HAL
open science

Organizing Radical Species in the Solid State with Halogen Bonding.

Marc Fourmigué, Julien Lieffrig

To cite this version:

Marc Fourmigué, Julien Lieffrig. Organizing Radical Species in the Solid State with Halogen Bonding.. Topics in Current Chemistry, Springer, pp.91-113, 2015, 10.1007/128_2014_604 . hal-01141728

HAL Id: hal-01141728

https://univ-rennes.hal.science/hal-01141728v1

Submitted on 26 May 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Contents

1 Introduction
2 Radicals as Halogen Bond Donors
  2.1 Halogenated Trioxytriangulene Radical
  2.2 TTF Radical Cations Salts: Toward Chiral Conductors
    2.2.1 IodoTTFs with Non-Centrosymmetric ClO_4^- Anion
    2.2.2 IodoTTFs with Halogen Bonding to Chiral Anions
    2.2.3 Chiral iodoTTF salts
  2.3 Paramagnetic Metal Complexes with Halogenated Ligands
    2.3.1. Halopyridine complexes of metal halides
    2.3.2. Spin Crossover cooperativity and halogen bonding

M. Fourmigué and J. Lieffrig
Institut des Sciences Chimiques de Rennes, Université Rennes 1 & CNRS, Campus de Beaulieu, 35042 Rennes, France
e-mail: marc.fourmigue@univ-rennes1.fr

3 Radicals as Halogen Bond Acceptors
3.1 Nitronyl radicals
3.2 Metal complexes with essentially metallic spin density
3.3 Metal complexes with non-innocent ligands
4 Halogen-Bonded Charge Transfer Salts
5 Summary, Conclusions, and Outlook
References

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.

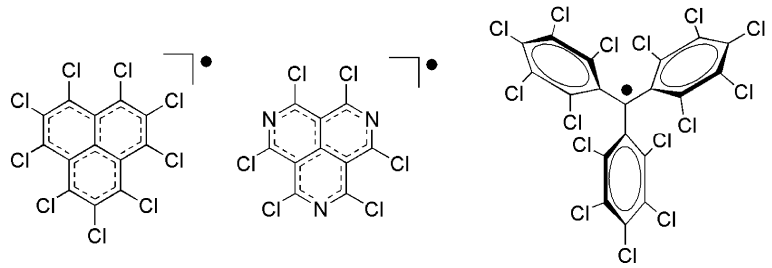

Fig. 1 Examples of heavily chlorinated carbon-based radicals. The crystal structure of the triazahexachlorophenalenyl is not known.

In that respect, the brominated trioxytriangulene (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 extend by the halogen bonding interactions, an important issue for the engineering of magnetic properties, particularly when associated with spin crossover (SCO) systems.

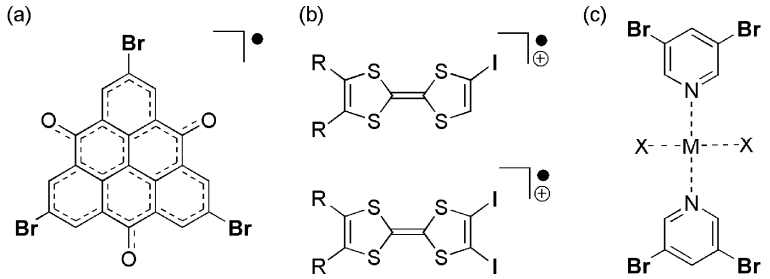

Fig. 2 Structures of radical, halogen bond donors described in Section 2.

2.1 Halogenated Trioxytriangulene 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 trioxytriangulene 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 Br_3TOT, 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 des Waals radii. The other oxygen atom O(1) is engaged in a cyclic $R_2^2(10)$ 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.

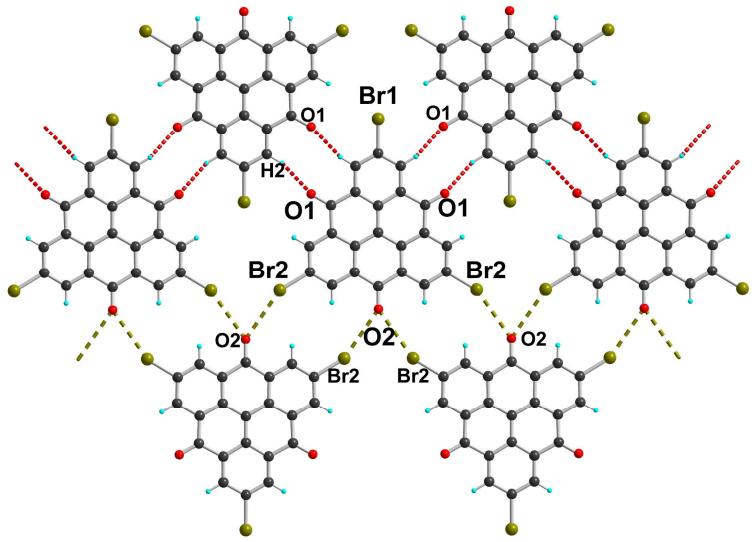

Fig. 3 Projection view of the crystal structure of Br_3TOT, perpendicular to the molecular plane, showing the C–Br(2)•••O(2) halogen bond [Br(2)•••O(2): 3.21 Å; C–Br(2)•••O(2): 156.4°; Br(2)•••O(2)=C: 144.6°] and C–H(2)•••O(1) [H(2)•••O(1): 2.44 Å; C–H(2)•••O(1): 150.7°: H(2)•••O(1)=C: 153.4°] hydrogen 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 (I_3^-, IBr_2^-, ...) [18], polyhalometallates, polycyanometallates, polythiocyanatometallates [19] to cluster anions such as $[Re_6Se_6(CN)_6]^{4-}$ [20,21] or $[Mo_3S_7Cl_6]^{2-}$ [22] or polymeric anionic networks such as $[PbI_3]_\infty^-$ [23], the layered $[Pb_{5/6}\square_{1/6}I_2]^-$ system with a PbI_2 structure [24] or complex cadmium thiocyanate lacunar networks such as $[Cd_3(NCS)_8]^{2-}$ and $[Cd_5(SCN)_{14}]^{4-}$ [25].

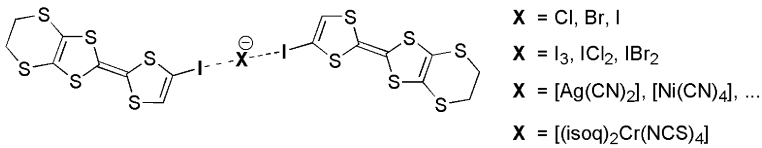

Fig. 4 Examples of halogen bonded TTF salts.

