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Chiral, flexible binaphthol-substituted tetrathiafulvalenes

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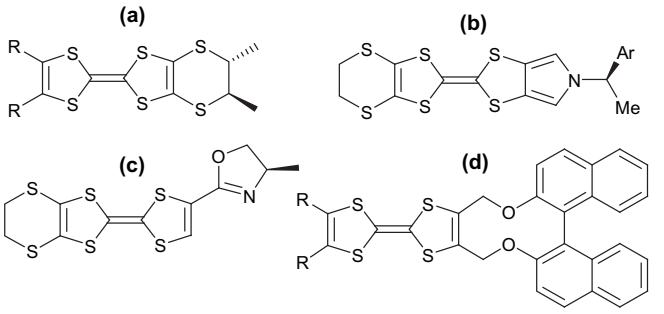
ABSTRACT

Novel chiral tetrathiafulvalene derivatives incorporating one or two binapthol moieties are described where two flexible (Ar–O)–CH_2–CH_2–S–(TTF) links generate a large 14-membered ring on one or both sides of the TTF core. The symmetric donor molecule with two chiral binaphthol moieties has been prepared as enantiopure (*RR*) or (*SS*) isomer, as well as diastereomeric mixture containing the (*RR*), (*SS*), and *meso* (*RS*)=(*SR*) forms. Other unsymmetrically substituted derivatives bearing one single chiral binaphthol substituent on one side were also prepared in their enantiopure (*R*) and (*S*) forms and as racemic mixture. X-ray crystal structure determinations of different donor molecules show that the TTF tend to associate into face-to-face dyads with a strong folding of the dithiole rings along the S···S hinge while the binaphthol moieties adopt a *cisoid* conformation with a dihedral angle between naphthyl rings in the range 80–85°. The racemic EDT/TTF derivative allowed for the isolation of two crystalline charge-transfer compounds with the electron acceptors TCNQ and $TCNQF_4$. The donor and acceptor molecules are organized into homo-dyads in the TCNQ neutral complex, insulating and diamagnetic. On the other hand, a full charge transfer occurs in the $TCNQF_4$ salt, with weakly interacting chiral TTF cation and $TCNQF_4$ anion radicals.

1. Introduction

Following the early days of molecular conductors based on partially oxidized donor molecules, such as perylene or tetrathiafulvalene,[1] different recent strategies have been developed to combine into multifunctional materials metallic conductivity with other interesting properties,[2] such as, for example, ferromagnetism,[3] or chirality. Chiral conductors are particularly appealing for the observation of a new phenomenon, referred to as the electrical magneto-chiral anisotropy effect.[4] As recently reviewed by Avarvari and Wallis,[5] two main strategies have emerged in the last years for the elaboration of organic conductors derived from the prototypical tetrathiafulvalene (TTF) donor molecule. The first one is based on the synthesis of chiral TTF donor molecules, for further electrocrystallization with a variety of anions; the second one takes advantage of the availability of various chiral anions, such as antimony tartrate[6] or camphorsulfonate[7] to be used as electrolytes in electrocrystallization experiments with achiral TTFs.

Based on the TTF approach (Scheme 1), the very first chiral tetrathiafulvalene described to date, was reported by Wallis and Dunitz in a tetramethyl derivative of BEDT/TTF,[8] and was followed by a large number of other chiral TTF derivatives.[9] More recently, TTF oxazoline derivatives[10] afforded a complete series of chiral organic metals with (*R*)-, (*S*)- and racemic salts,[11,12] highly sensitive to the eventual presence of disorder in the racemic salts. As another source of chirality, atropo-isomers as found in binaphthol derivatives, are available with very high enantiomeric purity,[13] and their introduction on a tetrathiafulvalene core would favor chiral solid state organizations through a combination of π–π interactions and overlap interactions of open-shell molecules.



Scheme 1. Examples of chiral TTF derivatives based on point chirality (a–c) and axial chirality (d).

Actually, only a few TTF derivatives incorporating a binaphthyl moiety have been described to date. Most of them are based on a single binaphthol platform bearing a TTF moiety coupled to each naphthalene ring, through either conjugated[14] or non-conjugated linkers,[15,16] affording in all cases highly flexible molecules with two TTF moieties per binaphthol unit. On the other hand, monomeric TTFs bearing one or two binaphthol moieties were only

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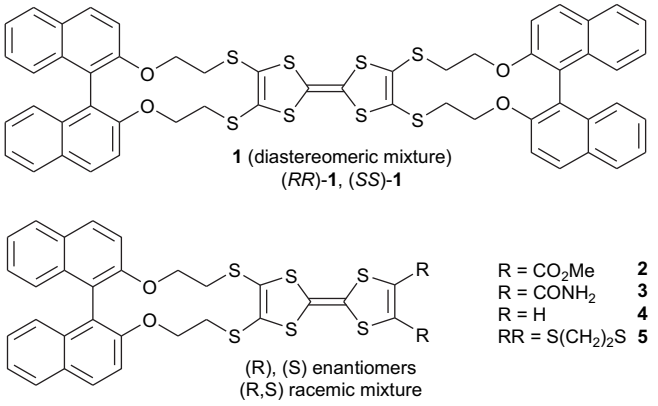
reported very recently.[17] These molecules, described in Scheme 1d, adopt a rigid structure with a constrained 10-membered ring incorporating the binaphthol moiety and limiting the possibility for intermolecular interactions in the solid state. Looking for a less constrained, extended link between the TTF and binaphthol moieties, we envisioned the novel tetrathiafulvalene derivatives **1**–**5** (Scheme 2), where the binaphthol moiety is now anchored to the TTF core through two flexible $-CH_2-CH_2-S-$ links generating a larger 14-membered ring. Accordingly, molecule **1** incorporating two chiral binaphthol moieties has been prepared as enantiopure (*RR*) and (*SS*) isomers, as well as diastereomeric mixture containing the (*RR*), (*SS*), and *meso* (*RS*)=(*SR*) forms. Other unsymmetrically substituted derivatives **2**–**5** with one single chiral binaphthol substituent were prepared in their enantiopure (*R*) and (*S*) forms and as racemic mixture. The geometry adopted by the different donor molecules in their crystalline state will be analyzed in details, as well as their electrochemical properties. The favorable redox potential and extended geometry of racemic EDT/TTF derivative (*R*,*S*)-**5** allowed for the isolation of two charge-transfer compounds with the electron acceptors TCNQ and $TCNQF_4$, whose structure and properties will be analyzed in details.



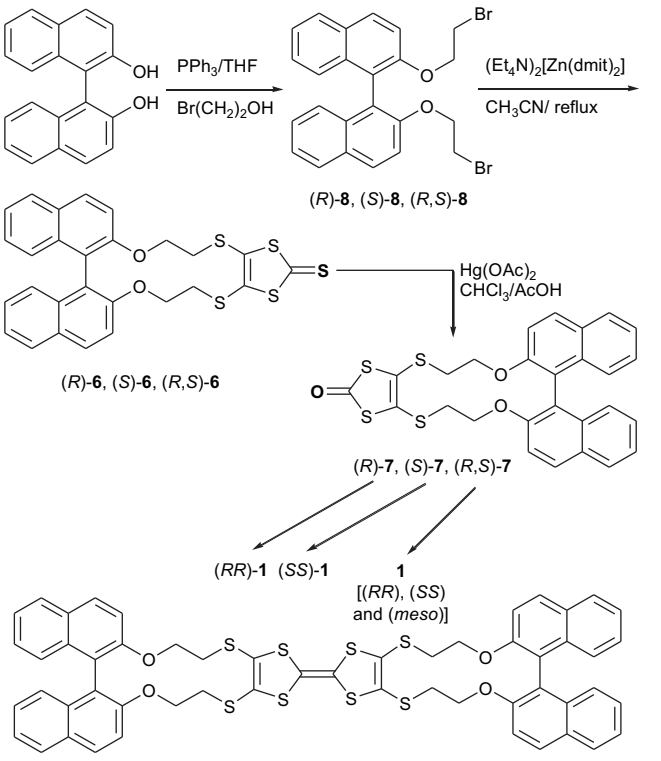
Scheme 2.

2. Results and discussion

2.1. Syntheses

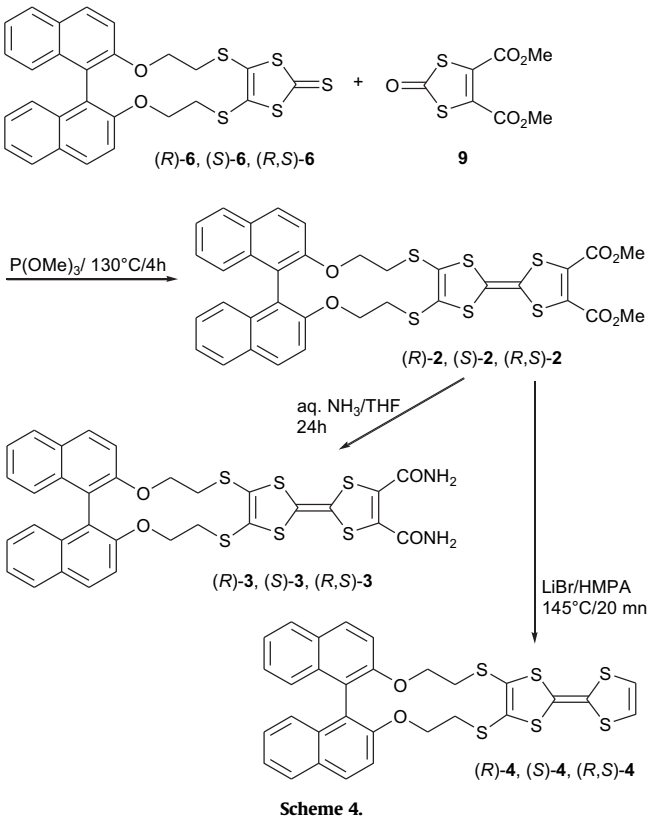
The preparation of all TTFs described here (Scheme 3) is based on phosphite-mediated cross coupling reactions involving the chiral trithiocarbonate **6** or the dithiocarbonate **7**. The key chiral intermediate **6** has been prepared in two steps from 1,1′-bi-2-naphthol (abbreviated as binaphthol in the following). As described by Zhu et al. with the (*R*) isomer of binaphthol,[15] the Mitsunobu reaction between binaphthol and 2-bromoethanol afforded the dibromo derivative **8** in ≈60% yield. Alkylation of $(Et_4N)_2[Zn(dmit)_2]$ with (*R*)-**8**, (*S*)-**8** or (*R*,*S*)-**8** was conducted in high dilution conditions to favor the formation of cyclic trithiocarbonate (*R*)-**6**, (*S*)-**6** and racemic (*R*,*S*)-**6**, affording the three compounds in 80–85% yield. Oxymercuration with $Hg(OAc)_2$ afforded the corresponding dithiocarbonates **7** in excellent yields. Coupling of the latter in the presence of $P(OMe)_3$ afforded the symmetrically substituted TTF **1** in 70–75% yield, either as a pure enantiomer (*RR*)-**1** and (*SS*)-**1** when starting from (*R*)-**6** and (*S*)-**6**, respectively, while the coupling reaction of the racemic (*R*,*S*)-**6** afforded the diastereoisomeric mixture which could not be separated by silica gel chromatography.

