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Tetrathiafulvalene-hydroxyamides and -oxazolines: hydrogen bonding, chirality, and a radical cation salt

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Abstract—Racemic and enantiopure ethylenedithio-tetrathiafulvalene (EDT-TTF) derivatives featuring β-hydroxyamide or oxazoline (OX) groups bearing methyl or isopropyl substituents have been synthesized starting from the corresponding amino alcohols. Crystal structure analysis shows in the case of the racemic methyl-\beta-hydroxyamide donor the development of a unique hydrogen bond network, characterized by short C=O···H-O and N-H···O-H intermolecular distances. The enantiopure (S)-EDT-TTF-methyl-OX crystallizes in the monoclinic non-centrosymmetric space group $P2_1$, whereas the isopropyl counterparts, (R)-and (S)-EDT-TTF-isopropyl-OX, crystallize in the orthorhombic non-centrosymmetric space group $P2_12_12_1$. All of them adopt a *s*-trans conformation in which TTF and oxazoline units are coplanar. Electrocrystallization experiments with the racemic EDT-TTF-methyl-OX, in the presence of $(nBu_4)_2Mo_6Cl_{14}$ as supporting electrolyte, afford a radical cation salt, formulated as $[(\pm)$ -EDT-TTF-methyl-OX]₂Mo₆Cl₁₄, in which the donors associate in strong dimers, which further stack along the b direction to form quasi-homochiral helix-like ribbons.

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1. Introduction

The introduction of chirality within conducting molecular materials based on tetrathiafulvalene (TTF) derivatives, a well known class of organosulfur electron donors extensively studied in the search for molecular conductors and superconductors,¹ currently receives a growing interest, also encouraged by Rikken et al.'s recent report of electrical magnetochiral anisotropy in chiral carbon nanotubes.² This feature is in line with the quest for multifunctional molecular materials, a trend of much interest in contemporary materials science, aiming at combining in the solid state at least two physical properties, such as conductivity and optical activity.³ The question of whether the chirality influences the electrical properties of TTF based radical cation salts had been previously addressed by Dunitz and others, but the lack of suitable enantiopure materials together with their racemic form did not allow deeper investigations.⁴ Yet, structural differences between racemic and enantiomeric forms may occur, since enantiopure radical cation salts are expected to suffer less from structural disorder than the racemates, whose crystal

structures may accommodate the enantiomers exchanging places. It is well established that structural disorder can strongly influence the electronic conductivity in molecular conductors,⁵ therefore the chirality can already play a paramount role at this level. A straightforward strategy to introduce chirality within TTF based materials lies in the utilization of chiral TTF's as precursors for radical cation salts, although the complementary strategy, consisting of the use of chiral counter-ions with achiral donors can be envisioned, as recently described in the BEDT-TTF (bisethylenedithio-tetrathiafulvalene) salt with the chiral anti-mony (L)-tartrate dimer, $[Sb_2(L-tart)_2]^{2-.6}$ The advantage of the former strategy, despite more synthetically-demanding efforts than for the second one, is that, once the synthesis of a chiral donor optimized, a large panel of anions, be they chiral or achiral, can be explored.



The first examples of enantiopure TTF derivatives were described by Dunitz and Wallis,⁷ and since then other chiral TTF's were synthesized, most of them featuring a functionalized BEDT-TTF skeleton.8 The latter, along with closely related donors, have been recently extensively

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surveyed by Wallis et al.⁴ Moreover, enantiopure TTF derivatives containing chiral binaphthyl frameworks⁹ or oxazoline rings¹⁰ were also synthesized. The latter were tested as ligands in the catalytic allylic substitution reaction, showing though a rather modest catalytic activity.

In a recent communication we briefly described the straightforward synthesis of EDT-TTF (ethylenedithiotetrathiafulvalene) substituted with a chiral 4-methyloxazoline and a diphenylphosphino group.¹¹ The chirality provided by the oxazoline ring is perfectly controlled and easily introduced in the synthesis by the use of racemic or enantiopure amino alcohols. By synthesizing the EDT-TTF-Me-Oxazolines (EDT-TTF-OX), our purpose was to access a class of chiral donors, which could serve as precursors for chiral molecular materials. Indeed, this strategy proved to be highly promising for future developments, since we succeeded in preparing the first complete series of mixedvalence metallic salts based on chiral tetrathiafulvalenes bearing the (R)-, (S)-, or racemic (+)-methyl-oxazoline heterocycle and the AsF_6^- monoanion. The single crystal conductivity for the enantiopure salts was one order of magnitude higher than that of the racemic one, very likely because of the structural disorder observed in the latter.¹² In the present paper, we describe the detailed synthesis and characterization of chiral EDT-TTF-\beta-hydroxyamides and -oxazolines, in methyl and isopropyl series, in their racemic and (R) and (S) enantiopure forms. In depth analyses of crystal structures of racemic Me-hydroxyamide, enantiopure (S)-Me-oxazoline and (R) and (S)-iPr-oxazolines are presented, along with that of a radical cation salt of racemic EDT-TTF-Me-oxazoline with the $Mo_6Cl_{14}^{2-}$ anion, obtained upon electrocrystallization.

