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New redox active ligands involving a tetrathiafulvalene vinylogue backbone

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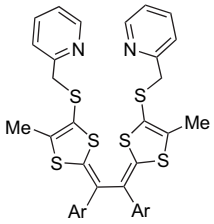
ABSTRACT

Two synthetic approaches towards a new bisthiopicoline substituted vinylogous tetrathiafulvalene (TTFV) are described. As evidenced by electrochemistry and ^{1}H NMR studies, this redox active ligand shows excellent coordinating properties towards Zn^{2+} metal ion.

1. Introduction

In recent years, a large amount of work has been devoted to the search of novel hybrid organic–inorganic architectures based on tetrathiafulvalene (TTF) due to their unique electronic properties.[1] A novel trend in this research area consists in grafting various coordination functions onto the TTF core, leading to numerous redox active ligands mainly as O,[2,3] S,[4] N,[5–8] P[9,10] ligands or mixed (P,N),[11] (N,S),[12] (P,S)[10a] ligands. Among these ligands, some TTFs have been used as redox-responsive receptors towards metal ions and have also shown their efficiency as redox probes.[4] A first π-extended TTF framework, functionalized with binding site groups for transition metal groups (Ni^{2+}, Pd^{2+} and Pb^{2+}), acting as a highly effective redox sensor was very recently reported.[13] As part of our ongoing research, we focused on the studies of electroactive ligands based on a tetrathiafulvalene vinylogue (TTFV) core, acting as potential redox receptors.[14] These TTFV, unlike simple TTF, exhibit different motions upon electron transfer, depending on the structure of the molecule,[15] and we have recently shown that the complexation to a metal ion can interfere with the electrochemically triggered molecular movement.[14] In order to further explore the intrinsic properties of these TTFV as electroactive ligands, we have decided to focus our attention on TTFV bearing two thiopicoline functions. Indeed, in the TTF series, bis-substituted thiopicoline TTF derivatives have shown their efficiency to form octahedral complexes with various divalent transition metal ions.[12] As the TTFV substituted on the central conjugation are non-planar molecules,[16] we investigated the functionalization of each dithiole ring in order to facilitate the complexation with one metal ion, sandwiched by the two coordination functions of the same TTFV. In this paper, we first describe two synthetic approaches to reach the target molecules. Then, we present the complexation studies of the dithiafulvenes precursors as well as the complexation study carried out on the TTFV in the presence of Zn^{2+} ions.



Ar = C_6H_5, C_6H_4CN

2. Results and discussion

2.1. Synthesis and redox properties of the donor molecules

TTFV can easily be synthesized from dithiafulvenes (DTF) through their chemical oxidative coupling.[16] In the literature, DTF are generally prepared according to a Wittig[17] or Wadsworth–Emmons[18] type reaction between a phosphonium or phosphonate in basic medium with an aldehyde. The DTF **2a** and **2b** functionalized by a thiopicoline group were prepared from the reaction of the dithiolyl phosphonate anion generated by treating **1** with *n*-BuLi followed by the addition of benzaldehyde or *p*-cyanobenzaldehyde (Scheme 1). It can be observed on the NMR spectra

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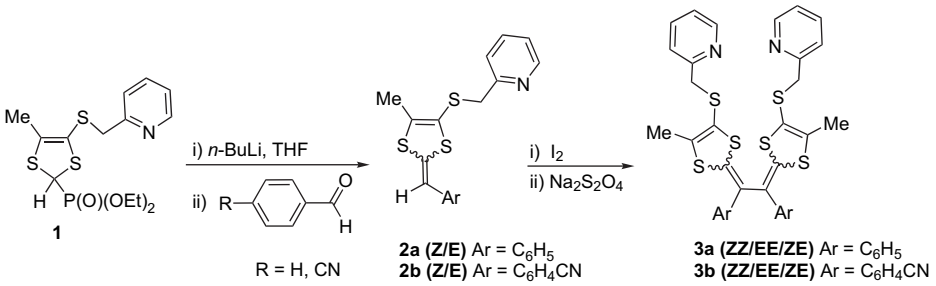


Scheme 1.

that both dithiafulvenes **2a** and **2b** exist as *Z* and *E* isomers, inseparable by column chromatography.

We investigated the redox properties of electroactive dithiafulvenes **2a** and **2b** using cyclic voltammetry. Both voltammograms show similar trends: at the first anodic scan, an irreversible oxidation wave and upon successive scans, the appearance of a novel reversible oxidation system at a lower oxidation potential than the first one (Fig. 1). This behaviour indicates that a novel redox active derivative TTFV **3** is formed upon oxidation, resulting from the coupling of two dithiafulvene radical cations followed by the deprotonation of the dimer.[19] Upon repetitive sweeps, the intensity of the irreversible oxidation wave decreases while the one of the reversible system increases.

