Novel Dissymmetric Tetrathiafulvalenes as Precursors of Organic Metals: Synthesis, X-ray Crystal Structures, Electrochemical Properties and Study of Their Radical Cations

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Two new dissymmetric π-electron donors, ethylenethioethylenedithiotetrathiafulvalene (ETEDT-TTF) and ethylenethiotetrathiafulvalene (ET-TTF), based on the combination of bis(ethylenethio)tetrathiafulvalene (BET-TTF) with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and tetrathiafulvalene (TTF), have been synthesized and characterized. The direct synthesis of these donors by means of the coupling of the corresponding thiones or ketones in $P(OMe)_3$ works well only for ETEDT-TTF. For ET-TTF, an alternative route has been used, in which the bis(carboxylate) derivative, ethylenethiobis(methoxycarbonyl)tetrathiafulvalene (ETDC M-TTF), is first synthesized and then decarboxylated. The crystal packings of neutral ETEDT-TTF and ET-TTF very closely resemble those of the related symmetrical donors BEDT-TTF and TTF, respectively. In contrast, the packing of the ETDC M-TTF donor is completely different, being dictated by the hydrogen bonds formed by the carbonyl groups. The electron donor ability of the new compounds has been investigated by cyclic voltammetry: ETEDT-TTF and ET-TTF are good donors, much better than ETDC M-TTF, in accordance with the electron-withdrawing character of the methoxycarbonyl substituent. The three donors form stable radical cations that have been characterized by means of UV/Vis and EPR spectroscopy. The EPR studies indicate that there is some spin density on the external sulfur atoms, which is important for the preparation of charge transfer salts with high electronic dimensionality. Indeed, a variety of properties, from stable metals to insulators, is displayed by the charge transfer salts and complexes which have been obtained with ETEDT-TTF and ET-TTF.

Introduction

The development of new organic conductors based on π-electron donors derived from tetrathiafulvalene (TTF) analogues derives to a large degree from interest in organic metals and superconductors. Very good results have been achieved with radical ion salts formed by tetrathiafulvalenes bearing substituents incorporating sulfur atoms: The bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) donor has to date provided the largest number of superconducting derivatives.[1] So far, this donor forms the salt with the highest T_c, 12.8 K.[2] The presence of sulfur atoms external to the tetrathiafulvalene core promotes intermolecular interactions that enhance the electronic dimensionality of the salts, avoiding the structural changes that promote metal-to-insulator transitions in 1D conductors and hence allowing the transition to the superconducting state. The size and aromaticity of fused heterocyclic ring substituents in TTF derivatives, and also the number and position of the sulfur atoms in those substituents, influence the packing of the donor molecules in the crystalline radical cation salts. As a consequence it is possible, by modifying the substituents on the TTF core, to obtain a wide range of structures and physical properties.

Following this approach to the preparation of new organic conductors, many tetrathiafulvalene derivatives with external sulfur atoms have been synthesized.[3] We have been extensively studying one of them, bis(ethylenethio)tetrathiafulvalene (BET-TTF),[4−6] which has two five-membered rings external to the TTF core, with one sulfur atom in the α position of each ring, and forms several salts with metallic properties.[7] This donor gives rise in some cases to mixtures of the *E* and *Z* isomers in its derived salts, which promote disorder in most of the crystal structures. The presence of disorder or defects in the crystals of organic metals is one of the causes of the metal-to-insulator transitions preventing the appearance of superconductivity.

In the search for new TTF-based building blocks able to form organic metals that lack any possibility of isomerism, we have synthesized dissymmetric donors based on the combination of half of the skeleton of BET-TTF and the totally symmetrical donors TTF and BEDT-TTF.

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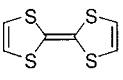
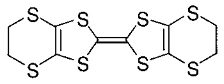
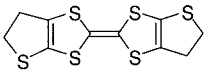


TTF



BEDT-TTF



***E*-BET-TTF**

We present here the synthesis and a detailed study of the structure and electrochemical properties of the new dissymmetric π-electron donors: ethylenethioethylenedithio-tetrathiafulvalene (ETEDT- TTF), ethylenethiobis(methoxycarbonyl)tetrathiafulvalene (ETDCM-TTF), and ethylenethiotetrathiafulvalene (ET-TTF). Additionally, we describe the characterization in solution of the derived radical cations, by EPR and optical spectroscopy. From the new ETEDT-TTF and ET-TTF donors we have obtained some charge transfer complexes and radical ion salts, which exhibit metallic properties.

