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Article

Halogen Bonding Interactions in DDQ Charge Transfer Salts with Iodinated TTFs

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Abstract: Oxidation of 3,4-ethylenedithio-3'-iodo-tetrathiafulvalene (EDT-TTF-I) and 3,4-ethylenedithio-3',4'-diiodo-tetrathiafulvalene (EDT-TTF-I_2) with DDQ afforded two different salts formulated as (EDT-TTF-I)(DDQ) and (EDT-TTF-I_2)$_2$(DDQ)·(CH_3CN), both characterized with a full charge transfer to the DDQ acceptor moiety and by short and linear halogen bonding interactions between the iodine atom as halogen bond donor, and the carbonyl oxygen or the nitrile nitrogen atoms of reduced DDQ.

Keywords: charge-transfer salts; halogen bonding; tetrathiafulvalene; crystal structure; iodine; magnetism

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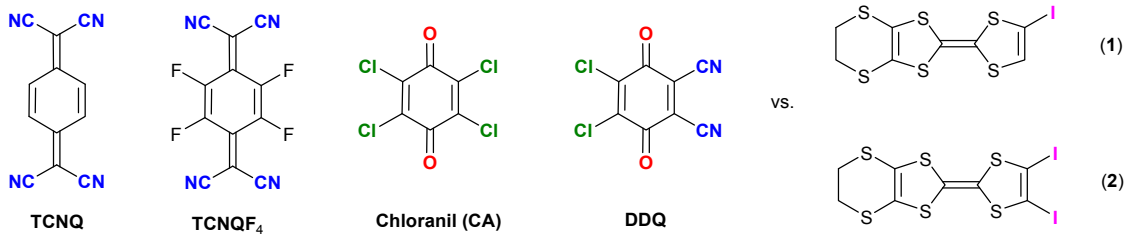
1. Introduction

In the search for novel molecular materials based on radical donor and acceptor molecules, many efforts have been devoted to the introduction of additional non-bonding interactions such as hydrogen bonding to orient and control the solid state association of radical molecules [1], in the hope to favor novel supramolecular arrangements. These efforts were mainly concentrated on cation radical salts of tetrathiafulvalene derivatives, obtained by electrocrystallization with various anions acting as hydrogen

bond or halogen bond acceptors. Charge–transfers salts such as the prototypical TTF-TCNQ or TTF-CA (CA: chloranil) are also amenable to such supramolecular strategies. Most examples rely on TTF derivatives functionalized with hydrogen bond donor groups (−CH_2OH, −CONHR), and chemically oxidized with TCNQ [2] or $TCNQF_4$ [3,4]. Halogen bonding interactions were also explored in charge-transfer salts, particularly by Iyoda [5] and Bryce [6], as in $(EDT\text{-}TTFCl_2)_2(TCNQF_4)$ [7]. Note that, due to their strong electronegativity, the functionalization of the TTF core with electron-withdrawing halogen atoms rises the oxidation potential of the TTF molecules, making often impossible their oxidation with TCNQ itself whose reduction potential amounts to 0.17 V (*vs*. SCE). Thus stronger oxidants such as the tetrafluoro TCNQ ($TCNQF_4$; E_{red} = 0.53 V *vs*. SCE) had to be considered [3,4,7]. In all these examples, the TCNQ derivatives act as halogen bond acceptors only through their nitrile functionality.

Scheme 1. Acceptor and donor molecules, for charge transfer salts as well as for halogen bonding interactions.



In this paper, we want to describe our recent results involving DDQ (2,3-dichloro-5,6-dicyanobenzoquinone, E_{red} = 0.53 V *vs*. SCE) as a powerful oxidant toward iodinated TTFs, toward the formation of novel charge-transfer salts with original halogen bonding patterns. Note that only one example of halogenated TTF with DDQ has been mentioned, but without crystal structure or composition [8]. Furthermore, DDQ is not only a strong oxidant comparable to $TCNQF_4$ but offers potentially three different halogen bonding acceptor sites, the carbonyl oxygen atoms, the nitrile nitrogen atoms and the chlorine atoms. We describe here the salts obtained upon oxidation of two iodinated TTF, namely 3,4-ethylenedithio-3'-iodo-tetrathiafulvalene (**1**) and 3,4-ethylenedithio-3',4'-diiodo-tetrathiafulvalene (**2**) with DDQ. As originally reported by Imakubo and Kato [9], these two donor molecules have been already engaged in a variety of cation radical salts upon electrocrystallization with anions acting as halogen bond acceptors such as halides [9,10], polyhalides [11], halometallates [12,13], cyanometallates [9,14,15] or thiocyanatometallates [16,17], but not in charge transfer salts, comparable to the reported example of $EDT\text{-}TTFCl_2$ with $TCNQF_4$ mentioned above [7].

