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Chirality in molecular conductors from enantiopure or racemic coordination complexes

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There has been growing interest in recent years in the synthesis of multifunctional materials that exhibit both chirality and electrical conductivity. These materials can exhibit electrical magnetochiral anisotropy (eMChA) or the chirality induced spin selectivity (CISS) effect. Several families of chiral tetrathiafulvalene (TTF)-based donor molecules have been successfully used with acceptors or simple anions to prepare chiral molecular conductors. Chiral materials have also been obtained by employing racemic or enantiopure counter anions with chiral or achiral TTF donors. Most recently, enantiopure molecular conductors of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) and 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene (BDH-TTP) have been obtained through chiral induction from a racemic mixture of a coordination complex, which provides the anion. This Frontier article provides an overview of chiral molecular conductors and a summary of progress to date. It highlights future perspectives on how chirality can be introduced into molecular conductors by employing enantiopure or racemic coordination complexes, which also have the potential to introduce magnetism into the multifunctional material.

Introduction

The effect of chirality on the electrical properties of a material has only recently been experimentally observed owing to the lack of enantiopure materials with there being no examples in nature. Of interest in chiral conductors are the physical

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molecular organic conductors and molecular structures, and also the study of molecular structures in general. He has collaborated with groups in France, Canada and Japan and continues to do research.



phenomena of electrical magnetochiral anisotropy (eMChA)¹ and the chirality induced spin selectivity (CISS) effect.² Measuring the conducting behaviour of a material as a function of temperature in both enantiomeric forms as well as the racemate provides an understanding of the effects of chirality on the conductivity, or superconductivity, of a material.

eMChA occurs when a pair of isostructural enantiomeric materials, *e.g.* existing in enantiomorphic space groups, show different conductivities in an applied magnetic field depending upon their handedness and upon the direction of the electric current and the applied magnetic field. eMChA was first reported in 2001 in bismuth helices³ and 2002 in single-walled carbon nanotubes,⁴ and then in 2014 in the first molecular chiral conductor based on TTF,⁵ which will be the type of material that is the focus of this Frontier article (Fig. 1).

The effect of chirality on superconductivity was first reported in an individual nanotube of tungsten disulphide.⁶ In an achiral material, the current flows equally in both directions, but in WS₂ nanotubes, the superconductivity has been shown to reflect the chiral structure where the forward and backward current flows are not equivalent in an applied magnetic field.⁶ Further reports of superconductivity in non-centrosymmetric materials⁷ provide an intriguing prospect for exploration of exotic superconducting properties, quantum phenomena and non-trivial Cooper pairing.

Another physical phenomenon of interest in chiral conducting materials is the CISS effect. First reported in 1999, the CISS effect has implications for many fields including enantio-separation, chiral spintronics, and electron-transfer processes.⁸ Electrons with a certain spin can traverse the material more easily depending on the handedness of the chiral material owing to the CISS effect. The CISS effect has recently been observed in a molecular superconductor derived from BEDT-TTF, which crystallises in space group *P*2₁, owing to the

handedness of the relative arrangement of achiral anions and cations in κ -(BEDT-TTF)₂Cu(NCS)₂.⁹

Radical-cation salts

Molecular materials provide an advantage over traditional continuous-lattice solids because of their ability to achieve multifunctionality and enable observation of interplay between properties within the same material. Organic-inorganic hybrid salts consist of two molecular layers in the same single crystal, where each layer gives its own individual distinct properties to the material. Crystal engineering of TTF-based radical-cation salts has proved to be a valuable route to high-quality single crystals combining together chirality and conductivity in salts, which can be synthesised in both enantiomeric forms and as a racemate. These salts have produced a wide variety of electronic ground states and exhibit many interesting phenomena such as superconductivity, spin-Peierls transition and quantum spin-liquid behavior. The electrical conductivity arises from the inter-TTF sulphur-sulphur close contacts and the variety is due to the multitude of donor packing arrangements that are possible (Fig. 2). Radical-cation salts are built up of alternating stacks of conducting BEDT-TTF layers and insulating anion layers. Subtle changes in the packing of the anion layer can therefore have pronounced effects on the packing of the donor layer, *e.g.* through hydrogen-bonding interactions with the terminal ethylene groups of the BEDT-TTF molecules. The donor packing arrangement and sulphur-sulphur contacts and their electronic properties can be tuned by the size and shape of the anions and by their packing arrangement in the insulating layers of the salt.

Since the discovery of the first metallic salt TTF-TCNQ (TCNQ = tetracyanoquinodimethane) in 1973¹¹ and the first molecular superconductor (TMTSF)₂PF₆ (TMTSF = tetramethyl-tetraselenafulvalene) in 1980,¹² a large number of organic donor molecules have been synthesised. The organic donor molecule BEDT-TTF has been the most extensively used in radical-cation salts because it has given a large number of superconductors with many simple and polyatomic anions as well as coordination complexes. The highest superconducting *T*_c values to date are 14.2 K under applied pressure for β' -(BEDT-TTF)₂ICl₂¹³ and 11.6 K at ambient pressure for κ -(BEDT-TTF)₂Cu[N(CN)₂]Br.¹⁴

This Frontier article will present examples of four approaches that have been employed to combine chirality with conductivity in TTF-based radical-cation salts: using chiral TTF-based donors, chiral anions, and chiral guest solvent molecules or through chiral induction.

