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Structural study and electrical conductivity of salts based on functionalized TTF containing peripheral selenium atoms†

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Five new substituted tetrathiafulvalene derivatives containing the acetoxyphenyl group as a side-chain have been synthesized using a Wittig-type condensation. Four of them contain peripheral selenium atoms. From cyclic voltammetry data, the electron donor abilities of the obtained compounds have been found to be similar to that of BEDT-TTF. The crystal structures of three of these new donors have been determined. A series of radical cation salts derived from these donors has been obtained by electrocrystallization; the electrical conductivity of these phases measured on compressed powder pellets range from 5×10^{-4} to 4×10^{-5} S cm^{-1}. Charge transfer complexes have also been chemically prepared by using TCNQ as an electron acceptor; the electrical conductivity of their compressed powders range from 0.3 to 0.5 S cm^{-1}. The crystal structure of one of these charge transfer complexes has been determined and shows that the donor and the acceptor entities form regular segregated stacks; its rather high conductivity, actually measured on powder, is in agreement with this structural feature.

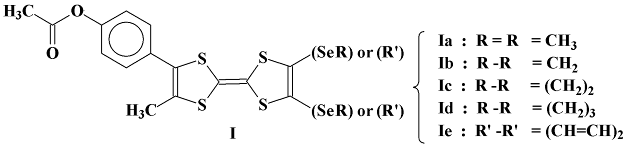
Introduction

Over the last few years, the main research topics in the field of conducting organic materials have been devoted to the stabilization of their metallic state by increasing their dimensionality.[1,2] This has been achieved in particular by introducing functions such as amine, alcohol, ester or amide onto tetrathiafulvalene (TTF) derivatives used as precursors.[3–8] Therefore, many functionalized molecules derived from TTF have been prepared and used more or less successfully.

In some cases, radical cation salts, based on TTF derivatives functionalized by one or two hydroxylated chains, were obtained as semi-conducting materials; in spite of the existence of (donor···anion···donor) interactions involving the OH groups, very weak electronic delocalization occurred. Moreover, the absence of a mixed valence state within the salts and unfavourable stacking modes of the TTF units due to steric hindrance induced by the chains attached to the TTF core may explain the poor conductive properties of the compounds.[7]

Conversely, in other cases, for instance, when TTF units bear an amide function (–CONH$_2$ and –CONHR), highly conducting salts were obtained.[5,6] These salts exhibited a structure consisting of stacks of organic molecules that allows the necessary electronic delocalization as well as effective (donor···anion···donor) interactions giving rise to the required two-dimensional character responsible for the stabilization of their metallic state down to 0.47 K.[6]

Within this framework, we developed and studied a series of TTF derivatives **I** (i) functionalized by the acetoxyphenyl group and (ii) containing, in some cases, peripheral selenium atoms which may induce two-dimensional intermolecular interactions.



I

The synthesis, electrochemical behaviour and structural characterization of these precursors containing an ester group, and the synthesis and electrical characterization of their radical cation salts and charge transfer complexes with TCNQ are reported below. The structural study of the charge transfer complex (**Ic**)$_2$TCNQ is also reported. Moreover, it is worth noting that compounds **I** are also interesting precursors to the corresponding hydroxylated-TTF (hydroxyphenyl group)[9,10] and to singly bridged bis-TTF involving the ester group as a linker.[11,12]

Experimental

Synthesis

Compounds **I** were prepared using the Wittig-type condensation[13–15] described in Scheme 1.

The starting salts (type 1[13] and 2[9]) were isolated following the appropriate procedures described in the literature.[13,9] The Wittig condensation was then carried out in acetonitrile at room temperature using a triphenylphosphonium salt **1** and a dithiolium salt **2** in the presence of triethylamine.[16,17] As expected, the reaction provided a mixture containing mainly

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams and a table of selected torsion angles for **Ic**–**e** and (**Ic**)$_2$–TCNQ. See http://www.rsc.org/suppdata/jm/b3/b308514g/

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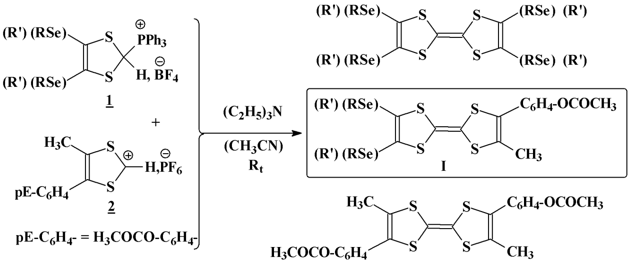

Scheme 1

the target compound **I** which was separated from the two symmetrical species by column chromatography on silica gel using CH_2Cl_2–hexane (1 : 2) as eluent. The pure samples were isolated in quite a low yield and analysed by mass spectrometry, ^1H-NMR and elemental analysis as reported in Table 1.

