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Chiral 1,2-dithiine as sulfur rich electron acceptor.

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ABSTRACT: The selective synthesis of both enantiomers of a sulfur rich electron acceptor containing two 1-phenylethyl groups of the same chirality and a chiral axis is described. Cyclisation into enantiopure dithiine has been induced by the presence of chiral substituent on the nitrogen atom of thiazoline-2-thione dithiolate precursor.

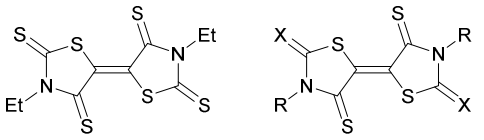
Introduction

The introduction of chirality on π-electron donor or acceptor precursors of conducting materials is stimulated by the potential synergistic effect referred to as electrical magneto-chiral anisotropy (eMChA) effect.[1] Accordingly, π-donor molecules such as chiral tetrathiafulvalenes (TTF)[2] have been prepared and the electrical magnetochiral anisotropy was evidenced in crystals of the enantiopure radical cation salts (DMEDT-TTF)$_2$ClO$_4$, confirming the chiral character of charge transport in these crystalline molecular materials.[3] Chiral π-electron acceptors exhibiting easily accessible redox potentials and thus able to form charge transfer salts are still rare in the literature. Nonetheless, a few metal bis(1,2-dithiolene)

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complexes, which act as electron acceptors and bear chiral substituents, can also be quoted.[4-8] We recently reported the synthesis of a sulfur rich electron acceptor, DEBTTT (chart 1), which is an excellent candidate for the elaboration of air-stable n-channel organic field effect transistors.[9]

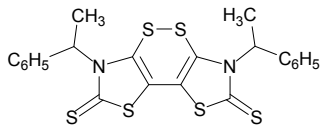
Chart 1



DEBTTT

Thus, we developed a series of various sulfur rich electron acceptors (Chart 1) with different electron affinity starting from different protected forms of N-alkyl-2-chalcogenoxo-1,3-thiazoline-4,5-dithiolate ligand.[9,10,11] As our strategy to form the thiazoline core allows for the introduction of diverse substituents on the nitrogen atom, we decided to insert on this heterocyclic ring a chiral substituent in order to generate a chiral acceptor. Herein, we report that using a protected dithiolene ligand bearing a 1-phenylethyl group on the nitrogen, all the chemical routes used previously to form DEBTTT and analogues, unexpectedly led to an electroactive dithiine acceptor **3** exhibiting three elements of chirality, the two stereogenic centers and an axial chirality due to the dithiine (Chart 2).

Chart 2



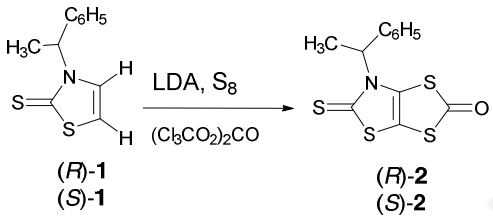
(*R,R,M*)-**3**
(*S,S,P*)-**3**

Results and Discussion

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For this purpose, we prepared a protected form of the dithiolene ligand which has proved to be a good starting derivative for other substituted acceptors (Scheme 1). The bicyclic derivatives *(R)*-**2** and *(S)*-**2** were prepared from the enantiopure *(R)*-, and *(S)*-3-(1-phenylethyl)-1,3-thiazoline-2-thione **1**[7] after a sequence of lithiation/sulfuration to generate the dithiolate which is further trapped *in situ* with triphosgene to generate **2**.

