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Hal···Hal interactions in a series of three isostructural salts of halogenated tetrathiafulvalenes. Contribution of the halogen atoms to the HOMO–HOMO overlap interactions

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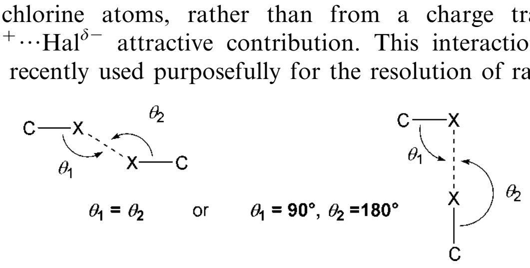
The halogenated tetrathiafulvalenes, Br_2-EDT-TTF and I_2-EDT-TTF were prepared by the coupling route from the corresponding 4,5-dibromo- or 4,5-diiodo-1,3-dithiole-2-thione. In the isostructural series, $(Br_2\text{-EDT-TTF})_2IBr_2$, $(Br_2\text{-EDT-TTF})_2I_3$ and $(I_2\text{-EDT-TTF})_2I_3$, noted **$Br_2$/$IBr_2$**, **$Br_2$/$I_3$** and **$I_2$/$I_3$** respectively, short (3.42–3.60 Å) and directional Hal···Hal interactions are identified between donor molecules and with the anions, stabilising rare β′ phases. These interactions play not only a structural role but also contribute to the electronic dispersion thanks to sizeable coefficients on the halogen atoms in the HOMOs of Br_2-EDT-TTF and I_2-EDT-TTF. The three salts behave as Mott insulators as reflected by a high room temperature conductivity (0.5 S cm^{-1}) with an activation energy which increases in the order **Br_2/IBr_2** (730 K), **Br_2/I_3** (1260 K), **I_2/I_3** (1330 K) and a weak magnetic susceptibility, which decreases abruptly below 150 K with no sign of an antiferromagnetic ground state.

Introduction

Intermolecular halogen···halogen interactions have been identified for a long time in the solid state structure of halogenated molecules but their nature is still a matter of debate. Either the presence of an attractive force,[1] often referred to as "donor–acceptor", "charge-transfer", "HOMO–LUMO" interactions, "incipient electrophilic and nucleophilic attack" or a decreased repulsion[2] of close-packed non-spherical atoms have been proposed. On the basis of statistical studies performed on the Cambridge Structural Database (CSD), Desiraju and Parthasarathy[3] showed that Hal···Hal interactions could be divided into two groups according to their geometrical features. While both are characterised by Hal···Hal distances significantly shorter than the sum of the van der Waals radii of the contacting atoms (Cl···Cl: 3.5 Å, Br···Br: 3.7 Å, I···I: 4.0 Å),[4] the shortest distances were found with the geometry described in Scheme 1 with $\theta_1 = 90°$ and $\theta_2 = 180°$. These geometrical preferences were shown[5] to originate from the electrostatic forces and repulsion anisotropy arising both from the quadrupolar lone pair electron density of the chlorine atoms, rather than from a charge transfer $Hal^{\delta+}\cdots Hal^{\delta-}$ attractive contribution. This interaction has been recently used purposefully for the resolution of racemic bromoalkanes[6] as well as for the elaboration of novel organic conductors based on halogenated tetrathiafulvalenes.[7,8] In the latter indeed, short Hal···Hal contacts were observed, between halogenated donor molecules as well as between the donor molecules and halogenated anions. Since the halogen atoms in those tetrathiafulvalenes are directly connected to the π redox core, we wanted to investigate to what extent they would not only contribute to the *structural* solid state arrangement through Hal···Hal short contacts but also could take part in the *electronic* delocalisation of the conduction electrons. To that aim, we have prepared the dibromo derivative of EDT-TTF, Br_2-EDT-TTF,[8] by a novel route which avoids the lithiation of EDT-TTF and investigated its cation radical salts with various anions. The successful electrocrystallisation of a conducting 2 : 1 salt with the linear IBr_2^- anion $(Br_2\text{-EDT-TTF})_2(IBr_2)$ prompted us to investigate the preparation of possible *isostructural* salts by introducing slight modifications on the system, substituting iodine atoms for the bromine ones, either on the donor molecule (I_2-EDT-TTF *vs.* Br_2-EDT-TTF) or on the anion (I_3^- *vs.* IBr_2^-) or on both. Such isostructural series offer invaluable opportunities for evaluating the effects of substitutional changes on the electronic properties of the solids, and open routes for alloying strategies when different behaviours are identified. This strategy has been successfully used in the field of molecular conductors such as (i) the isostructural Bechgaard salts[9] where different anions (ClO_4^-, PF_6^-, Br^-, ...) generate a variety of ground states (CDW, SDW, superconductivity, ...),[10] (ii) the superconducting A_3C_{60} (A = K; Rb, Cs) in which the critical temperature increases with the anion size,[11] or (iii) the λ-$(BEDS)_2(MX_4)$ series with M = Fe^{III}, Ga^{III}, X = Cl, Br.[12] Other examples are also found in molecular antiferromagnets, such as the perovskite series



