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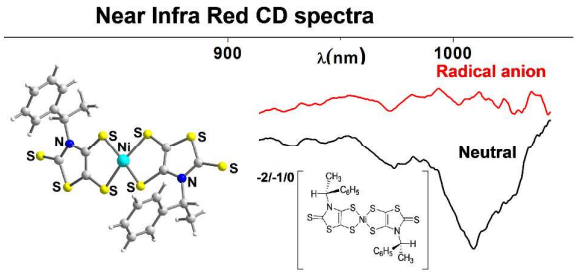
TOC



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Abstract

Enantiomerically pure dianionic, monoanionic and neutral dithiolene complexes formulated as [Ni*((R,R)*-CHMePh-thiazdt)$_2$]$^{-2,-1,0}$ and [Ni*((S,S)*-CHMePh-thiazdt)$_2$]$^{-2,-1,0}$ (CHMePh-thiazdt : N-(1-phenylethyl)-1,3-thiazoline-2-thione-4,5-dithiolate) have been synthesized from the enantiopure N-(1-phenylethyl)-1,3-thiazoline-2-thione precursors. The electrochemical and spectro-electrochemical investigations carried out on these complexes show that the CHMePh-thiazdt ligands act as electron rich ligands and that the complexes are strong near infrared (NIR) absorbers in the range of 800-1100 nm for the neutral species and 1050-1500 nm for the reduced radical anion species. Circular dichroism (CD) thin layer spectro-electrochemical experiments carried out on the neutral (*R,R*) enantiomer, [Ni*((R,R)*-CHMePh-thiazdt)$_2$], revealed a redox switching of CD-active bands, not only in the UV–vis but also in the NIR region.

Introduction

Nickel bis(dithiolene) complexes exhibit versatile and unique properties, associated with different redox states, for potential applications in optics and electronics.[1] For instance, these dithiolene complexes are strong near infrared (NIR) absorbers in the range of 700-1400 nm, and this absorption range can be tuned not only with the electron withdrawing or releasing ability of the ligand but also by controlling the degree of oxidation of the complex.[2] The

introduction of chirality in such metal dithiolene complexes has also recently emerged,[3] either to generate NIR chiro-optical effects[4] or for the possible observation, in conducting dithiolene salts,[5] of electrical magneto-chiral anisotropy,[6] as recently reported in fully organic conductors.[7] Interestingly,[4] the chirality of cholesterol substituents was transferred to the NIR response of the complexes only in a gel supramolecular organisation, but was absent in the diluted molecular complexes. There is therefore an important issue to be able to introduce chirality in the close vicinity of NIR-absorbing square-planar dithiolene complexes. In that respect, two strategies have been essentially reported to prepare such chiral salts: either the chirality is introduced by the counter-ion associated with the anionic metal dithiolene complex[5,8] or a chiral substituent is covalently linked to the dithiolene ligand.[3]

Our current interest on metal dithiolene complexes involving the N-alkyl-1,3-thiazoline-2-thione-4,5-dithiolate (R-thiazdt) ligand[9,10,11,12] prompted us to investigate the synthesis of chiral ligands on this attractive platform. Indeed, the thiazoline core offers the possibility of numerous structural modifications which can be brought through the substituent on the nitrogen atom. Therefore, we decided to investigate the synthesis of a thiazoline core bearing a chiral substituent and to use this chiral precursor in the preparation of homoleptic dithiolene complexes of general formula [Ni(R*-thiazdt)$_2$] (Chart 1), with a chiral center very close to the two metallacycles. The enantiopure (*R*- or *S*-) and racemic, commercially available 1-phenyl-ethylamine was chosen here for a first proof of concept. Herein, we report the synthesis of the enantiopure nickel dithiolene complexes together with spectroscopic and electrochemical investigations in solution. The X-ray crystal structures, magnetic properties as well as the chiroptical properties will be also presented, demonstrating for the first time a circular dichroism effect in the NIR region in diluted solution.

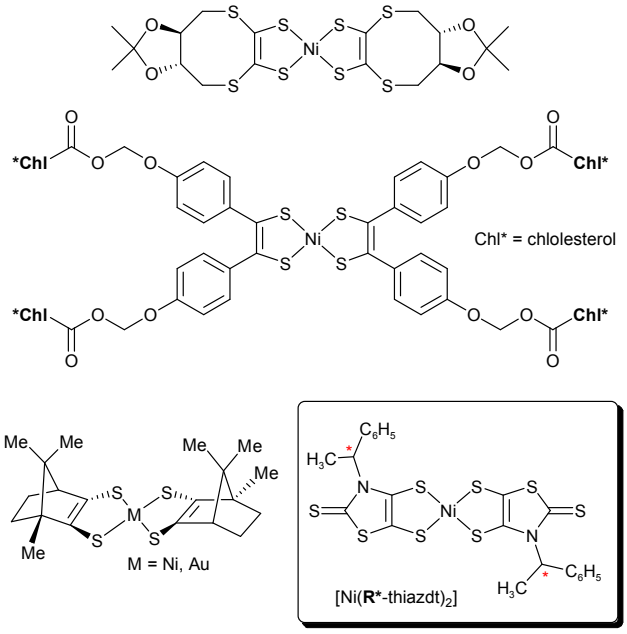
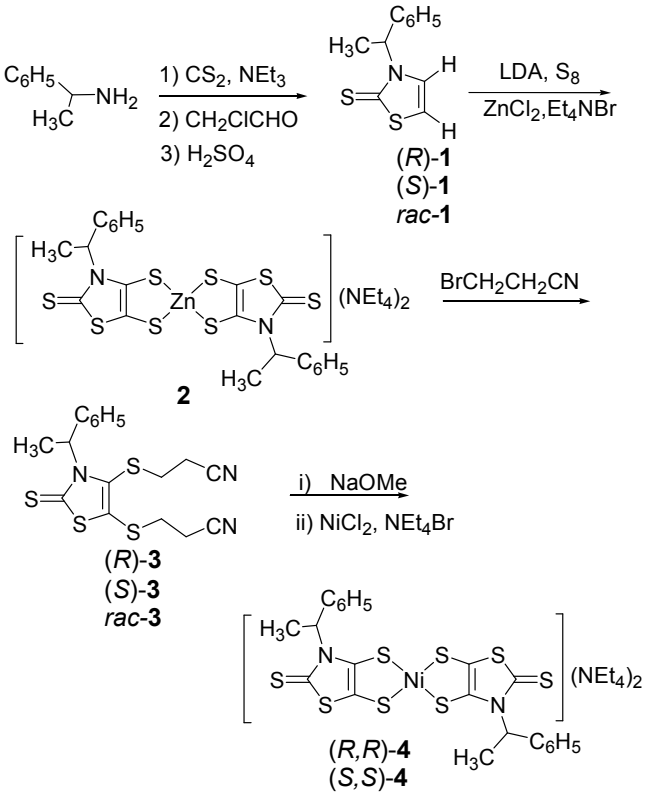