Electrochemical characterization

The redox properties of compounds **Ia–Ie** were determined by cyclic voltammetry. Each experiment was performed on a platinum electrode, in dry CH_2Cl_2 at room temperature, with a SCE reference electrode and n-Bu_4NPF_6 as the supporting electrolyte. A scan rate of 100 mV s^{-1} was used. As expected, all compounds show two one-electron reversible waves. The half-wave potentials $E_{1/2}ox_1$ and $E_{1/2}ox_2$ are reported in Table 2.

The $E_{1/2}ox_1$ values of compounds **Ia–Id** are found to be lower than that of BEDT-TTF (0.620 V) taken as a reference. This is indicative of good electron donor abilities which make these compounds suitable for use in the synthesis of charge-transfer complexes and radical cation salts.

It is also interesting to note that going from compound **Ib** to compound **Id** the $E_{1/2}ox_1$ value is shifted towards less anodic potentials as the ring strain of the peripheral heterocycles decreases. Moreover, when compared with the redox potentials of the unsubstituted parent compound TTF ($E_{1/2}ox_1 = 0.495$ V; $E_{1/2}ox_2 = 0.936$ V), these data show that the combined electron withdrawing effects of both the acetoxyphenyl substituent and the hydrocarbonselenium chains (or cycle) in donors **I** are almost compensated by the opposite effect of the methyl group also present on the TTF core.

Synthesis and characterization of salts and complexes derived from donors I

Tentative preparation and characterization of some radical cation salts derived from compounds **I** were undertaken. A few perchlorate, triiodide and hexafluorophosphate salts were obtained as crystals of poor quality by electrocrystallization of donors **Ib**, **Ic** and **Ie** in an organic solvent. The radical cation salts were prepared by galvanostatic electrochemical oxidation of donors **I** at a platinum electrode, in a 15 ml U-shaped cell containing a glass frit membrane, using n-Bu_4NClO_4, n-Bu_4NI_3 or n-Bu_4NPF_6 (0.5 M in THF) as the supporting electrolyte and by applying a current within the range 3–5 μA (0.25–0.40 μA cm^2). In addition, some charge transfer complexes were isolated by a chemical redox reaction between a donor of the type **I** series and TCNQ as the electron acceptor.[1,2] In each experiment, equimolar amounts (0.1 mmol.) of donor **I** and TCNQ were separately dissolved in boiling acetonitrile and then mixed. The resulting dark solution was then stored at room temperature for several days. The precipitate was then separated by filtration and analysed.[18,19] One of these complexes, *i.e.* $(\mathbf{Ic})_2$TCNQ, was obtained as plate-like crystals of sufficient quality to undergo a structural study by X-ray diffraction.

The electrical conductivities of the isolated radical cation salts and charge transfer complexes were measured using a two-probe technique[20] on compressed pellets. The results are collected in Table 3.

Crystal structure determinations

Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) was used for all measurements. Diffraction data sets for **Id** and $(\mathbf{Ic})_2$–TCNQ were collected at room temperature using a CAD4

