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Review

Electroactive oxazoline ligands

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ABSTRACT

This review deals with the synthesis, properties and applications of electroactive oxazoline ligands. The redox active units include ferrocene and tetrathiafulvalene derivatives. The different synthetic methods for their preparations are reviewed, together with the solid state structures. Metal complexes based on these ligands are described. The ferrocene–oxazolines have been mainly used as electrochemical sensors, while tetrathiafulvalene (TTF)–oxazolines have served as precursors for chiral molecular precursors, in which the role of chirality is emphasized. Moreover, examples of catalytic reactions in which TTF–oxazolines are involved are also discussed. Finally, an example of a poly(thiophene-oxazoline) provided with supramolecular chirality which can be modulated by various factors is presented.

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1. Introduction

The ligands based on at least one chiral oxazoline unit, acting as N-donor site, have known a tremendous development in the last 15 years, mainly motivated by the continuous need of highly efficient catalytic systems in the field of the enantioselective catalysis [1]. The most widely employed oxazoline ligands for catalytic purposes are those containing a second coordinating function to insure a chelating system, such as a phosphine group, within the famous family of the phosphine–oxazolines [1,2], or a second oxazoline ring to provide the extensive series of the bis(oxazolines) (BOX) [1,3]. It is thus clear that the very large majority of the reports in the literature concerning these ligands deal with catalysis issues, and the review articles published so far discuss mainly, besides the synthetic strategies, their use in various catalytic processes, with, sometimes, deeper insights in their coordination chemistry [3b,3f]. Throughout these investigations, it was undoubtedly emphasized that the substitution pattern of the oxazoline rings plays a paramount role in the stability and reactivity of the corresponding metal complexes, through a fine tuning of steric and electronic effects. Besides the oxazoline ring itself, a very important structural feature of the ligand is related to the nature of the backbone to which the second coordinating group, e.g. a phosphine or another oxazoline, is possibly tethered, which will ultimately determine the size and conformation of the metallacycles formed upon coordination. In the case of

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the phosphine–oxazolines the most common backbones are aryl groups [2d], while in the bis(oxazolines) the two rings are very often connected by diversely substituted methylene groups [3], thus providing in both situations six-member ring metallacycles. However, even though a large variety of such types of backbones have been envisaged, generally they do not bring an additional property to the system, which eventually increases its complexity and functionality. In this respect, special types of backbones are those provided with reversible electron oxidation/reduction character. The use of electroactive moieties in the structure of the oxazoline based ligands could in principle allow for the modulation of the electronic properties of the ligand, and possibly of the coordinated metal, by changing its oxidation state. The concept of the redox modulation of the catalytic activity of a complex has been already illustrated in several systems based on metallocene containing ligands [4], and in our opinion this direction could be the subject of a much more extensive development in the future. Inversely, when a platform is provided with physical properties, they could be interplayed or combined with the characteristics brought by the oxazoline ring(s) attached to this platform, i.e. chirality and coordination chemistry, into multifunctional systems. This peculiar type of electroactive oxazolines, containing redox active moieties such as ferrocenes (Fc) (Part 2), tetrathiafulvalenes (TTF) (Part 3) or others (Part 4), has never been reviewed so far in the literature from the perspective of the mutual influence between ligand and backbone properties, and this constitutes the topic of the present review article. We will focus exclusively on the synthesis and properties of those systems where the electroactivity of the platform has been put forward across diverse fields of application.

2. Ferrocene–oxazolines (Fc–Ox)

Ferrocene is one of the most useful electroactive units, extensively used in the structure of diverse ligands for catalytic applications, especially because of its stability and relative ease of functionalization, and also for its planar chirality in substituted derivatives [5]. Nevertheless, despite its attractive redox properties [6], implying a fully reversible one-electron couple ferrocene/ferricinium Fc/Fc^+ at a potential around +0.4 V *vs*. SCE, very few catalytic systems have been described to take advantage of a possible redox modulation of the catalytic activity [4b,7], none of them containing oxazolines as coordinating groups. This is somewhat surprising when considering the large number of ferrocene–oxazolines described so far in the literature [1,8], with various uses in asymmetric catalysis. However, the electroactivity of the ferrocene unit proved to be useful for the electrochemical sensing of diverse metal cations within a series of oxazoline based ligands. It is known that redox active units can show a change of their electrochemical behavior in solution upon interaction or complexation with a guest species [9], and this represents an important area in the molecular recognition field. We have therefore addressed this peculiar aspect of ferrocene–oxazolines in the following, having in mind that homogenous catalysis processes using similar electroactive ligands could be also investigated in this respect.

2.1. Synthesis

The use of a series of ferrocene–oxazolines as electrochemical sensors has been reported by Bryce and co-workers [10]. The synthetic procedure for the preparation of the ligands **1a–b**, previously described [11], consists in the reaction of the ferrocene acid chloride with amino-alcohols in basic conditions, followed by the cyclization of the intermediary hydroxyamides upon treatment with tosyl chloride (TsCl) in the presence of catalytic amounts of 4-dimethylaminopyridine (DMAP) (Scheme 1).

Additionally, the ligand **2**, containing a *trans*-ethene spacer between the oxazoline ring and the electroactive unit, has been also prepared within the same frame. However, the synthesis involved this time a Horner–Wadsworth–Emmons condensation between ferrocene-carboxaldehyde and an oxazoline-phosphonate derivative [10] (Scheme 2).

The structure of **2** has been confirmed by single crystal X-ray analysis, which evidenced the *trans* configuration of the ethylene bridge and the (*S*) configuration of the stereogenic center.

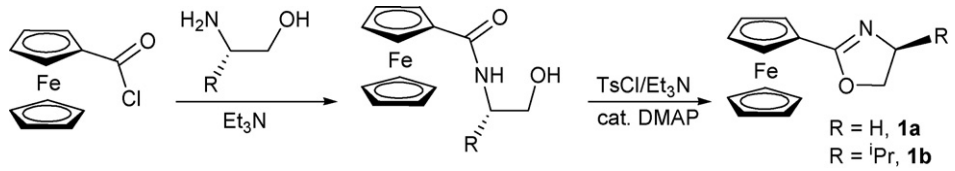
2.2. Sensing properties

The three ligands show the usual reversible redox wave of the ferrocene unit. Upon titration with metal perchlorate salts, a second reversible wave, anodically shifted, appears depending on the metallic center. Remarkably, addition of only 0.1 equivalents of Ca^{2+} ion was sufficient to afford a second oxidation wave for all the three ligands, thus demonstrating strong binding ($>10^4$) between the metal and the neutral ligand. Conversely, 1 equivalent of Mg^{2+} was necessary in the case of **1b** and **2** to observe the second redox process, while the recognition threshold of this ion by the ligand **1a** was one order of magnitude lower. The ligands **1a** and **1b** were also sensitive to the presence of the Cu^{2+} ion at a detection limit of 1 equivalent, although the resulting complex was highly sensitive to air and moisture. The observed anodic shifts ΔE range between 310 and 360 mV for the detection of Mg^{2+} and Ca^{2+} by the ligands **1a** and **1b**, while smaller ΔE values of 160 and 190 mV were measured in the case of the ligand **2** (Table 1). This difference is very likely related to the higher special separation between the redox center and the binding site in the latter, thus precluding efficient through-space electrostatic communication. Most importantly though is the absence of any sizeable change in the CV curves of all the three ligands when other metal cations such as Li^+, Na^+, K^+, Cs^+, Ba^{2+}, Ag^+ were added, at concentrations as high as 2500 mol%. This clearly demonstrates a very good selectivity of the three ligands for Mg^{2+} and Ca^{2+} recognition over the other cations.