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-TTFI$_2$ also contribute to the band dispersion as the HOMO of such TTFs exhibits no-zero coefficients on the halogen atoms. Note also that in most cases, the counter ion acting as Lewis based is centrosymmetric, affording halogen bonded systems with high symmetry. An illustrative counter example is obtained with the tetrahedral ClO_4^- 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 magneto-resistance 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 ClO_4^- Anion

Both EDT-TTFI$_2$ [33] and tTTF-I [34] were reported to form halogen bonded salts with the ClO_4^- anion (Fig. 5). In the 1:1 (EDT-TTFI$_2$)(ClO_4) salt, the EDT-TTFI$_2^{\bullet+}$ radical cations are associated two-by-two into face-to face dyads allowing for a strong σ overlap of the frontier orbitals [1].

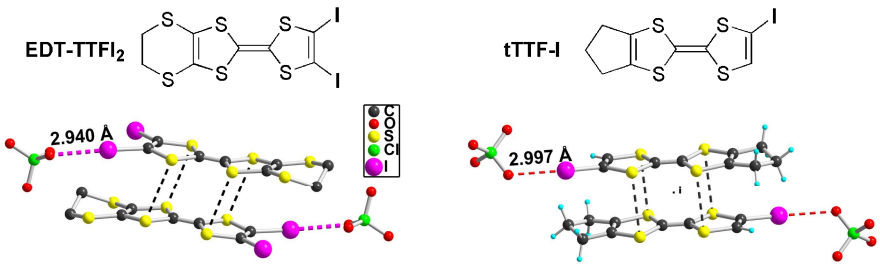

Fig. 5 Detail of the 1:1 ClO_4^- salts with EDT-TTFI$_2$ (left) and tTTF-I (right) showing the I•••O halogen bonds and the face-to-face interaction between radical species

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)(ClO_4), 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 $(tTTF\text{-}I)_2ClO_4$, where two oxygen atoms of the ClO_4^- 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.

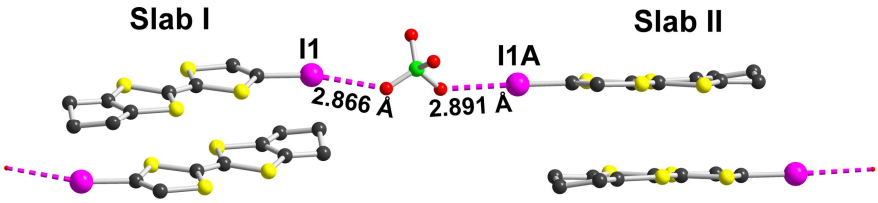

Fig. 6 Detail of the two crystallographically independent conducting slabs in $(tTTF\text{-}I)_2ClO_4$

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-$TTFI_2$ 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-$TTFI_2$ 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-$TTFI_2$ 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-TTFI$_2$ 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.

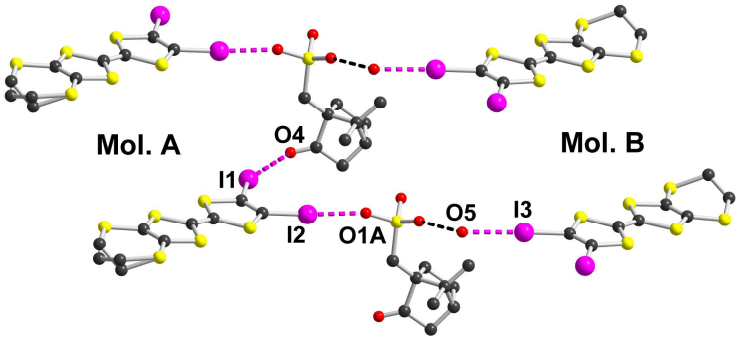

Fig. 7 Detail of the asymmetric unit in (EDT-TTFI$_2$)$_2$(*D*-camphorsulfonate). Halogen bonds with red dotted lines: I(1)•••O(4) 3.02 Å, I(2)•••O(1A) 2.68 Å, I(3)•••O(5) 2.84 Å. Hydrogen bond between water molecule and sulfonate moiety as black dotted line.

It should be stressed also that the racemic salt obtained with DL-camphorsulfonate is no 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-TTFI$_2^{+0.5}$ molecule is still present with the shortest O•••I distances above 2.81Å, 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-TTFI$_2$ is replaced by a 1,3-dimethyl-1,3-propylene substituent in Me$_2$PDT-TTFI$_2$ [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.

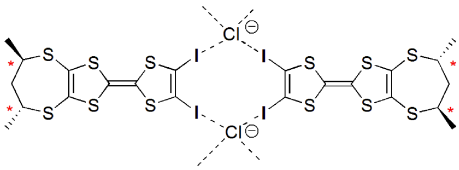

Fig. 8 The chiral Me_2PDT-$TTFI_2$ and the structural motif observed in its chloride salt.

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*-$[MCl_2(4\text{-}X'\text{-py})_2]$ (M = Pd, Pt; X' = Cl, Br) and *trans*-$[PdI_2(4\text{-I-py})_2]$. While no specific magnetic interactions can be expected from these low spin d^8 complexes, other examples were reported incorporating $S = ½$ ions, in d^7 Co^{2+} or d^9 Cu^{2+} species.

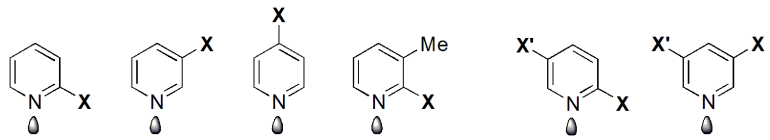

Fig. 9 Mono- and dihalopyridines used in the coordination of metal halides (X, X' = Cl, Br, I)

Several CuX_2 complexes with halogenated pyridine ligands were reported, as in *trans*-$[CuCl_2(3\text{-Cl-py})_2]$ [45], or $[CuX_2(2\text{-Br-py})_2]$ and -$[CuX_2(3\text{-Br-py})_2]$ [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 [CuX_2(3-Br-py)$_2$] but less than the sum of the r_{vdW} by ~0.24 Å in the *ortho*-substituted analog [CuX_2(2-Br-py)$_2$] (Fig. 10). Magnetic data for [$CuBr_2$(2-Br-py)$_2$] show an absence of any interactions, with a perfect Curie-type behavior [46].

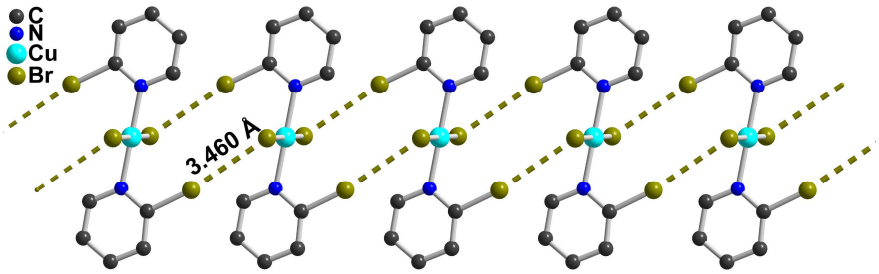

Fig. 10 View of the halogen bonded chains in [$CuBr_2$(2-Br-py)$_2$]. The Br•••Br distance, 3.46 Å, is to be compared with the sum of van der Waals radii, namely 3.70 Å.