2. Results and Discussion

Diffusion of a CH_3CN solution of DDQ on top of a CH_2Cl_2 solution of either **1** or **2** afforded after several days dark parallelepipedic crystals. X-ray crystal structure analyses give the formulations (**1**)DDQ and $(\mathbf{2})_2(DDQ)\cdot(CH_3CN)$ respectively, that is with 1:1 and 2:1 stoichiometry with **1** and **2** respectively. This different behavior might be related to the relative redox potential of **1** and **2**, when compared with the reduction potential of DDQ. Indeed, the first oxidation potential of the two donor

molecules amounts to 0.46 and 0.57 V *vs*. SCE (in CH_3CN with Bu_4NPF_6 0.1 M as electrolyte at 1 V s^{-1} scan rate) for **1** and **2** respectively, a difference which illustrates the electron withdrawing nature of the iodine atom on the TTF core. With the first reduction potential of DDQ found at 0.53 V in the same conditions, it clearly appears that DDQ is an oxidant strong enough to favour a full charge transfer with **1** while a contrasted situation can be anticipated with **2**. A similar borderline situation has been already reported when **1** and **2** are oxidized in the presence of $[Ni(mnt)_2]^{1-}$ [18], affording a fully oxidized $\mathbf{1}^{+\cdot}$ molecule in $[\mathbf{1}^{+\cdot}]_2[Ni(mnt)_2^{2-}]$, but a mixed valence salt with **2** in $[\mathbf{2}]_2^{+}[Ni(mnt)_2]^{1-}$.

2.1. Structural and Magnetic Properties of (1)(DDQ)

(**1**)(DDQ) crystallizes in the triclinic system, space group $P\bar{1}$ with both donor **1** and DDQ in general position in the unit cell (Figure 1). Intramolecular bond lengths within the TTF core in **1** and the DDQ molecule are highly sensitive to their oxidation state. As shown in Tables 1,2, by comparison with reference compounds, a full charge transfer between **1** and DDQ has occurred, leading unambiguously to a $(\mathbf{1}^{+\cdot})(DDQ^{-\cdot})$ formulation. In the solid state, the $\mathbf{1}^{+\cdot}$ cations are associated into face-to-face homo-dyads, which interact laterally along *a*-axis. A projection view of these dyads (Figure 2a) shows a typical bond-over-ring overlap, with a short plane-to-plane distance of 3.27 Å and a calculated $\beta_{HOMO-HOMO}$ interaction energy of 0.71 eV. On the other hand, the $DDQ^{-\cdot}$ radical anions are stacked to form alternated chains running along *a*-axis with two different overlap modes shown in Figure 2b,c. Plane-to-plane distances amount to 2.79 and 3.42 Å respectively, demonstrating the strong dimerization of the DDQ chains. It is further confirmed by the calculated $\beta_{LUMO-LUMO}$ interaction energies for the two overlap modes, which amount to 0.65 and 0.04 eV respectively. It should be stressed here that these strong overlap between respectively $\mathbf{1}^{+\cdot}$ and $DDQ^{-\cdot}$ species let us infer that the radical species are strongly associated into the bonding combination of respectively the TTF's HOMO and the DDQ LUMO. This is confirmed by the temperature dependence of the magnetic susceptibility of the salt, which exhibits an essentially diamagnetic behavior, with a Curie tail associated to 2.5% magnetic defaults.

Figure 1. Projection view (along *a*) of the unit cell of (**1**)(DDQ).

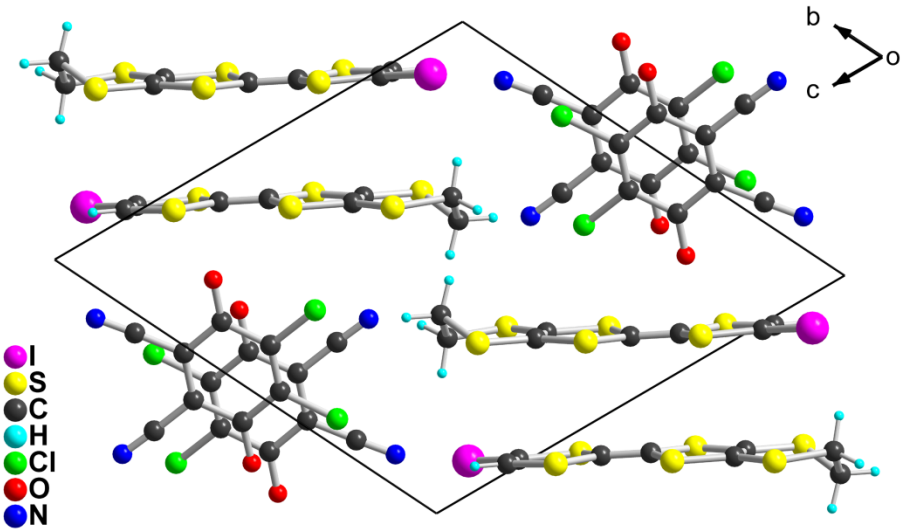


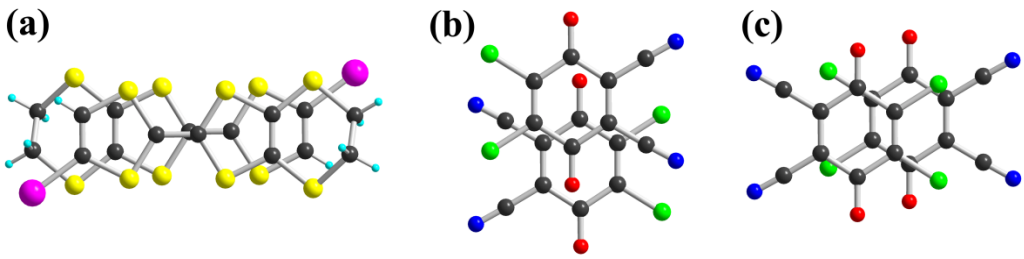
Table 1. Intramolecular bond lengths (in Å) in the TTF core of **1** (averaged values). The formal charge of each molecule is given as ρ, C_i and C_o are the inner and outer C atoms in the TTF core.