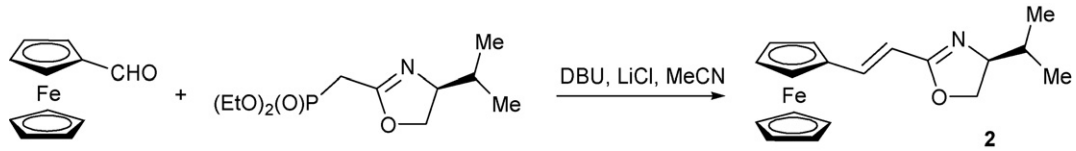
Worth noting is also the large binding enhancement, illustrated by the K_1/K_2 ratio between the complexation equilibrium constants of the neutral and oxidized forms of the ligands. The fact that the ligand–metal interaction strength decreases at such extent upon oxidation of the ferrocene unit demonstrates the usefulness of the electroactivity in the modulation of the coordinating properties of the ligand, without any structural change.

3. Tetrathiafulvalenes–oxazolines (TTF–Ox)

Tetrathiafulvalene (TTF) and its derivatives represent a most useful class of organic sulfur rich electron donors [12], extensively employed, since more than 30 years, as precursors for molecular conductors [13]. Besides, new applications of TTF derivatives, such as organic field effect transistors [14], fluorescence switchable systems, or cation and anion sensors [15], have emerged in the last decade. It is therefore not surprising that TTF derivatives have been covalently associated with coordinating groups within electroactive ligands such as TTF-phosphines or TTF-pyridines [16]. In the corresponding transition metal complexes, the coordinated metallic center might play a templating role to assemble at least two TTF units in its coordination sphere, or might provide an additional property such as magnetism or luminescence. In this last situation one would end up upon oxidation of TTFs with multifunctional systems in which the conducting properties would coexist



Scheme 1. Synthesis of Fc–oxazolines **1a–b**.



Scheme 2. Synthesis of **2**.

or interplay with another physical property. Another attractive field of investigations is represented by the homogenous catalysis, since, as in the case of the ferrocene based ligands, the modulation of the catalytic activity of the coordinated metal should be in principle possible upon changing the oxidation state of the TTF, providing that through-space or through-bond communication between the two units take place. Worth noting is the fact that TTF derivatives can be switched reversibly between three oxidation states, i.e. neutral TTF, radical cation $TTF^{+\bullet}$ and dication TTF^{2+}, thus enlarging the modulation propensity with respect to ferrocene derivatives. Thus, the covalent attachment of at least one oxazoline ring to a TTF unit to provide TTF–oxazoline (TTF–Ox) derivatives certainly presents several advantages. Besides the well known coordinating properties of mono- or bidentate oxazoline containing ligands [3b,f], they are relatively easily obtained as pure enantiomers, which allows in principle the access to electroactive precursors for chiral molecular conductors [17], a direction of much current interest in the field of the molecular multifunctional materials. Alternatively, as pointed out in Section 1, oxazoline derivatives proved to be efficient ligands in a large number of catalytic processes [1]. As a matter of fact, the first report concerning TTF–Ox by Bryce addressed exclusively this last point, through the preparation of a series of TTF–mono-oxazolines [18]. It was only several years later that Réthoré et al. reported EDT–TTF–Ox and EDT–TTF–phosphinooxazolines (TTF–PHOX) derivatives with a twofold objective: precursors for chiral molecular conductors and ligands for enantioselective catalysis [19]. In this section we will discuss the various aspects related to the synthesis, crystalline structures and coordination chemistry of TTF–Ox, together with their applications in the fields of molecular materials and homogenous catalysis. Contrary to the Fc–Ox previously described, utilization of TTF–Ox as redox sensors has not been reported so far, although this is the subject of active investigations in our group.

3.1. Synthesis and crystalline structures

As pointed out above, the first examples of TTFs containing chiral oxazoline rings (**3a–c**) have been described by Chesney and Bryce [18], with the objective to use them as electroactive ligands in the asymmetric allylic alkylation reaction. They were synthesized in a four step sequence starting from TTF, which was first lithiated, and then quenched with carbon dioxide. The resulting acid was transformed into acid chloride, which was further reacted with enantiopure amino-alcohols of (*S*) configuration, followed by cyclization of the intermediate β-hydroxyamides in the presence of PPh_3, CCl_4 and Et_3N (Scheme 3).

Alternatively, the same authors described the TTF–Ox **6** with a *trans*-ethene spacer between the two units, prepared by a Wittig–Horner condensation of an oxazoline-phosphonate and formyl-TTF (Scheme 4).

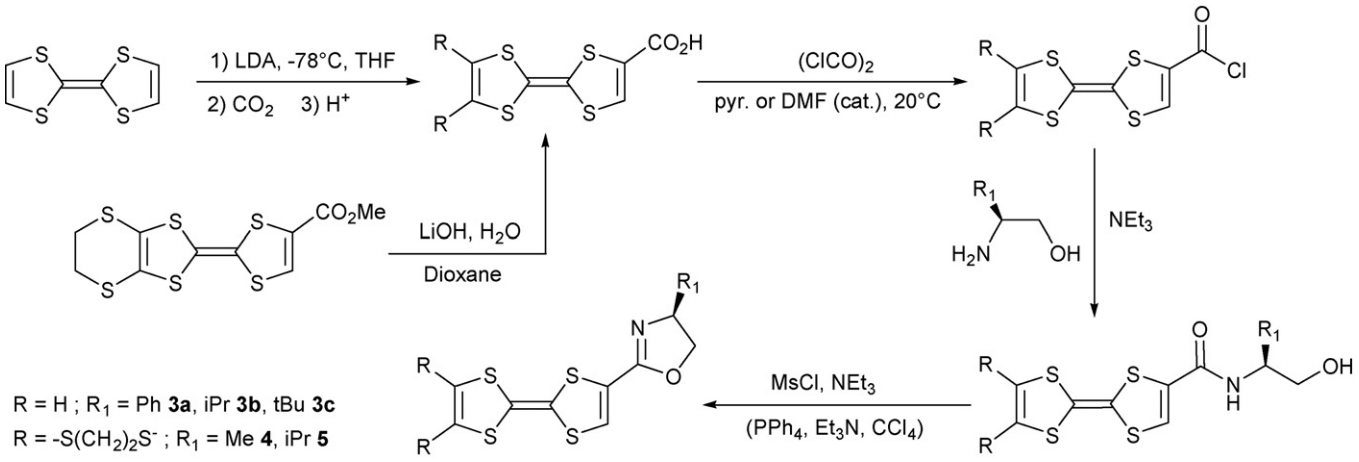
The EDT–TTF–Ox derivatives **4** and **5** have been prepared in both racemic and enantiopure forms *R* and *S*, upon reaction of the EDT–TTF acid chloride with alaninol (**4**) and valinol (**5**), followed by cyclization of the β-hydroxyamides in the presence of methanesulfonyl chloride (mesyl chloride, MsCl) and NEt_3 [19,20]. The methyl-oxazolines were prepared mainly as precursors for crystalline radical cation salts, while the isopropyl derivatives were expected to be more efficient as ligands in catalytic processes. Single crystal X-ray structures have been determined only for the enantiopure derivatives of **4** and **5**. They crystallize in the chiral space groups monoclinic $P2_1$ (**4**) and orthorhombic $P2_12_12_1$ (**5**), with different packing patterns, i.e. herringbone type and perpendicular dimers, respectively (Fig. 1).

Interesting to note is the planar conformation of these donors, with dihedral angles between the oxazoline rings and the TTF mean planes of only a few degrees (Fig. 2).

