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Cyanobenzene–Ethylenedithio–Tetrathiafulvalene Salts with ClO_4^-: Bilayer Polymorphs and Different Stoichiometries

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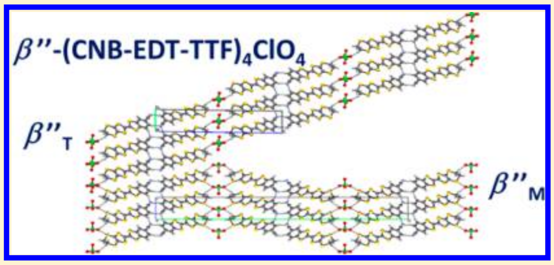
Supporting Information

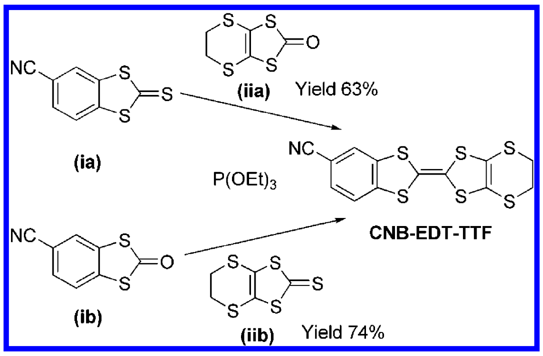


ABSTRACT: The electrocrystallization from dichloromethane or tetrahydrofuran solutions of the dissymmetrical bis(ethylenedithio)-tetrathiafulvalene (ET) derivative cyanobenzene–ethylenedithio–tetrathiafulvalene (CNB-EDT-TTF) in the presence of perchlorate anion ClO_4^- affords two different polymorphs of salts with 4:1 stoichiometry, a previously described triclinic phase β''_T-$(CNB\text{-}EDT\text{-}TTF)_4ClO_4$ (**1a**), and a new monoclinic phase β''_M-$(CNB\text{-}EDT\text{-}TTF)_4ClO_4$, (**1b**), as well as a compound with 1:1 stoichiometry, $(CNB\text{-}EDT\text{-}TTF)ClO_4$ (**2**), depending on the solvent and crystallization conditions. The special conditions necessary for the growth of the unusual 4:1 salts, requiring low current densities to oxidize the donors and subsequent slow diffusion controlled association processes, are discussed. Both 4:1 polymorphs present a bilayer structure of the donors induced by head-to-head C–N···H pairing interactions associated with a combination of $R^2_2(10)$ and $R^2_4(10)$ synthons between donors in nearby layers. These polymorphs share the same β''-type donor packing pattern in the layers, but the anions which are disordered over two possible orientations in the triclinic phase appear ordered in the monoclinic one, with a doubling of the interlayer cell axis, due to an alternation of the orientation of the molecules in the bilayers. The 1:1 salt **2** presents a crystal structure with dimerized donors stacks. The donor molecules in nearby stacks are connected by a helical network of C–N···H pairing interactions. A new polymorph of the neutral donor β-CNB-EDT-TTF (**3**) is also described.

INTRODUCTION

Recently we have shown that the dissymmetrical TTF derivative cyanobenzene–ethylenedithio–tetrathiafulvalene (CNB-EDT-TTF)[1] (Scheme 1) is a good electron donor that when electrocrystallized in the presence of small anions A, such as I_3^-, ClO_4^-, or PF_6^-, under specific conditions leads to a novel series of charge transfer salts with general formula $(CNB\text{-}EDT\text{-}TTF)_4A$.[2] These compounds present two-dimensional (2D) metallic properties and are characterized by a unique bilayer structure of the donors, promoted by a specific combination of effective C–N···H–C interactions, leading to a head-to-head arrangement of donor molecules in paired layers (bilayers).[2] Both the unique bilayer structure of the donors and the unusual stoichiometry may give rise to specific new physical properties making the study of these compounds particularly appealing.

Scheme 1. Two Synthetic Pathways for Cyanobenzene–Ethylenedithio–Tetrathiafulvalene (CNB-EDT-TTF)[a]



[a] On top the previous procedure[1] and on the bottom the present modification with higher yield.

The comparison of the new $(CNB\text{-}EDT\text{-}TTF)_4A$ salts with those based on symmetrical donors derived from TTF such as BEDT-TTF (ET), that have been reported in quite large numbers and intensively studied during the last decades, cannot be avoided.[3] The compounds based on symmetrical donors occur mainly with a 2:1 stoichiometry with formula $(ET)_2A$ and are characterized by a large structural diversity with several polymorphs associated with different donor packing patterns in single layer arrangements.[4−6] Associated with the different

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crystal structures, it has been observed a rich diversity of interesting physical properties ranging from Mott insulators, anti-ferromagnets, 2D metals, or even superconductors.[3,7−10] A similar or even more complex structural diversity is expected to occur in the bilayer salts based on CNB-EDT-TTF. Indeed in the first bilayer compounds $(\text{CNB-EDT-TTF})_4\text{A}$ reported so far, in spite of the disordered nature of the anions and the average nature of the crystal structures reported, there is already evidence for a rich structural diversity. For A = I_3^- several polymorphs, corresponding to β''- and κ-type donor packing patterns or to different degrees of disorder of the linear triiodide anion, have been already observed with superconductivity found at ambient pressure below 3.2K for κ-$(\text{CNB-EDT-TTF})_4\ I_3$.[11]

In this context, the study of all the possible structures of the CNB-EDT-TTF salts in general and specifically the conditions in which crystals of the different polymorphs of $(\text{CNB-EDT-TTF})_4\text{A}$ can be obtained emerges as a complex task of fundamental importance to understand these novel bilayer compounds and in the establishment of correlations with their physical properties.

