

Article

β'' -(CNB-EDT-TTF)₄BF₄; Anion Disorder Effects in Bilayer Molecular Metals

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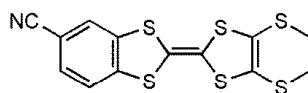


Abstract: The preparation and characterization of new salts based on the dissymmetrical TTF derivative CNB-EDT-TTF (cyanobenzene-ethylenedithio-tetrathiafulvalene) and BF₄[−] anions, are reported. Depending on the electrocrystallization conditions salts with different stoichiometries, (CNB-EDT-TTF)BF₄ and β'' -(CNB-EDT-TTF)₄BF₄, can be obtained. The 1:1 salt is an electrical insulator isostructural to the ClO₄ analogue previously described. The 4:1 salt is a new member of the family of 2D metals of this donor with different small anions X, (CNB-EDT-TTF)₄X, characterized by a bilayer arrangement of the donors and it was obtained in a monoclinic polymorph with a β'' -type donor packing pattern. The small anions in this compound are severely disordered between the donor bilayers, which present slightly larger lattice parameters than the isostructural ClO₄ analogue. Both electrical conductivity and thermoelectric power measurements in single crystals denote metallic properties as predicted by electronic band structure calculations. As a consequence of the anion disorder the metallic regime of the electrical conductivity denotes electronic localization effects with a progressive increase of resistivity below ~25 K. Because of the larger lattice parameters the intermolecular interactions and electronic bandwidth are decreased compared to other (CNB-EDT-TTF)₄X salts. The large and positive thermoelectric power *S* of this compound (~110 μ V/K in the range 100–330 K) and its electrical conductivity σ = 20 S/cm at room temperature lead to a power factor $S^2\sigma$ = 24 μ W/K²m, quite large among molecular conductors, placing these compounds as potential candidates for thermoelectric materials.

Keywords: molecular conductors; bilayer metals; radical cation salts; CNB-EDT-TTF; thermoelectrics

1. Introduction

It has been recently shown that the dissymmetrical TTF derivative cyanobenzene-ethylenedithio-tetrathiafulvalene (CNB-EDT-TTF) (Scheme 1) is an electron donating molecule that when combined with small anions X such as ClO₄[−], PF₆[−], and I₃[−], leads to a family of radical cation salts of composition (CNB-EDT-TTF)₄X and characterized by a unique donor bilayer structure [1]. This bilayer arrangement is promoted by an effective arrangement of hydrogen bond dimeric C–N...H–C interactions involving the cyano groups, as a combination of R²₂(10) and R²₂(8) synthons in a two-dimensional network. These (CNB-EDT-TTF)₄X compounds have been obtained in several polymorphic phases associated with different donor packing patterns or anion ordering schemes [2,3] and for κ -type packing pattern some of these 2D metals have shown superconductivity at low temperatures [2].



Scheme 1. CNB-EDT-TTF.

The donor bilayer structure confers to these salts unusual metallic properties associated to high band filling, large electronic effective masses and quasi degenerated 2D Fermi surfaces, making the study of this type of bilayer metallic systems quite attractive. However the range of stability of the (CNB-EDT-TTF)₄X salts was found so far restricted to linear, tetrahedral or octahedral anions of size comparable to ClO₄[−], PF₆[−], and I₃[−], and for instance with a larger anion such as FeBr₄[−], a salt of different stoichiometry (CNB-EDT-TTF)₂FeBr₄ and distinct structure is obtained instead [4]. These findings directed our attention towards exploring new CNB-EDT-TTF salts with comparable small anions and in this contribution we report the salts obtained with the smaller tetrahedral anion BF₄[−]. With this small tetrahedral anion salts with both 4:1 and 1:1 stoichiometries were obtained.

2. Materials and Methods

2.1. General Information

CNB-EDT-TTF was prepared following a previous described procedure [5] which was more recently improved [3]. *n*-Bu₄N BF₄ (Sigma Aldrich, Darmstadt, Germany) was purified by recrystallization from ethyl acetate. Dichloromethane and tetrahydrofuran (THF) were freshly distilled immediately before use.

