A Methyl Substituted Thiophenic-TTF Donor and its Salts

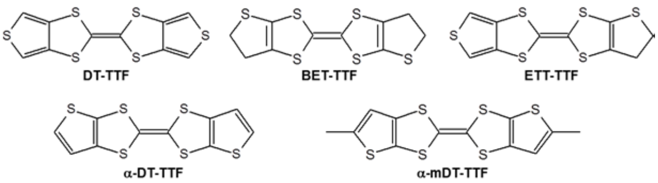
Rafaela A. L. Silva,[a] Isabel C. Santos,[a] Elsa B. Lopes,[a] Sandra Rabaça,[a] Sergi Galindo,[b] Marta Mas-Torrent,[b] Concepció Rovira,[b] Manuel Almeida [a] and Dulce Belo*[a]

Abstract: α-methyldithiophene-tetrathiafulvalene (α-mDT-TTF), the first alkyl substituted thiophenic-TTF electronic donor, as well as some of its charge transfer salts are reported. The crystal structure of α-mDT-TTF is composed of molecular stacks aligned parallel to each other. Its cyclic voltammetry shows higher electron donor ability than the unsubstituted analogue α-DT-TTF. This material has been employed as a semiconductor in an organic field effect transistor, giving a mobility of 4x10^{-4} cm^2/Vs. Two charge transfer salts of this donor with [M(mnt)$_2$]$^-$ anions (mnt=maleonitriledithiolate), with M=Co and Au, were obtained by electrocrystallization presenting unusual stoichiometries: (α-mDT-TTF)[Co(mnt)$_2$] (**2**) and (α-mDT-TTF)$_3$[Au(mnt)$_2$]$_2$ (**3**). In the cobalt compound the donor molecules are fully oxidized and the Co complex is dimerized presenting a semiconducting behavior (7x10^{-3} S/cm). The gold compound is composed by alternated stacks of donor trimers and pairs of anions.

Introduction

The tetrathiafulvalene derivatives fused with thiophene moieties are a class of sulfur rich electronic donors that have given rise to materials with interesting and unusual electrical and magnetic properties.[1] For instance the DT-TTF donor (DT-TTF= dithiophene-tetrathiafulvalene) when combined in charge transfer salts with [M(mnt)$_2$] (mnt= maleonitriledithiolate) anions, can either present spin-ladder systems with the diamagnetic anions M= Au and Cu[2] or systems with delocalized electrons in DT-TTF stacks interacting with localized magnetic moments with the paramagnetic anions M= Ni and Pt.[3] The analogous compounds with ETT-TTF donor (ETT-TTF=ethylenethio-thiophene-tetrathiafulvalene) have the same type of ladder structure of donors but due to disorder in the position of the thiophenic sulfur atoms they do not present a spin-ladder behavior.[4] In spite of a similar orientation disorder a spin-ladder magnetic system was found in α-DT-TTF salts (α-DT-TTF= alpha-dithiophene-tetrathiafulvalene) which behave as weakly disordered spin-ladder systems.[5] These electronic donors based on thiophene moieties fused tetrathiafulvalene have also attracted considerable interest as active materials in OFETs (OFET=Organic Field-Effect Transistor).[6] A very high mobility of up to 6.2 cm^2/Vs has been reported for the alpha polymorph of DT-TTF crystals.[7] In spite of presenting a similar structure with good 3D interactions, a mobility of one order of magnitude smaller has been observed in ETT-TTF donor, which has been attributed to the structural disorder.[8] Lower mobilities have been observed in α-DT-TTF having a different structure with less extended interactions.[5]

Therefore it seems of obvious interest to explore similar donors with different substituent groups and to see how the physical properties are changed by the possible structural differences induced by these substituents. With such aim we selected α-mDT-TTF (**1**) a substituted α-DT-TTF derivative with a methyl group[9] which is expected to modulate the packing pattern of the donor molecules in the solid state. In this paper we report the crystal structure and OFET properties of (**1**) as well as charge transfer salts of this donor with [Co(mnt)$_2$] and [Au(mnt)$_2$] anions.



Scheme 1.

Results and Discussion

α-mDT-TTF (**1**) was synthesized by self-coupling of the corresponding 5-methylthieno[2,3-*d*][1,3]-dithiole-2-thione in trimethyl phosphite, following a previously described procedure.[9] This compound is soluble in common organic solvents and orange plate-shaped crystals suitable for X-ray measurements were obtained by recrystallization from 3:1 acetone/isopropanol solutions.

