

Pyridyldithiafulvenes as Precursors of Coordination-Driven Self-Assembled Redox Active Macrocycle

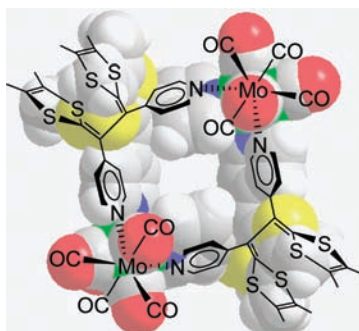
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ABSTRACT



A novel redox active macrocycle including two vinyllogous tetrathiafulvalenes (TTFVs) and two molybdenum tetracarbonyl fragments has been synthesized thanks to the coordination-driven self-assembly of complementary angular derivatives. Pyridyl vinyllogous TTFVs have been deliberately elaborated for that purpose, using the oxidative coupling of pyridyldithiafulvenes (DTF). Cyclic voltammetry, IR and NMR spectroscopies, and single-crystal X-ray crystallography of the target molecules have been investigated.

Redox active *N*-ligands involving a tetrathiafulvalene (TTF) backbone as the electroactive moiety have recently received a lot of attention as precursors of conducting or magnetic materials through their association to transition metal complexes.¹ Among the different functional groups used to confer an *N*-ligand character to the TTF, pyridine represents the most promising one. Indeed, pyridyl-substituted TTFs, where pyridine has been grafted either directly or through a spacer group on the TTF core, led to a variety of hybrid organic–inorganic structures and recently to original metal directed orthogonal based TTF dimers.^{1–4} Dithiafulvenes (DTF) are another class of electroactive molecules. An interesting aspect of the DTF chemistry is their ability to

form vinyllogous tetrathiafulvalenes (TTFV) by oxidative coupling when they are monosubstituted (Scheme 1).⁵ Therefore, the synthesis of monodentate DTF ligand would open the way to bidentate TTFV ligand, which has been little investigated in the area of redox active ligands.⁶ Concerning pyridyl-functionalized DTF,⁷ only those substituted with two

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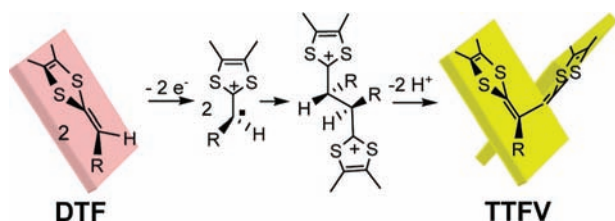
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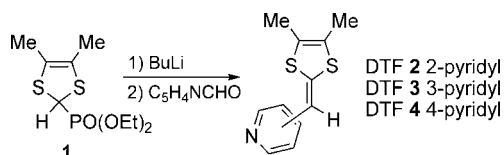
Scheme 1. Oxidative Dimerization of DTF into TTFV



pyridyl moieties, preventing the formation of TTFV, have been used as chelating ligands.⁸ The main difference between TTF and TTFV is their structural shape as TTF are planar molecules while TTFV substituted on the central conjugation (R) are nonplanar molecules (Scheme 1).^{5–7,9} Consequently, functionalization of TTFV with pyridine units will generate divergent bidentate ligands which could assemble with complementary angular metal complexes into macrocyclic structures.¹⁰ Thus, we decided to investigate the synthesis of vinyllogous TTFs bearing two pyridyl substituents on the central conjugation, thanks to the oxidative coupling of the appropriate DTF, and to study the coordinating ability of these derivatives toward molybdenum carbonyl fragment, Mo(CO)₄, in the construction of coordination-driven self-assembled macrocycle.

The DTF derivatives **2**, **3**, and **4** were prepared according to a Wittig–Horner-type reaction of the 4,5-dimethyl-1,3-dithiolylphosphonate anion generated from **1** in the presence of BuLi with 2-, 3-, or 4-pyridine carboxaldehyde (Scheme 2).