2. Results and discussion

In order to introduce a chirality center on the oxazoline ring, our first choice to use a methyl substituent was motivated by the concern to have a minimum steric bulk, provided by the redox inert oxazoline part of the donor, in the radical cation salts of EDT-TTF-OX. This feature would favor a maximization of π - π overlap and van der Waals intermolecular interactions in the solid state. Secondly, in a parallel series of donors, an isopropyl substituent was used instead of methyl, in order to gain in solubility, but also to insure a steric protection for potential catalytic applications.

2.1. Synthesis

It is well established that EDT-TTF-COCl (1) smoothly reacts with primary amines to afford in good yields secondary amides.¹³ Paralleling this strategy, two racemic

 (\pm) or enantiopure (R) and (S) amino alcohols, namely alaninol and valinol, were reacted with 1, and, after stirring at room temperature for up to 12 h and chromatographic work up, the corresponding EDT-TTF- β -hydroxyamides 2a-c and 3a-c were isolated and characterized by spectroscopic methods and elemental analysis (Scheme 1). An X-ray crystal structure analysis was undertaken for compound 2a (vide infra). Note these are the first examples of TTF's bearing both amide and alcohol functional groups, whereas numerous homofunctional derivatives of either amide,^{13,14} thioamide¹⁵ or alcohol¹⁶ type were described so far. Subsequently, cyclization reactions in the presence of methanesulfonyl chloride (MsCl) and triethylamine were performed on β -hydroxyamides to yield the series 4a-c (methyl) and **5a–c** (isopropyl) of (\pm) , (R) and (S) EDT-TTF-oxazolines (EDT-TTF-OX). All analytical data and elemental analyses are in good agreement with the proposed structures. Suitable single crystals for X-ray analysis were obtained for the enantiopure donors 4c, 5b and 5c.

2.2. X-ray crystal structures of donors

Suitable single crystals for the β -hydroxyamide **2a** were obtained upon recrystallization in ethyl acetate. The donor crystallizes in the monoclinic system, space group $P2_1/c$, with one independent molecule in the unit cell. As expected for a racemic mixture, both enantiomers, related to each other through the inversion center, are present in the structure. Selected bond lengths are listed in Table 1.

All values are typical for a neutral TTF, which, in this case, is moderately folded along both S...S hinges, that is, 15.33(18)° for S1...S2 and 19.9(3)° for S3...S4, as often encountered within crystalline structures of such neutral donors. The amide group is coplanar with the TTF unit, and disposed in an antiparallel manner with respect to C7=C8 and C9=O1 double bonds, as evidenced in Figure 1. Certainly, the most peculiar feature in the crystalline structure of 2a is the hydrogen bond network established thanks to amide and alcohol groups. As observed for another β -hydroxyamide,¹⁷ both functionalities participate as hydrogen bond donor and acceptor groups, with the carbonyl oxygen atom O1 acting as acceptor towards the alcoholic proton H2 and the amidic proton H1 as donor towards the alcoholic oxygen atom O2. The consequence of the balance between these requirements and the typical intermolecular S...S van der Waals contacts and stacking tendency of TTF type derivatives, is the organization of the donors in infinite ladders along a, through two types of hydrogen bond motifs (Fig. 1). Indeed, according to M. Etter's nomenclature,¹⁸ one can identify $R_2^2(14)$ and $R_2^2(10)$ rings, characterized by short and rather linear hydrogen bonds of C=O···H-O and N-H···O-H type, respectively.



Scheme 1. Reagents and conditions: (i) (\pm), (*R*) or (*S*)-alaninol for 2a–c and valinol for 3a–c, NEt₃, THF, 12 h, rt; (ii) NEt₃, THF, MsCl at 0 °C, then 20 h at 50 °C.

	2a	4c	5b	5c	$(4a)_2Mo_6Cl_{14}$
		Bond le	engths (Å)		
C3-C4	1.322(11)	1.336(5)	1.317(9)	1.314(8)	1.338(8)
C5-C6	1.339(8)	1.339(4)	1.335(8)	1.332(7)	1.398(7)
C7–C8	1.337(10)	1.333(5)	1.342(12)	1.322(10)	1.330(8)
C7–C9	1.500(10)	1.449(5)	1.448(14)	1.468(13)	1.454(8)
C17-C18					1.393(8)
C5-S4	1.752(7)	1.756(3)	1.749(7)	1.753(7)	1.723(5)
C5–S3	1.761(7)	1.748(3)	1.760(7)	1.766(6)	1.716(5)
C6-S2	1.761(7)	1.753(3)	1.743(7)	1.731(6)	1.732(5)
C6-S1	1.751(7)	1.763(3)	1.760(7)	1.761(6)	1.712(5)
		Torsion	angles (°)		
S1…S2	15.33(18)	5.8(2)	13.5(3)	14.6(3)	0.43(9)
S3…S4	19.9(3)	3.1(2)	21.6(5)	21.0(5)	3.95(9)
S7…S8					2.73(6)
S9…S10					2.56(13)
Oxazoline…TTF (s-trans)		7.3(5)	8.7(6)	10.1(7)	3.9(2) (N1)
Oxazoline…TTF (s-trans)					15.3(4) (N2A)
oxazoline…TTF (s-cis)					18.6(5) (N2B)