Scheme 1

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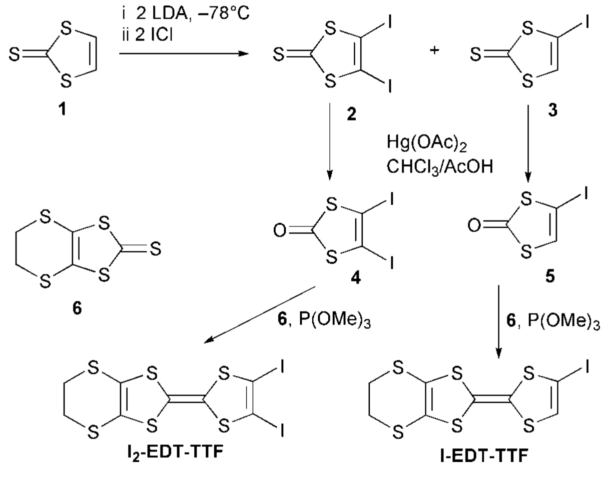
(TTF)$_3$(Mo$_3$X$_8$Y$_6$)Z with X, Y, Z = Cl, Br, I,[13] or the heteroleptic [Cp$_2$M(dmit)$^{+\bullet}$][X$^-$] complexes with M = Mo, W and X$^-$ = PF$_6^-$, AsF$_6^-$, SbF$_6^-$.[14]

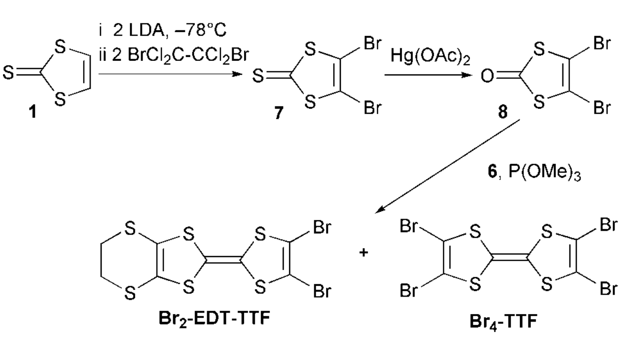
Results

Syntheses

Two routes have been described for the preparation of halogenated EDT-TTF. Both involve the metallation of either EDT-TTF itself or the vinylene trithiocarbonate **1** (Scheme 2) and further reaction with electrophilic halogenating agents. The first route has been mainly used for the preparation of the chloro- and bromo- derivatives;[8] its main drawback lies in the low yields of those reactions due to the reactivity of the dithioethylene bridge of EDT-TTF in the presence of two equivalents of lithiating agent.[15,16] The second route involving the halogenation of the vinylene trithiocarbonate **1** and further P(OMe)$_3$-assisted cross-coupling has been described for the synthesis of I$_4$TTF[7c] as well as several mono- and diiodo-tetrathiafulvalenes.[17] In our hands, this route afforded, in variable proportions, a mixture of the mono- and diiodo derivatives **2** and **3** which were separated by chromatography. Oxymercuration to **4** and **5** with Hg(OAc)$_2$ and coupling of **6** with either **4** or **5** afforded I$_2$-EDT-TTF and I-EDT-TTF. The synthetic route described above for the iodo derivatives has been exemplified here to the dibromo derivatives **7** and **8** (Scheme 3) to afford Br$_2$-EDT-TTF[8] *via* this coupling route[17] together with the symmetrically substituted Br$_4$-TTF.



Scheme 2



Scheme 3

Structural properties

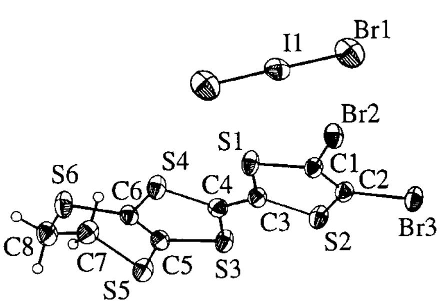


Fig. 1 ORTEP drawing of Br$_2$-EDT-TTF in (Br$_2$-EDT-TTF)$_2$IBr$_2$. Thermal ellipsoids are drawn at the 50% probability level.