On the other hand, the analogous 2,5-dibromopyridine derivatives, formulated as [$CuCl_2$(2,5-Br_2-py)$_2$] and [$CuBr_2$(2,5-Br_2-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 Cl•••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, [$CuCl_2$(2,5-Br_2-py)$_2$], adopts a structure comparable with that of [$CuBr_2$(2-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*-[$CoCl_2$(3,5-X_2py)$_2$], 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.

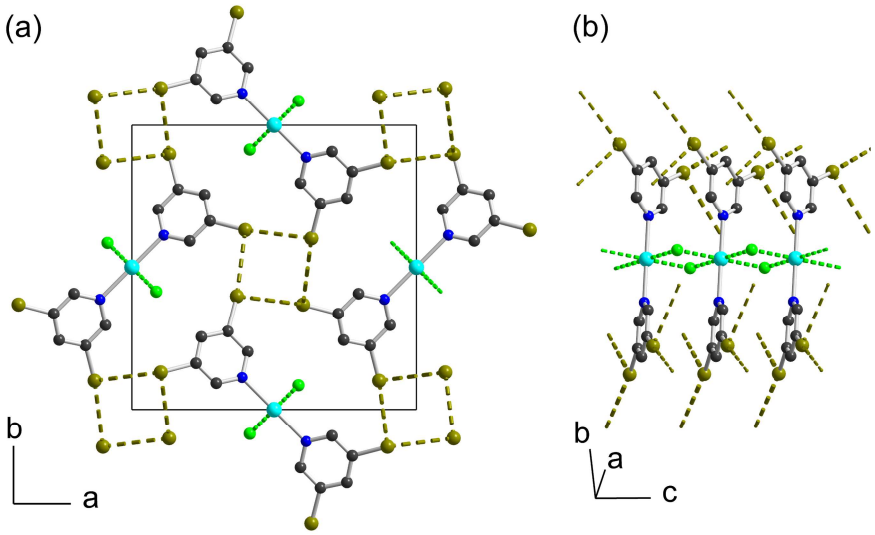

Fig. 11 Views of *trans*-[$CoCl_2$(3,5-Br_2py)$_2$] with, (a) projection along the *c* axis showing the tetrameric halogen bonded motif and, (b) the $CoCl_2$ chain running along *c*.

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).

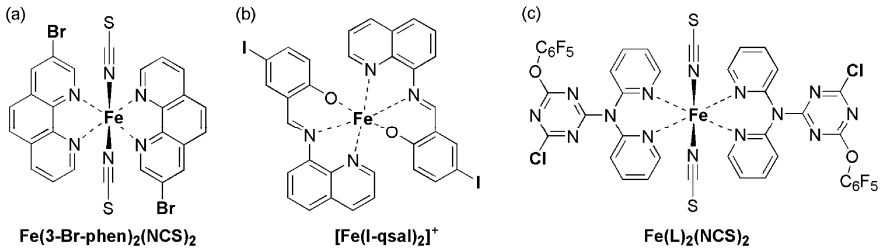

Fig. 12. Metal complexes with halogenated ligands exhibiting spin crossover conversion

The Fe^{II} $[Fe(phen)_2(NCS)_2]$ 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 $[Fe(3\text{-Br-phen})_2(NCS)_2]$•S (S = 0.5 MeOH, 2 CH_2Cl_2, 0.5 Me_2CO) [52], which exhibit magnetic features atypical of the classic $[Fe(phen)_2(NCS)_2]$ [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 Br•••S distance at 91% the sum of the r_{vdW}.

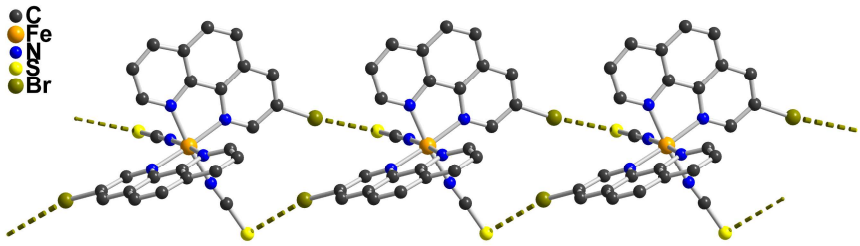

Fig. 13 Br•••S interactions in $[Fe(3\text{-Br-phen})_2(NCS)_2]$•2 CH_2Cl_2

Another example of SCO system involves the Fe^{III} $[Fe(Iqsal)_2]^+$ species, as $[Ni(dmit)_2]^-$ 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 $[Ni(dmit)_2]^-$ is also paramagnetic, but is shown here in this Section on SCO compounds for completeness. As shown in Fig. 14, a directional I•••S interaction takes place between cationic and anionic moieties [54]. The $[Ni(dmit)_2]^-$ 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 $T_{½}\downarrow$ = 150 K, characterized with an abrupt decrease of the $\chi_M T$ product. One remarkable feature is that the I•••S distance found at 3.690(2) at 293 K and 3.634(3) Å at 175 K, above $T_{½}\downarrow$, 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 $[Ni(dmit)_2]$ dimer suggest that the halogen-bond interactions between the cation and the anion compete with the π-stacking interactions between the face-to-face $[Ni(dmit)_2]$ anions.

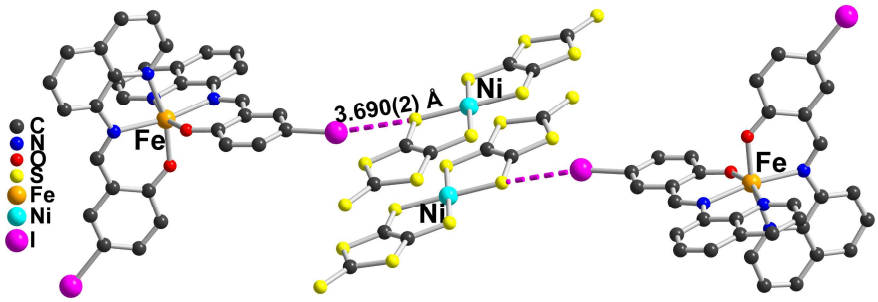

Fig. 14 I•••S interactions in the RT structure of $[Fe(Iqsal)_2][Ni(dmit)_2]\bullet CH_3CN\bullet H_2O$.

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 pentofluorophenyloxy 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.