Chart 1. Examples of reported chiral dithiolene complexes[3,4] and the desired [Ni(R*-thiazdt)$_2$] complex derived from 1-phenylethylamine

Results and Discussion

Syntheses. The dithiolene complexes were prepared either from the enantiopure or the racemic mixture of 1-phenylethylamine according to the chemical route described in Scheme 1. The (*R*)-, (*S*)- and (*R,S*)-3-(1-phenylethyl)-1,3-thiazoline-2-thione **1** were prepared according to a modified procedure of Sandström.[13] Addition of carbon disulfide and triethylamine to a suspension of 1-phenylethylamine leads to the dithiocarbamate salt which reacts with chloroacetaldehyde. Cyclization and dehydration in the presence of sulfuric acid affords the 1,3-thiazoline-2-thione (*R*)-, (*S*)- and *rac*-**1** in 55 % yield.[14] In order to form the organic dithiolate protected form of the ligand, the N(-1-phenylethyl)-4,5-bis(cyanoethylthio)-1,3-thiazoline-2-thione **3** where the two thiolates are protected by cyanoethyl groups, we choose a two-step approach. The first step consists in the formation of the dithiolate which is trapped with $ZnCl_2$ as described in Scheme 1.[9b]



Scheme 1. Synthetic procedure toward (*R,R*) and (*S,S*)-**4**

Subsequent reaction of this Zn salt **2** with 3-bromopropionitrile affords organic dithiolate protected form **3**. Even if this route is longer than the direct formation of **3** from **1**, it allows an easier isolation of **3**, thanks to the precipitation in the first step of the Zn salt **2**. It is worth mentioning that at room temperature the ^{1}H NMR spectra of (*R*)-, (*S*)- and *rac*-**3** exhibit two broad unresolved signals, one for the C–H at 7.12 ppm (Fig. 1) and the other one at 2.22 ppm for the CH_2 of one cyanoethyl chain. This is reminiscent of what was observed for other N(-1-phenylethyl)-thiazoline-2-thione derivatives where broad signals were attributed to the presence of two rotamers designated as the rotamer *syn* and *anti,* depending on the orientation of the smallest substituent (C–H) in the plane of the thiazole ring (Chart 2).[13,15] A temperature-dependent ^{1}H NMR study in $CDCl_3$ was carried out on (*S*)-**3** from ambient temperature to 223 K. Upon lowering the temperature, the broad signal observed at 7.12 ppm,

for the C–H, becomes a quadruplet at 233 K indicating that at this temperature one of the rotamers strongly predominates. Similar results have been observed in previous studies related to other N-(1-phenylethyl)-1,3-thiazoline-2-thiones, substituted in the 4 and 5 positions, where it was demonstrated that these compounds exist predominantly in the *anti* form.[13]

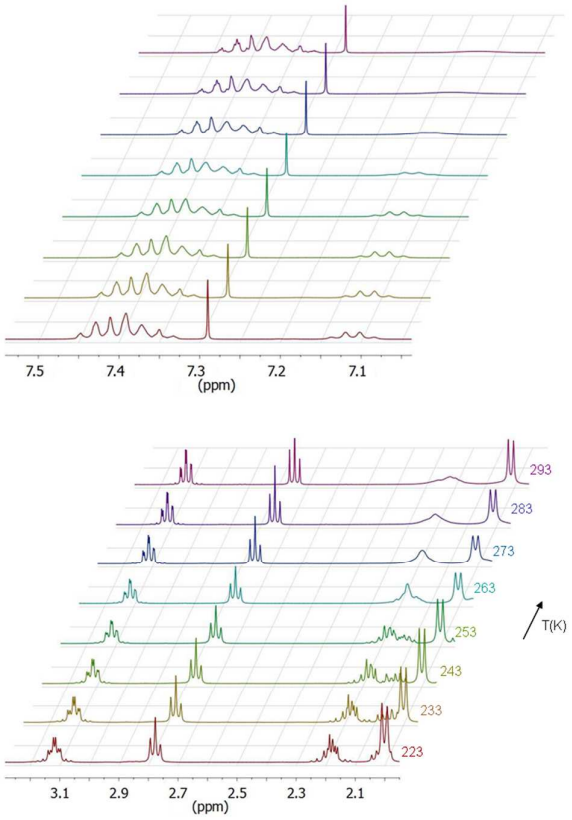


Fig. 1 ^{1}H NMR spectra of the phenyl and the benzylic protons of (*S*)-**3** (top) and the methyl and the cyanoethyl groups (bottom) at various temperature.

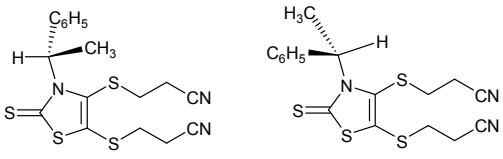


Chart 2.

Single crystals of good-quality for X-ray diffraction studies were obtained by slow diffusion of diethyl ether into a concentrated solution of (*S*)-**3** in dichloromethane. Figure 2 shows the two crystallographic independent molecules, for the structure solved in the orthorhombic system, space group $P2_12_12_1$. Both crystallographically independent molecules (*S*)-**3** exhibit a planar thiazole skeleton with the C^*–H of the chiral substituent oriented towards the C=S thione, that is the *anti* rotamer (Chart 2). The C–H bonds lie in the plane of the thiazole ring with short C–H•••S distances (2.5662(1) and 2.577(1) Å). Within this *anti* conformer, as observed in the NMR ^{1}H study, the phenyl group exerts a strong shielding effect on the closest cyanoethyl group.