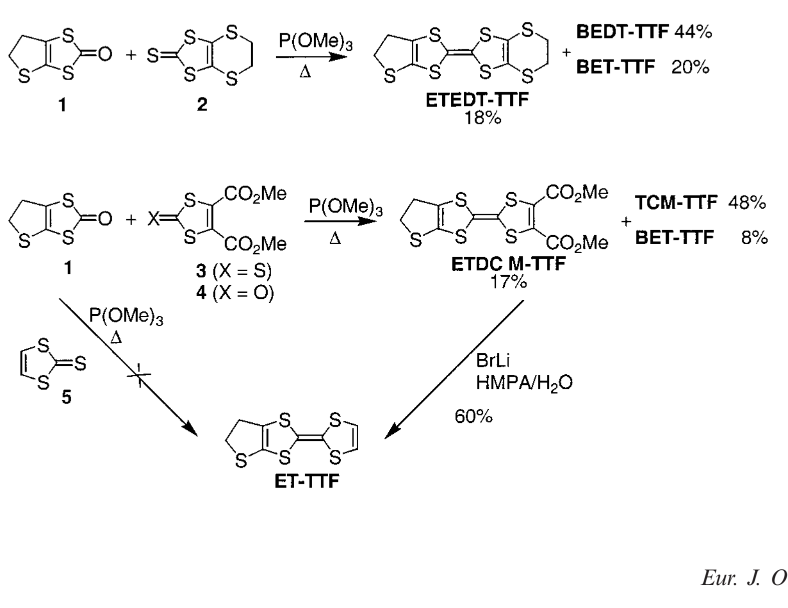
Results and Discussion

Synthesis

The synthesis of the donors ETEDT-TTF and ETDC M-TTF was performed by the cross-coupling of the appropriate ketones or thiones in neat boiling trimethyl phosphite, as shown in Scheme 1. The coupling of 4,5-ethylenethio-1,3-dithiol-2-one (**1**)[5] and 4,5-ethylenedithio-1,3-dithiole-2-thione (**2**)[8] gave rise to a mixture of the desired donor, ETEDT-TTF, and the symmetrical by-products BET-TTF and BEDT-TTF, which were separated by column chromatography. Because of the formation of these symmetrical derivatives, the yield of ETEDT-TTF is low (18%). Similar yields were obtained by replacing the thione **2** with the corresponding ketone, 4,5-ethylenedithio-1,3-dithiol-2-one.[9] The yield obtained in the synthesis of ET-TTF by the direct cross-coupling of ketone **1** with 1,3-dithiole-2-thione (**5**) was almost zero and an alternative route was used. Thus, the bis(methoxycarbonyl)-substituted TTF derivative ETDC M-TTF was synthesized first, by coupling of the appropriate ketones with trimethyl phosphite, and the resulting donor then was decarboxylated to yield the unsubstituted derivative ET-TTF. The yield of the first step, although still quite poor (17%), was higher when the 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-one (**4**)[10] was used for coupling with ketone **1** instead of the analogous thione **3**.[11,14] The coupling of ketones **1** and **4** also gives significant amounts of the corresponding symmetrical donors, BET-TTF and tetrakis(methoxycarbonyl)tetrathiafulvalene (TC M-TTF), which were efficiently separated by column chromatography. In spite of the poor yields, this cross-coupling route was our preferred choice for obtaining these TTF-based derivatives, since the precursor ketone **1** is easily prepared in gram amounts.[5] In contrast, the corresponding 4,5-ethylenethio-1,3-dithiole-2-thione, that would be expected to function as the precursor of dithiolium ion needed for the more convenient Wittig-like coupling reactions described for the synthesis of disymmetric TTFs,[12] is much more difficult to obtain in good yields.[4,13]

Molecular and Crystal Structures

To investigate the role of the sulfur atoms in the intermolecular contacts of the new donors, we have performed an X-ray crystallographic analysis of the three donors ETEDT-TTF,[14] ETDC M-TTF and ET-TTF, using single-crystal X-ray diffraction. The crystallographic parameters are given in Table 1and the molecular structures and corresponding atomic numberings are shown in Figure 1a, 2a and 3a. As can be seen in Figure 1a, the ETEDT-TTF molecule deviates significantly from planarity. As in the case of the symmetrical derivative BEDT-TTF,[15] a folding of the dithiole rings along the S···S hinge (around 8° in one part and around 15° in the other) and a boat conformation of the six-membered ring are observed. On the other hand, the five-membered ring substituent is almost planar, as is also the case in the ETDC M-TTF derivative (Figure 3a) and the symmetrical derivative BET-TTF.[3,15b] In contrast, the



Scheme 1

Table 1. Crystallographic data of the new donors

Donor	ETEDT-TTF	ETDC M-TTF	ET-TTF
Empirical formula	$C_{10}H_8S_7$	$C_{12}H_{10}O_4S_5$	$C_8H_6S_5$
M	352.58	378.5	262.43
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	6.427(1)	7.438(3)	7.375(1)
b [Å]	13.888(5)	9.678(2)	12.037(2)
c [Å]	15.405(3)	11.605(4)	11.752(3)
α [°]	90	79.02(2)	90
β [°]	92.18(2)	76.91(3)	102.06(1)
γ [°]	90	75.64(2)	90
V [Å^3]	1374.0(6)	780.2(2)	1020.2(3)
Z	4	2	4
Temperature [K]	293	293	213
$D_{calcd.}$ [g cm^{-3}]	1.704	1.611	1.709
μ [mm^{-1}]	1.119	0.752	1.080
F(000)	720	388	536
Crystal size [mm]	0.42 × 0.09 × 0.07	0.34 × 0.10 × 0.05	0.32 × 0.32 × 0.11
Crystal color	red	purple	orange
θ range for data collection [°]	3.22 to 20.52	1.82 to 29.96	3.00 to 22.50
Index ranges	$0 \le h \le 6$	$-10 \le h \le 10$	$0 \le h \le 7$
	$-13 \le k \le 0$	$-13 \le k \le 13$	$-1 \le k \le 12$
	$-15 \le l \le 15$	$0 \le l \le 16$	$-12 \le l \le 12$
Unique reflections	1386	4540	1330
R_{int}	0.0945	0.0378	0.0194
Reflections with $I > 2\sigma(I)$	405	1985	1132
Max. and min. transmission	0.9984−0.9091	0.9997−0.9520	1.000−0.852
Data/restraints/parameters	1386/61/174	4540/0/191	1273/0/118
Weighting parameters a, b	$a = 0.1045$, $b = 0$	$a = 0.0597$, $b = 0$	
No. of refined parameters	174	191	118
wR^2 (all data)	0.2447	0.1386	0.0688
R^1 (observed data)	0.0803	0.0571	0.0281
Goodness of fit on F^2	0.842	0.887	1.082
Max, min electron density [eÅ^{-3}]	0.535, −0.636	0.455, −0.336	0.212, −0.244

ethylene group of the ET-TTF molecule is folded, with the S5−C9−C8 part forming a dihedral angle of 144° with the TTF plane (Figure 2a).

