

TTF-Annulated Phenanthroline and Unexpected Oxidative Cleavage of the C=C Bond in Its Ruthenium(II) Complex

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Tetrathiafulvalene (TTF) and 1,10-phenanthroline have been fused together via a simple and efficient synthetic procedure that provides a new bidentate ligand, 4',5'-ethylenedithiotetrathiafulvenyl[4,5-*f*]-[1,10]phenanthroline (EDT-TTF-phen, **1**). Its ruthenium(II) complex exhibits a unique packing of TTF subunits in the solid state. In an acetonitrile solution, [Ru(bpy)₂](PF₆)₂ undergoes facile oxidative cleavage of the C=C double bond, which cannot be observed in the dark or under anaerobic conditions. This points to the photocatalytic role played by the ruthenium(II) chromophore in this conversion.

The field of multifunctional materials is expanding quickly, with molecule-based solids gaining great interest over the past decade. Among these, a lot of attention has been devoted to materials incorporating tetrathiafulvalene (TTF) and its derivatives. This interest is fueled by the large number of synthetic conductors and semiconductors that are based on these redox-active molecules. Attempts have been made to derivatize TTF with functional groups capable of binding to transition-metal ions. Such binding may enhance the synergy between the conducting properties of the organic substructure and optical or magnetic properties of the metal ions. In particular, thiolate,¹ phosphine,² carboxylate,³ acetylacetonate,⁴ and pyridyl⁵ derivatives have been used for this purpose.

1,10-Phenanthroline (phen) and 2,2'-bipyridine (bpy) are important chelating ligands in coordination chemistry because they exhibit high binding affinities toward transition-metal ions. Complexes such as [Ru(bpy)₃](PF₆)₂ and Fe(phen)₂(NCS)₂ have become “guinea pigs” for the fields of photochemistry and spin crossover, respectively. Until now, however, examples of TTF molecules derivatized with the phen or bpy functionality have been rare. Bpy was appended to the TTF unit through thiomethylene, ethynyl, and amido bridges.⁶ Decurtins and co-workers fused TTF with dipyrrophenazines.⁷ In a somewhat similar approach, a diazafluorene derivative of TTF also was reported.⁸

Herein, we report the syntheses and properties of TTF-annulated phen and its ruthenium(II) complex, as well as a facile, ruthenium-catalyzed photooxidative cleavage of the C=C double bond of the TTF unit accompanied by recrystallization of the reactant to the oxidized product under mother liquor.

4',5'-Ethylenedithiotetrathiafulvenyl[4,5-*f*]-[1,10]phenanthroline (EDT-TTF-phen, **1**) was prepared in good yield via a synthetic procedure that employs readily available and inexpensive reactants (Scheme 1). The synthesis starts with 5,6-dibromo-1,10-phenanthroline (**2**). While the Almeida group has reported recently that 5,6-bis(benzylthio)-1,10-phenanthroline (**3**) is obtained in 71% yield using a Pd₂(dba)₃-catalyzed reaction between **2** and benzylthiol in the presence of bis[2-(diphenylphosphino)phenyl] ether and *t*-BuOK (48 h at 120 °C),⁹ we discovered that a simple reaction between **2** and sodium benzylthiolate (generated *in situ* from benzylthiol and sodium hydride) provides a comparable yield of **3** but in just 12 h at room temperature and without a catalyst.

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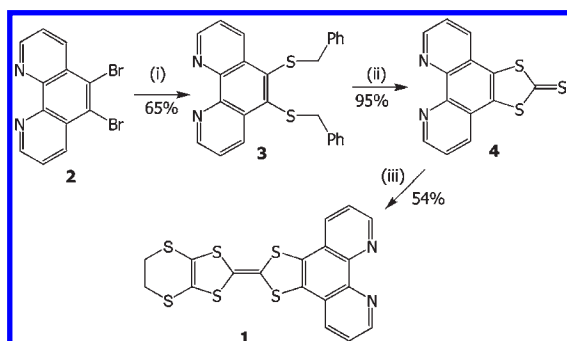
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Scheme 1. Synthesis of **1**^a

^a (i) NaH, C₆H₅CH₂SH, DMF, 12 h; (ii) AlCl₃, benzene, 24 h; NaOH, CS₂, reflux, 2 h; (iii) 4,5-ethylenedithio-1,3-dithiol-2-one, P(OEt)₃, reflux, 12 h.