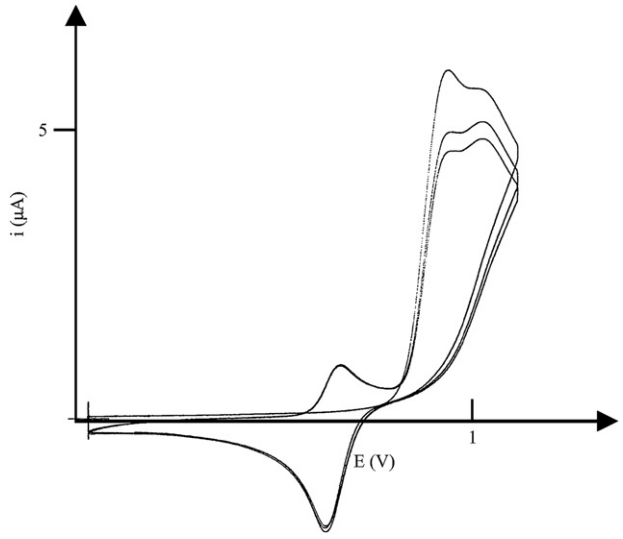
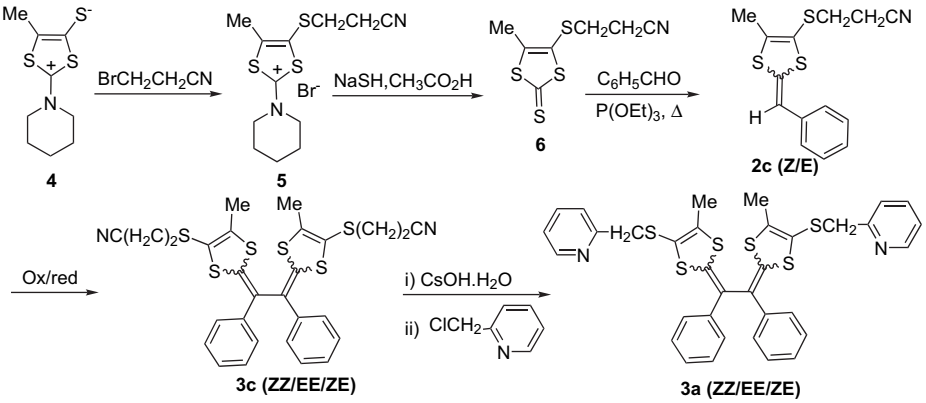


Figure 1. Cyclic voltammogram of **2b** in CH_2Cl_2 with 0.1 M *n*-Bu_4NPF_6 and *E* in V versus SCE scanning rate 100 mV/s.

One can observe the influence of the cyano electron withdrawing group on the oxidation potentials of the dithiafulvenes, as for DTF **2b** the E_{pa} amounts to 0.84 V versus SCE while for the DTF **2a** E_{pa} decreases to 0.79 V versus SCE. In order to prepare quantitatively the TTFV **3a** and **3b**, we also performed the chemical oxidative coupling of **2a** and **2b** in the presence of iodine; the formed dicationic species in the medium being then reduced with $Na_2S_2O_4$. Work up of the reaction leads to the neutral TTFV **3a** and **3b** in rather low yields (38 and 7%, respectively) (Scheme 1). The TTFV **3a**,**b** were obtained as a mixture of three isomers (*ZZ*/*EE*/*ZE*) in a statistical ratio, as observed on ^{1}H NMR spectra but could not be separated by column chromatography.

We also investigated another approach to insert the coordination function in the last synthetic step. One attractive possibility consists in preparing a TTFV containing cyanoethylthio-protected thiolate groups; a strategy well developed by Becher and Simonsen.[20] The thiolate can be easily deprotected in basic medium and further alkylated with various electrophiles. Nevertheless, the synthesis of a dithiafulvene according to Scheme 1 involves the generation of the phosphonate anion with *n*-BuLi, which would also deprotect the thiolate. Therefore, we investigated another route to the TTFV **3a** involving the phosphite mediated cross-coupling of a dithiole thione with an aldehyde, a route compatible with the basic-sensitive protected thiolate group.[21] This synthetic strategy starts from dithiole mesoionic **4**[22] as described in Scheme 2. Alkylation of **4** with 3-bromopropionitrile in refluxing CH_2Cl_2 followed by treatment of dithiolium salt **5** with $NaSH{\cdot}H_2O$ in acidic medium allows the formation of dithiole-2-thione **6** in 70% yield. A mixture of dithiole **6** and benzaldehyde was then heated in stoichiometric amounts, in neat triethyl phosphite at 100 °C for 6 h. Dithiafulvene **2c** was obtained in 88% yield as a mixture of *Z* and *E* isomers.

