

Syntheses, Characterization, and Properties of Ru(II) Complexes Based on π -conjugated Terpyridine Ligand with Tetrathiafulvalene Moiety

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Abstract

Two ruthenium(II) complexes [Ru(TTF-terpy)(terpy)][PF₆]₂ (terpy = 2,2':6',2''-terpyridine) (**1**) and [Ru(TTF-terpy)₂][PF₆]₂ (**2**) were synthesized by reactions of Ru(terpy)(dmsO)₂Cl₂ or *cis*-Ru(dmsO)₄Cl₂ with 4'-tetrathiafulvalene-2,2':6',2''-terpyridine (**TTF-terpy**), respectively. The crystal structure of **1** has been determined by X-ray crystallography. In the crystal of complex **1**, molecules are seized together into 1D chains *via* π – π stacking interactions. The electrochemical and spectroscopic properties of these compounds have been studied. The results show that these Ru(II) complexes show stepwise redox processes in solution, and are promising building blocks for the construction of multi-functional materials.

Keywords: Tetrathiafulvalene; Terpyridine ligand; Redox chemistry; Spectroscopic electrochemistry

1. Introduction

During the past decades, the field of multifunctional materials with molecule-based solids has gaining great interest. In particular, materials based on electrical conductivity and magnetic or optical interactions are currently the subject of intense investigation.¹ Recently, in order to obtain multi-functional molecular materials, much attention has been devoted to association of the electrochemically active tetrathiafulvalene (TTF) core with optical or magnetic properties of the metal ions bridged by various functional groups.^{2–5} To date, many TTF substituted derivatives have been reported, which might enable electron transfer and communication between the localized spins (d electrons) and the mobile π electrons.^{6–8} For further enhancing the interaction of this π -d system, it is important to shorten the distance between the metal ions and TTF units by designing new π -conjugated ligands.

2,2':6',2''-terpyridine (terpy) is a planar tridentate ligand with powerful binding abilities toward transition-metal ions, and it usually acts as an electronic acceptor.⁹ El-Ghayoury and Sallé et al. have successfully prepared

the TTF-based terpyridine ligand, 4'-tetrathiafulvalene-2,2':6',2''-terpyridine (**TTF-terpy**) for the first time in 2013.¹⁰ For **TTF-terpy**, the TTF unit is directly connected to the terpyridine which significantly decreases the distance between the metal ion and TTF units. Later, we have developed a more simple and efficient synthetic route for the incorporation of TTF into terpyridine, and firstly reported the series of their Fe(II) complexes.¹¹

Ru(II) complexes have been most intensely studied among the transition-metal complexes.¹² For example, the C₂-symmetric diphosphine/diamine based Ru(II) complexes can be used as excellent catalyst precursors in asymmetric transfer hydrogenation of acetophenone.¹³ Tris(2,2'-bipyridyl) Ru(II) complex show high photoluminescence and electroluminescence efficiency in light-emitting devices.¹⁴ Ru(II) polypyridyl complex with a terpyridine/phenylimidazo[4,5-f]-phenanthroline hybrid was investigated as an effective turn on luminescence sensor for H₂PO₄[–].¹⁵ Introduction of redox active ligands into Ru(II) complexes often generates unique photochemical and electrochemical properties of the complexes.^{8a,16,17} As an extension of our work, we investigated the reaction of

the ligand **TTF-terpy** with Ru(II) precursors. In this paper, two novel ruthenium(II) complexes [Ru(TTF-terpy)(terpy)][PF₆]₂ (**1**) and [Ru(TTF-terpy)₂][PF₆]₂ (**2**), were synthesized by coordination reactions of Ru(terpy)(dmsO)₂Cl₂ or *cis*-Ru(dmsO)₄Cl₂ with **TTF-terpy**, respectively (Scheme 1). Their spectroscopic and electrochemical properties were studied. The crystal structure of complex **1** is described.

2. Experimental

2.1. Materials and Physical Measurements

Formyltetrathiafulvalene, Ru(dmsO)₄Cl₂ and RuCl₂(terpy)dmsO were synthesized according to the literature procedure.¹⁸ All solvents were purified by standard techniques prior to use. Moisture or air sensitive reactions were carried under a nitrogen atmosphere.

