

Article

Electroactive Bisiminopyridine Ligands: Synthesis and Complexation Studies

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Abstract: The condensation reaction of (4-(6,7-dimethyldithio-tetrathiafulvalene)-aniline) with 2,6-diformylpyridine afforded an electroactive Schiff base (N,N,N) pincer (**3**). This pincer was reacted with Zn(II) cation to yield the corresponding Zinc chloride complex (**4**). The crystal structure of the newly prepared electroactive zinc complex reveals that the tetrathiafulvalene (TTF) is neutral and the zinc cation is pentacoordinated. The two chlorines are involved in a set of hydrogen bonds giving rise to a 2D supramolecular grid arrangement. The electronic absorption properties and the electrochemical behavior have been elucidated. These two compounds are promising for the construction of crystalline radical cation salts.

Keywords: tetrathiafulvalene; Schiff base; transition metal complex; cyclic voltammetry; UV-Vis spectroscopy

1. Introduction

Tetrathiafulvalene (TTF) and its derivatives have attracted much interest because of their electron-donating ability and their attractive reversible redox properties. They have therefore been widely used as donor components in the preparation of molecular conductors and superconductors [1–3].

However, one challenge is the construction of multifunctional molecular materials that can exhibit interplay between one or more physical properties such as magnetic properties and electrical conductivity [4–5]. In order to address this challenge, considerable effort has been devoted in associating the TTF moiety with an inorganic component and various organic mono- or polydentate ligands, and their corresponding electroactive metal complexes have therefore been reported [6]. For example, metal complexes of phosphines [7–12], dithiolates [13], acetylacetonates [14], pyridines [15–17], bipyridines [18,19] and more recently of Schiff bases [20–22] have been synthesized. Pyridine based Schiff bases ligands such as 2,6-*bis*(imino)pyridyl, with chelating abilities, form stable complexes, with various transition metals, which have been extensively used as catalysts for olefin polymerization [23,24].

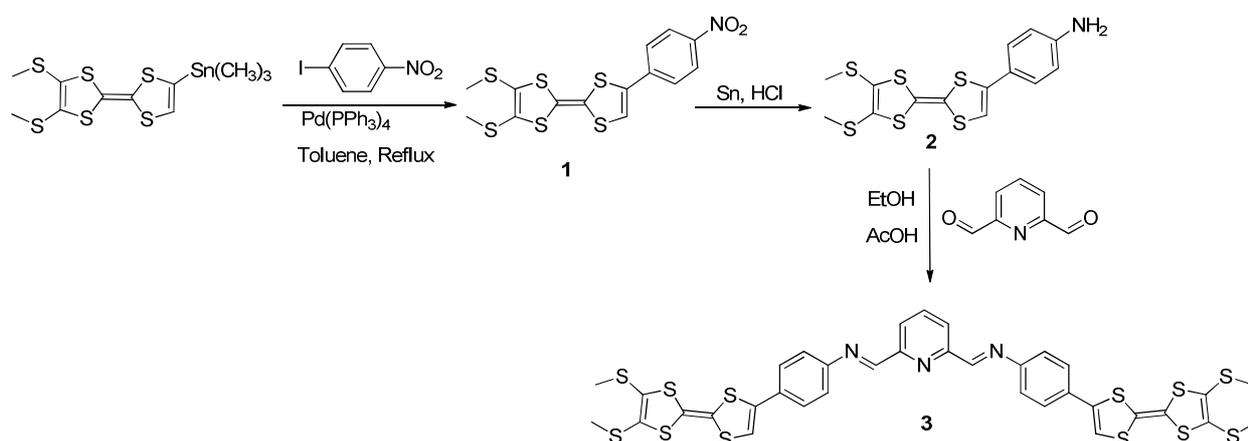
In order to obtain electroactive transition metal complexes with original structural and electronic properties, we report herein the synthesis of the **TTF₂-BisIm-Py (3)** that can act as an (*N,N,N*) pincer. The TTF based donor with monoaniline moiety, (4-(6,7-dimethyldithio-tetrathiafulvalene)-aniline) (**2**), has been chosen for the Schiff base condensation reaction with 2,6-diformylpyridine. The reaction of this TTF based tridentate pincer with zinc metal cation afforded a new electroactive metal complex.