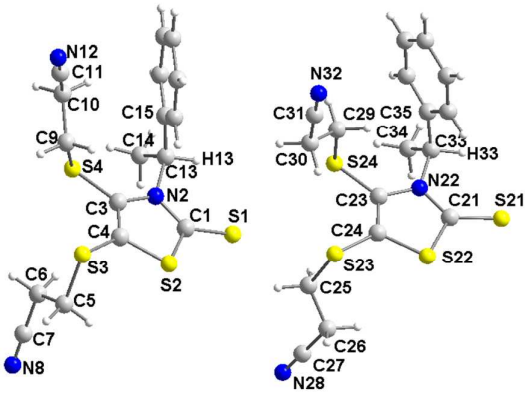


Fig. 2 Molecular structures of the two crystallographically independent molecules (*S*)-**3**

Deprotection of the dithiolate precursor **3** was performed in basic medium using NaOMe,[16] followed by addition of $NiCl_2$ and Et_4NBr, to afford the dianionic dithiolene complexes **4** as dark red crystalline material (Scheme 1). The reaction was conducted on the enantiopure (*R*)-**3** and (*S*)-**3** affording respectively the dianionic complexes (*R,R*)-**4** and (*S,S*)-**4**. Attempts to analyze the dianionic complexes by H^1 NMR spectroscopy were unsuccessful due to the fact that these complexes, as their methyl analogues $[NEt_4][Ni(Me\text{-}thiazdt)_2]$,[9b] are easily oxidized in solution upon exposure to traces of air to the paramagnetic radical anion species. This was confirmed by the investigation of their redox properties by cyclic voltammetry (CV). These

studies were carried out in CH_3CN using $[Bu_4N][PF_6]$ as the supporting electrolyte and the redox potentials of (*R,R*)-**4** and (*S,S*)-**4** are collected in Table 1 together with those of $[NEt_4][Ni(Me\text{-}thiazdt)_2]$ and $[NBu_4]_2[Ni(dmit)_2]$[17] for comparison. The Ni complexes **4** exhibit two reversible oxidation waves at E^1 = –0.33 V and E^2 = +0.25 V *vs* SCE, corresponding to the oxidation of the dianionic species into the radical anion and then to the neutral species (Fig. 3). A third irreversible redox process is also observed at E_{pa}^3 = +0.86 V *vs* SCE (E_{pa} = anodic peak potential) associated with the oxidation of the neutral complex into the radical cation. Comparison with the Ni dithiolene complexes belonging to the same family, $[NEt_4][Ni(Me\text{-}thiazdt)_2]$, and investigated in the same conditions, shows no difference of redox potentials, indicating that the presence of the –C*HMePh substituent on the thiazole ring has no significant effect. On the contrary, comparison with the well-known $Ni(dmit)_2$ derivative shows a cathodic shift of about 150 mV for the potential of the –2/–1 redox process for **4**, confirming the electron rich character of the thiazole dithiolene ligands.

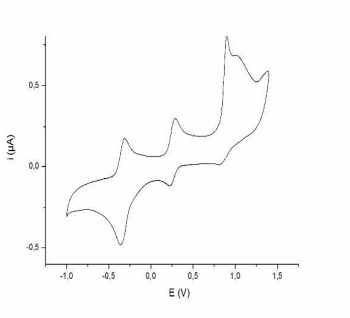


Fig. 3 Cyclic voltammogram of of (*R,R*)-**4** in CH_3CN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 100 $mV.s^{-1}$. Pt working electrode.

Table 1 Redox potentials for the Ni complexes in CH_3CN with $[NBu_4][PF_6]$ 0.1 M, E in V *vs* SCE, v = 100 $mV.s^{-1}$.

	E^1	E^2	$E_{pa}{}^3$
4	–0.33	+0.25	0.86*
[Ni(Me-thiazdt)$_2$]	–0.29	+0.20/0.01[a]	
[Ni(*DL*-bordt)$_2$][b,c]	–1.20	–0.43	+1.00*
[Ni(dmit)$_2$][17]	–0.175	+0.34/0.228[a]	

*Not fully reversible process. [a] E_{pa}/E_{pc} : anodic and cathodic peak potentials. [b]E values have been determined in CH_2Cl_2 [c] DL-bordt stands for bornylenedithiolate.

In order to generate the radical anion species, (*R,R*)-**4** and (*S,S*)-**4** were reacted with one equivalent of $[Cp_2Fe][PF_6]$. The resulting anionic complexes (*R,R*)-**5** and (*S,S*)-**5**, $[NEt_4]$[Ni*((R)*-CHMePh-thiazdt)$_2$] were then crystallized in an acetonitrile/toluene solution, and crystals of the enantiopure (*R,R*)-**5** suitable for an X-ray diffraction study were obtained.

Structural Properties. Complex (*R,R*)-**5** crystallizes in the monoclinic system, space group C2 with both Et_4N^+ cation and [Ni*((R)*-CHMePh-thiazdt)$_2$]$^{-\bullet}$ radical anion located in general position in the unit cell. The molecular structure represented in Figure 4 shows a slightly distorted square planar geometry around the Ni atom and the formation of the *trans*-isomer. Concerning the thiazole skeleton, the C–H groups of the chiral substituents are oriented towards the thione bonds leading to the *anti/anti* rotamer (Chart 3) as observed for the organic precursor **3** (Chart 2).