Elemental analyses for C, H and N were determined using a Perkin-Elmer 240C analyzer. Infrared spectra were recorded in the 400–4000 cm⁻¹ region by Vector22 Bruker spectrophotometer with KBr pellets. Spectroelectrochemical measurements were performed in a thin-layer cell (optical length 0.2 cm) in which an ITO glass electrode was set in the indicated solvent containing the compound to be studied (the concentration is around 1 × 10⁻⁴ M) with 0.1 M Bu₄NClO₄ as the supporting electrolyte. A platinum wire and Ag/AgCl in a saturated aqueous KCl solution were used as counter and reference electrodes, respectively. The cell was put into the spectrophotometer to monitor spectral changes during electrolysis. UV-VIS spectra were obtained on a UV-3100 spectrophotometer. Mass spectra were determined with an Autoflex II TM instru-

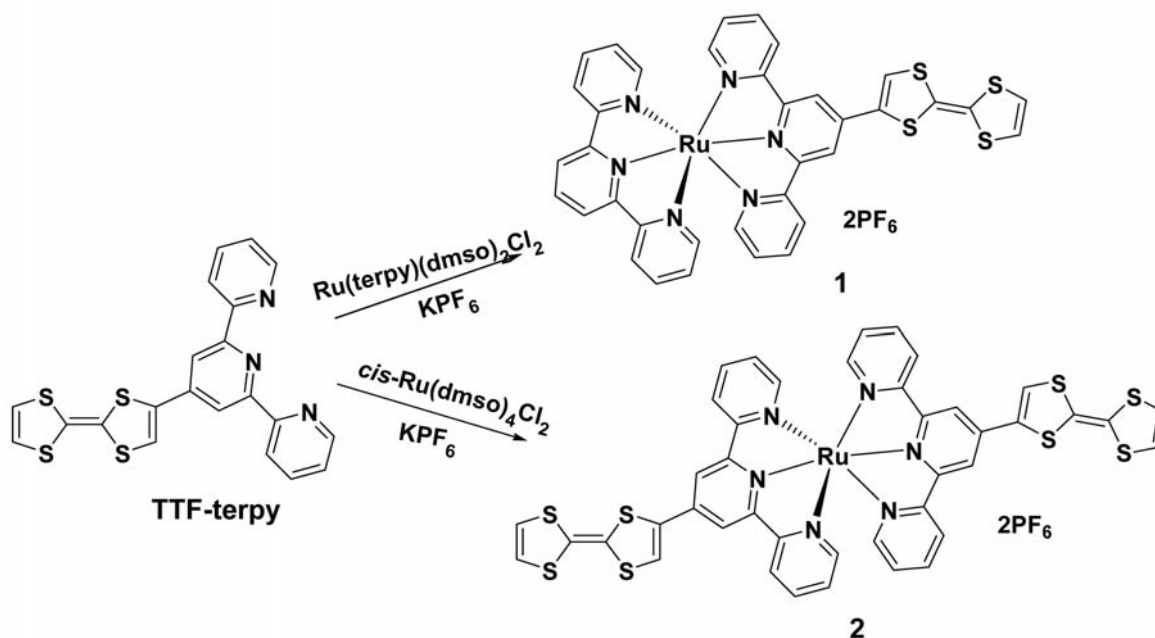
ment for ESI-MS. Cyclic voltammetry was performed on an Im6eX electrochemical analytical instrument, with a glassy carbon as the working electrode, platinum wire as the counter electrode, Ag/AgCl electrode containing sat. KCl served as the reference electrode, and 0.1 M *n* Bu₄NClO₄ as the supporting electrolyte.

2.2. Preparation of [Ru(TTF-terpy)(terpy)][PF₆]₂ (**1**).

A mixture of RuCl₂(terpy)dmsO (48.5 mg, 0.1 mmol) and TTF-terpy (43.5 mg, 0.1 mmol) in 6 mL ethanol was refluxed for 24 h. The solution was concentrated to about 2 mL, and then, KPF₆ (92 mg, 0.5 mmol) in methanol (1 mL) was added. The solution was stirred for 30 min, and the solvent evaporated. The crude product was purified by column chromatography on silica gel (acetone: H₂O: saturated aqueous KPF₆ (v/v) 100 : 4 : 0.4). Complex **1** was isolated in 67% yield (71 mg) as a reddish-brown solid. IR (KBr, cm⁻¹): 3061m, 2993w, 2909w, 1597m, 1583s, 1566s, 1535m, 1468m, 1449m, 1391s, 1083s, 1011m, 878m, 838s, 777s, 725m, 624m, 558s. ESI-MS, *m/z*: 385.3 [(M-2PF₆)²⁺]/2. Anal. Calcd for C₃₆H₂₄F₁₂N₆P₂RuS₄: C, 40.79; H, 2.28; N, 7.93. Found: C, 40.89; H, 2.32; N, 7.86%.

