

Dimensionality and Electrical Properties in Organic Synthetic Metals—Current Results through Selected Recent Examples

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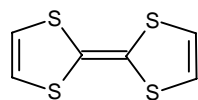
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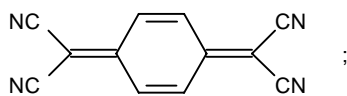
In this article on synthetic metals and organic superconductors, we recall, from the literature data, how an increase in dimensionality appeared to be a key element to stabilize the metallic character of TTF-based materials and to possibly increase T_c in superconducting salts. We then reviewed, through the main trends currently developed, the results obtained during the last decade in the search for new salts and complexes that might display a higher dimensionality associated with a higher electrical conductivity. Typical examples taken from the recent literature are given to illustrate the most interesting findings to date. © 2002 Elsevier Science (USA)

INTRODUCTION

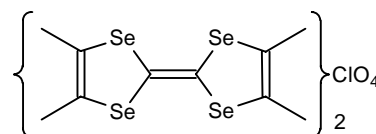
Today, it is common to talk about organic metals (1,2). However, we must remember that before the 1950s, organic compounds were still regarded as insulating matter despite the fact that Mc Coy and Moore (3), as early as in 1911, claimed that organic derivatives might exhibit metallic behavior and that, 50 years later, Little (4) predicted that it was possible to obtain a superconducting state in appropriate organic molecules. Of course, we know that these predictions are now reality since the discovery in 1973 of the highly conducting charge transfer complex TTF-TCNQ (5) and of the superconducting radical cation salts (TMTSF)₂PF₆ and (TMTSF)₂ClO₄ in 1980 and 1981 respectively (6,7).



TTF
(tetrathiafulvalene)



TCNQ
(tetracyanoquinodimethane)



TMTSF
(tetramethyltetraselenafulvalene)

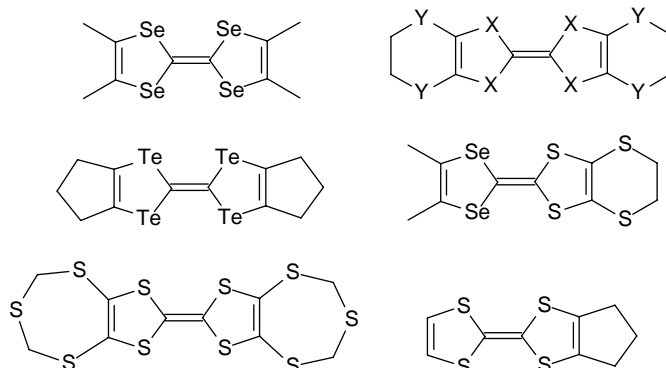
DIMENSIONALITY AND ELECTRICAL PROPERTIES

Results from the 1970s to the 1990s

From the discovery of TTF-TCNQ as the first synthetic metal, intensive efforts were made in order to understand such electrical phenomena while, besides TCNQ and TTF, new charge transfer complexes (CTC) and radical ion salts (SIR) were prepared from other acceptors and donors (see Tables 1 and 2) giving new organic metals and superconductors.

However, most of the work was devoted to the search for new TTF derivatives able to lead to salts electrically more effective. Hence, many changes were made on this donor leading, for example, to the synthesis of a wide variety of selenium derivatives, unsymmetrically substituted compounds, polychalcogenated TTF, etc.

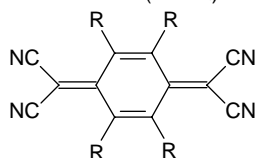
The following are selected examples of polychalcogenated and unsymmetrically substituted donors:



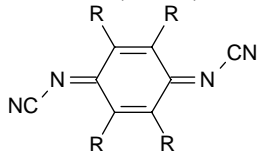
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TABLE 1
Types of Acceptor Used in Organic Salts

Tetracyanoquinodimethane (TCNQ) and derivatives

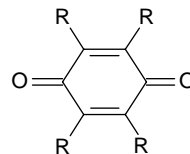


Dicyanoquinonediimine (DCNQI) and derivatives

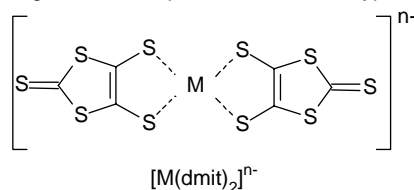


Buckminster fullerene : C₆₀

Quinones and derivatives



Organometallic species of dithiolene type



As shown in Table 3, each new family of donor gave rise to major improvements in the electrical properties of the resulting salts.

- The detailed analysis of the results obtained until the 1990s allowed to clearly describe the physical concepts responsible for such electrical properties (see the very useful review article by Bryce (14)), and to correlate the anisotropic electrical conductivity of these materials with their crystal and electronic structures as is summarized in the following typical examples:

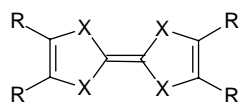
- The high conductivity observed in TTF-TCNQ in the range of 300–56 K (Fig. 1; D.O. Cowan *et al.*, 1986) was associated both with a crystal structure composed of regular segregated stacks of donors and acceptors (Fig. 2; R.H. Blessing *et al.*, 1974) and to a partial electron transfer between these two species. Moreover, down to 58 K, the semiconducting behavior of this CTC was

related to the Peierls distortion (lattice distortion) encountered in all quasi-one-dimensional systems (14) which causes the electron localization responsible for the lack of conductivity.

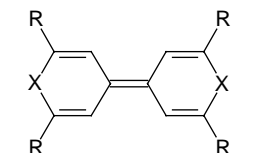
- Similar observations were made with the mixed valence salts TMTTF₂X (X = ClO₄, PF₆). A quasi-regular stacking of the organic molecules was found. It allowed a good π-overlap within the stacks (Fig. 3) associated with a partial band filling due to the exchange of one electron per two TMTSF molecules, making these salts highly conducting and even superconducting at very low temperatures. It is here worthy of note that these quasi-one-dimensional compounds become superconducting at only very low temperature (T_c around 1 K).

- With the polysulfur donor BEDT-TTF (15–17) a tremendous progress was made even if the same salt could lead to different types of molecular packing

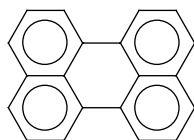
TABLE 2
Types of Donor Used in Organic Salts



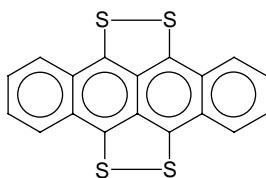
Tetrachalcogenofulvalene



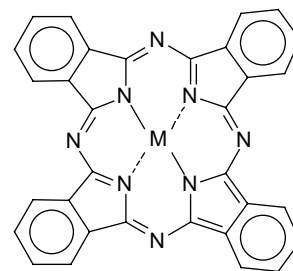
Bis(chalcogenopyranylidene)



Perylene

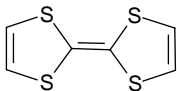
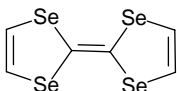
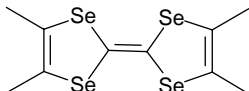
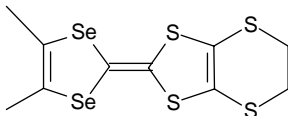
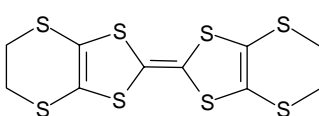


Tetrathiatetracene



Phthalocyanines

TABLE 3
Improvements in the Electrical Properties of CTC and SIR as a Function of TTF Nature

π donor	CTC or SIR
	1973: TTF-TCNQ The first organic metal: $\sigma_{RT} = 500 \text{ S cm}^{-1}$; $T_{M-1} = 58 \text{ K}$ (5) 1986: The first superconducting CTC (8)
	1974: TSF-TCNQ Metallic state retained down to 28 K (9)
	1980: (TMTSF) ₂ PF ₆ The first organic superconductor under pressure: 12 kbar; $T_c = 0.9 \text{ S cm}^{-1}$ (6) 1981: (TMTSF) ₂ ClO ₄ The first organic superconductor under ambient pressure: $T_c = 1.4 \text{ K}$ (7)
	1987: DMET ₂ AuCl ₂ The first organic superconductor based on an asymmetrical TTF: $T_c = 0.83 \text{ K}$ (10)
	1983: (BEDT-TTF) ₂ ReO ₄ The first organic superconductor under ambient pressure derived from poly-sulfur TTF: 4.5 kbar; $T_c = 2 \text{ K}$ (11) 1990: (BEDT-TTF) ₂ Cu[N(CN) ₂]Cl The highest T_c found in an organic superconductor under pressure: 0.3 kbar; $T_c = 12.8 \text{ K}$ (12) (BEDT-TTF) ₂ Cu[N(CN) ₂]Br The highest T_c found in an organic superconductor under ambient pressure: $T_c = 1.6 \text{ K}$ (13)

termed α , β and κ phases (18). As illustrated in (BEDT-TTF)₂BrO₄ (Fig. 4) (19) such salts showed a quasi-two-dimensional structure through short S...S interactions. These two-dimensional interactions gave