The unsymmetrically substituted TTFs *ortho*-diesters **2** incorporating one single binaphthol moiety are useful starting units toward the corresponding primary amides **3**, while their decarboxylation gives access to the simplest TTF derivatives of the series, compounds **4**. Compounds **2**, either as pure enantiomers or



Scheme 3. Synthesis of the chiral intermediates **6** and **7** and the symmetrically substituted TTF **1**.

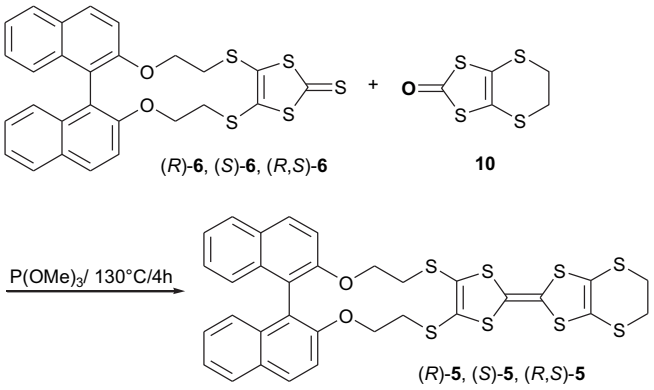
as racemic mixture, were prepared by phosphite-mediated cross coupling reaction of trithiocarbonate **6** with an excess of 4,5-bis-(carboxymethyl)-1,3-dithiole-2-one (**9**) (Scheme 4), affording the diesters **2** in 55% yield after recrystallization. TTF *ortho*-diesters derivatives have been reported to react cleanly to the



Scheme 4.

corresponding *ortho*-diamides upon reaction with an excess of ammonia or primary amines.[18,19] Indeed, reaction of (*R*)-**2**, (*S*)-**2** and racemic (*R*,*S*)-**2** with aqueous ammonia afforded the corresponding primary diamides (*R*)-**3**, (*S*)-**3** and racemic (*R*,*S*)-**3** in excellent yields (90%) as microcrystalline orange powders. Decarboxylation of the diesters in the presence of LiBr at elevated temperatures,[20] was also successfully attempted and provided unsubstituted (*R*)-**4**, (*S*)-**4**, and racemic (*R*,*S*)-**4** compounds as orange crystals.

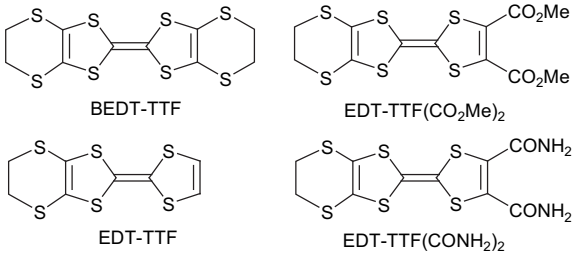
The preparation of the ethylenedithio (EDT) derivatives **5** is based on similar cross coupling reactions, involving the trithiocarbonates **6** with an excess of dithiocarbonate **10**. The cross coupling product **5** is isolated after separation from the symmetrical products **1** and BEDT/TTF in 85% yield. Note that the alternative coupling with the dithiocarbonate **7** and the trithiocarbonate analog of **10** afforded the desired product in significantly lower yields (45–60%) (Scheme 5).



Scheme 5.

Cyclic voltammetry experiments were performed on all newly prepared TTF derivatives, in order to determine the donor capability, by comparison with known compounds. All TTF exhibit two characteristic reversible oxidation waves (Table 1 and Figs. S1–5). No differences are observed between the isomers of the same compounds. As seen from Table 1, the redox potentials for **1** closely matches those reported for BEDT/TTF, demonstrating that our substitution pattern incorporating the binaphthol moiety does not modify significantly the redox ability of the TTF core. A similar trend is observed for the other substituted TTFs **2**–**5** whose redox potentials closely match those of the corresponding derivatives with a simple ethylenedithio substituent.

Table 1
Cyclic voltammetry data for TTFs **1**–**5** and reference compounds (in V vs SCE)



Compound	Solvent	$E^1_{1/2}$	$E^2_{1/2}$	Ref.
1	CH_2Cl_2	0.56	0.95	This work
5	CH_2Cl_2	0.52	0.92	This work
BEDT/TTF	$Cl(CH_2)_2Cl$	0.56	0.96	21
2	CH_2Cl_2	0.68	1.09	This work
EDT/TTF(CO$_2$Me)$_2$	CH_3CN	0.64[a]	0.95[a]	22
3	CH_2Cl_2	0.68	0.88	This work
EDT/TTF(CONH$_2$)$_2$	THF	0.73	0.96	19
4	CH_2Cl_2	0.45	0.92	This work
EDT/TTF	CH_3CN	0.44	0.75	20

[a] Versus Ag/AgCl.

2.2. Molecular and solid state structures of 1, 2, and 4

Good quality crystals could be obtained for the enantiopure bis(binaphthol) compounds (*RR*)-**1** and (*SS*)-**1** upon recrystallization from CH_2Cl_2/pentane. They both crystallize in the monoclinic system, space group C2, with the molecule and the pentane located on the twofold axis (Fig. 1). The TTF core exhibits strong distortions from planarity with a folding of the central dithiole ring along the S···S hinge, which amounts to 23.6 (1)°. The twist angle between the two naphthyl moieties is found at 83.95 (3), that is, a *cisoid* conformation, close however to the perpendicular orientation (90°).

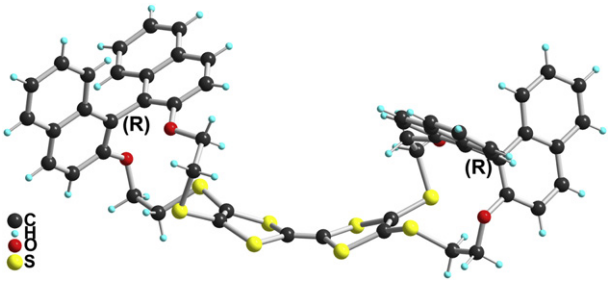
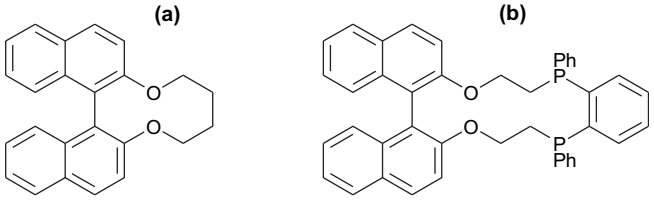


Fig. 1. View of (*RR*)-1.

This behavior contrasts with that observed on other binaphthol derivatives where the two oxygen atoms are included in a cycle. 10-membered derivatives, such as the TTF derivatives described earlier[17] (Scheme 1d) or the butylene derivative (Scheme 6a) exhibit a systematic *cisoid* conformation with a dihedral angle between the two naphthyl ring around 65–75°. The only structurally characterized derivative with a 14-membered ring (Scheme 6b) adopts a *transoid* conformation with a dihedral angle of 112.13°,[23] demonstrating the flexibility of these molecules even when constrained in cycles.



Scheme 6.

Crystals of the racemic diester (*R*,*S*)-**2** were obtained by recrystallisation from CH_2Cl_2/petrol ether. (*R*,*S*)-**2** crystallizes in the triclinic system, space group *P*−1, with one molecule in the asymmetric unit (Fig. 2a). The (*R*) and (*S*) isomers are associated into inversion-centered dyads, with again a strong folding of the dithiole rings along the S···S hinge, 19.01 (8)° along S1···S2, 20.01 (8)° along S3···S4, while the shortest intermolecular S···S distances amount to 3.64 Å, at van der Waals contact. As observed in (*RR*)- and (*SS*)-**1**, an almost perpendicular orientation between the two naphthyl rings was found, with a dihedral angle of 86.20 (3)°.