In this paper we report results from a study focused on salts of this donor with the ClO_4 anion obtained by electrocrystallization for which it was previously described an average structure with β''-type packing pattern of the donors in bilayers, with a strong anion disorder. In this work a new polymorph of the salt with the 4:1 stoichiometry and a β''-type of donor packing are described, as well as a new compound with 1:1 stoichiometry, $(\text{CNB-EDT-TTF})\text{ClO}_4$ (**2**).

■ EXPERIMENTAL SECTION

General Methods. Crystals of charge transfer salts **1a**, **1b**, and **2** (Figure 1) were obtained by electrocrystallization, at room temperature, from a dichloromethane or a tetrahydrofuran solutions of the CNB-EDT-TTF donor and the corresponding electrolyte. Electrocrystallization was performed in H-shaped two-compartment cells separated by a glass frit with Pt electrodes and under galvanostatic conditions. In the preparation of the electrocrystallization cells special care was taken to avoid the presence of water. Before use, the cells were dried for at least 12 h in the oven at 60 °C, the electrocrystallization reagents were stored under a vacuum at least during 48 h, in the case CNB-EDT-TTF donor at 60 °C and in the case $n\text{-Bu}_4\text{NClO}_4$ between 80 and 100 °C. The used commercially available $n\text{-Bu}_4\text{NClO}_4$ (Aldrich) was also purified by recrystallization in dichloromethane and diethyl ether. The solvents were also purified using standard procedures[12] and freshly distilled immediately before its use. CNB-EDT-TTF was prepared following a modification to the previously described procedure,[1] based on the heterocoupling between 5,6-dihidro[1,3]dithiol[4,5-*b*][1,4]dithiine-2-thione (**ib**) and 2-oxo-benzo[d][1,3]dithiol-5-carbonitrile (**iib**) instead of the corresponding ketone and thione (**ia, iia**), which was used with improved yield (Scheme 1). This reversed ketone-thione combination was found to provide a higher yield (~74%) with an almost complete suppression of the homocoupling side products. Under these conditions, silica gel column chromatography was not necessary to the separation and isolation of the desired product that could be directly purified by a simple recrystallization in dichloromethane.

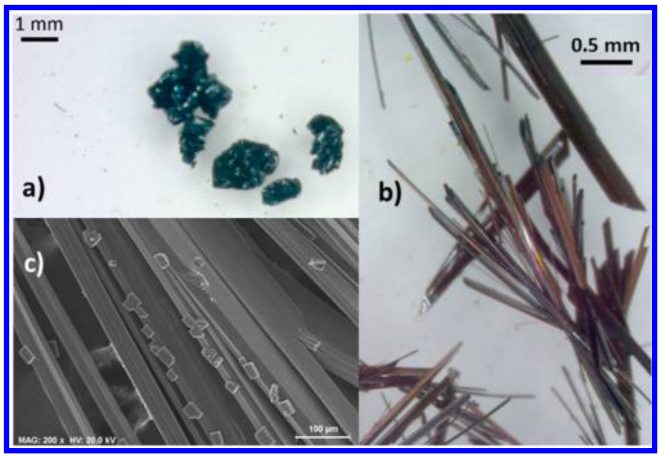

Figure 1. Typical crystals, obtained by electrocrystallization: (a) $(\text{CNB-EDT-TTF})\text{ClO}_4$ (**2**); (b) β''-$(\text{CNB-EDT-TTF})_4\text{ClO}_4$ (**1a** and **1b**); (c) SEM image of block shaped crystals of **2** nucleated on the surfaces of elongated platelet shaped crystals of **1a** or **1b**.

CNB-EDT-TTF. In freshly destilled triethyl phosphite (4 mL), 2-oxo-benzo[d][1,3]dithiol-5-carbonitrile (**ib**) (1.1 mmol, 0.21 g) and 5,6-dihidro[1,3]dithiol[4,5-*b*][1,4]dithiine-2-thione (**iib**) (1.0 mmol, 0.24 g) were heated to reflux for 8 h under N_2, leading to the formation of an orange precipitate. The precipitate was filtered and washed with cold methanol and dried under a vacuum. The product was purified by recrystallization with hot dichloromethane yielding orange needle-shaped crystals. Yield 74%.

β''-$(\text{CNB-EDT-TTF})_4\text{ClO}_4$ (1a, 1b). A dichloromethane solution of the donor CNB-EDT-TTF (3.3×10^{-3} M) and $n\text{-Bu}_4\text{N ClO}_4$ (6×10^{-3} M) was added to an H-shaped cell. The system was sealed under nitrogen, and the current was gradually increased from 0.2 μA cm^{-2} to 0.5 μA cm^{-2} during the first 3 days of the electrocrystallization. After approximately more 18 days of applying a current density of 0.5 μA cm^{-2}, metallic shining dark brown elongated platelet-shaped crystals grown on the anode, both triclinic (**1a**) and monoclinic (**1b**), were collected and washed with dichloromethane.