Scheme 2. Synthesis of Pyridyl-DTFs 2–4



The molecular structures of **2** and **4**, deduced from X-ray structure analysis, show that both dithiafulvenes exhibit

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planar geometry with similarities in the bond lengths (Figure 1). Interestingly, for **2**, only the *s-cis* conformer was obtained

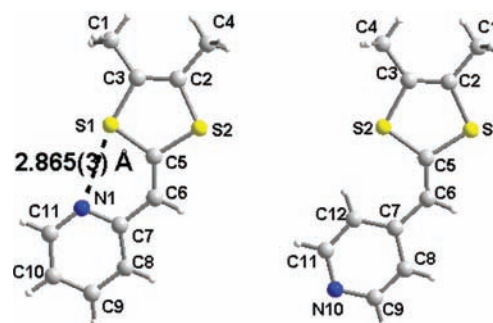


Figure 1. Molecular structure of DTF **2** (left) and **4** (right).

with a short distance between the sulfur atom of the dithiole ring and the nitrogen atom of 2.865(3) Å. This distance is much shorter than the sum of the van der Waals radii of 3.35 Å (N 1.5 Å and S 1.85 Å) indicating the existence of a stabilizing intramolecular interaction.¹¹

All these DTF derivatives **2–4** exhibit similar UV–vis spectra with a strong electronic absorption band at 391–375 nm followed by a weaker absorption band around 450 nm in dichloromethane. This low-energy absorption band is ascribed to an intramolecular charge transfer (ICT) between the dithiafulvene unit, as the electron-donating moiety, and the pyridine core, as the electron-accepting part.

The electrochemical properties of the DTFs **2–4** were studied by cyclic voltammetry in dichloromethane solution. On the first anodic scan, these DTFs exhibit similar redox behavior as two close irreversible oxidation waves, corresponding to the oxidation of the dithiafulvene core into its cation radical and to the oxidation of the pyridine, are successively observed ($E_{ox} = 0.71$ and 1.18 V vs SCE for DTF **2**, $E_{ox} = 0.77$ and 0.87 V vs SCE for DTF **3**, and $E_{ox} = 0.85$ and 1.15 V vs SCE for DTF **4**). The oxidation potentials correlate linearly with the Hammett para substituent (σ_p) constant (Figure 2).¹² Upon recurrent scans, the three DTFs **2–4** behave differently. Indeed, for DTFs **3** and **4**, a novel redox process appears on the voltammogram at a lower oxidation potential than the irreversible one (Figure 2), while for DTF **2**, no modification occurs. This indicates that upon oxidation, DTFs **3** and **4** form a novel electroactive derivative in the medium, typical for dithiafulvenes known to form vinyllogous TTFs upon oxidative coupling (Scheme 1). The redox signature of formed TTFV appears at lower oxidation potentials than the starting DTF.⁵ Contrariwise, the lack of reactivity of DTF **2** remains surprising and two interpretations can be envisioned, either the coupling of **2** is too slow at the cyclic voltammetry time scale, or the intramolecular S \cdots N interaction hinders the electro-oxidative coupling.

We also performed a chemical oxidation of the three derivatives **2–4** using AgBF₄ as the oxidizing agent followed by a reduction of the formed dicationic species TTFV²⁺, in these conditions, with Na₂S₂O₄. As expected, after the

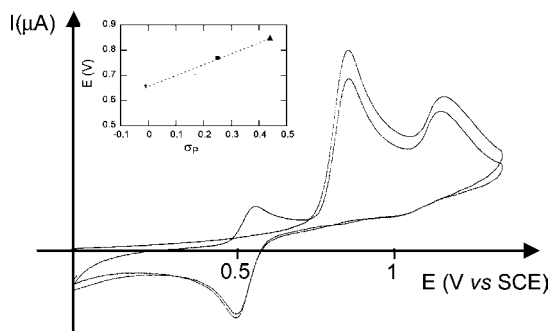
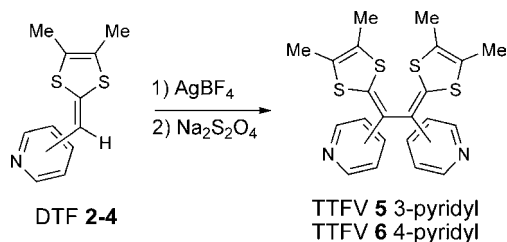