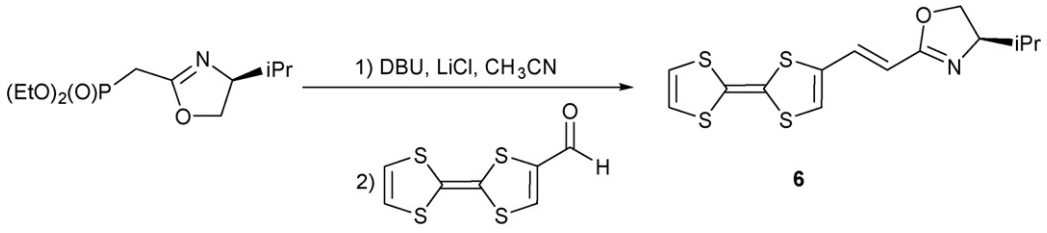
Table 1
Cyclic voltammetry data, ref. Ag/AgCl.

Ligand–M	$E^{1/2}$ free (mV)	$E^{1/2}$ complex (mV)	ΔE (mV)	Min. M^{2+} [a]	Max. M^{2+} [b]	K_1/K_2 [c]
1a–Mg	670	1000	330	0.1	3	3.8×10^5
1a–Ca	670	980	310	0.1	1	1.7×10^5
1a–Cu	670	920	250	1	2	1.7×10^4
1b–Mg	680	1040	360	1	5	1.2×10^6
1b–Ca	680	1040	360	0.1	3	1.2×10^6
1b–Cu	680	1000	320	1	2	2.5×10^5
2–Mg	650	840	190	1	15	1.6×10^3
2–Ca	650	810	160	0.1	3	5.1×10^2

[a] Minimum equivalents of $M(ClO_4)_2$ salt to observe the appearance of a second oxidation process.
[b] Minimum equivalents of $M(ClO_4)_2$ salt to observe the disappearance of the ligand free oxidation process.
[c] Binding enhancement for the complexation of the metal cations [9a], with the equilibrium constants K_1 and K_2 corresponding to the complexation by the neutral and oxidized ligand, respectively.



Scheme 3. Synthesis of TTF–Ox **3a–c** (only *S*) and EDT–TTF–Ox **4–5** (*rac*, *R* and *S*).



Scheme 4. Synthesis of TTF–Ox **6** (only *S*).

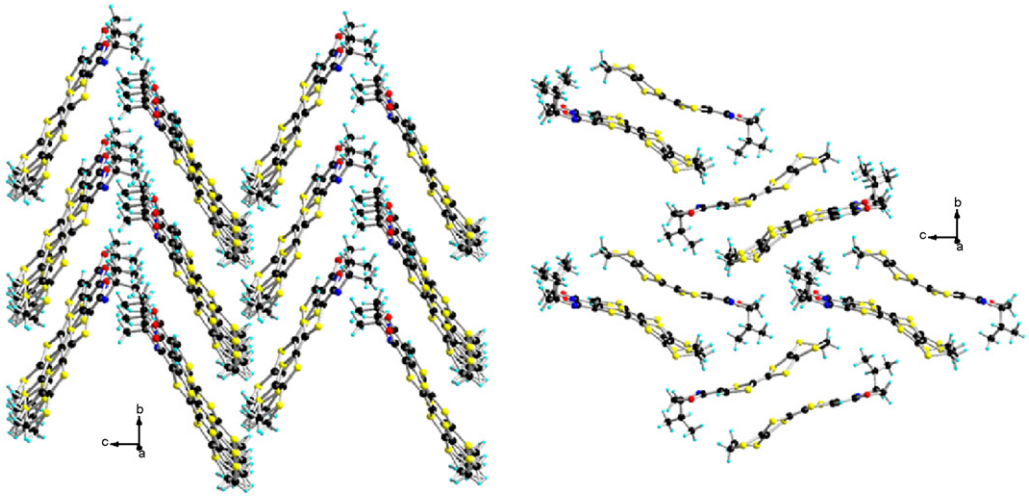


Fig. 1. Packing of donors in the crystalline structures of (*S*)-**4** (left) and (*S*)-**5** (right) [20].

The planar conformation corresponds also to the equilibrium geometry calculated in the gas phase by the DFT method for a model system. However, the calculations yielded two stable conformations corresponding to energy minima, characterized by either *s-trans*, as experimentally observed, or *s-cis* arrangements of the adjacent C=N and C=C double bonds (Scheme 5).

The calculated energy difference between them is only 1.41 kcal mol^{-1} in favor of the *s-trans* conformation [21], suggesting that packing forces or other intermolecular interactions in the solid state are more likely responsible for the experimental observed structure than its intrinsic stability with respect to the *s-cis* conformation. For both optimized structures, the dihedral angles between

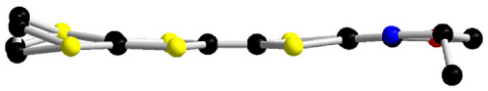
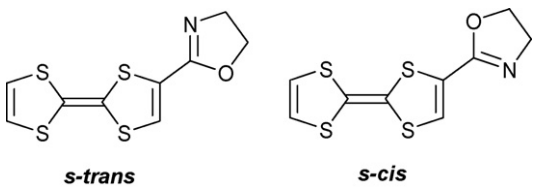


Fig. 2. Solid state conformation of (*S*)-**4**. Hydrogen atoms have been omitted.



Scheme 5. Stable planar conformations of TTF–Ox.

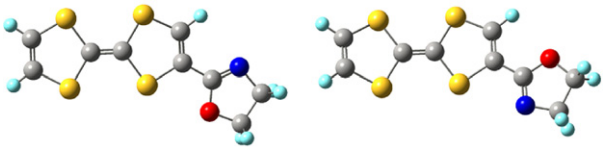


Fig. 3. Equilibrium geometries for TTF–Ox *s-cis* (left) and TTF–Ox *s-trans* (right) [21].

the oxazoline ring and the TTF mean plane are 0° (Fig. 3). The HOMO is as expected of TTF-π type, while the LUMO is delocalized over the oxazoline and the adjacent dithiole motifs.

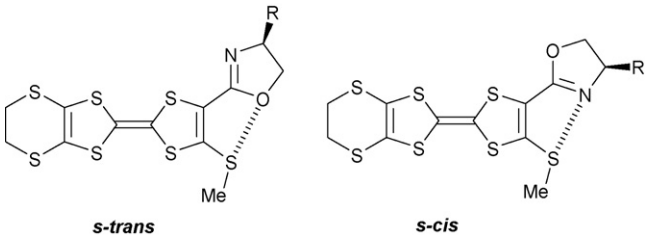
The same type of calculations has been performed for the radical cation derived from the model TTF–Ox, and once again the two planar conformations *s-cis* and *s-trans* represent energy minima, with a ΔE of 1.38 kcal mol^{-1} in favor of the latter [21]. This very likely suggests that small variations in the electrocrystallization conditions aimed at obtaining crystalline radical cation salts might induce preferential crystallization of either one or both conformations (*vide infra*).

Interestingly, the donors EDT–TTF–Ox can be further functionalized, as they still contain one vinylic proton which can be abstracted with strong bases such as lithium diisopropylamide (LDA). This strategy was employed for the preparation of chelating EDT–TTF–phosphinooxazolines (TTF–PHOX) **7–8**, after trapping the lithiated TTF–Ox with Ph_2PCl (Scheme 6) [19,22]. These derivatives were synthesized with the main objective to be investigated as ligands in homogenous catalytic reactions (*vide infra*).

Alternatively, racemic and enantiopure EDT–TTF–Ox **9–10** containing an appended thiomethyl group SMe *ortho* to the oxazoline ring were synthesized through the use, in the cross-coupling reaction, of an appropriate thione [23]. The subsequent steps parallel those of the preparation of the EDT-TTF–Ox **4–5** (Scheme 7).

The compounds **9–10** were synthesized with the primary objective to investigate on the occurrence of intramolecular non-bonded interactions of S···O (*s-trans*) or S···N (*s-cis*) type between the S atom of the thiomethyl group and the heteroatoms of the oxazoline ring (Scheme 8).