The electron donor ability of α-mDT-TTF was evaluated by cyclic voltammetry in dichloromethane solutions (10^{-3} M). Two pairs of quasi reversible waves, typical of TTF-based donors, were observed centered at -58 mV and +388 mV versus ferrocene/ferrocenium, the first being ascribed to the couple [α-mDT-TTF]^0/[α-mDT-TTF]$^+$ and a second +388 mV ascribed to the couple [α-mDT-TTF]$^+$/[α-mDT-TTF]$^{2+}$. The shape of the voltammograms (Figure SI1) with well-defined pairs of waves indicative of quasi-reversible redox processes, contrasts with those of DT-TTF, α-DT-TTF or BET-TTF where other association processes are visible and adsorbed species are formed on the electrode.[10] This is certainly a consequence of the higher solubility of the methyl substituted molecule. By analyzing Table 1, where the redox potential values obtained for **1** are compared with those reported for related thiophenic-TTF donors, it becomes evident that **1** has a higher electron donor ability than the unsubstituted analogue, α-DT-TTF[10], and higher than the *tert*-butyl substituted dithiophene-TTF (α-tDT-TTF).[11] The only related compound, so far, easier to oxidize than **1** is BET-TTF, the non-aromatic thiophenic-TTF donor.

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[a] C^{2}TN, Instituto Superior Técnico, Universidade de Lisboa,
Estrada Nacional 10, P-2695-066 Bobadela LRS, Portugal.
E-mail: dbelo@ctn.ist.utl.pt
Homepage: http://c2tn.tecnico.ulisboa.pt/grupos-de-investigacao/estado-solido/
[b] Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC) and CIBER-BBN, Campus UAB, E-08193 Bellaterra, Spain.

Table 1. Oxidation potentials of thiophene-TTF type donors. The values between brackets are half wave potentials ($E_{1/2}$). Potentials are relative to ferrocene/ferrocenium ($E_{1/2}$ = 0.566 V in dichloromethane vs SCE).

Donor	$E_{1,\ D^0/D^+}$ (mV)	$E_{2,\ D^+/D^{2+}}$ (mV)
α-tDT-TTF*[11]	(410)*	(770)*
DT-TTF[10]	219	692
α-DT-TTF[10]	-3	407
α-mDT-TTF	(-58)	(388)
BET-TTF[10]	-108	327

*Data collected in benzonitrile vs SCE.[11] Potentials were normalized with the ferrocene/ferrocenium redox potential of $E_{1/2}$ = 0.44 V vs SCE.

In spite of the good electron donor properties the preparation of charge transfer salts by electrocrystallization is hindered due to their significantly high solubility not favoring crystallization in dichloromethane and other solvents. Nevertheless crystals of two salts with $[M(mnt)_2]^-$ anions were obtained by electrocrystallization from dichloromethane solutions: (α-mDT-TTF)[Co(mnt)$_2$] (**2**) and (α-mDT-TTF)$_3$[Au(mnt)$_2$]$_2$ (**3**). No 2:1 donor:acceptor salts, that are the most abundant stoichiometry with the other donors, could be isolated with [M(mnt)$_2$] anions. The crystal structure and refinement data for compounds **1**-**3**, are given in Table 2.

Compound **1** crystallizes in the triclinic system, space group P-1. The unit of cell contains one α-mDT-TTF molecule in an inversion center. The molecule is essentially planar and shows orientation disorder in the terminal thiophenic sulphur atom, as denoted by the occupation factor of 67 and 33% for S3/C4 and S3A/C4A atom pairs, respectively (Figure 1). The bond lengths values are within the range observed in related neutral TTF donors ($d_{C1=C1*}$=1.343(7) Å) (Table SI1).

The crystal structure (Figure 2) is composed by stacks of the α-mDT-TTF neutral molecule along *a*. In the stacks the molecules are slipped along their long axis (Figure 2b) and although the average intermolecular plane distance is 3.552 Å, there are no contacts below the sum of the atomic van der Waals radii. The peripheric methyl group prevents short interactions along the molecules long axis. The most relevant interactions are side-by-side short $S\cdots S$ contacts between molecules in neighboring stacks along *c* (Figure 2c and Table SI2). This network of interactions is accomplished both by $S_{TTFCore}\cdots S_{TTFCore}$ and $S_{Thiophenic}\cdots S_{TTFCore}$, and therefore is not fully extended since it is broken up by the disorder of the thiophenic sulphur atom.

