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Organizing radical species in the solid state with halogen bonding

Marc Fourmigué and Julien Lieffrig

Abstract The electronic properties (conductivity, magnetism) of radical systems in the solid state essentially depends on (i) the extend of delocalization of the spin density in the molecule and (ii) the intermolecular interactions between radicals. Halogen bond has proven very efficient to engineer such magnetic or conducting structures and recent advances along these lines are reviewed here. Three situations are considered, (i) halogenated radical species acting as halogen bond donors, as found in iodotetrathiafulvalene-based chiral conductors or bilayer systems, and in spin crossover (SCO) complexes with halogenated ligands, (ii) radical species acting as halogen bond acceptors, such as neutral nitronyl species or anionic, mixed-valence dithiolene complexes, interacting with closed-shell halogen bond donors (iodoperfluoro alkanes and arenes, iodo- or bromo pyridinium cations) and finally (iii) charge transfer salts where both halogen bond donor and acceptor are radical species.

Keywords radical, halogen bond, magnetism, spin crossover, chirality, organic conductors, charge transfer, nitronyl, tetrathiafulvalene, dithiolene

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1 Introduction

Radical species are particularly investigated in the solid state for their magnetic (and eventually conductive) properties, which intimately depend on the interaction pathways that establish between them [1,2]. In that respect, intermolecular interactions are expected to play two strikingly different roles. They can introduce some control elements on the solid state organization of the radical species, and accordingly contribute to the specific magnetic and/or conductive properties of the material induced by its crystal structure. However, this structural role can be further complemented by an added functionality, i.e. the introduction of a new electronic interaction path for radical interactions or delocalization (electronic control) *through* the non-bonding interaction, provided some spin density or orbital overlap takes place. Such effects have been reported for hydrogen bonding interactions [3–5] and the question arises if they could be also investigated with halogen bonding interactions, as they have proven to be very good and predictable crystal engineering tools [6,7]. The halogen bond "structural" approach to control the solid state associations of radical species has been investigated in the last twenty years and several reviews are available until 2008 which describes the use of halogen bonding in molecular conductors [8], in conducting or magnetic systems [9,10]. In this chapter, we want to complement these reviews by more recent results on this topic, but with a special highlight on those situations where radical interactions or delocalization (electronic control) through the halogen bond were investigated and eventually identified. This contribution will be organized into three main sections, the first one dedicated to radical molecules or complexes acting as halogen bond donors, the second one describing radical molecules or complexes acting as halogen bond acceptors, and finally a third section reporting on charge transfer salts where both halogen bond donor and acceptor are also radical species, a rare situation which provides an opportunity to indeed evaluate the electronic interactions between radical species. Note that in the following, intermolecular distances will be compared with the sum of van der Waals radii, as defined by Bondi [11], with H: 1.20; N: 1.55; O: 1.52; F: 1.47; S: 1.80; Cl: 1.75; Br: 1.85 and I: 1.98 Å.

2 Radicals as Halogen Bond Donors

In order to act as halogen bond donors, molecules need to be not only in their radical form but also need to bear halogen atoms as substituents. Furthermore, as for any halogen bond interactions (see other chapters in this book), the strongest effects are anticipated with the most polarizable bromine and iodine atoms. Such molecules are actually extremely rare among neutral radicals, either C-centered or N–O centered ones. In the latter, halogen bonding interactions within halogenated neutral nitroxides have been indeed identified [9], the main information being that the oxygen atom in N–O• based radical species is able to act as an efficient halogen bond acceptor. Such situation will be detailed in Section 3.1.

Also, many neutral organic radicals are based on heavily chlorinated aryl derivatives (Fig. 1) such as the perchlorophenalenyl or the polychlorotriphenyl radicals [12,13]. When described, the X-ray crystal structures of such compounds show inevitably intermolecular Cl•••Cl contacts, without identifying particularly short ones. In perchlorophenalenyl for example, the steric interactions between the Cl atoms in *peri* position in the molecules leads to a strong distortion from planarity which induces a ruffled molecular structure [13]. As a consequence, the shortest intermolecular Cl•••Cl distances within the stacks amount to 3.78 Å, above the sum of van der Waals radii (3.50 Å). The bromo or iodo analogs of such complexes were not described, probably for stability reasons.

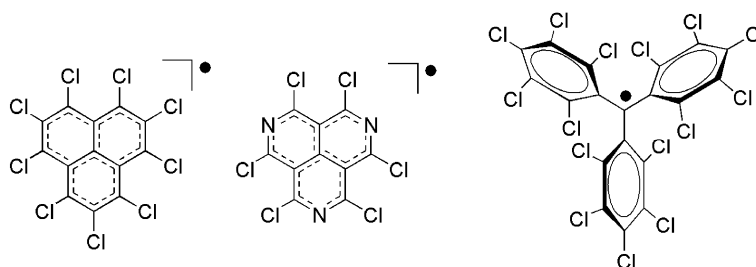


Fig. 1 Examples of heavily chlorinated carbon-based radicals. The crystal structure of the triazahexachlorophenalenyl is not known.

In that respect, the brominated trioxyltriangulene (Fig. 2a) described below in Section 2.1 is an exception which deserves special mention. Besides, the other efficient source of stable radical species acting as halogen bond donors remains the cation radical of iodinated tetrathiafulvalene derivatives (Fig. 2b). It has been shown indeed that these radical species are not only stable, but able to act as efficient halogen bond donors, thanks to the iodine activation by the cationic state of the TTF core. In the last years, the halogen bonding interaction with iodinated TTFs has been purposely used to favor very specific solid state structures, such as chiral, non-centrosymmetric or hexagonal organizations, as detailed in Section 2.2. A third possibility is associated with cationic and paramagnetic coordination

complexes, with halogenated organic ligands (Fig. 2c). The solid state organization of such complexes was shown to be controlled to some extent by the halogen bonding interactions, an important issue for the engineering of magnetic properties, particularly when associated with spin crossover (SCO) systems.

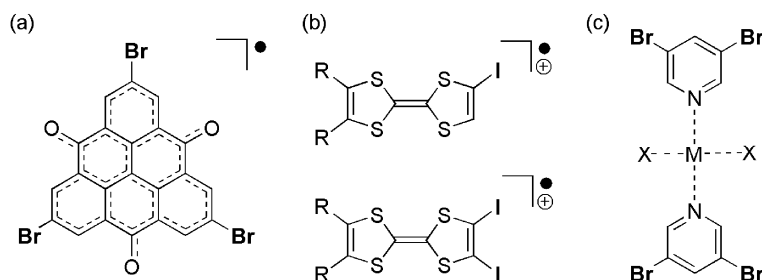


Fig. 2 Structures of radical, halogen bond donors described in Section 2.