Table 1. Selected bond lengths (Å) and torsion dihedral angles (°) for 2a, 4c, 5b, 5c and $(4a)_2Mo_6Cl_{14}$

Furthermore, the donors stack along b, with the shortest S \cdots S intermolecular distance amounting at 3.58 Å. Clearly, the presence of amide and alcohol groups within the same donor allows original hydrogen bond supramolecular patterns in the TTF series, with respect to homofunctional derivatives, whose crystalline structures have been recently extensively reviewed.¹⁹



In the case of oxazoline derivatives **4** and **5**, two planar conformations are possible, namely *s*-*cis* and *s*-*trans*, if one considers the mutual orientations of the C7=C8 and C9=N double bonds. In the crystalline structure of **4b**, previously published,¹¹ the conformation was *s*-*trans*, with TTF and oxazoline units lying in the same plane. Single crystals of **4c**



Figure 1. Hydrogen bond network in the crystalline structure of **2a**. Hydrogen atoms at C11 and C12 have been omitted for clarity. Intermolecular distances (Å) and angles (°): O1…O2A (-x, 1-y, -z) 2.62, O1…H2A 1.96, O1–H2A–O2A 137.0 for R²₂(14) ring; N1…O2B (-1-x, 1-y, -z) 2.82, H1…O2B 1.99, N1–H1–O2B 160.0 for R²₂(10) ring.

were obtained upon recrystallization in a THF/cyclohexane 1:1 mixture. Like its enantiomeric counterpart **4b**, the oxazoline **4c** crystallized in the monoclinic non-centrosymmetric space group $P2_1$, with one independent molecule in the unit cell. Note the *s*-trans conformation (Fig. 2) of the donor, with bond lengths in the typical range for a neutral TTF and only slight folding about S…S hinges. TTF and oxazoline units are coplanar, with the corresponding dihedral angle amounting at $7.3(5)^{\circ}$, an important feature in view of obtaining radical cation salts based on EDT-TTF-Me-OX **4a–c**.

The donors 4c stack along the b direction, leading to a herring bone type packing (Fig. 3), which is the mirror image of the 4b packing.

Furthermore, formation of isopropyl-oxazolines **5a–c** was also confirmed by X-ray diffraction analyses, on single crystals obtained upon slow evaporation of a ethyl acetate solution, for both enantiomers R (**5b**) and S (**5c**). They are isostructural and crystallized in the non-centrosymmetric orthorhombic space group $P2_12_12_1$, with one independent molecule in the unit cell. As represented in Figure 4, **5b** and **5c** are the images each other in a mirror plane, and, like their methyl analogue **4c**, adopt a quasi-planar *s-trans* conformation, with torsion angles TTF····oxazoline amounting at 8.7(6) and 10.1(7)°, respectively. Geometrical parameters (Table 1) are in the expected range.

Interestingly, the packing of **5b** and **5c** is completely different when compared with **4b**, since in these cases the



Figure 2. ORTEP view of (*S*)-EDT-TTF-OX **4c** (thermal ellipsoids set at 50% probability).



Figure 3. Packing diagram of 4c.



Figure 4. View of the two enantiomers 5b and 5c.

donors arrange in pairs, almost perpendicular to each other along b, as observed in Figure 5.

2.3. Redox properties of donors

In order to evaluate the redox properties of the donors synthesized so far we have performed cyclic voltammetry experiments to determine the oxidation potentials and the



Figure 5. Packing diagram of 5c.

reversibility of the processes. The corresponding half-wave potentials for all the compounds are listed in Table 2.

Both mono-electronic oxidations are fully reversible, with potential values very similar to that of EDT-TTF-amides (0.66 and 0.92 V vs SCE for $E_1^{1/2}$ and $E_2^{1/2}$, respectively).¹³ As already mentioned (vide supra),¹² we recently described a first complete series of mixed-valence metallic salts obtained upon electrocrystallization of the donors **4a**–**c** with the AsF₆⁻ monoanion. This time the (TBA)₂Mo₆Cl₁₄ dianionic salt was used as supporting electrolyte in a series of electrocrystallization experiments with the same **4a**–**c** donors. Unlike the case of the AsF₆⁻ monoanion, with the Mo₆Cl₁₄⁻ dianion only the racemic TTF-OX **4a** afforded suitable single crystals for X-ray analysis, of a salt formulated as (**4a**)₂Mo₆Cl₁₄, whereas crystalline plates of poor quality were obtained for the enantiopure **4b** and **4c**.