Table 1 Characteristics of compounds **Ia–Ie**

Compound **I**	Yield (%)	Mp/°C	^1H-NMR ($CDCl_3$, ppm)	Mass Spec.	Elemental Analysis (%) Calcd/Found
Ia: R = R = CH_3 $C_{17}H_{16}O_2S_4Se_2$	15	116	2.03 (s, 3H): CH_3 2.31 (s, 3H): CH_3CO 2.33 (s, 6H): 2 × $SeCH_3$ 7.23 (m, 4H): C_6H_4	M^+: 538	C 37.92; H 2.97 C 37.78; H 2.95
Ib: R–R = –CH_2– $C_{16}H_{12}O_2S_4Se_2$	12	148	2.03 (s, 3H): CH_3 2.31 (s, 3H): CH_3CO 4.93 (s, 2H): $SeCH_2Se$ 7.22 (m, 4H): C_6H_4	M^+: 522	C 36.78; H 2.29 C 36.67; H 2.46
Ic: R–R = $(CH_2)_2$ $C_{17}H_{14}O_2S_4Se_2$	20	164	2.03 (s, 3H): CH_3 2.31 (s, 3H): CH_3CO 3.31 (s, 4H): $(CH_2)_2$ 7.20 (m, 4H): C_6H_4	M^++3: 539	C 38.05; H 2.61 C 38.17; H 2.60
Id: R–R = $(CH_2)_3$ $C_{18}H_{16}O_2S_4Se_2$	16	193	2.02 (s, 3H): CH_3 2.31 (s, 3H): CH_3CO 2.76 (m, 6H): $(CH_2)_3$ 7.22 (m, 4H): C_6H_4	M^+: 550	C 38.27; H 2.90 C 38.91; H 2.86
Ie: R′–R′ = $(CH{=}CH)_2$ $C_{19}H_{14}O_2S_4$	31	161	2.04 (s, 3H): CH_3 2.30 (s, 3H): CH_3CO 7.09 (m, 4H): Benzo 7.30 (m, 4H): C_6H_4	M^+: 402	C 56.71; H 3.48 C 56.40; H 3.36

Table 2 Half-wave potentials of compounds **Ia–Ie**

Compound **I**	BEDT-TTF[a] (reference)	**Ia**	**Ib**	**Ic**	**Id**	**Ie**
$E_{1/2}ox_1$/V	0.620	0.542	0.562	0.558	0.548	0.632
$E_{1/2}ox_2$/V	1.039	0.984	1.018	1.014	1.017	1.099

[a] BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene. Cyclic voltammetry measurements were performed in CH_2Cl_2 on a Pt electrode *versus* SCE at room temperature with NBu_4PF_6 (0.1 M) as the supporting electrolyte. A scan rate of 100 mV s^{-1} was used.

Table 3 Characteristics and electrical conductivities of complexes and salts derived from donors of type **I**

Donor (type **I**)	**Ia**	**Ib**	**Ic**	**Id**	**Ib**	**Ic**	**Ic**	**Ie**	**Ie**
TCNQ or anion	TCNQ	TCNQ	TCNQ	TCNQ	ClO_4	ClO_4	I_3	PF_6	I_3
Mp/°C	148	188	169	180	220	200	170	168	220
Colour Morphology[a]	Green	Black	Black	Black	Green	Black	Black	Black	Black
	Ndl	Pwd	Plt	Pwd	Pwd	Ndl	Pwd	Plt	Pwd
σ/S cm^{-1}[b]	0.3	0.4	0.5	6×10^{-7}	1×10^{-5}	5×10^{-4}	4×10^{-5}	1×10^{-5}	9×10^{-5}

[a] Ndl = needles, Pwd = powder, Plt = platelets. [b] Electrical conductivity: measurements achieved on compressed pellets using a two probe technique.

Table 4 Crystal data and structure determination details for **Ic**, **Id**, **Ie**, and (**Ic**)$_2$–TCNQ

Compound	**Ic**	**Id**	**Ie**	(**Ic**)$_2$–TCNQ
Formula	$C_{17}H_{14}O_2S_4Se_2$	$C_{18}H_{16}O_2S_4Se_2$	$C_{19}H_{14}O_2S_4$	$C_{23}H_{16}N_2O_2S_4Se_2$
M	536.4	550.5	402.5	638.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$I2/a$ (n° 15)[c]
a/Å	10.4533(6)	6.641(2)	15.0129(8)	30.154(8)
b/Å	17.2668(9)	23.033(5)	9.4620(6)	4.052(4)
c/Å	11.5179(6)	13.830(3)	13.3550(8)	39.317(9)
β/°	112.10(1)	101.19(2)	109.64(1)	91.40(3)
V/Å^3	1926.1(2)	2075.2(9)	1786.8(2)	4802(5)
Z	4	4	4	8
μ/mm^{-1}	4.30	3.98	0.54	3.45
Measured/independent refl. (R_{int})	33791/4550 (0.051)	4428/4071 (0.036)	30356/4272 (0.079)	5512/2945 (0.076)
Observed refl. [$I > 2\sigma(I)$]	3582	2102	3855	1715
$R(F)$[a] (observed refl.)	0.036	0.033	0.050	0.048
$R_w(F^2)$[b] (all refl.)	0.100	0.126	0.138	0.131

[a] $R(F) = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $I2/a$ is a non-standard setting of space group n° 15, the standard setting is $C2/c$. The setting $I2/a$ has been chosen to reduce correlations during the refinement process. The unit cell parameters in $C2/c$ are a = 48.95 Å, b = 4.05 Å, c = 30.15 Å, β = 126.6°.