2. Results and Discussion

2.1. Synthesis and Characterization

The protocol followed for the synthesis of the new (2,6-*bis*(4-(4',5'-*bis*(methylthio)-[2,2'-*bi*(1,3-dithiolydene)]-4-yl)aniline)-iminopyridine) pincer (**3**, **TTF₂-BisIm-Py**) is presented in Figure 1.

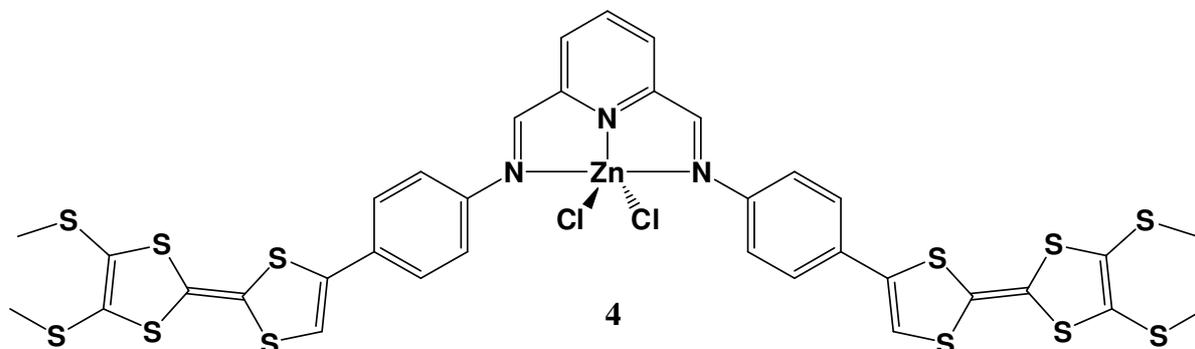
Figure 1. Synthesis scheme of the **TTF₂-BisIm-Py** Pincer (**3**).



The starting stannic derivative (6,7-dimethyldithio-2-trimethyltin-tetrathiafulvalene) was synthesized as previously described [25] and was reacted with 1-iodo-4-nitrobenzene under Stille coupling conditions to afford (1-(6,7-dimethyldithio-tetrathiafulvalene)-4-nitro-benzene) (**1**) in 67% yield [26]. Reduction of the nitro group to the amine was achieved using a mixture of HCl ethanolic solution in the presence of metallic tin [26]. The obtained amine (**2**) was further used in a condensation reaction with 2,6-diformylpyridine to afford the **TTF₂-BisIm-Py** pincer (**3**).