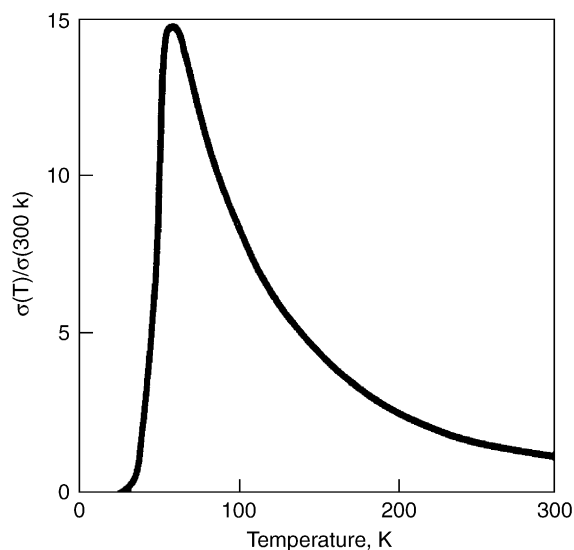


FIG. 1. Temperature dependence of the normalized conductivity of TTF-TCNQ.

rise to conducting sheets and very often to superconducting layers as seen with the κ (BEDT-TTF)₂Cu[N(CN)₂]Br salt (14). So not only BEDT-TTF and its derivatives provided the greatest number of superconducting salts known today, but also those exhibiting the highest T_c with values of 11.6 K at ambient pressure and

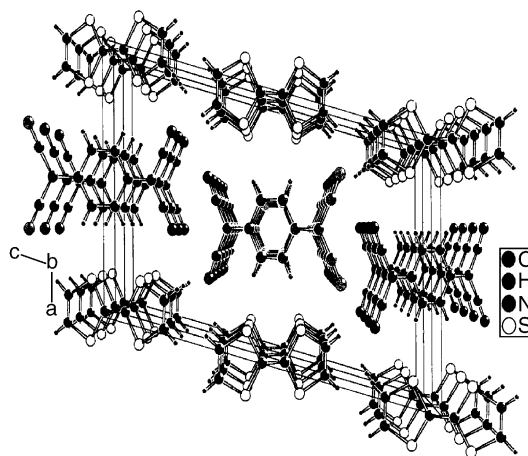
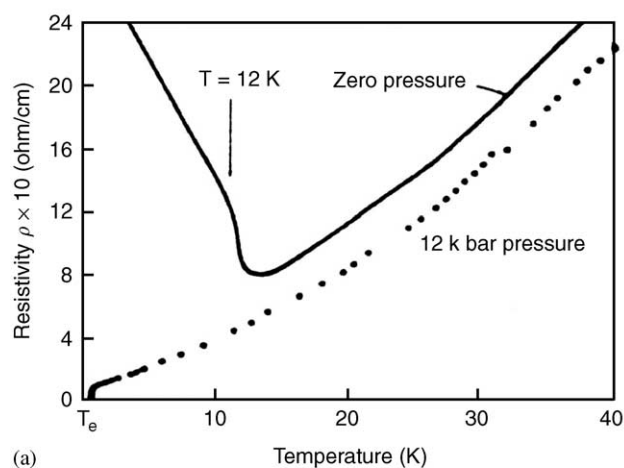


FIG. 2. Crystal structure of TTF-TCNQ: view of segregated stacking modes.



(b)

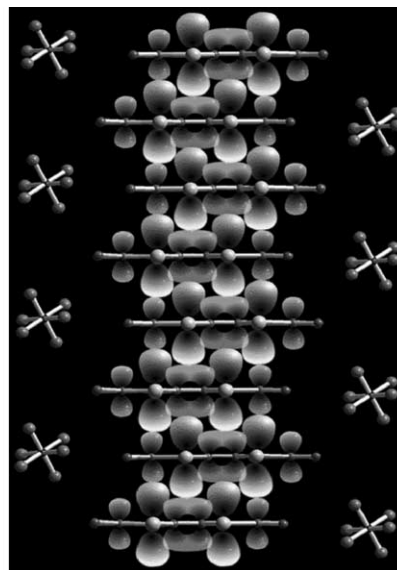


FIG. 3. (a) Temperature dependence of the resistivity at $P = 12$ kbar in $(\text{TMTSF})_2\text{PF}_6$ (D. Jerome *et al.*, 1980). (b) Orbital overlaps within the columnar stacking of $(\text{TMTSF})_2\text{PF}_6$ (from IMN, Nantes, 1999).

12.5 K at 0.3 kbar, respectively, found in $\kappa(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ (13) and $\kappa(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ (12).

• The use of non-centrosymmetric tetrathiafulvalenes confirmed the importance of increasing dimensionality on the improvements of electrical properties of TTF-based materials. Several salts derived from DMtM-TSF (Fig. 5) were found conducting down to 0.1 K (20). This result was also ascribed to the two-dimensional character of these salts (21).

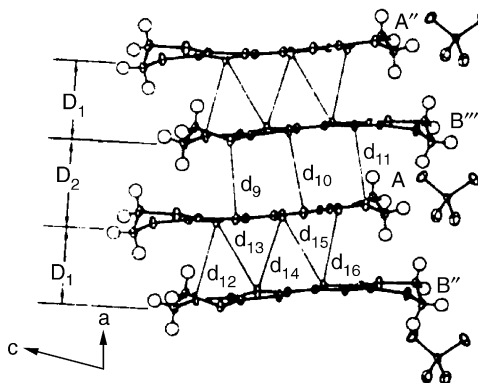
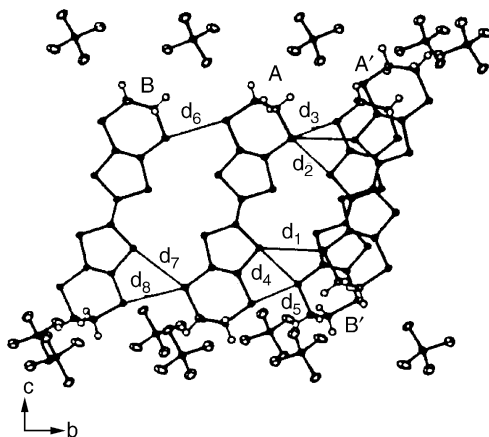
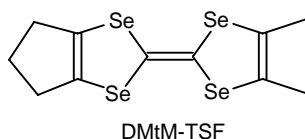


FIG. 4. Crystal structure of $(\text{BEDT-TTF})_2\text{BrO}_4$. View of $\text{S}\cdots\text{S}$ intermolecular contacts along the c -axis (interstack) and the b -axis (intrastack), respectively (from Ref. (19)).

Moreover, it is important to note that, despite their asymmetry, this type of donor leads to superconducting solids as was shown in several salts obtained, for example, from the DMET (22) and MDT-TTF (23) molecules.

Finally, from all these observations, it clearly emerged that increased dimensionality is, in the TTF-based materials, a crucial point to

(1) stabilize the metallic character of the conducting salts down to the lowest temperatures (0.1 K).

(2) increase the critical temperature (T_c) of the superconducting derivatives, a point which was strengthened in the early 1990s by the high values of T_c (18–45 K) found in a series of tridimensional alkaline fullerenes (17, 18).

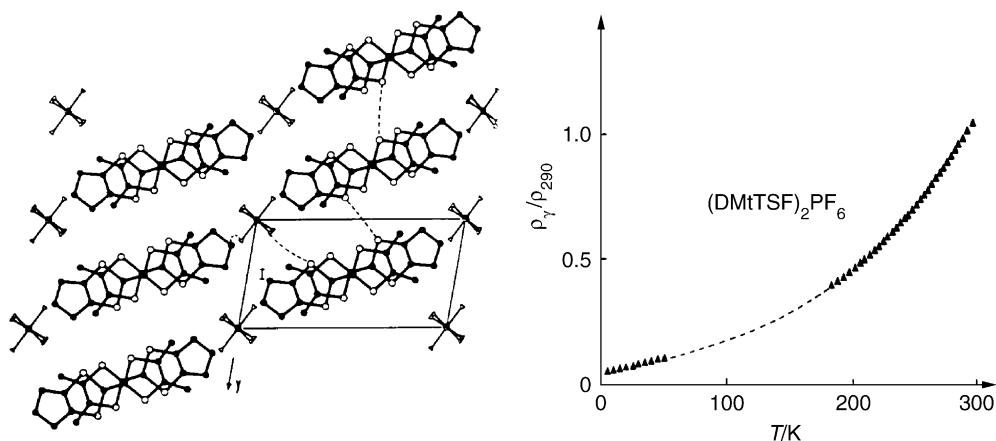


FIG. 5. View of inter- and intrastack Se...Se interactions in $(DMtM-TSF)_2AsF_6$ and temperature dependence of normalized electrical resistivity (from Refs. (20, 21)).