Enraf-Nonius diffractometer; data sets for **Ic** and **Ie** were collected at 180 K using a Xcalibur Oxford Instrument CCD diffractometer equipped with a nitrogen gas flow cooling device. Crystal data and relevant data collection and refinement parameters are listed in Table 4.‡ All intensity data were corrected for absorption. Structure solution and refinement (against F^2 using all reflections) were performed using standard procedures.[21–23]

All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located on difference-Fourier maps and their contributions were included in structure factor calculations using calculated positions and the riding model with isotropic temperature factors (not refined). However, for (**Ic**)$_2$–TCNQ, the carbon atoms were refined isotropically because of the small number of observed reflections and of the poor quality of the crystal.

Results and discussion

For discussion of the crystal structures, atoms are numbered according to Fig. 1. Selected bond lengths and angles are given in Table 5.

Neutral donors

The crystal structures of **Ie**, **Id** and **Ic** are shown on Figs. 2, 3 and 4 respectively.[24] In these structures the molecules have not formed stacks. The most striking feature is the difference in the conformations of these apparently closely related molecules. This is emphasized by comparison of the side view of the molecules shown in Fig. 5. A table of selected torsion angles (Table 6) has been deposited as supplementary material.†[24]

Probably, because of the conjugation between the external ring and the TTF core, the molecule **Ie** is almost planar with the exception of the phenyl ring bearing the acetoxyphenyl group. Owing to the free rotation allowed around the C(6)–C(7) and C(10)–O(1) bonds, it is surprising that the acetyl group lies almost exactly in the plane of the TTF core [the largest deviation from the plane defined by atoms S(1), S(2), S(3), S(4), C(3), C(4) is −0.12 Å for the outermost atom C(14)]. The other donor molecules **Id** and **Ic** are significantly bent and have a boat conformation. Taking as a reference the plane of the TTF core defined by atoms S(1), S(2), S(3), S(4), C(3), C(4) and setting as positive the rotation that brings atoms above this plane, the **Id** molecule displays angles $\alpha_1 = -21.5°$ and $\alpha_2 = -15.0°$ between the reference plane and the mean planes through atoms S(1), S(2), C(1), C(2), Se(1), Se(2) on one side and atoms S(3), S(4), C(5), C(6), C(7), C(15) on the other side, respectively. The same angles are $\alpha_1 = +21.2°$ and $\alpha_2 = +19.5°$ respectively for **Ic**.

Several TTF derivatives, in their neutral form, have been reported to adopt, in the solid state, such a boat conformation, for example BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene],[25] BEDO-TTF [bis(ethylenedioxo)tetrathiafulvalene],[26] EDT-TTF (ethylenedithiotetrathiafulvalene),[27] EDS-TTF (ethylenediselenotetrathiafulvalene),[28] or, more recently, ETEDT-TTF (ethylenethioethylenedithiotetrathiafulvalene).[29] A theoretical study by Whangbo *et al.*[30] on BEDT-TTF and BEDO-TTF has indicated that the most stable configuration for the isolated molecule would be the planar one (ethylene residues excluded), but the energy required to fold the molecule would be rather small and could be afforded by weak intermolecular interactions such as C–H···S (or C–H···O). In **Ie** no intermolecular S···S and only one H···S short distance (*i.e.* shorter than—but very close to—the sum of the van der Waals radii) is observed [C(15)–H···S(4): 2.843 Å]. In **Id** there is no intermolecular chalcogen···chalcogen short distance but three C–H···chalcogen contacts are observed [C(15)–H···S(3): 2.905 Å, C(12)–H···Se(1): 3.031 Å, C(14)–H···Se(1): 2.959 Å]. In **Ic** several intermolecular short distances are found

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‡ CCDC reference numbers 216047–216050. See http://www.rsc.org/suppdata/jm/b3/b308514g/ for crystallographic data in .cif or other electronic format.