$(\text{CNB-EDT-TTF})\text{ClO}_4$ (2). A tetrahydrofuran solution of the donor CNB-EDT-TTF (5×10^{-3} M) and $n\text{-Bu}_4\text{NClO}_4$ (2.5×10^{-3} M) was added to an H-shaped cell. The system was sealed under nitrogen, and after approximately 40 days of applying a constant current density of 1 μA cm^{-2}, black block-shaped crystals grown on the anode were collected and washed with dichloromethane.

Cyclic Voltammetry. Data were obtained using a BAS C3 Cell Stand. The voltammograms were obtained at room temperature, with scan rates in the range 1−5000 mV/s, Pt working and counter electrodes and an $Ag/AgNO_3$ reference electrode (10^{-3} M $AgNO_3$, 10^{-1} M $TBAPF_6$) immersed in acetonitrile. The studies were performed in dichloromethane solutions of compound **3** (10^{-3} M) using $n\text{-Bu}_4\text{NPF}_6$ (10^{-1} M) as the supporting electrolyte. The Pt working electrode was polished with 0.05 μm alumina on microcloth, thoroughly rinsed with distilled water and acetone prior to use in the electrochemical experiments. The potential sweeps were started from the open circuit potential in the cathodic direction. All the potentials presented in the present work are referred to the reference electrode.

X-ray Crystallography. Selected single crystals were mounted on a loop with protective oil and X-ray data were collected on a Bruker APEX II CCD detector diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) and operating in a φ and ω scans mode. A semi-empirical absorption correction was carried out using SADABS.[13] Data collection, cell refinement, and data reduction were done with the SMART and SAINT programs.[14] The structures were solved by direct methods using SIR97[15] and refined by full-matrix least-squares methods using the program SHELXL97[16] using the winGX software package.[17] 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.[18]

CCDC 1533003−1533006 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Scan Electron Microscopy (SEM). The morphology of the crystals was studied using scanning electron microscopy. The SEM observations were made using a Hitachi scanning electron microscope/S2400 operating at 20 kV and equipped for energy-dispersive spectroscopy (EDS) with a light element detector (EDS XFlash SDD).

RESULTS AND DISCUSSION

Different electrocrystallization trials following small variations from a general procedure previously described were made in order to find the best crystal growth conditions. During these tests it became evident that the electrocrystallization of the CNB-EDT-TTF salts presents specific characteristics quite different from many other charge transfer salts. First, in spite the fair solubility of the donor in solvents commonly used for electrocrystallization such as dichloromethane or tetrahydrofuran, well-formed crystals or even a microcrystalline product are only obtained under low current densities ∼0.5−1 μA/cm^2. Larger current densities lead to the formation of an amorphous material covering the electrode. It should be also noted that under such small current density conditions the growth of the first crystals only occurs after 2 or 3 days of electrocrystallization, indicating that the species being formed after oxidation on the electrode surface are relatively soluble. It is remarkable that often the crystals grow in the bottom of the cell, over donor crystals which may precipitate, while the electrode remains clean (Figure 2). To the best of our knowledge this type of crystal growth is unprecedented among electrocrystallization of molecular conductors, where the nucleation and growth of crystals on the anode is promptly induced[19−21] leading to well-formed crystals on the electrode even in the case of less soluble compounds.[22−24] These features support the previous speculation that the electrocrystallization of the CNB-EDT-TTF salts is based on a series of slow and diffusion controlled association processes, between donor cations generated at the electrode and neutral molecules in solution (such as $D^+ + nD \leftrightarrow D_{n+1}^+$, with $n \geq 1$), leading to products with solubility larger than most of the molecular conductors, and which due to a rather low solubility, crystals promptly grow directly on the electrode.

Figure 2. Dark crystals growing in the bottom of the electrocrystallization cell, over donor orange crystals which precipitate during the experiment.

Evidence for association processes occurring in solution after oxidation of the donor molecules, before the crystal growth, is provided by electrochemical studies which were performed in detail. Cyclic voltammetry studies show two redox processes at 0.405 and 0.850 V vs Ag/AgNO$_3$, previously ascribed to the (CNB-EDT-TTF)/(CNB-EDT-TTF)$^+$ and (CNB-EDT-TTF)$^+$/(CNB-EDT-TTF)$^{2+}$ couples.[1] In no case it is observed crossing of the curves with signs of formation of an insoluble product, as commonly observed in the formation of less soluble charge transfer salts.[22] It should be noted that these processes are not fully reversible since the difference between anodic and cathodic peak voltages is larger than 59 mV and the curve shape is quite dependent on the scan rate (Figure S1). Also the second oxidation process is strongly asymmetric with a sharp reduction peak denoting desorption process. The application of several diagnosis tests (current function and cathodic/anodic peak currents vs scan rate) to the first redox process as a function of the scan rate were made to infer about the mechanism of the redox reaction and coupled processes leading to the formation of the 4:1 compounds. However, results were not found corresponding to any simple coupled process, indicating instead the possibility of several or more complex chemical/electrochemical processes occurring simultaneously (Table S1, Figure S2).

The use of more concentrated donor solutions (3 mM) favors the nucleation in the bottom of the cell, often over crystals of an orange product that precipitates soon after the electrocrystallization current being turned on. The analysis of this precipitate and its UV−visible spectra corresponds to the CNB-EDT-TTF donor (Figure S3), suggesting that a new polymorph of the donor, with lower solubility, is being formed.