Chiral donor molecules

Using chiral donor molecules has proved to be the most promising route to introduce chirality into radical-cation salts.¹⁵ The first chiral TTF-type donor tetramethyl-(*S,S,S,S*)-BEDT-TTF



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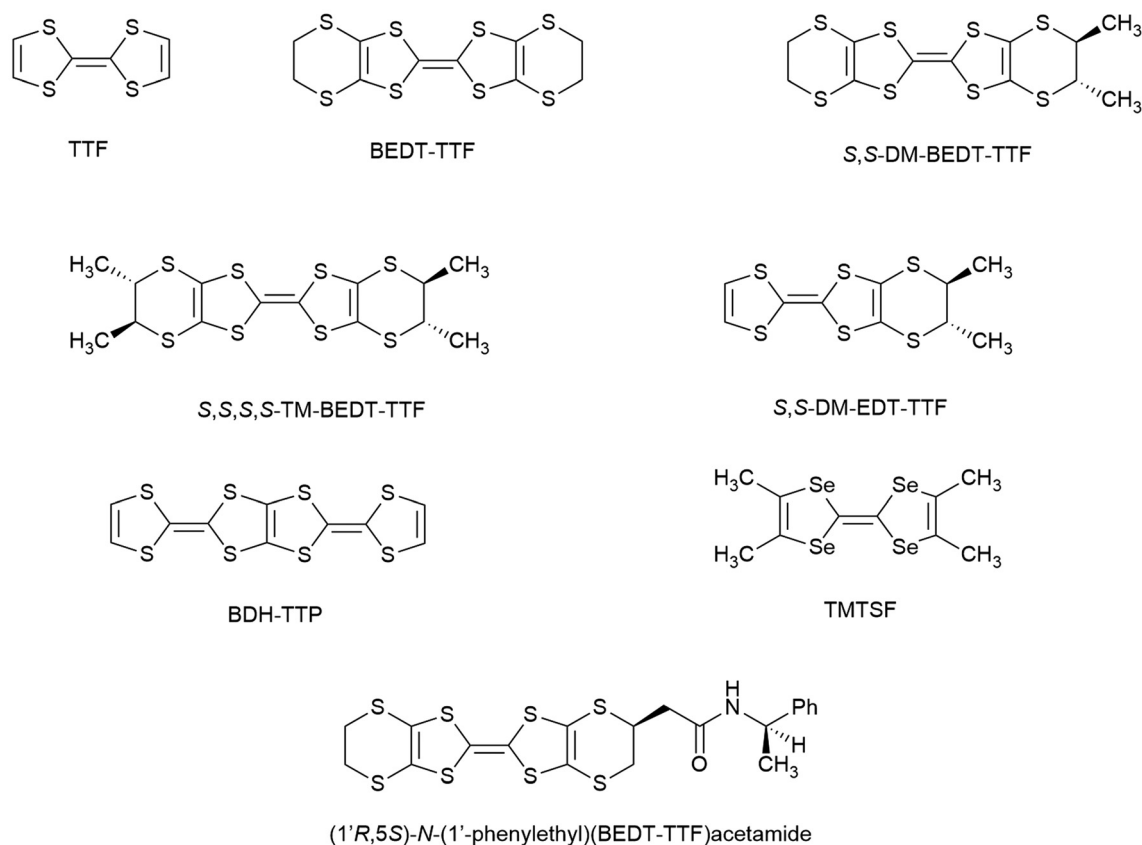
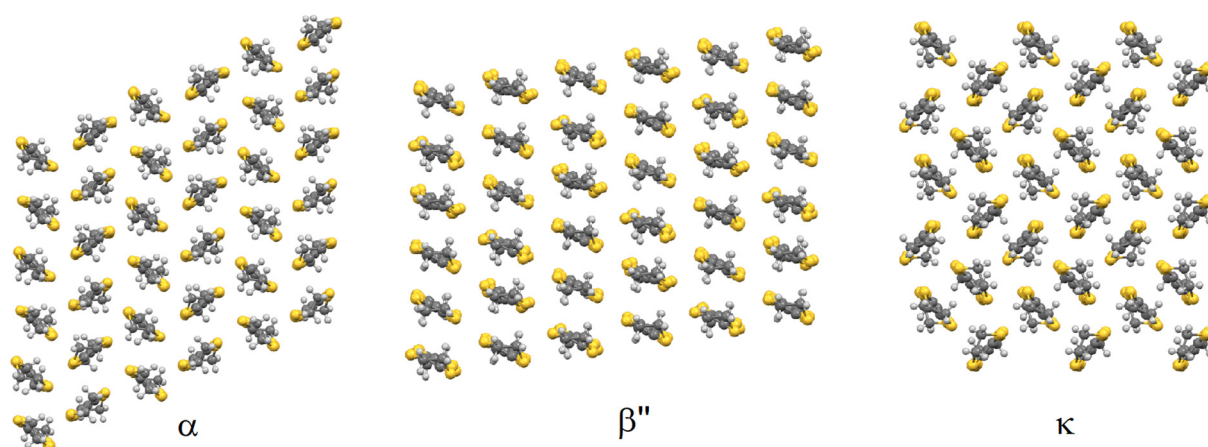


Fig. 1 Donor molecules.

Fig. 2 Alpha, beta'', and kappa BEDT-TTF packing arrangements.¹⁰

(TM-BEDT-TTF)¹⁶ (Fig. 1) has produced a number of radical-cation salts and many other enantiopure TTF derivatives have been synthesised with stereogenic carbon or sulphur atoms,¹⁵ axial chirality, *e.g.* TTF-BINOLs,¹⁷ TTF-helicenes,¹⁸ or spiro-TTFs.¹⁹

The first, and to date only, observation of eMChA in a bulk molecular conductor was reported in 2014 in a pair of enantiopure salts, *R,R* and *S,S*, of DM-EDT-TTF (dimethyl-

ethylenedithiotetrathiafulvalene).⁴ The enantiomers of DM-EDT-TTF crystallised with the anion ClO₄ in enantiomorphic space groups *P*_{6₂}22 and *P*_{6₄}22 and both were metals down to 40 K.