Electrochemical study of this dithiafulvene **2c** using cyclic voltammetry, leads to the same-patterned cyclic voltammogram as those obtained for **2a** and **2b**. The oxidation of **2c** into the cation radical occurs at E_{pa}=0.79 V versus SCE in CH_2Cl_2 (0.72 V vs SCE in CH_3CN). The chemical oxidative coupling of **2c** was investigated in



Scheme 2.

Table 1
Redox potentials of compounds **3a**–**3c**

	E in CH_3CN	E^1 in CH_2Cl_2	E^2 in CH_2Cl_2
3a	0.40	0.40	0.49
3b	0.50	0.55	–
3c	0.48	0.53	0.64

E in V versus SCE, Pt working electrode with 0.1 M n-Bu_4NPF_6, scanning rate 100 mV/s.

the presence of two different oxidizing agents, iodine[23] and $AgBF_4$.[24] The coupling reaction of **2c** was realized in the presence of 2 equiv of the oxidizing agent in refluxing dichloromethane under inert atmosphere followed by reduction of the medium with $Na_2S_2O_4$ (Scheme 2). The use of $AgBF_4$ allowed us to isolate **3c** in 70% yield while the oxidation with iodine afforded **3c** in lower yield (20%). The target molecule **3a** was prepared from **3c** by deprotection of the two thiolate functions with $CsOH\cdot H_2O$ followed by alkylation with picoline chloride. According to this strategy, **3a** was obtained in 80% yield, and the purification step was much easier to achieve than from the oxidative coupling reaction described in Scheme 1.

Redox behaviour of the three TTFV **3a**–**3c** has been studied by cyclic voltammetry in dichloromethane and in acetonitrile and the data are gathered in Table 1. All the derivatives exhibit only one single bielectronic reversible oxidation wave in acetonitrile. On the contrary, in dichloromethane, two distinct behaviours can be observed: either two close reversible monoelectronic waves for **3a** and **3c** or one bielectronic wave for **3b**. This behaviour is reminiscent to what was previously observed with other TTFV, where the redox behaviour was found to be strongly dependant both on the donating properties of the phenyl group and on the steric interactions on the central conjugation. As seen in Table 1, when decreasing the electron withdrawing strength, the bielectronic wave observed for **3b** splits into two close monoelectronic ones for **3a**.[25] This presence of the cyano group decreases also significantly the donating ability of the TTFV as the oxidation potential is positively shifted.

2.2. Metal complexes

Recently, Decurtins et al. showed that TTF derivatives substituted by two thiopicoline substituents can easily coordinate divalent metal ions such as Ni(II), Co(II), and Zn(II).[12] In order to follow the complexation not only through electrochemical studies but also through ^{1}H NMR studies, we realized these complexations only with the diamagnetic ion Zn^{2+}, either on the dithiafulvene **2b** or on the vinylogous TTF **3a**.

Addition of half equivalent of $ZnCl_2$ to an acetonitrile solution of **2b** and refluxing the medium for 1 h leads to a 2:1 complex where two dithiafulvenes **2b** are coordinated to one Zn^{2+} ion, Scheme 3. This complex $(\mathbf{2b})_2\cdot ZnCl_2$, has been isolated as a brown powder in 72% yield and fully characterized. Complexation of the metal ion has an influence on the ^{1}H NMR spectrum, especially on the set of signals attributed to the picoline group, which resonate at lower field. For instance, in $CDCl_3$ the methylene resonates at 4.03 ppm for the free ligand **2b** and at 4.31 ppm in $(\mathbf{2b})_2\cdot ZnCl_2$. We also investigated the redox behaviour of $(\mathbf{2b})_2\cdot ZnCl_2$ by cyclic voltammetry. As observed for **2b**, an irreversible peak is observed upon the first anodic scan while a reversible oxidation system appeared on the voltammogram upon successive scans, demonstrating the oxidative coupling of the dithiafulvene cores into the corresponding TTFV in solution. Two possibilities can be envisioned concerning the oxidative coupling since the two dithiafulvenes can form either a cyclic TTFV or a polymeric derivative via, respectively, an intra- or an intermolecular coupling. Actually it is interesting to note that the complexation does not modify the oxidation potential of the dithiafulvene core, as for $(\mathbf{2b})_2\cdot ZnCl_2$ E_{pa}=0.86 V versus SCE and for **2b** E_{pa}=0.85 V versus SCE in dichloromethane. Contrariwise, the reversible process due to TTFV formed in situ occurs at a higher oxidation potential (E=0.60 V vs SCE) than for metal-free TTFV **3b** at E=0.55 V versus SCE. In previous studies, we noticed that the only noticeable modification in terms of redox properties was a positive shift in the oxidation potentials when going from non-cyclic derivatives to cyclic ones, such as those represented on Chart 1. The derivatives **7**–**9** exhibit one reversible oxidation system at E=0.651 V for **7**, E=0.717 V for **8** (n=4) and E=0.736 V for **9** (n=3).[15] We can therefore conclude that the TTFV core formed here is the result of an intramolecular oxidative coupling and the positive shift observed is due to steric hindrance generated by the metal complexation. The complexation of $ZnCl_2$ constrains the binding groups linked to the dithiole rings, which induces in return a positive shift in the oxidation process. Unfortunately, when oxidizing $(\mathbf{2b})_2\cdot ZnCl_2$, either chemically or electrochemically, the resulting TTFV $(\mathbf{3b})\cdot ZnCl_2$ was not isolatable from the other salts formed in the medium.