We found the second step in the preparation of **1** to be the most challenging because attempts to isolate the intermediate 1,10-phenanthroline-5,6-dithiol led to untractable products. Thus, a one-pot approach was used in which the 1,3-dithiole-2-thione functionality was formed by reacting the in situ formed 1,10-phenanthroline-5,6-dithiolate dianion with CS₂ under basic conditions. Product **4** was obtained in 95% yield and recrystallized from acetonitrile.

It must be added that, very recently, an alternative route to **4** was reported in which 5,6-bis(2-cyanoethylsulfanyl)-1,10-phenanthroline is converted to **4** in a similar manner by cleaving the thioether groups with *t*-BuOK and converting the obtained dithiolate into 1,3-dithiole-2-thione using thiophosgene, with the resulting yield of 67%.¹⁰

The latter authors also reported that they were unsuccessful in preparing the corresponding symmetric TTF derivative by self-coupling of **4** in the presence of triethyl phosphite. Nevertheless, we successfully converted **4** to the asymmetric EDT-TTF-phen **1** by cross-coupling with 4,5-ethylenedithio-1,3-dithiol-2-one.

The crystal structure determination showed that the molecule of **1** is essentially planar (Figure 1a), with the exception of the ethylenedithio subunit, the C atoms of which are disordered over two positions at ~0.4 Å above and below the molecular plane. The molecules are stacked in columns along the *a* axis in a head-to-tail fashion (Figure S1 in the Supporting Information, SI) and exhibit π - π contacts with an interplanar separation of 3.56 Å. Large channels are present along the *a* axis, which are filled with disordered CHCl₃ molecules.

To show the suitability of **1** for the preparation of metal complexes, we reacted it with Ru(bpy)₂Cl₂ in refluxing ethanol. The subsequent addition of an ethanolic solution of NH₄PF₆ resulted in the precipitation of [Ru(bpy)₂(**1**)](PF₆)₂, which was recrystallized by the vapor diffusion of diethyl ether into an acetonitrile solution of the complex. A crystal structure analysis of this compound revealed that ligand **1** remains nearly planar (Figure 1b). Furthermore, the complex exhibits a unique packing of TTF moieties, in which an asymmetric unit includes three [Ru(bpy)₂(**1**)]²⁺ cations (Figure 2), with the plane-to-plane separation between TTF units being 3.44–3.78 Å. The identity of the complex was also confirmed by ¹H NMR spectroscopy (Figure S2 in the SI) and electrospray ionization mass spectrometry (Figure S3 in the SI).

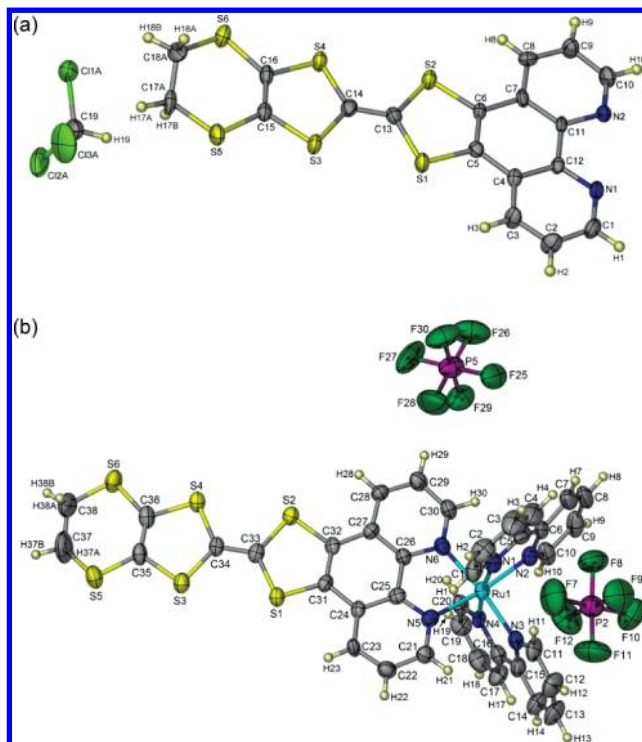


Figure 1. Crystal structures of **1**·CHCl₃ (a) and [Ru(bpy)₂(**1**)](PF₆)₂·3.5CH₃CN (b). In the latter, only one out of three crystallographically independent complexes is shown and the interstitial solvent molecules are omitted for clarity. (Thermal ellipsoids are at the 50% probability level.)