Results of the Last Decade: Trends in the Search for Increased Dimensionality

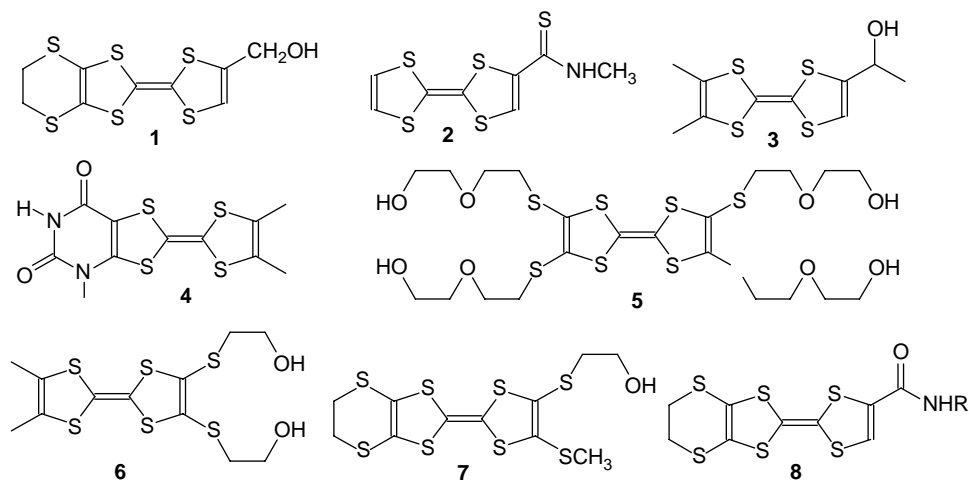
Since the 1990s new molecular systems have been prepared with the aim of obtaining increased dimensionality in conducting and superconducting TTF-based materials. Besides the synthesis of polychalcogenated non-centrosymmetric molecules still used, three main directions, often interconnected, were investigated: functionalization of the TTF core; extension of the conjugated π -system of the TTF; and oligomerization of TTF derivatives.

Functionalized TTF

The TTF core was functionalized by introducing substituents such as hydroxyl, amino, thioamido groups, etc. (Scheme 1) able to induce hydrogen bonds directly between adjacent donor molecules within the salt or

through donor-anion-donor interactions. The first results obtained with these compounds are summarized in a review article by Bryce (24).

It is shown that the best achievements are obtained in hydrated BEDT-TTF salts (25) while functionalized TTF **1**, **2** and **3**, which exhibit hydrogen bonding, give semiconducting SIR or insulating CTC due to disorder in $(1)_2ClO_4$, (26), a complete oxidation of donors in the 1:1 salt $(2)Br$ (24) and due to a mixed-stack structure in the insulating **3**-TCNQ complex (27). This is despite the fact that donors such as **4** (28) and the polyhydroxylated TTF **5** containing long side chains (29) give rise to crystal structures displaying quite strong N-H...O hydrogen bonds and uniform close stacking of the TTF rings respectively. More recently the crystal structure of semi-conducting salts of 1:1 stoichiometry **6**·Br and **7**·ClO₄ (two phases) obtained from donors **6** and **7** containing respectively one and two OH groups on a flexible side chain was studied (30). In each



SCHEME 1. Selected examples of functionalized TTF.

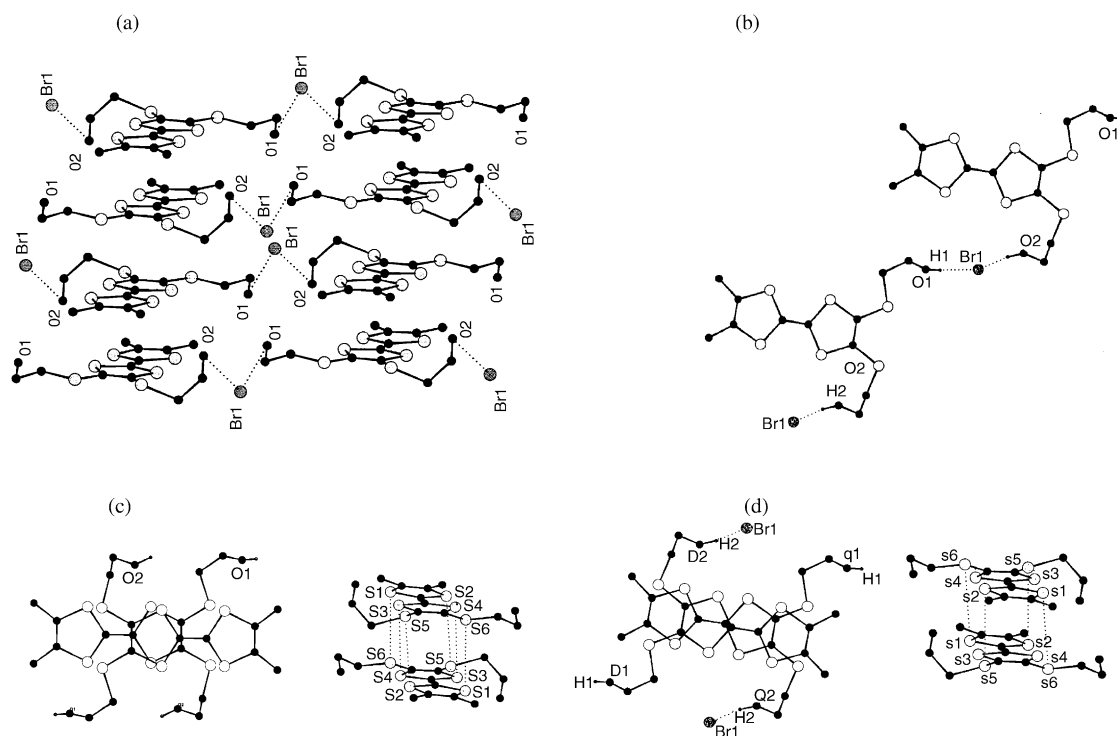


FIG. 6. Crystal structure of salt **6** · Br (30): (a) network of hydrogen bond (O–H...Br...H–O) between adjacent column of donors; (b) intermolecular hydrogen bond between two adjacent molecules through the Br anion, (c) (d) intra- and interdimer molecular overlaps respectively.

case, besides stacks of dimer arrangements, hydrogen bonds between the terminal OH groups of the TTF molecule and the anion (Br^- or ClO_4^-) were clearly observed (Fig. 6). Of course, the complete oxidation of the donor can explain their low conductivity which could also be caused by the “staircase-like” arrangement of the dimers associated with very weak intermolecular orbital overlaps. A very promising result was recently found in a series of SIR derived from amide-functionalized EDT-TTF **8a** ($R = \text{H}$) and **8b** ($R = \text{Me}$) (31, 32). In an interesting study of the interplay of π -overlap and hydrogen bonds, the presence of donor–anion hydrogen bonds was again clearly established in the 2:1 metallic salt **8a** · ReO_4 (33).

TTF with Extended π -Conjugation

The extension of the conjugated π -system of the TTF was regarded to be another strategy to develop two-dimensional electronic structures able to stabilize the metallic state down to low temperatures. This extension was carried out by inserting a conjugated spacer between either two half-TTF (1,3-dithiole cycle) or two TTF entities. Various families of compounds such as (a) vinylogues of TTF derivatives (34–40), (b) bis-fused TTF (41, 42), (c) benzo-fused TTF (43, 44), (d) conjugated bis-

TTF (45–48), and (e) directly linked bis-TTF (45–51) were prepared (Scheme 2), and their salts were studied.