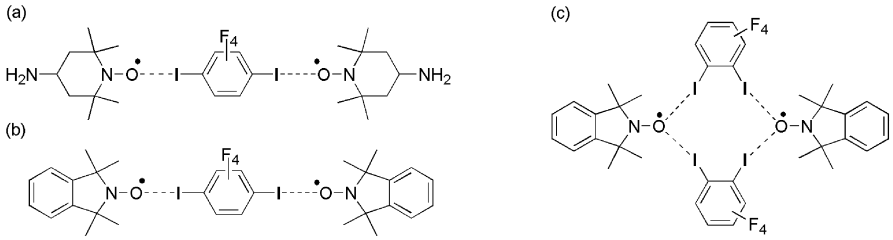

Fig. 15 Trimeric or tetrameric motifs observed in halogen bonded nitronyl radicals

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•••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.

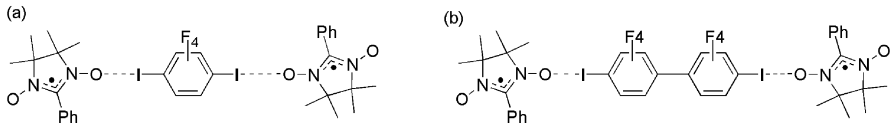

Fig. 16 Tetrameric motifs observed in halogen bonded nitronyl nitroxyde radicals

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•••X'–M [65-67]. This work was also recently extended to cyanometallates (C–X•••N≡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≡N•••X > 145°) or a longer interaction with the C≡N π-bond (C≡N•••X < 105°). 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 = ½ iodotetrathiafulvalenium cation.

3.3 Metal complexes with non-innocent ligands

Dithiolene complexes such as $[M(mnt)_2]^{-\bullet}$ and $[M(dmit)_2]^{-\bullet}$ (M = Ni, Pd, Pt) are paramagnetic species (S = ½) 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 $[Ni(mnt)_2]^{-\bullet}$ [72,73] or through the sulfur atoms in $[Pd(dmit)_2]^{-\bullet}$, [74] particularly when engaged in salt with iodinated tetrathiafulvalenium cations [9]. More recently, Kato et al. investigated mixed valence salts of $[Ni(dmit)_2]^{-\bullet}$ with non-magnetic halogenated cations such as N-Me-3,5-dihalopyridinium, N-Me-2,5-dihalopyridinium or N-ethyl-4-halothiazolium [75].

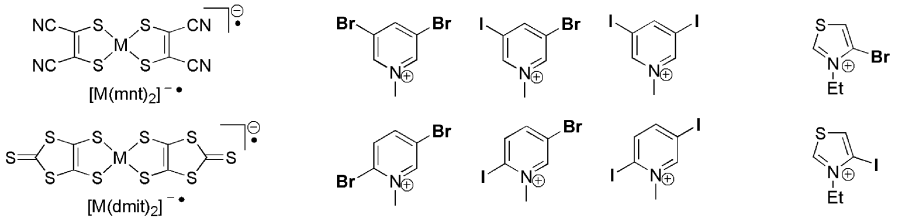

Fig. 17 Anionic dithiolene complexes and their halogenated cations

In all of them, strong I•••S interactions were identified together with C–H•••S hydrogen bonds, involving the outer thioketone S=C group of the dmit ligand, with I•••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 $[Ni(dmit)_2]$ complexes for one pyridinium cations. Such salts are obtained by electrocrystallization of the anionic $[Ni(dmit)_2]^{-\bullet}$, in the presence of the pyridinium cation. The latter is found in the solid state associated to two crystallographically independent $[Ni(dmit)_2]$ 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 $[Ni(dmit)_2]$ 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 $(3,5\text{-}I_2py)[Ni(dmit)_2]_2$ 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 $(tTTF\text{-}I)_2ClO_4$ [34].

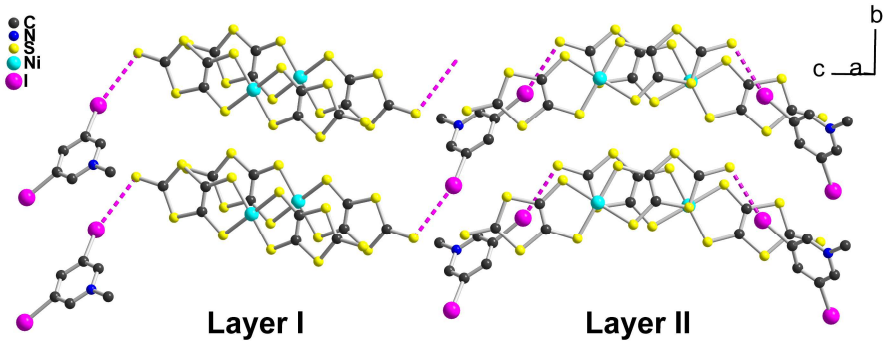

Fig. 18 Detail of the crystal structure of (3,5-I_2py)[Ni(dmit)$_2$]$_2$

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-Br_2Py)[Ni(dmit)$_2$]$_2$, (3,5-I_2py)[Ni(dmit)$_2$]$_3$, α-(3,5-I_2py)[Ni(dmit)$_2$]$_2$, β-(3,5-I_2py)[Ni(dmit)$_2$]$_2$ and (3,5-BrIpy)[Ni(dmit)$_2$]$_2$ [79]. Another series was developed with the 2,5-dihalopyridium 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 $TCNQ^{-\bullet}$ 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_{ox} = +0.47 V *vs*. SCE, a potential to high when compared with the reduction potential of TCNQ (E_{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 $TCNQF_2$ (E_{red} = +0.36 V), affording indeed an ionic salt formulated as $(EDT\text{-}TTF\text{-}I^{+0.5})_2(TCNQF_2^{-})$ with a slightly shorter N•••I interaction at 3.04 Å [86].

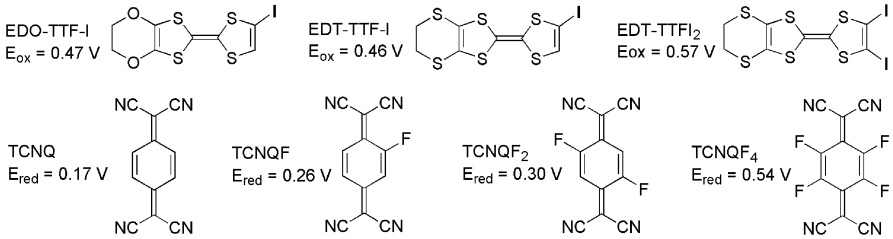

Fig. 19 Structures of halogenated TTFs and different TCNQs involved in charge transfer complexes and salts