In fact a different structure of the donor, corresponding to a new polymorph of the CNB-EDT-TTF donor, β-CNB-EDT-TTF (**3**) (Figure S4), could be obtained from X-ray diffraction in single crystals isolated from crystallizations upon the donor purification process.

The formation of this orange precipitate could be avoided by using less concentrated solutions, typically 0.5 mM. Under these conditions crystals from different phases of the charge transfer salt (CNB-EDT-TTF)$_4$ClO$_4$ could be obtained, eventually all in the same electrocrystallization. Using dichloromethane as solvent two different polymorphs with a 4:1 donor to acceptor stoichiometry were always obtained; in addition to the previously reported polymorph β''_T-(CNB-EDT-TTF)$_4$-ClO$_4$ (**1a**), crystals of a new monoclinic polymorph β''_M-(CNB-EDT-TTF)$_4$ClO$_4$, (**1b**) were also obtained, both as elongated plated-shaped dark crystals. These two polymorphs have the same color and shape and cannot be distinguished by visual inspection. Their electrical transport properties are also virtually identical to those already described for the monoclinic phase.[2] In addition to these two β'' salts with 4:1 stoichiometry, small amounts of distinct block-shaped crystals corresponding to a 1:1 salt (CNB-EDT-TTF)ClO$_4$ (**2**) were also obtained in minor amounts. The electrocrystallization of the 1:1 salt seems to be favored in dichloromethane by a lower concentration of the donor relatively to the concentration of the anion, and after several days (∼8) of electrocrystallization, starting with equimolar solutions of donor and anions, crystals of 1:1 salt can start nucleating on the top of 4:1 salts as shown in Figure 1c). SEM-EDS microanalysis of the large plate-shaped and small block-shaped crystals obtained under these conditions, using Cl and S lines, confirm a 4:1 and 1:1 stoichiometry, respectively. Using THF as solvent under similar electrocrystallization conditions, the crystals obtained were almost entirely larger block-shaped crystals of compound **2** (Figure 1a).

All these crystals were suitable for single crystal X-ray diffraction. Crystal and structural refinement data for compounds **1a**, **1b**, **2**, and **3** are listed in Table 1. Figure 3 and Figure 4 represent the ORTEP diagrams for the compounds **1b** and **2**. The ORTEP diagram of compound **1a** can be seen in Figure S6.

X-ray diffraction in selected new crystals of the β''_T-(CNB-EDT-TTF)$_4$ClO$_4$ (**1a**) lead to a structure resolution of better

Table 1. Crystal and refinement data for β''_T-(CNB-EDT-TTF)$_4$ClO$_4$ (**1a**), β''_M-(CNB-EDT-TTF)$_4$ClO$_4$ (**1b**), (CNB-EDT-TTF)ClO$_4$ (**2**) and CNB-EDT-TTF (**3**)[a]

$[D]_xA_y$ D = (CNB-EDT-TTF)	β''_T-$[D]_4ClO_4$ (**1a**)	β''_M-$[D]_4ClO_4$ (**1b**)	[D] ClO$_4$ (**2**)	β-[D] (**3**)
formula	$C_{26}H_{14}Cl_{0.50}N_2O_2S_{12}$	$C_{52}H_{28}ClN_4O_4S_{24}$	$C_{13}H_7ClNO_4S_6$	$C_{26}H_{14}N_2S_{12}$
molec mass	788.84	1577.67	469.01	739.11
T (K)	150(2)	150(2)	150(2)	150(2)
dimens (mm)	0.20 × 0.08 × 0.02	0.50 × 0.04 × 0.02	0.18 × 0.08 × 0.04	0.28 × 0.10 × 0.02
crystal color	dark brown	dark brown	black	orange
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/m$	$P2_1/c$	$P2_1/c$
a (Å)	4.8373(2)	4.88620(10)	9.5243(11)	31.9218(4)
b (Å)	5.8165(3)	54.9165(6)	8.3680(10)	7.79560(10)
c (Å)	27.7497(14)	5.76820(10)	21.405(2)	11.5358(2)
α (deg)	90.702(3)	90.00	90.00	90.00
β (deg)	91.645(2)	95.3680(10)	94.604(6)	93.6560(10)
γ (deg)	95.255(3)	90.00	90.00	90.00
volume (Å^3)	777.08(6)	1541.01(4)	1700.4(3)	2864.84(7)
Z	1	1	4	4
ρ_{calc} (g·cm^{-3})	1.686	1.700	1.832	1.714
h, k, l range	±5, ±6, −32/+33	±5, −66/+61, ±6	±11, ± 10, ±26	±38, −9/+8, ±14
θ_{max} (deg)	25.03	25.02	25.68	25.67
refl collected	7844	11419	25193	44033
refl unique	2644 [R_{int} = 0.0475]	2719 [R_{int} = 0.0395]	3237 [R_{int} = 0.0627]	5376 [R_{int} = 0.0383]
data/restraints/parameters	2644/31/217	2719/0/208	3237/0/226	5376/12/426
GOF on F^2	1.069	1.242	1.081	1.106
$R_1/\omega R_2$ [$I > 2\sigma I$]	0.0673/0.1584	0.0791/0.1736	0.0376/0.0963	0.0370/0.0761
$\Delta\rho$ max/min (e·Å^{-3})	0.863 and −0.674	1.275 and −1.165	0.874 and −0.456	0.591 and −0.330

[a] Crystallographic data (excluding structure factors) for **3**, **1a**, **1b**, and **2** were deposited with the Cambridge Crystallographic Data Centre with deposition numbers CCDC 1533003−1533006, respectively..