2.2. Synthesis

[CNB-EDT-TTF] BF₄ (1). A THF solution of the donor CNB-EDT-TTF (2.2×10^{-3} M) and *n*-Bu₄N BF₄ (1.1×10^{-2} M) was added to an H-shaped two-compartment cells separated by frit glass with Pt electrodes and sealed under nitrogen. After applying initially a current density of 0.5 μA/cm², during the first 3 days, then increased to 0.7 μA/cm² during more 20 days, black block shaped crystals grown on the anode were collected and washed with THF and dichloromethane.

β''-[CNB-EDT-TTF]₄ BF₄ (2). A dichloromethane solution of the donor CNB-EDT-TTF and *n*-Bu₄N BF₄ (both 2×10^{-3} M) was added to an H-shaped two-compartment cells separated by frit glass with Pt electrodes and sealed under nitrogen. After approximately 15 days of applying a constant current density of 1 μA/cm², dark brown elongated platelet shaped crystals grown on the anode were collected and washed with dichloromethane/ether.

2.3. X-ray Crystallography

Selected single crystals were mounted on a loop with protective oil and X-ray data was collected on a APEX II CCD detector diffractometer (Bruker, Billerica, Massachusetts, MA, USA) using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) and operating in a φ and ω scans mode. A semi empirical absorption correction was carried out using SADABS [6]. Data collection, cell refinement and data reduction were done with the SMART and SAINT programs [7]. The structures were solved by direct methods using SIR97 [8] and refined by full matrix least-squares methods using the program SHELXL97 [9] using the winGX software package [10]. 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 Mercury [11]. CCDC 1825988–1825989 contains 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.

Crystallographic data for compound 1, (CNB-EDT-TTF)BF₄: C₁₃H₇BF₄NS₆, M = 456.37 g·mol^{−1}, monoclinic, space group *P*2₁/*c*, *a* = 9.5066(9) Å, *b* = 8.3629(9) Å, *c* = 21.1593(13) Å, β = 95.984(6)°, *V* = 1673.1(3) Å³, *Z* = 4, ρ_{calc} = 1.812 g·cm^{−3}, μ(Mo *K*α) = 0.855 mm^{−1}, 5429 reflections measured, 2887 unique *R*_{int} = 0.0734, θ_{max} = 25.02°, *R*₁ = 0.0618 using 2887 Refl. > 2σ(*I*), ω*R*₂ = 0.1189, *T* = 150(2) K. CCDC 1825989.

Crystallographic data for compound 2, "-(CNB-EDT-TTF)₄BF₄: C₁₃H₇NS₆, M = 832.62 g·mol^{−1}, monoclinic, space group *P*2₁/*m*, *a* = 4.8418(13) Å, *b* = 55.724(15) Å, *c* = 5.9081(16) Å, β = 94.208(18)°, *V* = 1589.7(7) Å³, *Z* = 4, ρ_{calc} = 1.544 g·cm^{−3}, μ(Mo *K*α) = 0.847 mm^{−1}, 8106 reflections measured, 1584 unique *R*_{int} = 0.0747, θ_{max} = 20.64°, *R*₁ = 0.0764 using 1584 Refl. > 2σ(*I*), ω*R*₂ = 0.1727, *T* = 150(2) K. CCDC 1825988.

2.4. Electronic Band Structure Calculations

The tight-binding band structure calculations [12] were of the extended Hückel type and a modified Wolfsberg–Helmholtz formula was used to calculate the non-diagonal *H*_{μν} values [13]. All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double-ζ quality for C and N 2s and 2p, S 3s and 3p and of single-ζ quality for H1s. The ionization potentials, contraction coefficients and exponents were taken exactly as in our previous work for (CN-BEDT-TTF)₄I₃ [2]. Because of the different crystallographic cells the four different HOMO···HOMO intralayer interactions were defined as in the previous work on disordered (CN-BEDT-TTF)₄I₃ [2]: I, interaction along the stacks; II, lateral π-type interaction; III, interaction along the step-chains and IV, head to head interlayer interaction.

