

## Crystal structures and properties of the tetrathiafulvalene substituted bispyrazol ligand and its rhenium(I) tricarbonyl complex



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### ABSTRACT

The new tetrathiafulvalene-functionalized bispyrazole ligand (**L**) and the corresponding tricarbonyl rhenium(I) complex (**4**) have been synthesized and structurally characterized. Their absorption spectra and redox behaviors have been recorded, and the absorption spectral changes of **L** upon addition of NOPF<sub>6</sub> have also been studied in detail.

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Tetrathiafulvalene (TTF) and its derivatives (TTFs) are distinguished precursors for producing multifunctional materials, as their strong  $\pi$ -donors are capable of forming persistent radicals (TTF<sup>•+</sup> and TTF<sup>2+</sup>) [1,2]. In addition, these multifunctional materials always exhibit two or more properties with synergistic effects, such as conductivity and magnetism, luminescence, chirality and spin-crossover. Most interestingly, the properties can be improved by modifying the TTF moieties with various functional groups. Different TTF derivatives and their corresponding metal complexes have been synthesized and studied, for example, TTF–phosphine [3], –crown ethers [4], –oxazoline [5], –dithiolate [6], –acetylacetonate [7], –carboxyl [8], –pyridine [9], –bipyridine [10], –Schiff base [11] and –DNA [12].

The coordination chemistry of pyrazoles with unique two-nitrogen heterocycle has been extensively studied since 1972 [13]. Recently, such ligands have been used as building blocks in the synthesis of hydrogen-bonded networks [14]. In addition, the deprotonated forms of pyrazoles, namely pyrazolates, are usually acted as bridging ligands to construct polynuclear complexes [15,16]. Also the properties of the pyrazole ligands can be modified through the substitution of the protons, yielding a great diversity of pyrazole-derived ligands. Previously, we have reported the advantageous electrochemical and photophysical properties of the tricarbonyl (chloro) rhenium(I) complexes with a series of new

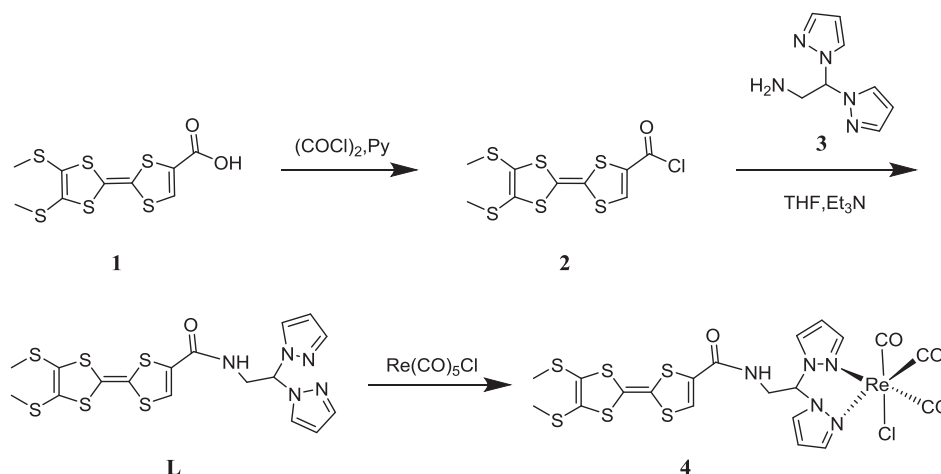
tetrathiafulvalene-substituted 3,5-dimethylpyrazole ligands. The results demonstrated that the novel tetrathiafulvalene–pyrazole ligands were useful for the preparation of new metal complexes with interesting properties [17]. In this paper, we have successfully synthesized another new TTF-based bispyrazole ligand with the amide bridge, N-(2,2-di(1H-pyrazol-1-yl)ethyl)-4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolyldiene)]-4-carboxamide (**L**) (Scheme 1). Then we have obtained a new rhenium (I) carbonyl complex, Re(CO)<sub>3</sub>(L)Cl (**4**), by the reaction of the TTF-bis(pyrazole) ligand and Re(CO)<sub>5</sub>Cl, which is structurally characterized. Finally, we investigated their spectroscopic and electrochemical properties by UV–vis and cyclic voltammetry, respectively.

4',5'-Bis(methylthio)-[2,2'-bi(1,3-dithiolyldiene)]-4-carboxylic acid (**1**) [18], 4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolyldiene)]-4-carbonyl chloride (**2**) [18] and 2,2'-bis(pyrazolyl)ethanamine (**3**) [19] were prepared according to literature procedures. As shown in Scheme 1, the TTF-bis(pyrazole) ligand (**L**) is synthesized by the acylation reaction between 4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolyldiene)]-4-carbonyl chloride and an excess of 2,2'-bis(pyrazolyl)ethanamine [20]. The <sup>1</sup>H NMR spectra exhibit signals at 6.12 ppm, which can be attributed to the proton on the amino group. It is also observed that the shape peak at 1566 cm<sup>-1</sup> is due to the stretching vibrations of the C=C and C=N bonds of the pyrazole group in infrared spectra.