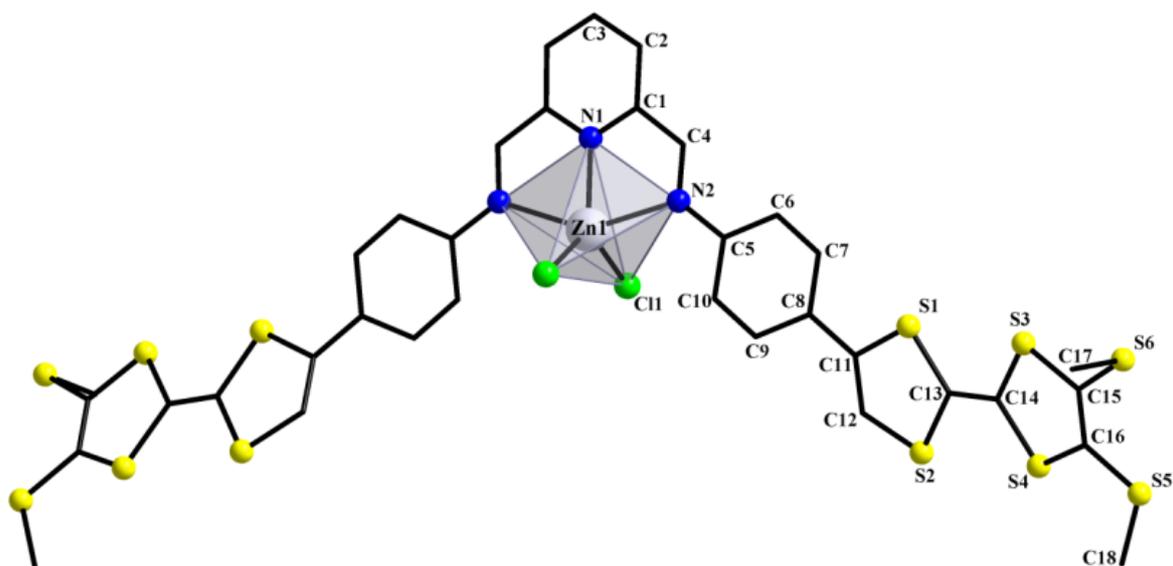
The **TTF₂-BisIm-Py** pincer was reacted with one equivalent of zinc chloride (ZnCl₂) in a dichloromethane/acetonitrile solvents mixture to afford good quality single crystals of [Zn(TTF₂-BisIm-Py) Cl₂] (**4**) (Figure 2) that were suitable for the X-ray crystal structure determination.

Figure 2. Schematic drawing of the zinc metal complex (**4**).



Single-crystal diffraction analysis revealed that the asymmetric unit (Figure 3) contains half of the molecule of complex (**4**). Within this complex the zinc ion is pentacoordinated, the coordination sphere being formed by the three nitrogen atoms of the pincer and two chlorines ions. For a more accurate description of the stereochemistry around the zinc ion, the τ parameter ($\tau = [(\alpha - \alpha')/60]$ [27], where α and α' are the *transoid* angles formed by the metal ion and the donor atoms within the basal plane), also known as Addison's parameter, was calculated to be $\tau = 0.47$. This indicates an intermediate between the two geometries corresponding number of five, square pyramidal and trigonal bipyramidal.

Figure 3. The crystal structure of complex **4** with the labeling scheme of the atoms. Hydrogen atoms have been omitted for clarity.



In the coordination polyhedron, Zn–(N/Cl)ligand distances are in the 2.052(5)–2.351(3) Å range. A selection of relevant bond lengths and angles are given in Table 1. In the complex, the planarity of the ligand is disrupted by the TTF-(SMe)₂ units, as proven by the value of the dihedral angle least-squares planes of the pyridyl group and the dithiole ring (23.55°). In the solid state, each of the two chlorine

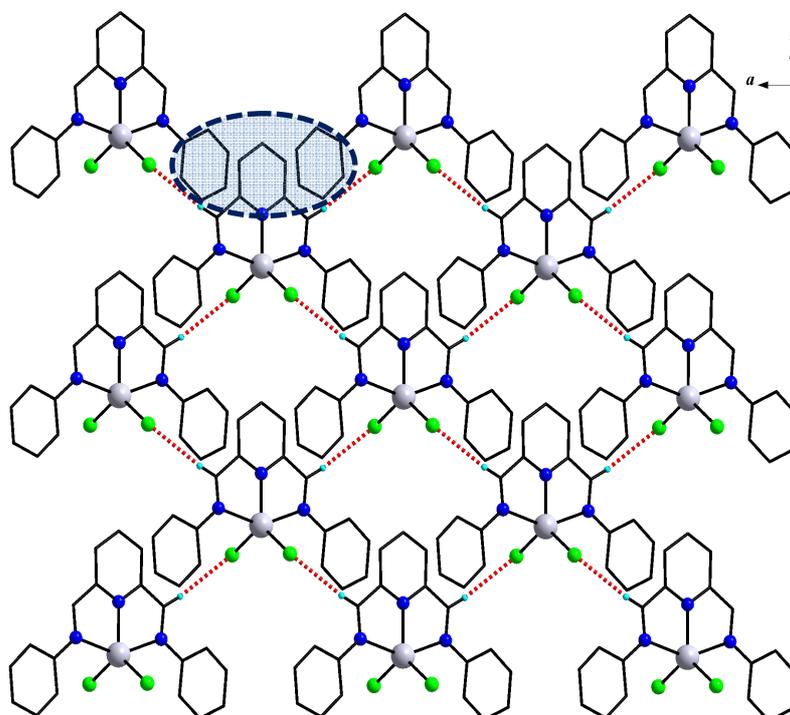
atoms coordinated to the zinc ion are involved in non-conventional hydrogen bonds with hydrogen atoms from other two neighboring molecules to generate a grid-like sheet represented in Figure 4.