Compound		ρ	C_i=C_i	C_i–S	C_o–S	C_o–C_o	Ref
Neutral **1**	mol A	0	1.332 (13)	1.763 (18)	1.759 (19)	1.331 (14)	[18]
	mol B		1.323 (14)	1.760 (17)	1.747 (16)	1.331 (13)	
$(\mathbf{1})_2[Ag(CN)_2]$		+0.5	1.373	1.739	1.746	1.347	[9]
$(\mathbf{1})_2[Ni(mnt)_2]$		+1	1.382 (19)	1.723 (25)	1.731 (3)	1.348 (19)	[18]
(**1**)(DDQ)		1	1.390 (7)	1.721 (6)	1.736 (6)	1.350 (8)	this work

Table 2. Characteristic intramolecular bond lengths (in Å) in DDQ in various salts (averaged values). The formal charge and wave number of nitrile stretching absorption in IR spectra, for each molecule, are given as ρ and ν_{CN} respectively.

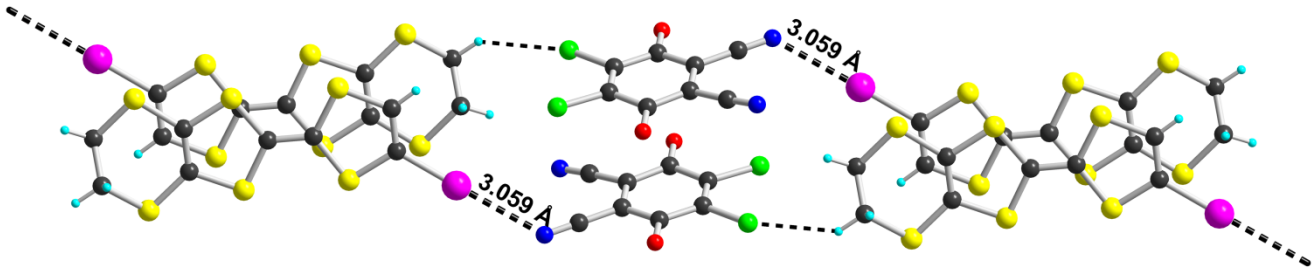
Compound	ρ	C=O	C_O–C_{Cl}	C_O–C_{CN}	C_{Cl}=C_{Cl}	C_{CN}=C_{CN}	ν_{CN} (cm^{-1})	Ref
DDQ	0	1.202	1.483	1.501	1.340	1.343	2234	[19]
(**1**)(DDQ)	–1	1.239 (5)	1.475 (7)	1.453 (8)	1.360 (6)	1.384 (6)	2202	–
$(\mathbf{2})_2$(DDQ)	–1	1.265 (10)	1.479 (15)	1.422 (17)	1.379 (12)	1.402 (12)	2212	–
(Et_4N)DDQ	–1	1.246	1.463	1.444	1.363	1.385	2217	[20]

Figure 2. Overlap interactions (**a**): within $(\mathbf{1}^{+\cdot})_2$ dyads, (**b**) and (**c**) within the chains of $(DDQ^{-\cdot})$ running along a.



As shown in Figure 3, halogen bonding interaction is observed between the iodine atom of **1** and the nitrogen atom of one cyano group of DDQ, together with a short C–H···Cl interaction. The I···N distance is much shorter than the sum of van der Waals radii (1.98 + 1.55 = 3.53 Å) or the contact distance predicted from anisotropic models [21] (r_{min}(I) + r_{max}(N) = 1.76 + 1.60 = 3.36 Å). The C–I···N angle of 175.6(2)° shows the strong halogen bond linearity but the I···N≡C angle at 131.6(4)° demonstrates that the interaction here is not optimal as the iodine atom does not point perfectly toward the nitrile lone pair. Much shorter and linear interactions were found for example in (**1**)$[Ag(CN)_2]$ with I···N distance at 2.88 Å and C–I···N and I···C≡N angles at 177° and 153° respectively [9].

Figure 3. Detail of the halogen bonding interactions in (**1**)(DDQ).