With respect to the supramolecular organization, ETEDT-TTF molecules are packed forming head-to-tail dimers (Figure 1b) sustained by C−H···S and C−H···C hydrogen bonds, as happens in BEDT-TTF[15] and other related dissymmetric donors such as dimethylethylenedithiodiselenadithiafulvalene (DMET)[16] and ethylenedithiotetrathiafulvalene (EDT-TTF).[17] The dimers are connected forming chains along the *a* direction and the chains are arranged perpendicularly to each other, avoiding the overlap of the dimers to form stacks (Figure 1b). This packing pattern is very similar to that of BEDT-TTF, DMET-TTF and EDT-TTF.[15−17] As observed in the crystal structure of BET-TTF,[4] there is disorder (59−41%) in the position of the S7 and C9 atoms of the ethylenethio groups of ETEDT-TTF (Figure 1a), but, in this case, the disorder is not due to *cis-trans* isomerism. In contrast to the above-mentioned compounds, no disorder was found in the crystal structure of ET-TTF.

The packing of the ET-TTF donor shows an angular pattern very similar to that of TTF, both compounds forming chains of molecules arranged in stacks. In contrast to TTF, which forms linear chains along the *c* direction and overlap along the *a* direction,[18,19] ET-TTF forms zig-zag chains along the *ac* direction (Figure 2b) that stack along the *b* axis in such a manner that the molecules form head-to-tail dimers but not stacks of molecules. The stacks of chains have two different orientations, with an angle of approximately 60 ° (Figure 2c). There are short S···S contacts along the chains (3.411 Å < S···S < 3.604 Å), between parallel chains (3.666 Å < S···S < 3.987 Å), and between nonparallel chains (S···S = 3.787 Å). There are also C−H···S and C−H···C contacts between parallel chains (C−H···S = 3.000 Å, C−H···C = 2.990 Å) and between chains of different orientation (2.856 Å < C−H···S < 3.059 Å), forming a 3D structure. Especially short C−H···S contacts (2.856 Å) are formed between C9−H of the molecules in one chain and S2 of molecules in the adjacent chains of different orientation. These packing characteristics could be the cause of the great distortion from the planarity observed for C9 in the ET-TTF molecule (Figure 2a).

ETDC M-TTF has crystal packing very different to the other derivatives described here, clearly dominated by the hydrogen bonds formed by the methoxycarbonyl groups. It forms stacks of molecules along the *a* axis, arranged head-to-tail along both the *a* and *b*−*c* directions (Figure 3b). There are hydrogen bonds along the stacks (2.428 Å < C−H···O < 2.614 Å), along the *b*−*c* direction (C−H···O = 2.473 Å) and in the *ab* direction (C−H···O = 2.765 Å), forming a 3D network (Figure 3c and 3d). There are also short intrastack S···S contacts (S···S = 3.939 Å) and others between adjacent stacks (3.470 Å < S···S < 3.684 Å).

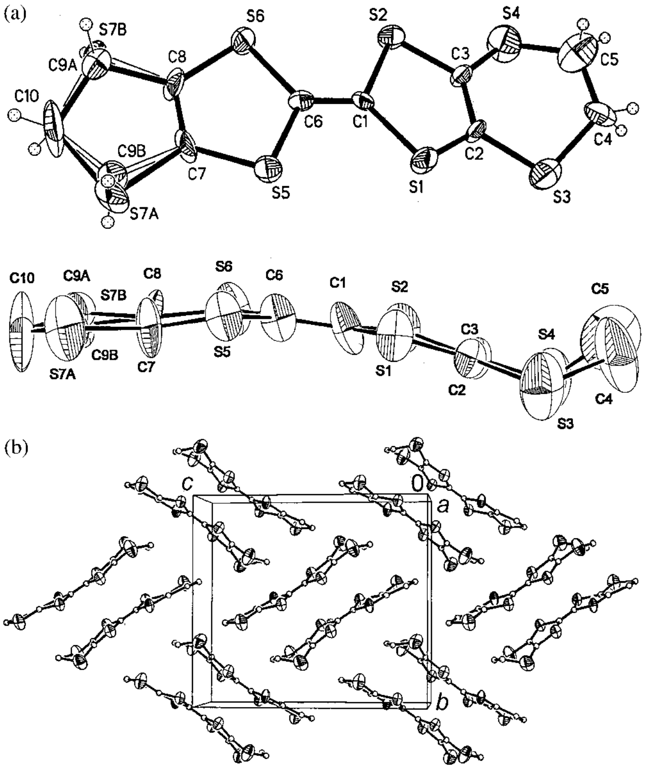


Figure 1. Crystal structure of ETEDT-TTF: (a) views of the molecular structure perpendicular and parallel to the plane of the TTF core; (b) view of the crystal packing along the *a* direction