There are currently no chiral superconductors with chiral donor molecules – in 1992, κ -[(*S,S*)-DM-BEDT-TTF]₂ClO₄ was reported to show superconductivity under applied pressure, but this has recently been revisited and shown not to be super-



conductivity, but rather current induced charge order melting.²⁰

The CISS effect has very recently been observed with enantiopure donor molecules DM-BEDT-TTF and TM-BEDT-TTF *via* electrochemistry.²¹ These enantiopure donor molecules have been chemisorbed onto gold and nickel surfaces to act as working electrodes in spin-dependent electrochemistry experiments. Spin-filtering ability is observed as a result of the CISS effect.²²

There are also many examples of TTF derivatives with chiral side chains attached to one or both ends of the molecule, which can induce a chiral packing arrangement in the molecular material, such as helical crystal packing arrangements.¹⁵ The enantiopure donor (1'*R*,5*S*)-*N*-(1'-phenylethyl)(BEDT-TTF) acetamide (Fig. 1) produces a 4 : 1 salt with TCNQ, which is a metal down to at least 4.2 K, the lowest temperature observed for a chiral molecular metal. When this salt is warmed up above 283 K, it undergoes a transition from a metal to an insulator, granting it room-temperature switching capabilities.²²

Chiral anions

Several racemic coordination complexes have been used as the anion in BEDT-TTF radical-cation salts. Racemic anions Fe(croconate)₃,²³ Cr(2,2'-bipy)(oxalate)₂,²⁴ Fe(chloranilate)₃,²⁵ Fe(chlorocyananilate)₃,²⁶ and TRISPHAT^{27,28} (Fig. 3) have produced racemic BEDT-TTF salts, which show semiconducting or insulating behaviour. The only example of an enantiopure coordination complex being employed is the antimony L-tartrate dianion (Fig. 3), which crystallises with BEDT-TTF as the semiconducting α-[ET]₃[Sb₂(L-tartrate)₂]-CH₃CN in the chiral space group *P*₂₁₂₁₂.²⁹ The opposing enantiomer yielded α-[ET]₃[Sb₂(D-tartrate)₂]-CH₃CN, which was confirmed by circular dichroism to produce an identical, but opposite, spectrum.²⁹ Both a chiral and a racemic BEDT-TTF salt have been obtained from the organic magnetic anion PROXYL-CONHCH₂SO₃ (PROXYL = 2,2,5,5-tetramethyl-pyrrolidin-1-oxyl).³⁰ β''-(BEDT-TTF)₂(S- and *rac*-PROXYL-CONHCH₂SO₃) are metallic at room temperature and have similar broad metal-insulator transitions. The chiral salt shows resistivity three orders of magnitude higher than the racemic salt at 30 K, differing only in a deviation in the C-H bond direction at the chiral centre.

Fe(chloranilate)₃³¹ and TRISPHAT²⁸ have also crystallised with the enantiopure donor molecule TM-BEDT-TTF to produce chiral semiconductors, though in both cases the anion is a racemate in the radical-cation salt. Isostructural β-[TM-BEDT-TTF]₃PPh₄[KFe(chloranilate)₃]-3H₂O radical-cation salts have been synthesised with the TM-BEDT-TTF donor in enantiopure *S,S,S,S*- and *R,R,R,R*-forms and also as a racemic mixture, crystallising in the *P*₁, *P*₁ and *P*₁ space groups, respectively.³¹ The radical-cation salts *S,S,S,S*- and *R,R,R,R*-[TM-BEDT-TTF](*rac*-TRISPHAT)-2CH₃CN crystallising in the space group *P*₁ were obtained from racemic TRISPHAT. When starting from enantiopure Δ-TRISPHAT, the anion racemised

under the conditions of electrochemical growth and both Δ and Λ TRISPHAT enantiomers were present to give the same structure as that obtained from the racemate.

Transition-metal coordination complexes, including the aforementioned iron- and chromium-based anions, have been used to introduce magnetism into (super)conducting radical-cation salts of BEDT-TTF. Tris(oxalato)metallate anions, M(C₂O₄)₃³⁻ (Fe(C₂O₄)₃³⁻ shown in Fig. 3), are the most commonly used in radical-cation salts of BEDT-TTF and have produced paramagnetic superconductors,³² ferromagnetic metals,³³ and antiferromagnetic metals.³⁴

M(C₂O₄)₃³⁻ with a counter cation has the ability to form a hexagonal 2D insulating anion layer with the hexagons accommodating guest molecules (Fig. 4).³² It is possible to make small changes to the packing of the insulating anion layers to tune the desired magnetic and conducting properties.³⁵ Changing the metal of M(C₂O₄)₃³⁻ can change the magnetic properties of the material,³⁵ and the bridging ability of the oxalato ligand can allow long-range magnetic order through the introduction of a second metal centre into the material.³³ The two faces of a 2D insulating M(C₂O₄)₃³⁻ anion layer are adjacent to conducting BEDT-TTF layers so that small changes in the structure of the M(C₂O₄)₃³⁻ anion layer will lead to changes in the BEDT-TTF packing and affect the conducting properties (Fig. 5). Changing the metal of M(C₂O₄)₃³⁻, the counter cation (H₃O⁺, K⁺, NH₄⁺, and Na⁺), and in particular, the guest molecule in the hexagonal cavity (Fig. 5), has a marked effect on the packing and thus the conducting behaviour of the neighbouring BEDT-TTF layers (Fig. 6).³⁵

In the superconducting series β''-(BEDT-TTF)₄[(A)M(C₂O₄)₃]-GUEST (A = cation H₃O⁺, NH₄⁺, K⁺; M = Fe³⁺, Cr³⁺, Ga³⁺, Ru³⁺, Mn³⁺, Rh³⁺, Co³⁺, Al³⁺),³⁵ crystallising in the monoclinic space group *C*2/*c*, the BEDT-TTF molecules pack in a β'' motif (Fig. 6 left). The guest solvent molecule within the hexagonal cavity of the anion layer (*e.g.* benzonitrile in Fig. 4 left) has its -C≡N bond aligned along the *b* axis directed towards the M(C₂O₄)₃³⁻ metal centre. Including longer guest molecules increases the length of the *b* axis and this affects the neighbouring BEDT-TTF layers by increasing the superconducting *T*_c.³⁶