2.3. Preparation of [Ru(TTF-terpy)(terpy)]₂[PF₆]₂ (**2**).

A mixture of Ru(dmsO)₄Cl₂ (48.4 mg, 0.1 mmol) and TTF-terpy (95.7 mg, 0.22 mmol) in 6 mL ethanol was refluxed for 24 h. The solution was concentrated to about 2 mL, and then KPF₆ (92 mg, 0.5 mmol) in methanol (1 mL)



Scheme 1. Synthetic Routes to complexes **1** and **2**.

was added. The solution was stirred for 30 min, and the solvent evaporated. The crude product was purified by column chromatography on silica gel (acetone: H₂O: saturated aqueous KPF₆ (v/v) 100 : 4 : 0.4). Complex **2** was isolated in 58% yield (73 mg) as a brown solid. IR (KBr, cm⁻¹): 3058m, 3009w, 2920w, 2850w, 1598m, 1583s, 1566s, 1535s, 1467s, 1421m, 1394s, 1088m, 1013m, 877m, 842s, 787s, 726m, 658m, 633m, 558m. ESI-MS, m/z: 486.3 [(M-2PF₆)²⁺]/2. Anal. Calcd for C₄₂H₂₆F₁₂N₆P₂RuS₄: C, 39.97; H, 2.08; N, 6.66. Found: C, 39.89; H, 2.14; N, 6.58%.

2. 4. X-ray Crystallography

The data were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation using a ω -2 θ scan

mode at 293 K. The collected data were reduced using the SAINT program,¹⁹ and multi-scan absorption corrections were performed using the SADABS program.²⁰ The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL.²¹ All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model.

The solid structures of complex **1** were determined by single-crystal X-ray diffraction. The crystallographic and data collection parameters are given in Table 1; selected bond lengths and angles are listed in Table 2.

3. Results and Discussion

3. 1. Synthesis and Characterization

The ligand **TTF-terpy** was prepared in one pot synthesis from formyltetrathiafulvalene, 2-acetylpyridine and ammonia in the presence of *t*-BuONa.¹¹ Complexes **1** and **2** were obtained by reactions of **TTF-terpy** with Ru(terpy)(dmso)₂Cl₂ or Ru(dmso)₄Cl₂ in reflux ethanol solution, respectively. In the infrared spectra of **1** and **2**, the sharp absorption bands of the counter anion (PF₆⁻) are located at 838 cm⁻¹ and 842 cm⁻¹, respectively. The positive ion electrospray mass spectra of these complexes are presented in Figures S1 and S2, they show full abundance of the parent peak which corresponds to {[M-2PF₆]/2}⁺. Red crystals of complex **1** suitable for structure determination were obtained by diffusion of ether into an acetonitrile solution of **1**.

3. 2. Crystal Structure Description of 1

Complex **1** crystallized in monoclinic system (space group $P 2_1/c$) and the asymmetric unit contains a complex cation, two PF₆⁻ anions and one CH₃CN molecule. As shown in Figure 1, the Ru(II) adopts a distorted octahedral

Table 1. Crystallographic data for **1**.

	1
empirical formula	C ₃₈ H ₂₇ F ₁₂ N ₇ P ₂ RuS ₄
M_r	1100.92
Cryst system	monoclinic
Space group	$P 2_1/c$
a (Å)	8.802(2)
b (Å)	40.985(9)
c (Å)	12.128(3)
α (°)	90.00
β (°)	100.66(4)
γ (°)	90.00
V (Å ³)	4299.7(17)
Z	4
ρ_c (g cm ⁻³)	1.701
$F(000)$	2200
T / K	293(2)
μ (Mo- K_α) / mm ⁻¹	0.725
Data / param. / restr.	8321 / 578 / 0
GOF	1.063
R_1, wR_2 ($I > 2\sigma(I)$)	0.0539 / 0.1326
R_1, wR_2 (all data)	0.0751 / 0.1354
Large diff. peak / hole (e Å ⁻³)	0.447 / -0.386

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**.