In all the donors, it is not only the sulfur atoms of the TTF core that are involved in the short intermolecular interactions, but also the external ones. These contacts contribute to an increase in the dimensionality of the structure, mainly in ETEDT-TTF and ET-TTF. These donors therefore are suitable for the preparation of radical ion salts with high electronic dimensionality if the appropriate directionality of the orbitals can be achieved in the derived salts. On the other hand, it is interesting to analyze which part of the molecule dictates the packing pattern in the crystal. In the case of ETDC M-TTF, as expected, the strong hydrogen bonds arising from the carbonyl groups dominate the crystal packing. For ETEDT-TTF and ET-TTF, the symmetrical part dominates over the dissymmetric one, since both of them have an angular packing similar to those of the symmetrical donors BEDT-TTF and TTF,[15b] differing completely from the planar sheet motif observed in BET-TTF.[4,15b] It is noteworthy that the same ETEDT-TTF packing pattern has been found in other dissymmetric derivatives of BEDT-TTF, such as DMET[16] and EDT-TTF.[17] In all cases an angular packing is found, with the molecules forming head-to-tail dimers and exhibiting a boat conformation in the six-membered ring. In all donors the TTF core is folded, although the most stable conformation for the TTF rings of BEDT-TTF is the planar one.[20] These characteristics arise from the energy gained through the formation of intermolecular S···H−C and C···H−C interactions in the dimers.

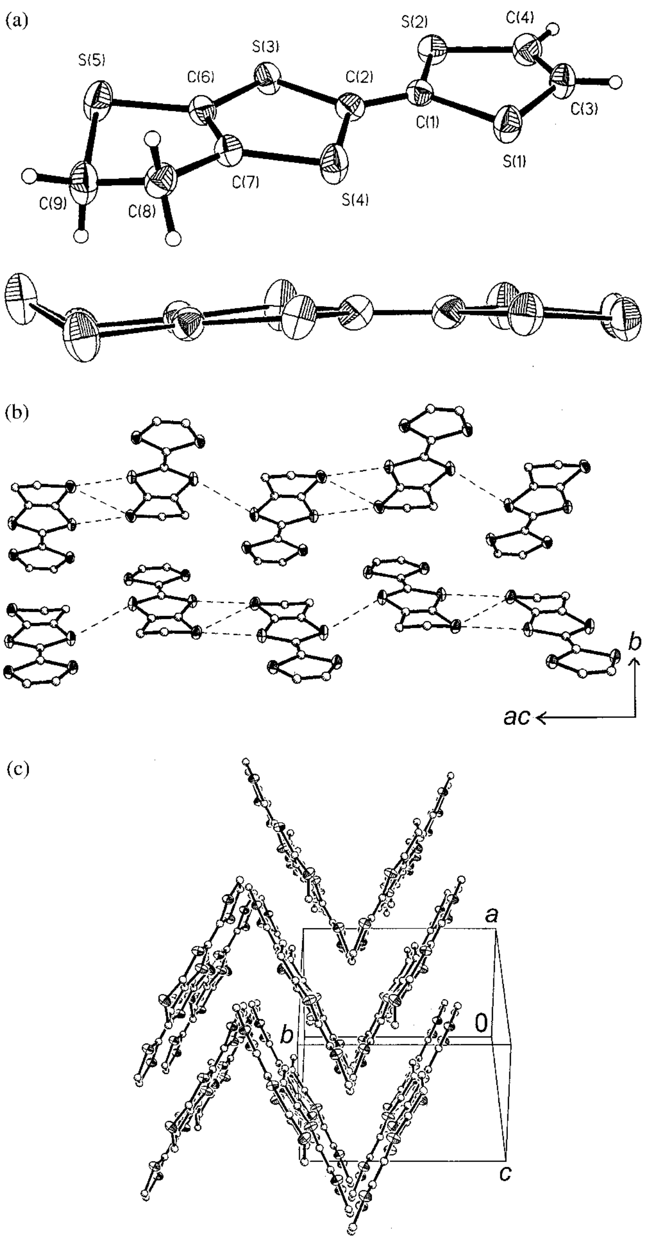


Figure 2. Crystal structure of ET-TTF: (a) views of the molecular structure perpendicular and parallel to the plane of the TTF core; (b) view of the chains of molecules and the short S···S contacts along the *ac* direction; (c) crystal packing along the *ac* direction

The redox properties of the new donors ETEDT-TTF, ETDC M-TTF and ET-TTF have been studied in solution by cyclic voltammetry, with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All donors exhibit two reversible one-electron redox waves, which indicates that they form stable cation radicals and dications. The values of the $E_{1/2}$ potentials in different solvents are given in Table 2, together with those of the corresponding symmetrical donors. Both ${}^{1}E_{1/2}$ and ${}^{2}E_{1/2}$ are considerably higher for ETDC M-TTF than for the other two donors; this is due to the electron-withdrawing character of the me-