It is known that this type of intra- or intermolecular interactions greatly contributes to the fine structure of the compounds [24]. Indeed, single crystal X-ray structures of **9** and **10** show planar conformations between the three units TTF, oxazoline and SMe, with short S···O distances (2.85–2.95 Å) and linear O···SMe arrangements (Fig. 4) [23].



Scheme 8. Non-bonded interactions in TTF–SMe–Ox.

Theoretical calculations at the DFT level demonstrate that the two planar conformations correspond to stable geometries which are isoenergetic. Moreover, geometry optimization in the case of the corresponding radical cations provided a similar result, and thus occurrence of the two configurations in crystalline radical cation salts based on these donors should be possible.

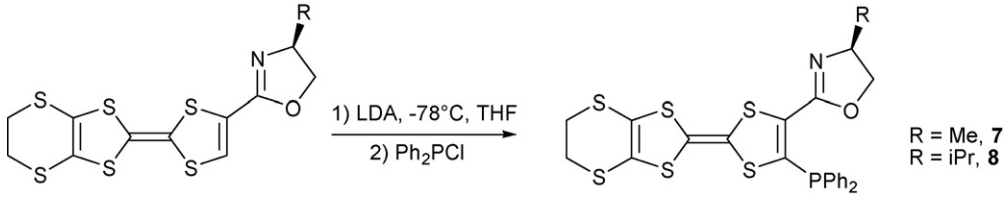
Very recently, EDT–TTF–bis(oxazoline) (TTF–BOX) donors **11** have been described, as a new family of multifunctional ligands [25]. Their synthesis involved the direct reaction between the EDT–TTF-diester and the (*R*)- or (*S*)-alaninol under heating in the presence of catalytic amounts of sodium hydride. Then, the intermediary bis(hydroxyamides) provided the corresponding bis(oxazolines) upon ring closure in classical conditions (Scheme 9).

Single crystal X-ray diffraction analysis for the (*S*,*S*) diastereomer shows that in the solid state the oxazoline rings are twisted with respect to the TTF mean plane (Fig. 5). The respective dihedral angles are 15° for OX1 and 51.5° for OX2. This feature is in sharp contrast with the planarity observed in the case of TTF–Ox and might result from the steric and electronic repulsion between the adjacent Ox units.

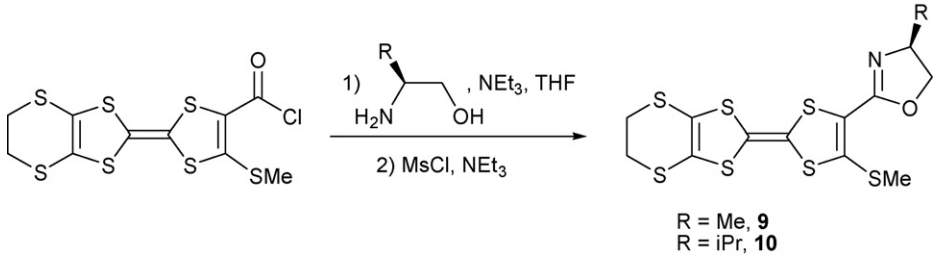
However in solution at room temperature the two oxazolines are equivalent, according to ^{1}H NMR spectroscopy. This new family of chiral donors is particularly interesting in the perspective of preparing radical cation salts and/or electroactive transition metal complexes.

3.2. Coordination chemistry

The metal complexes based on TTF–Ox and derived chelating ligands such as TTF–PHOX, TTF–SMe–Ox and TTF–BOX reported so far and structurally characterized in the solid state are summarized in the Scheme 10.



Scheme 6. Synthesis of TTF–PHOX **7–8**.



Scheme 7. Synthesis of TTF–SMe–Ox **9–10**.

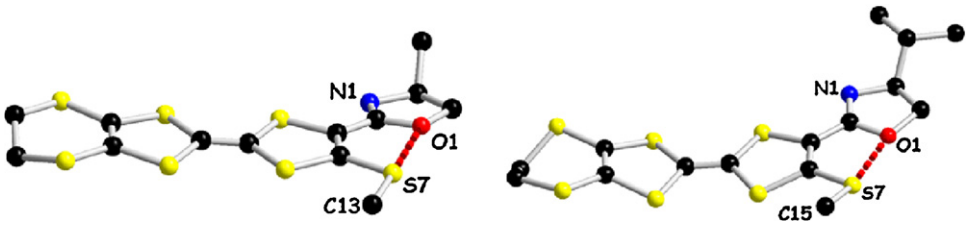
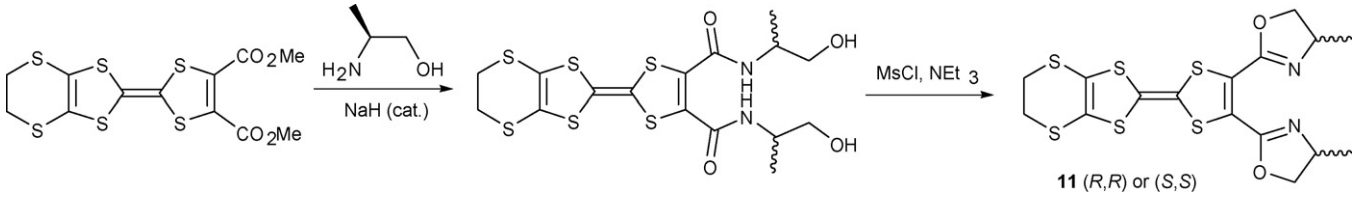


Fig. 4. Solid state conformation of (*S*)-**9** and (*S*)-**10**, with an emphasis on the short S···O contacts. Hydrogen atoms have been omitted [23].



Scheme 9. Synthesis of TTF–BOX **11**.

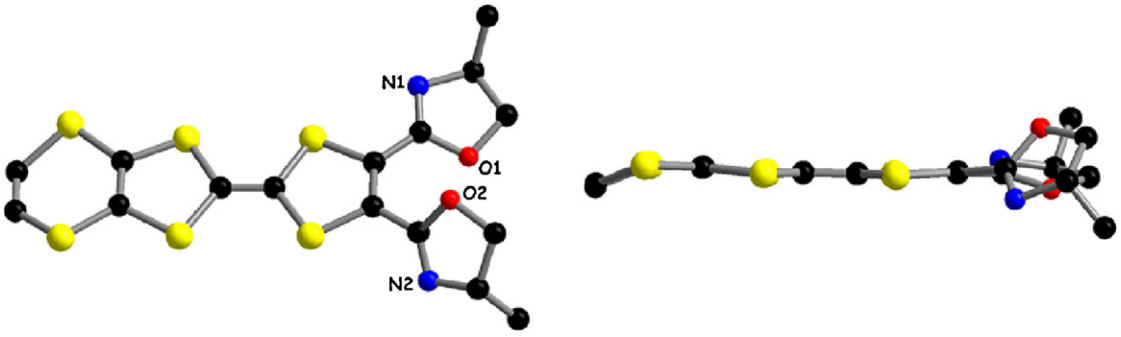
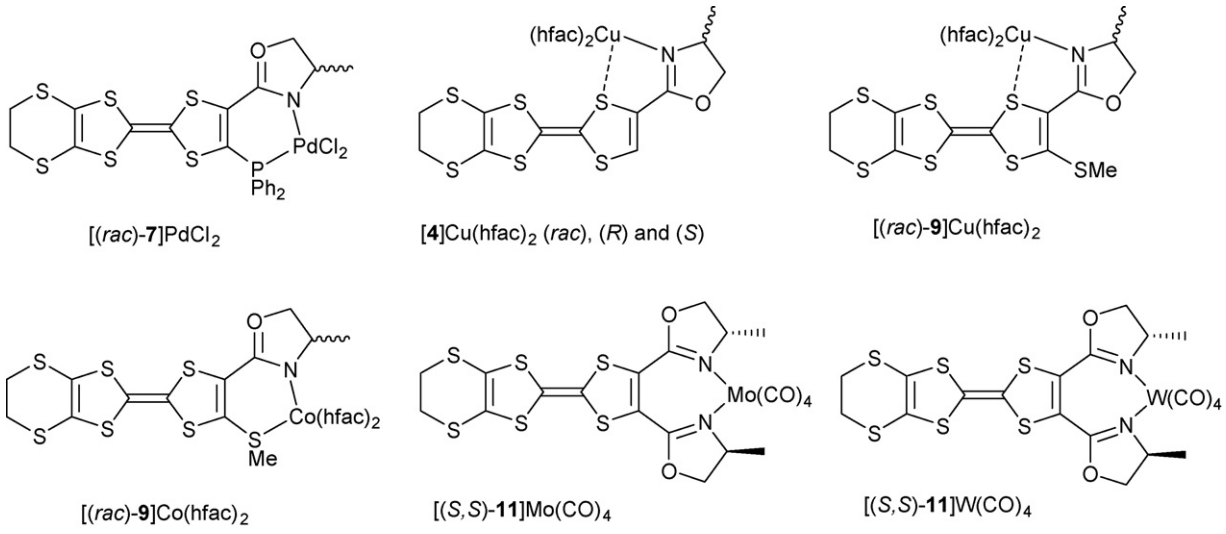