2.5. Electric Transport Properties

Electrical conductivity and thermoelectric power were measured in single crystals in the temperature range of 20–320 K, in a cell attached to the cold stage of a closed cycle helium refrigerator. In the first step, the thermoelectric power was measured by using a slow AC (ca. 10^{−2} Hz) technique [14], by attaching two φ = 25 μm diameter 99.999% pure Au wires (Goodfellow), thermally anchored to two quartz blocks, with Pt paint (Demetron 308A), to the extremities of an elongated sample as in a previously described apparatus [15], under computer control [16]. The oscillating thermal gradient was kept below 1 K and it was measured with a differential Au-0.05 at. % Fe vs. chromel thermocouple, and the sample temperature measured with a calibrated thermocouple of the same type. The absolute thermoelectric power of the samples was obtained after correction for the absolute thermopower of the Au leads, by using the data of Huebner [17]. In a second step two additional contacts between the previous ones, were similarly made in order to achieve a four-in-line contact configuration and electrical resistivity was measured imposing an AC current of 1 μA at 70 Hz and the voltage drop measured using a lock-in technique. Sample electrodes configuration was checked for unnested to nested voltage ratio, as defined by Schaffer et al. [18], which was kept below 5%.

3. Results

As previously observed with the anion ClO₄[−] depending on the solvent and electrocrystallization conditions salts with 1:1 and 4:1 donor:acceptor stoichiometries; (CNB-EDT-TTF)BF₄ (1) and (CNB-EDT-TTF)₄BF₄ (2) can be obtained, the first one as black block shaped crystals from tetrahydrofuran (THF) and the last one as thin dark brown platelet shaped crystals from dichloromethane solutions. For the 4:1 salt, among the several crystals tested only the monoclinic phase β''_M-(CNB-EDT-TTF)₄BF₄ could be observed with so far no evidence for the triclinic one described for ClO₄[−] [3]. These two BF₄ salts are isostructural with the analogues with ClO₄[−] anions [3] and therefore the description of their crystal structures will be only briefly summarized.

(CNB-EDT-TTF)BF₄ (1) crystallizes in the monoclinic system, space group *P*2₁/*c*. The asymmetric unit contains one independent donor molecule and one tetrahedral BF₄[−] anion located in general positions (Figure S1). The donor geometry is almost planar with exception of the dihydrodithiin ring which

presents the usual half-chair conformation with bond lengths (central C = C: C5–C6 = 1.374(9) Å) identical within experimental uncertainty to those observed in other 1:1 salts with this donor in monocationic state [3,4] (Table S1). The crystal structure of **1** consists in head-to-tail chains of CNB-EDT-TTF donors dimers stacked along *b*, as shown in Figure 1. Donors in nearby stacks with reversed tilting (related by a screw axis) are connected by a helical network of short C–N⋯H–C contacts at 2.546 Å. In addition there are several short S⋯S, S⋯C and S⋯F intermolecular contacts and hydrogen bonds listed in Table S2.

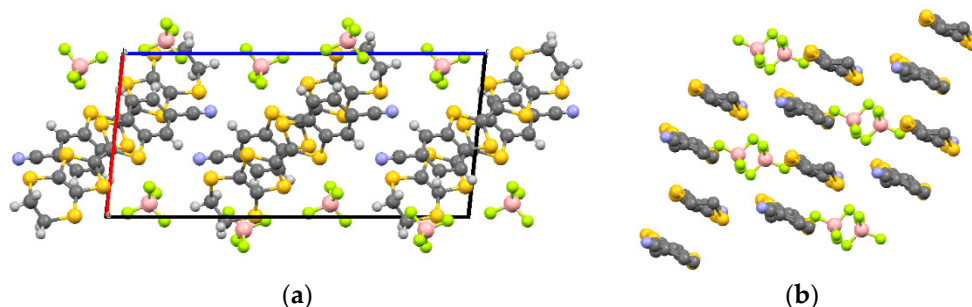


Figure 1. Crystal structure of (CNB-EDT-TTF) BF₄; (a) viewed along the axis; (b) partial view along the molecular long axis of a layer of head to tail donor dimers.