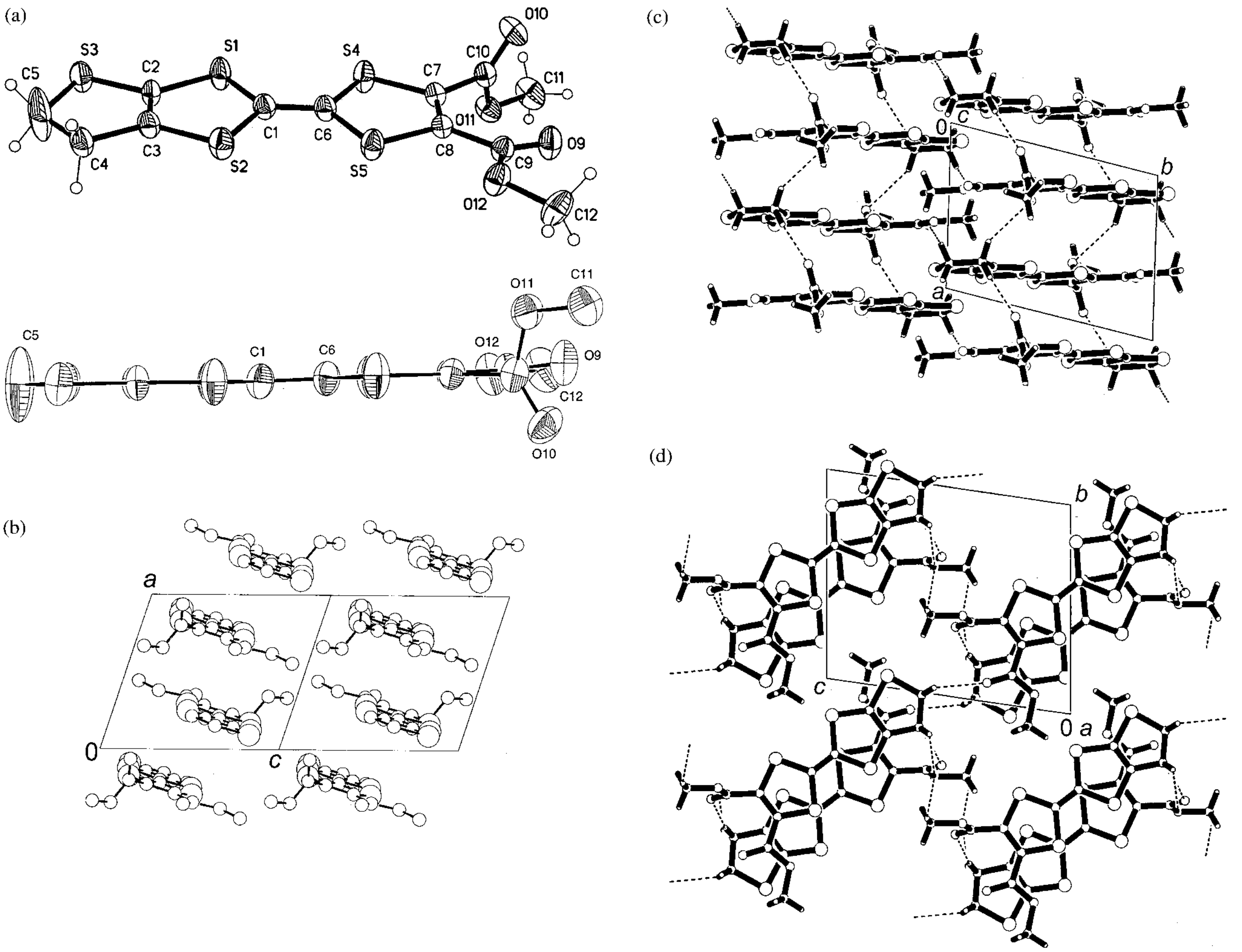


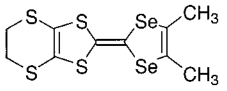
Figure 3. Crystal structure of ETDCM-TTF: (a) views of the molecular structure perpendicular and parallel to the plane of the TTF core; (b) projection of the crystal packing perpendicular to the *ac* plane; (c) and (d) views perpendicular to the *ab* and *bc* planes, respectively, showing the hydrogen bonds

Table 2. Cyclic voltammetry data of the new donors and the corresponding symmetrical ones

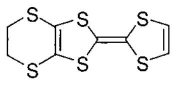
Donor	Solvent[a]	$E_{1/2}{}^1$ [V]	$E_{1/2}{}^2$ [V]	$\Delta E_{1/2}$ [V]	Ref.
TTF	DMF	0.390	0.620	0.230	[27]
	MeCN	0.367	0.748	0.381	[28]
BET-TTF	DMF	0.430	0.580	0.150	[4]
	MeCN	0.390	0.660	0.270	[b]
BEDT-TTF	DMF	0.630	0.751	0.121	[b]
	MeCN	0.567	0.829	0.262	[28]
TC M-TTF	DMF	0.800	1.080	0.280	[29][3f]
ETEDT-TTF	CH_2Cl_2	0.468	0.885	0.417	
	DMF	0.553	0.716	0.163	[b]
	MeCN	0.432	0.717	0.285	
ETDC M-TTF	CH_2Cl_2	0.624	1.098	0.474	[b]
	MeCN	0.578	0.916	0.338	
ET-TTF	CH_2Cl_2	0.431	0.902	0.471	
	DMF	0.456	0.674	0.218	[b]
	MeCN	0.373	0.706	0.333	

[a] Potentials vs. Ag/AgCl, Pt working and counter electrodes. – [b] This work.

thoxycarbonyl groups and indicates the poor donor properties of this compound. As can be observed, the values of the redox potentials of the dissymmetric donors are in all cases intermediate between those of the related symmetrical ones. All of them have small differences between the first and second oxidation potentials ($\Delta E_{1/2}$). This is a good characteristic for the preparation of molecular conductors, since this value is related to the intramolecular electronic repulsion, *U*. On lowering $\Delta E_{1/2}$, *U* decreases and the mobility of the electrons increases, resulting in greater conduction through the solid. ETEDT-TTF and ET-TTF are, therefore, good candidates for constructing radical ion salts and charge transfer complexes.