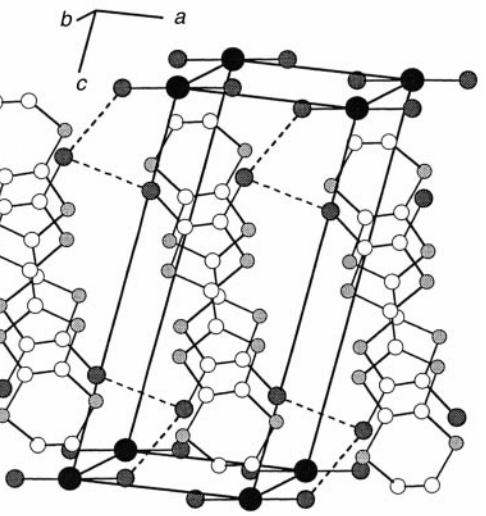


Fig. 2 A view of the unit cell of (Br$_2$-EDT-TTF)$_2$IBr$_2$ (**Br$_2$**/IBr$_2$). The dashed lines indicate the intermolecular Br···Br interactions.

Electrocrystallisation experiments of I$_2$-EDT-TTF and Br$_2$-EDT-TTF in the presence of *n*-Bu$_4$NI$_3$ or *n*-Bu$_4$NIBr$_2$ afforded three isostructural salts, of 2 : 1 stoichiometry, one with I$_2$-EDT-TTF, (I$_2$-EDT-TTF)$_2$(I$_3$) noted **I$_2$**/I$_3$ and two with Br$_2$-EDT-TTF, (Br$_2$-EDT-TTF)$_2$(I$_3$) noted **Br$_2$**/I$_3$ and (Br$_2$-EDT-TTF)$_2$(IBr$_2$) noted **Br$_2$**/IBr$_2$. Note that in the presence of *n*-Bu$_4$NI$_3$, another phase was often obtained and identified from its different crystal shape (plates instead of needles for **I$_2$**/I$_3$). Crystal structure resolution was hampered by strong disorder problems in the I$_3^-$ polymeric network and this salt will not be further discussed here.[18] **Br$_2$**/IBr$_2$, **Br$_2$**/I$_3$ and **I$_2$**/I$_3$ crystallise in the triclinic system, space group *P*1 with one donor molecule in a general position in the unit cell and one anion located on an inversion centre (Fig. 1). In the solid (Fig. 2), the partially oxidised donor molecules organise into inversion-centred diads with a bond-over-ring overlap and a short intra-diad plane-to-plane distance (Table 1). These diads arrange parallel to each other along *a* while they stack on top of each other with a lateral offset along *b* giving rise to organic slabs separated from each other by the anionic layers, a structural arrangement characteristic of the β′ phases of the BEDT-TTF salts (Fig. 3).[19] Furthermore, as shown in Fig. 2, Hal···Hal interactions are also identified (Table 1), between halogen atoms of two neighbouring donor molecules along *a* as well as between one halogen atom of the organic molecule and the terminal halogen of the counter anion. Both Hal···Hal interactions exhibit short Hal···Hal distances (Table 1) and a strong directionality: the angle values θ_1 and θ_2 defined in Scheme 1 are indeed close to 90 and 180° respectively in the three structures. Note also that the Hal···Hal distances do not change much when going from the Br···Br to the I···I interaction, illustrating the stronger interaction exhibited by the most polarisable iodine atoms. Four different $\beta_{\mathrm{HOMO}\cdots\mathrm{HOMO}}$ intermolecular interaction energies, which are a measure of the strength of the interaction between the HOMOs of adjacent molecules,[20] are identified in the organic conducting slab, as indicated on Fig. 3. The calculated values collected in

Table 1 Geometrical characteristics of the salts. The Hal···Hal distances can be compared with Σ_{vdW}(Br···Br) = 3.5 Å, Σ_{vdW}(Br···I) = 3.7 Å, Σ_{vdW}(I···I) = 4.0 Å. Definitions of θ_1 and θ_2 are given in Scheme 1

		Br$_2$/IBr$_2$	**Br$_2$/I$_3$**	**I$_2$/I$_3$**
Intra-diad plane-to-plane distance/Å		3.474(5)	3.49(1)	3.61(1)
Inter-diad plane-to-plane distance/Å		3.625(5)	3.65(1)	3.67(1)
Hal$_{donor}$···Hal$_{donor}$	Hal···Hal dist.	3.456(1) (Br···Br)	3.514(2) (Br···Br)	3.599(1) (I···I)
	θ_1	96.7(1)	97.6(3)	92.9(2)
	θ_2	152.0(1)	150.4(3)	155.8(2)
Hal$_{donor}$···Hal$_{anion}$	Hal···Hal dist.	3.422(1) (Br···Br)	3.509(1) (Br···I)	3.553(1) (I···I)
	θ_1	109.37(3)	110.53(3)	107.21(3)
	θ_2	164.6(1)	164.8(3)	164.9(2)

Table 2 show that the donor molecules are strongly associated through interaction I within inversion-centred diads which mainly interact with each other through interaction III and IV while a much weaker interaction II develops in the stacking direction. Since the β_{IV} value is twice as large as the β_{III} one, the structure can be tentatively described as chains running along $a+b$, weakly interacting with each other through interaction III along the a direction. The corresponding band structure (Fig. 4, full lines) and Fermi surface assuming a metallic filling of the bands[21] (Fig. 5, full lines) exhibit indeed a marked one-dimensional character in the three salts.

