ encountered in BEDT-TTF. This is particularly well illustrated by compounds **4a** ($E^1_{1/2}$ = 580 mV), **4b** ($E^1_{1/2}$ = 593 mV), **6b** ($E^1_{1/2}$ = 594 mV), which are very close to that of **BEDT-TTF** ($E^1_{1/2}$ = 590 mV). Of course, by decreasing the number of cyano substituents or replacing it by a hydroxy group less electro-attracting than –CN, Eox_1 decreases. This imply that the electron –donating ability is enhenced by the introduction of selenium atoms and hydroxyl groups.

It is also noteworthy that the $–XCH_3$ group exerts the same effect as the $–YCH_2CH_2OH$ chain as indicated through the $E^1_{1/2}$ values observed for **6b** ($E^1_{1/2}$ = 594 mV) and **4b** ($E^1_{1/2}$ = 593 mV) or **6c** ($E^1_{1/2}$ = 627 mV) and **4c** ($E^1_{1/2}$ = 628 mV).

Among all the synthesized target donors, only donor **3d**: 4,5-benzo-6,7-bis(2-cyanoethylseleno) tetrathiafulvalene crystallized in a Monoclinique crystalline system (P21/a space group). The structure is shown in Fig. 1 and the crystallographic parameters are given in Table 2.

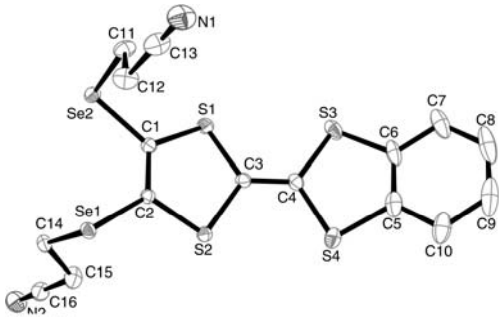


Fig. 1. Crystal structure of the donor 3d.

Table 2 . Crystallographic data of 3d.

	3d
Formule	$C_{16}H_{12}N_2S_4Se_2$
M ($g.mol^{-1}$)	518.44
T (K)	293(2)
Radiation, λ (Å)	0.71073
Système crist.	Monoclinique
Groupe d'espace	$P2_1/a$
a (Å)	7.034(10)
b (Å)	30.6416(6)
c (Å)	8.9082(2)
α (Å)	90
β (Å)	91.6352(8)
γ (Å)	90
V ($Å^3$)	1919.23(6)
Z	4
d_{calc} ($g.cm^{-3}$)	1.794
refl. Obs.($I>2\sigma(I)$)	7655/4342
R_1[a] Final, wR_2[b]	0.0441, 0.1082

[a] $R_1 = \sum||Fo| - |Fc|| / \sum |Fo|$. [b] $wR_2 = \{\sum[w (Fo^2 - Fc^2)^2] / \sum [w (Fo^2)^2]\}^{1/2}$

The crystalline structure consists of an pseudo-orthogonal arrangement of the molecules: the bond Se-C and the average plan of the molecule form a plane angle of approximately 95.5Å (Fig. 1).

We can observe that the molecules are almost arched (Fig. 2). Within the same tetramer, the molecules are presented biconvex once and another time biconcave. Between two close tetramers, we note the adoption of a parallel position between the arms selenocyanoethyle of two inserted molecules of each group (Fig. 2).

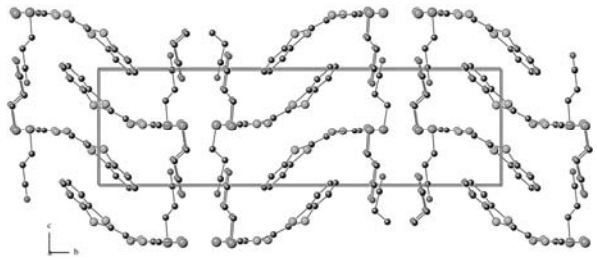


Fig. 2. Structure of 3d seen along the direction [100].

The radical cation salts (RCS) were prepared by galvanostatic electrochemical oxidation on a platinum electrode under constant current (5µA) in a 15 ml H-type cell from a solution of n-Bu_4NX (0.5 M, in dry THF) containing the donor (10^{-3} M).

Charge transfer complexes (CTC) are obtained by mixing donor and acceptor (TCNQ) in hot acetonitrile.
The electrical conductivity was measured on compressed powder or single crystals by the two-contacts method. The results of the different RCS and CTC are listed in Table 3. These results show a semi-conductor behaviour for all the synthesized materials.

Table 3. Crystal shape and electrical conductivity ($S.cm^{-1}$) of the RCS and CTC.

TTF	Br^-	NO_3^-	Cl^-	TCNQ
2a*	B. pl.[a] 10^{-6}	B. p.[c] 1.2×10^{-6}	B. pl.[a] 3.5×10^{-6}	N. R.[d]
2b	-	N. R.[d]	-	N. R.[d]
2c*	B. n.[b] $9.2\ 10^{-5}$	-	-	N. R.[d]
3b	-	N. R.[d]	-	N. R.[d]
3d	N. R.[d]	N. R.[d]	N. R.[d]	R. p.[e] 3.2×10^{-6}
4b	B. p.[c] $5.4\ 10^{-6}$	N. R.[d]	-	B. p.[c] 1.96×10^{-5}
4c	N. R.[d]	-	-	B. p.[b] 9.53×10^{-6}

[a] Black platelet, [b] Black needles, [c] Black powder, [d] negative result, [e]Red platelet.

4. Conclusions

Mono and dihydroxylated TTF derivatives were prepared using a chalcogenate protection-deprotection strategy [9,10] The study of these new donors by cyclic voltammetry showed that the presence of alcohol –OH functions and selenium atoms in one side or both sides of the TTF core has a similar effect to that observed for thioalkyl substituents BEDT-TTF. When we replace cyano substituents by a hydroxy group, the first oxidation potential decreases. It is also noteworthy that the $-XCH_3$ group exerts the same effect as the $-YCH_2CH_2OH$ chain as indicated through the $E^1_{1/2}$ values.

Only one donor (3d) gives single crystal and caracterized by X-ray method. From these donors, radical cation salts with different anions and charge transfer complexes with the acceptor TCNQ were obtained as powder or crystals. The results show a semi-conductor behaviour for all the synthesized materials.

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