2.1 Halogenated Trioxxytriangulene Radical

Following earlier work on the 6-oxophenalenoxyl neutral radical for its use as cathode-active materials for battery applications [14], Morita et al. recently introduced the trioxxytriangulene motif (noted TOT in the following), characterized by a SOMO and two degenerate LUMOs, which arise from the topological symmetry of the π -system [15]. Among these series, the tribromo derivative, noted Br₃TOT, forms a one-dimensional columnar structure stabilized by strong π - π stacking. The outside of these columns is covered by bromine and hydrogen atoms susceptible to act as halogen (respect. hydrogen) bond donors, and bromine atoms. The molecule is located on a mirror plane incorporating one bromine, Br(1) and one oxygen O(2) atoms, while Br(2) and O(1) are in general position. As shown in Fig. 3, Br(2) atoms from two coplanar molecules are halogen bonded to the oxygen O(2) atom located on a mirror plane, while the other bromine atom is essentially non-bonded. The Br(2)···O(2) distance is not very short, that is 95% the sum of van der Waals radii. The other oxygen atom O(1) is engaged in a cyclic R₂²(10) hydrogen bonded motif with a C-H group. Magnetic properties of this compound were not described, but their comparison with the known tris(*tert*-butyl) analog would be particularly interesting to investigate the role of the intermolecular interactions taking place between the columns. Another attractive perspective would be the preparation of the triodo analog.

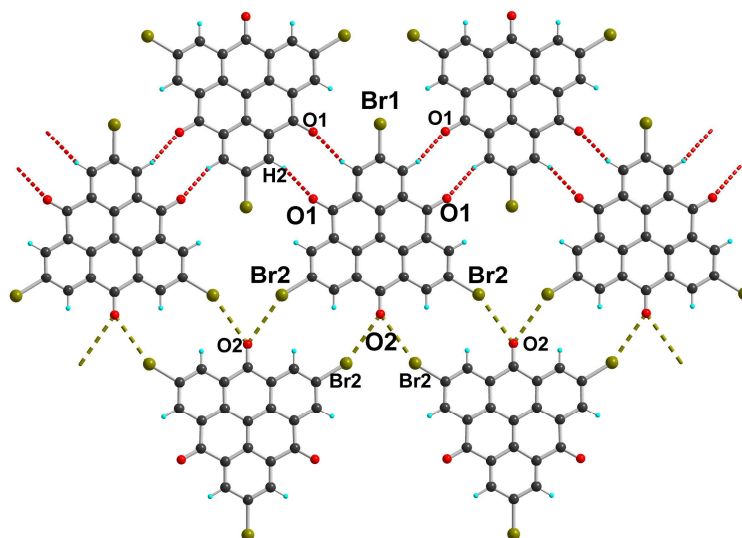


Fig. 3 Projection view of the crystal structure of Br₃TOT, perpendicular to the molecular plane, showing the C–Br(2)···O(2) halogen bond [Br(2)···O(2): 3.21 Å; C–Br(2)···O(2): 156.4°; Br(2)···O(2)=C: 144.6°] and C–H(2)···O(1) [H(2)···O(1): 2.44 Å; C–H(2)···O(1): 150.7°; H(2)···O(1)=C: 153.4°] hydrogen bonds

2.2 TTF Radical Cations Salts: Toward Chiral Conductors

Halogen-bonded TTF salts were first described by Kato in 1998 [16], from the electrocrystallization of EDT-TTF-I in the presence of counter ions acting as halogen bond acceptors, as detailed in Fig. 4. This topic has been reviewed in 2004 [8], and more recent results can be found in more general reviews [9,10]. Many different anions were used as halogen bond acceptors, from the simple halides [16,17] and polyhalides (I₃[−], IBr₂[−], ...) [18], polyhalometallates, polycyanometallates, polythiocyanatometallates [19] to cluster anions such as [Re₆Se₆(CN)₆]^{4−} [20,21] or [Mo₃S₇Cl₆]^{2−} [22] or polymeric anionic networks such as [PbI₃]_∞[−] [23], the layered [Pb_{5/6}□_{1/6}I₂][−] system with a PbI₂ structure [24] or complex cadmium thiocyanate lacunar networks such as [Cd₃(NCS)₈]^{2−} and [Cd₅(SCN)₁₄]^{4−} [25].

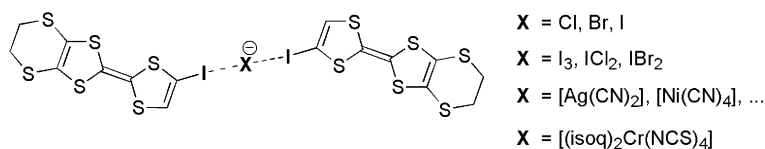


Fig. 4 Examples of halogen bonded TTF salts.

In essentially all cases, the halogen bonding interactions were shown to co-exist with the stacking of partially oxidized TTF derivatives, affording highly conducting salts. It was also demonstrated that the halogen atoms (Br, I) directly linked to the TTF core as in EDT-TTFI or EDT-TTFI₂ also contribute to the band dispersion as the HOMO of such TTFs exhibits non-zero coefficients on the halogen atoms. Note also that in most cases, the counter ion acting as Lewis base is centrosymmetric, affording halogen bonded systems with high symmetry. An illustrative counter example is obtained with the tetrahedral ClO₄[−] anion, as detailed below in section 2.2.1.

More recently, the XB interaction has been also used to tentatively favor the formation of *chiral conductors*. Indeed, as described by Rikken *et al.* [26], such conductors are expected to exhibit a weak magneto-chiral effect on the conductivity, which can be tentatively described as an added contribution to the magnetoresistance of a compound, only present in chiral compounds. This effect, first observed in chiral nanotubes [27] or in Bismuth twisted wires [28], has been a strong incentive in the domain of molecular conductors where the large chiral pool of organic molecules should allow for an easy functionalization with chiral substituents, either of the TTF core itself [29,30], or within chiral counter ions [31]. This ambitious objective was recently reached by Avarvari *et al.* [32], in a cation radical salt of a chiral BEDT-TTF derivative. In order to further enhance the structuring effect of a localized chiral center on the whole crystalline structures, intermolecular interactions such as hydrogen bonding [30] or halogen bonding can be also considered, as detailed below in sections 2.2.2 and 2.2.3.

2.2.1 IodoTTFs with Non-Centrosymmetric ClO₄[−] Anion

Both EDT-TTFI₂ [33] and tTTF-I [34] were reported to form halogen bonded salts with the ClO₄[−] anion (Fig. 5). In the 1:1 (EDT-TTFI₂)(ClO₄) salt, the EDT-TTFI₂^{•+} radical cations are associated two-by-two into face-to-face dyads allowing for a strong σ overlap of the frontier orbitals [1].