Table 2 Calculated $\beta_{HOMO\cdots HOMO}$ interaction energies (absolute values) in the three salts. Below each value is also given the calculated one for the hypothetical salts where hydrogen atoms are substituted for the halogen atoms on the donor molecules together with the corresponding variations (%)

	Br$_2$/IBr$_2$	**Br$_2$/I$_3$**	**I$_2$/I$_3$**
Interaction I	0.447	0.416	0.339
with H	0.391 (−12%)	0.349 (−16%)	0.225 (−33%)
Interaction II	0.040	0.038	0.003
with H	0.001^a	0.017^a	0.000^a
Interaction III	0.127	0.110	0.081
with H	0.118 (−7%)	0.102 (−7.3%)	0.069 (−15%)
Interaction IV	0.265	0.249	0.242
with H	0.255 (−3.8%)	0.240 (−3.8%)	0.229 (−5.4%)

^{a}The β values are to small to allow significant comparisons.

Electronic properties

The three salts exhibit room-temperature conductivity in the range 0.5–10 S cm^{-1} and a semi-conducting behaviour upon cooling (Fig. 6). The activation energies increase regularly with the size of the unit cell, in the order **Br$_2$/IBr$_2$** (730 K), **Br$_2$/I$_3$** (1260 K), **I$_2$/I$_3$** (1330 K). SQUID magnetic susceptibility measurements (Fig. 7) were performed on **Br$_2$/IBr$_2$** only since the other salts with I$_3^-$ might be polluted with other phases (see above) at different fields. The susceptibility, whose room temperature value is about 5.2×10^{-4} cm^3 mol^{-1}, is gradually reduced as the temperature is lowered down to 50 K, at which an anomaly appears. No field dependence could be observed between 2.5 and 150 K.

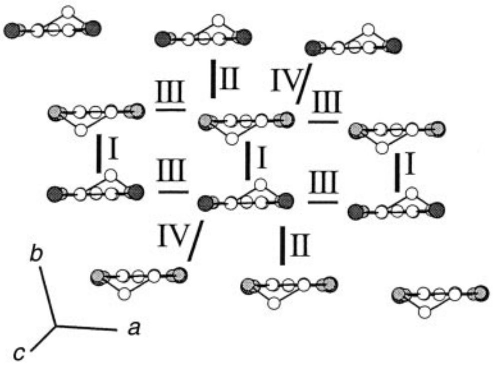


Fig. 3 A view of a single organic slab, viewed along the long axis of the donor molecules. The four different HOMO···HOMO intermolecular interactions are noted as I–IV (see text).

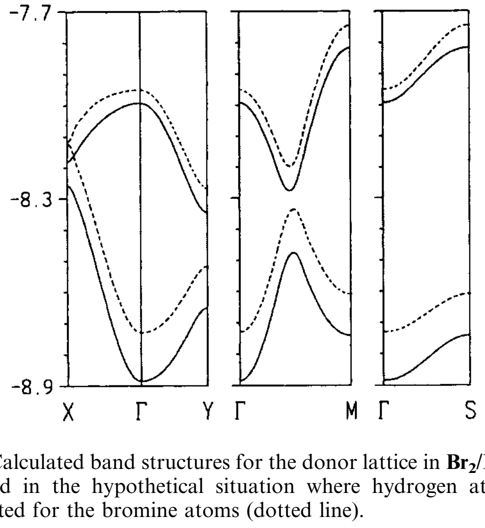


Fig. 4 Calculated band structures for the donor lattice in **Br$_2$/IBr$_2$** (full line) and in the hypothetical situation where hydrogen atoms are substituted for the bromine atoms (dotted line).

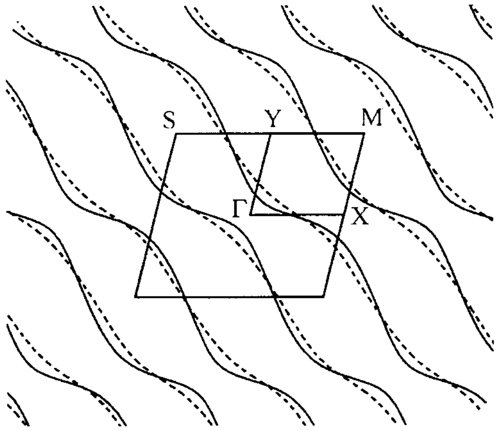


Fig. 5 Calculated Fermi surfaces (assuming a metallic band filling) in **Br$_2$/IBr$_2$** (full line) and in **I$_2$/I$_3$** (dotted line).