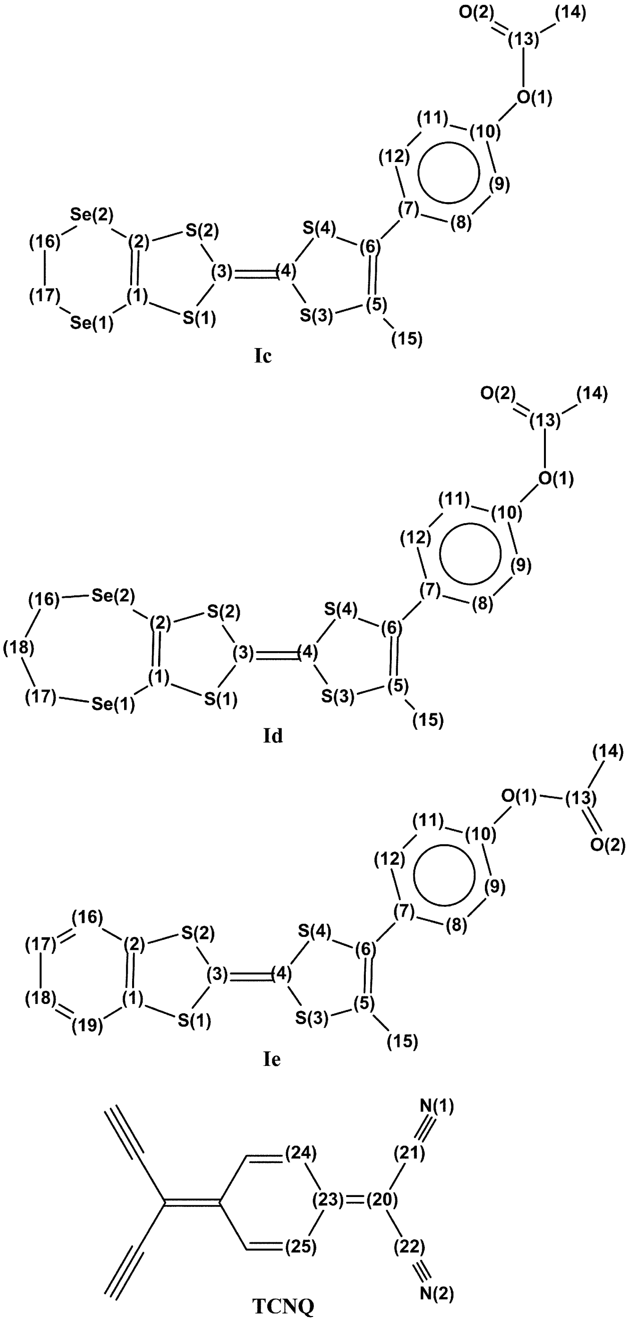

Fig. 1 Numbering scheme of the atoms used throughout the X-ray study. For the carbon atoms the symbol C is omitted for clarity.

[Se(1)···Se(2): 3.574 Å, Se(1)···S(1): 3.680 Å, Se(2)···S(3): 3.668 Å, S(1)···S(1): 3.330 Å, C(14)–H···S(2): 2.960 Å, C(15)–H···S(2): 2.903 Å]. These observations are qualitatively in agreement with the results of Whangbo *et al.*[30] on BEDT-TTF and BEDO-TTF. As a matter of fact, the molecule that is the most isolated in the solid state (**Ie**) exhibits the most planar configuration.

Another difference between **Ie** on the one hand and **Id** and **Ic** on the other hand is the position of the oxygen atom O(2) which is located on the same side as C(15) with regard to the C(6)···O(1) axis of **Ie** and located on the side opposite to C(15) for **Id** and **Ic**.

The charge transfer complex (Ic)$_2$–TCNQ

In the crystal, the donor and the acceptor entities pile up separately. Within a stack adjacent entities are related by the crystallographic translation $b = 4.052$ Å thus forming a regular stacking pattern. This feature is illustrated in Fig. 6 where the content of three unit cells piled up along the [010] axis has been drawn.[24] In the donor stacks the intermolecular distance defined as the distance between the mean planes through atoms S(1), S(2), S(3), S(4), C(3), C(4) is 3.72 Å and the overlapping

Table 5 Selected interatomic distances (Å) and bond angles (°) for **Ie**, **Id**, **Ic**, and (**Ic**)$_2$–TCNQ (e.s.d.'s in parentheses). For the sake of brevity C–C bond lengths of the phenyl rings are not listed and only bond angles involving the outermost atoms are reported. See Fig. 1 for numbering. Superscript ^{i} indicates an inversion through a centre of symmetry