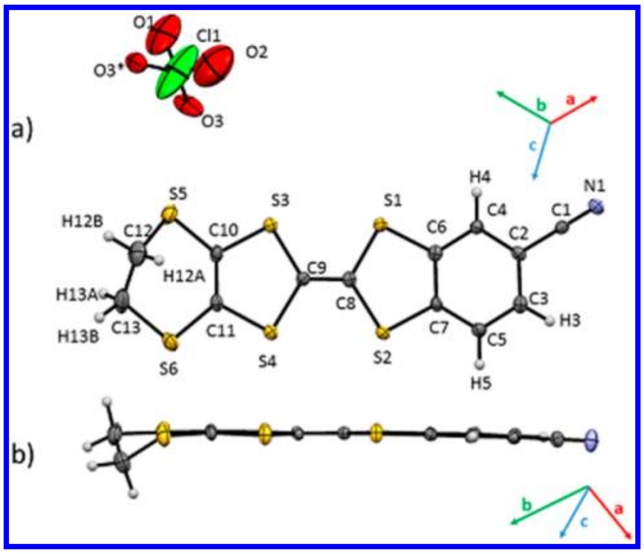

Figure 3. (a) ORTEP and atomic numbering schemes of β''_M-(CNB-EDT-TTF)$_4$ClO$_4$, (**1b**) with thermal ellipsoids at 50% probability level; (b) side view of the donor in **1b**.

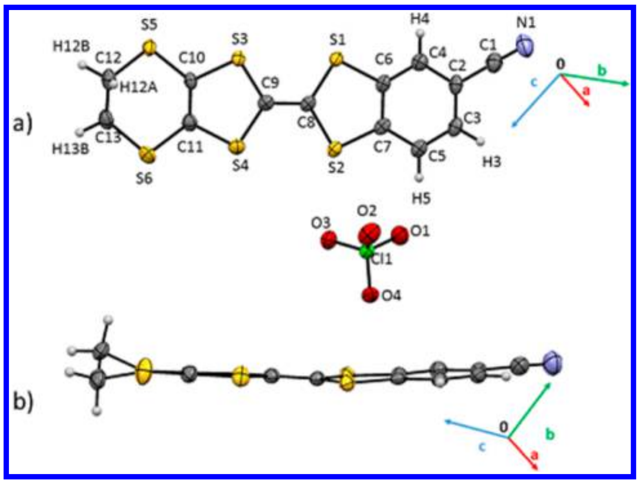

Figure 4. (a) ORTEP and atomic numbering schemes of (CNB-EDT-TTF)ClO$_4$ (**2**) with thermal ellipsoids at 50% probability level; (b) side view of the donor in **2**.

quality than the previously published one,[2] particularly concerning the disordered ClO$_4^-$ anion which appears with clearer-defined positions, as described in detail bellow. The unit cell is triclinic, $P\bar{1}$, with cell parameters a = 4.8373(2)Å, b = 5.8165(3)Å, c = 27.750(14) Å, α = 90.702(3)°; β = 91.645(2)°; γ = 95.255(3)°, and V = 777.08(6) Å^3.

The asymmetric unit contains one independent CNB-EDT-TTF donor molecule with all atoms located at general positions and one fragment of the partially occupied tetrahedral ClO$_4^-$ anion located near an inversion center. The chloride atom and two of the oxygen atoms (O1 and O2) have occupation factors of 0.25. The other oxygen atom (O3) has an occupation factor of 0.5. The coordination geometry of the ClO$_4^-$ anion is completed by the inversion center at [0.5, 0.5, 0.5] generating the fourth oxygen atom (O1* = 1 − x, 1 − y, 1 − z) (Figure 5a). These occupation factors correspond to a 4:1 a donor to acceptor stoichiometry.

These partially occupied positions for the Cl and O atoms, at distances clearly below the sum of the van der Waals radii imply anion disorder. As more clearly seen in Figure 5b, 5b1, and 5b2 these partially occupied positions can be seen as resulting from