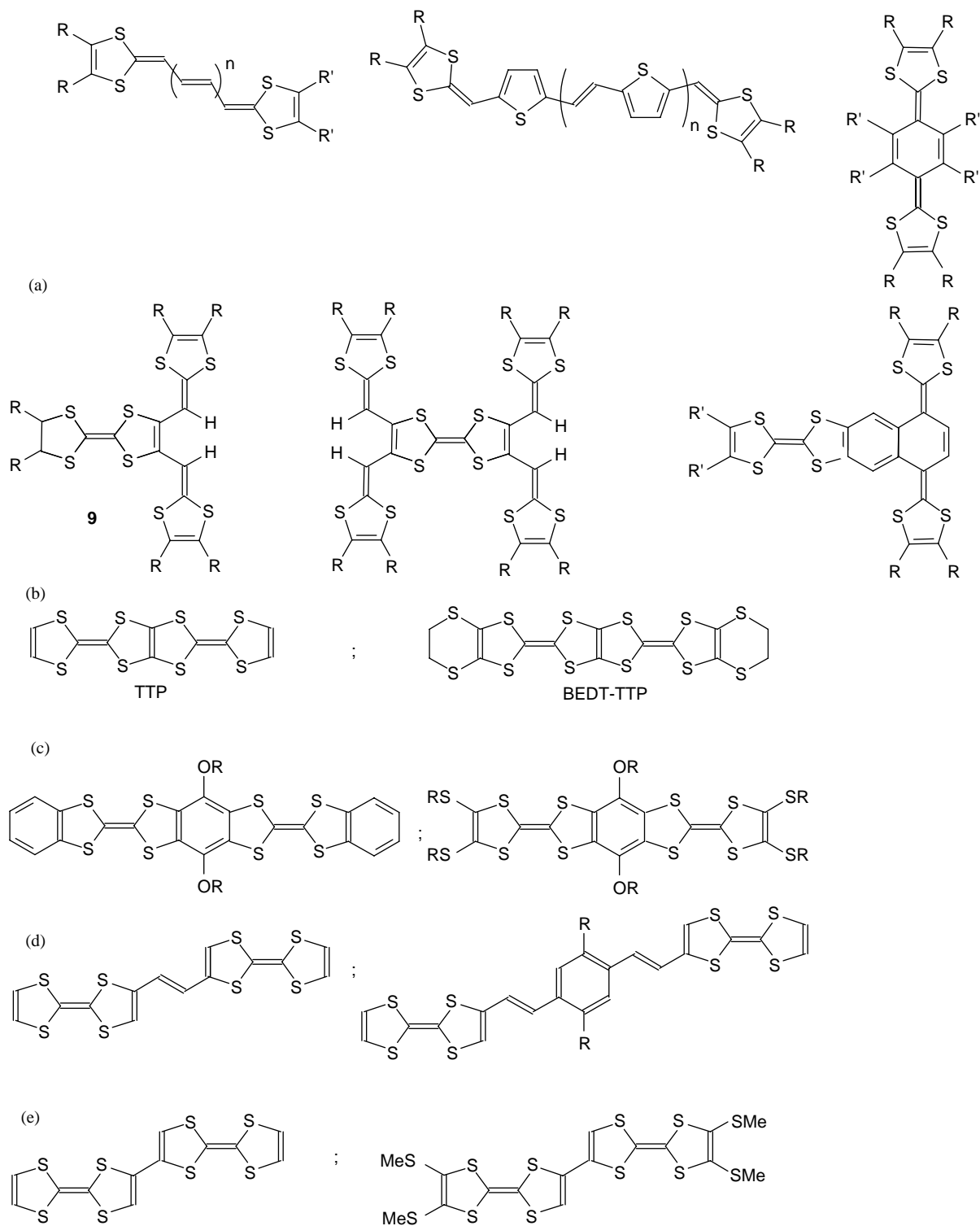
As all these series have been widely reviewed in different articles (24, 34, 42, 43, 52–54), we only briefly mention here some recent encouraging results obtained with these types of donors.

- As exemplified with **9**· ClO_4 (**9**: $R = \text{H}$) (37), many salts of the series (a) were found exhibiting both a 2D character and a relatively high electrical conductivity despite their 1:1 stoichiometry and hence their complete charge transfer. It was demonstrated that these interesting results were mainly due to the increased delocalization of the positive charge on the extended π system, which corresponds to decreasing on-site coulombic repulsions (34).

- Among the compounds of series (b) characterized by the central tetrathiapentalene (TTP) unit, the $(\text{DTEDT})_3 \text{Au}(\text{CN})_2$ salt was found as an ambient pressure superconductor below 4 K (41).

Furthermore, many salts metallic down to 1 K were reported by Misaki (41) and Yamada (55) groups respectively.

More recently, Misaki *et al.* discovered a stable metallic behavior down to 1.5–4.2 K with several salts derived from the selenium analogue donor DSEDS (56). In particular, the $(\text{DSEDS})_3 \text{TaF}_6$ salt revealed a two-dimensional β -type packing arrangement of the donor molecules (Fig. 7)


 SCHEME 2. Selected examples of extended π -conjugated TTF.

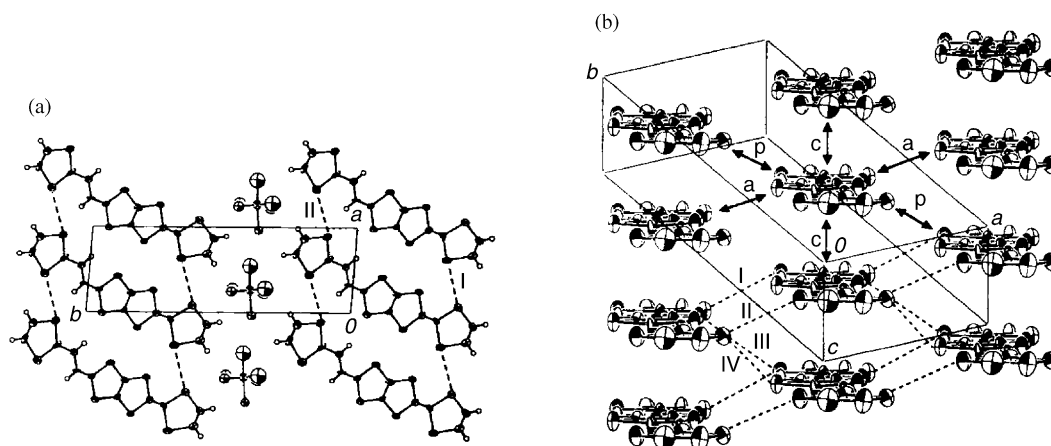
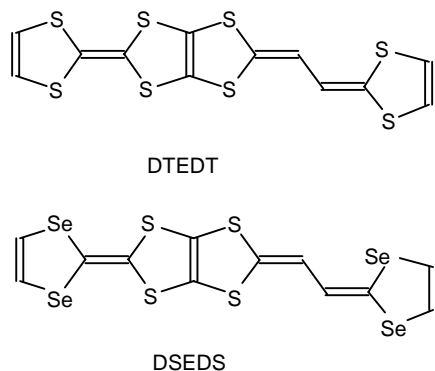


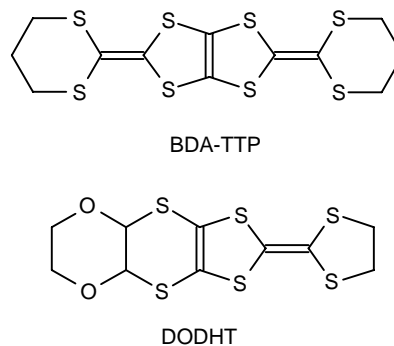
FIG. 7. Crystal structure of $(\text{DSEDS})_3\text{TaF}_6$ viewed (a) along the c -axis and (b) along the molecular long axis. I–IV represent the chalcogen–chalcogen intermolecular contacts (Reproduced with permission from The Royal Chemical Society; see Ref. (56)).

associated with short chalcogen–chalcogen intermolecular contacts (less than the sum of the van der Waals radii) between the stacks of donors. The closed ellipsoid found for the calculated Fermi surface indicated an electronic two-dimensional feature.



Recently, Yamada and co-workers presented a crucial result (57) by demonstrating that the TTF core is not essential to the production of organic superconductors. These authors described the first superconducting salts obtained from donors containing the TTP unit as the only π -electron system. These ambient-pressure superconductors β - $(\text{BDA-TTP})_2X$ ($X = \text{SbF}_6^-$, AsF_6^-) (Fig. 8) exhibited a T_c higher than 5 K. The values of the calculated intermolecular overlap integrals still suggested a two-dimensional electronic structure of these salts, even if a loose donor packing is observed. Moreover, tight-binding band calculations confirmed this 2D character and indicated closed Fermi surfaces. Such interesting superconducting properties were very recently found in radical cation salts of DODHT_2X type

($X = \text{AsF}_6$, PF_6) (58).



Dimeric and Oligomeric TTF

Following an idea proposed by Wudl in 1977 (59), the oligomerization of TTF derivatives, by linking together several TTF units, is now regarded as another possibility to increase dimensionality in CTC of TTF type. In this case TTF layers might be expected as a result of the covalent bonds introduced into the oligomeric precursors (Scheme 3).