Scheme 1



(*R*)-**1** (*S*)-**1** (*R*)-**2** (*S*)-**2**

Both enantiomers *(R)*-**2** and *(S)*-**2** were obtained as air stable compounds and crystals of sufficient quality for an X-ray diffraction study were obtained after slow concentration of a CH_2Cl_2 solution. The molecular structures of the two enantiomers, *(R)*-**2** and *(S)*-**2**, are represented in Figure 1. In both cases, the bicyclic framework is planar with the C-H in the same plane and oriented towards the C=S thione (Figure 1).[12]

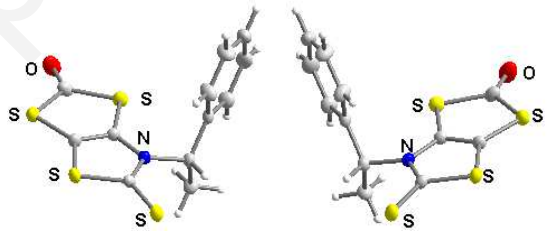


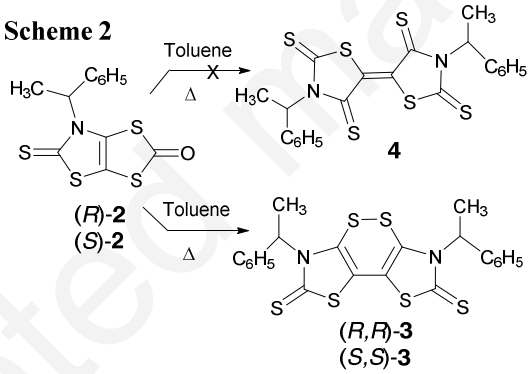
Figure 1. Molecular structures of bicycle *(R)*-**2** (right) and *(S)*-**2** (left). Ellipsoids are drawn at 50 % probability

Then we performed a thermal treatment of these bicyclic derivatives *(R)*-**2** and *(S)*-**2** in toluene. After the usual work up, we isolated crystals and performed an X-ray structure

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determination. Contrary to our expectations, we obtained the tricyclic structure **3** with the formation of a disulfide bridge, as shown in Scheme 2 and Figure 2. Compound **3** crystallizes with one molecule of S_8 (Figure S1). It is worth mentioning that the product formed and the yield of the reaction are not modified if the reaction is carried out in the presence of air or under inert atmosphere.[10] A plausible mechanism would be that upon the heat treatment the generated carbene, obtained after decarbonylation and the loss of sulfur, would dimerize into the acceptor **4**.[10] However, no trace of the expected acceptor **4** was detected in the medium. This acceptor **4** could be considered as the thioxo valence isomer of the dithiine **3**. We attempted to form **4** through either photolysis or thermolysis of a solution of **3**, but no electrocyclic ring opening was observed and the dithiine **3** was entirely recovered.

Scheme 2



As demonstrated by X-ray structure analyses of both enantiomers, the six-membered heterocyclic ring with a disulfide bridge is twisted, with a C-S-S-C torsion angle of 55.97 (17)° and 56.22(12)° for *(R,R)*-**3** and *(S,S)*-**3** respectively (Figure 2). This twist impedes the two thiazole rings to be coplanar and they form a dihedral angle of 27.98(8)° and 27.86(6)°. The bond lengths of the C-S-S-C moiety as well as the bond angles are in the usual range for such disulfide ring.[13-15] Interestingly the formation of the dithiine upon the heating of *(S)*-**2** leads to a twisted structure in the sense of a right handed helix *(P)* while the reaction of *(R)*-**2**

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generates a twisted heterocycle in the opposite direction left handed helix *(M)*. Both dithiines are exclusively the two enantiomeric forms, *(R,R,M)*-**3** and *(S,S,P)*-**3**.