Distances	**Ie**	**Id**	**Ic**	(**Ic**)$_2$–TCNQ
Se(1)–C(1)	—	1.893(5)	1.887(3)	1.877(7)
Se(1)–C(17)	—	1.966(6)	1.974(4)	1.943(9)
Se(2)–C(2)	—	1.900(5)	1.892(3)	1.883(7)
Se(2)–C(16)	—	1.948(7)	1.952(3)	1.944(9)
S(1)–C(1)	1.750(2)	1.757(5)	1.757(3)	1.752(7)
S(1)–C(3)	1.755(2)	1.762(6)	1.756(3)	1.739(7)
S(2)–C(2)	1.759(2)	1.748(5)	1.751(3)	1.748(8)
S(2)–C(3)	1.757(2)	1.764(5)	1.758(3)	1.745(7)
S(3)–C(4)	1.762(2)	1.752(5)	1.758(3)	1.731(7)
S(3)–C(5)	1.753(2)	1.750(5)	1.762(3)	1.731(8)
S(4)–C(4)	1.753(2)	1.734(5)	1.753(3)	1.735(7)
S(4)–C(6)	1.766(2)	1.771(5)	1.770(3)	1.761(7)
O(1)–C(10)	1.400(3)	1.406(7)	1.407(4)	1.404(8)
O(1)–C(13)	1.365(3)	1.294(10)	1.350(4)	1.348(10)
O(2)–C(13)	1.194(4)	1.202(11)	1.185(5)	1.190(11)
C(1)–C(2)	1.397(3)	1.327(7)	1.344(5)	1.308(9)
C(3)–C(4)	1.347(3)	1.335(7)	1.342(4)	1.349(10)
C(5)–C(6)	1.343(3)	1.333(7)	1.342(5)	1.356(11)
C(5)–C(15)	1.501(3)	1.506(7)	1.511(5)	1.504(12)
C(6)–C(7)	1.479(3)	1.474(6)	1.484(5)	1.460(10)
C(13)–C(14)	1.491(4)	1.461(10)	1.488(5)	1.477(11)
C(1)–C(19)	1.398(4)	—	—	—
C(2)–C(16)	1.400(3)	—	—	—
C(16)–C(17)	1.387(4)	—	1.469(5)	1.457(13)
C(16)–C(18)	—	1.517(10)	—	—
C(17)–C(18)	1.387(4)	1.501(10)	—	—
C(18)–C(19)	1.387(4)	—	—	—
C(20)–C(21)	—	—	—	1.431(11)
C(20)–C(22)	—	—	—	1.409(11)
C(20)–C(23)	—	—	—	1.420(10)
C(23)–C(24)	—	—	—	1.416(10)
C(23)–C(25)	—	—	—	1.420(9)
C(24)–C(25 ^{i})	—	—	—	1.340(11)
N(1)–C(21)	—	—	—	1.135(11)
N(2)–C(22)	—	—	—	1.118(11)
Angles	**Ie**	**Id**	**Ic**	(**Ic**)$_2$–TCNQ
C(10)–O(1)–C(13)	119.9(2)	121.7(6)	117.6(3)	118.5(6)
O(1)–C(13)–O(2)	123.3(3)	120.1(8)	123.1(3)	122.1(7)
O(1)–C(13)–C(14)	110.2(2)	115.9(7)	110.9(3)	111.6(7)
O(2)–C(13)–C(14)	126.4(3)	124.0(8)	126.0(3)	126.3(8)
Se(1)–C(17)–C(16)	—	—	118.1(3)	119.1(6)
Se(2)–C(16)–C(17)	—	—	114.1(3)	119.7(7)
Se(2)–C(16)–C(18)	—	116.7(5)	—	—
Se(1)–C(17)–C(18)	—	116.5(4)	—	—
C(16)–C(18)–C(17)	—	115.5(6)	—	—
C(2)–C(16)–C(17)	118.9(2)	—	—	—
C(16)–C(17)–C(18)	120.7(3)	—	—	—
C(17)–C(18)–C(19)	120.9(3)	—	—	—
C(18)–C(19)–C(1)	118.9(2)	—	—	—

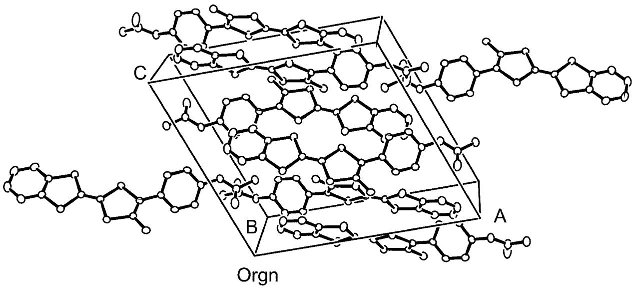

Fig. 2 Crystal structure of **Ie**. In this and subsequent figures hydrogen atoms are omitted for clarity.