Discussion

The three structures described here are characterised by a bond-over-ring diad formation, often encountered with similar unsymmetrically substituted TTFs. These diads arrange in a rare β′ structure through the side-by-side arrangement of the diads by translation along a, allowing for (and stabilised by) short Br···Br, Br···I and I···I interactions between radical

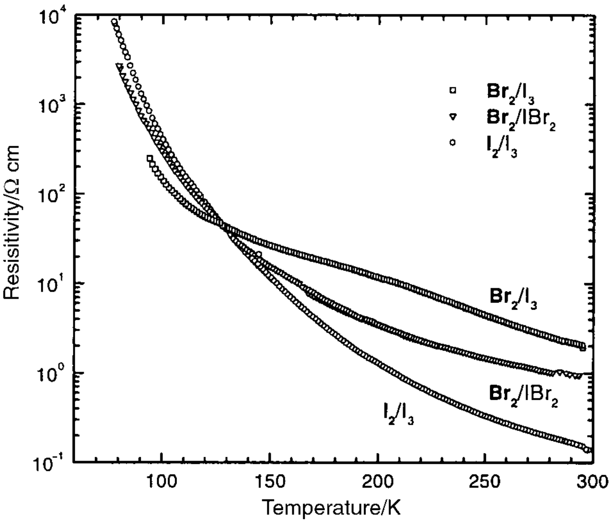


Fig. 6 Temperature dependence of the resistivity in the three salts.

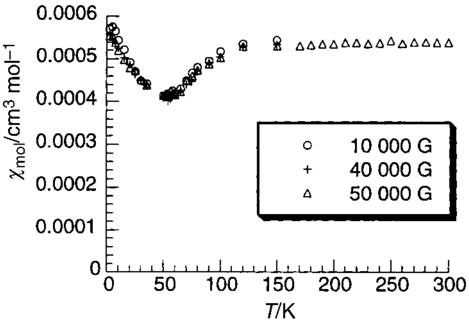


Fig. 7 Temperature dependence of the SQUID magnetic susceptibility in Br_2/IBr_2. Data have been corrected for sample diamagnetism and holder contribution.

cations with the $\theta_1 \approx 90°$, $\theta_2 \approx 180°$ characteristics. This is in contrast with the situation encountered in most radical cation salts of halogenated TTFs where only donor···anion Hal···Hal_{anion} or donor···donor Hal···S interactions are observed. This is all the more interesting since the orbital coefficients in the Br_2-EDT-TTF and I_2-EDT-TTF molecules (Fig. 8) exhibit sizeable coefficients on the halogen atoms. It is therefore expected that those Hal_{donor}···Hal_{donor} contacts might not only contribute to the structural stabilisation but also to the electronic delocalisation. In order to check this assumption, we performed the same β interaction energy calculations by substituting two hydrogen atoms for the halogen atoms of the donor molecules while keeping exactly the same relative orientations between a given donor molecule and its neighbours. The results are given in Table 2 and the variations in β values are systematically negative, demonstrating unambiguously the electronic contribution of the halogen atom to the overlap interactions. Furthermore, we note that the strongest variations (up to 33%) are observed in the I_2-EDT-TTF salt, highlighting the relative stronger contribution to the overlap of the iodine atoms in I_2-EDT-TTF when compared with the bromine ones in Br_2-EDT-TTF. Since the atomic coefficients on the Br and I atoms in the HOMOs are comparable (Fig. 8), this effect finds its origin in the more delocalised nature of the iodine electronic cloud. This halogen contribution is clearly identifiable in Fig. 4 where the band structure has been calculated (dashed lines) for an hypothetical salt where hydrogen atoms are substituted for the bromine atoms. Indeed, this substitution leads to a sizeable decrease of the dispersion.

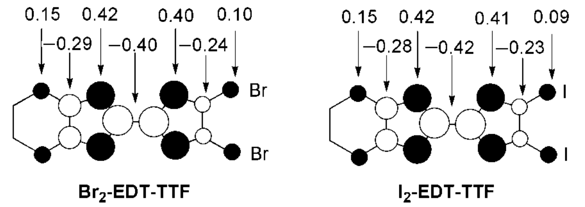


Fig. 8 Calculated (Extended Hückel) HOMO coefficients in Br_2-EDT-TFF and I_2-EDT-TTF.