The simpler TTF derivative **4** was also obtained in a crystalline form in its racemic mixture (*R*,*S*)-**4**. It crystallizes in the triclinic system, space group *P*−1, with one molecule in general position. The outer unsubstituted dithiole ring of the TTF core is disordered on two positions. As in (*R*,*S*)-**2**, the dithiole ring are folded, 20.66

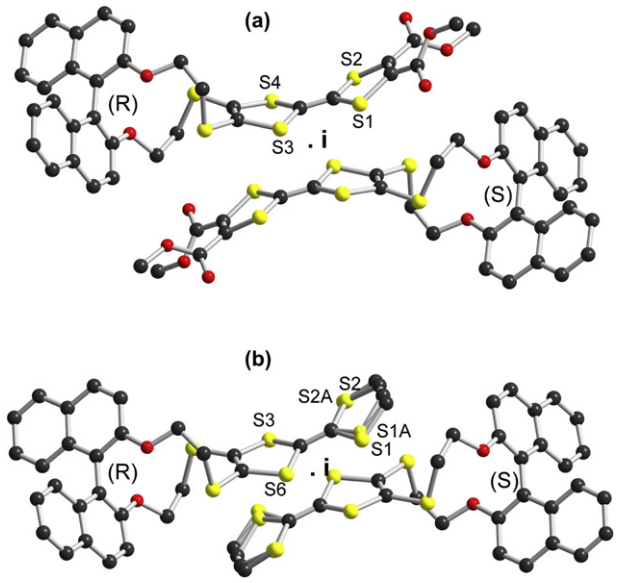


Fig. 2. Organization within centrosymmetric dyads in (a) racemic diester (*R*,*S*)-**2**, (b) racemic TTF (*R*,*S*)-**4**.

(9), 22 (1), and 16 (1)° along the S3···S6, S1···S2, and S1A···S2A hinges, respectively while the binaphthyl rings adopt a *cisoid* conformation with a dihedral angle of 79.91 (3). Intermolecular S···S distances within the inversion-centered dyads exceed 4 Å.

2.3. The EDT/TTF derivatives 5 and their salts

Chemical oxidation of the different donor molecules **1**–**5** with TCNQ or $TCNQF_4$ afforded crystals only with the racemic EDT/TTF derivative (*R*,*S*)-**5**. In the following, we will first describe the X-ray crystal structures obtained for the neutral enantiopure (*R*)-**5** and (*S*)-**5**, which will provide us with reference data for the intramolecular bond distances within the TTF core in **5**. In a second part, we will discuss the structures of the TCNQ and $TCNQF_4$ salts, in order to determine the degree of charge transfer within the two compounds, and its correlation with the electronic properties.

(*R*)-**5** and (*S*)-**5** are isostructural, they crystallize both in the orthorhombic system, space group $P2_12_12_1$, with two crystallographically independent molecules in the asymmetric unit, together with two CH_2Cl_2 molecules. Geometrical characteristics are collected in Table 2. Note again the strong distortion from planarity of the TTF core. In the solid state, the molecules are associated two-by-two (Fig. 3) with the shortest S···S intermolecular distance (3.74 Å) close the sum of van der Waals radii.

Reactions of the enantiopure (*R*)-**5** or (*S*)-**5** molecules with TCNQ or $TCNQF_4$ afforded only very soluble material, which could not be properly crystallized. On the other hand, slow cooling of warm CH_3CN solutions of racemic (*R*,*S*)-**5** with equimolar amount of TCNQ or $TCNQF_4$ afforded in both cases 1:1 compounds incorporating

Table 2
Structural characteristics of the EDT/TTF derivatives **5**. The *a* distance refers to the central C_i═C_i and *b* to the averaged C_i–S intramolecular distances. θ_1 and θ_2 are the folding angles of the dithiole ring, on the EDT and binaphthol side, respectively. θ_3 is the dihedral angle between naphthyl moieties

Compound	*a* (Å)	*b* (Å)	θ_1 (°)	θ_2 (°)	θ_3 (°)
(*R*)-**5** mol A	1.339 (5)	1.762 (3)	31.8 (2)	23.2 (2)	76.00 (6)
mol B	1.342 (5)	1.762 (3)	30.3 (2)	13.9 (2)	73.98 (6)
(*S*)-**5** mol A	1.341 (4)	1.762 (3)	31.3 (1)	22.8 (2)	76.26 (4)
mol B	1.344 (4)	1.761 (3)	30.1 (1)	13.6 (1)	74.24 (4)
[(*R*,*S*)-**5**](TCNQ)·CH_3CN	1.37 (1)	1.748 (9)	3.9 (6)	2.3 (6)	74.1 (1)
[(*R*,*S*)-**5**]·($TCNQF_4$)·(CH_3CN)$_2$	1.401 (5)	1.727 (5)	0.4 (2)	6.6 (2)	74.43 (7)

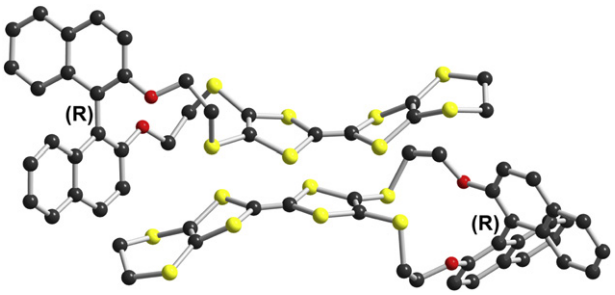


Fig. 3. Organization within dyads in neutral (*R*)-**5**.

acetonitrile and formulated, respectively as [(*R*,*S*)-**5**][TCNQ]·(CH_3CN) and [(*R*,*S*)-**5**][$TCNQF_4$]·(CH_3CN)$_2$.

The TCNQ compound crystallizes in the triclinic system, space group *P*–1, with donor and acceptor molecules in general position in the unit cell. As shown in Fig. 4, both donor (D) and acceptor (A) are organized into inversion-centered dyads, alternating along the *b* stacking axis into DDAADDAA mixed chains. Geometrical features collected in Table 2 show a strong planarization of the TTF core (θ_1 and θ_2 close to 0°) while the C_i═C_i (a) and C_i–S (b) intramolecular bond distances are slightly modified, when compared with the neutral (*R*)- or (*S*)-**5**, indicating some degree of charge transfer. Based on the large number of reported TCNQ salts, different correlations[24] between the charge of the molecule and the bond lengths within the TCNQ molecule have been reported. Applying those correlations to the TCNQ bond lengths in [(*R*,*S*)-**5**][TCNQ]·(CH_3CN), averaged in D_{2h} symmetry, gives calculated charges of ≈–0.25, thus indicating the possibility for a partial charge transfer in this TCNQ compound. The TTF and TCNQ homodyads interact only sideways as shown in Fig. 5. These unusual overlaps are associated with long inter-atomic distances; all S···S contacts in the TTF dyads exceed 3.68 Å, all C···C contacts in the TCNQ dyads exceed 3.54 Å. These geometrical features and the mixed-stack character are not in favor of a sizeable charge transfer, by contrast with other known BEDT/TTF salts with TCNQ itself.[25]

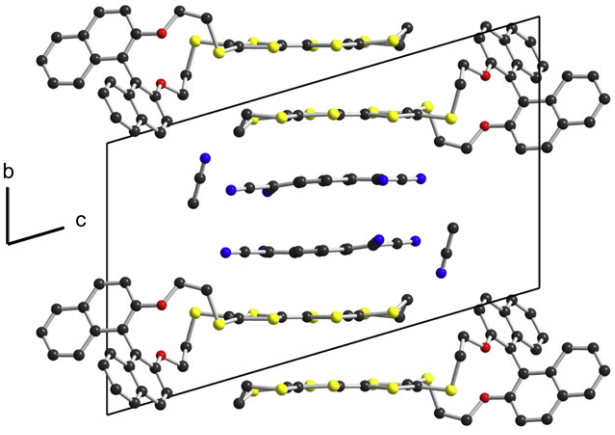


Fig. 4. Projection view along *a* of the unit cell of [(*R*,*S*)-5][TCNQ]·(CH_3CN).

The magnetic susceptibility of this TCNQ compound was determined in the 5–300 K temperature range and exhibits a temperature-independent diamagnetic behavior with χ_0=–7.6 10^{-4} cm^3 mol^{-1} with a Curie-type contribution of magnetic defaults accounting for less than 1% spin ½, demonstrating unambiguously the absence of charge transfer in this neutral complex. Conductivity measurements performed on this salt confirmed this zero charge transfer with a conductivity less than 10^{-6} S cm^{-1}.

The $TCNQF_4$ salt crystallizes in the triclinic system, space group *P*–1, with donor and acceptor molecules in general position in the

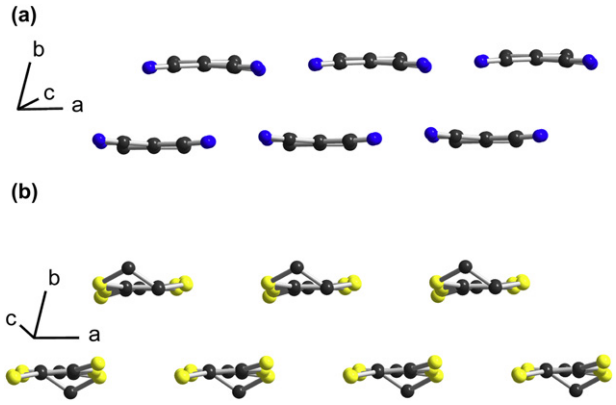


Fig. 5. View of the chains of dyads running along the *a* axis in [(*R*,*S*)-5][TCNQ]·(CH_3CN).

unit cell. Comparison of the bond distances within the TTF core with neutral (*R*)- or (*S*)-**5** (Table 2) shows a marked lengthening of the central C_i=C_i bond (a) with concomitant shortening of the C_i–S bonds (b), indicating clearly that the EDT/TTF **5** is here oxidized into the radical cation. This is further confirmed by the bond distances within the $TCNQF_4$ moiety as well as by the CN stretching vibration (2191, 2165 cm^{-1}).[26,27] The compound is thus formulated as [(*R*,*S*)-**5**]$^{+}$·[$TCNQF_4$]$^{-}$·(CH_3CN)$_2$. As shown in Fig. 6, the donor molecule is now fully planar and intercalated between $TCNQF_4$ molecules to form an alternated DADADA mixed-stack running along *a*. These chains are connected to each other along the *b* direction within (ab) layers (Fig. 6b) with the radical molecules interacting sideway along *b*.

