Ionic iridium complex coordinated with tetrathiafulvalene-fused phenanthroline ligand: Synthesis, photophysical, electrochemical and electrochemiluminescence properties

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1. Introduction

During the past decades, a lot of attention has been devoted to the design and synthesis of tetrathiafulvalene (TTF) derivatives since their excellent potential application in molecule-scale electronics and devices [1–5]. Among them, one of growing research interest is the combination of the electrochemically active properties of organic TTF units with magnetic or optical properties of inorganic metal ions to obtain new multifunctional molecular materials. Under this strategy, a variety of functional groups which are tailored for coordination toward diverse transition metal ions have been grafted to the TTF core [6–9]. Recently, we have reported the facile synthesis and properties of the chelating ligand, 4’5’-dimethylidithiotrifatulfalene(4,5-f][1,10]phenanthroline (L) [10], which is first described by Shatruk’s group [7b].

Due to their relatively short lifetime, significant Stokes shifts, and remarkable structure–function relationships, phosphorescent iridium(III) complexes have widely been employed in organic light-emitting diodes (OLEDs) devices [11], chemical sensors [12], fluorescent imaging [13], etc. Meanwhile as an important class of inorganic luminescent systems, iridium(III) complexes have also attracted wide interest in electrochemiluminescence (ECL) that the luminescence is generated by an electrochemical reaction without additional excitation source [14,15].

As an extension of our work, we investigated the reaction of the versatile TTF ligand L with cyclometalated iridium(III) complex. The unique π electron delocalized nature of TTF unit undergoing mixing valence state would allow the efficient incorporation of iridium luminophore into functional organic semiconductor. To date, only one paper on iridium(III) complex with tetrathiafulvalene fused ligand is reported [16]. Herein, we report the synthesis, characterization, electrochemical, photophysical and ECL behaviors of cationic iridium(III) complex, [Ir(ppy)2(L)]PF6 (1), which is based on tetrathiafulvalene fused phenanthroline (L) as NN ancillary ligand.

2. Results and discussion

Cationic iridium(III) complex 1 was prepared in good yield via a two-step procedure (Scheme 1) similar to the synthesis of [Ir(p-ppy)2(phen)]PF6 (phen = phenanthroline) [2] [11b,17]. It was characterized by elemental analysis, IR, 1H NMR and electrospray
solution (1:1, v/v) of electron-withdrawing inductive effect of the IrIII core, these two radical cation and then to the dication form. As a result of the oxidation potentials are positively shifted compared with the trostatic interactions between the TTF moieties and the IrIII core is not observed which is probably attributed to the electronic transitions have Metal–Ligand Charge Transfer (MLCT, $\pi^*_{\text{TTF}} \rightarrow \pi^*_{\text{phen}}$) and Ligand–Ligand Charge Transfer (LLCT, $\pi^*_{\text{phen}} \rightarrow \pi^*_{\text{phen}}$) character. The strong absorption peak in the ultraviolet region is mainly correlated to the electronic transitions from HOMO $-10$ to LUMO $+1$ and HOMO $-2$ to LUMO $+5$ and characteristic of $\pi^*_{\text{phen}}/\pi^*_{\text{TTF}} \rightarrow \pi^*_{\text{phen}}/\pi^*_{\text{TTF}}$ ILCT and $\pi^*_{\text{ppy}} \rightarrow \pi^*_{\text{ppy}}/\pi^*_{\text{TTF}}$ ILCT.

As depicted in Fig. 2, the absorption spectrum of complex 1 shows the following features: intense absorption bands below 350 nm, which are characteristic of the spin-allowed intraligand electron transfer (ILCT) from the electron-donor TTF core to the electron-acceptor phen unit, whereas the moderate absorption bands centered at 370 nm are found as the electronic transitions from orbitals (HOMO $-2$ and HOMO $-4$) to phen-localized LUMO. These electronic transitions have Metal–Ligand Charge Transfer (MLCT, $\pi^*_{\text{Ir}} \rightarrow \pi^*_{\text{phen}}$) and Ligand–Ligand Charge Transfer (LLCT, $\pi^*_{\text{phen}} \rightarrow \pi^*_{\text{phen}}$) character. The strong absorption peak in the ultraviolet region is mainly correlated to the electronic transitions from HOMO $-10$ to LUMO $+1$ and HOMO $-2$ to LUMO $+5$ and characteristic of $\pi^*_{\text{phen}}/\pi^*_{\text{TTF}} \rightarrow \pi^*_{\text{phen}}/\pi^*_{\text{TTF}}$ ILCT and $\pi^*_{\text{ppy}} \rightarrow \pi^*_{\text{ppy}}/\pi^*_{\text{TTF}}$ ILCT.