Each anion layer in these superconducting salts consists of only a single enantiomer of M(C₂O₄)₃³⁻ with the next layer consisting of only the opposite enantiomer to make the salt a racemate (Fig. 4 left and 5).³² Attempts to grow crystals of this salt starting from enantiopure Cr(C₂O₄)₃³⁻ produced no crystals initially, but once racemisation occurred in solution, racemic crystals began to grow.³⁷ However, these crystals were semiconducting polymorphs, crystallising in the space group *Pbcn*, owing to a different distribution of the enantiomers of M(C₂O₄)₃³⁻ (Fig. 4 right). In the *Pbcn* polymorph, a single anion layer does not contain a single enantiomer of M(C₂O₄)₃³⁻, but instead, each layer consists of alternating rows of Δ and Λ enantiomers, and the lattice is racemic (Fig. 4 right). This subtle change in the distribution of the enantiomers in the anion layer affects the packing of the guest molecule with the -C≡N group of the benzonitrile now disordered and directed towards the countercation instead of the



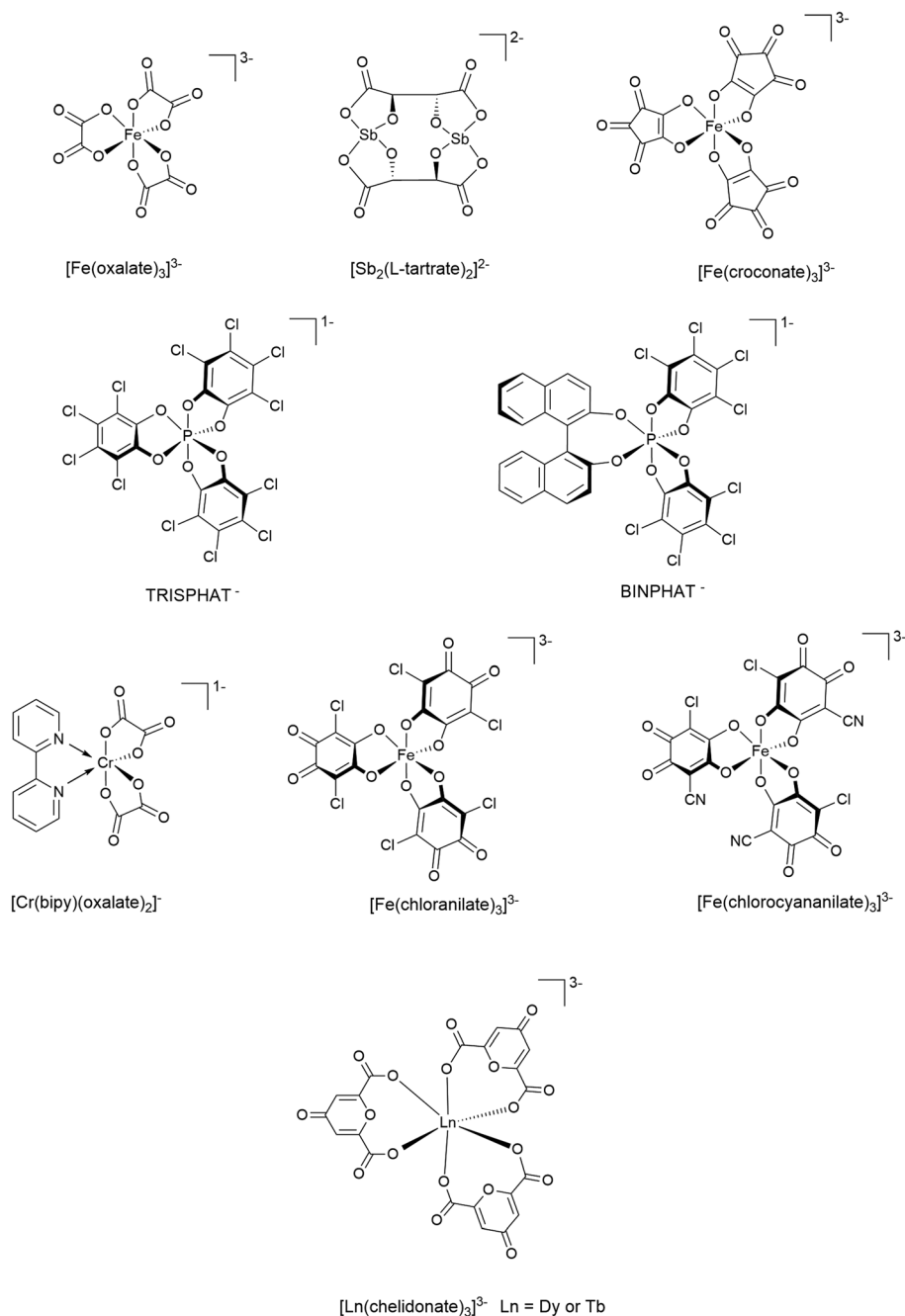
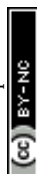


Fig. 3 Chiral and racemic coordination complex anions.