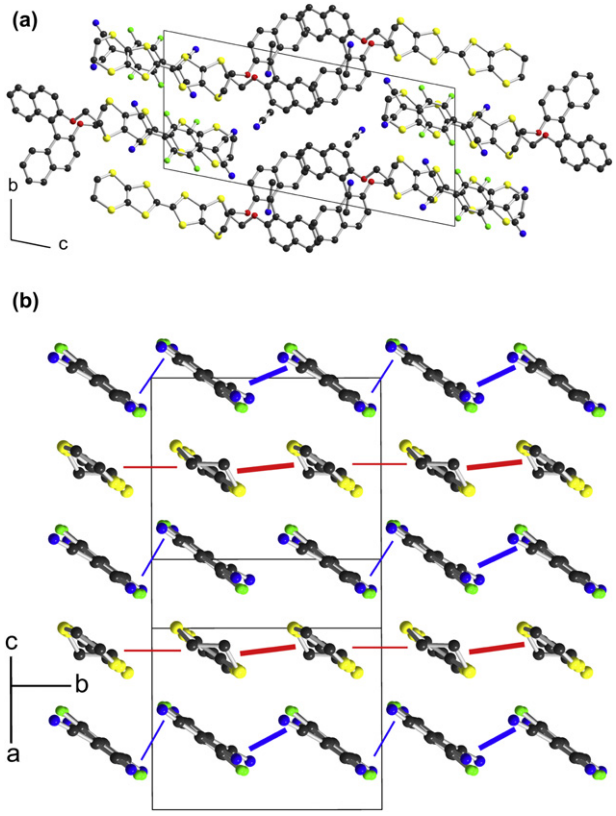


Fig. 6. (a) Projection view of the unit cell of [(*R*,*S*)-5][$TCNQF_4$]·(CH_3CN)$_2$ along *a*. Hydrogen atoms were omitted for clarity. (b) Solid state organization of the radical species. The thick and thin lines are associated with stronger and weaker overlap interactions between TTF in red, between $TCNQF_4$ LUMO in blue. The binaphthol moieties have been omitted for clarity.

The temperature dependence of the magnetic susceptibility of the $TCNQF_4^{-\bullet}$ salt (Fig. 7) confirms its biradical nature with a $\chi \cdot T$ value close to 0.6. The χT decrease at lower temperatures indicates the presence of antiferromagnetic interactions between the radicals. We have identified two different interactions within each chain, either built on the EDT/TTF **5** or $TCNQF_4$ molecules, highlighted in Fig. 6b with thick and thin lines, respectively (see also Fig. SII). The evolution of $\chi \cdot T$ versus T can be fitted as the sum of two contributions originating from each of the $EDT/TTF^{+\bullet}$ and $TCNQF_4^{-\bullet}$ radical species, both associated into inversion-centered dyads with a singlet-triplet behavior, that is, according to the following equation:

$$\chi = \chi_0 + x \cdot \chi_{\mathrm{Curie}} + (1-x)\frac{Ng^2\beta^2}{kT} \times \left[\frac{1}{3+\exp(-J_1/kT)} + \frac{1}{3+\exp(-J_2/kT)}\right]$$

where x is a fraction of paramagnetic defaults and J_1 and J_2 the two antiferromagnetic interactions associated with the radical dyads, which are found at −40 and −180 cm^{-1}, respectively. The shorter S···S intermolecular contacts observed within the TTF chains let us infer that the strongest interactions are due here to the TTF chains.

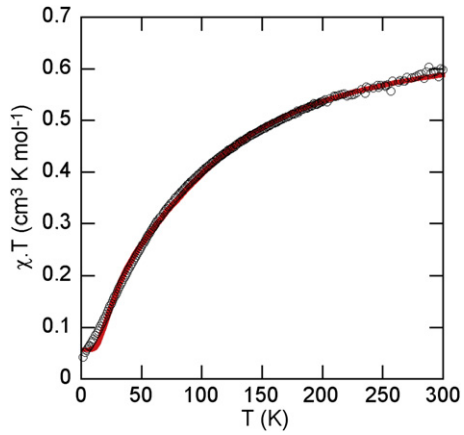


Fig. 7. Temperature dependence of the $\chi \cdot T$ product for [(*R*,*S*)-5][$TCNQF_4$].(CH_3CN)$_2$. The red solid line is a fit to the sum of two singlet-triplet systems, together with a Curie tail attributable to paramagnetic defaults.

3. Conclusions

In conclusion, we have described here a complete series of chiral binaphthol-based tetrathiafulvalene donor molecules where longer and flexible –S–(CH_2)$_2$– arms offer the possibility for direct intermolecular π–π interactions, as illustrated in the structures of the neutral derivatives **2**, **4**, and **5**, where molecules systematically associate into dyads with the TTF moieties facing each other through S···S van der Waals interactions. Furthermore, we have also demonstrated that such chiral donor molecules can be effectively oxidized into cation radical species, and are able to interact in the solid state, as illustrated here within two compounds of the racemic EDT/TTF derivative **5** with TCNQ and $TCNQF_4$. Electrocrystallization experiments aimed at isolating cation radical salts of these promising donor molecules, particularly in its enantiopure form, with various closed-shell counter ions are now in progress.

4. Experimental section

4.1. General

Enantiopure (*R*)-, (*S*)-, and racemic (*R*,*S*)-binaphthol were obtained from Aldrich and used as received. The zinc salt (Et_4N)$_2$[Zn(dmit)$_2$][28] and the dithiocarbonate **10**[29] were prepared

following published procedures. NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker Avance 300 spectrometer, chemical shifts are reported in parts per million referenced to TMS for ^{1}H and ^{13}C NMR. Cyclic voltammetry was carried out on a 1.5×10^{-3} M solution of TTF derivative in CH_2Cl_2 (anhydrous grade) containing 0.2 M *n*-Bu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured versus Saturated Calomel Electrode (SCE). Optical rotation was determined on a Perkin–Elmer 341 polarimeter with *c* given in g/100 mL. Circular dichroism spectra (Fig. S6–10) were recorded on a JASCO J-815 spectropolarimeter with 5 10^{-5} M solutions. Elemental analyses were performed at the CNRS Service de Microanalyse, Gif sur Yvette, France.

4.2. Synthesis of 2,2′-bis(2-bromoethoxy)-1,1′-binaphthyl 8

*4.2.1. Synthesis of racemic (R,S)-**8**.* To a solution of binaphthol (3.46 g, 12 mmol) and PPh_3 (9.5 g, 36.22 mmol) in THF (75 mL) at room temperature (rt) and under Ar is added dropwise during 2 h a mixture of 2-bromoethanol (2.56 mL, 36.04 mmol) and DEAD (azodicarboxylic acid diethyl ester, 40% solution in toluene, 16.5 mL, 36.3 mmol). After stirring overnight and solvent removal, the pale yellow oil is purified by chromatography on silica gel (CH_2Cl_2/petrol ether, 1:3). Recrystallisation from CH_2Cl_2/hexane at 5 °C gives (*R,S*)-**8** as white needles (3.3 g, 57%). Mp 106 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.99 (d, *J*=9.0 Hz, 2H), 7.91 (d, *J*=8.1 Hz, 2H), 7.45 (d, *J*=9.0 Hz, 2H), 7.42–7.32 (m, 2H), 7.32–7.22 (m, 2H), 7.17 (d, *J*=8.4 Hz, 2H), 4.35–4.14 (m, 4H), 3.25 (t, *J*=6.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 153.57, 134.05, 129.83, 129.73, 128.01, 126.57, 125.44, 124.19, 121.08, 116.38, 69.94, 29.23.

*4.2.2. Synthesis of (R)-**8**.* As described above for (*R,S*)-**8**, starting from (*R*)-binaphthol, one obtains (*R*)-**8** as white crystals (3.86 g, 64%). Mp 99 °C (lit.[15] 97.5–98.9 °C). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.97 (d, *J*=8.9 Hz, 2H), 7.89 (d, *J*=8.1 Hz, 2H), 7.43 (d, *J*=9.0 Hz, 2H), 7.37 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.25 (ddd, *J*=8.1, 5.6, 1.3 Hz, 2H), 7.17–7.10 (m, 2H), 4.32–4.12 (m, 4H), 3.23 (t, *J*=6.8 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 153.55, 134.03, 129.82, 129.71, 127.99, 126.55, 125.42, 124.17, 121.07, 116.37, 69.93, 29.18.

*4.2.3. Synthesis of (S)-**8**.* As described above for (*R,S*)-**8**, starting from (*S*)-binaphthol (5 g, 17.4 mmol), PPh_3 (12.2 g, 46.5 mmol) in THF (100 mL) with 2-bromoethanol (3.7 mL, 52.1 mmol) and DEAD (40% solution in toluene) (23.85 mL, 52.47 mmol), one obtains (*S*)-**8** as white crystals (5.7 g, 65%). Mp 98 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.01 (d, *J*=8.9 Hz, 2H), 7.93 (d, *J*=8.1 Hz, 2H), 7.47 (d, *J*=9.0 Hz, 2H), 7.41 (ddd, *J*=8.1, 6.6, 1.4 Hz, 2H), 7.29 (ddd, *J*=7.9, 6.6, 1.3 Hz, 2H), 7.24–7.18 (m, 2H), 4.36–4.17 (m, 4H), 3.27 (t, *J*=6.7 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 153.62, 134.10, 129.86, 129.78, 128.07, 126.62, 125.49, 124.23, 121.09, 116.40, 69.96, 29.33.