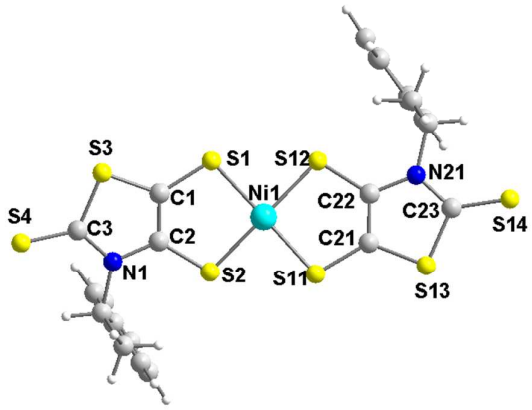
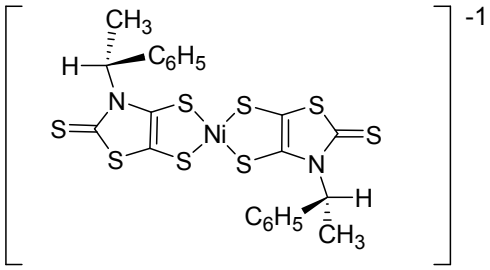
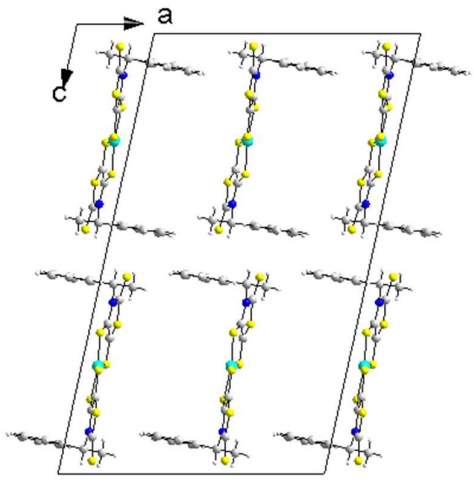


Fig. 4 Molecular structure of the radical anion [Ni*((R)*-CHMePh-thiazdt)$_2$]$^{\cdot -}$ in [NEt$_4$][Ni*((R)*-1-PhEt-thiazdt)$_2$] **5** showing the atom labelling.

Chart 3



(*R,R*)-5anti/anti



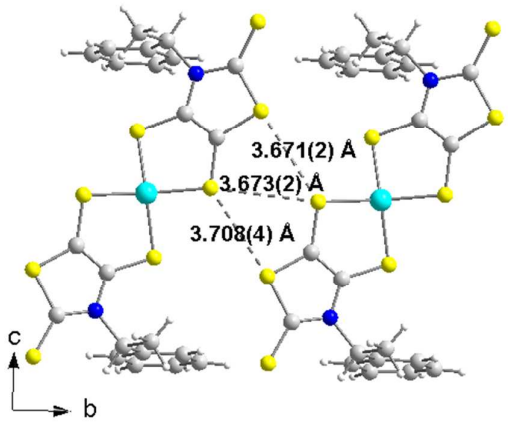


Fig. 5 Top: projection view along the *ac* plane of the unit cell of the monanionic radical (*R,R*)-**5** the NEt_4 groups have been omitted for clarity. Bottom: view of the shortest S•••S contacts in the chains of radical anions running along *b*.

In the solid state, the enantiopure complexes are isolated from each other by the Et_4N^+ counterion in the *ac* plane while several short lateral S•••S intermolecular contacts can be observed along the *b* axis (Fig. 5). Actually, steric hindrance due to the presence of the bulky N-1-phenylethyl substituent on the nitrogen impedes shorter lateral contacts in the *bc* plane. The temperature dependence of the magnetic susceptibility for the enantiopure monanionic radical (*R,R*)-**5** shows a weak Curie-type behavior with a magnetic susceptibility accounting for only 3.8% $S = ½$ species, demonstrating that the radical anions in (*R,R*)-**5** are interacting antiferromagnetically within the chains running along *b*, to such an extent that the remaining susceptibility in the investigated temperature range (5–300 K) is negligible.

Oxidation of the radical anion species, (*R,R*)-**5** and (*S,S*)-**5**, with one more equivalent of $[Cp_2Fe][PF_6]$ leads to the neutral species [Ni(CHMePh-thiazdt)$_2$] (*R,R*)-**6** and (*S,S*)-**6**. These neutral diamagnetic species have been investigated by ^{1}H NMR at room temperature where the signals associated with the benzylic protons are well resolved, compared to those observed for the protected ligands (*R*)-**3** and (*S*)-**3**. This indicates the presence of only one

rotamer at room temperature, most probably because of the steric hindrance generated by the metallacycles.

UV-vis-NIR spectroelectrochemical investigations UV-vis-NIR absorption spectra of freshly prepared solutions of the neutral dithiolene species in dichloromethane exhibit absorption bands in the UV-vis region between 250 and 450 nm and also in the near-IR region with a strong absorption band at 1013 nm (ε = 28 454 M^{-1} cm^{-1}). The gradual reduction of this neutral Ni complex to the monoanionic species induces the growth of a lower energy band in the near-IR region, at 1260 nm, concomitantly with the disappearance of the band at 1013 nm, as shown in Figure 6. These values are in accordance with those obtained on the Ni(Et-thiazdt)$_2$ analogue, where the neutral and monoanionic species exhibit indeed absorption bands at comparable wavelengths, i.e. 1030 nm (in toluene) and 1219 nm (in CH_2Cl_2), respectively.[18] These low-energy absorption bands are characteristic of square-planar nickel dithiolene complexes and are attributed to a π–π* transition of HOMO-LUMO character within these neutral species.[19]

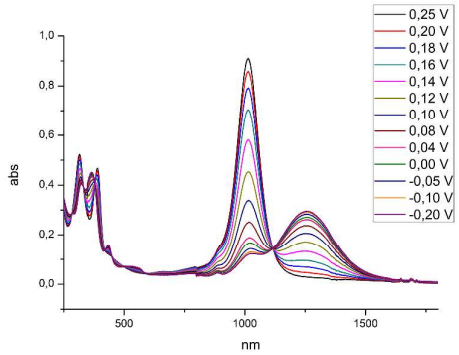


Fig. 6 UV-vis-NIR monitoring of the electrochemical reduction of [Ni(CHMePh-thiazdt)$_2$] (*R,R*)-**6** from 0.25V to -0.2 V in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte

As mentioned in the Introduction, the chiral character of these complexes opens perspectives toward the elaboration of electrochemically driven chiroptical switches.[20,21] Accordingly, the optical activity and circular dichroism of the dithiolene complexes, as well as some organic chiral precursors were investigated, in the UV-vis range as well as in the NIR range when possible. The optical activity of two organic precursors, the non-substituted thiazole **1** and the organic protected dithiolate form **3**, as well as the radical anion complex **5** are reported in Table 2, as specific and molar optical rotations at three different wavelengths, (436, 546 and 578 nm), in the visible range. Note that both enantiomers of **5**, (*R,R*)-**5** and (*S,S*)-**5,** exhibit practically no optical rotation ($|\alpha| < 0.002$) at 365 nm and between 546 nm and 589 nm but shows a weak optical activity at 436 nm($|\alpha| < 0.048$).