Table 1. Selected bond lengths (Å) and angles (°) for compound **4**.

bond	length (Å)	bond	length (Å)	bond	length (Å)
C11–C12	1.330(6)	C14–S4	1.761(5)	N1–Zn1	2.052(5)
C11–S1	1.774(4)	C15–C16	1.345(6)	N2–Zn1	2.351(3)
C12–S2	1.720(4)	C15–S6	1.743(4)	Cl1–Zn1	2.2345(13)
C13–C14	1.340(5)	C15–S3	1.769(4)	Zn1–Cl1 ⁱ	2.2345(13)
C13–S2	1.756(4)	C16–S5	1.742(4)	Zn1–N2 ⁱ	2.351(3)
C13–S1	1.759(4)	C18–S5	1.794(5)	H10–Cl1 ⁱ	3.1536(15)
C14–S3	1.758(4)	N1–C1 ⁱ	1.342(5)	Cl1–Cl1 ⁱ	3.8584(19)
angle	value (°)	angle	value (°)	angle	value (°)
N1–Zn1–Cl1	120.30(4)	N1–Zn1–N2 ⁱ	74.31(9)	Cl1–Zn1–N2	97.74(9)
N1–Zn1–Cl1 ⁱ	120.30(4)	Cl1–Zn1–N2 ⁱ	97.94(9)	Cl1 ⁱ –Zn1–N2	97.94(9)
Cl1–Zn1–Cl1 ⁱ	119.40(9)	N1–Zn1–N2	74.31(9)	N2 ⁱ –Zn1–N2	148.63(18)

ⁱ 2 – x, y, 0.5 – z.

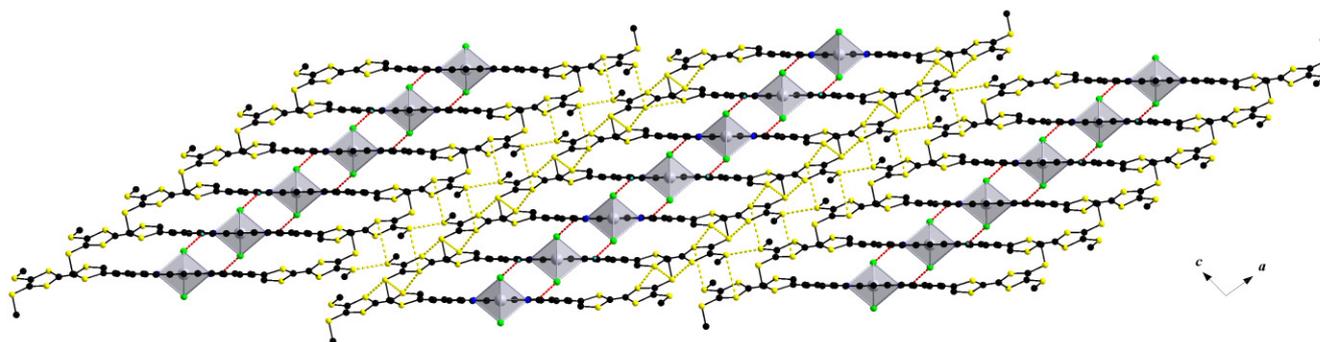
Figure 4. Front view of the 2D supramolecular layer in **4** reinforced by non-conventional hydrogen bonds (2.69 Å) (red dashed lines) and π – π stacking (highlighted by the blue circle). The TTF-(SMe)₂ units were omitted for clarity.