Table 2. Oxidation potentials (V vs SCE, nBu_4NPF_6 , 0.1 M in CH₂Cl₂ at 0.1 Vs⁻¹, at 20 °C)

	$E_1^{1/2}$	$E_2^{1/2}$	
2a-c	0.60	1.09	
3a-c	0.60	1.09	
4a-c	0.63	1.11	
5а-с	0.63	1.11	

2.4. Crystal structure of (4a)₂Mo₆Cl₁₄

The salt crystallizes in the monoclinic system, space group $P2_1/c$, with two independent donor molecules in general positions and two half-clusters located on inversion centers in the unit cell. According to the stoichiometry within the salt, both donor molecules are oxidized into radical cations, which is also confirmed by the variation of C=C and C-S central bonds, that is, elongation for C5=C6 and C17=C18 and shortening for C-S when compared to neutral donors (Table 1). As expected for fully oxidized donors the TTF units are practically planar, with folding angles about S...S hinges close to 0°. Interestingly, one donor (OX1) adopts a s-trans conformation, being coplanar with the TTF core, whereas the other (OX2) is disordered on two positions, corresponding to both R (0.75) and S (0.25) enantiomers on the same site, the first as s-trans and the second as s-cis conformers, with moderate TTF…oxazoline dihedral angles (Fig. 6 and Table 1).

There is no organic–inorganic segregation within the structure, but rather $Mo_6Cl_{14}^{2-}$ dianions wrapped in helixlike ribbons of donors developing along b (Fig. 7). Interestingly, the ribbons are homochiral if we consider only the major enantiomer (sof=0.75) in the case of OX2. As often observed in the case of fully oxidized TTF-based donors, the radical cations strongly dimerize within the ribbons, in a 'head-to-tail' conformation, to form dicationic $[(4a)_2]^{2+}$ species.

The dimerization occurs between the two independent donor molecules OX1 and OX2 and within this dyad there are intermolecular S…S contacts as short as 3.37-3.45 Å, with a $\beta_{HOMO-HOMO}$ interaction energy overlap, calculated by the extended Hückel method, amounting at 0.86 eV (interaction I). Longer intra-ribbon S…S contacts, in the



Figure 6. View of the two independent donor radical cations in the structure of $(4a)_2Mo_6Cl_{14}$. The bottom molecule corresponds to the disordered enantiomers on the same site, with the *S* one, in a *s*-*cis* conformation, having darkened bonds and the methyl carbon atom C24B in black. Hydrogen atoms have been omitted for clarity.



Figure 7. Mixed organic-inorganic slabs in the structure of $(4a)_2$ Mo₆Cl₁₄. Hydrogen atoms and oxazoline rings have been omitted for clarity. Calculated $\beta_{\text{HOMO-HOMO}}$ interaction energies are as follows: interaction **I** OX1···OX2 (-x, -y, 1-z) 0.86 eV, interaction **II** OX1···OX2 (x, 0.5-y, 0.5+z) 0.15 eV.

range of 3.6–3.8 Å, are observed between the dyads, with a much weaker interaction of only 0.15 eV (interaction II). Inter-ribbons S…S distances are over 4 Å, quite larger than the sum of van der Waals radii of two sulfur atoms.²⁰ The strong structural and energetic dimerization observed herein would, very likely, lead to an insulating behavior. Yet, the preparation of this radical cation salt demonstrates once again that the new class of donors is suitable for the synthesis of racemic or enantiopure molecular materials.

3. Conclusions

Two series of racemic and enantiopure EDT-TTF- β -hydroxyamides and EDT-TTF-oxazolines were

synthesized. X-ray crystal structure of the racemic methyl- β -hydroxyamide, with an emphasis on the hydrogen bond network in which both amide and alcohol groups are involved, is described. The hydrogen bond donor and acceptor requirements are entirely fulfilled by the establishment of C=O···H-O and N-H···O-H intermolecular interactions. Furthermore, X-ray structures of enantiopure S-methyl and R- and S-isopropyl oxazolines, which crystallized in non-centrosymmetric space groups, are analyzed. A radical cation salt involving the racemic EDT-TTF-methyloxazoline and the $Mo_6Cl_{14}^{2-}$ anion was synthesized. Its crystalline structure shows association of radical cations in dimers, characterized by a high energy overlap interaction, and formation of quasi-homochiral ribbons out of donor molecules. The use of these electroactive β -hydroxyamides and oxazolines as precursors for chiral molecular materials is currently being investigated.