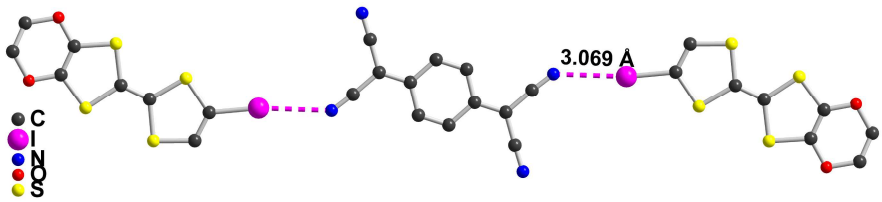

Fig. 20 Halogen-bonded trimers in neutral $(EDO\text{-}TTF\text{-}I)_2(TCNQ)$ [85]

The situation is however not so simple since moving from $TCNQF_2$ to the even more oxidizing $TCNQF_4$ afforded a 1:1 ionic salt, formulated as $(EDT\text{-}TTF\text{-}I^{+\bullet})(TCNQF_4^{-\bullet})$, 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, $EDT\text{-}TTFI_2$ [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 $TCNQF_4$. All four compounds exhibit the very same halogen bonded trimeric motif $(EDT\text{-}TTFI_2)(TCNQF_n)(EDT\text{-}TTFI_2)$, 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 $\Delta E = E_{red}(TCNQF_n) - E_{ox}(EDT\text{-}TTFI_2)$, 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-TTFI$_2$)$_2$(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.

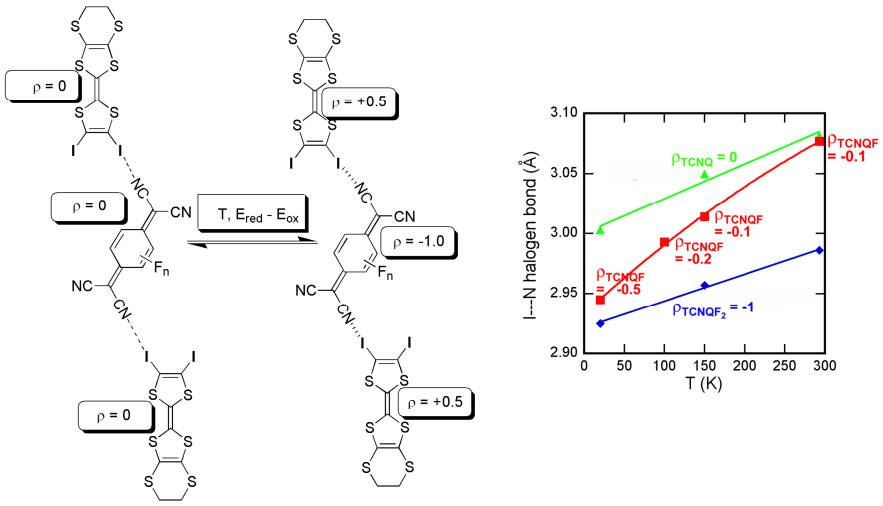

Fig. 21 Evolutions of the I•••N distance with charge and temperature within the (EDT-TTFI$_2$)$_2$(TCNQF$_n$) trimers, n = 0–2

Table 1. Evolutions of the TCNQF$_n$ charge (ρ) and the I•••N distance, within the series (EDT-TTFI$_2$)$_2$(TCNQF$_n$). ΔE stands for E_{red}(TCNQF$_n$) – E_{ox}(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	ρ ≈ –0.2	ρ ≈ –0.1	ρ ≈ –1	ρ ≈ –1
	I•••N = 3.08 Å	I•••N = 3.08 Å	I•••N = 2.99 Å	I•••N = 2.94 Å
T = 150 K	ρ ≈ –0.1	ρ ≈ –0.1	ρ ≈ –1.1	
	I•••N = 3.05 Å	I•••N = 3.01 Å	I•••N = 2.96 Å	
T = 100 K		ρ ≈ –0.2		
		I•••N = 2.99 Å		
T = 15 K	ρ ≈ –0.1	ρ ≈ –0.5	ρ ≈ –0.9	
	I•••N = 3.00 Å	I•••N = 2.94 Å	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 extend 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.

References

1. Fourmigué M (2012) The importance of π-interactions in crystal engineering. John Wiley & Sons Ltd. Chp. 6, pp143–162
2. Hicks RG (ed) (2010) Stable radicals. John Wiley & Sons Ltd.
3. Otsuka T, Okuno T, Awaga K, Inabe, T (1998) Crystal structures and magnetic properties of acid–base molecular complexes, (p-pyridyl nitronylnitroxide)$_2$X (X=hydroquinone, fumaric acid and squaric acid). J Mater Chem 8:1157-1163
4. Romero FM, Ziessel R, Bonnet M, Pontillon Y, Ressouche E, Schweitzer J, Delley B, Grand A, Paulsen C (2000) Evidence for Transmission of Ferromagnetic Interactions through Hydrogen Bonds in Alkyne-Substituted Nitroxide Radicals: Magnetostructural Correlations and Polarized Neutron Diffraction Studies. J Am Chem Soc 122:1298-1309
5. Maspoch D, Catala L, Gerbier P, Ruiz-Molina D, Vidal-Gancedo J, Wurst K, Rovira C, Veciana J (2002) Radical para-Benzoic Acid Derivatives: Transmission of Ferromagnetic Interactions through Hydrogen Bonds at Long Distances. Chem Eur J 8:3635-3645
6. Metrangolo P, Neukirch H, Pilati T, Resnati G (2005) Halogen bonding based recognition processes: A world parallel to hydrogen bonding. Acc Chem Res 38: 386-395.
7. Meyer F, Dubois P (2013) Halogen bonding at work: recent applications in synthetic chemistry and materials science. CrystEngComm 15: 3058-3071
8. Fourmigué M, Batail P (2004) Activation of Hydrogen- and Halogen-Bonding Interactions in Tetrathiafulvalene-Based Crystalline Molecular Conductors. Chem Rev 104:5379-5418