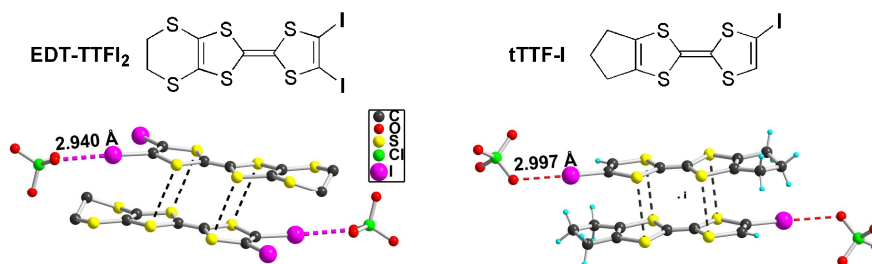


Fig. 5 Detail of the 1:1 ClO₄[−] salts with EDT-TTFI₂ (left) and tTTF-I (right) showing the I...O halogen bonds and the face-to-face interaction between radical species

The shortest I...O halogen bond is found at 84 % the sum of van des Waals radii. A similar 1:1 salt was also reported with tTTF-I, formulated as (tTTF-I)(ClO₄), with one I...O distance at 2.997 Å, i.e. 86% the sum of van des Waals radii.

A particularly interesting 2:1 salt was also isolated with tTTF-I, formulated as (tTTF-I)₂ClO₄, where two oxygen atoms of the ClO₄⁻ anion are engaged in I...O interactions, each of them however with a crystallographically independent tTTF-I molecule (Fig. 6) [34]. This asymmetry induced by the differential halogen bonding interaction is transferred to the whole salt, as each crystallographically independent molecule segregates into two crystallographically independent slabs. Band structure calculations for each of them gives a different Fermi level for an hypothetical common +0.5 charge for both tTTF-I molecules. Since there is only one Fermi level associated with the chemical potential of the salt, a charge transfer has necessarily to occur between both stacks, implying a deviation from a common +0.5 charge for each donor molecule.

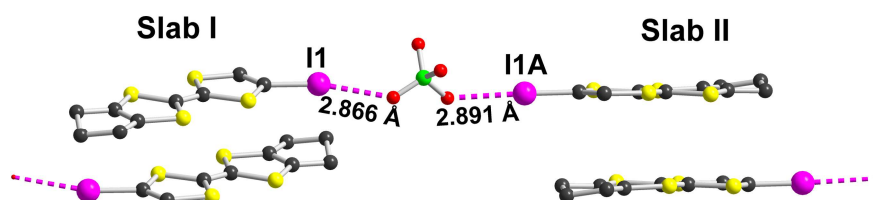


Fig. 6 Detail of the two crystallographically independent conducting slabs in (tTTF-I)₂ClO₄

2.2.2 IodoTTFs with Halogen Bonding to Chiral Anions

The electrocrystallization of iodoTTF derivatives such as EDT-TTF-I in the presence of chiral counter ions appears as a powerful way to introduce chiral center into halogen-bonded organic conductors, provided one has at hand chiral anionic species able to act as XB acceptors. We have shown that sulfonate anions are indeed efficient XB acceptors and various EDT-TTFI₂ salts were reported with 1,5-naphtalene-bis(sulfonate), 2,6-naphtalene-bis(sulfonate) or 2,6-anthracene-bis(sulfonate) [33]. Camphorsulfonate is a chiral anion, available both as enantiopure compound and racemic mixture. The electro-crystallization of EDT-TTFI₂ in the presence of the D-isomer afforded indeed a 2:1 salt with metallic conductivity and two-dimensional Fermi surface [35]. Interestingly, the two crystallographically independent EDT-TTFI₂ molecules exhibit a different XB pattern. Molecule A is halogen bonded both to the sulfonate and carbonyl moieties of D-camphorsulfonate anions while molecule B is only interacting with the oxygen atom of a water molecule (see Fig. 7 for structural XB characteristics). This diffe-

rentiation is associated to a departure from the averaged +0.5 charge on the two EDT-TTfI₂ molecules. Indeed, based on the comparison of intramolecular bond lengths, the compound is tentatively formulated as [A^{+0.75}B^{+0.25}][D-camphorsulfonate], i.e. with the most oxidized molecule A involved in the strongest intermolecular halogen-bond interactions, an observation to be correlated to the electrostatic contribution to halogen bond.

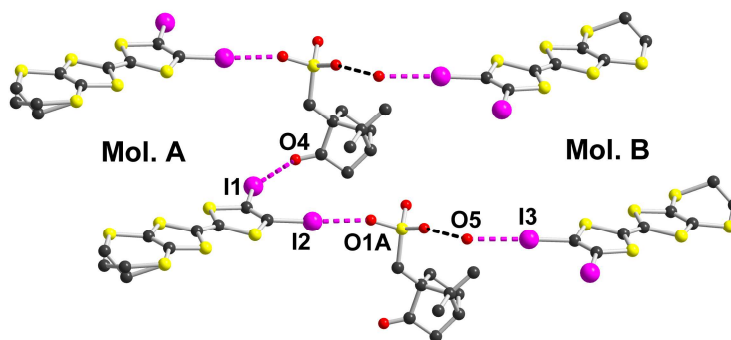


Fig. 7 Detail of the asymmetric unit in (EDT-TTfI₂)₂(D-camphorsulfonate). Halogen bonds with red dotted lines: I(1)···O(4) 3.02 Å, I(2)···O(1A) 2.68 Å, I(3)···O(5) 2.84 Å. Hydrogen bond between water molecule and sulfonate moiety as black dotted line.

It should be stressed also that the racemic salt obtained with DL-camphorsulfonate is not isostructural with its enantiopure counterpart [33]. Albeit a mixed-valence 2:1 salt was also obtained, it crystallizes with solvent inclusion, giving rise to a one-dimensional electronic structure and semi-conducting character. Halogen bonding interactions with the EDT-TTfI₂^{+0.5} molecule is still present with the shortest O···I distances above 2.81 Å, which is 80% the sum of van der Waals radii.

2.2.3 Chiral iodoTTF salts

Another approach to chiral conductors exhibiting halogen bonding in the solid state relies on the preparation of halogenated *and* chiral tetrathiafulvalene derivatives. Only one example has been reported to date, where the ethylene group of EDT-TTfI₂ is replaced by a 1,3-dimethyl-1,3-propylene substituent in Me₂PDT-TTfI₂ [36]. Its electrocrystallization with halide anions afforded a 2:1 mixed valence salt, whose conductivity is limited by the steric constraints imposed by the bulky dimethylpropylene moiety.

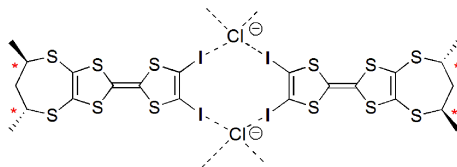


Fig. 8 The chiral Me₂PDT-TTFI₂ and the structural motif observed in its chloride salt.