Within this supramolecular layer developed in the *ab* crystallographic plane, each of the three six-membered aromatic rings of the ligand are stacked in a face to face manner (centroid...centroid 3.56 Å) with two other rings forming the triads highlighted in Figure 5. The crystal packing (Figure 5) reveals a segregation between the TTF units and the rest of the molecule that can be associated with the presence of numerous sulfur-sulfur interactions (intralayer S...S: S2...S3 3.59 Å, S2...S6 3.66 Å,

S4...S6 3.58 Å) reinforcing the above-mentioned layers but also connecting them into a 3D network (interlayer S...S: S3...S5 3.73 Å, S5...S5 3.30 Å).

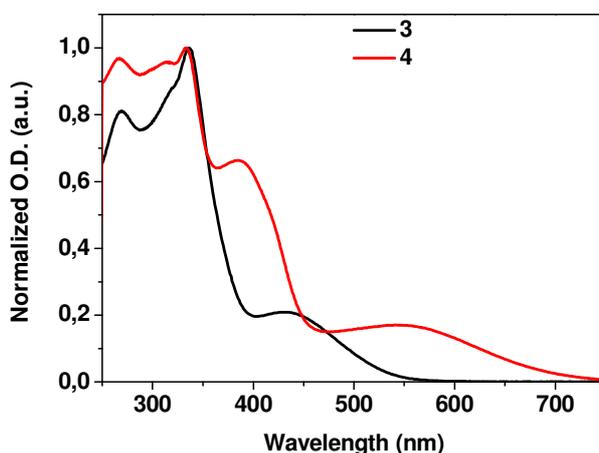
Figure 5. The crystal packing in **4** showing the non-conventional hydrogen bonds (red dashed lines) and S...S (yellow dashed lines) interactions.



2.2. UV-Vis Spectroscopy

The electronic absorption spectra of the **TTF₂-BisIm-Py** pincer (**3**) and of the **[Zn(TTF₂-BisIm-Py)Cl₂]** (**4**) complex were recorded in dichloromethane solution ($\sim 2 \cdot 10^{-5}$ M at room temperature; Figure 6). The **TTF₂-BisIm-Py** pincer exhibits two strong electronic absorption bands at $\lambda = 269$ nm and 336 nm which are assigned to the $\pi \rightarrow \pi^*$ absorption bands of the TTF and the phenyl ring. The broad band observed in the visible region at $\lambda_{\max} = 433$ nm is characteristic of the intramolecular charge transfer transition (ICT) from the highest occupied molecular orbital in the two TTFs to the lowest unoccupied molecular orbital in the electron-accepting pyridyl unit [20,28] and is responsible for the dark red color of this compound. Upon complexation of the pincer with zinc chloride (ZnCl_2), the electronic absorption spectrum presents the same features as the free ligand in the high energy region (<400 nm). However, the ICT transition is red shifted by about 80 nm indicating some effect on the electron acceptor behavior of this ligand upon complexation of zinc chloride. In addition, a shoulder (around 385 nm) is appearing, which is probably due to conformational change (all *trans* to all *cis*) of the pincer after complexation with zinc chloride.

Figure 6. Electronic absorption spectra of the pincer **3** and the zinc complex **4**.