Table **2**. Specific and molar optical rotations of compounds **1**, **3** and **5** in CH_2Cl_2, 0.5 10^{-3}g.mL^{-1}, 23°C)

	(*R*)-**1**[(a)]	(*S*)-**1**	(*R*)-**3**	(*S*)-**3**	(*R,R*)-**5**	(*S,S*)-**5**
$[\alpha]_{578}$	+325	–345	+258	–253	–	–
$[\alpha]_{546}$	+391	–407	+ 312	–305	–	–
$[\alpha]_{436}$					+1500	–1677
$[\Phi]_{578}$	+719	–764	1010	–990		
$[\Phi]_{546}$	+865	–901	1221	–1194		
$[\Phi]_{436}$					+11300	–12400

[(a)] Previously reported value $[\alpha]_D$ = +377 (c = 0.93, EtOH).[10]

Circular dichroism (CD) spectra in the UV-Visible range (Fig. 7) were recorded in CH_2Cl_2 at room temperature for the neutral complexes (*R,R*)- and (*S,S*)-**6**, together with those of starting thiazoline (*R*)- and (*S*)-**1** for comparison. These CD spectra of both enantiomers, for **1** and for **6**, exhibit mirror-image relationships. The spectrum for the (*R*)-**1** enantiomer exhibits a weak

negative band around 340 nm, a positive band at 320 nm and at shorter wavelengths a positive band at 270 nm. This spectrum is similar to the one reported for this compound by Sandström et al.[13] The CD spectrum of the (*S*)-**1** enantiomer is the mirror-image of the (*R*)-**1** spectrum. Besides some similarities in the short wavelengths such as a positive band at around 270 nm for (*R,R*)-**6**, the CD spectra of the neutral complexes (*R,R*)- and (*S,S*)-**6** exhibit two weak CD-active bands above 400 nm ((*R,R*)-**6**: $\Delta\varepsilon = -7.22$ M^{-1} cm^{-1}at 403 nm and $\Delta\varepsilon = -1.9$ M^{-1} cm^{-1}at 564 nm).

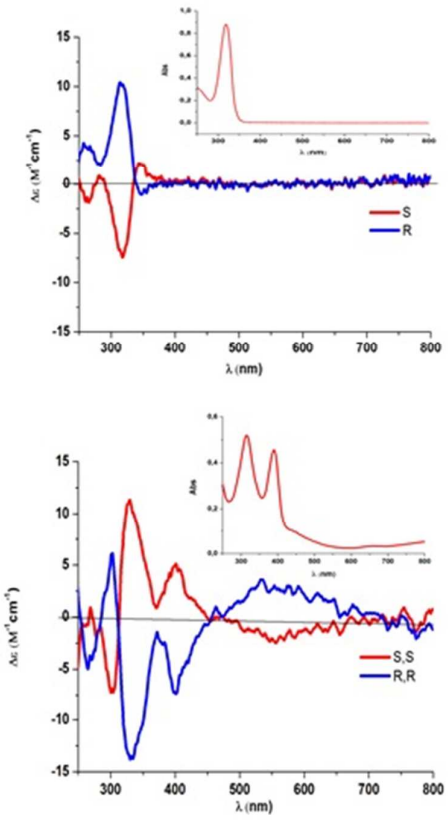


Fig. 7 CD spectra in CH_2Cl_2 (inserts : UV-vis absorption spectra) of thiazoline **1** (top) and of neutral complexes **6** (bottom).

In order to investigate the CD spectra of the other redox species such as the dianion in **4** and the radical anion in **5**, we set up a thin-layer spectro-electrochemical experiment on the CD spectrometer, starting with a solution of the neutral (*R,R*)-**6** enantiomer (Fig. 8). In the UV-vis region, the CD spectra of the electrogenerated radical anion (*R,R*)-**5** and the dianion (*R,R*)-**4** show some similarities, a positive band at 280 nm, a broad negative band ranging from 300 nm to 455 nm band with two maxima at 320 nm and 430 nm and a broad positive band from 455 nm to 660 nm. Most of these CD-active bands undergo changes in their intensities upon reduction accompanied with slight bathochromic shifts.

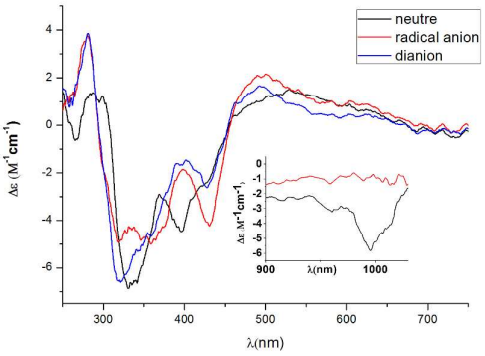


Fig. 8 CD spectra monitored electrochemically in CH_2Cl_2 at 293 K of the neutral (*R,R*)-**6**, radical anion (*R,R*)-**5** and dianion (*R,R*)-**4** complexes (insert :CD spectra from 900-1030 nm).

The CD spectra of the neutral and the radical anion species have been also investigated in the NIR region (insert Fig. 8), where both compounds are known to absorb (See Fig. 6). Remarkably, the neutral species exhibits a negative CD band centered around 1000 nm, related to its 1013 nm absorption. This CD active band in the NIR disappears upon reduction to the radical anion, while no clear CD signal can be observed for the radical anion species at lower energies, due to spectrophotometer limitations in the wavelength range. Note also that

the UV-vis-NIR CD spectra monitored electrochemically exhibit a very good reversibility, as the CD spectrum of the neutral complex (*R,R*)-**6** could be recovered from the dianionic and monoanionic complexes, upon oxidation.