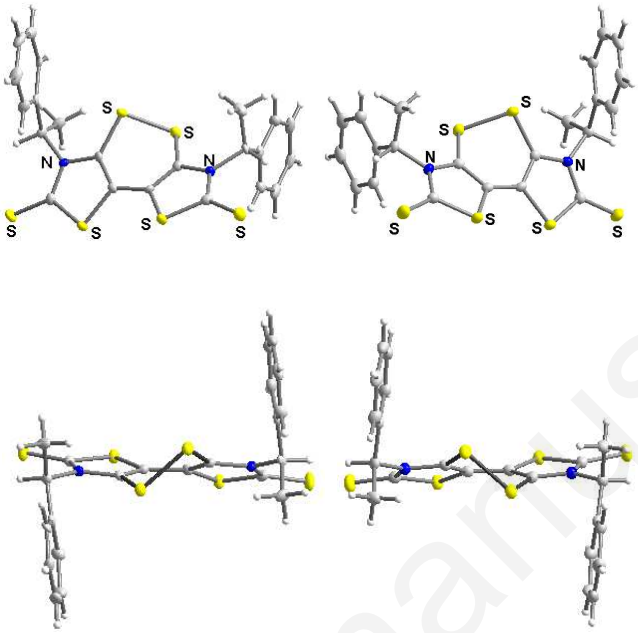
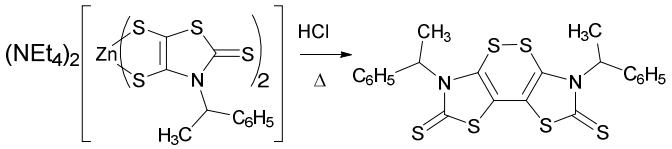


Figure 2. Molecular structures (top) and side views (bottom) of *(R,R,M)*-**3** (left) and (*S,S,P*)-**3** (right) . Ellipsoids are drawn at 50 % probability

We also attempted another approach that was previously successful for the synthesis of DEBTTT starting from a dianionic Zn bis(dithiolene) complex.[10] Thus, we attempted this approach to form similar acceptor skeleton (Scheme 3). Upon heating a dichloromethane solution of either the *(R,R)*-**5** or *(S,S)*-**5** Zn complex in the presence of HCl we noticed a deep change of color from yellow to purple as expected. There again, after the work up we obtained the same *(R,R,M)*-**3** and *(S,S,P)*-**3** tricyclic structures in 78 % and 87 % yield respectively. Actually, the formation of this tricyclic structure is reminiscent to what was obtained by Rauchfuss et al. from the thermal decomposition of $[Zn(dmit)_2]^{2-}$ in the presence of HCl, where the N-R is replaced by a S atom.[15]

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Scheme 3



The redox behavior of **3** was investigated by cyclic voltammetry in DMF with nBu_4NPF_6 as supporting electrolyte (Figure 3). For the two enantiomers, the CV displays two reversible redox systems indicating the stepwise formation of three redox states from the neutral to the radical anion and the fully reduced species $\mathbf{3}^{2-}$ (E_1= 0.10 V; E_2= -0.43 V vs SCE). This CV is close to those observed for DEBTTT and analogues where two reversible reduction processes were observed corresponding to the stepwise formation of the radical anion and dianion species. For comparison, we analysed the redox potentials of DEBTTT in DMF with nBu_4NPF_6. In these conditions, the CV shows two reversible reduction waves at similar potentials E_1= 0.11 V and E_2= -0.41 V vs SCE, indicating that **3** and DEBTTT are reduced at the same potentials.

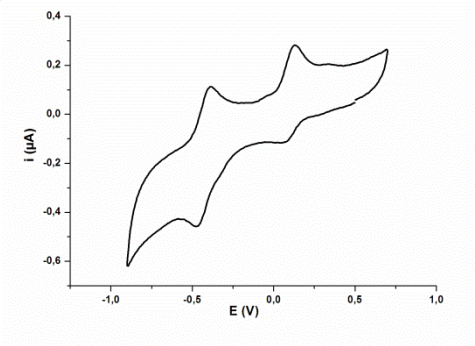
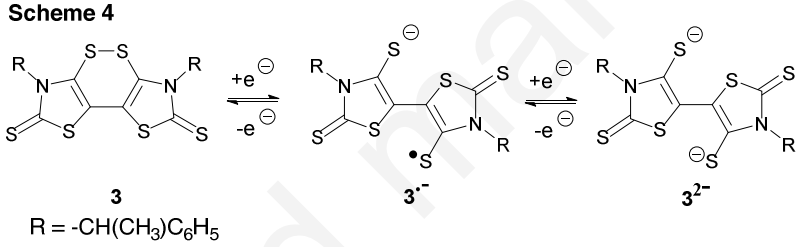