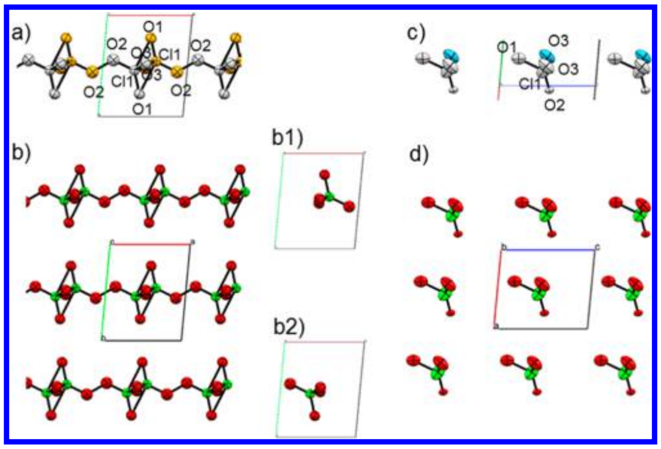

Figure 5. ORTEP diagrams at 20% probability level of ClO_4^- units in **1a** and **1b**. (a) The ClO_4^- units correspond to two equally populated positions slightly displaced along the *a*-axis, denoting both position disorder of the Cl and oxygen atoms in the interlayer cavities. Coloring scheme according to symmetry operations Yellow 1 − *x*, 1 − *y*, 1 − *z*, gray *x*, *y*, *z* in **1a**; (b) layer of disordered ClO_4^- units in **1a**; over two possible orientations, (b1) orientation I and (b2) orientation II. Note that the occupation factor for any of these orientations is 50%. (c) Chain of ClO_4^- units in **1b** with atom numbering scheme along *a*. Coloring scheme according to symmetry operations blue *x*, 1/2 − *y*, *z* gray *x*, *y*, *z*. (d) Layer of ClO_4^- units in **1b** corresponding only to orientation II in **1a**.

two possible orientations (I and II) of the ClO_4^- anions in two equally populated positions displaced along *a*.

The compound **1b** crystallizes in the monoclinic system, space group $P2_1/m$, with cell parameters a = 4.88620(10)Å, b = 54.9165(6)Å, c = 5.76820(10) Å, β = 95.3680(10)°, and V = 1541.01(4) Å^3. The unit cell of β''_M-(CNB-EDT-TTF)$_4$ClO$_4$ (**1b**) has twice the volume of the β''_T-(CNB-EDT-TTF)$_4$ClO$_4$ (**1a**), with the cell parameter *b* corresponding to a doubling of the cell parameter *c* on **1a**. The asymmetric unit of **1b** contains one independent CNB-EDT-TTF donor molecule with all atoms located at general positions and one disordered partially occupied tetrahedral ClO_4^- anion located on a symmetry plane. The structural refinement is also indicative of a 4:1 donor to acceptor stoichiometry as in **1a**. The chloride atom and two of the oxygen atoms (O1 and O2) are located on a mirror plane with occupation factors of 0.25. The other oxygen atom (O3) was refined with an occupation factor of 0.50. The mirror plane perpendicular to [0,1,0] generates the O3* atom (* = *x*, 1/2 − *y*, *z*) completing the tetrahedral coordination of the ClO_4^- anion. (Figure 5c) The positions of the ClO_4^-anions in **1b** correspond to only one of the two orientation observed previously in **1a** (Figure 5d).

The donor molecule, in compound **1a**, is essentially planar as in **1b** with exception of the dihydrodithiin ring which adopts a half-chair conformation with five coplanar atoms (Figure S6 and Figure 3, respectively). The central C═C bond length (C8−C9 = 1.357(8) Å (**1a**) and 1.339(9) Å (**1b**)) is identical to those previously observed in other 4:1 β''-(CNB-EDT-TTF)$_4$A salts with A = I_3,[11] PF_6.[2] Short contacts in compounds **1a** and **1b** are listed in Supporting Information, Table S3 and Table S4.

The donor intra-bilayer packing pattern in both β''_M- and β''_T-structures is essentially the same. The CNB-EDT-TTF molecules do not present any disorder in the dithiine ring as previously observed in the PF_6 salt and as commonly found in many ET salts. The donors are arranged head to head in bilayers through dipolar and bifurcated C−N···H interactions, described as a combination of dimeric $R^2_2(10)$ and $R^2_4(10)$ synthons, connecting almost coplanar molecules. The main difference between of β''_M- and β''_T- is the presence in the triclinic structure of a mirror plane responsible for a different repeat motif for the bilayers (Figure 6). In, β''_M-(CNB-EDT-TTF)$_4$ClO$_4$, the successive donor bilayers are related by a symmetry plane parallel to (*b*,*c*) through the anions, with donor molecules presenting an alternated tilted orientation along *a*, while in β''_T-(CNB-EDT-TTF)$_4$ClO$_4$ there is no such mirror plane and donor molecules in successive bilayers present the same tilt orientation. In view of the same donor packing pattern in two polymorphs, it is not surprising that no significantly different electronic transport properties where found in the different crystals measured.

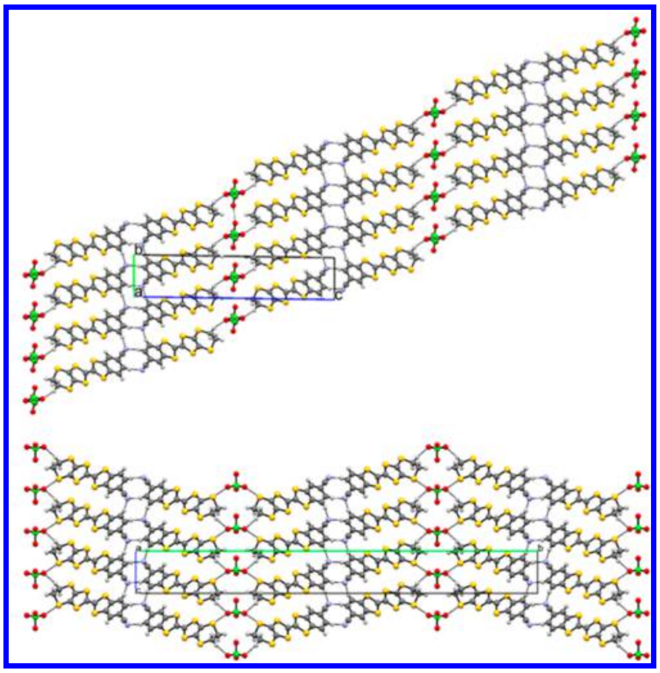

Figure 6. Crystal structures of **1a** (top) and **1b** (bottom), viewed along the *a* axis.