(CNB-EDT-TTF)₄BF₄ (**2**) crystallizes in the monoclinic system, space group P2₁/m, it is isostructural with the previously described monoclinic phase of the analogue with ClO₄ [3] but with cell parameters slightly larger. Figure 2 shows a projection of the crystal structure of **2** along the stacking axis (corresponding to *a*). The refinement of the crystal structure from different crystals measured was always severely limited by a large disorder associated with the anions which could not be clearly identified in several possible positions placed in a channel along *c* between the donor bilayers. However when a squeeze was applied leaving only the donors to be considered in the structural refinement, a fair agreement could be achieved. The asymmetric unit of **2** (Figure S2) contains one independent CNB-EDT-TTF donor molecule with all atoms located at general positions. The donor geometry and bond lengths (Table S3) are within experimental uncertainty identical to that previously observed in β''-(CNB-EDT-TTF)₄X salts. The donor crystal packing consist in the previously described β''-type bilayer structure of donors, with similar short intermolecular contacts listed in Table S4, and alternated tilting orientations of bilayers along *b*, the large cell parameter. A relevant difference is on the cell parameters *a* and *c*, slightly larger than those observed for ClO₄ in spite of the smaller anion size. This difference is certainly due to the severe anion disorder and it corresponds to a not so tight packing of the molecules in the layers.

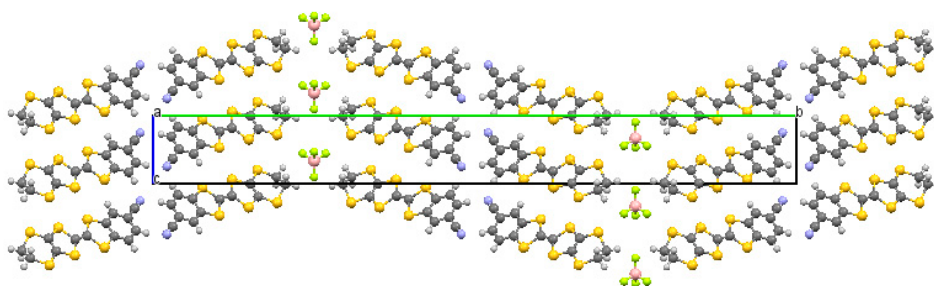


Figure 2. Crystal structure of β''-(CNB-EDT-TTF)₄BF₄ viewed along *a*.

The donor bilayer structure is due to a network of bifurcated C–N⋯H interactions in an efficient combination of R²₂(10) and R²₂(8) synthons between coplanar molecules (Figure 3a) with contact distances (N1⋯H3 at 2.624 Å, N1⋯H5 at 2.505 Å) comparable to those previously found

in β'' -(CNB-EDT-TTF)₄X salts [1–3]. However the stacking distance between successive planes of molecules interconnected by R²₂(10) and R²₂(8) synthons is slightly larger in this BF₄ salt. The three different intermolecular intralayer interactions I, II and III (I, along the stacks; II, lateral π -type and III, along the step-chains) are shown in Figure 3b. Figure 3a also shows the interaction IV between a pair of head to head molecules in adjacent layers. The magnitude of these interactions was evaluated under the extended Hückel approach and values obtained are listed in Table 1 and compared with those in the ClO₄, PF₆ and I₃ analogues. Interactions II and IV are practically identical, as a consequence of a quite similar network of C–N $\cdots$ H interactions, but interactions I and III are reduced as a consequence of a larger intermolecular spacing.