Table 2. Crystal and refinement data for (α-mDT-TTF) (**1**), (α-mDT-TTF)[Co(mnt)$_2$] (**2**) and (α-mDT-TTF)$_3$[Au(mnt)$_2$]$_2$ (**3**).[a]

Compound	α-mDT-TTF (**1**)	(α-mDT-TTF) [Co(mnt)$_2$] (**2**)	(α-mDT-TTF)$_3$ [Au(mnt)$_2$]$_2$ (**3**)
Formula	$C_{12}H_8S_6$	$C_{40}H_{16}Co_2N_8S_{20}$	$C_{52}H_{24}Au_2N_8S_{26}$
Molec. mass	344.54	1367.67	1988.29
T (K)	150(2)	120(2)	150(2)
Dimens. (mm)	0.60x0.12x0.06	0.08x0.06x0.04	0.20x0.10x0.05
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	P2$_1$/c	P2$_1$/c
a (Å)	5.9662(5)	7.2842(6)	15.9945(3)
b (Å)	7.5218(6)	27.6525(14)	18.5598(4)
c (Å)	8.3232(7)	12.0320(11)	11.7939(4)
α (°)	84.483(3)	90	90
β (°)	84.205(2)	99.825(2)	106.6940(10)
γ (°)	68.485(2)	90	90
Volume (Å^3)	345.01(5)	2388.0(3)	3353.51(15)
Z	1	2	2
ρ_{calc} (g.cm^{-3})	1.658	1.902	1.969
h, k, l range	-4–7, -7–8, ±9	±9, ±36, ±15	±19, ±22, ±14
θ_{max} (°)	27.09	11.20	27.07
Refl. collected	2009	41746	7737
Refl. indexed	1042	5669	6368
Refl. >2σ(I)	801	5519	5309
R1	0.05	0.05	0.03
ωR2	0.13	0.14	0.07

[a] Crystallographic data (excluding structure factors) for **1**, **2** and **3** was deposited with the Cambridge Crystallographic Data Centre with nos. CCDC 1413272, 1413270 and 1413271, respectively.

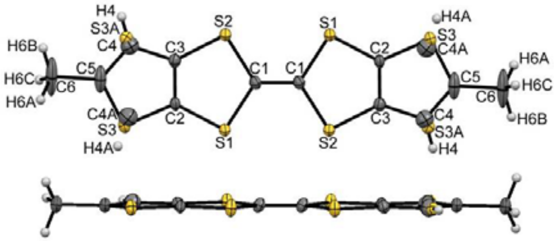

Figure 1. ORTEP and atomic numbering scheme of compound **1**, with thermal ellipsoids at 50% probability level.

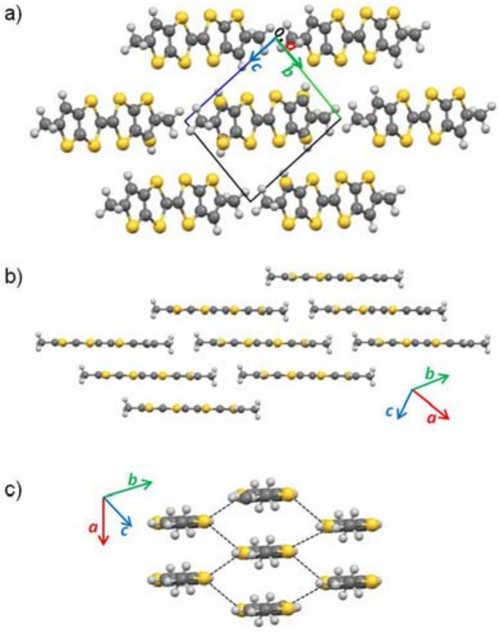

Figure 2. Crystal structure of compound **1**: a) view along the stacking axis *a*; b) partial view along the molecules short axis; c) view along the molecular long axis.