Table 3 Crystallographic data

	Br_2/IBr_2	**Br_2/I_3**	**I_2/I_3**
Formula	$C_{16}H_8Br_6IS_{12}$	$C_{16}H_8Br_4I_3S_{12}$	$C_{16}H_8I_7S_{12}$
Formula mass	1191.30	1285.28	1473.24
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P1	P1	P1
a/Å	6.7026(13)	6.7691(15)	7.0316(14)
b/Å	7.4586(15)	7.4923(12)	7.6515(15)
c/Å	15.789(3)	16.087(2)	16.138(3)
α/degrees	95.60(3)	95.599(12)	95.20(3)
β/degrees	98.47(3)	99.806(14)	98.54(3)
γ/degrees	104.20(3)	103.027(13)	103.49(3)
V/Å^3	749.5(3)	775.4(2)	827.8(3)
Z	1	1	1
Temperature/K	293(2)	293(2)	293(2)
d_{calc}/g cm^{-3}	2.639	2.753	2.955
μ/mm^{-1}	9.914	8.997	7.330
Data collected	7378	2951	8088
Ind. data	2718	2836	2975
R_{int}	0.0319	0.014	0.0721
$R(F)$	0.025	0.0501	0.0529
$wR(F^2)$	0.0528	0.1968	0.1207

The semi-conducting character of the salts together with the remarkably high room-temperature conductivity and a magnetic susceptibility value (at rt) of about 5.2×10^{-4} cm^3 mol^{-1}, which is in between the value for a localised spin system in an insulating state and that for a metallic system, demonstrates that we are in the presence of a magnetic semi-conductor in the Mott insulator regime.[22] Coming back to the three salts, we also observe in Table 2 a continuous decrease of all β values when going from Br_2/IBr_2 to Br_2/I_3 and finally I_2/I_3. The larger size of the halogen atoms, on the anion (I_3^-) or on the donor molecule (I_2-EDT-TTF), reflected by the unit cell increase (Table 3), pushes the molecules away from each other and increases the intermolecular S···S distances which control the essential part of the overlap interactions. These structural modifications are however not isotropic. In a localized description, there is one $S=\frac{1}{2}$ magnetic moment on each diad, interacting with each other through interactions II–IV. If we consider the evolution of the β_{II}–β_{IV} values within the series, the ratio $\beta_{IV}:\beta_{III}$ gives a clear indication of the anisotropy of the interaction network experienced by a given carrier localised on the inversion-centred diads (through β_I). We observe that this ratio amounts to 2 in Br_2/IBr_2, 2.25 in Br_2/I_3 and up to 3 in I_2/I_3. However, this change is almost exclusively due to the decrease of interaction III along the series, interaction IV remaining almost constant. This point is particularly important since the interaction III running along a is in fact controlled by the Hal···Hal interaction between donor molecules identified above. By increasing the size of the halogen atom, we specifically decrease this β_{III} interaction and consequently, the wrapping of the hypothetical Fermi surface also when going from Br_2/IBr_2 to I_2/I_3 as shown in Fig. 5. Despite this decrease, the interactions in the three salts are stronger than in the well known β′-(BEDT-TTF)$_2$ICl$_2$.[23] It is then understandable that, even if they are semiconductors, they are much better conductors than β′-(BEDT-TTF)$_2$ICl$_2$ itself (0.01 S cm^{-1}).[24] (see ref. 23 for the β values in this salt).

Furthermore, taking into account the dimeric nature of the unit bearing the localised electron, the strength of the interactions along the $(a+b)$ and a-directions are quite comparable and definitively larger as well as more similar than those along the corresponding directions in β′-(BEDT-TTF)$_2$ICl$_2$.

From the evolutions observed within theses series, we observed that the smallest halogen atoms, both on the donor molecules and the anion, afforded the strongest set on intermolecular interactions. Accordingly, the analogous salt of the chlorine-substituted Cl$_2$-EDT-TTF with for example the much smaller ICl$_2^-$ anion, if isostructural with the salts described here, would be highly interesting and routes are being developed for its preparation.

Experimental

4,5-Diodo-2-thioxo-1,3-dithiole (2) and 4-iodo-2-thioxo-1,3-dithiole (3)

To a solution of **1** (2 g, 14.9 mmol) in dry THF (30 mL) at −78 °C is added 2 eq. of LDA. After stirring for 3 h at −78 °C, the yellow suspension is treated with a solution of ICl (4.9 g, 30.2 mmol) in dry THF (20 mL). The suspension is left to warm to rt overnight and evaporated to dryness. The residue is extracted with CH$_2$Cl$_2$, washed with H$_2$O (200 mL), aq. NaHSO$_3$ (100 mL) and H$_2$O (200 mL) and dried over MgSO$_4$. Chromatography over SiO$_2$ (eluent CS$_2$) afforded **2** (2.1 g, 36.5%) followed by **3** (0.5 g, 13%). **2**: mp 170 °C (lit. 128 °C);[7c] ^{13}C NMR (CDCl$_3$/CS$_2$) δ 83.6 (C–I) 215.7 (C=S); SM (EI) *m*/*z* (I%) 386 (M$^+$, 96), 259 (50), 183 (9), 127 (32). Anal. Calcd for C$_3$I$_2$S$_3$ (found): C, 9.33 (10.07); I, 65.75 (64.97); S, 24.92 (24.97). **3**: mp 104 °C; ^{1}H NMR (CDCl$_3$) δ 7.26 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 70.2 (C–I), 134 (C–H), 215.3 (C=S); SM (EI) m/z (I%) 260 (M$^+$, 100), 184 (7), 133 (55); Anal. Calcd for C$_3$HIS$_3$ (Found): C,13?85 (14.52); H, 0.39 (0.35), I, 48.78 (48.05); S, 36.98 (35.11).