Figure 3. Cyclic voltammograms of (*S,S,P*)-**3** in DMF containing 0.1 M NBu_4PF_6. E in V *vs* SCE, scan rate 100 mVs^{-1}, Pt working electrode.

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Two mechanisms have been suggested for the reduction of 1,2-dithiine.[16] One proposed mechanism involves first the reduction of the disulfide into the radical anion followed by the rapid breaking of the S-S bond into a $S^{\bullet}$ and a S^{-}. Then the second electron transfer generates the dianionic species. The other mechanism suggests that the two electrons transfer occurs before the rapid cleavage of the S-S bond into the dithiolate.[17] The CV obtained for both enantiomers is in favor of the first of the two mechanisms, that is the reduction into the anion radical followed by the cleavage into the open structure of the radical anion as depicted in Scheme 4.

Scheme 4



The dithiines (*R*,*R*)-**3** and (*S*,*S*)-**3** exhibit absorption bands in the UV-vis region at λ_{max} (nm) (ε [$L.mol^{-1}cm^{-1}$]) = 354 (34400), 477 (4190) (Figure 4). This spectral signature is different to those of the acceptors such as DEBTTT which exhibits absorption bands at higher wavelengths (530 and 570 nm). The gradual reduction of (*S*,*S*)-**3** in 0.2 M CH_2Cl_2 nBu_4NPF_6 from 0.15 to -0.25 V leads to a diminution of UV visible absorption band at 354 nm and progressively to the appearance of new absorption bands at 400, 580, 680 and 810 nm characteristic to the formation of the anion radical species (Figure S2). It is really interesting to notice the perfect similarity of the UV-vis-NIR data of the radical anion form of the DEBTTT and the radical anion form of (*S*,*S*)-**3** confirming that the reduction of the disulfide

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into the radical anion is followed by a rapid breaking of the S-S bond into a $S^{\bullet}$ and a S^{-} (Figure 4 and Scheme 4).

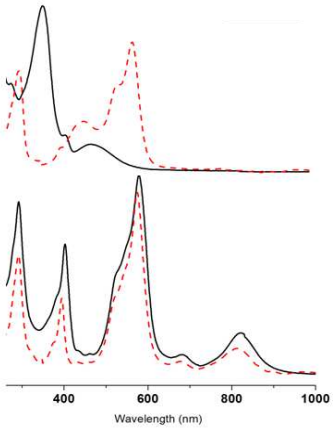


Figure 4. Comparison of the UV-vis-NIR spectra of (*S,S,P*)-**3** (black line) and DEBTTT (red dotted line) in neutral form (top) and radical anion form generated electrochemically (bottom)

The optical activity of the bicycle **2** and 1,2-dithiine **3** were also investigated, in the UV-vis range. The optical activity of these derivatives are reported in Table 1, as specific and molar optical rotations at four different wavelengths, (436, 546, 578 and 589 nm), in the visible range. Comparison of the chiroptical properties reveals an unexpected large increase in the values of the molar rotations between the precursor **2** and the dithiine acceptor **3**. For instance for the $[\Phi]_D$, the value for *(R,R,M)*-**3** is 20 times higher than the one for *(R)*-**2** (Table 1). These values for **3** are surprisingly large, almost the same order of magnitude as helicenes molar rotations.[18] The CD spectra of *(R)*-**2** and *(S)*-**2** as well as *(R,R,M)*-**3** and *(S,S,P)*-**3** recorded at room temperature in CH_2Cl_2, exhibit a perfect mirror-image relationship as expected for the opposite trace of two enantiomers (Figure 5).