Conclusions

In conclusion, we have described here the synthesis of a novel chiral Ni dithiolene complex where the chirality was provided by the dithiolene ligand, in the close proximity of the complex metallacycles. Electrochemical and spectro-electrochemical experiments showed that these Ni complexes exhibit four redox states from the dianion, radical anion, neutral to the radical cation with different UV-visible-near infrared (UV-vis-NIR) spectra. The spectro-electrochemical circular dichroism (CD) spectroscopy studies revealed changes in several CD active bands when reducing the neutral enantiopure complex (*R*,*R*)-**6** to the radical anion (*R*,*R*)-**5** and dianion (*R*,*R*)-**4**. Interestingly, the appearance of a CD-active band in the NIR region is observed in the neutral Ni dithiolene complex upon oxidation of the radical anion. These results suggest that chiral Ni-dithiolene complexes may be potentially used as redox chiroptical switches both in the UV-vis and NIR regions.[21]

Experimental section

General

All air-sensitive reactions were carried out under argon atmosphere. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300III spectrometer and chemical shifts are quoted in parts per million (ppm) referenced to tetramethylsilane. Optical rotation of the enantiopure compounds was determined with a Perkin-Elmer 341 polarimeter. The circular dichroism (CD) spectra were recorded with a Jasco spectropolarimeter J-815. Mass spectra were recorded with

Thermo-fisher Q-Exactive instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Elemental analysis were performed at the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Tetrahydrofuran was distilled from sodium-benzophenone. Column chromatography was performed using silica gel Merck 60 (70-260 mesh). The spectroelectrochemical setup was performed in CH_2Cl_2-[NBu_4][PF_6] 0.2 M. A Cary 5000 spectrophotometer was employed to record the UV-vis-NIR spectra. Cyclic voltammetry were carried out on a 10^{-3} M solution of the complex in CH_2Cl_2, containing 0.1 M nBu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 Vs^{-1} on a platinum disk electrode (A = 1mm^2). The potentials were measured *versus* Saturated Calomel Electrode.

Syntheses

(*R*)-, (*S*)- and (*R,S*)-3-(1-phenylethyl)-1,3-thiazoline-2-thione 1. To a suspension of 1-phenylethylamine (R/S, R or S) (12.8 mL, 0.1 mol) in 200 mL of diethyl ether at 0°C under nitrogen was slowly dropped triethylamine (14.6 mL, 0.105 mol) and carbon disulfide (6.34 mL, 0.105 mol). The mixture was stirred for 3 hours at 0°C and the precipitate was filtered off and washed with diethyl ether to afford 29.8 g of dithiocarbamate salt wich was used without further purification. Yield 100%. ^{1}H NMR (300 MHz, D_2O) δ 1.25 (t, 9H, $N(CH_2CH_3)_3$, J = 7.2 Hz), 1.50 (d, 3H, CH_3, J = 7.0 Hz), 3.18 (q, 6H, $N(CH_2CH_3)_3$, J = 7.2 Hz), 5.43 (q, 1H, CH, J = 7.0 Hz), 7.38 (m, 5H, Ar); ^{13}C NMR (75 MHz, D_2O) δ 8.6, 21.1, 45.9, 54.3, 126.2, 126.4, 127.4, 128.2, 128.5, 142.2. To a suspension of the dithiocarbamate salt (29.8 g, 0.1 mol) in acetonitrile (300 mL) was added chloroacetaldehyde (50 % solution in water, 25.4 mL, 0.2 mol). The mixture was stirred 24 hours at room temperature under nitrogen. The volume was reduced to approximatively 1/5 *in vacuo* and the solution was slowly added to a flask containing 20 mL of H_2SO_4 at 0°C. The mixture was stirred 15 min at 0°C, hydrolyzed with 120 mL of water, extracted with CH_2Cl_2 (3×80 mL), washed with water (3×50 mL) and

dried over $MgSO_4$. The concentrated solution was purified by chromatography on silica gel using CH_2Cl_2 as eluant to afford **1** as a brown thick oil.

(*R*)-**1** : Yield 54%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (t, 3H, CH_3, J = 6.9 Hz), 6.53 (m, 2H, =CH,*CH), 6.88 (d, 1H, CH, J = 4.8 Hz), 7.33 (m, 5H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 56.2, 111.2, 126.8, 128.2, 128,4, 128.8, 138.9, 186.0; HRMS (ESI) calcd for $C_{11}H_{11}NNaS_2^+$: 244.02306. Found: 244.0230.

(*S*)-**1**: Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (t, 3H, CH_3, J = 6.9 Hz), 6.53 (d, 1H, CH, J = 4.8 Hz), 6.59 (q, 1H, CH, J = 6.9 Hz), 6.88 (d, 1H, CH, J = 4.8 Hz), 7.33 (m, 5H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 56.2, 111.7, 126.9, 128.2, 128,4, 128.8, 138.9, 186,9; Anal. calcd for $C_{11}H_{11}NS_2$: C, 59.68; H 5.01; N, 6.33; S, 28.97. Found : C, 59.81; H, 5.01; N, 6.35; S, 28.80; HRMS (ESI) calcd for $C_{11}H_{11}NNaS_2^+$: 244.02306. Found: 244.0229.

(R/S)-**1** : Yield 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (t, 3H, CH_3, J = 6.9 Hz), 6.53 (m, 2H, =CH,*CH), 6.88 (d, 1H, CH, J = 4.8 Hz), 7.33 (m, 5H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.42, 56.2, 111.2, 126.8, 128.2, 128,4, 128.8, 138.9, 186.0; Anal calcd for $C_{11}H_{11}NS_2$: C, 59.68; H 5.01; N, 6.33; S, 28.97. Found : C, 59.41; H 5.03; N, 6.11; S, 28.86; HRMS (ESI) calcd for $C_{11}H_{11}NNaS_2^+$: 244.02306. Found: 244.0231.