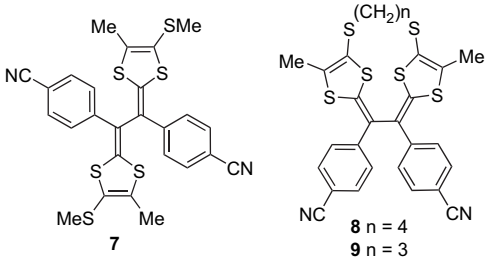
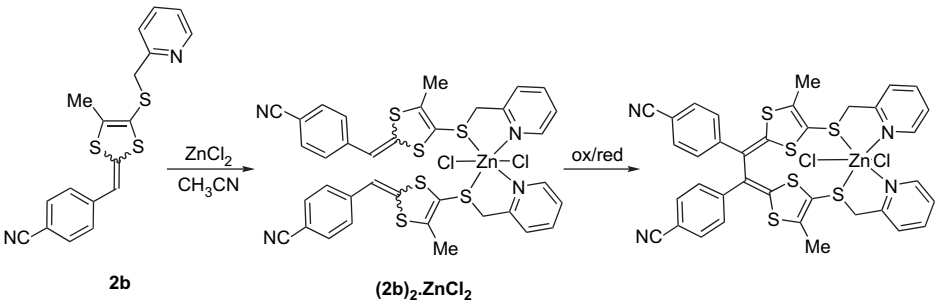
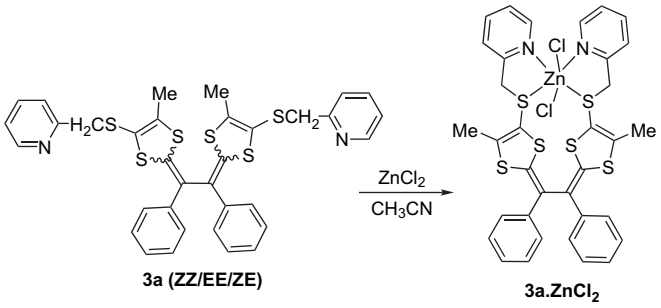


Chart 1.

To further understand the chelating abilities of these derivatives, $(\mathbf{3a})\cdot ZnCl_2$ has been directly prepared using similar reaction conditions, from preformed TTFV **3a** in the presence of 1 equiv of $ZnCl_2$. Filtration of the precipitate in suspension followed by analysis of both precipitate and filtrate show that the precipitate contains the remaining free ligand TTFV **3a** while the filtrate contains the 1:1



Scheme 3.

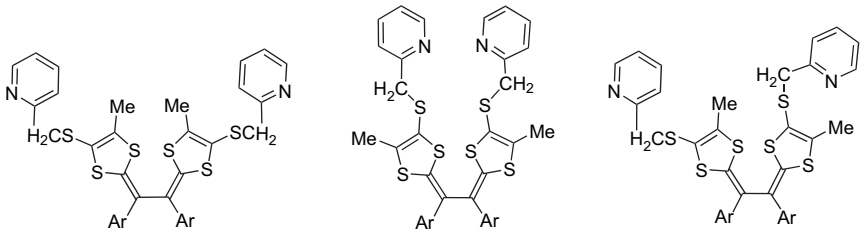


Scheme 4.

complex with **3a** as shown in Scheme 4. This reluctance of the TTFV **3a** to fully complex the Zn^{2+} cation is due to the fact that TTFV **3a** is obtained during its synthesis as a mixture of three isomers (*EE*/*EZ*/*ZZ*), which are represented below in Scheme 5.