To conclude this section on chiral conductors, it appears that the introduction of low symmetry counter ions systematically favor the presence of multiple crystallographically independent molecules, with then the possibility of different degrees of charge transfer, and competition with charge localization [37].

2.3 Paramagnetic Metal Complexes with Halogenated Ligands

2.3.1. Halopyridine complexes of metal halides

The ability of halometallates [38–40] (as well as cyano [41,42] and thiocyanato [19] analogs) to act as halogen bond acceptors has been extensively explored [43], particularly by Brammer *et al.*, and several series of salts with halo-pyridinium cations as halogen bond donors were reported.

Besides, neutral halopyridines (Fig. 9) were also used with a twin role, as they act as Lewis bases for metal coordination through the nitrogen atom and, simultaneously as halogen bond donor [44]. It is found for example in *trans*-[MCl₂(4-X'-py)₂] (M = Pd, Pt; X' = Cl, Br) and *trans*-[PdI₂(4-I-py)₂]. While no specific magnetic interactions can be expected from these low spin d⁸ complexes, other examples were reported incorporating $S = \frac{1}{2}$ ions, in d⁷ Co²⁺ or d⁹ Cu²⁺ species.

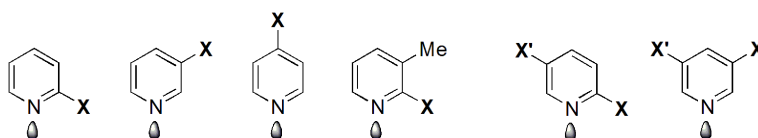


Fig. 9 Mono- and dihalopyridines used in the coordination of metal halides (X, X' = Cl, Br, I)

Several CuX₂ complexes with halogenated pyridine ligands were reported, as in *trans*-[CuCl₂(3-Cl-py)₂] [45], or [CuX₂(2-Br-py)₂] and -[CuX₂(3-Br-py)₂] [46]. The data indicates that the halogen bond interaction taking place between the coordinated chloro or bromo pyridine are much weaker than those observed in the cationic bromo or chloropyridinium salts, a clear indication of electrostatic activation in the salts. Furthermore, the bromine-halide distances are almost equal to the

sum of their van der Waals radii (r_{vdW}) in the *meta*-substituted $[\text{CuX}_2(3\text{-Br-py})_2]$ but less than the sum of the r_{vdW} by ≈ 0.24 Å in the *ortho*-substituted analog $[\text{CuX}_2(2\text{-Br-py})_2]$ (Fig. 10). Magnetic data for $[\text{CuBr}_2(2\text{-Br-py})_2]$ show an absence of any interactions, with a perfect Curie-type behavior [46].

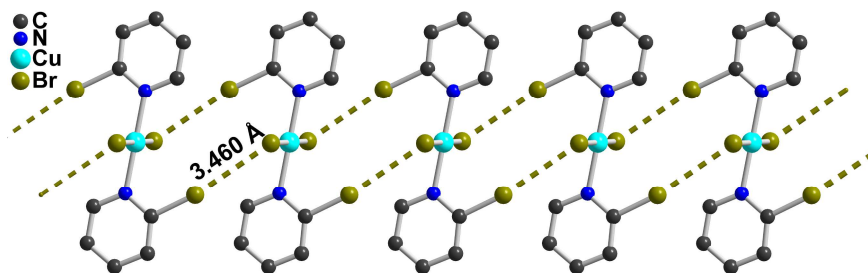


Fig. 10 View of the halogen bonded chains in $[\text{CuBr}_2(2\text{-Br-py})_2]$. The $\text{Br}\cdots\text{Br}$ distance, 3.46 Å, is to be compared with the sum of van der Waals radii, namely 3.70 Å.

On the other hand, the analogous 2,5-dibromopyridine derivatives, formulated as $[\text{CuCl}_2(2,5\text{-Br}_2\text{-py})_2]$ and $[\text{CuBr}_2(2,5\text{-Br}_2\text{-py})_2]$, are not isostructural and exhibit antiferro- or ferromagnetic interactions respectively [46,47]. The antiferromagnetic interactions in the copper chloride salt have been attributed, in spite of a relative long $\text{Cl}\cdots\text{Cl}$ distance (4.16 Å) to this two-halide exchange pathway, in accordance with a non-negligible spin density on the chloride ions (0.109). The copper bromide salt, $[\text{CuCl}_2(2,5\text{-Br}_2\text{-py})_2]$, adopts a structure comparable with that of $[\text{CuBr}_2(2\text{-Br-py})_2]$ (Fig. 10). Since the bromide are too far apart from each other, the proposed rationale for the observed ferromagnetic interaction is based on the orthogonal interaction between the very small spin density on the organic bromine (0.005), located along the C–Br bond, and the spin density of the bromide along the Cu–Br bond. Similar ferromagnetic interactions mediated by the halogen bonds were already reported in similar copper chloride and bromide with 2-chloro-3-methylpyridine and 2-bromo-3-methylpyridine [48].

The structures of *trans*- $[\text{CoCl}_2(3,5\text{-X}_2\text{py})_2]$, X = Cl, Br, are characterized (Fig. 11) by short XB interactions which develop in the *ab* plane, giving rise to original tetrameric motifs [49]. Magnetic interactions between cobalt ions are characteristic of linear cobalt chloride chain compounds, albeit the XB interactions limit here the magnetic interactions between the chains.

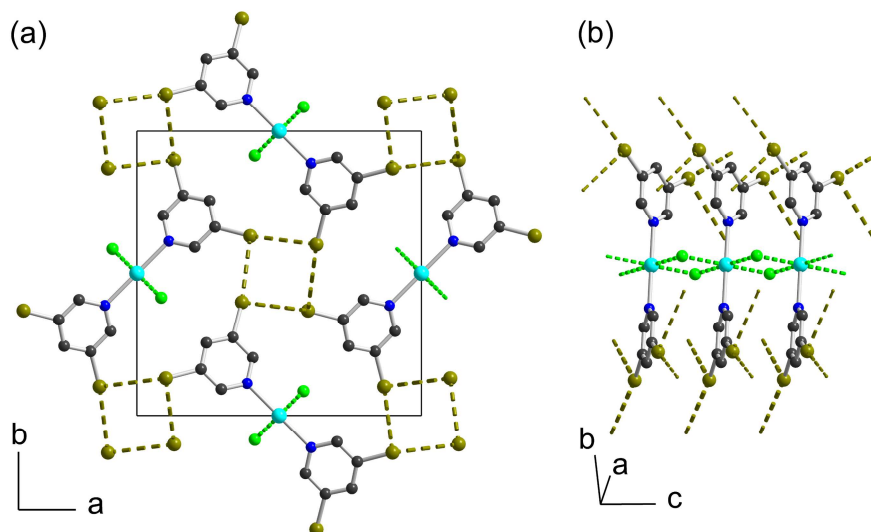


Fig. 11 Views of $\text{trans-[CoCl}_2(3,5\text{-Br}_2\text{py})_2]$ with, (a) projection along the c axis showing the tetrameric halogen bonded motif and, (b) the CoCl_2 chain running along c .