4,5-Diiodo-2-oxo-1,3-dithiole (4)

The trithiocarbonate **2** is dissolved in a mixture of chloroform (300 mL) and acetic acid (150 mL) and Hg(OAc)$_2$ (4.41 g, 13 mmol) is added. After stirring for 2 h, the suspension is filtered over Celite, the solution washed with H$_2$O (3 × 100 mL), dil. NaHCO$_3$ (3 × 100 mL) and H$_2$O and dried over MgSO$_4$. Chromatography over silica gel (eluent CS$_2$) afforded **4** (1.3 g, 68%). Mp 112–113 °C (lit. 97 °C).[7c] ^{13}C NMR (CDCl$_3$) δ 76.1 (C–I), 197.1 (C=O); MS (EI) *m*/*z* (I%) 370 (M$^+$, 79), 342 (45), 215 (84), 88 (100). Anal. Calcd for C$_3$I$_2$OS$_2$ (Found): C, 9.74 (10.24); O, 4.32 (4.58); S, 17.33 (16.20).

4-Iodo-2-oxo-1,3-dithiole (5)

Compound **1** (1.86 g, 5.8 mmol) is dissolved in a mixture of CHCl$_3$ (300 mL) and AcOH (150 mL) and Hg(OAc)$_2$ (4.4 g 13 mmol) is added. After stirring overnight, the suspension is filtered over Celite, the solution is washed with H$_2$O (3 × 100 mL), saturated NaHCO$_3$ (3 × 100 mL) and H$_2$O (3 × 100 mL) and finally dried over MgSO$_4$ and evaporated. Chromatography over SiO$_2$ (eluent CS$_2$) afforded **5** (1.4 g, 80.2%). Mp 110–111 °C. ^{1}H NMR (CDCl$_3$) δ 7.26; ^{13}C NMR (CDCl$_3$) δ 62.9 (C–I), 124 (C–H), 194.7 (C=O); MS (EI) *m*/*z* (I%) 244 (M$^+$, 85), 216 (54), 127 (27), 89 (100). Anal. Calcd for C$_3$HIOS$_2$ (Found): C, 14.76 (14.81); H, 0.41 (0.26); I, 51.99 (51.82); S, 26.28 (26.11).

4,5-Diiodo-4′,5′-(ethylenedithio)tetrathiafulvalene (I$_2$-EDT-TTF)

A solution of **4** (0.68 g, 1.83 mmol) and **6** (0.41 g, 1.83 mmol) in freshly distilled P(OMe)$_3$ (6.8 g, 30 eq.) is warmed to 60–80 °C for 4 h. After cooling, the precipitate obtained upon MeOH addition is washed with MeOH, and chromatographed over silica gel (eluent CS$_2$) affording I$_4$-TTF (40 mg, 6%, mp 186–187 °C (lit. 186 °C)[25]) followed by I$_2$-EDT-TTF (0.19 g, 20%) which is recrystallized from CHCl$_3$. Mp 190–191 °C (lit. 146–147 °C).[8a] (EI) *m*/*z* (I%) 546 (M$^+$, 74), 517 (63), 442 (14), 419 (13), 397 (26). Anal. Calcd for C$_8$H$_4$I$_2$S$_6$ (Found): C, 17.59 (17.61); H, 0.74 (0.54); I, 46.46 (45.27), S, 35.22 (33.38).

4-Iodo-4′,5′-(ethylenedithio)tetrathiafulvalene (I-EDT-TTF)

To a warm solution of **6** (552 mg, 2.46 mmol) in dry toluene (20 mL) is added a toluene solution (10 mL) of **5** (0.6 g, 2.46 mmol) and P(OMe)$_3$ (3.1 g, 25 mmol). After refluxing for 24 h, the solution is evaporated to dryness and extracted with CS$_2$. Chromatography on SiO$_2$ (eluent CS$_2$) to afford first (*Z,E*)I$_2$-TTF (100 mg, 12%) followed by I-EDT-TTF (160 mg, 28%). (*Z,E*)I$_2$-TTF: mp 186–187 (lit.[25] 186 °C). I-EDT-TTF: mp 140–141 °C (lit. 119–120 °C); MS (EI) *m*/*z* (I%) 419 (M$^+$, 75), 391 (92), 316 (35), 271 (54); Anal. Calcd for C$_8$H$_5$IS$_6$ (Found): C, 22.85 (23.18); H, 1.20 (1.18); I, 30.18 (30.24); S, 45.76 (45.47).