*2.2. Structural Properties of (**2**)$_2$(DDQ)·(CH$_3$CN)*

The mixed-valence salt with **2** is formulated as (**2**)$_2$(DDQ)·(CH$_3$CN). It crystallizes in the triclinic system, space group $P\bar{1}$ with two crystallographically independent TTF molecules **2**, one DDQ in general position and one acetonitrile solvent molecule. A projection of the unit cell along *a*-axis (Figure 4), shows that the donor molecules form layers, separated from each other by the acetonitrile and DDQ molecules. As shown in Table 2, the DDQ molecule appears as fully reduced radical anion form. Bond lengths within the TTF core (Table 3) in **2** are also comparable to those described in other mixed-valence (ρ = 0.5) salts of **2** [11−17]. Note that between the two crystallographically independent donor molecules **2**, the one bearing I3/I4 iodine atoms appears slightly more oxidized than molecule bearing I1/I2 iodine atoms. As shown in Figure 5, halogen bonding interactions develop at the interface between the mixed-valence slabs and the DDQ/CH$_3$CN layer. Both crystallographically independent molecules **2** show short contacts with DDQ^{-} anion. Very short and linear interactions are found with I(3) and I(4) atoms, with the carbonyl oxygen atoms, the nitrile nitrogen atoms of both the DDQ and the CH$_3$CN molecules. This donor molecule is also the one which appeared as the most oxidized one from comparison of intramolecular bond lengths (Table 4). Comparison of the two structures demonstrates that the reduced DDQ acts as a powerful halogen bond acceptor, involving the oxygen and nitrogen atoms. Earlier theoretical calculations of the charge and spin density in DDQ^{-} have shown a negative charge on the N, O and Cl atoms in the order −0.24, −0.20 and −0.18 [22], demonstrating a halogen bonding preference for the most negatively charged atoms. This behavior is in accordance with recent *ab initio* calculations showing that the electrostatic interaction between the positive σ-hole [23] located on the halogen atom along the C−Hal bond and Lewis bases such as pyridine is indeed the main component of the halogen bonding interaction [24].

Figure 4. Projection view (along *a*-axis) of the unit cell of (**2**)$_2$(DDQ)·(CH$_3$CN).

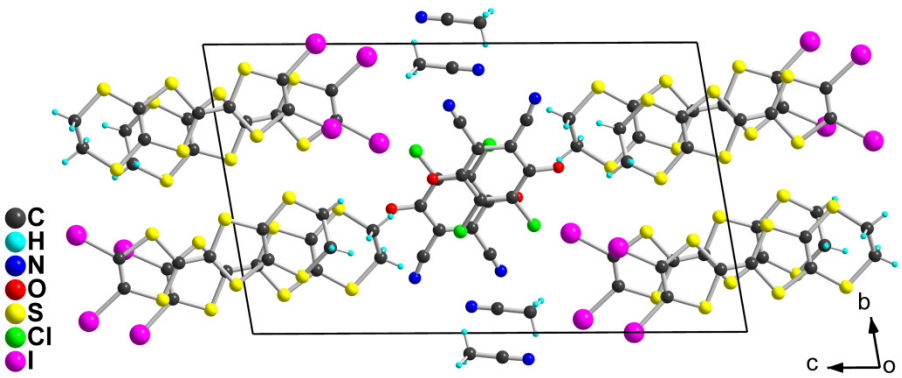


Table 3. Intramolecular bond lengths (in Å) in the TTF core of **2** (averaged values), depending on the actual charge (ρ). C_i and C_o are the inner and outer C atoms in the TTF core.

Compound		ρ	C_i=C_i	C_i–S	C_o–S	C_o–C_o	Ref
(**2**)$_2$(I_3)		+0.5	1.365 (29)	1.740 (20)	1.749 (20)	1.348 (16)	[11]
(**2**)$_2$(DDQ)	mol (I1,I2)	≈0.5	1.354 (9)	1.757 (8)	1.762 (8)	1.336 (9)	this work
	mol (I3,I4)	≈0.5	1.365 (9)	1.736 (8)	1.745 (8)	1.348 (9)	
(**2**)(I_3)		+1	1.40 (2)	1.718 (9)	–	–	[18]

Figure 5. Details of the halogen bonding interactions in (**2**)$_2$(DDQ)·(CH_3CN).

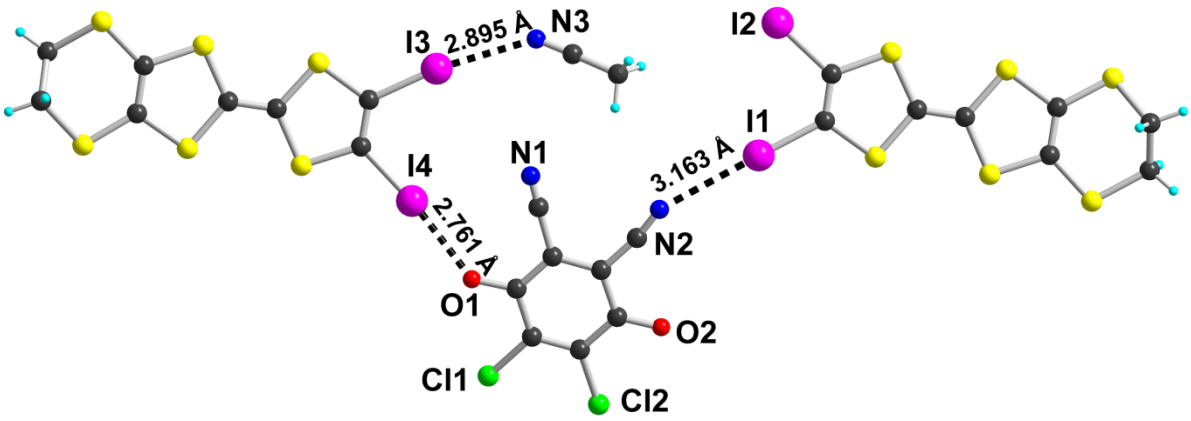


Table 4. Structural characteristics of the halogen bonding interactions in (**2**)$_2$(DDQ)·(CH_3CN). For atom numbering see Figure 5.