Ru(1)–N(1)	2.063(4)	Ru(1)–N(2)	1.956(4)
Ru(1)–N(3)	2.071(4)	Ru(1)–N(4)	2.045(4)
Ru(1)–N(5)	1.984(4)	Ru(1)–N(6)	2.069(4)
C(31)–C(32)	1.294(7)	C(33)–C(34)	1.292(7)
C(35)–C(36)	1.379(7)	C(33)–S(3)	1.775(5)
C(33)–S(4)	1.764(6)	C(34)–S(2)	1.757(6)
C(34)–S(1)	1.744(5)	N(1)–Ru(1)–N(3)	157.58(17)
N(2)–Ru(1)–N(4)	100.09(16)	N(2)–Ru(1)–N(6)	103.36(16)
N(4)–Ru(1)–N(5)	78.62(16)	N(5)–Ru(1)–N(6)	77.91(16)
N(1)–Ru(1)–N(2)	78.75(17)	N(1)–Ru(1)–N(4)	91.67(17)
N(1)–Ru(1)–N(5)	100.29(18)	N(1)–Ru(1)–N(6)	91.57(17)
N(3)–Ru(1)–N(2)	78.83(17)	N(3)–Ru(1)–N(4)	91.94(16)
N(3)–Ru(1)–N(5)	102.12(18)	N(3)–Ru(1)–N(6)	93.86(16)

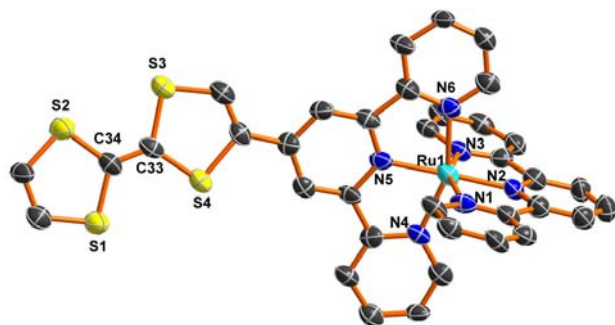


Figure 1. Thermal ellipsoid drawing with 50% probability of **1**. Counter anions, H atoms and solvent are omitted for clarity.

geometry, with the equatorial plane defined by N1, N2, N3 and N5. The axial N6–Ru1–N4 angle of $156.51(17)^\circ$ is significantly smaller than the ideal value of 180° caused by the shape of terpy units. While the sum of the equatorial angles N5–Ru1–N3, N3–Ru1–N2, N2–Ru1–N1, and N1–Ru1–N5 for complex **1** ($\approx 354.99^\circ$) is very close to the ideal value (360.00°), which ensures the planarity of equatorial plane. Among the Ru–N bond lengths, the bond distance of Ru(II) to the central terpy nitrogen (Ru1–N2, being $1.956(4)$ Å, and Ru1–N5, being $1.984(4)$ Å] is ca. 0.1 Å shorter than the other Ru–N distances ($2.045(4)$ – $2.071(4)$ Å), which is typical feature in the structure of other terpy–Ru(II) complexes.^{17a} The corresponding Ru–N bond lengths and angles in complex **1** are comparable to those found in similar Ru(terpy)₂²⁺ complexes, such as [Ru(terpy)(bpy')Cl]PF₆ (bpy' = 4-carboxy-4'-methyl-2,2'-bipyridine derivatives)^{22a}, [Ru(terpy)(PDA–N,N')-(OH₂)](ClO₄)₂ (PDA = 6-acetyl-6-hydroxy-1,10-phenanthroline-5-one).^{22b}

Complex **1** contains mutually orthogonal ligands, the **TTF-terpy** coordination plane (N4, N5, N6 and Ru1) forms a dihedral angle of $89.34(1)^\circ$ with the terpy coordination plane (N1, N2, N3 and Ru1). The five-membered ring (C31, S4, C33, S3, C32) is twisted out of the **TTF-terpy** coordination plane by $15.59(6)^\circ$. The TTF skeleton itself is almost planar, and the average deviation from a least-squares plane is 0.0300 Å. In addition, the dihedral angle between the two five-membered rings is only

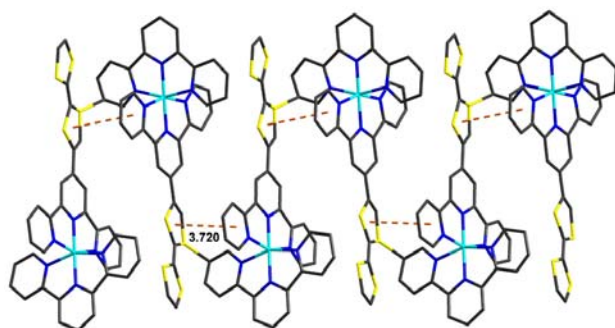


Figure 2. π – π stacking interactions found in **1** (H atoms are omitted for clarity).