(*R*)-, (*S*)- and (*R,S*)-3,3'-[3-(1-phenylethyl)-2-thioxo-2,3-dihydro-1,3-thiazole-4,5-diyl)bis(thio)]dipropanenitrile 3. To a -10°C cooled solution of thiazoline **1** (2 g, 9 mmol) in 90 mL of dry THF under nitrogen was added a solution of LDA prepared from diisopropylamine (1.96 mL, 13.5 mmol) and n-BuLi 1.6 M in hexane (8.5 mL, 13.5 mmol) in 20 mL of dry THF. After stirring for 30 min at -10°C, sulphur S_8 (434 mg, 13.5 mmol) was added and the solution was stirred for an additional 30 min. A solution of LDA (diisopropylamine 2.56 mL, 18.0 mmol and n-BuLi 1.6 M in hexane 11.3 mL, 18.0 mmol) in 40 mL of dry THF was added. The mixture was stirred for 3 hours and S_8 (578 mg, 18.0 mmol) was added. After 30 min $ZnCl_2$ (616 mg, 4.5 mmol) and NEt_4Br (1.9 g, 9.0 mmol)

were added. The reaction mixture was stirred overnight and the precipitate was filtered off and washed with diethyl ether to afford $[NEt_4]_2Zn(1\text{-phenylethyl-thiazdt})_2$] **2** as a yellow powder. The Zn salt **2** was used in the next step without further purification. (*R*)-**2** 62 % yield. Mp 222°C. ^{1}H NMR (300 MHz, CD_3CN) δ 1.16 (t, 24H, CH_3, J = 7.2 Hz), 1.93 (broad signal, 6H, CH_3), 3.12 (t, 16H, $N(CH_2CH_3)_3$, J = 7.2 Hz), 6.42 (broad signal, 2H, CH), 7.27 (m, 10H, Ar). ^{13}C NMR (75 MHz, CD_3CN) δ 7.6, 19.0, 48.1, 52.9, 127.6, 128.5, 129.4, 129.6, 129.7, 141.3, 184.1. (*S*)-**2** 67 % yield. Mp 239°C. ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ 1.15 (t, 24H, CH_3 , J = 7.2 Hz), 1.94 (broad signal, 6H, CH_3), 3.20 (t, 16H, $N(CH_2CH_3)_3$, J = 7.2 Hz), 6.35 (broad signal, 2H, CH), 7.24(m, 10H, Ar). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 7.1, 15.4, 51.4, 55.8, 126.2, 126.5, 126.6, 126.8, 127.7, 139.8, 180.8. (R/S)-**2** : 73 % yield. Mp 235°C. ^{1}H NMR (300MHz, $(CD_3)_2SO$) δ 1.15 (t, 24H, CH_3 , J = 7.2 Hz), 1.94 (broad signal, 6H, CH_3), 3.20 (t, 16H, $N(CH_2CH_3)_3$, J = 7.2 Hz), 6.37 (broad signal, 2H, CH), 7.22 (m, 10H, Ar). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ 7.0, 15.4, 51.3, 55.6, 126.1, 126.5, 126.6, 126.8, 127.5, 139.8, 179.12. To a solution of the zinc complex **2** (1 g, 1.12 mmol) in 40 mL of degased MeCN under nitrogen was added bromopropionitrile (3.65 mL, 11.20 mmol). The mixture was refluxed 24 hours and solvent was removed *in vacuo* and 150 mL of CH_2Cl_2 was added. The solution was washed with water (2×50 mL) and dried over $MgSO_4$. The concentrated solution was purified by chromatography on silica gel using CH_2Cl_2 as eluant to afford **3**. Recrystallisation in EtOH gave a white powder.

(*R*)-**3** : Yield 41 %, Mp = 108°C. ^{1}H NMR (300 MHz, $(CDCl_3)_2$ 1.97 (d, 3H, CH_3, J = 7.2 Hz), 2.19 (broad s, 4H, CH_2CN), 2.70 (t, 2H, SCH_2, J = 6.9 Hz), 3.09 (t, 2H, SCH_2, J = 6.9 Hz), 7.05 (broad signal, 1H, CH), 7.36 (m, 5H, Ar). ^{13}C NMR (75 MHz, $(CDCl_3)$ δ 16.4, 17.4, 18.6, 31.3, 31.4, 57.1, 117.0, 117.2, 126.5, 127.7, 127.8, 128.6, 135.7, 138.7, 188.6. UV-vis (CH_2Cl_2) λ (nm) (ε [$L.mol^{-1}cm^{-1}$]) 318 (15586); Anal. calcd for $C_{17}H_{17}N_3S_4$: C, 52.14; H

4.38; N, 10.73; S, 32.75. Found: C, 52.00; H 4.42; N, 10.70; S, 32.55. HRMS (ESI) calcd for $C_{17}H_{17}N_3NaS_4^+$: 414.0203. Found: 414.0201

(*S*)-**3** : Yield 40 %, Mp = 109°C. ^{1}H NMR (300 MHz, $(CDCl_3)_2$ 1.99 (d, 3H, CH_3, J = 7.2 Hz), 2.20 (broad s, 4H, CH_2CN), 2.72 (t, 2H, SCH_2, J = 6.9 Hz), 3.11 (t, 2H, SCH_2, J = 6.9 Hz), 7.10 (broad signal, 1H, CH), 7.38 (m, 5H, Ar).). ^{13}C NMR (75 MHz, $(CDCl_3)$ δ 16.3, 17.3, 18.5, 31.2, 31.3, 57.0, 117.0, 117.2, 126.5, 126.9, 127.6, 128.5, 135.6, 138.5, 188.4; UV-vis (CH_2Cl_2) λ (nm) (ε [L.mol^{-1}cm^{-1}]) 318 (14918); Anal. calcd for $C_{17}H_{17}N_3S_4$: C, 52.14; H 4.38; N, 10.73; S, 32.75. Found: C, 51.54; H 4.46; N, 10.64; S, 32.59. HRMS (ESI) calcd for $C_{17}H_{17}N_3NaS_4$ $[M^+Na]^+$: 414.0203. Found: 414.0203

(*R,S*)-**3** : Yield 38 %, Mp = 108°C. ^{1}H NMR (300MHz, $(CDCl_3)_2$ 1.97 (d, 3H, CH_3, J = 7.2 Hz), 2.19 (broad s, 4H, CH_2CN), 2.71 (t, 2H, SCH_2, J = 6.9 Hz), 3.08 (t, 2H, SCH_2, J = 6.9 Hz), 7.09 (broad signal, 1H, CH), 7.37 (m, 5H, Ar). ^{13}C NMR (75 MHz, $(CDCl_3)$ δ 16.5, 17.5, 18.6, 31.4, 31.6, 57.2, 117.0, 117.1, 126.5, 127.1, 127.8, 128.8, 135.9, 138.8, 188.8. UV-vis (CH_2Cl_2) λ (nm) (ε [L.mol^{-1}cm^{-1}]) 318 (15227); Anal. calcd for $C_{17}H_{17}N_3S_4$: C, 52.14; H 4.38; N, 10.73; S, 32.75. Found: C, 52.03; H 4.38; N, 10.73; S, 32.81; HRMS (ESI) calcd for $C_{17}H_{17}N_3NaS_4^+$: 414.0203. Found: 414.0201.

