Bilayer Molecular Metals Based on Dissymmetrical Electron Donors

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Supporting Information

ABSTRACT: The electrocrystallization from solutions of cyanobenzene-ethylenedithio-tetrathiafulvalene (CNB-EDT-TTF) in the presence of different anions X = ClO$_4$^{-}, PF$_6$^{-}, and I$_3$^{-}, affords a new type of 2D molecular metals with composition (CNB-EDT-TTF)$_4$X based on an unprecedented bilayer structure of the donors induced by effective head to head interdonor interactions through the nitrile groups, which is responsible for 2D metallic systems with unusual properties such as the higher band filling, larger effective mass of carriers, and almost degenerated double Fermi surfaces.

TTF derivatives have been at the basis of the majority of the organic conductors, reported in the last decades. An early trend soon established after the discovery of first organic metals and superconductors in the development of new electronic materials of this type was the preparation of electroactive molecules based on sulfur rich and extended \( \pi \)-systems capable to establish in the solid state interactions in more than one direction. The most successful molecular building blocks for this type of electronic materials have been sulfur and other chalcogen rich derivatives of TTF such as bis-ethylenedithio tetrathiafulvalene (ET) in salts with composition (ET)$_2$X where X can be a diversity of monoanions. Indeed this type of molecules has provided not only the large majority of organic metals and superconductors presently known but also many two-dimensional solids with a very rich diversity of electronic ground states, from superconducting, to insulating, antiferromagnetic, etc.

The crystal structures of these salts have a strong 2D character with donor molecules packed with their long axis parallel to each other in layers that alternate with anionic layers. The way the molecules are packed in a layer can be quite diverse, leading to a very rich variety of electronic properties. The most common structures associated with metallic and superconducting properties are the \( \alpha, \beta, \) and \( \kappa \)-phases depicted in Scheme 2. During the past few years some salts of this type of donors were found to present more complex structures where two different donor layers may alternate in the solid, but in all cases the layers have a thickness corresponding to the length of one donor molecule (monolayers).

We recently developed the dissymmetrical ET derivative cyanobenzene-ethylenedithio-tetrathiafulvalene (CNB-EDT-TTF) (Scheme 1), which through a weak hydrogen bond assisted interaction is capable to form effective dimeric interactions promoting the crystallization of its charge transfer salts with several small anions X into a new type of bilayer structures (Scheme 2) with metallic properties and composition (CNB-EDT-TTF)$_4$X.

Electrocrystallization of CNB-EDT-TTF from dichloromethane in the presence of salts of perchlorate, hexafluorophosphate, and triiodide leads to dark brown platelet crystals with metallic shine. Well-formed crystals are only obtained using moderate current densities (\( \sim 1 \mu \text{A/cm}^2 \)). Larger currents lead to a dark powder material with ill-defined composition, suggesting that after the oxidation of a donor molecule at the electrode the growth of salts with 4:1 donor to acceptor stoichiometry requires the association with neutral molecules in solution to allow the formation of partially oxidized tetrameric units (CNB-EDT-TTF)$_4$. Larger current probably does not allow the relatively slow, diffusion controlled, higher association process (Scheme S1).

Two distinct structural bilayer types have been observed in (CNB-EDT-TTF)$_4$X salts. For \( X = PF_6^- (1) \) and ClO$_4$^- (2), the crystal structure is triclinic \( \text{P}\overline{1} \) with one independent donor molecule per asymmetric unit. The donor molecules present in each layer an arrangement of \( \beta^- \)-type as observed in many ET salts with all molecules with the same orientation and conformation disorder in the dithiine ring in 1 (Figure S1a). The layers are however coupled in bilayers through the nitrile groups all pointing to the same side of the layers. The nitrile...
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Inorganic Chemistry

described as a R2\textsubscript{2}(10) side coupling between two molecules in each layer, which can be

where the molecules were essentially coplanar. The two donor

positions correspond to two different orientations of triiodide

$I_3$ and $I_1$ lie at the inversion

axis, respectively (top), and partial view of one donor layer along

the long axis of molecules (bottom). The arrows denote the different

intermolecular interactions.

![Figure 1. Crystal structure of I (left) and 3 (right); viewed along the a and b axis, respectively (top), and partial view of one donor layer along the long axis of molecules (bottom). The arrows denote the different intermolecular interactions.](image)

head coupling of two almost coplanar molecules in different

layers can be described as a dimeric R2\textsubscript{2}(10) homosynthon. In addition, through the bifurcated C−N···H interaction, there is a side coupling between two molecules in each layer, which can be described as a R2\textsubscript{2}(10) synthon (Figure S8). Although the C−N···H interactions are relatively weak it is worth referring that they are rather common among molecules with nitrile moieties.

The octahedral PF\textsubscript{6} anions present anomalous large displacement parameters with ill-defined positions (Figure S1) and low occupation factors corresponding to 0.5 atoms. The tetrahedral ClO\textsubscript{4} anions appear disordered over two almost equally populated positions slightly displaced along the a-axis, denoting both position disorder of the Cl atom and orientation disorder of the oxygen atoms in the interlayer cavities (Figure S3). This disorder is not so common in ET monolayer salts and may result from a weak correlation between the anion in different layers.