$2.84(1)^\circ$. The central C=C bond length of the TTF core is $1.292(7)$ Å, which is within the normal range for a neutral molecule.^{23,24}

In the solid state, the molecules of **1** are stacked in a head-tail fashion. The adjacent five-membered ring (containing S4, S3) and pyridine ring (containing N4) are approximately parallel to each other (the dihedral angle is $1.21(5)^\circ$), with a center-center distance of $3.720(6)$ Å, indicating the presence of face-to-face π – π stacking interactions, which further connect the molecules into one-dimensional chainlike structure along the *c* axis (Figure 2).

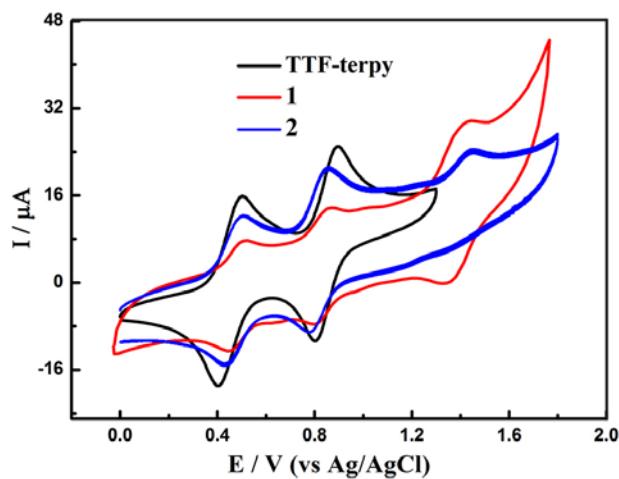


Figure 3. Cyclic voltammograms for **TTF-terpy**, complexes **1** and **2**.

3. 3. Electrochemical Properties

The redox properties of **1** and **2** were investigated using cyclic voltammetry in CH₂Cl₂/CH₃CN (1:1 ratio, $0.1 \text{ mol} \cdot \text{L}^{-1} n\text{-Bu}_4\text{NClO}_4$). As shown in Figure 3, three one-electron oxidation waves were observed in the potential region 0.0 to +1.8 V (vs Ag/AgCl). A comparison of their redox behaviors to that of **TTF-terpy** indicates that the first two oxidations around 0.48 V ($E_{1/2}^1$) and 0.83 V ($E_{1/2}^2$) are TTF based, which are derived from the successive oxidation of neutral TTF (TTF⁰) to the radical cation (TTF⁺) and then to the dication (TTF²⁺). Compared with the ligand **TTF-terpy**, upon complexation, the first oxidation potential is shifted to slightly more positive potential, which is the same as {TTF–Re(I)},^{4b, 4c} {TTF–[Ru₃(μ₃-O)]} complexes,²⁵ caused by the electron-withdrawing inductive effect of the metal core. However, the second oxidation potential is negatively shifted by 20 mV. This shift can be explained by the electronic interactions between the TTF unit and the Ru(terpy) unit caused by the shorter distance between them.¹¹ The third redox process at about $E_{1/2}^3 = 1.37 \text{ V}$ can be assigned to the Ru(II)-centered one-electron oxidation process.^{16a}

3. 4. Spectroscopic Properties

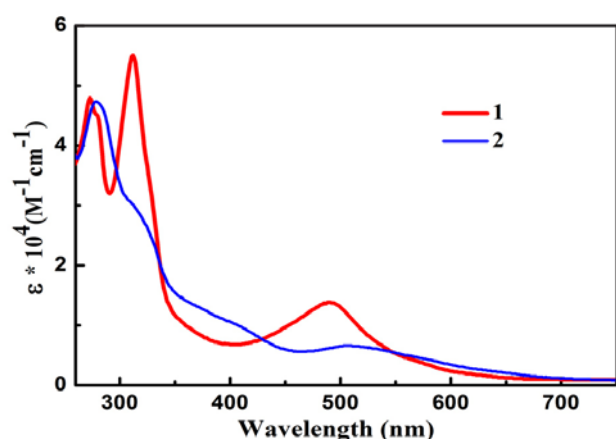


Figure 4. Absorption spectra of **1** and **2** (1×10^{-5} M) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1 ratio).