Moreover, as recently reported in a review article by Otsubo and co-workers (53), these oligomers which can display multi-stage redox behavior (60), might provide an opportunity to control the stoichiometry, band filling and molecular assembly in conducting salts. Numerous TTF oligomers have been synthesized so far, mainly as bis-TTF in which a flexible saturated spacer is used. They can be classified into three categories according to the nature,

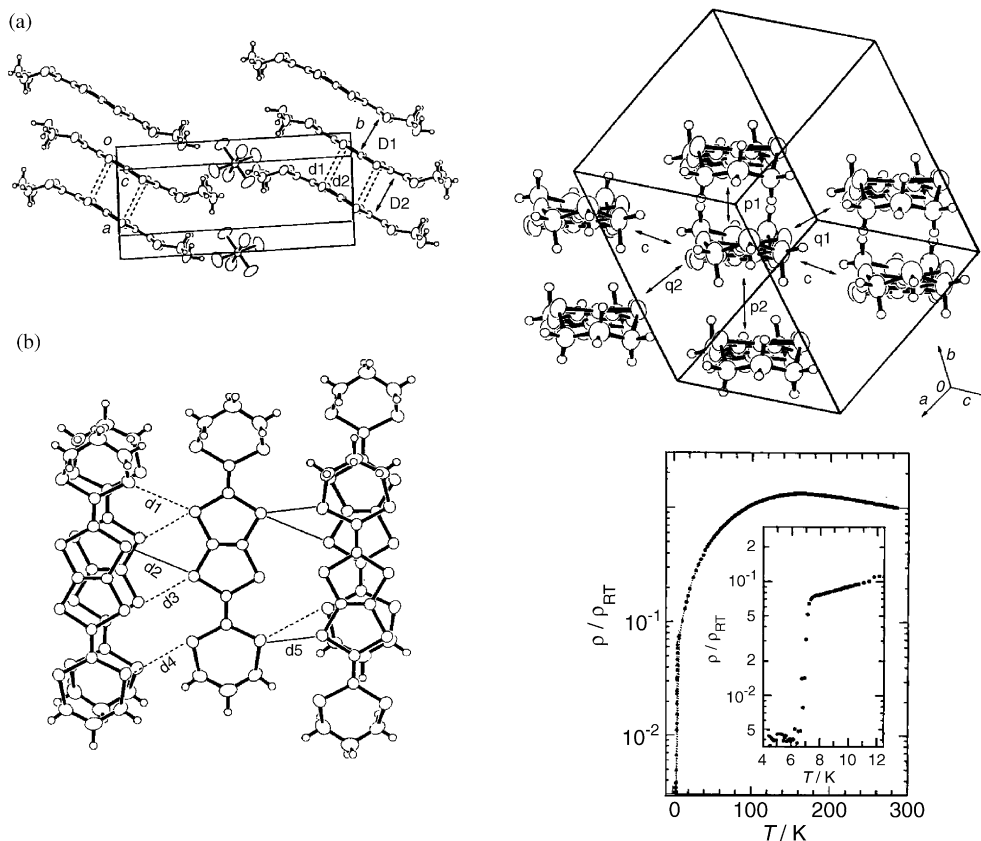
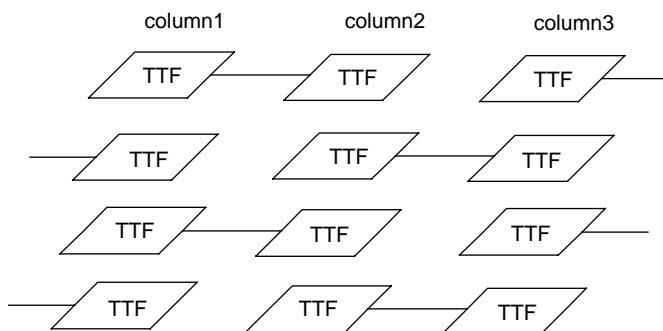
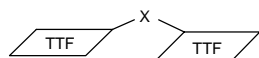


FIG. 8. Crystal structure of β -(BDA-TTP) $_2$ SbF $_6$. (a) d_1 and d_2 = intermolecular S...S contacts (less than the sum of van der Waals radii); D_1 and D_2 = interplanar distances of the BDA-TTP column. (b) d_1 , d_3 , d_4 = intermolecular S...S distances close to 3.70 Å and d_2 , d_5 = short intermolecular S...S contacts. Intermolecular overlap integrals in β -(BDA-TTP) $_2$ SbF $_6$; temperature dependence of the relative resistivity for β -(BDA-TTP) $_2$ SbF $_6$ (Reproduced with permission from The American Chemical Society; see Ref. (57)).

number and position of spacer groups:

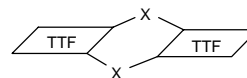
- single-bridged bis-TTF: type I:



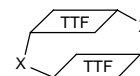
SCHEME 3.

- double-bridged bis-TTF : type II:

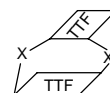
II a (macrocycle):



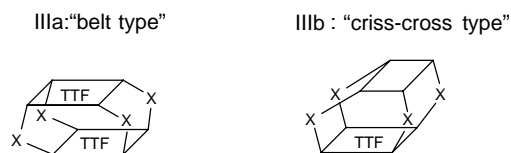
II b (cyclophane) (parallel)



II c (cyclophane) (orthogonal)



● quadruple-bridged bis-TTF: type III:



A large number of such bis-TTF have already been synthesized. Many of them, linked by a flexible chain, $X(\text{CH})_nX$ ($X = \text{S}, \text{Se}; n = 1, 2, 3, \dots$), were prepared by using two different multi-step strategies. The first one involves a cross-coupling reaction between two single-bridged dithiones or dithiolium salts (61, 62) and the second is based on the useful chalcogenolate protection-deprotection method developed by Becher and co-workers (63) and recently used to easily prepare a hexakis-(tetrathiafulvalene) exhibiting a relatively dense crystal packing structure (64). However, the main difficulty encountered remains the production of CTC and RIS as single crystals.

Materials obtained from bis-TTF of type I. Until now the most encouraging results were obtained by Sugawara (65) with a series of conducting salts (PF_6^- , ClO_4^- , BF_4^- , I_3^- , Cl^-) derived from the single-bridged bis-TTF **10**. Depending on the anion nature, three types of crystals were found. The semiconducting behavior observed in most of these D_2 -anion salts was explained by their α -type arrangement. On the other hand, the insulating and the metallic characters respectively found in the salts β -

$\text{10} \cdot \text{ClO}_4$ and $\beta' \text{-10} \cdot \text{Cl}(\text{H}_2\text{O})_x$ could be rationalized by their crystal structures. As shown in Fig. 9 for the chloride, both salts exhibit cyclophane-shaped conformers stacked along the a -axis (9a) with the arrangement of donors dimerized along the a -axis (9b). Whereas the unpaired electrons are localized within the dimers making the perchlorate insulating, in the chloride salt the dimerization is compensated for short $\text{S} \cdots \text{S}$ contacts observed in the other directions of the space-forming molecular stairs. The resulting tight packing of the salt, assigned to the polymeric nature of the counterion, induces the metallic behavior of the chloride down to 170 K.

Among these compounds of type I, conducting charge transfer complexes between the bis-TTF-ditelluride $(\text{TTFTe})_2$ and TCNQ (66) were also obtained. $(\text{TTFTe})_2 \cdot \text{TCNQ}$ showed an unusual crystal structure (Fig. 10) in which the flexibility of the ditelluride spacer allowed donor chain formation with plane-to-plane short $\text{S} \cdots \text{S}$ interactions. However, infinite stacks were not formed which can in part explain the semiconducting behavior observed for this CTC.

It is finally worthy of note that several series of radical cation salts were recently electrochemically prepared (67, 68) from bis-TTF of type I containing a longer spacer group: $X-(\text{CH}_2)_3-X$. Unfortunately from such donors, only powder or crystals of poor quality were obtained until now, preventing the study of their structure by X-ray diffraction. Low values of electrical conductivity were found and ascribed to likely structural disorder made easier by the increasing flexibility of such spacers.

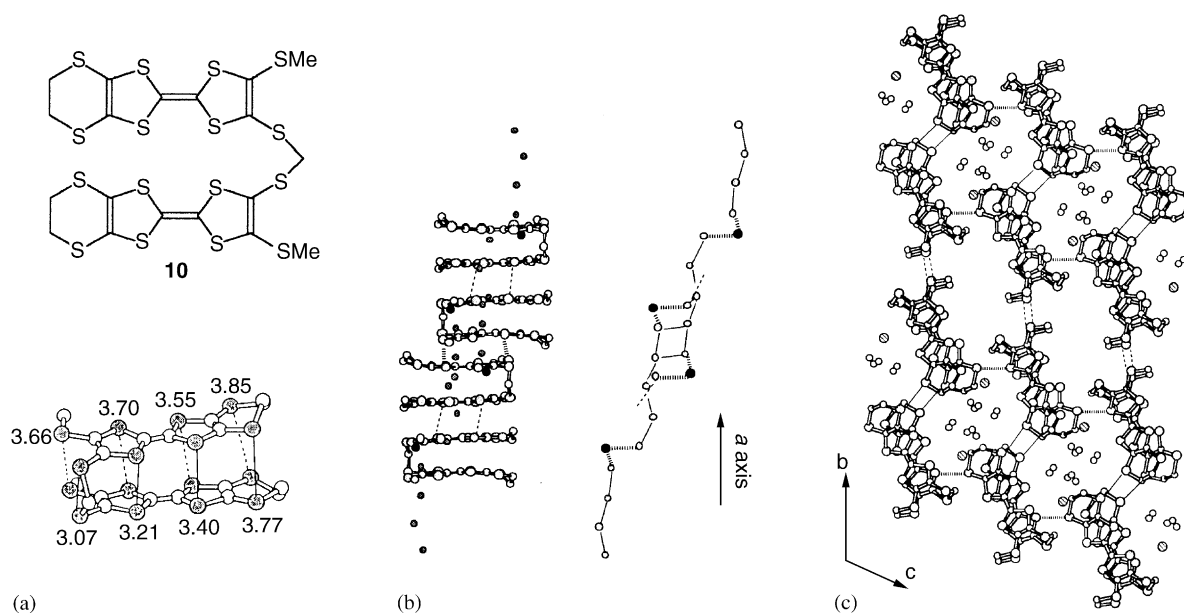


FIG. 9. Crystal structure of $\beta' \text{-10} \cdot \text{Cl}(\text{H}_2\text{O})_x$ salt. (a) Cyclophane-shape conformation of **10** in the salt. (b) Donor stacking and dimerization along the a -axis, polymeric hydrogen-bonded of the anion. (c) Projection of the structure in the bc plane, short intermolecular $\text{S} \cdots \text{S}$ contacts (dotted and solid lines) (Reproduced with permission from Taylor and Francis, Ltd., <http://www.tandf.co.uk/journals>; see Ref. (65)).