$\text{M}(\text{C}_2\text{O}_4)_3^{3-}$ metal centre (Fig. 4 right). Despite both $C2/c$ and $Pbcn$ salts being racemates, the distribution of Δ and Λ enantiomers leads to markedly different BEDT-TTF packing motifs, which gives rise to superconducting or semiconducting behaviour. In the $C2/c$ salt, the $\text{BEDT-TTF}^{0.5+}$ donors pack in a β'' motif, leading to metallic behaviour and superconductivity at low temperatures (Fig. 6 left), whilst in the $Pbcn$ salt, BEDT-TTF^{1+} dimers (red circle, Fig. 6 right) are surrounded by BEDT-TTF^0 monomers (blue circles, Fig. 6 right), resulting in semiconducting behaviour.³⁶

A recent report presented the first radical-cation salt of BEDT-TTF with a racemic nine-coordinate propeller-shaped lanthanide-based anion, which offers the possibility of including not only chirality but also magnetism or luminescence into these multifunctional materials. The labile $[\text{Ln}(\text{chelidonate})_3]^{3-}$ anions (Ln = Dy or Tb) are present at a 50 : 50 ratio in the salt with the enantiomers segregated into rows within each anion layer (Fig. 7).³⁸ The salt $\alpha\text{-(BEDT-TTF)}_5\text{Dy}(\text{chelidonate})_3\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}$ is a semiconductor, whilst the isomorphous Tb salt is a semimetal.



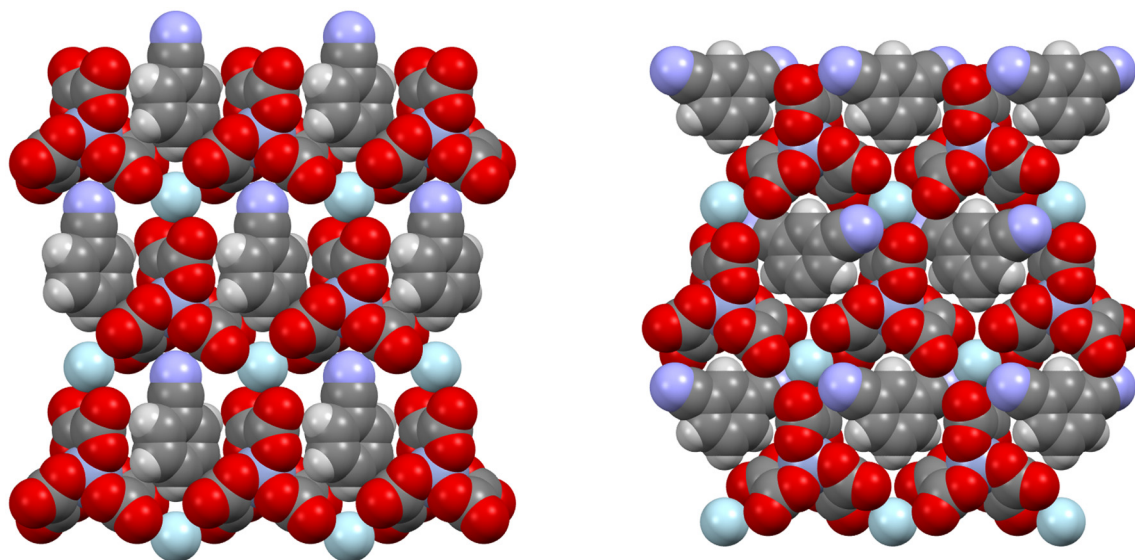


Fig. 4 Hexagonal anion layer in the $C2/c$ (left) and $Pbcn$ (right) $(BEDT-TTF)_4[(A)M(C_2O_4)_3] \cdot GUEST$ salts.

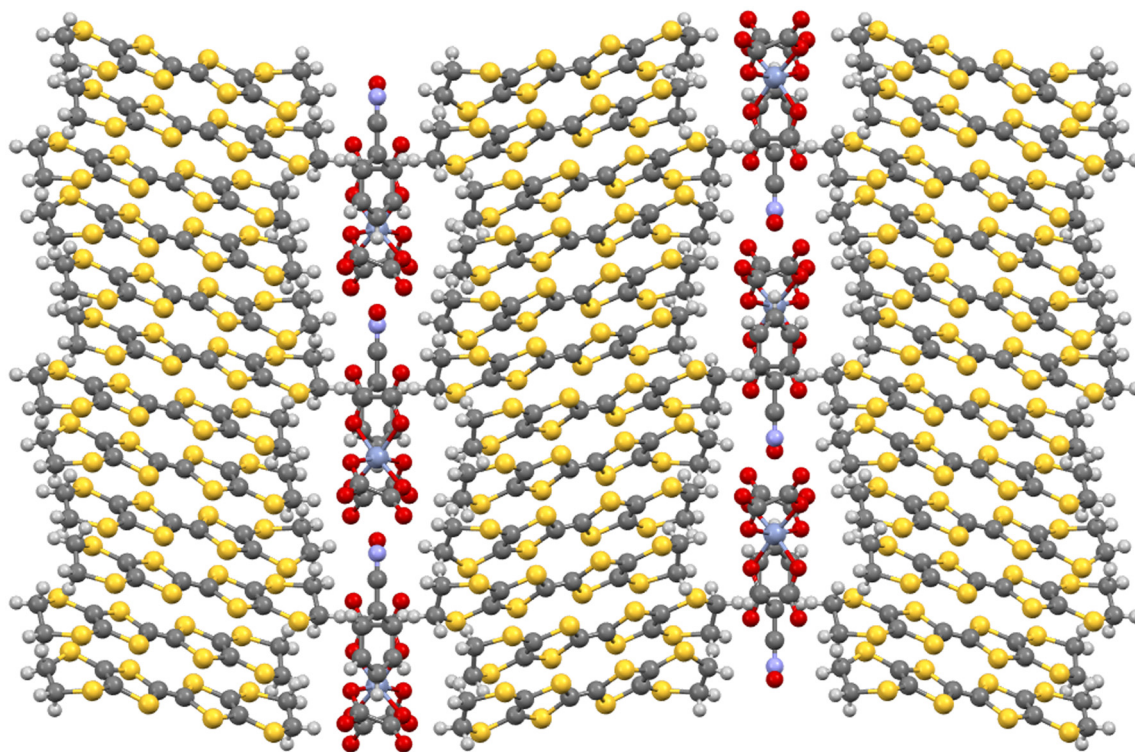


Fig. 5 Layered structure of $(BEDT-TTF)_4[(A)M(C_2O_4)_3] \cdot GUEST$ salts.