The absorption spectra of complexes **1** and **2** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1 ratio) at room temperature were measured. As depicted in Figure 4, intense absorptions relating to the admixture of intraligand ($\pi \rightarrow \pi^*$) transitions of the TTF moiety and the terpy moiety are observed in the range of 255–350 nm, which are red-shifted (about 35–41 nm) and more intense compared with the free ligand **TTF-terpy**. The red shift is reasonable since the energy of the LUMO localized on the terpy unit is lowered upon coordination to Ru(II).^{4c} In addition, complexes **1** and **2** also display broad bands at lower energy (350–650 nm), which could be assigned to the admixture of metal-to-ligand charge-transfer (MLCT, $d\pi(\text{Ru}) \rightarrow \pi^*(\text{TTF-terpy})$) and ligand-to-ligand charge-transfer (LLCT) transitions.^{11,26}

Spectroelectrochemical measurements were also carried out during the electrolysis of the solution of complexes **1** and **2** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1 ratio) at suitable

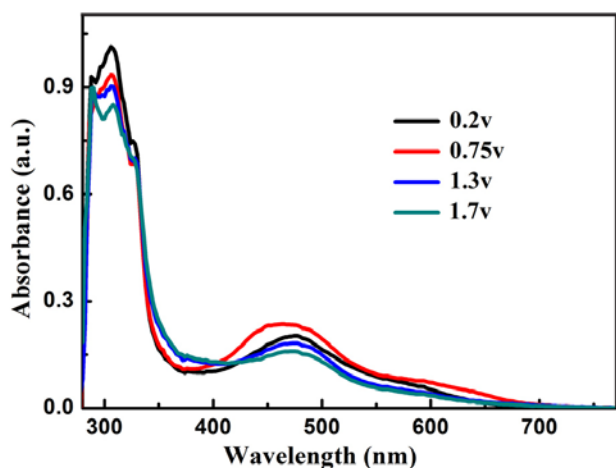


Figure 5. Spectroelectrochemistry of **1** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (0.1M Bu_4NClO_4).

constant potentials corresponding to its redox processes (Figures 5 and S3). The first stage of the electrochemical oxidation leads to the appearance of TTF radical cation bands around 448 nm. Upon the application the potential of 1.3 V, the electronic spectra show a decrease in the characteristic absorption of the radical cation bands ($\text{TTF}^{\cdot+}\text{-terpy}$) and the appearance of dication bands ($\text{TTF}^{2+}\text{-terpy}$) around 330–410 nm.

4. Conclusion

In summary, with the versatile ligand **TTF-terpy**, two novel ruthenium(II) complexes **1** and **2** were synthesized. The electrochemistry measurements suggested that these compounds display rich redox processes. On complexation, the two oxidation peaks of TTF backbone in **1** and **2** exhibit different shifts caused by electronic interactions between the TTF unit and the Ru(II) core. The electronic properties in the neutral TTF-terpy based compounds as well as in the radical cation $\text{TTF}^{\cdot+}\text{-terpy}$ and dication species $\text{TTF}^{2+}\text{-terpy}$ based compounds have been studied by spectroelectrochemical and absorption spectra. The results show that the versatile π -conjugated terpyridine ligand is useful for the preparation of multifunctional materials, and further work for exploring interesting conducting and magnetic materials is going on in our laboratory.

5. Supplementary Information

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 977059 (**1**). Copies of the data can be obtained free of charge via www.ccdc.ac.uk/contents/retrieving.html (or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

6. Acknowledgments

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Povzetek

Dva nova rutenijeva(II) kompleksa $[\text{Ru}(\text{TTF-terpy})(\text{terpy})][\text{PF}_6]_2$ (terpy = 2,2':6',2''-terpyridine) (**1**) in $[\text{Ru}(\text{TTF-terpy})_2][\text{PF}_6]_2$ (**2**) sta bila sintetizirana z reakcijo $\text{Ru}(\text{terpy})(\text{dmsO})_2\text{Cl}_2$ oziroma $\text{cis-Ru}(\text{dmsO})_4\text{Cl}_2$ s 4'-tetrathiafulvalen-2,2':6',2''-terpiridinom (**TTF-terpy**). S pomočjo rentgenske difrakcije je bila določena kristalna struktura **1**. V kristalu spojine **1** so molekule povezane v 1D verigo preko $\pi\cdots\pi$ interakcij. Elektrokemijske in spektroskopske lastnosti spojin so bile proučene. Rezultati kažejo postopen redoks proces Ru(II) kompleksov v raztopini in so obetavni gradniki večfunkcionalnih materialov.