Figure 2. Cyclic voltammogram of DTF **4** in CH_2Cl_2 , scan rate 100 mV/s. Inset: Correlation between the oxidation peak potential of DTF and the Hammett parameter σ_p (●, phenyl; ○, 2-pyridyl; ■, 3-pyridyl; ▲, 4-pyridyl; $R = 0.988$).

chemical oxidative coupling of **3** and **4**, the TTFVs **5** and **6** were indeed isolated (Scheme 3). On the other hand, the

Scheme 3. Synthesis of Bispyridyl-TTFVs **5** and **6**



oxidation of DTF **2** with AgBF_4 followed by the reduction with $\text{Na}_2\text{S}_2\text{O}_4$ did not afford any product resulting from an oxidative coupling. This unreactivity of **2** can be attributed to the stabilization of the cation radical into a planar geometry due to the S \cdots N intramolecular interaction, while the meta and para derivatives **3** and **4** lacking this interaction can adopt a tetrahedral structure at the bridging C atom necessary for the dimerization.¹³

The molecular structures of **5** and **6**, determined by X-ray structure analysis, shown in Figure 3, reveal that the donors are nonplanar. This common nonplanar geometry for all vinylogous TTF substituted on the central conjugation is due to steric hindrance. The two acute dihedral angles along the central C–C bond amount to 88.3(32)° and 89.3(30)° in **5** and to 76.46(32)° and 81.82(30)° in **6** for the two dithiole rings and the two pyridyl rings, respectively.

The redox behavior of **5** and **6** was also investigated by cyclic voltammetry in CH_2Cl_2 . The oxidation of the neutral TTFV to the dication occurs either in two close monoelec-

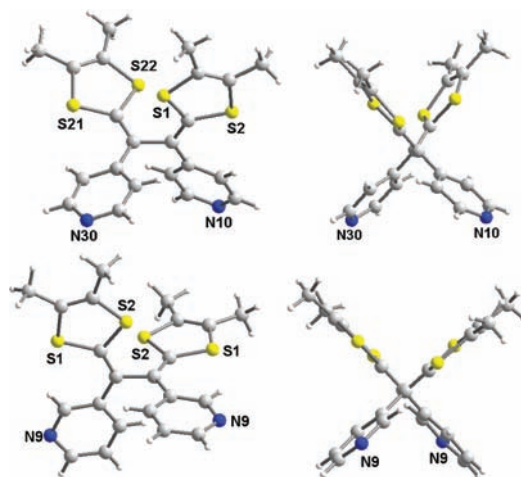


Figure 3. Molecular structures of TTFV **5** (bottom) and TTFV **6** (top).

tronic processes for **5** ($E_1 = 0.40$, $E_2 = 0.51$ V vs SCE) or in one bielectronic step for **6** ($E = 0.52$ V vs SCE) all of them being fully reversible. This different electron transfer behavior is correlated with the electron-withdrawing effect of the pyridyl substituents, as previously observed for other TTFV.⁹ This compression of potential, where the second electron transfer is easier than the first one, is more pronounced when increasing the withdrawing strength.⁹ The electron-withdrawing effect of the 4-pyridyl substituent is stronger than that of the 3-pyridyl group (Figure 2) and therefore the two mono-electronic processes in **5** coalesce into one bielectronic one in **6**.