9. Fourmigué M, (2008) Halogen bonding in Conducting or Magnetic Molecular Materials. Struct Bond 126:181
10. Metrangolo P, Meyer F, Pilati T, Resnati G, Terraneo G (2008) Halogen Bonding in Supramolecular Chemistry. Angew Chem Int Ed 47:6114-6127
11. Bondi A (1964) van der Waals Volumes and Radii. J Phys Chem 68:441-451
12. Veciana J, Ratera I (2010) in: Stable Radicals. Hicks RG (ed). John Wiley & Sons, Ltd. Chp 2, pp 33–80
13. Koutentis PA, Chen Y, Cao Y, Best TP, Itkis ME, Beer L, Oakley RT, Cordes AW, Brock CP, Haddon RC (2001) Perchlorophenalenyl Radical. J Am Chem Soc 123:3864-3871
14 Morita Y, Nishida S (2010) in Stable Radicals. Hicks RG (ed) John Wiley & Sons, Ltd.Chp. 3, pp 81–145
15. Morita Y, Nishida S, Murata T, Moriguchi M, Ueda A, Satoh M, Arifuku K, Sato K, Takui T (2011) Organic tailored batteries materials using stable open-shell molecules with degenerate frontier orbitals. Nature Mat 10:947-951
16. Imakubo T, Sawa H, Kato R (1995) 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 73:117-122
17. Imakubo T, Shirahata T, Hervé K, Ouahab L (2006) Supramolecular organic conductors based on diiodo-TTFs and spherical halide ion X− (X = Cl, Br). J Mater Chem 16:162-173
18. Domercq B, Devic T, Fourmigué M, Auban-Senzier P, Canadell E (2001) 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 11:1570-1575
19. Hervé K, Cador O, Golhen S, Costuas K, Halet JF, Shirahata T, Muto T, Imakubo T, Miyazaki A, Ouahab L (2006) Iodine 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 18:790-797
20. Ranganathan A, El-Ghayoury A, Mézière C, Harté E, Clérac R, Batail P (2006) 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 2878-2880
21. Barrès AL, El-Ghayoury A, Zorina LV, Canadell E, Auban-Senzier P, Batail P (2008) The 8:1:1 ternary hybrid framework in the system $[EDT\text{-}TTF^{\bullet+}]$ [1,4-bis(iodoethynyl)benzene] $[Re_6Se_8(CN)_6]^{4-}$: dual noncovalent expression of the octahedral halogen-bond hexa-acceptor nanonode. Chem. Commun 2194-2196
22. Alberola A, Fourmigué M, Gómez-García CJ, Llusar R, Triguero S (2008) Halogen bonding 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. 32:1103-1109
23. Devic T, Canadell E, Auban-Senzier P, Batail P (2004) $(EDT\text{-}TTF\text{-}I_2)_2PbI_3\bullet H_2O$: an ambient pressure metal with a β′ donor slab topology. J Mater Chem 14:135-137
24. Devic T, Evain M, Moëlo Y, Canadell E, Senzier P, Fourmigué M, Batail P (2003) Single Crystalline Commensurate Metallic Assemblages of π-slabs and CdI_2-Type Layers: Synthesis and Properties of $\beta\text{-}(EDT\text{-}TTF\text{-}I_2)_2[Pb_{5/6}\square_{1/6}I_2]_3$ and $\beta\text{-}(EDT\text{-}TTF\text{-}I_2)_2[Pb_{2/3+x}Ag_{1/3-2x}\square_xI_2]_3$, x = 0.05. J Am Chem Soc 125:3295-3301
25. Fourmigué M, Auban-Senzier P (2008) Anionic Layered Networks Reconstructed from $[Cd(SCN)_3]_\infty^-$ Chains in Pseudo One-Dimensional Conducting Salts of Halogenated Tetrathiafulvalenes. Inorg Chem 47:9979-9986
26. Rikken GLJA, Fölling J, Wyder P (2001) Electrical Magnetochiral Anisotropy. Phys Rev Lett 87:236602
27. De Martino A, Egger R, Tsvelik AM (2006) Nonlinear Magnetotransport in Interacting Chiral Nanotubes. Phys Rev Lett 97:076402
28. Krstic V, Rikken GLJA (2002) Magneto-chiral anisotropy of the free electron on a helix. Chem Phys Lett 364:51-56

29. Avarvari N, Wallis JD (2009) Strategies towards chiral molecular conductors. J Mater Chem 19, 4061-4076
30. Griffiths JP, Nie H, Brown RJ, Day P, Wallis JD (2005) Synthetic strategies to chiral organosulfur donors related to bis(ethylenedithio)tetrathiafulvalene. Org Biomol Chem 3:2155-2166
31. Galan-Mascaros J, Coronado E, Goddard PA, Singleton J, Coldea AI, Wallis JD, Coles SJ, Alberola A (2010) A Chiral Ferromagnetic Molecular Metal. J Am Chem Soc 132: 9271-9273
32. Pop F, Auban-Senzier P, Canadell E, Rikken GLJA, Avarvari N (2014) Electrical magnetochiral anisotropy in a bulk chiral molecular conductorNature Comm 5(3757): 1-6
33. Shin KS, Brezgunova M, Jeannin O, Roisnel T, Camerel F, Auban-Senzier P, Fourmigué M (2011) Strong Iodine···Oxygen Interactions in Molecular Conductors Incorporating Sulfonate Anions. Cryst Growth Des 11:5337-5345
34. Shin KS, Jeannin O, Brezgunova M, Dahaoui S, Aubert E, Espinosa E, Auban-Senzier P, Swietlik R, Frackowiak A, Fourmigué M (2014) Inter-layer charge disproportionation in the dual-layer organic metal $(tTTF\text{-}I)_2ClO_4$ with unsymmetrical I•••O halogen bond interactions. Dalton Trans 43:5280-5291
35. Brezgunova M, Shin KS, Auban-Senzier P, Jeannin O, Fourmigué M (2010) Combining halogen bonding and chirality in a two-dimensional organic metal $(EDT\text{-}TTF\text{-}I_2)_2$(*D*-camphorsulfonate)•$H_2O$. Chem Commun 3926-3928
36. Lieffrig J, Le Pennec R, Jeannin O, Auban-Senzier P, Fourmigué M (2013) Toward chiral conductors: combining halogen bonding ability and chirality within a single tetrathiafulvalene molecule. CrystEngComm 15:4408-4412
37. Lieffrig J, Jeannin O, Auban-Senzier P, Fourmigué M (2012) Chiral Conducting Salts of Nickel Dithiolene Complexes. Inorg. Chem 51:7144-7152
38. Libri S, Jasim NA, Perutz RN, Brammer L (2008) Metal Fluorides Form Strong Hydrogen Bonds and Halogen Bonds: Measuring Interaction Enthalpies and Entropies in Solution. J Am Chem Soc 130:7842-7844
39. Mínguez Espallargas G, Brammer L, Allan DR, Pulham CR, Robertson N, Warren JE, (2008) Noncovalent Interactions under Extreme Conditions: High-Pressure and Low-Temperature Diffraction Studies of the Isostructural Metal−Organic Networks $(4\text{-Chloropyridinium})_2[CoX_4]$ (X = Cl, Br). J Am Chem Soc 130:9058-9071
40. Awwadi F, Haddad SF, Willett RD, Twamley B (2010) The Analogy of C−Br···Br−C, C−Br•••Br−Fe, and Fe−Br•••Br−Fe Contacts: Crystal Structures of $(26DAPH)FeBr_4$ and $(26DA35DBPH)_2FeBr_4$•Br. Cryst Growth Des 10:158-164
41. Derossi S, Brammer L, Hunter CA, Ward MD (2009) Halogen Bonded Supramolecular Assemblies of $[Ru(bipy)(CN)_4]^{2-}$ Anions and N-Methyl-Halopyridinium Cations in the Solid State and in Solution. Inorg Chem 48:1666-1677
42. Ormond-Prout JE, Smart P, Brammer L (2012) Halogen Bonded Supramolecular Assemblies of $[Ru(bipy)(CN)_4]^{2-}$ Anions and N-Methyl-Halopyridinium Cations in the Solid State and in Solution. Cryst Growth Des 12:205−216
43. Bertani R, Sgarbossa P, Venzo A Lelj F, Amati M, Resnati G, Pilati T, Metrangolo P, Terraneo G (2010) Halogen bonding in metal–organic–supramolecular networks. Coord Chem Rev 254:677-695
44. Zordan F, Brammer L (2006) M−X···X'−C Halogen-Bonded Network Formation in MX_2(4-halopyridine)$_2$ Complexes (M = Pd, Pt; X = Cl, I; X' = Cl, Br, I). Cryst Growth Des 6:1374-1379
45. Mínguez Espallargas G, Hippler M, Florence AJ, Fernandes P, van de Streek J, Brunelli M, David WIF, Shamkland K, Brammer L (2007) Reversible Gas Uptake by a Nonporous Crystalline Solid Involving Multiple Changes in Covalent Bonding. J Am Chem Soc 129:15606-15614.
46. Awwadi FF, Willett DD, Haddad SF, Twamley B (2006) The Electrostatic Nature of Aryl−Bromine−Halide Synthons: The Role of Aryl−Bromine−Halide Synthons in the Crystal