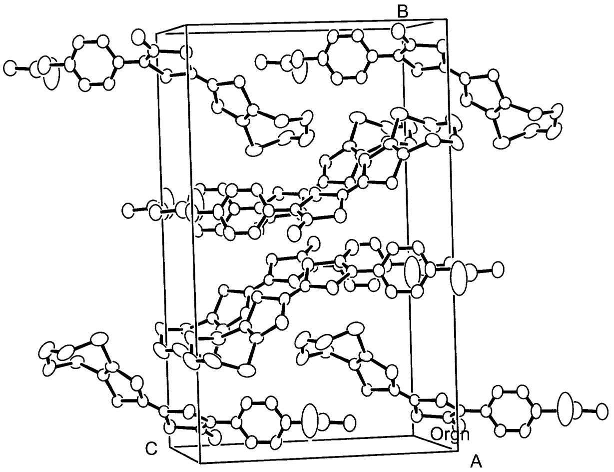

Fig. 3 Crystal structure of **Id**.

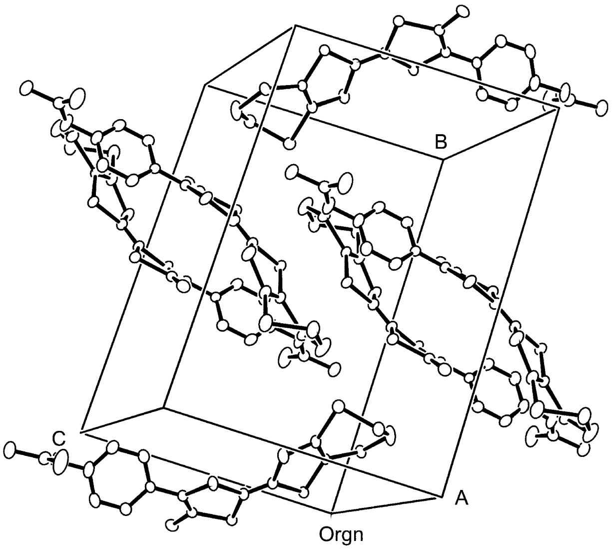

Fig. 4 Crystal structure of **Ic**.

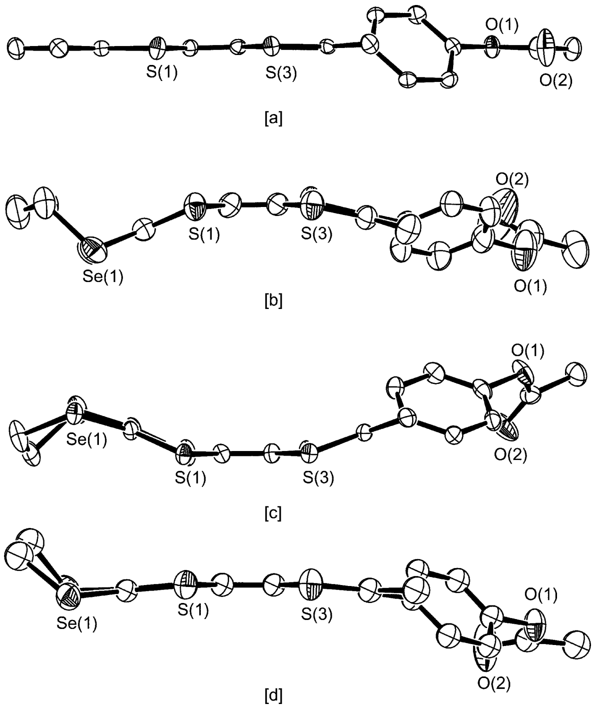

Fig. 5 Side view of the donor molecules. [a]: **Ie**; [b]: **Id**; [c]: **Ic**; [d]: **Ic** in (**Ic**)$_2$–TCNQ. In all these pictures the methyl carbon atom C(15) is directed towards the reader.