The electrical conductivity of α-mDT-TTF measured in single crystals is $6\text{x}10^{-8}$ S/cm at room temperature, significantly smaller than that of the unsubstituted analogue α-DT-TTF (3×10^{-6} S/cm).[5] The electronic mobility and the possibility to use this donor as a semiconductor was evaluated in OFET devices. The OFET structures were fabricated on Si/SiO_2 substrates with an interdigitated structure of gold contacts. Prior to the organic semiconductor deposition, the SiO_2 substrate was functionalised with an HMDS (hexamethyldisilazane) monolayer. Subsequently, a thin film layer of α-mDT-TTF was thermally evaporated. The device characteristics were measured in nitrogen atmosphere. A p-type behavior of α-mDT-TTF can be observed from the output characteristics shown in Figure 3, where an increment of negative gate voltage (V_{GS}) results in an increased measured current (I_{DS}), hence more holes are induced. The switch-on voltage (V_{SO}) is the voltage at which I_{SD} starts to increase. From the transfer characteristic (Figure 3), a V_{SO} of 0 V was extracted, which is the ideal value for low-voltage operation. Further, a threshold voltage (V_{TH}) of -4.4 V was calculated from the intercept with the x axis in the square root of the saturation current *vs* the gate voltage graph. A field-effect mobility μ_{FE} of about $4\text{x}10^{-4}$ cm^2/Vs was extracted in the saturation regime. This mobility value is an order of magnitude higher than that of the unsubstituted α-DT-TTF (5×10^{-5} cm^2/Vs)[10] and the *tert*-butyl substituted α-tDT-TTF ($5.8\text{x}10^{-5}$ cm^2/Vs).[11] In view of the X-ray powder pattern of the thin film layer of α-mDT-TTF (Figure SI3), the possible presence of more than one phase cannot be excluded, preventing the establishment of crystal structure-mobility correlations. The formation of polymorphs on surface different than the ones obtained in bulk is very common in organic semiconductors[12], and, in particular, also in TTFs. [7c, 13]

The topography of the α-mDT-TTF films was investigated by atomic force microscopy (AFM) in tapping mode. Figure 4 shows the top view AFM image where the formation of crystallites can be clearly observed. The grain structures have a size slightly lower than one μm. The rms surface roughness is 63 nm. The relatively low mobility values observed are limited both by the grain boundaries in these polycrystalline samples, polymorphism and strong anisotropy of electronic interactions in the crystal structure. For instance, in the crystal structure found for **1**, theoretical estimations of the intermolecular interactions along the different directions predict a strong 1D character with strong interactions along the stacking axis of the donors (*a*-axis) and interchain interactions at least two orders of magnitude smaller (Table SI3 and fig SI2).

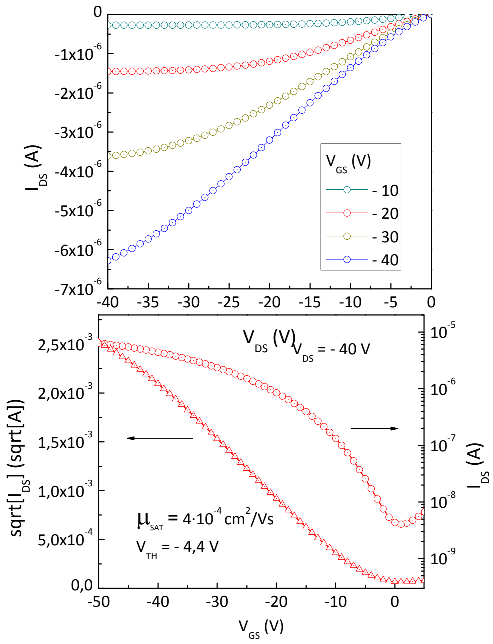

Figure 3. Output (top) and transfer (bottom) characteristics of an OFET based on a α-mDT-TTF thin film.

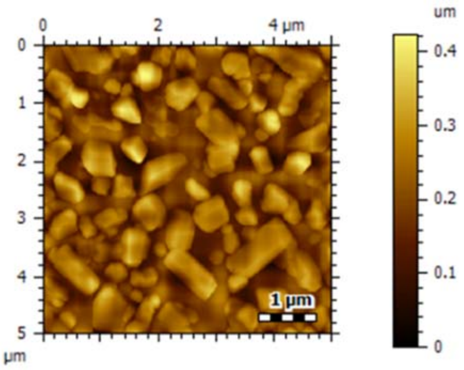

Figure 4. AFM image of a thin α-mDT-TTF layer on SiO_2 substrate.