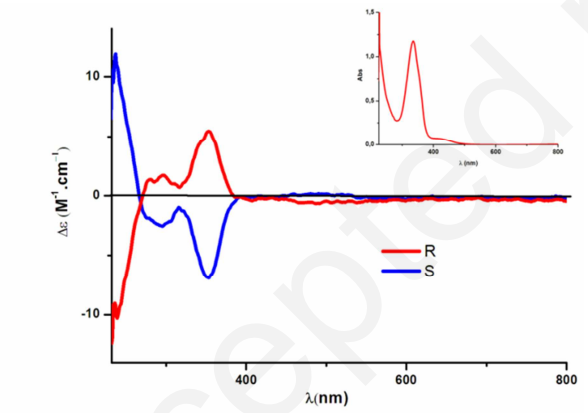
Table 1. Specific and molar optical rotations of compounds **2** and **3** in CH_2Cl_2, at 23°C.*

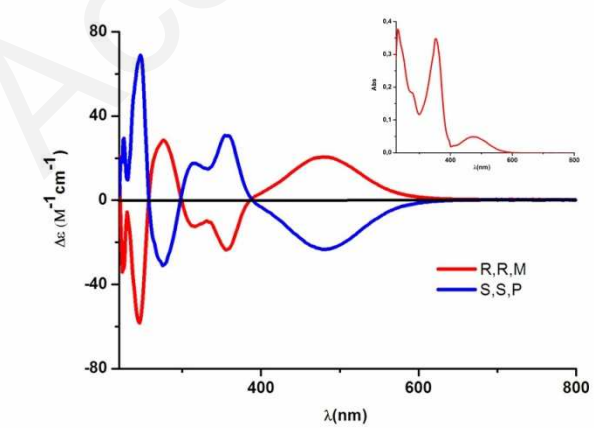
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	***(R)*-2**	***(S)*-2**	***(R,R,M)*-3**	***(S,S,P)*-3**
$[\alpha]_{436}$	+1034	-1065	-11505	12683
$[\alpha]_{546}$	+ 421	- 392	+ 5600	- 5975
$[\alpha]_{578}$	+ 340	- 334	+ 4553	- 4939
$[\alpha]_{589}$	+ 340	- 319	+ 4000	- 4451
$[\Phi]_{436}$	+3219	- 3314	-57796	+63714
$[\Phi]_{546}$	+ 1309	-1220	+ 28132	- 30016
$[\Phi]_{578}$	+ 1057	-1039	+ 22872	- 24811
$[\Phi]_{589}$	+ 1057	- 992	+ 20094	- 22360

* [α] Measured in 10^{-1} deg cm^2 g^{-1} and within an error of ± 10%. [Φ] in deg cm^2 $dmol^{-1}$

The large chiroptical properties of **3** relative to **2** may be due to the presence of the axial chirality generated by the distorted disulfide bridge. The S-S bond adopts a skewed conformation and thus these disulfides can adopt a right-handed screw sense *(P)* and a left-handed screw sense *(M)* which are not superimposable screws.





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Figure 5. CD spectra in CH_2Cl_2 (inserts: UV-vis absorption spectra) of **2** (top) and **3** (bottom).

Conclusions

In summary, this study shows that, independently of the chemical route used, the introduction of a chiral 1-phenylethyl substituent on the thiazoline-2-thione ring of a protected dithiolate form, favors the formation of a 1,2-dithiine skeleton with a stereocontrol of the axial chirality. This dithiine is an electroactive molecule which can be reversibly reduced into the radical anion and dianion as demonstrated through the electrochemical and spectro-electrochemical investigations. These results indicate that these enantiopure derivatives present interesting chiroptical and electrochemical properties which are of high interest for the elaboration of molecular materials.