The UV–vis-NIR spectra of complex 1 upon addition of oxidant nitrosonium hexafluorophosphate (NOPF$_6$) in CH$_2$Cl$_2$ solution was also investigated. As shown in Fig. 4, upon the addition of 1.0 equiv of oxidant NOPF$_6$, a weak broad band centered at 832 nm is observed, which results from the characteristic absorption band of the cationic radical TTF$^+$ [10,16], meanwhile, the initial absorbance at $\lambda = 262$ nm and 298 nm decrease. After the further oxidation with 1.0 equiv of NOPF$_6$, the TTF unit is oxidized to the dicaticonic state, the characteristic absorption band of TTF$^+$ disappears, and the absorption bands in the range 420–600 nm decreases. These phenomena are similar with the oxidation of the neutral TTF–Ir complex [16].

Unlike the rhenium complex CIRe(CO)$_3$(L) we reported before [10], complex 1 is luminescent at room temperature in dichloromethane solution which can be ascribe to the different photo-induced electron transfer efficiencies of the TTF unit. The corresponding photoluminescence data of complex 1 are summarized in Table 2. Fig. 5 shows the photoluminescence spectra in different conditions. Figs. S3–S5 show the lifetime curves of 1 in different solvents.

![Scheme 1. Synthetic routes to complex 1.](image1.png)

![Fig. 1. Cyclic voltammograms of compounds 1 and L (5 × 10$^{-4}$ M) in CH$_2$Cl$_2$/CH$_3$CN solution (1:1, v/v) of n-Bu$_4$NClO$_4$ (0.1 M) at a sweep rate of 100 mV/s.](image2.png)

![Fig. 2. Electronic absorption spectrum of 1 in CH$_2$Cl$_2$ solution together with the calculated oscillator strengths.](image3.png)
Upon excitation at 380 nm, complex 1 exhibits broad structureless band at about 607 nm in CH2Cl2 solution. According to the previous study, emission bands from LC states usually display vibronic progressions, while those from MLCT states are broad and featureless. Meanwhile, the MLCT states are known to be strongly temperature and solvent dependent [17,20]. For complex 1, a blue shift in the emission maxima about 41 nm with additional structure on going from fluid solution at room temperature to a rigid matrix at 77 K was observed (Fig. 5). And the emission maximum value occurs at higher energy in CH2Cl2 than that in more polar THF or CH3CN indicating that the excited state possesses a dominant MLCT character (Fig. 5). Thus we conclude that the emission of 1 gains larger contributions from MLCT state. With the 1.0 equiv of oxidant NOPF6 added, the emission intensity is remarkably decreased, and reaches the minimum after the addition of another 1.0 equiv of NOPF6 (Fig. S6), which is probably caused by photo-induced electron transfer from IrIII core to the oxidized TTF moiety.

The ECL performance of free ligand L, complex 1 and reference complex [Ir(ppy)2(phen)]PF6 (2) were studied in CH2Cl2 solution containing n-Bu4NClO4 as the supporting electrolyte and tri-n-propylamine (TPrA) as the coreactant. The typical ECL profile registered during a cyclic voltammetry is shown in Fig. 6. All the three compounds show broad oxidation peak, indicating the overlapped oxidation process. The ligand L is non-luminous, while for complex 1 and 2, the ECL emission occurs due to the reaction of IrIII core with TPrA radical, following the classic oxidative-reduction coreactant mechanism (Eqs. (1)-(5)) [14,15]. The ECL peak intensity of complex 1 is half that of complex 2, whose ECL emission occurs at higher potential. To examine the peak wavelength of ECL emission, the corresponding ECL spectrum of complex 1 is also achieved. As shown in Fig. 7, the maximum emission is about 627 nm, indicating the formation of the same excited state in photoluminescence and ECL.