DMET



EDT-TTF

Radical Cations

Radical cations of the new donors have been generated in isotropic solution by chemical oxidation with CF_3COOH in CH_2Cl_2. They were characterized by UV/Vis and electron paramagnetic resonance (EPR) spectroscopy (Table 3). In the visible range, all radical cations display new absorptions

Table 3. EPR and UV/Vis characteristics of the radical cations derived from the dissymmetric donors and their symmetrical counterparts

Donor[a]	g factor	a_{H} [mT][b]	a_{S} [mT][b]	λ [nm]
TTF[c]	2.0081	0.125 (4 H)	0.425 (4S)	
BEDT-TTF[c]	2.0074	≤ 0.005 (8 H)	0.370 (4S) ≤ 0.080 (4S)	960, 585 (sh) 485, 455
BET-TTF[d]	2.0077	0.257 (4 H)	0.425 (2S) 0.335 (2S)	
TC M-TTF[e]	2.0081	–	0.45 (4S)	
ETEDT-TTF[f]	2.0069	0.290 (2 H)	0.45 (1S) 0.35 (3S)	924, 568 (sh), 478, 457
ETDC M-TTF	2.0075	0.422 (2 H) 0.017 (2 H)	0.505 (1S) 0.375 (1S) 0.319 (2S)	852, 449, 313.5 (sh), 281 (sh)
ET-TTF	2.0075	0.317 (2 H) 0.105 (2 H)	0.472 (1S) 0.365 (1S) 0.355 (2S)	785, 519 (sh),466, 436, 413, 331 (sh)

[a] In CH_2Cl_2.– [b] Values obtained by simulation of the experimental spectra. – [c] From ref.[30,31] and ref.[22] – [d] From ref.[4] – [e] From ref.[31] – [f] In CH_3CN.

with respect to the neutral species. The observed absorptions are similar to those found in other oxidized TTF derivatives; the bands between 400 and 600 nm have been assigned to isolated radical cations, and the ones between 750 and 1000 nm to intermolecular charge transfer resulting from dimer formation.[21,22] In agreement with this assignment, the latter bands are strongly dependent on concentration and temperature. These bands are more intense for ETEDT-TTF and ET-TTF – those donors that form dimers in their crystal structure – than for ETDC M-TTF, in which the bulky methoxycarbonyl substituents can prevent dimer formation.

The isotropic solution EPR spectra of radical cations were recorded at 295 K. The three donors exhibit intense structured signals arising from the coupling of the unpaired electron with the hydrogen atoms. Figure 4 shows the spectrum of ETEDT-TTF.

In the three compounds, the biggest H coupling constant (a_{H}) is observed for the methylenic protons adjacent to the TTF core. It has different values for the three donors, indicating distinct spin density on the methylenic units. Only for ETDC M-TTF did we succeed in the observation of the small a_{H} value (0.017 mT) due to the protons of the other methylenic group (C5 in Figure 3a) (Table 3). Additional satellite lines, arising from hyperfine interactions with the natural abundance ^{33}S isotopes (a_{S}) of the TTF core, are also observed in all cases upon enlargement of the signals (Figure 4). The computer simulation of the EPR spectra of the three radical cations gives different ^{33}S coupling constants for each TTF core sulfur atom with different substituents (Table 3). By comparison with the related symmetrical TTF derivatives, and following the same semiempirical calculation procedure used for the assignment of the sulfur coupling constants of BET-TTF^{+},[4] a tentative assignment of a_{S} has been made. The highest value seems to correspond, in the three donors, to the sulfur atom adjacent to the methylenic group of the BET-TTF component, as was observed for BET-TTF.[4] The fact that the a_{S} values of the sulfur atoms adjacent to the sulfur atoms of the external rings are lower than those adjacent to the methylenic group indicates that there is some spin density in the exocyclic sulfur atoms. This fact is important for the formation of two-dimensional electronic band structures in the derived charge transfer salts, since these S atoms have to participate in intermolecular interactions.

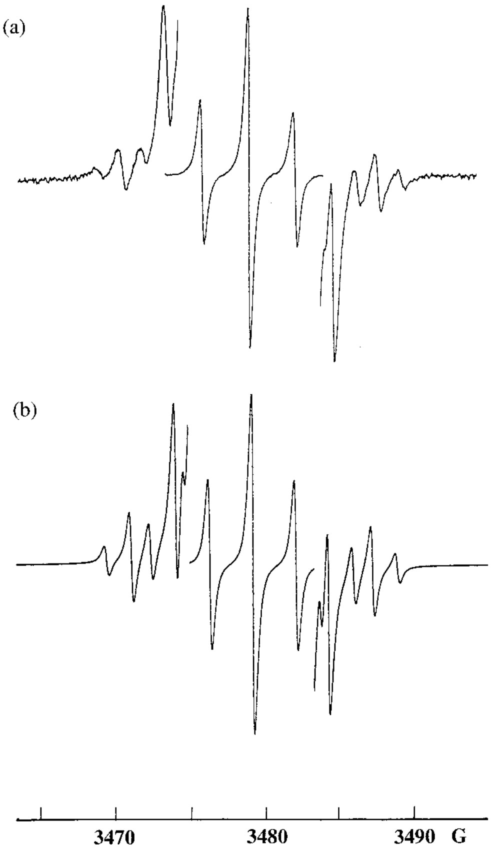


Figure 4. EPR spectrum of ETEDT-TTF radical cation at 295 K in CH_2Cl_2 under isotropic conditions; amplified signals show the satellite lines due to the ^{33}S hyperfine couplings: (a) experimental and (b) simulated spectra