4. Experimental

4.1. General comments

Dry CH₂Cl₂ was obtained by distillation over P₂O₅ and THF was distilled over sodium and benzophenone. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ¹H, 125.75 MHz for ¹³C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. MALDI-TOF MS spectra were recorded on Bruker Biflex-IIITM apparatus, equipped with a 337 nm N₂ laser. Elemental analyses were performed by the 'Service d'Analyse du CNRS' at Gif/ Yvette, France.

4.2. General procedure for β -hydroxy amides

In anhydrous THF (10 mL) 0.2 mL of the appropriate aminoalcohol (2.46 mmol) was diluted, and then 0.55 mL of dry triethylamine (3.95 mmol) was added. The colorless solution thus obtained was stirred for 10 min under N₂ before dropwise addition of a solution of freshly prepared ethylenedithio-tetrathiafulvalene carbonyl chloride (1) (0.700 g, 1.96 mmol) in 30 mL dry THF. The orange resulting solution was stirred for 6–12 h at room temperature. Then the mixture was filtered through a pad of Celite[®] and concentrated under reduced pressure. The crude product was chromatographed through silica gel, with THF as eluent, to give the hydroxy-amides as orange-red solids.

4.2.1. 2-(+/-)-*N*-(**1-Hydroxy-propy**])-ethylenedithiotetrathiafulvalene-amide (2a). From (+/-)-alaninol (0.19 g), orange solid (0.57 g, 73% yield), mp 166– 167 °C. ¹H NMR (CDCl₃): δ 1.24 (d, ³*J*=6.8 Hz, 3H, CH₃), 3.30 (s, 4H, S–*CH*₂–*CH*₂–S), 3.59 (dd, ²*J*=11.0 Hz, ³*J*=5.4 Hz, 1H of CH₂O), 3.72 (dd, ³*J*=11.0 Hz, ²*J*= 3.7 Hz, 1H of CH₂O), 4.14 (m, 1H, NH–*CH*–CH₂O), 5.76 (d, ³*J*=7.0 Hz, 1H, NH), 7.11 (s, 1H, =CH). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1615 ($\nu_{C=O}$), 3186 (ν_{OH}). *m/z* (MALDI-TOF): 395.08 (M⁺). Anal. Calcd for C₁₂H₁₃NO₂S₆: C, 36.43; H, 3.31; N, 3.54. Found: C, 36.53; H, 3.35; N, 3.42. **4.2.2. 2**-(*R*)-*N*-(**1**-Hydroxy-propyl)-ethylenedithio-tetrathiafulvalene-amide (2b). From (*R*)-alaninol (0.32 g, air sensitive) and 1.2 g of EDT-TTF-COCl, red solid (0.84 g, 63% yield), mp 148–150 °C. ¹H NMR (CDCl₃): δ 1.24 (d, ³*J*=6.8 Hz, 3H, CH₃), 3.30 (s, 4H, S–*CH*₂–*CH*₂–S), 3.60 (dd, ³*J*=11.0 Hz, ²*J*=5.4 Hz, 1H of CH₂O), 3.72 (dd, ³*J*= 11.0 Hz, ²*J*=3.7 Hz, 1H of CH₂O), 4.13 (m, 1H, NH–*CH*– CH₂O), 5.78 (d, ³*J*=7.3 Hz, 1H, NH), 7.11 (s, 1H, ==CH). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1615 ($\nu_{C=O}$), 3186 (ν_{OH}). *m*/ *z* (MALDI-TOF): 394.96 (M⁺). Anal. Calcd for C₁₂H₁₃NO₂S₆: C, 36.43; H, 3.31; N, 3.54. Found: C, 36.63; H, 3.37; N, 3.47.

4.2.3. 2-(*S*)-*N*-(**1-Hydroxy-propy**])-ethylenedithio-tetrathiafulvalene-amide (2c). From (*S*)-alaninol (0.26 g, air sensitive) and 1.05 g of EDT-TTF-COCl, red solid (0.93 g, 80% yield), mp 148–150 °C. ¹H NMR, IR and MS spectra are identical with those of **2b**. Anal. Calcd for $C_{12}H_{13}NO_2S_6$: C, 36.43; H, 3.31; N, 3.54. Found: C, 36.57; H, 3.41; N, 3.42.

4.2.4. 2-(+/-)-*N*-(**1-Hydroxy-3-methylbutyl**)-ethylenedithio-tetrathiafulvalene-amide (3a). From (+/-)-valinol (0.18 g), orange crystals (0.3 g, 52% yield), mp 176– 177 °C. ¹H NMR (CDCl₃): δ 0.96 (d, ³*J*=6.8 Hz, 3H, CH₃), 0.99 (d, ³*J*=6.8 Hz, 3H, CH₃), 1.93 (m, 1H, *CH*-(CH₃)₂), 3.30 (s, 4H, S-*CH*₂-*CH*₂-S), 3.74 (d, ³*J*=3.7 Hz, 2H, CH₂O), 3.79 (m, 1H, NH-*CH*-CH₂O), 5.75 (d, ³*J*=8.5 Hz, 1H, NH), 7.12 (s, 1H, =CH). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1615 ($\nu_{C=O}$), 3186 (ν_{OH}). *m*/*z* (MALDI-TOF): 423.03 (M⁺). Anal. Calcd for C₁₄H₁₇NO₂S₆: C, 39.69; H, 4.04; N, 3.31. Found: C, 39.82; H, 4.05; N, 3.24.