In the *EE* or *EZ* configuration, the two thiopicolines are too far away from each other to allow intramolecular complexation whereas in the *ZZ* configuration, they are much closer, which favours complexation to the metal ion.

As previously noticed for the DTF **2b**, comparison of the ^{1}H NMR spectra in $(CD_3)_2CO$ of the free ligand **3a** with the (**3a**)·$ZnCl_2$ complex shows that complexation influences the set of signals attributed to the picoline group, which resonate at lower field. The methylene group resonates at 4.04 ppm for **3a** and at 4.52 ppm in (**3a**)·$ZnCl_2$. Similarly, as can be seen in Figure 2, the signals



Scheme 5.

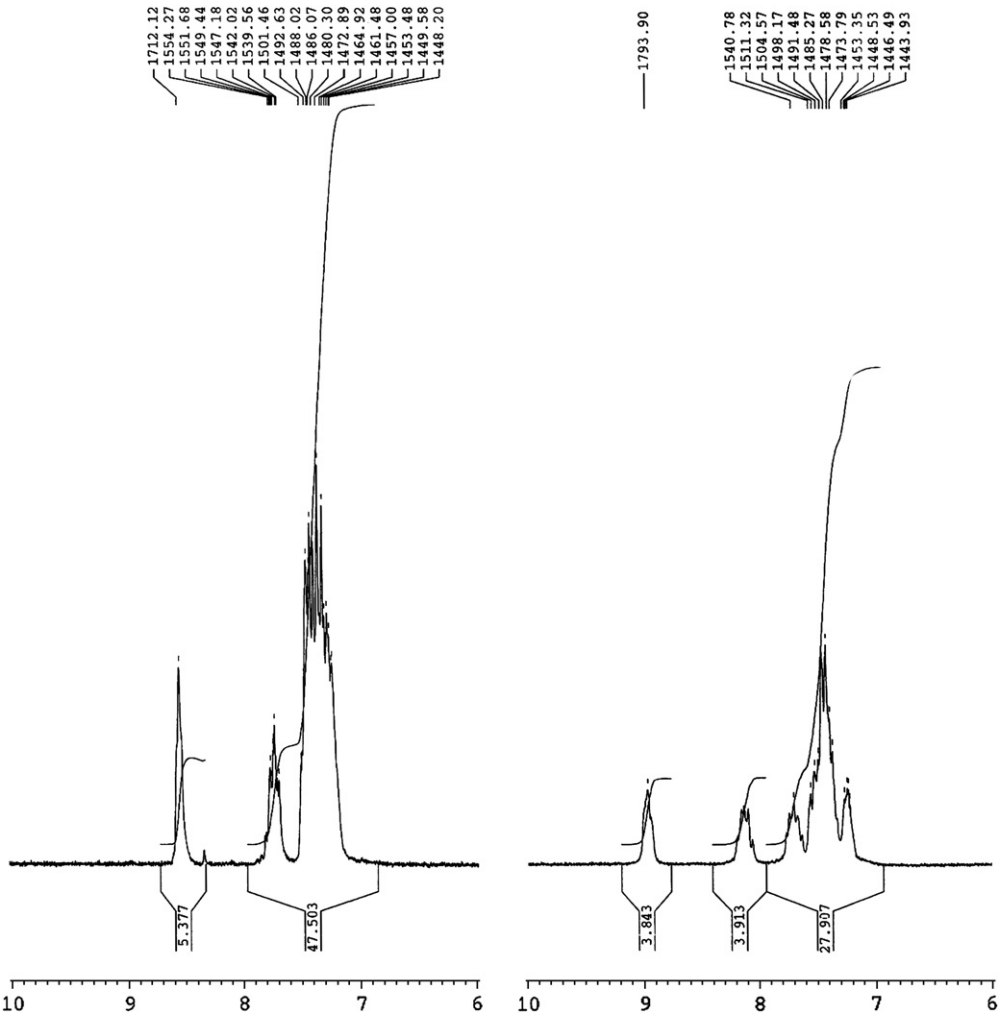


Figure 2. ^{1}H NMR ($(CD_3)_2CO$, 200 MHz) spectra of the aromatic protons of **3a** (left) and **3a**·$ZnCl_2$ (right).