Chiral guest molecules

A guest molecule is often included in these salts, which is the solvent used in the electrocrystallisation method of crystal growth. This limits the number of guest molecules that are possible to only those that can be used for electrocrystallisation. A chiral guest has been introduced using *sec*-phenethyl

alcohol as both enantiopure (*S*)- and racemic (*R/S*)-forms.³⁹ *sec*-Phenethyl alcohol is asymmetrical and also a larger guest compared to those used in the aforementioned β'' - $(BEDT-TTF)_4[(A)M(C_2O_4)_3] \cdot GUEST$ superconducting salts (*e.g.* benzonitrile, bromobenzene, and nitrobenzene). The asymmetrical *sec*-phenethyl alcohol molecules do not sit centrally within the hexagonal cavities of the anion layer and protrude



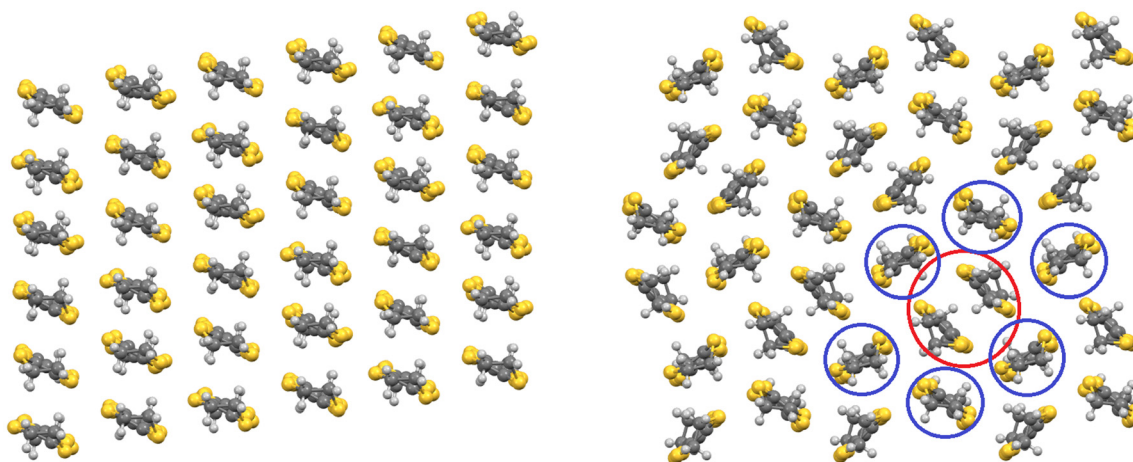


Fig. 6 Different packing arrangements in the BEDT-TTF donor layer in the *C2/c* (left) and *Pbcn* (right) $(\text{BEDT-TTF})_4[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{GUEST}$ salts.

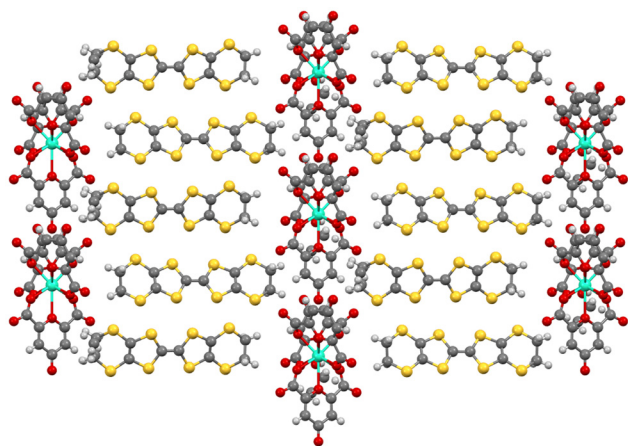


Fig. 7 Layered structure of the $\alpha\text{-(BEDT-TTF)}_5\text{M}(\text{clo})_3\cdot\text{EtOH}\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Tb}$ or Dy) salts.

on just one side of the anion layer. This leads to different BEDT-TTF donor packing motifs on either side of each anion layer, one α and the other β ". The enantiopure (*S*)- and racemic (*R/S*)-*sec*-phenethyl alcohol BEDT-TTF salts are isostructural but crystallise in *P1* and $\bar{P}1$ space groups, respectively. In the enantiopure salt, only the (*S*)-*sec*-phenethyl alcohol is present in the hexagonal cavity, whilst in the racemic salt, both *R* and *S* enantiomers of *sec*-phenethyl alcohol are present but disordered at a ratio of 58.5 : 41.5. Both enantiopure and racemic salts exhibit metal-insulator behavior, but a more pronounced metal-insulator transition is observed in the racemic salt as a result of the structural disorder.³⁹

Chiral induction

A series of $\text{BEDT-TTF}/\text{M}(\text{C}_2\text{O}_4)_3^{3-}$ salts has been obtained when using enantiopure (*R*)-(-)-carvone as a chiral guest mole-

cule. Using (*R*)-(-)-carvone alone produced no crystals, possibly due to the large size of the guest not fitting within the hexagonal cavities in the 2D $\text{M}(\text{C}_2\text{O}_4)_3^{3-}$ layer. However, using (*R*)-(-)-carvone mixed with a second solvent leads to this second solvent entering the radical-cation salt as the guest molecule, and the presence of (*R*)-(-)-carvone leads to chiral induction in tris(oxalato)metallates.⁴⁰ This series of salts contain either an enantiomeric excess of the complex anion or just the single enantiomer, $\Delta\text{-M}(\text{C}_2\text{O}_4)_3^{3-}$, despite starting from a racemic mixture. Crystallising in space groups *P2*₁, *P2*₁*2*₁*2*₁, or *P1*, these chiral salts are semiconductors having a formula of $(\text{BEDT-TTF})_3[(\text{A})\text{M}(\text{C}_2\text{O}_4)_3]\cdot\text{GUEST}$ ($\text{M} = \text{Al}^{3+}$, Cr^{3+} ; $\text{A} = \text{Li}^+$, Na^+ , NH_4^+) (Fig. 8) with a 3 : 1 ratio of donor : anion, compared to the 4 : 1 ratio in superconducting salts.⁴⁰