4.2.5. 2-(*R*)-*N*-(**1-Hydroxy-3-methylbutyl**)-ethylenedithio-tetrathiafulvalene-amide (3b). From (*R*)-valinol (0.472 g) and 1.28 g of EDT-TTF-COCl, orange solid (1.34 g, 88% yield), mp 163–164 °C. ¹H NMR (CDCl₃): δ 0.96 (d, ³*J*=6.8 Hz, 3H, CH₃), 0.98 (d, ³*J*=6.8 Hz, 3H, CH₃), 1.93 (m, 1H, *CH*-(CH₃)₂), 3.30 (s, 4H, S–*CH*₂–*CH*₂– S), 3.74 (d, ³*J*=4.2 Hz, 2H, CH₂O), 3.80 (m, 1H, NH–*CH*– CH₂O), 5.75 (d, ³*J*=8.5 Hz, 1H, NH), 7.12 (s, 1H, ==CH). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1615 ($\nu_{C=O}$), 3186 (ν_{OH}). *m*/*z* (MALDI-TOF): 422.91 (M⁺). Anal. Calcd for C₁₄H₁₇NO₂S₆: C, 39.69; H, 4.04; N, 3.31. Found: C, 39.91; H, 4.12; N, 3.17.

4.2.6. 2-(*S*)-*N*-(**1-Hydroxy-3-methylbutyl**)-ethylenedithio-tetrathiafulvalene-amide (**3c**). From (*S*)-valinol (0.556 g) and 1.48 g of EDT-TTF-COCl, orange solid (1.48 g, 84% yield), mp 163–164 °C. ¹H NMR, IR and MS spectra are identical with those of **3b**. Anal. Calcd for $C_{14}H_{17}NO_2S_6$: C, 39.69; H, 4.04; N, 3.31. Found: C, 39.89; H, 4.15; N, 3.18.

4.3. General procedure for oxazolines

To a solution of hydroxy-amide **2–3** (5.06 mmol) and dry triethylamine (1.5 mL, 10.76 mmol) in 150 mL of dry THF, cooled at 0 °C, was added in one portion methanesulfonyl chloride (0.8 mL, 10.34 mmol). After stirring at 0 °C for 30 min, another portion of triethylamine was added (6.3 mL, 45.2 mmol), then the reaction mixture was heated at 50 °C for approximately 20 h, that is, until the initially

formed mesylate disappeared, as monitored by TLC: AcOEt/cyclohexane 2:1. Then the mixture was filtered through a pad of Celite[®] and concentrated under reduced pressure. The crude product was chromatographed on silica gel (AcOEt/cyclohexane 2:1) to give a yellow-orange solid. Recrystallization in acetonitrile (or a mixture of THF and cyclohexane) affords orange crystalline solids.

4.3.1. (+/-)-2-(Ethylenedithio-tetrathiafulvalenyl)-4methyl-oxazoline (4a). From 0.2 g of 2a, orange-yellow solid (0.16 g, 83% yield), mp 181–186 °C. ¹H NMR (CDCl₃): δ 1.31 (d, ³*J*=6.6 Hz, 3H, CH₃), 3.29 (s, 4H, S– *CH*₂–*CH*₂–S), 3.88 (t, ³*J*=²*J*=7.9 Hz, 1H of CH₂O, H_{syn}/ CH₃), 4.31 (qdd, ³*J*=9.2 Hz, ³*J*=7.9 Hz, ³*J*=6.6 Hz, 1H, N–*CH*–CH₂O), 4.45 (dd, ³*J*=9.2 Hz, ²*J*=7.9 Hz, 1H of CH₂O, H_{anti}/CH₃), 6.97 (s, 1H, =CH). ¹³C NMR (CDCl₃): δ 21.8 (CH₃), 30.8, 30.9 (S–CH₂–CH₂–S), 63.1 (CH–N), 75.5 (CH₂O), 107.9, 114.3, 115.0, 116.5 (2C=C), 125.1 (=CH), 126.6 (=*C*–C=N), 157.3 (C=N). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1634 ($\nu_{C=N}$). *m*/*z* (MALDI-TOF): 376.93 (M⁺). Anal. Calcd for C₁₂H₁₁NOS₆: C, 38.17; H, 2.94; N, 3.71. Found: C, 38.05; H, 2.97; N, 3.62.