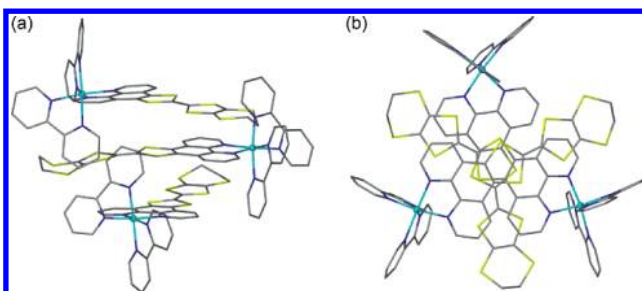


Figure 2. Side (a) and top (b) views of the packing of TTF-containing cations in the crystal structure of [Ru(bpy)₂(**1**)](PF₆)₂. The H atoms have been omitted for clarity. Color scheme: Ru, light blue; S, yellow; N, blue; C, gray.

A cyclic voltammogram of **1** (Figure 3) recorded in a 0.100 M acetonitrile/dichloromethane (3:2, v/v) solution¹¹ of (TBA)PF₆ (TBA = tetrabutylammonium) reveals two reversible oxidations at $E_{1/2}^{(1)} = 0.17$ and $E_{1/2}^{(2)} = 0.52$ V vs Fc/Fc⁺ (Fc = ferrocenium). Both oxidations are shifted to higher potentials as compared to unsubstituted TTF (−0.10 and 0.37 V),¹² as expected from the π -accepting nature of the phen moiety. [Ru(bpy)₂(**1**)](PF₆)₂ exhibits three reversible oxidations and two reversible reductions. A comparison of its redox behavior to that of **1** indicates that the first two oxidations at $E_{1/2}^{(1)} = 0.26$ and $E_{1/2}^{(2)} = 0.58$ V are TTF-based. They are shifted to slightly more positive potentials with respect to those observed for **1**. The third redox process

(11) The CH₃CN/CH₂Cl₂ solvent mixture was used to remove absorption effects manifested as a dramatic increase in the anodic current for the redox process observed at the most negative potential (Figure S7 in the SI).

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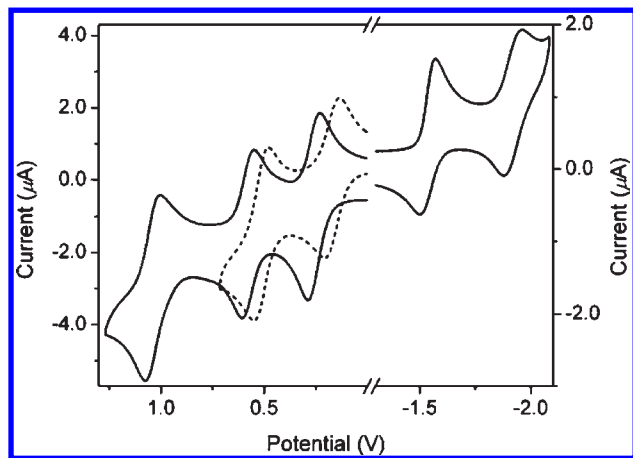


Figure 3. Cyclic voltammograms of **1** and $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ (dashed and solid lines, respectively) in a 0.100 M solution of $(\text{TBA})\text{PF}_6$ in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (3:2, v/v) at a sweep rate of 0.100 V/s (vs Fc/Fc^+).

at $E_{1/2}^{(3)} = 1.04$ V is due to oxidation of the Ru^{II} center. All three oxidations are similar to those reported earlier for $[\text{Ru}(\text{bpy})_2(\text{TTF-dppz})](\text{PF}_6)_2$ (0.29, 0.61, and 0.99 V).¹³ Reversible ligand-based reductions are also observed at $E_{1/2}^{(4)} = -1.54$ and $E_{1/2}^{(5)} = -1.92$ V.