Interaction	∑vdw (Å)	D_{anis} (Å)	I···(O,N) (Å)	C–I···(O,N) (°)	I···(O,N)–C (°)
I1···N2	3.53	3.36	3.163 (12)	178.2 (3)	147.8 (9)
I3···N3	3.53	3.36	2.895 (12)	171.0 (3)	139.2 (9)
I4···O1	3.50	3.30	2.761 (8)	178.2 (2)	138.7 (5)

∑vdw: sum of the van der Waals radii; D_{anis}: contact distance in the anisotropic model [21].

The mixed valence character of (**2**)$_2$(DDQ)·(CH_3CN) might favor a good conductivity for this ¾-filled salt. A side view of the conducting slab with calculated $\beta_{HOMO-HOMO}$ interaction energies is shown in Figure 6 (left), together with the calculated band structure (Figure 6, right). Based on the stoichiometry, the three lower bands are filled while the upper one is empty, with an indirect band gap of 40 meV. Temperature dependence of the resistivity (Figure 7) shows indeed a semiconducting behavior with a room temperature conductivity, σ_{RT} = 0.043 S cm^{-1} and an activation energy of 1220 K.

Figure 6. Left: Side view of the slab of partially oxidized **2** molecules in $(\mathbf{2})_2$(DDQ)·(CH_3CN) together with calculated $\beta_{HOMO-HOMO}$ interaction energies, $\beta_{a1} = -0.4742$, $\beta_{a2} = 0.1325$, $\beta_{b1} = 0.0648$, $\beta_{b2} = 0.1341$, $\beta_{ab1} = -0.2596$, $\beta_{ab2} = -0.0482$, $\beta_{ab3} = 0.1286$, $\beta_{ab4} = 0.0797$ eV. Right: Calculated band structure; Γ = (0, 0), X = (a*/2, 0), Y = (0, b*/2), M = (a*/2, b*/2).

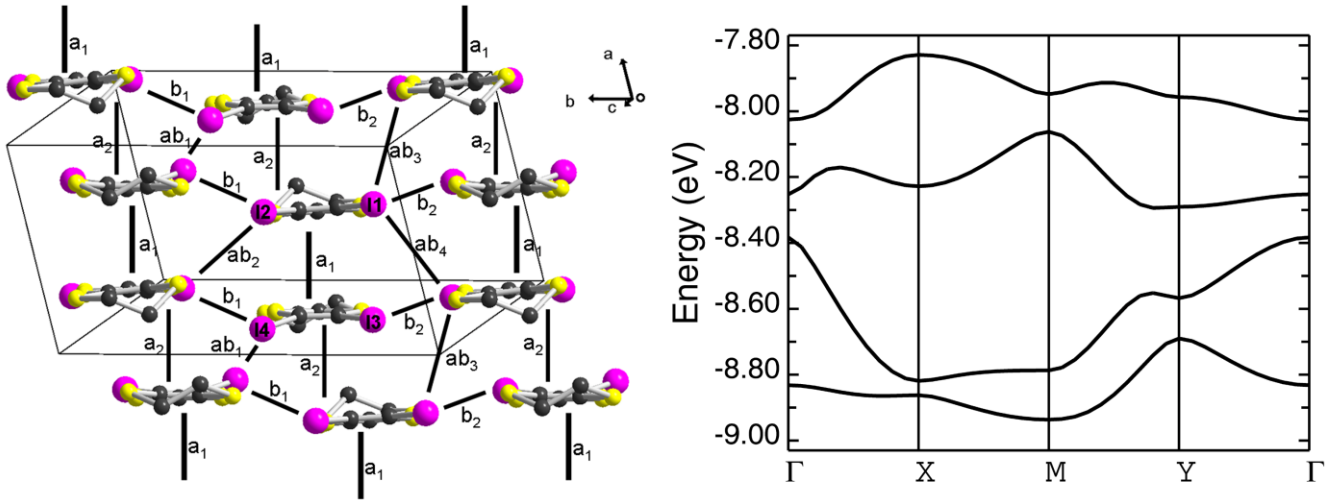
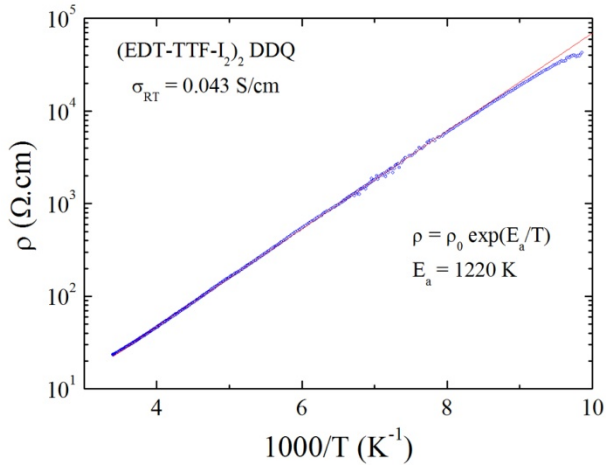


Figure 7. Temperature dependence of the resistivity of the mixed-valence salt $(\mathbf{2})_2$(DDQ)·(CH_3CN).