X-ray analysis of (α-mDT-TTF)[$Co(mnt)_2$] (**2**), was only possible by using synchrotron radiation at ID11 at ESRF in smaller crystals due to the quality of the larger crystals. **2** crystallizes in the monoclinic system, space group $P2_1/c$. The unit cell contains one monoanionic molecule of $[Co(mnt)_2]^-$ and one monocationic molecule of [α-mDT-TTF]$^+$, both at general positions. The cobalt bisdithiolene anions, $[Co(mnt)_2]^-$, present the usual dimerization with an inversion center connecting two units which are better described as $[Co(mnt)_2]_2^{2-}$. The Co atoms present a square pyramidal, 4 + 1, coordination geometry due to the formation of two apical Co–S bonds ($d_{Co\text{-}S1*}$=2.3772(12) Å) between distorted square based $[Co(mnt)_2]^-$ units (Figure 5b). The geometry of this dianionic dimer is identical to that observed in many cobalt(III) bisdithiolene complexes (Table SI4).[14]

The α-mDT-TTF unit with exception of the methyl hydrogen atoms is within experimental error, planar, and presents disorder in the sulphur atom of the thiophenic ring (55-45 % and 64-36 % for the pairs S7/S7A and S10/S10A, respectively) (Figure 5a

Table SI5). The length of central carbon-carbon double bond is longer than in compound **1**, ($d_{C9=C15}$=1.3916(1) Å), as expected for fully oxidized TTF derivatives.[15]

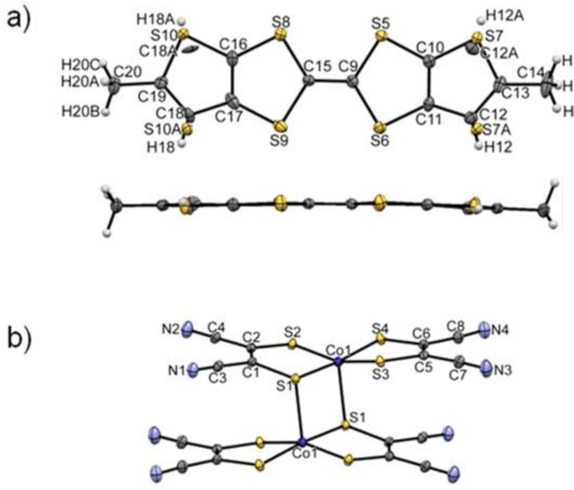

Figure 5. ORTEP and atomic numbering scheme of compound **2**, with thermal ellipsoids at 50% probability level.

The crystal structure is composed by alternating segregated stacks of anions and cations both along *a* (Figure 6a-b). Apart from the dimerization of molecules inside the stacks the crystal structure is essentially identical to that of DT-TTF [Cu(mnt)$_2$].[2d] The dimerization of the anions is reflected also in the cationic stacks since it induces a dimerization and alternation in the stacking pattern of the [α-mDT-TTF]$^+$ molecules. There is one dimer with top-to-top overlapping mode (Figure 6c) between molecules with interplanar distance (3.597 Å) and showing several short S···S contacts below the sum of vdW radii. Another dimer shows the overlap mode between molecules slightly displaced along their long axis (Figure 6d). Their interplanar distance is shorter (3.551 Å) but there is no relevant short interactions between them. The dimerized [Co(mnt)$_2$]$_2^{2+}$ units stack along *a* with no short contacts. Short interactions occur between anions and cations in neighboring stacks through short S···S interactions and N···H-C short hydrogen bonds, involving the cationic peripheric methyl group and the anionic nitrile group (Table SI6).

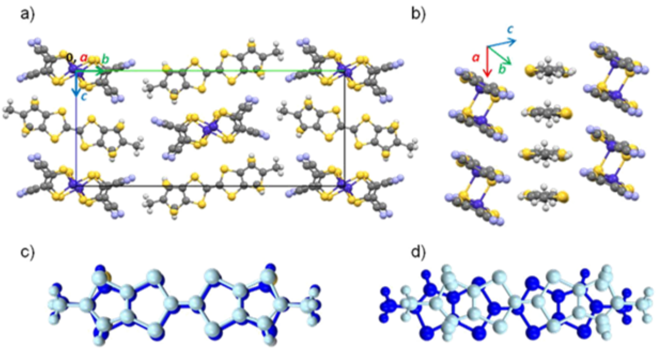

Figure 6. Crystal structure of **2**: a) view along the *a* axis; b) partial view showing neighboring stacks, along the molecules long axis; c) top-to-top overlapping mode of [α-mDT-TTF]$^+$; d) overlapping mode of [α-mDT-TTF]$^+$ molecules slightly displaced along their long axis.