Syntheses, Characterization, and Properties of Ru(II) Complexes Based on π -conjugated Terpyridine Ligand with Tetrathiafulvalene Moiety

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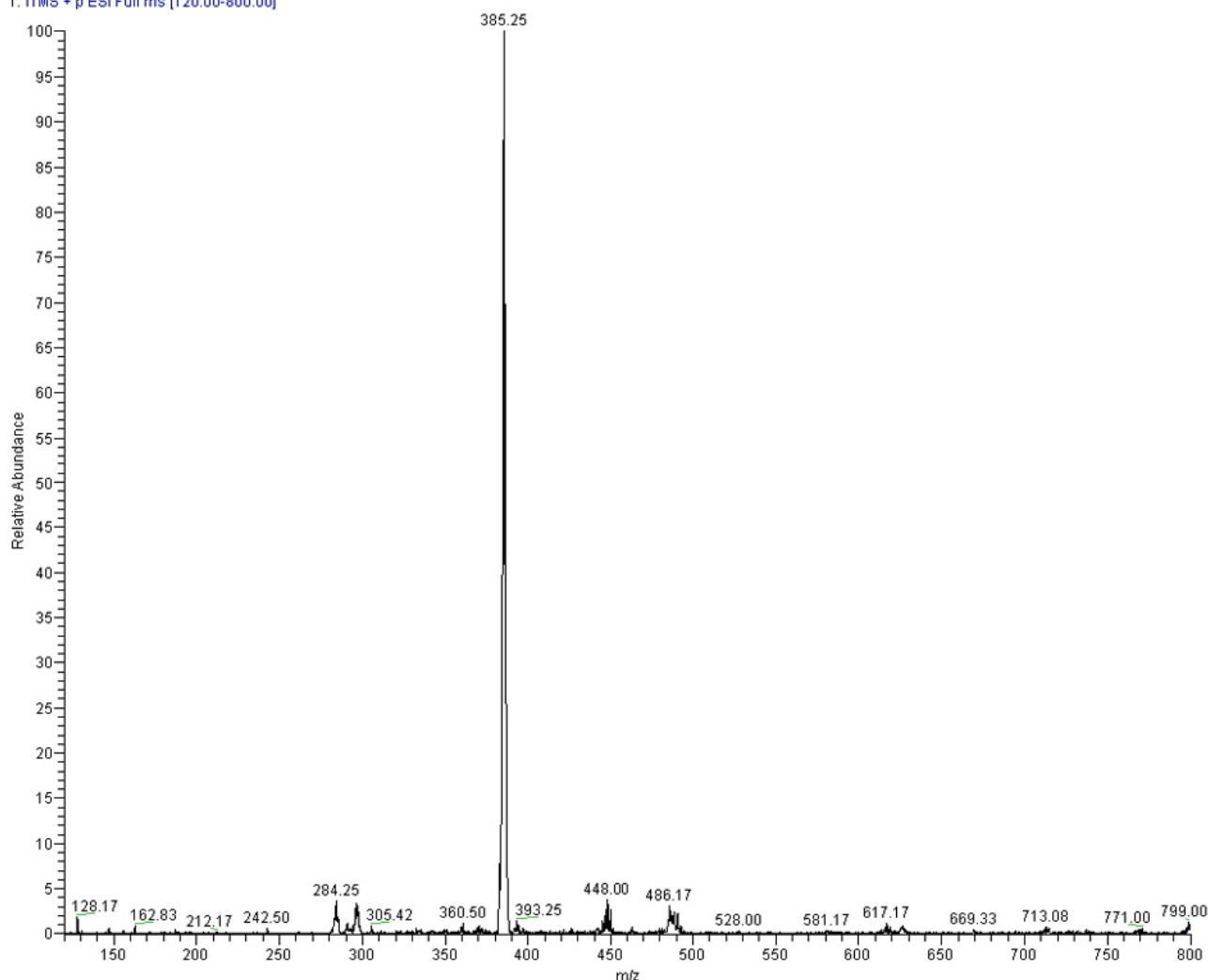


Fig. S1. ESI-MS of complex 1.