Similarly, chiral induction has been observed when adding a chiral solid additive during the electrocrystallisation of radical-cation salts starting from a racemic mixture of $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. The addition of enantiopure *L*-(+)-tartaric acid affords a semiconducting radical-cation salt $\alpha\text{-(BEDT-TTF)}_5[\text{D-Fe}(\text{C}_2\text{O}_4)_3]\cdot[\text{L-(+)-tartaric acid}]_2$, which contains only the single enantiomer $\Delta\text{-Fe}(\text{C}_2\text{O}_4)_3$, crystallising in the space group *C2*.⁴⁰ Using the same method with enantiopure (*R*)-(-)-3-hydroxytetrahydrofuran as the solid additive did not lead to resolution of the $\text{Fe}(\text{C}_2\text{O}_4)_3$ anion but the additive was included in the lattice to afford semiconducting $\alpha\text{-(BEDT-TTF)}_{12}[\text{Fe}(\text{oxalate})_3]_2\cdot(\text{H}_2\text{O})_{16}\cdot(\text{ethanol})\cdot(\text{R})\text{-(+)-3-hydroxytetrahydrofuran}$, crystallising in the space group *P2*₁.⁴¹

Spiroborate anions offer the possibility of more than one chiral centre: at the boron centre (if the bidentate ligand is asymmetrical) and on the ligand itself (if the ligand has a chiral centre). The huge pool of asymmetrical or chiral bidentate ligands available can lead to a great variety of sizes, shapes and packing modes, which has the potential to produce radical-cation salts with a wide variety of electrical properties and phenomena. Despite being labile at the boron centre, chiral crystallisation has been observed in radical-cation salts, which include only a single spiroborate enantiomer or a single pair of diastereomers.



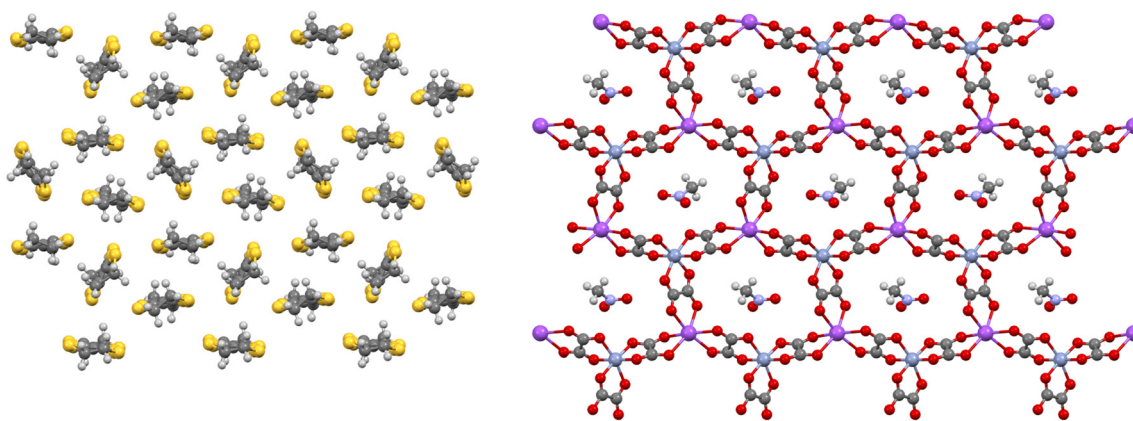


Fig. 8 Donor (left) and anion (right) layers in the 3 : 1 salt (BEDT-TTF)₃[NaCr(C₂O₄)₃]·nitromethane.

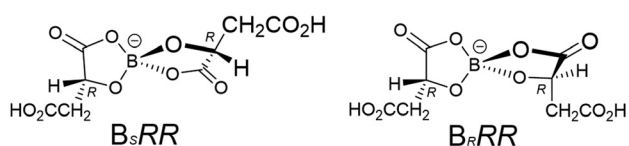


Fig. 9 The two spiroborate anions B_5RR (left) and B_6RR (right) obtained using *R*-malic acid.

The spiroborate anion $B(\text{malate})_2^-$ prepared from (*R*)-(-)-malic acid retains the (*R*) chirality on the malate ligands but is racemic at the boron centre, yielding the B_5RR and B_6RR enantiomers (Fig. 9). Upon electrocrystallisation with BEDT-TTF, the radical-cation salt contains only the B_5RR enantiomer, crystallising in the space group $P2_12_12_1$.⁴² When using racemic malic acid to synthesise the spiroborate anion, there are six enantiomers present: B_6RR and B_5RR with *R*-malate

ligands; B_6SS and B_5SS with *S*-malate ligands; and B_6RS and B_5RS with a mixture of both *R*- and *S*-malate ligands. Electrocrystallisation of a mixture of these six enantiomers with BEDT-TTF produces a radical-cation salt, which contains only the diastereomeric pair B_5RS and B_6RS .⁴²