In conclusion of this section, it appears that spin density on the halogen atoms of coordinated halogenated pyridines is extremely weak and that, as a consequence, magnetic interactions through the halogen bond cannot be expected to play an important role.

2.3.2. Spin Crossover cooperativity and halogen bonding

As illustrated above, the XB interactions introduce structural constraints which can play an important role in the solid state organization of magnetic systems. This can be particularly important in spin crossover systems (SCO) where the high spin/low spin (HS/LS) *conversion* can be turned into an abrupt structural *transition* in the presence of *cooperative* intermolecular interactions [50]. Only a few examples of complexes showing the involvement of halogen bonding in SCO have been described to date and involve either Fe^{II} or Fe^{III} complexes (Fig. 12).

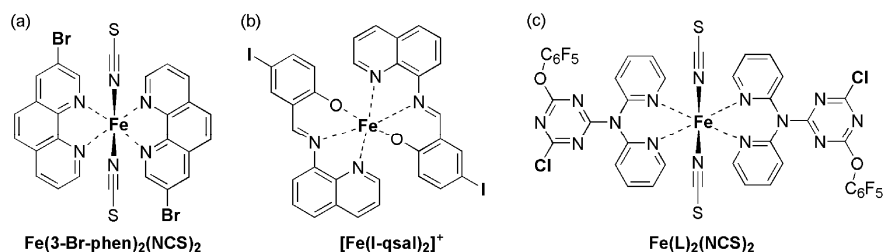


Fig. 12. Metal complexes with halogenated ligands exhibiting spin crossover conversion

The Fe^{II} $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ complex is regarded as the prototypical mononuclear SCO system, between a high temperature HS state ($S = 2$) to a low temperature LS state ($S = 0$) [51]. The observed abrupt transition has been extensively investigated and can be tentatively attributed to the presence of intermolecular π – π interactions. Among the various modifications of the phenanthroline ligand explored to date, the 3-bromophenanthroline (Fig. 12a) afforded a series of solvated iron thiocyanate complexes, formulated as $[\text{Fe}(\text{3-Br-phen})_2(\text{NCS})_2] \cdot \text{S}$ ($S = 0.5$ MeOH, 2 CH_2Cl_2 , 0.5 Me_2CO) [52], which exhibit magnetic features atypical of the classic $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ [51]. In the solid state (Fig. 13), a characteristic halogen bond interaction takes places between the bromine atom and the sulfur atom of the thiocyanate ligand. As already observed with non-coordinated NCS^- anion [53], the halogen bond donor points toward the sulfur atom, perpendicular to the C–S bond, with a $\text{Br} \cdots \text{S}$ distance at 91% the sum of the r_{vdW} .

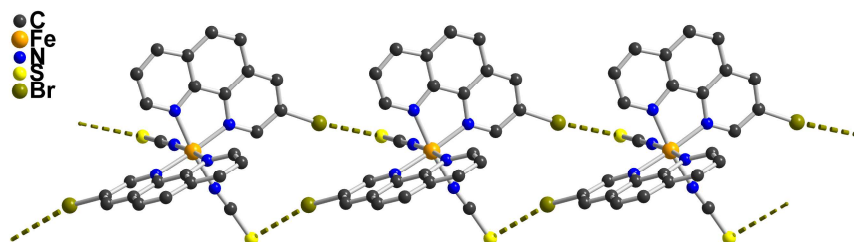


Fig. 13 $\text{Br} \cdots \text{S}$ interactions in $[\text{Fe}(\text{3-Br-phen})_2(\text{NCS})_2] \cdot 2 \text{CH}_2\text{Cl}_2$

Another example of SCO system involves the Fe^{III} $[\text{Fe}(\text{Iqsal})_2]^+$ species, as $[\text{Ni}(\text{dmit})_2]^-$ salt (dmit = 1,3-dithiole-3-thione-4,5-dimercapto) (Fig. 12b). This salt could have been described in the Section 4 dedicated to halogen bonded systems between two radical species as the $[\text{Ni}(\text{dmit})_2]^-$ is also paramagnetic, but is shown here in this Section on SCO compounds for completeness. As shown in Fig. 14, a directional $\text{I} \cdots \text{S}$ interaction takes place between cationic and anionic moieties [54]. The $[\text{Ni}(\text{dmit})_2]^-$ radical anions are organized into face-to-face dyads, in a way that parallel the one already observed with radical *cations*. A cooperative spin crossover occurs at $T_{1/2\downarrow} = 150$ K, characterized with an abrupt decrease of the $\chi_{\text{M}}T$ product. One remarkable feature is that the $\text{I} \cdots \text{S}$ distance found at 3.690(2) Å at 293 K and 3.634(3) Å at 175 K, above $T_{1/2\downarrow}$, actually increases abruptly up to 3.796(3) Å at 130 K, indicating that the halogen-bond interactions disappeared when crossing the SCO process. These observations along with the spin-singlet formation in the $[\text{Ni}(\text{dmit})_2]$ dimer suggest that the halogen-bond interactions between the cation and the anion compete with the π -stacking interactions between the face-to-face $[\text{Ni}(\text{dmit})_2]$ anions.

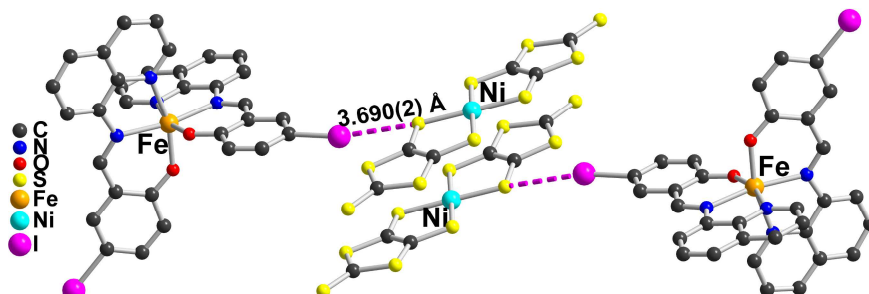


Fig. 14 I...S interactions in the RT structure of $[\text{Fe}(\text{Iqsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$.

The last example with the complex ligand L shown in Fig. 12c [55] exhibits a short Cl...F interaction between the strongly activated chlorine atom of the triazine ring and one fluorine atom of the pentafluorophenyl moiety. The Cl...F distance varies between, 2.969(4) Å and 3.013(4) Å in the LS and HS phase respectively, both notably shorter than the sum of van der Waals radii (3.22 Å). Together with other intermolecular interactions, this Cl...F contact is believed to contribute to the strongly cooperative SCO, characterized by an abrupt transition with hysteresis loop. These three rare examples demonstrate that halogen bonding interactions can indeed provide an efficient and powerful tool to modify and eventually control cooperativity in SCO systems. The extreme sensitivity to such complexes to minute modifications of their structural environment makes however difficult to fully rationalize the observed effects.