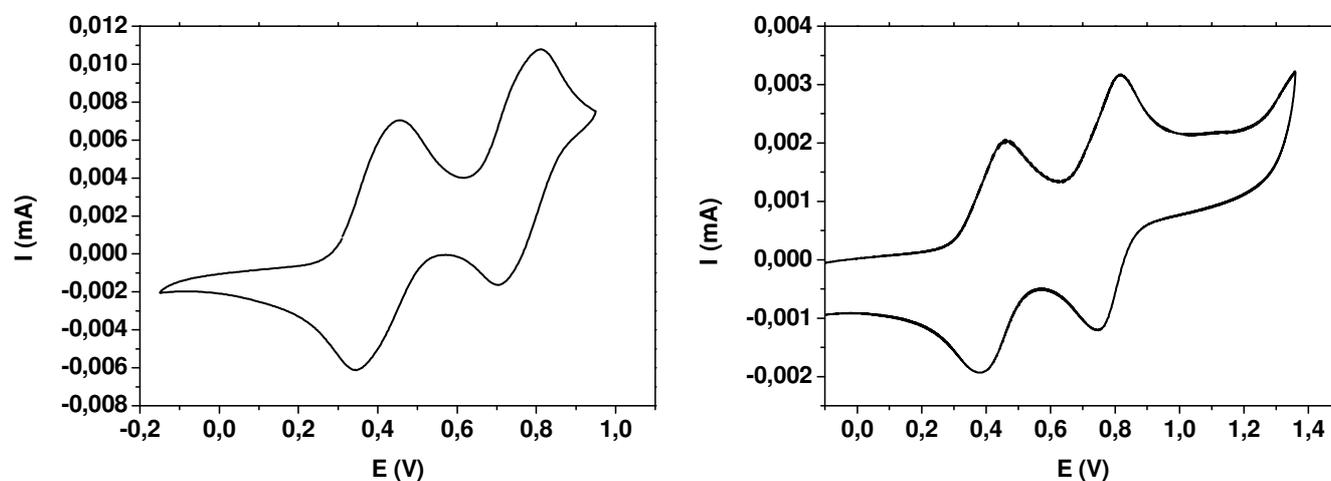


2.3. Electrochemistry

The electrochemical behaviors of the new pincer (**3**) and of the new complex (**4**) were examined by cyclic voltammetry (CV). The CV was performed in a three-electrode cell equipped with a platinum millielectrode, a platinum wire counter-electrode and a silver wire used as quasi-reference electrode. The electrochemical experiments were carried out under dry and oxygen-free atmosphere ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$) CH_3CN (5.10^{-4} M) with Bu_4NPF_6 (TBAP) (0.1 M) as supporting electrolyte. The voltammograms were recorded on an EGG PAR 273A potentiostat with positive feedback compensation. Based on repetitive measurements, absolute errors on potentials were estimated around $\pm 5 \text{ mV}$.

Cyclic voltammetry measurements (Figure 7) in the case of the pincer **TTF₂-BisIm-Py (3)** show two reversible oxidations waves (at $E_{1/2}^1 = 0.400 \text{ V}$ and $E_{1/2}^2 = 0.758 \text{ V vs. SCE}$). These potentials are anodically shifted from those of the free TTF (0.37 V vs. SCE) [1c]) because of the presence of the electrodeficient pyridine ring. The two oxidation bands, being broad, suggest very small differences between the oxidation potentials of the two TTF units present in the molecule. This behavior is similar to the one observed for *bis*(TTF) donors, described earlier by Avarvari *et al.* [29], separated by a triazine ring.

Figure 7. Cyclic voltammograms of both the pincer (**3**) (left) and of the zinc complex (**4**) (right) ($2 \times 10^{-5} \text{ M}$) in CH_3CN with $n\text{Bu}_4\text{NPF}_6$ (0.1 M).