This preference for certain enantiomers or diastereomers over others during electrocrystallisation has also been observed in radical-cation salts of spiroborates with mandelate ligands.⁴³ The first chiral radical-cation salt with the donor molecule BDH-TTF (Fig. 1) was grown from a racemic mixture of $B_5(S\text{-chloromandelate})_2$ [B_6SS and B_5SS] to afford the radical-cation salt $\kappa\text{-BDH-TTF}_2[B_5(S\text{-chloromandelate})_2]$, which includes only the B_5SS enantiomer, crystallising in the space group $P2_1$.⁴⁴ This salt is a metal down to at least 4.2 K, which is the lowest temperature that has been observed for a chiral molecular metal. Preference for certain enantiomers and diastereomers has also been observed in BEDT-TTF radical-cation

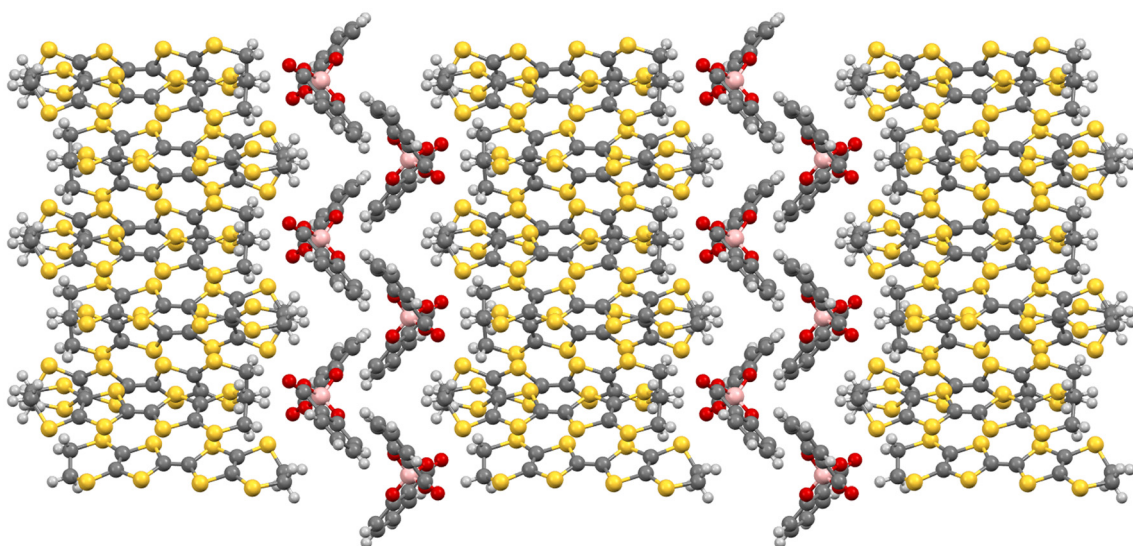


Fig. 10 Double anion layer in $\kappa\text{-(BEDT-TTF)}_2[B_6RS(\text{salicylate})_2]$.



salts of B(mandelate)₂ and B(chloromandelate)₂. When using enantiopure mandelate ligands, the crystals obtained *via* electrocrystallisation have a macromolecular helical morphology.⁴³

Electrocrystallisation of enantiopure *R,R*- or *S,S*-B[1,1'-bis(BINOL)]₂ with BEDT-TTF did not produce crystals, but starting from the racemic anion yielded crystals of the radical-cation salt (BEDT-TTF){B[1,1'-bis(BINOL)]₂}-THF, which contains a 1 : 1 mixture of *R,R*- and *S,S*-B[1,1'-bis(BINOL)]₂, but does not contain the *meso-R,S*-form.⁴⁵

Recently, a new quantum spin-liquid candidate has been found in a BEDT-TTF salt with the spiroborate anion B_{R/S}(salicylate)₂.⁴⁶ Despite first being proposed 50 years ago, the challenge of realizing a quantum spin liquid remains,^{47,48} which could be key to creating qubits for quantum computing or understanding the mechanism of high-temperature superconductivity.

Grown from racemic B_{R/S}(salicylate)₂, κ-(BEDT-TTF)₂-[B_{R/S}(salicylate)₂] (Fig. 10) is a 2D Mott insulator with a triangular lattice of BEDT-TTF molecules in the kappa packing arrangement (Fig. 2 right), crystallising in the space group *P*₂₁ as an inversion twin. There have previously been a few 2D molecular quantum spin-liquid candidates with a triangular lattice and *S* = ½ spin system, but this is the first example to have no inversion symmetry centre, which may show novel behaviour due to the low symmetry. The 6 K anomaly in the specific heat capacity data is 2 or 3 times larger than those of previous molecular quantum spin-liquid candidates κ-(BEDT-TTF)₂Cu₂(CN)₃ and EtMe₃Sb[Pd(dmit)₂]₂.⁴⁶ The anion layer in κ-(BEDT-TTF)₂[B_{R/S}(salicylate)₂] consists of two rows of the spiroborate anion (Fig. 10), resulting in a 2D salt with widely separated conducting donor layers.

Conclusions and outlook

The question of whether chirality has an effect on the electrical properties of a material has only recently been experimentally investigated, owing to the lack of enantiopure conducting materials. Challenges with obtaining high-quality crystalline materials have been overcome to allow molecular conducting materials to be prepared from enantiopure donors, anions, or guest solvents, as well as through chiral induction. A chiral molecular superconductor has also crystallised in the space group *P*₂₁ grown from an achiral donor and an achiral anion. Radical-cation salts offer the possibility of preparing families of materials in left-handed, right-handed, and racemic forms for direct comparison of their physical properties. Given the large number of radical-cation salts that have shown superconductivity over more than 40 years coupled with the multiple routes to introduce chirality into these systems highlighted in this Frontier article, there is a high likelihood that families of enantiopure metals, quantum spin-liquid candidates and superconductors can be discovered in this type of material.

Data availability

No new research data are presented in this Dalton Frontier article.

Conflicts of interest

There are no conflicts to declare.

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