3 Radicals as Halogen Bond Acceptors

The association of radical molecules acting as halogen bond acceptors is based on two conditions: (i) the presence of halogen bond donor moieties in the radical molecules and (ii) the availability of strong halogen bond donor molecules. This second point is essentially fulfilled with perfluorinated iodoalkanes and iodoarenes which have been used extensively in crystal engineering [6,7,10], and specifically here also with radical molecules. The first point gives us a way to classify the radical halogen bond acceptors. The interest for the solid state structure of radical molecules in the solid state is associated to their magnetic properties, which are intimately related to the spatial arrangement of the spin carriers in the crystal lattice. The introduction of XB interactions involving radical species might modify the way they interact with each other and accordingly their magnetic and/or transport properties. Three main classes of radical species acting as halogen bond acceptors are identified, and developed in the three following sections, nitronyl

radicals, paramagnetic metallic complexes, and metal complexes with non-innocent ligands.

3.1 Nitronyl radicals

As shown from theoretical [56,57] and temperature-dependent EPR studies [58], nitronyl radicals act as very good halogen bond donors and their co-crystallization with 1,4-diiodotetrafluorobenzene provided the very first example of an halogen bonded TEMPO radical, namely a trimeric entity obtained with 4-amino-TEMPO (Fig. 15a) [59]. This work was extended by Micallef to isoindoline nitroxide [60,61]: a similar trimeric entity was crystallized (Fig. 15b) while EPR spectroscopy performed in solution with pentafluoroiodobenzene indicated that halogen bonding induces indeed an increase in electron density at the nitroxide nitrogen nucleus and an increase in the nitroxide rotational correlation time. With 1,2-diiodotetrafluorobenzene [61,62], tetrameric motifs were isolated (Fig. 15c), with the NO group acting as simple or bifurcated halogen bond acceptor, allowing for a modulation of the magnetic properties, when compared with the radicals alone.

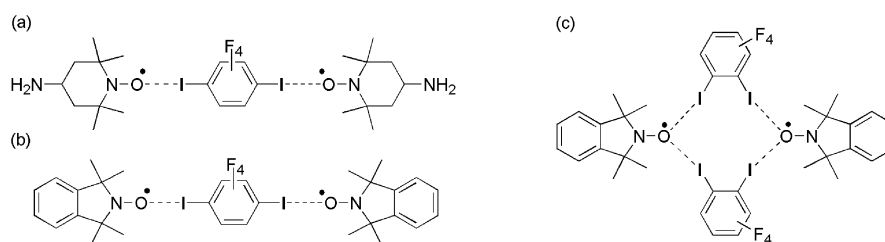


Fig. 15 Trimeric or tetrameric motifs observed in halogen bonded nitronyl radicals

Nitronyl nitroxyde radicals can also act as good halogen bonds acceptors and can act as bidendate donors, with a spin density delocalized on both NO groups [63]. Their co-crystallization with 1,4-diiodotetrafluorobenzene or the extended 4,4'-diiodooctafluoro-biphenyl (Fig. 16a,b) afforded indeed magnetic chains with very short $I\cdots O$ distances, below 80% the sum of van der Waals radii [64]. The lack of magnetic exchange through halogen bonds has been confirmed by EPR spectroscopy, and the magnetic interactions rely only on direct weak overlap between the radical species.

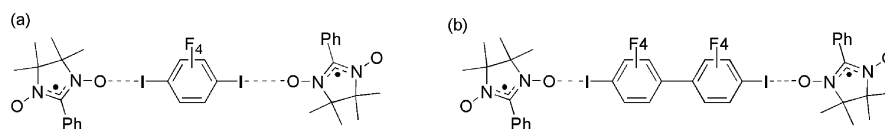


Fig. 16 Tetrameric motifs observed in halogen bonded nitronyl nitroxide radicals

3.2 Metal complexes with essentially metallic spin density

Paramagnetic metal complexes can act efficiently as halogen bond acceptors, and attractive interactions dominated by electrostatics were indeed described by Brammer et al. in a series of systematic studies on $C-X\cdots X'-M$ [65-67]. This work was also recently extended to cyanometallates ($C-X\cdots N\equiv C-M$) as halogen bond donors, in a series of halopyridinium salts of hexacyanometallates $[M(CN)_6]^{3-}$ ($M = Cr, Fe, Co$) [68]. The geometry of interaction of the halogen bond donor ($C-X$) with the cyanide ligand is either a shorter interaction predominantly with the *exo* lone pair of the nitrogen atom ($C\equiv N\cdots X > 145^\circ$) or a longer interaction with the $C\equiv N$ π -bond ($C\equiv N\cdots X < 105^\circ$). These studies provide important structural informations which can be further used when associating such paramagnetic complexes with radical species, particularly cation radical derived from tetrathiafulvalenes [8]. One can cite in this context halometallates such the $S = 5/2$ $Fe^{III} FeCl_4^-$ [69,70], cyanometallates such as $[Cr(CN)_6]^{3-}$ [71] or isothiocyanatometallates such as the $S = 3/2$ Cr^{III} $[Cr(isoq)_2(NCS)_4]^-$ complexes [19], all acting as halogen bond acceptors *vs.* iodinated tetrathiafulvalenium cations. In all reported examples however, the halogen bond was found to provide a very poor channel for super-exchange magnetic interactions between the paramagnetic complex and the $S = 1/2$ iodotetrathiafulvalenium cation.

3.3 Metal complexes with non-innocent ligands

Dithiolene complexes such as $[M(mnt)_2]^-$ and $[M(dmit)_2]^-$ ($M = Ni, Pd, Pt$) are paramagnetic species ($S = 1/2$) with a spin density strongly delocalized on the two dithiolene moieties. They have been acting as halogen bond acceptors, either through the CN group in $[Ni(mnt)_2]^-$ [72,73] or through the sulfur atoms in $[Pd(dmit)_2]^-$, [74] particularly when engaged in salt with iodinated tetrathiafulvalenium cations [9]. More recently, Kato et al. investigated mixed valence salts of $[Ni(dmit)_2]^-$ with non-magnetic halogenated cations such as N-Me-3,5-dihalopyridinium, N-Me-2,5-dihalopyridinium or N-ethyl-4-halothiazolium [75].