ETEDT-TTF and ET-TTF reacted with tetracyano-*p*-quinodimethane (TCNQ) to give crystalline mixed valence complexes. ETEDT-TTF gave a highly conductive TCNQ complex with metallic behavior down to 75 K. Several crystalline radical cation salts displaying conducting properties have also been prepared from ETEDT-TTF and ET-TTF. The best results were achieved with ETEDT-TTF, which forms salts that are stable organic metals with several octahedral counterions. ET-TTF, in contrast, has so far provided only one metallic salt; $(\text{ET-TTF})_x\text{AuI}_2$. This difference is probably due to the presence of additional external sulfur atoms in the ETEDT-TTF molecule, able to promote short S···S contacts in the solid. This structural characteristic can enhance the dimensionality of the electronic structures of the salts, which favors the metallic character, and avoid phase transitions to an insulating state. Indeed, the stable organic metallic salts $(\text{ETEDT-TTF})_2\text{XF}_6$ (X = P, As, Sb) have two-dimensional electronic structures.[23] More detailed studies of the physical and structural properties of these new compounds, as well as the preparation of new crystalline derivatives of ET-TTF and ETEDT-TTF donors, are in progress in our laboratory.

Summary and Conclusions

We have synthesized two new dissymmetric organic π-electron donors based on the combination of half of the skeleton of BET-TTF with those of BEDT-TTF and TTF. The structure of these new donors avoids the disorder caused by the *cis-trans* isomerism observed in BET-TTF. A third new dissymmetric donor, ETDC M-TTF, has also been obtained and characterized. X-ray structure analysis of the new donors ETEDT-TF and ET-TTF reveal that, although in ETEDT-TTF there is a crystallographical disorder in the peripheral sulfur atom of the BET-TTF-like moiety, the ET-TTF donor is completely ordered. Cyclic voltammetry data reveal that both compounds are good electron donors that form stable cation radicals in solution as ascertained by ESR and UV/Vis spectroscopy. Both donors give rise to charge transfer complexes and radical ion salts with conducting properties. The results presented show that the new donors ETEDT-TTF and ET-TTF are good building blocks for the synthesis of organic conductors and offer good prospects for obtaining stable metals and even superconductors

Experimental Section

FT-IR spectra were recorded with a Nicolet 710 spectrophotometer on KBr disks. − ^{1}H NMR and ^{13}C NMR spectra were measured with a Bruker Aspect 3000 at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C with TMS as internal reference. − UV/Vis-NIR absorption spectra were obtained with a Varian Cary 5 spectrophotometer. − EPR spectra were recorded with an X-Band Bruker ESP 300 E spectrometer, equipped with an ER 412HT temperature controller, a field frequency (F/F) lock accessory and a built-in NMR gaussmeter. − Melting points were determined with a Perkin−Elmer DSC 7. − Cyclic voltammetry was carried out with an EG & G PAR 263A potentiostat/galvanostat in a cell equipped with a double KCl (3M) bridge, using the following working conditions: Pt wire, Ag/AgCl as a reference electrode, scanning rate 50−100mV/s and Bu_4NPF_6 as a supporting electrolyte.

X-ray data for single crystals of ETEDT-TTF, ETDC M-TTF and ET-TTF were collected with an Enraf−Nonius CAD4 diffractometer using monochromatic Mo-K_α radiation ($\lambda = 0.71069$ Å). The cell parameters were determined from a least-squares refinement of 25 reflections randomly searched. Data were collected using an ω-2θ scan method. The MolEN[24] package was used for applying Lorentz polarisation and Ψ-scan empirical absorption corrections. The structures were solved by direct methods using the SHELXS97[25] program and refined by a full-matrix, least-squares method using the SHELXL97 program.[26] Least-squares calculation minimized $\Sigma w(\Delta F)^2$, being $w = [\sigma^2(F_o^2) + (a{\cdot}P)^2 + b{\cdot}P]^{-1}$, $P = (F_o^2 + 2{\cdot}F_c^2)/3$. Non-H atoms were anisotropically refined and H atoms were positioned in calculated positions and refined using a global isotropic temperature factor. Crystal parameters, data collection details and results of the refinements are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The deposition numbers are CCDC-139959, -139958, and -139961 for compounds ETEDT-TTF, ETDC M-TTF and ET-TTF, respectively. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB12 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