4.3. Synthesis of the trithiocarbonates 6

*4.3.1. Synthesis of racemic (R,S)-**6**.* To a solution of $(Et_4N)_2$[Zn(dmit)$_2$] (2.5 g, 3.6 mmol) in CH_3CN (3 L) is added (*R,S*)-**8** (3.35 g, 6.7 mmol) at rt. After stirring for five days under reflux, the cooled solution is evaporated, the residue taken in H_2O (500 mL) and extracted with CH_2Cl_2 (3×350 mL). The organic phase is washed with H_2O (3×350 mL), dried over $MgSO_4$, and the residue purified by chromatography on silica gel (CH_2Cl_2/petrol ether, 1:1) to afford the racemic (*R,S*)-**6** as a yellow powder (2.9 g, 81%). Mp 215–217 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J*=8.9 Hz, 2H), 7.80 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 2H), 7.34 (ddd, *J*=8.1, 6.4, 1.4 Hz, 2H), 7.25 (ddd, *J*=8.1, 6.4, 1.4 Hz, 2H), 7.19–7.11 (m, 2H), 4.22 (dt, *J*=10.1, 4.0 Hz, 2H), 4.08 (td, *J*=9.9, 3.2 Hz, 2H), 2.93 (dt, *J*=14.4, 3.4 Hz, 2H), 2.74 (ddd, *J*=14.2, 9.8, 4.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 211.98, 153.66, 140.64, 134.25, 129.50, 129.35, 127.98, 126.47, 125.31, 123.73, 119.66, 114.90, 66.26, 37.84. Elem. Anal. Calcd for $C_{27}H_{20}O_2S_5$ (536.01): C, 60.41; H, 3.76. Found: C, 59.99; H, 3.81.

*4.3.2. Synthesis of (R)-**6**.* As above for (*R,S*)-**6** starting from enantiopure (*R*)-**8** (2.65 g, 5.3 mmol). (*R*)-**6** is isolated as yellow crystals (2.45 g, 86%). Mp 135–137 °C. $[\alpha]_{Na}^{20}$ +964 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.99 (d, *J*=9.0 Hz, 2H), 7.89 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 2H), 7.34 (ddd, *J*=8.1, 6.4, 1.4 Hz, 2H), 7.24 (ddd, *J*=8.1, 6.4, 1.4 Hz, 2H), 7.15 (d, *J*=8.4 Hz, 2H), 4.31 (dt, *J*=10.1, 4.0 Hz, 2H), 4.18 (td, *J*=9.9, 3.2 Hz, 2H), 3.03 (dt, *J*=14.4, 3.5 Hz, 2H), 2.84 (ddd, *J*=14.2, 9.8, 4.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 211.97, 153.65, 140.61, 134.25, 129.50, 129.35, 127.98, 126.47, 125.30, 123.73, 119.67, 114.90, 66.26, 37.83. Elem. Anal. Calcd for $C_{27}H_{20}O_2S_5$ (536.01): C, 60.41; H, 3.76. Found: C, 60.18; H, 3.71.

*4.3.3. Synthesis of (S)-**6**.* As above for (*R,S*)-**6** starting from enantiopure (*S*)-**8** (4.5 g, 8.99 mmol). (*S*)-**6** is isolated as yellow crystals (4 g, 85%). Mp 130–132 °C. $[\alpha]_{Na}^{20}$ −970 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.05 (d, *J*=9.0 Hz, 1H), 7.95 (d, *J*=8.1 Hz, 2H), 7.45 (d, *J*=9.0 Hz, 2H), 7.39 (ddd, *J*=8.1, 6.7, 1.2 Hz, 2H), 7.27 (ddd, *J*=8.0, 6.7, 1.2 Hz, 2H), 7.16 (d, *J*=8.4 Hz, 2H), 4.33 (dt, *J*=10.0, 3.9 Hz, 2H), 4.24 (td, *J*=10.1, 3.0 Hz, 2H), 3.06 (dt, *J*=14.4, 3.2 Hz, 2H), 2.84 (ddd, *J*=14.3, 10.0, 4.2 Hz, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 212.84, 154.28, 141.69, 134.65, 129.89, 129.73, 128.49, 126.84, 125.56, 124.10, 119.74, 115.26, 66.56, 38.44. Elem. Anal. Calcd for $C_{27}H_{20}O_2S_5$ (536.01): C, 60.41; H, 3.76. Found C, 59.94; H, 3.68.

4.4. Synthesis of the dithiocarbonates 7

*4.4.1. Synthesis of (R,S)-**7**.* To a solution of the racemic 1,3-dithiole-2-thione (*R,S*)-**6** (1 g, 1.86 mmol) in a mixture $CHCl_3$/AcOH (50 mL, 3/2 v/v) is added $Hg(OAc)_2$ (1.8 g, 2.5 equiv, 5.65 mmol) at rt. After stirring for 4 h, the white insoluble is filtered on Celite and washed with CH_2Cl_2. The organic filtrate is washed with H_2O, satd $NaHCO_3$, H_2O, dried over $MgSO_4$, and concentrated. Chromatography on silica gel (CH_2Cl_2/petrol ether, 2:1) and recrystallisation from CH_2Cl_2/petrol ether afforded (*R,S*)-**7** as white needles (0.97 g, 95%). Mp 195 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.98 (d, *J*=9.0 Hz, 2H), 7.89 (d, *J*=8.1 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 2H), 7.37–7.32 (m, 2H), 7.27–7.21 (m, 2H), 7.16 (d, *J*=8.4 Hz, 2H), 4.29 (dt, *J*=9.9, 4.0 Hz, 2H), 4.18 (td, *J*=9.9, 3.2 Hz, 2H), 3.00 (dt, *J*=14.3, 3.4 Hz, 2H), 2.80 (ddd, *J*=14.2, 9.7, 4.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 189.49, 153.78, 134.28, 131.54, 129.46, 129.33, 127.96, 126.44, 125.32, 123.69, 119.68, 114.98, 66.22, 37.53. Elem. Anal. Calcd for $C_{27}H_{20}O_3S_4$ (520.71): C, 62.28; H, 3.87. Found: C, 62.08; H, 3.92.

*4.4.2. Synthesis of (R)-**7**.* As above for (*R,S*)-**7**, starting from the enantiopure 1,3-dithiole-2-thione (*R*)-**6** (1.9 g, 3.7 mmol) and $Hg(OAc)_2$ (2.85 g, 2.5 equiv, 8.94 mmol), one obtains (*R*)-**7** as a white powder (1.84 g, 100%). Mp 127–130 °C. $[\alpha]_{Na}^{20}$ +564 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.03 (d, *J*=8.9 Hz, 2H), 7.94 (d, *J*=8.1 Hz, 2H), 7.45 (d, *J*=9.0 Hz, 2H), 7.37 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.25 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.16–7.09 (m, 2H), 4.36 (dt, *J*=10.1, 4.0 Hz, 2H), 4.26 (td, *J*=10.0, 3.1 Hz, 2H), 3.08 (dt, *J*=14.4, 3.3 Hz, 2H), 2.85 (ddd, *J*=14.3, 9.9, 4.2 Hz, 2H). ^{13}C NMR (300 MHz, CD_2Cl_2, ppm): δ 189.84, 154.35, 134.63, 132.33, 129.81, 129.69, 128.41, 126.75, 125.51, 124.02, 119.74, 115.30, 66.52, 38.07. MS (MALDI-TOF) *m/z* 519.4 (M^+). Elem. Anal. Calcd for $C_{27}H_{20}O_3S_4$ (520.71): C, 62.28; H, 3.87. Found: C, 62.65; H, 4.46.

*4.4.3. Synthesis of (S)-**7**.* As above for (*R*)-**7**, starting from 1,3-dithiole-2-thione (*S*)-**6** (1 g, 1.86 mmol) and $Hg(OAc)_2$ (1.8 g, 2.5 equiv, 4.65 mmol), one obtains (*S*)-**7** as a white powder (0.97 g, 100%). Mp 125 °C. $[\alpha]_{Na}^{20}$ −560 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.04 (d, *J*=8.9 Hz, 2H), 7.95 (d, *J*=8.1 Hz, 2H), 7.45 (d,

J=9.0 Hz, 2H), 7.38 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.26 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.18–7.12 (m, 2H), 4.34 (dt, *J*=10.0, 4.0 Hz, 2H), 4.26 (td, *J*=10.0, 3.0 Hz, 2H), 3.06 (dt, *J*=14.4, 3.3 Hz, 2H), 2.83 (ddd, *J*=14.3, 9.9, 4.3 Hz, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 189.90, 154.39, 134.65, 132.48, 129.85, 129.69, 128.46, 126.81, 125.54, 124.06, 119.70, 115.30, 66.47, 38.10. Elem. Anal. Calcd for $C_{27}H_{20}O_3S_4$ (520.71): C, 62.28; H, 3.87. Found: C, 62.03; H, 3.94.

4.5. Synthesis of the symmetrically substituted TTFs (1)

*4.5.1. Synthesis of **1** (diastereoisomeric mixture).* A solution of the racemic 1,3-dithiole-2-one (*R*,*S*)-**7** (0.5 g, 0.96 mmol) in $P(OMe)_3$ (10 mL) is warmed to 130 °C during 5 h under Ar. After cooling to rt, the phosphite is evaporated and the residue purified by chromatography on silica gel (CH_2Cl_2/petrol ether 2:1). Recrystallisation from CH_2Cl_2/pentane afforded the diastereoisomeric mixture **1** [(*RR*) (*SS*) and *meso* form (*RS*)=(*SR*)] as a yellow powder (340 mg, 70%). Mp 260 °C. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.9 (d, *J*=9.0 Hz, 4H), 7.80 (d, *J*=8.0 Hz, 4H), 7.32 (d, *J*=9.0 Hz, 4H), 7.24 (t, *J*=7.3 Hz, 4H), 7.12 (t, *J*=7.4 Hz, 4H), 6.98 (d, *J*=8.4 Hz, 4H), 4.21–4.18 (m, 4H), 4.01–3.96 (m, 4H), 2.98–2.93 (m, 4H), 2.72–2.60 (m, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.45, 134.60, 131.70, 129.75, 129.69, 128.36, 126.70, 125.47, 124.01, 119.82, 115.73, 110.10, 67.15, 67.06, 37.48. MS (MALDI-TOF) *m*/*z* 1008.1 (M^+). Elem. Anal. Calcd for $C_{54}H_{40}O_4S_8$ (1009.41): C, 64.25; H, 3.99. Found: C, 64.02; H, 4.09.