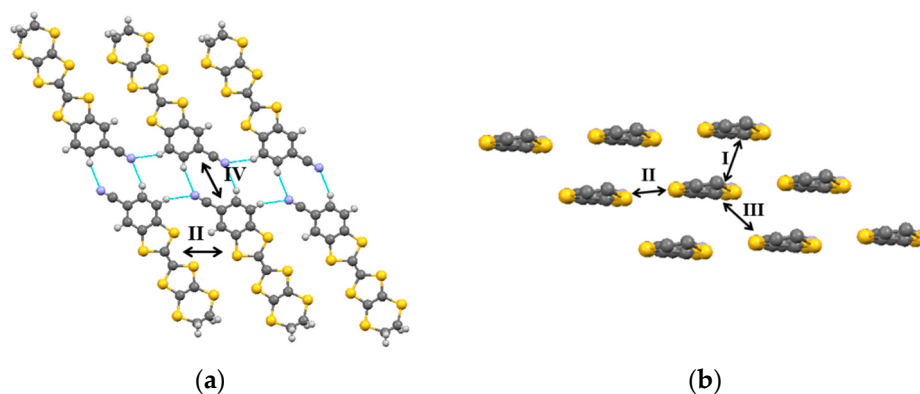


Figure 3. Details of donors packing in β'' -(CNB-EDT-TTF)₄BF₄: (a) partial view perpendicular to the donors with blue lines emphasizing C–N $\cdots$ H–C interactions, as a combination of R²₂(10) and R²₂(8) synthons in a two-dimensional network of coplanar donors; (b) View of one donor layer along the molecular long axis showing a β'' -type packing pattern, with identification of the distinct intralayer interactions I, II and III.

Table 1. Absolute values of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies (meV) for the different donor $\cdots$ donor interactions in the β'' -(CN-BEDT-TTF)₄X salts (I, along the stacks, II, lateral π -type, III, along the step-chains and IV, head to head interlayer interaction—See Figure 3).

Anion X	I	II	III	IV	Ref.
BF ₄	88	49	201	0.8	This work
ClO ₄	113	51	233	2.7	1
PF ₆	117	53	219	3.1	1
I ₃ (disordered phase)	125	51	220	0.6	2

The electronic band structure predicted on the basis of these calculated intermolecular interactions and the corresponding Fermi surface assuming an average charge 1/4+ for each donor molecule are depicted in Figure 4. Due to the small interlayer interaction IV, associated with head to head intermolecular contacts, the bands are split in two almost degenerated ones. The Fermi surface corresponds to two elliptical cylinders, as typical of β'' -salts [19], and their cross section area corresponds to about 1/8 of the first Brillouin Zone as previously calculated for identical β'' -(CNB-EDT-TTF)₄X salts [1,2].

The metallic properties predicted by these electronic band structure calculations are confirmed by the measurements of electrical transport properties in single crystals, shown in Figure 5 where they are compared with those previously reported for the ClO₄ and PF₆ analogues. The electrical resistivity, ρ (~ 0.05 – 0.06 Ω cm at room temperatures) upon cooling shows an almost linear decrease until about 50 K, reaches a broad and sample dependent minimum at ~ 25 – 30 K, followed by a gradual increase upon further cooling, reaching at 1.7 K values comparable to those at room temperature. This increase of resistivity at low temperatures, which was found slightly sample dependent, can be

due electron repulsion or most likely to localization effects induced by anion disorder [20]. Indeed no such minima of electrical resistivity was observed at this temperature range in the ClO_4 and PF_6 analogues where the anions were found not so severely disordered, and where the electrical resistivity presents a stronger temperature dependence in a more extended linear regime.

The thermopower S presents rather large positive values of $\sim 110 \mu\text{V/K}$ at room temperature, and it remains almost temperature independent down to 150 K. Upon cooling below this temperature the thermopower values start decreasing towards zero in a fashion approximately proportional to the temperature T , confirming the metallic nature of the compound and indicating that the conduction takes place in a continuum of states around the Fermi-level. The large positive values are consistent with the large band filling (7/8) predicted by the band structure calculations described above assuming an average $1/4+$ charge of each donor molecule. The thermopower values significantly larger than in the ClO_4 and PF_6 analogues are also consistent with the predicted smaller bandwidth of the BF_4 salt as a consequence of larger intermolecular spacing, which results in a larger density of states at the Fermi-level.