4.3.2. (*R*)-2-(Ethylenedithio-tetrathiafulvalenyl)-4methyl-oxazoline (4b). From 0.84 g of 2b, orange crystals (0.74 g, 92% yield), mp 202–203 °C. ¹H NMR (CDCl₃): δ 1.31 (d, ³*J*=6.7 Hz, 3H, CH₃), 3.29 (s, 4H, S–*CH*₂–*CH*₂–S), 3.88 (t, ³*J*=²*J*=7.9 Hz, 1H of CH₂O, H_{syn}/CH₃), 4.31 (qdd, ³*J*=9.2 Hz, ³*J*=7.9 Hz, ³*J*=6.7 Hz, 1H, N–*CH*–CH₂O), 4.45 (dd, ³*J*=9.2 Hz, ²*J*=7.9 Hz, 1H of CH₂O, H_{anti}/CH₃), 6.97 (s, 1H, =CH). ¹³C NMR (CDCl₃): δ 21.1 (CH₃), 30.1, 30.2 (S–CH₂–CH₂–S), 62.3 (CH–N), 74.8 (CH₂O), 107.1, 113.5, 114.3, 115.8 (2C=C), 124.3 (=CH), 125.9 (=*C*– C=N), 156.6 (C=N). IR (KBr, cm⁻¹): 1571 ($\nu_{C=C}$), 1634 ($\nu_{C=N}$). *m*/z (MALDI-TOF): 376.94 (M⁺). Anal. Calcd for C₁₂H₁₁NOS₆: C, 38.17; H, 2.94; N, 3.71. Found: C, 38.43; H, 2.93; N, 3.68.

4.3.3. (S)-2-(Ethylenedithio-tetrathiafulvalenyl)-4methyl-oxazoline (4c). From 0.93 g of 2c, orange crystals (0.65 g, 73% yield), mp 202–203 °C. ¹H NMR, ¹³C NMR, IR and MS spectra are identical with those of 4b. Anal. Calcd for $C_{12}H_{11}NOS_6$: C, 38.17; H, 2.94; N, 3.71. Found: C, 38.16; H, 2.87; N, 3.75.

4.3.4. (+/-)-2-(Ethylenedithio-tetrathiafulvalenyl)-4isopropyl-oxazoline (5a). From 0.25 g of 3a, orange solid (0.21 g, 88% yield), mp 156–157 °C. ¹H NMR (CDCl₃): δ 0.88 (d, ³*J*=6.7 Hz, 3H, CH₃), 0.97 (d, ³*J*=6.7 Hz, 3H, CH₃), 1.81 (m, 1H, *CH*–(CH₃)₂), 3.29 (s, 4H, S–*CH*₂–*CH*₂– S), 4.03 (m, 1H, N–*CH*–CH₂O), 4.06 (t, ³*J*=²*J*=7.3 Hz, 1H of CH₂O, H_{syn}/*i*Pr), 4.45 (dd, ²*J*=7.3 Hz, ³*J*=1.3 Hz, 1H of CH₂O, H_{anti}/*i*Pr), 6.95 (s, 1H, =CH). ¹³C NMR (CDCl₃): δ 18.6 (CH₃), 19.5 (CH₃), 30.8, 30.9 (S–CH₂–CH₂–S), 33.2 (*CH*–(CH₃)₂), 71.5 (CH–N), 73.5 (CH₂O), 107.7, 114.3, 115.0, 116.9 (2C=C), 125.2 (=CH), 126.3 (=*C*–C=N), 157.1 (C=N). IR (KBr, cm⁻¹): 1564 ($\nu_{C=C}$), 1641 ($\nu_{C=N}$). *m*/*z* (MALDI-TOF): 404.89 (M⁺). Anal. Calcd for C₁₄H₁₅NOS₆: C, 41.45; H, 3.73; N, 3.45. Found: C, 41.14; H, 3.86; N, 3.36.

4.3.5. (*R*)-2-(Ethylenedithio-tetrathiafulvalenyl)-4-isopropyl-oxazoline (5b). From 1.34 g of 3b, orange solid

Table 3. Crystal and structure refinement data for 2a, 4c, 5b, 5c and (4a)₂Mo₆Cl₁₄