(α-mDT-TTF)$_3$[Au(mnt)$_2$]$_2$ (**3**) crystallizes in the monoclinic system, space group P2$_1$/c. The unit cell is composed of two α-mDT-TTF donor molecules, one at an inversion center, and one [Au(mnt)$_2$]$^-$ anion molecule, at general position. As observed in **1** and **2** the donor molecules present a disorder in the position of the thiophenic sulphur atom (occupation factors of 42-58 %, 41-59 % 71-29% for S7/S7A, S10/S10A and S13/S13A pairs, respectively). One of the molecules presents a small boat type curvature (Figure 7a) and the other is planar, within experimental error (Figure 7b). The central carbon-carbon double bond length ($d_{C9=C15}$=1.353(6) Å and $d_{C21=C21*}$=1.417(6) Å)) (Table SI7) is in all cases slightly higher than in **1** and lower than in **2** suggesting different oxidation states for these two donor molecules (Table SI8).

The monoanion presents the usual square planar geometry (Figure 7c), with bond lengths and angles typically found in this type of gold bisdithiolate complexes (Table SI9). [2a), 5, 16]

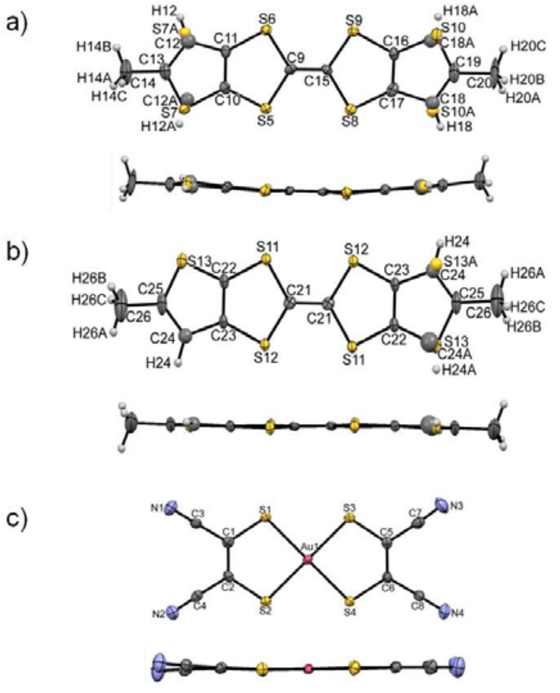

Figure 7. ORTEP view and atomic numbering scheme of compound **3**, with thermal ellipsoids at 50% probability level.

In the crystal structure of **3**, the donor molecules are arranged as trimers, (α-mDT-TTF)$_3^{2+}$, connected by four short $S_{TTFcore}\cdots S_{TTFCore}$ contacts (3.470, 3.487, 3.526 and 3.553 Å) and these trimers alternate with a pair of anions, along *b* (Figure 8) in a fashion similar to that found in (DT-TTF)$_3$[Au(dcdmp)$_2$]$_2$ (dcdmp=2,3-dicyano-5,6-dimercaptopyrazine).[17] There are no short interactions neither between anions within the pair, that are separated by an interplane distance of 3.464 Å, nor between the dicationic trimers and the pairs of anions along the stacks. The existent short contacts are side-by-side S···S between cations and anions in neighboring stacks (Table SI10). The donor sub-lattice is a network of donor trimers forming channels along *a*+*c*, which accommodate the anions (Figure 9).

The electric conductivity of (α-mDT-TTF) [Co(mnt)$_2$] measured in single crystals shows a semiconducting behavior with a room temperature value of 7x10^{-3} S/cm and an activation energy of

92 meV (Figure SI4). The thermopower presents a large negative value of ~-630 μV/K that increases on lowering the temperature (Figure SI4 and SI5) confirming the semiconducting behavior. These semiconducting properties are not surprising in view of the full oxidation and the strong dimerization of the donors.