Experimental Section

General procedures

All commercial chemicals were used without further purification unless otherwise noted. Tetrahydrofuran was distilled over sodium and benzophenone under nitrogen. Methylene chloride was dried by passing through activated alumina columns under nitrogen. All the NMR spectra were obtained in $CDCl_3$. Chemical shifts are reported in ppm and ^{1}H NMR spectra were referenced to residual $CHCl_3$ (7.26 ppm) and ^{13}C NMR spectra were referenced to $CHCl_3$ (77.2 ppm). Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. Mass spectra and elemental analysis were performed by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Cyclic voltammetry was carried out on a 10^{-3} M solution of **3** in DMF, containing 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte. Voltammograms

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were recorded at 0.1 Vs^{-1} on a platinum electrode and the potentials were measured *versus* Saturated Calomel Electrode (SCE). The spectroelectrochemical setup was referenced *versus* SCE in CH_2Cl_2-[NBu_4][PF_6] 0.2 M. Spectrophotometers were employed to record the UV-vis-NIR and IR spectra. The Zn salts (*R*,*R*)-**5** and (*S*,*S*)-**5** were prepared according to literature procedures.[7]

Synthesis

6-(1-phenylethyl)-5-thioxo-5,6-dihydro-[1,3]dithiolo[4,5,-d]thiazol-2-one **2**.

To a -10°C cooled solution of thiazoline **1** (500 mg, 2.26 mmol) in 40 mL of dry THF under nitrogen was added a solution of LDA prepared from diisopropylamine (0.50 mL, 3.39 mmol) and n-BuLi 1.6 M in hexane (2.12 mL, 3.39 mmol) in 10 ml of dry THF. After stirring for 30 min at -10°C, sulphur S_8 (108 mg, 3.39 mmol) was added and the solution was stirred for an additional 30 min. A solution of LDA (diisopropylamine 0.64 mL, 4.52 mmol and n-BuLi 1.6 M in hexane 2.83 mL, 4.52 mmol) in 15 mL of dry THF was added. The mixture was stirred for 3 hours and S_8 (145 mg, 4.52 mmol) was added. After 30 min triphosgen (1.34g, 4.5 mmol) was added at -10°C. The reaction mixture was stirred overnight at room temperature and water (5 mL) was slowly added. The solvent was evaporated *in vacuo*. Dichloromethane (50 mL) was added and the solution was washed with water (3×20 mL) and dried over $MgSO_4$. The concentrated solution was purified by chromatography on silica gel using CH_2Cl_2-petroleum ether (3/2) as eluent to afford **2** as a brown powder. Crystals of sufficient quality for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution.

(*R*)-**2** Yield 38 %. Mp 155°C (dec). ^{1}H NMR (300 MHz) δ 1.79 (d, 3H, ^3J = 7.0 Hz, CH_3), 6.86 (q, 1H, ^3J = 7.0 Hz, CH), 7.38 (m, 5H, H_{Ar}); ^{13}C NMR (75 MHz) δ 15.5 (CH_3), 57.2 (CH), 104.8 (C=C), 124.6 (Ar), 128.0 (Ar), 129.3 (Ar), 129.5 (Ar), 135.7 (C=C), 187.6 (C=S),

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189.2 (C=O); IR $\nu_{(C=S)}$ = 1274 cm^{-1}, $\nu_{(C=O)}$ = 1665 cm^{-1}; UV-vis (CH_2Cl_2) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 335 (14012); HRMS (ASAP) calcd for $C_{12}H_{10}NOS_4$ $[M+H]^+$: 311.96453 Found: 311.9642; Anal. calcd for $C_{12}H_9NOS_4$: C, 46.28 ; H, 2.91 ; N, 4.50. Found: C, 46.02 ; H, 2.81; N, 4.50.