	2a	4c	5b	5c	$(4a)_2Mo_6Cl_{14}$
Elemental formula	C ₁₂ H ₁₃ NO ₂ S ₆	C ₁₂ H ₁₁ NOS ₆	C ₁₄ H ₁₅ NOS ₆	C ₁₄ H ₁₅ NOS ₆	C ₂₄ H ₂₂ Cl ₁₄ Mo ₆ N ₂ O ₂ S ₁₂
Formula weight	395.64	377.58	405.63	405.63	1827.10
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P21/c	P21	P212121	P212121	P21/c
a (Å)	6.5992(9)	6.3167(5)	6.4416(5)	6.4450(6)	19.433
b (Å)	16.143(2)	7.7578(7)	14.3025(15)	14.313(2)	13.634
<i>c</i> (Å)	15.824(2)	16.2434(12)	19.3132(16)	19.360(2)	22.395
α (°)	90	90	90	90	90
β(°)	98.466(17)	99.960(9)	90	90	92.96
γ (°)	90	90	90	90	90
Cell volume, $V(Å^3)$	1667.4(4)	783.99(11)	1779.3(3)	1785.9(4)	5925.7
No. of formula units/cell, Z	4	2	4	4	4
Absorption coefficient (mm^{-1})	0.821	0.865	0.768	0.765	2.313
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Total no. of refl. measured	12937	6116	14353	11220	68687
No. of unique refl.	3056	2911	3455	3455	13514
No. of 'observed' refl. $(I > 2\sigma_I)$	1162	2719	1907	1247	8169
R_1 , wR_2 ('observed' data) ^a	0.057, 0.111	0.037, 0.101	0.058, 0.122	0.043, 0.071	0.044, 0.097
R_1 , wR_2 (all data) ^a	0.179, 0.140	0.040, 0.104	0.121, 0.145	0.150, 0.094	0.102, 0.115

^a $R(F_{o}) = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|; R_{w}(F_{o}^{2}) = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]]^{1/2}.$

(1.22 g, 95% yield), mp 150–151 °C. ¹H NMR (CDCl₃): δ 0.87 (d, ³*J*=6.7 Hz, 3H, CH₃), 0.97 (d, ³*J*=6.7 Hz, 3H, CH₃), 1.81 (m, 1H, *CH*–(CH₃)₂), 3.29 (s, 4H, S–*CH*₂–*CH*₂–S), 4.01–4.08 (m, 2H, N–*CH*–CH₂O and 1H of CH₂O, H_{syn}/*i*Pr), 4.33 (dd, ²*J*=7.4 Hz, ³*J*=1.3 Hz, 1H of CH₂O, H_{anti}/*i*Pr), 6.95 (s, 1H, =CH). ¹³C NMR (CDCl₃): δ 18.0 (CH₃), 18.9 (CH₃), 30.1, 30.2 (S–CH₂–CH₂–S), 32.5 (*CH*–(CH₃)₂), 70.9 (CH–N), 72.8 (CH₂O), 106.9, 113.6, 114.3, 116.2 (2C=C), 124.5 (=CH), 125.6 (=*C*–C=N), 156.4 (C=N). IR (KBr, cm⁻¹): 1564 ($\nu_{C=C}$), 1641 ($\nu_{C=N}$). *m/z* (MALDI-TOF): 404.90 (M⁺). Anal. Calcd for C₁₄H₁₅NOS₆: C, 41.45; H, 3.73; N, 3.45. Found: C, 41.59; H, 3.85; N, 3.41.

4.3.6. (*S*)-2-(Ethylenedithio-tetrathiafulvalenyl)-4-isopropyl-oxazoline (5c). From 1.48 g of 3c, orange solid (1.35 g, 95% yield), mp 150–151 °C. ¹H NMR, ¹³C NMR, IR and MS spectra are identical with those of 5b. Anal. Calcd for $C_{14}H_{15}NOS_6$: C, 41.45; H, 3.73; N, 3.45. Found: C, 41.47; H, 3.79; N, 3.36.

4.4. Electrocrystallization

Two-compartment cell was used together with platinum electrodes (2 cm long, 1 mm in diameter) and a current of 1 μ A at room temperature (20 ± 2 °C). [(*n*-Bu)₄N]₂Mo₆Cl₁₄ 0.015 M in CH₂Cl₂ (20 mL) was used as electrolyte with the donor **4a** (5 mg), dissolved in the anodic compartment. Electrolysis was performed during 7 days, after which air stable plate-shaped crystals were harvested on the anode and washed with little CH₂Cl₂.

4.5. X-ray crystallography

Details about data collection and solution refinement are given in Table 3. Data were collected on a Stoe Imaging Plate System (IPDS) for the structures **2a**, **4c**, **5b** and **5c** and on a Bruker-CCD System for the structure (**4a**)₂Mo₆Cl₁₄, both operating with a Mo K α X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on $F^{2,21}$ Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. All the heavy atoms, but C24A and C24B in the structure (**4a**)₂Mo₆Cl₁₄, have been refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 262767– 262771 (CIF files). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

4.6. Theoretical calculations

The overlap interaction energies ($\beta_{\text{HOMO-HOMO}}$) were of extended-Hückel type.²² A modified Wolfsberg-Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values.²³ Double- ζ orbitals for C, S, N and O were used.

4.7. Cyclic voltammetry

Cyclic voltammetry studies were performed in a threeelectrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/AgCl reference and a platinum wire counter-electrode. The electrolytic media involved a $0.1 \text{ mol } \text{L}^{-1}$ solution of (*n*-Bu₄N)PF₆ in dichloromethane. All experiments have been performed at room temperature at 0.1 V s⁻¹.

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