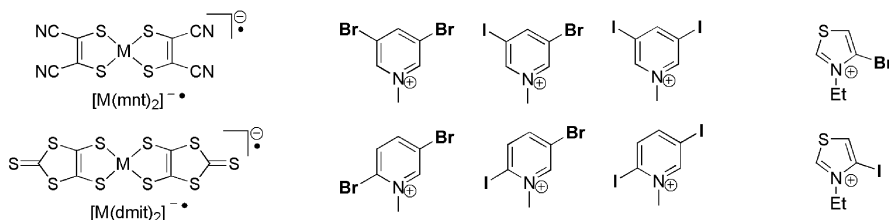


Fig. 17 Anionic dithiolene complexes and their halogenated cations

In all of them, strong $\text{I} \cdots \text{S}$ interactions were identified together with $\text{C}-\text{H} \cdots \text{S}$ hydrogen bonds, involving the outer thioketone $\text{S}=\text{C}$ group of the dmit ligand, with $\text{I} \cdots \text{S}$ distances at 3.27 and 3.49 Å [76]. The important point within these salts is their mixed valence character inferred from their stoichiometry, that is two $[\text{Ni}(\text{dmit})_2]$ complexes for one pyridinium cations. Such salts are obtained by electrocrystallization of the anionic $[\text{Ni}(\text{dmit})_2]^-$, in the presence of the pyridinium cation. The latter is found in the solid state associated to two crystallographically independent $[\text{Ni}(\text{dmit})_2]$ complexes, each of them forming two crystallographically independent conducting layers. The consequences are essentially twofold: (i) the two layers might exhibit different solid state arrangement of the partially oxidized $[\text{Ni}(\text{dmit})_2]$ complexes and accordingly different band structures and, (ii) the two independent complexes might have a formal charge deviating from the averaged -0.5 charge. Raman spectra in $(3,5\text{-I}_2\text{py})[\text{Ni}(\text{dmit})_2]_2$ indicated that the formal charge is the same in the two slabs, which exhibit different structures and transport properties (Fig. 18), with a localized state in Layer I and a two-dimensional closed Fermi surface in layer II. ^{13}C NMR showed evidence for the coexistence of localized spins (Layer I) and conduction π electrons (layer II) [77], while Shubnikov-de Haas and angular-dependent magnetoresistance oscillations clearly show that there exists a two-dimensional Fermi surface in layer II, whose spins are strongly coupled with the localized spins in layer I [78]. It is believed that the asymmetric environment mediated by the halogen (and weak hydrogen) bond interactions favors here the formation of such *bilayer systems*, as already mentioned above in Section 2.2.2 for $(\text{tTTF-I})_2\text{ClO}_4$ [34].

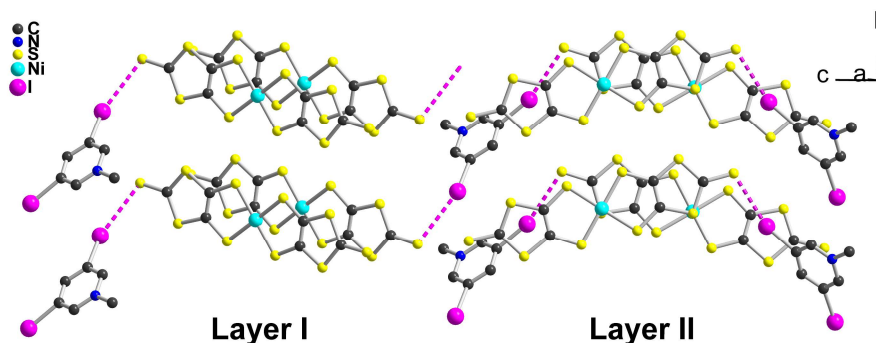


Fig. 18 Detail of the crystal structure of (3,5-I₂py)[Ni(dmit)₂]₂

Varying the electrocrystallization conditions or the nature of the halogens in the analogous 3,5-dibromo and 3,5-bromoiodopyridinium salts afforded a series of salts formulated as (3,5-Br₂Py)[Ni(dmit)₂]₂, (3,5-I₂py)[Ni(dmit)₂]₃, α -(3,5-I₂py)[Ni(dmit)₂]₂, β -(3,5-I₂py)[Ni(dmit)₂]₂ and (3,5-BrIpy)[Ni(dmit)₂]₂ [79]. Another series was developed with the 2,5-dihalopyridinium cations [80], as well as with N-ethyl-4-halothiazolium cations (see Fig. 17) [81].

4 Halogen-Bonded Charge Transfer Salts

This last section is dedicated to systems where both the halogen bond donor and the halogen bond acceptor are radical species. Such a rare situation is actually found in a few charge-transfer salts between *electron* donor and acceptor molecules. We have detailed above in Section 3 the possibility for radical species to act as halogen bond acceptors. In that respect, it is surprising that radical anion species such as TCNQ^{•-} were not reported until recently to form salts with halogenated cations where XB could be observed. Actually, neither its neutral complex with para-diiodobenzene [82], nor various pyridinium salts [83,84], exhibit any halogen bond interaction with the nitrile substituents of TCNQ. Perhaps the first mention is to be found in a charge-transfer complex with an iodinated TTF (Fig. 19), formulated as (EDO-TTF-I)₂(TCNQ) [85].

In this compound, a short and directional I^{•••}N interaction is found at 3.07 Å, between the centrosymmetric TCNQ molecule and the EDO-TTF-I electron donor (Fig. 20). A close inspection of the *intramolecular* bond lengths within both the TTF and TCNQ cores, shows however that an electron transfer didn't take place upon complex formation. In other words, we are in presence of a neutral, so-called charge-transfer complex (and not salt). This behavior finds its origin in the relative redox potentials of both molecules. EDO-TTF-I oxidizes indeed at $E_{\text{ox}} = +0.47$ V vs. SCE, a potential to high when compared with the reduction potential of TCNQ ($E_{\text{red}} = +0.17$ V). A very similar complex is obtained indeed with EDT-TTF-I (E_{ox}

= +0.46 V) [86], with a comparable I...N contact at 3.08 Å. These two examples demonstrate that the electron transfer, and ionic species, is not a necessary condition to observe the halogen bonding interaction between the iodine of the TTF derivative and the nitrile of TCNQ. The question then arises if this interaction is actually strengthened in the salts. For that purpose, TCNQ was replaced by the more oxidizing TCNQF₂ ($E_{\text{red}} = +0.36$ V), affording indeed an ionic salt formulated as (EDT-TTF-I^{+0.5})₂(TCNQF₂⁻) with a slightly shorter N...I interaction at 3.04 Å [86].