(*S*)-**2** Yield 57 %. Mp 154°C (dec). ^{1}H NMR (300 MHz) δ 1.79 (d, 3H, ^3J = 7.0 Hz, CH_3), 6.85 (q, 1H, ^3J = 7.0 Hz, CH), 7.38 (m, 5H, H_{Ar}); ^{13}C NMR (75 MHz) δ 15.5 (CH_3), 57.2 (CH), 104.8 (C=C), 124.6 (Ar), 128.0 (Ar), 129.2 (Ar), 129.4 (Ar), 135.6 (C=C), 187.5 (C=S), 189.2 (C=O); IR $\nu_{(C=S)}$ = 1274 cm^{-1}, $\nu_{(C=O)}$ = 1665 cm^{-1}; UV-vis (CH_2Cl_2) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 335 (14338); HRMS (ASAP) calcd for $C_{12}H_{10}NOS_4$ $[M+H]^+$: 311.96453 Found: 311.9644; Anal. calcd for $C_{12}H_9NOS_4$: C, 46.28 ; H, 2.91 ; N, 4.50. Found: C, 46.42 ; H, 2.92; N, 4.37.

Dithiin **3.**

Route **a** from bicycle **2**. A solution of compound **2** (100 mg ; 0.32 mmol) in toluene (10 mL) was refluxed for 7 hours. The solvent was evaporated *in vacuo*. The concentrated solution was purified by chromatography on silica gel using CH_2Cl_2-petroleum ether (3/2) as eluent to afford **3**. Crystals of (*R,R,M*)-**3** and (*S,S,P*)- **3** were obtained by slow concentration of fractions obtained after chromatography. The solvent of the combined fractions was reduced in volume under reduced pressure and the resulting precipitate was collected and washed with EtOH to give **3** as a purple powder. The enantiomer (*R,R,M*)-**3** was obtained in 52 % yield and the (*S,S,P*)-**3** in 62 % yield.

Route **b** from $[NEt_4]_2[Zn(PhMeCH\text{-}thiazdt)_2]$ **5**. To a suspension of Zinc complex **5** (250 mg, 0.28 mmol) in 25 mL of dry CH_2Cl_2 was added HCl 1M in diethyl ether (1.12 mL, 1.12 mmol). The reaction mixture was refluxed 24 hours then washed with water and dried over $MgSO_4$. The solvent was removed *in vacuo* and the concentrated solution was purified by

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chromatography on silica gel using CH_2Cl_2 as eluent to afford **3** as a dark purple powder. The enantiomer (*R,R,M*)-**3** was obtained in 78 % yield and the (*S,S,P*)- **3** in 87 % yield.

(*R,R,M*)-**3** Mp 225°C (dec). ^{1}H NMR (300 MHz) δ 1,90 (d, 6H, ^3J = 7.0 Hz, CH_3), 6.71 (q, 2H, ^3J = 7.0 Hz, CH), 7.19 (m, 4H, H_{Ar}), 7.35 (m, 6H, H_{Ar}); ^{13}C NMR (75 MHz) δ 15.2 (CH_3), 57.1 (CH), 117.0 (C=C), 124.2 (Ar), 127.2 (Ar), 128.9 (Ar), 129.3 (Ar), 138.8 (C=C), 185.7 (C=S); UV-vis (CH_2Cl_2) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 230 (37700), 354 (34700), 477 (4490); HRMS (ASAP) calcd $C_{22}H_{18}N_2NaS_6$ $[M+Na]^+$: 524.9692 Found: 524.9690; Anal. calcd for $C_{22}H_{18}N_2S_6$: C, 52.55 ; H, 3.61 ; N, 5.57 ; S, 38.27. Found: C, 52.46 ; H, 3.48 ; N, 5.23; S, 38.62.