(Ethylenethioethylenedithio)tetrathiafulvalene (ETEDT-TTF): A solution of 5,6-dihydrothieno[2,3-*d*]-1,3-dithiol-2-one (**1**) (0.500 g, 2.84 mmol) and 2,5,7,9-tetrathiabicyclo[4.3.0]non-1(6)-ene-8-thione (**2**) (0.637 g, 2.84 mmol) in freshly distilled trimethyl phosphite (9 mL) were heated to reflux under argon for 4 h. After cooling to room temperature, the precipitate formed was filtered off, washed with ether and dried (vacuum) to yield a red microcrystalline solid (0.622 g) containing ETEDT-TTF, BET-TTF and BEDT-TTF. The solid was extracted twice with dichloromethane and the resulting solution, which consisted mainly of ETEDT-TTF and BET-TTF, was concentrated to dryness (0.385 g) and chromatographed on silica gel, eluting with carbon disulfide, to afford ETEDT-TTF (0.177 g, 18%) as a red powder: m.p. 187.9 °C (dec.), onset at 186.6 °C. − ^{1}H NMR (C_6D_6): δ = 2.78 (2 H, t, *J* = 8.4 Hz), 2.17 (4 H, s), and 1.91 (2 H, t, *J* = 8.4 Hz). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.81 (2 H, t, *J* = 8.1 Hz), 3.40 (4 H, s), and 2.88 (2 H, t, *J* = 8.1 Hz). − ^{13}C NMR ([D$_6$]DMSO): δ = 125.24 (Csp^2), 123.8 (Csp^2), 113.2 (Csp^2), 106.3 (Csp^2), 32.9 (Csp^3), 31.1 (Csp^3), and 29.9 (Csp^3). − IR (KBr): ṽ = 2919, 2871, 2823, 1410, 1285, 1264, 1176, 1129, 1110, 1013, 911, 879, 767, 671, 500, and 450 cm^{-1}. − UV/Vis (CH_3CN): $\lambda_{\max}$ (log ε) = 465 (2.57), 340 (sh), 321 (4.15), 216 (4.27) nm. − MS; *m/z* (%): 352 (20.5) [M$^+$], 76 (100) [CS_2^+]. − $\text{C}_{10}\text{H}_8\text{S}_7$ (352.5932): calcd. C 34.06, H 2.29, S 63.65; found C 34.03, H 2.21, S 63.49.

[Ethylenethiobis(methoxycarbonyl)]tetrathiafulvalene (ETDC M-TTF): Ketone **1** (1.42 g, 8.07 mmol) and ketone **4** (3.78 g, 16.15 mmol) were heated to reflux in freshly distilled trimethyl phosphite (14 mL) under argon for 3 h. The mixture was allowed to cool and was filtered obtaining a red solid, BET-TTF (0.146 g), that was washed with ether. Addition of ether to the solution caused the precipitation of a violet solid, TC M-TTF (0.552 g), that was filtered off. The solution, which contained ETDC M-TTF, BET-TTF and TC M-TTF, was chromatographed (SiO$_2$, CH_2Cl_2/hexane, 3:2), to afford, in the second fraction from the column, ETDC M-TTF as a red-purple solid (0.528 g, 17%): m.p. 120.1 °C, onset at 118.8 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.83 (2 H, t, *J* = 8.1 Hz), 3.79 (6 H, s), and 2.90 (2 H, t, *J* = 8.1 Hz). − ^{13}C NMR ([D$_6$]DMSO): δ = 159.7 (C=O), 131.8 (CO−C−S), 125.5 (Csp^2), 123.8 (Csp^2), 120.9 (Csp^2), 105.9 (Csp^2), 54.2 (CH$_3$), 38.8 (Csp^3), and 32.9 (Csp^3). − IR (KBr): $\tilde{\nu}$ = 2951, 2924, 2847, 1735, 1713, 1654, 1583, 1539, 1520, 1436, 1252, 1096, 1018, 763, and 673 cm^{-1}. − UV/Vis (CH_3CN): λ_{max} (log ε) = 456 (3.02), 330 (sh), 309 (4.04) nm. − MS; *m/z* (%): 378 (100) [M$^+$]. − $C_{12}H_{10}S_5O_4$ (378.5070): calcd. C 38.08, H 2.66, S 42.35, O 16.91; found C 38.12, H 2.45, S 42.30, O 16.89.

(Ethylenethio)tetrathiafulvalene (ET-TTF): ETDC M-TTF (0.470 g, 1.24 mmol), LiBr (1.175 g, 13.5 mmol), HMPA (23.5 mL) and H_2O (2 drops) were heated under argon to 80 °C until the solution lost color. Then, the temperature was elevated to 150 °C, and the reaction mixture maintained at this temperature for 15 min. The dark brown solution was cooled to room temperature and H_2O (25 mL) was added, forming a suspension. The crude product was extracted with hot cyclohexane (5 × 230 mL), and the organic layer was washed with water (4 × 200 mL), dried ($MgSO_4$) and the solvent evaporated (0.351 g). ET-TTF was purified by a filtration through silica gel eluting with CH_2Cl_2/hexane (3:2), followed by recrystallization from toluene/CH_3CN (2:1). ET-TTF was obtained as orange crystals (0.195 g, 60%): m.p. 121.7 °C, onset at 120.01 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.75 (2 H, s), 3.81 (2 H, t, *J* = 8.1 Hz), and 2.86 (2 H, t, *J* = 8.1 Hz). − ^{13}C NMR ([D$_6$]DMSO): δ = 125.1 (Csp^2), 123.9 (Csp^2), 120.4 (Csp^2), 120.3 (Csp^2), 115.0 (Csp^2), 112.3 (Csp^2), 38.6 (Csp^3), and 32.9 (Csp^3). − IR (KBr): $\tilde{\nu}$ = 3058, 2923, 2889, 2833, 1652, 1539, 1497, 1419, 1293, 1255, 1131, 1089, 1011, 991, 878, 857, 796, 770, 732, 652, 493, 449, and 410 cm^{-1}. − UV/Vis (CH_3CN): λ_{max} (log ε) = 462 (2.47), 364 (sh), 329 (sh), 313 (4.12) nm. − MS; *m/z* (%): 262 (100) [M$^+$], 146 (100) [M$^+$ − $C_4H_4S_2$]. − $C_8H_6S_5$ (262.4354): calcd. C 36.61, H 2.30, S 61.08; found C 36.80, H 2.31, S 60.94.

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