Both TTFVs **5** and **6** are of potential interest for the construction of metallacycles through coordination-driven self-assembly, as they are bidentate redox active ligands with a twisted shape. However, TTFV **6** presents an advantage on TTFV **5** as the two coordinating sites are located in an almost perpendicular position and therefore chelation of a metal is not possible while with TTFV **5** both alternatives can be envisioned: chelation and coordination to two metallic atoms. As a first example, we investigated the reactivity of TTFV **6** ligand toward $\text{M}(\text{CO})_6$ using 1 equiv of $\text{Mo}(\text{CO})_6$ in refluxing toluene. Workup of the reaction mixture by chromatography on silica gel column leads to a powder that was analyzed by ^1H NMR. In the proton NMR spectrum, four sets of signals were observed at 1.99, 2.12, 6.91, and 8.28 ppm. The last two signals correspond to the pyridyl hydrogen signals. Compared with their chemical shift in the TTFV **6** precursor (7.25 and 8.50 ppm), they both are shifted upfield upon coordination. On the IR spectrum four stretching absorption bands were observed in the carbonyl region at 1821, 1880, 1926, and 2007 cm^{-1} characteristic of a $\text{Mo}(\text{CO})_4$ ¹⁴ fragment, which implies that two pyridyl fragments from two different TTFVs are coordinated to one molybdenum atom inducing the formation of only a macrocyclic structure (Scheme 4).

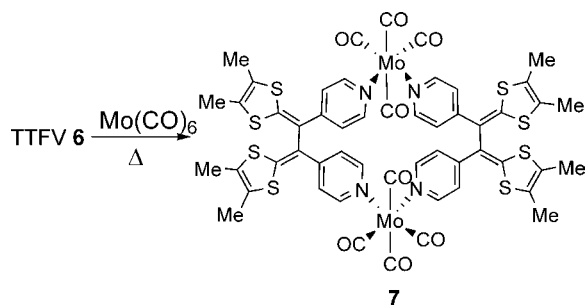
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Scheme 4. Synthesis of Metal-Directed Square Self-Assembled Redox Active Macrocycle **7**



X-ray crystal structure analysis confirmed our hypothesis concerning the formation of a self-organized structure **7** containing two TTFV **6** and two Mo(CO)₄ fragments (Figure 4). Indeed, due to complementarity of angle, size, and orientation of coordination moieties, the TTFV **6** and the *cis*-Mo(CO)₄ fragment, a square supramolecular structure is obtained. Within this architecture, the bond lengths of the TTFV are not modified compared to the free structure of **6**. Only, as the result of the coordination-driven self-assembly to Mo, the acute dihedral angle based on the central C–C bond for the two pyridyl rings respectively is enlarged as it amounts to 81.82(30)° in **6** and to 93.02(43)° in **7**.

As this macrocycle **7** contains four redox active units, the two TTFV cores and the two Molybdenum centers, we also studied its redox behavior by cyclic voltammetry in CH₂Cl₂. Interestingly, two redox systems are observed on the voltammogram at $E_1 = 0.48$ V and $E_2 = 0.74$ V vs SCE. Actually as already noticed from the ¹H NMR investigation, the coordination to Mo(CO)₄ exerts a releasing effect on the redox properties as the first oxidation potential is negatively shifted by 40 mV. The second oxidation process corresponds to the concomitant oxidation of the two radical cation of the TTFV into TTFV dication and the oxidation of the two metallic centers.

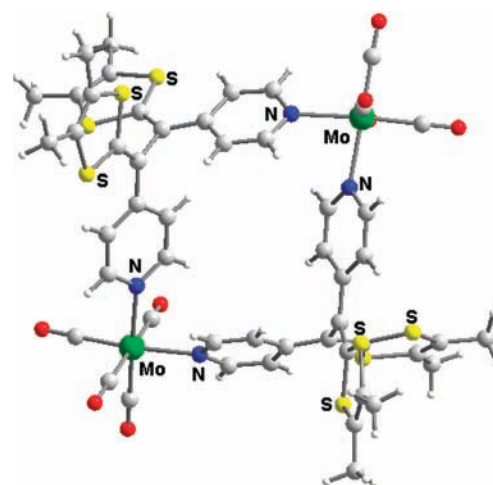


Figure 4. Molecular structure of the square macrocycle **7**.

In summary, we have shown that pyridyl-DTF is an excellent synthon for the elaboration of vinylogous TTFs, a novel class of electron-donor molecules able to form, via metal directed self-assembly, original macrocyclic structures. Further investigations will be devoted to the tuning of the size of the macrocycle as a function of the metallic fragments used, and to their controlled oxidation.

Supporting Information Available: Experimental conditions and characterization data for compounds **2–7** and X-ray data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre; deposition nos. 771254 –771258. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html.

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