*4.5.2. Synthesis of (RR)-**1**.* As described above, starting from the enantiopure 1,3-dithiole-2-one (*R*)-**6** (0.5 g, 0.96 mmol) in $P(OMe)_3$ (5 mL), one obtains (*RR*)-**1** as orange crystals (360 mg, 75%). Mp 220–222 °C. $[\alpha]_{Na}^{20}$ +1020 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.88 (d, *J*=8.9 Hz, 4H), 7.79 (d, *J*=8.0 Hz, 4H), 7.31 (d, *J*=9.0 Hz, 4H), 7.23 (ddd, *J*=8.1, 6.8, 1.2 Hz, 4H), 7.12 (ddd, *J*=8.1, 6.8, 1.3 Hz, 4H), 7.02–6.94 (m, 4H), 4.18 (dt, *J*=10.0, 4.0 Hz, 4H), 4.01 (td, *J*=9.9, 3.0 Hz, 4H), 2.94 (dt, *J*=14.3, 3.3 Hz, 4H), 2.70–2.64 (ddd, *J*=14.0, 9.8, 3.8 Hz, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.45, 134.62, 131.66, 129.75, 129.71, 128.36, 126.70, 125.49, 124.01, 119.87, 115.74, 110.12, 67.76, 67.07, 37.45. MS (MALDI-TOF) *m*/*z* 1008.02 (M^+). Elem. Anal. Calcd for $C_{54}H_{40}O_4S_8$ (1009.41): C, 64.25; H, 3.99. Found: C, 64.69; H, 4.08.

*4.5.3. Synthesis of (SS)-**1**.* As described above for (*RR*)-**1**, starting from the enantiopure 1,3-dithiole-2-one (*S*)-**6** (0.25 g, 0.48 mmol) in $P(OMe)_3$ (5 mL), one obtains (*SS*)-**1** as yellow crystals (160 mg, 75%). Mp 218–220 °C. $[\alpha]_{Na}^{20}$ −1014 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.88 (d, *J*=9.0 Hz, 4H), 7.80 (d, *J*=8.0 Hz, 4H), 7.31 (d, *J*=9.0 Hz, 4H), 7.27–7.19 (m, 4H), 7.15–7.08 (m, 4H), 6.98 (d, *J*=8.5 Hz, 4H), 4.18 (dt, *J*=9.8, 3.8 Hz, 4H), 4.00 (td, *J*=9.9, 2.8 Hz, 4H), 2.93 (dt, *J*=14.2, 3.1 Hz, 4H), 2.63 (ddd, *J*=14.0, 9.8, 3.8 Hz, 4H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.45, 134.60, 131.79, 129.76, 129.67, 128.38, 126.72, 125.48, 124.01, 119.76, 115.69, 110.13, 67.00, 37.50. Elem. Anal. Calcd for $C_{54}H_{40}O_4S_8$ (1009.41): C, 64.25; H, 3.99. Found: C, 63.63; H, 4.02.

4.6. Synthesis of the TTF diesters (2)

*4.6.1. Synthesis of (R,S)-**2**.* A solution of the racemic 1,3-dithiole-2-thione (*R*,*S*)-**6** (100 mg, 0.186 mmol) and bis(carboxymethyl)-1,3-dithiole-2-one **9** (233 mg, 5 equiv, 0.93 mmol) in $P(OMe)_3$ (5 mL) is heated to 130 °C for 4 h under Ar. After evaporation of the phospite under vacuum, the residue is purified by chromatography on silica gel (CH_2Cl_2/petrol ether, 2:1). Recrystallisation from CH_2Cl_2/petrol ether afforded (*R*,*S*)-**2** as red crystals (70 mg, 54%). Mp 235 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.95 (d, *J*=8.9 Hz, 2H), 7.87 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 2H), 7.32 (ddd, *J*=8.0, 6.7, 1.3 Hz, 2H), 7.22 (ddd, *J*=8.0, 6.7, 1.3 Hz, 2H), 7.13 (d, *J*=8.5 Hz, 2H), 4.24 (dt, *J*=10.1, 4.1 Hz, 2H), 4.04 (td, *J*=9.7, 3.1 Hz, 2H), 3.85 (s, 6H), 3.01 (dt, *J*=7.3, 3.2 Hz, 2H), 2.80–2.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 159.94, 153.93, 134.24, 132.00, 131.16, 129.42, 129.37, 127.92, 126.37, 125.28, 123.67, 119.77, 115.62, 112.53, 107.88, 66.91, 53.43, 37.08. MS (MALDI-TOF) *m*/*z* 721.9 (M^+). Elem. Anal. Calcd for $C_{34}H_{26}O_6S_6$ (722.96): C, 56.49; H, 3.62. Found: C, 55.99; H, 3.46.

*4.6.2. Synthesis of (R)-**2**.* As described above for (*R*,*S*)-**2**, starting from the enantiopure 1,3-dithiole-2-thione (*R*)-**6** (1 g, 1.86 mmol), one obtains (*R*)-**2** as a red powder (740 mg, 55%). Mp 147 °C. $[\alpha]_{Na}^{20}$ +678 (*c* 0.05, CH_2Cl_2). ^{1}H (300 MHz, $CDCl_3$, ppm): δ 7.95 (d, *J*=8.9 Hz, 2H), 7.87 (d, *J*=8.0 Hz, 2H), 7.37 (d, *J*=9.0 Hz, 2H), 7.32 (ddd, *J*=8.0, 6.7, 1.3 Hz, 2H), 7.22 (ddd, *J*=8.0, 6.7, 1.3 Hz, 2H), 7.13 (d, *J*=8.5 Hz, 2H), 4.23 (dt, *J*=10.0, 4.1 Hz, 2H), 4.04 (td, *J*=9.7, 3.1 Hz, 2H), 3.85 (s, 6H), 3.00 (dt, *J*=7.2, 3.3 Hz, 2H), 2.80–2.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 160.04, 154.03, 134.34, 132.09, 131.25, 129.52, 129.47, 128.02, 126.47, 125.37, 123.76, 119.87, 115.71, 112.62, 107.99, 67.00, 53.52, 37.17. MS (MALDI-TOF) *m*/*z* 722 (M^+). Elem. Anal. Calcd for $C_{34}H_{26}O_6S_6$ (722.96): C, 56.49; H, 3.62. Found: C, 56.19; H, 3.42.

*4.6.3. Synthesis of (S)-**2**.* As described above for (*R*,*S*)-**2** starting from the enantiopure 1,3-dithiole-2-thione (*S*)-**6** (1 g, 1.86 mmol), one obtains (*S*)-**2** as a red powder (740 mg, 55%). Mp 150 °C. $[\alpha]_{Na}^{20}$ −678 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.01 (d, *J*=8.9 Hz, 2H), 7.92 (d, *J*=8.0 Hz, 2H), 7.44 (d, *J*=9.0 Hz, 2H), 7.36 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.24 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.11 (d, *J*=8.5 Hz, 2H), 4.29 (dt, *J*=10.1, 3.9 Hz, 2H), 4.13 (td, *J*=9.9, 3.0 Hz, 2H), 3.86 (s, 6H), 3.07 (dt, *J*=6.9, 3.2 Hz, 2H), 2.84–2.70 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 160.31, 154.47, 134.59, 132.28, 131.95, 129.80, 129.72, 128.41, 126.73, 125.47, 124.03, 119.83, 115.85, 112.88, 108.04, 67.21, 53.85, 37.60. MS (MALDI-TOF) *m*/*z* 721.6 (M^+). Elem. Anal. Calcd for $C_{34}H_{26}O_6S_6$ (722.96): C, 56.49; H, 3.62. Found: C, 56.29; H, 3.59.

4.7. Synthesis of the TTF diamides (3)

*4.7.1. Synthesis of (R,S)-**3**.* To a solution of the racemic TTF diester (*R*,*S*)-**2** (100 mg, 0.138 mmol) in THF(20 mL) is added an aqueous solution of NH_3 (25% solution, 5 mL) at rt. After stirring for 24 h, the solvents are evaporated, the residue taken in THF, dried over $MgSO_4$, concentrated, and purified by chromatography on silica gel (THF/CH_2Cl_2, 1:3). Recrystallisation from THF/pentane afforded the racemic *ortho* diamide (*R*,*S*)-**3** as a pale orange powder (86 mg, 90%). Mp 278 °C. ^{1}H NMR (300 MHz, DMSO, ppm): δ 8.31 (s, 2H, NH_2), 8.07 (s, 2H, NH_2), 8.01 (d, *J*=9.1 Hz, 2H), 7.91 (d, *J*=8.0 Hz, 2H), 7.55 (d, *J*=9.1 Hz, 2H), 7.37–7.24 (m, 2H), 7.25–7.13 (m, 2H), 6.88 (d, *J*=8.4 Hz, 2H), 4.22–4 0.25 (m, 2H), 4.12–4.05 (m, 2H), 3.18–3.01 (m, 2H), 2.88–2.72 (m, 2H). ^{13}C NMR (300 MHz, DMSO, ppm): δ 160.60, 153.76, 133.58, 133.24, 130.74, 129.29, 128.79, 127.97, 126.27, 124.55, 123.37, 118.70, 115.71, 108.25, 107.71, 66.50, 36.58. MS (MALDI-TOF) *m*/*z* 691.9 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}N_2O_4S_6$ (692.93): C, 55.47; H, 3.49; N, 4.04. Found: C, 55.41; H, 3.68; N, 3.66.