For $X = I_3^−$ (3), the crystal is monoclinic P2\textsubscript{1}/c with two independent donor molecules per asymmetric unit. The donor molecules are arranged head to head in layers with a k-type arrangement, and again the layers are coupled in bilayers by identical C−N···H interactions with R2\textsubscript{2}(10) and R2\textsubscript{2}(10) synthons, which now involve nonequivalent molecules (Figures S6 and S8). In this compound as a consequence of the k-type packing the R2\textsubscript{2}(10) synthon involves molecules with a significant tilting angle at variance with the compounds 1 and 2 where the molecules were essentially coplanar. The two donor units within experimental uncertainty have identical molecular

structures (see Scheme 2).

The electronic properties of these bilayer salts can be understood in terms of the electronic band structure, which can be easily estimated from the crystal structure using the extended Hückel approach, which, in spite of its simplicity, has been quite successful in describing the properties of molecular conductors (Figure 2). The relevant $\beta_{\text{HOMO}−\text{HOMO}}$ intermo-

![Figure 2. Calculated electronic band structure (top) and Fermi surface (bottom) of 1 (left) and 2 (right).](image)

Table 1. Absolute Values of $\beta_{\text{HOMO}−\text{HOMO}}$ Intermolecular Interaction Energies (meV) in (CNB-EDT-TTF)$_4$X Crystals

<table>
<thead>
<tr>
<th>X</th>
<th>PF\textsubscript{6}</th>
<th>ClO\textsubscript{4}</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>$\beta_3$</th>
<th>$\beta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$</td>
<td>116.5</td>
<td>112.7</td>
<td>301.5</td>
<td>301.5</td>
<td>301.5</td>
<td>301.5</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>219.1</td>
<td>233.7</td>
<td>139.2</td>
<td>167.6</td>
<td>128.7</td>
<td>128.7</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>52.7</td>
<td>50.7</td>
<td>79.2</td>
<td>40.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>3.1</td>
<td>2.7</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the ClO\textsubscript{4}− and PF\textsubscript{6} salts with only one independent donor molecule and a β-type packing, between the intermolecular interactions between molecules in the same layer, $\beta_1$, $\beta_2$, $\beta_3$, characteristic of the β′-type packing, there is a smaller interaction $\beta_4$ between almost coplanar molecules in nearby layers connected through the C−N···H interactions. As a consequence of this interlayer interaction $\beta_4$, the usual 2D dispersive band is split into two closely spaced bands filled up to approximately 7/8, and the Fermi surface is two closely spaced cylinders with an area corresponding to almost 1/8 of the first Brillouin zone as shown in Figure 2.

In the I$_3^−$ salt there are four donor units in the unit cell of each layer (two inequivalent, depicted in red and blue in Figure 1)
with a k-type donor packing. The relevant distinct intermolecular interactions between molecules in the same layer now six (β1, β2, β12, β21, β22, β212), identified in Figure 1 (bottom right). There is also a weaker interaction (β3) between two inequivalent molecules in different layers, connected by the C–N–H interactions (Figure S6). The four donors per unit cell in each layer lead to four HOMO bands, which due to the weaker interlayer interaction the Fermi level is split each in two almost degenerated ones. The upper pair of bands are close to half filled. The corresponding Fermi surfaces are two closely spaced cylinders with an area corresponding to almost 1/2 of the first Brillouin zone.

The calculated electronic band structure of these compounds is confirmed by their electrical transport properties. The electrical conductivity measured in single crystals along their long axis b is of the order of 18, 22, and 28 S/cm for the ClO4, PF6, and I3 salts, respectively. In spite of the modest room temperature values, the conductivity presents in all cases a metallic behavior with a smooth decrease upon cooling (Figure 3). This decrease is almost proportional to temperature with the exception of a smooth anomaly between 110 and 140 K in 3 and an anomaly near 250 K for 2, possibly associated with donor charge and anion ordering, respectively. Thermoelectric power measurements decreasing toward zero upon cooling confirm the metallic behavior of these compounds (Figure 3). The large values of the ClO4 and PF6 salts, ~82 μV/K at 300 K, very large for a metallic system, are the result of a highly filled (7/8) band, while the smaller values of the iodine salt, ~28 μV/K at 300 K, are consistent with a system close to half filled, as predicted by the band calculations. Further studies at lower temperatures and under magnetic field are expected to confirm the above details of the band structure.

In conclusion we have shown how the nonsymmetrically cyano-substituted TTF derivative CNB-EDT-TTF can originate a new type of 2D metallic charge transfer salts with compositions (CNB-EDT-TTF)4X (X = ClO4−, PF6−, and I3−), based on a novel bilayer structure of the donors. The bilayer structure is induced by effective head to head interactions through the nitrile groups. These salts are certainly just the first examples of a new generation of molecular conductors expected to be obtained in the future with other anions, where interesting effects resulting from the higher band filling are expected to occur.

## ASSOCIATED CONTENT

### Supporting Information

Experimental and crystallography details, band structure calculations for 2, and CIF files for 1, 2, and 3. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01240.

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**Notes**

The authors declare no competing financial interest.

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# REFERENCES


(7) See Table S1 for detailed Crystallographic data for compounds 1 and 2. Additional selected bond lengths and selected short contacts can be found in Tables S2–S3 and Tables S4–S5 for compounds 1 and 2, respectively.

(8) See Table S1 for detailed crystallographic data of 3. Additional selected bond lengths, angles, and selected short contacts can be found in Tables S6–S7. Crystallographic details and a more detailed discussion are given in the Supporting Information.