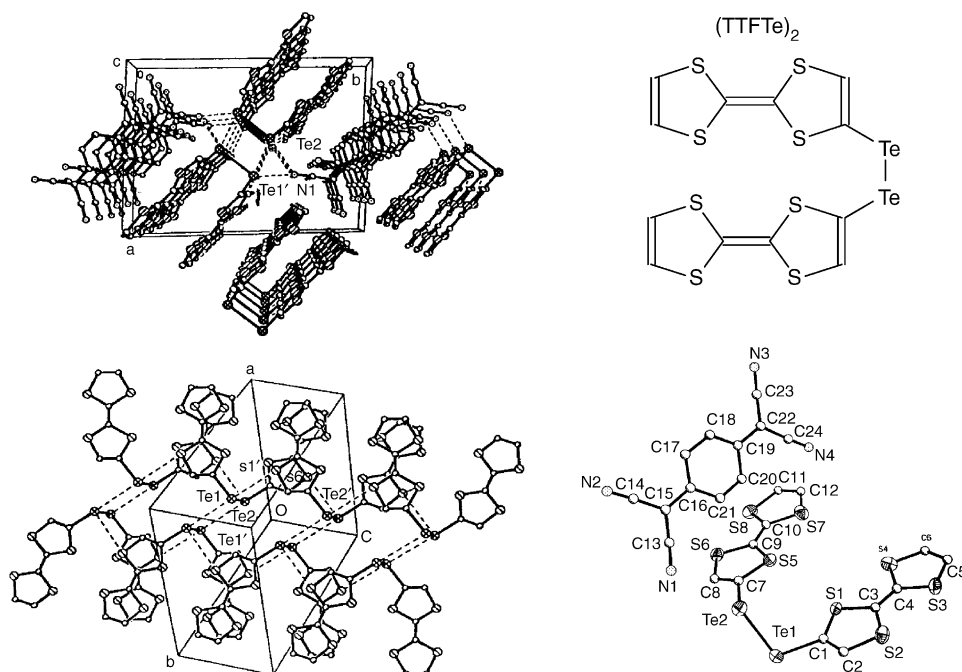
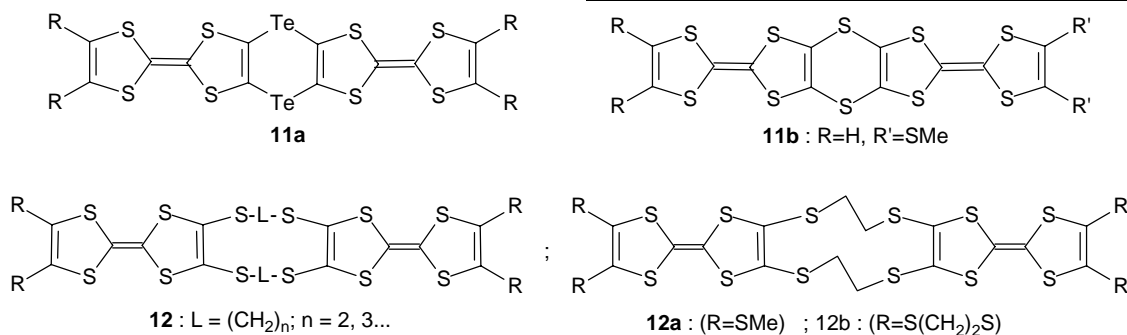


FIG. 10. Crystal structure of $(\text{TTFTe})_2 \cdot \text{TCNQ}$: view on the ab plane; chain of donor molecules. (Reproduced with permission from Wiley-VCH; see Ref. (66)).

Materials obtained from bis-TTF of type IIa (macrocycle). In this series of compounds, rigid fused TTF **11** containing two chalcogen atoms as spacers (69, 70) and bis-TTF **12** built from a more flexible double link (71–73) were prepared.

● In the structure of the metallic salt **12b**·ClO₄ (73), a V-shape conformation of the organic molecules (Fig. 12) and a donor packing showing a very promising three-dimensional arrangement were found. Nevertheless, an unexpected metal-insulating transition was



Concerning the non-planar donor **11a**, a conducting CTC with DMTCNQ ($\sigma = 6 \text{ S cm}^{-1}$) was obtained although its structure was not described (69). The same value of conductivity (6 S cm^{-1}) was found in the **11b**-TCNQ complex. A semiconducting behavior was observed despite the fact that the salt exhibited a partial degree of charge transfer in both donor and acceptor moieties and a “fir-tree”-like stacking arrangement of the donor (Fig. 11) with a high density of intra- and interstack S...S contacts (70).

In the family of more flexible macrocycles **12**, several salts and complexes derived from donors **12a** and **12b** were studied by Sugawara and co-workers.

observed at around 100 K. A likely one-dimensional electronic character was finally put forward to explain this result.

● Due to its U-shaped conformation, the same donor **12b** was found able to form inclusion complexes.

With the strong electron acceptor DDQ, the acceptor molecule occupied the donor cavity (Fig. 13) giving rise to the (**12b**)-DDQ salt in which the semiconducting behavior was rationalized by both the complete charge transfer and the mixed stack structure ...DAD-DAD... of the salt (74).

With the weak acceptor C₆₀, the inclusion complex (**12b**·C₆₀·CS₂) (Fig. 14) presented a low degree of charge

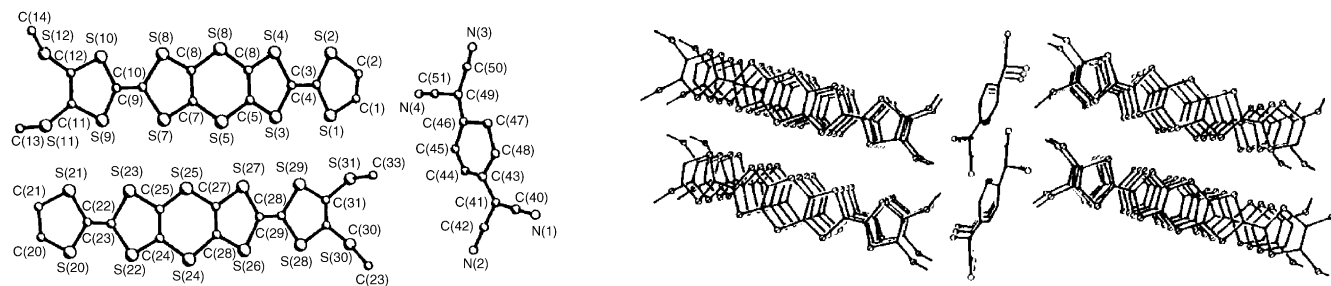


FIG. 11. Molecular structure of **11a**; packing diagram of $(\mathbf{11a})_2 \cdot \text{TCNQ}$, as viewed down the b -axis (Reproduced with permission from The Royal Society of Chemistry; see Ref. (70)).

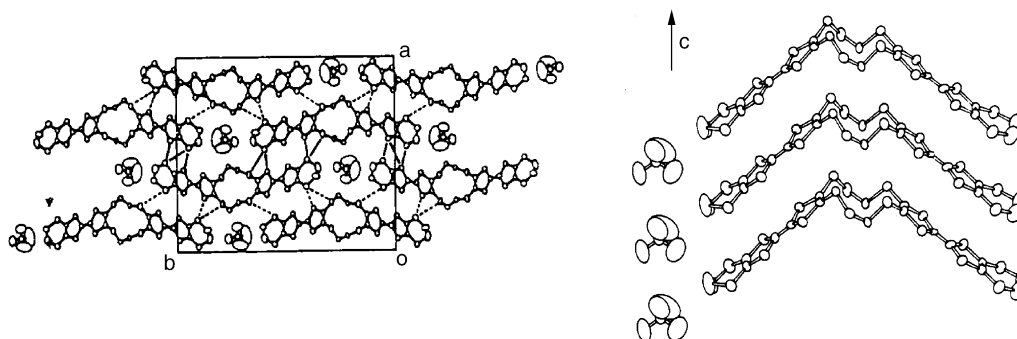


FIG. 12. Crystal structure of $\mathbf{12b} \cdot \text{ClO}_4$; projection along the c -axis and $\text{S} \cdots \text{S}$ interactions (solid and dashed lines). Donor column along the c -axis showing the V-shaped conformation of the donor molecules (Reproduced with permission from Elsevier Science; see Ref. (73)).

