Scientific paper

# New Iridium Complex Coordinated with Tetrathiafulvalene Substituted Triazole-pyridine Ligand: Synthesis, Photophysical and Electrochemical Properties

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#### **Abstract**

A new iridium(III) complex based on the triazole-pyridine ligand with tetrathiafulvalene unit,  $[Ir(ppy)_2(\mathbf{L})]PF_6$  (1), has been synthesized and structurally characterized. The absorption spectra, luminescent spectra and electrochemical behaviors of  $\mathbf{L}$  and  $\mathbf{1}$  have been investigated. Complex  $\mathbf{1}$  is found to be emissive at room temperature with maxima at 481 and 510 nm. The broad and structured emission bands are suggested a mixing of  ${}^3LC$  ( ${}^3\pi$ - $\pi^*$ ) and  ${}^3CT$  ( ${}^3MLCT$ ) excited states. The influence of iridium ion coordination on the redox properties of the TTF has also been investigated by cyclic voltammetry.

**Keywords:** Iridium(III) complexes; Tetrathiafulvalene; Triazole-pyridine ligands; Photoluminescence; Cyclic voltammetry

#### 1. Introduction

For several decades, tetrathiafulvalene (TTF) and its derivatives were extensively developed by scientists in photofunctional materials<sup>1-8</sup> because of their strongly electron-donating and attractive reversible redox properties. As a consequence, a large synthetic effort has also been devoted to the preparation of materials that exhibit

synergy or coexistence between conductivity and luminescence. Coordination of TTF-containing ligands to transition metal centers is typically achieved by functionalizing TTF with nitrogen atom.<sup>9</sup>

Very recently, we have reported a new nitrogen-containing TTF-based ligand, 2-(1-(2-((4',5'-bis(methylthio)-[2,2'-bi(1,3-dithiolylidene)]-4-yl)thio)ethyl)-1<math>H-1,2,3-triazol-4-yl)pyridine (**L**). Ligand **L** was used as the polyp-

**Scheme 1.** Synthetic routes of Ir(III) complex 1.

yridine N<sup>N</sup> ligand and binap/xantphos as diphosphines P<sup>P</sup> ligand to form two Cu(I) complexes, [Cu(I)(Binap) (L)]BF<sub>4</sub> and [Cu(I)(Xantphos)(L)]BF<sub>4</sub>, which exhibited advantageous electrochemical and photophysical properties. <sup>10</sup> The results hence led us to further design other metal complexes based on the TTF-containing thioethylbridged triazole-pyridine ligand.

Iridium(III) complexes have widely been employed in organic light-emitting devices (OLEDs), as they have high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tenability. 11-14 Therefore, the association of the redox-active TTF unit with cyclometalated iridium(III) complex is intriguing in coordination chemistry and material chemistry. In this work, we report the synthesis of a new bis-cyclometallated TTF-based iridium(III) complex with ppy as C^N ligand, [Ir(ppy)<sub>2</sub>(L)]PF<sub>6</sub> (1) (Scheme 1). Their electrochemical and photophysical properties are also investigated.

# 2. Experimental

#### 2. 1. Materials and Measurements

2-(1-(2-((4',5'-bis(methylthio)-[2,2'-bi(1,3-dithioly-lidene)]-4-yl)thio)ethyl)-1*H*-1,2,3-triazol-4-yl)pyridine (**L**) was synthesized in our previous work,<sup>8</sup> and an improved preparation method was used to synthesize the cyclometalated iridium chlorobridged dimer [Ir(ppy)<sub>2</sub>Cl]<sub>2</sub> in good yield.<sup>15</sup> All solvents were dried using standard procedures. Solvents used for electrochemistry and spectroscopy were spectroscopic grade.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AM 400 MHz instrument. Chemical shifts were reported in ppm relative to Me<sub>4</sub>Si as internal standard. FT–IR spectra were taken on a Nicolet 6700 FTIR spectrometer (400–4000 cm<sup>-1</sup>) with KBr pellets. ESI-MS spectra were recorded on an Esquire HCT–Agilent 1200 LC/MS spectrometer. The elemental analyses were performed on a Vario EL Cube Analyzer system. UV-vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F–7000 spectrophotometer.