\[
\text{[Ir(ppy)2(L)]}^+ + e^- \rightarrow \text{[Ir(ppy)2(L)]}^{2+} \quad (1)
\]
\[
\text{TPrA} - e^- \rightarrow \text{TPrA}^+
\]
\[
\text{TPrA}^+ \rightarrow \text{TPrA}^+ + H^+
\]
\[
\text{TPrA}^+ + \text{[Ir(ppy)2(L)]}^{2+} \rightarrow \text{[Ir(ppy)2(L)]}^{+} + \text{Pr}_2\text{N}^+
\]
\[
\text{[Ir(ppy)2(L)]}^{+} \rightarrow \text{[Ir(ppy)2(L)]}^{+} + hv
\]

### 3. Conclusion

In conclusion, the air-stable cationic-functionalized iridium(III) complex 1 based on tetraethiophene-fused phenanthroline as NN ancillary ligand is successfully synthesized and characterized. The electronic transition spectrum of 1 is calculated with TD-DFT, and a good agreement with the experimental data is observed. Interestingly, 1 is phosphorescent with maximum emission wavelength at 607 nm, and the ECL result shows the same excited state as photoluminescence. Complex 1

![Fig. 3. Selected molecular orbitals energy diagram and graphical representation for frontier molecular orbitals of 1.](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Main experimental and calculated optical transitions for 1.</th>
</tr>
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<tbody>
<tr>
<td>Orbital excitations</td>
<td>Transition</td>
</tr>
<tr>
<td>HOMO → LUMO + 1</td>
<td>ILCT</td>
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<tr>
<td>HOMO → LUMO</td>
<td>MLCT/ILCT</td>
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<tr>
<td>HOMO → LUMO</td>
<td>MLCT/ILCT</td>
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<tr>
<td>HOMO → LUMO + 1</td>
<td>ILCT</td>
</tr>
<tr>
<td>HOMO → LUMO + 5</td>
<td>ILCT</td>
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may be useful as photoelectric functional material, and more work is going on in our laboratory.

4. Experimental section

4.1. General procedures

The IR spectra were taken on a Vector22 Bruker spectrophotometer (400–4000 cm⁻¹) with KBr pellets. ¹H NMR spectra were measured on a Bruker AM 500 spectrometer. Chemical shifts were reported in ppm relative to Me₄Si as internal standard. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. Electrospray ionization mass spectrometry (ESI-MS) spectra were determined with LCQ Fleet instrument with CH₃CN as solvent. Cyclic voltammograms (CV) were recorded on an Im6eX electrochemical analytical instrument, with a polished Pt plate as the working electrode, a Pt foil as the counter electrode, Ag/AgCl as the reference electrode, and 0.1 M n-Bu₄NClO₄ as the supporting electrolyte. All the potentials were run at scan rates of 100 mV/s. UV–vis spectra were measured on a Shimadzu UV–3100 spectrophotometer. Photoluminescence spectra and photoluminescence lifetime measurement were carried out on an LS 55 and an Edinburgh Instruments FLS920 photometer. Photoluminescence spectra and photoluminescence lifetime measurement were carried out on an LS 55 and an Edinburgh FLS920P photometer. Photoluminescence spectra and photoluminescence lifetime measurement were carried out on an LS 55 and an Edinburgh FLS920P photometer.

4.2. Materials

All solvents were dried by standard methods and distilled prior to use. Solvents used for electrochemistry and spectroscopy were spectroscopic grade. Moisture-sensitive reactions were carried out under a nitrogen atmosphere. 4',5'-Dimethylthiodithiatrafulvenyl[4,5-f][1,10]phenanthroline (L), and cyclo metallated iridium chlorobridged dimer [Ir(ppy)₂Cl]₂ (ppy = 2-phenylpyridine) were synthesized according to the published procedures [10,11,21,22]. The luminescence quantum efficiencies were calculated by comparison of the fluorescence intensities (integrated areas) of a standard sample Ir(ppy)₃ and complex 1 according to Eq. (6) [22].