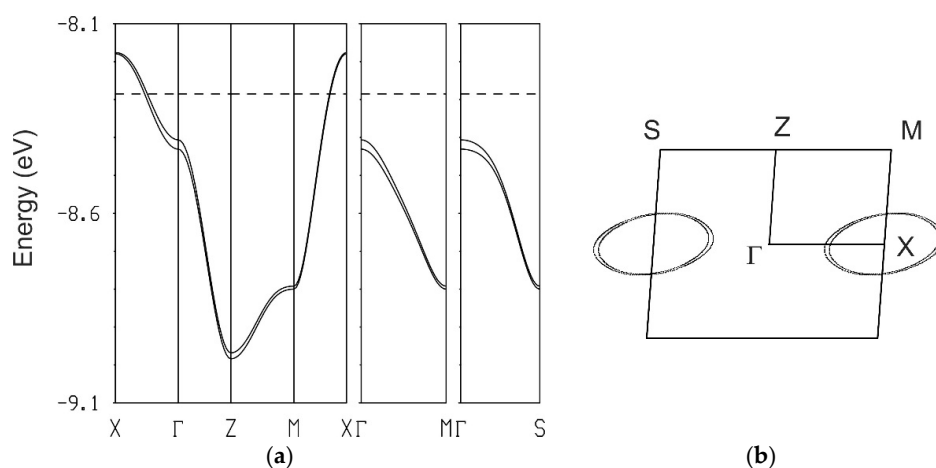


Figure 4. Calculated band structure (a) and Fermi surface (b) for $\beta''\text{-(CNB-EDT-TTF)}_4\text{BF}_4$ where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Z = (0, c^*/2)$, $M = (a^*/2, c^*/2)$ and $S = (-a^*/2, c^*/2)$. The dashed line in (a) refers to the Fermi level.

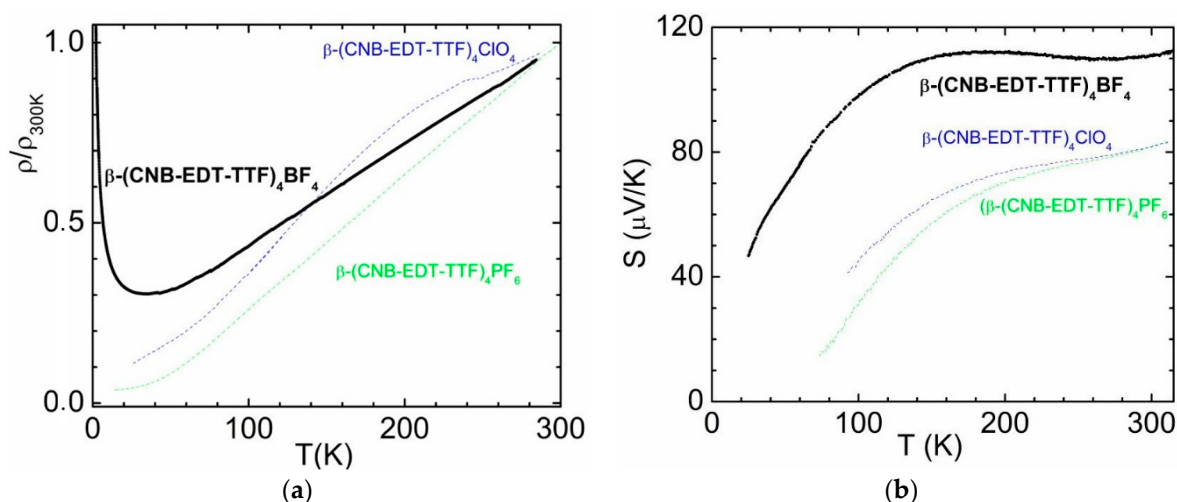


Figure 5. Temperature dependence of electrical resistivity ρ (a) and absolute thermoelectric power S ; (b) of $\beta''\text{-(CNB-EDT-TTF)}_4\text{BF}_4$ single crystals compared with corresponding data for $\beta''\text{-(CNB-EDT-TTF)}_4\text{ClO}_4$ and $\beta''\text{-(CNB-EDT-TTF)}_4\text{PF}_6$ (thin lines, from reference [1]).