$[NEt_4]_2[Ni(1\text{-phenylethyl-thiazdt})_2]$ (*S,S*)-4 and (*R,R*)-4. To a dry two necked flask containing thiazoline-2-thione **3** (225 mg, 0.58 mmol) 10 mL of 2M NaOMe was added under nitrogen at room temperature. The solution was stirred 1 hour and a solution of $NiCl_2$ (45 mg, 0.35 mmol) in 10 mL of dry EtOH was added. The reaction mixture was stirred 5 hours and a solution of NEt_4Br (72mg, 0.35 mmol) in 5mL of dry EtOH was added. The mixture was stirred overnight and the precipitate was filtered off, washed with EtOH to afford a red-brown powder (150mg). (*R,R*)-**4** and (*S,S*)-**4** in 65-69 % yield. Analysis of these dianion by ^{1}H NMR was not possible due to the presence of anion radical species in the medium.

[NEt$_4$][Ni(1-phenylethyl-thiazdt)$_2$] (*S,S*)-5 and (*R,R*)-5. To a solution of ferricinium hexafluorophosphate (53 mg, 0.16 mmol) in 10 mL of CH_2Cl_2 under inert atmosphere, the dianionic species **4** (140 mg, 0.16 mmol) was added. After stirring for 1 h, the addition of pentane (50 mL) afforded a precipitate which is filtered out. Recrystallization of the precipitate in acetonitrile gave crystals of the monoanionic species in 57% yield for **(*S,S*)-5** and in 77% yield for (*R,R*)-**5**.

(*S,S*)-**5** Mp > 250°C; Anal. calcd for $C_{30}H_{38}N_3S_8Ni$: C, 47.67; H, 5.07; N, 5.56. Found: C, 47.63; H 5.07; N, 5.56. HRMS (ESI) calcd for $A^-(C_{22}H_{18}N_2S_8Ni)$: 623.85947. Found: 623.8596; calcd for the ionization cluster $[2A^-,Et_4N^+]^-$: 1377.87797. Found: 1377.8788. UV-vis (CH_2Cl_2) λ (nm) (ε [L.mol^{-1}cm^{-1}]) 324 (16442), 366 (18846), 432 (6256), 1252 (13558). $[\alpha]_{436}^{25}$ =-1677, $[\Phi]_{436}^{25}$ =-12400.

(*R,R*)-**5.** Mp > 250°C; Anal. calcd for $C_{30}H_{38}N_3S_8Ni$: C, 47.67; H, 5.07; N, 5.56; S, 33.94. Found: C, 47.50; H, 5.02; N, 5.34; S,34.36. HRMS (ESI) calcd for $A^-(C_{22}H_{18}N_2S_8Ni)$: 623.85947. Found: 623.8601; calcd for the ionization cluster $[2A^-,Et_4N^+]^-$: 1377.87797. Found: 1377.8798. UV-vis (CH_2Cl_2) λ (nm) (ε [L.mol^{-1}cm^{-1}]) 323 (15220), 366 (18693), 432 (5720), 1250 (12870). $[\alpha]_{436}^{25}$ =+1500, $[\Phi]_{436}^{25}$ =+11300.

[Ni(1-phenylethyl-thiazdt)$_2$] (*S,S*)-6 and (*R,R*)-6. To a solution of ferricinium hexafluorophosphate (33 mg, 0.1 mmol) in 7 mL of CH_2Cl_2 under inert atmosphere, the monoanionic species **5** (75 mg, 0.1 mmol) was added. After stirring for 1 h, the addition of pentane afforded a precipitate which is filtered out in quantitative yield. ^{1}H NMR (300MHz, $CDCl_3$) δ 2.14 (d, 3H, CH_3, J = 7.2 Hz), 1.50 (q, 1H, CH, J = 6.9 Hz), 7.37 (m, 5H, Ar). UV-vis (CH_2Cl_2) λ (nm) (ε [L.mol^{-1}cm^{-1}]) 316 (23875), 390 (14462), 432 (5720), 1013 (28454).

Crystallography: Data were collected on an APEX II Bruker AXS diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure were solved by direct methods using the *SIR97* program,[22] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[23] with the aid of the *WINGX* program.[24] 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 3 for compounds for (*S*)-**3** and (*R, R*)-**5**. CCDC 1015857-1015858.

Table 3 Crystallographic data for (*S*)-**3** and (*R, R*)-**5**

Compound	(*S*)-**3**	(*R, R*)-**5**
Formula	$2(C_{17}H_{17}N_3S_4)$	$C_{30}H_{38}N_3NiS_8$
FW ($g\cdot mol^{-1}$)	783.15	755.88
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$C2$
a (Å)	8.5565(3)	16.624(4)
b (Å)	11.6085(3)	7.8685(14)
c (Å)	37.5518(10)	28.101(5)
α (°)	90	90
β (°)	90	102.325(7)
γ (°)	90	90
V ($Å^3$)	3729.95(19)	3591.2(12)
T (K)	150(2)	293(2)
Z	4	4
D_{calc} ($g\cdot cm^{-3}$)	1.395	1.398
μ (mm^{-1})	0.513	1.031
Total refls.	33125	15925
Uniq. refls. (R_{int})	8535 (0.0551)	7860 (0.0828)
Unique refls.(I>2σ(I))	7759	4396
R_1, wR_2	0.0365, 0.0756	0.0635,0.1283
R_1, wR_2 (all data)	0.042, 0.078	0.1250,0.1560
GoF	1.026	0.996

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