3. Experimental Section

3.1. Syntheses

The TTF derivatives **1** and **2** were prepared as previously described [11]. The charge-transfer salt with **1** was obtained by diffusion techniques in small glass tubes (Pasteur pipettes), with **1** (2.1 mg, 6.1×10^{-6} mol) dissolved in CH_2Cl_2 (2.5 mL) and layered with a solution of DDQ (3.3 mg, 14.5×10^{-6} mol) in CH_3CN (0.5 mL). Crystals were harvested after two weeks and washed with little CH_3CN. The charge-transfer salt with **2** was obtained by diffusion techniques in small glass tubes, with **2** (12.1 mg, 2.21×10^{-5} mol) dissolved in 1,1,2-trichloroethane (8 mL) and layered with a solution of DDQ (5.3 mg, 2.33×10^{-5} mol) in CH_3CN (2 mL). Crystals were harvested after two weeks and washed with little CH_3CN.

(**1**)(DDQ): IR (ATR) ν_{CN}: 2202 cm^{-1}. Elem. Anal. Calcd. for $C_{16}H_5Cl_2IN_2O_2S_6$: C, 29.68; H, 0.78; N, 4.33%. Found: C, 29.43; H, 1.06; N, 4.25.

(**2**)$_2$(DDQ)·(CH_3CN): IR (ATR) ν_{CN}: 2212 cm^{-1}. Only a few crystals of this phase were obtained, together with a 1:1 salt of poor crystallographic quality. Unit cell parameters of this 1:1 phase: a = 11.8443, b = 12.8752, c = 28.7860 Å, $\alpha = \beta = \gamma$ = 90.000, V = 4389.80(53) Å^3, system: orthorhombic, space group: Pnma. This mixing does not allow for elemental analysis of one single phase.

3.2. Crystallography

Single crystals were taken in a loop in oil and put directly under the N_2 stream at 150 K to avoid solvent losses. Data were collected on a Bruker SMART II diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS-97, SIR97) [25] and refined (SHELXL-97) by full-matrix least-squares methods [26], as implemented in the WinGX software package [27]. Absorption corrections were applied. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations, and not refined, with thermal parameters fixed as 1.2 times U_{eq} of the attached carbon atom. Further details of the crystal structures may be obtained from the Cambridge Crystallography Data Center, CCDC 871175 & 871176, free of charge, on application from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

(**1**)(DDQ): $C_{16}H_5Cl_2IN_2O_2S_6$, M = 647.38, triclinic, $P\bar{1}$, a = 7.0227(2), b = 12.6760(3), c = 13.1732(3) Å, α = 62.169(1), β = 76.282(1), γ = 78.615(1)°, V = 1002.31(4) Å^3, Z = 2, Dc = 2.145 g cm^{-3}, T = 150(2) K, 14723 reflections collected, 4566 unique (R_{int} = 0.0303) with among them 3871 with $I > 2\sigma(I)$, $R[I > 2\sigma(I)]$ = 0.0341, wR_2 (F^2, all data) = 0.0967, GoF = 1.083.

(**2**)$_2$(DDQ)·(CH_3CN): $C_{26}H_{11}Cl_2I_4N_3O_2S_{12}$, M = 1360.60, triclinic, $P\bar{1}$, a = 7.4173(9), b = 12.9354(15), c = 21.258(3) Å, σ = 79.600(4), β = 85.564(4), γ = 75.854(4)°, V = 1944.1(4) Å^3, Z = 2, Dc = 2.324 g cm^{-3}, T = 150(2) K, 23021 reflections collected, 8631 unique (R_{int} = 0.0373) with among them 6389 with $I > 2\sigma(I)$, $R[I > 2\sigma(I)]$ = 0.0426, wR_2 (F^2, all data) = 0.1444, GoF = 1.051.

3.3. Band Structure Calculations

The $\beta_{LUMO-LUMO}$ and $\beta_{HOMO-HOMO}$ interaction energies, the tight-binding band structure were calculated with the effective one-electron Hamiltonian of the extended Hückel method [28], as implemented in the Caesar 1.0 chain of programs [29]. The off-diagonal matrix elements of the Hamiltonian were calculated according to the modified Wolfsberg−Helmholz formula [30]. All valence electrons were explicitly taken into account in the calculations and the basis set consisted of double-ζ Slater-type orbitals for all atoms except H (ζ Slater-type orbital) using the Roothaan−Hartree−Fock wave functions of Clementi and Roetti [31].