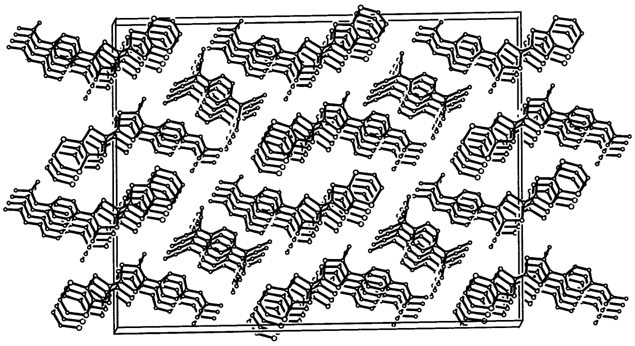

Fig. 6 Crystal structure of (**Ic**)$_2$–TCNQ. The picture is a projection down the [010] axis, tilted by about ten degrees to emphasize the stacking. The content of three unit cells piled up along the [010] axis has been drawn.

mode of the TTF cores is of the bond-over-ring type (Fig. 7a). In the acceptor stacks the intermolecular distance is 3.46 Å but the molecules are offset in such a way that the rings do not overlap (Fig. 7b). Thus, it is likely that the TCNQ entities do not much participate much in the conduction process. However the segregated regular stacks and the overlapping mode of the donor entities are favourable structural features for the setting of a conduction path, provided that the donor has been partially oxidized. As a matter of fact the conductivity of (**Ic**)$_2$–TCNQ measured on compressed pellets is relatively high ($\sigma_{\rm RT}$ = 0.5 S cm^{-1}). As, in addition, no chalcogen···chalcogen short contact is observed between stacks, we can expect that (**Ic**)$_2$–TCNQ would display pure 1D transport properties. Unfortunately the poor accuracy of the structure determination prevented us running band structure calculations. The charge transfer between **Ic** and TCNQ can be estimated by using the criterion, based on the bond lengths in TCNQ, developed by Flandrois and Chasseau.[31] From this criterion, it is deduced that the charge of TCNQ is close to −1 implying that each **Ic** entity has a partial charge of +0.5. However this result should only be considered as qualitative because of the low accuracy of the structural parameters.

In addition, it is interesting to compare the shape of the oxidized form of **Ic** to that of the neutral one (Fig. 5). The oxidized molecule is close to planarity (ethylene and acetoxyphenyl groups excluded): the characteristic folding angles (as

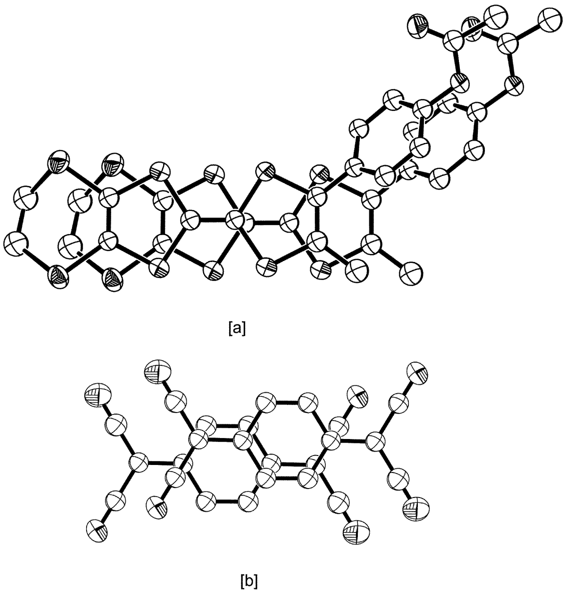

Fig. 7 [a] Overlapping mode of the **Ic** entities; projection onto the plane of the TTF core. [b] Overlapping mode of the TCNQ entities, projection onto the molecular plane.

defined above) are $\alpha_1 = -5.3°$ and $\alpha_2 = -5.4°$, to be compared with +21.2° and +19.5° respectively in neutral **Ic**. It has often been observed in other cases of TTF derivatives, that when the neutral donor is folded, its oxidized form is planar. Another strong difference between the two forms lies in the position of the ethylene group with respect to the plane defined by atoms S(1), S(2), C(1), C(2), Se(1), Se(2): keeping the same orientation for the molecule in the neutral form, *i.e.* C(15) directed towards the reader, the ethylene group is below this plane and in the oxidized form it is above this plane (Fig. 5c and 5d). There is no obvious reason other than weak intermolecular interactions (as discussed above) to explain this inversion in conformation.

Conclusion

In this series of new compounds, it has been found that a donor such as **Ic** could lead to a conducting TCNQ complex in spite of its bent conformation in the neutral form. From this result we hope to obtain improved electrical properties in salts of the phenylhydroxylated derivative of **Ic** (or other type **I** compounds) in which the occurrence of hydrogen bonds favours a two dimensional character. The conversion of compounds **Ia–Id** to the phenylhydroxylated species[9,10] and the synthesis of their radical cation salts and charge transfer complexes is now under way.

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