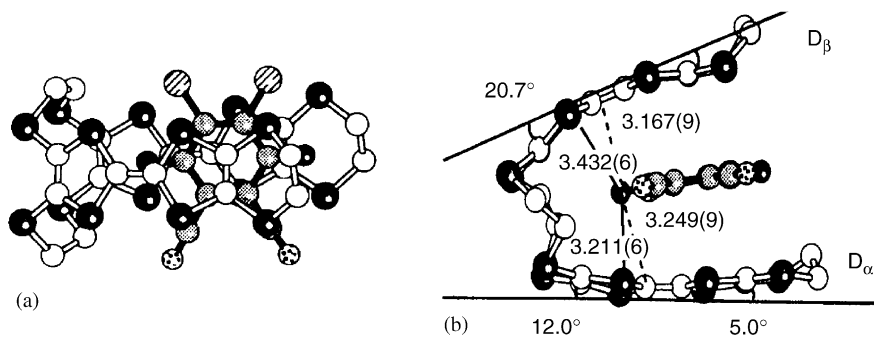


FIG. 13. Molecular structure of the inclusion complex $\mathbf{12b} \cdot \text{DDQ}$: (a) top view; (b) side view (Reproduced with permission from The Royal Society of Chemistry; see Ref. (74)).

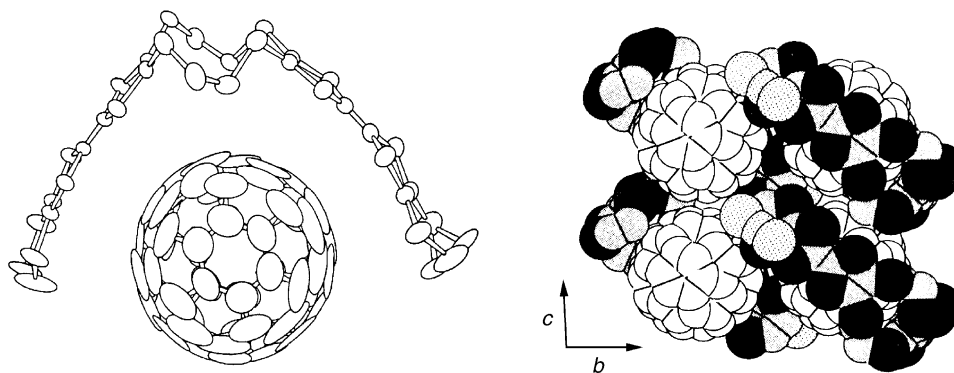


FIG. 14. Inclusion of a C_{60} acceptor molecule inside the cavity formed by the donor **12b**. Crystal packing of the complex $(\mathbf{12b} \cdot \text{C}_{60} \cdot \text{CS}_2)$ (Reproduced with permission from The Chemical Society of Japan; see Ref. (75)).

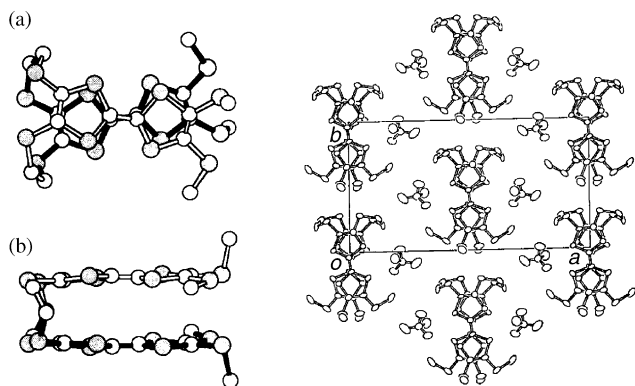


FIG. 15. Crystal structure of $12a \cdot (\text{ClO}_4)_2$ (a, b) Cyclophane conformation of $12a$. Projection of the structure in the ab plane (Reproduced with permission from Elsevier Science; see Ref. (76)).

transfer which would be responsible for the bad results of electrical conductivity (75).

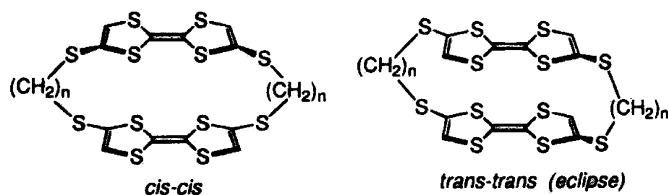
In the salt $12a \cdot (\text{ClO}_4)_2$ (76), the donor molecule takes again a cyclophane conformation with short $\text{S} \cdots \text{S}$ intramolecular distances associated with efficient overlaps. However, the U-shape donors (Fig. 11a and b) did not stack in column and therefore no significant interactions were observed between the adjacent donors along the b -axis (Fig. 15). This structural result and the fact that each TTF unit of the donor $12a$ was oxidized as a radical cation are consistent with the very low electrical conductivity ($2 \times 10^{-7} \text{ S cm}^{-1}$) measured in this salt.

Finally, among the bis-TTF of type IIa, compounds 12 , in which the length of the spacers ($n = 3$) was increased, were prepared and some of them were converted into salts (68). Unfortunately, as already seen above, the salts were

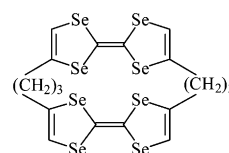
isolated only as powder or crystals of poor quality. Their very low electrical conductivity was again supposed to be mainly due to a structural disorder resulting in the too large flexibility of the corresponding donors.

We can also mention here the case of insulating ($10^{-7} \text{ S cm}^{-1}$) trihalogenides (I_3^- and IBr_2^-) of a macrocyclic tris-TTF which displays an unusual structure (77).

Materials obtained from bis-TTF IIb (parallel), and IIc (orthogonal). Many compounds IIb, isolated as different isomers (*cis/cis*; *cis/trans*; *trans/trans*), have been described until now (78–82) even if only a few of them have been studied as salts.



(13a : $n = 2$)



14

Recently, a series of radical cation salts were prepared from the double-bridged TTF $13a$. They were mostly found to

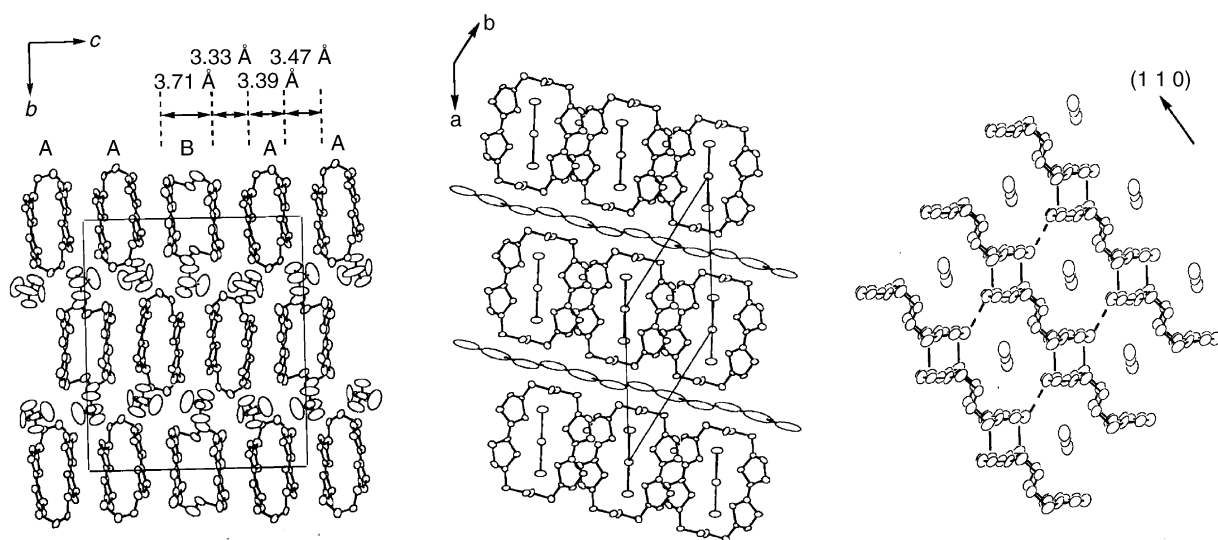
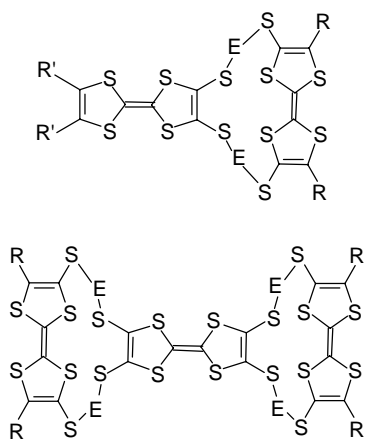


FIG. 16. (a) Packing diagram of $13a \cdot \text{ClO}_4$, a -axis projection. (b) Packing diagram of $13a \cdot (\text{I}_3)_2$: c -axis projection and side view of the donor sheet (Reproduced with permission from The American Chemical Society; see Ref. (81)).

be semiconductive and characterized by segregated stacks of the *trans/trans* (eclipse) form of the cationic species (81) (Fig. 16a). As an exception, the plate crystals of salt **13a**·(I₃)₂, which showed a conductivity of 28 S cm⁻¹ with a metallic behavior, presented a network of marked intermolecular S...S interactions of the *cis/cis* form of the organic cations (Fig. 16b). This result emphasized the crucial role played by the anion which in this typical case (I₃⁻ was in part found as a polymeric anion) enforces the donor to adopt a *cis/cis* geometry which turned in favor of donor sheet formation in **13a**·(I₃)₂.