The high temperature regime of large and almost temperature independent thermopower appears as a common feature of the β'' -salts of this donor. In this respect it is worth consider that the thermopower, which is the entropy per charge carrier weighted by their contribution to the total electrical conductivity, is directly related to the density of states at the Fermi level and the contribution $\sigma(E)$ of states with energy E close to the Fermi level, E_F , to the total conductivity σ [21]:

$$S = -k_B/e \int (E - E_F)/k_B T (\sigma(E)/\sigma) dE \quad (1)$$

Therefore the large thermopower of these 4:1 β'' -salts is a consequence of the large band filling placing the Fermi level in region of large effective mass. In contrast to the low temperature regime, with a $S\propto T$ behavior typical of metals, the high temperature regime with almost temperature independent thermopower can result from correlation effects in a narrow band, when the carrier mean free path becomes comparable to the lattice parameters and the transport mechanism becomes diffusive rather than coherent. Finally it should be mentioned that the measured thermopower value of $\sim 110 \mu\text{V/K}$ in β'' -(CNB-EDT-TTF) $_4\text{BF}_4$ is to the best of our knowledge the largest one observed in a molecular metallic system. Although the thermal conductivity of these molecular compounds was not yet measured, it is expected to be modest in view of the complex molecular structure ($\sim 1 \text{ W/Km}$) [22,23], the large thermopower values of these bilayer systems place them as good candidates for efficient thermoelectric materials. In fact from an electrical conductivity $\sigma = 20 \text{ S/cm}$ and thermoelectric power $S = 110 \mu\text{V/K}$, a power factor $PF = S^2\sigma = 24 \mu\text{W/K}^2\text{m}$ can be deduced, which is comparable to the best values reported so far for molecular materials such as $387 \mu\text{W/K}^2\text{m}$ in $(\text{TTT})\text{I}_3$ or $110 \mu\text{W/K}^2\text{m}$ in $\text{Cu}(\text{DMDCNQI})_2$ [1].

4. Conclusions

Based on the electron donor CNB-EDT-TTF and the small tetrahedral anion BF_4^- salts with 1:1 and 4:1 stoichiometries—(CNB-EDT-TTF) BF_4 and β'' -(CNB-EDT-TTF) $_4\text{BF}_4$ —can be obtained by electrocrystallization. The 1:1 salt is an electrical insulator but the 4:1 is a new member of the family of 2D metals with donor bilayer structure. Its structure and properties are comparable to the other compounds previously described, but the anions are more disordered and in spite of the smaller anion size the lattice parameters are slightly larger and intermolecular interactions smaller, while thermoelectric power becomes larger. The thermoelectric power of β'' -(CNB-EDT-TTF) $_4\text{BF}_4$, is very large, to the best of our knowledge the largest reported among molecular metallic systems, placing this family of bilayer compounds β'' -(CNB-EDT-TTF) $_4\text{X}$ as good candidates for efficient thermoelectric materials.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/8/4/142/s1>: Figure S1: ORTEP and atomic numbering schemes (top and side views) of (CNB-EDT-TTF) BF_4 (1). Thermal ellipsoids drawn at 50% probability level; Figure S2: ORTEP and atomic numbering schemes (top and side views) of (CNB-EDT-TTF) $_4\text{BF}_4$ (2). Thermal ellipsoids drawn at 50% probability level; Table S1: Bond lengths of compound 1; Table S2: Short contacts of compound 1; Table S3: Bond lengths of compound 2, Table S4: Short contacts of compound 2.

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Author Contributions: Sandra Rabaça and Manuel Almeida conceived and designed the experiments; Sandrina Oliveira and Vasco Gama performed the sample preparation and participated in all experiments; Isabel C. Santos analyzed the crystallographic data, Elsa B. Lopes and Gonçalo Oliveira measured the electric transport properties, Enric Canadell performed electronic band structure calculations, Sandra Rabaça and Manuel Almeida wrote the paper with the contributions from all authors.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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