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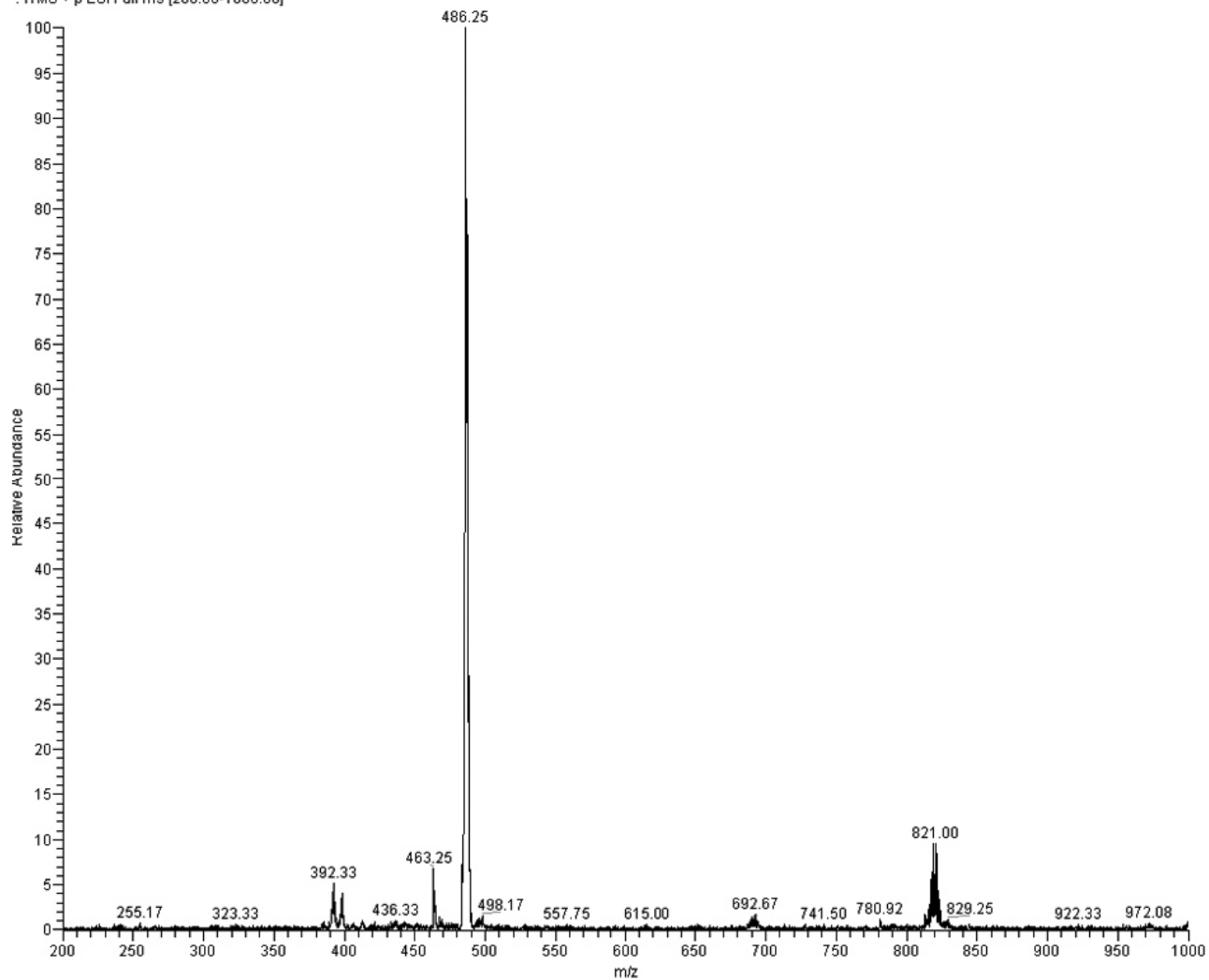


Fig. S2. ESI-MS of complex 2.

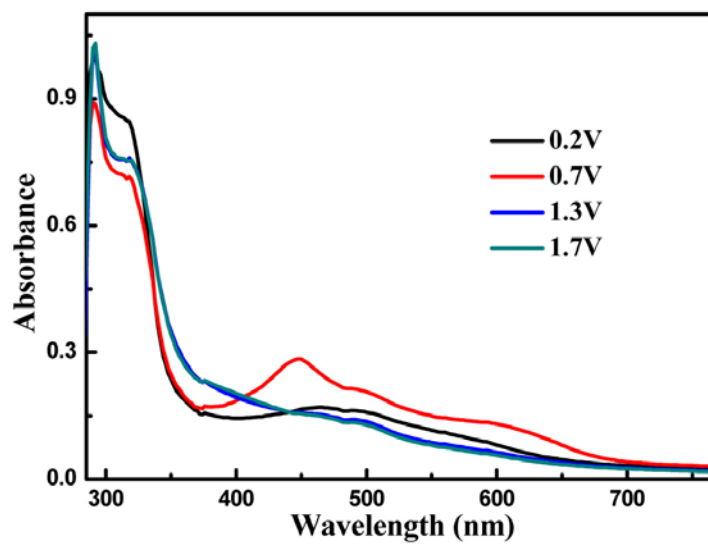


Fig. S3. Spectroelectrochemistry of 2 in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (0.1M Bu_4NClO_4).