*4.7.2. Synthesis of (R)-**3**.* As described above for (*R*,*S*)-**3**, starting from the enantiopure diester (*R*)-**2** (100 mg, 0.138 mmol). Recrystallisation from THF/pentane affordred the enantiopure diamide (*R*)-**3** as orange microcrystals (86 mg, 90%). Mp 267–268 °C. $[\alpha]_{Na}^{20}$ +320 (*c* 0.05, CH_2Cl_2). ^{1}H NMR (300 MHz, DMSO, ppm): δ 8.31 (s, 2H, NH_2), 8.06 (s, 2H, NH_2), 8.01 (d, *J*=9.0 Hz, 2H), 7.92 (d, *J*=8.0 Hz, 2H), 7.55 (d, *J*=9.0 Hz, 2H), 7.30 (t, *J*=7.3 Hz, 2H), 7.20 (t, *J*=7.5 Hz, 2H), 6.88 (d, *J*=8.4 Hz, 2H), 4.39–4.20 (m, 2H), 4.19–3.99 (m, 2H), 3.20–2.99 (m, 2H), 2.91–2.69 (m, 2H). ^{13}C NMR (75 MHz, DMSO, ppm): δ 160.60, 153.76, 133.58, 133.24, 130.73, 129.29, 128.79, 127.97, 126.27, 124.55, 123.37, 118.71, 115.71, 108.24, 107.72, 66.50,

36.57. MS (MALDI-TOF) *m/z* 691.9 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}N_2O_4S_6$ (692.93): C, 55.47; H, 3.49; N, 4.04. Found: C, 55.35; H, 3.66; N, 3.75.

*4.7.3. Synthesis of (S)-**3**.* As described above for (*R*)-**3**, starting from (*S*)-**2** (150 mg, 0.207 mmol), one obtains (*S*)-**3** as an orange cotton (132 mg, 92%). Mp 262 °C. $[\alpha]_{Na}^{20}$ −324 (*c* 0.05, CH_2Cl_2). ^1H NMR (300 MHz, DMSO, ppm): δ 8.33 (s, 2H, NH_2), 8.09 (s, 2H, NH_2), 8.01 (d, *J*=9.1 Hz, 2H), 7.91 (d, *J*=8.1 Hz, 2H), 7.55 (d, *J*=9.1 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 2H), 7.19 (t, *J*=7.6 Hz, 2H), 6.88 (d, *J*=8.4 Hz, 2H), 4.40–4.19 (m, 2H), 4.17–3.96 (m, 2H), 3.15–3.00 (m, 2H), 2.88–2.70 (m, 2H). ^{13}C NMR (75 MHz, DMSO, pm): δ 160.61, 153.75, 133.57, 133.24, 130.83, 129.29, 128.77, 127.98, 126.28, 124.55, 123.37, 118.65, 115.66, 108.28, 107.67, 66.44, 36.58. MS (MALDI-TOF) *m/z* 692 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}N_2O_4S_6$ (692.93): C, 55.47; H, 3.49; N, 4.04. Found: C, 55.04; H, 3.41; N, 4.01.

4.8. Synthesis of TTF (4)

*4.8.1. Synthesis of (R,S)-**4**.* To a solution of the racemic diester (*R*,*S*)-**2** (100 mg, 0.139 mmol) in HMPA (5 mL) is added LiBr (100 mg, 1.15 mmol) and the mixture is warmed to 145 °C during 20 nm, using a prealably heated oil bath. After rapid cooling, the solvent is evaporated under vacuum, the residue is taken into H_2O and extracted with CH_2Cl_2 (3×). The organic phase is washed with H_2O, dried over $MgSO_4$, and concentrated. Chromatography (silica gel, CH_2Cl_2/petrol ether 1:1) and recrystallisation from CH_2Cl_2/petrol ether afforded (*R*,*S*)-**4** as yellow crystals (70 mg, 84%). Mp 191 °C. ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.88 (d, *J*=9.0 Hz, 2H), 7.79 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=9.0 Hz, 2H), 7.23 (ddd, *J*=8.1, 6.8, 1.2 Hz, 2H), 7.11 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 6.98 (d, *J*=8.0 Hz, 2H), 6.28 (s, 2H), 4.19 (dt, *J*=10.1, 4.1 Hz, 2H), 4.02 (td, *J*=9.8, 3.1 Hz, 2H), 3.03–2.86 (m, 2H), 2.74–2.54 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.51, 134.60, 131.61, 129.75, 128.35, 126.65, 125.46, 123.98, 119.92, 119.41, 115.95, 114.98, 105.93, 67.31, 37.42. MS (MALDI-TOF) *m/z* 605.5 (M^+). Elem. Anal. Calcd for $C_{30}H_{22}O_2S_6$ (606.88): C, 59.37; H, 3.65. Found: C, 59.24; H, 3.68.

*4.8.2. Synthesis of (R)-**4**.* As described above for (*R*,*S*)-**4**, starting from the enantiopure diester (*R*)-**2** (100 mg, 0.139 mmol), one obtains after chromatography (*R*)-**4** as a yellow powder (70 mg, 84%). Mp 148 °C. $[\alpha]_{Na}^{20}$ +790 (*c* 0.05, CH_2Cl_2). ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.88 (d, *J*=9.0 Hz, 2H), 7.79 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=9.0 Hz, 2H), 7.23 (ddd, *J*=8.1, 6.8, 1.2 Hz, 2H), 7.12 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 6.98 (d, *J*=8.1 Hz, 2H), 6.28 (s, 2H), 4.19 (dt, *J*=10.1, 4.1 Hz, 2H), 4.02 (td, *J*=9.8, 3.1 Hz, 2H), 3.03–2.89 (m, 2H), 2.74–2.58 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.50, 154.50, 134.60, 131.61, 129.75, 129.73, 128.35, 126.65, 125.46, 123.97, 119.91, 119.41, 115.95, 114.97, 67.31, 37.41. MS (MALDI-TOF) *m/z* 605.7 (M^+). Elem. Anal. Calcd for $C_{30}H_{22}O_2S_6$ (606.88): C, 59.37; H, 3.65. Found: C, 59.06; H, 3.78.

*4.8.3. Synthesis of (S)-**4**.* As described above for (*R*,*S*)-**4**, starting from the enantiopure diester (*S*)-**2** (150 mg, 0.207 mmol), one obtains after chromatography (*S*)-**4** as a yellow powder (107 mg, 85%). Mp 145 °C. $[\alpha]_{Na}^{20}$ −794 (*c* 0.05, CH_2Cl_2). ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 8.00 (d, *J*=9.0 Hz, 2H), 7.91 (d, *J*=8.1 Hz, 2H), 7.44 (d, *J*=9.0 Hz, 2H), 7.36 (ddd, *J*=8.1, 6.8, 1.2 Hz, 2H), 7.24 (ddd, *J*=8.1, 6.8, 1.3 Hz, 2H), 7.11 (d, *J*=8.1 Hz, 2H), 6.40 (s, 2H), 4.30 (dt, *J*=10.1, 4.0 Hz, 2H), 4.13 (td, *J*=9.9, 3.0 Hz, 2H), 3.08 (dt, *J*=14.4, 3.5 Hz, 2H), 2.85–2.68 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.51, 134.60, 131.71, 129.77, 129.71, 128.38, 126.68, 125.46, 123.99, 119.85, 119.44, 115.92, 67.26, 37.45. MS (MALDI-TOF) *m/z* 605.7 (M^+). Elem. Anal. Calcd for $C_{30}H_{22}O_2S_6$ (606.88): C, 59.37; H, 3.65. Found: C, 59.41; H, 3.58.

4.9. Synthesis of the EDT/TTF derivatives (5)

*4.9.1. Synthesis of (R,S)-**5**.* A solution of the racemic 1,3-dithiole-2-thione (*R*,*S*)-**6** (0.15 g, 0.279 mmol) and EDT-substituted 1,3-dithiole-2-one **10** (0.3 g, 5 equiv, 1.44 mmol) in $P(OMe)_3$ (5 mL) is stirred at 130 °C for 5 h under Ar. After cooling to rt, the precipitated BEDT/TTF is filtered and the evaporated filtrate purified by chromatography on silica gel (CH_2Cl_2/petrol ether 1:1). Recrystallisation from CH_2Cl_2/ethanol afforded (*R*,*S*)-**5** as a yellow powder (155 mg, 80%). Mp 175 °C. ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.87 (d, *J*=8.9 Hz, 2H), 7.79 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=9.0 Hz, 2H), 7.24 (ddd, *J*=8.1, 6.7, 1.2 Hz, 2H), 7.11 (ddd, *J*=8.2, 6.7, 1.3 Hz, 2H), 7.01–6.94 (m, 2H), 4.18 (dt, *J*=10.2, 4.1 Hz, 2H), 4.01 (td, *J*=9.8, 3.1 Hz, 2H), 3.23 (s, 4H), 3.01–2.90 (m, 2H), 2.73–2.59 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.48, 134.58, 131.48, 129.77, 129.76, 128.37, 126.65, 125.44, 123.99, 119.95, 115.98, 114.30, 114.17, 108.64, 67.39, 37.50, 30.75. MS (MALDI-TOF) *m/z* 697.5 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}O_2S_8$ (697.05): C, 55.14; H, 3.47. Found: C, 54.59; H, 3.41.