# 2. 2. Synthesis of $[Ir(ppy)_2(L)]PF_6(1)$

A mixture of a dimer [Ir(ppy) $_2$ Cl] $_2$  (50 mg, 46.5 µmol) and **L** (58 mg, 93.0 µmol) was dissolved in 6 mL of DCM and MeOH (v/v = 1 : 1) and refluxed for 6 h under nitrogen. The orange-red solution was then cooled to room temperature and NH $_4$ PF $_6$  (38 mg, 0.23 mmol) was added to the solution. The mixture was stirred at room temperature for 4 h, and then evaporated to dryness. The solid was purified by column chromatography with DCM/MeOH (100 : 1) eluent to afford pure product **1** (54 mg, Yield: 50.5 %) as a yellow solid.  $^1$ H NMR (400 MHz, CDCl $_3$ ):  $\delta$  9.04 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.99 (t, J = 7.6 Hz, 1H),

7.90~7.92 (m, 2H), 7.82 (d, J = 4.2 Hz, 1H), 7.65~7.79 (m, 6H), 7.53 (d, J = 5.6 Hz, 1H), 6.88~7.08 (m, 6H), 6.40 (d, J = 7.2 Hz, 1H), 6.31 (d, J = 6.8 Hz, 1H), 5.97 (s, 1H), 4.63 (t, J = 6.0 Hz, 2H), 3.12~3.15 (m, 2H), 2.42 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.2, 167.6, 150.0, 149.9, 149.7, 149.5, 148.7, 148.5, 146.2, 143.8, 143.7, 139.7, 138.1, 138.0, 132.0, 131.9, 130.7, 130.2, 129.1, 127.9, 127.1, 126.6, 126.3, 124.8, 124.5, 123.5, 123.1, 122.8, 122.6, 121.6, 119.5, 119.4, 114.5, 108.9, 49.6, 34.8, 29.7; ESI-MS (m/z): 1001.0 [M-PF<sub>6</sub>]+. IR (cm<sup>-1</sup>): v = 3442 (m), 2922 (w), 2853 (w), 1608 (m), 1475 (m), 1422 (m), 1265 (w), 1100 (w), 842 (s), 756 (m), 556 (w). Anal. calcd. For C<sub>39</sub>H<sub>32</sub>F<sub>6</sub>IrN<sub>6</sub>PS<sub>7</sub>: C 40.86, H 2.81, N 7.33; found: C 40.95, H 2.96, N 7.45.

#### 2. 3. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed on a CHI 1210B electrochemical workstation, with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an aqueous saturated calomel electrode (SCE) as the reference electrode, and 0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte.

#### 3. Results and Discussion

#### 3. 1. Photophysical Properties

#### 3. 1. 1. Absorption Properties

The absorption spectra of **L** and **1** in dichloromethane solution at room temperature are depicted in Fig. 1. For ligand **L** and complex **1**, these strong absorption bands at a high energy ( $\lambda < 350$  nm) are assigned to spin-allowed intraligand ( $\pi \rightarrow \pi^*$ ) transitions of TTF-TzPy ligand (**L**) or ancillary ligand (ppy). The moderate absorption bands at lower energy (350–450 nm) correspond to intramolecular charge-transfer transition (ICT) for **L**<sup>16</sup> and metal-to-ligand charge-transfer (MLCT,  $d\pi(Ir) \rightarrow \pi^*(L)$ ) transition for **1**, respectively. 17,18

#### 3. 1. 2. Emission Properties

The relative emission spectra of ligand **L** and complex **1** in degassed CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature are also given in Fig. 1. Upon excitation at 438 nm, complex **1** displays two intense emission maxima at ca. 481 and 510 nm. As for **L**, the emission band occurs at about 462 nm ( $\lambda_{ex} = 363$  nm). Therefore the vibronically structured emission of **1** is probably derived from a mixing of  ${}^3LC$  ( ${}^3\pi$ - $\pi^*$ ) and  ${}^3CT$  ( ${}^3MLCT$ ) excited states. <sup>19,20</sup>

#### 3. 2. Electrochemical Properties

The electrochemical behaviors of the ligand L and iridium complex 1 were investigated by cyclic voltamme-