Structures of the trans-bis(2-bromopyridine)dihalocopper(II) and trans-bis(3-bromopyridine)dihalocopper(II) Complexes. Cryst Growth Des 6:1833-1836.
47. Awwadi FF, Haddad SF, Turnbull MM, Landee CP, Willett RD (2013) Copper–halide bonds as magnetic tunnels; structural, magnetic and theoretical studies of trans-bis(2,5-dibromopyridine)dihalo copper(II) and trans-bis(2-bromopyridine)dibromo copper(II). CrystEngComm, 15:3111-3118
48. Herringer SN, Turnbull MM, Landee CP, Wikaira JL (2011) Copper(II) complexes of 2-halo-3-methylpyridine: synthesis, structure, and magnetic behaviour of $Cu(2\text{-}X\text{-}3\text{-}CH_3py)_2X'_2$ [X, X′ = chlorine or bromine; py = pyridine]. Dalton Trans 40:4242-4252
49. Clemente-Juan JM, Coronado E, Minguez Espallargas G, Adams H, Brammer L (2010) Effects of halogen bonding in ferromagnetic chains based on Co(II) coordination polymers CrystEngComm 12:2339–2342
50. Halcrow MA (2011) Structure:function relationships in molecular spin-crossover complexes Chem Soc Rev 40:4119-4142
51 Gütlich P (1981) Spin-Crossover Materials: Properties and Applications. Struct Bond 44:83-195
52. Naik AD, Tinant B, Muffler K, Wolny Ja, Schünemann V, Garcia Y (2009) Relevance of supramolecular interactions, texture and lattice occupancy in the designer iron(II) spin crossover complexes. J Solid State Chem 182:1365-1376
53. Cauliez P, Polo V, Roisnel T, Llusar R, Fourmigué M (2010) The thiocyanate anion as a polydentate halogen bond acceptor. CrystEngComm 12:558-566
54. Fukuroi K, Takahashi K, Mochida T, Sakurai T, Ohta H, Yamamoto T, Einaga Y, Mori H (2014) Synergistic Spin Transition between Spin Crossover and Spin-Peierls-like Singlet Formation in the Halogen-Bonded Molecular Hybrid System: $[Fe(Iqsal)_2][Ni(dmit)_2]\bullet CH_3CN\bullet H_2O$. Angew. Chem. Int. Ed. 53:1983-1986
55. Nassirinia N, Amani S, Teat SJ, Roubeau O, Gamez P (2014) Enhancement of spin-crossover cooperativity mediated by lone pair–π interactions and halogen bonding. Chem Commun 50:1003-1005
56. Cimino P, Pavone M, Barone V (2007) Halogen Bonds between 2,2,6,6-Tetramethylpiperidine-N-oxyl Radical and C=HyFzI Species: DFT Calculations of Physicochemical Properties and Comparison with Hydrogen Bonded Adducts. J. Phys. Chem. A 111: 8482-8490
57. Zhao XR, Pang X, Yan XQ, Jin WJ (2013) Halogen Bonding or Hydrogen Bonding between 2,2,6,6-Tetramethylpiperidine-noxyl Radical and Trihalomethanes CHX_3 (X=CI, Br, I). Chin. J. Chem. Phys. 26:172-180
58. V. Mugnaini V, Punta C, Liantonio R, Metrangolo P, Recupero F, Resnati G, Pedulli GF, Lucarini M (2006) Noncovalent paramagnetic complexes: detection of halogen bonding in solution by ESR spectroscopy. Tetrahedron Lett 47:3265-3269
59. Boubekeur K, Syssa-Magalé JL, Palvadeau P, Schöllhorn B (2006) Self-assembly of nitroxide radicals via halogen bonding directional NO•••I interactions. Tetrahedron Lett 47:1249-1252
60. Hanson GR, Jensen P, McMurtrie J, Rintoul L, Micallef AS (2009) Halogen Bonding between an Isoindoline Nitroxide and 1,4-Diiodotetrafluorobenzene: New Tools and Tectons for Self-Assembling Organic Spin Systems. Chem Eur J 15:4156-4164.
61. Davy KJP, McMurtrie J, Rintoul L, Bernhardt PV, Micallef AS (2011) Vapour phase assembly of a halogen bonded complex of an isoindoline nitroxide and 1,2-diiodotetrafluorobenzene. CrystEngComm 13:5062-5070
62. Pang X, Zhao XR , Wang H, Sun HL, Jin WJ (2013) Modulating Crystal Packing and Magnetic Properties of Nitroxide Free Radicals by Halogen Bonding. Cryst Growth Des 13:3739-3745
63. Y. Hosokoshi Y, Tamura M, Nozawa K, Suzuki S, Kinoshita M, Sawa H, Kato R (1995) Magnetic properties and crystal structures of 2-hydro and 2-halo nitronyl nitroxide radical crystals. Synth Met 71:1795-1796