Fig. 5. Molecular structure of (*S,S*)-**11** (left) and side view (right). Hydrogen atoms have been omitted [25].

Note that other Pd(II) [22] and Ir(I) [26] complexes have been also prepared with TTF–PHOX ligands for catalytic purposes, without any solid state structural study though. The only metal complex containing a TTF–PHOX ligand analyzed by single crystal X-ray diffraction is the [(*rac*)-**7**]$PdCl_2$ synthesized by the direct reaction between the ligand and $PdCl_2$ [19]. Its crystal structure shows as expected chelation of the Pd center by the P,N ligand, with the metal lying in a square planar environment. A very interesting series of complexes has been obtained with the ligands TTF–Ox and TTF–SMe–Ox and the neutral fragment $Cu^{II}(hfac)_2$ [27]. The peculiarity of these complexes consists in the fact that besides the classical coordination of Cu(II) by the N atom of the oxazoline ring, there is establishment of a weaker coordinative interaction between the metal and the adjacent S atom of the TTF core, ranging between 2.95 and 3.04 Å (Fig. 6). This feature occurs even in the case of the TTF–SMe–Ox which is a potentially S,N chelating ligand, as observed with the $Co^{II}(hfac)_2$ fragment.



Scheme 10. Metal complexes structurally characterized based on TTF–Ox ligands.

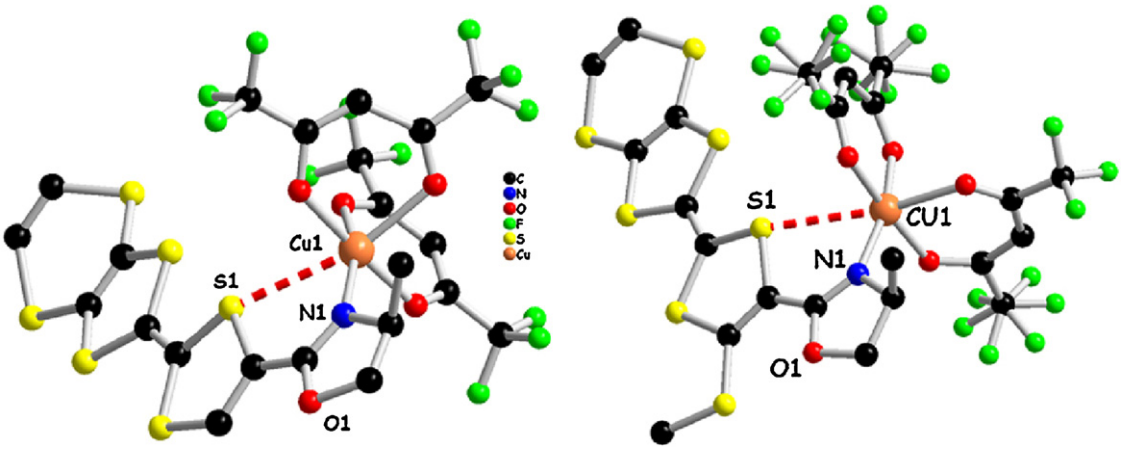


Fig. 6. Molecular structures of [(*S*)-**4**]Cu(hfac)$_2$ (left) and [(*rac*)-**9**]Cu(hfac)$_2$ (right). Hydrogen atoms have been omitted [27].

For both Cu(II) complexes, since the metallic centers are isolated each other as shown by the Cu···Cu distances of over 8 Å, magnetic susceptibility measurements are in agreement with a Curie type behavior.

The complexes [(*S,S*)-**11**]M(CO)$_4$ (M = Mo, W) have been described very recently [25]. They have been prepared upon thermal displacement of two piperidine ligands from the precursors M(CO)$_4$(L)$_2$ by one equivalent of TTF–BOX. Both complexes have been analyzed by single crystal X-ray analysis. They are isostructural, and, as anticipated, the coordination strereochemistry of the metal centers is octahedral, with the two oxazoline ligands twisted by about 40–49° out of the TTF mean plane (Fig. 7). There is therefore a local C_2 symmetry around the metal centers when taking into account only its coordination sphere, yet, the distortion of the ligand prevents the symmetry axis in the solid state.

However, in solution at room temperature the two oxazolines are equivalent, as demonstrated by ^{1}H NMR spectroscopy, and thus one can consider an averaged C_2 symmetric structure. Undoubtedly, the propensity of TTF–BOX to coordinate various metallic centers makes them very promising chiral electroactive ligands.

3.3. Conducting materials

All the TTF–Ox derivatives and their metal complexes are good electron donors, according to cyclic voltammetry measurements (Table 2).

In all cases the first oxidation process corresponds to the reversible generation of the TTF radical cation, showing that both the free ligands and also the metal complexes might be used as precursors for crystalline radical cation salts. As already mentioned, the methyl-oxazolines are probably more appropriate precursors, since they provide less steric hindrance than those with isopropyl substituents. Indeed, crystalline radical cation salts have been obtained by electrocrystallization with the series of the TTF–Ox **4**. In particularly, the use of these precursors allowed the preparation of the first complete series of chiral molecular conductors containing both enantiomers and also the racemic form. These mixed valence salts, formulated as (*rac*), (*R*) and (*S*)-[**4**]$_2$AsF$_6$, crystallize in the triclinic system, space group *P*-1 for the racemic and *P*1 for the enantiopure forms, with identical crystalline parameters [28]. A "classical" organic–inorganic segregation is observed in the molecular packing, with existence of organic layers formed by parallel columns of donors, an organization which is reminiscent of a β structural type [29] (Fig. 8). This arrangement, characterized by short S···S intrastack (3.65–3.75 Å) and interstack (3.25–3.45 Å) contacts, is similar for the three salts.

Table 2
Cyclic voltammetry data for TTF–Ox ligands and complexes.

Compound	$E_1^{1/2}$ (mV)	$E_2^{1/2}$ (mV)	Solvent, reference
3b	520	910	CH_3CN, Ag/AgCl
4,5	630	1110	CH_2Cl_2, SCE
7,8	630	1090	CH_2Cl_2, Ag/AgCl
9,10	630	1110	CH_2Cl_2, SCE
11	570	900	CH_3CN, SCE
[(*rac*)-**7**]$PdCl_2$	870	1250	CH_2Cl_2, Ag/AgCl
[**4**]Cu(hfac)$_2$	640	1120	CH_2Cl_2, SCE
[**11**]Mo(CO)$_4$	480	700[a]	CH_3CN, SCE
[**11**]W(CO)$_4$	490	730[a]	CH_3CN, SCE

[a] Partially reversible, metal centered redox process.