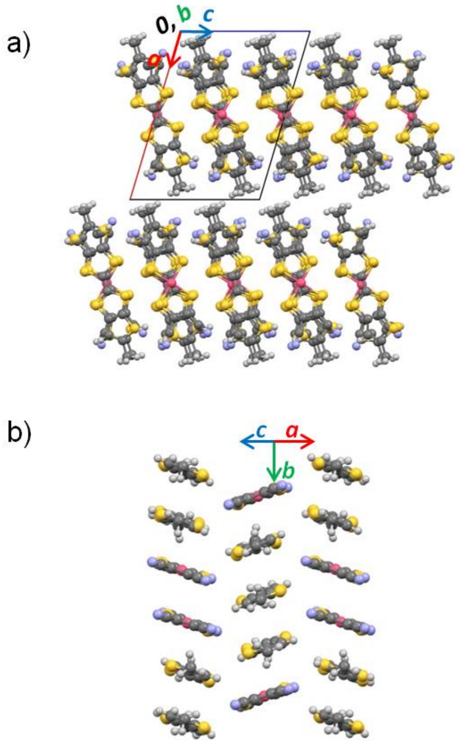

Figure 8. Crystal structure of **3**: a) view along the *b* axis; b) partial view along the molecules long axis.

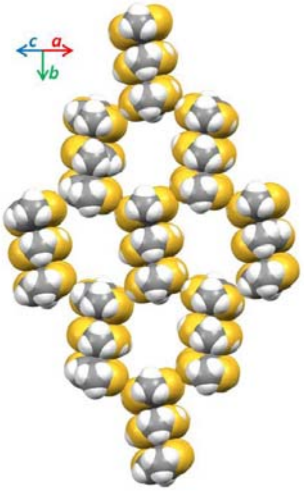

Figure 9. Partial view of the donor sub-lattice in the crystal structure of **3**.

Conclusions

The methyl substituted thiophenic-TTF donor α-mDT-TTF, has lower oxidation potentials than the unsubstituted analogue α-DT-TTF. The field-effect mobility value of this donor material in a polycrystalline thin film is an order of magnitude higher than that observed in the unsubstituted analogue possibly due to increased dimensionality of intermolecular interactions. The preparation of (α-mDT-TTF) $[Co(mnt)_2]$ and $(\alpha\text{-mDT-TTF})_3[Au(mnt)_2]_2$ derivatives demonstrates the ability of this donor to provide charge transfer salts. Unusual stoichiometries and interesting structures, completely different from those of unsubstituted donors, are obtained as a consequence of the methyl groups.

Experimental Section

General experimental conditions: All preparative procedures were performed under nitrogen atmosphere,unless otherwise stated. All solvents were purified following standard procedures. α-mDT-TTF was obtained following the procedure previously described.[9] The $(n\text{-}Bu_4N)[M(mnt)_2]$ (M= Au and Co) salts were also synthesized and purified by recrystallization as previously described. [18-19] Electrocrystallization was carried out in a two-compartment H-shaped cell, separated by frit glass, with Pt electrodes and under galvanostatic conditions. Dichloromethane was also purified using standard procedures and freshly distilled immediately before its use. Other chemicals were commercially obtained and used without any further purification.

(α-mDT-TTF)[Co(mnt)$_2$] (2) crystals were obtained by electrocrystallization, at room temperature, from a dichloromethane solution of the α-mDT-TTF donor and the tetrabutylammonium salt of $[Co(mnt)_2]$, in stoichiometric amounts. Under nitrogen and after ~8 days, using a current density of 1.5 $\mu A.cm^{-2}$, black plate-shaped crystals were grown on the anode.

(α-mDT-TTF)$_3$[Au(mnt)$_2$]$_2$ (3) small crystals were obtained by electrocrystallization in a dichloromethane solution of the donor and $n\text{-}Bu_4N[Au(mnt)_2]$, in stoichiometric amounts. The cell was sealed under nitrogen and after ~7 days of applying a current density of 0.5 $\mu A.cm^{-2}$, black plate-shaped crystals were collected.