64. Mínguez Espallargas G, Recuenco A, Romero FM, Brammer L, Libri S, (2012) One-dimensional organization of free radicals via halogen bonding. CrystEngComm 14, 6381-6383
65. Zordan F, Brammer L (2005) Supramolecular Chemistry of Halogens: Complementary Features of Inorganic (M−X) and Organic (C−X') Halogens Applied to M−X···X'−C Halogen Bond Formation. J Am Chem Soc 127:5979-5989
66 Mínguez Espallargas G, Brammer L, Sherwood P (2006) Designing Intermolecular Interactions between Halogenated Peripheries of Inorganic and Organic Molecules: Electrostatically Directed M–X···X'–C Halogen Bonds. Angew. Chem., Int. Ed. 45:435-440
67. Brammer L, Minguez Espallargas G Libri S (2008) Combining metals with halogen bonds. CrystEngComm 10, 1712-1727
68. Ormond-Prout JE, Smart P, Brammer L (2012) Cyanometallates as Halogen Bond Acceptors. Cryst growth Des 12:205-216
69. Nishijo J, Miyazaki A, Enoki T, Watanabe R, Kuwatani Y, Iyoda M (2005) d-Electron-Induced Negative Magnetoresistance of a π−d Interaction System Based on a Brominated-TTF Donor.Inorg Chem 44:2493-2506
70. Shirahata T, Kibune M, Maesato M, Kawashima T, Saito G, Imakubo T (2006) New organic conductors based on dibromo- and diiodo-TSeFs with magnetic and non-magnetic MX_4 counter anions (M = Fe, Ga; X = Cl, Br). J Mater Chem 16:3381-3390
71. Thoyon D, Okabe K, Imakubo T, Golhen S, Miyazaki A, Enoki T, Ouahab L (2002) Conducting Materials Containing Paramagnetic Hexacyanometallate $[Cr(CN)_6]^{3-}$ and Iodine Substituted Organic Donor [DIETS]. Mol Cryst Liq Cryst 376, 25-32
72. Nishijo J, Ogura E, Yamaura J, Miyazaki A, Enoki T, Takano T, Kuwatani Y, Iyoda M (2000) Molecular metals with ferromagnetic interaction between localized magnetic moments. Solid State Commun 116:661-664
73. Devic T, Domercq B, Auban-Senzier P, Molinié P, Fourmigué M (2002) 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 TTF Dyads. Eur J Inorg Chem, 2844-2849
74. Imakubo T, Sawa H, Kato R (1995) Synthesis and crystal structure of the molecular metal based on iodine-bonded π-donor, $(IEDT)[Pd(dmit)_2]$. Chem Commun 1097-1098
75. Kato R (2014) Development of π-Electron systems Based on $[M(dmit)_2]$ (M = Ni and Pd); dmit: 1,3-dithiole-2-thione-4,5-dithiolate) Anion Radicals. Bull Chem Soc Jpn 87, 355-374
76. Kosaka Y, Yamamoto HM, Nakao A, Tamura M, Kato R (2007) Coexistence of Conducting and Magnetic Electrons Based on Molecular π-Electrons in the Supramolecular Conductor $(Me\text{-}3,5\text{-}DIP)[Ni(dmit)_2]_2$. J Am Chem Soc 129, 3054-3055
77. Fujiyama S, Shitade A,Kanoda K, Kosaka Y, Yamamoto HM, Kato R (2008) Suppression of electronic susceptibility in metal–Mott-insulator alternating material $(Me\text{-}3,5\text{-}DIP)[Ni(dmit)_2]_2$ observed using C^{13} NMR. Phys Rev B 77:060403(R)
78. Hazama K, Uji S, Takahide Y, Kimata M, Satsukawa H, Harada A, Terashima T, Kosaka Y, Yamamoto HM, Kato R (2011) Fermi surface and interlayer transport in the two-dimensional magnetic organic conductor $(Me\text{-}3,5\text{-}DIP)[Ni(dmit)_2]_2$. Phys Rev B 83:165129
79. Kosaka Y, Yamamoto HM, Tajima A, Nakao A. Cui H, Kato R (2013) Supramolecular $Ni(dmit)_2$ salts with halopyridinium cations -development of multifunctional molecular conductors with the use of competing supramolecular interactions. CrystEngComm 15:3200-3211
80. Kusamoto T, Yamamoto HM, Tajima N, Oshima Y, Yamashita S, Kato R (2012) Bilayer Mott System Based on $Ni(dmit)_2$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) Anion Radicals: Two Isostructural Salts Exhibit Contrasting Magnetic Behavior. Inorg Chem 51:11645-11654
81. Kusamoto T, Yamamoto HM, Kato R (2013) Utilization of σ-Holes on Sulfur and Halogen Atoms for Supramolecular Cation···Anion Interactions in Bilayer $Ni(dmit)_2$ Anion Radical Salts. Cryst Growth Des13:4533-4541

82. Allen FH, Goud BS, Hoy VJ, Howard JAK, Desiraju GR (1994) Molecular recognition via iodo•••nitro and iodo•••cyano interactions: crystal structures of the 1:1 complexes of 1,4-diiodobenzene with 1,4-dinitrobenzene and 7,7,8,8-tetracyanoquinodimethane (TCNQ). Chem. Commun 2729-2730
83. Chen Y-C, Wang P-F, Liu G-X, Xu H, Ren X-M, Song Y, Ni Z-P (2008) Organic radical molecular solids based on $[(TCNQ)_n]^-$ (n = 1 or 2): Syntheses, crystal structures, magnetic properties and DFT analyses. J. Phys. Chem. Solids 69, 2445-2452
84. Liu G-X, Huang R-Y, Ren X-M (2008) Four novel ion-pair compounds consisting of 7,7,8,8-tetracyanoquinodimethane (TCNQ) radical: Syntheses, crystal structures and properties. J. Mol. Struct. 891:11-18
85. Iyoda M, Kuwatani Y, Ogura E, Hara K, Suzuki H, Takano T, Takeda K, Takano J, Ugawa K, Yoshida M, Matsuyama H, Nishikawa H, Ikemoto I, Kato T, Yoneyama N, Nishijo J, Miyazaki A, Enoki T, (2001) Syntheses, Structure and Conducting Properties of Halogenated Ethylene-dioxytetrathiafulvalenes. Heterocycles 54, 833-848
86. Lieffrig J, Jeannin O, Guizouarn T, Pascale Auban-Senzier P, Fourmigué M (2012) Competition between the C−H···N Hydrogen Bond and C−I•••N Halogen Bond in $TCNQF_n$ (n = 0, 2, 4) Salts with Variable Charge Transfer. Cryst Growth Des 12:4248−4257
87. Lieffrig J, Jeannin O, Frackowiak A, Olejniczak I, Swietlik R, Dahaoui S, Aubert E, Espinosa E, Auban-Senzier P, Fourmigué, M (2013) Charge-Assisted Halogen Bonding: Donor–Acceptor Complexes with Variable Ionicity. Chem Eur J 19:14804-14813
88. Lieffrig J, Jeannin O, Vacher A, Lorcy D, Auban-Senzier P, Fourmigué M (2014) C–I•••NC halogen bonding in two polymorphs of the mixed-valence 2:1 charge-transfer salt $(EDT\text{-}TTF\text{-}I_2)_2(TCNQF_4)$, with segregated versus alternated stacks. Acta Cryst B70:141-148