However, a most important difference, related to the structural disorder, is observed between the racemic and the two enantiopure salts. Accordingly, in the structure of the racemic salt the two enantiomers (*R*) and (*S*) occupy statistically the same crystallographic sites with occupational factors (s.o.f.) of 0.5 each, which corresponds to a structural disorder. On the contrary, this disorder is absent in the case of the enantiopure compounds, which crystallize with two independent molecules in the unit cell, one corresponding to the *s-cis*, and the other to the *s-trans* conformations (Fig. 9). Note that the oxazoline rings are coplanar with the adjacent TTF units, as also suggested by the theoretical calculations.

The direct consequence of this structural disorder feature is that, in spite of identical band structures and intermolecular energy interactions, the room temperature conductivity of the racemic salt (~10 S cm^{-1}) is one order of magnitude lower than the conductivity of the enantiopure salts (~100 S cm^{-1}), with the three compounds showing metallic like behavior down to 180–220 K [28]. This modulation of the structural disorder highlights one of the possible influences of the chirality on the conducting properties. The isostructural series of salts (*rac*), (*R*) and (*S*)-[**4**]$_2$PF$_6$, thus containing the smaller anion PF_6^- instead of AsF_6^-, shows the same features, i.e. occupational disorder in the racemic salt and metallic like conductivity for the three of them, with a room temperature value one order of magnitude higher for the enantiopure salts than for the racemic one [21].

A confirmation of the chirality/disorder/conductivity relationship was very recently reported through the synthesis of a novel series of chiral conducting salts based on the TTF–Ox donors **4** and the linear [Au(CN)$_2$]$^-$ monoanion [21]. Unlike the previous AsF$_6$ and PF$_6$ series, in the (*rac*)-[**4**]$_2$[Au(CN)$_2$] salt (and also in the enantiopure forms (*R*) and (*S*)) there is no structural disorder any more as far

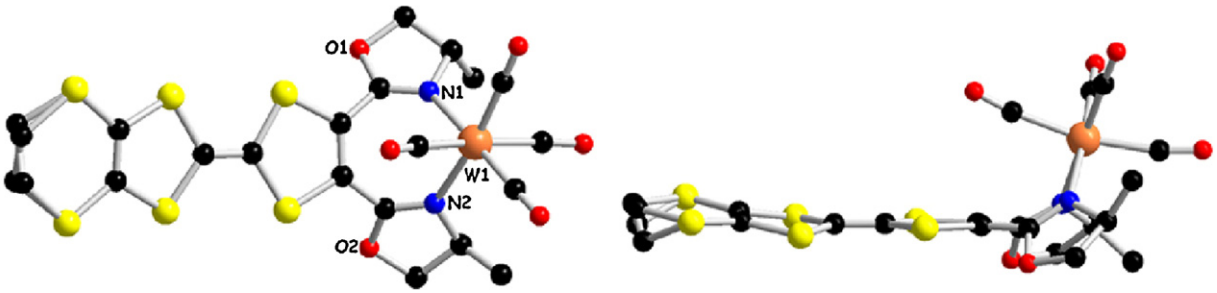


Fig. 7. Molecular structure of [(*S*,*S*)-**11**]W(CO)$_4$ (left) and side view (right). Hydrogen atoms have been omitted.

as the oxazoline rings are concerned. Only the *s-trans* conformation is observed this time (Fig. 10).

Since the donors adopt once again a β-type packing, with identical band diagrams and intermolecular energy interactions for the three salts, single crystal X-ray measurements have shown this time similar values for the room temperature conductivity, of 125–130 S cm^{-1}, with metallic like behavior down to around 250 K. The comparison of the three series of chiral salts highlights the versatility of these TTF–Ox donors.

Worth noting is also the series of racemic radical cation salts obtained with the TTF–SMe–Ox donor (*rac*)-**9** and the dianion $[Mo_6Cl_{14}]^{2-}$ [23]. The variation of the electrocrystallization solvent, i.e. CH_2Cl_2, CH_3CN, or a mixture of them, provided three salts with different donor/anion stoichiometries. Thus, an insulating salt formulated as [(*rac*)-**9**]$_2$[Mo_6Cl_{14}], with all the donors fully oxidized, was obtained by the use of CH_2Cl_2. For the mixed valence salts [(*rac*)-**9**]$_6$[Mo_6Cl_{14}]·2CH_3CN and [(*rac*)-**9**]$_4$[Mo_6Cl_{14}], obtained in CH_3CN and CH_3CN/CH_2Cl_2 mixture, respectively, single crystal resistivity measurements show semiconducting behavior. In line with the theoretical calculations results, suggesting the same energy for the planar conformations *s-cis* and *s-trans*, both of these have been found in the crystalline structures of this series of salts.

In view of these promising results it is clear that TTF–oxazolines and derivatives are valuable precursors for the preparation of chiral conductors. The use of paramagnetic metals in combination with chelating ligands such as the TTF–BOX **11** could also be envisaged within the frame of the multifunctional materials.

3.4. Catalytic applications

The first attempts to use TTF–Ox as ligands for a catalytic process have been reported by Chesney and Bryce [18]. The monooxazoline

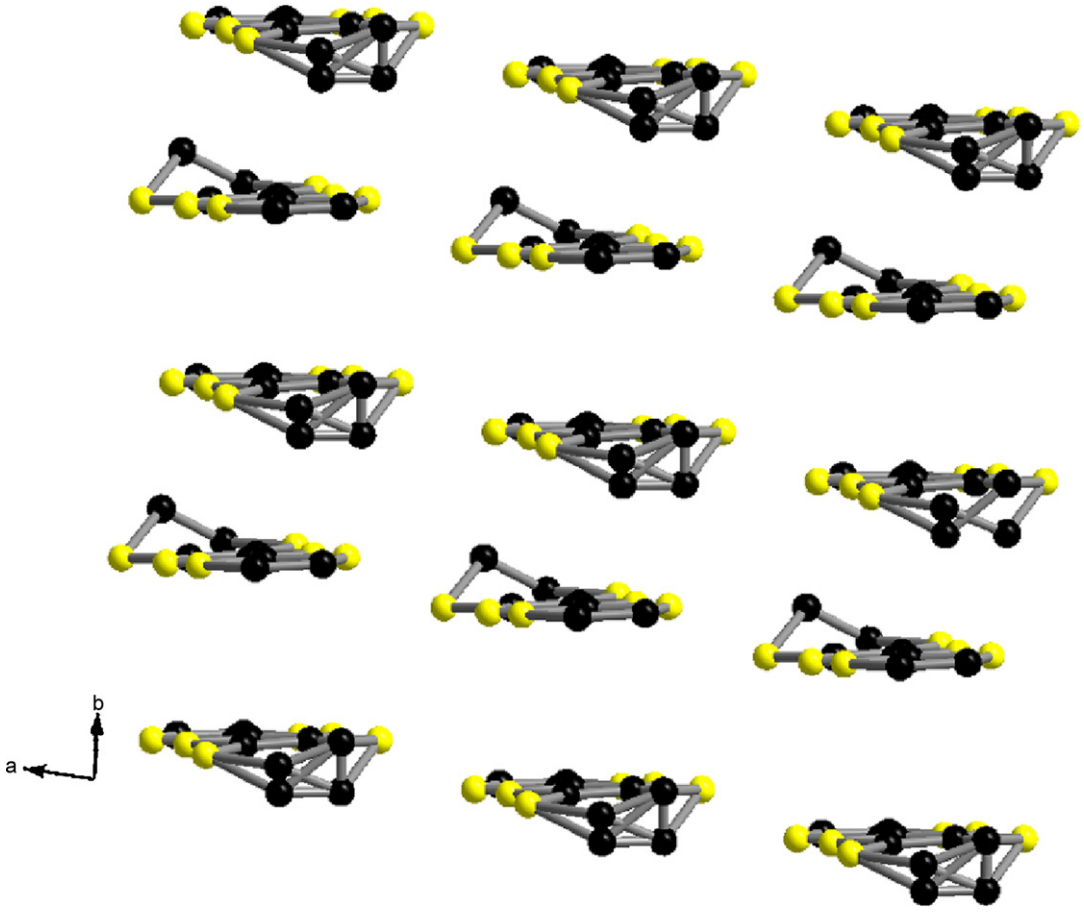


Fig. 8. Parallel columns of donors along *b* in the structure of [**4**]$_2$$AsF_6$. Hydrogen atoms and oxazoline rings have been omitted.