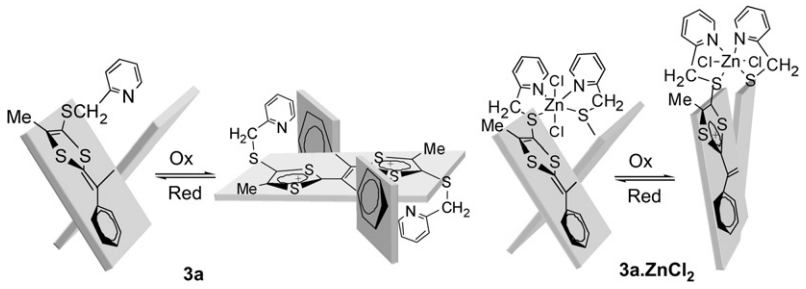


Figure 3. Schematic representation of the stretch motion for **3a** (left) and the clip motion for (**3a**)·$ZnCl_2$ (right) upon oxidation.

attributed to the pyridine proton exhibit significant chemical shift differences, for example, the closest proton from the nitrogen atom resonates at 8.56 ppm in **3a** while in (**3a**)·$ZnCl_2$ it is observed at 8.96 ppm.

The redox potentials of the complex (**3a**)·$ZnCl_2$ was investigated in dichloromethane by cyclic voltammetry. Complexation of the two dithiole rings through the thiopicoline groups modifies the shape of the voltammogram as only one reversible oxidation wave is observed at E=0.47 V versus SCE for (**3a**)·$ZnCl_2$ instead of the two close reversible oxidation processes observed for the free ligand **3a** (Table 1). The shift of the oxidation potential towards more positive value as well as the coalescence of the two monoelectronic waves into one bielectronic process has already been observed when passing from TTFV to their constrained cyclic TTFV.[15] This modification of the redox behaviour was the result of two different molecular motions generated by the electron transfer. Indeed a stretch movement was observed for the TTFV while a clip movement occurred for constrain cyclic TTFV. Therefore the modification of the shape of the voltammogram in (**3a**)·$ZnCl_2$ compared to **3a** implies that complexation impedes the stretch movement observed for TTFV (Fig. 3).

3. Conclusion

In summary we have presented two synthetic approaches to a novel redox active ligand able to coordinate divalent metal ions such as Zn^{2+}. Considering the fact that the binding sites of this ligand are far away from the redox active core, it is unlikely that the positive shift observed during the electrochemical investigations of the complex is the result of Coulombic repulsion between the oxidized TTFV core and the charged ion. Instead, due to the high stability of the complex, the Zn^{2+} plays the role of a linker between the two thiopicoline groups impeding the stretch molecular motions triggered by electron transfer. Consequently the oxidation of the TTFV core to the dication occurs in one bielectronic process in the complex instead of the two monoelectronic steps for the free ligand. Further work will be undertaken on the chelating ability of this redox active ligand towards other transition metal ions.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz with tetramethylsilane as internal reference. Elemental analysis results and Mass spectra were carried out at the Centre de Mesures Physiques de l'Ouest, Rennes. The dithiole phosphonate **1** was synthesized starting from dithiole mesoionic **4** according to published procedure.[18,26] Cyclic voltammetry were carried out on a 10^{-3} M solution of the compounds in dichloromethane or in acetonitrile, containing 0.1 M n-Bu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 V/s on a platinum disk electrode (A=1 mm^2). The potentials were measured versus saturated calomel electrode.

4.2. Synthesis

*4.2.1. Dithiafulvenes (**2a**) and (**2b**)*

To a solution of dithiole phosphonate **1** (1 g, 2.70 mmol) in THF (20 mL) under inert atmosphere and at −78 °C was added dropwise n-BuLi 1.6 M in hexane (1.82 mL, 2.97 mmol). After 30 min under stirring, the aldehyde was added (benzaldehyde: 0.30 mL; 4-cyanobenzaldehyde: 420 mg, 3.24 mmol). The reaction mixture was then allowed to reach room temperature and stirred for 12 h. The medium was concentrated in vacuo and CH_2Cl_2 (30 mL) was added. The organic phase was washed with water (2×50 mL), dried over $MgSO_4$ and concentrated. After column chromatography on silica gel using CH_2Cl_2/n-pentane 1:1 as eluent (R_f=0.65 for **2a**; R_f=0.60 for **2b**), Dithiafulvene **2a** and **2b** were obtained as thick oils.

*4.2.1.1. Compound **2a**.* Yield 42%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 3H, CH_3), 3.98 (s, 2H, CH_2), 6.42 (s, 1H, CH), 7.11–8.56 (m, 9H, CH Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.3, 41.8, 113.1, 113.3, 115.8, 122.2, 123.4, 125.5 126.6, 128.5, 132.5, 135.9, 136.5, 149.8, 157.1; HRMS calcd for $C_{17}H_{15}NS_3$: 329.0366, found: 329.0379.