Cyclic voltammetry: Cyclic voltammetry data were obtained using a BAS C3 Cell Stand. The voltammograms were obtained at room temperature, with a scan rate of 100 mV/s, Pt wire working and counter electrodes and a $Ag/AgNO_3$ reference electrode. The measurements were performed on fresh dichloromethane solutions with a concentration of 10^{-3} M that contained a 10^{-1} M concentration of tetrabutylammonium hexafluorophoshate ($n\text{-}Bu_4PF_6$) as the supporting electrolyte. Potentials were normalized with the ferrocene/ferrocenium redox potential, in dicloromethane, of $E_{1/2}$ = 0.266 V vs $Ag/AgNO_3$ ($E_{1/2 \text{ versus } Ag/AgNO3}$ + 300 mV= $E_{1/2 \text{ versus SCE}}$). This potential was measured in the same experimental conditions as the thiophenic-TTF type donors.

Preparation of Thin Film OFETs: The OFET structures were manufactured on thermally oxidized highly n-doped silicon wafers with a SiO_2 thickness of 200 nm (Si-Mat). The oxide acts as a gate insulator and the silicon wafer as the corresponding gate electrode. Laser lithography was used to define an interdigitated structure for source and drain contacts using a lift-off process. The thermally evaporated electrodes were composed of a thin 4 nm chromium adhesive layer and 35 nm of Au. They were configured as interdigitated fingers with a channel length of 25 µm and a channel width of 2.5 cm. Prior to the organic semiconductor deposition, the SiO_2 substrate was functionalized with an HMDS (hexamethyldisilazane) (Sigma Aldrich) monolayer. After the SiO_2 activation by ozone exposure (UVO Cleaner, Jelight Company) for 25 min, the substrate was immersed into 1 mM toluene solution for 4h. Subsequently, the excess HMDS was removed by immersion in clean toluene for 10 min in ultrasonic bath. Later on, the substrate was dried by nitrogen flow. Finally, α-mDT-TTF was thermally evaporated at a rate around 0.2 Å/s and a pressure lower than 10^{-6} mbar. Thereby, an OFET in a BGBC (bottom-gate bottom-contact) was fabricated. After the deposition of α-mDT-TTF, the samples were measured in an inert atmosphere inside of a glovebox. The electrical characterization was done with a Keithley2612A sourcemeter. The field-effect mobility and the threshold voltage were extracted in the saturation regime by using the relation:

$$\mu_{SAT} = \frac{2\,L}{W\,C_i}\left(\frac{\partial\sqrt{I_{SD\ ,SAT}}}{\partial V_{SG}}\right)^2$$

X-ray diffraction studies: In the case of $(\alpha\text{-mDT-TTF})_3[\mathrm{Au(mnt)_2}]_2$ (2) experiments were performed with a Bruker APEX II CCD detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å), in the φ and ω scans mode. A semi empirical absorption correction was carried out using SADABS.[20] Data collection, cell refinement and data reduction were done with the SMART and SAINT programs. [21] In the case of $(\alpha\text{-mDT-TTF})[\mathrm{Co(mnt)_2}]$ (3) single crystal X-ray diffraction was performed on a heavy-duty diffractometer at the Materials Science Beamline ID11 (ESRF, Grenoble, France) using a Frelon2K CCD detector.[22] After conversion of the frame file format, the data were indexed using SMART and integrated with SAINT.[21] They were scaled, combined and corrected for absorption using SADABS. The structures were solved by direct methods using SIR97[23] and refined by fullmatrix least-squares methods using the program SHELXL97[24] using the winGX software package.[25] Non-hydrogen atoms were refined with anisotropic thermal parameters whereas H-atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using ORTEP 3.[26]

Electrical Transport Properties: electrical conductivity and thermopower measurements in single crystals were performed in the temperature range of 50–320 K, using a measurement cell attached to the cold stage of a closed cycle helium refrigerator. In the first step, the thermopower was measured by using a slow ac (ca. 10-2 Hz) technique,[27] by attaching two 25 µm diameter 99.99 % pure Au wires (Goodfellow metals), thermally anchored to two quartz blocks, with Pt paint (Demetron 308A) to the extremities of an elongated sample as in a previously described apparatus,[28] controlled by a computer.[29] The oscillating thermal gradient was kept below 1 K and was measured with a differential Au-0.05 at. % Fe vs. chromel thermocouple of the same type. The absolute thermoelectric power of the sample was obtained after correction for the absolute thermopower of the Au leads, by using the data of Huebner. [30]

Intermolecular energy interactions calculations: the interaction energies were calculated[31] by employing the extended Hückel method.[32] The basis set consisted of Slater type orbitals of double-zeta quality. The exponents, contraction coefficients and atomic parameters were taken from previous work. [33]

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