After complexation, the oxidation potentials of the zinc metal complex (**4**) are slightly positively shifted (about 20 mV and 25 mV), suggesting that the zinc metal cation is affecting the oxidation potential of the TTF moieties by decreasing the electron density on the TTF units, a fact also suggested by the electronic absorption spectra. As a consequence of these electrochemical behaviors, we expect radical cation salts of both the TTF pincer and the corresponding zinc metal complex to form readily upon electrochemical oxidation into air-stable crystals [15].

3. Experimental Section

3.1. X-Ray Structure Determinations

Details about data collection and solution refinement are given in Table 2. X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer, operating with a Mo-K α ($\lambda = 0.71073 \text{ \AA}$) X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full matrix least-square procedures on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined. CCDC reference number: 871185 for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal Data and Structure Refinement for compound **4**.

complex	4
empirical formula	C ₃₅ H ₂₇ Cl ₂ N ₃ S ₁₂ Zn
fw	1010.59
<i>T</i> (K)	293(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	C2/c
unit cell dimensions:	
<i>a</i> (Å)	11.8152(16)
<i>b</i> (Å)	10.100(2)
<i>c</i> (Å)	35.579(6)
α (deg)	90
β (deg)	98.111(13)
γ (deg)	90
<i>V</i> (Å ³)	4202.2(12)
<i>Z</i>	4
<i>D</i> _c (g cm ⁻³)	1.597
abs coeff (mm ⁻¹)	1.340
θ range for data collection (deg)	1.16–27.54
reflections collected	4760
indep reflns	3371
completeness (%)	98.5
data/restraints/param	4760/0/243
GOF on F^2	1.197
final <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> 1 = 0.0597, <i>wR</i> 2 = 0.1051
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0968, <i>wR</i> 2 = 0.1227
largest diff. peak and hole (e Å ⁻³)	0.394 and -0.416

3.2. General

All the reactions were carried out under Argon and using HPLC solvents. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 spectrometer (operating at 500.04 MHz for ¹H and

125 MHz for ^{13}C) and Bruker Avance DRX 300 automatic spectrometer (operating at 300 MHz for ^1H , and 75 MHz for ^{13}C). Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; t, triplet. MALDI-TOF MS spectra were recorded on Bruker Biflex-IIITM apparatus, equipped with a 337 nm N₂ laser. Elemental analyses were recorded using a Flash 2000 Fisher Scientific Thermo Electron analyzer.

3.3. Synthesis of (1-(6,7-Dimethyldithio-tétrathiafulvalene)-4-nitro-benzene) (1)

1-Iodo-4-nitro-benzene (0.44 g, 1.78 mmol), 4-(trimethylstannyl)-4',5'-bis(methylthio)-tetrathiafulvalene (0.98 g, 2.14 mmol), and Pd(PPh₃)₄ as catalyst (10% mmol) were mixed in 40 mL of dry toluene and refluxed overnight under argon. The mixture was filtered over Celite and silica, washed with toluene and dichloromethane and dried under vacuum. The residue was purified by column chromatography (pentane/dichloromethane 1/1) to give 0.50 g of dark blue solid, yield: 67%. $^1\text{H-NMR}$ (300 MHz, CDCl₃) δ /ppm: 8.22 (d, 2H, $J^3 = 9$ Hz), 7.53 (d, 2H, $J^3 = 9$ Hz), 6.78 (s, 1H), 2.45 (s, 3H), 2.44 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl₃) δ /ppm: 147.0, 138.0, 133.7, 127.7, 126.6, 124.3, 118.3, 112.2, 109.6, 19.2; MS (MALDI-TOF): m/z : 416.9 ($M_{\text{th}} = 416.91$)