Compound **2** crystallizes in the monoclinic system, space group $P2_1/c$. The asymmetric unit contains one independent CNB-EDT-TTF donor molecule and one tetrahedral ClO_4^- anion located on general positions.

The donor molecule, in compound **2**, is essentially planar with exception of the dihydrodithiin ring which presents the usual half-chair conformation. The central C═C bond length (C8−C9 = 1.379(4) Å) are within experimental uncertainty identical to those observed in other 1:1 salts with donor in monocationic state (Table 2).

The crystal structure of **2** is made by head-to-tail chains of dimerized donors along *b* (Figure 7). Short contacts are observed between dimmers through C−S and C−C interactions. Along *a* the neighboring parallel chains are connected by several S−S interactions. Along *c* the neighboring chains are alternately tilted (72.2°) and connected by the C−N···H interactions (Figure 8); see Table S5 for short contact list. In this case, as for a previous 1:1 salt, the (CNB-EDT-TTF)FeBr$_4$, the bilayer structure is not observed.[25]

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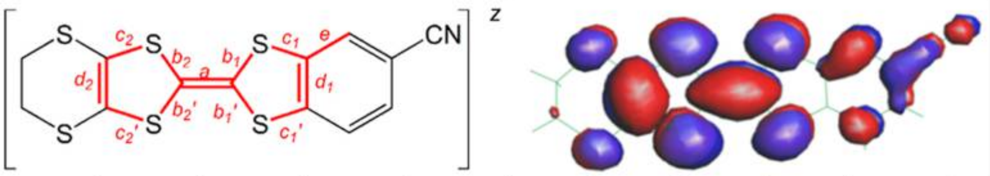
Table 2. Bond Lengths (Å) of (CNB-EDT-TTF)$^{+z}$ Donor in Different Compounds (CNB-EDT-TTF)$_n$A and in Different Oxidation States, from z = 0, to z = 1[b]

(CNB-EDT-TTF)$_n$A



A		z	δ	a	b1	b2	b1’	b2’	c1	c2	c1’	c2’	d1	d2	Ref
-	*β*-D 3	0	0,801	1.344(4)	1.764(3)	1.761(2)	1.764(2)	1.760(3)	1.755(2)	1.762(3)	1.753(3)	1.764(2)	1.408(3)	1.344(4)	a
			0,808	1.345(4)	1.766(2)	1.766(3)	1.762(3)	1.759(2)	1.754(3)	1.771(2)	1.754(2)	1.762(3)	1.405(3)	1.335(4)	
-	*α*-D	0	0,790	1.355(8)	1.753(7)	1.743(6)	1.758(7)	1.766(6)	1.758(5)	1.764(6)	1.744(6)	1.765(6)	1.413(8)	1.322(8)	1
ClO_4^-	**1a**	0.25	0,765	1.357(8)	1.759(6)	1.737(6)	1.745(6)	1.751(6)	1.751(6)	1.754(6)	1.750(5)	1.743(6)	1.402(8)	1.350(9)	a
ClO_4^-	**1b**	0.25	0,782	1.339(9)	1.763(6)	1.740(6)	1.748(6)	1.759(6)	1.743(6)	1.746(6)	1.748(6)	1.746(7)	1.401(9	1.353(10)	a
$[Au(mnt)_2]^-$		0.5	0,748	1.359(6)	1.748(5)	1.733(6)	1.744(5)	1.743(5)	1.738(4)	1.743(5)	1.757(5)	1.742(5)	1.391(7)	1.369(8)	25
$[Ni(mnt)_2)]^-$		0.5	0,753	1.360(4)	1.739(3)	1.732(3)	1.737(3)	1.734(3)	1.743(3)	1.742(3)	1.752(3)	1.746(3)	1.390(5)	1.346(5)	25
ClO_4^-	**2**	1	0,695	1.379(4)	1.729(3)	1.710(3)	1.729(3)	1.729(3)	1.746(3)	1.725(3)	1.735(3)	1.730(3)	1.402(4)	1.367(4)	a
$FeBr_4^-$		1	0,6985	1.38(2)	1.71(1)	1.70(1)	1.77(1)	1.71(1)	1.75(1)	1.75(1)	1.75(1)	1.73(1)	1.39(2)	1.39(2)	25

[a] This work. [b] Bonds are identified in the scheme below together with the HOMO diagram.[2] δ = (b + c) − (a + d).

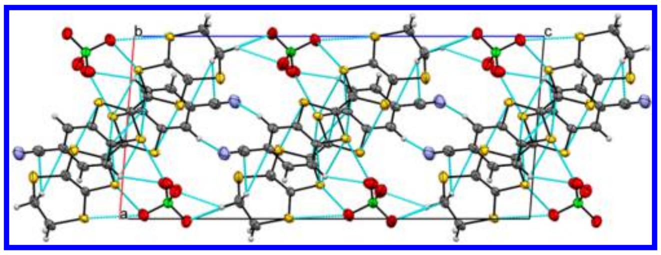


Figure 7. Crystal structures of **2** viewed along the *b* axis.