*4.2.1.2. Compound **2b**.* Yield 65%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 3H, CH_3), 4.03 (s, 2H, CH_2), 6.44 (s, 1H, CH), 7.20–7.30 (m, 3H, CH Ar), 7.49–7.71 (m, 4H, CH Ar), 8.57 (d, 1H, CH Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 42.2, 107.8, 111.3, 119.6, 122.9, 123.9, 127.8, 132.6, 136.8, 137.2, 138.2, 139.4, 141.1, 147.6, 150.0, 157.1; HRMS calcd for $C_{18}H_{14}N_2S_3$: 354.0319, found: 354.0307. Anal. Calcd for $C_{18}H_{14}N_2S_3$: C, 60.98; H, 3.98; N, 7.90. Found: C, 61.01; H, 3.95; N, 8.41.

*4.2.2. General procedure for the synthesis of TTFV (**3a**) and (**3b**) by oxidative coupling of (**2a**) and (**2b**)*

To a CH_2Cl_2 (40 mL) solution of dithiafulvene **2a** (1 g, 3.04 mmol) or **2b** (1.08 g, 3.04 mmol), under inert atmosphere, was added I_2 (2.02 g, 8 mmol) and the resulting solution was stirred under reflux for 1 h. To the reaction mixture a large excess of $Na_2S_2O_4$ (2 g) was added and the reaction mixture was stirred under reflux for 12 h. The reaction mixture was filtered on Celite and the organic phase was washed with water 2×50 mL, dried over $MgSO_4$. The solvent was removed and the residue was purified by silica gel column chromatography using CH_2Cl_2/Et_2O 9:1 as eluent. TTFV **3b** was obtained as a yellow thick oil. Yield 7%; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.75 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 4.05 (s, 2H, CH_2), 4.08 (s, 2H, CH_2), 7.19–7.75 (m, 14H, CH), 8.58 (m, 2H, CH). TTFV **3a** was obtained as a yellow thick oil. Yield 38%. Three isomers are observed on the ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 1.65 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 3.98 (s, 2H, CH_2), 4.04 (s, 2H, CH_2), 7.10–7.70 (m, 16H, CH), 8.56 (m, 2H, CH); ^{13}C NMR (75 MHz, CD_3Cl) δ 13.9, 41.7, 116.8, 122.2, 123.7, 124.2, 126.5, 126.6, 128.5, 136.2, 136.5, 136.7, 137.5, 149.8, 156.9; HRMS calcd for $C_{34}H_{28}N_2S_6$: 679.0475, found: 679.0477. Anal. Calcd for

$C_{34}H_{28}N_2S_6 \cdot 0.5CH_2Cl_2$: C, 59.27; H, 4.15; N, 4.01. Found: C, 59.44; H, 4.39; N, 3.94.

*4.2.3. 3-[(5-Methyl-2-thioxo-1,3-dithiol-4-yl)thio]propanenitrile (**6**)*

A solution of mesoionic-2-piperidino-1,3-dithiolium-4-thiolate **4** (13.9 g, 6 mmol) and 3-bromopropionitrile (9.4 g, 7 mmol) in CH_2Cl_2 was heated to reflux for 12 h. After evaporation of the solvent, the oil was washed several times with diethylether and dried. Dithiolium **5** was obtained in 93% yield as an oily product and used for the next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.48–1.60 (m, 6H, CH_2), 2.23 (s, 3H, CH_3), 2.66 (m, 2H, SCH_2), 2.87 (m, 2H, CH_2), 3.61 (m, 4H, NCH_2). A solution of dithiolium **5** (2 g, 5 mmol) and 2 g of $NaSH \cdot H_2O$ in DMF (20 mL) and acetic acid (20 mL) was stirred at 100 °C for 2 h. After cooling at room temperature, water (20 mL) and dichloromethane (40 mL) were added. The organic phase was washed with water (2×30 mL) and with $NaHCO_3$ (30 mL). The organic layer was separated and dried over Na_2SO_4. The solution was concentrated in vacuo and the residue was purified on column chromatography using ether/petroleum ether 1:2 as eluent to give **6** (820 mg) as yellow crystals in 70% yield. Mp=78–80 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H, CH_3), 2.74 (m, 2H, CH_2), 3.05 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.3, 18.6, 32.1, 117.3, 125.8, 148.6, 210.9. Anal. Calcd for $C_7H_7NS_4$: C, 36.02; H, 3.02; N, 6.00. Found: C, 35.75; H, 2.95; N, 5.75. FTIR (KBr) ν CN=2250 cm^{-1}.