The reaction of the ligand **L** and Re(CO)<sub>5</sub>Cl in toluene affords the corresponding tricarbonyl rhenium(I) complex, Re(L)(CO)<sub>3</sub>Cl (**4**) in high yield (83%) [21]. The metal complex is characterized by different methods such as IR, mass spectrometry, and <sup>1</sup>H NMR spectra. In IR spectra, three typical bands (around 2025, 1919 and 1882 cm<sup>-1</sup>)

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Scheme 1. Synthetic routes to **L** and **4**.

found in the CO stretching region for Re(I) complex **4** are in excellent agreement with the *facial* arrangement of the three coordinated C≡O groups [9a,17].

The structures of ligand **L** and complex **4** were determined at room temperature [22]. ORTEP drawings of **L** and **4** are shown in Fig. 1. In the solid state, the molecules of **L** are stacked in a head–tail fashion, leading to the formation of dimmers with shorter S⋯S contacts of 3.609 Å (Fig. 2). For the two crystals, the TTF units are not planar and adopt the obvious boat-like conformation [23]. Moreover, the central C=C bond length of the TTF core are 1.299(5) Å for **L** and 1.375(1) Å for **4**, which are within the range for a neutral TTF donor. Upon the coordination to rhenium(I) metal, the flexible ligand is totally distorted, with the dihedral angle of the two pyrazole rings [60.440(1)°] for **L** and [31.437(4)°] for **4**. In complex **4**, the ligand **L** coordinates with Re(I) by two nitrogen atoms forming a six-member metallacycle. The rhenium atom is also coordinated by three carbonyl ligands in a *fac* arrangement, as well as one chlorine atom. The average Re–C and Re–N

distances of 1.891 and 2.188 Å, respectively, are consistent with those found in similar rhenium tricarbonyl complexes [24].

The absorption spectra of the ligand **L** and complex **4** in dichloromethane at room temperature are measured (Fig. 3). For the ligand **L**, the absorption spectra show three absorption bands in 256–325 nm which are assigned to admixture of intraligand ( $\pi \rightarrow \pi^*$ ) transitions of the TTF moiety and the bispyrazole moiety. In addition, a weak broad absorption band at lower energy (360–540 nm) corresponds to the intramolecular charge-transfer from the HOMO in TTF to the LUMO in the pyrazole group [25]. Similarly, complex **4** displays absorption bands 2 around 285–325 nm in CH<sub>2</sub>Cl<sub>2</sub>, which could also be assigned to spin-allowed intraligand ( $\pi \rightarrow \pi^*$ ) transitions. Moreover, around 380–540 nm, the weak broad absorptions of complex **4** is attributed to a metal-to-ligand charge transfer (MLCT,  $d\pi(\text{Re}) \rightarrow \pi^*(\text{L})$ ) transition.

The UV–vis–NIR absorption spectra of ligand **L** is also measured in the presence of NOPF<sub>6</sub>. As shown in Fig. 4, it exhibits an absorption band of the TTF–bispyrazole ligand (**L**) at 420 nm. After oxidation

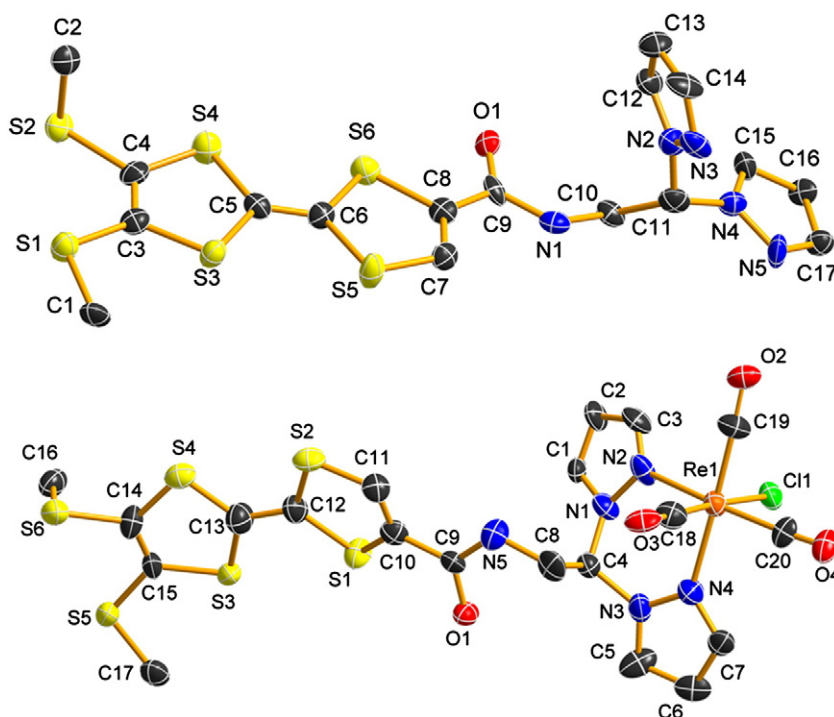


Fig. 1. ORTEP views of **L** (top) and **4** (bottom) with the atom-numbering scheme at 50% probability displacement ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

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