4. Conclusions

We have reported here the structural and electronic properties of novel charge-transfer salts of halogenated TTF **1** or **2** with DDQ, an acceptor molecule which provides three different possible

halogen acceptor sites, the carbonyl oxygen atoms, the nitrile nitrogen atoms and the chlorine atoms. While a 1:1 salt with full charge transfer has been isolated with the most easily oxidized monoiodo TTF **1**, a mixed-valence, conducting salt is obtained with the diiodo derivative **2**, which combines short and directional halogen bonding contacts with both oxygen and nitrogen atoms of DDQ, and a semi conducting behavior attributable to an indirect band gap, as deduced from band structure calculations. It is hoped that other oxidants than DDQ, with a lower reduction potential, might also favor the formation of conducting mixed-valence salts or eventually neutral complexes with possible neutral-ionic transition. This work is in progress and will be reported in due course.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

References and Notes

1. Fourmigué, M.; Batail, P. Activation of Hydrogen- and Halogen-Bonding Interactions in Tetrathiafulvalene-Based Crystalline Molecular Conductors. *Chem. Rev.* **2004**, *104*, 5379–5418.
2. Dolbecq, A.; Fourmigué, M.; Batail, P.; Coulon, C. From Racemic Mixtures of Chiral π-Donor molecules to Mixed Stacks of H-Bonded Centrosymmetrical Dimers of Cation and Anion Radicals with Singlet-Triplet Excitations: The Example of $[(\pm)Me_3TTF\text{-}C^*HMe(OH)^{\cdot+}]_2[TCNQ^{\cdot-}]_2$. *Chem. Mater.* **1994**, *6*, 1413–1418.
3. Baudron, S.A.; Mézière, C.; Heuzé, K.; Fourmigué, M.; Batail, P.; Auban-Senzier, P. Interplay of charge transfer, dimensionality and amide hydrogen bond network adaptability in $TCNQF_4$ complexes of EDO-TTF-$CONH_2$ and EDT-TTF-$CONH_2$. *J. Solid State Chem.* **2002**, *168*, 668–674.
4. Ono, G.; Terao, H.; Higuchi, S.; Sugawara, T.; Izuoka, A.; Mochida, T. One-dimensional double chain composed of carbamoylmethylthio-substituted TTF-based donor in ion radical salt. *J. Mater. Chem.* **2000**, *10*, 2277–2282.
5. Iyoda, M.; Kuwatani, Y.; Ogura, E.; Hara, K.; Suzuki, H.; Takano, T.; Takeda, K.; Takano, J.-I.; Ugawa, K.; Yoshida, M.; *et al*. Synthesis, structure and conducting properties of halogenated ethylenedioxytetrathiafulvalenes. *Heterocycles* **2001**, *54*, 833–848.
6. Batsanov, A.S.; Bryce, M.R.; Chesney, A.; Howard, J.A.K.; John, D.E.; Moore, A.J.; Wood, C.L.; Gershtenman, H.; Becker, J.Y.; Khodorkovsky, V.Y.; *et al*. Synthesis and crystal engineering of new halogenated tetrathiafulvalene (TTF) derivatives and their charge transfer complexes and radical ion salts. *J. Mater. Chem.* **2001**, *11*, 2181–2191.
7. Iyoda, M.; Suzuki, H.; Sasaki, S.; Yoshino, H.; Kikuchi, K.; Saito, K.; Ikemoto, I.; Matsuyama, H.; Mori, T. Charge-transfer complex and radical cation salt of a new donor EDT-$TTFCl_2$ unique conductivities and crystal structures. *J. Mater. Chem.* **1996**, *6*, 501–503.