*4.2.4. 2-Benzylidene-4,5-bis(methylthio)-1,3-dithiole (**2c**)*

To a suspension of 1,3-dithiole-2-thione (1 g, 4.3 mmol) in $P(OEt)_3$ (10 mL) was added benzaldehyde (460 mg, 4.3 mmol). The reaction mixture was stirred at 100 °C for 6 h. The solvent was removed under reduced pressure and the residue was purified on column chromatography using CH_2Cl_2 as eluent. The dithiole **2c** was obtained as a mixture of two isomers as a yellow oil in 88% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, 3H, CH_3), 2.66 (m, 2H, CH_2), 2.93 (m, 2H, CH_2), 6.50 (s, 1H, CH) for one isomer and 6.47 (s, 1H, CH) for the other one, 7.21–7.38 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.8, 18.4, 30.7, 114.1, 117.7, 125.9, 126.7, 128.6, 131.6, 136.3, 136.5, 137.3. Anal. Calcd for $C_{14}H_{13}NS_3$: C, 57.69; H, 4.50; N, 4.81. Found: C, 56.97; H, 4.49; N, 4.72. FTIR (KBr) ν CN=2249 cm^{-1}.

*4.2.5. Synthesis of TTFV (**3c**)*

To a solution of **2c** (430 mg, 1.5 mmol) in 10 mL of dry degassed CH_2Cl_2, $AgBF_4$ (580 mg, 3 mmol) was added at 0 °C. The solution was stirred at 0 °C for 2.5 h and then $Na_2S_2O_4$ (2 g) was added. After 30 min stirring the solution was washed with water (2×20 mL) and dried over Na_2SO_4. Chromatography over silica gel using ether/pentane (1:2) mixture as the eluent afforded the TTFV in 70% yield as a thick oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 6H, CH_3), 2.65 (m, 4H, CH_2), 2.92 (m, 4H, CH_2), 7.15–7.55 (m, 10H, Ar); HRMS calcd for $C_{28}H_{24}N_2S_6$: 580.0263, found: 580.0237. Anal. Calcd for $C_{28}H_{24}N_2S_6$: C, 57.99; H, 4.16; N, 4.82. Found: C, 57.55; H, 4.25; N, 4.88. FTIR (KBr) ν CN=2250 cm^{-1}.

4.3. Metal complexes

*4.3.1. Synthesis of complex (**2b**)$_2 \cdot ZnCl_2$*

To a solution of dithiafulvene **2b** (1 g, 2.82 mmol) in CH_3CN (40 mL), $ZnCl_2$ (192 mg, 1.41 mmol) dissolved in H_2O (5 mL) was added. The reaction mixture was stirred under reflux for 1 h and then 3 h at room temperature. The solvent was evaporated under reduced pressure and the complex (**2b**)$_2 \cdot ZnCl_2$ was precipitated by the addition Et_2O. The precipitate was washed with ether to afford (**2b**)$_2 \cdot ZnCl_2$ as a light brown compound (854 mg; 72%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.79 (s, 6H, CH_3), 4.31 (s, 4H, CH_2), 6.44 (s, 2H, CH), 7.24–7.28 (m, 4H, CH Ar), 7.34–7.37 (m, 4H, CH Ar), 7.57–7.63 (m, 4H, CH Ar), 7.84–8.07 (m, 2H, CH Ar), 8.88 (m, 2H, CH Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.2, 14.1, 39.1, 106.6, 110.5, 114.7, 118.1, 123.1, 124.9, 125.8, 131.3, 136.6, 137.1, 137.9, 139.6, 147.5, 147.9, 155.9, 206.4; HRMS calcd for $C_{36}H_{28}Cl_2N_4S_6Zn$ [M+H]: 842.9385, found: 842.9390. Anal. Calcd for ($C_{36}H_{28}Cl_2N_4S_6Zn.Et_2O$): C, 52.25; H, 4.16; N, 6.09. Found: C, 52.51; H, 3.81; N, 6.52.

*4.3.2. Synthesis of complex (**3a**)$\cdot ZnCl_2$*

Similar procedure as the one described above for **2b** using **3a** (250 mg, 0.3 mmol) and 1 equiv of $ZnCl_2$ (0.4 g, 0.3 mmol). The solvent was evaporated under reduced pressure and the uncomplexed **3a** and $ZnCl_2$ were precipitated by the addition Et_2O. The complex (**3a**)$\cdot ZnCl_2$ was obtained as a brown thick oil in 35% yield. ^{1}H NMR ($(CD_3)_2CO$, 200 MHz) δ 1.65 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 4.52 (s, 4H, CH_2), 7.2–7.6 (m, 12H, CH), 7.79 (m, 2H, CH), 8.15 (m, 2H, CH), 8.96 (m, 2H, CH); HRMS calcd for $C_{34}H_{28}Cl_2N_2S_6Zn$ [M+H]: 790.9324, found: 790.9355 and calcd for [M−Cl]: 754.9557, found: 754.9535.

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