Density functional theory calculations of the electronic structure of **1** reveal that the π -type highest occupied and lowest unoccupied molecular orbitals are centered on the EDT-TTF and phen fragments, respectively (Figure S4 in the SI), similarly to the nature of frontier orbitals in TTF-dppz.⁷ Therefore, the lowest-energy 402 nm band in the optical spectrum of **1** (Figure S5a in the SI) is assigned to the charge-transfer transition between the EDT-TTF and phen subunits.

$[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ exhibits a broad metal-to-ligand charge-transfer band with a maximum at 450 nm in an acetonitrile solution (Figure 4). The emission maximum is observed at 620 nm and red-shifted with respect to that of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (607 nm), while the quantum yield of 2.8% is somewhat lower than that reported for $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (6.2%),¹⁴ which is explained by luminescence quenching due to the presence of the TTF unit.¹³ A detailed investigation of other photophysical properties of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ is currently underway.

Both **1** and its ruthenium(II) complex are stable in the solid state and can be stored in air for prolonged periods of time. However, when $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ was crystallized from $\text{MeCN}/\text{Et}_2\text{O}$ and the crystals were allowed to remain under mother liquor for about 1 week, a complete transformation of this compound to a new crystalline solid was observed (Scheme 2). Crystal structure analysis revealed that the product contains 5,6-dithiocarbonato-1,10-phenanthroline (**5**) coordinated to the Ru^{II} center in place of **1** (Figure S6 in the SI). This facile oxidative cleavage of the C=C bond in the TTF unit does not occur when the $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ complex is kept under mother liquor in the dark or under an inert atmosphere. The role of the ruthenium(II) chromophore in this conversion is yet to be understood, and it might simply be to generate singlet oxygen that oxidizes the double bond. We currently are carrying out a detailed study of this unexpected conversion and will report our findings in due course.

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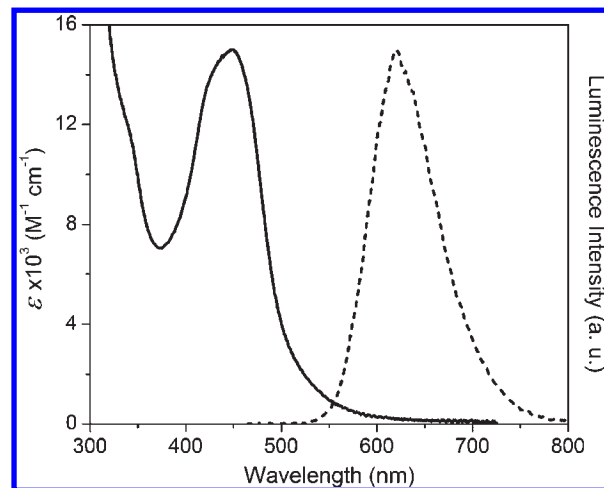
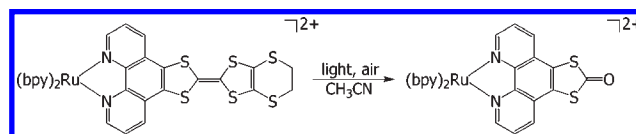


Figure 4. UV–visible absorption and emission spectra (solid and dashed lines, respectively) of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ in an acetonitrile solution. (For the full absorption spectrum, see Figure S5b in the SI.)

Scheme 2. Photoinduced Oxidation of $[\text{Ru}(\text{bpy})_2(\mathbf{1})](\text{PF}_6)_2$ to $[\text{Ru}(\text{bpy})_2(\mathbf{5})](\text{PF}_6)_2$ in an Acetonitrile Solution



It must be added that, while ruthenium(II) complexes have been used widely for such processes as photocatalytic water splitting and carbon dioxide to methane conversion,¹⁵ their applicability as photocatalysts for organic transformations is only beginning to receive attention,¹⁶ and one can anticipate that this research area will be rapidly expanding.

In summary, we successfully fused phen and TTF heterocycles using a convenient and inexpensive synthetic procedure. The obtained molecule **1** can serve as a promising ligand for the preparation of multifunctional metal complexes. We have shown that **1** forms a mononuclear ruthenium(II) complex with a unique arrangement of TTF moieties in the crystalline state. The ruthenium complex also shows unusual photoreactivity in solution that leads to facile oxidative cleavage of the C=C double bond in the TTF fragment. Currently, we are extending the use of ligand **1** to other transition-metal ions.

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Supporting Information Available: Complete experimental details, spectroscopic data, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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