4,5-Dibromo-2-thioxo-1,3-dithiole (7)

To a solution of **1** (5 g, 37.2 mmol) in dry THF (60 mL) at −78 °C is added 2 eq. of LDA. After stirring for 3 h at −78 °C, the yellow suspension is treated with a solution of 1,2-dibromo-1,1,2,2-tetrachloroethane (25 g, 76.7 mmol) in dry THF (50 mL). The suspension is left to warm to rt overnight and evaporated to dryness. The residue is extracted with CH$_2$Cl$_2$, washed with H$_2$O (200 mL), dried over MgSO$_4$. Chromatography over SiO$_2$ (eluent CS$_2$) afforded **7** after recrystallization from AcOEt (5.65 g, 52%). Mp 91–92 °C. MS (EI) *m*/*z* (I%) 292 (M$^+$, 100), 248 (10), 216 (44), 137 (76); ^{13}C NMR (CDCl$_3$) δ 106.7 (C=C), 207.8 (C=S). Anal. Calcd for C$_3$Br$_2$S$_3$ (Found): C, 12.34 (13.31); Br 54.72 (52.69); S, 32.94 (31.95).

4,5-Dibromo-2-oxo-1,3-dithiole (8)

As described for the preparation of **4**, from **7** (1.5 g, 5.13 mmol), one gets **8** after SiO$_2$ chromatography (0.9 g, 65%). Mp 62–63 °C. MS (EI) *m*/*z* (I%) 276 (M$^+$, 64), 248 (71), 169 (100), 137 (20); ^{13}C NMR (CDCl$_3$) δ 100.6 (C=C), 188.8 (C=O). Anal. Calcd for C$_3$Br$_2$OS$_2$ (Found): C, 10.06 (13.79); Br 57.91 (56.91); S, 23.24 (23.63).

4,5-Dibromo-4′,5′-(ethylenedithio)tetrathiafulvalene (Br$_2$-EDT-TTF)

A solution of **8** (1.5 g, 5.43 mmol) and **6** (1.22 g, 5.43 mmol) in freshly distilled P(OMe)$_3$ (20 mL, 30 eq.) is warmed at 60–70 °C overnight. After cooling, the precipitate obtained upon MeOH addition is washed with MeOH, and chromatographed over silica gel (eluent CS$_2$) affording Br$_4$-TTF (0.45 g, 32% after sublimation) followed by Br$_2$-EDT-TTF (0.67 g, 27%) which is recrystallized from CHCl$_3$. Mp 170 °C (lit. 167–168 °C).[8a] Anal. Calcd for C$_8$H$_4$Br$_2$S$_6$ (Found): C, 17.59 (17.61); H, 0.74 (0.54); Br, 46.46 (45.27), S, 35.22 (33.38). Crystals of Br$_2$-EDT-TTF exhibit a unit cell identical to that reported.[8a]

Electrocrystallisation experiments

Two-compartment cells with platinum electrodes ($l = 2$ cm, Ø = 1 mm) were used. The donor molecule (10 mg) in 1,1,2-trichloroethane (12 mL) with (n-Bu$_4$N$^+$)(IBr$_2^-$) or (n-Bu$_4$N$^+$)(I$_3^-$) (100 mg) as electrolyte was electrocrystallized at constant current (0.3 μA) during 3 weeks. Crystals were collected on the anode and washed with 1,1,2-trichloroethane.

X-Ray data collection and structure determination

Table 3 summarises the crystallographic details of data collection and structure refinement. Structures were solved by direct methods using SHELXS-86 and refined by the full-matrix least-squares method on F^2, using SHELXL-93 (G. M. Sheldrick, University of Göttingen, 1993) with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model). CCDC 155958–155960. See http://www.rsc.org/suppdata/jm/b1/b100103p/ for crystallographic files in .cif format.

Band structure calculations

The tight-binding band structure calculations[26] were of the extended-Hückel type.[27] A modified Wollsberg–Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values.[28] Double-ζ orbitals for C, S, Br and I were used. The exponents and parameters for C, S and H are taken from previous work.[29] The values employed for Br and I are as follows: 3.36 (0.6310), 2.044 (0.5050) and -22.07 eV for Br 4s, 2.92 (0.5822), 1.624 (0.5472) and -13.10 eV for Br 4p, 3.341 (0.6568), 2.046 (0.4869) and -18.0 eV for I 5s, 2.92 (0.6140), 1.671 (0.5258) and -12.7 eV for I 5p.

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