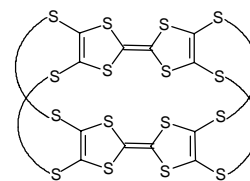
However it was recently shown that the stacking column of the *trans/trans* (eclipse) form of such cyclophane donors could also lead to highly conducting salt. It was demonstrated by using the selenium derivative **14** which showed effective chalcogen-chalcogen interactions within and between the stacks of the donors in the conducting 1:1 salt **14**·Au(CN)₂ (82).

In the series of double-bridged bis-TTF of type IIc in which the two TTF units are linked to each other in an orthogonal manner, several compounds have already been synthesized together with corresponding tris-TTF derivatives (83–85). However, no conducting salt or complex has been described so far.

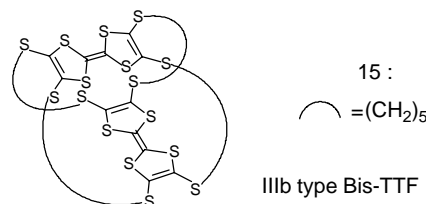


Materials obtained from bis-TTF IIIa (belt type) and IIIb (criss-cross type). Although the quadruple-bridged compounds of type IIIa have been obtained from various strategies (72,86,87), to our knowledge there is no salt described from such donors until now. However, from cyclophane bis-TTF of type IIIb (88,89), a series of radical cation salts exhibiting very low values of conductivity (10⁻⁶–10⁻⁷ S cm⁻¹) were studied. The crystal structure of the semiconducting salt **15**·Br allowed one to assign the low conductivity observed to an inclusion of an ethanol molecule inside the cavity of the donor preventing

intramolecular interactions between the two TTF units of the donor.



IIIa type bis-TTF



IIIb type Bis-TTF

More recently a semiconducting triiodide salt (3×10^{-6} S cm⁻¹) was obtained from a cage multi-bridged tris-tetrathiafulvalene macrocycle containing both flexible bis-(ethoxy)ethyl and dithioethyl linkers (90). While the crystal structure of the donor showed inclusion of a solvent molecule in the formed cavity, no more inclusion was found in the salt and the cavity had completely collapsed giving rise to a particular structure consistent with the low value of conductivity observed.

CONCLUSION

The search for new precursors of TTF type supposed to be able to lead to 2D or 3D salts exhibiting improved electrical performances has led, as reported here, to the synthesis of mainly three families of new donors:

- functionalized donors potentially able to induce hydrogen bonds in the resulting salts;
- donors possessing an extended π -conjugated system able to both reduce on-site coulombic repulsions and allow close molecular interactions;
- oligoTTF derivatives in which the covalent bridges linking the TTF units might prefigure the expected bidimensional structures in the corresponding materials.

In each of these families a large number of new molecules have been obtained by using various synthetic strategies and, despite only a few salts having been obtained, some encouraging results have come out providing good reasons to carry on with the intense efforts already made.

- From the functionalized TTF, the salts studied so far have generally shown the expected hydrogen bond formation. Unfortunately, the hydroxylated TTF such as **1**, **2**, **6** and **7** (26–27, 30) exhibited low values of conductivity due

to a complete oxidation of the donor and/or a structural disorder initiated by the more or less long side chain bearing the hydroxyl groups of the donor. However in this family of compounds, a promising result was recently depicted with TTF **8a** and **8b** containing an amide function. These donors not only allowed intrastack π -overlaps but also a network of hydrogen bonds through donor-anion interactions in metallic salts such as (**8a**·ReO₄) (33).

- In the family of donors containing an extended π -electron framework numerous compounds with various molecular architecture have been prepared. Very often, the decreasing coulombic repulsion expected in these extended conjugated systems is effectively observed as indicated through the relatively high electrical conductivity found in 1:1 salts obtained from vinylogues of TTF (37–40), a result recently confirmed (91). In this family of highly conjugated donors, other extremely interesting results have been obtained, in particular with donors containing the tetra-thiapentalene unit (DTEDT, DSEDS, BDA-TTP) (41, 55–57) which gave rise to series of metallic and even superconducting salts which presented the expected two-dimensional packing arrangement.

- The family of oligomeric TTF gave a great variety of results depending mainly on the nature, number and position of the spacer groups and also on the nature of the anion. This is clearly shown in the bis-TTF series.

- The single-bridged donors of type I gave metallic salts only if the length of the spacer is limited, as in donor **10** for example, which prevents a structural disorder due to a very large flexibility of the linkage. Moreover, the same donor led both to a semiconducting perchlorate (β -**10**·ClO₄) and to a conducting chloride (β' -**10**·Cl·H₂O_x) because the polymeric nature of the chloride (...Cl...H₂O...) induced short S...S contacts between the stacks of the cyclophane-shaped conformers **10**, not observed in the perchlorate salt.

The dependence of the crystal structure and the electrical properties with the length of the spacer groups was also observed in the series of double-bridged TTF of type IIa (73–76). Furthermore, as seen in **12b**·DDQ or **12b**·C₆₀·CS₂ complexes, the U-shape conformation was generally adopted by the donor-induced inclusion structures which prevent the electronic delocalization making these materials semiconducting. Nevertheless, this donor can also take a V-shape conformation and lead to a promising tridimensional structure associated with a metallic salt as seen in **12b**·ClO₄. This result shows again the important role played by the anion on the arrangement of the organic cation network, as was confirmed in the cyclophane series IIb with the donor **13a**. The compound showed a *cis/cis* configuration and short S...S intermolecular interactions in the metallic salt **13a**·(I₃)₂ and a *trans/trans* geometry with no efficient contact between the

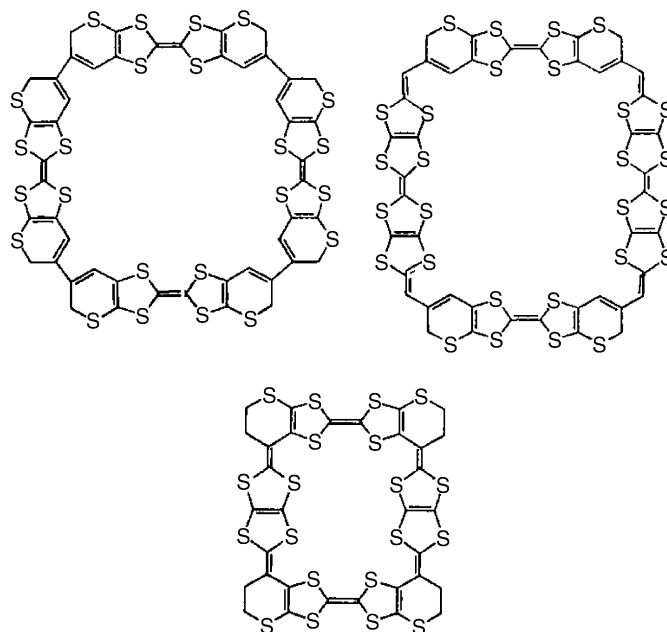
donors in the semiconducting salt **13a**·ClO₄. The situation strongly improved by replacing the sulfur atoms of the donor with selenium as exemplified with the metallic salt **14**·Au(CN)₂ (82).

Similar results were found with salts derived from quadruple-bridged donor IIIb of criss-cross type.

The low conductivity observed, in particular, in salt **15**·Br was related to an inclusion phenomenon already encountered in salts derived from double-bridged TTF IIa.

In conclusion, although the 2D κ (BEDT-TTF)₂Cu[N(CN)₂]Br salt still holds the record of T_c , very promising examples have been found in each of the three families of compounds investigated up to now. So even if guidelines are important in the synthesis of new species, the study of each specific case remains essential because, as still seen here, the same donor can lead to salts exhibiting completely opposite results and a very small modification of the donor can also induce drastic effects on the characteristics of the resulting complex. Molecules displaying the simplest architecture seem the better candidates to obtain well-organized 2D and 3D metallic salts (41, 55–57) although macrocyclic polychalcogenated molecules of type IV (18) to be synthesized might also be a source of highly conducting tridimensional materials. The introduction of too many TTF units in the oligomeric TTF or too long spacer chains generally lead to distorted structures not compatible with a high electrical conductivity. Such molecules today find a better interest in supramolecular chemistry and other applications (54, 92–96).

Hypothetical molecules of type IV:



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