8. Iyoda, M.; Kuwatani, Y.; Hara, K.; Ogura, E.; Suzuki, H.; Ito, H.; Mori, T. Halogenated *Bis*(methylthio)tetrathiafulvalenes as a Unique Donor System. *Chem. Lett.* **1997**, *26*, 599–600.
9. Imakubo, T.; Sawa, H.; Kato, R. Novel radical cation salts of organic π-donors containing iodine atom(s): the first application of strong intermolecular-I···X^- (X = CN, halogen atom) interaction to molecular conductors. *Synth. Metals* **1995**, *73*, 117–122.
10. Imakubo, T.; Shirahata, T.; Hervé, K.; Ouahab, L. Supramolecular organic conductors based on diiodo-TTFs and spherical halide ion X^- (X = Cl, Br). *J. Mater. Chem.* **2006**, *16*, 162–173.
11. Domercq, B.; Devic, T.; Fourmigué, M.; Auban-Senzier, P.; Canadell, E. Hal···Hal interactions in a series of three isostructural salts of halogenated tetrathiafulvalenes. Contribution of the halogen atoms to the HOMO–HOMO overlap interactions. *J. Mater. Chem.* **2001**, *11*, 1570–1575.
12. Alberola, A.; Fourmigué, M.; Gómez-García, C.J.; Llusar, R.; Triguero, S. Halogen halogen interactions with the $[Mo_3S_7Cl_6]^{2-}$ cluster anion in the mixed valence salt $[EDT\text{-}TTFI_2]_4[Mo_3S_7Cl_6]\cdot CH_3CN$. *New J. Chem.* **2008**, *32*, 1103–1109.
13. Devic, T.; Evain, M.; Moëlo, Y.; Canadell, E.; Senzier, P.; Fourmigué, M.; Batail, P. Single Crystalline Commensurate Metallic Assemblages of π-Slabs and CdI_2-type Layers: Synthesis and Properties of β-$[EDT\text{-}TTF\text{-}I_2]_2[Pb_{5/6}$ square $_{1/6}I_2]_3$ and β-$[EDT\text{-}TTF\text{-}I_2]_2[Pb_{2/3+x}Ag_{1/3-2x}$ square $_xI_2]_3$, $X = 0.05$. *J. Am. Chem. Soc.* **2003**, *125*, 3295–3301.
14. Imakubo, T.; Sawa, H.; Kato, R. Crystal engineering in molecular conductors based on iodine-bonded π-donors. *Synth. Metals* **1997**, *86*, 1847–1848.
15. Ranganathan, A.; El-Ghayoury, A.; Mézière, C.; Harté, E.; Clérac, R.; Batail, P. Balancing framework densification with charged, halogen-bonded-π-conjugated linkages: $[PPh_4]_2\{[E\text{-}TTF\text{-}I_2][Re_6Se_8(CN)_6]\}$ *vs.* $[PPh_4]_2[EDT\text{-}TTF\text{–}I]_2\{[EDT\text{-}TTF\text{-}I][Re_6Se_8(CN)_6]\}$. *Chem. Commun.* **2006**, *21*, 2878–2880.
16. Hervé, K.; Cador, O.; Golhen, S.; Costuas, K.; Halet, J.-F.; Shirahata, T.; Muto, T.; Imakubo, T.; Miyazaki, A.; Ouahab, L. Substituted tetrathiafulvalene radical cation salts with $[M(isoq)_2(NCS)_4]^-$ anions where $M = Cr^{III}$, Ga^{III}: role of I···S and S···S contacts on structural and magnetic properties. *Chem. Mater.* **2006**, *18*, 790–797.
17. Fourmigué, M.; Auban-Senzier, P. Anionic layered networks reconstructed from $[Cd(SCN)_3]_\infty^-$ chains in pseudo one dimensional conducting salts of halogenated tetrathiafulvalenes. *Inorg. Chem.* **2008**, *47*, 9979–9986.
18. Devic, T.; Domercq, B.; Auban-Senzier, P.; Molinié, P.; Fourmigué, M. Cyano-Halogen Interactions in $[EDT\text{-}TTF\text{-}I]_2[Ni(mnt)_2]$ and $[EDT\text{-}TTF\text{-}I_2]_2[Ni(mnt)_2]$ and Geometrical Evolutions within Mixed-Valence or Fully Oxidized Dyads. *Eur. J. Inorg. Chem.* **2002**, *2002*, 2844–2849.
19. Zanotti, G.; Bardi, R.; Del Pra, A. Structure of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). *Acta Crystallogr.* **1980**, *B36*, 168–171.
20. Zanotti, G.; Del Pra, A.; Bozio, R. Structure of tetraethylammonium-2,3-dichloro-5,6-dicyano-*p*-benzoquinone. *Acta Crystallogr.* **1982**, *B38*, 1225–1229.
21. Nyburg, S.C.; Faerman, C.H. A Revision of van der Waals Atomic Radii for Molecular Crystals: N, O, F, S, Cl, Se, Br and I Bonded to Carbon. *Acta Cryst* **1985**, *B41*, 274–279.

22. Miller, J.S.; Krusic, P.J.; Dixon, D.A.; Reiff, W.M.; Zhang, J.H.; Anderson, E.C.; Epstein, A.J. Radical Ion Salts of 2,3-Dichloro-5,6-dicyanobenzoquinone and Metallocenes. A Reexamination of their Magnetic and Spectroscopic Properties. *J. Am. Chem. Soc.* **1986**, *108*, 4459–4466.
23. Politzer, P.; Murray, J.S.; Lane, P. σ-Hole bonding and hydrogen bonding: Competitive interactions. *Int. J. Quantum Chem.* **2007**, *107*, 3046–3052.
24. Tsuzuki, S.; Wakisaka, A.; Ono, T.; Sonoda, T. Magnitude and Origin of the Attraction and Directionality of the Halogen Bonds of the Complexes of C_6F_5X and C_6H_5X (X = I, Br, Cl and F) with Pyridine. *Chem. Eur. J.* **2012**, *18*, 951–960.
25. Altomare, A.; Burla, M.C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.G.G.; Polidori, G.; Spagna, R. *SIR*97: a new tool for crystal structure determination and refinement. *J. Appl. Cryst.* **1999**, *32*, 115–119.
26. Sheldrick, G.M. *SHELX97—Programs for Crystal Structure Analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany, 1998.
27. Farrugia, L.J. *WinGX* suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.* **1999**, *32*, 837–838.
28. Whangbo, M.-H.; Hoffmann, R. The band structure of the tetracyanoplatinate chain. *J. Am. Chem. Soc.* **1978**, *100*, 6093–6098.
29. Ren, J.; Liang, W.; Whangbo, M.-H. *Crystal and Electronic Structure Analysis Using CAESAR*; PrimeColor Software, Inc.: Cary, NC, USA, 1998.
30. Ammeter, J.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. Counterintuitive orbital mixing in semiempirical and *ab initio* molecular orbital calculations. *J. Am. Chem. Soc*. **1978**, *100*, 3686–3692.
31. Clementi, E.; Roetti, C. Roothaan-Hartree-Fock atomic wavefunctions: Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms, $Z \leq 54$. *At. Data Nucl. Data Tables* **1974**, *14*, 177–478.

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