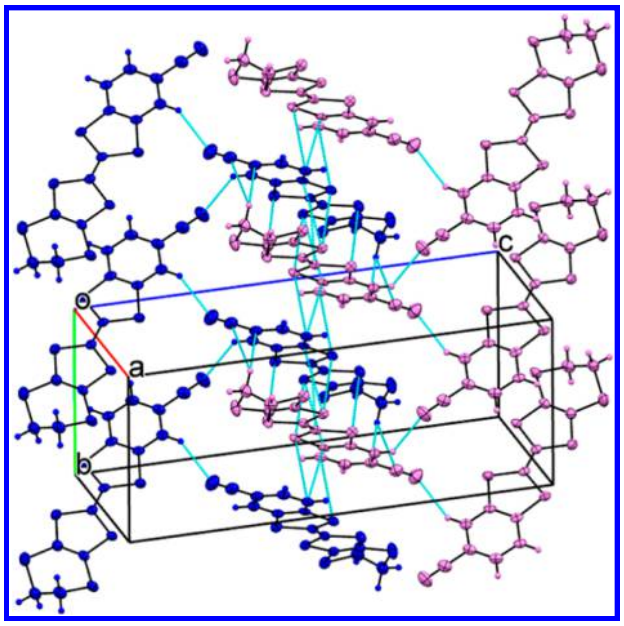


Figure 8. Alternated stacks along *a* of donor molecules in the crystal structure of **2**, the donors are connected to nearby donor stacks along *c* through C−N···H interactions. The anions were omitted for clarity.

Compound **3** crystallizes in the monoclinic system, space group $P2_1/c$, with cell parameters a = 31.9218(4) Å, b = 7.79560(10) Å, c = 11.5358(2) Å, β= 93.6560(10)°; and V = 2864.84(7) Å^3. This new donor structure (Figure S4) has two independent molecules in the asymmetric unit, both with disorder in the dithiine ring corresponding to half-chair conformations and one of the donor units presents also 50% disorder in the position of the cyano group. In spite of this disorder the structure of this new polymorph is of better quality than that previously described, presenting a lower uncertainty in bond lengths which however within experimental uncertainty are identical to the other donor polymorph previously reported.[1] The central C═C bond length (C9−C8 = 1.344(4) Å and C21−C22 = 1.345(4) Å) is typical of neutral TTF donors.[1] The crystal structure is made by piling up molecules head to tail forming stacks along the *b* axis (Figure S5) with short C−N···H−C contacts in the range 2.415−2.456 Å. Further details about the crystal structure are provided in Supporting Information (Table S2 and Figure S5).

The analysis of the donor bond lengths in the different compounds reveals as expected that the central C═C and C−S bond lengths of fully oxidized donors in **2**, which are comparable to those previously observed in the 1:1 salt (CNB-EDT-TTF)$FeBr_4$[25] present a larger deviation from those in the neutral donor (**1a** and **1b**) than those observed for the partially oxidized donors (Table S2). As one goes from the neutral donor **3** to the partially oxidized donors (**1a** and **1b**) and then to fully oxidized donors in **2**, a small but consistent increase in the central C═C and a decrease of the C−S bond lengths is observed as expected from the depopulation of the HOMO depicted in Table 2. In spite of the uncertainty of the bond lengths in different structures, this trend of variation is also observed in the comparison with other 1:1 and 1:2 salts.[25] This is further confirmed by the analysis of the function $\delta = (b + c) - (a + d)$, also shown in Table 2, which is more sensitive to the bond length variation upon oxidation.

■ CONCLUSIONS

In conclusion $(\text{CNB-EDT-TTF})_4\text{ClO}_4$ was obtained by electrocrystallization in dichloromethane in two different polymorphs. Besides the previously reported phase β''_T-$(\text{CNB-EDT-TTF})_4\text{ClO}_4$ reported here with better resolution, a new monoclinic phase β''_M-$(\text{CNB-EDT-TTF})_4\text{ClO}_4$, is now described. The 2D packing pattern of donors within the bilayers are identical in these two β''-polymorphs, but the donors molecules which in the triclinic phase have the same orientation in different layers, in the monoclinic phase present an alternation of orientation with a doubling of the interlayer cell parameter. Besides the alternation in donor orientation this unit cell doubling in the monoclinic phase is also associated with perchlorate anion ordering between two positions/orientations. The ClO_4^- anions in β''_M phase present only one of the two possible orientation observed in the triclinic phase. The experimental conditions favoring the preparation of any of these polymorphs of the 1:4 salts remain undetermined.

Besides the 4:1 salts, $(\text{CNB-EDT-TTF})\text{ClO}_4$ is also obtained by electrocrystallization. The growth of this 1:1 salt is favored in THF and by lower relative donor concentrations, which prevent the cationic donor association processes required for the growth of the 4:1 salts.

The present results in different perchlorate salts of CNB-EDT-TTF, put into evidence a new aspect of the polymorphism in salts of this donor. Besides the well-known polymorphism associated with different donor packing pattern in layers, as in single single layer ET salts and recently described in the bilayer $(\text{CNB-EDT-TTF})_4\text{I}_3$ salts with κ''- and β''-type, a new form of polymorphism associated with the orientation of donor molecules in β''-type consecutive layers is also present.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00257.

> Cyclic voltammograms, kinetic study, UV−vis absorption spectra, X-ray structural analysis, and selected short contact (PDF)

Accession Codes

CCDC 1533003−1533006 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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