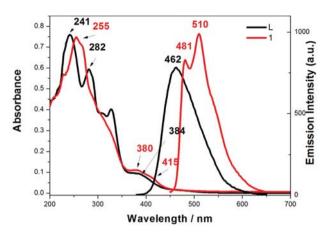


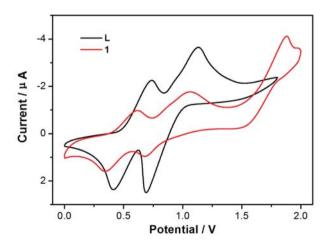
Fig. 1: UV and FL spectra of ligand L and complex 1 in CH<sub>2</sub>Cl<sub>2</sub>

try in  $\mathrm{CH_2Cl_2}$  solution (Fig. 2 and Table 1). Both compounds (**L** and **1**) exhibit two reversible one-electron oxidation processes, which are associated with the successive oxidation of the TTF unit to TTF<sup>+</sup> and TTF<sup>2+</sup>. Additionally, complex **1** show a irreversible oxidation peak ( $E_p^{\text{ox}}$ ) at 1.88 V, which is attributed to the metal-centered  $\mathrm{Ir}^{3+}/\mathrm{Ir}^{4+}$  oxidation couple. 21,22 In comparison with the ligand **L**, the two oxidation waves for complex **1** are shifted to more negative potentials. The observed results are different from the previous reported work, 23 it is possible that the triazole-pyridine unit is grafted on the TTF core through a non-conjugated spacer group, which is disadvantageous to intramolecular electron transfer and communications. 10

Table 1: Redox potentials of ligand  $\boldsymbol{L}$  and complex  $\boldsymbol{1}$ 

Compounds	$E_{1/2}^{-1}(V)^a$	$E_{1/2}^{2}(\mathbf{V})^{a}$	$E_p^{\text{ ox }} (\text{Ir}^{3+/4+}) (\text{V})$
L	0.57	0.91	_
1	0.48	0.87	1.88

 $^aE_{\rm 1/2}=1/2(E_{\rm pa}+E_{\rm pc}),$  where  $E_{\rm pa}$  and  $E_{\rm pc}$  are the anodic and cathodic peak potentials, respectively.



**Fig. 2:** Cyclic voltammograms for ligand L and complex 1 in  $CH_2Cl_2$  solution containing n-Bu<sub>4</sub> $NClO_4$  (0.1 M) at a sweep rate of 100 mV/s

#### 4. Conclusions

In conclusion, a new iridium(III) complex 1 based on tetrathiafulvalene-substituted triazole-pyridine ligand, has been synthesized and fully characterized by  $^1H$  NMR, has spectrometry, FTIR and elemental analyses. The photophysical and electrochemical properties have been measured and analyzed. The luminescent spectra show that the emissive state originates from mixed intraligand and metal-to-ligand charge transfer  $^3(\pi \rightarrow \pi^* + MLCT)$  transitions. The electrochemical studies reveal that 1 undergo reversible  $TTF/TTF^+/TTF^{2+}$  redox processes and one irreversible  $TTF/TTF^+/TTF^{2+}$  redox processes and one irreversible  $TTF/TTF^+/TTF^{2+}$  redox processes and one irreversible  $TTF/TTF^+/TTF^{2-}$  redox processes and  $TTF/TTF^+/T$ 

## 5. Acknowledgements

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### 6. Supplementary Material

<sup>1</sup>H NMR, <sup>13</sup>C NMR and ESI-MS spectra for iridium complex **1**.

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#### Povzetek

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Sintetiziran in strukturno okarakteriziran je nov iridijev(III) kompleks  $[Ir(ppy)_2(\mathbf{L})]PF_6$  (1) z vezanim triazol-piridinskim ligandom modificiranim s tetratiafulvensko skupino. Absorpcijski in luminiscenčni spekter ter elektrokemijske lastnosti  $\mathbf{L}$  in 1 so bili raziskani. Kompleks 1 emitira pri sobni temperature pri 481 in 510 nm. Široki in strukturirani emisijski trakovi so pripisani mešanju  $^3LC$  ( $^3\pi$ – $\pi$ \*) in  $^3CT$  ( $^3MLCT$ ) vzbujenih stanj. Vpliv koordinacije iridijevega iona na redoks lastnosti TTF skupine je bil raziskan s pomočjo ciklične voltametrije.