(*S,S,P*)-**3** Mp 225°C (dec). ^{1}H NMR (300 MHz) δ 1,90 (d, 6H, ^3J = 7.0 Hz, CH_3), 6.71 (q, 2H, ^3J = 7.0 Hz, CH), 7.19 (m, 4H, H_{Ar}), 7.35 (m, 6H, H_{Ar}); ^{13}C NMR (75 MHz) δ 15.2 (CH_3), 57.1 (CH), 117.0 (C=C), 124.2 (Ar), 127.2 (Ar), 128.9 (Ar), 129.3 (Ar), 138.8 (C=C), 185.7 (C=S); UV-vis (CH_2Cl_2) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 230 (37600), 354 (34400), 477 (4190); HRMS (ASAP) calcd $C_{22}H_{18}N_2NaS_6$ $[M+Na]^+$: 524.9692 Found: 524.9690; Anal. calcd for [$C_{22}H_{18}N_2S_6$ + $toluene_{0.25}$]: C, 54.25 ; H, 3.83 ; N, 5.33 ; S, 36.59. Found: C, 54.02 ; H, 3.97 ; N, 5.11; S, 36.94.

Crystallography

Data were collected on an APEXII, Bruker-AXS diffractometer. The structure were solved by direct methods using the SIR97 program,[19] and then refined with full-matrix least-square methods based on F^2 (SHELXL-97)[20] with the aid of the WINGX[21] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. Details of the final refinements are given in Table 2. CCDC 1486023-1486026.

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Table 2. Crystallographic data.

Compound	**(*R*)-2**	(*S*)-**2**	(*R*,*RM*)-**3**	(*S*,*S*,*P*)-**3**
Formula	$C_{12}H_9NOS_4$	$C_{12}H_9NOS_4$	$C_{22}H_{18}N_2S_6$, S_8	$C_{22}H_{18}N_2S_6$, S_8
FW ($g\cdot mol^{-1}$)	311.44	311.44	759.22	759.22
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.4177(2)	6.3994(14)	8.4457(6)	8.4463(2)
b (Å)	12.5899(5)	12.570(3)	15.3090(12)	15.3100(4)
c (Å)	16.6644(7)	16.622(4)	23.682(2)	23.6692(7)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V ($Å^3$)	1346.45(9)	1337.1(5)	3062.0(4)	3060.73(14)
T (K)	150(2)	150(2)	150(2)	150(2)
Z	4	4	4	4
D_{calc} ($g\cdot cm^{-3}$)	1.536	1.547	1.647	1.648
μ (mm^{-1})	0.690	0.695	1.013	1.013
Total refls.	12162	10644	14124	20181
Abs. Corr .	multi-scan	multi-scan	multi-scan	multi-scan
Uniq. refls. (R_{int})	3060(0.027)	3071(0.0578)	6330(0.0325)	6967(0.0298)
Unique refls. ($I > 2\sigma(I)$)	2958	2928	5535	6349
R_1, wR_2	0.0214, 0.0521	0.0302, 0.0714	0.0454, 0.0892	0.0302,0.0631
R_1, wR_2 (all data)	0.0226, 0.0527	0.0320, 0.0726	0.0581, 0.0944	0.0358, 0.0651
GoF	1.061	1.045	1.077	1.025
Flack parameter	0.02(3)	-0.03(6)	-0.11(9)	0.02(6)

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

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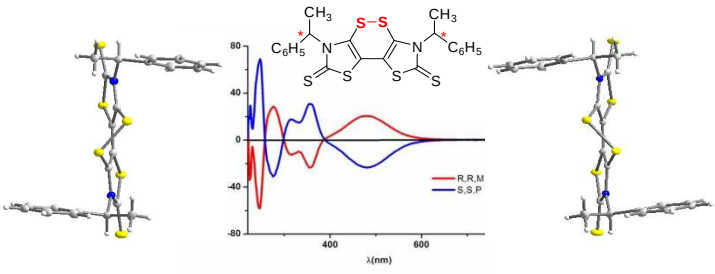
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Both enantiomers of a 1,2-dithiine containing two 1-phenylethyl groups of the same chirality were selectively synthetized and electrochemically and spectro-electrochemically characterized.

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