*4.9.2. Synthesis of (R)-**5**.* As described above for (*R*,*S*)-**5**, using the 1,3-dithiole-2-thione (*R*)-**6** (0.25 g, 0.46 mmol) and the dithiole-2-one **10** (0.5 g, 5 equiv, 2.4 mmol) afforded (*R*)-**5** as yellow crystals (0.27 g, 85%). Mp 170 °C. $[\alpha]_{Na}^{20}$ +770 (*c* 0.05, CH_2Cl_2). ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.85 (d, *J*=9.0 Hz, 2H), 7.77 (d, *J*=8.1 Hz, 2H), 7.29 (d, *J*=9.0 Hz, 2H), 7.22 (ddd, *J*=8.1, 6.8, 1.2 Hz, 2H), 7.10 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 6.97 (d, *J*=8.0 Hz, 2H), 4.14 (dt, *J*=10.1, 4.0 Hz, 2H), 3.99 (td, *J*=9.8, 3.1 Hz, 2H), 3.19 (s, 4H), 2.92 (dt, *J*=7.1, 3.3 Hz, 2H), 2.70–2.55 (m, 2H). ^{13}C (75 MHz, CD_2Cl_2, ppm): δ 154.49, 134.60, 131.57, 129.80, 129.75, 128.40, 126.68, 125.47, 124.01, 119.93, 115.96, 114.31, 114.21, 108.63, 67.35, 37.52, 30.76. MS (MALDI-TOF) *m/z* 697 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}O_2S_8$ (697.05): C, 55.14; H, 3.47. Found: C, 54.73; H, 3.34.

*4.9.3. Synthesis of (S)-**5**.* As described above for (*R*,*S*)-**5**. Using the enantiopure 1,3-dithiole-2-thione (*S*)-**6** (0.25 g, 0.46 mmol) and the dithiole-2-one **10** (0.5 g, 5 equiv, 2.4 mmol) afforded (*S*)-**5** as yellow crystals (0.27 g, 85%). Mp 171–172 °C. $[\alpha]_{Na}^{20}$ −764 (*c* 0.05, CH_2Cl_2). ^1H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.99 (d, *J*=8.9 Hz, 2H), 7.91 (d, *J*=8.1 Hz, 2H), 7.43 (d, *J*=9.0 Hz, 2H), 7.36 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.24 (ddd, *J*=8.1, 6.7, 1.3 Hz, 2H), 7.13–7.07 (m, 2H), 4.28 (dt, *J*=10.1, 4.0 Hz, 2H), 4.12 (td, *J*=9.9, 3.1 Hz, 2H), 3.34 (s, 4H), 2.92 (dt, *J*=7.1, 3.3 Hz, 2H), 2.83–2.70 (m, 2H). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 154.48, 134.58, 131.62, 129.80, 129.73, 128.41, 126.69, 125.46, 124.01, 119.87, 115.94, 114.26, 108.59, 67.31, 37.54, 30.74. MS (MALDI-TOF) *m/z* 697.4 (M^+). Elem. Anal. Calcd for $C_{32}H_{24}O_2S_8$ (697.05): C, 55.14; H, 3.47. Found: C, 55.02; H, 3.41.

4.10. The charge-transfer compounds of (*R*,*S*)-5 with TCNQ and $TCNQF_4$

With TCNQ. TCNQ (6 mg, 0.029 mmol) is added to a warm solution of the racemic donor (*R*,*S*)-**5** (10 mg, 0.0143 mmol) in CH_3CN (10 mL). The cooled solution deposited black crystals after 2 days. Filtration and washing with CH_3CN afforded the title compound (12 mg, 89%), a 1:1 complex formulated as [(*R*,*S*)-**5**](TCNQ)·CH_3CN from single crystal X-ray diffraction. IR: $\nu_{C\equiv N}$ 2202 cm^{-1}. Elem. Anal. Calcd for $C_{46}H_{31}N_5O_2S_8$ (942.31 g mol^{-1}): C, 58.63; H, 3.32; N, 7.43. Found: C, 58.42; H, 3.15; N, 6.96.

With $TCNQF_4$. $TCNQF_4$ (10 mg, 0.036 mmol) is added to a warm solution of the racemic donor (*R*,*S*)-**5** (15 mg, 0.0215 mmol) in CH_3CN (15 mL). The cooled solution deposited black crystals after 2 days. Filtration and washing with CH_3CN afforded the title compound (18 mg, 79%), a 1:1 complex formulated as [(*R*,*S*)-**5**](TCNQF_4)·$(CH_3CN)_2$ from single crystal X-ray diffraction. IR: $\nu_{C\equiv N}$

2191, 2165 cm^{-1}. Elem. Anal. Calcd for $C_{44}H_{24}F_4N_4O_2S_8$ (973.20 g mol^{-1}): C, 54.30; H, 2.49. Found: C, 52.99; H, 2.41.

4.11. Crystallography

Data were collected on a APEX II Brucker AXS diffractometer with Mo Kα radiation (λ=0.71073 Å). Structures were solved by direct methods (SHELXS97)[30] and refined (SHELXL-97)[30] by full-matrix least-squares methods as implemented in the WinGX software package.[31] An empirical absorption (multi-scan) correction was applied. Hydrogen atoms were introduced at calculated positions (riding model) included in structure factor calculation but not refined. A pentane molecule included in the structure of (*RR*)-**1** and (*SS*)-**1** was properly refined in the latter while an SQUEEZE procedure had to be used in the (*RR*) isomer. The crystals of the TCNQ complex [(*R*,*S*)-**5**]TCNQ·CH_3CN was twinned. CELLNOW was used to determine the orientation matrices of both components and TWINABS for absorption correction (see details in cif file) (Table 3).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 815024–815031. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 44(0) 1223 336033 or email: deposit@ccdc.cam.ac.uk].

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Supplementary data

Cyclic voltamogramm for all newly prepared TTF derivatives (Figs. S1–5), circular dichroism spectra for pairs of enantiomers, (*RR*)-**1** and (*SS*)-**1**, (*R*)-**2**, and (*S*)-**2**, (*R*)-**3** and (*S*)-**3**, (*R*)-**4**, and (*S*)-**4**,

Table 3
Crystallographic data

	(*RR*)-**1**·Pentane	(*SS*)-**1**·Pentane	(*R*,*S*)-**2**	(*R*,*S*)-**4**
Formula	$C_{59}H_{52}O_4S_8$	$C_{59}H_{52}O_4S_8$	$C_{34}H_{26}O_6S_6$	$C_{30}H_{22}O_2S_6$
Formula mass	1081.49	1081.57	722.91	606.84
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	C2	C2	*P*−1	*P*−1
T (K)	100 (2)	150 (2)	100 (2)	293 (2)
a/Å	39.3170 (11)	39.2936 (17)	8.0349 (10)	7.9067 (2)
b/Å	8.2662 (2)	8.3191 (3)	13.0347 (15)	12.8042 (3)
c/Å	8.2330 (2)	8.2604 (4)	15.7987 (19)	14.8200 (4)
α/degrees	90.0	90.0	79.400 (4)	73.164 (2)
β/degrees	96.7880 (10)	96.4540 (10)	81.871 (4)	79.895 (2)
γ/degrees	90.0	90.0	82.790 (4)	87.640 (3)
V/Å^3	2656.99 (12)	2683.1 (2)	1601.6 (3)	1413.70 (6)
Z	2	2	2	2
d_{calc}/g cm^{-3}	1.352	1.339	1.499	1.426
μ/mm^{-1}	0.384	0.380	0.474	0.512
Data collected	12569	10805	13024	30896
Ind. data	4620	5399	7819	6479
R_{int}	0.0227	0.0312	0.0221	0.0302
Obs data ($I>2\sigma(I)$)	4515	4763	6637	4961
Param. refined	299	316	417	389
R(*F*)	0.0264	0.0400	0.0325	0.0321
wR(F^2)	0.0756	0.1178	0.1134	0.0876
Flack param.	0.02 (5)	0.02 (7)	—	—
Residual *d*/e Å^{-3}	0.45, −0.31	0.70, −0.35	0.49, −0.45	0.19, −0.28

	(*R*)-**5**·CH_2Cl_2	(*S*)-**5**·CH_2Cl_2	[(*R*,*S*)-**5**)] TCNQ·CH_3CN	[(*R*,*S*)-**5**] $TCNQF_4$·$(CH_3CN)_2$
Formula	$C_{33}H_{26}Cl_2O_2S_8$	$C_{33}H_{26}Cl_2O_2S_8$	$C_{46}H_{31}N_5O_2S_8$	$C_{48}H_{30}F_4N_6O_2S_8$
Formula mass	781.92	781.92	942.24	1055.26
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	*P*−1	*P*−1
T (K)	100 (2)	150 (2)	150 (2)	150 (2)
a/Å	7.5235 (3)	7.5531 (2)	7.4318 (11)	9.0865 (10)
b/Å	19.4669 (7)	19.5746 (5)	13.938 (2)	11.0459 (13)
c/Å	46.2483 (17)	46.2788 (11)	22.315 (4)	23.991 (3)
α/degrees	90.0	90.0	73.395 (7)	100.389 (3)
β/degrees	90.0	90.0	86.882 (8)	100.027 (3)
γ/degrees	90.0	90.0	74.699 (7)	93.823 (3)
V/Å^3	6773.5 (4)	6842.3 (3)	2136.0 (6)	2320.4 (5)
Z	8	8	2	2
d_{calc}/g cm^{-3}	1.534	1.518	1.465	1.510
μ/mm^{-1}	0.717	0.710	0.465	0.450
Data collected	73890	63687	25778	19369
Ind. data	15549	15587	11183	10226
R_{int}	0.0520	0.0390	[a]	0.0368
Obs data ($I>2\sigma(I)$)	14142	14285	3952	6388
Param. refined	811	811	552	615
R(*F*)	0.0386	0.0295	0.0717	0.0487
wR(F^2)	0.1002	0.0975	0.2337	0.1604
Flack param.	−0.02 (4)	−0.02 (4)	—	—
Residual *d*/e Å^{-3}	0.38, −0.43	0.45, −0.37	0.55, −0.59	0.59, −0.55

[a] Twinned crystal. See text and cif file.

(*R*)-**5** and (*S*)-**5** (Figs. S6–10), views of the TTF/TTF and $TCNQF_4$/$TCNQF_4$ intermolecular interactions between radical species in $[(R,S)\text{-}\mathbf{5}]TCNQF_4\cdot(CH_3CN)_2$ (Fig. S11).

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