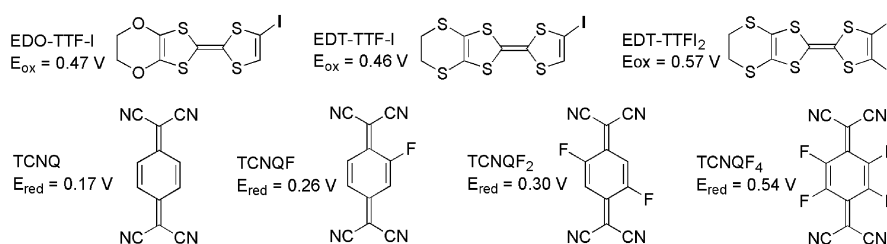


Fig. 19 Structures of halogenated TTFs and different TCNQs involved in charge transfer complexes and salts

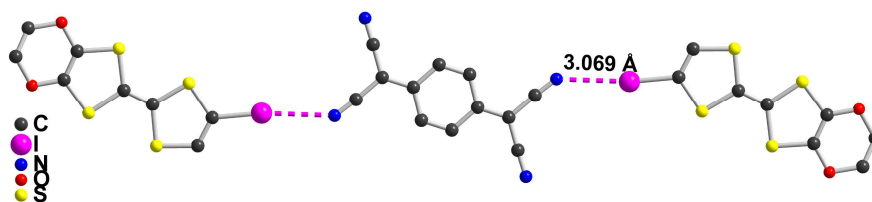


Fig. 20 Halogen-bonded trimers in neutral (EDO-TTF-I)₂(TCNQ) [85]

The situation is however not so simple since moving from TCNQF₂ to the even more oxidizing TCNQF₄ afforded a 1:1 ionic salt, formulated as (EDT-TTF-I⁺)(TCNQF₄⁻), where cations and anions are actually linked by a strong C-H...N hydrogen bond rather than the expected C-I...N halogen bond [86].

A similar series of compounds was obtained with the diiodo TTF derivative, EDT-TTFI₂ [87,88], where the competition with C-H...N hydrogen bond cannot take place. In order to establish a correlation between the halogen bond length and the degree of charge transfer, a complete series was crystallized from the less oxidizing TCNQ to the most oxidizing TCNQF₄. All four compounds exhibit the very same halogen bonded trimeric motif (EDT-TTFI₂)(TCNQF_n)(EDT-TTFI₂), $n = 0, 1, 2, 4$, similar to the one shown in Fig. 20. Three important conclusions were drawn from the structural, electronic and spectroscopic investigations of these series (Table 1, Fig. 21 and 22):

(i) the degree of electron transfer is directly correlated to the redox difference $\Delta E = E_{\text{red}}(\text{TCNQF}_n) - E_{\text{ox}}(\text{EDT-TTFI}_2)$, with ionic salts even when ΔE is slightly

negative, an indication of the coulombic stabilization of ionic forms in the solid state,

(ii) the degree of electron transfer can be modified with the temperature, with a neutral-to-ionic conversion observed upon cooling in the intermediate (EDT-TTFI₂)₂(TCNQF),

(iii) the degree of electron transfer is correlated to the length of the I•••N halogen bond. In other words, shorter halogen bonds are found with the most ionic compounds, indicated unambiguously an added electrostatic contribution to the halogen bond interaction.

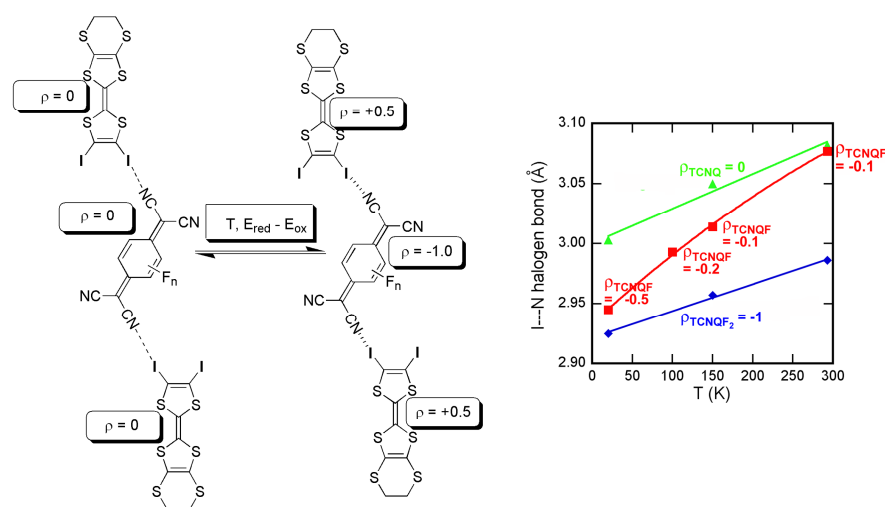


Fig. 21 Evolutions of the I•••N distance with charge and temperature within the (EDT-TTFI₂)₂(TCNQF_n) trimers, n = 0–2

Table 1. Evolutions of the TCNQF_n charge (ρ) and the I•••N distance, within the series (EDT-TTFI₂)₂(TCNQF_n). ΔE stands for $E_{\text{red}}(\text{TCNQF}_n) - E_{\text{ox}}(\text{EDT-TTFI}_2)$.

	TCNQ [87]	TCNQF [87]	TCNQF ₂ [87]	TCNQF ₄ [88]
ΔE (V)	-0.40	-0.31	-0.27	-0.03
T = 293K	$\rho \approx -0.2$ I•••N = 3.08 Å	$\rho \approx -0.1$ I•••N = 3.08 Å	$\rho \approx -1$ I•••N = 2.99 Å	$\rho \approx -1$ I•••N = 2.94 Å
T = 150 K	$\rho \approx -0.1$ I•••N = 3.05 Å	$\rho \approx -0.1$ I•••N = 3.01 Å	$\rho \approx -1.1$ I•••N = 2.96 Å	
T = 100 K		$\rho \approx -0.2$ I•••N = 2.99 Å		
T = 15 K	$\rho \approx -0.1$ I•••N = 3.00 Å	$\rho \approx -0.5$ I•••N = 2.94 Å	$\rho \approx -0.9$ I•••N = 2.93 Å	

5 Summary, Conclusions, and Outlook

A first very active research period, started at the end of the nineties, and aimed at investigating halogen bonding interactions essentially in organic conductors and radical nitronyl systems, has provided numerous examples of radical systems with solid state structures controlled to a large extent by halogen•••Lewis base interactions. While the contribution of halogen atoms to the band dispersion of organic metals was demonstrated, the preliminary assumptions that this intermolecular interaction could also work as a channel for magnetic interactions were not really fulfilled, essentially because the halogen atoms in radical halogen bond donors most often bear a very small part of the spin density. On the other hand, the predictability of halogen bonding associated to its strong linearity allowed for an efficient structural control of the solid state associations of radical species. We believe that this structural control can still play an important role in the tuning of intermolecular interactions, particularly in systems where cooperativity and delocalization play a crucial role. This is particularly true in molecular conductors and recent examples based on mixed valence salts, halogen bonded to non-centrosymmetric counter ions, provide novel bilayer conducting systems. Similarly, cooperativity effects are particularly involved in the nature of the spin crossover (SCO) between high spin and low spin states. Halogen bonding in the crystal structure of such SCO complexes opens the way to new structural organizations and new behaviors.

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