3.4. Synthesis of (4-(6,7-Dimethyldithio-tétrathiafulvalene)-aniline) (2)

To a solution of compound **1** (0.25 g, 0.59 mmol in 20 mL ethanol), Sn (0.14 g, 1.2 mmol) and HCl 35% (0.31 mL) were added and the mixture was refluxed for 4 h under argon. After the removal of the solvent, the crude was solubilised in ethyl acetate and washed several times with a NaOH solution (1 M) and water. The residue was purified by column chromatography with dichloromethane as eluent to give 0.23 g of an orange solid, yield: 99%. $^1\text{H-NMR}$ (300 MHz, CDCl₃) δ /ppm: 7.18 (d, 2H, $J^3 = 8.7$ Hz), 6.62 (d, 2H, $J^3 = 8.4$ Hz), 6.26 (s, 1H), 3.79 (broad s, 2H), 2.44 (s, 3H), 2.43 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl₃) δ /ppm: 146.9, 136.2, 127.6, 127.5, 122.8, 115.4, 114.9, 109.4, 106.3, 29.7, 19.2; MS (MALDI-TOF): m/z : 386.9 ($M_{\text{th}} = 386.94$).

3.5. (2,6-Bis(4-(4',5'-bis(Methylthio)-[2,2'-bi(1,3-dithiolylidene)]-4-yl)aniline)-iminopyridine) (3)

Compound **2** (0.115 g, 0.3 mmol) was solubilised in 50 mL ethanol, 2,6-Pyridinedicarboxaldehyde (0.019 g, 0.14 mmol) was added, followed by 3 drops of acetic acid and the mixture was refluxed overnight. After cooling the reaction, a red precipitate was formed which was filtered, washed with additional ethanol and dried to afford 116 mg of a red solid, yield: 94%. $^1\text{H-NMR}$ (300 MHz, CDCl₃) δ /ppm: 8.67 (s, 2H), 8.29 (d, 2H, $J^3 = 7.7$ Hz), 7.95 (t, 1H, $J^3 = 7.7$ Hz), 7.46 (d, 4H, $J^3 = 8.4$ Hz), 7.31 (d, 4H, $J^3 = 8.4$ Hz), 6.55 (s, 2H), 2.45 (s, 6H), 2.44 (s, 6H); $^{13}\text{C-NMR}$ (75 MHz, CDCl₃) δ /ppm: 160.2, 154.4, 150.6, 135.4, 130.9, 127.2, 123.5, 121.7, 113.2, 19.2; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 269 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 49260), 336 (60870), 433 (12670). Selected IR bands (cm^{-1}): 2916, 1621, 1567, 1454, 1411, 1212, 958, 835, 769. MS (MALDI-TOF): m/z : 873.6 ($M_{\text{th}} = 872.89$).

3.6. (2,6-Bis(4-(4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolylydene)]-4-yl)aniline)-iminopyridine) Zinc Chloride (**4**)

In a test tube, a solution of the pincer **3** (20 mg, 0.023 mmol) in CH₂Cl₂ (5 mL) was mixed with a solution of ZnCl₂ (3.1 mg, 0.023 mmol) in CH₃CN (3 mL) and ultrasonicated for 2 min. On top of the resulting solution a layer of 1:1 diethyl-ether mixture was added which led to the formation of good quality single crystals of complex **3** after 1 week. Yield: 18 mg (77%). $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 267 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 40750), 333 (42040), 385 sh, 550 (7290). Selected IR bands (cm⁻¹): 2916, 1622, 1568, 1457, 1418, 1215, 966, 888, 773.

4. Conclusions

As a first step towards the realization of multifunctional materials, a new TTF based pincer has been synthesized and its chelating ability has been investigated in respect to transition metal cations such as Zn(II). The crystal structure of the newly prepared electroactive zinc complex reveals that the TTF is neutral and the zinc cation is pentacoordinated. The two chlorines are involved in a set of hydrogen bonds giving rise to a 2D supramolecular grid arrangement. The electrochemical behavior of both the ligand and the neutral metal complex suggests that these compounds are useful candidates for the preparation of chemically and/or electrochemically oxidized radical cation crystalline salts. Further studies will be performed in order to investigate the complexation ability of this novel electroactive pincer on other metal cations such as Cu(II), Fe(II), Co(II), *etc.*

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Conflict of Interest

The authors declare no conflict of interest.

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