\[
\frac{\phi_{\text{unk}}}{\phi_{\text{std}}} = \frac{\frac{l_{\text{unk}}}{A_{\text{unk}}}}{\frac{l_{\text{std}}}{A_{\text{std}}}} \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2
\]

where \(\phi_{\text{unk}}\) is the luminescence quantum yield of the complex 1, \(\phi_{\text{std}}\) is the luminescence quantum yield of Ir(ppy)₃ solution, \(l_{\text{unk}}\) and \(l_{\text{std}}\) are the integrated fluorescence intensities of the complex 1 and Ir(ppy)₃, respectively. \(A_{\text{unk}}\) and \(A_{\text{std}}\) are the absorbances of the complex 1 and Ir(ppy)₃ at excitation wavelengths. The \(\eta_{\text{unk}}\) and \(\eta_{\text{std}}\) terms represent the refractive indices of the corresponding solvents (pure solvents were assumed). The \(\phi_{\text{std}}\) value of Ir(ppy)₃ has been revalued to be 0.42 [23].

4.3. Syntheses

4.3.1. [Ir(ppy)₂(L)]PF₆ (1)

Under a nitrogen atmosphere, a mixture of L (61 mg, 0.14 mmol) and [Ir(ppy)₂Cl]₂ (72 mg, 0.067 mmol) in 13 mL of CH₂Cl₂ and 5 mL of CH₃OH was refluxed for 4 h. Then the dark red solution was cooled to room temperature, and 8-fold excess of potassium hexafluorophosphate was added. The suspension was stirred for another 2 h and then was filtered. The filtrate was evaporated to dryness under reduced pressure. Purification was made by flash chromatography on a silica gel column using CH₂Cl₂/MeOH (v/v = 80:1) as the eluent to afford dark red crystalline solid in 80% yield. IR (KBr, cm⁻¹): 2920, 1607, 1582, 1478, 1420, 1314, 1267, 1163, 1062, 940, 841, 757, 722, 556. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.30 (d, J = 5.0 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 7.83 (dd, J = 5.5 Hz, 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 4H), 7.25 (d, J = 5.5 Hz, 2H), 7.11 (t, J = 7.5 Hz, 2H), 7.00 (t, J = 7.5 Hz, 2H), 6.91 (t, J = 6.5 Hz, 2H), 0.77 (s, 18H), 0.71 ppm. M.S. (ESI-MS): [M]⁺, 671 (100%).

4.3.2. [Ir(ppy)₂(Cl)(L)]PF₆ (2)

Under a nitrogen atmosphere, a mixture of L (61 mg, 0.14 mmol) and [Ir(ppy)₂Cl]₂ (72 mg, 0.067 mmol) in 13 mL of CH₂Cl₂ and 5 mL of CH₃OH was refluxed for 4 h. Then the dark red solution was cooled to room temperature, and 8-fold excess of potassium hexafluorophosphate was added. The suspension was stirred for another 2 h and then was filtered. The filtrate was evaporated to dryness under reduced pressure. Purification was made by flash chromatography on a silica gel column using CH₂Cl₂/MeOH (v/v = 80:1) as the eluent to afford dark red crystalline solid in 80% yield. IR (KBr, cm⁻¹): 2920, 1607, 1582, 1478, 1420, 1314, 1267, 1163, 1062, 940, 841, 757, 722, 556. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.30 (d, J = 5.0 Hz, 2H), 8.23 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 7.83 (dd, J = 5.5 Hz, 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 4H), 7.25 (d, J = 5.5 Hz, 2H), 7.11 (t, J = 7.5 Hz, 2H), 7.00 (t, J = 7.5 Hz, 2H), 6.91 (t, J = 6.5 Hz, 2H), 0.77 (s, 18H), 0.71 ppm. M.S. (ESI-MS): [M]⁺, 697 (100%).
2H), 6.39 (d, J = 7.5 Hz, 2H), 2.45 (s, 6H). MS (ESI-MS): m/z 949.17 [M – PF$_6$]$^+$, 144.92 PF$_6$. Anal. Calcd for C$_{40}$H$_{28}$S$_6$N$_4$PF$_6$Ir: C, 43.90; H, 2.24; N, 5.12. Found: C, 44.23; H, 2.24; N, 5.38%.

4.4. Computational details

The calculations were carried out with Gaussian 03 Program Package [18]. DFT and TD-DFT methods with no symmetry constraints were employed with the B3LYP. The LANL2DZ basis set was used to treat the iridium atom, the 6-31G* basis set was used to treat all other atoms.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.10.041.

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