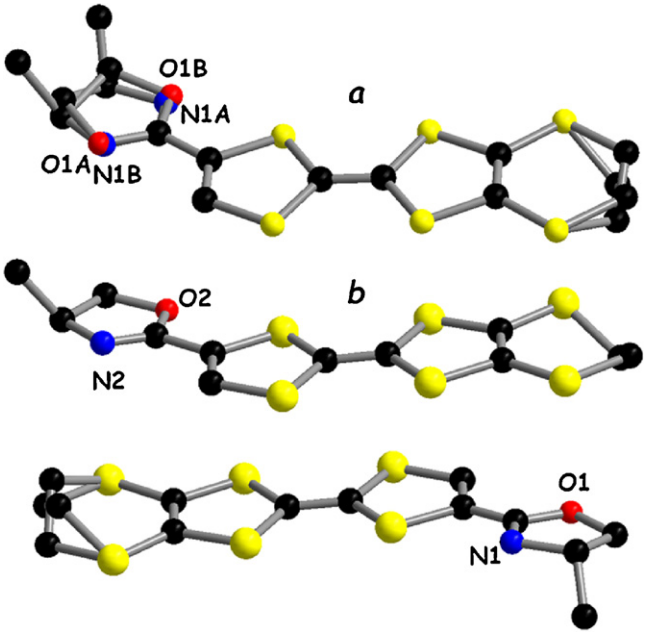


Fig. 9. Crystalline structures of (*rac*)-[**4**]$_2$AsF$_6$, showing the disorder of the oxazoline rings (a) and (*S*)-[**4**]$_2$AsF$_6$, showing the two independent molecules as *s-cis* (middle) and *s-trans* conformations (bottom) (b). Hydrogen atoms have been omitted [28].

ligands **3a–c** were used in the asymmetric allylic alkylation reaction [30] in the presence of the dimeric allylpalladium chloride precursors with the standard substrate diphenyl-allylic acetate and the sodium salt of dimethyl malonate as nucleophile (Scheme 11).

The results in terms of activity (up to 40% yield with **3b**) and selectivity (up to 33% ee with **3b**) were rather modest, which is not surprising when considering the monodentate nature of the ligands, although a chelation involving the adjacent TTF sulfur atom has been envisaged in order to explain the low ee values. Much better results in terms of selectivity have been obtained when the phosphinooxazolines **8** have been used in the same reaction [22]. For reaction times of 18 h, 10% conversion and 85% ee have been attained with (*R*)-**8**, while for prolonged reaction times up to 70 h the conversion reached 20%. The very modest value of the conversion can be reasonably explained by a deactivation of the catalyst by the lateral sulfur atoms of the EDT–TTF moiety, as the use of a mixture of this latter and the standard PHOX ligand [2d] lead to similar results. One possibility to circumvent this issue would be to test in the future a TTF–PHOX ligand without additional sulfur atoms as substituents. The other TTF–Ox ligands investigated in this study, such as TTF–Ox **4–5** and TTF–SMe–Ox **9–10**, gave only poor results. The use of the methyl substituted phosphinooxazoline **7** provoked a drastic decrease of the selectivity down to 30% ee. In order to evidence an influence of the TTF oxidation state on the catalytic process, the reaction has been performed as well with the oxidized TTF–PHOX **8**. Nevertheless, the activity and selectivity ware rather similar to those observed with the neutral ligands. It was pointed out that during the catalytic cycle the reduction of the TTF radical cation could occur, and thus the observation of any effect related to the TTF oxidation state would be hampered.

A second catalytic process investigated by the use of TTF–PHOX ligands and iridium (I) precursors was the hydrogenation of imines, a reaction for which the PHOX ligands proved their efficiency [31]. Thus, the hydrogenation of the *N*-benzylmethyl-phenylimine in the presence of the complexes [(**8**)Ir(COD)]$^+$X$^-$ (X = PF$_6$, BArF) was completed after several hours, with ee's up to 70% in the case of the non-coordinating anion BArF (tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) [26]. In contrast with the previous reaction, the oxidation of the ligand led to a massive decrease in activity (20% yield) and selectivity (23% ee) after 15 h.

It is clear that for both reactions it is however rather difficult to assess that during the catalytic cycle the TTF unit remains oxidized in radical cation or it is reduced back to the neutral species. The investigation of catalytic processes in which the metal intervenes only by its Lewis acidity would be an alternative to rule out possible redox equilibriums due to the change of the oxidation state of the metal. In this respect the use of the recently reported TTF–BOX ligands [25] holds much promise.

4. Miscellaneous

4.1. Polythiophene-oxazolines

An extremely interesting system based on optically active polythiophene (PT) aggregates has been described by Yashima et al. The synthetic procedure involved in the last step the reductive coupling of an appropriately functionalized thiophene-phenyl-oxazoline derivative [32] (Scheme 12). The polythiophene, thanks to the presence of the chiral oxazoline groups, adopt helical arrangements at

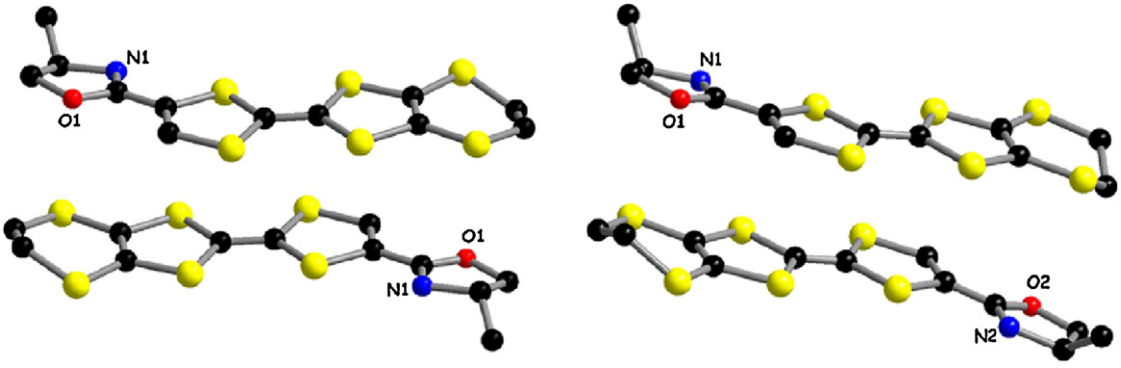
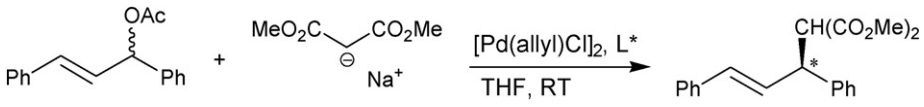


Fig. 10. Crystalline structures of (*rac*)-[**4**]$_2$[Au(CN)$_2$] (left) and (*R*)-[**4**]$_2$[Au(CN)$_2$] (right). Hydrogen atoms have been omitted [21].



Scheme 11. Asymmetric allylic alkylation with TTF–Ox ligands.

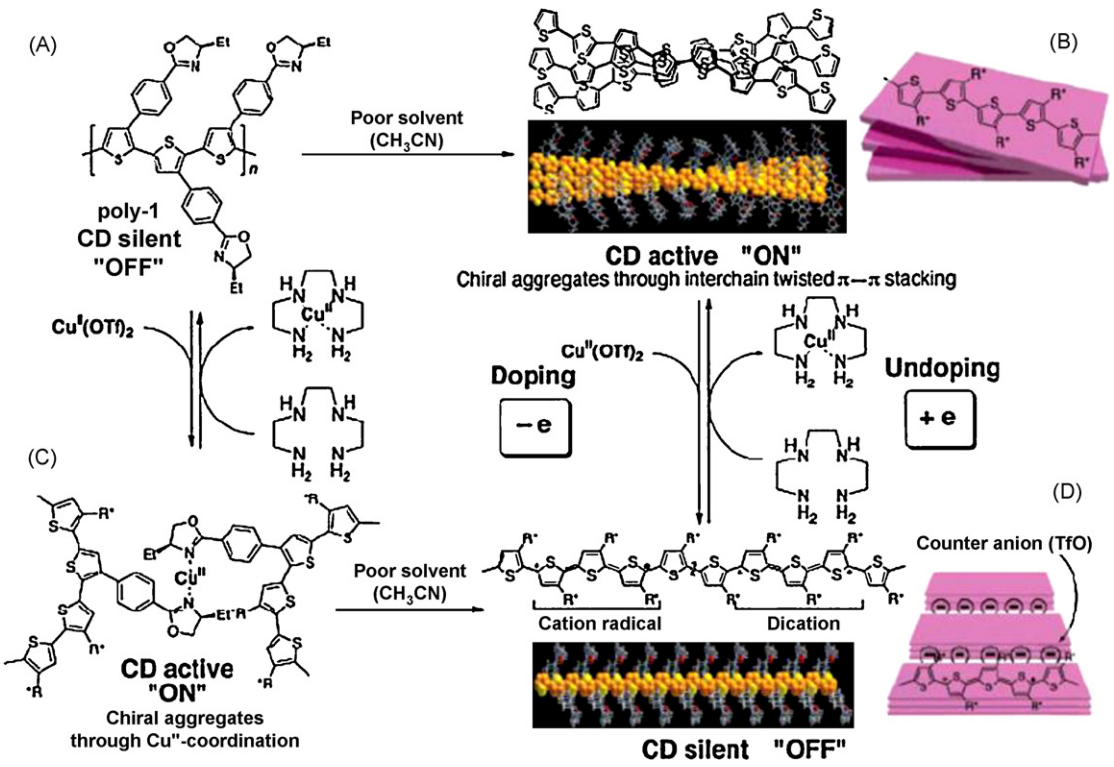


Fig. 11. Schematic illustrations of chiral supramolecular aggregates of poly(thiophene-oxazoline) [35].
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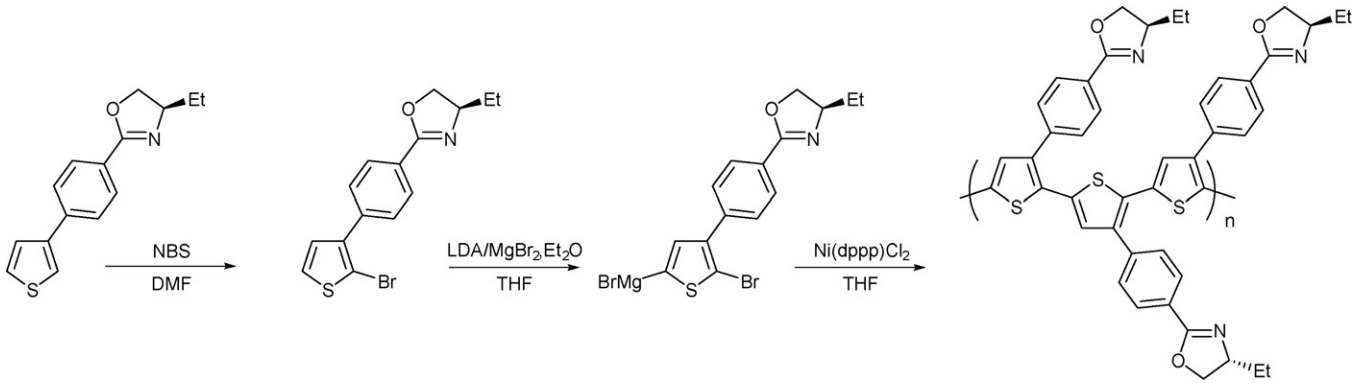
the supramolecular level, investigated by circular dichroism measurements.

The supramolecular chirality shown by these aggregates can be modulated by the solvent [33], transition metals coordinating the oxazoline units [34], and electron-induced processes [35], as ascertained by the reversible changes in the circular dichroism signal. The influence of these different factors is illustrated in Fig. 11.

Accordingly, the chiral polythiophene dissolved in a good solvent such as chloroform does not show any induced circular dichroism (ICD) signal in the π–π^* transition region of the main chain (Fig. 11A). Upon addition of acetonitrile, a poor solvent for this system, the polymer chains organize in chiral supramolecular aggregates (Fig. 11B), as confirmed by the appearance of a split-type ICD, with a first positive Cotton effect and a second negative Cotton effect, accompanied by a red-shift of around 200 nm (6800 cm^{-1}) of the absorption band. Formation of supramolecular aggregates can also be triggered by the addition of up to 0.5 equivalents of $Cu^{II}(OTf)_2$ in a chloroform solution of PT, thanks to the coordination of the oxazoline groups to the metallic centers (Fig. 11C). In this case the main absorption band exhibits a gradual blue shift of up to about 30 nm (1600 cm^{-1}) accompanied by the appearance of an ICD signal. Most remarkably, this process is totally reversible, since the treatment of the solution with triethylenetetramine (TETA) promotes the decomplexation of Cu(II), captured by the added amine, and thus the disappearance of the ICD. When $Cu(OTf)_2$ is added to the poor solvent containing solution of PT, a doping process of the polymer takes place, as confirmed by EPR measurements, leading to the untwisting of the supramolecular chiral aggregates (Fig. 11D). The color of the solution changes from purple to gray and the ICD signal completely vanishes. However, the reversibility of the process was evidenced also in this case by the use of TETA as complexing agent for Cu(I), accompanied by an electron transfer from the Cu–amine complex to the polymer. The switching processes demonstrated in the case of the chiral PT-oxazoline polymer, especially the redox control of the supramolecular chi-



Scheme 12. Synthesis of the regioregular poly[3-{4-((R)-4-ethyl-2-oxazolin-2-yl)phenyl}thiophene] [33].

rality, are very interesting in view of providing molecular devices with applicability in data storage and enantioselective electrodes.

5. Conclusions

In this review paper, we presented the electroactive oxazoline ligands mainly based on the ferrocene and TTF units, together with their coordination metallic complexes. We have focused our attention on those systems where the electroactivity of the ligand plays a role on a property. Accordingly, it turns out that the ferrocene–oxazolines have been used as electrochemical sensors, although the modulation of their reactivity in catalytic processes could be also envisaged. TTF–oxazolines proved to be excellent precursors for chiral molecular conductors, in which the role of the chirality has been highlighted through the modulation of the structural disorder, and hence its influence on the conducting properties. TTF–phosphinooxazolines have been employed mainly in catalytic processes. However, the modulation of the catalytic activity of the corresponding metal complexes with the oxidation state of the TTF unit has still to be proved. Promising donors as multifunctional ligands are also the recently reported TTF-bis(oxazolines). The utility of oxazolines has been proved also in the case of polythiophenes, for which the tuning of the supramolecular chirality has been achieved.

Acknowledgements

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